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1) Previously reported benzylic and related oxonium ions on unconstrained scaffolds.

As noted in the main text, there have been limited reports of benzylic and related oxonium ions on unconstrained scaffolds often with only partial characterisation; examples are shown in **Figure S1**.

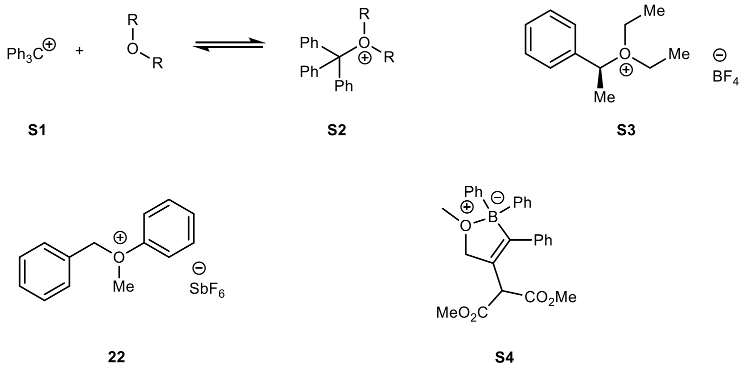


Figure S1. Examples of benzylic and related oxonium ions on unconstrained scaffolds.

1. The equilibrium of the trityl cation **S1** with ethers and acetals giving the corresponding oxonium ions **S2** has been studied by UV-Vis spectroscopy.[1-3]
2. Treatment of ethyl iodide with silver(I) tetrafluoroborate followed by filtration and addition of (*S*)-1-phenylethyl ethyl ether is reported to give (*S*)-diethyl(1-phenylethyl)oxonium tetrafluoroborate **S3** - no characterisation of the oxonium ion was reported.[4]
3. As discussed in the main text Olah reported the formation and characterisation by low temperature ^{1}H NMR of the thermally unstable oxonium ion **22**.[5]
4. The oxaborole zwitterion **S4** was recently reported.[6] As with Mascal's allylic oxonium ions,[7] although topologically allylic, it is not stereoelectronically allylic.

2) General experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 500 (500/125 MHz) and Bruker AV 400 (400/100 MHz) spectrometer. Proton and carbon chemical shifts are quoted in ppm and referenced to residual protonated solvent. Resonances are described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad), dd (double doublet) and so on. Coupling constants (*J*) are given in Hz and are rounded to the nearest 0.1 Hz. Low resolution mass spectra were recorded on a Fisons Platform spectrometer (ES). High resolution mass spectra were recorded by the mass spectrometry staff at the Chemistry Research Laboratory, University of Oxford, using a Bruker Daltronics microTOF spectrometer (ES) or a Micromass GCT (FI). *m/z* values are reported in Daltons. High resolution values are calculated to four decimal places from the molecular formula, all found values being within a tolerance of 5.0 ppm. Infrared spectra were recorded on a Bruker Tensor 27 Fourier Transform spectrometer using diamond ATR. Absorption maxima (ν_{max}) are described as strong, medium, weak and broad and are quoted in wavenumbers (cm^{-1}). Optical rotations were measured using a Perkin-Elmer 241 polarimeter in a cell of 1.0 dm path length (l). TLC was performed on Merck DC-Alufolien 60 F254 0.2 mm precoated plates and visualised using an acidic vanillin or basic potassium permanganate dip. Retention factors (R_f) are reported with the solvent system used in parentheses. Flash column chromatography was performed on Merck 60 silica (particle size 40 – 63 µm, pore diameter 60 Å) and the solvent system used is recorded in parentheses. All non-aqueous reactions were carried out in flame-dried glassware under an inert atmosphere of argon or nitrogen and employing standard techniques for handling air-sensitive materials. Solvents and commercially available reagents were dried and purified before use, as appropriate. Compounds were named using ChemDraw and the assignments of NMR spectra were done on MestReNova.

3) Note on HMBC

^{3}J ^{1}H-^{13}C coupling constants and hence ^{3}J HMBC correlations have a Karplus-like torsion angle dependence[8-10] as shown graphically below (**Figure S2**), hence in systems such as the [3.3.0]-bicyclic oxonium ions, $^{3}J_{\text{C-H}}$, $^{3}J_{\text{C-H'}}$, $^{3}J_{\text{C-H}}$ will likely have different values. Indeed, in the lowest energy conformation of the parent [3.3.0]-bicyclic oxonium ion (**Figure S17**), the torsion angle between the angular (orange) proton and the primary (blue) carbon atom is 112.2°, and in the second lowest energy conformer (**Figure S2**), the equivalent torsion angles are 108.9° and 119.6°, hence only a small $^{3}J_{\text{C-H}}$ would be expected. Therefore, the HMBC correlation between the orange proton and the blue carbon would be expected to be weak or not observed, in keeping with the experimental results illustrated in the main text (**Figure 2c** and in the Supplementary Data File – NMR spectra).

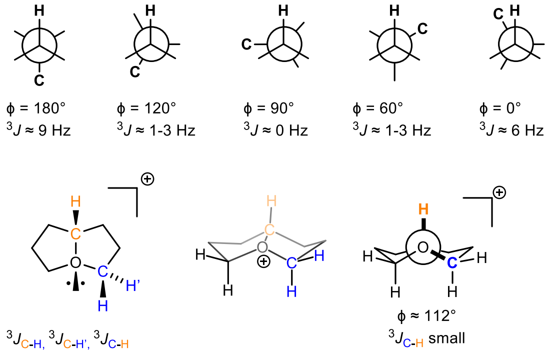


Figure S2. Angle dependence of ^{3}J ^{1}H-^{13}C coupling constants and relation to magnitude to ^{3}J ^{1}H-^{13}C coupling constants and hence magnitude of the corresponding HMBC correlations in [5.3.0]-bicyclic oxonium ions.

4) Synthesis of oxonium ion precursors (Part 1):

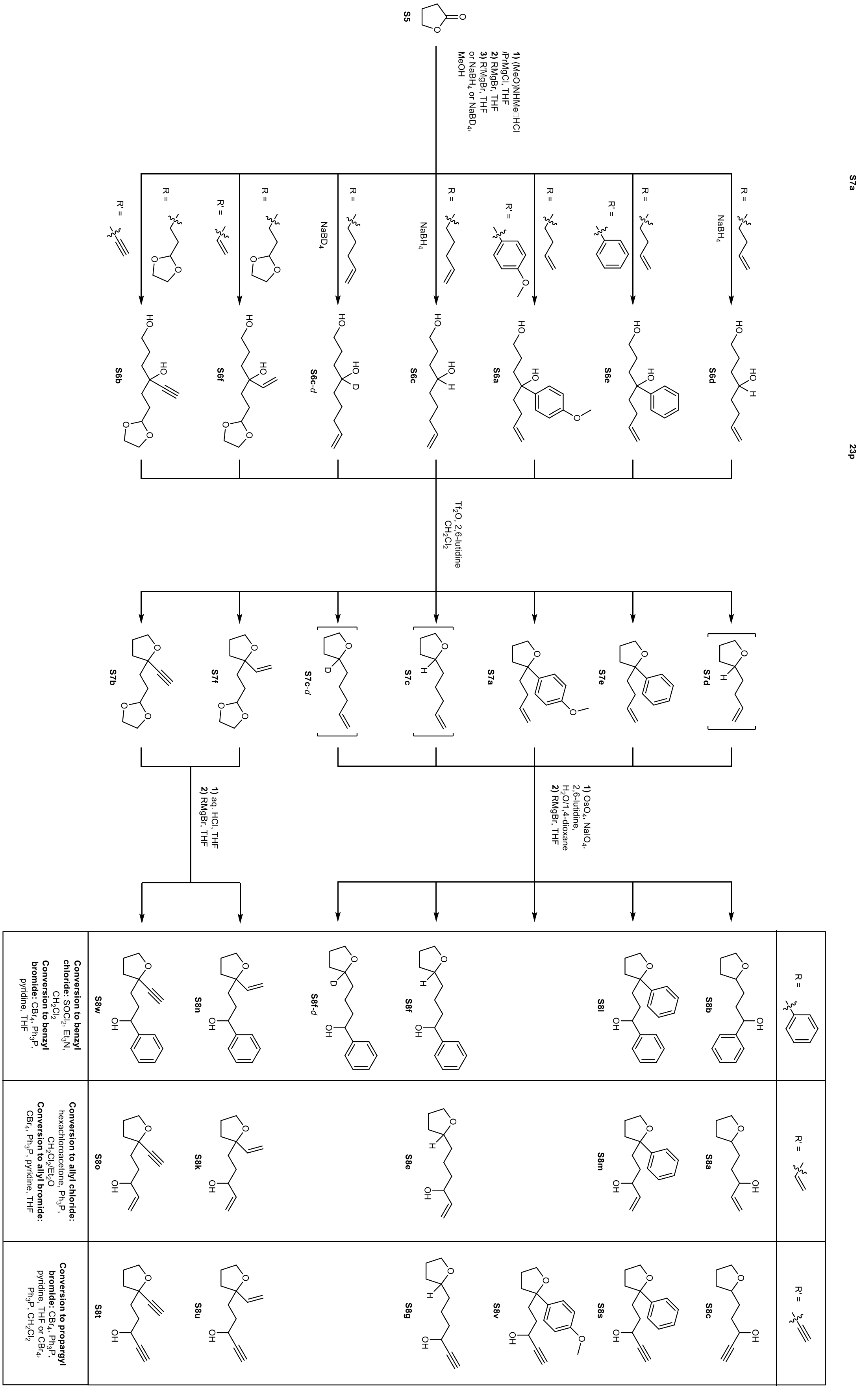


Figure S3. A general strategy for the synthesis of oxonium ion precursors **S8** and for conversion to benzylic, allylic and propargylic halides **23**.

General procedure A: Synthesis of diols S6 from γ-butyrolactone S5:

Step 1) *According to the procedures of Williams*[1]: γ-Butyrolactone **S5** (1.0 eq.) was dissolved in THF (0.5 M) followed by addition of (MeO)NHMe·HCl (1.55 eq). The insoluble (MeO)NHMe·HCl salt was broken up by vigorous stirring and/or sonication at room temperature before cooling the suspension to −20 °C. Isopropylmagnesium chloride (3.0 eq., 2.0 M solution in THF) was then added dropwise to the reaction mixture at −20 °C. After the addition, the reaction mixture was warmed to −10 °C and stirred for 20-30 minutes at this temperature. At this point the reaction was quenched with aqueous sat. NH_4Cl solution, and the aqueous layer was extracted three times with ethyl acetate. The organic layers were collected, dried with anhydrous $MgSO_4$, and concentrated under reduced pressure. Any remaining volatiles were further removed under high vacuum, and the crude Weinreb amide was carried forward to step 2 without further purification.

Step 2) Relevant Grignard reagents were prepared as follows:
But-3-en-1-ylmagnesium bromide: For 1.0 eq. of 4-bromobut-1-ene, magnesium (1.7 eq., grit) was suspended in dry THF (1.0 M w.r.t desired concentration of the Grignard reagent), followed by addition of 2 granules of elemental iodine, in which the liquid phase of the mixture turned from colourless to brown. The reaction mixture was then heated to 50 °C and stirred until the colour of the liquid phase change from brown to colourless or pale yellow. The reaction mixture was then cooled to room temperature. 4-Bromobut-1-ene (1.0 eq.) was then added dropwise to the reaction mixture, with careful control and monitoring of the reaction temperature, such that it does not exceed 50 °C. After the addition, the reaction mixture was cooled to room temperature, and successful generation of the desired Grignard reagent was signified by the formation of a deep grey liquid phase.

(2-(1,3-dioxolan-2-yl)ethyl)magnesium bromide: For 1.0 eq. of 2-(2-bromoethyl)-1,3-dioxolane, magnesium (1.7 eq., grit) was suspended in dry THF (1.0 M w.r.t desired concentration of the Grignard reagent), followed by addition of 2 granules of elemental iodine, in which the liquid phase of the mixture turned from colourless to brown. The reaction mixture was then heated to 50 °C and stirred until the colour of the liquid phase change from brown to colourless or pale yellow. The reaction mixture was then cooled to room temperature. 2-(2-bromoethyl)-1,3-dioxolane (1.0 eq.) was then added dropwise to the reaction mixture, with careful control and monitoring of the reaction temperature, such that it does not exceed **30 °C**. After the addition, the reaction mixture was cooled to room temperature, and successful generation of the desired Grignard reagent was signified by the formation of a deep grey liquid phase.

Pent-4-en-1-ylmagnesium bromide: For 1.0 eq. of 5-bromopent-1-ene, magnesium (1.7 eq., grit) was suspended in dry THF (1.0 M w.r.t desired concentration of the Grignard reagent), followed by addition of 2 granules of elemental iodine, in which the liquid phase of the mixture turned from colourless to brown. The reaction mixture was then heated to 50 °C and stirred until the colour of the liquid phase change from brown to colourless or pale yellow. The reaction mixture was then cooled to room temperature. 5-Bromopent-1-ene (1.0 eq.) was then added dropwise to the reaction mixture, with careful control and monitoring of the reaction temperature, such that it does not exceed 50 °C. After the addition, the reaction mixture was cooled to room temperature, and successful generation of the desired Grignard reagent was signified by the formation of a deep grey liquid phase.

Reaction of the Weinreb amide with Grignard reagents:
For 1.0 eq of the Weinreb amide, 2.1 eq. of Grignard reagent was prepared. The Grignard reagents (2.1 eq. 1.0 M in THF) prepared according to the general procedures above were cooled to 0 °C. The crude Weinreb amide (1.0 eq.) was dissolved in dry THF and added dropwise to the cold solution of

Grignard reagents. After addition, the reaction mixture was stirred at 0 °C for 1 hour and then warmed to room temperature. TLC analysis at this stage suggested complete consumption of starting materials. The reaction was quenched with aqueous sat. NH_4Cl solution, and the aqueous phase was extracted three times with ethyl acetate. The organic layers were collected, dried with anhydrous $MgSO_4$, and concentrated under reduced pressure. Any remaining volatiles were further removed under high vacuum, and the crude keto alcohols were carried forward to step 3 without further purification.

Step 3) For addition of Grignard reagents into the keto alcohols: The crude keto alcohols (1.0 eq.) were dissolved in dry THF (0.1 M) and cooled to 0 °C. Commercially available Grignard reagents (3.0 eq.) (Phenylmagnesium bromide, 3.0 M in Et_2O, vinylmagnesium bromide, 1.0 M in THF, ethynylmagnesium bromide 0.5 M in THF, or 4-methoxyphenylmagnesium bromide, 0.5 M in THF) was added to the cold solution of the corresponding keto alcohol accordingly. After addition, the reaction mixture was stirred at 0 °C for 1 hour and then warmed to room temperature. TLC analysis at this stage suggested complete consumption of starting materials. The reaction was quenched with aqueous sat. NH_4Cl solution, and the aqueous phase was extracted three times with ethyl acetate. The organic layers were collected, dried with anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude diols **S6** were then purified by flash column chromatography.

For reduction of the keto alcohols by $NaBH_4$ or $NaBD_4$: The crude keto alcohols (1.0 eq.) were dissolved in MeOH (0.1 M) and cooled to 0 °C. $NaBH_4$ or $NaBD_4$ (1.5 eq.) was added to the cold solution of the corresponding keto alcohol accordingly. After addition, the reaction mixture was stirred at 0 °C and then gradually warmed to room temperature overnight. TLC analysis at this stage suggested complete consumption of starting materials. The reaction was diluted with water, and the aqueous phase was extracted three times with dichloromethane. The organic layers were collected, dried with anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude diols **S6** were then purified by flash column chromatography.

General procedure B: Cyclization of diols S6 to provide tetrahydrofurans S7:

Diols **S6** (1.0 eq.) were dissolved in CH_2Cl_2 (0.01 M) followed by addition of 2,6-lutidine (2.1 eq.). The resultant solution was cooled to −78 °C and trifluoromethanesulfonic anhydride (1.1 eq.) was added. The reaction mixture was stirred at −78 °C for 1 hour and then warmed to room temperature. TLC analysis at this stage suggested complete consumption of starting materials. The reaction was quenched with aqueous sat. $NaHCO_3$ solution, and the aqueous phase was extracted three times with CH_2Cl_2. The organic layers were collected, quickly washed with 1.0 M aq. HCl solution to remove residual 2,6-lutidine, followed by a final wash with sat. $NaHCO_3$ solution to remove residual acids. The organic layer was then dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. *Caution: tetrahydrofurans **S7c** and **S7d** are volatile.* The crude tetrahydrofurans were then purified by flash column chromatography except tetrahydrofurans **S7c** and **S7d** due to their volatility. The crude tetrahydrofurans **S7c** and **S7d** were carried forward to the next step without further purification.

General procedure C: Oxidative cleavage of tetrahydrofurans S7d, S7e, S7a, S7c, S7f:

Tetrahydrofurans (1.0 eq.) were dissolved in a solution of 3:1 dioxane/H_2O (0.1 M) at room temperature. 2,6-Lutidine (1.96 eq.) was added, followed by cat. OsO_4 (2.5% in *t*BuOH). $NaIO_4$ (3.93 eq.) was added and the reaction mixture was stirred at room temperature for 1 hour. TLC analysis at this stage suggested complete consumption of starting materials. The reaction was diluted with a large excess of water and extracted three times with CH_2Cl_2. The organic layers were collected, quickly washed with 1.0 M aq. HCl solution to remove residual 2,6-lutidine, followed by a final wash with sat. $NaHCO_3$ solution to remove residual acids. The organic layer was then dried with anhydrous

$MgSO_4$ and concentrated under reduced pressure. The crude aldehydes were carried forward to the next step without further purification.

General procedure D: Deprotection of 1,3-dioxolanes S7b and S7f:
Tetrahydrofurans (1.0 eq.) were dissolved in THF (0.1 M) at room temperature followed by addition of 2.0 M aq. HCl (same volume as THF). The reaction mixture was stirred at room temperature for 2 hours. TLC analysis at this stage suggested complete consumption of starting materials. The reaction was diluted with a large excess of water and extracted three times with ethyl acetate. The organic layers were collected and washed with sat. $NaHCO_3$ solution to remove residual acids. The organic layer was then dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude aldehydes were carried forward to the next step without further purification.

General procedure E: Reaction of crude aldehydes with Grignard reagents:
The crude aldehydes (1.0 eq.) were dissolved in dry THF (0.1 M) and cooled to 0 °C. Commercially available Grignard reagents (2.0 eq.) (Phenylmagnesium bromide, 3.0 M in Et_2O, vinylmagnesium bromide, 1.0 M in THF, or ethynylmagnesium bromide 0.5 M in THF) was added to the cold solution of the corresponding aldehyde accordingly. After addition, the reaction mixture was stirred at 0 °C for 1 hour and then warmed to room temperature. TLC analysis at this stage suggested complete consumption of starting materials. The reaction was quenched with aqueous sat. NH_4Cl solution, and the aqueous phase was extracted three times with ethyl acetate. The organic layers were collected, dried with anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude alcohols **S8** were then purified by flash column chromatography.

General procedures F: Chlorination and bromination of alcohols S1:
For the synthesis of benzyl chlorides **23**: Alcohols **S8** (1.0 eq.) were dissolved in CH_2Cl_2 (0.1 M) at 0 °C. Et_3N (1.3 eq.) was added followed by the addition of $SOCl_2$ (1.3 eq.). The reaction was stirred at 0 °C for 1 hour and warmed to room temperature. TLC analysis at this stage suggested complete consumption of starting materials. The reaction was quenched with aqueous sat. $NaHCO_3$ solution, and the aqueous phase was extracted three times with CH_2Cl_2. The organic layers were collected, dried with anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude benzyl chlorides **23** were then purified by flash column chromatography.

For the synthesis of benzyl bromides, allyl bromides, and propargyl bromides **23** (**Method A**): *According to the procedure of Cooper*[2]: Alcohols **S8** (1.0 eq.), PPh_3 (2.4 eq.) and pyridine (1.1 eq.) were dissolved in THF (0.2 M) and stirred vigorously at room temperature. Then a solution of CBr_4 (1.1 eq.) and pyridine (0.6 eq.) in THF (1.0 M) was quickly added. The reaction was stirred at room temperature for 30 minutes. TLC analysis at this stage suggested complete consumption of starting materials. The reaction mixture was diluted with diethyl ether, stirred for 10 minutes, filtered and concentrated under reduced pressure. The crude benzyl bromides, allyl bromides, and propargylic bromides **23** were then purified by flash column chromatography.

For the synthesis of propargyl bromides **23** (**Method B**): *According to the procedure of Brimble*[3]: Alcohols **S8** (1.0 eq.) was dissolved in CH_2Cl_2 (0.1 M). CBr_4 (1.1 eq.) was added followed by PPh_3 (2.0 eq.). The reaction was stirred at room temperature for 2 hours. TLC analysis at this stage suggested complete consumption of starting materials. The reaction mixture was diluted with a large excess of ethyl acetate, stirred for 10 minutes, filtered and concentrated under reduced pressure. The crude propargylic bromides **23** were then purified by flash column chromatography.

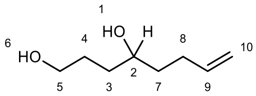
For the synthesis of allyl chlorides **23**: Alcohols **S8** (1.0 eq.) was dissolved in 1:1 Et_2O:CH_2Cl_2 (0.1

M) at 0 °C. Hexachloroacetone (1.3 eq.) and PPh$_3$ (1.3 eq.) were added and the reaction was stirred at 0 °C for 1 hour, then warmed to room temperature. TLC analysis at this stage suggested complete consumption of starting materials. The reaction was quenched with aqueous sat. NaHCO$_3$ solution, and the aqueous phase was extracted three times with CH$_2$Cl$_2$. The organic layers were collected, dried with anhydrous MgSO$_4$, and concentrated under reduced pressure. The crude allyl chlorides **23** were then purified by flash column chromatography.

Characterization data for the oxonium ion precursors (Part 1):

Note: As the oxonium ion precursors are prepared as 1:1 diastereomeric mixtures, the multiplicities of the peaks on ^{1}H NMR spectra are reported as multiplets (m) unless otherwise stated. Addtionally, these mixtures of diasteromers are given one number except for the alcohol **S8b** where the two diastereomers are labelled **S8b** and **S8b'** and the chloride **23b** where the two diasteoremers are labelled **23b** and **23b'** as these sets of diastereomers are formed in unequal ratios in the quenching of oxonium ion **24b**•Al(pftb)$_4$ (see section pS87).

Oct-7-ene-1,4-diol (S6d)



This compound was prepared according to General Procedure A.

Flash column chromatography eluent: 40% Acetone/Pet. Ether 40-60.

R$_f$ = 0.37 (40% Acetone/Pet. Ether 40-60)

Yield: 65% (613 mg) from 0.5 mL (565 mg) of **S6d**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.84 (ddtd, J = 16.9, 10.3, 7.2, 6.6, 2.3 Hz, 1H, **H9**), 5.05 (dq, J = 17.0, 1.8 Hz, 1H, **H10**), 4.97 (dq, J = 10.3, 1.8 Hz, 1H, **H10'**), 3.84 – 3.37 (m, 3H, **H2**, **H5**), 2.52 (s, 1H, **OH**), 2.30 – 1.94 (m, 3H, **OH**, **H8**), 1.74 – 1.66 (m, 2H, **H3**), 1.66 – 1.61 (m, 1H, **H4**), 1.61 – 1.53 (m, 2H, **H7**), 1.53 – 1.46 (m, 1H, **H4'**).

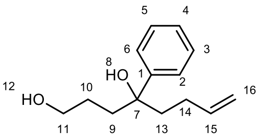
^{13}C NMR (101 MHz, CDCl$_3$) δ 138.7 (**C9**), 115.1 (**C10**), 71.6 (**C2**), 63.2 (**C5**), 36.7 (**C7**), 34.6 (**C4**), 30.3 (**C8**), 29.2 (**C3**).

IR (thin film, υ/cm^{-1}): 3314, 2927, 2869, 1640, 1447, 1260, 1014

HRMS (ESI): Found 167.10440, *m/z* calculated for C$_8$H$_{16}$O$_2$^{23}Na [M+Na]$^+$: 167.10425.

Spectroscopic data of **S6d** is in accordance with literature data.[4]

4-Phenyloct-7-ene-1,4-diol (S6e)



This compound was prepared according to General Procedure A.

Flash column chromatography eluent: 40% EA/Pet. Ether 40-60 to 60% EA/Pet. Ether 40-60

R$_f$ = 0.37 (60% EA/Pet. Ether 40-60)

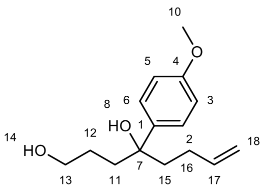
Yield: 62% (130 mg) from **S5**, in which a 100 mg fraction of the crude keto alcohol (622 mg) prepared from 0.5 mL (565 mg) of **S5** was used for this reaction.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.40 – 7.30 (m, 4H, **H2**, **H3**, **H5**, **H6**), 7.25 – 7.18 (m, 1H, **H4**), 5.78 (ddt, J = 16.8, 10.2, 6.4 Hz, 1H, **H15**), 5.01 – 4.80 (m, 2H, **H16**), 3.66 – 3.46 (m, 2H, **H11**), 3.04 (s, 1H, **OH**), 2.14 – 2.00 (m, 3H, **OH**, **H9**, **H12**, **H14**), 1.95 – 1.90 (m, 2H, **H9'**, **H13**), 1.88 – 1.77 (m, 1H, **H14'**), 1.54 – 1.46 (m, 1H, **H10**), 1.43 (dddd, J = 14.3, 8.1, 4.8, 3.1 Hz, 1H, **H10'**).

^{13}C NMR (126 MHz, CDCl$_3$) δ 146.0 (**C1**), 139.0 (**C15**), 128.3 (**C3**, **C5**), 126.5 (**C4**), 125.5 (**C2**,

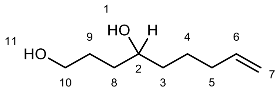
C6), 114.7 (**C16**), 76.9 (**C7**), 63.3 (**C11**), 42.6 (**C13**), 40.4 (**C9**), 28.2 (**C14**), 26.9 (**C10**).
IR (thin film, v/cm^{-1}): 3348, 2943, 1640, 1494, 1446, 1050, 1002, 908, 729, 700
HRMS (ESI): found 243.1357, m/z calculated for $C_{14}H_{20}O_2{}^{23}Na$ [M+Na]$^+$: 243.1356.

4-(4-Methoxyphenyl)oct-7-ene-1,4-diol (S6a)



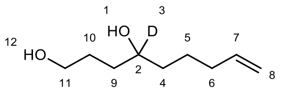
This compound was prepared according to General Procedure A.
Flash column chromatography eluent: 60% EA/Pet. Ether 40-60
R$_f$ = 0.12 (60% EA/Pet. Ether 40-60)
Yield: 46% (57 mg) from **S5**, in which a 53 mg fraction of the crude keto alcohol (622 mg) prepared from 0.5 mL (565 mg) of **S5** was used for this reaction.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.17 (m, 2H, **H2**, **H6**), 6.97 – 6.71 (m, 2H, **H3**, **H5**), 5.79 (dddd, *J* = 16.9, 10.1, 7.0, 5.7 Hz, 1H, **H17**), 4.95 (dt, *J* = 17.1, 1.8 Hz, 1H, **H18**), 4.91 (dt, *J* = 10.3, 1.7 Hz, 1H, **H18'**), 3.81 (s, 3H, **H10**), 3.68 – 3.50 (m, 2H, **H13**), 2.09 – 2.02 (m, 1H, **H16**), 2.00 (ddd, *J* = 14.3, 8.1, 6.2 Hz, 1H, **H11**), 1.93 – 1.86 (m, 4H, **H11'**, **H15**), 1.86 – 1.81 (m, 1H, **H16'**), 1.56 – 1.45 (m, 1H, **H12**), 1.47 – 1.39 (m, 1H, **H12'**).
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2 (**C4**), 139.1 (**C17**), 138.0 (**C1**), 126.6 (**C2**, **C6**), 114.8 (**C18**), 113.6 (**C3**, **C5**), 76.7 (**C7**), 63.4 (**C13**), 55.4 (**C10**), 42.6 (**C15**), 40.4 (**C11**), 28.3 (**C16**), 27.0 (**C12**).
IR (thin film, v/cm^{-1}): 3360, 2940, 1610, 1510, 1245, 1033
HRMS (ESI): Found 273.14606, *m/z* calculated for $C_{15}H_{22}O_3{}^{23}Na$ [M+Na]$^+$: 273.14612.

Non-8-ene-1,4-diol (S6c)



This compound was prepared according to General Procedure A.
Flash column chromatography eluent: 60% EA/Pet. Ether 40-60
R$_f$ = 0.12 (60% EA/Pet. Ether 40-60)
Yield: 70% (680 mg) from **S5**, in which a 900 mg fraction of the crude Weinreb amide (1.9 g) prepared from 1.0 mL (1.13 g) of **S5** was used for the synthesis of the crude keto alcohol (829 mg) for this reaction.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H, **H6**), 5.08 – 4.88 (m, 2H, **H7**), 3.86 – 3.53 (m, 3H, **H2**, **H10**), 2.28 – 1.89 (m, 4H, 2**OH**, **H5**), 1.78 – 1.60 (m, 3H, **H8**, **H9**), 1.60 – 1.36 (m, 5H, **H3**, **H4**, **H8'**).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8 (**C6**), 114.8 (**C7**), 71.9 (**C2**), 63.2 (**C10**), 37.2 (**C3**), 34.6 (**C8**), 33.8 (**C5**), 29.2 (**C9**), 25.1 (**C4**).
IR (thin film, v/cm^{-1}): 3324, 3076, 2932, 2861, 1640, 1438, 1338, 1053, 994, 908
HRMS (ESI): Found 159.1381, *m/z* calculated for $C_9H_{18}O_2$ [M+H]$^+$: 159.1380.

Non-8-ene-4-*d*-1,4-diol (S6c-*d*)



This compound was prepared according to General Procedure A.

Flash column chromatography eluent: 60% EA/Pet. Ether 40-60

R$_f$ = 0.12 (60% EA/Pet. Ether 40-60)

Yield: 43% (250 mg) from **S5**, in which a 472 mg fraction of the crude keto alcohol (840 mg) prepared from 0.5 mL (565 mg) of **S5** was used for this reaction.

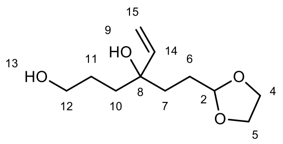
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H, **H7**), 5.01 (dq, J = 17.1, 1.7 Hz, 1H, **H8**), 4.96 (ddt, J = 10.2, 2.3, 1.2 Hz, 1H, **H8'**), 3.80 – 3.56 (m, 2H, **H11**), 2.22 – 2.00 (m, 4H, 2**OH**, **H6**), 1.74 – 1.66 (m, 2H, **H10**), 1.63 – 1.60 (m, 2H, **H4**), 1.58 – 1.50 (m, 1H, **H5**), 1.50 – 1.45 (m, 4H, **H4'**, **H9**), 1.45 – 1.38 (m, 1H, **H5'**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8 (**C7**), 114.8 (**C8**), 71.4 (1:1:1 triplet, $J_{C\text{-}D}$ = 21.0 Hz, **C2**), 63.2 (**C11**), 37.0 (**C9**), 34.4 (**C4**), 33.8 (**C6**), 29.2 (**C10**), 25.1 (**C5**).

IR (thin film, υ/cm^{-1}): 3309, 2926, 2857, 1640, 1054

HRMS (ESI): Found 160.1443, *m/z* calculated for $C_9H_{18}DO_2$ $[M+H]^+$: 160.1442.

4-(2-(1,3-Dioxolan-2-yl)ethyl)hex-5-ene-1,4-diol (S6f)



This compound was prepared according to General Procedure A.

Flash column chromatography eluent: 40% Acetone/Pet. Ether 40-60 **to** 60% Acetone/Pet. Ether 40-60

R$_f$ = 0.26 (60% Acetone/Pet. Ether 40-60)

Yield: 20% (154 mg) from **S5**, in which a 300 mg fraction of the crude keto alcohol (1.1 g) prepared from 1.0 mL (1.13 g) of **S5** was used for this reaction.

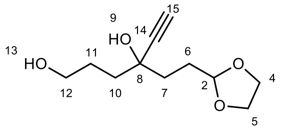
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74 (dd, J = 17.3, 10.8 Hz, 1H, **H14**), 5.26 (dd, J = 17.3, 1.4 Hz, 1H, **H15**), 5.16 (dt, J = 10.9, 1.4 Hz, 1H, **H15'**), 4.88 (t, J = 4.0 Hz, 1H, **H2**), 4.08 – 3.92 (m, 2H, **H4**), 3.92 – 3.78 (m, 2H, **H5**), 3.72 – 3.53 (m, 2H, **H12**), 1.83 – 1.71 (m, 3H, **H6**, **H10'**), 1.68 – 1.53 (m, 5H, **H7**, **H10**, **H11**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3 (**C14**), 113.8 (**C15**), 104.6 (**C2**), 74.7 (**C8**), 65.1 (**C4**, **C5**), 63.4 (**C12**), 38.5 (**C7**), 34.6 (**C10**), 27.9 (**C6**), 27.0 (**C11**).

IR (thin film, υ/cm^{-1}): 3385, 2925, 1410, 1139, 1028

HRMS (ESI): Found 239.12547, *m/z* calculated for $C_{11}H_{20}O_4{}^{23}Na$ $[M+Na]^+$: 239.12648.

4-(2-(1,3-Dioxolan-2-yl)ethyl)hex-5-yne-1,4-diol (S6b)



This compound was prepared according to General Procedure A.

Flash column chromatography eluent: 40% Acetone/Pet. Ether 40-60 **to** 60% Acetone/Pet. Ether 40-60

R$_f$ = 0.20 (40% Acetone/Pet. Ether 40-60)

Yield: 34% (344 mg) from **S5**, in which a 400 mg fraction of the crude keto alcohol (1.1 g) prepared from 1.0 mL (1.13 g) of **S5** was used for this reaction.

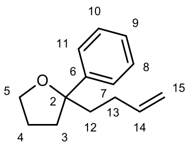
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.95 (t, *J* = 4.3 Hz, 1H, **H2**), 4.04 – 3.96 (m, 2H, **H5**), 3.92 – 3.85 (m, 1H, **H4**), 3.77 (dq, *J* = 10.4, 5.0 Hz, 1H, **H12'**), 3.68 (dt, *J* = 14.1, 5.2 Hz, 1H, **H12**), 2.48 (s, 1H, **H15**), 2.14 – 2.03 (m, 1H, **H6'**), 2.02 – 1.95 (m, 1H, **H6**), 1.92 (dddd, *J* = 11.7, 7.6, 4.8, 2.6 Hz, 1H, **H11'**), 1.87 – 1.79 (m, 4H, **H7**, **H10'**, **H11**), 1.81 – 1.72 (m, 1H, **H10**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 104.3 (**C2**), 86.4 (**C14**), 73.1 (**C15**), 70.3 (**C8**), 65.1 (**C4**, **C5**), 63.2 (**C12**), 39.7 (**C10**), 36.2 (**C7**), 28.9 (**C6**), 27.9 (**C11**).

IR (thin film, *υ*/cm^{-1}): 3385, 3283, 2925, 1025

HRMS (ESI): Found 237.10985, *m/z* calculated for $C_{11}H_{18}O_4{}^{23}Na$ [M+Na]$^+$: 237.10973.

2-(But-3-en-1-yl)-2-phenyltetrahydrofuran (S7e)



This compound was prepared according to General Procedure B.

Flash column chromatography eluent: 5% EA/Pet. Ether 40-60

R$_f$ = 0.74 (40% EA/Pet. Ether 40-60)

Yield: 56% (76 mg) from 150 mg of **S6e**

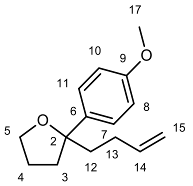
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.29 (m, 4H, **H7**, **H8**, **H10**, **H11**), 7.26 – 7.07 (m, 1H, **H9**), 5.75 (ddt, *J* = 16.7, 10.2, 6.4 Hz, 1H, **H14**), 4.93 (dq, *J* = 17.1, 1.8 Hz, 1H, **H15'**), 4.87 (dt, *J* = 10.4, 1.7 Hz, 1H, **H15**), 3.98 (q, *J* = 7.4 Hz, 1H, **H5'**), 3.89 (td, *J* = 8.0, 5.7 Hz, 1H, **H5**), 2.19 (ddd, *J* = 12.7, 8.0, 5.0 Hz, 1H, **H12'**), 2.14 – 2.01 (m, 2H, **H12**, **H13'**), 2.01 – 1.93 (m, 1H, **H4'**), 1.93 – 1.85 (m, 2H, **H3**), 1.85 – 1.71 (m, 2H, **H4**, **H13**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.7 (**C6**), 139.1 (**C14**), 128.2 (**C8**, **C10**), 126.5 (**C9**), 125.4 (**C7**, **C11**), 114.1 (**C15**), 86.6 (**C2**), 67.6 (**C5**), 41.7 (**C3**), 38.6 (**C12**), 29.0 (**C13**), 25.7 (**C4**).

IR (thin film, *υ*/cm^{-1}): 2974, 1640, 1446, 1053

HRMS (ESI): Found 203.14331, *m/z* calculated for $C_{14}H_{19}O$ [M+H]$^+$: 203.14304.

2-(But-3-en-1-yl)-2-(4-methoxyphenyl)tetrahydrofuran (S7a)



This compound was prepared according to General Procedure B.

Flash column chromatography eluent: 5% EA/Pet. Ether 40-60 to 10% EA/Pet. Ether 40-60

R$_f$ = 0.77 (50% EA/Pet. Ether 40-60)

Yield: 88% (270 mg) from 330 mg of **S6a**

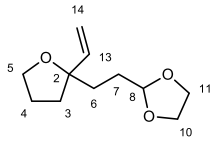
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.18 (m, 2H, **H7**, **H11**), 6.93 – 6.78 (m, 2H, **H8**, **H10**), 5.75 (ddt, *J* = 16.5, 10.2, 6.3 Hz, 1H, **H14**), 4.93 (dq, *J* = 17.2, 1.7 Hz, 1H, **H15'**), 4.86 (ddd, *J* = 10.2, 2.1, 1.3 Hz, 1H, **H15**), 3.95 (q, *J* = 8.1, 7.0 Hz, 1H, **H5'**), 3.87 (td, *J* = 8.1, 5.5 Hz, 1H, **H5**), 3.80 (s, 3H, **H17**), 2.16 (ddd, *J* = 12.2, 8.0, 4.7 Hz, 1H, **H12'**), 2.09 – 2.03 (m, 1H, **H13'**), 2.03 – 1.97 (m, 1H, **H12**), 1.97 – 1.89 (m, 1H, **H4'**), 1.89 – 1.84 (m, 2H, **H3**), 1.84 – 1.80 (m, 1H, **H13**), 1.79 – 1.72 (m, 1H, **H4**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2 (**C9**), 139.1 (**C14**), 138.6 (**C6**), 126.5 (**C7**, **C11**), 114.1 (**C15**), 113.5 (**C8**, **C10**), 86.4 (**C2**), 67.5 (**C5**), 55.4 (**C17**), 41.8 (**C3**), 38.5 (**C12**), 29.0 (**C13**), 25.7 (**C4**).

IR (thin film, *υ*/cm^{-1}): 2937, 1611, 1509, 1244, 1053

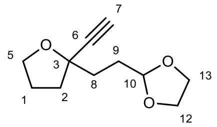
HRMS (ESI): Found 233.15367, *m/z* calculated for $C_{15}H_{21}O_2$ [M+H]$^+$: 233.15361.

2-(2-(2-Vinyltetrahydrofuran-2-yl)ethyl)-1,3-dioxolane (S7f)



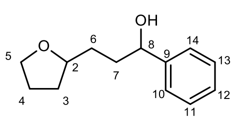
This compound was prepared according to General Procedure B.
Flash column chromatography eluent: 20% EA/Pet. Ether 40-60
R$_f$ = 0.60 (50% Acetone/Pet. Ether 40-60)
Yield: 71% (100 mg) from 154 mg of **S6f**
^{1}H NMR (500 MHz, CDCl$_3$) δ 5.76 (dd, *J* = 17.3, 10.7 Hz, 1H, **H13**), 5.18 (dd, *J* = 17.2, 1.8 Hz, 1H, **H14'**), 5.05 (dd, *J* = 10.6, 1.8 Hz, 1H, **H14**), 4.87 (t, *J* = 4.0 Hz, 1H, **H8**), 4.01 – 3.91 (m, 2H, **H11**), 3.88 – 3.77 (m, 4H, **H5**, **H10**), 1.91 – 1.79 (m, 3H, **H3'**, **H4**), 1.77 – 1.64 (m, 5H, **H3**, **H6**, **H7**).
^{13}C NMR (126 MHz, CDCl$_3$) δ 142.4 (**C13**), 112.9 (**C14**), 104.8 (**C8**), 84.8 (**C2**), 67.8 (**C5**), 65.0 (**C10**), 65.0 (**C11**), 35.9 (**C3**), 33.9 (**C6**), 29.1 (**C7**), 25.4 (**C4**).
IR (thin film, *υ*/cm^{-1}): 2960, 2873, 1403, 1311, 1034
HRMS (ESI): Found 221.11504, *m/z* calculated for $C_{11}H_{18}O_3{}^{23}Na$ [M+Na]$^+$: 221.11482.

2-(2-(2-Ethynyltetrahydrofuran-2-yl)ethyl)-1,3-dioxolane (S7b)



This compound was prepared according to General Procedures B.
Flash column chromatography eluent: 20% EA/Pet. Ether 40-60
R$_f$ = 0.32 (20% EA/Pet. Ether 40-60)
Yield: 97% (305 mg) from 344 mg of **S6b**
^{1}H NMR (400 MHz, CDCl$_3$) δ 4.96 – 4.89 (m, 1H, **H10**), 4.00 – 3.93 (m, 3H, **H5'**, **H12**), 3.93 – 3.89 (m, 1H, **H5**), 3.88 – 3.83 (m, 2H, **H13**), 2.42 (s, 1H, **H7**), 2.19 (ddd, *J* = 11.7, 8.2, 4.0 Hz, 1H, **H2'**), 2.15 – 2.06 (m, 1H, **H1'**), 2.03 – 1.95 (m, 1H, **H9'**), 1.95 – 1.92 (m, 1H, **H1**), 1.91 – 1.85 (m, 2H, **H8**, **H9**), 1.85 – 1.76 (m, 2H, **H2**, **H8**).
^{13}C NMR (101 MHz, CDCl$_3$) δ 104.4 (**C10**), 86.0 (**C6**), 79.0 (**C3**), 72.2 (**C7**), 67.8 (**C5**), 65.1 (**C12**, **C13**), 38.9 (**C2**), 34.8 (**C8**), 29.9 (**C9**), 25.5 (**C1**).
IR (thin film, *υ*/cm^{-1}): 3264, 2961, 1448, 1135, 1029
HRMS (ESI): Found 219.09932, *m/z* calculated for $C_{11}H_{16}O_3{}^{23}Na$ [M+Na]$^+$: 219.09917.

1-Phenyl-3-(tetrahydrofuran-2-yl)propan-1-ol (S8b/S8b')



This compound was prepared according to General Procedures B, C and then E.
Flash column chromatography eluent: 40% EA/Pet. Ether 40-60
R$_f$ = 0.46 (40% EA/Pet. Ether 40-60)
Yield: 21% (130 mg) from 430 mg of **S6d**
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.47 – 7.29 (m, 4H, **H10**, **H11**, **H13**, **H14**), 7.30 – 7.19 (m, 1H, **H12**), 4.84 – 4.61 (m, 1H, **H8**), 3.97 – 3.80 (m, 2H, **H2**, **H5'**), 3.80 – 3.64 (m, 1H, **H5**), 3.43 – 2.69 (m, 1H,

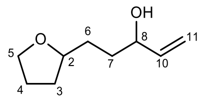
OH), 2.03 – 1.93 (m, 1H, **H3’**), 1.93 – 1.80 (m, 4H, **H4**, **H7**), 1.73 – 1.52 (m, 2H, **H6**), 1.51 – 1.39 (m, 1H, **H3**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.2 (**C9**), 145.0 (**C9**), 128.5 (**C11**, **C13**), 127.4 (**C12**), 126.0 (**C10**, **C14**), 125.9 (**C10**, **C14**), 79.7 (**C2**), 79.5 (**C2**), 74.7 (**C8**), 74.1 (**C8**), 68.0 (**C5**), 67.9 (**C5**), 37.0 (**C7**), 36.1 (**C7**), 32.7 (**C6**), 31.7 (**C6**), 31.5 (**C3**), 31.5 (**C3**), 25.8 (**C4**).

IR (thin film, *υ*/cm^{-1}): 3395, 2945, 1452, 1055

HRMS (ESI): Found 189.1275, *m/z* calculated for $C_{13}H_{17}O^+$ [M-OH]$^+$: 189.1274.

5-(Tetrahydrofuran-2-yl)pent-1-en-3-ol (S8a)



This compound was prepared according to General Procedures B, C and then E.

Flash column chromatography eluent: 20% EA/Pet. Ether 40-60 to 40% EA/Pet. Ether 40-60

R_f = 0.40 (50% EA/Pet. Ether 40-60)

Yield: 24% (52 mg) from 200 mg of **S6d**

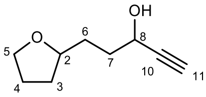
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 – 5.58 (m, 1H, **H10**), 5.42 – 5.16 (m, 1H, **H11’**), 5.16 – 4.96 (m, 1H, **H11**), 4.23 – 4.01 (m, 1H, **H8**), 3.96 – 3.78 (m, 2H, **H2**, **H5’**), 3.78 – 3.56 (m, 1H, **H5**), 3.08 – 2.41 (m, 1H, **OH**), 2.04 – 1.93 (m, 1H, **H3’**), 1.93 – 1.79 (m, 2H, **H4**), 1.76 – 1.56 (m, 4H, **H6**, **H7**), 1.56 – 1.37 (m, 1H, **H3**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4 (**C10**), 141.3 (**C10**), 114.5 (**C11**), 114.3 (**C11**), 79.6 (**C2**), 79.5 (**C2**), 73.1 (**C8**), 72.7 (**C8**), 67.9 (**C5**), 67.9 (**C5**), 34.5 (**C7**), 34.0 (**C7**), 32.1 (**C6**), 31.6 (**C3**), 31.6 (**C3**), 31.2 (**C6**), 25.8 (**C4**).

IR (thin film, *υ*/cm^{-1}): 3397, 2944, 1425, 1053

HRMS (ESI): Found 139.1117, *m/z* calculated for $C_9H_{15}O^+$ [M-OH]$^+$: 139.1117.

5-(Tetrahydrofuran-2-yl)pent-1-yn-3-ol (S8c)



This compound was prepared according to General Procedures B, C and then E.

Flash column chromatography eluent: 40% EA/Pet. Ether 40-60 to 60% EA/Pet. Ether 40-60

R_f = 0.37 (60% EA/Pet. Ether 40-60)

Yield: 38% (174 mg) from 430 mg of **S6d**

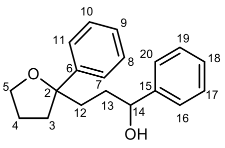
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 – 4.34 (m, 1H, **H8**), 3.95 – 3.80 (m, 2H, **H2**, **H5’**), 3.80 – 3.66 (m, 1H, **H5**), 3.27 – 3.12 (m, 1H, **H9**), 2.44 (m, 1H, **H11**), 2.07 – 1.94 (m, 1H, **H3’**), 1.93 – 1.83 (m, 4H, **H4**, **H7**), 1.83 – 1.75 (m, 1H, **H6’**), 1.73 – 1.61 (m, 1H, **H6**), 1.56 – 1.43 (m, 1H, **H3**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 85.1 (**C10**), 85.1 (**C10**), 79.4 (**C2**), 79.1 (**C2**), 72.8 (**C11**), 72.6 (**C11**), 68.0 (**C5**), 67.9 (**C5**), 62.4 (**C8**), 61.9 (**C8**), 34.9 (**C7**), 34.8 (**C7**), 31.7 (**C3**), 31.5 (**C6**), 31.4 (**C3**), 30.8 (**C6**), 25.8 (**C4**), 25.8 (**C4**).

IR (thin film, *υ*/cm^{-1}): 3365, 3288, 2950, 2111, 1029

HRMS (ESI): Found 137.0960, *m/z* calculated for $C_9H_{13}O^+$ [M-OH]$^+$: 137.0961.

1-Phenyl-3-(2-phenyltetrahydrofuran-2-yl)propan-1-ol (S8l)



This compound was prepared according to General Procedures C and then E.

Flash column chromatography eluent: 30% EA/Pet. Ether 40-60

R$_f$ = 0.43 (40% EA/Pet. Ether 40-60)

Yield: 61% (64 mg) from 76 mg of **S7e**

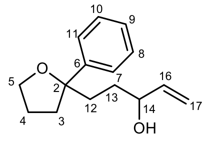
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.29 (m, 4H, **H7**, **H8**, **H10**, **H11**), 7.31 – 7.22 (m, 4H, **H16**, **H17**, **H19**, **H20**), 7.24 – 7.15 (m, 2H, **H9**, **H18**), 4.65 (dt, *J* = 8.4, 4.4 Hz, 0.5H, **H14**), 4.58 (ddd, *J* = 8.0, 4.5, 3.0 Hz, 0.5H, **H14**), 4.07 – 3.85 (m, 2H, **H5**), 3.18 – 2.74 (m, 1H, **OH**), 2.22 – 2.12 (m, 1H, **H3'**), 2.08 – 2.00 (m, 1H, **H3**), 2.00 – 1.95 (m, 1H, **H12'**), 1.95 – 1.87 (m, 1H, **H4'**), 1.87 – 1.80 (m, 1H, **H12**), 1.79 – 1.74 (m, 1H, **H4**), 1.73 – 1.66 (m, 1H, **H13'**), 1.61 – 1.52 (m, 1H, **H13**).

^{13}C NMR (101 MHz, CDCl$_3$) δ 146.4 (**C6**), 146.3 (**C6**), 145.1 (**C15**), 145.0 (**C15**), 128.4 (**C17**), 128.4 (**C17**), 128.2 (**C8**), 127.4 (**C18**), 127.2 (**C18**), 126.5 (**C9**), 126.0 (**C16**), 125.9 (**C16**), 125.4 (**C7**), 125.4 (**C7**), 86.9 (**C2**), 86.9 (**C2**), 74.9 (**C14**), 73.9 (**C14**), 68.0 (**C5**), 39.1 (**C3**), 39.1 (**C3**), 38.1 (**C12**), 34.3 (**C13**), 34.0 (**C13**), 25.7 (**C4**), 25.6 (**C4**).

IR (thin film, *υ*/cm^{-1}): 3404, 2949, 1446, 1028, 699

HRMS (ESI): Found 305.15121, *m/z* calculated for $C_{19}H_{22}O_2{}^{23}Na$ [M+Na]$^+$: 305.15120. Also ionized as [M-OH]$^+$: Found 265.15887, *m/z* calculated for $C_{19}H_{21}O$ [M-OH]$^+$: 265.15869.

5-(2-Phenyltetrahydrofuran-2-yl)pent-1-en-3-ol (S8m)



This compound was prepared according to General Procedures C and then E.

Flash column chromatography eluent: 20% EA/Pet. Ether 40-60

R$_f$ = 0.27 (20% EA/Pet. Ether 40-60)

Yield: 60% (386 mg) from 560 mg of **S7e**

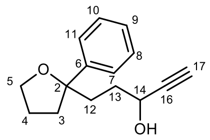
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.41 – 7.29 (m, 4H, **H7**, **H8**, **H10**, **H11**), 7.26 – 7.16 (m, 1H, **H9**), 5.94 – 5.65 (m, 1H, **H16**), 5.23 – 5.12 (m, 1H, **H17'**), 5.12 – 4.87 (m, 1H, **H17**), 4.17 – 3.97 (m, 2H, **H5'**, **H14**), 3.97 – 3.79 (m, 1H, **H5**), 2.63 – 2.36 (m, 1H, **OH**), 2.25 – 2.14 (m, 1H, **H3'**), 2.12 – 2.05 (m, 1H, **H3**), 2.04 – 1.99 (m, 0.5H, **12'**), 1.99 – 1.92 (m, 2H, **H4'**, **H12'**, **H12**), 1.91 – 1.85 (m, 0.5H, **H12**), 1.83 – 1.72 (m, 1H, **H4**), 1.56 – 1.50 (m, 0.5H, **H13'**), 1.50 – 1.42 (m, 0.5H, **H13'**), 1.42 – 1.36 (m, 0.5H, **H13**), 1.36 – 1.28 (m, 0.5H, **H13**).

^{13}C NMR (126 MHz, CDCl$_3$) δ 146.5 (**C6**), 146.3 (**C6**), 141.3 (**C16**), 141.3 (**C16**), 128.2 (**C8**, **C10**), 126.5 (**C9**), 125.4 (**C7**, **C11**), 114.4 (**C17**), 114.3 (**C17**), 86.9 (**C2**), 86.8 (**C2**), 73.4 (**C14**), 72.6 (**C14**), 67.9 (**C5**), 67.9 (**C5**), 39.2 (**C3**), 39.0 (**C3**), 38.6 (**C12**), 37.8 (**C12**), 32.1 (**C13**), 31.9 (**C13**), 25.7 (**C4**), 25.6 (**C4**).

IR (thin film, *υ*/cm^{-1}): 3402, 2949, 1445, 1260, 1050, 702

HRMS (ESI): Found 255.13559, *m/z* calculated for $C_{15}H_{20}O_2{}^{23}Na$ [M+Na]$^+$: 255.13555.

5-(2-Phenyltetrahydrofuran-2-yl)pent-1-yn-3-ol (S8s)



This compound was prepared according to General Procedures C and then E.

Flash column chromatography eluent: 20% EA/Pet. Ether 40-60 to 30% EA/Pet. Ether 40-60

R_f = 0.25 (20% EA/Pet. Ether 40-60)

Yield: 37% (26 mg) from 65 mg of **S7e** (Note: Oxidative cleavage in this case was carried out with cat. $RuCl_3$, $NaIO_4$ in $MeCN/H_2O$, according to Yang's procedure[5]).

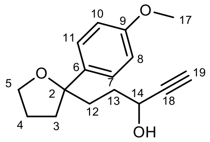
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 4H, **H7**, **H8**, **H10**, **H11**), 7.24 – 7.18 (m, 1H, **H9**), 4.39 – 4.29 (m, 1H, **H14**), 4.08 – 4.02 (m, 0.5H, **H5'**), 4.02 – 3.96 (m, 1H, **H5'**, **H5**), 3.96 – 3.89 (m, 0.5H, **H5**), 3.60 (d, *J* = 7.1 Hz, 0.5H, **OH**), 2.89 (dt, *J* = 5.2, 1.5 Hz, 0.5H, **OH**), 2.42 (d, *J* = 2.1 Hz, 0.5H, **H17**), 2.39 (d, *J* = 2.1 Hz, 0.5H, **H17**), 2.23 – 2.17 (m, 1H, **H3'**), 2.17 – 2.13 (m, 0.5H, **H12'**), 2.13 – 2.09 (m, 1H, **H3**, **H12'**), 2.09 – 2.04 (m, 1H, **H3**, **H12**), 2.00 – 1.92 (m, 1.5H, **H4'**, **H12**), 1.84 – 1.76 (m, 1H, **H4**), 1.76 – 1.69 (m, 0.5H, **13'**), 1.69 – 1.64 (m, 0.5H, **13'**), 1.63 – 1.53 (m, 1H, **13**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2 (**C6**), 145.8 (**C6**), 128.3 (**C8**, **C10**), 126.6 (**C9**), 125.4 (**C7**, **C11**), 86.7 (**C2**), 86.6 (**C2**), 85.2 (**C16**), 85.1 (**C16**), 72.7 (**C17**), 72.6 (**C17**), 68.1 (**C5**), 67.9 (**C5**), 62.6 (**C14**), 61.9 (**C14**), 39.7 (**C3**), 38.9 (**C3**), 38.2 (**C12**), 37.3 (**C12**), 32.9 (**C13**), 32.2 (**C13**), 25.6 (**C4**), 25.6 (**C4**).

IR (thin film, *υ*/cm^{-1}): 3386, 3287, 2955, 1445, 1030

HRMS (ESI): Found 253.12004, *m/z* calculated for $C_{15}H_{18}O_2{}^{23}Na$ $[M+Na]^+$: 253.11990. Also ionized as $[M-OH]^+$: Found 213.12758, *m/z* calculated for $C_{15}H_{27}O$ $[M-OH]^+$: 213.12739.

5-(2-(4-Methoxyphenyl)tetrahydrofuran-2-yl)pent-1-yn-3-ol (S8v)



This compound was prepared according to General Procedures C and then E.

Flash column chromatography eluent: 30% EA/Pet. Ether 40-60

R_f = 0.31 (20% EA/Pet. Ether 40-60)

Yield: 55% (37 mg) from 60 mg of **S7a**

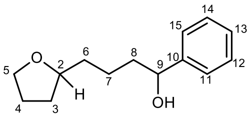
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 2H, **H7, H11**), 6.90 – 6.82 (m, 2H, **H8**, **H10**), 4.39 – 4.25 (m, 1H, **H14**), 4.08 – 3.97 (m, 1H, **H5'**), 3.97 – 3.87 (m, 1H, **H5**), 3.80 (s, 3H, **H17**), 3.67 – 2.84 (m, 1H, **OH**), 2.46 – 2.34 (m, 1H, **H19**), 2.21 – 2.11 (m, 1.5H, **H3'**, **H12'**), 2.11 – 2.01 (m, 2H, **H3**, **H12'**, **H12**), 2.01 – 1.90 (m, 1.5H, **H4'**, **H12**), 1.87 – 1.75 (m, 1H, **H4**), 1.74 – 1.68 (m, 0.5H, **H13'**), 1.67 – 1.62 (m, 0.5H, **H13'**), 1.62 – 1.57 (m, 1H, **H13**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4 (**C9**), 138.2 (**C6**), 137.8 (**C6**), 126.5 (**C11**), 113.7 (**C10**), 86.5 (**C2**), 86.4 (**C2**), 85.3 (**C18**), 85.2 (**C18**), 72.7 (**C19**), 72.6 (**C19**), 68.0 (**C5**), 67.8 (**C5**), 62.6 (**C14**), 61.9 (**C14**), 55.4 (**C17**), 39.7 (**C3**), 38.9 (**C3**), 38.3 (**C12**), 37.4 (**C12**), 33.0 (**C13**), 32.3 (**C13**), 25.6 (**C4**).

IR (thin film, *υ*/cm^{-1}): 3394, 3285, 1610, 1509, 1245, 1033, 832

HRMS (ESI): Found 261.14871, *m/z* calculated for $C_{16}H_{21}O_3$ $[M+H]^+$: 261.14852.

1-Phenyl-4-(tetrahydrofuran-2-yl)butan-1-ol (S8f)



This compound was prepared according to General Procedures B, C and then E.

Flash column chromatography eluent: 30% EA/Pet. Ether 40-60

R$_f$ = 0.40 (40% EA/Pet. Ether 40-60)

Yield: 41% (120 mg) from 210 mg of **S6c**

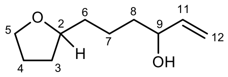
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38 – 7.31 (m, 4H, **H11**, **H12**, **H14**, **H15**), 7.27 (m, 1H, **H13**), 4.76 – 4.61 (m, 1H, **H9**), 3.89 – 3.80 (m, 1H, **H5'**), 3.81 – 3.73 (m, 1H, **H2**), 3.73 – 3.62 (m, 1H, **H5**), 1.99 – 1.91 (m, 1H, **H3'**), 1.91 – 1.79 (m, 2H, **H4'**, **H8'**), 1.79 – 1.70 (m, 1H, **H8**), 1.65 – 1.57 (m, 1H, **H6'**), 1.56 – 1.45 (m, 2H, **H6**, **H7'**), 1.44 – 1.30 (m, 2H, **H3**, **H7**).

^{13}C NMR (101 MHz, CDCl$_3$) δ 145.0 (**C10**), 145.0 (**C10**), 128.6 (**C12**, **C14**), 127.6 (**C13**), 126.0 (**C11**, **C15**), 79.4 (**C2**), 79.4 (**C2**), 74.7 (**C9**), 74.7 (**C9**), 67.8 (**C5**), 39.3 (**C8**), 39.2 (**C8**), 35.6 (**C6**), 35.6 (**C6**), 31.5 (**C3**), 31.5 (**C3**), 25.8 (**C4**), 23.0 (**C7**), 22.8 (**C7**).

IR (thin film, υ/cm^{-1}): 3403, 2931, 1453, 1028, 699

HRMS (ESI): Found 243.13568, *m/z* calculated for $C_{14}H_{20}O_2{}^{23}Na$ [M+Na]$^+$: 243.13555. Also ionized as [M-OH]$^+$: Found 203.14313, *m/z* calculated for $C_{14}H_{19}O$ [M-OH]$^+$: 203.14304.

6-(Tetrahydrofuran-2-yl)hex-1-en-3-ol (S8e)



This compound was prepared according to General Procedures B, C and then E.

Flash column chromatography eluent: 40% EA/Pet. Ether 40-60

R$_f$ = 0.31 (40% EA/Pet. Ether 40-60)

Yield: 33% (74 mg) from 210 mg of **S6c**

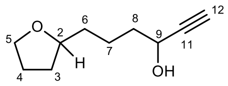
^{1}H NMR (400 MHz, CDCl$_3$) δ 5.96 – 5.70 (m, 1H, **H11**), 5.35 – 5.16 (m, 1H, **H12'**), 5.16 – 5.01 (m, 1H, **H12**), 4.23 – 4.03 (m, 1H, **H9**), 3.93 – 3.82 (m, 1H, **H5'**), 3.82 – 3.75 (m, 1H, **H2**), 3.75 – 3.64 (m, 1H, **H5**), 2.02 – 1.91 (m, 1H, **H3'**), 1.91 – 1.78 (m, 2H, **H4**), 1.74 – 1.64 (m, 1H, **OH**), 1.64 – 1.48 (m, 5H, **H6**, **H7'**, **H8**), 1.48 – 1.31 (m, 2H, **H3**, **H7**).

^{13}C NMR (101 MHz, CDCl$_3$) δ 141.4 (**C11**), 141.3 (**C11**), 114.8 (**C12**), 114.8 (**C12**), 79.5 (**C2**), 79.4 (**C2**), 73.3 (**C9**), 73.2 (**C9**), 67.8 (**C5**), 37.2 (**C8**), 37.1 (**C8**), 35.6 (**C6**), 35.6 (**C6**), 31.5 (**C3**), 31.5 (**C3**), 25.8 (**C4**), 22.4 (**C7**), 22.2 (**C7**).

IR (thin film, υ/cm^{-1}): 3406, 2935, 1644, 1459, 1065

HRMS (ESI): Found 171.13806, *m/z* calculated for $C_{10}H_{19}O_2$ [M+H]$^+$: 171.13796. Also ionized as [M-OH]$^+$: Found 153.12729, *m/z* calculated for $C_{10}H_{17}O$ [M-OH]$^+$: 153.12739.

6-(Tetrahydrofuran-2-yl)hex-1-yn-3-ol (S8g)



This compound was prepared according to General Procedures B, C and then E.

Flash column chromatography eluent: 30% EA/Pet. Ether 40-60

R$_f$ = 0.37 (40% EA/Pet. Ether 40-60)

Yield: 45% (100 mg) from 210 mg of **S6c**

^{1}H NMR (400 MHz, CDCl$_3$) δ 4.46 – 4.28 (m, 1H, **H9**), 3.95 – 3.81 (m, 1H, **H5'**), 3.83 – 3.75 (m, 1H, **H2**), 3.75 – 3.57 (m, 1H, **H5**), 2.55 – 2.32 (m, 1H, **H12**), 2.24 – 2.04 (m, 1H, **OH**), 2.04 – 1.94 (m, 1H, **H3'**), 1.94 – 1.83 (m, 2H, **H4**), 1.83 – 1.69 (m, 2H, **H8**), 1.66 – 1.50 (m, 4H, **H6**, **H7**), 1.50

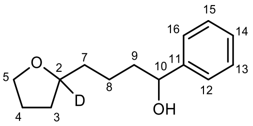
– 1.36 (m, 1H, **H3**).

^{13}C NMR (101 MHz, CDCl$_3$) δ 85.1 (**C11**), 79.4 (**C2**), 73.0 (**C12**), 72.9 (**C12**), 67.8 (**C5**), 62.3 (**C9**), 62.3 (**C9**), 37.7 (**C8**), 37.7 (**C8**), 35.2 (**C6**), 31.5 (**C3**), 31.5 (**C3**), 25.8 (**C4**), 22.1 (**C7**), 22.0 (**C7**).

IR (thin film, υ/cm^{-1}): 3362, 3288, 2942, 1460, 1036

HRMS (ESI): Found 191.10434, *m/z* calculated for $C_{10}H_{16}O_2{}^{23}Na$ [M+Na]$^+$: 191.10425. Also ionized as [M-OH]$^+$: Found 151.11172, *m/z* calculated for $C_{10}H_{15}O$ [M-OH]$^+$: 151.11174.

1-Phenyl-4-(tetrahydrofuran-2-yl-2-*d*)butan-1-ol (S8f-*d*)



This compound was prepared according to General Procedures B, C and then E.

Flash column chromatography eluent: 30% EA/Pet. Ether 40-60

R$_f$ = 0.33 (30% EA/Pet. Ether 40-60)

Yield: 58% (100 mg) from 250 mg of **S6c**-*d*

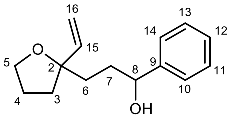
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.28 – 7.24 (m, 4H, **H12**, **H13**, **H15**, **H16**), 7.22 – 7.16 (m, 1H, **H14**), 4.62 – 4.53 (m, 1H, **H10**), 3.79 – 3.70 (m, 1H, **H5'**), 3.64 – 3.56 (m, 1H, **H5**), 2.32 – 2.13 (m, 1H, **OH**), 1.91 – 1.82 (m, 1H, **H3'**), 1.82 – 1.70 (m, 3H, **H4**, **H9'**), 1.70 – 1.60 (m, 1H, **H9**), 1.56 – 1.49 (m, 1H, **H7'**), 1.49 – 1.44 (m, 0.5H, **H8'**), 1.44 – 1.37 (m, 1.5H, **H7**, **H8'**), 1.37 – 1.29 (m, 1.5H, **H3**, **H8**), 1.29 – 1.20 (m, 0.5H, **H8**).

^{13}C NMR (101 MHz, CDCl$_3$) δ 145.1 (**C11**), 145.0 (**C11**), 128.5 (**C13**, **C15**), 127.5 (**C14**), 126.0 (**C12**, **C16**), 79.4 (**C2-protiated**), 79.4 (**C2-protiated**), 78.9 (1:1:1 triplet, $J_{C\text{-}D}$ = 21 Hz, **C2-deuterated**), 78.9 (1:1:1 triplet, $J_{C\text{-}D}$ = 21 Hz, **C2-deuterated**), 74.5 (**C10**), 74.5 (**C10**), 67.7 (**C5**), 39.3 (**C9**), 39.2 (**C9**), 35.4 (**C7**), 35.4 (**C7**), 31.4 (**C3**), 31.3 (**C3**), 25.8 (**C4**), 22.9 (**C8**), 22.7 (**C8**).

IR (thin film, υ/cm^{-1}): 3405, 2936, 1453, 1043, 699

HRMS (ESI): Found 244.1420, *m/z* calculated for $C_{14}H_{19}DO_2{}^{23}Na$ [M+Na]$^+$: 244.1418.

1-Phenyl-3-(2-vinyltetrahydrofuran-2-yl)propan-1-ol (S8n)



This compound was prepared according to General Procedures D and then E.

Flash column chromatography eluent: 20% EA/Pet. Ether 40-60 to 40% EA/Pet. Ether 40-60

R$_f$ = 0.46 (30% EA/Pet. Ether 40-60)

Yield: 67% (39 mg) from 50 mg of **S7f**

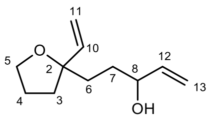
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.37 – 7.29 (m, 4H, **H10**, **H11**, **H13**, **H14**), 7.28 – 7.21 (m, 1H, **H12**), 5.73 (ddd, *J* = 17.4, 10.7, 7.0 Hz, 1H, **H15**), 5.20 (dt, *J* = 17.2, 1.5 Hz, 1H, **H16'**), 5.08 (dd, *J* = 10.6, 1.7 Hz, 1H, **H16**), 4.73 (dt, *J* = 7.7, 4.4 Hz, 0.5H, **H8'**), 4.65 (dt, *J* = 8.5, 3.4 Hz, 0.5H, **H8**), 3.99 – 3.73 (m, 2H, **H5**), 3.30 – 2.80 (m, 1H, **OH**), 1.92 – 1.81 (m, 4H, **H3'**, **H4**, **H7'**), 1.81 – 1.73 (m, 2H, **H6'**, **H7**), 1.73 – 1.66 (m, 1.5H, **H3**, **H6**), 1.66 – 1.60 (m, 0.5H, **H6**).

^{13}C NMR (126 MHz, CDCl$_3$) δ 145.3 (**C9**), 145.1 (**C9**), 142.2 (**C15**), 142.1 (**C15**), 128.5 (**C11**, **C13**), 128.4 (**C11**, **C13**), 127.4 (**C12**), 127.3 (**C12**), 126.0 (**C10**, **C14**), 125.9 (**C10**, **C14**), 113.3 (**C16**), 113.1 (**C16**), 85.3 (**C2**), 75.0 (**C8**), 74.0 (**C8**), 68.1 (**C5**), 68.1 (**C5**), 36.8 (**C6**), 36.5 (**C3**), 36.4 (**C3**), 35.6 (**C6**), 34.4 (**C7**), 34.0 (**C7**), 25.3 (**C4**), 25.2 (**C4**).

IR (thin film, υ/cm^{-1}): 3397, 1948, 1452, 1039, 699

HRMS (ESI): Found 255.13562, *m/z* calculated for $C_{15}H_{20}O_2{}^{23}Na$ [M+Na]$^+$: 255.13555. Also ionized as [M-OH]$^+$: Found 215.14320, *m/z* calculated for $C_{15}H_{19}O$ [M-OH]$^+$: 215.14304.

5-(2-Vinyltetrahydrofuran-2-yl)pent-1-en-3-ol (S8k)



This compound was prepared according to General Procedures D and then E.

Flash column chromatography eluent: 20% EA/Pet. Ether 40-60 to 40% EA/Pet. Ether 40-60

R_f = 0.46 (30% EA/Pet. Ether 40-60)

Yield: 55% (25 mg) from 50 mg of **S7f**

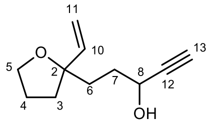
^{1}H NMR (500 MHz, CDCl$_3$) δ 5.93 – 5.79 (m, 1H, **H12**), 5.79 – 5.60 (m, 1H, **H10**), 5.26 – 5.12 (m, 2H, **H11’**, **H13’**), 5.12 – 4.99 (m, 2H, **H11**, **H13**), 4.21 – 4.00 (m, 1H, **H8**), 4.00 – 3.81 (m, 2H, **H5**), 2.86 – 2.40 (m, 1H, **OH**), 1.92 – 1.81 (m, 3H, **H3’**, **H4**), 1.77 – 1.69 (m, 3H, **H3**, **H6**), 1.69 – 1.64 (m, 0.5H, **H7’**), 1.63 – 1.57 (m, 1H, **H7’**, **H7**), 1.56 – 1.51 (m, 0.5H, **H7**).

^{13}C NMR (126 MHz, CDCl$_3$) δ 142.2 (**C10**), 142.1 (**C10**), 141.4 (**C12**), 141.3 (**C12**), 114.4 (**C13**), 114.3 (**C13**), 113.2 (**C11**), 113.1 (**C11**), 85.2 (**C2**), 85.2 (**C2**), 73.5 (**C8**), 72.6 (**C8**), 68.0 (**C5**), 36.5 (**C3**), 36.4 (**C3**), 36.3 (**C6**), 35.3 (**C6**), 32.1 (**C7**), 31.8 (**C7**), 25.3 (**C4**), 25.2 (**C4**).

IR (thin film, *υ*/cm^{-1}): 3406, 2923, 1456, 1041

HRMS (ESI): Found 205.12012, *m/z* calculated for $C_{11}H_{18}O_2{}^{23}Na$ [M+Na]$^+$: 205.11990. Also ionized as [M-OH]$^+$: Found 165.12741, *m/z* calculated for $C_{11}H_{17}O$ [M-OH]$^+$: 165.12739.

5-(2-Vinyltetrahydrofuran-2-yl)pent-1-yn-3-ol (S8u)



This compound was prepared according to General Procedures D and then E.

Flash column chromatography eluent: 20% EA/Pet. Ether 40-60 to 40% EA/Pet. Ether 40-60

R_f = 0.46 (30% EA/Pet. Ether 40-60)

Yield: 62% (31 mg) from 55 mg of **S7f**

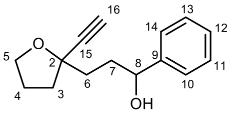
^{1}H NMR (400 MHz, CDCl$_3$) δ 5.74 (dd, *J* = 17.2, 10.6 Hz, 0.5H, **H10**), 5.74 (dd, *J* = 17.2, 10.7 Hz, 0.5H, **H10**), 5.20 (dd, *J* = 17.2, 1.7 Hz, 1H, **H11’**, **H11**), 5.10 (dd, *J* = 10.6, 1.7 Hz, 0.5H, **H11’**), 5.09 (dd, *J* = 10.7, 1.6 Hz, 0.5H, **H11**), 4.44 (dddd, *J* = 7.6, 6.2, 4.5, 2.0 Hz, 0.5H, **H8**), 4.38 (tdd, *J* = 6.8, 4.7, 1.8 Hz, 0.5H, **H8**), 3.98 – 3.81 (m, 2H, **H5**), 3.78 – 2.88 (m, 1H, **OH**), 2.52 – 2.34 (m, 1H, **H13**), 1.99 – 1.93 (m, 0.5H, **H6’**), 1.92 – 1.81 (m, 4.5H, **H3’**, **H4**, **H6’**, **H7’**), 1.80 – 1.70 (m, 3H, **H3**, **H6**, **H7**).

^{13}C NMR (101 MHz, CDCl$_3$) δ 142.0 (**C10**), 141.7 (**C10**), 113.6 (**C11**), 113.4 (**C11**), 85.2 (**C2**), 85.0 (**C12**), 85.0 (**C12**), 72.7 (**C13**), 72.6 (**C13**), 68.2 (**C5**), 68.0 (**C5**), 62.7 (**C8**), 61.9 (**C8**), 37.1 (**C3**), 36.3 (**C3**), 35.7 (**C6**), 34.9 (**C6**), 32.8 (**C7**), 32.1 (**C7**), 25.3 (**C4**), 25.2 (**C4**).

IR (thin film, *υ*/cm^{-1}): 3373, 3297, 1404, 1037

HRMS (ESI): Found 203.10440, *m/z* calculated for $C_{11}H_{16}O_2{}^{23}Na$ [M+Na]$^+$: 203.10425. Also ionized as [M-OH]$^+$: Found 163.11183, *m/z* calculated for $C_{11}H_{15}O$ [M-OH]$^+$: 163.11174.

3-(2-Ethynyltetrahydrofuran-2-yl)-1-phenylpropan-1-ol (S8w)



This compound was prepared according to General Procedures D and then E.

Flash column chromatography eluent: 20% EA/Pet. Ether 40-60 to 40% EA/Pet. Ether 40-60

R$_f$ = 0.46 (40% EA/Pet. Ether 40-60)

Yield: 55% (25 mg) from 40 mg of **S7b**

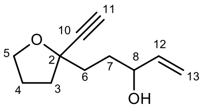
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.41 – 7.30 (m, 4H, **H10**, **H11**, **H13**, **H14**), 7.30 – 7.22 (m, 1H, **H12**), 4.80 (dt, *J* = 8.3, 4.2 Hz, 0.5H, **H8**), 4.72 (dt, *J* = 8.1, 4.1 Hz, 0.5H, **H8**), 4.01 – 3.95 (m, 1H, **H5’**), 3.95 – 3.86 (m, 1H, **H5**), 2.56 (d, *J* = 3.4 Hz, 0.5H, **OH**), 2.43 (s, 1H, **H16**), 2.41 – 2.38 (m, 1H, **OH**), 2.19 (dddd, *J* = 11.8, 8.2, 3.9, 1.5 Hz, 1H, **H6’**), 2.16 – 2.06 (m, 2H, **H4**, **H7**), 2.01 – 1.92 (m, 2H, **H4**, **H7**), 1.92 – 1.86 (m, 1H, **H3’**), 1.83 – 1.73 (m, 2H, **H3**, **H6**).

^{13}C NMR (126 MHz, CDCl$_3$) δ 144.8 (**C9**), 144.8 (**C9**), 128.6 (**C13**), 128.6 (**C13**), 127.6 (**C12**), 127.5 (**C12**), 126.1 (**C14**), 126.0 (**C14**), 85.9 (**C15**), 85.8 (**C15**), 79.2 (**C2**), 79.2 (**C2**), 74.7 (**C8**), 73.9 (**C8**), 72.5 (**C16**), 67.9 (**C5**), 39.2 (**C6**), 39.1 (**C6**), 37.2 (**C3**), 36.5 (**C3**), 35.0 (**C7**), 34.8 (**C7**), 25.5 (**C4**), 25.4 (**C4**).

IR (thin film, *υ*/cm^{-1}): 3405, 3288, 2956, 1452, 1260, 1025

HRMS (ESI): Found 253.12003, *m/z* calculated for $C_{15}H_{18}O_2{}^{23}Na$ [M+Na]$^+$: 253.11990. Also ionized as [M-OH]$^+$: Found 213.12753, *m/z* calculated for $C_{15}H_{17}O$ [M-OH]$^+$: 213.12739.

5-(2-Ethynyltetrahydrofuran-2-yl)pent-1-en-3-ol (S8o)



This compound was prepared according to General Procedures D and then E.

Flash column chromatography eluent: 20% EA/Pet. Ether 40-60 to 40% EA/Pet. Ether 40-60

R$_f$ = 0.37 (40% EA/Pet. Ether 40-60)

Yield: 52% (30 mg) from 63 mg of **S7b**

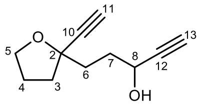
^{1}H NMR (500 MHz, CDCl$_3$) δ 6.02 – 5.74 (m, 1H, **H12**), 5.42 – 5.18 (m, 1H, **H13’**), 5.18 – 4.88 (m, 1H, **H13**), 4.31 – 4.08 (m, 1H, **H8**), 4.03 – 3.84 (m, 2H, **H5**), 2.56 – 2.33 (m, 1H, **H11**), 2.25 – 2.16 (m, 1H, **H3’**), 2.16 – 2.13 (m, 0.5H, **OH**), 2.14 – 2.05 (m, 1H, **H4’**), 2.06 – 2.02 (m, 0.5H, **OH**), 2.00 – 1.93 (m, 1H, **H4**), 1.92 – 1.87 (m, 1H, **H6’**, **H7’**), 1.86 – 1.77 (m, 3.5H, **H3**, **H6’**, **H6**, **H7’**, **H7**), 1.77 – 1.68 (m, 0.5H, **H7**).

^{13}C NMR (126 MHz, CDCl$_3$) δ 141.1 (**C12**), 114.8 (**C13**), 114.7 (**C13**), 86.0 (**C10**), 85.8 (**C10**), 79.2 (**C2**), 79.2 (**C2**), 73.1 (**C8**), 72.6 (**C8**), 72.4 (**C11**), 72.4 (**C11**), 67.9 (**C5**), 67.9 (**C5**), 39.2 (**C3**), 39.1 (**C3**), 36.7 (**C6**), 36.2 (**C6**), 32.8 (**C7**), 32.7 (**C7**), 25.5 (**C4**), 25.4 (**C4**).

IR (thin film, *υ*/cm^{-1}): 3403, 3293, 2953, 1445, 1034

HRMS (ESI): Found 203.10445, *m/z* calculated for $C_{11}H_{16}O_2{}^{23}Na$ [M+Na]$^+$: 203.10425. Also ionized as [M-OH]$^+$: Found 163.11171, *m/z* calculated for $C_{11}H_{15}O$ [M-OH]$^+$: 163.11174.

5-(2-Ethynyltetrahydrofuran-2-yl)pent-1-yn-3-ol (S8t)



This compound was prepared according to General Procedures D and then E.

Flash column chromatography eluent: 20% EA/Pet. Ether 40-60 to 40% EA/Pet. Ether 40-60

R$_f$ = 0.51 (40% EA/Pet. Ether 40-60)

Yield: 95% (17 mg) from 20 mg of **S7b**

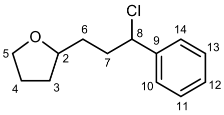
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.57 – 4.36 (m, 1H, **H8**), 4.06 – 3.85 (m, 2H, **H5**), 2.95 (d, *J* = 6.7 Hz, 0.5H, **OH**), 2.51 – 2.42 (m, 2H, **H11**, **H13**), 2.40 (d, *J* = 5.2 Hz, 0.5H, **OH**), 2.27 – 2.18 (m, 1H, **H3'**), 2.17 – 2.10 (m, 1.5H, **H4'**, **H7'**), 2.10 – 2.06 (m, 0.5H, **H7'**), 2.02 – 1.99 (m, 0.5H, **H6'**), 1.98 – 1.91 (m, 3.5H, **H4**, **H6'**, **H6**, **H7**), 1.87 – 1.80 (m, 1H, **H3**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 85.7 (**C10**), 85.4 (**C10**), 84.9 (**C12**), 84.8 (**C12**), 79.0 (**C2**), 78.9 (**C2**), 73.1 (**C13**), 73.0 (**C13**), 72.8 (**C11**), 72.6 (**C11**), 68.0 (**C5**), 67.9 (**C5**), 62.3 (**C8**), 61.8 (**C8**), 39.4 (**C3**), 39.1 (**C3**), 36.3 (**C6**), 35.7 (**C6**), 33.6 (**C7**), 33.3 (**C7**), 25.4 (**C4**), 25.4 (**C4**).

IR (thin film, υ/cm^{-1}): 3394, 3289, 2924, 1455, 1028

HRMS (ESI): Found 201.08880, *m/z* calculated for $C_{11}H_{14}O_2{}^{23}Na$ [M+Na]$^+$: 201.08860. Also ionized as [M-OH]$^+$: Found 161.09611, *m/z* calculated for $C_{11}H_{13}O$ [M-OH]$^+$: 161.09609.

2-(3-Chloro-3-phenylpropyl)tetrahydrofuran (23b/23b')



This compound was prepared according to General Procedures F.

Flash column chromatography eluent: 5% EA/Pet. Ether 40-60 to 10% EA/Pet. Ether 40-60

R$_f$ = 0.54 (10% EA/Pet. Ether 40-60)

Yield: 90% (187 mg) from 190 mg of **S8b**

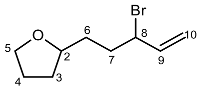
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 4H, **H10**, **H11**, **H13**, **H14**), 7.31 – 7.27 (m, 1H, **H12**), 5.00 – 4.83 (m, 1H, **H8**), 3.89 – 3.76 (m, 2H, **H2**, **H5'**), 3.75 – 3.66 (m, 1H, **H5**), 2.28 (dddd, *J* = 13.4, 10.6, 8.1, 4.8 Hz, 0.5H, **H7'**), 2.24 – 2.11 (m, 1H, **H7'**, **H7**), 2.11 – 2.05 (m, 0.5H, **H7'**), 2.02 – 1.93 (m, 1H, **H3'**), 1.92 – 1.80 (m, 2H, **H4**), 1.77 – 1.66 (m, 1H, **H6'**), 1.57 – 1.49 (m, 1H, **H6**), 1.48 – 1.40 (m, 1H, **H3**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.9 (**C9**), 141.9 (**C9**), 128.7 (**C11**, **C13**), 128.4 (**C12**), 127.1 (**C10**, **C14**), 127.1 (**C10**, **C14**), 78.9 (**C2**), 78.6 (**C2**), 67.9 (**C5**), 64.2 (**C8**), 63.8 (**C8**), 37.1 (**C7**), 36.9 (**C7**), 33.4 (**C6**), 33.1 (**C6**), 31.5 (**C3**), 31.5 (**C3**), 25.8 (**C4**), 25.8 (**C4**).

IR (thin film, υ/cm^{-1}): 2963, 1452, 1063, 697

HRMS (ESI): Ionized as [M-Cl]$^+$: Found 189.1275, *m/z* calculated for $C_{13}H_{17}O$ [M-Cl]$^+$: 189.1274.

2-(3-Bromopent-4-en-1-yl)tetrahydrofuran (23a)



This compound was prepared according to General Procedures F.

Flash column chromatography eluent: 5% EA/Pet. Ether 40-60 to 10% EA/Pet. Ether 40-60

R$_f$ = 0.34 (10% EA/Pet. Ether 40-60)

Yield: 61% (120 mg) from 141 mg of **S8a**

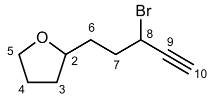
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.12 – 5.90 (m, 1H, **H9**), 5.27 – 5.16 (m, 1H, **H10'**), 5.11 – 4.93 (m, 1H, **H10**), 4.57 – 4.44 (m, 1H, **H8**), 3.89 – 3.83 (m, 1H, **H5'**), 3.83 – 3.76 (m, 1H, **H2**), 3.74 – 3.68 (m, 1H, **H5**), 2.14 – 2.04 (m, 1H, **H7'**), 2.04 – 1.94 (m, 2H, **H3'**, **H7**), 1.92 – 1.83 (m, 2H, **H4**), 1.73 – 1.64 (m, 1H, **H6'**), 1.63 – 1.57 (m, 1H, **H6**), 1.51 – 1.42 (m, 1H, **H3**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.5 (**C9**), 139.4 (**C9**), 116.5 (**C10**), 116.4 (**C10**), 78.8 (**C2**), 78.4 (**C2**), 67.9 (**C5**), 56.0 (**C8**), 55.6 (**C8**), 35.8 (**C7**), 35.5 (**C7**), 34.1 (**C6**), 33.7 (**C6**), 31.6 (**C3**), 31.5 (**C3**), 25.8 (**C4**), 25.8 (**C4**).

IR (thin film, υ/cm^{-1}): 2964, 1441, 1204, 1069

HRMS (ESI): Ionized as [M-Br]$^+$: Found 139.11171, *m/z* calculated for $C_9H_{15}O$ [M-Br]$^+$: 139.11174.

2-(3-Bromopent-4-yn-1-yl)tetrahydrofuran (23c)



This compound was prepared according to General Procedures F.

Flash column chromatography eluent: 5% EA/Pet. Ether 40-60 to 10% EA/Pet. Ether 40-60

R$_f$ = 0.69 (60% EA/Pet. Ether 40-60)

Yield: 40% (96 mg) from 174 mg of **S8c**

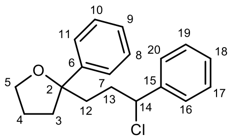
^{1}H NMR (400 MHz, CDCl$_3$) δ 4.62 – 4.49 (m, 1H, **H8**), 3.92 – 3.79 (m, 2H, **H2**, **H5'**), 3.76 – 3.65 (m, 1H, **H5**), 2.72 – 2.56 (m, 1H, **H10**), 2.26 – 2.13 (m, 1H, **H7'**), 2.12 – 2.04 (m, 1H, **H7**), 2.04 – 1.96 (m, 1H, **H3'**), 1.95 – 1.83 (m, 2H, **H4**), 1.80 – 1.70 (m, 2H, **H6**), 1.53 – 1.42 (m, 1H, **H3**).

^{13}C NMR (101 MHz, CDCl$_3$) δ 82.6 (**C9**), 78.4 (**C2**), 78.4 (**C2**), 75.2 (**C10**), 75.2 (**C10**), 67.9 (**C5**), 36.5 (**C7**), 36.5 (**C7**), 36.1 (**C8**), 35.9 (**C8**), 33.2 (**C6**), 33.2 (**C6**), 31.5 (**C3**), 31.5 (**C3**), 25.8 (**C4**).

IR (thin film, υ/cm^{-1}): 3291, 2944, 2114, 1443, 1064, 646

HRMS (ESI): Ionized as [M-Br]$^+$: Found 137.0961, *m/z* calculated for $C_9H_{13}O$ [M-Br]$^+$: 137.0961.

2-(3-Chloro-3-phenylpropyl)-2-phenyltetrahydrofuran (23l)



This compound was prepared according to General Procedures F.

Flash column chromatography eluent: 5% EA/Pet. Ether 40-60

R$_f$ = 0.57 (20% EA/Pet. Ether 40-60)

Yield: 86% (22 mg) from 24 mg of **S8l**

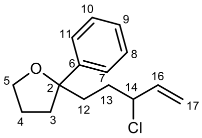
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35 – 7.29 (m, 6H, **H7**, **H8**, **H10**, **H11**, **H16**, **H20**), 7.29 – 7.26 (m, 3H, **H17**, **H18**, **H19**), 7.25 – 7.19 (m, 1H, **H9**), 4.80 (dd, *J* = 8.5, 5.4 Hz, 0.5H, **H14**), 4.72 (dd, *J* = 8.2, 6.3 Hz, 0.5H, **H14**), 3.99 – 3.84 (m, 2H, **H5**), 2.22 – 2.12 (m, 1.5H, **H3'**, **H13'**), 2.12 – 2.05 (m, 1H, **H12'**, **H13'**), 2.04 – 1.96 (m, 1.5H, **H3'**, **H12'**), 1.95 – 1.87 (m, 1H, **H4'**), 1.86 – 1.78 (m, 2H, **H12**, **H13**), 1.78 – 1.72 (m, 1H, **H4**).

^{13}C NMR (101 MHz, CDCl$_3$) δ 146.5 (**C6**), 146.3 (**C6**), 142.0 (**C15**), 141.9 (**C15**), 128.7 (**C17**), 128.7 (**C17**), 128.3 (**C8**), 128.3 (**C8**), 127.1 (**C18**), 127.1 (**C18**), 126.6 (**C9**), 125.4 (**C16**), 125.3 (**C7**), 86.4 (**C2**), 86.3 (**C2**), 67.8 (**C5**), 67.8 (**C5**), 64.4 (**C14**), 64.2 (**C14**), 39.8 (**C12**), 39.7 (**C12**), 39.2 (**C3**), 39.0 (**C3**), 35.1 (**C13**), 34.9 (**C13**), 25.6 (**C4**), 25.6 (**C4**).

IR (thin film, υ/cm^{-1}): 2959, 1446, 1261, 1028, 697

HRMS (ESI): Ionized as [M-Cl]$^+$: Found 265.15875, *m/z* calculated for $C_{19}H_{21}O$ [M-Cl]$^+$: 265.15869.

2-(3-Chloropent-4-en-1-yl)-2-phenyltetrahydrofuran (23m)



This compound was prepared according to General Procedures F.

Flash column chromatography eluent: 2% EA/Pet. Ether 40-60

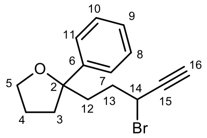
R$_f$ = 0.49 (10% EA/Pet. Ether 40-60)

Yield: 89% (26 mg) from 27 mg of **S8m**

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 – 7.29 (m, 4H, **H7**, **H8**, **H10**, **H11**), 7.26 – 7.19 (m, 1H, **H9**), 5.93 – 5.64 (m, 1H, **H16**), 5.30 – 5.12 (m, 1H, **H17'**), 5.12 – 4.96 (m, 1H, **H17**), 4.34 – 4.16 (m, 1H,

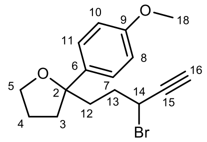
H14), 4.05 – 3.85 (m, 2H, **H5**), 2.29 – 2.12 (m, 1H, **H3'**), 2.12 – 2.01 (m, 1H, **H3**), 2.01 – 1.90 (m, 2H, **H4'**, **H12'**), 1.90 – 1.79 (m, 2H, **H12**, **H13'**), 1.79 – 1.71 (m, 1H, **H4**), 1.61 – 1.46 (m, 1H, **H13**).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5 (**C6**), 146.3 (**C6**), 138.8 (**C16**), 138.7 (**C16**), 128.3 (**C8**, **C10**), 128.2 (**C8**, **C10**), 126.6 (**C9**), 125.3 (**C7**, **C11**), 125.3 (**C7**, **C11**), 116.6 (**C17**), 116.5 (**C17**), 86.4 (**C2**), 86.3 (**C2**), 67.8 (**C5**), 63.7 (**C14**), 63.5 (**C14**), 39.2 (**C12**), 39.1 (**C3**), 39.0 (**C12**), 38.8 (**C3**), 33.4 (**C13**), 33.3 (**C13**), 25.7 (**C4**), 25.6 (**C4**).
IR (thin film, *υ*/cm^{-1}): 2951, 1445, 1053, 701
HRMS (ESI): Ionized as [M-Cl]$^+$: Found 215.14325, *m/z* calculated for $C_{15}H_{19}O$ [M-Cl]$^+$: 215.14304.

2-(3-Bromopent-4-yn-1-yl)-2-phenyltetrahydrofuran (23s)



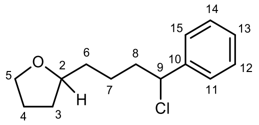
This compound was prepared according to General Procedures F.
Flash column chromatography eluent: 5% EA/Pet. Ether 40-60
R$_f$ = 0.66 (20% EA/Pet. Ether 40-60)
Yield: 95% (28 mg) from 23 mg of **S8s**
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 4H, **H7**, **H8**, **H10**, **H11**), 7.25 – 7.19 (m, 1H, **H9**), 4.47 – 4.35 (m, 1H, **H14**), 4.04 – 3.96 (m, 1H, **H5'**), 3.96 – 3.86 (m, 1H, **H5**), 2.61 (d, *J* = 2.4 Hz, 0.5H, **H16**), 2.58 (d, *J* = 2.4 Hz, 0.5H, **H16**), 2.23 – 2.14 (m, 1H, **H3'**), 2.13 – 2.07 (m, 1H, **H12'**), 2.07 – 1.98 (m, 3H, **H3**, **H12**, **H13'**), 1.98 – 1.90 (m, 1H, **H4'**), 1.85 – 1.77 (m, 1H, **H4**), 1.77 – 1.68 (m, 1H, **H13**).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7 (**C6**), 128.3 (**C8**, **C10**), 126.7 (**C9**), 125.3 (**C7**, **C11**), 86.2 (**C2**), 82.6 (**C15**), 75.1 (**C16**), 67.9 (**C5**), 39.6 (**C12**), 39.5 (**C12**), 39.2 (**C3**), 39.2 (**C3**), 36.6 (**C14**), 36.3 (**C14**), 34.7 (**C13**), 34.6 (**C13**), 25.6 (**C4**).
IR (thin film, *υ*/cm^{-1}): 3290, 2947, 1445, 1045, 701
HRMS (ESI): Ionized as [M-Br]$^+$: Found 213.12750, *m/z* calculated for $C_{15}H_{17}O$ [M-Br]$^+$: 213.12739.

2-(3-Bromopent-4-yn-1-yl)-2-(4-methoxyphenyl)tetrahydrofuran (23v)



This compound was prepared according to General Procedures F.
Flash column chromatography eluent: 2% EA/Pet. Ether 40-60 to 4% EA/Pet. Ether 40-60
R$_f$ = 0.31 (3% EA/Pet. Ether 40-60)
Yield: 84% (30 mg) from 28 mg of **S8v**
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 2H, **H7**, **H11**), 6.89 – 6.83 (m, 2H, **H8**, **H10**), 4.47 – 4.38 (m, 1H, **H14**), 3.99 – 3.93 (m, 1H, **H5'**), 3.93 – 3.86 (m, 1H, **H5**), 3.80 (s, 3H, **H18**), 2.62 – 2.56 (m, 1H, **H16**), 2.19 – 2.11 (m, 1H, **H3'**), 2.09 – 2.01 (m, 3H, **H3**, **H12'**, **H13'**), 2.01 – 1.96 (m, 1H, **H12**), 1.96 – 1.88 (m, 1H, **H4'**), 1.85 – 1.78 (m, 1H, **H4**), 1.78 – 1.71 (m, 1H, **H13**).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4 (**C9**), 138.1 (**C6**), 126.4 (**C7**, **C11**), 113.7 (**C8**, **C10**), 85.9 (**C2**), 82.7 (**C15**), 82.7 (**C15**), 75.1 (**C16**), 75.0 (**C16**), 67.8 (**C5**), 55.4 (**C18**), 39.6 (**C12**), 39.6 (**C12**), 39.2 (**C3**), 39.1 (**C3**), 36.6 (**C14**), 36.3 (**C14**), 34.8 (**C13**), 34.7 (**C13**), 25.6 (**C4**).
IR (thin film, *υ*/cm^{-1}): 3288, 2931, 1610, 1510, 1247, 1034
HRMS (ESI): Ionized as [M-Br]$^+$: Found 243.13814, *m/z* calculated for $C_{16}H_{19}O_2$ [M-Br]$^+$: 243.13796.

2-(4-Chloro-4-phenylbutyl)tetrahydrofuran (23f)



This compound was prepared according to General Procedures F.

Flash column chromatography eluent: 5% EA/Pet. Ether 40-60 to 10% EA/Pet. Ether 40-60

R$_f$ = 0.34 (10% EA/Pet. Ether 40-60)

Yield: 62% (34 mg) from 50 mg of **S8f**

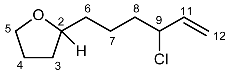
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H, **H11**, **H15**), 7.36 – 7.32 (m, 2H, **H12**, **H14**), 7.32 – 7.27 (m, 1H, **H13**), 4.92 – 4.80 (m, 1H, **H9**), 3.91 – 3.80 (m, 1H, **H5'**), 3.80 – 3.73 (m, 1H, **H2**), 3.73 – 3.60 (m, 1H, **H5**), 2.21 – 2.10 (m, 1H, **H8'**), 2.10 – 2.01 (m, 1H, **H8**), 2.00 – 1.90 (m, 1H, **H3'**), 1.90 – 1.79 (m, 2H, **H4**), 1.68 – 1.58 (m, 1H, **H7'**), 1.55 – 1.46 (m, 2H, **H6**), 1.46 – 1.29 (m, 2H, **H3**, **H7**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0 (**C10**), 142.0 (**C10**), 128.8 (**C12**, **C14**), 128.4 (**C13**), 127.1 (**C11**, **C15**), 79.2 (**C2**), 79.2 (**C2**), 67.8 (**C5**), 63.9 (**C9**), 63.8 (**C9**), 40.2 (**C8**), 40.2 (**C8**), 35.2 (**C6**), 35.1 (**C6**), 31.5 (**C3**), 25.8 (**C4**), 24.2 (**C7**), 24.1 (**C7**).

IR (thin film, υ/cm^{-1}): 2928, 1454, 1069, 697

HRMS (ESI): Ionized as $[M-Cl]^+$: Found 203.14315, *m/z* calculated for $C_{14}H_{19}O$ $[M-Cl]^+$: 203.14304.

2-(4-Chlorohex-5-en-1-yl)tetrahydrofuran (23e)



This compound was prepared according to General Procedures F.

Flash column chromatography eluent: 2% EA/Pet. Ether 40-60 to 4% EA/Pet. Ether 40-60

R$_f$ = 0.66 (20% EA/Pet. Ether 40-60)

Yield: 81% (36 mg) from 40 mg of **S8e**

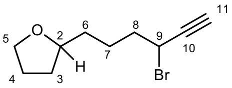
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.07 – 5.62 (m, 1H, **H11**), 5.42 – 5.17 (m, 1H, **H12'**), 5.17 – 5.02 (m, 1H, **H12**), 4.43 – 4.22 (m, 1H, **H9**), 3.91 – 3.83 (m, 1H, **H5'**), 3.83 – 3.75 (m, 1H, **H2**), 3.75 – 3.64 (m, 1H, **H5**), 2.01 – 1.94 (m, 1H, **H3'**), 1.93 – 1.77 (m, 4H, **H4**, **H8**), 1.61 – 1.54 (m, 2H, **H6'**, **H7'**), 1.54 – 1.48 (m, 2H, **H6**, **H7**), 1.48 – 1.39 (m, 1H, **H3**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.8 (**C11**), 116.7 (**C12**), 116.7 (**C12**), 79.2 (**C2**), 79.2 (**C2**), 67.8 (**C5**), 63.2 (**C9**), 63.2 (**C9**), 38.5 (**C8**), 38.4 (**C8**), 35.2 (**C6**), 35.1 (**C6**), 31.5 (**C3**), 25.8 (**C4**), 23.5 (**C7**), 23.4 (**C7**).

IR (thin film, υ/cm^{-1}): 2942, 1459, 1069, 924

HRMS (ESI): Ionized as $[M-Cl]^+$: Found 153.12749, *m/z* calculated for $C_{10}H_{17}O$ $[M-Cl]^+$: 153.12739.

2-(4-Bromohex-5-yn-1-yl)tetrahydrofuran (23g)



This compound was prepared according to General Procedures F.

Flash column chromatography eluent: 5% EA/Pet. Ether 40-60

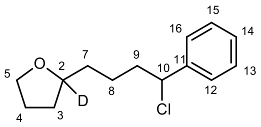
R$_f$ = 0.47 (10% EA/Pet. Ether 40-60)

Yield: 82% (35 mg) from 31 mg of **S8g**

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.55 – 4.40 (m, 1H, **H9**), 3.91 – 3.83 (m, 1H, **H5'**), 3.83 – 3.76 (m, 1H, **H2**), 3.76 – 3.62 (m, 1H, **H5**), 2.66 – 2.57 (m, 1H, **H11**), 2.09 – 2.03 (m, 2H, **H8**), 2.03 – 1.95 (m, 1H, **H3'**), 1.92 – 1.84 (m, 2H, **H4**), 1.70 – 1.63 (m, 1H, **H7'**), 1.63 – 1.57 (m, 1H, **H6'**, **H7**), 1.54

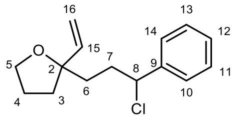
– 1.48 (m, 1H, **H6**), 1.48 – 1.41 (m, 1H, **H3**).
^{13}**C NMR** (126 MHz, CDCl$_3$) δ 82.6 (**C10**), 79.1 (**C2**), 79.1 (**C2**), 75.1 (**C11**), 67.9 (**C5**), 39.6 (**C8**), 39.5 (**C8**), 35.9 (**C9**), 35.9 (**C9**), 34.8 (**C6**), 31.5 (**C3**), 25.8 (**C4**), 24.4 (**C7**), 24.3 (**C7**).
IR (thin film, υ/cm^{-1}): 3292, 2943, 2114, 1459, 1066
HRMS (ESI): Ionized as [M-Br]$^+$: Found 151.11169, *m/z* calculated for C$_{10}$H$_{15}$O [M-Br]$^+$: 151.11174.

2-(4-Chloro-4-phenylbutyl)tetrahydrofuran-2-d (23f-*d*)



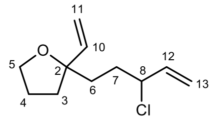
This compound was prepared according to General Procedures F.
Flash column chromatography eluent: 5% EA/Pet. Ether 40-60 to 10% EA/Pet. Ether 40-60
R$_f$ = 0.23 (5% EA/Pet. Ether 40-60)
Yield: 57% (62 mg) from 100 mg of **S8f-*d***
^{1}**H NMR** (500 MHz, CDCl$_3$) δ 7.40 – 7.36 (m, 2H, **H12**, **H16**), 7.36 – 7.32 (m, 2H, **H13**, **H15**), 7.32 – 7.27 (m, 1H, **H14**), 4.97 – 4.72 (m, 1H, **H10**), 4.05 – 3.77 (m, 1H, **H5'**), 3.77 – 3.61 (m, 1H, **H5**), 2.20 – 2.11 (m, 1H, **H9'**), 2.10 – 2.02 (m, 1H, **H9**), 1.98 – 1.91 (m, 1H, **H3'**), 1.91 – 1.80 (m, 2H, **H4**), 1.68 – 1.61 (m, 0.5H, **H8'**), 1.61 – 1.57 (m, 1H, **H7'**), 1.57 – 1.52 (m, 0.5H, **H8'**), 1.52 – 1.46 (m, 1H, **H7**), 1.46 – 1.44 (m, 0.5H, **H8**), 1.43 – 1.39 (m, 1H, **H3**), 1.39 – 1.32 (m, 0.5H, **H8**).
^{13}**C NMR** (126 MHz, CDCl$_3$) δ 142.0 (**C11**), 142.0 (**C11**), 128.8 (**C13**, **C15**), 128.8 (**C13**, **C15**), 128.4 (**C14**), 128.4 (**C14**), 127.1 (**C12**, **C16**), 79.2 (**C2-protiated**), 79.2 (**C2-protiated**), 78.7 (1:1:1 triplet, $J_{\text{C-H}}$ = 22 Hz, **C2-deuterated**), 78.7 (1:1:1 triplet, $J_{\text{C-H}}$ = 22 Hz, **C2-deuterated**), 67.8 (**C5**), 63.9 (**C10**), 63.8 (**C10**), 40.2 (**C9**), 40.2 (**C9**), 35.1 (**C7**), 35.0 (**C7**), 31.4 (**C3**), 25.8 (**C4**), 24.2 (**C8**), 24.1 (**C8**).
IR (thin film, υ/cm^{-1}): 2941, 1454, 1052, 696
HRMS (ESI): Ionized as [M-Cl]$^+$: Found 204.1494, *m/z* calculated for C$_{14}$H$_{18}$DO [M-Cl]$^+$: 204.1493.

2-(3-Chloro-3-phenylpropyl)-2-vinyltetrahydrofuran (23n)



This compound was prepared according to General Procedures F.
Flash column chromatography eluent: 5% EA/Pet. Ether 40-60
R$_f$ = 0.46 (10% EA/Pet. Ether 40-60)
Yield: 79% (23 mg) from 27 mg of **S8n**
^{1}**H NMR** (400 MHz, CDCl$_3$) δ 7.39 – 7.35 (m, 2H, **H10**, **H14**), 7.35 – 7.31 (m, 2H, **H11**, **H13**), 7.31 – 7.27 (m, 1H, **H12**), 5.73 (ddd, *J* = 17.2, 10.6, 2.1 Hz, 1H, **H15**), 5.18 (dt, *J* = 17.2, 1.9 Hz, 1H, **H16'**), 5.06 (dt, *J* = 10.6, 1.8 Hz, 1H, **H16**), 4.91 – 4.75 (m, 1H, **H8**), 3.97 – 3.60 (m, 2H, **H5**), 2.27 – 2.16 (m, 0.5H, **H7'**), 2.15 – 2.03 (m, 1.5H, **H7’**, **H7**), 1.91 – 1.84 (m, 2H, **H4**), 1.84 – 1.74 (m, 2H, **H3'**, **H6'**), 1.74 – 1.63 (m, 1H, **H3**), 1.60 – 1.46 (m, 1H, **H6**).
^{13}**C NMR** (101 MHz, CDCl$_3$) δ 142.3 (**C15**), 142.1 (**C15**), 142.1 (**C9**), 142.0 (**C9**), 128.7 (**C11**), 128.7 (**C11**), 128.3 (**C12**), 128.3 (**C12**), 127.2 (**C10**), 127.1 (**C10**), 113.2 (**C16**), 113.1 (**C16**), 84.8 (**C2**), 84.7 (**C2**), 67.8 (**C5**), 67.8 (**C5**), 64.5 (**C8**), 64.3 (**C8**), 37.4 (**C6**), 37.3 (**C6**), 36.4 (**C3**), 36.2 (**C3**), 35.2 (**C7**), 35.1 (**C7**), 25.3 (**C4**), 25.3 (**C4**).
IR (thin film, υ/cm^{-1}): 2951, 1454, 1041, 920, 697
HRMS (ESI): Ionized as [M-Cl]$^+$: Found 215.14323, *m/z* calculated for C$_{15}$H$_{19}$O [M-Cl]$^+$: 215.14304.

2-(3-Chloropent-4-en-1-yl)-2-vinyltetrahydrofuran (23k)



This compound was prepared according to General Procedures F.

Flash column chromatography eluent: 2% EA/Pet. Ether 40-60

R_f = 0.54 (10% EA/Pet. Ether 40-60)

Yield: 67% (11 mg) from 15 mg of **S8k**

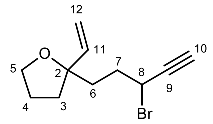
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 – 5.81 (m, 1H, **H12**), 5.81 – 5.67 (m, 1H, **H10**), 5.30 – 5.22 (m, 1H, **H13'**), 5.22 – 5.16 (m, 1H, **H11'**), 5.16 – 5.10 (m, 1H, **H13**), 5.10 – 5.04 (m, 1H, **H11**), 4.42 – 4.26 (m, 1H, **H8**), 3.90 – 3.77 (m, 2H, **H5**), 1.97 – 1.81 (m, 5H, **H3'**, **H4**, **H7**), 1.81 – 1.74 (m, 1H, **H6'**), 1.73 – 1.67 (m, 1H, **H3**), 1.66 – 1.59 (m, 1H, **H6**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3 (**C10**), 142.1 (**C10**), 138.8 (**C12**), 138.8 (**C12**), 116.7 (**C13**), 116.5 (**C13**), 113.1 (**C11**), 113.0 (**C11**), 84.8 (**C2**), 84.7 (**C2**), 67.9 (**C5**), 63.8 (**C8**), 63.6 (**C8**), 36.8 (**C6**), 36.5 (**C6**), 36.5 (**C3**), 36.1 (**C3**), 33.4 (**C7**), 33.3 (**C7**), 25.4 (**C4**), 25.3 (**C4**).

IR (thin film, υ/cm^{-1}): 2952, 1445, 1260, 1041, 921

HRMS (ESI): Ionized as $[M-Cl]^+$: Found 165.12755, *m/z* calculated for $C_{11}H_{17}O$ $[M-Cl]^+$: 165.12739.

2-(3-Bromopent-4-yn-1-yl)-2-vinyltetrahydrofuran (23u)



This compound was prepared according to General Procedures F.

Flash column chromatography eluent: 3% EA/Pet. Ether 40-60

R_f = 0.50 (10% EA/Pet. Ether 40-60)

Yield: 54% (37 mg) from 50 mg of **S8u**

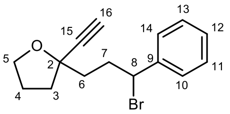
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (dd, J = 17.2, 10.7 Hz, 1H, **H11**), 5.21 (ddd, J = 17.2, 1.8, 1.0 Hz, 1H, **H12'**), 5.09 (dt, J = 10.7, 1.7 Hz, 1H, **H12**), 4.57 – 4.47 (m, 1H, **H8**), 3.95 – 3.77 (m, 2H, **H5**), 2.69 – 2.54 (m, 1H, **H10**), 2.12 – 2.06 (m, 1H, **H7’**), 2.06 – 1.99 (m, 1H, **H7**), 1.91 – 1.87 (m, 2H, **H4**), 1.87 – 1.84 (m, 1H, **H3'**), 1.84 – 1.80 (m, 2H, **H6**), 1.75 – 1.69 (m, 1H, **H3**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1 (**C11**), 142.0 (**C11**), 113.3 (**C12**), 113.3 (**C12**), 84.6 (**C2**), 82.7 (**C9**), 82.6 (**C9**), 75.2 (**C10**), 75.1 (**C10**), 67.9 (**C5**), 37.1 (**C6**), 37.1 (**C6**), 36.6 (**C3**), 36.6 (**C3**), 36.5 (**C8**), 36.3 (**C8**), 34.8 (**C7**), 34.7 (**C7**), 25.3 (**C4**).

IR (thin film, υ/cm^{-1}): 3293, 2962, 1444, 1260, 1038

HRMS (ESI): Ionized as $[M-Br]^+$: Found 163.11175, *m/z* calculated for $C_{15}H_{17}O$ $[M-Br]^+$: 163.11174.

2-(3-Bromo-3-phenylpropyl)-2-ethynyltetrahydrofuran (23w)



This compound was prepared according to General Procedures F.

Flash column chromatography eluent: 2% EA/Pet. Ether 40-60

R_f = 0.78 (20% EA/Pet. Ether 40-60)

Yield: 62% (40 mg) from 51 mg of **S8w**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 2H, **H10**, **H14**), 7.37 – 7.31 (m, 1H, **H11**, **H13**), 7.31 – 7.27 (m, 1H, **H12**), 5.11 – 4.70 (m, 1H, **H8**), 3.99 – 3.92 (m, 1H, **H5'**), 3.92 – 3.85 (m, 1H, **H5'**), 2.59 (dddd, J = 14.2, 11.5, 8.1, 5.0 Hz, 0.5H, **H7'**), 2.53 – 2.36 (m, 2.5H, **H7'**, **H7**, **H16**), 2.25 – 2.16

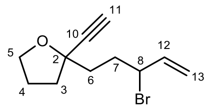
(m, 1H, **H3'**), 2.16 – 2.04 (m, 1H, **H4'**), 2.00 – 1.87 (m, 2H, **H4**, **H6'**), 1.85 – 1.74 (m, 1H, **H3**), 1.74 – 1.63 (m, 1H, **H6**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2 (**C9**), 142.1 (**C9**), 128.9 (**C13**), 128.9 (**C13**), 128.5 (**C12**), 127.5 (**C14**), 127.4 (**C14**), 85.8 (**C15**), 85.8 (**C15**), 78.8 (**C2**), 78.6 (**C2**), 72.6 (**C16**), 72.5 (**C16**), 67.8 (**C5**), 55.8 (**C8**), 55.3 (**C8**), 39.4 (**C6**), 39.2 (**C6**), 39.1 (**C3**), 35.9 (**C7**), 35.8 (**C7**), 25.4 (**C4**).

IR (thin film, *υ*/cm^{-1}): 3288, 2928, 1453, 1043, 697

HRMS (ESI): Ionized as [M-Br]$^+$: Found 213.12747, *m/z* calculated for $C_{11}H_{15}O$ [M-Br]$^+$: 213.12739.

2-(3-Bromopent-4-en-1-yl)-2-ethynyltetrahydrofuran (23o)



This compound was prepared according to General Procedures F.

Flash column chromatography eluent: 2% EA/Pet. Ether 40-60

R$_f$ = 0.54 (20% EA/Pet. Ether 40-60)

Yield: 51% (21 mg) from 30 mg of **S8o**

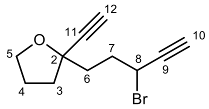
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 – 5.91 (m, 1H, **H12**), 5.30 – 5.17 (m, 1H, **H13'**), 5.14 – 4.98 (m, 1H, **H13**), 4.57 – 4.49 (m, 1H, **H8**), 4.02 – 3.84 (m, 2H, **H5**), 2.47 – 2.39 (m, 1H, **H11**), 2.28 – 2.17 (m, 2H, **H6'**, **H7'**), 2.17 – 2.05 (m, 2H, **H4'**, **H7**), 2.00 – 1.86 (m, 2H, **H3'**, **H4**), 1.85 – 1.72 (m, 2H, **H3**, **H6**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3 (**C12**), 139.2 (**C12**), 116.7 (**C13**), 116.5 (**C13**), 85.9 (**C10**), 85.8 (**C10**), 78.7 (**C2**), 78.6 (**C2**), 72.5 (**C11**), 72.4 (**C11**), 67.9 (**C5**), 67.8 (**C5**), 55.7 (**C8**), 55.3 (**C8**), 39.2 (**C6**), 39.1 (**C6**), 38.8 (**C3**), 38.6 (**C3**), 34.5 (**C7**), 34.5 (**C7**), 25.5 (**C4**), 25.4 (**C4**).

IR (thin film, *υ*/cm^{-1}): 3291, 2951, 1443, 1204, 1044

HRMS (ESI): Ionized as [M-Br]$^+$: Found 163.11185, *m/z* calculated for $C_{11}H_{15}O$ [M-Br]$^+$: 163.11174.

2-(3-Bromopent-4-yn-1-yl)-2-ethynyltetrahydrofuran (23t)



This compound was prepared according to General Procedures F.

Flash column chromatography eluent: 5% EA/Pet. Ether 40-60

R$_f$ = 0.66 (40% EA/Pet. Ether 40-60)

Yield: 74% (15 mg) from 15 mg of **S8t**

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.68 – 4.51 (m, 1H, **H8**), 4.02 – 3.77 (m, 2H, **H5**), 2.68 – 2.62 (m, 1H, **H10**), 2.49 – 2.42 (m, 1H, **H12**), 2.38 – 2.30 (m, 1H, **H7'**), 2.30 – 2.24 (m, 1H, **H7**), 2.24 – 2.17 (m, 1H, **H3'**), 2.16 – 2.06 (m, 1H, **H4'**), 2.01 – 1.92 (m, 3H, **H4**, **H6**), 1.87 – 1.79 (m, 1H, **H3**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 85.6 (**C11**), 85.6 (**C11**), 82.5 (**C9**), 82.4 (**C9**), 78.5 (**C2**), 75.4 (**C10**), 75.3 (**C10**), 72.6 (**C12**), 72.6 (**C12**), 67.9 (**C5**), 39.2 (**C3**), 38.0 (**C6**), 38.0 (**C6**), 36.0 (**C8**), 35.6 (**C8**), 35.4 (**C7**), 35.3 (**C7**), 25.4 (**C4**).

IR (thin film, *υ*/cm^{-1}): 3292, 2954, 2115, 1444, 1260, 1040

HRMS (ESI): Ionized as [M-Br]$^+$: Found 161.09620, *m/z* calculated for $C_{11}H_{13}O$ [M-Br]$^+$: 161.09609.

5) Synthesis of oxonium ion precursors (Part 2):

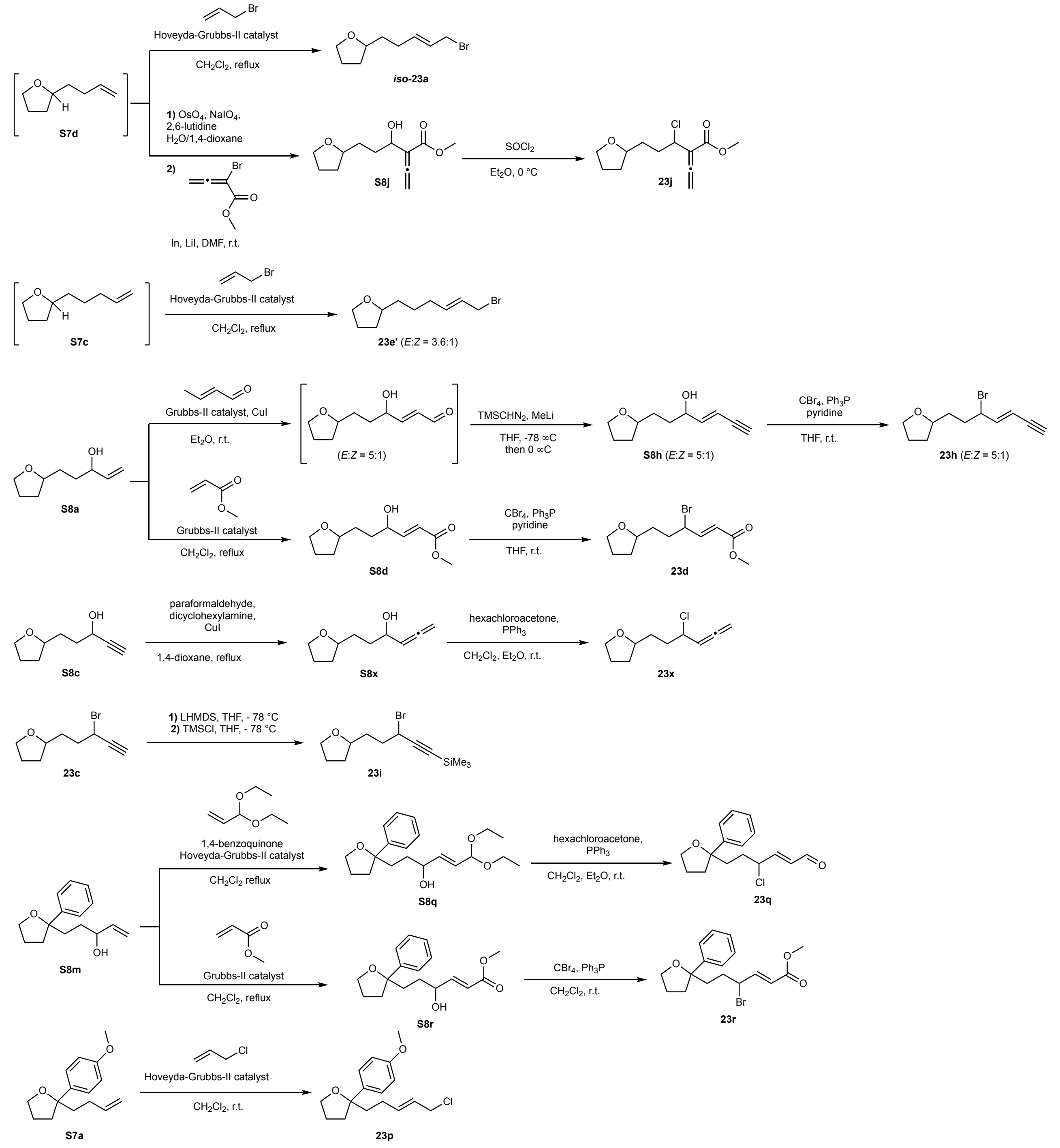
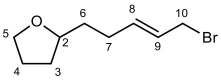


Figure S4. Synthesis of the remaining oxonium ion precursors **23**.

Characterization data for oxonium ion precursors (Part 2):

Note: As the oxonium ion precursors are prepared as 1:1 diastereomeric mixtures, the multiplicities of the peaks on ^{1}H NMR spectra are reported as multiplets (m) unless otherwise stated.

(*E*)-2-(5-Bromopent-3-en-1-yl)tetrahydrofuran (*iso*-23a)



Procedure: Crude **S7d** (300 mg, 2.4 mmol) was dissolved in dry and degassed CH_2Cl_2 (24 mL) at room temperature. Allyl bromide (2.1 mL, 24 mmol) was added to the reaction mixture. Hoveyda-Grubbs 2nd Generation catalyst (150 mg, 0.24 mmol) was added to the reaction mixture, and the reaction mixture was heated to reflux and stirred overnight. TLC analysis suggested complete consumption of starting materials at this stage. Volatiles were removed under reduced pressure and the crude was purified by flash column chromatography (10% Et_2O/Pet. Ether 40-60). The desired compound **23a'** was isolated as a yellow oil in 33% yield (170 mg).

R$_f$ = 0.47 (20% Et_2O /Pet. Ether 40-60)

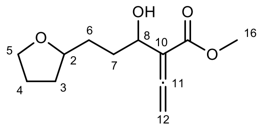
^{1}H NMR (500 MHz, CD_2Cl_2) δ 5.81 (dt, *J* = 15.0, 6.6 Hz, 1H, **H8**), 5.71 (dtt, *J* = 15.0, 7.5, 1.3 Hz, 1H, **H9**), 3.96 (d, *J* = 7.4 Hz, 2H, **H10**), 3.84 – 3.76 (m, 1H, **H5'**), 3.78 – 3.70 (m, 1H, **H2**), 3.65 (td, *J* = 7.9, 6.3 Hz, 1H, **H5**), 2.23 – 2.12 (m, 1H, **H7'**), 2.14 – 2.05 (m, 1H, **H7**), 1.95 (dddd, *J* = 11.6, 8.5, 6.5, 4.9 Hz, 1H, **H3'**), 1.91 – 1.77 (m, 2H, **H4**), 1.61 (dddd, *J* = 13.2, 9.4, 7.3, 5.9 Hz, 1H, **H6'**), 1.57 – 1.46 (m, 1H, **H6**), 1.42 (ddt, *J* = 11.9, 8.8, 7.7 Hz, 1H, **H3**).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 136.8 (**C8**), 127.1 (**C9**), 79.0 (**C2**), 68.0 (**C5**), 35.4 (**C6**), 34.3 (**C10**), 31.8 (**C3**), 29.5 (**C7**), 26.3 (**C4**).

IR (thin film, *υ*/cm^{-1}): 2934, 1441, 1204, 1068, 921

HRMS (ESI): Ionized as $[M-Br]^+$: Found 139.1117, *m/z* calculated for $C_9H_{15}O$ $[M-Br]^+$: 139.1117.

Methyl 3-hydroxy-5-(tetrahydrofuran-2-yl)-2-vinylidenepentanoate (S8j)



Procedure: Crude **S7d** (175 mg, 1.39 mmol) was dissolved in 3:1 1,4-dioxane/H_2O (14 mL) at room temperature. 2,6-Lutidine (0.32 mL, 1.96 mmol) was added followed by cat. OsO_4 (2.5 mol% in *t*BuOH). $NaIO_4$ (1.2 g, 5.46 mmol) was then added and the reaction was stirred for 1 hour. TLC analysis at this stage suggested complete consumption of starting materials. The reaction was diluted with a large excess of water and extracted three times with CH_2Cl_2. The organic layers were collected, quickly washed with 1.0 M aq. HCl solution to remove residual 2,6-lutidine, followed by a final wash with sat. $NaHCO_3$ solution to remove residual acids. The organic layer was then dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude aldehyde was carried forward to the next step without further purification. According to the procedures of Lee,[6] Indium ingot (100 mg, 0.86 mmol) was cut into small pieces and mixed with LiI (522 mg, 3.9 mmol) in DMF (3.0 mL) at room temperature. Methyl 2-bromobuta-2,3-dienoate (230 mg, 1.3 mmol) was added to the reaction mixture and stirred for 30 minutes. The crude aldehyde (110 mg, 0.86 mmol) was dissolved in DMF (2.2 mL) and added to the reaction mixture. The reaction mixture was stirred at room temperature for 48 hours. TLC analysis at this stage suggested complete consumption of starting materials. The reaction was quenched with sat. $NaHCO_3$ solution and extracted three times with ethyl acetate. The organic layers were collected, dried with anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude was purified by flash column chromatography (50% EA/ Pet. Ether 40-60 to 60% EA/ Pet. Ether 40-60). The desired compound **S8j** was isolated in 31% yield over 3 steps (98 mg, 0.43 mmol) as a colourless oil.

R$_f$ = 0.22 (50% EA/Pet. Ether 40-60)

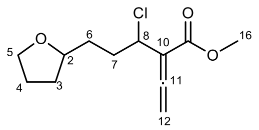
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.39 – 4.89 (m, 2H, **H12**), 4.54 – 4.33 (m, 1H, **H8**), 3.91 – 3.78 (m, 2H, **H2**, **H5'**), 3.83 – 3.57 (m, 3H, **H16**), 3.74 – 3.66 (m, 1H, **H5**), 3.65 – 3.26 (m, 1H, **OH**), 2.02 – 1.94 (m, 1H, **H3'**), 1.93 – 1.83 (m, 2H, **H4**), 1.81 – 1.75 (m, 1H, **H7'**), 1.75 – 1.67 (m, 2H, **H6'**, **H7**), 1.67 – 1.59 (m, 1H, **H6**), 1.50 – 1.40 (m, 1H, **H3**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 212.7 (**C11**), 167.6 (**C13**), 167.5 (**C13**), 103.5 (**C10**), 103.2 (**C10**), 81.1 (**C12**), 79.5 (**C2**), 79.2 (**C2**), 69.2 (**C8**), 69.1 (**C8**), 67.9 (**C5**), 67.9 (**C5**), 52.4 (**C16**), 32.7 (**C7**), 32.4 (**C7**), 32.2 (**C6**), 31.9 (**C6**), 31.6 (**C3**), 31.6 (**C3**), 25.8 (**C4**).

IR (thin film, *υ*/cm^{-1}): 3398, 2951, 1962, 1710, 1436, 1255, 1061

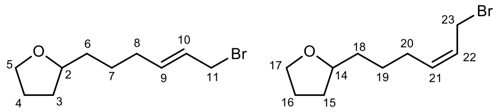
HRMS (ESI): Found 249.10951, *m/z* calculated for $C_{12}H_{18}O_4{}^{23}Na$ $[M+Na]^+$: 249.10973.

Methyl 3-chloro-5-(tetrahydrofuran-2-yl)-2-vinylidenepentanoate (23j)



Procedure: Alcohol **S8j** (20 mg, 0.088 mmol) was dissolved in dry Et_2O (0.88 mL) at 0 °C. Thionyl chloride (7.1 µL, 0.097 mmol) was added and the reaction mixture was stirred for 1 hour. TLC analysis at this stage suggested incomplete consumption of starting materials. Excess thionyl chloride (14.2 µL, 0.194 mmol) was added and the reaction was stirred for 1 hour. TLC analysis at this stage suggested complete consumption of starting materials. The reaction was quenched with sat. $NaHCO_3$ solution and extracted three times with ethyl acetate. The organic layers were collected, dried with anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude was purified by flash column chromatography (20% EA/ Pet. Ether 40-60). The desired compound **23j** was isolated in 56% yield (12 mg, 0.049 mmol) as a pale yellow oil.
R$_f$ = 0.50 (30% EA/Pet. Ether 40-60)
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.47 – 5.35 (m, 2H, **H12**), 4.84 – 4.78 (m, 1H, **H8**), 3.88 – 3.82 (m, 2H, **H2**, **H5'**), 3.80 – 3.77 (m, 3H, **H16**), 3.74 – 3.68 (m, 1H, **H5**), 2.11 – 2.04 (m, 1H, **H7'**), 2.04 – 1.99 (m, 1H, **H3'**), 1.97 – 1.93 (m, 1H, **H7**), 1.90 – 1.85 (m, 2H, **H4**), 1.79 – 1.73 (m, 1H, **H6'**), 1.63 – 1.57 (m, 1H, **H6**), 1.50 – 1.43 (m, 1H, **H3**).
^{13}C NMR (126 MHz, $CDCl_3$) δ 213.8 (**C11**), 213.7 (**C11**), 165.7 (**C13**), 103.9 (**C10**), 82.8 (**C12**), 82.8 (**C12**), 78.9 (**C2**), 78.3 (**C2**), 67.9 (**C5**), 57.2 (**C8**), 56.7 (**C8**), 52.7 (**C16**), 34.1 (**C7**), 33.7 (**C7**), 33.3 (**C6**), 32.9 (**C6**), 31.6 (**C3**), 31.5 (**C3**), 25.8 (**C4**), 25.8 (**C4**).
IR (thin film, υ/cm^{-1}): 2953, 1963, 1768, 1718, 1436, 1258, 1062
HRMS (ESI): Ionized as $[M-Cl]^+$: Found 209.11749, *m/z* calculated for $C_{12}H_{17}O_3$ $[M-Cl]^+$: 209.11722.

(*E*)-2-(6-bromohex-4-en-1-yl)tetrahydrofuran and (*Z*)-2-(6-bromohex-4-en-1-yl)tetrahydrofuran (23e')



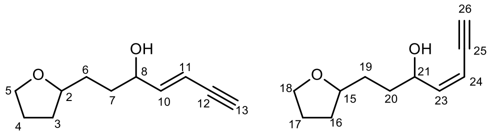
Procedure: Crude **S7d** (200 mg, 1.43 mmol) was dissolved in dry and degassed CH_2Cl_2 at room temperature. Allyl bromide (1.2 mL, 14.3 mmol) was added to the reaction mixture, followed by Hoveyda-Grubbs 2nd Generation catalyst (90 mg, 0.14 mmol). The reaction mixture was heated to reflux and stirred overnight. TLC analysis at this stage suggested complete consumption of starting materials. Volatiles were removed under reduced pressure and the crude was purified by flash column chromatography (10% Et_2O/Pet. Ether 40-60 to 20% Et_2O/Pet. Ether 40-60). The desired compound **23e'** was isolated as a yellow oil in 33% yield (110 mg, *E*:*Z* = 3.6:1).
R$_f$ = 0.43 (20% Et_2O /Pet. Ether 40-60)
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 – 5.74 (m, 1.3H, **H9**, **H22**), 5.74 – 5.66 (m, 1H, **H10**), 5.60 (dt, *J* = 10.6, 7.5 Hz, 0.3H, **H21**), 4.00 (d, *J* = 8.6 Hz, 0.6H, **H23**), 3.94 (dd, *J* = 7.4, 0.8 Hz, 2H, **H11**), 3.88 – 3.82 (m, 1.3H, **H5'**, **H17'**), 3.82 – 3.74 (m, 1.3H, **H2**, **H14**), 3.74 – 3.67 (m, 1.3H, **H5**, **H17**), 2.17 (qd, *J* = 7.2, 1.6 Hz, 0.6H, **H20**), 2.10 (q, *J* = 6.7 Hz, 2H, **H8**), 2.01 – 1.93 (m, 1.3H, **H3'**, **H15'**), 1.92 – 1.81 (m, 2.6H, **H4**, **H16**), 1.62 – 1.49 (m, 2.6H, **H6'**, **H7'**, **H18'**, **H19'**), 1.50 – 1.39 (m, 4H, **H3**, **H6**, **H7**, **H15**, **H18**, **H19**).
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.5 (**C9**), 135.8 (**C21**), 126.7 (**C10**), 125.7 (**C22**), 79.3 (**C2**, **C14**), 67.8 (**C5**, **C17**), 35.4 (**C18**), 35.3 (**C6**), 33.7 (**C11**), 32.2 (**C8**), 31.6 (**C15**), 31.5 (**C3**), 27.5 (**C23**),

27.1 (**C20**), 26.0 (**C19**), 25.9 (**C4**, **C16**), 25.7 (**C7**).

IR (thin film, υ/cm^{-1}): 2933, 1660, 1456, 1203, 1073, 964, 921

HRMS (ESI): Ionized as [M-Br]$^+$: Found 153.1274, *m/z* calculated for $C_{10}H_{17}O$ [M-Br]$^+$: 153.1274.

(*E*)-1-(tetrahydrofuran-2-yl)hept-4-en-6-yn-3-ol and (*Z*)-1-(tetrahydrofuran-2-yl)hept-4-en-6-yn-3-ol (S8h)



Procedure: Alcohol **S8a** (150 mg, 0.96 mmol) was dissolved in dry and degassed Et_2O (19.2 mL). Crotonaldehyde (0.4 mL, 4.8 mmol) was added, followed by Grubbs 2nd Generation catalyst (42 mg, 0.05 mmol) and CuI (13 mg, 0.07 mmol). The reaction mixture was stirred at room temperature overnight. TLC analysis at this stage suggested complete consumption of starting materials. Volatiles were removed under reduced pressure and the crude was quickly purified by flash column chromatography (50% EA/Pet. Ether 40-60 to 70% EA/Pet. Ether 40-60). The purified enal (120 mg, 0.65 mmol, *E*:*Z* = 5:1) was immediately used in the next step. MeLi (1.3 mL, 1.6 M in Et_2O) was added to dry THF (10 mL) at −78 °C. $TMSCHN_2$ (1.0 mL, 2.0 M in Et_2O) was added to the reaction mixture and stirred for 30 minutes. The crude enal (120 mg, 0.65 mmol) was dissolved in THF (3.0 mL) and was rapidly added to the reaction mixture. The reaction mixture was stirred at −78 °C for 1 hour, then warmed to 0 °C and stirred for 1 hour. TLC analysis at this stage suggested complete consumption of starting materials. The reaction was quenched with aq. HCl (1.0 M), extracted three times with ethyl acetate, the organic layers were collected and washed with sat. aq. $NaHCO_3$ to remove residual acid. The organic layer was dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude was purified by flash column chromatography (30% EA/Pet. Ether 40-60 to 50% EA/ Pet. Ether 40-60) to give the desired compound **S8h** in 48% yield over 2 steps (79 mg, 0.44 mmol, *E*:*Z* = 5:1).

R_f = 0.46 (70% EA/Pet. Ether 40-60)

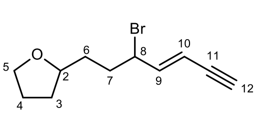
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 (ddd, *J* = 15.9, 5.2, 1.8 Hz, 1H, **H10**), 6.03 (dddd, *J* = 11.2, 8.2, 2.1, 0.9 Hz, 0.2H, **H23**), 5.74 (ddt, *J* = 16.0, 5.9, 2.0 Hz, 1H, **H11**), 5.51 (dddd, *J* = 11.1, 3.4, 2.4, 1.1 Hz, 0.2H, **H24**), 4.68 (m, 0.2H, **H21**), 4.22 (m, 1H, **H8**), 4.00 – 3.78 (m, 2.4H, **H2**, **H5'**, **H15**, **H18'**), 3.75 (m, 1.2H, **H5**, **H18**), 3.64 – 3.16 (m, 1.2H, **OH**), 3.13 (m, 0.2H, **H26**), 2.87 (m, 1H, **H13**), 2.05 – 1.94 (m, 1.2H, **H3'**, **H16'**), 1.94 – 1.81 (m, 2.4H, **H4**, **H17**), 1.78 – 1.67 (m, 2.6H, **H6'**, **H7'**, **H19'**, **H20**), 1.68 – 1.61 (m, 1.2H, **H6**, **H19**), 1.61 – 1.54 (m, 1H, **H7**), 1.52 – 1.42 (m, 1.2H, **H3**, **H16**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0 (**C10**), 147.8 (**C23**), 108.6 (**C24**), 108.5 (**C24**), 108.5 (**C11**), 108.2 (**C11**), 82.9 (**C26**), 82.1 (**C12**), 82.1 (**C25**), 79.6 (**C2**), 79.5 (**C2**), 79.4 (**C15**), 77.7 (**C13**), 77.6 (**C13**), 72.0 (**C8**), 71.3 (**C8**), 70.5 (**C21**), 69.9 (**C21**), 68.0 (**C5**, **C18**), 68.0 (**C5**, **C18**), 34.6 (**C7**), 34.3 (**C20**), 33.8 (**C7**), 33.6 (**C20**), 32.3 (**C6**), 32.1 (**C19**), 31.7 (**C3**, **C16**), 31.6 (**C3**, **C16**), 31.1 (**C19**), 30.9 (**C6**), 25.8 (**C4**, **C17**), 25.8 (**C4**, **C17**).

IR (thin film, υ/cm^{-1}): 3289, 2945, 2101, 1446, 1251, 1046

HRMS (ESI): Ionized as [M-OH]$^+$: Found 163.1118, *m/z* calculated for $C_{11}H_{15}O$ [M-OH]$^+$: 163.1117.

(*E*)-2-(3-bromohept-4-en-6-yn-1-yl)tetrahydrofuran and (*Z*)-2-(3-bromohept-4-en-6-yn-1-yl)tetrahydrofuran (23h)



Procedures: Alcohol **S1h** (70 mg, 0.39 mmol), PPh$_3$ (247 mg, 0.94 mmol) and pyridine (36.0 μL, 0.43 mmol) were dissolved in THF (2.1 mL) and stirred vigorously at room temperature. Then a solution of CBr$_4$ (143 mg, 0.43 mmol) and pyridine (24 μL, 0.27 mmol) in THF (0.5 mL) was quickly added. The reaction was stirred at room temperature for 30 minutes. TLC analysis at this stage suggested complete consumption of starting materials. The reaction mixture was diluted with diethyl ether, stirred for 10 minutes, filtered and concentrated under reduced pressure. The crude was purified by flash column chromatography (5% EA/Pet. Ether 40-60) to give the desired compound **23h** in 56% yield (53 mg, 0.22 mmol, *E*:*Z* = 5:1).

R$_f$ = 0.42 (10% EA/Pet. Ether 40-60)

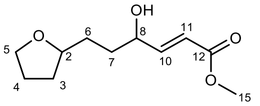
^{1}H NMR (400 MHz, CDCl$_3$) δ 6.31 (dd, *J* = 15.7, 9.4 Hz, 0.2H, **H9**), 6.12 (dt, *J* = 10.5, 1.4 Hz, 0.2H, **H22**), 5.65 (dt, *J* = 15.7, 2.4 Hz, 1H, **H10**), 5.47 (d, *J* = 10.6 Hz, 0.2H, **H23**), 5.07 (m, 0.2H, **H21**), 4.70 – 4.32 (m, 1H, **H8**), 3.95 – 3.75 (m, 2.4H, **H2**, **H5'**, **H15**, **H18'**), 3.71 (m, 1.2H, **H5**, **H18**), 3.37 – 3.16 (m, 0.2H, **H25**), 2.95 (m, 1H, **H12**), 2.20 – 2.06 (m, 1.2H, **H7'**, **H20'**), 2.05 – 1.96 (m, 2.3H, **H3'**, **H7'**, **H16'**, **H20'**), 1.91 – 1.84 (m, 2.4H, **H4**, **H17**), 1.70 – 1.64 (m, 1.2H, **H6'**, **H19'**), 1.63 – 1.54 (m, 1.2H, **H6**, **H19**), 1.50 – 1.41 (m, 1.2H, **H3**, **H16**).

^{13}C NMR (101 MHz, CDCl$_3$) δ 145.0 (**C9**), 145.0 (**C9**), 144.4 (**C22**), 144.4 (**C22**), 110.9 (**C10**), 110.8 (**C10**), 109.6 (**C23**), 109.6 (**C23**), 85.0 (**C25**), 85.0 (**C25**), 80.8 (**C11**, **C24**), 80.8 (**C11**, **C24**), 79.8 (**C12**), 79.7 (**C12**), 78.7 (**C2**), 78.6 (**C15**), 78.4 (**C15**), 78.4 (**C2**), 67.9 (**C5**, **C18**), 67.9 (**C5**, **C18**), 53.8 (**C8**), 53.4 (**C8**), 50.5 (**C21**), 50.3 (**C21**), 35.8 (**C20**), 35.6 (**C7**), 35.4 (**C7**), 33.9 (**C6**), 33.8 (**C19**), 33.6 (**C6**), 33.5 (**C19**), 31.5 (**C3**), 31.5 (**C3**), 31.4 (**C16**), 25.8 (**C4**), 25.8 (**C17**).

IR (thin film, *υ*/cm^{-1}): 3291, 2937, 2102, 1442, 1251, 1064, 955

HRMS (ESI): Did not ionize by ESI-MS.

Methyl (*E*)-4-hydroxy-6-(tetrahydrofuran-2-yl)hex-2-enoate (S8d)



Procedure: Alcohol **S8a** (40 mg, 0.26 mmol) was dissolved in dry and degassed CH$_2$Cl$_2$ (3.0 mL) at room temperature. Methyl acrylate (0.23 mL, 2.6 mmol) was added followed by Grubbs 2nd Generation catalyst (22 mg, 0.026 mmol), and the reaction mixture was heated to reflux and stirred overnight. TLC at this stage suggested complete consumption of starting material. Volatiles were removed under reduced pressure and the crude was purified by flash column chromatography (40% EA/ Pet. Ether 40-60) to give the desired compound **S8d** in 77% yield (43 mg, 0.20 mmol, *E*:*Z* > 20:1).

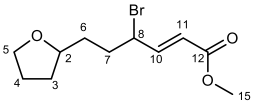
R$_f$ = 0.23 (40% EA/Pet. Ether 40-60)

^{1}H NMR (500 MHz, CDCl$_3$) δ 6.95 (dt, *J* = 15.6, 4.2 Hz, 1H, **H10**), 6.08 (ddd, *J* = 15.7, 7.8, 1.9 Hz, 1H, **H11**), 4.45 – 4.23 (m, 1H, **H8**), 3.95 (d, *J* = 3.4 Hz, 0.5H, **OH**), 3.93 – 3.80 (m, 2H, **H2**, **H5'**), 3.80 – 3.71 (m, 4H, **H5'**, **H15**), 3.57 (d, *J* = 5.9 Hz, 0.5H, **OH**), 2.05 – 1.94 (m, 1H, **H3'**), 1.94 – 1.84 (m, 2H, **H4**), 1.83 – 1.75 (m, 1.5H, **H6'**, **H7'**), 1.74 – 1.66 (m, 1H, **H6**, **H7'**), 1.65 – 1.53 (m, 1.5H, **H6**, **H7**), 1.52 – 1.42 (m, 1H, **H3**).

^{13}C NMR (126 MHz, CDCl$_3$) δ 167.4 (**C12**), 167.3 (**C12**), 151.0 (**C10**), 150.8 (**C10**), 119.9 (**C11**), 119.6 (**C11**), 79.6 (**C2**), 79.5 (**C2**), 71.2 (**C8**), 70.4 (**C8**), 68.1 (**C5**), 68.0 (**C5**), 51.7 (**C15**), 34.3 (**C7**),

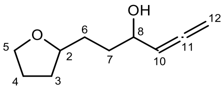
33.5 (**C7**), 32.4 (**C6**), 31.7 (**C3**), 31.6 (**C3**), 30.8 (**C6**), 25.8 (**C4**), 25.8 (**C4**).
IR (thin film, *υ*/cm^{-1}): 3399, 2949, 2865, 1721, 1658, 1436, 1272, 1166, 1040, 980, 925, 856
HRMS (ESI): Found 237.1099, m/z calculated for $C_{11}H_{18}O_4{}^{23}Na$ [M+Na]+: 237.1097.

Methyl (*E*)-4-bromo-6-(tetrahydrofuran-2-yl)hex-2-enoate (23d)



Procedure: Alcohol **S8d** (40 mg, 0.19 mmol), PPh_3 (163 mg, 0.62 mmol) and pyridine (25.0 µL, 0.30 mmol) were dissolved in THF (1.4 mL) and stirred vigorously at room temperature. Then a solution of CBr_4 (93 mg, 0.28 mmol) and pyridine (15 µL, 0.17 mmol) in THF (0.3 mL) was quickly added. The reaction was stirred at room temperature for 30 minutes. TLC analysis at this stage suggested complete consumption of starting materials. The reaction mixture was diluted with diethyl ether, stirred for 10 minutes, filtered and concentrated under reduced pressure. The crude was purified by flash column chromatography (30% EA/Pet. Ether 40-60 to 40% EA/Pet. Ether 40-60) to give the desired compound **23d** in 89% yield (47 mg, 0.17 mmol, *E*:*Z* > 20:1).
$\mathbf{R_f}$ = 0.49 (40% EA/Pet. Ether 40-60)
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 6.97 (ddd, *J* = 15.4, 9.1, 4.3 Hz, 1H, **H9**), 5.94 (ddd, *J* = 15.6, 2.8, 0.9 Hz, 1H, **H10**), 4.68 – 4.45 (m, 1H, **H8**), 3.93 – 3.77 (m, 2H, **H2**, **H5'**), 3.75 (s, 3H, **H15**), 3.74 – 3.63 (m, 1H, **H5**), 2.19 – 2.05 (m, 1H, **H7'**), 2.05 – 1.94 (m, 2H, **H3'**, **H7**), 1.94 – 1.81 (m, 2H, **H4**), 1.73 – 1.66 (m, 1H, **H6'**), 1.65 – 1.54 (m, 1H, **H6**), 1.50 – 1.38 (m, 1H, **H3**).
^{13}**C NMR** (126 MHz, $CDCl_3$) δ 166.4 (**C11**), 146.8 (**C9**), 146.8 (**C9**), 121.8 (**C10**), 121.7 (**C10**), 78.6 (**C2**), 78.3 (**C2**), 67.9 (**C5**), 52.0 (**C15**), 51.6 (**C8**), 51.1 (**C8**), 35.1 (**C7**), 34.9 (**C7**), 33.8 (**C6**), 33.4 (**C6**), 31.6 (**C3**), 31.5 (**C3**), 25.8 (**C4**), 25.8 (**C4**).
IR (thin film, *υ*/cm^{-1}): 2949, 1722, 1656, 1435, 1271, 1159
HRMS (ESI): Ionized as [M-Br]$^+$: Found 197.1174, *m/z* calculated for $C_{11}H_{17}O3$ [M-Br]$^+$: 197.1172.

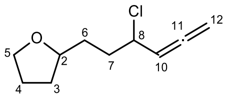
1-(Tetrahydrofuran-2-yl)hexa-4,5-dien-3-ol (S8x)



Procedure: According to the procedure of Ma[7]: Alcohol **S1c** (50 mg, 0.32 mmol) was mixed with paraformaldehyde (24 mg, 0.80 mmol) and CuI (31 mg, 0.16 mmol) in 1,4-dioxane (1.4 mL). Dicyclohexylamine (0.11 ml, 0.58 mmol) was then added. The reaction mixture was heated to reflux, stirred at this temperature, and the reaction progress was monitored by TLC analysis. Upon complete consumption of starting materials, the reaction was quenched with H_2O and extracted three times with Et_2O. The organic layers were collected, dried with anhydrous $MgSO_4$, filtered and concentrated. The crude was purified by flash column chromatography (40% EA/ Pet. Ether 40-60) to give the desired compound **S8x** as a colourless oil in 93% yield (50 mg, 0.30 mmol).
$\mathbf{R_f}$ = 0.20 (20% EA/Pet. Ether 40-60)
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 5.28 – 5.21 (m, 1H, **H10**), 4.89 – 4.79 (m, 2H, **H12**), 4.28 – 4.14 (m, 1H, **H8**), 3.92 – 3.79 (m, 2H, **H2**, **H5'**), 3.78 – 3.69 (m, 1H, **H5**), 3.04 – 2.45 (m, 1H, **OH**), 2.04 – 1.94 (m, 1H, **H3'**), 1.94 – 1.84 (m, 2H, **H4**), 1.77 – 1.71 (m, 1H, **H6'**), 1.71 – 1.64 (m, 3H, **H6**, **H7**), 1.53 – 1.41 (m, 1H, **H3**).
^{13}**C NMR** (101 MHz, $CDCl_3$) δ 207.2 (**C11**), 95.1 (**C10**), 94.9 (**C10**), 79.5 (**C2**), 79.5 (**C2**), 77.5 (**C12**), 69.8 (**C8**), 69.4 (**C8**), 67.9 (**C5**), 34.9 (**C6**), 34.4, (**C6**) 32.1 (**C7**), 31.6 (**C3**), 31.6 (**C3**), 31.4 (**C7**), 25.8 (**C4**), 25.8 (**C4**).
IR (thin film, *υ*/cm^{-1}): 3388, 2929, 1955, 1260, 1057

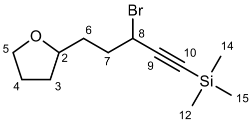
HRMS (ESI): Found 191.10439, *m/z* calculated for $C_{10}H_{16}O_2{}^{23}Na$ [M+Na]$^+$: 191.10425. Also ionized as [M-OH]$^+$: Found 151.11180, *m/z* calculated for $C_{10}H_{15}O$ [M-OH]$^+$: 151.11174.

2-(3-Chlorohexa-4,5-dien-1-yl)tetrahydrofuran (23x)



Procedure: Alcohols **S8x** (21 mg, 0.13 mmol) was dissolved in 1:1 Et_2O:CH_2Cl_2 (0.6 mL) at 0 °C. Hexachloroacetone (26 µL, 0.16 mmol) and PPh_3 (44 mg, 0.17 mmol) were added and the reaction was stirred at 0 °C for 1 hour, then warmed to room temperature. TLC analysis at this stage suggested complete consumption of starting materials. The reaction was quenched with aqueous sat. $NaHCO_3$ solution, and the aqueous phase was extracted three times with CH_2Cl_2. The organic layers were collected, dried with anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude was then purified by flash column chromatography (5% EA/ Pet. Ether 40-60) to give the desired compound **23x** in 69% yield (16 mg, 0.09 mmol) as a pale yellow oil.
R$_f$ = 0.57 (20% EA/Pet. Ether 40-60)
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 – 5.25 (m, 1H, **H10**), 5.02 – 4.76 (m, 2H, **H12**), 4.55 – 4.35 (m, 1H, **H8**), 3.93 – 3.76 (m, 2H, **H2**, **H5'**), 3.76 – 3.61 (m, 1H, **H5**), 2.09 – 1.96 (m, 2H, **H3'**, **H7'**), 1.94 – 1.80 (m, 3H, **H4**, **H7**), 1.79 – 1.68 (m, 1H, **H6'**), 1.68 – 1.59 (m, 1H, **H6**), 1.52 – 1.41 (m, 1H, **H3**).
^{13}C NMR (101 MHz, $CDCl_3$) δ 208.0 (**C11**), 94.0 (**C10**), 94.0 (**C10**), 78.9 (**C2**), 78.5 (**C2**), 78.1 (**C12**), 67.9 (**C5**), 60.5 (**C8**), 60.1 (**C8**), 35.7 (**C7**), 35.3 (**C7**), 33.0 (**C6**), 32.6 (**C6**), 31.6 (**C3**), 31.5 (**C3**), 25.9 (**C4**), 25.8 (**C4**).
IR (thin film, *υ*/cm^{-1}): 2924, 1953, 1456, 1260, 1028
HRMS (ESI): Ionized as [M-Cl]$^+$: Found 151.11176, *m/z* calculated for $C_{10}H_{15}O$ [M-OH]$^+$: 151.11174.

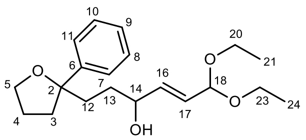
(3-Bromo-5-(tetrahydrofuran-2-yl)pent-1-yn-1-yl)trimethylsilane (23i)



Procedure: Bromide **23c** (12 mg, 0.055 mmol) was dissolve in dry THF (1.1 mL) at −78 °C. LHMDS (66 µL, 0.066 mmol, 1.0 M in THF) was added and the reaction mixture was stirred for 1 hour. TMSCl (8.4 µL, 0.066 mmol) was added and the reaction mixture was stirred until completion, in which the reaction progress was monitored by TLC analysis. Upon complete consumption of starting material, the reaction was quenched with sat. aq. NH_4Cl and extracted three times with ethyl acetate. The organic layers were collected, dried with anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude was purified by flash column chromatography (3% EA. Pet. Ether 40-60) to give the desired compound **23i** in 75% yield (12 mg, 0.041 mmol) as a colourless oil.
R$_f$ = 0.29 (5% EA/Pet. Ether 40-60)
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.65 – 4.43 (m, 1H, **H8**), 3.99 – 3.78 (m, 2H, **H2**, **H5'**), 3.72 (m, 1H, **H5**), 2.24 – 2.09 (m, 1H, **H7'**), 2.09 – 1.95 (m, 2H, **H3'**, **H7**), 1.95 – 1.82 (m, 2H, **H4**), 1.78 – 1.66 (m, 2H, **H6**), 1.55 – 1.40 (m, 1H, **H3**), 0.17 (s, 9H, **H12**, **H14**, **H15**).
^{13}C NMR (101 MHz, $CDCl_3$) δ 103.9 (**C9**), 92.3 (**C10**), 92.2 (**C10**), 78.5 (**C2**), 78.4 (**C2**), 67.9 (**C5**), 67.9 (**C5**), 37.5 (**C8**), 37.3 (**C8**), 36.7 (**C7**), 36.6 (**C7**), 33.4 (**C6**), 33.3 (**C6**), 31.5 (**C3**), 25.8 (**C4**), -0.1 (**C12**, **C14**, **C15**).
IR (thin film, *υ*/cm^{-1}): 2959, 2210, 1456, 1249, 1067
HRMS (ESI): Ionized as [M-Br]$^+$: Found 209.13584, *m/z* calculated for $C_{12}H_{21}OSi$ [M-Br]$^+$:

209.13562.

(*E*)-6,6-diethoxy-1-(2-phenyltetrahydrofuran-2-yl)hex-4-en-3-ol (S8q)



Procedure: Alcohol **S8m** (50 mg, 0.22 mmol) was dissolved in dry and degassed CH_2Cl_2 (2.2 mL). 3,3-Diethoxyprop-1-ene (0.17 mL, 1.1 mmol) was added, followed by 1,4-benzoquinone (2.4 mg, 0.022 mmol) and Hoveyda-Grubbs 2nd generation catalyst (7.0 mg, 0.011 mmol). The reaction was heated to reflux and stirred till completion. Upon complete consumption of starting materials as suggested by TLC analysis, the volatiles were removed under reduced pressure and the crude was purified by flash column chromatography (30% EA/ Pet. Ether 40-60 to 40% EA/ Pet. Ether 40-60) to give the desired compound **S8q** in 64% yield (47 mg, 0.14 mmol, *E*:*Z* > 20:1).

R$_f$ = 0.31 (40% EA/Pet. Ether 40-60)

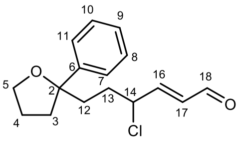
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 4H, **H7**, **H8**, **H10**, **H11**), 7.24 – 7.18 (m, 1H, **H9**), 5.77 (dt, *J* = 15.7, 5.6 Hz, 1H, **H16**), 5.64 (dd, *J* = 15.9, 4.8 Hz, 1H, **H17)**, 4.91 – 4.72 (m, 1H, **H18**), 4.11 (*p*, J = 5.9, 5.2 Hz, 0.5H, **H14**), 4.05 (dt, *J* = 8.9, 4.5 Hz, 0.5H, **H14**), 4.03 – 3.96 (m, 1H, **H5'**), 3.96 – 3.90 (m, 1H, **H5**), 3.66 – 3.55 (m, 2H, **H20'**, **H23'**), 3.52 – 3.41 (m, 2H, **H20**, **H23**), 2.70 (d, *J* = 3.7 Hz, 0.5H, **OH**), 2.49 (d, *J* = 4.9 Hz, 1H, **OH**), 2.24 – 2.13 (m, 1H, **H3'**), 2.10 – 2.02 (m, 1.5H, **H3**, **H12'**), 1.99 – 1.91 (m, 2H, **H4'**, **H12'**, **H12**), 1.91 – 1.85 (m, 0.5H, **H12**), 1.83 – 1.70 (m, 1H, **H4**), 1.54 – 1.49 (m, 0.5H, **H13'**), 1.49 – 1.43 (m, 0.5H, **H13'**), 1.43 – 1.37 (m, 0.5H, **H13**), 1.36 – 1.28 (m, 0.5H, **H13**), 1.22 – 1.14 (m, 6H, **H21**, **H24**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.4 (**C6**), 146.2 (**C6**), 137.1 (**C16**), 137.1 (**C16**), 128.3 (**C8**, **C10**), 127.4 (**C17**), 127.3 (**C17**), 126.5 (**C9**), 125.4 (**C7**, **C11**), 125.4 (**C7**, **C11**), 101.3 (**C18**), 101.2 (**C18**), 86.9 (**C2**), 86.8 (**C2**), 72.2 (**C14**), 71.4 (**C14**), 68.0 (**C5**), 67.9 (**C5**), 61.2 (**C20**, **C23**), 61.1 (**C20**, **C23**), 39.3 (**C3**), 39.1 (**C3**), 38.7 (**C12**), 37.8, (**C12**) 32.1 (**C13**), 31.9 (**C13**), 25.7 (**C4**), 25.5 (**C4**), 15.4 (**C21**, **C24**).

IR (thin film, *υ*/cm^{-1}): 3420, 2949, 1686, 1445, 1050

HRMS (ESI): Ionized as $[M-Br]^+$: Found 209.13584, *m/z* calculated for $C_{12}H_{21}OSi$ $[M-Br]^+$: 209.13562.

(*E*)-4-Chloro-6-(2-phenyltetrahydrofuran-2-yl)hex-2-enal (23q)



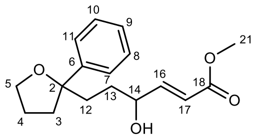
Procedure: Alcohols **S8q** (20 mg, 0.060 mmol) was dissolved in 1:1 Et_2O:CH_2Cl_2 (0.6 mL) at room temperature. Hexachloroacetone (12 µL, 0.078 mmol) and PPh_3 (20 mg, 0.078 mmol) were added and the reaction was stirred at room temperature. Upon complete consumption of starting material as suggested by TLC analysis, the reaction was quenched with aqueous sat. $NaHCO_3$ solution. The aqueous phase was extracted three times with CH_2Cl_2. The organic layers were collected, dried with anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude was then purified by flash column chromatography (10% EA/ Pet. Ether 40-60 to 20% EA/ Pet. Ether 40-60) to give the desired compound **23q** in 66% yield (11 mg, 0.039 mmol) as a pale yellow oil.

R$_f$ = 0.78 (50% EA/Pet. Ether 40-60)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.65 – 9.36 (m, 1H, **H18**), 7.36 – 7.31 (m, 4H, **H7**, **H8**, **H10**, **H11**), 7.25 – 7.20 (m, 1H, **H9**), 6.63 (dd, *J* = 15.5, 7.5 Hz, 0.6H, **H16**), 6.62 (dd, *J* = 15.5, 7.4 Hz, 0.4H,

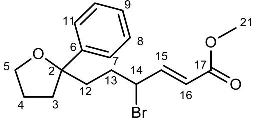
H16), 6.16 (ddd, *J* = 15.4, 7.7, 1.1 Hz, 0.6H, **H17**), 6.15 (ddd, *J* = 15.6, 7.6, 1.1 Hz, 0.4H, **H17**), 4.52 (td, *J* = 7.7, 4.7 Hz, 0.4H, **H14**), 4.47 – 4.24 (m, 0.6H, **H14**), 4.02 – 3.94 (m, 1H, **H5'**), 3.94 – 3.80 (m, 1H, **H5**), 2.24 – 2.15 (m, 1H, **H3'**), 2.12 – 2.03 (m, 1H, **H3**), 2.00 – 1.85 (m, 4H, **H4'**, **H12**, **H13'**), 1.83 – 1.74 (m, 1H, **H4**), 1.71 – 1.60 (m, 0.6H, **H13**), 1.60 – 1.50 (m, 0.4H, **H13**).
^{13}C NMR (126 MHz, $CDCl_3$) δ 193.2 (**C18**), 154.3 (**C16**), 154.2 (**C16**), 146.1 (**C6**), 145.9 (**C6**), 132.4 (**C17**), 132.2 (**C17**), 128.4 (**C8**, **C10**), 126.8 (**C9**), 126.8 (**C9**), 125.3 (**C7**, **C11**), 125.3 (**C7**, **C11**), 86.3 (**C2**), 86.1 (**C2**), 67.9 (**C5**), 67.9 (**C5**), 60.0 (**C14**), 59.8 (**C14**), 39.5 (**C3**), 39.2 (**C3**), 38.8 (**C12**), 38.7 (**C12**), 32.7 (**C13**), 32.7 (**C13**), 25.6 (**C4**), 25.6 (**C4**).
IR (thin film, *υ*/cm^{-1}): 2951, 1692, 1445, 1279, 1053
HRMS (ESI): Ionized as $[M-Cl]^+$: Found 243.13818, *m/z* calculated for $C_{16}H_{19}O_2$ $[M-Cl]^+$: 243.13796.

Methyl (*E*)-4-hydroxy-6-(2-phenyltetrahydrofuran-2-yl)hex-2-enoate (S8r)



Procedure: Alcohol **S8m** (50 mg, 0.22 mmol) was dissolved in dry and degassed CH_2Cl_2 (2.2 mL). Methyl acrylate (0.2 mL, 2.2 mmol) was added followed by Grubbs 2nd generation catalyst (20 mg, 0.022 mmol). The reaction was heated to reflux and stirred overnight. TLC analysis at this stage suggested complete consumption of starting materials. Volatiles were removed under reduced pressure and the crude was purified by flash column chromatography (30% EA/ Pet. Ether 40-60 to 40% EA/ Pet. Ether 40-60) to give the desired compound **S8r** in 69% yield (44 mg, 0.15 mmol, *E*:*Z* > 20:1) as a pale yellow oil.
R_f = 0.34 (40% EA/Pet. Ether 40-60)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 4H, **H7**, **H8**, **H10**, **H11**), 7.25 – 7.16 (m, 1H, **H9**), 6.86 (dd, *J* = 15.6, 4.1 Hz, 0.5H, **H16**), 6.84 (dd, *J* = 15.6, 4.5 Hz, 0.5H, **H16**), 6.03 (dd, *J* = 15.6, 1.9 Hz, 0.5H, **H17**), 6.02 (dd, *J* = 15.6, 1.8 Hz, 0.5H, **H17**), 4.28 (dddd, *J* = 9.8, 7.6, 4.5, 1.8 Hz, 0.5H, **H14**), 4.23 (dtd, *J* = 7.9, 3.9, 1.7 Hz, 0.5H, **H14**), 4.06 – 3.99 (m, 1H, **H5'**), 3.99 – 3.92 (m, 1H, **H5**), 3.73 (s, 1.5H, **H21**), 3.71 (s, 1.5H, **H21**), 3.45 (d, *J* = 3.7 Hz, 0.5H, **OH**), 3.36 (d, *J* = 5.5 Hz, 0.5H, **OH**), 2.25 – 2.15 (m, 1H, **H3'**), 2.12 – 2.01 (m, 2H, **H3**, **H12'**), 1.99 – 1.88 (m, 2H, **H4'**, **H12**), 1.84 – 1.72 (m, 1H, **H4**), 1.63 – 1.54 (m, 0.5H, **H13'**), 1.53 – 1.47 (m, 0.5H, **H13'**), 1.47 – 1.35 (m, 1H, **H13**).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3 (**C18**), 151.0 (**C16**), 150.7 (**C16**), 146.0 (**C6**), 145.7 (**C6**), 128.4 (**C8**, **C10**), 126.7 (**C9**), 125.4 (**C7**, **C11**), 119.7 (**C17**), 119.6 (**C17**), 86.9 (**C2**), 86.9 (**C2**), 71.4 (**C14**), 70.2 (**C14**), 68.2 (**C5**), 68.1 (**C5**), 51.7 (**C21**), 39.7 (**C3**), 39.4 (**C3**), 38.8 (**C12**), 37.3 (**C12**), 31.6 (**C13**), 31.2 (**C13**), 25.6 (**C4**), 25.5 (**C4**).
IR (thin film, *υ*/cm^{-1}): 3413, 1721, 1436, 1272, 1048
HRMS (ESI): Found 313.14108, *m/z* calculated for $C_{17}H_{22}O_4{}^{23}Na$ $[M+Na]^+$: 313.14103.

Methyl (*E*)-4-bromo-6-(2-phenyltetrahydrofuran-2-yl)hex-2-enoate (23r)



Procedure: Alcohol **S8r** (20 mg, 0.069 mmol) was dissolved in CH_2Cl_2 (1.4 mL). CBr_4 (23 mg, 0.069 mmol) was added followed by PPh_3 (36 mg, 0.14 mmol). The reaction was stirred at room temperature for 2 hours. TLC analysis at this stage suggested complete consumption of starting materials. The reaction mixture was diluted with a large excess of ethyl acetate, stirred for 10 minutes, filtered and concentrated under reduced pressure. The crude was then purified by flash column chromatography (5% EA/ Pet. Ether 40-60 to 10% EA/ Pet. Ether 40-60) to give the desired compound **23r** in 45% yield (11 mg, 0.031 mmol, *E*:*Z* > 20:1) as a colourless oil.

R$_f$ = 0.31 (10% EA/Pet. Ether 40-60)

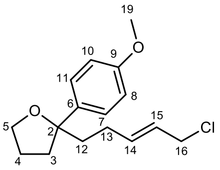
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36 – 7.30 (m, 4H, **H7**, **H8**, **H10**, **H11**), 7.25 – 7.20 (m, 1H, **H9**), 6.88 (dd, *J* = 15.5, 3.7 Hz, 0.5H, **H15**), 6.86 (dd, *J* = 15.5, 3.7 Hz, 0.5H, **H15**), 5.84 (dd, *J* = 15.5, 1.0 Hz, 0.5H, **H16**), 5.83 (dd, *J* = 15.5, 0.9 Hz, 0.5H, **H16**), 4.47 (td, *J* = 8.6, 5.5 Hz, 0.5H, **H14**), 4.40 (dt, *J* = 9.4, 7.0 Hz, 0.5H, **H14**), 4.02 – 3.94 (m, 1H, **H5'**), 3.94 – 3.86 (m, 1H, **H5**), 3.73 (s, 3H, **H21**), 2.22 – 2.13 (m, 1H, **H3'**), 2.09 – 2.01 (m, 1.5H, **H3**, **H12'**), 2.01 – 1.97 (m, 0.5H, **H13'**), 1.97 – 1.90 (m, 2H, **H4'**, **H12'**, **H13'**), 1.90 – 1.81 (m, 1H, **H12**), 1.80 – 1.74 (m, 1H, **H4**), 1.71 – 1.61 (m, 1H, **H13**).

^{13}C NMR (126 MHz, CDCl$_3$) δ 166.4 (**C17**), 146.9 (**C15**), 146.8 (**C15**), 146.2 (**C6**), 146.0 (**C6**), 128.4 (**C8**, **C10**), 126.7 (**C9**), 125.3 (**C7**, **C11**), 125.3 (**C7**, **C11**), 121.7 (**C16**), 121.5 (**C16**), 86.3 (**C2**), 86.2 (**C2**), 67.9 (**C5**), 67.8 (**C5**), 52.0 (**C21**), 51.9 (**C14**), 51.7 (**C14**), 40.1 (**C12**), 40.0 (**C12**), 39.3 (**C3**), 39.1 (**C3**), 33.1 (**C13**), 33.1 (**C13**), 25.6 (**C4**), 25.6 (**C4**).

IR (thin film, *υ*/cm^{-1}): 2949, 1723, 1655, 1435, 1272, 1048

HRMS (ESI): Ionized as [M-Br]$^+$, found 273.14865, *m/z* calculated for $C_{17}H_{21}O_3$ [M-Br]$^+$: 273.14852.

(*E*)-2-(5-Chloropent-3-en-1-yl)-2-(4-methoxyphenyl)tetrahydrofuran (23p)



Procedure: Compound **S7a** (50 mg, 0.22 mmol) was dissolved in dry and degassed CH_2Cl_2 (4.4 mL). Allyl chloride (88 μL, 1.08 mmol) was added followed by Hoveyda-Grubbs 2nd generation catalyst (14 mg, 0.022 mmol). The reaction was stirred at room temperature until completion. Upon complete consumption of starting materials as suggested by TLC analysis, all volatiles were removed under reduced pressure and the crude was purified by flash column chromatography (5% EA/ Pet. Ether 40-60 to 10% EA/ Pet. Ether 40-60) to give the desired compound **23p** in 68% yield (42 mg, 0.15 mmol, *E*:*Z* > 20:1) as a yellow oil.

R$_f$ = 0.56 (20% EA/Pet. Ether 40-60)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.30 – 7.22 (m, 2H, **H7**, **H11**), 6.91 – 6.82 (m, 2H, **H8**, **H10**), 5.69 (dtt, *J* = 15.2, 6.4, 1.2 Hz, 1H, **H14**), 5.52 (dtt, *J* = 15.5, 7.1, 1.4 Hz, 1H, **H15**), 4.00 – 3.92 (m, 3H, **H5'**, **H16**), 3.87 (td, *J* = 8.1, 5.5 Hz, 1H, **H5**), 3.80 (s, 3H, **H19**), 2.16 (ddd, *J* = 12.3, 7.9, 4.7 Hz, 1H, **H12'**), 2.10 – 2.04 (m, 1H, **H13'**), 2.04 – 1.99 (m, 1H, **H12**), 1.97 – 1.90 (m, 1H, **H4'**), 1.89 – 1.82 (m, 2H, **H3**), 1.81 – 1.74 (m, 2H, **H4**, **H13**).

^{13}C NMR (126 MHz, CDCl$_3$) δ 158.3 (**C9**), 138.4 (**C6**), 136.3 (**C14**), 126.5 (**C7**, **C11**), 125.7 (**C15**), 113.5 (**C8**, **C10**), 86.3 (**C2**), 67.6 (**C5**), 55.4 (**C19**), 45.7 (**C16**), 41.7 (**C3**), 38.6 (**C12**), 27.4 (**C13**), 25.6 (**C4**).

IR (thin film, *υ*/cm^{-1}): 2949, 1610, 1509, 1244, 1034

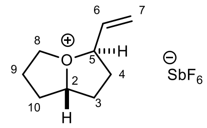
HRMS (ESI): Ionized as [M-Cl]$^+$, found 245.15384, *m/z* calculated for $C_{16}H_{21}O_2$ [M-Cl]$^+$: 245.15361.

6) Synthesis and characterization of monosubstituted oxonium ions

All of the oxonium ions, bar **24a**•SbF_6 were generated using $AgAl(pftb)_4$ given our extensive experience in both its use and synthesis.[11, 12] $AgSbF_6$ was also used for the formation of the oxonium ions **24m**•SbF_6 and **24l**•SbF_6 for comparison of the NMR data with the different counterions (some differences seen in both the ^{1}H and ^{13}C NMR spectra with the different anions (pages S53-S56, and Supporting Information (NMR) pages 192-216)). The different reactivity of **24m** and **24l** with the two counterions is detailed in the main text.

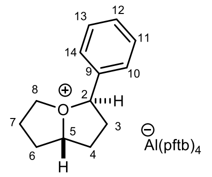
General procedure for the generation of monosubstituted oxonium ions 24: The monosubstituted oxonium ions **24** were generated from their halide precursors **23** (1.0 eq.) and $AgAl(pftb)_4{\cdot}CH_2Cl_2$ (or $AgSbF_6$) (1.1 eq.) in dry CD_2Cl_2 (0.7 mL) in a flame dried Young's NMR tube at their respective ***generation temperatures*** (see below). The halide precursor **23** (1.0 eq.) was quickly weighed out directly in the flame-dried Young's NMR tube, followed by the addition of dry CD_2Cl_2 (0.3 mL). ***Note:*** *The oxonium ions **24** were found to be only mildly sensitive to moisture, and thus temporary exposure to ambient conditions was tolerated.* The cap of the Young's NMR tube was closed, and the solution was mixed thoroughly by vigorous shaking, and the solution was incubated at the respective ***generation temperatures***. The silver salt ($AgAl(pftb)_4{\cdot}CH_2Cl_2$ or $AgSbF_6$) (1.1 eq.) was weighed out separately in a flame dried round bottom flask in a nitrogen-filled glove bag and dissolved in dry CD_2Cl_2 (0.4 mL) at room temperature. The room temperature solution of the silver salt was rapidly injected into the solution of the halide precursor **23** through the opening of the Young's NMR tube (not the opening of the cap). The cap of the Young's NMR tube was then closed, and the reaction mixture was thoroughly mixed by vigorous shaking. The silver halide precipitate generated upon the formation of monosubstituted oxonium ions **24** was allowed to settle at the bottom of the Young's NMR tube at their ***generation temperatures***. The monosubstituted oxonium ions **24** were then observed by NMR spectroscopy at their respective ***acquisition temperatures*** (see below).

(3*R**,7a*S**)-3-Vinylhexahydro-1*H*-furo[1,2-*a*]furan-4-ium hexafluoroantimonate 24a•SbF$_6$



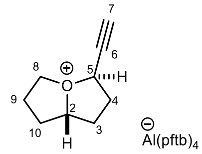
Generation temperature: 298K
Acquisition temperature: 298K
^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.97 (ddd, J = 16.9, 10.0, 8.4 Hz, 1H, **H6**), 5.83 (d, J = 16.9 Hz, 1H, **H7'**), 5.73 (d, J = 10.0 Hz, 1H, **H7**), 5.45 (ddt, J = 10.2, 7.8, 6.0 Hz, 1H, **H2**), 5.11 (ddd, J = 11.2, 8.5, 4.6 Hz, 1H, **H5**), 4.69 (ddd, J = 8.5, 6.6, 5.3 Hz, 1H, **H8'**), 4.50 (td, J = 8.2, 5.9 Hz, 1H, **H8**), 2.71 – 2.65 (m, 1H, **H4'**), 2.65 – 2.55 (m, 3H, **H3'**, **H9'**, **H10'**), 2.52 (ddd, J = 11.7, 5.1, 1.5 Hz, 1H, **H9**), 2.43 – 2.34 (m, 1H, **H4**), 2.33 – 2.20 (m, 2H, **H3**, **H10**).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 129.5 (**C6**), 128.3 (**C7**), 105.1 (**C2**), 104.4 (**C5**), 84.0 (**C8**), 34.8 (**C4**), 31.3 (**C3**), 30.9 (**C10**), 28.2 (**C9**).

(3*R**,7a*S**)-3-Phenylhexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24b•Al(pftb)$_4$



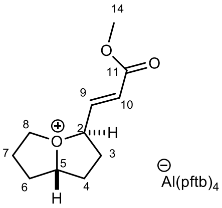
Generation temperature: 298K
Acquisition temperature: 298K
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.67 – 7.61 (m, 1H, **H12**), 7.60 – 7.55 (m, 2H, **H11**, **H13**), 7.50 – 7.44 (m, 2H, **H10**, **H14**), 5.62 (dtd, *J* = 10.9, 6.8, 5.5 Hz, 1H, **H5**), 5.41 (dd, *J* = 11.3, 4.8 Hz, 1H, **H2**), 4.56 (dt, *J* = 8.7, 6.3 Hz, 1H, **H8'**), 4.41 (ddd, *J* = 8.8, 7.6, 6.0 Hz, 1H, **H8**), 2.89 – 2.82 (m, 2H, **H3**), 2.82 – 2.76 (m, 1H, **H6'**), 2.73 – 2.63 (m, 1H, **H4'**), 2.62 – 2.51 (m, 2H, **H7**), 2.37 – 2.25 (m, 2H, **H4**, **H6**).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 133.3 (**C12**), 130.7 (**C11**, **C13**), 129.9 (**C9**), 128.4 (**C10**, **C14**), 106.3 (**C2**), 105.6 (**C5**), 84.1 (**C8**), 36.2 (**C3**), 32.1 (**C6**), 31.2 (**C4**), 28.1 (**C7**).

(3*R**,7a*S**)-3-Ethynylhexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24c•Al(pftb)$_4$



Generation temperature: 298K as a mixture of diastereomer, then sample left at 298K, or incubated at 313K and reaction progress monitored by ^{1}H NMR spectroscopy.
Acquisition temperature: 298K (single diastereomer)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.63 (tt, *J* = 8.9, 6.2 Hz, 1H, **H2**), 5.15 (ddd, *J* = 9.6, 5.2, 2.2 Hz, 1H, **H5**), 5.05 (ddd, *J* = 8.2, 6.5, 5.3 Hz, 1H, **H8'**), 4.48 (td, *J* = 8.3, 6.2 Hz, 1H, **H8**), 3.31 (d, *J* = 2.1 Hz, 1H, **H7**), 2.85 (dtd, *J* = 14.2, 5.4, 3.2 Hz, 1H, **H4'**), 2.78 (dtd, *J* = 13.2, 5.9, 3.4 Hz, 1H, **H3'**), 2.72 – 2.63 (m, 2H, **H4**, **H10'**), 2.63 – 2.53 (m, 2H, **H9**), 2.26 – 2.14 (m, 2H, **H3**, **H10**).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 107.6 (**C2**), 90.8 (**C5**), 86.8 (**C8**), 85.6 (**C7**), 72.4 (**C6**), 35.6 (**C4**), 31.1 (**C3**), 31.0 (**C10**), 28.2 (**C9**).

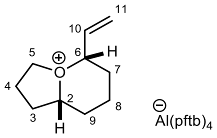
(3*R**,7a*S**)-3-((*E*)-3-Methoxy-3-oxoprop-1-en-1-yl)hexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24d•Al(pftb)$_4$



Generation temperature: 298K as a mixture of diastereomer, then incubated at 313K and reaction progress monitored by ^{1}H NMR spectroscopy.
Acquisition temperature: 298K (single diastereomer)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.85 (dd, *J* = 15.7, 7.8 Hz, 1H, **H9**), 6.32 (dd, *J* = 15.7, 0.9 Hz, 1H, **H10**), 5.60 (ddt, *J* = 10.4, 7.8, 6.2 Hz, 1H, **H5**), 5.04 (dddd, *J* = 10.8, 7.9, 4.7, 0.9 Hz, 1H, **H2**), 4.84 (dt, *J* = 8.4, 6.1 Hz, 1H, **H8'**), 4.41 (ddd, *J* = 8.5, 7.6, 6.2 Hz, 1H, **H8**), 3.82 (s, 3H, **H14**), 2.82 – 2.72 (m, 2H, **H3'**, **H4'**), 2.72 – 2.64 (m, 1H, **H6'**), 2.64 – 2.56 (m, 2H, **H7**), 2.49 (dddd, *J* = 14.1, 12.3,

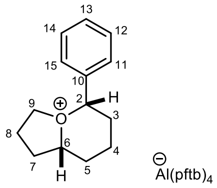
10.1, 5.8 Hz, 1H, **H3**), 2.31 – 2.24 (m, 1H, **H6**), 2.24 – 2.16 (m, 1H, **H4**).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 164.8 (**C11**), 135.0 (**C9**), 130.8 (**C10**), 108.0 (**C5**), 100.9 (**C2**), 86.0 (**C8**), 53.2 (**C14**), 34.8 (**C3**), 31.4 (**C4**), 30.8 (**C6**), 28.2 (**C7**).

(5*S**,8a*R**)-5-Vinyloctahydrofuro[1,2-*a*]pyran-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24e•Al(pftb)$_4$



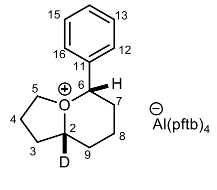
Generation temperature: 298K
Acquisition temperature: 298K
^{1}H NMR (500 MHz, CD_2Cl_2) δ 5.99 (dt, *J* = 17.1, 9.9, 9.5 Hz, 1H, **H10**), 5.81 (d, *J* = 9.9 Hz, 1H, **H11’**), 5.81 (d, *J* = 17.1 Hz, 1H, **H11**), 4.92 (ddd, *J* = 11.4, 9.2, 2.3 Hz, 1H, **H6**), 4.76 (q, *J* = 7.7 Hz, 1H, **H5’**), 4.48 (tdd, *J* = 11.3, 5.1, 2.0 Hz, 1H, **H2**), 4.27 (q, *J* = 8.3 Hz, 1H, **H5**), 2.60 (dq, *J* = 13.6, 5.4 Hz, 1H, **H3’**), 2.40 – 2.27 (m, 3H, **H3**, **H4**), 2.15 – 2.02 (m, 4H, **H7**, **H8’**, **H9’**), 1.91 – 1.84 (m, 1H, **H9**), 1.79 (dddd, *J* = 16.3, 11.7, 4.2, 2.0 Hz, 1H, **H8**).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 130.3 (**C10**), 129.5 (**C11**), 104.0 (**C6**), 102.7 (**C2**), 82.8 (**C5**), 32.0 (**C7**), 30.3 (**C9**), 30.2 (**C3**), 21.6 (**C8**), 20.6 (**C4**).

(5*S**,8a*R**)-5-Phenyloctahydrofuro[1,2-*a*]pyran-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24f•Al(pftb)$_4$



Generation temperature: 253K
Acquisition temperature: 253K
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.64 – 7.58 (m, 1H, **H13**), 7.58 – 7.52 (m, 2H, **H12**, **H14**), 7.49 – 7.43 (m, 2H, **H11**, **H15**), 5.39 (dd, *J* = 12.0, 2.2 Hz, 1H, **H2**), 4.60 (tdd, *J* = 11.3, 5.0, 1.8 Hz, 1H, **H6**), 4.22 (td, *J* = 8.4, 6.0 Hz, 1H, **H9’**), 4.02 (q, *J* = 8.3 Hz, 1H, **H9**), 2.60 (tdd, *J* = 12.1, 4.7, 2.5 Hz, 1H, **H7’**), 2.40 (dt, *J* = 16.4, 3.7 Hz, 2H, **H3’**, **H5’**), 2.31 – 2.20 (m, 1H, **H3**), 2.23 – 2.15 (m, 3H, **H4’**, **H8**), 2.17 – 2.07 (m, 1H, **H7**), 2.00 (dtd, *J* = 15.0, 11.9, 3.2 Hz, 1H, **H5**), 1.86 (qt, *J* = 13.1, 3.7 Hz, 1H, **H4**).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 133.0 (**C13**), 131.8 (**C10**), 130.4 (**C12**, **C14**), 126.3 (**C11**, **C15**), 104.8 (**C2**), 103.0 (**C6**), 83.0 (**C9**), 32.9 (**C3**), 30.0 (**C5**), 30.0 (**C7**), 22.0 (**C4**), 20.1 (**C8**).

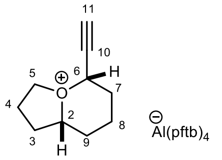
(5*S**,8a*R**)-5-Phenyloctahydrofuro[1,2-*a*]pyran-4-ium-8a-*d* tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24f-*d*•Al(pftb)$_4$



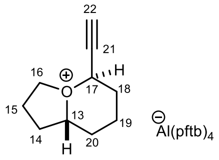
Generation temperature: 253K
Acquisition temperature: 253K
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.63 – 7.58 (m, 1H, **H14**), 7.57 – 7.52 (m, 2H, **H13**, **H15**), 7.48 –

7.42 (m, 2H, **H12**, **H16**), 5.38 (dd, *J* = 11.9, 2.2 Hz, 1H, **H6**), 4.22 (td, *J* = 8.4, 6.0 Hz, 1H, **H5'**), 4.01 (q, *J* = 8.8 Hz, 1H, **H5**), 2.58 (ddd, *J* = 13.1, 8.7, 2.3 Hz, 1H, **H3'**), 2.45 – 2.33 (m, 2H, **H7'**, **H9'**), 2.27 – 2.22 (m, 1H, **H7**), 2.22 – 2.14 (m, 3H, **H4**, **H8'**), 2.10 (dd, *J* = 12.8, 9.4 Hz, 1H, **H3**), 2.03 – 1.95 (m, 1H, **H9**), 1.86 (ddt, *J* = 16.3, 13.1, 6.5 Hz, 1H, **H8**).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 132.9 (**C14**), 131.7 (**C13**, **C15**), 130.3 (**C12**, **C16**), 128.9 (**C11**), 104.6 (**C6**), 102.4 (1:1:1 triplet, $J_{C\text{-}H}$ = 23.1 Hz, **C2**), 83.0 (**C5**), 32.9 (**C7**), 29.8 (**C3**, **C9**), 21.9 (**C8**), 20.0 (**C4**).

(5*S**,8a*R**)-5-Ethynyloctahydrofuro[1,2-*a*]pyran-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24g•Al(pftb)$_4$ and (5*R**,8a*R**)-5-Ethynyloctahydrofuro[1,2-*a*]pyran-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24g'•Al(pftb)$_4$ (ca. 1:1 diastereomeric mixture)



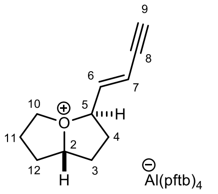
24g



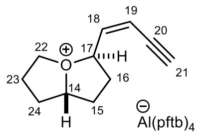
24g'

Generation temperature: 298K
Acquisition temperature: 298K
^{1}H NMR (500 MHz, CD_2Cl_2) δ 5.68 (dt, *J* = 4.3, 1.8 Hz, 1H, **H17**), 5.24 (td, *J* = 8.1, 6.7 Hz, 1H, **H5'**), 5.15 (dt, *J* = 11.8, 2.3 Hz, 1H, **H6**), 4.95 (tdd, *J* = 11.6, 5.0, 2.0 Hz, 1H, **H13**), 4.79 (q, *J* = 7.6 Hz, 1H, **H16'**), 4.70 (dt, *J* = 9.4, 7.3 Hz, 1H, **H16**), 4.59 (dt, *J* = 9.4, 8.0 Hz, 1H, **H5**), 4.60 – 4.52 (m, 1H, **H2**), 3.40 (d, *J* = 2.4 Hz, 1H, **H22**), 3.35 (d, *J* = 2.1 Hz, 1H, **H11**), 2.68 – 2.61 (m, 1H, **H3'**), 2.61 – 2.55 (m, 1H, **H14'**), 2.48 – 2.38 (m, 5H, **H4**, **H7'**, **H15**), 2.38 – 2.35 (m, 1H, **H20'**), 2.35 – 2.27 (m, 2H, **H9'**, **H18'**), 2.27 – 2.19 (m, 2H, **H7**, **H18**), 2.19 – 2.08 (m, 2H, **H3**, **H8'**), 2.09 – 1.98 (m, 3H, **H14**, **H19**), 1.97 – 1.84 (m, 2H, **H9**, **H20**), 1.77 (dtt, *J* = 14.6, 13.0, 3.7 Hz, 1H, **H8**).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 103.9 (**C2**), 98.7 (**C13**), 89.4 (**C6**), 87.8 (**C22**), 86.3 (**C17**), 85.7 (**C11**), 85.0 (**C5**), 83.8 (**C16**), 73.3 (**C10**), 71.0 (**C21**), 33.0 (**C7**), 30.8 (**C18**), 30.6 (**C20**), 30.5 (**C3**), 30.0 (**C9**), 29.5 (**C14**), 21.8 (**C15**), 21.5 (**C8**), 20.9 (**C4**), 17.8 (**C19**).

(3*R**,7a*S**)-3-((*E*)-But-1-en-3-yn-1-yl)hexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate (*E*)-24h•Al(pftb)$_4$ and (3*R**,7a*S**)-3-((*Z*)-But-1-en-3-yn-1-yl)hexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate (*Z*)-24h•Al(pftb)$_4$ (ca. 4:1 diastereomeric mixture)



(*E*)-**24h**

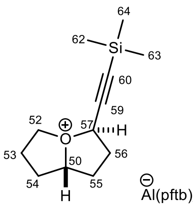


(*Z*)-**24h**

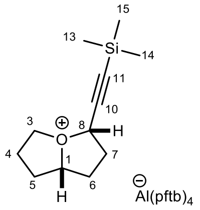
Generation temperature: 273K
Acquisition temperature: 273K
^{1}H NMR (500 MHz, CD_2Cl_2) δ 6.28 – 6.15 (m, 1.3H, **H6**, **H19**), 6.12 (dd, *J* = 15.8, 2.1 Hz, 1H, **H7**), 6.07 (ddd, *J* = 10.6, 9.5, 0.9 Hz, 0.3H, **H18**), 5.53 (ddd, *J* = 11.1, 9.2, 4.2 Hz, 0.3H, **H17**), 5.52 – 5.42 (m, 1.3H, **H2**, **H14**), 4.88 (ddd, *J* = 11.4, 8.6, 4.6 Hz, 1H, **H5**), 4.77 – 4.74 (m, 0.3H, **H22'**), 4.71 (dt, *J* = 8.7, 6.3 Hz, 1H, **H10'**), 4.52 (ddd, *J* = 8.4, 7.4, 5.7 Hz, 0.3H, **H22**), 4.35 (dt, *J* = 8.7, 6.7 Hz, 1H, **H10**), 3.60 (dd, *J* = 2.4, 0.9 Hz, 0.3H, **H21**), 3.38 (d, *J* = 2.1 Hz, 1H, **H9**), 2.76 – 2.65 (m, 2.5H, **H3'**,

H4’, **H15’**, **H16’**), 2.61 (m, 1.3H, **H12’**, **H24’**), 2.53 (m, 2.5H, **H11**, **H23**), 2.49 – 2.34 (m, 1.3H, **H4**, **H16**), 2.27 – 2.16 (m, 1.3H, **H12**, **H24**), 2.19 – 2.09 (m, 1.3H, **H3**, **H15**).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 132.8 (**C6**), 132.1 (**C18**), 122.6 (**C7**), 122.6 (**C19**), 105.8 (**C2**), 105.5 (**C14**), 103.6 (**C5**), 99.7 (**C17**), 89.1 (**C21**), 86.8 (**C20**), 85.3 (**C9**), 85.2 (**C22**), 84.2 (**C10**), 78.7 (**C8**), 34.5 (**C4**), 34.1 (**C16**), 31.7 (**C15**), 31.5 (**C3**), 30.7 (**C12**), 30.7 (**C24**), 28.0 (**C23**), 27.9 (**C11**).

(3*R,7a*S**)-3-((Trimethylsilyl)ethynyl)hexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24i•$Al(pftb)_4$ and (3*S**,7a*S**)-3-((Trimethylsilyl)ethynyl)hexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24i’•$Al(pftb)_4$ (ca. 1.4:1 diastereomeric mixture)**



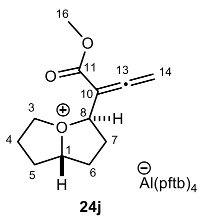
24i



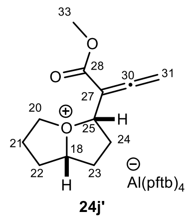
24i'

Generation temperature: 273K
Acquisition temperature: 273K
^{1}H NMR (500 MHz, CD_2Cl_2) δ 5.67 (dd, *J* = 6.5, 3.1 Hz, 0.7H, **H8**), 5.55 (ddt, *J* = 9.8, 8.3, 6.2 Hz, 1H, **H50**), 5.39 (tt, *J* = 9.1, 5.9 Hz, 0.7H, **H1**), 5.11 (dd, *J* = 10.0, 5.1 Hz, 1H, **H57**), 5.03 – 4.92 (m, 1.7H, **H3’**, **H52’**), 4.62 (ddd, *J* = 8.5, 6.9, 4.4 Hz, 0.7H, **H3**), 4.44 (td, *J* = 8.2, 6.3 Hz, 1H, **H52**), 2.81 – 2.76 (m, 1H, **H56’**), 2.76 – 2.70 (m, 1.7H, **H7’**, **H55’**), 2.69 – 2.63 (m, 1.4H, **H6’**, **H7**), 2.63 – 2.57 (m, 3.4H, **H4’**, **H5’**, **H54’**, **H56**), 2.57 – 2.53 (m, 2H, **H53**), 2.52 – 2.48 (m, 0.7H, **H4**), 2.34 (dtd, *J* = 13.5, 10.6, 9.3, 6.2 Hz, 0.7H, **H6**), 2.20 – 2.11 (m, 2H, **H54**, **H55**), 2.11 – 2.05 (m, 0.7H, **H5**), 0.25 (s, 6.3H, **H13**, **H14**, **H15**), 0.21 (s, 9H, **H62**, **H63**, **H64**).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 108.6 (**C11**), 106.8 (**C1**), 106.2 (**C50**), 104.8 (**C60**), 92.0 (**C10**), 91.9 (**C59**), 91.7 (**C57**), 89.3 (**C8**), 85.9 (**C52**), 81.3 (**C3**), 35.5 (**C56**), 35.4 (**C7**), 31.1 (**C55**), 30.7 (**C54**, **C5**), 30.0 (**C6**), 28.7 (**C4**), 27.9 (**C53**), -1.0 (**C62**, **C63**, **C64**), -1.0 (**C13**, **C14**, **C15**).

(3*R,7a*S**)-3-(1-Methoxy-1-oxobuta-2,3-dien-2-yl)hexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24j•$Al(pftb)_4$ and (3*S**,7a*S**)-3-(1-Methoxy-1-oxobuta-2,3-dien-2-yl)hexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24j’•$Al(pftb)_4$ (ca. 1.2:1 mixture of diastereomers)**



24j



24j'

Generation temperature: 253K
Acquisition temperature: 253K
^{1}H NMR (500 MHz, CD_2Cl_2) δ 5.87 – 5.84 (m, 0.8H, **H25**), 5.84 – 5.78 (m, 1.6H, **H31**), 5.77 – 5.68 (m, 2H, **H14**), 5.59 – 5.55 (m, 1H, **H8**), 5.53 (ddd, *J* = 10.9, 5.4, 2.2 Hz, 0.8H, **H18**), 5.45 (dq, *J* = 10.0, 6.3 Hz, 1H, **H1**), 4.87 (dt, *J* = 8.9, 6.2 Hz, 1H, **H3’**), 4.80 (td, *J* = 8.4, 5.8 Hz, 1H, **H3**), 4.52 (t, *J* = 7.4 Hz, 0.8H, **H20’**), 4.18 (ddd, *J* = 12.6, 7.6, 5.4 Hz, 0.8H, **H20**), 3.82 (s, 2.4H, **H33**), 3.81 (s, 3H, **H16**), 2.66 – 2.57 (m, 4.6H, **H6**, **H7’**, **H22’**, **H23’**), 2.56 – 2.49 (m, 2H, **H4’**, **H5’**), 2.49 – 2.42

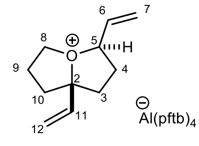
(m, 2.6H, **H4**, **H21'**, **H24'**), 2.35 – 2.28 (m, 2.4H, **H21**, **H23**, **H24**), 2.22 – 2.13 (m, 2H, **H5**, **H7**), 1.93 – 1.83 (m, 0.8H, **H22**).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 217.3 (**C30**), 215.8 (**C13**), 165.4 (**C11**), 164.5 (**C28**), 105.2 (**C1**), 104.6 (**C18**), 99.3 (**C8**), 97.8 (**C25**), 95.7 (**C10**), 93.9 (**C27**), 87.5 (**C3**), 85.4 (**C14**), 85.2 (**C31**), 79.7 (**C20**), 53.8 (**C16**, **C33**), 31.6 (**C22**), 31.1 (**C7**), 31.0 (**C6**), 30.1 (**C5**), 28.8 (**C23**), 28.1 (**C24**), 27.3 (**C4**), 26.9 (**C21**).

7) Synthesis and characterization of disubstituted oxonium ions

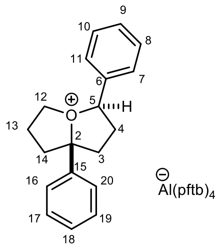
General procedure for the generation of disubstituted oxonium ions 24: The disubstituted oxonium ions **24** were generated from their halide precursors **23** (1.0 eq.) and $AgAl(pftb)_4{\cdot}CH_2Cl_2$ (or $AgSbF_6$) (1.1 eq.) in dry CD_2Cl_2 (0.7 mL) in a flame dried Young's NMR tube at their respective ***generation temperatures*** (see below). The halide precursor **23** (1.0 eq.) was quickly weighed out directly in the flame-dried Young's NMR tube, followed by the addition of dry CD_2Cl_2 (0.3 mL). ***Note:*** *The oxonium ions* ***24*** *were found to be only mildly sensitive to moisture, and thus temporary exposure to ambient conditions was tolerated.* The cap of the Young's NMR tube was closed, and the solution was mixed thoroughly by vigorous shaking, and the solution was incubated at the respective ***generation temperatures***. The silver salt ($AgAl(pftb)_4{\cdot}CH_2Cl_2$ or $AgSbF_6$) (1.1 eq.) was weighed out separately in a flame dried round bottom flask in a nitrogen-filled glove bag and dissolved in dry CD_2Cl_2 (0.4 mL) at room temperature. The room temperature solution of the silver salt was rapidly injected into the solution of the halide precursor **23** through the opening of the Young's NMR tube (not the opening of the cap). The cap of the Young's NMR tube was then closed, and the reaction mixture was thoroughly mixed by vigorous shaking. The silver halide precipitate generated upon the formation of disubstituted oxonium ions **24** was allowed to settle at the bottom of the Young's NMR tube at their ***generation temperatures***. The disubstituted oxonium ions **24** were observed by NMR spectroscopy at their respective ***acquisition temperatures*** (see below).

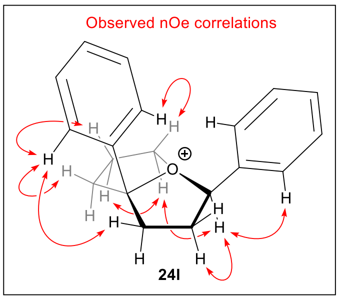
(3*R**,7a*S**)-3,7a-Divinylhexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24k•Al(pftb)$_4$



Generation temperature: 273K
Acquisition temperature: 273K
^{1}H NMR (500 MHz, CD_2Cl_2) δ 5.99 – 5.89 (m, 2H, **H6**, **H11**), 5.79 (d, *J* = 10.1 Hz, 1H, **H7'**), 5.78 (d, *J* = 16.9 Hz, 1H, **H7**), 5.53 (d, *J* = 11.1 Hz, 1H, **H12'**), 5.42 (d, *J* = 17.1 Hz, 1H, **H12**), 4.88 (ddd, *J* = 11.4, 8.8, 4.6 Hz, 1H, **H5**), 4.68 (dt, *J* = 9.0, 6.4 Hz, 1H, **H8'**), 4.38 (dt, *J* = 9.3, 6.5 Hz, 1H, **H8**), 2.67 – 2.63 (m, 1H, **H3'**), 2.63 – 2.58 (m, 1H, **H4'**), 2.57 – 2.53 (m, 2H, **H9**), 2.53 – 2.47 (m, 1H, **H10'**), 2.47 – 2.41 (m, 1H, **H4**), 2.41 – 2.36 (m, 1H, **H10**), 2.36 – 2.30 (m, 1H, **H3**).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 133.7 (**C11**), 129.3 (**C7**), 128.8 (**C6**), 119.4 (**C12**), 119.4 (**C2**), 105.4 (**C5**), 83.2 (**C8**), 36.0 (**C10**), 35.7 (**C3**), 33.5 (**C4**), 27.7 (**C9**).

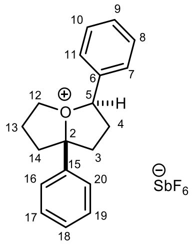
(3R*,7aS*)-3,7a-Diphenylhexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24l•Al(pftb)$_4$





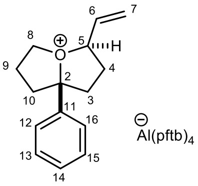
Generation temperature: 253K
Acquisition temperature: 253K
^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ 7.73 – 7.62 (m, 1H, **H9**), 7.61 – 7.57 (m, 2H, **H8**, **H10**), 7.57 – 7.53 (m, 2H, **H17**, **H19**), 7.53 – 7.50 (m, 1H, **H18**), 7.50 – 7.41 (m, 2H, **H7**, **H11**), 7.33 – 7.22 (m, 2H, **H16**, **H20**), 5.57 (dd, *J* = 11.9, 4.0 Hz, 1H, **H5**), 4.69 (dt, *J* = 9.0, 6.4 Hz, 1H, **H12'**), 4.63 (dt, *J* = 9.0, 6.4 Hz, 1H, **H12**), 3.22 – 3.02 (m, 1H, **H3'**), 2.82 – 2.73 (m, 3H, **H3**, **H4'**, **H14'**), 2.73 – 2.67 (m, 1H, **H4'**), 2.69 – 2.58 (m, 2H, **H13'**, **H14**), 2.50 (ddd, *J* = 14.1, 9.4, 5.5 Hz, 1H, **H13**).
^{13}C NMR (126 MHz, CD$_2$Cl$_2$) δ 137.9 (**C15**), 133.3 (**C9**), 130.5 (**C8**, **C10**), 130.3 (**C18**), 130.0 (**C17**, **C19**), 129.1 (**C7**, **C11**), 129.0 (**C6**), 124.0 (**C16**, **C20**), 119.8 (**C2**), 107.8 (**C5**), 84.0 (**C12**), 40.1 (**C14**), 38.9 (**C3**), 34.0 (**C4**), 27.6 (**C13**).

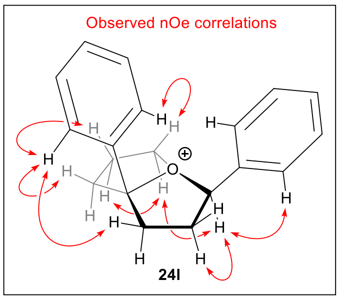
(3R*,7aS*)-3,7a-Diphenylhexahydro-1*H*-furo[1,2-*a*]furan-4-ium hexafluoroantimonate 24l•SbF$_6$



Generation temperature: 243K
Acquisition temperature: 243K
^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ 7.64 – 7.58 (m, 1H, **H9**), 7.58 – 7.55 (m, 2H, **H8**, **H10**), 7.55 – 7.53 (m, 2H, **H17**, **H19**), 7.53 – 7.51 (m, 2H, **H7**, **H11**), 7.52 – 7.45 (m, 1H, **H18**), 7.33 (m, 2H, **H16**, **H20**), 5.87 (dd, *J* = 12.2, 4.4 Hz, 1H, **H5**), 4.78 (q, *J* = 7.5 Hz, 1H, **H12'**), 4.68 (q, *J* = 6.5 Hz, 1H, **H12**), 3.02 (dd, *J* = 13.4, 5.3 Hz, 1H, **H3'**), 2.91 (td, *J* = 13.1, 5.2 Hz, 1H, **H3**), 2.85 (dd, *J* = 13.6, 6.9 Hz, 1H, **H14'**), 2.76 (dt, *J* = 14.4, 4.9 Hz, 1H, **H4'**), 2.70 (dt, *J* = 12.8, 6.1 Hz, 1H, **H13'**), 2.64 – 2.57 (m, 1H, **H4**), 2.57 – 2.51 (m, 1H, **H14**), 2.40 (tt, *J* = 13.8, 6.6 Hz, 1H, **H13**).
^{13}C NMR (126 MHz, CD$_2$Cl$_2$) δ 138.8 (**C15**), 132.0 (**C9**), 130.1 (**C6**), 129.8 (**C8**, **C10**), 129.4 (**C17**, **C19**), 129.3 (**C7**, **C11**), 129.1 (**C18**), 124.3 (**C16**, **C20**), 118.8 (**C2**), 106.7 (**C5**), 84.4 (**C12**), 39.8 (**C14**), 38.6 (**C3**), 34.3 (**C4**), 27.6 (**C13**).

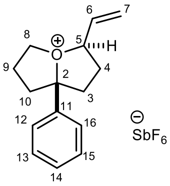
(3*R**,7a*S**)-7a-Phenyl-3-vinylhexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24m•Al(pftb)$_4$





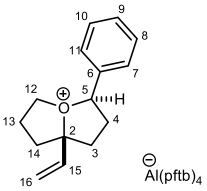
Generation temperature: 273K
Acquisition temperature: 273K
^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ 7.56 – 7.46 (m, 3H, **H13**, **H14**, **H15**), 7.25 – 7.18 (m, 2H, **H12**, **H16**), 6.08 (ddd, *J* = 17.2, 10.0, 8.9 Hz, 1H, **H6**), 5.88 (d, *J* = 10.0 Hz, 1H, **H7'**), 5.88 (d, *J* = 17.0 Hz, 1H, **H7**), 5.06 (ddd, *J* = 11.7, 8.9, 4.3 Hz, 1H, **H5**), 4.84 (dt, *J* = 9.0, 6.6 Hz, 1H, **H8'**), 4.58 (dt, *J* = 9.0, 6.4 Hz, 1H, **H8**), 2.87 (dd, *J* = 12.4, 5.5 Hz, 1H, **H3'**), 2.74 (ddd, *J* = 13.5, 7.3, 6.3 Hz, 1H, **H10'**), 2.68 (q, *J* = 6.6 Hz, 1H, **H10**), 2.65 – 2.56 (m, 3H, **H3**, **H4'**, **H9'**), 2.50 (tt, *J* = 13.3, 6.5 Hz, 1H, **H9**), 2.33 (tdd, *J* = 11.2, 9.7, 8.8, 5.8 Hz, 1H, **H4**).
^{13}C NMR (126 MHz, CD$_2$Cl$_2$) δ 138.0 (**C11**), 130.2 (**C7**), 130.2 (**C14**), 129.9 (**C13**, **C15**), 128.5 (**C6**), 123.8 (**C12**, **C16**), 119.3 (**C2**), 106.6 (**C5**), 84.0 (**C8**), 39.5 (**C10**), 39.1 (**C3**), 32.9 (**C4**), 27.5 (**C9**).

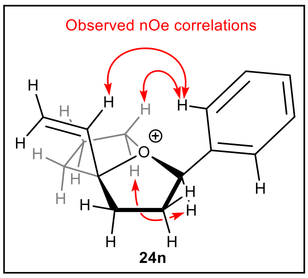
(3*R**,7a*S**)-7a-Phenyl-3-vinylhexahydro-1*H*-furo[1,2-*a*]furan-4-ium hexafluoroantimonate 24m•Al(pftb)$_4$



Generation temperature: 253K
Acquisition temperature: 253K
^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ 7.51 – 7.43 (m, 3H, **H13**, **H14**, **H15**), 7.28 – 7.21 (m, 2H, **H12**, **H16**), 6.05 (dt, *J* = 16.9, 9.4 Hz, 1H, **H6**), 5.96 (d, *J* = 16.8 Hz, 1H, **H7'**), 5.82 (d, *J* = 9.8 Hz, 1H, **H7**), 5.35 (td, *J* = 9.4, 9.0, 2.7 Hz, 1H, **H5**), 4.83 (dt, *J* = 8.2, 6.2 Hz, 1H, **H8'**), 4.74 (q, *J* = 7.8, 7.4 Hz, 1H, **H8**), 2.81 (dt, *J* = 13.4, 8.0, 5.9 Hz, 1H, **H10**), 2.78 – 2.73 (m, 2H, **H3**), 2.67 (dq, *J* = 13.7, 7.4, 6.2, 5.0 Hz, 1H, **H9'**), 2.65 – 2.57 (m, 1H, **H4'**), 2.56 (dd, *J* = 13.4, 5.0 Hz, 1H, **H10**), 2.39 (dp, *J* = 13.7, 8.0, 7.4, 6.2 Hz, 1H, **H9**), 2.22 (ddt, *J* = 14.2, 11.6, 9.0 Hz, 1H, **H4**).
^{13}C NMR (126 MHz, CD$_2$Cl$_2$) δ 139.0 (**C11**), 129.8 (**C7**), 129.5 (**C13**, **C15**), 129.3 (**C14**), 128.8 (**C6**), 124.0 (**C12**, **C16**), 117.9 (**C2**), 106.1 (**C5**), 84.2 (**C8**), 39.3 (**C10**), 38.9 (**C3**), 33.1 (**C4**), 27.6 (**C9**).

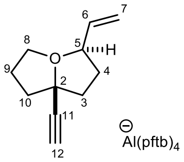
(3*R**,7a*S**)-3-Phenyl-7a-vinylhexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24n•Al(pftb)$_4$





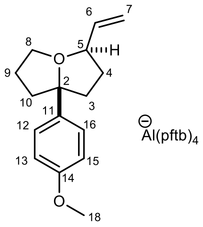
Generation temperature: 233K
Acquisition temperature: 233K
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.60 (t, *J* = 7.5 Hz, 1H, **H9**), 7.54 (t, *J* = 7.6 Hz, 2H, **H8**, **H10**), 7.44 (d, *J* = 7.4 Hz, 2H, **H7**, **H11**), 6.04 (dd, *J* = 17.1, 11.4 Hz, 1H, **H15**), 5.61 (d, *J* = 11.1 Hz, 1H, **H16'**), 5.51 (d, *J* = 17.0 Hz, 1H, **H16**), 5.38 (t, *J* = 8.4 Hz, 1H, **H5**), 4.50 (dt, *J* = 8.8, 6.1 Hz, 1H, **H12'**), 4.42 (dt, *J* = 8.9, 6.0 Hz, 1H, **H12**), 2.81 (dt, *J* = 13.4, 3.4 Hz, 1H, **H3'**), 2.78 – 2.72 (m, 2H, **H4**), 2.60 – 2.51 (m, 2H, **H13**), 2.51 – 2.48 (m, 1H, **H14'**), 2.48 – 2.40 (m, 2H, **H3**, **H14**).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 133.5 (**C15**), 132.7 (**C9**), 130.1 (**C8**, **C10**), 129.4 (**C6**), 128.6 (**C7**, **C11**), 119.6 (**C16**), 119.2 (**C2**), 106.0 (**C5**), 83.1 (**C12**), 36.1 (**C14**), 35.4 (**C3**), 34.9 (**C4**), 27.5 (**C13**).

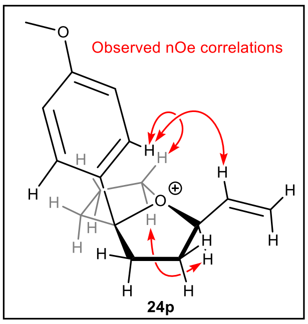
(3*R**,7a*S**)-7a-Ethynyl-3-vinylhexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24o•Al(pftb)$_4$



*Generated as a ca. 2.4:1 mixture of **24o** and **52** (for characterization of **52**, see below).
Generation temperature: 263K
Acquisition temperature: 263K
^{1}H NMR (500 MHz, CD_2Cl_2) δ 5.99 (ddd, *J* = 17.1, 10.2, 8.9 Hz, 1H, **H6**), 5.87 – 5.65 (m, 2H, **H7**), 4.88 (q, *J* = 8.5 Hz, 1H, **H5**), 4.82 (dt, *J* = 8.5, 6.0 Hz, 1H, **H8'**), 4.34 (ddd, *J* = 8.5, 7.2, 5.8 Hz, 1H, **H8**), 3.36 (s, 1H, **H12**), 2.92 – 2.80 (m, 1H, **H3'**), 2.81 – 2.75 (m, 1H, **H10'**), 2.75 – 2.69 (m, 3H, **H4**, **H9'**), 2.67 – 2.57 (m, 1H, **H9**), 2.56 – 2.49 (m, 1H, **H10**), 2.49 – 2.39 (m, 1H, **H3**).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 129.5 (**C7**), 128.8 (**C6**), 110.4 (**C2**), 106.0 (**C5**), 84.3 (**C12**), 83.5 (**C8**), 77.1 (**C11**), 38.5 (**C3**), 38.3 (**C10**), 35.0 (**C4**), 28.9 (**C9**).

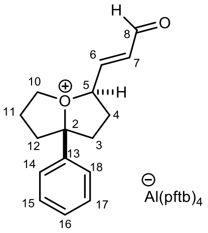
(3R*,7aS*)-7a-(4-Methoxyphenyl)-3-vinylhexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24p•Al(pftb)$_4$

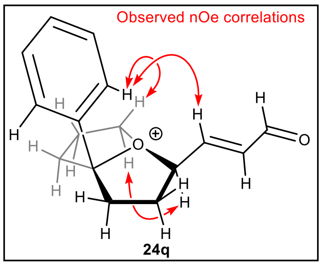




Generation temperature: 253K
Acquisition temperature: 253K
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.15 (d, *J* = 8.7 Hz, 2H, **H12**, **H16**), 6.98 (d, *J* = 8.8 Hz, 2H, **H13**, **H15**), 6.00 (dt, *J* = 17.2, 9.3 Hz, 1H, **H6**), 5.89 – 5.74 (m, 2H, **H7**), 4.97 (ddt, *J* = 11.4, 8.9, 4.4 Hz, 1H, **H5**), 4.77 (dt, *J* = 8.9, 6.5 Hz, 1H, **H8'**), 4.53 (dt, *J* = 9.1, 6.1 Hz, 1H, **H8**), 3.80 (s, 3H, **H18**), 2.86 (dd, *J* = 12.7, 5.6 Hz, 1H, **H3'**), 2.73 – 2.62 (m, 2H, **H10**), 2.61 – 2.55 (m, 1H, **H4'**), 2.55 – 2.51 (m, 2H, **H3**, **H9'**), 2.51 – 2.44 (m, 1H, **H9**), 2.32 (qd, *J* = 11.8, 10.8, 5.1 Hz, 1H, **H4**).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 160.8 (**C14**), 129.6 (**C7**), 129.3 (**C11**), 128.7 (**C6**), 125.6 (**C12**, **C16**), 121.2 (**C2**), 114.9 (**C13**, **C15**), 105.8 (**C5**), 83.4 (**C8**), 55.8 (**C18**), 39.4 (**C10**), 38.4 (**C3**), 33.1 (**C4**), 27.6 (**C9**).

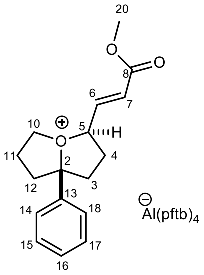
(3R*,7aS*)-3-((*E*)-3-Oxoprop-1-en-1-yl)-7a-phenylhexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24q•Al(pftb)$_4$

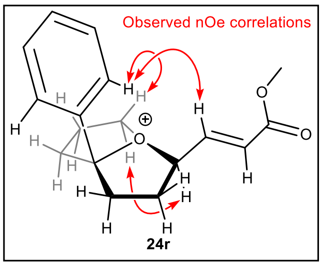




Generation temperature: 253K
Acquisition temperature: 253K
^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.65 (d, *J* = 7.3 Hz, 1H, **H8**), 7.53 (q, *J* = 4.3 Hz, 3H, **H15**, **H16**, **H17**), 7.31 – 7.18 (m, 2H, **H14**, **H18**), 6.81 (dd, *J* = 15.9, 7.8 Hz, 1H, **H6**), 6.49 (dd, *J* = 15.9, 7.2 Hz, 1H, **H7**), 5.25 (ddd, *J* = 12.1, 7.7, 4.9 Hz, 1H, **H5**), 4.97 (dt, *J* = 8.7, 6.6 Hz, 1H, **H10'**), 4.64 (dt, *J* = 8.9, 6.0 Hz, 1H, **H10**), 3.02 (ddd, *J* = 13.5, 5.5, 1.7 Hz, 1H, **H3'**), 2.82 – 2.78 (m, 1H, **H12'**), 2.78 – 2.74 (m, 1H, **H4'**), 2.74 – 2.70 (m, 1H, **H12**), 2.70 – 2.64 (m, 1H, **H3**, **H11'**), 2.64 – 2.58 (m, 1H, **H11**), 2.41 (qd, *J* = 12.7, 5.5 Hz, 1H, **H4**).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 192.5 (**C8**), 141.6 (**C6**), 137.9 (**C6**), 136.8 (**C13**), 130.8 (**C16**), 130.1 (**C15**, **C17**), 125.4 (**C2**), 123.8 (**C14**, **C18**), 100.5 (**C5**), 86.5 (**C10**), 39.2 (**C12**), 38.1 (**C3**), 33.5 (**C4**), 27.9 (**C11**).

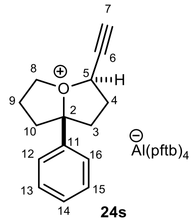
(3*R**,7a*S**)-3-((*E*)-3-Methoxy-3-oxoprop-1-en-1-yl)-7a-phenylhexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24r•$Al(pftb)_4$



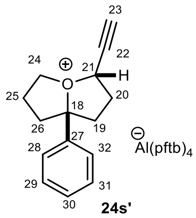


Generation temperature: 253K
Acquisition temperature: 253K
^{1}**H NMR** (500 MHz, CD_2Cl_2) δ 7.59 – 7.44 (m, 3H, **H15**, **H16**, **H17**), 7.29 – 7.09 (m, 2H, **H14**, **H18**), 6.94 (dd, *J* = 15.6, 8.7 Hz, 1H, **H6**), 6.37 (d, *J* = 15.6 Hz, 1H, **H7**), 5.14 (ddd, *J* = 12.8, 8.6, 4.4 Hz, 1H, **H5**), 4.92 (dt, *J* = 8.7, 6.4 Hz, 1H, **H10'**), 4.59 (dt, *J* = 8.8, 6.2 Hz, 1H, **H10**), 3.80 (s, 3H, **H20**), 2.95 (dd, *J* = 12.4, 5.4 Hz, 1H, **H3'**), 2.77 (dt, *J* = 13.0, 6.6 Hz, 1H, **H12'**), 2.73 – 2.69 (m, 1H, **H12**), 2.69 – 2.66 (m, 1H, **H4'**), 2.66 – 2.64 (m, 1H, **H3**), 2.64 – 2.60 (m, 1H, **H11'**), 2.56 (dt, *J* = 13.7, 6.6 Hz, 1H, **H11**), 2.44 – 2.38 (m, 1H, **H4**).
^{13}**C NMR** (126 MHz, CD_2Cl_2) δ 164.8 (**C8**), 137.2 (**C13**), 134.9 (**C6**), 131.2 (**C7**), 130.5 (**C16**), 130.0 (**C15**, **C17**), 123.8 (**C14**, **C18**), 123.5 (**C2**), 101.6 (**C5**), 85.7 (**C10**), 53.1 (**C20**), 39.3 (**C12**), 38.5 (**C3**), 33.4 (**C4**), 27.8 (**C11**).

(3*R**,7a*S**)-3-Ethynyl-7a-phenylhexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24s•$Al(pftb)_4$ and (3*S**,7a*S**)-3-Ethynyl-7a-phenylhexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24s'•$Al(pftb)_4$ (24s:24s' = 1.3:1)



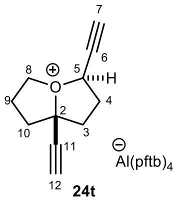
24s



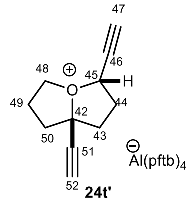
24s'

Generation temperature: 273K
Acquisition temperature: 273K
^{1}**H NMR** (500 MHz, CD_2Cl_2) δ 7.65 – 7.41 (m, 5.0H, **H13**, **H14**, **H15**, **H29**, **H30**, **H31**), 7.40 – 7.27 (m, 2H, **H12**, **H16**), 7.27 – 7.12 (m, 1.5H, **H28**, **H32**), 5.88 (dt, *J* = 5.9, 3.1 Hz, 0.8H, **H21**), 5.37 – 5.30 (m, 1H, **H5**), 5.22 (td, *J* = 8.7, 6.1 Hz, 0.8H, **H24'**), 5.17 (dt, *J* = 8.6, 6.1 Hz, 1H, **H8'**), 4.89 (ddd, *J* = 8.6, 7.1, 4.3 Hz, 0.8H, **H24**), 4.68 (td, *J* = 8.3, 6.1 Hz, 1H, **H8**), 3.56 (d, *J* = 2.3 Hz, 0.4H, **H23**), 3.39 (d, *J* = 2.1 Hz, 0.5H, **H7**), 2.86 – 2.80 (m, 3.3H, **H3'**, **H4'**, **H19'**), 2.79 – 2.75 (m, 3H, **H10'**, **H19**, **H26'**), 2.74 – 2.71 (m, 2H, **H20**), 2.71 – 2.65 (m, 3H, **H3**, **H25'**, **H26**), 2.64 – 2.56 (m, 3H, **H4**, **H9'**, **H10**), 2.55 – 2.48 (m, 1H, **H9**), 2.48 – 2.43 (m, 0.8H, **H25**).
^{13}**C NMR** (126 MHz, CD_2Cl_2) δ 137.4 (**C27**), 137.3 (**C11**), 130.6 (**C14**, **C30**), 130.1 (**C29**, **C31**), 130.1 (**C13**, **C15**), 124.1 (**C12**, **C16**), 123.8 (**C28**, **C32**), 123.4 (**C2**), 123.2 (**C18**), 91.4 (**C5**), 88.8 (**C23**), 88.5 (**C21**), 87.1 (**C8**), 85.9 (**C7**), 82.5 (**C24**), 72.4 (**C6**), 72.1 (**C22**), 38.9 (**C3**), 38.8 (**C26**), 38.8 (**C10**), 37.8 (**C19**), 35.0 (**C20**), 34.5 (**C4**), 28.4 (**C25**), 27.8 (**C9**).

(3*R**,7a*S**)-3,7a-Diethynylhexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24t•Al(pftb)$_4$ and (3*S**,7a*S**)-3,7a-Diethynylhexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24t’•Al(pftb)$_4$ (24t:24t’ = 1:1.1)



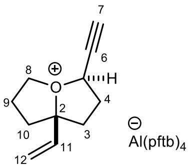
24t



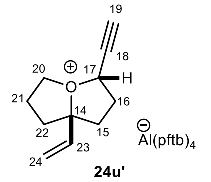
24t'

Generation temperature: 298K
Acquisition temperature: 298K
^{1}**H NMR** (400 MHz, CD$_2$Cl$_2$) δ 5.81 (dt, *J* = 6.6, 2.4 Hz, 1H, **H45**), 5.22 – 5.06 (m, 2H, **H5**, **H8’**), 5.02 (ddd, *J* = 9.4, 8.3, 6.0 Hz, 1H, **H48’**), 4.84 (ddd, *J* = 8.2, 7.0, 4.1 Hz, 1H, **H48**), 4.45 (td, *J* = 8.4, 5.8 Hz, 1H, **H8**), 3.51 (d, *J* = 2.2 Hz, 1H, **H47**), 3.48 (s, 1H, **H12**), 3.42 (s, 1H, **H52**), 3.34 (d, *J* = 2.2 Hz, 1H, **H7**), 3.18 – 3.01 (m, 1H, **H44’**), 2.98 – 2.89 (m, 3H, **H3’**, **H4**), 2.88 – 2.78 (m, 6H, **H9’**, **H10’**, **H43’**, **H44**, **H49’**, **H50’**), 2.76 – 2.63 (m, 3H, **H9**, **H43**, **H49**), 2.57 – 2.48 (m, 2H, **H3**, **H10**), 2.47 – 2.42 (m, 1H, **H50**).
^{13}**C NMR** (101 MHz, CD$_2$Cl$_2$) δ 115.0 (**C42**), 114.8 (**C2**), 91.0 (**C5**), 89.3 (**C47**), 88.1 (**C45**), 86.5 (**C8**), 86.2 (**C7**), 86.0 (**C12**), 85.7 (**C52**), 81.8 (**C48**), 76.9 (**C11**, **C51**), 72.3 (**C6**), 72.0 (**C46**), 38.6 (**C10**), 38.4 (**C50**), 38.3 (**C3**), 37.3 (**C43**), 37.0 (**C44**), 36.4 (**C4**), 30.5 (**C49**), 29.5 (**C9**).

(3*R**,7a*S**)-3-Ethynyl-7a-vinylhexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24u•Al(pftb)$_4$ and (3*S**,7a*S**)-3-Ethynyl-7a-vinylhexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24u’•Al(pftb)$_4$ (24u:24u’ = 1.2:1)



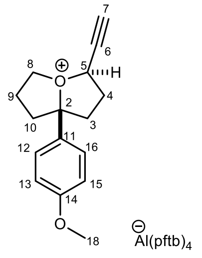
24u



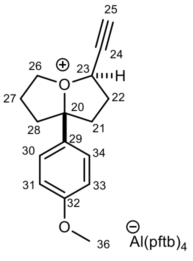
24u'

Generation temperature: 273K
Acquisition temperature: 273K
^{1}**H NMR** (500 MHz, CD$_2$Cl$_2$) δ 5.99 (dd, *J* = 17.1, 11.1 Hz, 1H, **H11**), 5.93 (dd, *J* = 17.1, 11.1 Hz, 1H, **H23**), 5.69 (dt, *J* = 6.7, 2.7 Hz, 1H, **H17**), 5.59 (d, *J* = 11.1 Hz, 1H, **H24’**), 5.56 (d, *J* = 11.6 Hz, 2H, **H12’**), 5.52 (d, *J* = 17.1 Hz, 1H, **H24**), 5.43 (d, *J* = 17.1 Hz, 1H, **H12**), 5.15 (ddd, *J* = 8.9, 5.6, 2.2 Hz, 1H, **H5**), 5.08 – 5.04 (m, 1H, **H8’**), 5.04 – 5.00 (m, 1H, **H20’**), 4.72 (ddd, *J* = 8.4, 6.9, 4.4 Hz, 1H, **H20**), 4.50 – 4.42 (m, 1H, **H8**), 3.47 (d, *J* = 2.2 Hz, 1H, **H19**), 3.29 (d, *J* = 2.1 Hz, 1H, **H7**), 2.87 – 2.77 (m, 2H, **H4’**, **H16’**), 2.72 – 2.63 (m, 4H, **H3’**, **H4**, **H16**, **H21’**), 2.62 – 2.52 (m, 6H, **H9**, **H10’**, **H15**, **H21’**, **H22’**), 2.43 – 2.37 (m, 1H, **H3**), 2.37 – 2.32 (m, 1H, **H10**), 2.33 – 2.26 (m, 1H, **H22**).
^{13}**C NMR** (126 MHz, CD$_2$Cl$_2$) δ 133.2 (**C11**), 133.1 (**C23**), 123.6 (**C2**), 123.1 (**C14**), 120.4 (**C24**), 119.9 (**C12**), 90.0 (**C5**), 88.4 (**C19**), 87.3 (**C17**), 86.2 (**C8**), 85.2 (**C7**), 81.5 (**C20**), 72.5 (**C6**), 72.1 (**C18**), 35.5 (**C3**), 35.4 (**C10**, **C22**), 35.3 (**C16**), 34.8 (**C4**), 34.4 (**C15**), 28.8 (**C21**), 28.0 (**C9**).

(3R^*,7aS^*)-3-Ethynyl-7a-(4-methoxyphenyl)hexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24v•Al(pftb)$_4$ and (3S^*,7aS^*)-3-Ethynyl-7a-(4-methoxyphenyl)hexahydro-1*H*-furo[1,2-*a*]furan-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 24v'•Al(pftb)$_4$ (24v:24v' = ca. 1.7-1.8:1)



24v



24v'

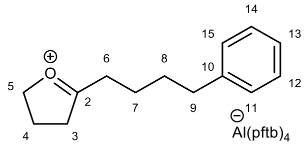
Generation temperature: 253K
Acquisition temperature: 233K
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.41 (m, 2H, **H12**, **H16**), 7.20 (m, 1H, **H30**, **H34**), 7.02 (m, 2H, **H13**, **H15**), 6.98 (m, 1H, **H31**, **H33**), 5.81 – 5.68 (m, 0.5H, **H23**), 5.15 – 5.10 (m, 1H, **H5**), 5.06 (td, *J* = 8.8, 5.9 Hz, 0.5H, **H26'**), 4.94 (dt, *J* = 9.1, 5.8 Hz, 1H, **H8'**), 4.77 (q, *J* = 7.0 Hz, 0.5H, **H26**), 4.44 (td, *J* = 8.4, 5.4 Hz, 1H, **H8**), 3.85 (s, 3H, **H18**), 3.81 (s, 1.5H, **H36**), 3.46 (d, *J* = 2.4 Hz, 0.5H, **H25**), 3.25 (d, *J* = 2.2 Hz, 1H, **H7**), 3.03 – 2.95 (m, 1H, **H3'**), 2.93 – 2.87 (m, 1H, **H10'**), 2.87 – 2.81 (m, 1H, **H4'**), 2.80 – 2.74 (m, 1.5H, **H21**, **H28'**), 2.74 – 2.69 (m, 1H, **H22**), 2.68 – 2.62 (m, 2.5H, **H3**, **H10**, **H27'**), 2.62 – 2.57 (m, 2H, **H4**, **H9'**), 2.57 – 2.53 (m, 0.5H, **H28**), 2.54 – 2.44 (m, 1.5H, **H9**, **H27**).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 163.1 (**C14**), 161.6 (**C32**), 140.8 (**C2**), 130.6 (**C20**), 128.6 (**C29**), 128.5 (**C11**), 128.2 (**C12**, **C16**), 126.4 (**C30**, **C34**), 115.2 (**C13**, **C15**), 114.9 (**C31**, **C33**), 87.4 (**C25**), 87.1 (**C5**), 86.3 (**C23**), 84.0 (**C8**), 83.7 (**C7**), 80.8 (**C26**), 73.4 (**C6**), 72.2 (**C24**), 56.1 (**C18**), 55.9 (**C36**), 38.1 (**C28**), 37.9 (**C3**), 37.8 (**C10**), 37.2 (**C21**), 35.0 (**C4**, **C22**), 29.6 (**C9**), 29.2 (**C27**).

8) Synthesis and characterization of rearranged oxonium ions

General procedures for the synthesis of oxocarbenium ions 33•Al(pftb)$_4$ **and 33-*d*•**Al(pftb)$_4$**:**

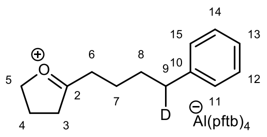
The oxocarbenium ions **33/33-*d*•**Al(pftb)$_4$ were generated by warming the oxonium ions **24f/24f-*d*•**Al(pftb)$_4$ above -20 °C in a Young's NMR tube, in which the oxonium ions **24f/24f-*d*•**Al(pftb)$_4$ was generated from chloride **23f/ 23f-*d*** (1.0 eq.) and AgAl(pftb)$_4$·CH_2Cl_2 (1.1 eq.) in dry CD_2Cl_2 (0.7 mL) at -20 °C in a flame dried Young's NMR tube, following the general procedures for the synthesis of monosubstituted oxonium ions (*see above*). The $AgCl_{(s)}$ precipitate generated upon the formation of oxonium ion **24f/24f-*d*•**Al(pftb)$_4$ was allowed to settle in the Young's NMR tube at -20 °C before the rearrangement of oxonium ions **24f/24f-*d*•**Al(pftb)$_4$ into oxocarbenium ions **33/33-*d*•**Al(pftb)$_4$ was observed by ^{1}H NMR spectroscopy by warming the sample to above -20 °C. The oxocarbenium ions **33/33-*d*•**Al(pftb)$_4$ were ultimately characterized by NMR spectroscopy at 25 °C.

5-(4-Phenylbutyl)-3,4-dihydro-2*H*-furan-1-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 35•Al(pftb)$_4$



Synthesised from 11.7 mg (0.049 mmol) of **23f** and 63.0 mg (0.054 mmol) of AgAl(pftb)$_4$·CH_2Cl_2.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.40 – 7.29 (m, 2H, **H11**, **H15**), 7.29 – 7.23 (m, 1H, **H13**), 7.23 – 7.18 (m, 2H, **H12**, **H14**), 5.72 (t, J = 8.1 Hz, 2H, **H5**), 3.72 (t, J = 8.2 Hz, 2H, **H3**), 3.32 (t, J = 7.1 Hz, 2H, **H6**), 2.71 (t, J = 7.2 Hz, 2H, **H9**), 2.64 (t, J = 8.1 Hz, 2H, **H4**), 1.95 – 1.86 (m, 2H, **H7**), 1.84 – 1.75 (m, 2H, **H8**).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 245.4 (**C2**), 141.5 (**C10**), 129.1 (**C12**, **C14**), 129.0 (**C11**, **C15**), 126.6 (**C13**), 94.4 (**C5**), 45.4 (**C3**), 39.0 (**C6**), 35.3 (**C9**), 30.6 (**C8**), 24.3 (**C7**), 20.7 (**C4**).

5-(4-Phenylbutyl-4-*d*)-3,4-dihydro-2*H*-furan-1-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 35-*d*•Al(pftb)$_4$

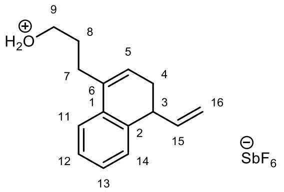


Synthesised from 7.7 mg (0.032 mmol) of **23f-*d*** and 41.0 mg (0.035 mmol) of AgAl(pftb)$_4$·CH_2Cl_2.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.35 – 7.29 (m, 2H, **H12**, **H14**), 7.26 – 7.20 (m, 1H, **H13**), 7.20 – 7.15 (m, 2H, **H11**, **H15**), 5.72 (tt, J = 8.2, 1.0 Hz, 2H, **H5**), 3.72 (dddt, J = 9.4, 7.5, 1.8, 0.8 Hz, 2H, **H3**), 3.36 – 3.29 (m, 2H, **H6**), 2.75 – 2.65 (m, 1H, **H9**), 2.64 (p, J = 8.2 Hz, 2H, **H4**), 2.00 – 1.85 (m, 2H, **H7**), 1.79 (m, 2H, **H8**).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 245.4 (**C2**), 141.1 (**C10**), 129.2 (**C12**, **C14**), 128.9 (**C11**, **C15**), 127.0 (**C13**), 94.4 (**C5**), 45.4 (**C3**), 39.0 (**C6**), 35.0 (1:1:1 triplet, $J_{\text{C-D}}$ = 19.2 Hz, **C9**), 30.6 (**C8**), 24.3 (**C7**), 20.7 (**C4**).

Procedure for the synthesis of oxonium ion 49a•SbF_6:

The oxonium ion **24m•**SbF_6 was intended to be generated from bromide **23m** (6.8 mg, 0.023 mmol) and $AgSbF_6$ (9.0 mg, 0.025 mmol) at room temperature in dry CD_2Cl_2 (0.7 mL), following the general procedure for the synthesis of disubstituted oxonium ions (*see above*). *Note: The bromide **23m** was isolated as a mixture of isomers and hence was not characterized. However, the use of chloride **23m**, which was characterized properly, was equally effective in carrying out this reaction.* A rearrangement reaction was observed over 1.5 hours that gave rise to the oxonium ion **49a•**SbF_6. The oxonium ion **49a**•SbF_6 was characterized by NMR spectroscopy at 25 °C.

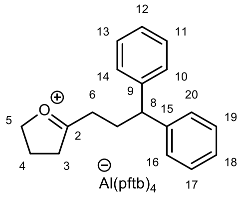
(3-(4-Vinyl-3,4-dihydronaphthalen-1-yl)propyl)oxonium hexafluoroantimonate 52•SbF_6



^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.46 – 7.33 (m, 3H, **H11**, **H12**, **H13**), 7.21 (dd, J = 7.6, 1.7 Hz, 1H, **H14**), 6.46 (ddd, J = 16.9, 9.6, 2.7 Hz, 1H, **H15**), 6.17 (dd, J = 5.5, 2.6 Hz, 1H, **H5**), 5.44 (dt, J = 9.5, 1.9 Hz, 1H, **H16'**), 4.84 (dt, J = 16.9, 2.0 Hz, 1H, **H16**), 4.15 – 4.01 (m, 2H, **H9**), 3.71 (dt, J = 7.1, 2.3 Hz, 1H, **H3**), 3.13 – 3.03 (m, 1H, **H7'**), 2.75 – 2.65 (m, 2H, **H4**), 2.67 – 2.57 (m, 1H, **H7**), 2.16 (dddd, J = 16.2, 10.0, 5.0, 2.5 Hz, 1H, **H8'**), 1.92 (dddd, J = 16.2, 8.2, 4.4, 2.3 Hz, 1H, **H8**).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 142.5 (**C6**), 140.0 (**C15**), 134.6 (**C2**), 131.5 (**C1**), 130.6 (**C14**), 129.6 (**C13**), 129.1 (**C12**), 125.6 (**C11**), 119.2 (**C5**), 105.2 (**C16**), 69.0 (**C9**), 40.7 (**C3**), 32.1 (**C7**), 30.5 (**C4**), 29.4 (**C8**).

Procedure for the synthesis of oxocarbenium ion 59•Al(pftb)$_4$:
The oxocarbenium ion **59**•Al(pftb)$_4$ was generated from chloride **23l** (10.0 mg, 0.033 mmol) and AgAl(pftb)$_4$·CH_2Cl_2 (42.0 mg, 0.037 mmol) in dry CD_2Cl_2 (0.7 mL), following the general procedures for the synthesis of disubstituted oxonium ions (*see above*). The reaction progress was observed by ^{1}H NMR spectroscopy from 0 °C to room temperature (**Figure S7**, *see below*). The oxonium ion **24l**•Al(pftb)$_4$ was observed as an intermediate, which is known to be generated exclusively at lower temperatures (-20 °C, see above). The oxocarbenium ion **59**•Al(pftb)$_4$ was characterized by NMR spectroscopy at -10 °C.

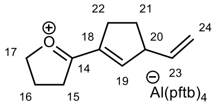
5-(3,3-Diphenylpropyl)-3,4-dihydro-2*H*-furan-1-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 59•Al(pftb)$_4$



^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.38 (m, 4H, **H11**, **H13**, **H17**, **H19**), 7.33 – 7.32 (m, 2H, **H12**, **H18**), 7.26 (m, 4H, **H10**, **H14**, **H16**, **H20**), 5.46 (t, J = 8.2 Hz, 2H, **H5**), 3.99 (t, J = 8.1 Hz, 1H, **H8**), 3.36 (t, J = 7.4 Hz, 4H, **H3**, **H6**), 2.76 (dt, J = 8.3, 6.5 Hz, 2H, **H7**), 2.35 (p, J = 8.2 Hz, 2H, **H4**).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 244.8 (**C2**), 142.6 (**C9**, **C15**), 129.7 (**C11**, **C13**, **C17**, **C19**), 128.1 (**C10**, **C14**, **C16**, **C20**), 128.0 (**C12**, **C18**), 93.5 (**C5**), 50.9 (**C8**), 45.2 (**C3**), 38.3 (**C6**), 31.2 (**C7**), 20.2 (**C4**).

Procedure for the synthesis of oxocarbenium ion 39•Al(pftb)$_4$ and 40•Al(pftb)$_4$:
The oxocarbenium ion **39**•Al(pftb)$_4$ was generated along with oxonium ion **24o**•Al(pftb)$_4$ as a 2.4:1 mixture (**24o**•Al(pftb)$_4$:**39**•Al(pftb)$_4$), following the general procedure for the synthesis of disubstituted oxonium ions (*see above*). The oxocarbenium ion was characterized by NMR spectroscopy at -10 °C. The mixture of oxonium ion **24o**•Al(pftb)$_4$ and oxocarbenium ion **39**•Al(pftb)$_4$ was converted to the oxocarbenium ion **40**•Al(pftb)$_4$ at 25 °C in ca. 1 hour (by NMR monitoring **Figure S5**). The oxocarbenium ion **40**•Al(pftb)$_4$ was characterized by NMR spectroscopy at 25 °C.

5-(3-Vinylcyclopent-1-en-1-yl)-3,4-dihydro-2*H*-furan-1-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 39•Al(pftb)₄



^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.31 (d, *J* = 2.7 Hz, 1H, **H19**), 5.87 – 5.65 (m, 1H, **H23**), 5.50 (t, *J* = 7.8 Hz, 2H, **H17**), 5.28 (d, *J* = 10.2 Hz, 1H, **H24'**), 5.26 (d, *J* = 16.8 Hz, 1H, **H24**), 3.95 (q, *J* = 6.8 Hz, 1H, **H20**), 3.79 (ddd, *J* = 9.3, 5.7, 2.7 Hz, 2H, **H15**), 2.92 – 2.80 (m, 1H, **H22'**), 2.81 – 2.75 (m, 1H, **H22**), 2.67 – 2.57 (m, 2H, **H16**), 2.56 – 2.49 (m, 1H, **H21'**), 2.04 (ddt, *J* = 12.7, 8.6, 7.1 Hz, 1H, **H21**).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 214.4 (**C14**), 186.0 (**C19** (not observed on ^{13}C spectrum, deduced from ^{1}H-^{13}C HMBC correlations)), 137.5 (**C18**), 134.3 (**C23**), 119.1 (**C24**), 88.9 (**C17**), 54.6 (**C20**), 39.0 (**C15**), 30.1 (**C21**), 29.7 (**C22**), 21.7 (**C16**).

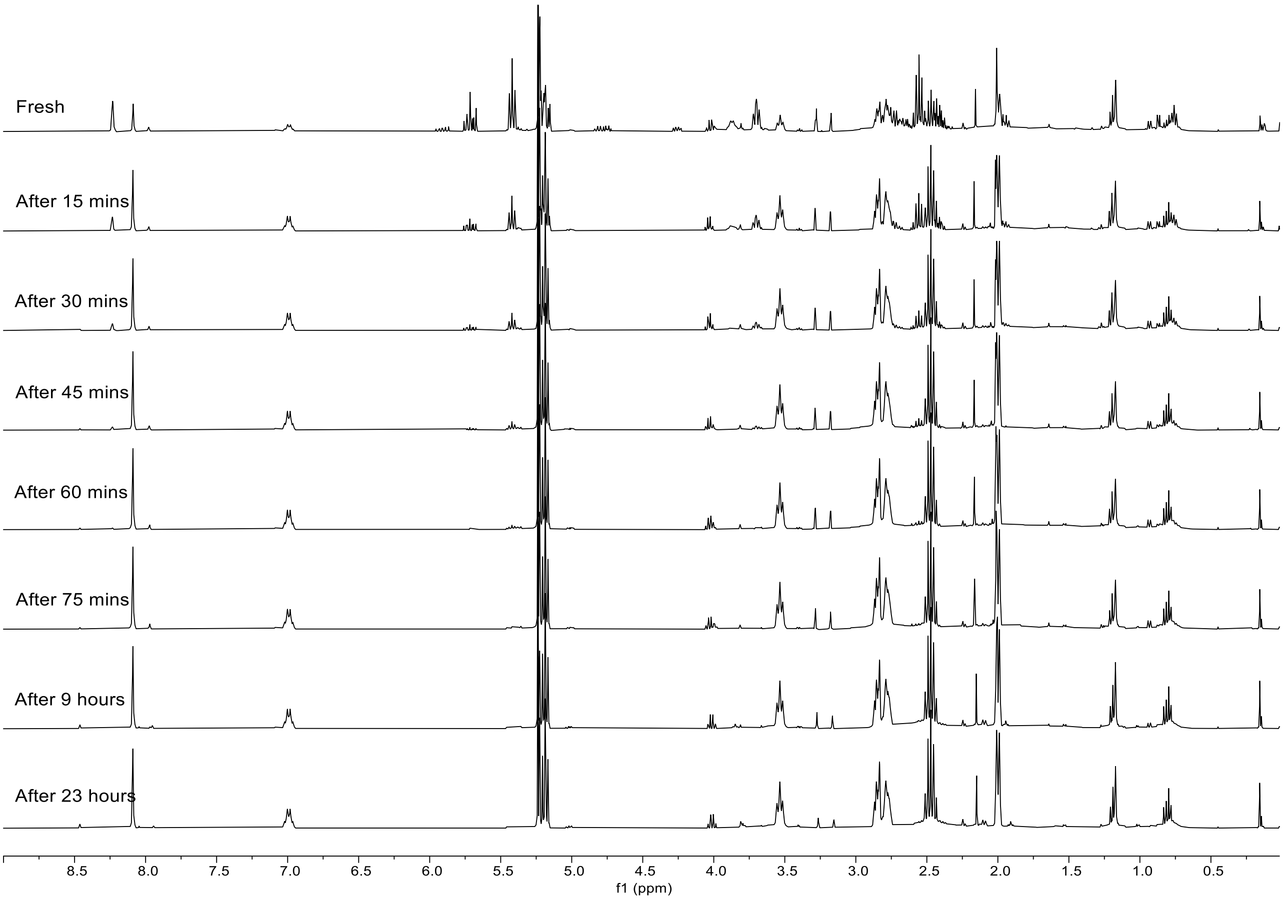
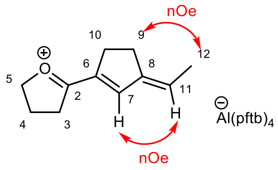


Figure S5. ^{1}H NMR monitoring of the conversion of oxonium ion **24o**•Al(pftb)₄ and oxocarbenium ion **39**•Al(pftb)₄ into oxocarbenium ion **40**•Al(pftb)₄.

(*E*)-5-(3-Ethylidenecyclopent-1-en-1-yl)-3,4-dihydro-2*H*-furan-1-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 40•Al(pftb)₄



^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.18 (s, 1H, **H7**), 7.09 (qt, *J* = 7.7, 2.5 Hz, 1H, **H11**), 5.28 (t, *J* = 7.6

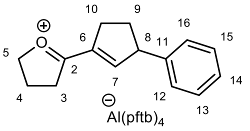
Hz, 2H, **H5**), 3.63 (t, *J* = 8.1 Hz, 2H, **H3**), 3.03 – 2.90 (m, 2H, **H10**), 2.90 – 2.77 (m, 2H, **H9**), 2.57 (p, *J* = 7.9 Hz, 2H, **H4**), 2.15 – 1.96 (m, 3H, **H12**).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 206.7 (**C2**), 175.7 (**C7**), 153.2 (**C11**), 151.8 (**C8**), 136.9 (**C6**), 85.8 (**C5**), 37.0 (**C3**), 28.9 (**C10**), 26.9 (**C9**), 22.5 (**C4**), 18.9 (**C12**).

Procedure for the synthesis of oxocarbenium ion 42•Al(pftb)$_4$:

The oxocarbenium ion **42**•Al(pftb)$_4$ was synthesized from the chloride **23w** (10.0 mg, 0.040 mmol) and AgAl(pftb)$_4$·CH_2Cl_2 (51.0 mg, 0.044 mmol) in dry CD_2Cl_2 (0.7 mL) at room temperature, following the general procedure for the synthesis of disubstituted oxonium ions (*see above*). The oxocarbenium ion **40**•Al(pftb)$_4$ was characterized by NMR spectroscopy at 25 °C.

5-(3-Phenylcyclopent-1-en-1-yl)-3,4-dihydro-2*H*-furan-1-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 42•Al(pftb)$_4$



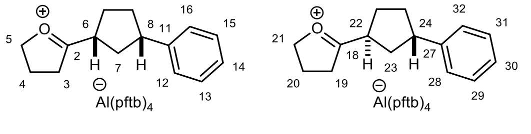
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.42 (t, *J* = 1.8 Hz, 1H, **H7**), 7.45 – 7.30 (m, 3H, **H13**, **H14**, **H15**), 7.25 – 7.06 (m, 2H, **H12**, **H16**), 5.55 (t, *J* = 7.7 Hz, 2H, **H5**), 4.55 – 4.45 (m, 1H, **H8**), 3.87 – 3.75 (m, 2H, **H3**), 3.13 – 3.00 (m, 1H, **H10'**), 3.00 – 2.88 (m, 1H, **H10**), 2.87 – 2.75 (m, 1H, **H9'**), 2.67 (p, *J* = 8.0 Hz, 2H, **H4**), 2.33 – 2.22 (m, 1H, **H9**).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 214.9 (**C2**), 186.0 (**C7**), 139.4 (**C11**), 137.8 (**C6**), 130.1 (**C13**, **C15**), 129.0 (**C14**), 128.2 (**C12**, **C16**), 89.3 (**C5**), 57.0 (**C8**), 39.4 (**C3**), 33.1 (**C9**), 30.5 (**C10**), 21.9 (**C4**).

Procedure for the synthesis of oxocarbenium ions 46•Al(pftb)$_4$:

The oxocarbenium ions **46**•Al(pftb)$_4$ was synthesized from the chloride **23n** (7.0 mg, 0.028 mmol) and AgAl(pftb)$_4$·CH_2Cl_2 (36.0 mg, 0.031 mmol) in dry CD_2Cl_2 (0.7 mL) at -20 °C, following the general procedure for the synthesis of disubstituted oxonium ions (*see above*). The oxocarbenium ion **44**•Al(pftb)$_4$ was characterized by NMR spectroscopy at -10 °C.

5-(3-Phenylcyclopentyl)-3,4-dihydro-2*H*-furan-1-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 46•Al(pftb)$_4$ (d.r. ca. 1:1)



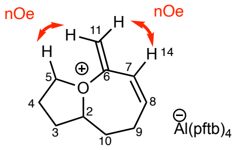
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.39 – 7.32 (m, 4H, **H13**, **H15**, **H29**, **H31**), 7.30 – 7.26 (m, 2H, **H14**, **H30**), 7.26 – 7.17 (m, 4H, **H12**, **H16**, **H28**, **H32**), 5.75 (t, *J* = 8.1 Hz, 2H, **H5**), 5.71 (t, *J* = 8.1 Hz, 2H, **H21**), 4.02 – 3.94 (m, 1H, **H22**), 3.94 – 3.88 (m, 1H, **H6**), 3.86 (t, *J* = 8.3 Hz, 2H, **H3**), 3.80 (q, *J* = 8.6 Hz, 2H, **H19**), 3.37 (ddd, *J* = 17.6, 11.1, 6.6 Hz, 1H, **H8**), 3.29 (q, *J* = 8.1, 6.7 Hz, 1H, **H24**), 2.75 – 2.61 (m, 5H, **H4**, **H7’**, **H20**), 2.61 – 2.53 (m, 1H, **H26’**), 2.53 – 2.48 (m, 1H, **H23’**), 2.48 – 2.42 (m, 1H, **H10’**), 2.41 – 2.32 (m, 3H, **H9’**, **H23**, **H26**), 2.32 – 2.25 (m, 1H, **H10**), 2.09 – 2.01 (m, 3H, **H7**, **H25**), 1.99 – 1.90 (m, 1H, **H9**).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 246.2 (**C2**), 246.1 (**C18**), 141.7 (**C11**), 141.3 (**C27**), 129.1 (**C13**, **C15**, **C29**, **C31**), 127.5 (**C14**), 127.3 (**C30**), 127.2 (**C12**, **C16**, **C28**, **C32**), 93.4 (**C5**), 93.3 (**C21**), 47.7 (**C22**), 47.3 (**C6**), 46.7 (**C8**), 45.9 (**C24**), 44.1 (**C3**), 44.1 (**C19**), 40.3 (**C7**), 38.6 (**C23**), 35.1 (**C25**), 33.2 (**C9**), 32.6 (**C26**), 30.6 (**C10**), 20.7 (**C4**, **C20**).

Procedure for the synthesis of vinyl oxonium ion 62•Al(pftb)$_4$:

The chloride **23x** (7.1 mg, 0.038 mmol) and AgAl(pftb)$_4$·CH_2Cl_2 (48.0 mg, 0.042 mmol) were mixed in dry CD_2Cl_2 (0.7 mL) at -20 °C following the general procedure for the synthesis of monosubstituted oxonium ions (*see above*). The resulting NMR sample was warmed above -20 °C and gave the vinyl oxonium ion **62**•Al(pftb)$_4$. The vinyl oxonium ion **62**•Al(pftb)$_4$ can also be prepared from **23x** and AgAl(pftb)$_4$·CH_2Cl_2 directly at room temperature. The vinyl oxonium ion **62**•Al(pftb)$_4$ was characterized by NMR spectroscopy at 0 °C.

5-Methylene-2,3,5,8,9,9a-hexahydro-1*H*-furo[1,2-*a*]oxepin-4-ium tetrakis((1,1,1,3,3,3-hexafluoro 2-(trifluoromethyl)propan-2-yl)oxy)aluminate 62•Al(pftb)$_4$



^{1}H NMR (500 MHz, CD_2Cl_2) δ 6.21 – 6.14 (m, 2H, **H7**, **H8**), 5.73 (ddt, J = 11.7, 6.8, 2.2 Hz, 1H, **H2**), 5.56 (d, J = 4.8 Hz, 1H, **H11'**), 5.46 (d, J = 4.8 Hz, 1H, **H11**), 4.88 (td, J = 6.8, 4.0 Hz, 1H, **H5'**), 4.78 (dt, J = 9.1, 6.7 Hz, 1H, **H5**), 2.65 – 2.61 (m, 2H, **H9**), 2.61 – 2.56 (m, 2H, **H3'**, **H10'**), 2.56 – 2.48 (m, 2H, **H4**), 2.38 (dq, J = 12.9, 9.0 Hz, 1H, **H3**), 2.25 – 2.18 (m, 1H, **H10**).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 155.3 (**C6**), 138.4 (**C8**), 119.0 (**C7**), 111.7 (**C11**), 108.4 (**C2**), 87.8 (**C5**), 29.0 (**C10**), 28.5 (**C3**), 24.9 (**C9**), 24.6 (**C4**).

9) Synthesis and characterization of oxonium and oxocarbenium ion quenching products

Procedure for the NMR monitoring and quenching of oxonium ion 24v•Al(pftb)$_4$ with cycloheptatriene to generate 28 and 28': The oxonium ion **24v**•Al(pftb)$_4$ was generated from bromide **23v** (11.1 mg, 0.034 mmol) and AgAl(pftb)$_4$·CH$_2$Cl$_2$ (44.0 mg, 0.038 mmol) in dry CD$_2$Cl$_2$ (0.7 mL) at -20 °C. The oxonium ion solution was quickly filtered into a Young's NMR tube maintained at -20 °C by a filter cannula and the ^{1}H NMR spectrum of the oxonium ion was acquired at -20 °C to confirm its generation. It was later found that the above oxonium ion generation/filtration procedure could also be carried out at room temperature without significant deterioration of oxonium ion quality. To the filtered solution of the oxonium ion **24v**•Al(pftb)$_4$ at -20 °C was then added cycloheptatriene (4.0 μL, 0.038 mmol) at the same temperature. The progress of the reaction at -20 °C (sample incubated inside the NMR spectrometer) and then at room temperature (sample taken out of the NMR spectrometer, equilibrated to room temperature and left for 30 minutes) was monitored by ^{1}H NMR at -20 °C for comparison with the ^{1}H NMR spectrum of **24v**•Al(pftb)$_4$ obtained at -20 °C. It was found that the oxonium ion **24v**•Al(pftb)$_4$ was almost unreactive towards cycloheptatriene at -20 °C but was rapidly consumed at room temperature in 30 minutes (**Figure S6**). The reaction mixture in the Young's NMR tube was concentrated and purified by flash column chromatography (5% EA/ Pet. Ether 40-60) to give the reduction products **28** and **28'** (42%, 0.013 mmol, **28**:**28'** = 1.7:1, inseparable mixture) as a colourless oil.

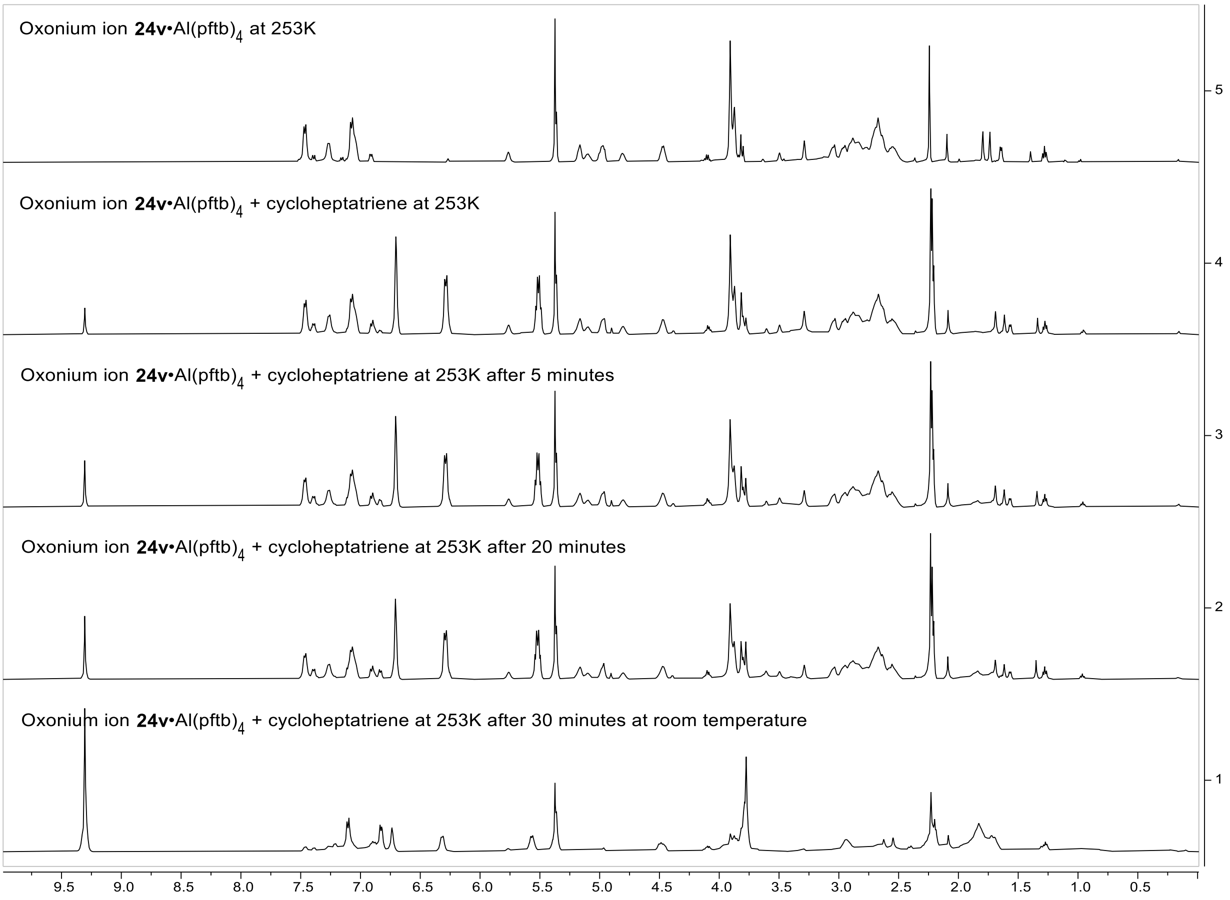
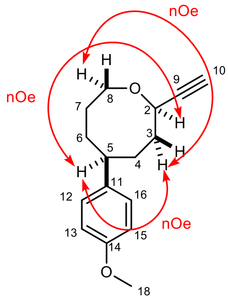
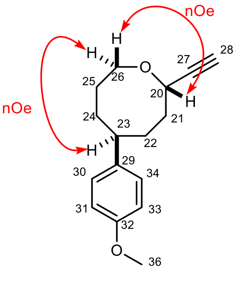


Figure S6. ^{1}H NMR monitoring at 253K of the reaction between oxonium ion **24v**•Al(pftb)$_4$ and cycloheptatriene.

(2*R,5*S**)-2-Ethynyl-5-(4-methoxyphenyl)oxocane 28 and (2*S**,5*S**)-2-ethynyl-5-(4-methoxy phenyl)oxocane 28’**



28

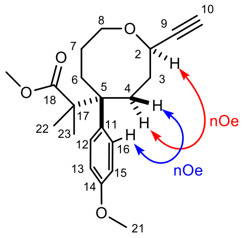


28'

R$_f$ = 0.34 (5% EA/ Pet. Ether 40-60)
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.12 – 7.04 (m, 5.4H, **H12**, **H16**, **H30**, **H34**), 6.87 – 6.77 (m, 5.4H, **H13**, **H15**, **H31**, **H33**), 4.47 (ddd, *J* = 9.7, 3.6, 2.1 Hz, 1.7H, **H2**), 4.40 (ddd, *J* = 9.1, 4.0, 2.2 Hz, 1H, **H20**), 4.02 (ddd, *J* = 12.5, 6.0, 4.3 Hz, 1H, **H26'**), 3.87 (ddd, *J* = 12.7, 10.9, 3.7 Hz, 1.7H, **H8'**), 3.78 (s, 8.1H, **H18**, **H36**), 3.78 (ddd, *J* = 23.4, 4.3, 2.8 Hz, 1.7H, **H8**), 3.65 (ddd, *J* = 11.9, 8.3, 3.6 Hz, 1H, **H26**), 2.99 (tt, *J* = 9.9, 9.5, 3.0 Hz, 1H, **H23**), 2.94 (dtd, *J* = 10.9, 6.8, 5.1, 3.6 Hz, 1.7H, **H5**), 2.47 (d, *J* = 2.1 Hz, 1H, **H28**), 2.41 (d, J = 2.2 Hz, 1.7H, **H10**), 2.27 – 2.17 (m, 1.7H, **H3'**), 2.11 (dddd, *J* = 14.9, 9.0, 4.0, 2.3 Hz, 1H, **H21'**), 2.00 (ddt, *J* = 14.7, 9.1, 2.9 Hz, 1H, **H22'**), 1.90 – 1.81 (m, 10.8H, **H3**, **H4'**, **H6**, **H21**, **H24**, **H25'**), 1.80 – 1.75 (m, 4.4H, **H4**, **H7'**, **H22**), 1.72 (m, 2.7H, **H7**, **H25**).
^{13}C NMR (126 MHz, CDCl$_3$) δ 157.7 (**C14**, **C32**), 143.0 (**C11**), 142.9 (**C29**), 127.8 (**C12**, **C16**, **C30**, **C34**), 113.9 (**C13**, **C15**, **C31**, **C33**), 84.2 (**C9**), 83.4 (**C27**), 73.1 (**C28**), 72.3 (**C10**), 68.6 (**C2**), 68.6 (**C20**), 68.0 (**C26**), 66.0 (**C8**), 55.4 (**C18**, **C36**), 44.3 (**C23**), 43.8 (**C5**), 34.2 (**C4**, **C21**, **C24**), 32.7 (**C6**), 32.6 (**C22**), 31.8 (**C3**), 29.9 (**C7**), 28.2 (**C25**).
IR (thin film, υ/cm^{-1}): 3284, 2928, 1610, 1510, 1244, 1090
HRMS (ESI): Ionized as [M+H]$^+$: Found 245.1537, *m/z* calculated for $C_{16}H_{21}O_2$ [M+H]$^+$: 245.1536.

General procedure for the quenching of oxonium ion 24v•Al(pftb)$_4$ with various π-nucleophiles: The oxonium ion **24v**•Al(pftb)$_4$ was generated from bromide **23v** (1.0 eq.) and AgAl(pftb)$_4$·CH$_2$Cl$_2$ (1.1 eq.) in dry CD$_2$Cl$_2$ (0.05 M) at -20 °C. The resulting oxonium ion solution was not filtered. To this solution at -20 °C was added cycloheptatriene (1.1 eq.) followed by the π-nucleophile (See below for specific equivalents). The reaction mixture was then warmed to room temperature and stirred at this temperature for 15 minutes (unless otherwise specified). The progress of the reaction was monitored by TLC analysis. The reaction was quenched with sat. aq. NaHCO$_3$ solution and excess TBAI when TLC analysis suggest complete consumption of starting material. The aqueous layer was extracted three times with dichloromethane, the organic layers were collected and dried with anhydrous MgSO$_4$, concentrated, and the crude was purified by flash column chromatography to give the desired products.

Methyl 2-((2*R**,5*R**)-2-ethynyl-5-(4-methoxyphenyl)oxocan-5-yl)-2-methylpropanoate 29



29

Flash column chromatography eluent: 20% EA/Pet. Ether 40-60

R_f = 0.31 (20% EA/Pet. Ether 40-60)

Yield: 81% (12 mg) in total as a 1.6:1 separable mixture of **31a** and **31a'** from 14 mg of **23v** and 2.0 equivalents of (1-Methoxy-2-methyl-1-propenyloxy)trimethylsilane.

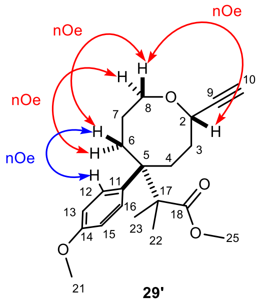
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.13 – 7.02 (m, 2H, **H12**, **H16**), 6.89 – 6.78 (m, 2H, **H13**, **H15**), 4.41 (ddd, *J* = 12.1, 5.6, 2.2 Hz, 1H, **H2**), 3.93 (ddd, *J* = 12.5, 5.5, 2.7 Hz, 1H, **H8'**), 3.81 (s, 3H, **H21**), 3.52 (s, 3H, **H25**), 3.48 (dt, *J* = 12.1, 6.2 Hz, 1H, **H8**), 2.60 (m, 1H, **H4'**), 2.54 (ddd, *J* = 17.2, 11.2, 2.7 Hz, 1H, **H6'**), 2.35 (d, *J* = 2.1 Hz, 1H, **H10**), 2.00 (ddd, *J* = 14.8, 7.0, 2.3 Hz, 1H, **H6**), 1.95 (m, 1H, **H4**), 1.84 (ddd, *J* = 16.0, 11.1, 5.5 Hz, 1H, **H3'**), 1.64 (dddd, *J* = 13.8, 11.7, 6.8, 1.9 Hz, 1H, **H3**), 1.58 – 1.49 (m, 2H, **H7**), 1.06 (s, 6H, **H22**, **H23**).

^{13}C NMR (126 MHz, CDCl$_3$) δ 177.5 (**C18**), 157.8 (**C14**), 133.0 (**C11**), 131.1 (**C12**, **C16**), 112.9 (**C13**, **C15**), 82.5 (**C9**), 74.1 (**C10**), 67.4 (**C2**), 64.1 (**C8**), 55.3 (**C21**), 51.6 (**C25**), 50.9 (**C17**), 49.8 (**C5**), 32.3 (**C3**), 28.1 (**C6**), 27.4 (**C4**), 25.9 (**C7**), 22.7 (**C22**, **C23**).

IR (thin film, *υ*/cm^{-1}): 3284, 2948, 1718, 1608, 1513, 1255, 1137

HRMS (ESI): Ionized as [M+Na]$^+$: Found 367.1881, *m/z* calculated for $C_{21}H_{28}O_4{}^{23}Na$ [M+Na]$^+$: 367.1880.

Methyl 2-((2*S**,5*R**)-2-ethynyl-5-(4-methoxyphenyl)oxocan-5-yl)-2-methylpropanoate 29'



29'

Flash column chromatography eluent: 20% EA/Pet. Ether 40-60

R_f = 0.30 (20% EA/Pet. Ether 40-60)

Yield: 81% (12 mg) in total as a 1.6:1 separable mixture of **31a** and **31a'** from 14 mg of **23v** and 2.0 equivalents of (1-Methoxy-2-methyl-1-propenyloxy)trimethylsilane

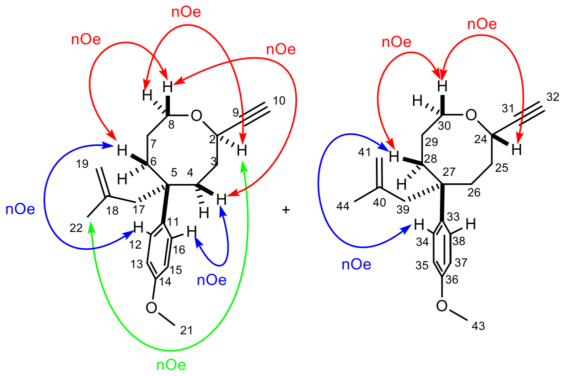
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.13 – 7.04 (m, 2H, **H12**, **H16**), 6.87 – 6.79 (m, 2H, **H13**, **H15**), 4.12 (ddd, *J* = 6.3, 4.2, 2.3 Hz, 1H, **H2**), 3.80 (s, 3H, **H21**), 3.74 (ddd, *J* = 12.7, 11.4, 5.2 Hz, 1H, **H8'**), 3.52 (s, 3H, **H25**), 3.42 (ddd, *J* = 12.6, 5.6, 2.9 Hz, 1H, **H8**), 2.50 (dd, *J* = 15.0, 10.5 Hz, 1H, **H6'**), 2.45 – 2.37 (m, 2H, **H4'**, **H10**), 2.32 (dtd, *J* = 15.1, 7.1, 2.5 Hz, 1H, **H4**), 2.09 (dd, *J* = 15.0, 8.2 Hz, 1H, **H6**), 1.85 – 1.73 (m, 2H, **H3**), 1.66 – 1.55 (m, 1H, **H7'**), 1.53 – 1.43 (m, 1H, **H7**), 1.09 (s, 3H, **H22**), 1.08 (s, 3H, **H23**).

^{13}C NMR (126 MHz, CDCl$_3$) δ 177.5 (**C18**), 157.8 (**C14**), 133.8 (**C11**), 130.8 (**C12**, **C16**), 112.9 (**C13**, **C15**), 84.5 (**C9**), 72.0 (**C10**), 68.6 (**C8**), 68.4 (**C2**), 55.3 (**C21**), 51.6 (**C25**), 50.7 (**C17**), 49.3 (**C5**), 31.2 (**C3**), 28.0 (**C6**), 26.0 (**C7**), 25.7 (**C4**), 22.7 (**C22**, **C23**).

IR (thin film, *υ*/cm^{-1}): 3283, 2949, 1719, 1464, 1188, 1096

HRMS (ESI): Ionized as $[M+Na]^+$: Found 367.1881, *m/z* calculated for $C_{21}H_{28}O_4{}^{23}Na$ $[M+Na]^+$: 367.1880.

(2*R,5*S**)-2-Ethynyl-5-(4-methoxyphenyl)-5-(2-methylallyl)oxocane 30 and (2*S**,5*S**)-2-ethynyl-5-(4-methoxyphenyl)-5-(2-methylallyl)oxocane 30'**



30 **30'**

Specific conditions: Reaction mixture was maintained at -20 °C and stirred at this temperature for 15 minutes after the addition of cycloheptatriene and methallyltrimethylsilane. TLC analysis at this stage suggested complete consumption of starting materials, and 2.0 eq. TBAOAc was added. This was followed by the general procedure for quenching the reaction and work-up.

Flash column chromatography eluent: 5% EA/Pet. Ether 40-60 to 10% EA/Pet. Ether 40-60

R_f = 0.47 (10% EA/Pet. Ether 40-60)

Yield: 74% (13.2 mg) in total as a 1.6:1 inseparable mixture of **31b** and **31b'** from 19.3 mg of **23v** and 10.0 equivalents of methallyltrimethylsilane.

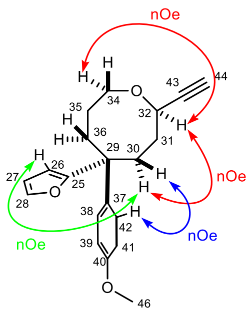
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.16 (m, 5.2H, **H12**, **H16**, **H34**, **H38**), 6.90 – 6.83 (m, 5.2H, **H13**, **H15**, **H35**, **H37**), 4.77 – 4.60 (m, 2.6H, **H19'**, **H41'**), 4.49 – 4.34 (m, 4.2H, **H2**, **H19**, **H41**), 4.23 (ddd, *J* = 7.2, 5.7, 2.2 Hz, 1H, **H24**), 3.99 – 3.86 (m, 2.6H, **H8'**, **H30'**), 3.82 – 3.76 (m, 7.8H, **H21**, **H43**), 3.57 (dt, *J* = 12.4, 7.0 Hz, 1.6H, **H8**), 3.50 (ddd, *J* = 12.7, 7.0, 4.4 Hz, 1H, **H30**), 2.44 (d, *J* = 2.1 Hz, 1H, **H32**), 2.39 (d, *J* = 2.2 Hz, 1.6H, **H10**), 2.35 – 2.28 (m, 1.6H, **H4'**), 2.27 – 2.22 (m, 5.2H, **H17**, **H39**), 2.22 – 2.17 (m, 1.6H, **H6'**), 2.15 – 2.06 (m, 3H, **H26**, **H28'**), 2.06 – 1.98 (m, 1H, **H28**), 1.98 – 1.86 (m, 4.8H, **H3'**, **H4**, **H6**), 1.86 – 1.82 (m, 2H, **H25**), 1.81 – 1.73 (m, 1.6H, **H3**), 1.73 – 1.67 (m, 1H, **H29'**), 1.63 (s, 3.2H, **H7**), 1.56 – 1.50 (m, 1H, **H29**), 1.12 (s, 4.8H, **H22**), 1.09 (s, 3H, **H44**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.6 (**C36**), 157.6 (**C14**), 143.3 (**C18**, **C40**), 138.5 (**C33**), 138.2 (**C11**), 128.7 (**C12**, **C16**), 128.4 (**C34**, **C38**), 114.7 (**C35**, **C37**), 114.6 (**C13**, **C15**), 113.5 (**C19**), 113.5 (**C41**), 84.4 (**C31**), 83.1 (**C9**), 73.6 (**C10**), 72.5 (**C32**), 69.8 (**C8**, **C30**), 69.4 (**C24**), 68.3 (**C2**), 55.3 (**C21**, **C43**), 52.1 (**C17**, **C39**), 43.8 (**C5**), 43.2 (**C27**), 34.1 (**C6**), 33.4 (**C28**), 31.3 (**C3**), 31.0 (**C25**), 30.5 (**C26**), 29.8 (**C4**), 25.5 (**C29**), 25.4 (**C7**), 24.6 (**C22**), 24.5 (**C44**).

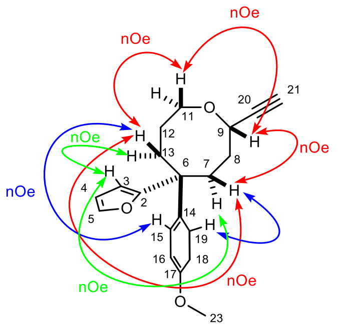
IR (thin film, υ/cm^{-1}): 3286, 2933, 1702, 1513, 1290, 1031

HRMS (ESI): Ionized as $[M+H]^+$: Found 299.2005, *m/z* calculated for $C_{20}H_{27}O_2$ $[M+H]^+$: 299.2006.

(2*R,5*R**)-2-Ethynyl-5-(furan-2-yl)-5-(4-methoxyphenyl)oxocane 31 and (2*S**,5*R**)-2-ethynyl-5-(furan-2-yl)-5-(4-methoxyphenyl)oxocane 31'**



31



31'

Flash column chromatography eluent: 10% EA/Pet. Ether 40-60 to 20% EA/Pet. Ether 40-60

R$_f$ = 0.17 (10% EA/Pet. Ether 40-60)

Yield: 52% (5.8 mg) in total as a 1:1.4 inseparable mixture of **31c** and **31c'** from 11 mg of **23v** and 20.0 equivalents of furan.

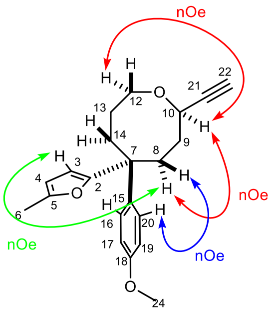
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.32 (d, *J* = 1.9 Hz, 1.4H, **H5**), 7.30 (d, *J* = 1.8 Hz, 1H, **H28**), 7.17 – 7.12 (m, 2H, **H38**, **H42**), 7.11 – 7.05 (m, 2.8H, **H15**, **H19**), 6.84 – 6.77 (m, 4.8H, **H16**, **H18**, **H39**, **H41**), 6.33 (dd, *J* = 3.2, 1.9 Hz, 1.4H, **H4**), 6.30 (dd, *J* = 3.2, 1.9 Hz, 1H, **H27**), 6.20 (d, *J* = 3.2 Hz, 1.4H, **H3**), 6.13 (d, *J* = 3.3 Hz, 1H, **H26**), 4.43 (td, *J* = 8.0, 2.0 Hz, 1.4H, **H9**), 4.36 (td, *J* = 7.2, 2.0 Hz, 1H, **H32**), 4.04 (dt, *J* = 12.7, 5.0 Hz, 1.4H, **H11'**), 3.99 (dt, *J* = 12.4, 6.0 Hz, 1H, **H34'**), 3.78 (s, 3H, **H46**), 3.77 (s, 4.2H, **H23**), 3.64 – 3.59 (m, 1.4H, **H11**), 3.59 – 3.54 (m, 1H, **H34**), 2.55 (ddd, *J* = 15.0, 8.5, 3.9 Hz, 1H, **H30'**), 2.52 – 2.47 (m, 1.4H, **H7'**), 2.46 – 2.40 (m, 3.8H, **H13'**, **H21**, **H44**), 2.41 – 2.34 (m, 2H, **H36'**, **H36**), 2.35 – 2.29 (m, 2.4H, **H13**, **H30**), 2.29 – 2.22 (m, 1.4H, **H7**), 1.92 – 1.84 (m, 4.8H, **H8**, **H31**), 1.77 – 1.66 (m, 2.4H, **H12'**, **H35'**), 1.65 – 1.57 (m, 2.4H, **H12**, **H35**).

^{13}C NMR (126 MHz, CDCl$_3$) δ 161.0 (**C25**), 160.6 (**C2**), 157.9 (**C17**, **C40**), 141.5 (**C5**, **C28**), 139.4 (**C14**), 139.1 (**C37**), 128.0 (**C38**, **C42**), 127.7 (**C15**, **C19**), 113.7 (**C16**, **C18**, **C39**, **C41**), 109.9 (**C4**), 109.8 (**C27**), 106.9 (**C3**), 106.3 (**C26**), 83.8 (**C43**), 83.2 (**C20**), 73.6 (**C21**), 73.0 (**C44**), 69.1 (**C32**), 68.8 (**C9**), 68.6 (**C34**), 67.3 (**C11**), 55.3 (**C23**, **C46**), 47.0 (**C29**), 46.6 (**C6**), 33.2 (**C13**, **C36**), 31.5 (**C7**), 31.2 (**C31**), 30.6 (**C8**), 29.9 (**C30**), 25.4 (**C12**), 25.3 (**C35**).

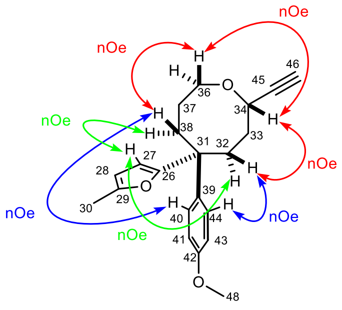
IR (thin film, υ/cm^{-1}): 3283, 2931, 1608, 1511, 1251, 1032

HRMS (ESI): Ionized as [M+H]$^+$: Found 311.1642, *m/z* calculated for $C_{20}H_{23}O_3$ [M+H]$^+$: 311.1642.

(2*R,5*R**)-2-ethynyl-5-(4-methoxyphenyl)-5-(5-methylfuran-2-yl)oxocane 32 and (2*S**,5*R**)-2-ethynyl-5-(4-methoxyphenyl)-5-(5-methylfuran-2-yl)oxocane 32'**



32



32'

Flash column chromatography eluent: 10% EA/Pet. Ether 40-60 to 20% EA/Pet. Ether 40-60

R$_f$ = 0.50 (20% EA/Pet. Ether 40-60)

Yield: 72% (9.3 mg) in total as a 1:1 inseparable mixture of **31d** and **31d'** from 13 mg of **23v** and 10.0 equivalents of 2-methylfuran.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.19 – 7.14 (m, 2H, **H16**, **H20**), 7.13 – 7.08 (m, 2H, **H40**, **H44**), 6.84

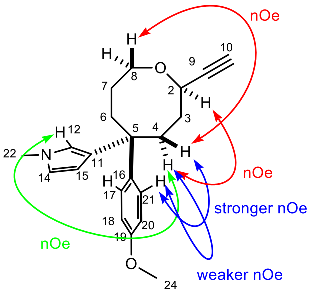
– 6.77 (m, 4H, **H17**, **H19**, **H41**, **H43**), 6.04 (d, *J* = 3.0 Hz, 1H, **H27**), 5.96 (d, *J* = 3.1 Hz, 1H, **H3**), 5.89 (dq, *J* = 3.2, 1.2 Hz, 1H, **H28**), 5.86 (dq, *J* = 3.1, 1.2 Hz, 1H, **H4**), 4.42 (ddd, *J* = 9.0, 5.9, 2.2 Hz, 1H, **H34**), 4.35 (ddd, *J* = 7.8, 5.5, 2.2 Hz, 1H, **H10**), 4.04 (dt, *J* = 12.7, 5.0 Hz, 1H, **H36'**), 3.99 (ddd, *J* = 12.4, 6.6, 5.5 Hz, 1H, **H12'**), 3.78 (s, 3H, **H48**), 3.77 (s, 3H, **H24**), 3.63 – 3.59 (m, 1H, **H36**), 3.59 – 3.54 (m, 1H, **H12**), 2.56 – 2.49 (m, 1H, **H8'**), 2.49 – 2.45 (m, 1H, **H32'**), 2.45 – 2.42 (m, 2H, **H22**, **H46**), 2.42 – 2.37 (m, 1H, **H38'**), 2.33 (tt, *J* = 5.8, 2.7 Hz, 2H, **H14**), 2.30 – 2.26 (m, 2H, **H8**, **H38**), 2.25 – 2.22 (m, 1H, **H32**), 2.21 (d, *J* = 1.0 Hz, 3H, **H6**), 2.20 (d, *J* = 1.0 Hz, 3H, **H30**), 1.96 – 1.82 (m, 4H, **H9**, **H33**), 1.79 – 1.70 (m, 1H, **H37'**), 1.69 – 1.57 (m, 3H, **H13**, **H37**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1 (**C2**), 158.6 (**C26**), 157.9 (**C18**, **C42**), 151.0 (**C5**, **C29**), 139.9 (**C39**), 139.5 (**C15**), 128.0 (**C16**, **C20**), 127.8 (**C40**, **C44**), 113.6 (**C17**, **C19**, **C41**, **C43**), 107.6 (**C27**), 107.0 (**C3**), 105.7 (**C28**), 105.6 (**C4**), 83.9 (**C21**), 83.3 (**C45**), 73.5 (**C46**), 72.9 (**C22**), 69.1 (**C10**), 68.8 (**C34**), 68.6 (**C12**), 67.3 (**C36**), 55.3 (**C24**, **C48**), 46.9 (**C31**), 46.5 (**C7**), 33.2 (**C14**, **C36**), 31.5 (**C32**, **C33**), 31.3 (**C9**), 30.5 (**C8**), 25.5 (**C37**), 25.3 (**C13**), 13.8 (**C6**, **C30**).

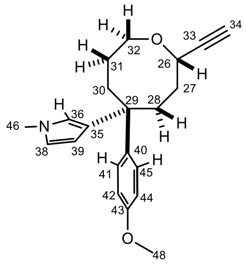
IR (thin film, υ/cm^{-1}): 3284, 2934, 1708, 1511, 1252, 1027

HRMS (ESI): Ionized as [M+Na]$^+$: Found 347.1626, *m/z* calculated for $C_{21}H_{24}O_3{}^{23}Na$ [M+Na]$^+$: 347.1618.

3-((2*R**,5*R**)-2-Ethynyl-5-(4-methoxyphenyl)oxocan-5-yl)-1-methyl-1*H*-pyrrole 33 and 3-((2*S**,5*R**)-2-Ethynyl-5-(4-methoxyphenyl)oxocan-5-yl)-1-methyl-1*H*-pyrrole 33'



33



33' (assigned by elimination)

Flash column chromatography eluent: 5% EA/Pet. Ether 40-60 to 10% EA/Pet. Ether 40-60

R$_f$ = 0.43 (20% EA/Pet. Ether 40-60)

Yield: 55% (7.5 mg) in total as a 1.5:1 inseparable mixture of **31e** and **31e'** from 15 mg of **23v** and 2.0 equivalents of *N*-methylpyrrole.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 3H, **H17**, **H21**), 7.24 – 7.18 (m, 2H, **H41**, **H45**), 6.85 – 6.75 (m, 5H, **H18**, **H20**, **H42**, **H44**), 6.50 (t, *J* = 2.5 Hz, 1H, **H38**), 6.49 (t, *J* = 2.4 Hz, 1.5H, **H14**), 6.33 (t, *J* = 2.1 Hz, 1H, **H36**), 6.23 (s, 1.5H, **H12**), 5.85 (dd, *J* = 2.9, 1.7 Hz, 2.5H, **H15**, **H39**), 4.39 (m, 2.5H, **H2**, **H26**), 4.01 (m, 2.5H, **H8'**, **H32'**), 3.78 (s, 4.5H, **H24**), 3.77 (s, 3H, **H48**), 3.60 (s, 3H, **H46**), 3.58 (m, 2.5H, **H8**, **H32**), 3.57 (s, 4.5H, **H22**), 2.54 (ddd, *J* = 14.8, 10.1, 2.1 Hz, 1H, **H4'**), 2.44 – 2.39 (m, 3.5H, **H6'**, **H10**, **H34**), 2.39 – 2.35 (m, 1H, **H28'**), 2.34 – 2.30 (m, 2H, **H30**), 2.30 – 2.27 (m, 1H, **H28**), 2.27 – 2.22 (m, 1.5H, **H6'**), 2.18 (ddd, *J* = 14.8, 7.8, 1.9 Hz, 1.5H, **H4**), 2.00 – 1.92 (m, 2.5H, **H3'**, **H27'**), 1.88 – 1.81 (m, 2.5H, **H3**, **H27**), 1.81 – 1.75 (m, 1H, **H31'**), 1.67 (p, *J* = 5.8 Hz, 3H, **H7**), 1.61 – 1.57 (m, 1H, **H31**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4 (**C19**, **C43**), 142.5 (**C40**), 141.9 (**C16**), 134.0 (**C11**), 133.1 (**C35**), 128.5 (**C17**, **C21**), 128.2 (**C41**, **C45**), 121.6 (**C14**, **C36**), 119.6 (**C36**), 119.2 (**C12**), 113.3 (**C18**, **C20**), 113.3 (**C42**, **C44**), 107.8 (**C39**), 107.5 (**C15**), 86.4 (**C33**), 83.9 (**C9**), 73.1 (**C34**), 73.0 (**C10**), 69.1 (**C26**), 68.9 (**C2**), 68.0 (**C8**), 67.6 (**C32**), 55.3 (**C24**, **C48**), 44.8 (**C29**), 44.6 (**C5**), 36.3 (**C46**), 36.3 (**C22**), 35.3 (**C6**), 35.2 (**C30**), 33.4 (**C28**), 33.1 (**C4**), 31.8 (**C27**), 31.8 (**C3**), 25.8 (**C31**), 25.7 (**C7**).

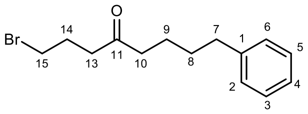
IR (thin film, υ/cm^{-1}): 3280, 2930, 1704, 1509, 1256, 1029

HRMS (ESI): Ionized as [M+Na]$^+$: Found 346.1777, *m/z* calculated for $C_{21}H_{25}O_2N^{23}Na$ [M+Na]$^+$:

346.1778.

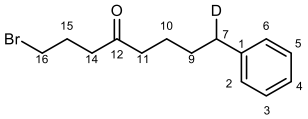
General procedures for the quenching of oxocarbenium ions 35•Al(pftb)$_4$ and 35-*d*•Al(pftb)$_4$: The oxocarbenium ion **35/35-*d*•**Al(pftb)$_4$ was generated at 10 °C over 9 hours from the oxonium ion **24f/24f-*d*•**Al(pftb)$_4$, which was generated from chloride **23f/23f-*d*** (1.0 eq.) and AgAl(pftb)$_4$·CH$_2$Cl$_2$ (1.1 eq.) in dry CD$_2$Cl$_2$ (0.7 mL) at -20 °C in a flame dried Young's NMR tube. The AgCl$_{(s)}$ precipitate generated upon the formation of oxonium ion **24f/24f-*d*•**Al(pftb)$_4$ was allowed to settle in the Young's NMR tube at -20 °C before the oxonium ion **24f/24f-*d*•**Al(pftb)$_4$ was observed by ^{1}H NMR spectroscopy at 10 °C. The NMR sample of the oxonium ion **24f/24f-*d*•**Al(pftb)$_4$ in the NMR spectrometer at 10 °C was then monitored over 9 hours to observe the rearrangement from **24f/24f-*d*•**Al(pftb)$_4$ to **35/35-*d*•**Al(pftb)$_4$. At the end of the NMR monitoring experiment, the sample was retrieved, the AgCl$_{(s)}$ precipitate filtered by the use of a filter cannula, and the resulting solution of **35/35-*d*•**Al(pftb)$_4$ was quenched by addition of tetrabutylammonium bromide (TBAB) (5.0 eq.) to give the ketone products **36**/**36**-*d*. On the other hand, the sample could be directly quenched with cycloheptatriene (1.1 eq.) without filtration to provide the tetrahydrofuran products **37**/**37**-*d*.

1-Bromo-8-phenyloctan-4-one 36



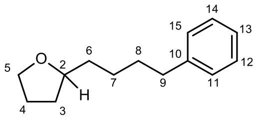
Flash column chromatography eluent: 5% EA/Pet. Ether 40-60 to 10% EA/Pet. Ether 40-60
R$_f$ = 0.49 (10% EA/Pet. Ether 40-60)
Yield: 52% (5.0 mg) from 8.2 mg of **23f**.
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.30 – 7.26 (m, 2H, **H3**, **H5**), 7.22 – 7.13 (m, 3H, **H2**, **H4**, **H6**), 3.44 (t, *J* = 6.4 Hz, 2H, **H15**), 2.62 (t, *J* = 7.0 Hz, 2H, **H7**), 2.59 (t, *J* = 7.0 Hz, 2H, **H13**), 2.44 (t, *J* = 6.8 Hz, 2H, **H10**), 2.11 (p, *J* = 6.7 Hz, 2H, **H14**), 1.68 – 1.58 (m, 4H, **H8**, **H9**).
^{13}C NMR (126 MHz, CDCl$_3$) δ 209.8 (**C11**), 142.3 (**C1**), 128.5 (**C2**, **C6**), 128.5 (**C3**, **C5**), 125.9 (**C4**), 43.0 (**C10**), 40.6 (**C13**), 35.9 (**C7**), 33.6 (**C15**), 31.1 (**C8**), 26.5 (**C14**), 23.6 (**C9**).
IR (thin film, *υ*/cm^{-1}): 2928, 1711, 1495, 1029
HRMS (ESI): Ionized as [M-Br]$^+$: Found 203.1432, *m/z* calculated for C$_{14}$H$_{19}$O [M-Br]$^+$: 203.1430.

1-Bromo-8-phenyloctan-4-one-8-*d* 36-*d*



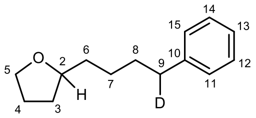
Flash column chromatography eluent: 5% EA/Pet. Ether 40-60 to 10% EA/Pet. Ether 40-60
R$_f$ = 0.49 (10% EA/Pet. Ether 40-60)
Yield: 46% (4.2 mg) from 7.7 mg of **23f**.
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.30 – 7.26 (m, 2H, **H3**, **H5**), 7.20 – 7.14 (m, 3H, **H2**, **H4**, **H6**), 3.44 (t, *J* = 6.4 Hz, 2H, **H16**), 2.65 – 2.55 (m, 3H, **H7**, **H14**), 2.44 (t, *J* = 7.0 Hz, 2H, **H11**), 2.11 (p, *J* = 6.7 Hz, 2H, **H15**), 1.68 – 1.57 (m, 4H, **H9**, **H10**).
^{13}C NMR (126 MHz, CDCl$_3$) δ 209.7 (**C12**), 142.2 (**C1**), 128.5 (**C2**, **C6**), 128.5 (**C3**, **C5**), 125.9 (**C4**), 43.0 (**C11**), 40.6 (**C14**), 35.5 (1:1:1 triplet, $J_{C\text{-}D}$ = 19.6 Hz, **C7**), 33.6 (**C16**), 31.0 (**C9**), 26.5 (**C15**), 23.6 (**C10**).
IR (thin film, *υ*/cm^{-1}): 2927, 1712, 1495, 1029
HRMS (ESI): Ionized as [M-Br]$^+$: Found 204.1495, *m/z* calculated for C$_{14}$H$_{19}$O [M-Br]$^+$: 204.1493

2-(4-Phenylbutyl)tetrahydrofuran 37



Flash column chromatography eluent: 5% EA/Pet. Ether 40-60
R$_f$ = 0.40 (5% EA/Pet. Ether 40-60), only stains with KMnO$_4$.
Yield: 69% (4.2 mg) from 7.1 mg of **23**.
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.30 – 7.24 (m, 2H, **H12**, **H14**), 7.20 – 7.14 (m, 3H, **H11**, **H13**, **H15**), 3.86 (ddd, *J* = 8.4, 7.2, 6.1 Hz, 1H, **H5'**), 3.78 (dddd, *J* = 7.8, 6.9, 6.5, 5.4 Hz, 1H, **H2**), 3.71 (td, *J* = 8.0, 6.2 Hz, 1H, **H5**), 2.62 (dd, *J* = 7.8 Hz, 2H, **H9**), 1.96 (dddd, *J* = 11.4, 8.5, 6.2, 4.6 Hz, 1H, **H3'**), 1.92 – 1.81 (m, 2H, **H4**), 1.69 – 1.63 (m, 2H, **H8**), 1.63 – 1.58 (m, 1H, **H7'**), 1.52 – 1.47 (m, 1H, **H7**), 1.47 – 1.44 (m, 1H, **H6'**), 1.44 – 1.40 (m, 1H, **H3**), 1.40 – 1.33 (m, 1H, **H6**).
^{13}C NMR (126 MHz, CDCl$_3$) δ 142.9 (**C10**), 128.6 (**C12**, **C14**), 128.4 (**C11**, **C15**), 125.8 (**C13**), 79.5 (**C2**), 67.8 (**C5**), 36.1 (**C9**), 35.7 (**C7**), 31.8 (**C8**), 31.5 (**C3**), 26.3 (**C6**), 25.9 (**C4**).
IR (thin film, *υ*/cm^{-1}): 2930, 1453, 1065
HRMS (ESI): Ionized as [M+H]$^+$: Found 205.1589, *m/z* calculated for C$_{14}$H$_{21}$O [M+H]$^+$: 205.1587.

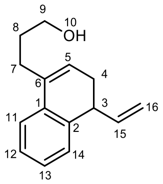
2-(4-Phenylbutyl-4-d)tetrahydrofuran 37-*d*



Flash column chromatography eluent: 5% EA/Pet. Ether 40-60
R$_f$ = 0.40 (5% EA/Pet. Ether 40-60), only stains with KMnO$_4$.
Yield: 68% (4.0 mg) from 7.0 mg of **23f**.
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31 – 7.22 (m, 2H, **H12**, **H14**), 7.21 – 7.12 (m, 3H, **H11**, **H13**, **H15**), 3.86 (ddd, *J* = 8.4, 7.2, 6.2 Hz, 1H, **H5'**), 3.78 (dddd, *J* = 7.8, 6.9, 6.5, 5.4 Hz, 1H, **H2**), 3.71 (td, *J* = 7.9, 6.3 Hz, 1H, **H5**), 2.63 – 2.57 (m, 1H, **H9**), 2.00 – 1.91 (m, 1H, **H3'**), 1.91 – 1.81 (m, 2H, **H4**), 1.68 – 1.62 (m, 2H, **H8**), 1.62 – 1.57 (m, 1H, **H7'**), 1.52 – 1.47 (m, 1H, **H7**), 1.47 – 1.44 (m, 1H, **H6'**), 1.44 – 1.40 (m, 1H, **H3**), 1.40 – 1.33 (m, 1H, **H6**).
^{13}C NMR (126 MHz, CDCl$_3$) δ 142.8 (**C10**), 128.5 (**C12**, **C14**), 128.4 (**C11**, **C15**), 125.8 (**C13**), 79.5 (**C2**), 67.8 (**C5**), 35.9 (**C7**), 35.7 (1:1:1 triplet, $J_{C\text{-}D}$ = 20.2 Hz, **C9**), 31.7 (**C8**), 31.5 (**C3**), 26.2 (**C6**), 25.9 (**C4**).
IR (thin film, *υ*/cm^{-1}): 2960, 1450, 1259, 1072, 1029
HRMS (ESI): Ionized as [M+H]$^+$: Found 206.1651, *m/z* calculated for C$_{14}$H$_{20}$DO [M+H]$^+$: 206.1650.

Procedure for the generation of Friedel-Crafts product 54:
The oxonium ion **24m•SbF$_6$** was intended to be generated from bromide **23m** (6.8 mg, 0.023 mmol) and AgSbF$_6$ (9.0 mg, 0.025 mmol) at room temperature in dry CD$_2$Cl$_2$ (0.7 mL). *Note: The bromide* ***23m*** *was isolated as a mixture of isomers and hence was not characterized. However, the use of chloride* ***23m****, which was fully characterized, was equally effective in carrying out this reaction.* A rearrangement reaction was observed over 1.5 hours that gave rise to the oxonium ion **52**•SbF$_6$. Neutralization of the reaction mixture with Et$_3$N (6.4 µL, 0.046 mmol), followed by evaporation of volatiles and purification by flash column chromatography (30% EA/ Pet. Ether 40-60 to 50% EA/ Pet. Ether 40-60) gave the product **54** (3.0 mg, 0.014 mmol, 61%) as a colourless oil.

3-(4-Vinyl-3,4-dihydronaphthalen-1-yl)propan-1-ol 54

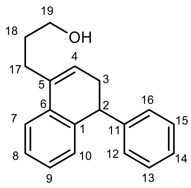


R_f = 0.50 (50% EA/Pet. Ether 40-60)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, J = 7.5 Hz, 1H, **H11**), 7.25 – 7.19 (m, 1H, **H12**), 7.19 – 7.15 (m, 2H, **H13**, **H14**), 5.96 (ddd, J = 17.4, 10.2, 7.7 Hz, 1H, **H15**), 5.83 (tt, J = 4.6, 1.1 Hz, 1H, **H5**), 5.07 (ddd, J = 10.2, 1.8, 0.8 Hz, 1H, **H16’**), 5.00 (dt, J = 17.1, 1.5 Hz, 1H, **H16**), 3.70 (d, J = 7.5 Hz, 2H, **H9**), 3.41 (q, J = 7.6 Hz, 1H, **H3**), 2.63 – 2.49 (m, 2H, **H7**), 2.44 (dt, J = 16.8, 5.7 Hz, 1H, **H4’**), 2.26 (ddd, J = 16.6, 8.2, 4.7 Hz, 1H, **H4**), 1.80 (h, J = 6.6 Hz, 2H, **H8**), 1.26 (s, 1H, **OH**).
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.9 (**C15**), 138.3 (**C2**), 135.9 (**C6**), 134.2 (**C1**), 127.6 (**C14**), 127.2 (**C13**), 126.8 (**C12**), 123.6 (**C5**), 123.1 (**C11**), 115.4 (**C16**), 62.8 (**C9**), 42.7 (**C3**), 31.4 (**C8**), 29.5 (**C4**), 29.1 (**C7**).
IR (thin film, υ/cm^{-1}): 3293, 2926, 1636, 1448, 1260, 1060
HRMS (ESI): Ionized as [M+H]$^+$: Found 215.14330, *m/z* calculated for $C_{15}H_{19}O$ [M+H]$^+$: 215.14304.

Procedure for the generation of Friedel-Crafts products 55:

The oxonium ion **24l**•SbF_6 was intended to be generated from chloride **23l** (9.0 mg, 0.030 mmol) and $AgSbF_6$ (11.3 mg, 0.033 mmol) at -10 °C in dry CD_2Cl_2 (0.7 mL). A rearrangement reaction was observed over 2 hours as the sample was warmed from -10 °C to room temperature. Neutralization of the reaction mixture with Et_3N (8.3 µL, 0.060 mmol), followed by evaporation of volatiles and purification by flash column chromatography (30% EA/ Pet. Ether 40-60 to 50% EA/ Pet. Ether 40-60) gave the product **55** (5.4 mg, 0.020 mmol, 68%) as a colourless oil.

3-(4-Phenyl-3,4-dihydronaphthalen-1-yl)propan-1-ol 55



R_f = 0.66 (50% EA/Pet. Ether 40-60)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, J = 7.8, 1.3 Hz, 1H, **H7**), 7.30 (t, J = 7.4 Hz, 2H, **H13**, **H15**), 7.25 – 7.21 (m, 2H, **H8**, **H14**), 7.21 – 7.15 (m, 2H, **H12**, **H16**), 7.11 (td, J = 7.5, 1.3 Hz, 1H, **H9**), 6.86 (dt, J = 7.6, 1.2 Hz, 1H, **H10**), 5.84 (t, J = 4.5 Hz, 1H, **H4**), 4.06 (dd, J = 9.3, 7.1 Hz, 1H, **H2**), 3.69 (t, J = 6.4 Hz, 2H, **H19**), 2.81 – 2.46 (m, 4H, **H3**, **H17**), 1.84 (dp, J = 14.0, 6.8 Hz, 2H, **H18**).
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.4 (**C11**), 139.2 (**C1**), 136.1 (**C5**), 134.8 (**C6**), 128.6 (**C12**, **C16**), 128.5 (**C13**, **C15**), 128.2 (**C10**), 127.2 (**C9**), 126.8 (**C8**), 126.5 (**C14**), 123.8 (**C4**), 123.0 (**C7**), 62.8 (**C19**), 44.3 (**C2**), 31.6 (**C3**), 31.4 (**C18**), 29.1 (**C17**).
IR (thin film, υ/cm^{-1}): 3270, 2925, 1650, 1444, 1260
HRMS (ESI): Ionized as [M+H]$^+$: Found 265.15873, *m/z* calculated for $C_{19}H_{21}O$ [M+H]$^+$: 265.15869.

Procedure for the quenching of oxocarbenium ion 59•Al(pftb)$_4$:

The oxocarbenium ion **59**•Al(pftb)$_4$ was generated from chloride **23l** (10.0 mg, 0.033 mmol) and AgAl(pftb)$_4$·CH_2Cl_2 (42.0 mg, 0.037 mmol) in dry CD_2Cl_2 (0.7 mL), which was observed by ^{1}H NMR spectroscopy from 0 °C to room temperature (**Figure S7**). The oxonium ion **24l**•Al(pftb)$_4$ was observed as an intermediate, which is known to be generated exclusively at lower temperatures (-20

°C, see above). The resultant solution containing the oxocarbenium ion **59**•Al(pftb)$_4$ was filtered and quenched with tetrabutylammonium bromide (53.2 mg, 0.165 mmol) at room temperature, concentrated and purified by flash chromatography (5% Acetone/ Pet. Ether 40-60 to 7% Acetone/ Pet. Ether 40-60) to give the products **60** (2.4 mg, 6.9 µmol, 21%) and **61** (3.7 mg, 0.014 mmol, 42%, *d.r.* = 3:1) which could be separated individually as colourless oils.

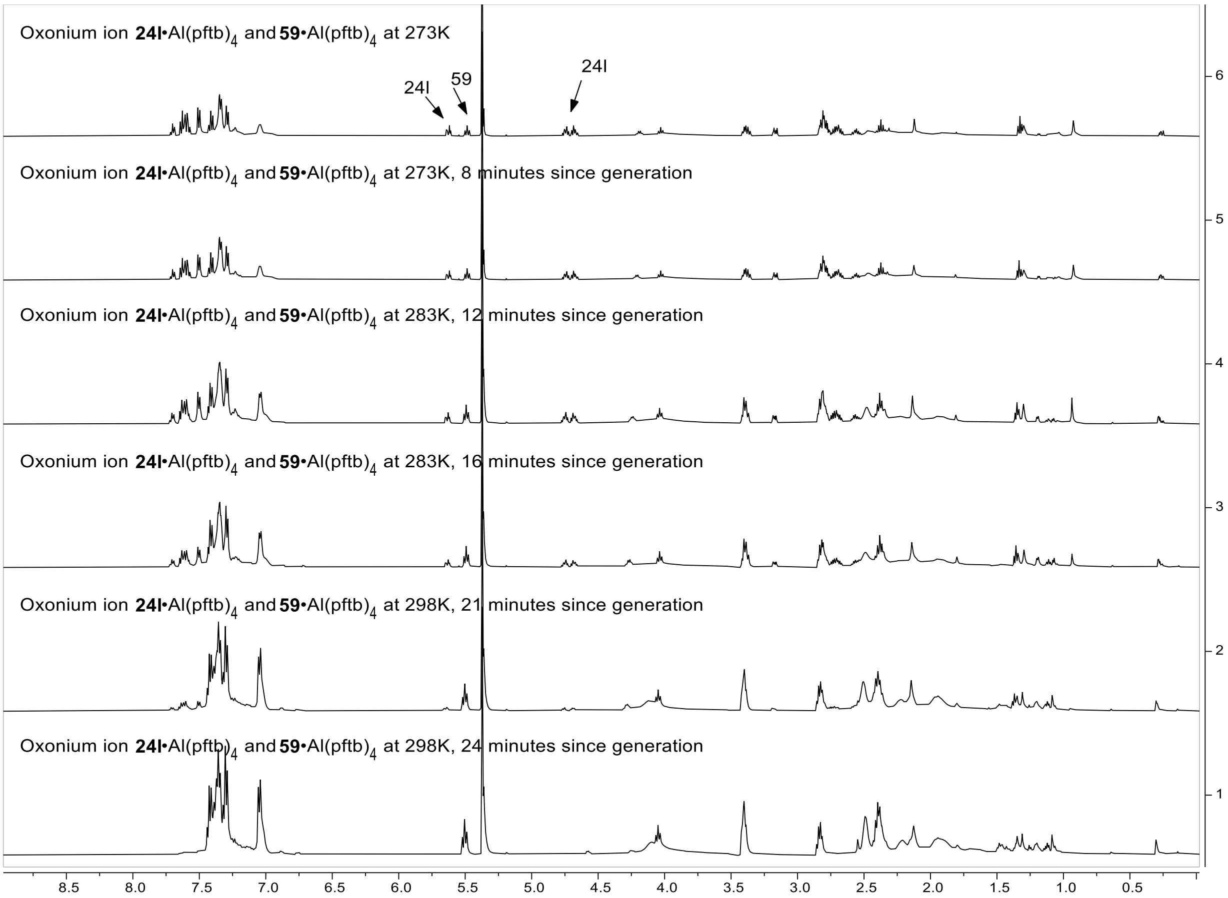
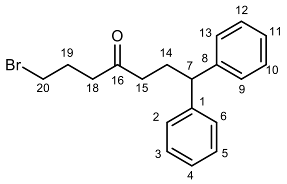


Figure S7. ^{1}H NMR monitoring experiment for the conversion of **24l**•Al(pftb)$_4$ to **59**•Al(pftb)$_4$ from 0 °C to room temperature.

7-Bromo-1,1-diphenylheptan-4-one 60



R$_f$ = 0.34 (10% Acetone/Pet. Ether 40-60)

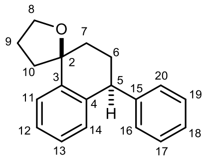
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31 – 7.26 (m, 4H, **H3**, **H5**, **H10**, **H12**), 7.25 – 7.21 (m, 4H, **H2**, **H6**, **H9**, **H13**), 7.21 – 7.16 (m, 2H, **H4**, **H11**), 3.89 (t, *J* = 7.6 Hz, 1H, **H7**), 3.41 (t, *J* = 6.4 Hz, 2H, **H20**), 2.51 (t, *J* = 7.0 Hz, 2H, **H18**), 2.42 – 2.37 (m, 2H, **H15**), 2.37 – 2.30 (m, 2H, **H14**), 2.07 (p, *J* = 6.7 Hz, 2H, **H19**).

^{13}C NMR (126 MHz, CDCl$_3$) δ 209.4 (**C16**), 144.4 (**C1**, **C8**), 128.7 (**C10**, **C12**, **C3**, **C5**), 128.0 (**C9**, **C13**, **C2**, **C6**), 126.5 (**C11**, **C4**), 50.6 (**C7**), 41.4 (**C15**), 40.8 (**C18**), 33.5 (**C20**), 29.3 (**C14**), 26.5 (**C19**).

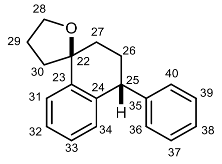
IR (thin film, *υ*/cm^{-1}): 2926, 1713, 1599, 1450, 1260, 1047

HRMS (ESI): Ionized as [M-Br]$^+$: Found 265.1587, *m/z* calculated for $C_{19}H_{21}O$ [M-Br]$^+$: 265.1587.

(2*R**,4'*S**)-4'-Phenyl-3',4,4',5-tetrahydro-2'*H*,3*H*-spiro[furan-2,1'-naphthalene] 61 and (2*R**,4'*R**)-4'-Phenyl-3',4,4',5-tetrahydro-2'*H*,3*H*-spiro[furan-2,1'-naphthalene] 61'



61



61'

R_f = 0.47 (10% Acetone/Pet. Ether 40-60)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.0, 1.4 Hz, 0.3H, **H31**), 7.47 (dd, *J* = 7.9, 1.4 Hz, 1H, **H11**), 7.33 – 7.28 (m, 2H, **H17**, **H19**), 7.28 – 7.22 (m, 0.9H, **H32**, **H37**, **H39**), 7.23 – 7.19 (m, 2H, **H12**, **H18**), 7.19 – 7.16 (m, 0.3H, **H38**), 7.14 – 7.11 (m, 2H, **H16**, **H20**), 7.11 – 7.08 (m, 0.3H, **H33**), 7.08 – 7.04 (m, 1.6H, **H13**, **H36**, **H40**), 6.86 (d, *J* = 7.8 Hz, 0.3H, **H34**), 6.76 (dt, *J* = 7.9, 1.3 Hz, 1H, **H14**), 4.23 – 4.17 (m, 1.3H, **H8'**, **H28'**), 4.16 – 4.13 (m, 0.3H, **H25**), 4.12 – 4.09 (m, 1H, **H5**), 4.09 – 4.05 (m, 1H, **H8**), 4.04 – 4.01 (m, 0.3H, **H28**), 2.27 (ddt, *J* = 14.0, 5.8, 3.2 Hz, 1H, **H6'**), 2.23 – 2.16 (m, 2.9H, **H9'**, **H10'**, **H26'**, **H29'**, **H30'**), 2.14 – 2.07 (m, 2.6H, **H9**, **H10**, **H29**, **H30**), 2.05 – 2.02 (m, 0.3H, **H26**), 2.02 – 1.98 (m, 0.3H, **H27'**), 1.98 – 1.95 (m, 2H, **H7**), 1.93 – 1.85 (m, 1H, **H6**), 1.70 (ddd, *J* = 13.2, 7.4, 2.8 Hz, 0.3H, **H27**).
^{13}C NMR (126 MHz, $CDCl_3$) δ 147.3 (**C15**), 147.0 (**C35**), 143.7 (**C3**), 143.2 (**C23**), 139.5 (**C4**), 139.0 (**C24**), 130.0 (**C34**), 129.6 (**C14**), 129.1 (**C36**, **C40**), 128.9 (**C16**, **C20**), 128.6 (**C17**, **C19**), 128.3 (**C37**, **C39**), 127.2 (**C33**), 127.0 (**C32**), 126.9 (**C13**), 126.7 (**C12**, **C31**), 126.3 (**C18**), 126.2 (**C11**), 126.1 (**C38**), 83.2 (**C2**), 82.8 (**C22**), 68.8 (**C8**), 68.6 (**C28**), 46.2 (**C5**), 44.9 (**C25**), 40.9 (**C10**), 40.7 (**C30**), 35.3 (**C7**), 32.2 (**C27**), 32.0 (**C6**), 30.4 (**C26**), 26.8 (**C29**), 26.6 (**C9**).
IR (thin film, *υ*/cm^{-1}): 2932, 2860, 1491, 1447, 1048, 908, 757, 729, 701.
HRMS (ESI): Ionized as $[M+H]^+$: Found 265.1588, *m/z* calculated for $C_{19}H_{21}O$ $[M+H]^+$: 265.1587.

Procedure for the quenching of oxocarbenium ion 42•$Al(pftb)_4$:

The oxocarbenium ion **42**•$Al(pftb)_4$ was generated from chloride **23w** (10.4 mg, 0.042 mmol) and $AgAl(pftb)_4{\cdot}CH_2Cl_2$ (53.0 mg, 0.046 mmol) at room temperature Tetrabutylammonium bromide (68.0 mg, 0.21 mmol) was added to the reaction mixture and stirred open to air at room temperature. TLC analysis at this stage suggested the formation of two spots that do not correspond to **23w** (First spot, **R_f** = 0.41 (5% EA/ Pet. Ether 40-60), a bright blue spot under 256nm UV irradiation on TLC plate. Second spot, **R_f** = 0.16 (5% EA/ Pet. Ether 40-60), UV active). Volatiles were removed and the residue was purified by flash column chromatography (5% EA/ Pet. Ether 40-60 to 15% EA/ Pet. Ether 40-60). It was observed that the spot corresponding to **R_f** = 0.41 was converted to the spot corresponding to **R_f** = 0.16 during flash column chromatography. The spot corresponding to **R_f** = 0.16 was found to be the fulvene product **43**, which was isolated as a yellow oil (2.5 mg, 0.012 mmol, 28%, *E*:*Z* = 1:1). *Note*: resonances we ascribe to the oxonium ion **24w**•$Al(pftb)_4$ could be observed by ^{1}H NMR at -40 °C which readily decayed with concomitant increase of the resonances of oxocarbenium ion **42w**•$Al(pftb)_4$ (**Figure S8**).

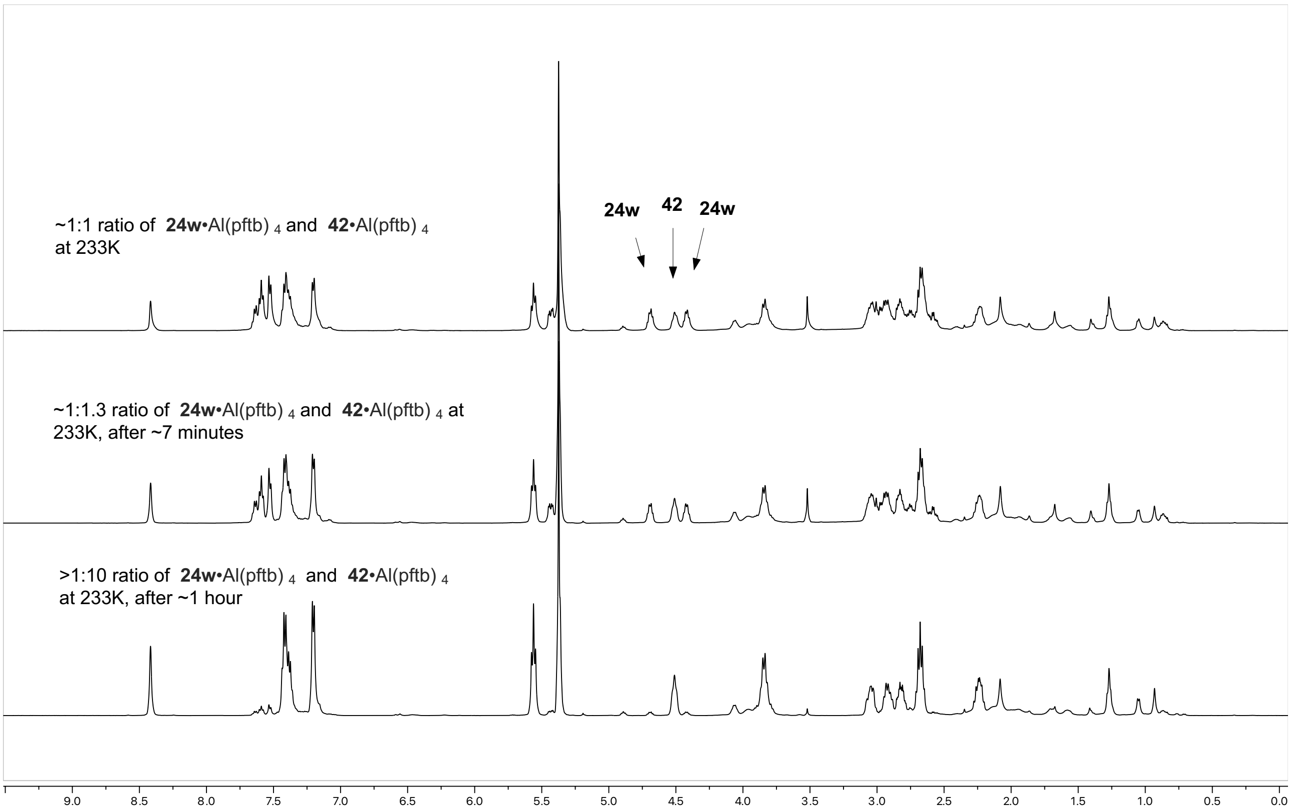
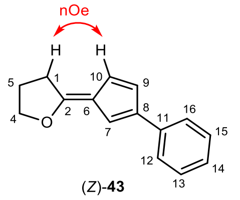
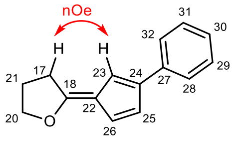


Figure S8. ^{1}H NMR monitoring experiment for the conversion of **24w**•Al(pftb)$_4$ to **42**•Al(pftb)$_4$ at -40 °C.

(*Z*)-2-(3-phenylcyclopenta-2,4-dien-1-ylidene)tetrahydrofuran (*Z*)-43 and (*E*)-2-(3-phenylcyclopenta-2,4-dien-1-ylidene)tetrahydrofuran (*E*)-43



(*Z*)-**43**



(*E*)-**43**

R$_f$ = 0.16 (5% EA/ Pet. Ether 40-60)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 – 7.50 (m, 4H, **H12**, **H16**, **H28**, **H32**), 7.39 – 7.28 (m, 4H, **H13**, **H15**, **H29**, **H31**), 7.24 – 7.11 (m, 2H, **H14**, **H30**), 6.90 (t, *J* = 2.0 Hz, 1H, **H7**), 6.78 (dd, *J* = 5.1, 1.8 Hz, 1H, **H25**), 6.76 (dd, *J* = 5.0, 1.8 Hz, 1H, **H9**), 6.74 (dd, *J* = 5.0, 2.1 Hz, 1H, **H26**), 6.70 (t, *J* = 2.0 Hz, 1H, **H23**), 6.56 (dd, *J* = 5.0, 2.2 Hz, 1H, **H10**), 4.49 (t, *J* = 6.9 Hz, 2H, **H5**), 4.48 (t, *J* = 6.9 Hz, 2H, **H21**), 3.19 (t, *J* = 7.7 Hz, 2H, **H1**), 3.18 (t, *J* = 7.7 Hz, 2H, **H17**), 2.23 (m, 4H, **H4**, **H20**).

^{13}C NMR (126 MHz, CDCl$_3$) δ 169.0 (**C2**), 169.0 (**C18**), 141.0 (**C8**), 140.2 (**C24**), 137.0 (**C11**, **C27**), 128.6 (**C13**, **C15**, **C31**), 126.5 (**C14**), 126.3 (**C29**), 126.0 (**C25**), 125.8 (**C12**, **C16**), 125.6 (**C32**, **C28**), 125.2 (**C9**), 123.2 (**C10**), 119.2 (**C6**), 119.2 (**C22**), 119.1 (**C26**), 116.1 (**C23**), 112.0 (**C7**), 73.9 (**C5**, **C21**), 30.4 (**C1**), 30.3 (**C17**), 24.1 (**C4**), 24.1 (**C20**).

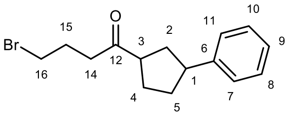
IR (thin film, *υ*/cm^{-1}): 2925, 1688, 1642, 1597, 1172

HRMS (ESI): Ionized as [M+H]$^+$: Found 211.11201, *m/z* calculated for $C_{15}H_{15}O$ [M+H]$^+$: 211.11174.

Procedure for the quenching of oxocarbenium ion 46•Al(pftb)$_4$:

The oxonium ion **24n**•Al(pftb)$_4$ was generated from chloride **23n** (7.3 mg, 0.029 mmol) and AgAl(pftb)$_4$·CH$_2$Cl$_2$ (37.0 mg, 0.032 mmol) in CD$_2$Cl$_2$ at -40 °C. Upon warming to room temperature, the oxonium in **24n**•Al(pftb)$_4$ was found to rearrange into the oxocarbenium ion **46**•Al(pftb)$_4$. The above process was also found to give the oxocarbenium ion **46**•Al(pftb)$_4$ using the following slightly modified conditions, where chloride **23n** (10.0 mg, 0.040 mmol) and AgAl(pftb)$_4$·CH$_2$Cl$_2$ (51.0 mg, 0.044 mmol) were mixed in CH_2Cl_2 at -20 °C and then warmed to room temperature. The difference in conditions employed was because the former condition allowed the characterization of oxonium ion **24n**•Al(pftb)$_4$. The solution containing the oxocarbenium ion **46**•Al(pftb)$_4$ was filtered and the filtrate was quenched with tetrabutylammonium bromide (64.0 mg, 0.2 mmol) at room temperature. Volatiles were removed and the residue was purified by flash column chromatography (2% EA/ Pet. Ether 40-60 to 5% EA/ Pet. Ether 40-60) to give the compound **47**(7.4 mg, 0.025 mmol, 63%, *d.r.* = 1:1) as a colourless oil.

4-Bromo-1-(3-phenylcyclopentyl)butan-1-one 47



R_f = 0.44 (5% EA/ Pet. Ether 40-60)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H, **H8**, **H10**), 7.27 – 7.22 (m, 2H, **H7**, **H11**), 7.22 – 7.17 (m, 1H, **H9**), 3.53 – 3.42 (m, 2H, **H16**), 3.20 – 3.14 (m, 0.5H, **H3’**), 3.14 – 3.04 (m, 1.5H, **H1**, **H3**), 2.76 – 2.62 (m, 2H, **H14**), 2.38 – 2.32 (m, 0.5H, **H2’**), 2.32 – 2.25 (m, 0.5H, **H2’**), 2.20 – 2.13 (m, 2.5H, **H5’**, **H15**), 2.13 – 2.08 (m, 1H, **H4'**, **H5’**), 2.06 (ddd, *J* = 9.5, 6.1, 2.8 Hz, 0.5H, **H4'**), 1.94 (ddd, *J* = 13.0, 6.7, 3.0 Hz, 0.5H, **H4**), 1.89 (dt, *J* = 8.0, 2.3 Hz, 0.5H, **H4**), 1.88 – 1.81 (m, 1H, **H2**), 1.77 – 1.68 (m, 1H, **H5**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.6 (**C12**), 211.4 (**C12**), 145.0 (**C6**), 144.5 (**C6**), 128.5 (**C8**, **C10**), 127.2 (**C7**, **C11**), 127.1 (**C7**, **C11**), 126.3 (**C9**), 126.2 (**C9**), 51.4 (**C3**), 50.8 (**C3**), 46.5 (**C1**), 45.1 (**C1**), 39.8 (**C14**), 39.6 (**C14**), 37.5 (**C2**), 36.4 (**C2**), 34.8 (**C5**), 33.9 (**C5**), 33.7 (**C16**), 29.1 (**C4**), 28.1 (**C4**), 26.6 (**C15**), 26.6 (**C15**).

IR (thin film, *υ*/cm^{-1}): 2952, 1707, 1601, 1493

HRMS (ESI): Ionized as [M-Br]$^+$: Found 215.14322, *m/z* calculated for $C_{15}H_{19}O$ [M-Br]$^+$: 215.14304.

Quenching of oxonium ion 24b with a series of σ- and π-nucleophiles Figure S9:

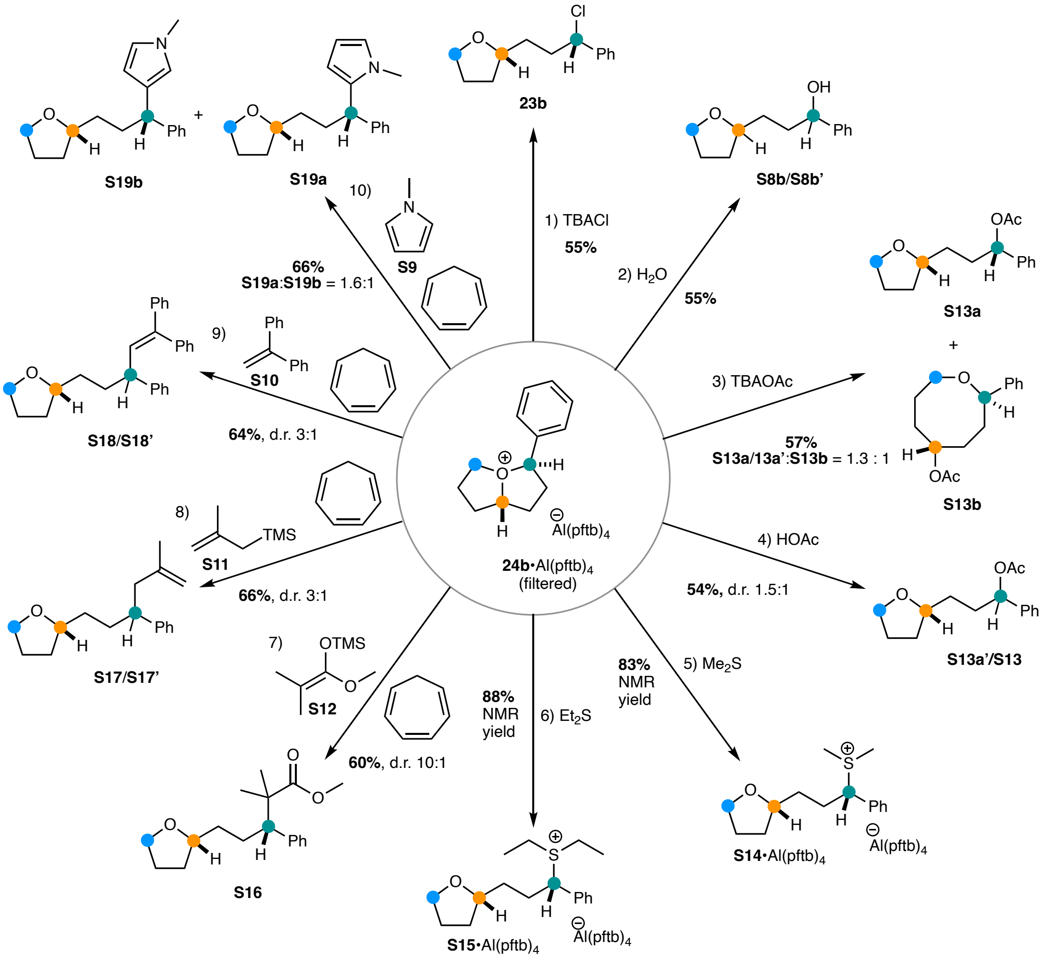


Figure S9. Quenching of oxonium ion **24b**•Al(pftb)$_4$ with a series of σ- and π-nucleophiles. Reagents and conditions: **1)** Filter off $AgCl_{(s)}$, 2.0 eq. Tetrabutylammonium chloride, CH_2Cl_2, r.t., 55% **2)** Filter off $AgCl_{(s)}$, 2.0 eq. H_2O, CH_2Cl_2, r.t., 1 min, *then* excess $NaHCO_{3(s)}$, 55% *d.r.* ~ 2 : 1. **3)** Filter off $AgCl_{(s)}$, 2.0 eq. Tetrabutylammonium acetate, CH_2Cl_2, r.t., 57% **S13a**:**S13b** = 1.3 : 1 **4)** Filter off $AgCl_{(s)}$, 2.0 eq. AcOH, r.t., 1 min, *then* excess $NaHCO_{3(s)}$, 54% *d.r.* ~ 2 : 1. **5)** Filter off $AgCl_{(s)}$, 1.5 eq. Me_2S, CD_2Cl_2, −20 °C, 83% NMR yield. **6)** Filter off $AgCl_{(s)}$, 1.2 eq. Et_2S, CD_2Cl_2, −20 °C, 88% NMR yield. **7)** 2.0 eq. Methyl trimethylsilyl dimethylketene acetal **S12**, 2.0 eq. cycloheptatriene, CH_2Cl_2, −20 °C to r.t., 30 mins, 54% *d.r.* ~ 10 : 1. **8)** 10.0 eq. Methallyltrimethylsilane **S11**, 2.0 eq. cycloheptatriene, CH_2Cl_2, −20 °C, 30 mins, *then* 2.0 eq. TBAOAc at −20 °C, 66% *d.r.* ~ 3 : 1. **9)** 10.0 eq. 1,1-diphenylethylene **S10**, 2.0 eq. cycloheptatriene, CH_2Cl_2, −20 °C to r.t., 30 mins, 64% *d.r.* ~ 2 : 1. **10)** 2.0 eq. *N*-methylpyrrole **S9**, 2.0 eq. cycloheptatriene, −20 °C, 15 mins, 66% **S19a**:**S19b** = 1.6:1. All relative stereochemical configurations in the products were inferred from the relative stereochemical configuration of the oxonium ion **24b**•Al(pftb)$_4$ (see below).

For the quenching of oxonium ion **24b**•Al(pftb)$_4$ with σ-nucleophiles (Entries 1-6), anionic nucleophiles, such as tetrabutylammonium chloride and tetrabutylammonium acetate provided, **23b**, **S13a** and **S13b** as single diastereomers with the relative configuration assumed to be that arising from S$_N$2 attack with inversion of configuration. Neutral nucleophiles such as water and acetic acid, which were expected to bring about reversible quenching, gave **S8b** and **S13a/S13a'** as mixtures of diastereomers with slight enrichment of one over the another. The major diastereomer **S13a** obtained from irreversible acetate quench was found to be a the minor diastereomer in the acetic acid quench, suggesting that **S13a** was formed under kinetic control. For the last two neutral nucleophiles Me_2S and Et_2S, they were found to provide a single diastereomer of their corresponding sulfonium ions **S14**•Al(pftb)$_4$ and **S15**•Al(pftb)$_4$ upon quenching at −20 °C, with the relative configuration assumed to be that arising from S$_N$2 attack with inversion of configuration. However, if the quenching was executed at room temperature, a diastereomeric mixture was obtained, with the sulfonium ions **S14**•Al(pftb) and **S15**•Al(pftb)$_4$ being the minor diastereomer. This observation was found to parallel that observed for the tetrabutylammonium acetate/acetic acid quench scenario, which suggests that quenching by Me_2S and Et_2S at −20 °C were under kinetic control. A series of experiments were performed to further elucidate the rationale of the observed stereochemical behavior of the sulfonium ions.

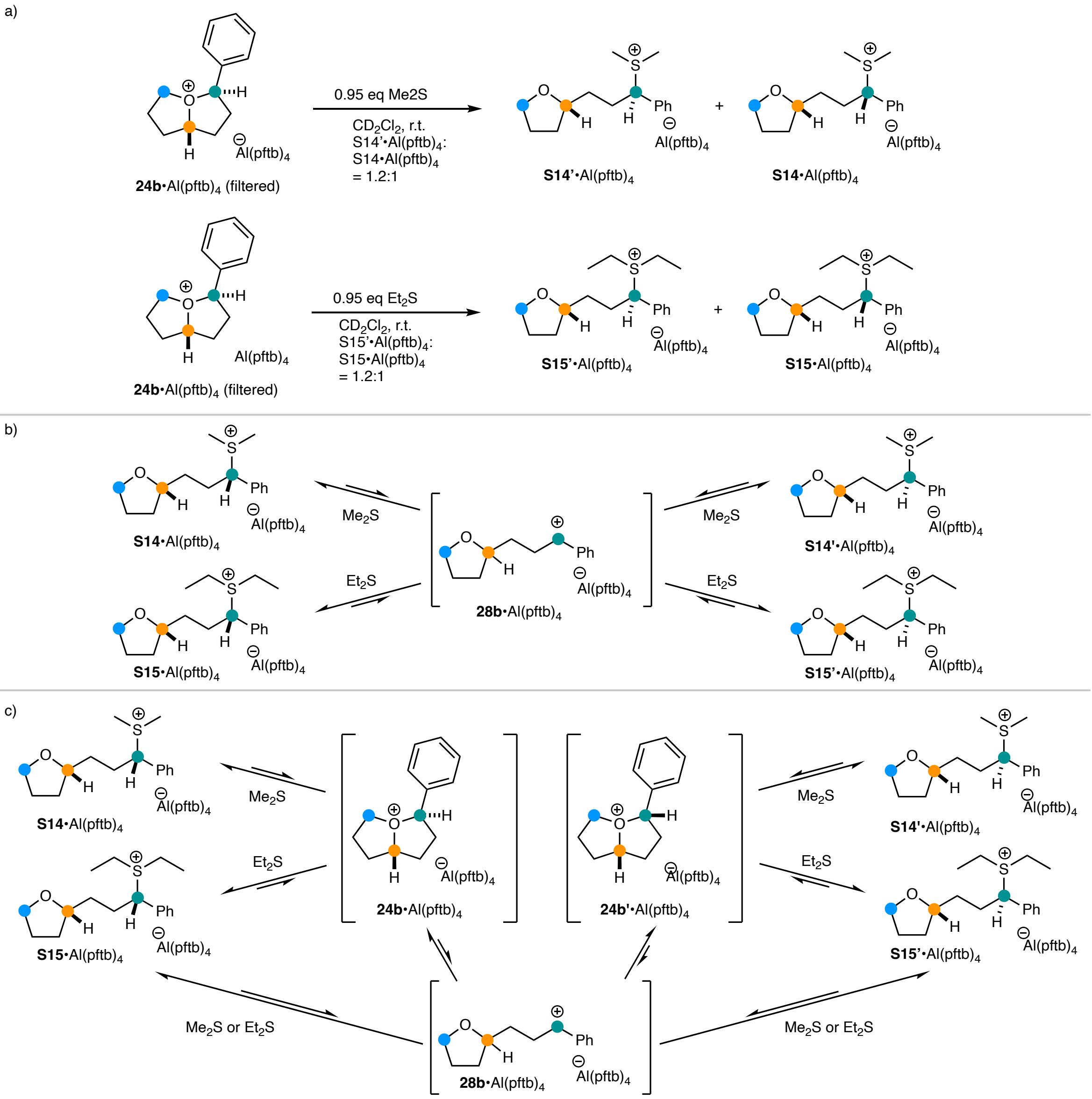
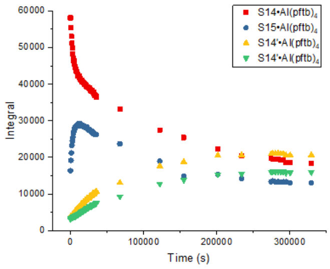


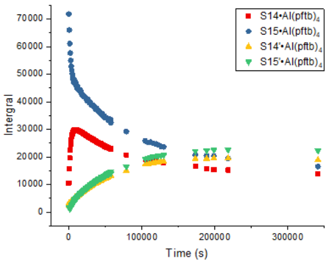
Figure S10. a) Reaction of oxonium ion **24b**•Al(pftb)$_4$ with sub-stoichiometric equivalents of dialkylsulfides at room temperature. **b)** Illustration of the sulfonium ion-carbenium ion mechanism. **c)** Illustration of the sulfonium ion-oxonium ion-carbenium ion mechanism.

The reaction of filtered oxonium ion **24b**•Al(pftb)$_4$ with 0.95 equivalents of either Me_2S or Et_2S at room temperature gave sulfonium ions **S14'**•Al(pftb)$_4$/**S14**•Al(pftb)$_4$ and **S15'**•Al(pftb)$_4$/**S15**•Al(pftb)$_4$ respectively, each having a ~1.2:1 diastereomeric ratio (**Figure S10a**). This suggested that the observed stereochemical behavior was not due to excess Me_2S or Et_2S in the reaction mixture. This therefore suggested that the generation of the major thermodynamically most stable diastereomer **S14'**•Al(pftb)$_4$ or **S15'**•Al(pftb)$_4$ at room temperature could occur even with limiting dialkylsulfide. Given this observation, two boundary scenarios of sulfide exchange in a mechanistic continuum could lead to the observed stereochemical outcome. On one end, an S$_N$1 process could be envisioned involving the direct ionization of the sulfonium ion **S14**•Al(pftb)$_4$ or **S15**•Al(pftb)$_4$ into the carbenium ion **28b**•Al(pftb)$_4$, followed by *direct, unselective quenching* of the carbenium ion **28b**•Al(pftb)$_4$ by the dialkylsulfides to give rise to a mixture of **S14'**•Al(pftb)$_4$/**S14**•Al(pftb)$_4$ and **S15'**•Al(pftb)$_4$/**S15**•Al(pftb)$_4$. If this mechanism (a sulfonium ion-carbenium ion mechanism) were predominant, an experiment with any arbitrary ratios of free Me_2S and Et_2S mixed with **S14**•Al(pftb)$_4$ would be expected to give rise to an increase in the concentration of both **S15**•Al(pftb)$_4$, **S14'**•Al(pftb)$_4$ and **S15'**•Al(pftb)$_4$. On the other hand, it could be envisioned that the regeneration of oxonium ion **24b**•Al(pftb)$_4$ *via* an intramolecular S_N2 process from the sulfonium ions **S14**•Al(pftb)$_4$ or **S15**•Al(pftb)$_4$ could precede the generation of carbenium ion **28b**•Al(pftb)$_4$. If this mechanism (a sulfonium ion-oxonium ion-carbenium ion mechanism) was predominant, an experiment with any arbitrary ratios of free Me_2S and Et_2S mixed with **S14**•Al(pftb)$_4$ is expected to first give rise to the conversion of **S14**•Al(pftb)$_4$ to **S15**•Al(pftb)$_4$ *due to the stereospecific nature of S_N2 processes*, followed by a slow build-up of **S14'**•Al(pftb)$_4$ and **S15'**•Al(pftb)$_4$ through **28b**•Al(pftb)$_4$ via the oxonium-carbocation equilibrium (**Figure S10b and c**).

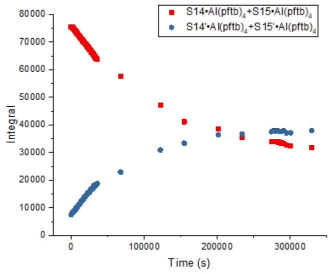
Experimentally, it was observed that in a mixture of 1.0 eq. **67**, 1.0 eq. free Me_2S and 1.5 eq. of free Et_2S, rapid conversion of **67** to **68** was observed before a slow build-up of **67'** and **68'**, in which the ratio of **67'**+**68'** : **67**+**68** reached 1.2 : 1 over ca. 4 days, in accordance with previous observation. The ratio of **67**:**68** and **67'**:**68'** was found to be 1.3-1.4 : 1, which coincides with the ratio of total Me_2S : total Et_2S in the system (1.4 : 1). Performing the experiment in the opposite way, beginning with sulfonium ion **68** instead of **67**, it was experimentally observed that rapid conversion of **68** to **67** occurred in a mixture of 1.0 eq. **68**, 0.3 eq. free Et_2S and 1.0 eq. free Me_2S before a slow build-up of **67'** and **68'**, in which the ratio of **67'**+**68'** : **67**+**68** reached 1.3 : 1 over ca. 4 days, also in accordance with previous observation. The ratio of **67**:**68** and **67'**:**68'** was found to be 1 : 1.2, which coincides with the ratio of total Me_2S : total Et_2S in the system (1 : 1.3) (**Figure S11**). These experimental observations suggest that the sulfonium ion-oxonium ion-carbenium ion mechanism is more likely to be responsible for the observed stereochemical behavior of the sulfonium ions. A quantitative kinetic analysis of this transformation was however not attempted due to slow decomposition of the sulfonium ions into unknown species over the time of the study (ca. 4 days).



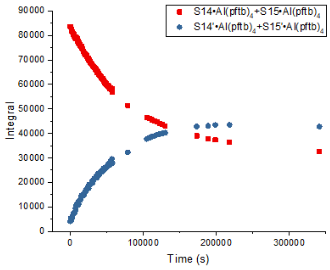
Sulfonium ion	Final Integral	Ratio
S14•Al(pftb)$_4$	18438	S14:S15 =1.4
S15•Al(pftb)$_4$	13048	
S14’•(Alpftb)$_4$	20677	S14’:S15’ =1.3
S14’•(Alpftb)$_4$	15981	



Sulfonium ion	Final Integral	Ratio
S14•Al(pftb)$_4$	13896	S14:S15 =1.2
S15•Al(pftb)$_4$	16470	
S14’•Al(pftb)$_4$	18844	S14’:S15’ =1.2
S15’•Al(pftb)$_4$	22275	



Sulfonium ion	Final Integral	Ratio
S14+S15	31867	1.2
S14’+S15’	37884	
S14+S15 from a)	31486	1.2
S14’+S15’ from a)	36658	



Sulfonium ion	Final Integral	Ratio
S14+S15	29572	1.3
S14’+S15	39657	
S14+S15 from a)	30366	1.4
S14’+S15’ from a)	41119	

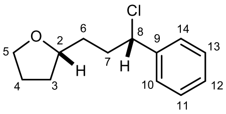
Figure S11. For both **a)** and **b)**: Plot on the left: Experiment beginning with sulfonium ion **S14**•Al(pftb)$_4$, with 1.0 eq. free Me_2S and 1.5 eq. of free Et_2S. Plot on the right: Experiment beginning with sulfonium ion **S15**•Al(pftb)$_4$, with 0.3 eq. free Et_2S and 1.0 eq. free Me_2S. **a)** Variation of the individual integrals of the benzylic C−H protons of sulfonium ions **S14**•Al(pftb)$_4$, **S15**•Al(pftb)$_4$, **S14'**•Al(pftb)$_4$ and **S15'**•Al(pftb)$_4$ over time. **b)** Variation of the sum of the integrals of the benzylic C−H proton of sulfonium ions **S14**•Al(pftb)$_4$, **S15**•Al(pftb)$_4$ and **S14'**•Al(pftb)$_4$, **S15'**•Al(pftb)$_4$ over.

For the quenching of oxonium **24b**•Al(pftb)$_4$ with π-nucleophiles (Entries 7-10), the reaction conditions employed were analogous to that for the reaction of oxonium ion **24v**•Al(pftb)$_4$. It was discovered that more nucleophilic π-nucleophiles, according to Mayr’s nucleophilicity parameters,[13, 14] gave higher diastereoselectivity in the reaction with the relative configuration of the major diastereomer assumed to be that arising from S_N2 attack with inversion of configuration. This is exemplified by the products **S16**, **S19a** and **S19b**, which were generated at least with 10 : 1 *d.r.* in the reaction. A control experiment in which **S16** was directly generated from a diastereomeric mixture of chlorides **23b** without the explicit preparation of oxonium ion **24b**•Al(pftb)$_4$ did not result in significant *d.r.* in the reaction. This therefore suggests the participation of oxonium ions **24b**•Al(pftb)$_4$ is crucial for diastereoselectivity.

General procedure for the quenching of oxonium ion 24b•Al(pftb)$_4$ with tetrabutylammonium chloride, and tetrabutylammonium acetate:

The oxonium ion **24b**•Al(pftb)$_4$ was generated from the chloride **23b** (1.0 eq.) and $AgAl(pftb)_4{\cdot}CH_2Cl_2$ (1.1 eq.) in CH_2Cl_2 (0.01 M) at room temperature. The solution of the oxonium ion **24b**•Al(pftb)$_4$ was then filtered, and the corresponding nucleophile (2.0 eq.) was added at room temperature. TLC analysis was then performed to monitor the progress of the reaction. The oxonium ion **24b**•Al(pftb)$_4$ manifests itself as a baseline spot on TLC (10% EA/ Pet. Ether 40-60) and the disappearance of the baseline spot was found to indicate completion of reaction. TLC analysis was also performed against the chloride starting material **23b**. Volatiles were then removed, and the residue was purified by flash column chromatography to give the corresponding products **23b**, **S13a** and **S13a'**.

(*S**)-2-((*S**)-3-chloro-3-phenylpropyl)tetrahydrofuran 23b



Flash column chromatography eluent: 5% EA/Pet. Ether 40-60 to 10% EA/Pet. Ether 40-60
R$_f$ = 0.47 (10% EA/ Pet. Ether 40-60)
Yield: 55% (5.5 mg) from 10.0 mg of **23b** and 22.0 mg of tetrabutylammonium chloride.
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.40 – 7.36 (m, 2H, **H10**, **H14**), 7.36 – 7.32 (m, 1H, **H11**, **H13**), 7.31 – 7.27 (m, 1H, **H12**), 4.89 (dd, *J* = 8.4, 6.1 Hz, 1H, **H8**), 3.84 (ddd, *J* = 8.5, 7.3, 6.2 Hz, 1H, **H5'**), 3.80 (tdd, *J* = 7.7, 6.4, 5.1 Hz, 1H, **H2**), 3.70 (td, *J* = 8.0, 6.4 Hz, 1H, **H5**), 2.21 (dddd, *J* = 13.5, 10.5, 8.4, 6.1 Hz, 1H, **H7'**), 2.14 (dddd, *J* = 13.5, 10.1, 8.0, 5.1 Hz, 1H, **H7**), 1.98 (dddd, *J* = 11.6, 8.5, 6.4, 4.8 Hz, 1H, **H3'**), 1.92 – 1.82 (m, 2H, **H4**), 1.72 (ddt, *J* = 13.5, 10.5, 5.1 Hz, 1H, **H6'**), 1.54 (dddd, *J* = 13.5, 10.1, 8.0, 5.6 Hz, 1H, **H6**), 1.45 (ddt, *J* = 12.0, 8.8, 7.6 Hz, 1H, **H3**).
^{13}C NMR (126 MHz, CDCl$_3$) δ 142.0 (**C9**), 128.8 (**C11**, **C13**), 128.4 (**C12**), 127.1 (**C10**, **C14**), 78.9 (**C2**), 67.9 (**C5**), 64.2 (**C8**), 37.2 (**C7**), 33.4 (**C6**), 31.5 (**C3**), 25.8 (**C4**).
Comparison of ^{1}H and ^{13}C NMR spectrum with a diastereomeric mixture of **23b** suggests the **23b** generated from the quenching of oxonium ion **24b**•Al(pftb)$_4$ by tetrabutylammonium chloride consists of a single diastereomer (**Figure S12**).

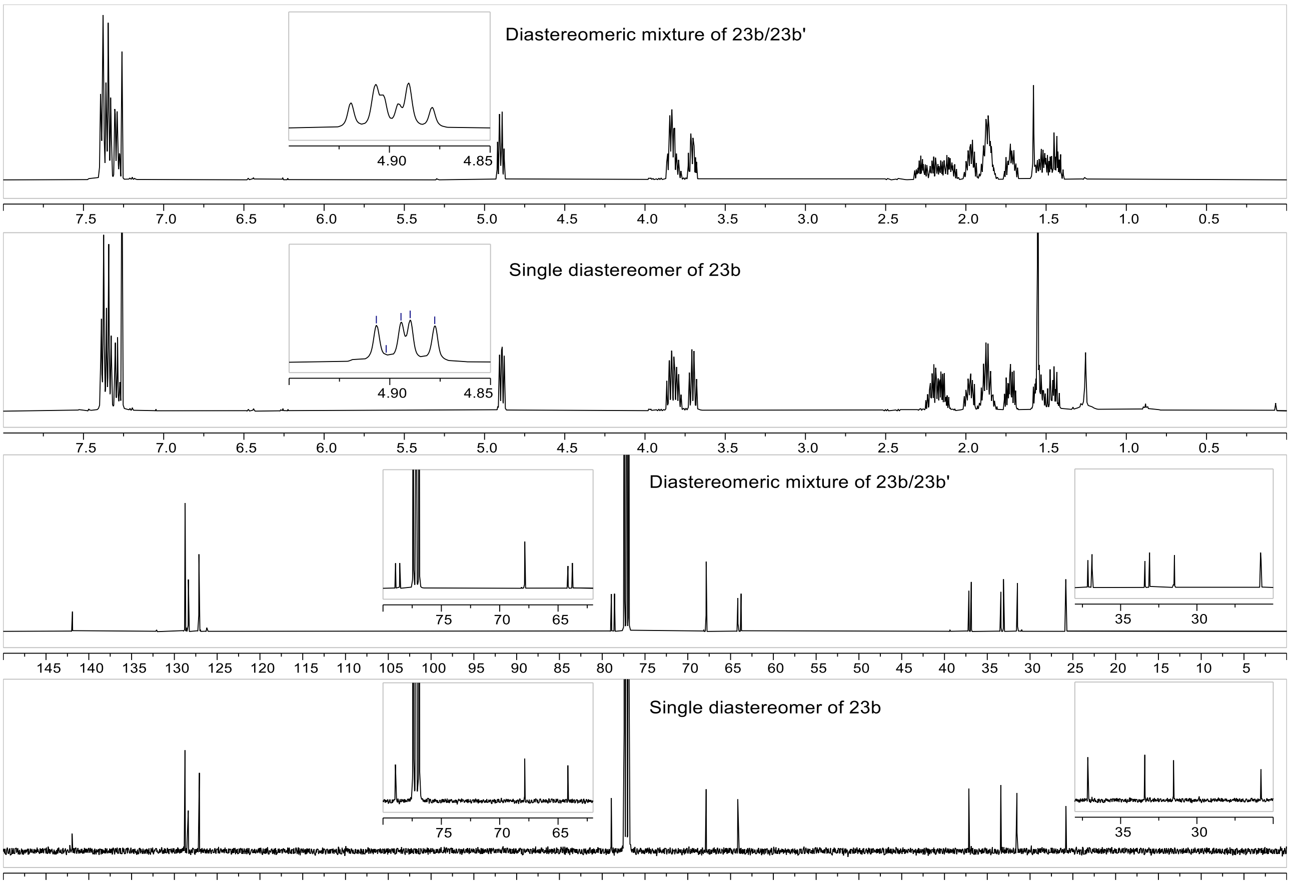
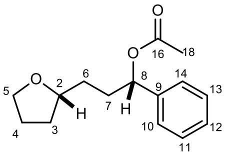


Figure S12. Comparison of ^{1}H and ^{13}C NMR spectra of a diastereomeric mixture of **23b/23b'** and a single diastereomer of **23b**.

(*S)-1-phenyl-3-((*S**)-tetrahydrofuran-2-yl)propyl acetate S13a**



Flash column chromatography eluent: 10% EA/Pet. Ether 40-60

R$_f$ = 0.31 (10% EA/ Pet. Ether 40-60)

Yield: 32% (3.5 mg) from 10.0 mg of **23b** and 24.0 mg of tetrabutylammonium acetate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.33 (m, 2H, **H11**, **H13**), 7.33 – 7.32 (m, 2H, **H10**, **H14**), 7.30 – 7.27 (m, 1H, **H12**), 5.74 (t, *J* = 6.9 Hz, 1H, **H8**), 3.82 (ddd, *J* = 8.3, 7.1, 6.2 Hz, 1H, **H5'**), 3.79 – 3.73 (m, 1H, **H2**), 3.69 (td, *J* = 7.9, 6.5 Hz, 1H, **H5**), 2.06 (s, 3H, **H18**), 2.00 – 1.95 (m, 1H, **H3'**), 1.95 – 1.89 (m, 2H, **H7**), 1.89 – 1.80 (m, 2H, **H4**), 1.54 – 1.46 (m, 2H, **H6**), 1.47 – 1.36 (m, 1H, **H3**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5 (**C16**), 140.7 (**C9**), 128.6 (**C11**, **C13**), 128.0 (**C12**), 126.7 (**C10**, **C14**), 79.0 (**C2**), 76.2 (**C8**), 67.8 (**C5**), 33.3 (**C7**), 31.7 (**C6**), 31.4 (**C3**), 25.8 (**C4**), 21.4 (**C18**).

IR (thin film, υ/cm^{-1}): 2926, 2854, 1734, 1371, 1235, 1023, 700.

HRMS (ESI): Ionized as $[M+Na]^+$: Found 271.1306, *m/z* calculated for $C_{15}H_{20}O_3{}^{23}Na$ $[M+Na]^+$: 271.1305.

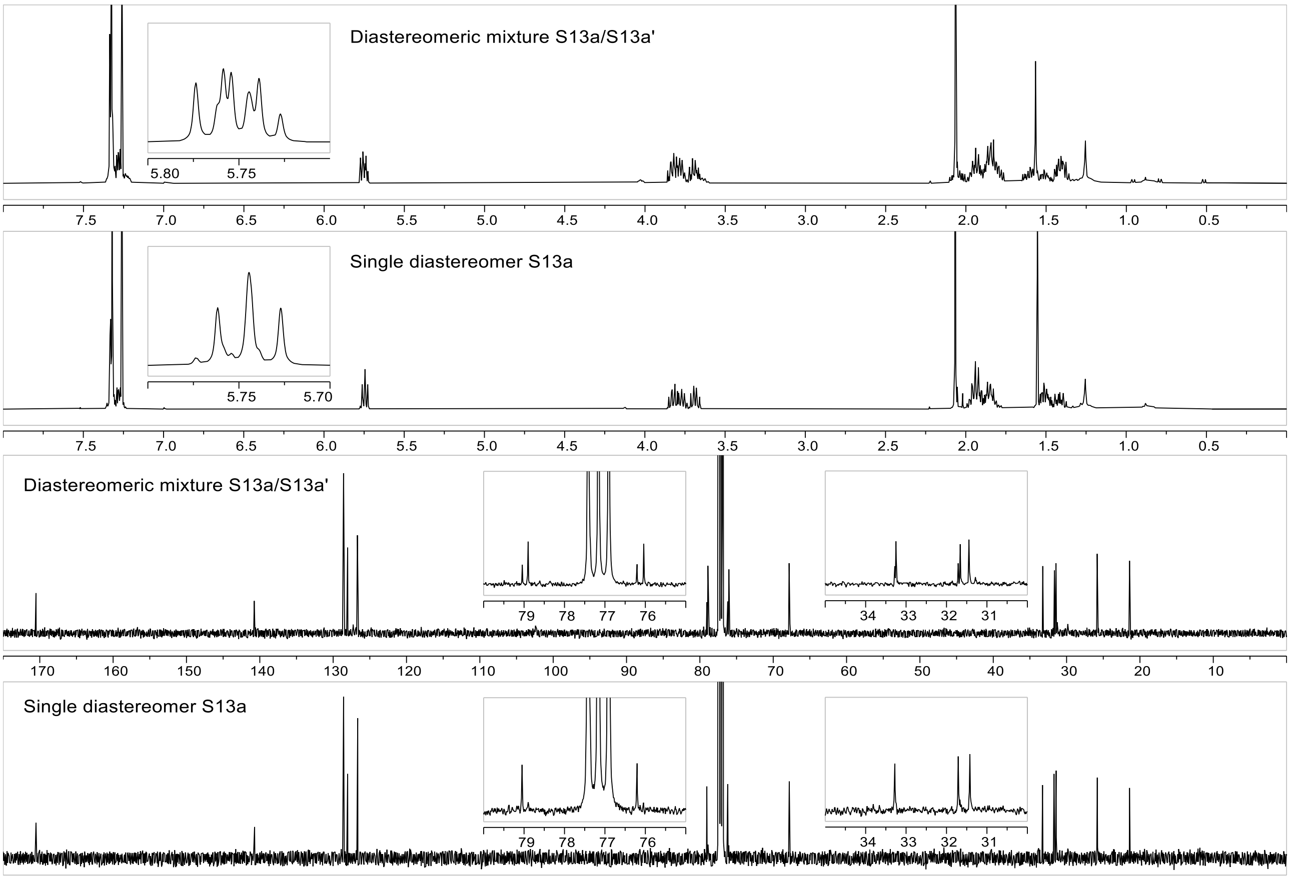
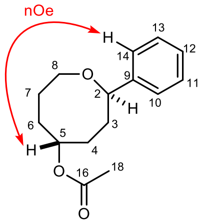


Figure S13. Comparison of ^{1}H and ^{13}C NMR spectra of diastereomeric mixture **S13** and **S13'** and single diastereomer **S13**.

(2*R**,5*R**)-2-phenyloxocan-5-yl acetate S13b

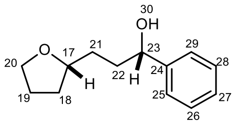


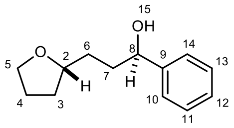
Flash column chromatography eluent: 5% EA/Pet. Ether 40-60 to 10% EA/Pet. Ether 40-60
R$_f$ = 0.44 (10% EA/ Pet. Ether 40-60)
Yield: 25% (2.8 mg) from 10.0 mg of **23b** and 24.0 mg of tetrabutylammonium acetate.
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.33 (s, 2H, **H11**, **H13**), 7.32 (s, 2H, **H10**, **H14**), 7.27 – 7.20 (m, 1H, **H12**), 5.36 (tt, *J* = 8.7, 3.5 Hz, 1H, **H5**), 4.45 (dd, *J* = 8.2, 3.2 Hz, 1H, **H2**), 3.91 (ddd, *J* = 12.0, 8.1, 3.1 Hz, 1H, **H8'**), 3.59 (dt, *J* = 12.0, 6.1, 3.2 Hz, 1H, **H8**), 2.11 – 2.02 (m, 1H, **H3'**), 2.02 (s, 3H, **H18**), 2.00 (d, *J* = 3.1 Hz, 1H, **H6'**), 1.99 – 1.93 (m, 1H, **H7'**), 1.89 – 1.80 (m, 2H, **H3**, **H4'**), 1.82 – 1.76 (m, 1H, **H4**), 1.79 – 1.71 (m, 2H, **H6**, **H7**).
^{13}C NMR (126 MHz, CDCl$_3$) δ 170.7 (**C16**), 143.5 (**C9**), 128.4 (**C11**, **C13**), 127.2 (**C12**), 125.9 (**C10**, **C14**), 80.4 (**C2**), 75.6 (**C5**), 69.6 (**C8**), 34.1 (**C3**), 32.4 (**C6**), 30.9 (**C4**), 26.2 (**C7**), 21.7 (C**18**).
IR (thin film, *υ*/cm^{-1}): 2935, 1719, 1254, 906, 727, 700
HRMS (ESI): Ionized as [M+Na]$^+$: Found 271.1305, *m/z* calculated for $C_{15}H_{20}O_3{}^{23}Na$ [M+Na]$^+$: 271.1305.

General procedure for the quenching of oxonium ion 24b•Al(pftb)$_4$ with water and acetic acid:

The oxonium ion **24b**•Al(pftb)$_4$ was generated from the chloride **23b** (1.0 eq.) and AgAl(pftb)$_4$·CH$_2$Cl$_2$ (1.1 eq.) in CH$_2$Cl$_2$ (0.01 M) at room temperature. The solution of the oxonium ion **24b**•Al(pftb)$_4$ was then filtered, and the corresponding nucleophile (2.0 eq.) was added at room temperature. After stirring for 1 minute (extended stirring to 5 minutes led to significant decrease in yield), the reaction was quenched with sat. aq. NaHCO$_3$ solution. The reaction mixture was further diluted with water and the aqueous layer was extracted three times with CH$_2$Cl$_2$. The organic layers were collected and dried with anhydrous MgSO$_4$, concentrated and purified by flash column chromatography to give the corresponding products **S8b**, and **S13a** and **S13a'**.

(*S**)-1-phenyl-3-((*S**)-tetrahydrofuran-2-yl)propan-1-ol S8b and (*R**)-1-phenyl-3-((*S**)-tetrahydrofuran-2-yl)propan-1-ol S8b'





Flash column chromatography eluent: 40% EA/Pet. Ether 40-60
R$_f$ = 0.13 (10% EA/Pet. Ether 40-60)
Yield: 55% (5.0 mg) from 10.0 mg of **23b** and 1.4 µL of H$_2$O.
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.39 – 7.31 (m, 6H, **H10**, **H11**, **H13**, **H14**, **H25**, **H26**, **H28**, **H29**), 7.26 – 7.23 (m, 1.5H, **H12**, **H27**), 4.75 (dd, *J* = 7.5, 5.1 Hz, 0.5H, **H23**), 4.70 (t, *J* = 6.4 Hz, 1H, **H8**), 3.98 – 3.86 (m, 1.5H, **H5'**, **H20'**), 3.86 – 3.80 (m, 1.5H, **H2**, **H17**), 3.80 – 3.69 (m, 1.5H, **H5**, **H20**), 3.35 (s, 1H, **OH**), 2.86 (s, 0.5H, **OH**), 2.06 – 1.94 (m, 1.5H, **H3'**, **H18'**), 1.94 – 1.82 (m, 6H, **H4**, **H7**, **H19**, **H22**), 1.70 – 1.64 (m, 2.5H, **H6**, **H21'**), 1.62 – 1.53 (m, 0.5H, **H21**), 1.52 – 1.40 (m, 1.5H, **H3**, **H18**).
^{13}C NMR (126 MHz, CDCl$_3$) δ 145.2 (**C9**), 145.0 (**C24**), 128.5 (**C11**, **C13**, **C26**, **C28**), 127.4 (**C12**,

C27), 126.0 (**C10**, **C14**, **C25**, **C29**), 79.7 (**C2**), 79.5 (**C17**), 74.7 (**C8**), 74.1 (**C23**), 68.0 (**C5**), 68.0 (**C20**), 37.0 (**C7**), 36.1 (**C22**), 32.7 (**C6**), 31.7 (**C3**, **C18**), 31.5 (**C21**), 25.8 (**C4**, **C19**).

Comparison of ^{1}H and ^{13}C NMR spectrum with **S8b/S8b'** synthesised as is a 1:1 diastereomeric mixture, suggests, that **S8b/S8b'** generated from the quenching of oxonium ion **24b•**Al(pftb)$_4$ by water is enriched of one diastereomer over the other (*d.r.* = 2:1) (**Figure S14**).

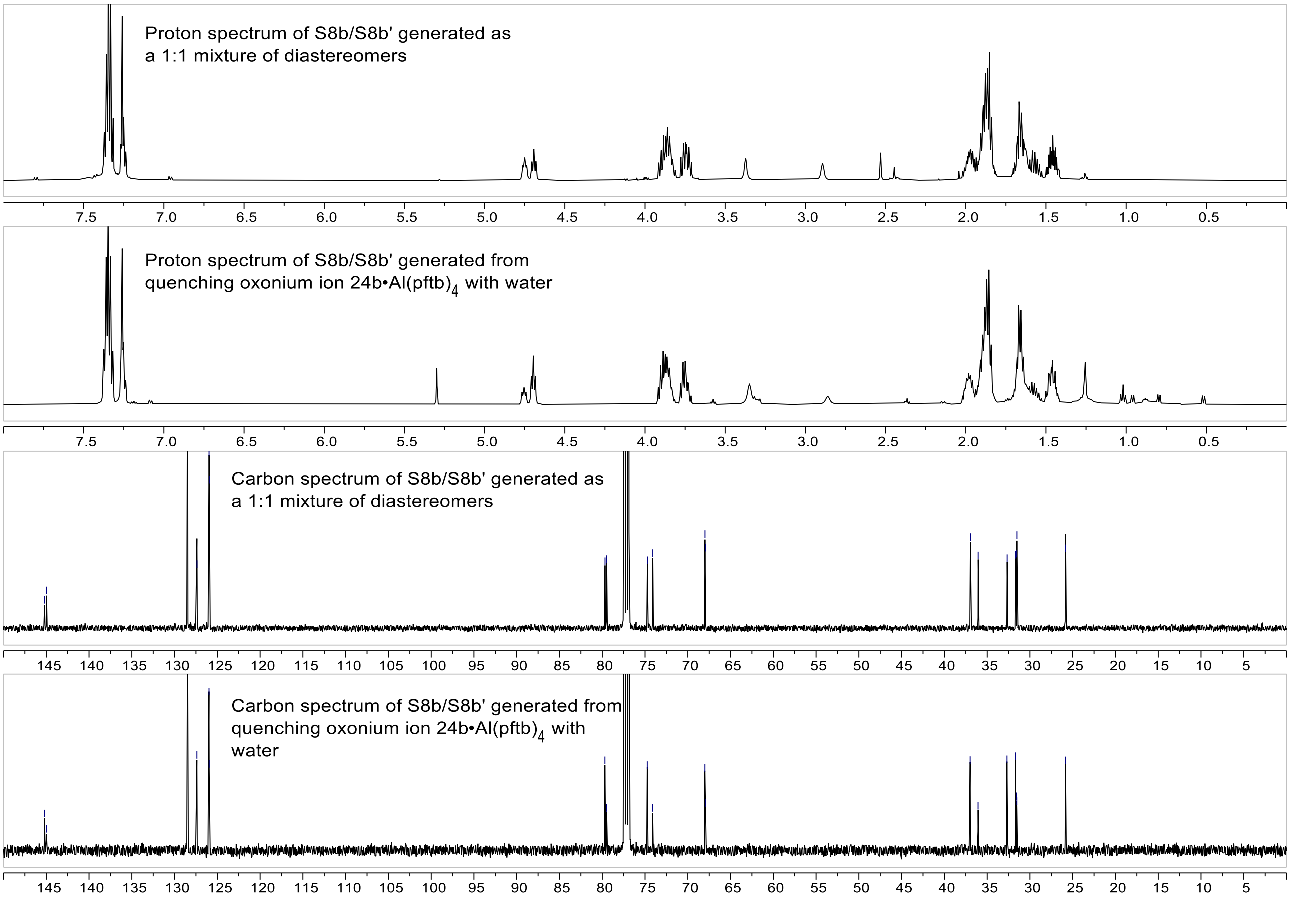
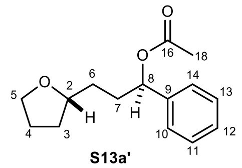
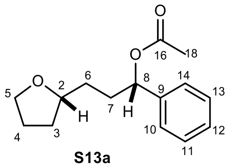


Figure S14. Comparison of ^{1}H and ^{13}C NMR spectra of **S8b/S8b'** generated as a 1:1 mixture of diastereomers and **S8b/S8b'** formed from quenching oxonium ion **24b•**Al(pftb)$_4$ with water.

(*R**)-1-phenyl-3-((*S**)-tetrahydrofuran-2-yl)propyl acetate S13a' and (*S**)-1-phenyl-3-((*S**)-tetrahydrofuran-2-yl)propyl acetate S13a



S13a'



S13a

Flash column chromatography eluent: 10% EA/Pet. Ether 40-60

R$_f$ = 0.31 (10% EA/ Pet. Ether 40-60)

Yield: 54% (6.1 mg, 66a':66a = 2:1) from 10.0 mg of **23b** and 4.6 μL of acetic acid.

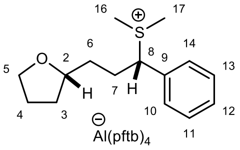
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35 – 7.31 (m, 4H, **H10**, **H11**, **H13**, **H14**), 7.30 – 7.27 (m, 1H, **H12**), 5.97 – 5.45 (m, 1H, **H8**), 3.87 – 3.80 (m, 1H, **H5'**), 3.80 – 3.74 (m, 1H, **H2**), 3.73 – 3.65 (m, 1H, **H5**), 2.08 – 2.03 (m, 3H, **H18**), 2.11 – 2.00 (m, 0.8H, **H7'**), 1.99 – 1.94 (m, 1H, **H3'**), 1.94 – 1.90 (m, 0.8H, **H7'**), 1.90 – 1.83 (m, 2H, **H4**), 1.83 – 1.76 (m, 0.8H, **H7**), 1.66 – 1.58 (m, 0.8H, **H6'**), 1.54 – 1.46 (m, 0.8H, **H6**), 1.46 – 1.36 (m, 1.8H, **H3**).

^{13}C NMR (126 MHz, CDCl$_3$) δ 170.5 (**C16**), 140.8 (**C9**), 140.7 (**C9**), 128.6 (**C11**, **C13**), 128.0 (**C12**), 126.7 (**C10**, **C14**), 126.6 (**C10**, **C14**), 79.0 (**C2**), 78.9 (**C2**), 76.2 (**C8**), 76.0 (**C8**), 67.8 (**C5**), 33.3

(**C7**), 33.2 (**C7**), 31.7 (**C6**), 31.7 (**C6**), 31.4 (**C3**), 31.4 (**C3**), 25.8 (**C4**), 25.8 (**C4**), 21.4 (**C18**).
IR (thin film, υ/cm^{-1}): 2926, 2855, 1734, 1371, 1233, 1021, 700
HRMS (ESI): Ionized as $[M+Na]^+$: Found 271.1306, *m/z* calculated for $C_{15}H_{20}O_3{}^{23}Na$ $[M+Na]^+$: 271.1305.
Comparison of ^1H and ^{13}C NMR spectrum with **S13a**, which is a single diastereomer, suggests **S13a'** and **S13** generated from the quenching of oxonium ion **24b**•Al(pftb)$_4$ with acetic acid consists of a diastereomeric mixture with an enrichment of one diastereomer over the other (*d.r.* = 2:1).

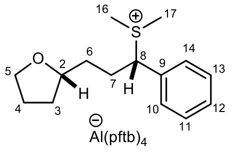
General procedure for the quenching of oxonium ion 24b•Al(pftb)$_4$ with Me$_2$S and Et$_2$S:
The oxonium ion **24b**•Al(pftb)$_4$ was generated from the chloride **23b** (1.0 eq.) and AgAl(pftb)$_4$·CH$_2$Cl$_2$ (1.0 eq.) in CD$_2$Cl$_2$ (0.7 mL) at room temperature. The solution of the oxonium ion **24b**•Al(pftb)$_4$ was then filtered into a flame dried Young's NMR tube and cooled to -20 °C. The corresponding nucleophiles (1.5 eq. Me$_2$S, 1.2 eq. Et$_2$S) were added at -20 °C. The corresponding sulfonium ions **S14**•Al(pftb)$_4$ and **S15**•Al(pftb)$_4$ were characterized by NMR spectroscopy at -20 °C, and their NMR yields were determined with reference to an electronic standard using QUANTAS. Alternatively, the oxonium ion **24b**•Al(pftb)$_4$ was generated from the chloride **23b** (1.0 eq.) and AgAl(pftb)$_4$·CH$_2$Cl$_2$ (1.0 eq.) in CH$_2$Cl$_2$ (0.05 M). The solution of the oxonium ion **24b**•Al(pftb)$_4$ was then filtered into a flame dried Young's NMR tube and the volatiles were removed under a stream of dry nitrogen followed by evacuation under reduced pressure. The residue was dissolved in CD$_2$Cl$_2$ (0.7 mL). The reason for the switch in solvent was that CH$_2$Cl$_2$ allowed for the use of extra solvent for the complete transfer of the oxonium ion **24b**•Al(pftb)$_4$ into the Young's NMR tube. The corresponding nucleophiles (0.95 eq. Me$_2$S, 0.95 eq. Et$_2$S) were then added at room temperature. The corresponding sulfonium ions **S14**•Al(pftb)$_4$, **S14'**•Al(pftb)$_4$, **S15**•Al(pftb)$_4$ and **S15'**•Al(pftb)$_4$ were then characterized by NMR spectroscopy. *See reaction monitoring section below for the variation in concentrations of each sulfonium ion species over time.*

Dimethyl((*S)-1-phenyl-3-((*S**)-tetrahydrofuran-2-yl)propyl)sulfonium tetrakis((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)oxy)aluminate S14•Al(pftb)$_4$**

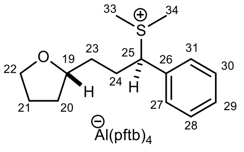


NMR Yield: 83%, using an electronic standard (QUANTAS).
^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ 7.62 – 7.53 (m, 3H, **H11**, **H12**, **H13**), 7.35 – 7.25 (m, 2H, **H10**, **H14**), 4.57 (dd, *J* = 9.3, 7.0 Hz, 1H, **H8**), 3.86 – 3.80 (m, 1H, **H2**), 3.80 – 3.75 (m, 1H, **H5'**), 3.69 (dt, *J* = 8.5, 6.8 Hz, 1H, **H5**), 2.73 (s, 3H, **H16**), 2.39 (s, 3H, **H17**), 2.39 – 2.27 (m, 2H, **H7**), 1.97 (dq, *J* = 12.1, 6.3 Hz, 1H, **H3'**), 1.84 (p, *J* = 6.8 Hz, 2H, **H4**), 1.65 (dddd, *J* = 14.1, 8.2, 5.9, 2.8 Hz, 1H, **H6'**), 1.53 (ddt, *J* = 14.4, 9.7, 7.2 Hz, 1H, **H6**), 1.39 (dq, *J* = 12.1, 8.1 Hz, 1H, **H3**).
^{13}C NMR (126 MHz, CD$_2$Cl$_2$) δ 132.0 (**C12**), 130.7 (**C11**, **C13**), 129.4 (**C10**, **C14**), 128.2 (**C9**), 77.8 (**C2**), 68.3 (**C5**), 62.5 (**C8**), 31.8 (**C3**), 31.7 (**C6**), 28.1 (**C7**), 25.8 (**C4**), 24.6 (**C16**), 22.3 (**C17**).

Dimethyl((*S**)-1-phenyl-3-((*S**)-tetrahydrofuran-2-yl)propyl)sulfonium tetrakis((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)oxy)aluminate S14•Al(pftb)$_4$ and Dimethyl((*R**)-1-phenyl-3-((*S**)-tetrahydrofuran-2-yl)propyl)sulfonium tetrakis((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)oxy)aluminate S14'•Al(pftb)$_4$



S14•Al(pftb)$_4$



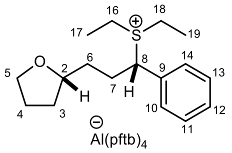
S14'•Al(pftb)$_4$

NMR Yield: Not determined. **67'**:**67** = 1.2:1

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.61 – 7.53 (m, 6.6H, **H11**, **H12**, **H13**, **H28**, **H29**, **H30**), 7.37 – 7.27 (m, 4.4H, **H10**, **H14**, **H27**, **H31**), 4.73 (dd, *J* = 10.2, 5.4 Hz, 1.2H, **H25**), 4.61 (dd, *J* = 9.1, 7.0 Hz, 1H, **H8**), 3.90 – 3.83 (m, 2.2H, **H2**, **H19**), 3.83 – 3.75 (m, 2.2H, **H5'**, **H22'**), 3.75 – 3.68 (m, 2.2H, **H5**, **H22**), 2.80 (s, 3.6H, **H33**), 2.75 (s, 3H, **H16**), 2.47 (s, 3.6H, **H34**), 2.42 (s, 3H, **H17**), 2.41 – 2.38 (m, 2H, **H7**), 2.38 – 2.33 (m, 2.4H, **H24**), 2.05 – 1.94 (m, 2.2H, **H3'**, **H20'**), 1.91 – 1.86 (m, 2H, **H4**), 1.86 – 1.79 (m, 2.4H, **H21**), 1.73 – 1.64 (m, 2.2H, **H6'**, **H23'**), 1.62 – 1.55 (m, 1H, **H6**), 1.47 – 1.39 (m, 1H, **H3**), 1.40 – 1.32 (m, 2.2H, **H20**, **H23**).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 132.5 (**C12**), 132.3 (**C29**), 131.1 (**C11**, **C13**), 131.0 (**C28**, **C30**), 129.7 (**C27**, **C31**), 129.7 (**C10**, **C14**), 129.4 (**C26**), 129.1 (**C9**), 80.0 (**C19**), 78.0 (**C2**), 68.6 (**C22**), 68.6 (**C5**), 64.0 (**C25**), 63.6 (**C8**), 32.4 (**C20**), 32.3 (**C3**), 32.1 (**C23**), 32.0 (**C6**), 30.0 (**C24**), 28.6 (**C7**), 26.1 (**C4**), 26.0 (**C21**), 25.3 (**C16**), 25.1 (**C33**), 23.5 (**C34**), 22.9 (**C17**).

Diethyl((*S**)-1-phenyl-3-((*S**)-tetrahydrofuran-2-yl)propyl)sulfonium tetrakis((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)oxy)aluminate S15•Al(pftb)$_4$

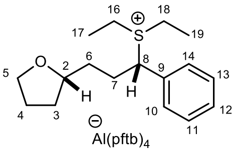


NMR Yield: 88%, using an electronic standard (QUANTAS).

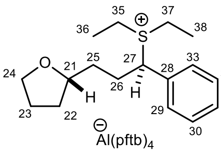
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.62 – 7.45 (m, 3H, **H11**, **H12**, **H13**), 7.39 – 7.22 (m, 2H, **H10**, **H14**), 4.60 (dd, *J* = 10.0, 6.2 Hz, 1H, **H8**), 3.84 – 3.79 (m, 1H, **H2**), 3.78 – 3.73 (m, 1H, **H5'**), 3.67 (q, *J* = 7.1 Hz, 1H, **H5**), 3.18 (dt, *J* = 15.1, 7.8 Hz, 1H, **H16'**), 3.10 (dt, *J* = 14.3, 7.2 Hz, 1H, **H16**), 2.79 (dt, *J* = 14.9, 7.5 Hz, 1H, **H18'**), 2.64 (dq, *J* = 14.5, 7.4 Hz, 1H, **H18**), 2.39 – 2.23 (m, 2H, **H7**), 1.95 (dq, *J* = 12.6, 6.5 Hz, 1H, **H3'**), 1.83 (p, *J* = 7.0 Hz, 2H, **H4**), 1.56 (t, *J* = 7.4 Hz, 4H, **H6'**, **H17**), 1.48 (ddd, *J* = 14.2, 7.1, 2.8 Hz, 1H, **H6**), 1.37 (dq, *J* = 11.9, 7.9 Hz, 1H, **H3**), 1.28 (t, *J* = 7.5 Hz, 3H, **H19**).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 131.7 (**C12**), 130.7 (**C11**, **C13**), 129.2 (**C9**), 129.1 (**C10**, **C14**), 77.5 (**C2**), 68.2 (**C5**), 58.2 (**C8**), 31.9 (**C16**), 31.7 (**C3**), 31.5 (**C6**, **C18**), 28.4 (**C7**), 25.7 (**C4**), 9.2 (**C19**), 8.6 (**C17**).

Diethyl((*S**)-1-phenyl-3-((*S**)-tetrahydrofuran-2-yl)propyl)sulfonium tetrakis((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)oxy)aluminate S15•Al(pftb)$_4$ and diethyl((*R**)-1-phenyl-3-((*S**)-tetrahydrofuran-2-yl)propyl)sulfonium tetrakis((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)oxy)aluminate S15'•Al(pftb)$_4$



S15•Al(pftb)$_4$



S15'•Al(pftb)$_4$

NMR Yield: Not determined. **68'**:**68** = 1.2:1

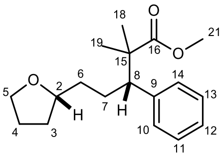
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.61 – 7.52 (m, 6.6H, **H11**, **H12**, **H13**, **H30**, **H31**, **H32**), 7.39 – 7.30 (m, 4.4H, **H10**, **H14**, **H29**, **H33**), 4.82 (dd, *J* = 11.3, 4.3 Hz, 1.2H, **H27**), 4.64 (dd, *J* = 9.6, 6.4 Hz, 1H, **H8**), 3.88 – 3.76 (m, 4.4H, **H2**, **H5'**, **H21**, **H24'**), 3.76 – 3.60 (m, 2.2H, **H5**, **H24**), 3.23 (q, *J* = 7.4 Hz, 2.4H, **H37**), 3.18 (q, *J* = 7.4 Hz, 2H, **H18**), 2.90 – 2.77 (m, 3.4H, **H16'**, **H35**), 2.77 – 2.64 (m, 1H, **H16**), 2.49 – 2.35 (m, 2H, **H7**), 2.35 – 2.21 (m, 2.4H, **H26**), 2.03 – 1.92 (m, 2.2H, **H3'**, **H22'**), 1.91 – 1.79 (m, 4.4H, **H4**, **H23**), 1.66 – 1.49 (m, 11H, **H6**, **H19**, **H25**, **H38**), 1.47 – 1.34 (m, 2.2H, **H3**, **H22**), 1.31 (t, *J* = 7.5 Hz, 3H, **H17**), 1.28 (t, *J* = 7.5 Hz, 3.6H, **H36**).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 132.2 (**C12**), 132.0 (**C31**), 131.1 (**C11**, **C13**), 131.0 (**C30**, **C32**), 130.1 (**C28**), 129.8 (**C9**), 129.6 (**C29**, **C33**), 129.4 (**C10**, **C14**), 80.2 (**C21**), 77.8 (**C2**), 68.6 (**C24**), 68.5 (**C5**), 59.7 (**C27**), 59.6 (**C8**), 33.1 (**C18**), 32.8 (**C37**), 32.5 (**C16**), 32.4 (**C35**), 32.4 (**C22**), 32.1 (**C3**), 32.1 (**C25**), 31.8 (**C6**), 30.7 (**C26**), 28.9 (**C7**), 26.1 (**C4**), 26.0 (**C23**), 9.7 (**C17**), 9.5 (**C36**), 9.3 (**C19**), 9.1 (**C38**).

General procedure for the quenching of oxonium ion 24b•Al(pftb)$_4$ with π-nucleophiles:

The oxonium ion **24b**•Al(pftb)$_4$ was generated from the chloride **23b** (1.0 eq.) and AgAl(pftb)$_4$·CH_2Cl_2 (1.0 eq.) in CH_2Cl_2 (0.05 M) at room temperature. The solution containing the oxonium ion 24•Al(pftb)$_4$b was not filtered. The solution containing the oxonium ion **24b**•Al(pftb)$_4$ was cooled to -20 °C, and cycloheptatriene (2.0 eq.) was added followed by the corresponding π-nucleophiles (equivalents specified below). The reaction mixture was then warmed to room temperature and stirred for 30 minutes unless otherwise specified. The progress of the reaction was followed by TLC analysis. The oxonium ion **24b**•Al(pftb)$_4$ manifests itself as a baseline spot on TLC (10% EA/ Pet. Ether 40-60) and the disappearance of the baseline spot was found to indicate completion of reaction. TLC analysis was also performed against the chloride starting material **23b**. The reaction mixture was then quenched with sat. aq. $NaHCO_3$ solution and excess TBAI. The aqueous layer was extracted three times with CH_2Cl_2, the organic layers were collected, dried with anhydrous $MgSO_4$, concentrated and purified by flash chromatography.

Methyl (*S**)-2,2-dimethyl-3-phenyl-5-((*R**)-tetrahydrofuran-2-yl)pentanoate S16



Flash column chromatography eluent: 10% EA/Pet. Ether 40-60 to 20% EA/Pet. Ether 40-60

R_f = 0.38 (10% EA/ Pet. Ether 40-60)

Yield: 54% (8.5 mg, *d.r.* > 10:1) from 12.0 mg of **23b**, 11.0 µL of cycloheptatriene and 22.0 µL of methyl trimethylsilyl dimethylketene acetal.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H, **H11**, **H13**), 7.23 – 7.18 (m, 1H, **H12**), 7.18 – 7.13 (m, 2H, **H10**, **H14**), 3.79 – 3.74 (m, 1H, **H5'**), 3.74 – 3.69 (m, 1H, **H2**), 3.68 – 3.64 (m, 1H, **H5**), 3.63 (s, 3H, **H21**), 2.97 (dd, *J* = 12.2, 3.0 Hz, 1H, **H8**), 1.94 (dddd, *J* = 13.4, 12.2, 10.8, 5.5 Hz, 1H, **H7'**), 1.91 – 1.84 (m, 1H, **H3'**), 1.79 (dq, *J* = 8.9, 6.6 Hz, 2H, **H4**), 1.53 (dddd, *J* = 13.5, 10.7, 5.6, 3.0 Hz, 1H, **H7**), 1.35 – 1.24 (m, 2H, **H3**, **H6'**), 1.25 – 1.17 (m, 1H, **H6**), 1.15 (s, 3H, **H19**), 1.02 (s, 3H, **H18**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.5 (**C16**), 140.2 (**C9**), 129.9 (**C10**, **C14**), 128.0 (**C11**, **C13**), 126.8 (**C12**), 79.2 (**C2**), 67.7 (**C5**), 53.2 (**C8**), 51.8 (**C21**), 46.9 (**C15**), 34.4 (**C6**), 31.5 (**C3**), 26.8 (**C7**), 25.8 (**C4**), 24.4 (**C18**), 21.0 (**C19**).

IR (thin film, *υ*/cm^{-1}): 2947, 1727, 1453, 1130

HRMS (ESI): Ionized as $[M+Na]^+$: Found 313.1775, *m/z* calculated for $C_{18}H_{26}O_3{}^{23}Na$ $[M+Na]^+$: 313.1774.

A control experiment was performed using the following procedure for the generation of a diastereomeric mixture of **S16**, where the π-nucleophile (methyl trimethylsilyl dimethylketene acetal) and cycloheptatriene were premixed with the chloride **23b** before halide abstraction with $AgAl(pftb)_4{\cdot}CH_2Cl_2$. This operation was expected to allow immediate quenching of the incipient carbocation, upon halide abstraction, by methyl trimethylsilyl dimethylketene acetal. Therefore, no significant diastereoselectivity was expected. Indeed, the **S16** generated by this method was found to be a 1:1.4 diastereomeric mixture, as opposed to the highly diastereoselective result obtained (d.r. ~ 10:1) by the procedure where the oxonium ion **24b•**$Al(pftb)_4$ was explicitly generated before the addition of the π-nucleophiles.

Procedure for the generation of a diastereomeric mixture of S16: The chloride **23b** (10.0 mg, 0.044 mmol) was mixed with cycloheptatriene (9.2 µL, 0.088 mmol) and methyl trimethylsilyl dimethylketene acetal (18.0 µL, 0.088 mmol) in dry CH_2Cl_2 (1.1 mL). To this mixture was added $AgAl(pftb)_4{\cdot}CH_2Cl_2$ (51.0 mg, 0.044 mmol) at -20 °C and warmed to room temperature. TLC analysis at this stage suggested the complete consumption of starting materials. The reaction was quenched with sat. aq. $NaHCO_3$ and excess TBAI. The aqueous layer was extracted with CH_2Cl_2 three times and the organic layers were collected, concentrated, and the residue was purified by flash column chromatography (20% EA/ Pet. Ether 40-60) to give **S16** (68%, 0.030 mmol, *d.r.* = 1:1) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H, **H11**, **H13**), 7.23 – 7.18 (m, 1H, **H12**), 7.17 – 7.13 (m, 2H, **H10**, **H14**), 3.82 – 3.74 (m, 1H, **H5'**), 3.74 – 3.69 (m, 1H, **H2**), 3.69 – 3.64 (m, 1H, **H5**), 3.65 – 3.59 (m, 3H, **H21**), 2.98 – 2.96 (m, 0.4H, **H8**), , 2.96 – 2.91 (m, 0.6H, **H8**), 1.99 – 1.92 (m, 0.4H, **H7'**), 1.91 – 1.84 (m, 1H, **H3'**), 1.83 – 1.77 (m, 2H, **H4**), 1.77 – 1.72 (m, 0.6H, **H7'**), 1.68 (tdd, *J* = 13.4, 5.6, 3.3 Hz, 0.6H, **H7**), 1.53 (dddd, *J* = 13.5, 10.7, 5.6, 3.0 Hz, 0.4H, **H7**), 1.38 – 1.33 (m, 0.6H, **H6'**), 1.33 – 1.26 (m, 1.4H, **H3**, **H6'**), 1.26 – 1.18 (m, 1H, **H6**), 1.18 – 1.12 (m, 3H, **H18**), 1.05 – 0.99 (m, 3H, **H19**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.5 (**C16**), 178.3 (**C16**), 140.4 (**C9**), 140.2 (**C9**), 129.9 (**C14**), 129.8 (**C14**), 128.0 (**C13**), 128.0 (**C13**), 126.8 (**C12**), 126.8 (**C12**), 79.5 (**C2**), 79.2 (**C2**), 67.7 (**C5**), 67.7 (**C5**), 53.2 (**C8**), 53.2 (**C8**), 51.8 (**C21**), 46.9 (**C15**), 46.9 (**C15**), 34.4 (**C6**), 34.4 (**C6**), 31.4 (**C3**), 31.4 (**C3**), 26.9 (**C7**), 26.8 (**C7**), 25.8 (**C4**), 25.7 (**C4**), 24.4 (**C19**), 24.3 (**C19**), 21.3 (**C18**), 21.0 (**C18**).
A comparison between the ^{1}H and ^{13}C NMR spectra of the **S16** generated by the two different methods further supports the **S16** generated through the explicitly generated oxonium ion is enriched in one diastereomer over the other by ca. 10:1 (**Figure S15**).

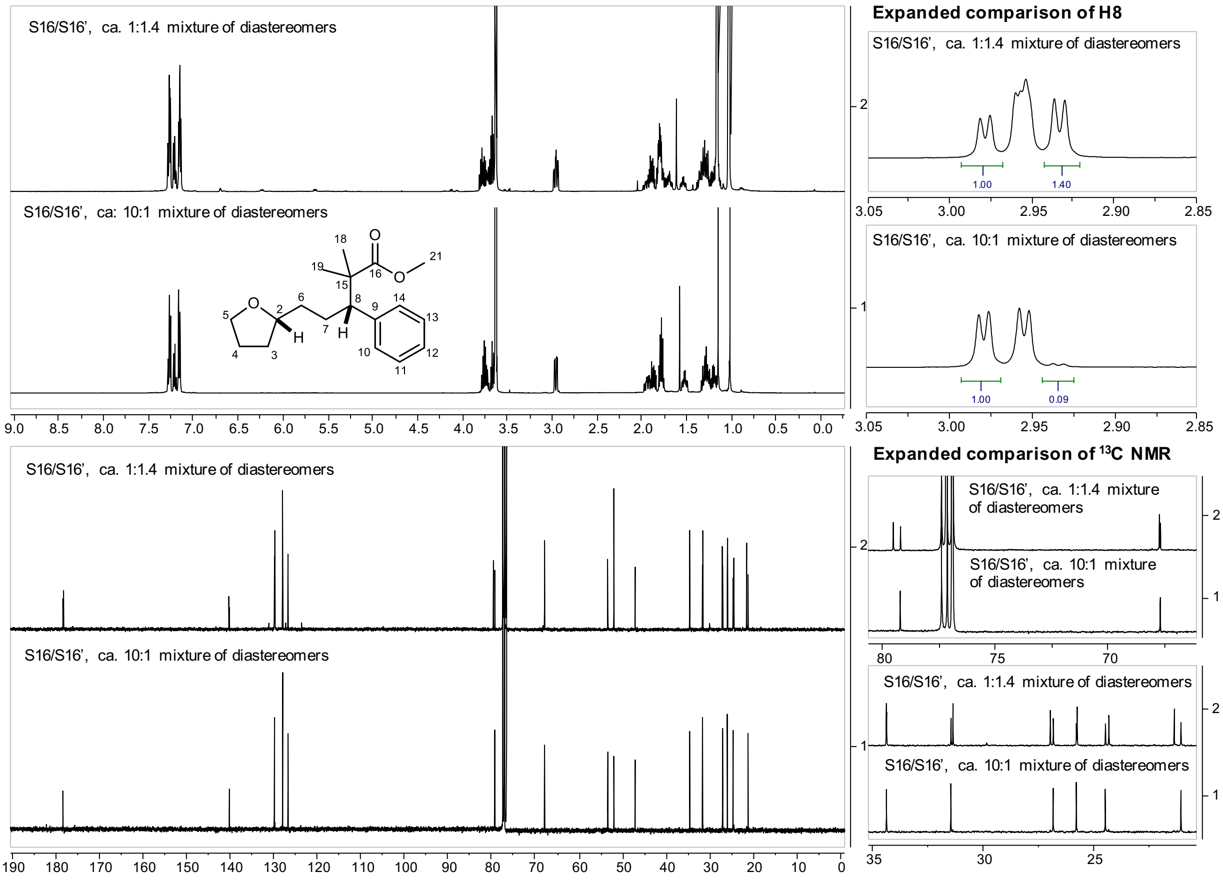
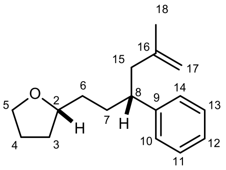


Figure S15. Comparison of ^{1}H and ^{13}C NMR spectra of **S16/S16'** generated by two different methods.

(*R**)-2-((*R**)-5-methyl-3-phenylhex-5-en-1-yl)tetrahydrofuran S17



Flash column chromatography eluent: 5% EA/Pet. Ether 40-60

R$_f$ = 0.34 (10% EA/ Pet. Ether 40-60)

Yield: 66% (10.0 mg, *d.r.* ~ 3:1) from 14.0 mg of **23b**, 13.0 µL of cycloheptatriene and 0.11 mL of methallyltrimethylsilane.

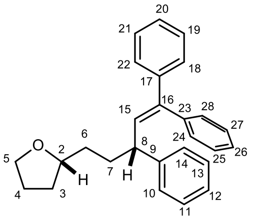
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 2H, **H11**, **H13**), 7.19 – 7.10 (m, 3H, **H10**, **H12**, **H14**), 4.68 – 4.52 (m, 2H, **H17**), 3.84 – 3.75 (m, 1H, **H5'**), 3.75 – 3.70 (m, 1H, **H2**), 3.70 – 3.62 (m, 1H, **H5**), 2.80 – 2.65 (m, 1H, **H8**), 2.41 – 2.22 (m, 2H, **H15**), 1.96 – 1.86 (m, 1H, **H3'**), 1.86 – 1.76 (m, 2.3H, **H4**, **H7'**), 1.73 – 1.61 (m, 4.4H, **H7'**, **H18**), 1.56 – 1.48 (m, 0.3H, **H7**), 1.48 – 1.42 (m, 0.3H, **H6'**), 1.42 – 1.27 (m, 2.4H, **H3**, **H6'**), 1.27 – 1.18 (m, 0.3H, **H6**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5 (**C9**), 145.4 (**C9**), 144.0 (**C16**), 144.0 (**C16**), 128.4 (**C11**, **C13**), 127.8 (**C10**, **C14**), 126.1 (**C12**), 112.2 (**C17**), 79.7 (**C2**), 79.4 (**C2**), 67.7 (**C5**), 67.7 (**C5**), 45.7 (**C15**), 44.3 (**C8**), 44.1 (**C8**), 34.0 (**C6**), 33.7 (**C6**), 33.3 (**C7**), 32.8 (**C7**), 31.5 (**C3**), 31.4 (**C3**), 25.8 (**C4**), 25.8 (**C4**), 22.5 (**C18**).

IR (thin film, *υ*/cm^{-1}): 2930, 1452, 1030

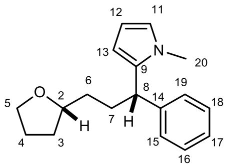
HRMS (ESI): Ionized as $[M+H]^+$: Found 245.1902, *m/z* calculated for $C_{17}H_{25}O$ $[M+H]^+$: 245.1900.

(*R**)-2-((*R**)-3,5,5-triphenylpent-4-en-1-yl)tetrahydrofuran S18



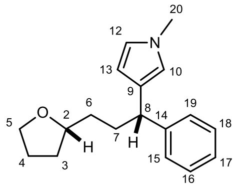
Flash column chromatography eluent: 2% EA/Pet. Ether 40-60 to 5% EA/Pet. Ether 40-60
R_f = 0.53 (10% EA/ Pet. Ether 40-60)
Yield: 64% (15.4 mg, *d.r.* ~ 2:1) from 14.6 mg of **23b**, 13.0 µL of cycloheptatriene and 0.12 mL of 1,1-diphenylethene.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 1H, **H25**, **H27**), 7.36 – 7.32 (m, 1H, **H26**), 7.32 – 7.27 (m, 2H, **H11**, **H13**), 7.27 – 7.24 (m, 2H, **H19**, **H21**), 7.24 – 7.21 (m, 3H, **H12**, **H18**, **H22**), 7.21 – 7.17 (m, 3H, **H10**, **H14**, **H20**), 7.16 – 7.13 (m, 2H, **H24**, **H28**), 6.25 (d, *J* = 10.4 Hz, 1H, **H15**), 3.86 – 3.78 (m, 1H, **H5'**), 3.74 – 3.63 (m, 2H, **H2**, **H5**), 3.40 (ddd, *J* = 10.6, 8.4, 6.3 Hz, 1H, **H8**), 1.94 – 1.89 (m, 1H, **H3'**), 1.89 – 1.86 (m, 1H, **H7'**), 1.86 – 1.77 (m, 2H, **H4**), 1.77 – 1.69 (m, 1H, **H7**), 1.68 – 1.56 (m, 0.7H, **H6'**), 1.55 – 1.46 (m, 0.3H, **H6'**), 1.46 – 1.39 (m, 0.3H, **H6**), 1.39 – 1.32 (m, 1H, **H3**), 1.32 – 1.26 (m, 0.7H, **H6**).
^{13}C NMR (126 MHz, $CDCl_3$) δ 145.4 (**C16**), 145.3 (**C16**), 142.5 (**C17**), 141.4 (**C9**), 140.2 (**C23**), 140.2 (**C23**), 133.0 (**C15**), 130.1 (**C24**, **C28**), 128.7 (**C11**, **C13**), 128.7 (**C11**, **C13**), 128.3 (**C25**, **C27**), 128.2 (**C19**, **C21**), 127.5 (**C14**, **C10**), 127.4 (**C22**, **C18**), 127.4 (**C12**), 127.2 (**C26**), 127.1 (**C26**), 126.2 (**C20**), 79.4 (**C2**), 79.4 (**C2**), 67.7 (**C5**), 45.5 (**C8**), 45.5 (**C8**), 34.3 (**C7**), 34.1 (**C7**), 33.7 (**C6**), 33.7 (**C6**), 31.4 (**C3**), 31.4 (**C3**), 25.8 (**C4**), 25.8 (**C4**).
IR (thin film, *υ*/cm^{-1}): 2937, 1492, 1030
HRMS (ESI): Ionized as $[M+H]^+$: Found 369.2214, *m/z* calculated for $C_{27}H_{29}O$ $[M+H]^+$: 369.2213.

1-Methyl-2-((*S**)-1-phenyl-3-((*R**)-tetrahydrofuran-2-yl)propyl)-1*H*-pyrrole S19a



Flash column chromatography eluent: 10% EA/Pet. Ether 40-60 to 20% EA/Pet. Ether 40-60
R_f = 0.28 (10% EA/ Pet. Ether 40-60)
Yield: 66% (10.1 mg, **72a**:**72b** = 1.6:1, separable by flash column chromatography) from 12.8 mg of **23b**, 12.0 µL of cycloheptatriene and 10.0 µL of *N*-methylpyrrole.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 2H, **H16**, **H18**), 7.17 – 7.13 (m, 1H, **H17**), 7.12 – 7.08 (m, 2H, **H15**, **H19**), 6.51 (dd, *J* = 3.1, 1.5 Hz, 1H, **H11**), 6.15 (dd, *J* = 3.0, 1.5 Hz, 1H, **H13**), 6.10 (t, *J* = 3.1 Hz, 1H, **H12**), 3.86 – 3.82 (m, 1H, **H8**), 3.82 – 3.80 (m, 1H, **H5'**), 3.80 – 3.76 (m, 1H, **H2**), 3.68 (td, *J* = 8.0, 6.5 Hz, 1H, **H5**), 3.29 (s, 3H, **H20**), 2.08 (dddd, *J* = 12.5, 10.9, 7.0, 5.4 Hz, 1H, **H7'**), 2.01 (ddt, *J* = 10.7, 5.2, 2.8 Hz, 1H, **H7**), 1.98 – 1.92 (m, 1H, **H3'**), 1.89 – 1.80 (m, 2H, **H4**), 1.62 – 1.55 (m, 1H, **H6'**), 1.55 – 1.47 (m, 1H, **H6**), 1.42 (dq, *J* = 11.9, 7.9 Hz, 1H, **H3**).
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.1 (**C14**), 135.6 (**C9**), 128.6 (**C16**, **C18**), 128.1 (**C15**, **C19**), 126.3 (**C17**), 121.7 (**C11**), 106.4 (**C12**), 105.8 (**C13**), 79.5 (**C2**), 67.7 (**C5**), 43.8 (**C8**), 34.3 (**C6**), 34.0 (**C20**), 33.4 (**C7**), 31.5 (**C3**), 25.8 (**C4**).
IR (thin film, *υ*/cm^{-1}): 2945, 1690, 1491, 1260, 1067, 1030
HRMS (ESI): Ionized as $[M+H]^+$: Found 270.1854, *m/z* calculated for $C_{18}H_{24}ON$ $[M+H]^+$: 270.1852.

1-Methyl-3-((S*)-1-phenyl-3-((R*)-tetrahydrofuran-2-yl)propyl)-1*H*-pyrrole S19b

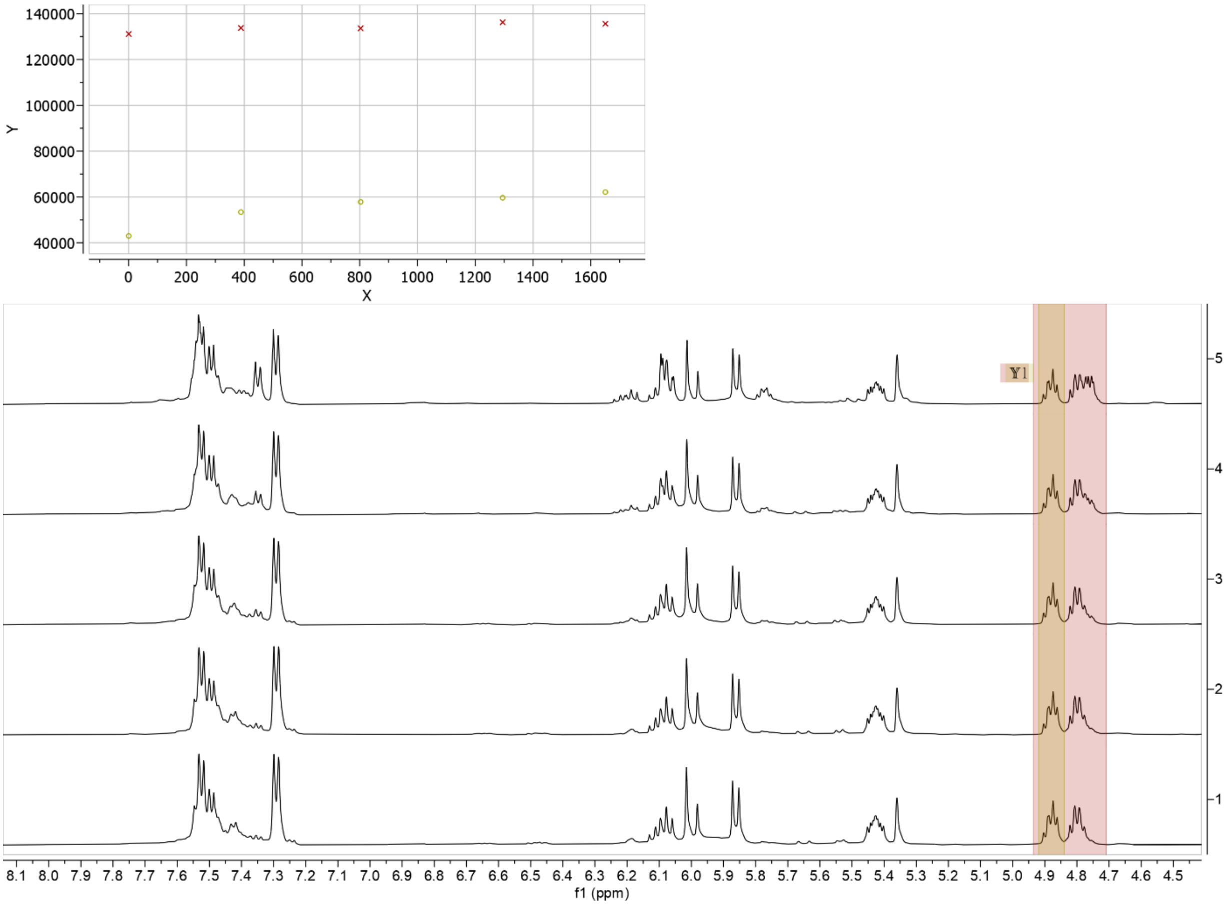


Flash column chromatography eluent: 10% EA/Pet. Ether 40-60 to 20% EA/Pet. Ether 40-60
$\mathbf{R_f}$ = 0.25 (10% EA/ Pet. Ether 40-60)
Yield: 66% (10.1 mg, **S19a**:**S19b** = 1.6:1, separable by flash column chromatography) from 12.8 mg of **23b**, 12.0 μL of cycloheptatriene and 10.0 μL of *N*-methylpyrrole.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (m, 4H, **H15**, **H16**, **H18**, **H19**), 7.15 (m, 1H, **H17**), 6.49 (t, *J* = 2.5 Hz, 1H, **H12**), 6.34 (t, *J* = 2.1 Hz, 1H, **H10**), 5.97 (t, *J* = 2.5 Hz, 1H, **H13**), 3.85 – 3.79 (m, 1H, **H5'**), 3.82 – 3.76 (m, 1H, **H2**), 3.75 (d, *J* = 7.8 Hz, 1H, **H8**), 3.68 (td, *J* = 7.9, 6.4 Hz, 1H, **H5**), 3.56 (s, 3H, **H20**), 2.07 – 1.96 (m, 2H, **H7**), 1.94 (dddd, *J* = 11.6, 8.4, 6.4, 4.9 Hz, 1H, **H3'**), 1.88 – 1.78 (m, 2H, **H4**), 1.54 – 1.43 (m, 2H, **H6**), 1.41 (ddt, *J* = 11.9, 8.7, 7.7 Hz, 1H, **H3**).
IR (thin film, υ/cm^{-1}): 2928, 1686, 1452, 1260, 1066, 1024
HRMS (ESI): Ionized as $[M+H]^+$: Found 270.1855, *m/z* calculated for $C_{18}H_{24}ON$ $[M+H]^+$: 270.1852.

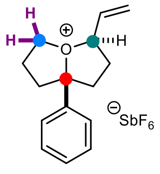
10) Data for stereochemical equilibration and kinetic isotopic effect experiments:

NMR monitoring of the conversion of 24m’•SbF$_6$ to 24m•SbF$_6$ at 0°C Figure S16, Figure S17:

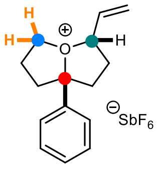
Data selection:



ARR_DATA(I)	Y(X)	Y1(X)	Y2(X)	Y3(X)
1651	135471	62862.1	125724.2	9746.8
1295	136118	59729.4	119458.8	16659.2
803	133588	58225.5	116451	17137
389	133779	53977.6	107955.2	25823.8
0	131108	43342.9	86685.8	44422.2



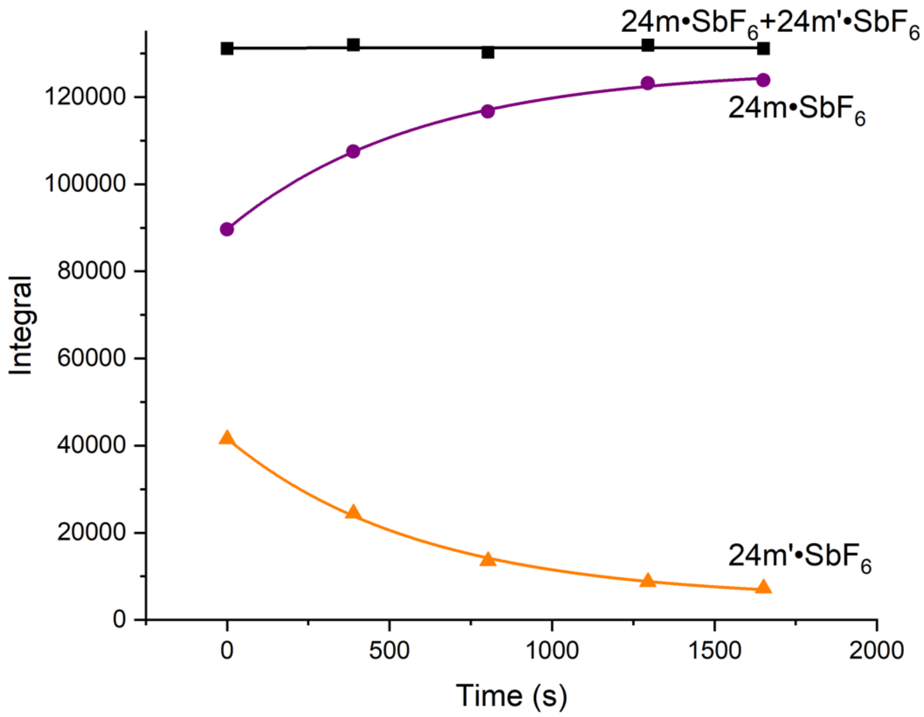
24m•SbF$_6$



24m'•SbF$_6$

Figure S16. Data selection for NMR monitoring of the conversion of **24m’**•SbF$_6$ to **24m**•SbF$_6$ at 0°C. Y(X) = Total integral; Y1(X) = Integral of one purple C–H resonance of **24m**•SbF$_6$; Y2(X) = Total integral of **24m**•SbF$_6$; Y3(X) = Total integral of **24m’**•SbF$_6$. Derivation of total integrals of **24m**•SbF$_6$ and **24m’**•SbF$_6$: Y1(X)*2 = Total Integral of **24m**•SbF$_6$; Y(X) – Total Integral of **24m**•SbF$_6$ = Total Integral of **24m’**•SbF$_6$

Plotting Y(X) (**24m**•SbF$_6$+**24m'**•SbF$_6$), Y(2)X (**24m**•SbF$_6$), and Y(3)X (**24m'**•SbF$_6$) against time:



Exponential form of first-order kinetic equation from best fit of the decay of **24m'**•SbF$_6$:

$$[A] = 10889 + 33366e^{-0.0019864t}$$

Reaction half-life = $\frac{0.693}{0.0019864}$ = 349 s, 5.82 minutes.

Experimental reaction barrier from Eyring equation:

$$k = \frac{\kappa k_B T}{h} e^{\frac{-\Delta G^{\ddagger}}{RT}}$$

$$0.0019864 = \frac{(1)(1.381 \times 10^{-23})(273)}{6.626 \times 10^{-34}} e^{\frac{-\Delta G^{\ddagger}}{(8.314)(273)}}$$

$$0.0019864 = (5.69 \times 10^{12}) e^{\frac{-\Delta G^{\ddagger}}{(8.314)(273)}}$$

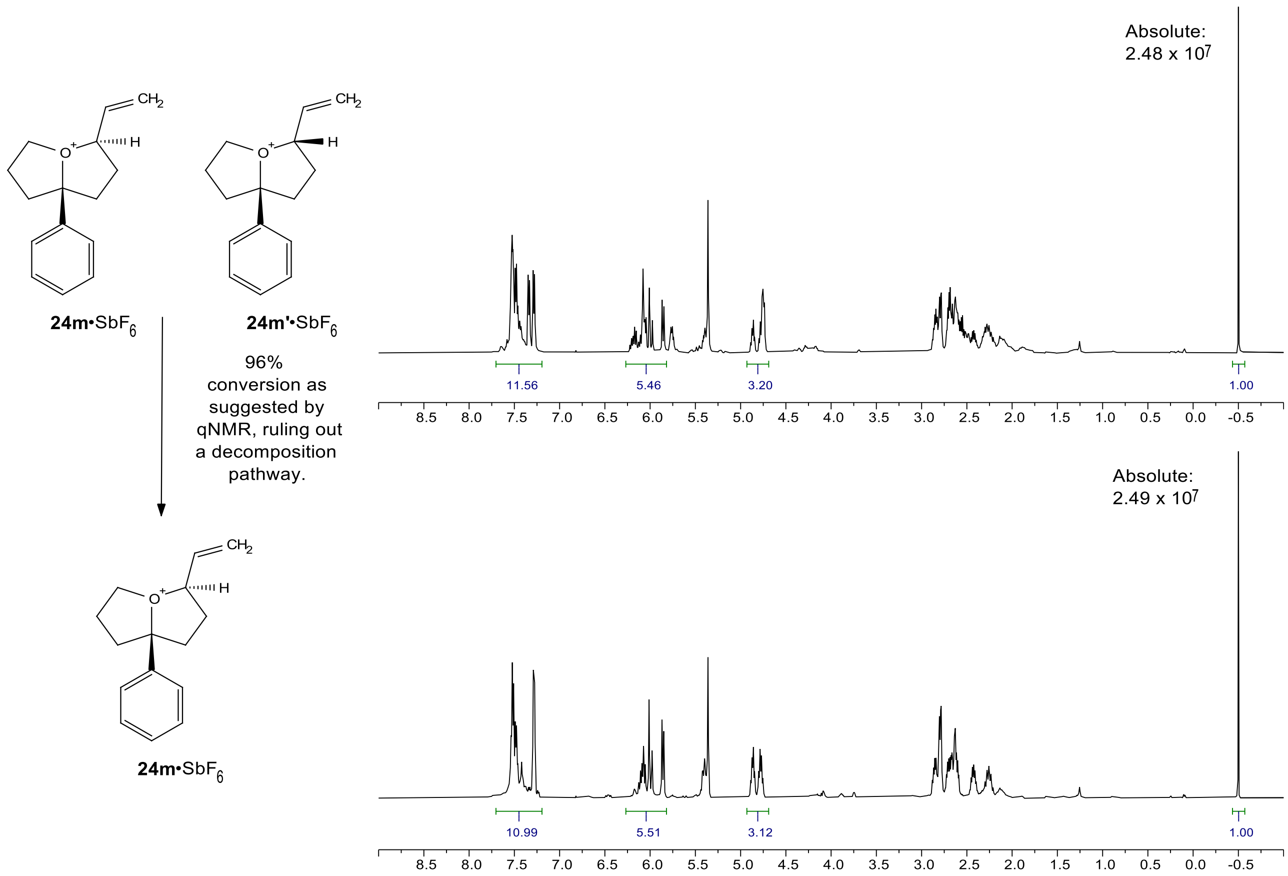
$$0.0019864 = (5.69 \times 10^{12}) e^{\frac{-\Delta G^{\ddagger}}{(8.314)(273)}}$$

$$3.49 \times 10^{-16} = e^{\frac{-\Delta G^{\ddagger}}{(8.314)(273)}}$$

$$-35.6 = \frac{-\Delta G^{\ddagger}}{(8.314)(273)}$$

$$-35.6 = \frac{-\Delta G^{\ddagger}}{(8.314)(273)}$$

$$\Delta G = 19.3\ kcal\ mol^{-1}$$



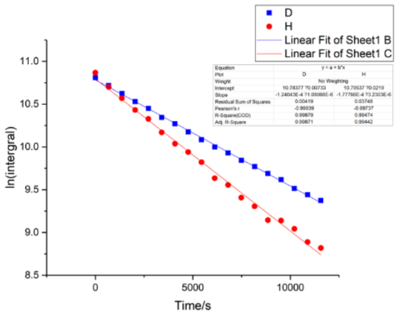
24m•SbF_6 **24m'**•SbF_6

96% conversion as suggested by qNMR, ruling out a decomposition pathway.

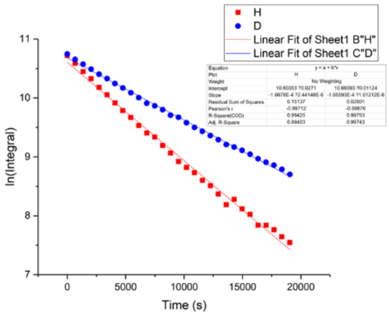
24m•SbF_6

Figure S17. qNMR experiment rules out decomposition pathway (Note: This is a separate experiment from the kinetics experiment as described above.)

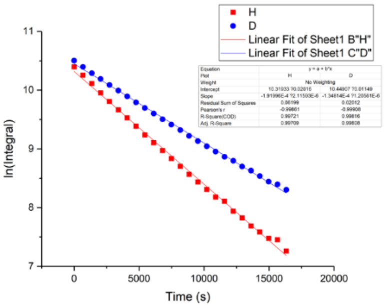
Kinetic isotope effect of intramolecular hydride transfer of oxonium ion 24f•Al(pftb)$_4$:*



Equation	y = a + b*x	
Plot	D	H
Weight	No Weighting	
Intercept	10.78377 ?0.00733	10.79537 ?0.0219
Slope	-1.24043E-4 ?1.08068E-6	-1.77766E-4 ?3.2303E-6
Residual Sum of Squares	0.00419	0.03748
Pearson's r	-0.99939	-0.99737
R-Square(COD)	0.99879	0.99474
Adj. R-Square	0.99871	0.99442



Equation	y = a + b*x	
Plot	H	D
Weight	No Weighting	
Intercept	10.60353 ?0.0271	10.68093 ?0.01124
Slope	-1.6678E-4 ?2.44148E-6	-1.05593E-4 ?1.01212E-6
Residual Sum of Squares	0.15137	0.02601
Pearson's r	-0.99712	-0.99876
R-Square(COD)	0.99425	0.99753
Adj. R-Square	0.99403	0.99743



Equation	y = a + b*x	
Plot	H	D
Weight	No Weighting	
Intercept	10.31933 ?0.02016	10.44907 ?0.01149
Slope	-1.91996E-4 ?2.11593E-6	-1.34814E-4 ?1.20561E-6
Residual Sum of Squares	0.06199	0.02012
Pearson's r	-0.99861	-0.99908
R-Square(COD)	0.99721	0.99816
Adj. R-Square	0.99709	0.99808

1st	H	D
k (x10^{-4} s$^{-1)}$	1.778	1.240
KIE	1.434	

2nd	H	D
k (x10^{-4} s$^{-1)}$	1.668	1.056
KIE	1.580	

3rd	H	D
k (x10^{-4} s$^{-1)}$	1.920	1.348
KIE	1.424	

Average KIE: 1.479 ± 0.071

* the error in the KIE (±0.071) represents the standard deviation of the 3 measurements.

1) Computational methods

Density functional theory (DFT) calculations were performed with Gaussian 16, Rev. C.01 and conformational analyses were performed with CREST.[15, 16]

Workflow for oxonium ^{13}C and ^{1}H NMR prediction: Conformers were generated with CREST at the GFN2-xTB level of theory[17] with GBSA solvation. Those within 6 kcal/mol of the global minimum were then optimized at the B3LYP/6-31+G(d,p) level of theory.[18-22] Frequency calculations were performed to confirm these structures were minima and to evaluate Gibbs energies at 298K. M06-2X/6-311+G(2d,p) single-point energies[23] were then evaluated. Isotropic shielding tensors were computed with gauge including atomic orbitals (GIAO) at the mPW1PW91/6-311+G(2d,p) level of theory[24] with PCM solvation (dichloromethane).[25] ^{13}C and ^{1}H NMR isotropic chemical shifts were obtained from the shielding tensors using scaling factors reported by Tantillo (slope = −1.0710 for ^{1}H and −1.0462 for ^{13}C; intercept= 31.8217 for ^{1}H and 186.7538 for ^{13}C) available from the cheshirenmr.info website.[26] For symmetry-related, non-diastereotopic protons, computed values were averaged before comparison with experimental data. Boltzmann-weighting was performed to account for conformational flexibility. Mean absolute deviations (MADs) were determined between experimental and computed chemical shifts for each set of carbon and proton chemical shifts. For this comparison, we only used atoms in the bicyclic framework (i.e. ^{1}H and ^{13}C NMR chemical shifts of the ring protons and carbons), since predictions of alkene vs. alkyne vs. aromatic environments introduce different systematic errors. This workflow (B3LYP optimization, M06-2X single-point energies, mPW1PW91 chemical shifts) implements the best-in-class methods recommended by Goodman for computational elucidation of relative configuration.[27] Computed chemical shifts at the mPW1PW91/6-311+G(2d,p)//B3LYP/6-31+G(d,p) level of theory were recently applied to assign the relative stereochemistry of various oxonium ions, with a mean absolute deviation (MAD) with respect to experimental spectra of 1.4-1.8 ppm (^{13}C) and 0.13-0.15 ppm (^{1}H), sufficient to distinguish diastereomeric structures.[28]

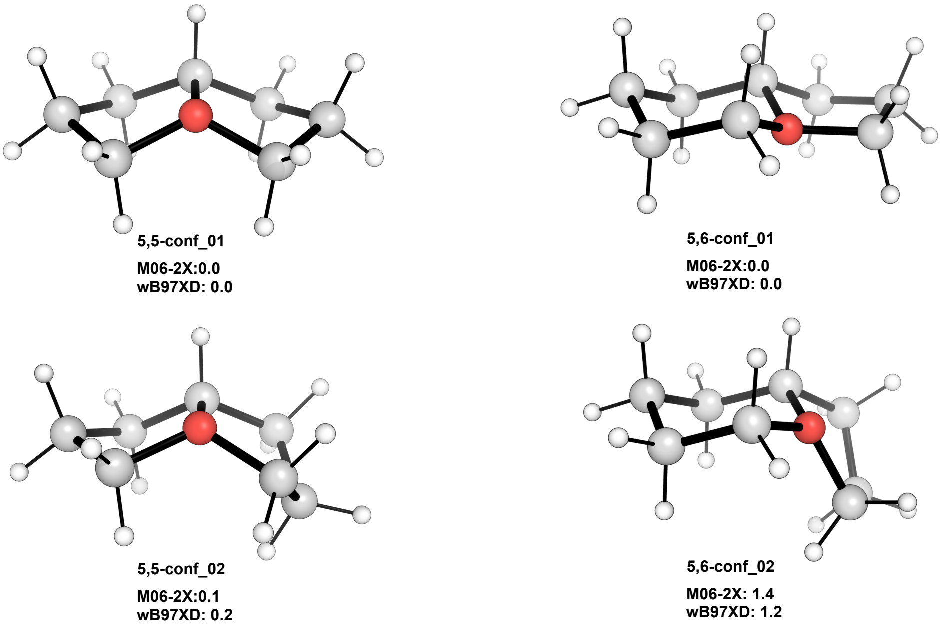
Workflow for mechanistic evaluation: Ground and transition state structures were optimized at the B3LYP/6-31+G(d,p) level of theory and confirmed by vibrational analyses. M06-2X/def2-TZVP and wB97XD/def2-TZVP single point energies were evaluated with SMD solvation (dichloromethane). Single point corrected Gibbs free energies were evaluated for all species at 298 K with *GoodVibes* 3.0.1.[29] A quasi-harmonic treatment was applied (frequency cut-off of 100 cm^{-1}) to vibrational entropies. Predicted kinetic isotope effects were computed without scaling vibrational frequencies using the Bigeleisen-Mayer equation and a Bell correction for tunnelling implemented with the *Kinisot* package**.**[30]

2) Conformational analysis of bicyclic oxonium ions

Conformers of the parent 5,5- and 5,6-bicyclic oxoniums:[*]

In our computational studies, we found that all 5,5-fused bicyclic oxonium ions adopt 5,5-*cis* fused conformations (shown for unsubstituted systems in **Figure S18**). There are two low-energy *cis*-fused conformations (conf_01 and conf_02) that differ by the pucker of one of the five-membered rings. These conformers are similar in stability. 5,5-*trans* fused structures are not energy minima: upon geometry optimization they spontaneously undergo inversion at oxygen to form 5,5-*cis* fused bicyclic structures.

In contrast, we found that 5,6-fused bicyclic oxonium ions universally favor a 5,6-*trans* fused conformation (i.e., over *5,6-cis*). The trans-fused conformer is more stable by > 1 kcal/mol.



5,5-conf_01
M06-2X:0.0
wB97XD: 0.0

5,6-conf_01
M06-2X:0.0
wB97XD: 0.0

5,5-conf_02
M06-2X:0.1
wB97XD: 0.2

5,6-conf_02
M06-2X: 1.4
wB97XD: 1.2

Figure S18. Most important conformations of 5,5- and 5,6-fused bicyclic oxonium ions. M06-2X/def2-TZVP//B3LYP/6-31+G(d,p) and wB97XD/def2-TZVP//B3LYP/6-31+G(d,p) relative Gibbs energies in dichloromethane (kcal/mol).

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[*] the [3.3.0]-bicyclic oxonium ions and the [4.3.0]-bicyclic oxonium ions are referred to as the 5,5- and 6.5-bicylic oxonium ions in this section of the document.

Representative conformers of substituted 5,5-bicyclic oxoniums:

We have studied the conformations of 5,5-fused bicyclic oxoniums with an exocyclic substituent (e.g., a vinyl group in diastereomers **24a** and **24a’** shown in **Figure S19**. As above, there are no stable *trans*-fused conformers for these species - upon geometry optimization they spontaneously undergo inversion at oxygen to form 5,5-*cis* fused bicyclic structures. For **24a**, there are two main conformers of similar energy. **24a’**, the diastereomer of **24a**, is less stable by around 2 kcal/mol, and there are three main conformations present.

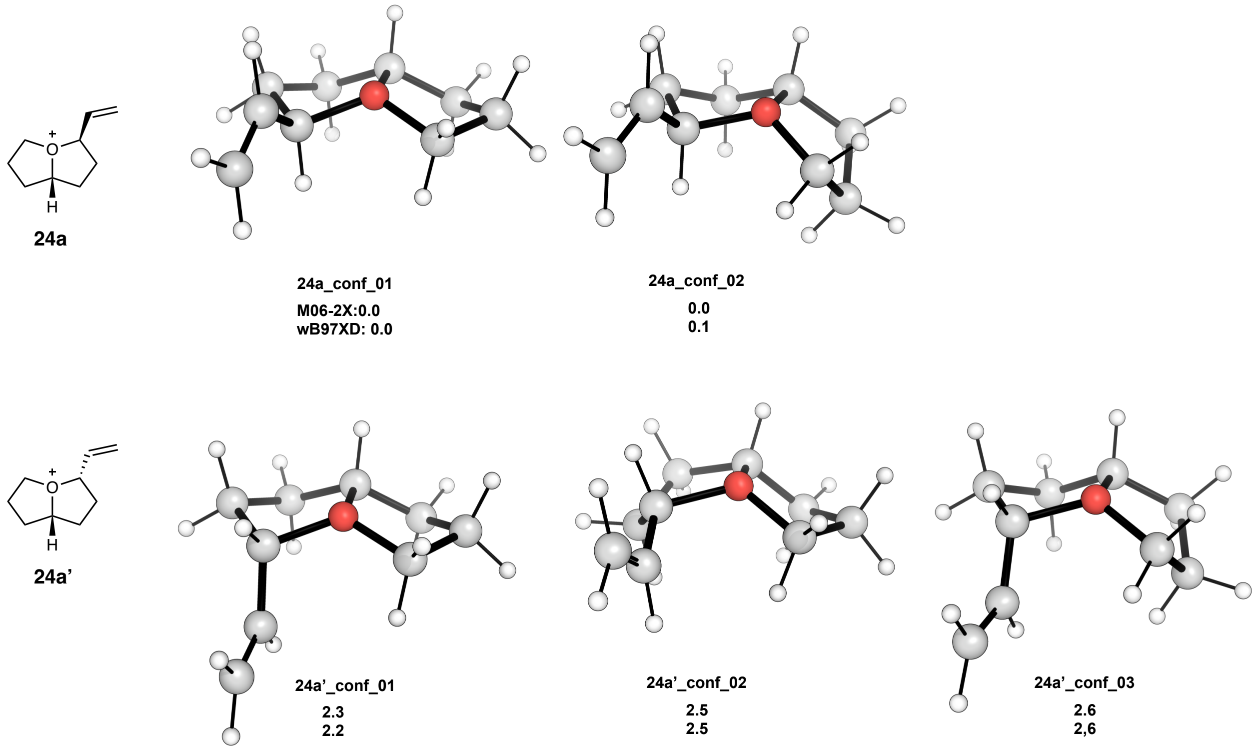


Figure S19. Low energy conformations of 5,5-fused bicyclic oxonium **24a**/**24a’**. M06-2X/def2-TZVP//B3LYP/6-31+G(d,p) and wB97XD/def2-TZVP//B3LYP/6-31+G(d,p) relative Gibbs energies in dichloromethane (kcal/mol).

Representative conformers of substituted 5,6-bicyclic oxoniums:

In our studies 5,6-fused bicyclic oxonium ions universally favor the 5,6-*trans* fused (i.e., over *5,6-cis*) conformation by 1.4 – 2.4 kcal/mol. For vinyl-substituted **24e** (**Figure S20**), there is a strong preference for a single conformation in which the substituent occupies an equatorial position on the chair-shaped 6-membered ring, which is *trans*-fused. Diastereomer **24e'**, is less stable by around 1 kcal/mol: the vinyl substituent is axial in the most stable conformer, while there is a second conformer a further 2 kcal/mol higher in energy in which the 6-membered ring adopts a twist-boat conformation.

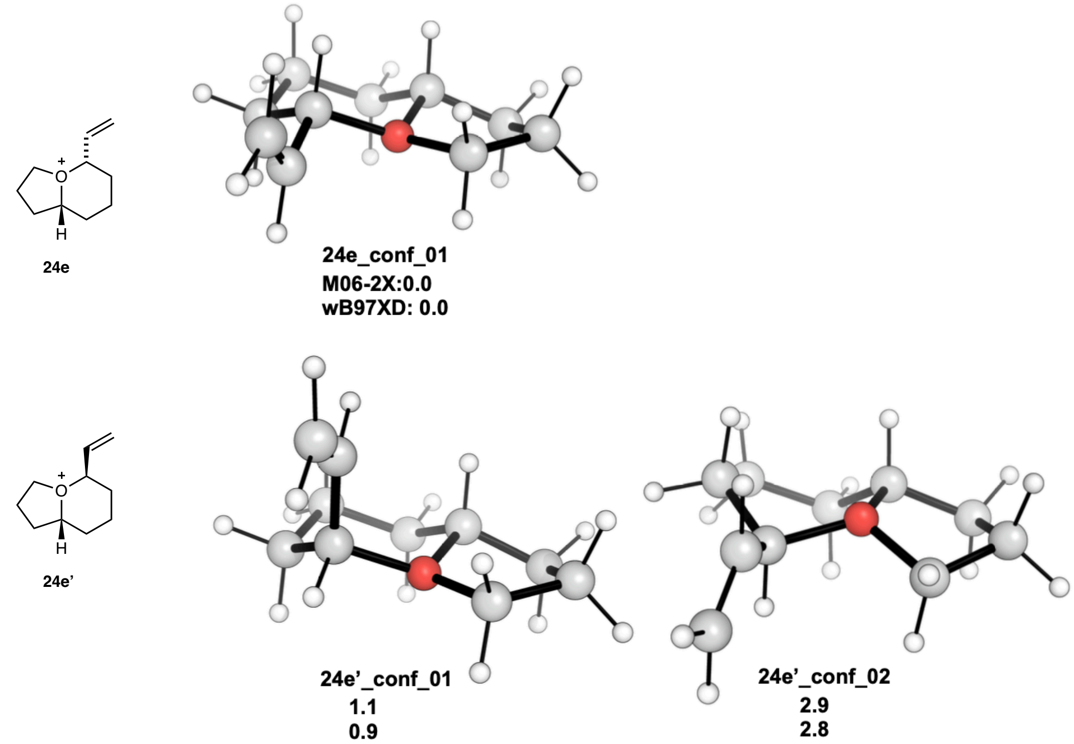
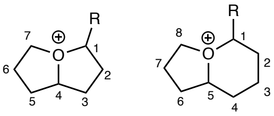


Figure S20. Low energy conformations of 5,6-fused bicyclic oxonium **24e**/**24e'**. M06-2X/def2-TZVP//B3LYP/6-31+G(d,p) and wB97XD/def2-TZVP//B3LYP/6-31+G(d,p) relative Gibbs energies in dichloromethane (kcal/mol).

3) ^{13}C and ^{1}H NMR predictions for bicyclic oxonium ions

In previous computational NMR studies of oxonium ions, MAD values wrt experiment for correct structural assignments were 1.4-1.8 ppm (^{13}C) and 0.13-0.15 ppm (^{1}H). In each case below, we compare two computed diastereomeric structures against an experimental spectrum using the ^{1}H and ^{13}C NMR chemical shifts of the ring protons and carbons to confirm the relative stereochemical assignment. Cheshire scaling parameters were applied to ^{13}C (Slope: -1.0462; Intercept: 186.7538) and ^{1}H (Slope: -1.0710; Intercept: 31.8217) computed isotropic shielding tensors. In the vast majority of cases, the MAE values for both nuclei pointed to the same stereochemical assignment. For **24i**, computed ^{13}C and ^{1}H spectra suggest **24i** matches the experimental chemical shift data more closely for ^{1}H; ^{13}C comparisons are similar. However, taken together with the data for diastereomer 2, for which **24i'** matches more closely for both nuclei, **24i** is the more likely assignment. Computed ^{13}C and ^{1}H spectra of diastereomers suggest **24c** match the experimental chemical shift data more closely for ^{13}C; for ^{1}H **24c** matches more closely at the C-1 epimeric stereocenter. The stereochemical assignment for **24c** was made by analogy with **24i** and **24i'** and by comparison with the relative configuration of the other [3.3.0]-bicyclic oxonium ions in Figure 2 of the manuscript.

Note: the atom numbering used below differs from that used in the experimental section of the ESI.



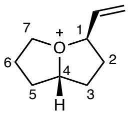
For the 5,5-oxonium ions ([3.3.0]-bicyclic oxonium ions) both ^{1}H and ^{13}C NMR experimental resonances, C-4/H-4 and C-1/H-1 appear at higher chemical shift than the resonances for C-7/H-7 and this trend is reproduced computationally for both proton and carbon for all of the 5,5-oxonium ions in Figure 2.

It is generally the case (with some exceptions) with both ^{1}H and ^{13}C NMR the order of chemical shifts is C4 > C1 >> C7 however, the C4 and C1 resonances are close in chemical shift hence the ordering of C4 and C1 chemical shifts is not always exactly reproduced computationally.

With the 5,6-oxonoium ions ([4.3.0]-bicyclic oxonium ions) the ordering of the ^{1}H and ^{13}C NMR chemical shifts of C-1/H-1, C-5/H-5 and C-8/H-8 is generally reproduced computationally.

5,5-fused structures (mono-substituted)

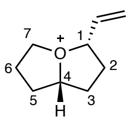
24: Computed ^{13}C and ^{1}H spectra of diastereomers suggest **24a** matches the experimental chemical shift data more closely for both nuclei.



24a *2 low-energy conformers*

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	104.4	105.9	1.5
2	34.8	37.0	2.2
3	31.3	32.7	1.4
4	105.2	105.7	0.5
5	30.9	31.8	0.9
6	28.2	31.0	2.8
7	84.0	81.1	-2.9
		MAE	**1.7**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	5.11	4.83	-0.28
2a	2.39	2.45	0.06
2b	2.68	2.52	-0.16
3a	2.26	2.16	-0.10
3b	2.60	2.51	-0.09
4	5.45	5.23	-0.22
5a	2.26	2.10	-0.16
5b	2.60	2.46	-0.14
6a	2.52	2.47	-0.05
6b	2.60	2.50	-0.10
7a	4.50	4.08	-0.42
7b	4.69	4.44	-0.25
		MAE	**0.17**

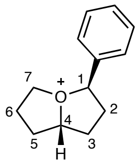


24a' *3 low-energy conformers*

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	104.4	102.4	-2.0
2	34.8	36.3	1.5
3	31.3	30.6	-0.7
4	105.2	104.6	-0.6
5	30.9	31.8	0.9
6	28.2	32.4	4.2
7	84.0	76.1	-7.9
		MAE	**2.5**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	5.11	5.33	0.22
2a	2.39	2.40	0.01
2b	2.68	2.85	0.17
3a	2.26	2.21	-0.05
3b	2.60	2.45	-0.15
4	5.45	5.10	-0.35
5a	2.26	1.92	-0.34
5b	2.60	2.41	-0.19
6a	2.52	2.53	0.01
6b	2.60	2.60	0.00
7a	4.50	4.12	-0.38
7b	4.69	4.23	-0.46
		MAE	**0.19**

24b: Computed ^{13}C and ^{1}H spectra of diastereomers suggest **24b** matches the experimental chemical shift data significantly more closely for both nuclei.

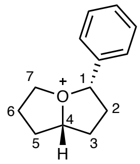


24b

2 low-energy conformers

Atom No.	^{13}C$_{expt}$ ppm	^{13}C$_{pred}$ ppm	Error (ppm)
1	106.3	109.1	2.8
2	36.2	37.9	1.7
3	31.2	33.3	2.1
4	105.6	104.0	-1.6
5	32.1	31.9	-0.2
6	28.1	31.0	2.9
7	84.1	80.5	-3.6
		MAE	**2.1**

Atom No.	^{1}H$_{expt}$ ppm	^{1}H$_{pred}$ ppm	Error (ppm)
1	5.41	5.42	0.01
2a/2b	2.85	2.77	-0.08
3a	2.30	2.32	0.02
3b	2.67	2.65	-0.02
4	5.62	5.34	-0.28
5a	2.30	2.16	-0.14
5b	2.80	2.49	-0.31
6a/b	2.57	2.47	-0.10
7a	4.41	4.11	-0.30
7b	4.56	4.12	-0.44
		MAE	**0.17**



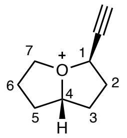
24b'

2 low-energy conformers

Atom No.	^{13}C$_{expt}$ ppm	^{13}C$_{pred}$ ppm	Error (ppm)
1	106.3	112.1	5.8
2	36.2	28.4	-7.8
3	31.2	31.1	-0.1
4	105.6	100.2	-5.4
5	32.1	32.5	0.4
6	28.1	28.9	0.8
7	84.1	77.5	-6.6
		MAE	**3.8**

Atom No.	^{1}H$_{expt}$ ppm	^{1}H$_{pred}$ ppm	Error (ppm)
1	5.41	6.16	0.75
2a/2b	2.85	2.69	-0.16
3a	2.30	2.42	0.12
3b	2.67	2.69	0.02
4	5.62	5.13	-0.49
5a	2.30	1.95	-0.35
5b	2.80	2.38	-0.42
6a/b	2.57	2.23	-0.34
7a	4.41	3.64	-0.77
7b	4.56	3.62	-0.94
		MAE	**0.44**

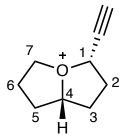
24c: Computed spectra of diastereomers suggest **24c** matches the experimental chemical shift data more closely for ^{13}C; for ^{1}H **24c** matches more closely at the epimeric stereocenter.



24c *3 low-energy conformers*

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	90.8	91.5	0.7
2	35.6	38.6	3.0
3	31.1	32.5	1.4
4	107.6	107.9	0.3
5	31.0	31.6	0.6
6	28.2	31.3	3.1
7	86.8	83.7	-3.1
		MAE	**1.7**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	5.15	5.06	-0.09
2a	2.67	2.66	-0.01
2b	2.85	2.76	-0.09
3a	2.20	2.19	-0.01
3b	2.78	2.55	-0.23
4	5.63	5.37	-0.26
5a	2.20	2.10	-0.10
5b	2.67	2.49	-0.18
6a/6b	2.58	2.54	-0.04
7a	4.48	4.19	-0.29
7b	5.05	4.77	-0.28
		MAE	**0.14**

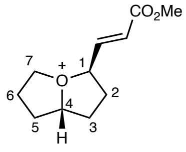


24c' *3 low-energy conformers*

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	90.8	88.9	-1.9
2	35.6	38.1	2.5
3	31.1	31.1	0.0
4	107.6	108.6	1.0
5	31.0	31.7	0.7
6	28.2	31.7	3.5
7	86.8	79.8	-7.0
		MAE	**2.4**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	5.51	5.06	-0.45
2a	2.66	2.66	0.00
2b	2.83	2.76	-0.07
3a	2.35	2.19	-0.16
3b	2.50	2.55	0.05
4	5.27	5.37	0.10
5a	2.06	2.10	0.04
5b	2.44	2.49	0.04
6a/6b	2.58	2.54	-0.04
7a	4.43	4.19	-0.24
7b	4.83	4.77	-0.05
		MAE	**0.11**

24d: Computed ^{13}C and ^{1}H spectra of diastereomers suggest **24d** matches the experimental chemical shift data more closely for both nuclei.

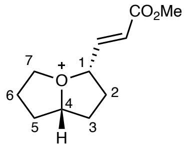


24d

3 low-energy conformers

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	100.9	102.3	1.4
2	34.8	37.3	2.5
3	31.4	32.8	1.4
4	108.0	107.3	-0.7
5	30.8	31.6	0.8
6	28.2	31.4	3.2
7	86.0	82.1	-3.9
		MAE	**2.0**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	5.04	4.91	-0.13
2a	2.49	2.54	0.05
2b	2.76	2.57	-0.19
3a	2.21	2.21	0.00
3b	2.76	2.57	-0.19
4	5.60	5.33	-0.27
5a	2.27	2.12	-0.15
5b	2.68	2.48	-0.20
6a/6b	2.60	2.52	-0.08
7a	4.41	4.07	-0.34
7b	4.84	4.46	-0.38
		MAE	**0.18**



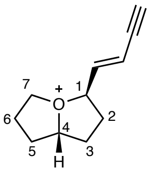
24d'

2 low-energy conformers

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	100.9	103.5	2.6
2	34.8	32.7	-2.1
3	31.4	31.4	0.0
4	108.0	103.9	-4.1
5	30.8	31.2	0.4
6	28.2	28.7	0.5
7	86.0	79.8	-6.2
		MAE	**2.3**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	5.04	5.44	0.40
2a	2.49	2.38	-0.11
2b	2.76	2.47	-0.29
3a	2.21	2.28	0.07
3b	2.76	2.53	-0.23
4	5.60	5.23	-0.37
5a	2.27	2.13	-0.14
5b	2.68	2.42	-0.26
6a/6b	2.60	2.28	-0.32
7a	4.41	4.22	-0.19
7b	4.84	4.37	-0.47
		MAE	**0.26**

(*E*)-24h: Computed ^{13}C and ^{1}H spectra of diastereomers suggest **(*E*)-24h** matches the experimental chemical shift data more closely for both nuclei.

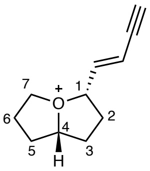


(*E*)-24h

3 low-energy conformers

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	103.6	107.9	4.3
2	34.5	36.8	2.3
3	31.5	33.0	1.5
4	105.8	104.3	-1.5
5	30.7	31.9	1.2
6	27.9	31.5	3.6
7	84.2	80.5	-3.7
		MAE	**2.6**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	4.88	4.94	0.06
2a	2.42	2.49	0.07
2b	2.70	2.54	-0.16
3a	2.14	2.19	0.05
3b	2.70	2.53	-0.17
4	5.47	5.16	-0.31
5a	2.20	2.07	-0.13
5b	2.61	2.45	-0.16
6a/6b	2.53	2.50	-0.03
7a	4.35	4.01	-0.34
7b	4.71	4.44	-0.27
		MAE	**0.16**



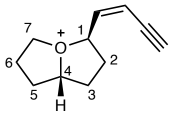
(*E*)-24h'

3 low-energy conformers

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	103.6	109.1	5.5
2	34.5	33.5	-1.0
3	31.5	31.5	0.0
4	105.8	101.4	-4.4
5	30.7	31.6	0.9
6	27.9	30.4	2.5
7	84.2	76.8	-7.4
		MAE	**3.1**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	4.88	5.52	0.64
2a	2.42	2.35	-0.07
2b	2.70	2.60	-0.10
3a	2.14	2.24	0.10
3b	2.70	2.50	-0.20
4	5.47	5.04	-0.43
5a	2.20	1.96	-0.24
5b	2.61	2.37	-0.24
6a/6b	2.53	2.40	-0.13
7a	4.35	4.13	-0.22
7b	4.71	4.18	-0.53
		MAE	**0.26**

(*Z*)-24h: Computed ^{13}C and ^{1}H spectra of diastereomers suggest **(*Z*)-24h** matches the experimental chemical shift data more closely for both nuclei.

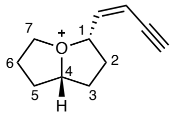


(*Z*)-24h

3 low-energy conformers

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	99.7	102.3	2.6
2	34.1	34.5	0.4
3	31.8	34.2	2.4
4	105.5	104.3	-1.2
5	30.7	30.3	-0.4
6	28.0	27.9	-0.1
7	85.2	83.4	-1.8
		MAE	**1.3**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	5.53	5.20	-0.33
2a	2.42	2.47	0.05
2b	2.70	2.66	-0.04
3a	2.14	2.19	0.05
3b	2.70	2.54	-0.16
4	5.47	5.38	-0.09
5a	2.20	2.20	0.00
5b	2.61	2.42	-0.19
6a/6b	2.53	2.39	-0.14
7a	4.52	4.31	-0.21
7b	4.75	4.43	-0.32
		MAE	**0.14**



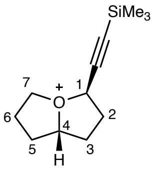
(*Z*)-24h'

3 low-energy conformers

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	99.7	101.3	1.6
2	34.1	33.5	-0.6
3	31.8	31.2	-0.6
4	105.5	102.3	-3.2
5	30.7	31.6	0.9
6	28.0	30.7	2.7
7	85.2	76.7	-8.5
		MAE	**2.6**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	5.53	6.03	0.50
2a	2.42	2.35	-0.07
2b	2.70	2.64	-0.06
3a	2.14	2.23	0.09
3b	2.70	2.52	-0.18
4	5.47	5.09	-0.38
5a	2.20	1.93	-0.27
5b	2.61	2.38	-0.23
6a/6b	2.53	2.42	-0.11
7a	4.52	4.21	-0.31
7b	4.75	4.21	-0.54
		MAE	**0.25**

24i (diastereomer 1): Computed ^{13}C and ^{1}H spectra of diastereomers suggest **24i** matches the experimental chemical shift data more closely for ^{1}H; ^{13}C comparisons are similar. However, taken together with the data for diastereomer 2, for which **24i’** matches more closely for both nuclei, **24i** seems the more likely assignment.

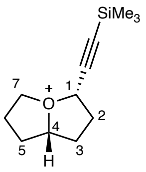


24i

3 low-energy conformers

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	91.7	95.0	3.3
2	35.5	38.8	3.3
3	31.1	33.0	1.9
4	106.2	105.1	-1.1
5	30.7	31.8	1.1
6	27.9	31.5	3.6
7	85.9	82.2	-3.7
		MAE	**2.6**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	5.11	5.14	0.03
2a	2.60	2.60	0.00
2b	2.78	2.70	-0.08
3a	2.15	2.18	0.03
3b	2.72	2.51	-0.21
4	5.55	5.22	-0.33
5a	2.15	2.07	-0.08
5b	2.60	2.46	-0.14
6a/6b	2.55	2.53	-0.02
7a	4.44	4.11	-0.33
7b	4.98	4.70	-0.28
		MAE	**0.14**



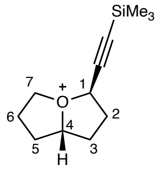
24i’

5 low-energy conformers

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	91.7	93.3	1.6
2	35.5	37.2	1.7
3	31.1	31.4	0.3
4	106.2	105.4	-0.8
5	30.7	32.1	1.4
6	27.9	31.2	3.3
7	85.9	78.5	-7.4
		MAE	**2.4**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	5.11	5.59	0.48
2a	2.60	2.55	-0.05
2b	2.78	2.73	-0.05
3a	2.15	2.32	0.17
3b	2.72	2.48	-0.24
4	5.55	5.13	-0.42
5a	2.15	1.98	-0.17
5b	2.60	2.40	-0.20
6a/6b	2.55	2.52	-0.03
7a	4.44	4.34	-0.10
7b	4.98	4.76	-0.22
		MAE	**0.19**

24i (diastereomer 2): Computed ^{13}C and ^{1}H spectra of diastereomers suggest **24i’** matches more closely for both nuclei.

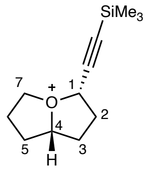


24i

3 low-energy conformers

Atom No.	^{13}C$_{expt}$ ppm	^{13}C$_{pred}$ ppm	Error (ppm)
1	89.3	95.0	5.7
2	35.5	38.8	3.3
3	30.0	33.0	3.0
4	106.8	105.1	-1.7
5	30.7	31.8	1.1
6	28.7	31.5	2.8
7	81.3	82.2	0.9
		MAE	**2.6**

Atom No.	^{1}H$_{expt}$ ppm	^{1}H$_{pred}$ ppm	Error (ppm)
1	5.67	5.14	-0.53
2a	2.66	2.60	-0.06
2b	2.72	2.70	-0.02
3a	2.34	2.18	-0.16
3b	2.66	2.51	-0.15
4	5.39	5.22	-0.17
5a	2.08	2.07	-0.01
5b	2.60	2.46	-0.14
6a	2.51	2.53	0.02
6b	2.60	2.53	-0.07
7a	4.62	4.11	-0.51
7b	4.98	4.70	-0.28
		MAE	**0.18**



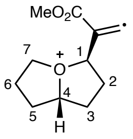
24i’

5 low-energy conformers

Atom No.	^{13}C$_{expt}$ ppm	^{13}C$_{pred}$ ppm	Error (ppm)
1	89.3	93.3	4.0
2	35.5	37.2	1.7
3	30.0	31.4	1.4
4	106.8	105.4	-1.4
5	30.7	32.1	1.4
6	28.7	31.2	2.5
7	81.3	78.5	-2.8
		MAE	**2.2**

Atom No.	^{1}H$_{expt}$ ppm	^{1}H$_{pred}$ ppm	Error (ppm)
1	5.67	5.59	-0.08
2a	2.66	2.55	-0.11
2b	2.72	2.73	0.01
3a	2.34	2.32	-0.02
3b	2.66	2.48	-0.18
4	5.39	5.13	-0.26
5a	2.08	1.98	-0.10
5b	2.60	2.40	-0.20
6a	2.51	2.52	0.01
6b	2.60	2.53	-0.07
7a	4.62	4.34	-0.28
7b	4.98	4.76	-0.22
		MAE	**0.13**

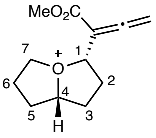
24j (diastereomer 1): Computed ^{13}C and ^{1}H spectra of diastereomers suggest **24j** matches the experimental chemical shift data more closely for both nuclei.



24j *3 low-energy conformers*

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	99.3	101.5	2.2
2	31.1	33.5	2.4
3	31.1	33.1	2.0
4	105.3	104.8	-0.5
5	30.1	31.3	1.2
6	27.3	30.0	2.7
7	87.6	85.3	-2.3
		MAE	**1.9**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	5.56	5.56	0.00
2a	2.19	2.45	0.26
2b	2.61	2.67	0.06
3a/3b	2.61	2.34	-0.27
4	5.45	5.23	-0.22
5a	2.19	2.12	-0.07
5b	2.52	2.42	-0.10
6a	2.46	2.38	-0.08
6b	2.52	2.49	-0.03
7a	4.80	4.42	-0.38
7b	4.87	4.83	-0.04
		MAE	**0.14**

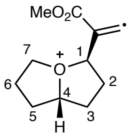


24j' *4 low-energy conformers*

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	99.3	104.0	4.7
2	31.1	30.5	-0.6
3	31.1	30.9	-0.2
4	105.3	102.7	-2.6
5	30.1	31.6	1.5
6	27.3	28.7	1.4
7	87.6	79.8	-7.8
		MAE	**2.7**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	5.56	5.65	0.09
2a	2.19	2.39	0.20
2b	2.61	2.65	0.04
3a/3b	2.61	2.40	-0.21
4	5.45	5.16	-0.29
5a	2.19	2.07	-0.12
5b	2.52	2.37	-0.15
6a	2.46	2.28	-0.18
6b	2.52	2.45	-0.07
7a	4.80	4.28	-0.52
7b	4.87	4.51	-0.36
		MAE	**0.20**

24j (diastereomer 2): Computed ^{13}C and ^{1}H spectra of diastereomers suggest **24j'** matches the experimental chemical shift data more closely for both nuclei.

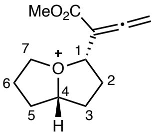


24j

3 low-energy conformers

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	97.8	101.5	3.7
2	28.1	33.5	5.4
3	28.8	33.1	4.3
4	104.6	104.8	0.2
5	31.6	31.3	-0.3
6	26.9	30.0	3.1
7	79.7	85.3	5.6
		MAE	**3.3**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	5.85	5.56	-0.29
2a	2.30	2.45	0.15
2b	2.46	2.67	0.21
3a	2.30	2.19	-0.11
3b	2.61	2.49	-0.12
4	5.53	5.23	-0.30
5a	1.89	2.12	0.23
5b	2.61	2.42	-0.19
6a	2.30	2.38	0.08
6b	2.46	2.49	0.03
7a	4.18	4.42	0.24
7b	4.52	4.83	0.31
		MAE	**0.19**



24j'

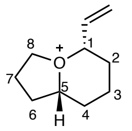
4 low-energy conformers

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	97.8	104.0	6.2
2	28.1	30.5	2.4
3	28.8	30.9	2.1
4	104.6	102.7	-1.9
5	31.6	31.6	0.0
6	26.9	28.7	1.8
7	79.7	79.8	0.1
		MAE	**2.1**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	5.85	5.65	-0.20
2a	2.30	2.39	0.09
2b	2.46	2.65	0.19
3a	2.30	2.38	0.08
3b	2.61	2.43	-0.18
4	5.53	5.16	-0.37
5a	1.89	2.07	0.18
5b	2.61	2.37	-0.24
6a	2.30	2.28	-0.02
6b	2.46	2.45	-0.01
7a	4.18	4.28	0.10
7b	4.52	4.51	-0.01
		MAE	**0.14**

5,6-fused structures (mono-substituted)

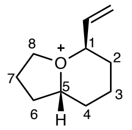
24e: Computed ^{13}C and ^{1}H spectra of diastereomers suggest **24e** matches the experimental chemical shift data more closely for both nuclei.



24e *1 low-energy conformer*

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	104.0	104.8	0.8
2	32.0	33.3	1.3
3	21.6	23.0	1.4
4	30.3	30.7	0.4
5	102.7	100.8	-1.9
6	30.2	32.2	2.0
7	20.6	23.3	2.7
8	82.8	81.1	-1.7
		MAE	**1.5**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	4.92	4.91	-0.01
2a/2b	2.09	1.98	-0.11
3a	1.79	1.75	-0.04
3b	2.09	1.97	-0.12
4a	1.88	1.82	-0.06
4b	2.09	2.16	0.07
5	4.48	4.43	-0.05
6a	2.33	2.02	-0.31
6b	2.60	2.36	-0.24
7a/7b	2.33	2.21	-0.12
8a	4.27	4.29	0.02
8b	4.76	4.34	-0.42
		MAE	**0.13**

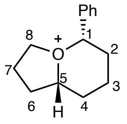


24e' *2 low-energy conformers*

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	104.0	100.7	-3.3
2	32.0	30.9	-1.1
3	21.6	19.0	-2.6
4	30.3	31.1	0.8
5	102.7	95.7	-7.0
6	30.2	32.2	2.0
7	20.6	24.8	4.2
8	82.8	78.5	-4.3
		MAE	**3.2**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	4.92	5.09	0.17
2a/2b	2.09	2.14	0.05
3a	1.79	1.86	0.07
3b	2.09	1.91	-0.18
4a	1.88	1.89	0.01
4b	2.09	2.20	0.11
5	4.48	4.62	0.14
6a	2.33	1.96	-0.37
6b	2.60	2.32	-0.28
7a/7b	2.33	2.18	-0.15
8a	4.27	4.20	-0.07
8b	4.76	4.45	-0.31
		MAE	**0.16**

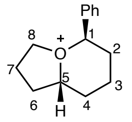
24f: Computed ^{13}C and ^{1}H spectra of diastereomers suggest **24f** matches the experimental chemical shift data much more closely for both nuclei.



24f *1 low-energy conformer*

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	104.8	107.6	2.8
2	32.9	34.3	1.4
3	22.0	24.0	2.0
4	30.0	30.9	0.9
5	103.0	100.7	-2.3
6	30.0	32.4	2.4
7	20.1	23.0	2.9
8	83.0	81.3	-1.7
		MAE	**2.1**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	5.39	5.45	0.06
2a	2.24	2.09	-0.15
2b	2.40	2.47	0.07
3a	1.86	1.88	0.02
3b	2.19	2.09	-0.10
4a	2.00	1.96	-0.04
4b	2.40	2.24	-0.16
5	4.60	4.55	-0.05
6a	2.12	2.05	-0.07
6b	2.60	2.38	-0.22
7a/7b	2.19	2.12	-0.07
8a	4.02	3.83	-0.19
8b	4.22	3.99	-0.23
		MAE	**0.11**

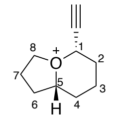


24f' *3 low-energy conformers*

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	104.8	101.8	-3.0
2	32.9	30.2	-2.7
3	22.0	19.4	-2.6
4	30.0	28.9	-1.1
5	103.0	100.0	-3.0
6	30.0	32.9	2.9
7	20.1	24.9	4.8
8	83.0	79.1	-3.9
		MAE	**3.0**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	5.39	5.58	0.19
2a	2.24	2.21	-0.03
2b	2.40	2.52	0.12
3a	1.86	2.05	0.19
3b	2.19	2.08	-0.11
4a	2.00	2.16	0.16
4b	2.40	2.27	-0.13
5	4.60	5.13	0.53
6a	2.12	2.04	-0.08
6b	2.60	2.47	-0.13
7a/7b	2.19	2.08	-0.11
8a	4.02	3.88	-0.14
8b	4.22	3.89	-0.33
		MAE	**0.17**

24g (diastereomer 1): Computed ^{13}C and ^{1}H spectra of diastereomers suggest **24g** matches the experimental chemical shift data much more closely for both nuclei.

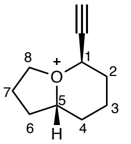


24g

1 low-energy conformer

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	89.4	90.4	1.0
2	33.0	34.9	1.9
3	21.5	23.1	1.6
4	30.0	30.6	0.6
5	104.0	102.5	-1.5
6	30.5	32.4	1.9
7	20.9	23.6	2.7
8	85.0	83.7	-1.3
		MAE	**1.5**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	5.15	5.15	0.00
2a	2.23	2.19	-0.04
2b	2.42	2.25	-0.17
3a	1.77	1.75	-0.02
3b	2.14	1.99	-0.15
4a	1.91	1.85	-0.06
4b	2.31	2.16	-0.15
5	4.56	4.47	-0.09
6a	2.14	2.07	-0.07
6b	2.64	2.40	-0.24
7a/7b	2.42	2.30	-0.12
8a	4.59	4.61	0.02
8b	5.24	4.80	-0.44
		MAE	**0.12**



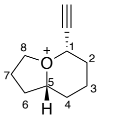
24g'

1 low-energy conformer

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	89.4	86.8	-2.6
2	33.0	32.7	-0.3
3	21.5	19.5	-2.0
4	30.0	31.1	1.1
5	104.0	98.2	-5.8
6	30.5	31.7	1.2
7	20.9	25.0	4.1
8	85.0	82.6	-2.4
		MAE	**2.4**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	5.15	5.45	0.30
2a	2.23	2.11	-0.12
2b	2.42	2.33	-0.09
3a	1.77	2.00	0.23
3b	2.14	1.85	-0.29
4a	1.91	2.22	0.31
4b	1.31	1.87	0.56
5	4.56	4.94	0.38
6a	2.14	2.39	0.25
6b	2.64	2.01	-0.63
7a/7b	2.42	2.32	-0.10
8a	4.59	4.67	0.08
8b	5.24	4.50	-0.74
		MAE	**0.31**

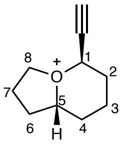
24g (diastereomer 2): Computed ^{13}C and ^{1}H spectra of diastereomers suggest **24g'** matches the experimental chemical shift data much more closely for both nuclei.



24g *1 low-energy conformer*

Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	86.3	90.4	4.1
2	30.8	34.9	4.1
3	17.8	23.1	5.3
4	30.6	30.6	0.0
5	98.7	102.5	3.8
6	29.5	32.4	2.9
7	21.8	23.6	1.8
8	83.8	83.7	-0.1
		MAE	**2.7**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1	5.68	5.15	-0.53
2a	2.23	2.19	-0.04
2b	2.31	2.25	-0.06
3a/3b	2.04	1.87	-0.17
4a	1.91	1.85	-0.06
4b	2.37	2.16	-0.21
5	4.95	4.47	-0.48
6a	2.04	2.07	0.03
6b	2.58	2.40	-0.18
7a/7b	2.42	2.30	-0.12
8a	4.70	4.61	-0.09
8b	4.79	4.80	0.01
		MAE	**0.16**



24g' *1 low-energy conformer*

Atom No.	13C/ppm	pred	Err
1	86.3	86.8	0.5
2	30.8	32.7	1.9
3	17.8	19.5	1.7
4	30.6	31.1	0.5
5	98.7	98.2	-0.5
6	29.5	31.7	2.2
7	21.8	25.0	3.2
8	83.8	82.6	-1.2
		MAE	**1.5**

Atom No.	1H/ppm	pred	Err
1	5.68	5.45	-0.23
2a	2.23	2.11	-0.12
2b	2.31	2.33	0.02
3a/3b	2.04	1.92	-0.12
4a	1.91	1.87	-0.04
4b	2.37	2.22	-0.15
5	4.95	4.94	-0.01
6a	2.04	2.01	-0.03
6b	2.58	2.39	-0.19
7a/7b	2.42	2.32	-0.10
8a	4.70	4.67	-0.03
8b	4.79	4.50	-0.29
		MAE	**0.11**

4) Mechanistic analysis of bicyclic oxonium ions

Equilibration of diastereomeric oxonium ions: We computed the equilibration of 5,5-fused oxonium ion **24m** as studied experimentally in Figure 4 in the main text (**Figure S21**). We located transition structures and carbenium ion intermediates corresponding to the cleavage of the three distinct C–O bonds (pathways a, b and c where only pathways b and c can lead to stereochemical inversion). Consistent with experiment where equilibration at 0 °C results in the conversion of a mixture of diastereomers to solely **24m**, this diastereomer is computed to be thermodynamically more stable than **24m'**, by around 2 kcal/mol. Formation of a primary carbocation (pathway a) is extremely unfavorable as expected, is unviable for all of the oxonium ions studied and does not lead to stereochemical inversion. In contrast, formation of an allylic carbocation (pathway b) is accessible, with a barrier of 21-22 kcal/mol from **24m** (19-21 kcal/mol from **24m'**), which compares favorably with the measured barrier of 19.4 kcal/mol. Although the benzylic carbocation **27m** is the most stable carbenium ion intermediate for this process, the barrier for ring-opening is higher (27-28 kcal/mol) to form this species.

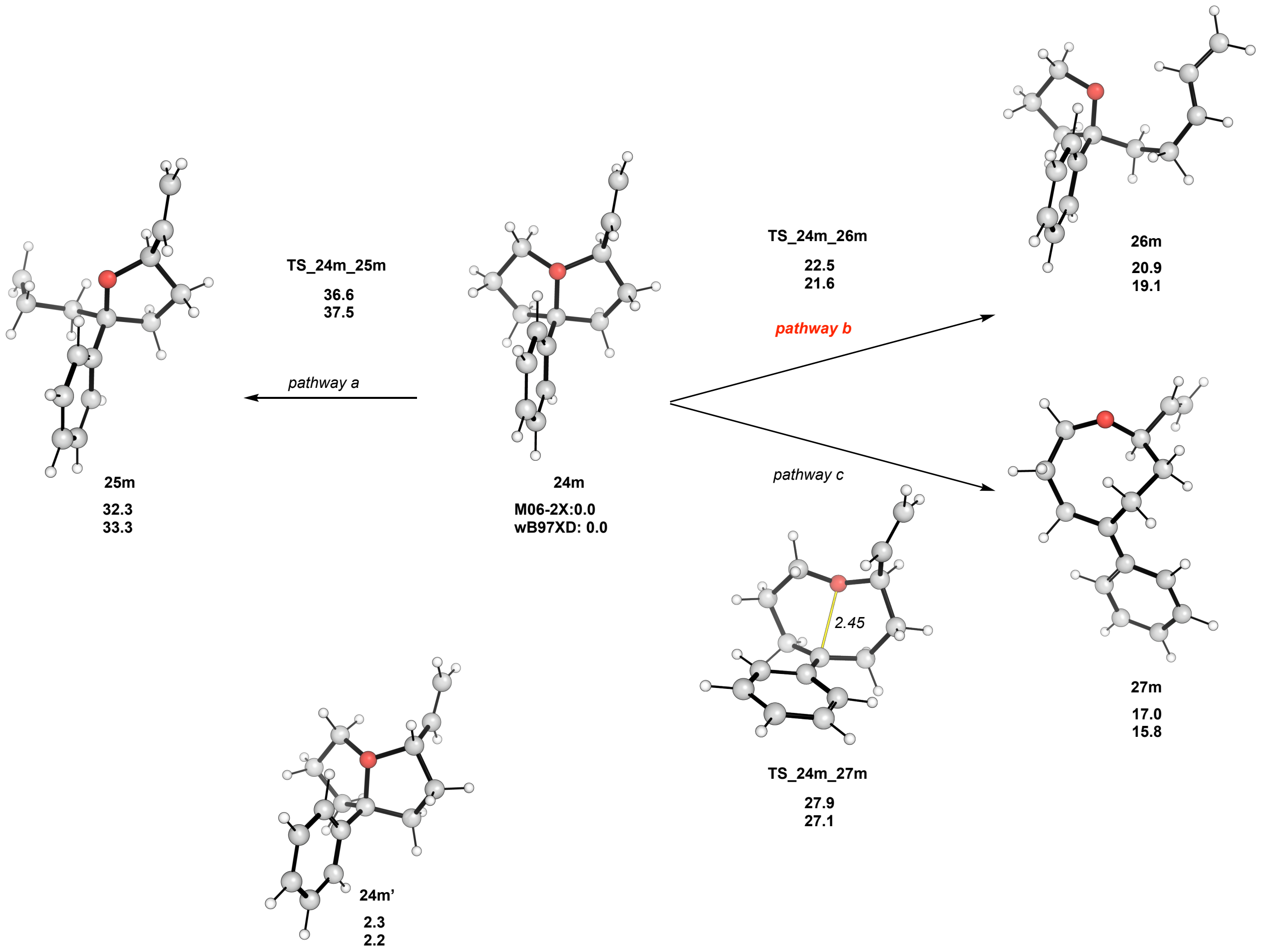


Figure S21. Equilibration of **24m/24m'** via carbenium ion forming pathways a, b, and c. M06-2X/def2-TZVP//B3LYP/6-31+G(d,p) and wB97XD/def2-TZVP//B3LYP/6-31+G(d,p) relative Gibbs energies in dichloromethane (kcal/mol). Forming/breaking bond distances in Å.

We also studied the equilibration of **24v/24v’** (**Figure S22**), which shows fluxionality even at -40 °C (Figure 5 in the main text). In this case, the electron-rich *p*-methoxyphenyl substituent aids the formation of a benzylic carbocation, with a barrier that is much lower than that obtained for **24m**. The barrier for ring-opening is 15-17 kcal/mol, which is consistent with equilibration at low temperatures. We expect that this (pathway c) will be significantly favored over formation of a propargylic cation (pathway b) for this substrate.

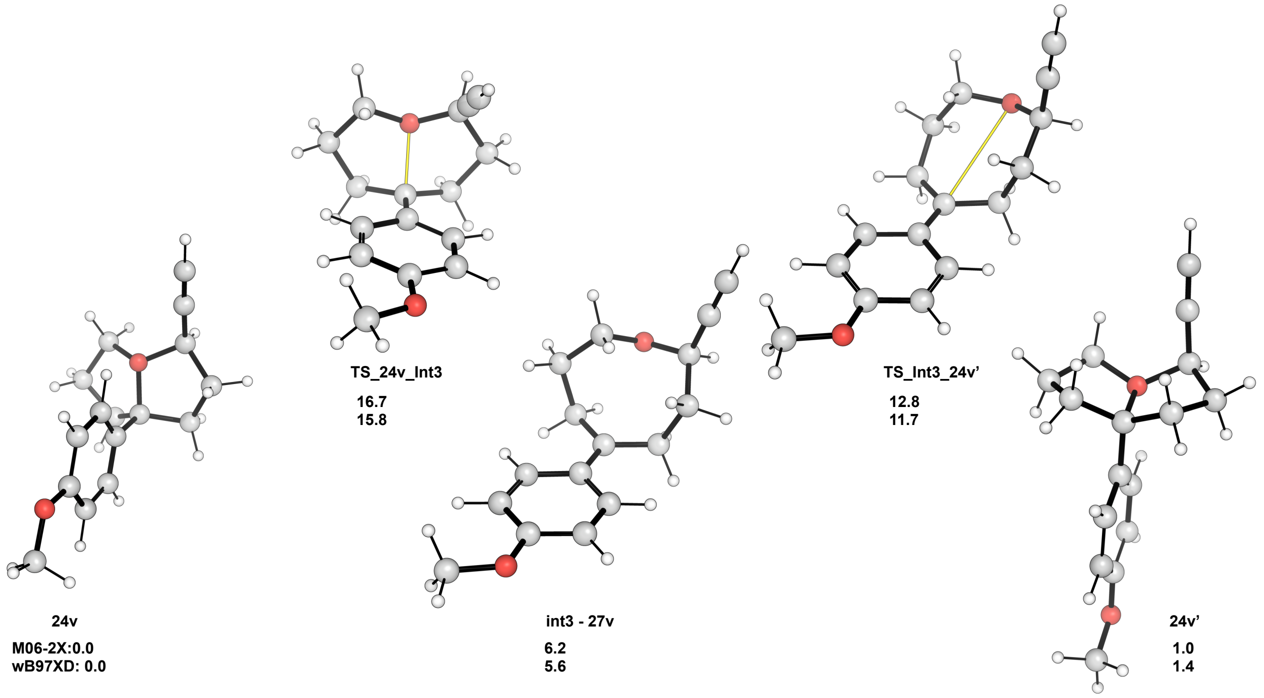


Figure S22. Equilibration of **24v/24v’** via carbenium ion forming pathway c. M06-2X/def2-TZVP//B3LYP/6-31+G(d,p) and wB97XD/def2-TZVP//B3LYP/6-31+G(d,p) relative Gibbs energies in dichloromethane (kcal/mol). Forming/breaking bond distances in Å.

Conversion of 24f to 35: We located transition structures for the conversion of **24f** to carbenium ion **26f**, and for the intramolecular hydride-transfer forming oxocarbenium **35** (**Figure S23**) as discussed in Figures 6 and 7 in the main text. Consistent with experiment the H-transfer is rate-determining. This TS is chair-shaped, with a C–H–C angle of 140° along the transferring axis. Consistent with an exothermic/exergonic step in forming the stabilized oxocarbenium, H-transfer is highly asynchronous, with a breaking C–H distance of 1.17 Å and a forming C–H distance of 1.71 Å. These two factors contribute to a relatively small primary KIE – the computationally predicted value (using Kinisot) for TS-33 is 1.85, which is qualitatively consistent with the experimentally observed value of 1.48.

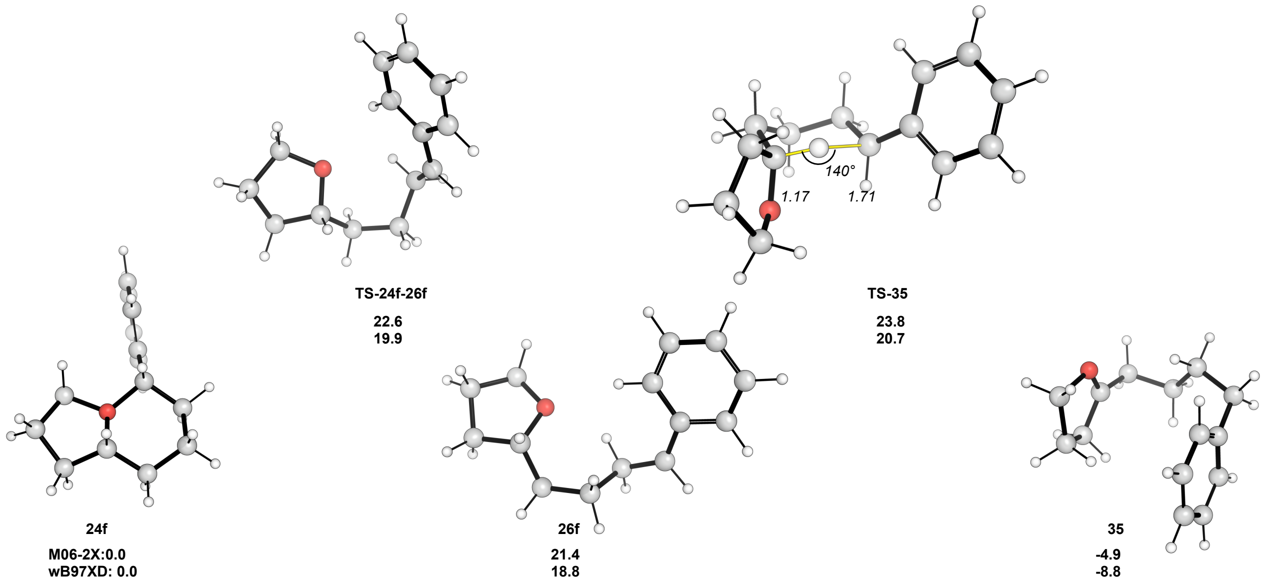
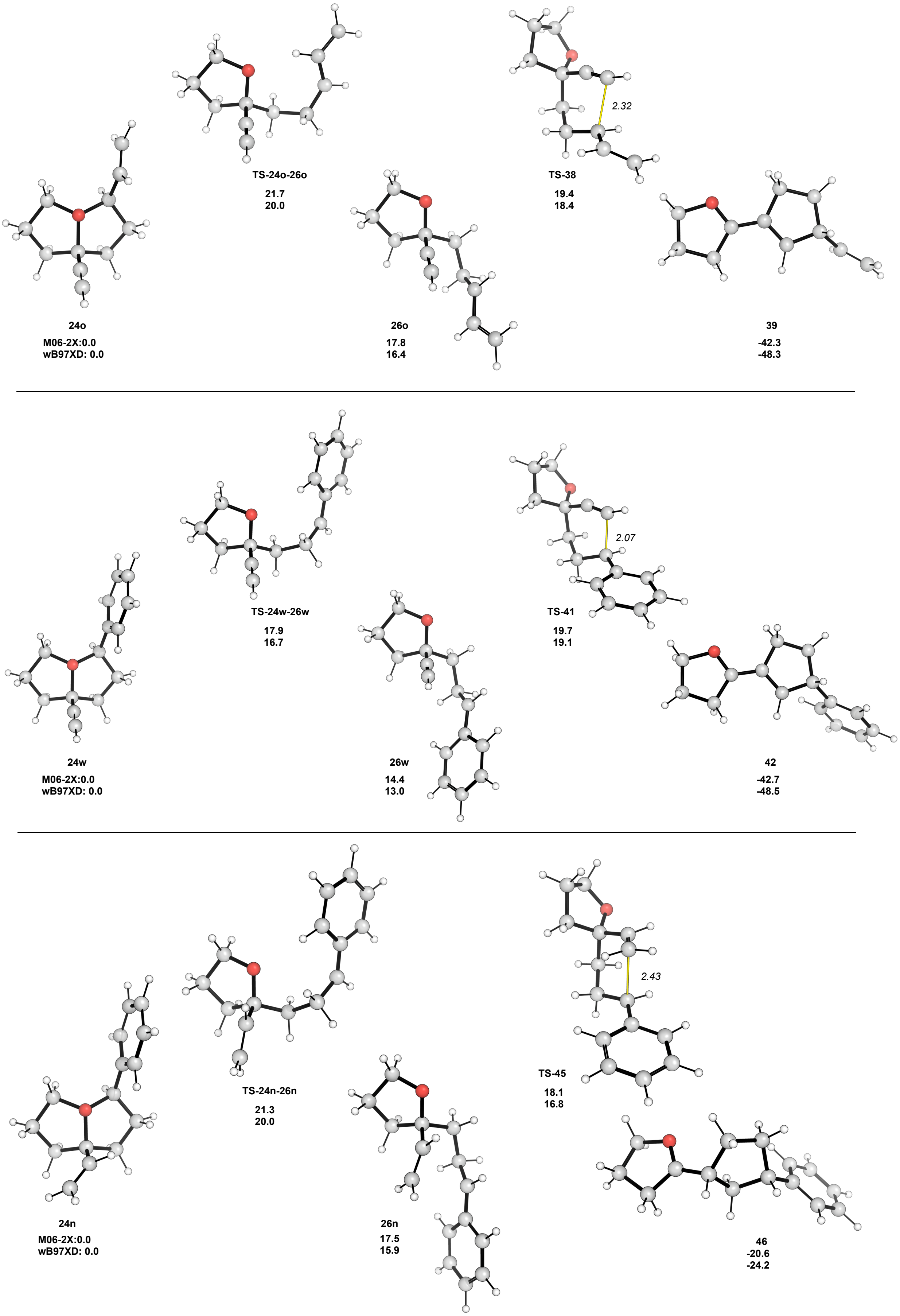


Figure S23. Conversion of **24f** to **35** via intramolecular hydride-transfer in carbenium ion **26f**. M06-2X/def2-TZVP//B3LYP/6-31+G(d,p) and wB97XD/def2-TZVP//B3LYP/6-31+G(d,p) relative Gibbs energies in dichloromethane (kcal/mol). Forming/breaking bond distances in TS-**35** in Å.

Friedel-Crafts pinacol reactions of 24o, 24w, 24n: We located transition structures and intermediates for the conversion of disubstituted 5,5-fused oxonium ions **24o, 24w, 24n** into the corresponding oxocarbenium ions **39**, **42**, **46** via a Friedel-Crafts pinacol rearrangement (**Figure S24**) as discussed in Figure 8 in the main text.
For each of the three systems we studied, rearrangement from the allylic/benzylic carbenium to the oxocarbenium occurred in a single elementary step. However, this process is highly asynchronous: C-C formation begins to occur in each TS, while 1,2-migration does not begin to occur until later along the Intrinsic Reaction Coordinate (IRC). This concerted, asynchronous mechanism avoids the intermediacy of a high-energy linear or secondary carbocation (**Figure S25**). Comparing the propargylic and benzylic cations **24w** and **24n**, the six-membered TS leading to the rearrangement is expected to be more stable for the latter (despite the much smaller thermodynamic driving force for this transformation), presumably since less bending is required (vs. the alkyne) to achieve the chair-shaped geometry required.

Consistent with experiment, the rearrangement of **24w** is computed to occur more readily than for **24o**: this is predicted to result from the greater stability of the benzylic vs. allylic carbocation in the first step of these transformations. The computed barriers around 20 to 22 kcal/mol are also consistent with processes occurring in the range of 0 °C to rt.



24o
M06-2X:0.0
wB97XD: 0.0

TS-24o-26o
21.7
20.0

26o
17.8
16.4

TS-38
19.4
18.4

39
-42.3
-48.3

24w
M06-2X:0.0
wB97XD: 0.0

TS-24w-26w
17.9
16.7

26w
14.4
13.0

TS-41
19.7
19.1

42
-42.7
-48.5

24n
M06-2X:0.0
wB97XD: 0.0

TS-24n-26n
21.3
20.0

26n
17.5
15.9

TS-45
18.1
16.8

46
-20.6
-24.2

Figure S24. Friedel-Crafts pinacol rearrangements of **24o, 24w, 24n**. M06-2X/def2-TZVP//B3LYP/6-31+G(d,p) and wB97XD/def2-TZVP//B3LYP/6-31+G(d,p) relative Gibbs energies in dichloromethane (kcal/mol). Forming bond distances in Å.

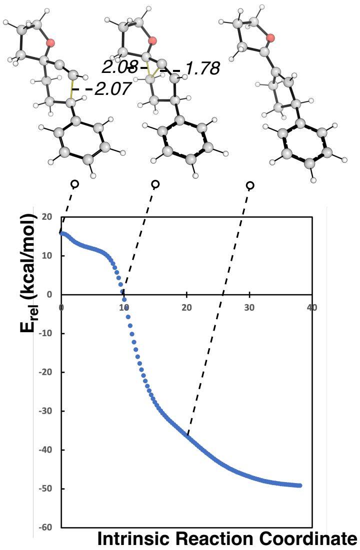


Figure S25. Intrinsic Reaction Coordinate following **TS-41** showing evolution to the oxocarbenium ion without intervening intermediates. B3LYP/6-31+G(d,p) relative energies in (kcal/mol). Forming/breaking bond distances in Å.

Friedel Crafts reactions of 24l and 24m:

We studied the competing ipso- and ortho-Friedel Crafts processes that can occur from the benzylic and allylic carbenium ions generated for C4-phenyl substituted oxonium ions (main text Figures 9 and 10). For ipso-alkylation, we located a transition structure (TS-2b) that evolves to oxocarbenium ion **5 9/int-3b** in a single step without the formation of a stable phenonium ion intermediate (**Figure S26**): this process corresponds formally to a cationic Smiles (Hayashi) rearrangement. In contrast, for alkylation at the ortho-position (via TS-2a), a dearomatized intermediate (int 3a) is formed which can undergo either a 1,2-hydride shift (forming oxocarbenium ion **59/int-3b**), or proton transfer to the ether oxygen can result in formation of alcohol **55**. For the diphenyl substituted oxonium ion **24l** we find that ipso addition is favored (i.e., **ts-2b** is more favorable than **ts-2a**), while for the vinyl, phenyl disubstituted oxonium ion **24m**, ortho addition is favored (i.e., **ts-2a** is more favorable than **ts-2b**) (**Figure S27**). The intramolecular 1,4-proton-transfer from carbon to oxygen leads to a stable product (**int-4**) leading to **61**, however, the computed barriers are relatively high: this process could also be promoted by a solvent molecule.

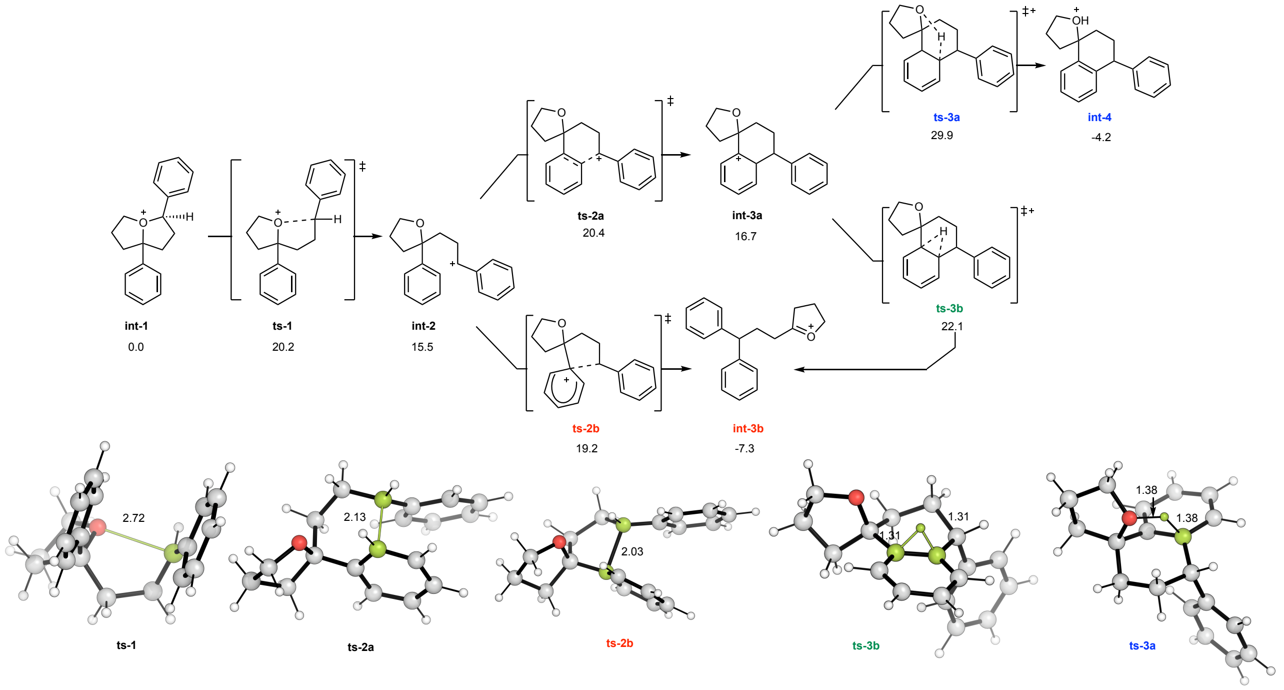


Figure S26. Friedel Crafts reactions of **24l**. M06-2X/def2-TZVP//B3LYP/6-31+G(d,p) and wB97XD/def2-TZVP//B3LYP/6-31+G(d,p) relative Gibbs energies in dichloromethane (kcal/mol). Breaking/forming bond distances in Å.

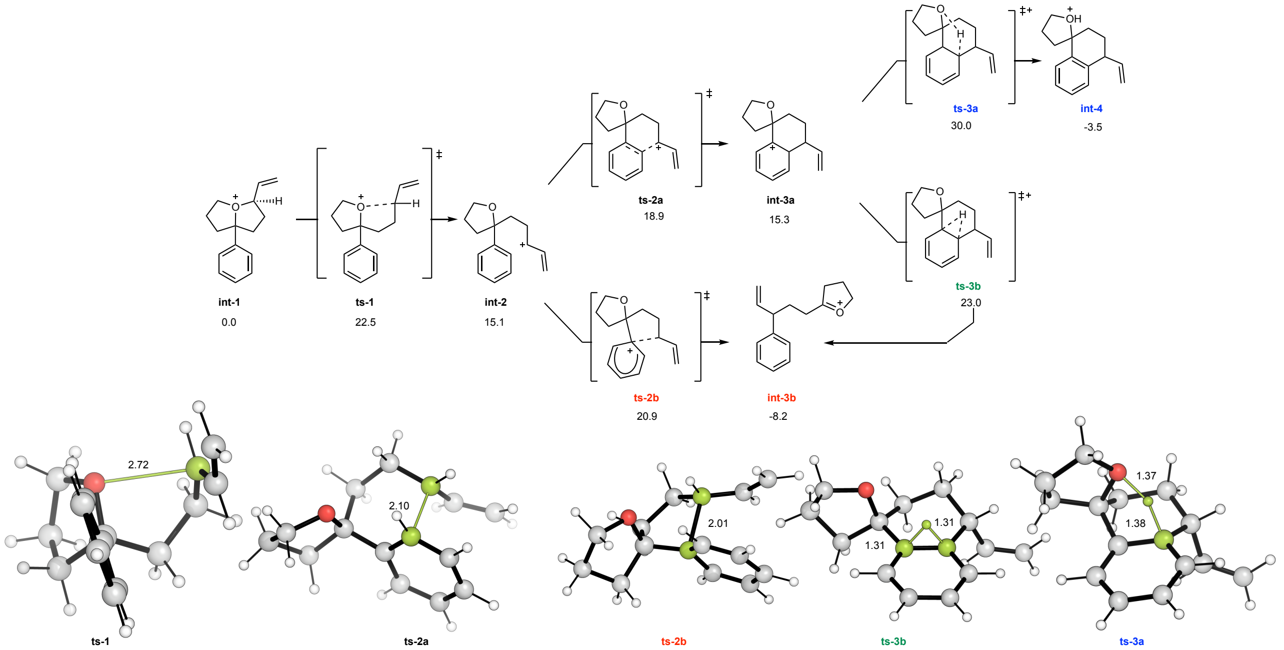


Figure S27. Friedel Crafts reactions of **24m**. M06-2X/def2-TZVP//B3LYP/6-31+G(d,p) and wB97XD/def2-TZVP//B3LYP/6-31+G(d,p) relative Gibbs energies in dichloromethane (kcal/mol). Breaking/forming bond distances in Å.

Rearrangement of 23x: We located transition structures and intermediates for the rearrangement of allenyl-substituted 5,5-fused oxonium **23x** to vinyl oxonium ion **63** (**Figure S28**). There is a single low energy conformation of **63**, which has a 5,7 *cis*-fused ring, minimized allylic-1,3 strain to the *exo*-methylene group. We also compared the predicted ^{13}C and ^{1}H NMR spectra for **63** against experiment, which gives similar levels of accuracy to other oxonium ions.

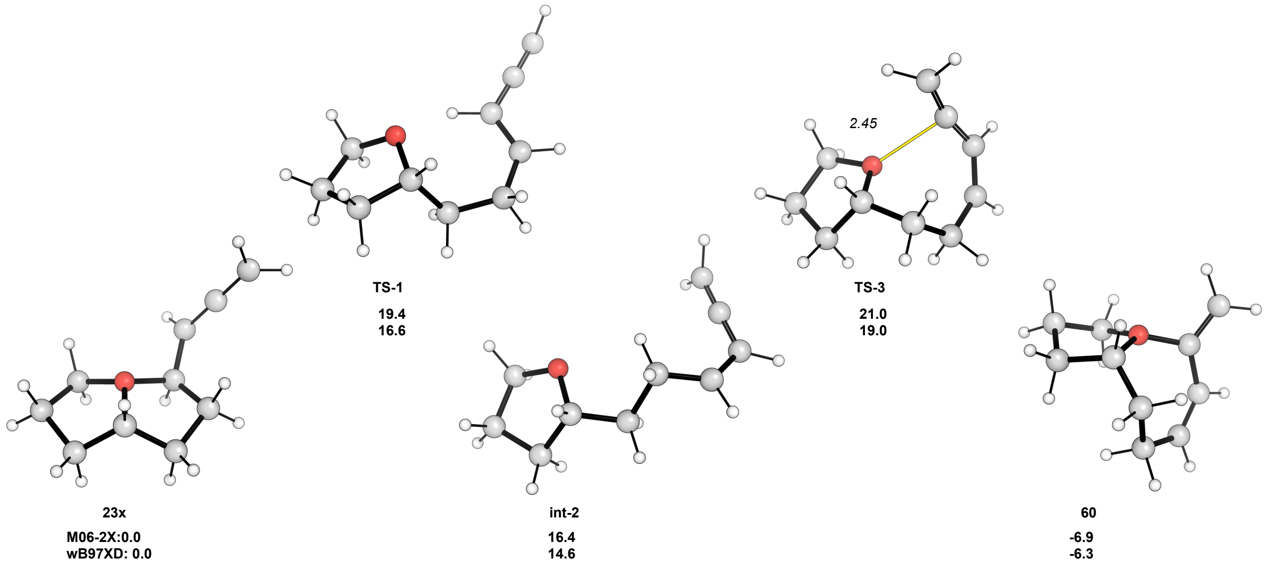
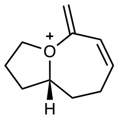
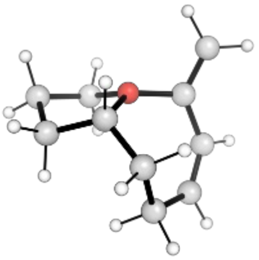


Figure S28. Rearrangements of **23x** to vinyl oxonium ion **60**. M06-2X/def2-TZVP//B3LYP/6-31+G(d,p) and wB97XD/def2-TZVP//B3LYP/6-31+G(d,p) relative Gibbs energies in dichloromethane (kcal/mol). Forming bond distance in Å.



62



Atom No.	$^{13}C_{expt}$ ppm	$^{13}C_{pred}$ ppm	Error (ppm)
1	111.7	116.1	4.4
2	155.3	157.1	1.8
3	119.0	118.9	-0.1
4	138.4	143.7	5.3
5	24.9	27.7	2.8
6	29	29.0	0.0
7	108.4	110.0	1.6
8	28.5	28.9	0.4
9	24.6	26.6	2.0
10	87.8	87.5	-0.3
		MAE	**1.9**

Atom No.	$^{1}H_{expt}$ ppm	$^{1}H_{pred}$ ppm	Error (ppm)
1a	5.56	5.68	0.12
1b	5.46	5.49	0.03
3	6.18	6.19	0.01
4	6.18	6.26	0.08
5a/5b	2.62	2.70	0.08
6a	2.22	2.04	-0.18
6b	2.59	2.62	0.03
7	5.73	5.63	-0.10
8a	2.38	2.38	0.00
8b	2.59	2.42	-0.17
9a/b	2.52	2.40	-0.12
10a	4.78	4.54	-0.24
10b	4.88	4.61	-0.27
		MAE	**0.11**

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6) Cartesian Coordinates

21

Parent 5,5 oxonium 01

C	-1.29849	-1.20706	0.16716
C	-2.22555	-0.02033	-0.04729
C	-1.32681	1.20348	0.22654
H	-1.19469	1.35648	1.30283
H	-1.74400	2.12035	-0.19734
C	0.00000	0.85908	-0.43026
C	1.32668	1.20345	0.22695
H	1.74375	2.12063	-0.19634
H	1.19434	1.35573	1.30331
C	2.22555	-0.02018	-0.04737
H	2.60443	-0.00962	-1.07364
H	3.08251	-0.06716	0.62896
C	1.29859	-1.20701	0.16691
H	1.13363	-1.44168	1.22194
O	0.00002	-0.70303	-0.37980
H	0.00032	1.05145	-1.50504
H	1.53961	-2.10577	-0.40023
H	-1.53950	-2.10589	-0.39987
H	-1.13337	-1.44154	1.22220
H	-2.60463	-0.01013	-1.07349
H	-3.08236	-0.06715	0.62924

21

Parent 5,5 oxonium 02

C	-1.30655	-1.22324	-0.10869
C	-1.89697	-0.05046	0.65330
H	-1.52015	-0.02625	1.68077
H	-2.98675	-0.11572	0.69893
C	-1.42127	1.17735	-0.15071
H	-1.43896	2.09282	0.44639
H	-2.06003	1.33392	-1.02425
C	0.00477	0.84854	-0.58670
C	1.17128	1.20727	0.32026
H	1.60480	2.16653	0.02623
H	0.84221	1.29002	1.36212
C	2.16068	0.04076	0.14717

H	2.70022	0.11788	-0.80139
H	2.89701	-0.00784	0.95324
C	1.26618	-1.18686	0.15857
H	0.95437	-1.47811	1.16445
O	0.03261	-0.71123	-0.56235
H	0.20935	1.07482	-1.63392
H	-1.83753	-1.46065	-1.03168
H	-1.11897	-2.13084	0.46421
H	1.62485	-2.04702	-0.40549

24

Parent 5,6 oxonium 01

C	1.63319	-1.22234	-0.11339
C	0.27255	0.80360	0.33285
C	1.64323	1.22927	-0.15161
C	2.53704	-0.00439	0.11112
H	1.63423	-1.94125	0.70817
H	1.77127	-1.72715	-1.06962
H	1.60502	1.47908	-1.21652
H	1.99516	2.10822	0.39386
H	3.40086	-0.02946	-0.55583
H	2.90766	0.00419	1.13927
H	0.24439	0.70069	1.42539
C	-0.97572	1.48006	-0.19440
C	-0.91860	-1.46295	0.22005
C	-2.17233	-0.75706	-0.26775
C	-2.24099	0.70224	0.21077
H	-0.99804	2.49660	0.21465
H	-3.12336	1.18644	-0.21607
H	-0.90643	1.57098	-1.28473
H	-2.36250	0.73364	1.30129
H	-0.86599	-1.56070	1.30980
H	-0.75670	-2.43095	-0.25575
H	-2.20458	-0.80290	-1.36215
H	-3.03087	-1.32914	0.10139
O	0.25245	-0.63361	-0.18987

24

Parent 5,6 oxonium 02

C	-1.26504	-1.29519	0.39440
C	-0.36138	0.78495	-0.67139
C	-1.85452	0.93084	-0.41985

C	-2.17365	-0.10252	0.68501
H	-1.73639	-2.09723	-0.17432
H	-0.74537	-1.69251	1.26702
H	-2.10098	1.94855	-0.10750
H	-2.41418	0.71076	-1.33315
H	-1.96219	0.30650	1.67574
H	-3.22442	-0.39867	0.66479
H	-0.07197	0.95899	-1.71065
C	0.58115	1.47440	0.30406
C	1.15964	-1.30915	-0.54276
C	2.04452	-0.58557	0.45395
C	2.01750	0.93222	0.21756
H	0.55815	2.54365	0.06373
H	2.64385	1.43578	0.95872
H	0.20167	1.37422	1.32822
H	2.44719	1.16322	-0.76585
H	1.48749	-1.17736	-1.57637
H	1.01903	-2.37165	-0.34159
H	1.73285	-0.82157	1.47901
H	3.05894	-0.98347	0.33661
O	-0.22287	-0.73489	-0.53630

25

24a

C	-0.60419	-1.65476	-0.14355
C	-1.88029	-1.34967	0.62176
H	-1.65532	-1.07828	1.65828
H	-2.55056	-2.21235	0.64058
C	-2.48235	-0.15952	-0.15332
H	-3.17866	0.42278	0.45578
H	-3.02313	-0.51293	-1.03561
C	-1.28391	0.69373	-0.57060
C	-0.80219	1.80431	0.35276
H	-1.23222	2.76495	0.05798
H	-1.10263	1.60506	1.38761
C	0.72753	1.77873	0.21372
H	1.04968	2.22579	-0.73265
H	1.23370	2.30872	1.02463
C	1.09133	0.30081	0.25132
C	2.35020	-0.13533	-0.40486
C	3.27247	-0.86955	0.22613

H	4.20871	-1.13277	-0.25524
H	3.13650	-1.21367	1.24895
H	2.51222	0.21320	-1.42293
H	0.98799	-0.11338	1.25889
O	-0.10338	-0.30290	-0.54562
H	-1.31606	1.01267	-1.61338
H	-0.77346	-2.18388	-1.08282
H	0.19858	-2.13523	0.41476

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24a’

C	-0.71774	-1.56650	-0.39347
H	-0.09357	-1.94201	0.41841
H	-0.56646	-2.15305	-1.29950
O	-0.25239	-0.18165	-0.71099
C	1.22539	0.27902	-0.55232
H	1.66471	0.01133	-1.51397
C	1.90201	-0.41581	0.57836
C	2.91868	-1.26436	0.38924
H	3.45004	-1.70486	1.22697
H	3.26704	-1.53205	-0.60570
H	1.59271	-0.15000	1.58798
C	0.99763	1.78266	-0.37402
H	0.87862	2.26096	-1.35081
H	1.85424	2.24294	0.12396
C	-0.29778	1.90404	0.45286
C	-1.23130	0.86979	-0.15335
H	-1.72801	1.24049	-1.05338
C	-2.15851	0.02886	0.70807
H	-1.76657	-0.05454	1.72748
H	-3.15547	0.47309	0.76272
C	-2.17134	-1.34480	0.00784
H	-2.52125	-2.14546	0.66403
H	-2.81623	-1.32577	-0.87574
H	-0.11595	1.68789	1.51052
H	-0.72700	2.90677	0.38568

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24b

C	1.37829	-1.66809	-0.13607
H	1.28301	-1.74297	-1.22276
H	0.62799	-2.28261	0.35960

C	2.80995	-1.84519	0.35077
H	2.82495	-2.08739	1.41768
H	3.31018	-2.65474	-0.18635
C	3.45755	-0.47101	0.08554
H	4.36874	-0.32318	0.67044
H	3.71263	-0.35882	-0.97378
C	2.38247	0.52924	0.48439
H	2.35778	0.70118	1.56287
C	2.16119	1.81026	-0.30942
H	2.65662	2.65810	0.17027
H	2.56991	1.70978	-1.32063
C	0.63175	1.97830	-0.35362
H	0.24395	2.36185	0.59456
H	0.30871	2.66128	-1.14366
C	0.09225	0.57971	-0.62719
H	0.31440	0.26973	-1.65302
C	-1.31159	0.23013	-0.25574
C	-1.82648	0.50851	1.02197
C	-3.14588	0.18299	1.33001
C	-3.96657	-0.41188	0.36446
C	-3.46348	-0.68828	-0.90833
C	-2.13750	-0.37512	-1.21509
H	-1.75035	-0.59006	-2.20817
H	-4.09815	-1.14674	-1.65976
H	-4.99598	-0.65717	0.60604
H	-3.53728	0.39687	2.31942
H	-1.20035	0.96959	1.78046
O	1.07895	-0.25528	0.23709

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24b’

C	-0.94208	-1.57432	-0.10693
H	-0.32738	-1.42514	0.78129
H	-0.40524	-2.16941	-0.84397
C	-2.35485	-2.03666	0.21664
H	-2.82298	-2.49794	-0.65821
H	-2.34835	-2.77209	1.02503
C	-3.07472	-0.73424	0.60217
H	-4.16303	-0.82550	0.56121
H	-2.79976	-0.41997	1.61560
C	-2.57656	0.26951	-0.42737

H	-3.09999	0.16635	-1.37962
C	-2.37244	1.72608	-0.00609
H	-2.52489	2.39427	-0.85850
H	-3.09038	2.00743	0.76876
C	-0.91839	1.81173	0.48737
H	-0.54609	2.84005	0.48827
H	-0.82359	1.42434	1.50576
C	-0.12789	0.97203	-0.49643
H	-0.15391	1.40940	-1.49608
C	1.23634	0.46383	-0.18311
C	2.08095	0.11925	-1.25430
C	3.37153	-0.35061	-1.01670
C	3.83724	-0.47203	0.29625
C	3.01162	-0.12019	1.36840
C	1.71714	0.34385	1.13292
H	1.09872	0.62552	1.97916
H	3.37791	-0.20027	2.38682
H	4.84502	-0.82933	0.48341
H	4.01535	-0.60983	-1.85092
H	1.72708	0.22800	-2.27654
O	-1.16072	-0.23190	-0.73855

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24c

C	-0.72345	-1.58394	0.34250
C	-2.17084	-1.38824	-0.08346
H	-2.31861	-1.73645	-1.10998
H	-2.84813	-1.94955	0.56487
C	-2.38375	0.13615	0.02250
H	-2.53294	0.43696	1.06496
C	-1.09956	0.73708	-0.52804
C	-0.46639	1.96829	0.10416
H	-0.73250	2.87154	-0.45063
C	1.04763	1.69437	0.06028
H	1.61107	2.32275	0.75407
C	1.17290	0.22288	0.46286
C	2.34938	-0.49423	0.03193
C	3.35996	-1.07018	-0.29458
H	4.25584	-1.57527	-0.58792
H	0.98660	0.08381	1.53391
O	-0.05616	-0.37203	-0.22961

H	1.45739	1.84042	-0.94297
H	-0.81127	2.09195	1.13624
H	-1.08941	0.77661	-1.61919
H	-3.24969	0.47095	-0.55398
H	-0.58311	-1.54707	1.42621
H	-0.21124	-2.44354	-0.08763

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24c’

C	-0.99986	-1.36523	-0.62858
H	-0.37725	-1.98382	0.01919
H	-1.09540	-1.80478	-1.62102
O	-0.27234	-0.06637	-0.82304
C	1.25707	0.03742	-0.78068
H	1.55788	-0.18796	-1.80601
C	1.82377	-0.90597	0.16354
C	2.36907	-1.67582	0.91960
H	2.85561	-2.35367	1.58907
C	1.41444	1.51538	-0.40024
H	1.28341	2.13517	-1.29211
H	2.40824	1.70479	0.00938
C	0.29000	1.76535	0.62242
C	-0.91967	1.05667	0.03664
H	-1.42939	1.65947	-0.71850
C	-1.89079	0.27701	0.90471
H	-1.39931	-0.06080	1.82295
H	-2.74840	0.89491	1.18289
C	-2.30223	-0.92089	0.02489
H	-2.73981	-1.73476	0.60827
H	-3.03114	-0.61790	-0.73257
H	0.55182	1.34445	1.59787
H	0.09156	2.83227	0.75120

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24d

C	1.76638	-1.66650	-0.20581
H	1.56210	-1.65090	-1.27982
H	1.01647	-2.25290	0.32353
C	3.21645	-1.99059	0.12341
H	3.31107	-2.30657	1.16656
H	3.59026	-2.79889	-0.50984
C	3.95541	-0.65917	-0.12246

H	4.92796	-0.63030	0.37512
H	4.11680	-0.49513	-1.19325
C	3.02205	0.39914	0.44500
H	3.11476	0.49949	1.52852
C	2.82898	1.73976	-0.24793
H	3.44387	2.51312	0.21930
H	3.11476	1.67225	-1.30299
C	1.32413	2.03534	-0.10611
H	1.07935	2.38348	0.90267
H	0.97650	2.79047	-0.81536
C	0.63821	0.69881	-0.38101
H	0.66412	0.44083	-1.44455
C	-0.70148	0.47802	0.22263
C	-1.77940	0.14111	-0.49539
H	-1.74116	-0.02521	-1.56916
C	-3.11084	-0.00305	0.17273
O	-3.29130	0.13194	1.36619
O	-4.05673	-0.30405	-0.72596
C	-5.40213	-0.46883	-0.21044
H	-5.42476	-1.28439	0.51482
H	-5.73245	0.45591	0.26635
H	-6.01407	-0.70099	-1.07977
H	-0.80556	0.64426	1.29372
O	1.62971	-0.26275	0.28932

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24d’

C	-1.59025	-1.53611	-0.80781
H	-0.65263	-1.69582	-0.27379
H	-1.49553	-1.82633	-1.85397
C	-2.80596	-2.09462	-0.07885
H	-3.63881	-2.23984	-0.77332
H	-2.57520	-3.05960	0.37903
C	-3.14309	-1.01249	0.96666
H	-4.16352	-1.10994	1.34553
H	-2.45665	-1.06356	1.81856
C	-2.96332	0.29445	0.21348
H	-3.81824	0.52353	-0.42727
C	-2.40125	1.53446	0.88772
H	-3.20304	2.21254	1.19029
H	-1.83386	1.26487	1.78397

C	-1.49036	2.17293	-0.17966
H	-2.08452	2.69069	-0.93861
H	-0.78853	2.89253	0.24843
C	-0.73795	1.00066	-0.81874
H	-0.53287	1.13743	-1.88110
C	0.45732	0.52577	-0.06945
C	1.65704	0.36008	-0.63999
H	1.82909	0.51828	-1.70182
C	2.83189	-0.04297	0.19637
O	2.76051	-0.30902	1.38030
O	3.94670	-0.07352	-0.54071
C	5.16695	-0.44549	0.15049
H	5.06710	-1.45062	0.56429
H	5.94585	-0.40974	-0.60838
H	5.36852	0.26528	0.95399
H	0.37207	0.37015	1.00533
O	-1.86038	-0.06245	-0.80865

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24e

C	-1.20570	0.25962	0.21364
C	-1.15178	1.71266	-0.25161
H	-2.07254	2.18625	0.10619
H	-1.19254	1.73026	-1.34731
C	0.08059	2.47858	0.24930
H	0.06649	3.49322	-0.15836
H	0.04245	2.57971	1.34168
C	1.37740	1.76688	-0.16324
C	1.39372	0.34154	0.34375
C	2.46256	-0.61917	-0.13450
H	3.39344	-0.47686	0.41998
H	2.66755	-0.45356	-1.19692
C	1.84739	-2.01206	0.11465
H	2.26472	-2.76830	-0.55305
H	2.03449	-2.33386	1.14246
C	0.34165	-1.84426	-0.11973
H	-0.01712	-2.22632	-1.07405
H	-0.28337	-2.21299	0.69388
O	0.14794	-0.35330	-0.20075
H	1.28117	0.30418	1.43519
H	2.25229	2.27684	0.25595

H	1.49337	1.76717	-1.25347
H	-1.21791	0.17140	1.30597
C	-2.29712	-0.53873	-0.41625
C	-3.22821	-1.18025	0.29647
H	-4.05603	-1.68860	-0.18751
H	-3.21063	-1.20238	1.38376
H	-2.35236	-0.50872	-1.50323

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24e’

C	1.23242	-0.18353	0.56957
C	1.53148	1.30121	0.78609
H	2.61983	1.41774	0.75033
H	1.21401	1.57206	1.79934
C	0.85019	2.22805	-0.23446
H	1.08311	3.26613	0.01842
H	1.25238	2.05953	-1.24083
C	-0.67492	2.02733	-0.23747
C	-1.03564	0.58374	-0.52044
C	-2.45569	0.09819	-0.30264
H	-3.08534	0.33060	-1.16504
H	-2.88840	0.58154	0.57923
C	-2.29951	-1.42307	-0.09397
H	-3.13876	-1.85019	0.45857
H	-2.23527	-1.93619	-1.05735
C	-0.98949	-1.58769	0.68194
H	-1.11315	-1.70254	1.75940
H	-0.32425	-2.35317	0.28107
O	-0.30676	-0.26450	0.51477
H	-0.64955	0.25274	-1.49117
H	-1.14634	2.64631	-1.00926
H	-1.10518	2.32590	0.72582
H	1.45138	-0.76288	1.46913
C	1.83458	-0.82695	-0.63681
C	2.52407	-1.97134	-0.56757
H	3.00289	-2.39618	-1.44422
H	2.65654	-2.50951	0.36858
H	1.75527	-0.30145	-1.58564

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24f

C	-0.01327	0.71777	-0.53378

C	-0.48383	2.05710	0.02321
H	0.14009	2.82240	-0.45175
H	-0.26463	2.09768	1.09541
C	-1.97170	2.33948	-0.22767
H	-2.24157	3.29688	0.22687
H	-2.15867	2.44134	-1.30472
C	-2.85152	1.22051	0.34892
C	-2.46073	-0.12327	-0.22702
C	-3.03768	-1.39451	0.36159
H	-4.04164	-1.58645	-0.02498
H	-3.10056	-1.30808	1.45104
C	-2.03310	-2.48544	-0.06399
H	-2.04172	-3.33783	0.61813
H	-2.27364	-2.85575	-1.06406
C	-0.66102	-1.80097	-0.06997
H	-0.02937	-2.03261	0.78534
H	-0.10028	-1.92796	-0.99636
O	-0.98228	-0.33652	0.06900
H	-2.53302	-0.12287	-1.32271
H	-3.90681	1.39064	0.10682
H	-2.77154	1.18510	1.44191
H	-0.19924	0.64398	-1.61081
C	1.39639	0.32397	-0.21101
C	1.87653	0.32451	1.11003
C	3.20151	-0.02022	1.37375
C	4.06373	-0.35304	0.32285
C	3.59677	-0.34752	-0.99329
C	2.26578	-0.01766	-1.25831
H	1.90823	-0.01216	-2.28519
H	4.26397	-0.59929	-1.81134
H	5.09696	-0.61227	0.53131
H	3.56462	-0.02182	2.39657
H	1.22005	0.58687	1.93470

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24f’

C	0.02168	0.73186	-0.38912
C	0.47569	2.00708	0.30827
H	0.32565	1.88360	1.38599
H	-0.21312	2.79902	-0.00120
C	1.93907	2.39669	-0.00888

H	1.97203	3.10692	-0.84016
H	2.36293	2.91445	0.85677
C	2.80397	1.17231	-0.37090
C	2.43409	-0.06138	0.42449
C	3.11936	-1.37054	0.04469
H	3.96726	-1.56682	0.70552
H	3.49779	-1.31199	-0.98155
C	2.02821	-2.45010	0.15654
H	2.26544	-3.34303	-0.42664
H	1.87355	-2.75344	1.19631
C	0.79097	-1.75821	-0.38175
H	0.78242	-1.67262	-1.47253
H	-0.16206	-2.13707	-0.01816
O	0.93548	-0.38135	0.17570
H	2.45193	0.11896	1.50179
H	3.86437	1.37625	-0.18285
H	2.72801	0.93812	-1.43973
H	0.24924	0.75284	-1.45938
C	-1.40199	0.31636	-0.16386
C	-2.23736	0.11488	-1.27246
C	-3.57980	-0.22682	-1.09226
C	-4.09117	-0.38400	0.19762
C	-3.26144	-0.19312	1.30849
C	-1.92472	0.16139	1.13124
H	-1.29171	0.30923	2.00145
H	-3.65855	-0.31448	2.31129
H	-5.13311	-0.65308	0.33960
H	-4.22088	-0.37124	-1.95595
H	-1.84439	0.23688	-2.27895

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24g

C	-1.23519	0.14698	0.43529
C	-1.39511	1.56070	-0.13214
H	-2.31288	1.96944	0.30331
H	-1.55971	1.48062	-1.21180
C	-0.19255	2.46352	0.17488
H	-0.34745	3.43831	-0.29573
H	-0.12382	2.64527	1.25527
C	1.11634	1.83973	-0.33437
C	1.32632	0.46386	0.25908

C	2.42028	-0.43794	-0.27361
H	3.38765	-0.17775	0.16320
H	2.49580	-0.33537	-1.36075
C	1.96550	-1.85562	0.13339
H	2.39032	-2.62268	-0.51702
H	2.27546	-2.07599	1.15826
C	0.43659	-1.84214	0.03516
H	0.02940	-2.30232	-0.86320
H	-0.07711	-2.21473	0.92211
O	0.09845	-0.37646	-0.10031
H	1.33154	0.49551	1.35641
H	1.97666	2.45633	-0.04999
H	1.11556	1.76845	-1.42827
H	-1.10609	0.15456	1.52507
C	-2.28127	-0.77154	0.03744
C	-3.20180	-1.49121	-0.27008
H	-4.01766	-2.12593	-0.54464

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24g’

C	-1.07386	0.60262	0.78738
C	-1.87236	-0.70164	0.90577
H	-2.93035	-0.42870	0.96790
H	-1.60034	-1.17266	1.85674
C	-1.61694	-1.66502	-0.26249
H	-2.17508	-2.58948	-0.09108
H	-1.99887	-1.23388	-1.19539
C	-0.11779	-1.98397	-0.40465
C	0.69617	-0.71913	-0.57827
C	2.20662	-0.75470	-0.46829
H	2.65812	-1.06749	-1.41307
H	2.51375	-1.46110	0.30951
C	2.59095	0.69593	-0.10152
H	3.55729	0.74670	0.40397
H	2.64838	1.31425	-1.00108
C	1.46740	1.19679	0.81093
H	1.69449	1.16096	1.87659
H	1.05649	2.16685	0.52801
O	0.37513	0.17768	0.62357
H	0.36826	-0.14191	-1.45018
H	0.06052	-2.61465	-1.28309

H	0.24752	-2.53533	0.46985
H	-1.06075	1.14072	1.73925
C	-1.45320	1.48694	-0.30321
C	-1.81119	2.24033	-1.17827
H	-2.13538	2.90529	-1.95077

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(*E*)-24h

C	-0.94642	-1.63967	0.22326
H	-0.73573	-1.59561	1.29543
H	-0.22253	-2.27393	-0.28663
C	-2.41003	-1.92352	-0.08513
H	-2.52324	-2.27478	-1.11511
H	-2.80916	-2.69304	0.58021
C	-3.09622	-0.55675	0.11305
H	-4.06923	-0.50725	-0.38196
H	-3.24616	-0.34720	1.17760
C	-2.12190	0.44138	-0.49543
H	-2.22001	0.50812	-1.58123
C	-1.88109	1.80038	0.14740
H	-2.47117	2.57673	-0.34605
H	-2.16657	1.78103	1.20464
C	-0.36787	2.03843	-0.00464
H	-0.11202	2.33803	-1.02637
H	0.00384	2.81125	0.67307
C	0.28132	0.69903	0.32644
H	0.22850	0.47307	1.39617
C	1.61456	0.40464	-0.24141
C	2.62109	-0.08113	0.51670
H	2.44568	-0.28772	1.57370
C	3.93226	-0.33277	0.04427
C	5.06569	-0.56240	-0.31926
H	6.06281	-0.75979	-0.64823
H	1.77259	0.63198	-1.29271
O	-0.76075	-0.26333	-0.32175

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(*E*)-24h’

C	-0.82758	-1.55513	-0.68628
H	0.06709	-1.73989	-0.08974
H	-0.68788	-1.90388	-1.70941
C	-2.11368	-2.01300	-0.00891

H	-2.91181	-2.14367	-0.74577
H	-1.96722	-2.96707	0.50338
C	-2.44676	-0.86483	0.96432
H	-3.49235	-0.88209	1.28160
H	-1.81828	-0.91663	1.85993
C	-2.13675	0.39159	0.16667
H	-2.94162	0.64866	-0.52647
C	-1.53662	1.62233	0.82652
H	-2.31030	2.35596	1.06634
H	-1.03087	1.35255	1.75933
C	-0.53782	2.16732	-0.21263
H	-1.06510	2.67945	-1.02305
H	0.17375	2.87217	0.22403
C	0.19443	0.94003	-0.76021
H	0.44216	1.00897	-1.81982
C	1.32851	0.43660	0.04727
C	2.49393	0.06024	-0.52492
H	2.58694	0.07948	-1.61201
C	3.64401	-0.35185	0.19051
C	4.65046	-0.71057	0.76345
H	5.53576	-1.02256	1.27396
H	1.23528	0.44365	1.13090
O	-1.01103	-0.07519	-0.77099

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24i

C	2.22051	1.60728	0.44671
H	2.20812	1.48608	1.53341
H	1.41828	2.26845	0.12203
C	3.60445	1.91694	-0.10584
H	3.52959	2.33799	-1.11287
H	4.12600	2.64060	0.52539
C	4.30459	0.54270	-0.12995
H	5.16952	0.53187	-0.79776
H	4.64614	0.26267	0.87235
C	3.22836	-0.41795	-0.61452
H	3.12371	-0.41213	-1.70157
C	3.09901	-1.81808	-0.02915
H	3.58116	-2.55665	-0.67450
H	3.57591	-1.86834	0.95558
C	1.58278	-2.05552	0.08454

H	1.13249	-2.28048	-0.88622
H	1.33426	-2.86765	0.77206
C	1.02850	-0.73329	0.61736
H	1.30099	-0.58123	1.66833
C	-0.35304	-0.42098	0.36681
C	-1.54034	-0.19668	0.19457
Si	-3.37394	0.13305	-0.06997
C	-4.21473	-0.13868	1.59134
H	-5.29271	0.03693	1.49854
H	-4.07524	-1.16356	1.95065
H	-3.83011	0.54545	2.35481
C	-3.97086	-1.08356	-1.37515
H	-3.83529	-2.12050	-1.05045
H	-3.43912	-0.95090	-2.32317
H	-5.03921	-0.93323	-1.56875
C	-3.51409	1.91878	-0.65205
H	-3.12557	2.61871	0.09512
H	-2.97329	2.08192	-1.59018
H	-4.56605	2.17167	-0.82783
O	1.92685	0.27049	-0.15041

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24i’

C	1.98407	1.43143	-0.99406
H	0.92919	1.55990	-0.74626
H	2.17451	1.66957	-2.04026
C	2.92770	2.08003	0.01095
H	3.91699	2.23396	-0.43033
H	2.54573	3.05253	0.33126
C	2.99282	1.06310	1.16778
H	3.86298	1.22390	1.80930
H	2.09296	1.11907	1.78900
C	3.07230	-0.28353	0.46923
H	4.07867	-0.50096	0.10356
C	2.38694	-1.51621	1.03701
H	3.09889	-2.14254	1.58027
H	1.58479	-1.23080	1.72412
C	1.81386	-2.24008	-0.19518
H	2.60432	-2.74245	-0.76084
H	1.05297	-2.97759	0.06618
C	1.20619	-1.12000	-1.04796

H	1.25771	-1.30792	-2.12254
C	-0.09675	-0.65178	-0.63549
C	-1.23293	-0.32650	-0.32729
Si	-3.00340	0.13778	0.11863
C	-3.38161	-0.66083	1.77971
H	-2.71238	-0.29703	2.56650
H	-3.29145	-1.75107	1.73187
H	-4.40842	-0.42658	2.08337
C	-4.09342	-0.53224	-1.25955
H	-3.83428	-0.09362	-2.22864
H	-5.14344	-0.29334	-1.05489
H	-4.01121	-1.62067	-1.34535
C	-3.05354	2.01861	0.21319
H	-2.38238	2.40574	0.98731
H	-4.06804	2.35054	0.46228
H	-2.78160	2.47946	-0.74226
O	2.29092	-0.02638	-0.84181

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24j

C	1.30102	-1.66438	0.38051
H	1.12396	-2.02378	-0.63449
H	0.50214	-1.99631	1.04016
C	2.71681	-1.89505	0.88075
H	2.76181	-1.80307	1.97023
H	3.06744	-2.89438	0.61088
C	3.53254	-0.78119	0.19587
H	3.74300	-1.04126	-0.84686
H	4.48537	-0.59681	0.69813
C	2.63292	0.44449	0.26677
H	2.71728	0.96961	1.22072
C	2.52805	1.40041	-0.91205
H	3.19787	2.25455	-0.78372
H	2.80388	0.89232	-1.84223
C	1.04996	1.82201	-0.93539
H	0.83844	2.56679	-0.16234
H	0.75281	2.24362	-1.89916
C	0.27481	0.54083	-0.66804
H	0.26904	-0.13383	-1.52678
C	-1.10664	0.63741	-0.09043
C	-1.53344	1.70534	0.56260

C	-1.97235	2.74967	1.20101
H	-1.88459	2.82772	2.28273
H	-2.45874	3.56775	0.67337
C	-1.98384	-0.55929	-0.31935
O	-1.55220	-1.57824	-0.83586
O	-3.23437	-0.38258	0.09495
C	-4.14630	-1.49599	-0.09674
H	-5.09980	-1.14850	0.29563
H	-3.79135	-2.36838	0.45473
H	-4.22364	-1.73467	-1.15875
O	1.21580	-0.16506	0.34274

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24j’

C	-1.00221	-1.25130	1.00791
H	-0.57273	-0.47706	1.64501
H	-0.30908	-2.08162	0.88238
C	-2.42311	-1.62438	1.40524
H	-2.52643	-1.66186	2.49254
H	-2.69160	-2.60639	1.00456
C	-3.27746	-0.51771	0.76437
H	-3.21374	0.41202	1.34145
H	-4.33170	-0.79439	0.68384
C	-2.65837	-0.34029	-0.61305
H	-2.97199	-1.12580	-1.30289
C	-2.62813	1.04797	-1.25246
H	-3.48907	1.63982	-0.93096
H	-2.66905	0.96460	-2.34198
C	-1.29487	1.67701	-0.81186
H	-1.35679	2.08889	0.20037
H	-0.98487	2.48405	-1.48068
C	-0.30040	0.53308	-0.86314
H	-0.09842	0.19334	-1.88046
C	0.98976	0.64152	-0.11000
C	1.25875	1.65907	0.69167
C	1.55580	2.66238	1.46387
H	1.99471	3.57137	1.05696
H	1.39380	2.61953	2.53887
C	2.00151	-0.42908	-0.41547
O	1.72267	-1.38298	-1.12003
O	3.18037	-0.21571	0.16440

C	4.21514	-1.20179	-0.09328
H	3.89699	-2.18065	0.26976
H	4.42095	-1.25305	-1.16368
H	5.08506	-0.84600	0.45491
O	-1.17735	-0.66201	-0.35847

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24v

C	2.53213	-0.87540	-1.51259
H	3.54869	-1.15176	-1.21992
H	2.54583	-0.19710	-2.36511
C	1.59609	-2.06853	-1.62778
H	0.71539	-1.81114	-2.22200
H	2.09824	-2.91360	-2.10518
C	1.20626	-2.36648	-0.16857
H	0.32239	-3.00339	-0.10694
H	2.02790	-2.86795	0.35403
C	0.93467	-0.99021	0.45162
C	1.44750	-0.73763	1.87835
H	0.63003	-0.81236	2.59786
H	2.21148	-1.47458	2.14864
C	2.05061	0.67474	1.84512
H	1.27497	1.44406	1.81915
H	2.70762	0.87438	2.69480
C	2.85208	0.69527	0.54204
H	3.76828	0.10000	0.63001
C	3.11938	1.98182	-0.06246
C	3.37944	3.06368	-0.53321
H	3.60573	4.02378	-0.94572
O	1.94383	-0.10778	-0.37475
C	-0.45405	-0.43935	0.17789
C	-1.55302	-1.14509	0.68813
C	-2.85946	-0.68957	0.50789
C	-3.09013	0.50021	-0.20150
C	-1.99547	1.21486	-0.71476
C	-0.69854	0.75275	-0.52435
H	0.12275	1.32956	-0.93428
H	-2.18434	2.13249	-1.26147
O	-4.30889	1.03309	-0.44045
C	-5.47488	0.36477	0.05067
H	-5.45901	0.29836	1.14433

H	-5.56786	-0.63601	-0.38584
H	-6.31737	0.97911	-0.26451
H	-3.67998	-1.26445	0.91898
H	-1.40593	-2.06691	1.24580

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24v'

C	-2.27526	1.47348	-1.06361
H	-3.34629	1.46913	-0.85773
H	-2.08133	1.55791	-2.13296
C	-1.49214	2.43196	-0.17598
H	-0.53326	2.68889	-0.63322
H	-2.05414	3.35506	-0.01383
C	-1.28145	1.64043	1.12710
H	-0.49660	2.07905	1.74603
H	-2.20618	1.60557	1.71243
C	-0.89072	0.23381	0.66343
C	-1.44116	-0.96223	1.44975
H	-0.67440	-1.37545	2.10745
H	-2.29950	-0.66343	2.05924
C	-1.87050	-1.97532	0.37653
H	-1.00068	-2.44337	-0.09183
H	-2.52072	-2.75853	0.77012
C	-2.61303	-1.12328	-0.66045
H	-2.52187	-1.49809	-1.68258
C	-3.99361	-0.82013	-0.32931
C	-5.16172	-0.63945	-0.07597
H	-6.19539	-0.48459	0.15051
O	-1.74926	0.13288	-0.65291
C	0.56497	0.09166	0.25039
C	0.98696	-0.17644	-1.06219
C	2.33690	-0.30857	-1.36645
C	3.30954	-0.17842	-0.36181
C	2.90192	0.08772	0.95547
C	1.54371	0.22008	1.24612
H	1.25825	0.42326	2.27556
H	3.62514	0.19326	1.75461
O	4.59303	-0.32458	-0.75871
C	5.64287	-0.20751	0.20654
H	5.65103	0.79010	0.65978
H	5.54927	-0.97364	0.98437

H	6.56733	-0.36294	-0.34820
H	2.66176	-0.51340	-2.38091
H	0.26370	-0.28201	-1.86316

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C	-1.79750	1.11170	-0.88780
C	-0.79131	2.03665	-0.25570
C	-0.17031	1.54121	1.06072
C	0.86170	0.43576	0.95681
C	2.12864	0.70678	0.14822
C	2.45601	-0.60413	-0.59197
C	1.09818	-1.13571	-1.00241
H	1.02065	-2.21665	-1.11169
H	0.65210	-0.61982	-1.85544
O	0.26949	-0.79207	0.20436
C	-1.16234	-1.08080	0.17238
C	-1.97633	-0.20286	-0.66735
H	-2.82138	-0.69983	-1.13698
C	-1.52131	-2.16841	0.85342
H	-2.56224	-2.47223	0.87074
H	-0.80237	-2.76681	1.40088
H	2.96055	-1.31661	0.06706
H	3.09265	-0.43626	-1.46388
H	2.93879	1.01155	0.81530
H	1.96343	1.51717	-0.56728
H	1.08195	0.00741	1.93659
H	-0.96491	1.23884	1.75124
H	0.35311	2.37174	1.55223
H	-1.30801	2.98068	-0.04654
H	-0.01966	2.30742	-0.99061
H	-2.49318	1.58878	-1.57454