Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Enantioselective rhodium-catalysed insertion of trifluorodiazoethanes into tin hydrides

Stephen Hyde,[a] Janis Veliks,[a] David M. H. Ascough,[a] Robert Szpera,[a] Robert S. Paton,[a,b] Véronique Gouverneur*[a]

[a]Department of Chemistry, University of Oxford, Chemistry Research Laboratory, Mansfield Road, OX1 3TA, UK [b] Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA.

ARTICLE INFO

Article history:
Received
Received in revised form
Accepted

Available online

Keywords:
Stannane
Asymmetric insertion
trifluorodiazoethane
Silane
Germanium hydride

ABSTRACT

Aryl substituted 2,2,2-trifluorodiazoethanes undergo rhodium(II)-catalysed insertion reactions with tin hydrides affording the corresponding α-(trifluoromethyl)benzyl stannanes. This reactivity contrasts with that of diazo esters which predominantly afford CH_2 reduction products in the presence of tin hydrides. The first example of asymmetric insertion into tin hydrides using diazo compounds is also described. In addition, this system extends to asymmetric germanium hydride and silane insertion.

1. Introduction

The insertion of diazo compounds into carbon-hydrogen and heteroatom-hydrogen bonds is well-documented.[1,2,3,4] Insertion reactions where X-H (X = C, Si, S, O, N, B, P) bonds are cleaved by Rh, Cu, or other metal carbenoid intermediates, have been well studied both in racemic[5,6,7,8,9,10,11] and asymmetric[12,13] settings. Insertion into trialkyltin hydrides has received relatively little attention, despite several early reports supporting the feasibility of such insertion with carbenes.[14,15,16] In 1995, Landais and co-workers reported an isolated example of trialkyltin hydride insertion with diazo esters (Figure 1a).[17] Wang later showed that tin hydride enables the reduction of diazo carbonyl compounds, a process resulting from *in situ* protodestannylation of the tin hydride insertion product (Figure 1b).[18]. More recently, the groups of Wang and Bi have disclosed insertion into the Sn-H bond leading to stable benzyltributylstannanes.[19,20] Both methods generate the diazo intermediate *in situ* from a tosyl- or nosylhydrazone, however neither system offer a route to asymmetric insertion (Figure 1c and 1d). Our group extended X-H insertion to trifluorodiazoalkanes.[21] Under Cu catalysis, Si-H, S-H, N-H, B-H, and P-H bonds were successfully cleaved, and an asymmetric protocol was developed for silanes and boranes (Figure 1e). However, tributyltin hydride gave a low yield of the insertion product under our standard reaction conditions. Herein, we report the successful development of a rhodium catalyzed tributyltin hydride insertion with aryl-substituted 2,2,2-trifluorodiazoethanes, as well as extension to an asymmetric catalytic protocol (Figure 1f). This system is also suitable for asymmetric insertion into germanium hydrides and silanes.

2. Results and discussion

The starting materials for this study, aryl-substituted 2,2,2-trifluorodiazoethanes, were prepared according to previously reported literature procedures.[22,23] Optimization studies of the tributyltin hydride insertion reaction were performed using 4-(1-diazo-2,2,2-trifluoroethyl)-1,1'-biphenyl (**1a**) as the model substrate (Table 1). Under our previously reported conditions,[21] involving slow addition over one hour of diazo compound to a mixture of $Cu(MeCN)_4PF_6$ (4 mol%) and tributyltin hydride (2 equivs), only 26% of the desired product **2a** was obtained, in addition to the reduced product.

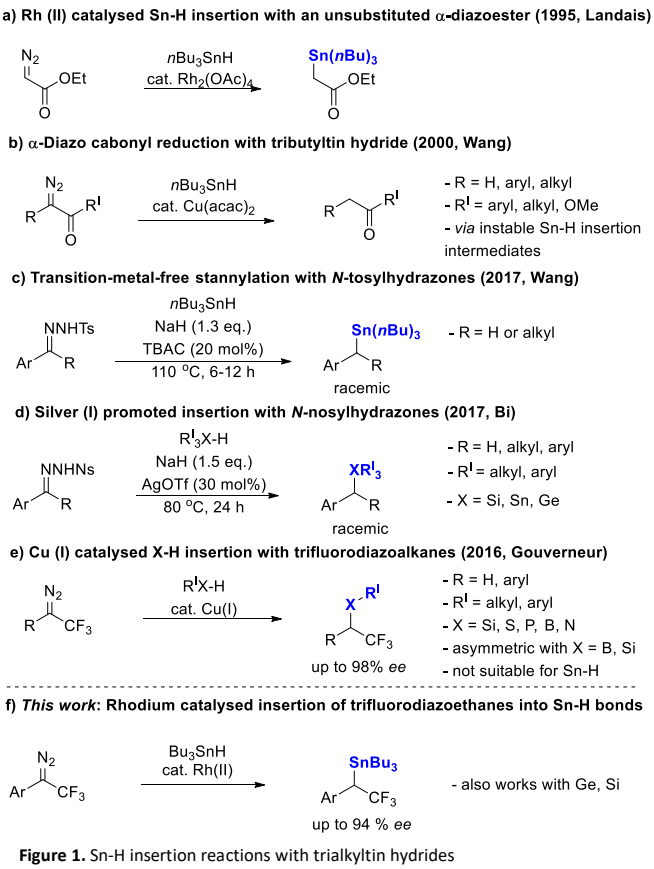
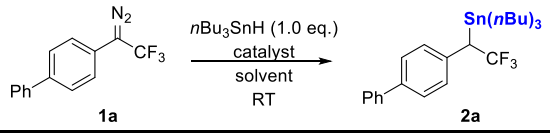


Figure 1. Sn-H insertion reactions with trialkyltin hydrides

(Table 1, entry 1). Decreasing the amount of nBu$_3$SnH to 1.0 equivalents and changing the order of addition were not beneficial (Table 1, entries 2 and 3). Under Rh$_2$(OAc)$_4$ catalysis, comparably poor results were obtained (entry 4). When the reaction was performed by fast addition of Rh(II) catalyst to an equimolar mixture of diazo compound **1a** and nBu$_3$SnH in dichloromethane in an open vial, almost instantaneous evolution of nitrogen and disappearance of the characteristic orange colour of the diazo compound **1a** was observed (Table 1, entry 5). The desired insertion product **2a** was isolated in 64% yield. Cu(II) and Rh(I) were ineffective for this transformation (entries 6 and 7). Screening various solvents highlighted dichloromethane as the optimum solvent for Sn-H insertion (entry 5 vs. entries 8-11).

Table 1. Optimization studies for Sn-H insertion[a]



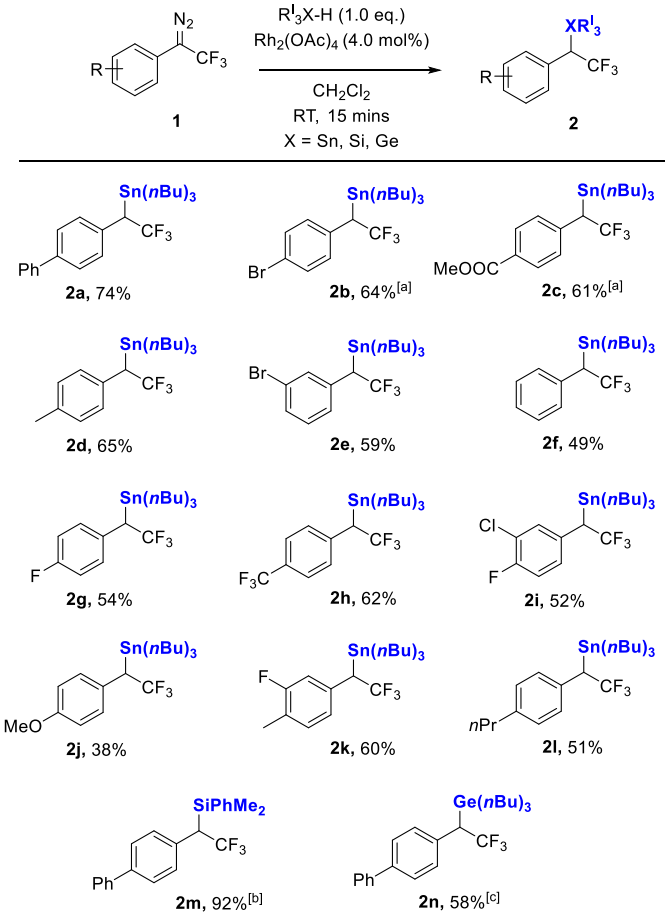
Entry	Catalyst	Solvent	Procedure[c]	Yield[d]
1[b]	Cu(MeCN)$_4$PF$_4$	CH_2Cl_2	**A**	26
2	Cu(MeCN)$_4$PF$_4$	CH_2Cl_2	**B**	4
3	Cu(MeCN)$_4$PF$_4$	CH_2Cl_2	**C**	traces
4	Rh$_2$(OAc)$_4$	CH_2Cl_2	**A**	25
5	Rh$_2$(OAc)$_4$	CH_2Cl_2	**C**	64
6	Cu(OAc)$_2$	CH_2Cl_2	**C**	traces
7	Rh(PPh)$_3$Cl	CH_2Cl_2	**C**	(6)
8	Rh$_2$(OAc)$_4$	$CHCl_3$	**C**	(43)
9	Rh$_2$(OAc)$_4$	Toluene	**C**	(59)
10	Rh$_2$(OAc)$_4$	Hexane	**C**	(43)
11	Rh$_2$(OAc)$_4$	DCE	**C**	(45)
12	**Rh$_2$(OAc)$_4$**	**CH_2Cl_2**	**D**	**74**
13	Rh$_2$(OAc)$_4$[e]	CH_2Cl_2	**D**	67
14	Rh$_2$(OAc)$_4$[f]	CH_2Cl_2	**D**	74

[a] All reactions performed on a 0.1 mmol scale with 1.0 eq. of **1a** and nBu$_3$SnH, with 4.0 mol% catalyst loading, unless stated otherwise. [b] 2.0 eq. of nBu$_3$SnH. [c] Procedure A: Syringe pump addition of **1a** solution to a mixture of cat. and nBu$_3$SnH in dichloromethane over 1h. Procedure B: Syringe pump addition of **1a** and nBu$_3$SnH solution to a catalyst suspension in dichloromethane over 1h. Procedure C: **1a** and nBu$_3$SnH added to vial and dissolved in dichloromethane (not degassed). The catalyst was then added. Procedure D: **1a** and nBu$_3$SnH added to a vial and dissolved in dichloromethane under anhydrous conditions. In a separate vial was added the catalyst and dichloromethane. The mixture of **1a** and nBu$_3$SnH was added to the catalyst suspension. [d] All yields are those of isolated products unless stated otherwise. ^{1}H and ^{19}F NMR yields, using ethyl trifluoroacetate as internal reference, are shown in parenthesis. [e] 2 mol% of catalyst. [f] 10 mol% of catalyst.

When the reaction was performed under an argon atmosphere with degassed dichloromethane, and the reagent mixture quickly transferred to the catalyst under inert atmosphere, the yield of the desired product **2a** was further improved to 74% (entry 12). The use of 4 mol% of Rh$_2$(OAc)$_4$ was optimal for this transformation (entry 12 vs. 13 and 14).

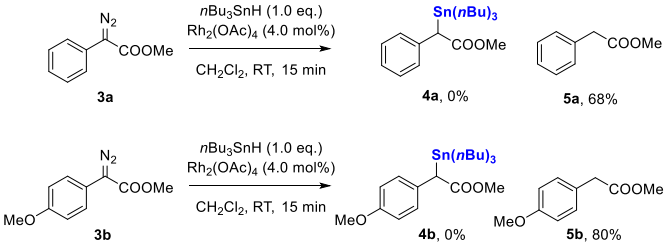
After optimisation of the reaction conditions, the substrate scope was investigated. Various substituents such as alkyl, aryl, halide, and CF_3 are tolerated on the phenyl group giving good to moderate yields of the insertion products **2**. The limitations for this transformation are highlighted by the electron rich methoxy- substituted substrate **1j** which gives a low yield of 38%.

This procedure was also efficient for PhMe$_2$SiH and nBu$_3$GeH insertion, delivering silane **2m** and organogermanium **2n** in good yields.



Scheme 1. Rhodium-catalysed insertion into Sn-H bonds with aryl substituted trifluorodiazoethanes. All reactions performed on 0.1 mmol scale following procedure D (table 1) unless stated otherwise. All yields are those of isolated products. [a] Procedure C. [b] 1.0 eq. of PhMe$_2$SiH instead of nBu$_3$SnH. [c] 1.0 eq. of nBu$_3$GeH instead of nBu$_3$SnH.

When these reaction conditions were applied to diazo esters **3a** and **3b**, the crude ^{1}H NMR spectra indicated mixtures of stannanes **4** and reduction products **5**, and upon workup, only the latter were isolated (scheme 2). These examples highlight the instability of α-carbonyl stannanes, which is consistent with previous literature.[18]



Scheme 2. Reactivity of diazo esters towards nBu$_3$SnH

Given that Wang proposed that α-carbonyl stannanes undergo protodestannylation via a putative radical pathway, radical stabilization enthalpies (RSE), which are derived from bond dissociation enthalpies (BDE), may account for the difference in stability of the stannane products. Due to the paucity of experimental tin bond dissociation enthalpies, we performed quantum mechanical calculations in Gaussian 09 rev. D.0.1.[24] Computation of tin bond dissociation enthalpies is challenging, due to relativistic effects, and

lack of experimental data for benchmarking. Grindley and Boyd have benchmarked organotin bond dissociation energies, finding a strong method dependence; we use the B3LYP/SDB-aug-cc-pVTZ//B3LYP/def2-SVPD level of theory described by the latter.[25,26] We also computed the corresponding proto derivatives using the higher G4 method for comparison and confirm good correlation of RSEs (see SI).[27]

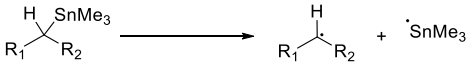


Table 2. Computed bond enthalpies in kcal/mol[a]

Entry	Stannane	R_1	R_2	BDE	RSE
1	**6a**	H	H	63.6	0.0 (defined)
2	**6b**	H	CO_2Et	58.6	5.0
3	**6c**	C_6H_5	CF_3	47.2	16.4
4	**6d**	C_6H_5	CH_3	41.8	21.8
5	**6e**	C_6H_5	CO_2Me	42.7	20.9

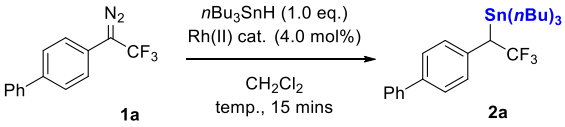
[a] Values computed at the B3LYP/SDB-aug-cc-pVTZ//B3LYP/def2-SVPD level of theory, BDE – bond dissociation enthalpy, RSE – radical stabilization energy.

Of the compounds calculated, the RSE corresponding to stannane **6b** (5.0 kcal/mol) is lower than the other compounds investigated by at least 10 kcal/mol (Table 2, entry 2). This is consistent with the low propensity for this compound to undergo protodestannylation via a radical pathway. In contrast, the phenyl-substituted ester **6e** has a much higher RSE (20.9 kcal/mol) consistent with the protodestannylation observed experimentally (Table 2, entry 5).[18] Compound **6c** has significantly lower RSE than the non-fluorinated derivative **6d** with RSEs of 16.4 kcal/mol and 21.8 kcal/mol respectively (Table, entries 3 and 4). This is consistent with reports of the destabilizing effect of trifluoromethyl substitution on carbon-centered radicals.[28] Additionally, we find the RSE corresponding to **6d** and the phenyl substituted ester **6e** to be similar (RSE = 21.8 kcal/mol and 20.9 kcal/mol respectively).

Despite asymmetric heteroatom-hydrogen insertion reactions with diazo compounds having been extensively studied for many nucleophiles,[12] to date there are no examples of catalytic enantioselective Sn-H insertion reactions. This is possibly due to α-diazo carbonyl compounds generating unstable stannane insertion products.[18] Since aryl 2,2,2-trifluorodiazoethanes are converted into stable Sn-H insertion products, we sought to develop an asymmetric protocol.

Optimization studies for an asymmetric insertion reaction were performed by testing a range of chiral Rh(II) catalysts (Table 3, entries 1 to 4). For operational simplicity, the chiral catalyst was added to a solution of diazo compound **1a** and tributyltin hydride in dichloromethane in an open vial, a process which allowed for the rapid identification of Rh_2(S-tertPTTL)$_4$ as the most efficient catalyst affording **2a** in 90% ee but low yield (entry 4).[29,30] When the reaction was performed under inert atmosphere in degassed solvent, a significant improvement of yield was achieved in addition to slight increase of enantioselectivity (entry 5). Decreasing temperature improved ee, however the yield was diminished (entries 6 and 7). At -78 °C, enantioenriched stannane **2a** was isolated in 57% yield and 94% ee.

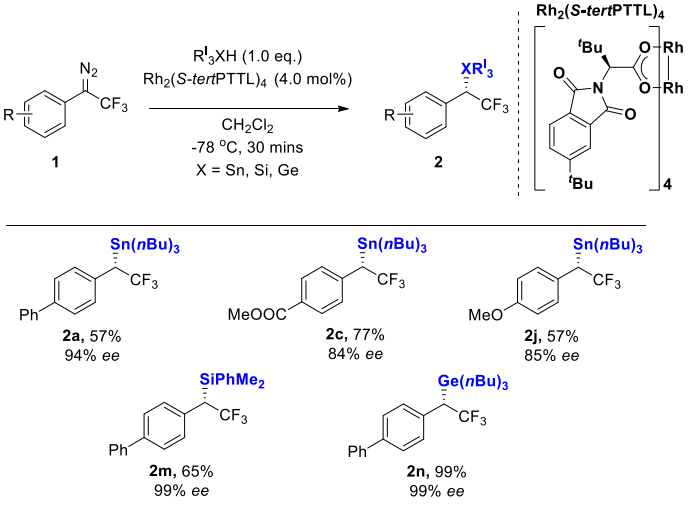
Table 3. Optimization studies for asymmetric insertion **1a** into nBu$_3$SnH[a]



Entry	Procedure	Catalyst	T/ °C	Yield 2a/ %	*ee*/ %
1	A	Rh_2(*S*-DOSP)$_4$	RT	78	7
2	A	Rh_2(*R*-PTAD)$_4$	RT	19	79
3	A	Rh_2(*R*-BTPCP)$_4$	RT	78	-26
4	A	Rh_2(*S*-*tert*PTTL)$_4$	RT	36	-90
5	B	Rh_2(*S*-*tert*PTTL)$_4$	RT	82	-91
6	B	Rh_2(*S*-*tert*PTTL)$_4$	0	74	-92
7[c]	B	Rh_2(*S*-*tert*PTTL)$_4$	-78	57	-94

Yields are those of isolated products. [a] Procedure A: Diazo and stannane added to vial and dissolved in dichloromethane. To the mixture was added the catalyst. Procedure B: (anhydrous conditions) Diazo and stannane added to a vial and dissolved in dichloromethane. In a separate vial was added the catalyst and more dichloromethane. The diazo/stannane mixture was added to the catalyst suspension. [c] Reaction time 30 minutes.

Comparable results were achieved when electron poor ester **1c** and electron rich 4-methoxy substituted diazo compound **1j** were subjected to the asymmetric insertion protocol, affording stannanes **2c** and **2j** with good to moderate yields with good enantioselectivities. In addition, these optimized reaction conditions were highly efficient for $PhMe_2SiH$ and nBu$_3$GeH asymmetric insertion, affording silane **2m** and organogermanium **2n** in good and excellent yields respectfully, both with 99% ee (scheme 3).



Scheme 3. Asymmetric rhodium-catalysed insertion into X-H bonds (X = Sn, Ge, Si) with trifluorodiazoethanes. Absolute configuration determined by comparison of $[\alpha]^D$ value of **2m** with that reported in the literature.[21] Absolute configuration of other substrates assigned by analogy with **2m**.

3. Conclusion

In summary, we have developed a Rh(II) catalysed trialkyltin hydride insertion reaction into 1-aryl-2,2,2-trifluorodiazoethanes. In contrast to products of Sn-H insertion of α-carbonyl diazo compounds, the α-(trifluoromethyl)benzyl stannanes are bench stable. In addition, the first asymmetric tin hydride insertion with diazo compounds has been disclosed delivering enantioenriched α-(trifluoromethyl)benzyl stannanes. The use of the stannane products in palladium catalyzed cross coupling is challenging due to their propensity to undergo β-fluoride elimination. However, a recent report has demonstrated that secondary α-(trifluoromethyl)benzyl tosylates can

undergo cross coupling without β-fluoride elimination, suggesting that the same might possible for the corresponding stannanes disclosed within.[31]

4. Experimental

4.1 General Information

All NMR spectra were recorded on Bruker DPX200, AV400 or AV500 spectrometers and are reported as chemical shifts (δ) in parts per million (ppm). ^{1}H and ^{13}C NMR spectra are referenced relative to residual undeuterated solvent peak. ^{19}F NMR spectra are referenced relative to $CFCl_3$. Coupling constants (J) are reported in units of hertz (Hz). The following abbreviations are used to describe multiplets: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintuplet), sept (septet), m (multiplet), br (broad). High resolution mass spectra (HRMS, m/z) were recorded on a Bruker MicroTOF spectrometer using electrospray ionization (ESI), electron ionisation (EI) or chemical ionisation (CI). Infrared spectra were recorded as neat compound using a Bruker Tensor 27 FT-IR spectrometer. Absorptions are reported in wavenumbers (cm^{-1}) and only peaks of interest are reported. Melting points of solids were measured on a Griffin apparatus and are uncorrected. Thin layer chromatographies (TLC) were performed using Merck aluminium-foil baked plates precoated with Kieselgel 60 F254. The products were visualized using UV fluorescence (254 nm) or potassium permanganate stain. Flash column chromatography columns were performed over Merck silica gel C60 (40 60 μm) using eluent systems as described for each experiment. All solvents and chemicals were purchased from Sigma-Aldrich, Acros, Alfa Aesar, Fluorochem or Apollo Scientific, and used without further purification, unless stated otherwise.

4.2 Preparation of diazo substrates **1**

All diazo compounds **1** were prepared from the corresponding trifluoroacetophenones, either via general procedure A followed by general procedure B, or in a telescoped process using general procedure C. The trifluoroacetophenones were prepared according to literature procedures.[23,32]

General procedure A: preparation of hydrazone diazo precursors **1'**

Procedure from Wang et al.[33] To a round bottom flask equipped with a reflux condenser was added tosylhydrazide (1.0 eq.) and the minimum quantity of solvent (either methanol or toluene according to individual substrates) needed to dissolve the hydrazide at reflux (approximately 1.5 M). Subsequently the reaction was cooled to room temperature and trifluoroacetophenone (1.0 eq.) was added in one portion. The reaction mixture was then stirred at 65 °C (MeOH) or 90 °C (Toluene) over 4-16 h (monitored by TLC). The solution was cooled to room temperature or 0 °C, at which point the product precipitated out of solution (precipitation can be induced by addition of pentane). The precipitate was collected by vacuum filtration and washed with pentane, in which case it was used without further purification. If no precipitation occurred, the solvent was removed under reduced pressure and the residue used in the next step without further purification. Hydrazone derivatives were found to be unstable on silica gel.

General procedure B: preparation of diazo substrates **1**

CAUTION: diazo compounds are presumed to be toxic and potentially explosive and should be handled with care, in a fume hood.[34] Procedure from Xu et al.[35] The Tosyl hydrazone (1.0 eq.) was refluxed in a solution of KOH (2 eq.) in MeOH (0.4 M) for 1 h or until the colour of the solution no longer intensified. The reaction was then cooled to room temperature and diluted with water. The crude product was extracted with CH_2Cl_2 or pentane (see individual substrates for details), washed with saturated solutions of $NaHCO_3$ and brine, dried with $MgSO_4$, concentrated under reduced pressure, and purified by silica gel chromatography.

General procedure C: telescoped preparation of diazo substrates **1**

CAUTION: diazo compounds are presumed to be toxic and potentially explosive and should be handled with care, in a fume hood.[34] To a mixture of tosyl hydrazine (1.0 eq.) in MeOH (1.5 M) was added ketone (1.0 eq). The reaction mixture was heated to reflux for 18 h then allowed to cool to room temperature. Solvent was evaporated under reduced pressure and the residue triturated with pentane, dried under vacuum and used in subsequent steps without additional purification. To the residue was added KOH (2.0 equiv.) in MeOH (0.4 M) and the reaction mixture heated to reflux for 1–2 hours, during which the characteristic red colour of diazo compounds appeared. The reaction mixture was allowed to cool to room temperature, poured into water and extracted with pentane (x3). The combined organic layers were dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography.

N'-(1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (**1'a**)

Prepared following general procedure A from the corresponding trifluoroacetophenone (6.7 g, 36 mmol.), in toluene (90 °C, 12 h). Purified by precipitation upon cooling to room temperature and subsequent filtration. Obtained as an off-white solid (11.4 g, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.84 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 7.73 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 7.60 (m, 2H), 7.50 (m, 2H), 7.43 (m, 1H), 7.35 (m, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 144.7, 141.6 (q, $^{2}J_{CF}$ = 35.7 Hz), 139.7, 134.7, 130.1, 129.3, 128.9, 128.8, 128.6, 128.2, 127.4, 124.0, 120.2 (q, $^{1}J_{CF}$ = 271 Hz), 21.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.1 (s, 3F). Data consistent with literature values.[23]

4-(1-diazo-2,2,2-trifluoroethyl)-1,1'-biphenyl (**1a**)

Prepared following general procedure B from tosylhydrazone **1'a** (7.41 g, 17.1 mmol). Purified by silica gel chromatography (pentane) and obtained as a orange/red solid (1.86 g, 40 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (m, 2H), 7.29 (m, 2H), 7.23 (m, 2H), 7.14 (m, 1H), 6.81 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 129.2, 128.0, 127.9, 127.7, 127.6, 126.3 (q, $^{1}J_{CF}$ = 270 Hz), 125.6, 123.2, 122.1 (C=N_2 not observed). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.4 (s, 3F). Data consistent with literature values.[36]

N'-(1-(4-bromophenyl)-2,2,2-trifluoroethylidene)-4-methylbenzenesulfonohydrazide (**1'b**)

Prepared following general procedure A from 4'-bromo-2,2,2-trifluoroacetophenone (2.43 g, 9.6 mmol.) in toluene (90 °C, 12 h). Purified by precipitation upon cooling to room temperature and subsequent filtration. Obtained as an off-white solid (3.72 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H) 7.81 (m, 2H), 7.60 (m, 2H), 7.36 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H), 7.15 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 140.5 (q, $^{2}J_{CF}$ = 36.0 Hz), 134.5, 133.7, 130.1, 130.0, 128.4, 126.8, 124.3, 120.0 (q, $^{1}J_{CF}$ = 273 Hz), 21.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.2 (s, 3F). Data consistent with literature values.[33]

1-bromo-4-(1-diazo-2,2,2-trifluoroethyl)benzene (**1b**)

Prepared following general procedure B from tosylhydrazone **1'b** (3.5 g, 8.3 mmol.). Purified by silica gel chromatography (pentane) and obtained as a deep-red liquid (1.21 g, 55 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (m, 2H), 6.97 (d, $^{3}J_{HH}$ = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.5, 125.7 (q, $^{1}J_{CF}$ = 270

Hz), 123.8, 122.9, 119.7 (C=N_2 not observed). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.6 (s, 3F). Data consistent with literature values.[23]

methyl-4-(2,2,2-trifluoro-1-(2-tosylhydrazineylidene)ethyl)benzoate (**1'c**)

Prepared following general procedure A from corresponding trifluoroacetophenone (3.0 g, 12.9 mmol.) in toluene (90 °C, 12 h). Purified by precipitation upon cooling to room temperature and subsequent filtration. Obtained as an off-white solid (4.36 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96, (s, 1H), 7.84 (m, 2H), 7.35 (m, 4H), 7.15 (d, 2H), 2.49 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 145.0, 140.4 (q, $^2J_{CF}$ = 36.5 Hz), 134.5, 133.2, 131.2, 130.0, 129.7, 128.6, 128.2, 120.0 (q, $^1J_{CF}$ = 273.0 Hz), 53.0, 21.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.1 (s, 3F). Data consistent with literature values.[23]

methyl 4-(1-diazo-2,2,2-trifluoroethyl)benzoate (**1c**)

Prepared following a modification of general procedure B: To a solution of tosylhydrazone **1'c** (1.12 g, 2.8 mmol.) in MeOH (10 mL) was added NaOMe (303 mg, 5.6 mmol., 2 eq.). A condenser was attached, and the reaction mixture refluxed for 1 h. The reaction was cooled to room temperature and diluted with water. The crude product was extracted with CH_2Cl_2, washed with saturated solutions of $NaHCO_3$ and brine, dried with $MgSO_4$, concentrated under reduced pressure, and purified by silica gel chromatography (pentane/CH_2Cl_2 90:10) and obtained as an orange solid (414 mg, 63 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 6.73 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 3.60 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.4, 126.3, 125.2 (q, $^1J_{CF}$ = 269.0 Hz), 124.1, 123.3, 122.5, 119.2 (C=N_2 not observed). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.5 (s, 3F). Data consistent with literature values.[23]

4-methyl-N'-(2,2,2-trifluoro-1-(p-tolyl)ethylidene)benzenesulfonohydrazide (**1'd**)

Prepared following general procedure A from 2,2,2-trifluoro-1-(p-tolyl)ethan-1-one (1.0 g, 5.31 mmol.) in methanol (65 °C, 18 h). Purified by cooling to room temperature and subsequent filtration and washing with pentane. Obtained as a white solid (0.73 g, 38 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 1H) 7.81 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.32 (m, 4H), 7.13 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 2.42 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 142.1, 141.8 (q, $^2J_{CF}$ = 35.8 Hz), 134.6, 130.7, 129.9, 128.0, 122.1, 119.0 (q, $^1J_{CF}$ = 275 Hz), 21.7, 21.5 (C=N_2 not observed). ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.4 (s, 3F). Data consistent with literature values.[33]

1-(1-diazo-2,2,2-trifluoroethyl)-4-methylbenzene (**1d**)

Prepared following general procedure B from tosylhydrazone **1'd** (0.72 g, 2.0 mmol), purified by silica gel chromatography (pentane) and obtained as a red liquid (169 mg, 42 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 6.75 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 1.98 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.2, 130.7, 126.9 (q, $^1J_{CF}$ = 270 Hz), 123.1, 120.6, 60.2 (q, $^2J_{CF}$ = 43.9 Hz), 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.5 (s, 3F). Data consistent with literature values.[23]

1-bromo-3-(1-diazo-2,2,2-trifluoroethyl)benzene (**1e**)

Prepared following general procedure C from 3'-bromo-2,2,2-trifluoroacetophenone (2.0 g, 7.9 mmol.). Purified by silica gel column chromatography (pentane) and obtained as a red oil (120 mg, 6 % over two steps). ^{1}H NMR (500 MHz, C_6D_6): 7.02 – 6.88 (m, 2H), 6.55 (t, J = 7.9 Hz, 1H), 6.52 – 6.45 (m, 1H). ^{13}C NMR (125 MHz, C_6D_6): δ 130.6, 128.7, 125.8, 125.5 (q, $^1J_{CF}$ = 269.3 Hz), 124.7, 123.5, 120.4, (C=N_2 not observed). ^{19}F NMR (471 MHz, C_6D_6) δ -57.5 (s, 3F). IR (neat) υ/ cm^{-1}: 3071, 2082, 1594, 1561, 1481, 1349, 1324, 1261, 1172, 1106, 993, 968, 860, 773, 760, 710, 700, 678.[39]

4-methyl-N'-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonohydrazide (**1'f**)

Prepared following general procedure A from trifluoroacetophenone (2.09 g, 12 mmol.), in methanol (65 °C, 12 h). Purified by precipitation upon cooling to room temperature and subsequent filtration. Obtained as an off-white solid (2.79 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H) 7.81 (m, 2H), 7.50 (m, 3H), 7.35 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 7.25 (m, 2H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 141.4 (q, $^2J_{CF}$ = 35.7 Hz), 134.6, 130.1, 130.1, 128.3, 128.1, 125.3, 120.1 (q, $^1J_{CF}$ = 273 Hz), 21.8 (unable to see C=N_2). ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.2 (s, 3F). Data consistent literature values.[22]

(1-diazo-2,2,2-trifluoroethyl)benzene (**1f**)

Prepared following general procedure B from tosylhydrazone **1'f** (2.91 g, 8.5 mmol.). Purified by silica gel chromatography (pentane) and obtained as a volatile red liquid (544 mg, 35 %). ^{1}H NMR (400 MHz, C_6D_6) δ 7.42 (m, 2H), 7.21 (m, 1H), 7.12 (d, $^3J_{HH}$ = 8.2 Hz, 2H). ^{13}C NMR (126 MHz, C_6D_6) δ 130.0, 126.7 (q, $^1J_{CF}$ = 269 Hz), 126.5, 123.9, 122.9 (C=N_2 not observed). ^{19}F NMR (376 MHz, C_6D_6) δ - 57.3 (s, 3F). Data consistent with literature values.[22]

4-methyl-N'-(2,2,2-trifluoro-1-(4-fluorophenyl)ethylidene)benzenesulfonohydrazide (**1'g**)

Prepared following general procedure A from 2,2,2,4'-tetrafluoroacetophenone (1.0 g, 5.20 mmol.) in methanol (65 °C, 12 h). Purified by cooling to room temperature and subsequent filtration and washing with pentane. Obtained as a white solid (1.45 g, 77 %). Used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.80 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.29-7.19 (m, 4H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.2 (d, $^1J_{CF}$ = 252.7 Hz), 145.2, 134.5, 130.9, 130.8, 130.0, 128.2, 120.1 (q, $^1J_{CF}$ = 274.9 Hz), 117.7, 117.5, 21.8. ^{19}F NMR (377 MHz, $CDCl_3$): δ -68.4 (s, 3F), -106.6 (m, 1F). Data consistent with literature values.[33]

1-(1-diazo-2,2,2-trifluoroethyl)-4-fluorobenzene (**1g**)

Prepared following general procedure B from tosylhydrazone **1'g** (1.45 g, 4.0 mmol). Purified by silica gel chromatography (pentane) and obtained as a orange/red liquid (250 mg, 31 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.06 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.7 (d, $^1J_{CF}$ = 246.8 Hz), 126.0 (q, $^1J_{CF}$ = 269.2 Hz), 124.4 (dq, J = 8.1, 1.4 Hz), 119.4 (d, J = 3.5 Hz), 116.8 (d, J = 22.3 Hz), (C=N_2 not observed). ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.6 (s, 3F), -115.9 (s, 1F). IR (neat) υ/ cm^{-1}: 3054, 2080, 1512, 1334, 1306, 1270, 1240, 1167, 1099, 957, 825, 735, 609. HRMS (ESI, negative) calculated for $C_8H_3F_4N_2$- ([M-H]-): 203.0238, observed: 203.0233.

1-(1-diazo-2,2,2-trifluoroethyl)-4-(trifluoromethyl)benzene (**1h**)

Prepared following general procedure C from 4'-trifluoromethyl-2,2,2-trifluoroacetophenone (1.01 g, 4.2 mmol.). Purified by silica gel column chromatography (pentane) and obtained as a yellow oil (46 mg, 4 % over two steps). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73–7.50 (m, 2H), 7.22–7.07 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 128.3, 128.0 (q, $^2J_{CF}$ = 32.9 Hz), 126.5 (q, J = 3.9 Hz), 125.2 (q, $^1J_{CF}$ = 269.7 Hz), 124.0 (q, $^1J_{CF}$ = 271.8 Hz), 122.0 (d, J = 1.0 Hz), (C=N_2 not observed). ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.4 (s, 3F), -62.6 (s, 3F). IR (neat) υ/ cm^{-1}: 2931, 2859, 2088, 1619, 1523, 1325, 1280, 1206, 1169, 1110, 1069, 1016, 958, 831, 738.[39]

2-chloro-4-(1-diazo-2,2,2-trifluoroethyl)-1-fluorobenzene (**1i**)

Prepared following general procedure C from the corresponding trifluoroacetophenone (1.0 g, 4.4 mmol). Purified by silica gel column chromatography (pentane) and obtained as a red oil (14 mg, 2 % over two

steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (t, J = 8.6 Hz, 1H), 7.13 (dd, J = 6.4, 2.4 Hz, 1H), 6.98-6.94 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.6 (d, $^1J_{CF}$ = 249.8 Hz), 126.7, 125.6 (q, $^1J_{CF}$ = 269.4 Hz), 124.6 (d, J = 1.3 Hz), 122.3 (m), 121.1 (d, J = 4.2 Hz), 117.9 (d, J = 22.0 Hz), (C=N_2 not observed). ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.5 (s, 3F), -118.1 (td, J = 7.2, 4.2 Hz, 1F). IR (neat) υ/ cm^{-1}: 2925, 2853, 2237, 2172, 2089, 2011, 1599, 1504, 1466, 1324, 1257, 1194, 1145, 1066, 814, 704, 628, 617.[39]

4-methyl-N'-(2,2,2-trifluoro-1-(4-methoxyphenyl)ethylidene)benzenesulfonohydrazide (**1'j**)

Prepared following general procedure A from 4'-methoxy-2,2,2-trifluoroacetophenone (4.08 g, 20 mmol.) in methanol (65 °C, 12 h). Purified by precipitation upon cooling to room temperature and subsequent filtration. Obtained as a pale-yellow solid (2.31 g, 28%). ^{1}H NMR (400 MHz, CD_3OD) δ 7.80-7.79 (m, 2H), 7.43 (m, 2H), 7.32-7.30 (m, 2H), 7.09-7.06 (m, 2H), 3.87 (s, 3H), 2.45 (s, 3H), (unable to see N-H). ^{13}C NMR (100 MHz, CD_3OD) δ 161.5, 144.1, 141.0 (q, $^2J_{CF}$ = 38.9 Hz), 135.3, 129.8, 129.2, 127.7, 120.4 (q, $^1J_{CF}$ = 274 Hz), 118.9, 114.2, 54.2, 20.0. ^{19}F NMR (376 MHz, CD_3OD) δ -65.5 (s, 3F). Data consistent with literature values.[23]

1-(1-diazo-2,2,2-trifluoroethyl)-4-methoxybenzene (**1j**)

Prepared following general procedure B from tosylhydrazone **1'j** (2.0 g, 5.38 mmol.). Purified by basic alumina gel chromatography (hexane) and obtained as a red solid (139 mg, 12 %). ^{1}H NMR (500 MHz, C_6D_6) δ 6.75-6.73 (m, 2H), 6.60 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 3.21 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.6 (s, 3F). Data consistent with literature values.[37]

4-(1-diazo-2,2,2-trifluoroethyl)-2-fluoro-1-methylbenzene (**1k**)

Prepared following general procedure C from the corresponding trifluoroacetophenone (1.8 g, 8.7 mmol.). Purified by silica gel column chromatography (pentane) and obtained as a red oil (47 mg, 2 % over two steps). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.24 (t, J = 8.2 Hz, 1H), 6.86 – 6.71 (m, 2H), 2.26 (d, $^4J_{HF}$ = 1.9 Hz, 3H). ^{13}C NMR (126 MHz, Methylene Chloride-d2) δ 162.4 (d, J = 244.9 Hz), 133.1 (d, J = 6.1 Hz), 126.2 (q, J = 269.0 Hz), 123.4 (d, J = 9.1 Hz), 123.2 (d, J = 17.3 Hz), 118.3 (d, J = 3.3 Hz), 109.6 (d, J = 26.2 Hz), 14.4 (C=N_2 not observed). ^{19}F NMR (376 MHz, $CDCl_3$): δ -56.0 (s, 3F), -114.3 (m, 1F). IR (neat) υ/ cm^{-1}: 2960, 2933, 2867, 2082, 1629, 1579, 1514, 1354, 1327, 1295, 1273, 1235, 1204, 1104, 1009, 875, 862, 807, 760, 734, 644. Compound **1k** was found to be unstable under various ionisation techniques and HRMS could therefore not be obtained.

4-methyl-N'-(2,2,2-trifluoro-1-(4-propylphenyl)ethylidene)benzenesulfonohydrazide (**1'l**)

Prepared following general procedure A from 4'-N-propyl-2,2,2-trifluoroacetophenone (1.0 g, 4.60 mmol.) in methanol (65 °C, 12 h). Purified by cooling to room temperature and subsequent filtration and washing with pentane. Obtained as a white solid (1.33 g, 75 %). Used without further purification. ^{1}H NMR (400 MHz, CDCl3): δ 7.98 (s, 1H), 7.81 (d, J = 8.3 Hz, 2H), 7.36 7.31 (m, 4H), 7.14 (d, J = 8.0 Hz, 2H), 2.63 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 2.46 (s, 3H), 1.71, 1.62 (m, 2H), 0.97 (t, $^3J_{HH}$ = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 146.9, 145.0, 142.0 (q, $^2J_{CF}$ = 35.6 Hz), 134.7, 130.2, 130.0, 128.1, 122.5, 120.1 (q, $^1J_{CF}$ = 274.9 Hz), 77.2, 38.1, 24.3, 21.8, 14.0. ^{19}F NMR (377 MHz, $CDCl_3$): δ -68.3 (s, 3F). MP 108-109 °C. IR (neat) υ/ cm^{-1}: 3171, 2964, 2924, 2857, 1359, 1170, 1119, 1070, 999, 811, 684. HRMS (ESI, positive) calculated for $C_{18}H_{20}F_3N_2O_2S^+$ ([M+H]$^+$): 385.1192, observed: 385.1202.

1-(1-diazo-2,2,2-trifluoroethyl)-4-propylbenzene (**1l**)

Prepared following general procedure B from tosylhydrazone **1'l** (1.33 g, 3.46 mmol), purified by silica gel chromatography (pentane) and obtained as a orange/red liquid (194 mg, 25 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 7.03 (d, $^3J_{HH}$ = 7.9 Hz, 2H), 2.60 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 1.70-1.61 (m, 2H), 0.96 (t, 3JHH = 7.3 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$): δ -57.4 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.9, 129.7, 125.7 (q, $^1J_{CF}$ = 268.6 Hz), 122.5, 120.5, 37.6, 24.6, 13.9, (C=N_2 not observed). IR (neat) υ/ cm^{-1}: 2963, 2934, 2874, 2079, 1516, 1345, 1276, 1167, 1145, 1105, 957, 835, 799, 738, 640. HRMS (ESI, negative) calculated for $C_{11}H_{10}F_3N_2^-$ ([M-H]-): 227.0802, observed: 227.0556.

4.3 Diazo insertion reaction

General procedure D: $CF_3C(Ar)N_2$ Insertion into $n$$Bu_3SnH$ under inert atmosphere

A flame dried, argon purged vial was charged with aryl 2,2,2-trifluorodiazoethane **1** (1.0 eq., 0.1 mmol), $n$$Bu_3SnH$ (26.5 µL, 1.0 eq, 0.1 mmol) and degassed CH_2Cl_2 (0.7 mL). In a separate flame dried, argon purged vial was added $Rh_2(OAc)_4$ (1.8 mg, 4 mol%, 0.004 mmol) and degassed CH_2Cl_2 (0.5 mL). Diazo compound and $n$$Bu_3SnH$ solution were added to the $Rh_2(OAc)_4$ suspension over <1 min at room temperature. After evolution of N_2 had stopped and characteristic orange/red colour of diazo compound had disappeared, the reaction progress was monitored by TLC. Typically, the reaction was complete in less than 15 minutes. The reaction mixture was filtered through a short plug of silica gel eluting with CH_2Cl_2, evaporated under reduced pressure and the crude product purified by silica gel column chromatography.

General procedure E: $CF_3C(Ar)N_2$ Insertion into $n$$Bu_3SnH$ in an open vial

To a solution of aryl 2,2,2-trifluorodiazoethane **1** (1.0 eq, 0.1 mmol) and $n$$Bu_3SnH$ (26.5 µL, 1.0 eq, 0.1 mmol) in CH_2Cl_2 (1.2 mL) in an open vial was added $Rh_2(OAc)_4$ (1.77 mg, 4 mol%, 0.004 mmol). After evolution of N_2 had stopped and characteristic orange/red colour of diazo compound had disappeared, the reaction progress was monitored by TLC. Typically, the reaction was complete in less than 15 min. The reaction mixture was filtered through a short plug of silica gel eluting with CH_2Cl_2, evaporated under reduced pressure and the crude product purified by silica gel column chromatography.

General Procedure F: Asymmetric $CF_3C(Ar)N_2$ insertion into $n$$Bu_3SnH$

A flame dried, argon purged vial was charged with aryl 2,2,2-trifluorodiazoethane **1** (1.0 eq, 0.1 mmol), $n$$Bu_3SnH$ (26.5 µL, 1.0 eq, 0.1 mmol) and degassed CH_2Cl_2 (0.7 mL). In a separate flame dried, argon purged vial was added Rh_2(S-tertPTTL)$_4$ (1.77 mg, 4 mol%, 0.004 mmol) and degassed CH_2Cl_2 (0.5 mL) and the mixture was cooled down to -78 °C. The diazo compound and $n$$Bu_3SnH$ solution were added to the Rh_2(S-tertPTTL)$_4$ suspension over <1 min at -78 °C. After evolution of N_2 had stopped and characteristic orange/red colour of diazo compound had disappeared, the reaction progress was monitored by TLC. Typically, the reaction was complete in less than 30 min. The reaction mixture was filtered through a short plug of silica gel eluting with CH_2Cl_2, evaporated under reduced pressure and the crude product was purified by silica gel column chromatography.

(1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethyl)tributylstannane (**2a**)

Prepared following general procedure D. Purified by silica gel column chromatography (pentane) and obtained as a colourless oil (39 mg, 74 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.58 (m, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.22 (d, J = 8.2 Hz, 2H), 3.23 (q, $^3J_{HF}$ = 13.7 Hz, 1H), 1.47-1.39 (m, 6H), 1.28 (m, 6H), 0.97 (m, 6H), 0.87 (t, $^3J_{HH}$ = 7.3 Hz,

9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.9, 138.7, 135.8 (q, J = 3.8 Hz), 129.7 (q, $^1J_{CF}$ = 274.3 Hz), 128.9, 128.3, 127.5, 127.3, 127.0, 38.9 (q, 2JCF = 30.9 Hz), 28.8, 27.4, 13.7, 10.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ -55.7 (d, $^3J_{FH}$ = 13.6 Hz, 3F). IR (neat) υ/ cm^{-1}: 3031, 2956, 2923, 2872, 2854, 1907, 1729, 1612, 1600, 1519, 1488, 1463, 1416, 1377, 1345, 1306, 1281, 1261, 1238, 1204, 1123, 1101, 1075, 1039, 1008, 960, 912, 878, 848, 823, 764, 740, 727, 695, 668, 614. HRMS (CI) calculated for $C_{14}H_{10}F_2^+$([M-*n*Bu_3SnF]$^+$): 216.0751, observed: 216.0753; calculated for $C_{12}H_{27}Sn^+$ ([*n*Bu_3Sn]$^+$): 291.1129, observed: 291.1145.[38] Asymmetric reaction was performed using general procedure F. The product (+)-(**2a**) was obtained in 57 % yield with this procedure. 94 % ee, HPLC conditions; Chiralpak IA column, hexane = 100%, flow rate = 1.0 mL/min, 25 °C, wavelength = 254 nm, tR = 5.89 min for minor isomer, tR = 6.72 min for major isomer: $[\alpha]^{D}_{25}$ = +55.7 (c 1.46, MeOH).

(1-(4-bromophenyl)-2,2,2-trifluoroethyl)tributylstannane (**2b**)

Prepared following general procedure E. Purified by silica gel column chromatography (pentane) and obtained as a colourless oil (34 mg, 64 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 3.12 (q, $^3J_{HF}$ = 13.6 Hz, 1H), 1.45-1.37 (m, 6H), 1.29-1.24 (m, 6H), 0.99-0.90 (m, 6H), 0.87 (t, $^3J_{HH}$ = 7.3 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.9, 131.9, 130.7 (q, $^1J_{CF}$ = 275.0 Hz), 129.5, 119.6, 38.7 (q, $^2J_{CF}$ = 31.2 Hz), 28.7, 27.4, 13.7, 10.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -55.9 (d, $^3J_{FH}$ = 13.5 Hz, 3F). IR (neat) υ/ cm^{-1}: 2957, 2924, 2872, 2854, 1895, 1731, 1592, 1490, 1463, 1412, 1377, 1350, 1339, 1301, 1264, 1238, 1196, 1127, 1100, 1076, 1039, 1011, 960, 941, 875, 843, 809, 769, 747, 721, 691, 671, 649. HRMS (CI) calculated for $C_{12}H_{27}Sn^+$ ([*n*Bu_3Sn]$^+$): 291.1129, observed: 291.1138.[38]

methyl 4-(2,2,2-trifluoro-1-(tributylstannyl)ethyl)benzoate (**2c**)

Prepared following general procedure E. Purified by silica gel column chromatography (100% pentane to pentane/CH_2Cl_2 1:1) and obtained as a colourless oil (31 mg, 61 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.19 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 3.90 (s, 3H), 3.25 (q, $^3J_{HF}$ = 13.5 Hz, 1H), 1.45-1.31 (m, 6H), 1.25 (m, 6H), 1.01-0.89 (m, 6H), 0.85 (t, $^3J_{HH}$ = 7.3 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.0, 142.5 (q, J = 4.0 Hz), 130.2, 129.3 (q, $^1J_{CF}$ = 275.0 Hz), 127.5, 127.4, 52.2, 39.7 (q, $^2J_{CF}$ = 31.2 Hz), 28.7, 27.4, 13.7, 10.6. ^{19}F NMR (377 MHz, $CDCl_3$): δ -55.3 (d, $^3J_{FH}$ = 13.2 Hz, 3F). IR (neat) υ/ cm^{-1}: 2956, 2925, 2873, 2855, 1724, 1610, 1436, 1348, 1275, 1239, 1184, 1112, 1021, 962, 860, 771, 711. HRMS (CI) calculated for $C_{22}H_{36}F_3O_2Sn^+$ ([M+H]$^+$): 509.1689, observed: 509.1677. Asymmetric reaction was performed using general procedure F. The product (+)-(**2c**) was obtained in 77 % yield with this procedure. 84 % ee, HPLC conditions; Chiralpak IA column, hexane = 100%, flow rate = 1.0 mL/min, 25 °C, wavelength = 254 nm, tR = 10.50 min for major isomer, tR = 12.13 min for minor isomer: $[\alpha]^{D}_{25}$ = + 1.0 (c 1.26, MeOH).

tributyl(2,2,2-trifluoro-1-(p-tolyl)ethyl)stannane (**2d**)

Prepared following general procedure D. Purified by silica gel column chromatography (pentane) and obtained as a colourless oil (30 mg, 65 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.08 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.1 Hz, 2H), 3.12 (q, $^3J_{HF}$ = 13.8 Hz, 1H), 2.31 (s, 3H), 1.47-1.32 (m, 6H), 1.26 (m, 6H), 0.99-0.90 (m, 6H), 0.86 (t, $^3J_{HH}$ = 7.3 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 135.4, 133.4 (q, J = 3.9 Hz), 129.7 (q, $^1J_{CF}$ = 275.0 Hz), 129.5, 127.9, 38.7 (q, $^2J_{CF}$ = 30.8 Hz), 28.8, 27.4, 21.1, 13.7, 10.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ -56.0 (d, $^3J_{FH}$ = 13.7 Hz, 3F). IR (neat) υ/ cm^{-1}: 2957, 2923, 2872, 2855, 1513, 1463, 1342, 1309, 1241, 1199, 1123, 1103, 1074, 1042, 876, 808, 719.43, 665. HRMS (CI) calculated for $C_9H_8F_2^+$([M-*n*Bu_3SnF]$^+$): 154.0594, observed: 154.0585; calculated for $C_{12}H_{27}Sn^+$ ([*n*Bu_3Sn]$^+$): 291.1129, observed: 291.1129.[38]

(1-(3-bromophenyl)-2,2,2-trifluoroethyl)tributylstannane (**2e**)

Prepared following general procedure D. Purified by silica gel column chromatography (pentane) and obtained as a colourless oil (31 mg, 59 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.29 (m, 2H), 7.15 (t, J = 8.1 Hz, 1H), 7.07 (d, J = 7.9 Hz, 1H), 3.12 (q, $^3J_{HF}$ = 13.5 Hz, 1H), 1.45-1.34 (m, 6H), 1.27 (m, 6H), 1.01-0.90 (m, 6H), 0.87 (t, $^3J_{HH}$ = 7.3 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 139.3-139.1 (m), 130.7, 130.3, 129.3 (q, $^1J_{CF}$ = 275.0 Hz), 128.9, 126.3, 122.9, 38.9 (q, $^2J_{CF}$ = 31.2 Hz), 28.7, 27.4, 13.7, 10.6. ^{19}F NMR (377 MHz, $CDCl_3$): δ -55.7 (d, $^3J_{FH}$ = 13.4 Hz, 3F). IR (neat) υ/ cm^{-1}: 2957, 2923, 2872, 2854, 1593, 1563, 1475, 1378, 1341, 1239, 1195, 1128, 1088, 1039, 996, 877, 779, 713, 692, 620. HRMS (CI) calculated for $C_{12}H_{27}Sn^+$ ([*n*Bu_3Sn]$^+$): 291.1129, observed: 291.1132.[38]

tributyl(2,2,2-trifluoro-1-phenylethyl)stannane (**2f**)

Prepared following general procedure D. Purified by silica gel column chromatography (pentane) and obtained as a colourless oil (22 mg, 49 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (s, 2H), 7.17-7.13 (m, 3H), 3.16 (q, $^3J_{HF}$ = 13.7 Hz, 1H), 1.43-1.36 (m, 6H), 1.26 (m, 6H), 0.97-0.90 (m, 6H), 0.86 (t, $^3J_{HH}$ = 7.3 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 136.6 (q, J = 3.9 Hz), 129.7 (q, $^1J_{CF}$ = 274.9 Hz), 128.8, 127.9, 125.8, 39.2 (q, $^2J_{CF}$ = 30.9 Hz), 28.7, 27.4, 13.7, 10.5. ^{19}F NMR (377 MHz, $CDCl_3$): δ -55.8 (d, $^3J_{FH}$ = 13.5 Hz, 3F). IR (neat) υ/ cm^{-1}: 2957, 2924, 2872, 2854, 1601, 1495, 1456, 1356, 1277, 1240, 1203, 1125, 1074, 1034, 874, 757, 698, 671, 615. HRMS (CI) calculated for $C_8H_6F_2^+$([M-*n*Bu_3SnF]$^+$): 140.0438 observed: 140.0426; calculated for $C_{12}H_{27}Sn^+$ ([*n*Bu_3Sn]$^+$): 291.1129, observed: 291.1135.[38]

tributyl(2,2,2-trifluoro-1-(4-fluorophenyl)ethyl)stannane (**2g**)

Prepared following general procedure D. Purified by silica gel column chromatography (pentane) and obtained as a colourless oil (25 mg, 54 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 (dd, J = 8.4, 5.4 Hz, 2H), 6.98 (t, J = 8.7 Hz, 2H), 3.13 (q, $^3J_{HF}$ = 13.6 Hz, 1H), 1.46-1.34 (m, 6H), 1.26 (m, 6H), 1.00-0.89 (m, 6H), 0.86 (t, $^3J_{HH}$ = 7.3 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.2 (d, $^1J_{CF}$ = 244.5 Hz), 132.4 (q, J = 3.9 Hz), 129.5 (q, $^1J_{CF}$ = 274.9 Hz), 129.5 (q, J = 7.8 Hz), 115.6 (d, J = 21.3 Hz), 38.3 (q, $^2J_{CF}$ = 31.2 Hz), 28.7, 27.4, 13.7, 10.5. ^{19}F NMR (471 MHz, $CDCl_3$): δ -56.4 (d, $^3J_{FH}$ = 3.6 Hz, 3F), -117.3 (m, 1F). IR (neat) υ/ cm^{-1}: 2958, 2924, 2873, 2855, 1607, 1509, 1464, 1420, 1342, 1272, 1246, 1228, 1200, 1161, 1117, 1094, 1042, 961, 876, 825, 791, 721, 664. HRMS (CI) calculated for $C_8H_5F_3^+$([M-*n*Bu_3SnF]$^+$): 158.0343 observed: 158.0330; calculated for $C_{12}H_{27}Sn^+$ ([*n*Bu_3Sn]$^+$): 291.1129, observed: 291.1133.[38]

tributyl(2,2,2-trifluoro-1-(4-(trifluoromethyl)phenyl)ethyl)stannane (**2h**)

Prepared following general procedure D. Purified by silica gel column chromatography (pentane) and obtained as a colourless oil (32 mg, 62 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 3.24 (q, $^3J_{HF}$ = 13.4 Hz, 1H), 1.49–1.32 (m, 6H), 1.32–1.16 (m, 6H), 1.02–0.90 (m, 6H), 0.86 (t, $^3J_{HH}$ = 7.3 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.0, 129.1 (q, $^1J_{CF}$ = 271.8 Hz), 127.8 (q, $^2J_{CF}$ = 32.7 Hz), 127.6 (t, J = 1.4 Hz), 125.6 (q, J = 3.5 Hz), 124.2 (q, $^1J_{CF}$ = 271.8 Hz), 39.2 (q, $^2J_{CF}$ = 31.3 Hz), 28.5, 27.2, 13.5, 10.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ -55.5 (d, $^3J_{FH}$ = 13.4 Hz, 3F), -62.4 (3F). IR (neat) υ/ cm^{-1}: 2959, 2925, 2874, 2856, 1620, 1582, 1519, 1464, 1423, 1378, 1326, 1286, 1240, 1202, 1166, 1121, 1103, 1069, 1019, 960, 909, 879, 849, 825, 767, 742, 690, 671. HRMS (CI) calculated for $C_{12}H_{27}Sn^+$ ([*n*Bu_3Sn]$^+$): 291.1129, observed: 291.1129.[38]

tributyl(1-(3-chloro-4-fluorophenyl)-2,2,2-trifluoroethyl)stannane (**2i**)

Prepared following general procedure D, on 0.05mmol scale. Purified by silica gel column chromatography (pentane) and obtained as a colourless oil (13 mg, 52 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17 (dd, J = 6.9, 2.3 Hz, 1H), 7.06 (t, J = 8.7 Hz, 1H), 7.00-6.97 (m, 1H), 3.09 (q, $^3J_{HF}$ = 13.4 Hz, 1H), 1.44-1.38 (m, 6H), 1.30-1.23 (m, 6H), 0.99-0.92 (m, 6H), 0.87 (t, $^1J^{HH}$ = 7.3 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.5 (d, $^1J_{CF}$ = 247.8 Hz), 134.1-133.8 (m), 129.8, 129.3 (q, $^1J_{CF}$

= 275.0 Hz), 127.5 (d, J = 7.0 Hz), 121.2 (d, J = 17.9 Hz), 116.8 (d, J = 21.0 Hz), 38.2 (q, $^{2}J_{CF}$ = 31.5 Hz), 28.7, 27.4, 13.7, 10.6. ^{19}F NMR (377 MHz, $CDCl_3$): δ -56.2 (d, $^{3}J_{FH}$ = 13.2 Hz, 3F), -119.6- (m, 1F). IR (neat) υ/ cm^{-1}: 2958, 2924, 2855, 1499, 1236, 1230, 1109. HRMS (CI) calculated for $C_8H_4ClF_3^+$ ([M-*n*Bu_3SnF]$^+$): 191.9954 observed: 191.9974; calculated for $C_{12}H_{27}Sn^+$ ([*n*Bu_3Sn]$^+$): 291.1129, observed: 291.1146.[38]

tributyl(2,2,2-trifluoro-1-(4-methoxyphenyl)ethyl)stannane (**2j**)

Prepared following general procedure D. Purified by preparative TLC (5% EtOAc in cyclohexane) and obtained as a colourless oil (18.3 mg, 38 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11–7.02 (m, 2H), 6.87–6.79 (m, 2H), 3.79 (s, 3H), 3.09 (q, $^{3}J_{HF}$ = 13.8 Hz, 1H), 1.49 1.30 (m, 6H), 1.26 (h, J = 7.3 Hz, 6H), 1.02–0.87 (m, 6H), 0.86 (t, $^{3}J_{HH}$ = 7.3 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.9, 129.8 (q, $^{1}J_{CF}$ = 274.9 Hz), 129.3, 128.5 (q, J = 4.2 Hz), 114.2, 55.4, 38.1 (q, $^{2}J_{CF}$ = 30.9 Hz), 28.8, 27.4, 13.7, 10.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ -56.5 (d, $^{3}J_{FH}$ = 13.6 Hz, 3F). IR (neat) υ/ cm^{-1}: 2956, 2924, 2872, 2854, 1612, 1581, 1511, 1464, 1443, 1423, 1377, 1351, 1307, 1283, 1250, 1235, 1202, 1180, 1122, 1100, 1075, 1038, 961, 931, 875, 849, 821, 775, 747, 726, 687, 665. HRMS (CI) calculated for $C_9H_8F_2O^+$ ([M-*n*Bu_3SnF]$^+$): 170.0543, observed: 170.0520; calculated for $C_{12}H_{27}Sn^+$ ([*n*Bu_3Sn]$^+$): 291.1129, observed: 291.1116.[38] Asymmetric reaction was performed using general procedure F. The product (-)-(**2j**) was obtained in 57 % yield with this procedure. 85 % ee, HPLC conditions; Chiralpak IC column, hexane = 100%, flow rate = 1.0 mL/min, 25 °C, wavelength = 254 nm, tR = 9.20 min for major isomer, tR = 10.11 min for minor isomer: $[\alpha]^{D}_{25}$ = -0.6 (c 0.46, MeOH).

tributyl(2,2,2-trifluoro-1-(3-fluoro-4-methylphenyl)ethyl)stannane (**2k**)

Prepared following general procedure D. Purified by silica gel column chromatography (pentane) and obtained as a colourless oil (14.5 mg, 60 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.13–7.02 (m, 1H), 6.88–6.74 (m, 2H), 3.11 (q, $^{3}J_{HF}$ = 13.6 Hz, 1H), 2.23 (d, J = 1.9 Hz, 3H), 1.50–1.34 (m, 6H), 1.34–1.13 (m, 6H), 1.04–0.89 (m, 6H), 0.86 (t, $^{3}J_{HH}$ = 7.2 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.4 (d, $^{1}J_{CF}$ = 244.6 Hz), 136.2 (dd, J = 7.8, 3.9 Hz), 131.7 (d, J = 5.8 Hz), 129.5 (q, $^{1}J_{CF}$ = 274.8 Hz), 123.3 (d, J = 3.1 Hz), 122.1 (d, J = 17.2 Hz), 114.4 (d, J = 23.2 Hz), 39.2–38.2 (m), 28.7, 27.4, 14.3 (d, J = 3.3 Hz), 13.7, 10.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -56.0 (d, $^{3}J_{FH}$ = 13.5 Hz, 3F), -117.2 (ddd, J = 10.6, 8.4, 2.2 Hz, 1F). IR (neat) υ/ cm^{-1}: 2957, 2925, 2873, 2855, 627, 1579, 1510, 1463, 1425, 1378, 1340, 1290, 1272, 1238, 1207, 1150, 1128, 1075, 1041, 999, 958, 876, 851, 817, 787, 755, 710, 683. HRMS (CI) calculated for $C_9H_7F_3^+$ ([M-*n*Bu_3SnF]$^+$): 172.0500, observed: 173.0472; calculated for $C_{12}H_{27}Sn^+$ ([*n*Bu_3Sn]$^+$): 291.1129, observed: 291.1122.[38]

tributyl(2,2,2-trifluoro-1-(4-propylphenyl)ethyl)stannane (**2l**)

Prepared following general procedure D. Purified by silica gel column chromatography (pentane) and obtained as a colourless oil (25 mg, 51 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.08 (d, J = 8.2 Hz, 2H), 7.04 (d, J = 8.2 Hz, 2H), 3.13 (q, $^{3}J_{HF}$ = 13.8 Hz, 1H), 2.55 (t, J = 7.6 Hz, 2H), 1.62 (m, 2H), 1.45-1.31 (m, 6H), 1.25 (m, 6H), 0.98 0.89 (m, 9H), 0.85 (t, $^{3}J_{HH}$ = 7.3 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 140.2, 133.6 (q, J = 3.9 Hz), 129.8 (q, $^{1}J_{CF}$ = 274.8 Hz), 128.8, 127.9, 38.7 (q, $^{2}J_{CF}$ = 30.7 Hz), 37.7, 28.8, 27.4, 24.6, 13.9, 13.7, 10.4. ^{19}F NMR (377 MHz, $CDCl_3$): δ -56.0 (d, $^{3}J_{FH}$ = 13.8 Hz, 3F). IR (neat) υ/ cm^{-1}: 2958, 2926, 2872, 2855, 1512, 1463, 1343, 1240, 1198, 1125, 1106, 1041, 877, 668. HRMS (CI) calculated for $C_{11}H_{12}F_2^+$ ([M-*n*Bu_3SnF]$^+$): 182.0907, observed: 182.0905; calculated for $C_{12}H_{27}Sn^+$ ([*n*Bu_3Sn]$^+$): 291.1129, observed: 291.1136.[38]

(1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethyl)dimethyl(phenyl)silane (**2m**)

Prepared following general procedure D, with substitution of *n*Bu_3SnH for $PhMe_2SiH$ (15.3 µL, 1.0 eq, 0.1 mmol). Purified by silica gel column chromatography (5-15% CH_2Cl_2 in pentane) and obtained as a white solid in 92% yield (34 mg, 0.09 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.3 Hz, 2H), 7.49-7.41 (m, 4H), 7.40-7.30 (m, 6H), 7.06 (d, J = 8.1 Hz, 2H), 3.16 (q, J = 12.9 Hz, 1H), 0.48 (s, 3H), 0.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.7, 139.5, 135.3, 134.3, 132.9 (q, J = 3.2 Hz), 129.8, 129.5, 128.9, 128.3 (q, J = 277.7 Hz, CF_3), 127.9, 127.4, 127.1, 127.1, 43.8 (q, J = 27.7 Hz), -3.4, -3.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.5 (t, J = 13.0 Hz, 3F). IR (neat) υ/ cm^{-1} 3071, 3031, 2963, 2905, 2362, 2284, 1488, 1239, 1151, 1133, 1068, 810, 764, 739, 695, 649. HRMS (EI) calculated for $C_{22}H_{21}F_3Si^+$ (M^+): 370.1359, observed: 370.1363. The asymmetric reaction was performed using general procedure F, with substitution of *n*Bu_3SnH for $PhMe_2SiH$ (15.3 µL, 1.0 eq, 0.1 mmol). Purified by silica gel column chromatography (5-15% CH_2Cl_2 in pentane). The product (+)-(**2m**) was obtained in 65 % and 99 % ee, HPLC conditions; Chiralcel OJ-H column, hexane/^{i}PrOH = 99:1, flow rate = 1.0 mL/min, 25 °C, wavelength = 250 nm, tR = 15.06 min for major isomer, tR = 20.53 min for minor isomer: $[\alpha]^{D}_{25}$ = + 75.8 (c 0.85, MeOH).

(1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethyl)tributylgermane (**2n**)

Prepared following general procedure D, with substitution of *n*Bu_3SnH for *n*Bu_3GeH (25.8 µL, 1.0 eq, 0.1 mmol). Purified by silica gel column chromatography (pentane) and obtained as a colourless oil in 58% yield (28 mg, 0.06 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.58 (m, 2H), 7.56-7.53 (m, 2H), 7.47-7.42 (m, 2H), 7.37-7.33 (m, 1H), 7.25 (d, J = 7.7 Hz, 2H), 3.15 (q, 3JHF = 13.2 Hz, 1H), 1.34-1.24 (m, 12H), 0.92-0.83 (m, 15H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.8, 139.3, 134.3, 129.0, 128.9 (q, $^{1}J_{CF}$ = 276.8 Hz), 128.9, 127.4, 127.3, 127.1, 41.0 (q, $^{2}J_{CF}$ = 28.8 Hz), 27.0, 26.6, 13.8, 12.7. ^{19}F NMR (377 MHz, $CDCl_3$): δ -57.1 (d, $^{3}J_{FH}$ = 13.2 Hz, 3F). IR (neat) υ/ cm^{-1}: 3032, 2956, 2927, 2871, 2857, 1910, 1600, 1520, 1488, 1464, 1416, 1378, 1344, 1306, 1281, 1262, 1242, 1205, 1141, 1131, 1109, 1063, 1008, 964, 912, 884, 855, 826, 765, 743, 729, 695, 681, 654, 616. HRMS (CI) calculated for $C_{26}H_{41}F_3GeN^+$ ([M+NH_4]$^+$): 498.2397, observed: 498.2435. The asymmetric reaction was performed using general procedure F, with substitution of *n*Bu_3SnH for *n*Bu_3GeH (25.8 µL, 1.0 eq, 0.1 mmol). The product (+)-(**2n**) was obtained in 99 % yield with this procedure. 99 % ee, HPLC conditions; Chiralpak IC column, hexane = 100%, flow rate = 1.0 mL/min, 25 °C, wavelength = 254 nm, tR = 6.15 min for major isomer, tR = 6.97 min for minor isomer: $[\alpha]^{D}_{25}$ = +54.3 (c 3.46, MeOH).

Acknowledgments

Financial support was provided by the EPSRC (S.H.), a CASE Studentship with AstraZeneca (S.H.), the Swiss National Foundation (J.V.), and the EPSRC Centre for Doctoral Training in Synthesis for Biology and Medicine (EP/L015838/1) (D. M. H. A. and R. S.).

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