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Supporting Information

Palladium(II)-Catalyzed Synthesis of Sulfinates from Boronic Acids and DABSO: A Redox-Neutral, Phosphine-Free Transformation

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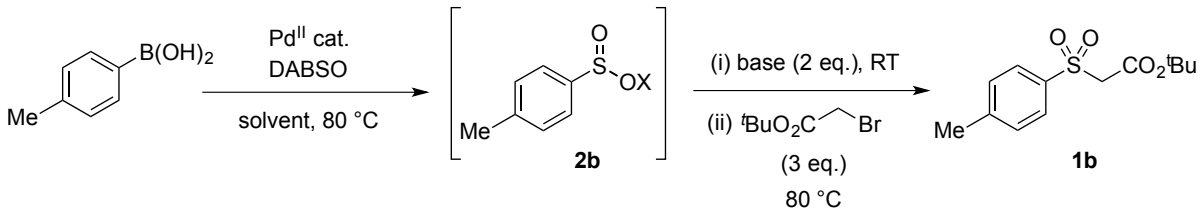
Supporting Information

Table. Screening of conditions for the two-step boronic acid sulfination (**1b**).



Entry	Solvent	Pd source (mol %)	Base	Yield (2b) [a]	Yield (1b) [a]
1	Dioxane/EtOH	$Pd(OAc)_2$ (10)	Et_3N	0%	-
2	Dioxane/^{t}BuOH	$Pd(OAc)_2$ (10)	Et_3N	0%	-
3	Dioxane/IPA	$Pd(OAc)_2$ (10)	Et_3N	0%	-
4	Dioxane	$Pd(OAc)_2$ (10)	Et_3N	0%	-
5	MeOH	$Pd(OAc)_2$ (10)	Et_3N	84% [b]	82%
6	Dioxane/MeOH	$PdCl_2$ (10)	Et_3N	86% [b]	83%
7	Dioxane/MeOH	$Pd(TFA)_2$ (10)	Et_3N	81% [b]	81%
8	Dioxane/MeOH	$Pd(OAc)_2$ (5)	Et_3N	93% [b]	89% [c]
9	Dioxane/MeOH	$Pd(OAc)_2$ (5) [d]	Et_3N	76% [b]	-
10	Dioxane/MeOH	$Pd(OAc)_2$ (5) [e]	Et_3N	0% [f]	-
11	Dioxane/MeOH	$Pd(OAc)_2$ (5) [g]	Et_3N	0% [f]	-
12	Dioxane/MeOH	$Pd(OAc)_2$ (3)	Et_3N	91% [b]	86% [c]
13	Dioxane/MeOH	$Pd(OAc)_2$ (10)	DIPEA	-	78%
14	Dioxane/MeOH	$Pd(OAc)_2$ (10)	K_2CO_3	-	70%
15	Dioxane/MeOH	$Pd(OAc)_2$ (10)	Cs_2CO_3	-	78%

Reaction Conditions: Boronic acid (0.25 mmol, 1 equiv), Pd cat. (3-10 mol%), DABSO (1 equiv), base (2 equiv), solvent [0.16 M].[a] HPLC yields relative to benzophenone as an internal standard. [b] Observed with 3-6% of homocoupled product [c] Isolated yields. [d] With DABSO (0.6 equiv). [e] With *N*-methylmorphiline·SO_2. [f] Starting material and biphenyl formation observed. [g] With $K_2S_2O_5$ (2 equiv).

General considerations

Chemicals were purchased from Sigma Aldrich, Alfa Aesar, Apollo Scientific or Acros Organics and used without further purification unless otherwise stated. Solvents were purchased from Sigma Aldrich, Fisher Scientific or Rathburn and unless otherwise mentioned, used directly without further purification. 'Petrol' refers to the fraction of light petroleum ether boiling in the range 40-60 °C. Anhydrous (KF titration < 10 ppm) THF, DCM, CH_3CN, Et_2O, MeOH and toluene were obtained from an in-house Grubbs solvent drying system (Innovative Technology Inc. PS-400-7) having passed through dried alumina columns. 1,4-Dioxane was purified prior to use by stirring over CaH_2 for 24 hr before distilling onto activated 4Å molecular sieves. DABCO was prepared in accordance with previous publications.[8c]

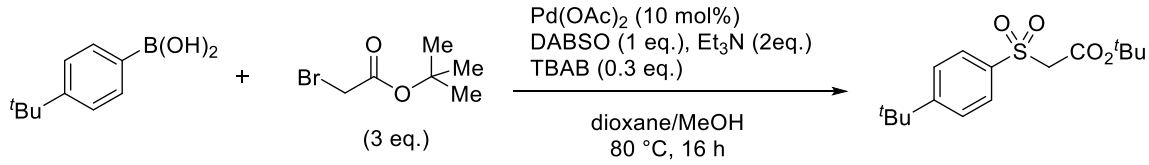
Reactions were performed with continuous magnetic stirring, under an atmosphere of nitrogen (passed through a Drierite®filled tube), unless otherwise stated, and all glassware was dried in an oven (>200 °C, overnight) and allowed to cool under vacuum (10 mbar) prior to use. Flash column chromatography was performed using Apollo scientific silica gel 60 (particle size 0.040-0.063 nm) with the indicated eluents. Thin Layer Chromatography (TLC) analysis was carried out on Merck Kieselgel 60 PF254 pre-coated aluminium backed sheets and visualised either by UV fluorescence (254 nm) and/or by staining with potassium permanganate ($KMnO_4$).

NMR spectra were recorded at ambient temperature on a Brüker AVIII400 (400 MHz) spectrometer or AVII500 (500 MHz). Chemical shifts (δ) are reported in parts per million (ppm) and referenced relative to the residual solvent peak(s) (as specified). Coupling constants (*J*) are given in Hertz (Hz) and rounded to the nearest 0.5 Hz. Assignments were made on the basis of chemical shifts, coupling constants, COSY, HSQC and comparison with spectra of related compounds. Signal multiplicities are denoted as: s, singlet; d, doublet; t, triplet; q, quartet; quin., quintet; sext., sextet; hept., heptet; m, multiplet; br., broad. Multiplicities are reported as observed.

Melting points were measured using a Leica Gallen III hot-stage microscope. Low resolution mass spectra were recorded on a Fisons Platform spectrometer (ESI). High resolution mass spectra were measured by the internal service at the University of Oxford using a Bruker Daltronics microTOF spectrometer. *m/z* ratio values are reported in Daltons; high resolution

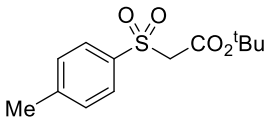
values are calculated to four decimal places from the molecular formula, all found within a tolerance of 5 ppm. Infrared spectra were determined neat using a Bruker Tensor 27 FT spectrometer with an internal range of 600-4000 cm^{-1}.

General Procedure A for the synthesis of sulfones from boronic acids, DABSO, and alkyl halides as exemplified by the preparation of *tert*-butyl 2-{[4-(*tert*-butyl)phenyl]sulfonyl}acetate (1a)



To a reaction tube was added DABSO (60 mg, 0.25 mmol), *tert*-butylphenylboronic acid (45 mg, 0.25 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), TBAB (24 mg, 0.075 mmol), Et_3N (70 μL, 0.50 mmol) and *tert*-butylbromoacetate (110 μL, 0.75 mmol). After addition of dioxane (0.8 mL) and MeOH (0.8 mL) the resulting mixture was heated at 80 ºC and stirred at this temp. for 16 hr. The reaction mixture was allowed to cool to room temp. and filtered through a plug of silica before removing the solvent *in vacuo*. Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as a white solid (52 mg, 83%); mp 107-108 °C (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* 8.5, 2H, Ar-*H*), 7.60 (d, *J* 8.5, 2H, Ar-*H*), 4.05 (s, 2H, CH_2), 1.37 (s, 18H, Ar-CMe_3 and CMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 158.1, 136.0, 128.4, 126.2, 83.5, 62.2, 35.3, 31.0, 27.7; IR ν_{max} (neat)/cm^{-1} 2982, 1730 (CO), 1591, 1495, 1328 (SO_2), 1143 (SO_2); LRMS (ESI) *m/z* 330 (100%, $[M+NH_4]^+$), 335 (80%, $[M+Na]^+$), 647 (30%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 335.1283 $[M+Na]^+$, $C_{16}H_{24}O_4SNa$ requires *m/z* 335.1288.

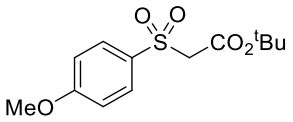
tert-Butyl 2-tosylacetate (1b)



Prepared according to general procedure A using *p*-tolylphenylboronic acid (33 mg, 0.25 mmol). Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as a white solid (54 mg, 79%); mp 56-57 °C (CH_2Cl_2) [lit.[1] mp 57-58 °C]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* 8.5, 2H, Ar-*H*), 7.30 (d, *J* 8.5, 2H, Ar-*H*), 3.94 (s,

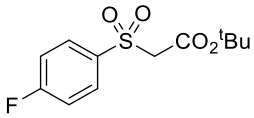
2H, CH_2), 2.39 (s, 3H, Ar*Me*), 1.31 (s, 9H, CMe_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 145.2, 136.0, 129.7, 128.6, 83.6, 62.2, 27.7, 21.7; LRMS (ESI) *m/z* 293 (30%, $[M+Na]^+$), 563 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 293.0817 $[M+Na]^+$, $C_{13}H_{18}O_4SNa$ requires *m/z* 293.0818. Data in accordance with that previously reported.[1]

***tert*-Butyl 2-[(4-methoxyphenyl)sulfonyl]acetate (1c)**



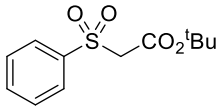
Prepared according to general procedure A using *p*-methoxyphenylboronic acid (38 mg, 0.25 mmol). Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as a colourless oil (52 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* 9.0, 2H, Ar-*H*), 6.96 (d, *J* 9.0, 2H, Ar-*H*), 3.94 (s, 2H, CH_2), 3.82 (s, 3H, OCH_3), 1.33 (s, 9H, CMe_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 161.6, 130.8, 130.5, 114.3, 83.5, 62.4, 55.7, 27.8; LRMS (ESI) *m/z* 309 (30%, $[M+Na]^+$), 595 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 309.0767 $[M+Na]^+$, $C_{13}H_{18}O_5SNa$ requires *m/z* 309.0767. Data in accordance with that previously reported.[2]

***tert*-Butyl 2-[(4-fluorophenyl)sulfonyl]acetate (1d)**



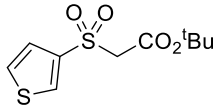
Prepared according to general procedure A using *p*-fluorophenylboronic acid (35 mg, 0.25 mmol). Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as a colourless oil (45 mg, 66%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.87 (m, 2H, Ar-*H*), 7.22-7.15 (m, 2H, Ar-*H*), 3.97 (s, 2H, CH_2), 1.32 (s, 9H, CMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1 (d, J_{CF} 257.5), 161.3, 135.0 (d, J_{CF} 3.5), 131.6 (d, J_{CF} 9.5), 116.5 (d, J_{CF} 22.5), 83.8, 62.1, 27.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -102.6; IR ν_{max} (neat)/cm^{-1} 2982, 1730 (CO), 1590, 1495, 1328 (SO_2), 1144 (SO_2), 1083; LRMS (ESI) *m/z* 297 (30%, $[M+Na]^+$), 571 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 297.0568 $[M+Na]^+$, $C_{12}H_{15}O_4FSNa$ requires *m/z* 297.0567.

***tert*-Butyl 2-(phenylsulfonyl)acetate (1e)**



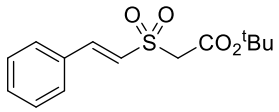
Prepared according to general procedure A using potassium phenyltrifluoroborate (46 mg, 0.25 mmol) and heating at 100 ºC. Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as a colourless oil (44 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.86 (m, 2H, Ar-*H*), 7.65-7.59 (m, 1H, Ar-*H*), 7.52 (dd, *J* 8.5, 7.0, 2H, Ar-*H*), 3.97 (s, 2H, CH_2), 1.30 (s, 9H, CMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 139.0, 134.1, 129.2, 128.6, 83.7, 62.1, 27.7; LRMS (ESI) *m/z* 279 (30%, $[M+Na]^+$), 535 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 279.0660 $[M+Na]^+$, $C_{12}H_{16}O_4SNa$ requires *m/z* 279.0662. Data in accordance with that previously reported.[3]

***tert*-Butyl 2-(thiophen-3-ylsulfonyl)acetate (1f)**



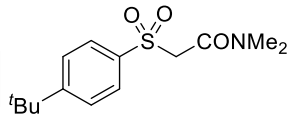
Prepared according to general procedure A using thienyl-3-boronic acid (32 mg, 0.25 mmol). Purification by flash column chromatography (petrol/Et_2O 1:1) afforded the titled sulfone as a colourless oil (40 mg, 61%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* 3.0, 1.5, 1H, Ar-*H*), 7.41 (dd, *J* 5.0, 3.0, 1H, Ar-*H*), 7.38 (dd, *J* 5.0, 1.5, 1H, Ar-*H*), 3.99 (s, 2H, CH_2), 1.34 (s, 9H, CMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 139.3, 133.7, 128.0, 126.5, 83.7, 62.3, 27.8; LRMS (ESI) *m/z* 285 (40%, $[M+Na]^+$), 547 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 285.0225 $[M+Na]^+$, $C_{10}H_{14}O_4S_2Na$ requires *m/z* 285.0226. Data in accordance with that previously reported.[2]

tert-Butyl (_E_)-2-(styrylsulfonyl)acetate (1g)



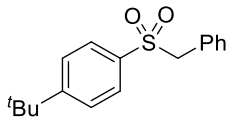
Prepared according to general procedure A using potassium *trans*-styryltrifluoroborate (37 mg, 0.25 mmol). Purification by flash column chromatography (petrol/Et_2O 7:3) afforded the titled sulfone as a colourless oil (30 mg, 45%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* 15.5, 1H, PhC*H*), 7.46 (dd, *J* 7.5, 2.0, 2H, Ar-*H*), 7.40-7.33 (m, 3H, Ar-*H*), 7.00 (d, *J* 15.5, 1H, SO_2C*H*), 3.93 (s, 2H, CH_2), 1.41 (s, 9H, CMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 145.2, 132.1, 131.6, 129.2, 128.7, 125.0, 83.9, 61.3, 27.9; IR ν_{max} (neat)/cm^{-1} 2937, 1726 (CO), 1623, 1493, 1301 (SO_2), 1149 (SO_2), 1091; LRMS (ESI) *m/z* 305 (70%, [M+Na]$^+$), 587 (100%, [2M+Na]$^+$); HRMS (ESI) found *m/z* 305.0816 [M+Na]$^+$, $C_{14}H_{18}O_4SNa$ requires *m/z* 305.0818.

2-[(4-(_tert_-Butyl)phenyl)sulfonyl]-_N_,_N_-dimethylacetamide (1h)



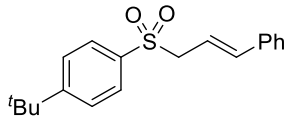
Prepared according to general procedure A using *tert*-butylphenylboronic acid (45 mg, 0.25 mmol) and 2-bromo-*N*,*N*-dimethylacetamide (90 μL, 0.75 mmol). Purification by flash column chromatography (petrol/Et_2O 1:4) afforded the titled sulfone as a colourless oil (57 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* 8.5, 2H, Ar-*H*), 7.50 (d, *J* 8.5, 2H, Ar-*H*), 4.17 (s, 2H, CH_2), 3.10 (s, 3H, N*Me*), 2.91 (s, 3H, N*Me*), 1.28 (s, 9H, CMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 158.1, 136.1, 128.3, 126.2, 59.9, 38.7, 36.1, 35.3, 31.1; IR ν_{max} (neat)/cm^{-1} 2962, 1649 (CO), 1593, 1494, 1398, 1317 (SO_2), 1154, (SO_2), 1081; LRMS (ESI) *m/z* 306 (20%, [M+Na]$^+$), 589 (100%, [2M+Na]$^+$); HRMS (ESI) found *m/z* 306.1133 [M+Na]$^+$, $C_{14}H_{21}NO_3SNa$ requires *m/z* 306.1134.

1-(Benzylsulfonyl)-4-(*tert*-butyl)benzene (1i)



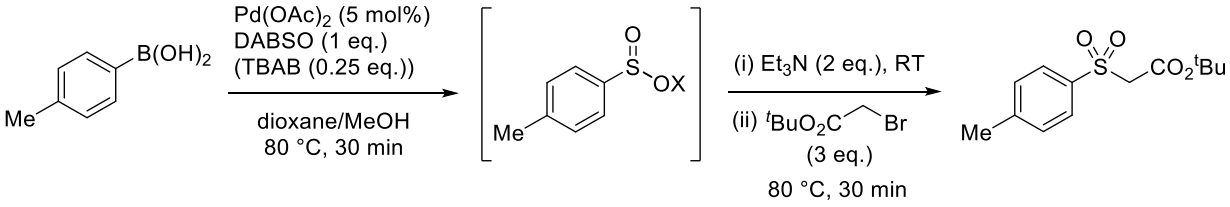
Prepared according to general procedure A using *tert*-butylphenylboronic acid (45 mg, 0.25 mmol) and benzyl bromide (90 μL, 0.75 mmol). Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as a white solid (54 mg, 75%); mp 102-103 °C (CH_2Cl_2) [lit.[4] mp 98-101 °C]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* 8.5, 2H, Ar-*H*), 7.48 (d, *J* 8.5, 2H, Ar-*H*), 7.38-7.31 (m, 1H, Ar-*H*), 7.32-7.26 (m, 2H, Ar-*H*), 7.13 (d, *J* 7.0, 2H, Ar-*H*), 4.32 (s, 2H, CH_2), 1.36 (s, 9H, CMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 135.0, 130.9, 128.7, 128.5, 128.5, 128.3, 125.9, 63.0, 35.3, 31.1; LRMS (ESI) *m/z* 311 (70%, $[M+Na]^+$), 599 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 311.1076 $[M+Na]^+$, $C_{17}H_{20}O_2SNa$ requires *m/z* 311.1076. Data in accordance with that previously reported.[4]

1-(*tert*-Butyl)-4-(cinnamylsulfonyl)benzene (1j)



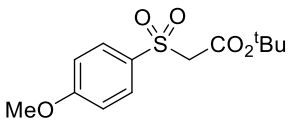
Prepared according to general procedure A using *tert*-butylphenylboronic acid (45 mg, 0.25 mmol) and 3-bromo-1-phenyl-1-propene (148 mg, 0.75 mmol). Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as a yellow solid (42 mg, 52%); mp 117-118 °C (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* 8.5, 2H, Ar-*H*), 7.57 (d, *J* 8.5, 2H, Ar-*H*), 7.38-7.26 (m, 5H, Ar-*H*), 6.42 (dt, *J* 16.0, 1.0, 1H, PhC*H*), 6.15 (dt, *J* 16.0, 7.5, 1H, CH_2C*H*), 3.97 (dd, *J* 7.5, 1.0, 2H, CH_2), 1.37 (s, 9H, CMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 139.1, 135.9, 135.5, 128.7, 128.5, 128.4, 126.6, 126.1, 115.3, 60.6, 35.3, 31.1; IR ν_{max} (neat)/cm^{-1} 2928, 1588, 1490, 1306 (SO_2), 1155 (SO_2), 1038; LRMS (ESI) *m/z* 337 (100%, $[M+Na]^+$), 651 (80%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 337.1234 $[M+Na]^+$, $C_{19}H_{22}O_2SNa$ requires *m/z* 337.1233.

General Procedure B for the two-step synthesis of sulfones from boronic acids, DABSO, and alkyl halides as exemplified by the preparation of *tert*-butyl 2-tosylacetate (1b)



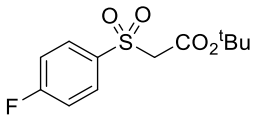
To a reaction tube was added DABSO (60 mg, 0.25 mmol), *p*-tolylboronic acid (33 mg, 0.25 mmol) and $Pd(OAc)_2$ (2.8 mg, 0.0125 mmol). After addition of dioxane (0.8 mL) and MeOH (0.8 mL) the resulting mixture was heated at 80 ºC and stirred at this temp. for 30 min. The reaction was then allowed to cool to room temp., Et_3N (70 μL, 0.50 mmol) added and the mixture stirred for 1 min. *tert*-Butylbromoacetate (110 μL, 0.75 mmol) was then added and the reaction was heated at 80 ºC and stirred at this temp. for 30 min. The reaction mixture was allowed to cool to room temp. and filtered through a plug of silica before removing the solvent *in vacuo*. Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as a white solid (60 mg, 88%). Data as outlined above.

***tert*-Butyl 2-[(4-methoxyphenyl)sulfonyl]acetate (1c)**



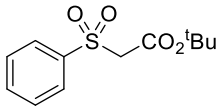
Prepared according to general procedure B using *p*-methoxyphenylboronic acid (38 mg, 0.25 mmol) and TBAB (20 mg, 0.0625 mmol). Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as a colourless oil (54 mg, 78%). Data as outlined above.

***tert*-Butyl 2-[(4-fluorophenyl)sulfonyl]acetate (1d)**



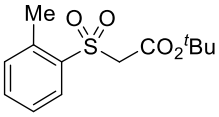
Prepared according to general procedure B using *p*-fluorophenylboronic acid (35 mg, 0.25 mmol) and TBAB (20 mg, 0.0625 mmol). Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as a colourless oil (57 mg, 83%). Data as outlined above.

***tert*-Butyl 2-(phenylsulfonyl)acetate (1e)**



Prepared according to general procedure B using phenylboronic acid (30 mg, 0.25 mmol). Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as a colourless oil (59 mg, 91%). Data as outlined above.

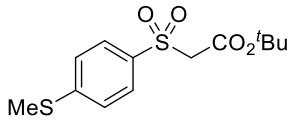
***tert*-Butyl 2-(*o*-tolylsulfonyl)acetate (1k)**



Prepared according to general procedure B using 2-methylphenylboronic acid (33 mg, 0.25 mmol) and running the first step for 3hr. Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as a yellow solid (46 mg, 68%); mp 65-66 °C (CH_2Cl_2) [lit.[2] mp 66-67 °C]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* 8.0, 1.5, 1H, Ar-*H*), 7.47 (app. td, *J* 7.5, 1.5, 1H, Ar-*H*), 7.34-7.31 (m, 1H, Ar-*H*), 7.29 (ddd, *J* 7.5, 1.5, 0.5, 1H, Ar-*H*), 4.02 (s, 2H, CH_2), 2.65 (s, 3H, Ar*Me*), 1.22 (s, 9H, CMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 138.2, 137.1, 134.1, 132.7, 130.7, 126.5, 83.5, 61.6, 27.6, 20.3; LRMS (ESI) *m/z* 293 (40%, $[M+Na]^+$), 563 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 293.0817

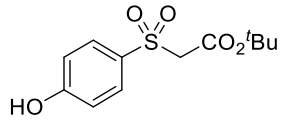
$[M+Na]^+$, $C_{13}H_{18}O_4SNa$ requires *m/z* 293.0818. Data in accordance with that previously reported.[2]

***tert*-Butyl 2-{[4-(methylthio)phenyl]sulfonyl}acetate (1l)**



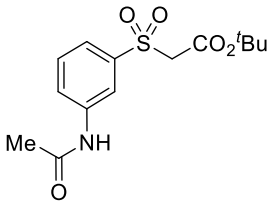
Prepared according to general procedure B using 4-(methylthio)phenylboronic acid (42 mg, 0.25 mmol) and TBAB (20 mg, 0.0625 mmol) and running the first step for 1 hr. Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as an off-white solid (62 mg, 82%); mp 44-45 °C (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* 8.5, 2H, Ar-*H*), 7.37 (d, *J* 8.5, 2H, Ar-*H*), 4.04 (s, 2H, C*H*$_2$), 2.56 (s, 3H, S*Me*), 1.42 (s, 9H, C*Me*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 147.9, 134.5, 128.8, 125.2, 83.7, 62.2, 27.7, 14.7; LRMS (ESI) *m/z* 325 (40%, $[M+Na]^+$), 627 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 325.0537 $[M+Na]^+$, $C_{13}H_{18}O_4S_2Na$ requires *m/z* 325.0539. Data in accordance with that previously reported.[2]

***tert*-Butyl 2-[(4-hydroxyphenyl)sulfonyl]acetate (1m)**



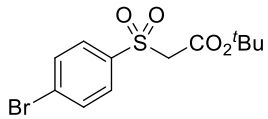
Prepared according to general procedure B using 4-hydroxyphenylboronic acid (34 mg, 0.25 mmol) and TBAB (20 mg, 0.0625 mmol) and running the first step for 1 hr. Purification by flash column chromatography (petrol/Et_2O 2:3) afforded the titled sulfone as a colourless oil (58 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* 9.0, 2H, Ar-*H*), 6.85 (d, *J* 9.0, 2H, Ar-*H*), 3.96 (s, 2H, C*H*$_2$), 1.34 (s, 9H, C*Me*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 161.3, 131.0, 129.7, 116.0, 84.1, 62.5, 27.8; IR ν_{max} (neat)/cm^{-1} 3386 (br. OH), 1728 (CO), 1602, 1586, 1302 (SO_2), 1289, 1135 (SO_2); LRMS (ESI) *m/z* 295 (20%, $[M+Na]^+$), 567 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 295.0610 $[M+Na]^+$, $C_{12}H_{26}O_5SNa$ requires *m/z* 295.0611. Data in accordance with that previously reported.[2]

***tert*-Butyl 2-[(3-acetamidophenyl)sulfonyl]acetate (1n)**



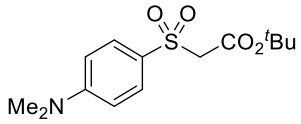
Prepared according to general procedure B using 3-acetamidophenylboronic acid (45 mg, 0.25 mmol) and TBAB (20 mg, 0.0625 mmol) and running the first step for 1 hr. Purification by flash column chromatography (petrol/EtOAc 3:7) afforded the titled sulfone as a colourless oil (60 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (ddd, *J* 8.0, 2.0, 1.0, 1H, Ar-*H*), 7.90 (s, 1H, CON*H*), 7.85 (app. t, *J* 2.0, 1H, Ar-*H*), 7.58 (ddd, *J* 8.0, 2.0, 1.0, 1H, Ar-*H*), 7.47 (app. t, *J* 8.0, 1H, Ar-*H*), 4.00 (s, 2H, CH_2), 2.15 (s, 3H, CO*Me*), 1.29 (s, 9H, CMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 161.1, 139.3, 139.2, 130.1, 125.2, 123.4, 118.9, 83.9, 61.9, 27.7, 24.6; IR ν_{max} (neat)/cm^{-1} 3356 (NH), 2982, 1730 ((OR)C=O), 1675 ((NH)C=O), 1538, 1480, 1302 (SO_2), 1256, 1139 (SO_2); LRMS (ESI) *m/z* 336 (100%, $[M+Na]^+$), 649 (20%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 336.0873 $[M+Na]^+$, $C_{14}H_{19}NO_5SNa$ requires *m/z* 336.0876.

***tert*-Butyl 2-[(4-bromophenyl)sulfonyl]acetate (1o)**



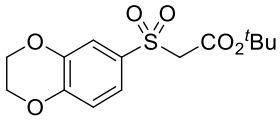
Prepared according to general procedure B using 4-bromophenylboronic acid (50 mg, 0.25 mmol) and TBAB (20 mg, 0.0625 mmol). Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as an off-white solid (49 mg, 58%); mp 74-75 °C (CH_2Cl_2) [lit.[2] mp 73-74 °C]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* 8.5, 2H, Ar-*H*), 7.66 (d, *J* 8.5, 2H, Ar-*H*), 3.96 (s, 2H, CH_2), 1.33 (s, 9H, CMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 137.9, 132.5, 130.2, 129.6, 84.0, 62.0, 27.7; LRMS (ESI) *m/z* 357 (90%, $[M(^{79}Br)+Na]^+$), 359 (100%, $[M(^{81}Br)+Na]^+$); HRMS (ESI) found *m/z* 358.9745 $[M(^{81}Br)+Na]^+$, $C_{12}H_{15}O_4{}^{81}BrSNa$ requires *m/z* 358.9746. Data in accordance with that previously reported.[2]

***tert*-Butyl 2-[(4-(dimethylamino)phenyl)sulfonyl]acetate (1p)**



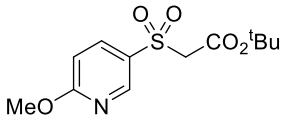
Prepared according to general procedure B using 4-dimethylaminophenylboronic acid (41 mg, 0.25 mmol) and TBAB (20 mg, 0.0625 mmol). Purification by flash column chromatography (petrol/Et_2O 2:3) afforded the titled sulfone as an off-white solid (39 mg, 52%); mp 98-99 °C (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* 9.0, 2H, Ar-*H*), 6.62 (d, *J* 9.0, 2H, Ar-*H*), 3.90 (s, 2H, CH_2), 3.00 (s, 6H, NMe_2), 1.34 (s, 9H, CMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 153.7, 130.3, 123.9, 110.7, 83.1, 62.7, 40.1, 27.8; IR ν_{max} (neat)/cm^{-1} 2975, 1722 (CO), 1599, 1314 (SO_2), 1295, 1148 (SO_2), 1082; LRMS (ESI) *m/z* 322 (70%, $[M+Na]^+$), 621 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 322.1081 $[M+Na]^+$, $C_{14}H_{21}NO_4SNa$ requires *m/z* 322.1084.

***tert*-Butyl 2-{(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)sulfonyl}acetate (1q)**



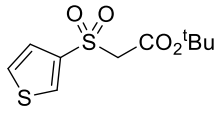
Prepared according to general procedure B using 1,4-benzodioxane-6-boronic acid (45 mg, 0.25 mmol) and TBAB (20 mg, 0.0625 mmol). Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as an off-white solid (67 mg, 85%); mp 78-79 °C (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* 2.5, 1H, Ar-*H*), 7.44 (dd, *J* 8.5, 2.5, 1H, Ar-*H*), 7.03 (d, *J* 8.5, 1H, Ar-*H*), 4.50-4.18 (m, 4H, OCH_2), 4.01 (s, 2H, CH_2), 1.43 (s, 9H, CMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 148.6, 143.6, 131.3, 122.3, 118.3, 117.9, 83.5, 64.6, 64.1, 62.4, 27.8; IR ν_{max} (neat)/cm^{-1} 2986, 2934, 1736 (CO), 1495, 1311 (SO_2), 1157 (SO_2), 1074; LRMS (ESI) *m/z* 337 (50%, $[M+Na]^+$), 651 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 337.0714 $[M+Na]^+$, $C_{14}H_{18}O_6SNa$ requires *m/z* 337.0716.

***tert*-Butyl 2-[(6-methoxypyridin-3-yl)sulfonyl]acetate (1r)**



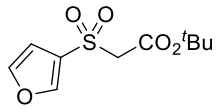
Prepared according to general procedure A using 2-methoxy-5-pyridylboronic acid (38 mg, 0.25 mmol). Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as a colourless oil (38 mg, 53%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (dd, *J* 2.5, 0.5, 1H, Ar-*H*), 8.05 (dd, *J* 9.0, 2.5, 1H, Ar-*H*), 6.90 (dd, *J* 9.0, 0.5, 1H, Ar-*H*), 4.06 (overlapping s, 5H, CH_2 and OCH_3), 1.45 (s, 9H, CMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 161.4, 149.5, 138.6, 128.1, 111.4, 84.0, 62.5, 54.5, 27.8; LRMS (ESI) *m/z* 288 (50%, $[M+Na]^+$), 597 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 288.0898 $[M+H]^+$, $C_{12}H_{18}NO_5S$ requires *m/z* 288.0900. Data in accordance with that previously reported.[2]

***tert*-Butyl 2-(thiophen-3-ylsulfonyl)acetate (1f)**



Prepared according to general procedure G using thienyl-3-boronic acid (32 mg, 0.25 mmol) and TBAB (20 mg, 0.0625 mmol). Purification by flash column chromatography (petrol/Et_2O 1:1) afforded the titled sulfone as a colourless oil (42 mg, 64%). Data as outlined above.

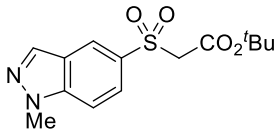
***tert*-Butyl 2-(furan-3-ylsulfonyl)acetate (1s)**



Prepared according to general procedure B using furan-3-boronic acid (28 mg, 0.25 mmol) and TBAB (20 mg, 0.0625 mmol). Purification by flash column chromatography (petrol/Et_2O 2:3) afforded the titled sulfone as a yellow oil (29 mg, 48%); ^{1}H NMR (400 MHz, $CDCl_3$)

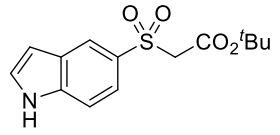
δ 7.97 (dd, *J* 1.5, 1.0, 1H, Ar-*H*), 7.47 (app. t, *J* 2.0, 1H, Ar-*H*), 6.69 (dd, *J* 2.0, 1.0, 1H, Ar-*H*), 3.98 (s, 2H, CH_2), 1.38 (s, 9H, CMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 147.9, 144.7, 126.9, 109.3, 83.9, 62.3, 27.8; IR ν_{max} (neat)/cm^{-1} 2982, 1729 (CO), 1498, 1327 (SO_2), 1152 (SO_2), 1008; LRMS (ESI) *m/z* 269 (70%, $[M+Na]^+$), 515 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 269.0454 $[M+Na]^+$, $C_{10}H_{14}O_5SNa$ requires *m/z* 269.0454.

tert-Butyl 2-[(1-methyl-1H-indazol-5-yl)sulfonyl]acetate (1t)



Prepared according to general procedure B using 1-methylindazole-5-boronic acid (44 mg, 0.25 mmol) and TBAB (20 mg, 0.0625 mmol). Purification by flash column chromatography (petrol/Et_2O 1:1) afforded the titled sulfone as an off-white solid (56 mg, 72%); mp 98-99 °C (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (dd, *J* 2.0, 1.0, 1H, Ar-*H*), 8.19 (d, *J* 1.0, 1H, Ar-*H*), 7.93 (dd, *J* 9.0, 2.0, 1H, Ar-*H*), 7.57 (app. dt, *J* 9.0, 1.0, 1H, Ar-*H*), 4.17 (s, 3H, N*Me*), 4.10 (s, 2H, CH_2), 1.39 (s, 9H, CMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 141.4, 134.8, 131.1, 125.2, 124.5, 123.2, 109.6, 83.6, 62.5, 36.0, 27.7; IR ν_{max} (neat)/cm^{-1} 3010, 2947, 1719 (CO), 1410, 1319 (SO_2), 1157 (SO_2); LRMS (ESI) *m/z* 333 (10%, $[M+Na]^+$), 643 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 333.0878 $[M+Na]^+$, $C_{14}H_{18}N_2O_4SNa$ requires *m/z* 333.0880.

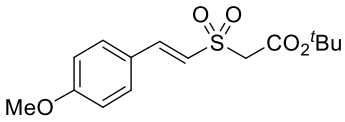
tert-Butyl 2-[(1H-indol-5-yl)sulfonyl]acetate (1u)



Prepared according to general procedure B using 5-indolylboronic acid (40 mg, 0.25 mmol) and TBAB (20 mg, 0.0625 mmol) and running the first step for 1 hr. Purification by flash column chromatography (petrol/Et_2O 1:4) afforded the titled sulfone as an off-white solid (46 mg, 62%); mp 102-103 °C (CH_2Cl_2) [lit.[2] mp 104-105 °C];; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (br. s, 1H, N*H*), 8.20 (app. dt, *J* 2.0, 1.0, 1H, Ar-*H*), 7.64 (dd, *J* 8.5, 2.0, 1H, Ar-*H*),

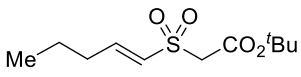
7.45 (app. dt, *J* 8.5, 1.0, 1H, Ar-*H*), 7.30 (dd, *J* 3.5, 2.0, 1H, Ar-*H*), 6.62 (ddd, *J* 3.5, 2.0, 1.0, 1H, Ar-*H*), 4.00 (s, 2H, CH_2), 1.26 (s, 9H, CMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 138.4, 129.9, 127.4, 127.0, 123.0, 121.3, 111.6, 104.2, 83.4, 62.8, 27.7; LRMS (ESI) *m/z* 318 (10%, $[M+Na]^+$), 613 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 318.0769 $[M+Na]^+$, $C_{14}H_{17}NO_4SNa$ requires *m/z* 318.0771. Data in accordance with that previously reported.[2]

***tert*-Butyl (*E*)-2-[(4-methoxystyryl)sulfonyl]acetate (1v)**



Prepared according to general procedure B using trans-2-(4-methoxyphenyl)vinylboronic, acid (45 mg, 0.25 mmol) and TBAB (20 mg, 0.0625 mmol). Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as a colourless oil (35 mg, 45%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* 15.5, 1H, SO_2CHCH), 7.41 (d, *J* 9.0, 2H, Ar-*H*), 6.86 (d, *J* 9.0, 2H, Ar-*H*), 6.82 (d, *J* 15.5, 1H, SO_2CH), 3.91 (s, 2H, CH_2), 3.78 (s, 3H, O*Me*), 1.40 (s, 9H, CMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 162.0, 144.9, 130.6, 124.7, 122.0, 114.6, 83.8, 61.5, 55.48, 27.9; IR ν_{max} (neat)/cm^{-1} 2979, 1728 (CO), 1601, 1512, 1309 (SO_2), 1129 (SO_2), 1026; LRMS (ESI) *m/z* 335 (50%, $[M+Na]^+$), 647 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 335.0922 $[M+Na]^+$, $C_{15}H_{20}O_5SNa$ requires *m/z* 335.0924.

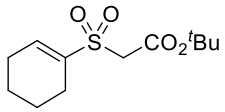
***tert*-Butyl (*E*)-2-(pent-1-en-1-ylsulfonyl)acetate (1w)**



Prepared according to general procedure B using penten-1-yl-boronic acid (29 mg, 0.25 mmol) and TBAB (20 mg, 0.0625 mmol) and running the first step for 1 hr. Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as a colourless oil (23 mg, 37%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (dt, *J* 15.0, 7.0, 1H, SO_2CHCH), 6.43 (dt, *J* 15.0, 1.5, 1H, SO_2CH), 3.82 (s, 2H, SO_2CH_2), 2.18-2.25 (m, 2H, $CHCH_2$), 1.50-1.44 (m, 2H, CH_3CH_2), 1.43 (s, 9H, CMe_3), 0.90 (t, *J* 7.5, 3H, CH_2CH_3); ^{13}C NMR (100 MHz,

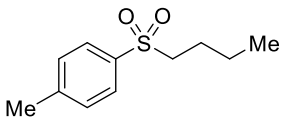
$CDCl_3$) δ 161.9, 150.0, 128.2, 83.8, 60.9, 33.5, 27.9, 20.8, 13.6; IR ν_{max} (neat)/cm^{-1} 2965, 1730 (CO), 1635, 1323 (SO_2), 1294, 1132 (SO_2); LRMS (ESI) *m/z* 271 (70%, $[M+Na]^+$), 519 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 271.0971 $[M+Na]^+$, $C_{11}H_{20}O_4SNa$ requires *m/z* 271.0975.

tert-Butyl 2-(cyclohex-1-en-1-ylsulfonyl)acetate (1x)



Prepared according to general procedure B using 1-cyclohexen-1-yl-boronic acid (32 mg, 0.25 mmol) and TBAB (20 mg, 0.0625 mmol) and running the first step for 1 hr. Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as a white solid (60 mg, 92%); mp 52-53 °C (CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 6.99 (tt, *J* 4.0, 2.0, 1H, CH_2CH), 3.87 (s, 2H, SO_2CH_2), 2.43-2.39 (m, 2H, CH_2), 2.35-2.29 (m, 2H, CH_2), 1.85-1.77 (m, 2H, CH_2), 1.72-1.65 (m, 2H, CH_2), 1.49 (s, 9H, CMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 141.4, 138.0, 83.4, 58.4, 27.8, 25.6, 23.5, 21.9, 20.8; IR ν_{max} (neat)/cm^{-1} 2948, 1723 (CO), 1644, 1311 (SO_2), 1288, 1134 (SO_2); LRMS (ESI) *m/z* 283 (60%, $[M+Na]^+$), 543 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 283.0972 $[M+Na]^+$, $C_{12}H_{20}O_4SNa$ requires *m/z* 283.0975.

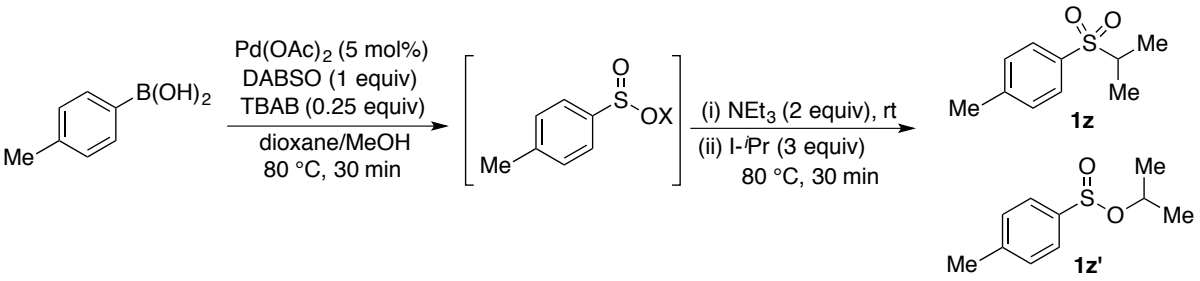
1-(Butylsulfonyl)-4-methylbenzene (1y)



Prepared according to general procedure B using *p*-tolylboronic acid (33 mg, 0.25 mmol) and *n*-butyl iodide (85 μL, 0.75 mmol). Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as a colourless oil (41 mg, 77%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* 8.0, 2H, Ar-*H*), 7.38 (d, *J* 8.0, 2H, Ar-*H*), 3.17-3.00 (m, 2H, SO_2CH_2), 2.48 (s, 3H, Ar*Me*), 1.70 (tt, *J* 8.0, 6.5, 2H, $SO_2CH_2CH_2$), 1.41 (app. sext., *J* 7.5, 2H, CH_3CH_2), 0.91 (t, *J* 7.5, 3H, CH_3CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 136.3, 129.9, 128.1, 56.2, 24.7, 21.6 (2C), 13.5; LRMS (ESI) *m/z* 235 (30%, $[M+Na]^+$), 447 (100%,

[2M+Na]$^+$); HRMS (ESI) found *m/z* 235.0762 [M+Na]$^+$, $C_{11}H_{16}O_2SNa$ requires *m/z* 235.0763. Data in accordance with that previously reported.[5]

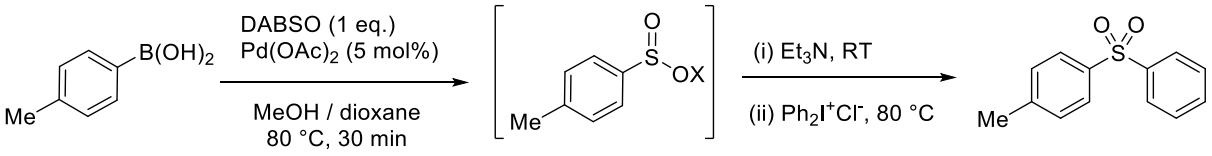
1-(*Iso*propylsulfonyl)-4-methylbenzene (1z) and 1z'



Prepared according to general procedure B using *p*-tolylboronic acid (33 mg, 0.25 mmol) and *iso*propyl iodide (75 μL, 0.75 mmol). Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone **1z** as a white solid (28 mg, 52%) and sulfinic acid ester **1z'** as a colourless oil; **1z**: mp 76-77 °C (CH_2Cl_2) [lit.[6] mp 76-77 °C]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* 8.5, 2H, Ar-*H*), 7.29 (d, *J* 8.5, 2H, Ar-*H*), 3.10 (hept., *J* 7.0, 1H, C*H*(CH_3)$_2$), 2.38 (s, 3H, Ar*Me*), 1.21 (d, *J* 7.0, 6H, CHC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 134.0, 129.7, 129.1, 55.6, 21.6, 15.8; LRMS (ESI) *m/z* 221 (20%, [M+Na]$^+$), 419 (100%, [2M+Na]$^+$); HRMS (ESI) found *m/z* 221.0607 [M+Na]$^+$, $C_{10}H_{14}O_2SNa$ requires *m/z* 221.0607. Data in accordance with that previously reported.[6]

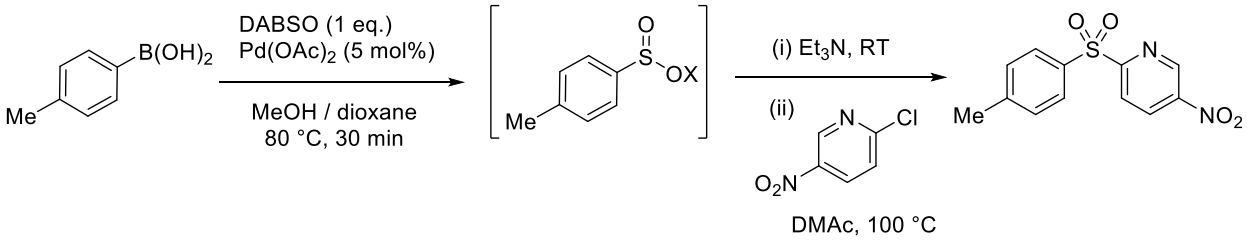
1z': ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* 8.0 Hz, 2H, Ar-*H*), 7.26 (d, *J* 8.0 Hz, 2H, Ar-*H*), 4.53 (hept., *J* 6.0 Hz, 1H, C*H*CH_3), 2.35 (s, 3H, Ar*Me*), 1.31 (d, *J* 6.0 Hz, 3H, CHC*H*$_3$), 1.18 (d, *J* 6.0 Hz, 3H, CHC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 142.5, 129.6, 125.0, 72.7, 24.0, 23.8, 21.5; LRMS (ESI) *m/z* 199 (60%, [M+H]$^+$), 221 (100%, [M+Na]$^+$), 419 (50%, [2M+Na]$^+$); HRMS (ESI) found *m/z* 221.0607 [M+Na]$^+$, $C_{10}H_{14}O_2SNa$ requires *m/z* 221.0607. Data in accordance with that previously reported.[7]

Synthesis of 1-methyl-4-(phenylsulfonyl)benzene (1aa)



To a reaction tube was added DABSO (60 mg, 0.25 mmol), *p*-tolylboronic acid (33 mg, 0.25 mmol) and $Pd(OAc)_2$ (2.8 mg, 0.0125 mmol). After addition of dioxane (0.8 mL) and MeOH (0.8 mL) the resulting mixture was heated at 80 ºC and stirred at this temp. for 30 min. The reaction was then allowed to cool to room temp., Et_3N (70 μL, 0.50 mmol) added and the mixture stirred for 1 min. Following this, diphenyliodonium chloride (237 mg, 0.75 mmol) was added and the resulting mixture was heated at 80 ºC and stirred at this temp. for 6hr. The reaction mixture was allowed to cool to room temp. and filtered through a plug of silica before removing the solvent *in vacuo*. Purification by flash column chromatography (petrol/Et_2O 3:2) afforded the titled sulfone as a white solid (47 mg, 81%); mp 124-125 °C (CH_2Cl_2) [lit.[10] mp 124-125 °C]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* 8.5, 2H, Ar-*H*), 7.76 (d, *J* 8.5, 2H, Ar-*H*), 7.53-7.36 (m, 3H, Ar-*H*), 7.22 (d, *J* 8.5, 2H, Ar-*H*), 2.32 (s, 3H, Ar*Me*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 142.0, 138.7, 133.0, 129.9, 129.2, 127.7, 127.5, 21.6; LRMS (ESI) *m/z* 255 (100%, $[M+Na]^+$), 487 (90%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 255.0450 $[M+Na]^+$, $C_{13}H_{12}O_2SNa$ requires *m/z* 255.0450. Data in accordance with that previously reported.[10]

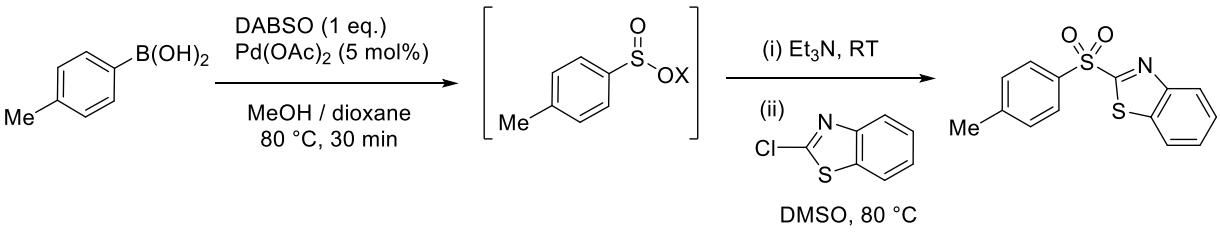
Synthesis of 5-nitro-2-tosylpyridine (1ab)



To a reaction tube was added DABSO (60 mg, 0.25 mmol), *p*-tolylboronic acid (33 mg, 0.25 mmol) and $Pd(OAc)_2$ (2.8 mg, 0.0125 mmol). After addition of dioxane (0.8 mL) and

MeOH (0.8 mL) the resulting mixture was heated at 80 ºC and stirred at this temp. for 30 min. The reaction was then allowed to cool to room temp., Et_3N (70 μL, 0.50 mmol) added and the mixture stirred for 1 min. Following this, the solvents were removed *in vacuo* and 2-chloro-5-nitropyridine (80 mg, 0.50 mmol) and DMAc (1.5 mL) were added. The resulting mixture was heated at 100 ºC and stirred at this temp. for 1hr. After cooling, water (10 mL) and EtOAc (15 mL) were added, the two phases separated and the aqueous layer extracted with EtOAc (2 × 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. Purification by flash column chromatography (petrol/Et_2O 1:1) afforded the titled sulfone as an off-white solid (41 mg, 60%); mp 146-147 °C (CH_2Cl_2) [lit.[9] mp 144-145 °C]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (dd, *J* 2.5, 0.5, 1H, Ar-*H*), 8.62 (dd, *J* 8.5, 2.5, 1H, Ar-*H*), 8.33 (dd, *J* 8.5, 0.5, 1H, Ar-*H*), 7.88 (d, *J* 8.5, 2H, Ar-*H*), 7.30 (d, *J* 8.5, 2H, Ar-*H*), 2.37 (s, 3H, Ar*Me*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 146.0, 145.7, 145.1, 134.3, 133.5, 130.1, 129.5, 122.4, 21.8; LRMS (ESI) *m/z* 301 (100%, $[M+Na]^+$); HRMS (ESI) found *m/z* 301.0254 $[M+Na]^+$, $C_{12}H_{10}N_2O_4SNa$ requires *m/z* 301.0254. Data in accordance with that previously reported.[8]

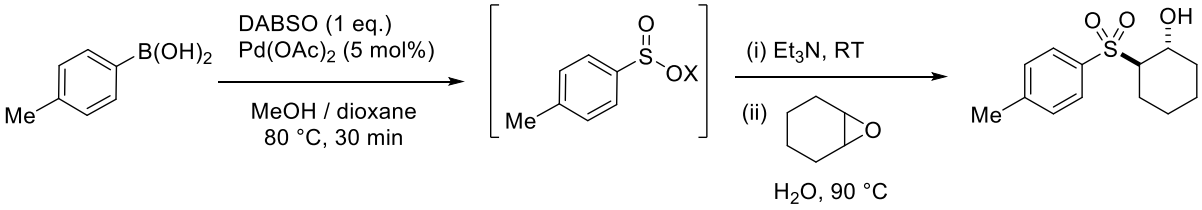
Synthesis of 2-tosylbenzo[*d*]thiazole (1ac)



To a reaction tube was added DABSO (60 mg, 0.25 mmol), *p*-tolylboronic acid (33 mg, 0.25 mmol) and $Pd(OAc)_2$ (2.8 mg, 0.0125 mmol). After addition of dioxane (0.8 mL) and MeOH (0.8 mL) the resulting mixture was heated at 80 ºC and stirred at this temp. for 30 min. The reaction was then allowed to cool to room temp., Et_3N (70 μL, 0.50 mmol) added and the mixture stirred for 1 min. Following this, the solvents were removed *in vacuo* and 2-chlorobenzothiazole (100 μL, 0.75 mmol) and DMSO (1.5 mL) were added. The resulting mixture was heated at 80 ºC and stirred at this temp. for 2 hr. After cooling, water (10 mL) and EtOAc (15 mL) were added, the two phases separated and the aqueous layer extracted with EtOAc (2 × 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and

the solvent removed *in vacuo*. Purification by flash column chromatography (petrol/Et_2O 3:1) afforded the titled sulfone as a white solid (30 mg, 41%); mp 133-134 °C (CH_2Cl_2) [lit.[8] mp 130-132 °C]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-8.04 (m, 1H, Ar-*H*), 7.97 (d, *J* 8.5, 2H, Ar-*H*), 7.89-7.86 (m, 1H, Ar-*H*), 7.54-7.42 (m, 2H, Ar-*H*), 7.30 (d, *J* 8.5, 2H, Ar-*H*), 2.35 (s, 3H, Ar*Me*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 152.9, 145.9, 137.0, 135.5, 130.2, 129.0, 127.8, 127.5, 125.5, 122.2, 21.8; LRMS (ESI) *m/z* 312 (40%, $[M+Na]^+$), 601 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 312.0124 $[M+Na]^+$, $C_{14}H_{11}NO_2S_2Na$ requires *m/z* 312.0123. Data in accordance with that previously reported.[9]

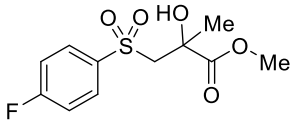
General procedure C for the synthesis of *β*-hydroxysulfones as exemplified by the preparation of 2-tosylcyclohexan-1-ol (1ad)



To a reaction tube was added DABSO (60 mg, 0.25 mmol), *p*-tolylboronic acid (33 mg, 0.25 mmol) and $Pd(OAc)_2$ (2.8 mg, 0.0125 mmol). After addition of dioxane (0.8 mL) and MeOH (0.8 mL) the resulting mixture was heated at 80 ºC and stirred at this temp. for 30 min. The reaction was then allowed to cool to room temp., Et_3N (70 μL, 0.50 mmol) added and the mixture stirred for 1 min. Following this, the solvents were removed *in vacuo* and cyclohexene oxide (125 μL, 1.25 mmol) and H_2O (1.5 mL) added. The resulting mixture was heated at 90 ºC and stirred at this temp. for 6hr. After cooling, sat. NH_4Cl (10 mL) and subsequently CH_2Cl_2 (10 mL) were added, the two phases separated and the aqueous layer extracted with CH_2Cl_2 (2 × 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. Purification by flash column chromatography (petrol/Et_2O 1:4) afforded the titled sulfone as an off-white solid (44 mg, 69%) mp 125-126 °C (CH_2Cl_2) [lit.[11] mp 123 °C]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* 8.5, 2H, Ar-*H*), 7.32 (d, *J* 8.5, 2H, Ar-*H*), 4.29 (s, 1H, O*H*), 3.82 (td, *J* 10.0, 5.0, 1H, C*H*OH), 2.89 (ddd, *J* 12.0, 10.0, 4.0, 1H, SC*H*CH_2), 2.40 (s, 3H, Ar*Me*), 2.09-2.02 (m, 1H, CH(OH)CH_2), 1.87-1.80 (m, 1H, SCHCH_2), 1.66-1.60 (m, 2H, CH_2), 1.32-1.05 (m, 4H, 1 × CH(OH)CH_2, 1 × SCHCH_2

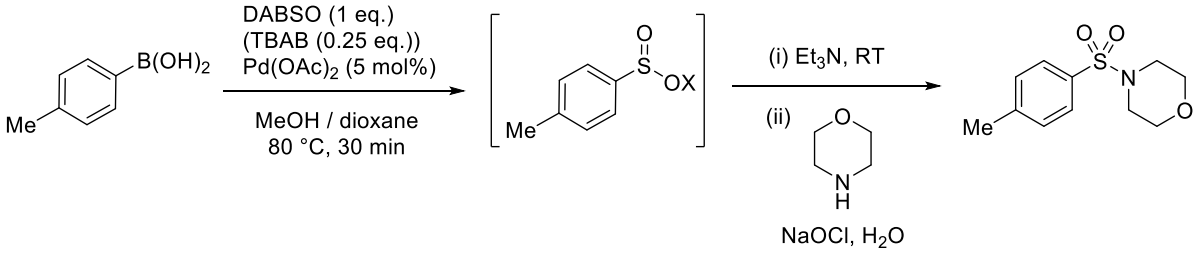
and C*H*$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 133.7, 129.9, 129.1, 68.9, 68.2, 34.1, 25.7, 24.6, 23.6, 21.7; LRMS (ESI) *m/z* 277 (20%, $[M+Na]^+$), 531 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 277.0876 $[M+Na]^+$, $C_{13}H_{18}O_3SNa$ requires *m/z* 277.0869. Data in accordance with that previously reported.[11]

Methyl 3-[(4-fluorophenyl)sulfonyl]-2-hydroxy-2-methylpropanoate (1ae)



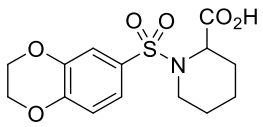
Prepared according to general procedure C using *p*-fluorophenylboronic acid (35 mg, 0.25 mmol), TBAB (20 mg, 0.0625 mmol) and methyl 2-methylglycidate (130 μL, 1.25 mmol). Purification by flash column chromatography (petrol/Et_2O 1:4) afforded the titled sulfone as an off-white solid (40 mg, 58%); mp 66-67 °C (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.81 (m, 2H, Ar-*H*), 7.15 (dd, *J* 9.0, 8.0, 2H, Ar-*H*), 3.77 (s, 3H, CO_2*Me*), 3.70 (d, *J* 15.0, 1H, SO_2CH_2), 3.59 (br. s, 1H, O*H*), 3.49 (d, *J* 15.0, 1H, SO_2CH_2), 1.38 (s, 3H, C(OH)*Me*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 165.8 (d, J_{CF} 256.5), 136.7 (d, J_{CF} 3.0), 131.1 (d, J_{CF} 10.0), 116.4 (d, J_{CF} 23.0), 72.3, 63.9, 53.6, 27.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -103.3; IR ν_{max} (neat)/cm^{-1} 3468 (br. OH), 3080, 2952, 1750 (CO), 1590, 1316 (SO_2), 1145 (SO_2), 1083; LRMS (ESI) *m/z* 299 (100%, $[M+Na]^+$), 575 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 299.0362 $[M+Na]^+$, $C_{11}H_{13}O_5FSNa$ requires *m/z* 299.0360.

General Procedure D for the synthesis of substituted sulfonamides as exemplified by the preparation of 4-tosylmorpholine (3a)



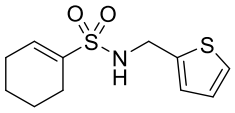
To a reaction tube was added DABSO (60 mg, 0.25 mmol), *p*-tolylboronic acid (33 mg, 0.25 mmol) and $Pd(OAc)_2$ (2.8 mg, 0.0125 mmol). After addition of dioxane (0.8 mL) and MeOH (0.8 mL) the resulting mixture was heated at 80 ºC and stirred at this temp. for 30 min. The reaction was then allowed to cool to room temp., Et_3N (70 μL, 0.50 mmol) added and the mixture stirred for 1 min. Following this, the solvents were removed *in vacuo* and water (1.5 mL) and morpholine (110 μL, 1.25 mmol) were added. NaOCl (14.5 % aqueous solution, 320 μL, 0.75 mmol) was added to the mixture at 0 ºC and the reaction was allowed to warm to room temp. and stirred at this temp. for 16 hr. $NaS_2O_{3(aq)}$ (10 mL) was added and the mixture stirred for a further 20 mins. The aqueous mixture was then extracted with CH_2Cl_2 (3 × 15 mL) and the combined organic extracts were subsequently washed with 1M $HCl_{(aq)}$ (1 × 30 mL). The organic layer was dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. Purification by flash column chromatography (petrol/Et_2O 1:1) afforded the titled sulfonamide as a white solid (49 mg, 82%); mp 148-149 °C (CH_2Cl_2) [lit.[12] mp 148-150 °C]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* 8.5, 2H, Ar-*H*), 7.35 (d, *J* 8.5, 2H, Ar-*H*), 3.77-3.69 (m, 4H, NCH_2CH_2), 3.02-2.94 (m, 4H, NCH_2CH_2), 2.46 (s, 3H, Ar*Me*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 132.0, 129.7, 127.9, 66.1, 46.0, 21.5; LRMS (ESI) *m/z* 264 (100%, $[M+Na]^+$), 505 (80%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 264.0951 $[M+Na]^+$, $C_{11}H_{15}NO_3SNa$ requires *m/z* 264.0952. Data in accordance with that previously reported.[12]

1-{(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)sulfonyl}piperidine-2-carboxylic acid (3b)



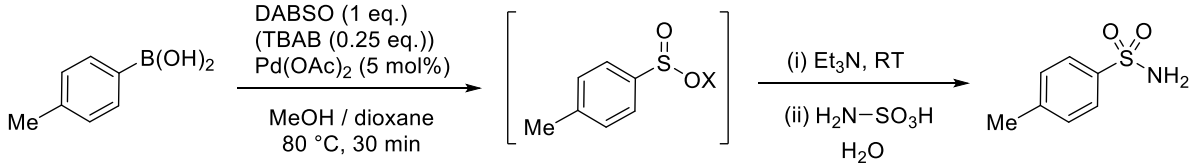
Prepared according to general procedure D using 1,4-benzodioxane-6-boronic acid (45 mg, 0.25 mmol), TBAB (20 mg, 0.0625 mmol) and and (*D*,*L*)-pipecolinic acid (161 mg, 1.25 mmol). The aqueous acid wash (extracted with EtOAc) gave the pure titled sulfonamide as an off-white solid (46 mg, 56%) without further purification; mp 123-124 °C (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* 2.0, 1H, Ar-*H*), 7.21 (dd, *J* 8.5, 2.0, 1H, Ar-*H*), 6.85 (d, *J* 8.5, 1H, Ar-*H*), 4.67 (app. d, *J* 6.0, 1H, C*H*CO_2H), 4.25 (s, 4H, OCH_2), 3.70-3.62 (m, 1H, NCH_2), 3.12 (td, *J* 12.5, 3.0, 1H, NCH_2), 2.10-2.03 (m, 1H, CH_2), 1.79-1.50 (m, 3H, CH_2), 1.47-1.16 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 147.4, 143.5, 132.1, 120.9, 117.5, 116.8, 64.6, 64.2, 54.7, 42.5, 27.5, 24.5, 20.0; IR ν_{max} (neat)/cm^{-1} 2940 (br. OH), 1715 (CO), 1493, 1315 (SO_2), 1285, 1150 (SO_2), 1055; LRMS (ESI) *m/z* 326 (100%, $[M-H]^-$); HRMS (ESI) found *m/z* 326.0698 $[M-H]^-$, $C_{14}H_{16}NO_6SNa$ requires *m/z* 326.0693.

***N*-(Thiophen-2-ylmethyl)cyclohex-1-ene-1-sulfonamide (3c)**



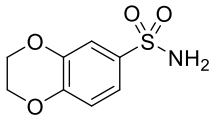
Prepared according to general procedure D using 1-cyclohexen-1-yl-boronic acid (32 mg, 0.25 mmol), TBAB (20 mg, 0.0625 mmol) and 2-thiophenemethylamine (120 μL, 1.25 mmol) and running the first step for 1 hr. Purification by flash column chromatography (petrol/Et_2O 1:1) afforded the titled sulfonamide as a white solid (53 mg, 82%); mp 120-121 °C (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.26 (m, 1H, Ar-*H*), 6.98 (overlapping m, 2H, Ar-*H*), 6.85 (tt, *J* 3.5, 1.5, 1H, CH_2C*H*), 4.51 (t, *J* 6.0, 1H, N*H*), 4.39 (d, *J* 6.0, 2H, NHCH_2), 2.36-2.18 (m, 4H, CH_2), 1.74-1.67 (m, 2H, CH_2), 1.64-1.57 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 138.0, 137.6, 126.9, 126.7, 125.7, 41.7, 25.3, 23.0, 21.8, 20.9; IR ν_{max} (neat)/cm^{-1} 3265 (NH), 2947, 1724, 1434, 1311 (SO_2), 1292, 1140 (SO_2), 1050; LRMS (ESI) *m/z* 280 (70%, $[M+Na]^+$), 537 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 280.0437 $[M+Na]^+$, $C_{11}H_{15}NO_2S_2Na$ requires *m/z* 280.0436.

General procedure E for the synthesis of unsubstituted sulfonamides as exemplified by the preparation of 4-methylbenzenesulfonamide (3d)



To a reaction tube was added DABSO (60 mg, 0.25 mmol), *p*-tolylboronic acid (33 mg, 0.25 mmol) and $Pd(OAc)_2$ (2.8 mg, 0.0125 mmol). After addition of dioxane (0.8 mL) and MeOH (0.8 mL) the resulting mixture was heated at 80 ºC and stirred at this temp. for 30 min. The reaction was then allowed to cool to room temp., Et_3N (70 μL, 0.50 mmol) added and the mixture stirred for 1 min. Following this, the solvents were removed *in vacuo* and water (1.5 mL) and hydroxylamine-*O*-sulfonic acid (141 mg, 1.25 mmol) added. The resulting mixture was stirred at room temp. for 2 hr before adding $NaHCO_{3(aq.)}$ (10 mL) and extracting with CH_2Cl_2 (3 × 15 mL). The organic layer was dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. Purification by flash column chromatography (petrol/Et_2O 1:4) afforded the titled sulfonamide as a white solid (37 mg, 87 %); mp 138-139 °C (CH_2Cl_2) [lit.[13] mp 136-138 °C]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* 8.5, 2H, Ar-*H*), 7.24 (d, *J* 8.5, 2H, Ar-*H*), 4.84 (br s, 2H, NH_2), 2.36 (s, 3H, Ar*Me*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 139.0, 129.7, 126.5, 21.6; LRMS (ESI) *m/z* 194 (100%, $[M+Na]^+$); HRMS (ESI) found *m/z* 194.0249 $[M+Na]^+$, $C_7H_9NO_2SNa$ requires *m/z* 194.0246. Data in accordance with that previously reported.[13]

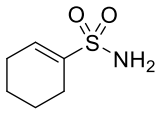
2,3-Dihydrobenzo[*b*][1,4]dioxine-6-sulfonamide (3e)



Prepared according to general procedure E using 1,4-benzodioxane-6-boronic acid (45 mg, 0.25 mmol) and TBAB (20 mg, 0.0625 mmol). Purification by flash column chromatography (petrol/Et_2O 3:7) afforded the titled sulfonamide as a white solid (30 mg, 56 %); mp 194-195 °C (CH_2Cl_2); ^{1}H NMR (400 MHz, MeOD-d_4) δ 7.28-7.23 (overlapping s, 1H, Ar-*H* and

dd, *J* 8.5, 2.0, 1H, Ar-*H*), 6.85 (app. dt, *J* 8.5, 1.0, 1H, Ar-*H*), 4.23-4.16 (m, 4H, OCH_2); ^{13}C NMR (100 MHz, MeOD-d_4) δ 147.0, 143.5, 136.1, 119.2, 117.1, 115.2, 64.5, 64.2; IR ν_{max} (neat)/cm^{-1} 3231 (NH), 2923, 1583, 1498, 1321 (SO_2), 1284, 1146 (SO_2), 1060; LRMS (ESI) *m/z* 238 (90%, $[M+Na]^+$), 453 (100%, $[2M+Na]^+$); HRMS (ESI) found *m/z* 238.0144 $[M+Na]^+$, $C_8H_9NO_4SNa$ requires *m/z* 238.0145.

Cyclohex-1-ene-1-sulfonamide (3f)



Prepared according to general procedure E using 1-cyclohexen-1-yl-boronic acid (32 mg, 0.25 mmol) and TBAB (20 mg, 0.0625 mmol) and running the first step for 1 hr. Purification by flash column chromatography (petrol/Et_2O 1:4) afforded the titled sulfonamide as a colourless oil (27 mg, 67 %); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (tt, *J* 4.0, 1.5, 1H, CH_2CH), 4.74 (br. s, 2H, NH_2), 2.31-2.38 (m, 2H, CH_2), 2.20-2.14 (m, 2H, CH_2), 1.74-1.65 (m, 2H, CH_2), 1.61-1.53 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 135.7, 25.1, 23.0, 21.9, 20.9; IR ν_{max} (neat)/cm^{-1} 3323 (NH), 3233 (NH), 2927, 1558, 1433, 1315 (SO_2), 1151 (SO_2); LRMS (ESI) *m/z* 184 (100%, $[M+Na]^+$); HRMS (ESI) found *m/z* 184.0405 $[M+Na]^+$, $C_6H_{11}NO_2SNa$ requires *m/z* 184.0403.

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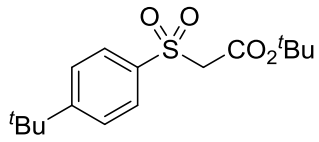
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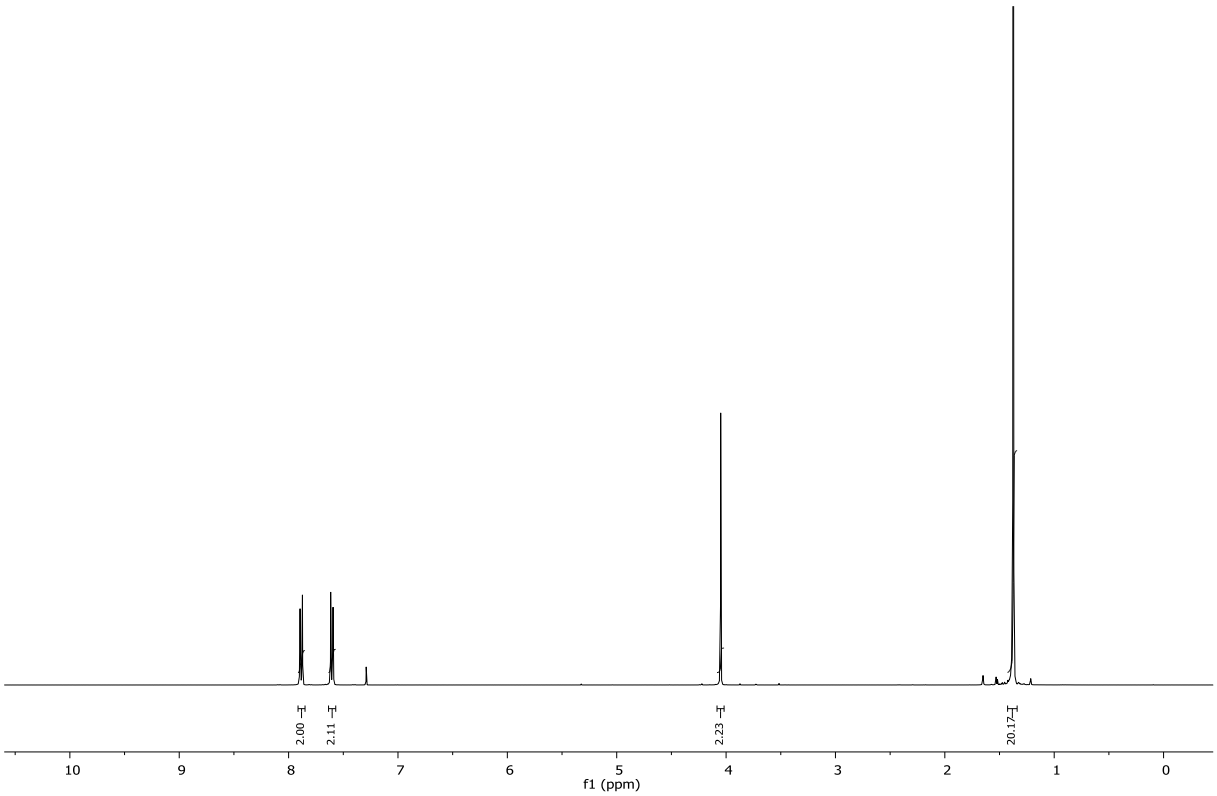
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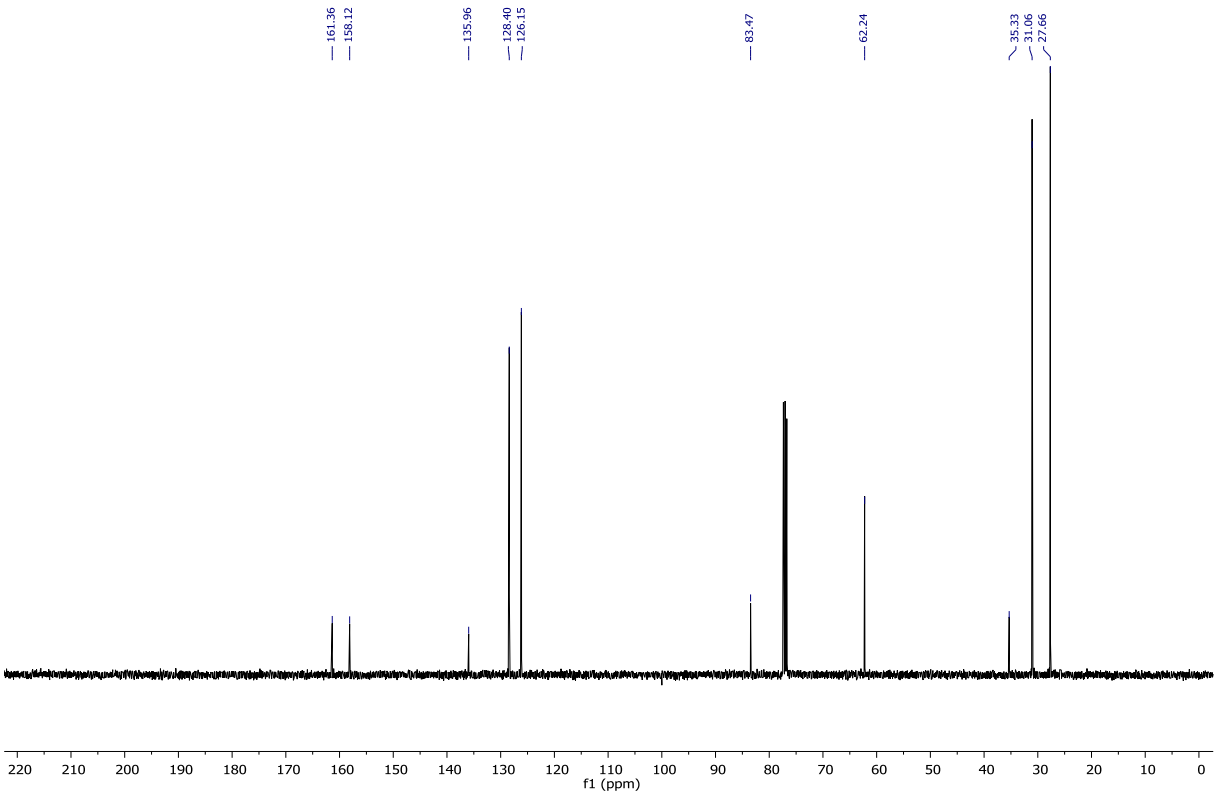
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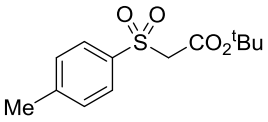
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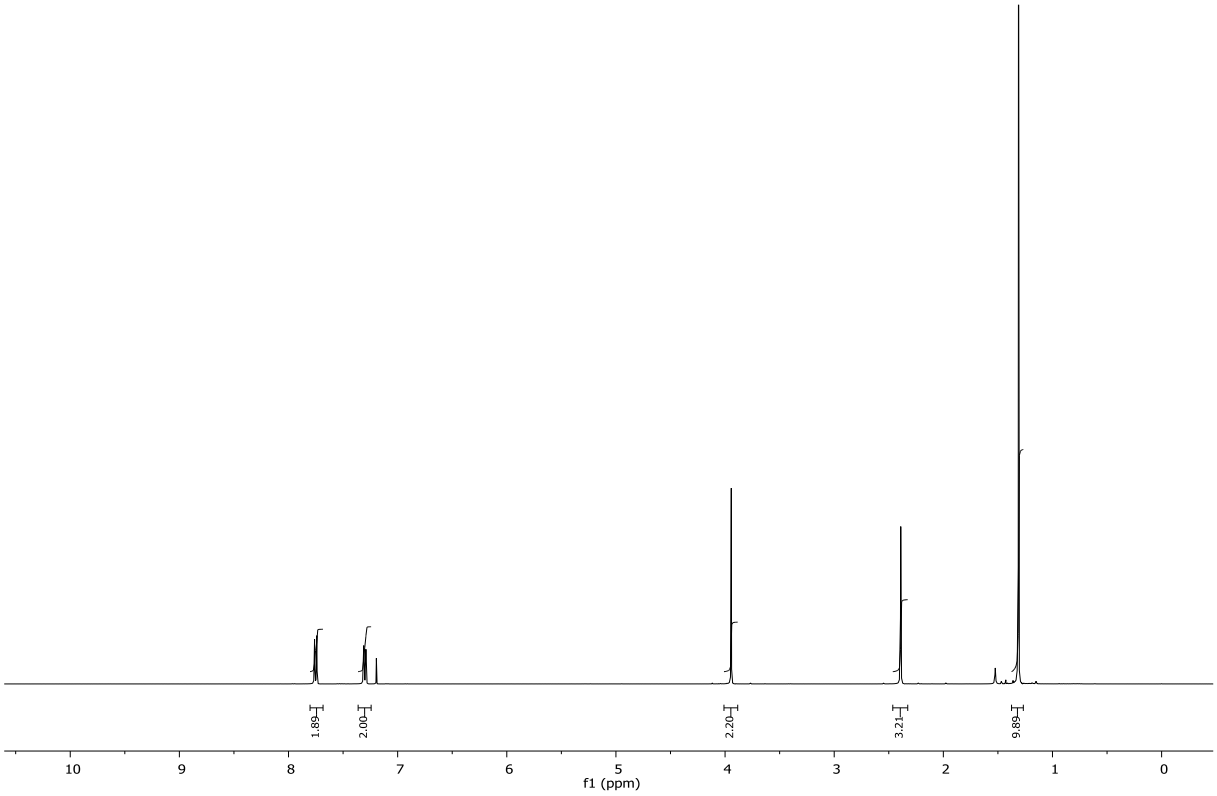
S
CO2tBu
Me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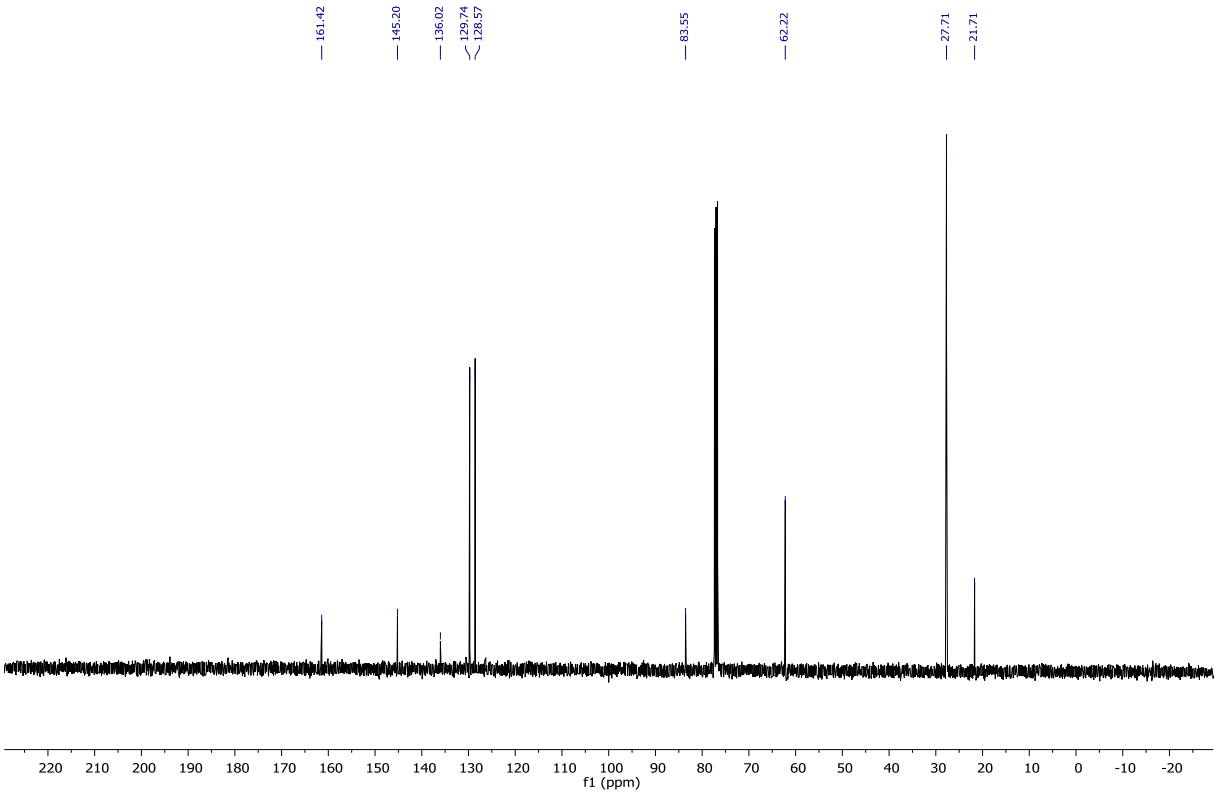
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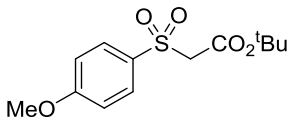
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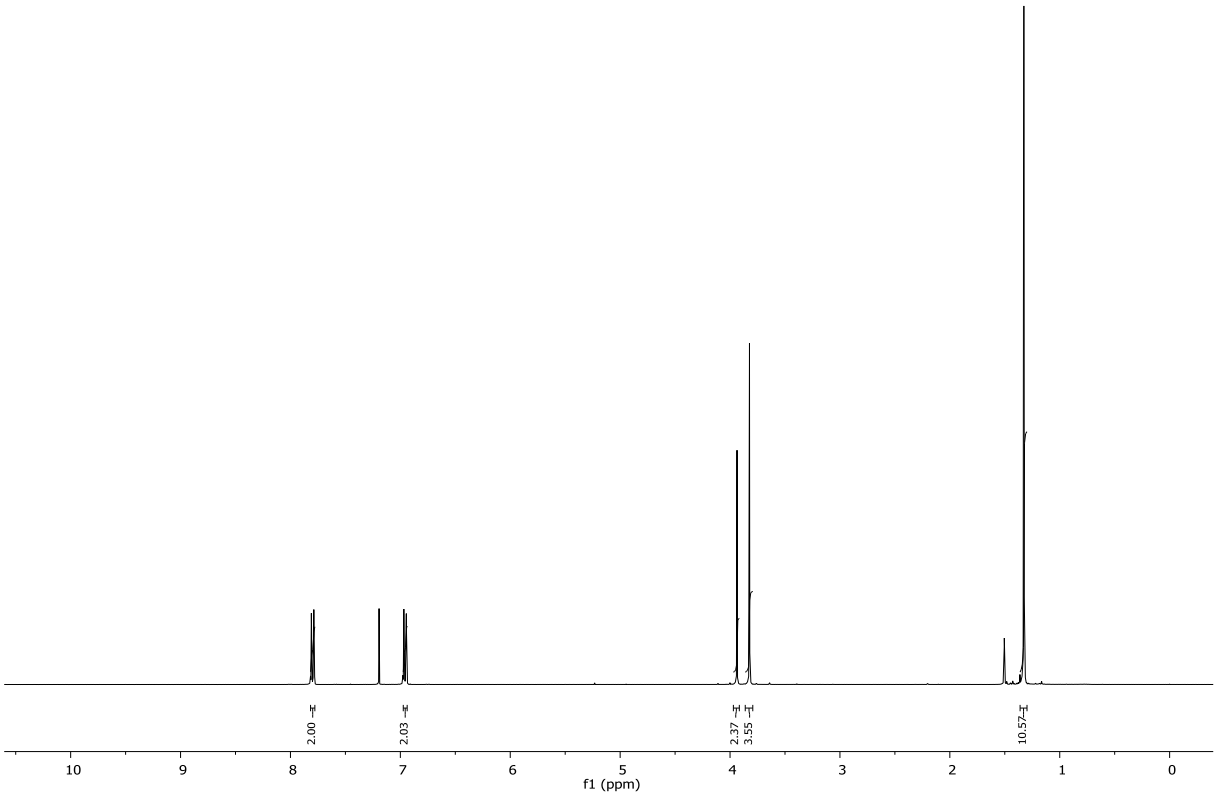
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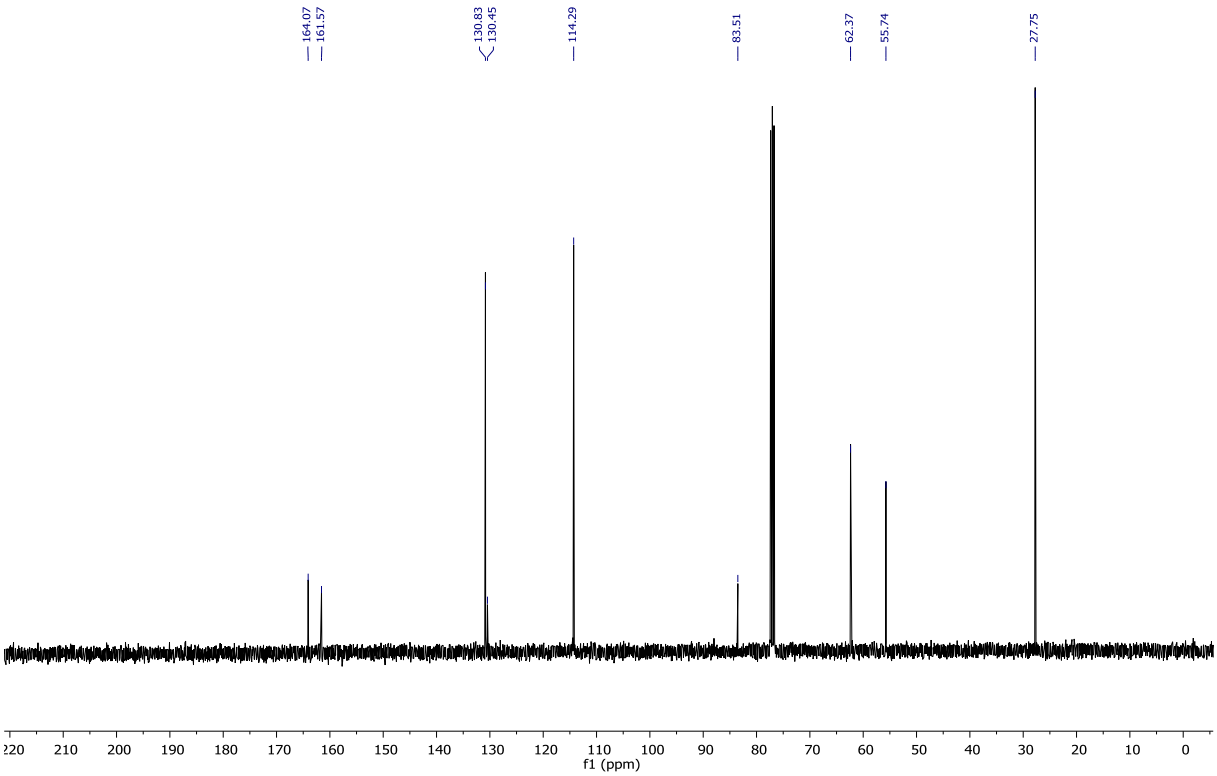
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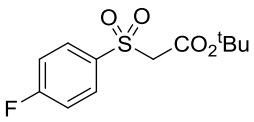
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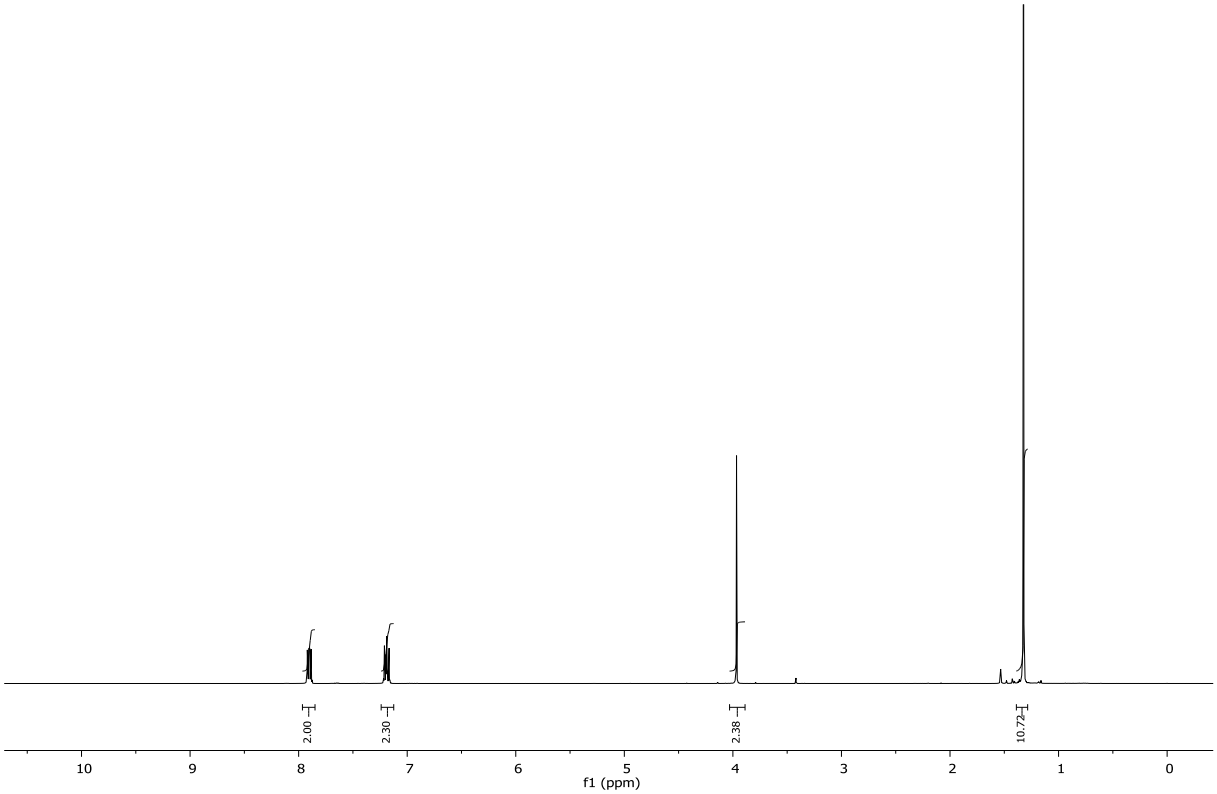
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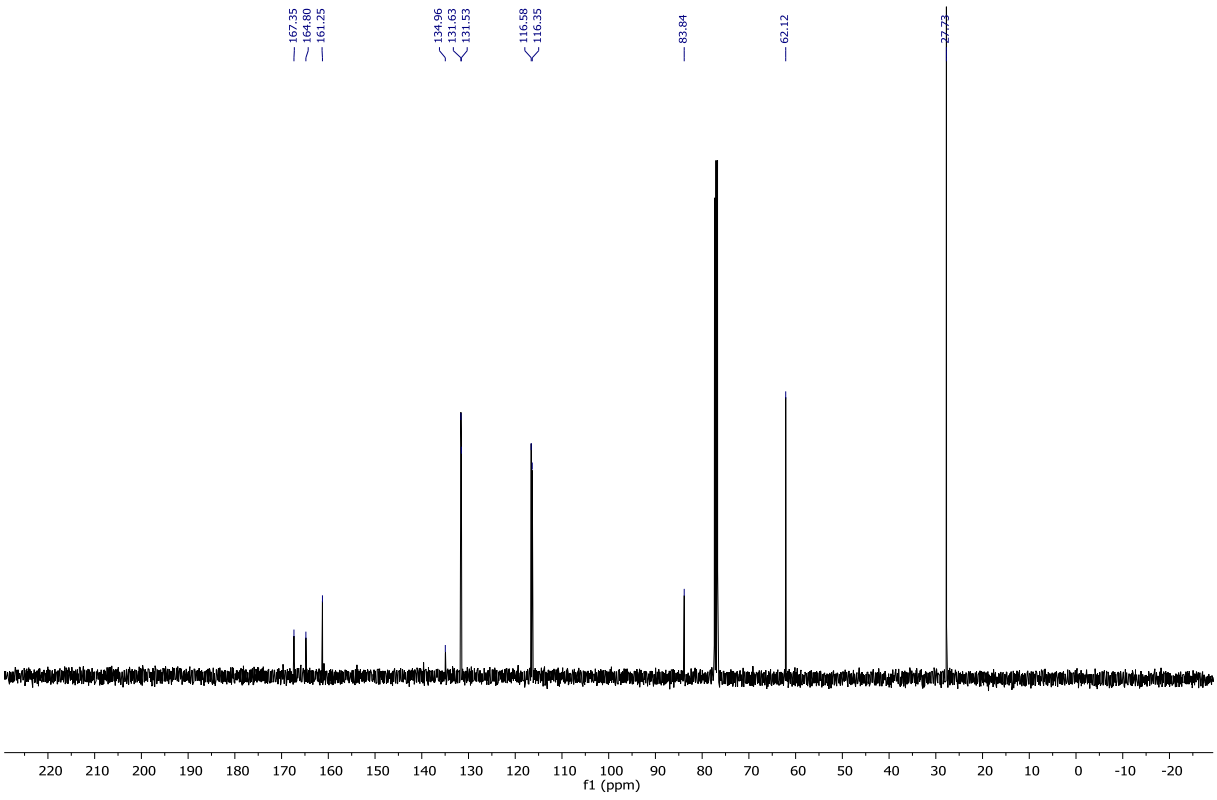
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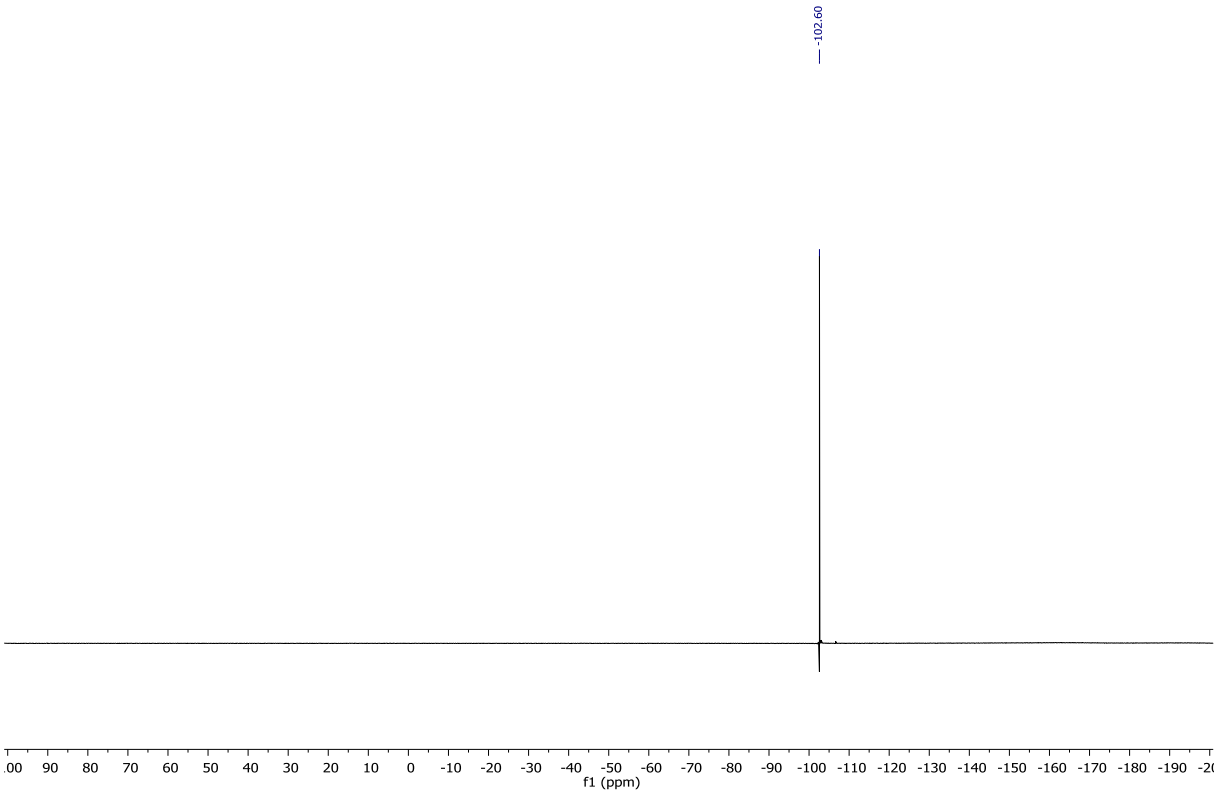
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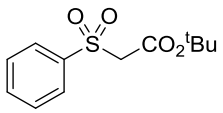
f1 (ppm)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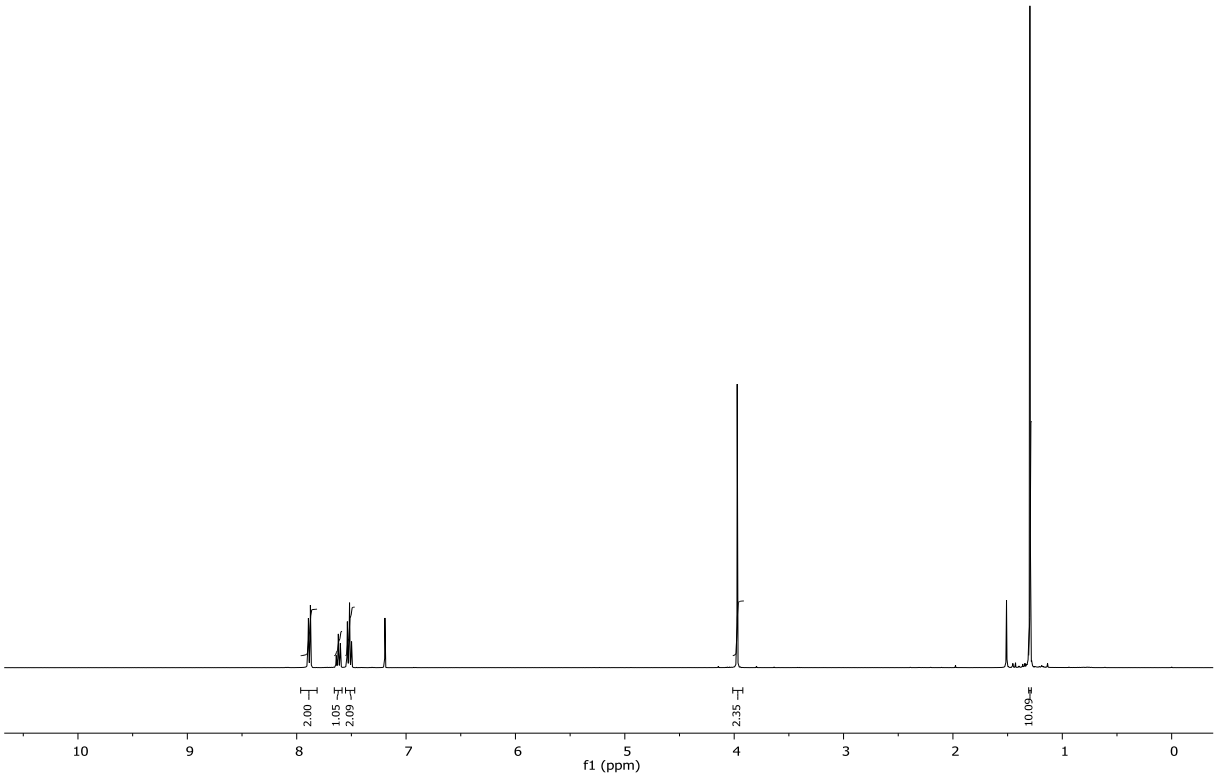
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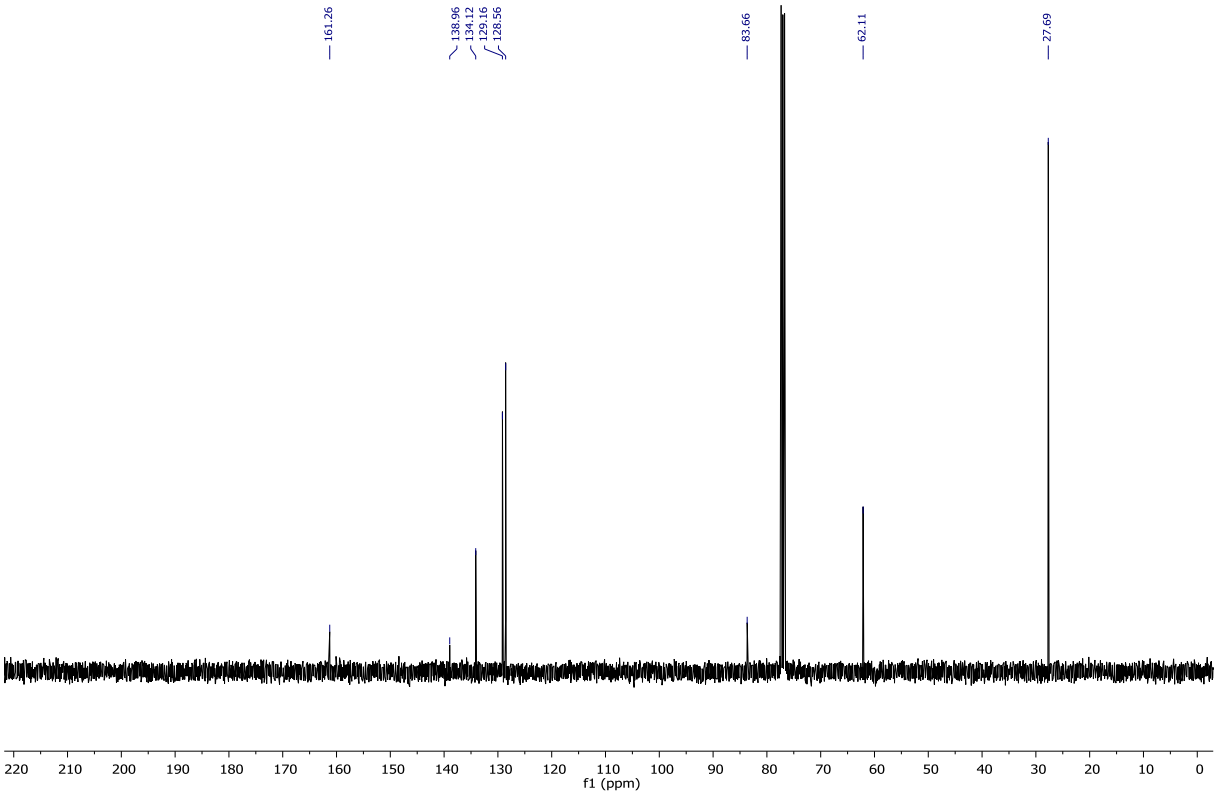
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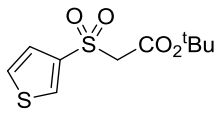
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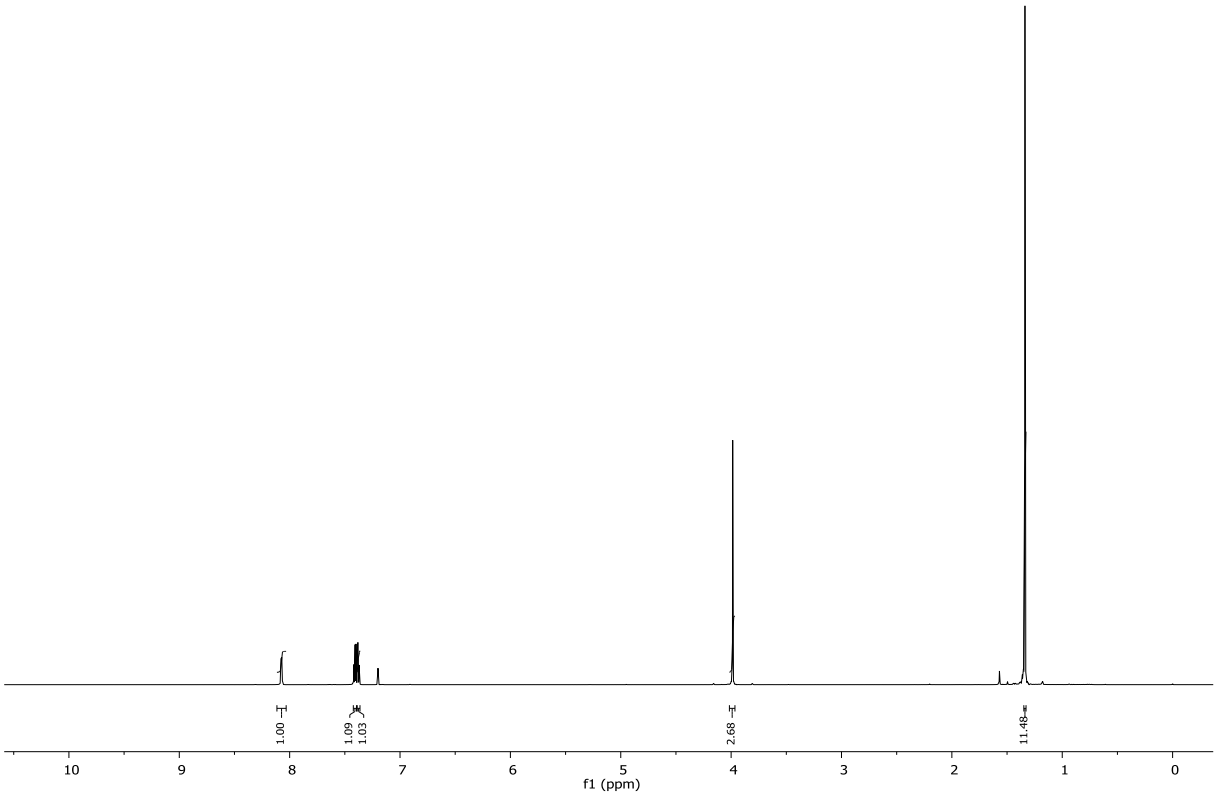
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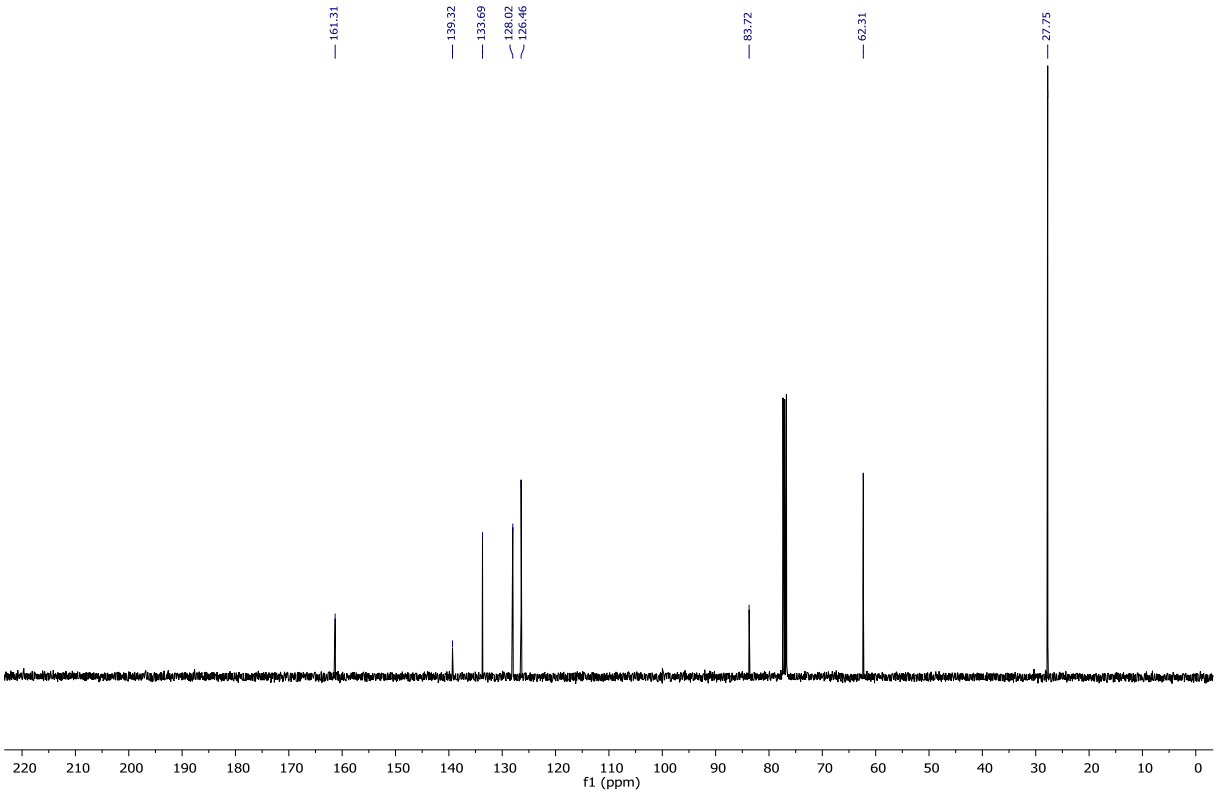
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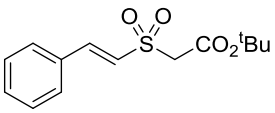
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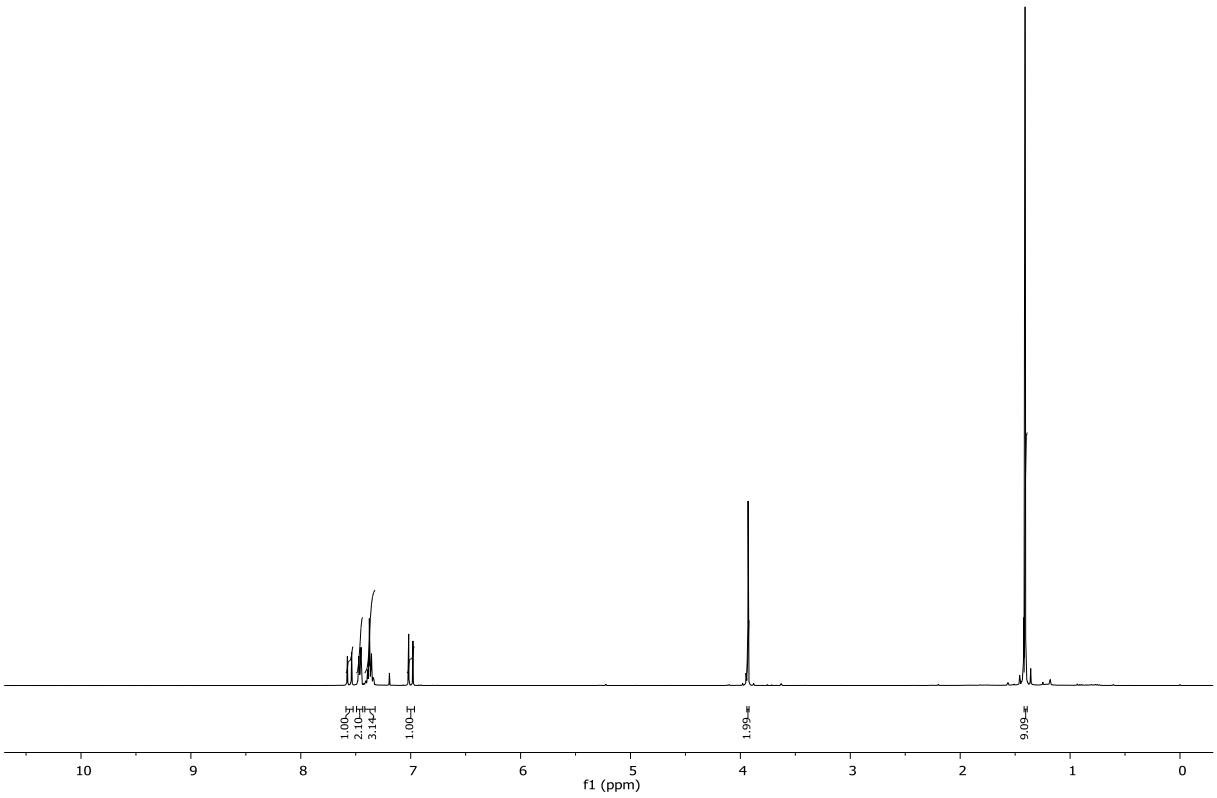
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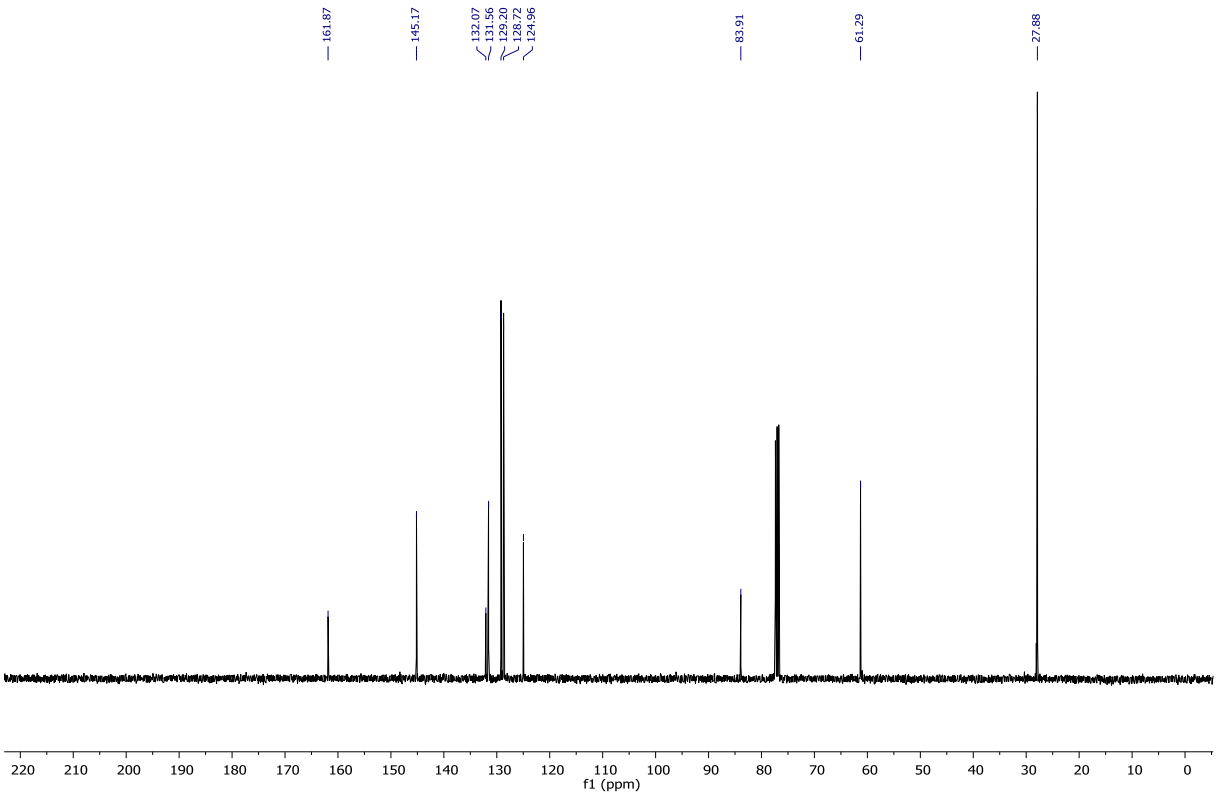
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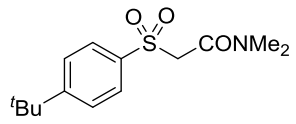
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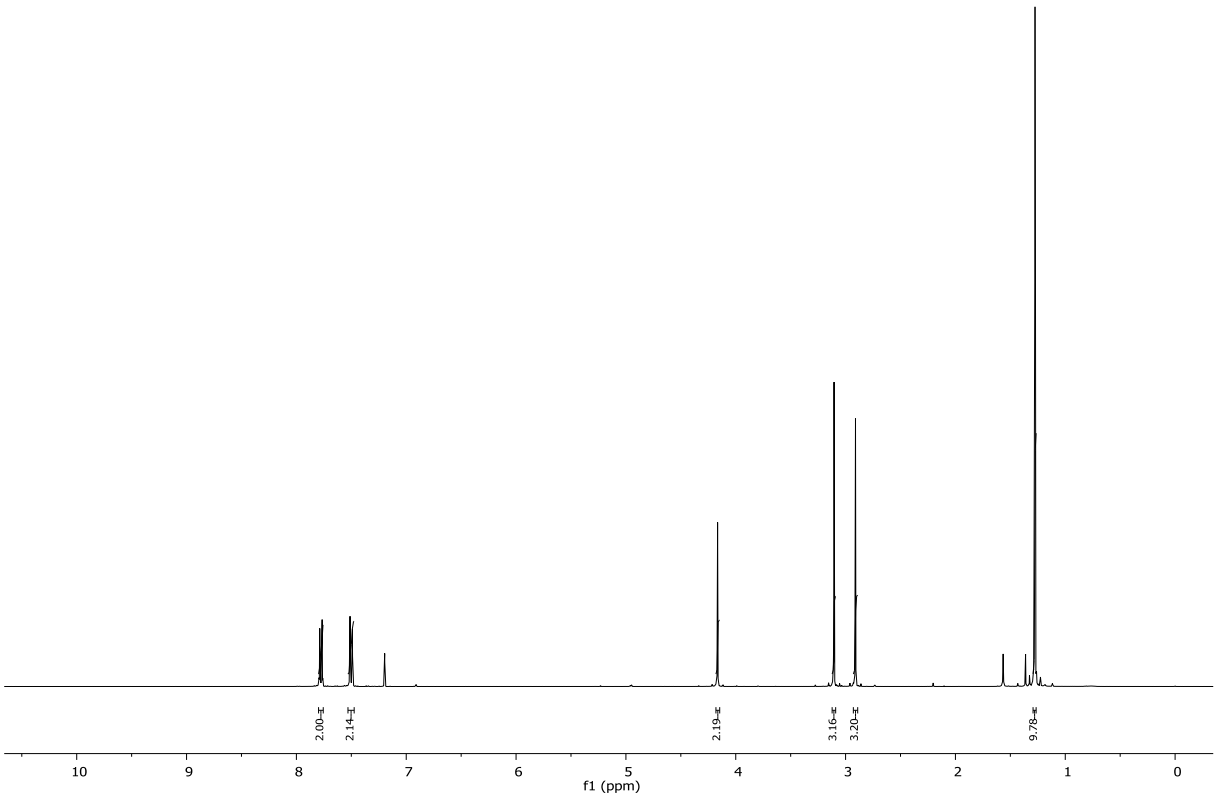
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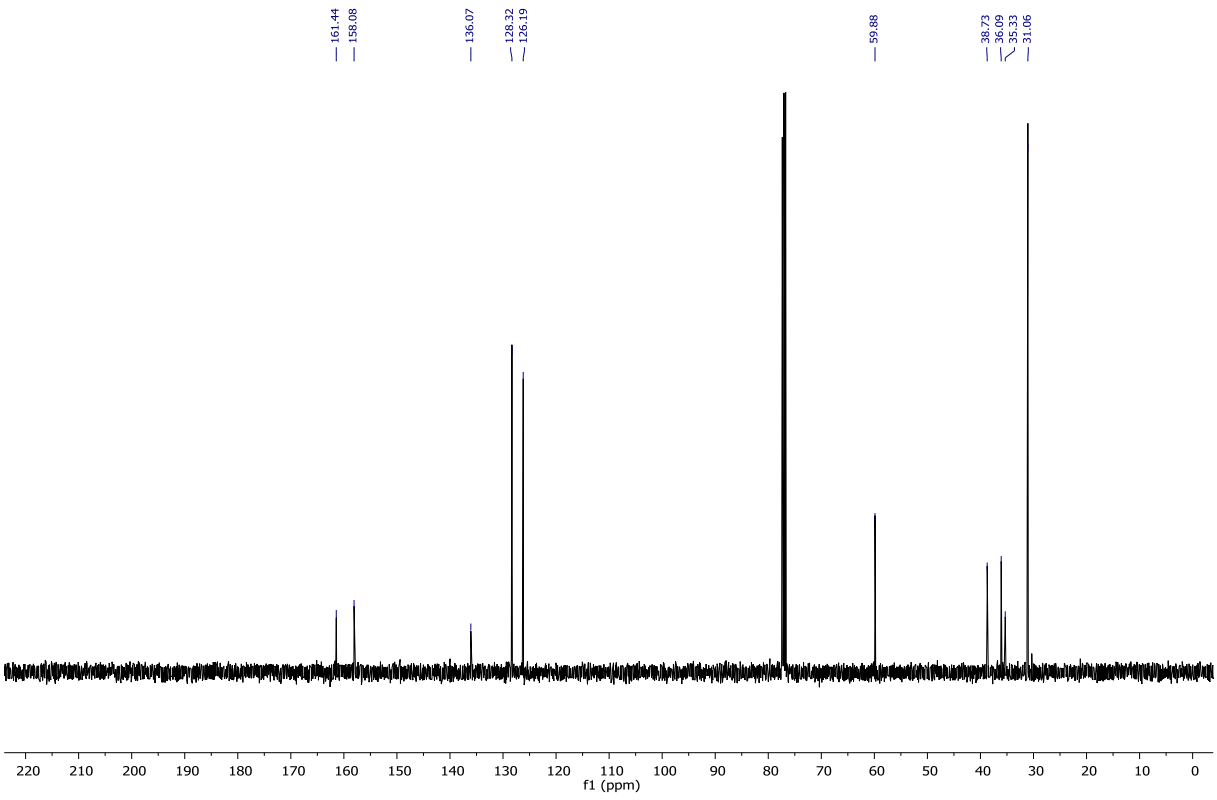
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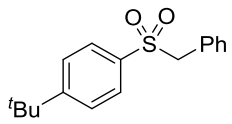
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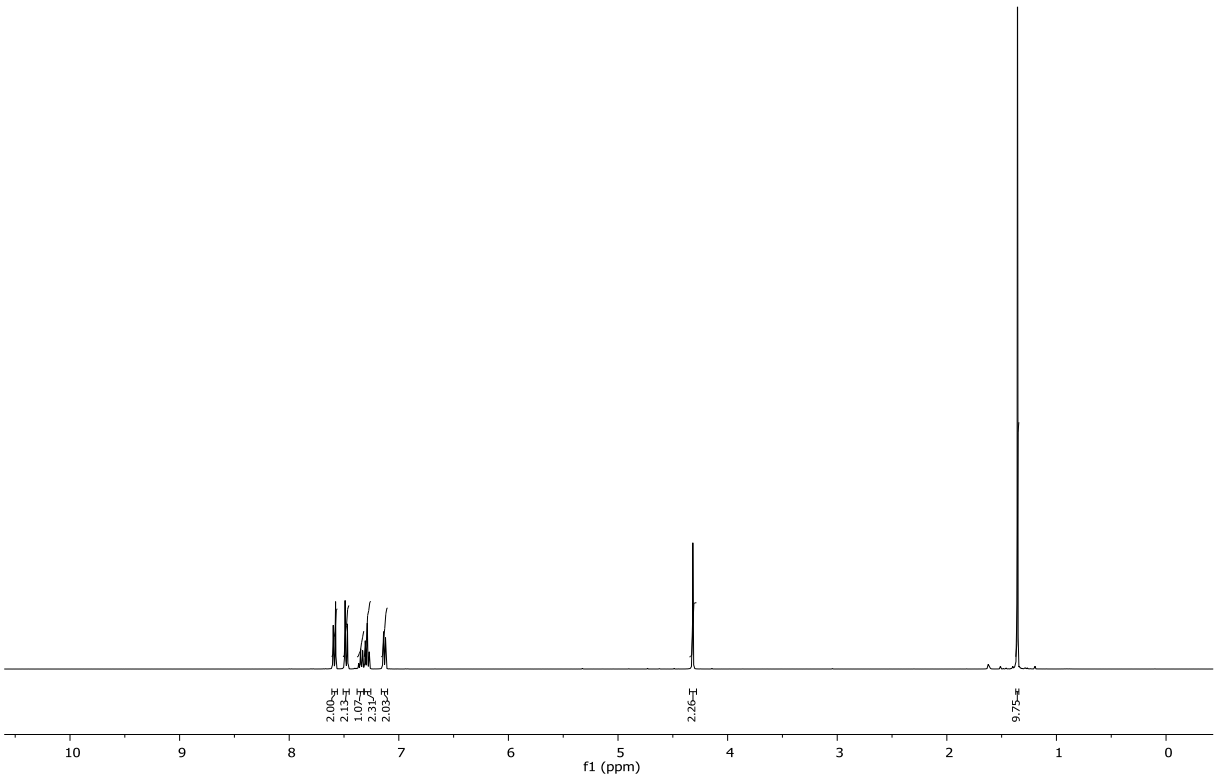
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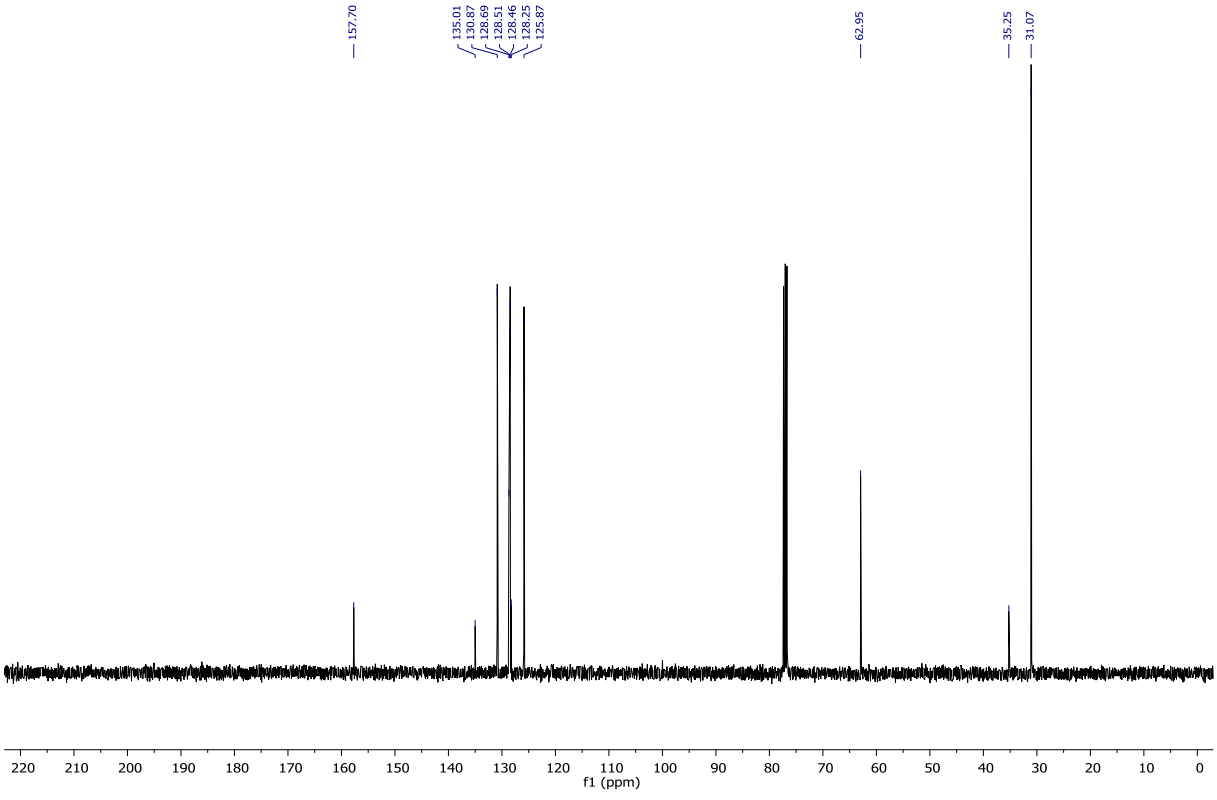
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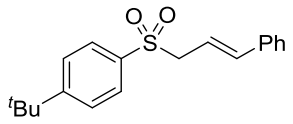
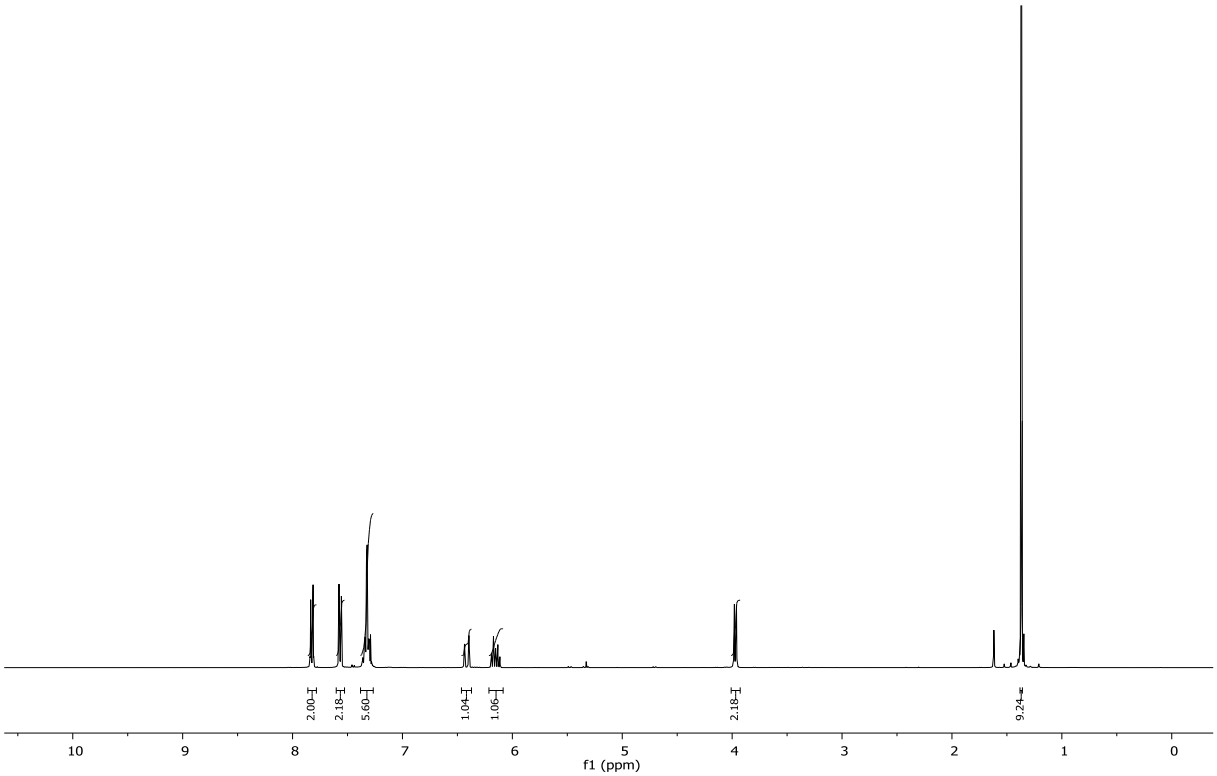
0
f1 (ppm)


O
O
S
Ph
tBu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2.18
5.60
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1.06
2.18
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10
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8
7
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5
4
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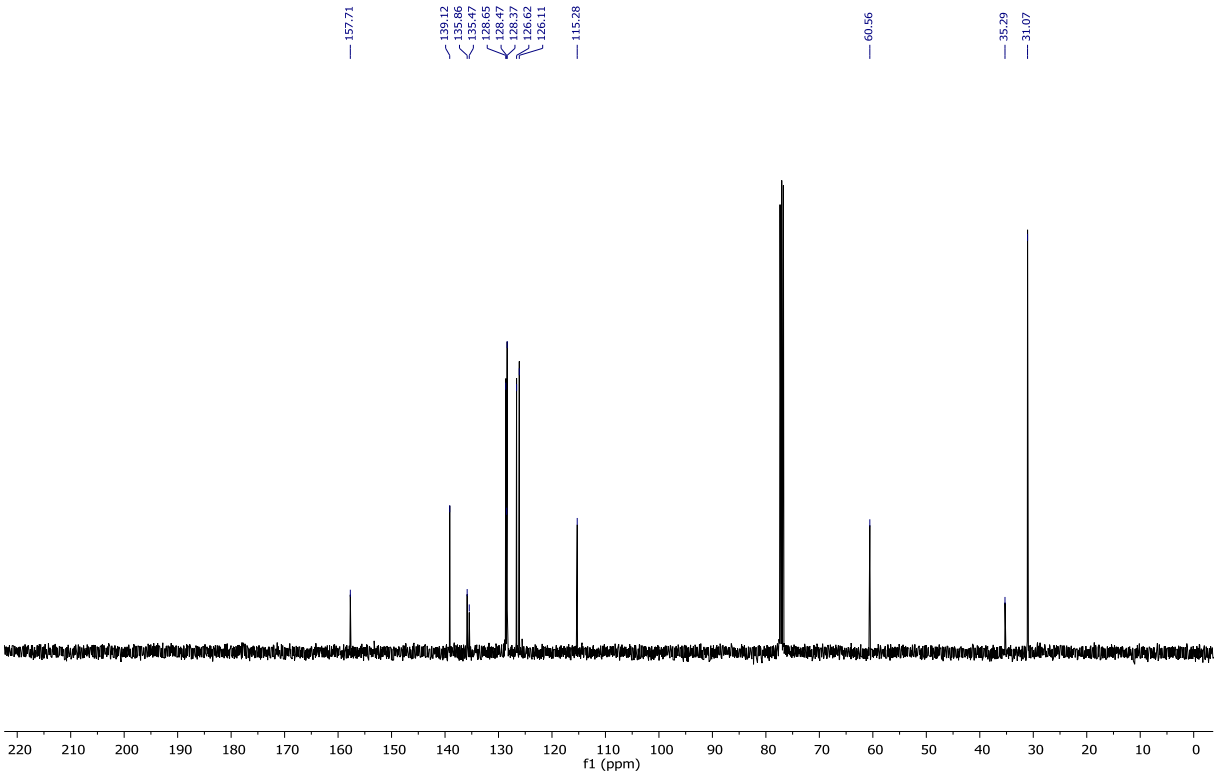
2
1
0
f1 (ppm)


157.71
139.12
135.86
135.47
128.65
128.47
128.37
126.62
126.11
115.28
60.56
35.29
31.07
220
210
200
190
180
170
160
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140
130
120
110
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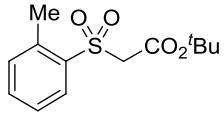
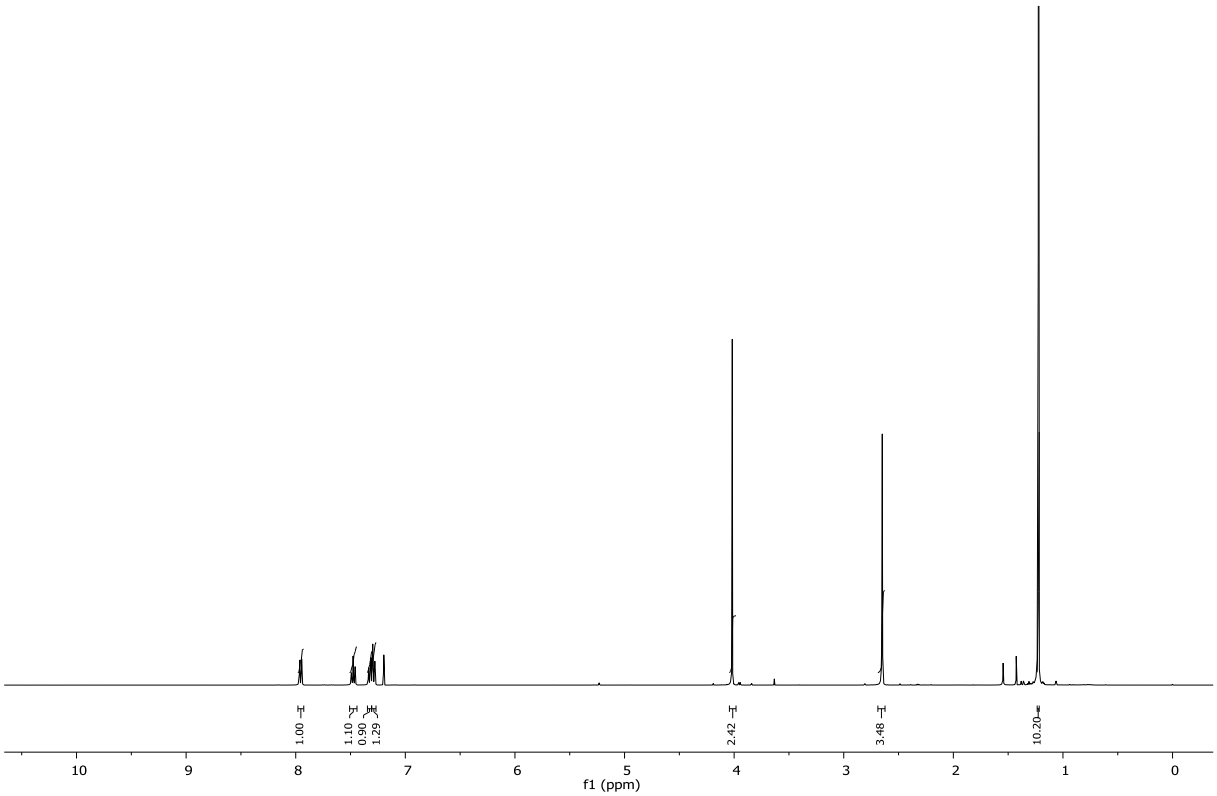
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
O
O
S
CO2tBu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10
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7
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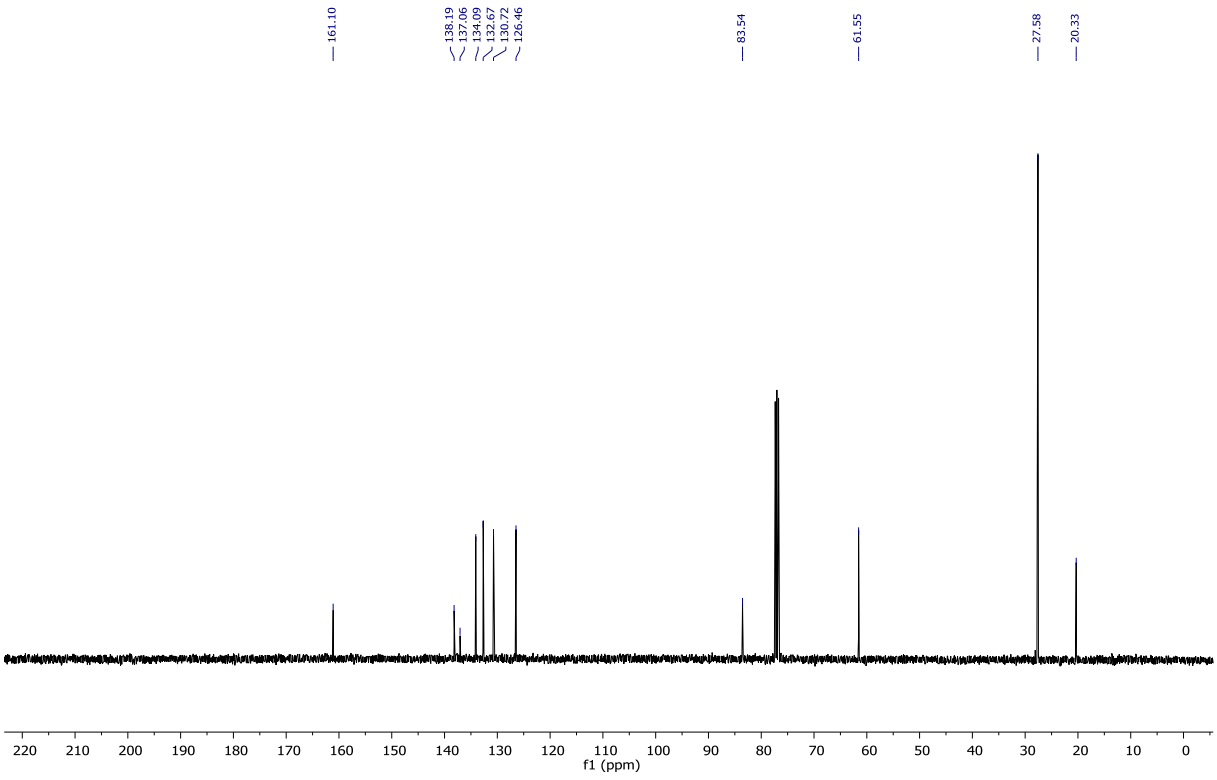
5
4
3
2
1
0
f1 (ppm)


161.10
138.19
137.06
134.09
132.67
130.72
126.46
83.54
61.55
27.58
20.33
220
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200
190
180
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130
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90
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50
40
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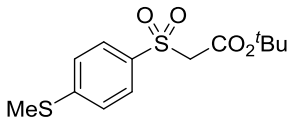
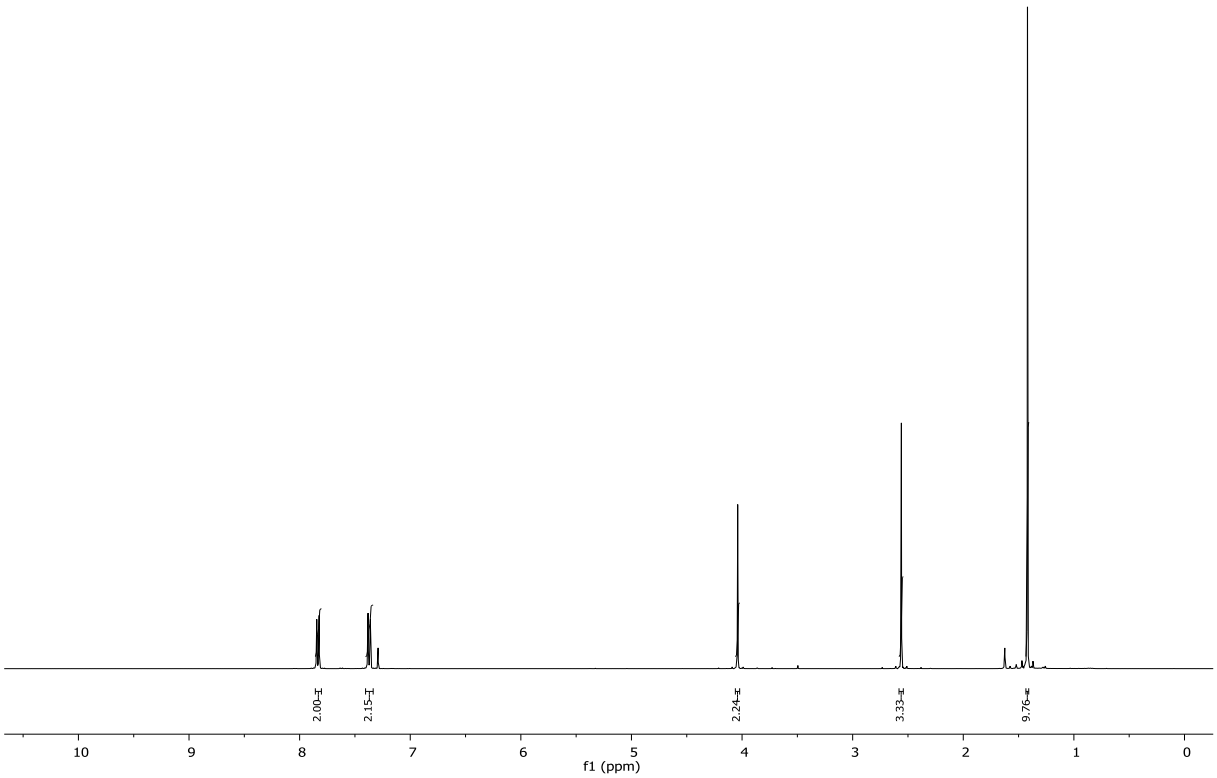
10
0
f1 (ppm)


O
O
S
CO2tBu
MeS


2.00
2.15
2.24
3.33
9.76
10
9
8
7
6
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4
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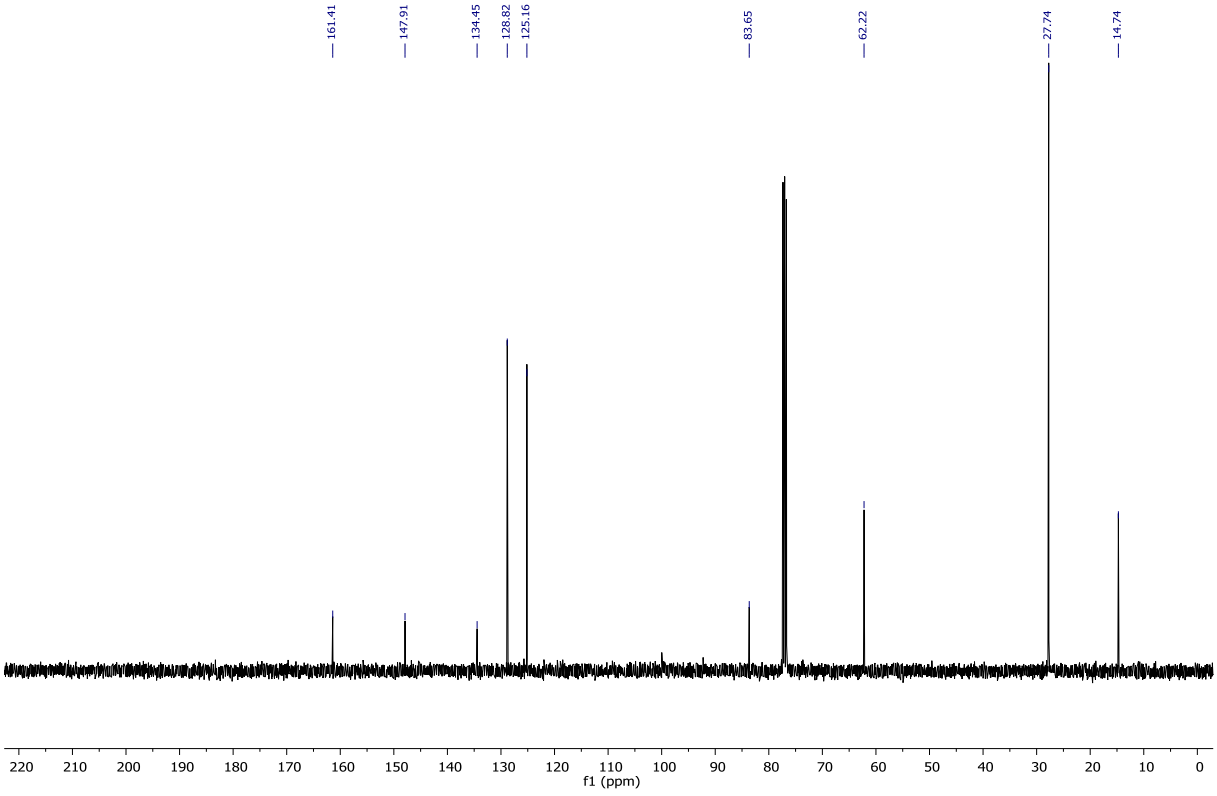
2
1
0
f1 (ppm)


161.41
147.91
134.45
128.82
125.16
83.65
62.22
27.74
14.74
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210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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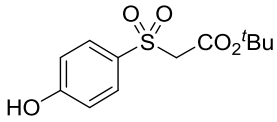
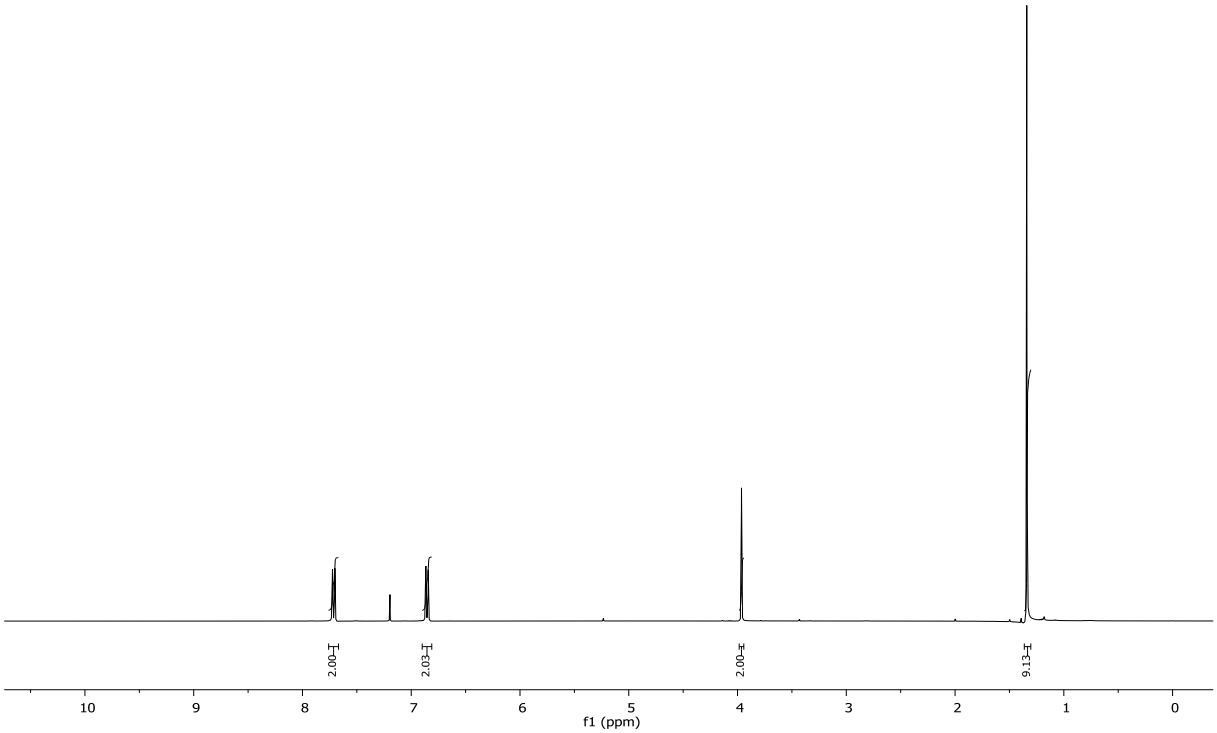
50
40
30
20
10
0
f1 (ppm)


O
O
S
CO2tBu
HO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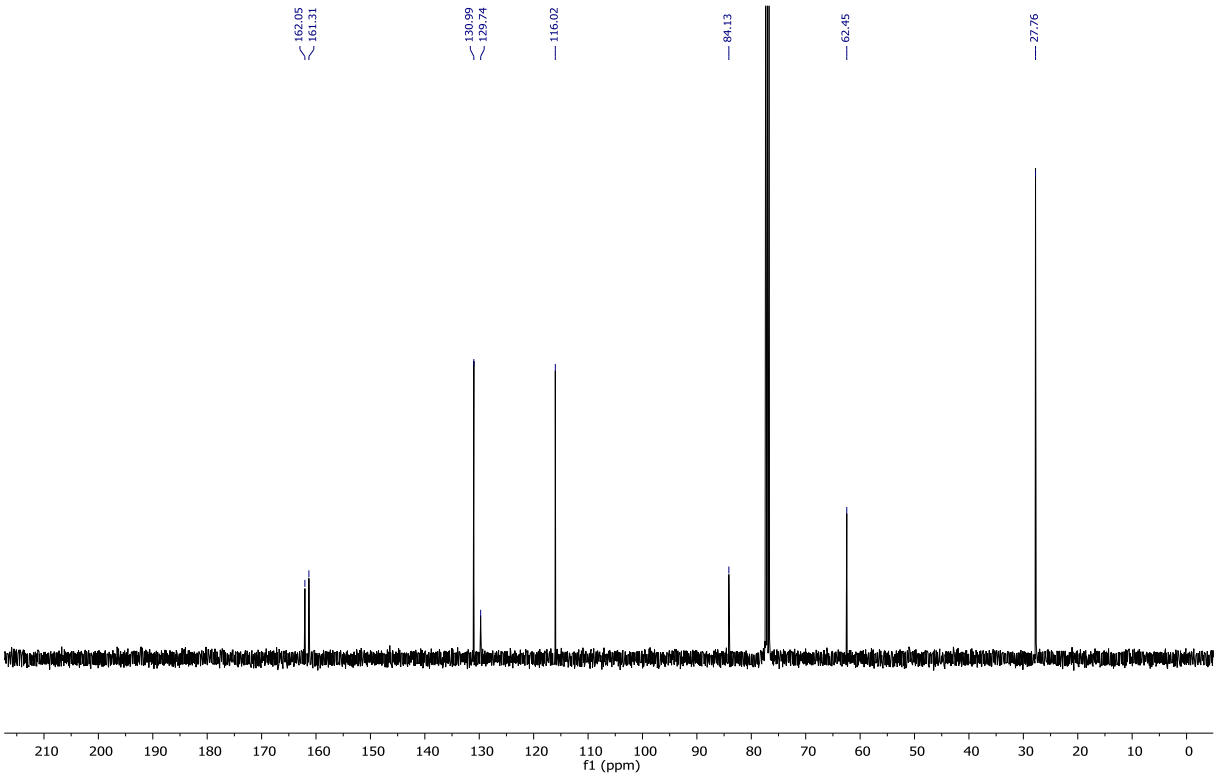
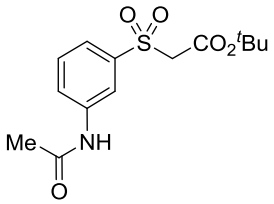
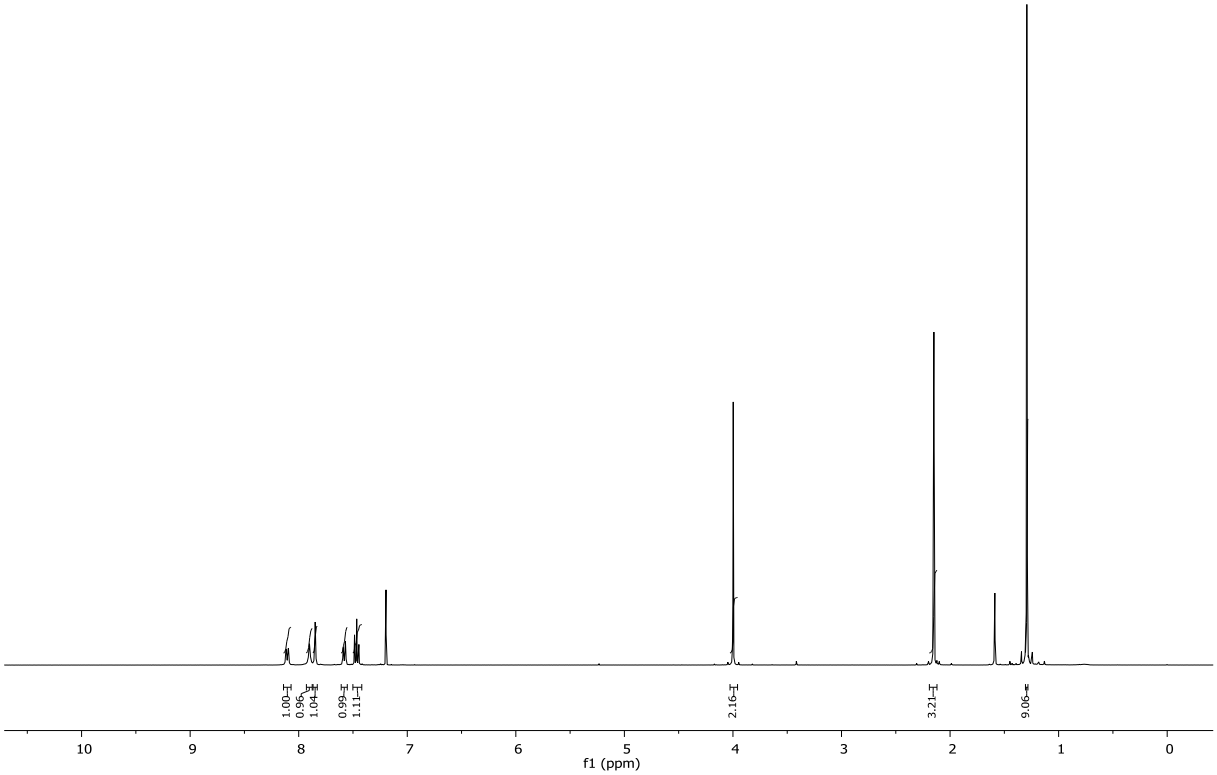
2.03
2.00
9.13
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


162.05
161.31
130.99
129.74
116.02
84.13
62.45
27.76
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
S
CO2tBu
Me
NH
O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0.96
1.04
0.99
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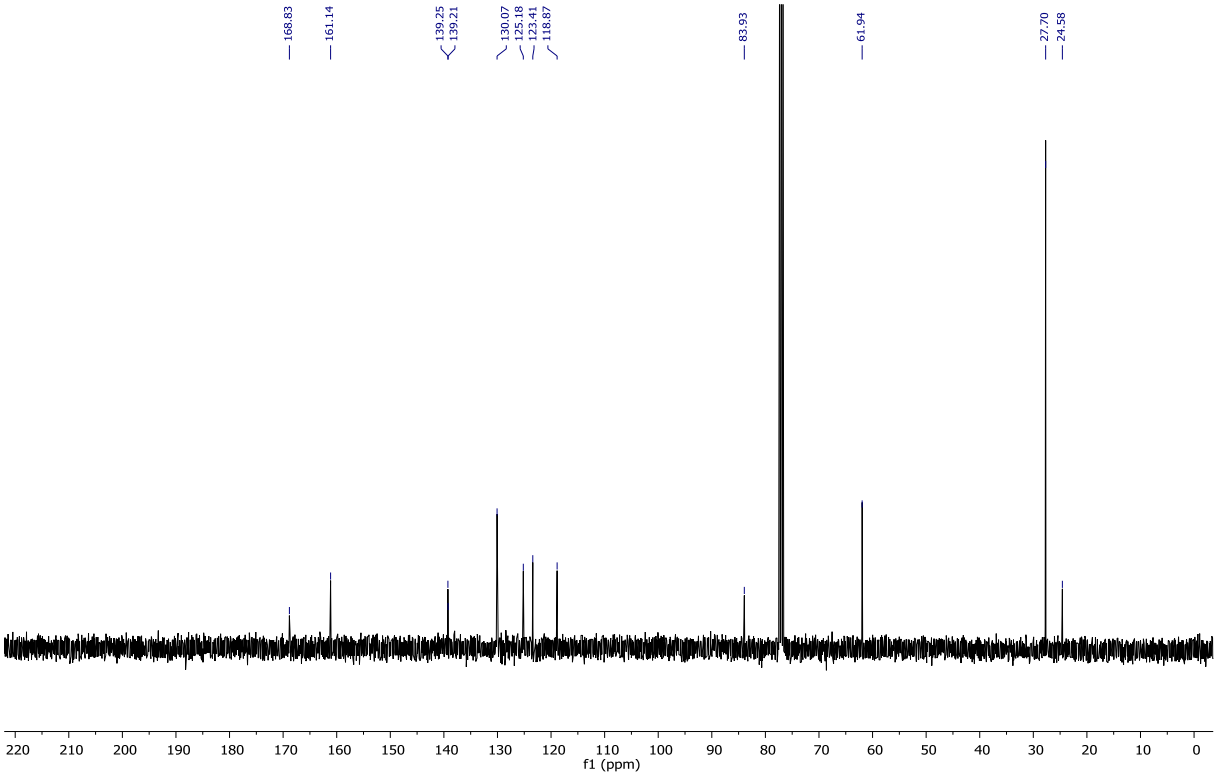
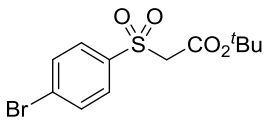
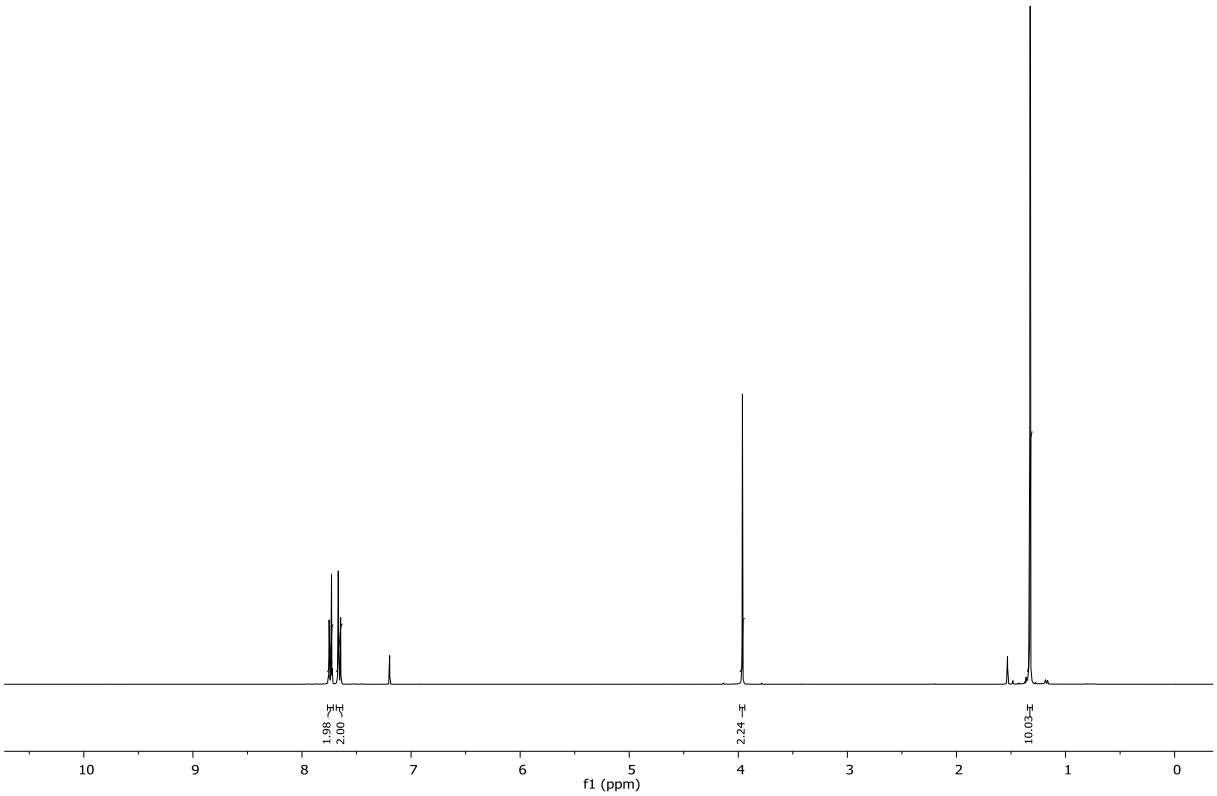
3.21
9.06
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


168.83
161.14
139.25
139.21
130.07
125.18
123.41
118.87
83.93
61.94
27.70
24.58
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
S
CO2tBu
Br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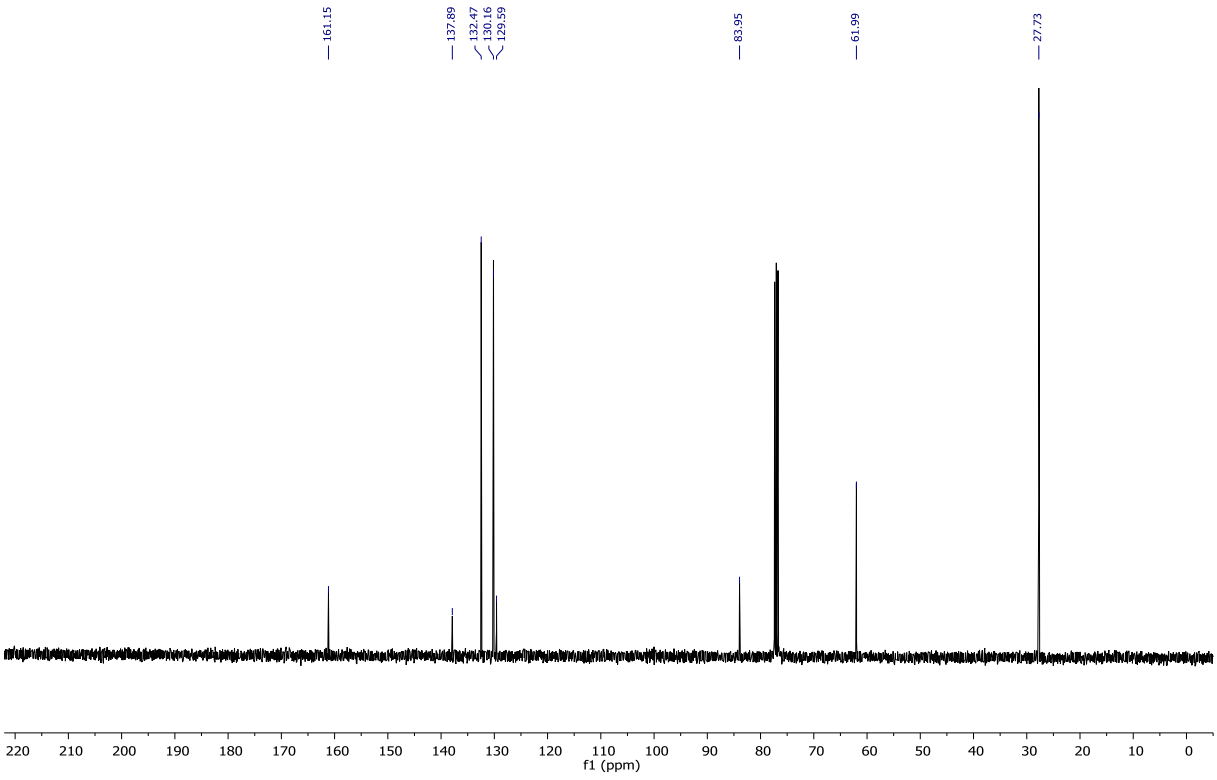
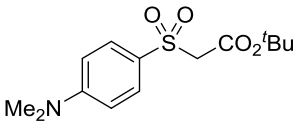
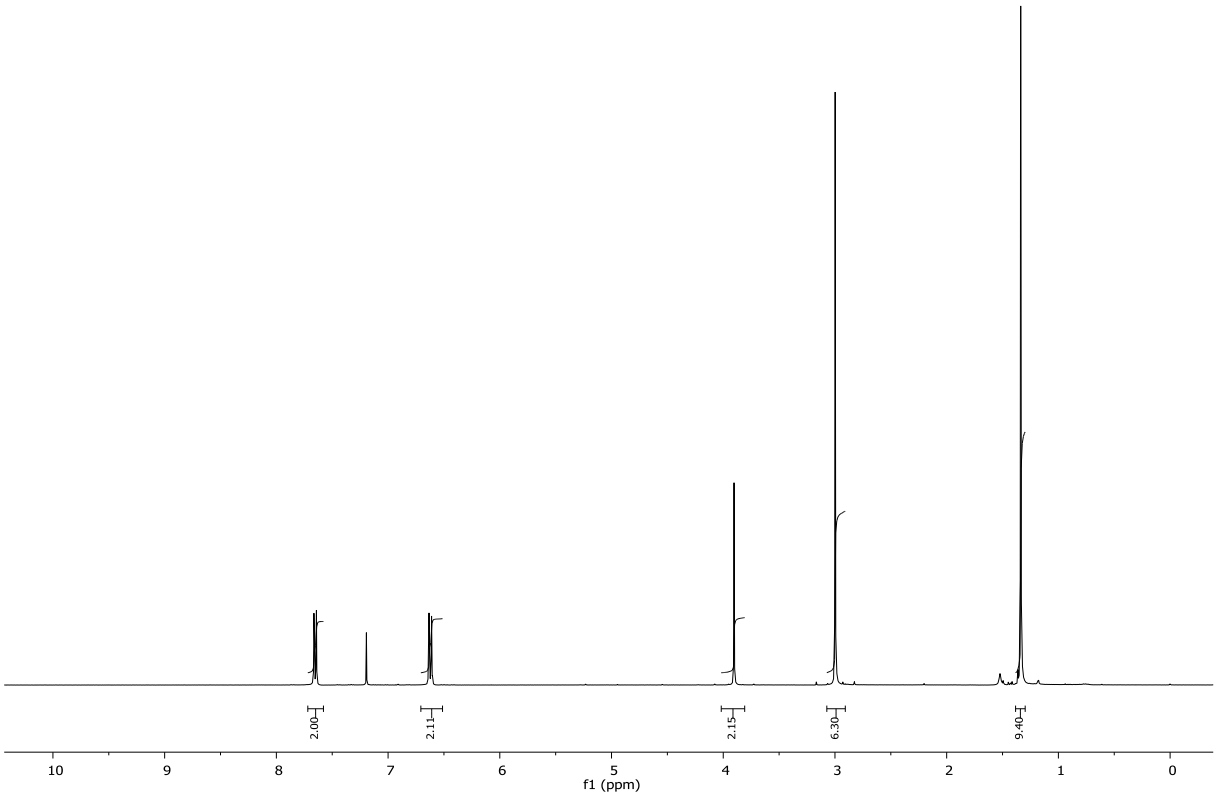
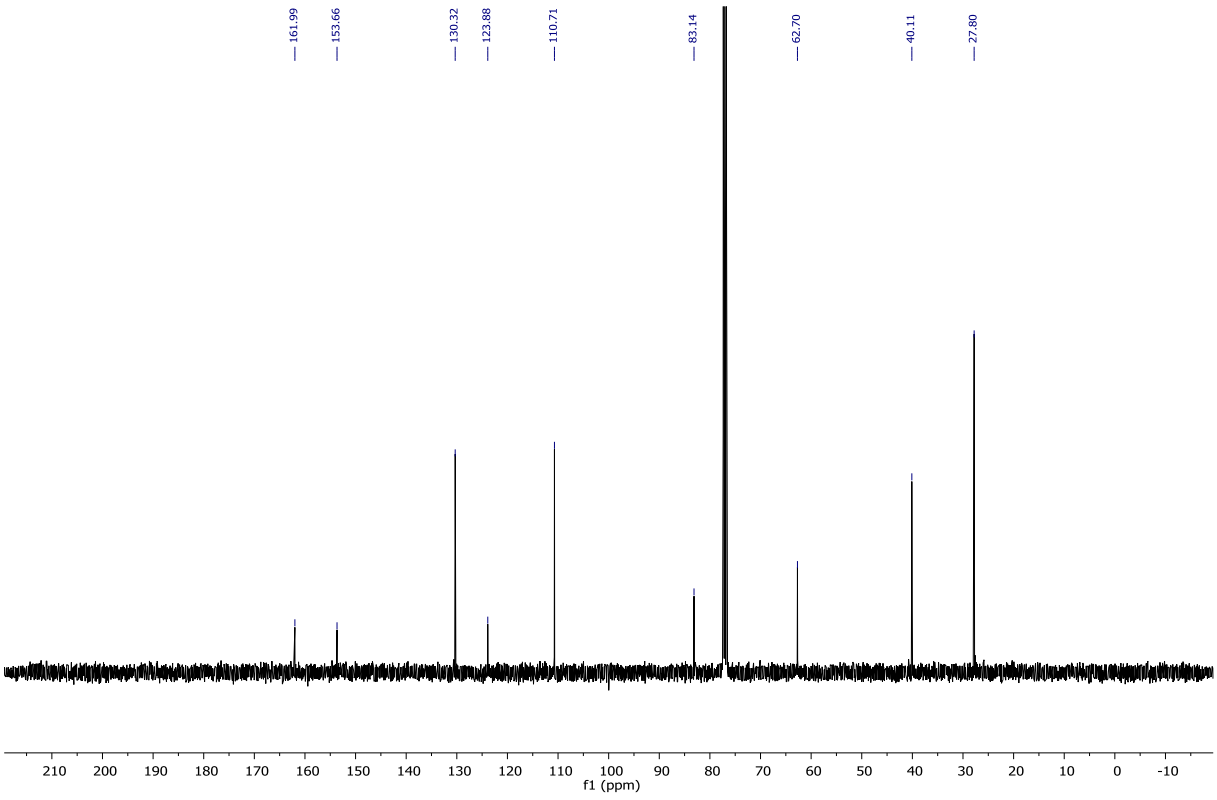
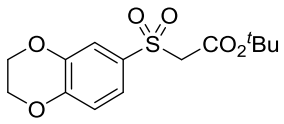
2.24
10.03
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

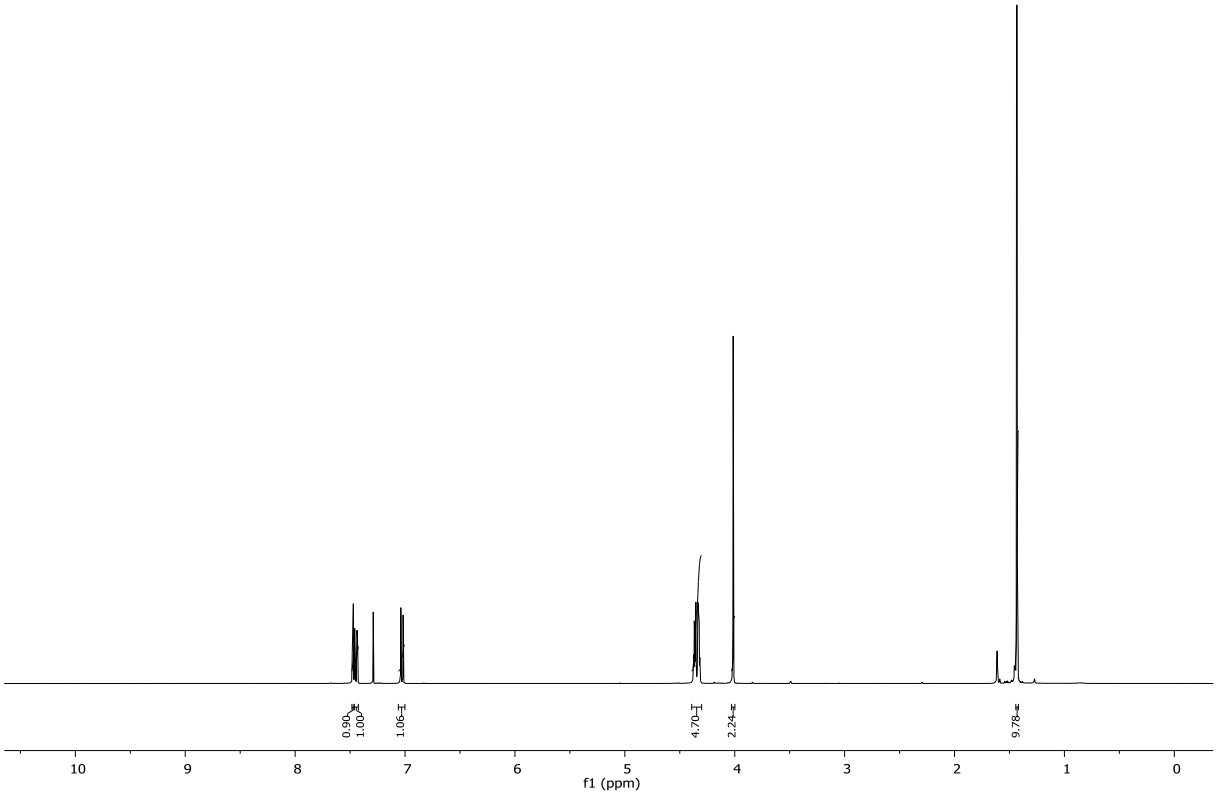

161.15
137.89
132.47
130.16
129.59
83.95
61.99
27.73
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
S
CO2tBu
Me2N


2.00
2.11
2.15
6.30
9.40
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


161.99
153.66
130.32
123.88
110.71
83.14
62.70
40.11
27.80
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
O
S
O
O
CO2tBu


0.90
1.00
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4.70
2.24
9.78
10
9
8
7
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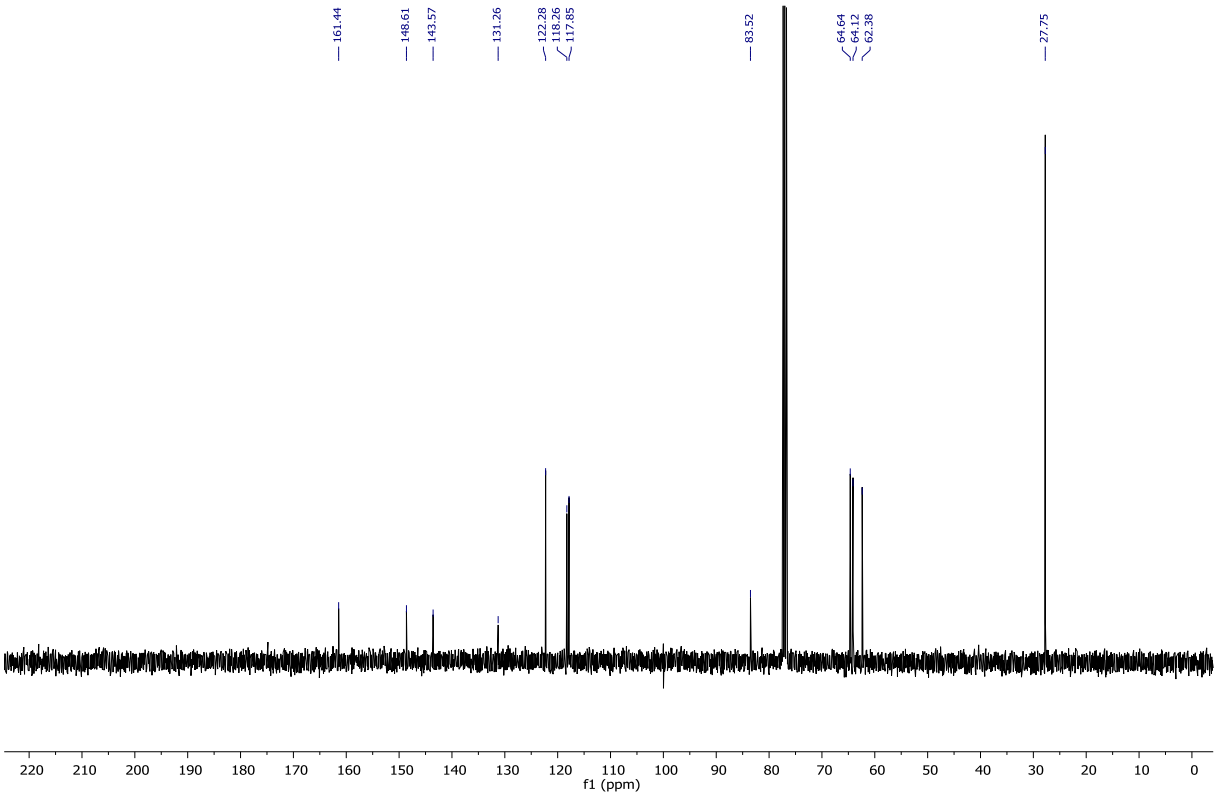
5
4
3
2
1
0
f1 (ppm)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131.26
122.28
118.26
117.85
83.52
64.64
64.12
62.38
27.75
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210
200
190
180
170
160
150
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130
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110
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90
80
70
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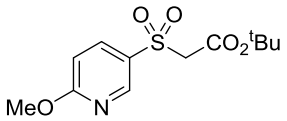
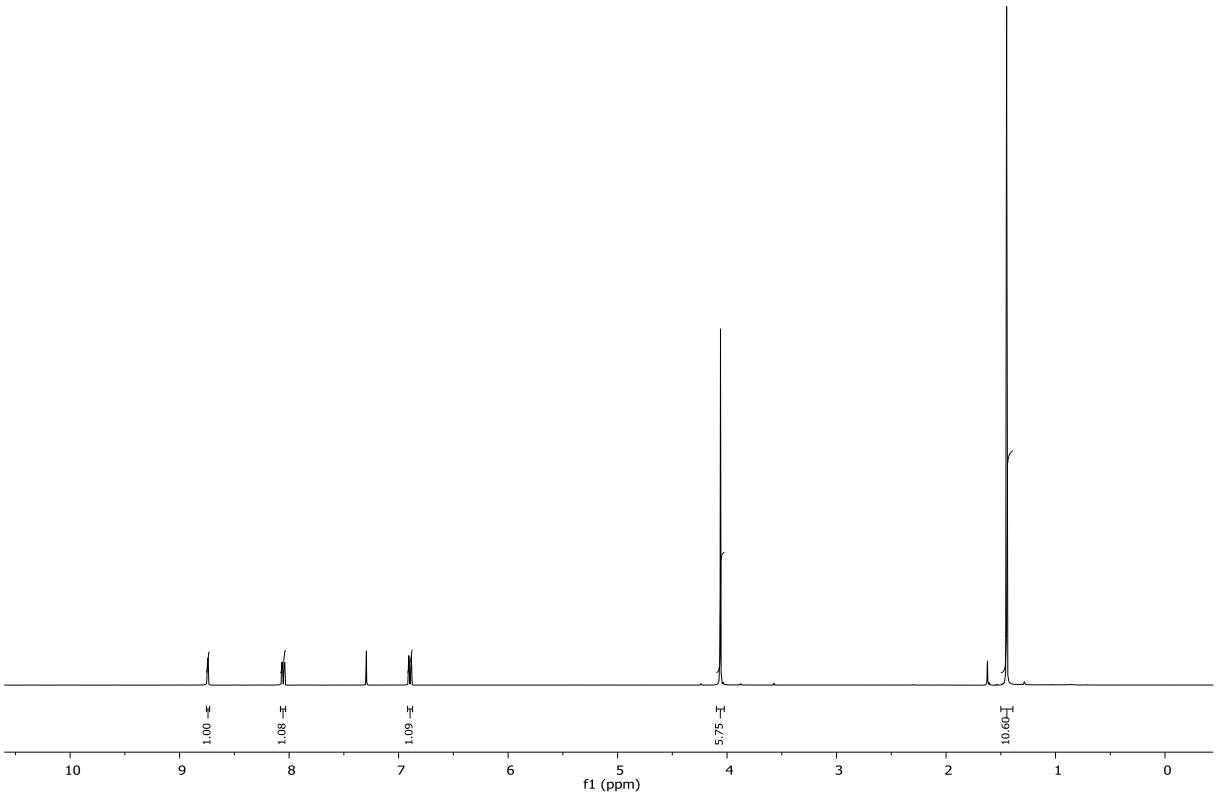
50
40
30
20
10
0
f1 (ppm)


O
O
S
CO2tBu
MeO
N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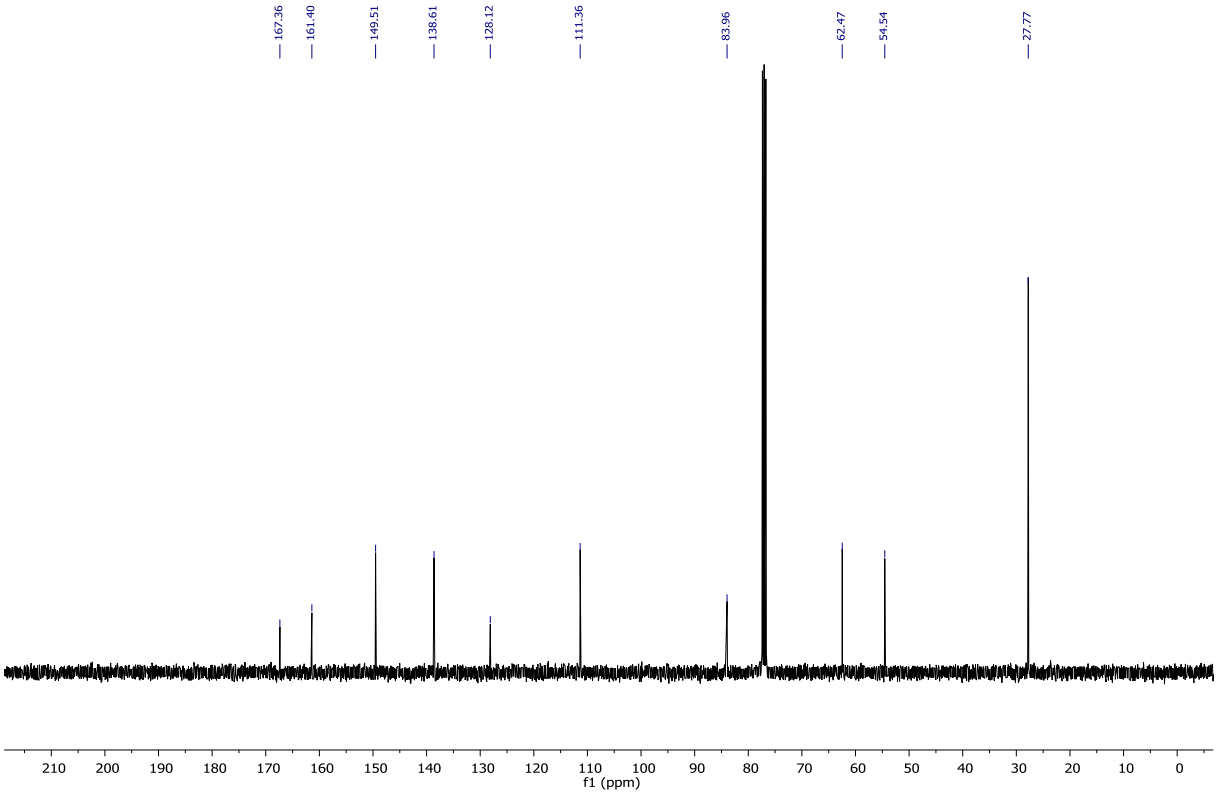
1.08
1.09
5.75
10.60
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


167.36
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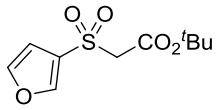
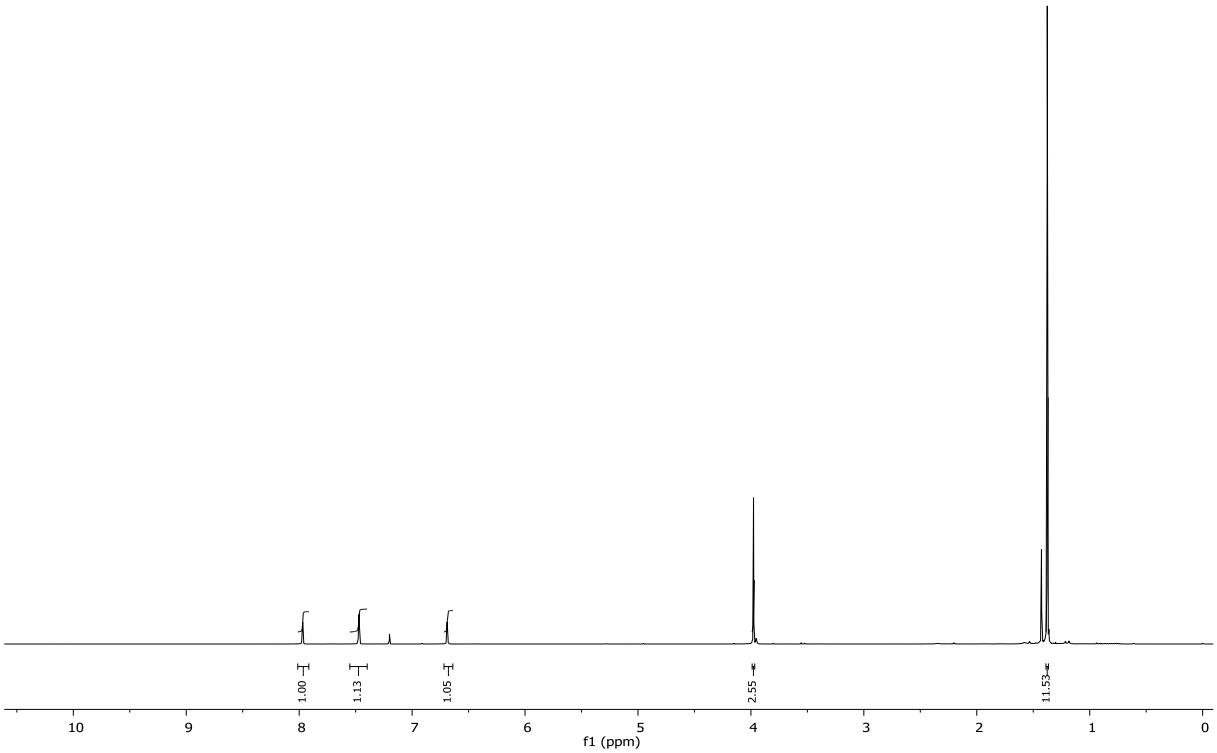
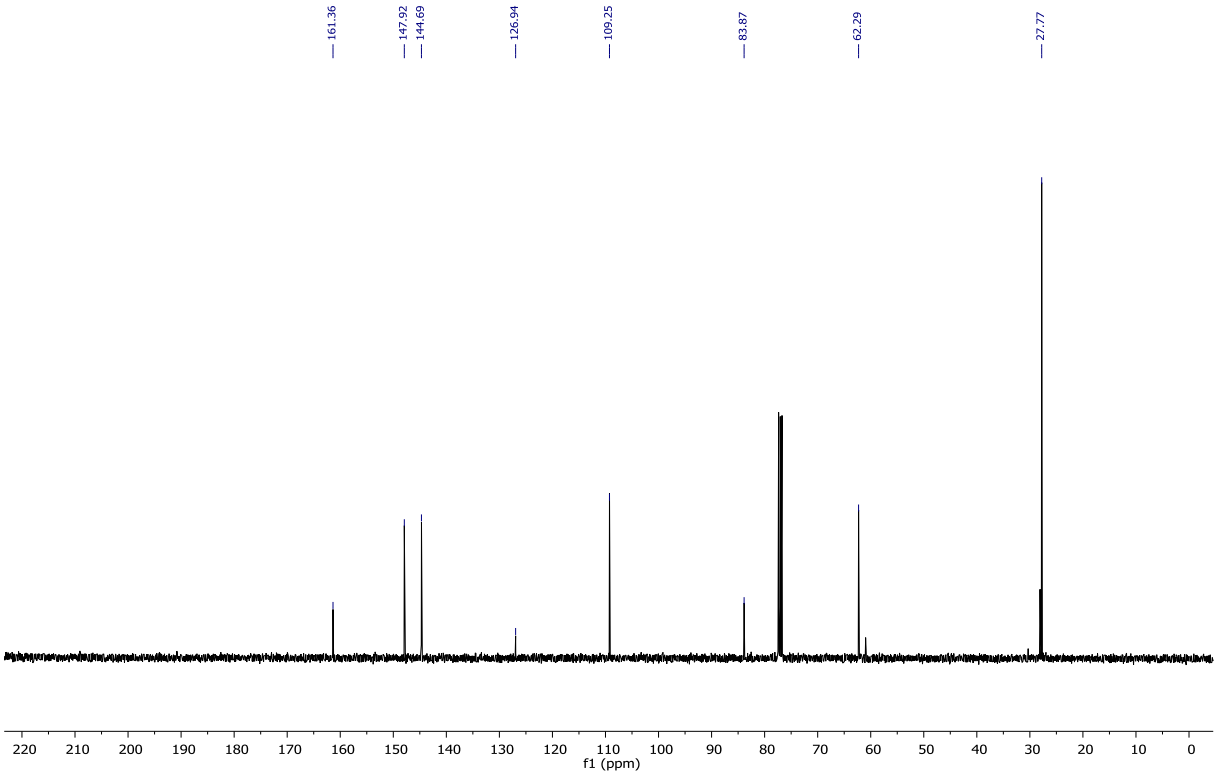
149.51
138.61
128.12
111.36
83.96
62.47
54.54
27.77
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
S
CO2tBu
O


1.00
1.13
1.05
2.55
11.53
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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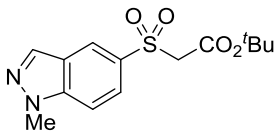
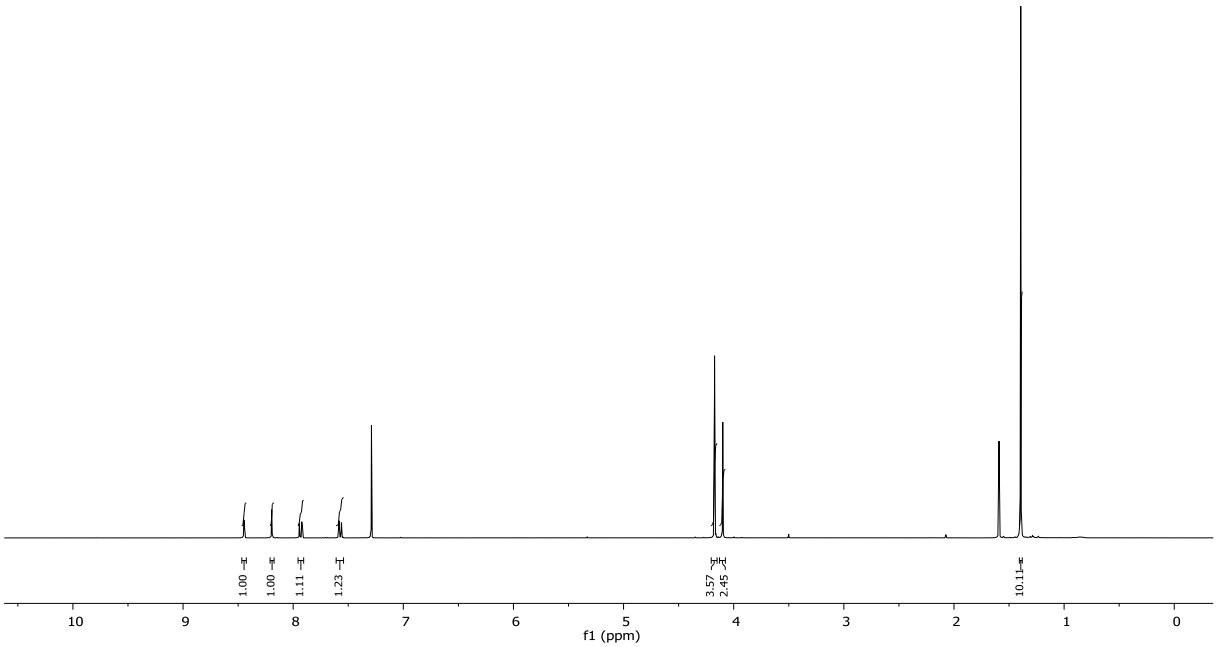
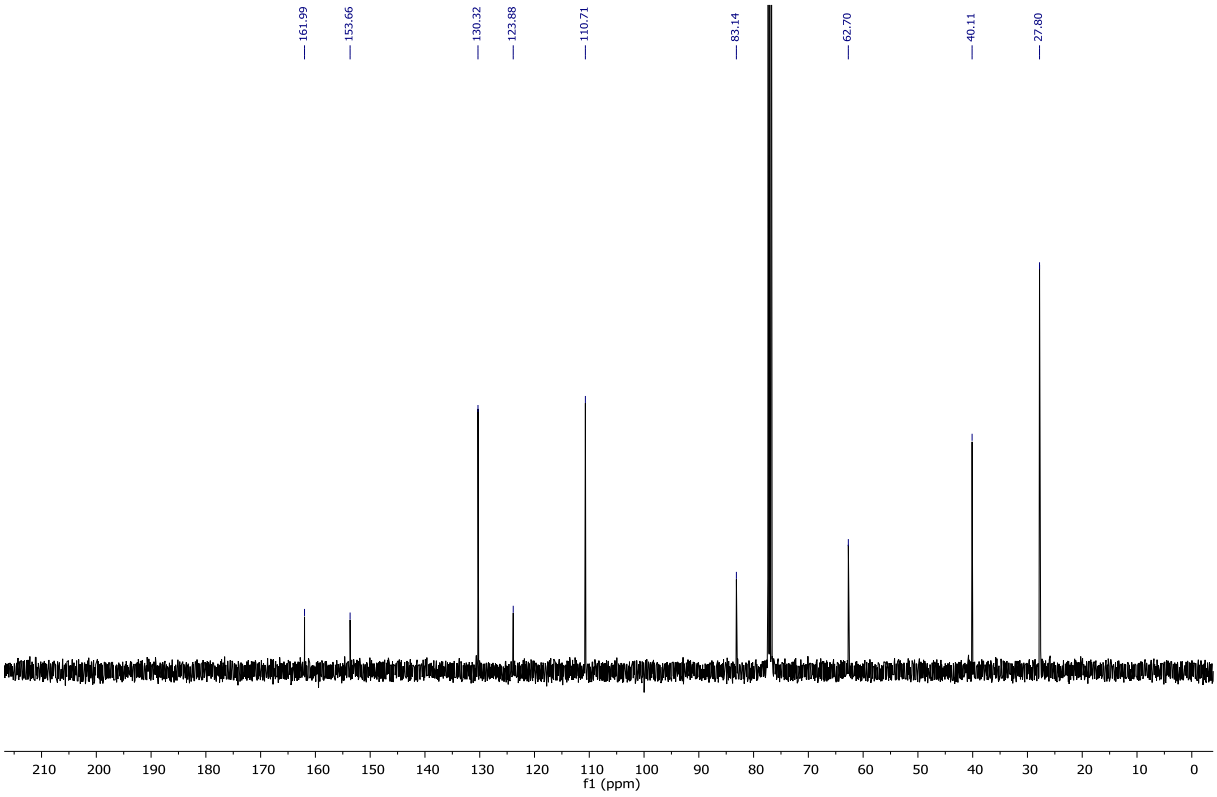
126.94
109.25
83.87
62.29
27.77
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
S
CO2tBu
N
N
Me


1.00
1.00
1.11
1.23
3.57
2.45
10.11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


161.99
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130.32
123.88
110.71
83.14
62.70
40.11
27.80
210
200
190
180
170
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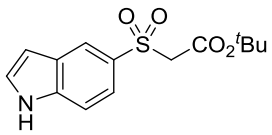
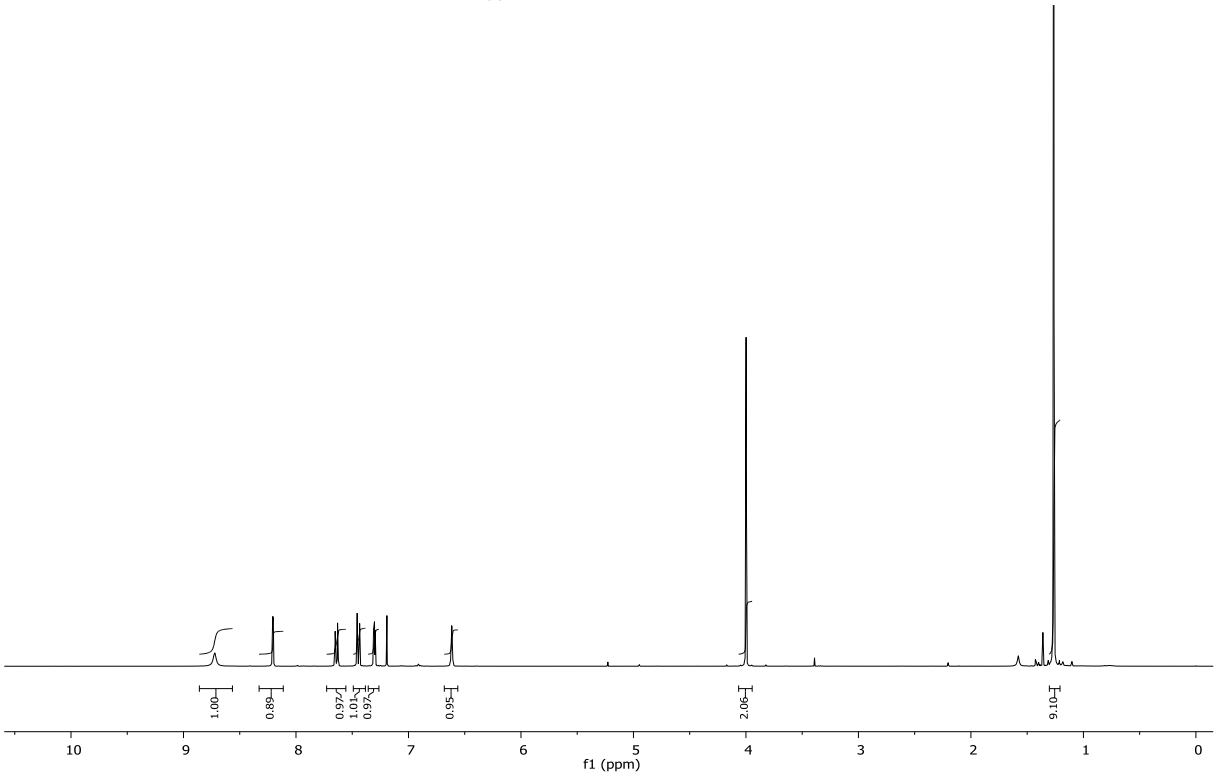
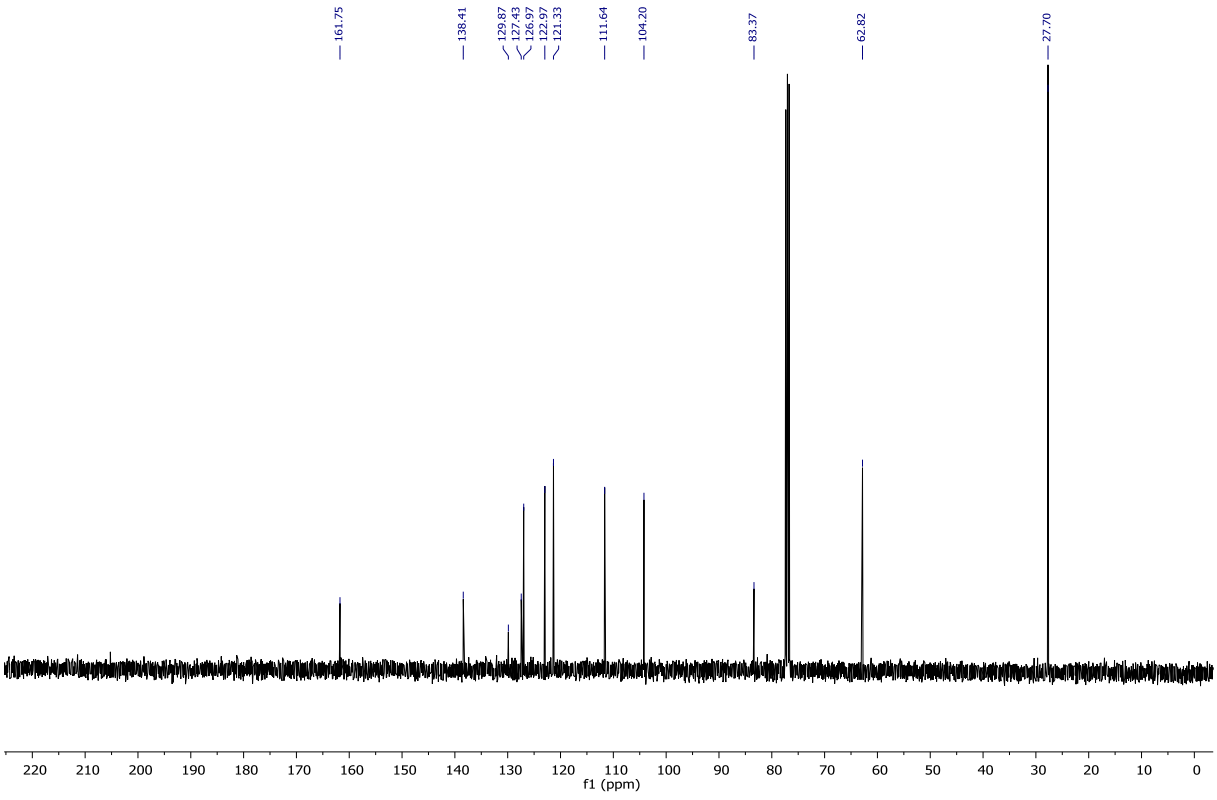
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
S
CO2tBu
N
H


1.00
0.89
0.97
1.01
0.97
0.95
2.06
9.10
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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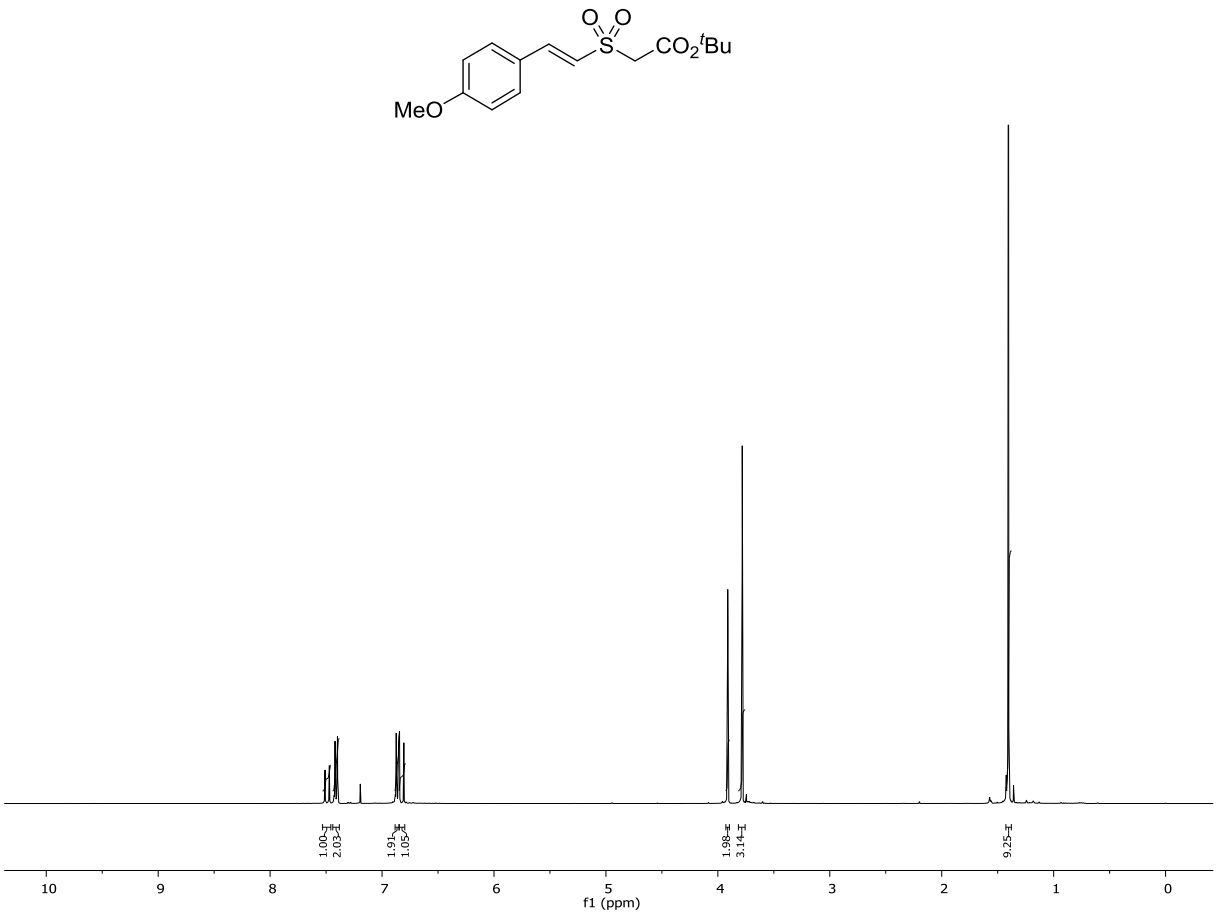
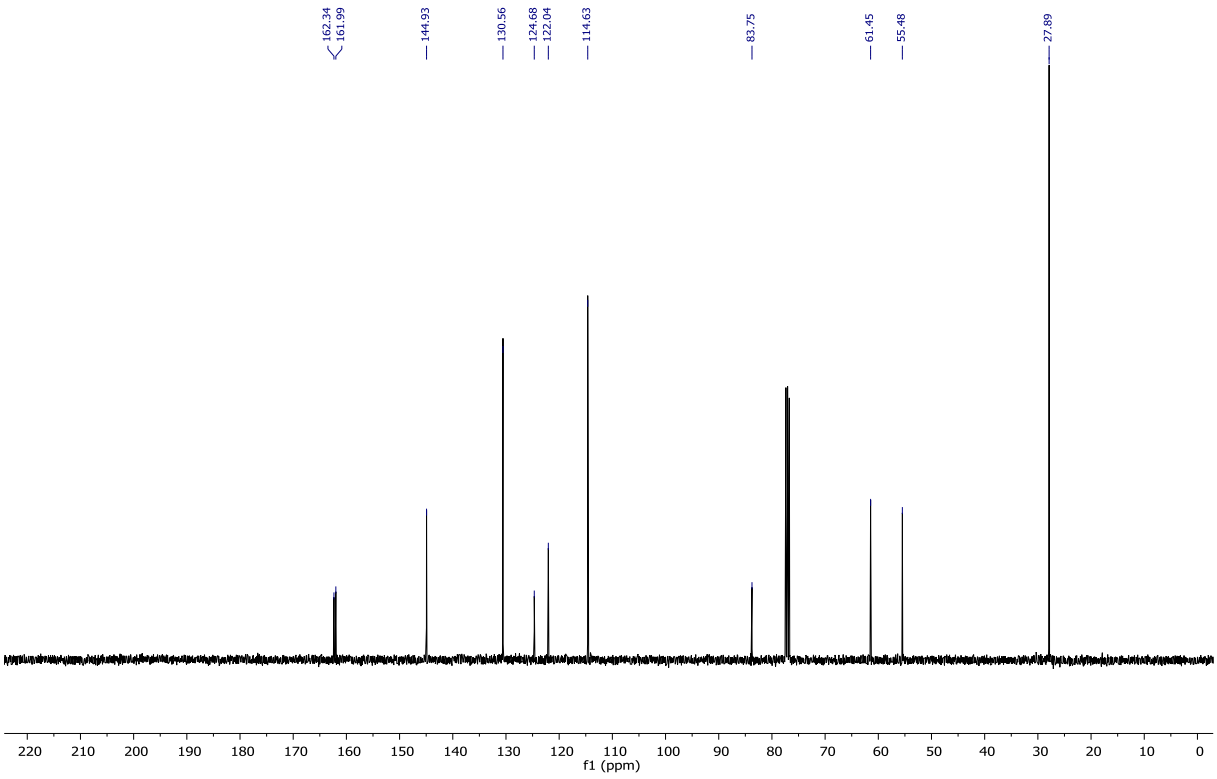
138.41
129.87
127.43
126.97
122.97
121.33
111.64
104.20
83.37
62.82
27.70
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
S
CO2tBu
MeO
1.00
2.03
1.91
1.05
1.98
3.14
9.25
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


162.34
161.99
144.93
130.56
124.68
122.04
114.63
83.75
61.45
55.48
27.89
220
210
200
190
180
170
160
150
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130
120
110
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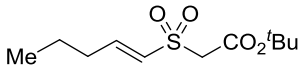
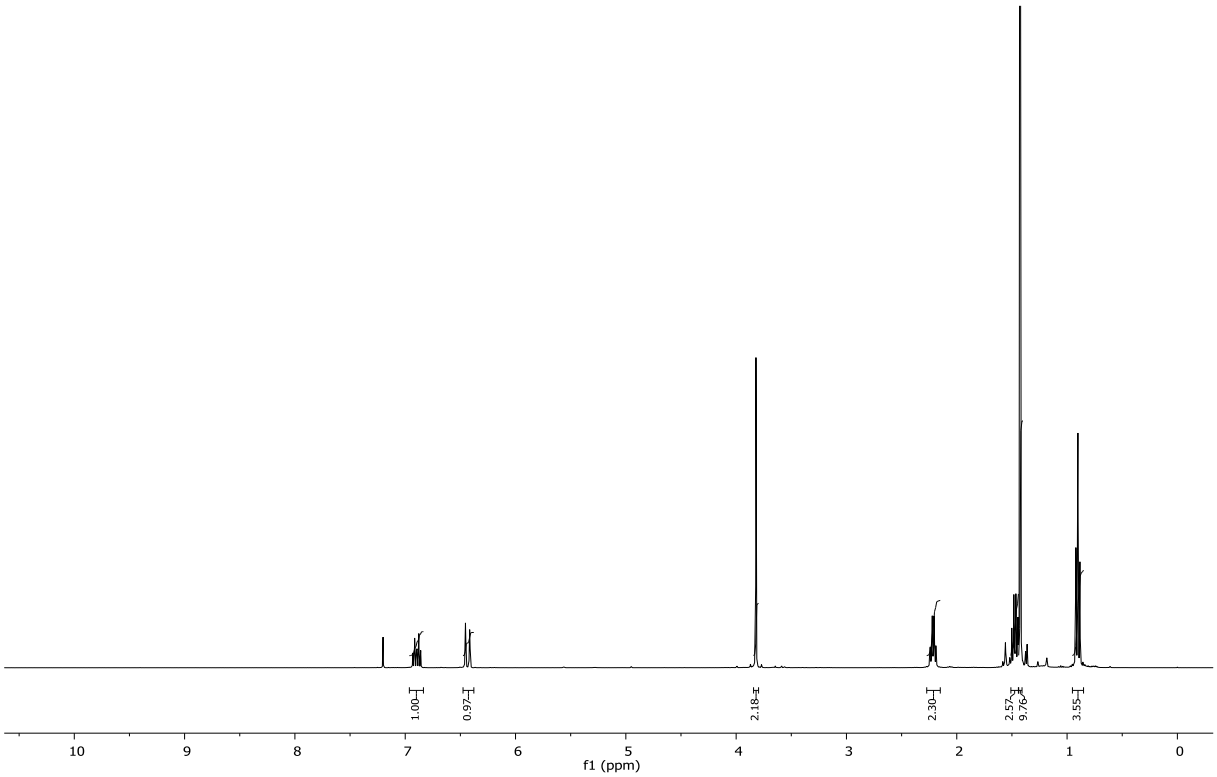
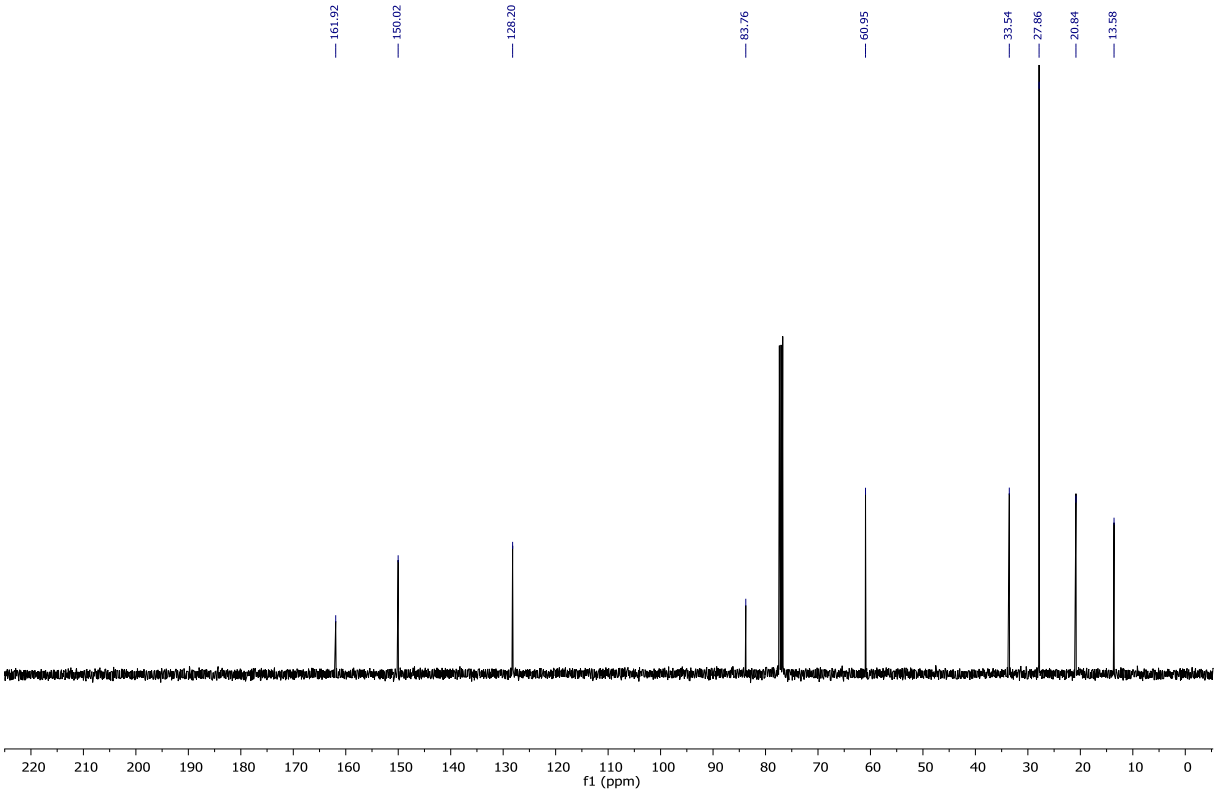
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
S
Me
CO2tBu


1.00
0.97
2.18
2.30
2.57
9.76
3.55
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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128.20
83.76
60.95
33.54
27.86
20.84
13.58
220
210
200
190
180
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90
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50
40
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20
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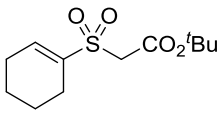
f1 (ppm)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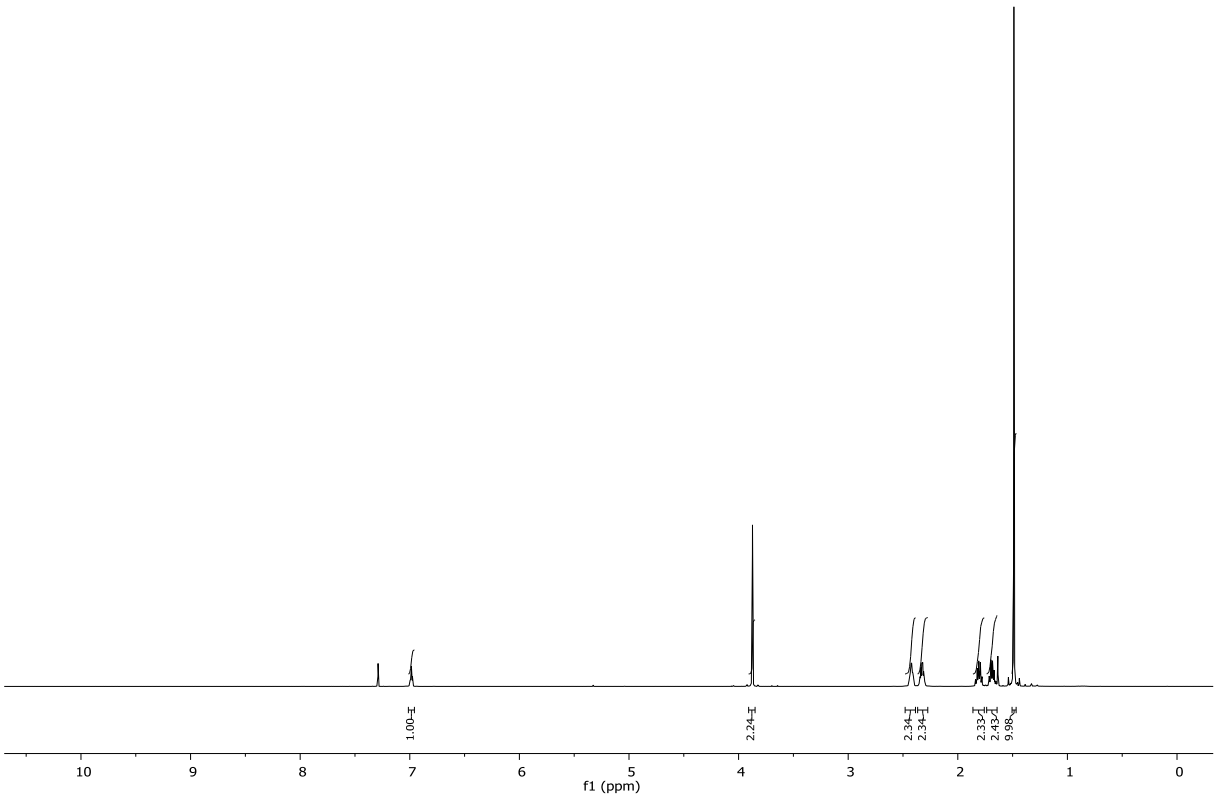
O
S
CO2tBu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2.24
2.34
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2.43
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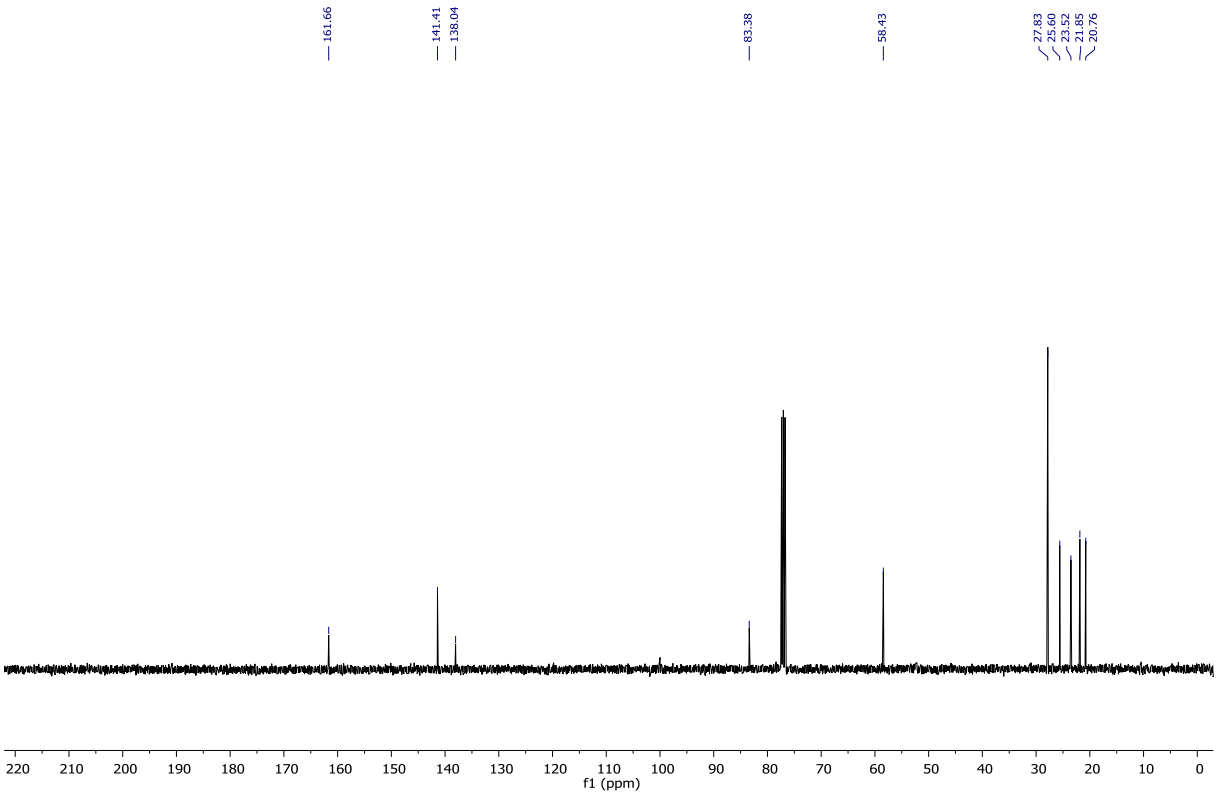
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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138.04
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58.43
27.83
25.60
23.52
21.85
20.76
220
210
200
190
180
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50
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10
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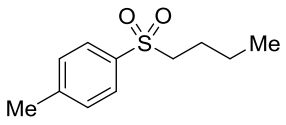
f1 (ppm)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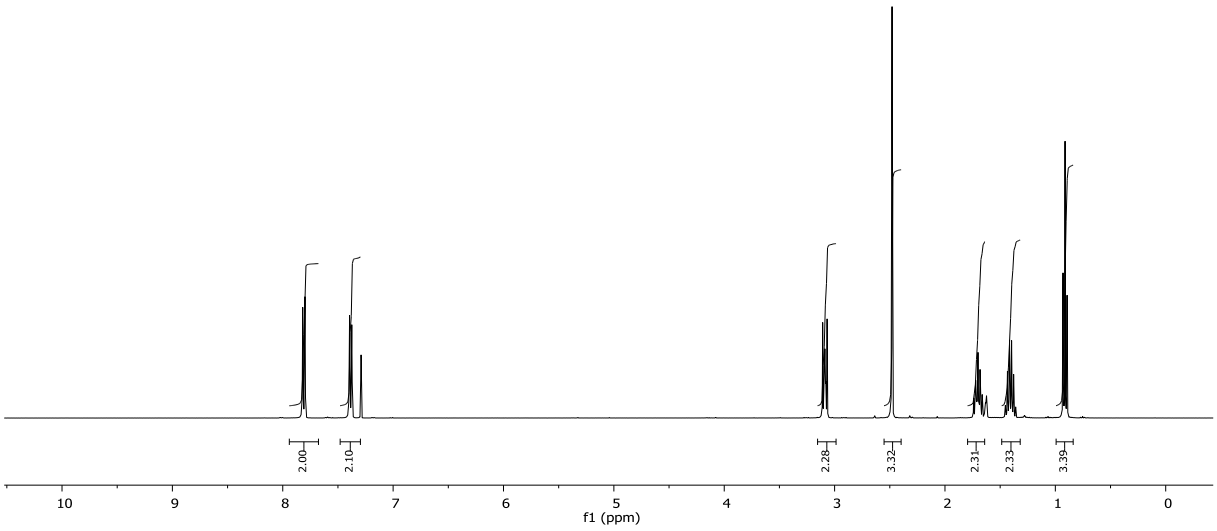
O
S
Me
Me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2.28
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2.33
3.39
10
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7
6
5
4
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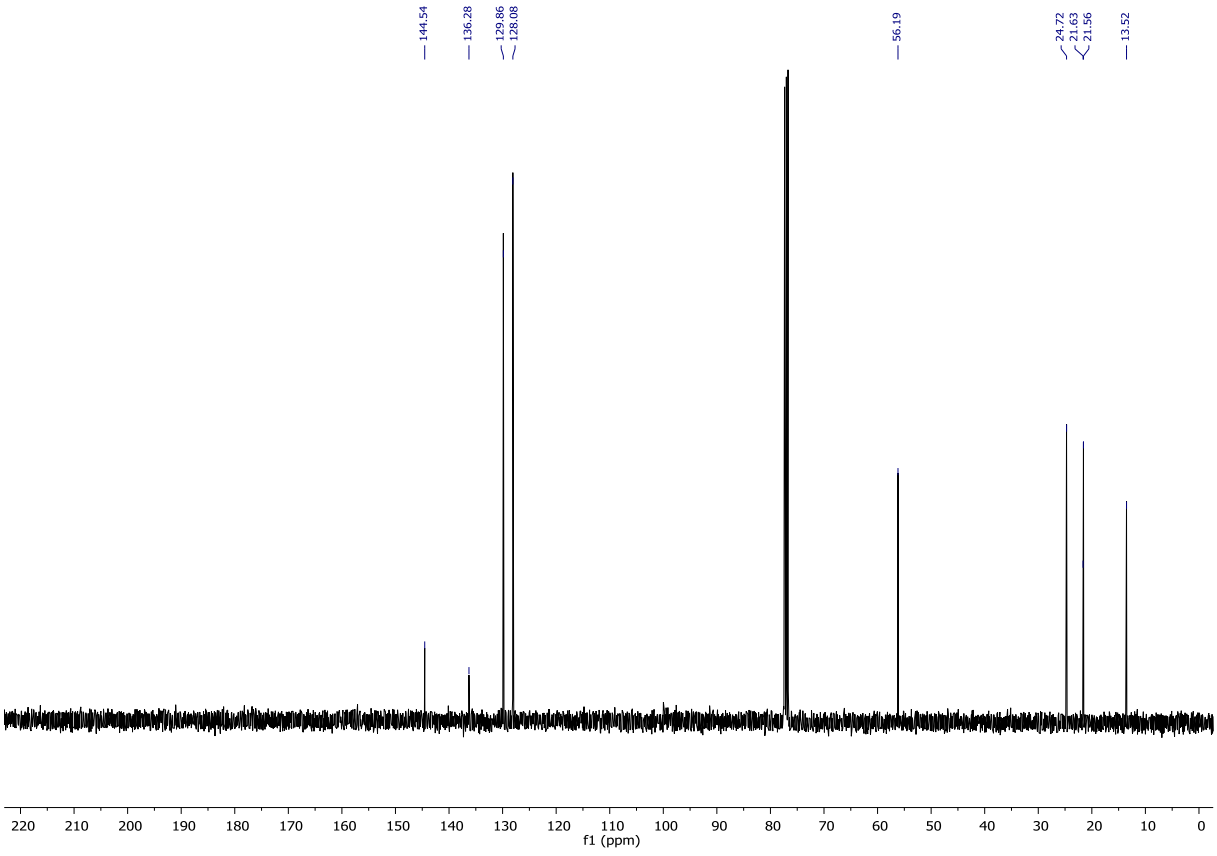
2
1
0
f1 (ppm)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136.28
129.86
128.08
56.19
24.72
21.63
21.56
13.52
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210
200
190
180
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70
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50
40
30
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10
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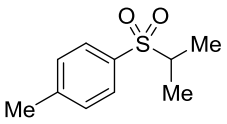
f1 (ppm)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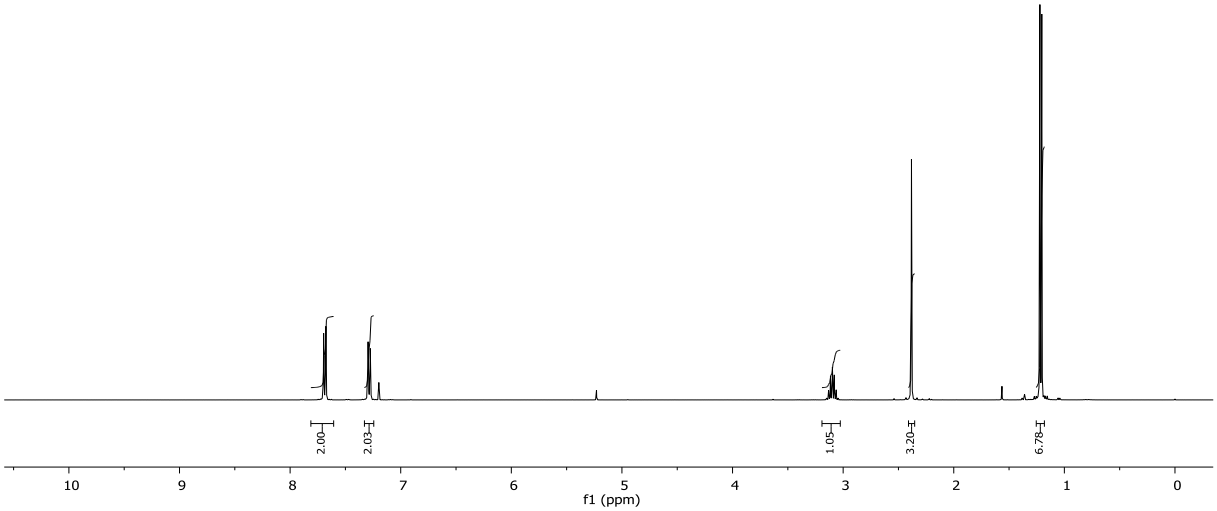
O
S
Me
Me
Me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6.78
10
9
8
7
6
5
4
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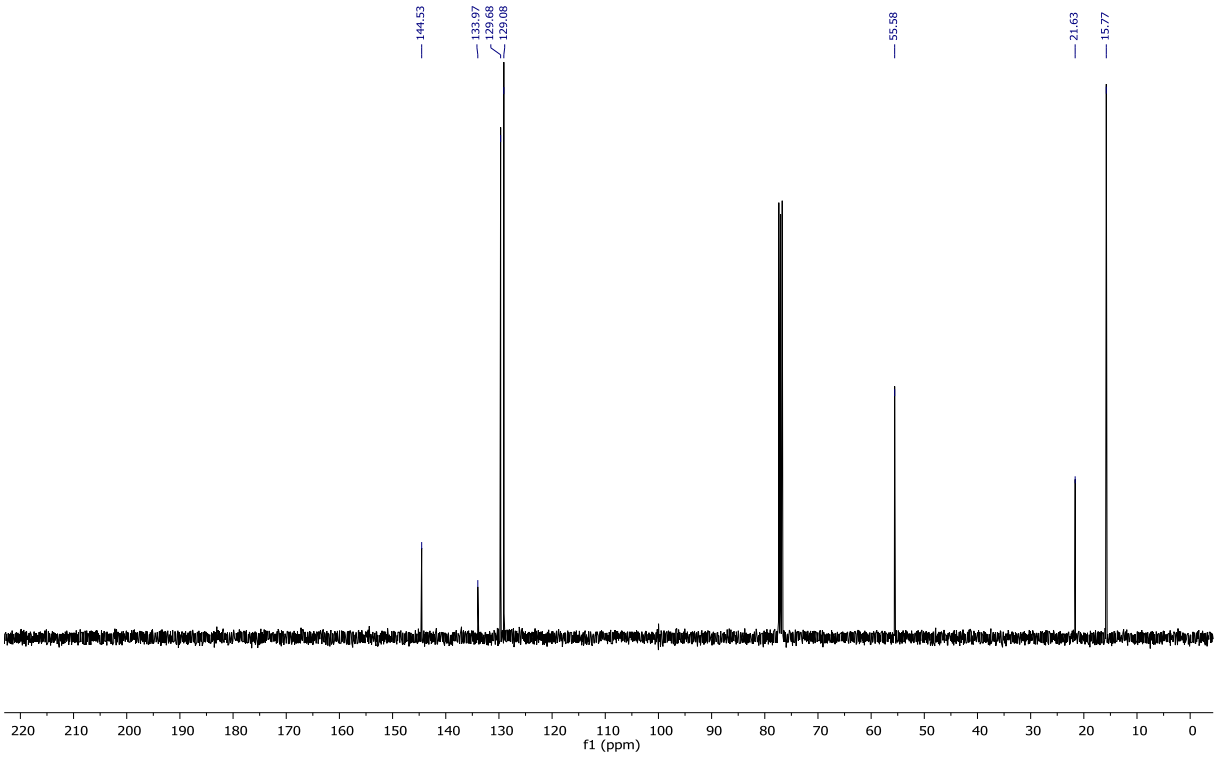
1
0
f1 (ppm)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129.08
55.58
21.63
15.77
220
210
200
190
180
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90
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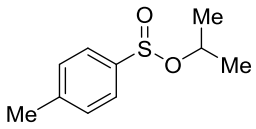
f1 (ppm)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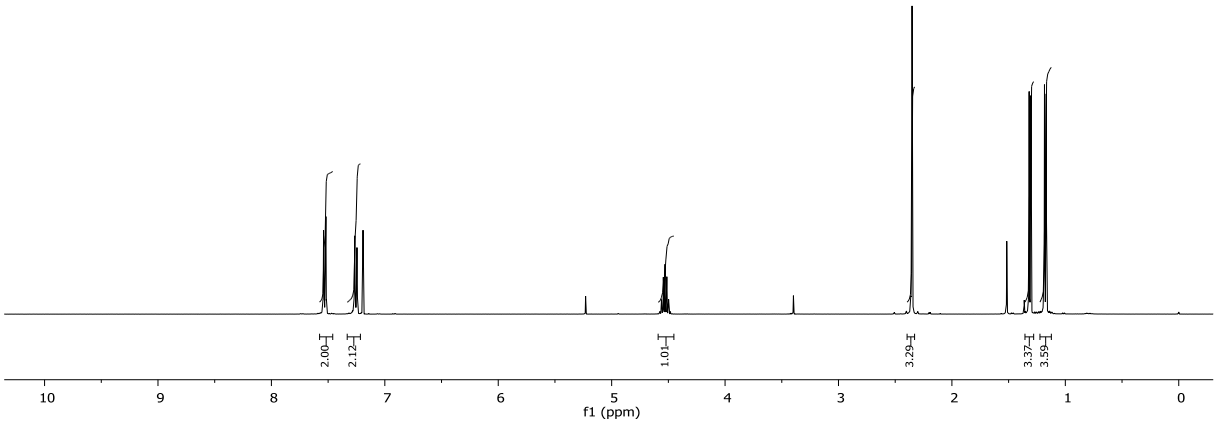
Me
S
O
Me
Me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2.12
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3.29
3.37
3.59
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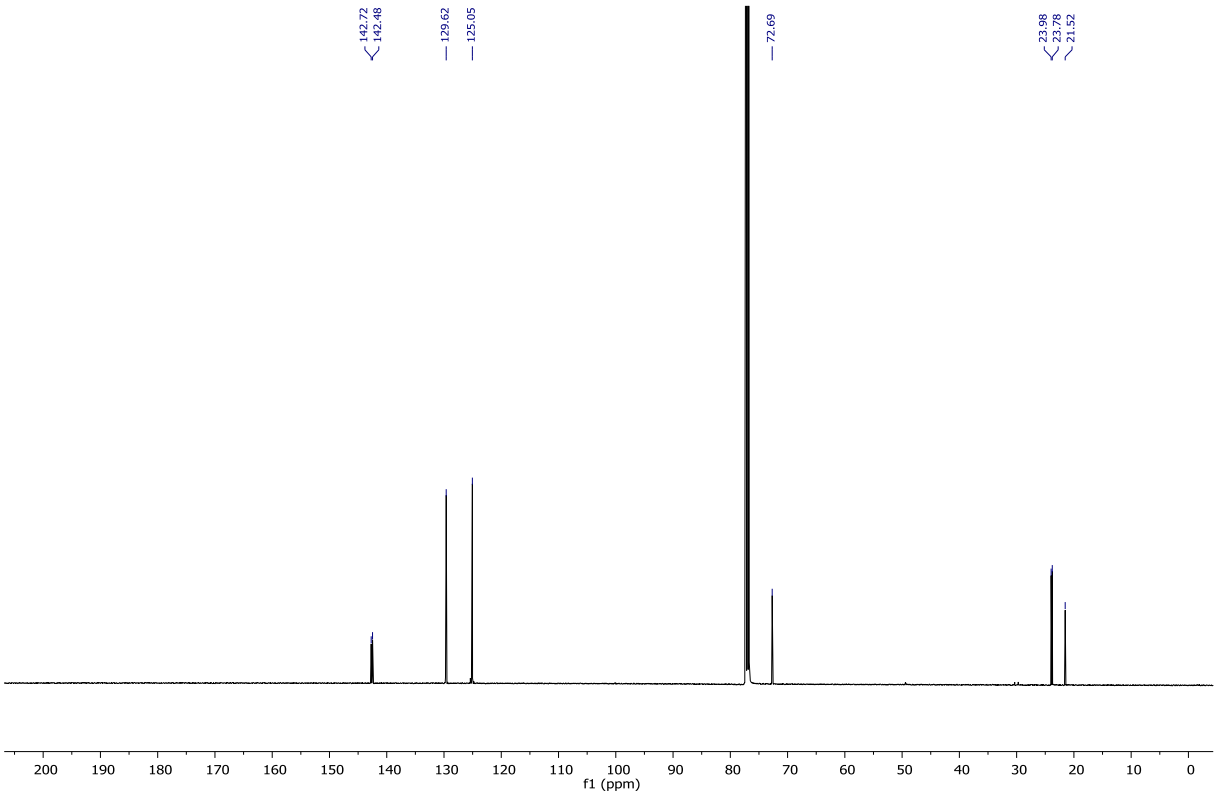
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


142.72
142.48
129.62
125.05
72.69
23.98
23.78
21.52
200
190
180
170
160
150
140
130
120
110
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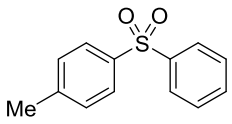
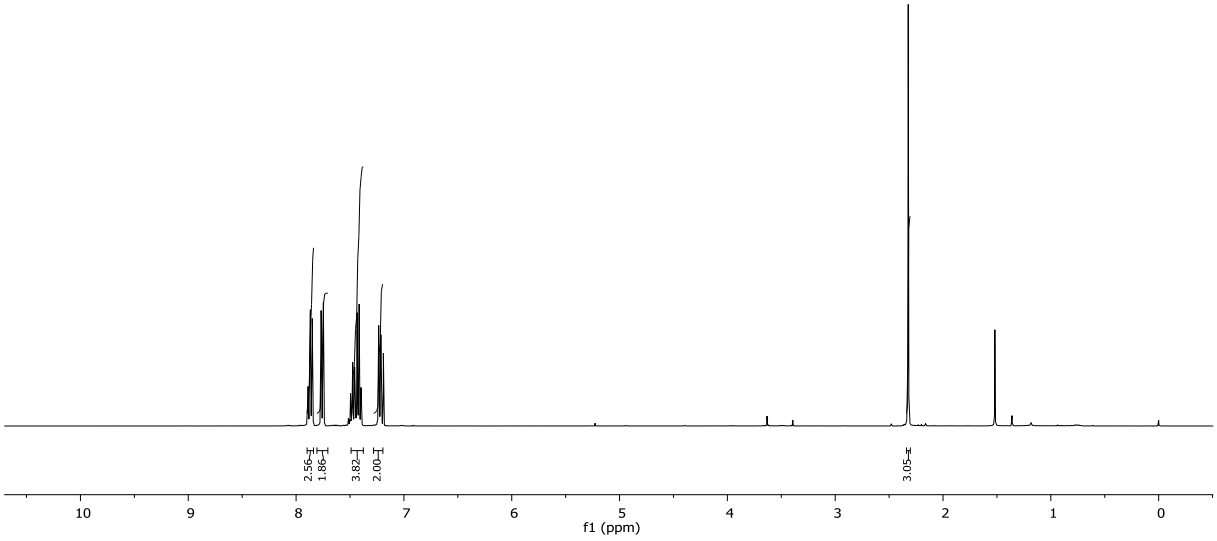
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
S
Me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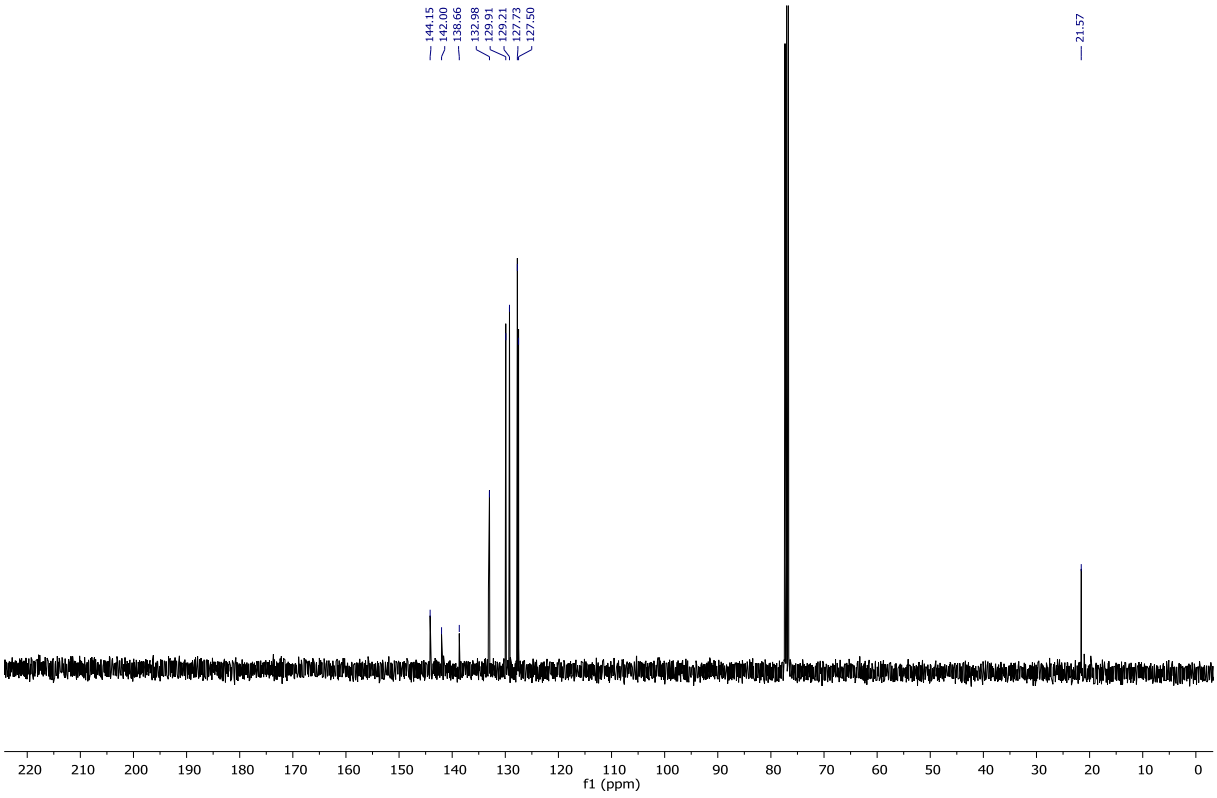
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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142.00
138.66
132.98
129.91
129.21
127.73
127.50
21.57
220
210
200
190
180
170
160
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130
120
110
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90
80
70
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50
40
30
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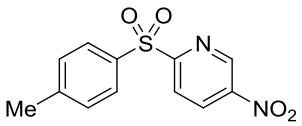
10
0
f1 (ppm)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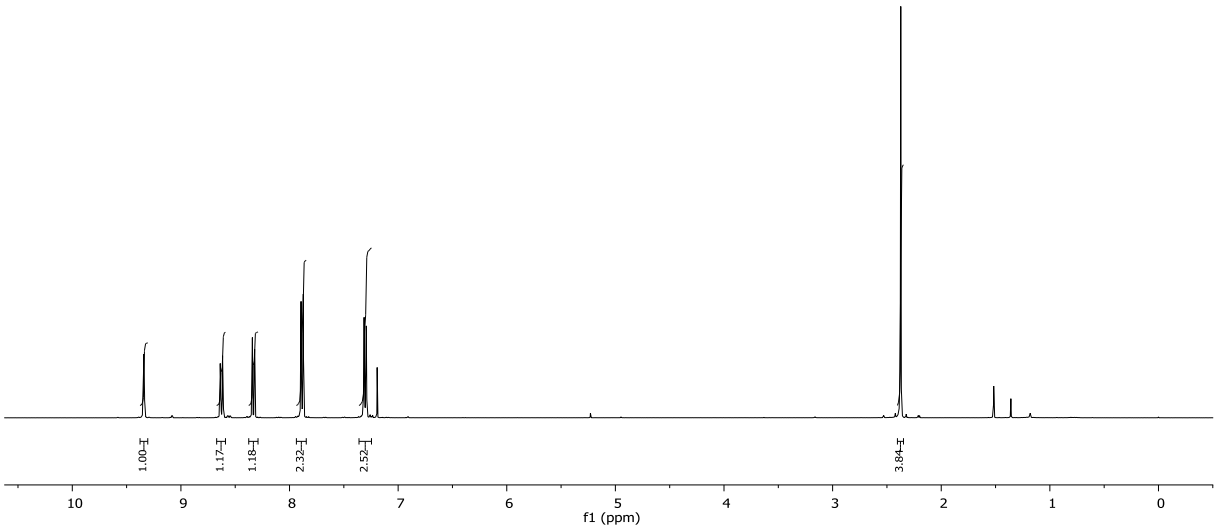
O
S
N
Me
NO2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1.17
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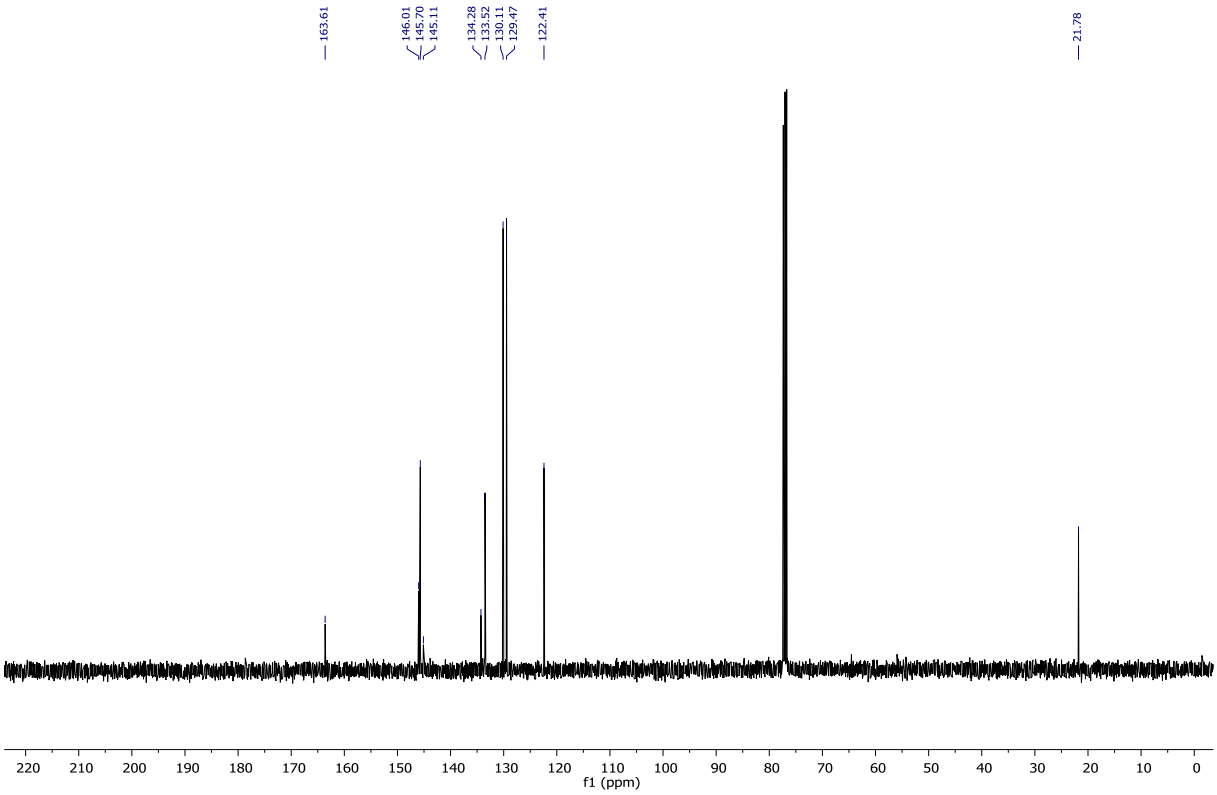
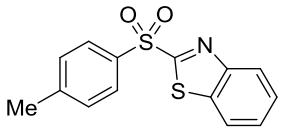
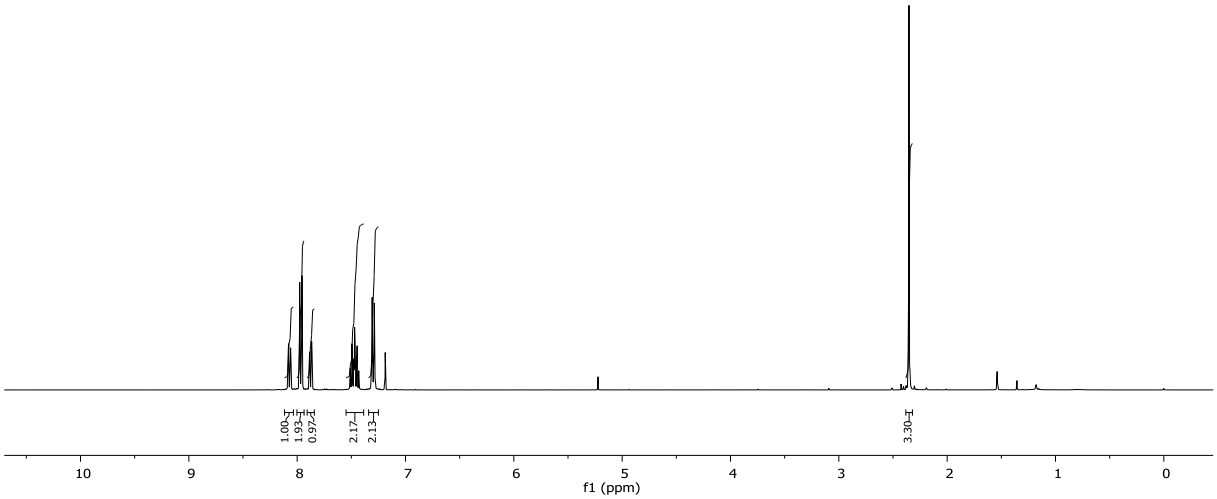
2.52
3.84
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


163.61
146.01
145.70
145.11
134.28
133.52
130.11
129.47
122.41
21.78
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
S
N
S
Me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1.93
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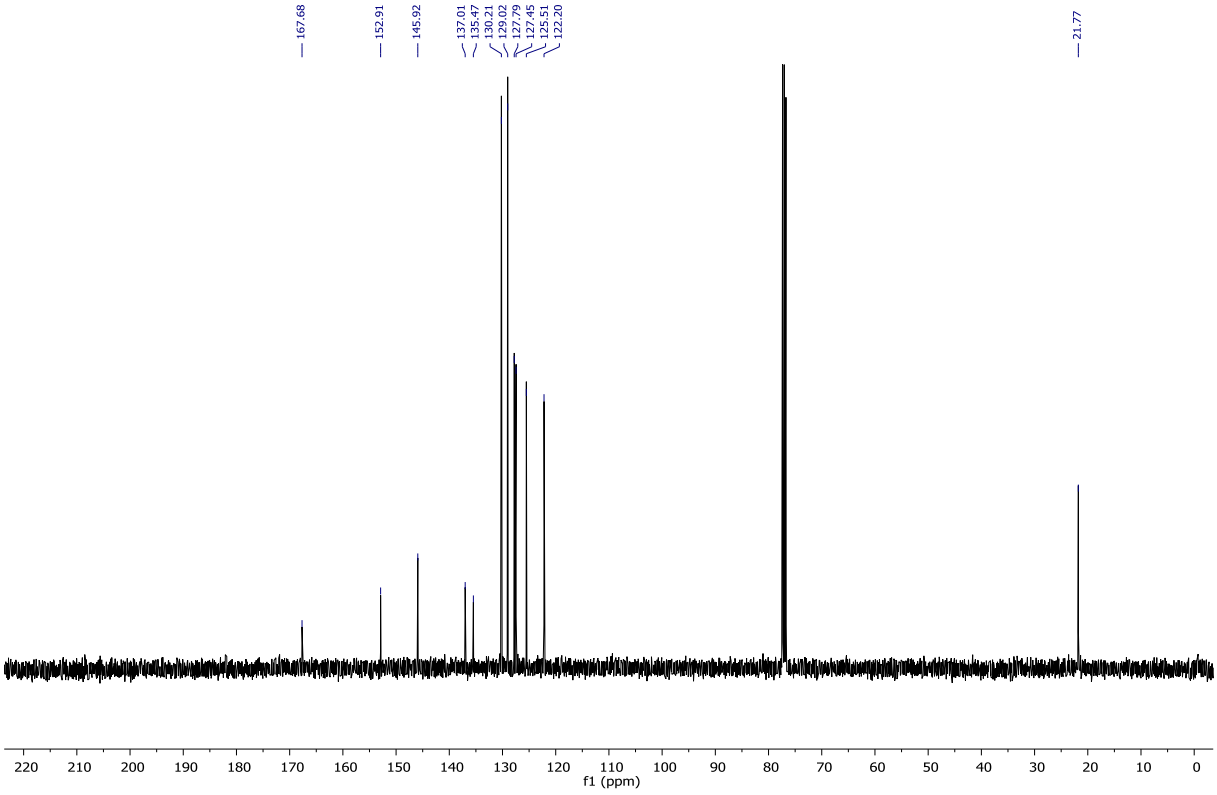
2.13
3.30
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


167.68
152.91
145.92
137.01
135.47
130.21
129.02
127.79
127.45
125.51
122.20
21.77
220
210
200
190
180
170
160
150
140
130
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110
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90
80
70
60
50
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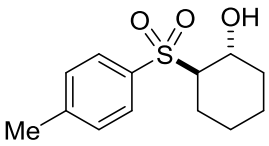
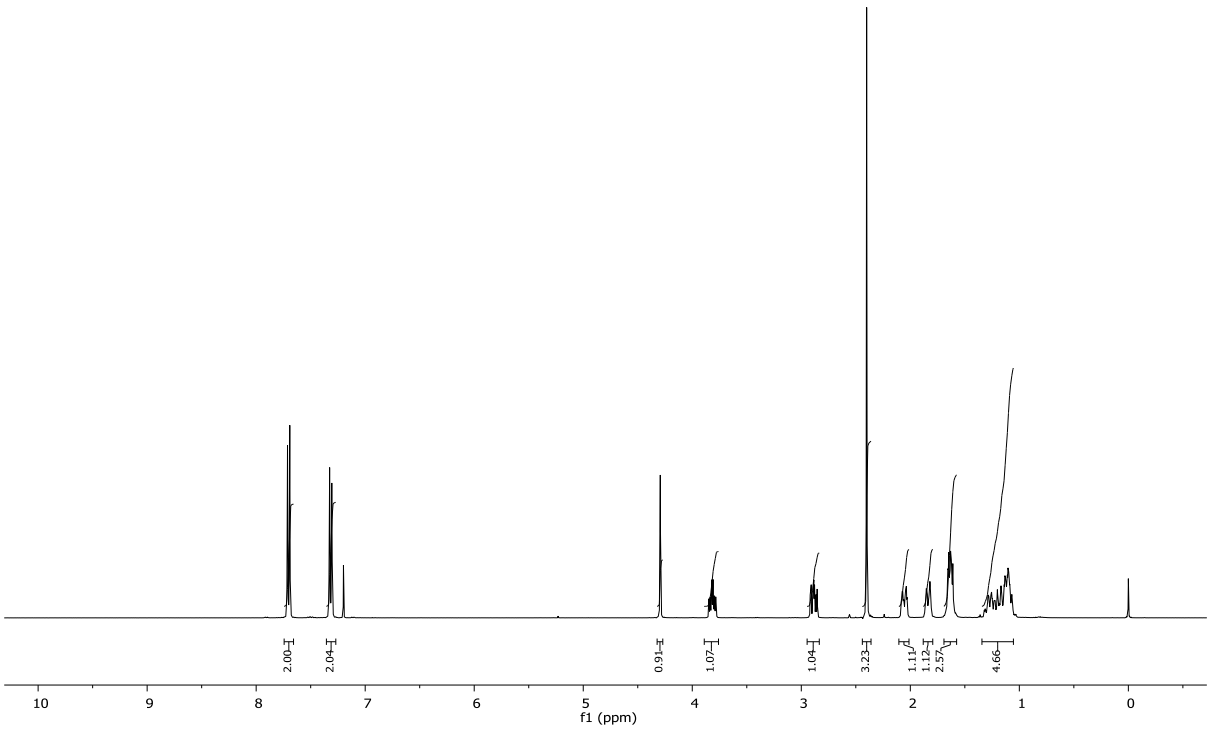
30
20
10
0
f1 (ppm)


O
O
OH
S
Me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1.07
1.04
3.23
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1.12
2.57
4.66
10
9
8
7
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5
4
3
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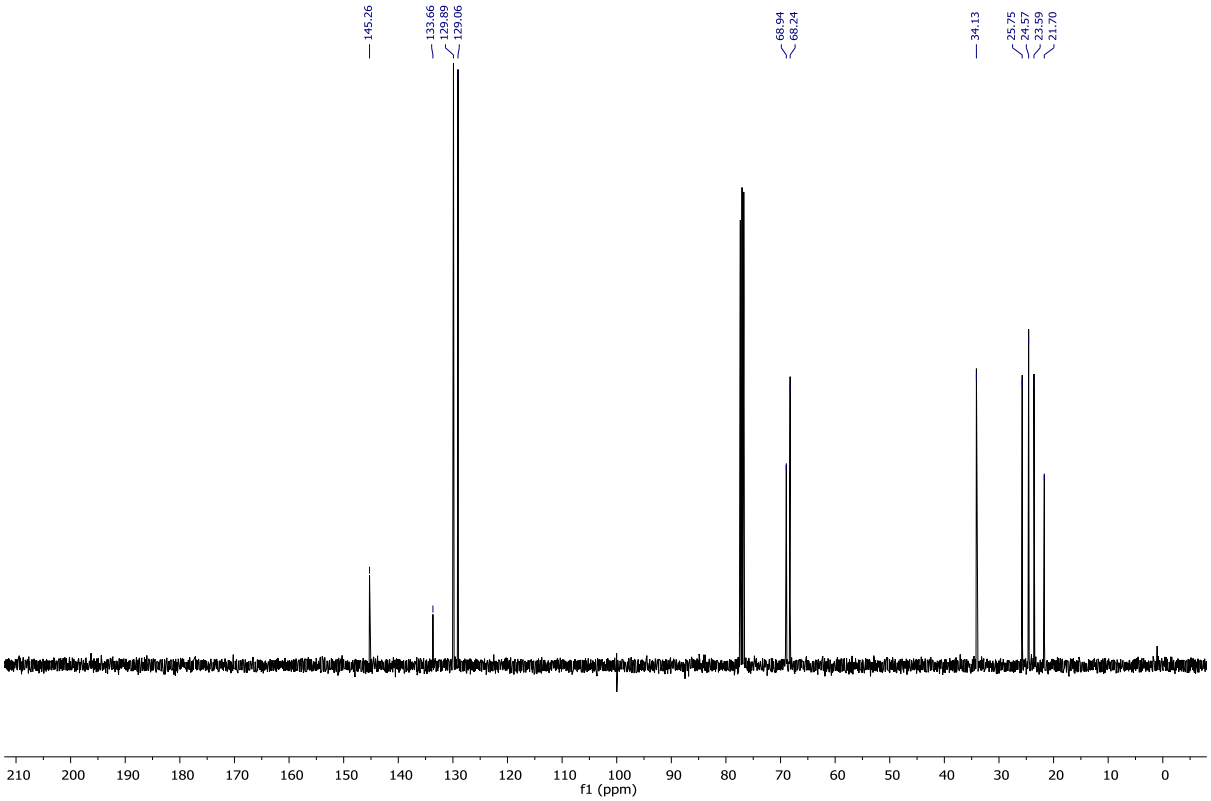
1
0
f1 (ppm)


145.26
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129.89
129.06
68.94
68.24
34.13
25.75
24.57
23.59
21.70
210
200
190
180
170
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150
140
130
120
110
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90
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70
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50
40
30
20
10
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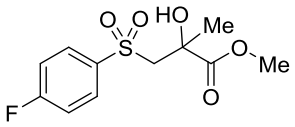
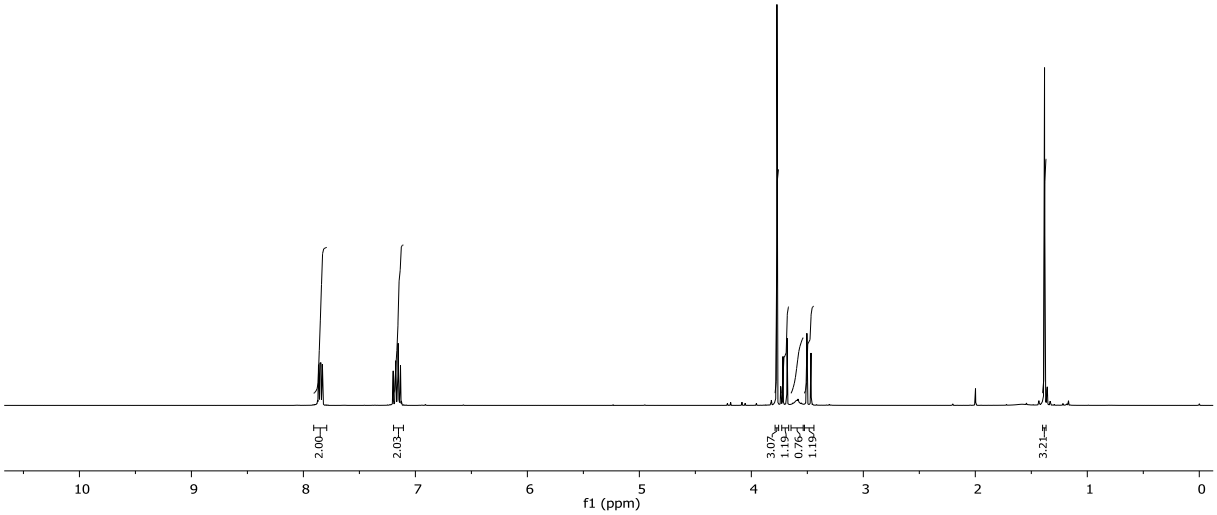
f1 (ppm)


O
O
HO
Me
S
O
Me
O
F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9
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7
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5
4
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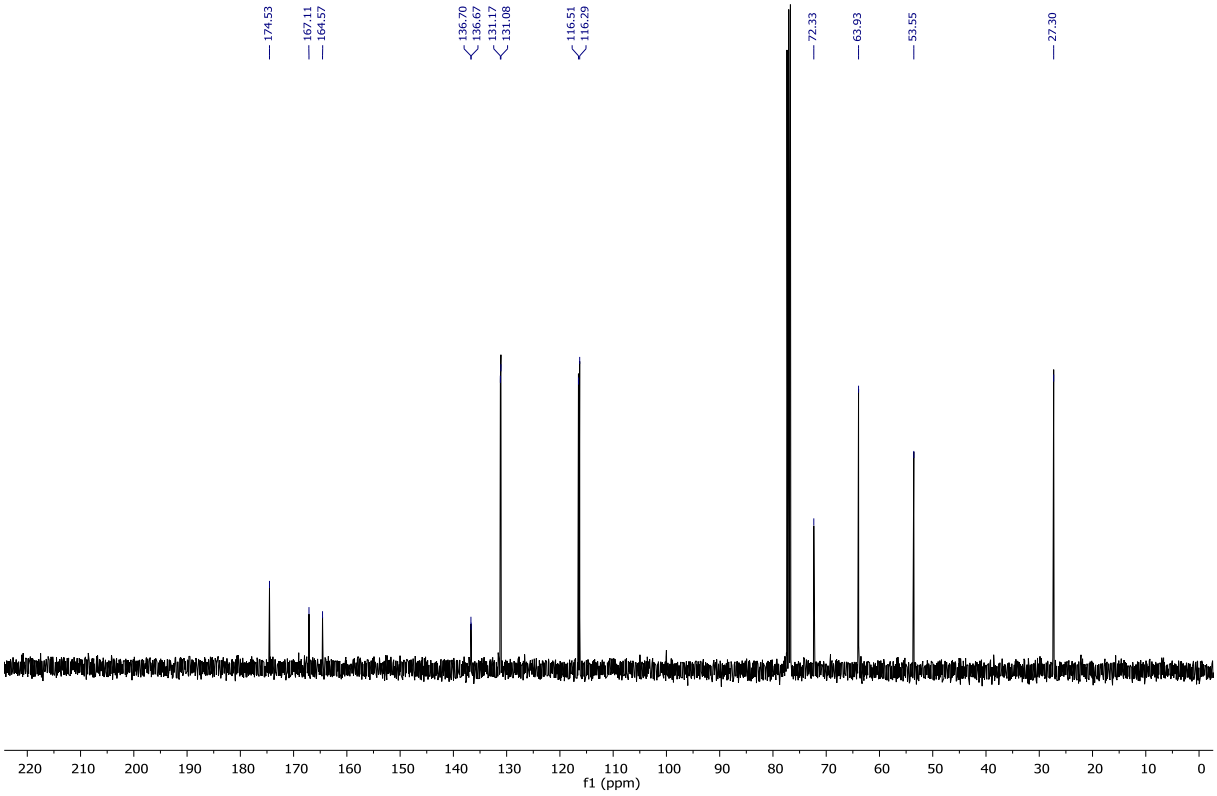
1
0
f1 (ppm)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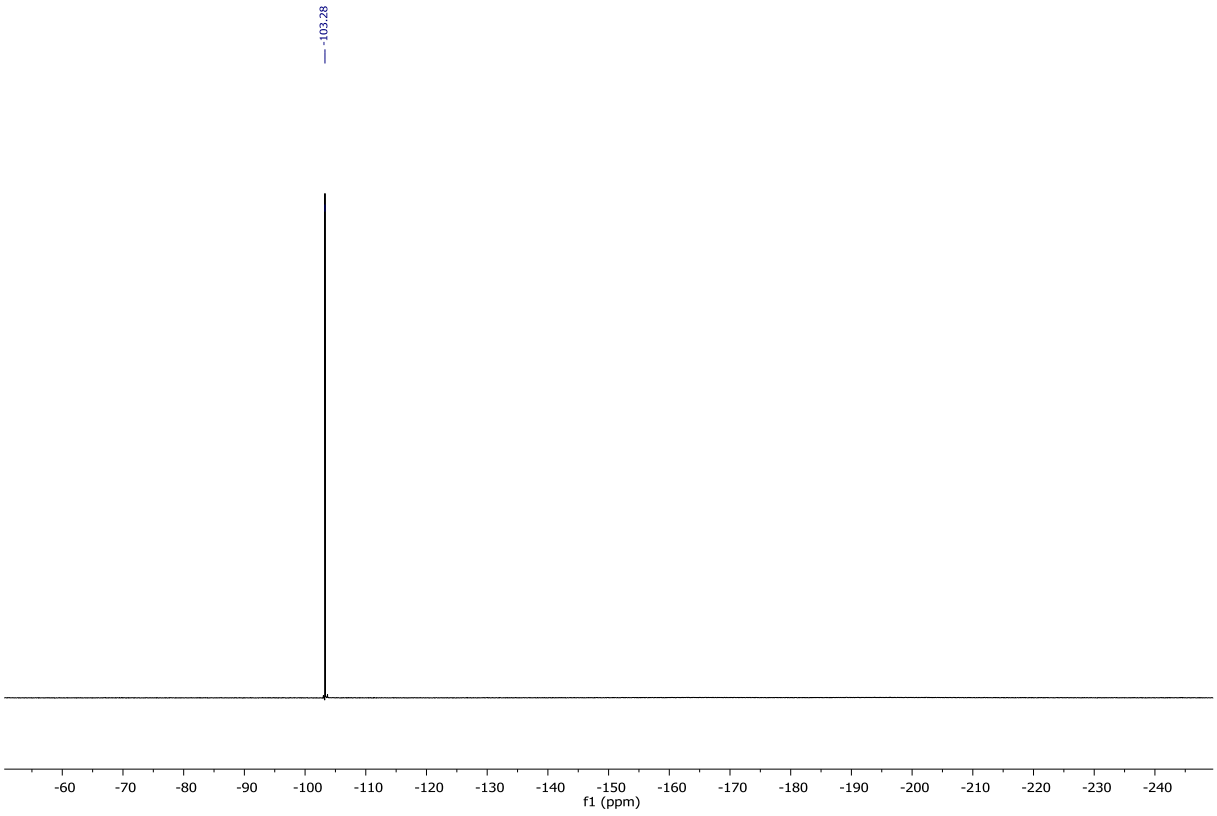
136.70
136.67
131.17
131.08
116.51
116.29
72.33
63.93
53.55
27.30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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-70
-80
-90
-100
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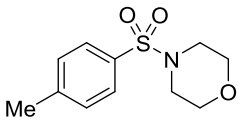
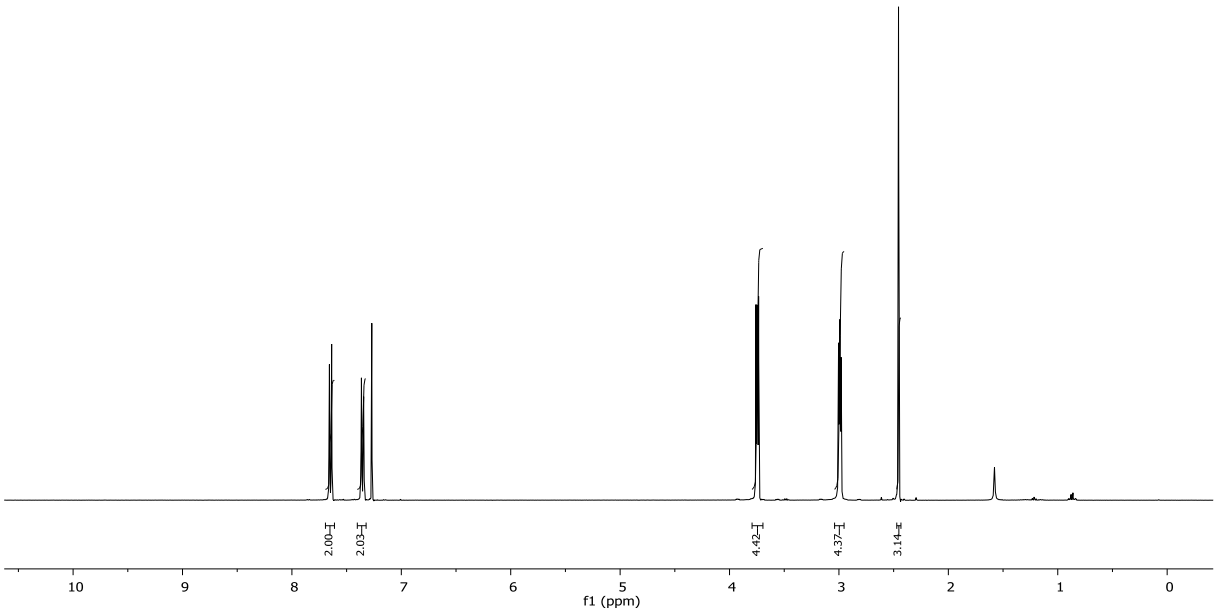
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)


O
O
S
N
O
Me


2.00
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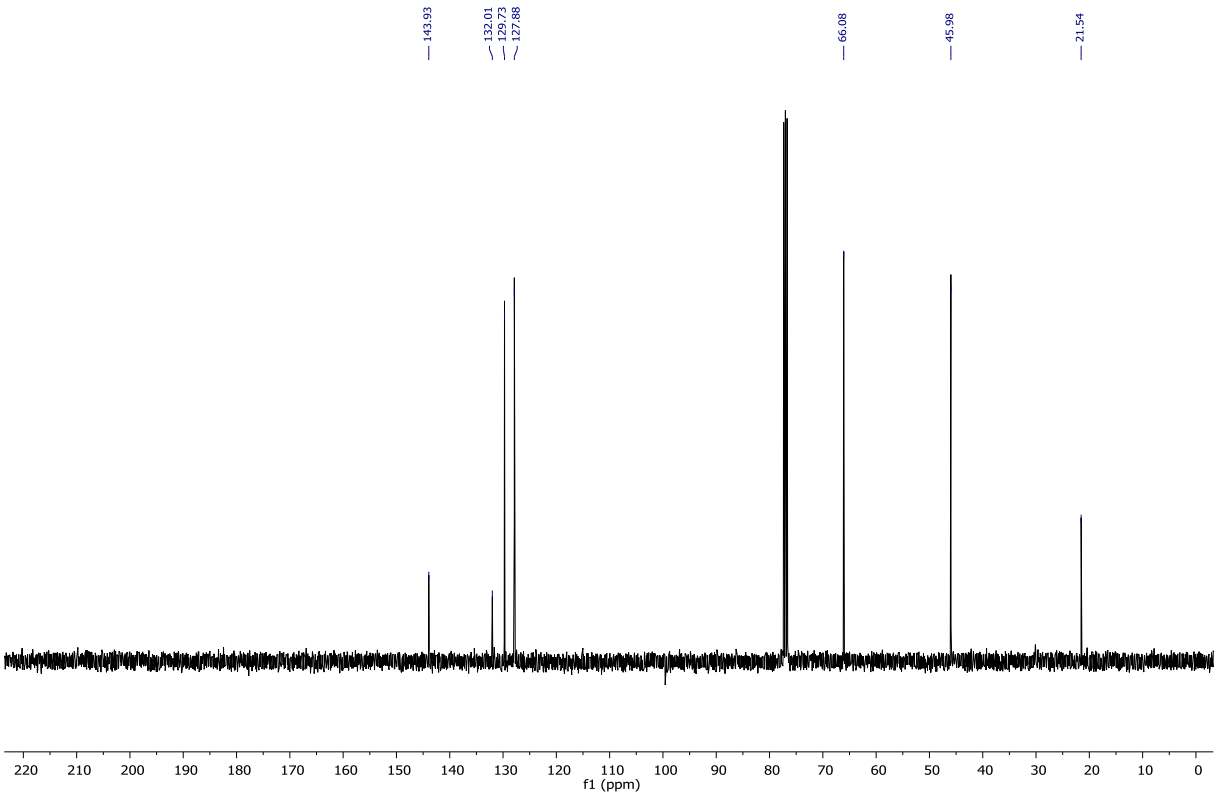
4.37
3.14
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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66.08
45.98
21.54
220
210
200
190
180
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130
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90
80
70
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50
40
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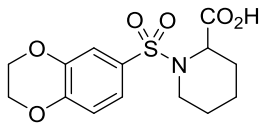
10
0
f1 (ppm)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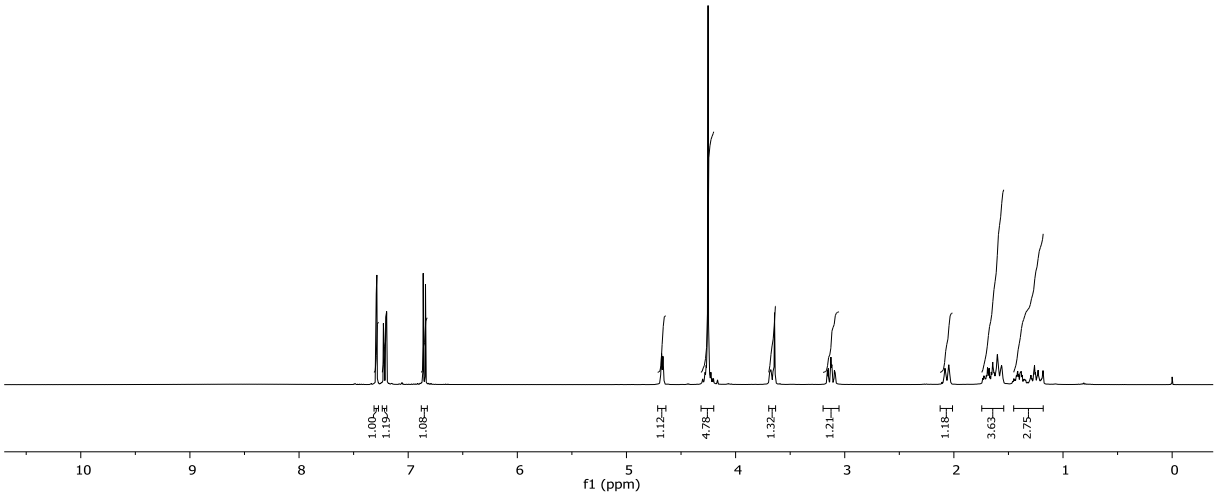
S
N
CO2H
O
O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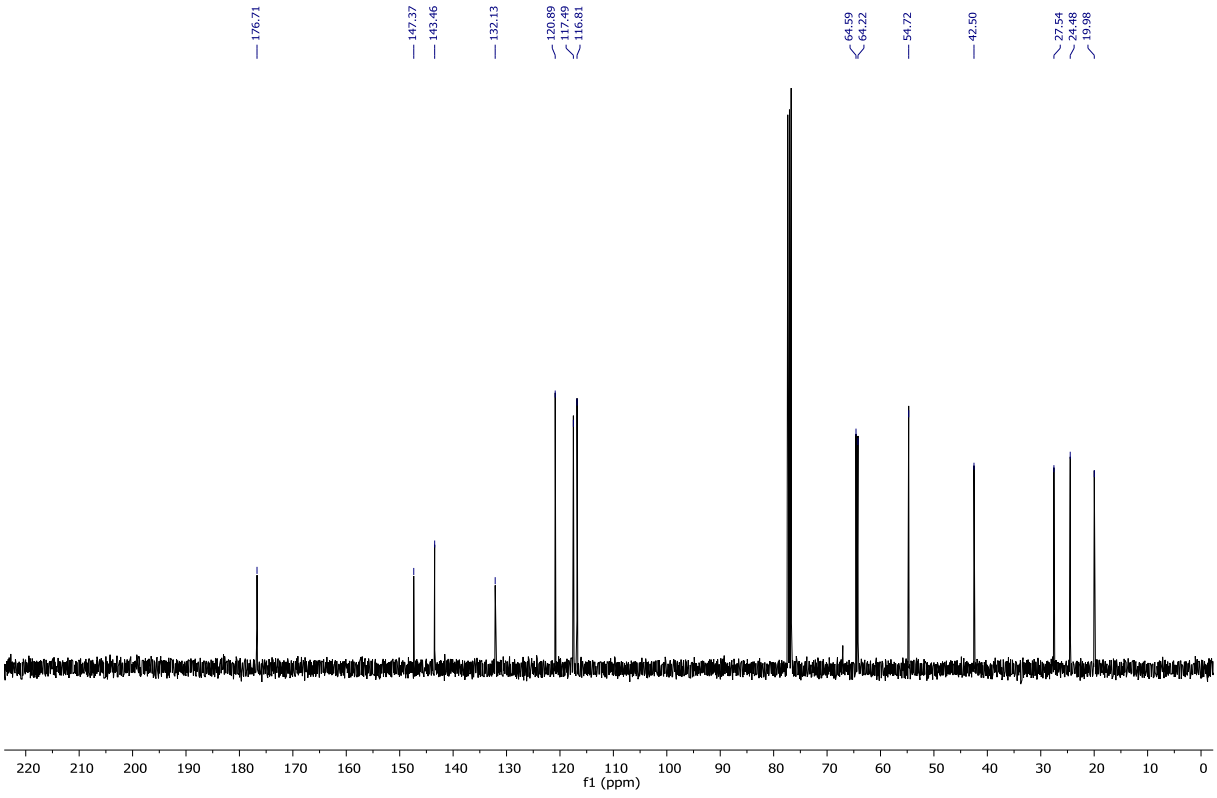
1.12
4.78
1.32
1.21
1.18
3.63
2.75
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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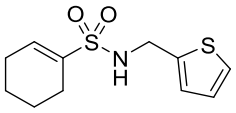
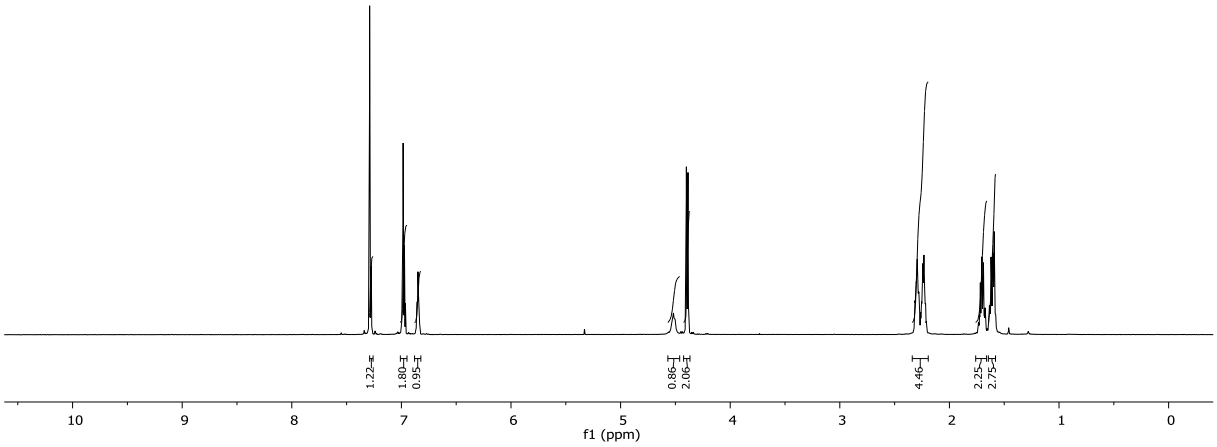
117.49
116.81
64.59
64.22
54.72
42.50
27.54
24.48
19.98
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
S
N
H
S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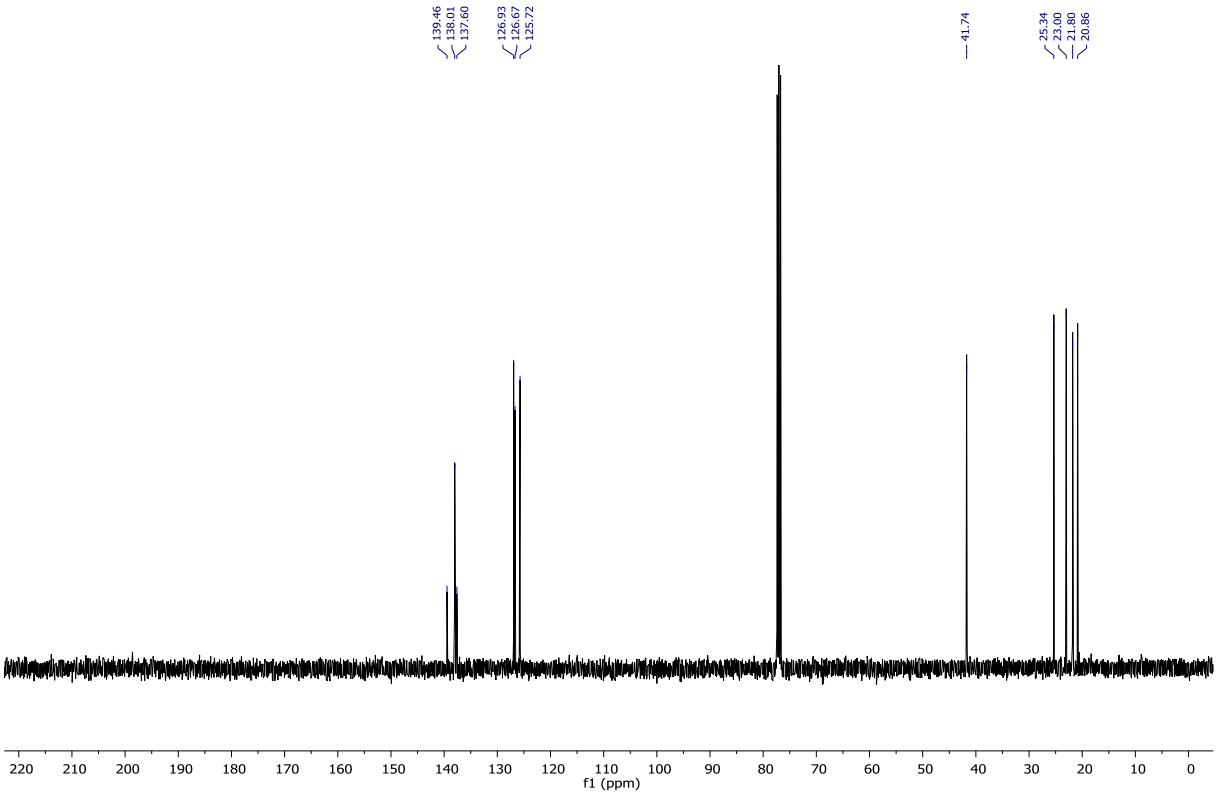
0.95
0.86
2.06
4.46
2.25
2.75
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


139.46
138.01
137.60
126.93
126.67
125.72
41.74
25.34
23.00
21.80
20.86
220
210
200
190
180
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110
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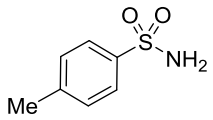
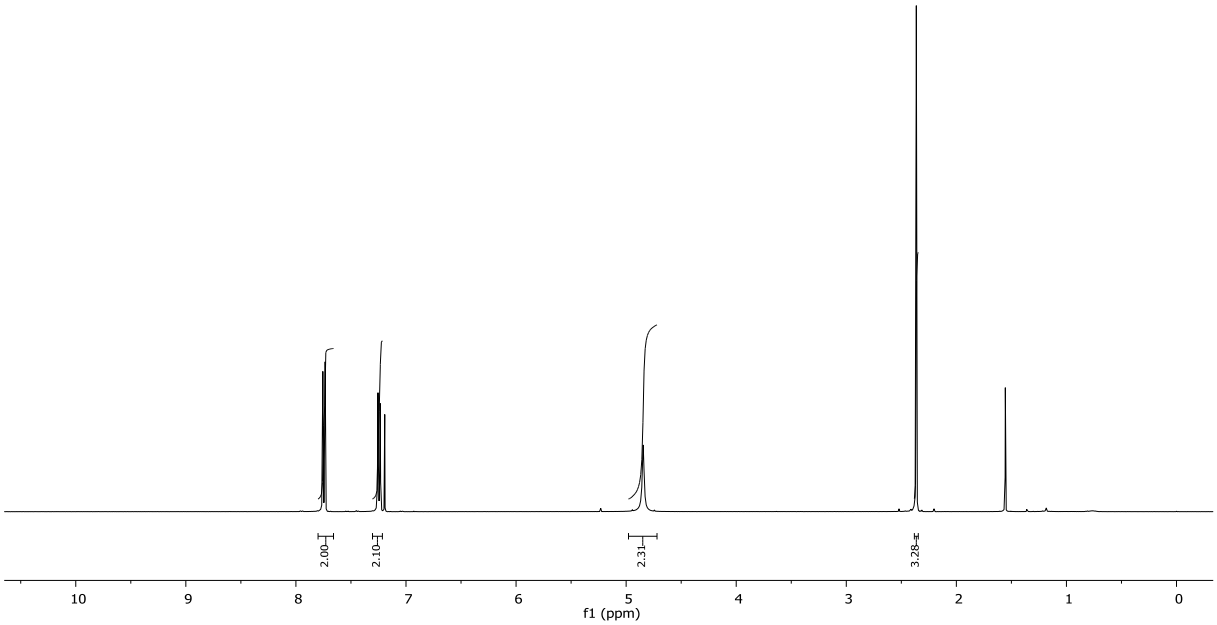
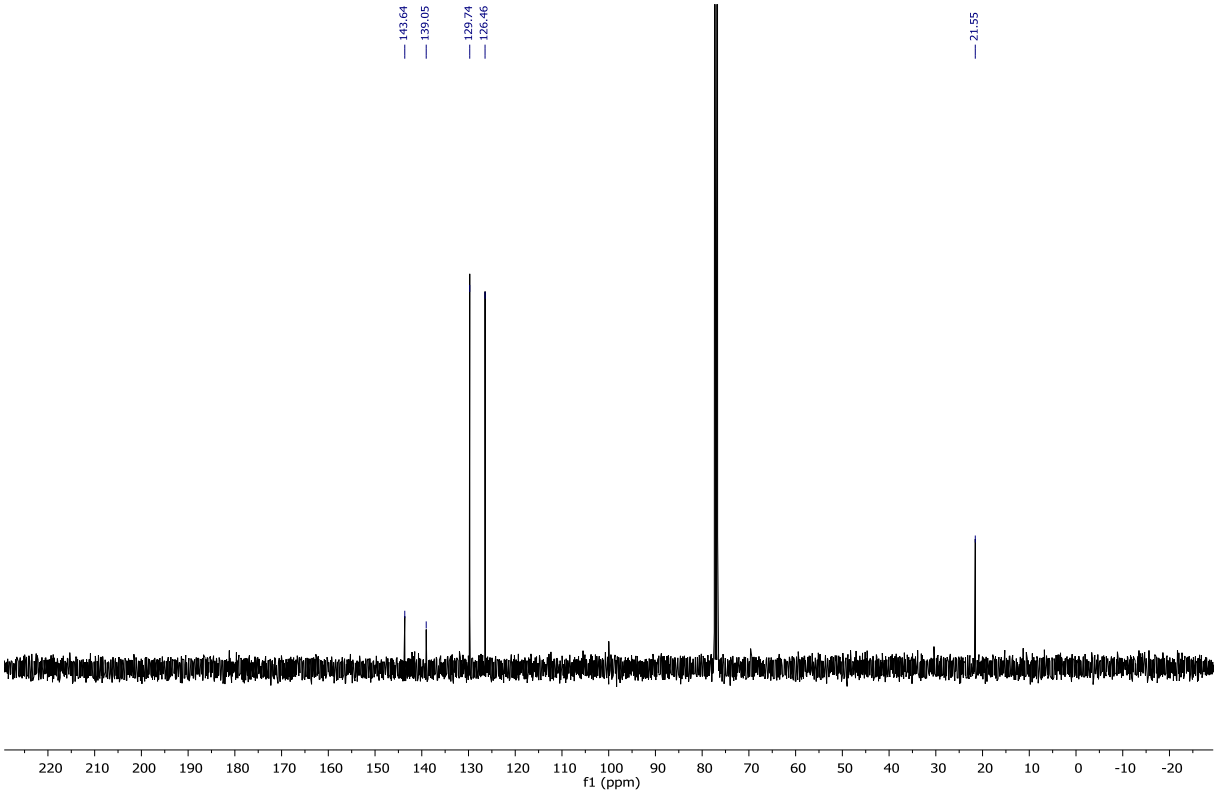
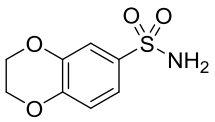
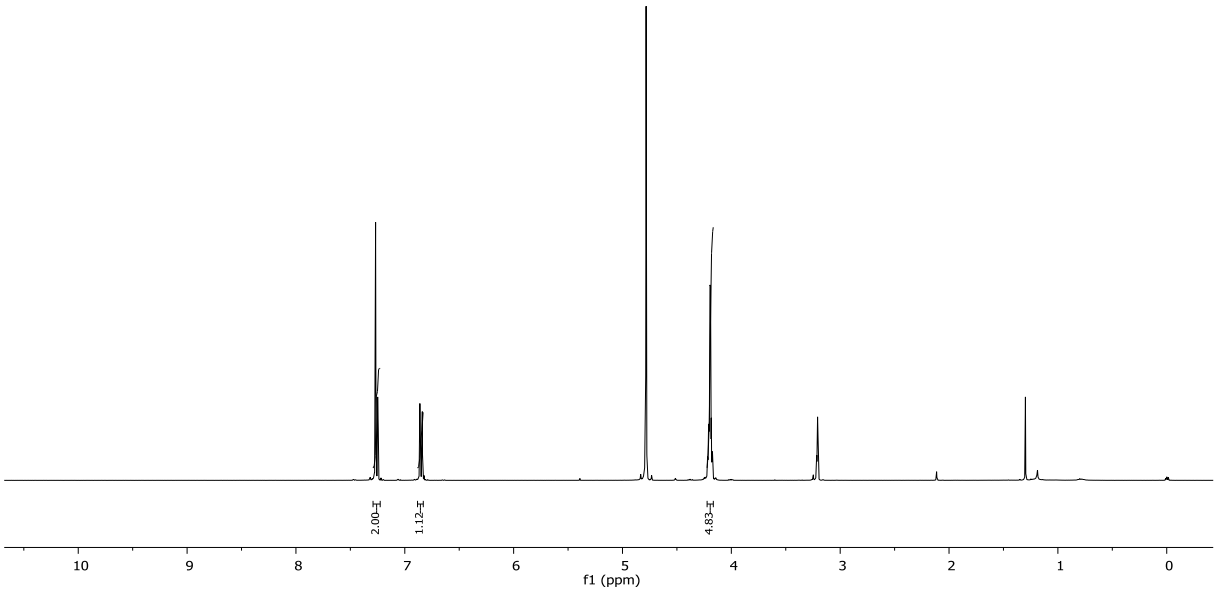
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

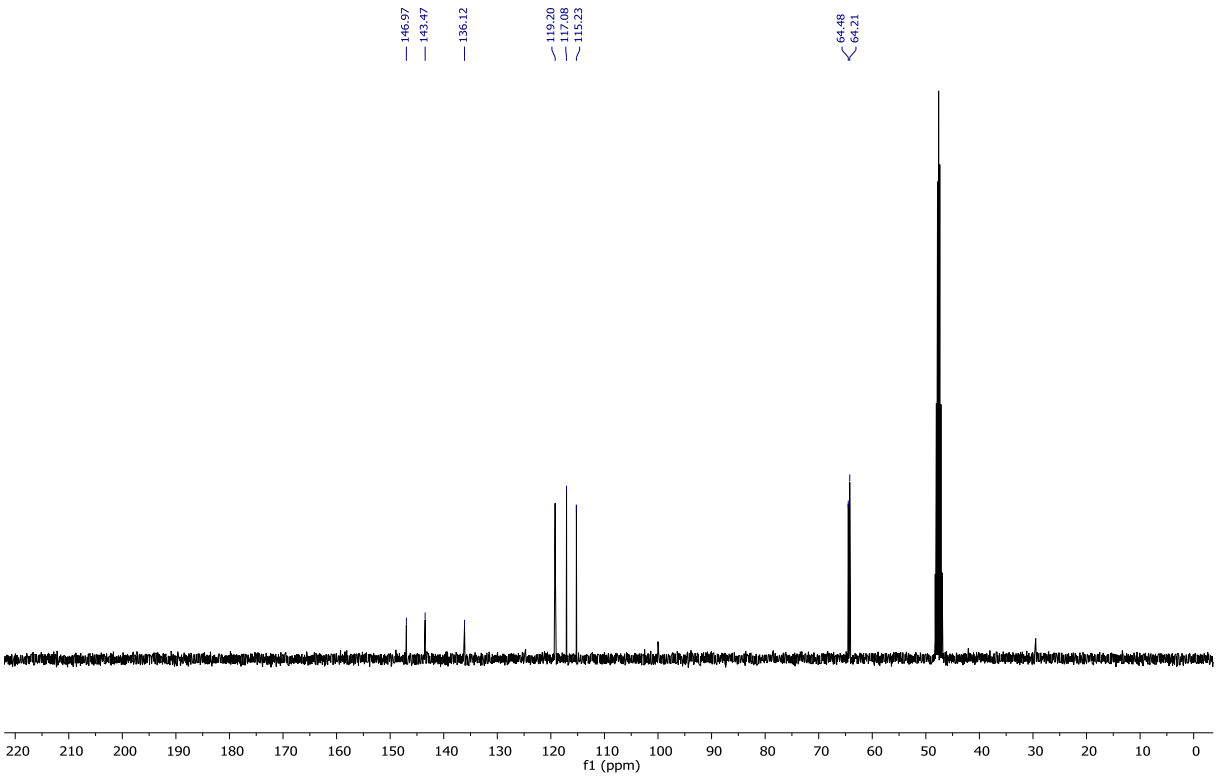

O
O
S
NH2
Me

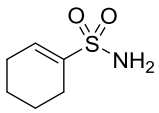

2.00
2.10
2.31
3.28
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

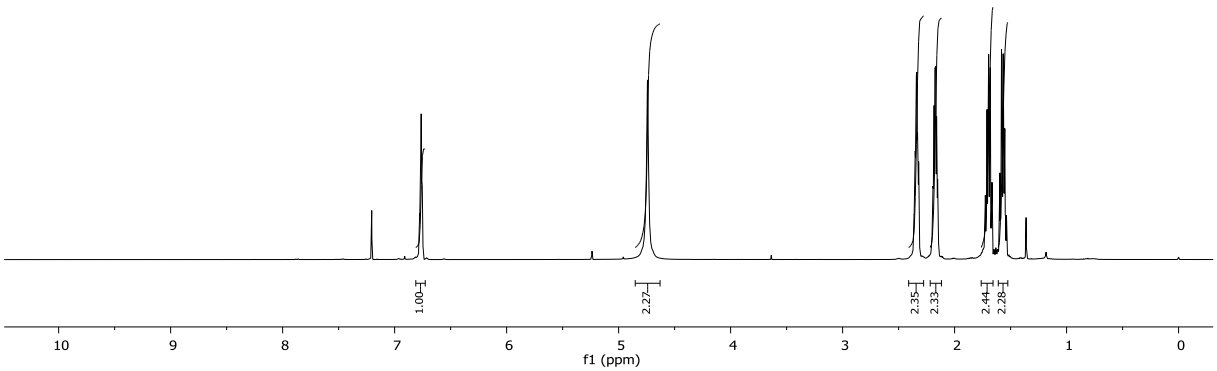

143.64
139.05
129.74
126.46
21.55
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

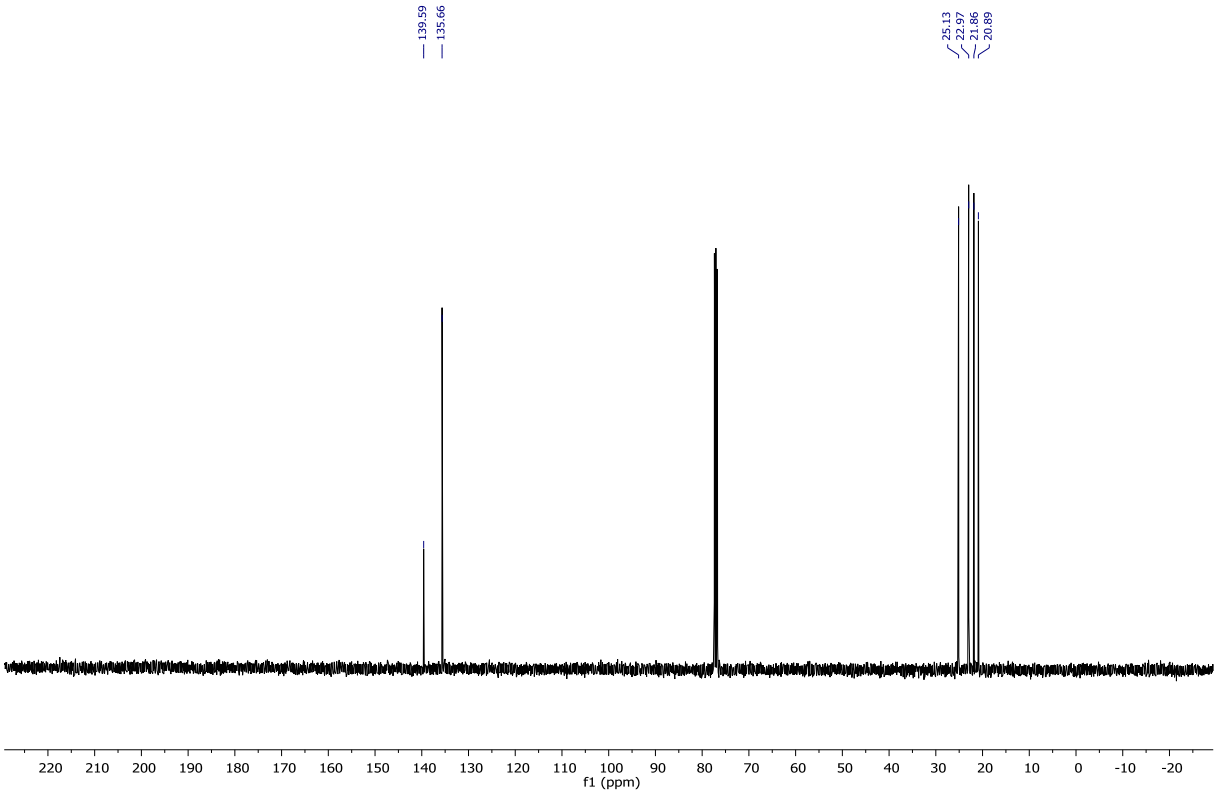

O
O
S
NH2
O
O


2.00
1.12
4.83
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


146.97
143.47
136.12
119.20
117.08
115.23
64.48
64.21
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
S
NH2


1.00
2.27
2.35
2.33
2.44
2.28
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


139.59
135.66
25.13
22.97
21.86
20.89
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)