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Supporting Information

Tuning the Lewis Acidity of Boranes in Frustrated Lewis Pair Chemistry: Implications for the Hydrogenation of Electron-Poor Alkenes

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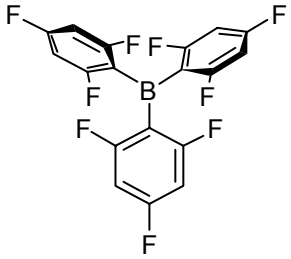
General procedures: All reactions were carried out in flame-dried glassware under Ar. All the solvents were purified by distillation over the drying agents indicated and were transferred under Ar. CH_2Cl_2 (CaH_2), hexane and toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker DPX 300 or AV 400 spectrometer in the solvents indicated; ^1H and ^{13}C chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale. All commercially available compounds (Acros, Fluka, Lancaster, Alfa Aesar, Aldrich) were used as received unless stated otherwise.

General procedure for the synthesis of tris(fluorophenyl)boranes:

The corresponding di- or trifluoro-substituted bromobenzene (3 eq.) was dissolved in freshly distilled THF (0.05 M) and cooled to -20 °C. At this temperature *i*-PrMgCl (3 eq., 2.0 M in Et_2O) was added dropwise. The reaction mixture was then allowed to reach 0 °C and after 1 h at this temperature cooled again to -50 °C. Subsequently, BF_3•Et_2O (1 eq.) was added dropwise and after 1 h the cooling bath was removed and the reaction mixture warmed to room temperature within another hour. Removal of all volatiles and sublimation of the remaining solid (120 °C, 1•10^{-3} mbar) afforded the desired boranes as white solids.

Compound 4: Prepared following the general procedure from 1-bromo-2,4,6-trifluorobenzene (0.57 mL, 4.8 mmol), *i*-PrMgCl (2.0 M in Et_2O, 2.4 mL, 4.8 mmol) and BF_3•Et_2O (0.20 mL, 1.6 mmol). White solid (550 mg, 85%).



^{1}H NMR (300 MHz, CD_2Cl_2) δ = 6.68 (dd, *J* = 8.9, 8.0 Hz, 6H) ppm.

^{13}C NMR (75 MHz, CD_2Cl_2) δ = 100.8 (ddd, *J* = 30.2, 25.0, 3.2 Hz), 166.5 (dt, *J* = 252.2, 14.9 Hz), 167.1 (dt, *J* = 255.1, 16.8 Hz) ppm.

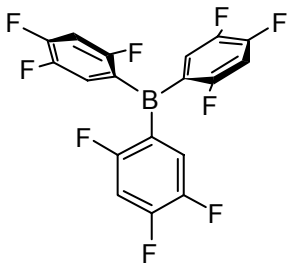
^{11}B NMR (96 MHz, CD_2Cl_2) δ = 59.4 ppm.

^{19}F NMR (282 MHz, CD_2Cl_2) δ = -100.9 (t, *J* = 10.1 Hz, 3F), -96.4 (d, *J* = 9.9 Hz, 6F) ppm.

IR (neat) $\tilde{\nu}$ = 720, 838, 875, 891, 998, 1022, 1113, 1164, 1224, 1291, 1326, 1412, 1424, 1479, 1518, 1579, 1602, 1629, 3112 cm^{-1}.

HRMS *calcd.* for $C_{18}H_6BF_9$: 404.041883; *found*: 404.041906.

Compound 5: Prepared following the general procedure from 1-bromo-2,4,5-trifluorobenzene (0.50 mL, 4.2 mmol), *i*-PrMgCl (2.0 M in Et_2O, 2.1 mL, 4.2 mmol) and BF_3•Et_2O (0.18 mL, 1.4 mmol). White solid (425 mg, 75%).



^{1}H NMR (300 MHz, CD_2Cl_2) δ = 6.97-7.05 (m, 3H), 7.16 (dt, *J* = 9.8, 5.5 Hz, 3H) ppm.

^{13}C NMR (75 MHz, CD_2Cl_2) δ = 106.3 (dd, *J* = 31.6, 20.3 Hz), 125.5 (ddd, *J* = 17.6, 9.0, 2.1 Hz), 147.4 (ddd, *J* = 246.0, 12.1, 3.4 Hz), 154.1 (dt, *J* = 257.9, 14.1 Hz), 162.6 (ddd, *J* = 250.7, 9.7, 2.1 Hz) ppm.

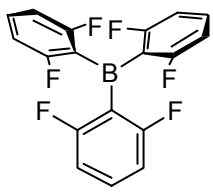
^{11}B NMR (96 MHz, CD_2Cl_2) δ = 61.8 ppm.

^{19}F NMR (282 MHz, CD_2Cl_2) δ = -143.9 (dd, *J* = 22.1, 15.7 Hz, 3F), -126.0 (dd, *J* = 22.1, 8.8 Hz, 3F), -100.4 (dd, *J* = 15.8, 8.6 Hz, 3F) ppm.

IR (neat) $\tilde{\nu}$ = 681, 719, 746, 778, 815, 893, 1040, 1085, 1128, 1140, 1183, 1193, 1276, 1298, 1393, 1419, 1491, 1618, 3080, 3476, 3547 cm^{-1}.

HRMS *calcd.* for $C_{18}H_6BF_9$: 404.041883; *found*: 404.041715.

Compound 6: Prepared following the general procedure from 1-bromo-2,6-difluorobenzene (1.0 mL, 8.8 mmol), *i*-PrMgCl (2.0 M in Et_2O, 4.4 mL, 8.8 mmol) and BF_3•Et_2O (0.37 mL, 2.9 mmol). White solid (609 mg, 59%).



^{1}H NMR (300 MHz, CD_2Cl_2) δ = 6.91 (t, *J* = 8.2 Hz, 6H), 7.46-7.56 (m, 3H) ppm.

^{13}C NMR (75 MHz, CD_2Cl_2) δ = 111.6 (dd, *J* = 26.5, 1.7 Hz), 135.5 (t, *J* = 11.6 Hz), 165.5 (dd, *J* = 250.5, 11.9 Hz) ppm.

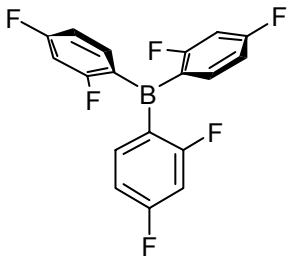
^{11}B NMR (96 MHz, CD_2Cl_2) δ = 63.6 ppm.

^{19}F NMR (282 MHz, CD_2Cl_2) δ = -99.8 ppm.

IR (neat) $\tilde{\nu}$ = 699, 732, 780, 871, 966, 1120, 1169, 1211, 1239, 1283, 1316, 1439, 1558, 1614, 3503 cm^{-1}.

HRMS *calcd.* for $C_{18}H_9BF_6$: 350.070153; *found*: 350.070229.

Compound 7: Prepared following the general procedure from 1-bromo-2,4-difluorobenzene (1.0 mL, 8.8 mmol), *i*-PrMgCl (2.0 M in Et_2O, 4.4 mL, 8.8 mmol) and BF_3•Et_2O (0.37 mL, 2.9 mmol). White solid (408 mg, 41%).



^{1}H NMR (300 MHz, CD_2Cl_2) δ = 6.86 (dt, *J* = 9.5, 2.3 Hz, 3H), 6.97 (dt, *J* = 8.3, 2.4 Hz, 3H), 7.36 (q, *J* = 7.8 Hz, 3H) ppm.

^{13}C NMR (75 MHz, CD_2Cl_2) δ = 104.1 (dd, *J* = 29.2, 24.5 Hz), 111.7 (dd, *J* = 20.4, 3.3 Hz), 140.4 (t, *J* = 9.8 Hz), 165.6 (dd, *J* = 74.2, 12.7 Hz), 169.0 (dd, *J* = 72.5, 12.6 Hz) ppm.

^{11}B NMR (96 MHz, CD_2Cl_2) δ = 63.0 ppm.

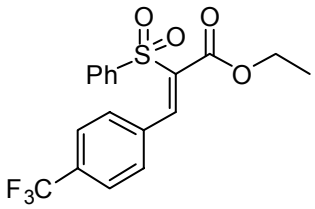
^{19}F NMR (282 MHz, CD_2Cl_2) δ = -104.1 (d, *J* = 11 Hz, 3F), -95.7 (d, *J* = 11 Hz, 3F) ppm.

IR (neat) $\tilde{\nu}$ = 674, 712, 732, 742, 815, 849, 968, 1081, 1090, 1113, 1136, 1227, 1248, 1289, 1402, 1495, 1575, 1596, 3075 cm^{-1}.

HRMS *calcd.* for $C_{18}H_9BF_6$: 350.070154; *found*: 350.070459.

Alkylidene disulfones,[1] sulfonoesters[2] and nitroalkenes[3] were prepared accordingly to the procedures described in the literature. The spectroscopic and analytic characterization of those not reported follows:

Compound 19: **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 1.11 (t, *J* = 7.1 Hz, 3H), 4.19 (q, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 4H), 7.60-7.68 (m, 3H), 7.96 (d, *J* = 7.5 Hz, 2H), 8.01 (s, 1H) ppm.



^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.6, 62.9, 123.6 (q, *J* = 268.6 Hz), 125.5, 125.8 (q, *J* = 3.8 Hz), 128.7, 129.2, 129.9, 132.7 (q, *J* = 32.8 Hz), 134.0, 135.3, 135.3, 137.8, 139.6, 142.0, 162.5 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ = -63.1 ppm.

IR (neat) $\tilde{\nu}$ = 685, 730, 830, 909, 1016, 1067, 1086, 1115, 1151, 1217, 1320, 1373, 1448, 1623, 1724, 2988 cm^{-1}.

HRMS *calcd*. for $C_{18}H_{15}F_3O_4S$: 407.053534; *found*: 407.053511.

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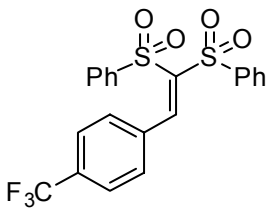
[1] a) S. Sulzer-Mossé, A. Alexakis, J. Mareda, G. Bollot, G. Bernardinelli, Y. Filinchuk, *Chem. Eur. J.* **2009**, *15*, 3204-3220; b) H. Asahara, H. Mayr, *Chem. Asian J.* **2012**, *7*, 1401-1407

[2] D. A. R. Happer, B. E. Steenson, *Synthesis,* **1980**, 806-807.

[3] a) P. J. Black, G. Cami-Kobeci, M. G. Edwards, P. A. Slatford, M. K. Whittlesey, J. M. J. Williams, *Org. Biomol. Chem.* **2006**, 116-125; b) S. Cai, X. Zhao, X. Wang, Q. Liu, Z Li, D. Z. Wan, *Angew. Chem. Int. Ed.* **2012**, *51*, 8050-8053

Compound 22: **^{1}H NMR** (400 MHz, CD_2Cl_2) δ = 7.32-7.39 (m, 2H), 7.42-7.54 (m, 4H), 7.54-7.60 (m, 1H), 7.69 (dd, *J* = 16.4, 8.3 Hz, 4H), 7.77-7.84 (m, 1H), 8.10 (dd, *J* = 8.4, 1.2 Hz, 2H), 8.73 (s, 1H) ppm.



^{13}C NMR (101 MHz, CD_2Cl_2) δ = 124.6 (q, *J* = 263.0 Hz), 125.6 (q, *J* = 3.7 Hz), 128.5, 129.4, 129.6, 129.8, 130.0, 134.8, 134.9, 135.1, 132.6 (q, *J* = 31.6 Hz), 139.9, 140.5, 147.8, 150.7 ppm.

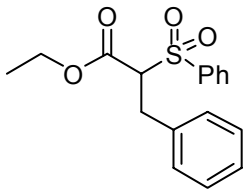
^{19}F NMR (376 MHz, CD_2Cl_2) δ = -63.3 ppm.

IR (neat) $\tilde{\nu}$ = 658, 683, 719, 739, 753, 832, 945, 999, 1018, 1065, 1081, 1110, 1124, 1149, 1319, 1408, 1448, 1479, 1595, 3007, 3071 cm^{-1}.

HRMS *calcd*. for $C_{21}H_{15}F_3O_4S_2Na$: 475.025608; *found*: 475.025730.

Reduction products: All nitroalkanes obtained after reduction of the corresponding nitroolefines were known products.[4]

Compound 26: After hydrogenation following the general procedure it was purified by flash chromatography (SiO_2; hexanes : ethyl acetate, 6:1) to afford a colourless oil (64 mg, 97%).



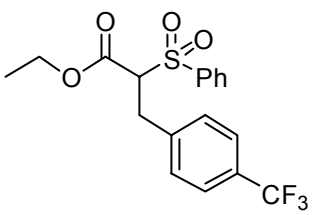
^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.99 (t, *J* = 7.1 Hz, 3H), 3.23 (dd, *J* = 16.5, 9.0 Hz, 1H), 3.42 (dd, *J* = 13.6, 3.4 Hz, 1H), 3.97 (qd, *J* = 7.1, 2.8 Hz, 2H), 4.20 (dd, *J* = 11.9, 3.5 Hz, 1H), 7.09-7.16 (m, 2H), 7.18-7.31 (m, 4H), 7.55-7.64 (m, 2H), 7.66-7.76 (m, 1H), 7.90-7.99 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 12.8, 31.7, 61.3, 71.3, 126.4, 127.9, 128.0, 128.3, 128.5, 133.5, 134.7, 136.33, 164.41 ppm.

IR (neat) $\tilde{\nu}$ = 699, 722, 749, 800, 849, 1024, 1083, 1144, 1196, 1228, 1260, 1322, 1369, 1447, 1369, 1447, 1495, 1585, 1603, 1736, 2936, 2983, 3027, 3063 cm^{-1}.

HRMS *calcd*. for $C_{17}H_{18}O_4SNa$: 341.081805; *found*: 341.081546.

Compound 27: After hydrogenation following the general procedure it was purified by flash chromatography (SiO_2; hexanes : ethyl acetate, 6:1) to afford a colourless oil (57 mg, 97%).



^{1}H NMR (300 Mz, $CDCl_3$) δ = 1.00 (t, *J* = 7.1 Hz, 3H), 3.25-3.39 (m, 1H), 3.49 (dd, *J* = 13.7, 3.5 Hz, 1H), 3.98 (q, *J* = 6.1 Hz, 2H),

[4] S. Cai, X. Zhao, X. Wang, Q. Liu, Z. Li, D. Z. Wang, *Angew. Chem. Int. Ed.* **2012**, *51*, 8050.

4.20 (dd, *J* = 11.6, 3.7 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.48-7.67 (m, 4H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.89-8.01 (m, 2H) ppm.

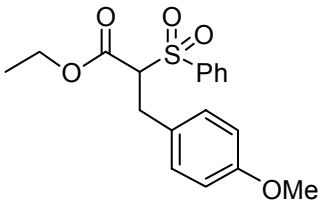
^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.8, 32.4, 62.5, 71.9, 125.9 (q, *J* = 3.7 Hz), 129.3, 129.5, 129.6, 129.9 (q, *J* = 33.4 Hz), 134.6, 137.3, 140.0, 165.1 ppm. (*C*F_3 signal not observed).

^{19}F NMR (282 MHz, $CDCl_3$) δ = -62.9 ppm.

IR (neat) $\tilde{\nu}$ = 687, 721, 737, 758, 825, 852, 876, 1018, 1066, 1083, 1109, 1121, 1145, 1194, 1231, 1260, 1321, 1370, 1419, 1448, 1585, 1618, 1735, 2986, 3070 cm^{-1}.

HRMS *calcd.* for $C_{18}H_{17}F_3O_4SNa$: 409.069186; *found*: 409. 068888.

Compound 28: After hydrogenation following the general procedure it was purified by flash chromatography (SiO_2; hexanes : ethyl acetate, 6:1) to afford a colourless oil (48 mg, 65%).



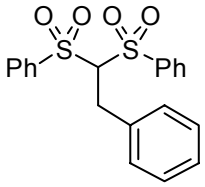
^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.99 (t, *J* = 7.1 Hz, 3H), 3.17 (dd, *J* = 13.6, 12.0 Hz, 1H), 3.35 (dd, *J* = 13.7, 3.5 Hz, 1H), 3.96 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 4.15 (dd, *J* = 11.9, 3.5 Hz, 1H), 6.72-6.84 (m, 2H), 7.00-7.09 (m, 2H), 7.53-7.64 (m, 2H), 7.64-7.75 (m, 1H), 7.86-7.98 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 13.8, 31.9, 55.3, 62.2, 72.5, 114.3, 127.5, 129.2, 129.5, 130.0, 134.4, 137.3, 158.9, 165.43 ppm.

IR (neat) $\tilde{\nu}$ = 688, 722, 735, 753, 822, 852, 874, 1031, 1083, 1110, 1144, 1178, 1196, 1248, 1310, 1321, 1369, 1391, 1447, 1465, 1512, 1584, 1612, 1734, 2383, 2937, 2984, 3067 cm^{-1}.

HRMS *calcd.* for $C_{18}H_{20}O_5S$: 371.092363; *found*: 371.092279.

Compound 29: After hydrogenation following the general procedure it was purified by flash chromatography (SiO_2; hexanes : ethyl acetate, 2:1) to afford a crystalline white solid (74.5 mg, 98%).



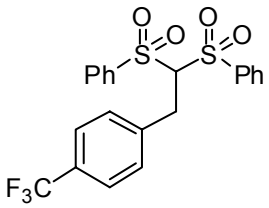
^{1}H NMR (400 MHz, CD_2Cl_2) δ = 3.51 (d, *J* = 5.8 Hz, 2H), 4.78 (t, *J* = 5.8 Hz, 1H), 6.98-7.00 (m, 2H), 7.16-7.20 (m, 3H), 7.51-7.55 (m, 4H), 7.66-7.71 (m, 2H), 7.81-7.84 (m, 4H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 31.6, 85.2, 127.5, 129.0, 129.6, 129.7, 135.0, 136.6, 138.6 ppm.

IR (neat) $\tilde{\nu}$ = 685, 697, 710, 727, 737, 755, 764, 777, 806, 838, 854, 899, 928, 997, 1006, 1022, 1077, 1141, 1152, 1178, 1205, 1265, 1306, 1318, 1327, 1345, 1446, 1455, 1479, 1497, 1584, 1604, 2929, 3030, 3064 cm^{-1}.

HRMS *calcd.* for $C_{20}H_{18}O_4S_2Na$: 409.053872; *found*: 409.054162.

Compound 30: After hydrogenation following the general procedure it was purified by flash chromatography (SiO_2; hexanes : ethyl acetate, 2:1) (88 mg, 95%).



^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.60 (d, *J* = 5.5 Hz, 2H), 4.72 (t, *J* = 5.6 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 11.6 Hz, 2H), 7.53 (d, *J* = 7.7 Hz 4H), 7.66 (d, *J* = 7.4 Hz, 2H), 7.85 (d, *J* = 7.7 Hz, 4H) ppm.

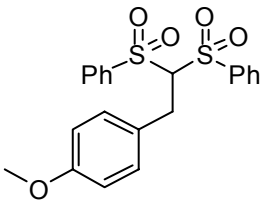
^{13}C NMR (75 MHz, $CDCl_3$) δ = 31.3, 85.0, 124.1 (*J* = 262.2 Hz), 125.8 (q, *J* = 3.8 Hz), 129.3, 129.4, 129.6, 129.8 (q, *J* = 36.6 Hz), 134.9, 138.1, 140.5 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ = -62,7 ppm.

IR (neat) $\tilde{\nu}$ = 686, 736, 758, 787, 823, 853, 911, 999, 1019, 1067, 1078, 1122, 1155, 1260, 1323, 1420, 1448, 1584, 1619, 1708, 2931, 3071 cm^{-1}.

HRMS *calcd.* for $C_{21}H_{17}F_3O_4S_2Na$: 477.041262; *found*: 477.041384

Compound 31: After hydrogenation following the general procedure it was purified by flash chromatography (SiO_2; hexanes : ethyl acetate, 2:1) (82 mg, 96%).



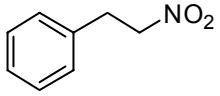
^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.48 (d, *J* = 5.5 Hz, 2H), 3.76 (s, 3H), 4.69 (t, *J* = 5.5 Hz, 1H), 6.71 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 4H), 7.66 (t, *J* = 7.5 Hz, 2H), 7.86 (dd, *J* = 8.3, 1.0 Hz, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 30.7, 55.4, 85.6, 114.2, 128.3, 129.2, 129.6, 129.9, 134.6, 138.4, 158.8 ppm.

IR (neat) $\tilde{\nu}$ = 724, 756, 793, 821, 850, 907, 998, 1032, 1078, 1109, 1148, 1178, 1247, 1311, 1325, 1447, 1478, 1513, 1584, 1612, 2257, 2837, 2963, 3007, 3067 cm^{-1}.

HRMS *calcd.* for $C_{21}H_{20}O_5S_2Na$: 439.064436; *found*: 439.064528.

Compound 38: After hydrogenation following the general procedure it was purified by flash chromatography (SiO_2; hexanes : ethyl acetate, 6:1) to afford a colourless oil (35.5 mg, 95%).



^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.31 (t, *J* = 7.3 Hz, 2H), 4.63 (t, *J* = 7.3 Hz, 2H), 7.01-7.65 (m, 5H) ppm.

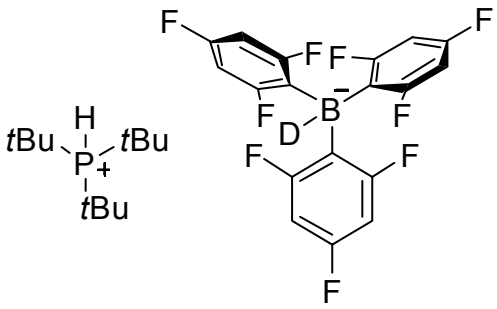
^{13}C NMR (101 MHz, $CDCl_3$) δ = 33.9, 76.9, 127.9, 129.1, 129.4, 136.6 ppm.

IR (neat) $\tilde{\nu}$ = 697, 750, 862, 907, 1030, 1083, 1183, 1223, 1377, 1431, 1455, 1496, 1547, 2923, 3031 cm^{-1}.

HRMS *calcd.* for $C_8H_9NO_2$: 151.063331; *found*: 151.063262.

Deuterium labelling experiments:

Synthesis of [^{t}Bu$_3$PH][DB(2,4,6-F-Ph)$_3$]: A solution of ^{t}Bu$_3$P (0.45 ml, 0.9 mmol, 2.0 M in toluene) was added to a stirring solution of 360 mg (0.9 mmol) of tris(2,4,6-trifluorophenyl)borane in 9.1 ml of toluene (0.1 M). Bubbling of D_2 to the clear solution immediately forms a white precipitate. The volume of the resulting suspension was then reduced to the half and 6 ml of *n*-pentane are added. After removing of the solvent by filtration, the residue is washed twice with 6 ml *n*-pentane and further purified by column chromatography affording (SiO_2; CH_2Cl_2) 155 mg (30%) of [^{t}Bu$_3$PH][DB(2,4,6-F-Ph)$_3$] as a white solid.



^{1}H NMR (300 MHz, CD_3CN) δ = 1.60 (d, *J* = 15.5 Hz, 27H), 5.40 (d, *J* = 443.7 Hz, 1H), 6.39 (dd, *J* = 9.5, 7.1 Hz, 6H) ppm.

^{13}C NMR (75 MHz, CD_3CN) δ = 30.3, 98.5 (dd, *J* = 36.6, 37.3 Hz), carbon atoms directly attached to F were not observed.

^{11}B NMR (96 MHz, CD_2Cl_2) δ = -25.6 ppm.

^{19}F NMR (282 MHz, CD_2Cl_2) δ = -119.9, -99.8 ppm.

^{31}P NMR (122 MHz, CD_2Cl_2) δ = 57.1 ppm.

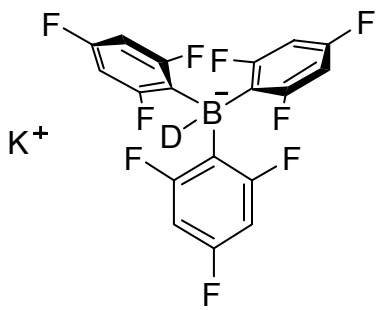
IR (neat) $\tilde{\nu}$ = 674, 739, 809, 890, 934, 942, 994, 1031, 1101, 1156, 1177, 1206, 1281, 1309, 1321, 1380, 1401, 1436, 1463, 1473, 1484, 1514, 1582, 1617, 1689, 1764, 2922, 2980, 3004, 3085 cm^{-1}.

ESI MS(pos.) [^{t}Bu$_3$PH]$^+$ = 203 m/z.

ESI MS(neg.) [DB(2,4,6-F-Ph)$_3$]$^-$ = 406 m/z.

HRMS *calcd.* for $C_{18}H_6DBF_9$: 406.056535; *found*: 406.056621.

Synthesis of K[DB(2,4,6-F-Ph)$_3$]: A solution of [^{t}Bu$_3$PH][DB(2,4,6-F-Ph)$_3$] (188 mg, 0.31 mmol) in THF (10 mL) was treated with KH (19 mg, 0.47 mmol) and the resulting suspension stirred for 1 hour at r.t. Filtration afforded a transparent solution that was evaporated in vacuum. The white precipitate thus obtained was washed with pentane (4 x 4 mL) and dried in vacuum affording the desired salt (110 mg, 80%).



^{1}H NMR (300 MHz, CD_3CN) δ = 6.40 (dd, *J* = 9.6, 7.2 Hz, 6H) ppm.

^{11}B NMR (96 MHz, CD_2Cl_2) δ = -26.1 ppm.

^{19}F NMR (282 MHz, CD_2Cl_2) δ = -120.6, -100.2 (t, *J* = 3.4 Hz) ppm.

Synthesis of [HDABCO][DB(2,4,6-F-Ph)$_3$]: A solution of 35 mg DABCO•HCl in acetonitrile (5.0 ml) was added dropwise under argon to a stirring solution of K[DB(2,4,6-F-Ph)$_3$] (100 mg, 0.23 mmol) in acetonitrile (2.3 ml, 0.1 M) and stirred over night. The resulting suspension was filtered off, the filtrate evaporated and the residue washed three times with *n*-pentane (5 ml). The white solid thus obtained was dried under high vacuum affording 88 mg (74%) of [HDABCO][DB(2,4,6-F-Ph)$_3$]. **^{1}H NMR** (300 MHz, CD_3CN) δ = 3.05 (s, 12H), 6.41 (dd, *J* = 9.5, 7.1 Hz, 6H), 7.37 (br s, 1H) ppm; **^{13}C NMR** (75 MHz, CD_3CN) δ = 45.5, 98.5 (dd, *J* = 37.0, 36.3 Hz), 161.1 (dt, *J* = 238.2 Hz, 17.1 Hz), 167.4 (dm, *J* = 239.1 Hz); **^{1}B NMR** (96 MHz, CD_3CN) δ = -26.0 ppm; **^{19}F NMR** (282 MHz, CD_3CN) δ = -120.6, -100.2 ppm; **IR** (neat) $\tilde{\nu}$ = 669, 688, 745, 760, 785, 835, 870, 992, 1054, 1101, 1159, 1281, 1321, 1406, 1464, 1515, 1583, 1620, 1697, 1777, 2983, 3094 cm^{-1}; **ESI(pos.)** $[HDABCO]^+$ = 113 m/z; **ESI(neg.)** $[DB(2,4,6\text{-}F\text{-}Ph)_3]^-$ = 406 m/z; **HRMS** *calcd.* for $C_{18}H_6DBF_9$: 406.056535; *found*: 406.056617.

Stoichiometric reduction of diethyl benzylidenmalonate with [HDABCO][DB(2,4,6-F-Ph)$_3$]: 12.4 µl (0.055 mmol) of diethyl benzylidenmalonate were added to a stirring solution of [HDABCO][DB(2,4,6-F-Ph)$_3$] (28.6 mg, 0.055 mmol) in CD_2Cl_2. The resulting solution was heated to 50°C and followed by GC-MS. After 1 hour the reaction was completed. Then, the solvent was removed and the residue purified by column chromatography (SiO2, hexanes : ethyl acetate, 10:1) affording the D-labelled product . **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.21 (t, *J* = 7.1 Hz, 3H9, 1.22 (t, *J* = 7.1 Hz, 3H), 3.20 (d, *J* = 7.8 Hz, 1H), 3.67 (d, *J* = 7.8 Hz, 1H), 4.12-4.20 (m, 4H), 7.19-7.22 (m, 3H), 7.26-7.30 (m, 2H) ppm.

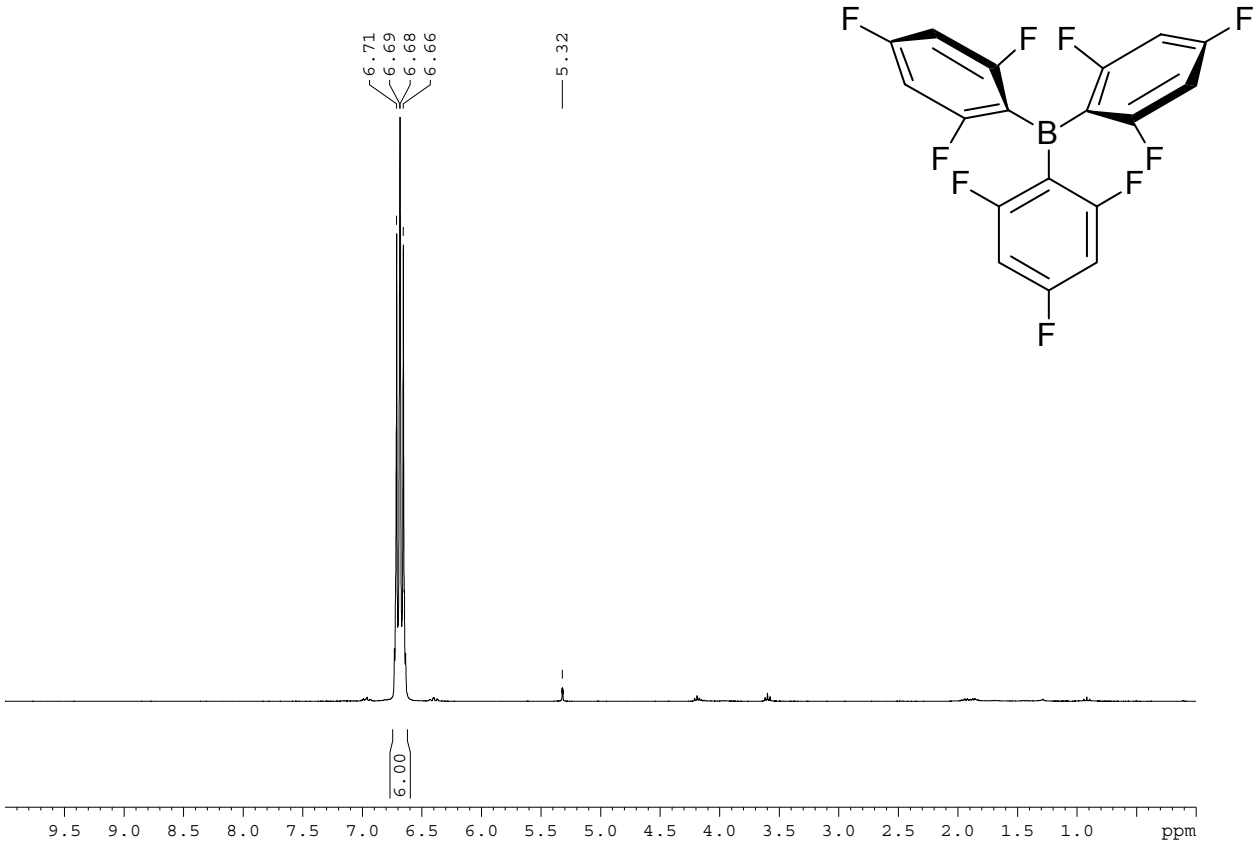
^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.1, 34.5 (t, *J* = 20.2 Hz), 53.9, 61.5, 126.8, 128.6, 128.9, 134.0 ppm.

IR (neat) $\tilde{\nu}$ = 662, 699, 744, 786, 855, 909, 1033, 1095, 1148, 1175, 1207, 1256, 1368, 1451, 1496, 1605, 1729, 2983 cm^{-1}.

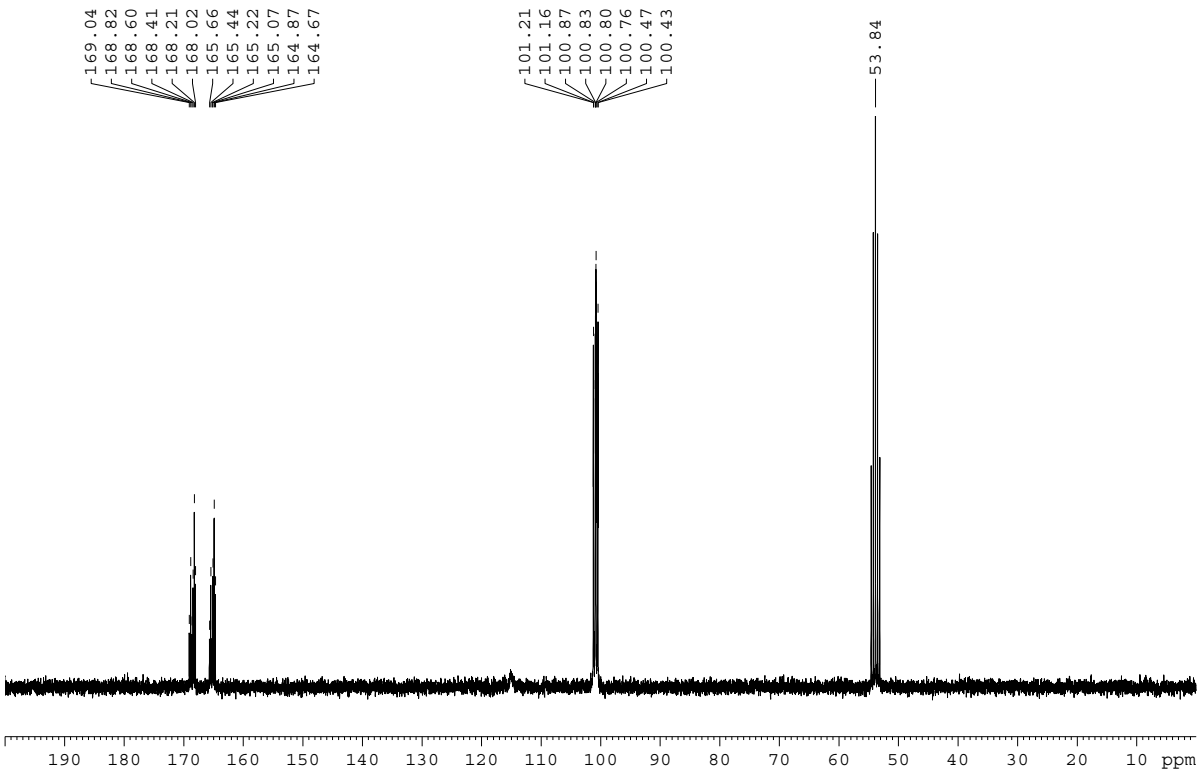
HRMS *calcd.* for $C_{14}H_{17}DO_4Na$: 274.116002; *found*: 274.115865.

Selected NMR experiments

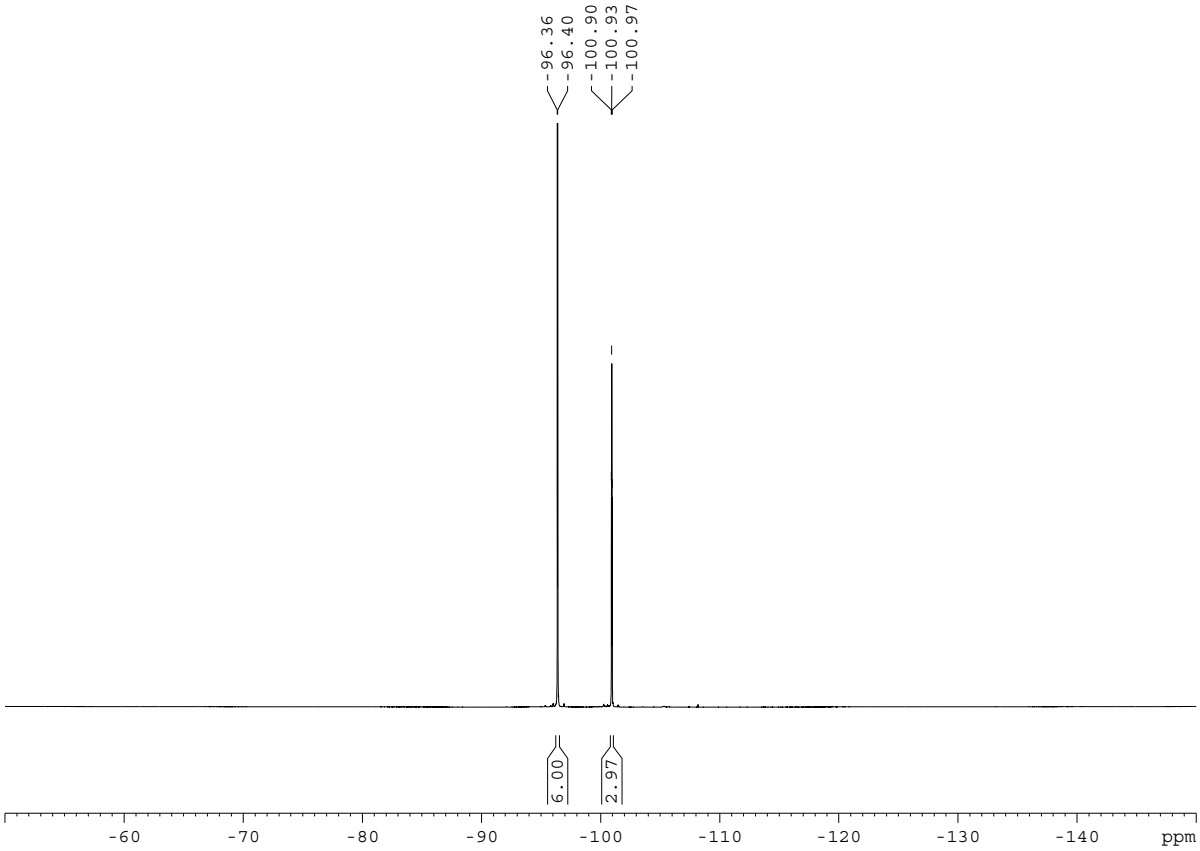
^{1}H NMR (300 MHz, CD_2Cl_2)



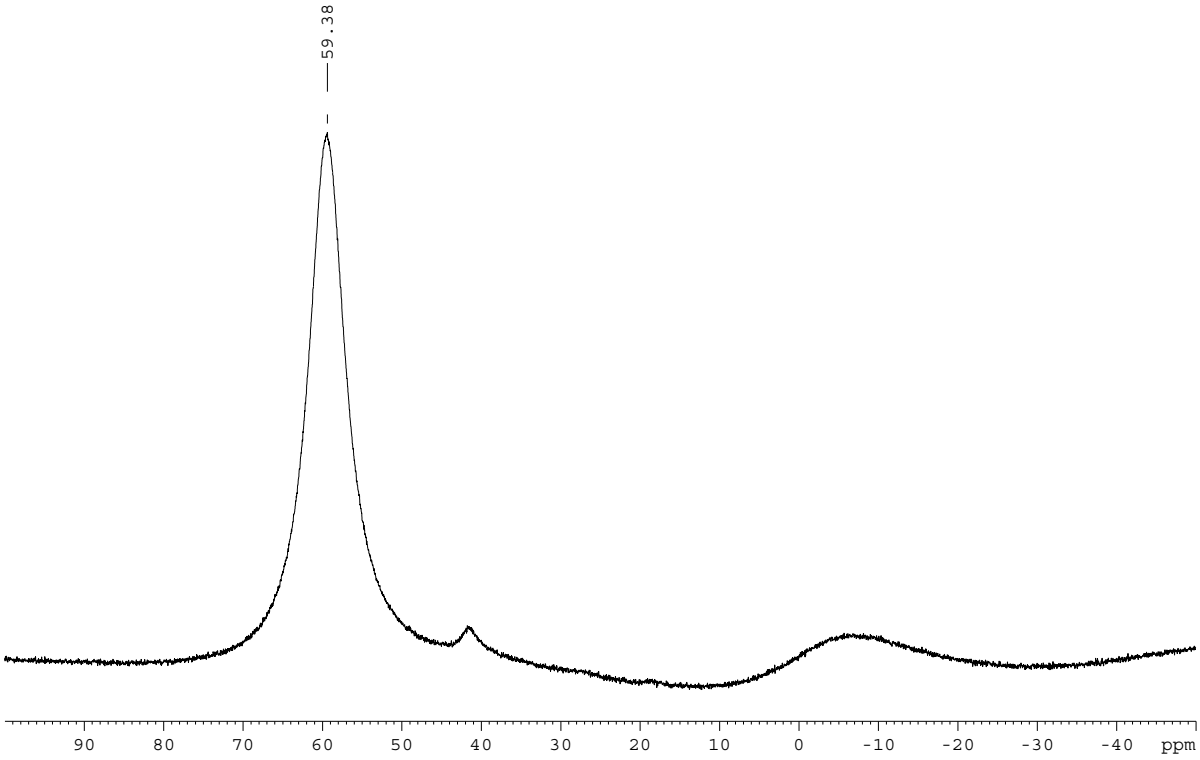
^{13}C NMR (75 MHz, CD_2Cl_2)



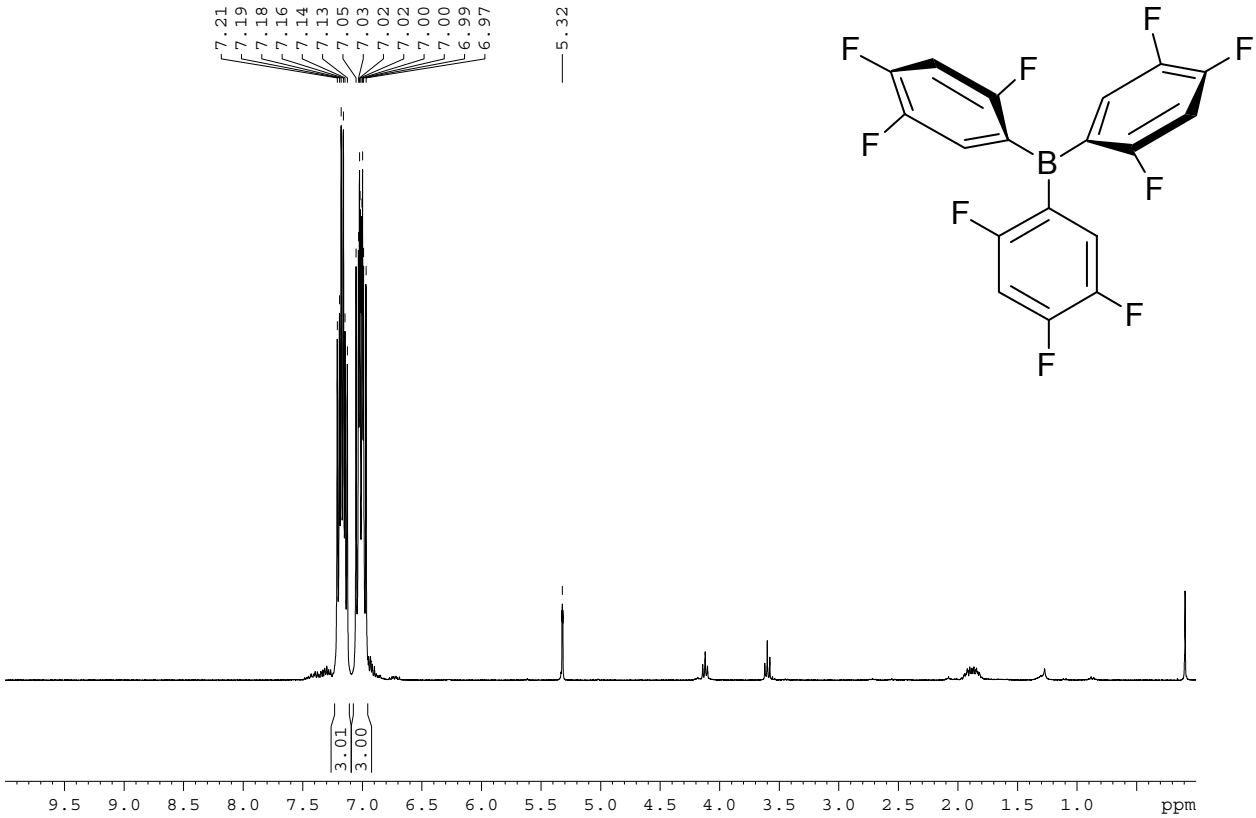
^{19}F NMR (75 MHz, CD_2Cl_2)



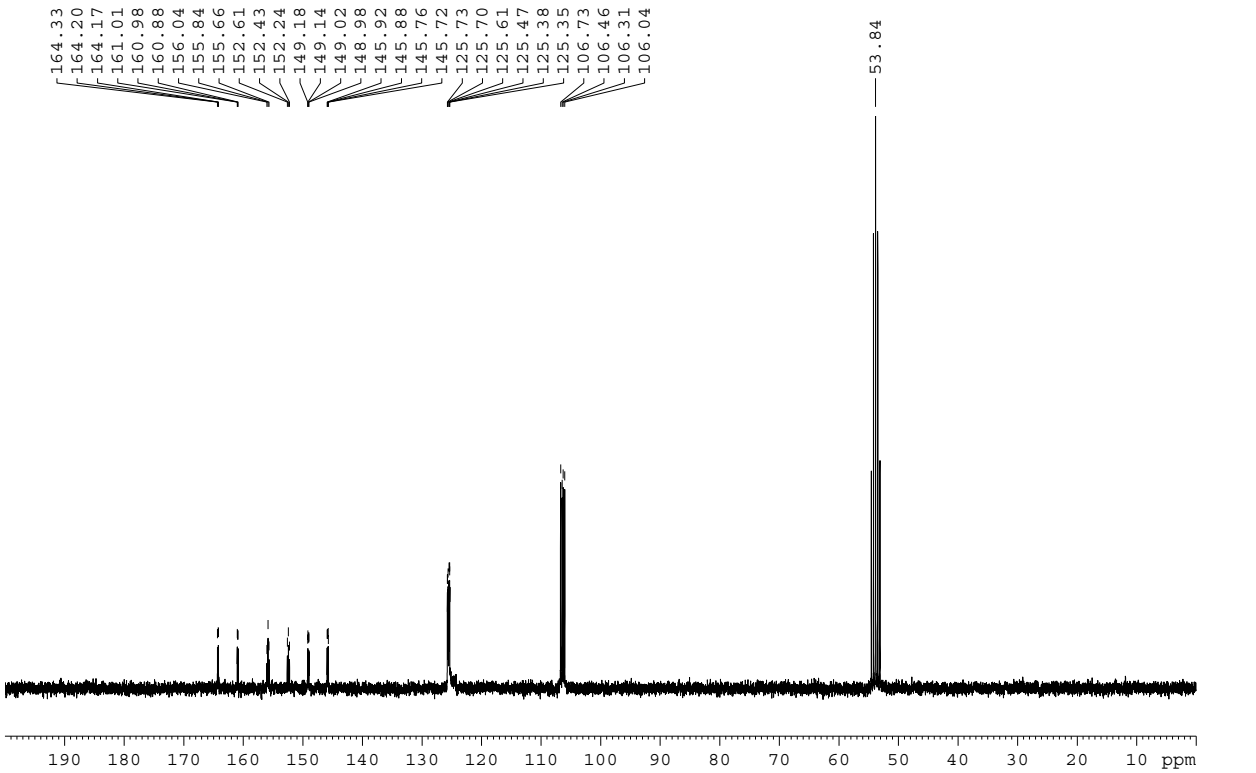
^{11}B NMR (96 MHz, CD_2Cl_2)



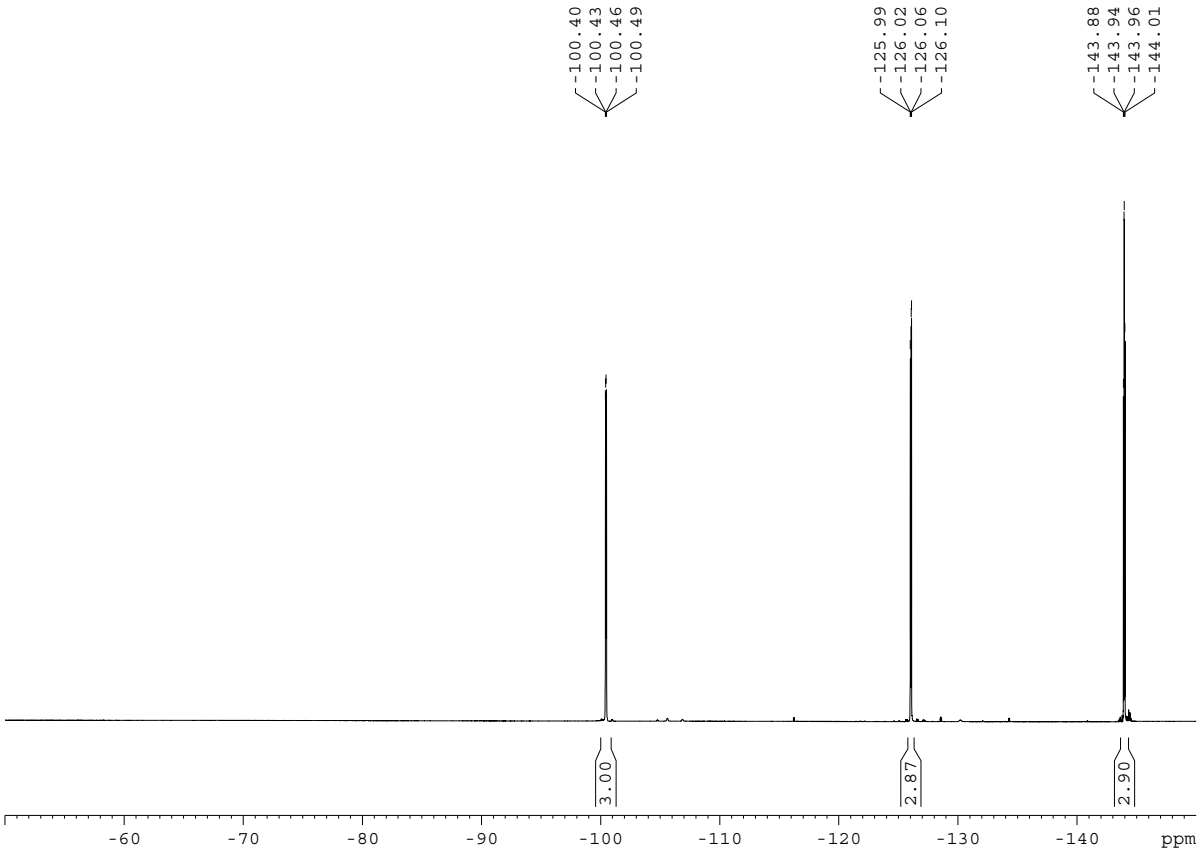
^{1}H NMR (300 MHz, CD_2Cl_2)



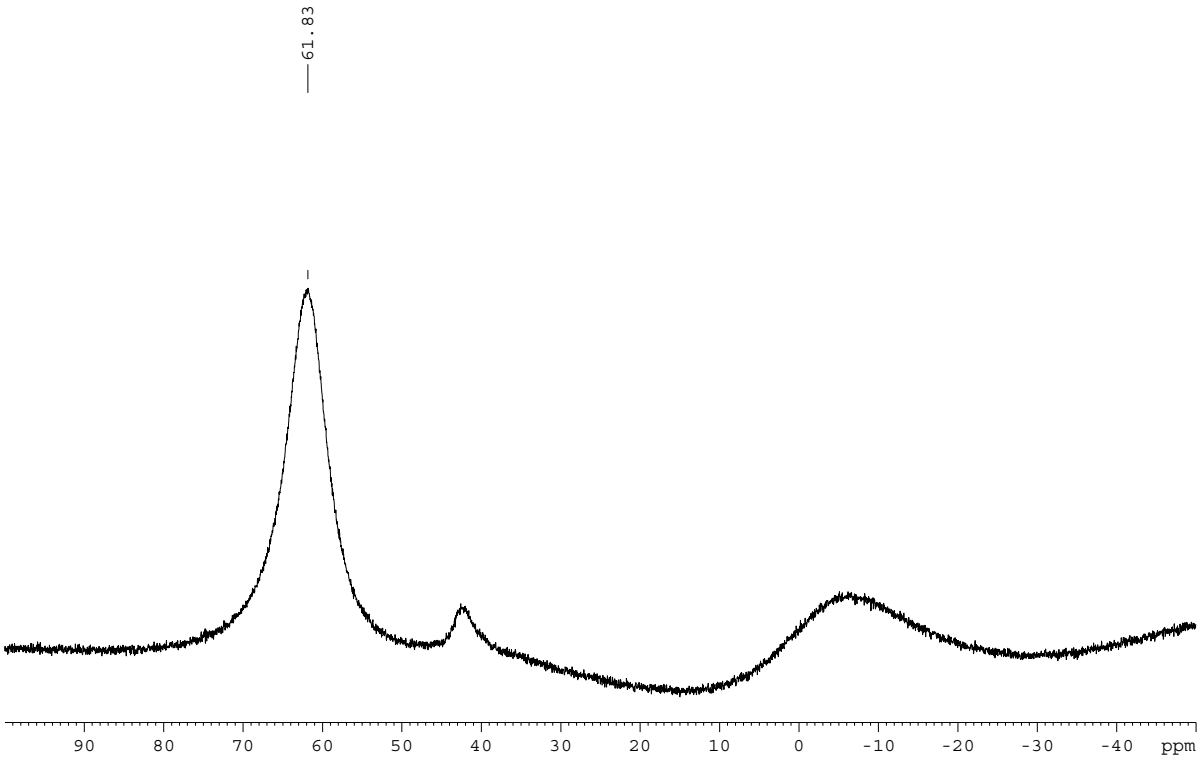
^{13}C NMR (75 MHz, CD_2Cl_2)



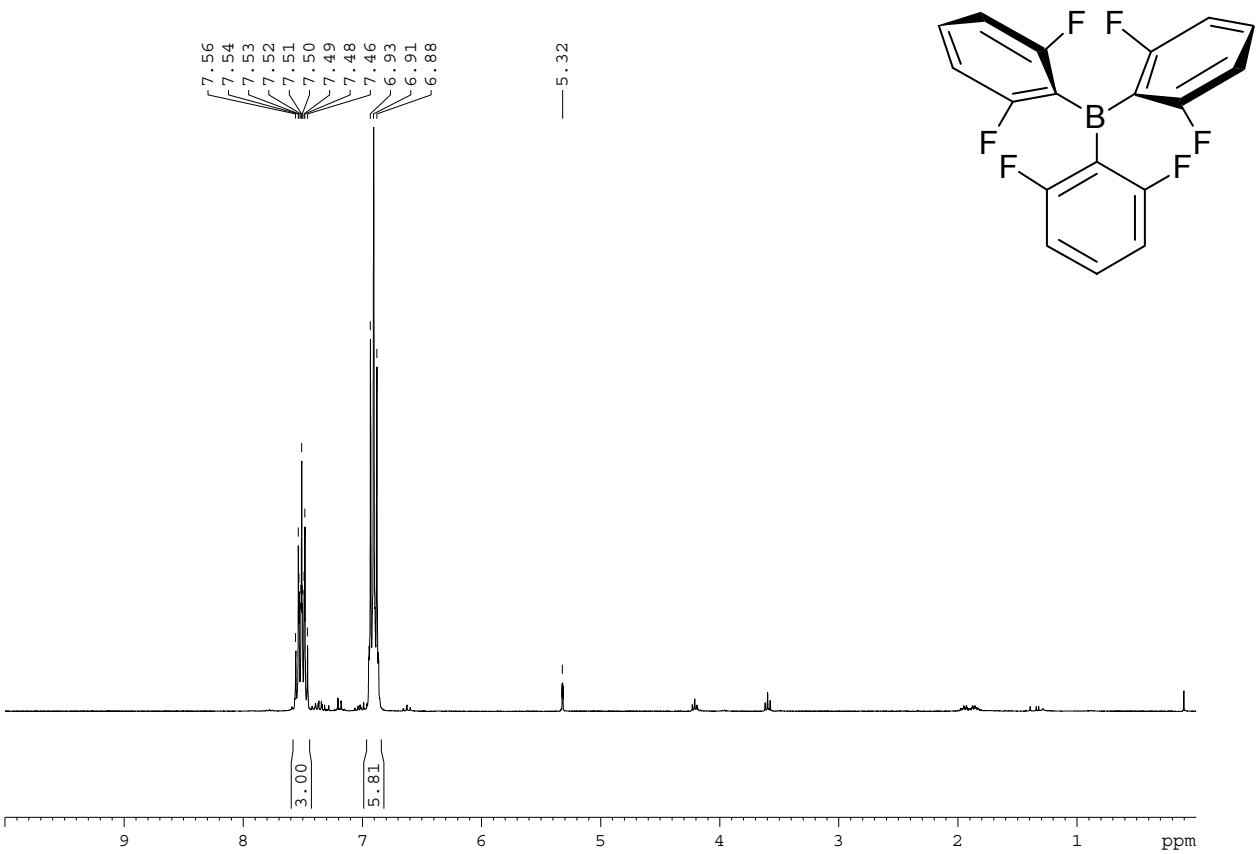
^{19}F NMR (75 MHz, CD_2Cl_2)



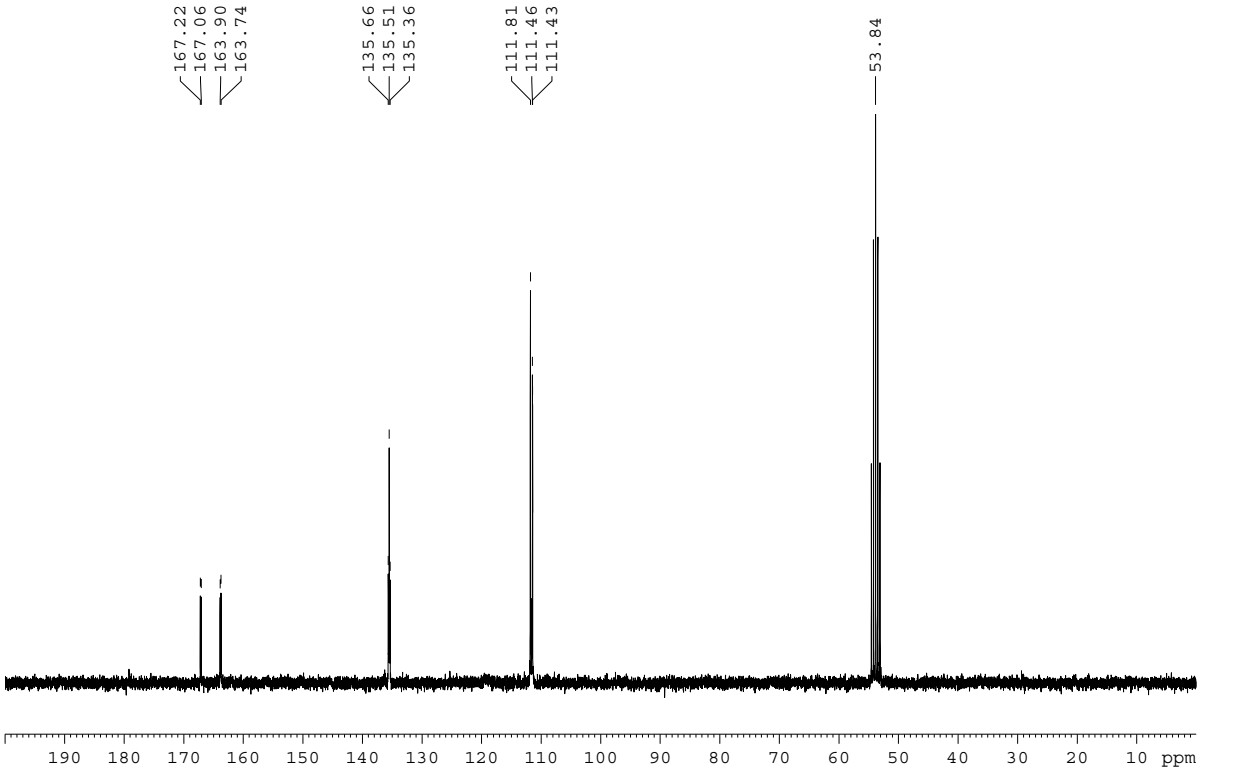
^{11}B NMR (96 MHz, CD_2Cl_2)



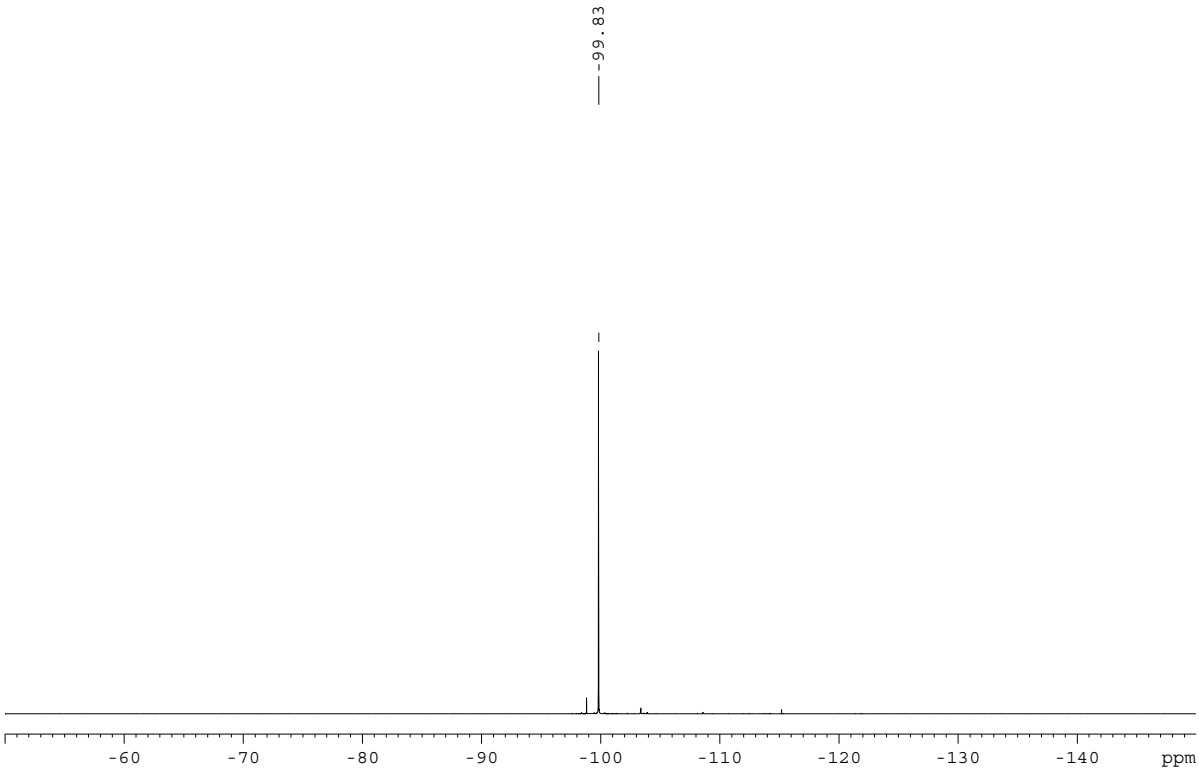
^{1}H NMR (300 MHz, CD_2Cl_2)



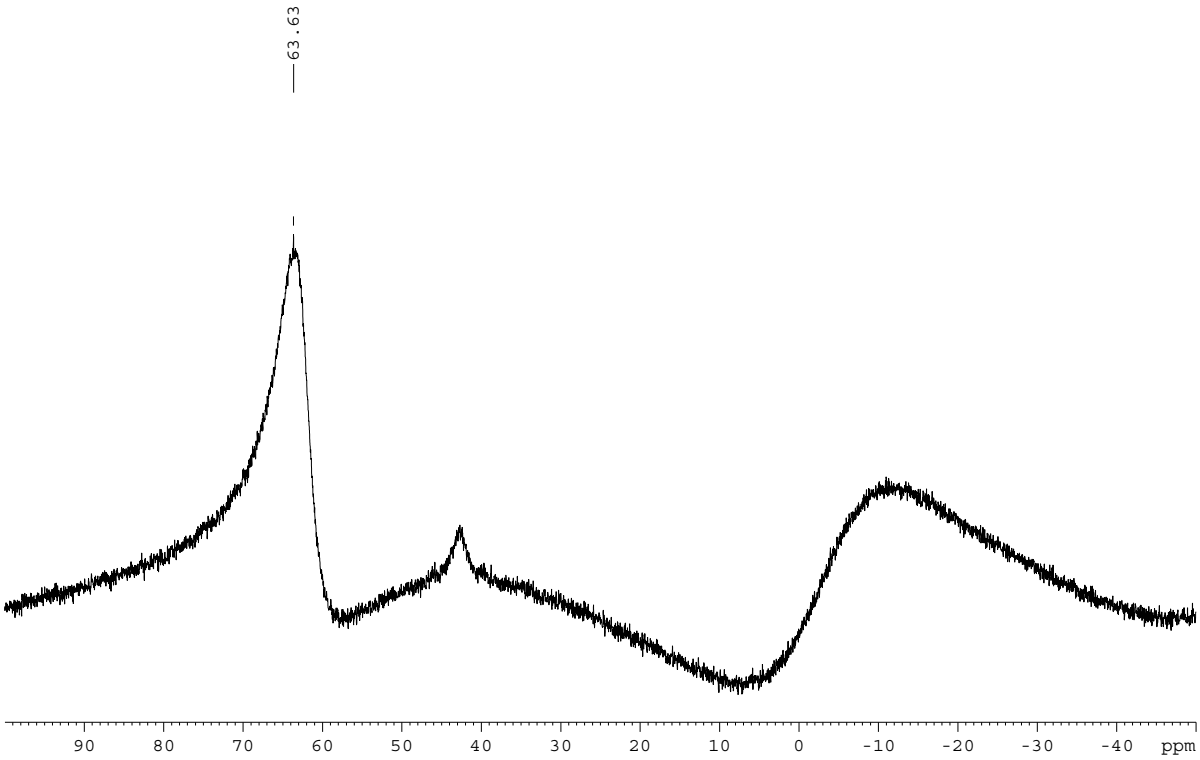
^{13}C NMR (75 MHz, CD_2Cl_2)



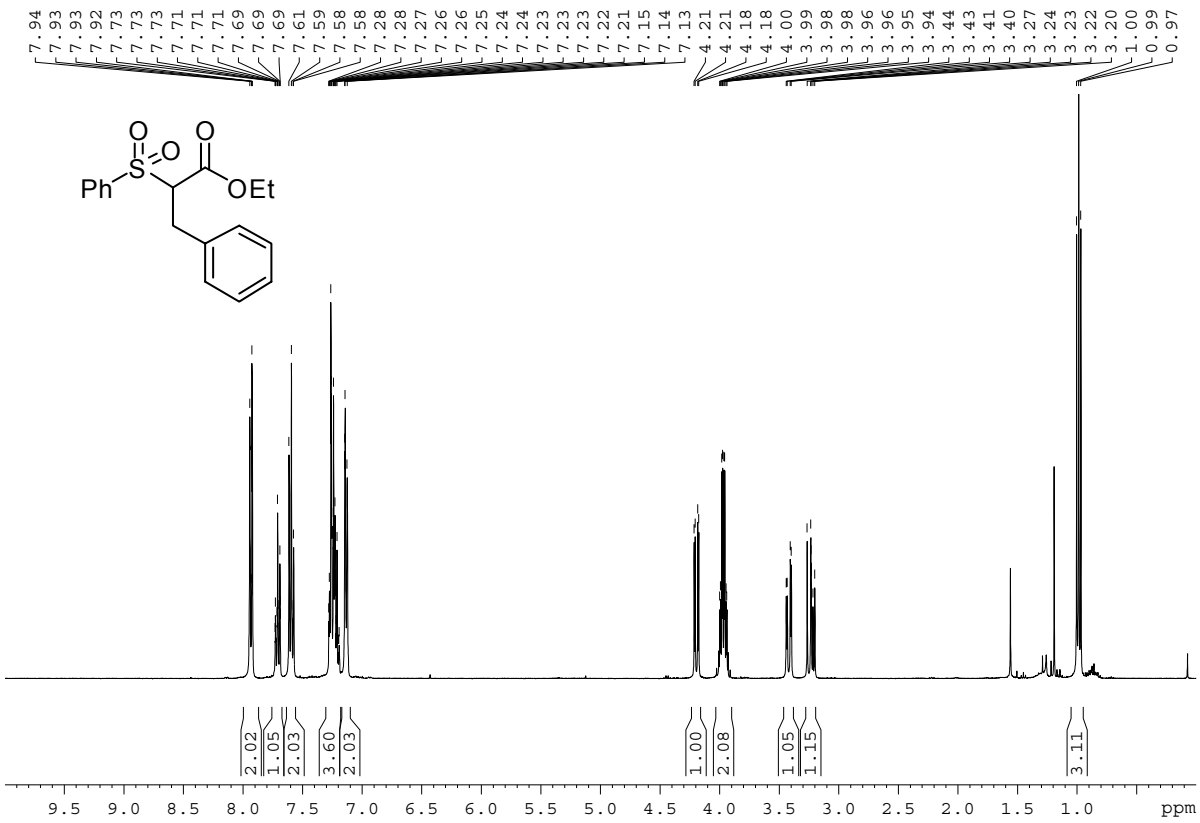
^{19}F NMR (75 MHz, CD_2Cl_2)



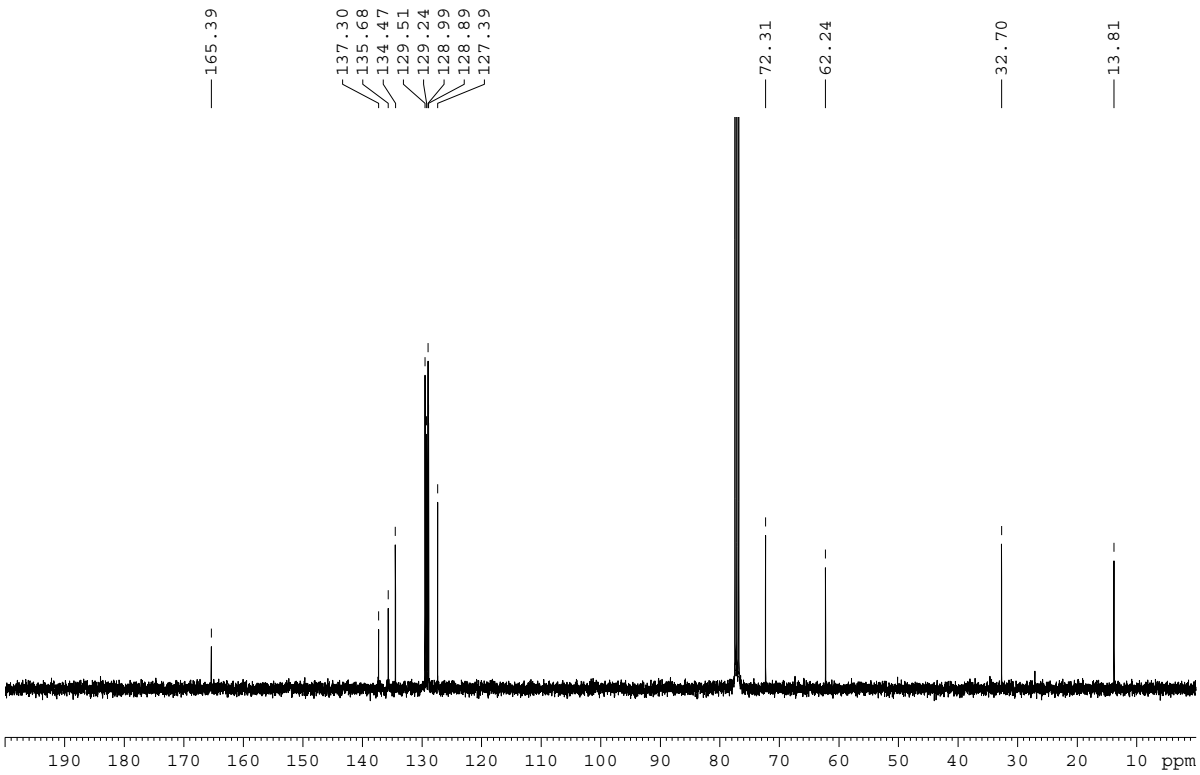
^{11}B NMR (96 MHz, CD_2Cl_2)



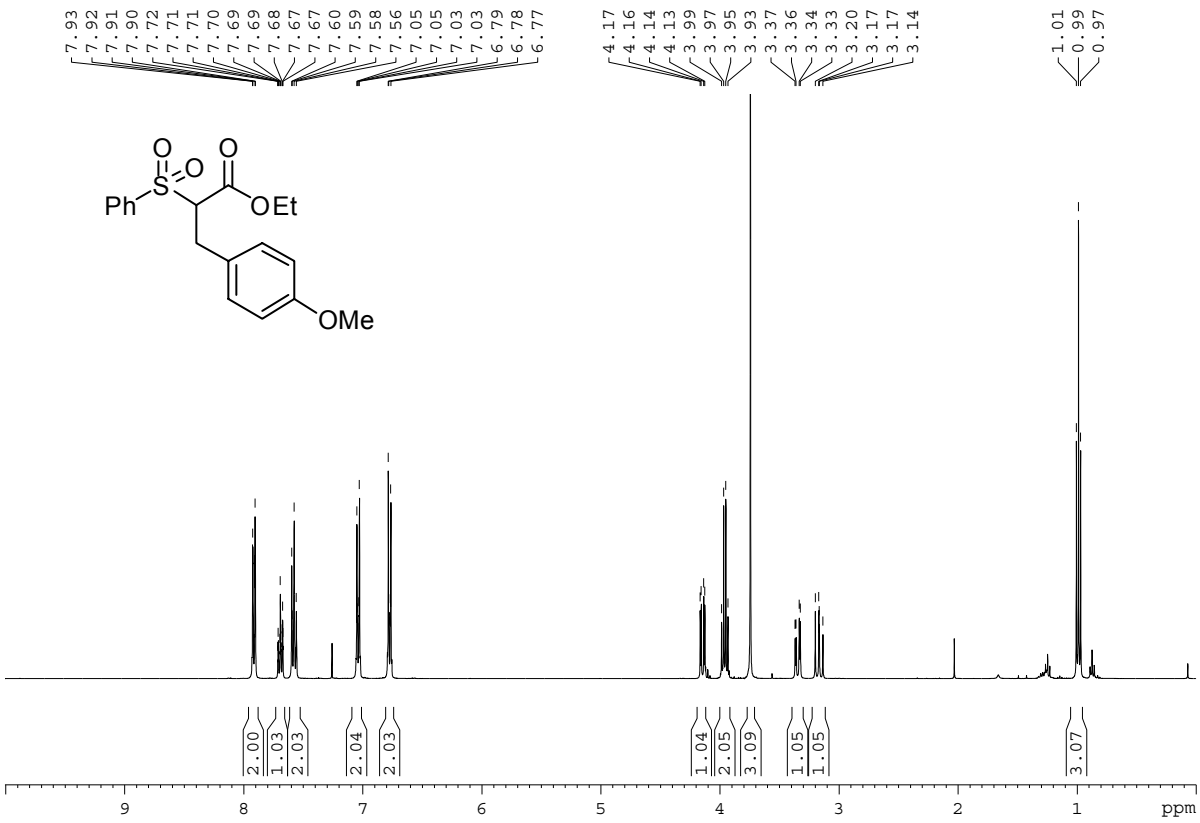
^{1}H NMR (400 MHz, $CDCl_3$)



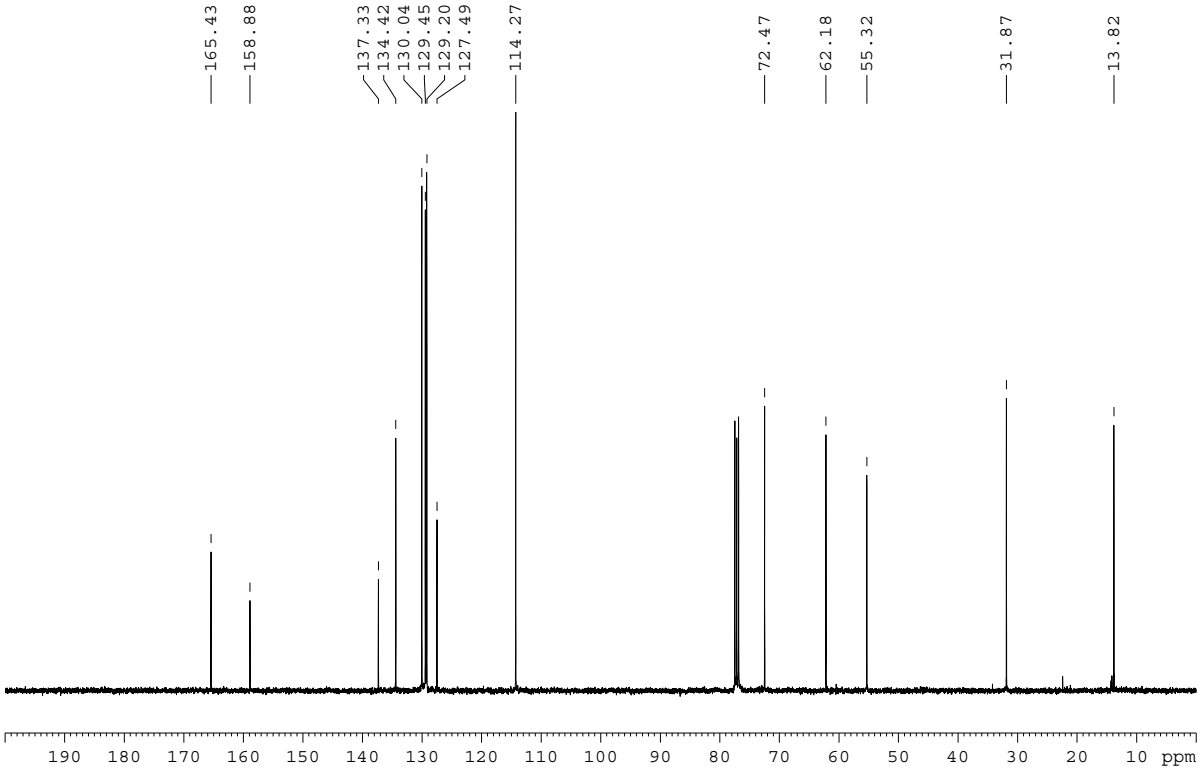
^{13}C NMR (101 MHz, $CDCl_3$)



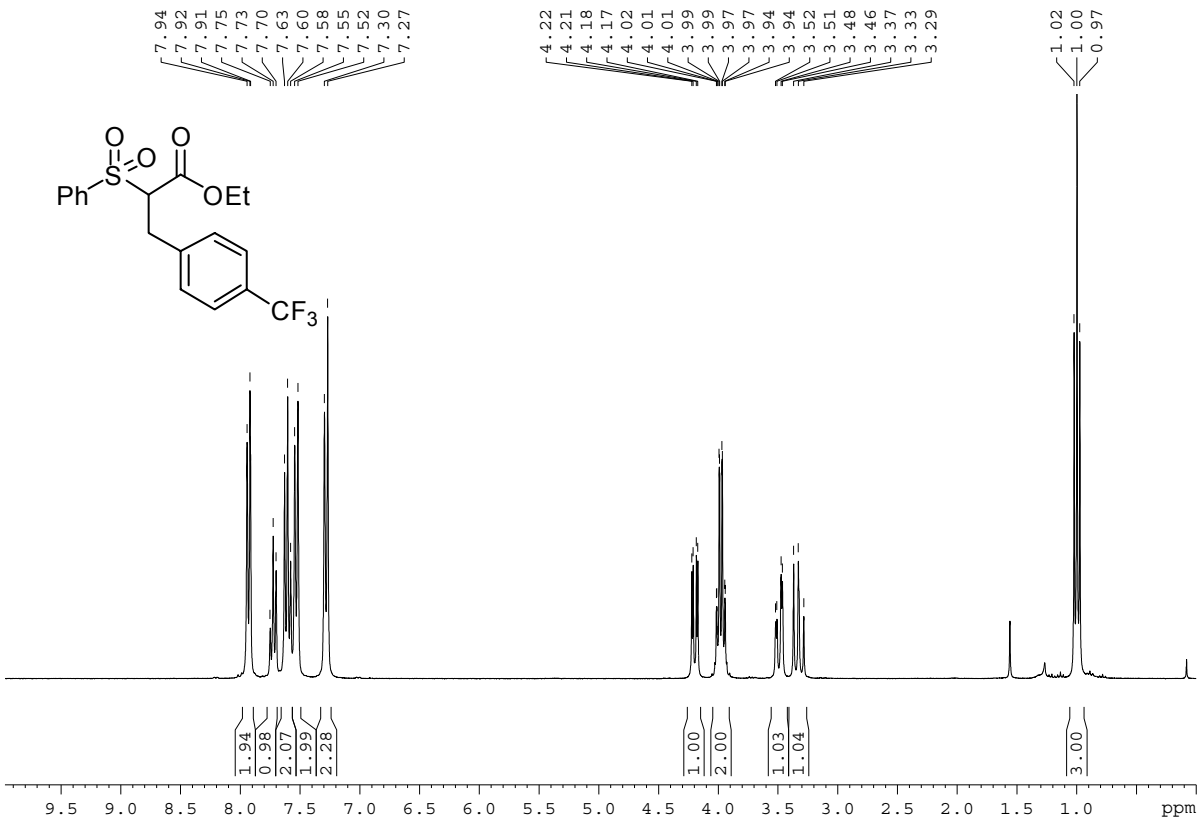
^{1}H NMR (400 MHz, $CDCl_3$)



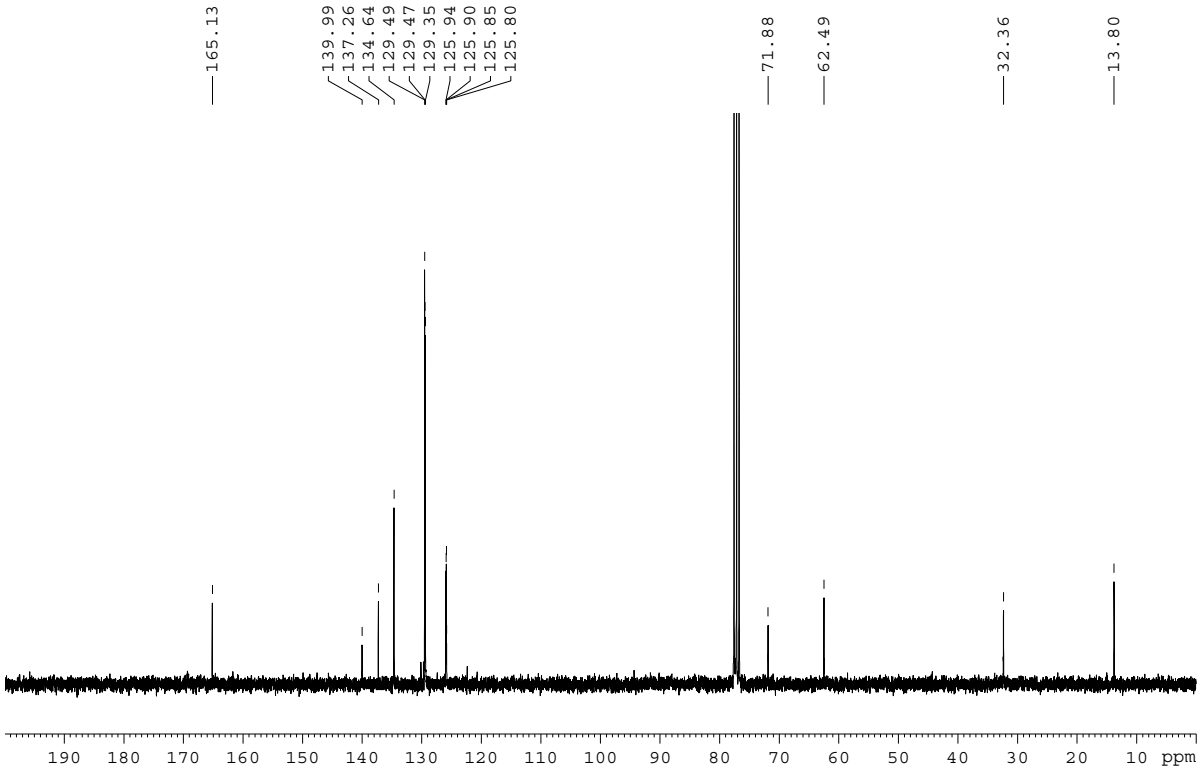
^{13}C NMR (101 MHz, $CDCl_3$)



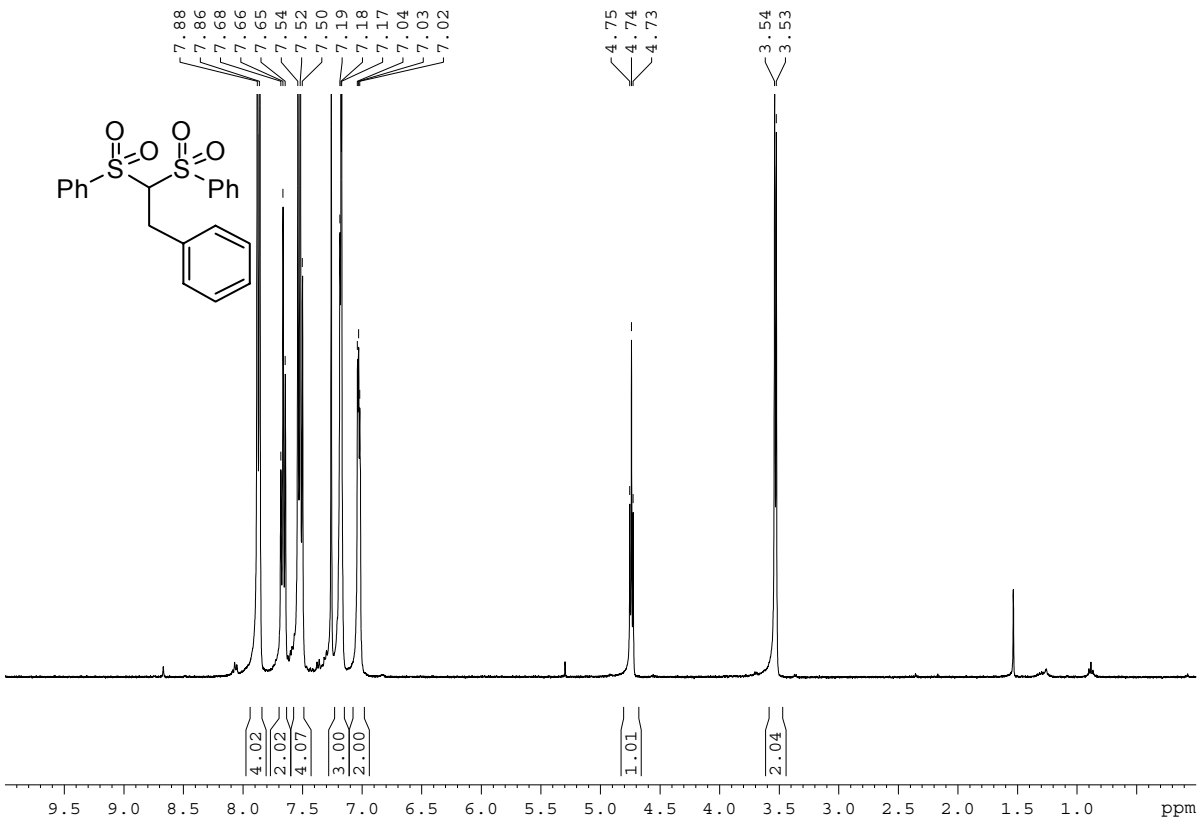
^{1}H NMR (300 MHz, $CDCl_3$)



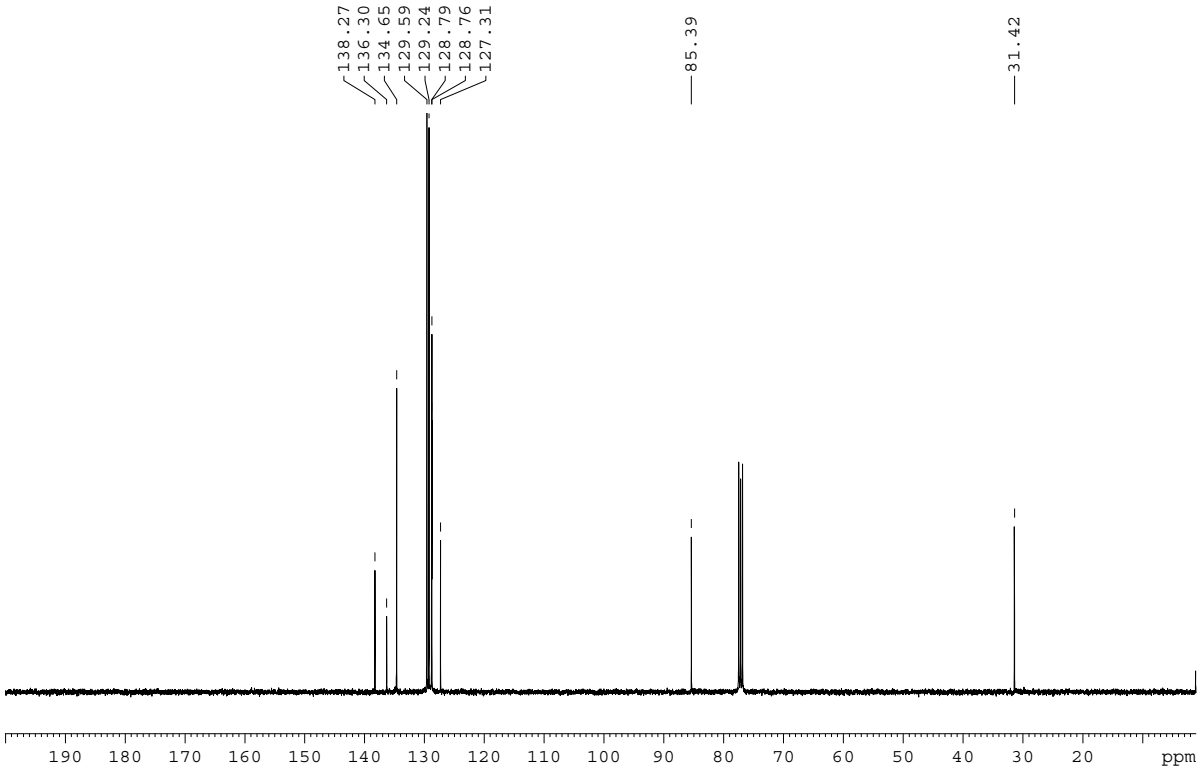
^{13}C NMR (75 MHz, $CDCl_3$)



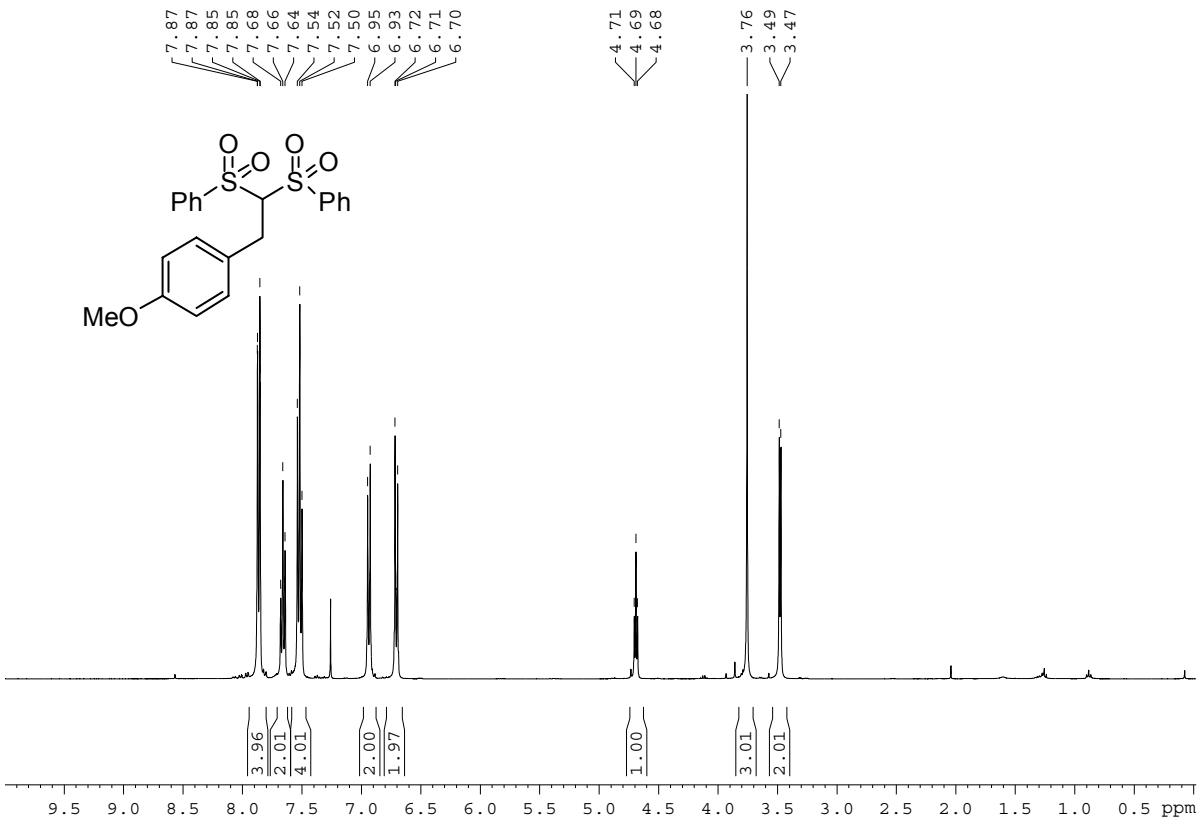
^{1}H NMR (400 MHz, $CDCl_3$)



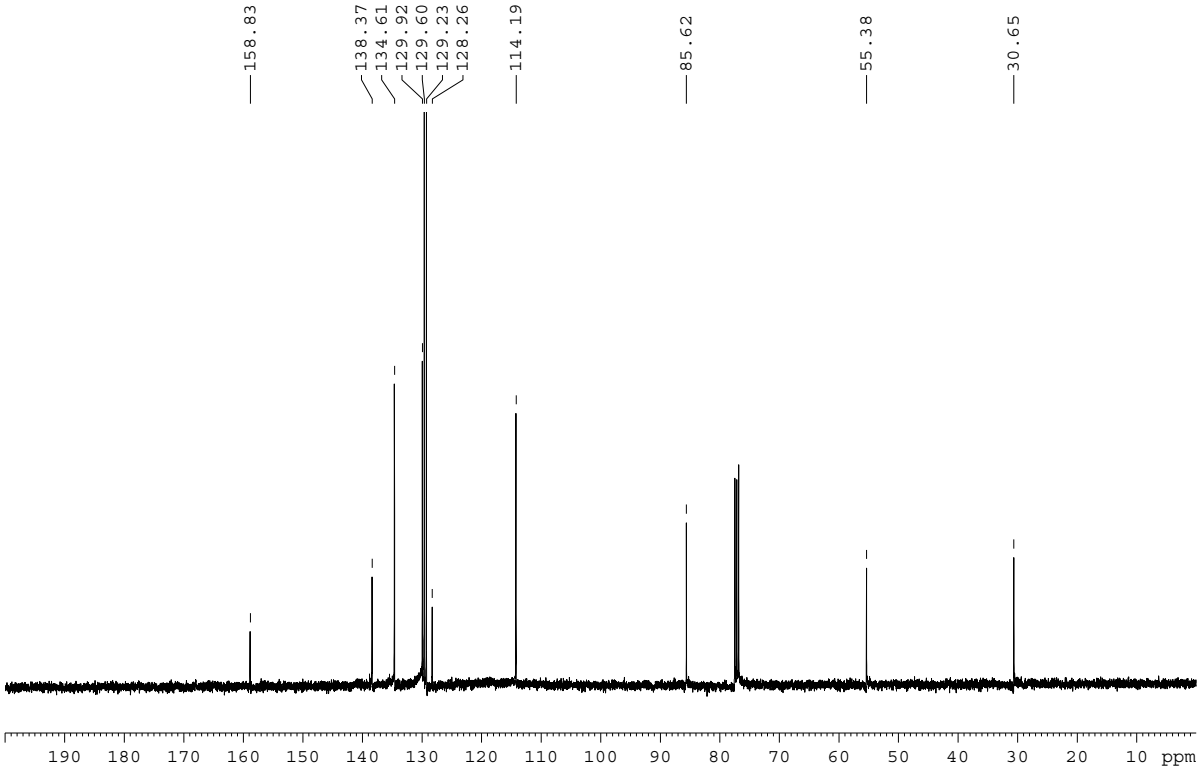
^{13}C NMR (101 MHz, $CDCl_3$)



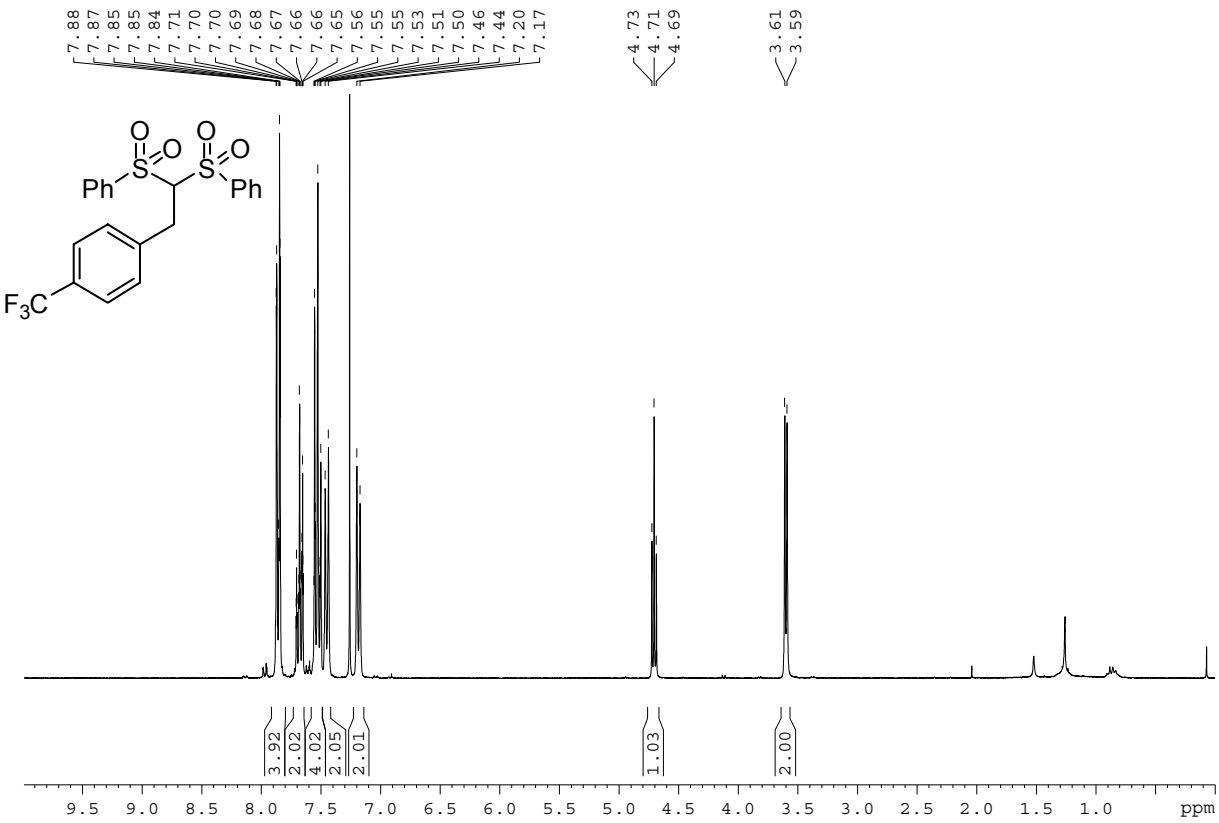
^{1}H NMR (400 MHz, $CDCl_3$)



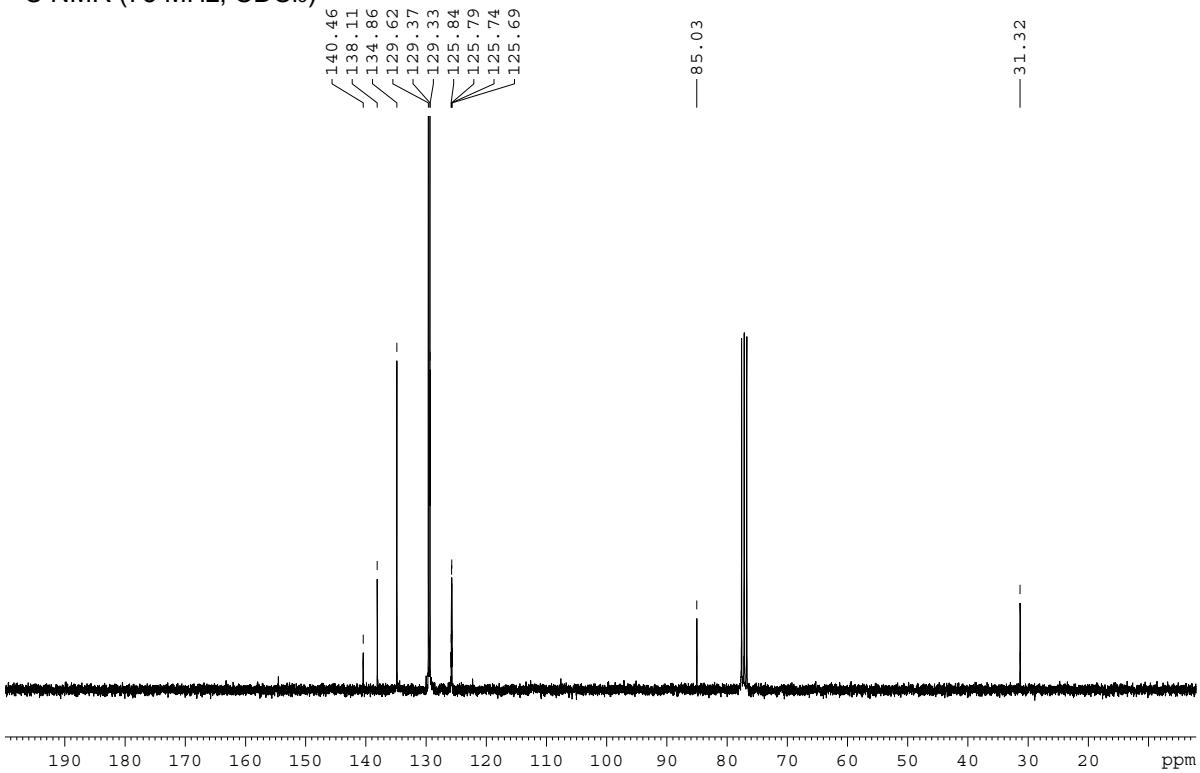
^{13}C NMR (101 MHz, $CDCl_3$)



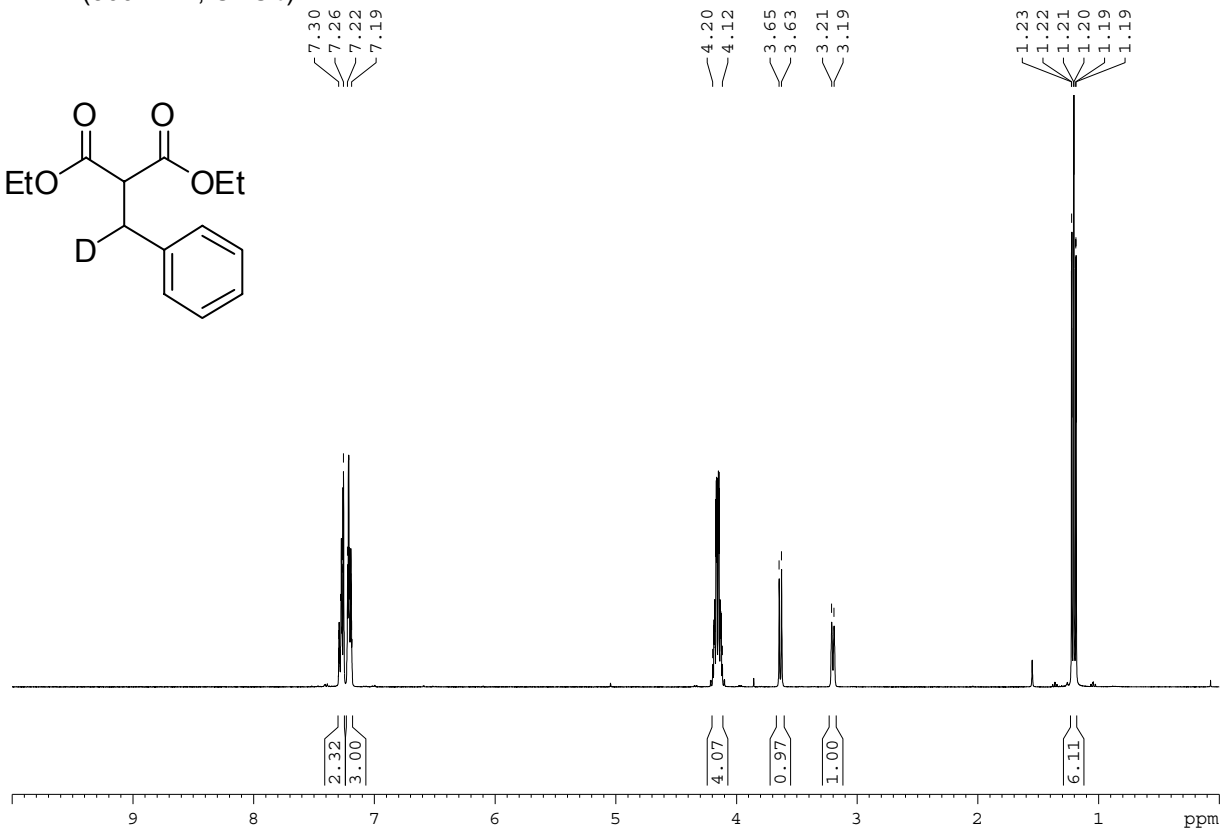
^{1}H NMR (300 MHz, $CDCl_3$)



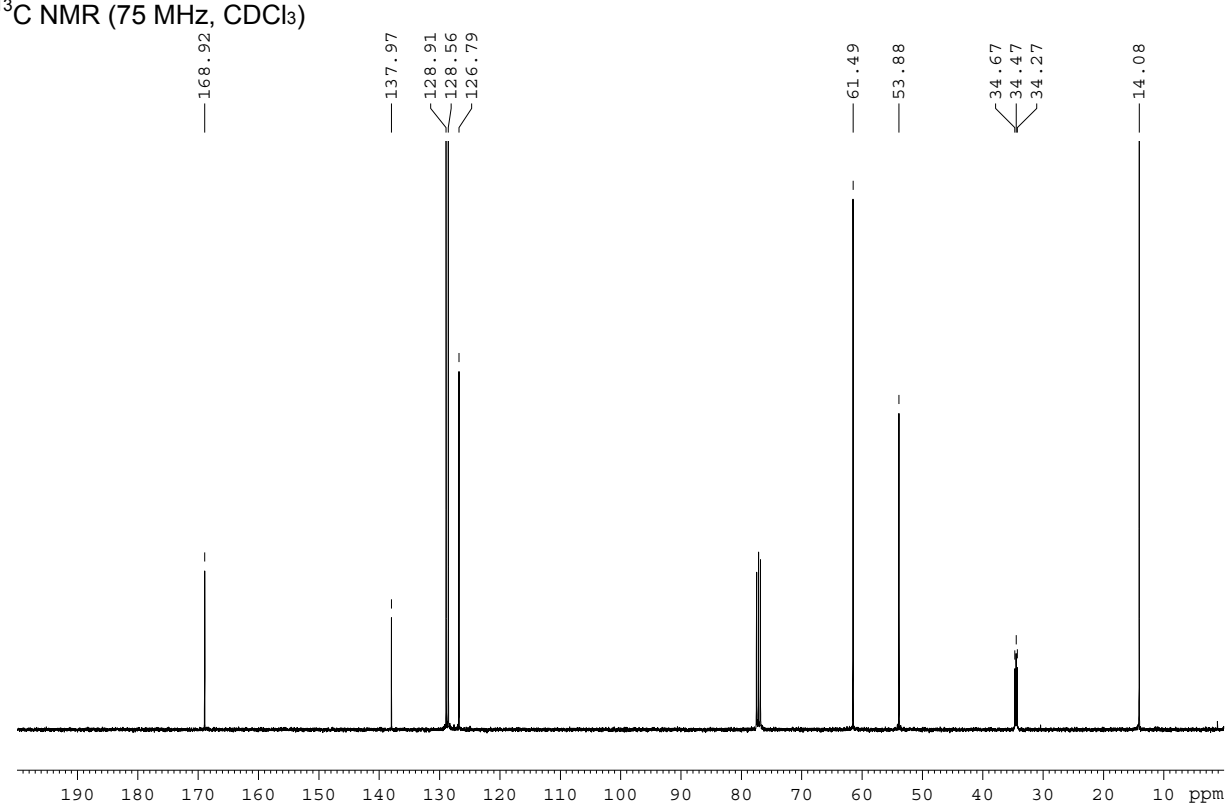
^{13}C NMR (75 MHz, $CDCl_3$)



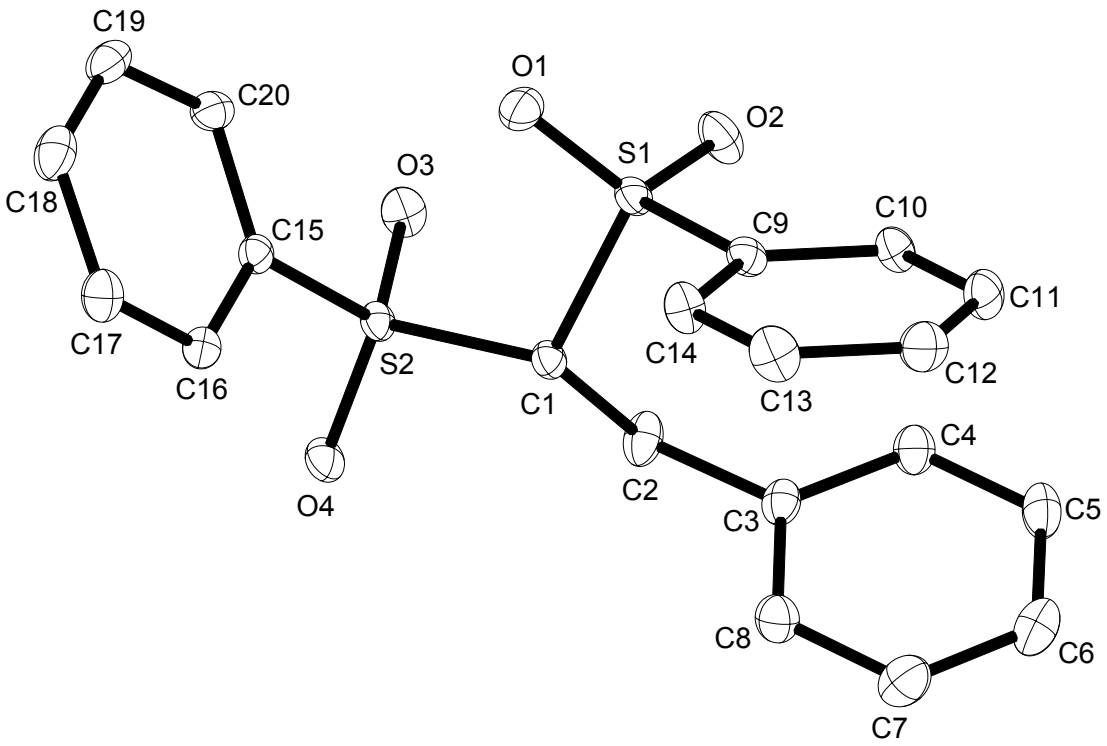
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

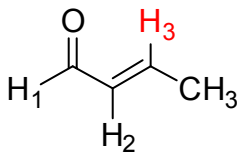


X-Ray Analysis:



Empirical formula	$C_{20}H_{18}O_4S_2$	
Colour	colourless	
Formula weight	386.46 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	p 2_1/c, (no. 14)	
Unit cell dimensions	a = 8.0772 (5) Å	α= 90°.
	b = 20.4379(12) Å	β= 95.577(5)°.
	c = 10.9593 (8) Å	γ = 90°.
Volume	1800.6(2) Å^3	
Z	4	
Density (calculated)	1.426 Mg · m^{-3}	
Absorption coefficient	0.319 mm^{-1}	
F(000)	808 e	
Crystal size	0.47 x 0.11 x 0.08 mm^3	
θ range for data collection	2.73 to 33.09°.	
Index ranges	$-12 \le h \le 12$, $-31 \le k \le 31$, $-16 \le l \le 16$	
Reflections collected	37122	
Independent reflections	6831 [R_{int} = 0.0379]	
Reflections with I>2σ(I)	5533	
Completeness to θ = 27.50°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.97556 and 0.90249	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6831 / 0 / 235	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2σ(I)]	R_1 = 0.0380	w R^2 = 0.0976
R indices (all data)	R_1 = 0.0527	w R^2 = 0.1048
Largest diff. peak and hole	0.911 and -0.655 e · Å^{-3}	

Assessment of the relative Lewis acidity by Childs' method:



Lewis acid	Proton Δδ (ppm)[a]				Relative Acidity (%)
	H_1	H_2	H_3	H_4	
3	-0,60	0,70	0,94	0,33	100
4	-0,52	0,55	0,66	0,23	70
5	-0,51	0,57	0,69	0,24	73
7	-0,50	0,60	0,63	0,23	67
6	-0,41	0,48	0,53	0,18	56

[a] Chemical shifts were determined in CD_2Cl_2, (0.1 M).