Practical Radical Cyclizations with Arylboronic Acids and Trifluoroborates

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Supporting Information

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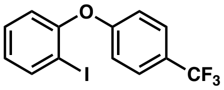
General Experimental

All reactions were carried out under an air atmosphere, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous material, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica plates (60F-254), using ultra violet (UV) light as the visualizing agent and potassium permanganate ($KMnO_4$) as a developing agent. Flash silica gel chromatography was performed using E. Merck silica gel (60, particle size

0.043–0.063 mm). Nuclear magnetic resonance (NMR) spectra were recorded on Bruker DRX-600, DRX-500, AV-400, and Varian INOVA-399 instruments and were calibrated using residual undeuterated solvent as an internal reference ($CHCl_3$ @ 7.26 ppm for ^1H NMR, 77.16 ppm for ^{13}C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. For boron-containing compounds, the carbon attached to boron is generally not observed in ^{13}C NMR spectra due to quadrupolar relaxation. High resolution mass spectra (HRMS) were recorded on an Agilent LC/MSD TOF mass spectrometer by electrospray ionization time of flight reflectron experiments. Infra red (IR) experiments were recorded on a Perkin Elmer Spectrum BX FTIR spectrometer. Melting points were recorded on a Fisher–Johns 12-144 melting point apparatus and are uncorrected.

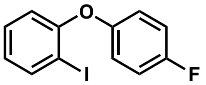
General Method for Chan–Evans–Lam coupling

A mixture of 2-iodophenol (220 mg, 1 mmol, 1 equiv), arylboronic acid (1.5 mmol, 1.5 equiv), anhydrous $Cu(OAc)_2$ (218 mg, 1.2 mmol, 1.2 equiv), triethylamine (0.7 mL, 5 mmol, 5 equiv), pyridine (0.81 mL, 5 mmol, 5 equiv) and powdered 4 Å molecular sieves (100 mg) in anhydrous CH_2Cl_2 (10 mL) was stirred at room temperature for 48 h. The reaction contents were filtered through a plug of silica gel and the filtrate was concentrated in vacuo. Purification by silica gel chromatography (9:1 hexanes/EtOAc) afforded chromatographically and spectroscopically pure product.



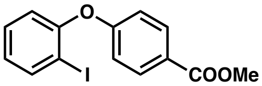
1-Iodo-2-(4-(trifluoromethyl)phenoxy)benzene (S1)

Using 2-iodophenol and 4-(trifluoromethyl)phenylboronic acid in a Chan–Evans–Lam coupling as described above, the title compound was obtained (90%) as a colorless oil; IR (neat) ν_{max} 3064, 1616, 1512, 1464, 1324, 1239, 1166, 1122, 1065, 1013, 837, 768, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.9 Hz, 1.4 Hz, 1 H), 7.59 (d, *J* = 8.6 Hz, 2 H), 7.39 – 7.35 (m, 1 H), 7.03 – 6.97 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 155.2, 140.4, 130.1, 127.4 (q, J_{CF} = 3.8 Hz), 126.8, 121.2, 117.4, 89.9; quartet from CF_3 and the quaternary carbon were not observed; HRMS (ESI-TOF) calcd. for $C_{13}H_8F_3IOH^+$ [M + H$^+$] 362.9499, found 362.9485.



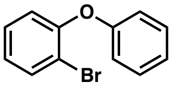
1-(4-Fluorophenoxy)-2-iodobenzene (S2)

Using 2-iodophenol and 4-fluorophenylboronic acid in a Chan−Evans−Lam coupling as described above, the title compound was obtained (83%) as a colorless oil; IR (neat) ν_{max} 3063, 1498, 1464, 1438, 1215, 1190, 1019, 847, 832, 816, 775, 749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 7.9 Hz, 1.4 Hz, 1 H), 7.64 – 7.62 (m, 1 H), 7.38 (m, *J* = 8.6 Hz, 2 H), 7.29 (m, *J* = 9.2, 4.5 Hz, 2 H), 7.21 – 7.16 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 157.4 (d, J_{CF} = 92.1 Hz), 152.8 (d, J_{CF} = 2.7 Hz), 140.1, 129.9, 125.5, 120.2 (d, J_{CF} = 8.2 Hz), 118.9, 116.6 (d, J_{CF} = 23.4 Hz), 88.6; Did not ionize in HRMS (ESI-TOF); GC/MS, M$^+$ 314.



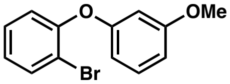
Methyl 4-(2-iodophenoxy)benzoate (S3)

Using 2-iodophenol and 4-(methoxycarbonyl)phenylboronic acid in a Chan−Evans−Lam coupling as described above, the title compound was obtained (71%) as a colorless oil; IR (neat) ν_{max} 2997, 2949, 1717, 1605, 1503, 1464, 1435, 1279, 1237, 1162, 1110, 1019, 766, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.9 Hz, 2 H), 7.89 (d, *J* = 7.9 Hz, 1 H), 7.36 (td, *J* = 7.7 Hz, 0.6 Hz, 1 H), 7.03 (d, *J* = 8.1 Hz, 1 H), 6.98 – 6.92 (m, 3H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 161.2, 155.2, 140.3, 131.9, 130.1, 126.8, 124.9, 121.4, 117.0, 90.0, 52.2; HRMS (ESI-TOF) calcd. for $C_{14}H_{11}IO_3H^+$ [M + H$^+$] 354.9826, found 354.98635.



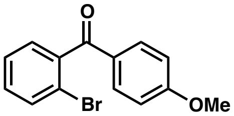
1-Bromo-2-phenoxybenzene (S4)

To a suspension of NaO*t*Bu (1.06 g, 11 mmol, 1.1 equiv) in THF (36 mL) was added 2-bromophenol (1.16 mL, 10 mmol, 1.0 equiv) at 0 °C. The reaction mixture was stirred at 0 °C for 15 min, and diphenyliodonium trifluoromethanesulfonate (5.16 g, 12 mmol, 1.2 equiv) was added in one portion. The reaction mixture was stirred at 40 °C for 3 h. The reaction mixture was quenched with H_2O at 0 °C, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by silica gel chromatography (9:1 hexanes/EtOAc) afforded the title compound (33%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.0 Hz, 1.6 Hz, 1 H), 7.33 – 7.29 (m, 2 H), 7.25 – 7.21 (m, 1 H), 7.10 – 7.06 (m, 1 H), 6.99 (td, *J* = 7.7 Hz, 1.5 Hz, 1 H), 6.95 – 6.92 (m, 3 H). See: Hu, J.; Koehmainen, E.; Knuutinen, J. *Magn. Reson. Chem.* **2000**, *38*, 375–378.



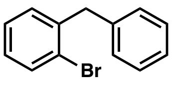
1-Bromo-2-(3-methoxyphenoxy)benzene (S5)

A mixture of copper(I) iodide (210 mg, 1.1 mmol, 0.1 equiv), Cs_2CO_3 (5.40 g, 16.5 mmol, 1.5 equiv), 3-methoxyphenol (1.64 g, 13.2 mmol, 1.2 equiv), 1,2-dibromobenzene (2.59 g, 11 mmol, 1.0 equiv), and *N*,*N*-dimethylglycine (340 mg, 3.3 mmol, 0.3 equiv) in anhydrous 1,4-dioxane (44 mL) under an argon balloon was stirred at room temperature for 30 min and then at 115 °C overnight. The reaction mixture was cooled to room temperature, filtered through Celite, and the filtrate was concentrated in vacuo. Purification by silica gel chromatography (9:1 hexanes/EtOAc) afforded the title compound (30%) as a colorless oil; R_f = 0.67 (4:1 hexanes/EtOAc); IR (neat) ν_{max} 1604, 1594, 1578, 1486, 1468, 1261, 1226, 1135, 1044, 951, 844, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.61 (m, 1 H), 7.29 – 7.20 (m, 2 H), 7.04 – 6.99 (m, 2 H), 6.67 – 6.64 (m, 1 H), 6.55 – 6.51 (m, 2 H), 3.78 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.1, 158.2, 153.6, 133.6, 130.3, 128.8, 125.3, 121.1, 110.2, 109.1, 104.3, 55.5; HRMS (ESI-TOF) calcd. for $C_{13}H_{11}BrO_2H^+$ [M + H$^+$] 279.0015, found 279.0005.



(2-Bromophenyl)(4-methoxyphenyl)methanone (S6)

A solution of 2-bromobenzoyl chloride (0.52 mL, 878 mg, 4 mmol) in $CHCl_3$ (1.03 mL) was added at –15 °C to anhydrous aluminum chloride (572 mg, 1.04 mol) in $CHCl_3$ (1.44 mL) and the resulting mixture stirred for 15 min at room temperature. Anisole (0.52 mL, 519 mg, 4.8 mmol, 1.2 equiv) in $CHCl_3$ (0.4 mL) was then added dropwise, and the mixture was stirred at room temperature for 12 h. The reaction mixture was quenched with 2 N aqueous HCl (1 mL), the layers were separated, and the aqueous layer was extracted with $CHCl_3$ (3 × 2 mL). The organic layers were combined, washed with 2 N aqueous HCl (3 × 1 mL), saturated aqueous $NaHCO_3$ (2 × 1 mL), brine (2 × 1 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was recrystallized from MeOH to afford the title compound (880 mg, 76%) as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.8 Hz, 2 H), 7.63 (d, *J* = 7.6 Hz, 1 H), 7.43 – 7.39 (m, 1 H), 7.35 – 7.31 (m, 2 H), 6.94 (d, *J* = 8.8 Hz, 2 H), 3.87 (s, 3 H). See: Moorthy, J. N.; Samanta, S. *J. Org. Chem.* **2007**, *72*, 9786–9789.



1-Benzyl-2-bromobenzene (S7)

A solution of 2-bromobenzylbromide (250 mg, 1.22 mmol) in benzene (3 mL) was treated with $AlCl_3$ in THF (0.05 ml, 0.5 M) under argon balloon. The solution was refluxed for 5 h. The reaction mixture was extracted with Et_2O (10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by silica gel chromatography (100% hexanes) afforded the title compound (200 mg, 81%) as a colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.30 (t, *J* = 7.2 Hz, 2 H), 7.24 – 7.19 (m, 4 H), 7.14 (dd, *J* = 7.7, 1.7 Hz, 1 H), 7.08 (td, *J* = 7.6, 1.7 Hz, 1 H), 4.13 (s, 2 H). See: Odedra, A.; Datta, S.; Liu, R.-S. *J. Org. Chem.* **2007,** *72*, 3289–3292.

General Methods for 1,2-addition followed by oxidation

Method A (iodoarenes)

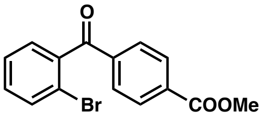
A solution of iodoarene (1 mmol) in THF (10 mL) at –40 °C was treated with *i*PrMgCl (2.3 M, 1.05 mmol, 1.05 equiv) in Et_2O. After 1 h at –40 °C, 2-bromobenzaldehyde (1.05 mmol, 1.05 equiv) was added. After stirring for 3 h, the reaction mixture was diluted with saturated aqueous NH_4Cl (15 mL) and EtOAc (30 mL). The layers were separated, and the aqueous layer was extracted with EtOAc. The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by silica gel chromatography (100% hexanes → 4:1 hexanes/EtOAc) afforded the benzylic alcohol. This intermediate was dissolved in CH_2Cl_2 (4 mL) and treated with MnO_2 (10.0 mmol, 10 equiv). The reaction mixture was stirred at room temperature overnight, filtered through Celite, and concentrated in vacuo. Purification by silica gel chromatography (100% hexanes → 4:1 hexanes/EtOAc) afforded chromatographically and spectroscopically pure product.

Method B (bromoarenes)

A solution of bromoarene (1 mmol) in THF (2.5 mL) at 0 °C was treated with *i*PrMgCl•LiCl (1.0 mL, 1 mmol, 1.0 M, 1 equiv) in THF dropwise. The reaction mixture was stirred at 0 °C for 2−3 h, then treated with a solution of 2-bromobenzaldehyde (0.9 mmol, 0.9 equiv) in THF (0.5 mL). The ice bath was removed and the reaction mixture was stirred at room temperature for 2 h. The reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by silica gel chromatography (100% hexanes → 4:1 hexanes/EtOAc) afforded the benzylic alcohol. This intermediate was dissolved in CH_2Cl_2 (4 mL) and treated with MnO_2 (10.0 mmol, 10 equiv). The reaction mixture was stirred at room temperature overnight, filtered through Celite, and concentrated in vacuo. Purification by silica gel chromatography (100% hexanes → 4:1 hexanes/EtOAc) afforded chromatographically and spectroscopically pure product.

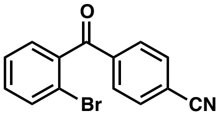
Method C (fluoroarenes)

A solution of fluoroarene (1 mmol, 1.0 equiv) in THF (1 mL) at –78 °C was treated dropwise with *n*BuLi in hexanes (1.0 mmol, 1 equiv). The solution was stirred for 30 min, then treated with 2-bromobenzaldehyde (1.0 mmol) in THF (1 mL) at –78 °C. The solution was stirred at –78 °C for 30 min, then allowed to warm to 0 °C before quenching with saturated aqueous NH_4Cl. The mixture was extracted with EtOAc, washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by silica gel chromatography (100% hexanes → 4:1 hexanes/EtOAc) afforded the benzylic alcohol. This intermediate was dissolved in CH_2Cl_2 (4 mL) and treated with MnO_2 (10.0 mmol, 10 equiv). The mixture was stirred at room temperature overnight, filtered through Celite, and concentrated in vacuo. Purification by silica gel chromatography (100% hexanes → 4:1 hexanes/EtOAc) afforded chromatographically and spectroscopically pure product.



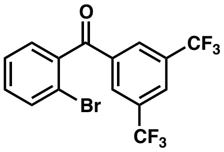
Methyl 4-(2-bromobenzoyl)benzoate (S8)

Method A. Yield: 85% as a white solid; m.p. 63 °C; IR (neat) ν_{max} 3057, 3001, 2952, 1720, 1674, 1434, 1271, 1245, 1104, 928, 764, 731 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.09 (d, *J* = 8.3 Hz, 2 H), 7.83 (d, *J* = 8.4 Hz, 2 H), 7.62 (d, *J* = 7.8 Hz, 1 H), 7.43 – 7.33 (m, 3 H), 3.91 (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.4, 166.3, 140.2, 139.6, 134.5, 133.5, 131.8, 130.1, 130.0, 129.4, 127.6, 119.7, 52.7; HRMS (ESI-TOF) calcd. for $C_{15}H_{11}BrO_3H^+$ [M + H$^+$] 318.9964, found 318.9976.



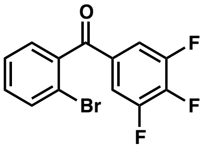
4-(2-Bromobenzoyl)benzonitrile (S9)

Method B. Yield: 60% as a white solid; m.p. 116 °C; IR (neat) ν_{max} 3063, 2924, 2231, 1676, 1588, 1429, 1310, 1283, 1249, 929, 855, 753, 677 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 (d, *J* = 8.3 Hz, 2 H), 7.76 (d, *J* = 8.3 Hz, 2 H), 7.66 (d, *J* = 7.8 Hz, 1 H), 7.48 – 7.35 (m, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 194.7, 139.6, 139.5, 133.6, 132.7, 132.2, 130.5, 129.5, 127.8, 119.7, 118.1, 117.0; HRMS (ESI-TOF) calcd. for $C_{14}H_8BrNOH^+$ [M + H$^+$] 285.9862, found 285.9861.



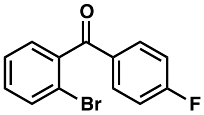
(3,5-Bis(trifluoromethyl)phenyl)(2-bromophenyl)methanone (S10)

Method B. Yield: 54% as a white solid; m.p. 68 °C; IR (neat) ν_{max} 1686, 1379, 1278, 1242, 1178, 1135, 911, 749, 681 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.24 (s, 2 H), 8.10 (s, 1 H), 7.70 (dd, *J* = 7.9, 1.1 Hz, 1 H), 7.52 – 7.39 (m, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 193.2, 138.8, 138.0, 133.8, 132.6 (q, J_{CF} = 34.2 Hz), 132.6, 130.1 – 129.9 (m), 129.6, 128.0, 126.8 (dt, J_{CF} = 7.4 Hz, 3.7 Hz), 123.0 (q, J_{CF} = 271.6 Hz), 119.7; HRMS (ESI-TOF) calcd. for $C_{15}H_7BrF_6OH^+$ [M + H$^+$] 396.9675, found 396.9660.



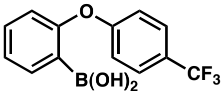
(2-Bromophenyl)(3,4,5-trifluorophenyl)methanone (S11)

Method C. Yield: 45% as a colorless oil; IR (neat) ν_{max} 3076, 1676, 1618, 1588, 1508, 1470, 1430, 1297, 1281, 1204, 1150, 1072, 1055, 1040, 1026, 876, 848, 822, 778, 753, 735, 679 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.63 (d, J = 7.9 Hz, 1 H), 7.57 – 7.51 (m, 1 H), 7.45 – 7.36 (m, 3 H), 7.09 (tdd, J = 8.9 Hz, 6.7 Hz, 2.1 Hz, 1 H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 191.5, 154.5 (ddd, J_{CF} = 258.8 Hz, 10.1 Hz, 3.2 Hz), 151.3 (dt, J_{CF} = 262.3 Hz, 10.8 Hz, 4.0 Hz) 141.6, 140.2 (dt, J_{CF} = 253.9, 15.3 Hz), 134.3, 133.1, 130.1, 128.5, 125.9 (ddd, J_{CF} = 13.3 Hz, 6.6 Hz, 2.4 Hz), 123.5 (ddd, J_{CF} = 7.7 Hz, 3.7 Hz, 1.7 Hz), 120.2, 112.8 (dd, J_{CF} = 17.8 Hz, 3.9 Hz); HRMS (ESI-TOF) calcd. for $C_{13}H_6BrF_3OH^+$ [M + H$^+$] 314.9627, found 314.9624.



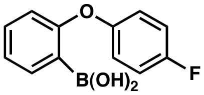
(2-Bromophenyl)(4-fluorophenyl)methanone (S12)

Method C. Yield: 68% as a colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.86 – 7.82 (m, 2 H), 7.64 (s, 1 H), 7.43 (t, J = 7.4 Hz, 1 H), 7.39 – 7.32 (m, 2 H), 7.14 (t, J = 8.5 Hz, 2 H). See: Bachmann, W. E.; Chu, E. J.-H. *J. Am. Chem. Soc.* **1935**, *57*, 1095–1097.



(2-(4-(Trifluoromethyl)phenoxy)phenyl)boronic acid (S13)

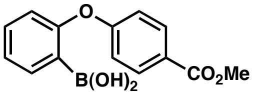
According to the “in situ quench” method of Reider,[2] a solution of aryl iodide (530 mg, 1.67 mmol, 1.0 equiv, azeotroped with benzene 2 × 5 mL) and (iPrO)$_3$B (0.46 mL, 2.01 mmol, 1.2 equiv, freshly distilled over sodium metal) in toluene–THF (4:1 v/v, 3.4 mL) at −78 °C under argon balloon was treated with nBuLi (0.84 mL, 2.4 M in hexanes, 1.2 equiv) dropwise via syringe pump over 30 min. The reaction mixture was stirred at −78 °C for an additional 30 min, then allowed to warm to −20 °C. The reaction mixture was quenched by the addition of 2 N aqueous HCl (3 mL), and the mixture was allowed to warm to room temperature. The layers were separated, and the aqueous layer was extracted with EtOAc (2 × 20 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by silica flash chromatography (4:1 hexanes/EtOAc) afforded the title compound (490 mg, 62%) as a white solid; m.p. 137–139 °C; R_f = 0.37 (4:1 hexanes/EtOAc); IR (neat) ν_{max} 3527, 3374, 1604, 1478, 1448, 1414, 1321, 1227, 1155, 1063, 855, 745 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, J = 7.3 Hz, 1 H), 7.65 (d, J = 8.1 Hz, 2 H), 7.43 (t, J = 7.7 Hz, 1 H), 7.22 (t, J = 7.2 Hz, 1 H), 7.16 (d, J = 8.1 Hz, 2 H), 6.80 (d, J = 8.2 Hz, 1 H), 6.41 (s, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.0, 158.8, 137.4, 133.2, 127.6 (q, J_{CF} = 3.7 Hz), 126.7 (q, J_{CF} = 32.9 Hz), 124.4, 124.1 (q, J_{CF} = 271.6 Hz), 119.7, 117.5; HRMS (ESI-TOF) calcd. for $C_{13}H_{10}BF_3O_3H^+$ [M + H$^+$] 283.0748, found 283.0745.



(2-(4-Fluorophenoxy)phenyl)boronic acid (S14)

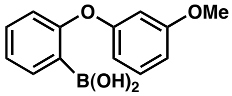
According to the “in situ quench” method of Reider,[2] a solution of aryl iodide (250 mg, 0.80 mmol, 1.0 equiv, azeotroped with benzene 2 × 3 mL) and (iPrO)$_3$B (0.22 mL, 0.96 mmol, 1.2 equiv, freshly distilled over sodium metal) in toluene–THF (4:1 v/v, 2.0 mL) at −78 °C under argon balloon was treated with nBuLi (0.37 mL, 2.4 M in hexanes, 1.1 equiv) dropwise via syringe pump over 30 min. The reaction mixture was stirred at −78 °C for an additional 30 min, then allowed to warm to −20

°C. The reaction mixture was quenched by the addition of 2 N aqueous HCl (1.5 mL), and the mixture was allowed to warm to room temperature. The layers were separated, and the aqueous layer was extracted with EtOAc (2 × 10 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by silica flash chromatography (4:1 hexanes/EtOAc) afforded the title compound (26 mg, 14%) as a white solid; m.p. 84–86 °C; R_f = 0.39 (4:1 hexanes/EtOAc); IR (neat) ν_{max} 3402, 1601, 1503, 1479, 1446, 1339, 1201, 1045, 850, 764 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 7.2 Hz, 1 H), 7.36 (t, J = 7.8 Hz, 1 H), 7.13 (t, J = 7.2 Hz, 1 H), 7.12 – 7.06 (m, 4 H), 6.67 (d, J = 8.2 Hz, 1 H), 5.93 (s, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.8, 160.6, 159.0, 151.2 (d, J_{CF} = 2.8 Hz), 137.2, 133.0, 123.2, 122.1, 122.1, 117.0, 116.8, 115.6; HRMS (ESI-TOF) calcd. for $C_{12}H_{10}BFO_3H^+$ [M + H^+] 233.0780, found 233.0780.



(2-(4-(Methoxycarbonyl)phenoxy)phenyl)boronic acid (*S*15)

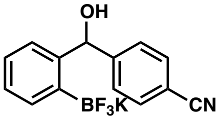
A dry and nitrogen-flushed 10-mL flask equipped with a magnetic stirrer and a septum was charged with aryl iodide (245 mg, 0.69 mmol, 1 equiv) and (iPrO)$_3$B (0.30 mL, 1.31 mmol, 1.9 equiv). THF was then added (1.4 mL). The reaction mixture was cooled to 0 °C, and iPrMgCl•LiCl (0.76 mL, 1.0 M in THF, 0.76 mmol, 1.1 equiv) was added dropwise over 5 min. The mixture was stirred for 30 min a 0 °C before 0.5 M HCl was added. The solution was stirred for 5 min and then diluted with EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2 × 15 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by silica flash chromatography (4:1 hexanes/EtOAc) afforded the title compound (136 mg, 72%) as a white solid; m.p. 75–85 °C; R_f = 0.19 (4:1 hexanes/EtOAc); IR (neat) ν_{max} 3377, 1719, 1603, 1478, 1444, 1432, 1275, 1214, 1163, 875, 754, 693 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 2 H), 7.97 (d, J = 7.1 Hz, 1 H), 7.40 (t, J = 8.6 Hz, 1 H), 7.19 (t, J = 7.2 Hz, 1 H), 7.08 (d, *J* = 8.5 Hz, 2 H), 6.80 (d, *J* = 8.2 Hz, 1 H), 6.36 (s, 2 H), 3.91 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 161.8, 160.0, 137.3, 133.0, 132.0, 131.8, 130.1, 124.3, 120.2, 119.0, 117.7, 117.3, 52.3; HRMS (ESI-TOF) calcd. for $C_{14}H_{13}BO_5H^+$ [M + H^+] 273.0929, found 273.0922.



(2-(3-Methoxyphenoxy)phenyl)boronic acid (S16)

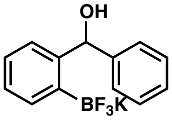
A solution of *n*BuLi in THF (1.24 mL, 2.3 M, 2.86 mmol, 1.05 equiv) was added dropwise to a solution of 1-bromo-2-(3-methoxyphenoxy)benzene (760 mg, 2.72 mmol) in anhydrous THF (9.5 mL) at −78 °C. The resulting mixture was stirred at −78 °C for 45 min and freshly distilled (Na) (iPrO)$_3$B (1.57 mL, 6.8 mmol, 2.5 equiv) was added. The mixture was stirred at −78 °C for 1 h and then at room temperature for a further 1 h. Et_2O (9 mL) and 1 M HCl (9 mL) were added at 0 °C. The mixture was stirred at 0 °C for 10 min, at room temperature for 1 h, and then extracted with Et_2O. The combined organic extracts were washed with H_2O, brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by silica flash chromatography (4:1 hexanes/EtOAc) afforded the title compound (400 mg, 64%) as a white solid; m.p. 71–74 °C; R_f = 0.29 (4:1 hexanes/EtOAc); IR (neat) ν_{max} 3411, 1602, 1478, 1442, 1335, 1200, 1140, 1040, 949, 850, 762, 685 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.1 Hz, 1 H), 7.34 (d, *J* = 7.7 Hz, 1 H), 7.27 – 7.23 (m, 1 H), 7.12 – 7.10 (m, 1 H), 6.76 – 6.73 (m, 2 H), 6.66 – 6.62 (m, 2 H), 6.22 (s, 2 H), 3.77 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.2, 161.2, 156.7, 137.0, 132.9, 130.6, 123.3, 116.5, 112.4, 110.6, 106.3, 55.6; HRMS (ESI-TOF) calcd. for $C_{13}H_{13}BO_4H^+$ [M + H^+] 245.0980, found 245.0978.

Direct addition to 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde followed by treatment with KHF_2



Trifluoroborate (S17)

A solution of 4-iodobenzonitrile (437 mg, 1.91 mmol) in THF (19 mL) at –40 °C was treated with *i*PrMgCl (1.05 mL, 2.0 M, 2.01 mmol, 1.05 equiv) in THF. After 1 h at –40 °C, 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (490 mg, 2.11 mmol, 1.1 equiv) in THF (1 mL) was added slowly. After stirring for 3 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (15 mL) and EtOAc (30 mL). The layers were separated and the aqueous layer was extracted with EtOAc. The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. A concentrated solution of the pinacol boronate ester (390 mg, 1.16 mmol) in MeOH (2 mL) at room temperature was treated with a solution of saturated aqueous KHF_2 (0.85 mL, 4.5 M, 3.84 mmol, 3.3 equiv). The solution was stirred for 15 min. The solvent was removed in vacuo and pinacol was removed by evaporation (4 ×) from MeOH–H_2O (1:1 v/v). The crude product was extracted with acetone (4 × 2 mL) then hot acetone (2 mL), filtered, and concentrated in vacuo to afford a slightly yellow solid (385 mg). The solid was washed with Et_2O and recrystallized from acetone/Et_2O to afford a white solid (255 mg, 42 % two steps); m.p. 201 °C; IR (neat) ν_{max} 3538, 3058, 2864, 2229, 1698, 1600, 1447, 1254, 1195, 1097, 985, 949, 923, 882, 821, 748, 697 cm^{-1}; ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 6.5 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.88 (d, *J* = 7.1 Hz, 1H), 5.86 (d, *J* = 9.1 Hz, 1H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 154.8 (d, *J* = 4.7 Hz), 152.5, 132.5, 129.3, 128.0, 126.8, 126.5, 122.0, 119.8, 110.5, 80.8; Did not ionize in HRMS (ESI-TOF).

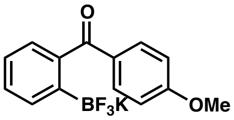


Trifluoroborate (S18)

A solution of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (308 mg, 1.34 mmol) in THF (2 mL) at –40 °C was treated with phenylmagnesium bromide (2.94 mL, 0.91 M, 2.68 mmol, 2 equiv) in THF. The resulting solution was then allowed to warm to room temperature and stirred for 1 h. The reaction mixture was cooled to 0 °C, and carefully quenched by adding saturated aqueous NH_4Cl solution (0.5 mL). The reaction contents were extracted with EtOAc (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. A concentrated solution of the pinacol boronate ester (180 mg, 0.79 mmol) in MeOH (2 mL) at room temperature was treated with a solution of saturated aqueous KHF_2 (0.58 mL, 4.5 M, 2.6 mmol, 3.3 equiv). The solution was stirred for 15 min. The solvent was removed in vacuo and pinacol was removed by evaporation (4 ×) from MeOH–H_2O (1:1 v/v). The crude product was extracted with acetone (4 × 2 mL) then hot acetone (2 mL), filtered, and concentrated in vacuo. The solid was washed with Et_2O and recrystallized from acetone/Et_2O to afford a white solid (183 mg, 47 % two steps); m.p. 228 °C; IR (neat) ν_{max} 3576, 3331, 3204, 3061, 3026, 2920, 1453, 1198, 1098, 1043, 994, 976, 946, 760, 697 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 7.40 – 7.36 (m, 2 H), 7.29 – 7.25 (m, 2 H), 7.19 – 7.15 (m, 1 H), 7.08 – 7.01 (m, 2 H), 6.85 – 6.75 (m, 1 H), 5.77 (d, *J* = 9.1 Hz, 1 H); ^{13}C NMR (150 MHz, CD_3CN) δ 153.8, 149.0, 129.0, 128.9, 127.2, 126.9, 126.5, 122.3, 81.3; Did not ionize in HRMS (ESI-TOF).

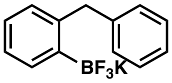
General Method for Miyaura borylation followed by treatment with KHF_2

A microwave vial was charged with $PdCl_2(CH_3CN)_2$ (0.02 mmol), SPhos (0.08 mmol) and aryl halide (1.0 mmol), evacuated, and backfilled with argon. Anhydrous 1,4-dioxane (0.60 mL) was added via syringe, through the septum, followed by Et_3N (0.21 mL, 1.5 mmol, 1.5 equiv) and pinacol borane (0.23 mL, 1.5 mmol, 1.5 equiv). The septum was exchanged for a microwave vial cap, and the reaction mixture was degassed with argon for 10 min. The reaction mixture was stirred at 110 °C until the aryl halide was consumed as determined by TLC (1−2 h). The mixture was filtered through a small plug of silica gel and concentrated in vacuo. Purification by silica gel chromatography (100% hexanes → 4:1 hexanes/EtOAc) afforded the corresponding pinacol boronate ester. A concentrated solution of the pinacol boronate ester in MeOH (2 mL) at room temperature was treated with a saturated aqueous solution of KHF_2 (4.5 M, 3 equiv). The mixture was stirred for 30 min. The solvent was removed in vacuo and pinacol was removed by evaporation (4 ×) from MeOH–H_2O (1:1 v/v). The solid was dried thoroughly and extracted with acetone (3 ×) and then with hot acetone (1 ×). The organic layer was filtered and evaporated to dryness. The crude product was washed with Et_2O (3 ×) and recrystallized from acetone/Et_2O to afford chromatographically and spectroscopically pure product.



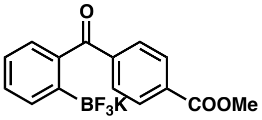
Trifluoroborate (S19)

Yield: 40% (two steps) as a white solid; m.p. 179 °C; IR (neat) ν_{max} 3628, 3052, 3007, 2936, 2841, 1709, 1654, 1593, 1509, 1290, 1253, 1178, 1150, 998, 946, 929, 846, 751, 696 cm^{-1}; ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 7.73 (dd, J = 11.5, 8.4 Hz, 3 H), 7.28 (t, J = 7.3 Hz, 1 H), 7.16 (t, J = 7.5 Hz, 1 H), 6.98 (dd, J = 19.7, 8.1 Hz, 3 H), 3.88 (s, 3 H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 201.7, 164.1, 144.1, 134.1 (q, J_{CF} = 2.5 Hz), 133.4, 132.3, 128.5, 126.4, 125.4, 113.9, 55.9; HRMS (ESI-TOF) calcd. for $C_{15}H_{14}BO_3^+$ $[M - F_3K + OMe]^+$ 253.1033, found 253.1032.



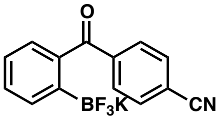
Trifluoroborate (S20)

Yield: 54% (two steps) as a white solid; m.p. 170 °C; IR (neat) ν_{max} 3627, 3058, 3025, 2917, 2850, 1596, 1494, 1437, 1208, 953, 752, 700 cm^{-1}; ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 7.59 – 7.55 (m, 1 H), 7.31 – 7.06 (m, 5 H), 6.95 – 6.78 (m, 3 H), 4.20 (s, 2 H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 145.4, 144.9, 133.1 (q, J_{CF} = 3.2 Hz), 130.4, 129.0, 128.6, 126.4, 125.7, 124.5, 41.1. Did not ionize in HRMS (ESI-TOF).



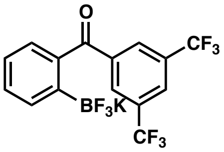
Trifluoroborate (S21)

Yield: 30% (two steps) as a white solid; m.p. 234 °C; IR (neat) ν_{max} 3627, 1723, 1666, 1437, 1405, 1283, 1192, 1108, 951, 932, 753, 724 cm^{-1}; ^{1}H NMR (400 MHz, CD_3CN) δ 8.03 (d, *J* = 8.4 Hz, 2 H), 7.81 (d, *J* = 8.4 Hz, 2 H), 7.64 (d, *J* = 7.3 Hz, 1 H), 7.36 (t, *J* = 7.2 Hz, 1 H), 7.23 (t, *J* = 7.5 Hz, 1 H), 7.06 (d, *J* = 7.5 Hz, 1 H), 3.88 (s, 3 H); ^{13}C NMR (150 MHz, CD_3CN): δ 202.3, 177.5, 167.1, 143.6, 142.7, 134.1, 133.7 (d, J_{CF} = 2.2 Hz), 130.9, 129.8, 129.1, 126.1, 52.9; HRMS (ESI-TOF) calcd. for $C_{16}H_{14}BO_4^+$ [M − F_3K + OMe]$^+$ 281.0985, found 281.0992.



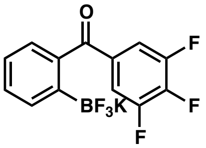
Trifluoroborate (S22)

Yield: 33% (two steps) as a white solid; m.p. 253 °C; IR (neat) ν_{max} 3630, 3052, 2233, 1669, 1285, 1256, 1191, 1049, 950, 930, 858, 754, 709, 689 cm^{-1}; ^{1}H NMR (400 MHz, CD_3CN) δ 7.83 (d, *J* = 8.4 Hz, 2 H), 7.77 (d, *J* = 8.5 Hz, 2 H), 7.63 (d, *J* = 7.2 Hz, 1 H), 7.36 (t, *J* = 7.4 Hz, 1 H), 7.24 (t, *J* = 7.4 Hz, 1 H), 7.06 (d, *J* = 7.5 Hz, 1 H); ^{13}C NMR (150 MHz, CD_3CN) δ 201.8, 143.2, 142.7, 133.7, 133.0, 131.2, 129.3, 126.3, 126.1, 119.3, 116.0; HRMS (ESI-TOF) calcd. for $C_{14}H_8BF_3NO^-$ [M − K^+] 274.0651, found 274.0659.



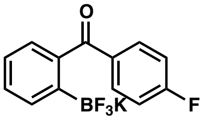
Trifluoroborate (S23)

Yield: 36% (two steps) as a white solid; m.p. 211 °C; IR (neat) ν_{max} 3631, 3059, 1713, 1677, 1615, 1379, 1275, 1245, 1182, 1129, 1109, 1001, 948, 911, 753, 681 cm^{-1}; ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.24 (s, 2 H), 8.15 (s, 1 H), 7.66 (d, *J* = 7.4 Hz, 1 H), 7.32 (t, *J* = 7.3 Hz, 1 H), 7.21 (td, *J* = 7.4, 1.2 Hz, 1 H), 7.13 (d, *J* = 7.5 Hz, 1 H); ^{13}C NMR (150 MHz, $(CD_3)_2CO$) δ 199.6, 142.3, 141.7, 133.8 (q, J_{CF} = 2.4 Hz), 131.6 (q, J_{CF} = 33.4 Hz), 130.8 (q, J_{CF} = 3.9 Hz), 129.5, 126.4, 126.3 (d, J_{CF} = 2.6 Hz), 125.9 (dt, J_{CF} = 7.7 Hz, 3.8 Hz), 124.3 (q, J_{CF} = 272.0 Hz); HRMS (ESI-TOF) calcd. for $C_{16}H_{10}BF_6O_2^+$ [M − F_3K + OMe]$^+$ 259.0678, found 259.0677.



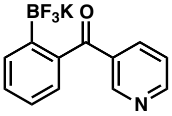
Trifluoroborate (S24)

Yield: 40% (two steps) as a white solid; m.p. 263 °C; IR (neat) ν_{max} 3059, 1681, 1509, 1630, 1509, 1463, 1308, 1270, 1194, 1059, 1016, 949, 923, 856, 831, 747, 688 cm^{-1}; ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.67 (d, *J* = 7.4 Hz, 1 H), 7.33 – 7.31 (m, 2 H), 7.17 (d, *J* = 9.6 Hz, 3 H); ^{13}C NMR (150 MHz, $(CD_3)_2CO$) δ 197.9, 153.6 (ddd, J_{CF} = 252.5, 10.1, 2.6 Hz), 151.5 (ddd, J_{CF} = 259.5, 10.3, 3.8 Hz), 144.5, 140.5 (dt, J_{CF} = 248.8, 15.5 Hz), 134.0 (d, J_{CF} = 3.0 Hz), 129.5, 128.0 – 127.9 (m), 127.2 (d, J_{CF} = 9.0 Hz), 126.6, 125.9, 112.2 (dd, J_{CF} = 17.7, 4.2 Hz); HRMS (ESI-TOF) calcd. for $C_{14}H_9BF_3O_2^+$ [M − F_3K + OMe]$^+$ 277.0650, found 277.0645.



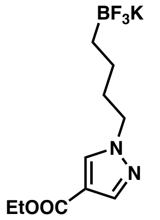
Trifluoroborate (S25)

Yield: 29% (two steps) as a white solid; m.p. 207 °C; IR (neat) ν_{max} 3634, 3054, 1662, 1596, 1504, 1286, 1258, 1232, 1193, 1149, 1103, 1050, 951, 931, 852, 752 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.68 (dd, *J* = 8.7, 5.8 Hz, 2 H), 7.49 (d, *J* = 7.4 Hz, 1 H), 7.27 – 7.20 (m, 3 H), 7.16 (t, *J* = 7.4 Hz, 1 H), 6.93 (d, *J* = 7.5 Hz, 1 H); ^{13}C NMR (150 MHz; DMSO-d$_6$) δ 199.4, 164.4 (d, J_{CF} = 250.0 Hz), 143.0, 135.1, 132.5, 132.4, 127.4, 125.1, 124.5, 114.8 (d, J_{CF} = 21.8 Hz); HRMS (ESI-TOF) calcd. for $C_{14}H_{11}BFO_2^+$ [M – F_3K + OMe]$^+$ 241.0833, found 241.0829.



Trifluoroborate (S26)

To the bromide (159 mg, 0.61 mmol) in a microwave reaction vial equipped with a stir bar was added bis(pinacolato)diboron (308 mg, 1.21 mmol), anhydrous KOAc (179 mg, 1.82 mmol). The vial was sealed with a septum, and anhydrous 1,4-dioxane (2.5 mL) was added under argon balloon. The reaction mixture was degassed by bubbling with argon while sonicating for 10 min. $PdCl_2(dppf)\bullet CH_2Cl_2$ (25 mg, 0.03 mmol) was then quickly added followed by an additional 5 min of degassing. The septum was then quickly replaced with a Teflon rupture disk under a blanket of argon. The reaction mixture was stirred at 100 °C in an oil bath for 17 h. The reaction mixture was then cooled to room temperature, filtered through a Celite plug, and concentrated in vacuo. The crude product was purified via flash column chromatography on silica gel eluting with 50% EtOAc/hexanes. The boronate ester (contaminated with bis(pinacolato)diboron) was then dissolved in MeOH (2 mL) followed by the addition of saturated aqueous KHF_2 (~4.5 M, 0.4 mL) and stirred for 30 min. The reaction mixture was then concentrated on the rotovap. Pinacol was then azeotropically removed by dissolving the crude BF_3K salt in MeOH/H_2O (1:1 v/v, 3 mL) and concentrating on the rotary evaporator a total of four times followed by drying under high-vacuum for 1 h. The BF_3K salt was rinsed with hot acetone (5 × 10 mL) and concentrated to yield a pale yellow foam. The foam was then dissolved in a minimal amount of acetone and crystallized with Et_2O at 0 °C, yielding the title compound (43%) as a white solid; m.p. 160–162 °C; IR (neat) ν_{max} 3060, 1674, 1582, 1416, 1188, 945, 926 cm^{-1}; ^1H NMR (600 MHz, $(CD_3)_2CO$) δ 8.85 (d, *J* = 2.1 Hz, 1 H), 8.65 (dd, *J* = 4.8, 1.8 Hz, 1 H), 8.01 – 7.98 (m, 1 H), 7.67 (d, *J* = 7.4 Hz, 1 H), 7.39 (dd, *J* = 5.0 Hz, 1 H), 7.29 (t, *J* = 7.4 Hz, 1 H), 7.17 (t, *J* = 7.4 Hz, 1 H), 7.05 (d, *J* = 7.5 Hz, 1 H); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 201.8, 153.3, 152.1, 143.3, 137.8, 134.7, 134.0, 129.0, 126.2, 125.9, 123.8; HRMS (ESI-TOF) calcd. for $C_{12}H_8BF_3KNO$ 289.0288 (did not ionize). See: Harrowven, D. C.; Sutton, B. J.; Coulton, S. *Org. Biomol. Chem.* **2003**, *1*, 4047–4057. (bromide)



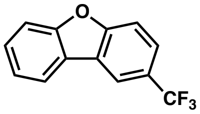
Heterocycle alkyltrifluoroborate (*S*27)

To a solution of 2-(4-bromobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (131.5 mg, 0.5 mmol) in CH_3CN (1 ml) was added ethyl 1*H*-pyrazole-4-carboxylate (210 mg, 1.5 mmol, 3 equiv) and K_2CO_3 (345 mg, 2.5 mmol, 5 equiv). The reaction mixture was stirred at 90 °C for 2 h. The crude product was partitioned between EtOAc and H_2O. The layers were separated, and the aqueous layer was extracted with EtOAc. The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by silica gel chromatography (100% hexanes → 1:1 hexanes/EtOAc) afforded the pinacol boronate ester (110 mg, 0.59 mmol). A concentrated solution of the pinacol boronate ester (90 mg, 0.28 mmol) in MeOH at room temperature was treated with a solution of saturated aqueous KHF_2 (0.20 mL, 4.5 M, 0.92 mmol, 3.3 equiv). The solution was stirred for 15 min. The solvent was removed in vacuo and pinacol was removed by serial evaporation (4 ×) from MeOH–H_2O (1:1 v/v). The crude product was extracted with acetone (4 × 2 mL), then hot acetone (2 mL), filtered, and concentrated in vacuo. The solid was washed with Et_2O

and recrystallized from acetone/Et_2O to afford the title compound (80 mg, 53 % two steps) as a white solid; m.p. 138 °C; IR (neat) ν_{max} 3564, 3132, 2981, 2929 1708, 1554, 1410, 1219, 1113, 1088, 1028, 983, 938, 843, 767, 722 cm^{-1}; ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 7.95 (s, 1 H), 7.62 (s, 1 H), 4.07 (q, *J* = 7.1 Hz, 2 H), 3.97 (t, *J* = 7.3 Hz, 2 H), 1.66 (quintet, *J* = 7.4 Hz, 2 H), 1.15 – 1.09 (m, 5 H), 0.03 (dq, *J* = 14.9 Hz, 7.2 Hz, 2 H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 163.4, 140.8, 133.4, 115.0, 60.2, 53.4, 34.2, 23.2 (d, J_{CF} = 2.4 Hz), 14.7; Did not ionize in HRMS (ESI-TOF).

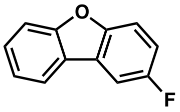
Standard Procedure for "borono-Pschorr" cyclization

To a solution of boronic acid or trifluoroborate (0.1 mmol, 1.0 equiv) in trifluorotoluene (0.5 mL) and water (0.48 mL) was added silver(I) nitrate (20 μL, 1 M, 0.02 mmol, 0.2 equiv). Potassium persulfate (81.1 mg, 0.3 mmol, 3.0 equiv) was then added in one portion and the reaction mixture was stirred vigorously at 60 °C for 1 h. The mixture was extracted with EtOAc (5 ×). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by silica gel chromatography (100% hexanes → 4:1 hexanes/EtOAc) afforded chromatographically and spectroscopically pure product.



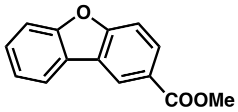
2-(Trifluoromethyl)dibenzo[*b*,*d*]furan (1)

Yield: 73% (gram-scale: 65%) as a white solid; m.p. 97 °C; IR (neat) ν_{max} 2922, 1453, 1352, 1334, 1319, 1274, 1164, 1105, 1053, 898, 826, 770, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1 H), 8.00 (d, *J* = 7.5 Hz, 1 H), 7.73 (d, *J* = 8.2 Hz, 1 H), 7.67 – 7.61 (m, 2 H), 7.53 (t, *J* = 7.3 Hz, 1 H), 7.41 (t, *J* = 7.5 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.5, 157.7, 129.1, 126.2 (q, J_{CF} = 32.3 Hz), 125.4 (q, J_{CF} = 271.9 Hz,), 125.4, 125.1 (q, J_{CF} = 3.6 Hz), 124.2, 124.2, 121.8, 119.2 (q, J_{CF} = 4.0 Hz), 112.9, 112.8; Did not ionize in HRMS (ESI-TOF).



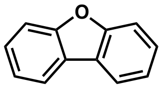
2-Fluorodibenzo[*b*,*d*]furan (2)

Yield: 69%; ^{1}H NMR (400 MHz; CDCl$_3$) δ 7.92 (d, *J* = 7.7 Hz, 1 H), 7.62 – 7.56 (m, 2 H), 7.52 – 7.46 (m, 2 H), 7.37 – 7.33 (m, 1 H), 7.17 (td, *J* = 9.0, 2.7 Hz, 1 H). See: *J. Am. Chem. Soc.* **2009**, *131*, 4194–4195.



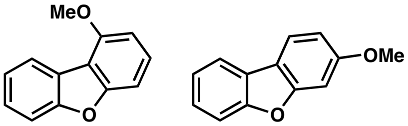
Methyl dibenzo[*b*,*d*]furan-2-carboxylate (3)

Yield: 57%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.69 (d, *J* = 1.4 Hz, 1 H), 8.19 (dd, *J* = 8.6 Hz, 1.7 Hz, 1 H), 8.01 (d, *J* = 7.7 Hz, 1 H), 7.61 – 7.59 (m, 2 H), 7.51 (td, *J* = 7.8, 1.1 Hz, 1 H), 7.42 – 7.38 (m, 1 H), 3.99 (s, 3 H). See: *Org. Lett.* **2004**, *6*, 3739–3742.



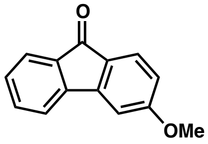
Dibenzo[*b*,*d*]furan (4)

Yield: 65%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 (d, *J* = 7.7 Hz, 1 H), 7.58 (d, *J* = 8.2 Hz, 1 H), 7.47 (t, *J* = 7.7 Hz, 1 H), 7.35 (t, *J* = 7.5 Hz, 1 H). See: *J. Am. Chem. Soc.* **2009**, *131*, 4194–4195.



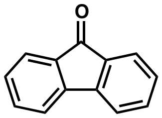
1-Methoxydibenzo[*b*,*d*]furan (5a) and 3-methoxydibenzo[*b*,*d*]furan (5b)

Yield: 41%, inseparable mixture (5:1 *para*:*ortho*); major isomer (**5a**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.6 Hz, 1 H), 7.55 (d, *J* = # Hz, 1 H), 7.42 (dt, *J* = # Hz, 1 H), 7.39 (t, *J* = # Hz, 1 H), 7.34 (dt, *J* = # Hz, 1 H), 7.21 (d, *J* = # Hz, 1 H), 6.80 (d, *J* = # Hz, 1 H), 4.06 (s, 3 H). See: Oliveira, A. M. A. G.; Raposo, M. M. M.; Oliveira-Campos, A. M. F.; Griffiths, J.; Machado, A. E. H. *Helv. Chim. Acta* **2003**, *86*, 2900–2907.



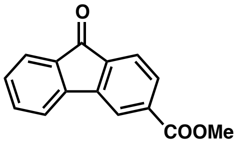
3-Methoxy-9*H*-fluoren-9-one (6)

Yield: 43%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.8, 3.2 Hz, 2 H), 7.50 – 7.45 (m, 2 H), 7.30 (td, *J* = 7.0, 0.6 Hz, 1 H), 7.03 (d, *J* = 1.9 Hz, 1 H), 6.75 (dd, *J* = 8.1, 1.5 Hz, 1 H), 3.92 (s, 3 H). See: Moorthy, J. N.; Samanta, S. *J. Org. Chem.* **2007**, *72*, 9786–9789.



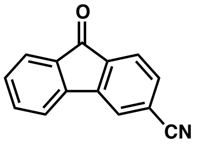
Fluorenone (7)

Yield: 30% as a yellow solid from CH_2 and 41% from CHOH; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.4 Hz, 2 H), 7.43 – 7.37 (m, 4 H), 7.20 (t, *J* = 7.2 Hz, 2 H). See: Tilly, D.; Fu, J.; Zhao, B.; Alessi, M.; Castanet, A.-S.; Snieckus, V.; Mortier, J. *Org. Lett.* **2010**, *12*, 68–71.



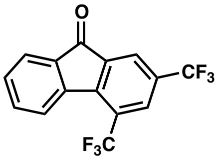
Methyl 9-oxo-9*H*-fluorene-3-carboxylate (8)

Yield: 67% as a yellow solid; m.p. 145 °C; IR (neat) ν_{max} 3055, 2960, 1713, 1420, 1277, 1247, 1189, 1102, 921, 728, 661 cm^{-1}; 1H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1 H), 7.98 (d, *J* = 7.6 Hz, 1 H), 7.69 (t, *J* = 7.4 Hz, 2 H), 7.59 (d, *J* = 7.4 Hz, 1 H), 7.53 (t, *J* = 7.4 Hz, 1 H), 7.33 (t, *J* = 7.4 Hz, 1 H), 3.97 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 166.3, 144.6, 143.9, 137.6, 137.6, 135.7, 135.4, 134.3, 131.0, 129.8, 124.8, 124.2, 121.4, 121.0, 52.8; HRMS (ESI-TOF) calcd. for $C_{15}H_{10}O_3H^+$ [M + H$^+$] 239.0703, found 239.0703. See: Harget, A. J.; Warren, K. D.; Yandle, J. R. *J. Chem. Soc. B.* **1968**, 214–218.



9-Oxo-9*H*-fluorene-3-carbonitrile (9)

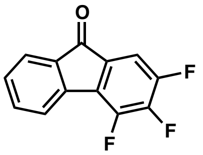
Yield: 77% from C(O) and 55% from CHOH; ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.19 (s, 1 H), 7.92 (d, *J* = 7.4 Hz, 1 H), 7.81 (q, *J* = 8.5 Hz, 2 H), 7.70 (t, *J* = 6.7 Hz, 2 H), 7.50 (t, *J* = 7.5 Hz, 1 H). See: Harget, A. J.; Warren, K. D.; Yandle, J. R. *J. Chem. Soc. B.* **1968**, 214–218.



2,4-Bis(trifluoromethyl)-9*H*-fluoren-9-one (10)

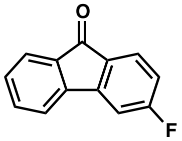
Yield: 61% as a yellow solid; m.p. 124 °C; IR (neat) ν_{max} 3119, 2924, 1729, 1633, 1388, 1292, 1275, 1247, 1155, 1140, 1118, 909, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1 H), 8.03 (s, 1 H), 7.93 (d, *J* = 7.7 Hz, 1 H), 7.81 (d, *J* = 7.4 Hz, 1 H), 7.63 (t, *J* = 7.7 Hz, 1 H), 7.49 (t, *J* = 7.5 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.4, 146.2, 141.2, 137.4, 136.7, 135.1, 132.4 (q, J_{CF} = 34.1 Hz), 132.1, 129.4 – 129.2 (m), 126.2

(q, J_{CF} = 5.5 Hz), 125.9, 125.7 (q, J_{CF} = 34.6 Hz), 124.9 (q, J_{CF} = 3.7 Hz), 123.8 (q, J_{CF} = 273.2 Hz); Did not ionize in HRMS (ESI-TOF); GC/MS, M^+ 316.



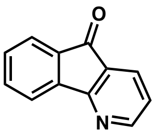
2,3,4-Trifluoro-9*H*-fluoren-9-one (11)

Yield: 71% as a yellow solid; m.p. sublimes; IR (neat) ν_{max} 3076, 1714, 1625, 1601, 1506, 1464, 1249, 1090, 876, 801, 761, 738, 690 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.96 – 7.92 (m, 1 H), 7.88 (d, *J* = 7.6 Hz, 1 H), 7.71 – 7.65 (m, 2 H), 7.46 (td, *J* = 7.5, 0.7 Hz, 1 H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 189.0, 156.2 (dd, J_{CF} = 256.5, 10.3 Hz), 149.6 – 147.7 (m), 142.9, 141.6 – 141.6 (m), 140.8 (dt, *J* = 250.9, 16.2 Hz), 137.0, 134.7, 131.6, 125.5, 123.3, 118.1 (d, J_{CF} = 10.8 Hz), 108.6 (d, J_{CF} = 21.3 Hz); HRMS (ESI-TOF) calcd. for $C_{13}H_5F_3OH^+$ [M + H^+] 235.0365, found 235.0363.



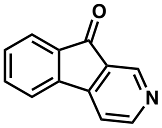
3-Fluoro-9*H*-fluoren-9-one (12)

Yield: 65%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (m, *J* = 7.9, 5.4 Hz, 2 H), 7.51 (m, *J* = 6.3 Hz, 2 H), 7.36 – 7.32 (m, 1 H), 7.20 (dd, *J* = 8.3, 2.2 Hz, 1 H), 6.95 (td, *J* = 8.6, 2.2 Hz, 1 H). See: Thirunavukkarasu, V. S.; Parthasarathy, K.; Cheng, C.-H. *Angew. Chem., Int. Ed.* **2008**, *47*, 9462–9465.



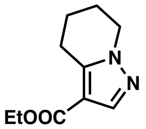
5*H*-Indeno[1,2-*b*]pyridin-5-one (13)

Major (R_f = 0.57 in 4:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.63 (d, *J* = 5.0 Hz, 1 H), 7.90 (d, *J* = 7.4 Hz, 1 H), 7.86 (d, *J* = 7.4 Hz, 1 H), 7.73 (d, *J* = 7.4 Hz, 1 H), 7.61 (t, *J* = 7.4 Hz, 1 H), 7.44 (t, *J* = 7.4 Hz, 1 H), 7.22 (d, *J* = 5.2 Hz, 1 H), 7.21 (d, *J* = 5.2 Hz, 1 H).



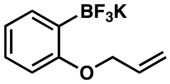
9*H*-Indeno[2,1-*c*]pyridin-9-one (14)

Minor (R_f = 0.34 in 4:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.87 (s, 1 H), 8.65 (d, *J* = 1.1 Hz, 1 H), 7.76 (d, *J* = 7.3 Hz, 1 H), 7.66 (d, *J* = 7.3 Hz, 1 H), 7.60 (t, *J* = 7.4 Hz, 1 H), 7.53 – 7.47 (m, 2 H). See: Stauffer, K. J.; Williams, P. D.; Selnick, H. G.; Nantermet, P. G.; Newton, C. L.; Homnick, C. F.; Zrada, M. M.; Lewis, S. D.; Lucas, B. J.; Krueger, J. A.; Pietrak, B. L.; Lyle, E. A.; Singh, R.; Miller-Stein, C.; White, R. B.; Wong, B.; Wallace, A. A.; Sitko, G. R.; Cook, J. J.; Holahan, M. A.; Stranieri-Michener, M.; Leonard, Y. M.; Lynch, Jr., J. J.; McMasters, D. R.; Yan, Y. *J. Med. Chem.* **2005**, *48*, 2282–2293.



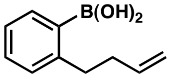
Ethyl 4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyridine-3-carboxylate (15)

Yield: 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1 H), 4.27 (q, *J* = 7.1 Hz, 2 H), 4.15 (t, *J* = 6.1 Hz, 2 H), 3.06 (t, *J* = 6.4 Hz, 2 H), 2.07 – 2.01 (m, 2 H), 1.91 – 1.85 (m, 2 H), 1.33 (t, *J* = 7.1 Hz, 3 H). See: Allin, S. M.; Barton, W. R. S.; Bowman, W. R.; Bridge, E.; Elsegood, M. R. J.; McInally, T.; McKee, V. *Tetrahedron* **2008**, *64*, 7745–7758.



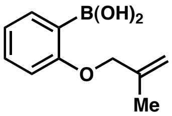
Potassium aryltrifluoroborate (S28)

A concentrated solution of 2-(allyloxyphenyl)boronic acid (1.50 g, 8.43 mmol) in MeOH (10 mL) at room temperature was treated with a saturated aqueous solution of KHF_2 (~4.5 M, 6 mL). Within 5 min, a white suspension was obtained. The spin bar was removed, and the suspension was concentrated in vacuo. The white solid was extracted with hot acetone, and the acetone layer was concentrated in vacuo, affording the title compound (750 mg, 40%) as a white solid; m.p. 215 °C; IR (neat) ν_{max} 1192, 954, 927, 734 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 7.42 (d, *J* = 6.5 Hz, 1 H), 7.10 (t, *J* = 7.5 Hz, 1 H), 6.81 (t, *J* = 7.2 Hz, 1 H), 6.78 (d, *J* = 8.2 Hz, 1 H), 6.13 – 6.04 (m, 1 H), 5.45 (d, *J* = 17.2 Hz, 1 H), 5.23 (d, *J* = 10.5 Hz, 1 H), 4.52 (d, *J* = 5.0 Hz, 2 H); ^{13}C NMR (150 MHz, CD_3CN) δ 162.4, 135.6, 134.4 (q, J_{CF} = 2.8 Hz), 128.1, 120.9, 117.8, 112.4, 69.4; HRMS (ESI-TOF) calcd. for $C_9H_8BF_3OH^+$ [M – KH + H^+] 201.0693, found 201.0700. See: Morgan, J.; Pinhey, J. T. *J. Chem. Soc., Perkin Trans. I* **1993**, 1673−1676. (boronic acid) See: Barluenga, J.; Fañanás, F. J.; Sanz, R.; Marcos, C.; Trabada, M. *Org. Lett.* **2002**, *4*, 1587−1590. (bromide)



(2-(But-3-en-1-yl)phenyl)boronic acid (S29)

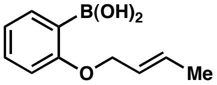
According to the "in situ quench" method of Reider,[2] a solution of aryl bromide (495 mg, 2.20 mmol, 1.0 equiv, azeotroped with benzene 2 × 5 mL) and $(iPrO)_3B$ (0.54 mL, 2.20 mmol, 1.0 equiv, freshly distilled over sodium metal) in toluene−THF (4:1 v/v, 12 mL) at −78 °C under argon was treated with *n*BuLi (0.96 mL, 2.3 M in hexanes, 1.0 equiv) dropwise via syringe pump over 30 min. The reaction was mixture stirred at −78 °C for an additional 60 min, then allowed to warm to −20 °C. The reaction mixture was quenched by the addition of 2 N aqueous HCl (10 mL), and the mixture was allowed to warm to room temperature. The layers were separated, and the aqueous layer was extracted with Et_2O (2 × 20 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by silica flash chromatography (12:1 → 3:1 hexanes/EtOAc) afforded the title compound (236 mg, 57%) as a white solid; m.p. 83–84 °C; R_f = 0.24 (3:1 hexanes/EtOAc); IR (neat) ν_{max} 1596, 1441, 1334, 1292, 910, 754, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 7.7, 1.4 Hz, 1 H), 7.49 (td, *J* = 7.6, 1.5 Hz, 1 H), 7.33 – 7.28 (m, 2 H), 5.99 – 5.89 (m, 1 H), 5.07 – 4.98 (m, 2 H), 3.32 (t, *J* = 7.9 Hz, 2 H), 2.51 – 2.45 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 138.4, 137.8, 132.4, 130.2, 125.6, 115.1, 37.2, 35.2; HRMS (ESI-TOF) calcd. for $C_{10}H_{13}BO_2H^+$ [M + H^+] 177.1081, found 177.1076. See: Molander, G. A.; Sandrock, D. L. *J. Am. Chem. Soc.* **2008**, *130*, 15792–15793. (bromide)



(2-((2-Methylallyl)oxy)phenyl)boronic acid (S30)

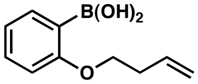
According to the "in situ quench" method of Reider,[2] a solution of aryl iodide (4.1 g, 14.96 mmol, 1.0 equiv, azeotroped with benzene 2 × 10 mL) and $(iPrO)_3B$ (4.6 mL, 17.95 mmol, 1.2 equiv, freshly distilled over sodium metal) in toluene–THF (4:1 v/v, 60 mL) at −78 °C under argon balloon was treated with *n*BuLi (7.80 mL, 2.3 M in hexanes, 1.2 equiv) dropwise via syringe pump over 30 min. The reaction mixture was stirred at −78 °C for an additional 60 min, then allowed to warm to −20 °C. The reaction mixture was quenched by the addition of 2 N aqueous HCl (40 mL), and the mixture was allowed to warm to room temperature. The layers were separated, and the aqueous layer was extracted with Et_2O (2 × 60 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by silica flash chromatography (10:1 → 2:1 hexanes/EtOAc) afforded the title compound (2.6 g, 81%) as a white solid; m.p. 51–52 °C (hexanes); R_f = 0.50 (3:1 hexanes/EtOAc); IR (neat) ν_{max} 3400, 1600, 1447, 1338, 1217, 1017, 758 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.3, 1.6 Hz, 1 H), 7.44 – 7.40 (m, 1 H), 7.03 (t, *J*

= 7.3 Hz, 1 H), 6.90 (d, *J* = 8.4 Hz, 1 H), 5.91 (s, 2 H), 5.11 – 5.10 (m, 1 H), 5.06 – 5.05 (m, 1 H), 4.55 (s, 2 H), 1.86 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 140.1, 137.0, 132.9, 121.5, 114.3, 111.4, 72.4, 19.7; HRMS (ESI-TOF) calcd. for $C_{10}H_{13}BO_3H^+$ [M + H^+] 193.1030, found 193.1035. See: Casaschi, A.; Grigg, R.; Sansano, J. M. *Tetrahedron* **2000**, *56*, 7553–7560. (iodide)



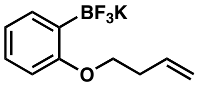
(*E*)-(2-(But-2-en-1-yloxy)phenyl)boronic acid (*S*31)

According to the "in situ quench" method of Reider,[2] a solution of aryl iodide (1.16 g, 4.23 mmol, 1.0 equiv, azeotroped with benzene 2 × 10 mL) and $(iPrO)_3B$ (1.04 mL, 4.44 mmol, 1.05 equiv, freshly distilled over sodium metal) in toluene−THF (4:1 v/v, 21 mL) at −78 °C under argon was treated with *n*BuLi (1.93 mL, 2.3 M in hexanes, 5.36 mmol, 1.05 equiv) dropwise via syringe pump over 30 min. The reaction was stirred at −78 °C for an additional 60 min, then allowed to warm to −20 °C. The reaction mixture was quenched by the addition of 2 N aqueous HCl (20 mL), and the mixture was allowed to warm to room temperature. The layers were separated, and the aqueous layer was extracted with Et_2O (2 × 40 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by silica flash chromatography (10:1 → 2:1 hexanes/EtOAc) afforded the title compound (687 mg, 85%, 5:1 *E*:*Z*) as a white solid; m.p. 55−60 °C (hexanes); R_f = 0.48 (3:1 hexanes/EtOAc); IR (neat) ν_{max} 3366, 1599, 1446, 1341, 1221, 997, 968, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.3, 1.9 Hz, 1 H), 7.42 (ddd, *J* = 8.3, 7.4, 1.9 Hz, 1 H), 7.02 (td, *J* = 7.3, 0.8 Hz, 1 H), 6.90 (d, *J* = 8.3 Hz, 1 H), 5.92 (s, 2 H), 5.94 – 5.71 (m, 2 H), 4.55 (d, *J* = 6.2 Hz, 2 H), 1.80 – 1.77 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 137.0, 132.9, 132.2, 125.4, 121.4, 111.4, 69.4, 18.0; HRMS (ESI-TOF) calcd. for $C_{10}H_{13}BO_3H^+$ [M + H^+] 193.1030, found 193.1033. See: Kita, Y.; Nambu, H.; Ramesh, N. G.; Anilkumar, G.; Matsugi, M. *Org. Lett.* **2001**, *3*, 1157−1160. (iodide)



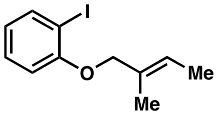
(2-(But-3-en-1-yloxy)phenyl)boronic acid (S32)

According to the "in situ quench" method of Reider,[2] a solution of aryl bromide (1.34 g, 5.90 mmol, 1.0 equiv, azeotroped with benzene 2 × 5 mL) and (iPrO)$_3$B (1.64 mL, 7.08 mmol, 1.2 equiv, freshly distilled over sodium metal) in toluene−THF (4:1 v/v, 12 mL) at −78 °C under argon was treated with *n*BuLi (3.08 mL, 2.3 M in hexanes, 1.2 equiv) dropwise via syringe pump over 30 min. The reaction mixture was stirred at −78 °C for an additional 60 min, then allowed to warm to −20 °C. The reaction mixture was quenched by the addition of 2 N aqueous HCl (10 mL), and the mixture was allowed to warm to room temperature. The layers were separated, and the aqueous layer was extracted with Et_2O (2 × 20 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by silica flash chromatography (10:1 → 3:1 hexanes/EtOAc) afforded the title compound (951 mg, 84%) as a white solid; m.p. 79–81 °C (hexanes); R_f = 0.45 (3:1 hexanes/EtOAc); IR (neat) ν_{max} 3371, 1600, 1574, 1449, 1343, 1225, 1052, 903, 761 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.3, 1.5 Hz, 1 H), 7.45 – 7.40 (m, 1 H), 7.03 (t, *J* = 7.3 Hz, 1 H), 6.90 (d, *J* = 8.4 Hz, 1 H), 6.34 (s, 2 H), 5.93 – 5.85 (m, 1 H), 5.29 – 5.25 (m, 1 H), 5.23 – 5.20 (m, 1 H), 4.14 (t, *J* = 6.2 Hz, 2 H), 2.62 (q, *J* = 6.4 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 137.1, 134.3, 132.9, 121.3, 118.3, 110.8, 67.0, 34.0; HRMS (ESI-TOF) calcd. for $C_{10}H_{13}BO_3H^+$ [M + H$^+$] 193.1030, found 193.1031. See: Shi, L.; Narula, C. K.; Mak, K. T.; Kao, L.; Xu, Y.; Heck, R. F. *J. Org. Chem.* **1983**, *48*, 3894–3900. (bromide)



Potassium aryltrifluoroborate (S33)

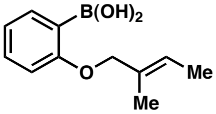
According to the method of Darses,[1] the arylboronic acid (192 mg, 1.0 mmol, 1.0 equiv) in MeOH (1.0 mL) at room temperature was treated with a saturated aqueous solution of KHF_2 (~4.5 M, 0.7 mL, ~3.3 equiv). Within 5 min, a white suspension was obtained. The spin bar was removed, and the suspension was concentrated in vacuo. The white solid was extracted with hot acetone, and the acetone layer was concentrated in vacuo, affording the title compound (226 mg, 89%) as a white solid; m.p. 176–178 °C; IR (neat) ν_{max} 1597, 1475, 1438, 1187, 935, 738 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 7.42 (d, J = 6.3 Hz, 1 H), 7.10 (td, J = 7.8, 1.9 Hz, 1 H), 6.82 – 6.79 (m, 2 H), 6.01 – 5.94 (m, 1 H), 5.19 – 5.14 (m, 1 H), 5.09 – 5.06 (m, 1 H), 3.99 (t, J = 7.1 Hz, 2 H), 2.48 (q, J = 7.0 Hz, 2 H); ^{13}C NMR (150 MHz, CD_3CN) δ 162.7, 136.3, 134.5 (q, J_{CF} = 3.3 Hz), 128.2, 121.0, 117.1, 112.9, 68.6, 34.5; HRMS (ESI-TOF) calcd. for $C_{10}H_{10}BF_3OH^+$ [M – KH + H^+] 215.0855, found 215.0868.



(*E*)-1-Iodo-2-((2-methylbut-2-en-1-yl)oxy)benzene (S34)

A solution of 2-iodophenol (1.10 g, 5.0 mmol, 1.0 equiv) and (*E*)-1-iodo-2-methylbut-2-ene (1.47 g, 7.5 mmol, 1.5 equiv) in acetone (5 mL) was treated with powdered, oven-dried K_2CO_3 (6.5 mmol, 1.3 equiv). The reaction mixture was stirred at reflux for 3 h, then concentrated in vacuo. The residue was diluted with H_2O (10 mL) and extracted with EtOAc (3 × 10 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by silica flash chromatography (100% hexanes) afforded the title compound (1.36 g, 94%, 5:3 *E*:*Z*) as a colorless oil. R_f = 0.50 (20:1 hexanes/Et_2O); IR (neat) ν_{max} 1581, 1469, 1437, 1274, 1241, 1016, 996, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.75 (m, 1 H), 7.30 – 7.24 (m, 1 H), 6.84 – 6.80 (m, 1 H), 6.72 – 7.67 (m, 1 H), 5.70 – 5.65 (m, 1 H), 4.44 (br s, 2 H), 1.88 – 1.54 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 139.5, 131.3, 129.4, 123.3, 122.5, 112.7, 86.9, 75.0, 13.8, 13.4; HRMS (ESI-TOF) calcd. for $C_{11}H_{13}IONa^+$ [M + Na^+] 310.9903, found 310.9889. See: Janusz, J. M.;

Young, P. A.; Scherz, M. W.; Enzweiler, K.; Wu, L. I.; Gan, L.; Pikul, S.; McDow-Dunham, K. L.; Johnson, C. R.; Senanayake, C. B.; Kellstein, D. E.; Green, S. A.; Tulich, J. L.; Rosario-Jansen, T.; Magrisso, I. J.; Wehmeyer, K. R.; Kuhlenbeck, D. L.; Eichhold, T. H.; Dobson, R. L. M. *J. Med. Chem* **1998**, *41*, 1124–1137. (similar substrate)



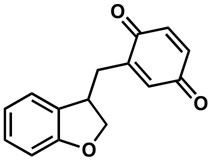
(*E*)-(2-((2-Methylbut-2-en-1-yl)oxy)phenyl)boronic acid (S35)

According to the "in situ quench" method of Reider,[2] a solution of aryl iodide (1.09 g, 3.98 mmol, 1.0 equiv, azeotroped with benzene 2 × 10 mL) and (iPrO)$_3$B (0.96 mL, 4.38 mmol, 1.1 equiv, freshly distilled over sodium metal) in toluene–THF (4:1 v/v, 19 mL) at −78 °C under argon was treated with *n*BuLi (1.90 mL, 2.3 M in hexanes, 4.38 mmol, 1.1 equiv) dropwise via syringe pump over 30 min. The reaction mixture was stirred at −78 °C for an additional 60 min, then allowed to warm to −20 °C. The reaction mixture dwas quenched by the addition of 2 N aqueous HCl (15 mL), and the mixture was allowed to warm to room temperature. The layers were separated, and the aqueous layer was extracted with Et$_2$O (2 × 30 mL). The organic layers were combined, dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. Purification by silica flash chromatography (10:1 → 2:1 hexanes/EtOAc) afforded the title compound (653 mg, 68%, 5:3 *E*:Z) as a colorless oil; R$_f$ = 0.42 (3:1 hexanes/EtOAc); IR (neat) ν_{max} 3404, 1599, 1446, 1337, 1319, 1213, 1133, 990, 756 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.87 – 7.84 (m, 1 H), 7.45 – 7.40 (m, 1 H), 7.05 – 6.90 (m, 2 H), 6.19 (s, 2 H), 5.69 – 5.57 (m, 1 H), 4.62 – 4.49 (m, 3 H), 1.85 – 1.63 (m, 7 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 164.2, 136.9, 132.9, 130.9, 125.2, 121.3, 111.4, 74.9, 21.7, 13.5; HRMS (ESI-TOF) calcd. for C$_{11}$H$_{15}$BO$_3$H$^+$ [M + H$^+$] 207.1187, found 207.1190.

Standard Procedure for tandem radical cyclization/trap

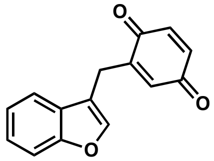
To a solution of 1,4-benzoquinone (0.1 mmol, 1.0 equiv) in trifluorotoluene (0.5 mL) and water (0.5 mL) were added the arylboronic acid or trifluoroborate (0.15 mmol, 1.5 equiv), silver(I) nitrate (0.02 mmol, 0.2 equiv), and potassium persulfate (0.3 mmol, 3.0 equiv). The reaction mixture was stirred vigorously at 60 °C for 60 min. The reaction mixture was diluted with EtOAc (3 mL) and washed with 5% aqueous $NaHCO_3$ (3 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 3 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification was performed by silica gel chromatography to yield chromatographically and spectroscopically pure product.

Compounds **16** and **17** were obtained as a 5:1 mixture in 71% yield, separable by silica gel chromatography. As such, they are described individually.



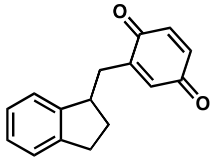
2-((2,3-Dihydrobenzofuran-3-yl)methyl)cyclohexa-2,5-diene-1,4-dione (16)

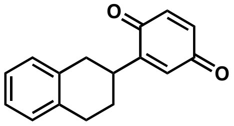
A yellow oil; $R_f = 0.50$ (100% CH_2Cl_2); IR (neat) ν_{max} 3378, 2923, 1654, 1598, 1480, 1452, 1226, 1194, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.8 Hz, 1 H), 7.12 (d, *J* = 7.1 Hz, 1 H), 6.86 (t, *J* = 7.4 Hz, 1 H), 6.82 – 6.74 (m, 2 H), 6.80 (d, *J* = 7.1 Hz, 1 H), 6.45 (d, *J* = 1.0 Hz, 1 H), 4.56 (t, *J* = 8.8 Hz, 1 H), 4.24 (dd, *J* = 9.1, 5.0 Hz, 1 H), 3.71 – 3.64 (m, 1 H), 2.86 (dd, *J* = 14.2, 5.9 Hz, 1 H), 2.64 (dd, *J*= 14.2, 8.2 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.5, 187.4, 159.8, 146.1, 136.9, 136.6, 134.1, 129.3, 129.0, 124.6, 120.8, 110.0, 76.1, 40.6, 35.2; HRMS (ESI-TOF) calcd. for $C_{15}H_{12}O_3H^+$ [M + H^+] 241.0859, found 241.0865.



2-(Benzofuran-3-ylmethyl)cyclohexa-2,5-diene-1,4-dione (17)

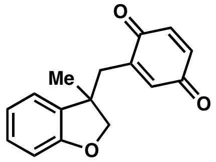
A yellow oil; R_f = 0.60 (100% CH_2Cl_2); IR (neat) ν_{max} 3411, 3062, 1654, 1600, 1452, 1289, 1184, 1095, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1 H), 7.50 (d, J = 8.2 Hz, 1 H), 7.42 (d, J = 7.8 Hz, 1 H), 7.31 (t, J = 7.1 Hz, 1 H), 7.23 (t, J = 7.1 Hz, 1 H), 6.81 (d, J = 10.1 Hz, 1 H), 6.72 (dd, J = 10.0, 2.5 Hz, 1 H), 6.47 – 6.45 (m, 1 H), 3.84 (br s, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.7, 187.3, 155.6, 146.8, 143.4, 136.8, 136.6, 133.2, 127.3, 124.8, 123.0, 119.5, 115.0, 111.9, 23.3; HRMS (ESI-TOF) calcd. for $C_{15}H_{10}O_3H^+$ [M + H^+] 239.0703, found 239.0700.





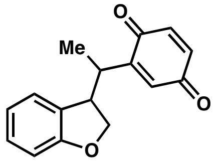
2-((2,3-Dihydro-1*H*-inden-1-yl)methyl)cyclohexa-2,5-diene-1,4-dione (18) and 2-(1,2,3,4-Tetrahydronaphthalen-2-yl)cyclohexa-2,5-diene-1,4-dione (19)

An amber oil (1:1 mixture in 61% yield, inseparable by silica gel chromatography); R_f = 0.70 (100% CH_2Cl_2); IR (neat) ν_{max} 2929, 1654, 1598, 1293, 908, 750 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.24 – 7.06 (m, 4 H), 6.81 – 6.78 (m, 1 H), 6.76 – 6.73 (m, 1 H), 6.58 (br s, 1 H), 3.40 – 3.36 (m, 0.5 H), 3.20 – 3.16 (m, 0.5 H), 3.01 – 2.89 (m, 2.5 H), 2.88 – 2.81 (m, 0.5 H), 2.71 (dd, J = Hz, 0.5 H), 2.46 (dd, J = 14.2, 9.6 Hz, 0.5 H), 2.24 – 2.18 (m, 0.5 H), 2.04 – 2.01 (m, 0.5 H), 1.77 – 1.65 (m, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.0, 187.8, 187.6, 187.1, 152.9, 148.0, 145.9, 143.8, 137.2, 136.9, 136.5, 136.2, 135.7, 135.2, 133.7, 131.3, 129.1, 129.0, 127.0, 126.4, 126.2, 126.0, 124.8, 123.8, 43.4, 35.0, 35.0, 33.2, 31.9, 31.2, 29.0, 28.1; HRMS (ESI-TOF) calcd. for $C_{16}H_{14}O_2H^+$ [M + H^+] 239.1067, found 239.1071.



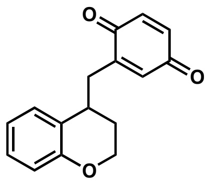
2-((3-Methyl-2,3-dihydrobenzofuran-3-yl)methyl)cyclohexa-2,5-diene-1,4-dione (20)

The standard procedure was followed with a reaction time of 60 min to provide the product (76%; gram scale: 60%) as a yellow-orange solid; m.p. 75−77 °C; R_f = 0.47 (4:1 hexanes/EtOAc); IR (neat) ν_{max} 2963, 1655, 1597, 1480, 1294, 976, 754 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (t, *J* = 7.7 Hz, 1 H), 7.09 (d, *J* = 7.3 Hz, 1 H), 6.92 (t, *J* = 7.4 Hz, 1 H), 6.73 – 6.70 (m, 2 H), 6.62 (dd, *J* = 10.0 Hz, 2.4 Hz, 1 H), 5.84 – 5.82 (m, 1 H), 4.38 (d, *J* = 8.8 Hz, 1 H), 4.01 (d, *J* = 9.0 Hz, 1 H), 2.95 (d, *J* = 12.6 Hz, 1 H), 2.39 (d, *J* = 12.6 Hz, 1 H), 1.45 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.5, 187.2, 159.6, 144.9, 136.8, 136.2, 134.7, 132.8, 129.0, 122.9, 121.1, 110.2, 81.6, 46.9, 39.2, 24.4; HRMS (ESI-TOF) calcd. for $C_{16}H_{14}O_3H^+$ [M + H$^+$] 255.1016, found 255.1020.



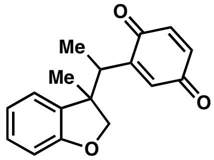
2-(1-(2,3-Dihydrobenzofuran-3-yl)ethyl)cyclohexa-2,5-diene-1,4-dione (21)

The standard procedure was followed with a reaction time of 60 min to provide the product (64%, 1:1 d.r.) as an amber oil; R_f = 0.60 (100% CH_2Cl_2); IR (neat) ν_{max} 3382, 1653, 1597, 1479, 1452, 1190, 749 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 – 7.13 (m, 3 H), 6.96 (d, *J* = 7.3 Hz, 1 H), 6.87 (t, *J* = 7.4 Hz, 1 H), 6.82 – 6.75 (m, 6 H), 6.73 – 6.71 (m, 1 H), 6.43 – 6.42 (m, 1 H), 6.30 (d, *J* = 1.8 Hz, 1 H), 4.58 (t, *J* = 9.0 Hz, 1 H), 4.40– 4.36 (m, 2 H), 4.33 – 4.30 (m, 1 H), 3.66 – 3.61 (m, 1 H), 3.58 – 3.54 (m, 1 H), 3.39 – 3.33 (m, 1 H), 3.23 – 3.17 (m, 1 H), 1.06 (d, *J* = 7.0 Hz, 3 H), 1.05 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.6, 187.6, 187.4, 187.1, 160.7, 160.3, 150.7, 150.6, 137.2, 137.2, 136.3, 136.2, 133.1, 132.4, 129.1, 129.1, 128.0, 126.9, 125.7, 124.8, 120.8, 120.3, 109.9, 109.9, 75.9, 73.3, 46.0, 45.1, 36.6, 35.6, 14.4, 13.9; HRMS (ESI-TOF) calcd. for $C_{16}H_{14}O_3Na^+$ [M + Na$^+$] 277.0835, found 277.0839.



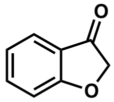
2-(Chroman-4-ylmethyl)cyclohexa-2,5-diene-1,4-dione (22)

The Standard Procedure was followed with a reaction time of 60 min to provide the product (54%) as an amber oil; R_f = 0.60 (100% CH_2Cl_2); IR (neat) ν_{max} 2929, 1654, 1489, 1292, 1223, 1067, 757 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.7 Hz, 1 H), 7.14 – 7.10 (m, 1 H), 6.88 (td, *J* = 7.5, 1.2 Hz, 1 H), 6.82 (dd, *J* = 8.2, 1.2 Hz, 1 H), 6.81 (d, *J* = 10.0 Hz, 1 H), 6.77 (dd, *J* = 10.1, 2.5 Hz, 1 H), 6.58 – 6.56 (m, 1 H), 4.20 – 4.18 (m, 2 H), 3.09 – 3.05 (m, 1 H), 3.00 (ddd, *J* = 13.7, 4.8, 1.3 Hz, 1 H), 2.57 – 2.53 (m, 1 H), 2.04 – 1.99 (m, 1 H), 1.74 – 1.70 (m, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.6, 187.5, 154.5, 147.1, 137.0, 136.6, 134.5, 129.4, 128.1, 124.8, 120.5, 117.2, 62.8, 36.8, 32.8, 26.5; HRMS (ESI-TOF) calcd. for $C_{16}H_{14}O_3H^+$ [M + H$^+$] 255.1016, found 255.1019.



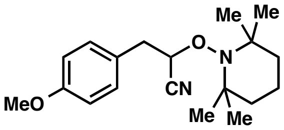
2-(1-(3-Methyl-2,3-dihydrobenzofuran-3-yl)ethyl)cyclohexa-2,5-diene-1,4-dione (23)

The standard procedure was followed with a reaction time of 60 min to provide the product (30%, 7:4 d.r.) as an amber oil; R_f = 0.60 (100% CH_2Cl_2); IR (neat) ν_{max} 3396, 2968, 1672, 1654, 1596, 1479, 1457, 1187, 1033, 753 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.6 Hz, 1 H), 6.96 (d, *J* = 7.4 Hz, 1 H), 6.84 (t, *J* = 7.4 Hz, 1 H), 6.70 (d, *J* = 7.5 Hz, 1 H), 6.64 – 6.59 (m, 2 H), 6.42 (s, 1 H), 4.62 (d, *J* = 9.3 Hz, 1 H), 4.09 (d, *J* = 9.3 Hz, 1 H), 3.40 (q, *J* = 6.9 Hz, 1 H), 1.35 (s, 3 H), 1.11 (d, *J* = 7.1 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.4, 186.6, 159.8, 150.7, 136.8, 135.8, 135.8, 133.2, 129.0, 124.4, 120.4, 110.0, 80.8, 49.1, 38.5, 24.6, 14.8; HRMS (ESI-TOF) calcd. for $C_{17}H_{16}O_3H^+$ [M + H$^+$] 269.1172, found 269.1182.



Benzofuran-3(2*H*)-one (24)

Isolated in a control experiment, following the Standard Procedure except omitting 1,4-benzoquinone. The title compound (~20% yield) was isolated using silica gel chromatography and verified by spectral comparison: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.7 Hz, 1 H), 7.62 (t, *J* = 7.8 Hz, 1 H), 7.15 (d, *J* = 8.4 Hz, 1 H), 7.10 (t, *J* = 7.4 Hz, 1 H), 4.63 (s, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.1, 174.2, 138.0, 124.2, 122.2, 121.3, 113.8, 74.8. See: Inoue, A.; Kitagawa, K.; Shinokubo, H.; Oshima, K. *J. Org. Chem.* **2001**, *66,* 4333–4339.



3-(4-Methoxyphenyl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanenitrile (S36)

4-Methoxyphenylboronic acid (46 mg, 0.3 mmol, 1.5 equiv) in CH_2Cl_2 (1.0 mL) and water (1.0 mL) was treated with TEMPO (31 mg, 0.2 mmol, 1.0 equiv), acrylonitrile (66 μL, 1.0 mmol, 5.0 equiv), silver(I) nitrate (6.8 mg, 0.04 mmol, 0.2 equiv), and potassium persulfate (162 mg, 0.6 mmol, 3.0 equiv). The reaction mixture was stirred vigorously at 23 °C for 90 min. The reaction was treated with ascorbic acid (106 mg, 0.6 mmol, 3.0 equiv) and stirred at 23 °C for 10 min. The reaction mixture was extracted with Et_2O (3 × 3 mL). The organic layers were combined, dried over

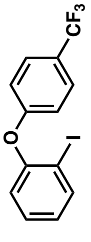
Na_2SO_4, filtered, and concentrated in vacuo. Purification was performed by silica gel chromatography (1:1 CH_2Cl_2/hexanes → 100% CH_2Cl_2) to yield the product (31 mg, 50%) as a pale yellow residue; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.6 Hz, 2 H), 6.87 (d, *J* = 8.6 Hz, 2 H), 4.74 (t, *J* = 6.7 Hz, 1 H), 3.80 (s, 3 H), 3.13 – 3.05 (m, 2 H), 1.59 – 1.40 (m, 5 H), 1.35 – 1.31 (m, 1 H), 1.27 (s, 3 H), 1.13 (s, 3 H), 1.09 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 131.0, 127.9, 126.9, 119.4, 114.3, 114.1, 75.5, 61.2, 60.1, 55.4, 40.1, 40.0, 38.6, 34.1, 33.8, 20.7, 20.5, 17.1. See: Heinrich, M. R.; Wetzel, A.; Kirschstein, M. *Org. Lett.* **2007**, *9*, 3833–3835.

References

(1) Darses, S.; Michaud, G.; Genet, J.-P. *Eur. J. Org. Chem.* **1999**, 1875–1883.

(2) Li, W.; Nelson, D. P.; Jensen, M. S.; Hoerrner, R. S.; Cai, D.; Larsen, R. D.; Reider, P. J. *J. Org. Chem.* **2002**, *67*, 5394–5397.

^{1}H and ^{13}C NMR Spectra for New Compounds



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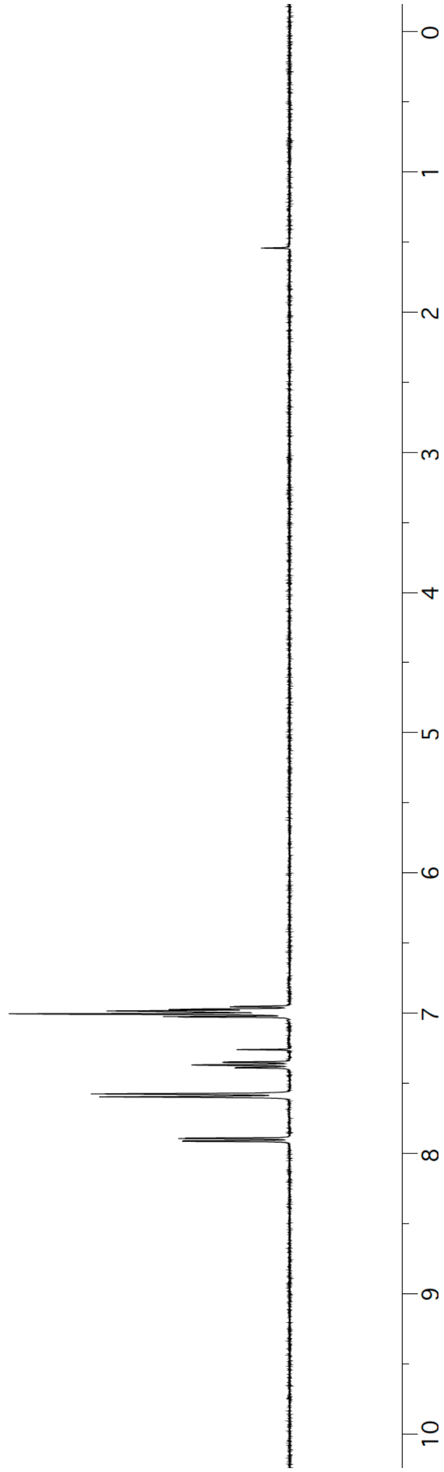

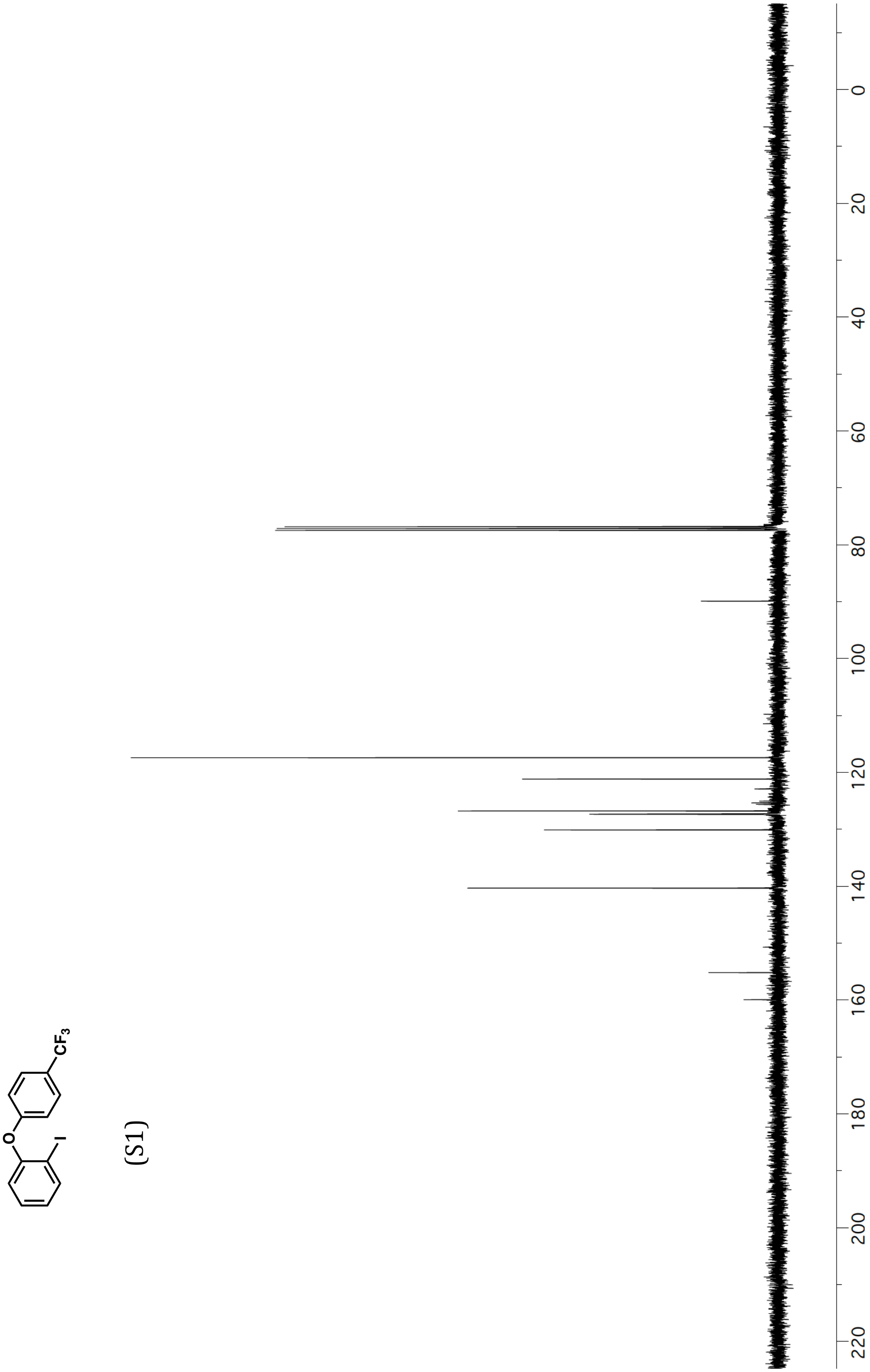

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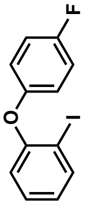

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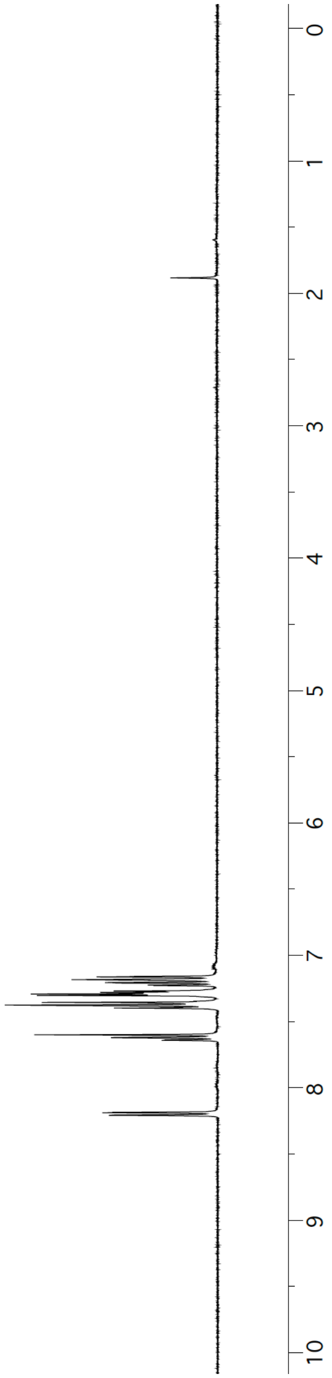

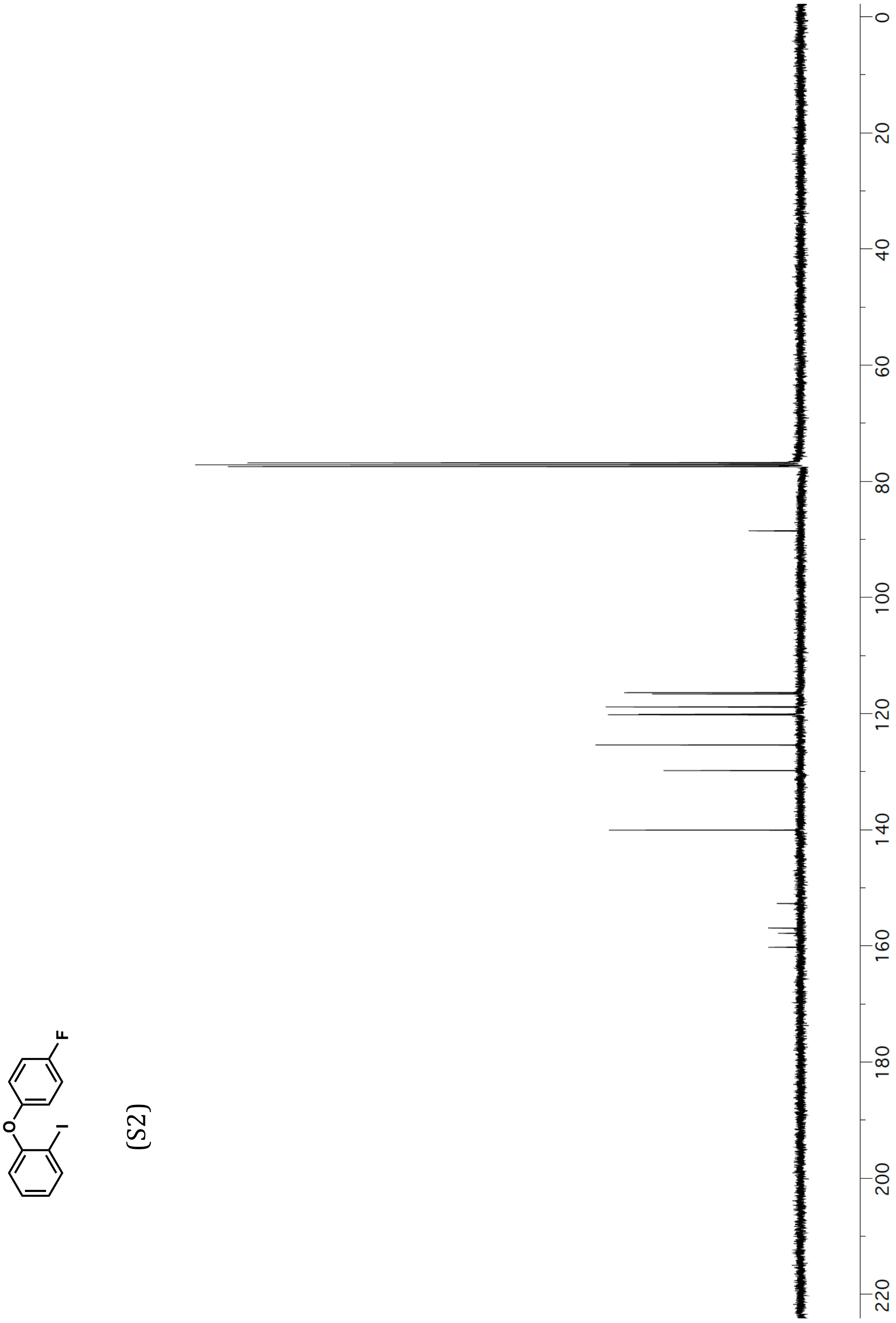

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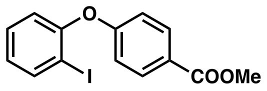

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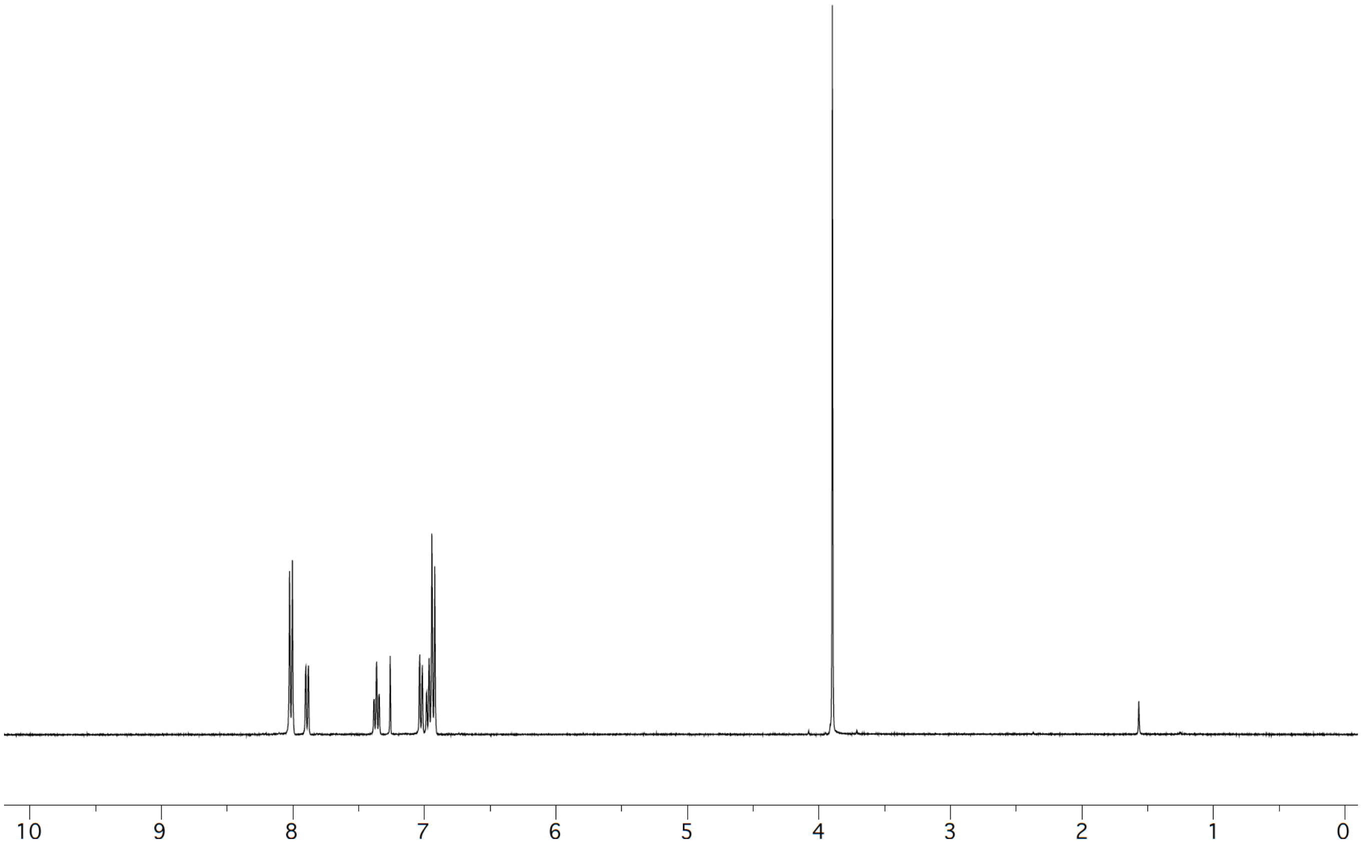

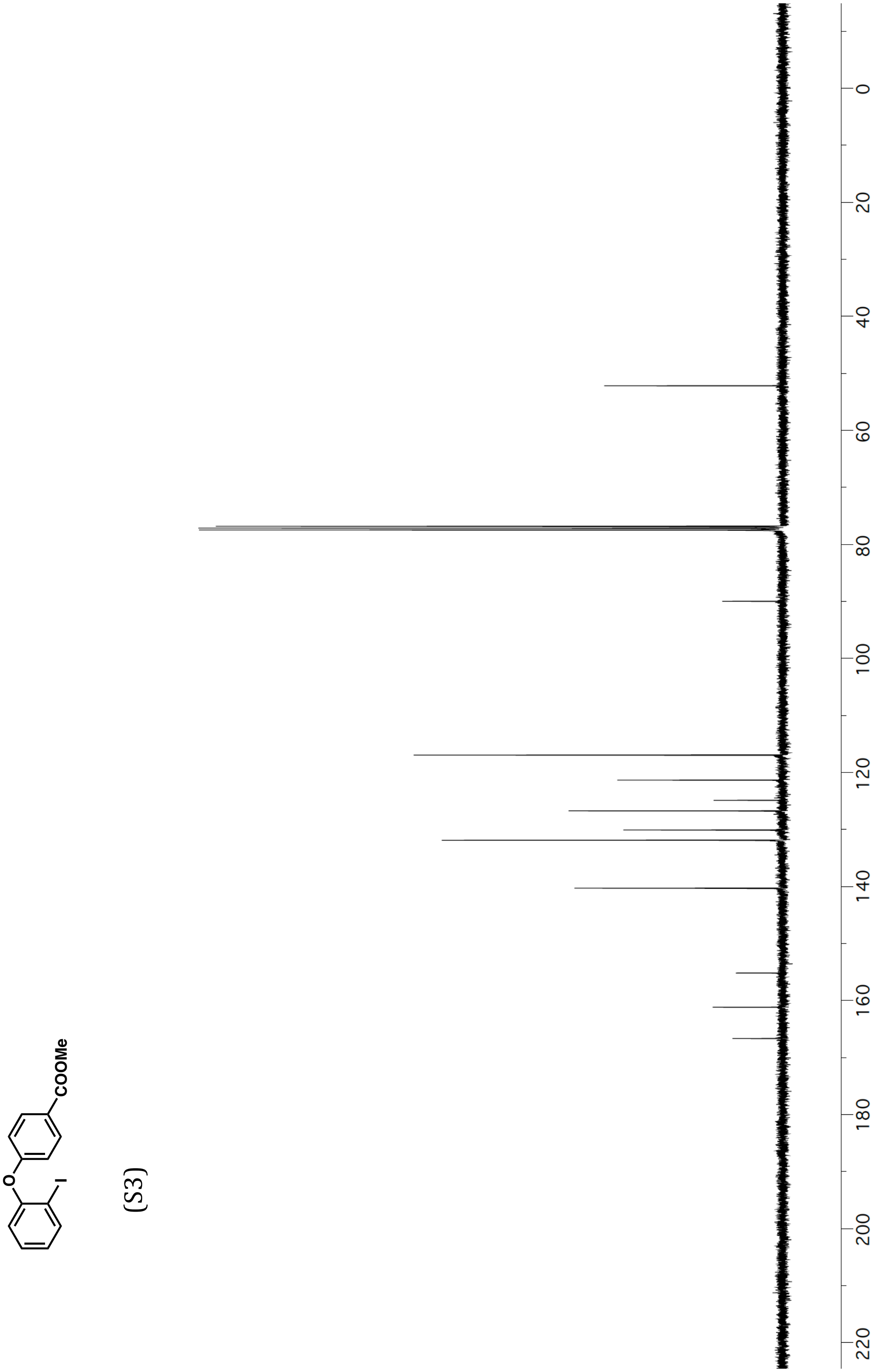

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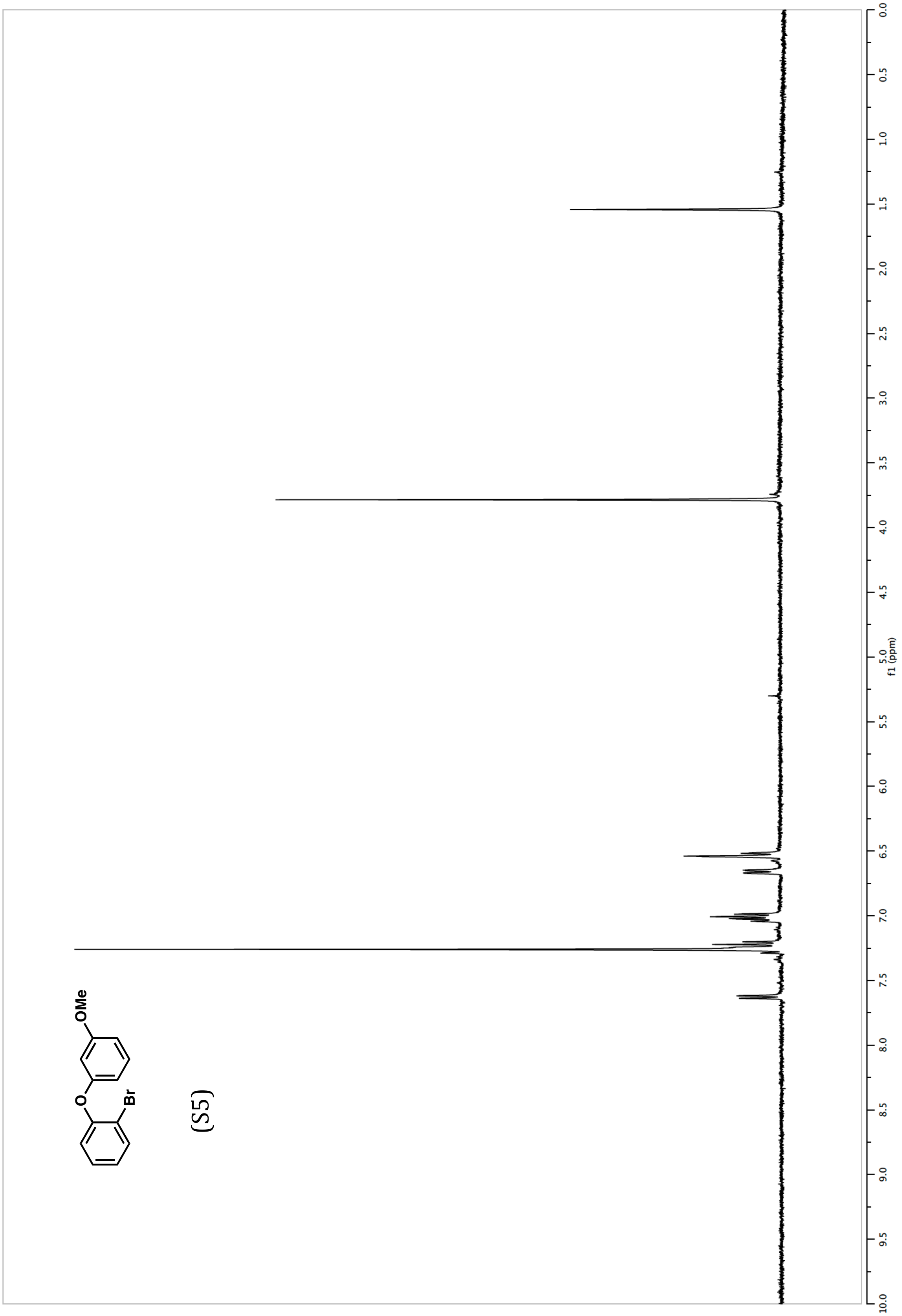
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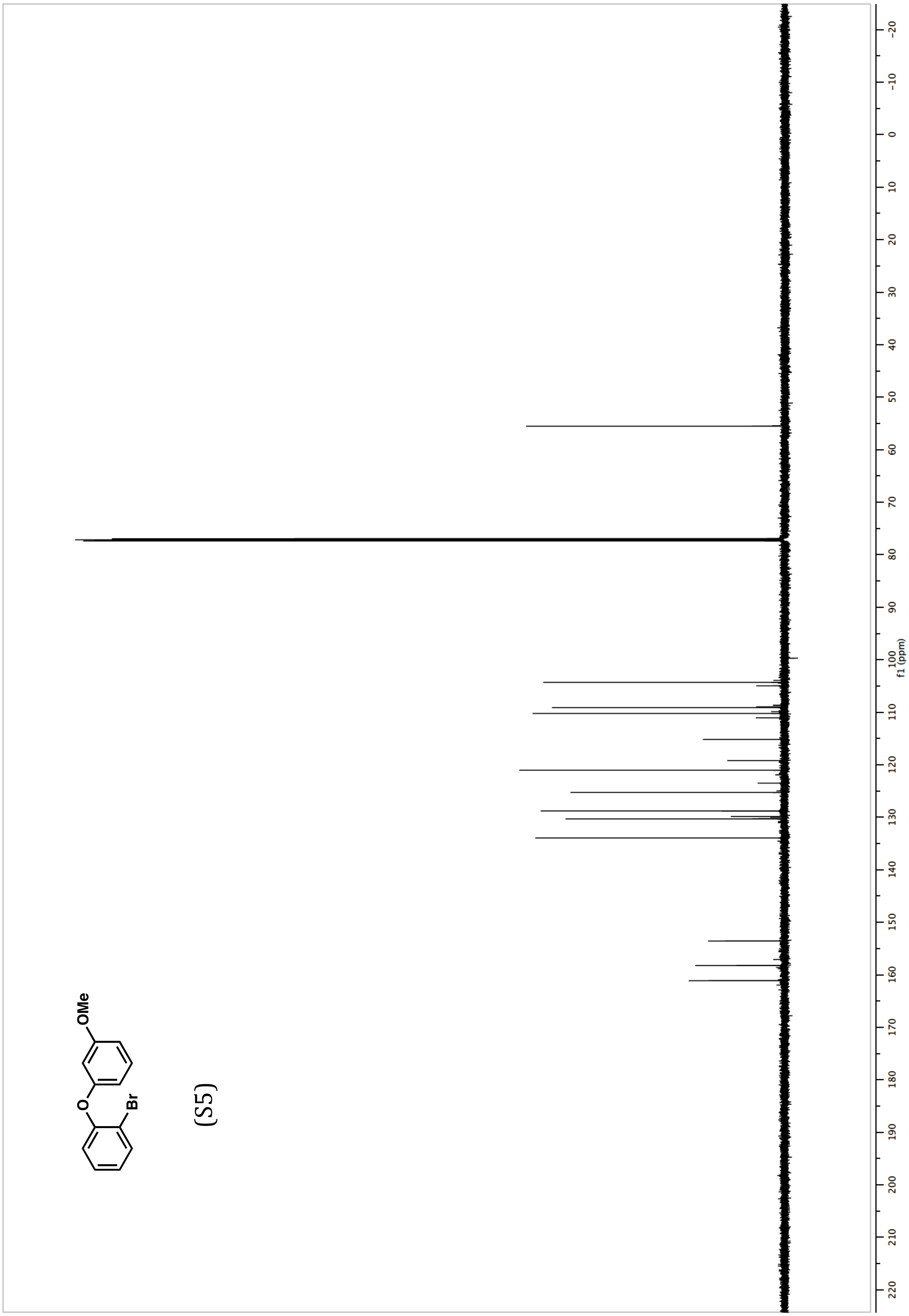
(S5)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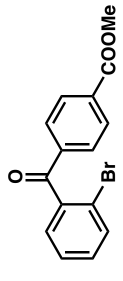
f1 (ppm)

(S5)



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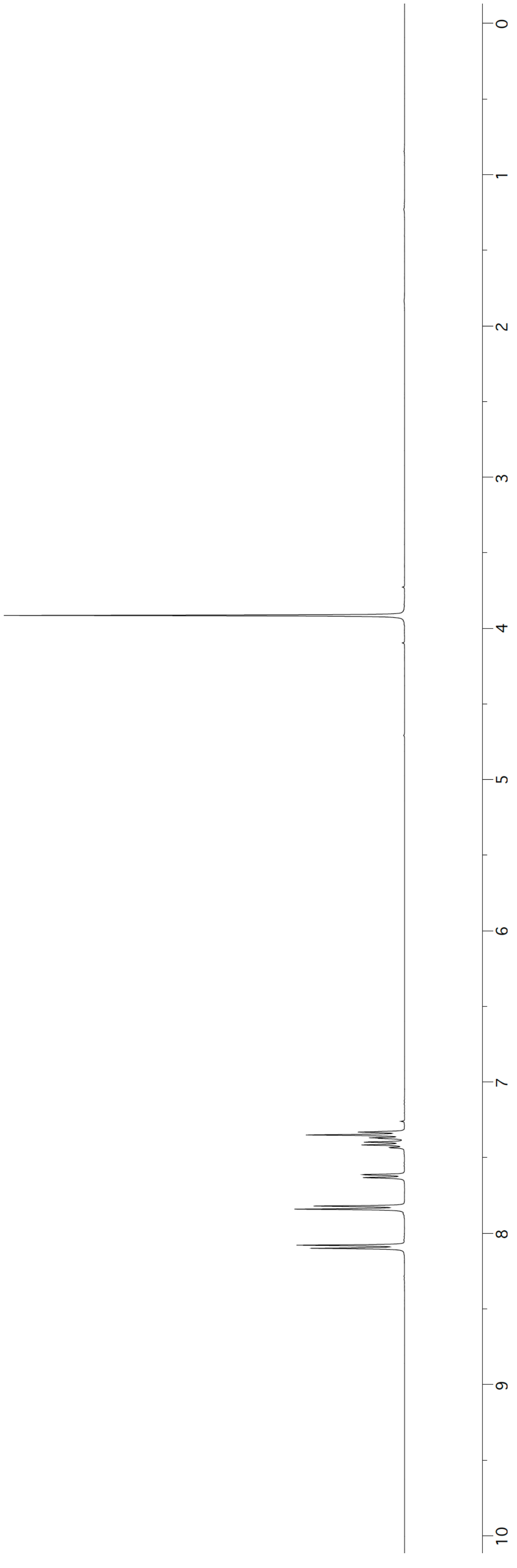

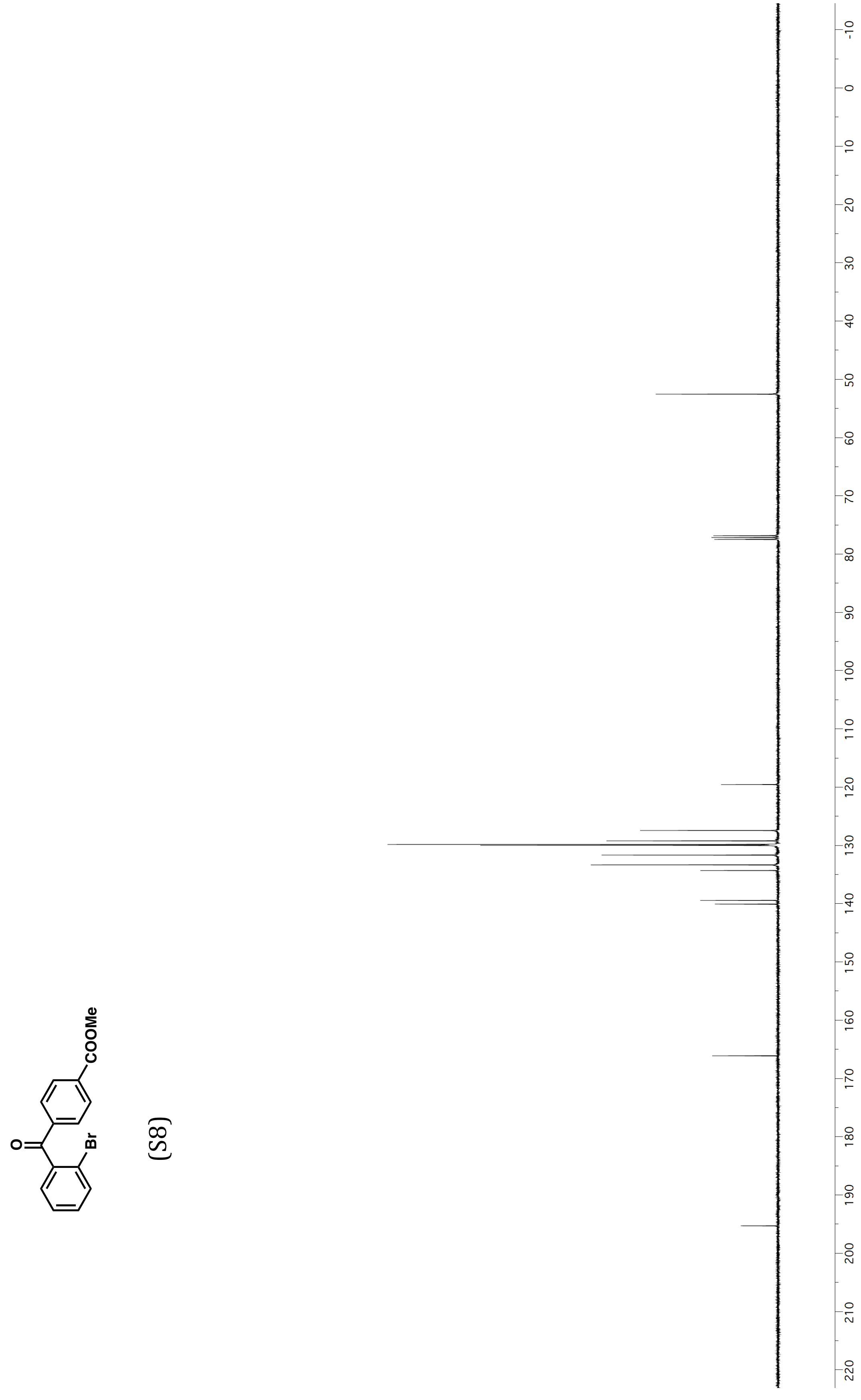
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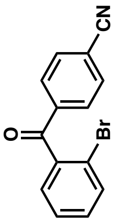
(S8)



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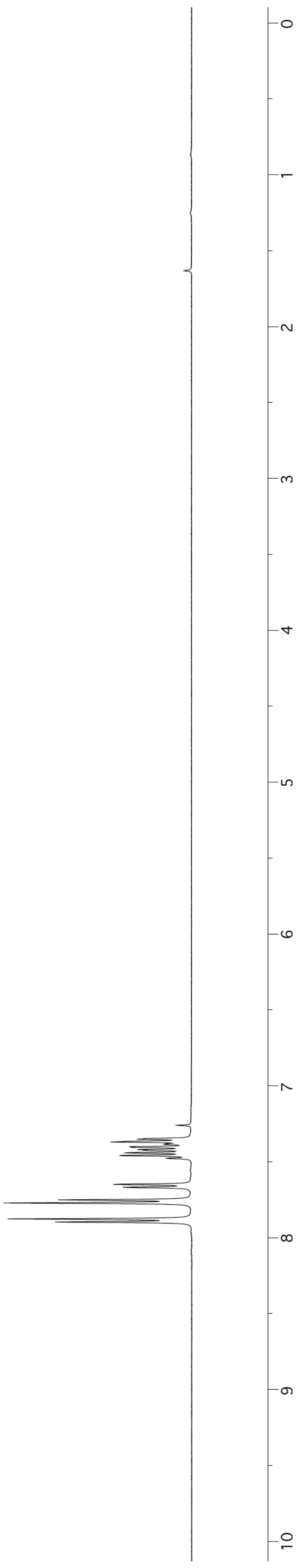

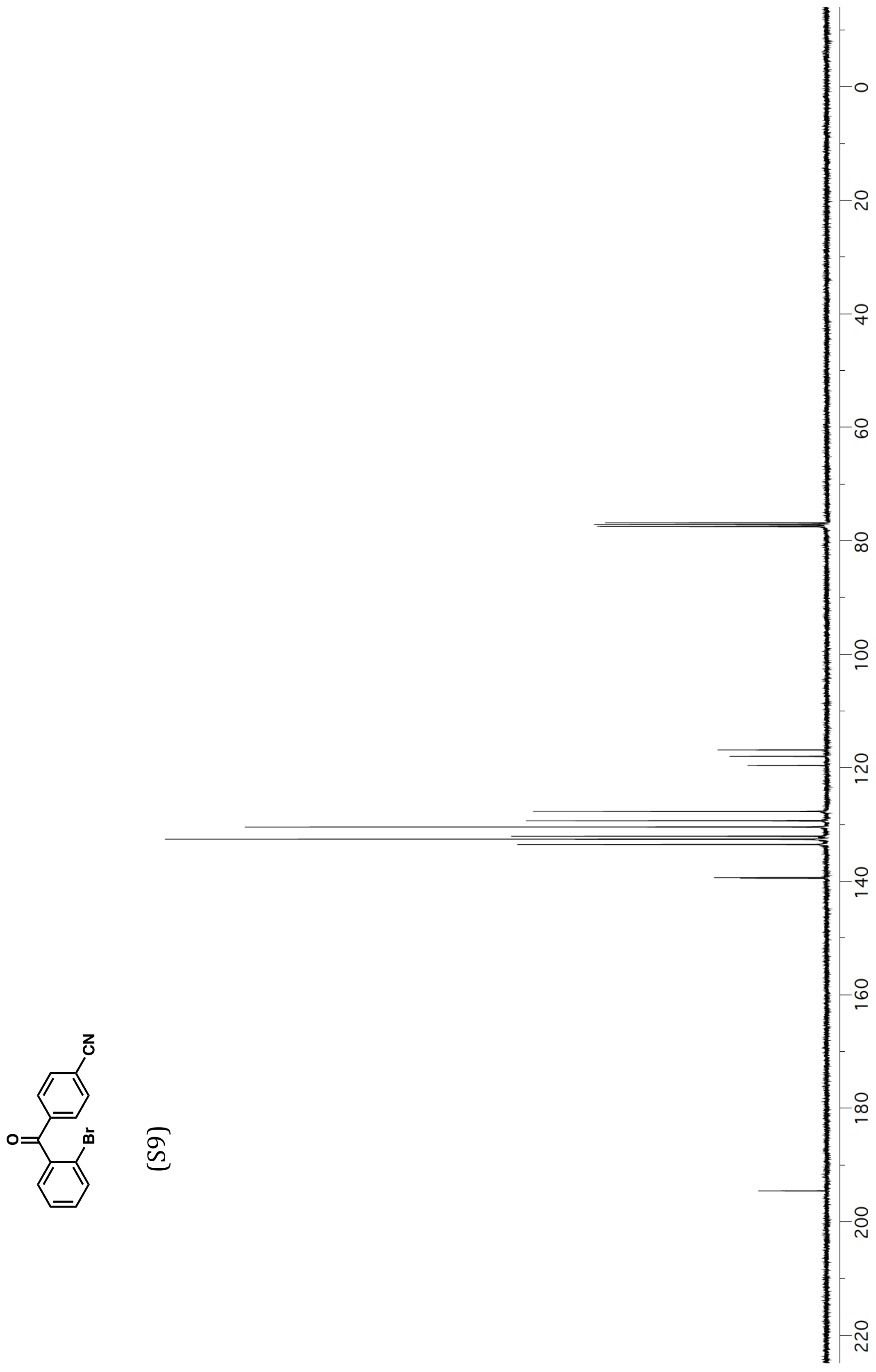

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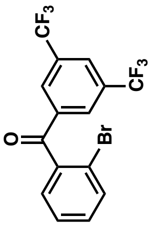

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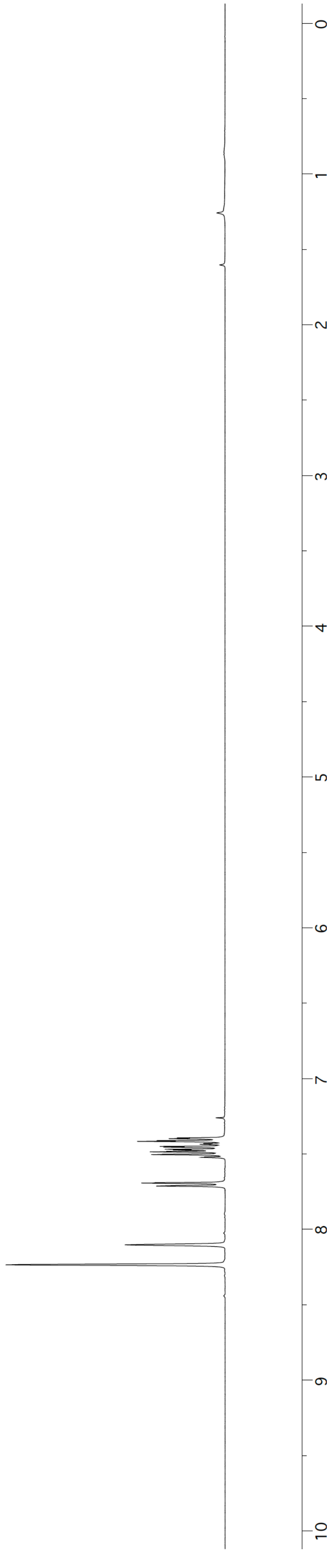

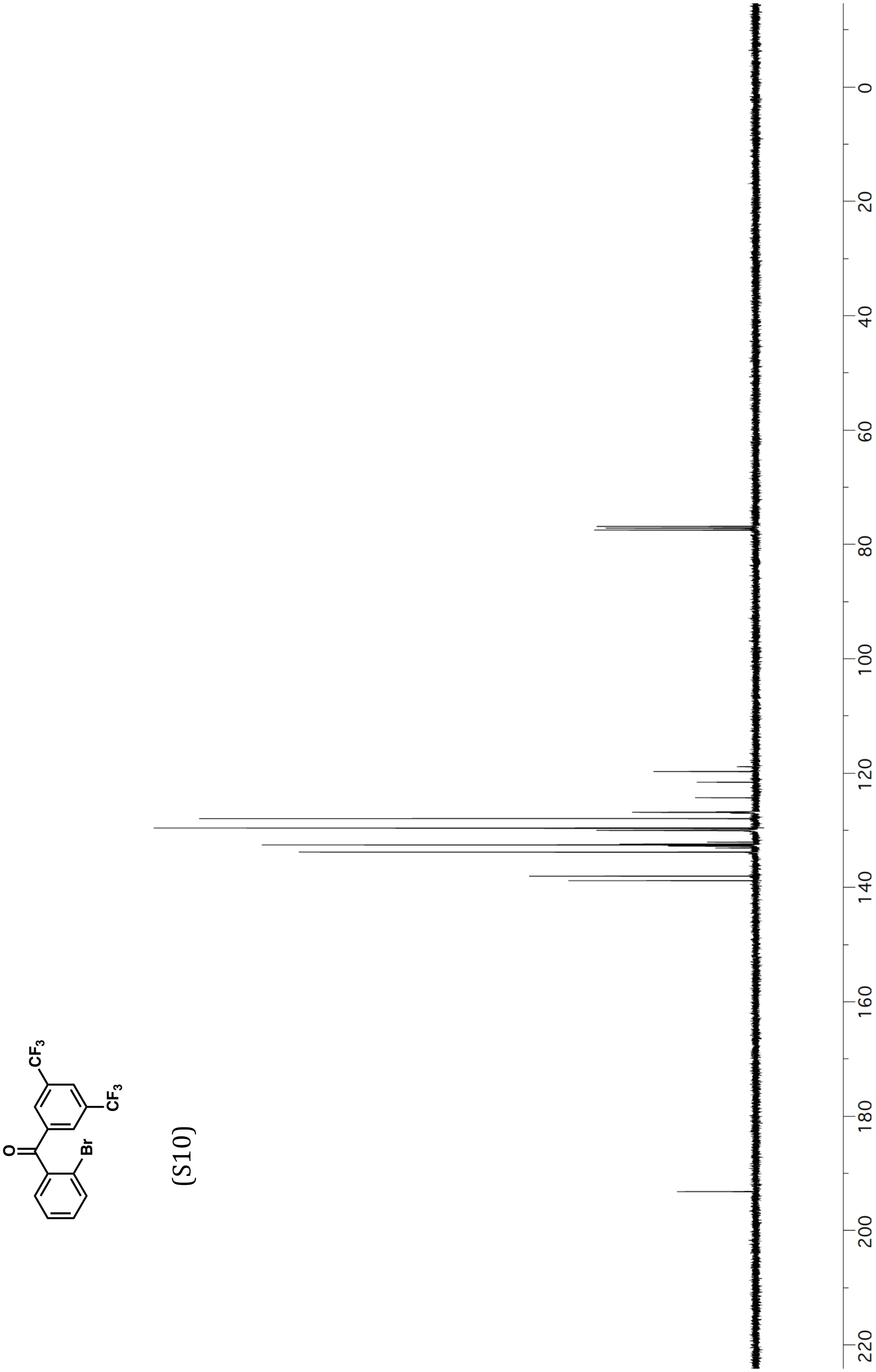

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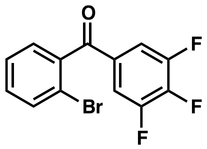

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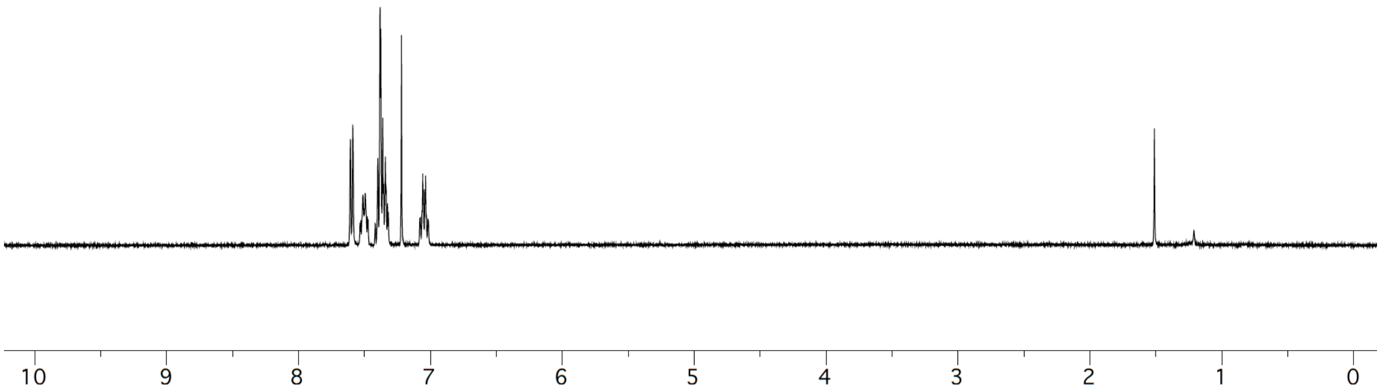

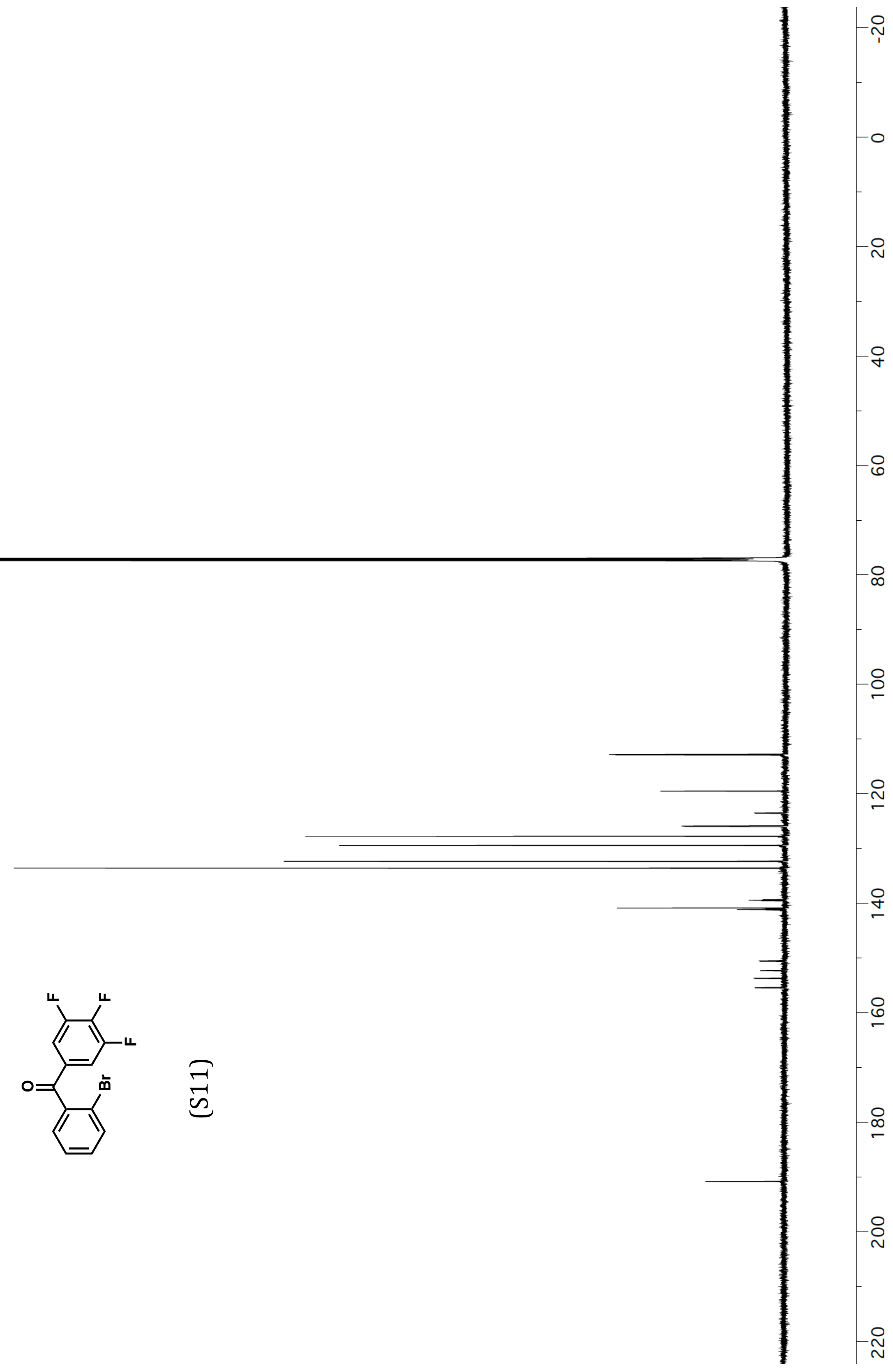

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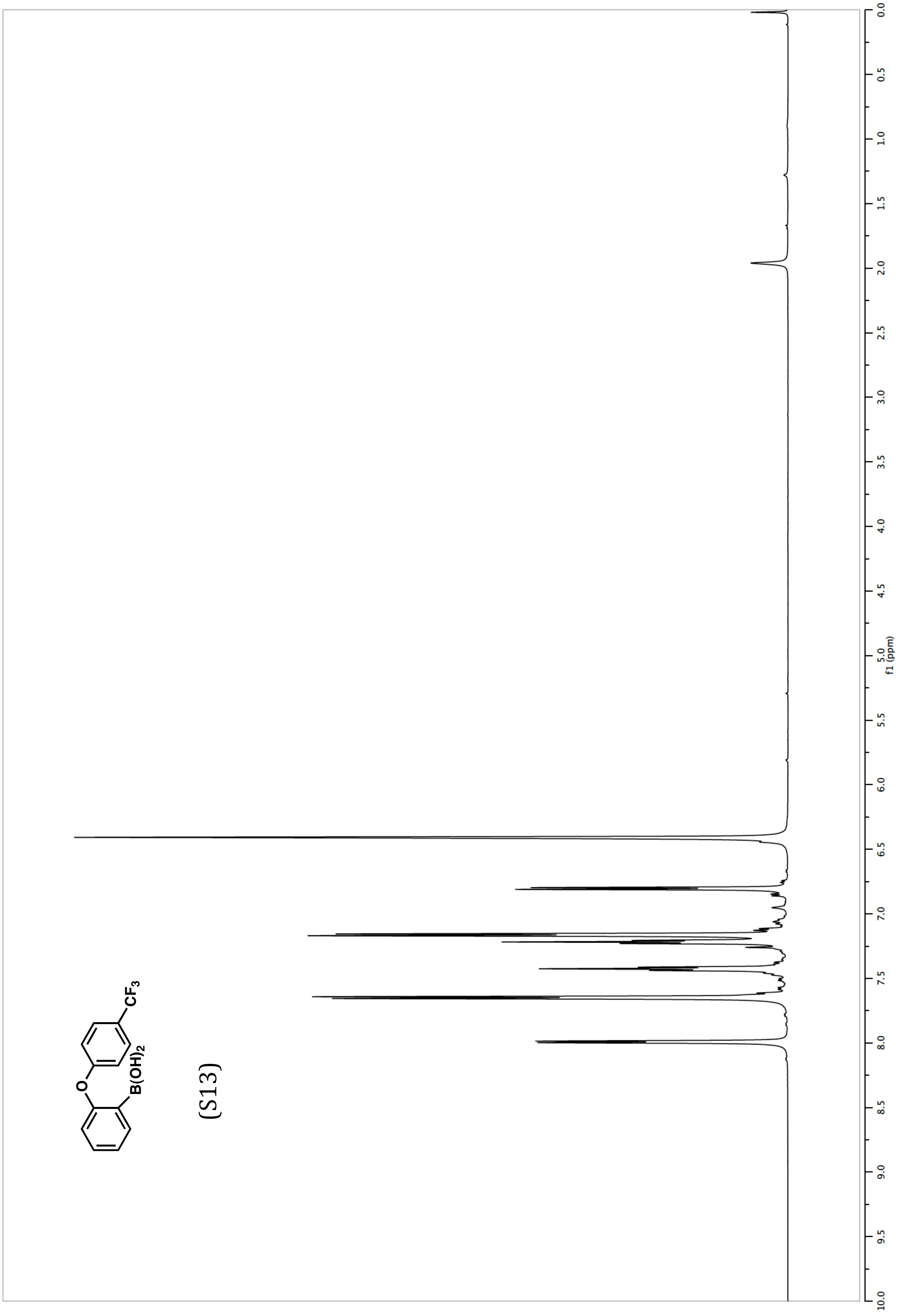

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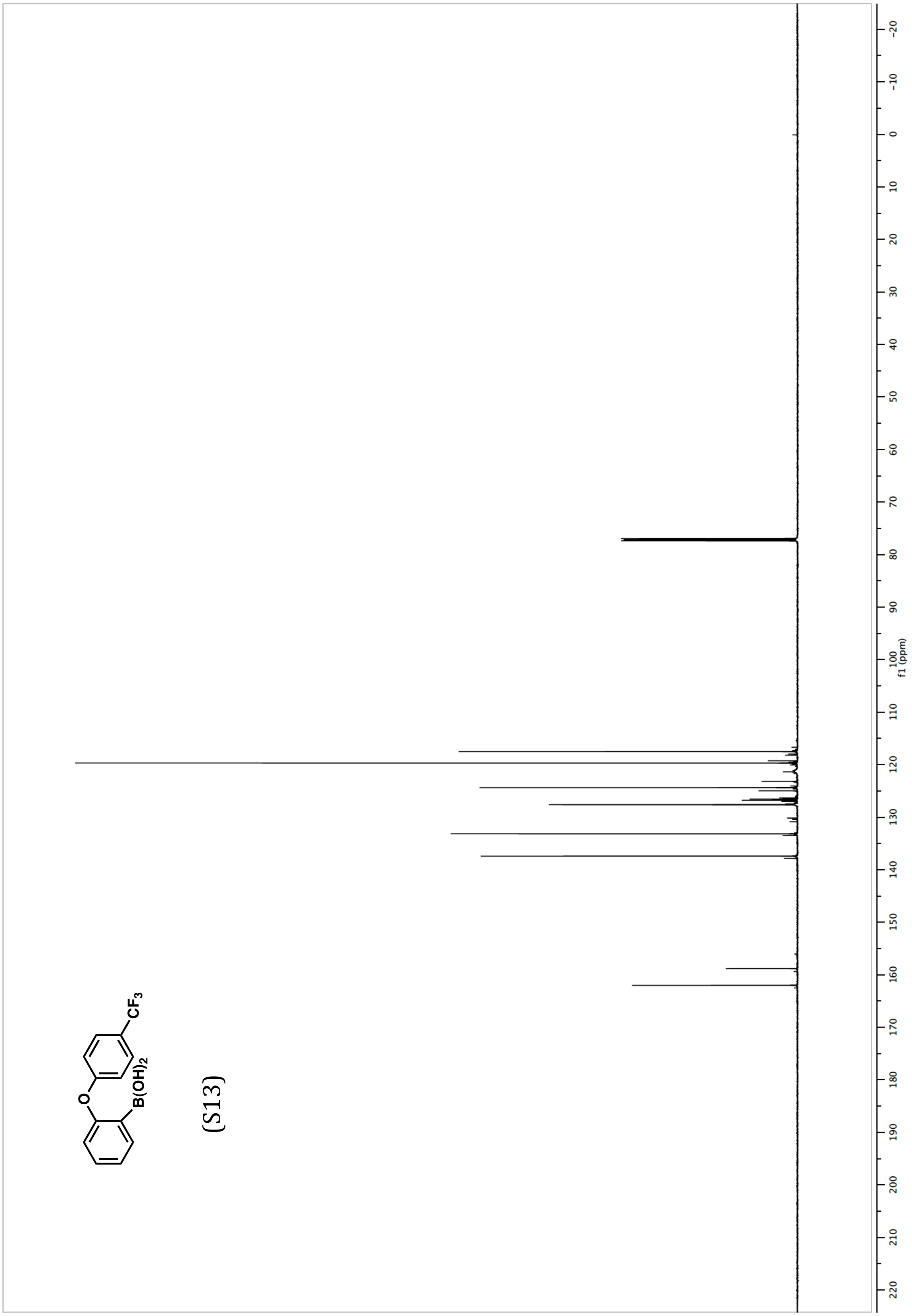

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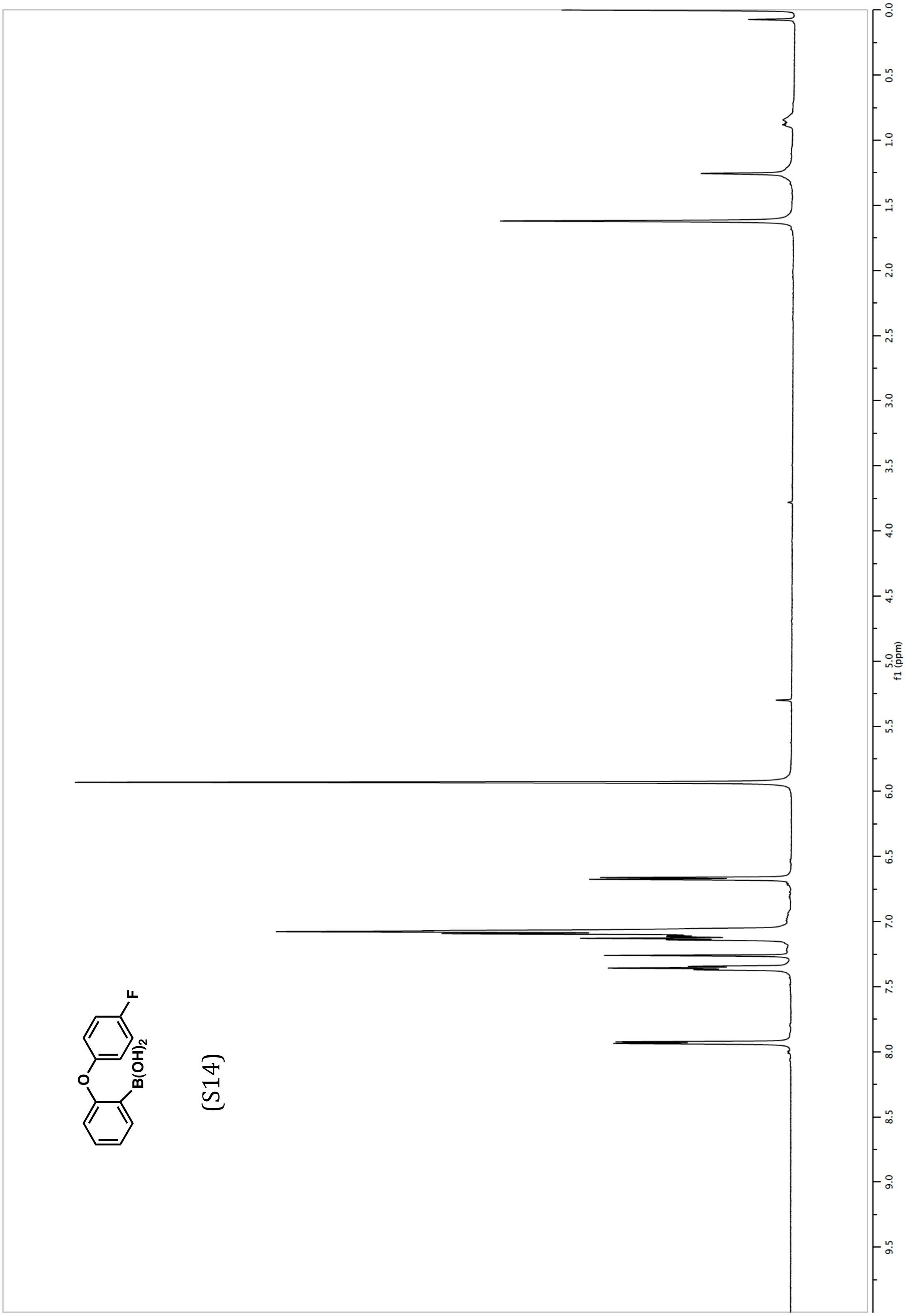
(S13)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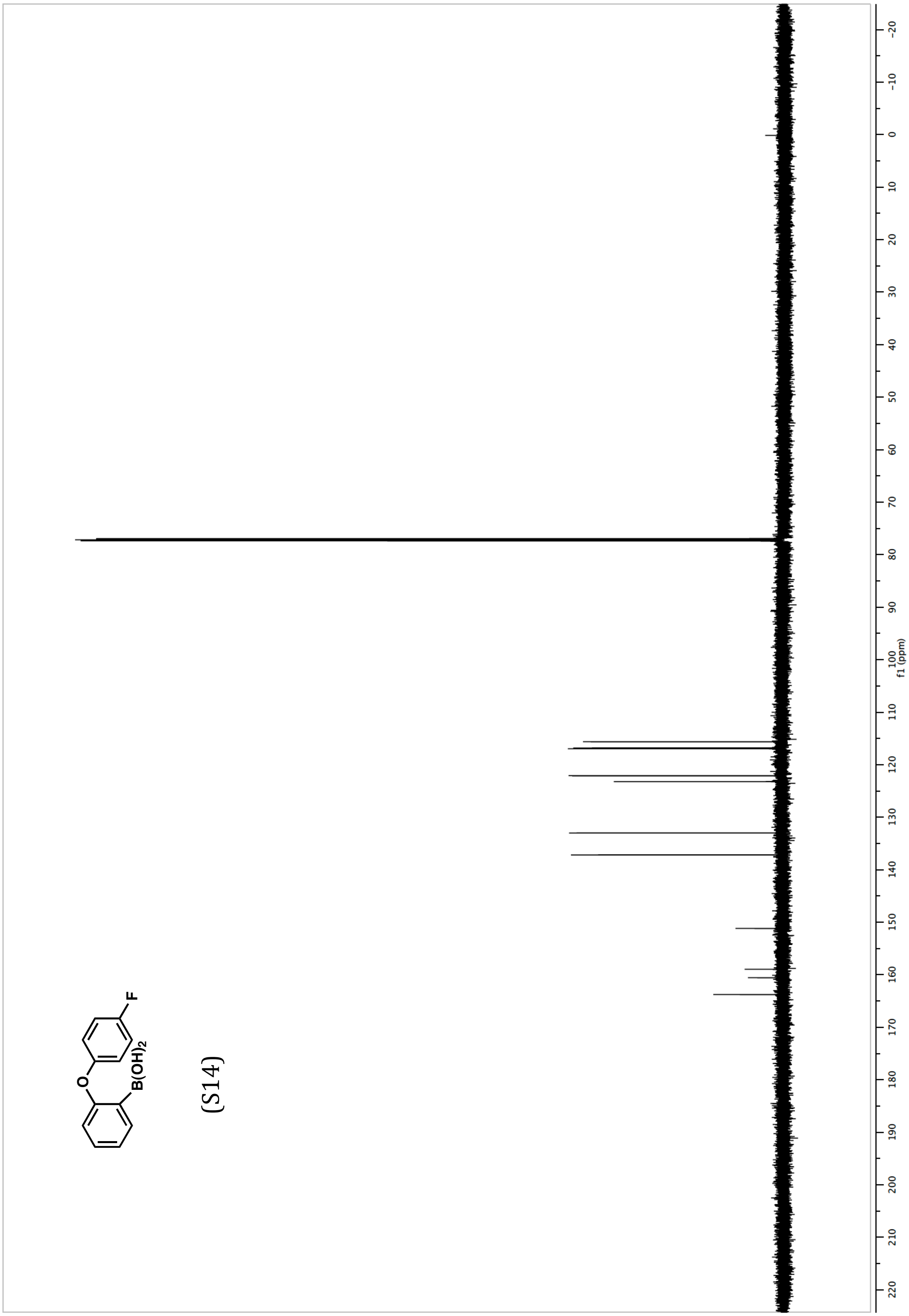
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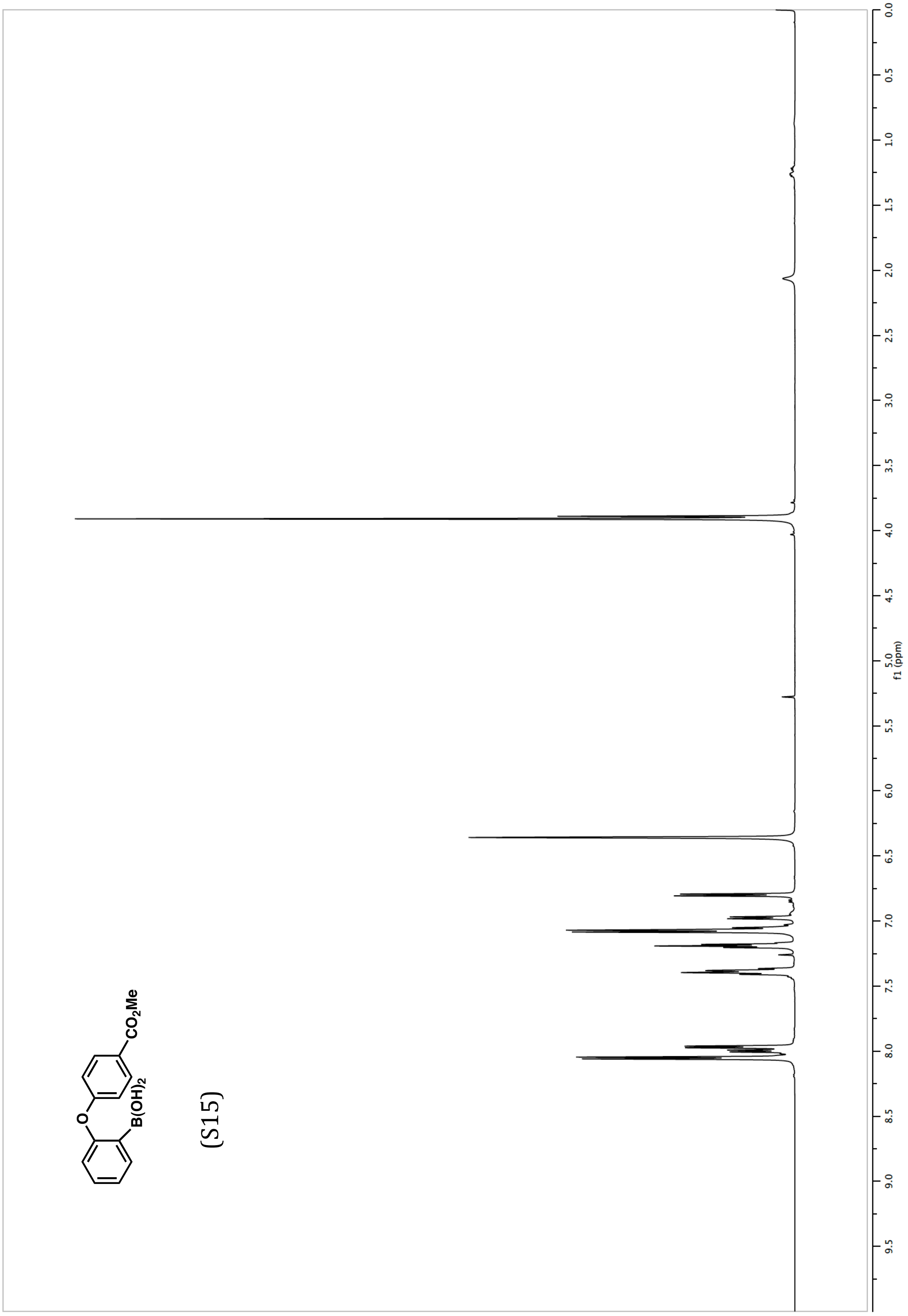
f1 (ppm)

(S14)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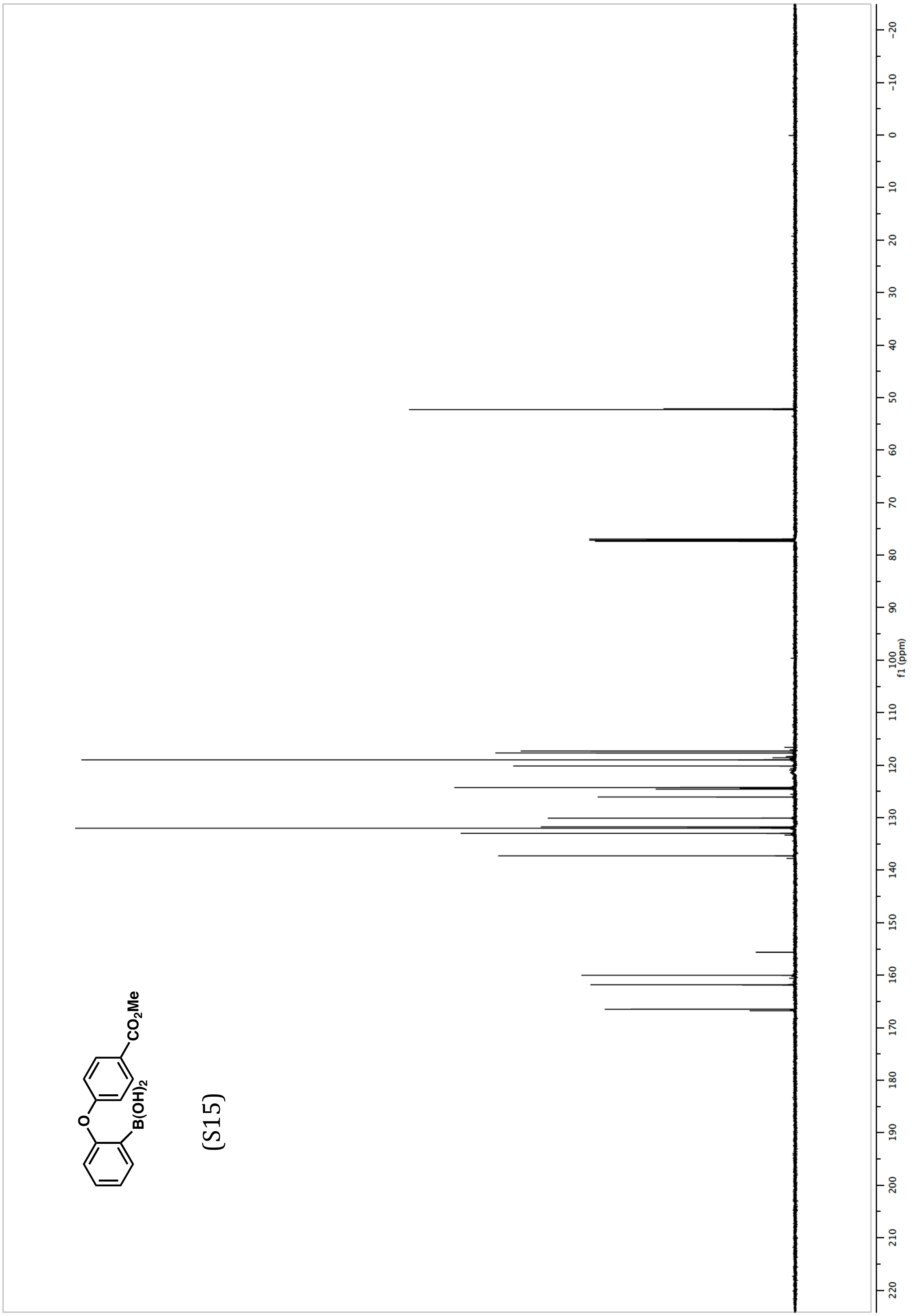
(S15)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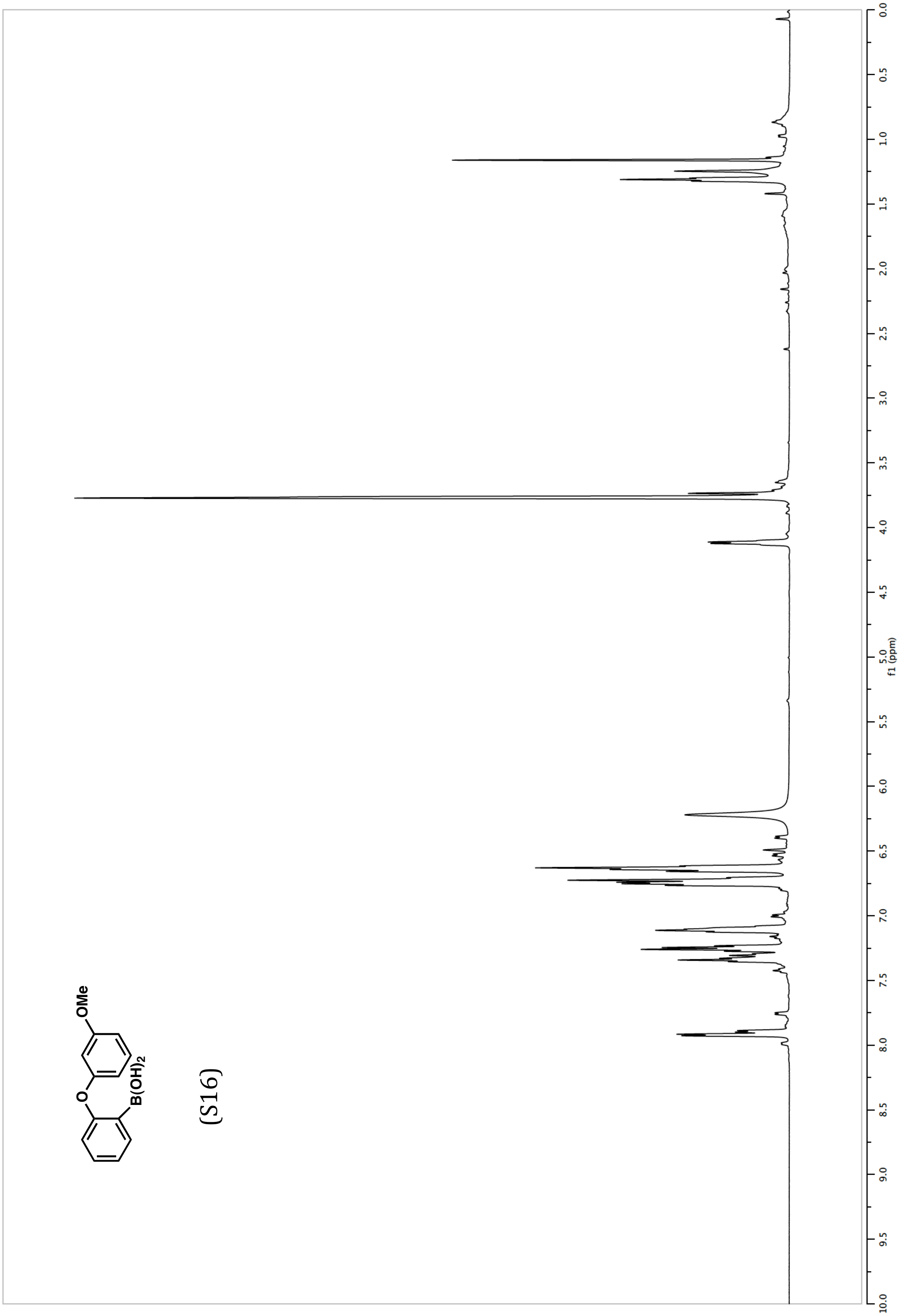
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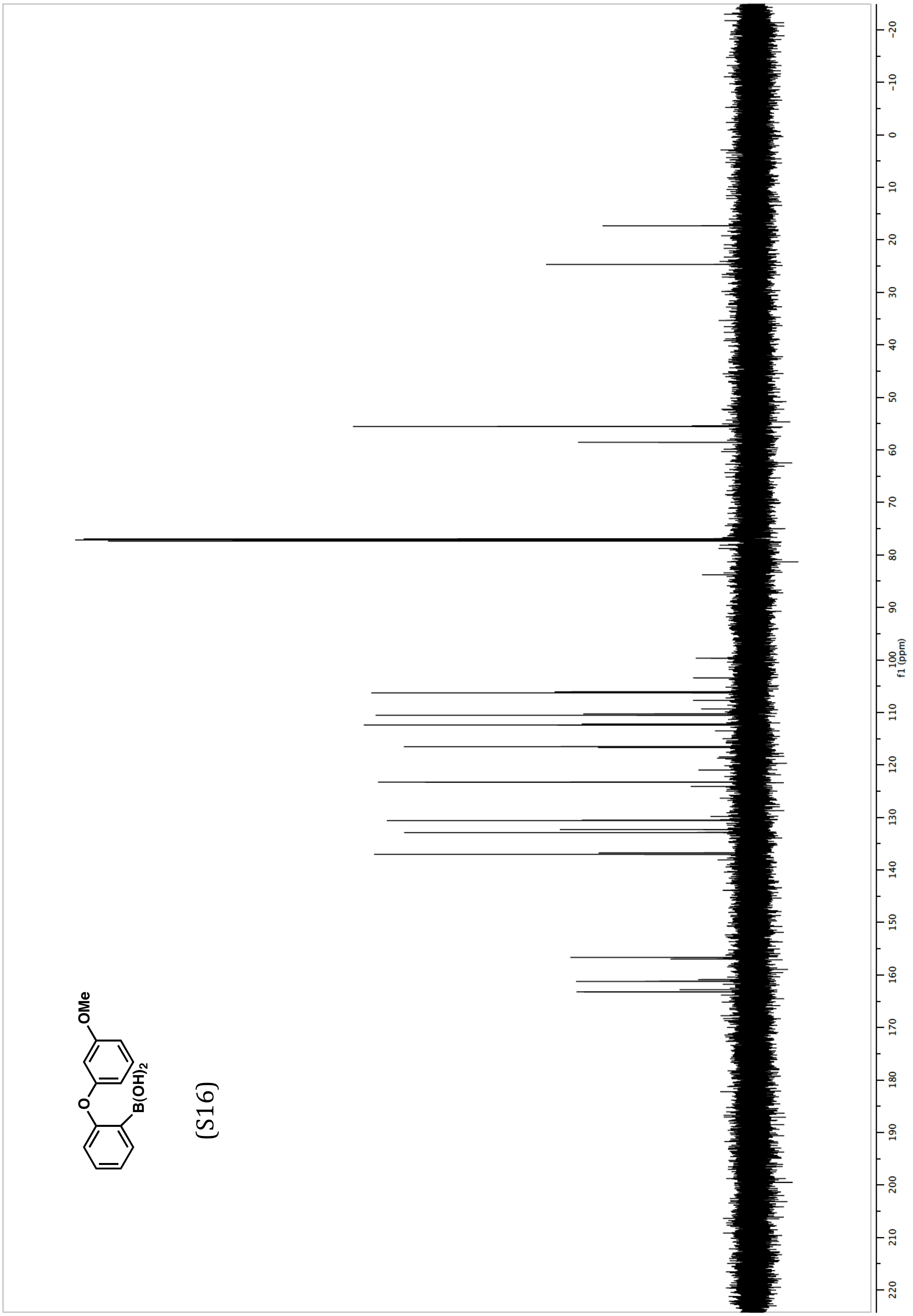
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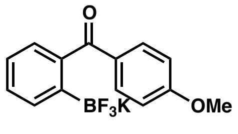
(S16)



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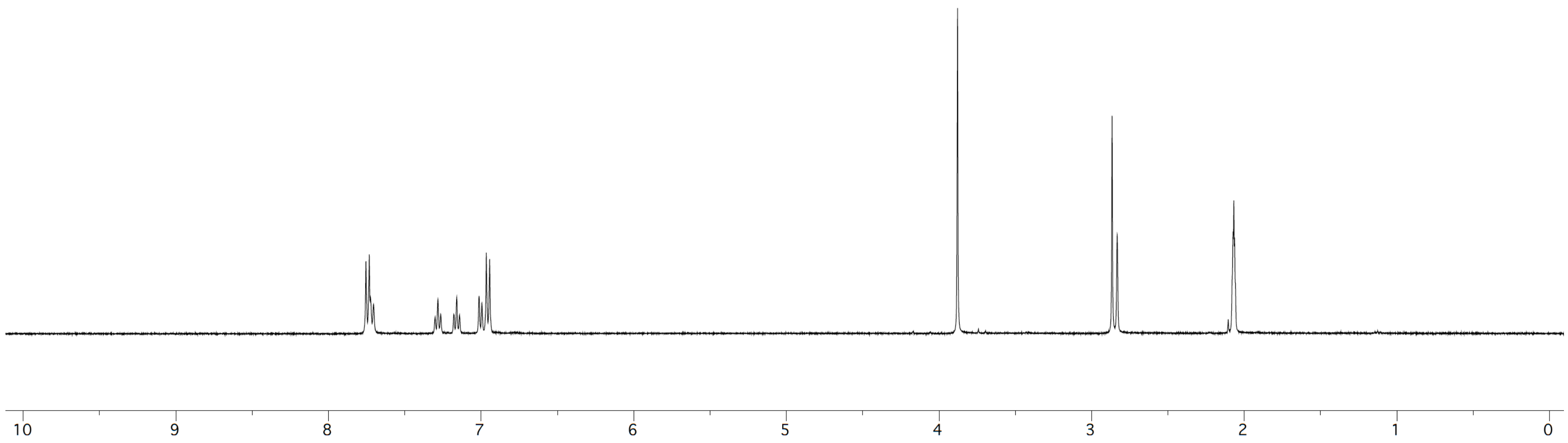

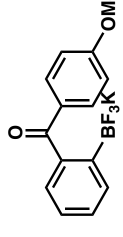
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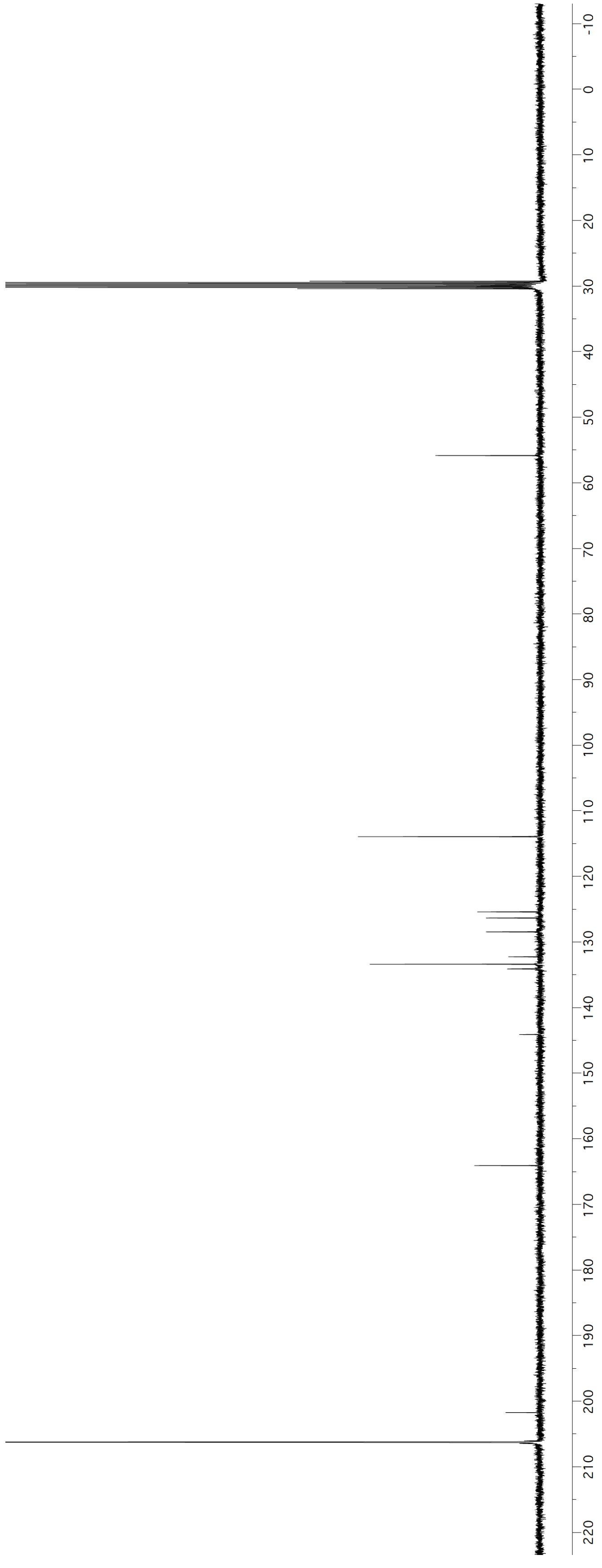
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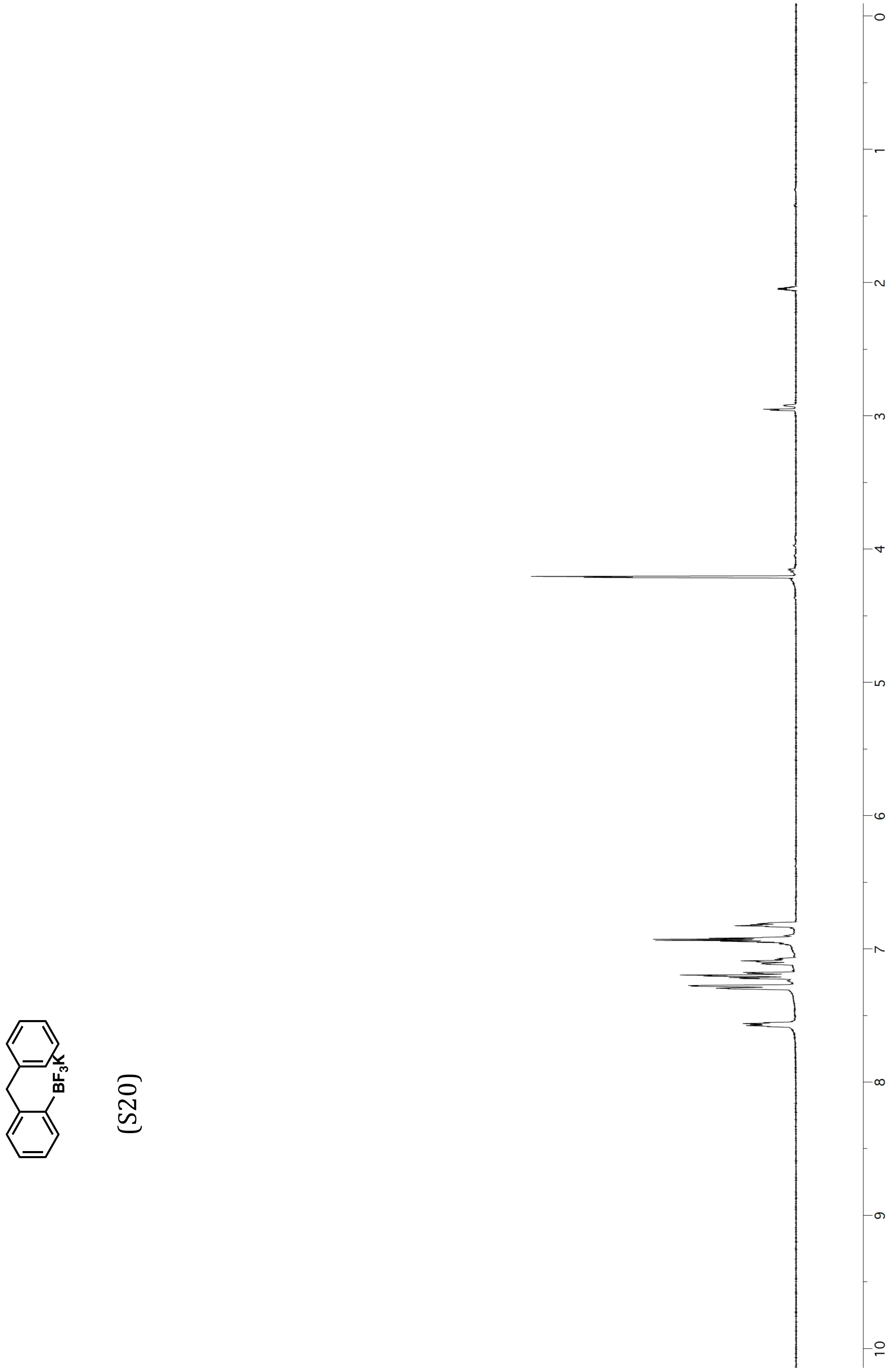

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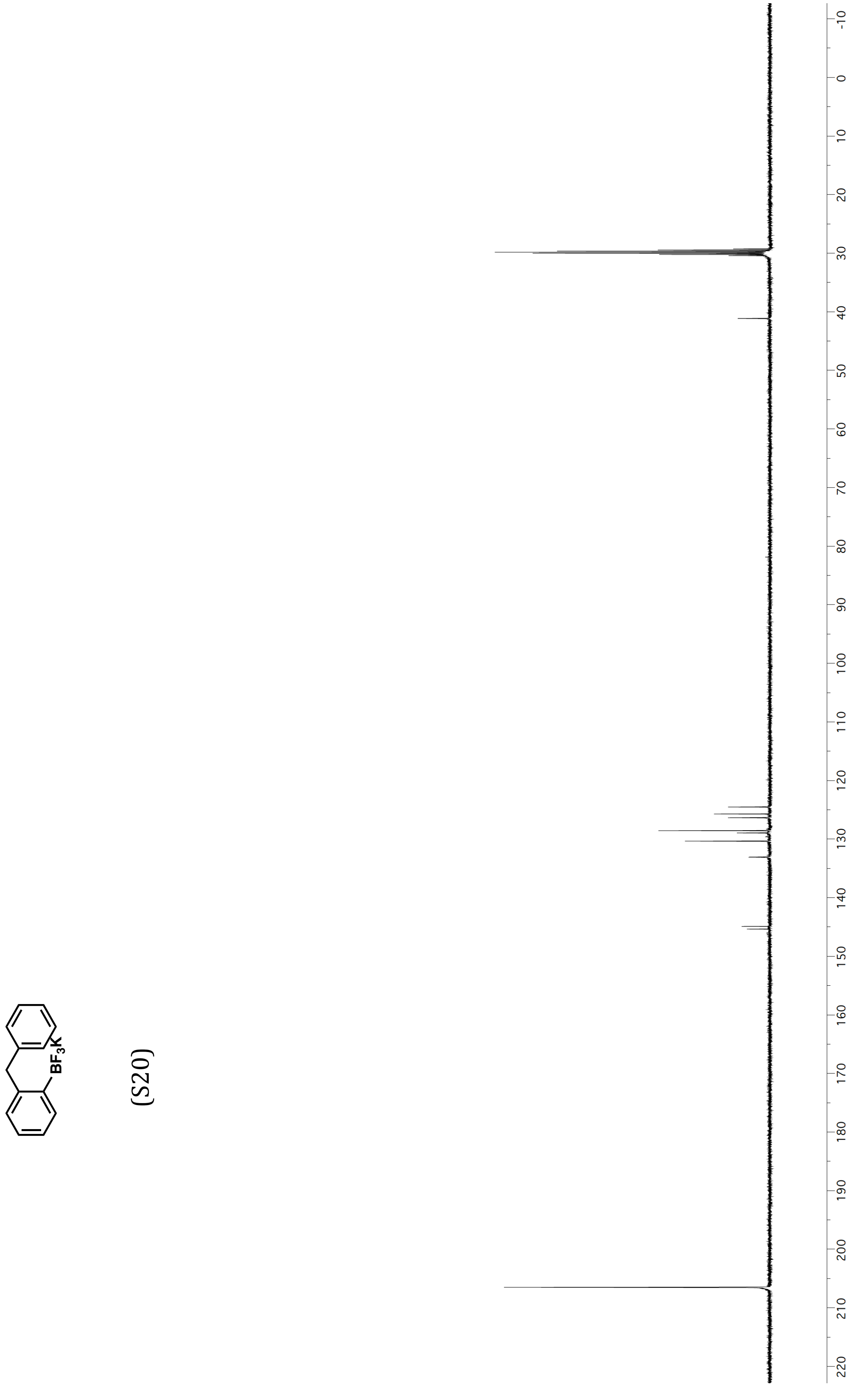
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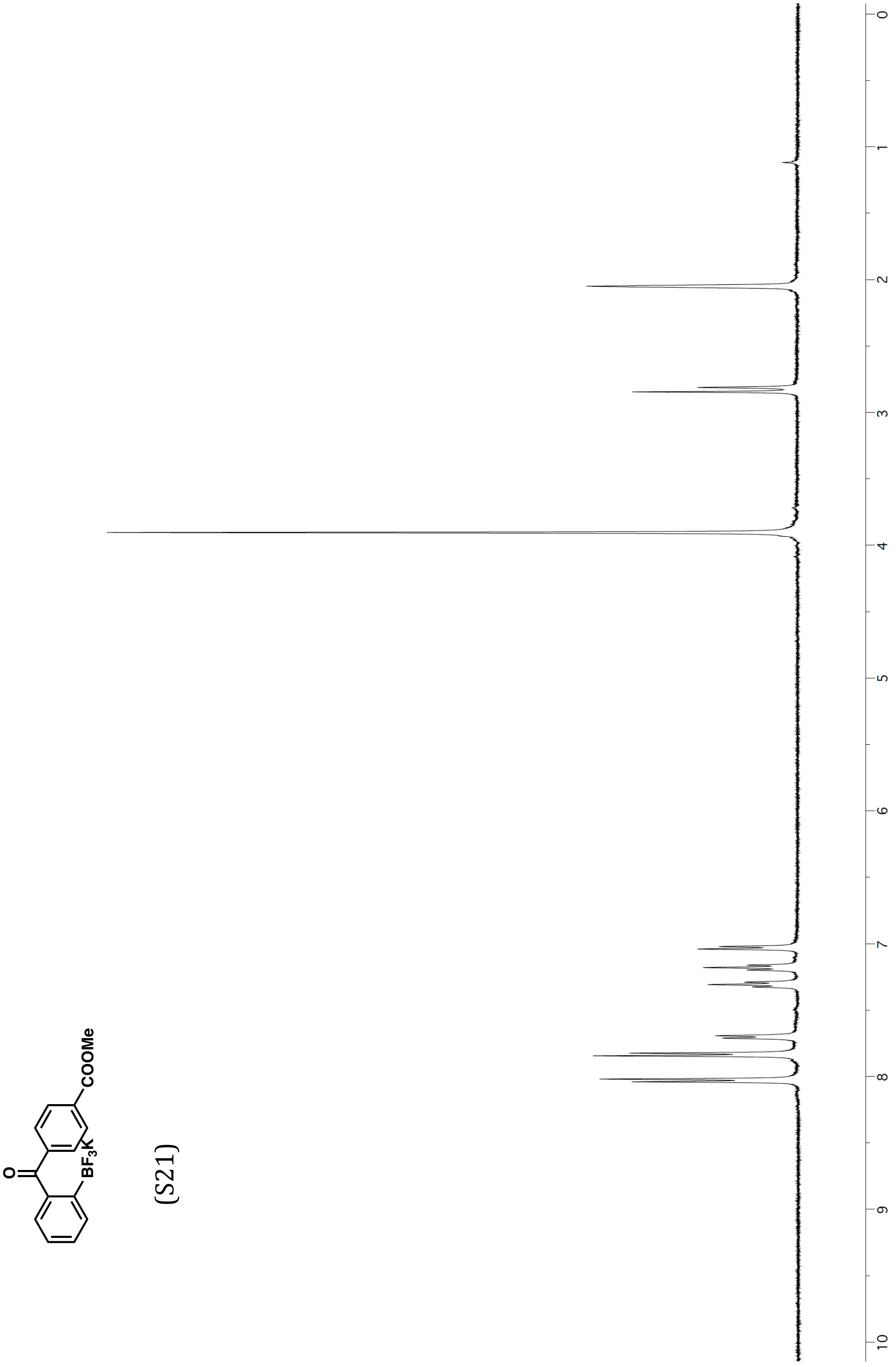
(S20)



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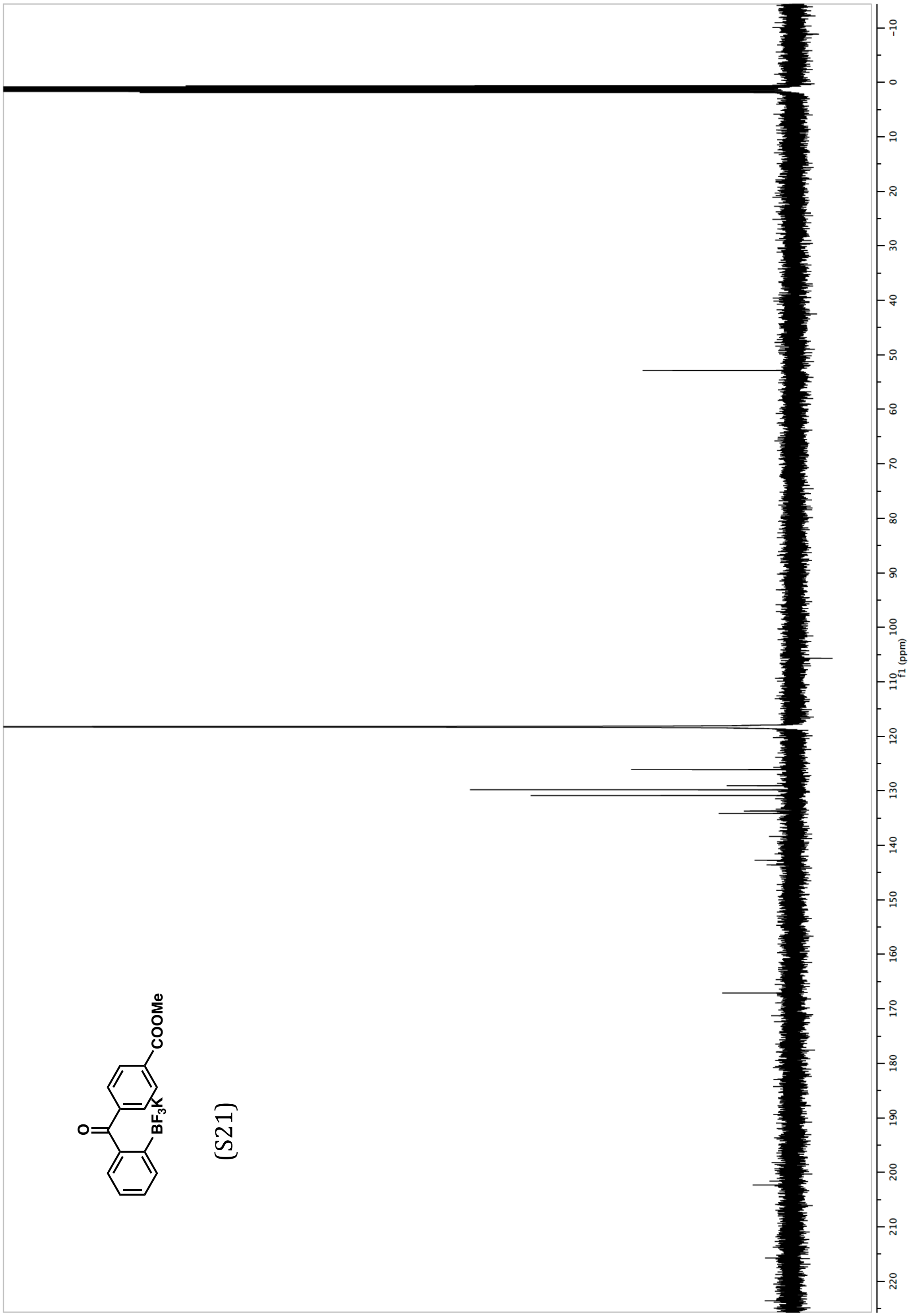
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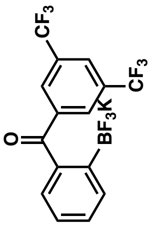
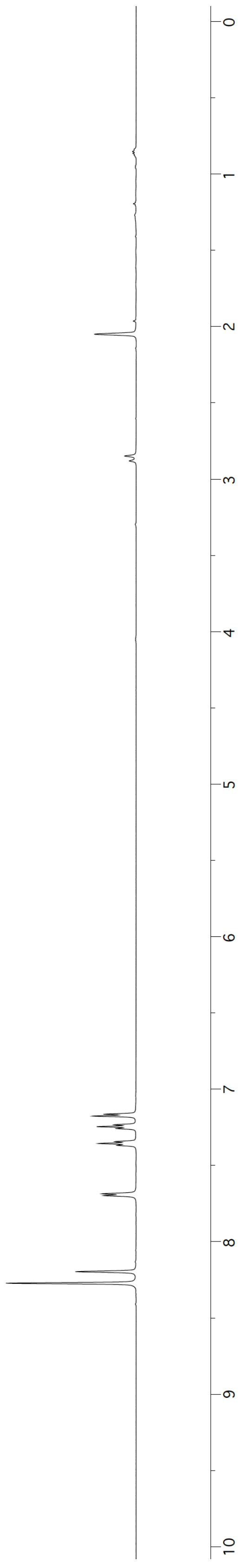
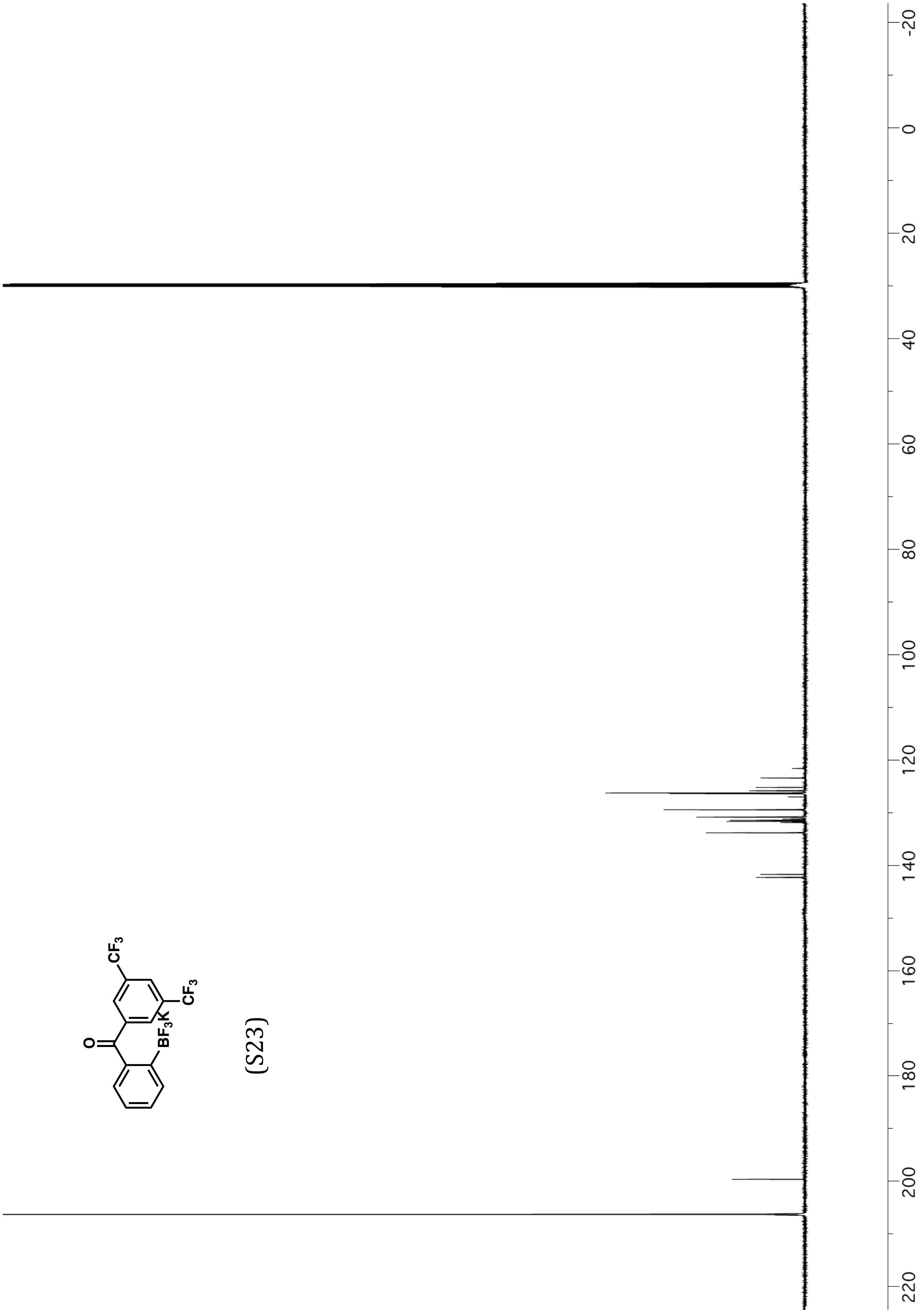
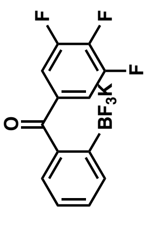


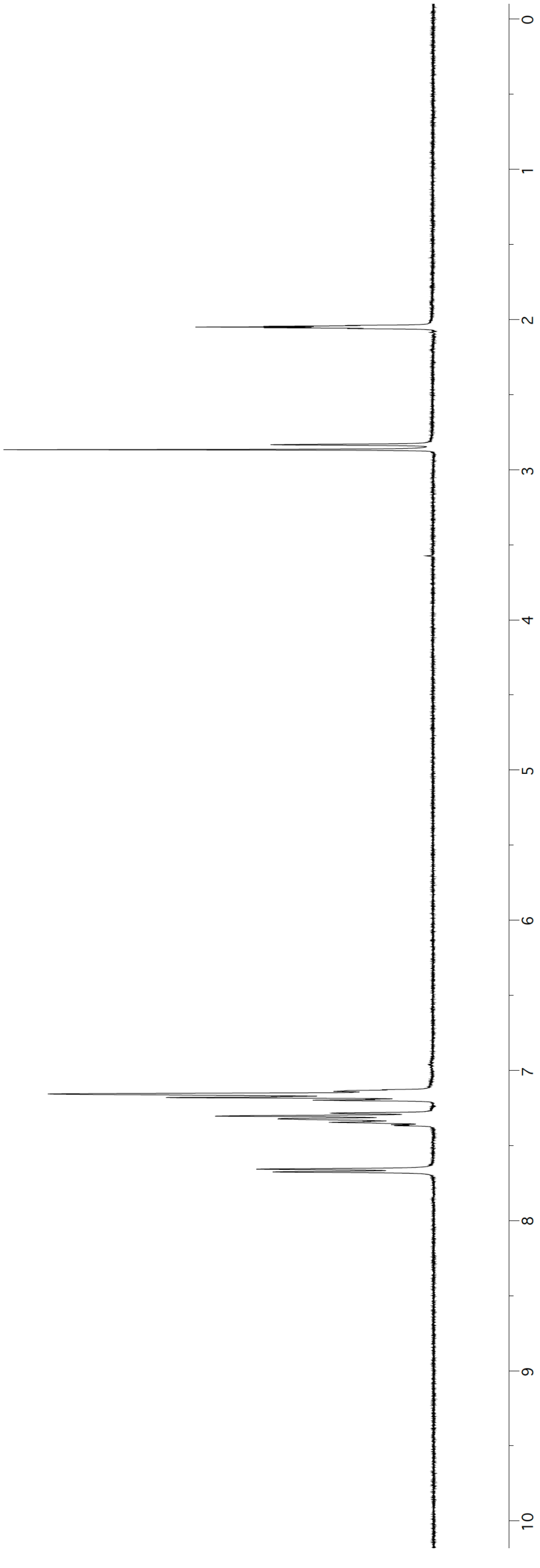
(S23)

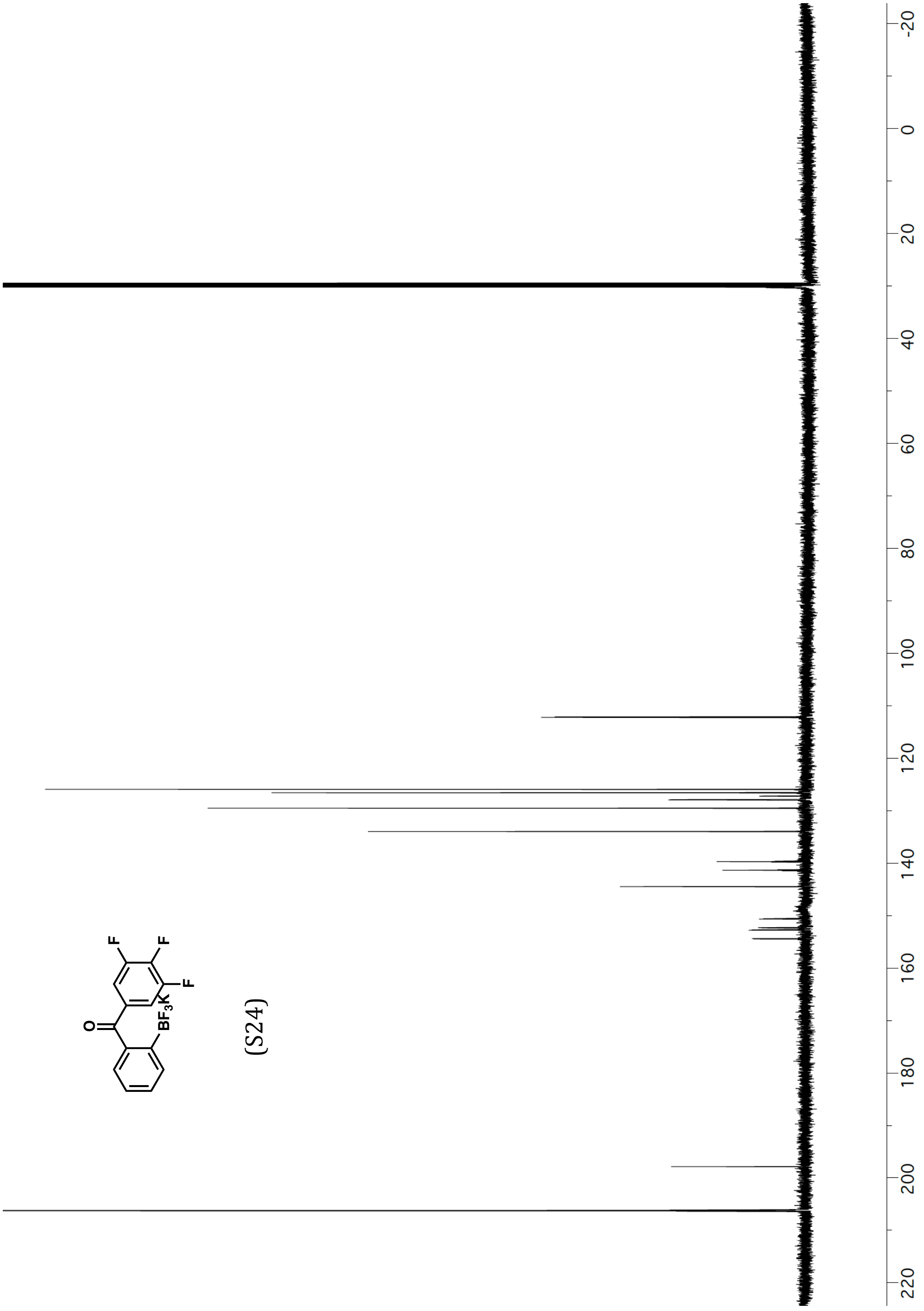



(S23)

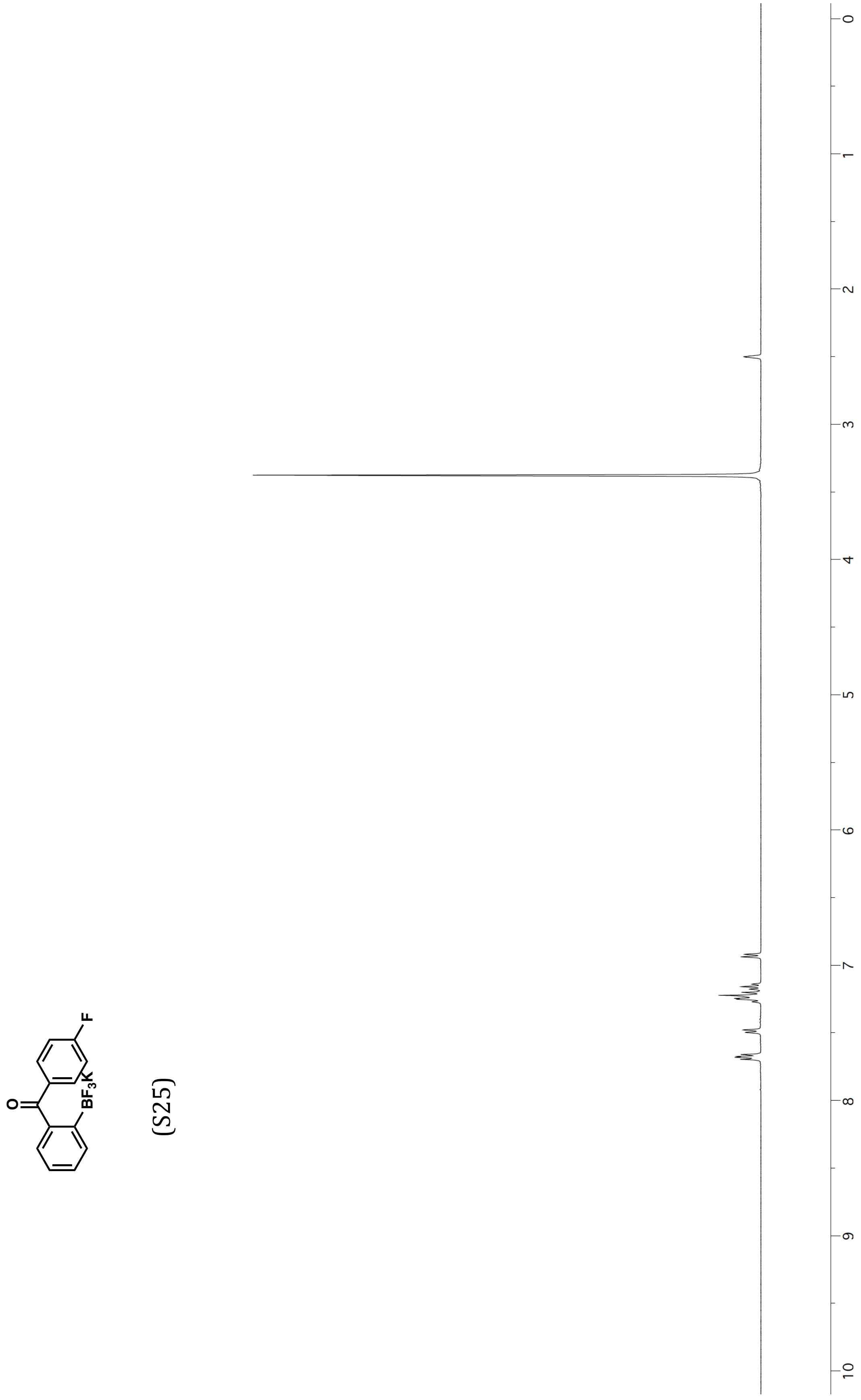


(S24)

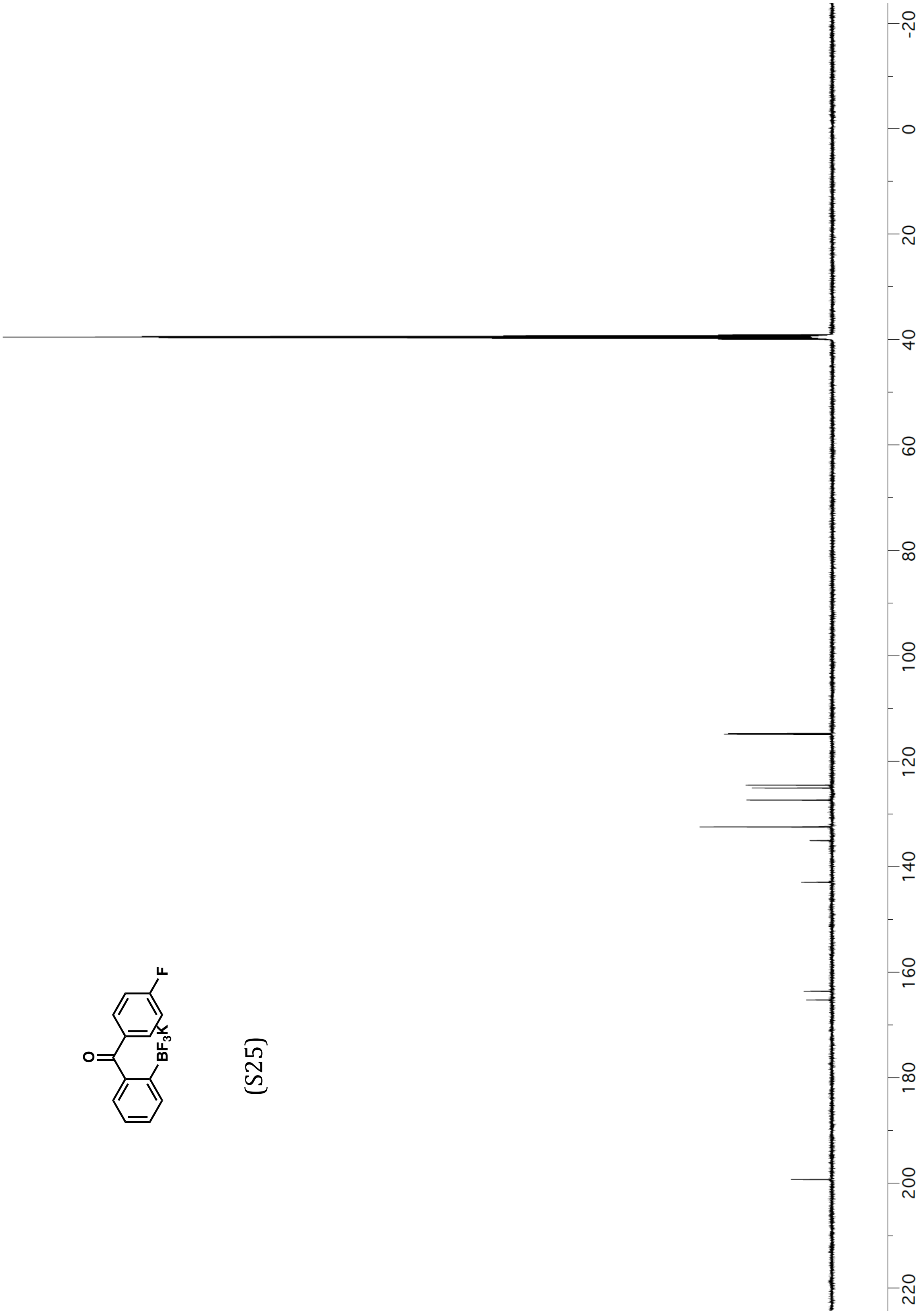




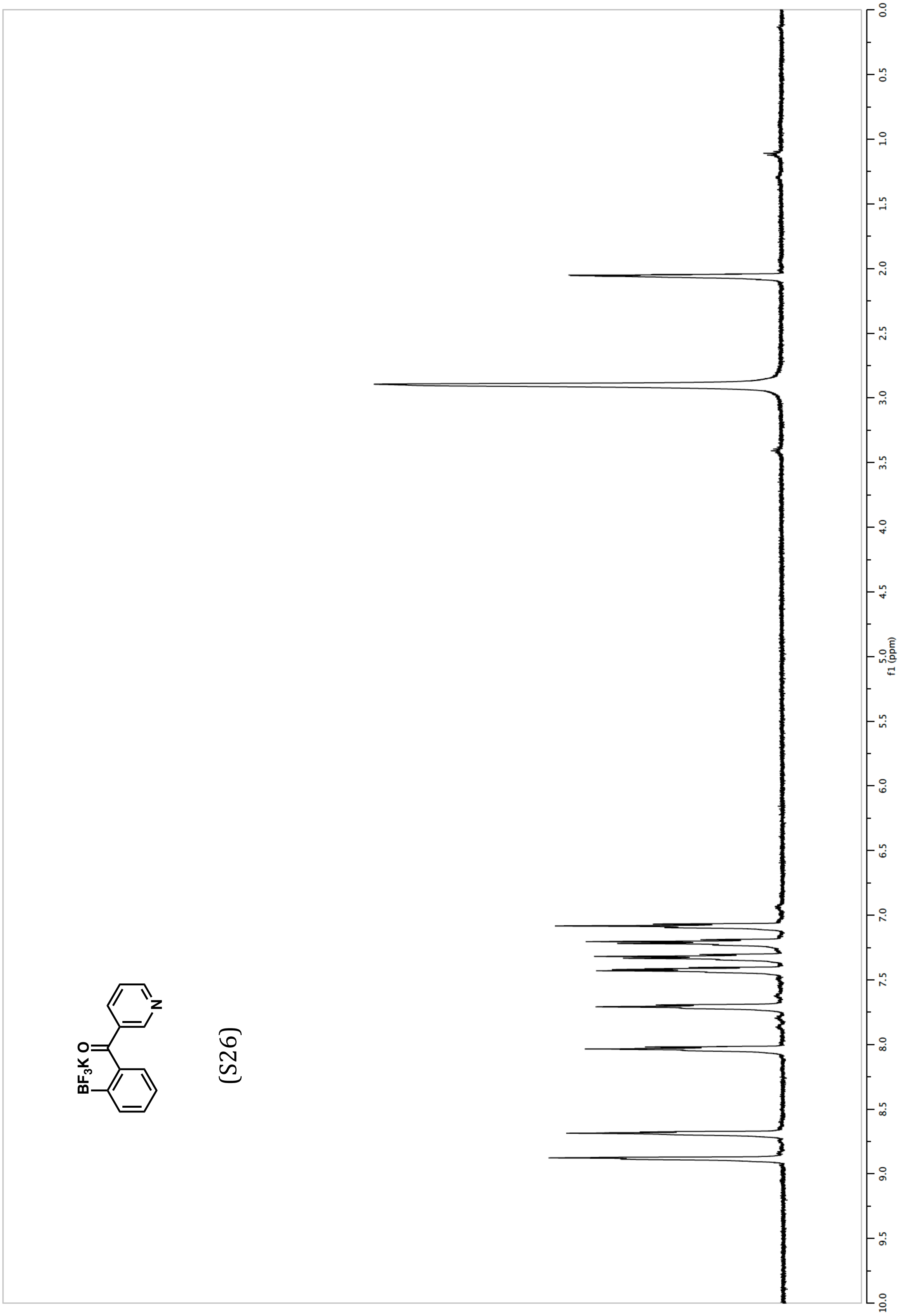
(S24)



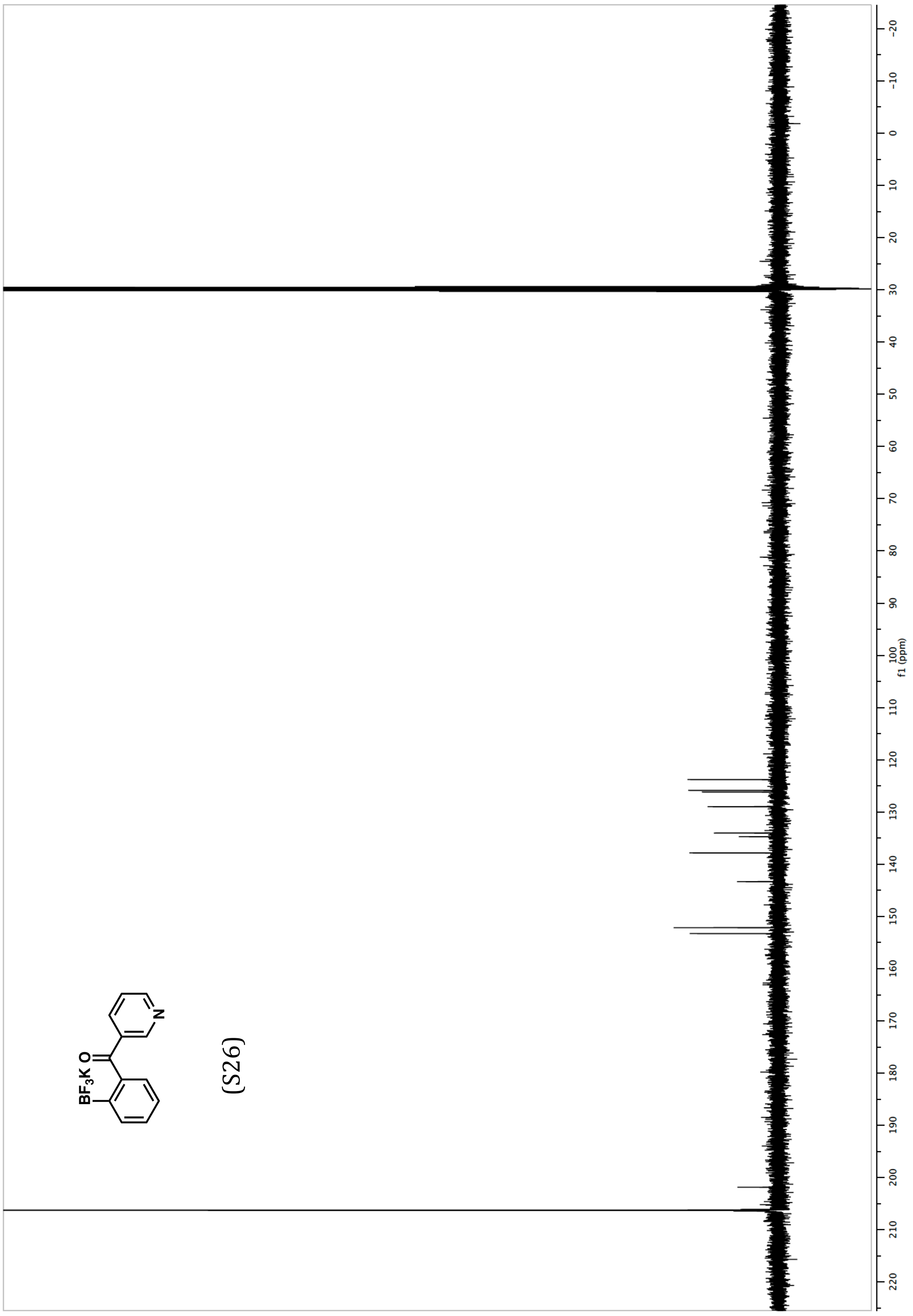
(S25)



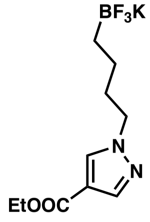
(S25)


BF3K O
N
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
f1 (ppm)

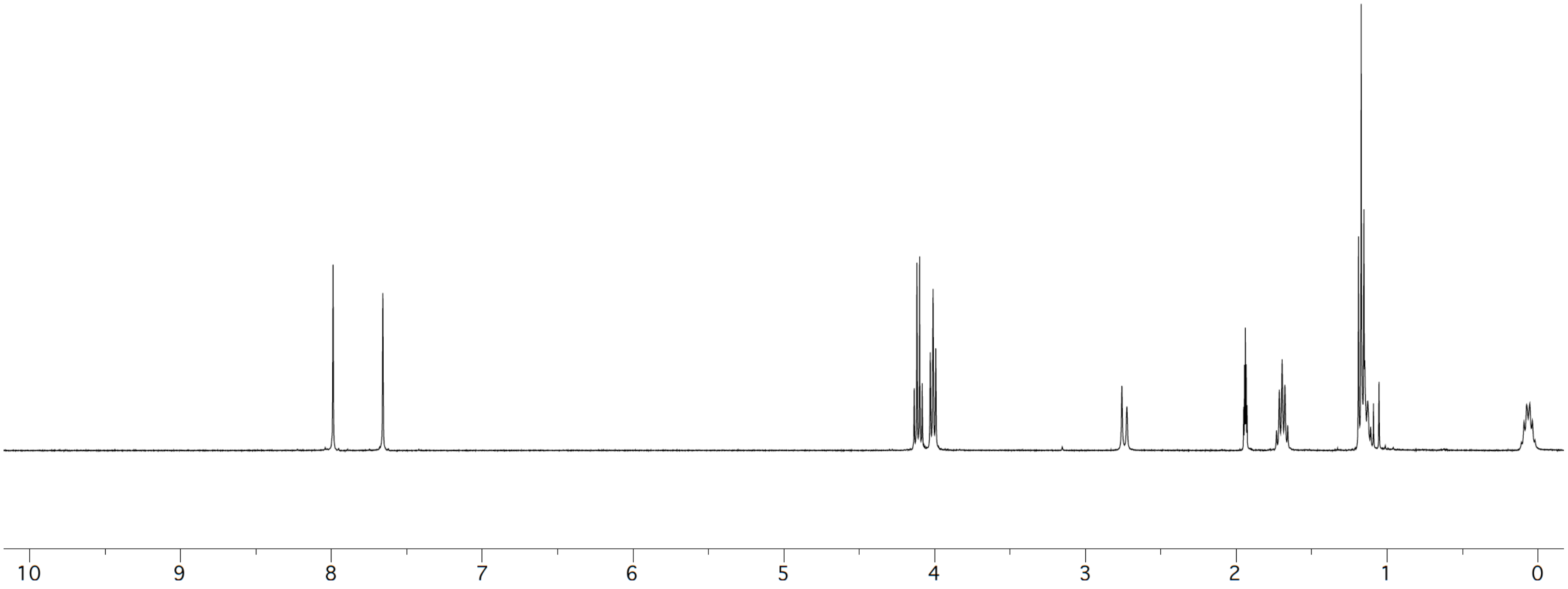
(S26)

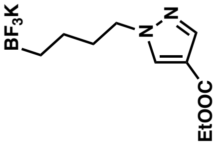

(S26)

BF3K O
N
f1 (ppm)
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220

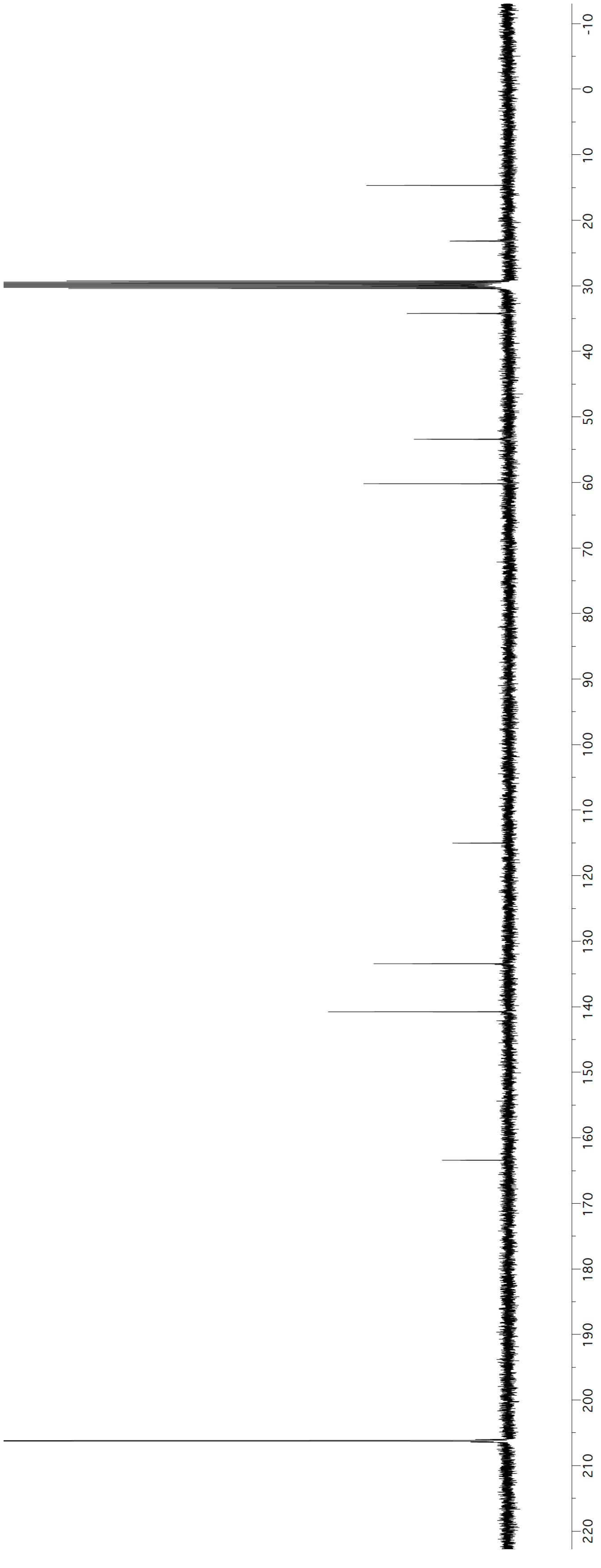


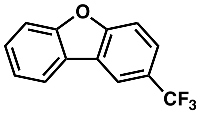
(S27)



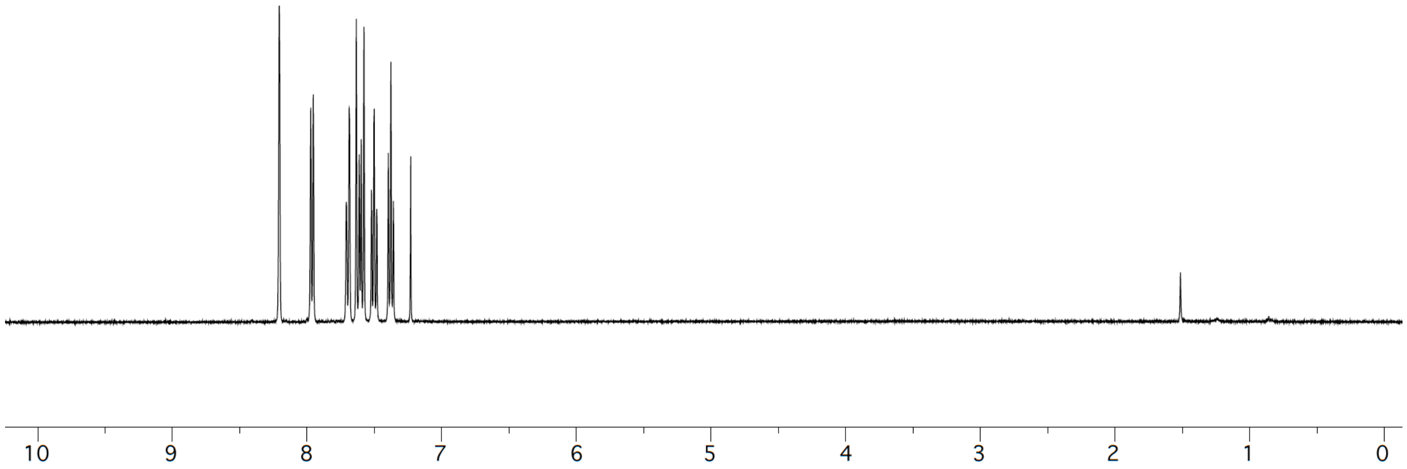

BF3K
N
N
EtOOC

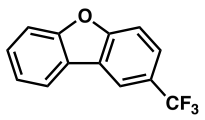
(S27)


-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220

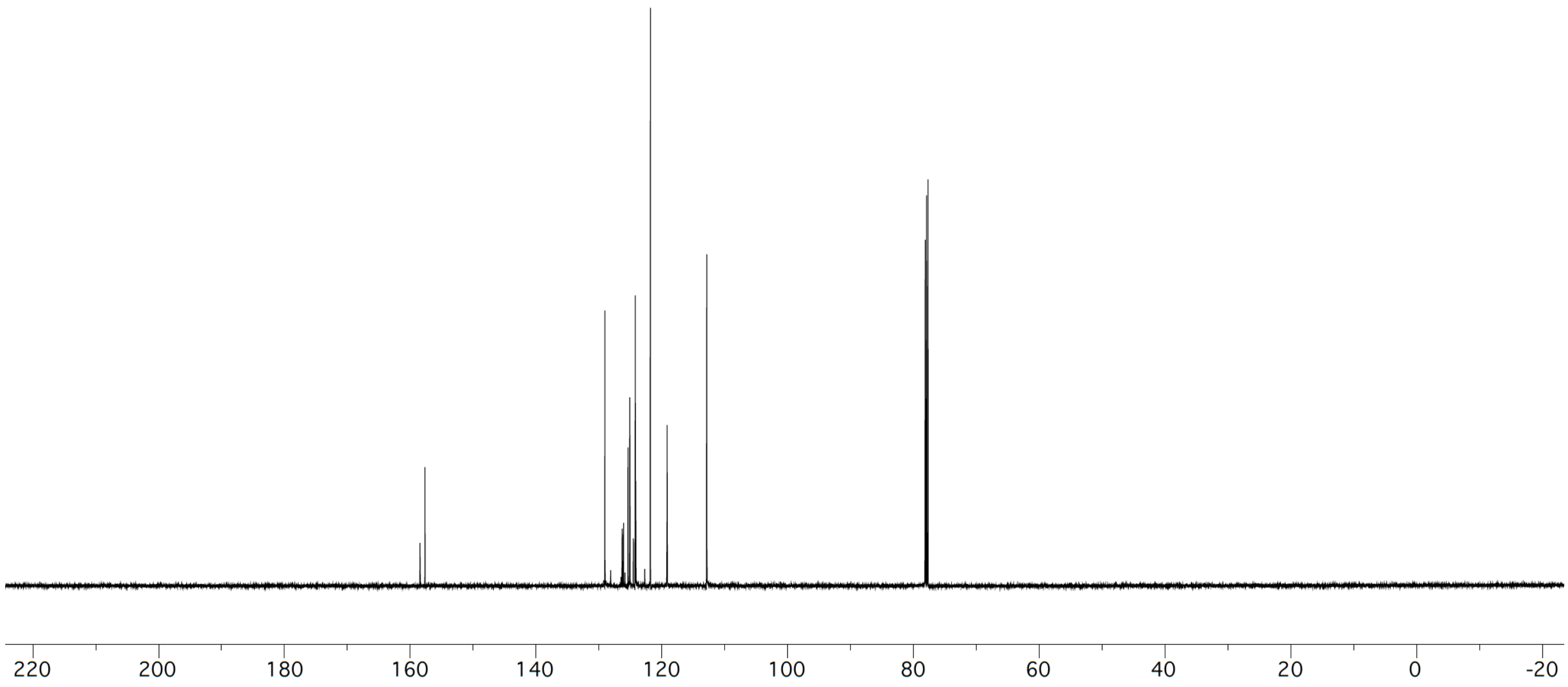


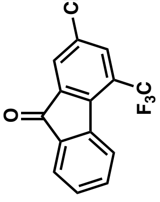
(1)



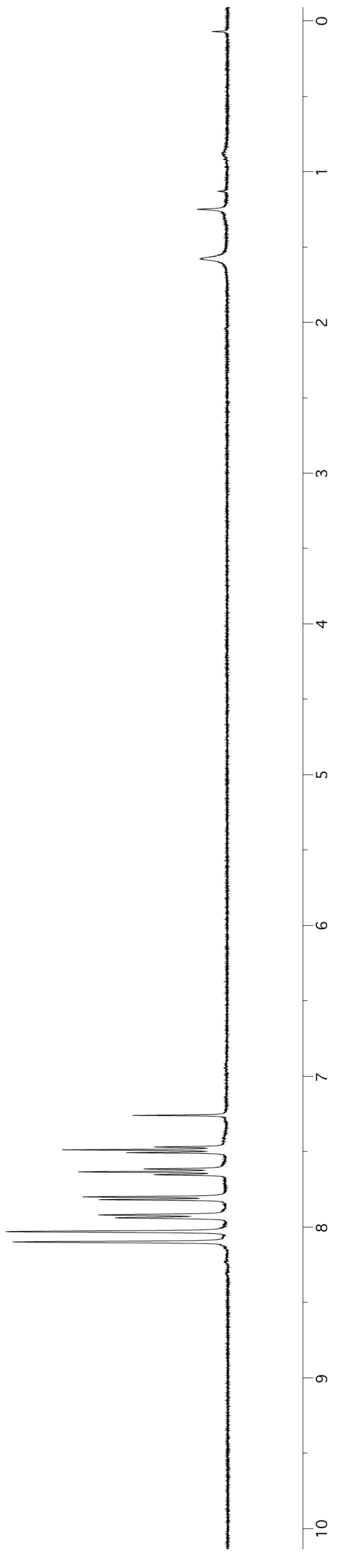


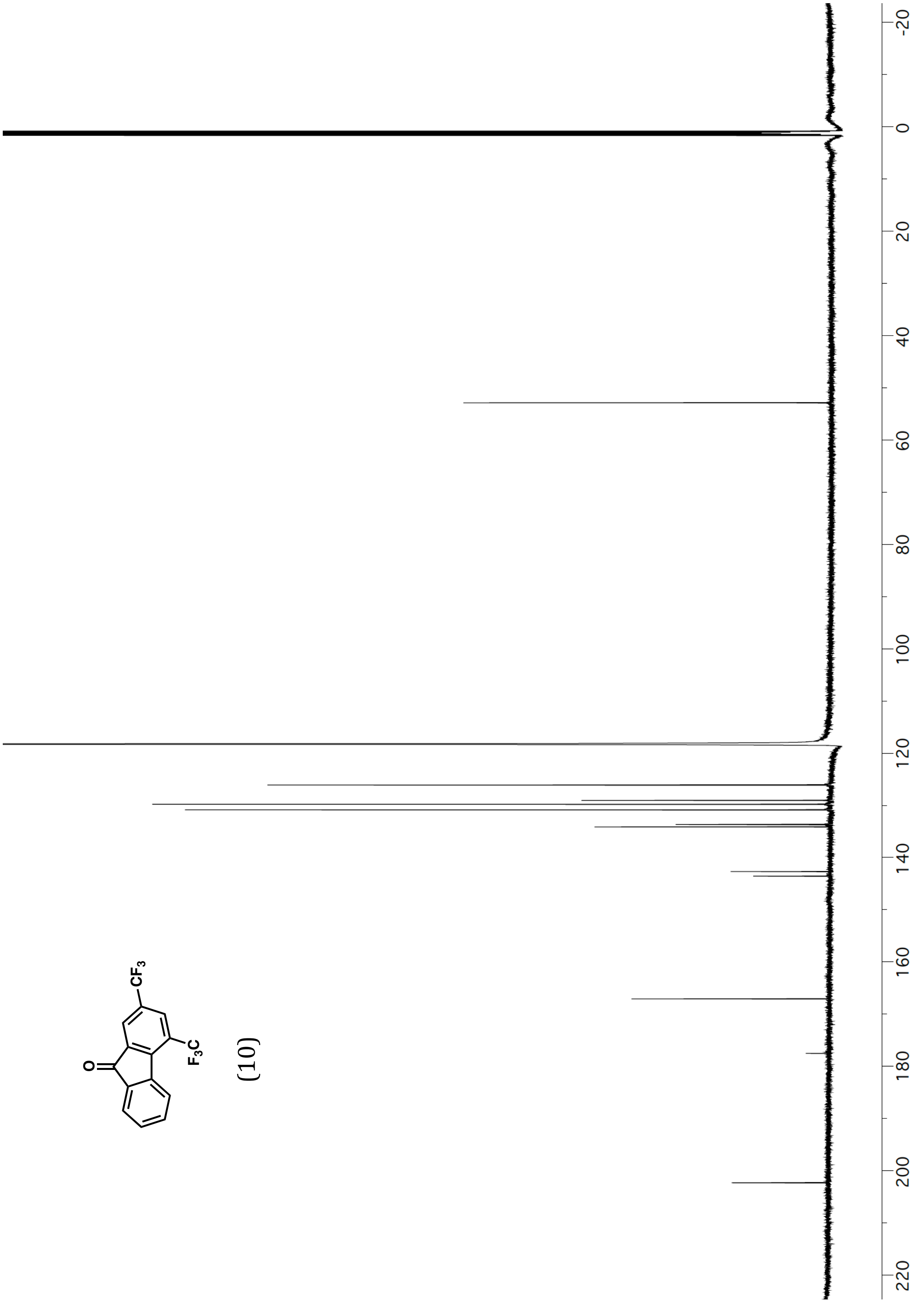
(1)



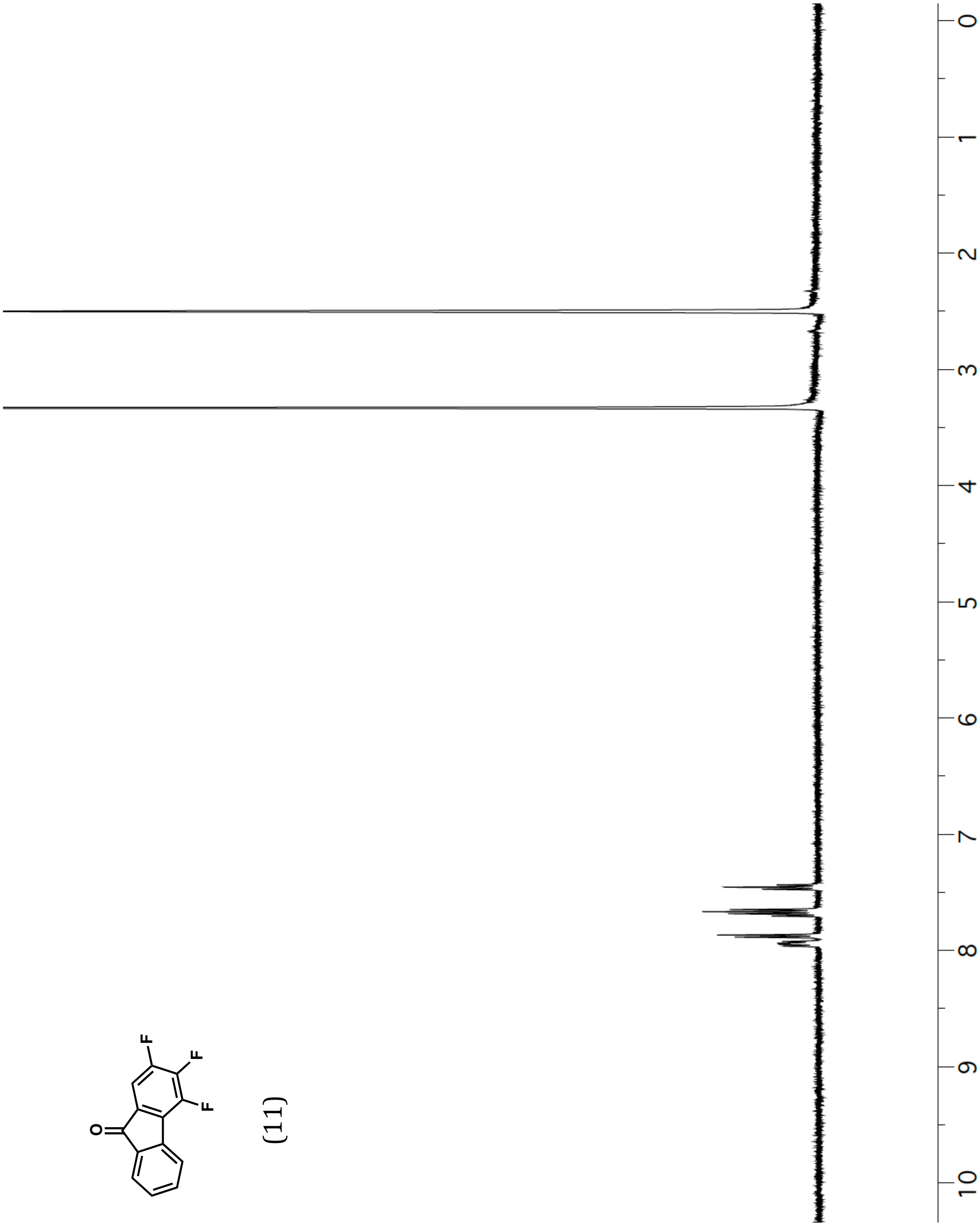


(10)

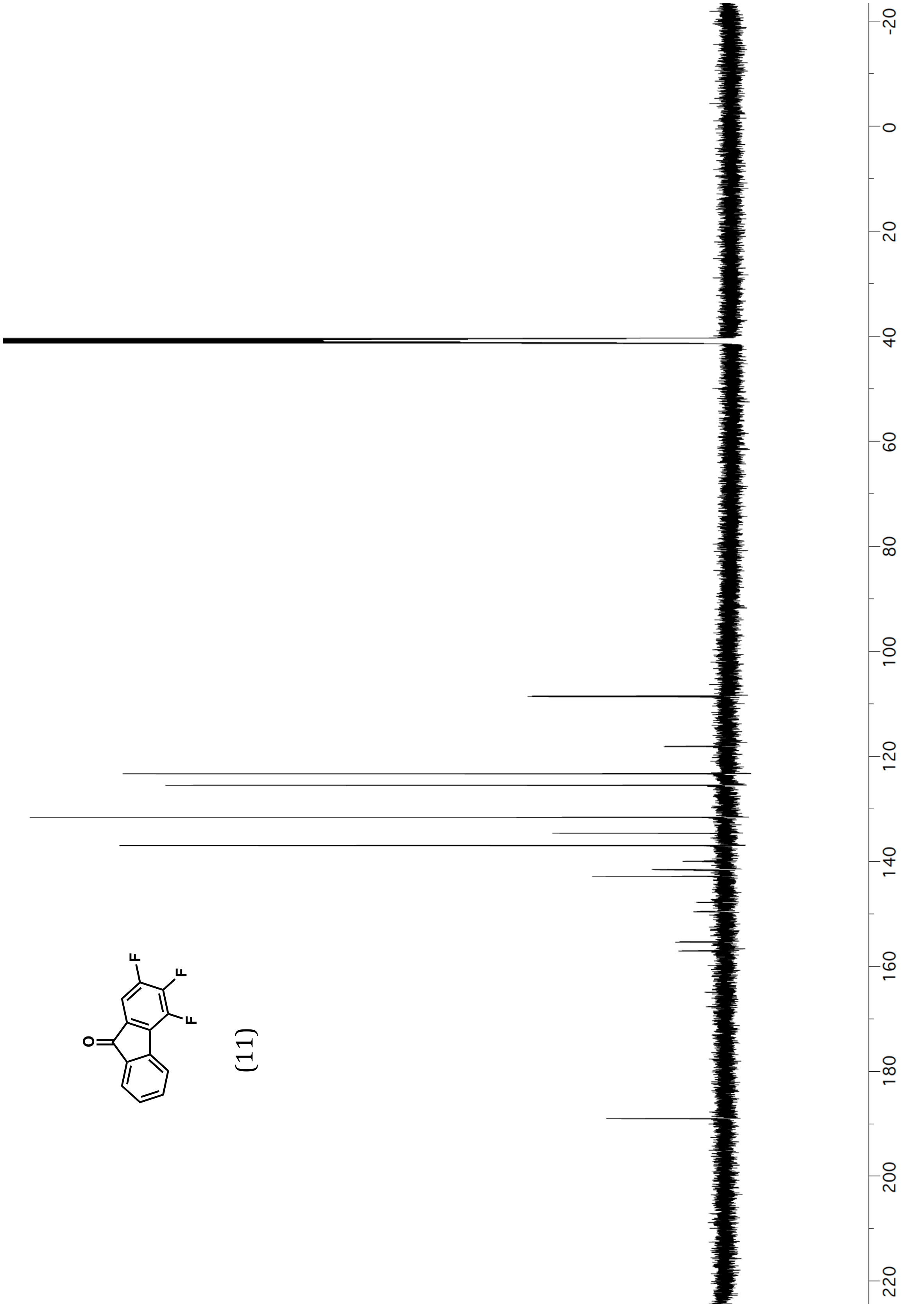




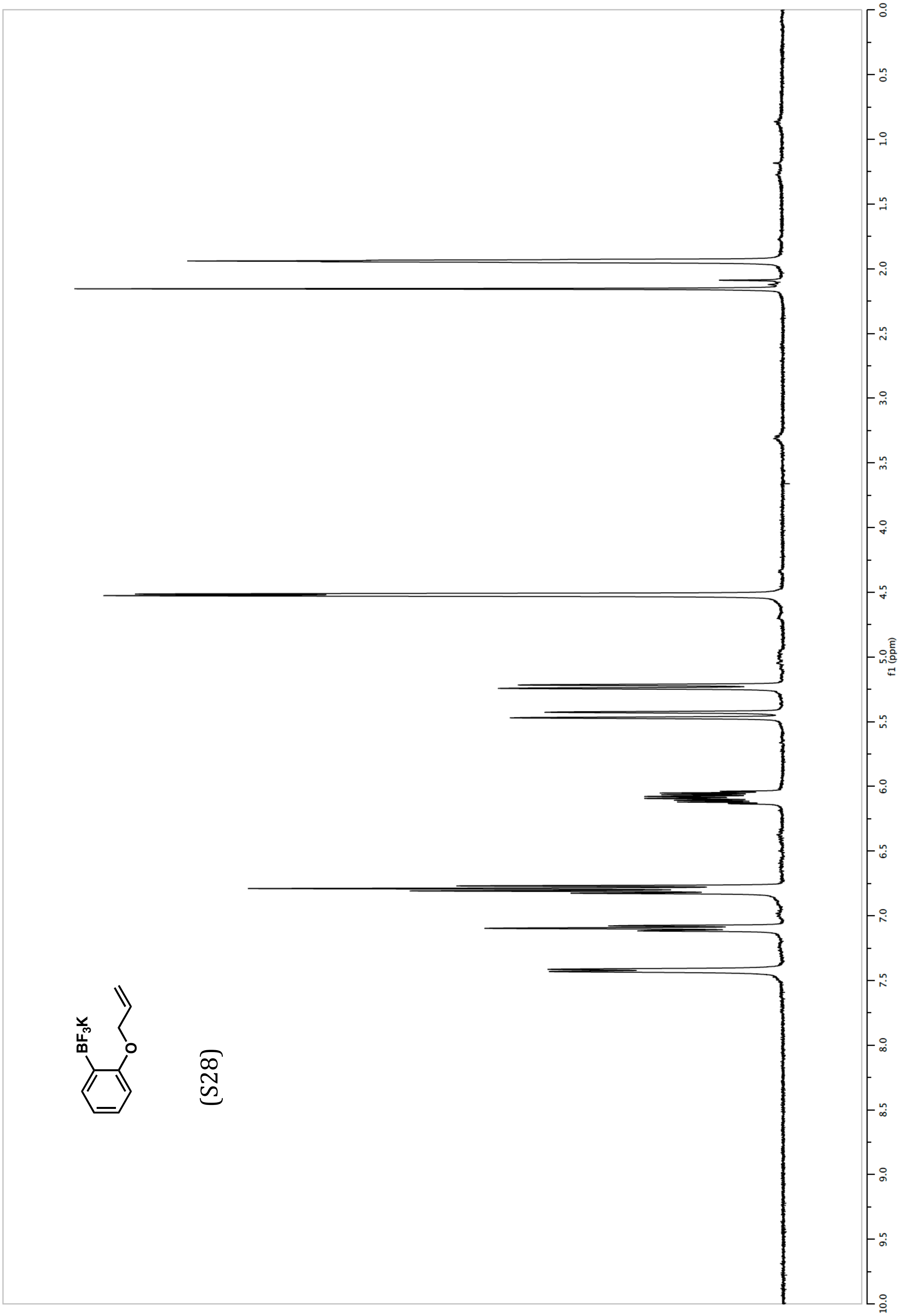
(10)



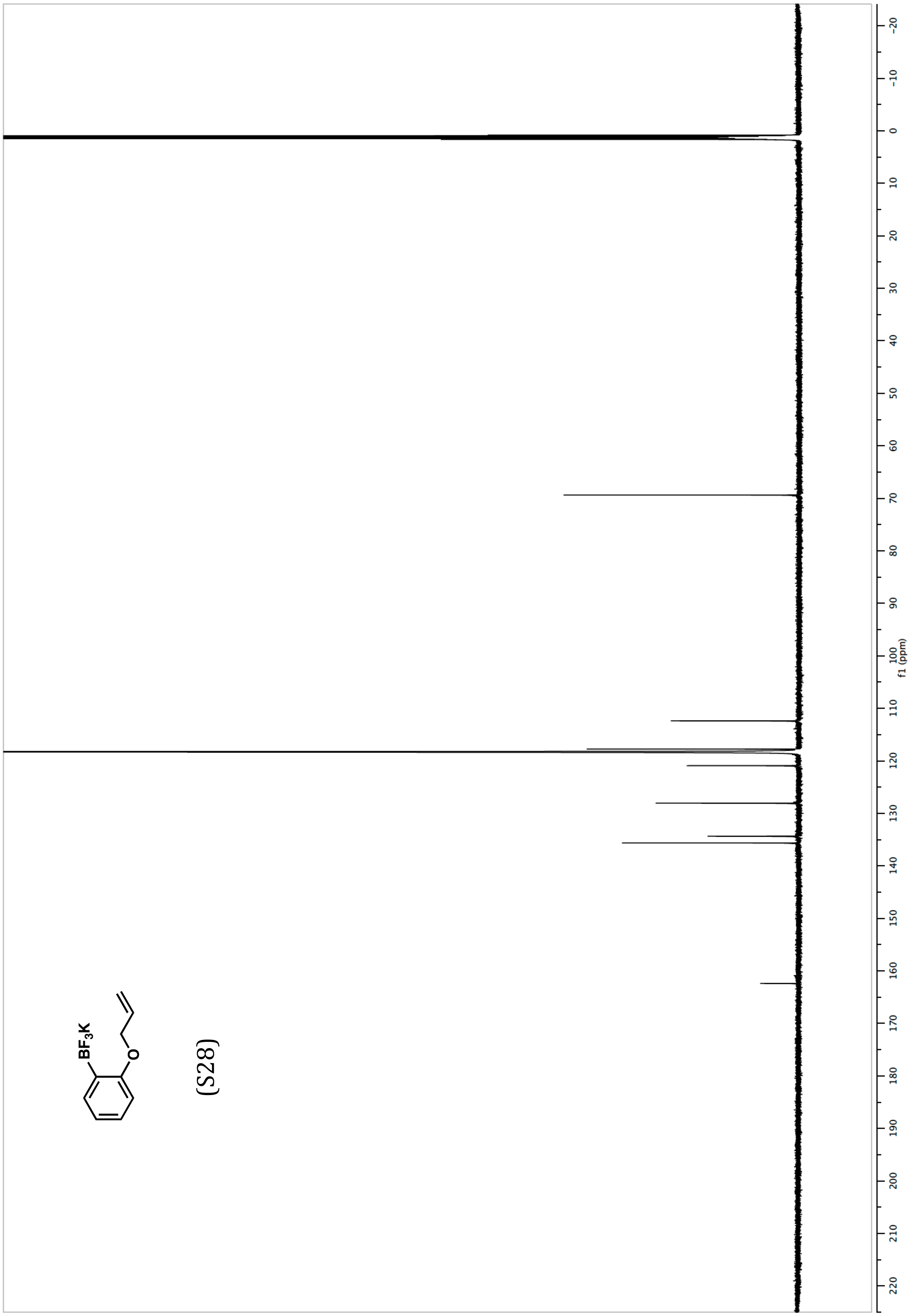
(11)

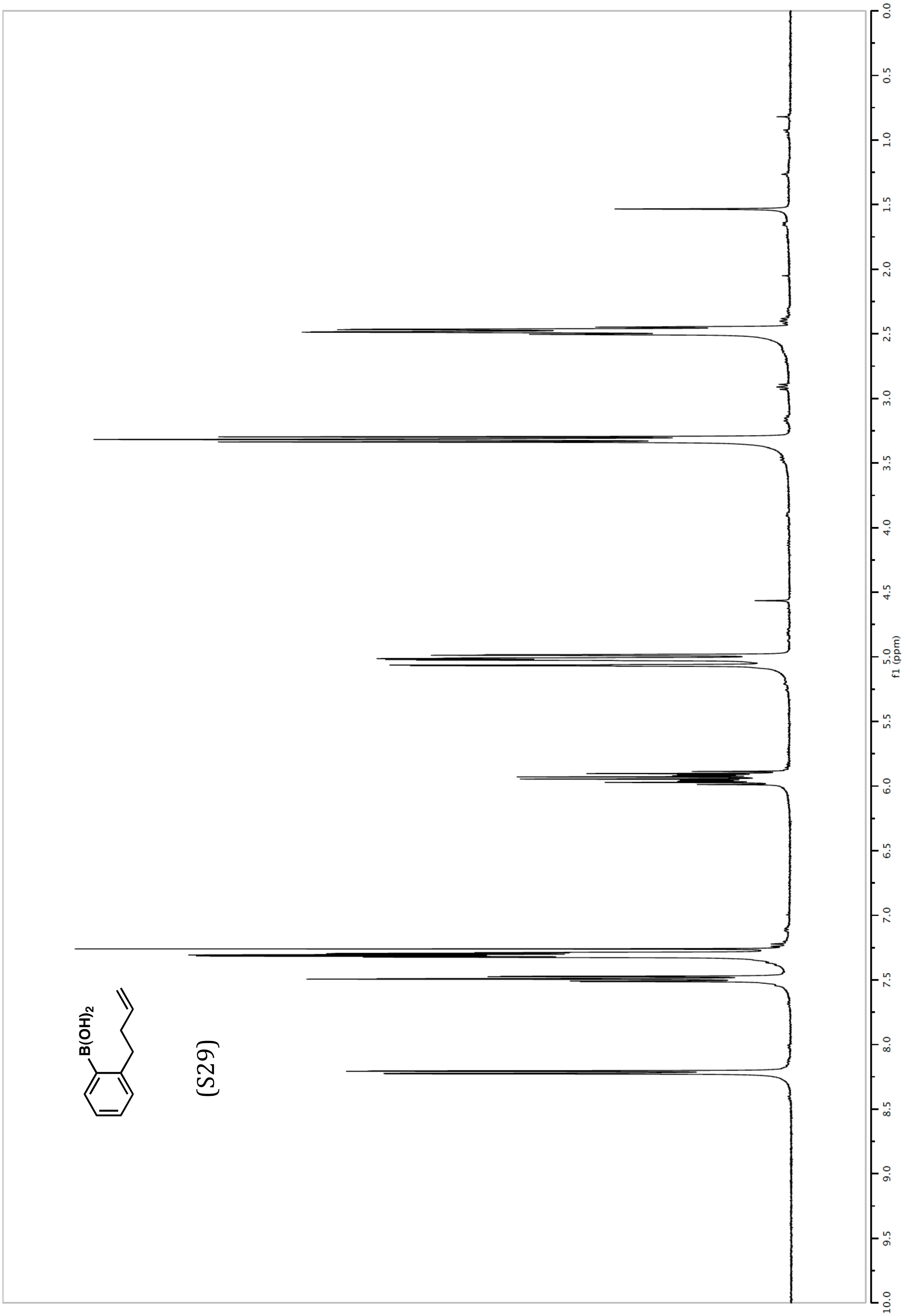


(11)


(S28)

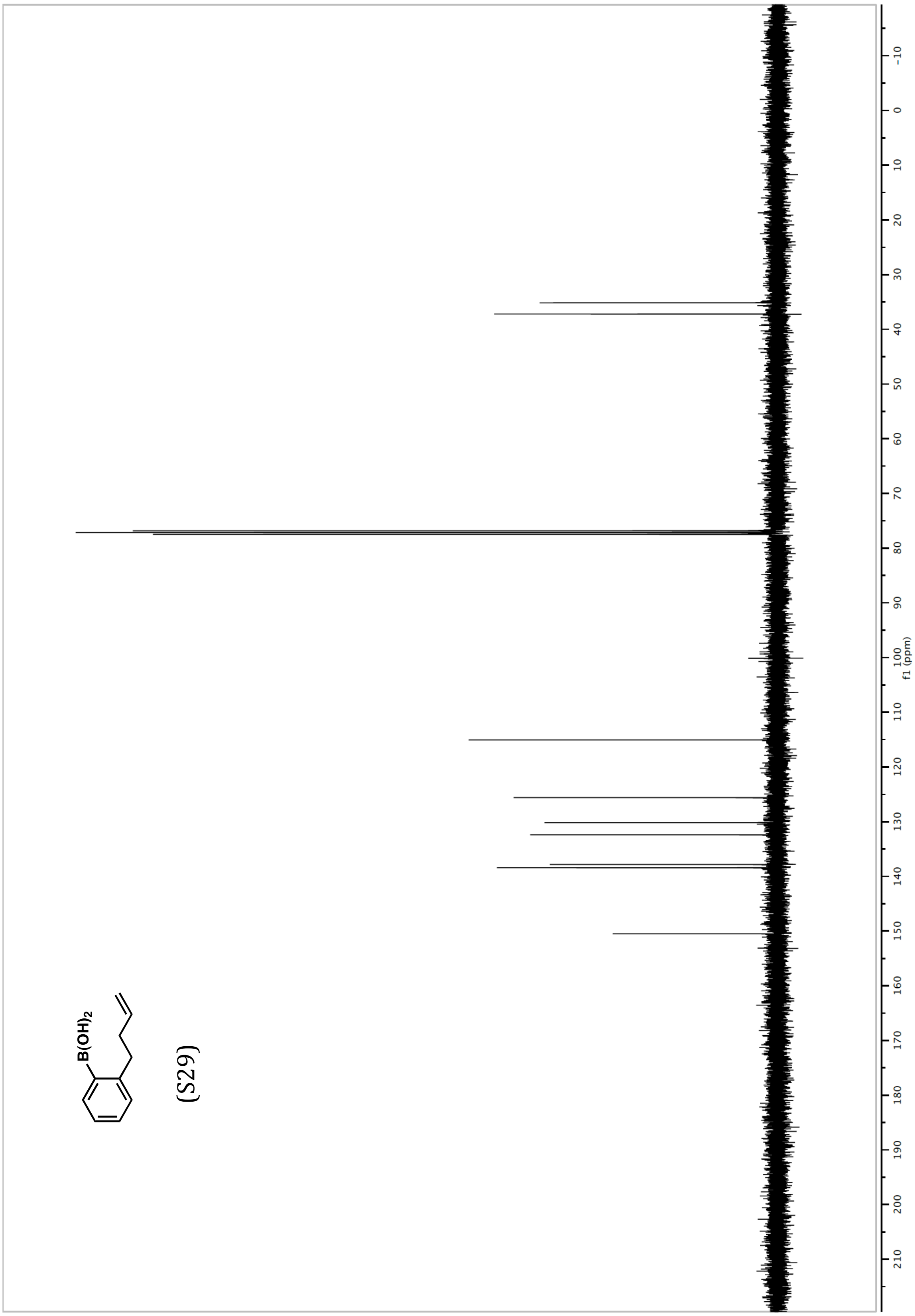
BF3K
O
f1 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0



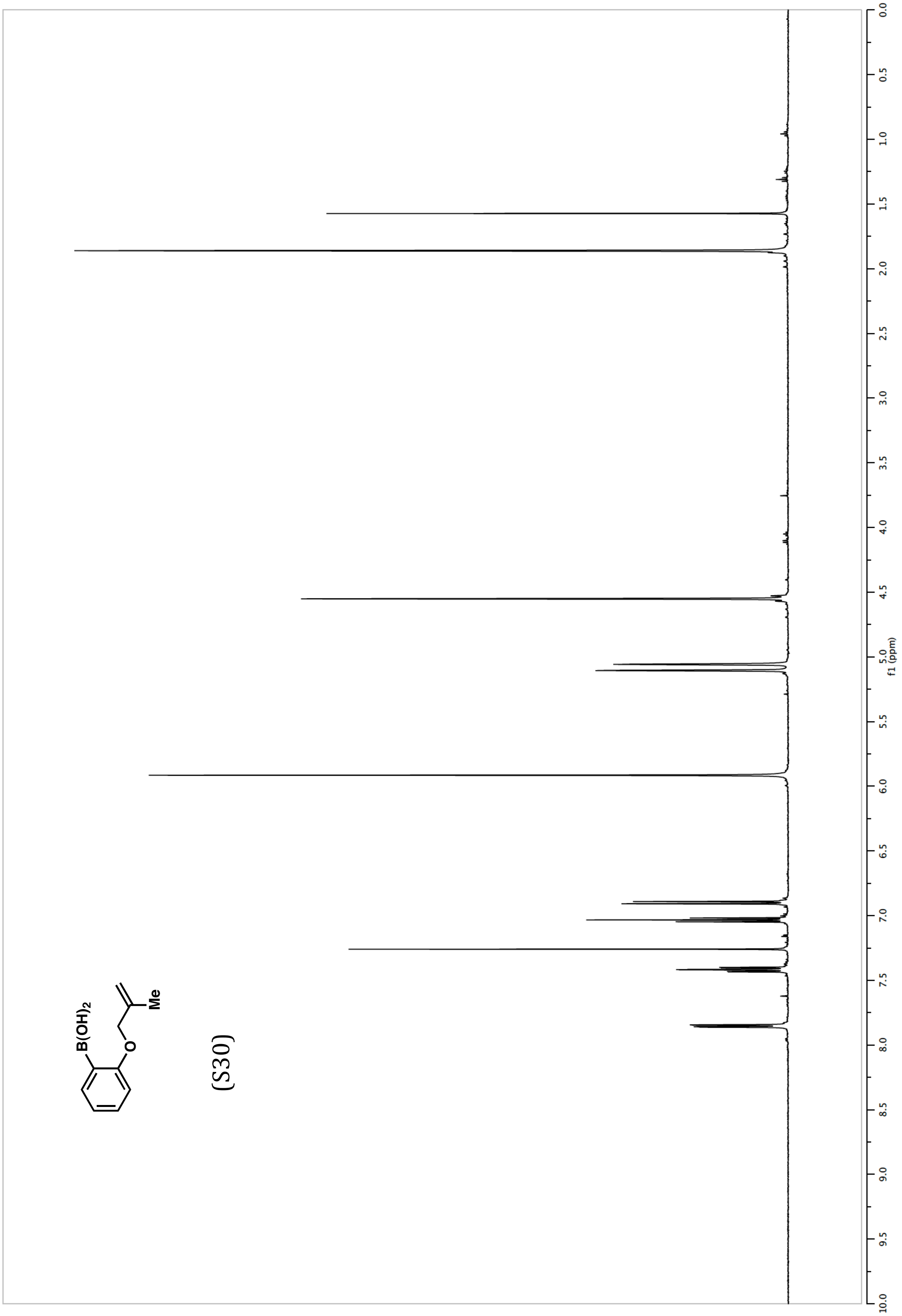


(S29)

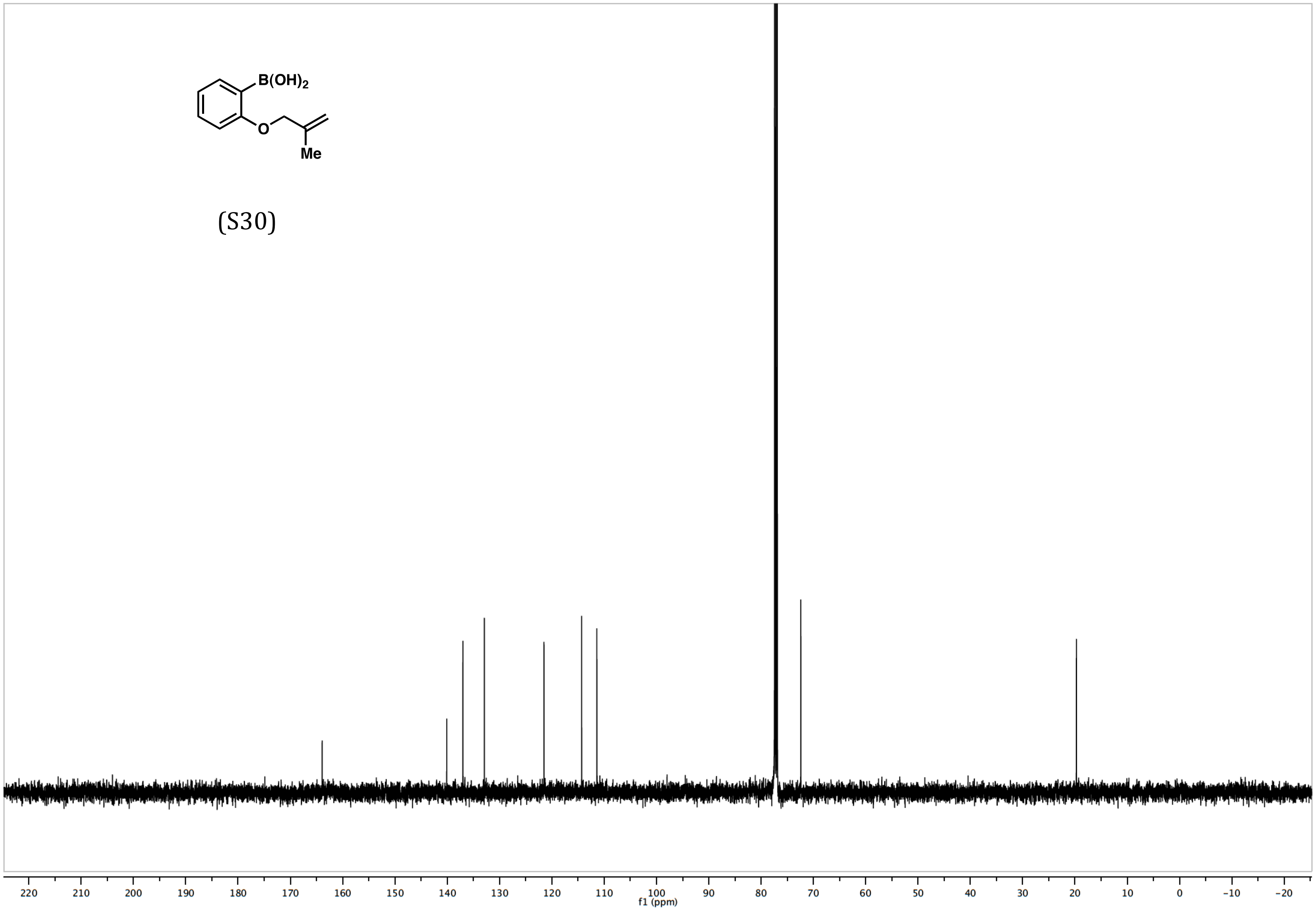
B(OH)₂
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

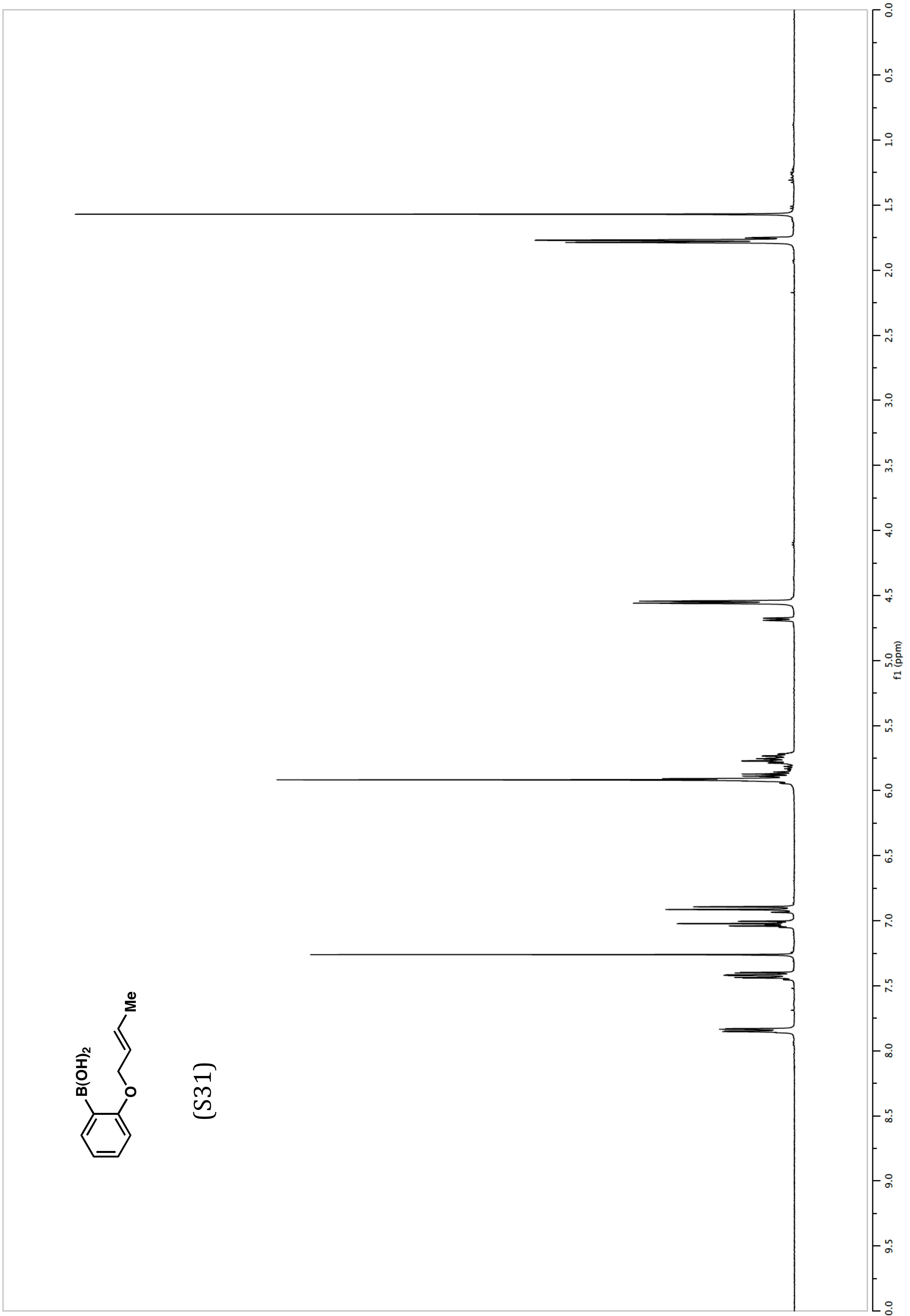
B(OH)2
f1 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

(S29)

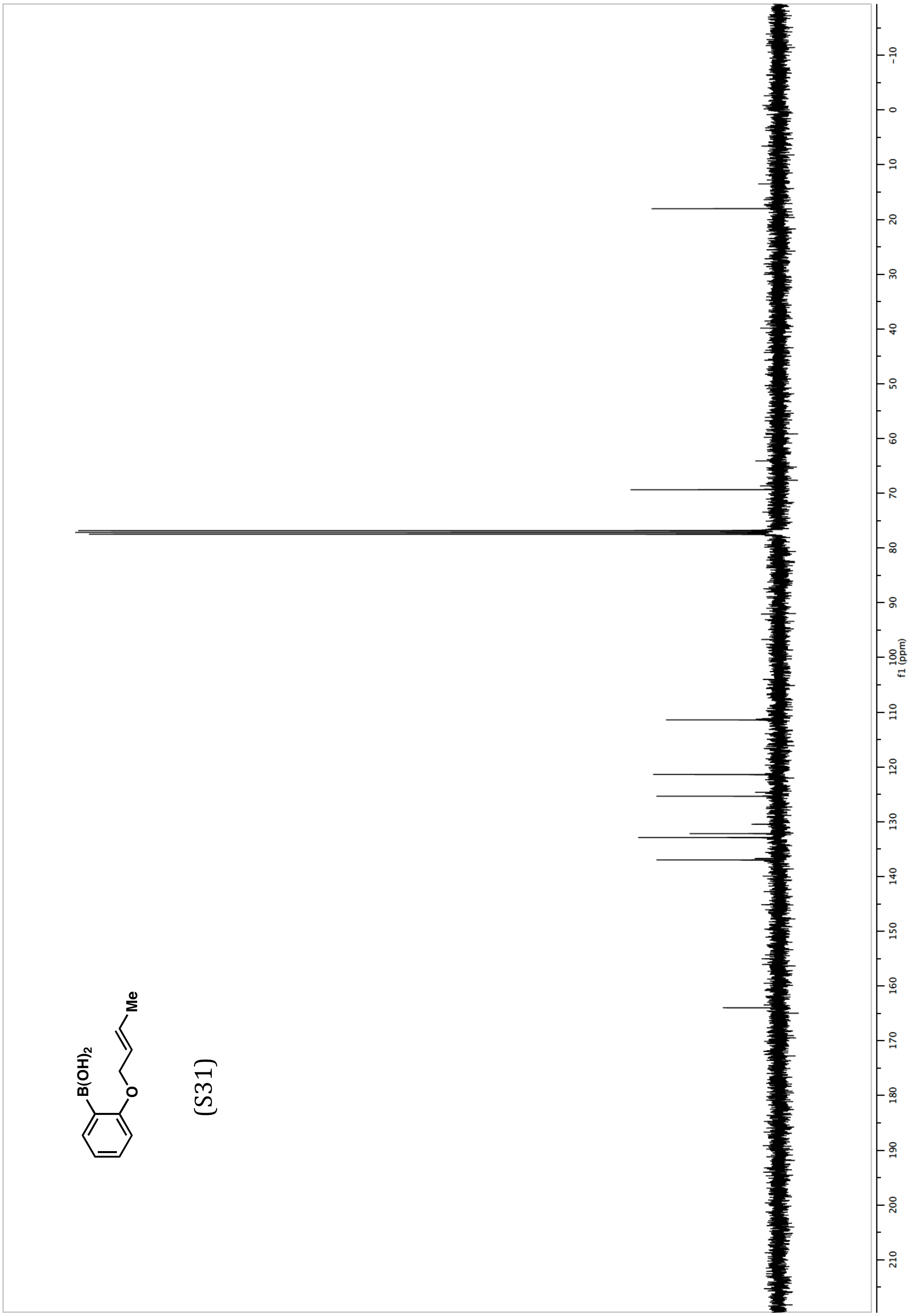

B(OH)2
O
Me
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
f1 (ppm)

(S30)


(S30)
B(OH)$_2$
O
Me
220
210
200
190
180
170
160
150
140
130
120
110
100
f1 (ppm)
90
80
70
60
50
40
30
20
10
0
−10
−20

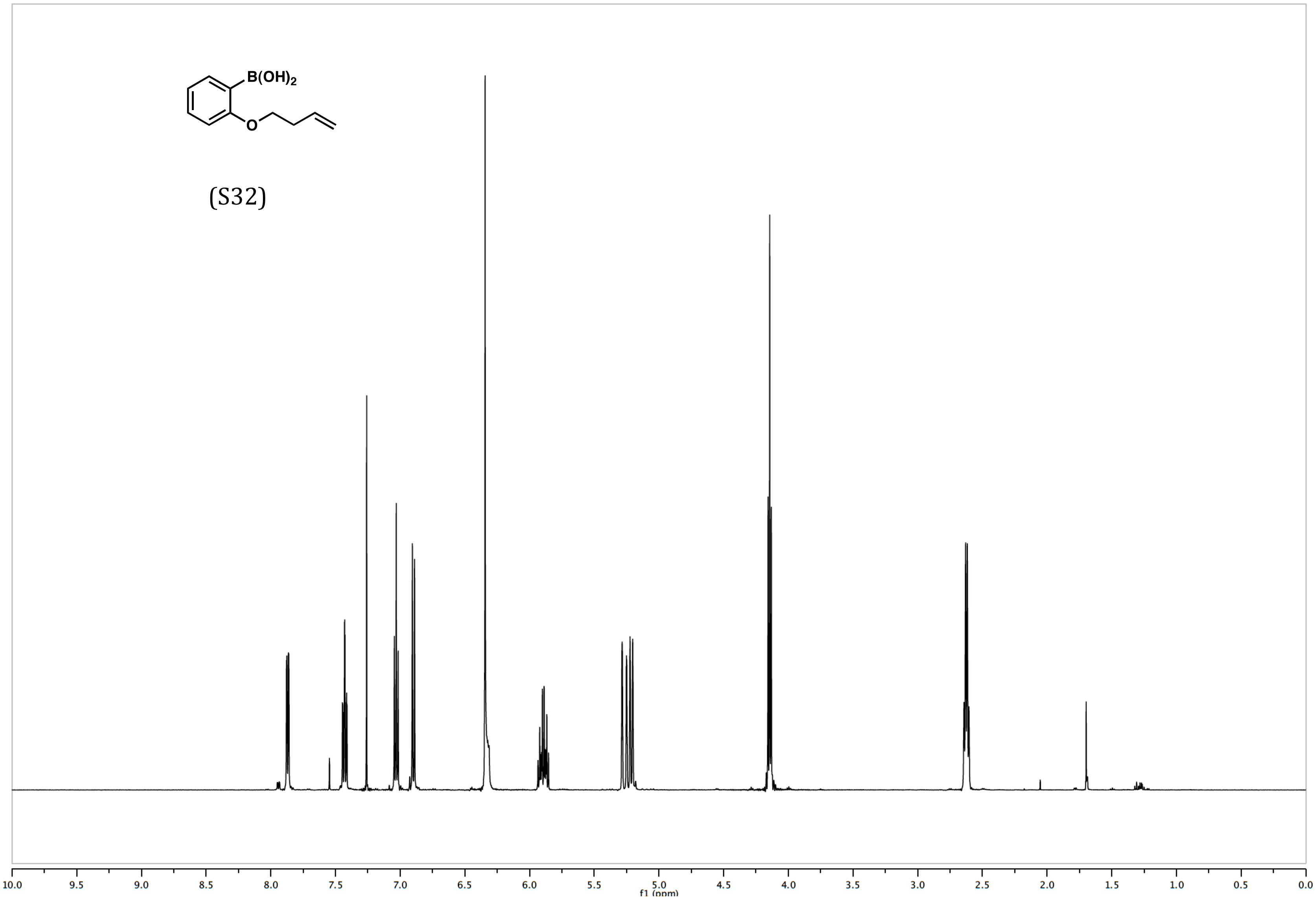

B(OH)2
O
Me
f1 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0

(S31)



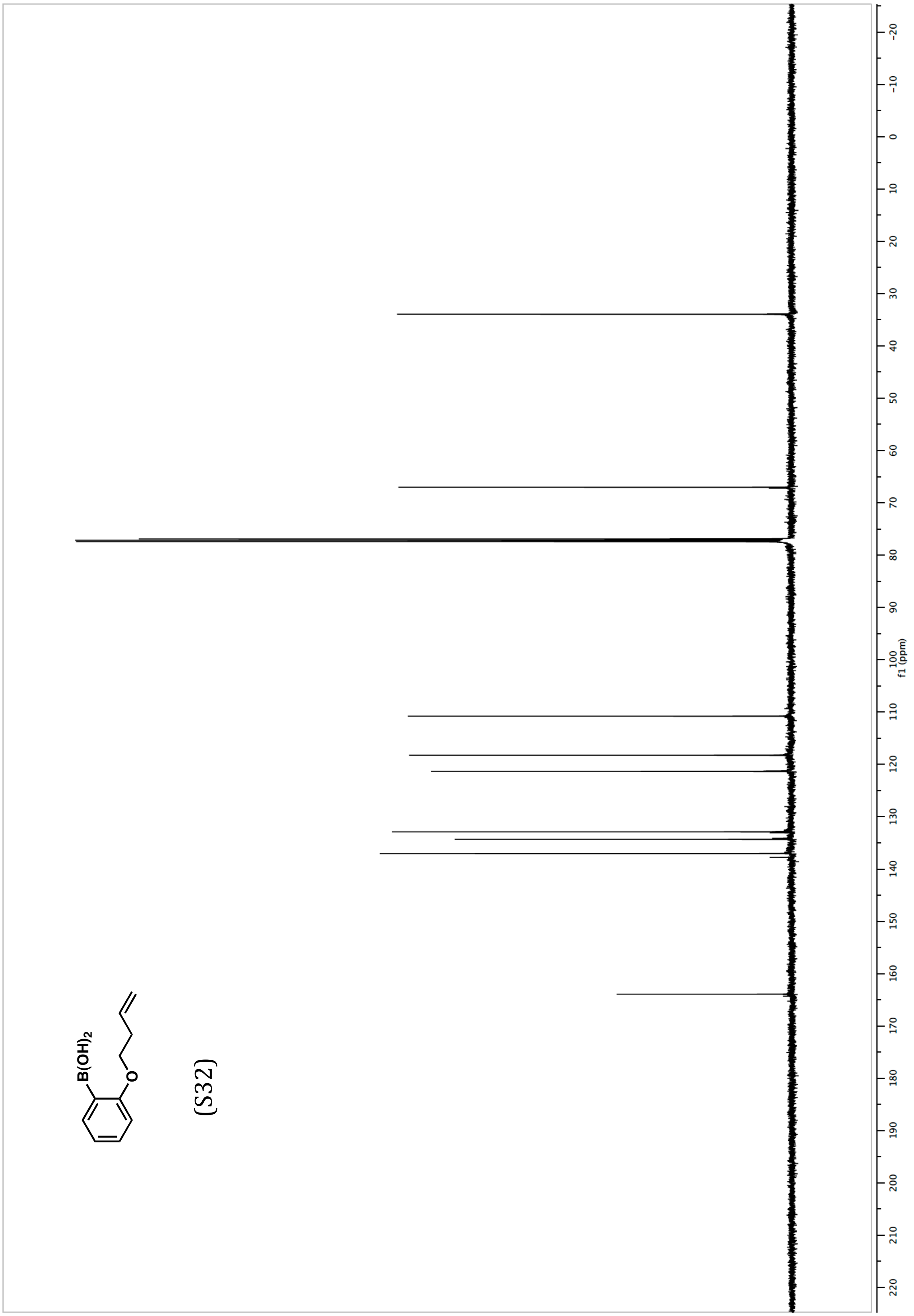
B(OH)2
O
Me
f1 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

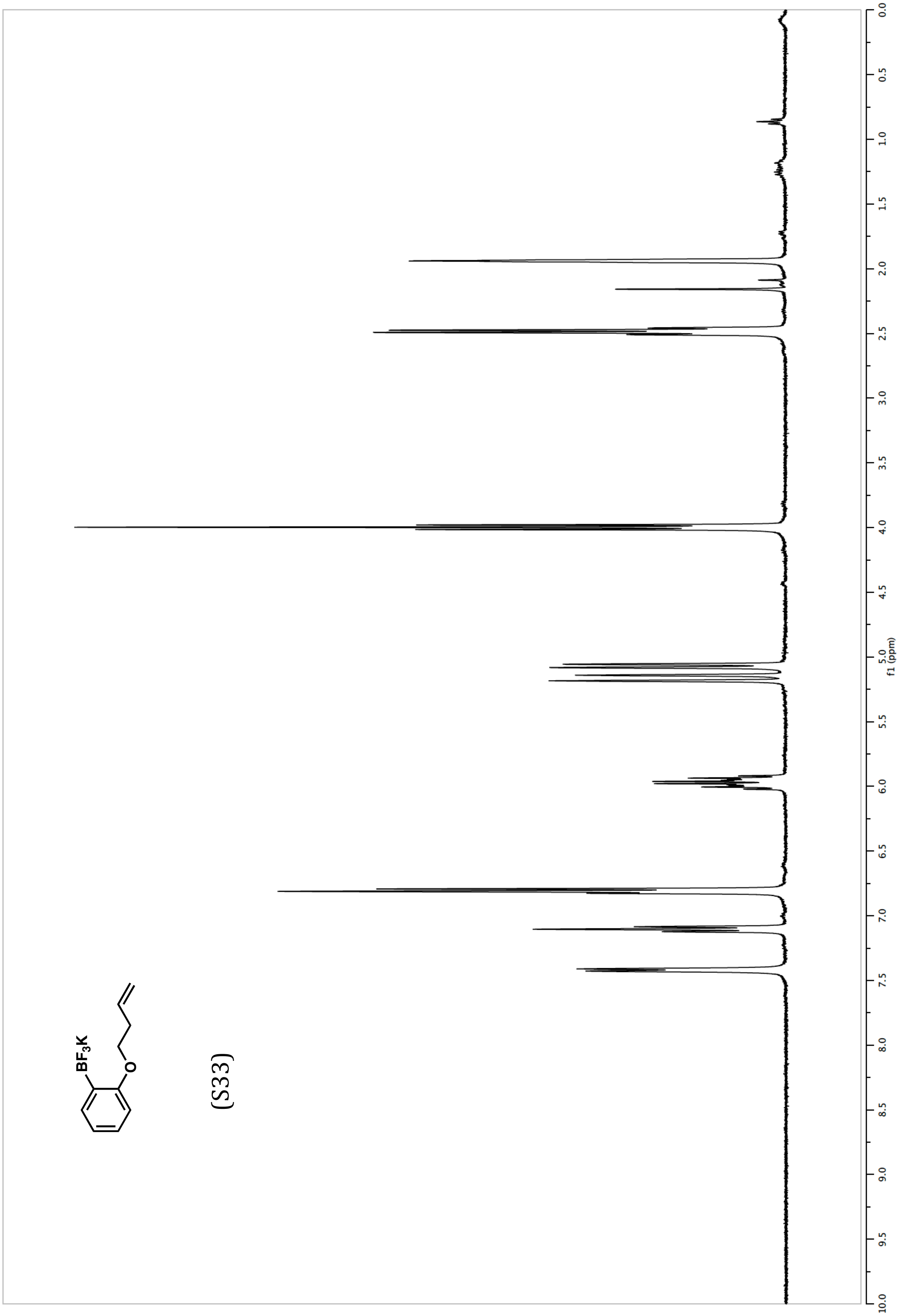
(S31)



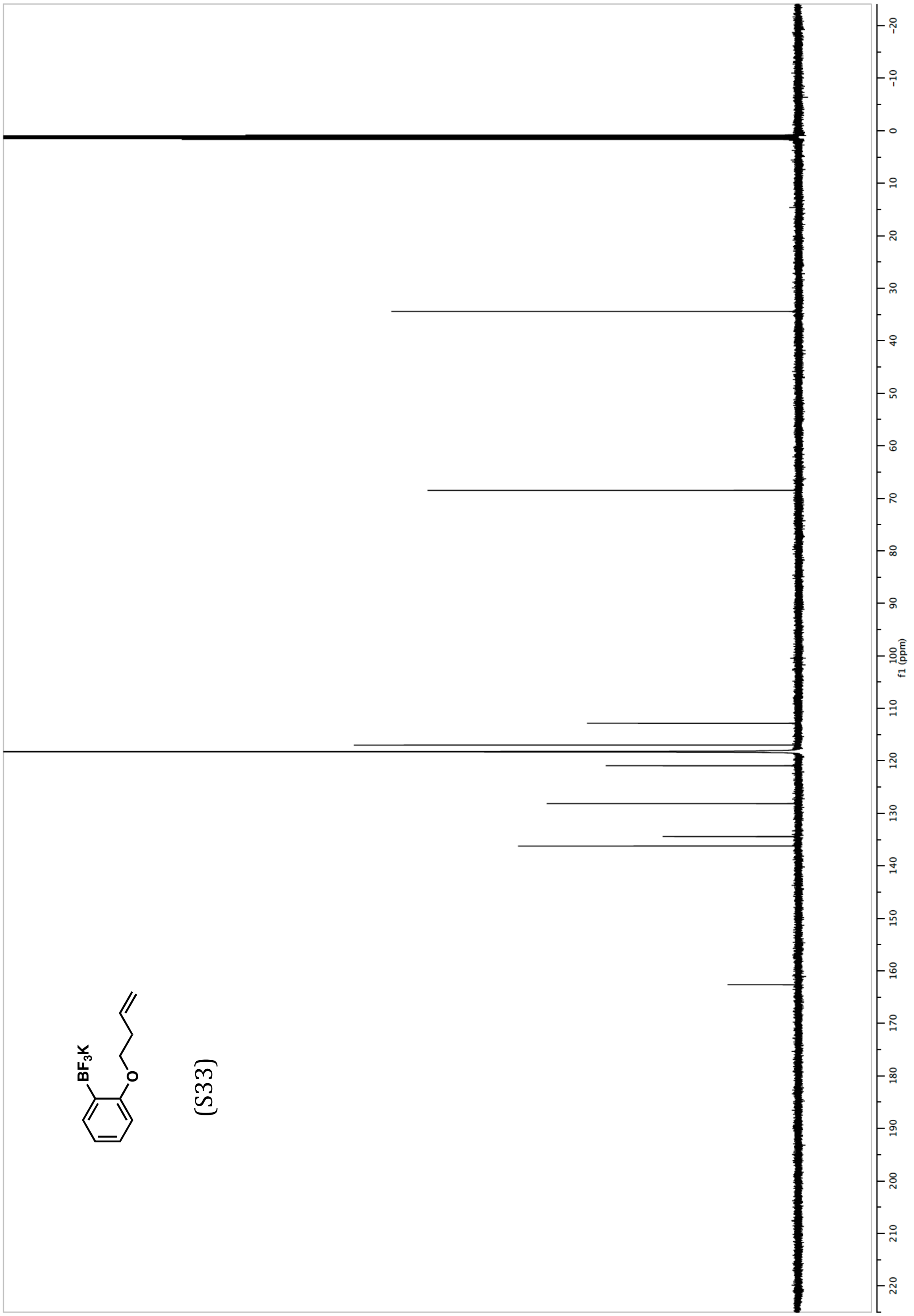
(S32)

B(OH)$_2$
O
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


B(OH)₂
O
(S32)
f1 (ppm)
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220

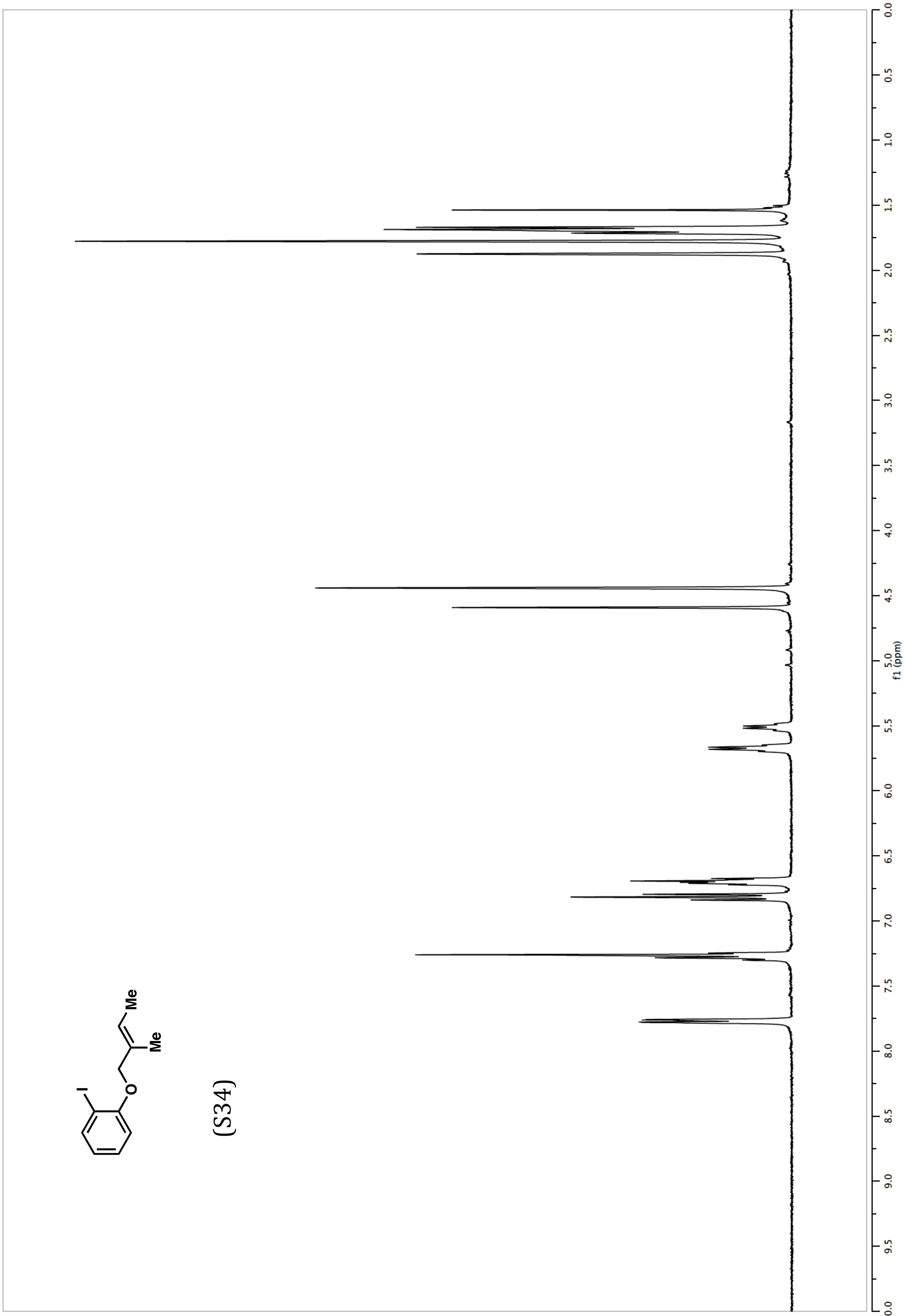

BF$_3$K
O
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0

(S33)



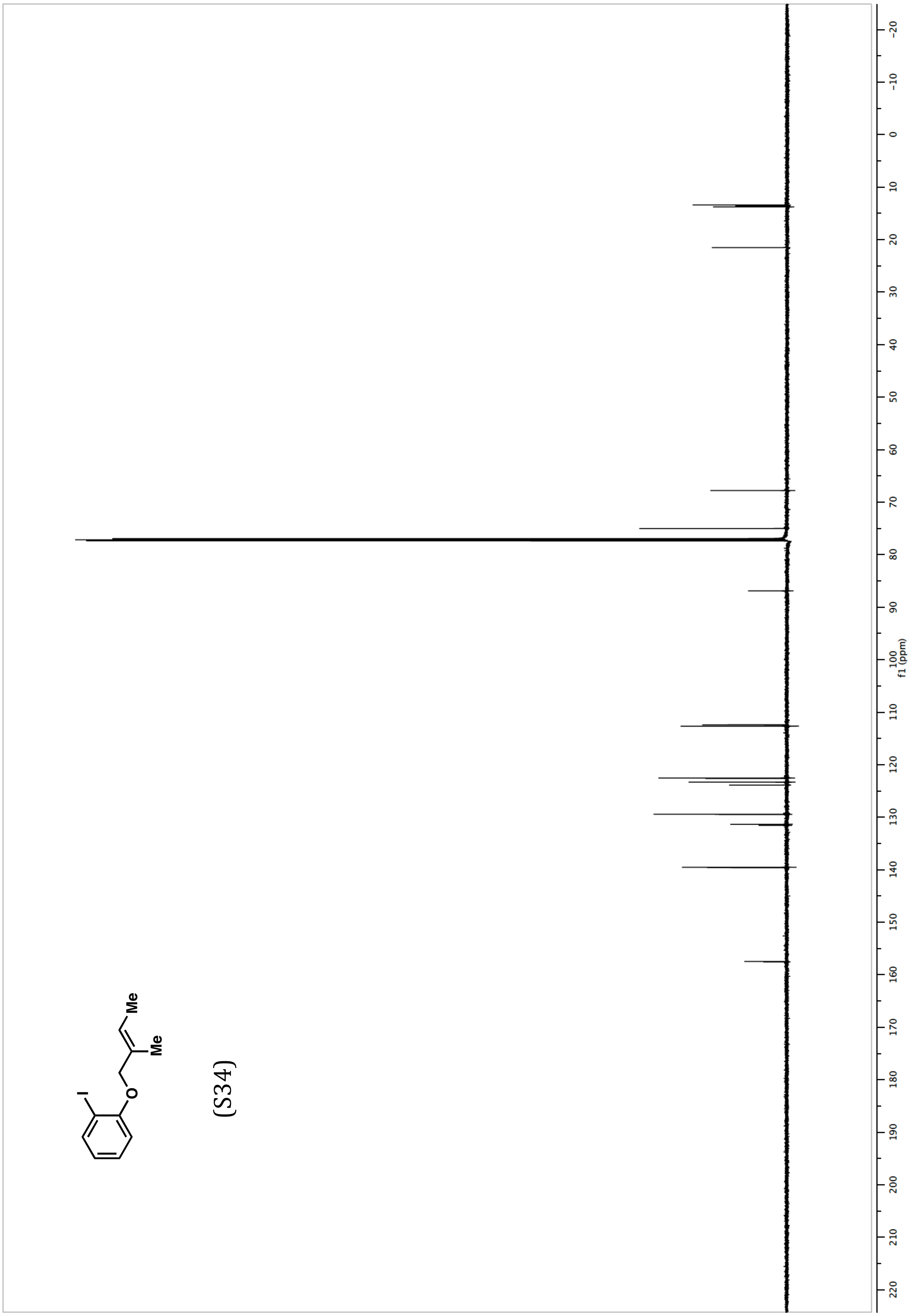
(S33)

BF$_3$K
O
-20
-10
0
10
20
30
40
50
60
70
80
90
100
f1 (ppm)
110
120
130
140
150
160
170
180
190
200
210
220



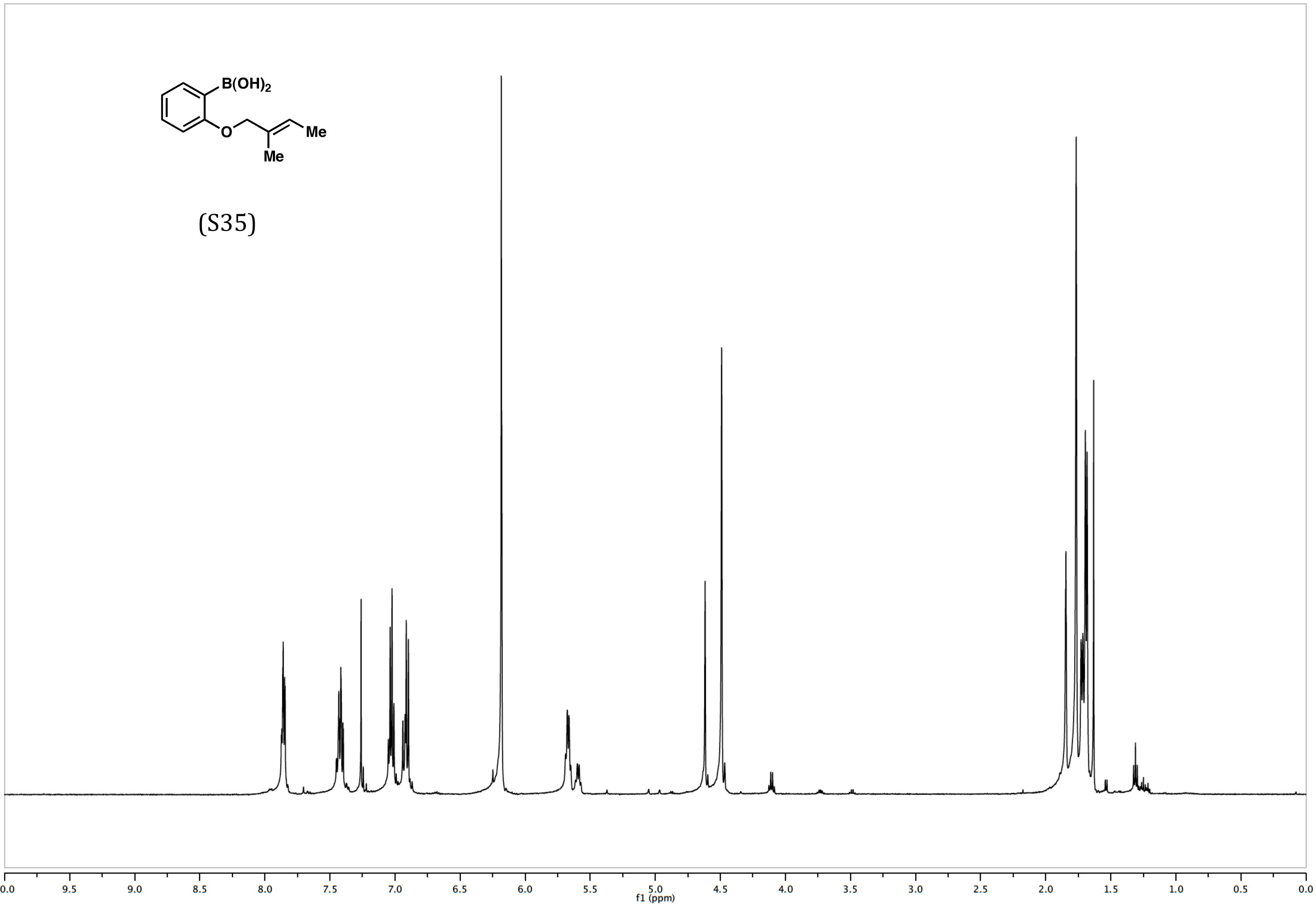
(S34)

I
O
Me
Me
f1 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0

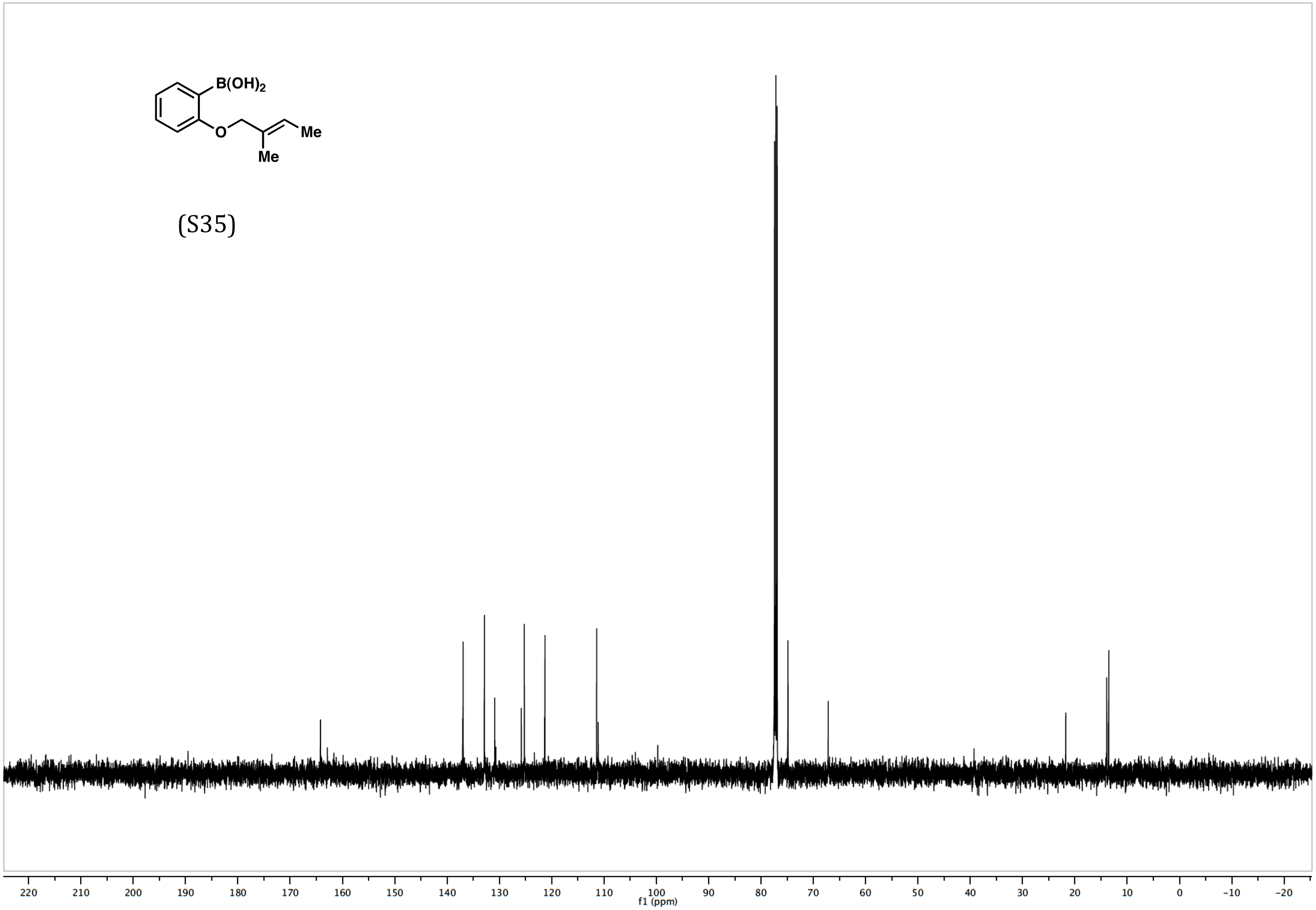


I
O
Me
Me
-20
-10
0
10
20
30
40
50
60
70
80
90
100
f1 (ppm)
110
120
130
140
150
160
170
180
190
200
210
220

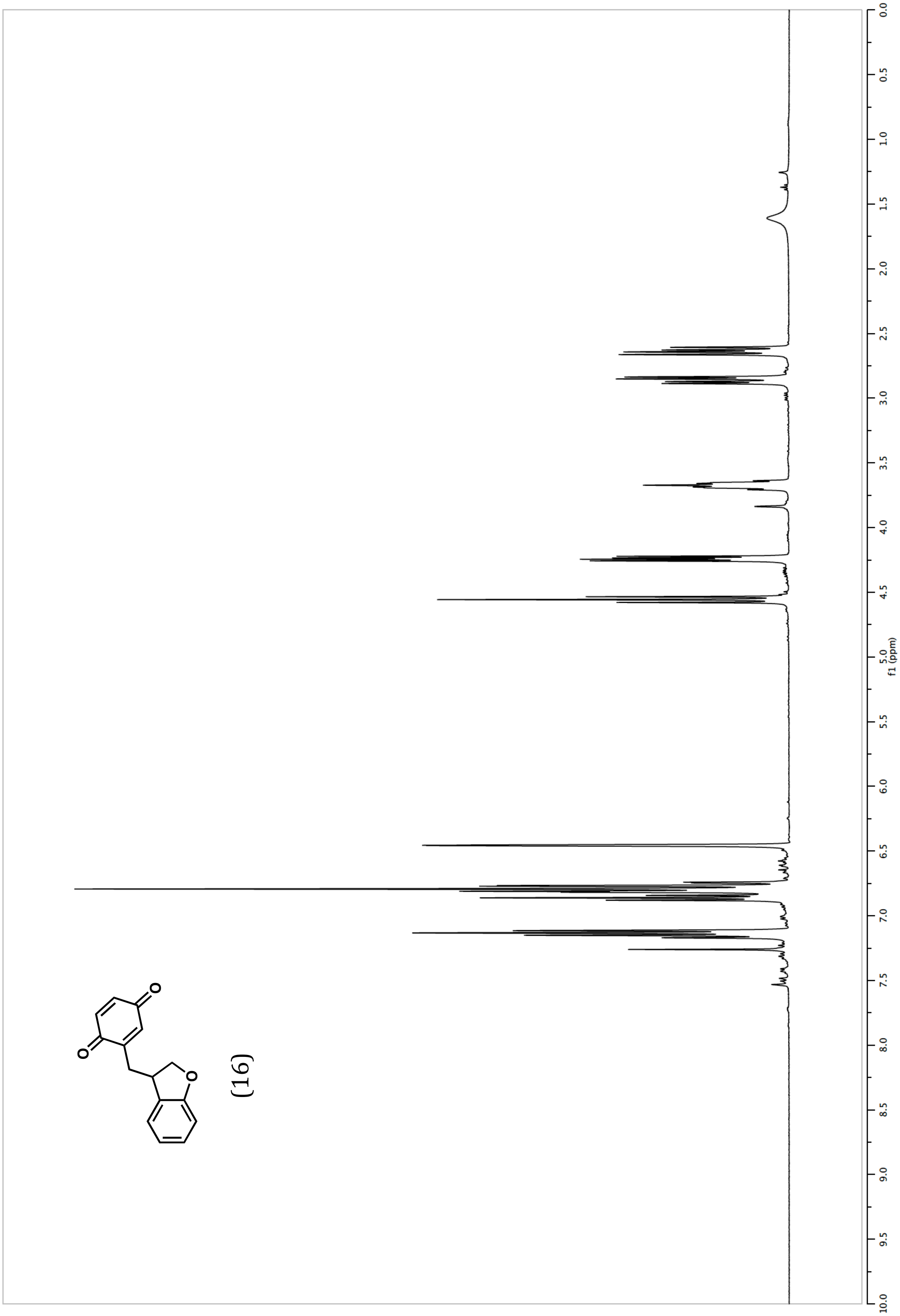
(S34)


B(OH)2
O
Me
Me
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

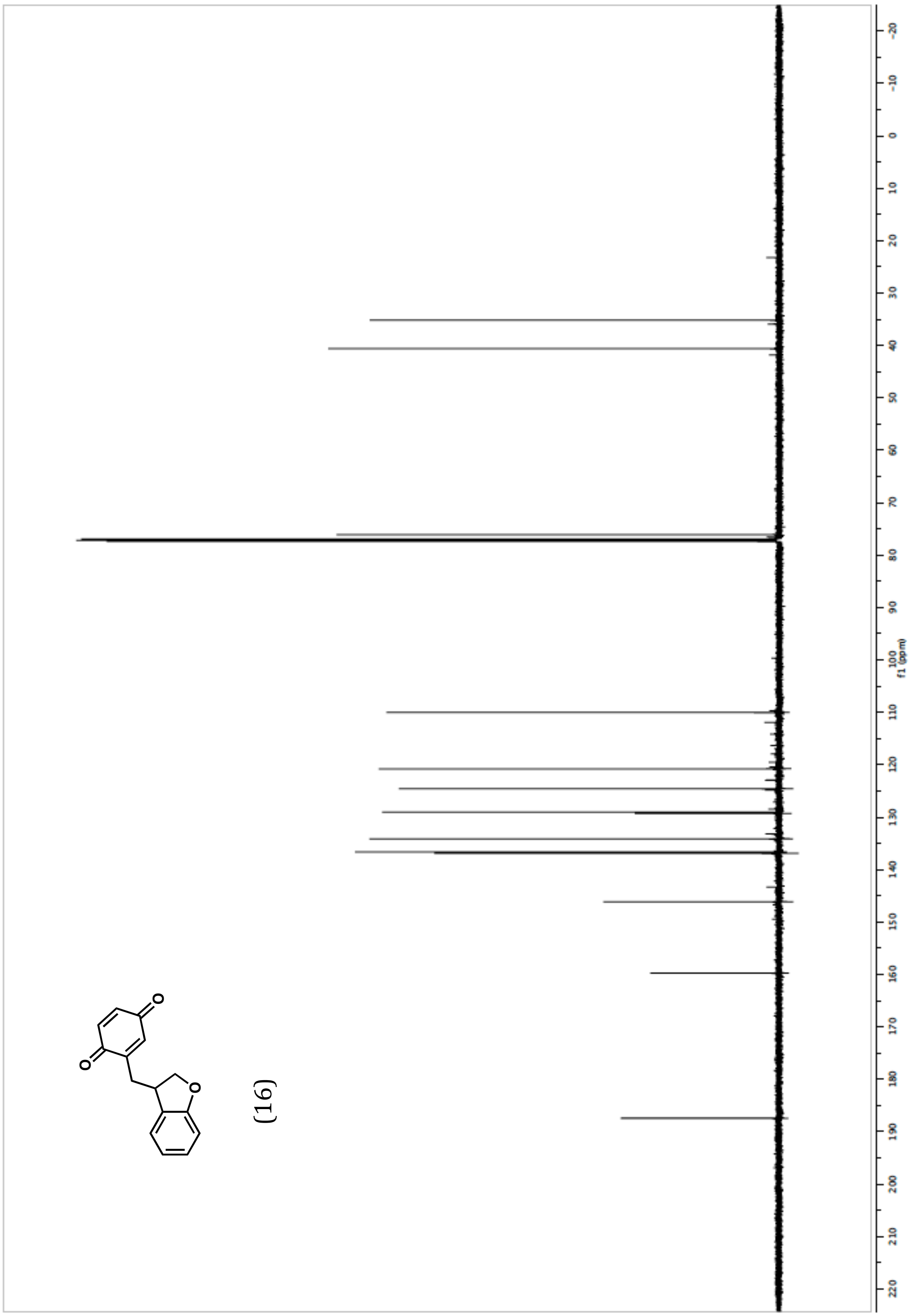
(S35)


B(OH)$_2$
O
Me
Me
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)

(S35)

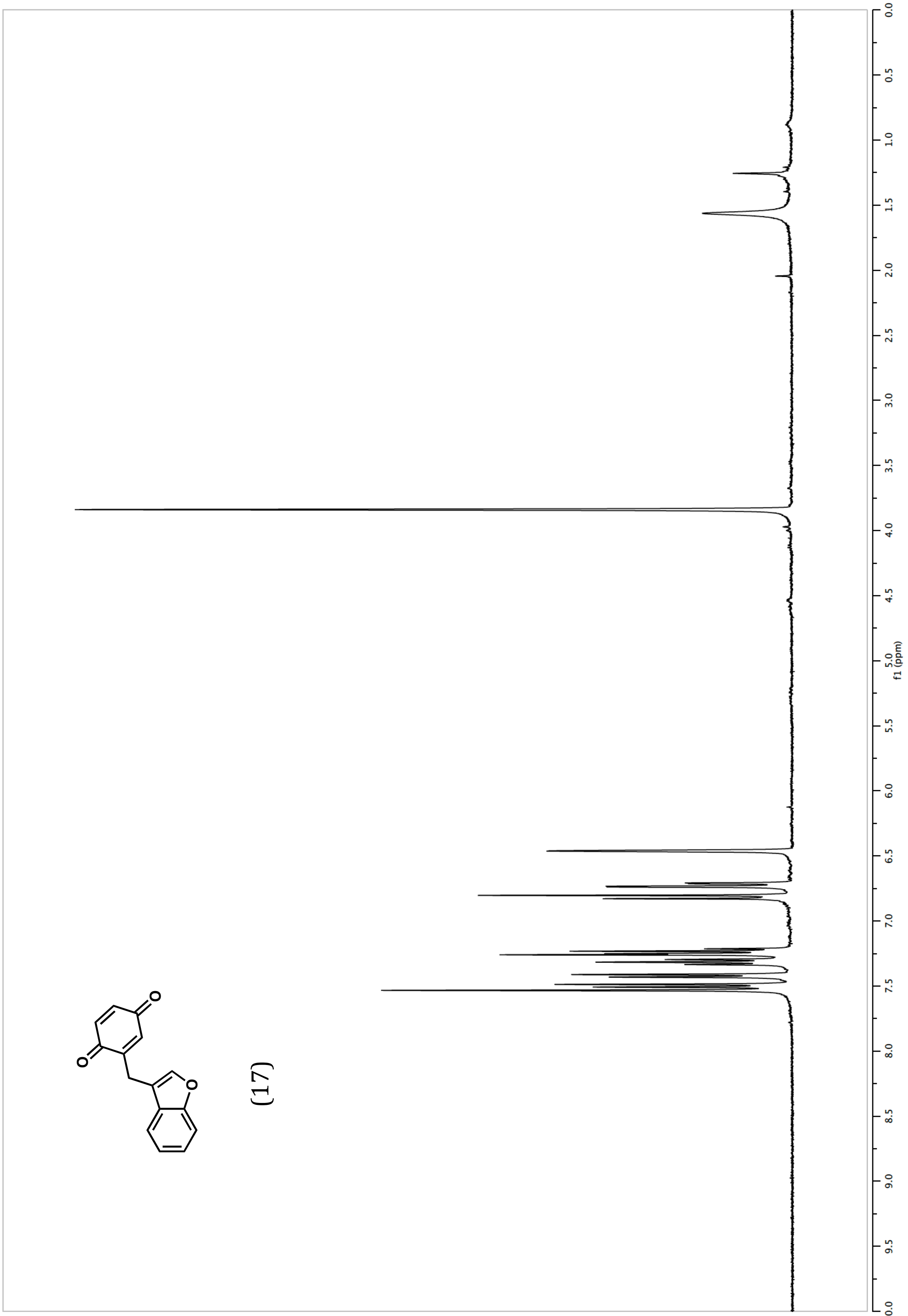


(16)

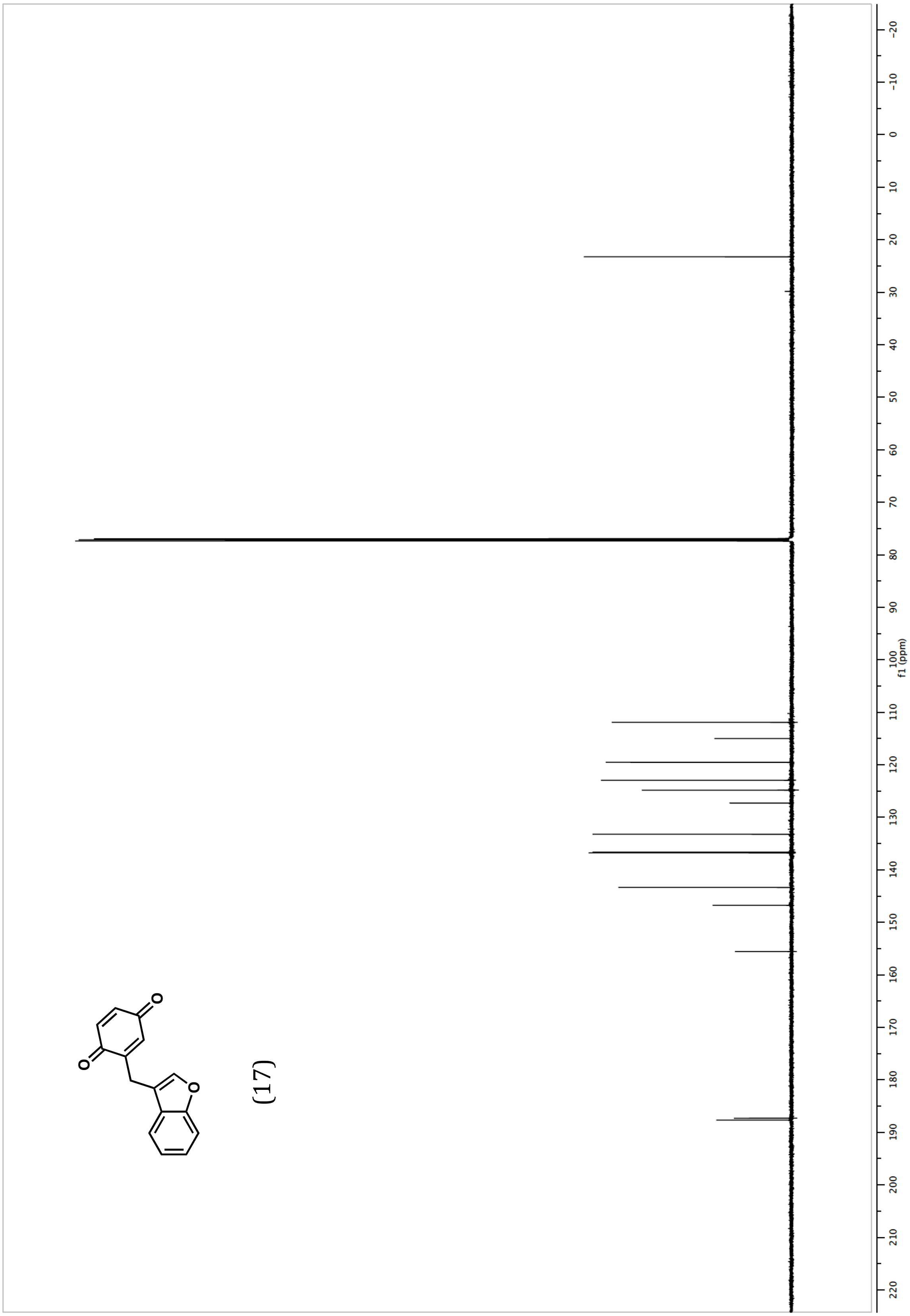


(16)

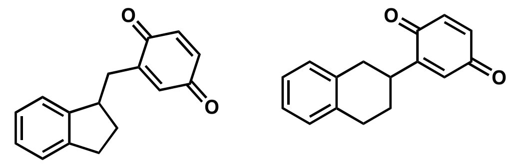
f1 (ppm)
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220


(17)

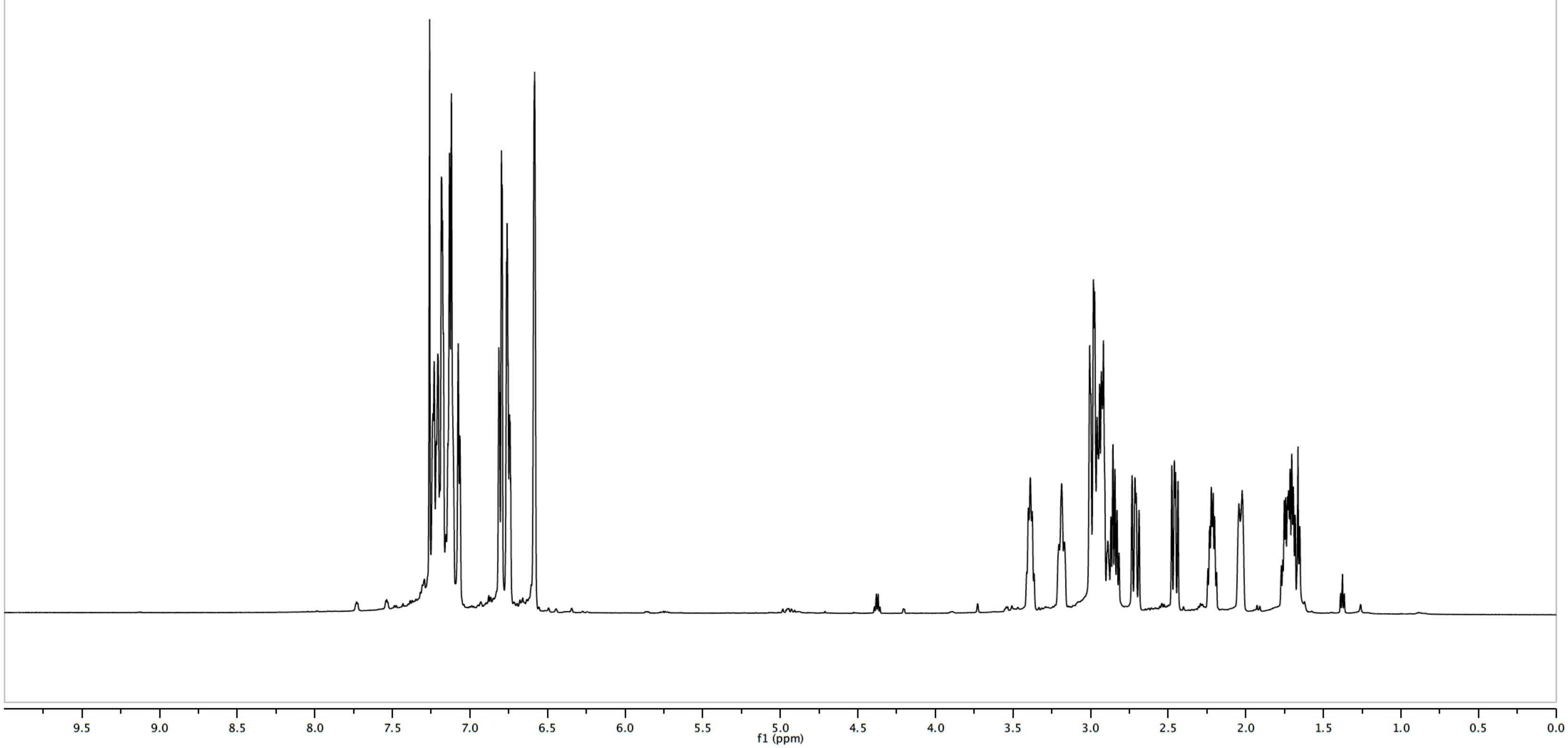
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
O
O
O

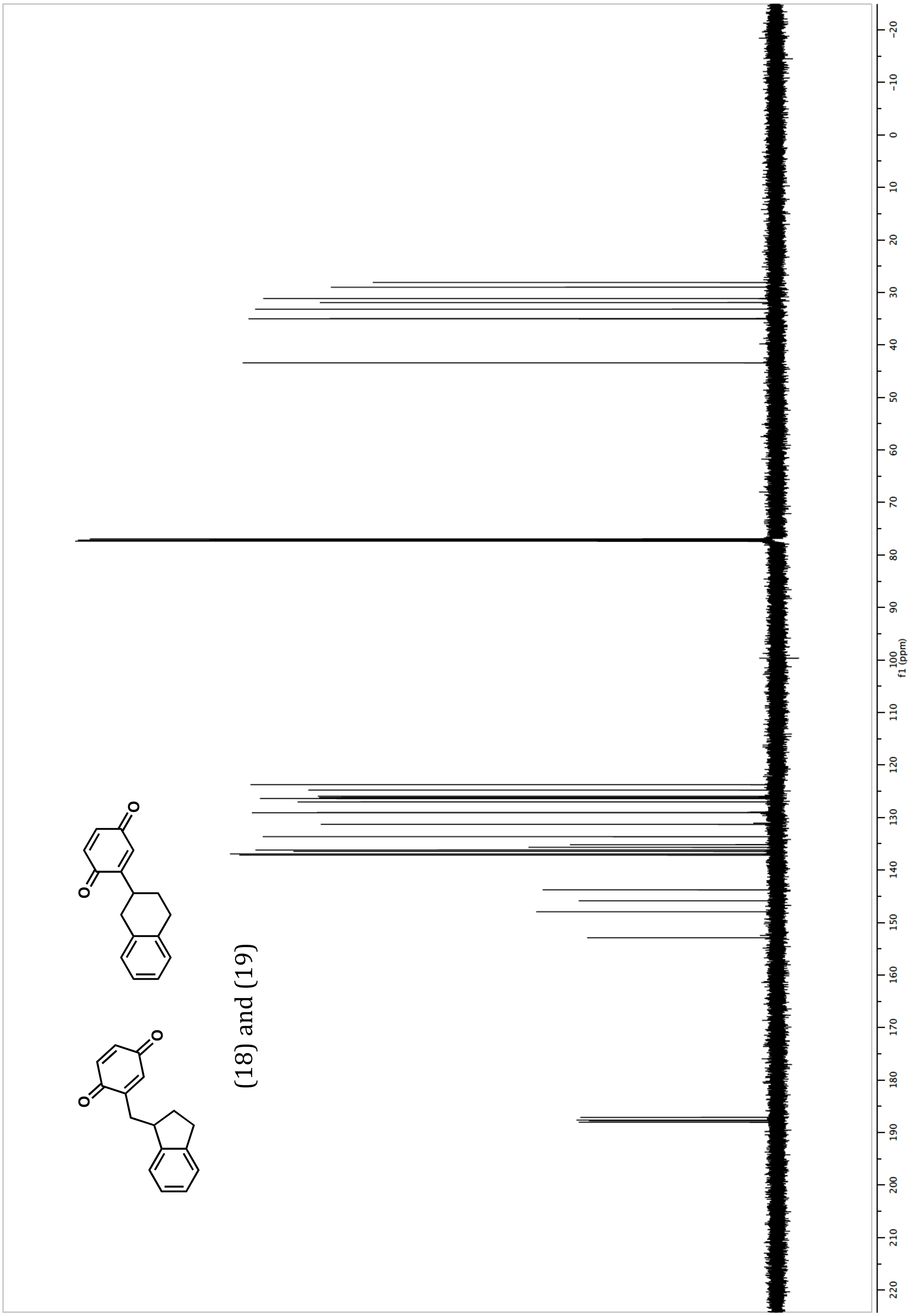

-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
f1 (ppm)

(17)



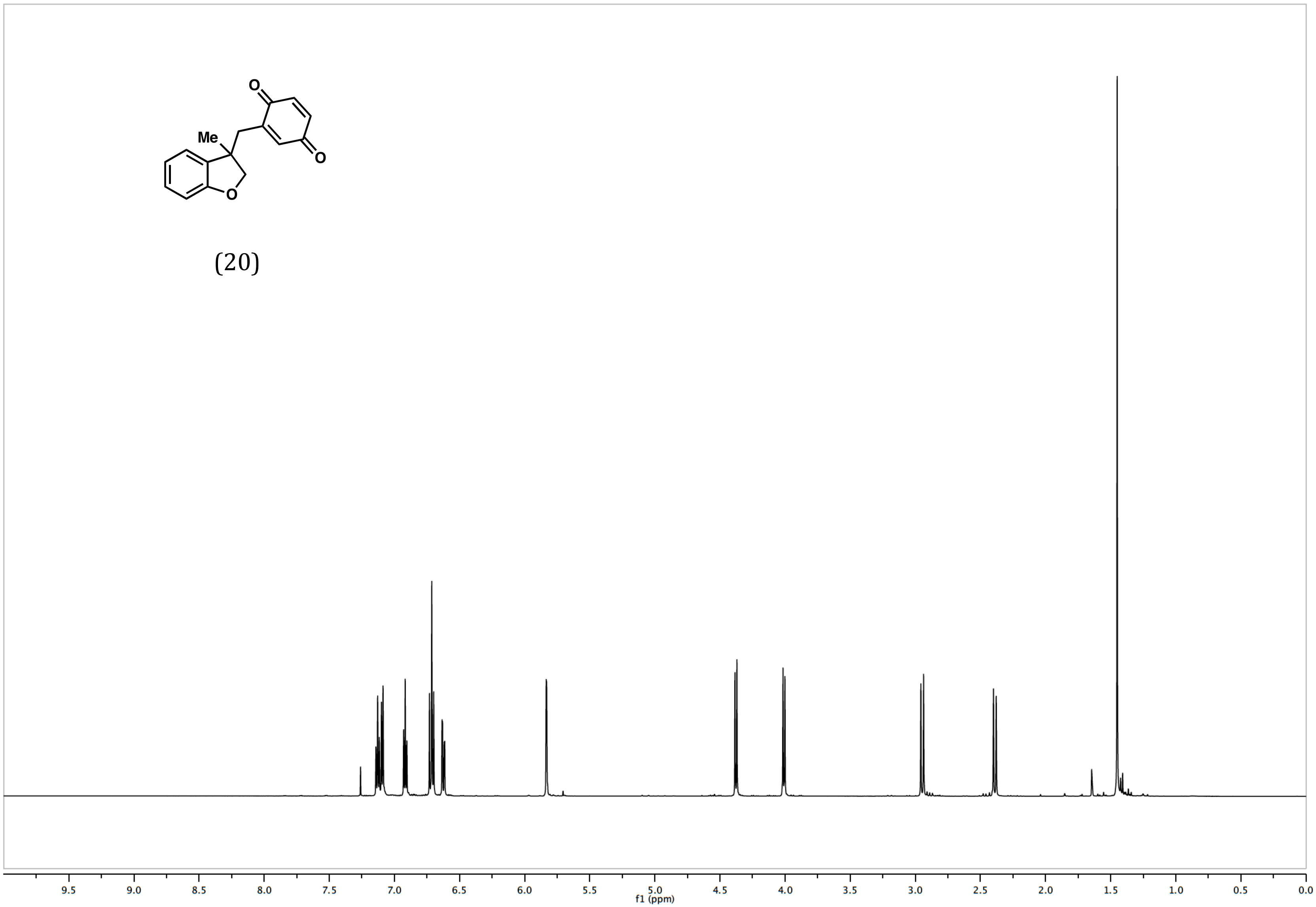
(18) and (19)



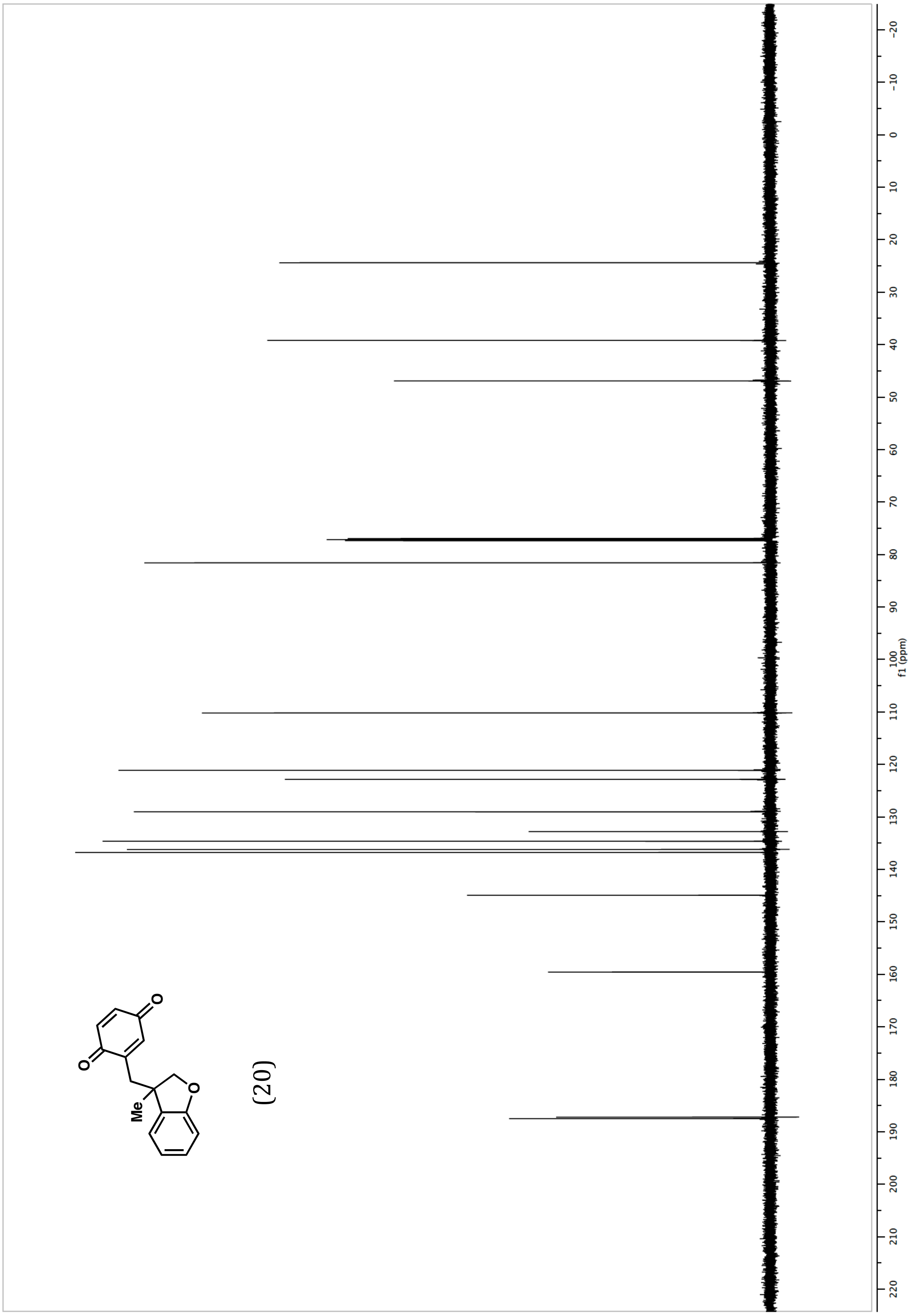


(18) and (19)

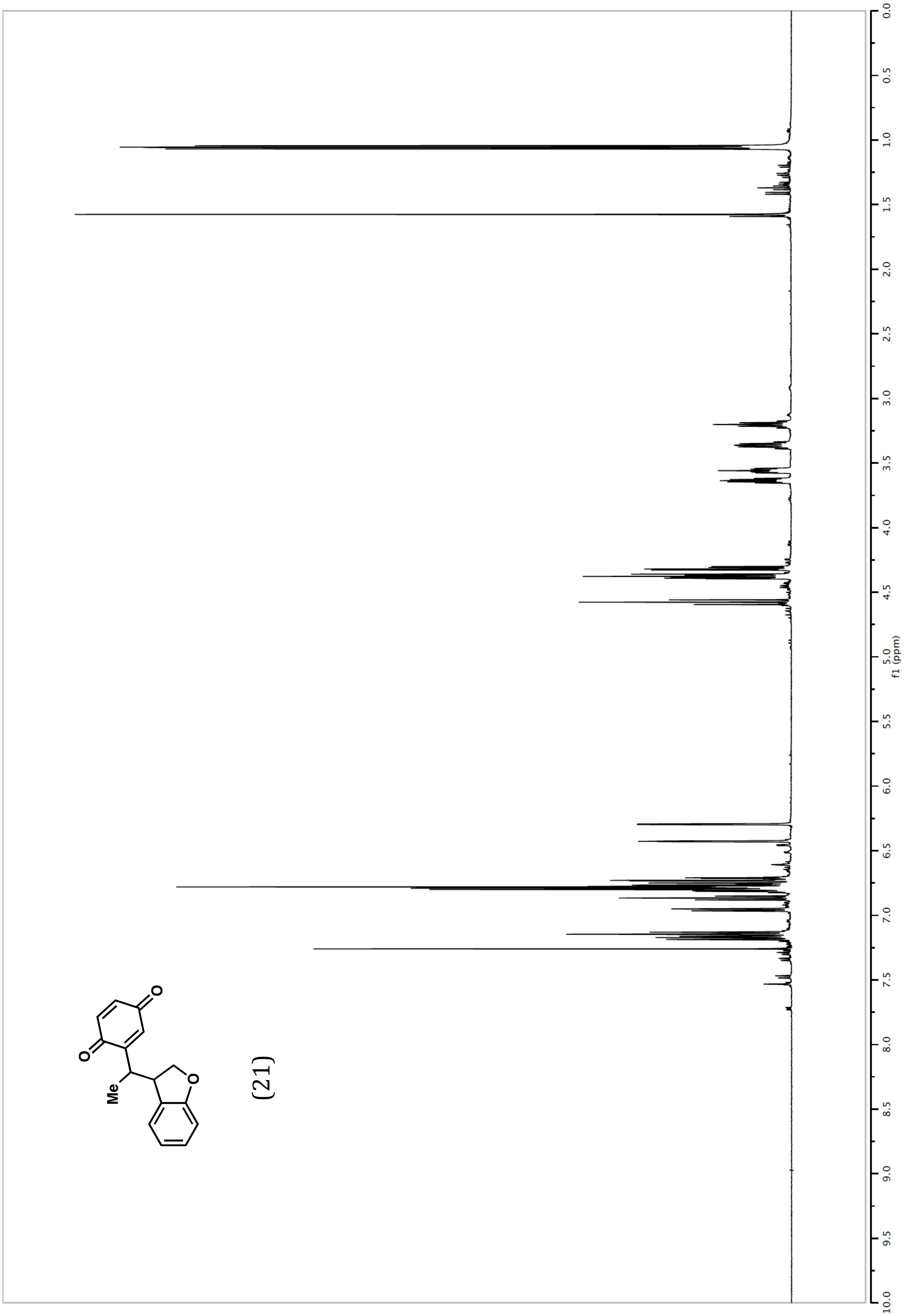
f1 (ppm)
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220


Me
O
O
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

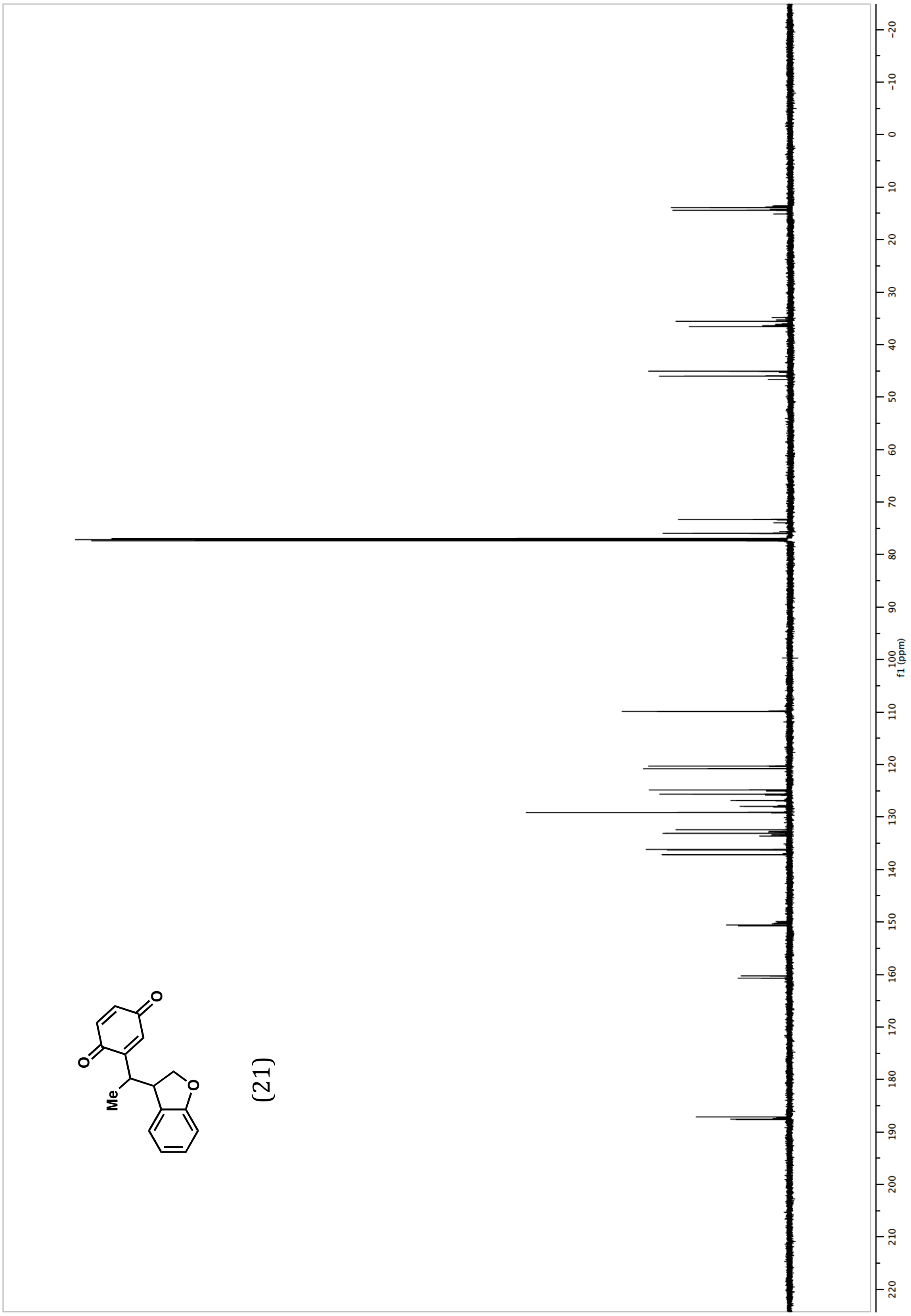
(20)


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

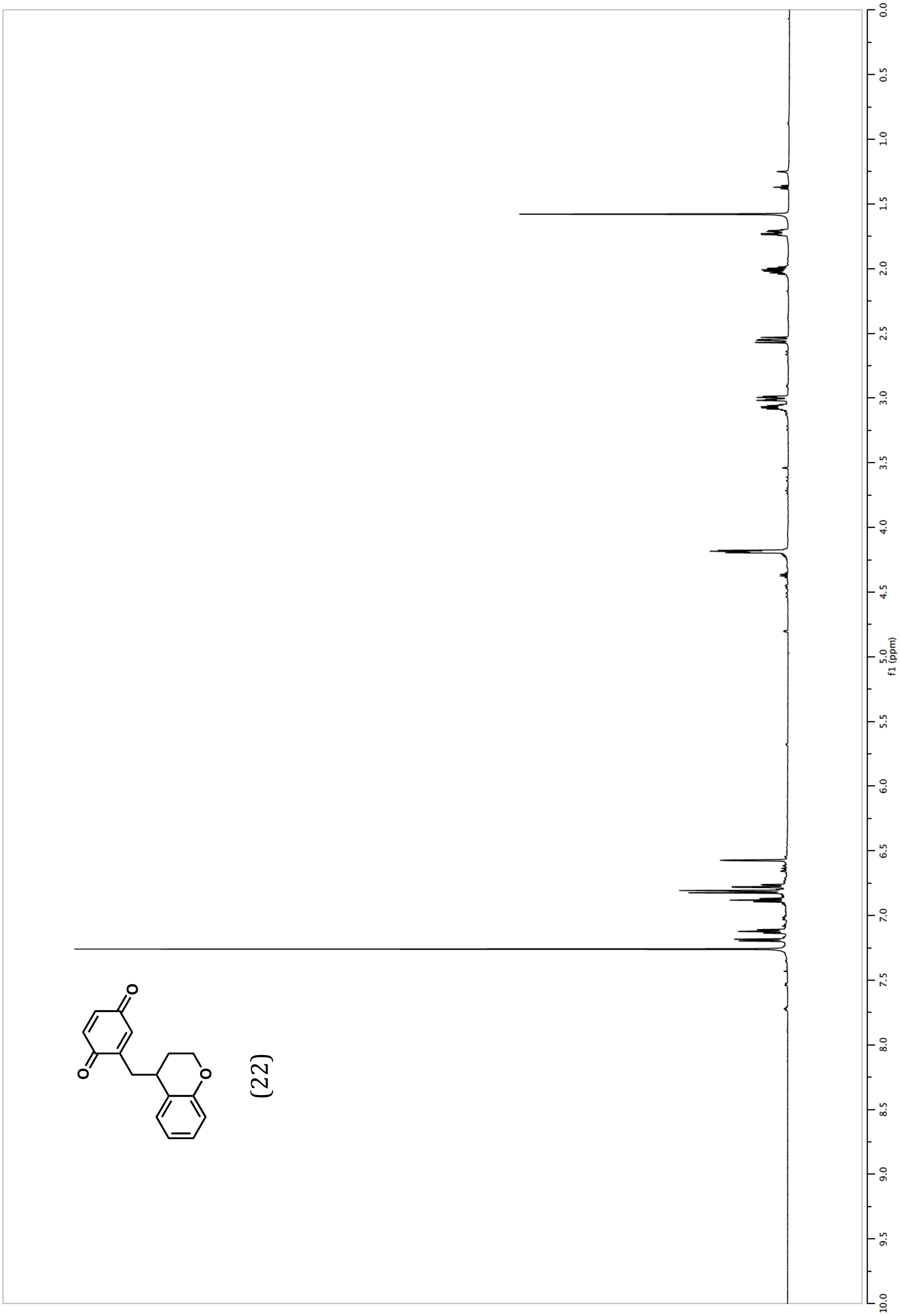
(20)


f1 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
Me
O
O
O

(21)


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

(21)



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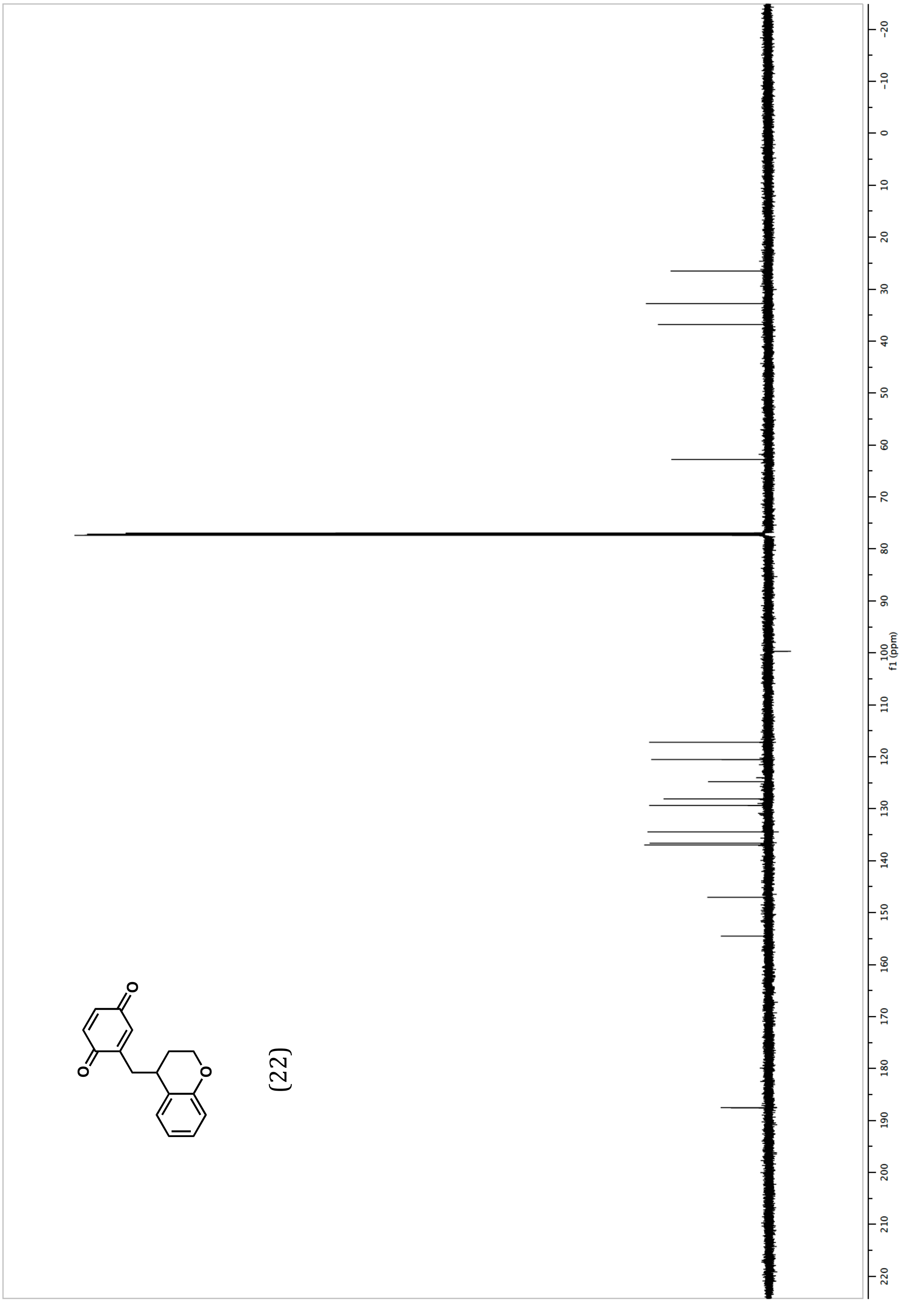
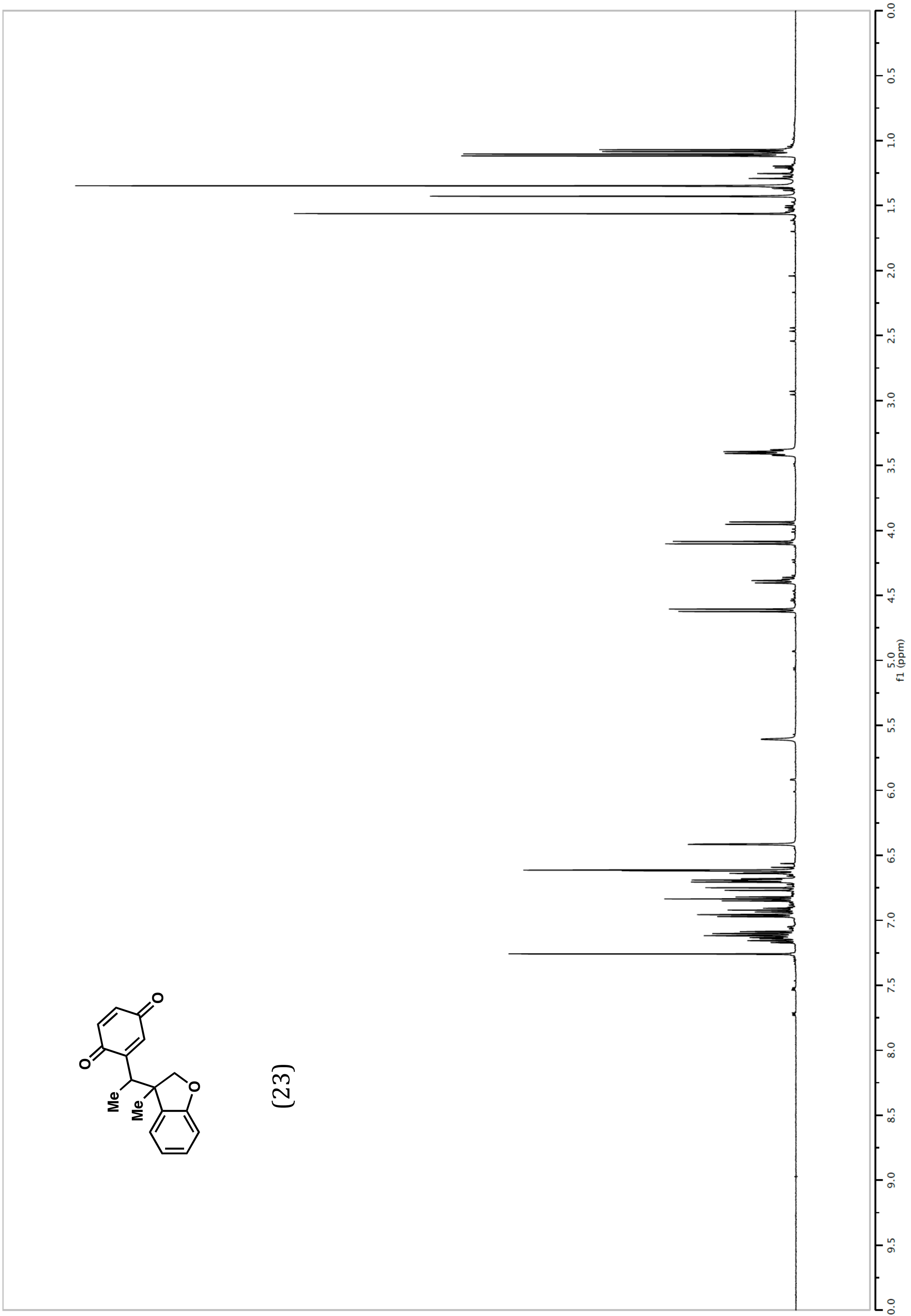
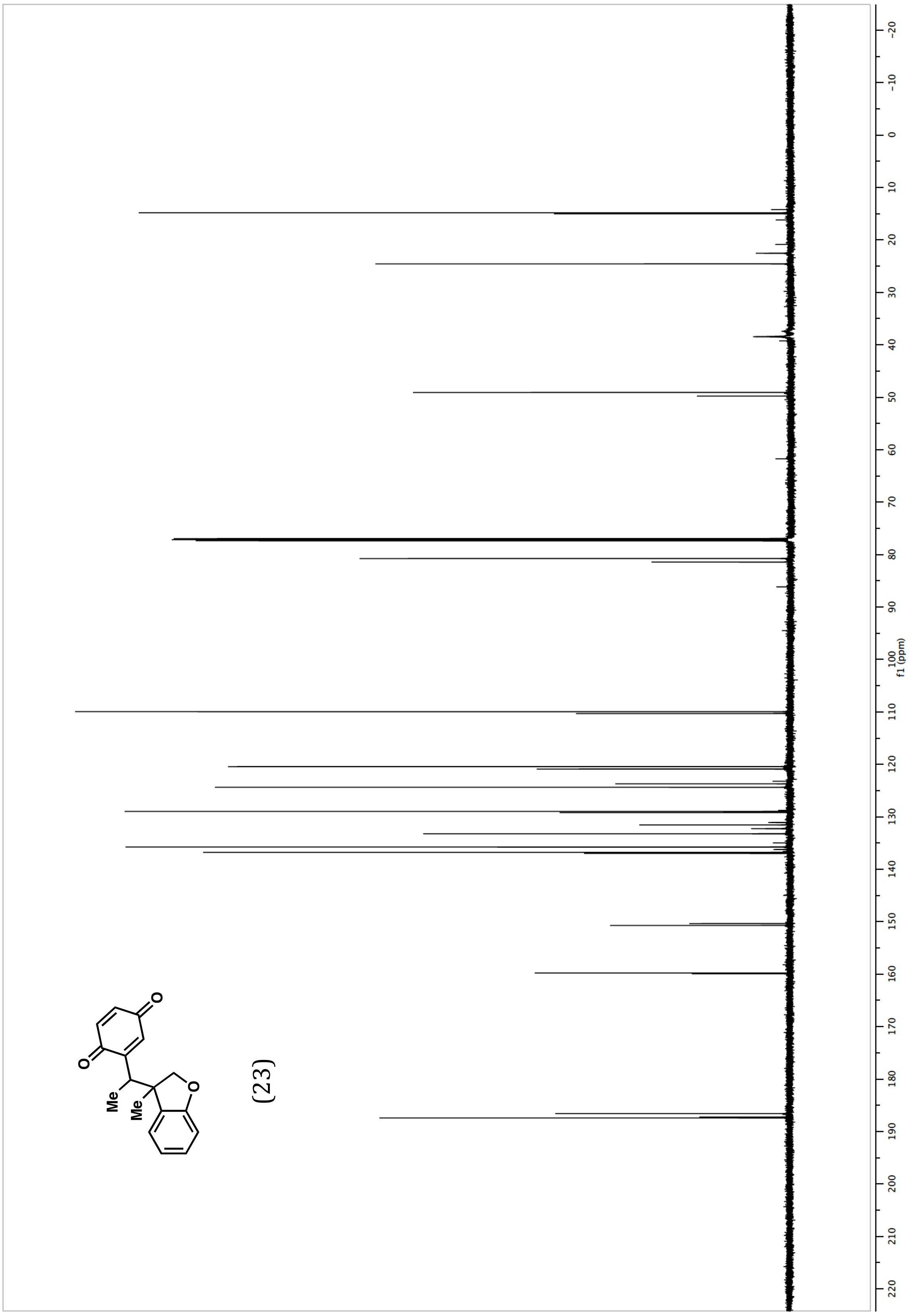

f1 (ppm)
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220

(22)


Me
Me
O
O
O
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0

(23)


(23)

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