Supporting Information

Iron-Catalysed Enantioselective Suzuki–Miyaura Coupling of Racemic Alkyl Bromides

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1. General.

All reactions dealing with air- or moisture-sensitive compounds were carried out in well-dried reaction vessels under a positive pressure of dry argon. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a PTFE cannula. Flash column chromatography was performed on Flash column chromatography was performed on Wakogel 60N, 38–100 μm or on a Biotage SP1 Flash Purification System with prepacked silica cartridges. Preparative recycling gel permeation chromatography (GPC) was performed with a Japan Analytical Industry LC-9204 instrument equipped with JAIGEL-1H/JAIGEL-2H columns using chloroform as an eluent.

^1H and ^{13}C NMR spectra were recorded on a JEOL ECS-400NR NMR spectrometer (391.8 and 98.5 MHz, respectively). The ^1H chemical shift

values are reported in parts per million (ppm, δ scale) and referenced to the ^{1}H resonance of tetramethylsilane (δ 0.00). The ^{13}C chemical shift values are reported in parts per million, and referenced to the ^{13}C resonance of $CDCl_3$ (δ 77.16). Data are presented as: chemical shift, multiplicity, coupling constant in Hertz (Hz) and signal area integration in natural numbers. NMR yield was determined for a crude product by ^{1}H NMR analysis by using 1,1,2,2-tetrachloroethane as an internal standard.

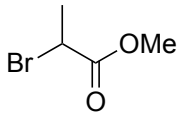
GC analysis was conducted with Shimadzu GC-2010 and GC-2010 Plus instruments equipped with an FID detector and a capillary column, ZB-1MS (Phenomenex Inc., 10 m × 0.10 mm i.d., 0.10 μm film thickness). GC yield was determined for a crude product using undecane as a internal standard.

The er values were determined by GC or HPLC analysis using a chiral stationary column. IR spectra were recorded on PerkinElmer Spectrum One FT-IR spectrometers, and reported in cm^{-1}.High-resolution mass spectra (HRMS) were obtained using electron ionization (EI) on a JEOL JMS-700 mass spectrometer.

Unless otherwise noted, commercially available materials were used without purification. Tetrahydrofuran (THF), purchased from Wako Pure Chemical Industries, Ltd. (Wako), was distilled over benzophenone ketyl. Water content of the solvents was determined with a Karl Fischer Moisture Titrator (MKC-610, Kyoto Electronics Company) to be less than 15 ppm. Metal salts were purchased, and purities, commercial suppliers and production numbers are as follows: $FeCl_2$ (99.998%, Aldrich Inc., 429368), $MgBr_2$ (≥99.99%, Aldrich Inc., 495093).

2. Preparation of Starting Materials

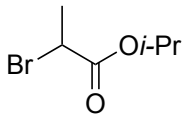
Methyl 2-bromopropionate



To a solution of 2-bromopropionic acid (0.9 mL, 10 mmol) in MeOH (5 mL) was added thionyl chloride (0.9 mL, 12 mmol) at 0 °C, and then the mixture was stirred at room temperature for 12 h. The reaction mixture was quenched with sat. $NaHCO_3$ aq. (30 mL) and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The organic layers were combined, dried with $MgSO_4$, and filtered. The solvent was removed under reduced pressure to afford the crude product. The crude product was purified by distillation to give the title product as a colorless liquid (800 mg, 48%).

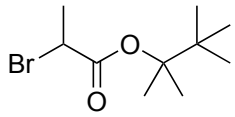
^{1}H NMR ($CDCl_3$) δ 1.83 (d, J = 6.9 Hz, 3H), 3.79 (s, 3H), 4.39 (q, J = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.8, 39.9, 53.1, 170.8; Anal. calcd for $C_4H_7BrO_2$, C, 28.77; H, 4.23. found C, 28.91; H, 4.24. All analytical data are in good accordance with those reported in the literature[1].

Isopropyl 2-bromopropionate



To a solution of 2-bromopropionic acid (0.9 mL, 10 mmol) in *i*-PrOH (5 mL) was added thionyl chloride (0.9 mL, 12 mmol) at 0 °C, and then the mixture was stirred at room temperature for 12 h. The reaction mixture was quenched with sat. $NaHCO_3$ aq. (30 mL) and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The organic layers were combined, dried with $MgSO_4$, and filtered. The solvent was removed under reduced pressure to afford the crude product. The crude product was purified by distillation to give the title product as a colorless liquid (1.24 g, 64%).
^{1}H NMR ($CDCl_3$) δ 1.28 (d, J = 6.3 Hz, 6H), 1.81 (d, J = 7.0 Hz, 3H), 4.32 (q, J = 7.0 Hz, 1H), 5.06 (hept, J = 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.5, 21.67, 21.70, 40.8, 69.7, 169.9; Anal. calcd for $C_6H_{11}BrO_2$, C, 36.95; H, 5.68. found C, 36.93; H, 5.64. All analytical data are in good accordance with those reported in the literature[1].

2,3,3-Trimethylbut-2-yl 2-bromopropionate

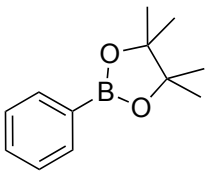


To a solution of 2-bromopropionic acid (3.6 mL, 40 mmol) in Et_2O (40 mL) was added trifluoroacetic anhydride (7.4 mL, 52 mmol) at room temperature, and the mixture was stirred for 18 h. After addition of 2,3,3-trimethylbutan-2-ol (15.59 g, 134 mmol), the resulting solution was stirred at 40 °C for 5 days. The reaction mixture was added to a solution of $NaHCO_3$ (10.2 g, 120 mmol) in water (100 mL), and the aqueous layer was extracted with EtOAc (20 mL × 3). The organic layers were combined, dried with $MgSO_4$, and filtered. The solvent was removed under reduced pressure to afford the crude product. The crude product was purified by distillation to give the title product as a colorless liquid (1.10 g, 11%).
^{1}H NMR ($CDCl_3$) δ 1.00 (s, 9H), 1.52 (s, 6H), 1.79 (d, J = 7.0 Hz, 3H), 4.30 (q, J = 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.2, 20.4, 21.9, 25.3 (3C), 38.7, 42.6, 89.2, 169.2; Anal. calcd for $C_{10}H_{19}BrO_2$, C, 47.82; H, 7.63. found C, 48.08; H, 7.64. All analytical data are in good accordance with those reported in the literature[2].

Synthesis of 4,4,5,5,-Tetramethyl-2-aryl-1,3,2-dioxaborolanes

General Procedure A: Arylboronic acid and pinacol (1.2 equiv) were dissolved in THF with molecular sieves 4 Å at room temperature, and the mixture was stirred at the temperature for 12 h. Then the solvent was evaporated in vacuo, and excess pinacol was removed by silica gel column chromatography (toluene = 100%).

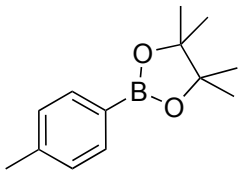
2-Phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



The title product was synthesized according to the general procedure A using phenylboronic acid (7.87 g, 65 mmol) and pinacol (9.18 g, 78 mmol). The product was obtained as a colorless solid (12.5 g, 94%) after distillation.

^{1}H NMR ($CDCl_3$) δ 1.34 (s, 12H), 7.36 (tt, J = 7.0, 1.1 Hz, 2H), 7.45 (tt, J = 7.4, 1.6 Hz, 1H), 7.81 (d, J = 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ25.0 (4C), 83.9 (2C), 127.8 (2C), 131.4, 134.9 (2C); Anal. calcd for $C_{12}H_{17}BO_2$, C, 70.63; H, 8.40. found C, 70.44; H, 8.39. All analytical data are in good accordance with those reported in the literature[3].

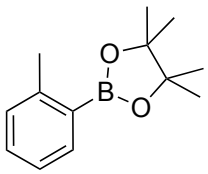
4,4,5,5-Tetramethyl-2-(*p*-tolyl)-1,3,2-dioxaborolane



The title product was synthesized according to the general procedure A using *p*-tolylboronic acid (1.35 g, 10 mmol) and pinacol (1.39 g, 12 mmol). The product was obtained as a white solid (1.45 g, 66%) after distillation.

^{1}H NMR ($CDCl_3$) δ 1.33 (s, 12H), 2.36 (s, 3H), 7.18 (dd, J = 8.1, 0.5 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.9, 25.0 (4C), 83.7 (2C), 128.7 (2C), 134.9 (2C), 141.5; Anal. calcd for $C_{13}H_{19}BO_2$, C, 71.59; H, 8.78. found C, 71.46; H, 8.79. All analytical data are in good accordance with those reported in the literature[4].

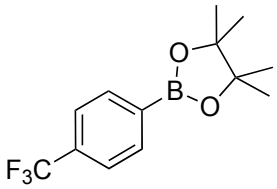
4,4,5,5-Tetramethyl-2-(*o*-tolyl)-1,3,2-dioxaborolane



The title product was synthesized according to the general procedure A using *o*-tolylboronic acid (1.35 g, 10 mmol) and pinacol (1.39 g, 12 mmol). The product was obtained as a colorless liquid (1.81 g, 83%) after distillation.

^{1}H NMR ($CDCl_3$) δ 1.34 (s, 12H), 2.54 (s, 3H), 7.13–7.17 (m, 2H), 7.31 (td, J = 7.5, 1.6 Hz,1H), 7.76 (dd, J = 7.6, 1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 22.4, 25.0 (4C), 83.5 (2C), 124.8, 129.9, 130.9, 136.0, 145.0; Anal. calcd for $C_{13}H_{19}BO_2$, C, 71.59; H, 8.78. found C, 71.64; H, 8.79. All analytical data are in good accordance with those reported in the literature[4].

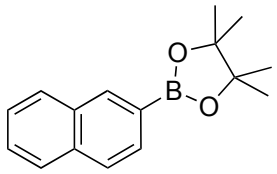
4,4,5,5-Tetramethyl-2-(4-trifluoromethylphenyl)-1,3,2-dioxaborolane



The title product was synthesized according to the general procedure A using 4-trifluoromethylphenylboronic acid (1.04 g, 5 mmol) and pinacol (0.83 g, 7 mmol). The product was obtained as a white solid (0.68 g, 47%) after recrystallization (MeOH / hexane).

^{1}H NMR ($CDCl_3$) δ 1.35 (s, 12H), 7.61 (d, J = 8.3 Hz, 2H), 7.91 (d, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 25.0 (4C), 84.4 (2C), 124.3 (q, J = 272.4 Hz), 124.5 (d, J = 3.8 Hz, 2C), 133.0 (q, J = 32.9 Hz), 135.2 (2C); Anal. calcd for $C_{13}H_{16}BF_3O_2$, C, 57.39; H, 5.93. found C, 57.18; H, 6.02. All analytical data are in good accordance with those reported in the literature[4].

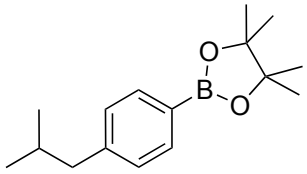
4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane



The title product was synthesized according to the general procedure A using 2-naphthylboronic acid (1.72 g, 10 mmol) and pinacol (1.17 g, 10 mmol). The product was obtained as a colorless solid (2.04 g, 80%).

^{1}H NMR ($CDCl_3$) δ 1.39 (s, 12 H), 7.48 (m, 2 H), 7.81–7.84 (m, 3H), 7.85–7.89 (m, 1H), 8.37 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 24.9 (4C), 83.9 (2C), 125.8, 127.0 (2C), 127.7, 128.7, 130.4, 132.8, 135.0, 136.2; Anal. calcd for $C_{16}H_{19}BO_2$, C, 75.62; H, 7.54. found C, 75.51; H, 7.57. All analytical data are in good accordance with those reported in the literature[5].

4,4,5,5-Tetramethyl-2-[4-(2-methylpropyl)phenyl]-1,3,2-dioxaborolane

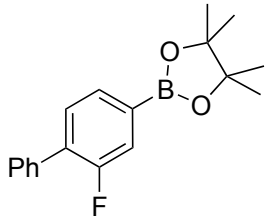


The title product was synthesized according to the general procedure A using 4-(2-methylpropyl)phenylboronic acid (0.99 g, 6 mmol) and pinacol (0.83 g, 7 mmol). The product was obtained as a colorless liquid (0.84 g, 57%) after distillation.

IR (neat, cm^{-1}) 2955, 1612, 1466, 1398, 1358, 1318, 1272, 1215, 1143, 1089, 1022, 963, 860, 735, 658; ^{1}H NMR ($CDCl_3$) δ 0.89 (d, J = 6.6 Hz, 6H), 1.34 (s, 12H), 1.87 (hept, J = 6.9 Hz, 1H), 2.48 (d, J = 7.2 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 22.5 (2C), 25.0 (4C), 30.3, 45.8, 83.8 (2C), 128.7 (2C), 134.8 (2C), 145.3; HRMS (EI$^+$): m/z [M]$^+$ calcd for

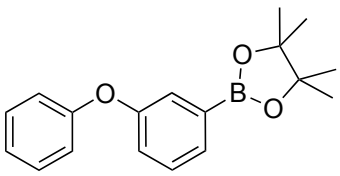
$C_{16}H_{25}BO_2$ 260.1951, found 260.1950. Anal. calcd for $C_{16}H_{25}BO_2$, C, 73.86; H, 9.69. found C, 73.83; H, 9.73.

4,4,5,5-Tetramethyl-2-(2-fluoro-4-biphenylyl)-1,3,2-dioxaborolane



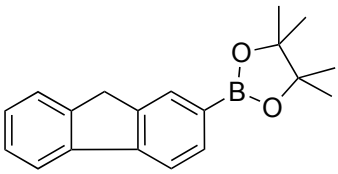
The title product was synthesized according to the general procedure A using 2-fluoro-4-biphenylboronic acid (1.24 g, 6 mmol) and pinacol (1.08 g, 9 mmol). The product was obtained as a white solid (1.31 g, 77%) after recrystallization (hexane / toluene).
IR (neat, cm^{-1}) 2977, 1517, 1404, 1355, 1327, 1202, 1140, 1089, 965, 913, 851, 770, 727, 702, 681; ^1H NMR ($CDCl_3$) δ 1.36 (s, 12H), 7.37 (m, 1H), 7.42–7.47 (m, 3H), 7.56–7.59 (m, 3H), 7.63 (dd, J = 7.6, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 24.9, 84.2 (2C), 122.0 (J = 20.7 Hz), 127.9, 128.5 (2C), 129.1 (2C), 130.3, 130.7, 131.8 (J = 13.1 Hz), 135.8, 159.5 (J = 248.9 Hz); HRMS (EI^+): m/z $[M]^+$ calcd for $C_{18}H_{20}BFO_2$ 298.1544, found 298.1543. Anal. calcd for $C_{18}H_{20}BFO_2$, C, 72.51; H, 6.76. found C, 72.36; H, 6.75.

4,4,5,5-Tetramethyl-2-(3-phenoxyphenyl)-1,3,2-dioxaborolane



The title product was synthesized according to general procedure A using 3-phenoxybenzeneboronic acid (1.0 g, 5 mmol) and pinacol (0.67 g, 6 mmol). The product was obtained as a white solid (1.14 g, 82%) after recrystallization (hexane).
IR (neat, cm^{-1}) 2981, 1594, 1576, 1487, 1423, 1353, 1325, 1307, 1237, 1140, 1069, 966, 921, 856, 789, 706, 695, 672; ^1H NMR ($CDCl_3$) δ 1.33 (s, 12H), 6.98 (d, J = 7.6 Hz, 2H), 7.05–7.12 (m, 2H), 7.29–7.36 (m, 3H), 7.48 (d, J = 2,5 Hz, 1H), 7.56 (dt, J = 7.3, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 24.9 (4C), 83.9 (2C), 118.5 (2C), 122.3, 122.9, 125.3, 129.2, 129.7(2C), 129.8, 156.5, 157.7; HRMS (EI^+): m/z $[M]^+$ calcd for $C_{18}H_{21}BO_3$ 296.1587, found 296.1589. Anal. calcd for $C_{18}H_{21}BO_3$, C, 73.00; H, 7.15. found C, 73.06; H, 7.17.

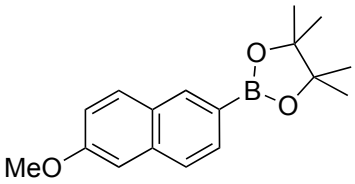
4,4,5,5-Tetramethyl-2-(2-fluorenyl)-1,3,2-dioxaborolane



Bis(pinacolato)diboron (1.54 g, 6 mmol), 2-bromofluorene (1.22g, 5 mmol), potassium acetate (0.32 g, 3 mmol) and [1,1'-bis(diphenylphosphino)ferrocene]paradium(II) dichloride (28 mg, 0.1 mmol) were dissolved in 1,4-dioxane (5 mL), and the mixture was stirred at 90 °C for 45 h. Then water (3 mL) was added to the reaction mixture and the aqueous layer was extracted with EtOAc (20 mL × 3). The organic layers were combined, dried with $MgSO_4$, and filtered. The solvent was removed under reduced pressure to afford the crude product. The title product was obtained as a white solid (0.83 g, 57%) after recycling GPC.

IR (neat, cm^{-1}) 2975, 1613, 1418, 1353, 1313, 1266, 1143, 1079, 963, 856, 771, 736, 664; ^1H NMR ($CDCl_3$) δ 1.37 (s, 12H), 3.60 (s, 2H), 7.30–7.41 (m, 2H), 7.55 (d, J = 7.4 Hz, 1H), 7.78–7.50 (m, 3H), 8.00 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 24.0 (4C), 36.7, 83.9 (2C), 119.3, 120.4, 125.1, 126.7, 127.2, 131.3, 133.4, 141.5, 142.5, 143.9, 144.6; HRMS (EI^+): m/z $[M]^+$ calcd for $C_{19}H_{21}BO_2$ 292.1638, found 292.1637. Anal. calcd for $C_{19}H_{21}BO_2$, C, 78.10; H, 7.24. found C, 78.23; H, 7.25.

4,4,5,5-Tetramethyl-2-(6-methoxynaphthalen-2-yl)-1,3,2-dioxaborolane



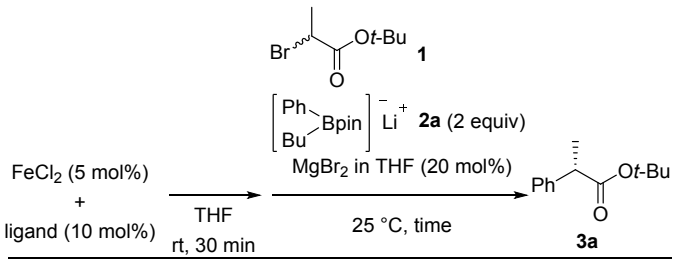
To a solution of 2-bromo-4-methoxynaphthalene (4.71 g, 20 mmol) in toluene-THF (4:1 v/v, 80 mL), BuLi (14.5 mL, 1.66 M in hexane, 24 mmol) was added dropwise over 7 min at -78°C, and the mixture was stirred at that temperature for 30 min. Then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.12 mL, 30 mmol) was added dropwise over 5 min. The reaction mixture was stirred for 1 h and warmed up to room temperature. After stirring for 30 h, The reaction mixture was quenched by a solution of NH_4Cl (1.78g, 33 mmol) in water (30 mL). The aqueous layer was extracted with EtOAc (20 mL × 3). The organic layers were combined, dried with $MgSO_4$, and filtered. The solvent was removed under reduced pressure to afford the crude product. The title product was obtained as a white solid (5.40 g, 95%) after filtration using MeOH.

^1H NMR ($CDCl_3$) δ 1.38 (s, 12H), 3.92 (s, 3H), 7.12–7.14 (m, 2H), 7.71 (d, J = 8.2 Hz, 1H), 7.79 (t, J = 10.9 Hz, 2H), 8.29 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 24.9 (4C), 55.3, 83.8 (2C), 105.6, 118.7, 125.9, 128.4, 130.2, 131.1, 136.0, 136.4, 158.5; Anal. calcd for $C_{17}H_{21}BO_3$, C, 71.86; H, 7.45. found C, 71.95; H, 7.40. All analytical data are in good accordance with those reported in the literature[6].

3. Iron-Catalyzed Enantioselective Coupling

General Procedure B: To a solution of arylboronic acid pinacol ester (1.1 mmol) in THF (2 mL), BuLi (0.65 mL, 1.60 M in hexane, 1.05 mmol) was added at -40 °C. The mixture was stirred at that temperature for 30 min, and then at 0 °C for 30 min. The solvent was removed under reduced pressure at room temperature. To the residual borate, THF (1.1 mL) was added. This borate (1.0 M, in THF) was used for the following cross coupling.

To a flame–dried schlenk flask filled up with argon gas, $FeCl_2$ (3.6 mg, 5 mol%), (*R,R*)-QuinoxP* (16.4 mg, 10 mol%), and THF (0.5 mL) were added. This mixture was stirred at 25 °C for 30 minutes. Then undecane (36.44 mg, 0.2331 mmol), lithium borate (1.0 M THF solution, 1.0 mL, 1.00 mmol), *tert*-butyl 2-bromopropionate (104.36 mg, 0.4991 mmol) and $MgBr_2$ (0.2 M THF solution, 0.50 mL, 0.10 mmol) were added. This mixture was stirred at 25 °C for 5 hours, and quenched with sat. NH_4Cl aq. (2 mL) and the aqueous layer was extracted with EtOAc (2 mL x 4). The organic layers were combined, dried with $MgSO_4$, and filtered. The solvent was removed under reduced pressure to afford the crude product.



entry	chiral ligand	time	yield [%] (er)[a]
1	(*R,R',S,S'*)-DuanPhos	2 h	>99 (66:34)
2	(*S,S*)-Ph-BPE	6 h	73 (57:43)
3	(*S,S*)-BOX **1**	28 h	95 (76:24)
4	(*S,S*)-BOX **2**	5 h	>99 (49:51)
5	(*S,S*)-BOX **3**	5 h	95 (61:39)
6	(*R,R*)-BOX **4**	64 h	61 (23:77)
7	(*S,S*)-BOX **5**	4 h	87 (56:44)
8	(*S,S*)-BOX **6**	22 h	18 (52:48)[b]
9	(*R*)-PHOX	4 h	>99 (40:60)
10	(*R*)-MonoPhos	3 h	98 (50:50)
11	(*S*)-DTBM-SEGPHOS	3 h	>99 (48:52)
12	No Ligand	1 h	98

[a] The yield and er value were determined by GC and HPLC, respectively.

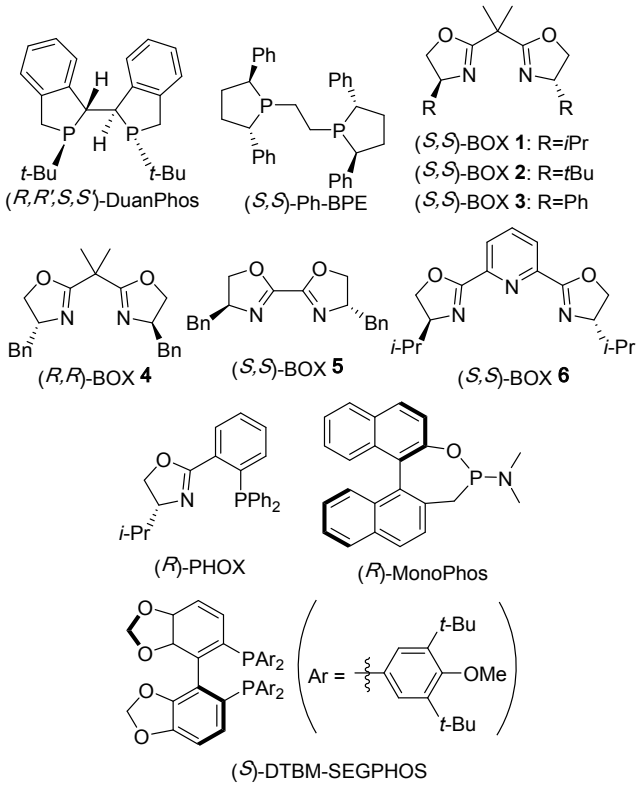
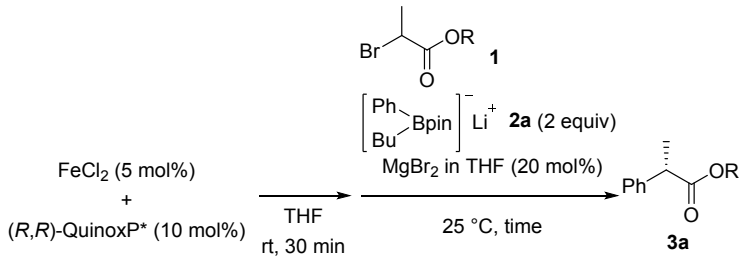


Table S1. Ligand screening for iron-catalyzed enantioselective coupling of α-bromopropionate with phenyl boron reagent.

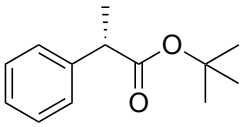


entry	R	time (h)	yield [%] (er)[a]
1	Me	4	95 (56:44)
2	*i*-Pr	5	82 (73:27)
3	*t*-Bu	5	99 (84:16)
4		6	92 (85:15)

[a] The yield and er value were determined by NMR and HPLC, respectively.

Table S2. Optimization of alkyl bromides for iron-catalyzed enantioselective coupling with phenyl boron reagent.

tert-Butyl (*S*)-2-phenylpropionate

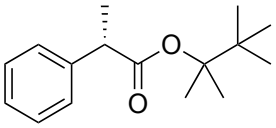


The reaction was performed according to the general procedure B: the corresponding lithium borate (0.40 mL, 1.0 M in THF, 0.40 mmol) and *tert*-butyl 2-bromopropionate (39.8 mg, 0.19 mmol) were used. The product was obtained in 99% yield with 84:16 er.

The er was determined by HPLC on a CHIRALCEL OJ-3R column (4.6 mm i.d., 150 mm length) under the following conditions: 50 % CH_3CN aq, 1.0 mL/min, 25 °C, retention times (t_r) = 14.8 min (major) and 18.21 min (minor).

^{1}H NMR ($CDCl_3$) δ 1.39 (s, 9H), 1.45 (d, J = 7.2 Hz, 3H), 3.61 (q, J = 7.1 Hz, 1H), 7.21–7.31 (m, 5H). The NMR spectrum is in good accordance with with previous literature data[7].

2,3,3-Trimethylbut-2-yl (S)-2-phenylpropionate

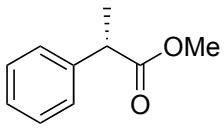


The reaction was performed according to the general procedure B: the corresponding lithium borate (0.60 mL, 1.0 M in THF, 0.60 mmol) and 2,3,3-trimethylbut-2-yl 2-bromopropionate (76.5 mg, 0.30 mmol) were used. The product was obtained in 92% yield with 85:15 er.

The er was determined by HPLC on a CHIRALCEL OJ-3R column (4.6 mm i.d., 150 mm length) under the following conditions: 60 % CH_3CN aq, 1.0 mL/min, 25 °C, retention times (t_r) = 13.3 min (major) and 16.8 min (minor).

^{1}H NMR ($CDCl_3$) δ 0.83 (s, 9H), 1.38 (s, 3H), 1.46 (s, 3H), 1.47 (d, *J* = 6.5 Hz, 3H), 3.63 (q, *J* = 7.2 Hz, 1H), 7.21–7.34 (m, 5H). The NMR spectrum is in good accordance with with previous literature data[7].

Methyl (S)-2-phenylpropionate

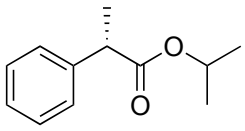


The reaction was performed according to the general procedure B: the corresponding lithium borate (1.0 mL, 1.0 M in THF, 1.0 mmol) and methyl 2-bromopropionate (81.3 mg, 0.49 mmol) were used. The product was obtained in 88% yield with 56:44 er.

The er was determined by HPLC on a CHIRALCEL OJ-3R column (4.6 mm i.d., 150 mm length) under the following conditions: 50 % CH_3CN aq, 1.0 mL/min, 25 °C, retention times (t_r) = 6.5 min (major) and 7.1 min (minor).

^{1}H NMR ($CDCl_3$) δ 1.50 (d, *J* = 7.2 Hz, 3H), 3.66 (s, 3H), 3.72 (q, *J* = 7.2 Hz, 1H), 7.23–7.34 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 18.6, 45.4, 52.0, 127.1, 127.5 (2C), 128.6 (2C), 140.6, 175.0; The NMR spectrum is in good accordance with with previous literature data[8].

isopropyl (*S*)-2-phenylpropionate



The reaction was performed according to the general procedure B: the corresponding lithium borate (0.60 mL, 1.0 M in THF, 0.60 mmol) and isopropyl 2-bromopropionate (58.4 mg, 0.30 mmol) were used. The product was obtained in 82% yield with 75:25 er.

The er was determined by HPLC on a CHIRALCEL OD-3 column (4.6 mm i.d., 150 mm length) under the following conditions: hexane, 1.0 mL/min, 3 °C, retention times (t_r) = 23.1 min (major) and 27.4 min (minor).

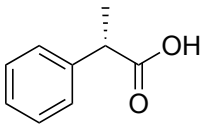
^{1}H NMR ($CDCl_3$) δ 1.13 (d, *J* = 6.2 Hz, 3H) 1.22 (d, *J* = 6.3 Hz, 3H), 1.48 (d, *J* = 7.2 Hz, 3H), 3.67(q, *J* = 7.2 Hz, 1H), 4.99 (sept, *J* = 6.3 Hz, 1H), 7.22–7.35 (m, 5H). The NMR spectrum is in good accordance with with previous literature data[9].

Synthesis of *α*-arylpropionic acid

General procedure C: Coupling reaction was performed according to the general procedure B. Then, to a solution of the crude product in CH_2Cl_2 (1.5 mL) was added trifluoroacetic acid (0.38 mL, 5 mmol) at room temperature, and the mixture was stirred for 6 h. Then the reaction mixture was quenched by sat. $NaHCO_3$ aq. (5 mL). The aqueous layer was extracted with CH_2Cl_2 (2mL x 5). The organic layers were combined, and extracted with 2 M NaOH aq. (2 mL x 5) to separate the desired carboxylic acid

from other byproducts. Then the aqueous layers were combined and washed with hexane (2 mL x 10). To the aqueous layer, 2 M HCl aq was added to adjust the pH 3. Finally, the acidic aqueous layer was extracted by CH_2Cl_2 (2 mL x 5). The organic layers were combined, dried with $MgSO_4$, and filtered. The solvent was removed under reduced pressure to afford the semi-purified product.

(*S*)-2-phenylpropionic acid

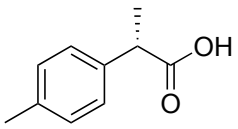


The reaction was performed according to the general procedure C: the corresponding lithium borate (0.40 mL, 1.0 M in THF, 0.40 mmol) and *tert*-butyl 2-bromopropionate (39.8 mg, 0.19 mmol) were used. The semi-purified product was further purified by silica gel column chromatography (hexane/EtOAc = 95/5 to 40/60) to give the title product in 95% yield (27.2 mg) with 84:16 er as a yellow liquid.

The er was determined by HPLC on a CHIRALCEL OJ-3R column (4.6 mm i.d., 150 mm length) under the following conditions: 10 mM H_3PO_4 aq/CH_3CN = 75/25, 1.0 mL/min, 25 °C, retention times (t_r) = 15.3 min (major) and 16.9 min (minor).

^{1}H NMR ($CDCl_3$) δ 1.51 (d, *J* = 7.2 Hz, 3H), 3.74 (q, *J* = 7.2 Hz, 1H), 7.25–7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 18.1, 45.3, 127.4, 127.6 (2C), 128.8 (2C), 139.7, 180.5; Anal. calcd for $C_9H_{10}O_2$, C, 71.98; H, 6.71. found C, 71.75; H, 6.82. $[\alpha]^{20}_D$ +51.0 (c 0.47, EtOH). Analytical data are in good accordance with those reported in the literature[10].

(*S*)-2-(4-methylphenyl)propionic acid



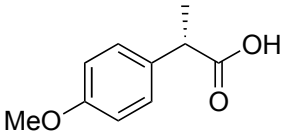
The reaction was performed according to the general procedure C: the corresponding lithium borate (0.40 mL, 1.0 M in THF, 0.40 mmol) and *tert*-butyl 2-bromopropionate (35.8 mg, 0.17 mmol) were used. The semi-purified product was further purified by silica gel column chromatography (hexane/EtOAc = 95/5 to 40/60) to give the title product in 90% yield (25.4 mg) with 81:19 er as a yellow liquid.

The er was determined by HPLC on a CHIRALCEL OD-3 column (4.6 mm i.d., 150 mm length) under the following conditions: hexane/*i*-PrOH/TFA = 99/1/0.1, 1.0 mL/min, 20 °C, retention times (t_r) = 11.6 min (minor) and 13.3 min (major).

^{1}H NMR ($CDCl_3$) δ 1.50 (d, *J* = 7.2 Hz, 3H), 2.33 (s, 3 H), 3.70 (q, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.3, 21.2, 45.0, 127.6 (2C), 129.5 (2C), 137.0,

137.2, 180.4; Anal. calcd for $C_{10}H_{12}O_2$, C, 73.15; H, 7.37. found C, 72.57; H, 7.59. $[\alpha]^{20}_D$ + 49.0 (c 0.34, EtOH). All analytical data are in good accordance with those reported in the literature[10].

(*S*)-2-(4-methoxyphenyl)propionic acid

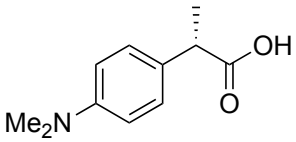


The reaction was performed according to general procedure C: the corresponding lithium borate (0.40 mL, 1.0 M in THF, 0.40 mmol) and *tert*-butyl 2-bromopropionate (48.2 mg, 0.23 mmol) were used. The semi-purified product was further purified by silica gel column chromatography (hexane/EtOAc = 95/5 to 40/60) to give the title product in 85% yield (35.2 mg) with 82:18 er as a white solid.

The er was determined by HPLC on a CHIRALCEL OD-3 column (4.6 mm i.d., 150 mm length) under the following conditions: hexane/*i*-PrOH/TFA = 99/1/0.1, 1.0 mL/min, 25 °C, retention times (t_r) = 27.6 min (minor) and 30.3 min (major).

^{1}H NMR ($CDCl_3$) δ 1.49 (d, *J* = 7.2 Hz, 3H), 3.69 (q, *J* = 7.2 Hz, 1 H), 3.79 (s, 3H), 6.86 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.2, 44.5, 55.4, 114.2 (2C), 128.7 (2C), 132.0, 159.0, 180.8; Anal. calcd for $C_{10}H_{12}O_3$, C, 66.65; H, 6.71. found C, 66.54; H, 6.79. $[\alpha]^{20}_D$ + 36.6 (c 0.51, EtOH). All analytical data are in good accordance with those reported in the literature[11].

(*S*)-2-[4-(dimethylamino)phenyl]propionic acid

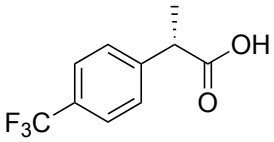


The reaction was performed according to general procedure C: the corresponding lithium borate (1.00 mL, 1.0 M in THF, 1.00 mmol) and *tert*-butyl 2-bromopropionate (104.9 mg, 0.50 mmol) were used. The semi-purified product was further purified by silica gel column chromatography (hexane/EtOAc = 95/5 to 40/60) to give the title product in 89% yield (86.0 mg) with 82:18 er as a white solid.

The er was determined by HPLC on a CHIRALCEL OD-3 column (4.6 mm i.d., 150 mm length) under the following conditions: hexane/*i*-PrOH/TFA = 95/5/0.1, 1.0 mL/min, 25 °C, retention times (t_r) = 9.8 min (minor) and 10.9 min (major).

^{1}H NMR ($CDCl_3$) δ 1.47 (d, *J* = 7.2 Hz, 3H), 2.92 (s, 6 H), 3.64 (q, 7.2 Hz, 1H), 6.70 (d, *J* = 8.8 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.2, 40.9 (2C), 44.4, 113.1 (2C), 128.0, 128.4 (2C), 150.0, 180.8; Anal. calcd for $C_{11}H_{15}NO_2$, C, 68.37; H, 7.82; N, 7.25. found C, 68.38; H, 7.92; N, 6.92. $[\alpha]^{20}_D$ + 37.5 (c 0.53, EtOH). All analytical data are in good accordance with those reported in the literature[12].

(*S*)-2-[4-(trifluoromethyl)phenyl]propionic acid

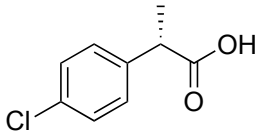


The reaction was performed according to general procedure C: the corresponding lithium borate (0.40 mL, 1.0 M in THF, 0.40 mmol) and *tert*-butyl 2-bromopropionate (43.45 mg, 0.21 mmol) were used. The semi-purified product was further purified by silica gel column chromatography (hexane/EtOAc = 95/5 to 40/60) to give the title product in 81% yield (36.9 mg) with 76:24 er as a yellow solid.

The er was determined by HPLC on a CHIRALCEL OJ-3R column (4.6 mm i.d., 150 mm length) under the following conditions: 10 mM H_3PO_4 aq/CH_3CN = 75/25, 1.0 mL/min, 25 °C, retention times (t_r) = 24.6 min (minor) and 28.3 min (major).

^{1}H NMR ($CDCl_3$) δ 1.54 (d, *J* = 7.2 Hz, 3H), 3.81 (q, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ18.2, 45.4, 124.2 (q, *J* = 172.4), 125.8 (d, *J* = 3.8 Hz, 2C), 128.2 (2C), 129.9 (q, *J* = 31.9 Hz), 143.7, 180.2; Anal. calcd for $C_{10}H_9F_3O_2$: C, 55.05; H, 4.16. found C, 55.55; H, 4.38. $[\alpha]^{20}_D$ + 23.2 (c 0.54, EtOH). All analytical data are in good accordance with those reported in the literature[13].

(*S*)-2-(4-chlorophenyl)propionic acid

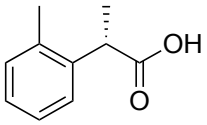


The reaction was performed according to general procedure C: the corresponding lithium borate (1.00 mL, 1.0 M in THF, 1.00 mmol) and *tert*-butyl 2-bromopropionate (100.3 mg, 0.48 mmol) were used. The semi-purified product was further purified by silica gel column chromatography (hexane/EtOAc = 95/5 to 40/60) to give the title product in 83% yield (72.9 mg) with 84:16 er as a yellow solid.

The er was determined by HPLC on a CHIRALCEL OD-3R column (4.6 mm i.d., 150 mm length) under the following conditions: 10 mM H_3PO_4 aq/CH_3CN = 80/20, 1.0 mL/min, 25 °C, retention times (t_r) = 43.9 min (major) and 46.5 min (minor).

^{1}H NMR ($CDCl_3$) δ 1.49 (d, *J* = 7.2 Hz, 3H), 3.71 (q, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.23–7.31 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 18.2, 44.9, 129.0 (2C), 129.1 (2C), 133.5, 138.3, 189.6; Anal. calcd for $C_9H_9ClO_2$, C, 58.55; H, 4.91. found C, 58.62; H, 5.16. $[\alpha]^{20}_D$ + 33.6 (c 0.48, EtOH). All analytical data are in good accordance with those reported in the literature[11].

(*S*)-2-(2-methylphenyl)propionic acid

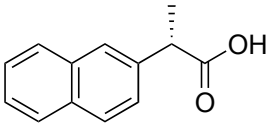


The reaction was performed according to general procedure C: the corresponding lithium borate (0.40 mL, 1.0 M in THF, 0.40 mmol) and *tert*-butyl 2-bromopropionate (42.2 mg, 0.20 mmol) were used. The semi-purified product was further purified by silica gel column chromatography (hexane/EtOAc = 95/5 to 40/60) to give the title product in 65% yield (21.4 mg) with 88:12 er as a yellow solid.

The er was determined by HPLC on a CHIRALCEL OD-3R column (4.6 mm i.d., 150 mm length) under the following conditions: 10 mM H_3PO_4 aq/CH_3CN = 75/25, 1.0 mL/min, 25 °C, retention times (t_r) = 17.1 min (major) and 20.1 min (minor).

^{1}H NMR ($CDCl_3$) δ 1.49 (d, *J* = 7.2 Hz, 3H), 2.38 (s, 3 H), 3.98 (q, *J* = 7.1 Hz, 1H), 7.16–7.21 (m, 3H), 7.28–7.30 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 17.7, 19.8, 41.2, 126.6, 126.7, 127.3, 130.7, 136.1, 138.5, 180.7; Anal. calcd for $C_{10}H_{12}O_2$, C, 73.15; H, 7.37. found C, 72.69; H, 7.55 $[\alpha]^{20}_D$ + 55.4 (c 0.43, EtOH). All analytical data are in good accordance with those reported in the literature[13, 14].

(*S*)-2-(naphthalen-2-yl)propionic acid

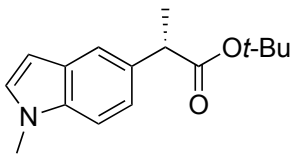


The reaction was performed according to general procedure C: the corresponding lithium borate (0.60 mL, 1.0 M in THF, 0.60 mmol) and *tert*-butyl 2-bromopropionate (62,4 mg, 0.30 mmol) were used. The semi-purified product was further purified by silica gel column chromatography (hexane/EtOAc = 95/5 to 40/60) to give the title product in 91% yield (54.2 mg) with 77:23 er as a white solid.

The er was determined by HPLC on a CHIRALCEL OJ-3R column (4.6 mm i.d., 150 mm length) under the following conditions: 10 mM H_3PO_4 aq/CH_3CN = 70/30, 1.0 mL/min, 25 °C, retention times (t_r) = 33.5 min (major) and 37.0 min (minor).

^{1}H NMR ($CDCl_3$) δ 1.60 (d, *J* = 7.2 Hz, 3H), 3.90 (q, *J* = 7.1 Hz, 1H), 7.42–7.49 (m, 3H), 7.75 (s, 1H), 7.79–7.81 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 18.1, 45.4, 125.7, 125.9, 126.2, 126.3, 127.6, 127.8, 128.4, 132.7, 133.4, 137.1, 180.2; Anal. calcd for $C_{13}H_{12}O_2$, C, 77.98; H, 6.04. found C, 77.37; H, 6.05. $[\alpha]^{20}_D$ + 35.5 (c 0.36, EtOH). Analytical data are in good accordance with those reported in the literature[11].

***Tert*-butyl (*S*)-2-(1-methyl-1H-indol-5-yl) propionate**

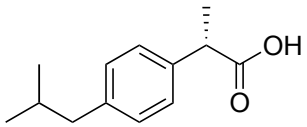


The reaction was performed according to general procedure B: the corresponding lithium borate (1.00 mL, 1.0 M in THF, 1.00 mmol) and *tert*-butyl 2-bromopropionate (100.7 mg, 0.48 mmol) were used. The semi-purified product was further purified by GPC to give the title product in 61% yield (75.6 mg) with 81:19 er as a white solid.

The er was determined by HPLC on a CHIRALCEL OJ-3R column (4.6 mm i.d., 150 mm length) under the following conditions: 55% CH_3CN aq, 1.0 mL/min, 25 °C, retention times (t_r) = 13.0 min (major) and 17.0 min (minor).

IR (neat, cm^{-1}) 2972, 2936, 1710, 1513, 1492, 1447, 1424, 1365, 1339, 1311, 1248, 1152, 1139, 1086, 1052, 1014, 875, 847, 803, 784, 762, 736, 682; ^1H NMR ($CDCl_3$) δ 1.38 (s, 9H), 1.49 (d, J = 7.2 Hz, 3H), 3.70 (q, J = 7.2 Hz, 1H), 3.75 (s, 3H), 6.43 (dd, J = 3.1, 0.8 Hz, 1H), 7.01 (d, J = 3.1 Hz, 1H), 7.17 (dd, J = 8.4, 1.7 Hz, 1H), 7.25 (d, J = 8.5 Hz, 1H), 7.53 (s, 1H); ^{13}C NMR ($CDCl_3$) δ19.3, 28.1 (3C), 33.0, 46.6, 80.2, 101.0, 109.2, 119.5, 121.4, 128.7, 129.2, 132.4, 135.0, 174.8; HRMS (EI^+): *m*/*z* $[M]^+$ calcd for $C_{16}H_{21}NO_2$ 259.1572, found 259.1575. Anal. calcd for $C_{16}H_{21}NO_2$, C, 74.10; H, 8.16; N, 5.40. found C, 74.03; H, 8.25; N, 5.31. $[\alpha]^{20}_D$ + 26.3 (c 0.50, EtOH).

(*S*)-2-[(2-methylpropyl)phenyl]propionic acid [(*S*)-ibuprofen]

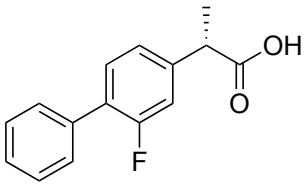


The reaction was performed according to general procedure C: the corresponding lithium borate (1.00 mL, 1.0 M in THF, 1.00 mmol) and *tert*-butyl 2-bromopropionate (100.4 mg, 0.48 mmol) were used. The semi-purified product was further purified by silica gel column chromatography (hexane/EtOAc = 95/5 to 40/60) to give the title product in 95% yield (93.6 mg) with 82:18 er as a yellow liquid.

The er was determined by HPLC on a CHIRALCEL OJ-3R column (4.6 mm i.d., 150 mm length) under the following conditions: 10 mM H_3PO_4 aq/CH_3CN = 70/30, 1.0 mL/min, 25 °C, retention times (t_r) = 45.4 min (minor) and 49.3 min (major).

^1H NMR ($CDCl_3$) δ 0.89 (d, J = 6.6 Hz, 6H), 1.49 (d, J = 7.1 Hz, 3H), 1.84 (hept, J = 6.8 Hz, 1H), 2.44 (d, J = 7.2 Hz, 2H), 3.70 (q, J = 7.2 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.2, 22.5 (2C), 30.3, 45.1, 45.2, 127.4(2C), 129.5 (2C), 137.1, 141.0, 181.0; Anal. calcd for $C_{13}H_{18}O_2$, C, 75.69; H, 8.80. found C, 75.57; H, 8.94. $[\alpha]^{20}_D$ +28.9 (c 0.51, EtOH). Analytical data are in good accordance with those reported in the literature[7].

(*S*)-2-(2-fluoro-4-biphenylyl)propionic acid [(*S*)-flurbiprofen]

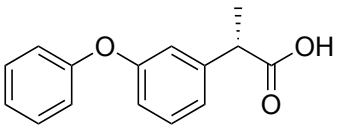


The reaction was performed according to general procedure C: the corresponding lithium borate (1.00 mL, 1.0 M in THF, 1.00 mmol) and *tert*-butyl 2-bromopropionate (100.7 mg, 0.48 mmol) were used. The semi-purified product was further purified by silica gel column chromatography (hexane/EtOAc = 95/5 to 40/60) to give the title product in 56% yield (61.1 mg) with 81:19 er as a yellow solid.

The er was determined by HPLC on a CHIRALCEL OJ-3R column (4.6 mm i.d., 150 mm length) under the following conditions: 10 mM H_3PO_4 aq/CH_3CN = 70/30, 1.0 mL/min, 25 °C, retention times (t_r) = 58.5 min (minor) and 62.3 min (major).

^{1}H NMR ($CDCl_3$) δ 1.55 (d, *J* = 7.2 Hz, 3H), 3.78 (q, *J* = 7.2 Hz, 1H), 7.12–7.18 (m, 2H), 7.48–7.35 (m, 4H), 7.52 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.1, 45.0, 115.5 (*J* = 23.5 Hz), 123.8, 127.9, 128.3 (*J* = 13.1 Hz), 128.6 (2C), 129.1 (2C), 131.0, 135.5, 141.0, 159.8 (*J* = 249.0 Hz), 180.4; Anal. calcd for $C_{15}H_{13}FO_2$, C, 73.76; H, 5.36. found C, 73.37; H, 5.46. $[\alpha]^{20}_D$ + 23.8 (c 0.49, EtOH). All analytical data are in good accordance with those reported in the literature[15].

(*S*)-2-(3-phenoxyphenyl)propionic acid [(*S*)-phenoprofen]

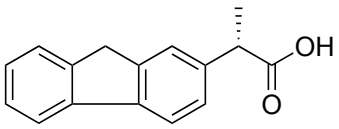


The reaction was performed according to general procedure C: the corresponding lithium borate (1.00 mL, 1.0 M in THF, 1.00 mmol) and *tert*-butyl 2-bromopropionate (107.8 mg, 0.52 mmol) were used. The semi-purified product was further purified by silica gel column chromatography (hexane/EtOAc = 95/5 to 40/60) to give the title product in 52% yield (64.9 mg) with 82:18 er as a yellow liquid.

The er was determined by HPLC on a CHIRALCEL OJ-3R column (4.6 mm i.d., 150 mm length) under the following conditions: 10 mM H_3PO_4 aq/CH_3CN = 70/30, 1.0 mL/min, 25 °C, retention times (t_r) = 61.2 min (major) and 68.3 min (minor).

^{1}H NMR ($CDCl_3$) δ 1.50 (d, *J* = 7.2 Hz, 3H), 3.71 (q, *J* = 7.2 Hz, 1H), 6.88 (ddd, *J* = 8.2, 2.5, 0.86 Hz, 1H), 7.00–7.02 (m, 3H), 7.06 (d, *J* = 7.8 Hz, 1H), 7.10 (tt, *J* = 7.3, 1.1 Hz, 1H), 7.28–7.35 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 18.0, 45.1, 117.5, 118.2, 119.0 (2C), 122.4, 123.4, 129.8 (2C), 129.9, 141.7, 156.9, 157.5, 179.8; Anal. calcd for $C_{15}H_{14}O_3$, C, 74.36; H, 5.82. found C, 74.27; H, 5.86. $[\alpha]^{20}_D$ + 26.6 (c 0.52, EtOH).Analytical data are in good accordance with those reported in the literature[15].

(*S*)-2-(2-fluorenyl)propionic acid [(*S*)-cicloprofen]

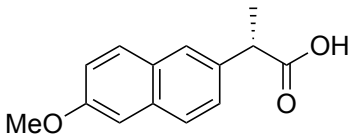


The reaction was performed according to general procedure C: the corresponding lithium borate (1.00 mL, 1.0 M in THF, 1.00 mmol) and *tert*-butyl 2-bromopropionate (103.9 mg, 0.50 mmol) were used. The semi-purified product was further purified by silica gel column chromatography (hexane/EtOAc = 95/5 to 40/60) to give the title product in 49% yield (58.0mg) with 81:19 er as a white solid.

The er was determined by HPLC on a CHIRALCEL OJ-3R column (4.6 mm i.d., 150 mm length) under the following conditions: 10 mM H_3PO_4 aq/CH_3CN = 70/30, 1.0 mL/min, 25 °C, retention times (t_r) = 73.7 min (minor) and 80.2 min (major).

^{1}H NMR ($CDCl_3$) δ 1.57 (d, *J* = 7.2 Hz, 3H), 3.82 (q, *J* = 7.1 Hz, 1H), 3.88 (s, 2H), 7.27–7.38 (m, 3H), 7.51–7.53 (m, 2H), 7.72–7.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 18.5, 37.0, 45.6, 120.0, 120.1, 124.4, 125.1, 126.5, 126.8, 126.9, 138.5, 141.2, 141.4, 143.4, 143.9, 180.8; Anal. calcd for $C_{16}H_{14}O_2$, C, 80.65; H, 5.92; Found: C, 80.32; H, 5.97. $[\alpha]^{20}_D$ + 36.7 (c 0.49, EtOH). All analytical data are in good accordance with those reported in the literature[16].

(*S*)-2-(6-methoxynaphth-2-yl)propionic acid [(*S*)-naproxen]



The reaction was performed according to general procedure C: the corresponding lithium borate (151 mg, 0.53 mmol) and *tert*-butyl 2-bromopropionate (48.0 mg, 0.23 mmol) were used. The semi-purified product was further purified by silica gel column chromatography (hexane/EtOAc = 95/5 to 40/60) to give the title product in 83% yield (42.3 mg) with 80:20 er as a yellow liquid.

The er was determined by HPLC on a CHIRALPAK AD-3R column (4.6 mm i.d., 150 mm length) under the following conditions: 10 mM H_3PO_4 aq/CH_3CN = 70/30, 1.0 mL/min, 25 °C, retention times (t_r) = 18.1 min (minor) and 21.1 min (major).

^{1}H NMR ($CDCl_3$) δ 1.57 (d, *J* = 7.2 Hz, 3H), 3.86 (q, *J* = 7.2 Hz, 1H), 3.90 (s, 3H), 7.09–7.14 (m, 2H), 7.40 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.68 (d, *J* = 8.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 18.1, 45.3, 55.3, 105.6, 119.0, 126.1, 126.2, 127.2, 128.9, 129.3, 133.8, 134.9, 157.7, 180.5; Anal. calcd for $C_{16}H_{14}O_2$, C, 80.65; H, 5.92; Found: C, 80.32; H, 5.97. $[\alpha]^{20}_D$ + 29.8 (c 0.44, EtOH). All analytical data are in good accordance with those reported in the literature[11].

4. Synthesis and stoichiometric reaction of $FeCl_2$/(*R*,*R*)-QuinoxP* and $FeCl_2$/(*R*,*R*)-BenzP*

Synthesis of $FeCl_2$/(*R*,*R*)-BenzP*: $FeCl_2$/(*R*,*R*)-BenzP* was synthesized according to the previously reported method.[S17]

Synthesis of $FeCl_2$/(*R*,*R*)-QuinoxP*: To a mixture of $FeCl_2$ (16.6 mg, 0.13 mmol) and (*R*,*R*)-QuinoxP* (32.7 mg, 0.12 mmol) was added EtOH (1.0 ml), and the mixture was stirred at 50 ºC for 3h. After filtration, the filtrate was condensed and recrystallized from Et_2O and hexane to afford the iron complex (32.2 mg, 66% yield). ^{1}H NMR (*d*-THF) δ 7.67, 8.80, 9.0, 91.73; Anal. calcd for $C_{18}H_{28}Cl_2FeN_2P_2$ C, 46.88; H, 6.12, N, 6.08 found C, 46.83; H, 6.06; N, 6.00. HRMS (FAB$^+$): *m*/*z* $[M]^+$ calcd for $C_{18}H_{28}Cl_2FeN_2P_2$ 460.0455, found 460.0455.

Stoichiometric reaction of iron complex with phenyl borate: To a mixture of $FeCl_2$/(*R*,*R*)-QuinoxP* (9.2 mg, 0.02 mmol) and (*R*,*R*)-QuinoxP* (6.7 mg, 0.02 mmol) in *d*-THF (0.5 ml) was added lithium phenylborate (0.84 M *d*-THF solution, 0.12 ml, 0.1 mmol), which was generated according to the general procedure B, and $MgBr_2$ (0.2 M *d*-THF solution, 0.1 ml, 0.02 mmol). The mixture was stirred at 25 °C, and conversion of the iron complex was monitored by the change of the signal at 91.73 ppm in ^{1}H NMR. The same reaction was performed by using $FeCl_2$/(*R*,*R*)-BenzP* (8.2 mg, 0.02 mmol) and (*R*,*R*)-BenzP* (5.6 mg, 0.02 mmol).

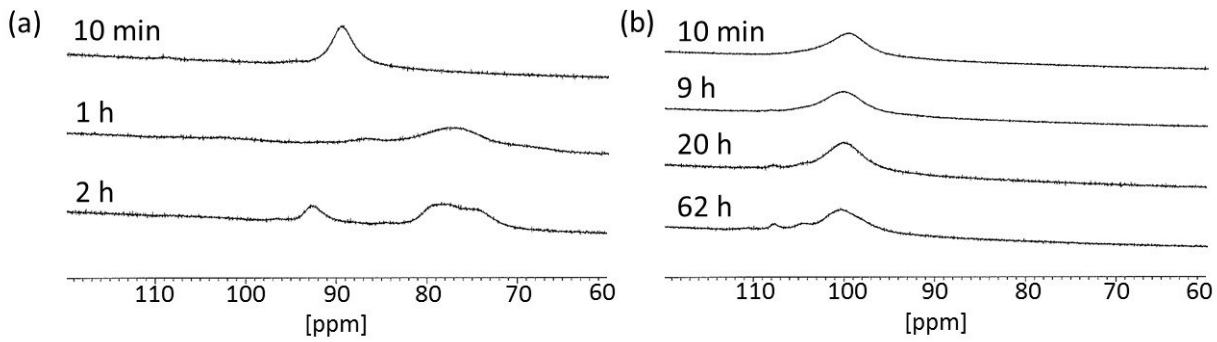


Figure S1. Stoichiometric reaction of (a) $FeCl_2$/(*R*,*R*)-QuinoxP* and (b) $FeCl_2$/(*R*,*R*)-BenzP* with phenyl boron reagent **2a** in the presence of $MgBr_2$

5. DFT Calculation

All calculations were carried out by using the Gaussian 09 program packages.[S18] Geometry optimizations were performed at B3LYP/6-311G** with GD3BJ empirical dispersion.[S19] Vibrational frequencies were calculated at the same level to characterize each stationary points (no imaginary frequencies for minima and one imaginary frequency for transition states).

Energies and optimized structures at recombination and reductive elimination step are shown in Figure S2 and S3. Reaction of iron complex **C** (S=2) with alkyl radical produce complex **D** (S=3/2). Optimization of the transition state at this recombination failed because this process would be almost barrierless as is the case with our previous report of iron-catalyzed enantioselective coupling with Grignard reagents.[S17] The resulting complex **D** undergo reductive elimination with an activation barrier of 11.8 kcal/mol to afford the complex **B** (S=3/2) and the product.

Iron complex **D** has a distorted trigonal bipyramidal structure, where distance of Fe–C_{ipso} (Ph) and Fe–C_{ipso} (alkyl) is 1.98 and 2.05 Å, respectively. In **TS**, distance of Fe–C_{ipso} (alkyl) is obviously elongated (2.27 Å), and on the other hand that of Fe–C_{ipso} (Ph) hardly changes compared with complex **D**. However, C_{ipso} (Ph) is significantly distorted in **TS** as shown by the dihedral angle of ∠C1C2C3Fe (Figure S2b and S2c). Our previous report about theoretical calculation of iron-catalyzed enantioselective coupling of Grignard reagents also suggested such structural changes at reductive elimination (elongation of Fe–C_{ipso} (alkyl) and deformation of C_{ipso} (Ph)).[S17]

Table S3. Gibbs free energy (G) at 298.150 K and 1.0000 atm.

	G (hartree)	G (kcal/mol)
FePhBr/(*R*,*R*)-QuinoxP* **C**	-5564.62479	-3491857.70197
Alkyl radical generated from **1a**	-424.999265	-266691.288780
FePhBr(alkyl)/(*R*,*R*)-QuinoxP* **D**	-5989.646488	-3758563.067684
FeBr/(*R*,*R*)-QuinoxP* **B**	-5332.962659	-3346487.398149
Transition state at reductive elimination **TS**	-5989.627694	-3758551.274261
Product **3a**	-656.697378	-412084.171668

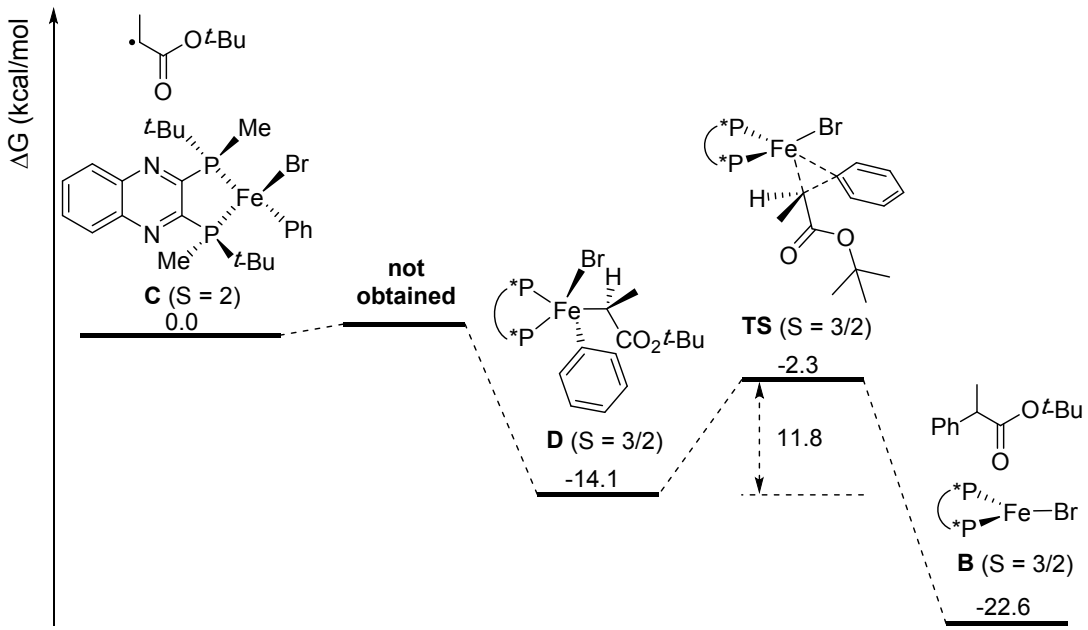


Figure S2. Energy profile for recombination and reductive elimination step.

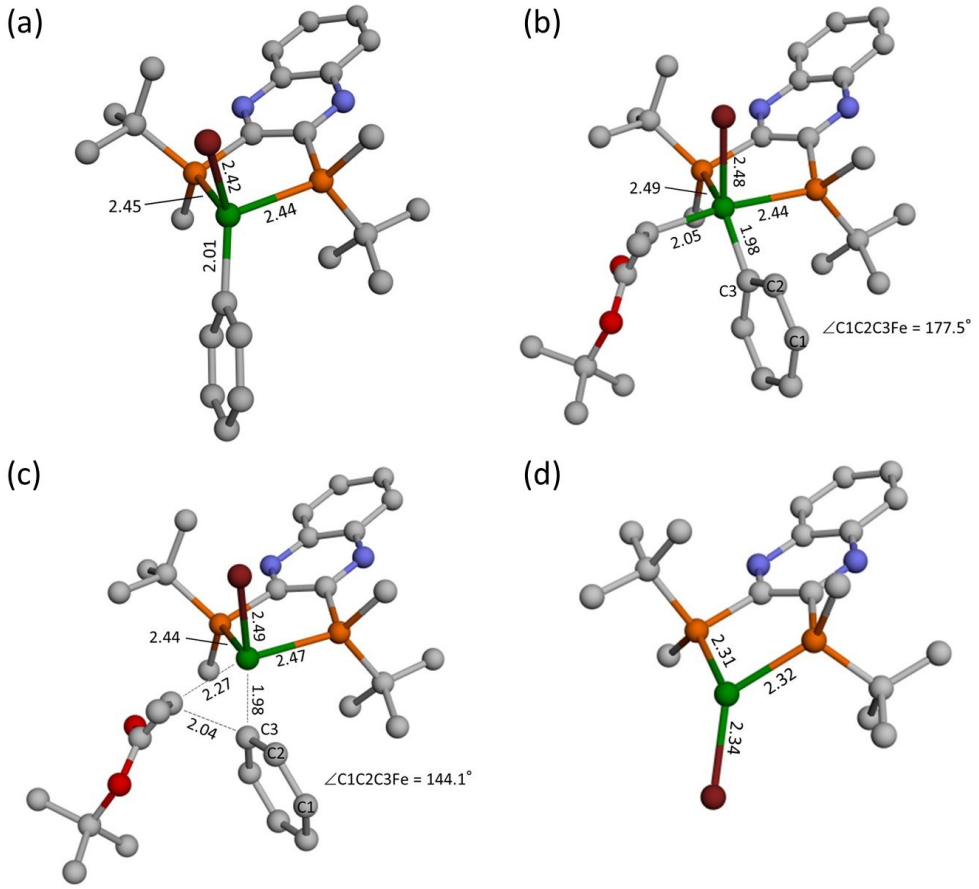


Figure S3. Optimized structure of (a) **C**, (b) **D**, (c) **TS**, and (d) **B**. The bond lengths are given in Å. H atoms are omitted for clarity: grey; C: green; Fe: red; Br: orange; P: purple; N.

Cartesian coordinates for optimized compounds.

FePhBr/(*R*,*R*)-QuinoxP* **C**

C	1.701439	0.329487	-0.52425
C	1.580576	-0.81132	0.341616
C	3.856407	-1.09096	0.278651
C	3.966986	-0.00905	-0.64471
P	-0.10394	-1.39858	0.853634
P	0.201637	1.357693	-0.91273
C	0.189188	-1.95931	2.571813
H	-0.6444	-2.58754	2.887674
H	1.130851	-2.50108	2.653632
H	0.20546	-1.07318	3.20724
C	0.139145	1.177454	-2.74254
H	-0.59367	1.8737	-3.15214
H	1.119728	1.368876	-3.1785
H	-0.17256	0.163065	-2.98853
C	0.732988	3.139682	-0.59798
C	-0.33057	-2.95685	-0.18257
C	0.710187	-4.03501	0.136405
H	0.542926	-4.89869	-0.51569
H	1.729172	-3.67973	-0.01808
H	0.626583	-4.37962	1.169062
C	-1.7477	-3.47649	0.114294
H	-1.93644	-4.37	-0.48907
H	-1.86264	-3.75935	1.163834
H	-2.50884	-2.7338	-0.12911
C	-0.23624	-2.53469	-1.65636
H	-0.99156	-1.78497	-1.89815
H	0.752058	-2.13966	-1.90395
H	-0.41763	-3.40362	-2.29579
C	-0.57241	3.955744	-0.59852
H	-0.33345	5.01512	-0.46339
H	-1.11425	3.857646	-1.54397
H	-1.23455	3.649992	0.213291
C	1.695554	3.679586	-1.66274
H	1.988783	4.698408	-1.38921
H	2.594032	3.067441	-1.73416
H	1.225772	3.728853	-2.64769
C	1.383466	3.198875	0.792876
H	0.738569	2.762528	1.557891
H	2.347223	2.686545	0.803912
H	1.558203	4.245633	1.059833
Fe	-1.6551	0.433162	0.396345
C	-3.29475	-0.16458	-0.6101
C	-3.36576	-0.25948	-2.01081
C	-4.43793	-0.57321	0.102523
C	-4.49466	-0.74891	-2.66796

H	-2.52139	0.055675	-2.61855	H	3.473856	-0.93116	-0.00432
C	-5.57303	-1.06499	-0.53954	C	0.99549	-0.07696	-0.00054
H	-4.44433	-0.5084	1.187525	O	1.015014	-1.29691	-0.0002
C	-5.60273	-1.15796	-1.93021	O	-0.12631	0.683382	-0.00097
H	-4.51242	-0.80893	-3.7517	C	-1.46341	0.070749	0.000098
H	-6.43608	-1.3735	0.041815	C	-2.38714	1.286032	0.0002
H	-6.48371	-1.54069	-2.43379	C	-1.65917	-0.75985	-1.26912
Br	-1.62769	1.539227	2.543947	H	-1.00022	-1.62573	-1.27613
N	2.865094	0.690851	-1.02192	H	-2.69561	-1.10292	-1.32262
N	2.64045	-1.48176	0.741784	H	-1.45532	-0.14957	-2.1523
C	5.239199	0.348573	-1.15096	C	-1.65787	-0.75898	1.270081
C	5.022977	-1.77694	0.692343	H	-1.45308	-0.14819	2.152701
C	6.353427	-0.33907	-0.73817	H	-2.69434	-1.10178	1.324816
H	7.329846	-0.06666	-1.12047	H	-0.99912	-1.62501	1.277042
C	6.245281	-1.40431	0.190604	H	-3.43106	0.964533	0.00074
H	7.140901	-1.92783	0.502901	H	-2.20947	1.899466	0.8858
H	5.296762	1.170429	-1.85357	H	-2.21031	1.8991	-0.88582
H	4.91202	-2.58995	1.398817				

FePhBr(alkyl)/(*R*,*R*)-QuinoxP* **D**

Alkyl radical generated from **1a**				C	-2.34115	-0.66614	-0.55885
C	2.183305	0.755292	-0.0006	C	-2.52479	0.669778	-0.06353
H	2.048097	1.829976	-0.00064	C	-4.79332	0.440867	-0.28012
C	3.537429	0.156787	0.000357	C	-4.60542	-0.83222	-0.89448
H	4.115093	0.4846	-0.87355	P	-1.0431	1.738588	0.228284
H	4.110021	0.476467	0.880745	P	-0.66304	-1.46572	-0.45452

C	-1.59228	2.860796	1.563722	H	0.560199	-3.27763	1.676349
H	-0.83607	3.632333	1.708657	C	-1.60816	-4.11921	-0.88422
H	-2.55592	3.306183	1.321519	H	-1.86895	-5.08212	-0.43284
H	-1.67274	2.269817	2.474548	H	-2.50395	-3.69936	-1.34029
C	-0.25134	-1.71968	-2.22834	H	-0.86748	-4.31315	-1.66253
H	0.610262	-2.38177	-2.27994	C	-2.06716	-3.09196	1.367461
H	-1.103	-2.13203	-2.76873	H	-1.75484	-2.35723	2.110718
H	0.032806	-0.765	-2.66652	H	-3.0619	-2.83109	1.007253
C	-1.05462	-3.20237	0.216411	H	-2.13555	-4.06602	1.862183
C	-1.05021	2.816954	-1.33537	Fe	0.745597	0.175101	0.783539
C	-2.43004	3.423035	-1.62863	C	2.042884	1.580138	0.264651
H	-2.33843	4.081793	-2.49856	C	2.659607	1.628003	-0.98656
H	-3.17862	2.666198	-1.85807	C	2.332245	2.589887	1.189663
H	-2.80172	4.023049	-0.79698	C	3.52316	2.670553	-1.32183
C	-0.04027	3.959753	-1.14019	H	2.478368	0.842708	-1.71214
H	0.011017	4.54175	-2.06585	C	3.19749	3.632052	0.861541
H	-0.35479	4.638425	-0.34492	H	1.881298	2.565397	2.176914
H	0.959043	3.600516	-0.9137	C	3.791747	3.678771	-0.39906
C	-0.62715	1.924605	-2.50802	H	3.987884	2.693655	-2.30198
H	0.361796	1.49674	-2.34564	H	3.407527	4.408201	1.589691
H	-1.3419	1.11455	-2.67011	H	4.462761	4.490089	-0.65655
H	-0.58859	2.519482	-3.42563	C	2.428038	-0.92569	1.189995
C	0.260248	-3.78652	0.759505	H	1.822486	-1.75804	1.550102
H	0.099534	-4.84126	1.004079	C	3.327687	-0.3902	2.288376
H	1.076373	-3.71618	0.039394	H	3.904844	0.469761	1.951867

H	2.727709	-0.09328	3.150358	H	6.43622	0.359453	-0.80072
H	4.037705	-1.1564	2.620489	H	7.335392	-0.9438	-1.60769
C	3.082135	-1.37598	-0.06018	H	6.916308	-1.07937	0.112704
O	2.525396	-2.02401	-0.93806	Br	-0.3331	-0.15371	2.99273
O	4.366708	-0.98684	-0.13691				
C	5.253479	-1.39548	-1.23601	FeBr/(*R*,*R*)-QuinoxP* **B**			
C	6.570793	-0.72231	-0.85931	Fe	-2.08533	0.304327	0.193639
C	5.395958	-2.91773	-1.23647	P	-0.52336	-1.26149	0.886093
H	4.456243	-3.39665	-1.50537	C	-0.73175	-2.93272	0.025154
H	6.163537	-3.21342	-1.95631	C	-0.64787	-2.66504	-1.48568
H	5.701846	-3.26568	-0.247	C	1.135416	-0.65159	0.305188
C	4.748215	-0.86785	-2.5792	C	1.204144	0.635552	-0.32704
H	4.648401	0.21766	-2.54355	C	3.441469	0.326949	-0.71282
H	5.474377	-1.11832	-3.35719	C	3.390507	-0.91638	-0.01575
H	3.788533	-1.31053	-2.83671	P	-0.3117	1.702414	-0.31525
N	-3.36099	-1.36807	-1.00423	C	0.126813	3.007371	0.98161
N	-3.72233	1.187657	0.097014	C	0.454884	2.261485	2.283584
C	-5.73035	-1.55775	-1.35317	C	-0.16941	2.56547	-1.93057
C	-6.10356	0.94532	-0.10599	C	-0.13883	-1.67824	2.638449
C	-6.99035	-1.0395	-1.18168	C	-2.1454	-3.42068	0.384533
H	-7.855	-1.59436	-1.52576	C	0.30992	-3.97511	0.446359
C	-7.17827	0.214975	-0.54986	C	1.306772	3.892171	0.566514
H	-8.1834	0.598463	-0.42142	C	-1.13533	3.863237	1.178618
H	-5.56186	-2.51986	-1.82059	H	-0.85248	3.415654	-1.94402
H	-6.218	1.910524	0.371149	H	0.853537	2.887852	-2.12229

H	-0.48414	1.865789	-2.70601	C	4.670019	0.77375	-1.25107
H	-0.95237	-2.27086	3.058496	C	5.803864	0.014441	-1.08797
H	0.798311	-2.23065	2.710765	H	6.746892	0.354884	-1.49868
H	-0.05373	-0.75386	3.210483	C	5.7564	-1.21251	-0.38365
H	1.542858	4.588394	1.378431	H	6.663957	-1.79242	-0.26556
H	2.197092	3.301944	0.3479	H	4.510421	-2.61046	0.682747
H	1.070092	4.48596	-0.31851	H	4.680206	1.718494	-1.78028
H	-0.9447	4.636797	1.929375	Br	-4.1291	-0.05689	-0.89696
H	-1.43399	4.364264	0.254699				
H	-1.98148	3.261629	1.520948	Transition state at reductive elimination **TS**			
H	-0.36943	1.613345	2.592469	C	-1.5945	4.02589	2.818531
H	1.350423	1.644976	2.182614	C	-2.49157	3.754013	1.786947
H	0.632405	2.983069	3.086628	C	-2.22828	2.724939	0.884444
H	-2.33933	-4.37027	-0.12403	C	-1.07039	1.935849	0.978156
H	-2.25101	-3.59614	1.458978	C	-0.1867	2.236141	2.029436
H	-2.9095	-2.70533	0.074697	C	-0.4343	3.263359	2.938986
H	0.136613	-4.89918	-0.11537	Fe	-0.654	0.464938	-0.33437
H	1.325633	-3.63342	0.252489	C	-2.92227	-0.47021	2.110497
H	0.228862	-4.21826	1.508308	C	-4.11848	-0.25456	1.3178
H	-1.40167	-1.94088	-1.80366	O	-4.22534	-1.18466	0.341001
H	0.33773	-2.29115	-1.77426	C	-5.39499	-1.22338	-0.55258
H	-0.82751	-3.59635	-2.03115	C	-5.51857	0.082389	-1.33904
N	2.211705	-1.38831	0.477754	P	0.629946	-1.30525	0.773577
N	2.324586	1.096683	-0.83946	C	0.485847	-3.05543	0.084799
C	4.574198	-1.67274	0.144897	C	0.906461	-3.00352	-1.3906

C	2.424371	-0.87827	0.520889	H	2.405171	-3.78677	0.839038
C	2.809578	0.068625	-0.4921	H	1.03704	-4.15225	1.89454
C	5.018037	-0.31117	0.006947	H	-1.14977	-4.42532	-0.25279
C	4.6336	-1.20763	1.047628	H	-1.33378	-3.49111	1.22857
P	1.493831	0.987339	-1.42845	H	-1.64267	-2.72945	-0.34302
C	2.083656	2.773247	-1.55184	H	0.272139	-2.31902	-1.95578
C	2.485387	3.257652	-0.15208	H	1.951499	-2.70364	-1.50284
C	0.577971	-1.49974	2.599093	H	0.797816	-3.99904	-1.83109
C	1.717287	0.292216	-3.11483	H	1.123922	4.612175	-2.16425
C	0.850862	3.560284	-2.03498	H	0.481772	3.192209	-2.99624
C	3.249764	2.953035	-2.53183	H	0.034791	3.504048	-1.31203
C	1.350035	-4.06115	0.852533	H	3.553824	4.00502	-2.5313
C	-1.00179	-3.43483	0.188557	H	4.10558	2.343476	-2.24348
Br	-1.80933	-0.34428	-2.29288	H	2.964326	2.696367	-3.55395
C	-2.69987	0.295247	3.357491	H	1.672946	3.131417	0.563794
O	-4.9231	0.637534	1.529226	H	3.370666	2.735319	0.214895
C	-5.06523	-2.38728	-1.48326	H	2.722275	4.325109	-0.19918
C	-6.64868	-1.51999	0.272175	H	-2.95682	2.521858	0.105638
H	-0.31114	-2.06209	2.882969	H	0.727838	1.657457	2.15066
H	1.474954	-2.00889	2.949055	H	-3.40315	4.33472	1.694239
H	0.516852	-0.51076	3.052238	H	0.270473	3.467723	3.738905
H	1.115875	0.872152	-3.81518	H	-1.79981	4.822384	3.52519
H	2.767309	0.309325	-3.40747	H	-2.30191	-1.31638	1.850294
H	1.339521	-0.72776	-3.12787	H	-3.0966	-0.25829	4.222487
H	1.244431	-5.04719	0.388581	H	-1.64028	0.472976	3.540849

H	-3.21789	1.252574	3.312282	H	1.245322	2.404966	2.109509
H	-6.87325	-0.69779	0.949573	H	-0.46036	2.745053	1.767282
H	-7.49926	-1.66655	-0.3986	H	0.023087	1.142633	2.332393
H	-6.50996	-2.43496	0.853937	C	-0.72953	1.012393	-0.40366
H	-4.57795	0.303058	-1.84484	O	-1.09634	1.335884	-1.50659
H	-6.30041	-0.03052	-2.09532	O	-1.35396	0.131523	0.397512
H	-5.77869	0.910518	-0.68309	C	-2.54026	-0.62224	-0.05576
N	3.322062	-1.47938	1.273052	C	-2.85055	-1.50739	1.147692
N	4.077704	0.31894	-0.74398	C	-3.69126	0.34283	-0.33575
C	5.629647	-1.82851	1.838256	H	-3.46741	0.980899	-1.18809
C	6.391702	-0.06632	-0.22988	H	-4.59934	-0.22726	-0.54805
C	6.954597	-1.57018	1.588702	H	-3.87865	0.969625	0.539483
H	7.721135	-2.04479	2.189452	C	-2.17571	-1.46757	-1.27533
C	7.337301	-0.68695	0.548148	H	-1.30247	-2.08648	-1.05649
H	8.389962	-0.50168	0.371147	H	-3.01145	-2.12733	-1.52169
H	5.310707	-2.5013	2.624448	H	-1.95707	-0.83992	-2.13692
H	6.658599	0.616043	-1.02705	C	1.649887	0.508284	0.111757
H	-4.14532	-2.18059	-2.03108	C	1.602598	-0.70857	0.800616
H	-4.93408	-3.30718	-0.90848	C	2.737412	0.762267	-0.72576
H	-5.8786	-2.53525	-2.19765	C	2.624062	-1.64211	0.658437
				H	0.756092	-0.92712	1.438641
Product **3a**				C	3.761826	-0.17082	-0.86866
C	0.542854	1.542798	0.252853	H	2.779956	1.698343	-1.27167
H	0.81808	2.409988	-0.34935	C	3.708387	-1.37648	-0.1759
C	0.32158	1.98373	1.707384	H	2.573303	-2.58044	1.199154

H	4.599276	0.045027	-1.52217
H	4.503543	-2.10471	-0.28544
H	-3.732	-2.11967	0.944886
H	-2.00928	-2.16954	1.362562
H	-3.04605	-0.89616	2.031073

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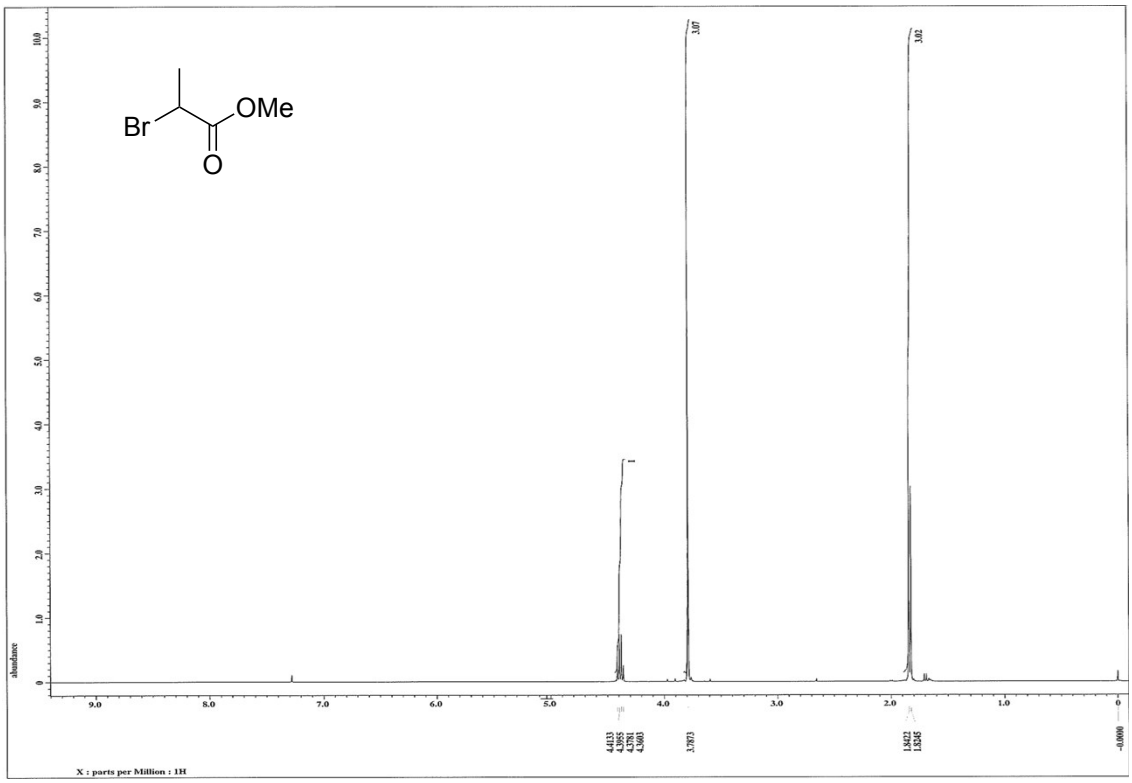
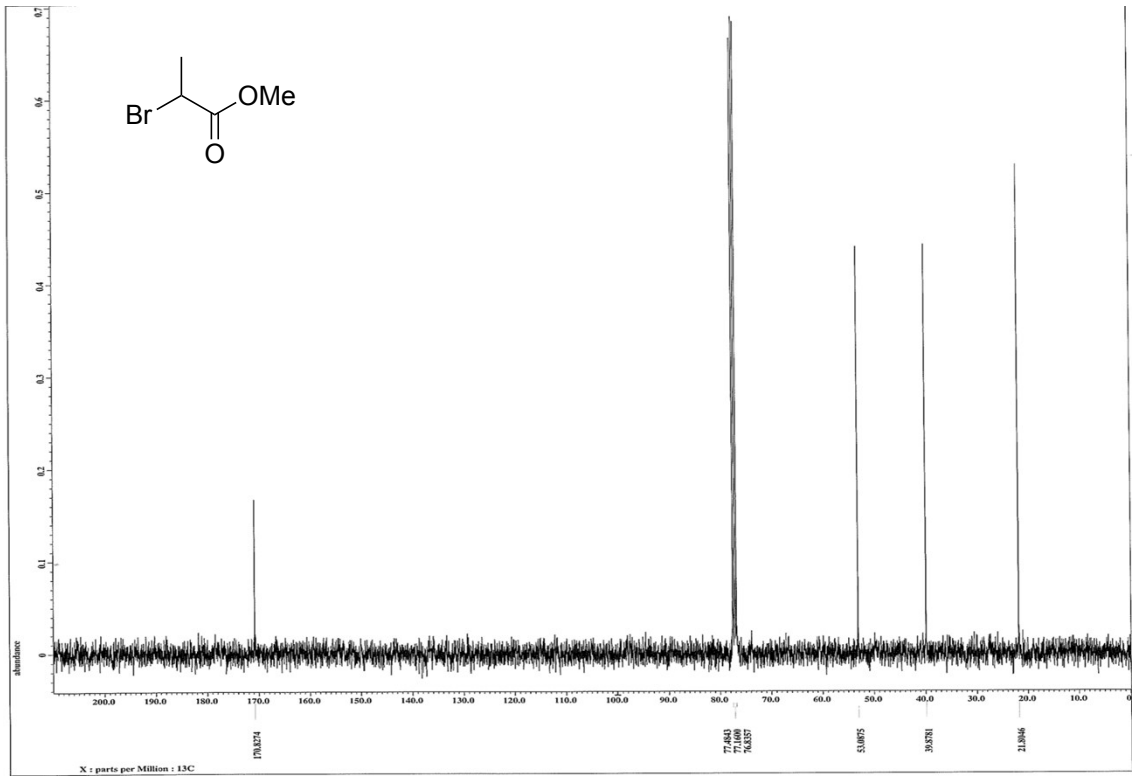
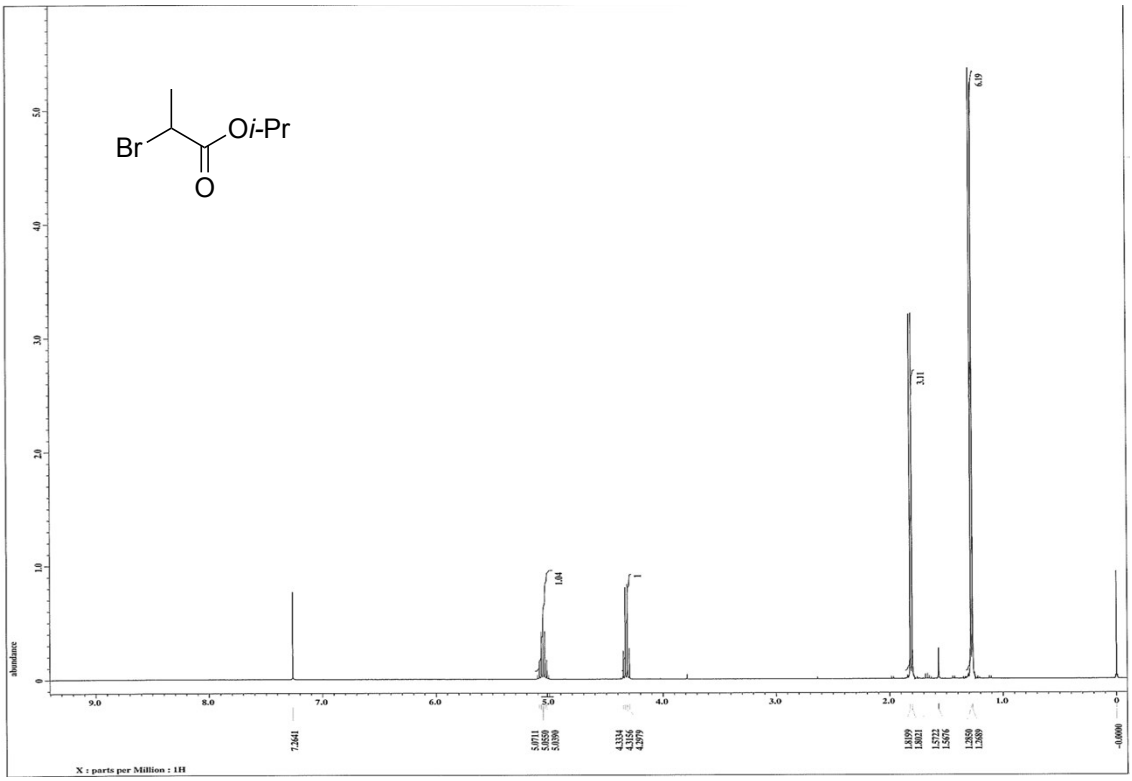
7. ^{1}H and ^{13}C NMR spectra

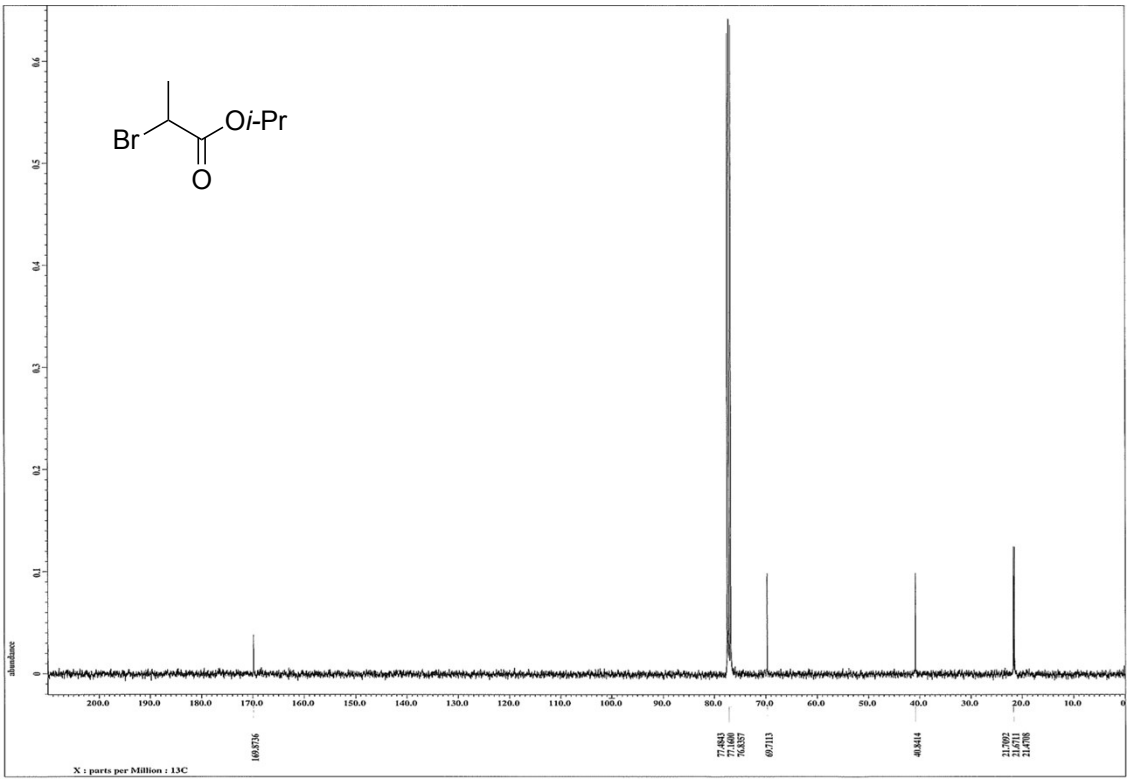
Methyl 2-bromopropionate



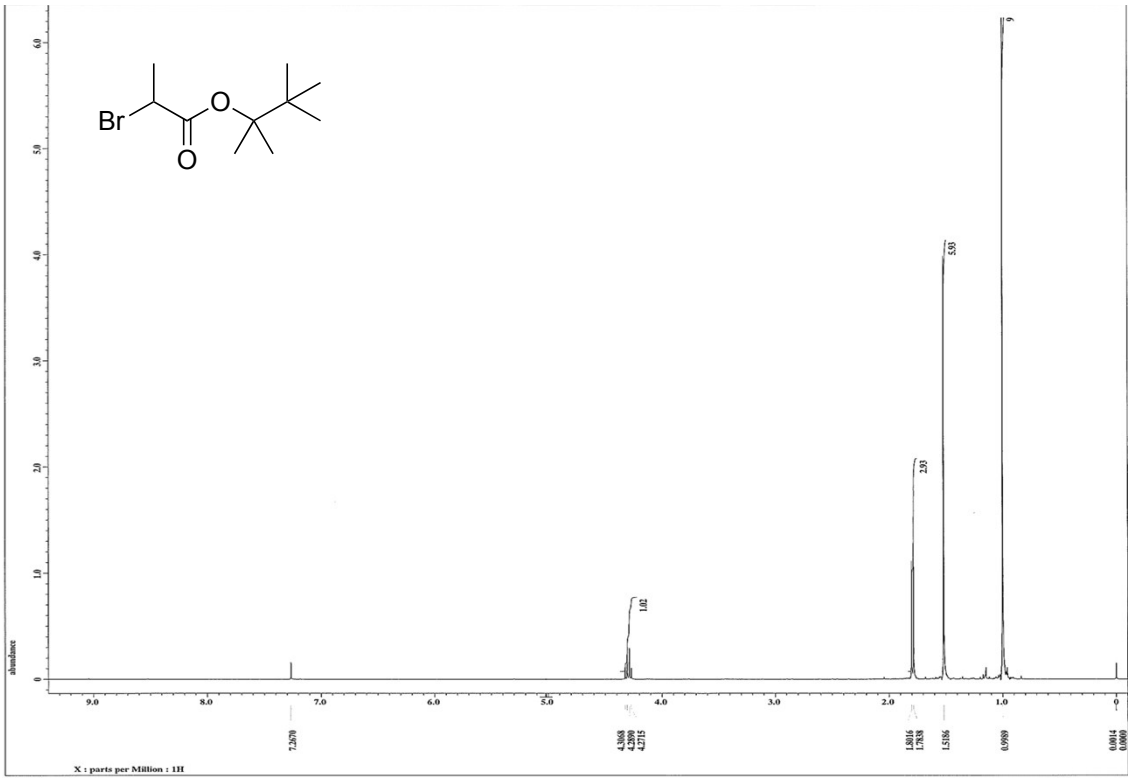


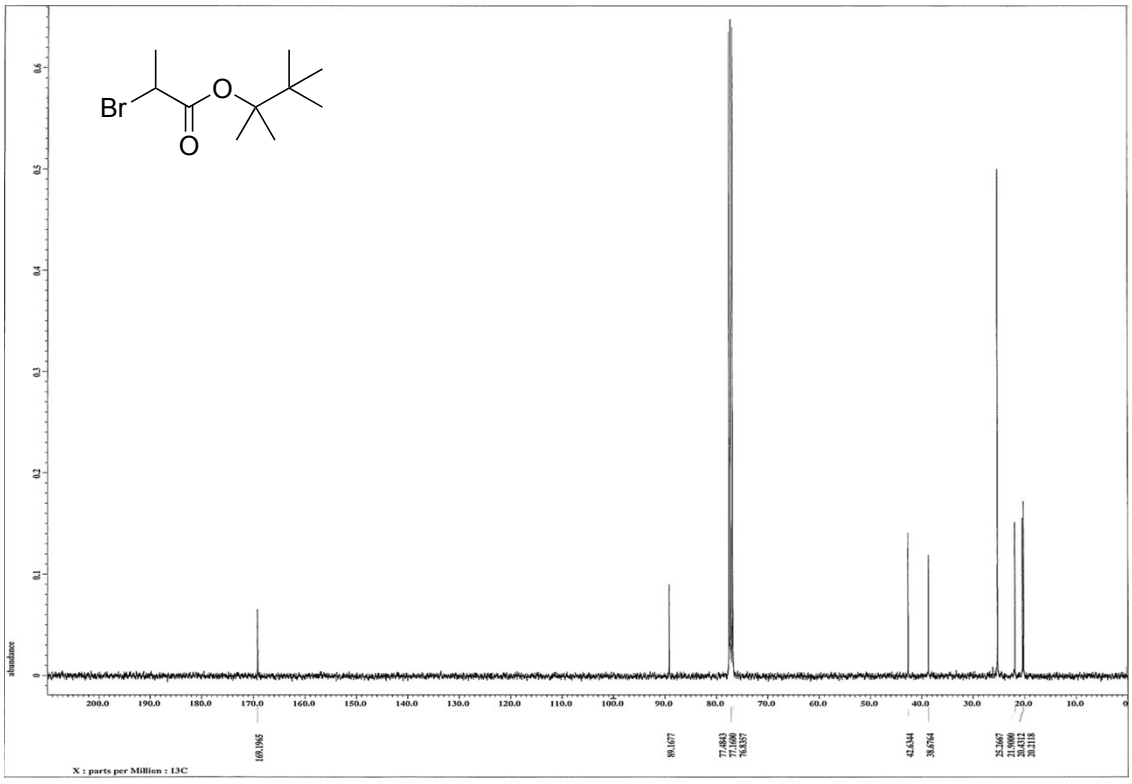
Isopropyl 2-bromopropionate



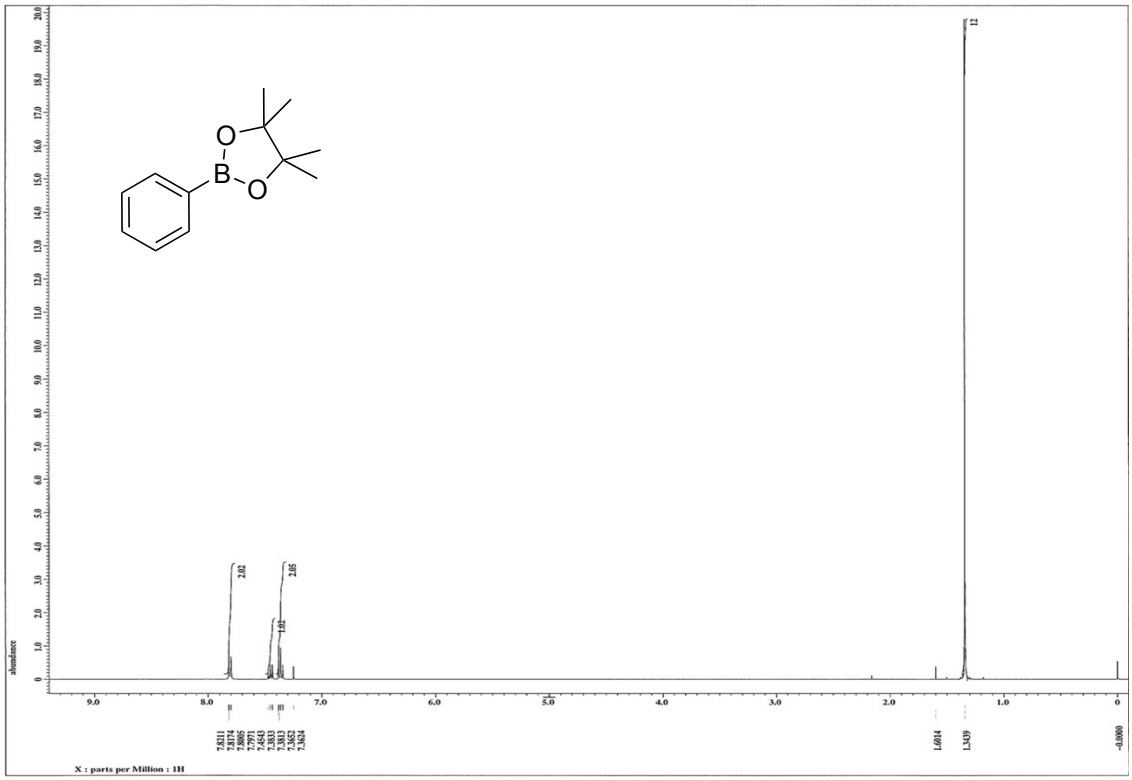


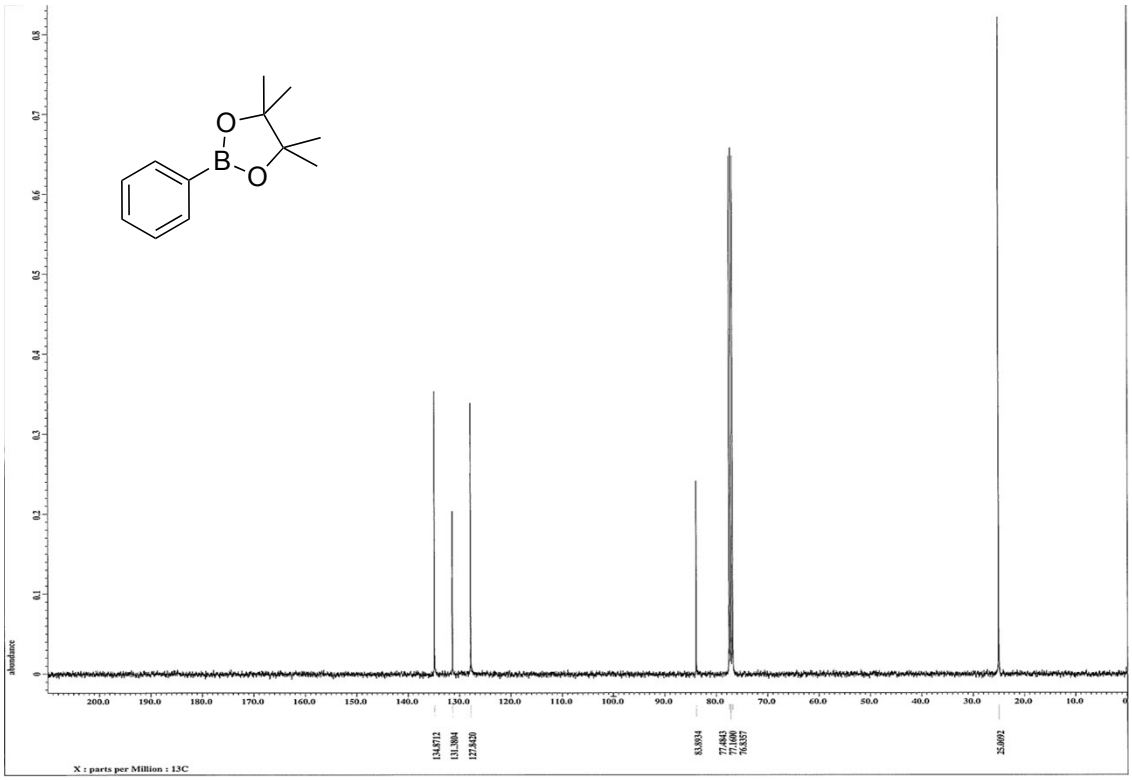
2,3,3-Trimethylbut-2-yl 2-bromopropionate





2-Phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane





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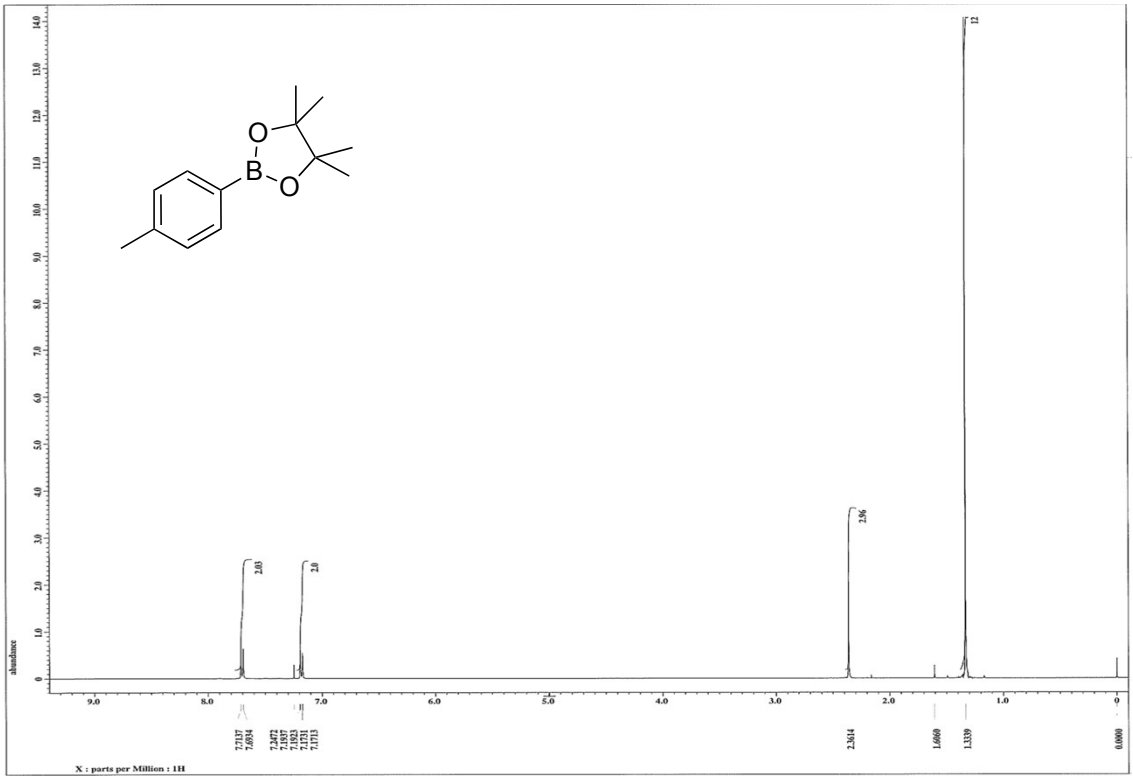

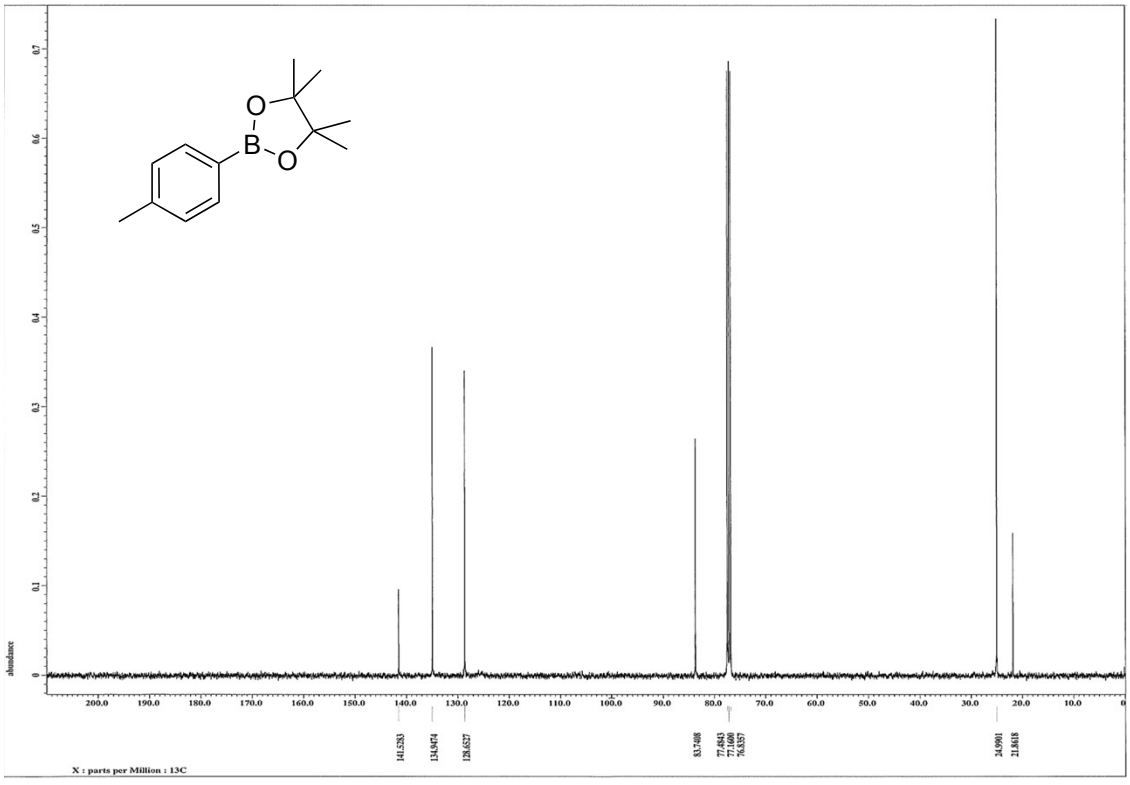

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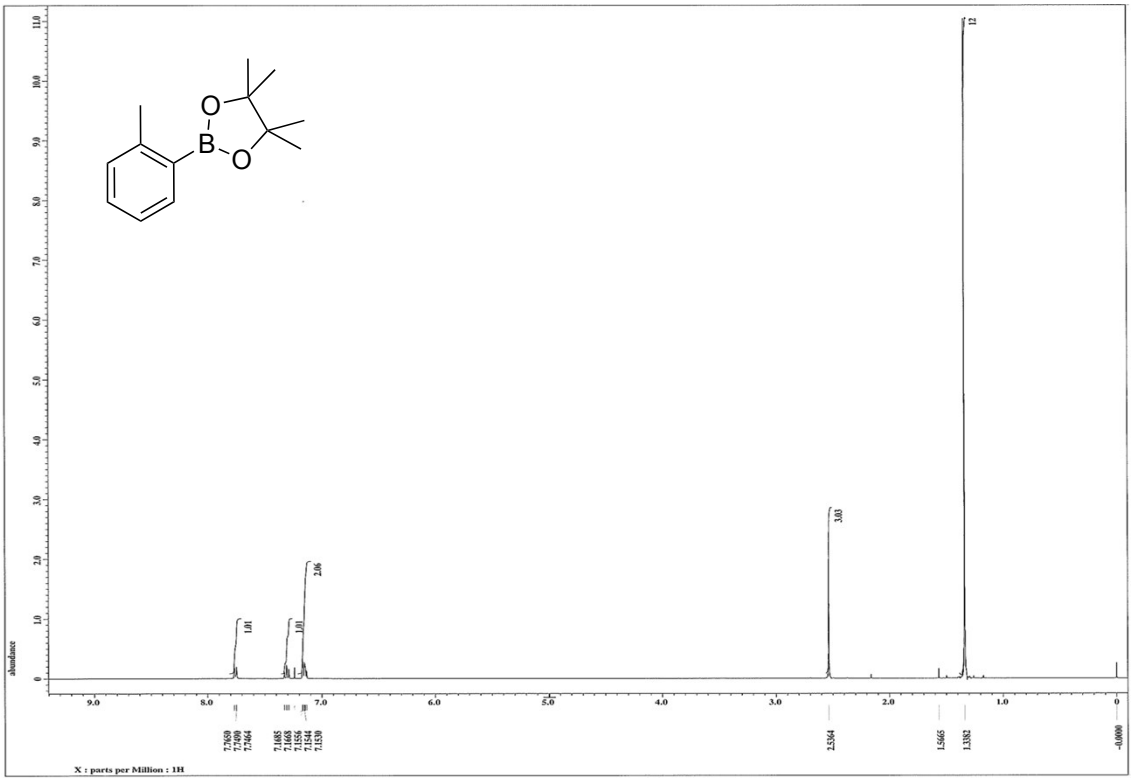

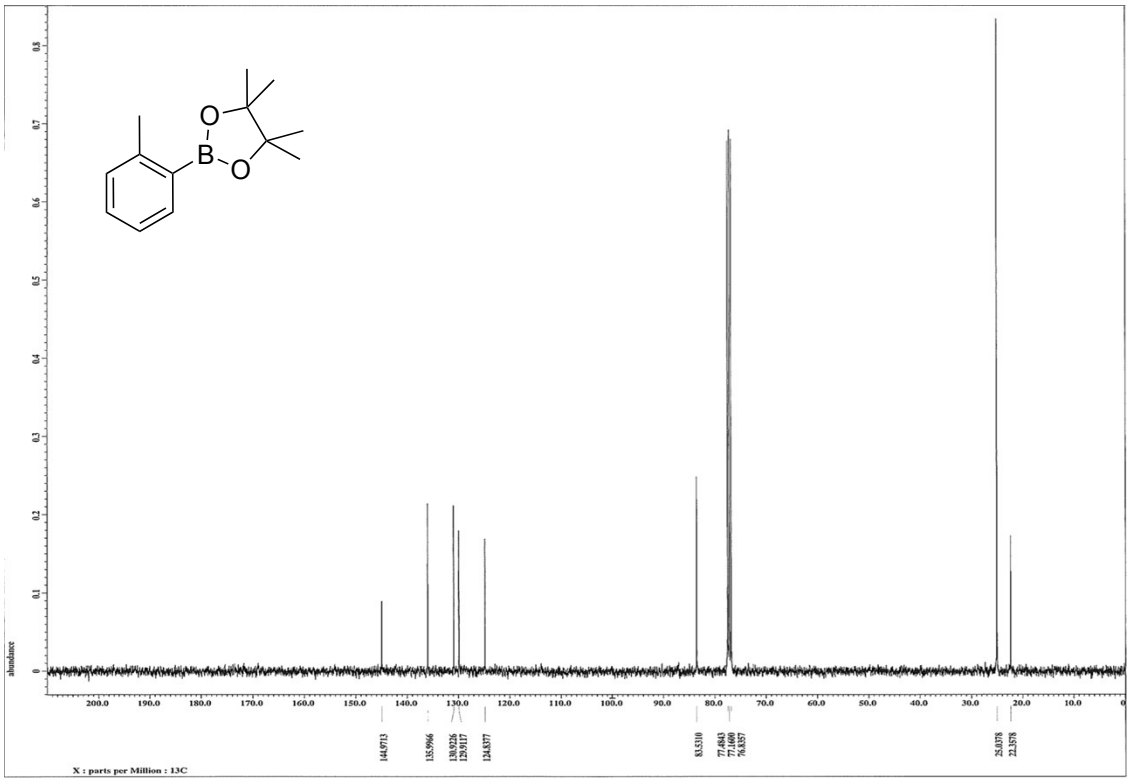

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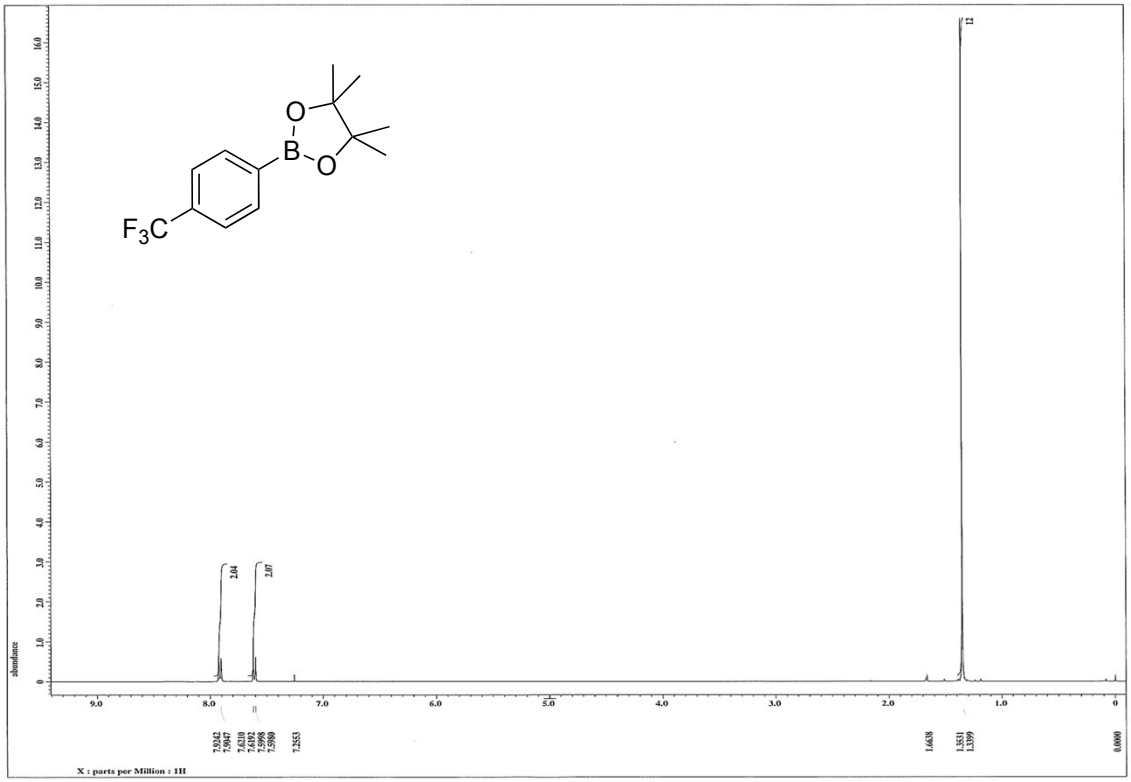

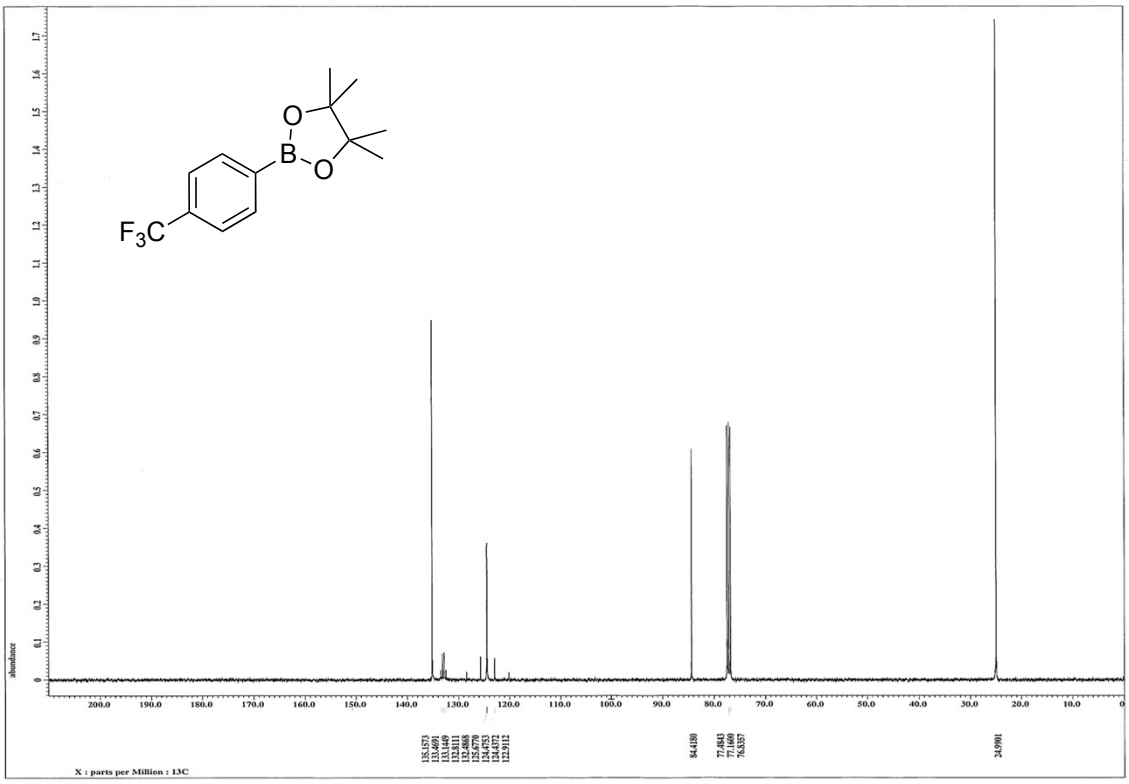

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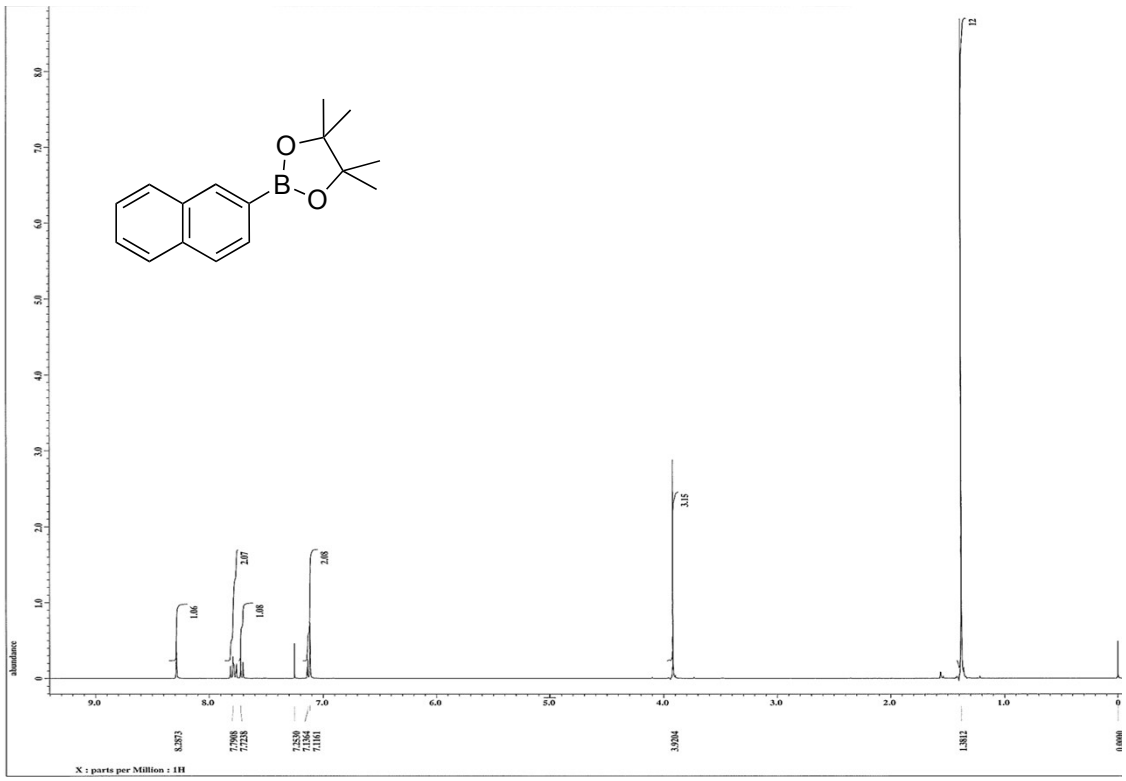

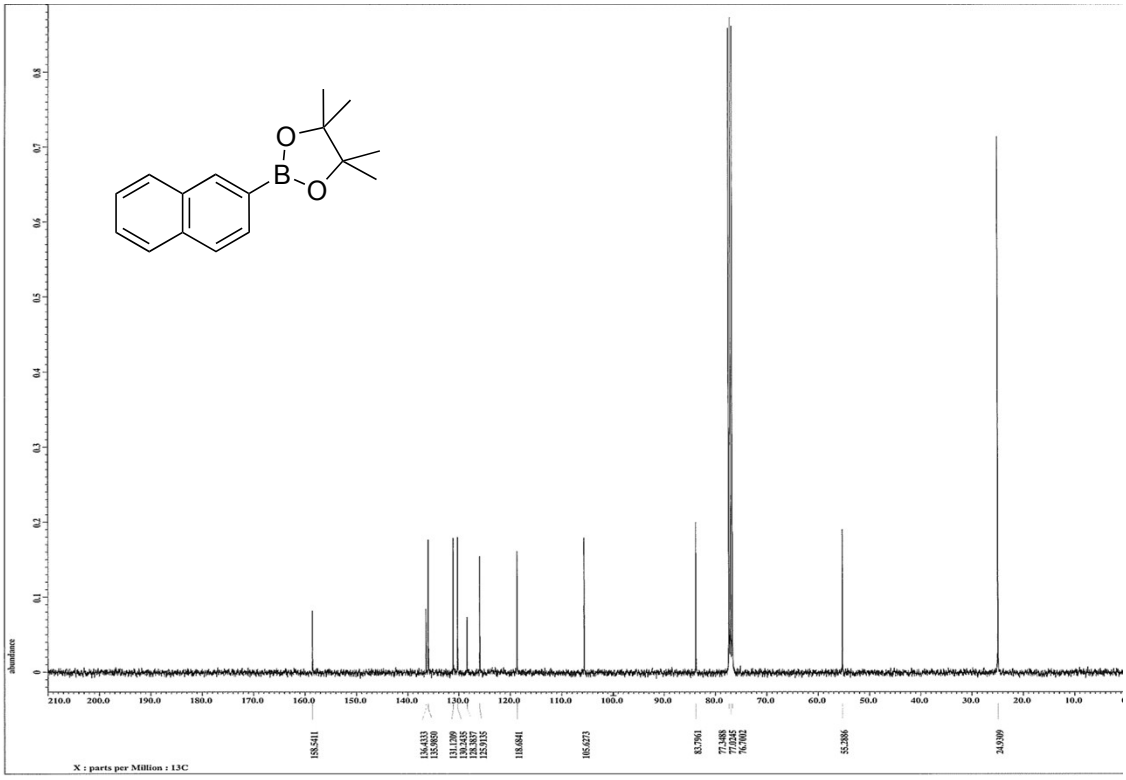

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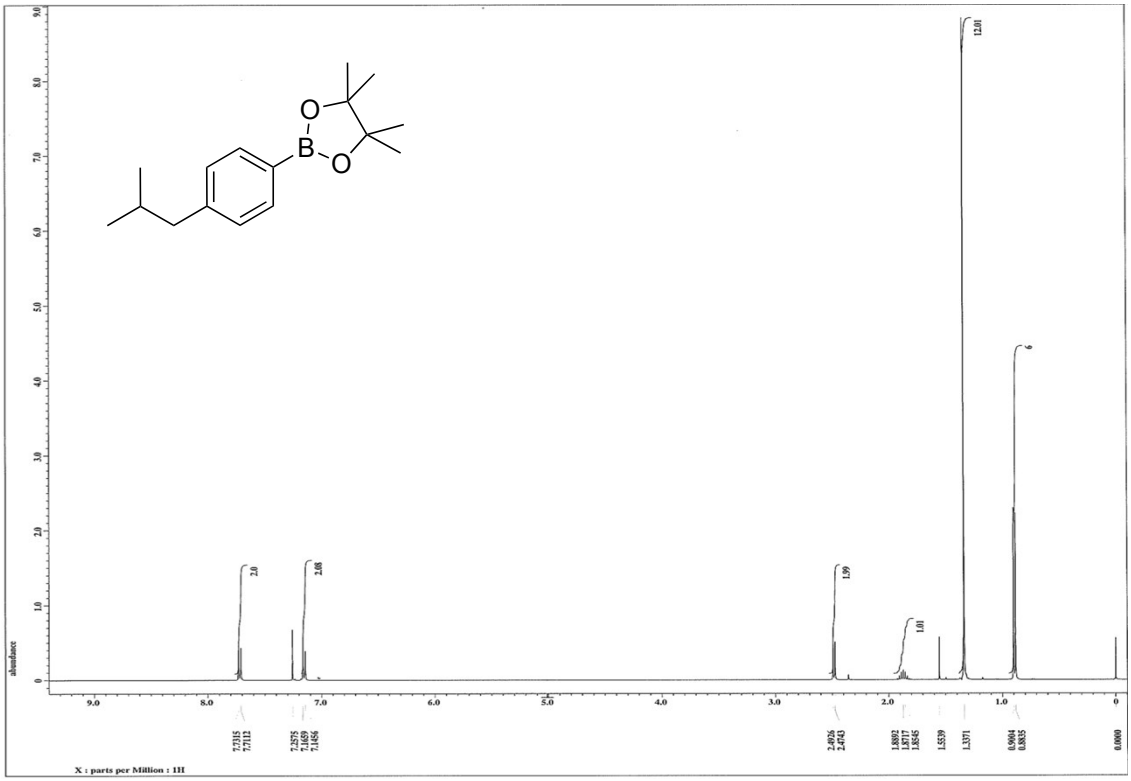

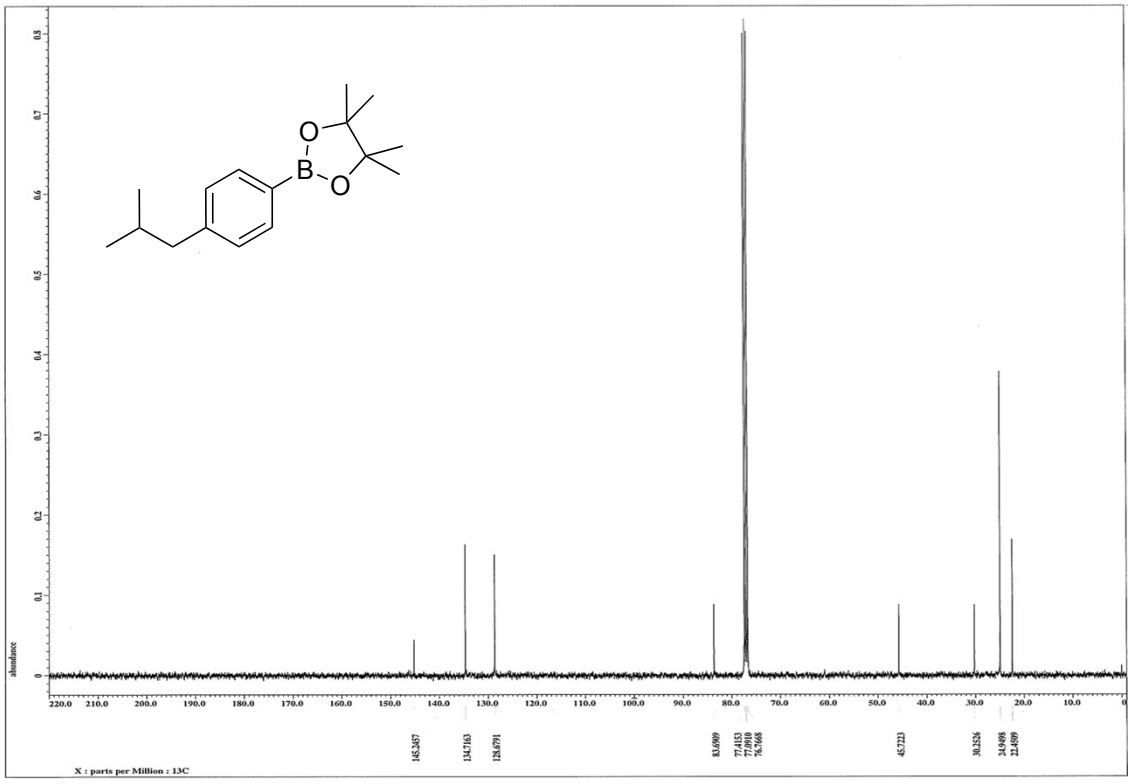

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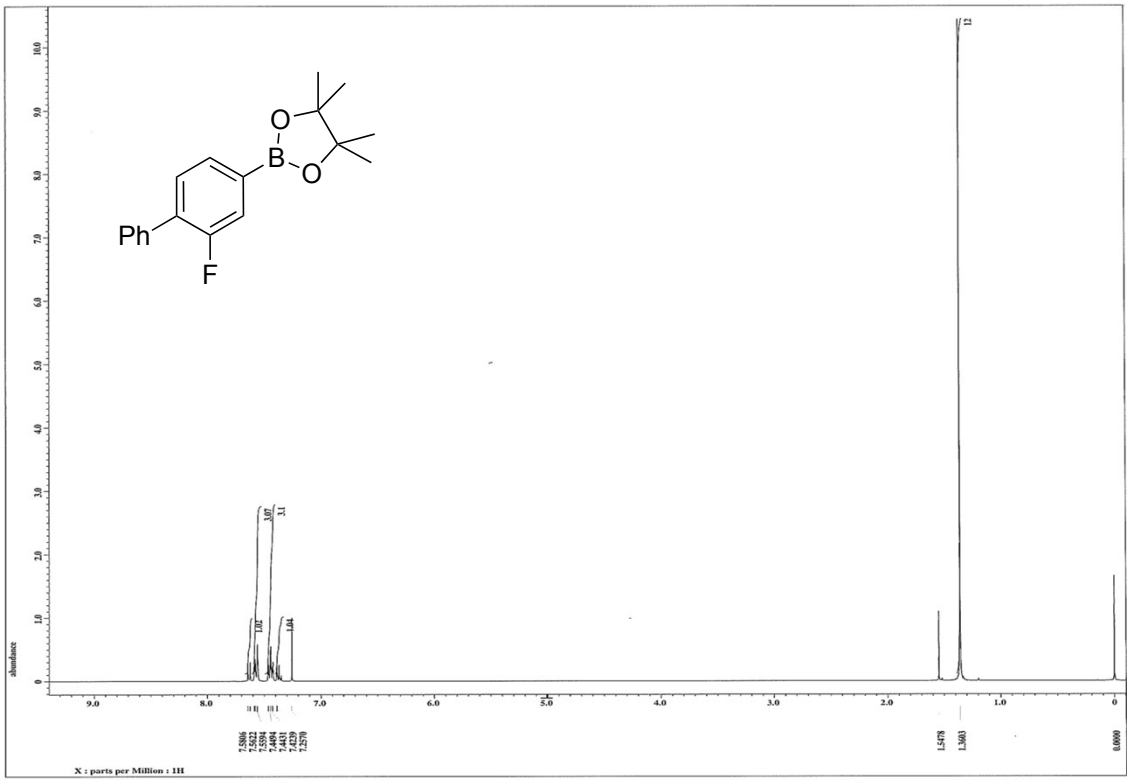
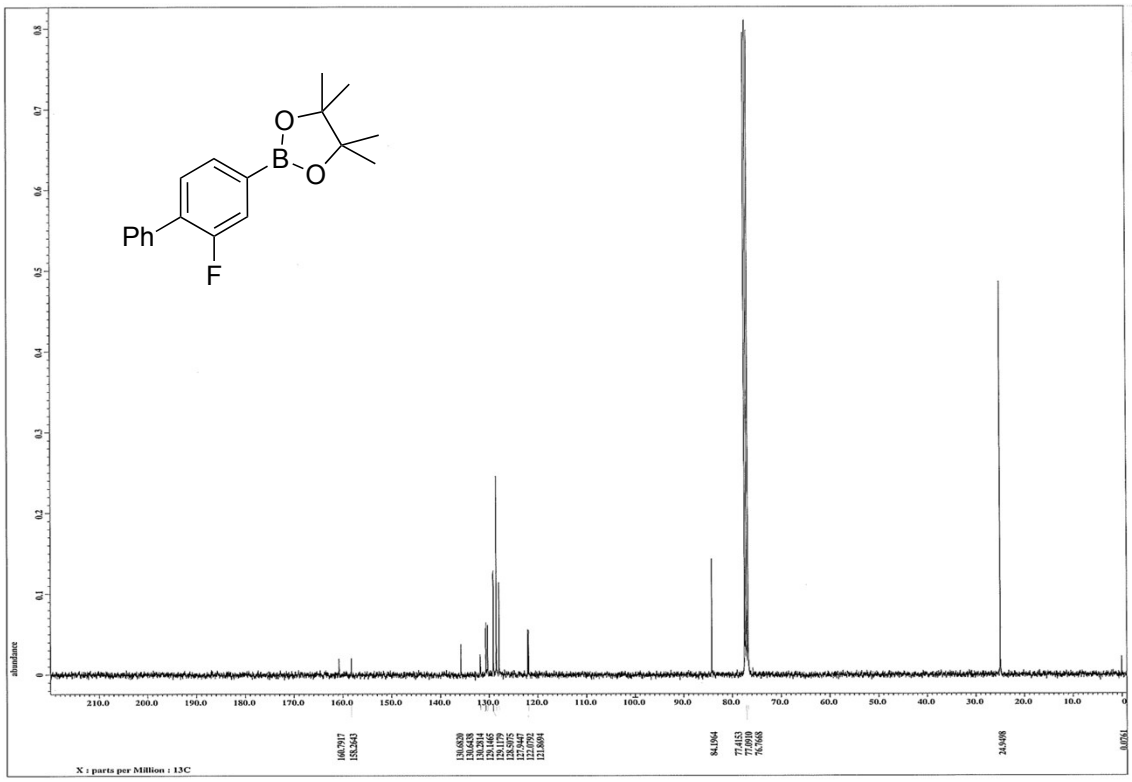
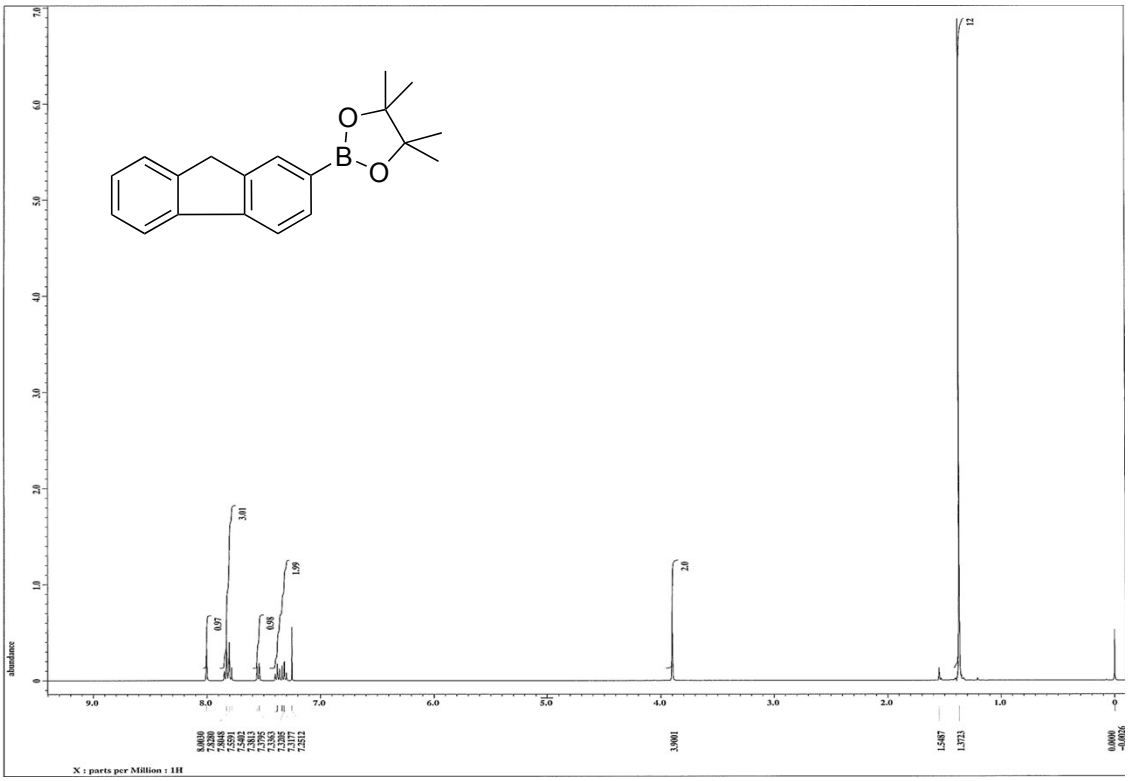
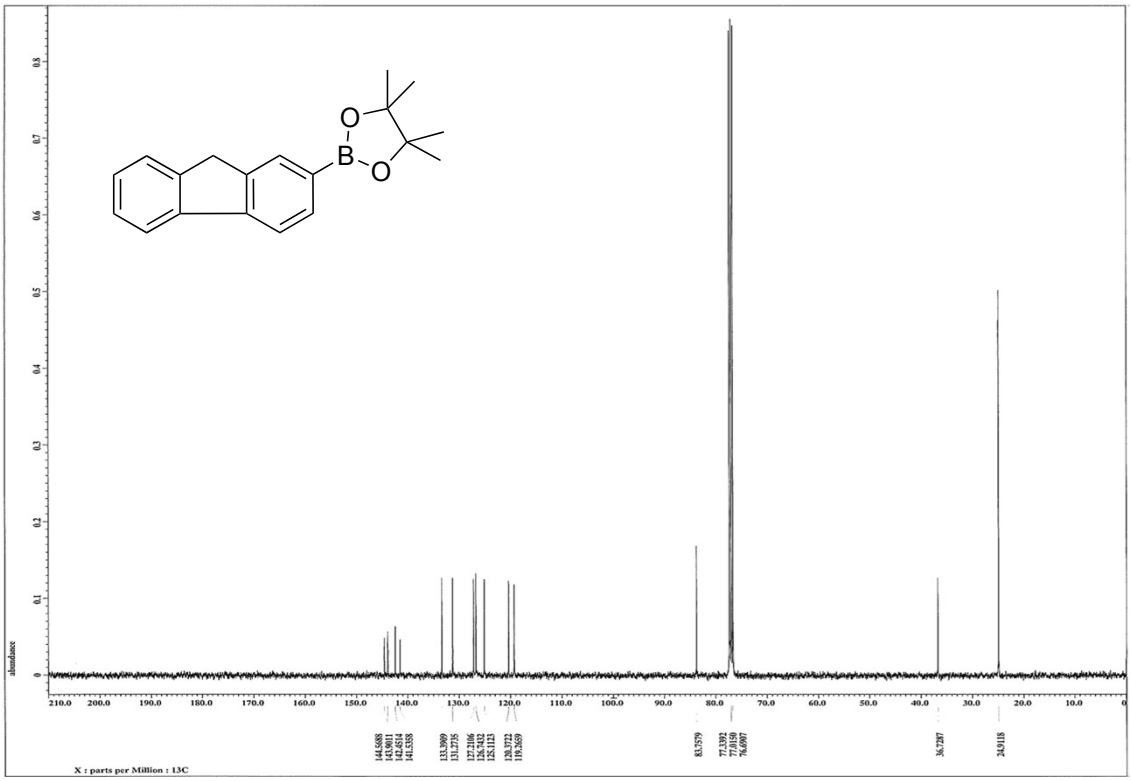




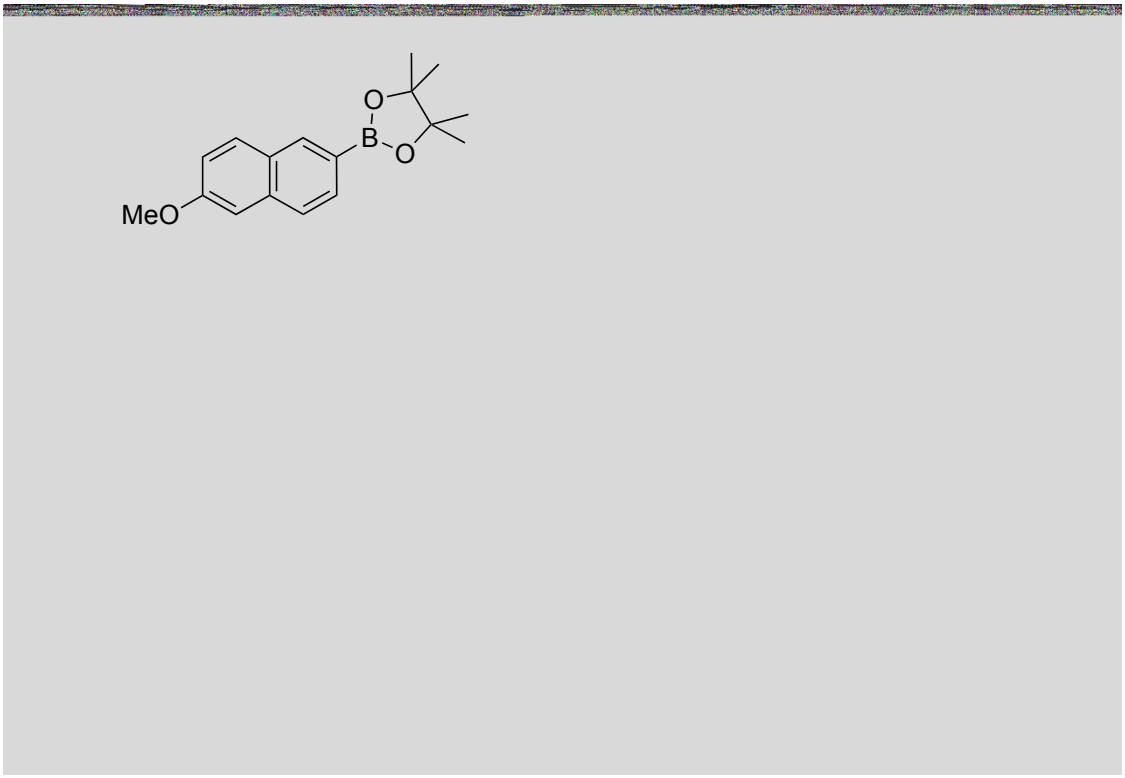
4,4,5,5-Tetramethyl-2-(3-phenoxyphenyl)-1,3,2-dioxaborolane

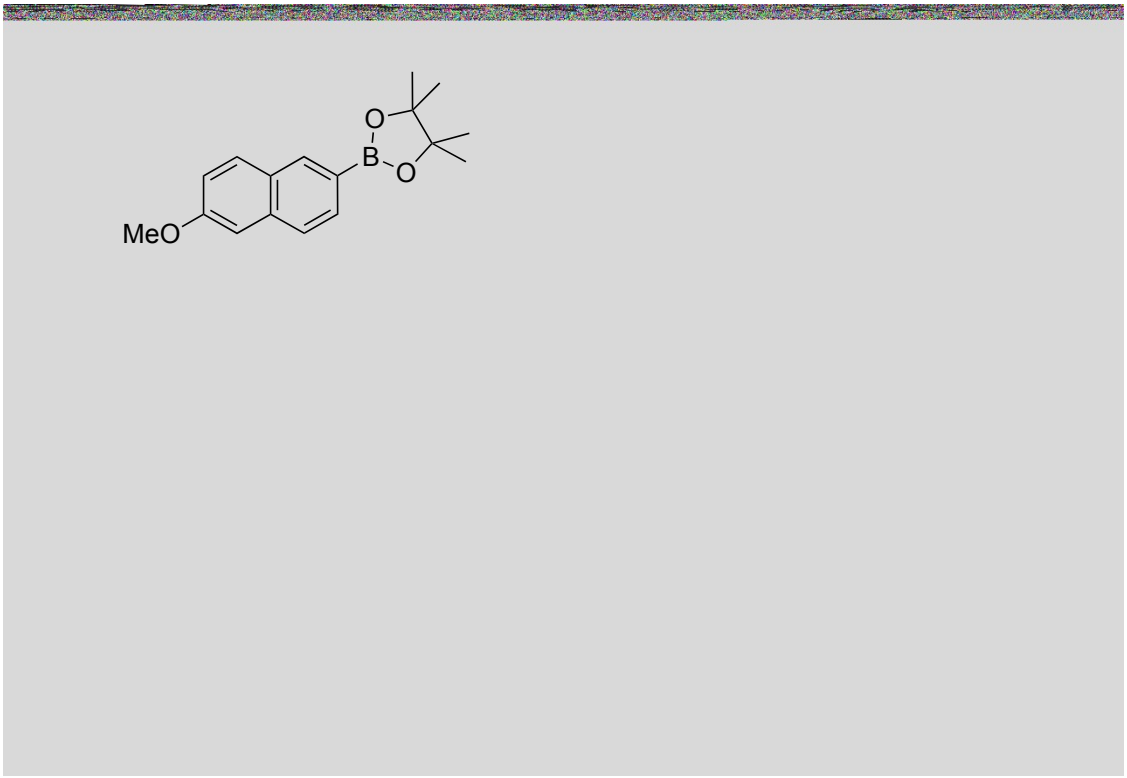
4,4,5,5-Tetramethyl-2-(2-fluorenyl)-1,3,2-dioxaborolane



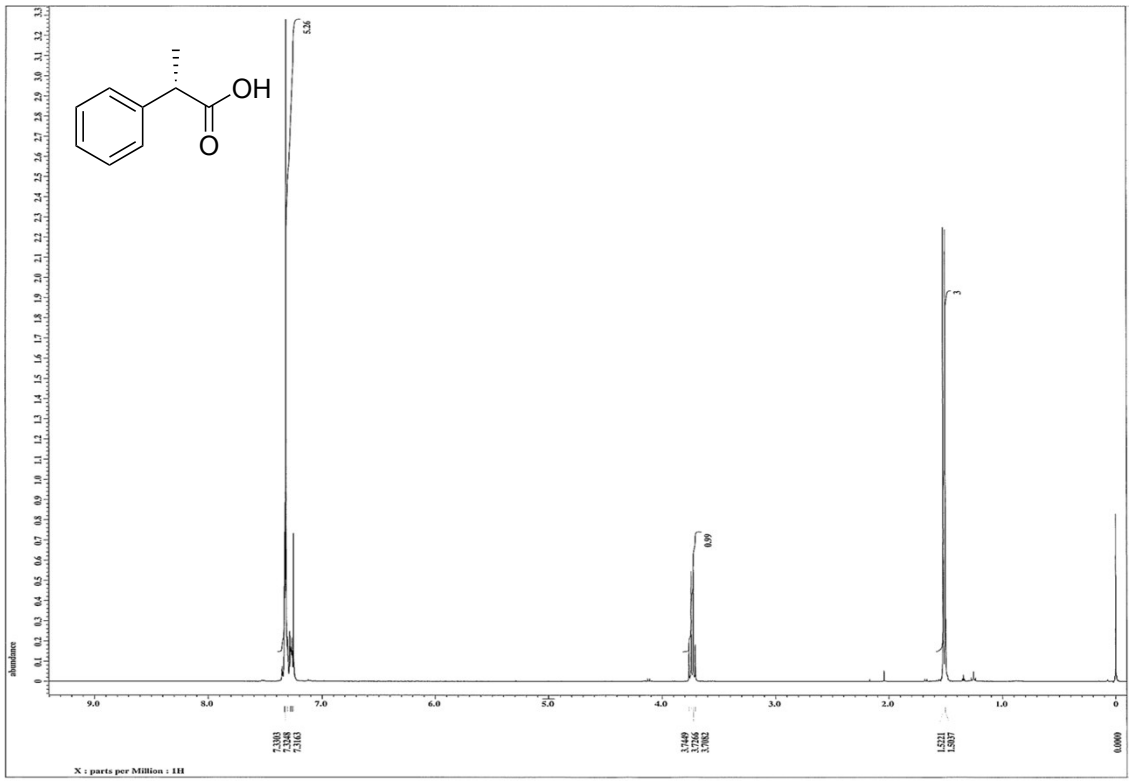


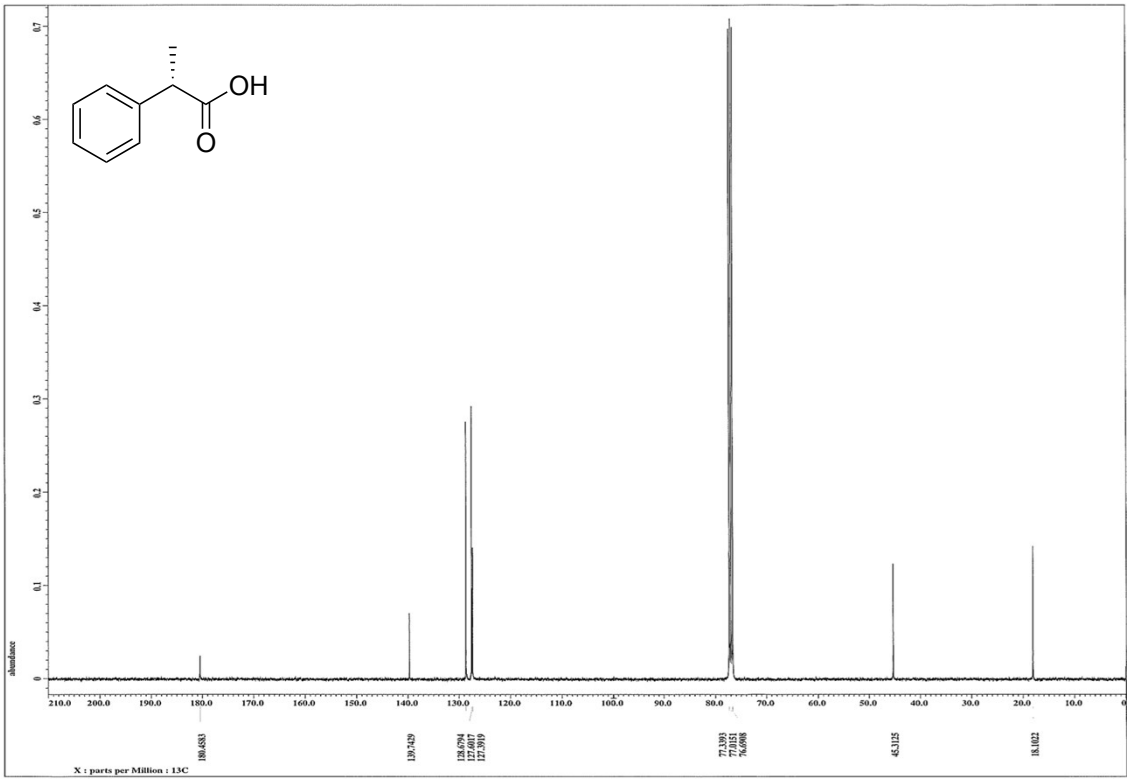
4,4,5,5-Tetramethyl-2-(6-methoxynaphthalen-2-yl)-1,3,2-dioxaborolane



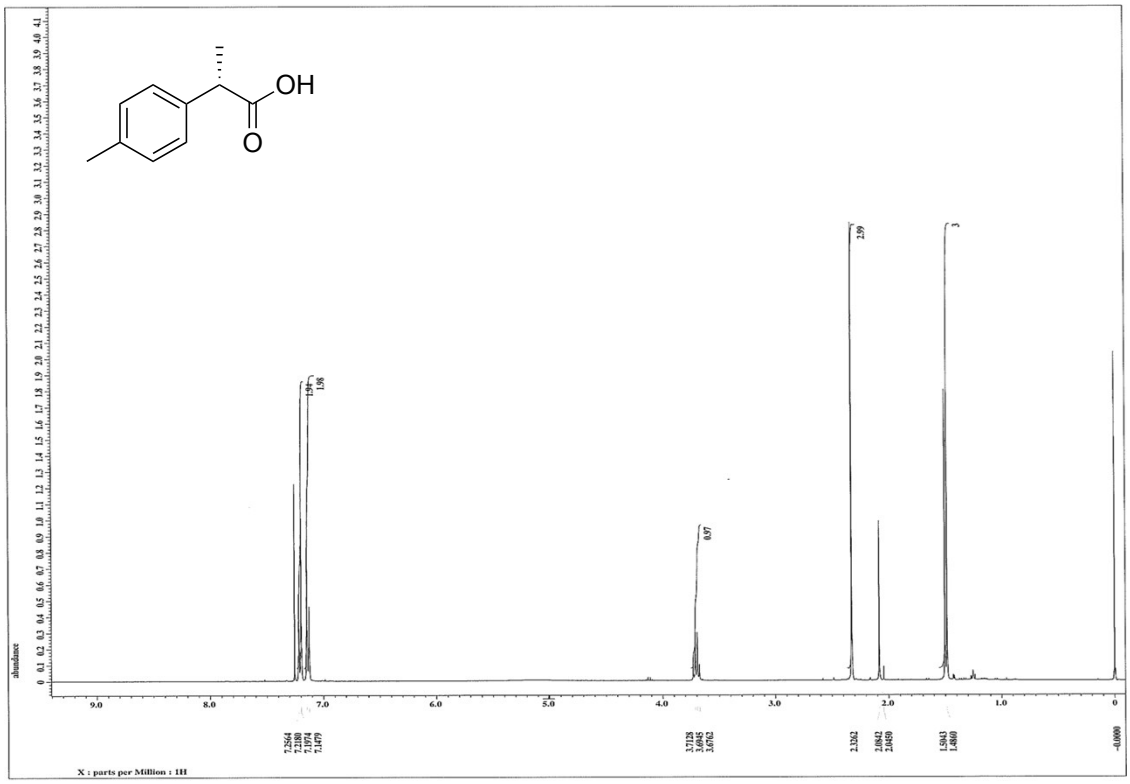


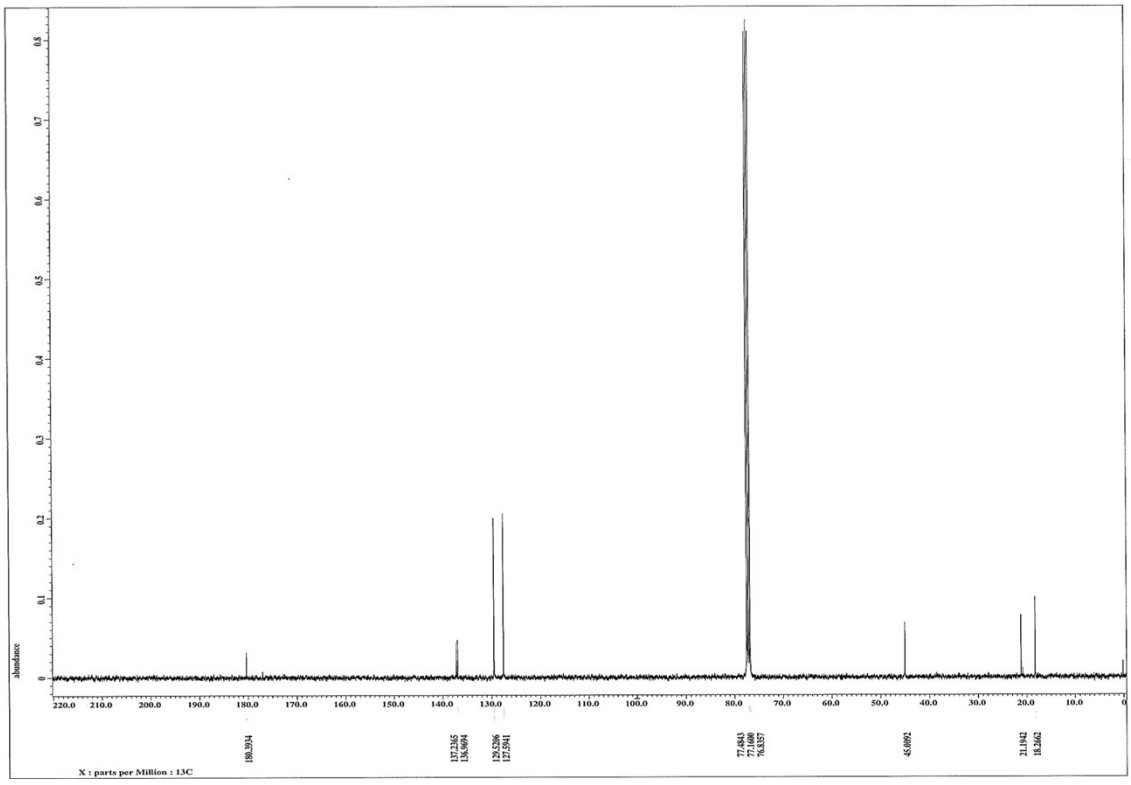
(*S*)-2-phenylpropionic acid



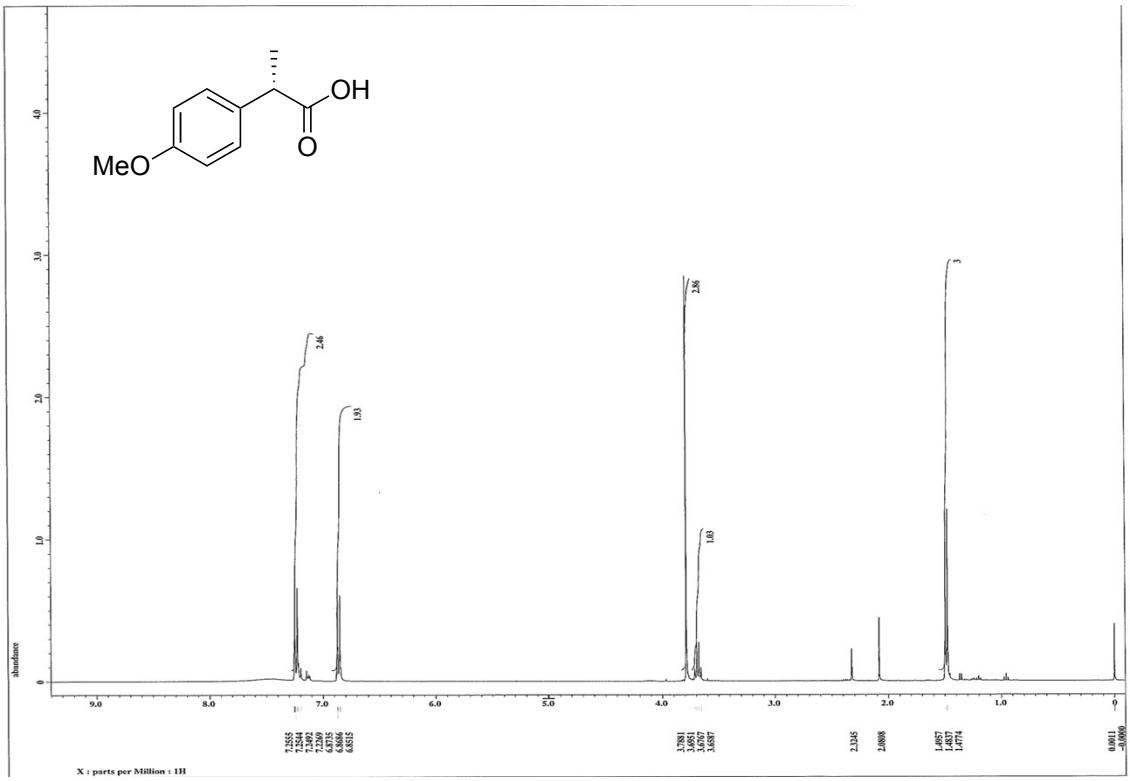


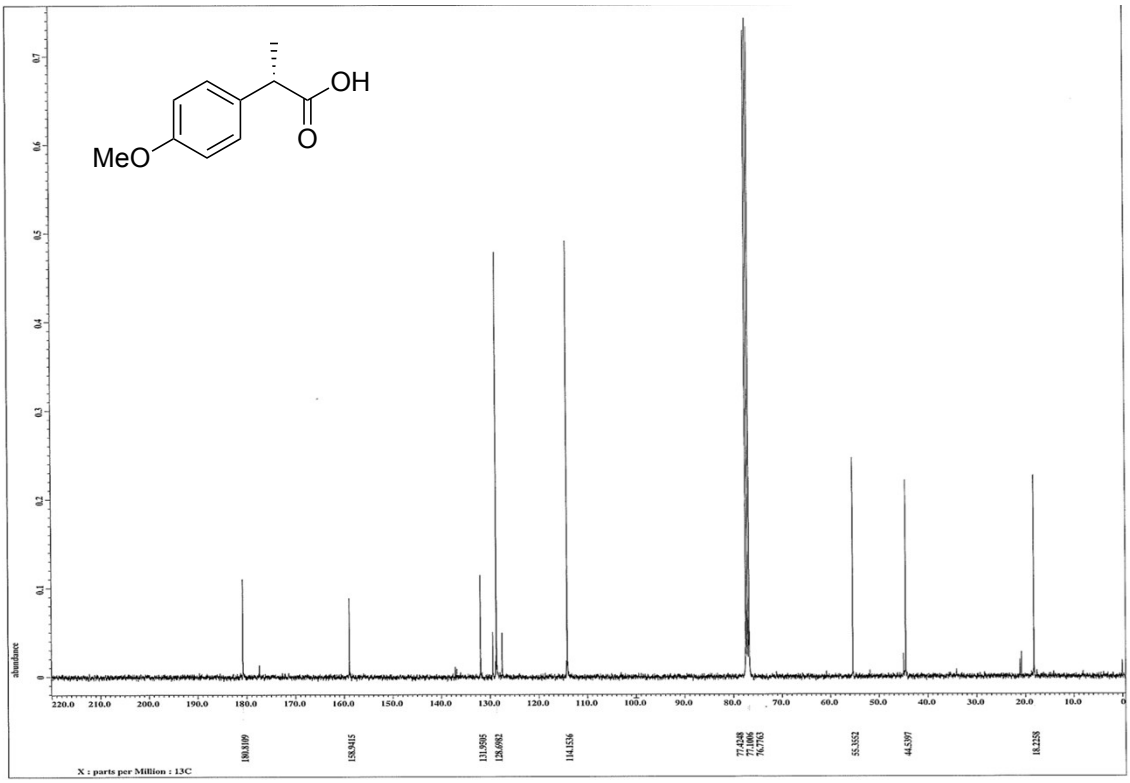
(*S*)-2-(4-methylphenyl)propionic acid



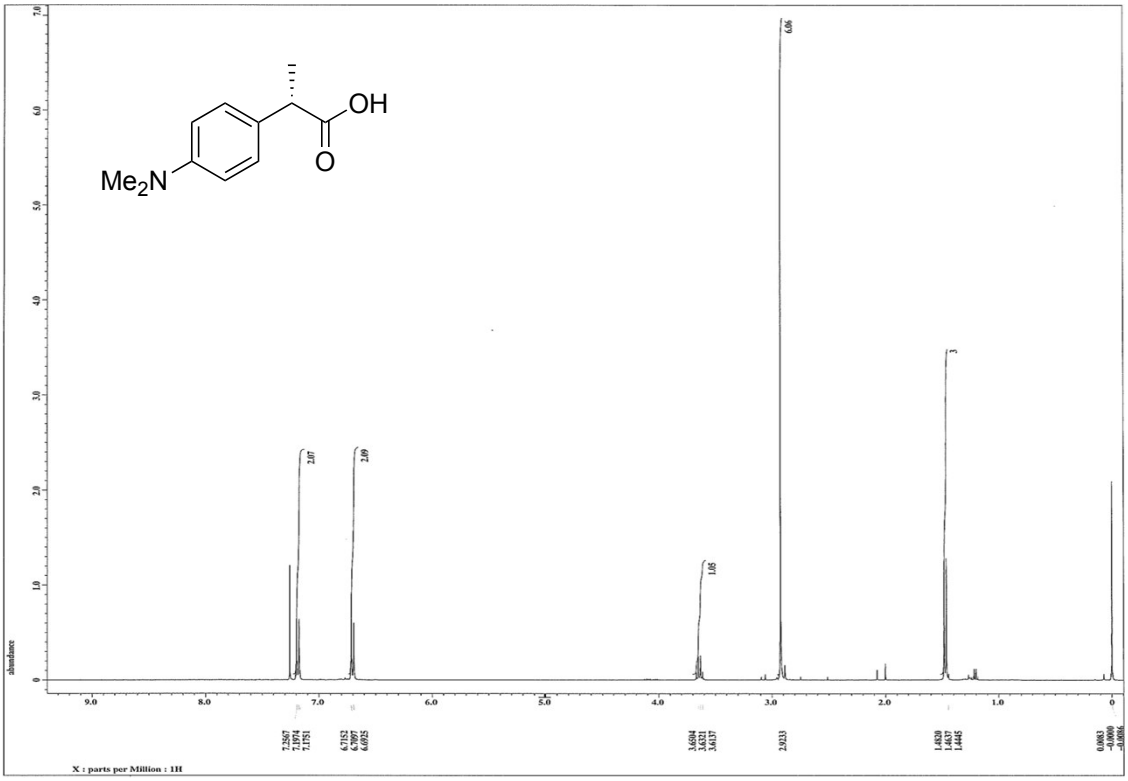


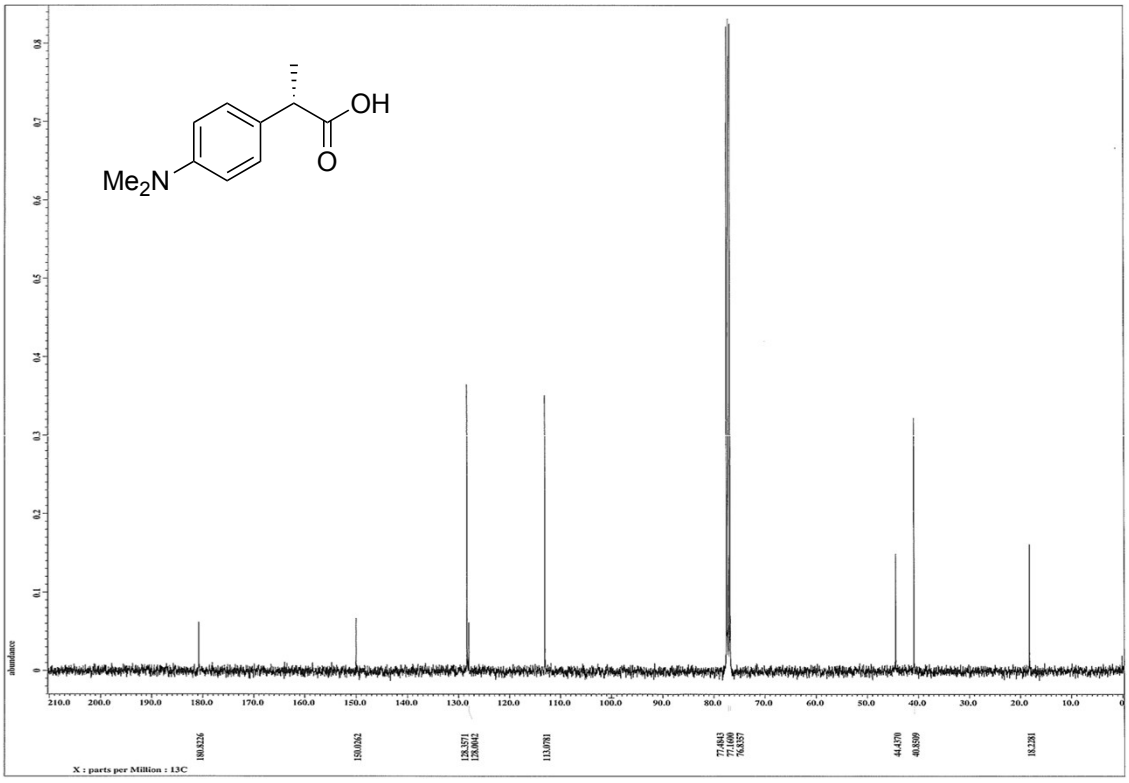
(*S*)-2-(4-methoxyphenyl)propionic acid



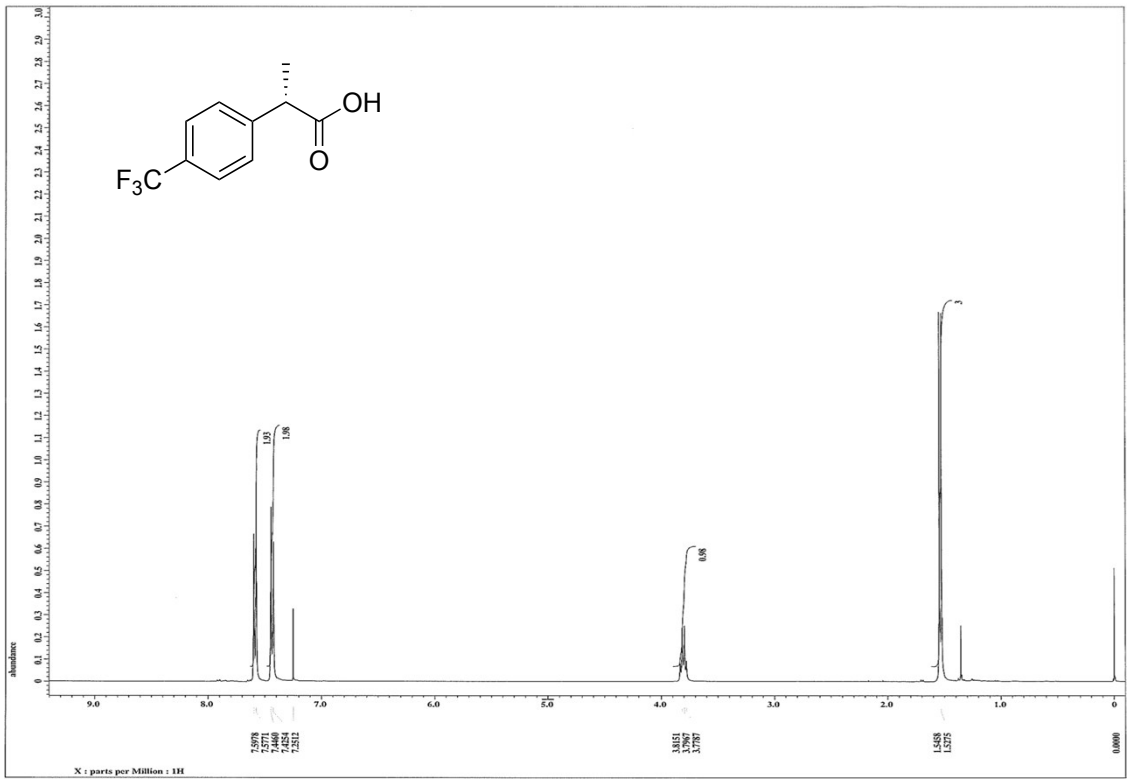


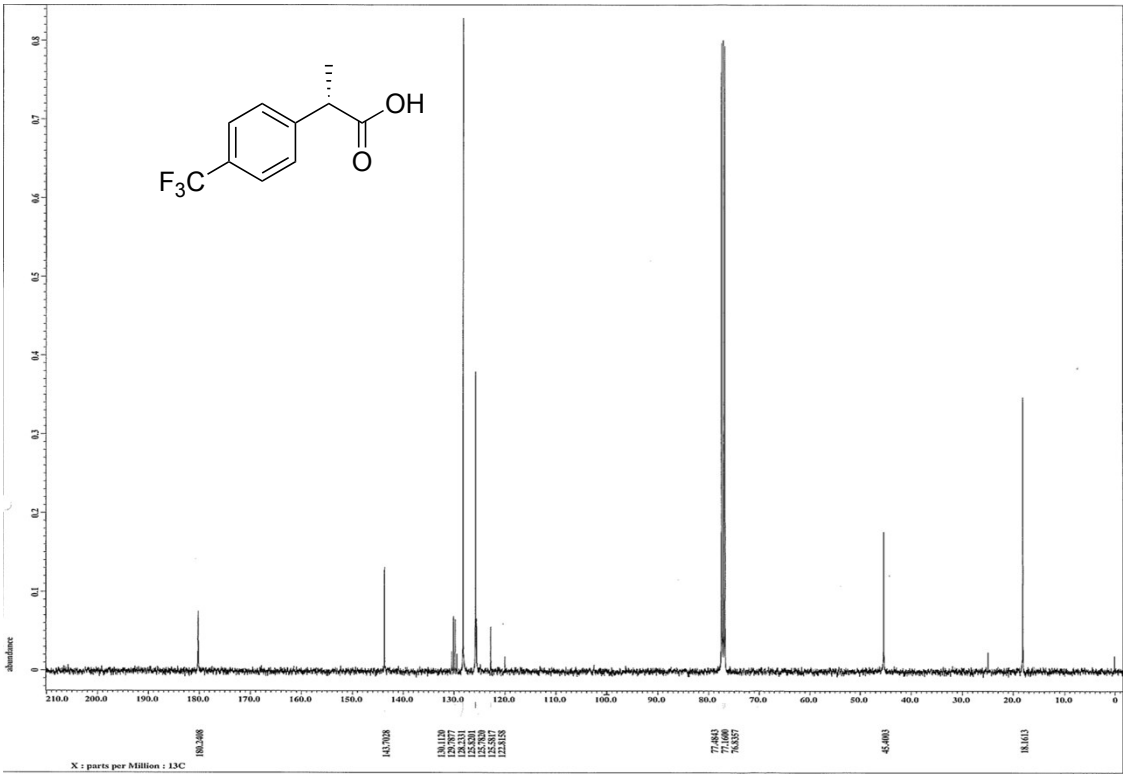
(*S*)-2-[4-(dimethylamino)phenyl]propionic acid



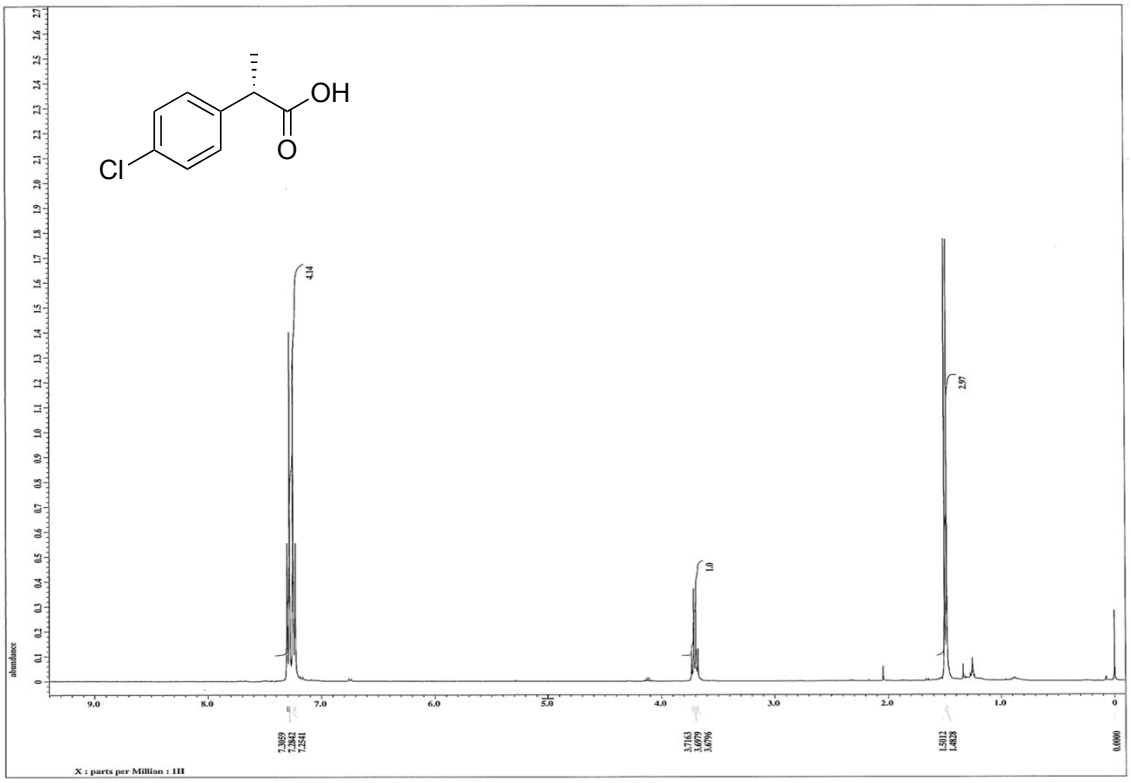


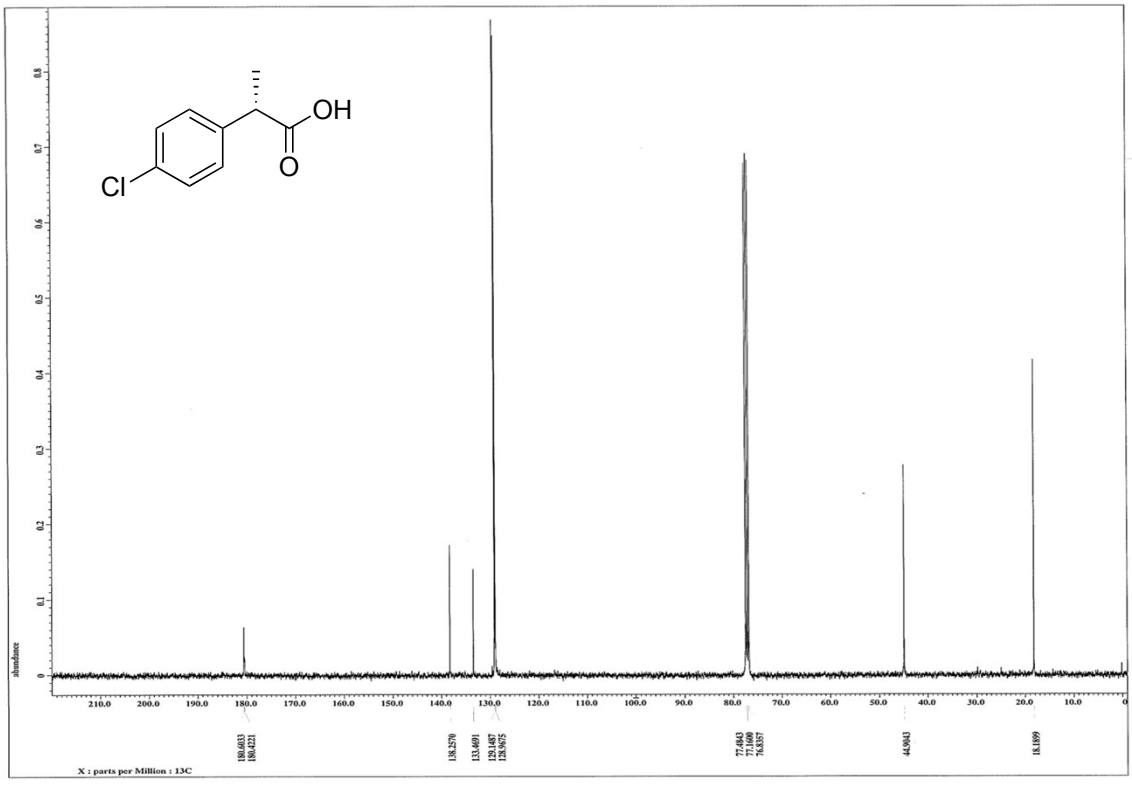
(*S*)-2-[4-(trifluoromethyl)phenyl]propionic acid



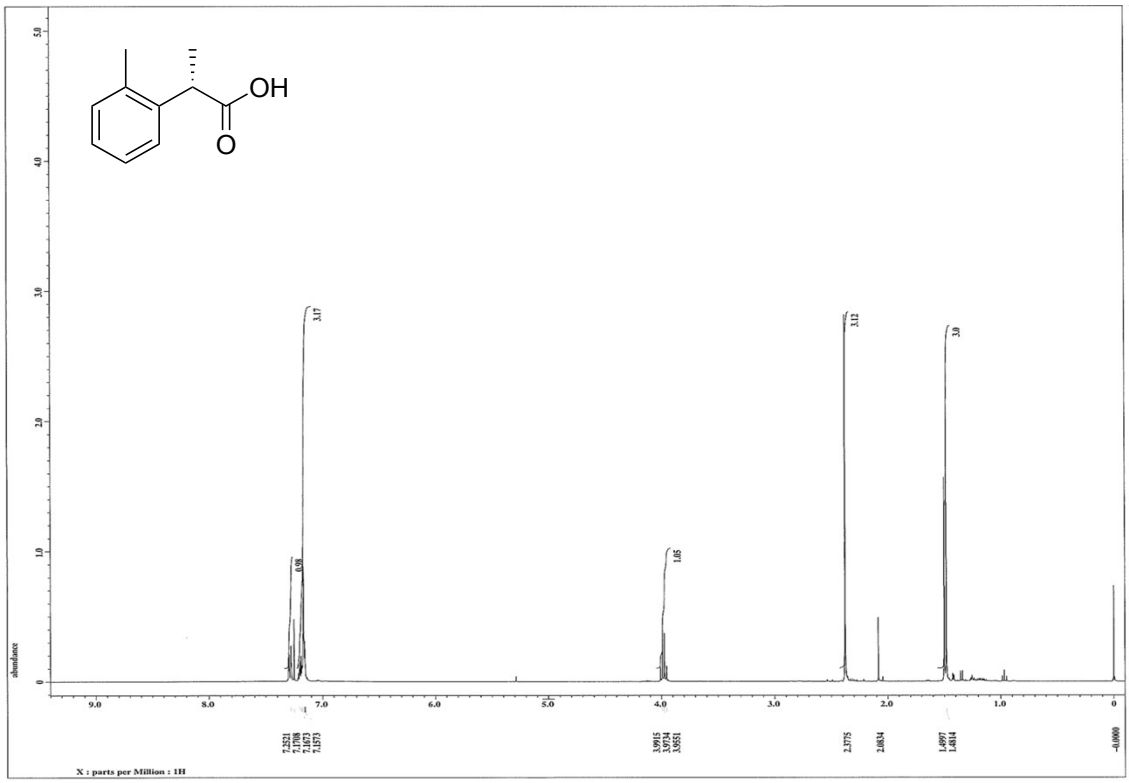


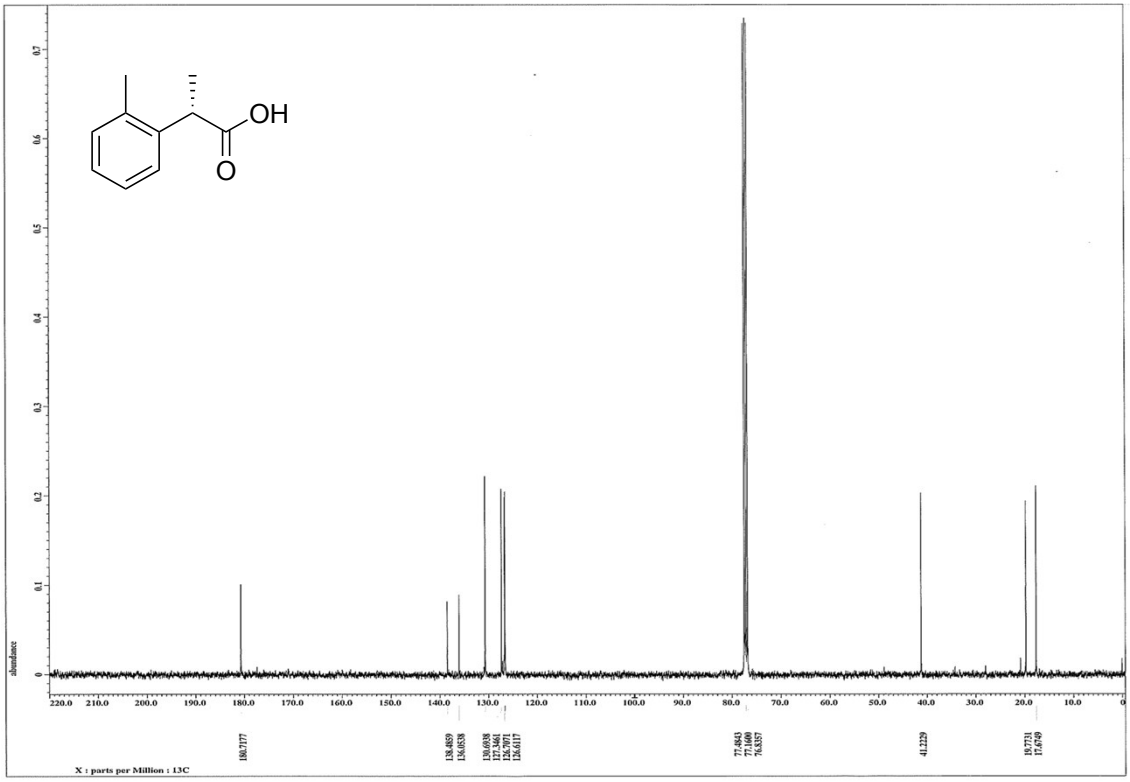
(*S*)-2-(4-chlorophenyl)propionic acid



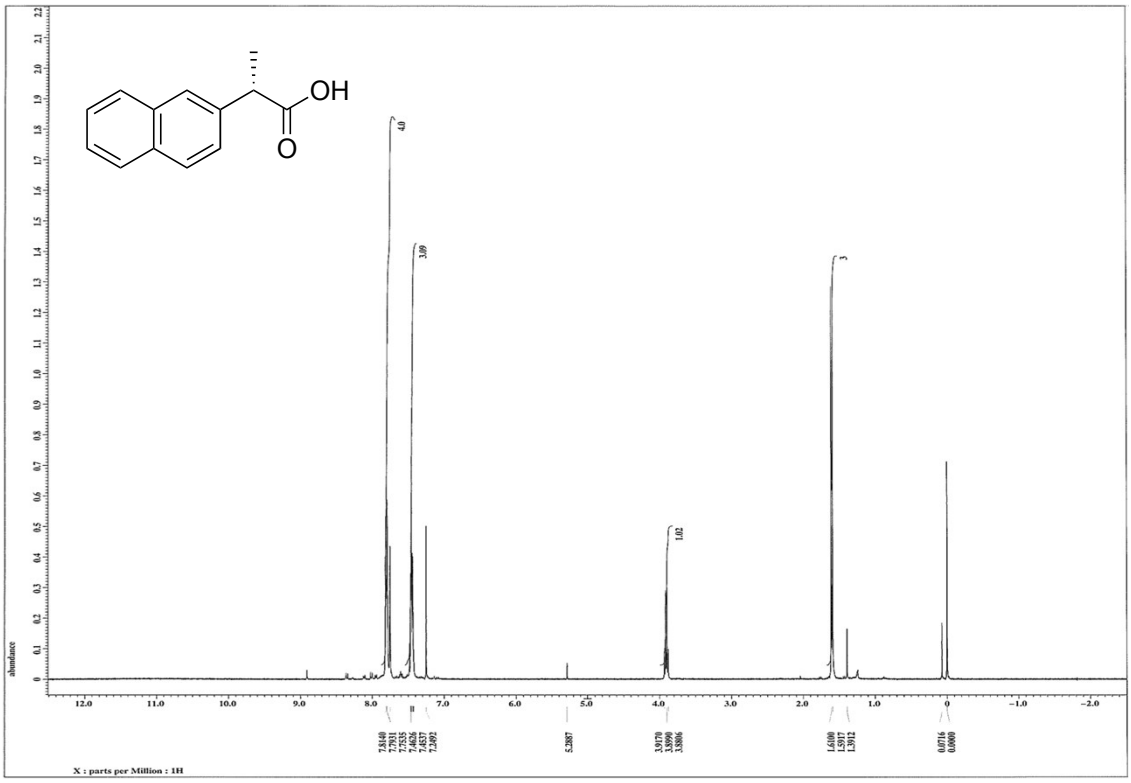


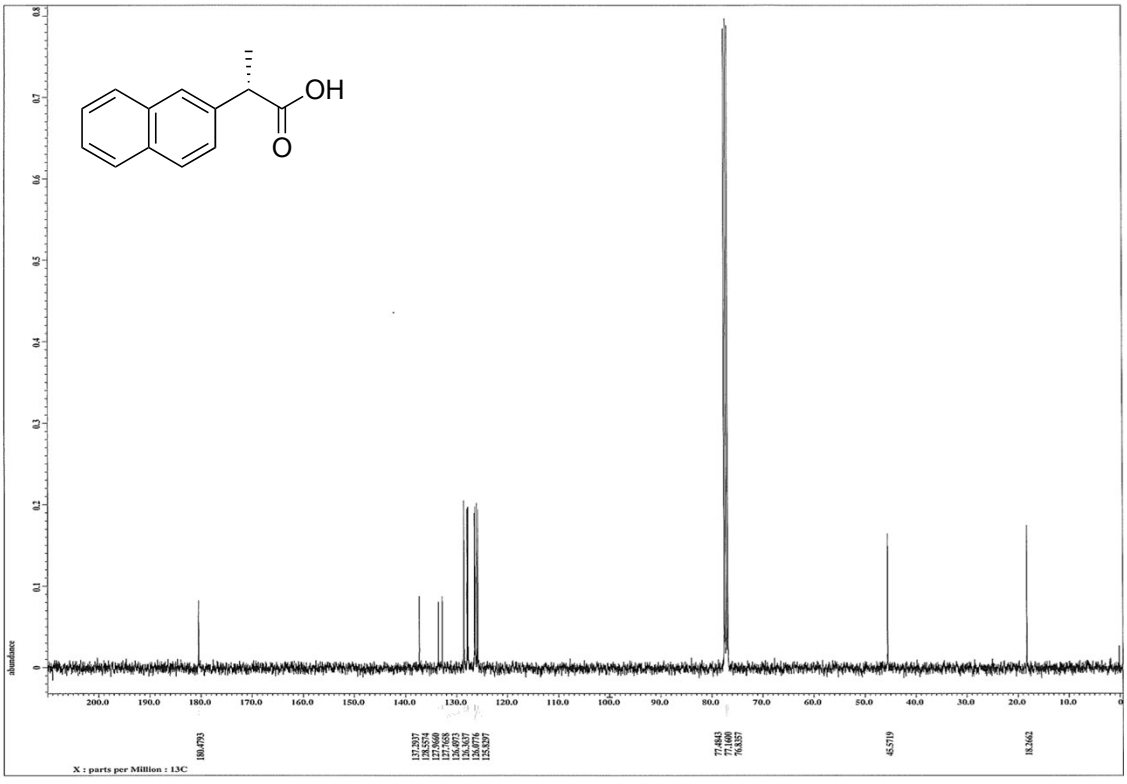
(*S*)-2-(2-methylphenyl)propionic acid



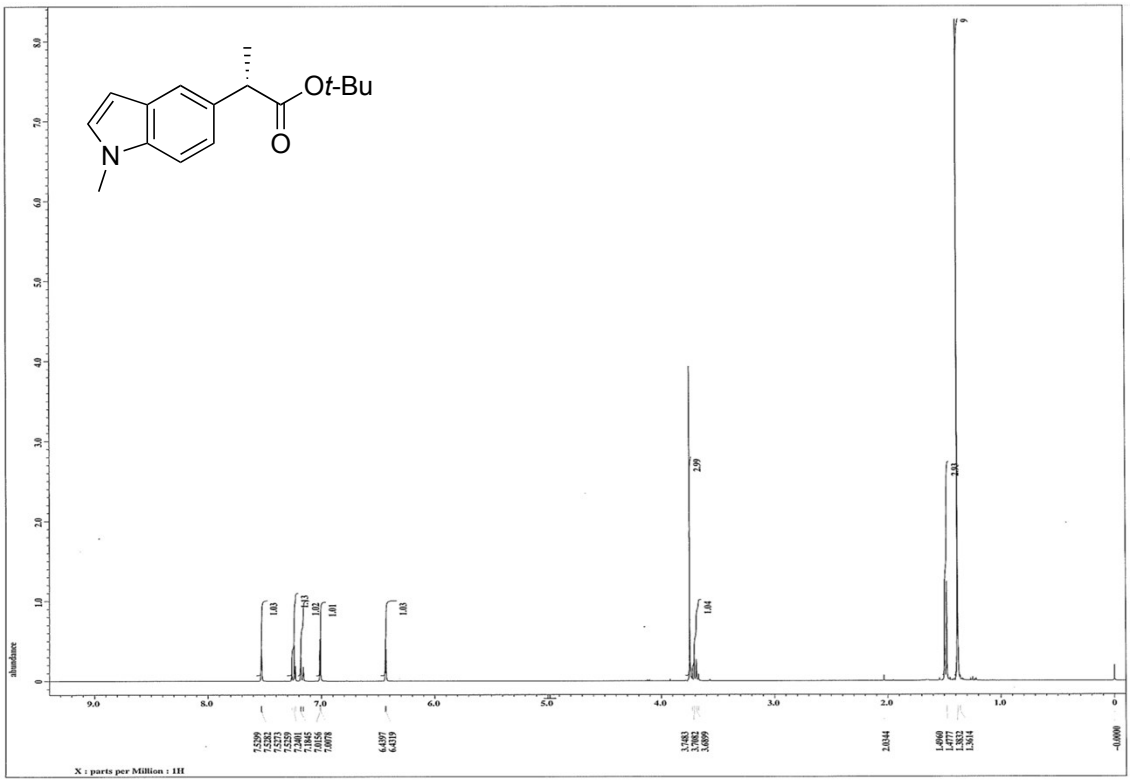


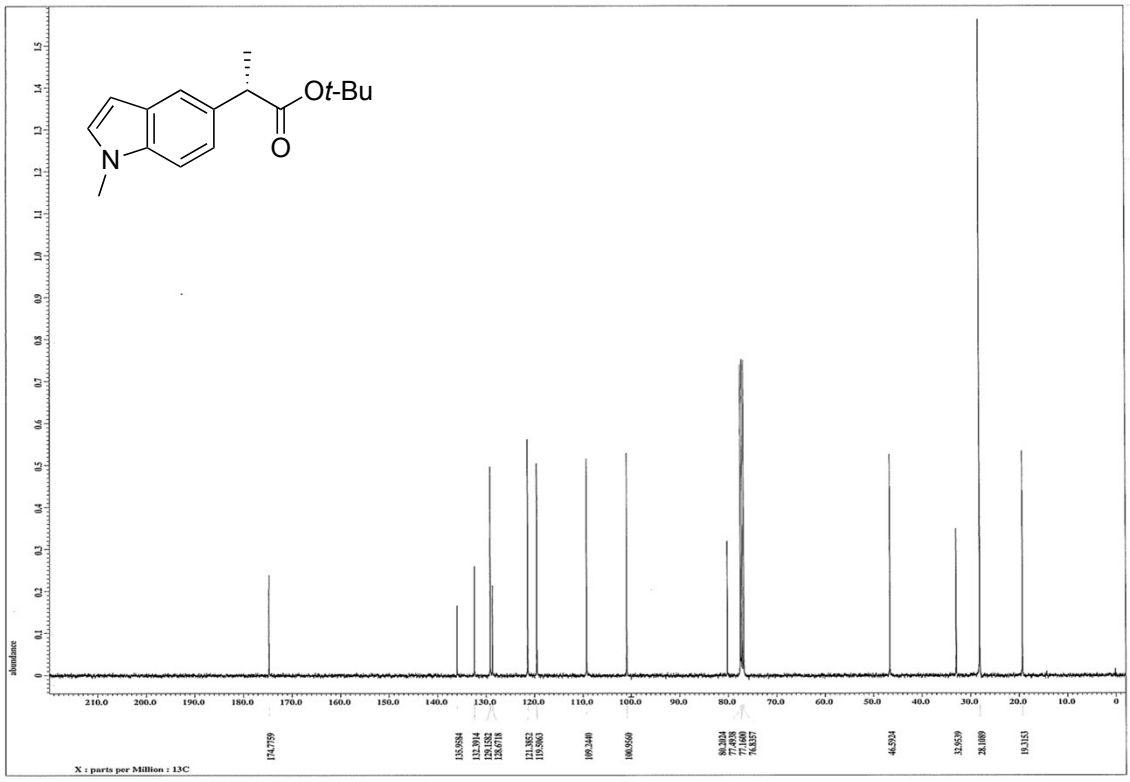
(*S*)-2-(naphthalen-2-yl)propionic acid



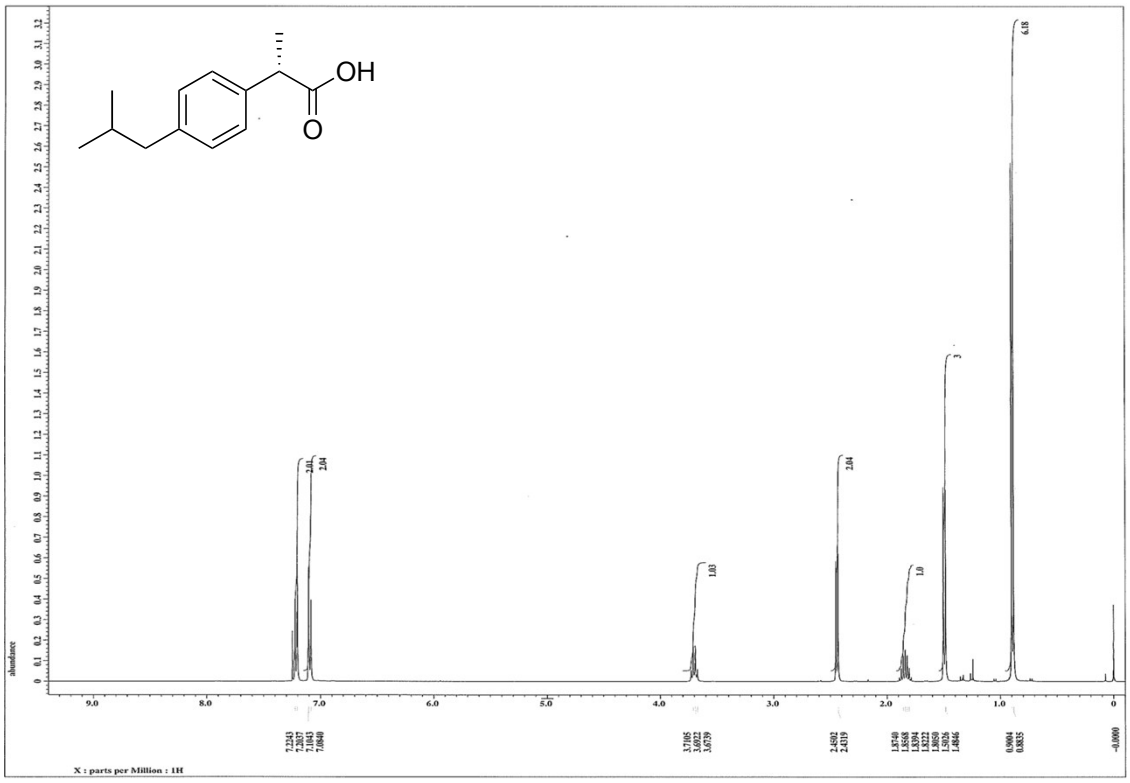


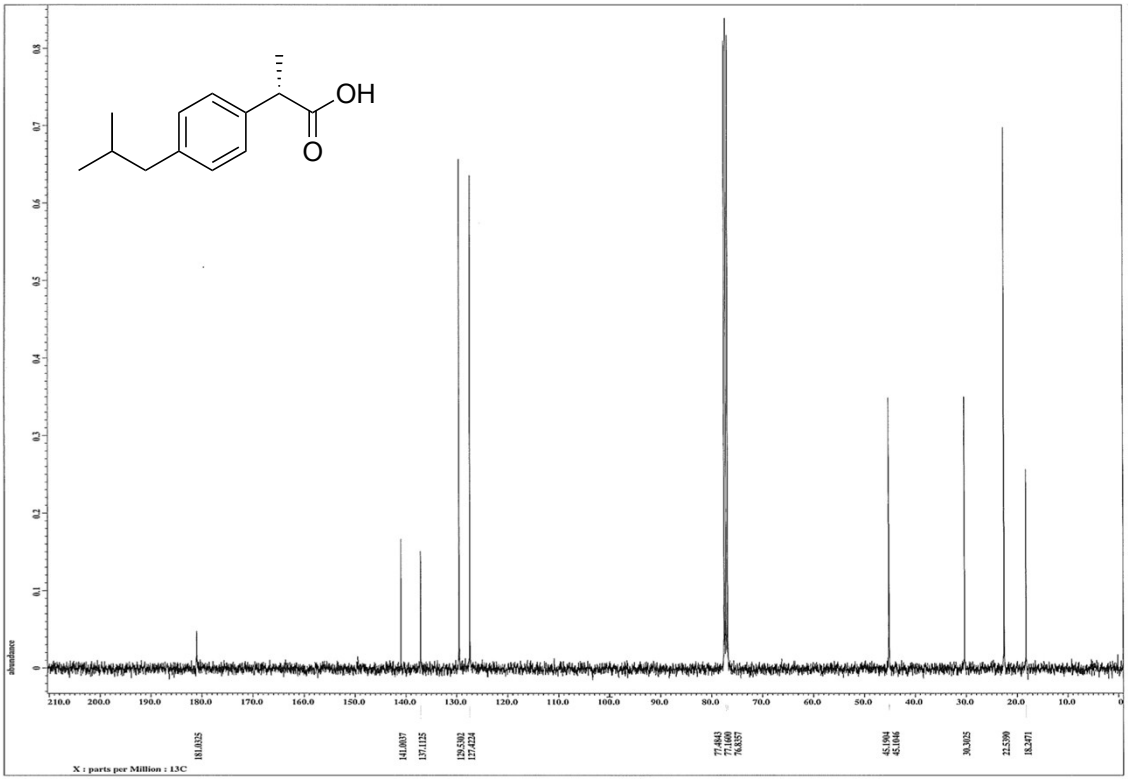
***Tert*-butyl (*S*)-2-(1-methyl-1H-indol-5-yl) propionate**



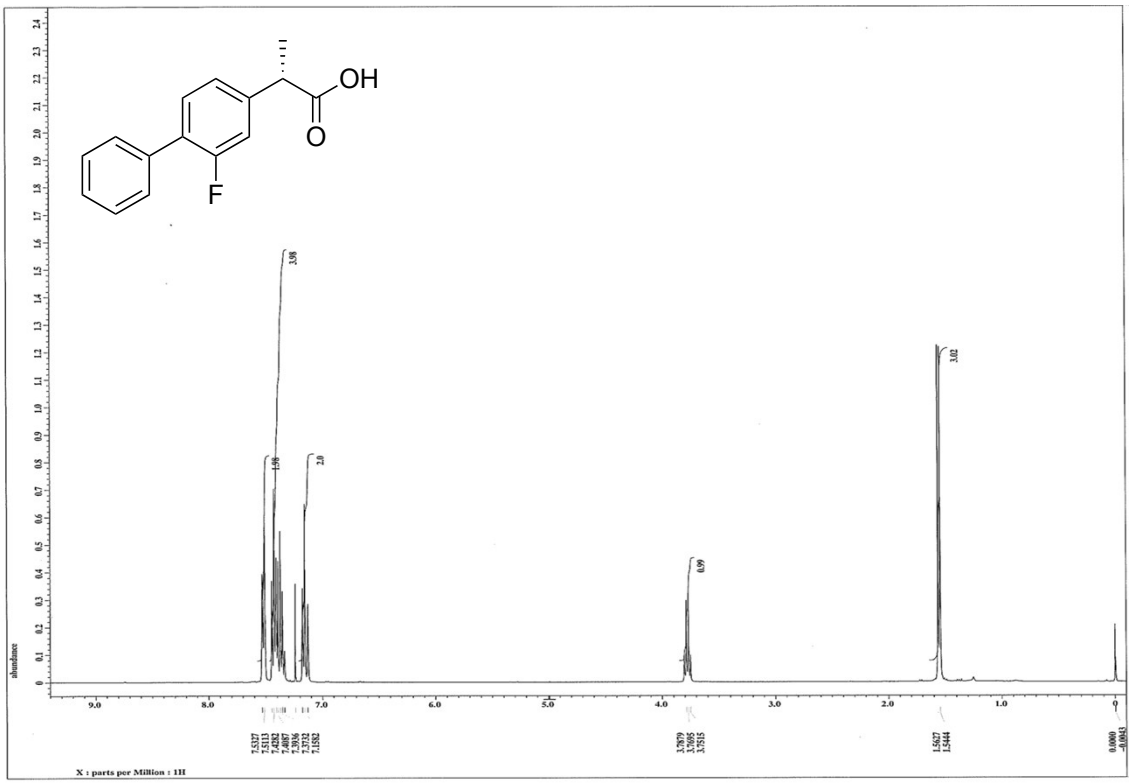


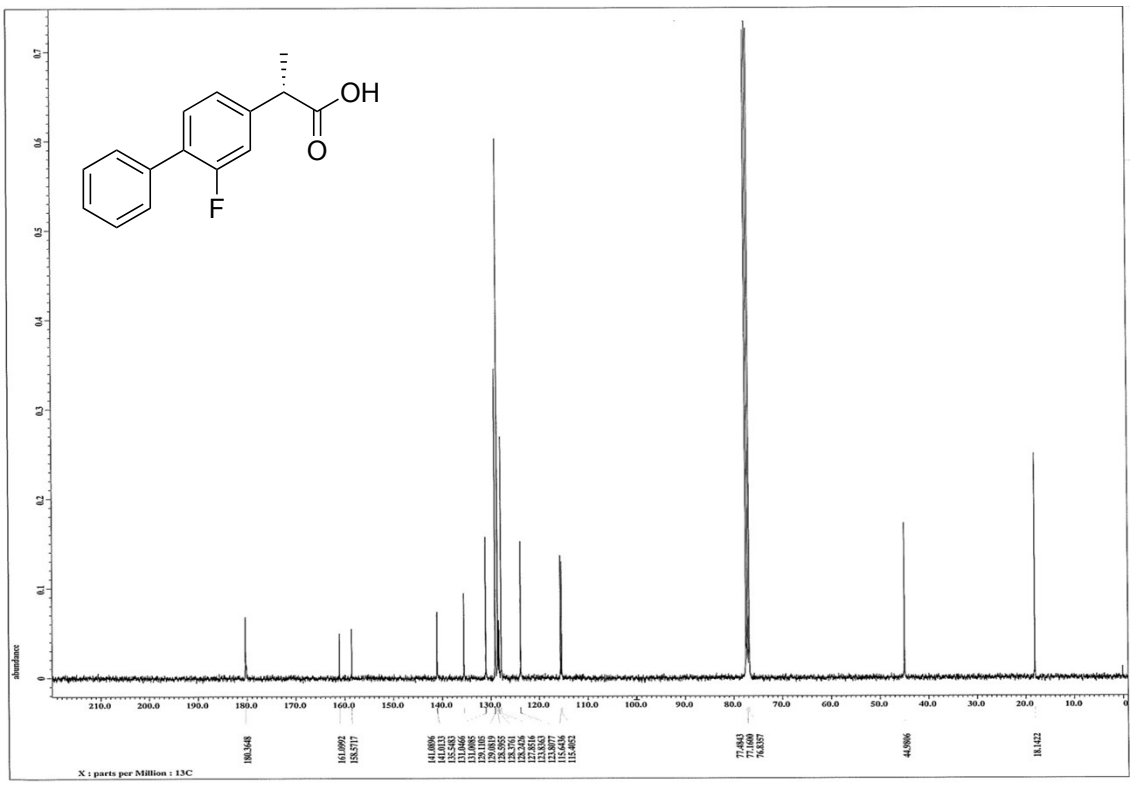
(*S*)-2-[(2-methylpropyl)phenyl]propionic acid [(*S*)-ibuprofen]



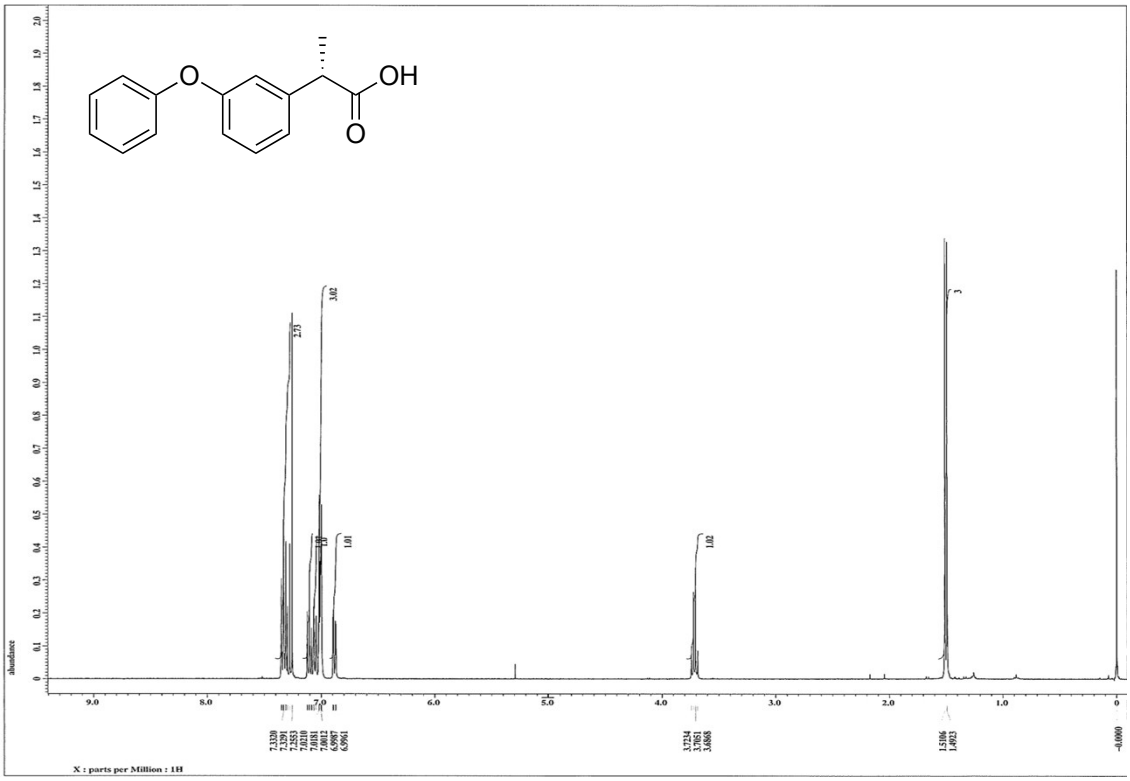


(*S*)-2-(2-fluoro-4-biphenylyl)propionic acid [(*S*)-flurbiprofen]

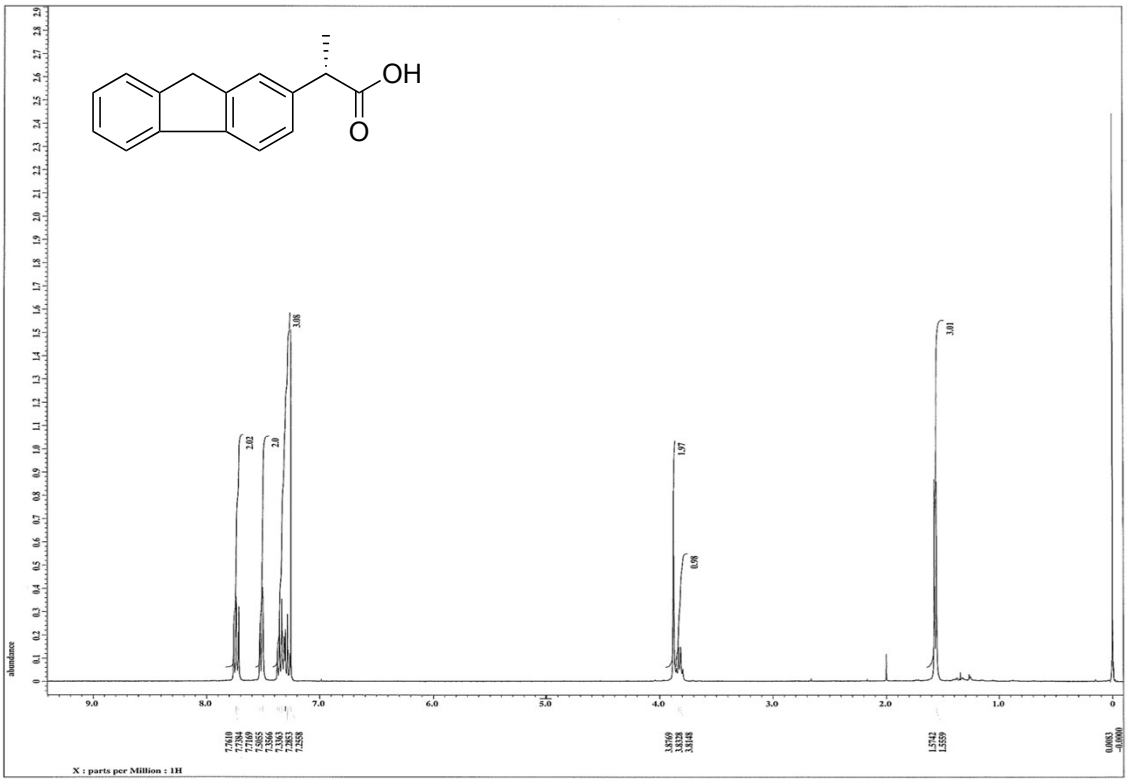




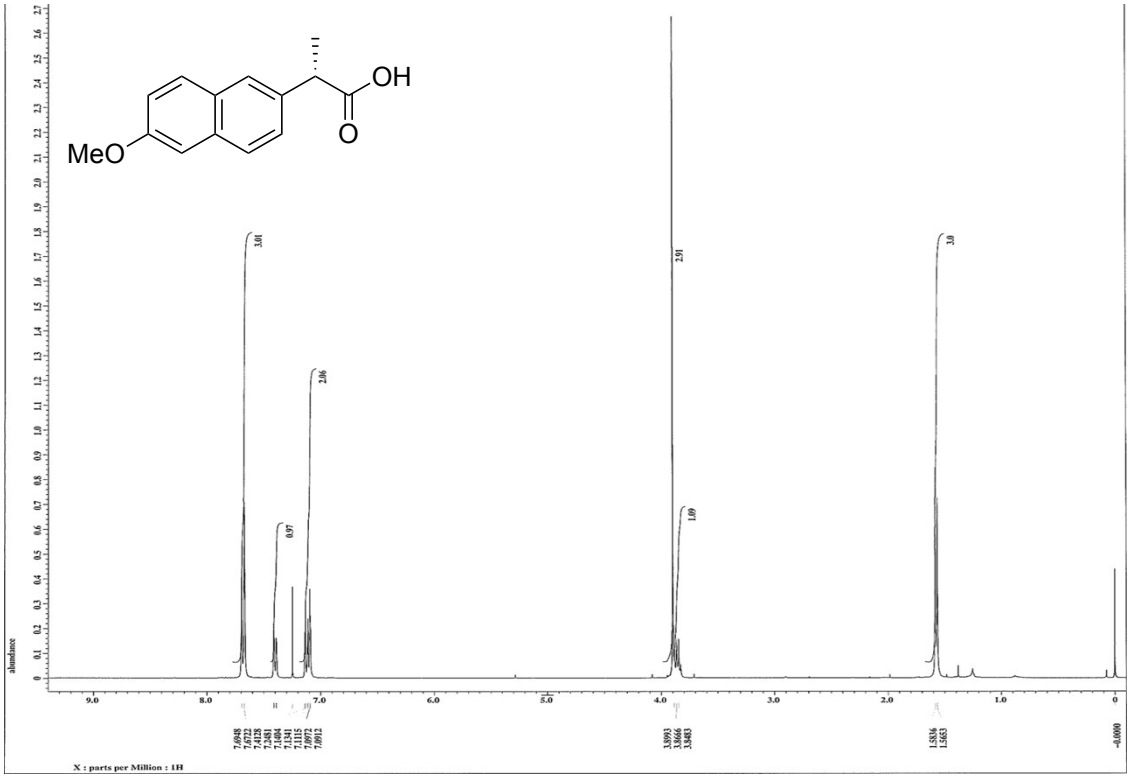
(*S*)-2-(3-phenoxyphenyl)propionic acid [(*S*)-phenoprofen]

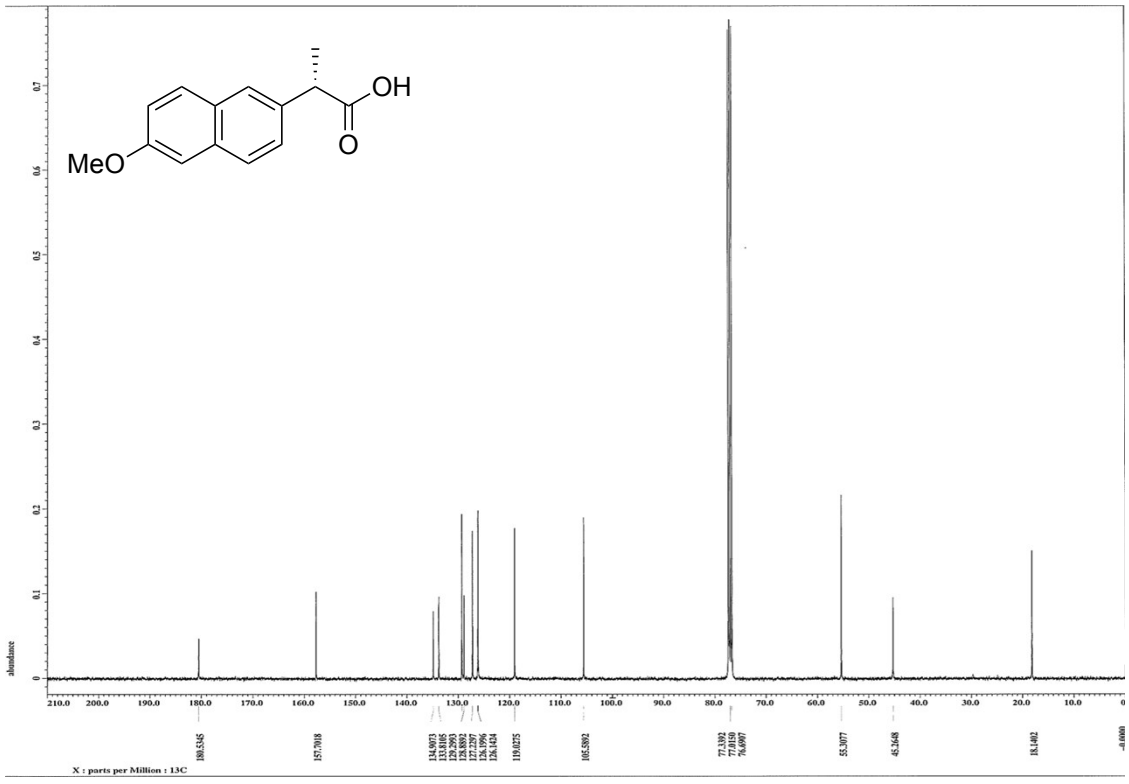


(*S*)-2-(2-fluorenyl)propionic acid [(*S*)-cicloprofen]



(*S*)-2-(6-methoxynaphth-2-yl)propionic acid [(*S*)-naproxen]





$FeCl_2$/(*R*,*R*)-QuinoxP*