

Supplementary Information for

Silyl Phosphorus and Nitrogen Donor Chelates for Homogeneous *ortho* Borylation Catalysis

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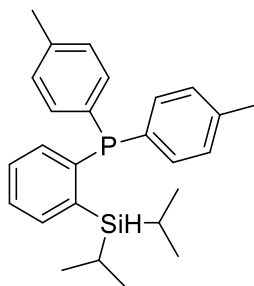
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General Methods. All reactions were conducted in a nitrogen filled glove-box. THF was distilled from sodium benzophenone solutions. All other solvents were used as received from Sigma-Aldrich (Sure/Seal™) and were stored in the glove-box. All other commercially available materials were used as received. ¹H and ¹³C NMR spectra were recorded on a Varian VXR-500 or Varian Unity-500-Plus spectrometer (499.74 and 125.67 MHz respectively) and referenced to residual solvent signals. ¹¹B spectra were recorded on Varian VXR-500 operating at 160.41 MHz respectively.

(2-(diisopropylsilyl)phenyl)di-*p*-tolylphosphane (SiPBz) (5)

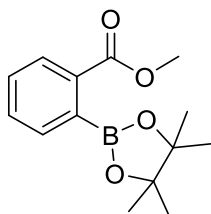


(2-bromophenyl)di-*p*-tolylphosphine was synthesized on 10 mmol scale reaction following a previously reported procedure in 95% (3.507 g) isolated yield (final work up was performed in air).¹ (2-bromophenyl)di-*p*-tolylphosphine (3.507 g, 9.5 mmol) was added to a Schlenk flask containing a magnetic stir bar and kept under gentle stream of nitrogen through the synthesis. Dry diethyl ether (50 mL) was added via syringe, and the flask was cooled to – 78 °C. *n*-BuLi (4.0 mL, 10 mmol, 2.5 M) was added dropwise via syringe and the mixture was allowed to warm to room temperature over 1 h. The reaction mixture was cooled back to – 78 °C, and diisopropylchlorosilane (1.70 mL, 10.0 mmol) was added dropwise over 15 min. The resulting mixture was warmed to reach room temperature and stirred for 4 hours. In a nitrogen-filled glove box, the mixture was then filtered and the precipitate washed with toluene. Volatiles were removed from the filtrate under reduced pressure and the product was isolated as a white solid in 88% (3.840 g) yield. ¹H NMR (500 MHz, C₆D₆) δ 1.01 (d, *J* = 7.4 Hz, 6H), 1.17 (d, *J* = 7.3 Hz, 6H), 1.47 (m, 2H), 1.98 (s, 6H), 4.57 (m, 1H), 6.90 (d, *J* = 7.8 Hz, 4H), 7.08-7.02 (m, 2H), 7.31 (d, *J* = 7.8 Hz, 4H), 7.36-7.33 (m, 1H), 7.62-7.58 (m, 1H); ¹³C NMR (125 MHz, C₆D₆) 12.1 (d, *J* = 6.7 Hz), 19.3 (d, *J* = 10.5 Hz), 21.2, 127.7, 129.1 (d, *J* = 6.7 Hz), 133.6 (d, *J* = 19.1 Hz), 134.0, 134.5 (d, *J* = 10.5 Hz), 136.7 (d, *J* = 15.3 Hz), 138.1, 142.9, 143.2, 144.3 (d, *J* = 10.4 Hz); ³¹P

NMR (202 MHz, C₆D₆) δ -9.82. (s). HRMS (ESI) m/z calcd for C₂₆H₃₄PSi [M + H]⁺ 405.2167, found 405.2159.

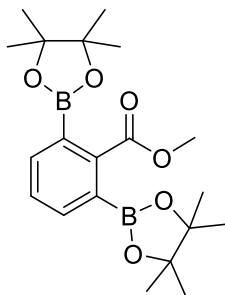
General procedure for *ortho*-directed borylation of methyl benzoates. In a nitrogen filled glovebox, [Ir(OMe)(cod)]₂ (8.3 mg, 0.0125 mmol) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. To the tube, 1 equiv. B₂Pin₂ (254.0 mg), SiPBz (0.0250 mmol, 10.0 mg), and 1.0 mmol methyl benzoate substrate were also added, and the reaction vessel was sealed and heated at 80 °C for 16h. The reaction mixture was allowed to return to room temperature and was exposed to air. The volatiles were then removed under reduced pressure and the product was purified by passing it through a short plug of SiO₂ eluting with MTBE. Additional purifications were performed as described below.

Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**6a**)



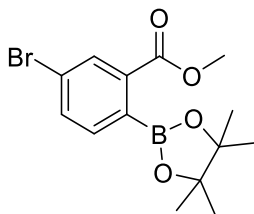
In a glove box, [Ir(OMe)(cod)]₂ (3.3 mg, 0.0050 mmol), SiPBz (0.0100 mmol, 4.0 mg), and anhydrous, degassed THF (1.0 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1 min at room temperature. Methylbenzoate (276.0 mg, 2.0 mmol) was added to the tube and lastly bis(pinacolato)diboron (254.0 mg, 1.0 mmol) was added as a solid, the reaction vessel was sealed and heated at 60 °C. Reaction progress was monitored by GC over 1 hour intervals. After 3 hours, (100% GC conversion based on B₂pin₂) the reaction mixture was allowed to return to room temperature and was exposed to air. The volatiles were then removed under reduced pressure and the product was purified by column chromatography; hexanes: EtOAc (12:1) to hexanes: EtOAc (9:1) as a pale yellow- oil (190.0 mg, 72% yield based on B₂Pin₂ (5% diborylated product, **6b**, was observed in crude); ¹H NMR (500 MHz, CDCl₃) δ 1.42 (s, 12H), 3.91 (s, 3H), 7.42 (dt, J = 2.5, 8.4 Hz, 1H), 7.53-7.48 (m, 2H), 7.94 (d, J = 7.8 Hz, 1H).²

Methyl 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6b)



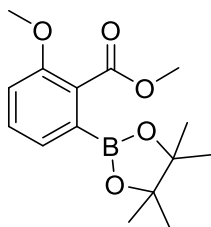
The reaction was performed using 1.0 mmol substrate (126 μ l), $[\text{Ir}(\text{OMe})(\text{cod})]_2$ $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (16.6 mg, 0.0250 mmol), 0.5 equiv B_2Pin_2 (254.0 mg), SiPBz (0.0500 mmol, 20.0 mg). The product was obtained by recrystallization from MeOH/ H_2O as a white solid (244.0 mg, 63% isolated yield); ^1H NMR (500 MHz, CDCl_3) δ 1.35 (s, 24H), 3.89 (s, 3H), 7.43 (d, $J = 7.3$ Hz, 1H), 7.70 (d, $J = 7.4$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 24.8, 52.0, 84.0, 128.9, 135.4, 141.7, 170.6; ^{11}B NMR (160 MHz, CDCl_3) δ 31.0 (br s); HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{31}\text{B}_2\text{O}_6$ $[\text{M} + \text{H}]^+$ 389.2307, found 389.2307.

Methyl 5-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6c)



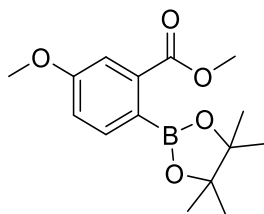
The reaction was performed using 0.5 mmol substrate (107.5 mg), $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (16.6 mg, 0.0250 mmol), 2 equiv B_2Pin_2 (254.0 mg), SiPBz (0.0500 mmol, 20.0 mg). Purified by column chromatography; hexanes: EtOAc (9:1). The product was obtained as yellow oil (139 mg, 60% yield (95% assay yield by ^1H NMR)); ^1H NMR (500 MHz, CDCl_3) δ 1.40 (s, 12H), 3.91 (s, 3H), 7.37 (d, $J = 7.8$ Hz, 1H), 7.64 (dd, $J = 2.0, 7.8$ Hz, 1H), 8.07 (s, $J = 1.5$ Hz, 1H).³

Methyl 2-methoxy-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6d)



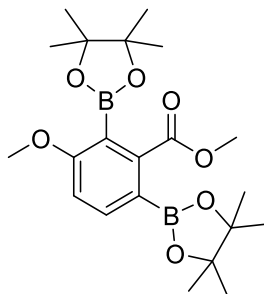
The reaction was performed using 1.0 mmol substrate (166.0 mg), $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (8.3 mg, 0.0125 mmol), 1.25 equiv B_2Pin_2 (317.0 mg), SiPBz (0.0250 mmol, 10.0 mg). The product was obtained by recrystallization from MeOH/ H_2O as brown crystals (240.0 mg, 82% yield); ^1H NMR (500 MHz, CDCl_3) δ 1.32 (s, 12H), 3.83 (s, 3H), 3.88 (s, 3H), 7.02 (d, $J = 8.3$ Hz, 1H), 7.32 (d, $J = 6.4$ Hz, 1H), 7.38 (t, $J = 7.3$ Hz, 1H).⁴

Methyl 5-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6e)



Purified by column chromatography; hexanes: EtOAc (9:1). The product was obtained as yellow oil (193.0 mg, 66% yield) Spectrum contains minor amounts of methyl 3-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate ^1H NMR (500 MHz, CDCl_3) δ 1.39 (s, 12H), 3.83 (s, 3H), 3.89 (s, 3H), 7.05 (dd, $J = 2.4, 8.3$ Hz, 1H), 7.45-7.42 (m, 2H).⁴

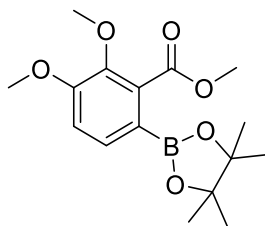
Methyl 3-methoxy-2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6e')



Purified by column chromatography; hexanes: EtOAc (9: 1). The product was obtained as yellow powder (20.0 mg, 5% yield); ^1H NMR (500 MHz, CDCl_3) δ 1.34 (s, 12H), 1.39 (s, 12H), 3.79 (s, 3H), 3.87 (s, 3H), 6.93 (d, $J = 8.3$ Hz, 1H), 7.50 (d, $J = 7.9$ Hz, 1H); ^{13}C NMR (125 MHz,

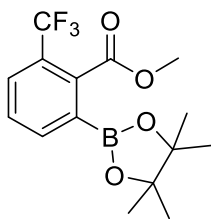
CDCl₃) δ 24.8, 24.9, 52.1, 55.6, 83.6, 83.8, 112.3, 135.4, 139.0, 163.6, 169.3; ¹¹B NMR (160 MHz, CDCl₃) δ 31.0 (br, s); HRMS (ESI) m/z calcd for C₂₁H₃₃B₂O₇ [M + H]⁺ 419.2420, found 419.2434.

Methyl 2,3-dimethoxy-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6f)



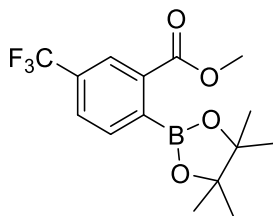
The compound was obtained via recrystallization with MeOH/H₂O as white crystals (227.0 mg, 70% yield); ¹H NMR (500 MHz, CDCl₃) δ 1.30 (s, 12H), 3.85 (s, 3H), 3.88 (s, 3H), 3.89 (s, 3H), 6.94 (d, *J* = 8.3 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 24.8, 52.2, 55.8, 61.6, 83.8, 112.6, 131.8, 134.6, 145.4, 155.0, 168.7; ¹¹B NMR (160 MHz, CDCl₃) δ 30.0 (br, s); HRMS (ESI) m/z calcd for C₁₆H₂₄BO₆ [M + H]⁺ 323.1669, found 323.1677. Structure determination was done by single crystal X-ray diffraction studies.

Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trifluoromethyl)benzoate (6g)



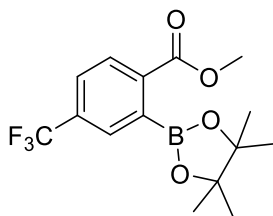
The compound was obtained via recrystallization with MeOH/H₂O, as black crystals (270.0 mg, 82% yield); ¹H NMR (500 MHz, CDCl₃) δ 1.34 (s, 12H), 3.92 (s, 3H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 7.9, Hz, 1H).⁴

Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trifluoromethyl)benzoate (6h)



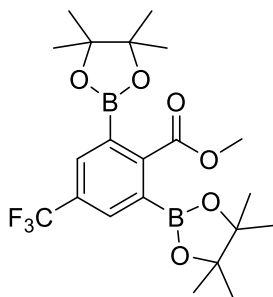
The compound was obtained via recrystallization with MeOH/H₂O, as brown powder (266.0 mg, 81% yield); ¹H NMR (500 MHz, CDCl₃) δ 1.42 (s, 12H), 3.95 (s, 3H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.76 (dd, *J* = 1.0, 7.8 Hz, 1H), 8.19 (s, 1H).⁴

Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trifluoromethyl)benzoate (6i)



The compound purified by column chromatography; hexanes: EtOAc (9:1), and obtained as yellow oil (163.0 mg, 49% yield); ¹H NMR (500 MHz, CDCl₃) δ 1.43 (s, 12H), 3.95 (s, 3H), 7.69 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.74 (s, 1H), 8.04 (d, *J* = 8.3 Hz, 1H).⁴

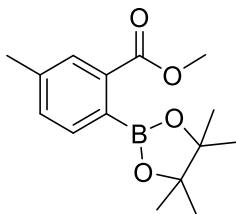
Methyl 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trifluoromethyl)benzoate (6i')



The compound purified by column chromatography; hexanes: EtOAc (9:1), and was obtained as brown crystals (77.0 mg, 17% yield); ¹H NMR (500 MHz, CDCl₃) δ 1.34 (s, 24H), 3.89 (s, 3H), 7.93 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 24.7, 52.3, 84.5, 124.9 (*J* = 272.7 Hz), 130.7 (*J* = 32.4 Hz), 132.6 (*J* = 3.8 Hz), 145.9, 169.8; ¹⁹F NMR (470 MHz, CDCl₃) δ -62.8 (s); ¹¹B NMR

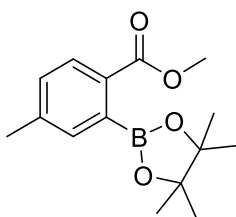
(160 MHz, CDCl₃) δ 31.0 (br, s); HRMS (ESI) m/z calcd for C₂₁H₃₀B₂F₃O₆ [M + H]⁺ 457.2188, found 457.2198.

Methyl 5-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6j)



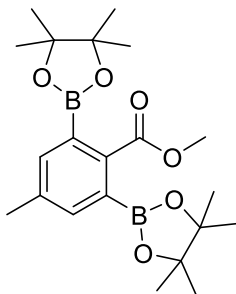
The compound purified by column chromatography; hexanes: EtOAc (9:1) and was obtained as yellow oil (227.0 mg, 82% yield); ¹H NMR (500 MHz, CDCl₃) δ 1.42 (s, 12H), 2.38 (s, 3H), 3.91 (s, 3H), 7.34 (d, J = 7.4 Hz, 1H), 7.41 (d, J = 7.3 Hz, 1H), 7.76 (s, 1H).³

Methyl 4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6k)



The product was obtained via column chromatography; hexanes: EtOAc (9:1), as white powder (135.0 mg, 49% yield); ¹H NMR (500 MHz, CDCl₃) δ 1.43 (s, 12H), 2.38 (s, 3H), 3.90 (s, 3H), 7.22 (dd, J = 1.0, 7.9 Hz, 1H), 7.29 (s, 1H), 7.85 (d, J = 7.8 Hz, 1H).³

Methyl 4-methyl-2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6k')



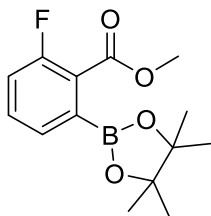
The product was obtained by column chromatography; hexanes: EtOAc (9:1), as brown crystals (54.0 mg, 13% yield); ¹H NMR (500 MHz, CDCl₃) δ 1.36 (s, 24H), 2.35 (s, 3H), 3.87 (s, 3H), 7.45 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 21.2, 24.8, 51.9, 83.9, 135.4, 137.7, 139.3, 170.3;

^{11}B NMR (160 MHz, CDCl_3) δ 30.0 (br, s); HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{33}\text{B}_2\text{O}_6$ $[\text{M} + \text{H}]^+$ 403.2471, found 403.2462.

Reaction was optimized for catalyst loading, temperature and time:

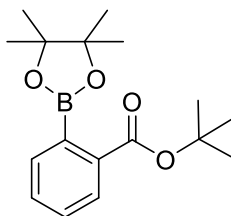
In a glove box, $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (3.3 mg, 0.0050 mmol), SiPBz (0.0100 mmol, 4.0 mg), and anhydrous, degassed THF (1.0 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1 min at room temperature. Methyl 4-methylbenzoate (150.2 mg, 1.0 mmol) was added to the tube and lastly bis(pinacolato)diboron (254.0 mg, 1.0 mmol) was added as solid, the reaction vessel was sealed and heated at 60 °C. Reaction progress was monitored by GC over 1 hour intervals. After 3 hours, (100% GC conversion based on B_2pin_2) the reaction mixture was allowed to return to room temperature and was exposed to air. The volatiles were then removed under reduced pressure and the product was purified by column chromatography; hexanes: EtOAc (9:1). **6K** and **6K'** were obtained in 55% (152.0 mg) and 10% (41.2 mg) isolated yield.

Methyl 2-fluoro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6I)



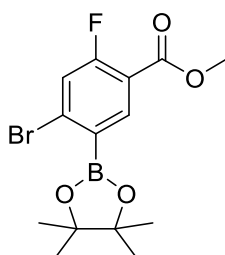
Product was purified by column chromatography; hexanes: EtOAc (9:1) as yellow oil (281.0 mg, 84% yield); ^1H NMR (500 MHz, CDCl_3) δ 1.36 (s, 12H), 3.92 (s, 3H), 7.16 (m, 1H), 7.46 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 24.9, 53.0, 84.6, 118.8 ($J = 21.0$ Hz), 124.9 ($J = 13.3$ Hz), 130.1 ($J = 3.8$ Hz), 133.2 ($J = 8.6$ Hz), 160.3 ($J = 251.8$ Hz), 166.1; ^{19}F NMR 470 MHz, CDCl_3) δ -115.0 (s); ^{11}B NMR (160 MHz, CDCl_3) δ 31.0 (br, s); HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{19}\text{BFO}_4$ $[\text{M} + \text{H}]^+$ 281.1363, found 281.1371.

tert-Butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6m)



In a glove box, $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (3.3 mg, 0.0050 mmol), SiPBz (0.0100 mmol, 4.0 mg), and anhydrous, degassed THF (1.0 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1 min at room temperature. tert-Butyl benzoate (178.2 mg, 1.0 mmol) was added to the tube and lastly bis(pinacolato)diboron (254.0 mg, 1.0 mmol) was added as solid, the reaction vessel was sealed and heated at 80 °C. Reaction progress was monitored by GC over 2 hour intervals. After 16 hours, (80% GC conversion based on B_2pin_2) the reaction mixture was allowed to return to room temperature and was exposed to air. The volatiles were then removed under reduced pressure and the product was purified by column chromatography; hexanes: Et_2O (4:1) as a white solid (192.0 mg, 63% yield). No diborylated product was observed in crude; ^1H NMR (500 MHz, CDCl_3) δ 1.42 (s, 12H), 1.58 (s, 9H), 7.34 (m, 1H), 7.43-7.49 (m, 2H), 7.82 (d, $J = 7.8$ Hz, 1H).⁴

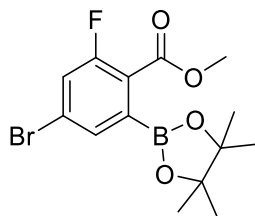
Methyl 4-bromo-2-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6n)



The reaction was performed using 1.0 mmol substrate (233.0 mg), $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (8.3 mg, 0.0125 mmol), 1 equiv B_2Pin_2 (254.0 mg), 4,4'-di-tert-butyl bipyridine (6.7 mg, 0.0250 mmol), 1 mL hexanes. Product was obtained via recrystallization with $\text{MeOH}/\text{H}_2\text{O}$ as a pale white powder (370 mg, 80% yield) Spectrum contains minor amounts of 4-bromo-2-fluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate; ^1H NMR (500 MHz, CDCl_3) δ 1.38 (s, 12H), 3.97 (s, 3H), 7.40 (d, $J = 10.3$ Hz, 1H), 8.23 (d, $J = 8.3$ Hz, 1H), Aromatic couplings are due to H-F couplings; ^{13}C NMR (125 MHz, CDCl_3) δ 24.8 ($J = 10.5$ Hz), 52.4, 84.6, 117.1 ($J = 8.6$ Hz), 121.8 ($J = 24.8$ Hz), 133.7 ($J = 9.5$ Hz), 140.2 ($J = 1.9$ Hz), 163.6 ($J = 268$), 164.2; ^{19}F NMR 470

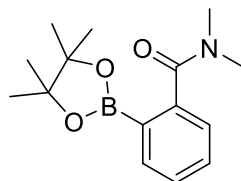
MHz, CDCl₃) δ -104.6 (s); ¹¹B NMR (160 MHz, CDCl₃) δ 30.0 (br, s); HRMS (ESI) *m/z* calcd for C₁₃H₁₄BBrFO₄ [M - CH₃ + H]⁺ 343.0155, found 343.0160.

Methyl 4-bromo-2-fluoro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6o)



Purified by column chromatography; hexanes: EtOAc (8.5: 1). Yellow Oil (255.0 mg, 70% yield); ¹H NMR (500 MHz, CDCl₃) δ 1.38 (s, *J*=0.9 Hz, 12H), 3.93 (s, *J* = 1.5 Hz, 3H), 7.35 (d, *J* = 9.3 Hz, 1H), 7.53 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 24.7, 52.8, 84.6, 121.4 (*J* = 24.8 Hz), 122.7 (*J* = 12.4 Hz), 126.1 (*J* = 8.6 Hz), 132.0 (*J* = 3.8 Hz), 160.9 (*J* = 261.3 Hz), 166.2; ¹⁹F NMR (470 MHz, CDCl₃) δ -109.7 (s); ¹¹B NMR (160 MHz, CDCl₃) δ 30.0 (br, s); HRMS (ESI) *m/z* calcd for C₁₃H₁₄BBrFO₄ [M - CH₃ + H]⁺ 343.0155, found 343.0150.

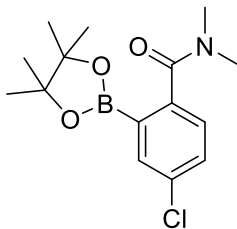
***N,N*-Dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (8a)**



In a glove box, [Ir(OMe)(cod)]₂ (8.3 mg, 0.0125 mmol), SiPBz (0.0250 mmol, 10.0 mg), bis(pinacolato)diboron (254.0 mg, 1 mmol) and anhydrous, degassed THF (4.5 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1 min at room temperature. *N,N*-Dimethyl benzamide (149.0 mg, 1.0 mmol) was added to the tube, the reaction vessel was sealed and heated at 80 °C. Reaction progress was monitored by GC over 4 hour intervals. After 16 hours, (86% GC conversion) the reaction mixture was allowed to return to room temperature and was exposed to air. The volatiles were then removed under reduced pressure and the product was purified by passing it through a short plug of SiO₂ eluting (hexane/EtOAc = 1/1). The product was isolated by precipitation from hexane. White solid (206.2 mg) in 75% isolated yield. ¹H NMR (500 MHz, CDCl₃) δ 1.31 (s, 12H), 2.97 (br s, 6H),

7.30 (dd, $J = 7.5, 0.6$ Hz, 1H), 7.37 (dt, $J = 7.5, 1.5$ Hz, 1H), 7.45 (dt, $J = 7.5, 1.5$ Hz, 1H), 7.80 (dd, $J = 7.5, 0.6$ Hz, 1H).⁴

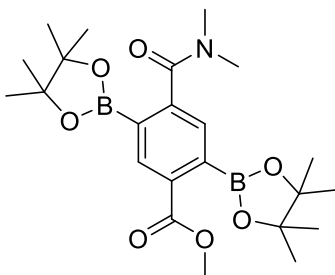
4-chloro-*N,N*-dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (8b)



In a glove box, [Ir(OMe)(cod)]₂ (8.3 mg, 0.0125 mmol), SiPBz (0.0250 mmol, 10.0 mg), bis(pinacolato)diboron (254.0 mg, 1.0 mmol) and anhydrous, degassed THF (4.5 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1 min at room temperature. 4-Chloro *N,N*-dimethyl benzamide (183.6 mg, 1.0 mmol) was added to the tube, the reaction vessel was sealed and heated at 80 °C. Reaction progress was monitored by GC over 4 hour intervals. After 16 hours, 95% conversion was observed. The reaction was stopped and mixture was allowed to return to room temperature and was exposed to air. The volatiles were then removed under reduced pressure and the product was purified by passing it through a short plug of SiO₂ eluting with (hexane/EtOAc = 1/1). The product was isolated by precipitation from hexane. White solid (263.1 mg) in 85% isolated yield was obtained.

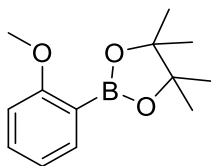
¹H NMR (500 MHz, CDCl₃) δ ppm 1.31 (s, 12 H) 3.00 (br. s., 6 H) 7.26 (d, $J=8.3$, 1 H) 7.40 (d, $J=8.3$ Hz, 1 H) 7.76 (s, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ ppm 24.9, 83.6, 127.1, 130.6, 134.5, 135.1, 139.7, 171.5; ¹¹B NMR (160 MHz, CDCl₃) δ ppm 27.3 (s); HRMS (ESI) m/z calcd for C₁₅H₂₂BClNO₃ [M + H]⁺ 310.1384, found 310.1386.

Methyl 4-(dimethylcarbamoyl)-2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (8c)



In a glove box, $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (8.3 mg, 0.0125 mmol), SiPBz (0.0250 mmol, 10.0 mg), bis(pinacolato)diboron (508.0 mg, 2 mmol) and anhydrous, degassed THF (4.5 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1 min at room temperature. Methyl 4-(dimethylcarbamoyl)benzoate (207.0 mg, 1.0 mmol) was added to the tube, the reaction vessel was sealed and heated at 100 °C. Reaction progress was monitored by GC over 4 hour's intervals. After 16 hours the reaction mixture was allowed to return to room temperature and was exposed to air. The volatiles were then removed under reduced pressure and the product was purified by passing it through a short plug of SiO_2 eluting with (hexane/EtOAc = 1/1). The product was isolated by precipitation from hexane. White solid (436.0 mg) in 95% isolated yield. ^1H NMR (500 MHz, CDCl_3) δ ppm 1.31 (s, 12 H) 1.41 (s, 12 H) 2.75 (br. s., 3 H) 3.09 (br. s., 3 H) 3.93 (s, 3 H) 7.42 (s, 1 H) 8.37 (s, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ ppm 24.8, 24.9, 52.4, 84.0, 84.2, 129.5, 132.8, 135.3, 146.0, 168.0, 171.7; ^{11}B NMR (160 MHz, CDCl_3) δ ppm 30.2 (s); HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{36}\text{B}_2\text{NO}_7$ $[\text{M} + \text{H}]^+$ 460.2686, found 460.2684.

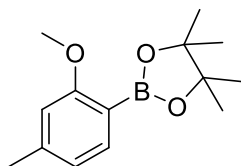
2-(2-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8d)



In a glove box, $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (8.3 mg, 0.0125 mmol), SiPBz (0.0250 mmol, 10.0 mg), bis(pinacolato)diboron (254.0 mg, 1 mmol) and anhydrous, degassed THF (3 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1 min at room temperature. Anisole (108.0 mg, 1.0 mmol) was added to the tube; the reaction vessel was sealed and heated at 100 °C. Reaction progress was monitored by GC over 4 hour intervals. After 12 hours all of bis(pinacolato)diboron was consumed and no further conversion was observed, the reaction mixture was allowed to return to room temperature and was exposed to air. The volatiles were then removed under reduced pressure and the product was characterized as mixture of 6:1:2 (ortho: meta+para: diborylation) with 55% total GC conversion, (for better

clarity of isomeric ratio on $^1\text{H NMR}$ of crude material, some starting material was removed under vacuum).⁵

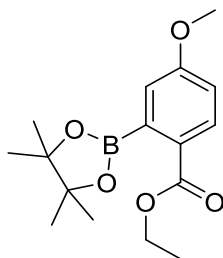
2-(2-methoxy-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8e)



In a glove box, $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (8.3 mg, 0.0125 mmol), SiPBz (0.0250 mmol, 10.0 mg), bis(pinacolato)diboron (254.0 mg, 1 mmol) and anhydrous degassed THF (3 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1 min at room temperature. 3-Methyl anisole (122.0 mg, 1.0 mmol) was added to the tube; the reaction vessel was sealed and heated at 100 °C. Reaction progress was monitored by GC over 4 hour intervals. After 12 hours, all bis(pinacolato)diboron was consumed and 46% GC conversion based on substrate and no further was observed (crude mixture contained 7% of the meta isomer). The reaction mixture was allowed to return to room temperature and was exposed to air. The volatiles were then removed under reduced pressure and product was purified by Kugelrohr distillation. The product was isolated as white solid (86.0 mg) in 35 % isolated yield.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ ppm 1.32 (s, 12 H) 2.33 (s, 3 H) 3.8 (s, 3 H) 6.65 (s, 1 H) 6.74 (d, $J=7.4$ Hz, 1 H) 7.55 (d, $J=7.5$ Hz, 1 H).⁶

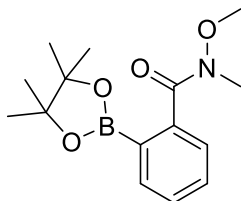
Ethyl 4-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (8f)



In a glove box, $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (8.3 mg, 0.0125 mmol), SiPBz (0.0250 mmol, 10.0 mg), bis(pinacolato)diboron (254.0 mg, 1.0 mmol) and anhydrous, degassed *n*-hexane (1 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1

min at room temperature. Ethyl 4-methoxybenzoate (180.0 mg, 1.0 mmol) was added to the tube, the reaction vessel was sealed and heated at 80 °C, and reaction progress was monitored by GC. After 12 hours 90% conversion was observed and reaction mixture was allowed to return to room temperature and was exposed to air. Purification with column chromatography (gradient from hexane/EtOAc = 9/1 to hexane/EtOAc = 4/1) resulted in ethyl 4-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (226.0 mg) as oil with 77% isolated yield. (5% conversion to ethyl 4-methoxy-2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate was observed by ¹H NMR of the crude reaction mixture and by GC). ¹H NMR (500 MHz, CDCl₃) δ ppm 1.37 (t, *J*=7.1 Hz, 3H) 1.43 (s, 12 H) 3.86 (s, 3 H) 4.36 (q, *J*=7.3 Hz, 2 H) 6.88 (dd, *J*=8.8, 2.5 Hz, 1 H) 6.95 (d, *J*=2.5 Hz, 1 H) 7.91 (d, *J*=8.8 Hz, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ ppm 14.4, 24.9, 55.4, 60.9, 84.0, 114.1, 116.8, 126.0, 130.7, 162.4, 167.7; ¹¹B NMR (160 MHz, CDCl₃) δ ppm 31.1 (s); HRMS (ESI) *m/z* calcd for C₁₆H₂₄BO₅ [M + H]⁺ 307.1720, found 307.1726.

N-Methoxy-N-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (8g)

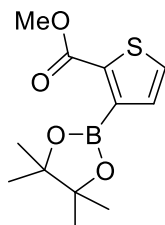


In a glove box, [Ir(OMe)(cod)]₂ (8.3 mg, 0.0125 mmol), SiPBz (0.0250 mmol, 10.0 mg), bis(pinacolato)diboron (254.0 mg, 1.0 mmol) and anhydrous, degassed THF (4.5 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1 min at room temperature. *N*-Methoxy-*N*-methylbenzamide (165.0 mg, 1.0 mmol) was added to the tube; the reaction vessel was sealed and heated at 80 °C. Reaction progress was monitored by GC over 4 hour intervals. After 12 hours the reaction mixture was allowed to return to room temperature and was exposed to air. The volatiles were then removed under reduced pressure and the product was purified by silica column chromatography (gradient from CHCl₃ to 2% MeOH: 98% CHCl₃). Colorless viscose oil (244.4 mg) was obtained in 84% isolated yield.

¹H NMR (500 MHz, CDCl₃) δ ppm 1.32 (s, 12 H) 3.34 (br. s., 3 H) 3.50 (br. s., 3 H) 7.38 - 7.46 (m, 2 H) 7.49 - 7.55 (m, 1 H) 7.72 - 7.77 (m, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ ppm 25.0, 34.03, 61.0, 83.32, 126.5, 128.0, 128.1, 128.7, 129.5, 130.03, 130.6, 132.2, 133.6 (br);

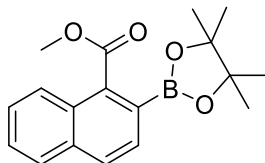
(Presumably, due to interaction of NOME group with pinacol group some peaks in ^1H NMR and ^{13}C NMR are broad). ^{11}B NMR (160 MHz, CDCl_3) δ ppm 27.8 (br,s) ; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{23}\text{BNO}_4$ $[\text{M} + \text{H}]^+$ 292.1723, found 292.1728.

Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-carboxylate (8h)



In a glove box, $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (8.3 mg, 0.0125 mmol), SiPBz (0.0250 mmol, 10.0 mg), bis(pinacolato)diboron (254.0 mg, 1.0 mmol) and anhydrous, degassed *n*-hexane (2 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1 min at room temperature. Thiophene-2-carboxylic acid methyl ester (142.0 mg, 1.0 mmol) was added to the tube; the reaction vessel was sealed and heated at 80 °C. Reaction progress was monitored by GC over 1 h interval. After 1h, the reaction mixture was allowed to return to room temperature and was exposed to air. 85% GC conversion was observed (ratio 3 position: 5 position: diborylated: 14:1:1). The volatiles were then removed under reduced pressure and Kugelrohr distillation resulted in a white solid (174.2 mg) in 65% isolated yield. ^1H NMR (500 MHz, CDCl_3) δ 1.42 (s, 12H), 3.9 (s, 3H), 7.19 (d, $J = 4.9$ Hz, 1H), 7.5 (d, $J = 4.9$ Hz, 1H).⁷

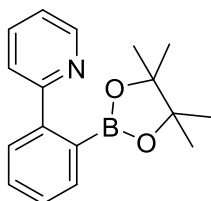
Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-naphthoate (8i)



In a glove box, $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (8.3 mg, 0.0125 mmol), SiPBz (0.025 mmol, 10.0 mg), bis(pinacolato)diboron (254.0 mg, 1.0 mmol) and anhydrous, degassed *n*-hexane (1 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1 min at room temperature. Methyl 1-naphthoate (186.0 mg, 1.0 mmol) was added to the tube, the reaction vessel was sealed and heated at 80 °C, Reaction progress was monitored by GC. After 8h full conversion was observed and the reaction mixture was allowed to return to room temperature and was exposed to air. Purification with column chromatography (dichloromethane)

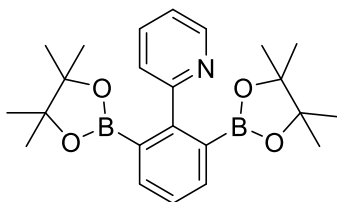
resulted in colorless oil (265.0 mg) in 85% isolated yield. ^1H NMR (500 MHz, CDCl_3) δ ppm 1.39 (s, 12 H) 4.03 (s, 3 H) 7.50 - 7.58 (m, 2 H), 7.78 (d, $J=8.3$ Hz, 1 H) 7.83 - 7.89 (m, 1 H) 7.9 (d, $J=8.3$ Hz, 1 H) 8.1 (d, $J=8.3$ Hz, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ ppm 24.9, 52.4, 84.2, 125.5, 127.0, 127.0, 128.1, 129.4, 129.5, 134.4, 137.0, 170.5; ^1H NMR (500 MHz, C_6D_6) δ ppm 1.12 (s, 12 H) 3.77 (s, 3 H) 7.17 - 7.21 (m, 1 H) 7.25 (ddd, $J=8.3, 6.9, 1.5$ Hz, 1 H) 7.51 (d, $J=8.3$ Hz, 1 H) 7.59 (d, $J=7.8$ Hz, 1 H) 8.01 (d, $J=8.3$ Hz, 1 H) 8.35 (d, $J=8.3$ Hz, 1 H); ^{13}C NMR (125 MHz C_6D_6) δ ppm 24.5, 51.6, 83.7, 125.7, 126.8, 126.9, 128.1, 129.1, 129.8, 129.9, 134.7, 138.4, 169.7; ^{11}B NMR (160 MHz, CDCl_3) δ ppm 31.1 (s); HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{22}\text{BO}_4$ [$\text{M} + \text{H}$] $^+$ 313.1614, found 313.1612.

2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyridine (8j)



In a glove box, $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (8.3 mg, 0.0125 mmol), SiPBz (0.0250 mmol, 10.0 mg), bis(pinacolato)diboron (254.0 mg, 1.0 mmol) and anhydrous, degassed THF (2 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1 min at room temperature. 2-Phenyl pyridine (202.0 mg, 1.3 mmol) was added to the tube, the reaction vessel was sealed and heated at 60 $^\circ\text{C}$, and reaction progress was monitored by GC. After 2h the reaction mixture was allowed to return to room temperature and was exposed to air. After removal of solvent, purification using silica column chromatography (hexane/EtOAc = 1/3) resulted in a white solid (182 mg) 65% isolated yield. (15% of diborylated material was observed in crude reaction mixture by GC, which was characterized as **8j'** by independent synthesis, see below). ^1H NMR (500 MHz, CDCl_3) δ ppm 1.45 (s, 12H), 7.27–7.44 (m, 3H), 7.68 (d, $J = 7.8$ Hz, 1H), 7.75 (d, $J = 7.3$ Hz, 1H), 7.83 (d, $J = 8.3$ Hz, 1H), 7.99 (td, $J = 7.8, 1.5$ Hz, 1H), 8.70 (d, $J = 5.4$ Hz, 1H).⁸

2-(2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyridine (8j')



In a glove box, $[\text{Ir}(\text{OMe})(\text{cod})_2]$ (8.3 mg, 0.0125 mmol), SiPBz (0.0250 mmol, 10.0 mg), bis(pinacolato)diboron (508.0 mg, 2.0 mmol) and anhydrous, degassed THF (2 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1 min at room temperature. 2-phenyl pyridine (155.2 mg, 1.0 mmol) was added to the tube, the reaction vessel was sealed and heated at 60 °C, and reaction progress was monitored by GC. After 24 hours the reaction mixture was allowed to return to room temperature and was exposed to air. Solvent was removed under reduced pressure. Upon addition of hexane to the mixture white solid precipitate. White solid (264.4 mg) with 65 % isolated yield (15% of monoborylated material was observed in GC of crude reaction mixture). ^1H NMR (500 MHz, CDCl_3) δ ppm 1.42 (s, 24 H) 7.37 (m, 2 H) 7.79 (d, $J=7.34$ Hz, 2 H) 7.91 - 7.96 (t, $J=7.83$ Hz, 1 H) 8.68 (d, $J=5.4$ Hz, 1 H) 8.81 (d, $J=7.8$ Hz, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ ppm 26.1, 82.0, 121.6, 122.4, 129.9, 134.9, 141.6, 142.6, 157.7; ^{11}B NMR (160 MHz, CDCl_3) δ ppm 21.6 (s); HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{32}\text{B}_2\text{NO}_4$ $[\text{M} + \text{H}]^+$ 408.2517, found 408.2526

Borylation of Chlorobenzene

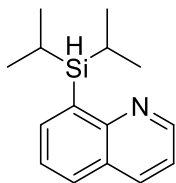
In a glove box, $[\text{Ir}(\text{OMe})(\text{cod})_2]$ (8.3 mg, 0.0125 mmol), SiPBz (0.0250 mmol, 10.0 mg), bis(pinacolato)diboron (127.0 mg, 0.5 mmol) and anhydrous, degassed THF (1 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1 min at room temperature. Chlorobenzene (56.0 mg, 0.5 mmol) was added to the tube; the reaction vessel was sealed and heated at 80 °C. The reaction was stopped after 16 hours, and the mixture was allowed to return to room temperature and was exposed to air. The volatiles were then removed under reduced pressure and the product was characterized as mixture of isomers, with ortho: (meta+para) being 1:3 after 55% conversion.

IrCODSiPBz (9)

In a nitrogen filled glove box, [Ir(OMe)(cod)]₂ (100.0 mg, 0.151 mmol) was fully dissolved in a minimum amount of *n*-hexane (30 mL) in a 100 mL flask, SiPBz (121.0 mg, 0.302 mmol) was added to the flask as a solid. Upon addition of SiPBz, the solution turned a deep red color. After 15 minutes, ³¹P NMR showed full consumption of free phosphine. Then the solvent was fully removed under vacuum and the crude was dissolved in a minimal amount of pentane and stored in a -30 °C freezer. Dark red crystals were obtained after 2 days (100.1 mg, 47% isolated yield).

Structure determination was made by single crystal X-ray diffraction studies. ¹H NMR (500 MHz, C₄D₈O, d₈-THF) δ ppm 0.97 (d, *J*=7.4 Hz, 6 H), 1.02 (d, *J*=7.4 Hz, 6 H), 1.55 - 1.63 (m, 2 H), 1.63 - 1.70 (m, 2 H), 1.75 - 1.85 (m, 2 H), 1.97 - 2.07 (m, 2 H), 2.07 - 2.18 (m, 2 H), 2.26 - 2.40 (s, 6 H), 3.77 (m, 2 H), 5.38 (m, 2 H), 7.10 - 7.23 (m, 5 H), 7.28 (td, *J*=7.24, 1.77 Hz, 1 H), 7.38 - 7.53 (m, 5 H), 7.71 (d, *J*=7.1 Hz, 1 H); ¹³C NMR (125 MHz, C₄D₈O, d₈-THF) δ ppm 19.7, 21.2 (d, *J*=2.8 Hz), 21.5 (d, *J*=2.3 Hz), 30.3 (d, *J*=2.9 Hz), 34.3 (d, *J*=2.9 Hz), 77.7 (d, *J*=12.4 Hz), 81.3, 129.2, 129.3, 129.76, 129.84, 130.1, 132.3 (d, *J*=5.7 Hz), 133.6, 133.9, 134.2, 134.3, 135.2 (d, *J*=22.7 Hz), 140.69, 140.71, 148.6, 157.2, 157.6; ³¹P NMR (202 MHz, C₄D₈O, d₈-THF) δ ppm 52.8 (s)

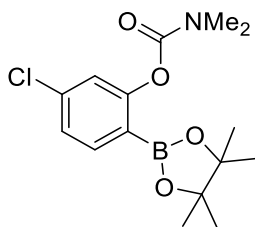
8-(diisopropylsilyl)quinolone (QSi) (10)



sec-Butyllithium (1.3 M in cyclohexane, 7.25 mL, 9.45 mmol) was added dropwise *via* syringe to a magnetically stirred solution of 8-bromoquinoline (1.955 g, 9.4 mmol) in 35.00 mL of Tetrahydrofuran at -78°C over 5 min, followed by stirring for an additional 15 min at this temperature. Diisopropylchlorosilane (1.59 mL, 9.3 mmol), was then added dropwise *via* syringe over 10 min, and the resulting mixture was allowed to warm to ambient temperature over 2 h. After removal of the solvent and volatiles, the crude mixture was subjected to silica column using hexane. Product was obtained as colorless liquid (1.970 g), in 87% yield. ¹H NMR (500 MHz, C₆D₆) δ ppm 1.14 (d, *J*=7.3 Hz, 6 H), 1.30 (d, *J*=7.3 Hz, 6 H) 1.82 (m, 2 H) 4.50 (t, *J*=3.9

Hz, 1 H) 6.75 (dd, $J=8.3, 3.9$ Hz, 1 H) 7.23 (dd, $J=8.1, 6.6$ Hz, 1 H) 7.42 (dd, $J=8.3, 1.5$ Hz, 1 H) 7.52 (dd, $J=8.3, 2.0$ Hz, 1 H) 8.02 (dd, $J=6.8, 1.5$ Hz, 1 H) 8.67 (dd, $J=4.4, 2.0$ Hz, 1 H); ^{13}C NMR (125 MHz, C_6D_6) δ ppm 12.7, 20.17, 20.22, 121.3, 126.7, 129.9, 136.4, 138.9, 139.7, 149.9, 153.4; HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{22}\text{NSi}$ $[\text{M} + \text{H}]^+$ 244.1521, found 244.1527.

5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl dimethylcarbamate (12a)



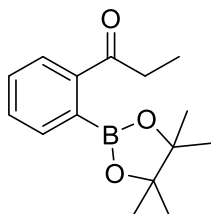
In a glove box, $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (8.3 mg, 0.0125 mmol), QSi (0.0250 mmol, 6.1 mg), bis(pinacolato)diboron (254.0 mg, 1.0 mmol) and anhydrous, degassed THF (1 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1 min at room temperature. 3-Chlorophenyl dimethylcarbamate (200.0 mg, 1.0 mmol) was added to the tube; the reaction vessel was sealed and heated at 80 °C. Reaction progress was monitored by GC. After 4h, 93% conversion was observed and the reaction mixture was allowed to return to room temperature and was exposed to air. Purification with column chromatography (gradient from dichloromethane to dichloromethane/EtOAc, 98/2) resulted in pale yellow oil (195.0 mg) with 60% isolated yield.

^1H NMR (500 MHz, CDCl_3) δ ppm 1.30 (s, 12 H) 3.00 (s, 3 H) 3.12 (s, 3 H) 7.11 (d, $J=1.5$ Hz, 1 H) 7.18 (dd, $J=7.8, 2.0$ Hz, 1 H) 7.69 (d, $J=8.3$ Hz, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ ppm 24.9, 36.5, 36.7, 83.6, 122.8, 125.2, 137.0, 137.6, 155.1, 156.8; ^{11}B NMR (160 MHz, CDCl_3) δ 30.0 (br, s); HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{22}\text{BClNO}_4$ $[\text{M} + \text{H}]^+$ 326.1333 found 326.1324.

Method B

The reaction was performed using 0.5 mmol substrate (99.5 mg), $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (8.3 mg, 0.0125 mmol), 2 equiv B_2Pin_2 (254.0 mg), SiPBz (0.0250 mmol, 10.0 mg) (5.0 mol %), 1.5 ml THF. Purified by column chromatography; hexanes: EtOAc (8.5:1) using Alizarin as an indicator. The compound was isolated as a clear gel (26.0 mg, 12 % yield).

1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-one (12b)



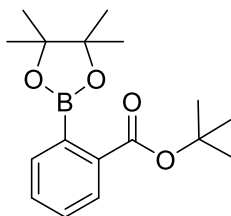
In a glove box, $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (8.3 mg, 0.0125 mmol), QSi (0.0250 mmol, 6.1 mg), bis(pinacolato)diboron (254.0 mg, 1 mmol) and anhydrous, degassed THF (1 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1 min at room temperature. propiophenone (134.0 mg, 1.0 mmol) was added to the tube, the reaction vessel was sealed and heated at 80 °C. Reaction progress was monitored by GC. After 1h the reaction mixture was allowed to return to room temperature and was exposed to air (82% GC conversion). Purification with column chromatography (hexane/EtOAc) resulted in a white solid (182.2 mg) with 70% isolated yield (NMR shows 3% starting material).

^1H NMR (500 MHz, CDCl_3) δ ppm 1.24 (t, $J=7.3$ Hz, 3 H) 1.45 (s, 12 H) 3.01 (q, $J=7.3$ Hz, 2 H) 7.43 (ddd, $J=7.9, 5.3, 2.9$ Hz, 1 H) 7.52 - 7.55 (m, 2 H) 7.82 (d, $J=7.8$ Hz, 1 H).⁹

Borylation of anisole using QSi (10)

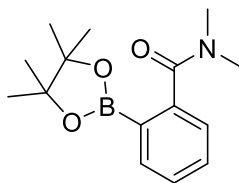
In a glove box, $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (8.3 mg, 0.0125 mmol), QSi (0.0250 mmol, 6.1 mg), and anhydrous, degassed THF (3 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1 min at room temperature. Anisole (108.0 mg, 1.0 mmol) was added to the tube and lastly, bis(pinacolato)diboron (254.0 mg, 1.0 mmol) was added as a solid; the reaction vessel was sealed and heated at 80 °C. Reaction progress was monitored by GC over 4 hour intervals. After 12 hours no further conversion was observed, the reaction mixture was allowed to return to room temperature and was exposed to air. The volatiles were then removed under reduced pressure and the product was characterized as mixture of 1.6:4.2:1.0 (ortho: meta+para: diborylation) with 40% total GC conversion.

Borylation of tert-Butyl benzoate using QSi (10)



In a glove box, $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (3.3 mg, 0.0050 mmol), QSi (0.0100 mmol, 3.0 mg), and anhydrous, degassed THF (1.0 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1 min at room temperature. tert-Butyl benzoate (178.2 mg, 1.0 mmol) was added to the tube and lastly bis(pinacolato)diboron (254.0 mg, 1.0 mmol) was added as a solid, the reaction vessel was sealed and heated at 80 °C. Reaction progress was monitored by GC over 1 hour intervals. After 3 hours, (91% GC conversion based on benzoate) the reaction mixture was allowed to return to room temperature and was exposed to air. The volatiles were then removed under reduced pressure and the product was purified by column chromatography; hexanes: Et₂O (4:1) to afford a white solid (238.0 mg, 78% yield). No diborylated product was observed in the crude reaction; ¹H NMR was identical to the previous report.⁴

Borylation of N,N-dimethylbenzamide using QSi (10)

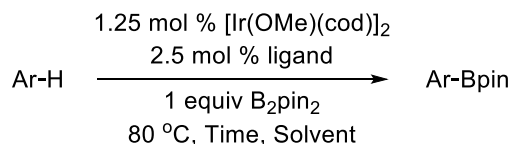


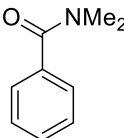
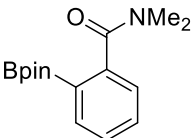
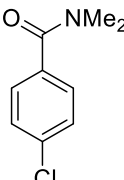
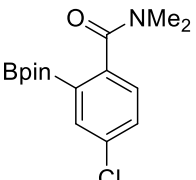
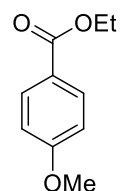
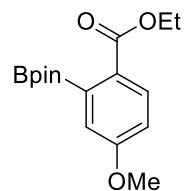
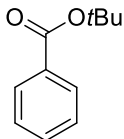
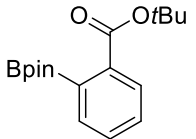
In a glove box, $[\text{Ir}(\text{OMe})(\text{cod})]_2$ (8.3 mg, 0.0125 mmol), SiPBz (0.0250 mmol, 10.0 mg), bis(pinacolato)diboron (254.0 mg, 1.0 mmol) and anhydrous, degassed THF (4.5 mL) were placed in a 15 mL pressure tube containing a magnetic stir bar, and the mixture was stirred for 1 min at room temperature. N,N-Dimethyl benzamide (149.0 mg, 1.0 mmol) was added to the tube, the reaction vessel was sealed and heated at 80 °C. Reaction progress was monitored by GC over 1 hour intervals. After 4 hours, (90% GC conversion) the reaction mixture was allowed to return to room temperature and was exposed to air. The volatiles were then removed under reduced

pressure and the product was purified by passing it through a short plug of SiO₂ eluting (hexane/EtOAc = 1/1). The product was isolated by precipitation from hexane. A white solid (220.2 mg) was isolated in 80% yield. ¹H NMR was identical to the previous report.⁴

Borylation of benzamides (7a and 8a) and benzoates (7f and tert-butyl benzoate) using QSi (10) vs SiPbz (5)

Reactions were performed under identical conditions as described for analogues reaction using SiPbz (5).



Entry	Substrate	Product	Ligand	Solvent	Time (h)	% yield
1			SiPbz	THF	16	75
			QSi	THF	4	80
2			SiPbz	THF	16	85
			QSi	THF	2	85
3			SiPbz	Hex	12	77 ^a
			QSi	Hex	2	75 ^b
4 ^c			SiPbz	THF	16	63
			QSi	THF	3	78

^a5% diborylation was obtained. ^b15% diborylation was obtained. ^c0.5 mol % [Ir(OMe)(cod)]₂ and 1.0 mol % ligand was used.

Figure 1. Methyl 2,3-dimethoxy-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6f)

The following are 50% thermal ellipsoidal drawings of the molecule in the asymmetric cell with various amount of labeling.

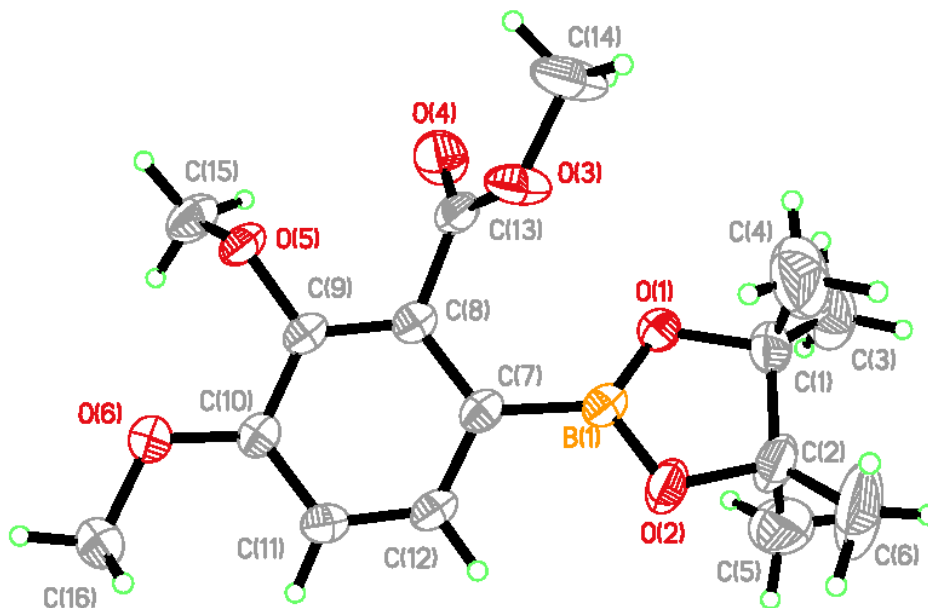


Table 1 Crystal data and structure refinement for 6f

Empirical formula	C ₁₆ H ₂₃ O ₆ B
Formula weight	322.15
Temperature/K	172.99
Crystal system	monoclinic
Space group	C2/c
a/Å	23.4123(4)

b/Å	9.0701(2)
c/Å	18.5703(3)
α /°	90
β /°	118.6010(10)
γ /°	90
Volume/Å ³	3462.24(12)
Z	8
ρ_{calc} /mg/mm ³	1.236
m/mm ⁻¹	0.767
F(000)	1376.0
Crystal size/mm ³	0.427 × 0.31 × 0.194
Radiation	CuK α (λ = 1.54178)
2 Θ range for data collection	8.604 to 144.228°
Index ranges	-27 ≤ h ≤ 28, -11 ≤ k ≤ 10, -22 ≤ l ≤ 22
Reflections collected	15915
Independent reflections	3362[R(int) = 0.0246]
Data/restraints/parameters	3362/0/215
Goodness-of-fit on F ²	1.075
Final R indexes [I >= 2 σ (I)]	R ₁ = 0.0663, wR ₂ = 0.1903

Final R indexes [all data] $R_1 = 0.0701$, $wR_2 = 0.1943$

Largest diff. peak/hole / $e \text{ \AA}^{-3}$ 0.86/-0.43

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 6f. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$
O1	1320.0(8)	1095.9(17)	6643.7(9)	38.1(4)
O2	1459.9(10)	2890.2(18)	7567.6(9)	47.8(5)
O3	2101.8(8)	2235(2)	5836.4(11)	46.6(5)
O4	1224.7(10)	1693.5(19)	4651.8(10)	52.0(5)
O5	1220.9(7)	4947.1(17)	4302.8(9)	34.4(4)
O6	629.6(8)	7349.4(18)	4500.2(10)	39.6(4)
C1	1640.2(15)	389(3)	7450.6(15)	51.4(7)
C2	1551.7(18)	1496(3)	7999.4(16)	58.0(8)
C3	1396(2)	-1110(3)	7399(2)	82.6(12)
C4	2376.1(19)	351(6)	7696(3)	95.8(14)
C5	866(2)	1211(5)	7959(3)	92.4(14)
C6	2017(3)	1671(5)	8859(2)	127(2)
C7	1093.9(9)	3801(2)	6122.0(12)	29.0(4)

C8	1197.3(9)	3763(2)	5433.9(12)	27.4(4)
C9	1040.6(9)	4956(2)	4908.8(11)	28.1(4)
C10	756.6(10)	6226(2)	5038.0(12)	30.2(5)
C11	634(1)	6257(2)	5700.4(13)	32.5(5)
C12	811(1)	5069(2)	6230.7(12)	32.0(5)
C13	1492.2(11)	2450(2)	5249.7(12)	32.2(5)
C14	2422.7(16)	943(4)	5740(2)	68.7(9)
C15	695.6(13)	4716(3)	3490.8(14)	47.4(6)
C16	415.4(12)	8711(3)	4679.4(15)	42.5(6)
B1	1300.4(11)	2552(3)	6779.6(14)	30.8(5)

Table 3 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 6f. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+\dots+2hka \times b \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	46.4(9)	39.6(9)	25.7(7)	0.5(6)	15.0(7)	9.8(7)
O2	81.7(13)	33.6(9)	27.2(8)	1.2(6)	25.3(8)	-4.1(8)
O3	33.7(8)	56.0(11)	50.7(10)	-14.4(8)	20.7(8)	9.6(7)
O4	70.0(12)	38.0(9)	38.6(9)	-11.7(7)	18.3(9)	-1.9(8)
O5	38.7(8)	43.6(9)	29.2(7)	1.0(6)	22.9(7)	0.4(6)

O6	52.6(10)	35.4(8)	37.3(8)	5.6(6)	26.6(7)	5.6(7)
C1	70.6(18)	45.2(14)	31.4(12)	7.5(10)	18.7(12)	18.6(13)
C2	111(2)	33.8(13)	32.0(12)	2.8(10)	36.3(15)	-4.5(14)
C3	135(4)	39.7(16)	56.6(19)	0.7(13)	33(2)	0.4(18)
C4	66(2)	125(4)	95(3)	53(3)	38(2)	43(2)
C5	147(4)	72(2)	116(3)	23(2)	109(3)	20(2)
C6	234(6)	61(2)	31.2(16)	7.9(15)	19(2)	1(3)
C7	26.0(9)	37.5(11)	23.7(9)	-1.8(8)	12.0(8)	-3.9(8)
C8	22.5(9)	34.6(10)	23.5(9)	-3.3(7)	9.8(7)	-3.8(7)
C9	26.0(9)	37.2(11)	23.5(9)	-2.2(8)	13.6(8)	-3.5(8)
C10	29.8(10)	34.9(11)	25.9(9)	0.8(8)	13.3(8)	-1.9(8)
C11	31.8(10)	37.4(11)	30.5(10)	-4.6(8)	16.8(9)	1.6(8)
C12	30.8(10)	44.2(12)	24.8(9)	-2.3(8)	16.4(8)	-1.3(9)
C13	39.3(11)	33.9(11)	30.1(10)	-1.7(8)	22.0(9)	-3.6(9)
C14	59.6(18)	71(2)	80(2)	-15.7(17)	37.4(17)	24.1(15)
C15	55.2(15)	62.4(16)	27.3(11)	-2.5(10)	22.0(11)	0.2(12)
C16	50.1(14)	34.6(12)	43.5(13)	2.2(9)	22.8(11)	3.2(10)
B1	28.2(11)	39.5(13)	25.9(11)	-1.0(9)	14.0(9)	-1.9(9)

Table 4 Bond Lengths for 6f.

Atom Atom Length/Å			Atom Atom Length/Å		
O1	C1	1.464(3)	C1	C3	1.459(4)
O1	B1	1.350(3)	C1	C4	1.558(5)
O2	C2	1.457(3)	C2	C5	1.591(6)
O2	B1	1.361(3)	C2	C6	1.447(5)
O3	C13	1.332(3)	C7	C8	1.410(3)
O3	C14	1.448(3)	C7	C12	1.389(3)
O4	C13	1.196(3)	C7	B1	1.563(3)
O5	C9	1.378(2)	C8	C9	1.384(3)
O5	C15	1.433(3)	C8	C13	1.496(3)
O6	C10	1.356(3)	C9	C10	1.407(3)
O6	C16	1.431(3)	C10	C11	1.391(3)
C1	C2	1.514(4)	C11	C12	1.383(3)

Table 5 Bond Angles for 6f.

Atom Atom Atom Angle/°				Atom Atom Atom Angle/°			
B1	O1	C1	106.49(17)	C12	C7	B1	118.51(18)
B1	O2	C2	106.77(18)	C7	C8	C13	121.67(18)

C13	O3	C14	115.7(2)	C9	C8	C7	121.10(19)
C9	O5	C15	114.58(16)	C9	C8	C13	117.22(17)
C10	O6	C16	117.04(17)	O5	C9	C8	119.29(18)
O1	C1	C2	103.32(19)	O5	C9	C10	119.91(18)
O1	C1	C4	105.2(2)	C8	C9	C10	120.51(18)
C2	C1	C4	107.9(3)	O6	C10	C9	116.38(18)
C3	C1	O1	110.4(2)	O6	C10	C11	124.80(19)
C3	C1	C2	119.1(3)	C11	C10	C9	118.82(19)
C3	C1	C4	110.0(3)	C12	C11	C10	119.72(19)
O2	C2	C1	103.70(19)	C11	C12	C7	122.88(18)
O2	C2	C5	103.6(3)	O3	C13	C8	111.12(17)
C1	C2	C5	108.7(3)	O4	C13	O3	123.8(2)
C6	C2	O2	110.3(3)	O4	C13	C8	125.1(2)
C6	C2	C1	122.8(4)	O1	B1	O2	113.9(2)
C6	C2	C5	106.3(4)	O1	B1	C7	126.06(19)
C8	C7	B1	124.53(19)	O2	B1	C7	120.0(2)
C12	C7	C8	116.91(19)				

Table 6 Torsion Angles for 6f.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C1	C2	O2	-23.6(3)	C9	C8	C13	O3	114.6(2)
O1	C1	C2	C5	86.2(3)	C9	C8	C13	O4	-64.5(3)
O1	C1	C2	C6	-149.1(4)	C9	C10	C11	C12	2.0(3)
O5	C9	C10	O6	5.1(3)	C10	C11	C12	C7	-1.9(3)
O5	C9	C10	C11	-174.13(18)	C12	C7	C8	C9	1.9(3)
O6	C10	C11	C12	-177.07(19)	C12	C7	C8	C13	-179.38(18)
C1	O1	B1	O2	-11.3(3)	C12	C7	B1	O1	150.4(2)
C1	O1	B1	C7	170.9(2)	C12	C7	B1	O2	-27.2(3)
C2	O2	B1	O1	-4.6(3)	C13	C8	C9	O5	-6.6(3)
C2	O2	B1	C7	173.3(2)	C13	C8	C9	C10	179.45(18)
C3	C1	C2	O2	-146.4(3)	C14	O3	C13	O4	-4.0(3)
C3	C1	C2	C5	-36.6(4)	C14	O3	C13	C8	176.9(2)
C3	C1	C2	C6	88.1(5)	C15	O5	C9	C8	106.7(2)
C4	C1	C2	O2	87.4(3)	C15	O5	C9	C10	-79.3(2)
C4	C1	C2	C5	-162.8(3)	C16	O6	C10	C9	-172.58(19)
C4	C1	C2	C6	-38.1(4)	C16	O6	C10	C11	6.6(3)
C7	C8	C9	O5	172.17(17)	B1	O1	C1	C2	21.5(3)

C7 C8 C9 C10 -1.7(3)	B1 O1 C1 C3 149.9(3)
C7 C8 C13 O3 -64.2(2)	B1 O1 C1 C4 -91.5(3)
C7 C8 C13 O4 116.7(2)	B1 O2 C2 C1 17.7(3)
C8 C7 C12 C11 0.0(3)	B1 O2 C2 C5 -95.7(3)
C8 C7 B1 O1 -32.2(3)	B1 O2 C2 C6 150.9(4)
C8 C7 B1 O2 150.1(2)	B1 C7 C8 C9 -175.53(18)
C8 C9 C10 O6 178.94(18)	B1 C7 C8 C13 3.2(3)
C8 C9 C10 C11 -0.3(3)	B1 C7 C12 C11 177.54(19)

Table 7 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 6f.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H3A	922	-1085	7169	124
H3B	1594	-1546	7948	124
H3C	1509	-1703	7044	124
H4A	2442	-311	7325	144
H4B	2627	-7	8260	144
H4C	2522	1346	7655	144
H5A	885	297	8251	139

H5B	529	1122	7384	139
H5C	762	2037	8215	139
H6A	2459	1675	8927	191
H6B	1972	852	9172	191
H6C	1935	2605	9059	191
H11	430	7091	5788	39
H12	736	5123	6689	38
H14A	2155	70	5672	103
H14B	2848	823	6228	103
H14C	2482	1064	5256	103
H15A	524	3716	3447	71
H15B	854	4841	3092	71
H15C	350	5435	3377	71
H16A	-6	8563	4661	64
H16B	371	9453	4273	64
H16C	735	9048	5228	64

Crystal Data. C₁₆H₂₃O₆B, $M = 322.15$, monoclinic, $a = 23.4123(4) \text{ \AA}$, $b = 9.0701(2) \text{ \AA}$, $c = 18.5703(3) \text{ \AA}$, $\beta = 118.6010(10)^\circ$, $V = 3462.24(12) \text{ \AA}^3$, $T = 172.99$, space group C2/c (no. 15), $Z = 8$, $\mu(\text{CuK}\alpha) = 0.767$, 15915 reflections measured, 3362 unique ($R_{\text{int}} = 0.0246$) which were used in all calculations. The final wR_2 was 0.1943 (all data) and R_1 was 0.0663 ($I > 2\sigma(I)$).

Figure 2. IrCODSiPbz (9)

The following are 50% thermal ellipsoidal drawings of the molecule in the asymmetric cell with various amount of labeling

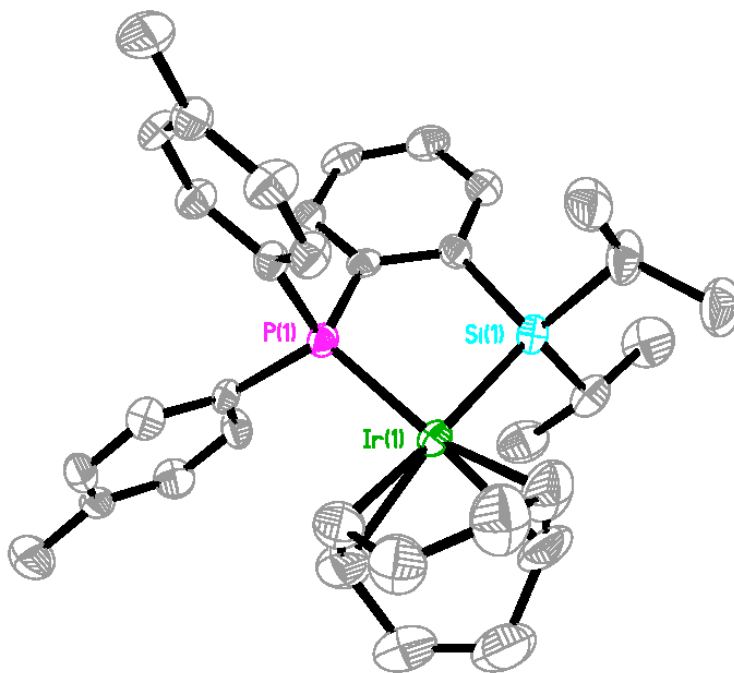


Table 1 Crystal data and structure refinement for 9

Empirical formula	C ₃₄ H ₄₄ IrPSi
Formula weight	703.95
Temperature/K	173.15
Crystal system	triclinic
Space group	P-1
a/Å	9.9128(11)
b/Å	10.2416(11)
c/Å	16.4821(18)

$\alpha/^\circ$	77.3150(10)
$\beta/^\circ$	86.7650(10)
$\gamma/^\circ$	69.1190(10)
Volume/ \AA^3	1524.8(3)
Z	2
$\rho_{\text{calc}}/\text{mg}/\text{mm}^3$	1.533
m/mm^{-1}	4.491
F(000)	708.0
Crystal size/ mm^3	$0.10 \times 0.092 \times 0.073$
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection	4.358 to 50.38 $^\circ$
Index ranges	$-11 \leq h \leq 11, -12 \leq k \leq 12, -19 \leq l \leq 19$
Reflections collected	28194
Independent reflections	5481[R(int) = 0.0621]
Data/restraints/parameters	5481/48/340
Goodness-of-fit on F^2	1.060
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0395, wR_2 = 0.0819$
Final R indexes [all data]	$R_1 = 0.0519, wR_2 = 0.0884$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	1.19/-0.95

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 9. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
Ir1	4582.2(3)	2779.6(3)	2879.2(2)	25.08(9)
P1	2438.2(17)	2567.3(17)	2683.2(10)	22.7(4)
Si1	5470.3(19)	994.8(19)	2077.0(11)	26.2(4)
C1	3665(9)	4768(9)	3394(5)	49.9(16)
C2	4035(10)	3579(9)	4045(5)	54.4(17)
C3	5417(10)	2942(11)	4585(6)	69.2(19)
C4	6723(11)	2927(12)	4112(6)	75(2)
C5	6722(9)	2648(11)	3257(6)	62.8(18)
C6	6270(10)	3661(10)	2546(7)	63.4(18)
C7	5631(11)	5262(10)	2517(7)	70.7(19)
C8	4560(10)	5695(9)	3136(6)	58.1(17)
C9	2594(7)	1009(6)	2264(4)	23.2(14)
C10	3896(7)	398(7)	1893(4)	26.4(14)
C11	3965(8)	-644(7)	1459(4)	34.6(16)
C12	2844(8)	-1140(7)	1439(4)	36.3(17)
C13	1601(8)	-585(7)	1858(4)	34.1(16)
C14	1458(7)	505(7)	2259(4)	29.5(15)
C15	1363(6)	2459(7)	3612(4)	24.5(14)
C16	1707(7)	1184(7)	4195(4)	31.3(15)
C17	1056(8)	1127(8)	4956(4)	37.3(17)
C18	55(7)	2342(8)	5168(4)	31.8(16)

C19	-289(7)	3612(7)	4587(4)	31.5(15)
C20	356(7)	3669(7)	3818(4)	30.8(15)
C21	-637(9)	2253(10)	6011(5)	53(2)
C22	1246(7)	4053(7)	1930(4)	26.2(14)
C23	1763(8)	5083(7)	1473(4)	34.5(16)
C24	896(8)	6180(8)	871(4)	40.1(18)
C25	-500(7)	6305(7)	695(4)	33.3(16)
C26	-999(7)	5275(8)	1148(4)	35.1(17)
C27	-169(7)	4179(7)	1757(4)	31.4(16)
C28	-1417(9)	7515(8)	36(5)	49(2)
C29	6218(8)	1409(9)	1000(5)	45(2)
C30	7794(9)	1332(10)	997(5)	58(2)
C31	5260(9)	2830(9)	474(5)	52(2)
C32	6884(7)	-706(7)	2705(4)	35.0(16)
C33	7549(9)	-1913(8)	2263(6)	58(2)
C34	6267(9)	-1220(9)	3537(5)	52(2)

Table 3 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 9. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+\dots+2hka \times b \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir1	21.24(14)	26.01(14)	29.25(15)	-4.56(10)	-0.53(10)	-10.49(11)
P1	19.0(8)	26.0(9)	22.9(8)	-3.3(7)	1.2(7)	-9.1(7)

Si1	21.1(9)	23.7(9)	32.6(10)	-5.4(8)	3.5(8)	-7.4(8)
C1	50(3)	48(3)	65(4)	-32(3)	3(3)	-21(3)
C2	58(4)	64(4)	57(4)	-25(3)	1(3)	-33(3)
C3	68(4)	80(4)	70(4)	-20(3)	-17(3)	-34(3)
C4	60(4)	78(4)	90(4)	-31(4)	-27(3)	-17(3)
C5	39(3)	71(4)	94(4)	-41(3)	-15(3)	-23(3)
C6	50(4)	63(4)	96(4)	-33(3)	11(3)	-34(3)
C7	68(4)	60(4)	93(4)	-21(3)	15(3)	-33(3)
C8	61(4)	46(3)	76(4)	-25(3)	7(3)	-24(3)
C9	25(3)	24(3)	17(3)	2(3)	-5(3)	-8(3)
C10	26(4)	30(4)	22(3)	-3(3)	3(3)	-10(3)
C11	33(4)	38(4)	34(4)	-13(3)	1(3)	-10(3)
C12	41(4)	31(4)	39(4)	-7(3)	-8(3)	-14(3)
C13	33(4)	32(4)	38(4)	-3(3)	-13(3)	-15(3)
C14	24(4)	35(4)	28(3)	-4(3)	-2(3)	-9(3)
C15	15(3)	30(4)	30(3)	-8(3)	2(3)	-9(3)
C16	28(4)	33(4)	28(4)	-5(3)	8(3)	-7(3)
C17	42(4)	34(4)	29(4)	3(3)	-2(3)	-10(4)
C18	27(4)	48(4)	28(4)	-14(3)	3(3)	-19(3)
C19	30(4)	33(4)	32(4)	-12(3)	7(3)	-10(3)
C20	32(4)	24(3)	35(4)	0(3)	1(3)	-11(3)
C21	58(6)	65(6)	39(5)	-15(4)	9(4)	-23(5)

C22	24(4)	25(3)	28(3)	-3(3)	2(3)	-9(3)
C23	29(4)	36(4)	35(4)	2(3)	1(3)	-13(3)
C24	42(5)	36(4)	38(4)	10(3)	-7(3)	-18(4)
C25	32(4)	28(4)	33(4)	-5(3)	-3(3)	-3(3)
C26	21(4)	42(4)	37(4)	-7(3)	-8(3)	-5(3)
C27	29(4)	34(4)	32(4)	-2(3)	-3(3)	-13(3)
C28	49(5)	48(5)	36(4)	2(4)	-12(4)	-8(4)
C29	31(4)	48(5)	49(5)	3(4)	10(4)	-15(4)
C30	40(5)	75(6)	53(5)	1(5)	12(4)	-25(5)
C31	48(5)	57(5)	37(4)	5(4)	5(4)	-12(4)
C32	29(4)	25(4)	48(4)	-2(3)	-6(3)	-9(3)
C33	57(6)	30(4)	76(6)	-17(4)	-10(5)	3(4)
C34	57(6)	48(5)	46(5)	5(4)	-15(4)	-18(4)

Table 4 Bond Lengths for 9.

Atom Atom Length/Å			Atom Atom Length/Å		
Ir1	P1	2.2597(16)	C10	C11	1.389(9)
Ir1	Si1	2.3764(18)	C11	C12	1.381(10)
Ir1	C1	2.246(8)	C12	C13	1.377(10)
Ir1	C2	2.217(8)	C13	C14	1.380(9)
Ir1	C5	2.194(8)	C15	C16	1.384(9)
Ir1	C6	2.161(8)	C15	C20	1.383(9)

P1	C9	1.829(6)	C16	C17	1.376(9)
P1	C15	1.821(6)	C17	C18	1.388(10)
P1	C22	1.819(6)	C18	C19	1.377(9)
Si1	C10	1.928(7)	C18	C21	1.515(10)
Si1	C29	1.904(7)	C19	C20	1.386(9)
Si1	C32	1.924(7)	C22	C23	1.391(9)
C1	C2	1.386(12)	C22	C27	1.402(9)
C1	C8	1.500(11)	C23	C24	1.379(9)
C2	C3	1.530(12)	C24	C25	1.385(10)
C3	C4	1.470(13)	C25	C26	1.377(10)
C4	C5	1.498(13)	C25	C28	1.503(9)
C5	C6	1.357(13)	C26	C27	1.373(9)
C6	C7	1.523(12)	C29	C30	1.536(10)
C7	C8	1.452(12)	C29	C31	1.525(10)
C9	C10	1.391(9)	C32	C33	1.502(10)
C9	C14	1.397(9)	C32	C34	1.533(10)

Table 5 Bond Angles for 9.

Atom Atom Atom Angle/°				Atom Atom Atom Angle/°			
P1	Ir1	Si1	83.53(6)	C7	C6	Ir1	108.2(6)
C1	Ir1	P1	96.0(2)	C8	C7	C6	115.7(8)
C1	Ir1	Si1	168.7(2)	C7	C8	C1	115.1(7)

C2	Ir1	P1	96.8(2)	C10	C9	P1	115.8(5)
C2	Ir1	Si1	155.1(2)	C10	C9	C14	121.1(6)
C2	Ir1	C1	36.2(3)	C14	C9	P1	123.0(5)
C5	Ir1	P1	169.6(3)	C9	C10	Si1	117.1(5)
C5	Ir1	Si1	95.2(2)	C11	C10	Si1	125.9(5)
C5	Ir1	C1	87.3(3)	C11	C10	C9	116.9(6)
C5	Ir1	C2	80.0(3)	C12	C11	C10	122.6(7)
C6	Ir1	P1	154.0(3)	C13	C12	C11	119.4(7)
C6	Ir1	Si1	95.0(3)	C12	C13	C14	119.9(6)
C6	Ir1	C1	80.5(3)	C13	C14	C9	120.0(6)
C6	Ir1	C2	95.2(3)	C16	C15	P1	119.6(5)
C6	Ir1	C5	36.3(3)	C20	C15	P1	121.5(5)
C9	P1	Ir1	113.8(2)	C20	C15	C16	118.0(6)
C15	P1	Ir1	114.9(2)	C17	C16	C15	120.7(6)
C15	P1	C9	105.9(3)	C16	C17	C18	121.4(6)
C22	P1	Ir1	113.6(2)	C17	C18	C21	120.4(7)
C22	P1	C9	103.1(3)	C19	C18	C17	118.0(6)
C22	P1	C15	104.5(3)	C19	C18	C21	121.6(7)
C10	Si1	Ir1	107.4(2)	C18	C19	C20	120.7(6)
C29	Si1	Ir1	120.9(3)	C15	C20	C19	121.2(6)
C29	Si1	C10	104.5(3)	C23	C22	P1	119.4(5)
C29	Si1	C32	107.6(3)	C23	C22	C27	117.8(6)

C32	Si1	Ir1	110.8(2)	C27	C22	P1	122.8(5)
C32	Si1	C10	104.2(3)	C24	C23	C22	120.2(6)
C2	C1	Ir1	70.8(5)	C23	C24	C25	122.3(6)
C2	C1	C8	124.1(8)	C24	C25	C28	120.9(6)
C8	C1	Ir1	110.0(5)	C26	C25	C24	117.1(6)
C1	C2	Ir1	73.1(5)	C26	C25	C28	122.0(7)
C1	C2	C3	127.2(8)	C27	C26	C25	122.1(6)
C3	C2	Ir1	106.5(6)	C26	C27	C22	120.6(6)
C4	C3	C2	113.4(8)	C30	C29	Si1	114.6(6)
C3	C4	C5	114.8(8)	C31	C29	Si1	112.4(5)
C4	C5	Ir1	111.8(6)	C31	C29	C30	110.5(6)
C6	C5	Ir1	70.5(5)	C33	C32	Si1	116.1(5)
C6	C5	C4	125.8(9)	C33	C32	C34	110.8(6)
C5	C6	Ir1	73.2(5)	C34	C32	Si1	110.3(5)
C5	C6	C7	124.0(9)				

Table 6 Torsion Angles for 9.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Ir1	P1	C9	C10	-18.1(5)	C9	P1	C22	C27	60.7(6)
Ir1	P1	C9	C14	166.1(4)	C9	C10	C11	C12	-4.5(10)
Ir1	P1	C15	C16	-78.0(5)	C10	C9	C14	C13	-2.2(9)
Ir1	P1	C15	C20	91.6(5)	C10	C11	C12	C13	0.3(11)

Ir1 P1 C22 C23 7.3(6)	C11 C12 C13 C14 3.1(10)
Ir1 P1 C22 C27 -175.7(5)	C12 C13 C14 C9 -2.2(10)
Ir1 C1 C2 C3 98.2(9)	C14 C9 C10 Si1 -171.3(5)
Ir1 C1 C8 C7 9.9(10)	C14 C9 C10 C11 5.4(9)
Ir1 C2 C3 C4 40.3(10)	C15 P1 C9 C10 -145.2(5)
Ir1 C5 C6 C7 101.0(9)	C15 P1 C9 C14 39.0(6)
Ir1 C6 C7 C8 36.4(11)	C15 P1 C22 C23 133.2(5)
P1 C9 C10 Si1 12.8(6)	C15 P1 C22 C27 -49.8(6)
P1 C9 C10 C11 -170.5(5)	C15 C16 C17 C18 -1.0(11)
P1 C9 C14 C13 173.4(5)	C16 C15 C20 C19 0.3(10)
P1 C15 C16 C17 170.3(5)	C16 C17 C18 C19 1.1(11)
P1 C15 C20 C19 -169.5(5)	C16 C17 C18 C21 -179.4(7)
P1 C22 C23 C24 177.0(6)	C17 C18 C19 C20 -0.4(10)
P1 C22 C27 C26 -176.2(5)	C18 C19 C20 C15 -0.2(10)
Si1 C10 C11 C12 171.8(5)	C20 C15 C16 C17 0.3(10)
C1 C2 C3 C4 -40.7(13)	C21 C18 C19 C20 -179.9(7)
C2 C1 C8 C7 89.7(11)	C22 P1 C9 C10 105.3(5)
C2 C3 C4 C5 -35.6(13)	C22 P1 C9 C14 -70.5(6)
C3 C4 C5 Ir1 11.6(12)	C22 P1 C15 C16 156.9(5)
C3 C4 C5 C6 92.7(12)	C22 P1 C15 C20 -33.5(6)
C4 C5 C6 Ir1 -103.3(9)	C22 C23 C24 C25 -0.2(11)
C4 C5 C6 C7 -2.4(15)	C23 C22 C27 C26 0.9(10)

C5 C6 C7 C8	-45.2(13)	C23 C24 C25 C26	-0.2(11)
C6 C7 C8 C1	-31.4(13)	C23 C24 C25 C28	179.9(7)
C8 C1 C2 Ir1	-101.6(8)	C24 C25 C26 C27	0.9(10)
C8 C1 C2 C3	-3.4(14)	C25 C26 C27 C22	-1.3(11)
C9 P1 C15 C16	48.4(6)	C27 C22 C23 C24	-0.2(10)
C9 P1 C15 C20	-142.0(5)	C28 C25 C26 C27	-179.2(7)
C9 P1 C22 C23	-116.3(6)		

Table 7 Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for 9.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H1	2602	5280	3294	60
H2	3185	3391	4331	65
H3A	5319	3503	5018	83
H3B	5532	1950	4871	83
H4A	7570	2183	4430	90
H4B	6839	3861	4063	90
H5	7519	1761	3173	75
H6	6811	3399	2040	76
H7A	6429	5599	2584	85
H7B	5183	5753	1958	85
H8A	3904	6686	2914	70

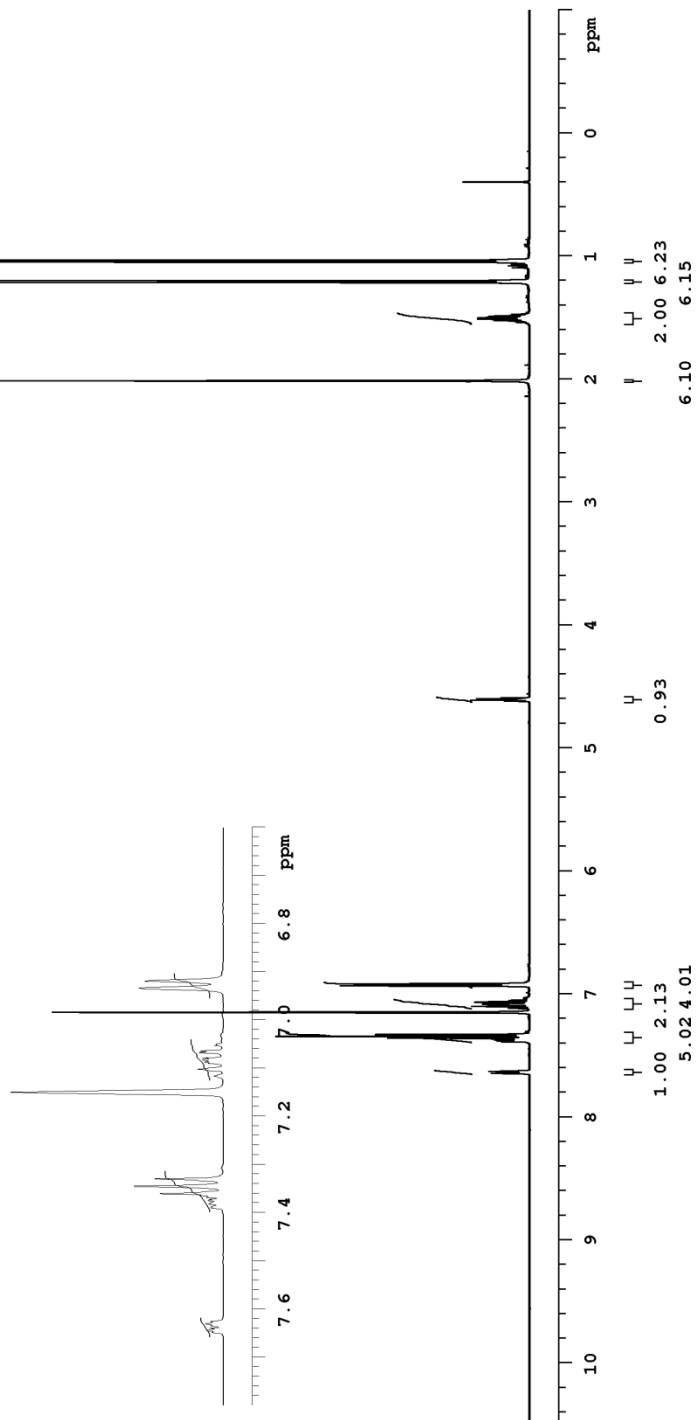
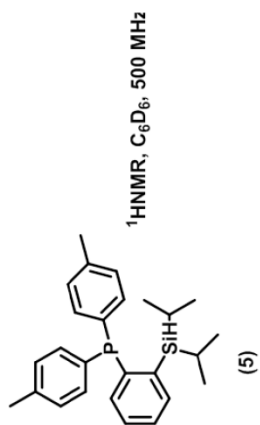
H8B	5061	5705	3636	70
H11	4816	-1030	1166	41
H12	2930	-1857	1139	44
H13	842	-952	1871	41
H14	588	912	2532	35
H16	2400	339	4070	38
H17	1296	237	5343	45
H19	-976	4457	4716	38
H20	101	4555	3426	37
H21A	-163	2603	6378	80
H21B	-530	1257	6254	80
H21C	-1665	2844	5948	80
H23	2716	5030	1576	41
H24	1269	6873	568	48
H26	-1947	5325	1035	42
H27	-557	3500	2064	38
H28A	-1473	7158	-461	73
H28B	-986	8259	-105	73
H28C	-2391	7918	245	73
H29	6200	651	712	54
H30A	7852	2128	1215	87
H30B	8145	1396	427	87

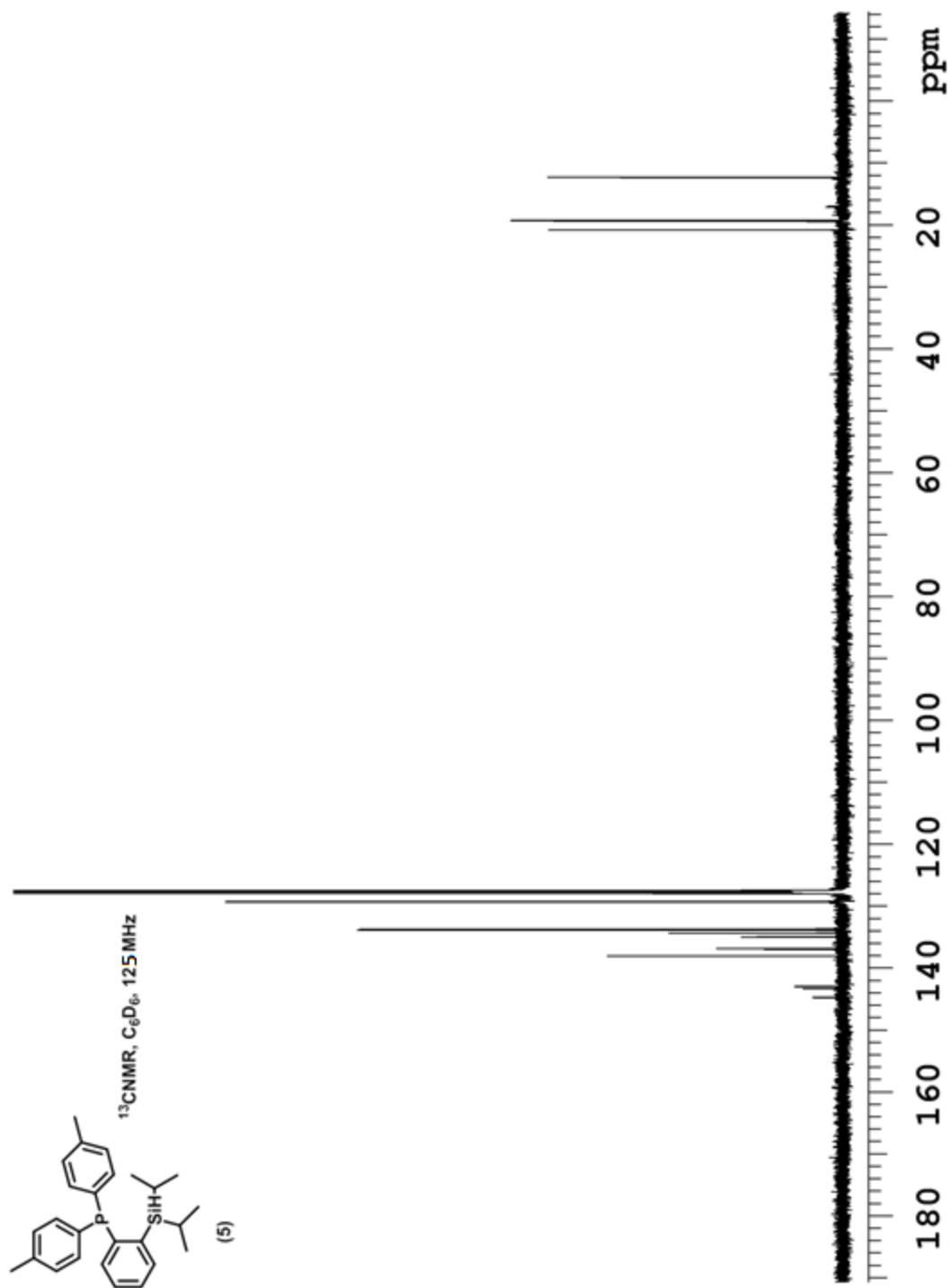
H30C 8390	424	1349	87
H31A 4272	2836	451	78
H31B 5632	2951	-91	78
H31C 5261	3615	722	78
H32 7692	-418	2844	42
H33A 6810	-2287	2152	87
H33B 8327	-2677	2611	87
H33C 7942	-1563	1735	87
H34A 5926	-444	3840	79
H34B 7020	-2041	3869	79
H34C 5458	-1505	3434	79

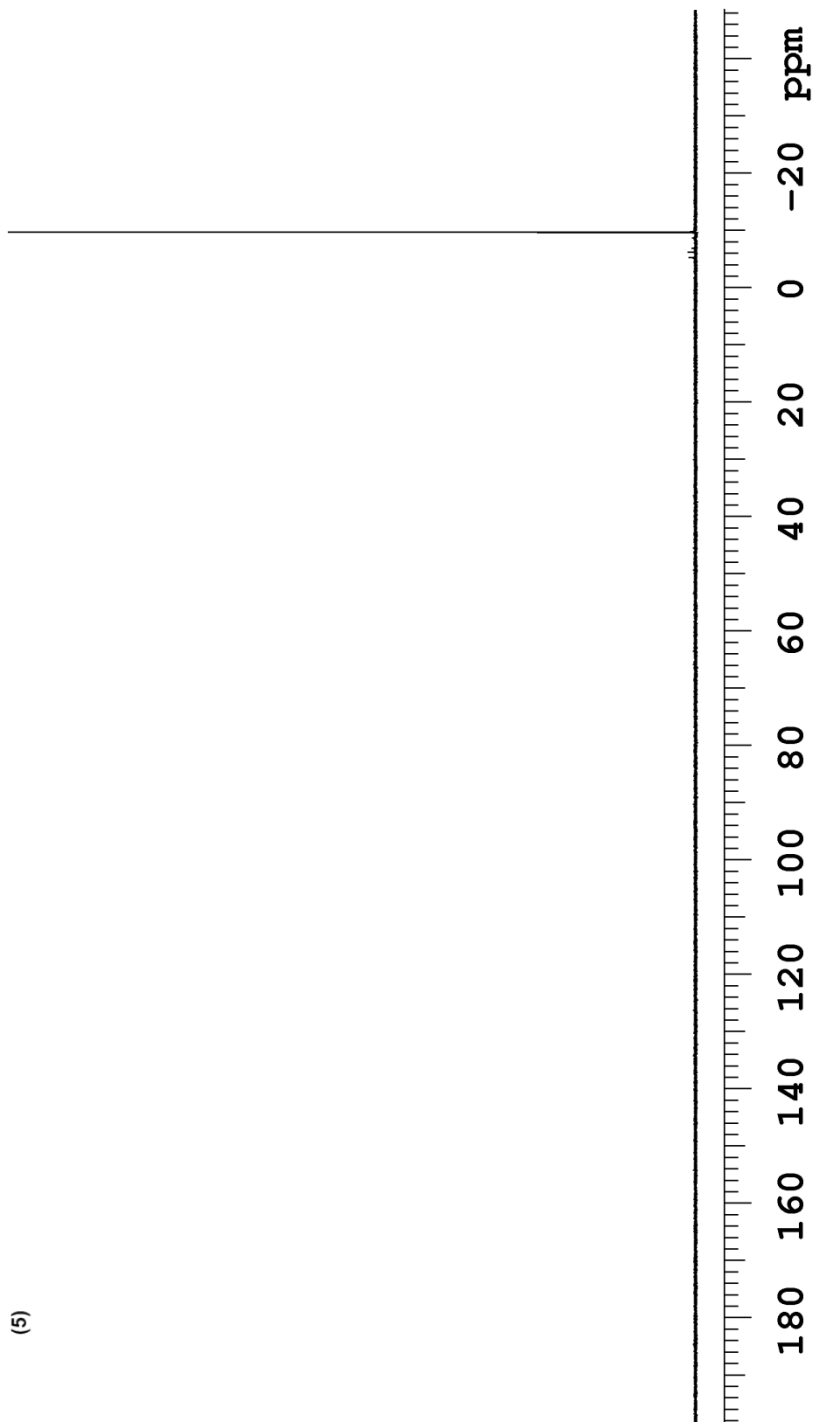
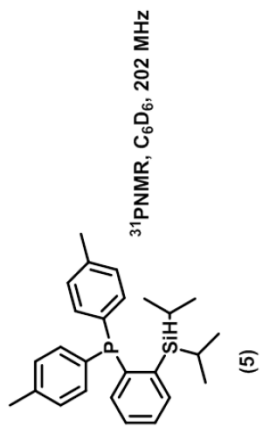
Crystal Data. $C_{34}H_{44}IrPSi$, $M=703.95$, triclinic, $a = 9.9128(11) \text{ \AA}$, $b = 10.2416(11) \text{ \AA}$, $c = 16.4821(18) \text{ \AA}$, $\alpha = 77.3150(10)^\circ$, $\beta = 86.7650(10)^\circ$, $\gamma = 69.1190(10)^\circ$, $V = 1524.8(3) \text{ \AA}^3$, $T = 173.15$, space group P-1 (no. 2), $Z = 2$, $\mu(\text{MoK}\alpha) = 4.491$, 28194 reflections measured, 5481 unique ($R_{\text{int}} = 0.0621$) which were used in all calculations. The final wR_2 was 0.0884 (all data) and R_1 was 0.0395 ($I > 2\sigma(I)$).

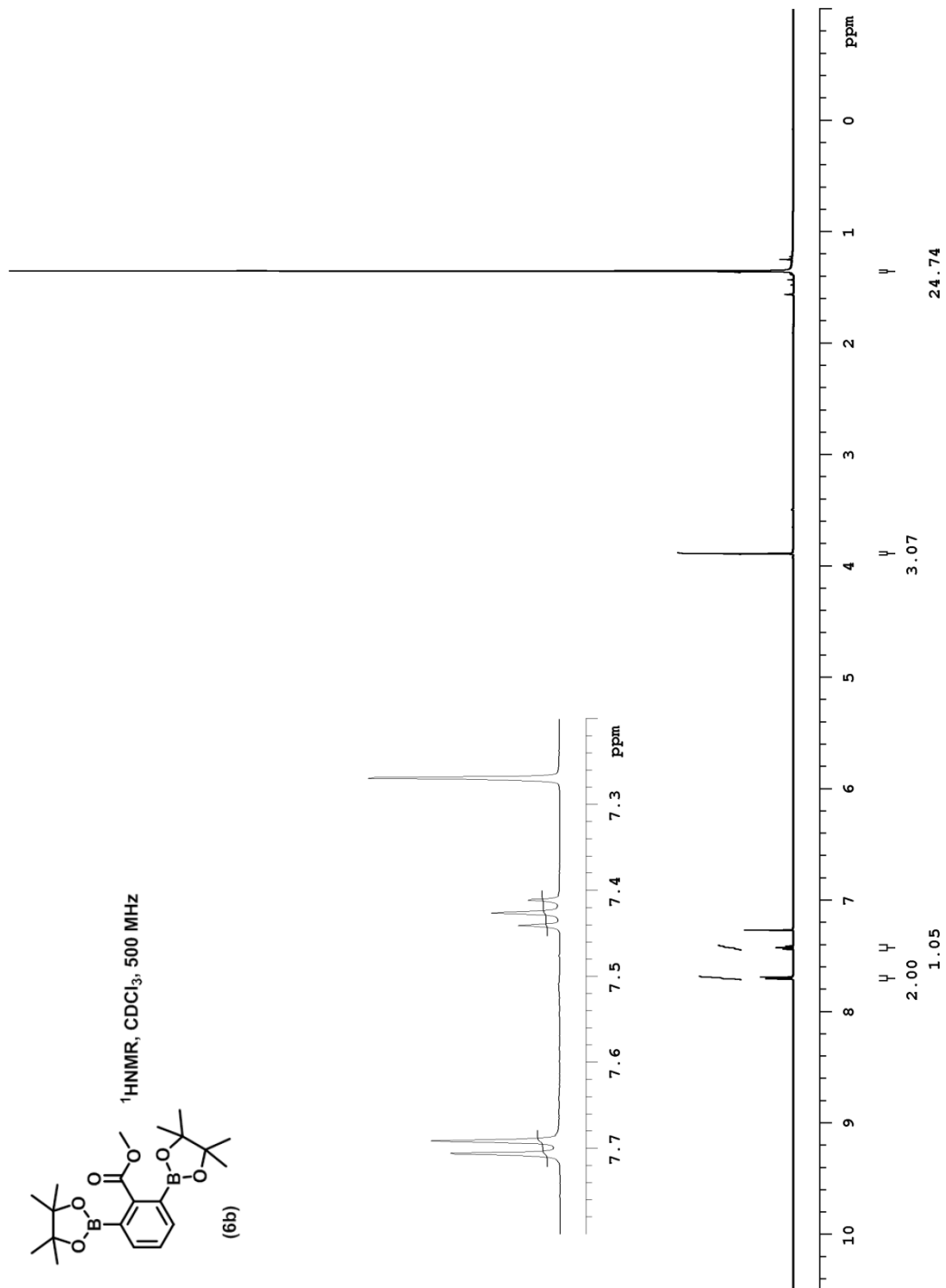
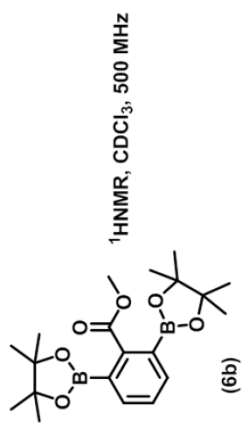
References

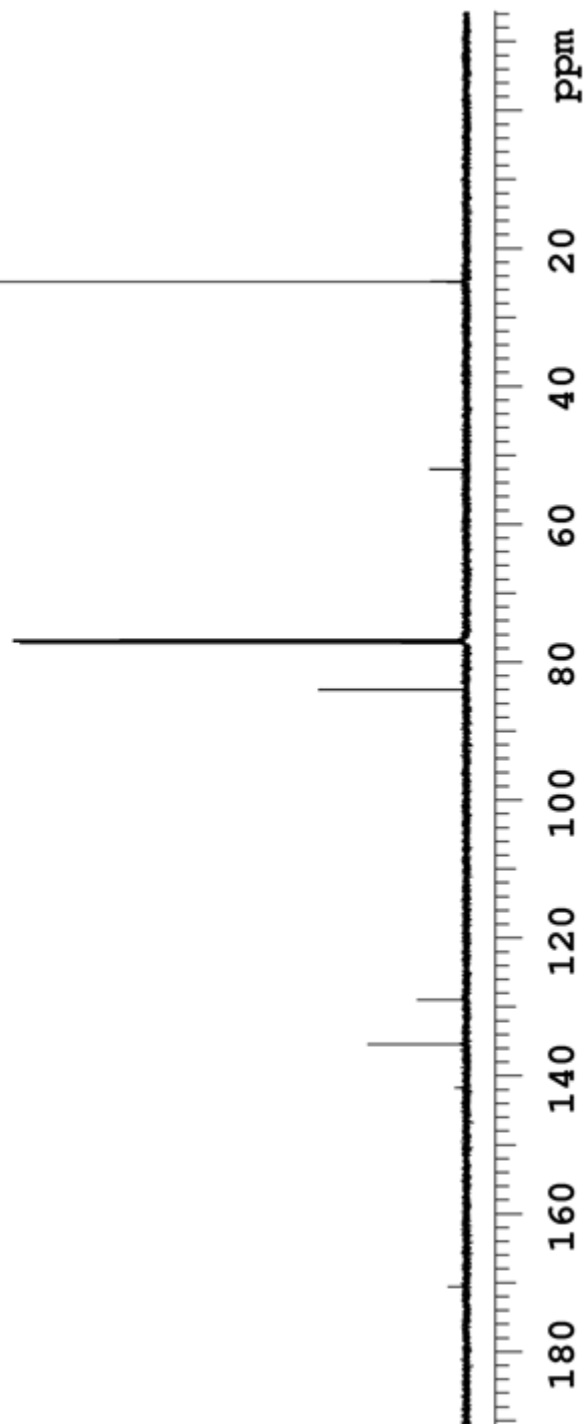
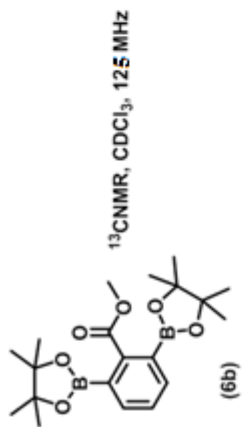
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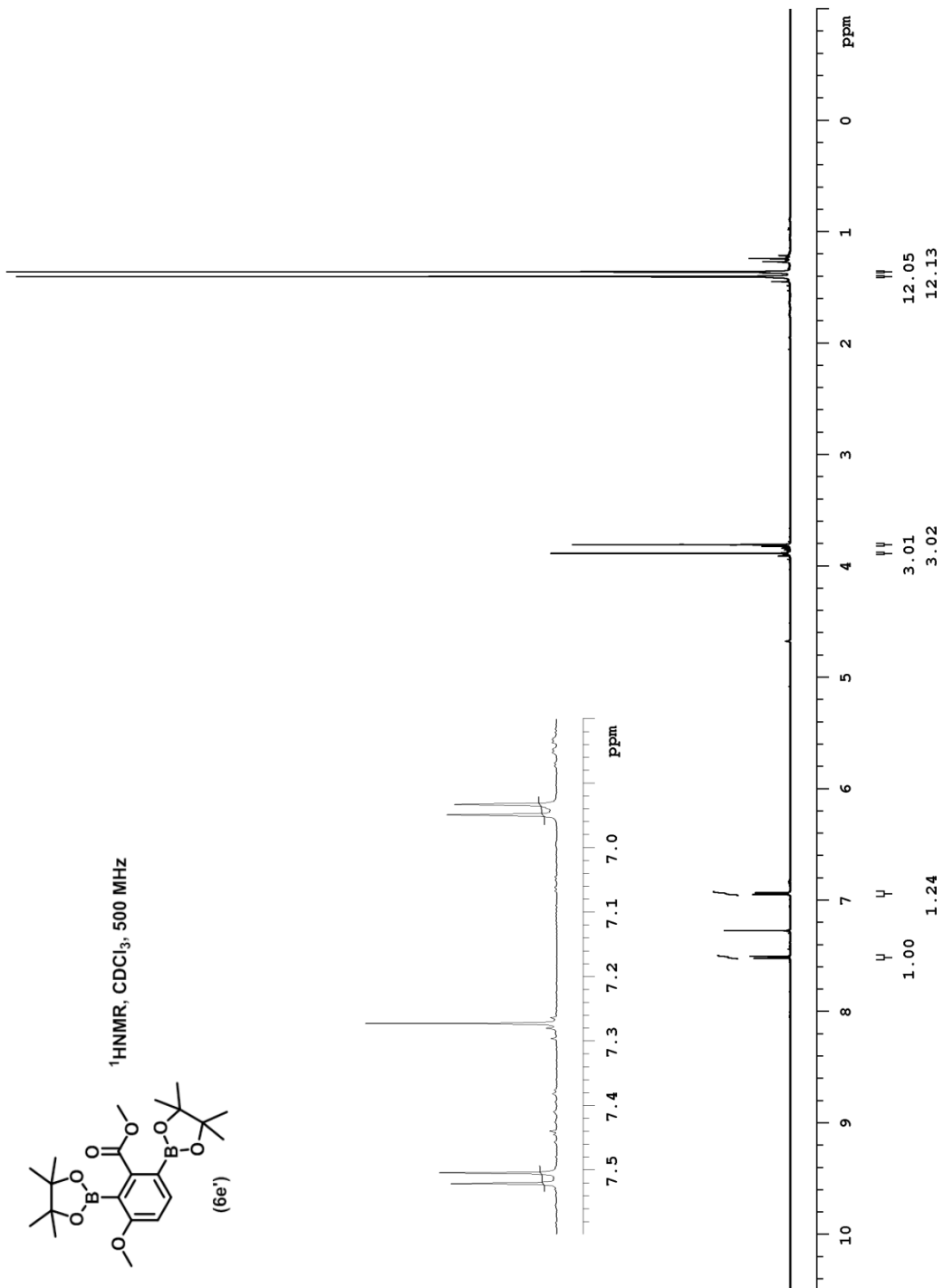
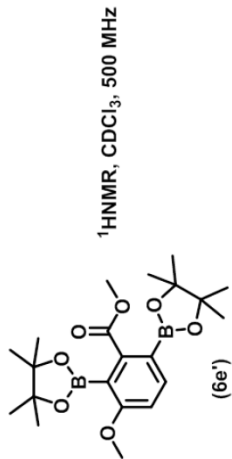


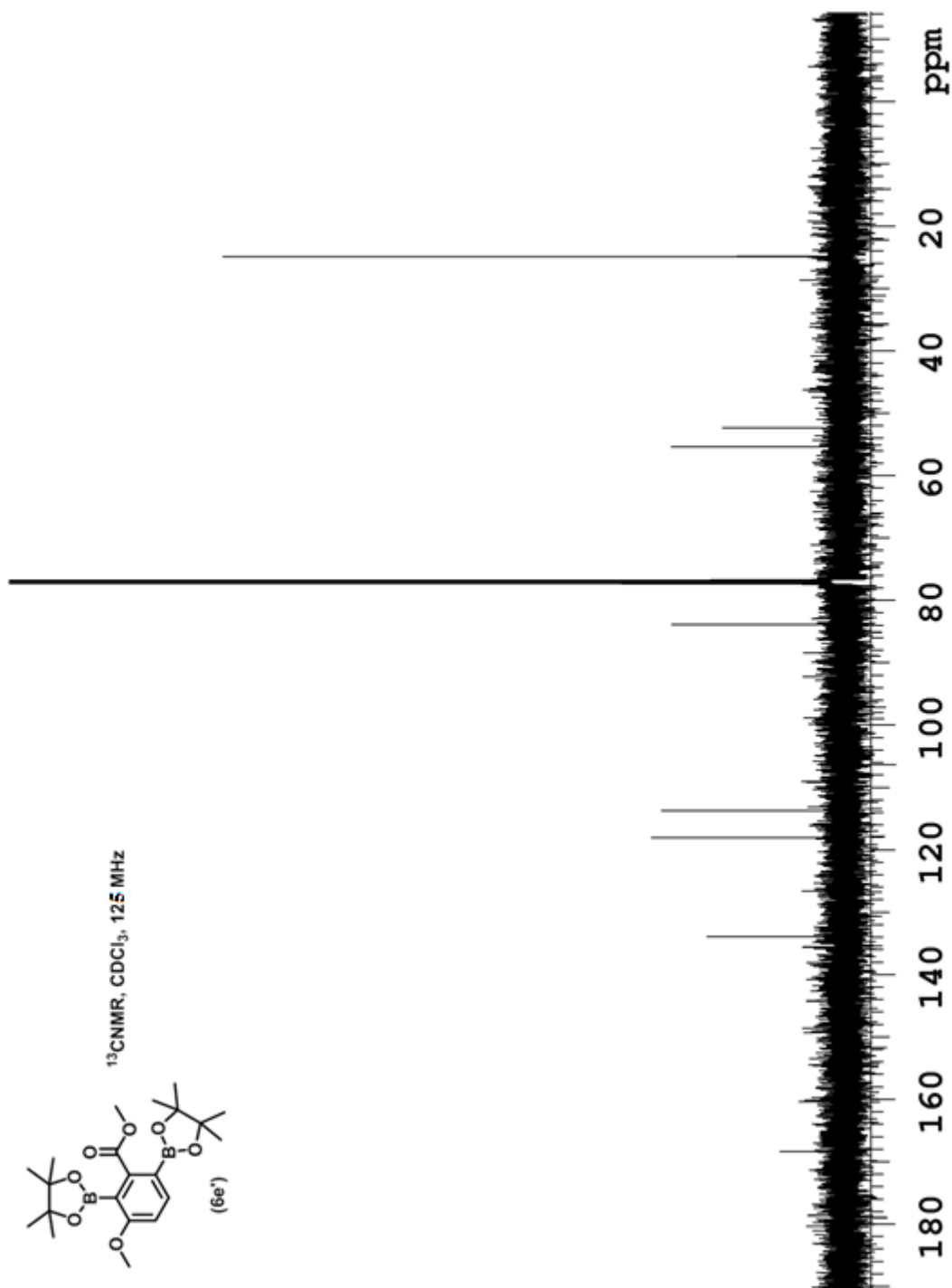
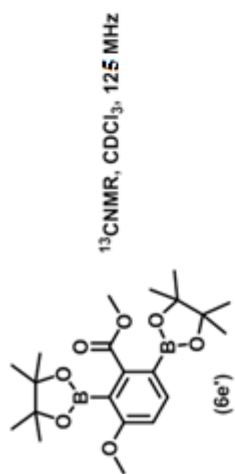


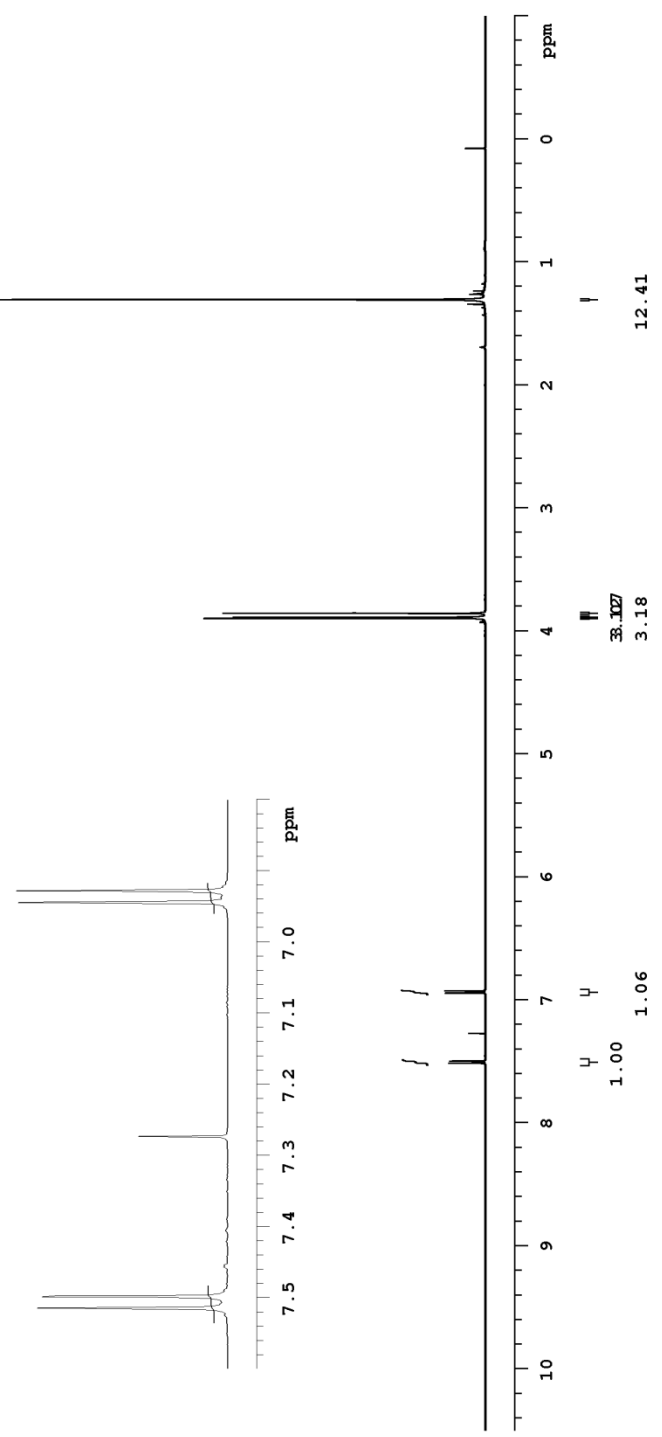
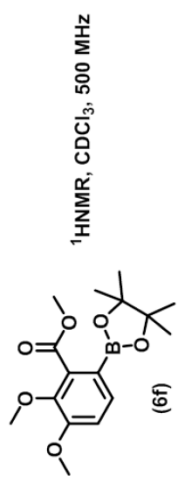


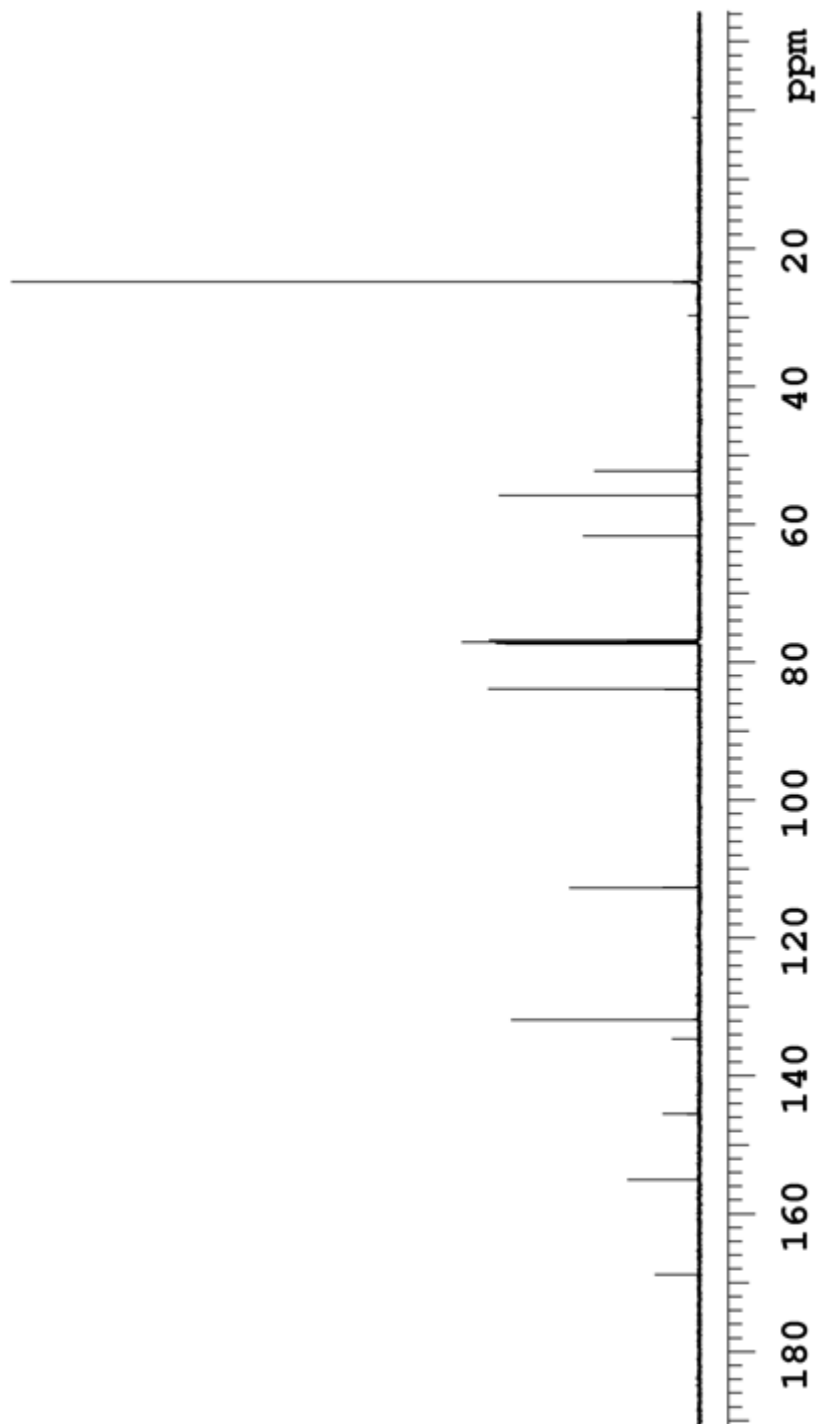
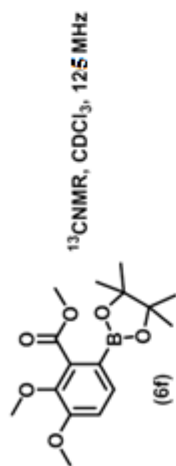


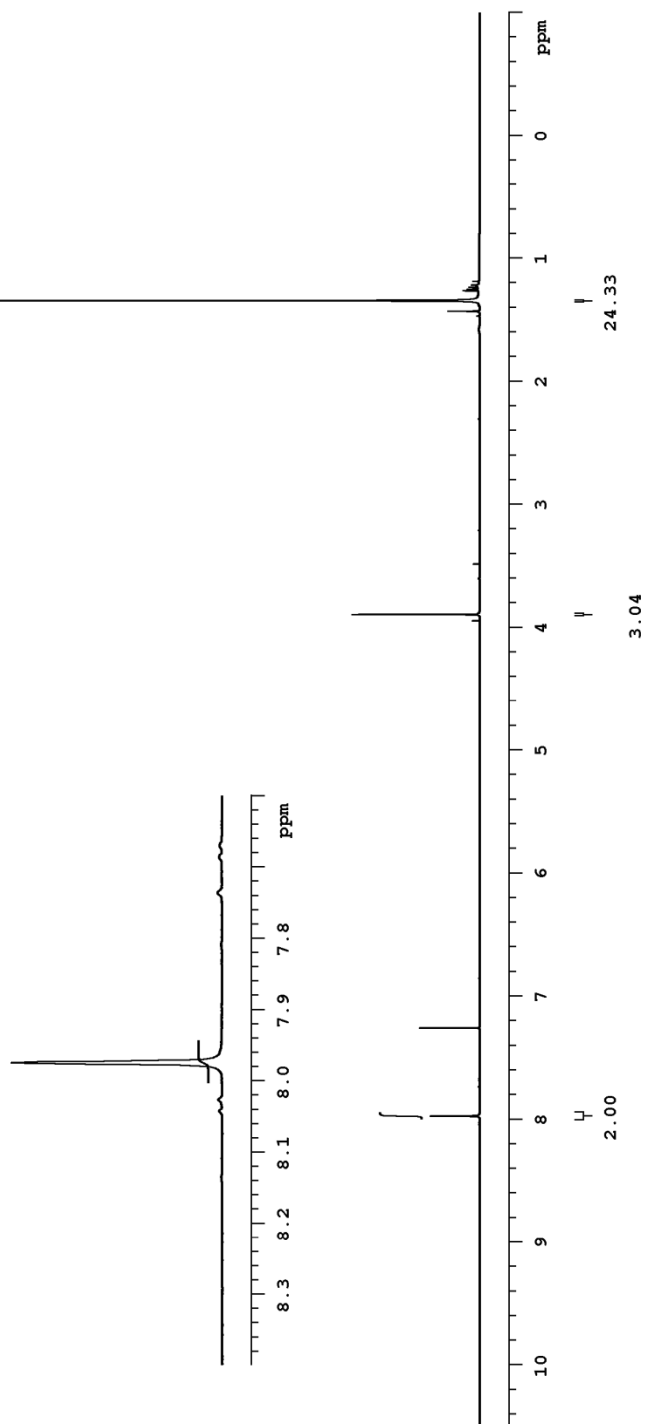
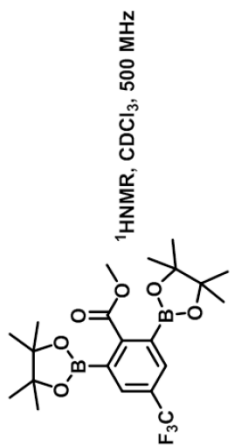


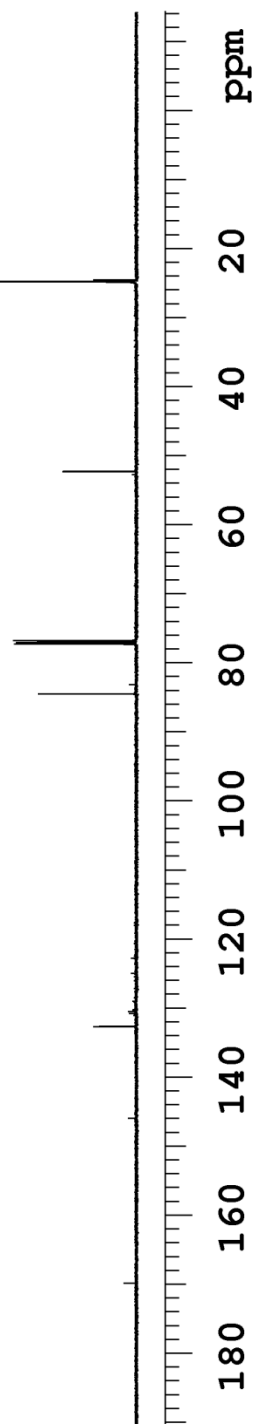
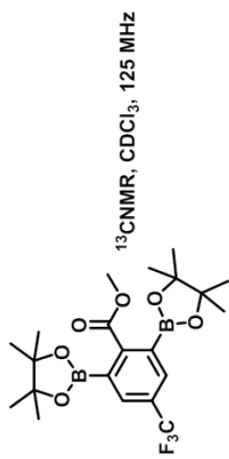


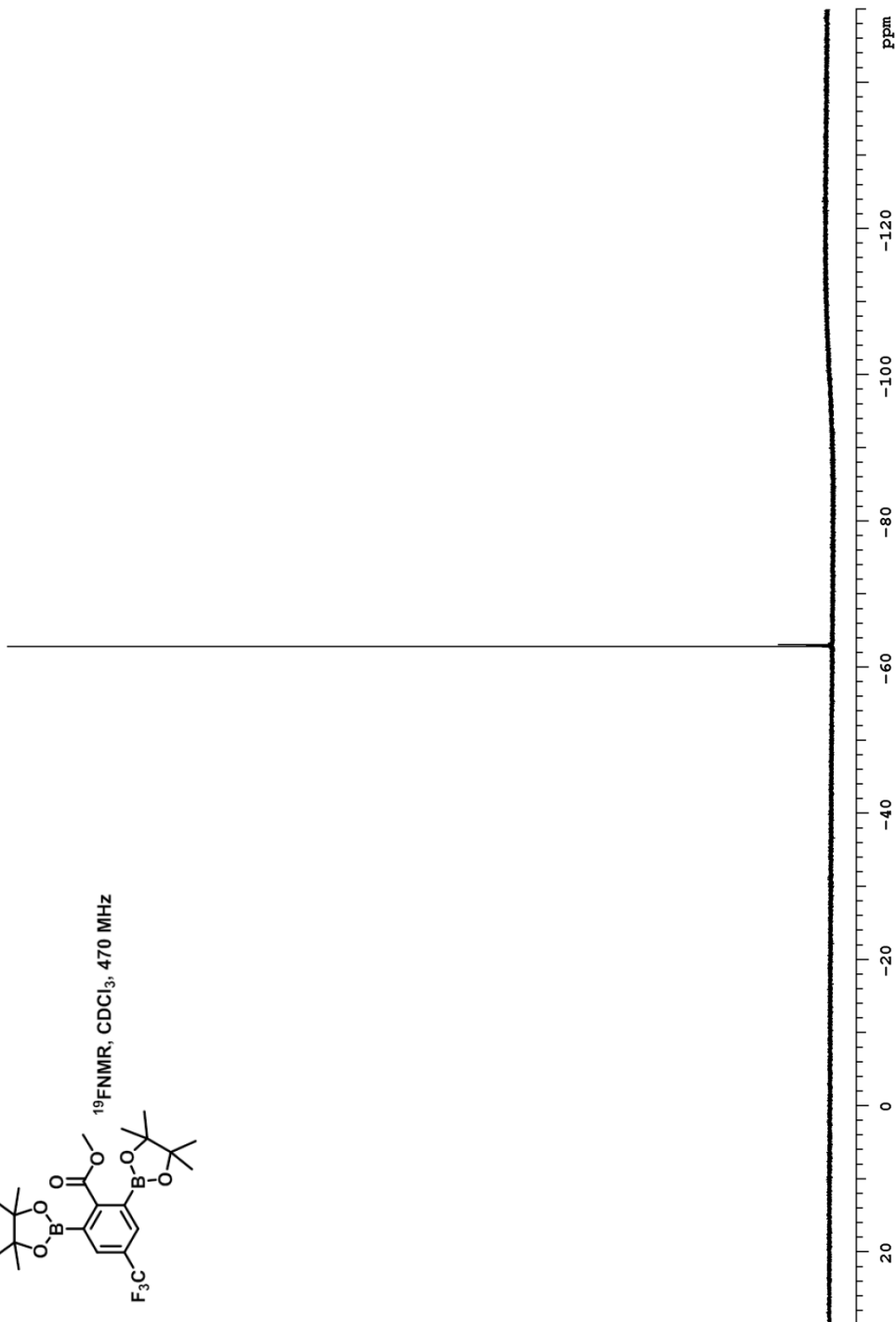
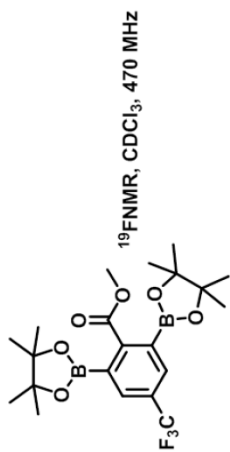


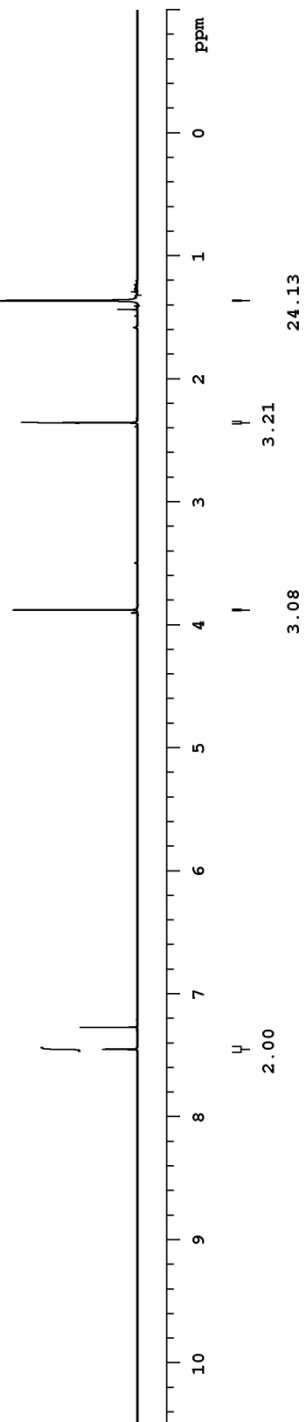
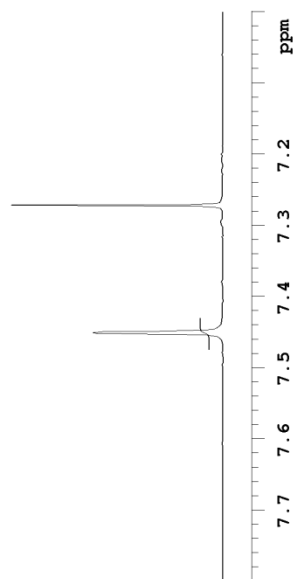
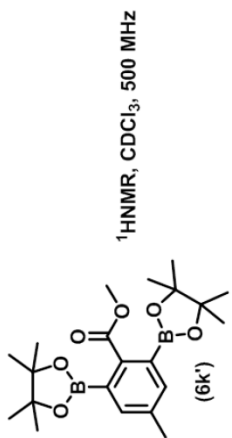


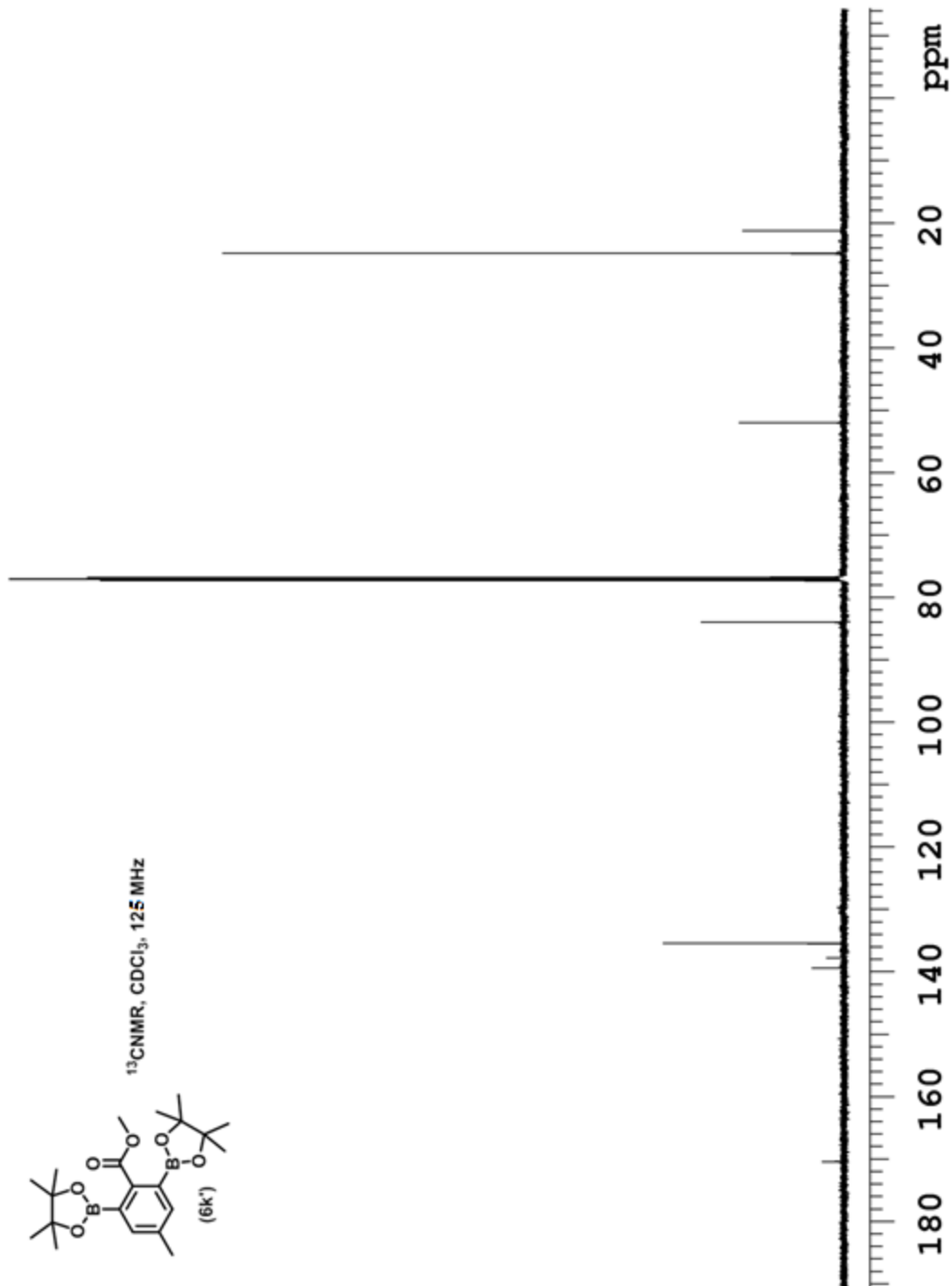
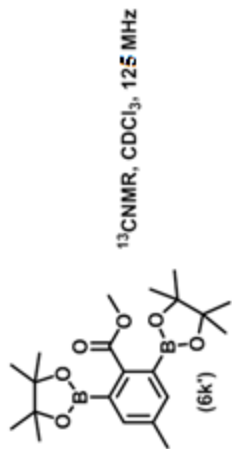


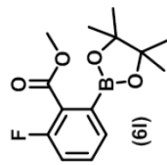




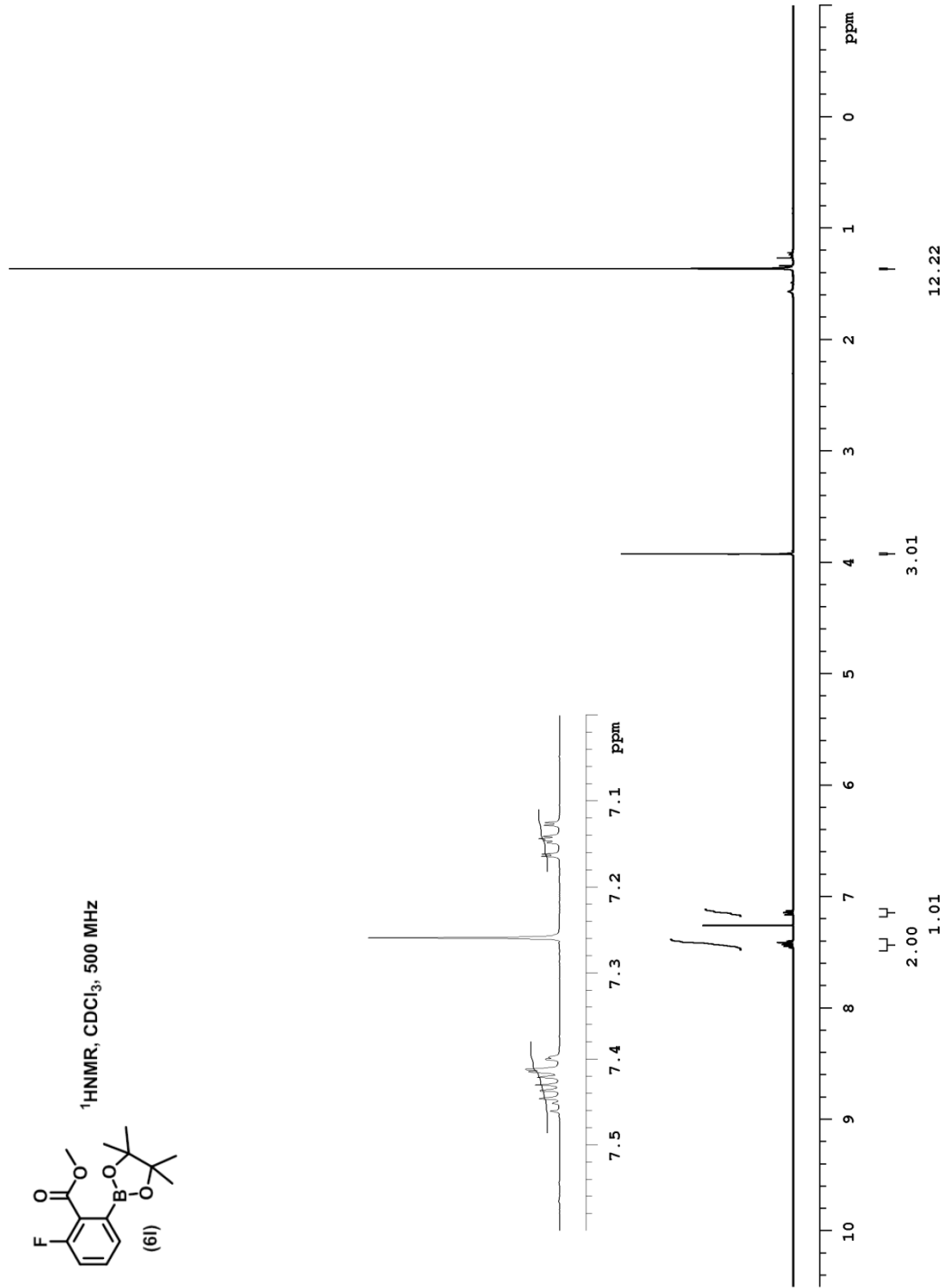


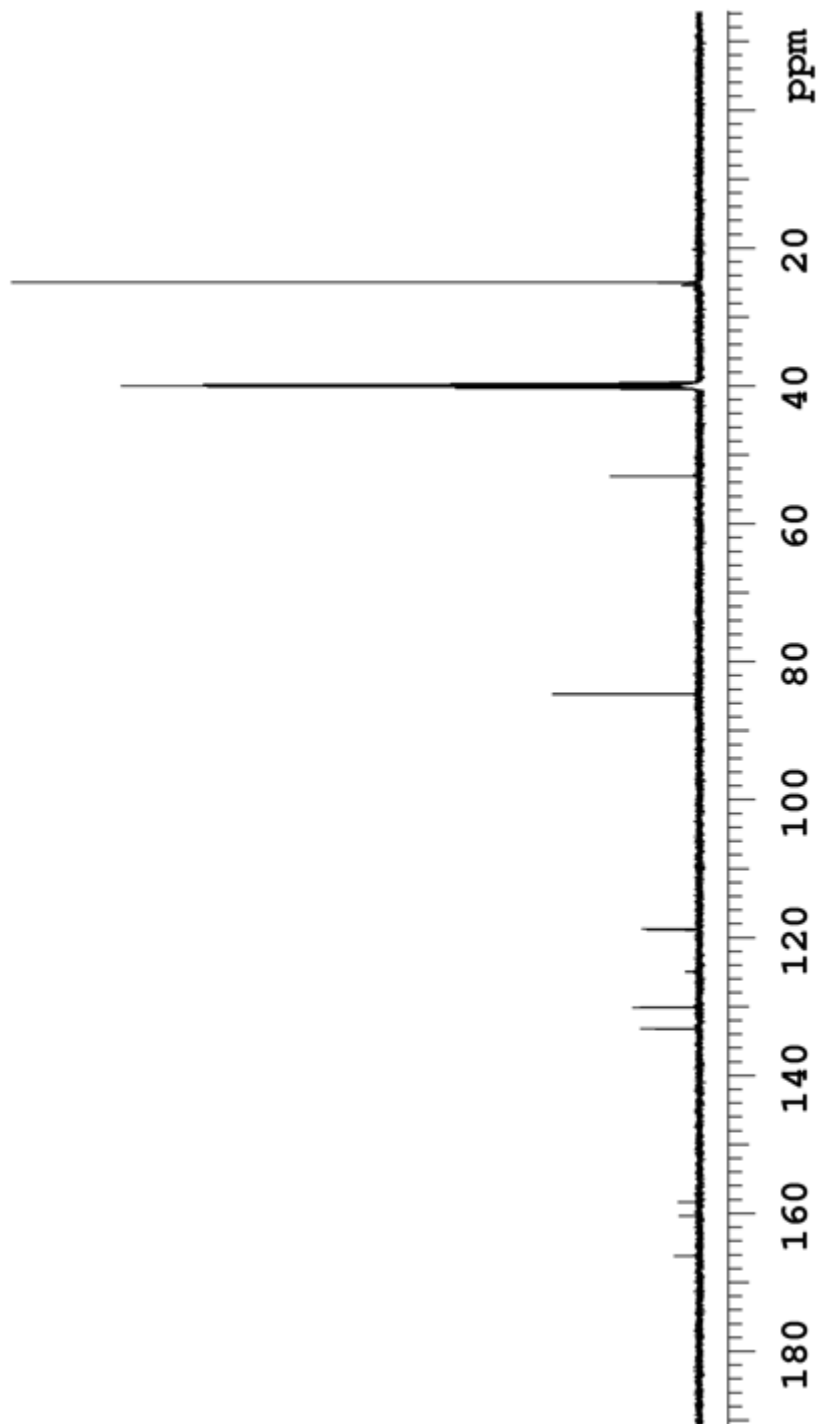


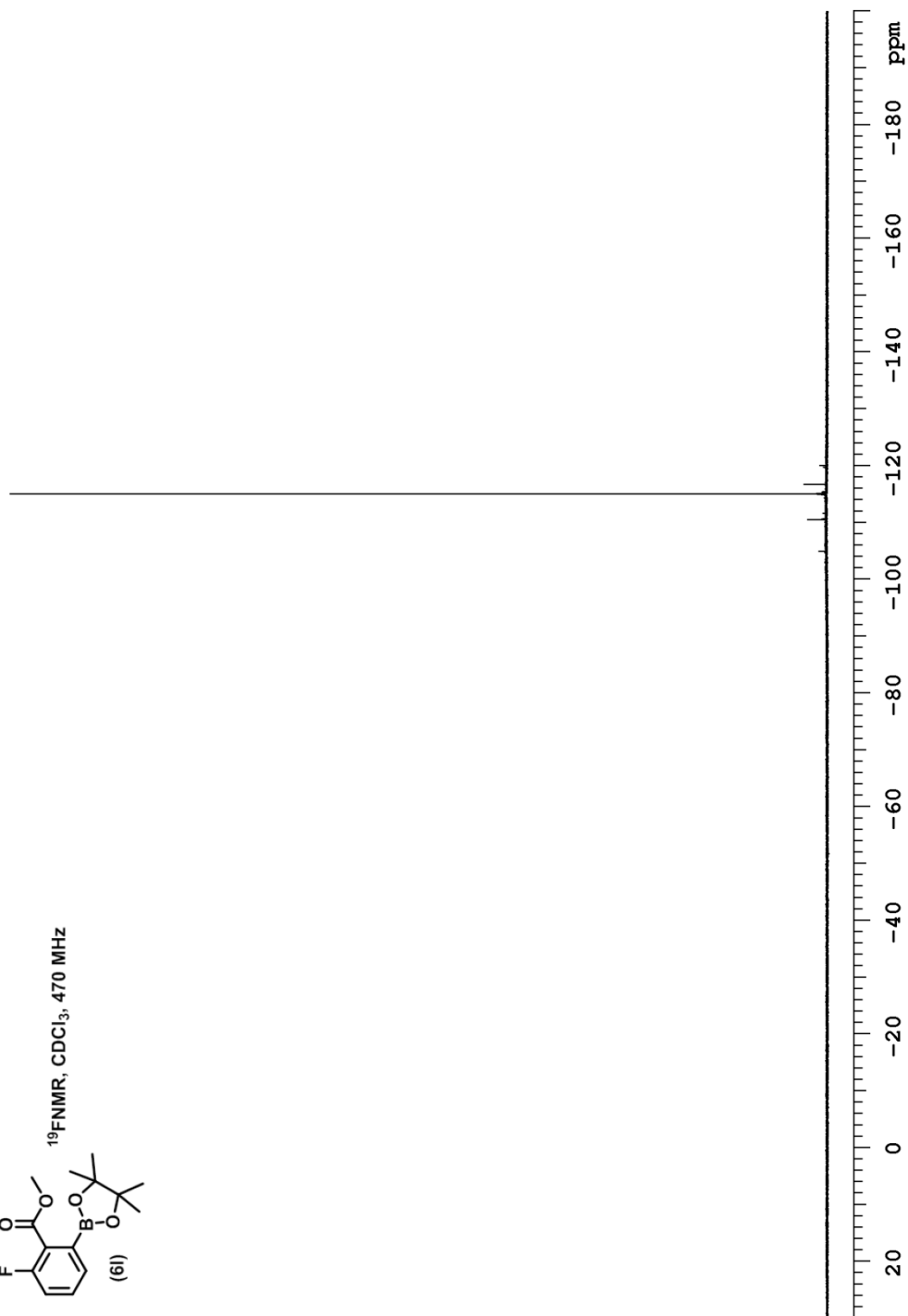


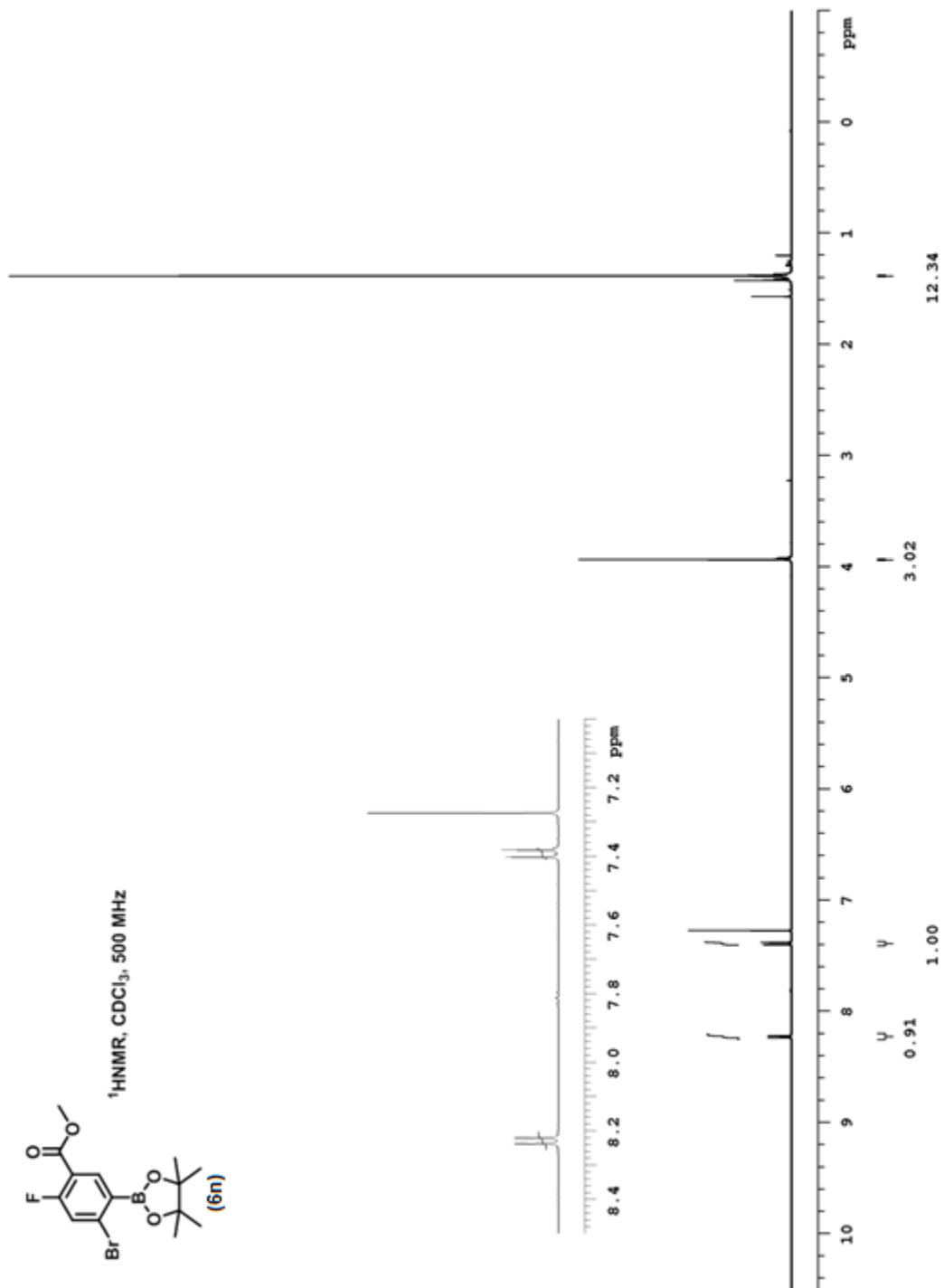
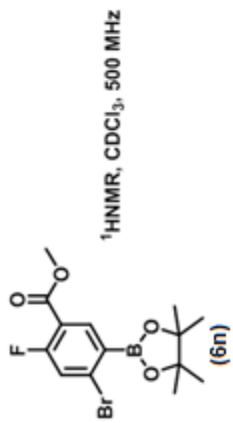


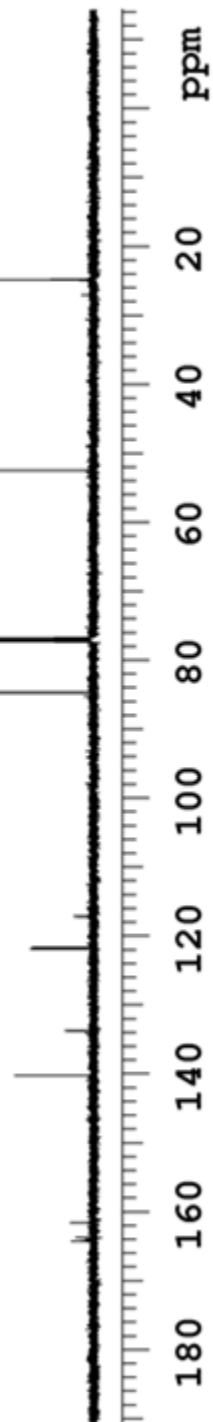
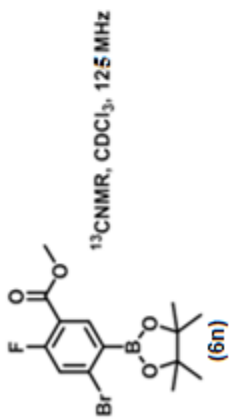
¹HNMR, CDCl₃, 500 MHz

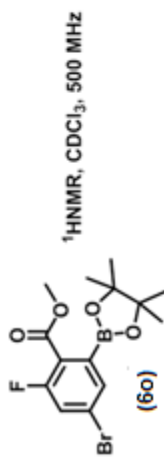




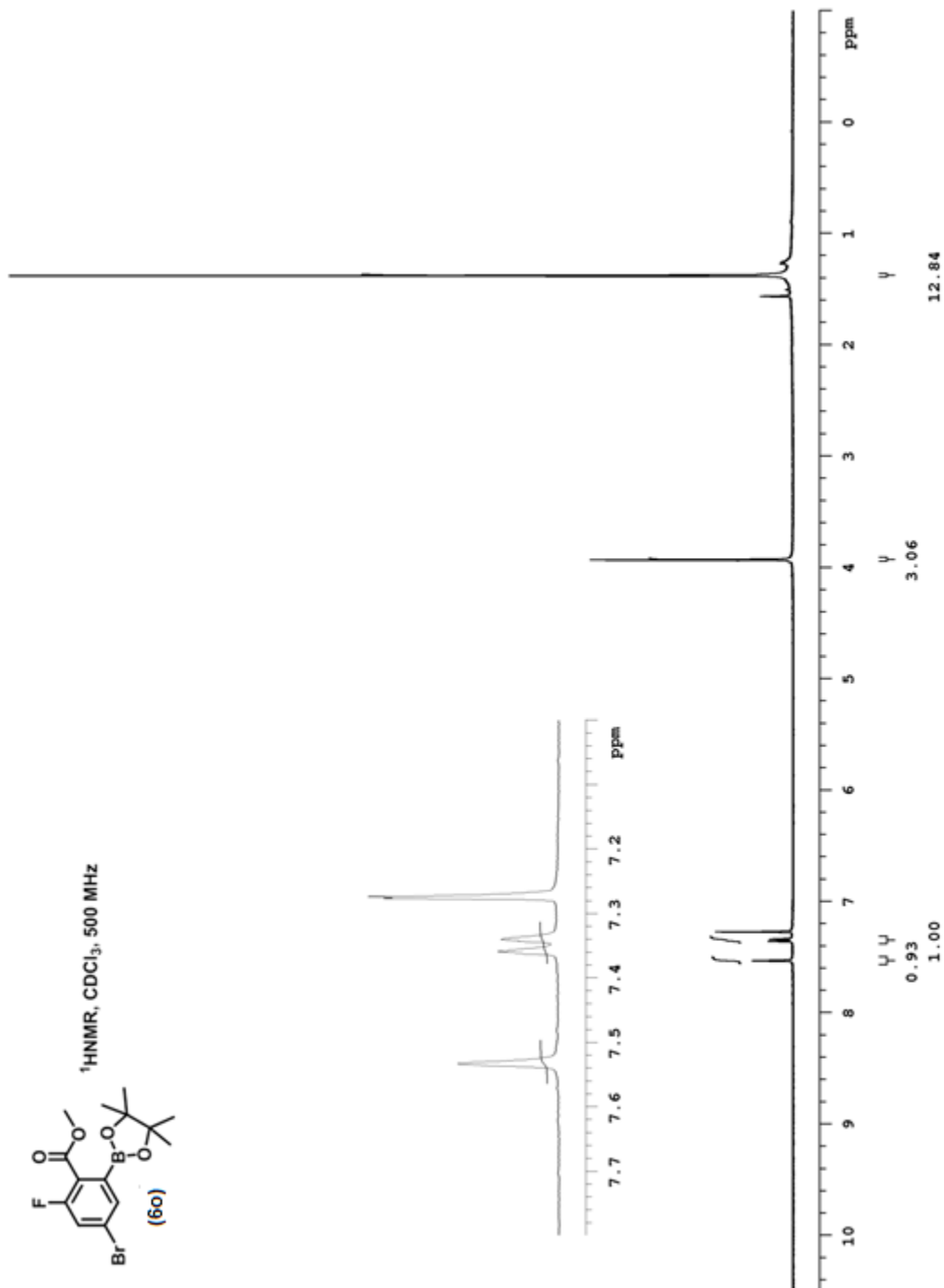


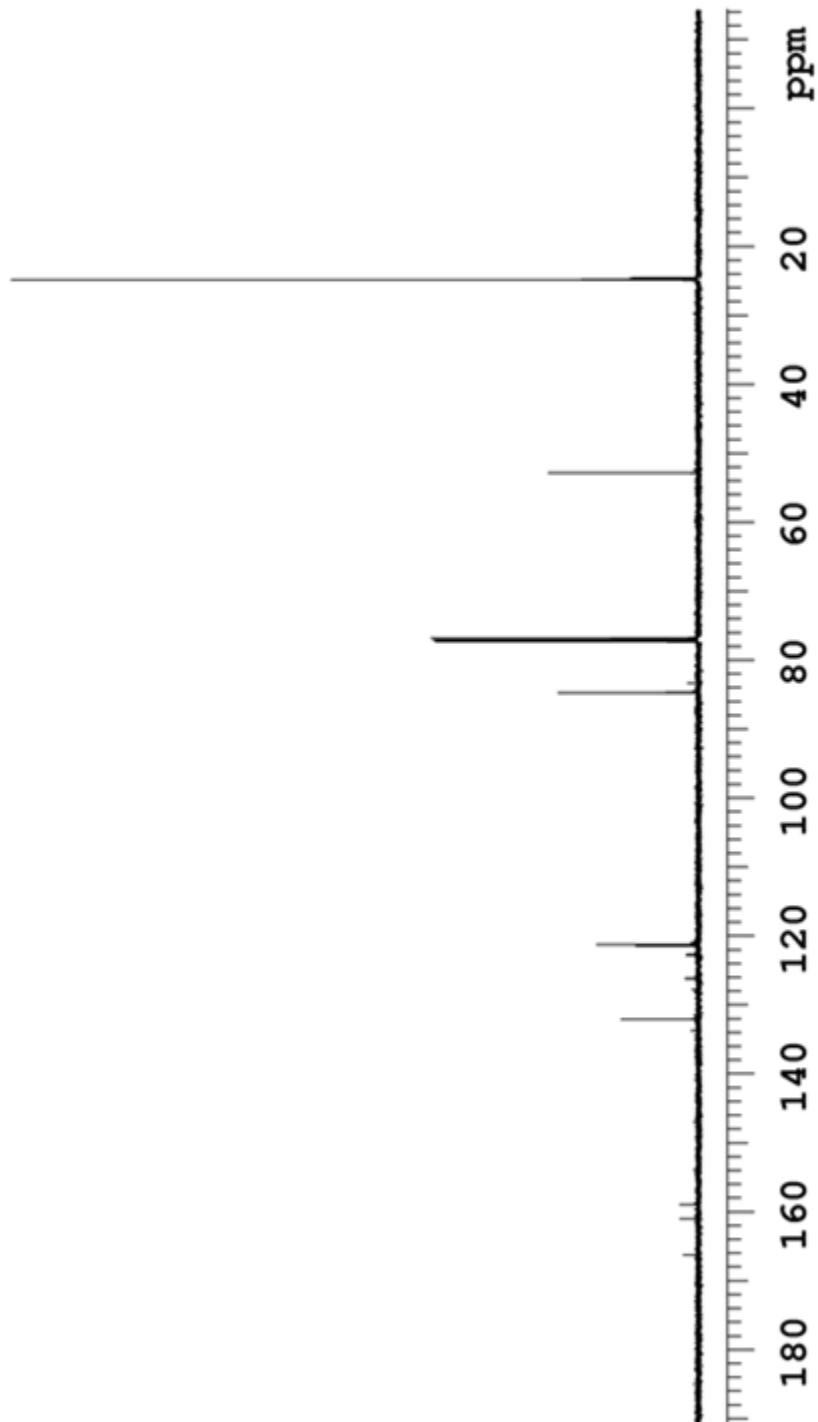
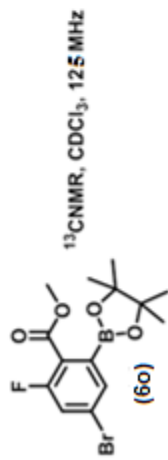


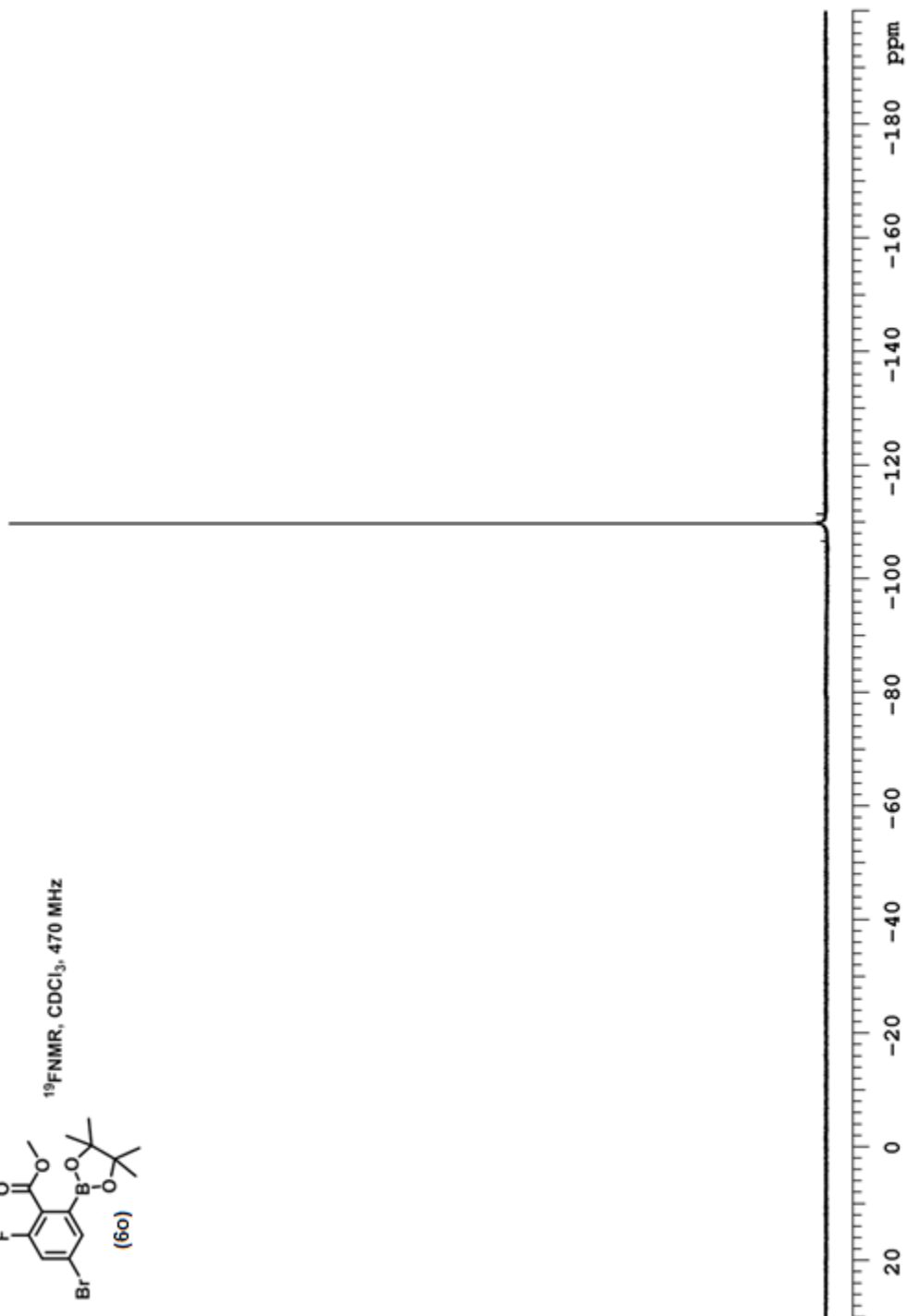
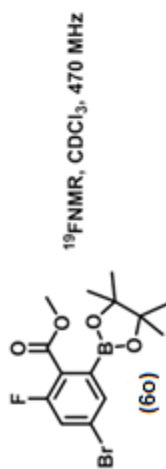


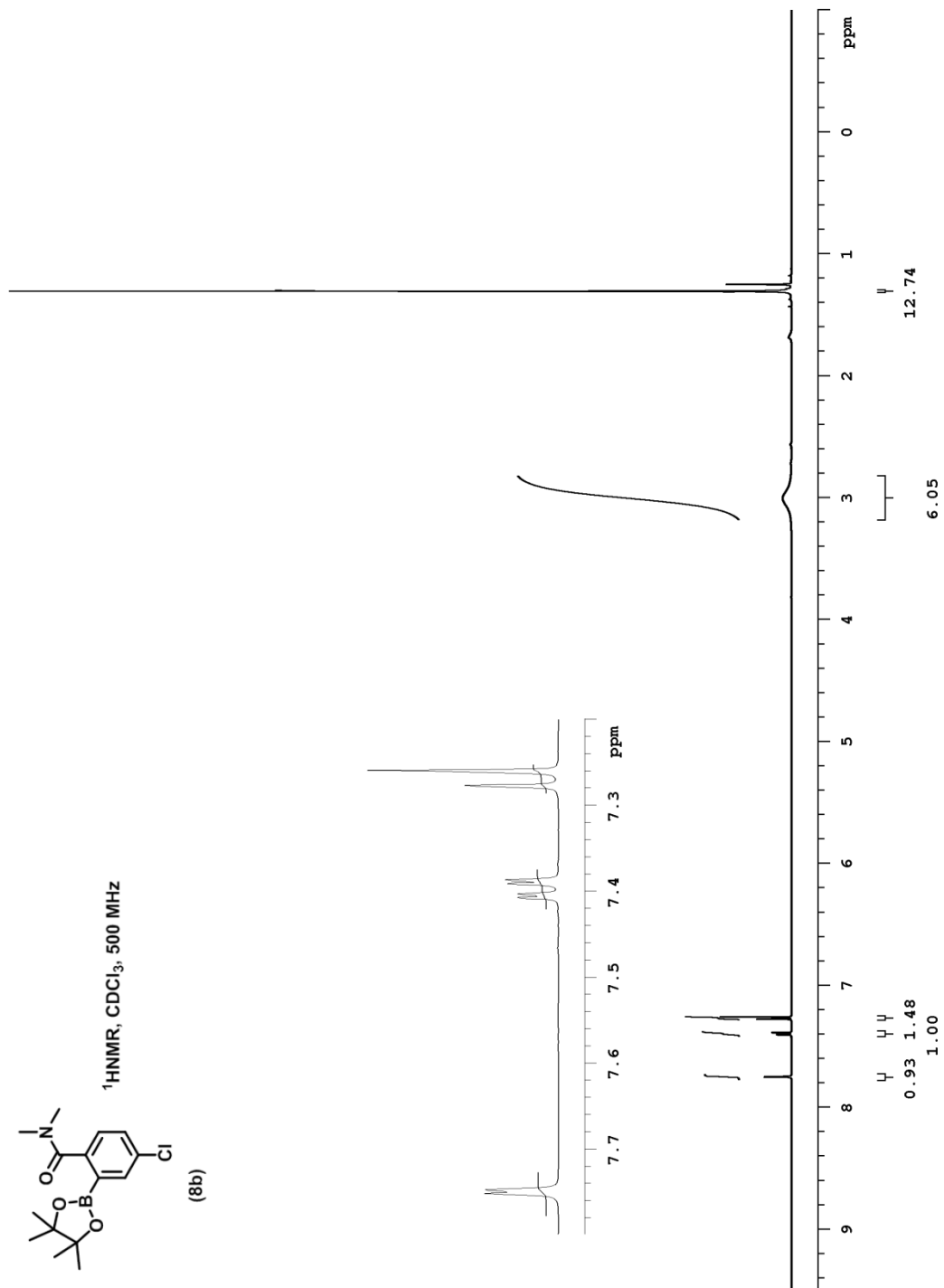
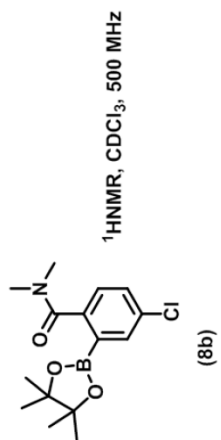


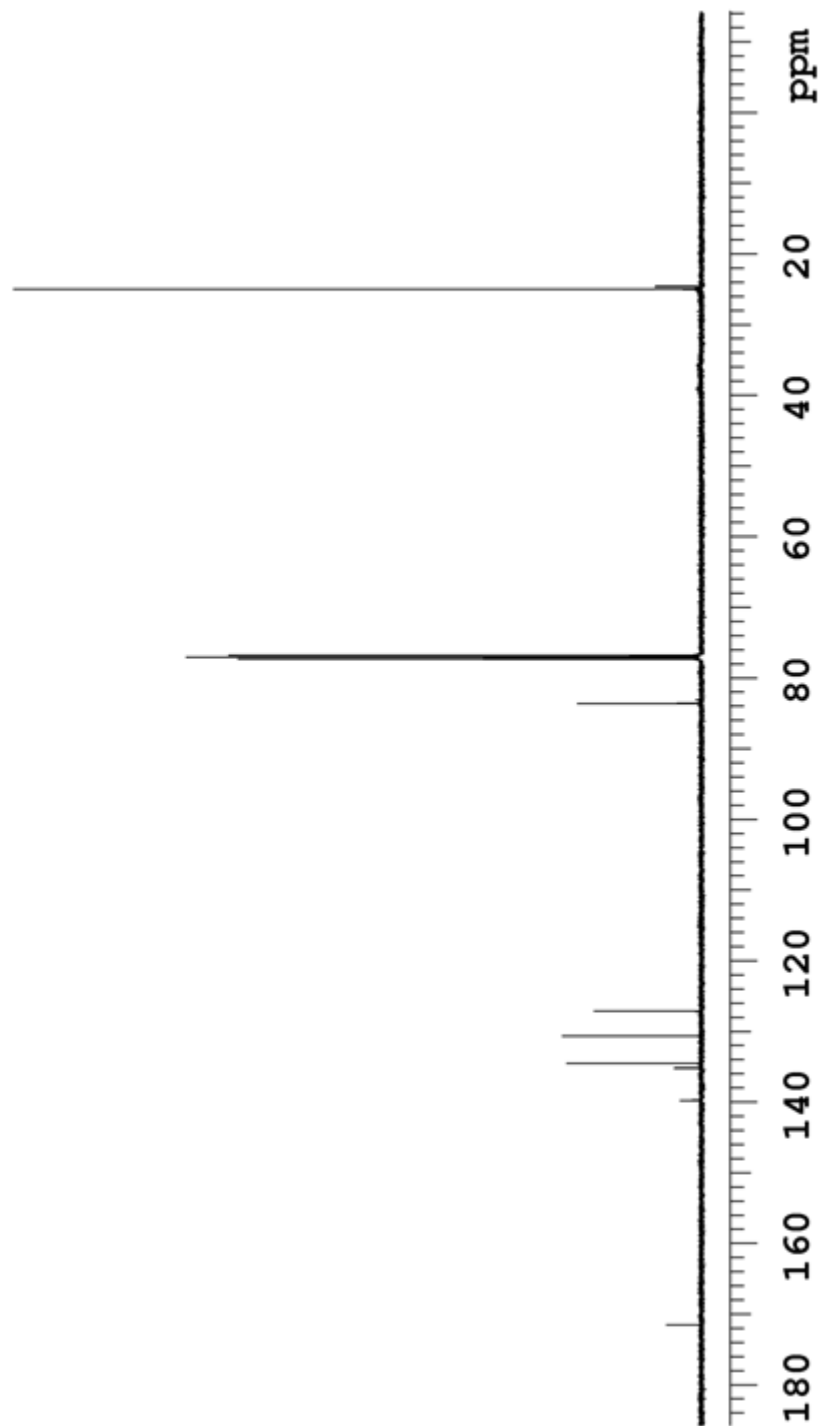
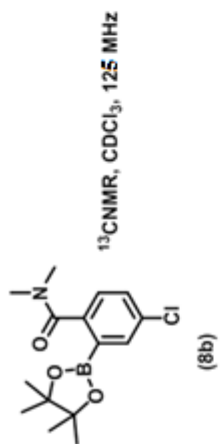
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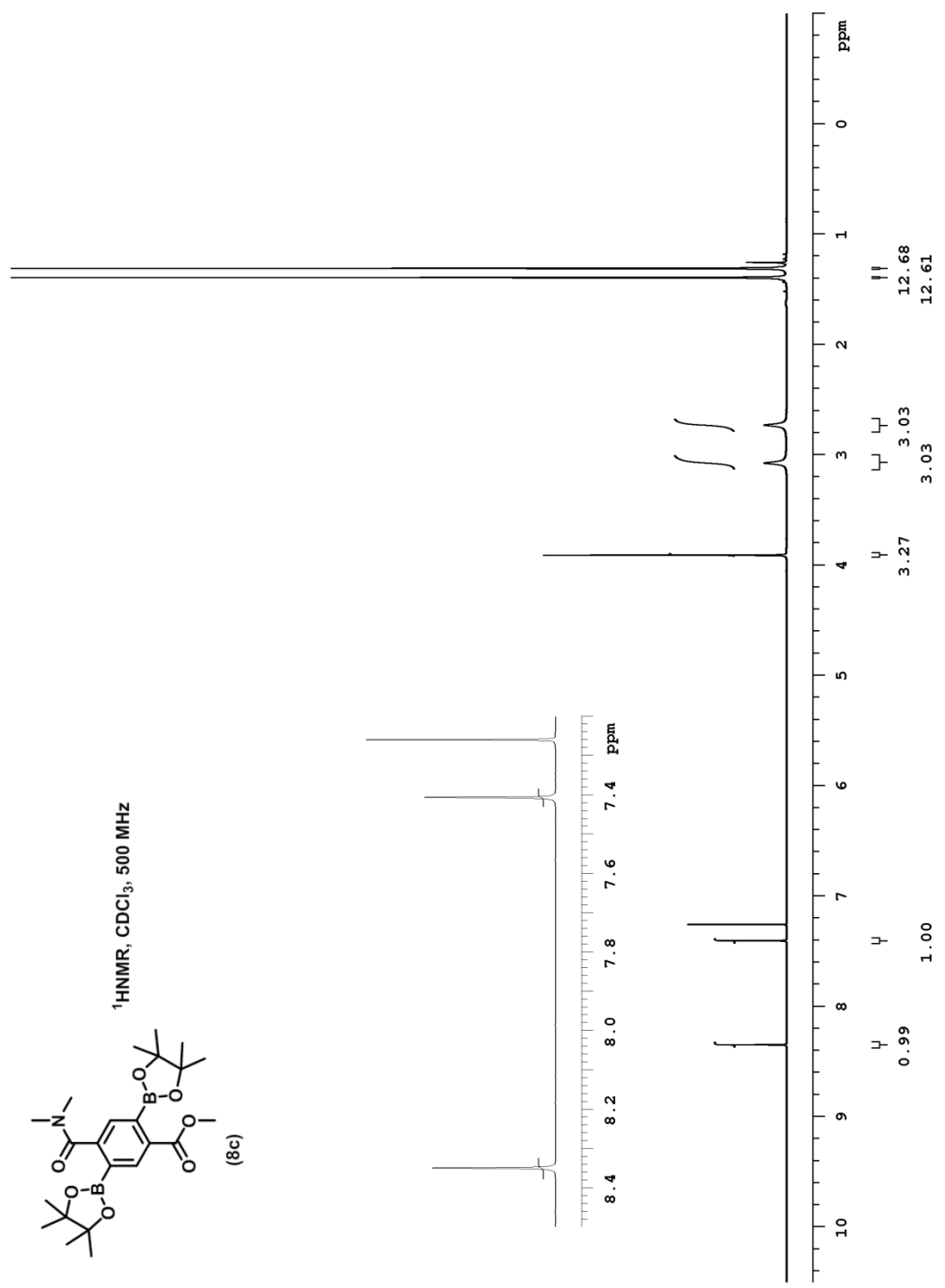
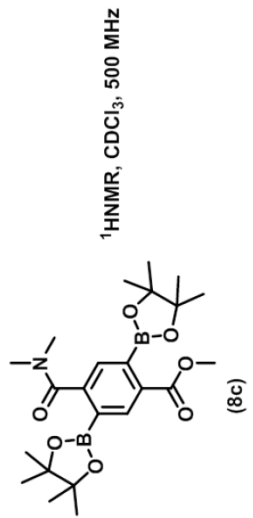


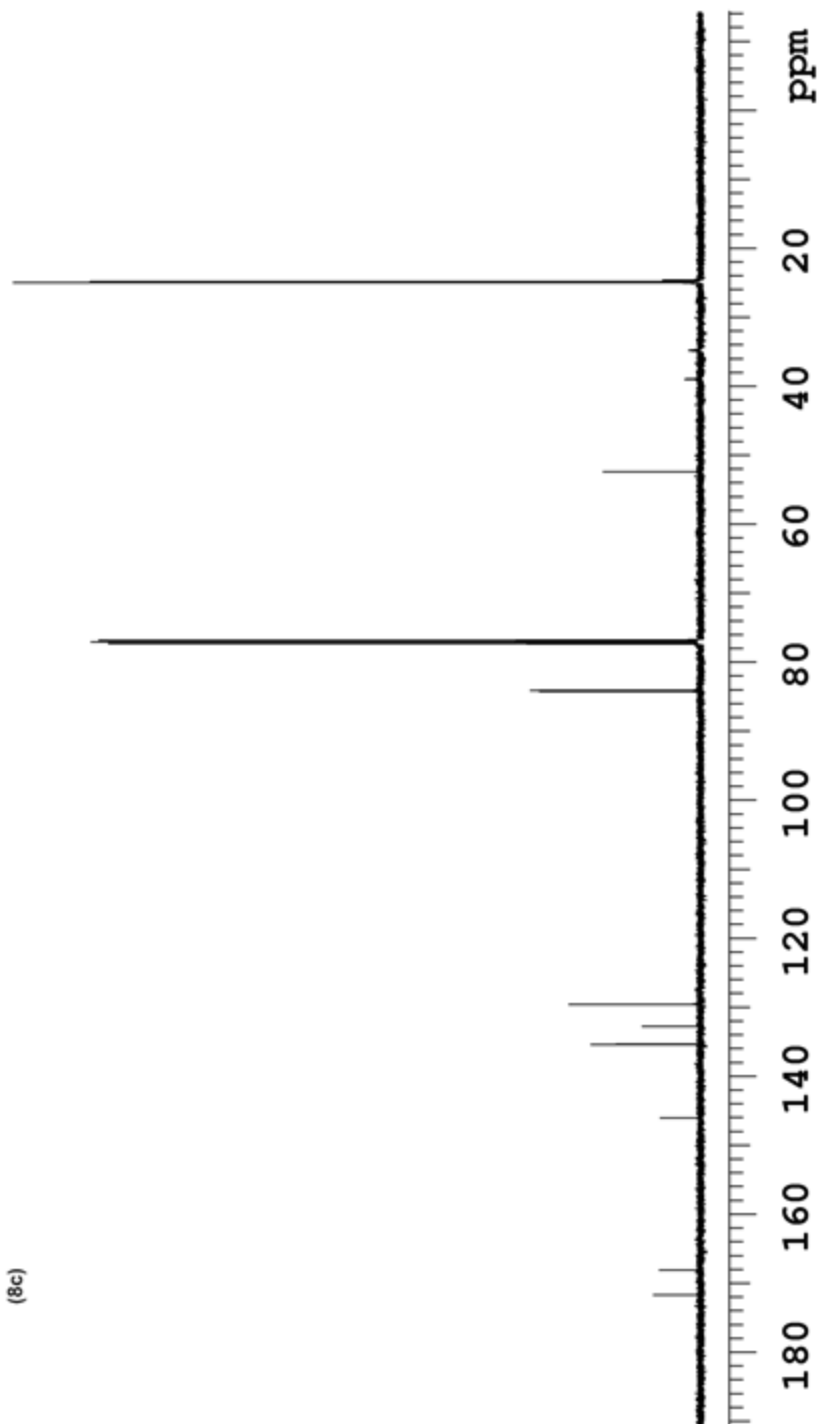
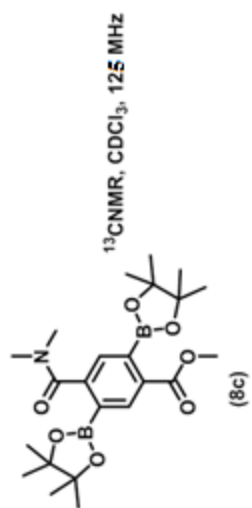




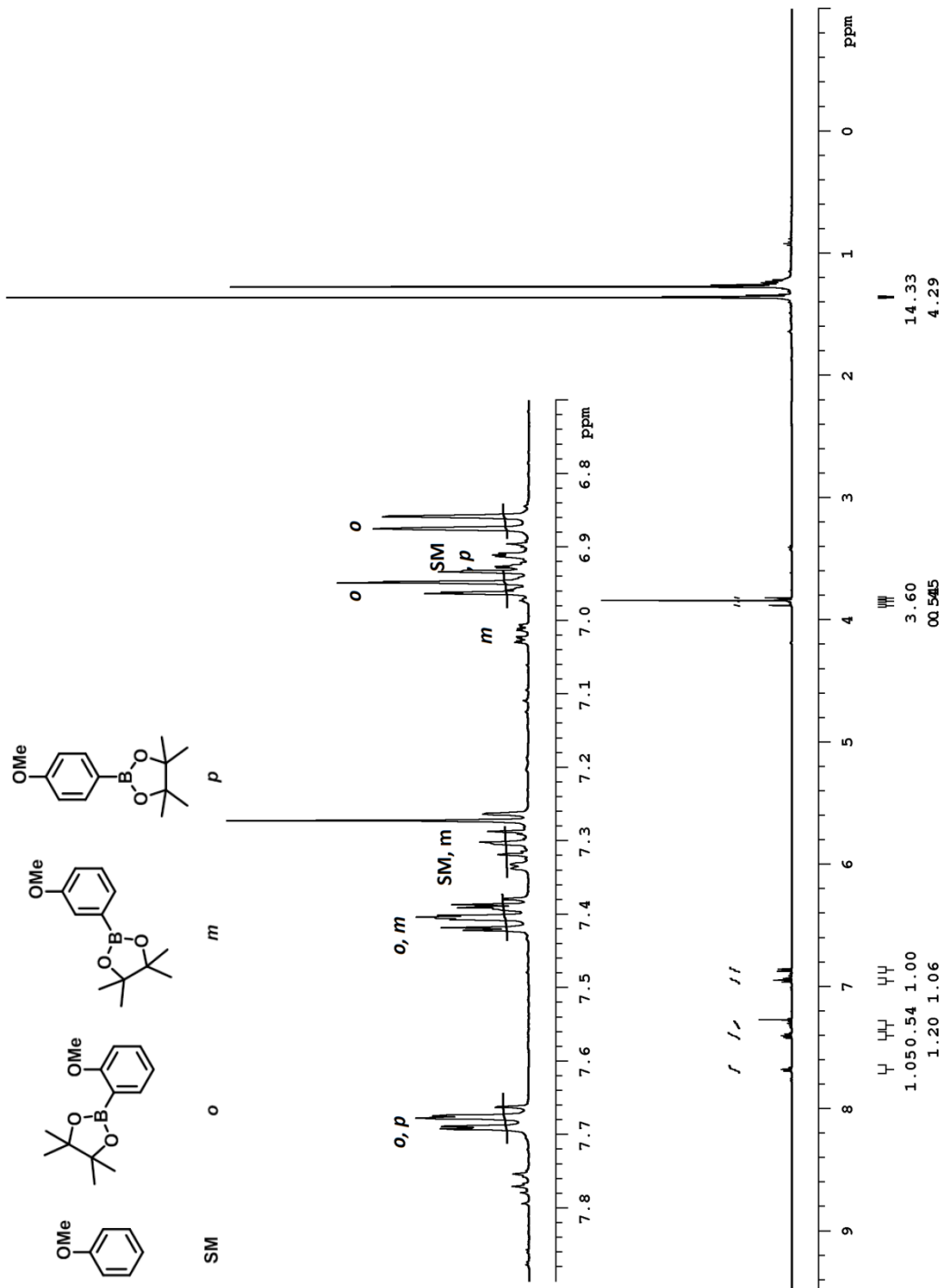


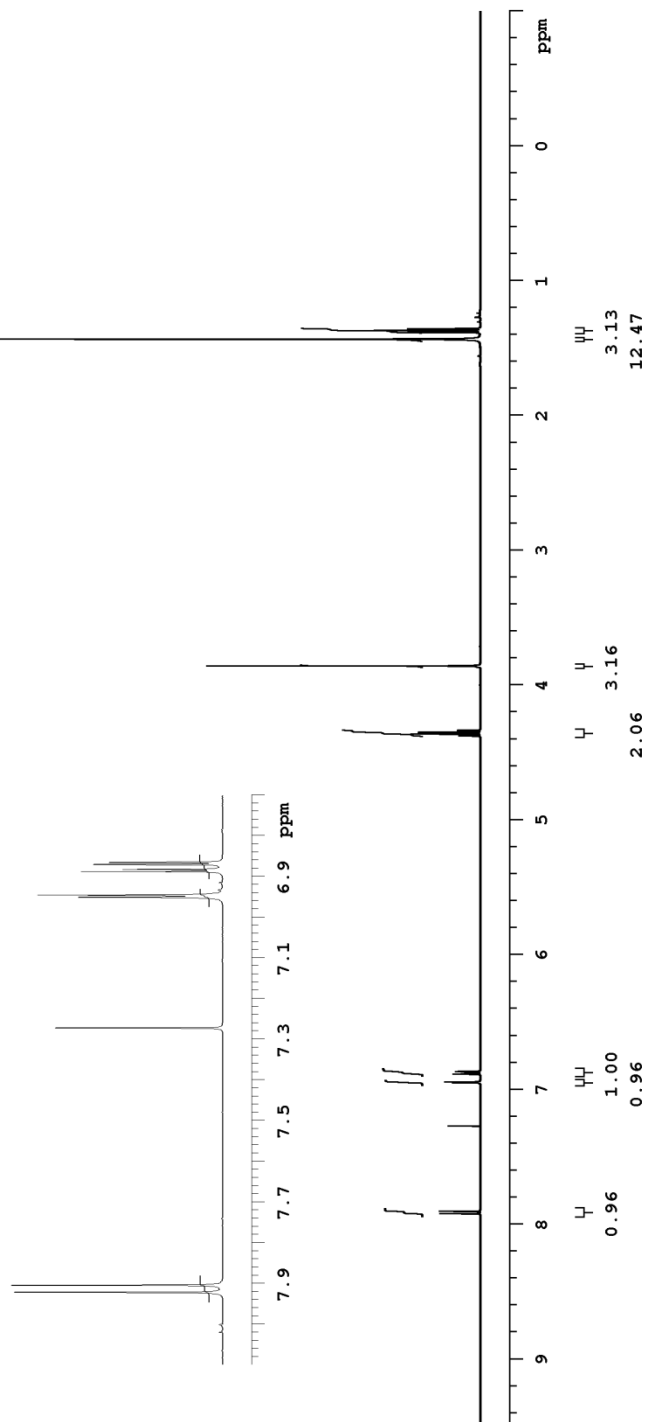
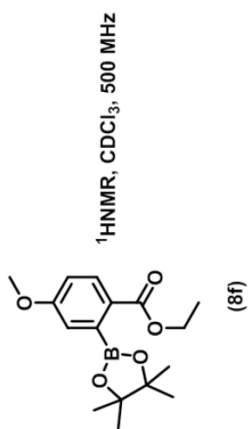


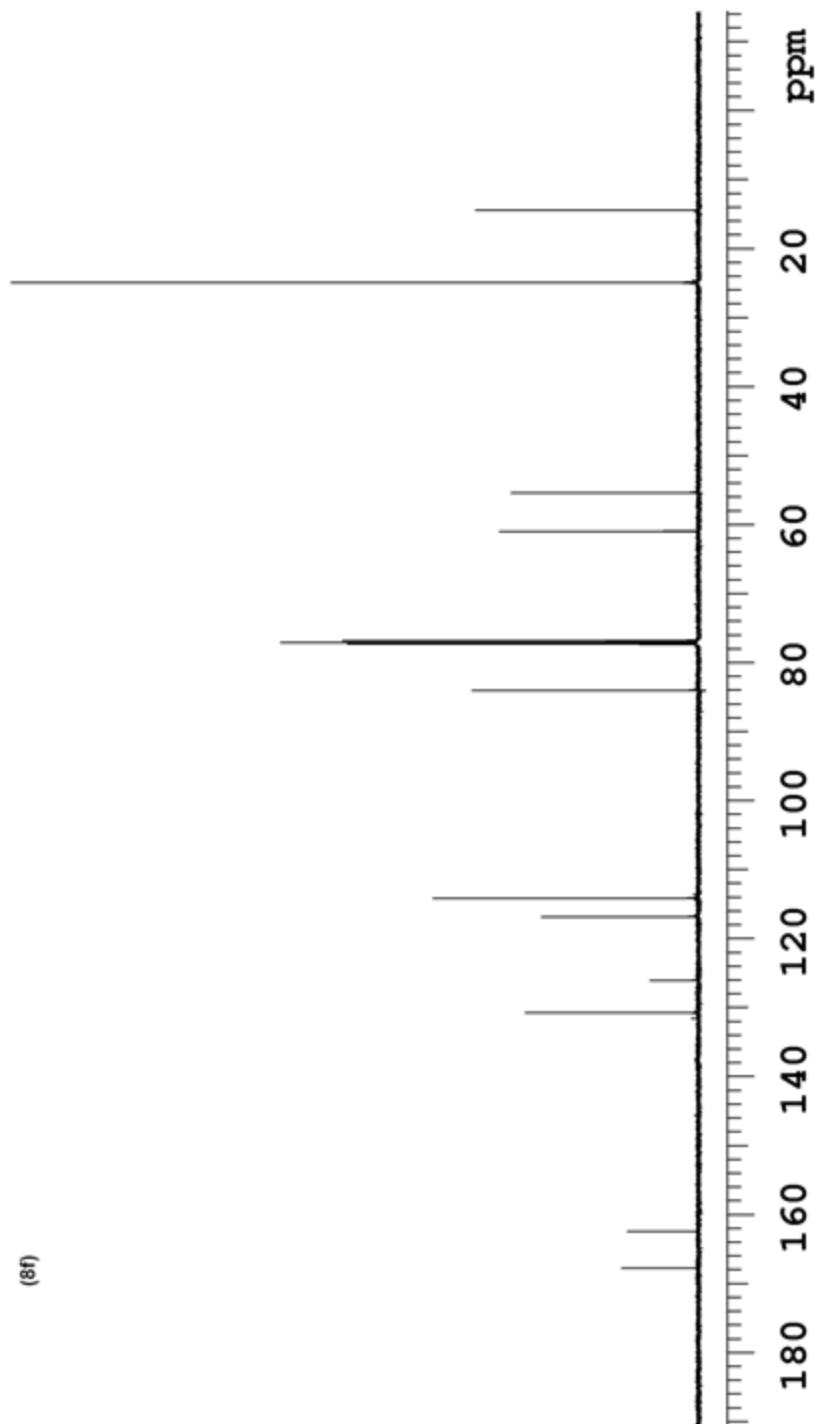
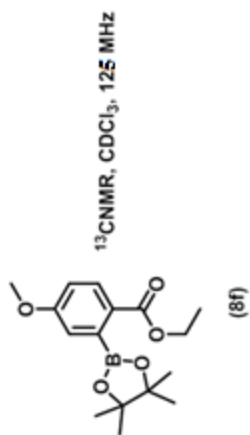


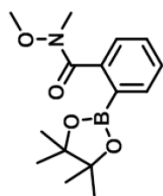


(8d), ¹H NMR, CDCl₃, 500 MHz



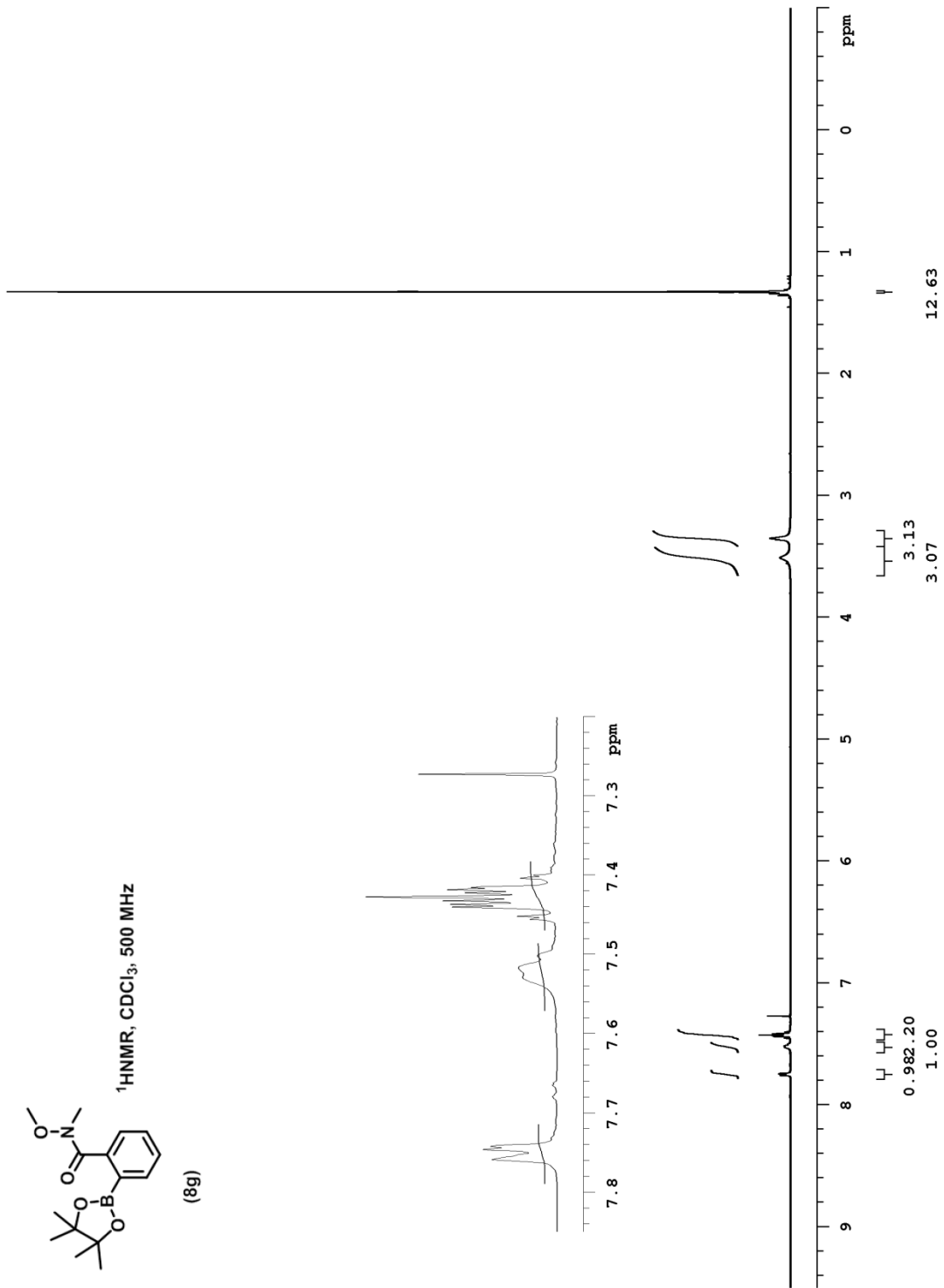


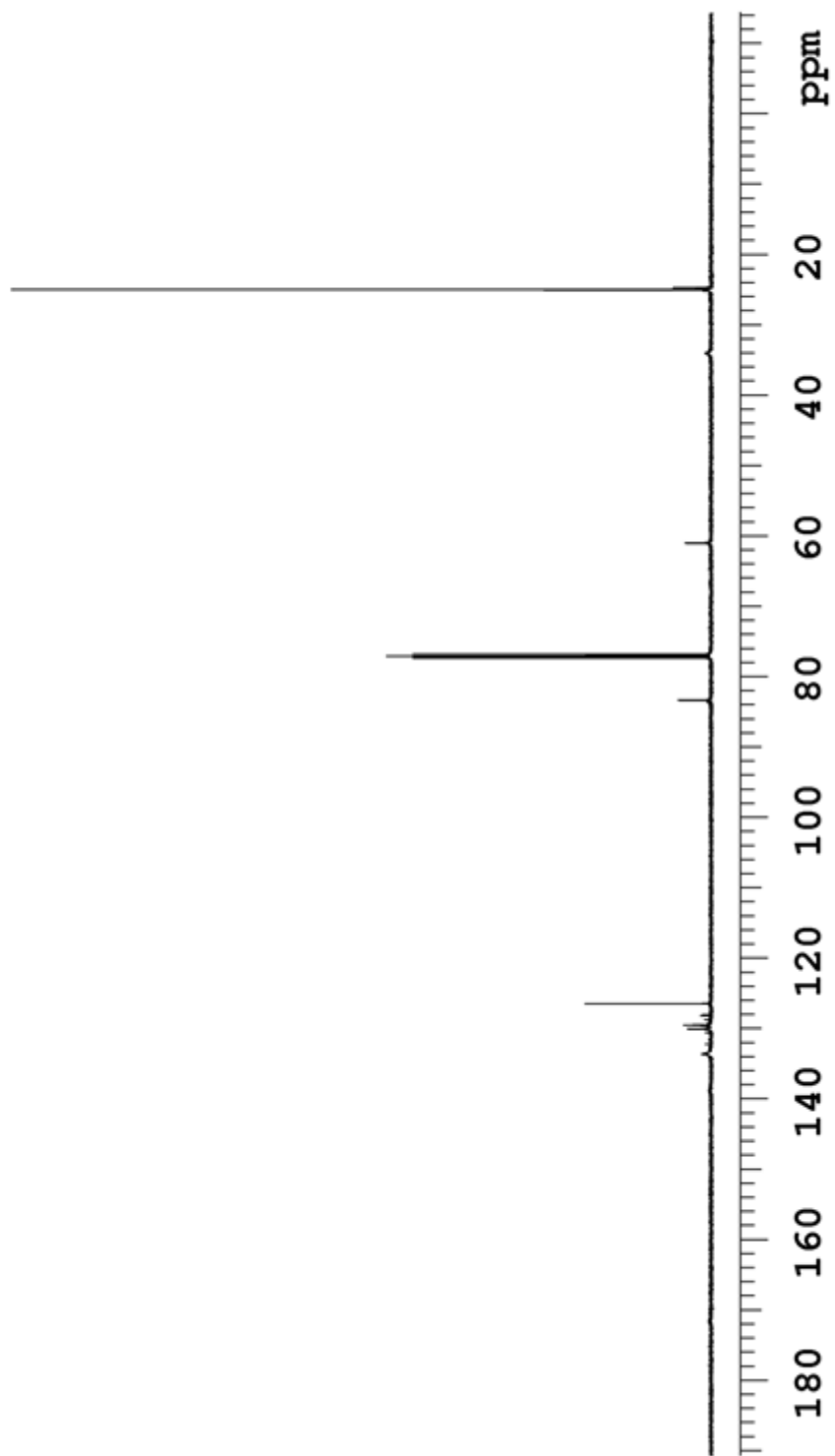
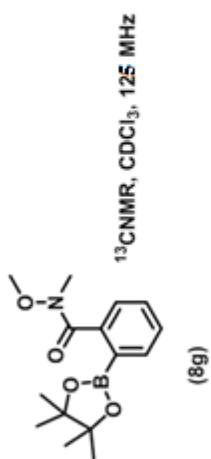


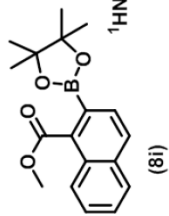


(8g)

¹HNMR, CDCl₃, 500 MHz

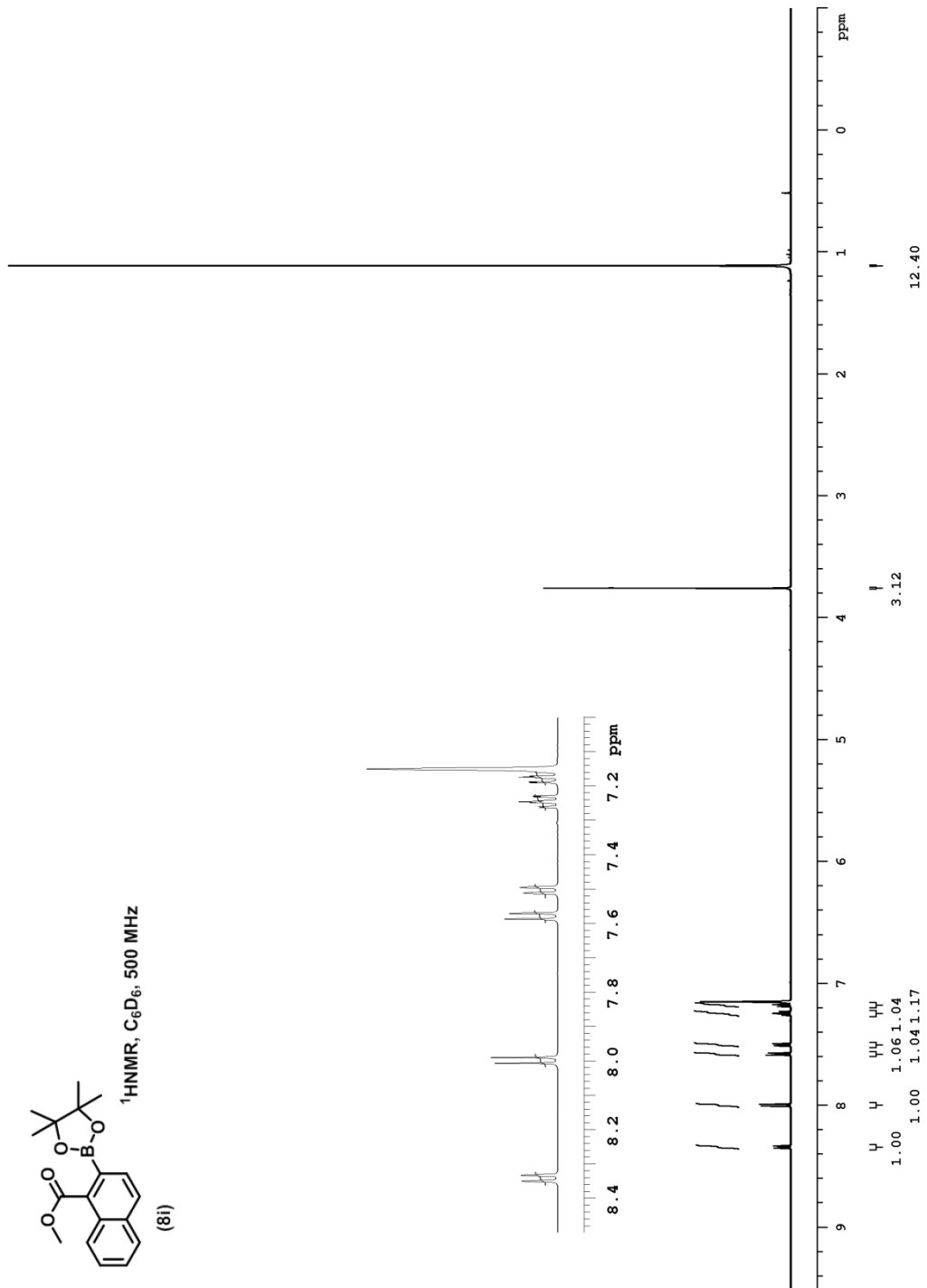


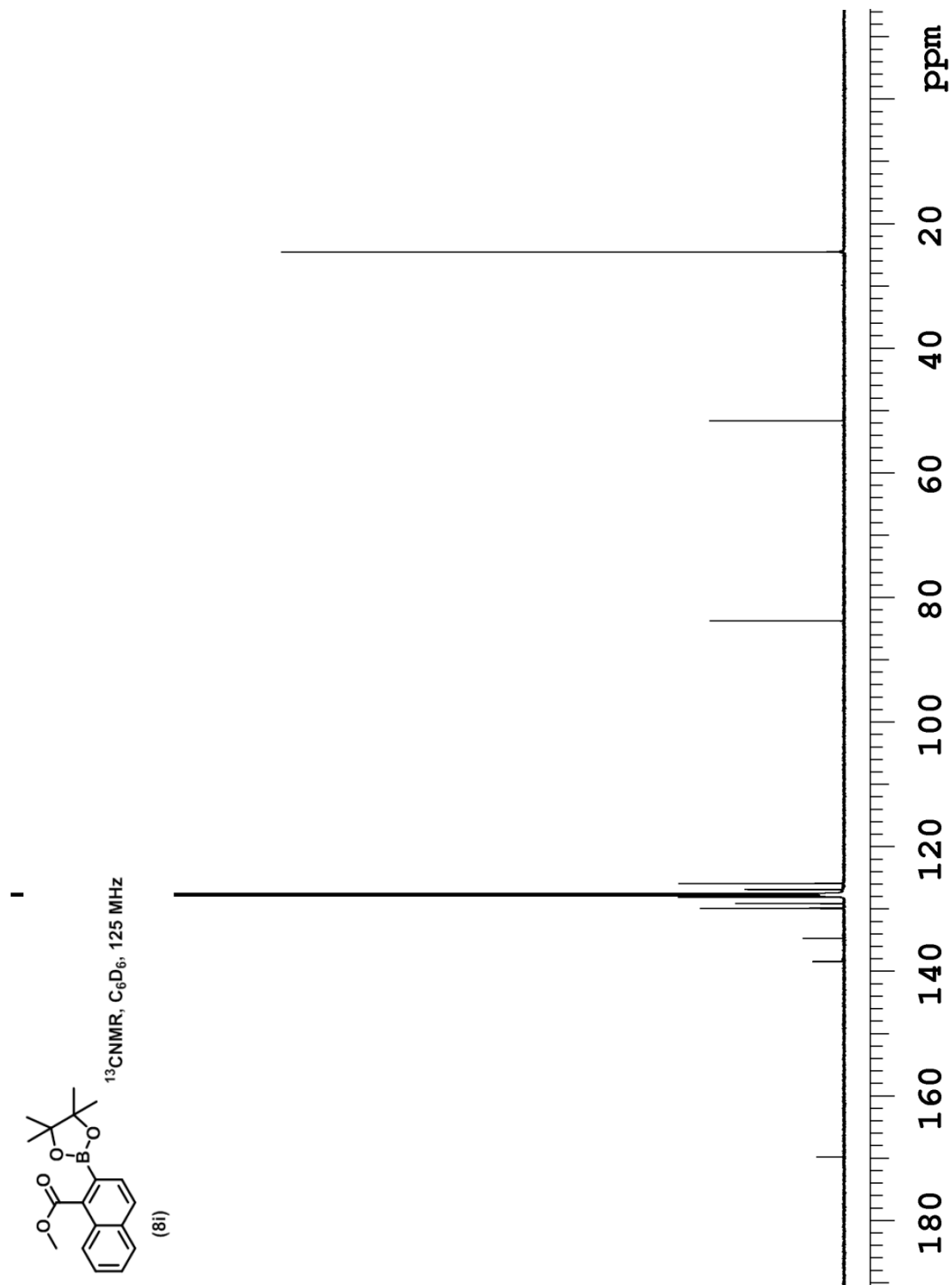


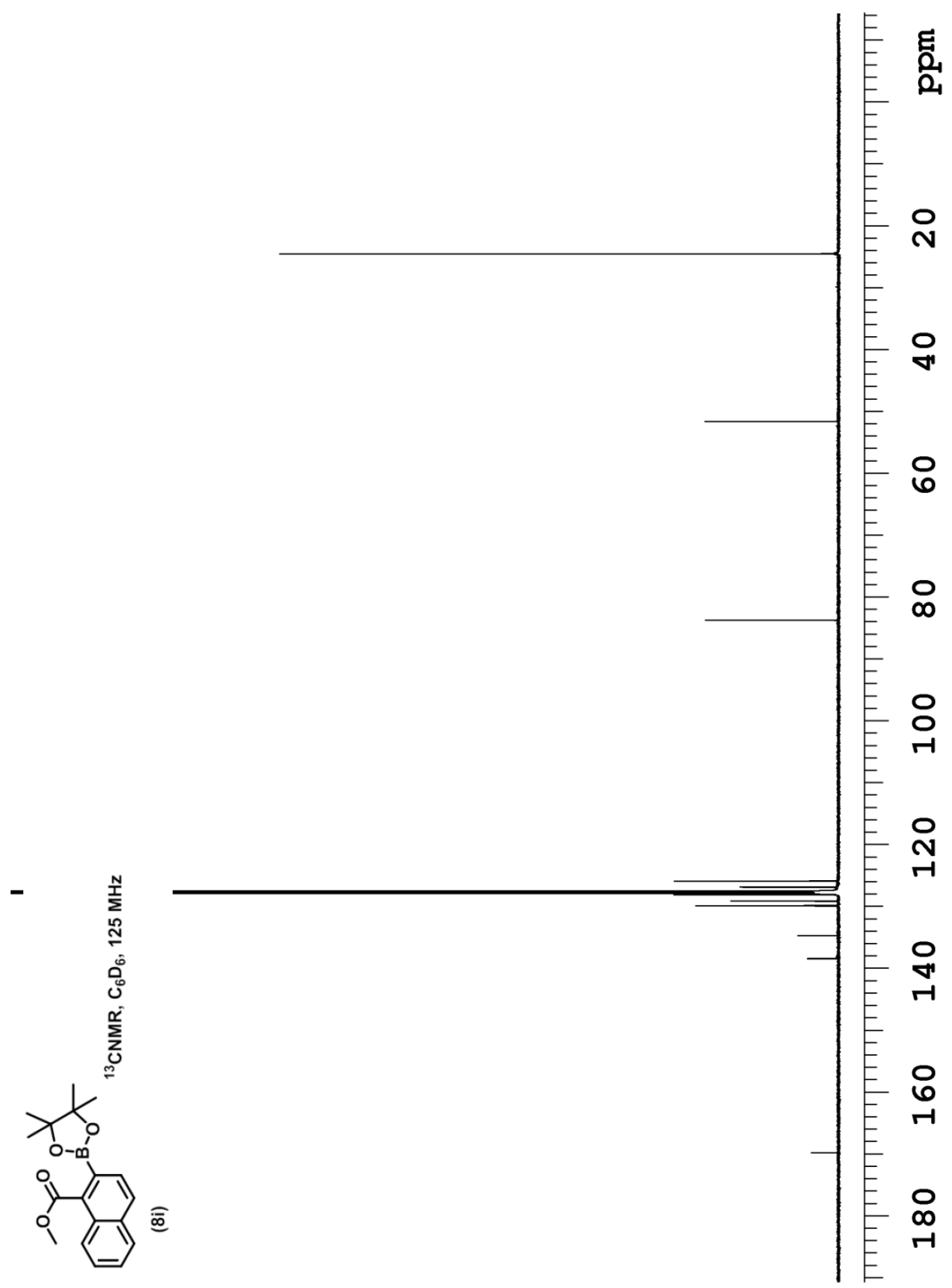


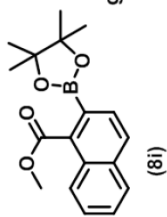
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(8i)

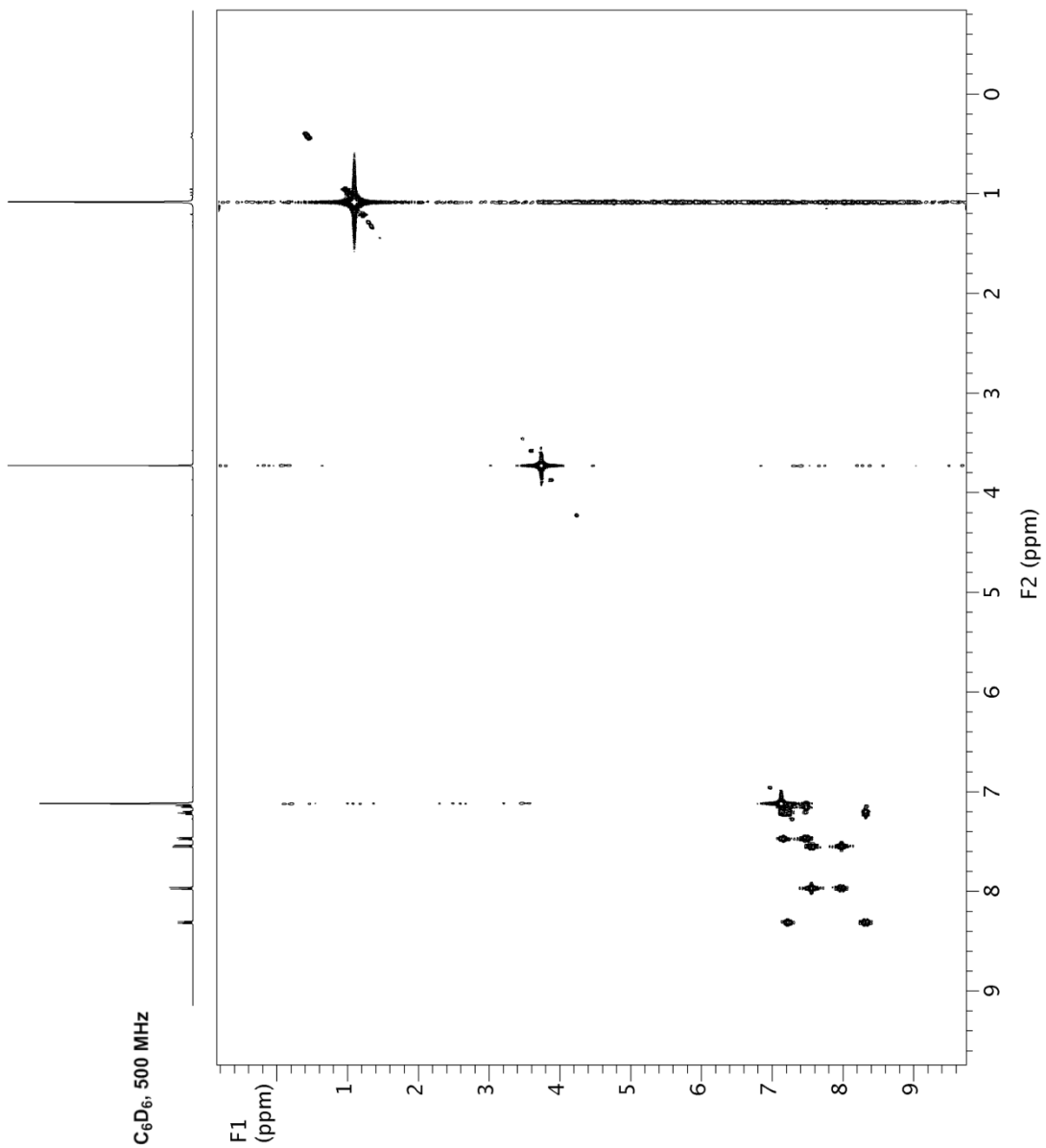


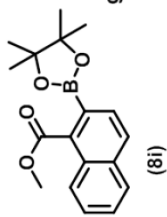




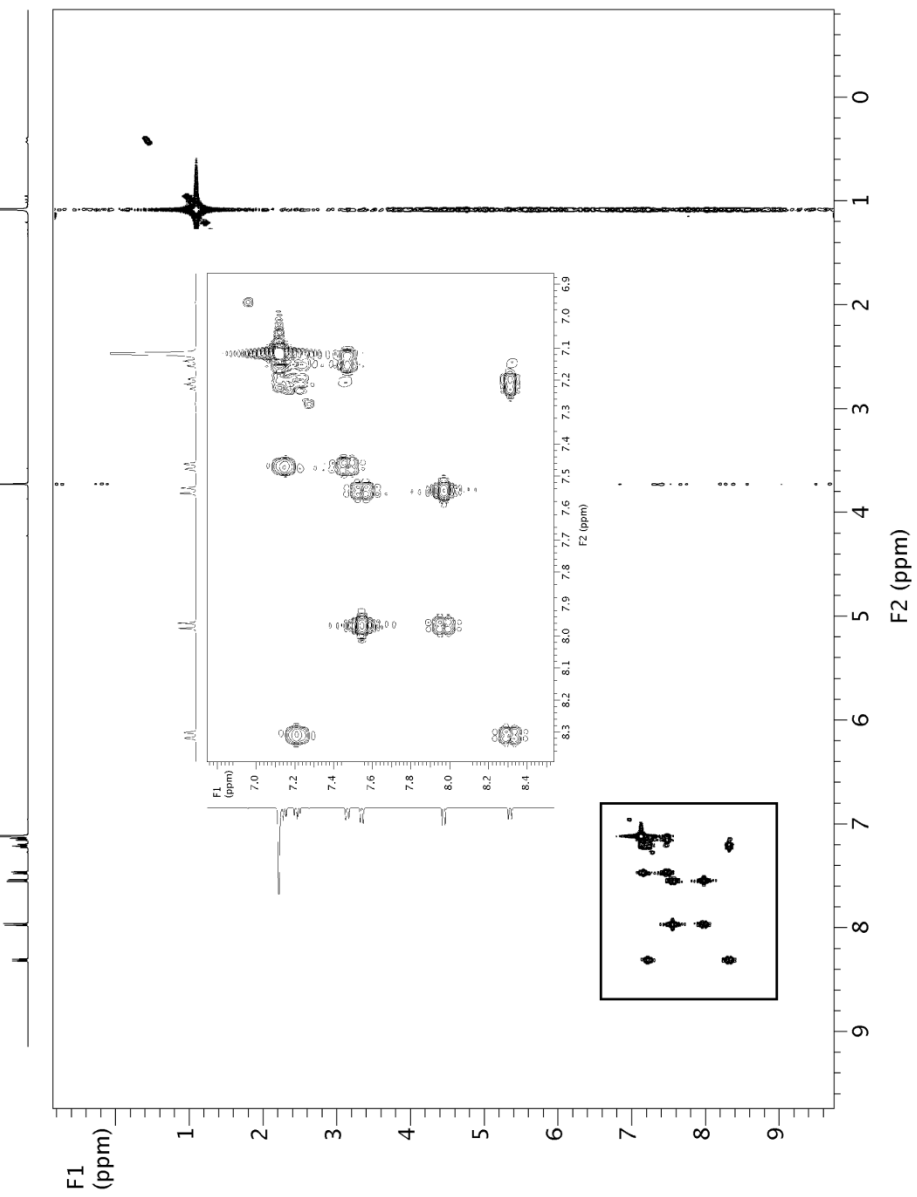


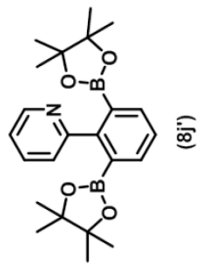
gCOSY, C₆D₆, 500 MHz



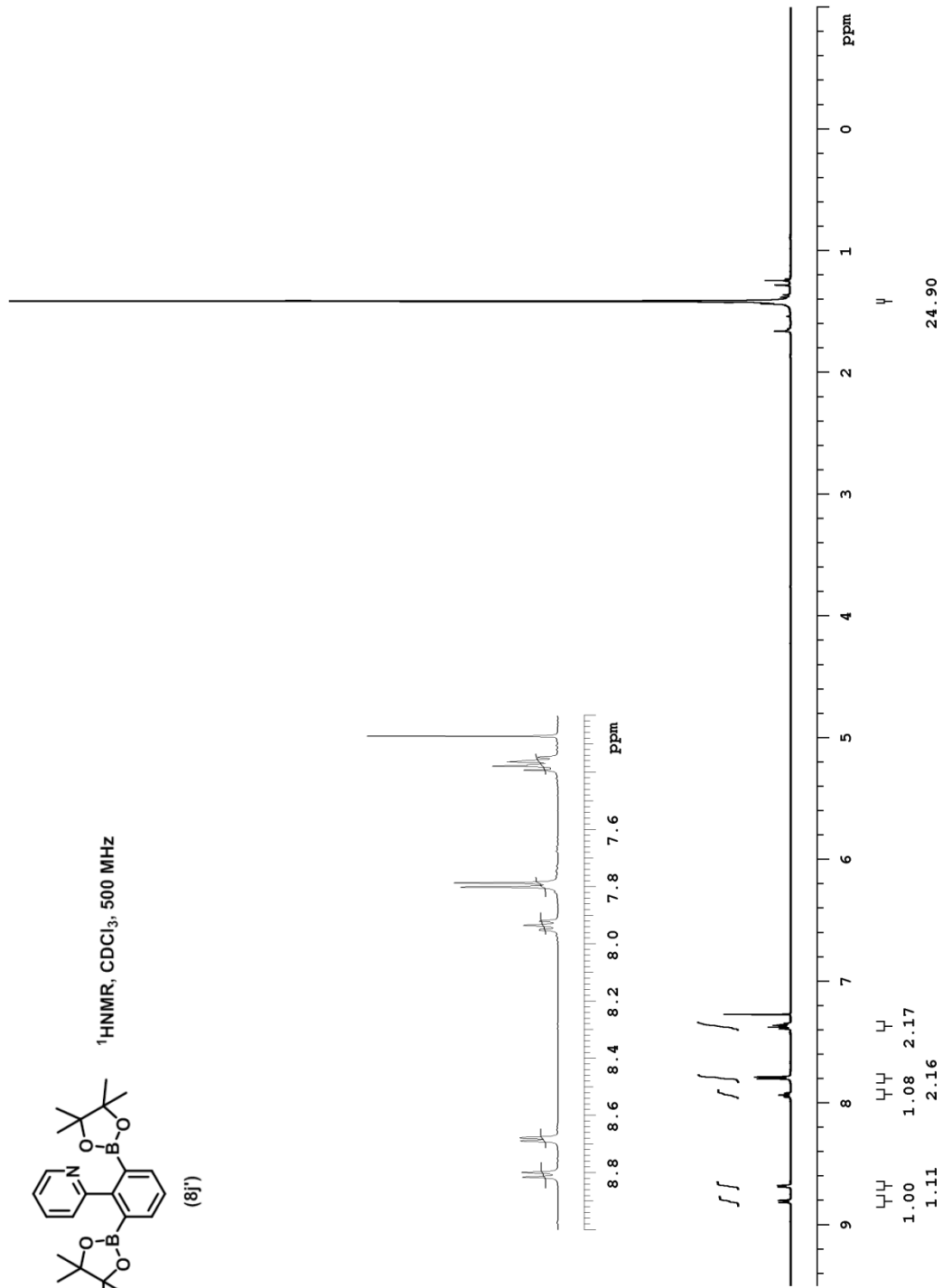


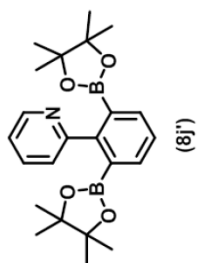
gCOSY, C₆D₆, 500 MHz



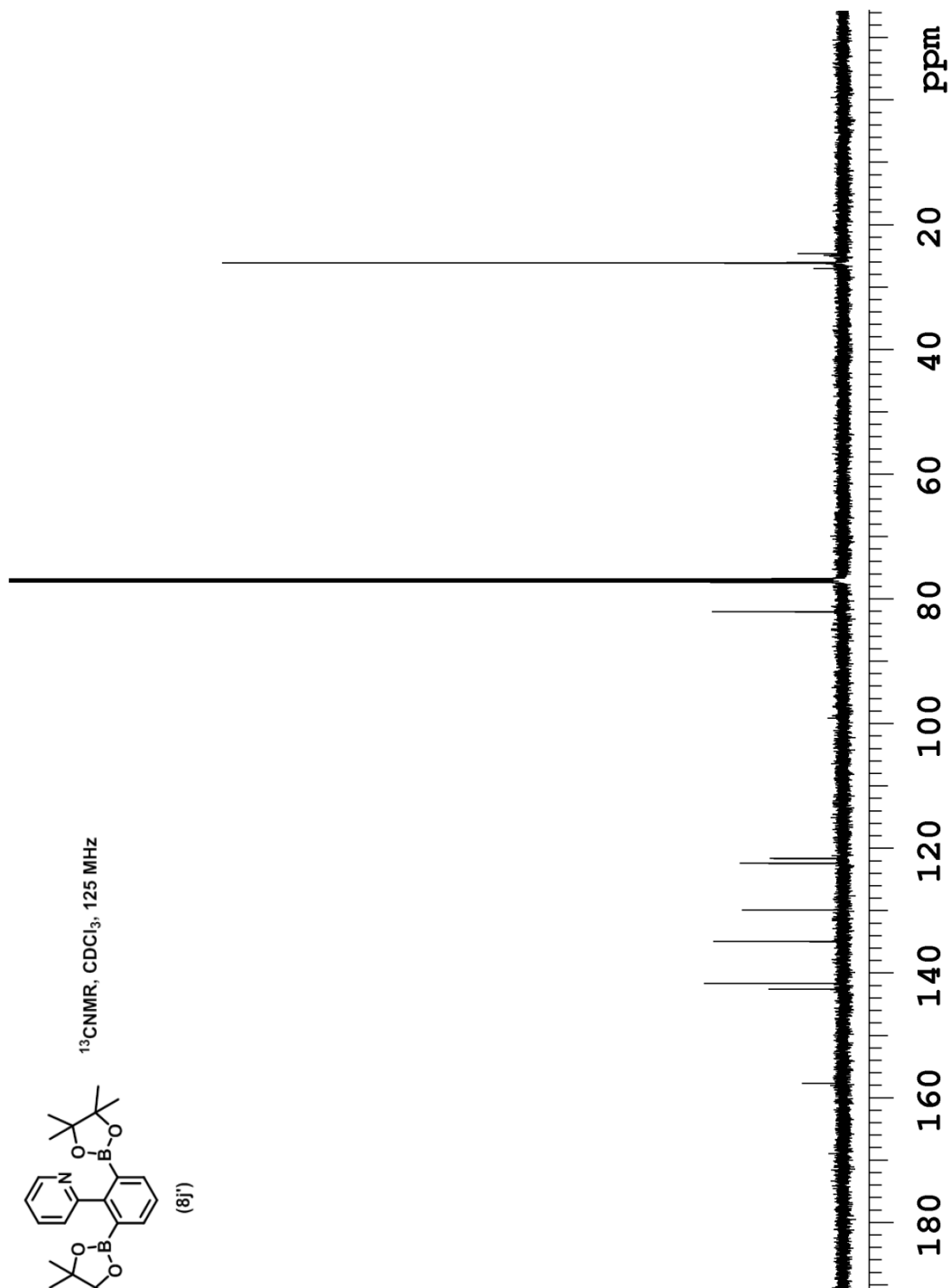


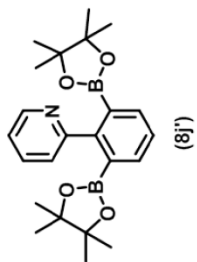
¹HNMR, CDCl₃, 500 MHz



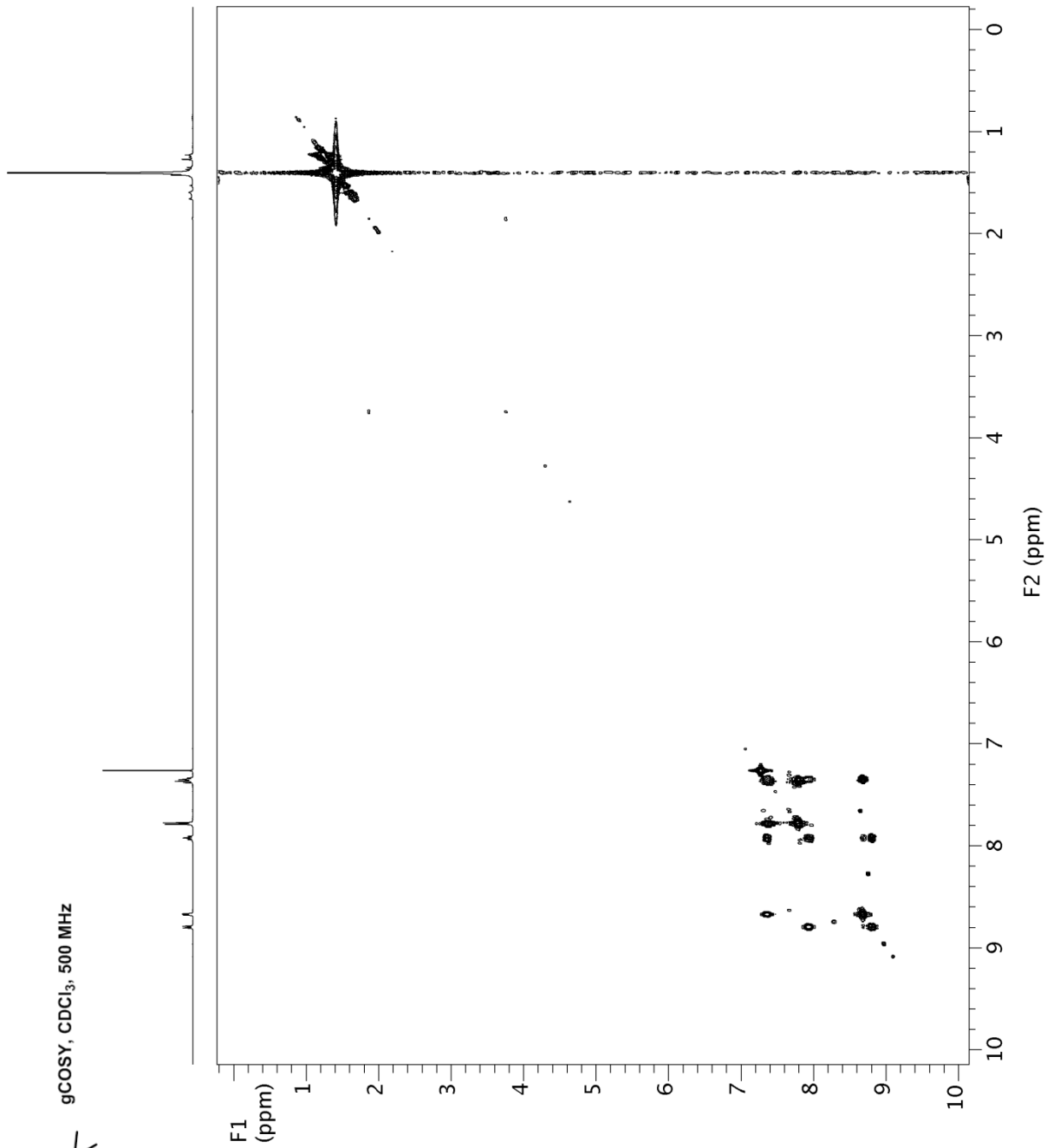


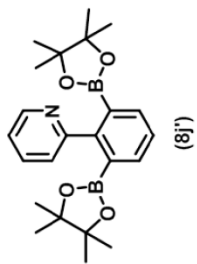
¹³CNMR, CDCl₃, 125 MHz



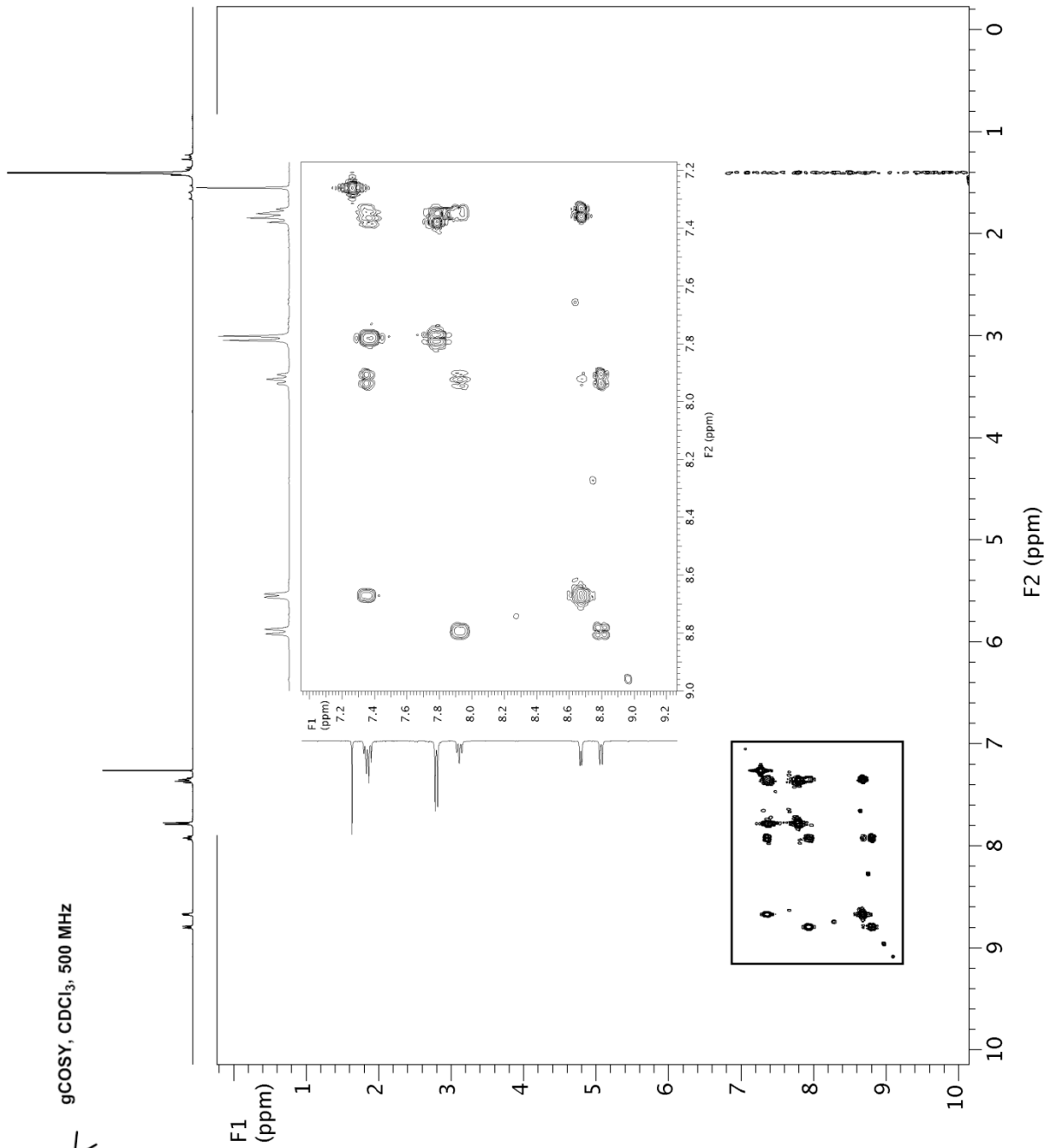


gCOSY, CDCl₃, 500 MHz

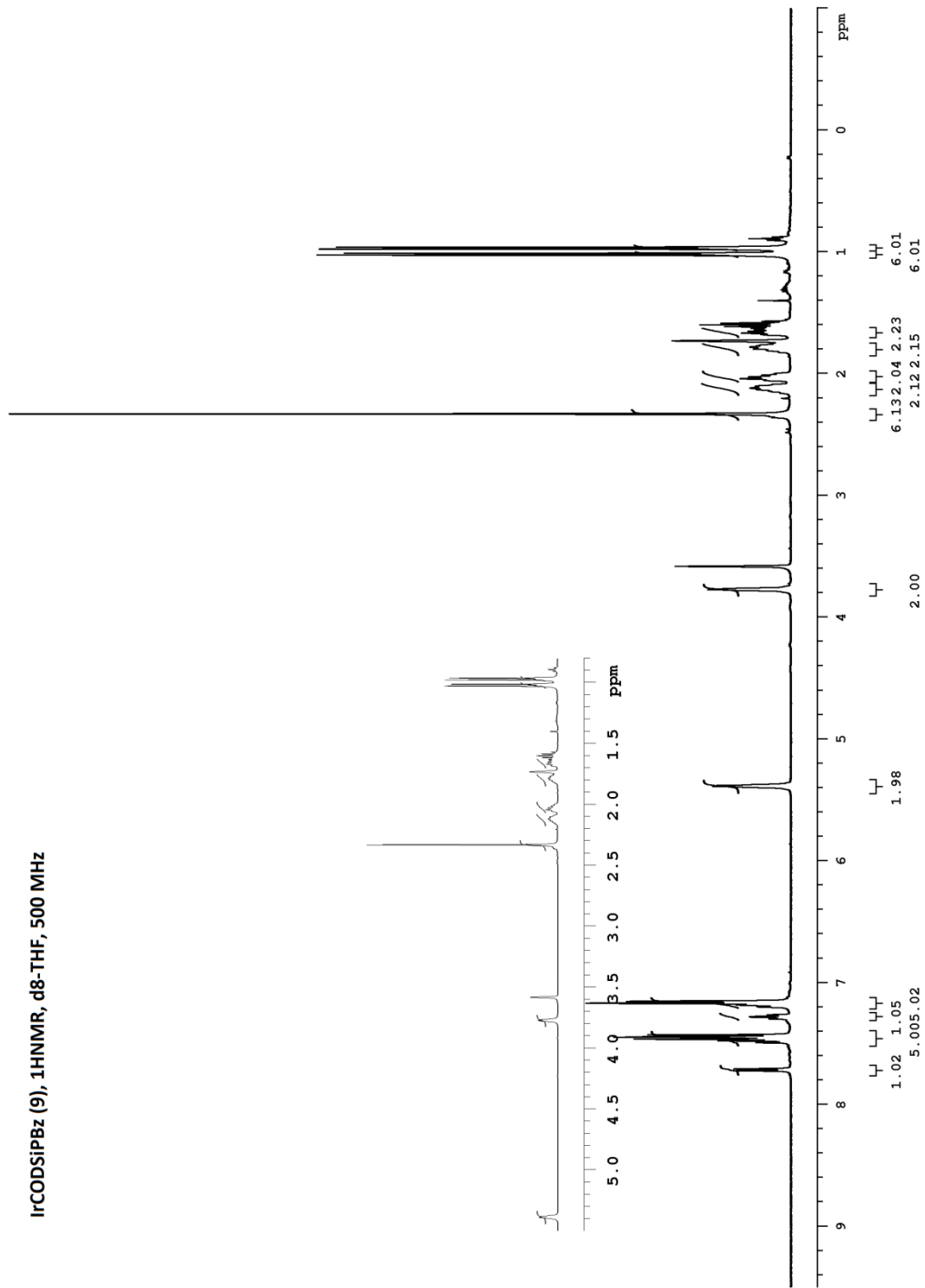




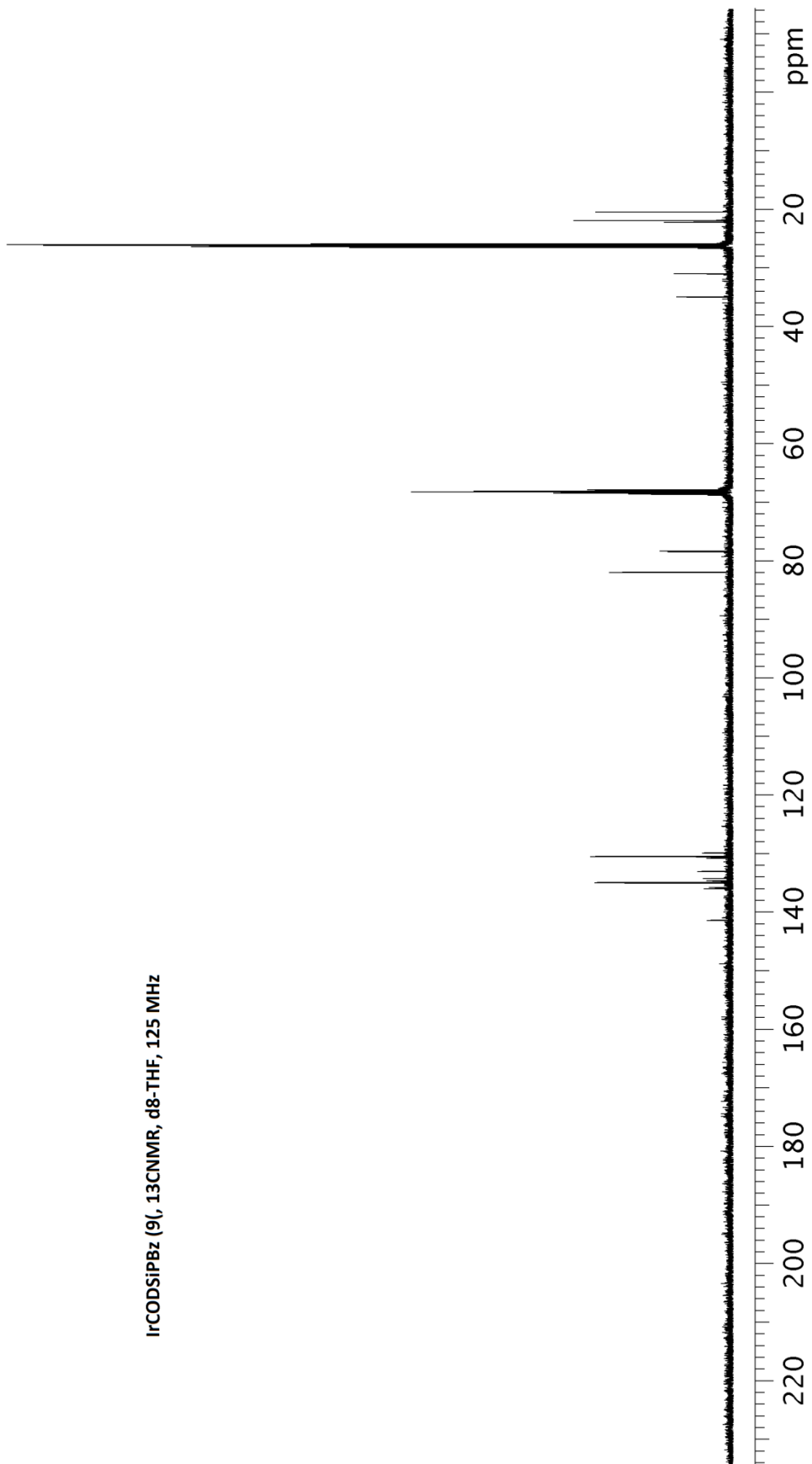
gCOSY, CDCl₃, 500 MHz



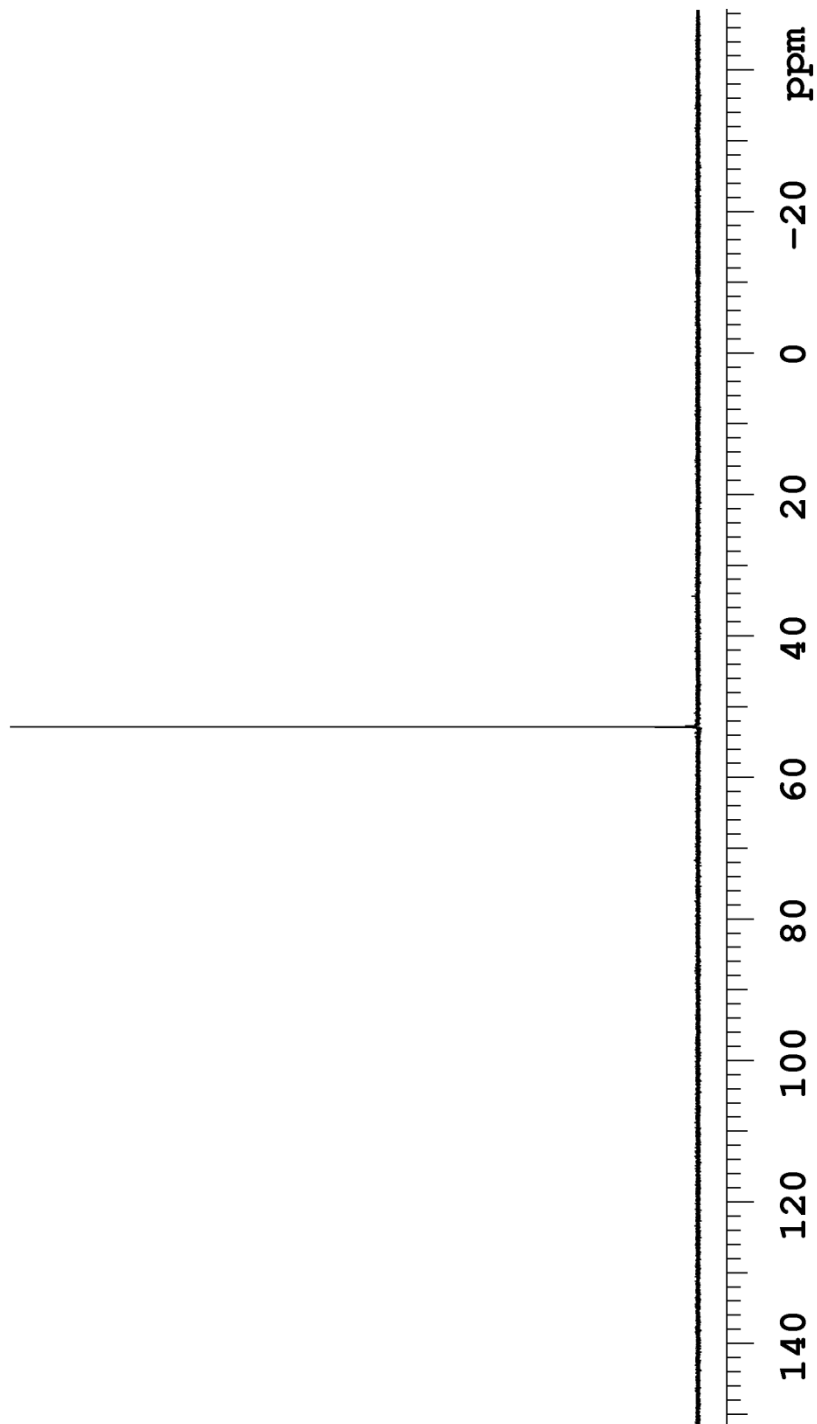
IrCODSiPBz (9), ¹H NMR, d8-THF, 500 MHz

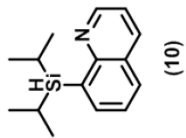


IrCODSiPBz (9), ¹³CNMR, d8-THF, 125 MHz

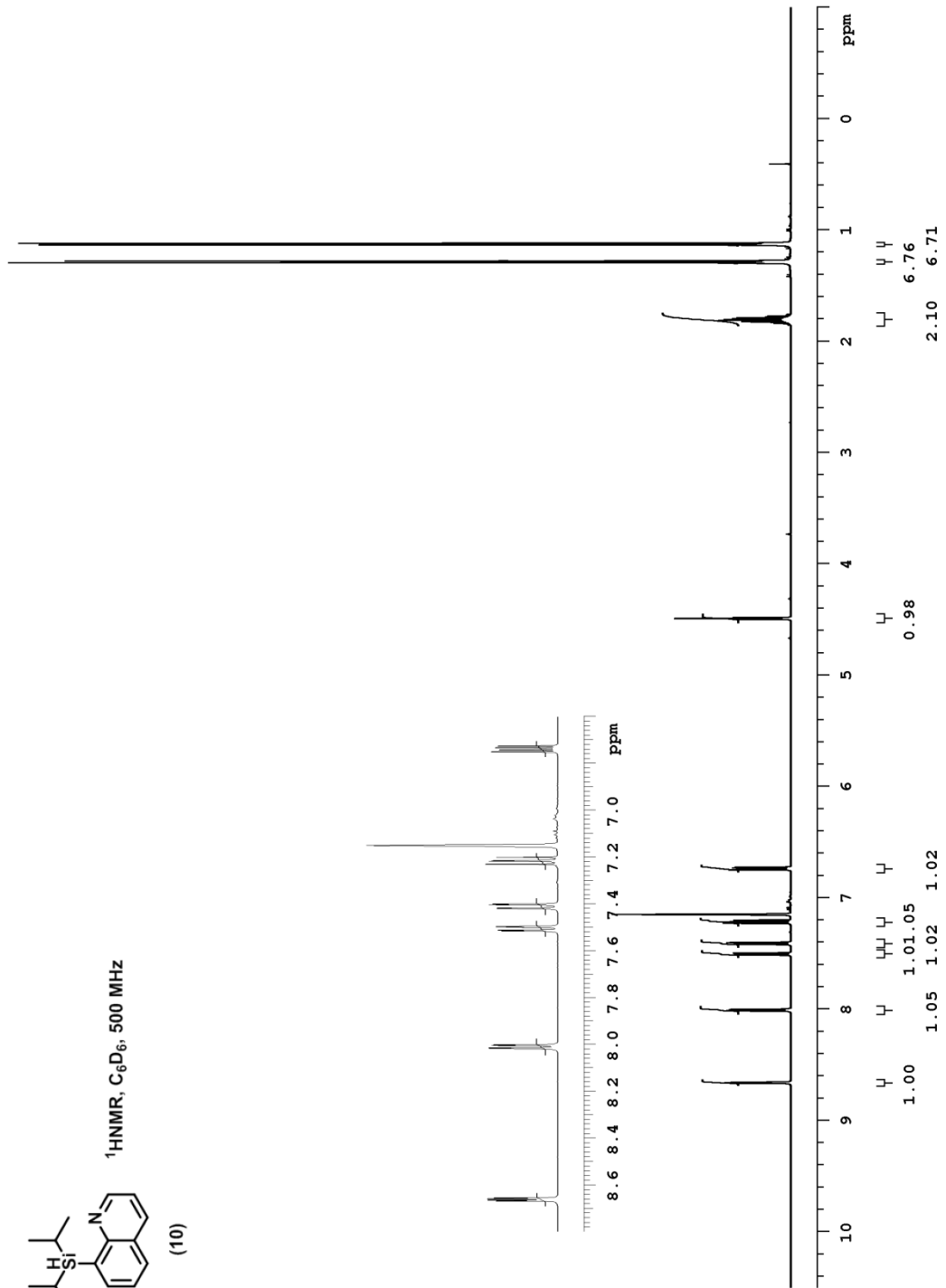


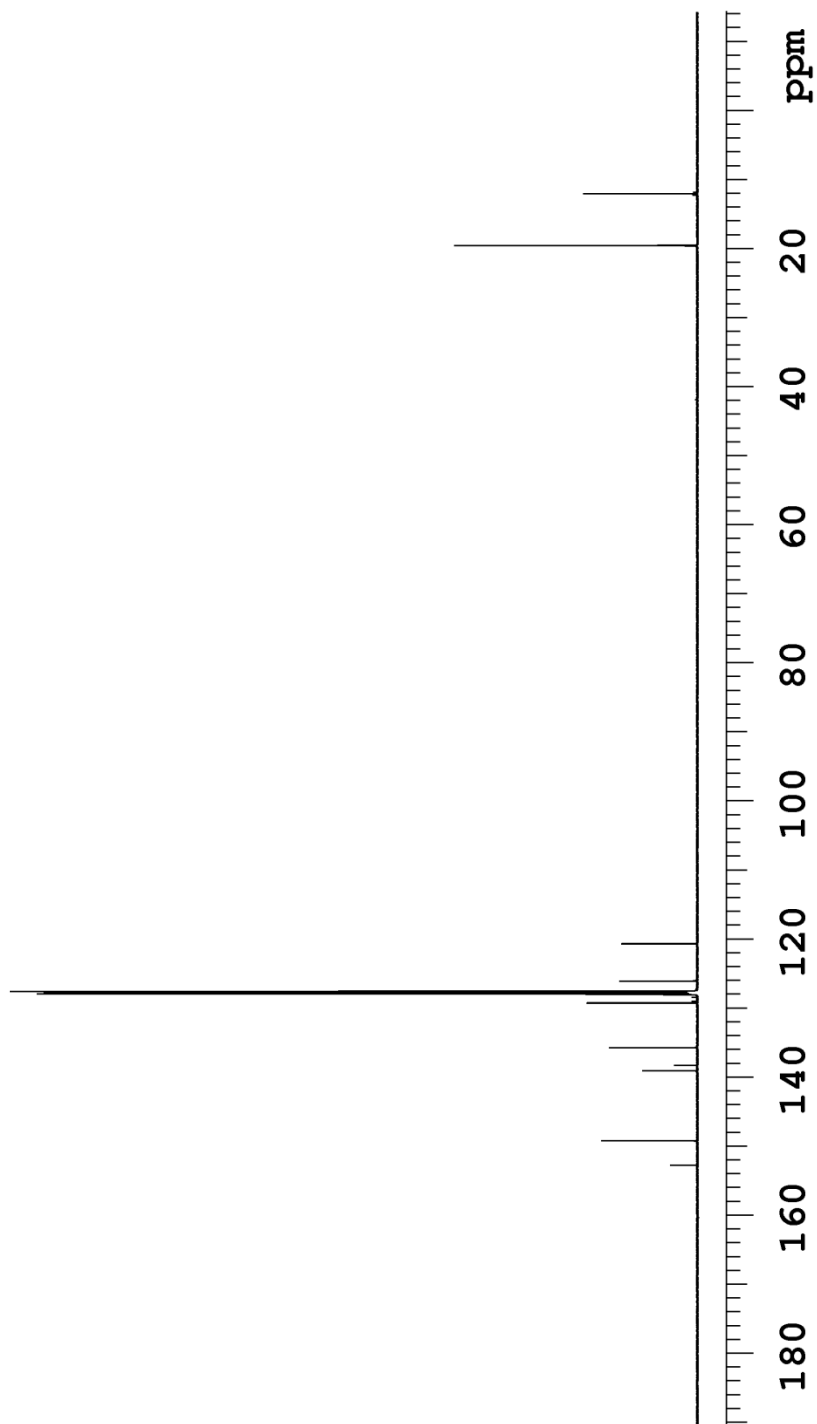
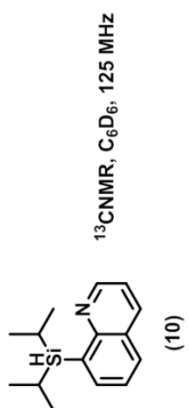
IrCODSIPbz (9), 31PNMIR, d8-THF, 202 MHz

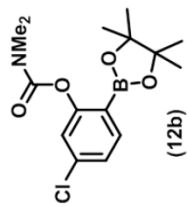




¹HNMR, C₆D₆, 500 MHz







¹HNMR, CDCl₃, 500 MHz

