# Supplementary Information for

# New Air-Stable *Si, S*-Chelating Ligand for Ir-Catalyzed Directed *ortho* C–H Borylation

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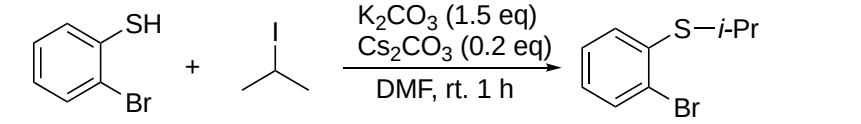
# 1. General

**General.** Unless otherwise noted, all reactions were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230-400 mesh silica gel containing a fluorescent indicator. Visualization was accomplished by exposure to a UV lamp. All the products in this article are compatible with standard silica gel chromatography. Column chromatography was performed on silica gel (200-300 mesh) using standard methods.

**Structural Analysis**. NMR spectra were measured on a Bruker Avance-400 spectrometer and chemical shifts (δ) are reported in parts per million (ppm). $^{1}$H NMR spectra were recorded at 400 MHz in NMR solvents and referenced internally to corresponding solvent resonance, and $^{13}$C NMR spectra were recorded at 100 MHz and referenced to corresponding solvent resonance. Carbons bearing boron substituents were generally not observed due to quadrupolar relaxation. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), bs (broad singlet) and bq (broad quartet). Infrared spectra were collected on a Thermo Fisher Nicolet 6700 FT-IR spectrometer using ATR (Attenuated Total Reflectance) method. Absorption maxima (ν max) are reported in wavenumbers (cm$^{-1}$). High resolution mass spectra (HRMS) were acquired with an APCI or ESI source.

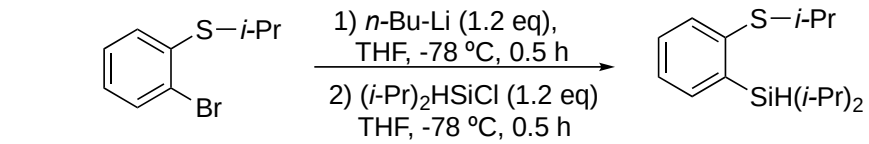
**Materials.** Commercial reagents and solvent were purchased from J&K, Sigma-Aldrich, Alfa Aesar, Acros Organics, Strem Chemicals, TCI, Adamas-beta, Energy chemicals and used as received unless otherwise stated.

# 2. Synthesis of diisopropyl(2-(isopropylthio)phenyl)silane




2-Bromothiophenol 1-Bromo-2-isopropylthiobenzene

**Preparation of 1-Bromo-2-isopropylthiobenzene.** To a suspension of $K_2CO_3$ (0.74 g, 5.35 mmol) and $Cs_2CO_3$ (0.24 g, 0.75 mmol) in DMF (9 ml), 2-bromothiophenol (0.5 g, 3.57 mmol) was added. After stirring for 30 min, 2-iodopropane (0.41 mL, 0.7 g, 7.49 mmol) was added and reaction mixture was stirred for 1 hour at room temperature. Then mixture was poured into water (5 mL), extracted with diethyl ether (3 × 6 mL), combined organic phases were washed with water, brine and dried. Solvent was evaporated to dryness to obtain **5b** as a yellow oil (0.62 g, 3.39 mmol, yield 96%) after purification by silica gel flash chromatography (EtOAc/PE = 1:50 v/v)

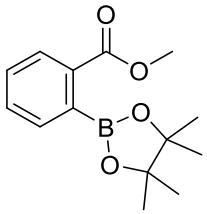



1-Bromo-2-isopropylthiobenzene *Si,S*-Ligand

**Preparation of *Si,S*-Ligand**：1-Bromo-2-isopropylthiobenzene (245mg, 1 mmol) was dissolved in THF at -78 °C, then *n*-BuLi (0.75 mL, 1.2 mmol) was added dropwise, stirred for 30min, then raise the temperature to room temperature and added The $(i\text{-Pr})_2$SiHCl (250 $\mu$L, 1.2 mmol), stir for 8 hours, 5 mL of saturated sodium carbonate to quench the reaction solution, 5×3 mL of ether to extract, brine and dried. Solvent was evaporated to dryness to obtain *Si,S*-ligand as colorless oil (202 mg, yield 76%) after purification by silica gel flash chromatography (EtOAc/PE = 1:50 v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.3 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.3 Hz, 1H), 3.99 (t, *J* = 4.0 Hz, 1H), 3.34 (hept, *J* = 6.7 Hz, 1H), 1.32 (ddp, *J* = 11.3, 7.3, 4.0 Hz, 2H), 1.23 (d, *J* = 6.7 Hz, 6H), 1.04 (d, *J* = 7.3 Hz, 6H), 0.89 (d, *J* = 7.4 Hz, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 142.6, 138.5, 137.1, 130.9, 125.5, 77.3, 77.0, 76.7, 38.9, 23.0, 19.4, 19.2, 11.6. HRMS (ESI+, m/Z): Calculated for 289.14222, found: 289.14170.

## 3. General procedure for *ortho*-directed borylation of methyl benzoates.

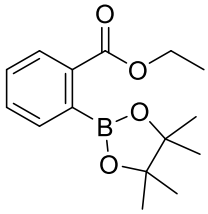
In a nitrogen filled glovebox, $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) was dissolved in 0.5 mL 2-Me-THF in a 10 mL pressure tube containing a magnetic stir bar, then the $[IrOMe(cod)]_2$ stir in advance with *Si,S*-ligand for 1h, Then 0.5 mmol methyl benzoate substrate and 1.2 equiv. $B_2pin_2$ (154 mg) 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. Additional purifications were performed as described below.




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

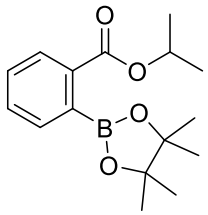
The general procedure was followed using methyl benzoate (68.1 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, the resulting mixture was allowed to stir 16 hours at 80 °C. The $^1$H NMR yields of **2a** was 67%, **2a** was obtained as pale yellow oil (78.6 mg, 60%) after purification by silica gel flash chromatography (EtOAc/PE = 1:20 v/v). $^1$H NMR (400 MHz,

$CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.55-7.47 (m, 2H), 7.45-7.36 (m, 1H), 3.91 (s, 3H), 1.42 (s, 12H); $^{13}C$ NMR (100 MHz, $CDCl_3$) 168.4, 133.4, 132.1, 131.8, 128.9, 128.7, 84.0, 52.3, 24.8; The spectral data were in accordance with literature[(1)].



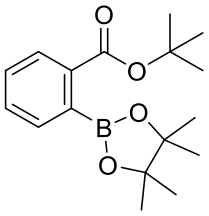
**Ethyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2b)**

The general procedure was followed using ethyl benzoate (75.1 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si*,*S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, the resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **2b** was 75%, **2b** was obtained as colorless oil (86.9 mg, 63%) after purification by silica gel flash chromatography (EtOAc/PE = 1:20 v/v). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 1H), 7.51-7.49 (m, 2H), 7.42-7.38 (m, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.42 (s, 12H), 1.38 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100MHz, $CDCl_3$) 168.1, 133.8, 132.1, 131.7, 128.8, 128.5, 84.0, 61.2, 24.9, 14.3; The spectral data were in accordance with literature [(1).]



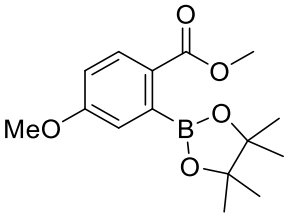
**Isopropyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2c)**

The general procedure was followed using isopropyl benzoate (82.1 mg, 0.5 mmol, 1.0 equiv. ), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si*,*S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **2c** was 81%. **2c** was obtained as colorless oil (101.5 mg, 70%) after purification bysilica gel flash chromatography (EtOAc/PE = 1:20 v/v). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.50-7.48 (m, 2H), 7.41-7.37 (m, 1H), 5.30 (hept, *J* = 6.0 Hz, 1H), 1.43 (s, 12H), 1.36 (d, *J* = 6.0 Hz, 6H); $^{13}C$ NMR(100 MHz, $CDCl_3$) 167.6, 134.4, 131.9, 131.6, 128.7, 128.3, 83.9, 68.7, 24.9, 21.9; The spectral data were in accordance with literature[(1)].



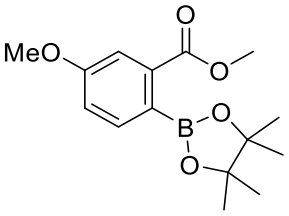
***tert*-Butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2d)**

The general procedure was followed using *tert*-butyl benzoate (89.1 mg, 0.5 mmol, 1.0 equiv.), [IrOMe(cod)]$_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si*,*S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1$H NMR yields of **2d** was70%. **2d** was obtained as white solid (89.7 mg, 59%) after purification by silica gel flash chromatography (EtOAc/PE = 1:20 v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.47-7.46 (m, 2H), 7.38-7.34 (m, 1H), 1.58 (s, 9H), 1.42 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) 167.5, 135.9, 131.8, 131.3, 128.6, 128.1, 83.8, 81.3, 28.2, 24.9; The spectral data were in accordance with literature(1).



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

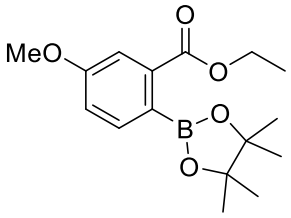
The general procedure was followed using methyl *p*-anisate (83.1 mg, 0.5 mmol, 1.0 equiv.), [IrOMe(cod)]$_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si*,*S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1$H NMR yields of **2d** was 65%. **2d** was obtained as white solid (86.1 mg, 59%) after purification by silica gel flash chromatography (EtOAc/PE = 1:20 v/v). $^1$H NMR (400 MHz, $CDCl_3$) 7.91 (d, *J* = 8.8 Hz, 1H), 6.94 (d, *J* = 2.8 Hz, 1H), 6.88 (dd, *J* = 8.7, 2.8 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 1.43 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) 168.1, 162.5, 131.0, 125.6, 117.0, 114.2, 84.1, 55.4, 52.1, 24.9. The spectral data were in accordance with literature[4].



**Methyl 5-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2f)**

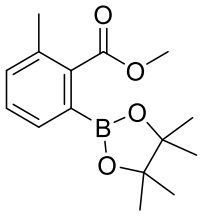
The general procedure was followed using methyl 3-methoxybenzoate (83 mg, 0.5 mmol, 1.0 equiv.), [IrOMe(cod)]$_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si*,*S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and

$B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **2f** was 62%. **2f** was obtained as yellow oil (73mg, 50%) after purification by silica gel flash chromatography (EtOAc/PE = 1:20 v/v). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.45-7.43 (m, 2H), 7.05 (dd, *J* = 2.4, 8.0 Hz, 1H), 3.91 (s, 3H), 3.84 (s, 3H), 1.40 (s, 12H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 168.4, 160.3, 135.6, 133.9, 118.0, 113.7, 83.9, 55.3, 52.3, 24.9; The spectral data were in accordance with literature[(2)].



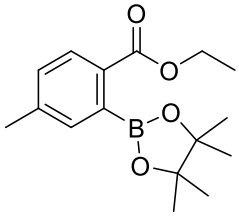

**Ethyl 5-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2g)**

The general procedure was followed using ethyl 3-methoxybenzoate (90 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **2g** was 60%. **2g** was obtained as yellow oil (75mg, 49%) after purification by silica gel flash chromatography (EtOAc/PE = 1:20 v/v). $^1H$ NMR (400 MHz, $CDCl_3$) 7.45-7.42 (m, 2H), 7.04 (dd, *J* = 2.8, 8.4 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.40 (s, 12H), 1.38 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): 168.0, 160.3, 136.1, 133.8, 117.6, 113.7, 83.9, 61.3, 55.3, 24.9,14.3; The spectral data were in accordance with literature[(4)].



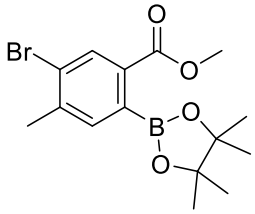

**Methyl 2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2h)**

The general procedure was followed using methyl 2-methylbenzoate (77.0 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **2h** was 60%, **2h** was obtained as yellow oil (69 mg, 50%) after purification by silica gel flash chromatography (EtOAc/PE = 1:20 v/v). $^1H$ NMR (400MHz, $CDCl_3$) δ 7.54 (d, *J* = 6.8 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.27-7.24 (m, 1H), 3.89 (s, 3H), 2.39 (s, 3H), 1.33 (s, 12H). $^{13}C$ NMR (100 MHz, $CDCl_3$) 170.7, 137.5, 135.4, 132.7, 131.7, 129.4, 84.0, 52.1, 24.8, 20.0; The spectral data were in accordance with literature[(1)].



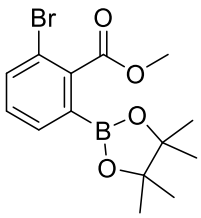
**Methyl 4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2i)**

The general procedure was followed using methyl 4-methylbenzoate (82.0 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si*,*S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **2i** was 71%, **2i** was obtained as white solid (85.5 mg, 59%) after purification by silica gel flash chromatography (EtOAc/PE = 1:20 v/v). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H), 7.04 (dd, *J* = 2.8, 8.4 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 1.44 (s, 12H), 1.38 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 168.1, 142.2, 132.7, 131.0, 129.5, 128.7, 83.9, 61.0, 28.4, 24.9, 21.5, 14.4; $^{11}B$ NMR (128.4 MHz, CDCl3) δ 31.2, HRMS($ESI^+$, m/Z): Calculated for 291.17622, found: 291.17576. point 135-137 °C.



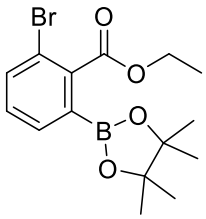
**Methyl 5-bromo-4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2j)**

The general procedure was followed using methyl 3-bromo-4-methylbenzoate (114.0 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si*,*S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **2j** was 63%, **2j** was obtained as white solid (92mg, 52%) after purification by silica gel flash chromatography (EtOAc/PE = 1:20 v/v). $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.34 (s, 1H), 3.90 (s, 3H), 2.43 (s, 3H), 1.42 (s, 12H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 167.2, 142.2, 134.4, 132.8, 132.7, 125.7, 84.2, 52.4, 24.9, 23.0. $^{11}B$ NMR (128.4 MHz, $CDCl_3$) δ 31.3, HRMS($ESI^+$, m/Z): Calculated for 354.06380, found: 354.06421. Point 251-253 °C.



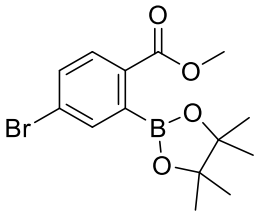
**Methyl 2-bromo-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2k)**

The general procedure was followed using methyl 2-bromo-benzoate (107.0 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **2k** was 78%, **2k** was obtained as yellow oil (119.7mg, 70%) after purification by silica gel flash chromatography (EtOAc/PE = 1:20 v/v). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 9.2 Hz, 1H), 7.26 (dd, *J* = 3.6, 8.4 Hz, 1H), 3.92 (s, 3H), 1.32 (s, 12H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 168.8, 140.8, 135.1, 133.7, 130.2, 119.2, 84.5, 52.5, 24.8; The spectral data were in accordance with literature[3].



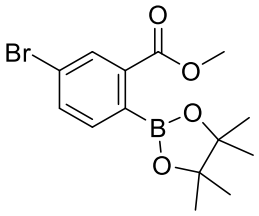

**Ethyl 2-bromo-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2l)**

The general procedure was followed using ethyl 2-bromobenzoate (114.0 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80°C. The $^1H$ NMR yields of **2l** was 68%, **2l** was obtained as white solid (106.2mg, 60%) after purification by silica gel flash chromatography (EtOAc/PE = 1:20 v/v). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.26 (dd, *J* = 3.6, 7.6 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.32 (s, 12H); $^{13}C$ NMR (100 MHz, $CDCl_3$) 168.4, 141.1, 135.1, 133.8, 130.0, 119.2, 84.4, 61.7, 24.8, 14.1; $^{11}B$ NMR (128.4 MHz, $CDCl_3$) δ 30.0, HRMS ($ESI^+$, m/Z): Calculated for 355.07108, found: 355.06957. Point 217-219 °C



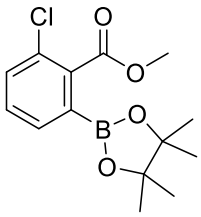

**Methyl 4-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2m)**

The general procedure was followed using methyl 4-bromobenzoate (107.0 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **2m** was 70%,**2m** was obtained as yellow oil (104.3mg, 61%) after purification by silica gel flash chromatography (EtOAc/PE = 1:20 v/v). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 1H), 7.61 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H), 1.42 (s, 12H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 167.8, 135.1, 132.1(5), 132.1(4) 130.3, 127.6, 84.4, 52.5, 24.9; The spectral data were in accordance with literature[3].



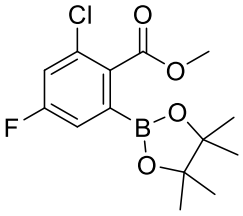
**Methyl 5-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2n)**

The general procedure was followed using methyl 3-bromobenzoate (107.0 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **2n** was 70%, **2n** was obtained as yellow oil (99.2 mg, 58%) after purification by silica gel flash chromatography. (EtOAc/PE = 1:20 v/v).$^1H$ NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.65 (d, $J$ = 8.0 Hz, 1H), 7.37 (d, $J$ = 8.0 Hz, 1H), 3.92 (s, 3H), 1.41 (s, 12H); $^{13}C$ NMR(100 MHz, $CDCl_3$) δ 167.2, 135.4, 134.7, 133.8, 131.8, 123.4, 84.3, 52.6, 24.8; The spectral data were in accordance with literature[(3)].



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

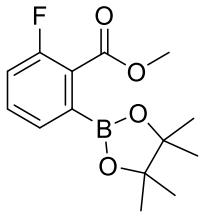
The general procedure was followed using methyl 2-chlorobenzoate (85.0 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **2o** was 83%, **2o** was obtained as yellow oil (101.3mg, 68%) after purification by silica gel flash chromatography (EtOAc/PE = 1:20 v/v).$^1H$ NMR (400 MHz, $CDCl_3$) δ 7.67 (d, $J$ = 8.4 Hz, 1H), 7.47 (d, $J$ = 9.2 Hz, 1H), 7.33 (dd, $J$ = 3.6, 7.6 Hz, 1H), 3.92 (s, 3H), 1.32 (s, 12H). $^{13}C$ NMR (100 MHz, $CDCl_3$) 168.3, 138.4, 133.1, 131.9, 130.7, 130.1, 84.5, 52.5, 24.8; The spectral data were in accordance with literature[(1)].



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

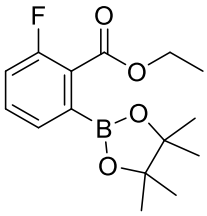
The general procedure was followed using methyl 2-chloro-4-fluorobenzoate (94.0 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **2p** was 92%, **2p** was obtained as yellow oil (113.8mg,

72%) after purification by silica gel flash chromatography (EtOAc/PE = 1:30 v/v). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 4.0, 8.0 Hz, 1H), 7.20 (dd, *J* = 4.0, 8.0 Hz, 1H), 3.91 (s, 3H), 1.33 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.7, 134.2, 120.0, 119.8, 119.3, 119.1, 84.8, 52.7, 24.8; The spectral data were in accordance with literature(1).



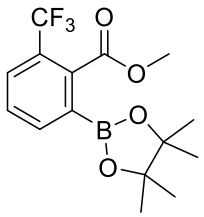

**Methyl 2-fluoro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2q)**

The general procedure was followed using methyl 2-fluorobenzoate (77.0 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^{1}$H NMR yields of **2q** was 70%, **2q** was obtained as yellow oil (81.8mg, 58%) after purification by silica gel flash chromatography (EtOAc/PE = 1:30 v/v). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.47-7.40 (m, 2H), 7.17-7.12 (m, 1H), 3.93 (s, 3H), 1.37 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.9, 161.4, 158.8, 132.5, 129.1 (*J* = 3.6 Hz), 124.1, 117.9 (*J* = 21.9 Hz), 84.3, 52.7, 24.8; The spectral data were in accordance with literature(2).



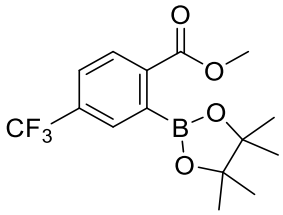

**Ethyl 2-fluoro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2r)**

The general procedure was followed using ethyl 2-fluorobenzoate (84.0 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^{1}$H NMR yields of **2r** was 72%, **2r** was obtained as yellow oil (88.5mg, 60%) after purification by silica gel flash chromatography (EtOAc/PE = 1:20 v/v). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.46-7.41 (m, 2H), 7.16-7.11 (m, 1H), 4.41 (q, *J* = 8.0 Hz, 2H), 1.39 (t, *J* = 8.0 Hz, 3H), 1.36 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.7, 161.2, 158.7, 132.2 (d, *J* = 8.0 Hz), 129.2 (d, *J* = 3.6 Hz), 124.8 (d, *J* = 13.1 Hz), 117.9 (d, *J* = 21.9 Hz), 84.3, 61.8, 24.9, 14.2; The spectral data were in accordance with literature(1).



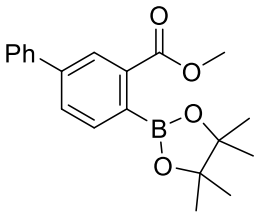
**Ethyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trifluoromethyl)benzoate (2s)**

The general procedure was followed using methyl 2-(trifluoromethyl)benzoate (102.0 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si*,*S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **2s** was 59%, **2s** was obtained as yellow oil (86.3mg, 52%) after purification by silica gel flash chromatography (EtOAc/PE = 1:30 v/v).$^1H$ NMR (400 MHz, $CDCl_3$) δ 7.97 (d, $J$ = 7.6 Hz, 1H), 7.74 (d, $J$ = 8.0 Hz, 1H), 7.52 (t, $J$ = 8.0 Hz, 1H), 3.91 (s, 3H), 1.33 (s, 12H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 168.6, 138.3, 137.3 (q, $J_{C-F}$ = 2.3 Hz), 128.9, 128.3 (q, $J_{C-F}$ = 4.5 Hz), 127.6 (q, $J_{C-F}$ = 32.0 Hz), 126.4 (q, $J_{C-F}$ = 274.2 Hz), 84.5, 52.6, 24.7 The spectral data were in accordance with literature(2).




**Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trifluoromethyl)benzoate (2t)**

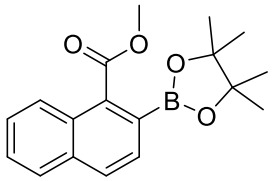
The general procedure was followed using methyl 4-(trifluoromethyl)benzoate (102.0 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si*,*S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **2t** was 76%, **2t** was obtained as yellow oil (103 mg, 62%) after purification by silica gel flash chromatography (EtOAc/PE = 1:30 v/v).$^1H$ NMR (400 MHz, $CDCl_3$) δ 8.04 (d, $J$ = 8.4 Hz, 1H), 7.74 (s, 1H), 7.68 (d, $J$ = 9.2 Hz, 1H), 3.95 (s, 3H), 1.43 (s, 12H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 167.4, 136.7, 133.3 (q, $J_{C-F}$ = 32.2 Hz), 129.1 (q, $J_{C-F}$ = 3.7 Hz), 126.0 (q, $J_{C-F}$ = 3.6 Hz), 123.9 (q, $J_{C-F}$ = 272.9 Hz), 84.6, 52.7, 24.9; The spectral data were in accordance with literature(1).




**Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-3-carboxylate (2u)**

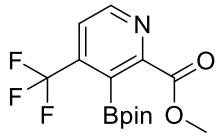
The general procedure was followed using methyl [1,1'-biphenyl]-3-carboxylate (106.0 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si*,*S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **2u** was 72%, **2u** was obtained as white solid (107.1mg, 63%) after purification by silica gel flash chromatography (EtOAc/PE = 1:30 v/v).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 1.2, 7.2 Hz, 1H), 7.48-7.41 (m, *J* = 28 Hz, 2H)7.38-7.33 (m, *J* = 20 Hz, 5H), 3.65 (s, 3H), 1.34 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.6, 140.6, 139.6, 138.0, 133.4, 132.4, 129.0, 128.5,128.2, 127.3, 84.3, 52.0, 24.8; The spectral data were in accordance with literature(1).



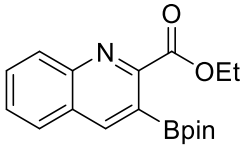

**Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-naphthoate (4a)**

The general procedure was followed using methyl 1-naphthoate (93.0 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si*,*S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1$H NMR yields of **4a** was 57%,**4a** was obtained as white solid (70.2 mg, 45%) after purification by silica gel flash chromatography (EtOAc/PE = 1:20 v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.1 (d, *J* = 8.3 Hz, 1 H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.86-7.84 (m, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.54-7.52 (m, 2H), 4.01 (s, 3H), 1.38 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.5, 137.0, 134.5, 129.5(2), 129.4(9), 129.4(6), 128.2, 127.1, 127.0, 125.5, 84.2, 52.5, 24.9; The spectral data were in accordance with literature(2).



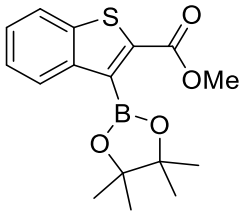

**Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trifluoromethyl)picolinate (4b)**

The general procedure was followed using methyl 4-(trifluoromethyl)picolinate (102.5 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si*,*S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Methy-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1$H NMR yields of **4b** was 72%, **4b** was obtained as white solid (112.5 mg, 68%) after purification by silica gel flash chromatography (EtOAc/PE = 1:4 v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.09 (s, 1H), 4.01 (s, 3H), 1.39 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.4, 153.9, 146.9 (q, *J* = 3.8 Hz), 138.4 (q, *J* = 3.5 Hz), 128.1 (q, *J* = 33.1 Hz), 124.4 (q, *J* = 271.3 Hz), 121.7, 85.0, 53.5, 24.8. $^{19}$F NMR(376.5 MHz, $CDCl_3$), δ -62.7 (s); $^{11}$B NMR (128.4 MHz, $CDCl_3$) δ 31.6, HRMS (ESI+, m/Z): Calculated for 331.12027 , found: 331.12730 .



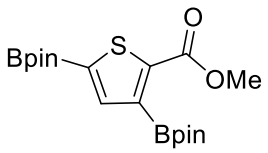
**Ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinoline-2-carboxylate (4c)**

The general procedure was followed using ethyl quinoline-2-carboxylate (100.5 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **4c** was 67%, **4c** was obtained as white solid (90mg, 55%) after purification by silica gel flash chromatography (EtOAc/PE = 1:2 v/v). $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.24 (d, $J$ = 8.4 Hz, 1H), 7.85 (d, $J$ = 8.0 Hz, 1H), 7.71 (t, $J$ = 8.0 Hz, 1H), 7.62 (t, $J$ = 7.6 Hz, 1H), 4.56 (q, $J$ = 7.2 Hz 2H), 1.50 (t, $J$ = 7.2 Hz 3H). 1.45(s, 12H). $^{13}C$ NMR (100 MHz, $CDCl_3$) 167.4, 151.8, 147.5, 142.7, 130.5, 130.3, 128.2, 128.0, 127.6, 84.4, 62.5, 24.8, 24.8, 14.3.; $^{11}B$ NMR (128.4 MHz, $CDCl_3$) δ 30.6, HRMS (ESI+, m/Z): Calculated for 328.17147, found: 328.17134. Point 246-248 °C



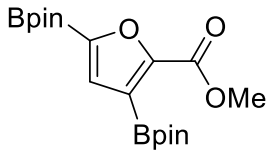

**Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[b]thiophene-2-carboxylate (4d)**

The general procedure was followed using methyl benzo[b]thiophene-2-carboxylate (96 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **4d** was 93%, **4d** was obtained as white solid (135.1mg, 85%) after purification by silica gel flash chromatography (EtOAc/PE = 1:10 v/v), $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.90-7.84 (m, 2H), 7.45-7.37 (m, 2H), 3.94 (s, 3H), 1.49 (s, 12H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 163.7, 142.5, 142.4, 137.7, 126.7, 125.9, 124.8, 122.5, 84.7, 52.5, 25.0, 24.6; The spectral data were in accordance with literature[(4)].



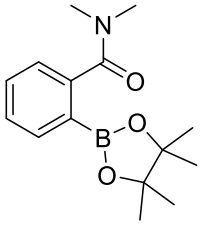

**Methyl 3,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-carboxylate (4e)**

The general procedure was followed using methyl thiophene-2-carboxylate (71 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Methy-THF, the resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **4e** was 84%, **4e** was obtained as pale yellow oil (94.5 mg, 80%) after purification by silica gel flash chromatography (EtOAc/PE = 1:20 v/v). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 3.87 (s, 3H), 1.38 (s, 12H), 1.33 (s, 12H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 162.9, 143.9, 141.8, 84.5, 84.3, 83.1, 52.2, 24.8; The spectral data were in accordance with literature [(4)]



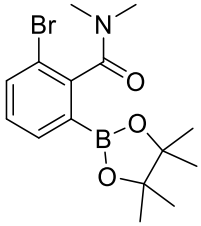

**Methyl 3,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan-2-carboxylate (4f)**

The general procedure was followed using methyl furan-2-carboxylate (62 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Methy-THF, The resulting mixture was allowed to stir 16 hours at 80 ℃. The $^1H$ NMR yields of **4f** was 60%, **4f** was obtained as white solid (90.7 mg, 56%) after purification by silica gel flash chromatography (EtOAc/PE = 1:20 v/v). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 3.89(s, 3H), 1.36 (s, 12H). 1.33(s, 12H). $^{13}C$ NMR (100 MHz, $CDCl_3$) 159.3, 151.6, 128.8, 84.6, 84.3, 83.1, 52.0, 24.7; The spectral data were in accordance with literature [(4)]




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

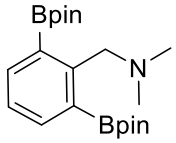
The general procedure was followed using *N,N*-dimethylbenzamide (74.5 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **4g** was 60%, **4g** was obtained as white solid (67.4 mg, 49%) after purification by silica gel flash chromatography (EtOAc/PE = 1:2 v/v). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 3.00 (bs, 6H), 1.25 (s, 12H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 172.5, 142.6, 135.0, 130.9, 128.2, 125.5, 83.5, 25.0; The spectral data were in accordance with literature[(1)].




**2-Bromo-*N,N*-dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (4h)**

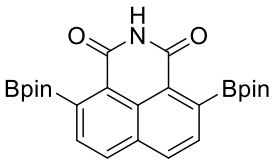
The general procedure was followed using 2-bromo-*N,N*-dimethylbenzamide (113.5 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1H$ NMR yields of **4h** was 52%, **4h** was obtained as white solid (79.4 mg, 47%) after purification by silica gel flash chromatography (EtOAc/PE = 1:2 v/v). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* =7.2 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 3.10 (s, 1H), 2.77 (s, 3H), 1.30 (s, 12H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 169.5, 144.1, 135.2, 134.4, 129.1, 119.4,

84.1, 38.1, 34.4, 24.9; $^{11}$B NMR (128.4 MHz, $CDCl_3$) δ 30.0 ppm; HRMS (ESI$^+$, m/Z): Calculated for 354.08706, found: 354.08711. Point 215-217 °C.




**1-(2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-*N,N*-dimethylmethanamine (4i)**

The general procedure was followed using *N,N*-dimethyl-1-phenylmethanamine (67.5 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, The resulting mixture was allowed to stir 16 hours at 80 °C. The $^1$H NMR yields of **4i** was 96%, **4i** was obtained as pale yellow solid (80.1 mg, 93%) after purification by vacuum distillation and filtration of a short silica gel column (EtOAc). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, $J$ = 7.6 Hz, 2H), 7.20 (t, $J$ = 7.2 Hz, 1H), 4.15 (s, 2H), 2.60 (s, 6H), 1.29 (s, 24H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 146.2, 134.5, 126.4, 81.6, 66.6, 45.8, 25.8, 24.8; The spectral data were in accordance with literature[1].



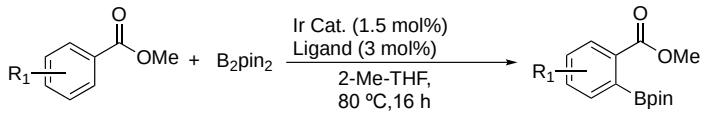

**4,9-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (4j)**

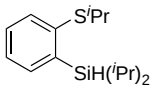
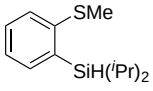
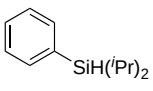
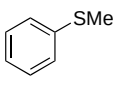
The general procedure was followed using 1H-benzo[de]isoquinoline-1,3(2H)-dione (98.5 mg, 0.5 mmol, 1.0 equiv.), $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), *Si,S*-ligand (4 mg, 0.015 mmol, 0.03 equiv.) and $B_2pin_2$ (154 mg, 0.6 mmol, 1.2 equiv.) in 0.5 mL of 2-Me-THF, the resulting mixture was allowed to stir 16 hours at 80 °C. The $^1$H NMR yields of **4j** was 85%, **4j** was obtained as pale yellow oil (101 mg, 82%) after purification by silica gel flash chromatography (EtOAc/PE = 1:20 v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.17 (d, $J$ = 8.0 Hz, 2H), 7.73 (d, $J$ = 8.0 Hz, 2H), 1.49 (s, 24H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.3, 133.2, 132.0, 129.8, 128.3, 125.3, 84.6, 24.8; $^{11}$B NMR (128.4 MHz, $CDCl_3$) δ 31.2, HRMS (ESI+, m/Z): Calculated for 449.21810, found: 449.22831.

# 4 Control experiment for *ortho*-directed borylation using different ligands.

In a nitrogen filled glovebox, $[IrOMe(cod)]_2$ (5 mg, 0.0075 mmol, 0.015 equiv.), ligand (0.015 mmol, 0.03 equiv.) was dissolved in 0.5 mL 2-Me-THF in a 10 mL pressure tube containing a magnetic stir bar, in the optimized condition: the $[IrOMe(cod)]_2$ stir in advance with *Si,S*-ligand for 1h, then 0.5 mmol methyl benzoate substrate and 1.2 equiv. $B_2pin_2$ were also added, and the reaction vessel was sealed and heated at 80 °C for 16h. Standard purification were carried out and the reaction yields were listed in Table S1.

**Table S1. Control Experiment of Ligand toward *ortho*-directed borylation**




| Ligand |  |  |  |  |
|---|---|---|---|---|
| Yield of **2** | 66% | 64% | trace | 10% |



# 5. References


(1) Wang, G.; Liu,L.; Wang, H.; Ding, Y,; Zhou, J.; Mao, S.; Li, P. *J. Am. Chem. Soc*. **2017**, *139*, 91

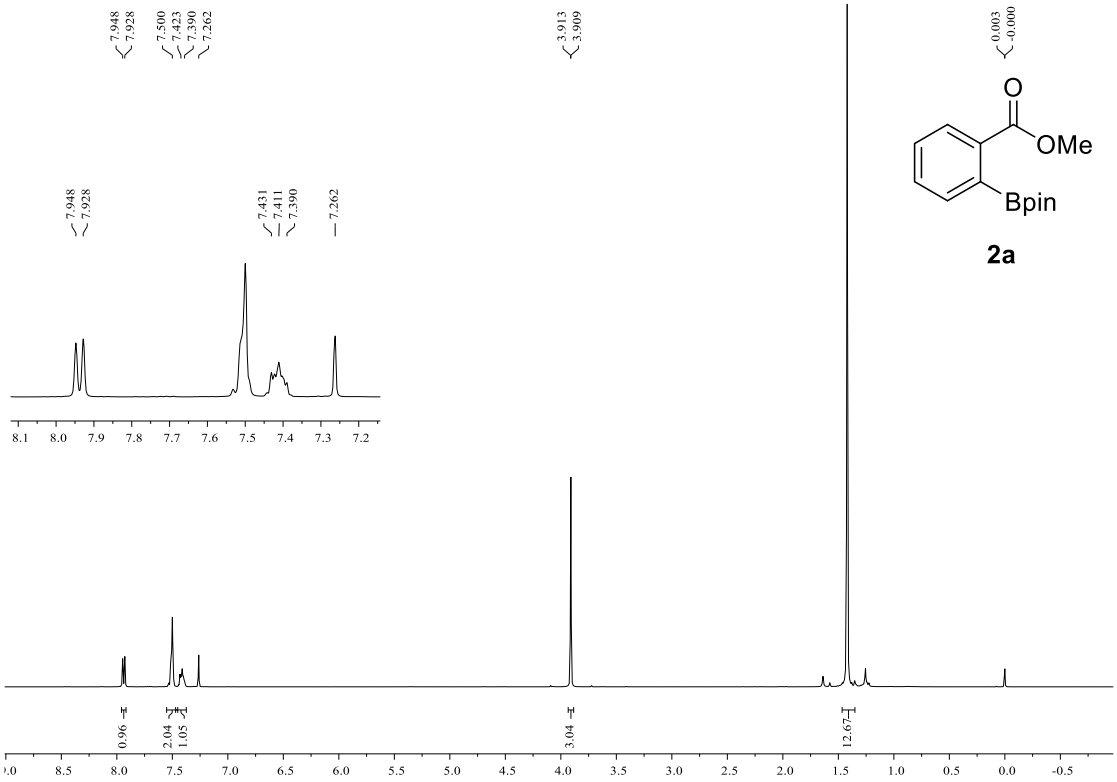
(2) Ghaffari, B.; Preshlock, S. M.; Plattner, D. L.; Staples, R. J.; Maligres, P. E.; Krska, S. W.; Maleczka, R. E.; Smith,M. R. III. *J. Am. Chem. Soc.* **2014**, *136*, 14345.

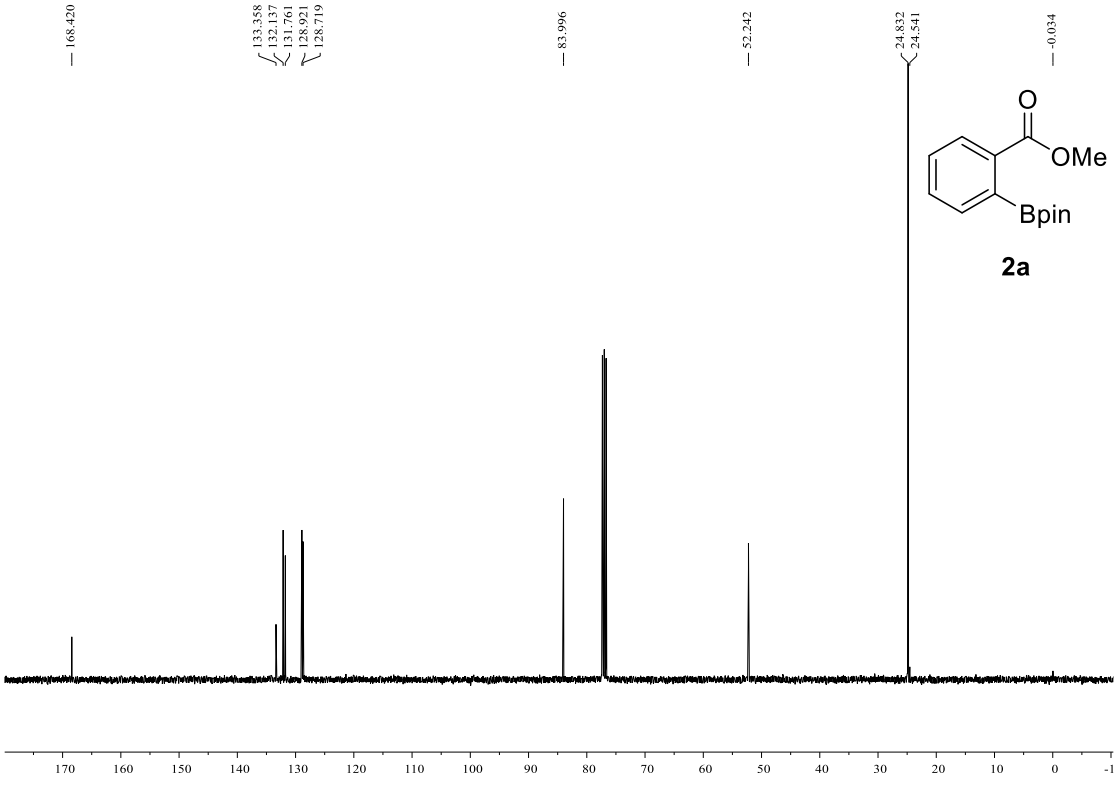
(3) Ishiyama, T.; Isou, H.; Kikuchi, T.; Miyaura, N. *Chem. Commun*. **2010**, *46*, 159

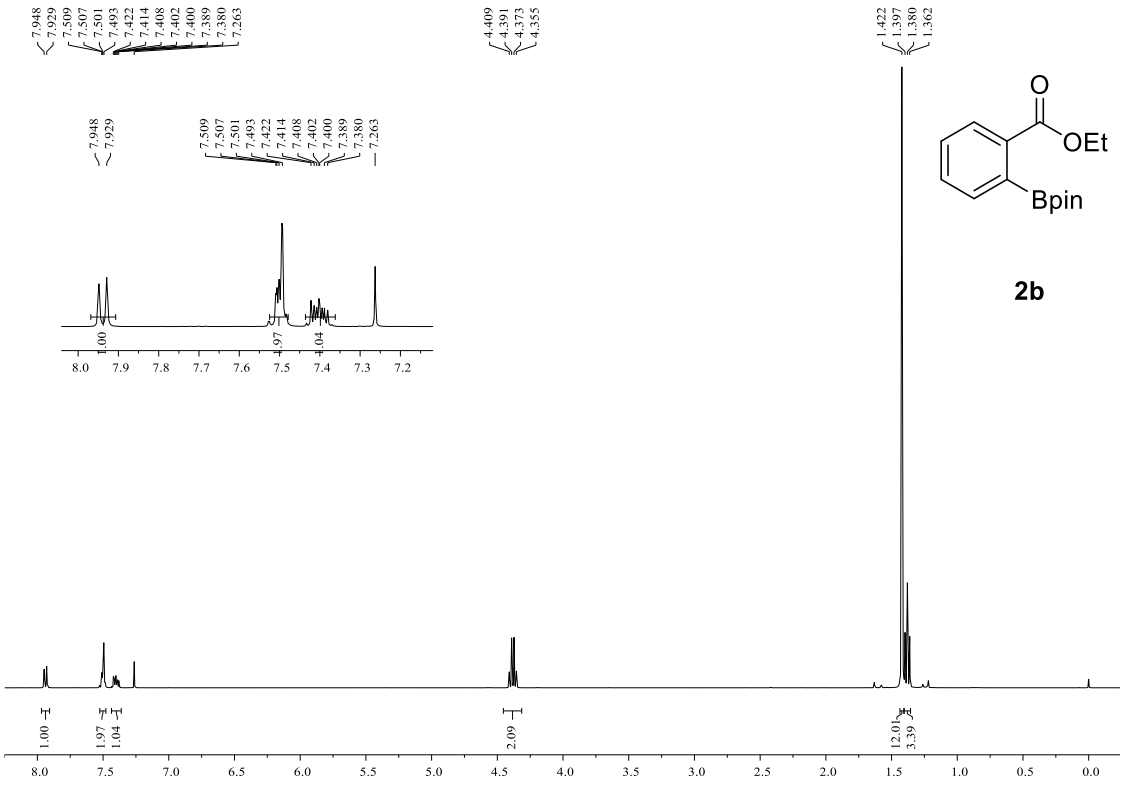
(4) Kawamorita, S.; Ohmiya, H.; Sawamura, M.; J. Org. Chem. 2010, 75, 3855

(5) Kinuta, H.; Tobisu, M.; Chatani,N.; *J. Am. Chem. Soc.* **2015**, *137*, 1593−1600

# 6. Copies of NMR Spectra

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7.501
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7.422
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7.402
7.400
7.389
7.380
7.263
4.409
4.391
4.373
4.355
1.422
1.397
1.380
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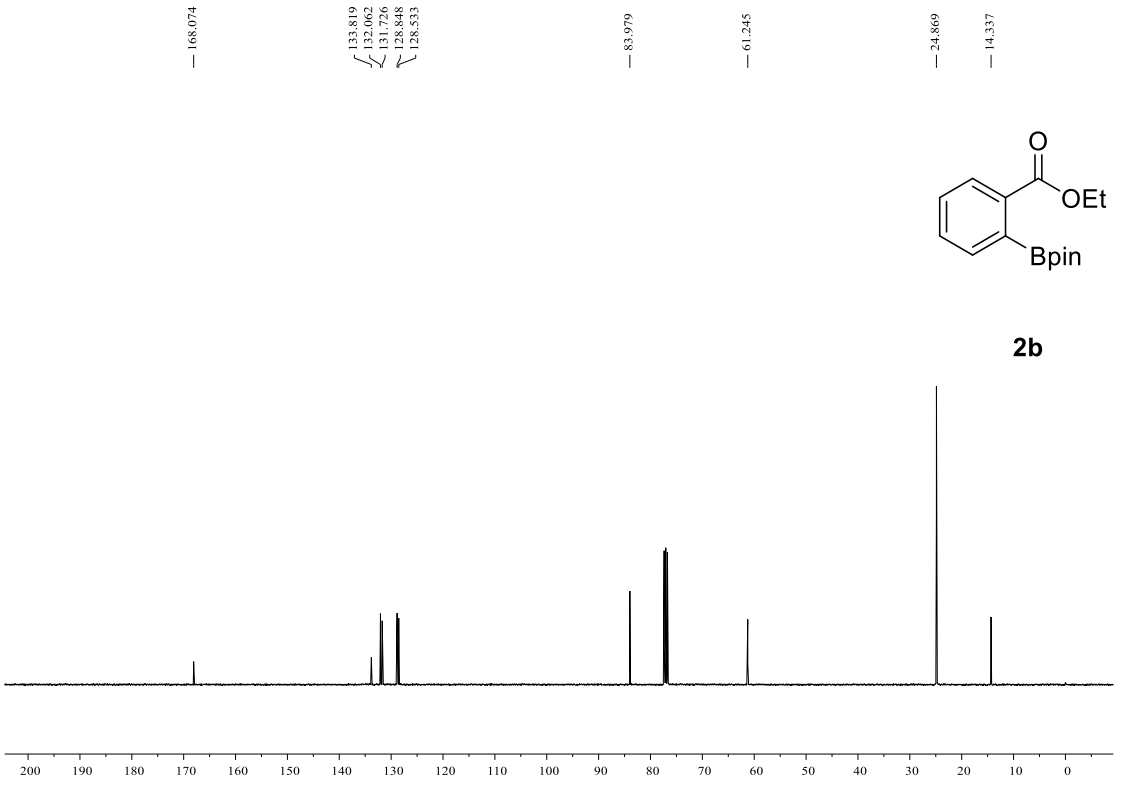
O
OEt
Bpin
1.00
1.97
1.04
2.09
12.01
3.39

**2b**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83.979
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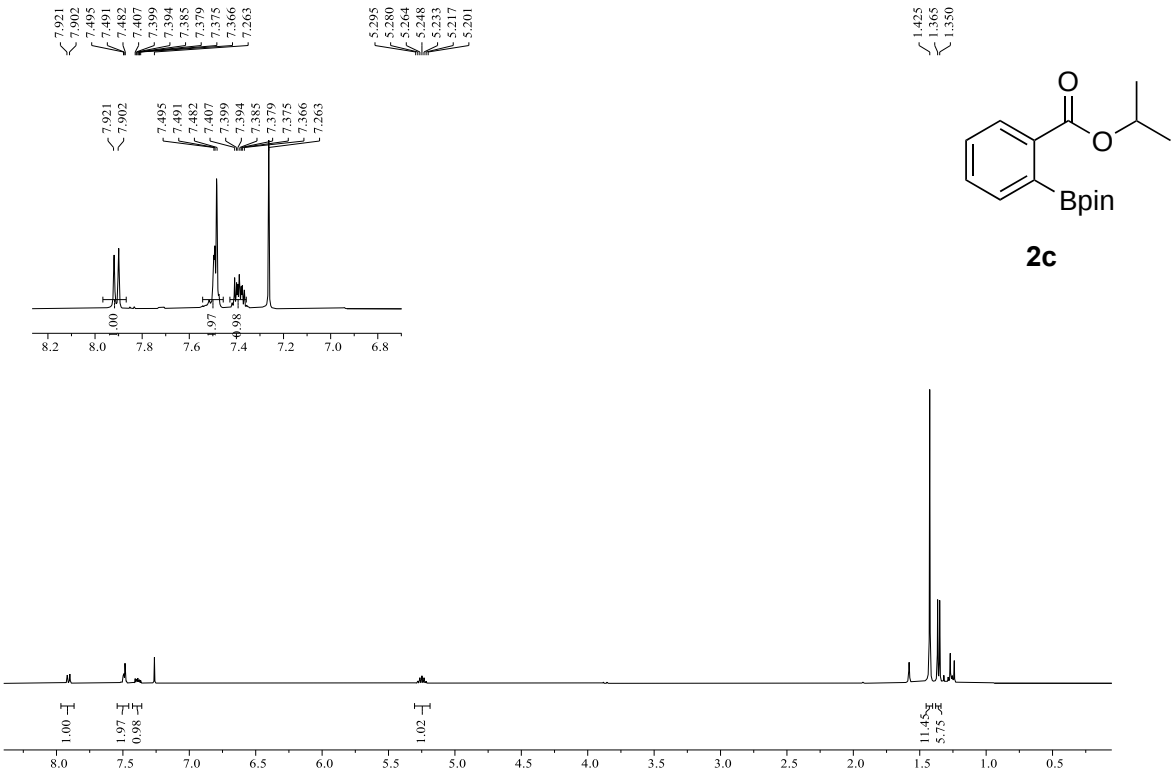
OEt
Bpin

**2b**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5.280
5.264
5.248
5.233
5.217
5.201
1.425
1.365
1.350
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0.98
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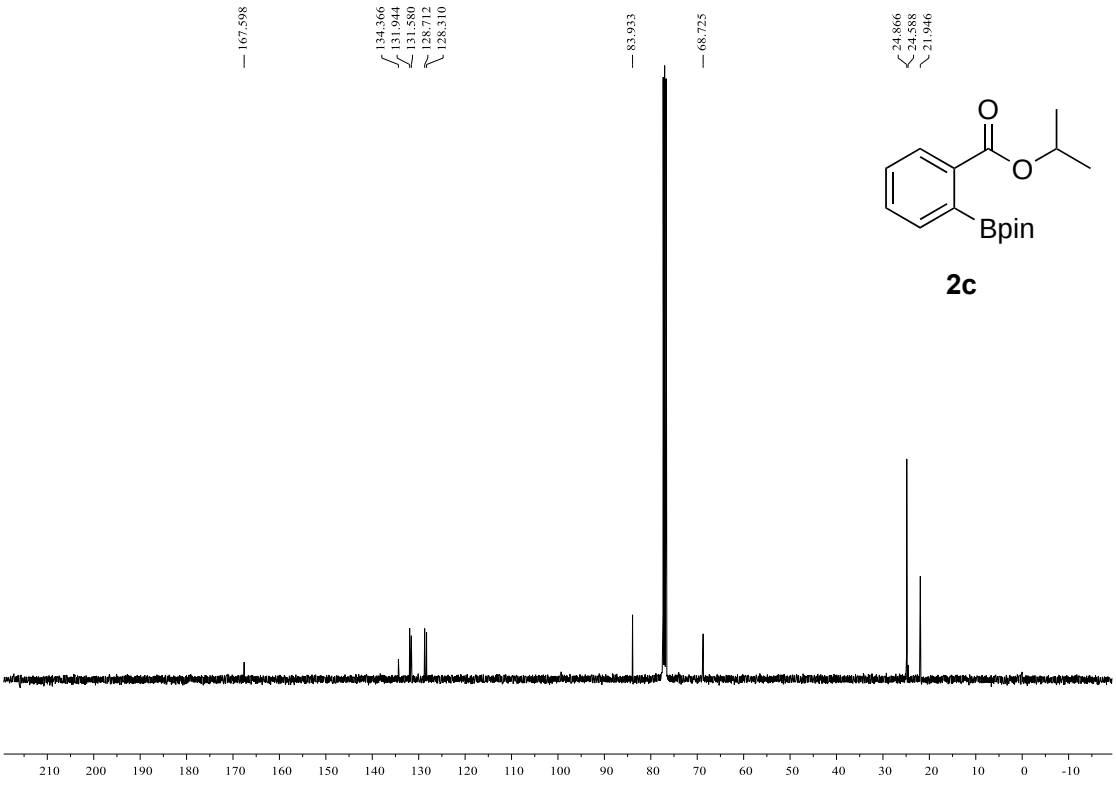
O
O
Bpin

**2c**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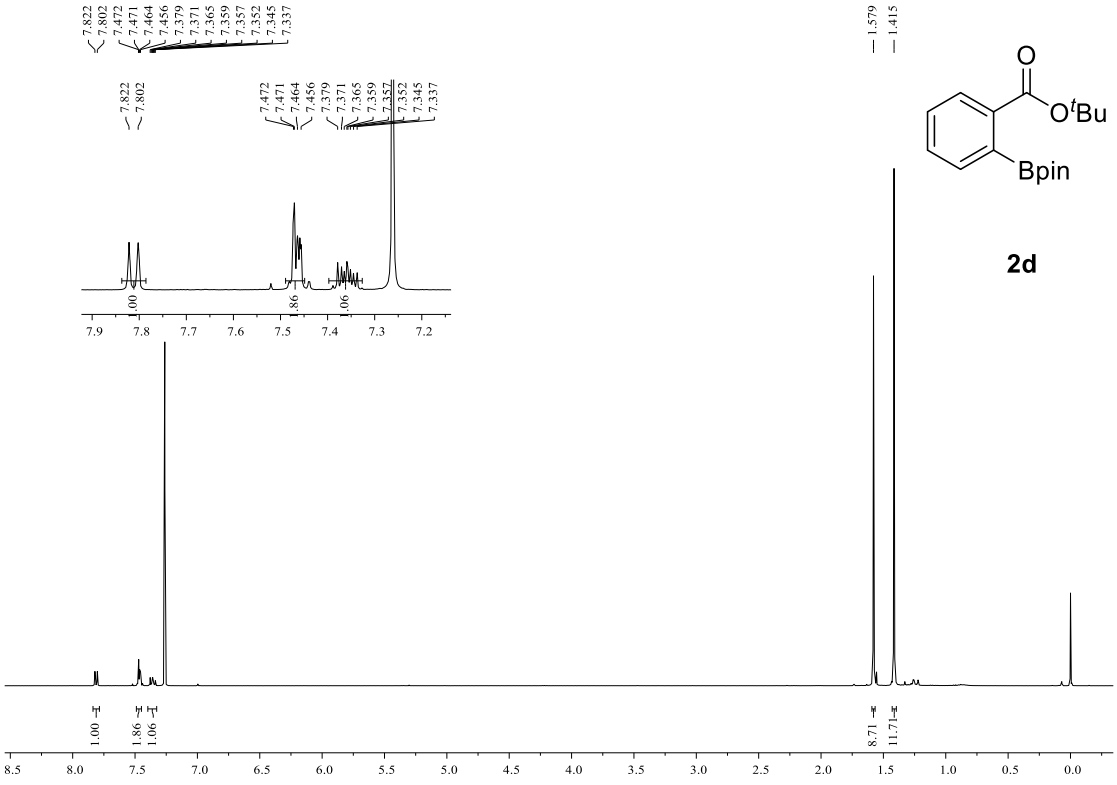
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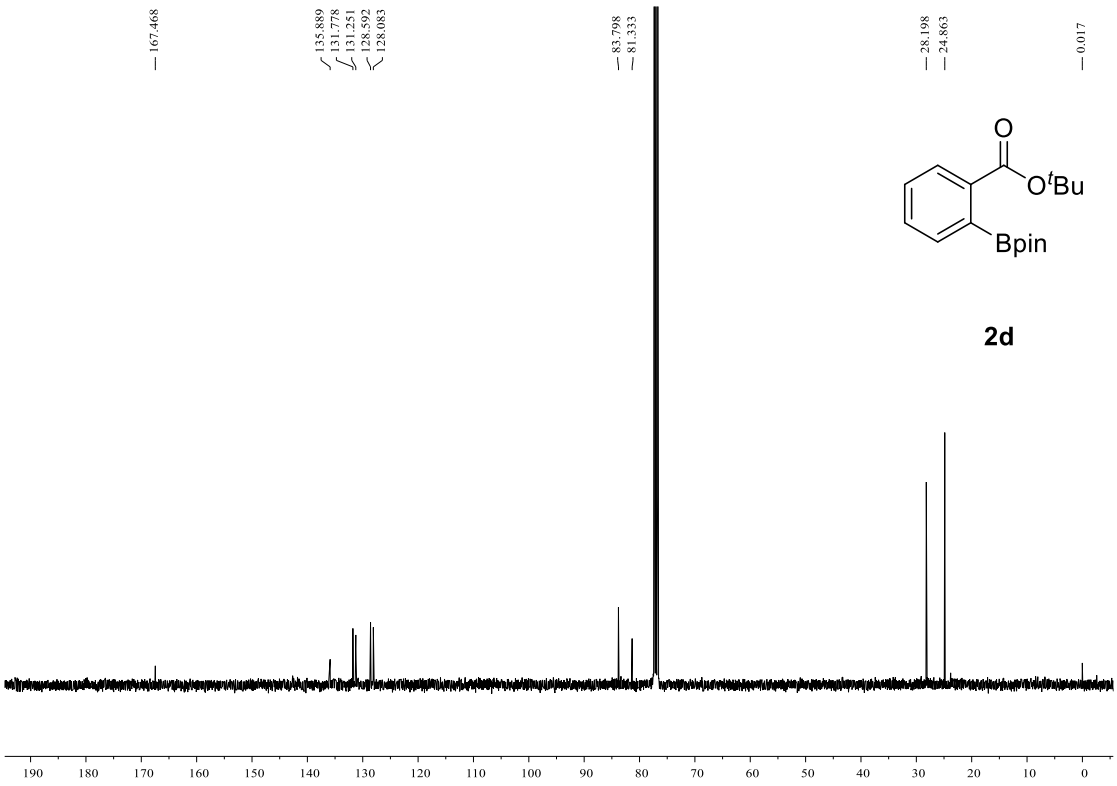
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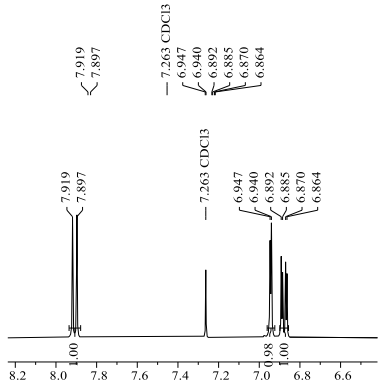
Bpin

**2d**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7.4
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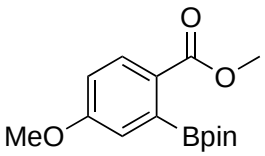
6.8
6.6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MeO
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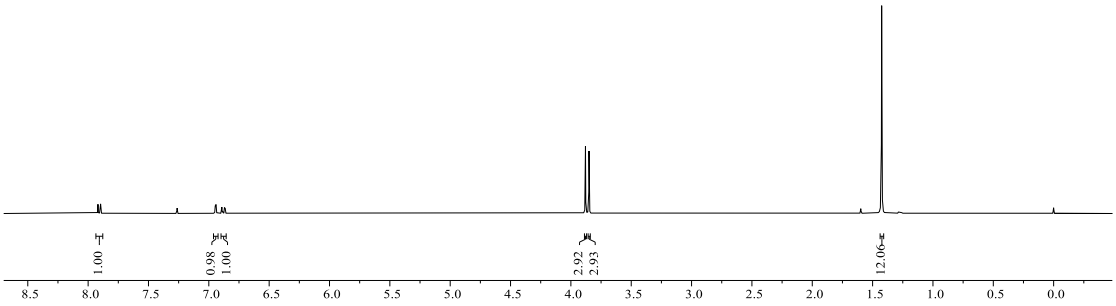
**2e**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0.000
1.00
0.98
1.00
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12.06
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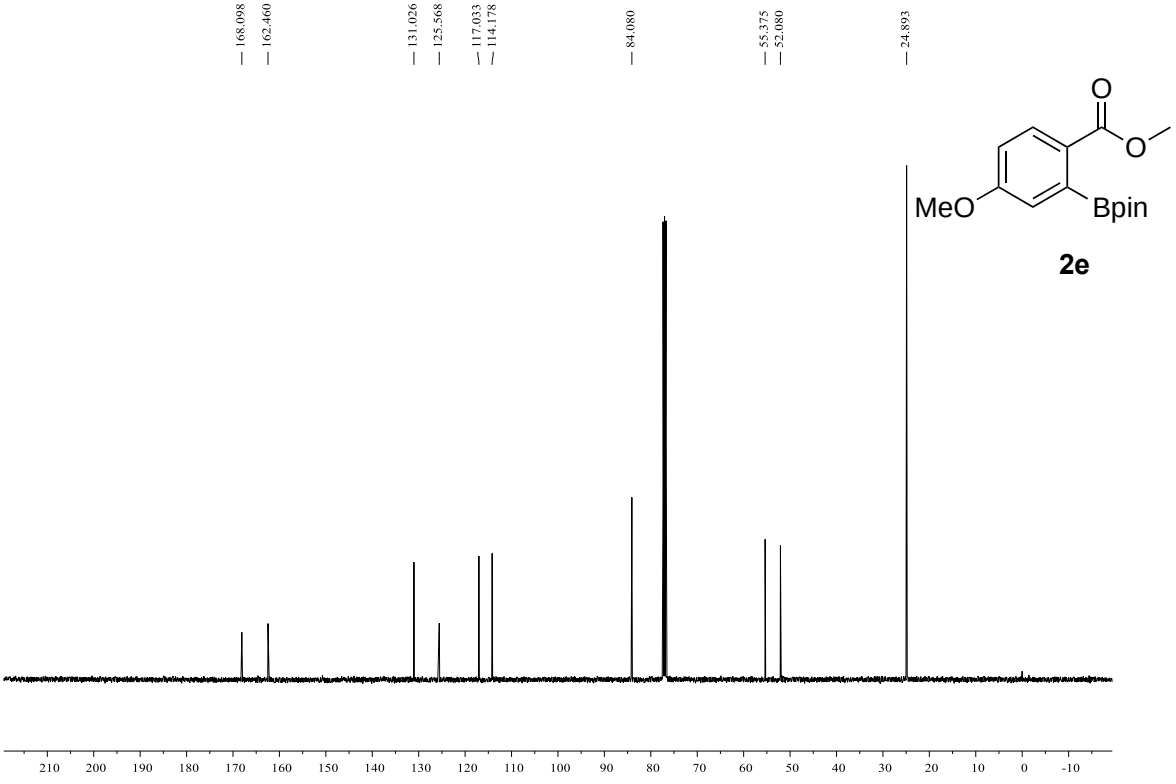
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170
160
150
140
130
120
110
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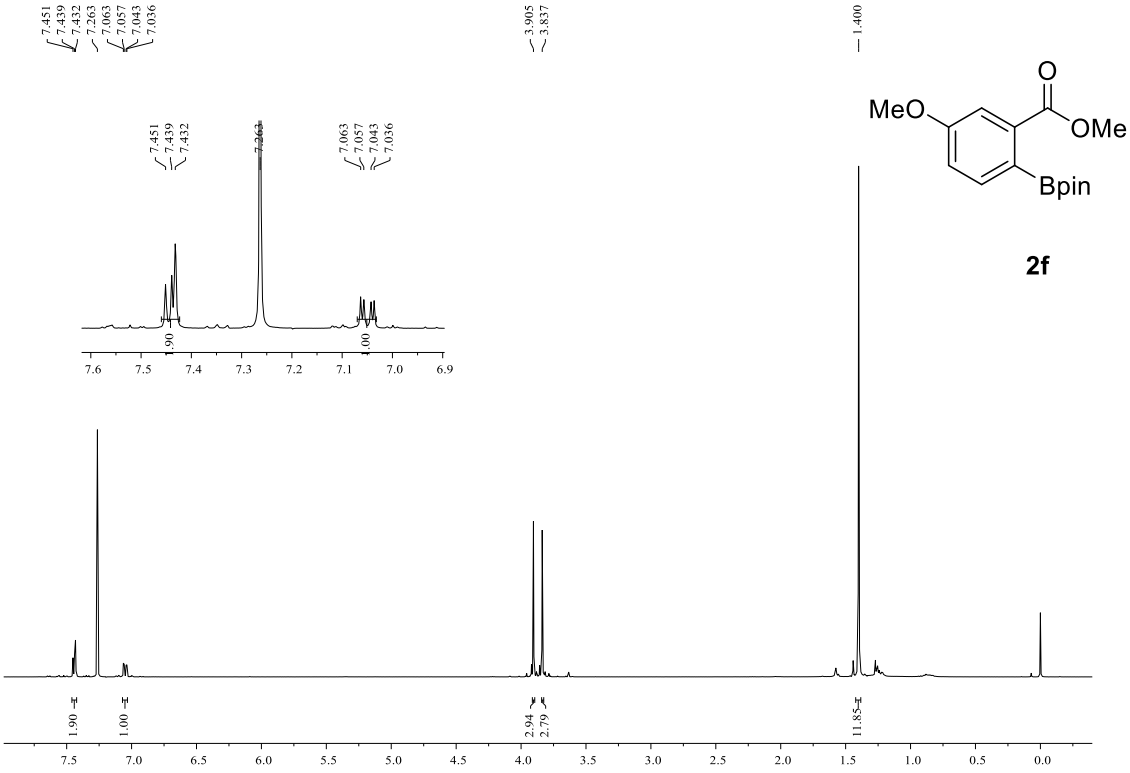
70
60
50
40
30
20
10
0
-10


O
O
MeO
Bpin

**2e**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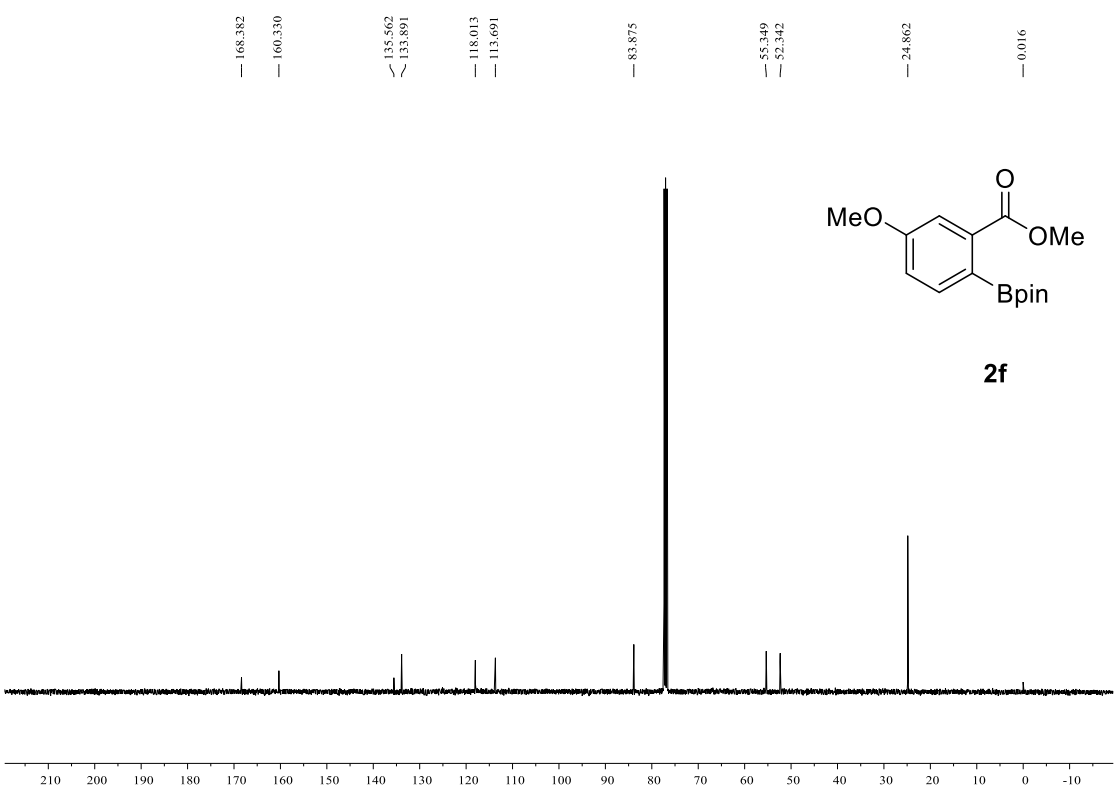
**2f**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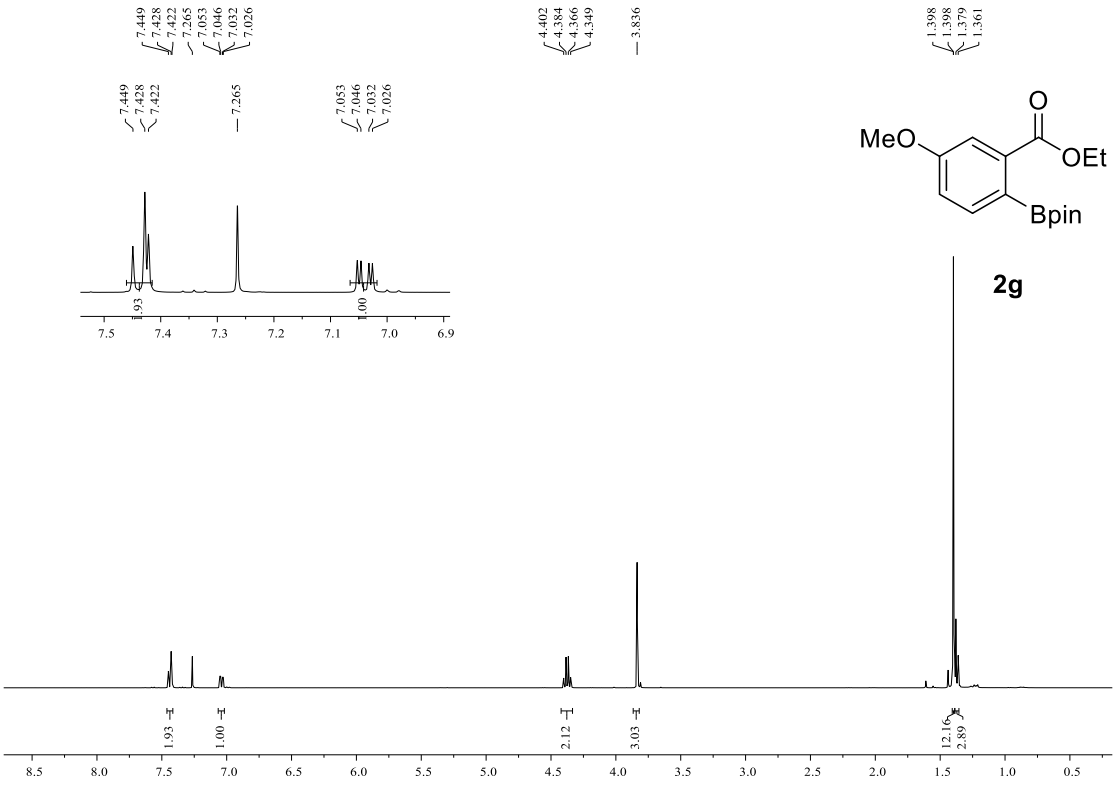
**2f**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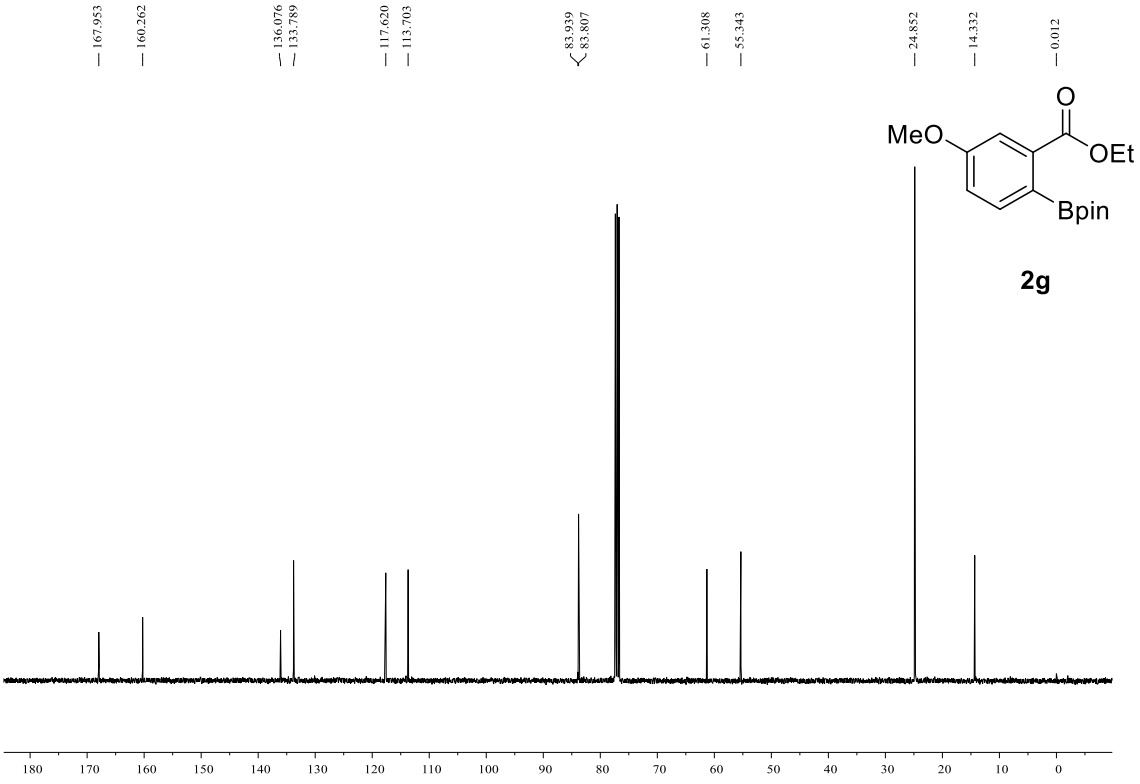
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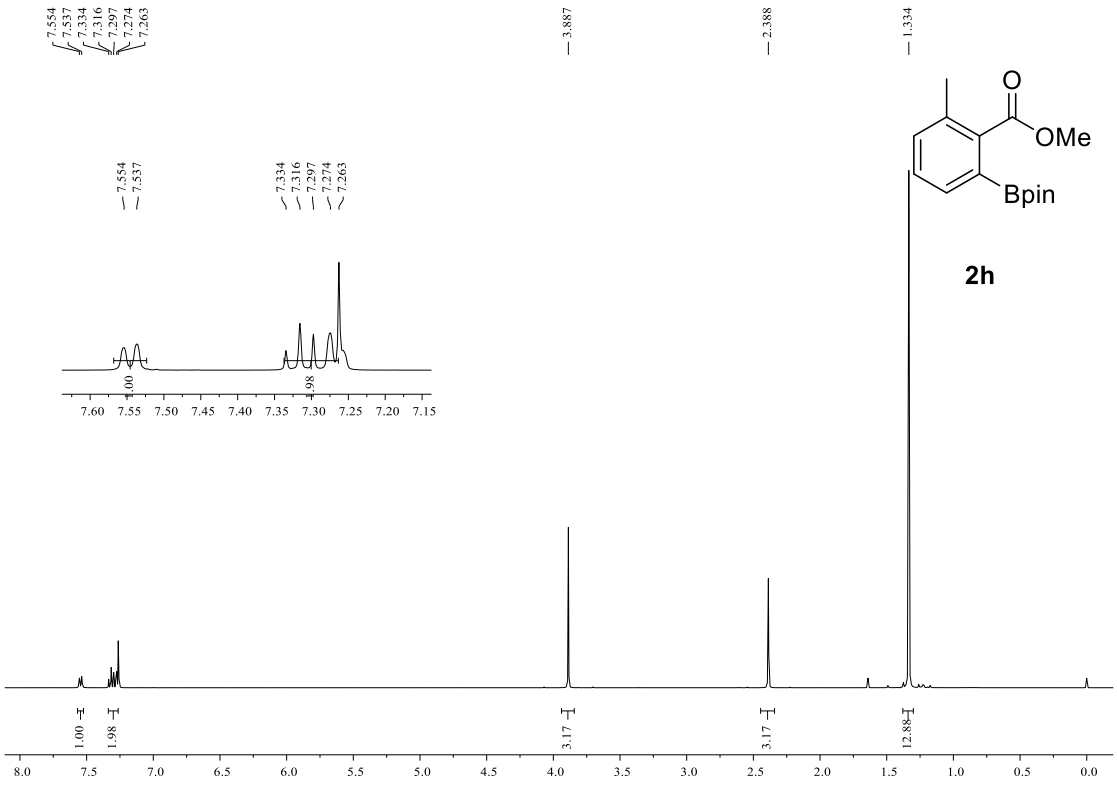
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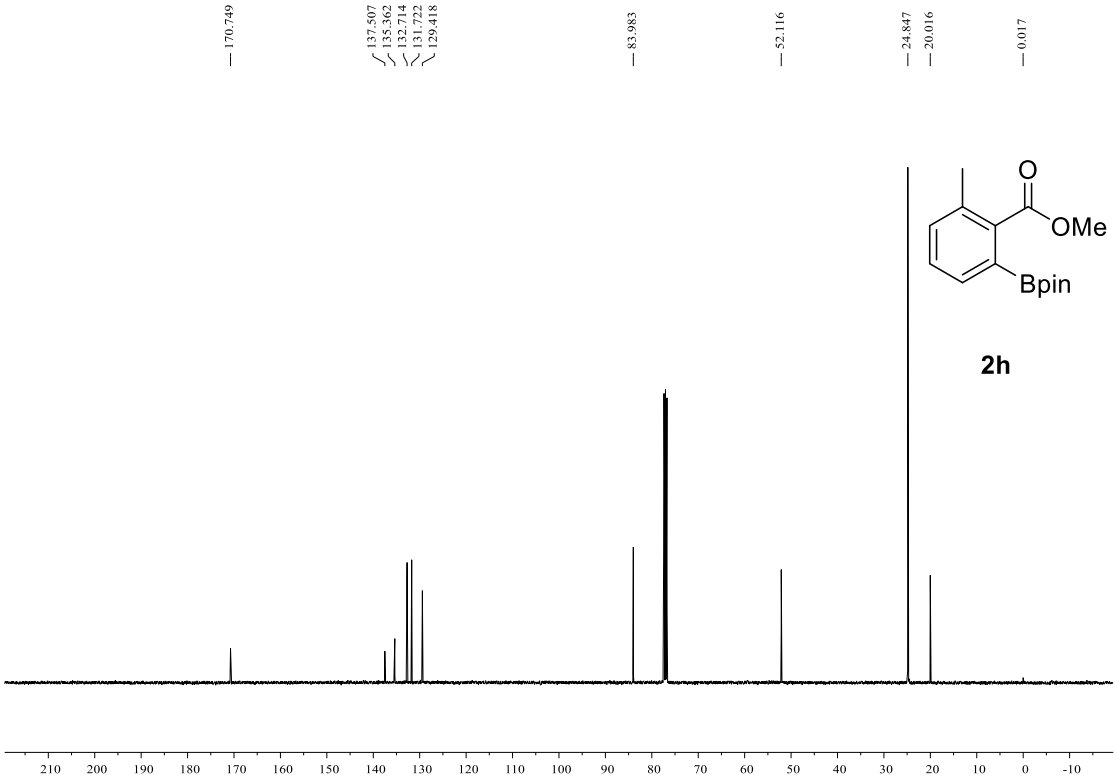
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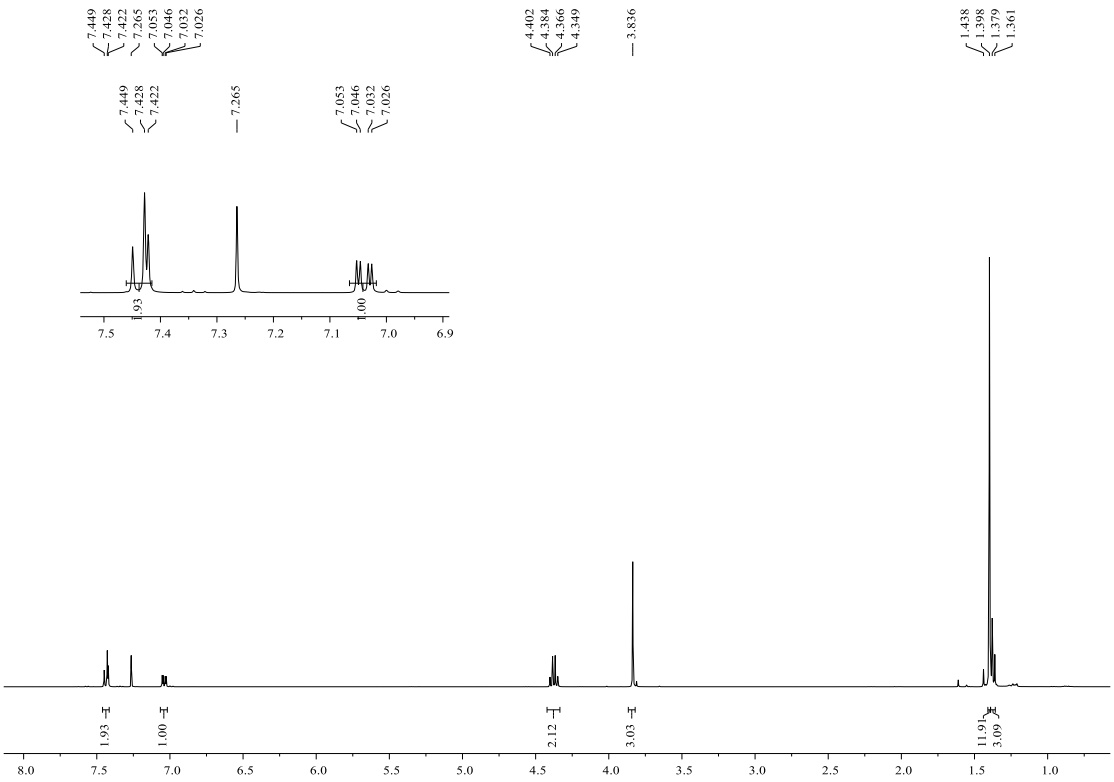
OMe
Bpin
2h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7.422
7.265
7.053
7.046
7.032
7.026
4.402
4.384
4.366
4.349
3.836
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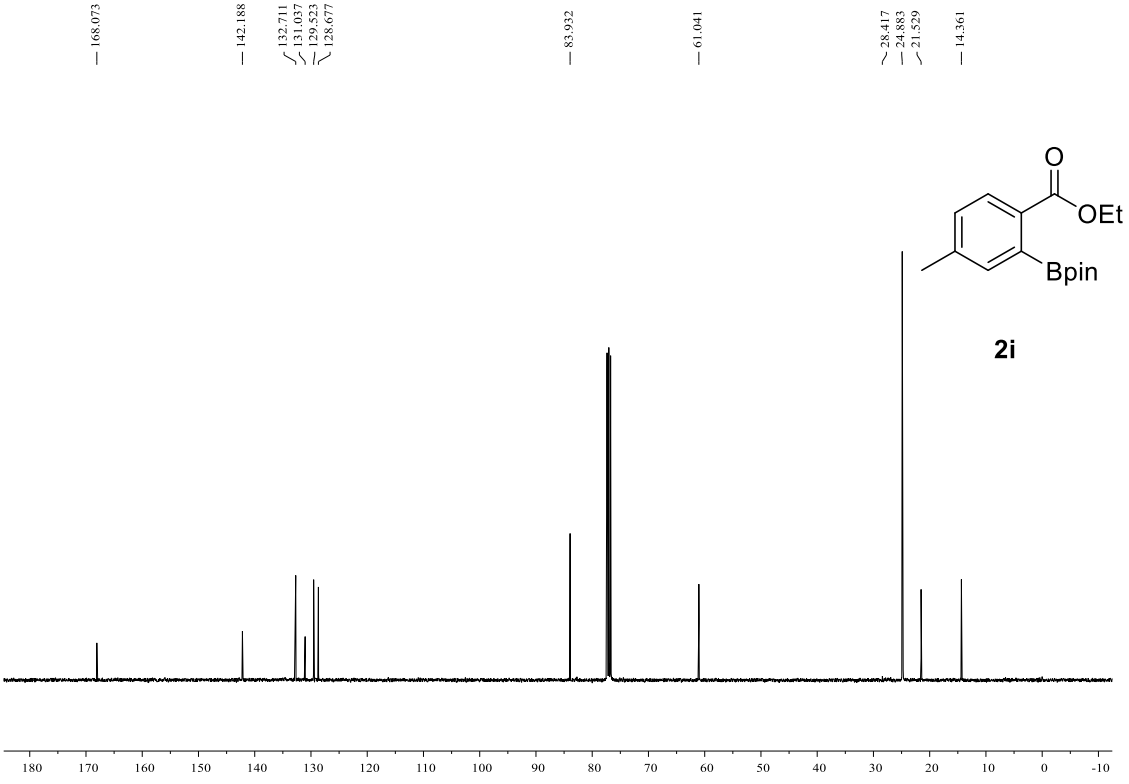
1.398
1.379
1.361
1.93
1.00
2.12
3.03
11.91
3.09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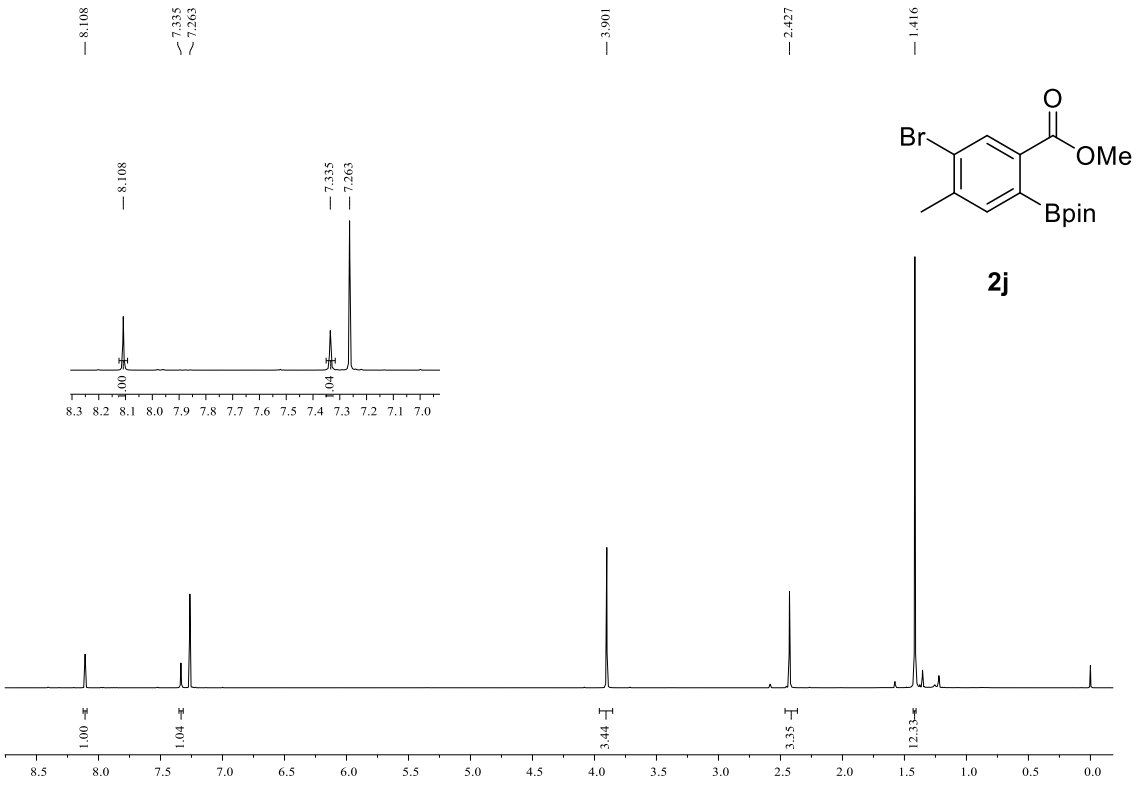
128.677
83.932
61.041
28.417
24.883
21.529
14.361


O
OEt
Bpin

**2i**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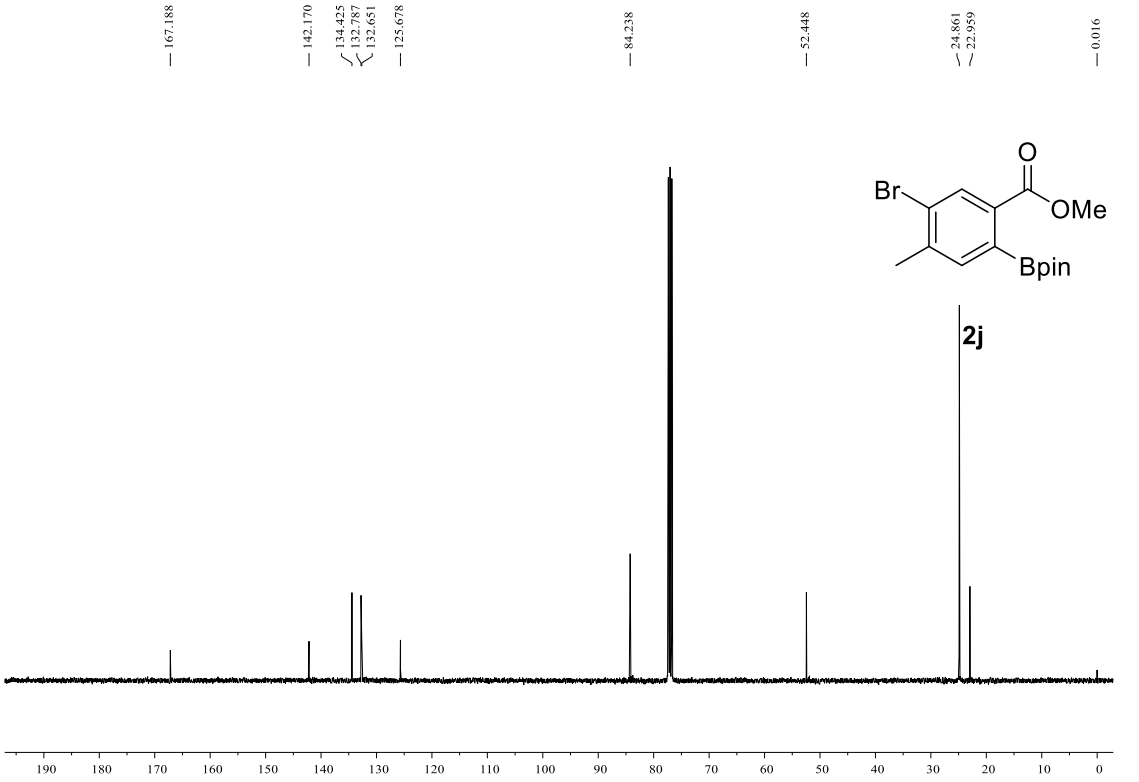
1.416
Br
O
OMe
Bpin
2j
1.00
1.04
3.44
3.35
12.33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52.448
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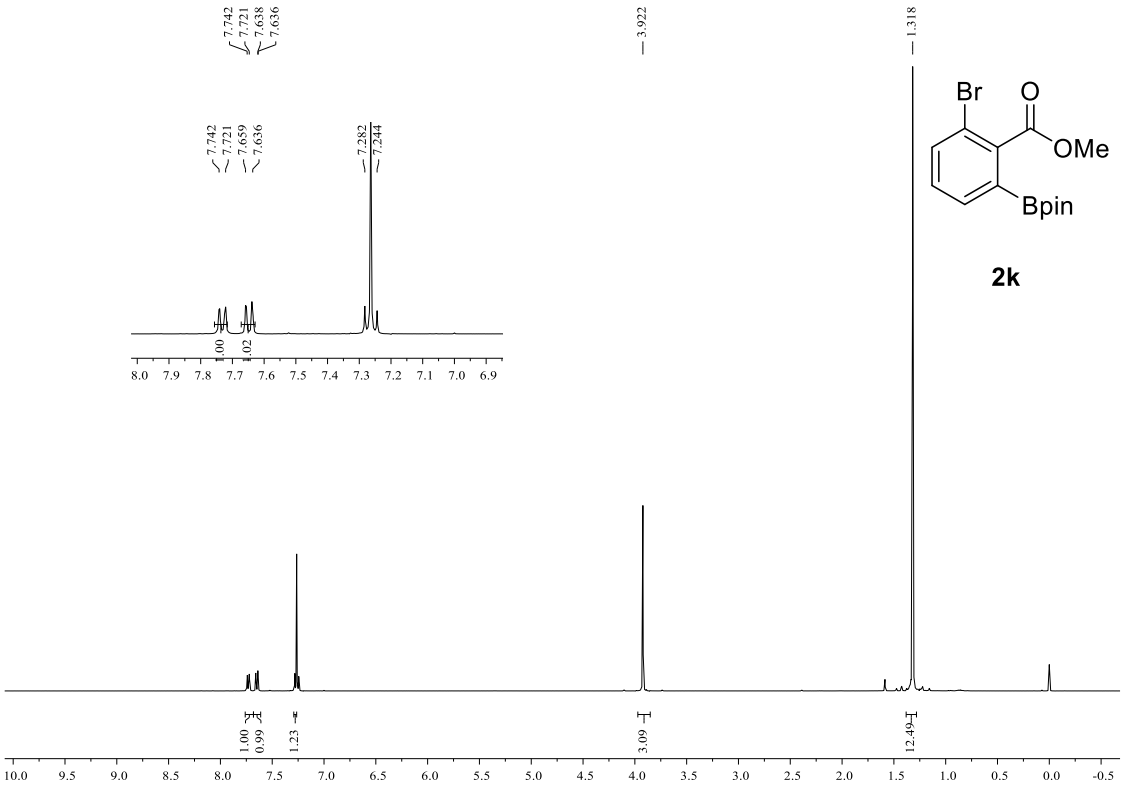
0.016
Br
O
OMe
Bpin
2j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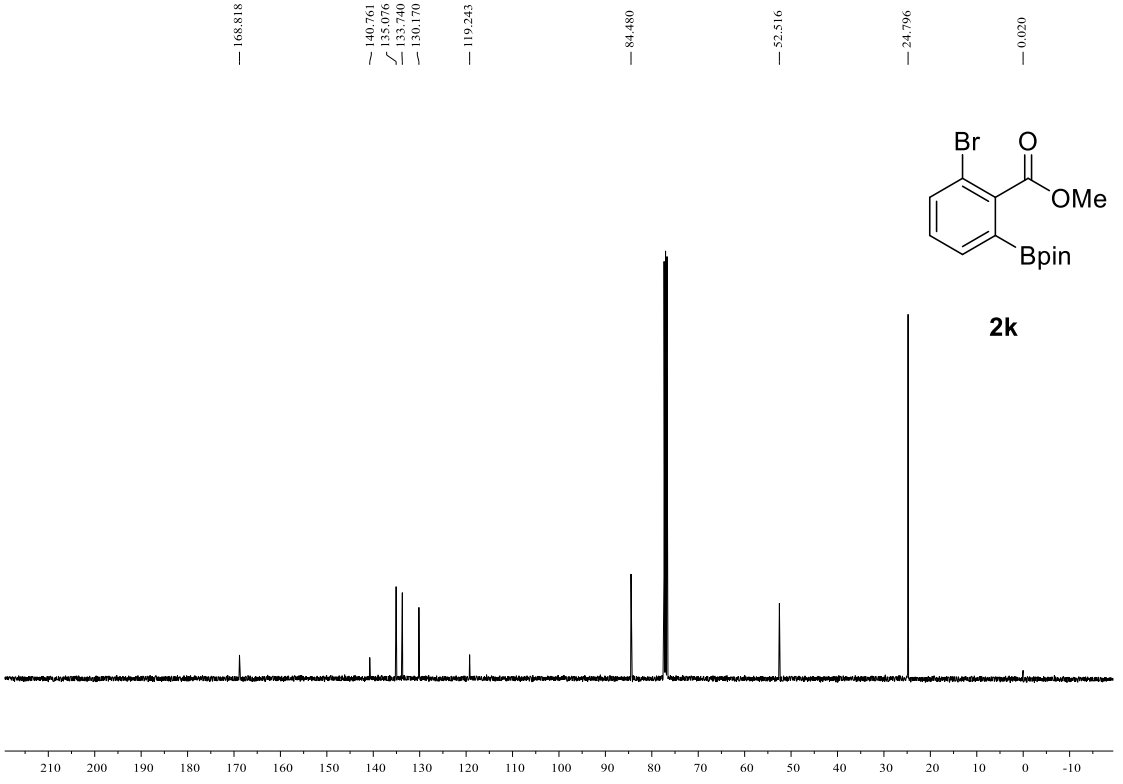
7.638
7.636
3.922
1.318
7.742
7.721
7.659
7.636
7.282
7.244
1.00
1.02
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
Br
O
OMe
Bpin
2k
1.00
0.99
1.23
3.09
12.49
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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119.243
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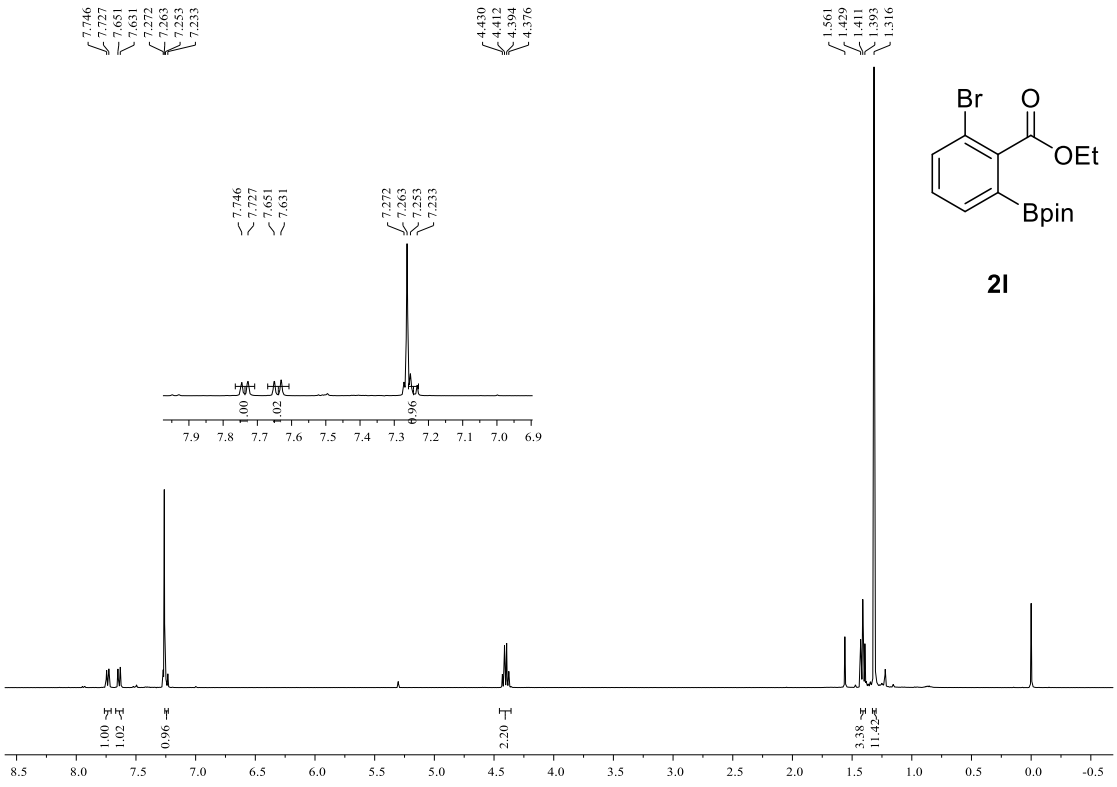
0.020
Br
O
OMe
Bpin
2k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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7.253
7.233
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4.412
4.394
4.376
1.561
1.429
1.411
1.393
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Br
O
OEt
Bpin
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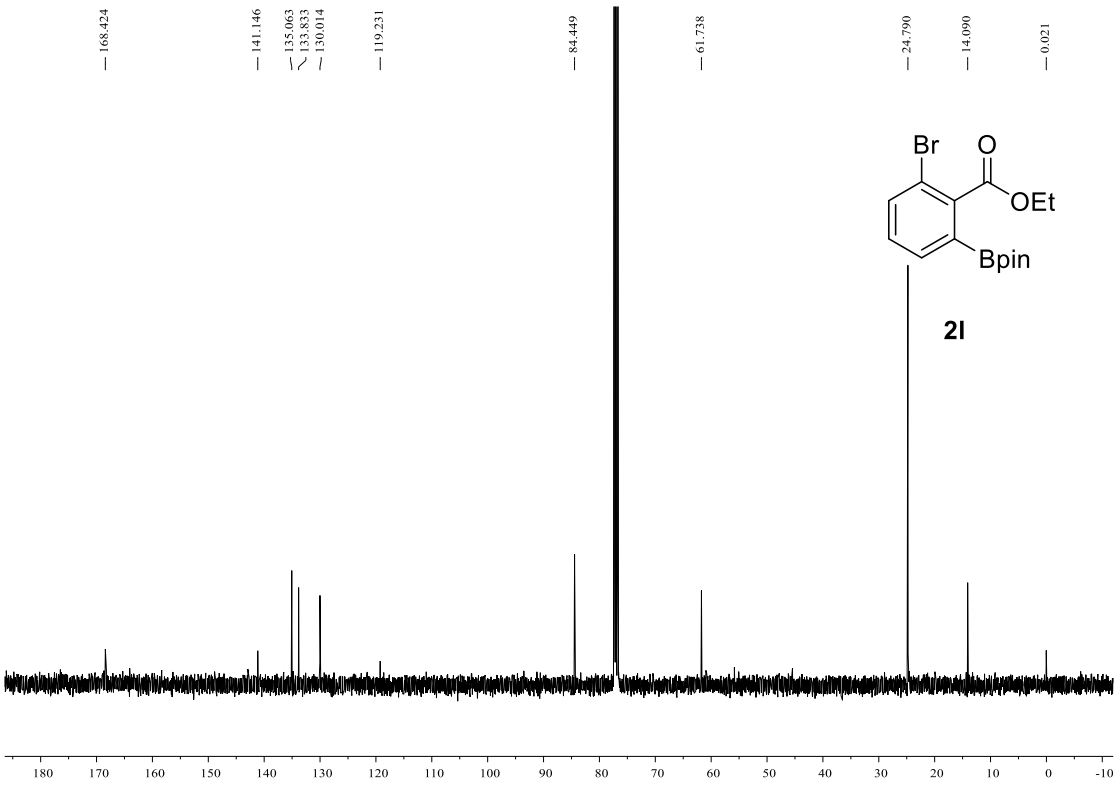
1.02
0.96
2.20
3.38
11.42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141.146
135.063
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119.231
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61.738
24.790
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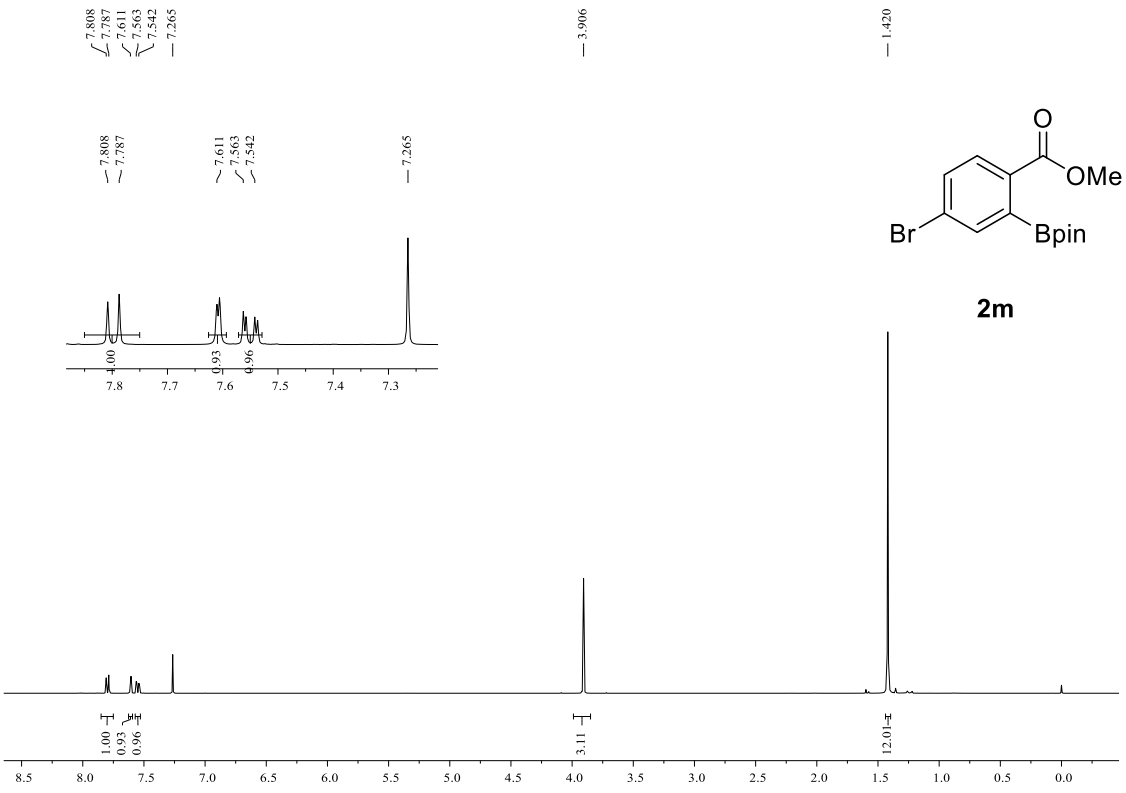
0.021
Br
O
OEt
Bpin
2l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7.787
7.611
7.563
7.542
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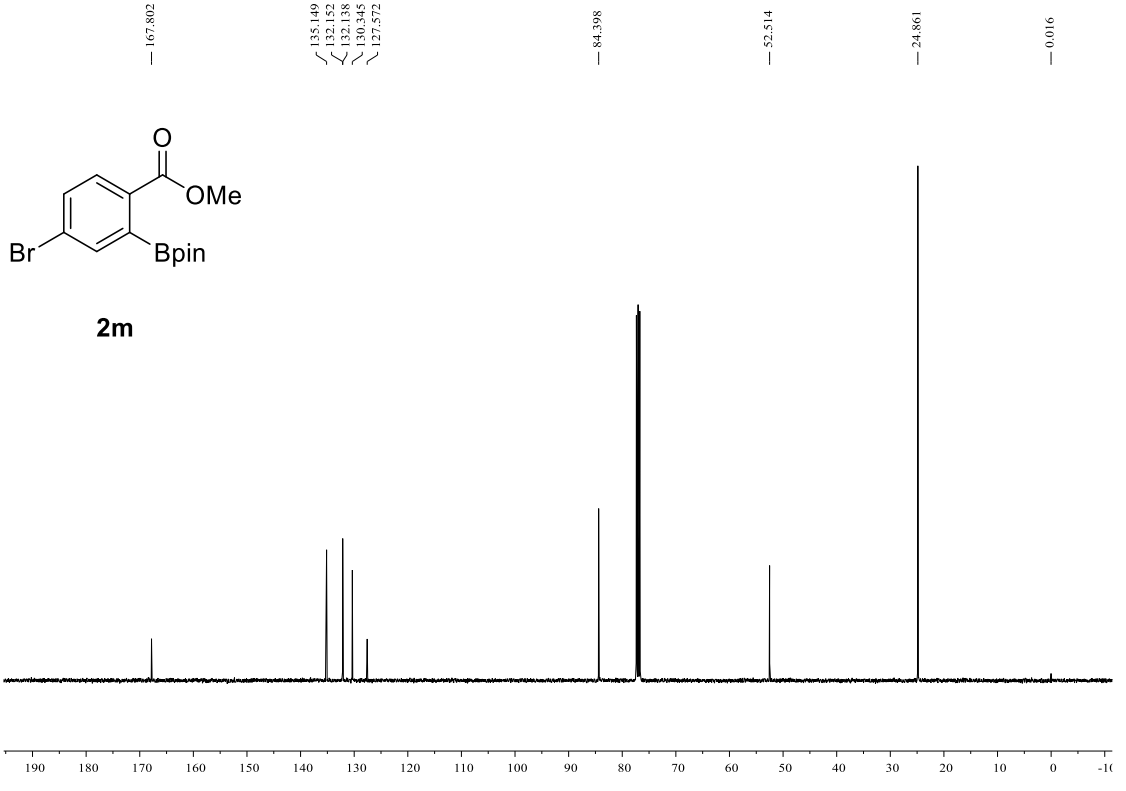
3.906
1.420
1.00
0.93
0.96
3.11
12.01
O
OMe
Br
Bpin

**2m**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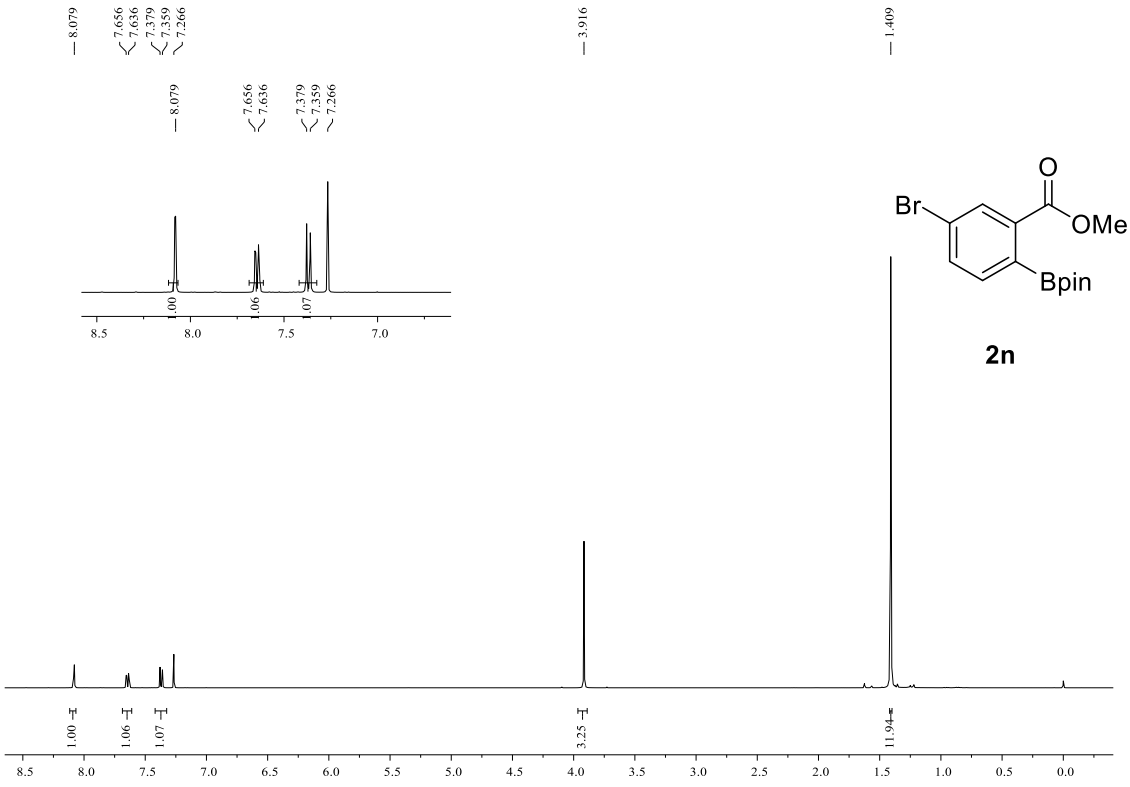
135.149
132.152
132.138
130.345
127.572
84.398
52.514
24.861
0.016
O
OMe
Br
Bpin

**2m**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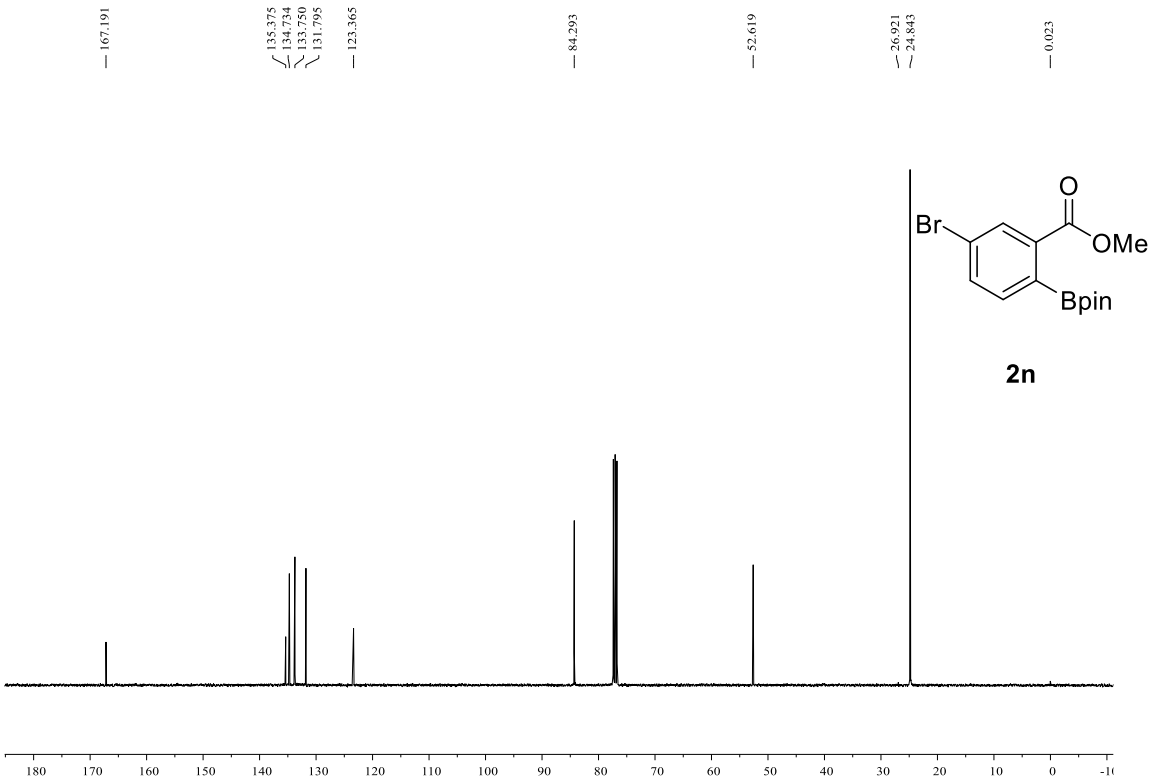
7.656
7.636
7.379
7.359
7.266
3.916
1.409
1.00
1.06
1.07
3.25
11.94
Br
O
OMe
Bpin

**2n**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135.375
134.734
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131.795
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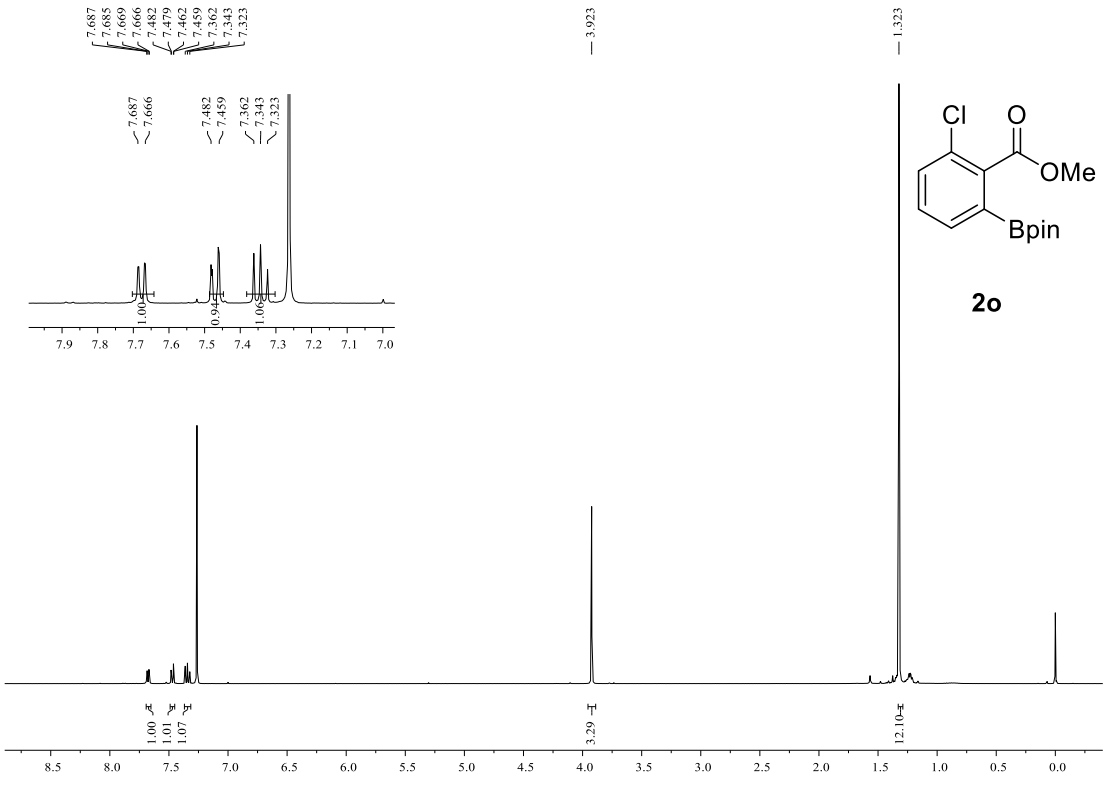
84.293
52.619
26.921
24.843
0.023
Br
O
OMe
Bpin

**2n**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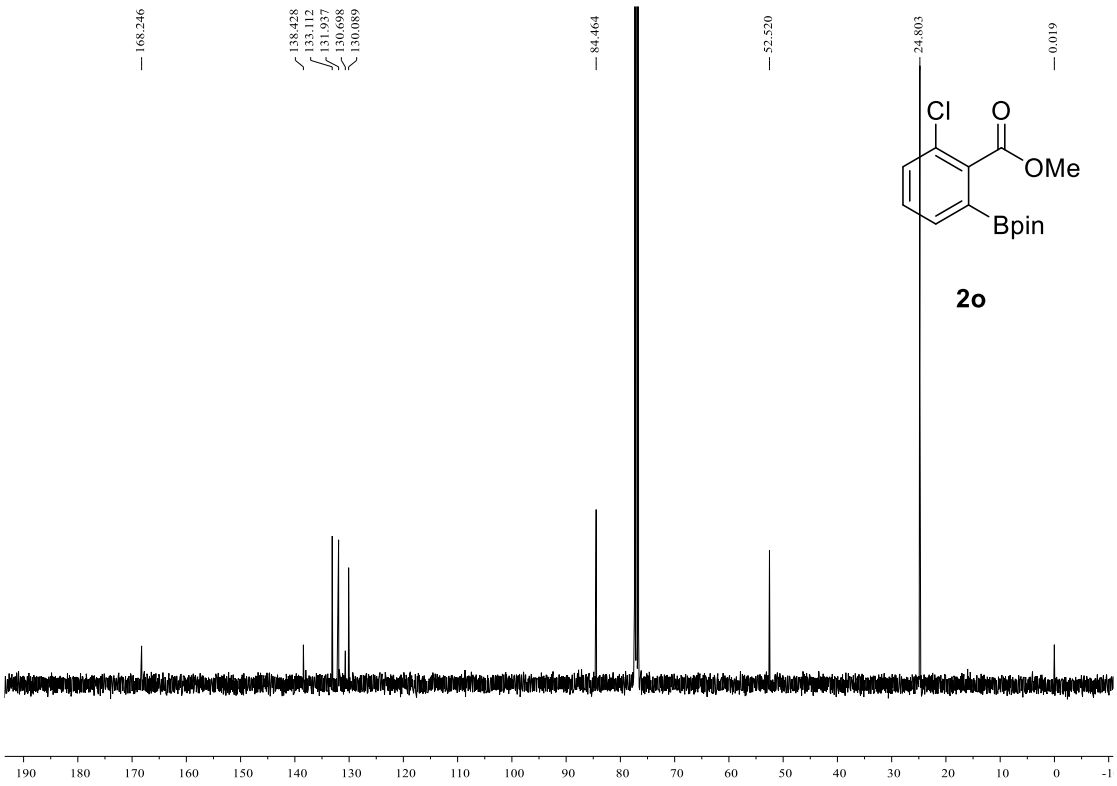
7.685
7.669
7.666
7.482
7.479
7.462
7.459
7.362
7.343
7.323
3.923
1.323
Cl
O
OMe
Bpin
1.00
0.94
1.06
1.00
1.01
1.07
3.29
12.10

**2o**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138.428
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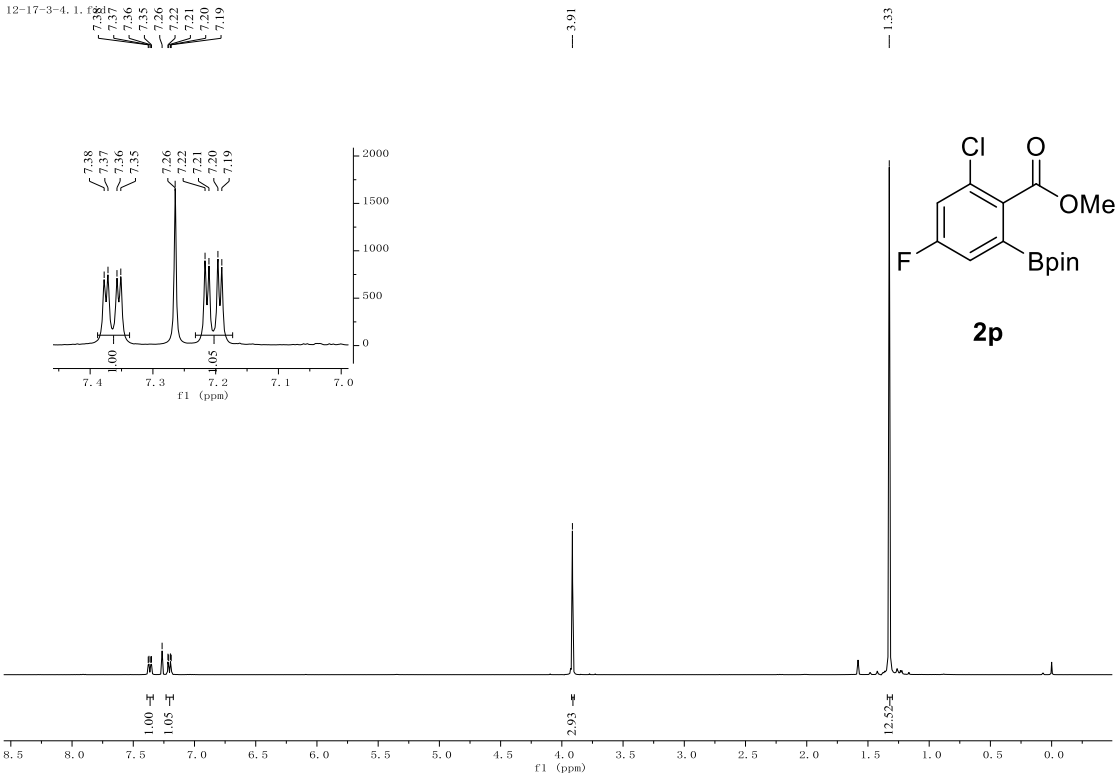
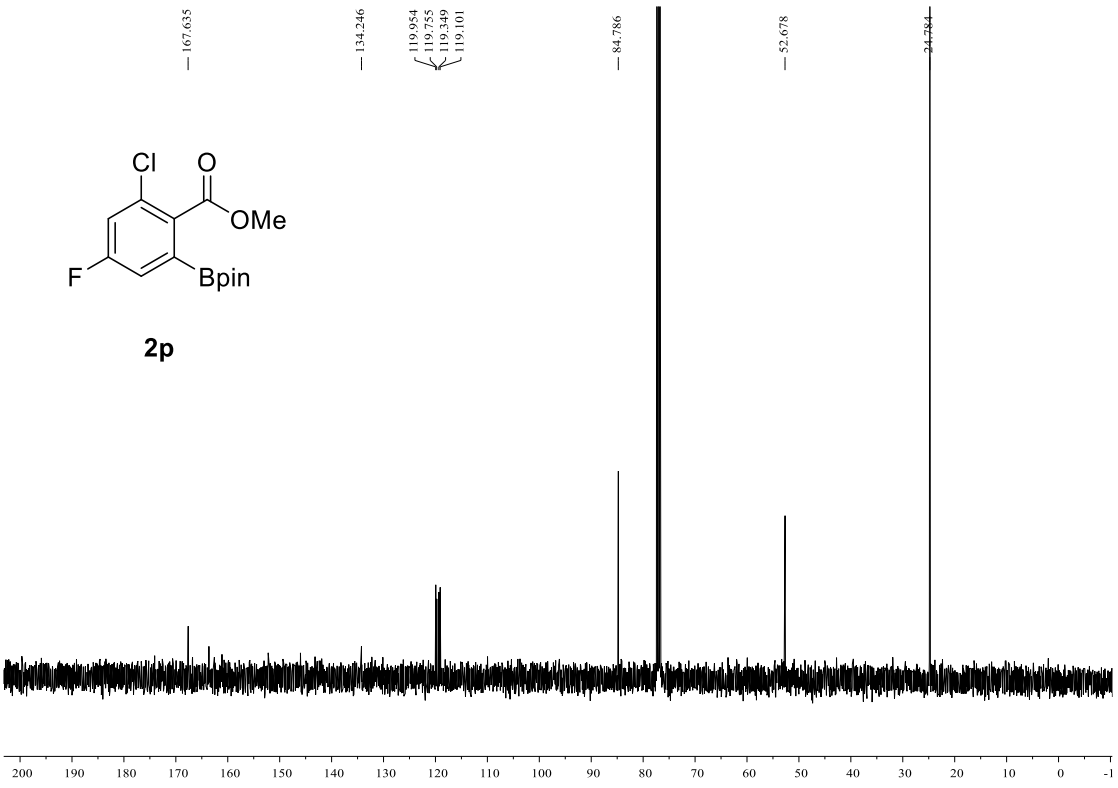
130.698
130.089
84.464
52.520
24.803
0.019
Cl
O
OMe
Bpin

**2o**


12-17-3-4.1.fid
7.38
7.37
7.36
7.35
7.26
7.22
7.21
7.20
7.19
3.91
1.33
Cl
O
OMe
F
Bpin
2p
1.00
1.05
2.93
12.52
f1 (ppm)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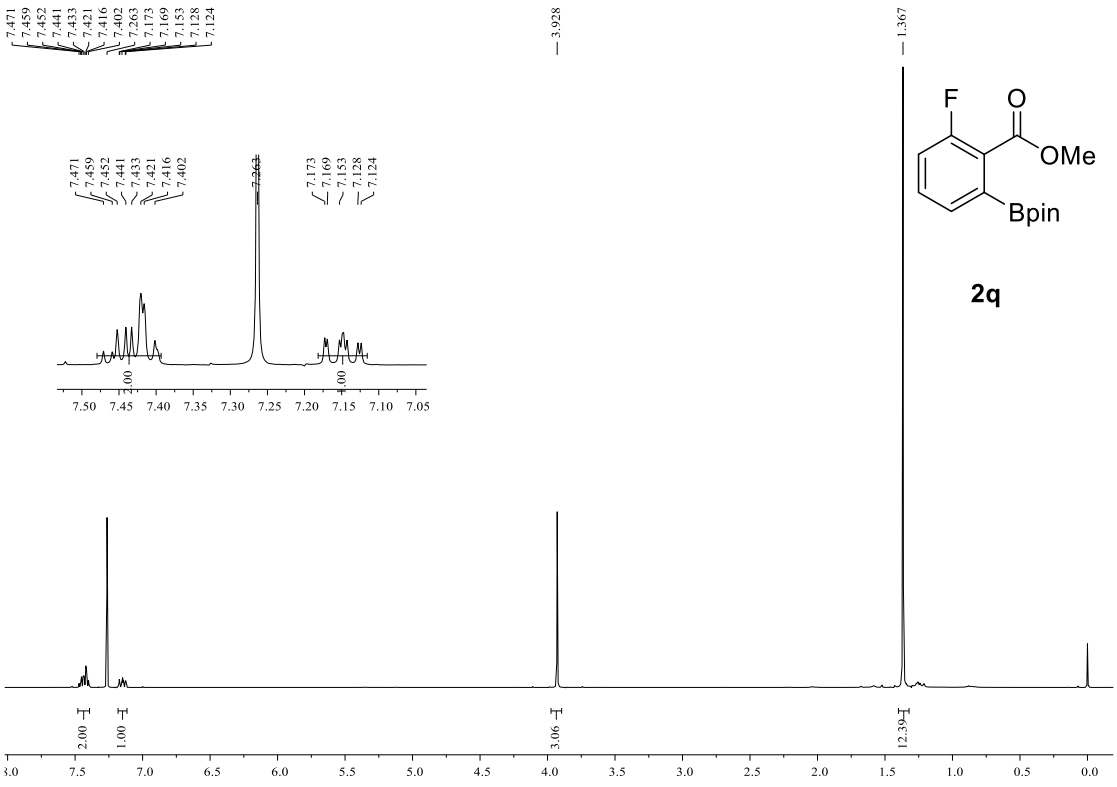
119.954
119.755
119.349
119.101
84.786
52.678
24.784
Cl
O
OMe
F
Bpin
2p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7.459
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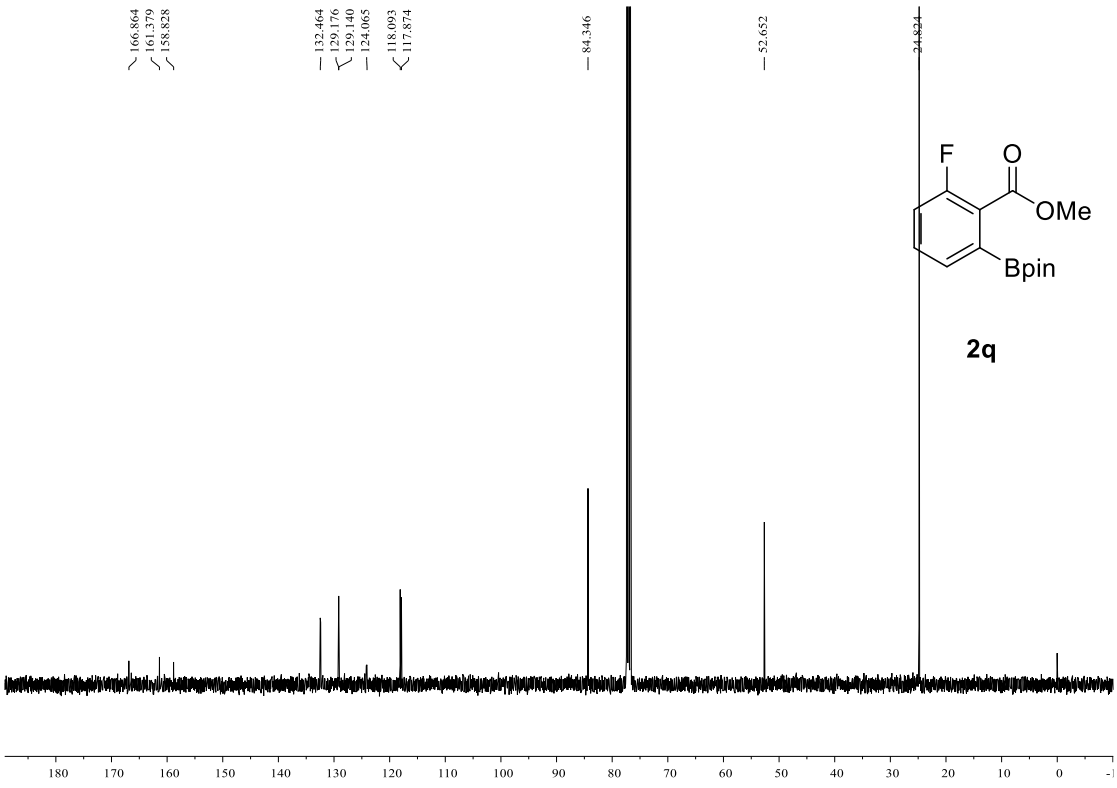
7.441
7.433
7.421
7.416
7.402
7.263
7.173
7.169
7.153
7.128
7.124
3.928
1.367
F
O
OMe
Bpin
2q
2.00
1.00
3.06
12.39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158.828
132.464
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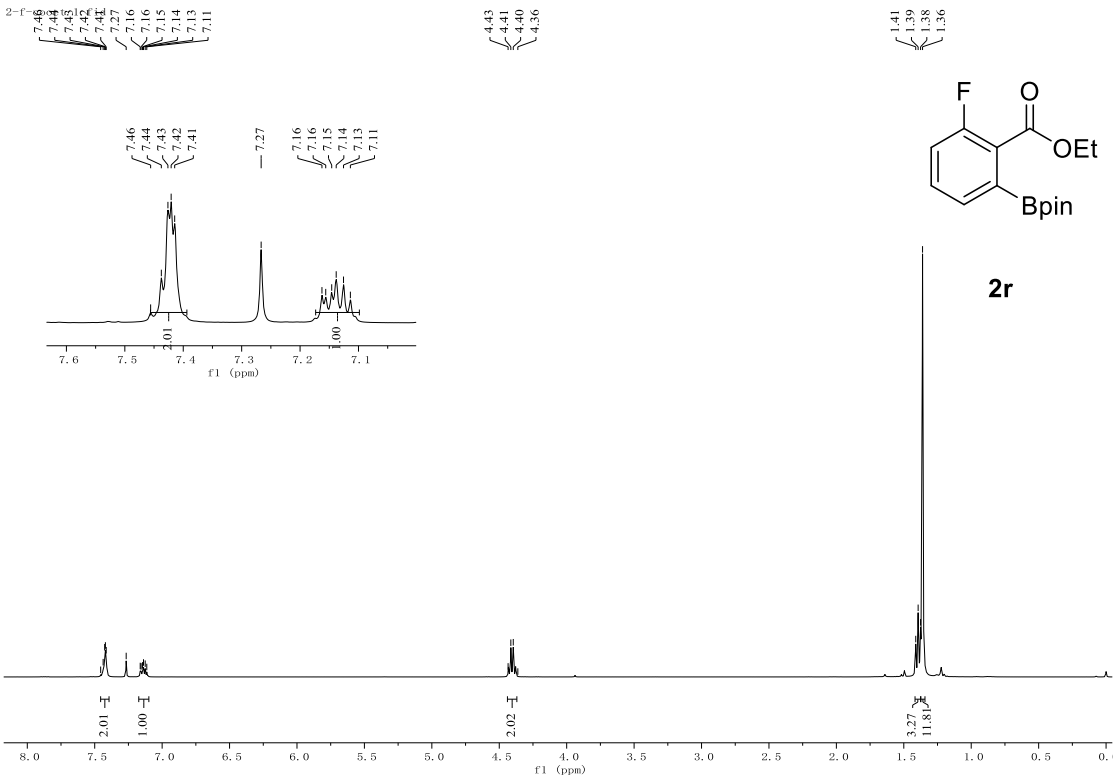
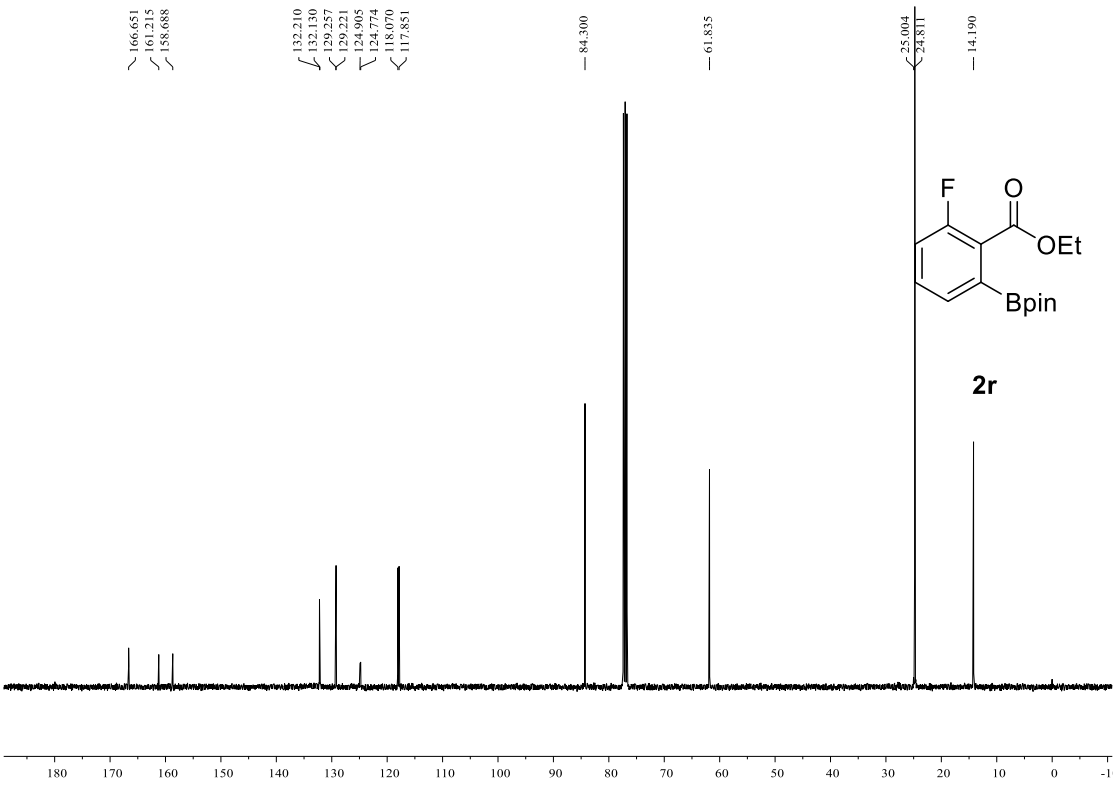
129.140
124.065
118.093
117.874
84.346
52.652
24.824
F
O
OMe
Bpin
2q


7.46
7.44
7.43
7.42
7.41
7.27
7.16
7.16
7.15
7.14
7.13
7.11
4.43
4.41
4.40
4.36
1.41
1.39
1.38
1.36
F
O
OEt
Bpin
2r
2.01
1.00
2.02
3.27
11.81
f1 (ppm)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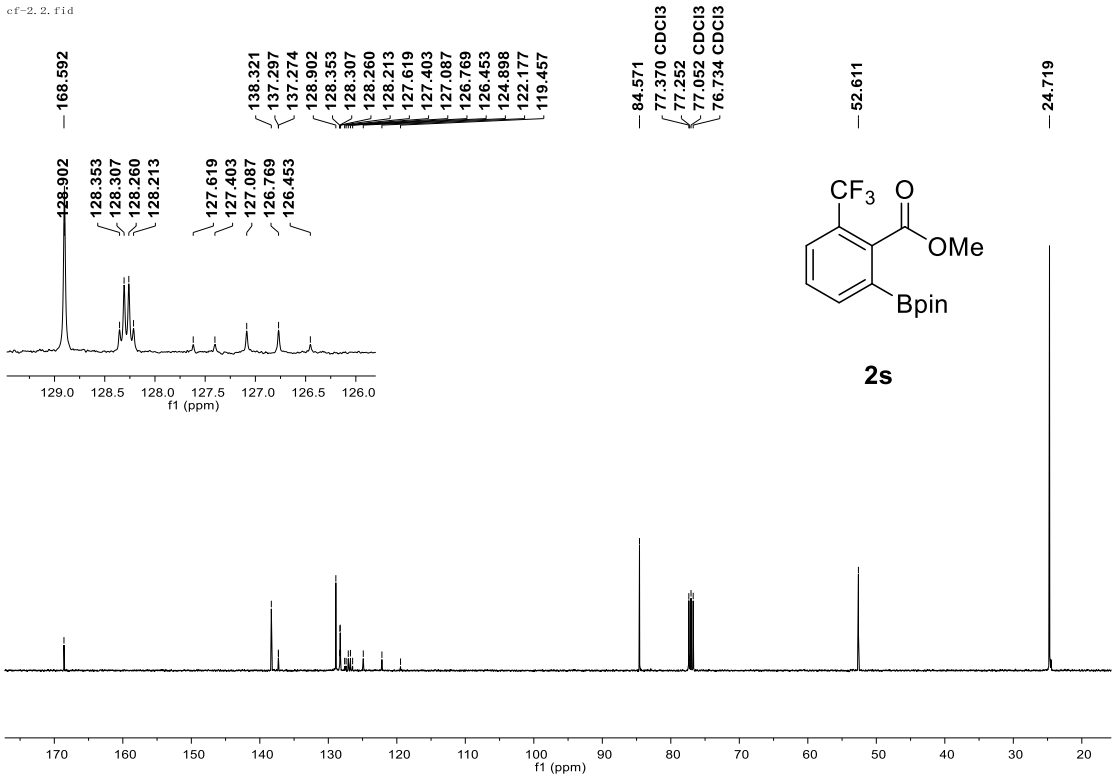
132.130
129.257
129.221
124.905
124.774
118.070
117.851
84.300
61.835
25.004
24.811
14.190
F
O
OEt
Bpin
2r


cf-2.1.fid
7.987
7.968
7.749
7.729
7.538
7.519
7.499
7.276
3.913
1.325
0.93
1.00
0.99
3.00
12.39
f1 (ppm)
CF3
O
OMe
Bpin
2s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128.902
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128.307
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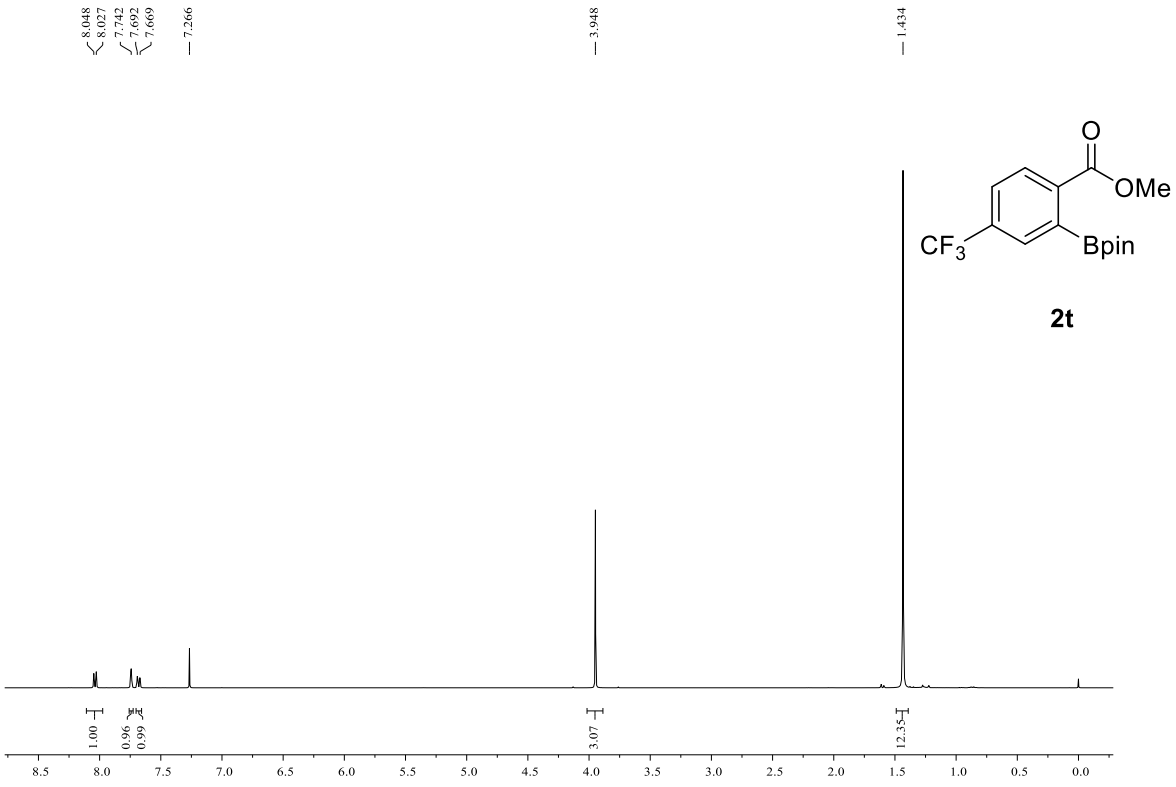
128.213
127.619
127.403
127.087
126.769
126.453
124.898
122.177
119.457
84.571
77.370 CDCl3
77.252
77.052 CDCl3
76.734 CDCl3
52.611
24.719
f1 (ppm)
CF3
O
OMe
Bpin
2s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7.669
7.266
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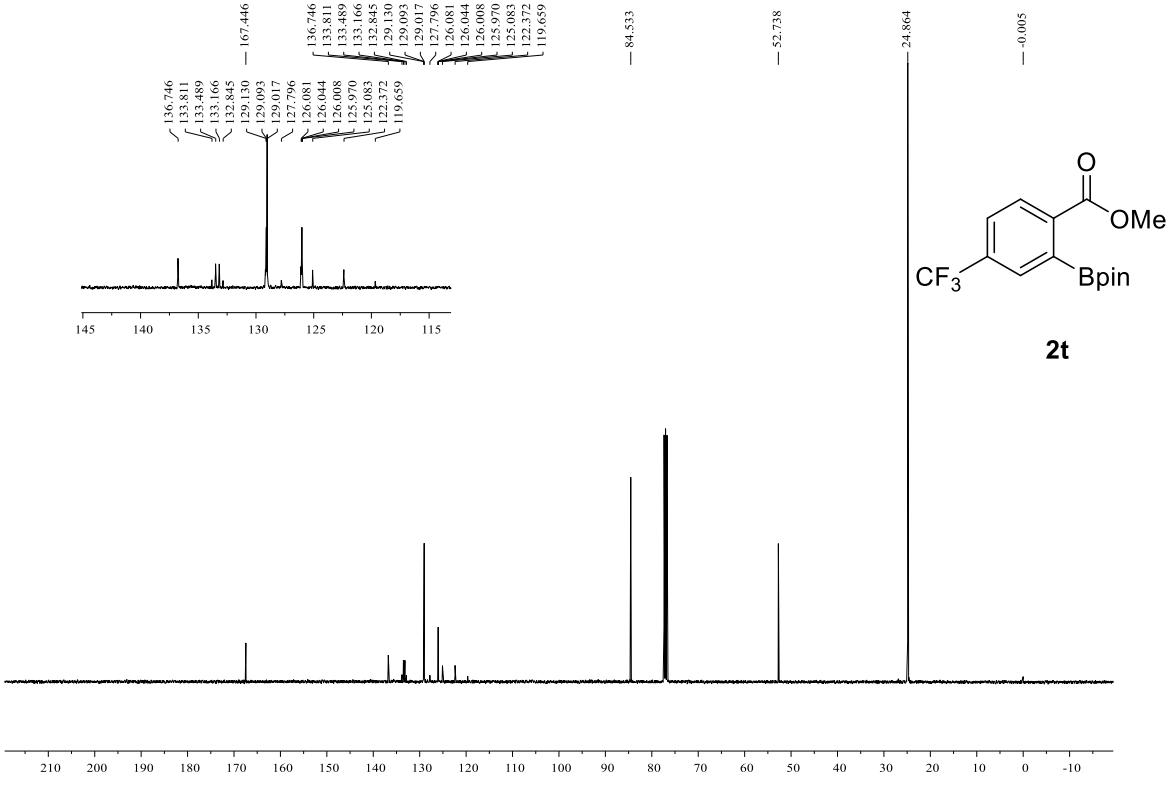
1.434
O
OMe
CF3
Bpin
2t
1.00
0.96
0.99
3.07
12.35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129.093
129.017
127.796
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126.044
126.008
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119.659
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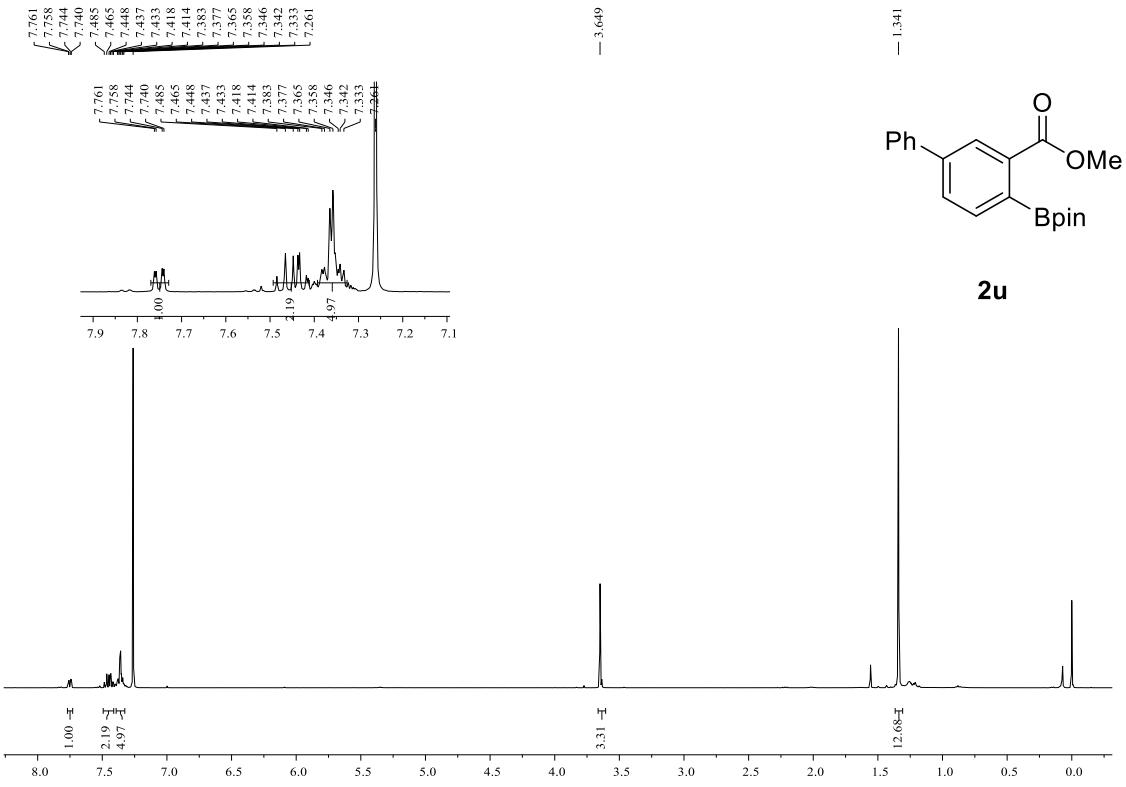
24.864
-0.005
O
OMe
CF3
Bpin
2t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7.740
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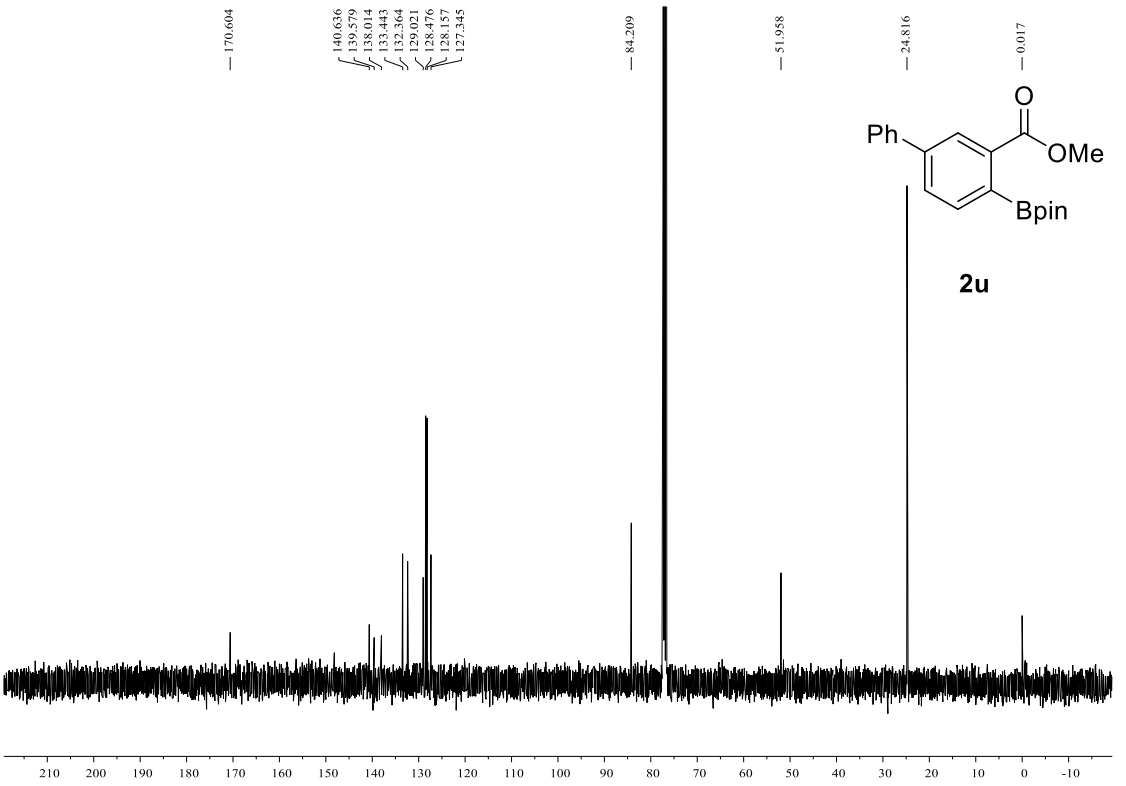
7.465
7.448
7.437
7.433
7.418
7.414
7.383
7.377
7.365
7.358
7.346
7.342
7.333
7.261
3.649
1.341
Ph
O
OMe
Bpin
2u
1.00
2.19
4.97
3.31
12.68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128.157
127.345
84.209
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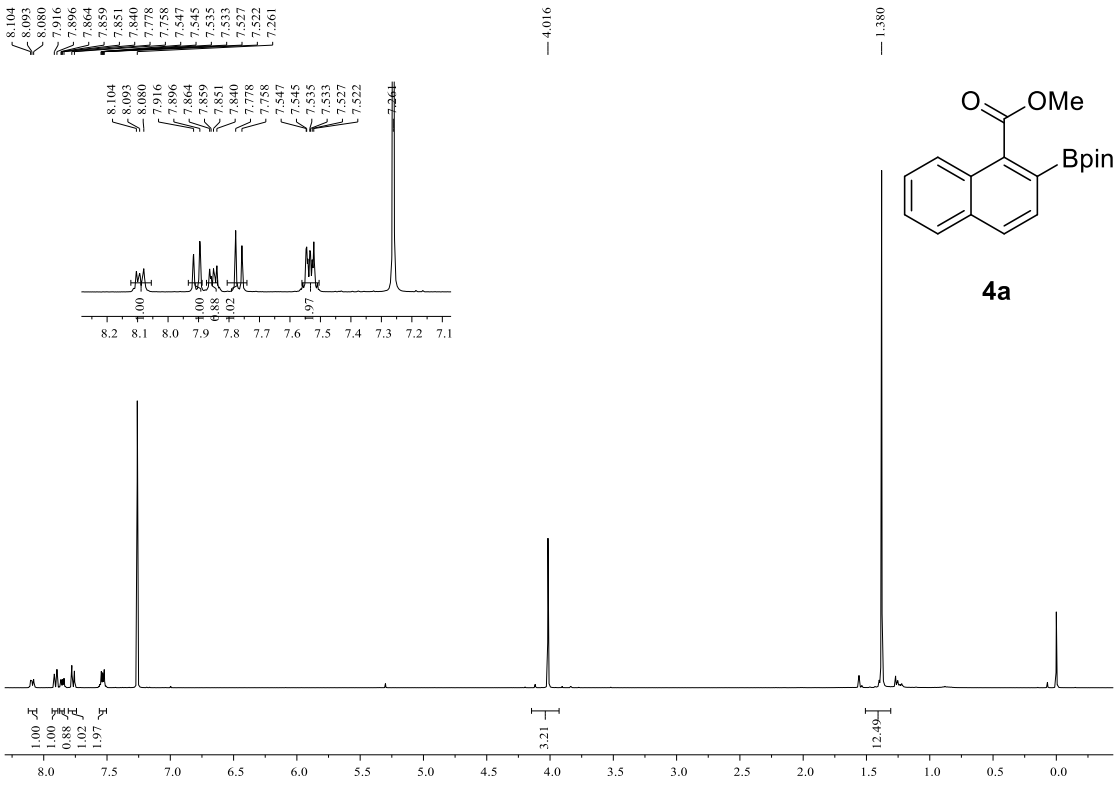
0.017
Ph
O
OMe
Bpin
2u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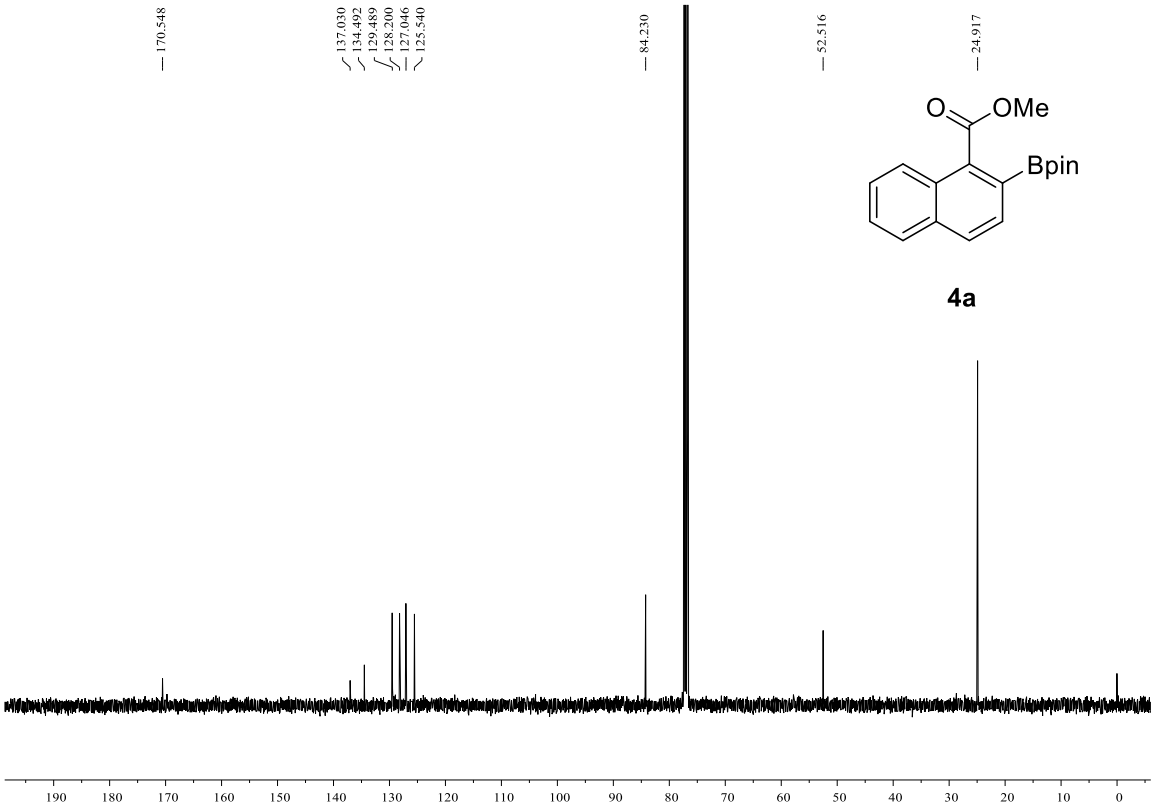
7.864
7.859
7.851
7.840
7.778
7.758
7.547
7.545
7.535
7.533
7.527
7.522
7.261
4.016
1.380
O
OMe
Bpin
4a
1.00
1.00
0.88
1.02
1.97
3.21
12.49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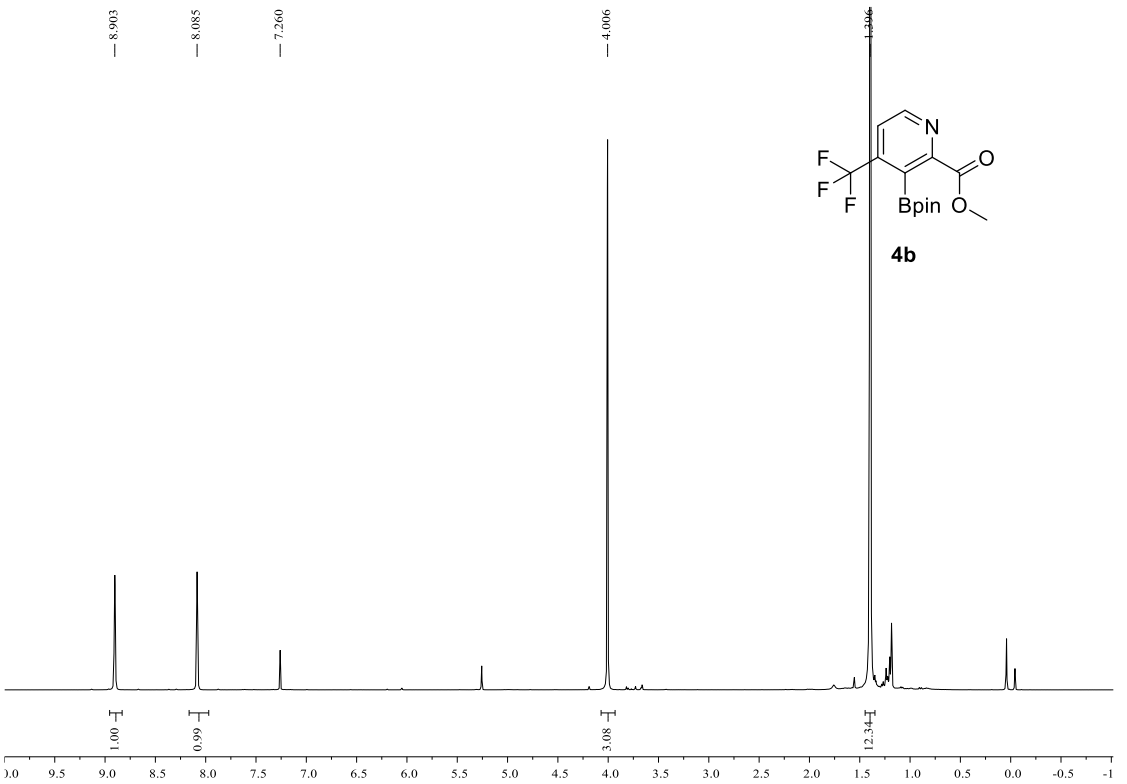
129.489
128.200
127.046
125.540
84.230
52.516
24.917
O
OMe
Bpin
4a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8.085
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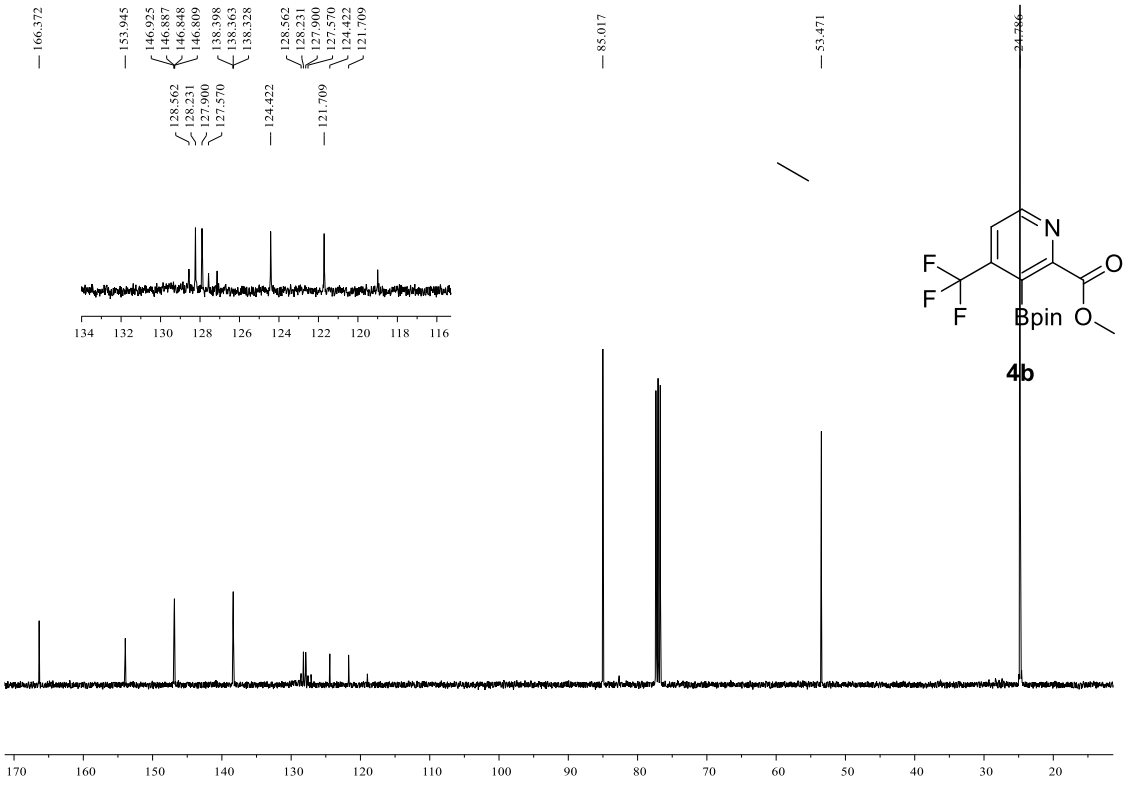
4.006
1.396
1.00
0.99
3.08
12.34
F
F
F
N
O
Bpin
O

**4b**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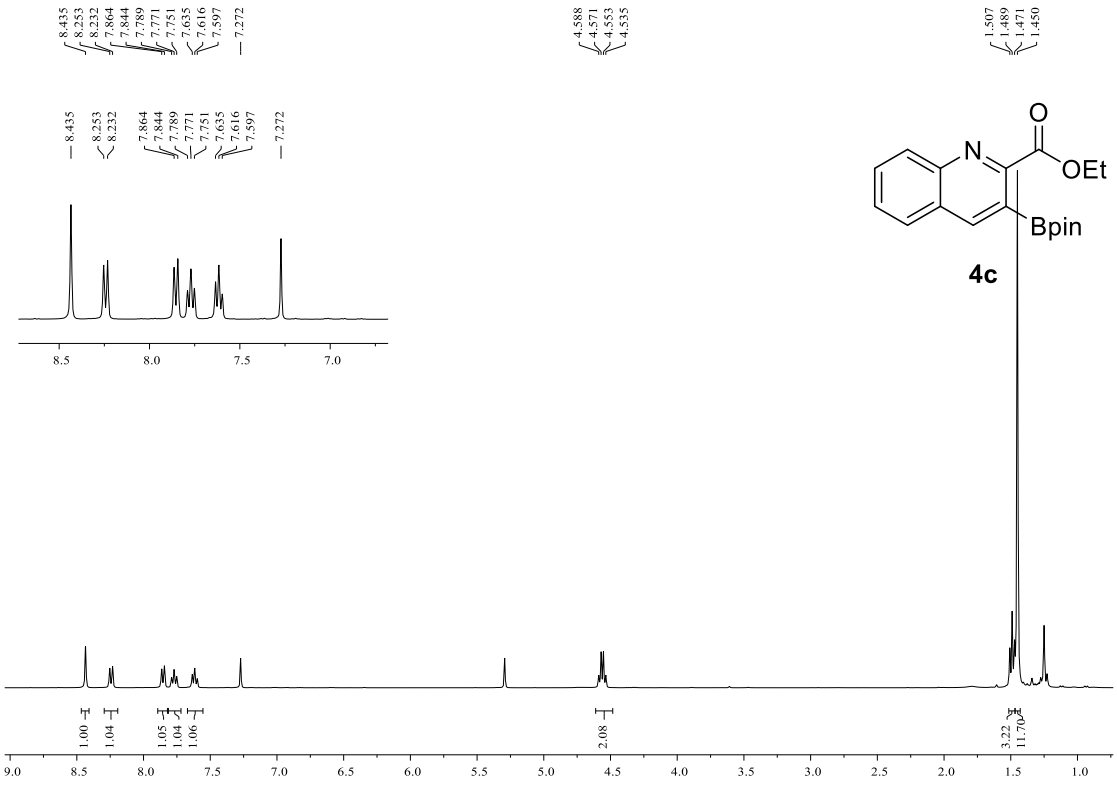
146.887
146.848
146.809
138.398
138.363
138.328
128.562
128.231
127.900
127.570
124.422
121.709
85.017
53.471
24.786
F
F
F
N
O
Bpin
O

**4b**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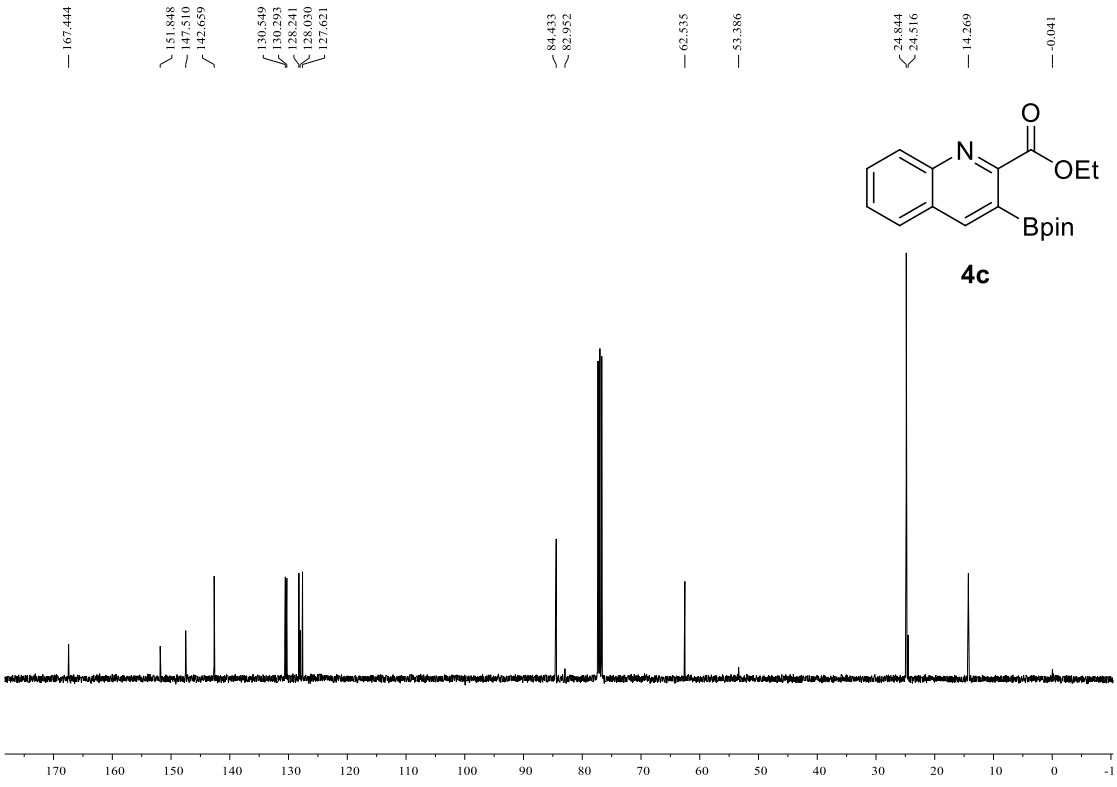
8.253
8.232
7.864
7.844
7.789
7.771
7.751
7.635
7.616
7.597
7.272
4.588
4.571
4.553
4.535
1.507
1.489
1.471
1.450
O
N
OEt
Bpin
4c
1.00
1.04
1.05
1.04
1.06
2.08
3.22
11.70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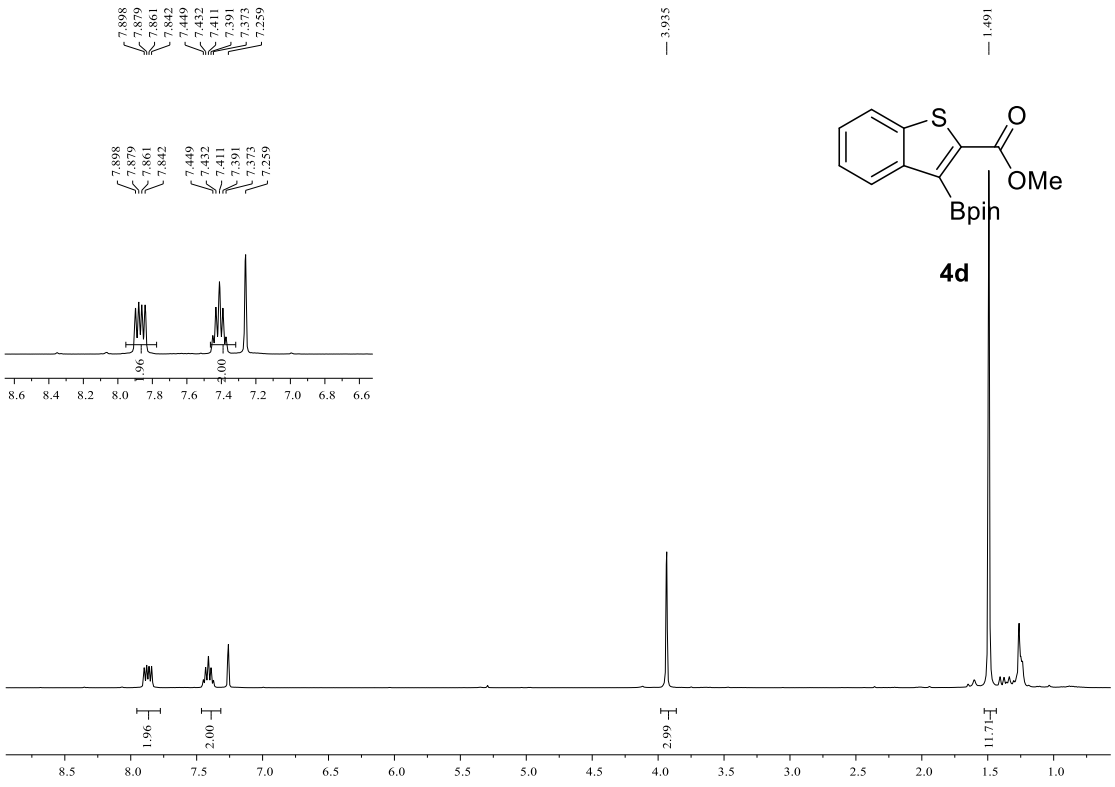
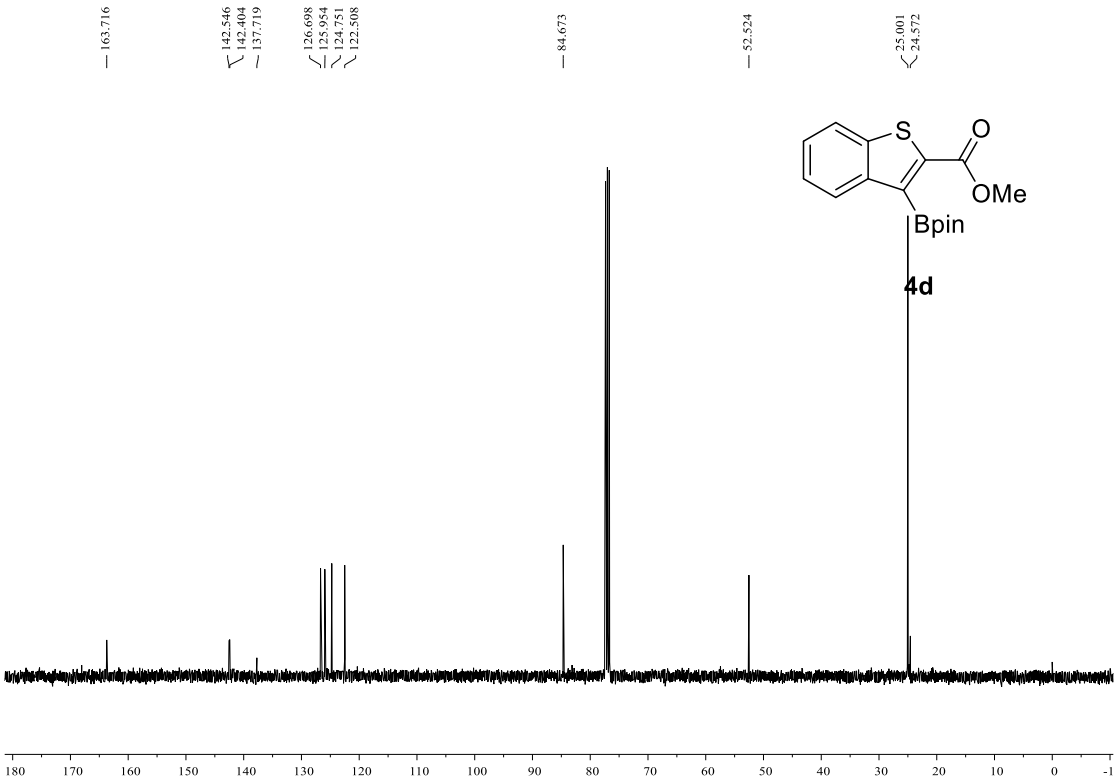
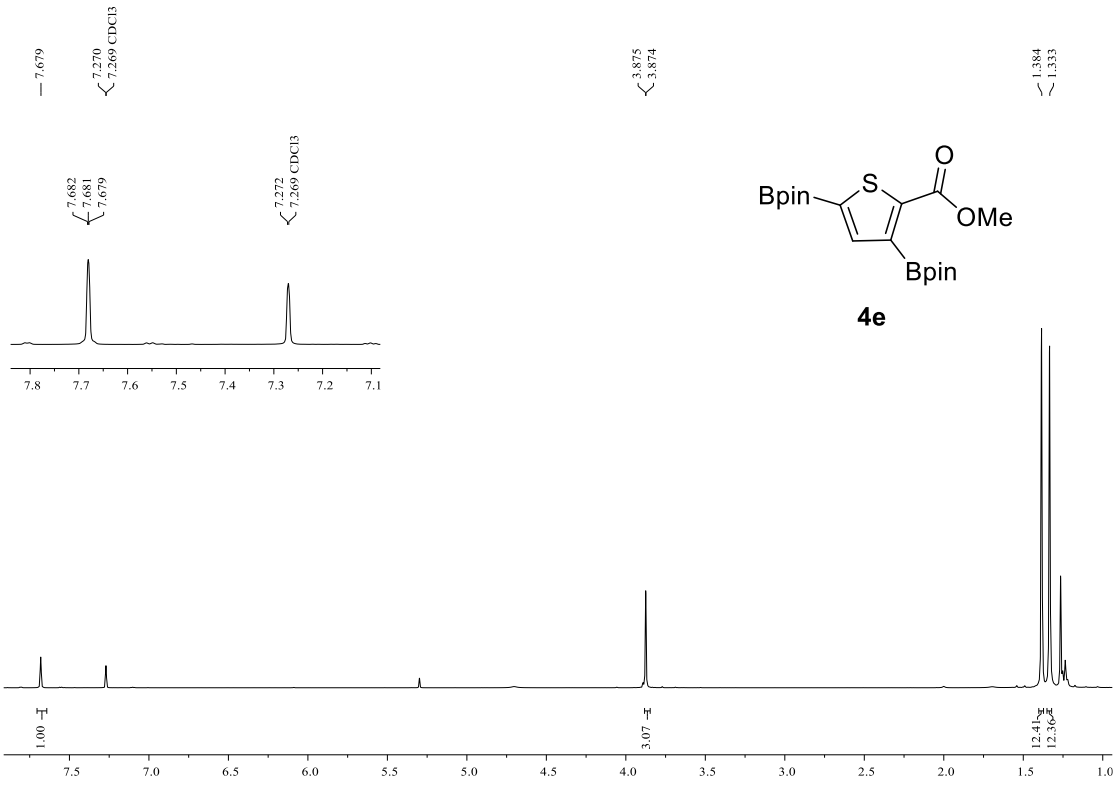
151.848
147.510
142.659
130.549
130.293
128.241
128.030
127.621
84.433
82.952
62.535
53.386
24.844
24.516
14.269
-0.041
O
N
OEt
Bpin
4c


7.898
7.879
7.861
7.842
7.449
7.432
7.411
7.391
7.373
7.259
3.935
1.491
S
O
OMe
Bpin
4d
1.96
2.00
2.99
11.71


163.716
142.546
142.404
137.719
126.698
125.954
124.751
122.508
84.673
52.524
25.001
24.572
S
O
OMe
Bpin
4d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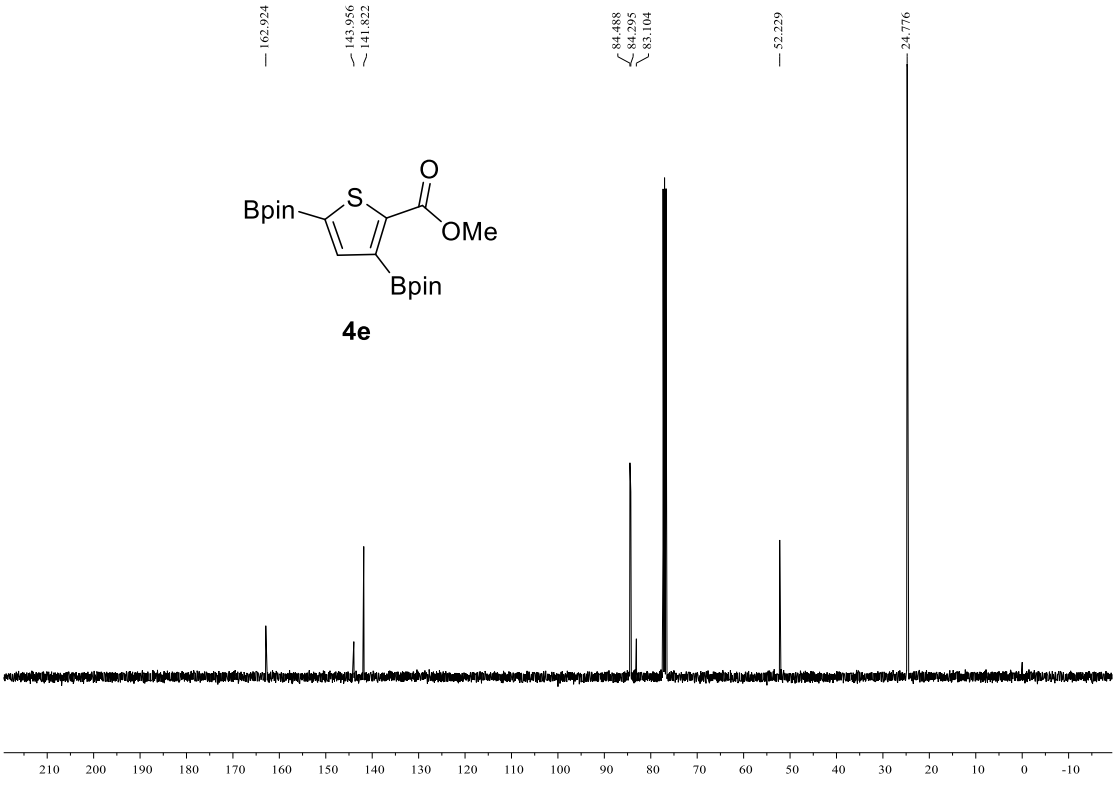
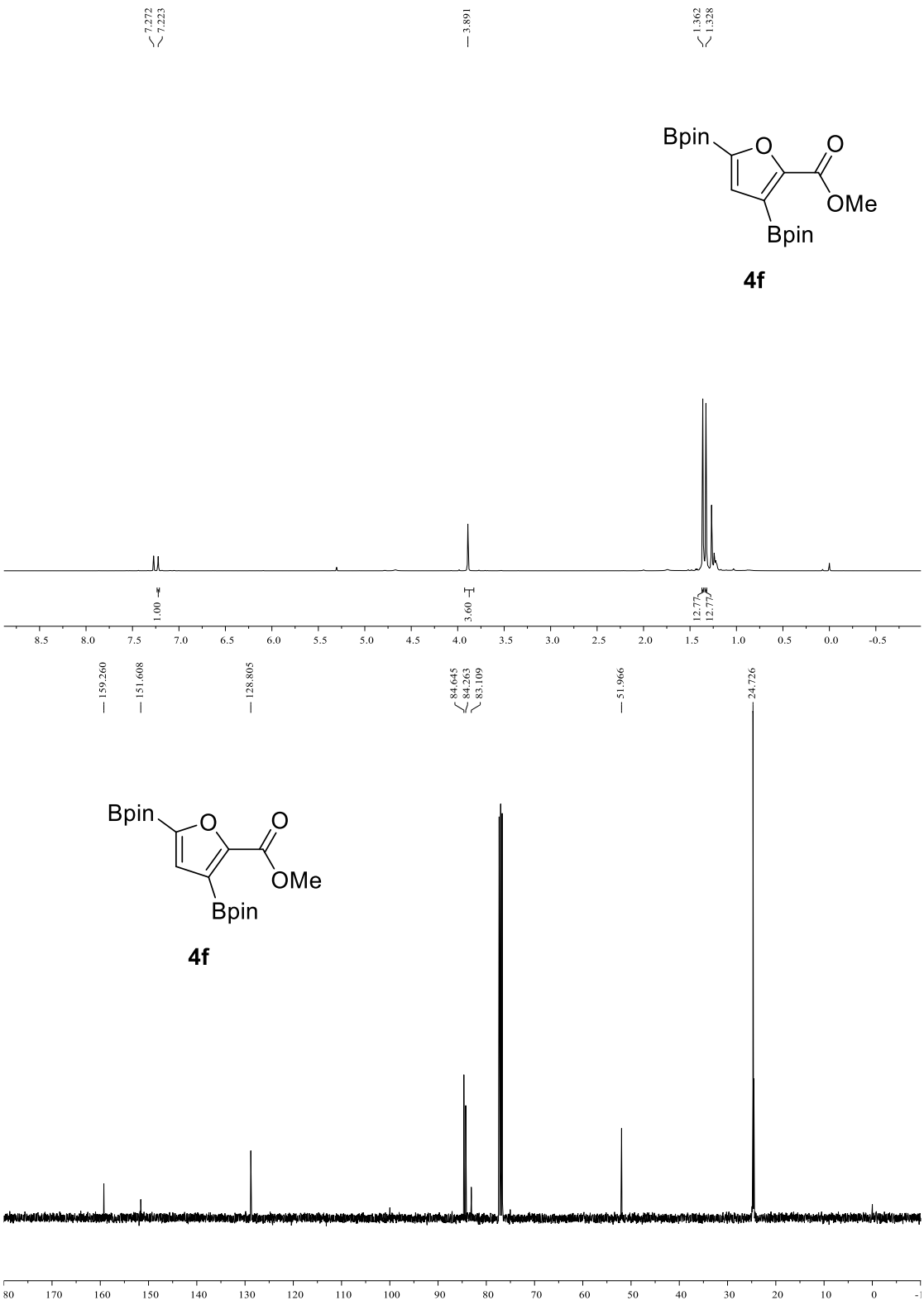
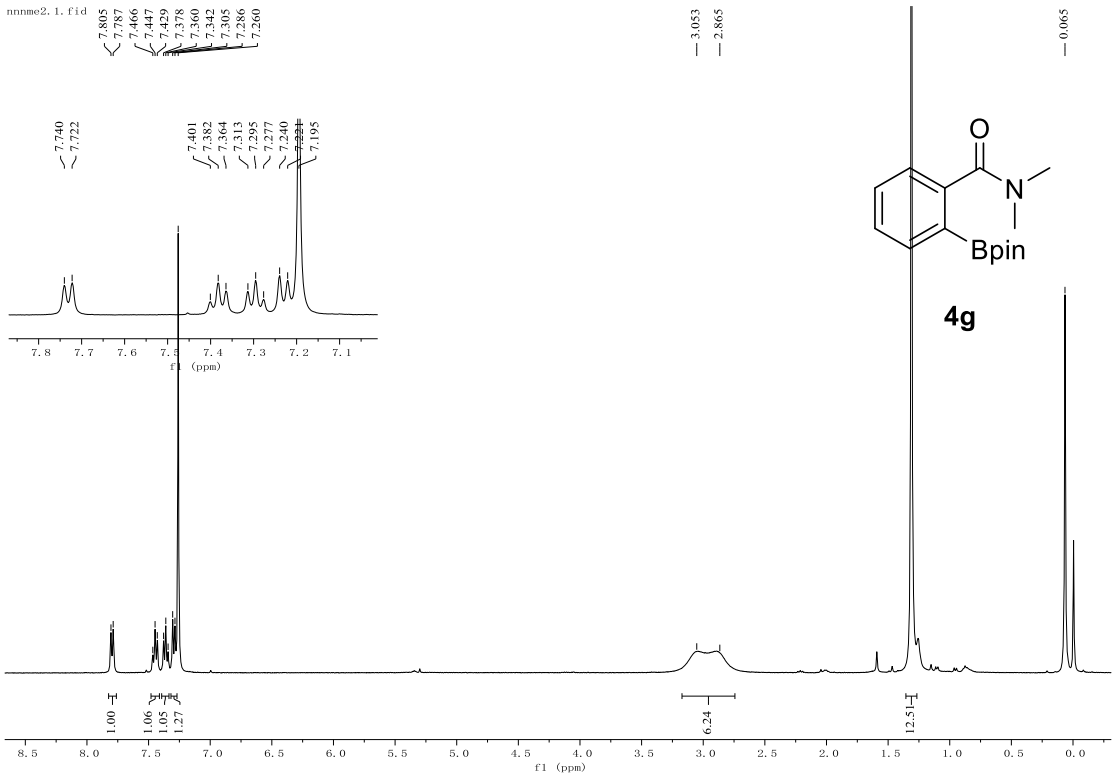
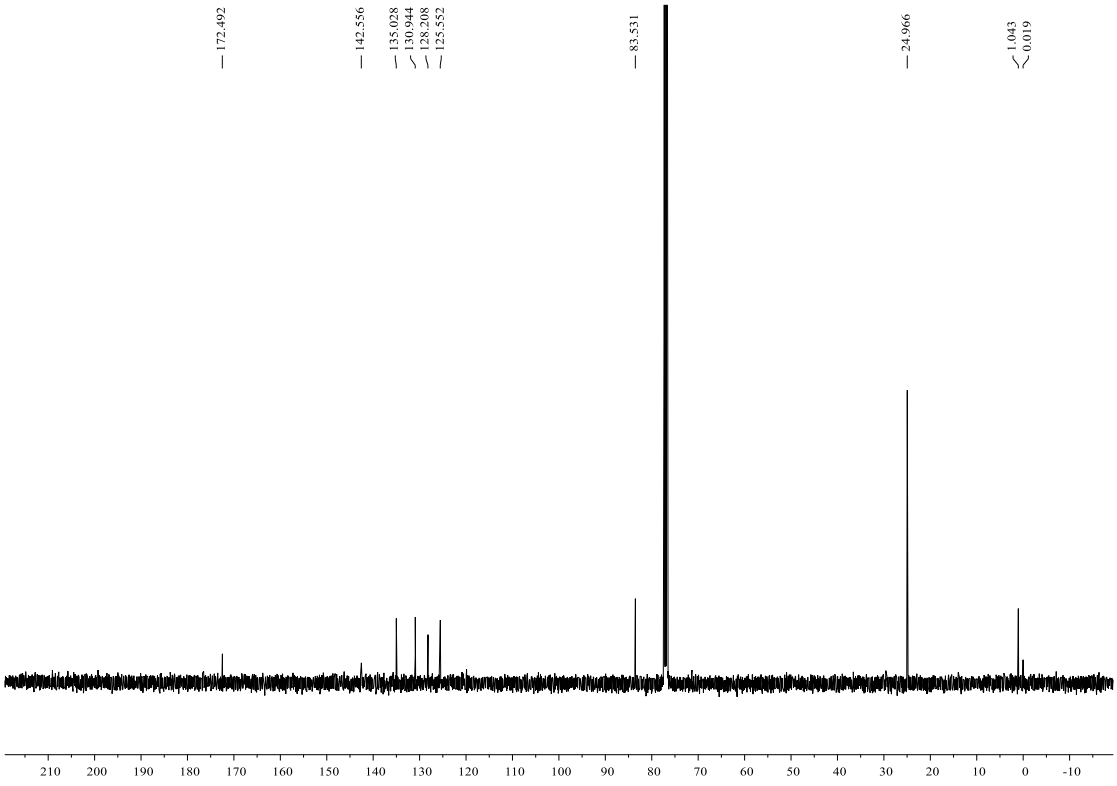
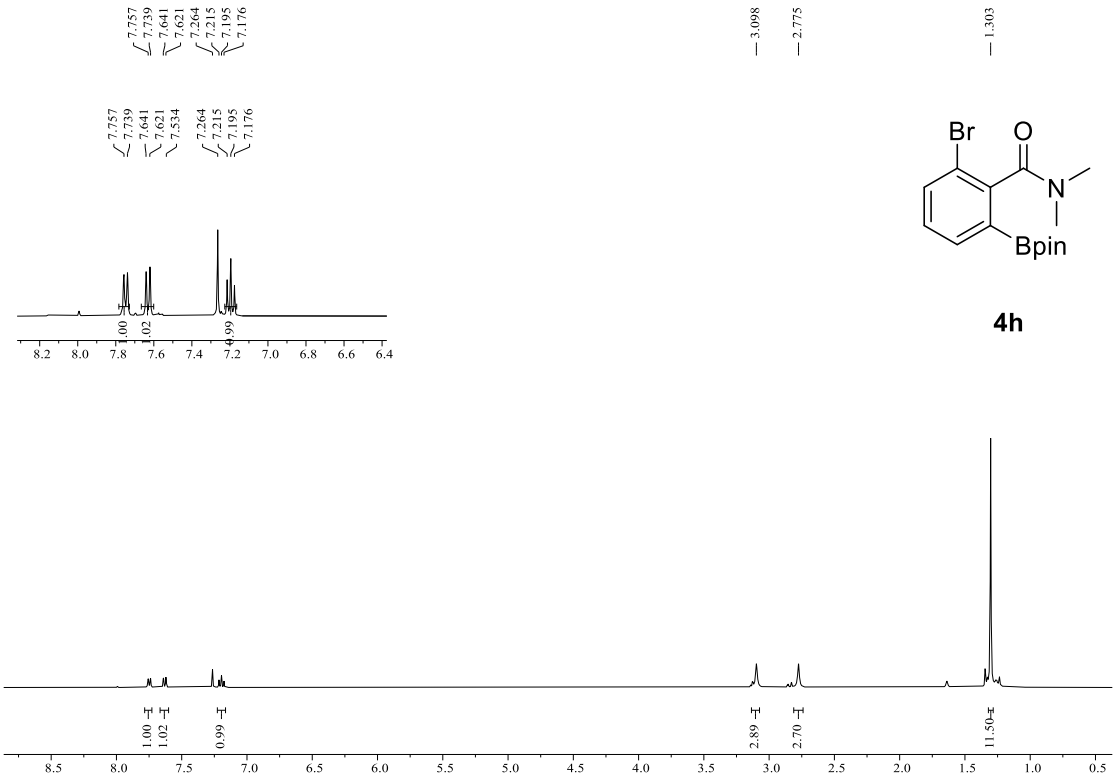
7.270
7.269 CDCl3
3.875
3.874
1.384
1.333
7.682
7.681
7.679
7.272
7.269 CDCl3
Bpin
S
O
OMe
Bpin
4e
1.00
3.07
12.41
12.36

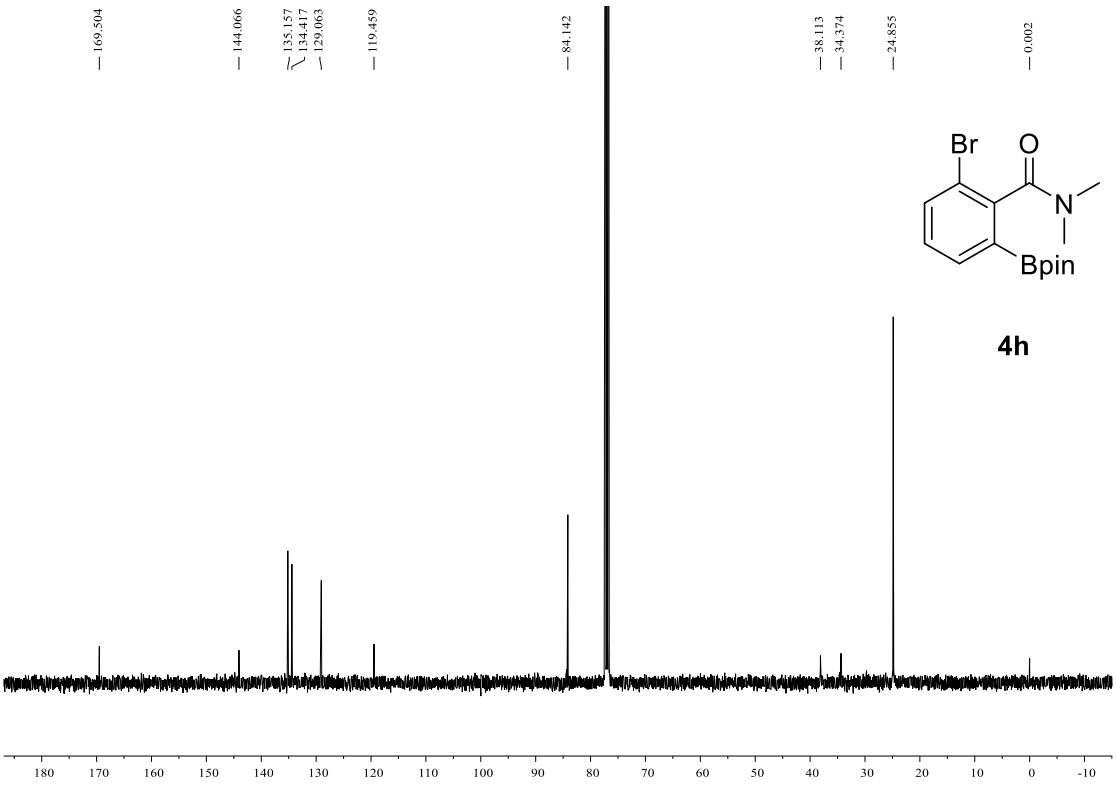

162.924
143.956
141.822
84.488
84.295
83.104
52.229
24.776
Bpin
S
O
OMe
Bpin
4e

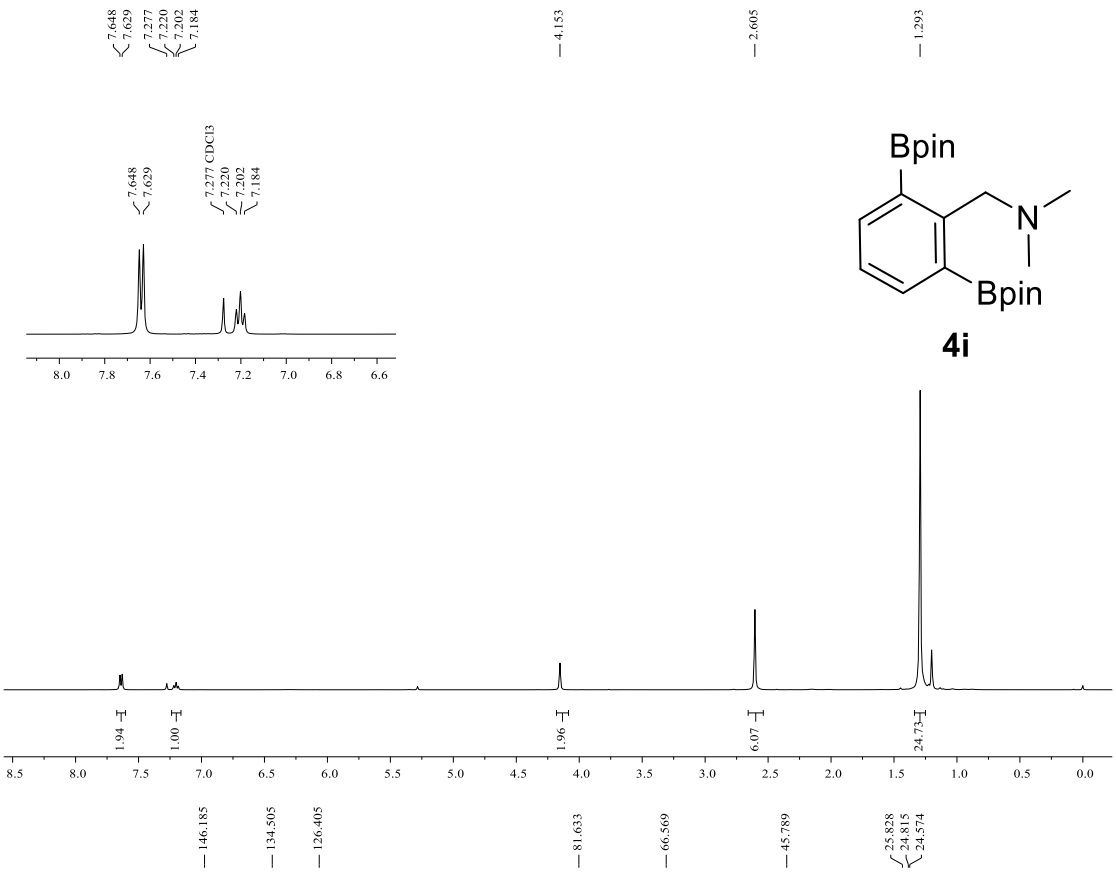

7.272
7.223
3.891
1.362
1.328
Bpin
O
O
OMe
Bpin
4f
1.00
3.60
12.77
12.79
159.260
151.608
128.805
84.645
84.263
83.109
51.966
24.726
Bpin
O
O
OMe
Bpin
4f

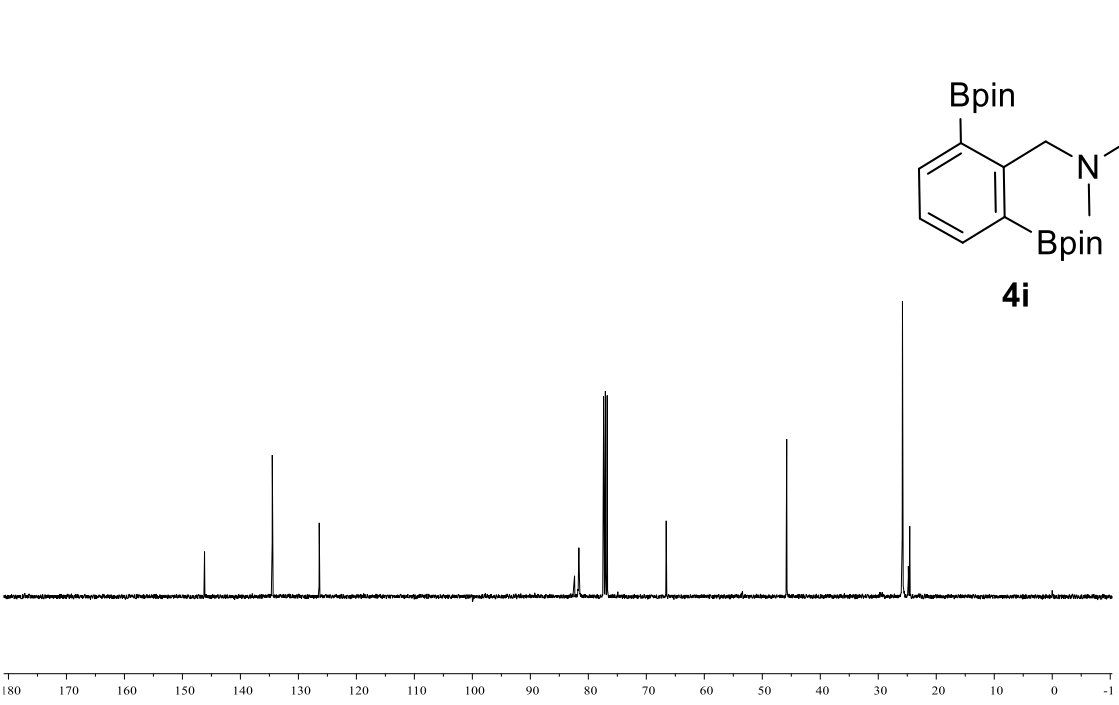

nnnme2.1.fid
7.805
7.787
7.466
7.447
7.429
7.378
7.360
7.342
7.305
7.286
7.260
3.053
2.865
0.065
7.740
7.722
7.401
7.382
7.364
7.313
7.295
7.277
7.240
7.221
7.195
O
N
Bpin
4g
1.00
1.06
1.05
1.27
6.24
12.51
f1 (ppm)

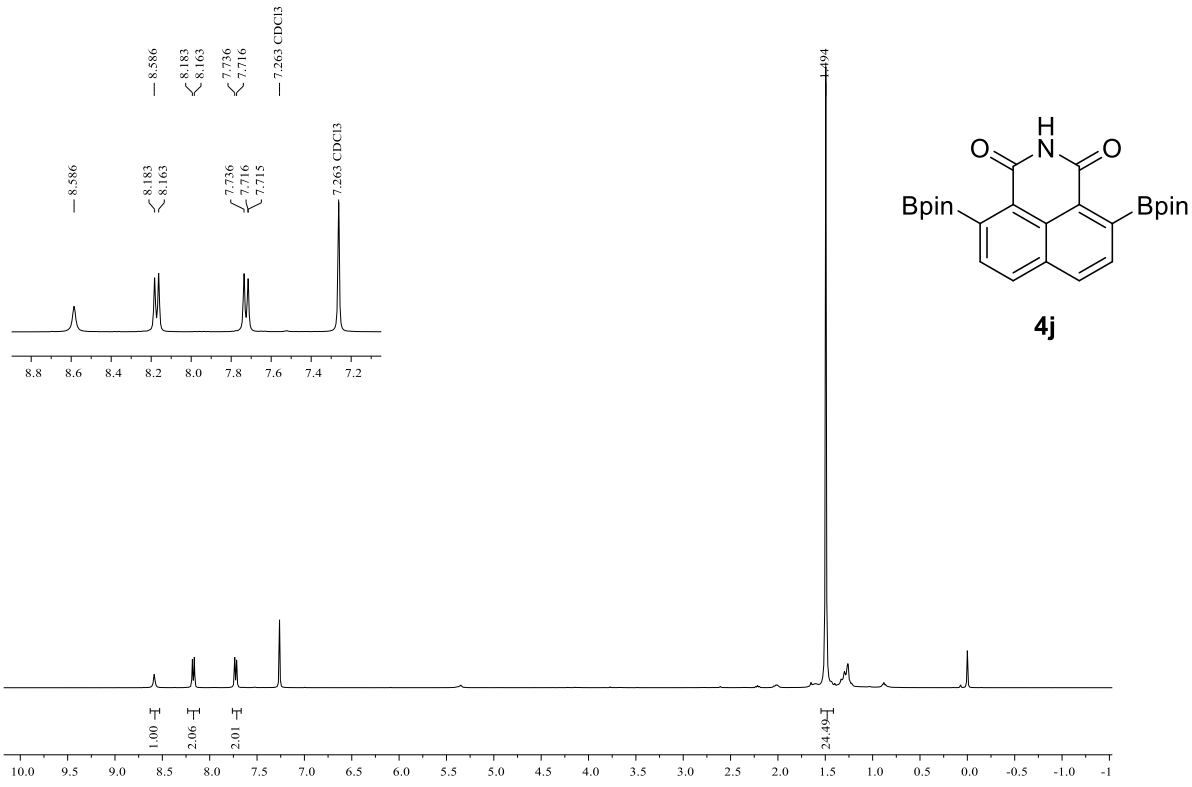

172.492
142.556
135.028
130.944
128.208
125.552
83.531
24.966
1.043
0.019


7.757
7.739
7.641
7.621
7.264
7.215
7.195
7.176
3.098
2.775
1.303
7.534
1.00
1.02
4.99
Br
O
N
Bpin
4h
1.00
1.02
0.99
2.89
2.70
11.50

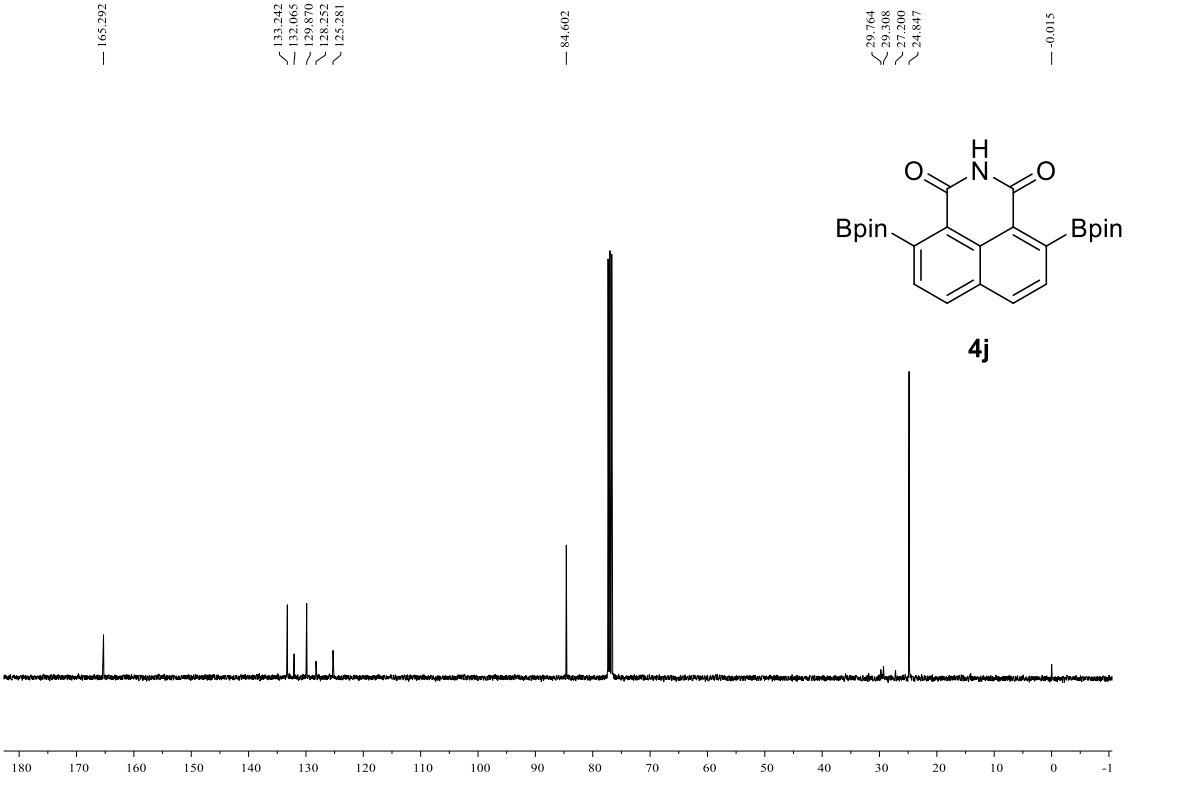

169.504
144.066
135.157
134.417
129.063
119.459
84.142
38.113
34.374
24.855
0.002
Br
O
N
Bpin
4h


7.648
7.629
7.277
7.220
7.202
7.184
4.153
2.605
1.293
7.277 CDCl3
Bpin
N
Bpin
4i
1.94
1.00
1.96
6.07
24.73

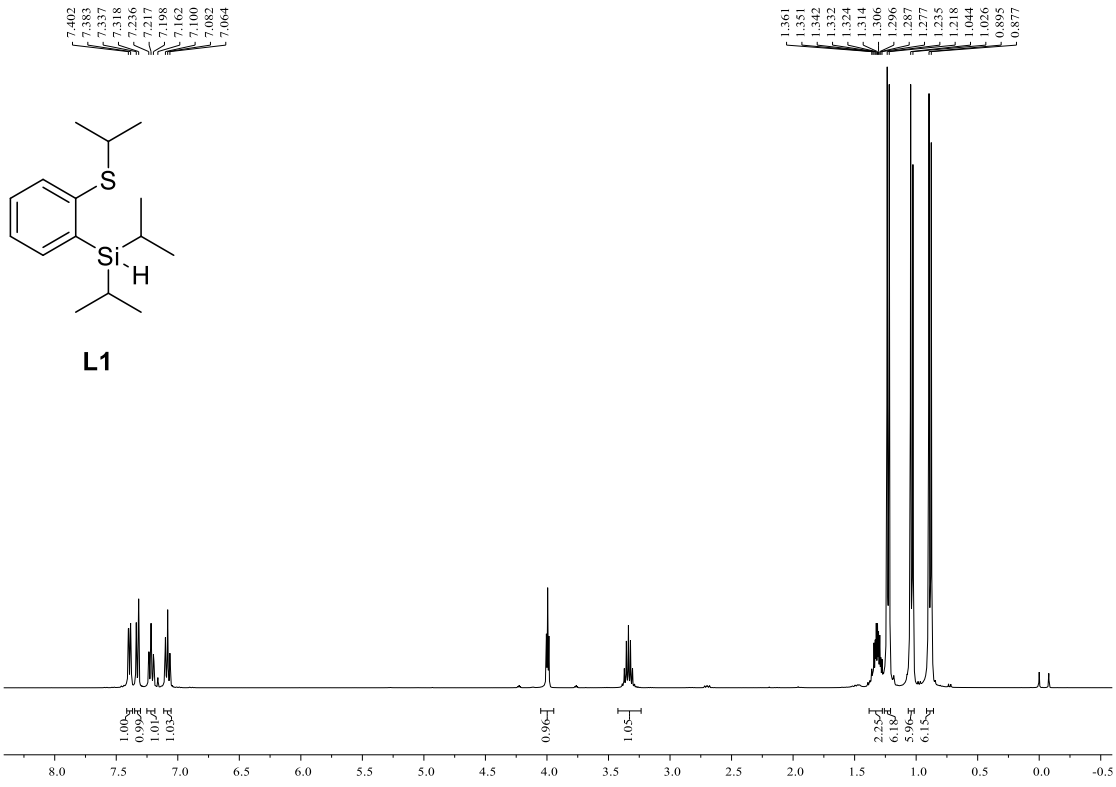

146.185
134.505
126.405
81.633
66.569
45.789
25.828
24.815
24.574
Bpin
N
Bpin
4i


8.586
8.183
8.163
7.736
7.716
7.715
7.263 CDCl3
1.494
1.00
2.06
2.01
24.49
Bpin
Bpin
H
N
O
O

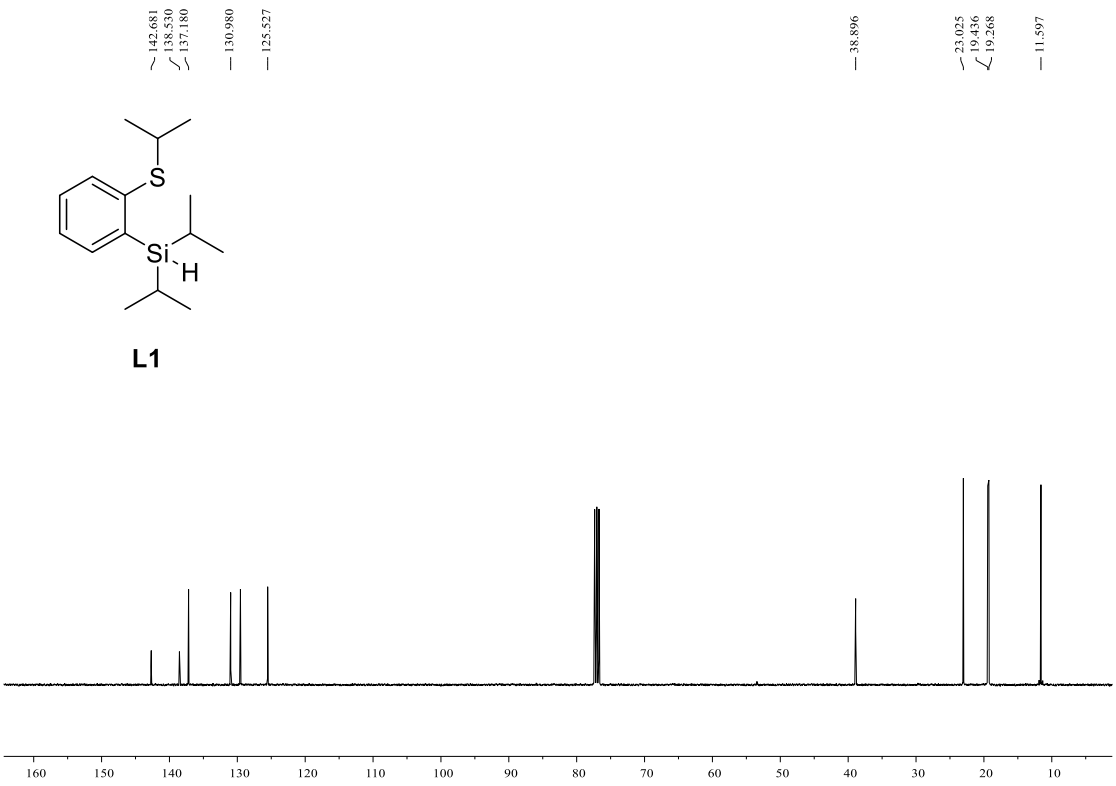
**4j**


165.292
133.242
132.065
129.870
128.252
125.281
84.602
29.764
29.308
27.200
24.847
0.015
Bpin
Bpin
H
N
O
O

**4j**


7.402
7.383
7.337
7.318
7.236
7.217
7.198
7.162
7.100
7.082
7.064
1.361
1.351
1.342
1.332
1.324
1.314
1.306
1.296
1.287
1.277
1.235
1.218
1.044
1.026
0.895
0.877
S
Si
H
1.00
0.99
1.01
1.03
0.96
1.05
2.25
6.18
5.96
6.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

**L1**


142.681
138.530
137.180
130.980
125.527
38.896
23.025
19.436
19.268
11.597
S
Si
H
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

**L1**