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Supplementary Information

Photoinduced Aerobic C–S Borylation of Aryl Sulfides

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1. General information

Unless otherwise noted, all reactants or reagents were obtained from commercial suppliers and used as received. Thioanisole, B_2pin_2, benzoquinone, and 2,6-lutidine were obtained from Energy Chemical (Shanghai, China). 1,4-Dioxane was obtained from Sinopharm Chemical Reagent (Shanghai, China). Photoreactor with blue LED was obtained from Wuhan JinboTianhua Instrument Equipment Co., Ltd. Otherwise noted, all reactions were performed in a 50 mL test tube under air atmosphere. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Analytical thin-layer chromatography (TLC) was performed using Leyan (Shanghai Haohong Scientific Co., Ltd., China). The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with silica gel (200–300 mesh). Gas chromatography (GC) analysis was conducted on a Shimadzu GC-2030 instrument equipped with a Rtx-1 column (30 m × 0.25 mm, Dell) with naphthalene as an internal standard. GCMS analysis was conducted on a Shimadzu GCMS-QP2010 instrument equipped with a Rtx-5MS column (30 m × 0.25 mm, Dell). Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to residual peak of $CDCl_3$ (δ 7.26 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.16 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplets, dt = doublet of triplets, td = triplet of doublets, q = quartet, m = multiplets, v = virtual coupling, br = broad signal), coupling constant (Hz), and integration. High resolution mass spectra (HRMS) were obtained from Thermo Fisher LTQ Orbitrap LCMS with electrospray ionization (ESI). UV-vis absorption spectra were recorded on a Shimadzu UV-2700 spectrophotometer.

2. Synthesis of starting materials

Thioanisole, methyl *p*-tolyl sulfide, 1-methoxy-4-methylsulfanylbenzene, 1-(4-methylsulfanylphenyl)ethanone, 4-methylsulfanylbenzonitrile, 4-chlorothioanisole, 4,4,5,5-tetramethyl-2-(4-methylsulfanylphenyl)-1,3,2-dioxaborolane, ethyl phenyl sulfide, benzyl phenyl sulfide, propan-2-ylsulfanylbenzene, diphenyl sulfide were purchased from commercial sources and used as received. Unless otherwise noted, all other sulfide derivatives were prepared according to the procedures reported in the literature. The methylation of sulfide derivatives was conducted according to the procedures reported in the literature[1].

1c[1], **1d**[1], **1e**[1], **1f**[1], **1g**[1], **1h**[1], **1j**[1], **1k**[3], **1l**[2], **1m**[3], **1n**[3], **1o**[3], **1p**[3], **1r**[3], **1s**[2], **1u**[9], **1x**[1], **1y**[3], **1z**[1], **1ab**[2] were prepared according to the procedures reported in the literatures.

3. Photoinduced Aerobic C–S Borylation of Aryl Sulfides

Reaction optimization: An oven-dried 50 mL test tube equipped with a magnetic stirring bar was charged with **1a** (0.2 mmol, 24.8 mg), benzoquinone (0.04 mmol, 4.3 mg), B_2pin_2 (1.0 mmol, 253.9 mg), and solvent (0.2 mL) under air atmosphere. Then the tube was put in a photoreactor equipped with LED. After stirring the reaction mixture under LED light illumination at room temperature for 72 hours, the mixture was diluted with ethyl acetate. The yield of product **2a** was determined by GC and calibrated using naphthalene as internal standard.

General Procedure: An oven-dried 50 mL test tube equipped with a magnetic stirring bar was charged with aryl sulfides (0.2 mmol), benzoquinone (0.04 mmol, 4.3 mg), B_2pin_2 (1.0 mmol, 253.9 mg) in 1,4-dioxane (0.2 mL) under air atmosphere. Then the tube was closed with a cap and put in a photoreactor equipped with blue LED. After stirring the reaction mixture under LED light illumination at room temperature for 72 hours, the solvent was evaporated under reduced pressure and the residue was directly purified by flash column chromatography over silica gel eluting with petroleum ether/ethyl acetate to afford the corresponding product.

Note: The reactions of **1k**, **1p** and **1s** were conducted using 30 mol% of 2,6-lutidine as the additive. The reactions of **1j**, **1o**, **1r** and **1v** were conducted extending the reaction time to five days.

Photoreactor: The photoreactors used in this research were bought from Wuhan JinBoTianHua Instrument (Figure S1 and Figure S2: blue LEDs, light intensity = 64.8 mw/cm^2, 5 W for every light bulb; the distance between the lamp and the test tube is around 0.8 cm; every test tube was irradiated by one light bulb from the bottom).

Figure S1. Photoreactor used in this research (5 W blue LEDs)

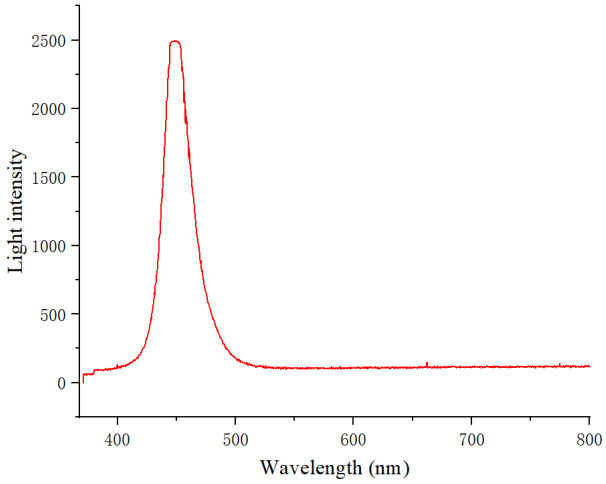
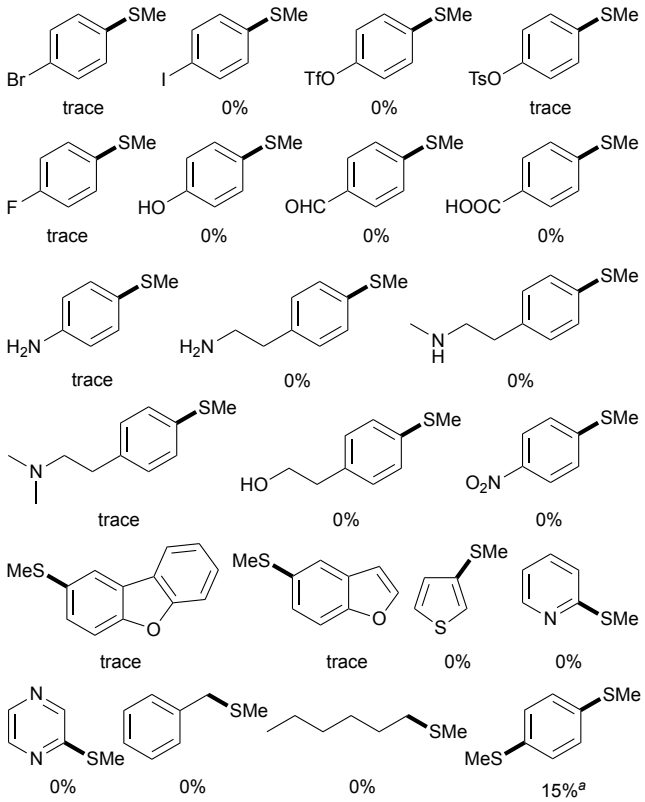


Figure S2. Spectrum of photoreactor (λ_{max} = 450 nm)

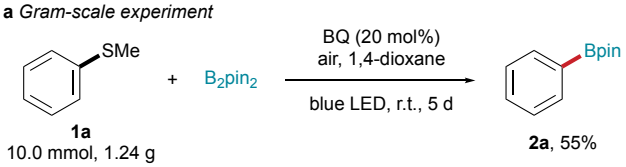
Unsuccessful substrates:



Reaction conditions: substrate (0.2 mmol), B_2pin_2 (1.0 mmol), BQ (0.04 mmol), 1,4-dioxane (0.2 mL), air, 5 W blue LED, room temperature, 72 h. [a] 15% of diborylated product.

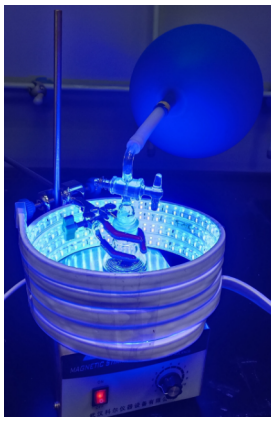
4. Synthetic application

a *Gram-scale experiment*



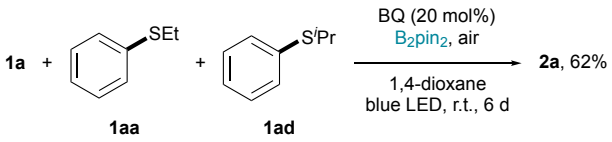
1a
10.0 mmol, 1.24 g

2a, 55%



An oven-dried 50-mL flask equipped with a magnetic stirring bar was charged with **1a** (10.0 mmol, 1.24 g), B_2pin_2 (50.0 mmol, 12.70 g), and 1,4-dioxane (10.0 mL) under air atmosphere. The flask with an air balloon was put in a photoreactor equipped with blue LED. After stirring the reaction mixture under LED light illumination at room temperature for 5 days, the solvent was evaporated under reduced pressure and the residue was directly purified by flash column chromatography over silica gel eluting with petroleum ether to afford **2a** (1.122 g, 55% yield).

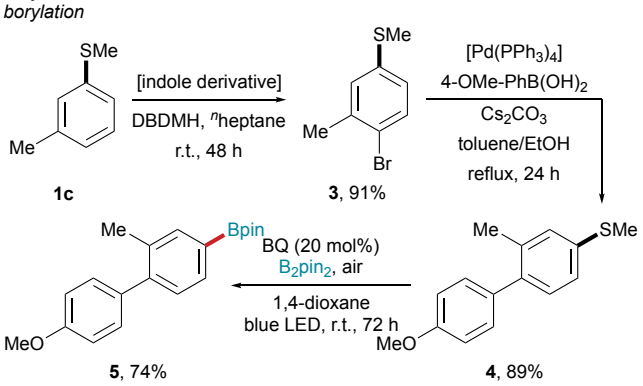
b *C–S borylation of mixed aryl sulfides*



1aa **1ad**

An oven-dried 50 mL test tube equipped with a magnetic stirring bar was charged with **1a** (0.1 mmol, 12.4 mg), **1aa** (0.1 mmol, 13.8 mg), **1ad** (0.1 mmol, 15.2 mg), benzoquinone (0.06 mmol, 6.5 mg), B_2pin_2 (1.5 mmol, 380.9 mg) and 1,4-dioxane (0.3 mL) under air atmosphere. Then the tube was put in a photoreactor equipped with blue LED. After stirring the reaction mixture under LED light illumination at room temperature for 6 days, the yield of product **2a** was determined by GC and calibrated using naphthalene as internal standard.

c *Synthesis of trisubstituted arenes via SMe-directed transformation and C–S borylation*



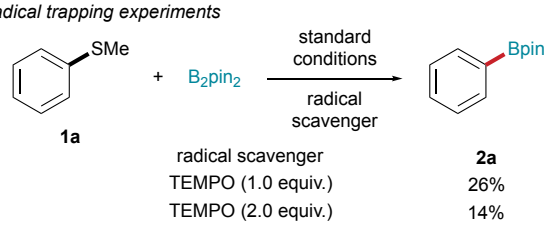
Compound **3** was prepared according to the procedures reported in the literature[4]. To a mixture of methyl(*m*-tolyl)sulfane **1c** (0.5 mmol, 69.1 mg) and catalyst methyl 2-pentyl-indole-3-carboxylate (0.025 mmol, 6.1 mg) in ^{n}heptane (1.0 mL) was added 1,3-dibromo-5,5- dimethylhydantoin (0.525 mmol, 150.1 mg) in the absence of light. The reaction mixture was stirred at room temperature for 48 h. The solvent was then evaporated under reduced pressure and the residue was directly purified by flash column chromatography over silica gel eluting with ethyl acetate/petroleum ether to provide compound **3** (98.7 mg, 91% yield) as a colorless oil.

Compound **4** was prepared according to the procedures reported in the literature[5]. In a dry 25 mL Schlenk-tube (4-bromo-3-methylphenyl)(methyl)sulfane **3** (86.8 mg, 0.4 mmol), (4-methoxyphenyl)boronic acid (73.0 mg, 0.48 mmol), Pd $(PPh_3)_4$ (9.2 mg, 8 μmol), and Cs_2CO_3 (391.0 mg, 1.2 mmol) were added consecutively and suspended in 3 mL toluene and 1.5 mL EtOH. The suspension was then heated at reflux for 24 h. The reaction mixture was allowed to cool to r.t., diluted with TBME and filtered through a pad of celite. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2; hexane: EtOAc 10:1) which resulted in a pale red oil **4** (87.0 mg, 89 % yield).

Compound **5** was prepared according to the following procedures. An oven-dried 50 mL test tube equipped with a magnetic stirring bar was charged with compound **4** (0.2 mmol, 48.3 mg), benzoquinone (0.04 mmol, 4.3 mg), B_2pin_2 (1.0 mmol, 253.9 mg) in 1,4-dioxane (0.2 mL) under air atmosphere. Then the tube was put in a photoreactor equipped with blue LED. After stirring the reaction mixture under LED light illumination at room temperature for 72 hours, the solvent was evaporated under reduced pressure and the residue was directly purified by flash column chromatography over silica gel eluting with ethyl acetate/petroleum ether to provide compound **5** (48.0 mg, 74% yield) as a white solid.

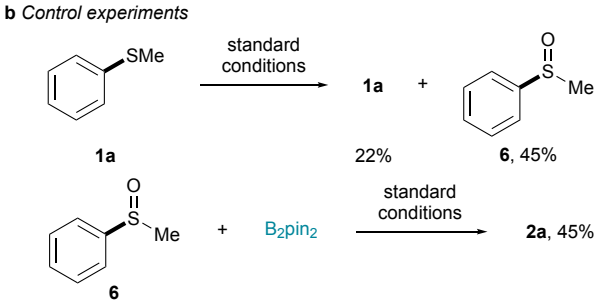
5. Mechanistic studies

a *Radical trapping experiments*



An oven-dried 50 mL test tube equipped with a magnetic stirring bar was charged with **1a** (0.2 mmol, 24.8 mg), B_2pin_2 (1.0 mmol, 253.9 mg), benzoquinone (0.04 mmol, 4.3 mg), radical scavenger (0.2 mmol or 0.4 mmol), and 1,4-dioxane (0.2 mL) under air atmosphere. Then the tube was put in a photoreactor equipped with blue LED. After stirring the reaction mixture under LED light illumination at room temperature for 72 hours, the mixture was diluted with ethyl acetate. The yield of product **2a** was determined by GC and calibrated using naphthalene as internal standard.

b *Control experiments*



An oven-dried 50 mL test tube equipped with a magnetic stirring bar was charged with **1a** (0.2 mmol, 24.8 mg), benzoquinone (0.04 mmol, 4.3 mg) and solvent (0.2 mL) under air atmosphere. Then the tube was put in a photoreactor equipped with LED. After stirring the reaction mixture under LED light illumination at room temperature for 72 hours, the mixture was diluted with ethyl acetate. The yields of **1a** and **6** were determined by GC and calibrated using naphthalene as internal standard.

An oven-dried 50 mL test tube equipped with a magnetic stirring bar was charged with **6** (0.2 mmol, 28.0 mg), benzoquinone (0.04 mmol, 4.3 mg), B_2pin_2 (1.0 mmol, 253.9 mg), and solvent (0.2 mL) under air atmosphere. Then the tube was put in a photoreactor equipped with LED. After stirring the reaction mixture under LED light illumination at room temperature for 72 hours, the mixture was diluted with ethyl acetate. The yield of product **2a** was determined by GC and calibrated using naphthalene as internal standard.

c *UV-Vis absorption experiments*

The UV-Vis absorption of BQ with different concentrations were tested, which indicated that it could absorb light at 450 nm and probably act as photosensitizer.

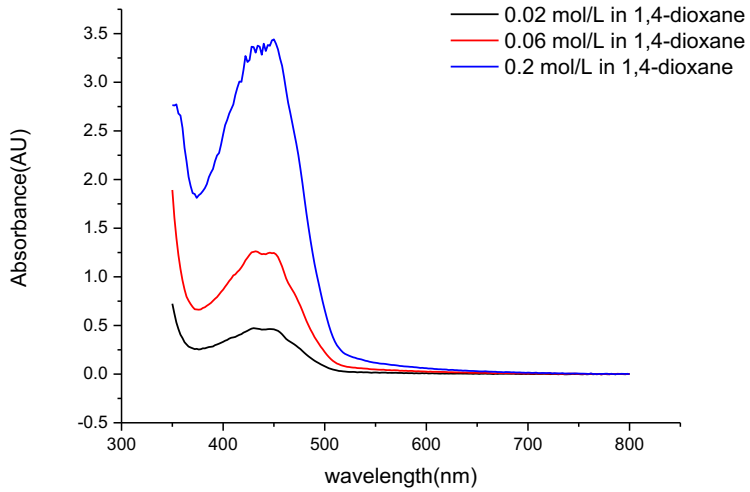
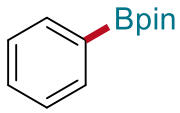


Figure S3 UV-Vis absorption experiments

6. Analytical data of starting materials and products

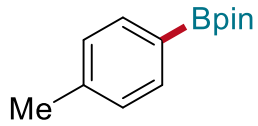
4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (2a)[2]



2a

2a (29.0 mg, 71%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 6.4 Hz, 2H), 7.55 (t, J = 7.9 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 1.43 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8, 131.3, 127.7, 83.7, 24.9.

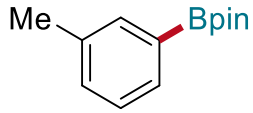
4,4,5,5-tetramethyl-2-(*p*-tolyl)-1,3,2-dioxaborolane (2b)[2]



2b

2b (31.8 mg, 73%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 7.7 Hz, 2H), 2.44 (s, 3H), 1.41(s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 134.9, 128.6, 83.7, 25.0 , 21.9.

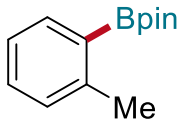
4,4,5,5-tetramethyl-2-(*m*-tolyl)-1,3,2-dioxaborolane (2c)[2]



2c

2c (27.9 mg, 64%) was obtained as a colorless oil after flash chromatography (SiO_2, petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 2H), 7.32 – 7.28 (m, 2H), 2.39 (s, 3H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 135.4, 132.2, 131.9, 127.8, 83.8, 25.0, 21.4.

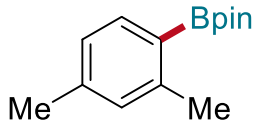
4,4,5,5-tetramethyl-2-(*o*-tolyl)-1,3,2-dioxaborolane(2d)[2]



2d

2d (22.3 mg, 52%) was obtained as a colorless oil after flash chromatography (SiO_2, petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.38 (td, *J* = 7.5, 1.5 Hz, 1H), 7.26 – 7.20 (m, 2H), 2.62 (s, 3H), 1.41 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 135.9, 130.9, 129.9, 124.8, 83.5, 24.9, 22.3.

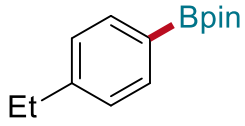
2-(2,4-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)[6]



2e

2e (33.9 mg, 73%) was obtained as a colorless liquid after flash chromatography (SiO_2, petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.06 (d, *J* = 6.0 Hz, 2H), 2.60(s, 3H), 2.39(s, 3H), 1.41 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 140.9, 136.2, 130.8, 125.6, 83.3, 25.0, 22.2, 21.6.

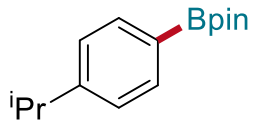
2-(4-isopropylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f)[7]



2f

2f (27.8 mg, 60%) was obtained as a colorless liquid after flash chromatography (SiO_2, petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.34 (s, 12H), 1.24 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 135.0, 127.5, 83.7, 29.3, 25.0, 15.6.

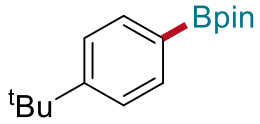
2-(4-isopropylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2g)[8]



2g

2g (26.1 mg, 53%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.96 (hept, *J* = 6.9 Hz, 1H), 1.39 (s, 12H), 1.31 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 135.1, 126.0, 83.7, 34.4, 24.9, 24.0.

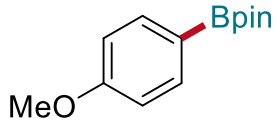
2-(4-(*tert*-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2h)[8]



2h

2h (26.5 mg, 51%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 1.33 (d, *J* = 4.8 Hz, 21H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 134.8, 124.8, 83.8, 35.0, 31.3, 25.0.

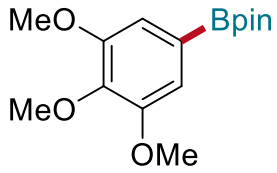
2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i)[2]



2i

2i (18.7 mg, 40%) was obtained as a colorless liquid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 1.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 136.6, 113.4, 83.6, 55.1, 25.0.

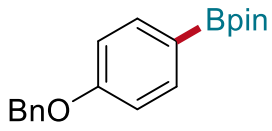
2-(3,4,5-trimethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j)[10]



2j

2j (24.7 mg, 42%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 7.2 Hz, 2H), 3.84 (d, *J* = 13.4 Hz, 9H), 1.29 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 140.7, 111.2, 83.8, 60.7, 56.0, 24.8.

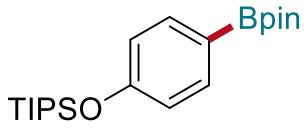
2-[4-(Methoxymethoxy) phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)[2]



2k

2k (34.1 mg, 55%) was obtained as a colorless liquid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.6 Hz, 2H), 7.49 – 7.31 (m, 5H), 7.00 (d, *J* = 8.6 Hz, 2H), 5.11 (s, 2H), 1.36 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 136.9, 136.6, 128.7, 128.1, 127.6, 114.3, 83.7, 69.8, 25.0.

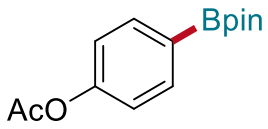
3-(3,4,5-trimethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2l)[2]



2l

2l (49.6 mg, 66%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 6.88 (dd, *J* = 8.6, 1.9 Hz, 2H), 1.30 (s, 12H), 1.27 (dt, *J* = 8.8, 7.4 Hz, 3H), 1.11 (d, *J* = 7.3 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 136.6, 119.5, 83.6, 118.0, 25.0, 18.0, 12.8.

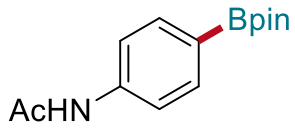
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl acetate (2m)[3]



2m

2m (29.9 mg, 57%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 2.29 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 153.2, 136.3, 121.1, 84.0, 24.9, 21.2.

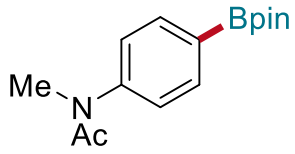
N-[4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]acetamide (2n)[11]



2n

2n (21.4 mg, 41%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.74 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H), 2.10 (s, 3H), 1.32 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 140.9, 135.8, 118.8, 83.8, 24.9, 24.7.

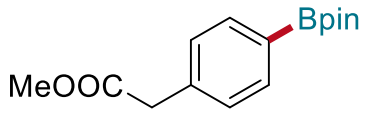
N-methyl-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide (2o)[3]



2o

2o (42.9 mg, 78%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 3.23 (s, 3H), 1.85 (s, 3H), 1.32 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5,147.1, 136.3, 126.3, 84.1, 37.1, 24.9, 22.5.

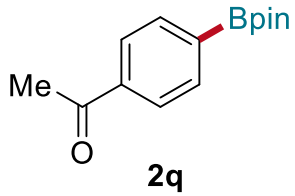
Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2p)[3]



2p

2p (30.3 mg, 55%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 3.66 (d, J = 14.2 Hz, 5H), 1.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 137.2, 135.2, 128.8, 83.9, 52.2, 41.6, 25.0.

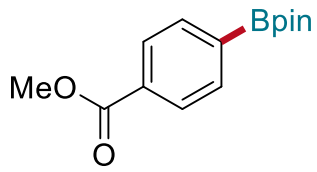
1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethanone (2q)[12]



2q

2q (34.4 mg, 70%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (q, J = 8.3 Hz, 4H), 2.59 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5,139.0, 135.0, 127.3, 84.3, 26.8, 24.9.

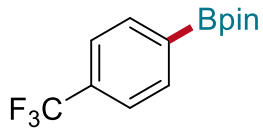
Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2r)[2]



2r

2r (33.0 mg, 63%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 2H), 7.86 (d, J = 8.1 Hz, 2H), 3.90 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 134.7, 132.4, 128.7, 84.2, 52.2, 25.0.

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

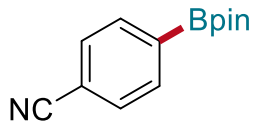


2s

2s (21.7 mg, 40%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.8 Hz, 2H), 7.62 (d, J = 7.9 Hz, 2H), 1.36 (s, 12H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 133.0 (q, $J_{C\text{-}F}$ = 32 Hz), 124.3 (q, $J_{C\text{-}F}$ = 4 Hz), 124.2 (q, $J_{C\text{-}F}$ = 269 Hz), 84.3, 24.9.

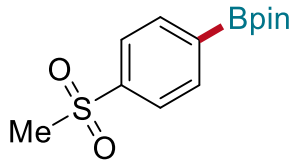
4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (2t)[2]



2t

2t (23.4 mg, 51%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 131.1, 118.8, 114.5, 84.5, 24.8.

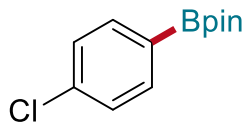
1-4,4,5,5-tetramethyl-2-(4-(methylsulfonyl)phenyl)-1,3,2-dioxaborolane (2u)[13]



2u

2u (27.6 mg, 49%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.3 Hz, 2H), 7.91 (d, J = 8.3 Hz, 2H), 3.03 (s, 3H), 1.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.7,135.7, 126.4, 84.6, 44.5, 25.0.

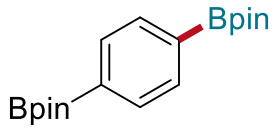
2-(4-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2v)[13]



2v

2v (30.0 mg, 63%) was obtained as a colorless liquid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 1.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 136.2, 128.1, 84.0, 24.9.

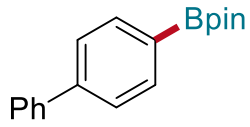
1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (2w)[3]



2w

2w (34.9 mg, 53%) was obtained as a brown solid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 4H), 1.35 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.0, 84.0, 25.0.

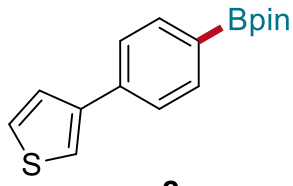
2-[1,1'-biphenyl]-4-yl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2x)[3]



2x

2x (30.2 mg, 54%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.2 Hz, 2H), 7.76 – 7.63 (m, 4H), 7.49 (dd, J = 10.3, 4.7 Hz, 2H), 7.41 (d, J = 7.3 Hz, 1H), 1.42 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 141.1, 135.4, 128.9, 127.7, 127.3, 126.6, 83.9, 25.0.

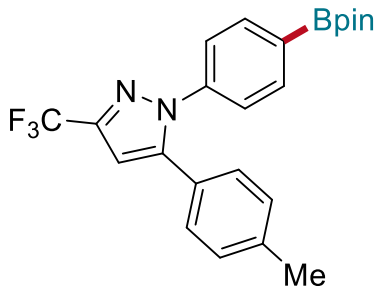
3-[1,1'-biphenyl]-4-yl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2y)[3]



2y

2y (30.9 mg, 54%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.9 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.52 (dd, J = 2.7, 1.1 Hz, 1H), 7.46 – 7.37 (m, 2H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.1 , 84.0 , 121.1, 125.8, 126.4 , 126.5, 135.5, 138.5 , 142.4.

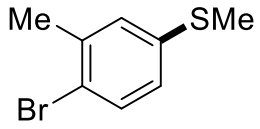
2-(9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2z)



2z

2z (52.2 mg, 61%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.16 – 7.06 (m, 4H), 6.71 (s, 1H), 2.35 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 143.6, 143.2, 141.6, 139.2, 135.6, 129.5, 128.8, 126.4, 124.6, 105.7, 84.2, 25.0, 21.4. HRMS (ESI) m/z calced for $C_{23}H_{24}BF_3N_2O_2$ $[M+H]^+$: 429.1956 found 429.1922.

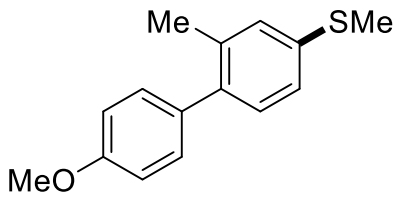
(4-bromo-3-methylphenyl)(methyl)sulfane (3)[4]



3

3 (62.8 mg, 91%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.3 Hz, 1H), 7.11 (s, 1H), 6.93 (d, J = 10.6 Hz, 1H), 2.46 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 137.7, 132.6, 128.9, 125.5, 121.4, 23.0, 16.1.

(4'-methoxy-2-methyl-[1,1'-biphenyl]-4-yl)(methyl)sulfane (4)

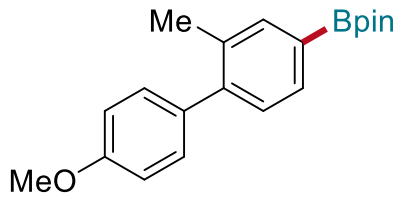


4

4 (87.0 mg, 89%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.7 Hz, 2H), 7.19 – 7.13 (m, 3H), 6.96 (d, J = 8.7 Hz,

2H), 3.86 (s, 3H), 2.52 (s, 3H), 2.27 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 138.7, 136.8, 136.2, 133.8, 130.5, 130.4, 128.6, 124.2, 113.6, 55.4, 29.8, 20.7, 16.1; HRMS (ESI) m/z calced for C15H16OS $[M+H]^+$: 245.0902 found 245.0916.

2-(4'-methoxy-2-methyl-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)[14]



5

5 (48.0 mg, 74%) was obtained as a white solid after flash chromatography (SiO_2, petroleum ether/ ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) 7.84 –7.61 (m, 2H), 7.26 (s, 3H), 6.96 (d, J = 6.4 Hz, 2H), 3.86 (d, J = 1.8 Hz, 3H), 2.30 (s, 3H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 144.6, 136.9, 134.9, 134.3, 132.3, 130.3, 129.5, 113.6, 83.9, 55.4, 25.0, 20.5.

7. References

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8. NMR spectra of starting materials and products

Figure S4. ^{1}H NMR spectrum of 2a in $CDCl_3$ (400 MHz)

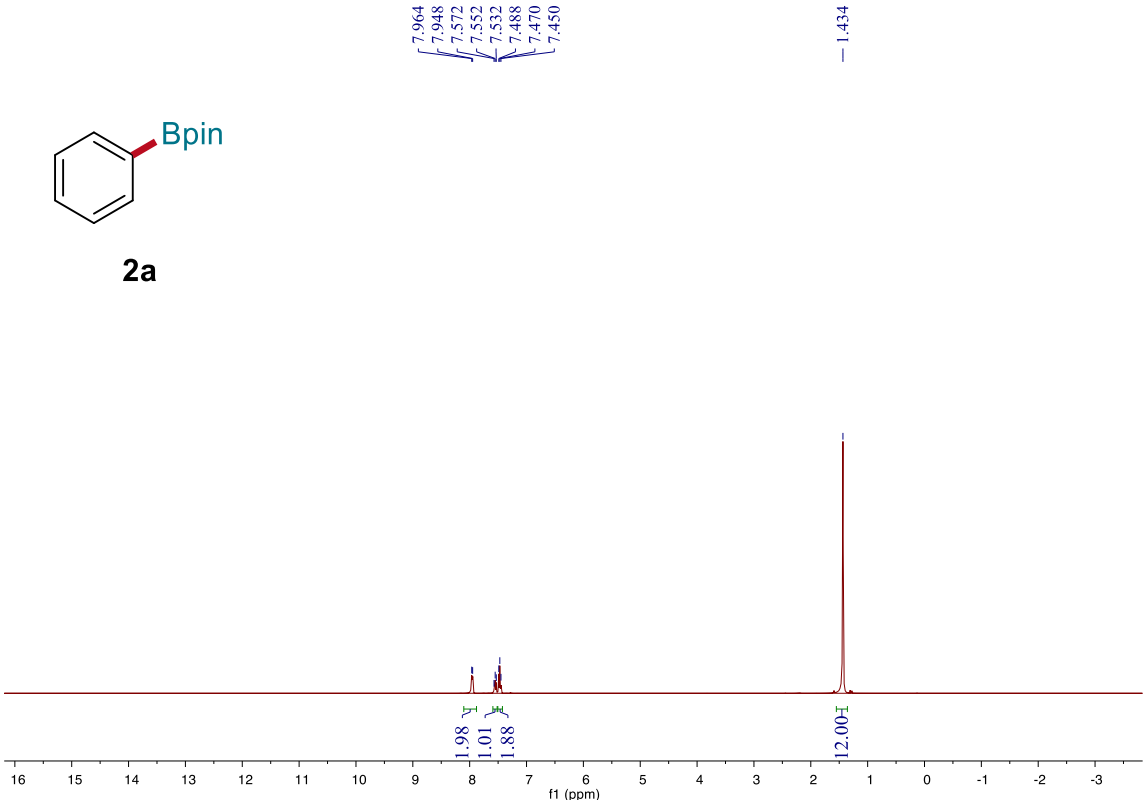

Figure S5. ^{13}C NMR spectrum of 2a in $CDCl_3$(100 MHz)

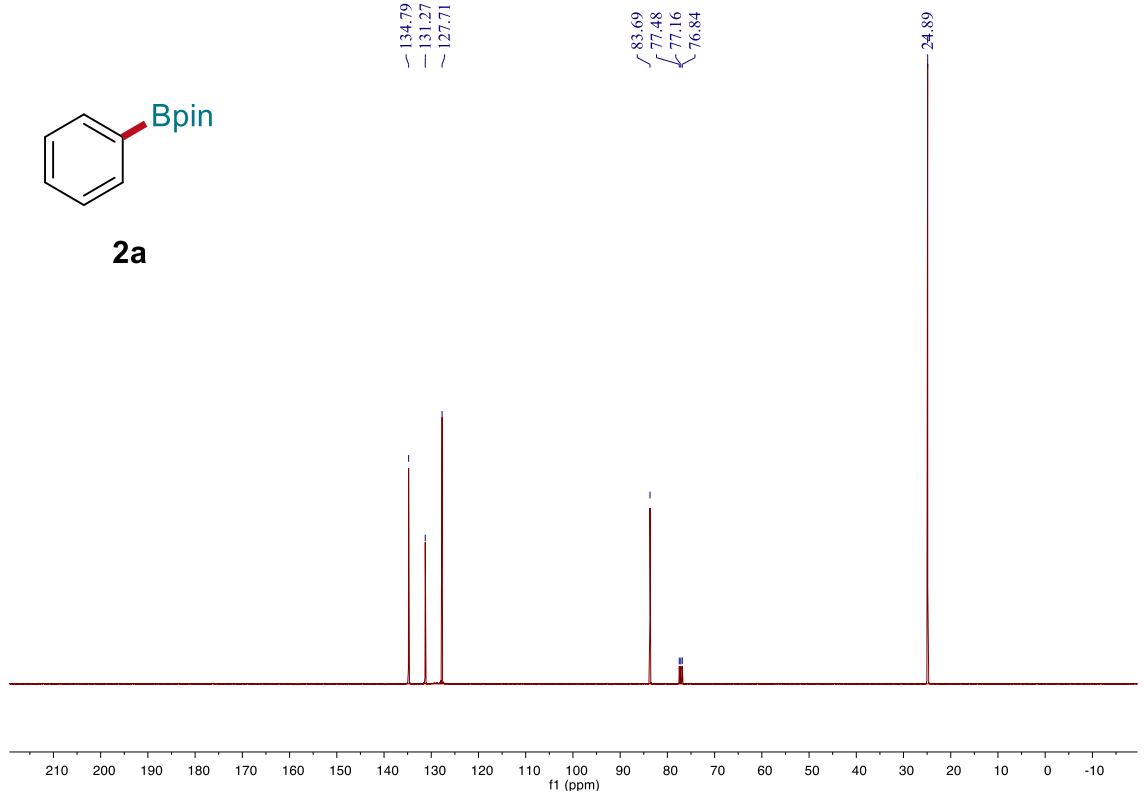

Figure S6. ^{1}H NMR spectrum of 2b in $CDCl_3$ (400 MHz)

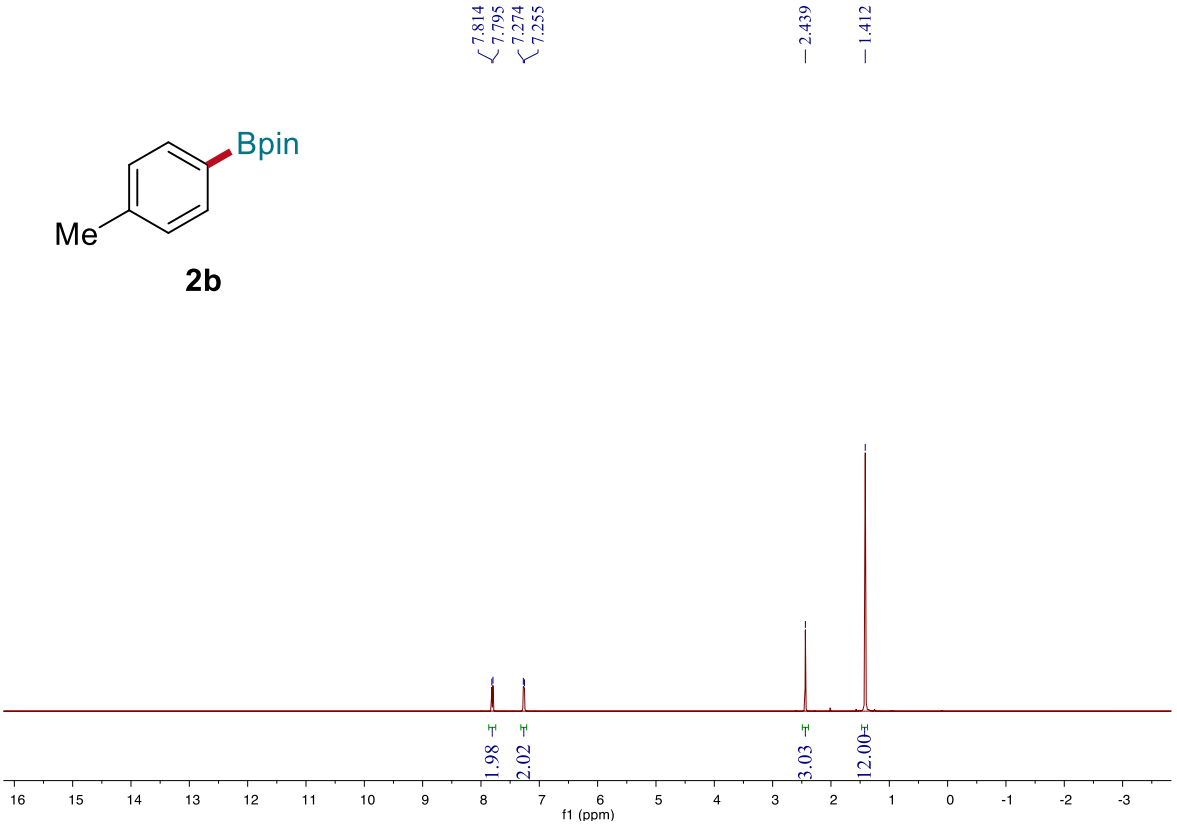

Figure S7. ^{13}C NMR spectrum of 2b in $CDCl_3$ (100 MHz)

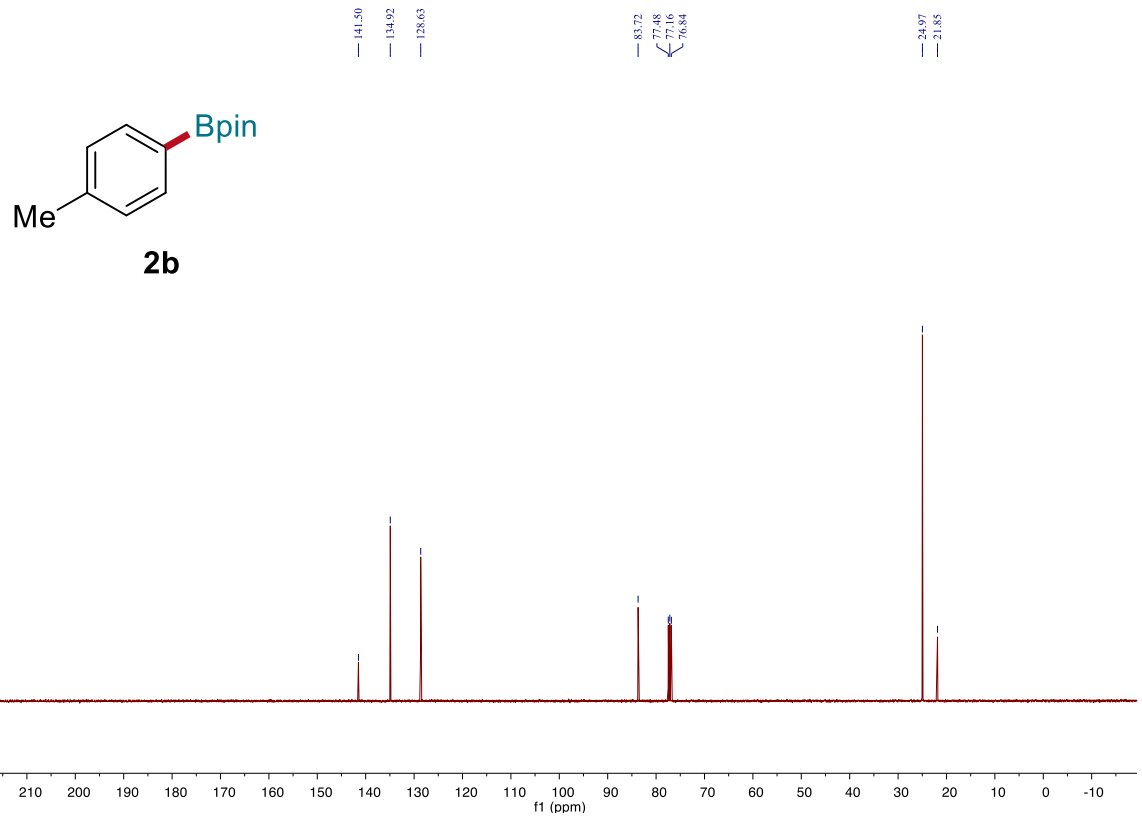

Figure S8. ^{1}H NMR spectrum of 2c in $CDCl_3$ (400 MHz)

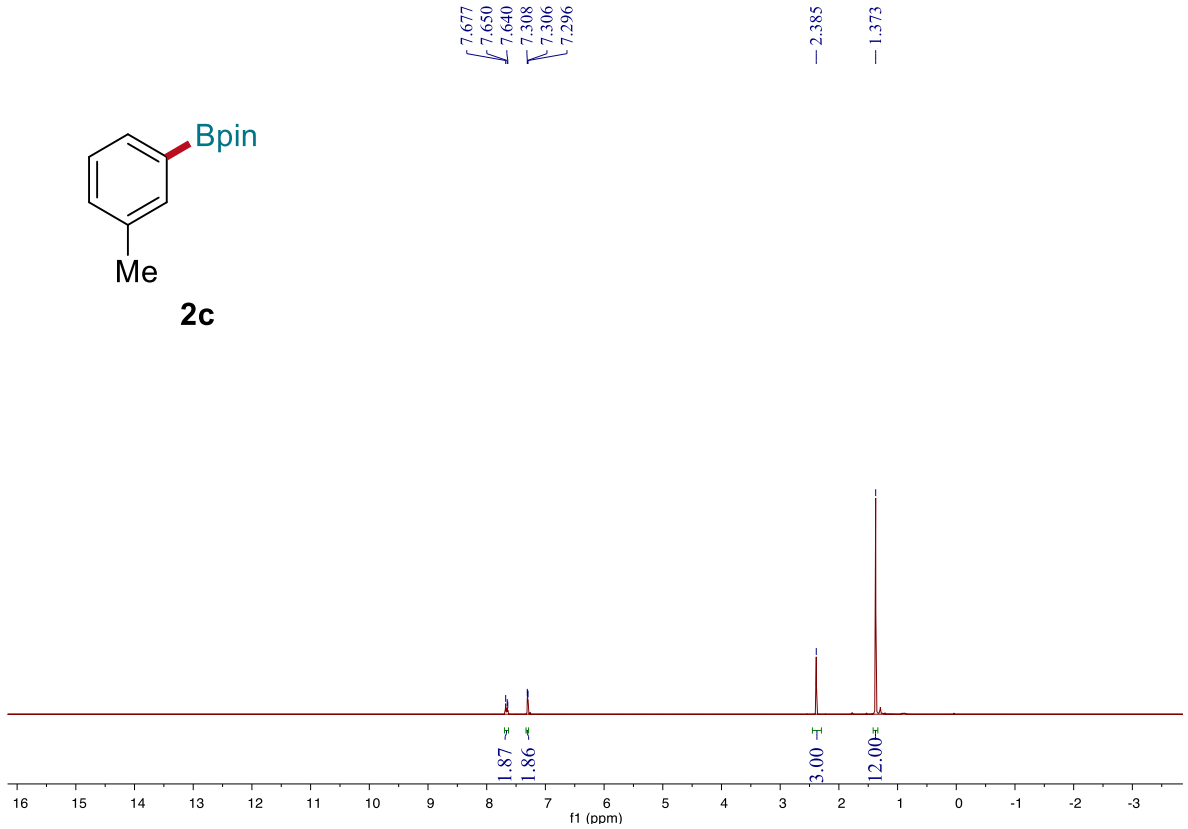

Figure S9. ^{13}C NMR spectrum of 2c in $CDCl_3$ (100 MHz)

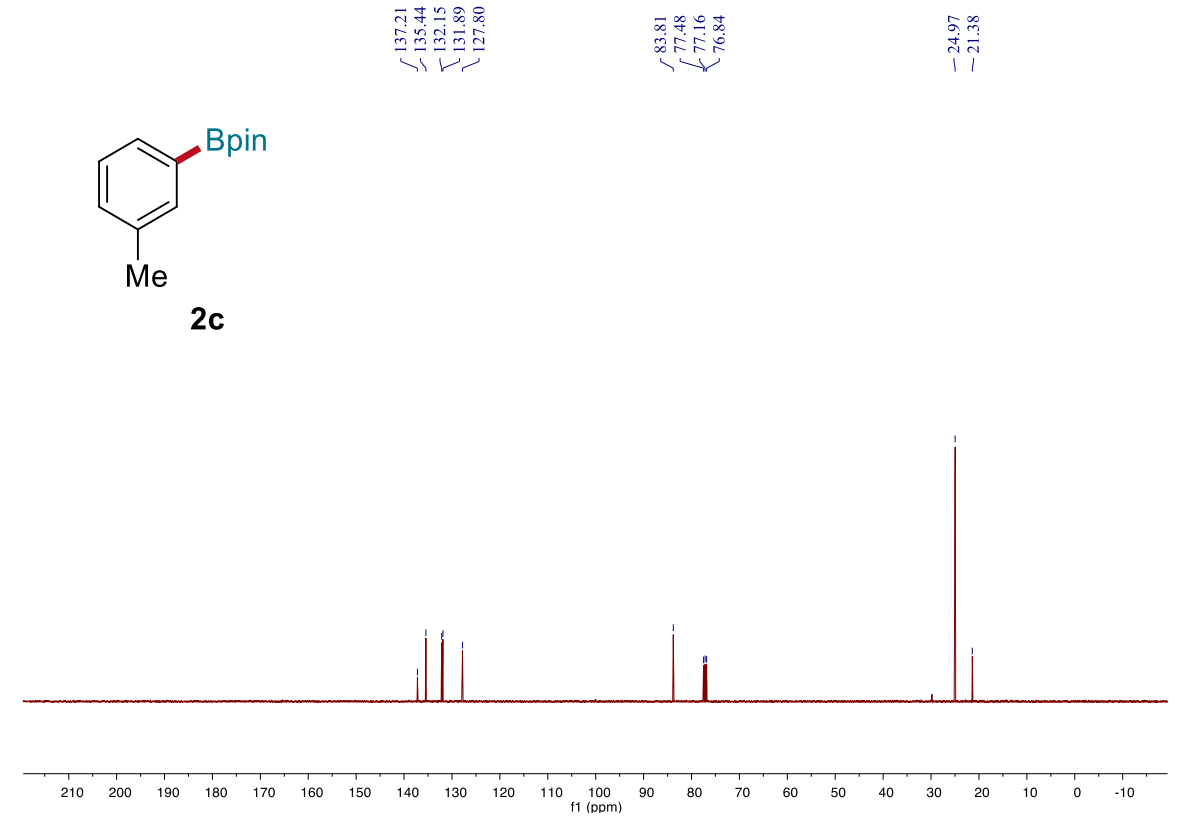

Figure S10. ^{1}H NMR spectrum of 2d in $CDCl_3$ (400 MHz)

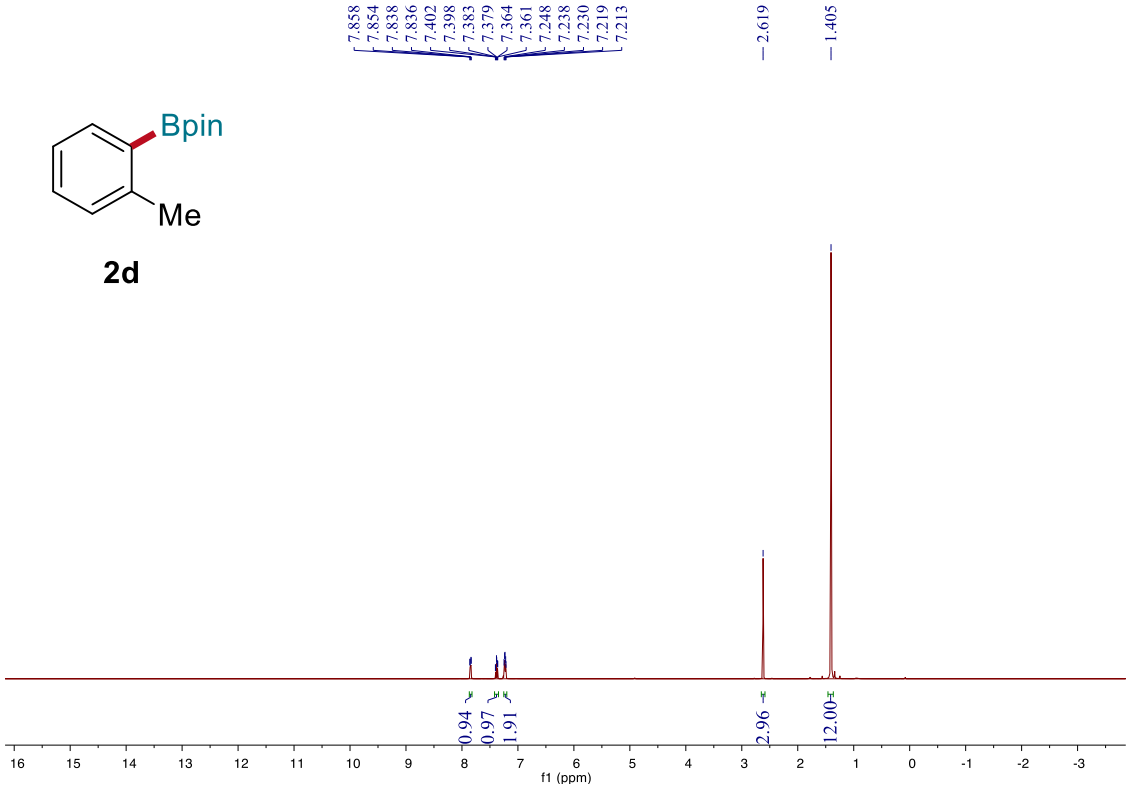

Figure S11. ^{13}C NMR spectrum of 2d in $CDCl_3$ (100 MHz)

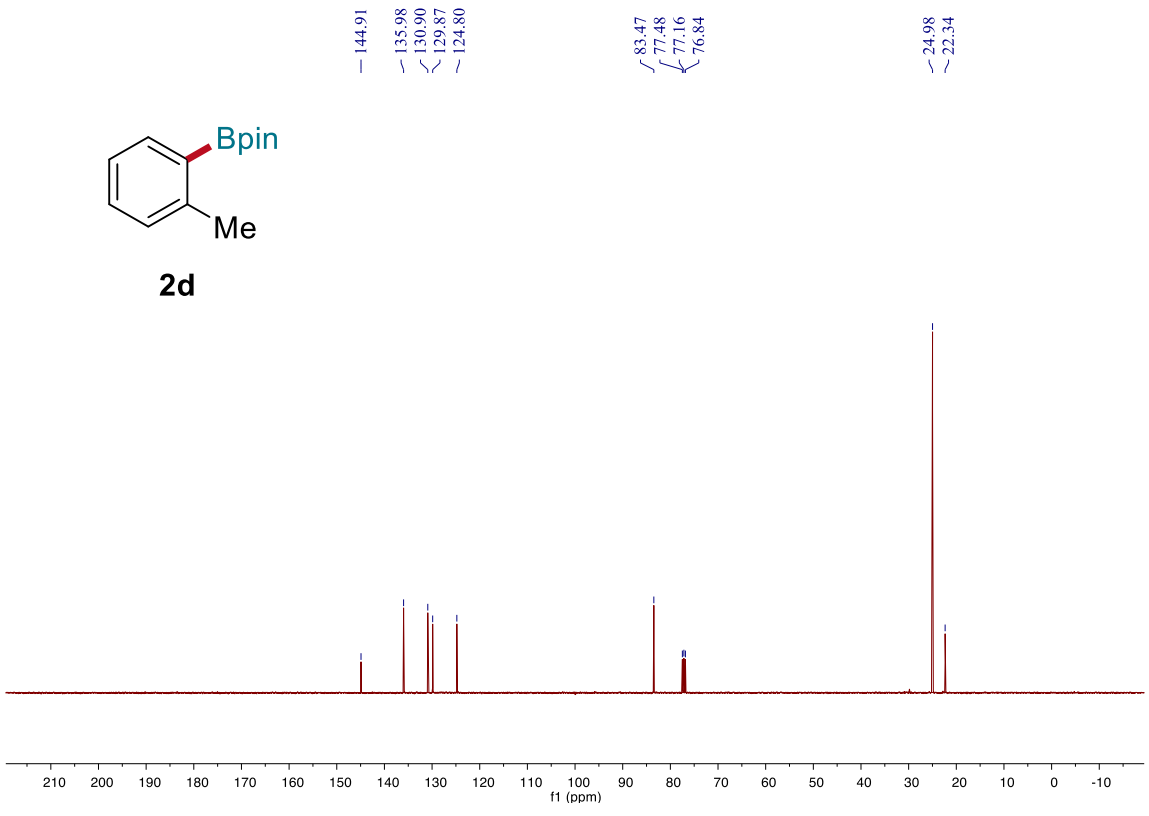

Figure S12. ^{1}H NMR spectrum of 2e in $CDCl_3$ (400 MHz)

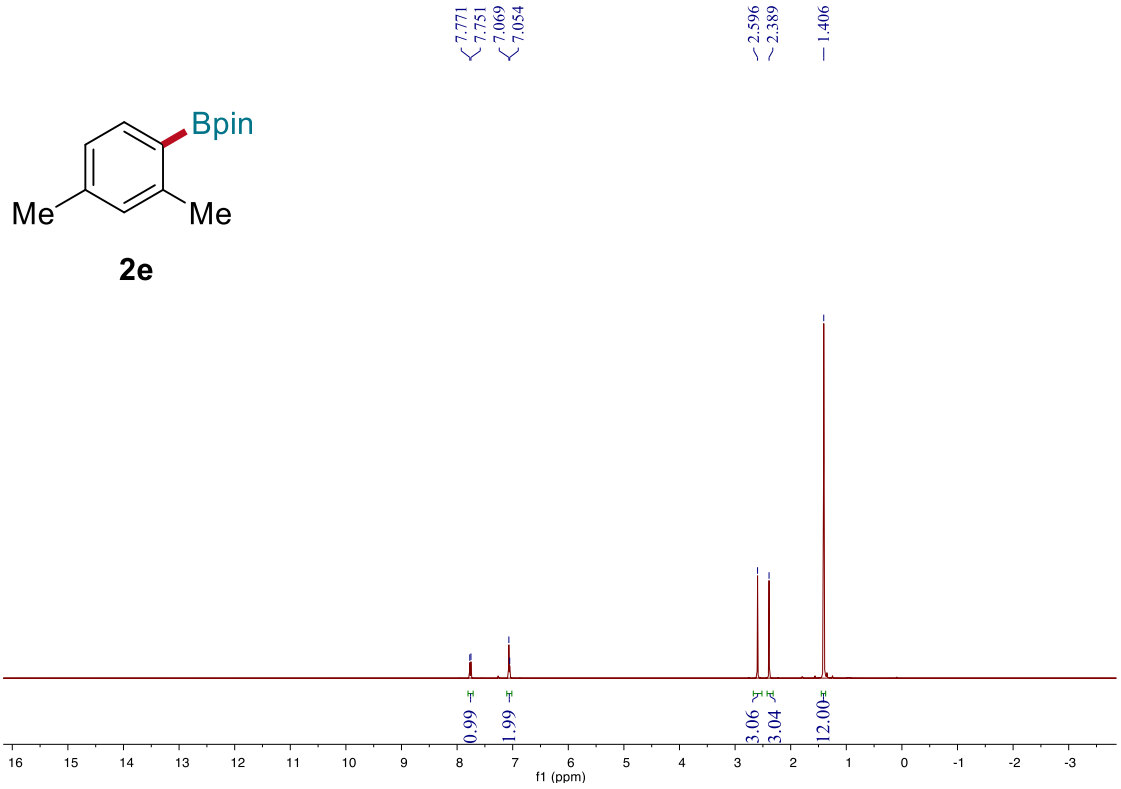

Figure S13. ^{13}C NMR spectrum of 2e in $CDCl_3$ (100 MHz)

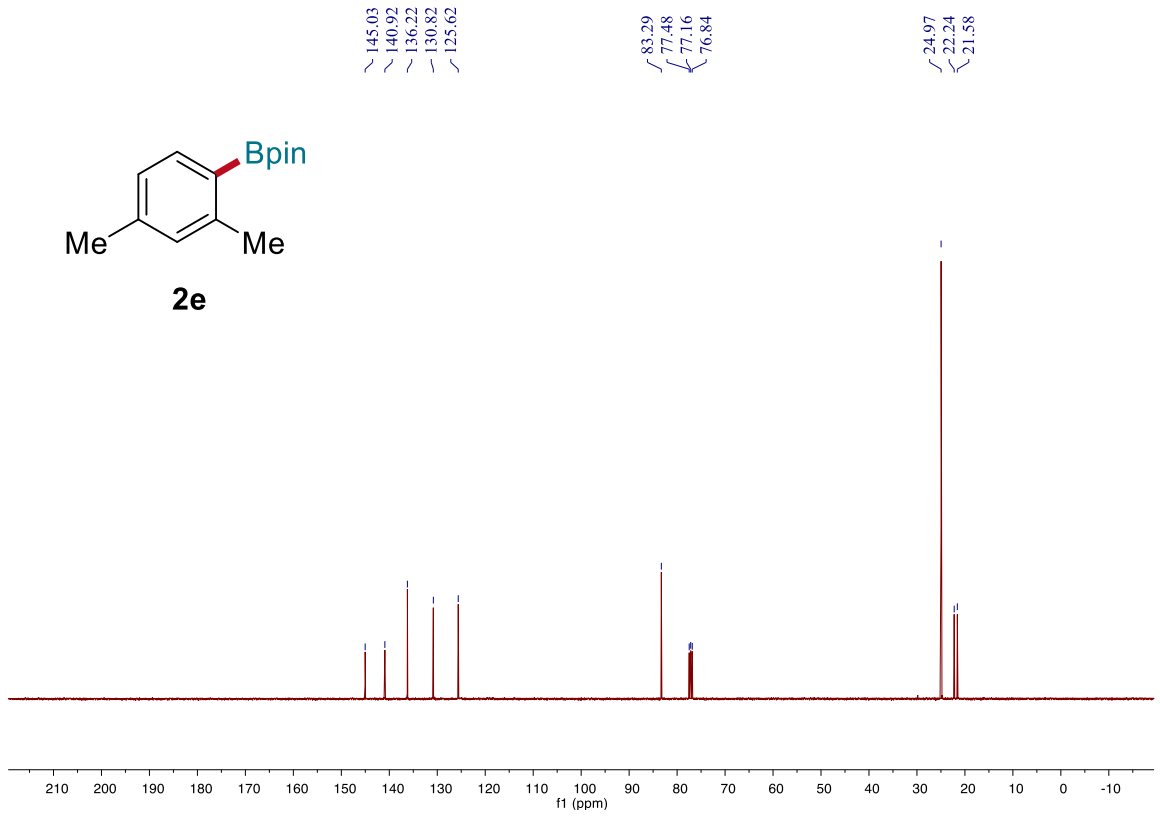

Figure S14. ^{1}H NMR spectrum of 2f in $CDCl_3$ (400 MHz)

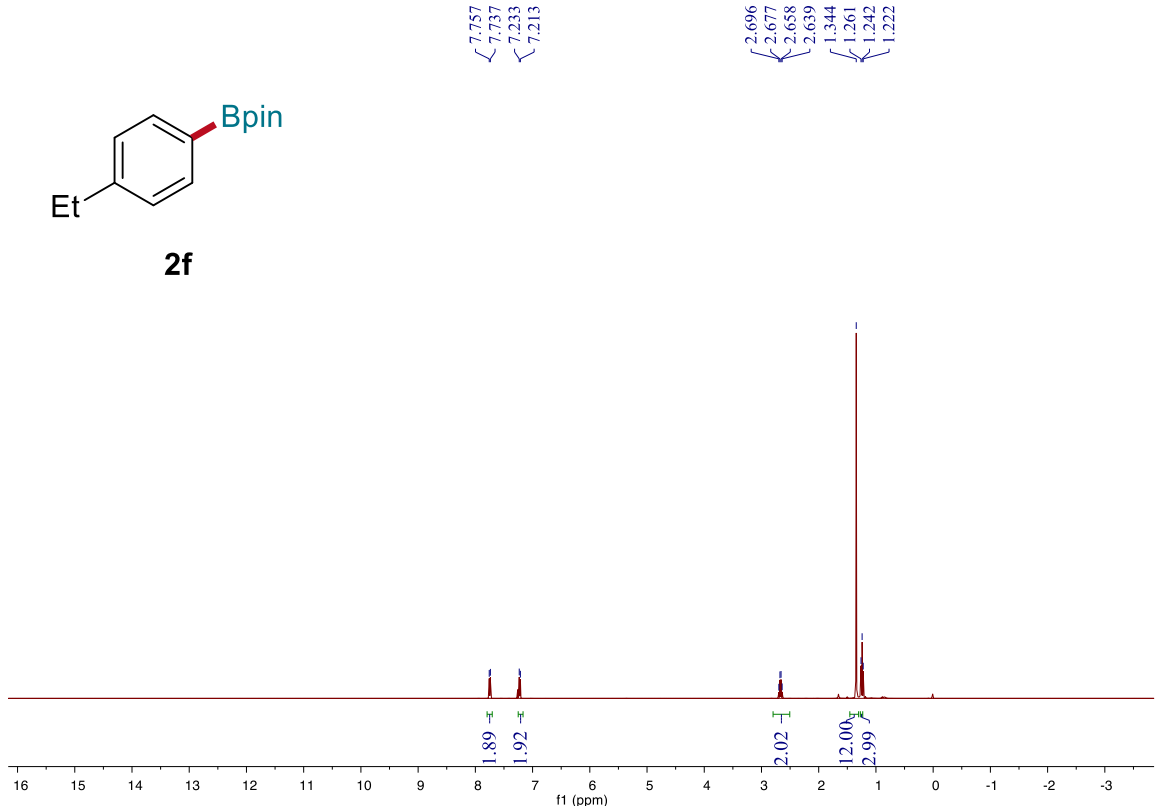

Figure S15. ^{13}C NMR spectrum of 2f in $CDCl_3$ (100 MHz)

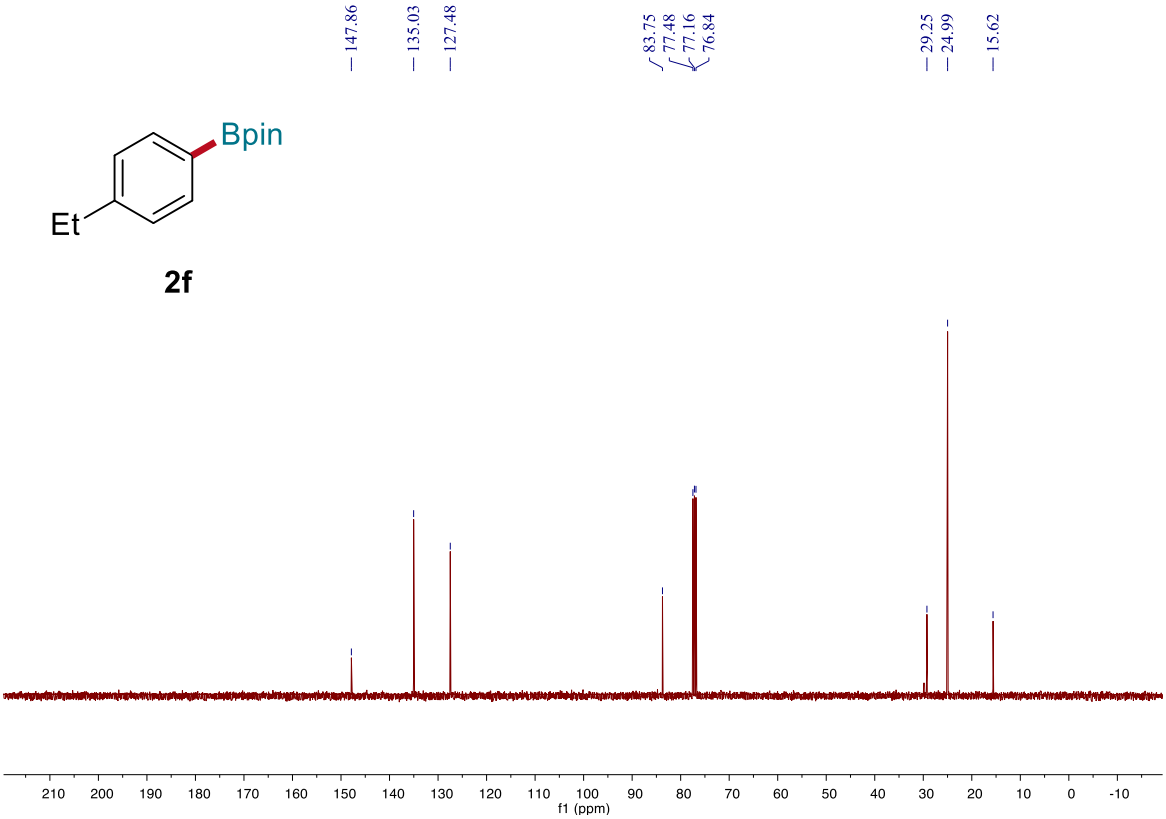

Figure S16. ^{1}H NMR spectrum of 2g in $CDCl_3$ (400 MHz)

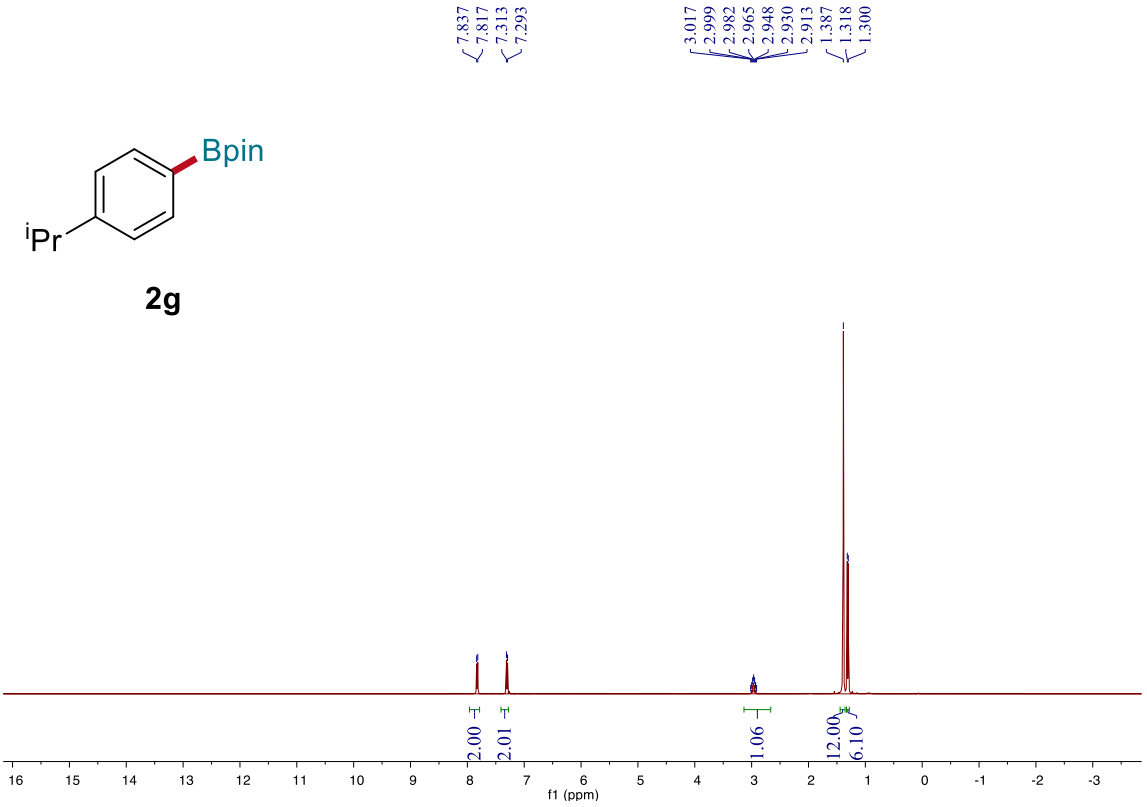

Figure S17. ^{13}C NMR spectrum of 2g in $CDCl_3$ (100 MHz)

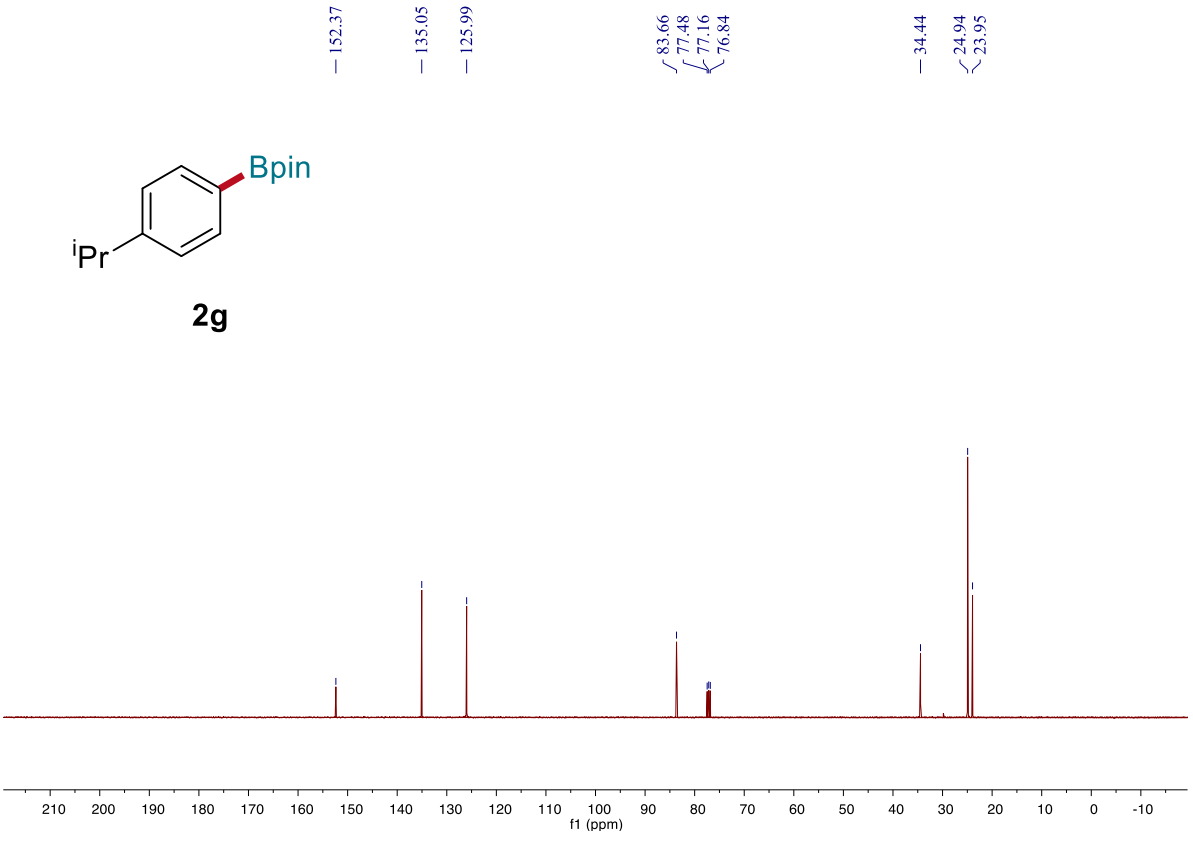

Figure S18. ^{1}H NMR spectrum of 2h in $CDCl_3$ (400 MHz)

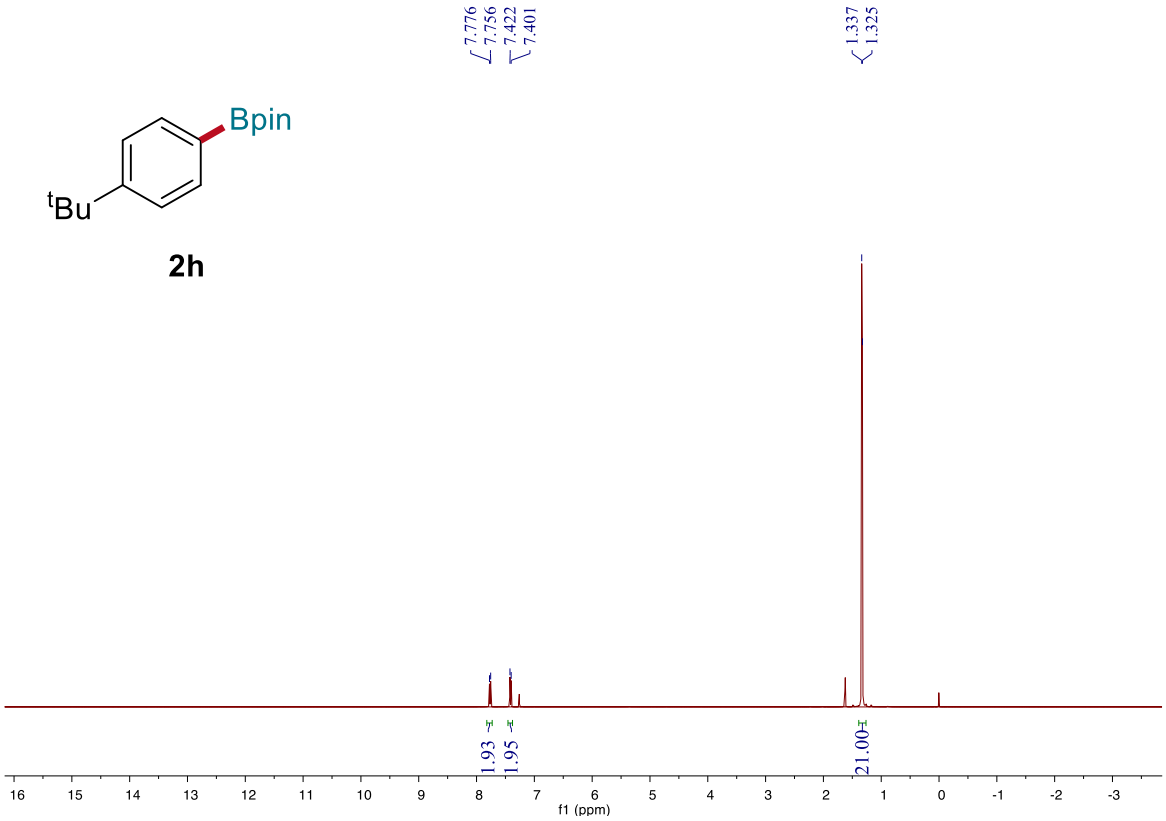

Figure S19. ^{13}C NMR spectrum of 2h in $CDCl_3$ (100 MHz)

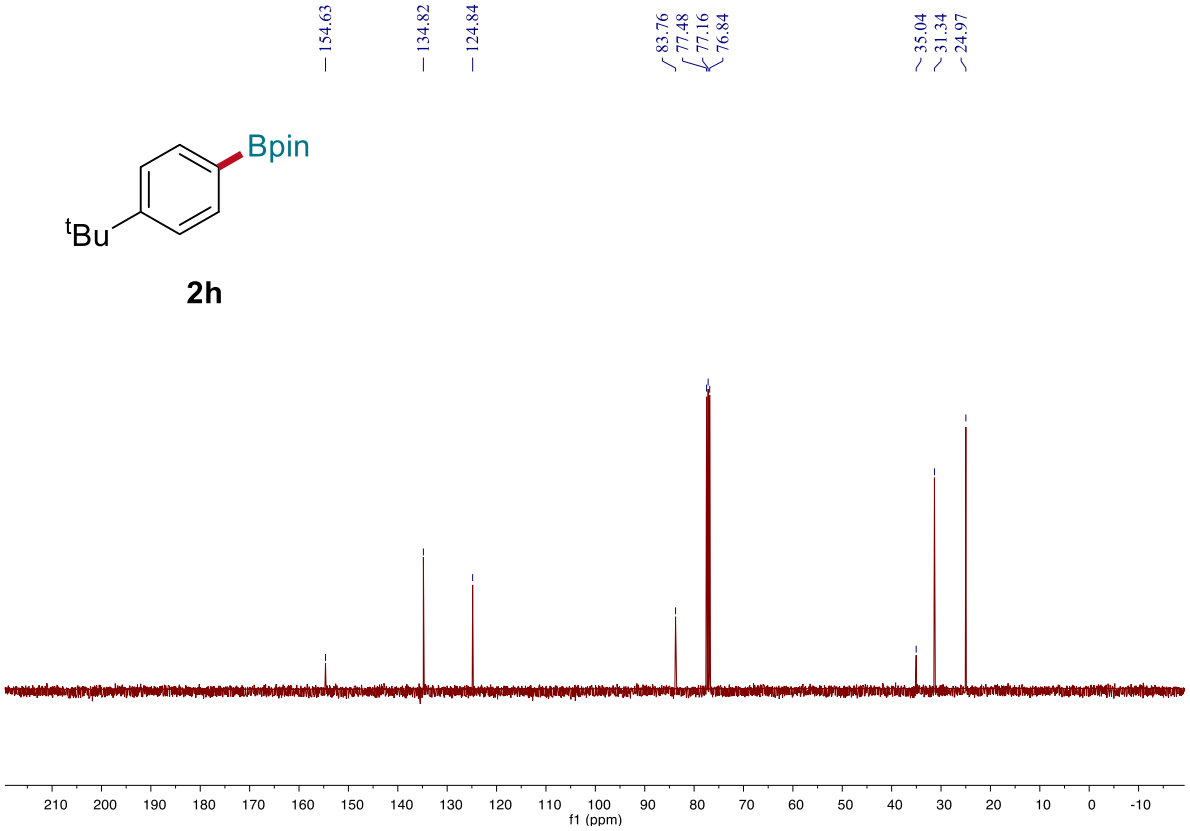

Figure S20. ^{1}H NMR spectrum of 2i in $CDCl_3$ (400 MHz)

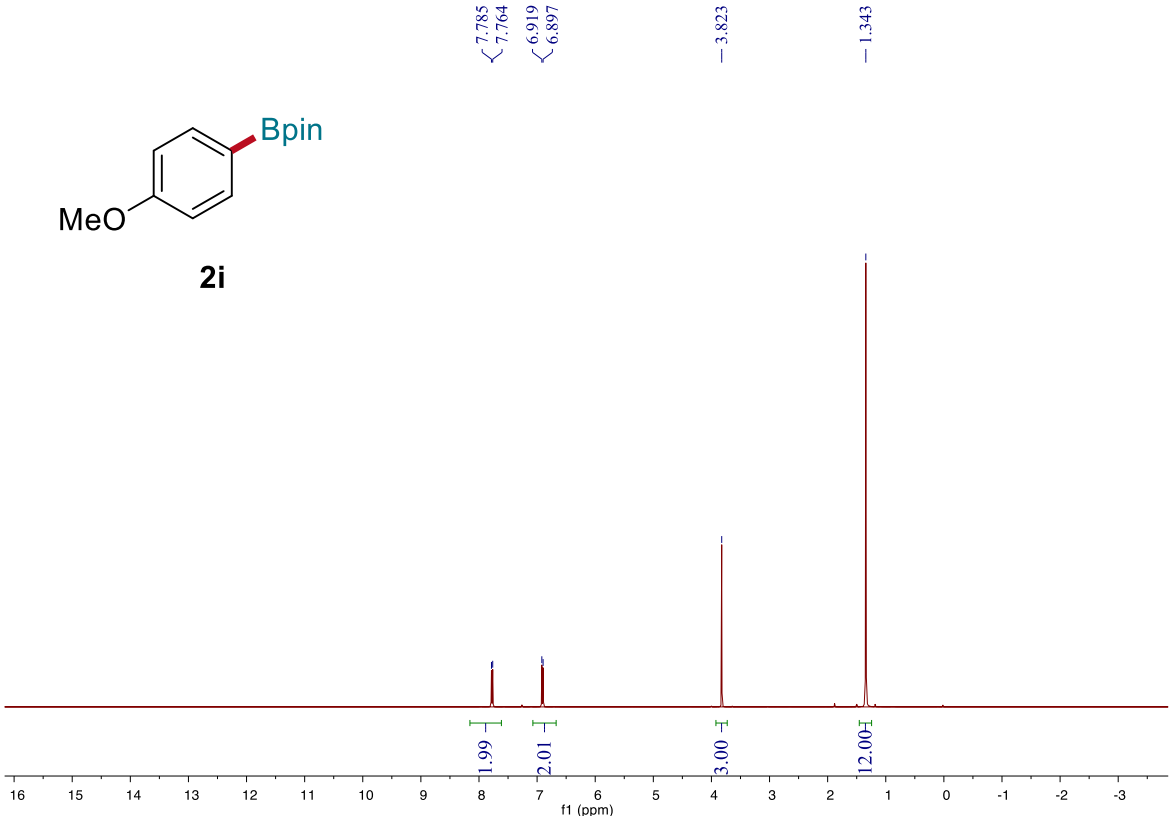

Figure S21. ^{13}C NMR spectrum of 2i in $CDCl_3$ (100 MHz)

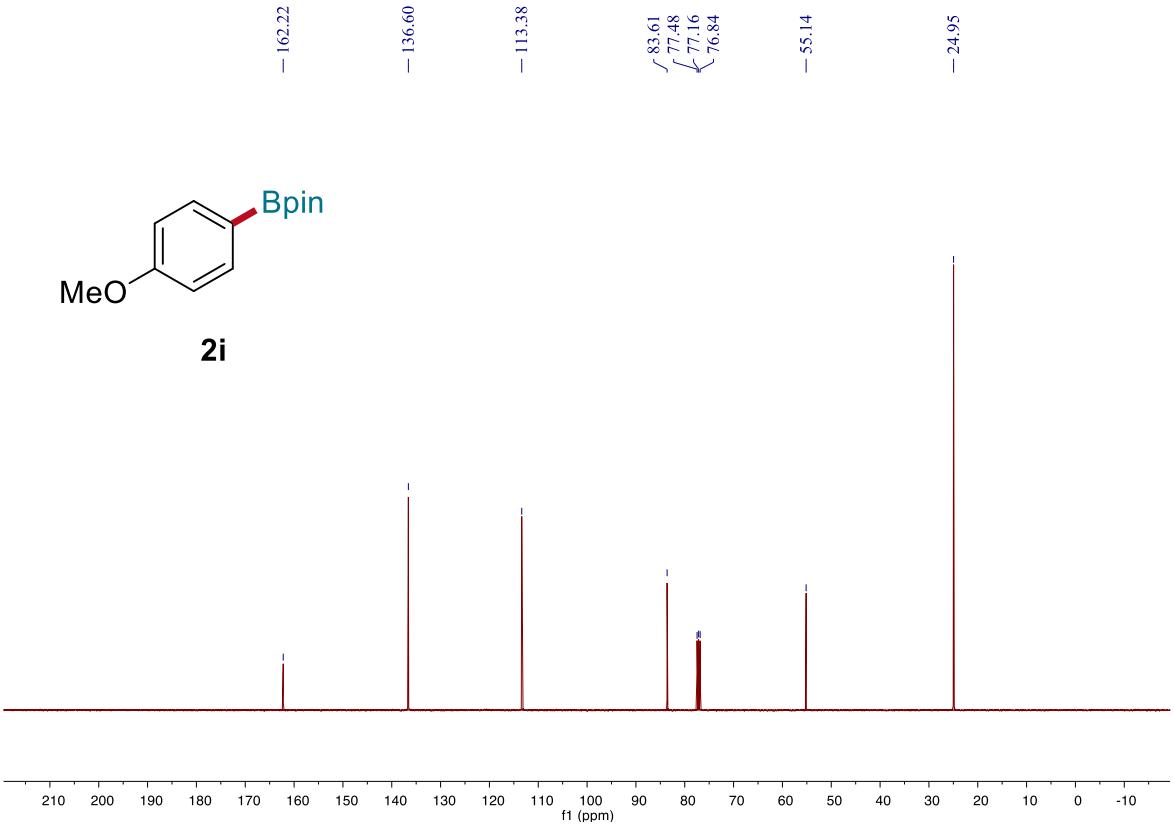

Figure S22. ^{1}H NMR spectrum of 2j in $CDCl_3$ (400 MHz)

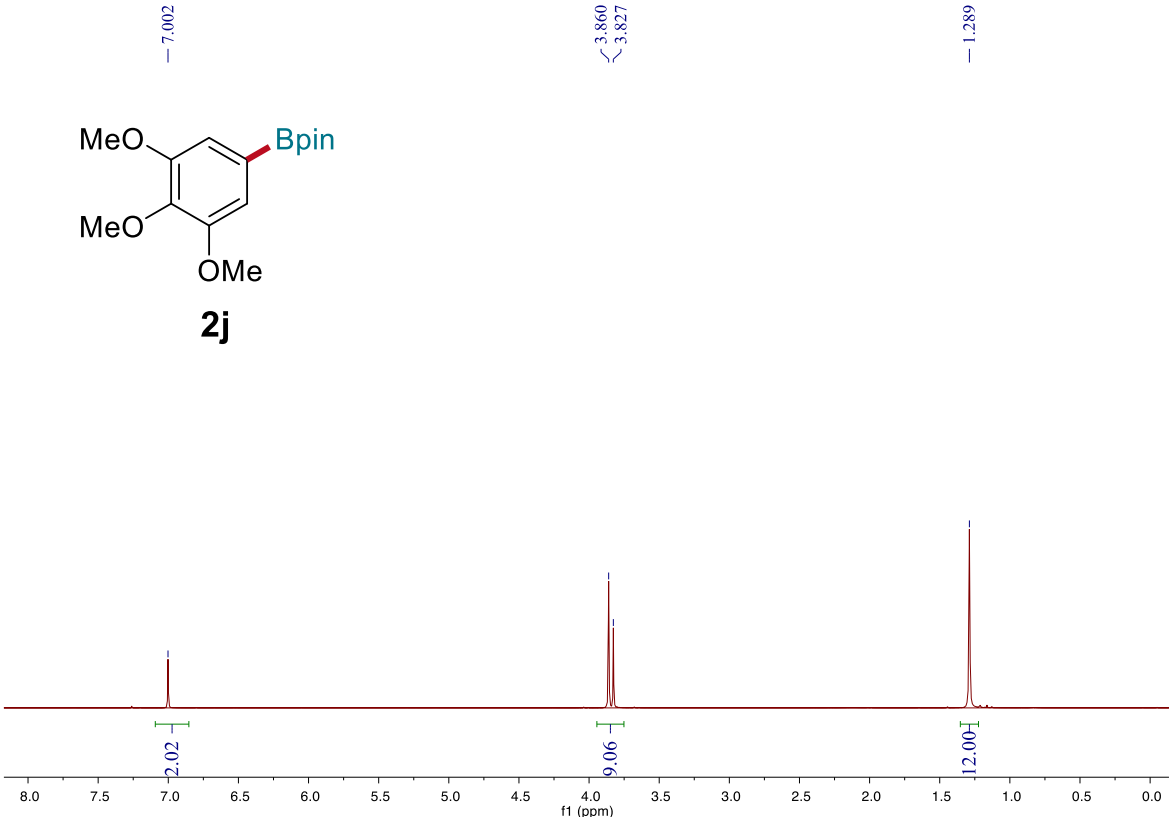

Figure S23. ^{13}C NMR spectrum of 2j in $CDCl_3$ (100 MHz)

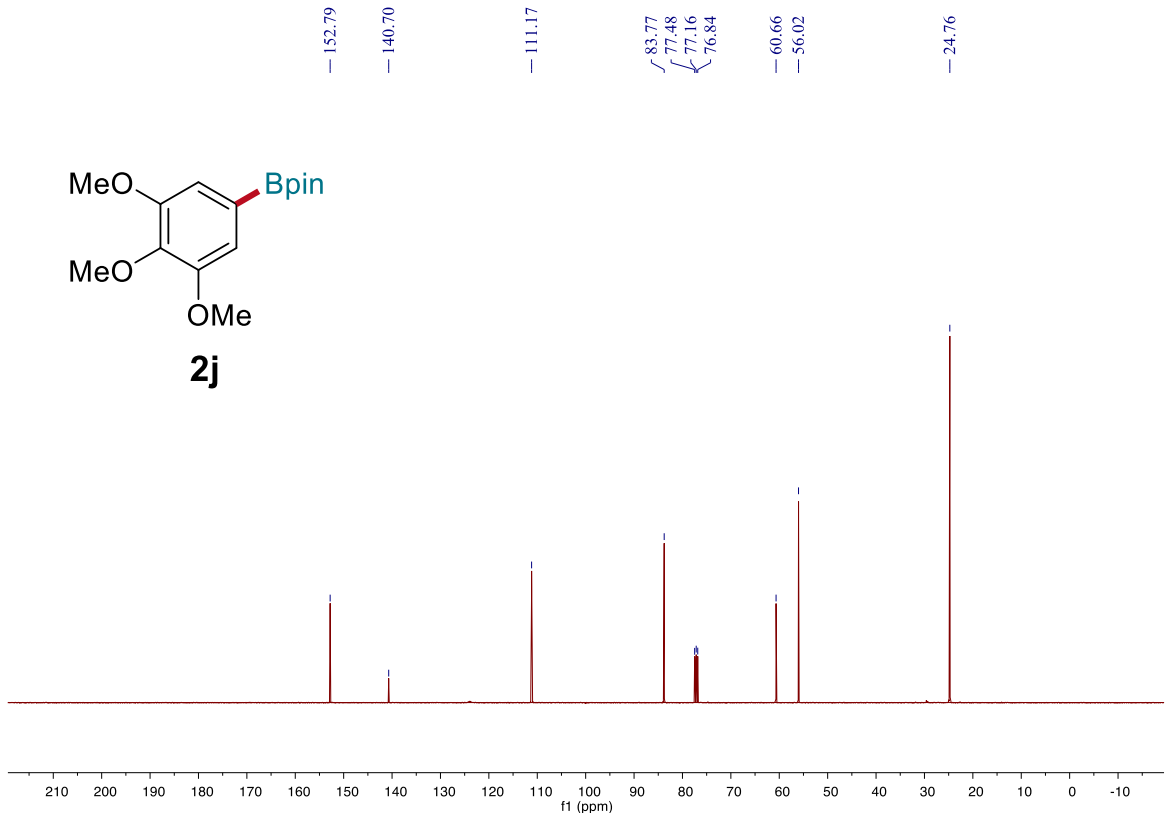

Figure S24. ^{1}H NMR spectrum of 2k in $CDCl_3$ (400 MHz)

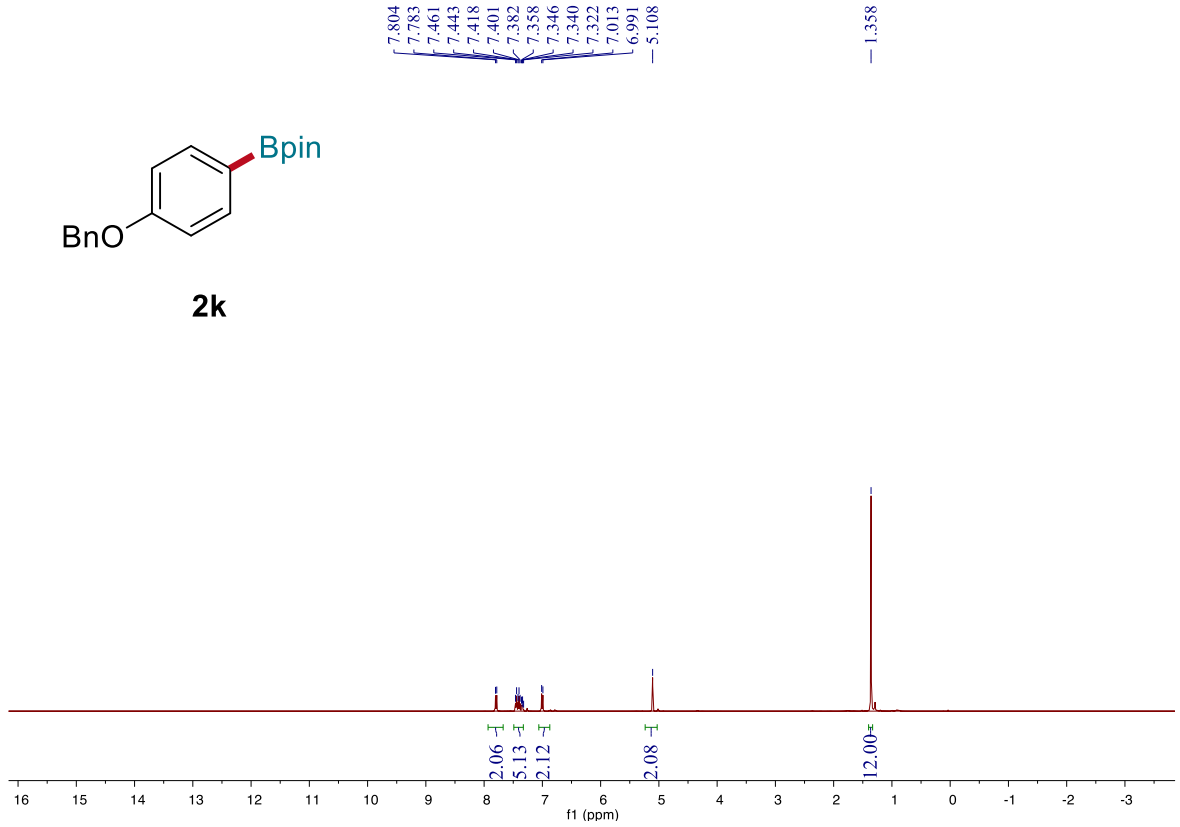

Figure S25. ^{13}C NMR spectrum of 2k in $CDCl_3$ (100 MHz)

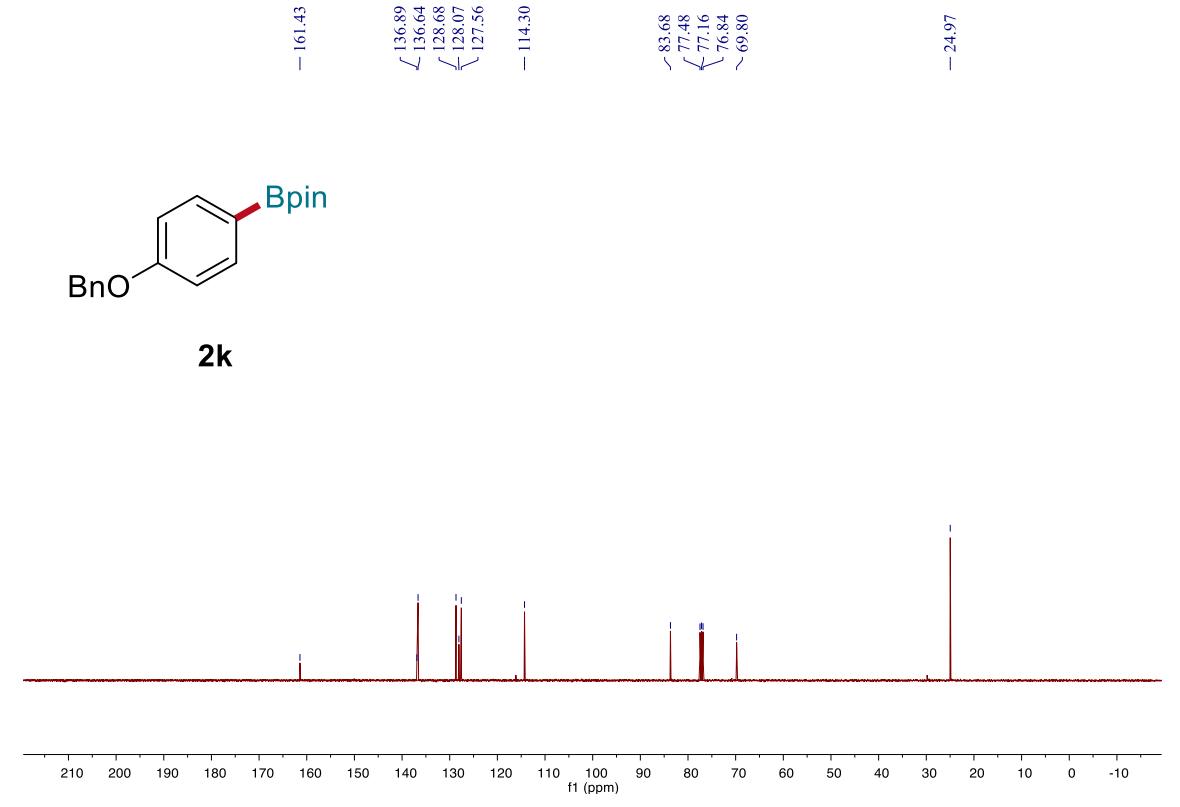

Figure S26. ^{1}H NMR spectrum of 2l in $CDCl_3$ (400 MHz)

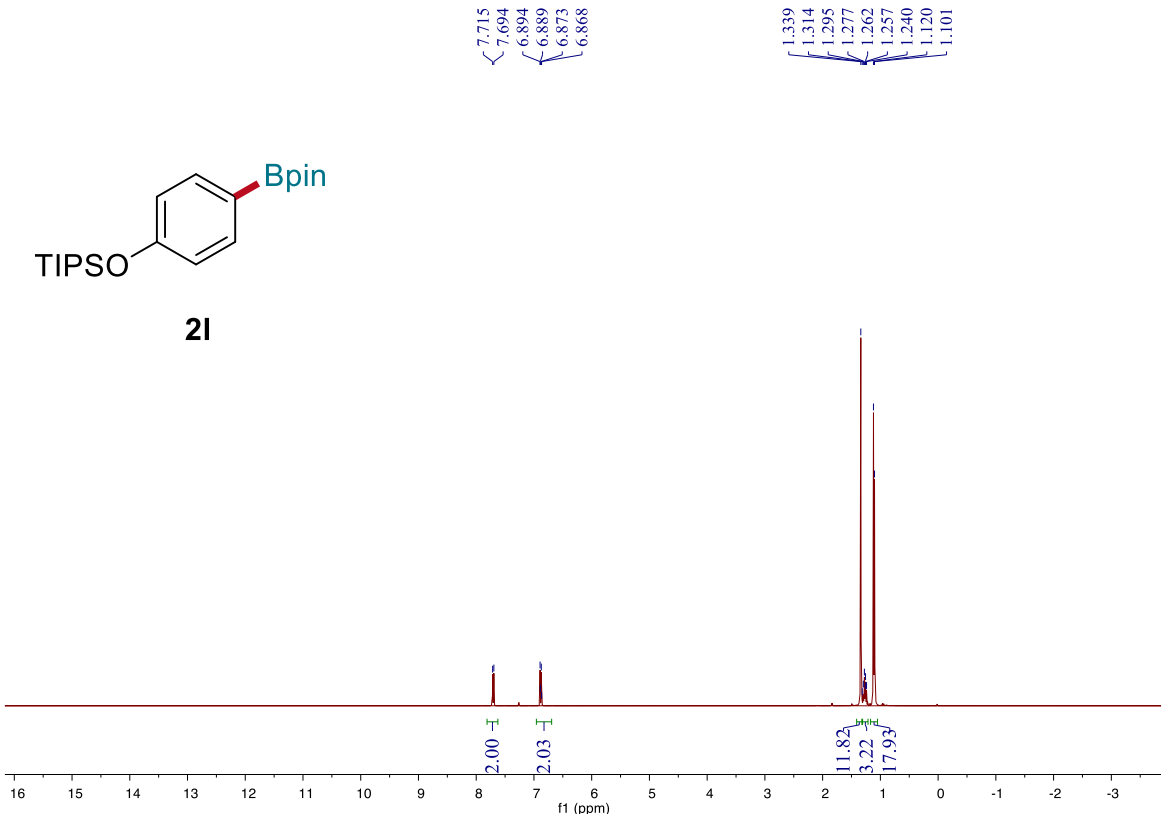

Figure S27. ^{13}C NMR spectrum of 2l in $CDCl_3$ (100 MHz)

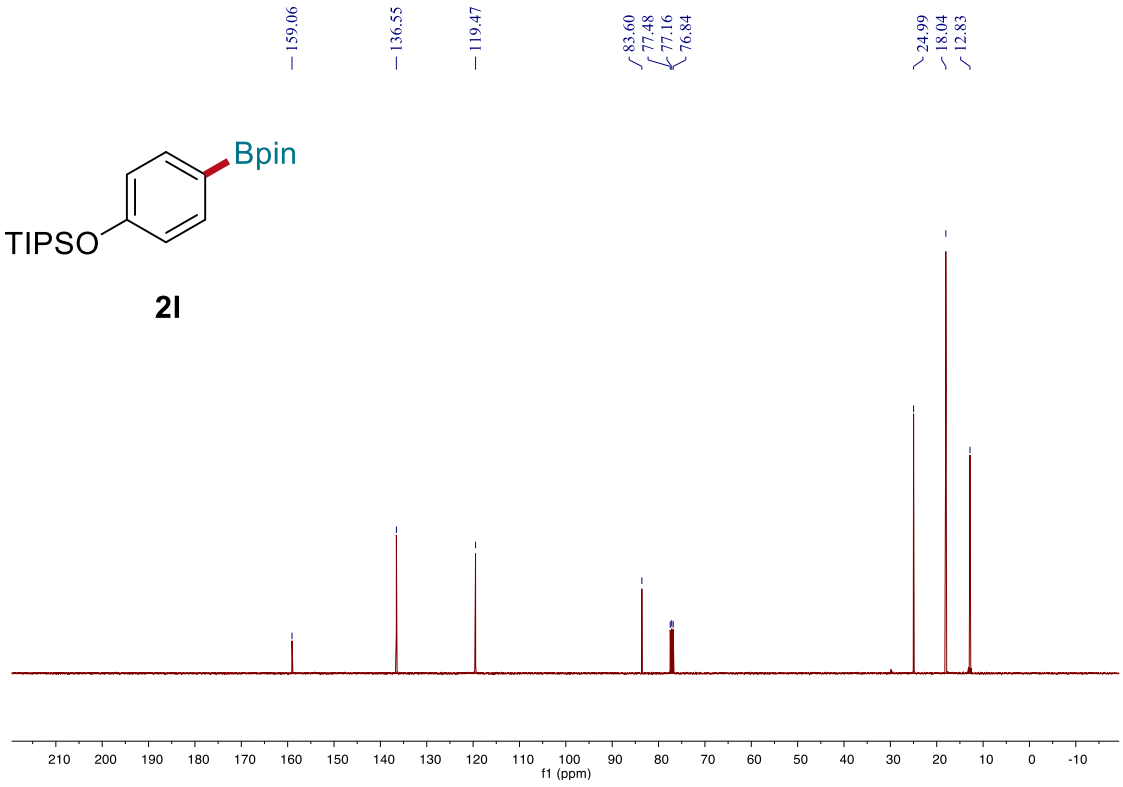

Figure S28. ^{1}H NMR spectrum of 2m in $CDCl_3$ (400 MHz)

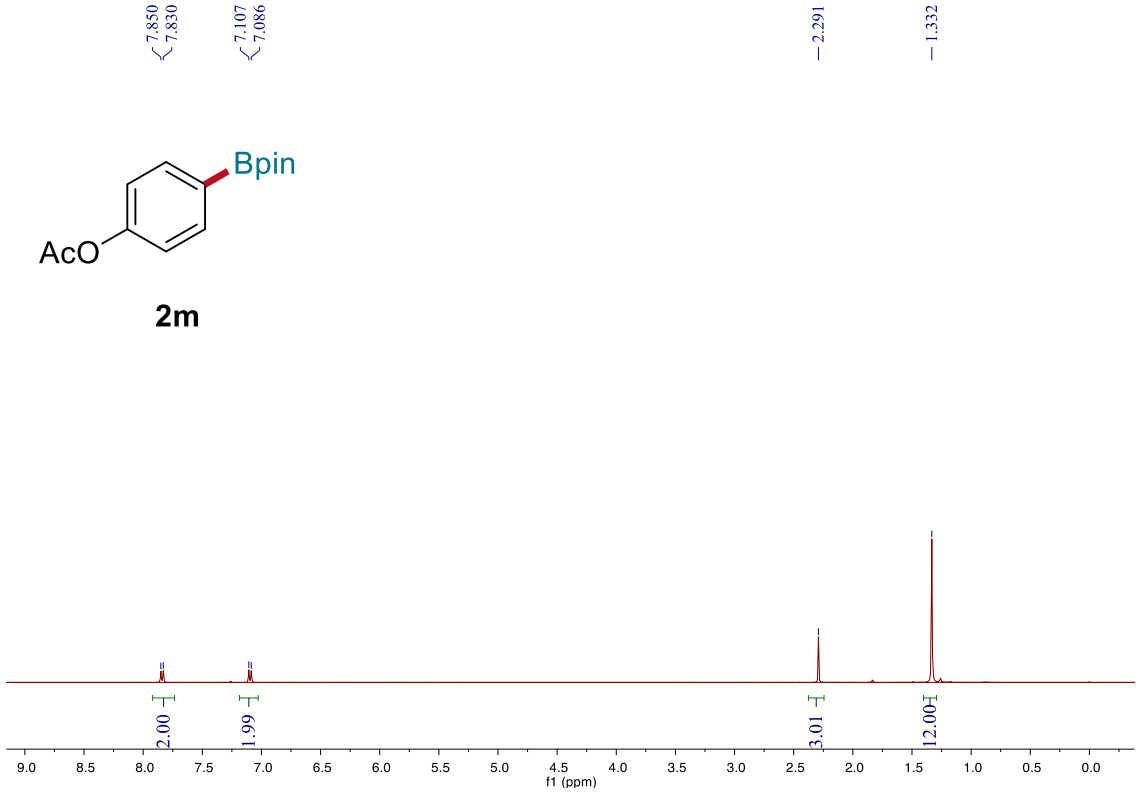

Figure S29. ^{13}C NMR spectrum of 2m in $CDCl_3$ (100 MHz)

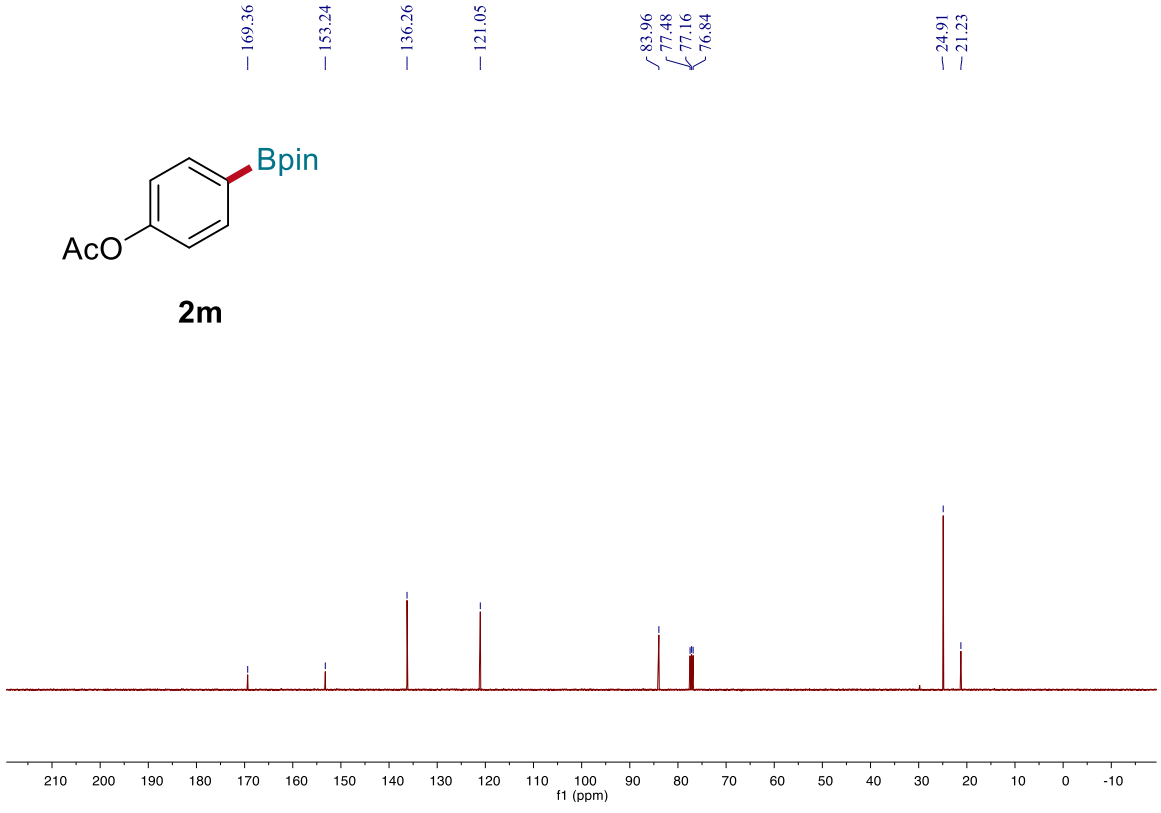

Figure S30. ^{1}H NMR spectrum of 2n in $CDCl_3$ (400 MHz)

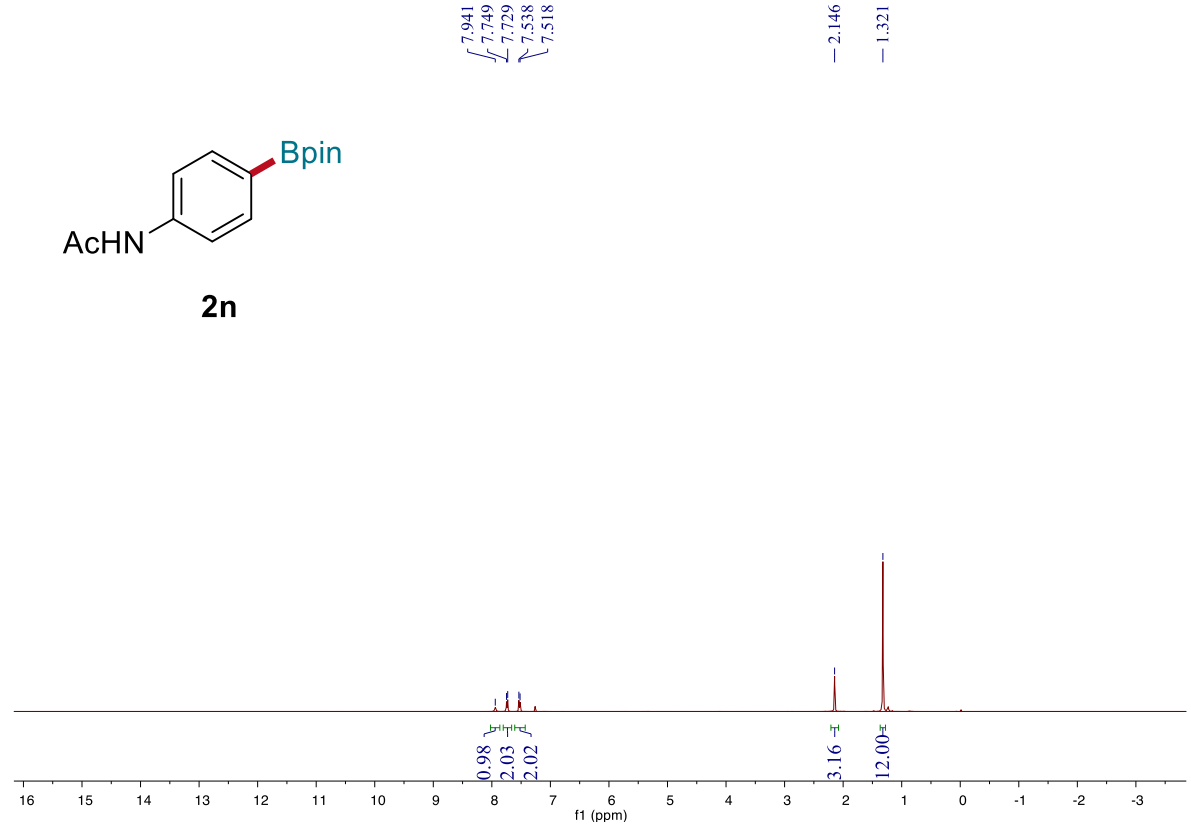

Figure S31. ^{13}C NMR spectrum of 2n in $CDCl_3$ (100 MHz)

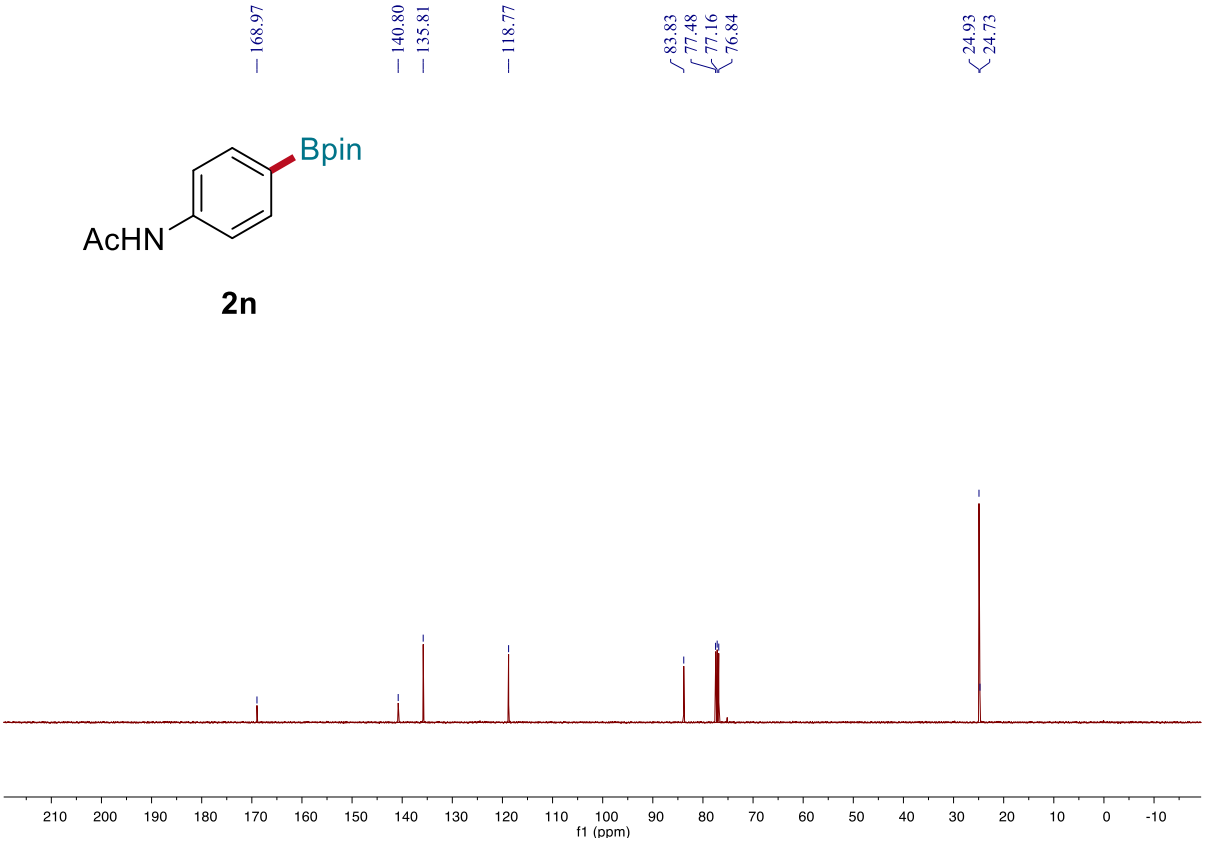

Figure S32. ^{1}H NMR spectrum of 2o in $CDCl_3$ (400 MHz)

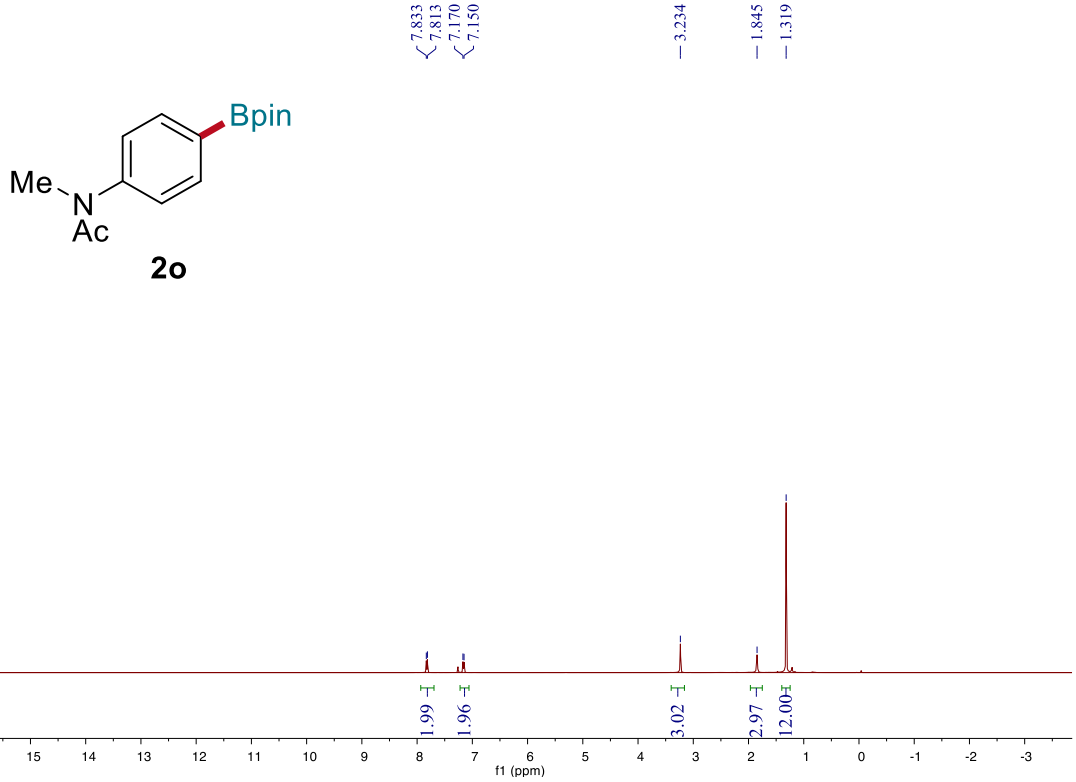

Figure S33. ^{13}C NMR spectrum of 2o in $CDCl_3$ (100 MHz)

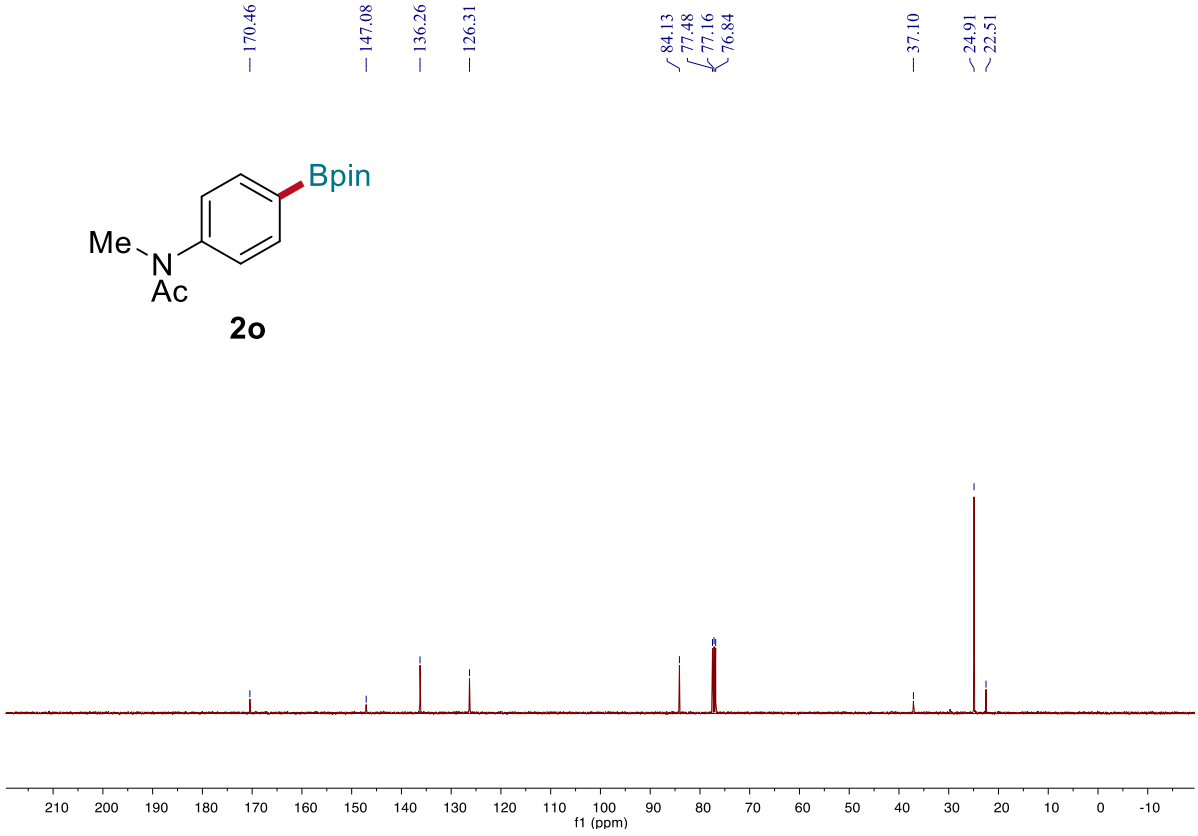

Figure S34. ^{1}H NMR spectrum of 2p in $CDCl_3$ (400 MHz)

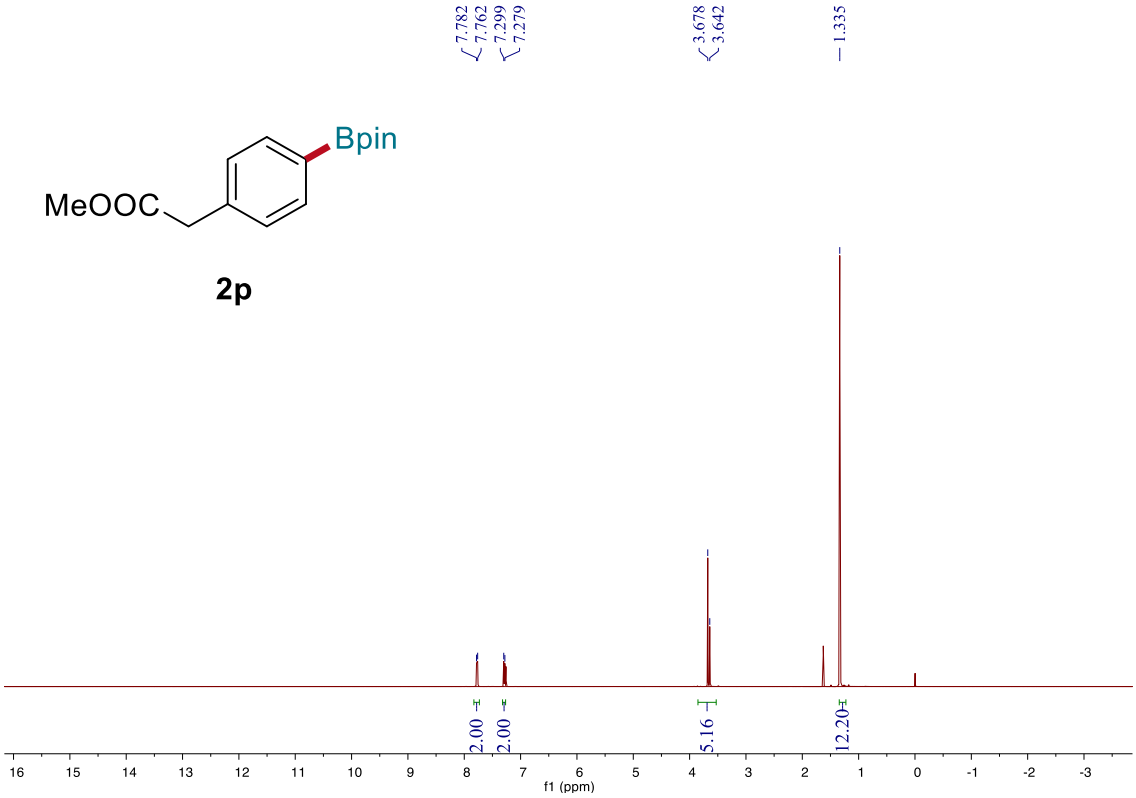

Figure S35. ^{13}C NMR spectrum of 2p in $CDCl_3$ (100 MHz)

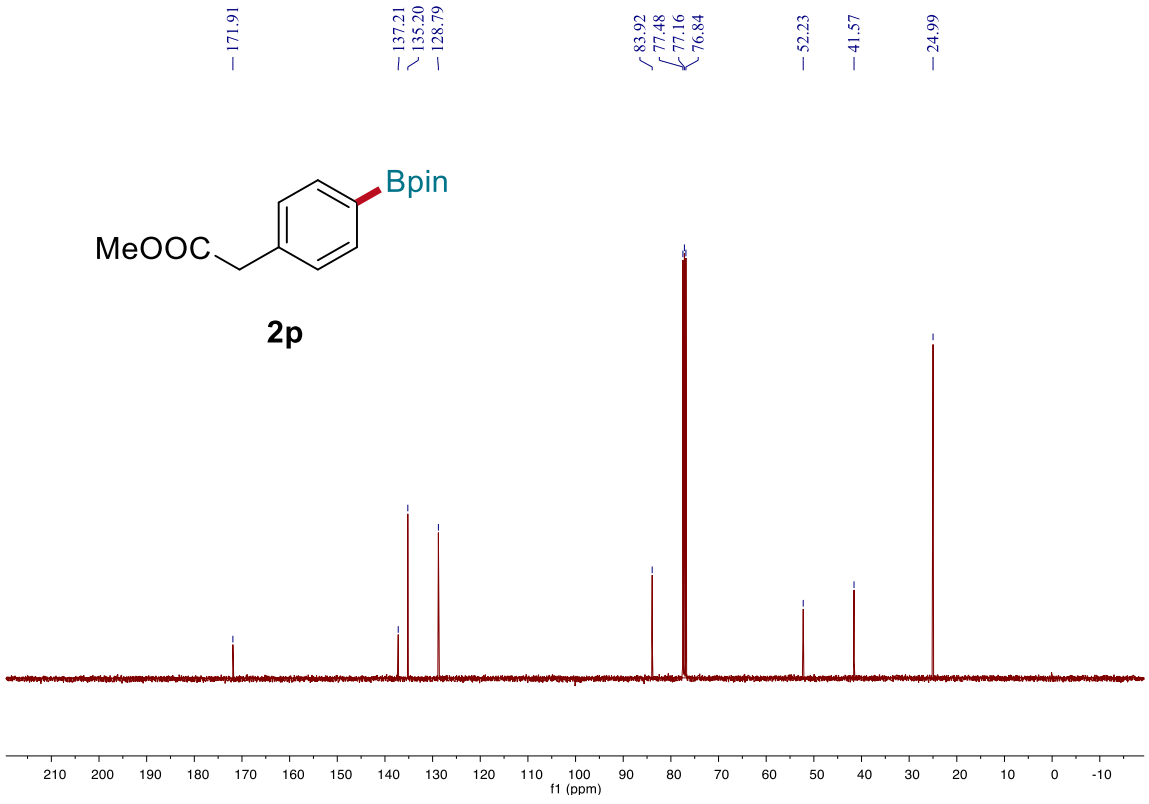

Figure S36. ^{1}H NMR spectrum of 2q in $CDCl_3$ (400 MHz)

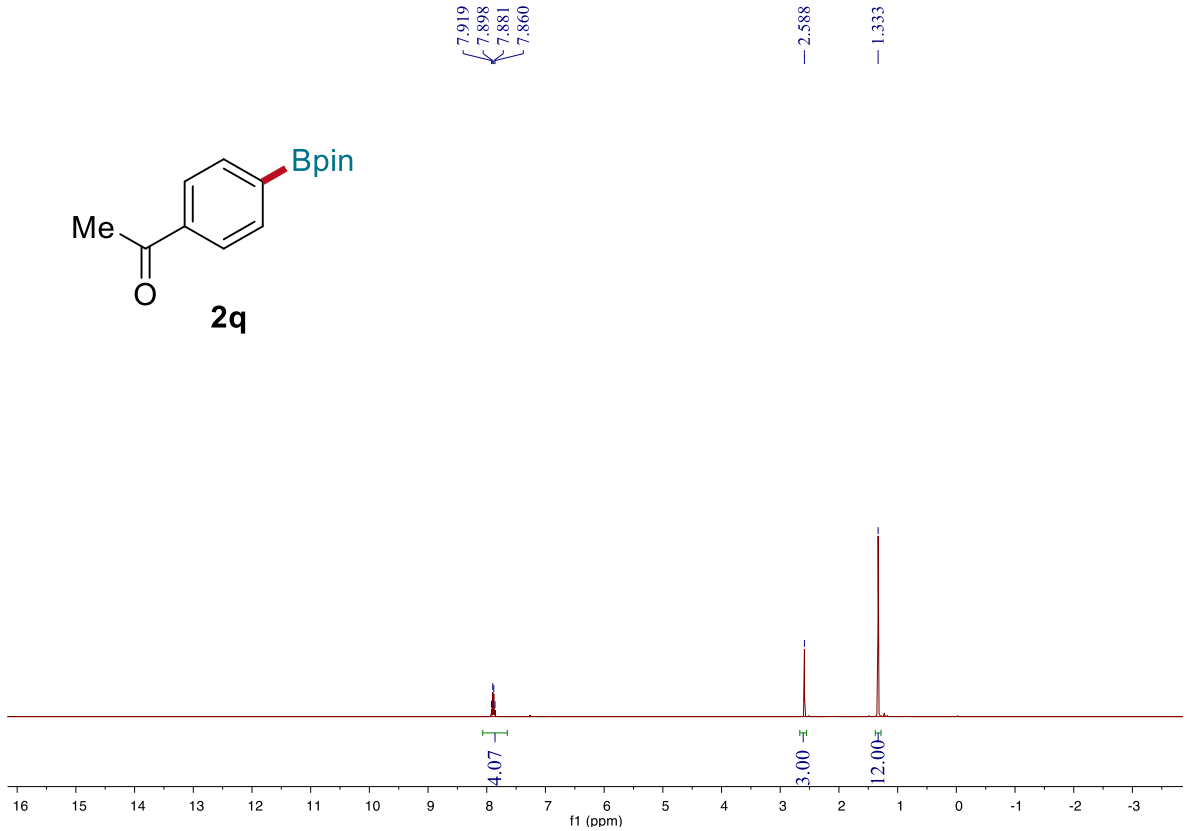

Figure S37. ^{13}C NMR spectrum of 2q in $CDCl_3$ (100 MHz)

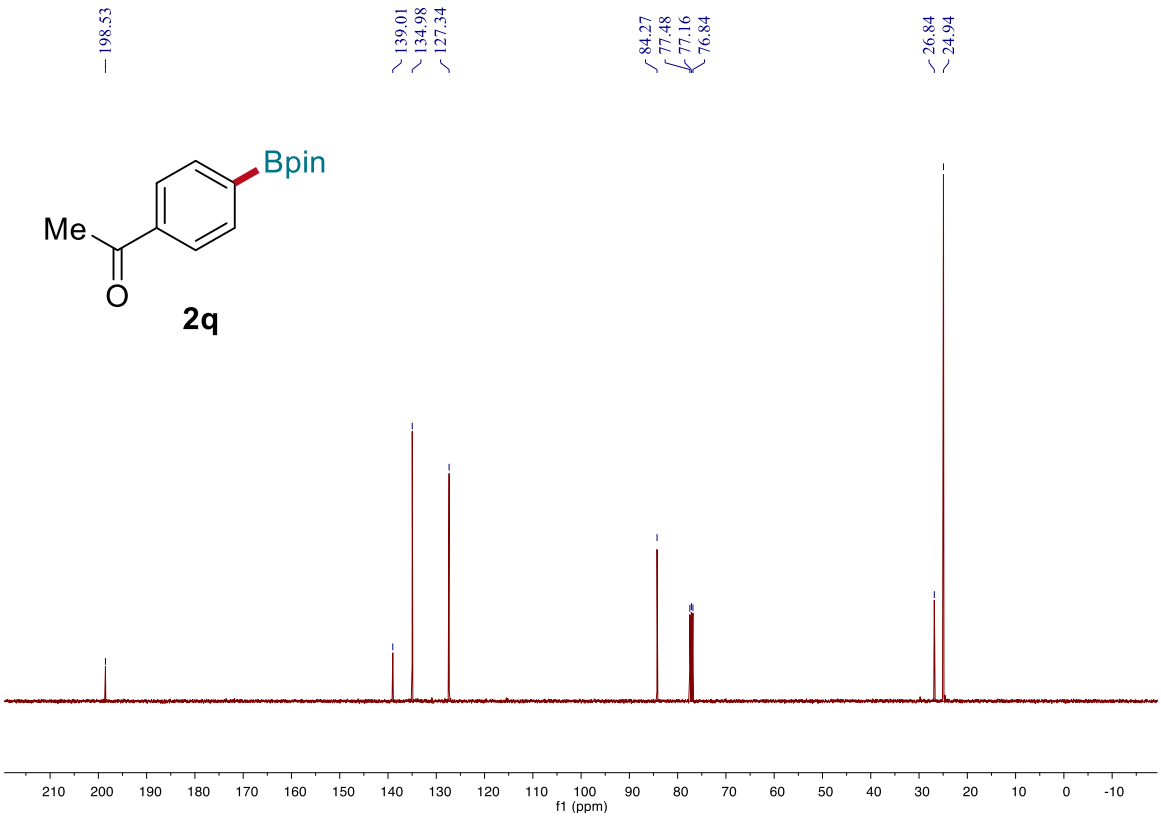

Figure S38. ^{1}H NMR spectrum of 2r in $CDCl_3$ (400 MHz)

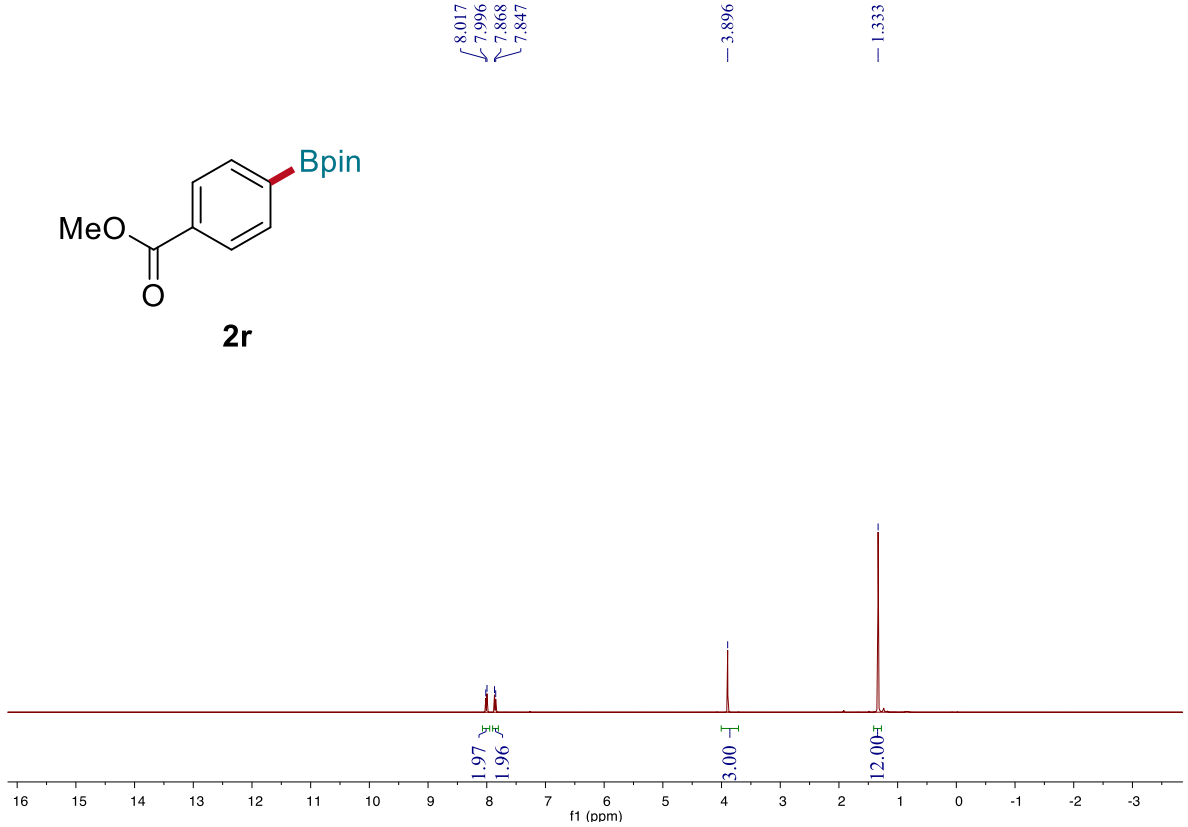

Figure S39. ^{13}C NMR spectrum of 2r in $CDCl_3$ (100 MHz)

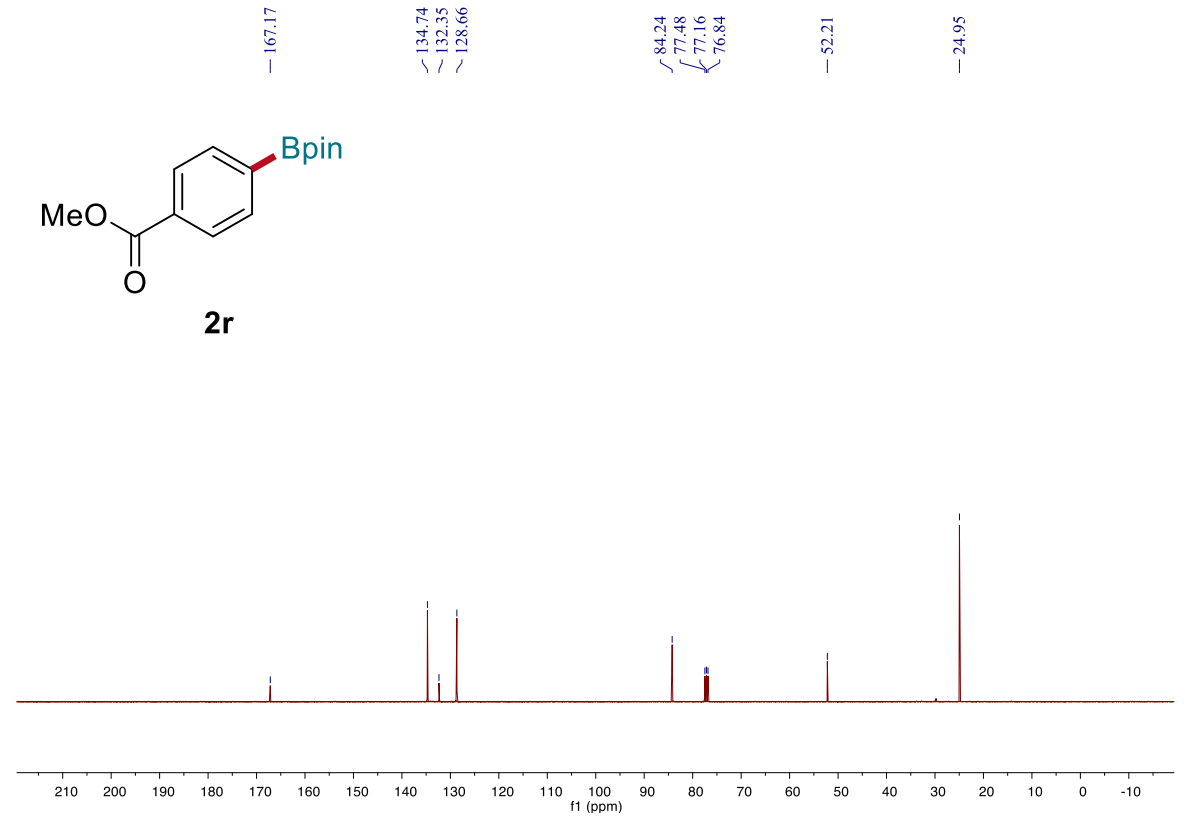

Figure S40. ^{1}H NMR spectrum of 2s in $CDCl_3$ (400 MHz)

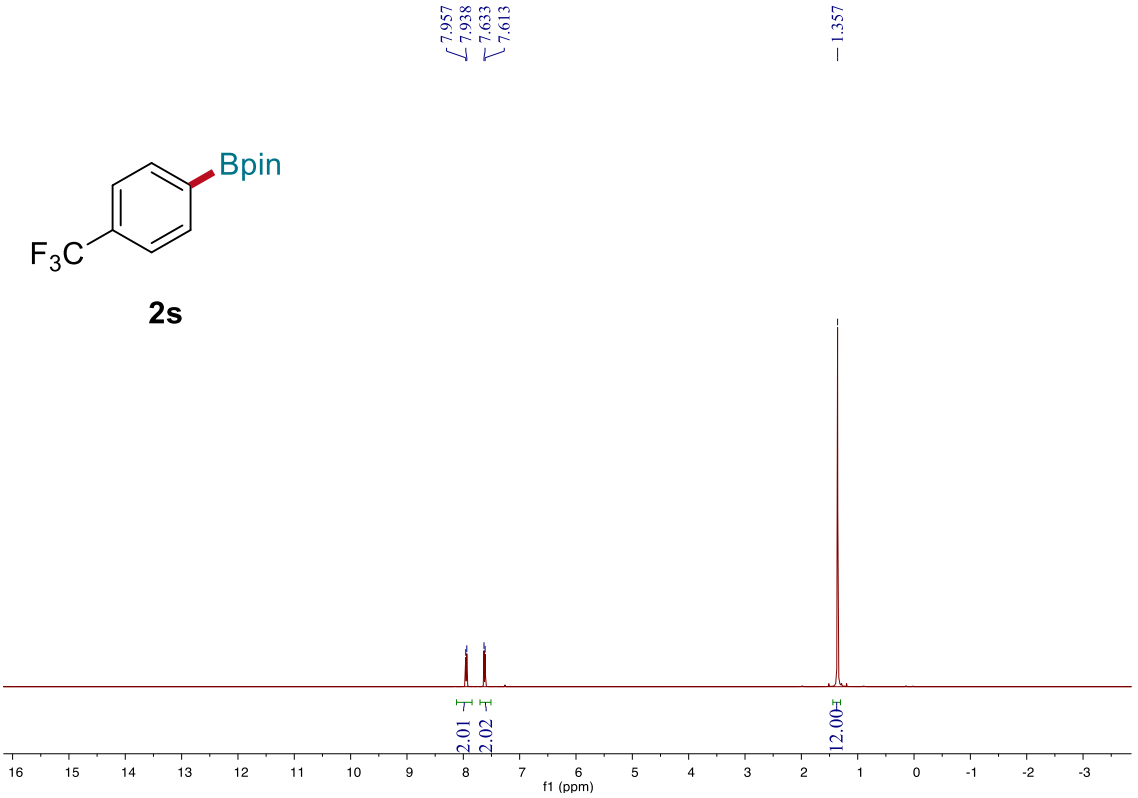

Figure S41. ^{13}C NMR spectrum of 2s in $CDCl_3$ (100 MHz)

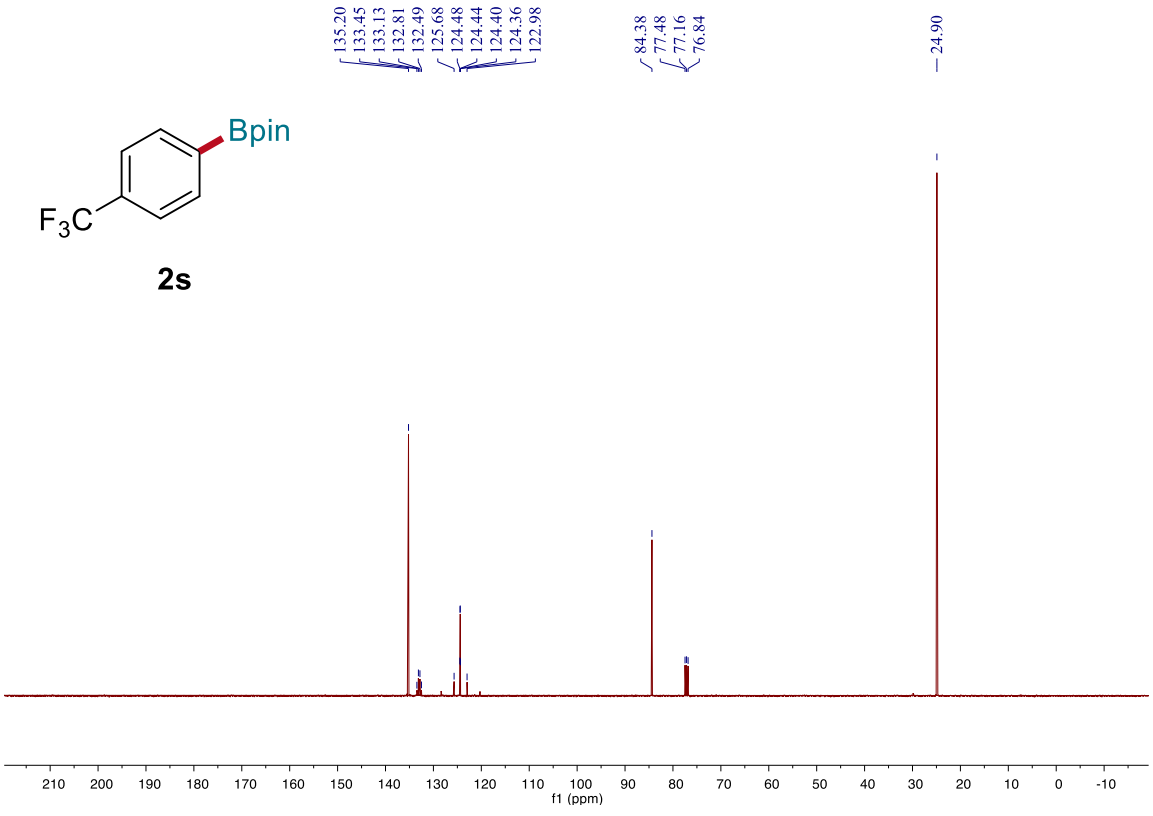

Figure S42. ^{1}H NMR spectrum of 2t in $CDCl_3$ (400 MHz)

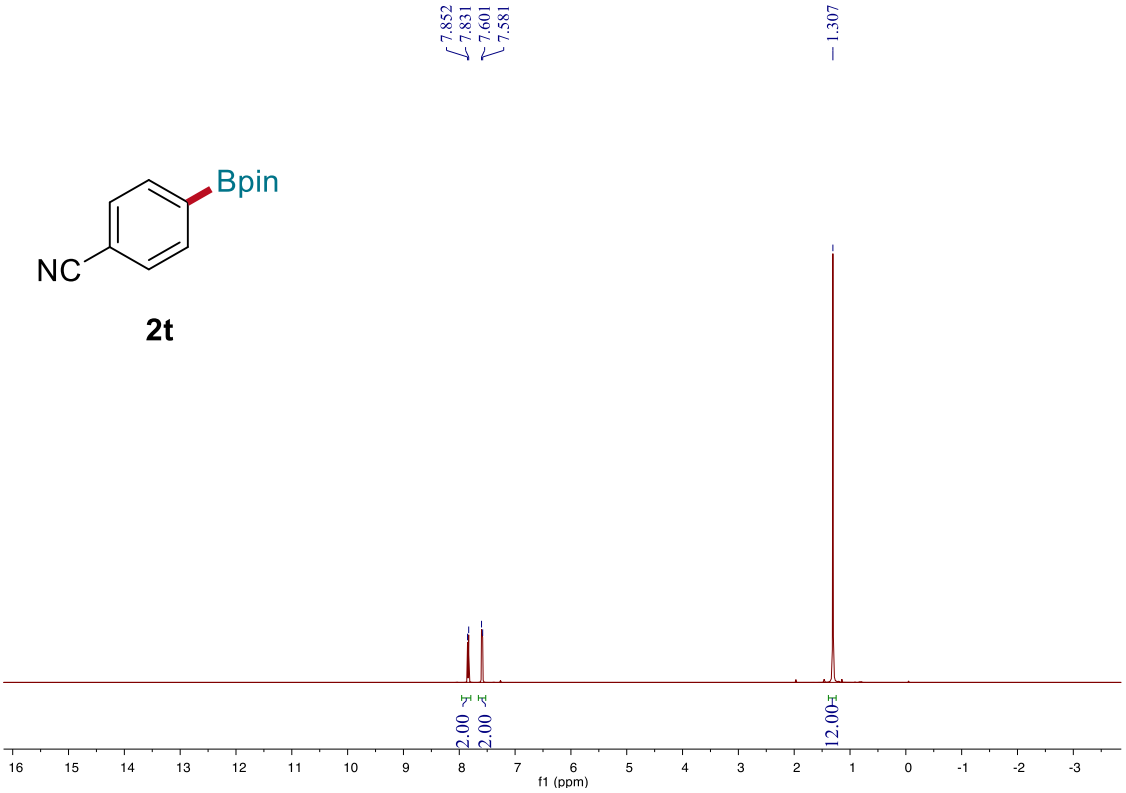

Figure S43. ^{13}C NMR spectrum of 2t in $CDCl_3$ (100 MHz)

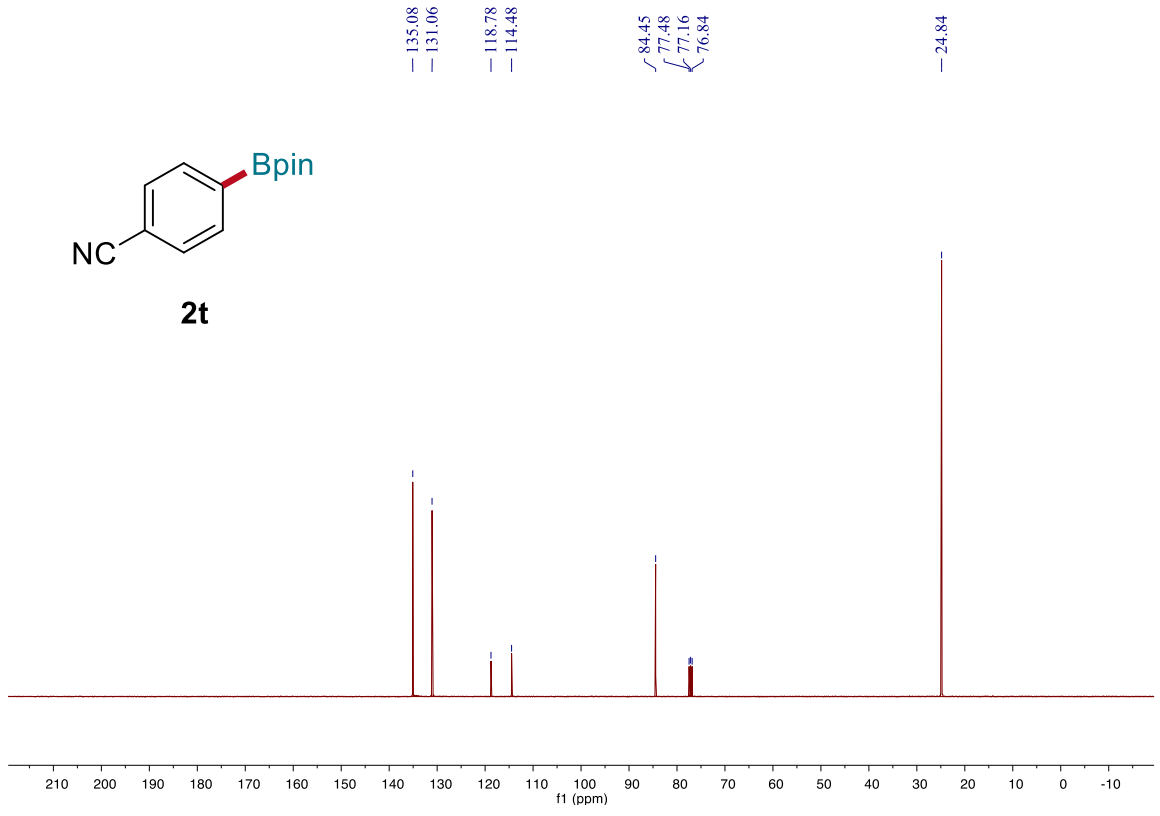

Figure S44. ^{1}H NMR spectrum of 2u in $CDCl_3$ (400 MHz)

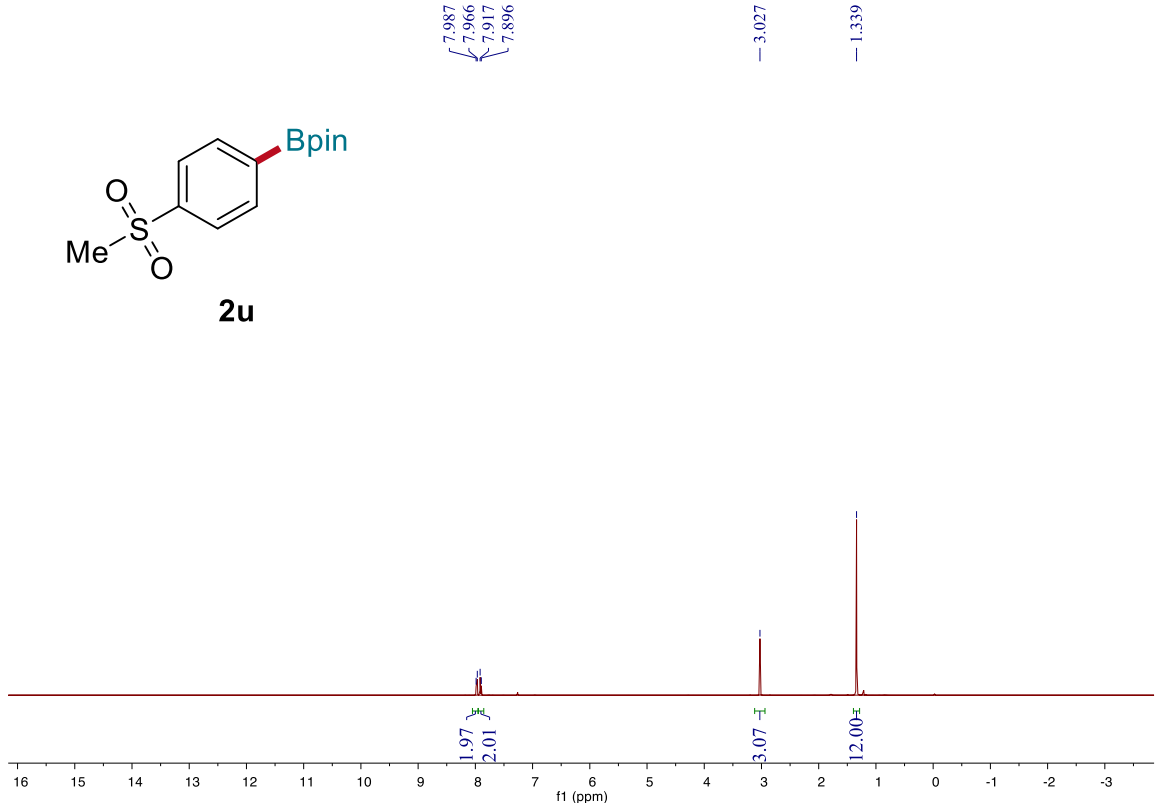

Figure S45. ^{13}C NMR spectrum of 2u in $CDCl_3$ (100 MHz)

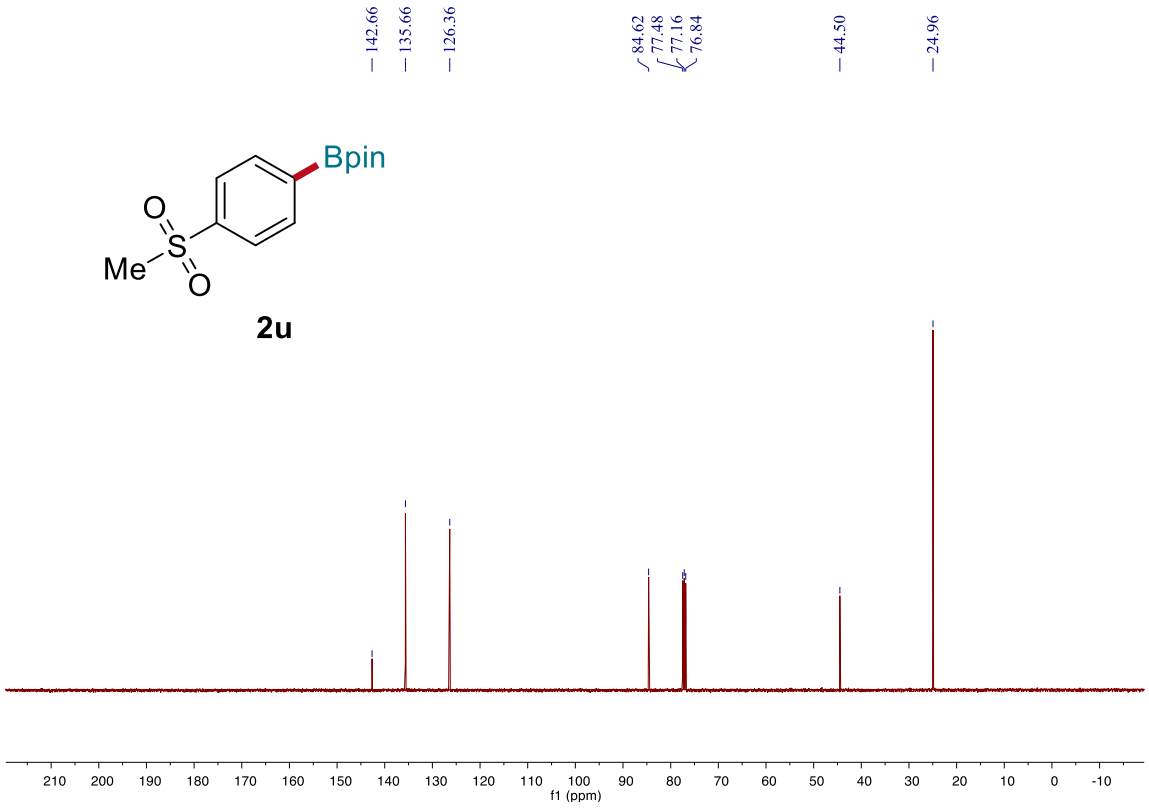

Figure S46. ^{1}H NMR spectrum of 2v in $CDCl_3$ (400 MHz)

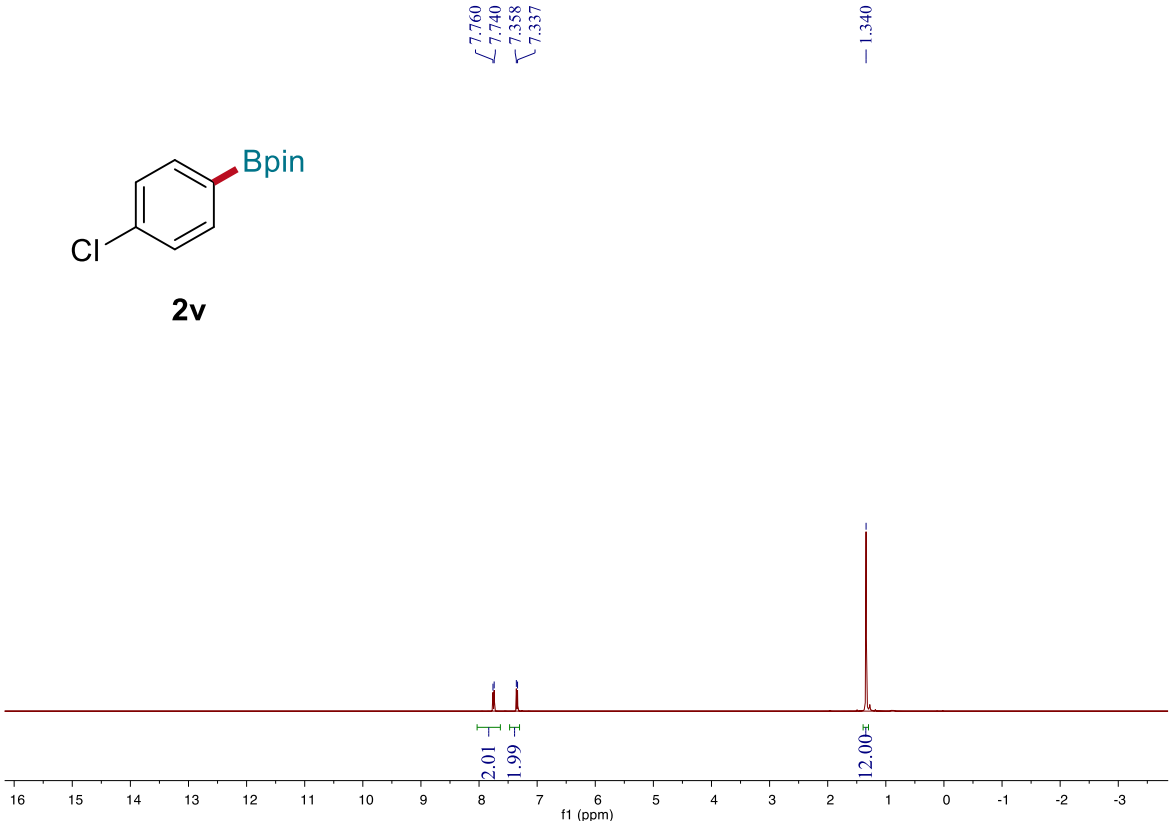

Figure S47. ^{13}C NMR spectrum of 2v in $CDCl_3$ (100 MHz)

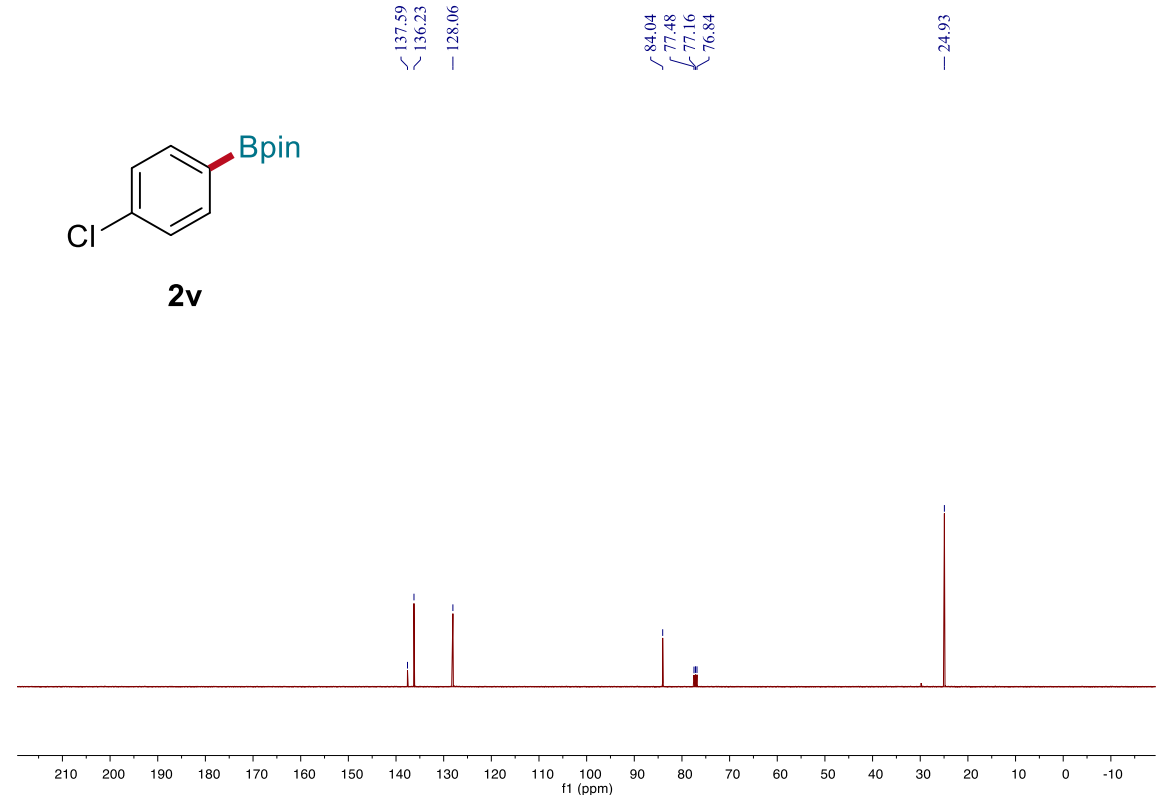

Figure S48. ^{1}H NMR spectrum of 2w in $CDCl_3$ (400 MHz)

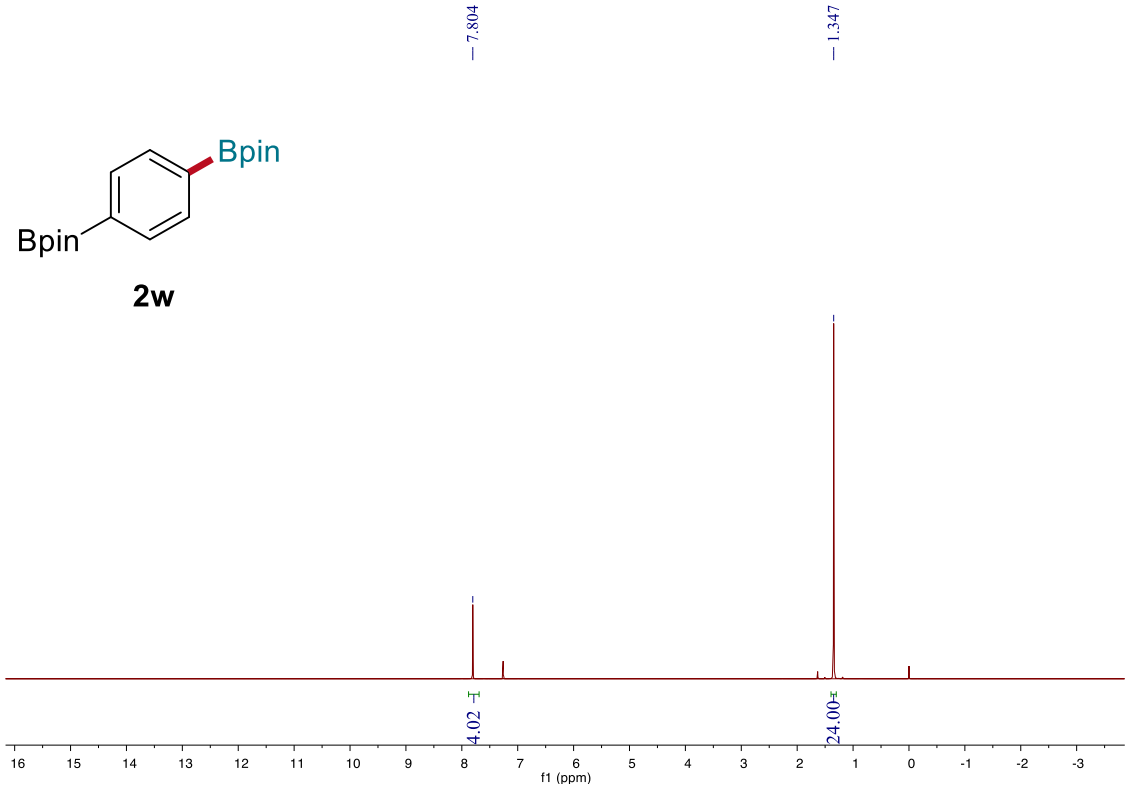

Figure S49. ^{13}C NMR spectrum of 2w in $CDCl_3$ (100 MHz)

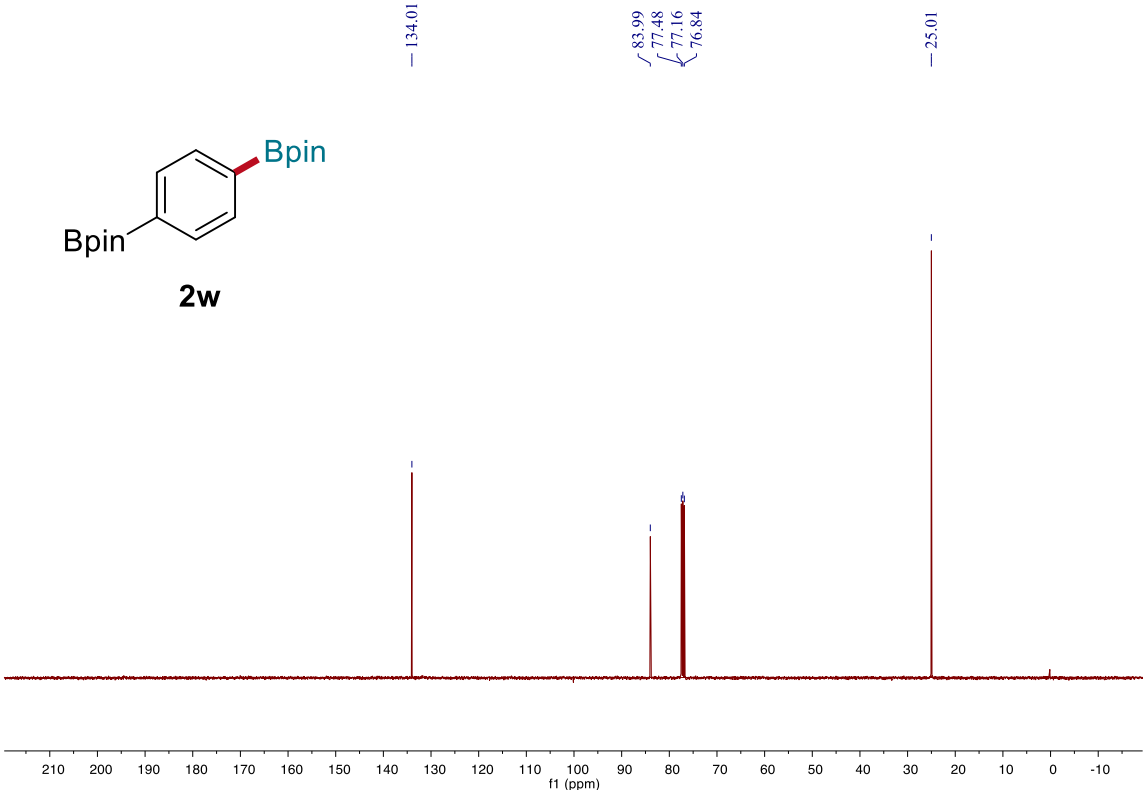

Figure S50. ^{1}H NMR spectrum of 2x in $CDCl_3$ (400 MHz)

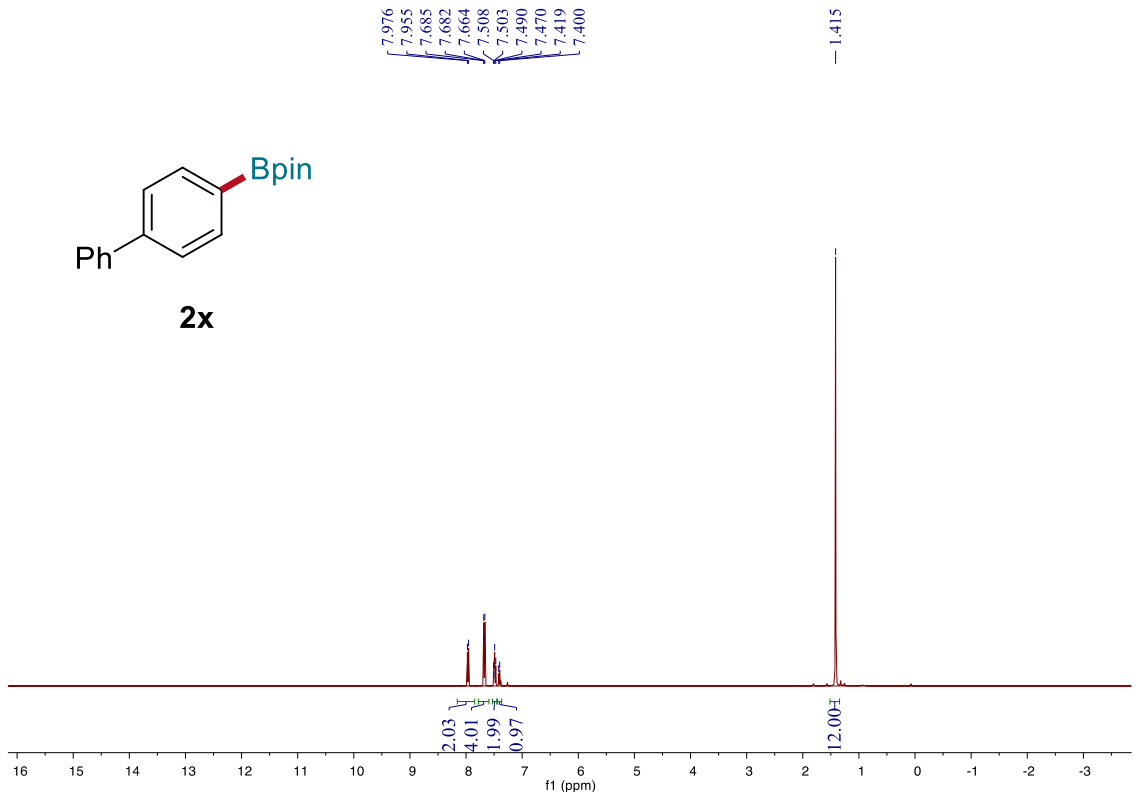

Figure S51. ^{13}C NMR spectrum of 2x in $CDCl_3$ (100 MHz)

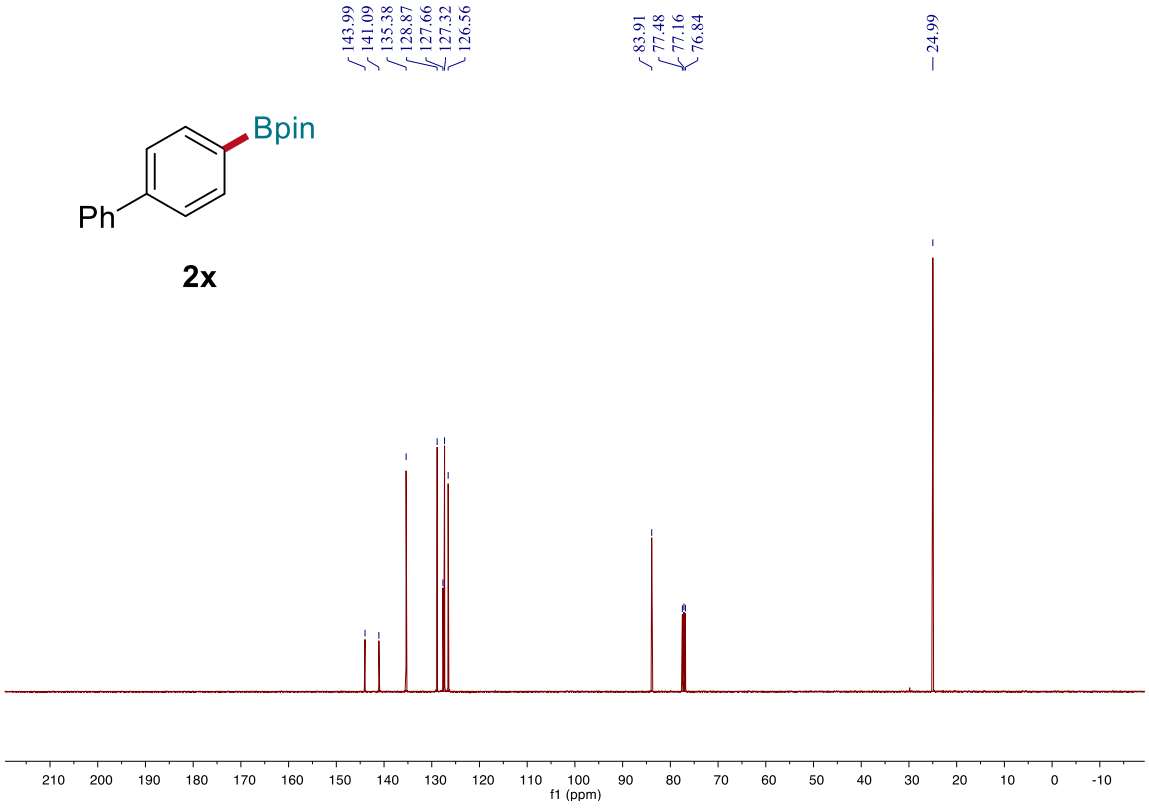

Figure S52. ^{1}H NMR spectrum of 2y in $CDCl_3$ (400 MHz)

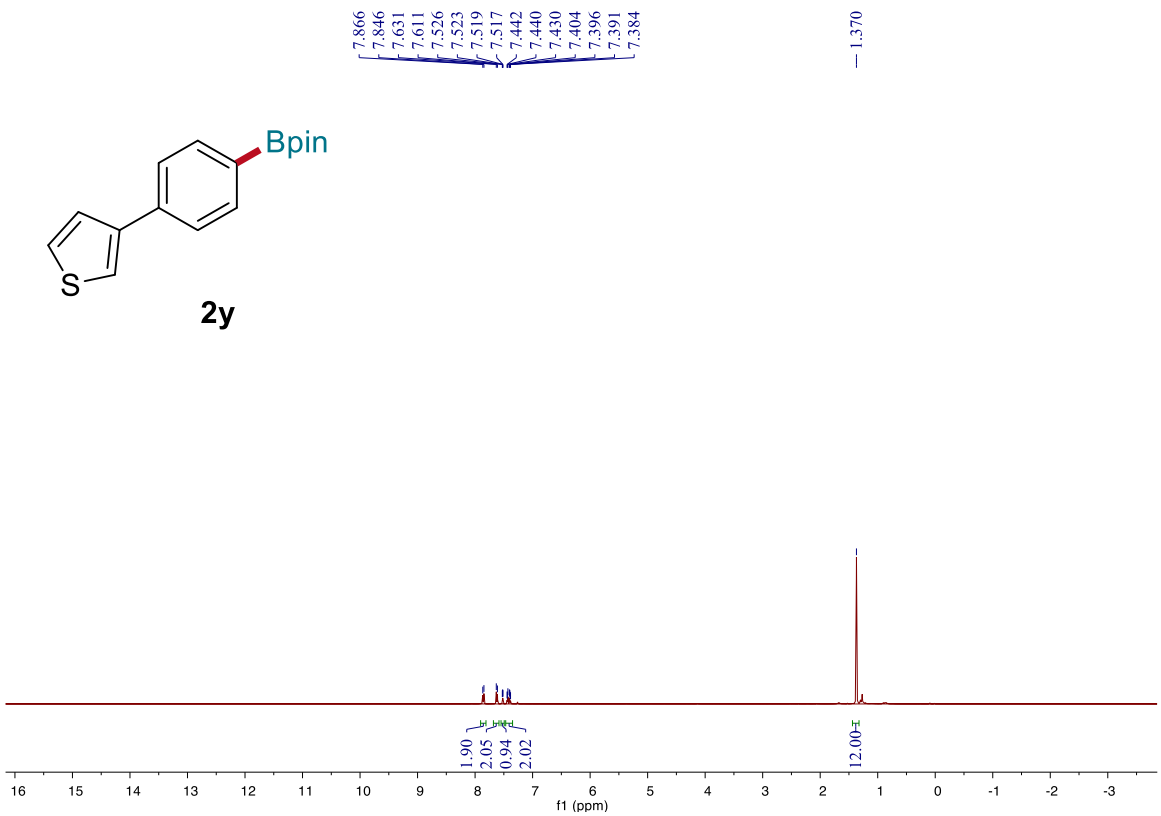

Figure S53. ^{13}C NMR spectrum of 2y in $CDCl_3$ (100 MHz)

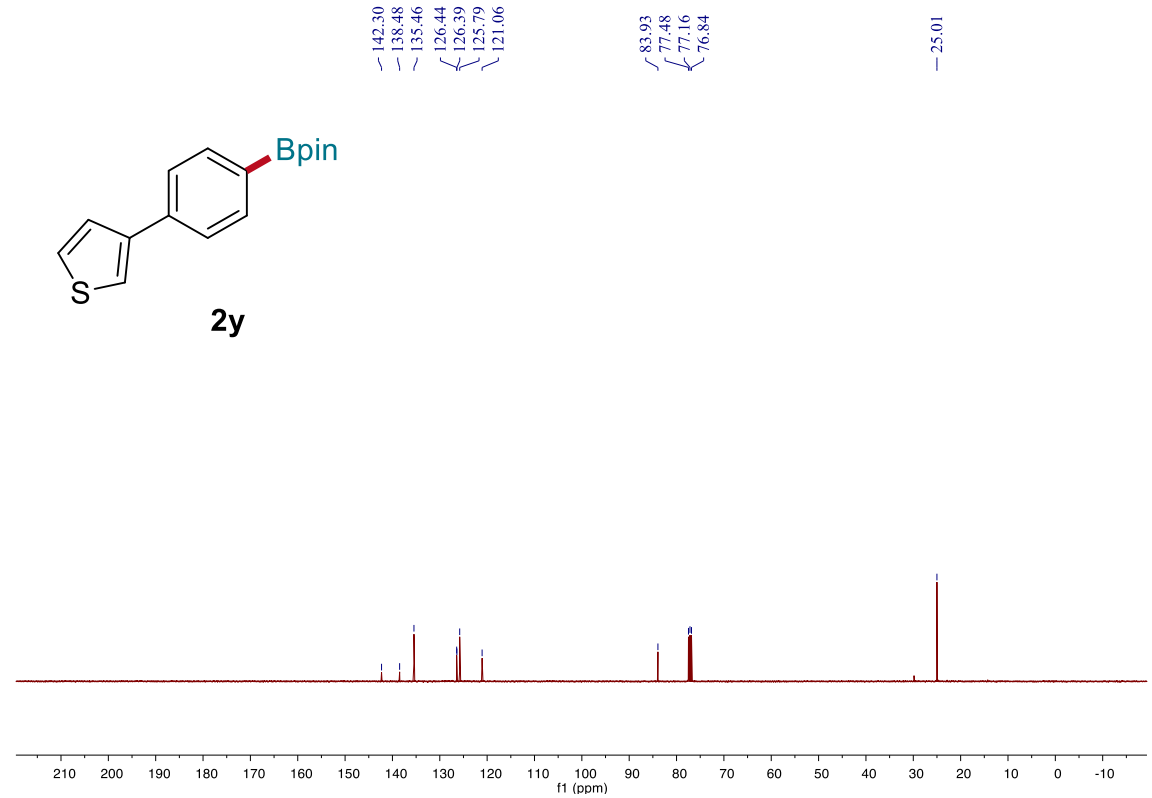

Figure S54. ^{1}H NMR spectrum of 2z in $CDCl_3$ (400 MHz)

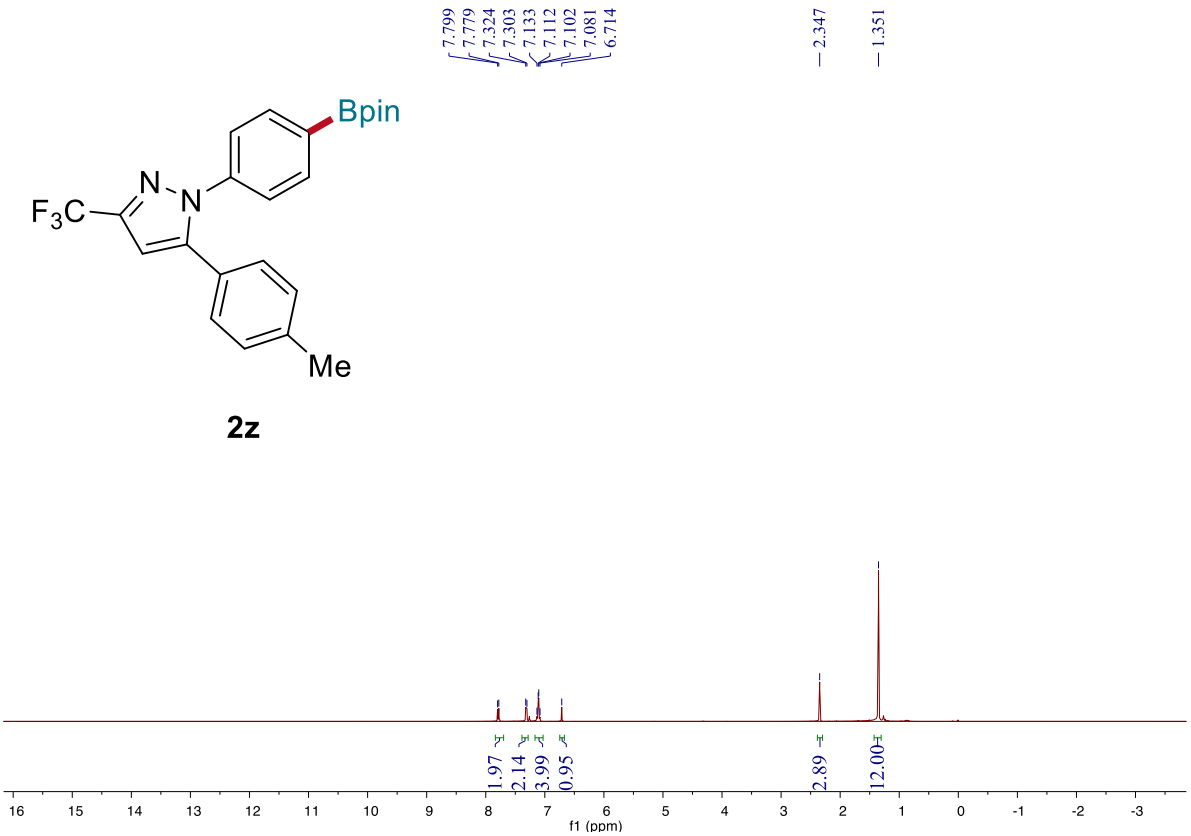

Figure S55. ^{13}C NMR spectrum of 2z in $CDCl_3$ (100 MHz)

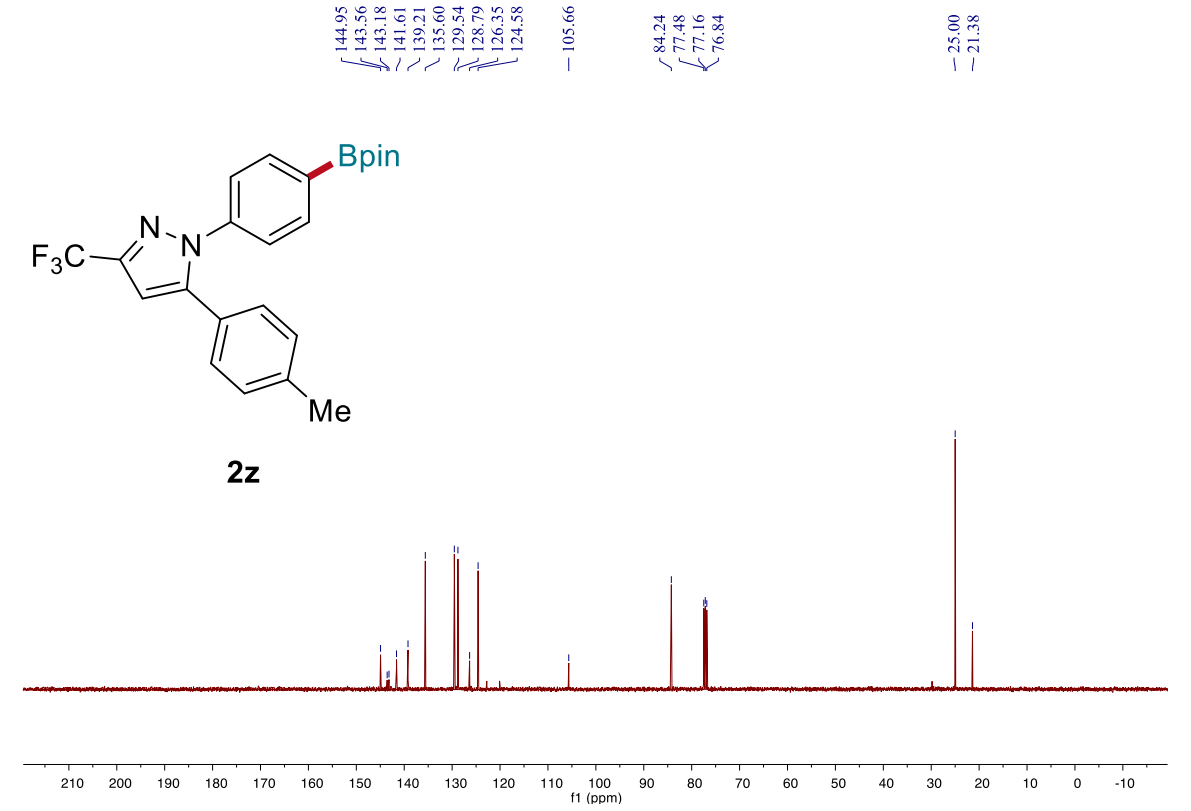

Figure S56. ^{1}H NMR spectrum of 2 in $CDCl_3$ (400 MHz)

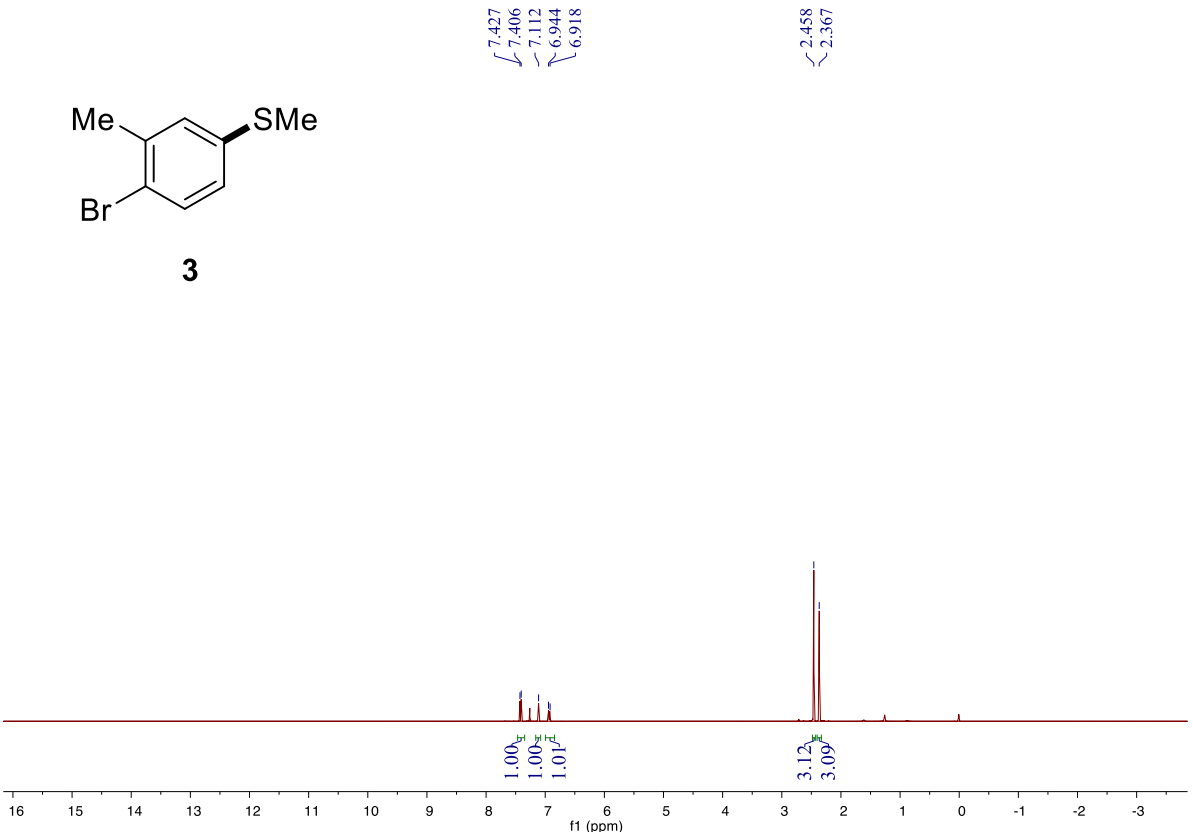

Figure S57. ^{13}C NMR spectrum of 2 in $CDCl_3$ (100 MHz)

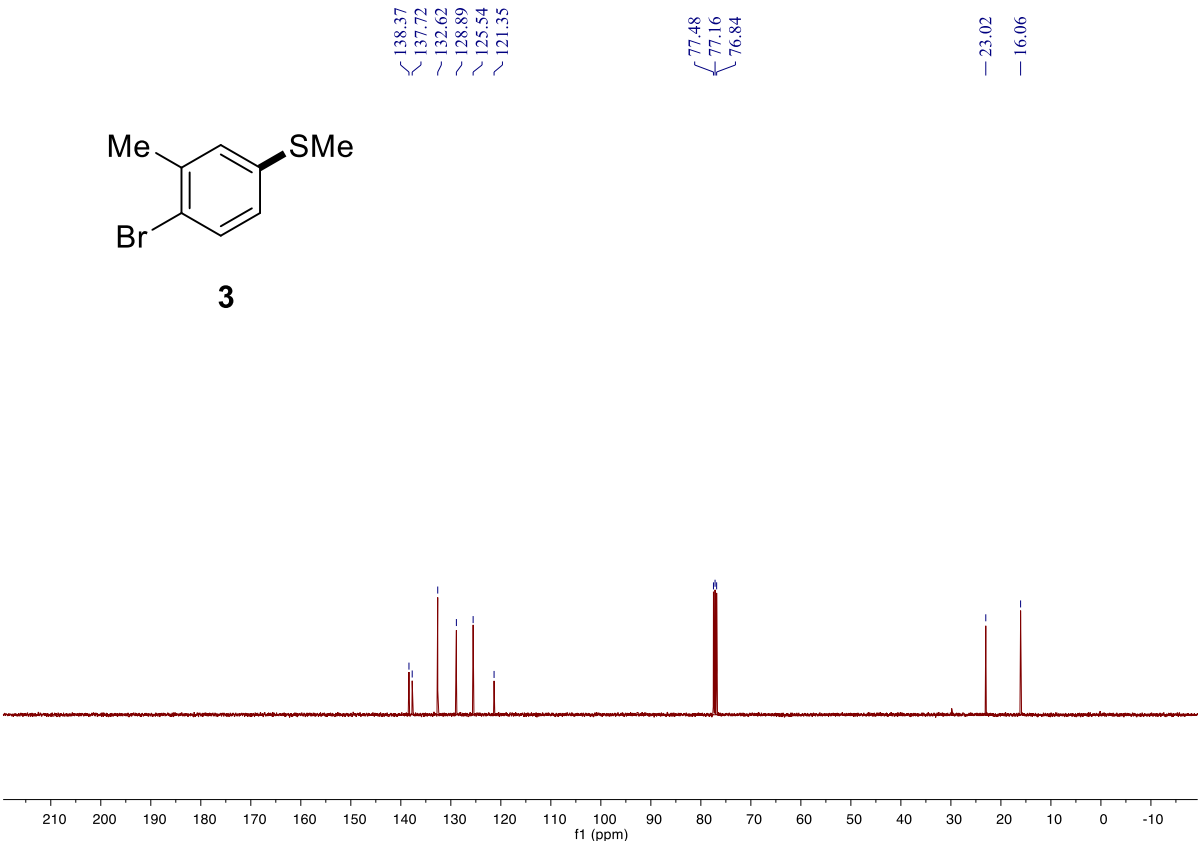

Figure S58. ^{1}H NMR spectrum of 3 in $CDCl_3$ (400 MHz)

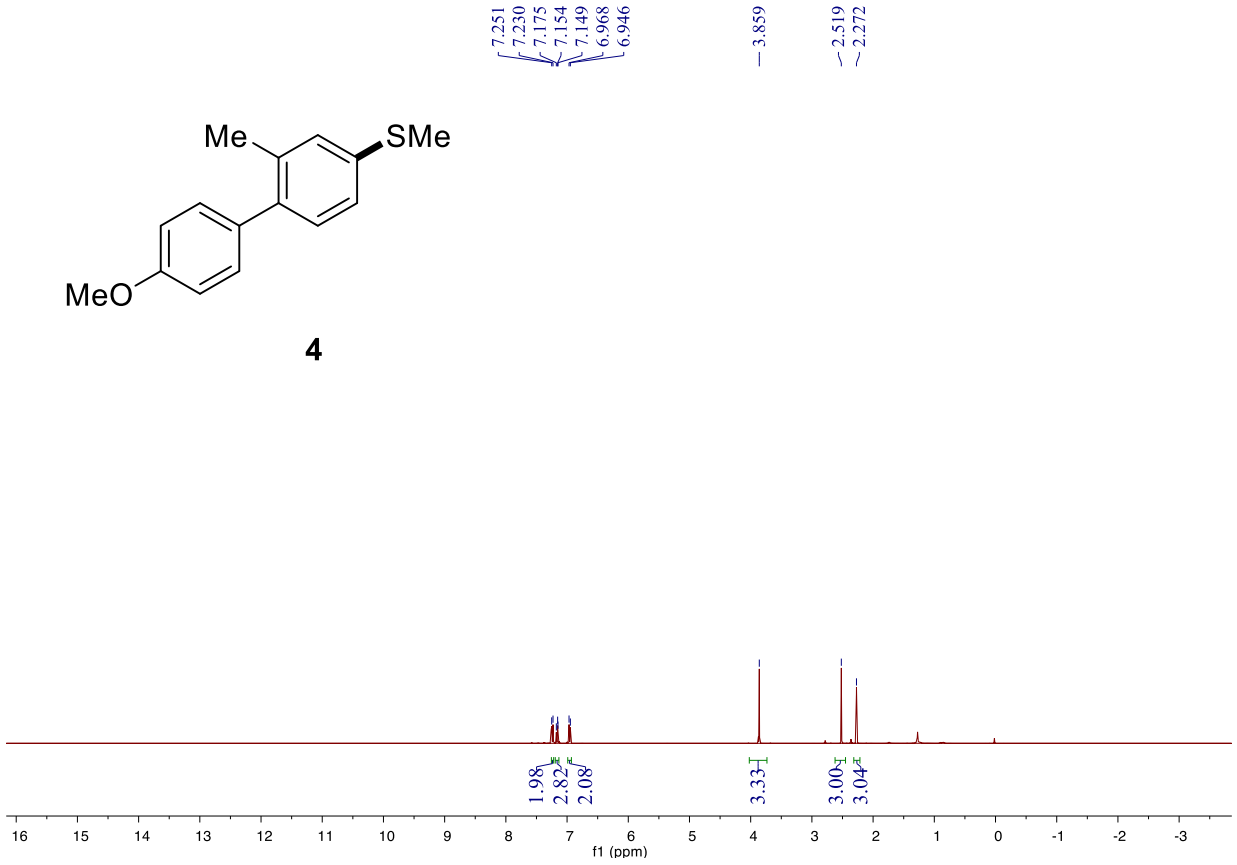

Figure S59. ^{13}C NMR spectrum of 3 in $CDCl_3$ (100 MHz)

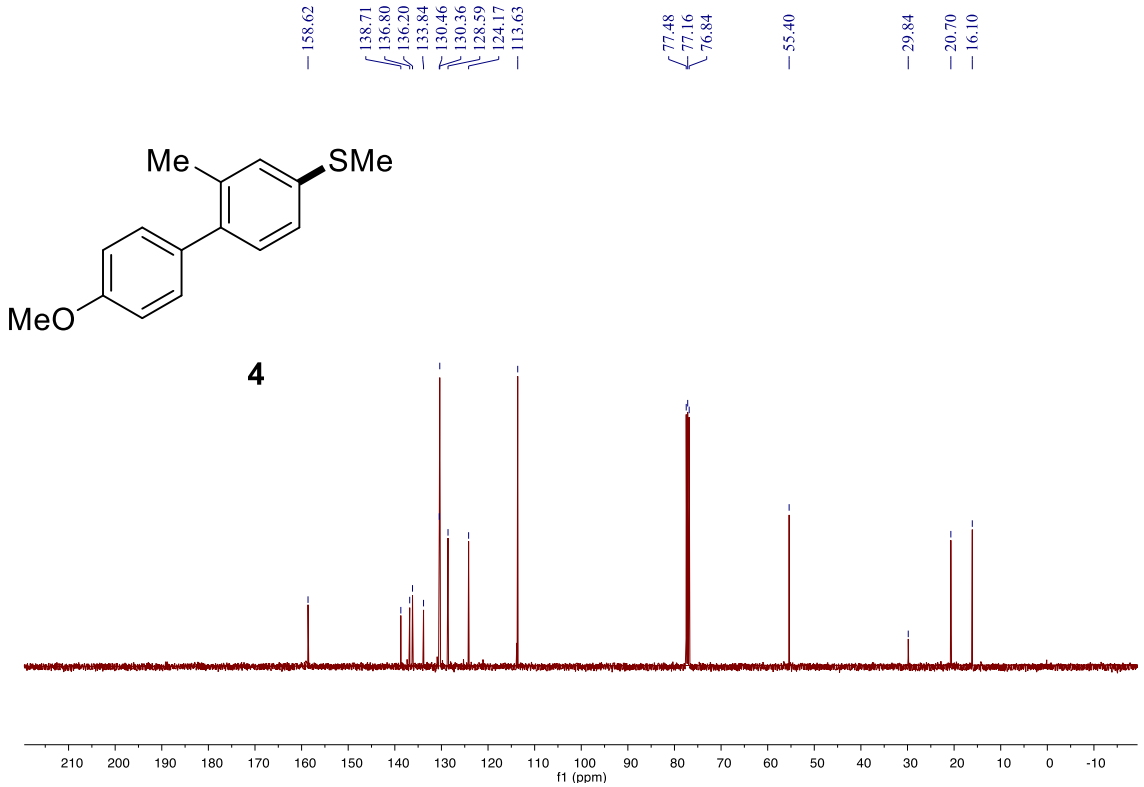

Figure S60. ^{1}H NMR spectrum of 4 in $CDCl_3$ (400 MHz)

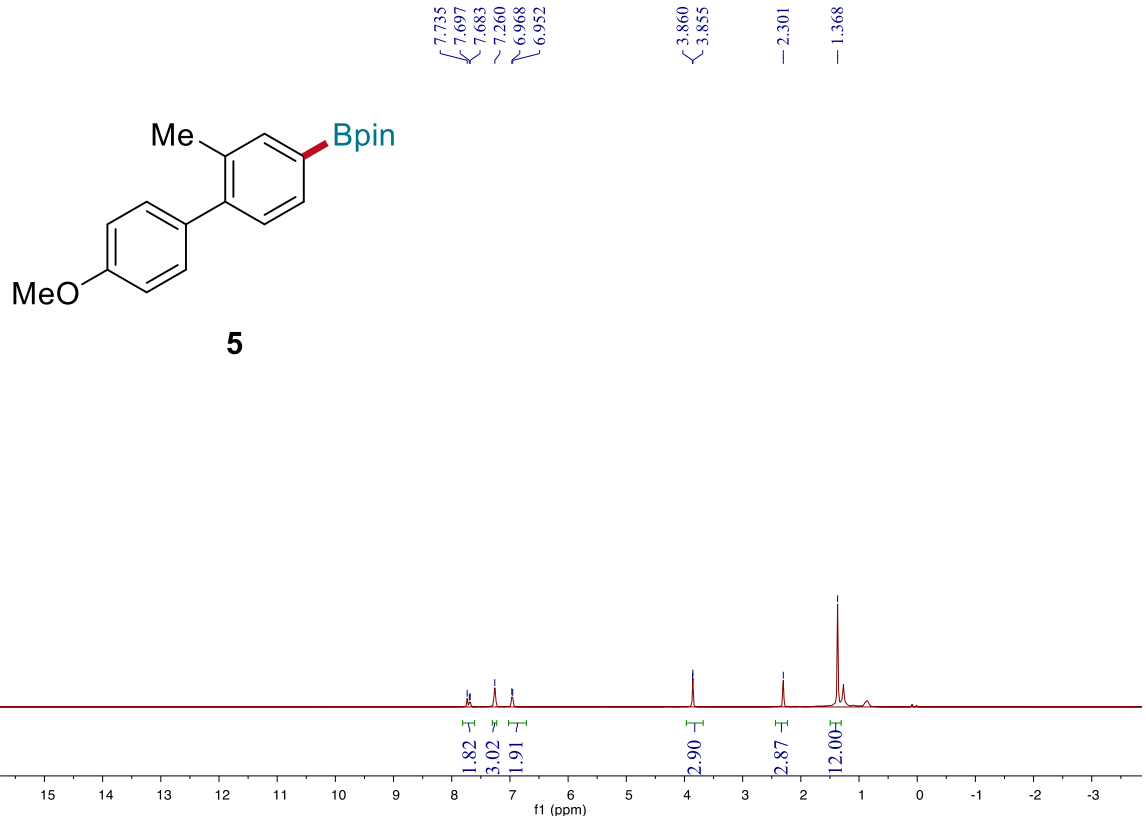

Figure S61. ^{13}C NMR spectrum of 4 in $CDCl_3$ (100 MHz)