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Supporting Information

Modular Functionalization of Arenes in a Triply Selective Sequence: Rapid C(sp^2) and C(sp^3) Coupling of C−Br, C−OTf, and C−Cl Bonds Enabled by a Single Palladium(I) Dimer

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Contents

General information

Reagents and starting materials

Unless otherwise stated, all reagents and starting materials were commercially available and used as received. The Pd$^{(I)}$ dimer $[Pd(\mu\text{-}I)PtBu_3]_2$ **1** was prepared according to the reported literature procedure.[1] The aryl triflate starting materials were prepared according to a reported literature procedure,[2] with the obtained characterization data consistent with that previously reported. All boronic acids were recrystallized from water and dried under reduced pressure prior to use.

Solvents.

Tetrahydrofuran (THF) and dichloromethane were purified by the Pure Solvent PS-MD-5 solvent drying system from Innovative Technology. Anhydrous N-methyl-2-pyrrolidinone (NMP) was purchased from Sigma Aldrich. *n*-Hexane and ethyl acetate were technical grade.

Experimental Techniques.

The work-up of all reactions and the isolation of products were carried out in a fume hood using standard techniques. Whether a reaction was performed under an argon or air atmosphere is specified in the experimental procedure.

Characterization.

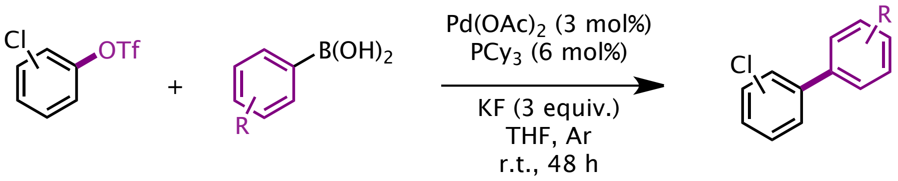
All ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR and $^{19}F\{^{1}H\}$ NMR spectra were recorded at ambient temperature either on a Varian V-NMRS 600 or Varian V-NMRS 400 spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) and were referenced to the residual solvent peak for the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra. Coupling constants (J) are given in Hz. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), sext (sextet), m (multiplet), dd (doublet of doublets) and br (broad), and the term *app* indicates an apparent multiplicity.

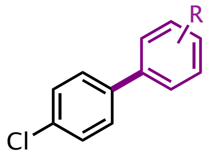
High Resolution Mass Spectrometric (HRMS) analyses were performed on a Thermo Scientific LTQ Orbitrap XL (ESI), or on a Finnigan SSQ 7000, EI: 70 eV (EI).

Gas Chromatography - Mass Spectrometry (GC-MS) analyses were performed using an Agilent Technologies 5975 series MSD mass spectrometer coupled with an Agilent Technologies 7820A gas chromatograph (with an Agilent 19091s-433 HP-SMS column (30 m x 0.250 µm x 0.25 µm)). The molecular ion fragment is indicated by an 'M', with other fragments indicated using a 'Fr' when specifying whether the fragment contains ^{35}Cl or ^{37}Cl.

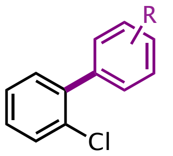
Investigations of the scope of a reported C-OTf selective strategy

Table S1: Investigation of the generality of the Suzuki cross-coupling protocol previously identified by Fu and co-workers to yield selective arylation of 4-chlorophenyl triflate.

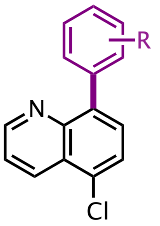




R = 2 -CH_3: 90% (87%*)
4-OCH_3: 26%
4-CF_3: 22%



R = 2-CH_3: 9%
4-OCH_3: 17%
4-CF_3: 17%



R = 2 -CH_3: <5%
4-OCH_3: <5%
4-CF_3: 0%

Reactions were performed in accordance with the procedure reported by Fu *et al*[3]

Reaction Conditions: Chloroaryl triflate (0.4 mmol, 1 equiv.), aryl-$B(OH)_2$ (0.4 mmol, 1 equiv.), $Pd(OAc)_2$ (3 mg, 0.012 mmol, 0.03 equiv.), PCy_3 (7 mg, 0.024 mmol, 0.06 equiv.), KF (70 mg, 1.2 mmol, 3 equiv.) and THF (0.3 mL) were added to a 5 mL vial in a glovebox under an argon atmosphere, and stirred for 48 hours. The solvent was then removed *in vacuo*, the internal standard (4-(trifluoromethoxy)anisole, 60 uL, 0.4 mmol, 1 equiv.) and $CDCl_3$ (*ca.* 0.6 mL) was added and the mixture filtered through a pad of celite (3-4 cm in a Pasteur pipette). The reaction mixture was then analyzed using GC-MS and NMR spectroscopy, with ^1H (and ^{19}F where appropriate) NMR spectroscopy used to determine the extent of conversion to the product (as shown in Table S1).

Experimental procedures and compound characterization data

C-OTf selective cross-coupling reactions

Method A:

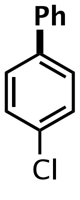
A solution of the appropriate alkyl/aryl magnesium halide (in either THF, 2-MeTHF or Et_2O, 0.6 mmol, 1.5 equiv.*) and $ZnCl_2$ (1M in THF, 0.65 mL, 1.6 equiv.*) were added to a dry 16 mL vial under an argon atmosphere and stirred for 20 minutes. The vial was then opened to air and a solution of the appropriate aryl triflate (0.4 mmol, 1 equiv.) and the $Pd^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) in NMP (1 mL) was added, followed by NMP (2 x 0.5 mL) used to wash the vial containing the aryl triflate/$Pd^{(I)}$-I-dimer mixture. The reaction mixture was stirred for 10 minutes, and the crude reaction mixture was then purified by silica gel column chromatography.

**Unless otherwise stated below*

Method B:

A solution of the appropriate alkyl/aryl magnesium halide (in either THF, 2-MeTHF or Et_2O, 0.6 mmol, 1.5 equiv.*) and $ZnCl_2$ (1M in THF, 0.65 mL, 1.6 equiv.*) were added to a dry 16 mL vial under an argon atmosphere and stirred for 20 minutes. The vial was then opened to air and NMP (1mL) was added, and then a solution of the appropriate aryl triflate (0.4 mmol, 1 equiv.) and the $Pd^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) in NMP (0.5 mL) was added slowly over 1 minute, followed by NMP (0.5 mL) used to wash the vial containing the aryl triflate/$Pd^{(I)}$-I-dimer mixture. The reaction mixture was stirred for 10 minutes, and the crude reaction mixture was then purified by silica gel column chromatography.

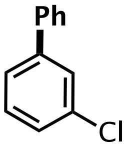
**Unless otherwise stated below*



2

4-Chloro-1,1'-biphenyl

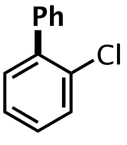
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.61) in 96% yield (73.6 mg) as a white solid. M.p. = 72-74 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.55 (m, 2H), 7.53 – 7.51 (m, 2H), 7.46 - 7.43 (m, 2H), 7.42 – 7.40 (m, 2H), 7.38 – 7.35 (m, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 140.0, 139.6, 133.4, 128.9, 128.9, 128.4, 127.6, 127.0. MS (70 eV, EI): *m/z* (%) 191 (4) ^{37}Cl-$[M+H]^+$, 190 (33) [^{37}Cl-M^+], 189 (13) ^{35}Cl-$[M+H]^+$, 188 (100) [^{35}Cl-M^+], 153 (16), 152 (47), 151(14), 76 (11), 75 (5). The data are in agreement with those previously reported in the literature.[4]



3

3-Chloro-1,1'-biphenyl

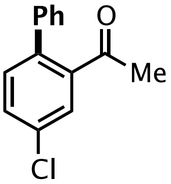
Method B. The title compound was obtained after purification using flash column chromatography on silica gel using hexane ($R_f = 0.58$) in 79% yield (60 mg) as a colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 3H), 7.49 - 7.45 (m, 3H), 7.41 – 7.33 (m, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 143.1, 139.8, 134.6, 130.0, 128.9, 127.9, 127.3, 127.3, 127.1, 125.3. MS (70 eV, EI): *m/z* (%) 191 (4) ^{37}Cl-[M+H]$^+$, 190 (33) [^{37}Cl-M$^+$], 189 (13) ^{35}Cl-[M+H]$^+$, 188 (100) [^{35}Cl-M$^+$], 153 (17), 152 (44), 151(12), 76 (12), 75 (4). The data are in agreement with those previously reported in the literature.[4]



4

2-Chloro-1,1'-biphenyl

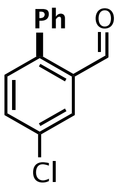
Method B. The title compound was obtained after purification using flash column chromatography on silica gel using hexane ($R_f = 0.63$) in 80% yield (61.0 mg) as a colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.49 – 7.44 (m, 4H), 7.42 – 7.39 (m, 1H), 7.37 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.35 - 7.32 (m, 1H), 7.31 - 7.29 (m, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 140.5, 139.4, 132.5, 131.4, 129.9, 129.4, 128.5, 128.0, 127.6, 126.8. MS (70 eV, EI): *m/z* (%)191 (4) ^{37}Cl-[M+H]$^+$, 190 (34) [^{37}Cl-M$^+$], 189 (13) ^{35}Cl-[M+H]$^+$, 188 (100) [^{35}Cl-M$^+$], 153 (23), 152 (54), 151 (17), 76 (18). The data are in agreement with those previously reported in the literature.[5]



5

1-(4-Chloro-[1,1'-biphenyl]-2-yl)ethanone

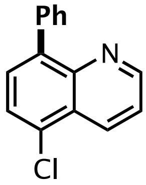
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using 6% ethyl acetate in hexane ($R_f = 0.44$) in 70% yield (64 mg) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 2.1 Hz, 1H), 7.47 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.45 - 7.41 (m, 3H), 7.34 – 7.31 (m, 3H), 1.98 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 203.3, 142.0, 139.5, 138.8, 133.7, 131.6, 130.6, 128.8, 128.7, 128.3, 127.8, 30.3. MS (70 eV, EI): *m/z* (%) 233 (3) ^{37}Cl-[M+H]$^+$, 232 (19) [^{37}Cl-M$^+$], 231 (24) ^{35}Cl-[M+H]$^+$, 230 (58) [^{35}Cl-M$^+$], 229 (50), 218 (4) ^{37}Cl-[Fr+H]$^+$, 217 (33) [^{37}Cl-Fr$^+$], 216 (14) ^{35}Cl-[Fr+H]$^+$, 215 (100) [^{35}Cl-Fr$^+$], 153 (14), 152 (95), 151 (26), 76 (11). The data are in agreement with those previously reported in the literature.[6]



6

4-Chloro-[1,1'-biphenyl]-2-carbaldehyde

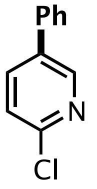
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using 6% ethyl acetate in hexane ($R_f = 0.48$) in 75% yield (66.1 mg) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.99 (d, *J* = 2.3 Hz, 1H), 7.60 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.50 - 7.46 (m, 3H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.36 – 7.35 (m, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 191.1, 144.2, 136.6, 134.7, 134.3, 133.4, 132.2, 130.0, 128.6, 128.5, 127.4. MS (70 eV, EI): *m/z* (%) 219 (3) ^{37}Cl-[M+H]$^{+}$, 218 (26) [^{37}Cl-M^{+}], 217 (41) ^{35}Cl-[M+H]$^{+}$, 216 (81) [^{35}Cl-M^{+}], 215 (96), 190 (9) ^{37}Cl-[Fr+H]$^{+}$, 189 (4) [^{37}Cl-Fr^{+}], 188 (30) ^{35}Cl-[Fr+H]$^{+}$, 187 (2) [^{35}Cl-Fr^{+}], 182 (6), 181 (40), 153 (34), 152 (100), 151 (32), 150 (17), 151 (26), 126 (8), 76 (20), 75 (11), 74(6). The data are in agreement with those previously reported in the literature.[7]



7

8-Chloro-5-phenylquinoline

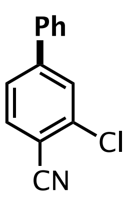
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using 6% ethyl acetate in hexane (R_f = 0.27) in 81% yield (78.2 mg) as a white solid. M.p. = 112-114°C. ^{1}H NMR (600 MHz, CDCl$_3$) δ 9.01 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.65 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.71 – 7.66 (m, 4H), 7.54 – 7.50 (m, 3H), 7.46 - 7.43 (m, 1H). ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ 150.7, 146.6, 140.2, 138.8, 133.0, 130.6, 130.5, 129.9, 128.1, 127.7, 126.6, 126.4, 121.7. HRMS (ESI) calculated for $C_{15}H_{11}N^{35}Cl$: 240.05745 [M+H]$^{+}$, Found: 240.05750.



8

2-Chloro-5-phenylpyridine

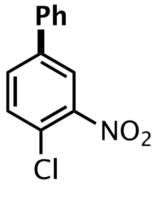
Method A, using 1.15 equiv. phenyl zinc chloride (0.46 mmol). The title compound was obtained after purification using flash column chromatography on silica gel using 4% ethyl acetate in hexane (R_f = 0.25) in 78% yield (73.6 mg) as a white solid. M.p. = 53-54°C. ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.61 (d, *J* = 2.3 Hz, 1H), 7.84 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.49 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.44 – 7.39 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ 150.3, 148.0, 137.2, 136.5, 135.6, 129.2, 128.5, 127.0, 124.2. MS (70 eV, EI): *m/z* (%) 192 (4) ^{37}Cl-[M+H]$^{+}$, 191 (33) [^{37}Cl-M^{+}], 190 (14) ^{35}Cl-[M+H]$^{+}$, 189 (100) [^{35}Cl-M^{+}], 154 (24), 153 (8), 128 (9), 127 (22), 126 (9). The data are in agreement with those previously reported in the literature.[8]



9

3-Chloro-[1,1'-biphenyl]-4-carbonitrile

Method A. The title compound was obtained after purification using flash column chromatography on silica gel using 6% ethyl acetate in hexane (R_f = 0.34) in 92% yield (79.1 mg) as a white solid. M.p. = 99-101 °C. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.74 – 7.72 (m, 2H), 7.58 – 7.57 (m, 3H), 7.51 – 7.48 (m, 2H), 7.46 – 7.44 (m, 1H). ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ 147.2, 137.9, 137.2, 134.2, 129.2, 128.4 (br), 127.2, 125.8, 116.1, 111.6. HRMS (ESI) calculated for $C_{13}H_8N^{35}Cl$: 213.03398 [M]$^{+}$, Found: 213.03302.

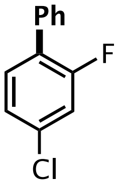


10

4-Chloro-3-nitro-1,1'-biphenyl

Method A. The title compound was obtained after purification using flash column chromatography on silica gel using 5% ethyl acetate in hexane ($R_f = 0.38$) in 87% yield (81 mg) as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 2.1 Hz, 1H), 7.73 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.52 – 7.47 (m, 2H), 7.46 – 7.41 (m, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 148.2, 141.2, 137.5, 132.2, 131.5, 129.3, 128.8, 126.9, 125.7, 123.9. HRMS (EI) calculated for $C_{12}H_8O_2N^{35}Cl$: 233.02381 $[M]^+$, Found: 233.02287.

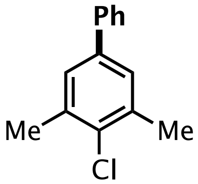
For the large scale reaction Method A was also followed, using 4-chloro-3-nitrophenyl trifluoromethanesulfonate (1 g, 3.27 mmol, 1 equiv.), phenyl zinc chloride (5 mmol, 1.5 equiv.), Pd$^{(I)}$-I-dimer **1** (73 mg, 0.082 mmol, 0.025 equiv.) in NMP (17 mL). After reaction completion (10 minutes) diethyl ether (30 mL) was added to the reaction mixture, and the mixture was washed with water (5 x 20 mL). The organic layer was collected, and the combined water washings were extracted with diethyl ether (3 x 20 mL). The combined organic layers were then washed with brine, dried with Na_2SO_4, and the product **10** was isolated and characterized as described above.



11

4-Chloro-2-fluoro-1,1'-biphenyl

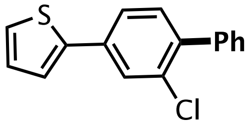
Method B. The title compound was obtained after purification using flash column chromatography on silica gel using hexane ($R_f = 0.70$) in 78% yield (65 mg) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 2H), 7.47-7.45 (m, 2H), 7.41 - 7.37 (m, 2H), 7.23 – 7.19 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 159.5 (d, *J* = 251.5 Hz), 134.7, 133.8 (d, *J* = 10.3 Hz), 131.4 (d, *J* = 4.3 Hz), 128.9 (d, *J* = 2.9 Hz), 128.6, 128.0, 127.7 (d, *J* = 13.7 Hz), 124.8 (d, *J* = 3.7 Hz), 116.8 (d, *J* = 26.4 Hz). ^{19}F{^{1}H} NMR (564 MHz, $CDCl_3$) δ -115.32 (m). HRMS (ESI) calculated for $C_{12}H_8F^{35}Cl$: 206.02931 $[M]^+$, Found: 206.02834.



12

4-Chloro-3,5-dimethyl-1,1'-biphenyl

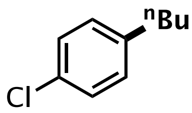
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using hexane ($R_f = 0.62$) in 72% yield (62.7 mg) as a white solid. M.p. = 47-49°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.4 Hz, 2H), 7.43 (dd, *J* = 7.7, 7.6 Hz, 2H), 7.36 - 7.34 (m, 1H), 7.31 (s, 2H), 2.45 (s, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 140.4, 139.0, 136.5, 133.9, 128.7, 127.3, 127.1, 127.0, 20.9. MS (70 eV, EI): *m/z* (%) 219 (5) ^{37}Cl-$[M+H]^+$, 218 (33) [^{37}Cl-M^+], 217 (16) ^{35}Cl-$[M+H]^+$, 216 (100) [^{35}Cl-M^+], 182 (5), 181 (35), 178 (14), 166 (26), 165 (44), 152 (7), 89 (10). The data are in agreement with those previously reported in the literature.[9]



13

2-(2-Chloro-[1,1'-biphenyl]-4-yl)thiophene

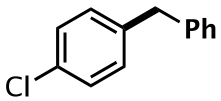
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.30) in 60% yield (65.3 mg) as a white solid. M.p. = 94-96°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 1.4 Hz, 1H), 7.55 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.49 – 7.44 (m, 4H), 7.41 - 7.39 (m, 1H), 7.37 – 7.33 (m, 3H), 7.12 – 7.11 (m, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 142.4, 139.2, 138.9, 134.9, 132.9, 131.7, 129.4, 128.2, 128.1, 127.7, 127.1, 125.6, 124.3, 123.9. HRMS (ESI) calculated for $C_{16}H_{11}S^{35}Cl$: 270.02645 $[M]^+$, Found: 270.02635.



14

1-Butyl-4-chlorobenzene

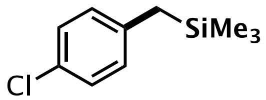
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.70) in 90% yield (61 mg) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 2.64 – 2.55 (m, 2H), 1.59 (*app.* p, *J* = 7.6 Hz, 2H), 1.36 (*app.* sext, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 141.3, 131.2, 129.7, 128.3, 35.0, 33.6, 22.3, 13.93. MS (70 eV, EI): *m/z* (%) 171 (1) $^{37}Cl\text{-}[M+H]^+$, 170 (9) $[^{37}Cl\text{-}M^+]$, 169 (3) $^{35}Cl\text{-}[M+H]^+$, 168 (28) $[^{35}Cl\text{-}M^+]$, 133 (4), 128 (5) $^{37}Cl\text{-}[Fr+H]^+$, 127 (37) $[^{37}Cl\text{-}Fr^+]$, 126 (15) $^{35}Cl\text{-}[Fr+H]^+$, 125 (100) $[^{35}Cl\text{-}Fr^+]$, 103 (7), 91 (15), 77 (6), 63 (4). The data are in agreement with those previously reported in the literature.[10]



15

1-Benzyl-4-chlorobenzene

Method A. The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.38) in 89% yield (72 mg) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.31 – 7.28 (m, 2H), 7.28 – 7.24 (m, 1H), 7.21 (d, *J* = 7.4 Hz, 2H), 7.17 – 7.13 (m, 2H), 3.99 (s, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 140.6, 139.6,131.9, 130.3, 128.9, 128.6, 128.6, 126.3, 41.3. MS (70 eV, EI): *m/z* (%) 205 (2) $^{37}Cl\text{-}[M+H]^+$, 204 (14) $[^{37}Cl\text{-}M^+]$, 203 (7) $^{35}Cl\text{-}[M+H]^+$, 202 (43) $[^{35}Cl\text{-}M^+]$, 167 (100), 152 (18), 139 (4), 128 (2) $^{37}Cl\text{-}[Fr+H]^+$, 127 (3) $[^{37}Cl\text{-}Fr^+]$, 126 (2) $^{35}Cl\text{-}[Fr+H]^+$, 125 (5) $[^{35}Cl\text{-}Fr^+]$, 91 (5), 82 (9), 63 (4). The data are in agreement with those previously reported in the literature.[11]

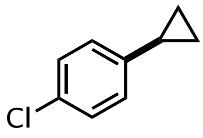


16

(4-Chlorobenzyl)trimethylsilane

Method A. The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.71) in 81% yield (64 mg) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 – 7.16 (m, 2H), 6.96 – 6.90 (m, 2H), 2.06 (s, 2H), 0.00 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 129.5, 129.2, 128.2, 26.5, -2.0. MS (70 eV, EI): *m/z* (%) 201 (1) $^{37}Cl\text{-}[M+H]^+$, 200 (7) $[^{37}Cl\text{-}M^+]$, 199 (3) $^{35}Cl\text{-}[M+H]^+$, 198 (19) $[^{35}Cl\text{-}M^+]$, 186 (1) $^{37}Cl\text{-}[Fr+H]^+$, 185 (4) $[^{37}Cl\text{-}Fr^+]$, 184 (2) $^{35}Cl\text{-}[Fr+H]^+$, 183 (11) $[^{35}Cl\text{-}Fr^+]$, 155 (5) $[^{37}Cl\text{-}Fr^+]$, 153

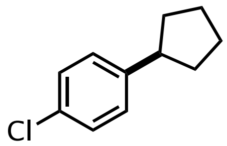
(1) [^{35}Cl-Fr$^+$], 127 (3) [^{37}Cl-Fr$^+$], 125 (8) [^{35}Cl-Fr$^+$], 105 (4), 89 (9), 73 (100), 63 (6). The data are in agreement with those previously reported in the literature.[12]



17

1-Chloro-4-cyclopropylbenzene

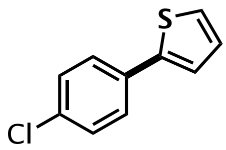
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using hexane ($R_f = 0.57$) in 83% yield (50 mg) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 2H), 7.07 – 6.93 (m, 2H), 1.90 – 1.85 (m, 1H), 1.02 – 0.95 (m, 2H), 0.69 – 0.66 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 142.5, 130.9, 128.3, 127.0, 14.9, 9.3. MS (70 eV, EI): *m/z* (%) 155 (2) ^{37}Cl-[M+H]$^+$, 154 (13) [^{37}Cl-M$^+$], 153 (5) ^{35}Cl-[M+H]$^+$, 152 (40) [^{35}Cl-M$^+$], 127 (4) ^{37}Cl-[Fr+H]$^+$, 125 (12) ^{35}Cl-[Fr+H]$^+$, 117 (100), 101 (4), 89 (12), 75 (7), 63 (8), 51 (4). The data are in agreement with those previously reported in the literature.[13]



18

1-Chloro-4-cyclopentylbenzene

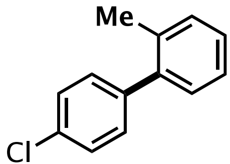
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using hexane ($R_f = 0.72$) in 79% yield (57 mg) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.20 – 2.16 (m, 2H), 3.01 – 2.94 (m, 1H), 2.12 – 2.03 (m, 2H), 1.87 – 1.78 (m, 2H), 1.76 – 1.64 (m, 2H), 1.60 – 1.53 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 145.0, 131.2, 128.4, 128.3, 45.3, 34.6, 25.5. MS (70 eV, EI): *m/z* (%) 183 (3) ^{37}Cl-[M+H]$^+$, 182 (20) [^{37}Cl-M$^+$], 181 (7) ^{35}Cl-[M+H]$^+$, 180 (61) [^{35}Cl-M$^+$], 154 (3) [^{37}Cl-Fr$^+$], 153 (21) ^{35}Cl-[Fr+H]$^+$, 152 (10) [^{35}Cl-Fr$^+$], 151 (62), 145 (100), 141 (5) ^{37}Cl-[Fr+H]$^+$, 140 (26) [^{37}Cl-Fr$^+$], 139 (12) ^{35}Cl-[Fr+H]$^+$, 138 (80) [^{35}Cl-Fr$^+$], 127 (12) ^{37}Cl-[Fr+H]$^+$, 125 (30) ^{35}Cl-[Fr+H]$^+$, 115 (48), 103 (21), 91 (25), 77 (12), 63 (7), 51 (6). The data are in agreement with those previously reported in the literature.[14]



19

2-(4-Chlorophenyl)thiophene

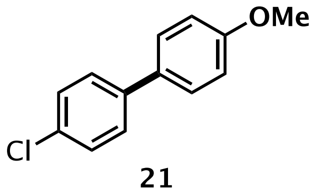
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using hexane ($R_f = 0.57$) in 73% yield (57 mg) as a white solid. M.p. = 82-84 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.51 (m, 2H), 7.40 – 7.33 (m, 2H), 7.32 – 7.27 (m, 2H), 7.09 (dd, *J* = 4.9, 3.8 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 143.1, 133.2, 132.9, 129.0, 128.2, 127.1, 125.2, 123.5. MS (70 eV, EI): *m/z* (%) 197 (4) ^{37}Cl-[M+H]$^+$, 196 (37) [^{37}Cl-M$^+$], 195 (12) ^{35}Cl-[M+H]$^+$, 194 (100) [^{35}Cl-M$^+$], 159 (4), 151 (5) [^{37}Cl-Fr$^+$], 149 (15) [^{35}Cl-Fr$^+$], 138 (2) [^{37}Cl-Fr$^+$], 136 (4) [^{35}Cl-Fr$^+$], 115 (19), 97 (4). The data are in agreement with those previously reported in the literature.[15]



20

4'-Chloro-2-methyl-1,1'-biphenyl

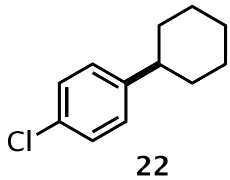
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.46) in 87% yield (70 mg) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.25 (m, 5H), 7.22 (d, *J* = 7.3 Hz, 1H), 2.29 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 140.7, 140.3, 135.3, 132.8, 130.5, 130.4, 129.7, 128.3, 127.6, 125.9, 20.4. MS (70 eV, EI): *m/z* (%) 205 (4) ^{37}Cl-[M+H]$^{+}$, 204 (30) [^{37}Cl-M^{+}], 203 (15) ^{35}Cl-[M+H]$^{+}$, 202 (90) [^{35}Cl-M^{+}], 167 (100), 152 (36), 139 (8), 115 (8), 82 (18), 63 (5). The data are in agreement with those previously reported in the literature.[16]



21

4-Chloro-4'-methoxy-1,1'-biphenyl

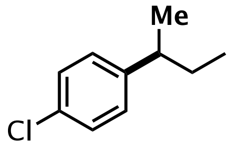
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using 5% ethyl acetate in hexane (R_f = 0.49) in 90% yield (79 mg) as a white solid. M.p. = 111-113 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.44 (m, 4H), 7.43 – 7.35 (m, 2H), 7.03 – 6.94 (m, 2H), 3.86 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 159.4, 139.3, 132.7, 132.5, 128.8 128.0, 127.9, 114.3, 55.4. MS (70 eV, EI): *m/z* (%) 221 (4) ^{37}Cl-[M+H]$^{+}$, 220 (33) [^{37}Cl-M^{+}], 219 (14) ^{35}Cl-[M+H]$^{+}$, 218 (100) [^{35}Cl-M^{+}], 206 (2) ^{37}Cl-[Fr+H]$^{+}$, 205 (15) [^{37}Cl-Fr^{+}], 204 (6) ^{35}Cl-[Fr+H]$^{+}$, 203 (45) [^{35}Cl-Fr^{+}], 175 (36), 152 (7), 139 (25), 76 (4). The data are in agreement with those previously reported in the literature.[17]



22

1-Chloro-4-cyclohexylbenzene

Method A. The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.74) in 74% yield (57 mg) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 2H), 7.15 – 7.11 (m, 2H), 2.57 – 2.36 (m, 1H), 1.88 – 1.81 (m, 4H), 1.78 – 1.71 (m, 1H), 1.45 – 1.30 (m, 4H), 1.28 – 1.22 (m, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 146.5, 131.3, 128.3, 128.2, 44.0, 34.4, 26.8, 26.0.MS (70 eV, EI): *m/z* (%) 197 (3) ^{37}Cl-[M+H]$^{+}$, 196 (22) [^{37}Cl-M^{+}], 195 (9) ^{35}Cl-[M+H]$^{+}$, 194 (67) [^{35}Cl-M^{+}], 159 (20), 154 (3) [^{37}Cl-Fr^{+}], 153 (22) ^{35}Cl-[Fr+H]$^{+}$, 152 (10) [^{35}Cl-Fr^{+}], 151 (65), 141 (4) ^{37}Cl-[Fr+H]$^{+}$, 140 (33) [^{37}Cl-Fr^{+}], 139 (11) ^{35}Cl-[Fr+H]$^{+}$, 138 (100) [^{35}Cl-Fr^{+}], 127 (19) ^{37}Cl-[Fr+H]$^{+}$, 126 (6) [^{37}Cl-Fr^{+}], 125 (46) ^{35}Cl-[Fr+H]$^{+}$, 115 (32), 103 (18), 91 (19), 77 (11), 63 (4), 51 (4). The data are in agreement with those previously reported in the literature.[14]

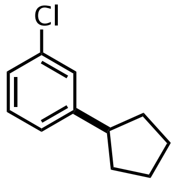


23

1-(*sec*-Butyl)-4-chlorobenzene

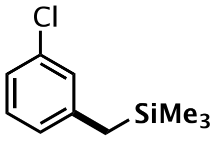
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.71) in 78% yield (53 mg) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 2.59 (m, 1H), 1.63 – 1.55 (m, 2H), 1.24 (d, *J* = 7.0 Hz, 3H), 0.83 (t, *J* = 7.4 Hz, 3H).

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 146.1, 131.3, 128.4, 128.3, 41.2, 31.1, 21.8, 12.2. MS (70 eV, EI): *m/z* (%) 171 (1) ^{37}Cl-[M+H]$^+$, 170 (6) [^{37}Cl-M$^+$], 169 (3) ^{35}Cl-[M+H]$^+$, 168 (20) [^{35}Cl-M$^+$], 142 (3) ^{37}Cl-[Fr+H]$^+$, 141 (33) [^{37}Cl-Fr$^+$], 140 (9) ^{35}Cl-[Fr+H]$^+$, 139 (100) [^{35}Cl-Fr$^+$], 125 (14), 115 (5), 103 (37), 77 (13). The data are in agreement with those previously reported in the literature.[18]


24

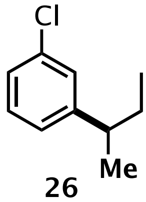
1-Chloro-2-cyclopentylbenzene

Method B. The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.54) in 69% yield (50.0 mg) as a colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 – 7.19 (m, 2H), 7.15 – 7.11 (m, 2H), 2.99 - 2.93 (m, 1H), 2.09 - 2.04 (m, 2H), 1.84 - 1.77 (m, 2H), 1.72 - 1.65 (m, 2H), 1.60 – 1.53 (m, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 148.7, 134.0, 129.4, 127.2, 125.8, 125.3, 45.6, 34.5, 25.4. MS (70 eV, EI): *m/z* (%) 183 (2) ^{37}Cl-[M+H]$^+$, 182 (22) [^{37}Cl-M$^+$], 181 (8) ^{35}Cl-[M+H]$^+$, 180 (66) [^{35}Cl-M$^+$], 154 (3) [^{37}Cl-Fr$^+$], 153 (10) ^{35}Cl-[Fr+H]$^+$, 152 (6) [^{35}Cl-Fr$^+$], 151 (33), 146 (12), 145 (100), 141 (10) ^{37}Cl-[Fr+H]$^+$, 140 (27) [^{37}Cl-Fr$^+$], 139 (24) ^{35}Cl-[Fr+H]$^+$, 138 (77) [^{35}Cl-Fr$^+$], 125 (24), 117 (37), 116 (21), 115 (44), 103 (24), 91 (31), 77 (12).


25

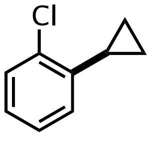
(3-Chlorobenzyl)trimethylsilane

Method B. The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.90) in 78% yield (62 mg) as a colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ7.15 – 7.12 (m, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.99 (s, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 2.07 (s, 2H), 0.00 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 142.8, 133.9,129.3, 127.9, 126.2, 124.0, 27.0, -2.0. MS (70 eV, EI): *m/z* (%) 200 (5) [^{37}Cl-M$^+$], 198 (14) [^{35}Cl-M$^+$], 201 (1) ^{37}Cl-[M+H]$^+$, 200 (7) [^{37}Cl-M$^+$], 199 (3) ^{35}Cl-[M+H]$^+$, 198 (19) [^{35}Cl-M$^+$], 185 (3) [^{37}Cl-Fr$^+$], 184 (1) ^{35}Cl-[Fr+H]$^+$, 183 (8) [^{35}Cl-Fr$^+$], 155 (3) [^{37}Cl-Fr$^+$], 127 (1) [^{37}Cl-Fr$^+$], 125 (3) [^{35}Cl-Fr$^+$], 105 (3), 89 (5), 75 (4), 74 (8), 73 (100). The data are in agreement with those previously reported in the literature.[12]


26

1-(*sec*-Butyl)-3-chlorobenzene

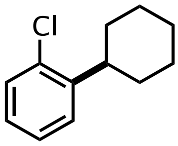
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.67) in 88% yield (60 mg) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 1H), 7.18 – 7.14 (m, 2H), 7.06 (d, *J* = 7.6 Hz, 1H), 2.61 – 2.54 (m, 1H), 1.59 (p, *J* = 7.3 Hz, 2H), 1.23 (d, *J* = 7.0 Hz, 3H), 0.82 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 149.8, 134.0, 129.5, 127.2, 125.9, 125.3, 41.5, 31.0, 21.7, 12.2. HRMS (EI) calculated for $C_{10}H_{13}{}^{35}Cl$: 168.07003 [M], Found: 168.07015.



27

1-Chloro-2-cyclopropylbenzene

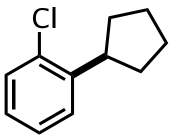
Method B. The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.68) in 66% yield (40.0 mg) as a colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.9 Hz, 1H), 7.17 - 7.15 (m, 1H), 7.11 - 7.08 (m, 1H), 6.94 – 6.92 (m, 1H), 2.22 - 2.18 (m, 1H), 1.03 – 0.99 (m, 2H), 0.70 – 0.67 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 140.9, 135.2, 129.1, 126.6, 126.6, 126.0, 13.3, 8.0. HRMS (ESI) calculated for $C_9H_9{}^{35}Cl$: 152.03873 $[M]^+$, Found: 152.03932.



28

1-Chloro-2-cyclohexylbenzene

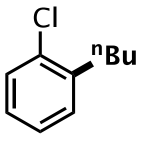
Method B. The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.63) in 79% yield (62.4 mg) as a colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.28 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.24 – 7.21 (m, 1H), 7.13 - 7.10 (m, 1H), 3.07 – 3.00 (m, 1H), 1.91 – 1.86 (m, 4H), 1.81 – 1.78 (m, 1H), 1.50 - 1.43 (m, 2H), 1.41 – 1.35 (m, 2H), 1.32 - 1.24 (m, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 144.8, 133.5, 129.4, 127.2, 126.9, 126.8, 40.5, 33.1, 26.9, 26.2. HRMS (EI) calculated for $C_{12}H_{15}{}^{35}Cl$: 194.08568 $[M]^+$, Found: 194.08598.



29

1-Chloro-2-cyclopentylbenzene

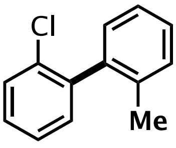
Method B. The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.70) in 73% yield (53.1 mg) as a colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.23 - 7.20 (m, 1H), 7.12 – 7.10 (m, 1H), 3.45 (*app*. p, *J* = 8.5 Hz, 1H), 2.13 – 2.08 (m, 2H), 1.86 - 1.79 (m, 2H), 1.75 – 1.69 (m, 2H), 1.61 – 1.55 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 143.6, 134.1, 129.4, 127.1, 126.8, 126.8, 42.1, 33.2, 25.4. HRMS (EI) calculated for $C_{11}H_{13}{}^{35}Cl$: 180.07003 $[M]^+$, Found: 180.07043.



30

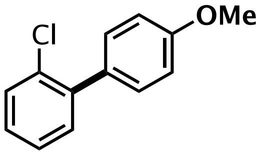
1-Butyl-2-chlorobenzene

Method B. The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.81) in 75% yield (51.0 mg) as a colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.9 Hz, 1H), 7.22 – 7.16 (m, 2H), 7.13 - 7.11 (m, 1H), 2.74 – 2.72 (m, 2H), 1.63 – 1.58 (m, 2H), 1.43 - 1.37 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 140.4, 133.9, 130.3, 129.4, 127.0, 126.6, 33.3, 31.9, 22.5, 14.0. MS (70 eV, EI): *m/z* (%) 171 (1) $^{37}Cl\text{-}[M+H]^+$, 170 (11) $[^{37}Cl\text{-}M^+]$, 169 (5) $^{35}Cl\text{-}[M+H]^+$, 168 (32) $[^{35}Cl\text{-}M^+]$, 133 (6), 128 (10) $^{37}Cl\text{-}[Fr+H]^+$, 127 (35) $[^{37}Cl\text{-}Fr^+]$, 126 (30) $^{35}Cl\text{-}[Fr+H]^+$, 125 (100) $[^{35}Cl\text{-}Fr^+]$, 103 (7), 91 (33), 89 (10). The data are in agreement with those previously reported in the literature.[20]


31

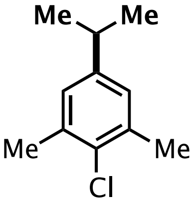
2-Chloro-2'-methyl-1,1'-biphenyl

Method B. The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.63) in 81% yield (68.0 mg) as a colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 1H), 7.32 – 7.29 (m, 4H), 7.28 – 7.24 (m, 2H), 7.17 – 7.15 (m, 1H), 2.14 (s, 3H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 140.6, 139.4, 136.2, 133.4, 131.0, 129.8, 129.4, 129.4, 128.6, 127.9, 126.6, 125.5, 19.8. MS (70 eV, EI): *m/z* (%) 205 (3) ^{37}Cl-[M+H]$^{+}$, 204 (24) [^{37}Cl-M^{+}], 203 (12) ^{35}Cl-[M+H]$^{+}$, 202 (72) [^{35}Cl-M^{+}], 168 (14), 167 (100), 166 (35), 165 (84), 164 (11), 139 (9), 82 (23). The data are in agreement with those previously reported in the literature.[21]


32

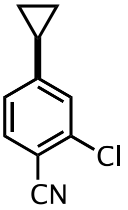
2-Chloro-4'-methoxy-1,1'-biphenyl

Method B. The title compound was obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane (R_f = 0.66) in 85% yield (77.1 mg) as a colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (dd, J = 7.9, 1.3 Hz, 1H), 7.43 – 7.40 (m, 2H), 7.35 (dd, J = 7.6, 1.8 Hz, 1H), 7.33 - 7.30 (m, 1H), 7.28 – 7.26 (m, 1H), 7.01 – 6.99 (m, 2H), 3.87 (s, 3H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 159.1, 140.1, 132.6, 131.8, 131.4, 130.6, 129.9, 128.2, 126.8, 113.5, 55.3. MS (70 eV, EI): *m/z* (%) 221 (5) ^{37}Cl-[M+H]$^{+}$, 220 (34) [^{37}Cl-M^{+}], 219 (15) ^{35}Cl-[M+H]$^{+}$, 218 (100) [^{35}Cl-M^{+}], 206 (1) ^{37}Cl-[Fr+H]$^{+}$, 205 (9) [^{37}Cl-Fr^{+}], 204 (4) ^{35}Cl-[Fr+H]$^{+}$, 203 (26) [^{35}Cl-Fr^{+}], 177 (12), 176 (4), 175 (35), 152 (8), 151 (8), 149 (13), 140 (12), 139 (33). The data are in agreement with those previously reported in the literature.[21]


33

2-Chloro-5-isopropyl-1,3-dimethylbenzene

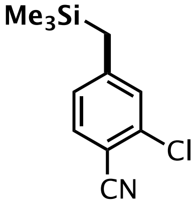
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.74) in 94% yield (69 mg) as a colourless oil, as a 94:6 mixture of the branched:linear isomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.95 (s, 2H), 2.83 (sext, J = 6.9 Hz, 1H), 2.38 (s, 6H), 1.24 (s, 3H), 1.23 (s, 3H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 146.7, 135.9, 131.8, 126.5, 33.5, 24.0, 20.8. HRMS (EI) calculated for $C_{11}H_{15}{}^{35}Cl$: 182.08568 [M]$^{+}$, Found: 182.08582.


34

2-Chloro-4-cyclopropylbenzonitrile

Method A, using 1.15 equiv. cyclopropyl zinc chloride (0.46 mmol). The title compound was obtained after purification using flash column chromatography on silica gel using 6% ethyl acetate in hexane (R_f = 0.30) in 72% yield (52.1 mg) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, J = 8.1 Hz, 1H), 7.15 (d, J = 1.5 Hz, 1H), 7.01 (dd, J = 8.1, 1.5 Hz, 1H), 1.93 - 1.89 (m, 1H), 1.14 – 1.10 (m, 2H), 0.80 – 0.77 (m, 2H). $^{13}C\{^{1}H\}$ NMR (151 MHz,

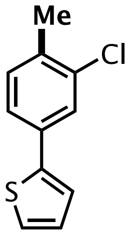
$CDCl_3$) δ 152.1, 136.7, 133.7, 126.8, 124.3, 116.4, 109.7, 15.8, 10.9. HRMS (ESI) calculated for $C_{10}H_8N^{35}ClNa$: 200.02375 $[M+Na]^+$, Found: 200.02353.



35

2-Chloro-4-((trimethylsilyl)methyl)benzonitrile

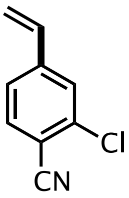
Method A, using 1.15 equiv. (trimethylsilyl)methyl zinc chloride (0.46 mmol). The title compound was obtained after purification using flash column chromatography on silica gel using 6% ethyl acetate in hexane ($R_f = 0.42$) in 88% yield (80.0 mg) as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$) 7.50 (d, *J* = 8.0 Hz, 1H), 7.13 – 7.12 (m, 1H), 6.97 – 6.95 (m, 1H), 2.16 (s, 2H), 0.01 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 149.0, 136.5, 133.5, 129.0, 126.7, 116.5, 108.5, 28.3, -2.0. HRMS (ESI) calculated for $C_{11}H_{14}N^{35}ClSiNa$: 246.04762 $[M+Na]^+$, Found: 246.04784.



36

2-(3-Chloro-4-methylphenyl)thiophene

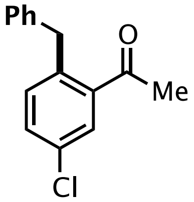
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using hexane ($R_f = 0.63$) in 80% yield (66.8 mg) as a white solid. M.p. = 45-47°C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 1.4 Hz, 1H), 7.40 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.28 (d, *J* = 4.4 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.09 - 7.07 (m, 1H), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 142.9, 135.1, 134.8, 133.6, 131.3, 128.1, 126.3, 125.0, 124.1, 123.3, 19.8. HRMS (ESI) calculated for $C_{11}H_9S^{35}Cl$: 208.01080 $[M]^+$, Found: 208.01084.



37

2-Chloro-4-vinylbenzonitrile

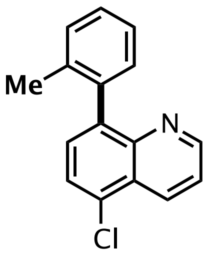
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using 6% ethyl acetate in hexane ($R_f = 0.32$) in 79% yield (52.0 mg) as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 1H), 7.51 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.89 (d, *J* = 17.5 Hz, 1H), 5.50 (d, *J* = 10.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 143.4, 137.1, 134.3, 134.0, 127.4, 124.8, 119.2, 116.1, 111.8. HRMS (EI) calculated for $C_9H_6N^{35}Cl$: 163.01833 $[M]^+$, Found: 163.01731.



38

1-(2-Benzyl-5-chlorophenyl)ethanone

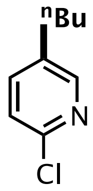
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using 5% ethyl acetate in hexane ($R_f = 0.43$) in 86% yield (84 mg) as a pale yellow oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 2.1 Hz, 1H), 7.36 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.22 – 7.15 (m, 2H), 7.11 (d, *J* = 7.5 Hz, 2H), 4.23 (s, 2H), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 201.0, 140.3, 139.7, 138.9, 133.1, 132.0, 131.2, 129.1, 128.7, 128.4, 126.2, 38.6, 29.7. HRMS (ESI) calculated for $C_{15}H_{13}O^{35}ClNa$: 267.05471 $[M+Na]^+$, Found: 267.05527.



39

5-Chloro-8-(*o*-tolyl)quinoline

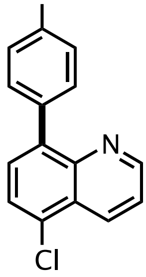
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane (R_f = 0.44) in 86% yield (86 mg) as a viscous yellow oil. ^1H NMR (600 MHz, $CDCl_3$) δ 8.97 (dd, *J* = 4.1, 1.7 Hz, 1H), 8.66 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.51 (dd, *J* = 8.6, 4.1 Hz, 1H), 7.42 – 7.27 (m, 4H), 2.06 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 150.9, 147.1, 140.8, 139.1, 136.9, 132.9, 130.6, 130.2, 130.1, 129.8, 128.0, 126.4, 126.3, 125.5, 121.7, 20.5. HRMS (ESI) calculated for $C_{16}H_{13}N^{35}Cl$: 254.07310 $[M+H]^+$, Found: 254.07262.



40

5-Butyl-2-chloropyridine

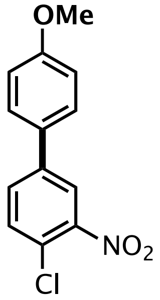
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane (R_f = 0.51) in 70% yield (47 mg) as a colourless oil. ^1H NMR (600 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.45 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.23 (d, *J*= 8.1 Hz, 1H), 2.63 – 2.54 (m, 2H), 1.58 (*app* p, *J* = 7.6 Hz, 2H), 1.35 (*app* sext., *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 149.6, 148.8, 138.7, 136.9, 123.8, 33.1, 31.9, 22.1, 13.8. HRMS (ESI) calculated for $C_9H_{12}N^{35}ClNa$: 192.05505 $[M+Na]^+$, Found: 192.05557.



41

5-Chloro-8-(4-fluorophenyl)quinoline

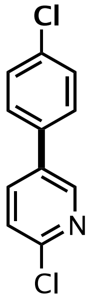
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane (R_f = 0.49) in 75% yield (77 mg) as a pale yellow solid. M.p. = 124-126 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.99 (dd, *J* = 4.0, 1.4 Hz, 1H), 8.65 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.67 – 7.59 (m, 3H), 7.54 (dd, *J* = 8.5, 4.1 Hz, 1H), 7.22 – 7.16 (m, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 163.3, 161.7, 150.7, 146.4, 139.1, 134.7 (d, *J* = 3.1 Hz), 133.1, 132.2 (d, *J* = 8.0 Hz), 130.7, 129.8, 126.7 126.4, 121.8, 115.0 (d, *J* = 21.3 Hz). $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$) δ -115.0. HRMS (ESI) calculated for $C_{15}H_{10}N^{35}ClF$: 258.04803 $[M+H]^+$, Found: 258.04800.



42

4-Chloro-4'-methoxy-3-nitro-1,1'-biphenyl

Method A. The title compound was obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane ($R_f = 0.29$) in 88% yield (93 mg) as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 2.1 Hz, 1H), 7.67 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 160.2, 148.2, 140.8, 132.1, 130.9, 129.8, 128.1, 124.8, 123.3, 114.7, 55.4. HRMS (ESI) calculated for $C_{13}H_{10}O_3N^{35}ClNa$: 286.02414[M+Na]$^+$, Found: 286.02444.



43

2-Chloro-5-(4-chlorophenyl)pyridine

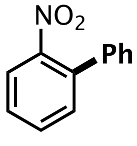
Method A. The title compound was obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane ($R_f = 0.47$) in 62% yield (55 mg) as a white solid. M.p. = 109-111 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (d, *J* = 2.2 Hz, 1H), 7.80 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.49 – 7.43 (m, 4H), 7.39 (d, *J* = 8.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 150.7, 147.8, 137.0, 134.9, 134.8, 134.5, 129.4, 128.3, 124.3. MS (70 eV, EI): *m/z* (%) 226 (10) ^{37}Cl-[M+H]$^+$, 225 (65) [^{37}Cl-M$^+$], 224 (14) ^{35}Cl-[M+H]$^+$, 223 (100) [^{35}Cl-M$^+$], 190 (6) [^{37}Cl-Fr$^+$], 189 (3) ^{35}Cl-[Fr+H]$^+$, 188 (18) [^{35}Cl-Fr$^+$], 162 (4), 153 (22), 126 (9), 75 (6). The data are in agreement with those previously reported in the literature.[22]

C-Cl cross-coupling reactions

General Method:

A solution of the appropriate alkyl/aryl magnesium halide (in either THF, 2-MeTHF or Et_2O, 0.8 mmol, 2 equiv.) and $ZnCl_2$ (1M in THF, 0.85 mL, 2.1 equiv.) were added to a dry 16 mL vial under an argon atmosphere and stirred for 20 minutes. In a separate vial the appropriate aryl chloride (0.4 mmol, 1 equiv.), the $Pd^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) and NMP (2 mL) were added, the vial was evacuated and put under an argon atmosphere. The alkyl/aryl zinc halide mixture was then brought into a 3 mL syringe and added slowly to the NMP solution over 15 minutes at room temperature.* Once addition was complete the reaction mixture was stirred for a further 10 minutes, and the crude reaction mixture was then purified by silica gel column chromatography.

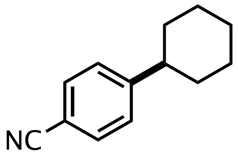
**Unless otherwise stated below*



44

2-Nitro-1,1'-biphenyl

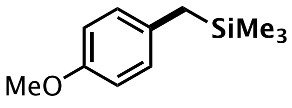
The title compound was obtained after purification using flash column chromatography on silica gel using 5% ethyl acetate in hexane (R_f = 0.23) in 89% yield (71 mg) as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.51 – 7.47 (m, 1H), 7.47 – 7.39 (m, 4H), 7.34 (d, *J* = 7.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 149.3, 137.4, 136.3, 132.3, 132.0, 128.7, 128.2, 128.2, 127.9, 124.1. MS (70 eV, EI): *m/z* (%) 199 (M^+, 19), 182 (44), 171 (45), 152 (100), 127 (16), 115 (66), 76 (25), 63 (14). The data are in agreement with those previously reported in the literature.[23]



45

4-Cyclohexylbenzonitrile

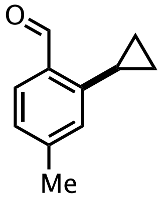
The title compound was obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane (R_f = 0.58) in 92% yield (68 mg) as a yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 2.56 - 2.53 (m, 1H), 1.86 - 1.84 (m, 4H), 1.77 - 1.75 (m, 1H), 1.43 – 1.35 (m, 4H), 1.28 - 1.22 (m, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) 153.5, 132.2, 127.7, 119.2, 109.5, 44.7, 34.0, 26.6, 25.9. MS (70 eV, EI): m/z (%) 185 (M^+, 34), 142 (22), 130 (18), 129 (100), 128 (8), 116 (27), 115 (10). The data are in agreement with those previously reported in the literature.[24]



46

(4-Methoxybenzyl)trimethylsilane

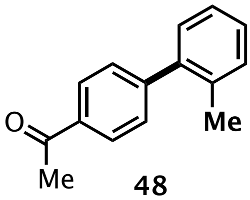
The reaction was performed at 80 °C, and the title compound was obtained after purification using flash column chromatography on silica gel using 5% ethyl acetate in hexane (R_f = 0.65) in 60% yield (47 mg) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.92 (d, *J* = 7.3 Hz, 2H), 6.79 (d, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 2.02 (s, 2H), -0.01 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 156.5, 132.3, 128.8, 113.6, 55.2, 25.7, -1.9. MS (70 eV, EI): *m/z* (%) 194 (M^+, 21), 179 (100), 149 (5), 121 (20), 73 (97). The data are in agreement with those previously reported in the literature.[25]



47

2-Cyclopropyl-4-methylbenzaldehyde

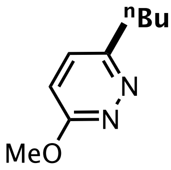
The title compound was obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane (R_f = 0.33) in 83% yield (53 mg) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.52 (s, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 6.91 (s, 1H), 2.66 – 2.58 (m, 1H), 2.36 (s, 3H), 1.08 – 1.03 (m, 2H), 0.79 – 0.75 (m, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 192.3, 146.1, 144.9, 132.6, 130.4, 127.1, 126.9, 21.9, 11.7, 8.41. HRMS (ESI) calculated for $C_{11}H_{13}O$: 161.09609 $[M+H]^+$, Found: 161.09595



48

1-(2'-Methyl-[1,1'-biphenyl]-4-yl)ethanone

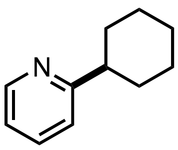
The title compound was obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane (R_f = 0.32) in 93% yield (78 mg) as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 – 7.98 (m, 2H), 7.46 – 7.42 (m, 2H), 7.36 – 7.18 (m, 4H), 2.66 (s, 3H), 2.29 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 197.8, 147.0, 140.7, 135.6, 135.2, 130.5, 129.5, 129.5, 128.2, 127.9, 126.0, 26.7, 20.4. MS (70 eV, EI): *m/z* (%) 210 (M^+, 46), 195 (100), 165 (37), 152 (29), 115 (7), 97 (7), 82 (6). The data are in agreement with those previously reported in the literature.[26]



49

3-Butyl-6-methoxypyridazine

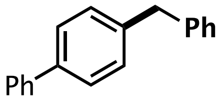
The reaction was performed at 50 °C, and the title compound was obtained after purification using flash column chromatography on silica gel using 20% ethyl acetate in hexane (R_f = 0.27) in 76% yield (51 mg) as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (d, *J* = 9.1 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 4.07 (s, 3H), 2.87 – 2.82 (m, 2H), 1.73 – 1.65 (m, 2H), 1.36 (sext, *J* = 7.4 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 163.8, 159.0, 129.2, 117.3, 54.5, 35.1, 31.5, 22.2, 13.8. HRMS (ESI) calculated for $C_9H_{15}ON_2$: 167.11789 $[M+H]^+$, Found: 167.11810



50

2-Cyclohexylpyridine

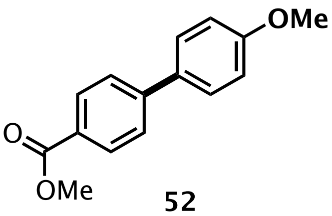
The title compound was obtained after purification using flash column chromatography on silica gel using 20% ethyl acetate in hexane (R_f = 0.50) in 71% yield (46.1 mg) as a yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 – 8.51 (m, 1H), 7.60 - 7.57 (m, 1H), 7.14 (d, J = 7.9 Hz, 1H), 7.09 - 7.06 (m, 1H), 2.69 (tt, J = 12.0, 3.4 Hz, 1H), 1.95 - 1.93 (m, 2H), 1.87 – 1.83 (m, 2H), 1.77 - 1.72 (m, 1H), 1.55 - 1.48 (m, 2H), 1.44 - 1.37 (m, 2H), 1.32 - 1.34 (m, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) 166.5, 149.0, 136.3, 121.0, 46.6, 32.9, 26.6, 26.1. MS (70 eV, EI): *m/z* (%) 161 (M^+, 40), 160 (28), 133 (14), 132 (70), 130 (9), 120 (13), 118 (21), 117 (25), 107 (20), 104 (8), 106 (100), 93 (36), 79 (17). The data are in agreement with those previously reported in the literature.[27]



51

4-Benzyl-1,1'-biphenyl

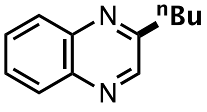
The reaction was performed at 80 °C, and the title compound was obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.14) in 78% yield (77 mg) as a white solid. M.p. = 84-85 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 2H), 7.60 – 7.57 (m, 2H), 7.50 – 7.45 (m, 2H), 7.42 – 7.21 (m, 8H), 4.08 (s, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 141.1, 141.0, 140.3, 139.1, 129.4, 129.0, 128.8, 128.6, 127.3, 127.1, 127.1, 126.2, 41.6. MS (70 eV, EI): *m/z* (%) 244 (M^+, 100), 229 (12), 215 (8), 165 (56), 152 (19), 139 (4), 115 (13). The data are in agreement with those previously reported in the literature.[28]



52

Methyl 4'-methoxy-[1,1'-biphenyl]-4-carboxylate

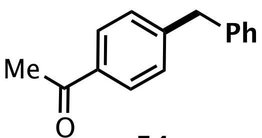
The title compound was obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane (R_f = 0.22) in 80% yield (69 mg) as a white solid. M.p.= 170-172 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.58 – 7.56 (m, 2H), 7.01 - 6.98 (m, 2H), 3.93 (s, 3H), 3.86 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) 167.1, 159.8, 145.2, 132.4, 130.1, 128.3, 128.2, 126.4, 114.3, 55.4 (d, J = 3.1 Hz) 52.1 (d, J = 2.87 Hz). MS (70 eV, EI): *m/z* (%) 243 ($[M+H]^+$, 16), 242 (M^+, 100), 227 (8), 212 (10), 211 (69), 199 (6), 183 (7), 168 (16), 152 (10), 140 (17), 139 (28), 105 (9). The data are in agreement with those previously reported in the literature.[29]



53

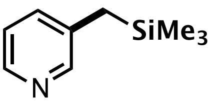
2-Butylquinoxaline

The title compound was obtained after purification using flash column chromatography on silica gel using 6% ethyl acetate in hexane (R_f = 0.44) in 85% yield (65 mg) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.06 - 8.01 (m, 2H), 7.73 – 7.66 (m, 2H), 3.01 – 2.98 (m, 2H), 1.84 – 1.79 (m, 2H), 1.44 (h, J = 7.4 Hz, 2H), 0.95 (t, J = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 157.7, 145.8, 142.2, 141.2, 129.9, 129.1, 128.9, 128.8, 36.2, 31.6, 22.6, 13.9. MS (70 eV, EI): *m/z* (%) 186 (M^+, 7), 157 (13), 145 (11), 144 (100), 143 (5), 102 (7), 76 (6). The data are in agreement with those previously reported in the literature.[30]


54

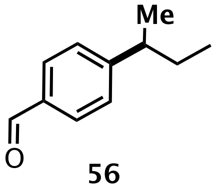
1-(4-Benzylphenyl)ethanone

The title compound was obtained after purification using flash column chromatography on silica gel using 5% ethyl acetate in hexane (R_f = 0.11) in 94% yield (79 mg) as a pale yellow oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.26 (m, 4H), 7.26 – 7.22 (m, 1H), 7.19 (d, *J* = 7.6 Hz, 2H), 4.04 (s, 2H), 2.58 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 197.8, 146.8, 140.1, 135.2, 129.1, 129.0, 128.7, 126.4, 41.9, 26.6. MS (70 eV, EI): *m/z* (%) 210 (M^+, 38), 195 (100), 165 (39), 152 (23), 115 (4), 91 (7). The data are in agreement with those previously reported in the literature.[31]


55

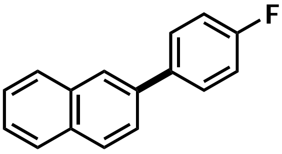
3-((Trimethylsilyl)methyl)pyridine

The reaction was performed at 80 °C, and the title compound was obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane (R_f = 0.09) in 81% yield (54 mg) as a pale yellow oil. ^1H NMR (600 MHz, $CDCl_3$) δ 8.31 (d, *J* = 4.1 Hz, 1H), 8.28 (s, 1H), 7.31 – 7.27 (m, 1H), 7.12 (dd, *J* = 7.7, 4.8 Hz, 1H), 2.03 (s, 2H), -0.01 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 149.2, 145.5, 136.1, 135.0, 123.0, 23.9, -2.1. MS (70 eV, EI): *m/z* (%) 165 (M^+, 44), 150 (13), 73 (100), 65 (5). The data are in agreement with those previously reported in the literature.[32]


56

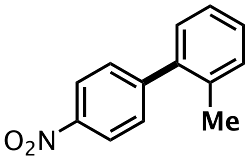
4-(*sec*-Butyl)benzaldehyde

The title compound was obtained after purification using flash column chromatography on silica gel using 5% ethyl acetate in hexane (R_f = 0.36) in 73% yield (48 mg) as a colourless oil, as a 85:15 mixture of the branched:linear isomers. ^1H NMR (600 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.72 – 2.65 (m, 1H), 1.62 (p, *J* = 7.3 Hz, 2H), 1.26 (d, *J* = 7.0 Hz, 3H), 0.82 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 192.1, 155.2, 134.6, 129.9, 127.7, 42.0, 30.9, 21.5, 12.1. HRMS (EI) calculated for $C_{11}H_{14}O$: 162.10392 [M], Found: 162.10330.


57

2-(4-Fluorophenyl)naphthalene

The reaction was performed at 80 °C, and the title compound was obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.29) in 71% yield (63 mg) as a white solid. M.p. = 105-107 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.95 – 7.85 (m, 3H), 7.73 – 7.65 (m, 3H), 7.57 – 7.48 (m, 2H), 7.22 – 7.16 (m, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 162.5 (d, J = 246.5 Hz), 137.6, 137.2 (d, J = 3.3 Hz), 133.6, 132.5, 129.0 (d, J = 7.9 Hz), 128.5, 128.2, 127.7, 126.4, 126.0, 125.7, 125.4, 115.7 (d, J = 21.4 Hz). $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$) δ -115.5. MS (70 eV, EI): *m/z* (%) 222 (M^+, 100), 110 (12), 98 (5). The data are in agreement with those previously reported in the literature.[33]



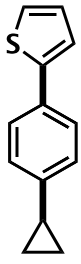
58

2-Methyl-4'-nitro-1,1'-biphenyl

The title compound was obtained after purification using flash column chromatography on silica gel using 5% ethyl acetate in hexane (R_f = 0.45) in 95% yield (81 mg) as a pale yellow solid. M.p. = 101-102 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.34 – 8.24 (m, 2H), 7.53 – 7.46 (m, 2H), 7.37 – 7.27 (m, 3H), 7.22 (d, J = 7.9 Hz, 1H), 2.28 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 148.8, 146.8, 139.6, 135.1, 130.7, 130.1, 129.4, 128.5, 126.1, 123.4, 20.4. MS (70 eV, EI): *m/z* (%) 213 (M^+, 100), 183 (10), 165 (90), 152 (59), 128 (16), 115 (21), 82 (10), 63 (8). The data are in agreement with those previously reported in the literature.[34]

Sequential cross-coupling of *bis*(pseudo)halogenated arenes

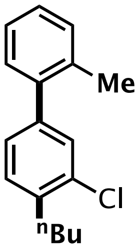
For all cases the solution of the appropriate alkyl/aryl magnesium halide (in either THF, 2-MeTHF or Et_2O, 1 equiv.) and $ZnCl_2$ (1M in THF, 1.1 equiv.) were added to a dry 16 mL vial under an argon atmosphere and stirred for 20 minutes prior to use.



59

2-(4-cyclopropylphenyl)thiophene

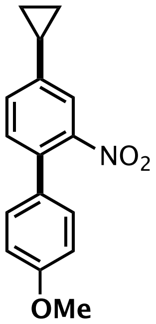
The vial containing the thiophen-2-yl-ZnCl solution (0.6 mmol, 1.5 equiv.) was opened to air and a solution of 4-bromophenyl trifluoromethanesulfonate (124 mg, 0.4 mmol, 1 equiv.) and the $Pd^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) in THF (1 mL) was added, followed by THF (2 x 0.5 mL) used to wash the vial containing the substrate/$Pd^{(I)}$-I-dimer mixture. The reaction mixture was stirred for 5 minutes at room temperature. NMP (2.5 mL) and the cyclopropyl-ZnCl solution (0.6 mmol, 1.5 equiv.) were then added to the reaction mixture, and the mixture was stirred for 10 minutes at room temperature in an open flask. The title compound was obtained after purification using flash column chromatography on silica gel using hexane ($R_f = 0.38$) in 66% yield (54 mg) as a white solid. M.p. = 63-65 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.25 (m, 2H), 7.10 – 7.07 (m, 3H), 1.94 - 1.90 (m, 1H), 1.02 – 0.98 (m, 2H), 0.75 – 0.72 (m, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 144.5, 143.5, 131.6, 127.9, 126.1, 125.9, 124.2, 122.5, 15.2, 9.4. HRMS (ESI) calculated for $C_{13}H_{13}S$: 201.07325 $[M+H]^+$, Found: 201.07307.



60

4'-Butyl-3'-chloro-2-methyl-1,1'-biphenyl

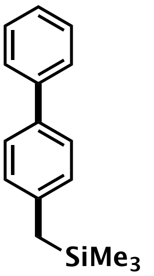
The vial containing the 2-tolyl-ZnCl solution (0.6 mmol, 1.5 equiv.) was opened to air and a solution of 4-bromo-2-chlorophenyl trifluoromethanesulfonate (136.1 mg, 0.4 mmol, 1 equiv.) and the $Pd^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) in THF (1 mL) was added, followed by THF (2 x 0.5 mL) used to wash the vial containing the substrate/$Pd^{(I)}$-I-dimer mixture. The reaction mixture was stirred for 5 minutes at room temperature. NMP (2.5 mL) and the ^{n}butyl-ZnCl solution (0.6 mmol, 1.5 equiv.) were then added to the reaction mixture, and the mixture was stirred for 10 minutes at room temperature in an open flask. The title compound was obtained after purification using flash column chromatography on silica gel using hexane ($R_f = 0.66$) in 72% yield (75 mg) as a colourless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 1.7 Hz, 1H), 7.28 – 7.21 (m, 5H), 7.16 (dd, *J* = 7.8, 1.7 Hz, 1H), 2.80 – 2.78 (m, 2H), 2.30 (s, 3H), 1.70 - 1.65 (m, 2H), 1.49 - 1.43 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) 141.0, 140.5, 138.8, 135.3, 133.5, 130.4, 129.9, 129.9, 129.7, 127.5, 127.5, 125.8, 33.1, 32.0, 22.6, 20.5, 14.0. HRMS (ESI) calculated for $C_{17}H_{13}{}^{35}Cl$: 258.11698 $[M]^+$, Found: 258.11707.



61

4-Cyclopropyl-4'-methoxy-2-nitro-1,1'-biphenyl

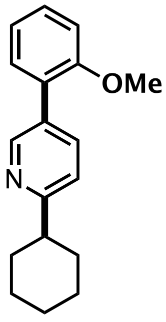
A solution of 4-chloro-3-nitrophenyl trifluoromethanesulfonate (122 mg, 0.4 mmol, 1 equiv.) and the Pd$^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) in NMP (1 mL) was added to a vial containing the cyclopropyl-ZnCl solution (0.52 mmol, 1.3 equiv.) under an argon atmosphere, followed by NMP (2 x 0.5 mL) used to wash the vial containing the substrate/Pd$^{(I)}$-I-dimer mixture. The reaction mixture was stirred for 10 minutes under an argon atmosphere, and then the 4-methoxyphenyl-ZnCl solution (0.8 mmol, 2 equiv.) was added slowly (*via* a 3 mL syringe) to the reaction mixture over 15 minutes at room temperature. Once addition was complete the reaction mixture was stirred for a further 10 minutes. The title compound was obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane (R_f = 0.41) in 78% yield (84 mg) as a green liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.30 – 7.27 (m, 2H), 7.23 – 7.21 (m, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 3.84 (s, 3H), 2.01 – 1.96 (m, 1H), 1.10 – 1.06 (m, 2H), 0.80 - 0.77 (m, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 159.5, 149.3, 144.7, 132.7, 131.7, 129.5, 129.5, 129.1, 121.1 (d, *J* = 2.8 Hz), 114.1, 55.3 (d, *J* = 4.4 Hz), 15.0, 9.8. HRMS (ESI) calculated for $C_{16}H_{16}NO_3$: 270.11247 $[M+H]^+$, Found: 270.11215.



62

([1,1'-Biphenyl]-4-ylmethyl)trimethylsilane

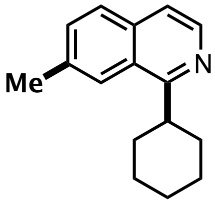
The vial containing the phenyl-ZnCl solution (0.56 mmol, 1.4 equiv.) was opened to air and a solution of 4-chlorophenyl trifluoromethanesulfonate(104 mg, 0.4 mmol, 1 equiv.) and the Pd$^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) in NMP (1 mL) was added, followed by NMP (2 x 0.5 mL) used to wash the vial containing the substrate/Pd$^{(I)}$-I-dimer mixture. The reaction mixture was stirred for 10 minutes at room temperature, and the crude reaction mixture was then filtered through a pad of silica washing with hexane (50 mL) and the filtrate concentrated *in vacuo*. The crude product was transferred to a vial containing the Pd$^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) and NMP (2 mL), the vial was evacuated and put under an argon atmosphere, and then placed in a reactor block at 80 °C. The solution of $(Me)_3SiCH_2$-ZnCl (0.8 mmol, 2 equiv.) was then added slowly (*via* a 3 mL syringe) to the reaction mixture over 15 minutes. Once addition was complete the reaction mixture was stirred for a further 10 minutes at 80 °C. The title compound was then obtained after purification using flash column chromatography on silica gel using hexane (R_f = 0.33) in 61% yield (58 mg) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J*= 8.3 Hz, 2H), 7.50 – 7.46 (m, 2H), 7.45 – 7.41 (m, 2H), 7.34 – 7.30 (m, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 2.14 (s, 2H), 0.04 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 141.2, 139.8, 136.7, 128.7, 128.4, 126.8, 126.8, 126.7, 26.8, -1.9. MS (70 eV, EI): *m/z* (%) 240 (M^+, 18), 165 (11), 152 (4), 73 (100). The data are in agreement with those previously reported in the literature.[35]



63

2-Cyclohexyl-5-(2-methoxyphenyl)pyridine

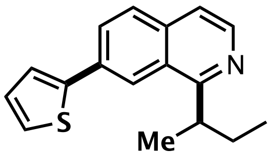
A solution of 6-chloropyridin-3-yl trifluoromethanesulfonate (105 mg, 0.4 mmol, 1 equiv.) and the Pd$^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) in NMP (1 mL) was added to a vial containing the 2-methoxyphenyl-ZnCl solution (0.42 mmol, 1.05 equiv.) under an argon atmosphere, followed by NMP (2 x 0.5 mL) used to wash the vial containing the substrate/Pd$^{(I)}$-I-dimer mixture. The reaction mixture was stirred for 10 minutes under an argon atmosphere, and then the cyclohexyl-ZnCl solution (0.8 mmol, 2 equiv.) was added slowly (*via* a 3 mL syringe) to the reaction mixture over 15 minutes at room temperature. Once addition was complete the reaction mixture was stirred for a further 10 minutes. The title compound was then obtained after purification using flash column chromatography on silica gel using 20% ethyl acetate in hexane ($R_f = 0.37$) in 80% yield (86 mg) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (d, J = 2.2 Hz, 1H), 7.79 (dd, J = 8.1, 2.3 Hz, 1H), 7.39 – 7.27 (m, 2H), 7.18 (d, J = 8.1 Hz, 1H), 7.06 – 7.02 (m, 1H), 6.99 (d, J = 8.2 Hz, 1H), 3.81 (s, 3H), 2.74 (tt, J = 12.0, 3.4 Hz, 1H), 2.04 – 1.97 (m, 2H), 1.91 – 1.84 (m, 2H), 1.80 – 1.73 (m, 1H), 1.62 – 1.52 (m, 2H), 1.48 – 1.39 (m, 2H), 1.35 – 1.26 (m, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 164.7, 156.6, 149.3, 137.2, 131.4, 130.6, 129.2, 127.2, 121.0, 120.2, 111.2, 55.5, 46.3, 33.0, 26.6, 26.1. HRMS (ESI) calculated for $C_{18}H_{22}ON$: 268.16959 $[M+H]^+$, Found: 268.17020.



64

1-Cyclohexyl-7-methylisoquinoline

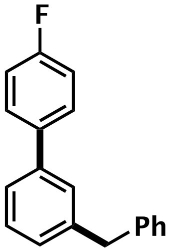
A solution of 7-bromo-1-chloroisoquinoline (97 mg, 0.4 mmol, 1 equiv.) and the Pd$^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) in THF (1 mL) was added to a vial containing the Me-ZnCl solution (0.52 mmol, 1.3 equiv.) under an argon atmosphere, followed by THF (2 x 0.5 mL) used to wash the vial containing the substrate/Pd$^{(I)}$-I-dimer mixture. The reaction mixture was stirred for 5 minutes at room temperature under an argon atmosphere. NMP (2.5 mL) was then added and the cyclohexyl-ZnCl solution (0.8 mmol, 2 equiv.) was added slowly (*via* a 3 mL syringe) to the reaction mixture over 15 minutes at room temperature. Once addition was complete the reaction mixture was stirred for a further 10 minutes. The title compound was then obtained after purification using flash column chromatography on silica gel using 15% ethyl acetate in hexane ($R_f = 0.37$) in 71% yield (64 mg) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, J = 5.6 Hz, 1H), 7.96 (s, 1H), 7.70 (d, J = 8.3 Hz, 1H), 7.47 (dd, J = 8.3, 1.2 Hz, 1H), 7.42 (d, J = 5.9 Hz, 1H), 3.54 (tt, J = 11.8, 3.2 Hz, 1H), 2.57 (s, 3H), 1.99 – 1.91 (m, 4H), 1.87 – 1.79 (m, 3H), 1.59 – 1.50 (m, 2H), 1.44 – 1.36 (m, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 164.9, 141.2, 136.6, 134.6, 131.7, 127.3, 126.4, 123.5, 118.6, 41.3, 32.6, 26.9, 26.3, 22.2. HRMS (ESI) calculated for $C_{16}H_{20}N$: 226.15903 $[M+H]^+$, Found: 226.15916.



65

1-(*sec*-Butyl)-7-(thiophen-2-yl)isoquinoline

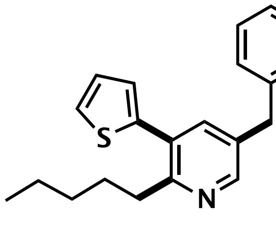
A solution of 7-bromo-1-chloroisoquinoline (97 mg, 0.4 mmol, 1 equiv.) and the Pd$^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) in THF (1 mL) was added to a vial containing the thiophen-2-yl-ZnCl solution (0.6 mmol, 1.5 equiv.) under an argon atmosphere, followed by THF (2 x 0.5 mL) used to wash the vial containing the substrate/Pd$^{(I)}$-I-dimer mixture. The reaction mixture was stirred for 5 minutes at room temperature under an argon atmosphere. NMP (2.5 mL) was then added and the *sec*-butyl-ZnCl solution (0.8 mmol, 2 equiv.) was added slowly (*via* a 3 mL syringe) to the reaction mixture over 15 minutes at room temperature. Once addition was complete the reaction mixture was stirred for a further 10 minutes. The title compound was then obtained after purification using flash column chromatography on silica gel using 15% ethyl acetate in hexane ($R_f = 0.45$) in 70% yield (76 mg) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (d, $J = 5.6$ Hz, 1H), 8.40 (s, 1H), 7.91 (dd, $J = 8.5, 1.7$ Hz, 1H), 7.82 (d, $J = 8.5$ Hz, 1H), 7.49 – 7.43 (m, 2H), 7.37 (dd, $J = 5.1, 1.0$ Hz, 1H), 7.15 (dd, $J = 5.0, 3.7$ Hz, 1H), 3.75 (sext, $J = 6.8$ Hz, 1H), 2.09 – 2.00 (m, 1H), 1.84 – 1.76 (m, 1H), 1.44 (d, $J = 6.8$ Hz, 3H), 0.93 (t, $J = 7.4$ Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 165.9, 144.0, 142.0, 135.6, 132.9, 128.3, 128.2, 128.1, 127.1, 125.6, 123.9, 121.1, 118.6, 37.8, 29.7, 20.2, 12.4. HRMS (ESI) calculated for $C_{17}H_{18}NS$: 268.11545 $[M+H]^+$, Found: 268.11542.



66

3-Benzyl-4'-fluoro-1,1'-biphenyl

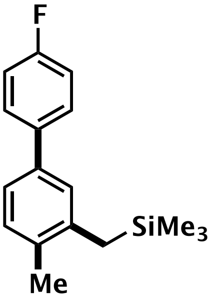
The vial containing the 4-fluorophenyl-ZnCl solution (0.6 mmol, 1.5 equiv.) was opened to air and a solution of 1-bromo-3-chlorobenzene (77 mg, 0.4 mmol, 1 equiv.) and the Pd$^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) in THF (1 mL) was added, followed by THF (2 x 0.5 mL) used to wash the vial containing the substrate/Pd$^{(I)}$-I-dimer mixture. The reaction mixture was stirred for 5 minutes at room temperature, and the crude reaction mixture was then filtered through a pad of silica washing with hexane (100 mL) and the filtrate concentrated *in vacuo*. The crude product was transferred to a vial containing the Pd$^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) and NMP (2 mL), the vial was evacuated and put under an argon atmosphere, and then placed in a reactor block at 80 °C. The solution of benzyl-ZnCl (0.8 mmol, 2 equiv.) was then added slowly (*via* a 3 mL syringe) to the reaction mixture over 15 minutes. Once addition was complete the reaction mixture was stirred for a further 10 minutes at 80 °C. The title compound was then obtained after purification using flash column chromatography on silica gel using hexane ($R_f = 0.09$) in 78% yield (80 mg) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 2H), 7.47 – 7.32 (m, 5H), 7.31 – 7.19 (m, 4H), 7.18 – 7.13 (m, 2H), 4.10 (s, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 162.5 (d, $J = 246.1$ Hz), 141.8, 141.0, 140.5, 137.4 (d, $J = 3.0$ Hz), 129.0, 129.0, 128.8 (d, $J = 8.1$ Hz), 128.6, 128.0, 127.7, 126.2, 124.9, 115.6 (d, $J = 21.3$ Hz), 42.1. $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$) δ -115.7. HRMS (EI) calculated for $C_{19}H_{15}F$: 262.11523 [M], Found: 262.11609.



67

5-Benzyl-2-pentyl-3-(thiophen-2-yl)pyridine

The vial containing the thiophen-2-yl-ZnCl solution (0.44 mmol, 1.1 equiv.) was opened to air and a solution of 3-bromo-5-chloropyridin-2-yl trifluoromethanesulfonate (136 mg, 0.4 mmol, 1 equiv.) and the Pd$^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) in THF (1 mL) was added, followed by THF (2 x 0.5 mL) used to wash the vial containing the substrate/Pd$^{(I)}$-I-dimer mixture. The reaction mixture was stirred for 5 minutes at room temperature. NMP (2.5 mL) and the pentyl-ZnCl solution (0.6 mmol, 1.5 equiv.) were then added to the reaction mixture, and the mixture was stirred for 10 minutes at room temperature in an open flask. The 5-chloro-2-pentyl-3-(thiophen-2-yl)pyridine intermediate was isolated using flash column chromatography on silica gel using 5% ethyl acetate in hexane (R_f = 0.40). This compound was transferred to a vial containing the Pd$^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) and NMP (2 mL), the vial was evacuated and put under an argon atmosphere, and then placed in a reactor block at 80 °C. The solution of benzyl-ZnCl (0.8 mmol, 2 equiv.) was then added slowly (*via* a 3 mL syringe) to the reaction mixture over 15 minutes. Once addition was complete the reaction mixture was stirred for a further 10 minutes at 80 °C. The title compound was then obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane (R_f = 0.33) in 77% yield (99 mg) as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, *J* = 2.1 Hz, 1H), 7.43 (d, *J* = 2.2 Hz, 1H), 7.36 (dd, *J* = 5.1, 0.9 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.25 – 7.18 (m, 3H), 7.08 (dd, *J* = 5.1, 3.6 Hz, 1H), 7.02 (dd, *J* = 3.5, 1.0 Hz, 1H), 3.97 (s, 2H), 2.88 – 2.85 (m, 2H), 1.72 – 1.66 (m, 2H), 1.33 – 1.28 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.3, 148.8, 140.8, 139.8, 138.6, 133.4, 129.2, 128.8, 128.7, 127.2, 126.9, 126.4, 125.9, 38.5, 35.5, 31.8, 29.7, 22.5, 14.0. HRMS (ESI) calculated for $C_{21}H_{24}NS$: 322.16240 $[M+H]^+$, Found: 322.16302.

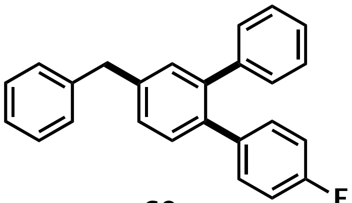


68

((4'-Fluoro-4-methyl-[1,1'-biphenyl]-3-yl)methyl)trimethylsilane

The vial containing the (4-fluorophenyl)-ZnCl solution (0.6 mmol, 1.5 equiv.) was opened to air and a solution of 4-bromo-2-chlorophenyl trifluoromethanesulfonate (136.5 mg, 0.4 mmol, 1 equiv.) and the Pd$^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) in THF (1 mL) was added, followed by THF (2 x 0.5 mL) used to wash the vial containing the substrate/Pd$^{(I)}$-I-dimer mixture. The reaction mixture was stirred for 5 minutes at room temperature. NMP (2.5 mL) and the methyl-ZnCl solution (0.6 mmol, 1.5 equiv.) were then added to the reaction mixture, and the mixture was stirred for 10 minutes at room temperature in an open flask. The 3-chloro-4'-fluoro-4-methyl-1,1'-biphenyl intermediate was isolated using flash column chromatography on silica gel using hexane (R_f = 0.59).

This compound was transferred to a vial containing the Pd$^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) and NMP (2 mL), the vial was evacuated and put under an argon atmosphere, and then placed in a reactor block at 80 °C. The solution of ((trimethylsilyl)methyl)-ZnCl (0.8 mmol, 2 equiv.) was then added slowly (*via* a 3 mL syringe) to the reaction mixture over 15 minutes. Once addition was complete the reaction mixture was stirred for a further 10 minutes at 80 °C. The title compound was obtained after purification using flash column chromatography on silica gel using hexane ($R_f = 0.59$) in 63% yield (69 mg) as a colourless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 2H), 7.20 - 7.18 (m, 2H), 7.16 (s, 1H), 7.14 – 7.10 (m, 2H), 2.29 (s, 3H), 2.18 (s, 2H), 0.07 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 162.2 (d, J = 245.4 Hz), 139.5, 137.6, 137.6, 133.8, 130.6, 128.4 (d, J = 8.0 Hz), 127.3, 122.7, 115.5 (d, J = 21.2 Hz), 23.9, 20.0, -1.3. $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$) δ -116.5. HRMS (ESI) calculated for $C_{17}H_{21}FSi$: 272.13911 $[M+H]^+$, Found: 272.13902.



69

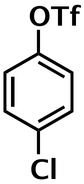
4'-Benzyl-4-fluoro-1,1':2',1''-terphenyl

The vial containing the phenyl-ZnCl solution (0.6 mmol, 1.5 equiv.) was opened to air and a solution of 2-bromo-4-chlorophenyl trifluoromethanesulfonate (136 mg, 0.4 mmol, 1 equiv.) and the Pd$^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) in THF (1 mL) was added, followed by THF (2 x 0.5 mL) used to wash the vial containing the substrate/Pd$^{(I)}$-I-dimer mixture. The reaction mixture was stirred for 5 minutes at room temperature, and then the 5-chloro-[1,1'-biphenyl]-2-yl trifluoromethanesulfonate intermediate was isolated using flash column chromatography on silica gel using 5% ethyl acetate in hexane ($R_f = 0.58$). The separate vial containing the 4-fluorophenyl-ZnCl solution (0.6 mmol, 1.5 equiv.) was opened to air and a solution of the isolated compound and the Pd$^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) in NMP (1 mL) was added, followed by NMP (2 x 0.5 mL) used to wash the vial containing the substrate/Pd$^{(I)}$-I-dimer mixture. The mixture was stirred for 10 minutes at room temperature in an open flask, after which the 4'-chloro-4-fluoro-1,1':2',1''-terphenyl intermediate was isolated using flash column chromatography on silica gel using hexane ($R_f = 0.40$). This compound was transferred to a vial containing the Pd$^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) and NMP (2 mL), the vial was evacuated and put under an argon atmosphere, and then placed in a reactor block at 80 °C. The solution of benzyl-ZnCl (0.8 mmol, 2 equiv.) was then added slowly (*via* a 3 mL syringe) to the reaction mixture over 15 minutes. Once addition was complete the reaction mixture was stirred for a further 10 minutes at 80 °C. The title compound was then obtained after purification using flash column chromatography on silica gel using hexane ($R_f = 0.18$) in 57% yield (77 mg) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 3H), 7.29 – 7.26 (m, 3H), 7.24 – 7.18 (m, 5H), 7.12 – 7.09 (m, 2H), 7.08 – 7.05 (m, 2H), 6.91 – 6.86 (m, 2H), 4.06 (s, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 161.7 (d, J = 245.5 Hz), 141.4, 140.8, 140.7, 140.6, 137.4, 137.3 (d, J = 3.3 Hz), 131.4 (d, J = 7.9 Hz), 131.2, 130.7, 129.9, 129.0, 128.6, 128.1, 128.0, 126.6, 126.3, 114.8 (d, J = 21.2 Hz), 41.7. $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$) δ -116.4 (m). HRMS (EI) calculated for $C_{25}H_{19}F$: 338.14653 [M], Found: 338.14597

Synthesis of aryl trifluoromethanesulfonate starting materials

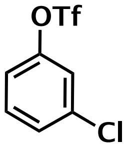
General Method:

To a dry 250 mL round-bottomed flask was added the appropriate phenol (9.0 mmol, 1 equiv.) and dichloromethane (20 mL) under an argon atmosphere, followed by the addition of triethylamine (18.9 mmol, 2.1 equiv.). The mixture was stirred at room temperature for 5 minutes, and was then cooled to -78 °C and trifluoromethanesulfonic anhydride (9.9 mmol, 1.1 equiv.) was added dropwise. The reaction mixture was then allowed to warm to room temperature and stirred for an additional 12 hours. Water (or saturated aqueous $NaHCO_3$ for basic products) was then added and the reaction mixture was extracted with diethyl ether. The combined organic layers were concentrated under reduced pressure and the crude mixture was then purified by silica gel column chromatography.



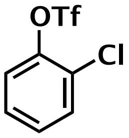
4-Chlorophenyl trifluoromethanesulfonate

The title compound was obtained after purification using flash column chromatography on silica gel using hexane ($R_f = 0.47$) in 93% yield (2.18 g) as a colourless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 2H), 7.25 – 7.22 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 147.8, 134.3, 130.4, 122.7, 118.7 (q, J = 320.9 Hz). ^{19}F{^{1}H} NMR (564 MHz, $CDCl_3$) δ -72.70. MS (70 eV, EI): *m/z* (%) 263 (1) ^{37}Cl-[M+H]$^+$, 262 (18) [^{37}Cl-M$^+$], 261 (4) ^{35}Cl-[M+H]$^+$, 260 (46) [^{35}Cl-M$^+$], 196 (8), 130 (4) ^{37}Cl-[Fr+H]$^+$, 129 (36) [^{37}Cl-Fr$^+$], 128 (7) ^{35}Cl-[Fr+H]$^+$, 127 (100) [^{35}Cl-Fr$^+$], 101 (29), 99 (86), 75 (13), 73 (28), 69 (46), 63 (27). The data are in agreement with those previously reported in the literature.[36]



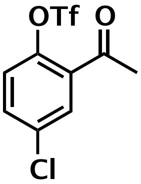
3-Chlorophenyl trifluoromethanesulfonate

The title compound was obtained after purification using flash column chromatography on silica gel using hexane ($R_f = 0.50$) in 96 % yield (2.25 g) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 2H), 7.31 (s, 1H), 7.22 – 7.18 (m, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 149.5, 135.6, 130.9, 128.8, 122.0, 119.70, 118.6 (d, J = 320.2 Hz). ^{19}F{^{1}H} NMR (564 MHz, $CDCl_3$) δ -72.75. MS (70 eV, EI): *m/z* (%) 263 (2) ^{37}Cl-[M+H]$^+$, 262 (22) [^{37}Cl-M$^+$], 261 (5) ^{35}Cl-[M+H]$^+$, 260 (58) [^{35}Cl-M$^+$], 198 (16), 196 (50), 130 (20) ^{37}Cl-[Fr+H]$^+$, 129 (12) [^{37}Cl-Fr$^+$], 128 (2) ^{35}Cl-[Fr+H]$^+$, 127 (35) [^{35}Cl-Fr$^+$], 102 (2) ^{37}Cl-[Fr+H]$^+$, 101 (32) [^{37}Cl-Fr$^+$], 100 (6) ^{35}Cl-[Fr+H]$^+$, 99 (100) [^{35}Cl-Fr$^+$], 92 (12), 73 (31), 69 (93), 62 (13). The data are in agreement with those previously reported in the literature.[37]



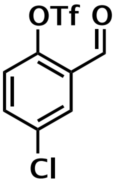
2-Chlorophenyl trifluoromethanesulfonate

The title compound was obtained after purification using flash column chromatography on silica gel using hexane ($R_f = 0.44$) in 96% yield (2.25 g) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 1H), 7.37 – 7.32 (m, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 145.7, 131.3, 129.2, 128.3, 127.3, 123.0, 118.6 (q, *J* = 320.6 Hz). ^{19}F{^{1}H} NMR (564 MHz, $CDCl_3$) δ -73.47.MS (70 eV, EI): *m/z* 263 (2) ^{37}Cl-[M+H]$^+$, 262 (28) [^{37}Cl-M$^+$], 261 (6) ^{35}Cl-[M+H]$^+$, 260 (74) [^{35}Cl-M$^+$], 198 (9), 196 (29), 130 (4) ^{37}Cl-[Fr+H]$^+$, 129 (29) [^{37}Cl-Fr$^+$], 128 (6) ^{35}Cl-[Fr+H]$^+$, 127 (87) [^{35}Cl-Fr$^+$], 111 (7), 102 (2) ^{37}Cl-[Fr+H]$^+$, 101 (33) [^{37}Cl-Fr$^+$], 100 (6) ^{35}Cl-[Fr+H]$^+$, 99 (100) [^{35}Cl-Fr$^+$], 92 (12), 75 (12), 73 (26), 69 (38), 62 (21). The data are in agreement with those previously reported in the literature.[38]



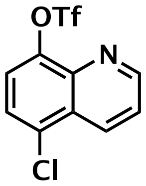
2-Acetyl-4-chlorophenyl trifluoromethanesulfonate

The title compound was obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane ($R_f = 0.57$) in 85% yield (2.31 g) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 2.6 Hz, 1H), 7.56 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.29 (d, *J* = 8.8 Hz, 1H), 2.63 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 195.3, 145.0, 134.5, 133.4, 133.3, 130. 7, 124.1, 118.5 (q, *J* = 320.8 Hz), 29.5. ^{19}F{^{1}H} NMR (564 MHz, $CDCl_3$) δ -73.14. MS (70 eV, EI): *m/z* (%) 305 (4) ^{37}Cl-[M+H]$^+$, 304 (34) [^{37}Cl-M$^+$], 303 (10) ^{35}Cl-[M+H]$^+$, 302 (89) [^{35}Cl-M$^+$], 290 (4) ^{37}Cl-[Fr+H]$^+$, 289 (38) [^{37}Cl-Fr$^+$], 288 (10) ^{35}Cl-[Fr+H]$^+$, 287 (100) [^{35}Cl-Fr$^+$], 225 (15), 223 (44), 169 (15) [^{37}Cl-Fr$^+$], 170 (2) ^{35}Cl-[Fr+H]$^+$, 171 (5) [^{35}Cl-Fr$^+$], 157 (18) ^{37}Cl-[Fr+H]$^+$, 156 (25) [^{37}Cl-Fr$^+$], 155 (8) ^{35}Cl-[Fr+H]$^+$, 154 (93) [^{35}Cl-Fr$^+$], 152 (52), 143 (33), 141 (98), 129 (27) ^{37}Cl-[Fr+H]$^+$, 128 (14) [^{37}Cl-Fr$^+$], 127 (7) ^{35}Cl-[Fr+H]$^+$, 126 (43) [^{35}Cl-Fr$^+$], 77 (62), 69 (84). The data are in agreement with those previously reported in the literature.[39]



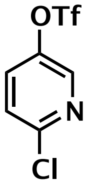
4-Chloro-2-formylphenyl trifluoromethanesulfonate

The title compound was obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane ($R_f = 0.67$) in 81% yield (2.10 g) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.22 (s, 1H), 7.96 (d, *J* = 2.7 Hz, 1H), 7.67 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 185.1, 148.1, 135. 6, 135.2, 130.3, 129.4, 124.0, 118.6 (q, *J* = 320.8 Hz). ^{19}F{^{1}H} NMR (564 MHz, $CDCl_3$) δ -72.68. MS (70 eV, EI): *m/z* (%) 291 (3) ^{37}Cl-[M+H]$^+$, 290 (28) [^{37}Cl-M$^+$], 289 (7) ^{35}Cl-[M+H]$^+$, 288 (73) [^{35}Cl-M$^+$], 225 (26), 223 (78), 158 (4) ^{37}Cl-[Fr+H]$^+$, 157 (51) [^{37}Cl-Fr$^+$], 156 (19) ^{35}Cl-[Fr+H]$^+$, 155 (100) [^{35}Cl-Fr$^+$], 154 (28), 138 (16), 129 (33) ^{37}Cl-[Fr+H]$^+$, 128 (7) [^{37}Cl-Fr$^+$], 127 (51) ^{35}Cl-[Fr+H]$^+$, 126 (11) [^{35}Cl-Fr$^+$], 110 (12), 101 (32), 99 (99), 69 (63), 62 (16). The data are in agreement with those previously reported in the literature.[40]



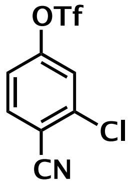
5-Chloroquinolin-8-yl trifluoromethanesulfonate

The title compound was obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane ($R_f = 0.46$) in 83% yield (2.33 g) as a white solid. M.p. = 80-82 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.10 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.60 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.66 - 7.64 (m, 2H), 7.56 (d, *J* = 8.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 152.1, 144.9, 141.5, 133.1, 131.5, 127.6, 125.8, 123.4, 120.9, 118.84 (q, *J* = 320.5 Hz). $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$) δ -73.69. HRMS (EI) calculated for $C_{10}H_5O_3N^{35}ClF_3S$: 310.96253 [M]$^+$, Found: 310.96241.



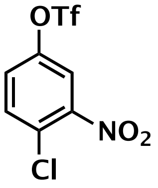
6-Chloropyridin-3-yl trifluoromethanesulfonate

The title compound was obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane ($R_f = 0.54$) in 93% yield (2.19 g) as a white solid. M.p. = 40-42 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (d, *J* = 3.0 Hz, 1H), 7.61 (dd, *J* = 8.8, 3.0 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 150.9, 145.6, 142.6, 131.8, 125.7, 118.6 (q, *J* = 321.3 Hz). $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$) δ -72.36. HRMS (EI) calculated for $C_8H_3O_3N^{35}ClF_3S$: 260.94688 [M]$^+$, Found: 260.94889.



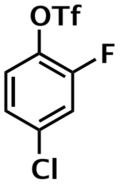
3-Chloro-4-cyanophenyl trifluoromethanesulfonate

The title compound was obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane ($R_f = 0.45$) in 88% yield (2.26 g) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.7 Hz, 1H), 7.50 (d, *J* = 2.4 Hz, 1H), 7.35 (dd, *J* = 8.7, 2.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 151.7, 139.0, 135.6, 123.6, 120.7, 118.6 (q, *J* = 321.1 Hz), 114.5, 113.9. $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$) δ -72.47. HRMS (EI) calculated for $C_8H_3O_3N^{35}ClF_3S$: 284.94688 [M]$^+$, Found: 284.94593.



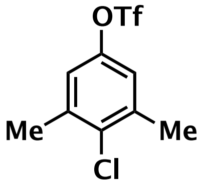
4-Chloro-3-nitrophenyl trifluoromethanesulfonate

The title compound was obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane ($R_f = 0.51$) in 85% yield (2.34 g) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 2.9 Hz, 1H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.49 (dd, *J* = 8.9, 2.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 148.1, 147.1, 133.7, 127.5, 126.3, 119.3, 118.6 (q, *J* = 321.1 Hz). $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$) δ -72.37. HRMS (EI) calculated for $C_7H_3O_5N^{35}ClF_3S$: 304.93671 [M]$^+$, Found: 304.93708.



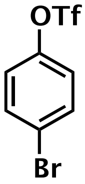
4-Chloro-2-fluorophenyl trifluoromethanesulfonate

The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R$_f$ = 0.52) in 98% yield (2.46 g) as a colourless oil. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.32 – 7.28 (m, 2H), 7.23 - 7.21 (m, 1H). ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ 153.5 (d, J = 257.2 Hz), 135.5 (d, J = 13.6 Hz), 134.9 (d, J = 8.8 Hz), 125.4 (d, J = 3.8 Hz), 124.3, 118.6 (q, J = 320.9 Hz), 118.4 (d, J = 21.3 Hz). ^{19}F{^{1}H} NMR (564 MHz, CDCl$_3$) δ -73.12, -124.13. MS (70 eV, EI): *m/z* (%) 281 (1) ^{37}Cl-[M+H]$^+$, 280 (10) [^{37}Cl-M$^+$], 279 (3) ^{35}Cl-[M+H]$^+$, 278 (27) [^{35}Cl-M$^+$], 214 (9), 148 (3) ^{37}Cl-[Fr+H]$^+$, 147 (35) [^{37}Cl-Fr$^+$], 146 (8) ^{35}Cl-[Fr+H]$^+$, 145 (100) [^{35}Cl-Fr$^+$], 119 (24), 117 (73), 81 (16), 69 (50). The data are in agreement with those previously reported in the literature.[41]



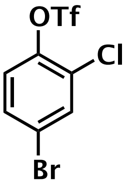
4-Chloro-3,5-dimethylphenyl trifluoromethanesulfonate

The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R$_f$ = 0.65) in 95% yield (2.47 g) as a colourless oil. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.01 (s, 2H), 2.41 (s, 6H). ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ 146.9, 138.7, 134.5, 120.8, 118.7 (q, J = 320.7 Hz), 20.9. ^{19}F{^{1}H} NMR (564 MHz, CDCl$_3$) δ -72.93. MS (70 eV, EI): *m/z* (%) 291 (2) ^{37}Cl-[M+H]$^+$, 290 (21) [^{37}Cl-M$^+$], 289 (6) ^{35}Cl-[M+H]$^+$, 288 (55) [^{35}Cl-M$^+$], 189 (12), 158 (3) ^{37}Cl-[Fr+H]$^+$, 157 (34) [^{37}Cl-Fr$^+$], 156 (9) ^{35}Cl-[Fr+H]$^+$, 155 (100) [^{35}Cl-Fr$^+$], 129 (23), 127 (60), 91 (47), 69 (18), 65 (12). The data are in agreement with those previously reported in the literature.[9]



3-Chloro-4-cyanophenyl trifluoromethanesulfonate

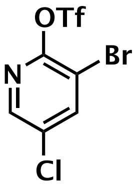
The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R$_f$ = 0.52) in 94% yield (2.58 g) as a colourless oil. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.59 – 7.57 (m, 2H), 7.18 – 7.15 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) 148.5, 133.4, 123.1, 122.0, 118.7 (q, J = 320.8 Hz). ^{19}F{^{1}H} NMR (564 MHz, CDCl$_3$) δ -72.73. MS (70 eV, EI): *m/z* (%): 306 (44) [^{81}Br-M$^+$], 304 (42) [^{79}Br-M$^+$], 173 (98), 171 (100), 143 (71), 145 (69), 69 (44), 63 (47). The data are in agreement with those previously reported in the literature.[2]



4-Bromo-2-chlorophenyl trifluoromethanesulfonate

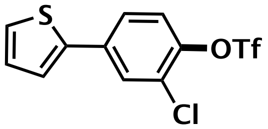
The title compound was obtained after purification using flash column chromatography on silica gel using hexane (R$_f$ = 0.50) in 88% yield (2.69 g) as a colourless oil. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.70 (d, J = 2.3 Hz, 1H), 7.48 (dd, J = 8.8, 2.3 Hz, 1H), 7.26 – 7.23 (m, 1H). ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ 144.8, 133.9, 131.5, 128.5, 124.2 122.1, 118.5 (q, J = 320.6 Hz). ^{19}F{^{1}H} NMR (564 MHz, CDCl$_3$) δ -73.28. MS (70 eV, EI): *m/z* (%) 342 (15) [^{37}Cl-^{81}Br-M$^+$], 340 (52) [^{35}Cl-^{81}Br-M$^+$] + [^{37}Cl-^{79}Br-M$^+$], 338 (39) [^{35}Cl-^{79}Br-M$^+$], 209 (25) [^{37}Cl-^{81}Br-Fr$^+$], 207 (100)

[^{35}Cl-^{81}Br-Fr^{+}] + [^{37}Cl-^{79}Br-Fr^{+}], 205 (80) [^{35}Cl-^{79}Br-Fr^{+}], 181 (16), 179 (64), 177 (49), 98 (10), 97 (9), 69 (49), 63 (48), 62 (21). The data are in agreement with those previously reported in the literature.[2]



3-Bromo-5-chloropyridin-2-yl trifluoromethanesulfonate

The title compound was obtained after purification using flash column chromatography on silica gel using 10% ethyl acetate in hexane (R_f = 0.67) in 85% yield (2.85 g) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 2.3 Hz, 1H), 8.08 (d, *J* = 2.3 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 151.2, 145.5, 143.4, 132.3, 118.4 (q, *J* = 320.8 Hz), 111.5. ^{19}F{^{1}H} NMR (564 MHz, $CDCl_3$) δ -72.89.MS (70 eV, EI): *m/z* (%) 343 (10) [^{37}Cl-^{81}Br-M^{+}],341 (37) [^{35}Cl-^{81}Br-M^{+}] and [^{37}Cl-^{79}Br-M^{+}], 339 (28) [^{35}Cl-^{79}Br-M^{+}], 277 (13), 251 (23), 249 (95), 247 (74), 198 (18), 196 (55), 182 (22), 180 (92), 153 (39), 127 (14), 72 (34), 69 (100), 64 (29). The data are in agreement with those previously reported in the literature.[2]

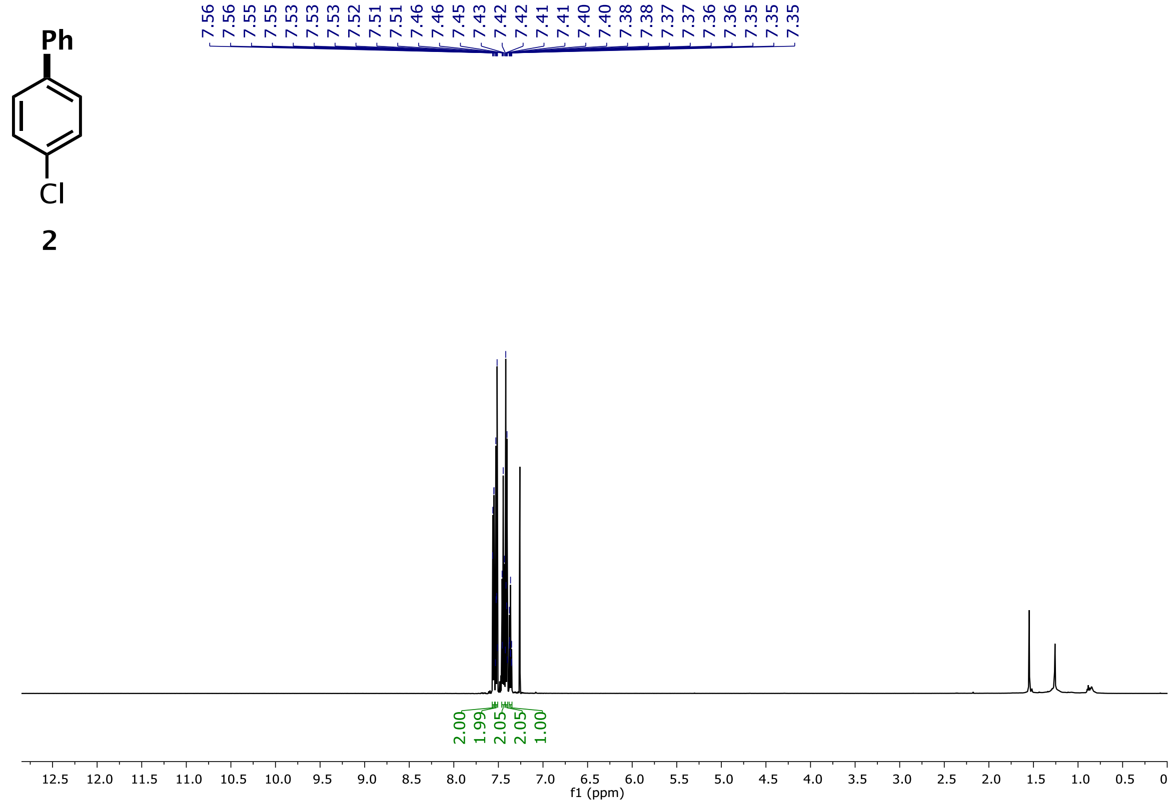


2-Chloro-4-(thiophen-2-yl)phenyl trifluoromethanesulfonate

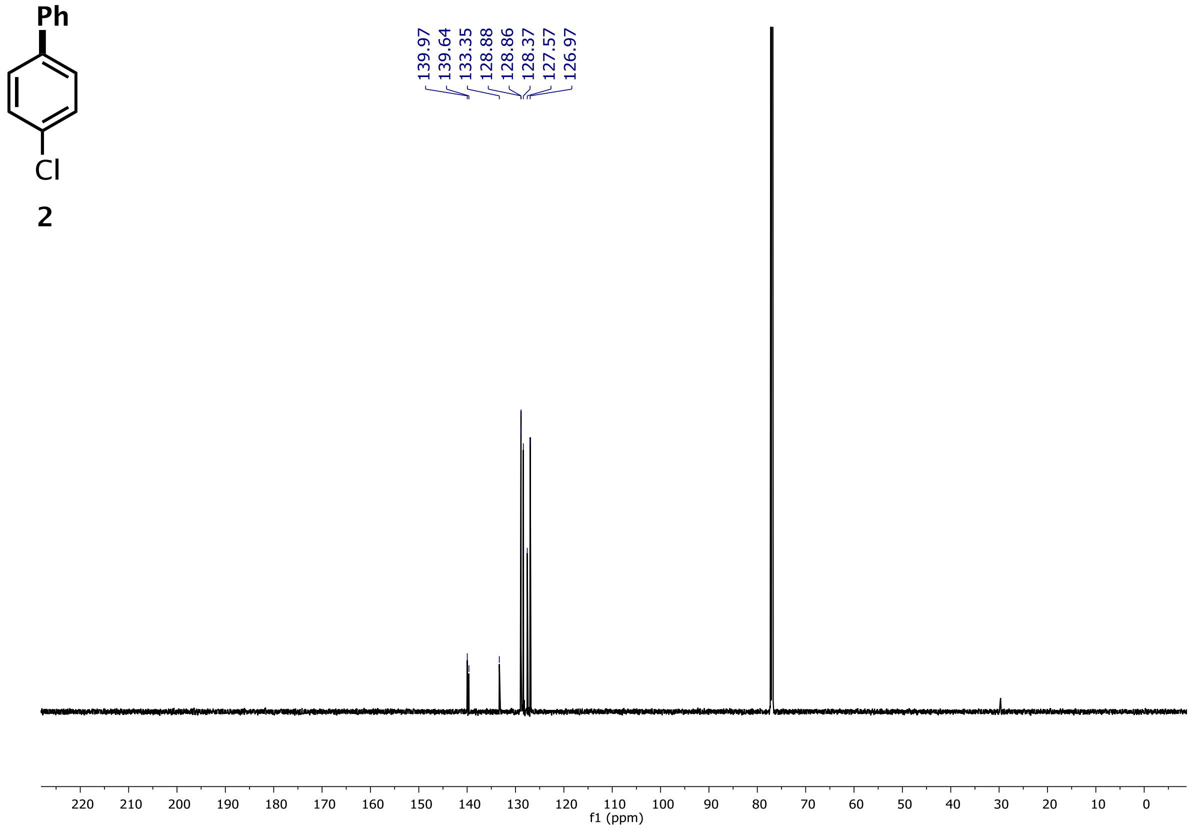
To a solution of 4-bromo-2-chlorophenyl trifluoromethanesulfonate (137 mg, 0.4 mmol, 1.0 equiv.) and the Pd$^{(I)}$-I-dimer **1** (8.7 mg, 0.01 mmol, 0.025 equiv.) in THF, phenyl-MgCl (1M in THF, 0.6 ml, 0.6 mmol, 1.5 equiv.) was added and stirred for 5 minutes. The title compound was then obtained after purification using flash column chromatography on silica gel using hexane ($R_f = 0.23$) in 90% yield (123.4 mg) as a green liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 2.2 Hz, 1H), 7.54 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.38 – 7.33 (m, 3H), 7.11 (dd, *J* = 4.9, 3.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) 144.4, 140.7, 135.9, 128.4, 128.1, 127.7, 126.7, 125.4, 124.9, 123.3, 118.60 (q, *J* = 320.6 Hz). $^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$) δ -73.33. HRMS (EI) calculated for $C_{11}H_6O_3{}^{35}ClF_3S_2$: 341.93935 $[M]^+$, Found: 341.93874.

Spectra

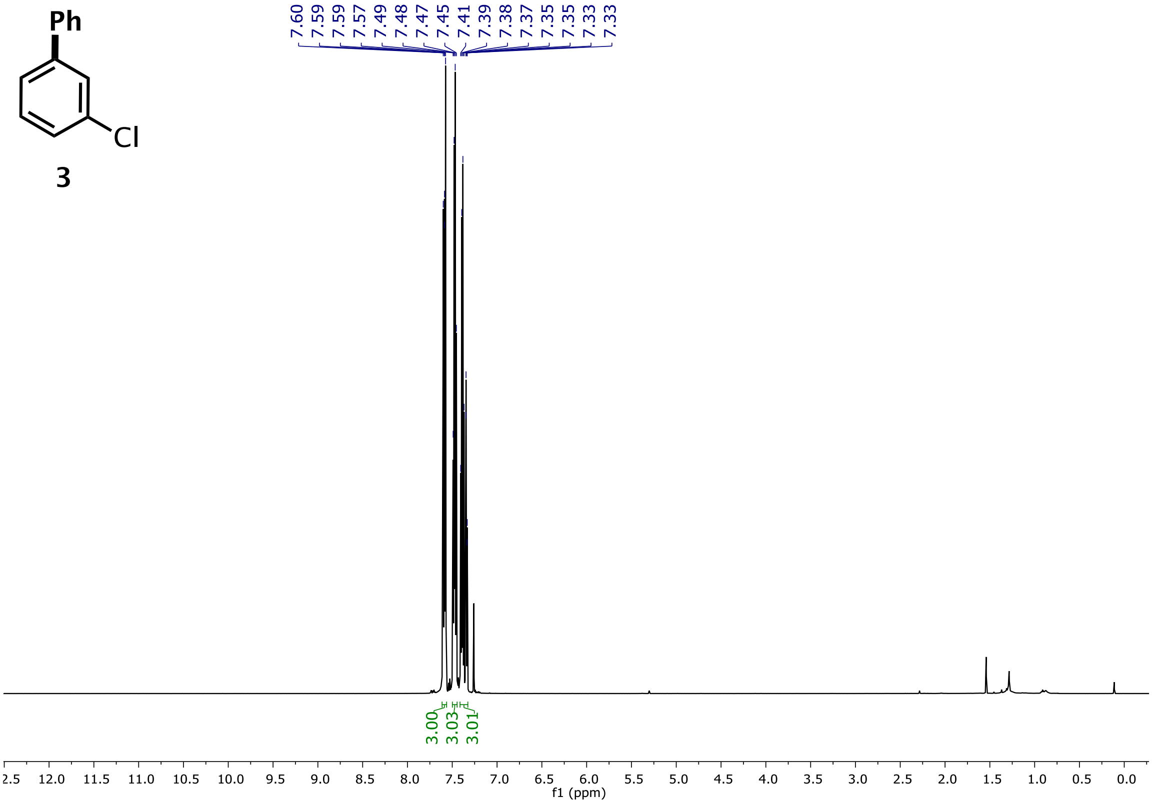
^{1}H (600 MHz, $CDCl_3$)



$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



^{1}H (600 MHz, CDCl$_3$)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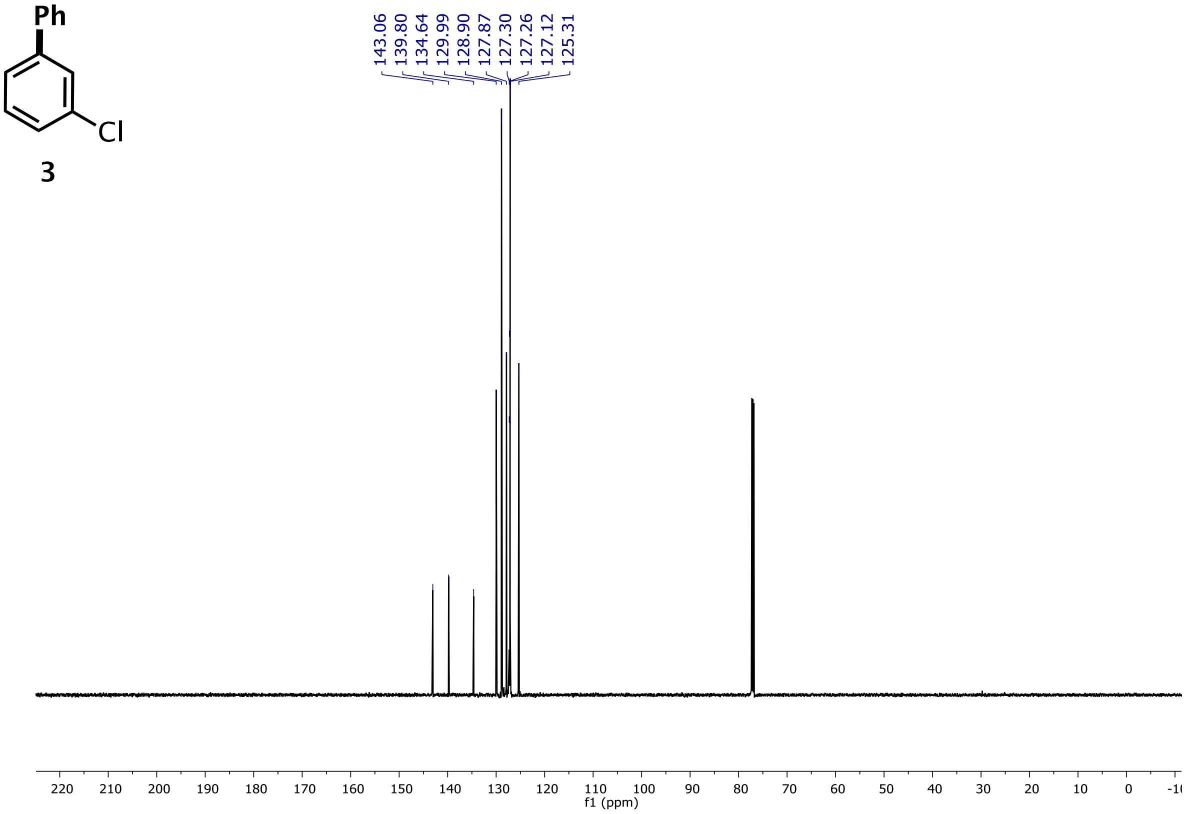
^{13}C{^{1}H} (151 MHz, CDCl$_3$)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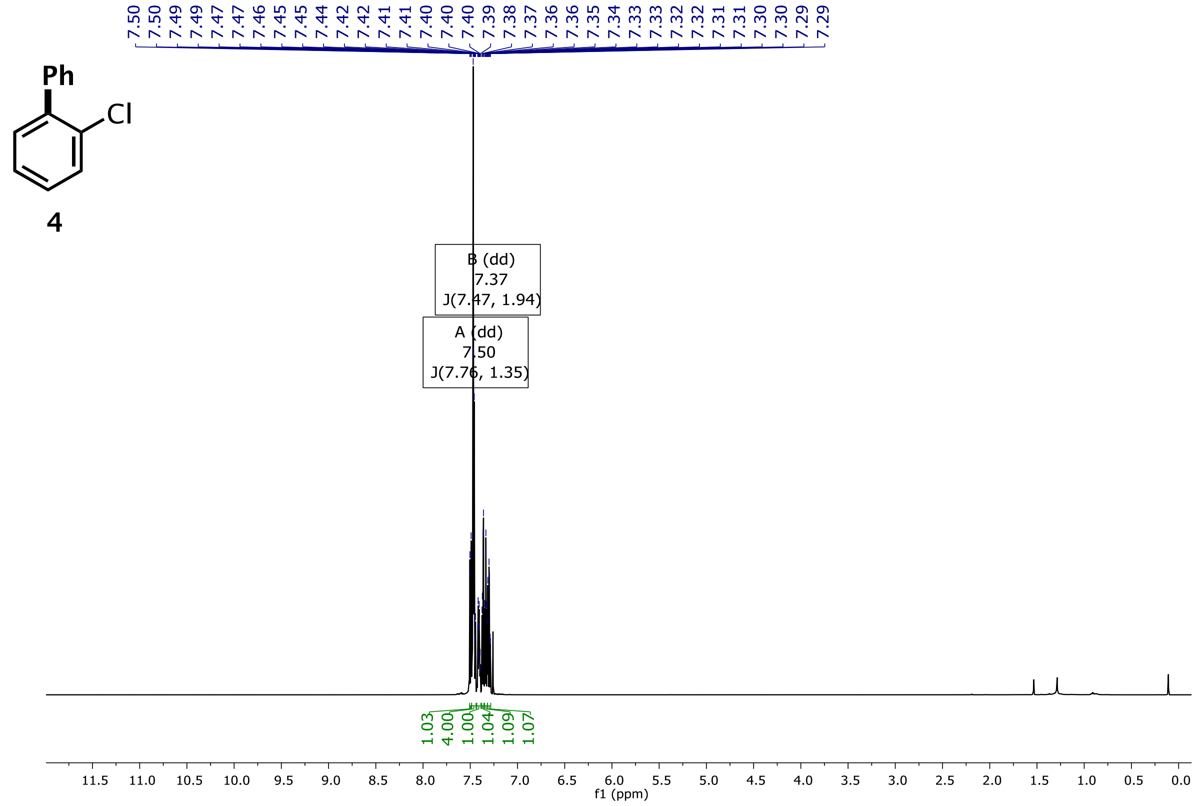
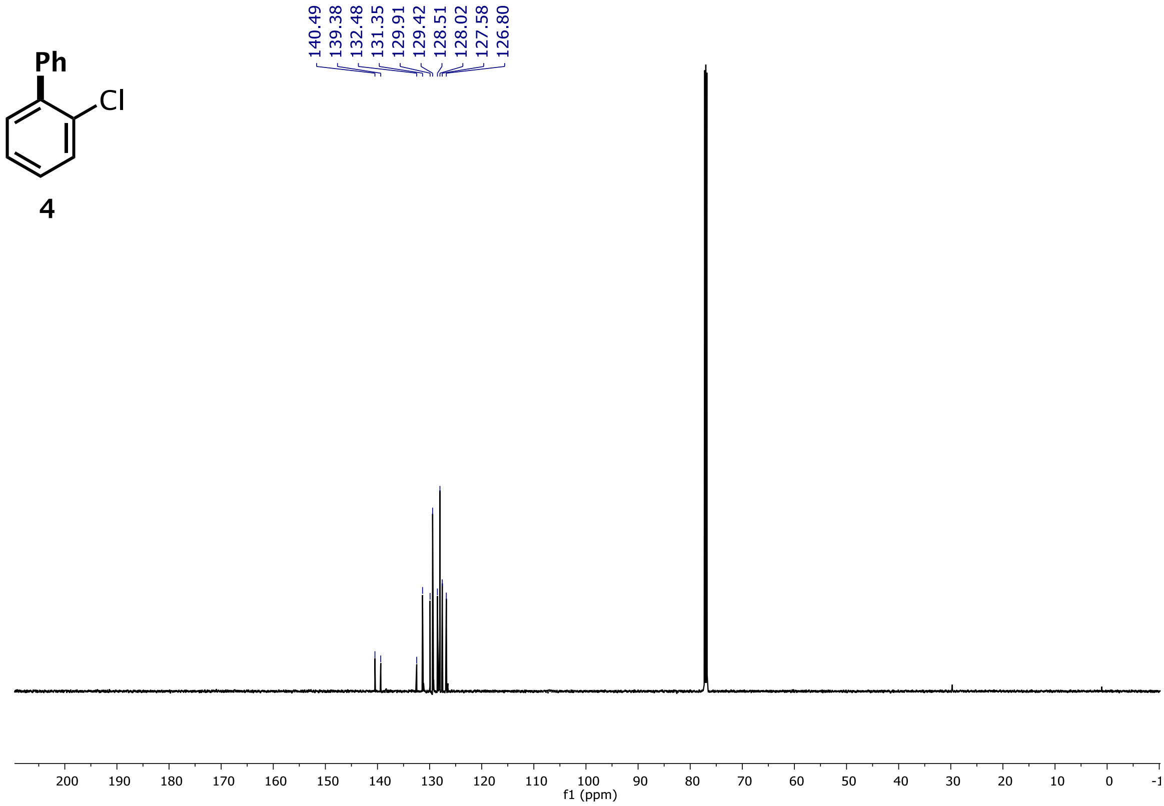
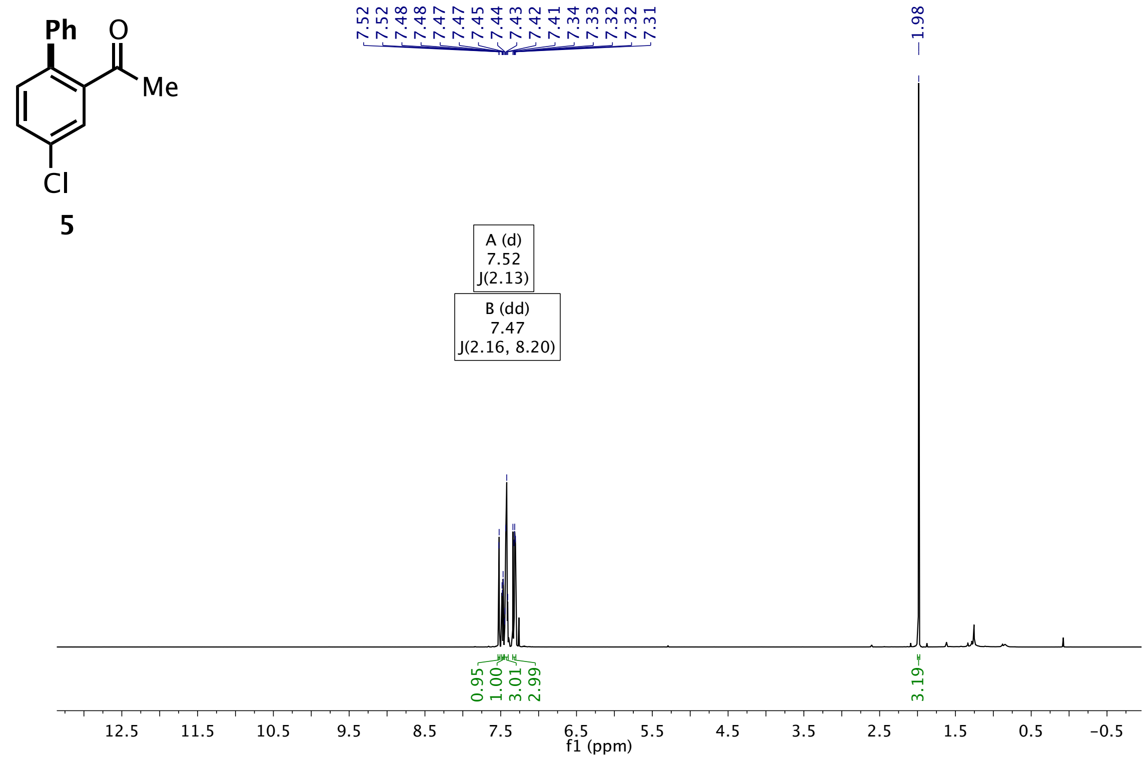
^{1}H (600 MHz, CDCl$_3$)



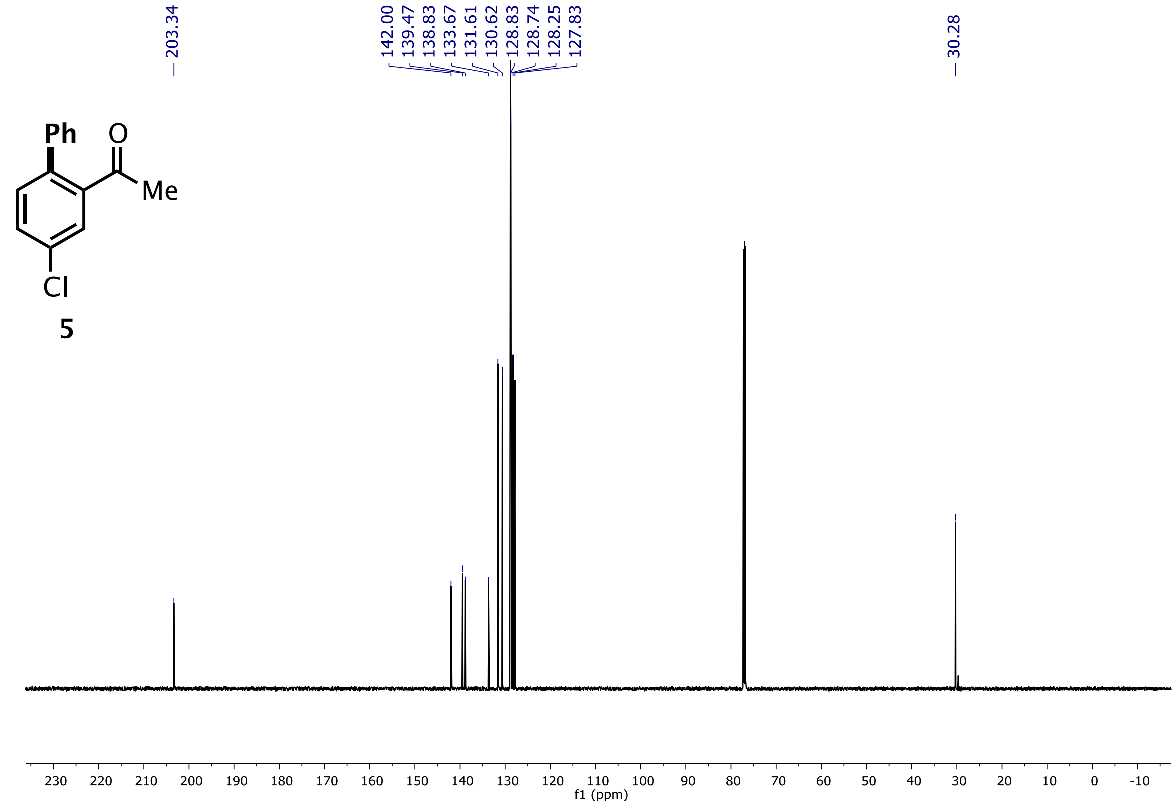
^{13}C{^{1}H} (151 MHz, CDCl$_3$)



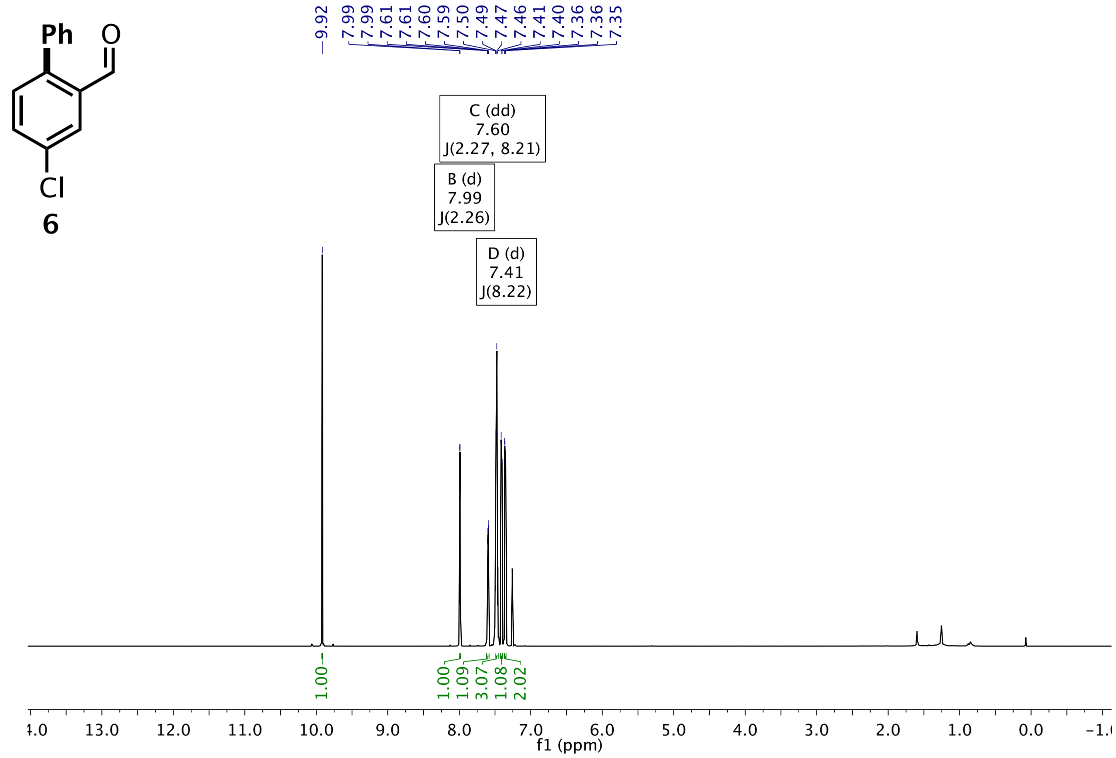
^1H (600 MHz, $CDCl_3$)



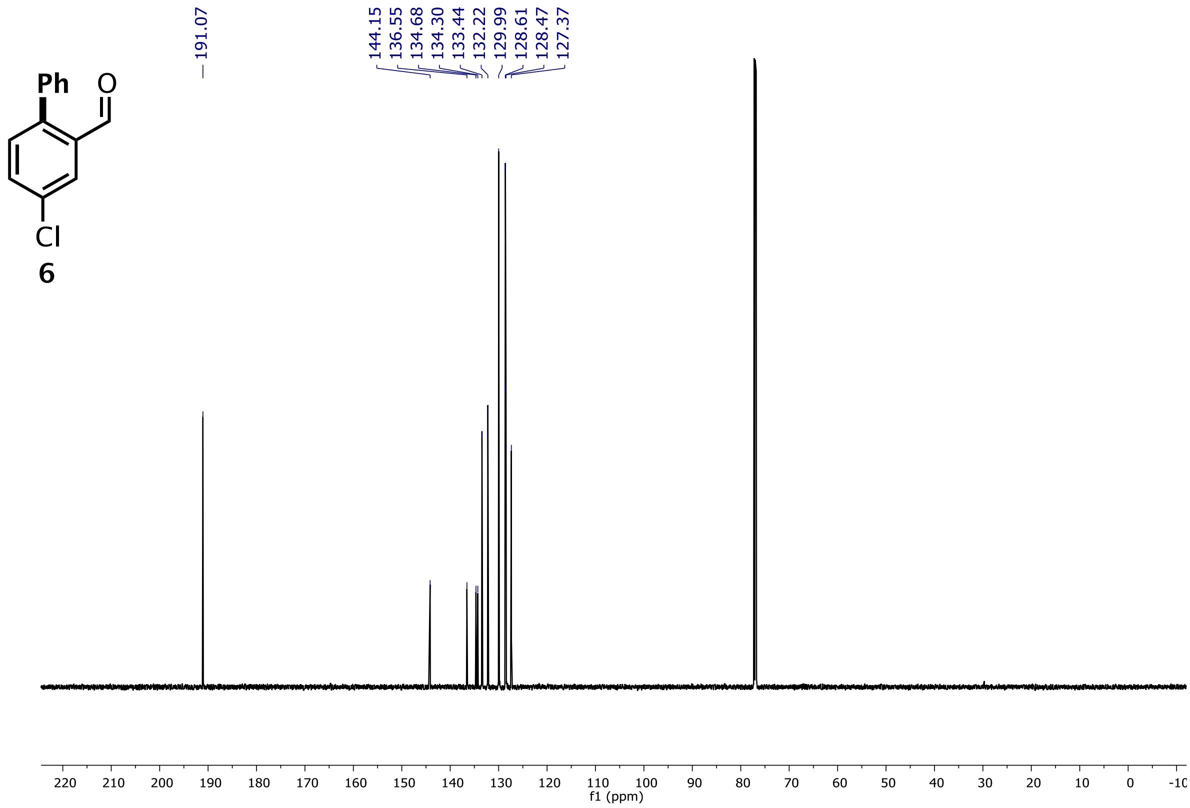
$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



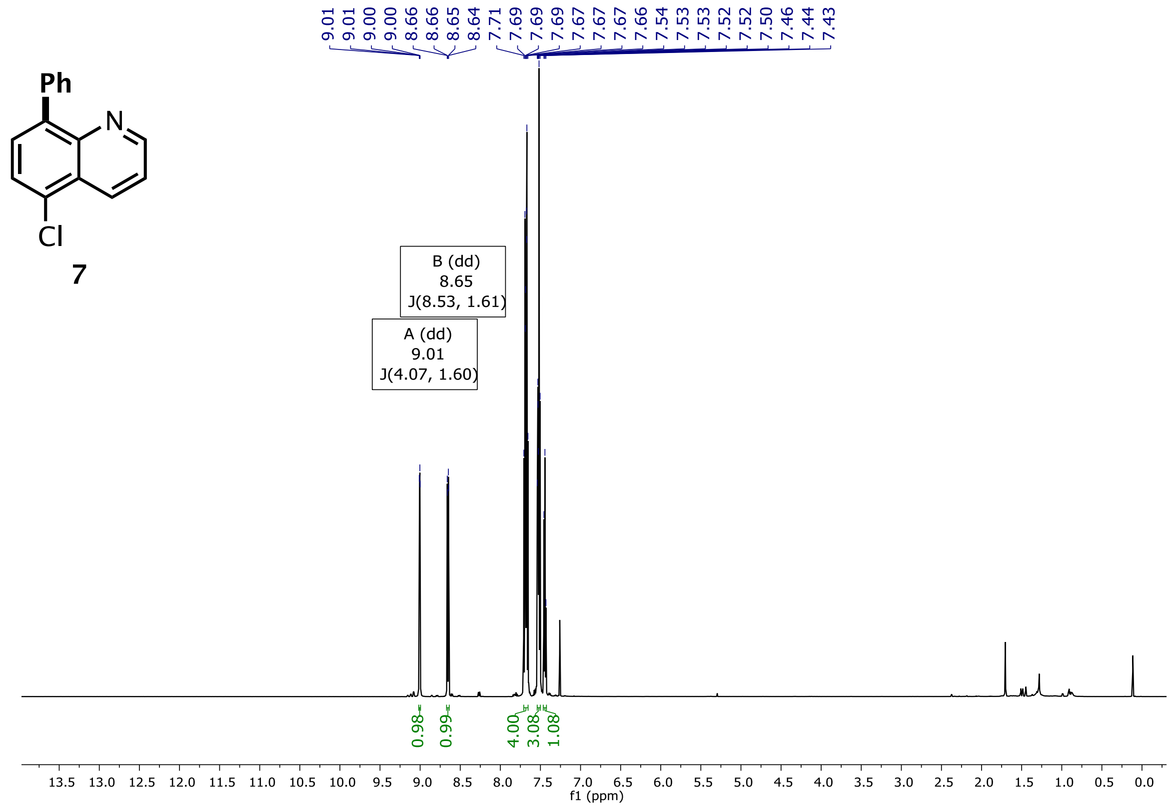
^{1}H (600 MHz, CDCl$_3$)



^{13}C{^{1}H} (151 MHz, CDCl$_3$)



^{1}H (600 MHz, CDCl$_3$)



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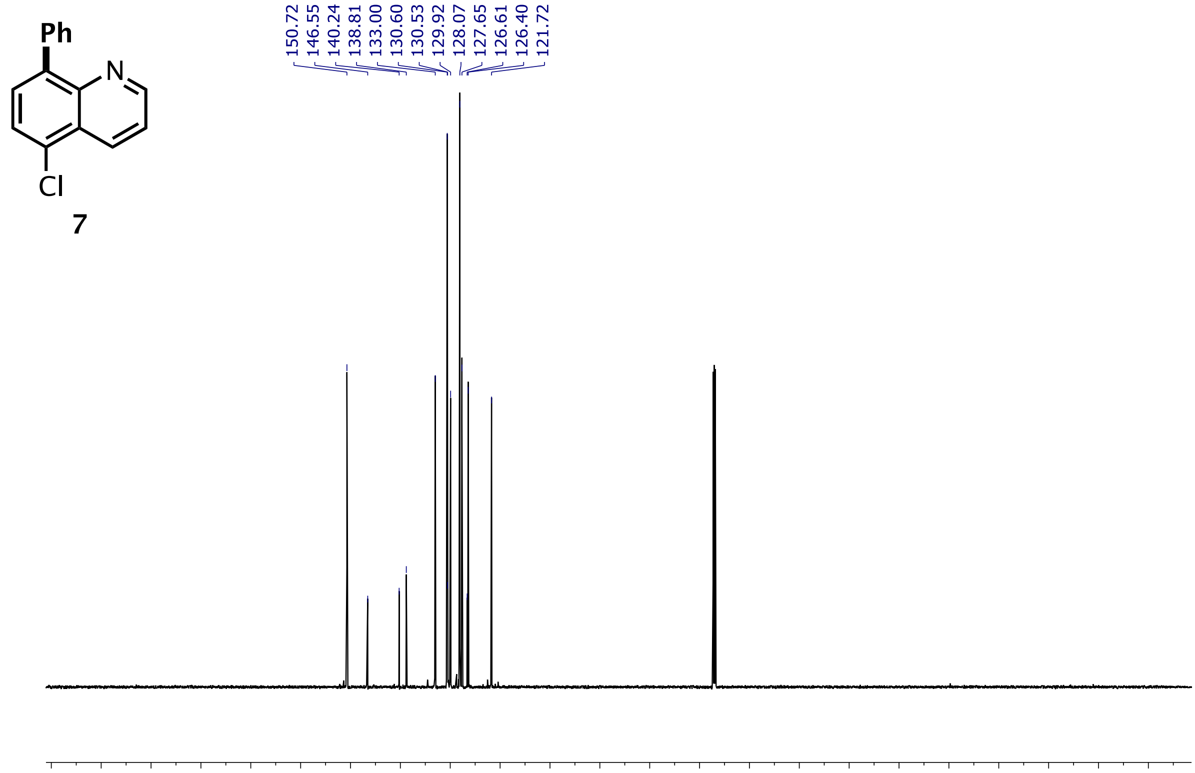
^{13}C{^{1}H} (151 MHz, CDCl$_3$)



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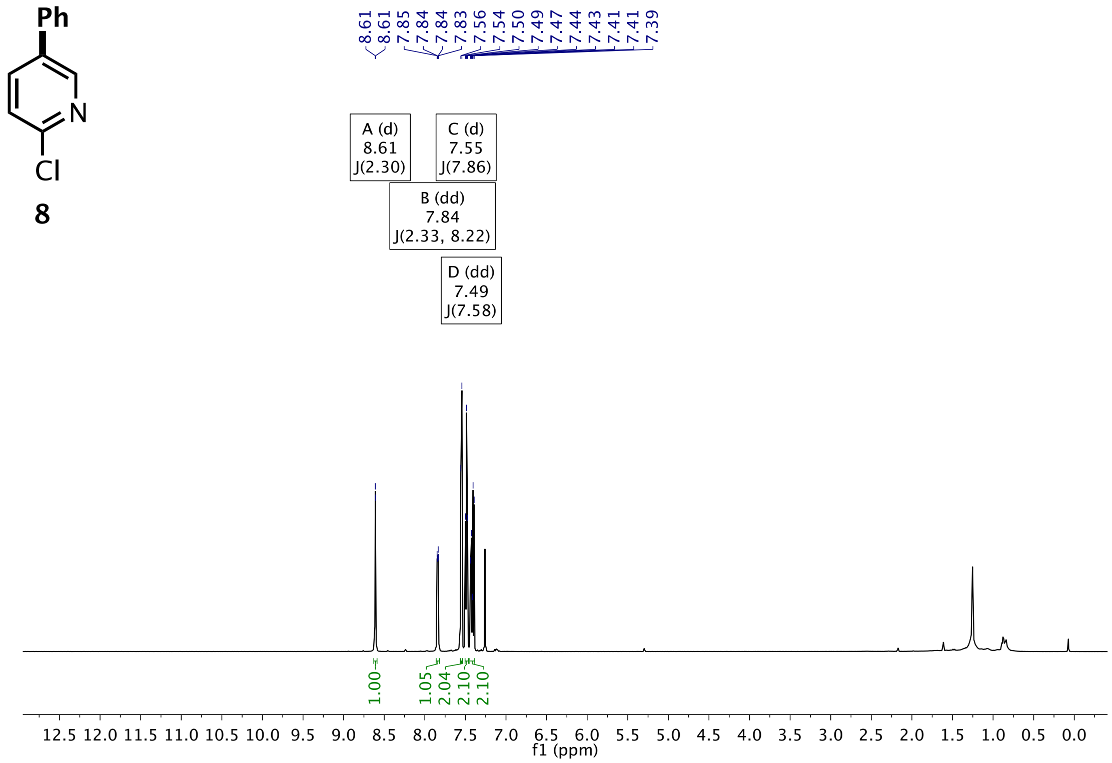
^{1}H (600 MHz, CDCl$_3$)



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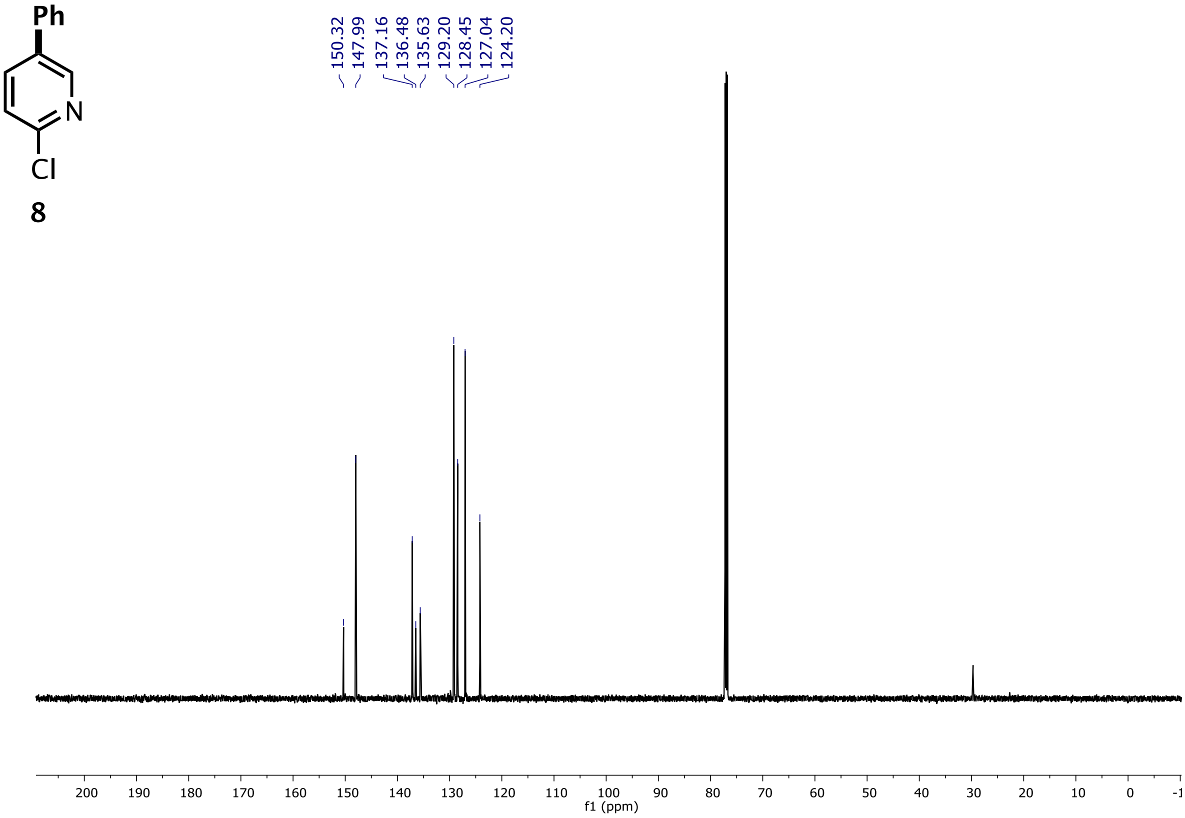

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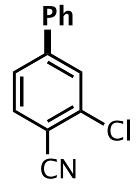

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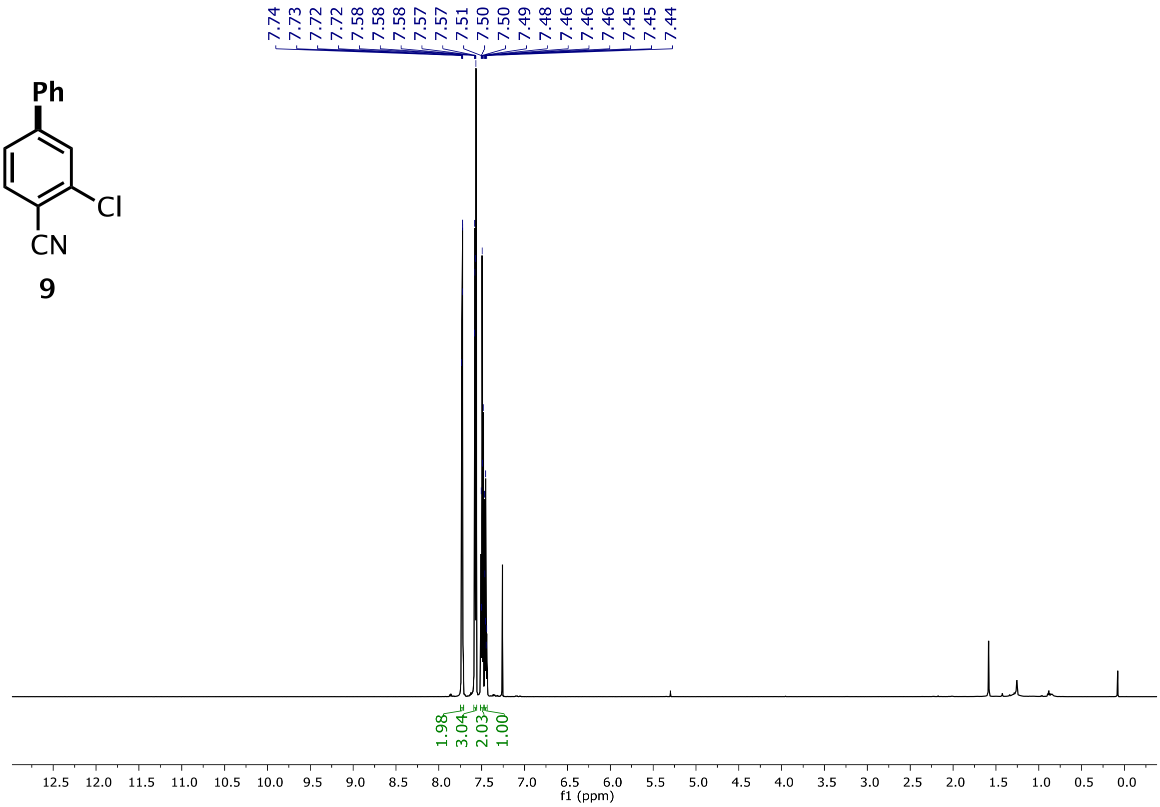
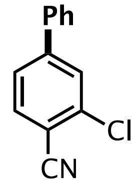


$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)



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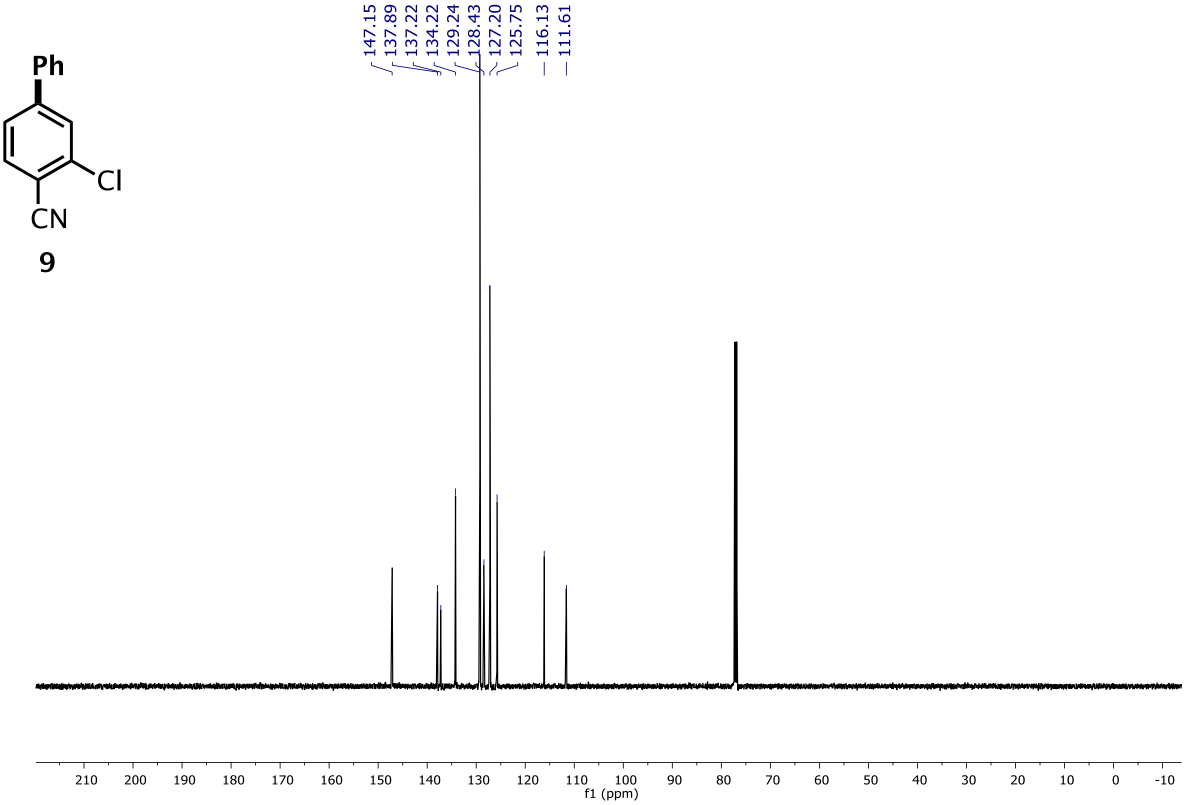
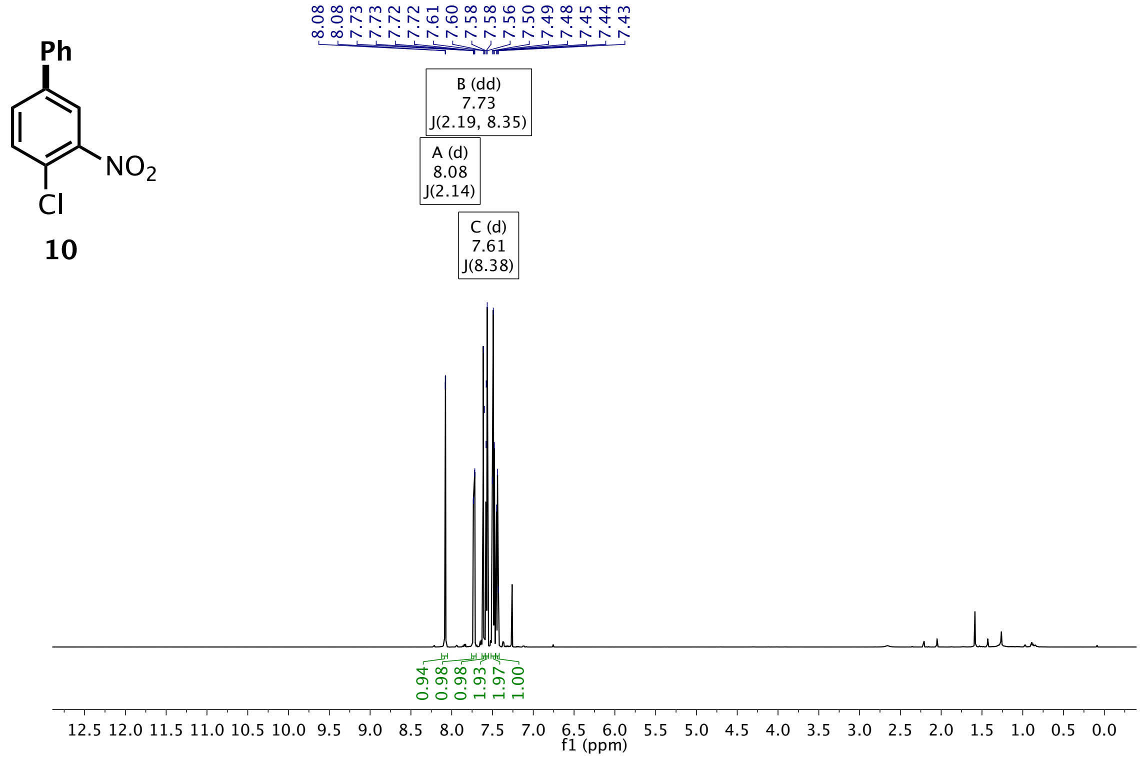
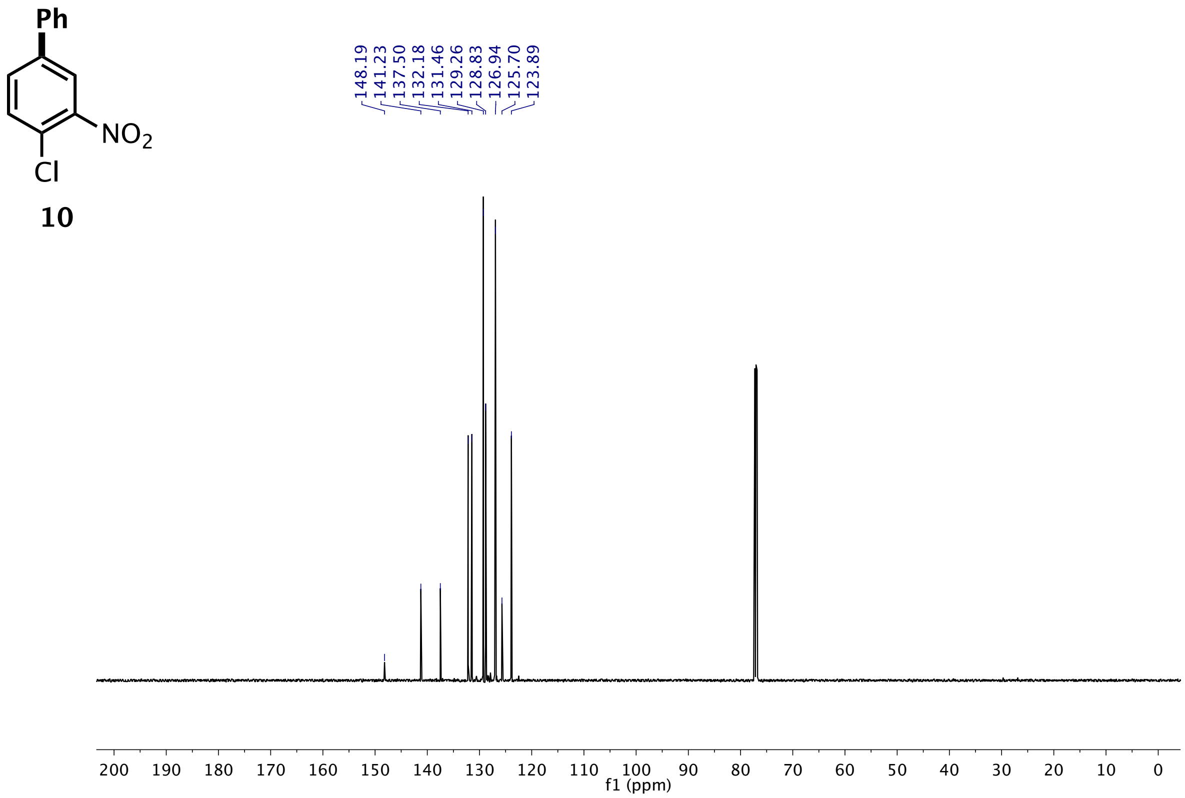


^{1}H (600 MHz, CDCl$_3$)



^{13}C{^{1}H} (151 MHz, CDCl$_3$)



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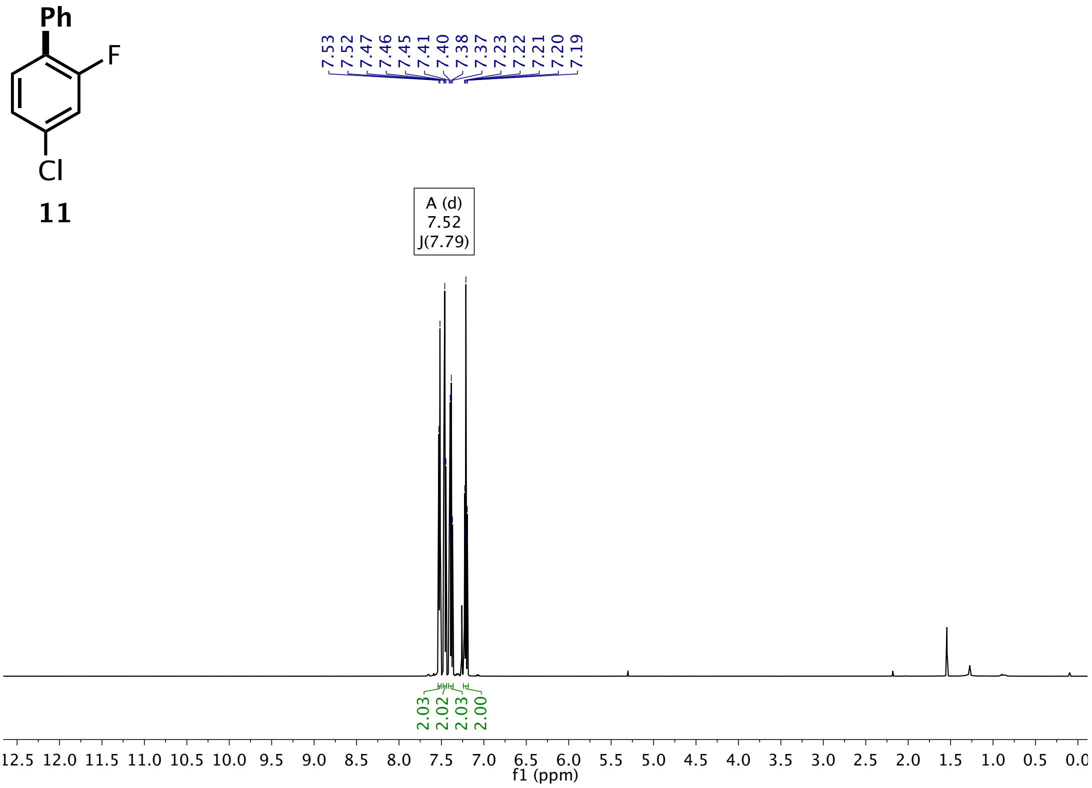
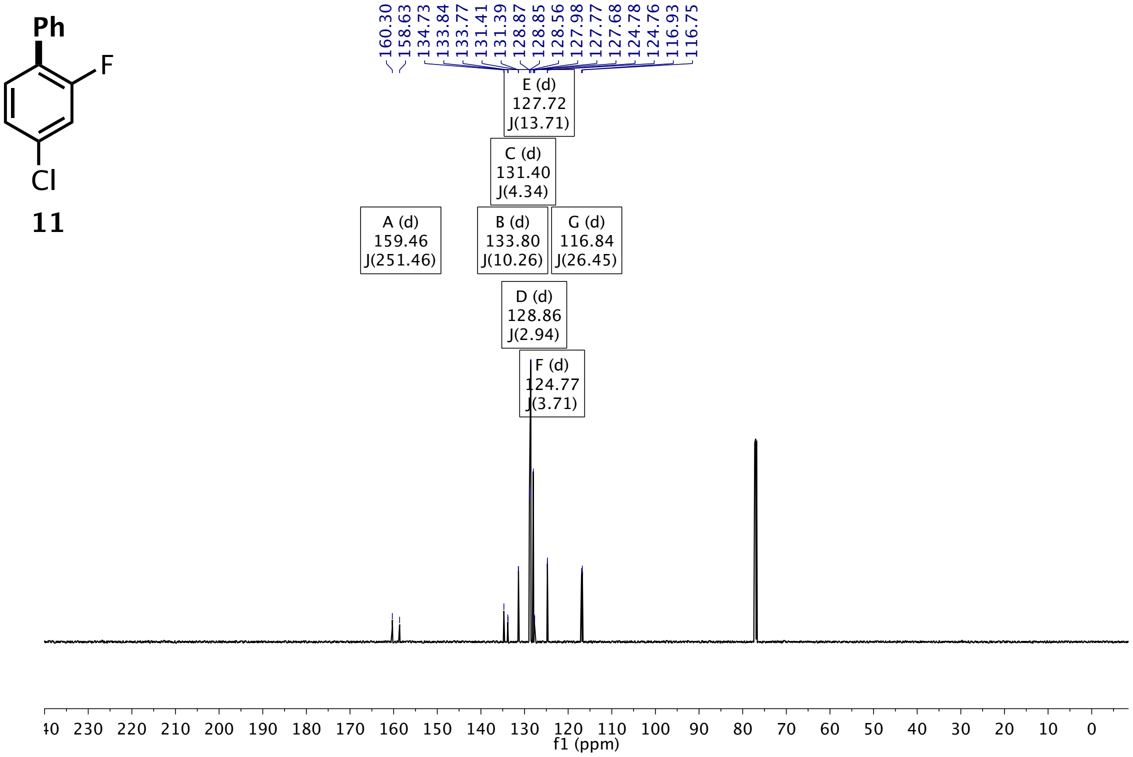
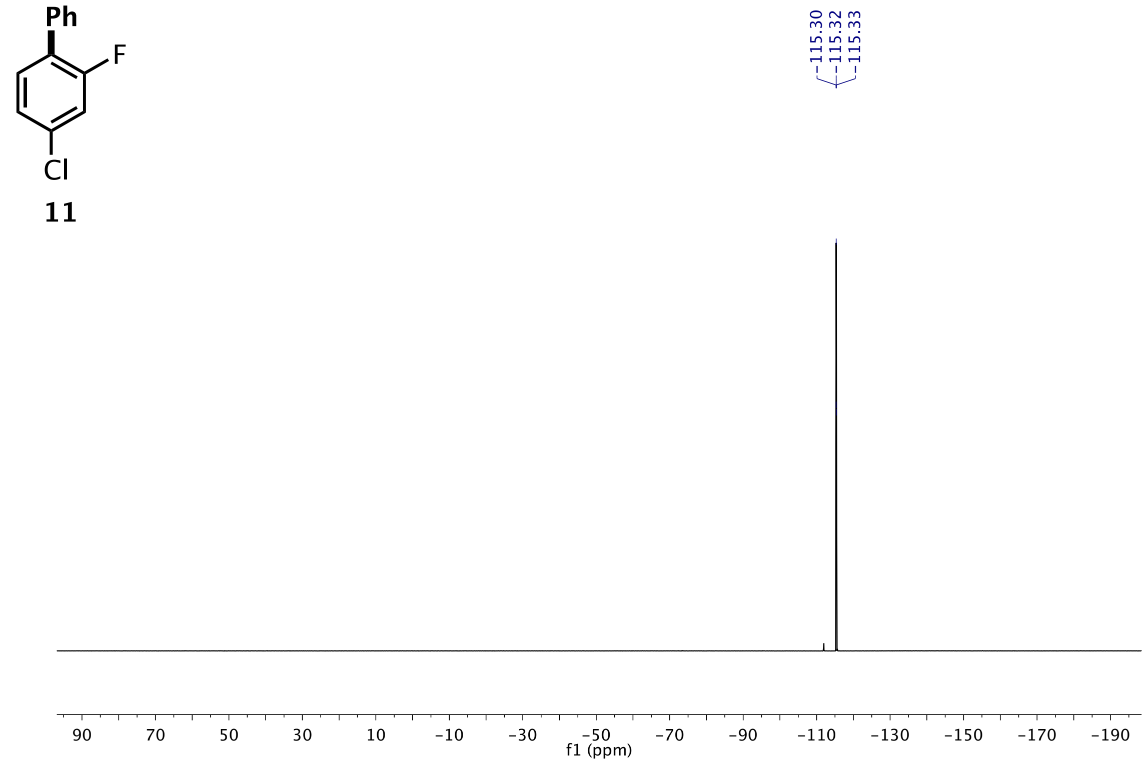


^{13}C{^{1}H} (151 MHz, CDCl$_3$)

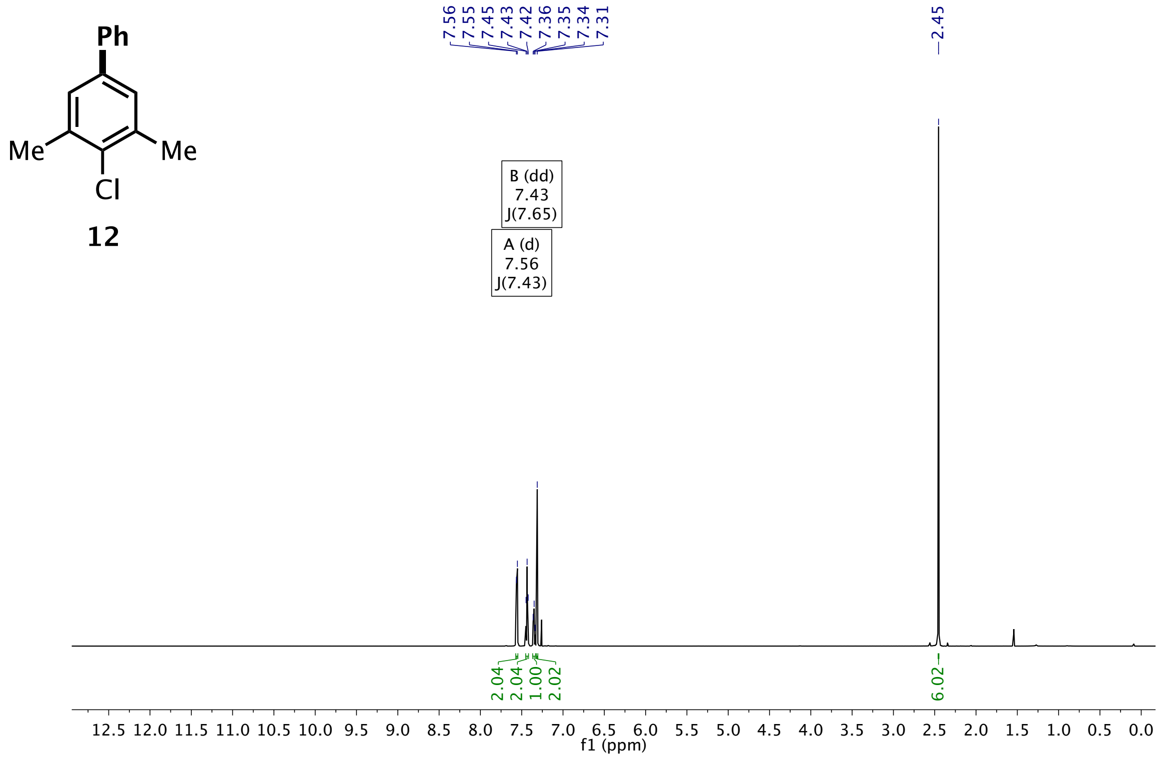


$^{19}F\{^{1}H\}$ (564 MHz, $CDCl_3$)



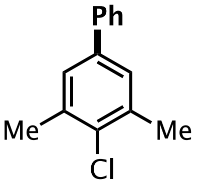
11

^{1}H (600 MHz, $CDCl_3$)



12

$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



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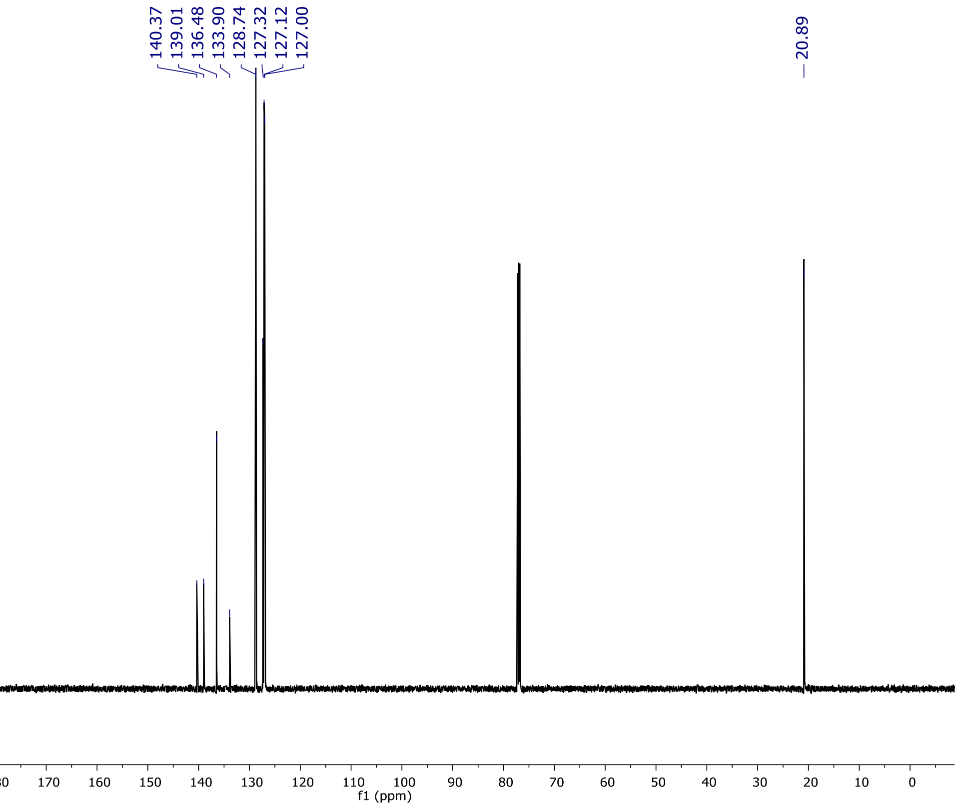
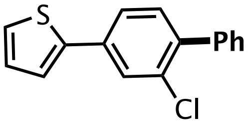


^1H (600 MHz, $CDCl_3$)



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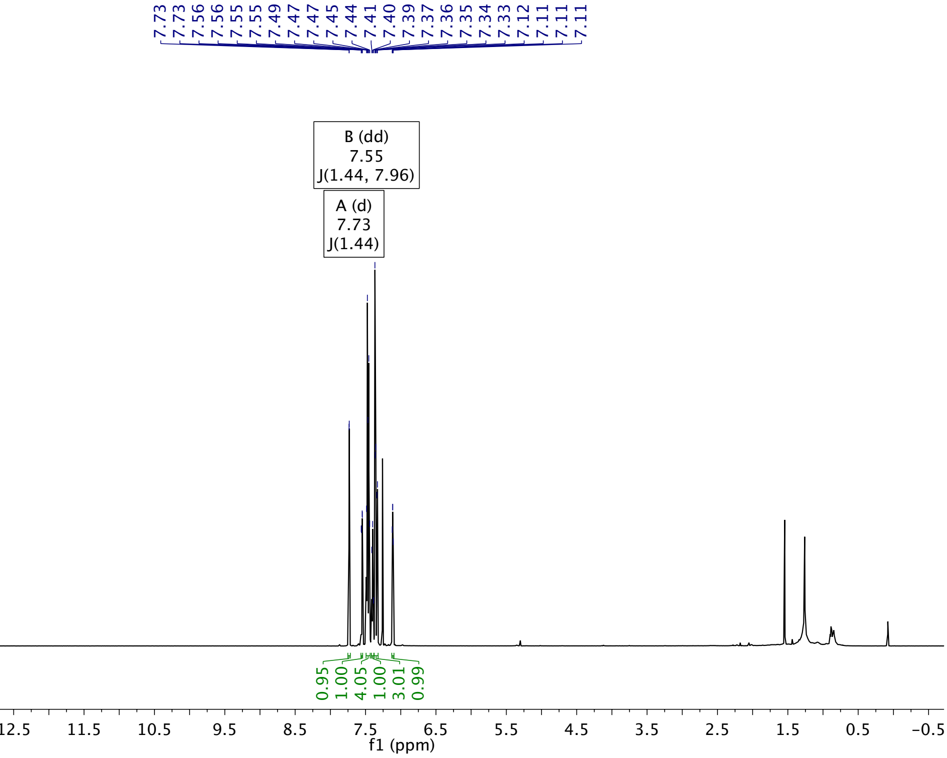
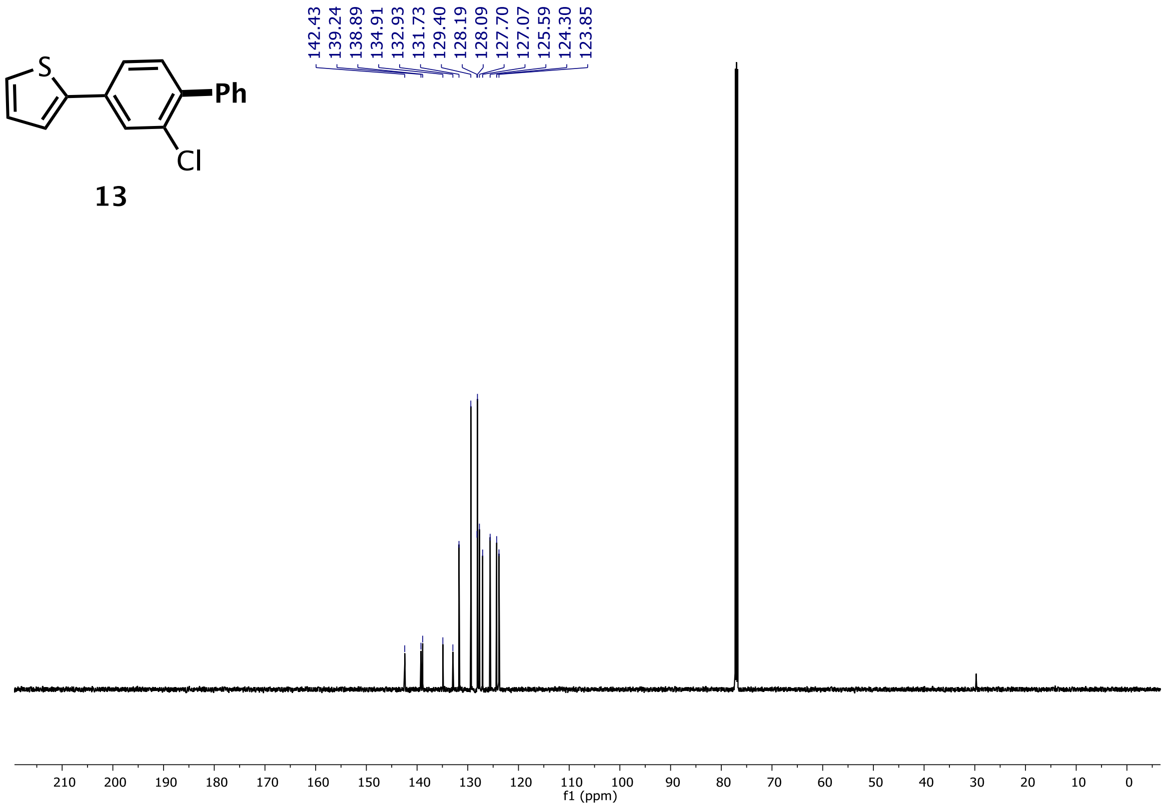


$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



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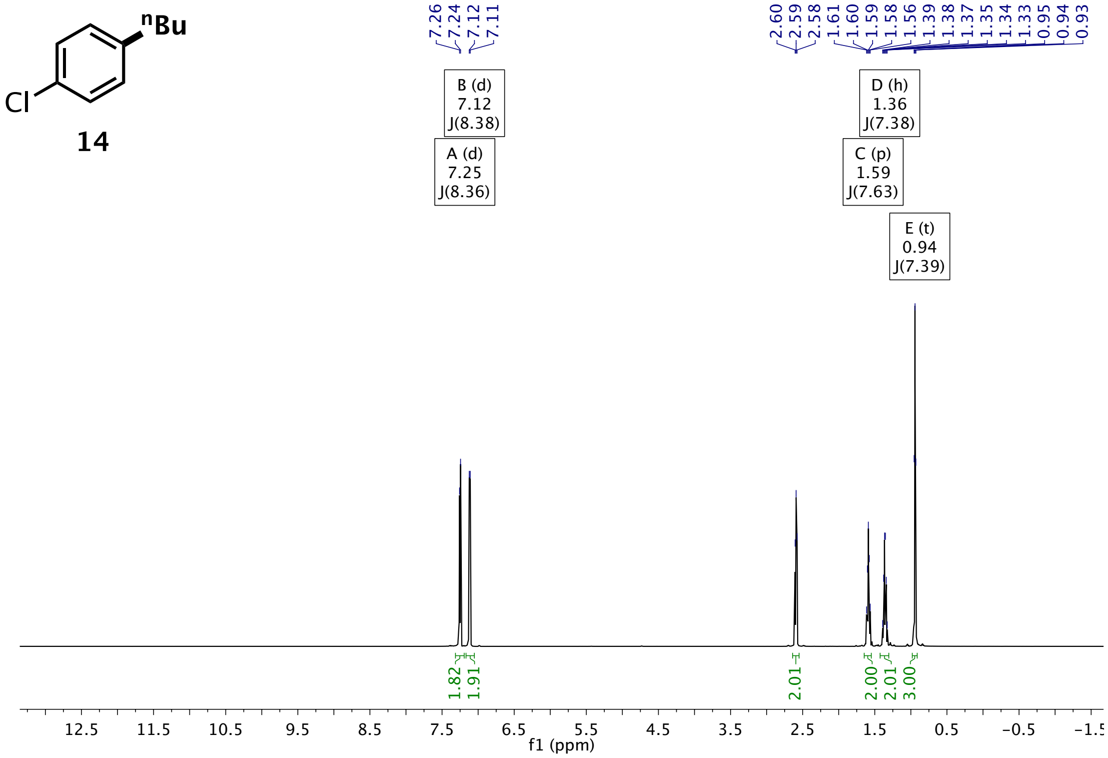
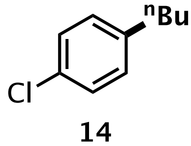
^1H (600 MHz, $CDCl_3$)



14

$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



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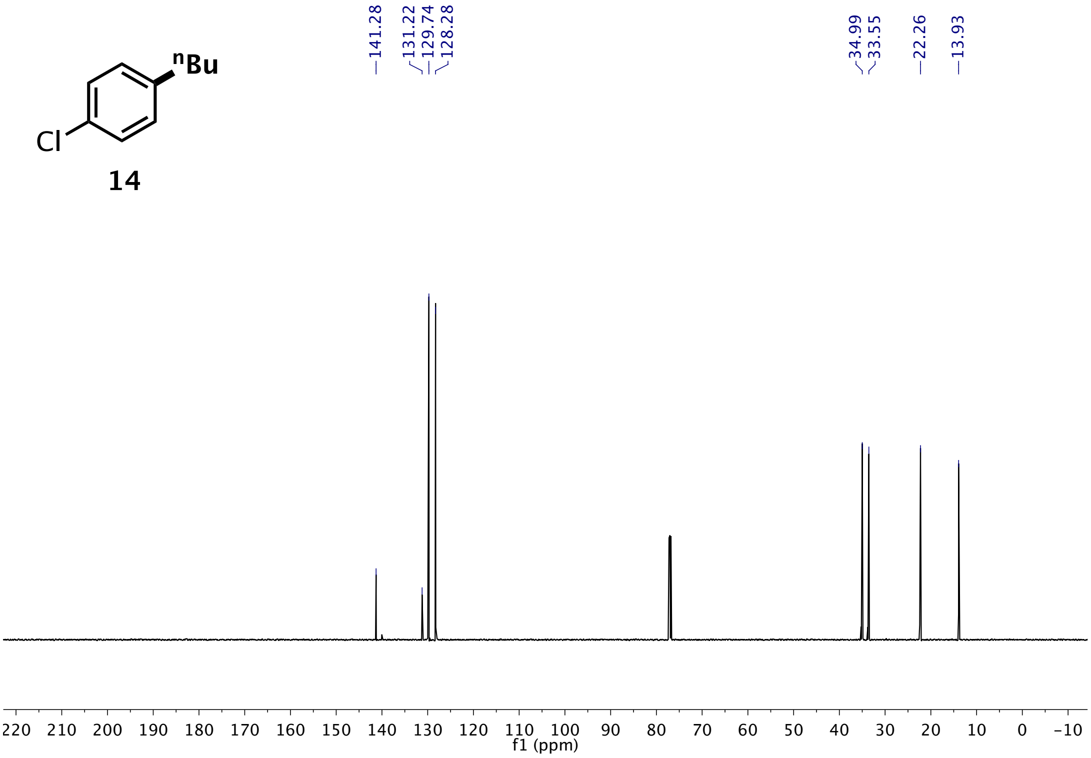
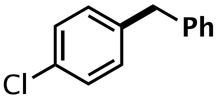


^1H (600 MHz, $CDCl_3$)



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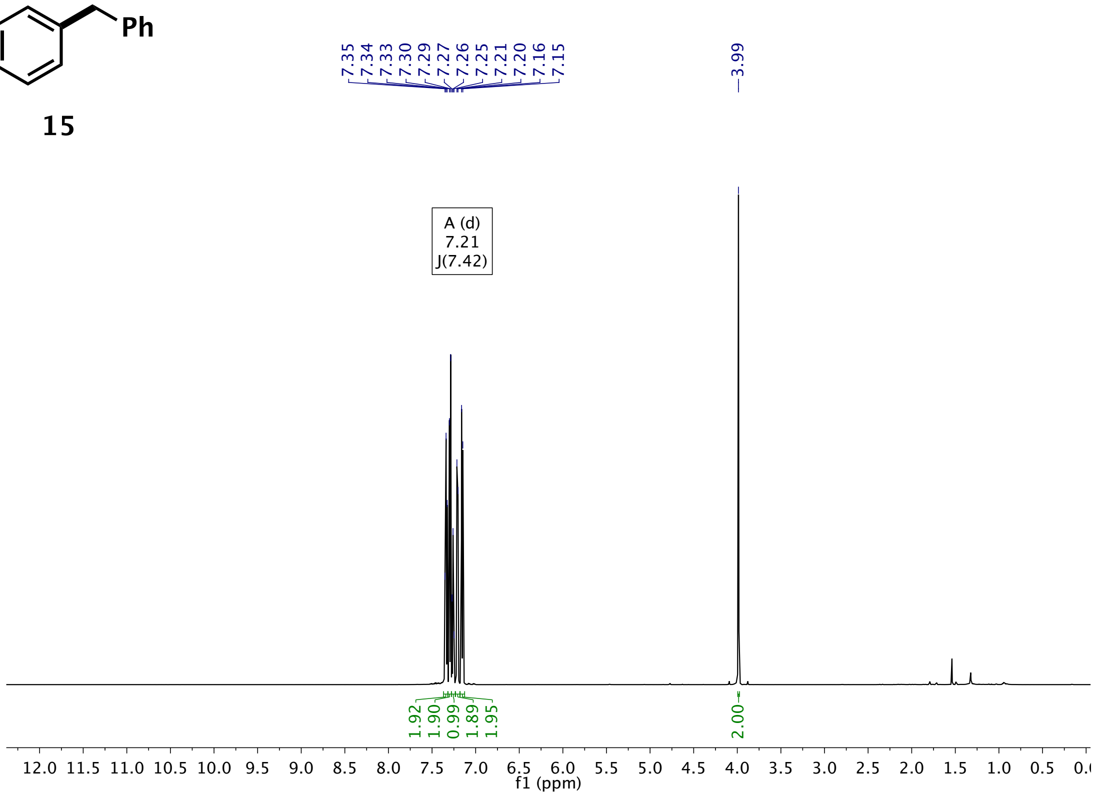
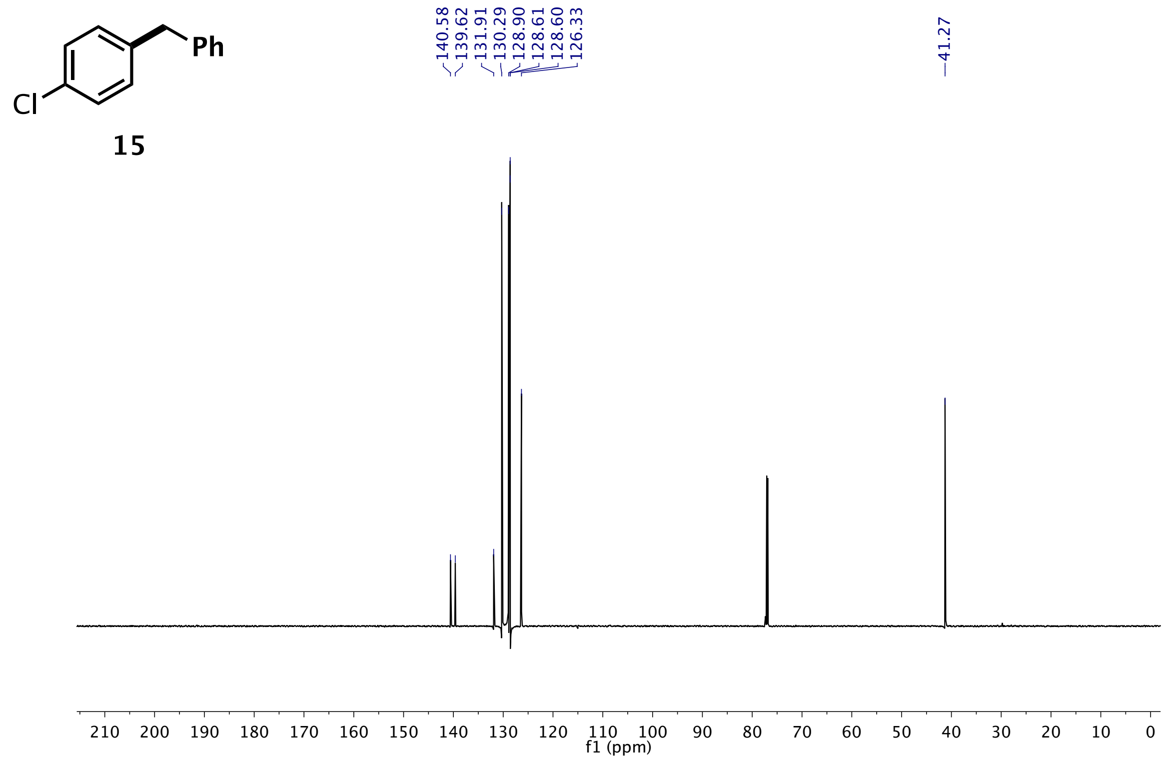


^{13}C{^{1}H} (151 MHz, CDCl$_3$)



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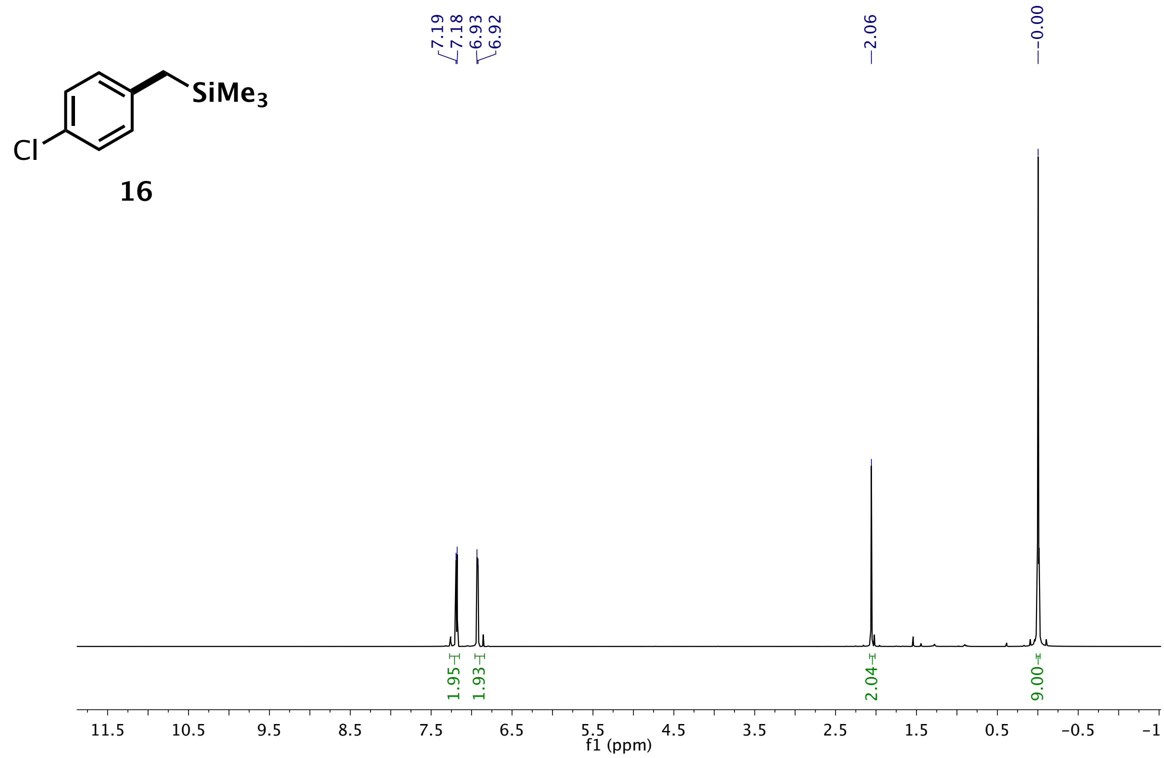
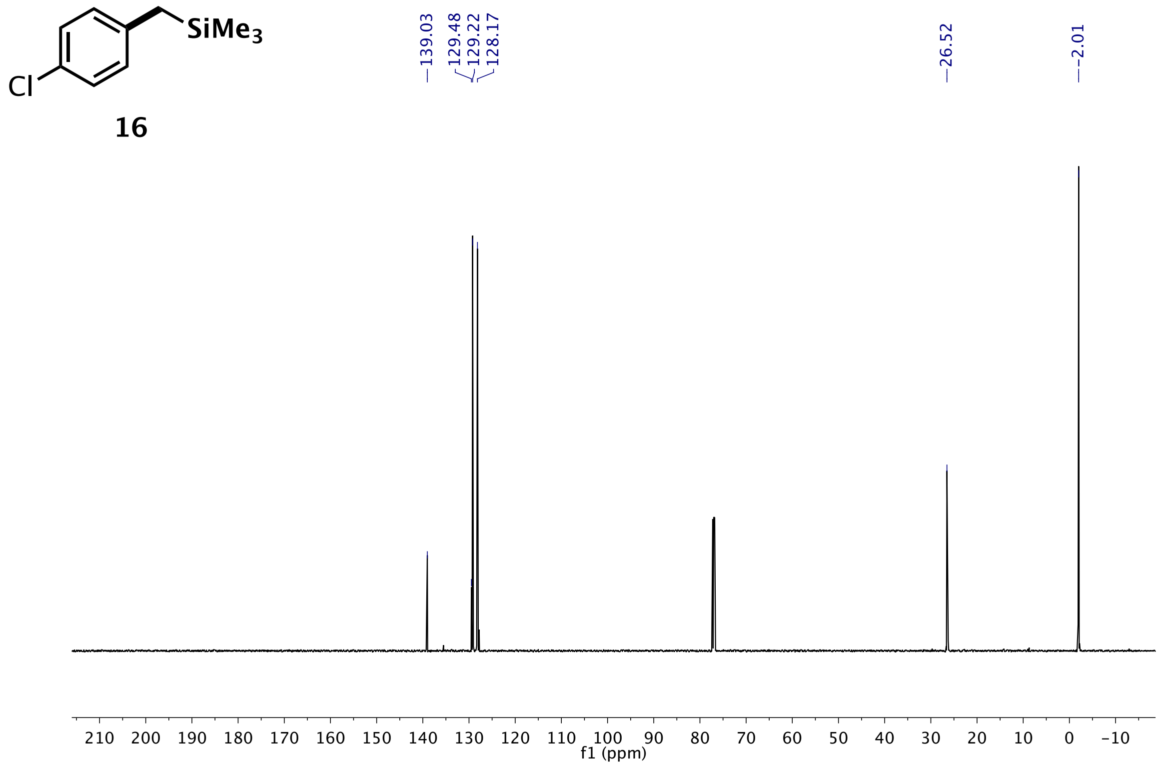


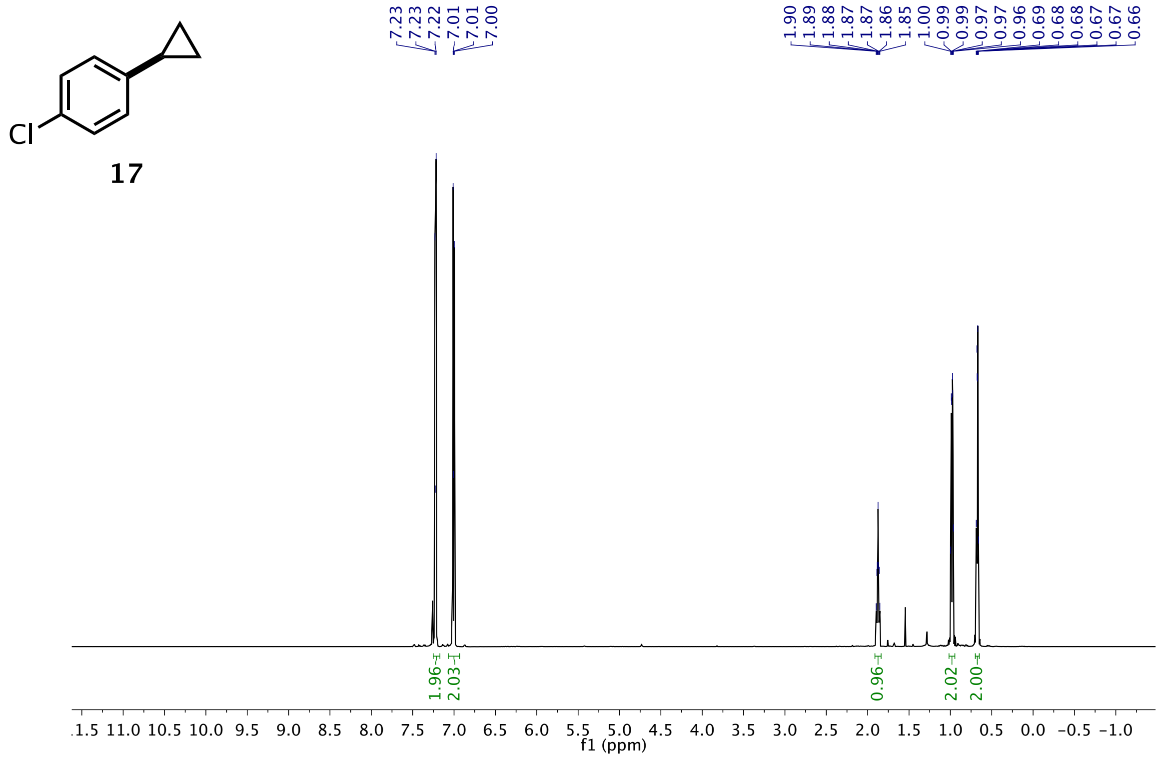
16

$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)



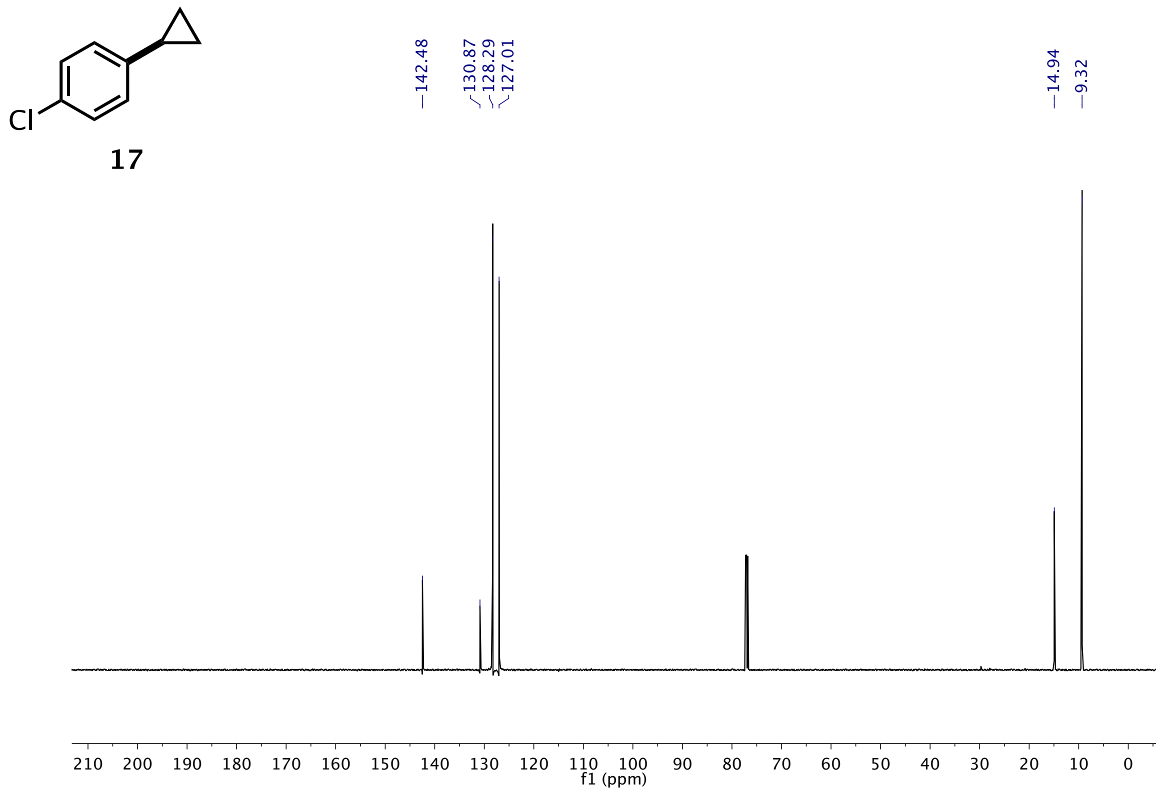
16

^{1}H (600 MHz, $CDCl_3$)



17

$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)



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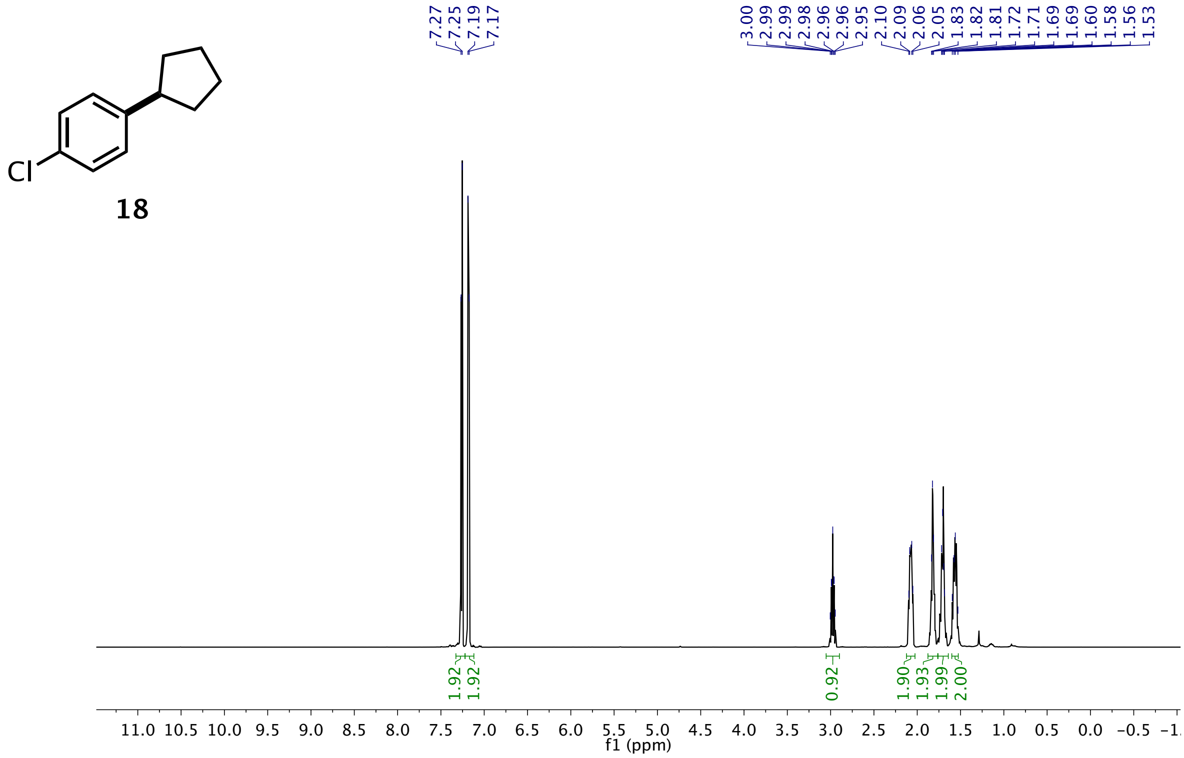

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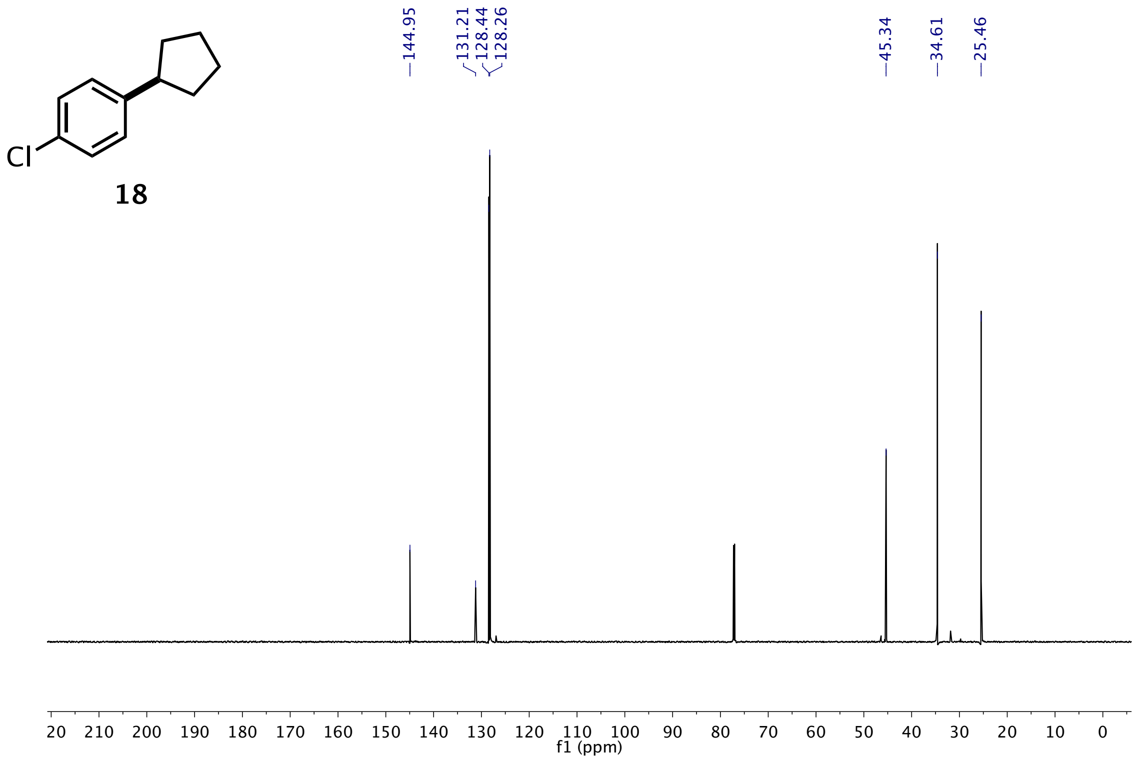
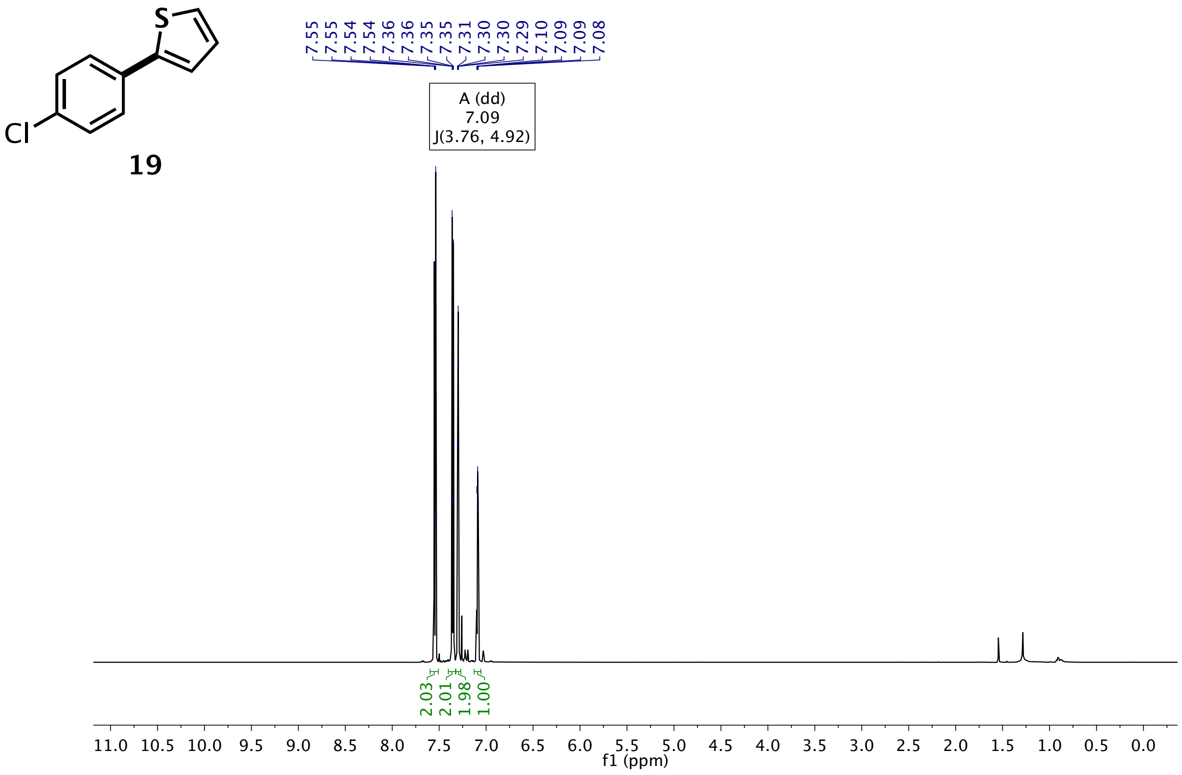


18

^1H (600 MHz, $CDCl_3$)



19

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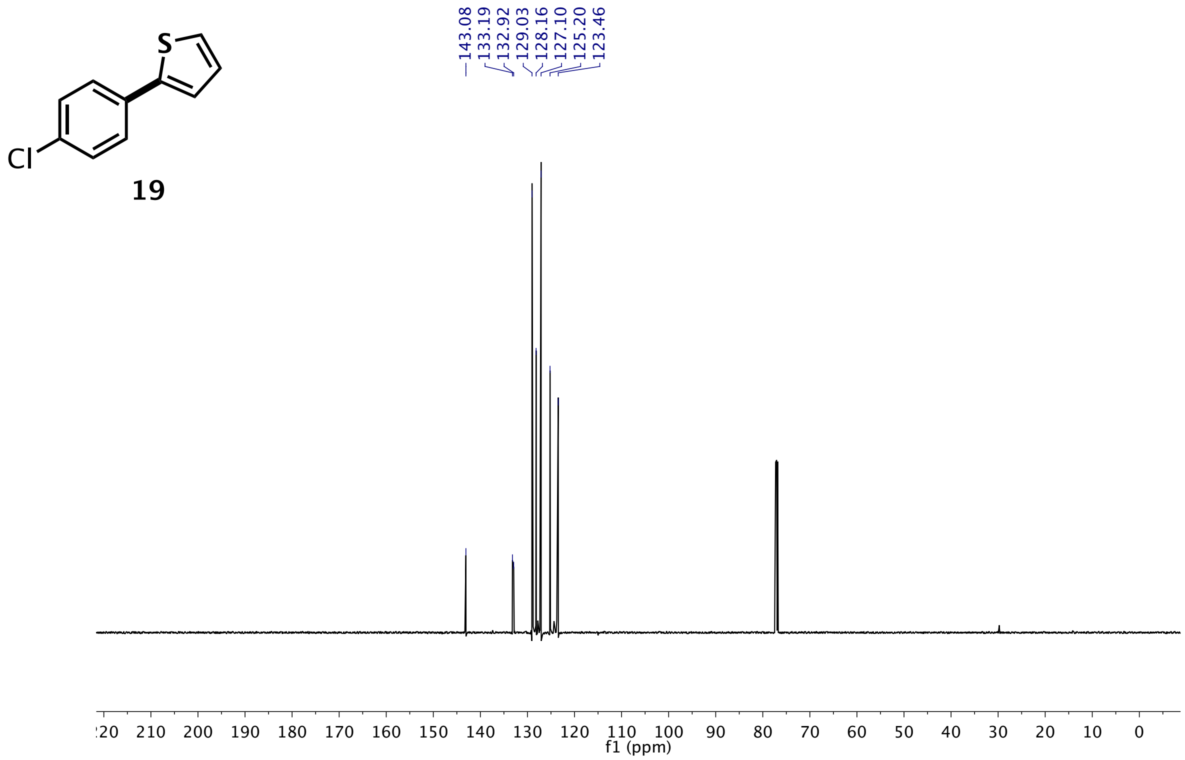
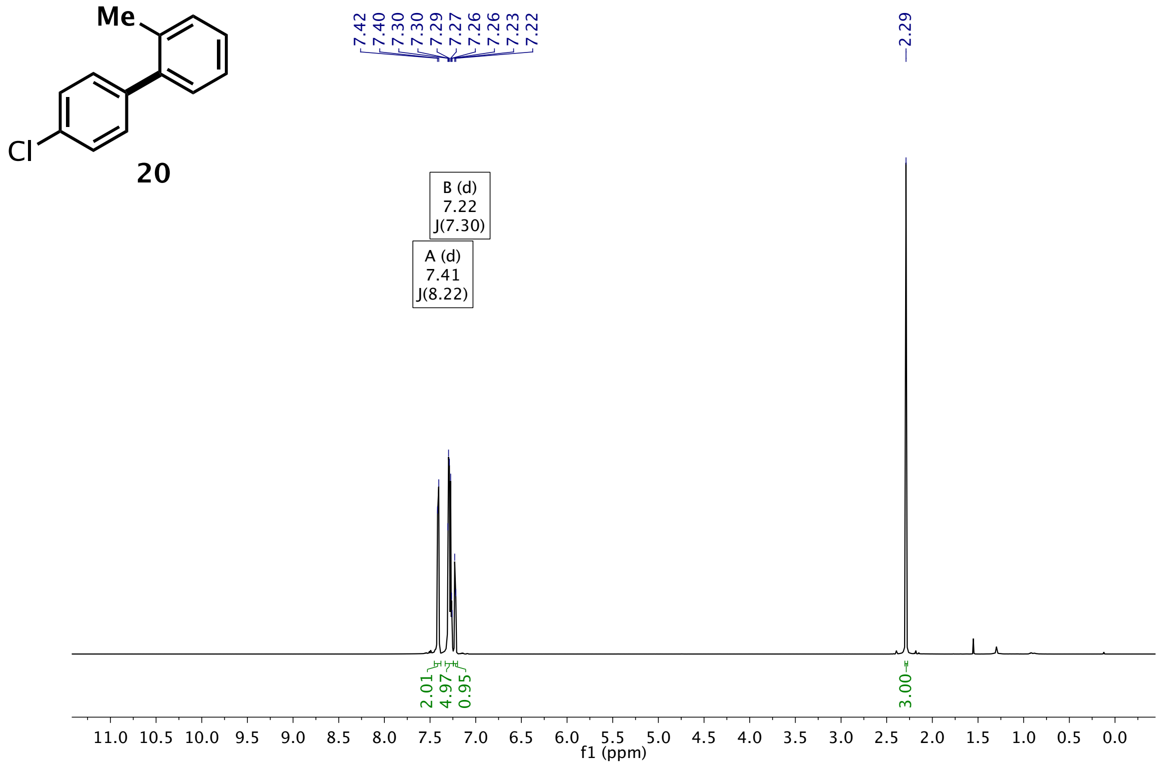


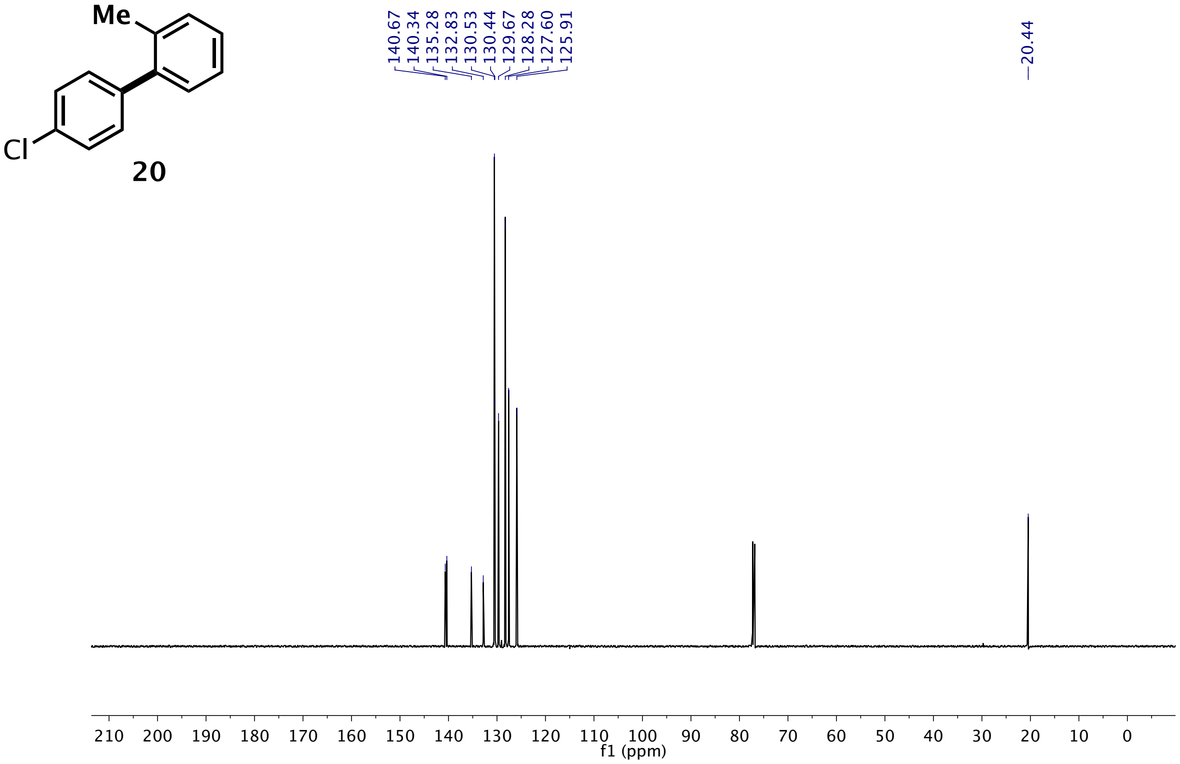
19

^1H (600 MHz, $CDCl_3$)



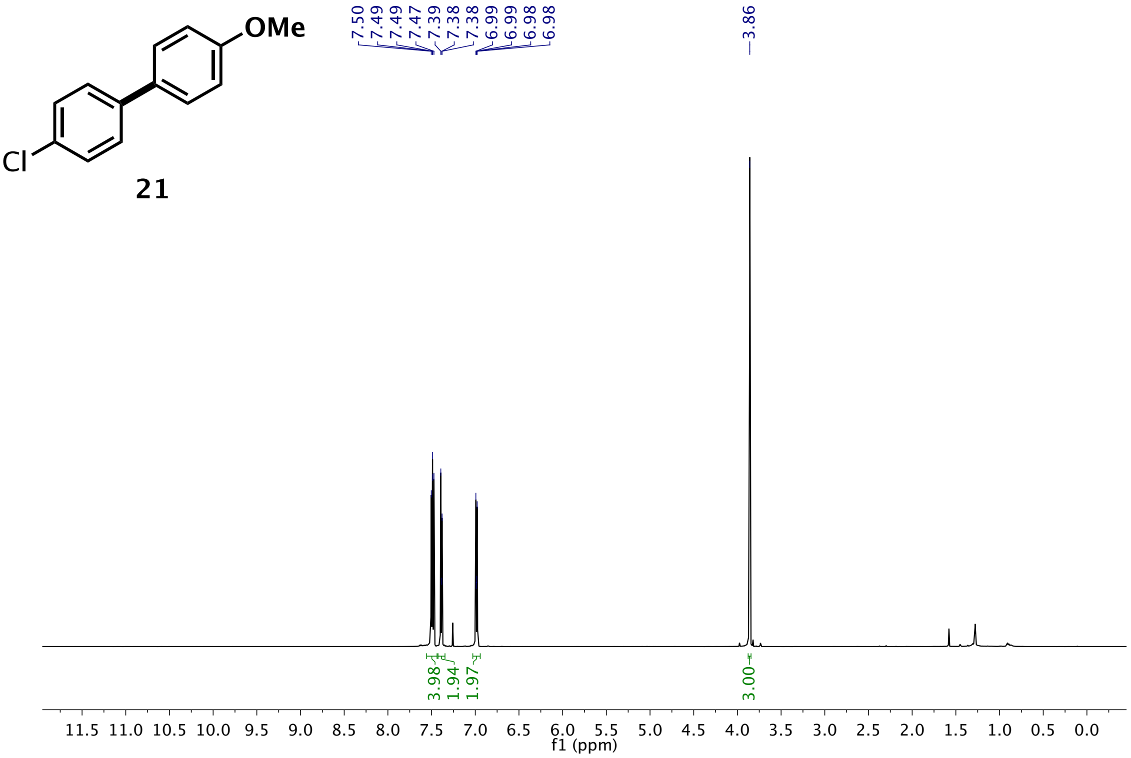
20

$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



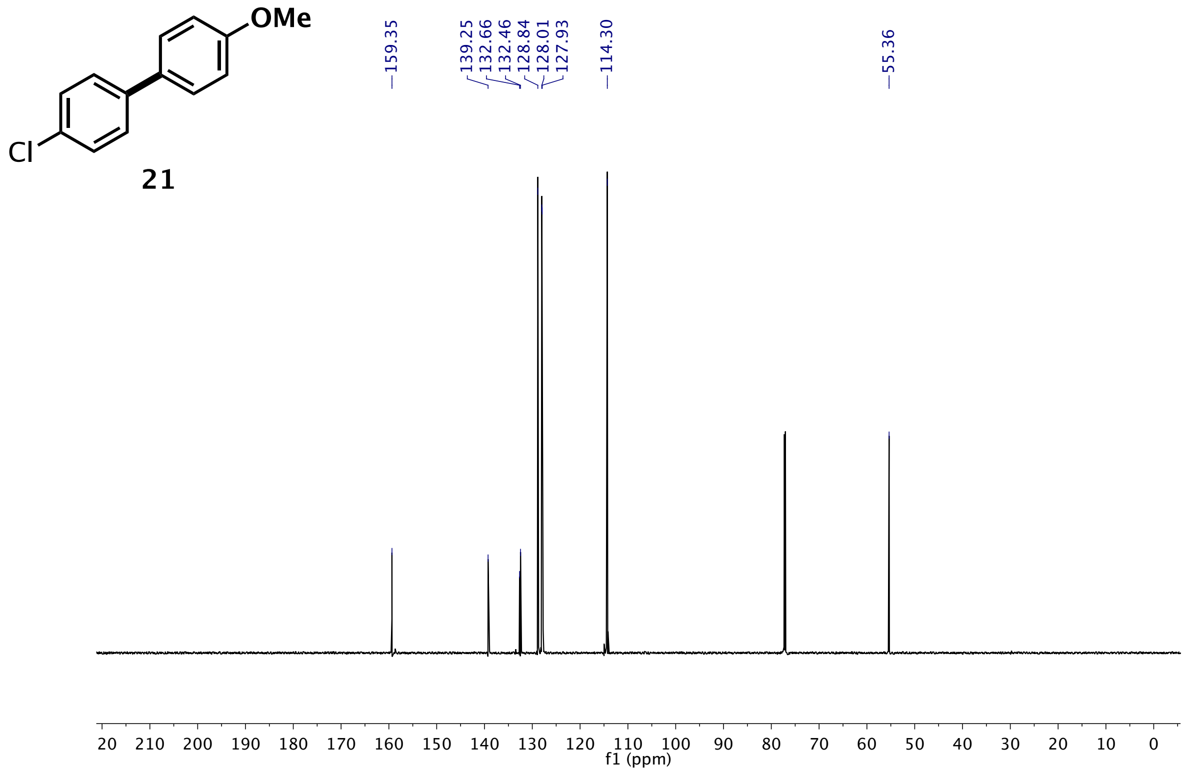
20

^1H (600 MHz, $CDCl_3$)



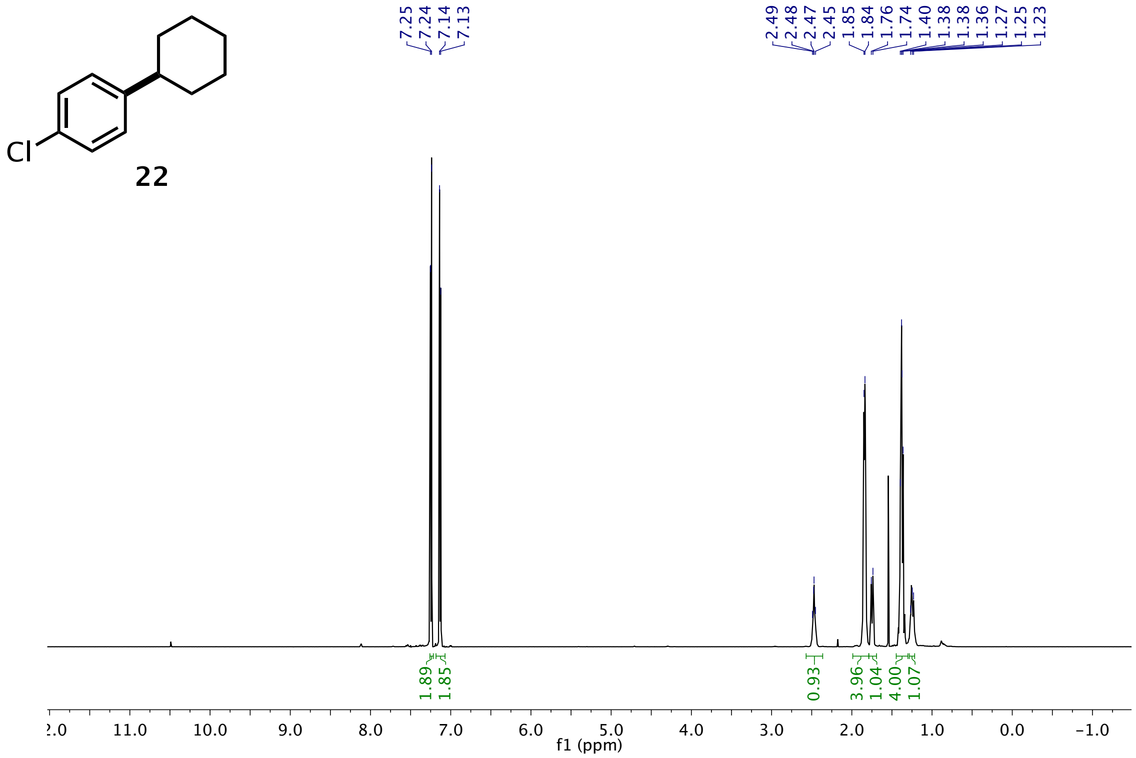
21

$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



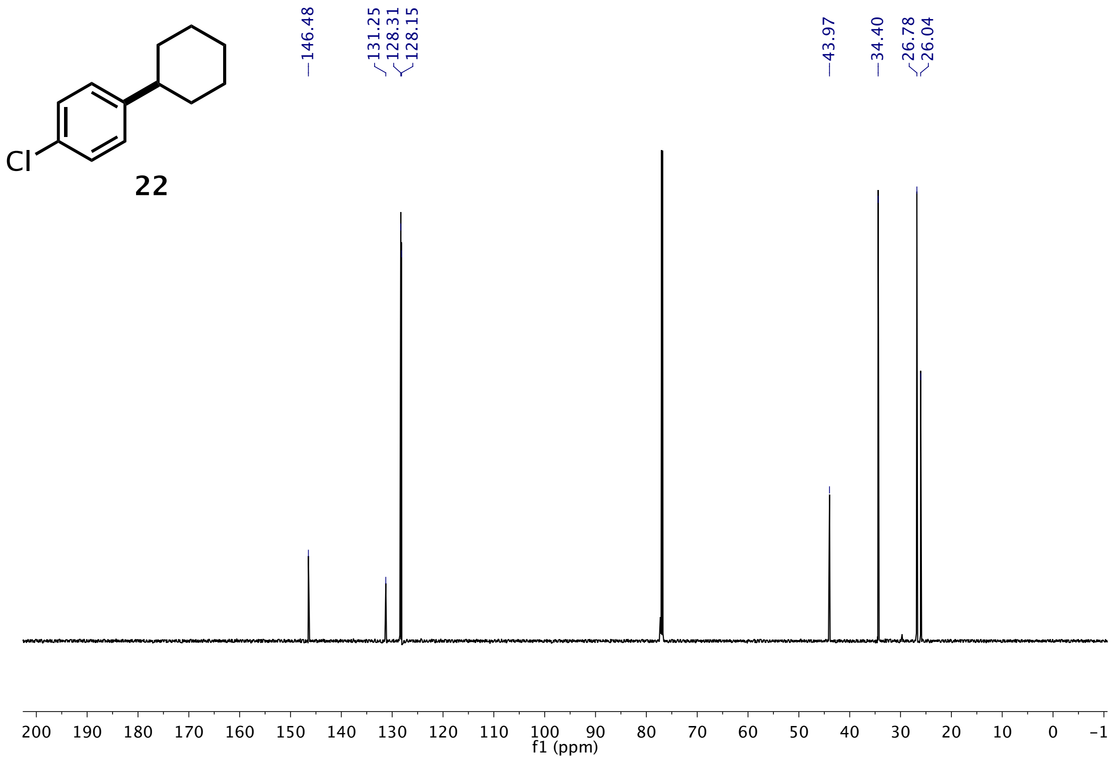
21

^1H (600 MHz, $CDCl_3$)

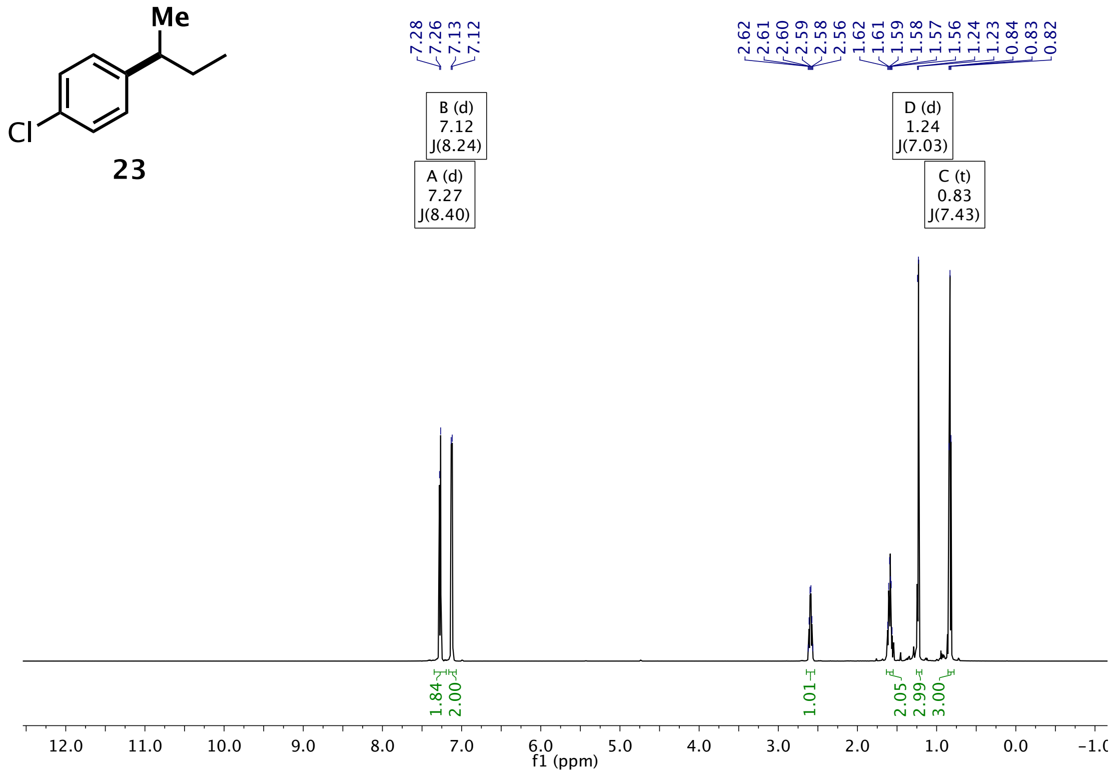


22

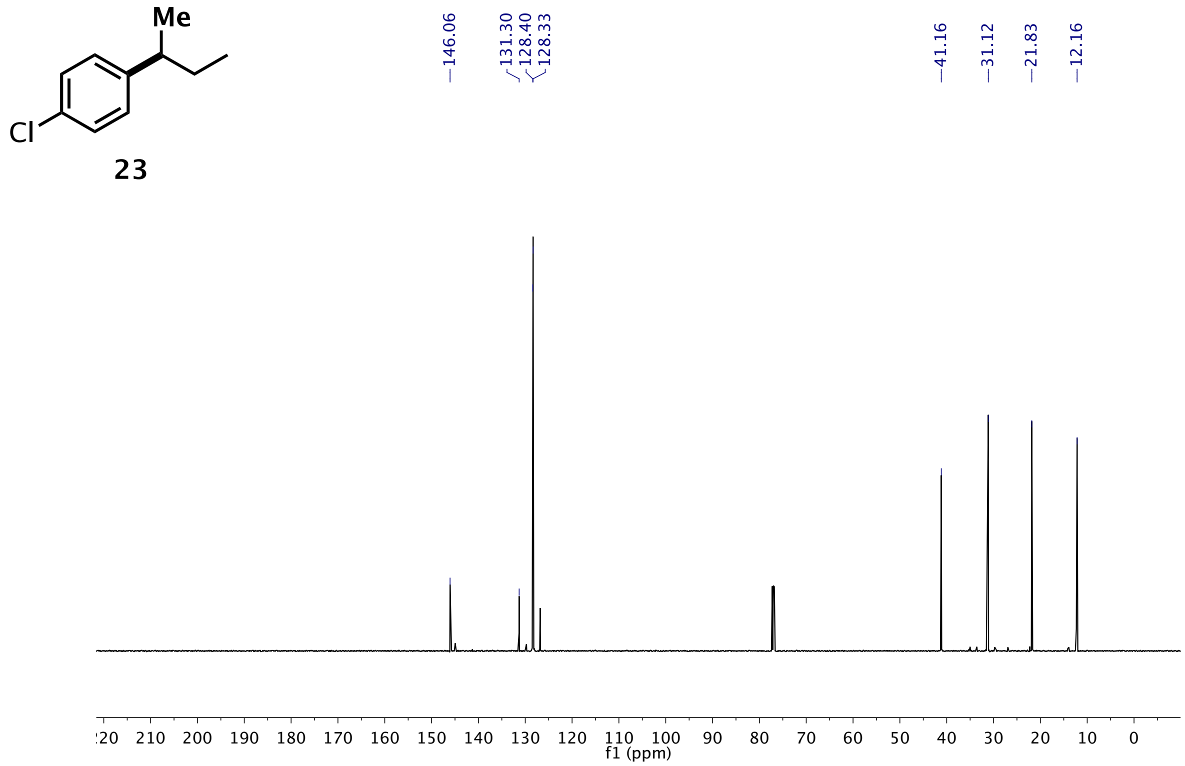
^{13}C{^{1}H} (151 MHz, CDCl$_3$)



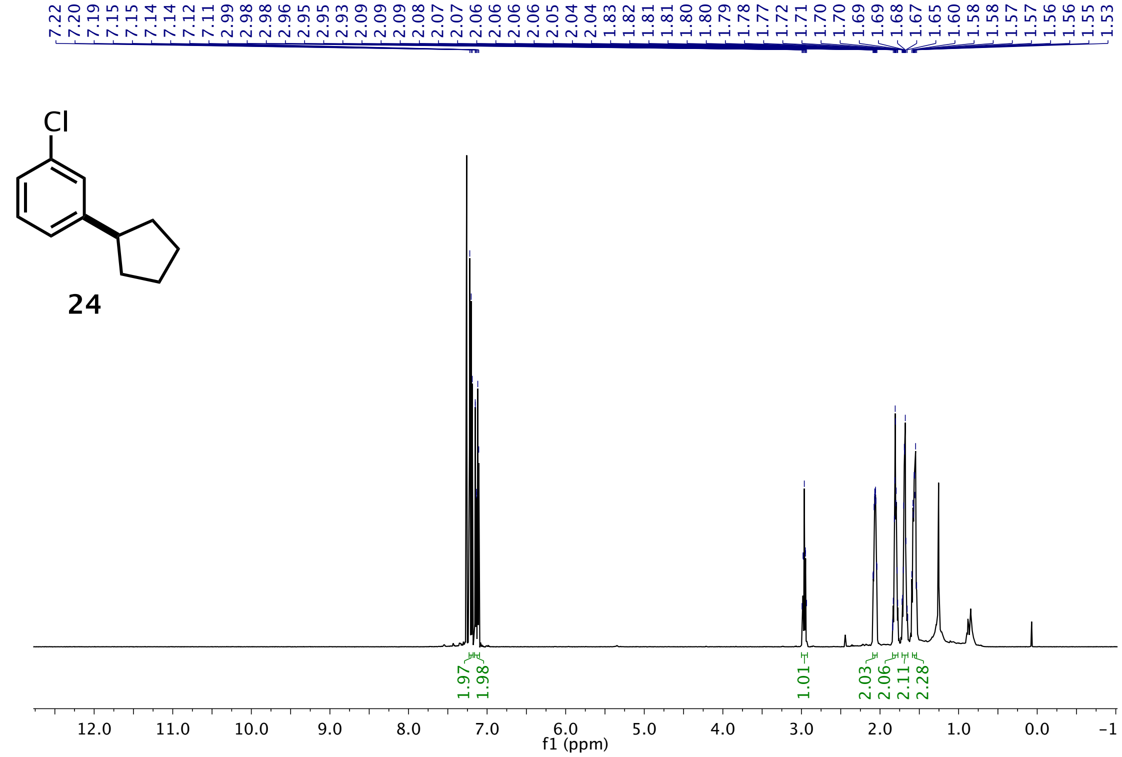
^{1}H (600 MHz, CDCl$_3$)



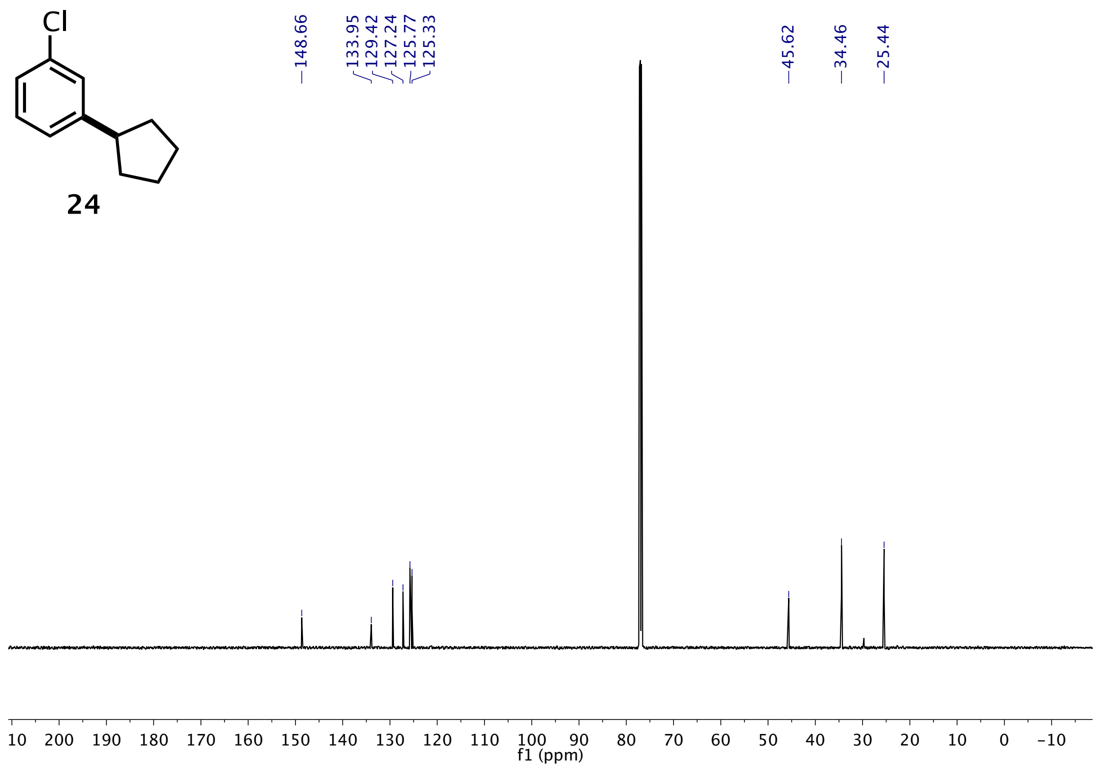
$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)



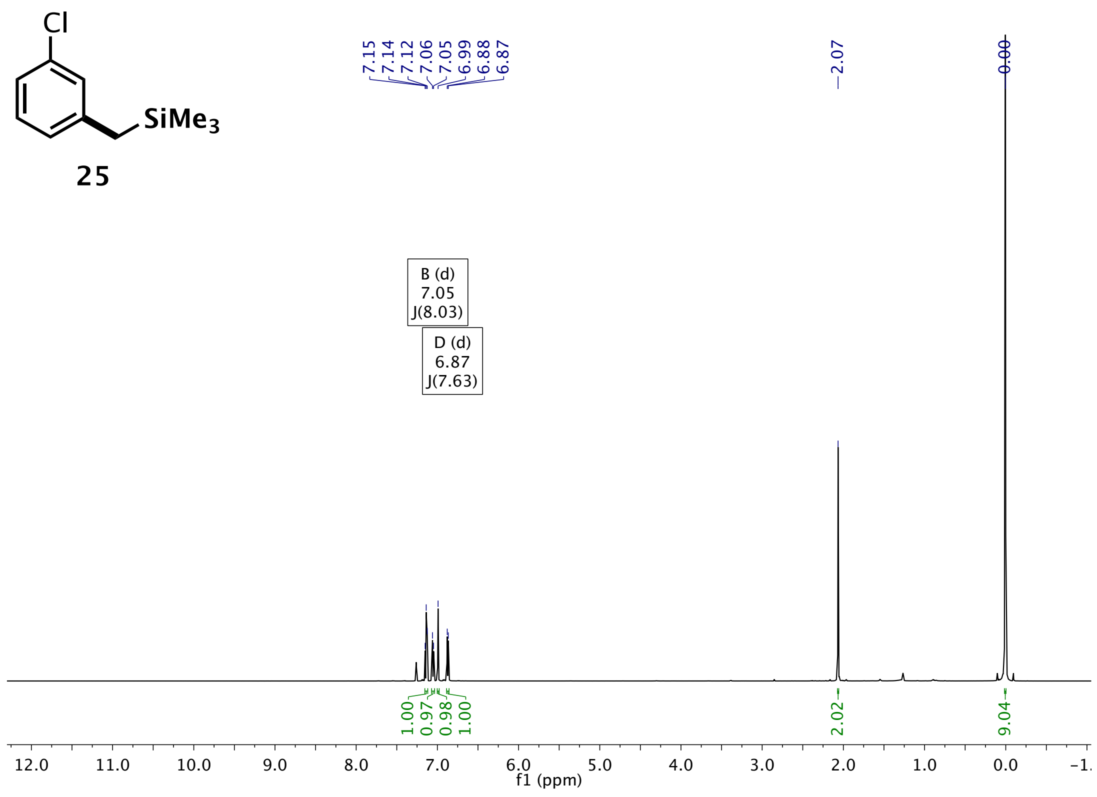
^{1}H (600 MHz, $CDCl_3$)



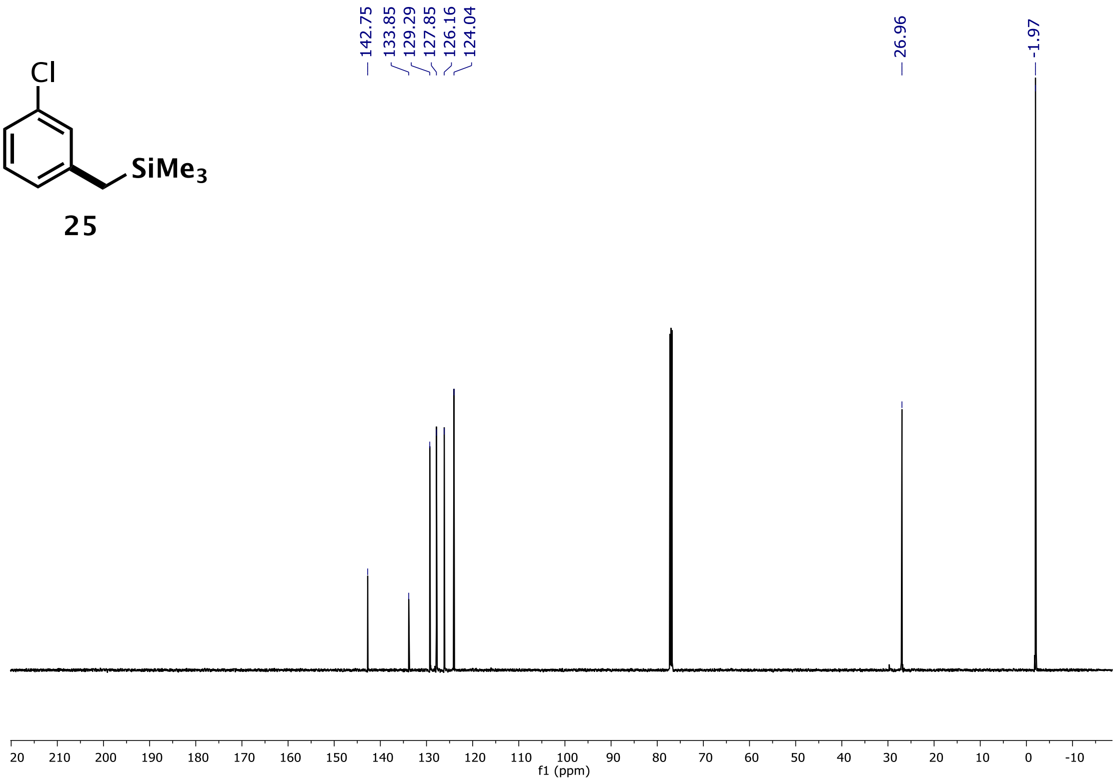
$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



^1H (600 MHz, $CDCl_3$)

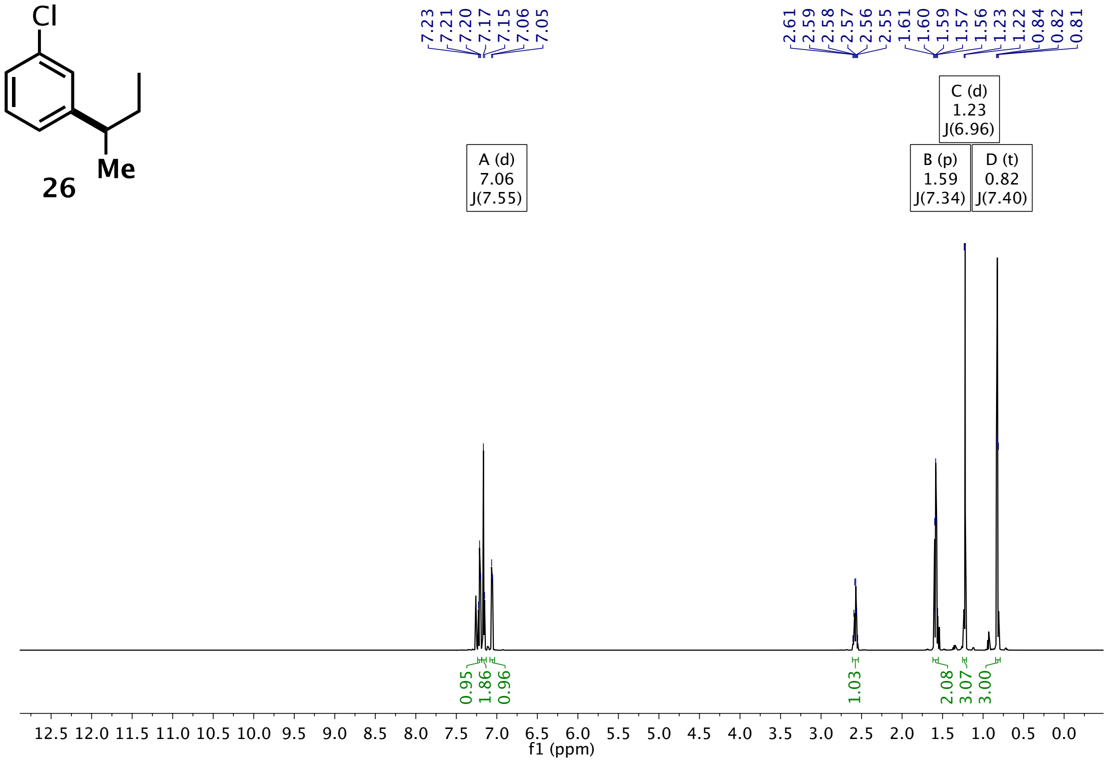


^{13}C{^{1}H} (151 MHz, CDCl$_3$)



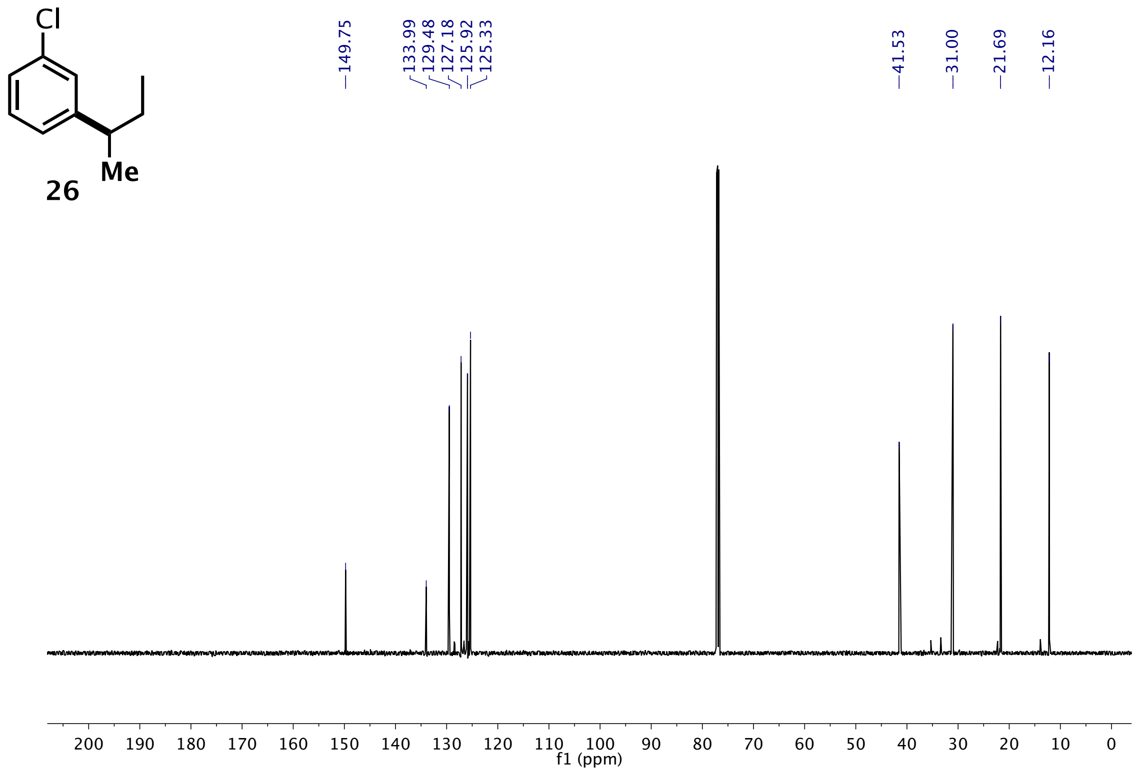
25

^{1}H (600 MHz, CDCl$_3$)



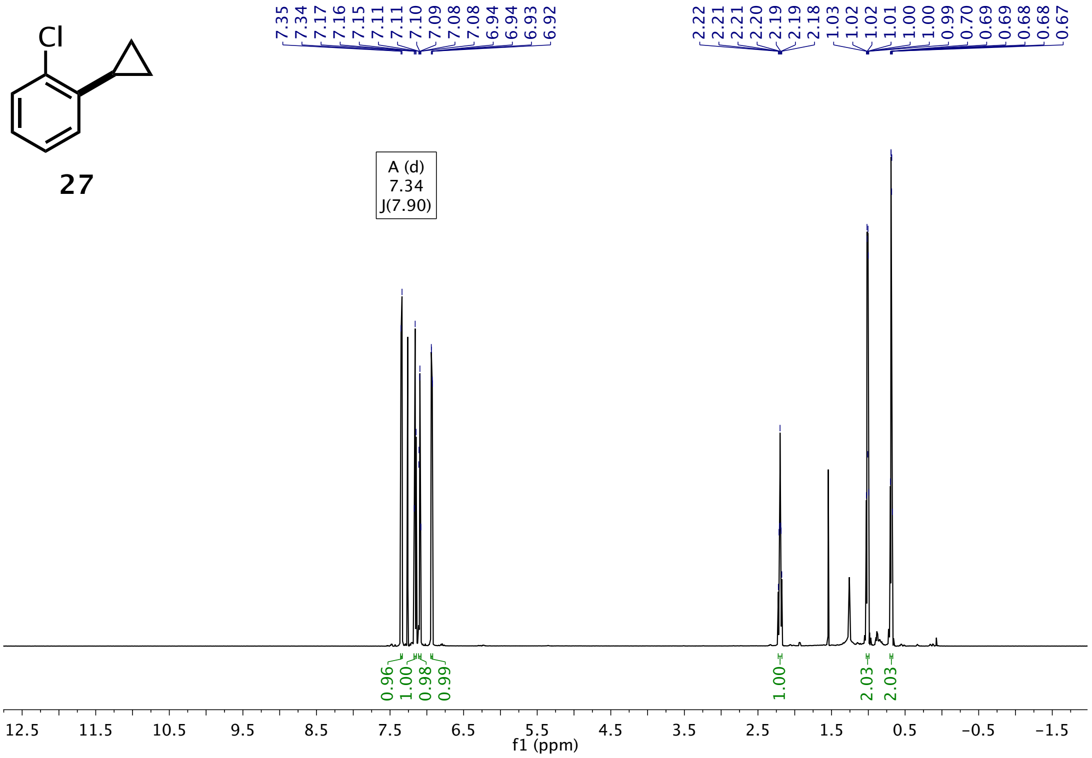
26

$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



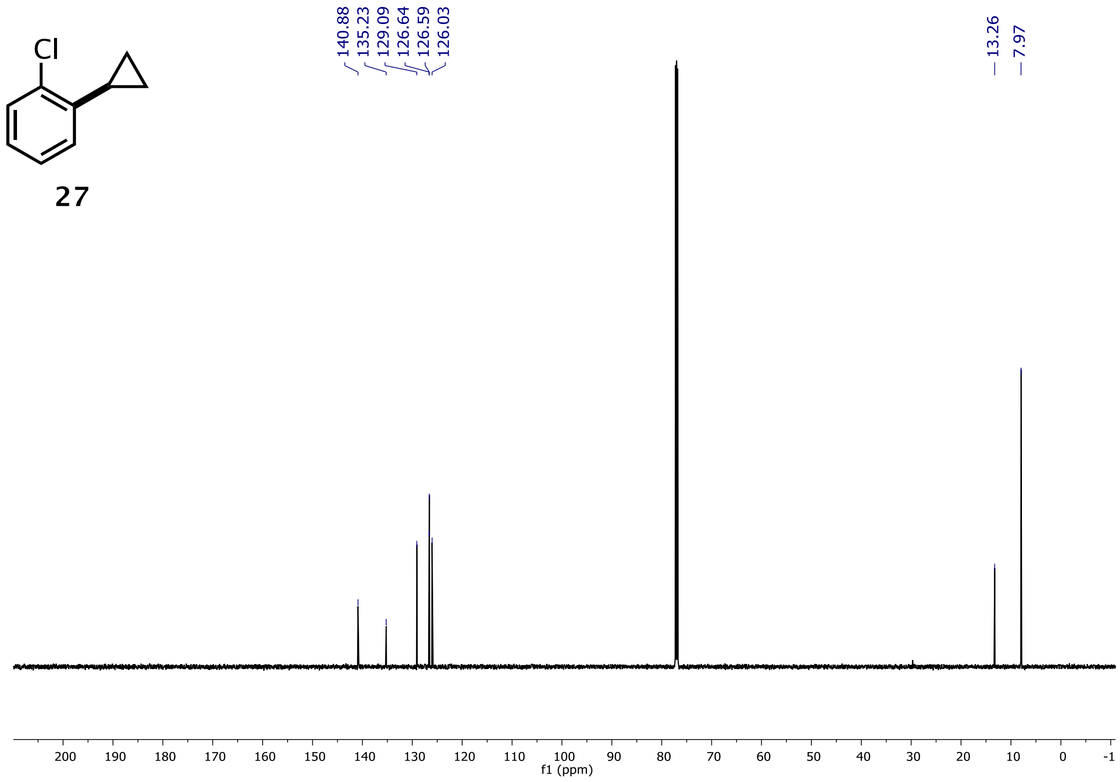
26

^1H (600 MHz, $CDCl_3$)



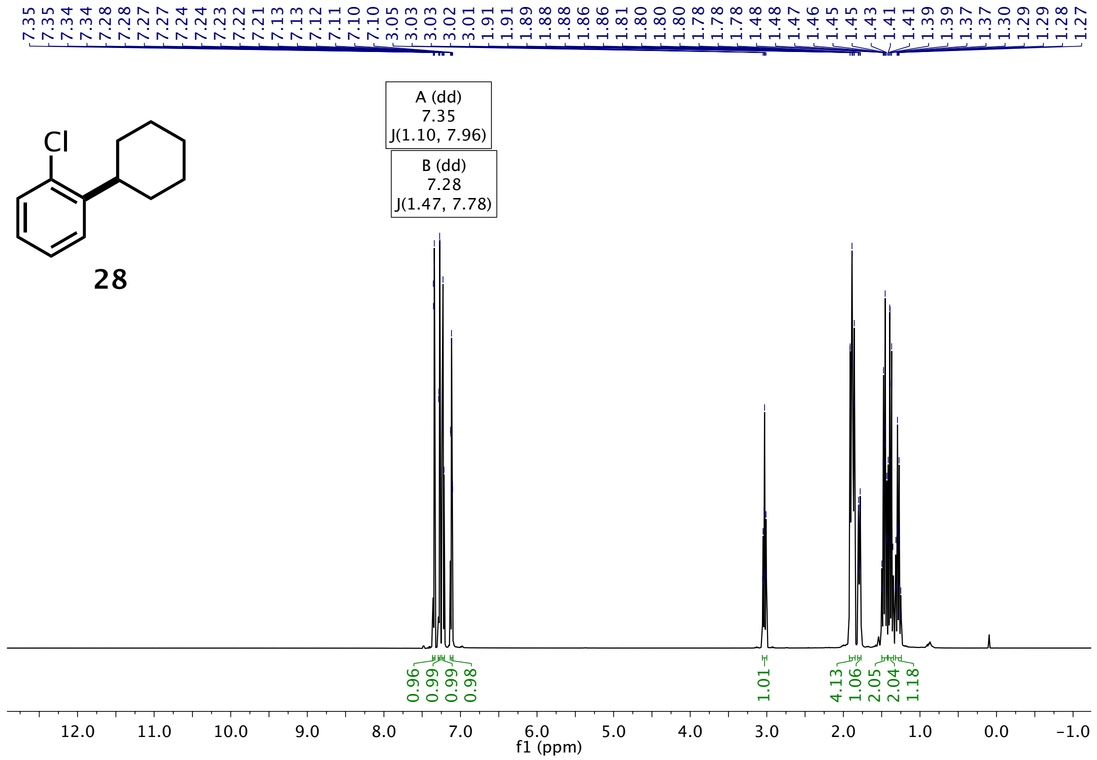
27

^{13}C{^{1}H} (151 MHz, $CDCl_3$)



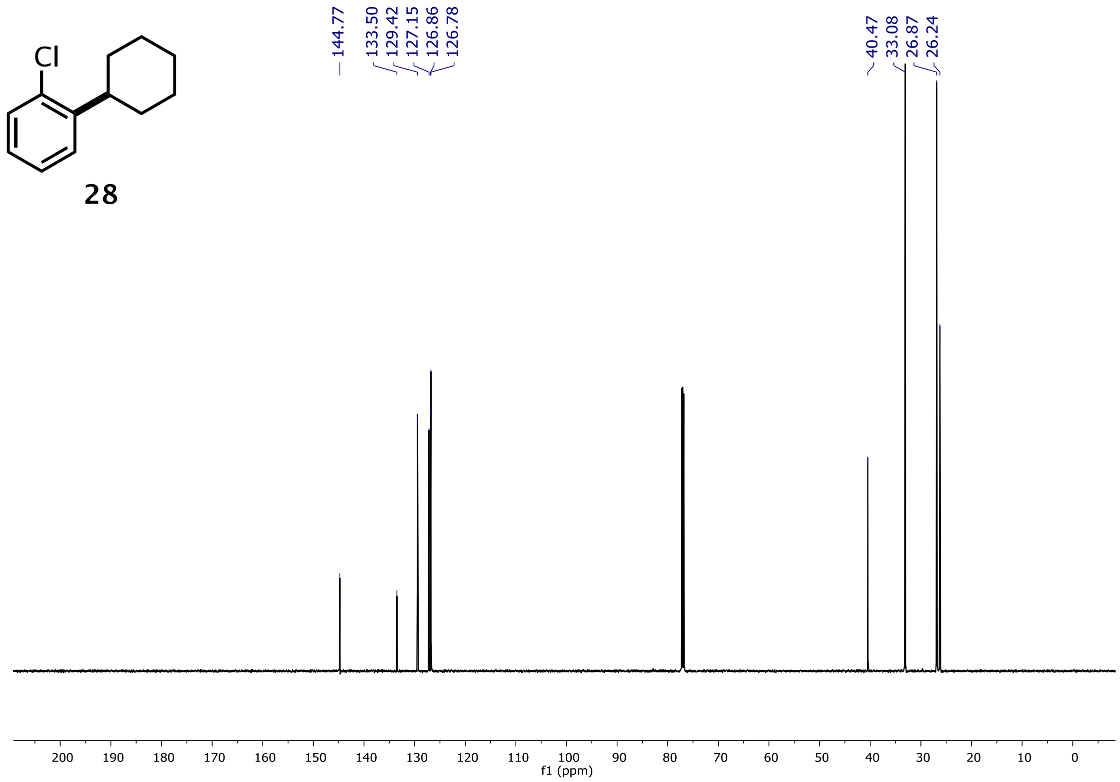
27

^{1}H (600 MHz, $CDCl_3$)



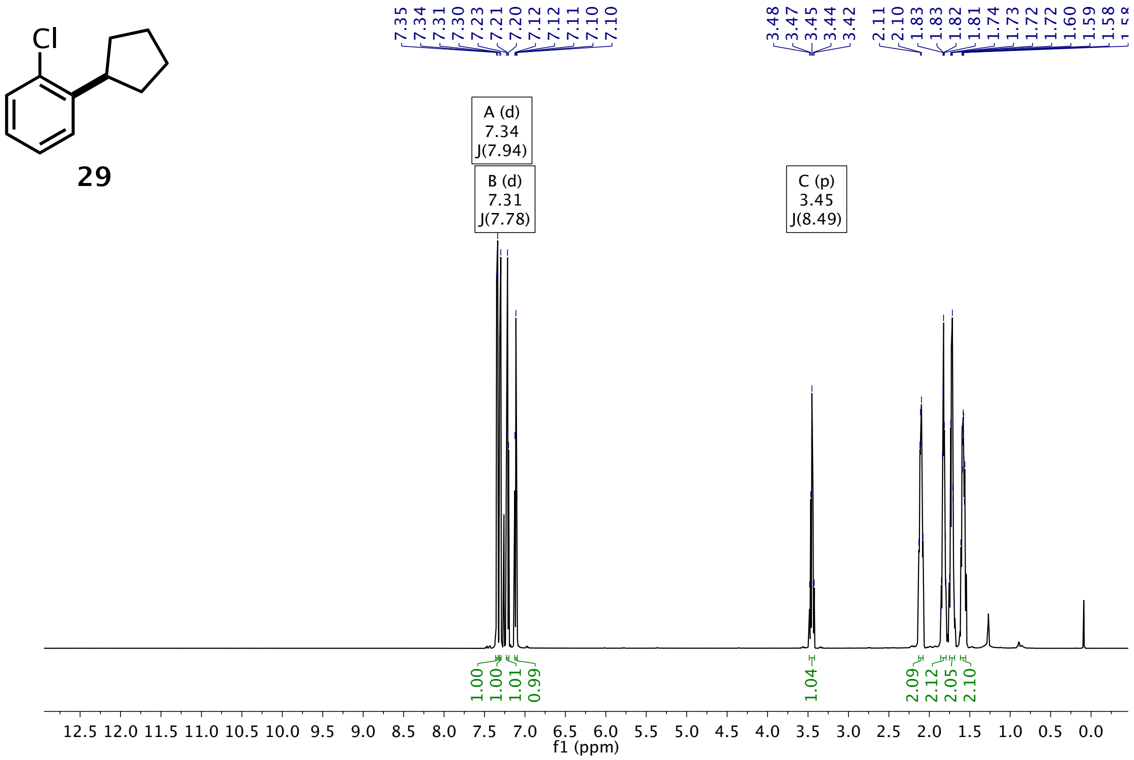
28

$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



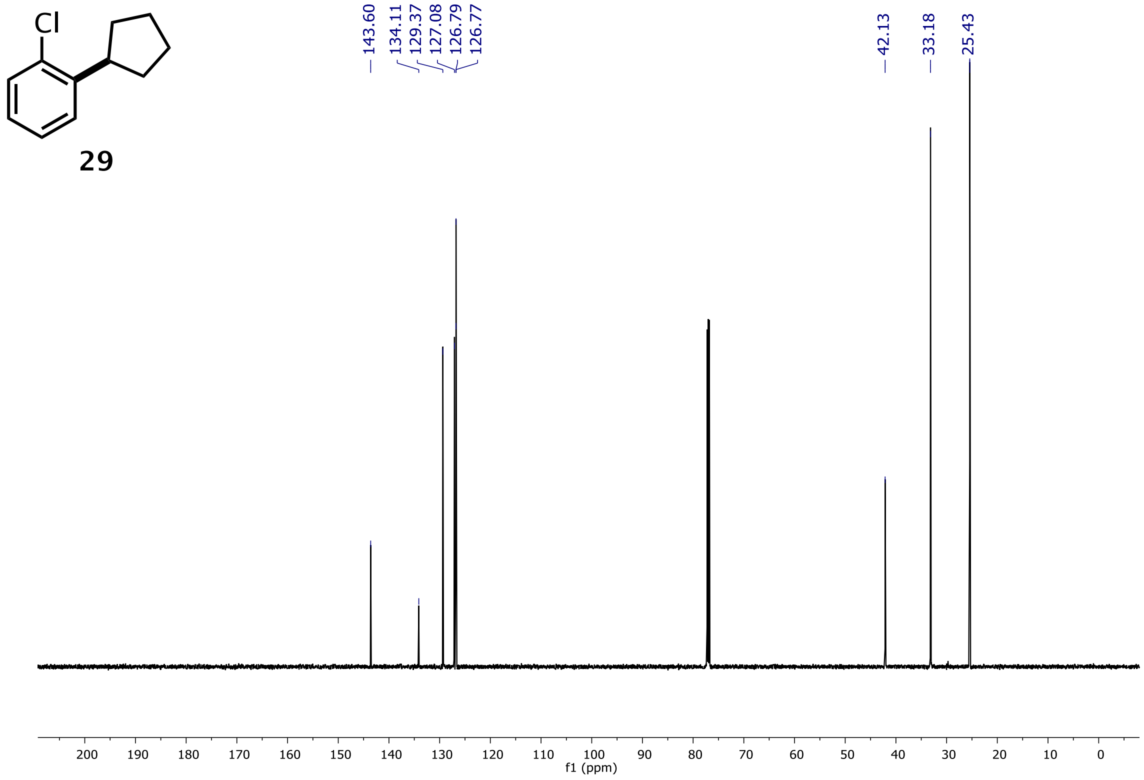
28

^1H (600 MHz, $CDCl_3$)



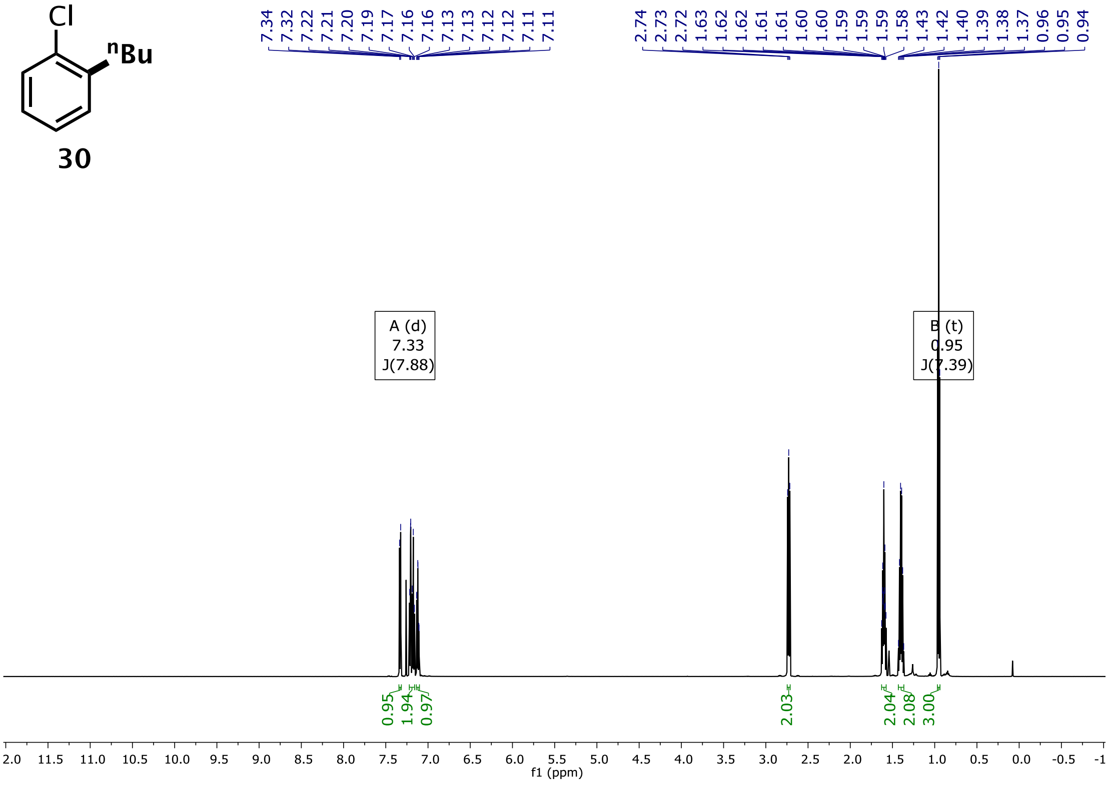
29

$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)



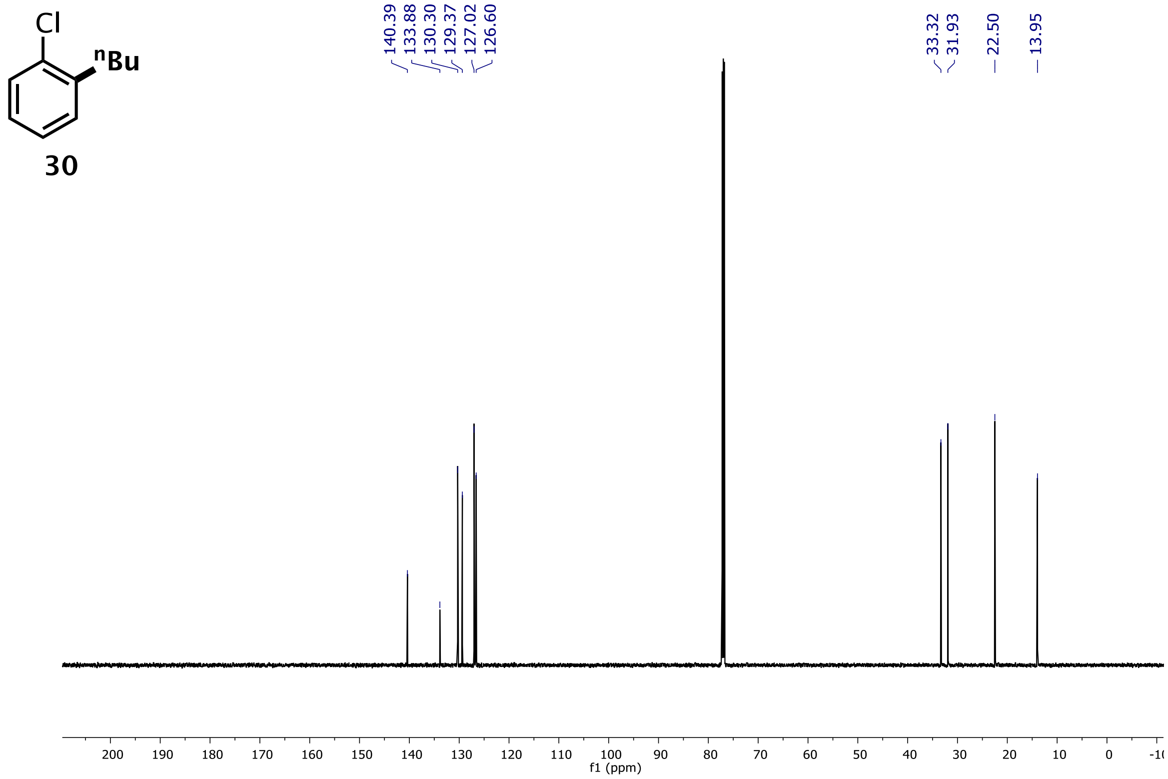
29

^{1}H (600 MHz, $CDCl_3$)

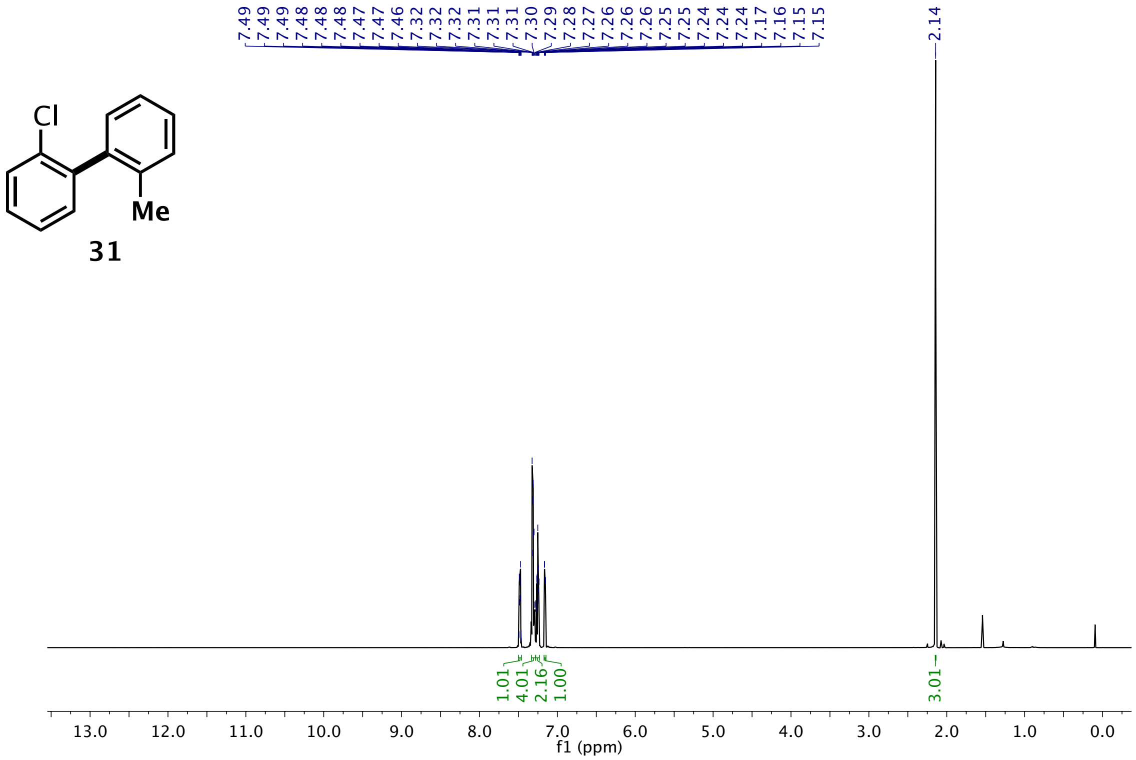


30

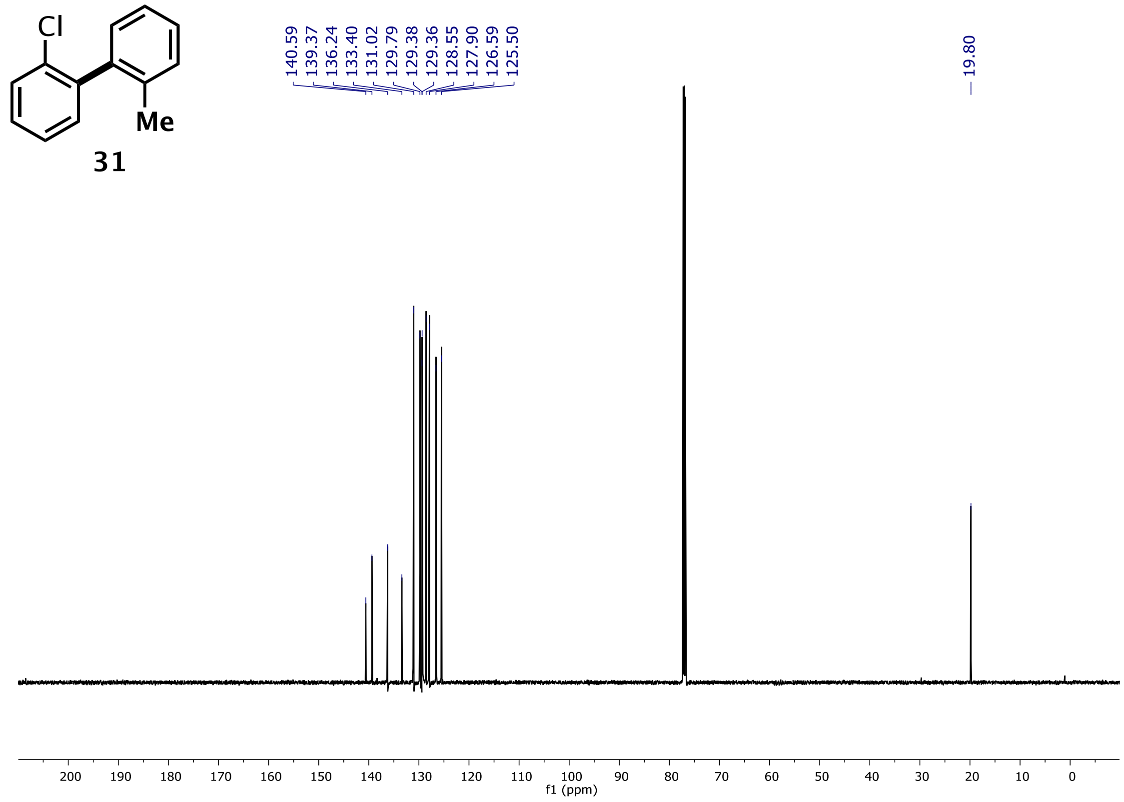
$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)


30

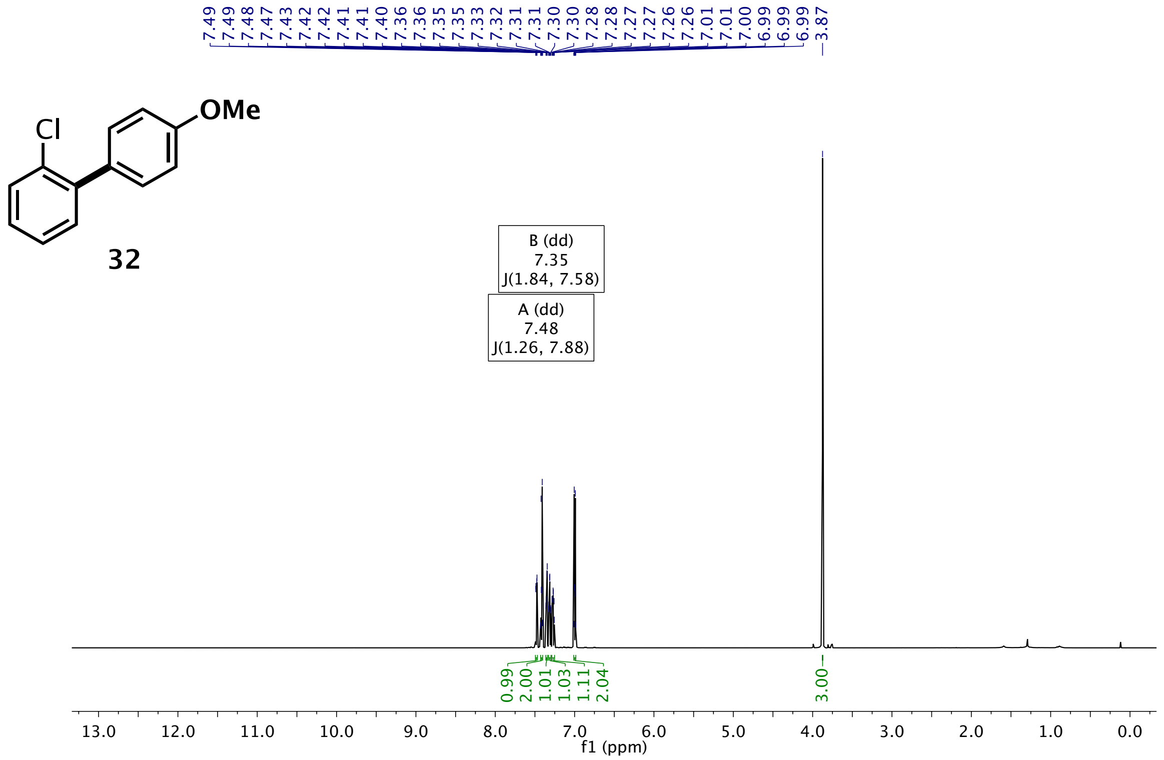
^{1}H (600 MHz, $CDCl_3$)


31

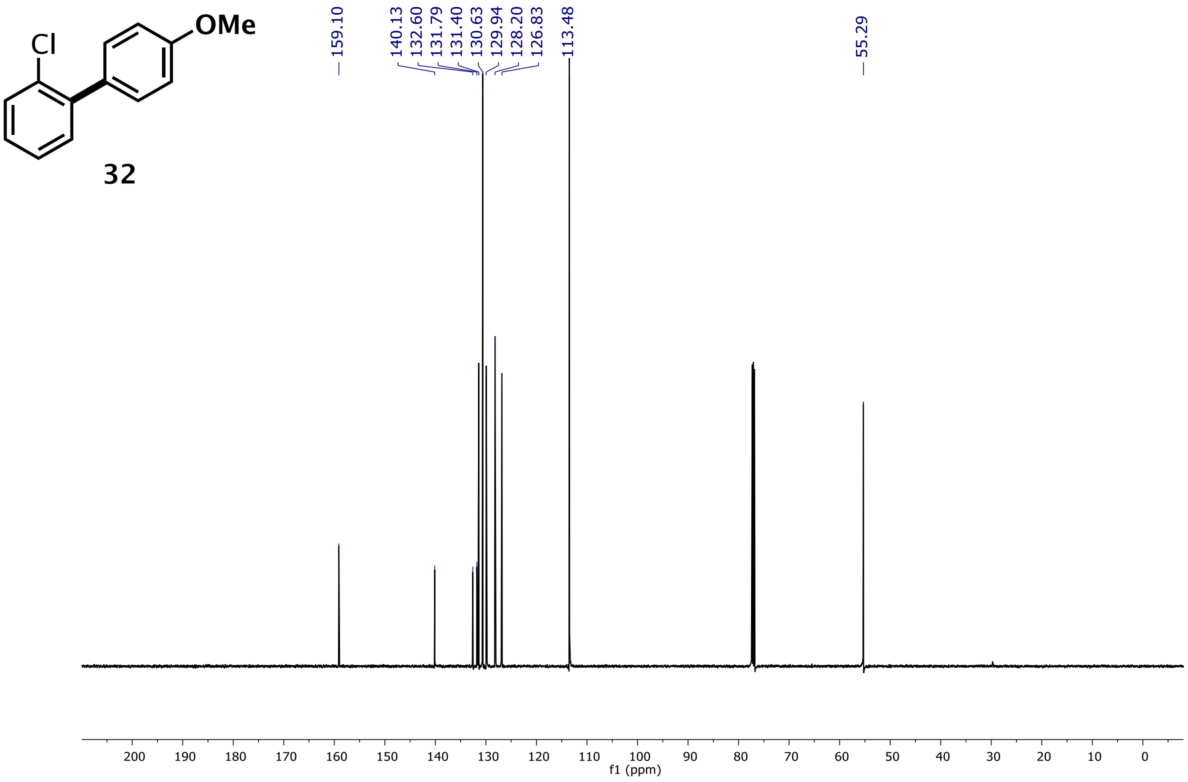
$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



^1H (600 MHz, $CDCl_3$)

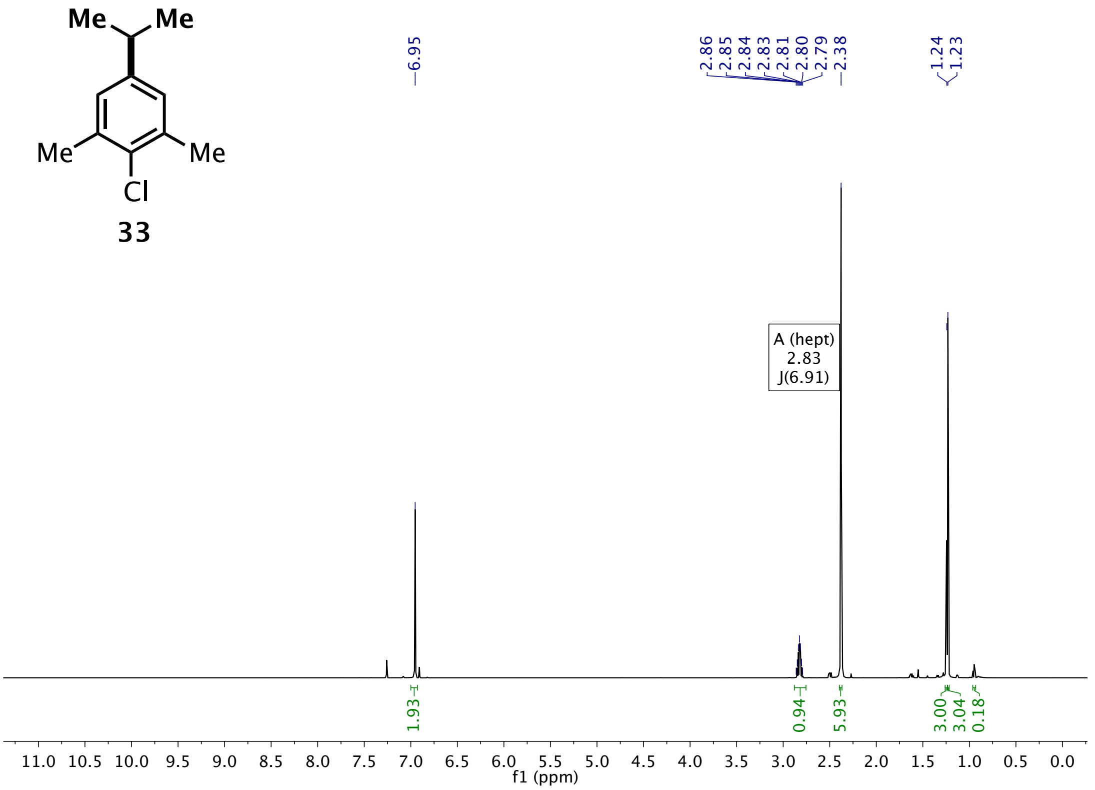


$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)



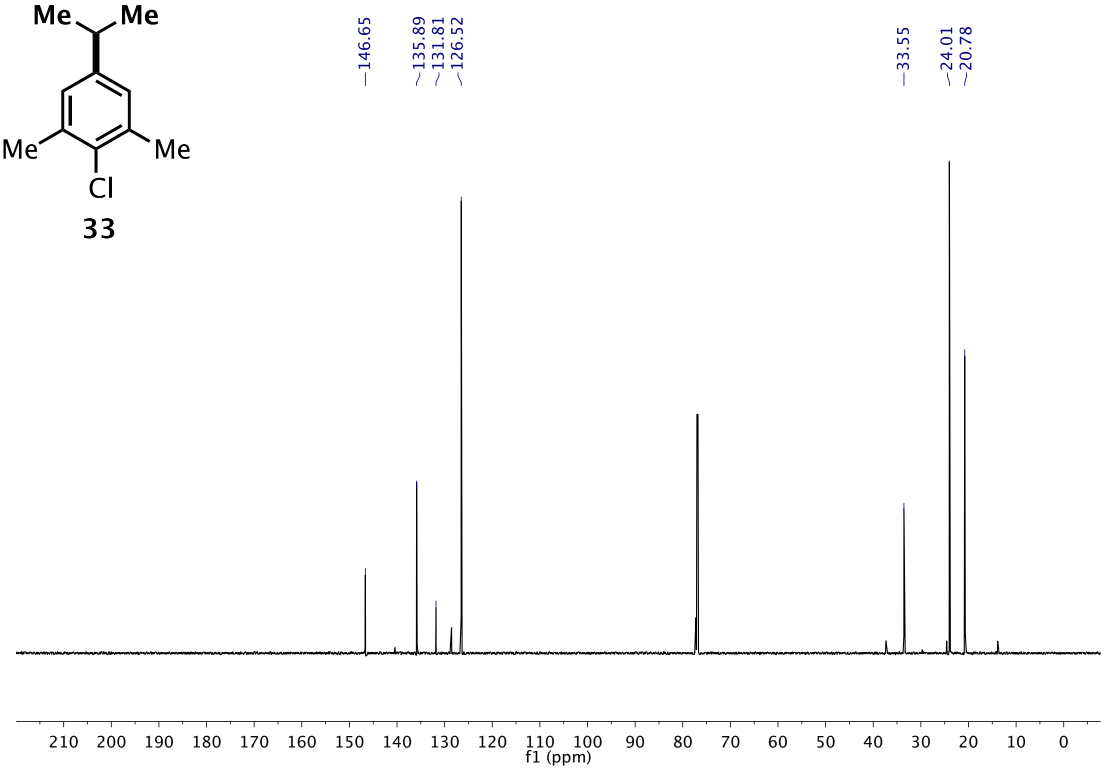
32

^{1}H (600 MHz, $CDCl_3$)



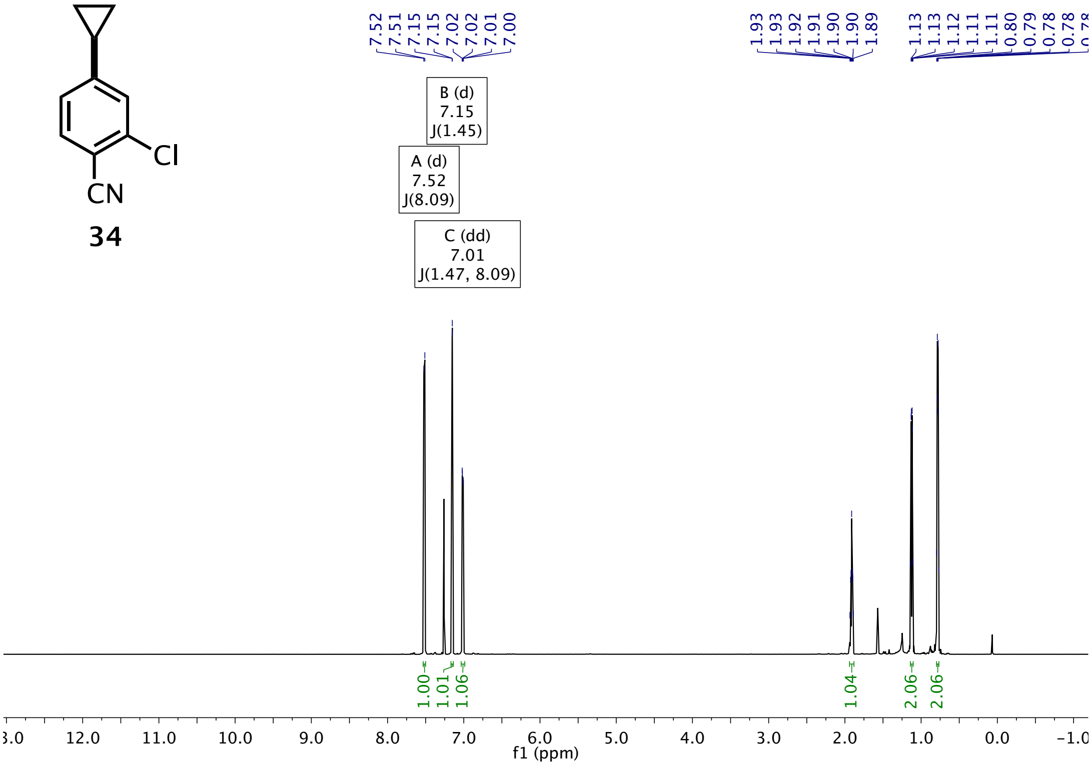
33

$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)



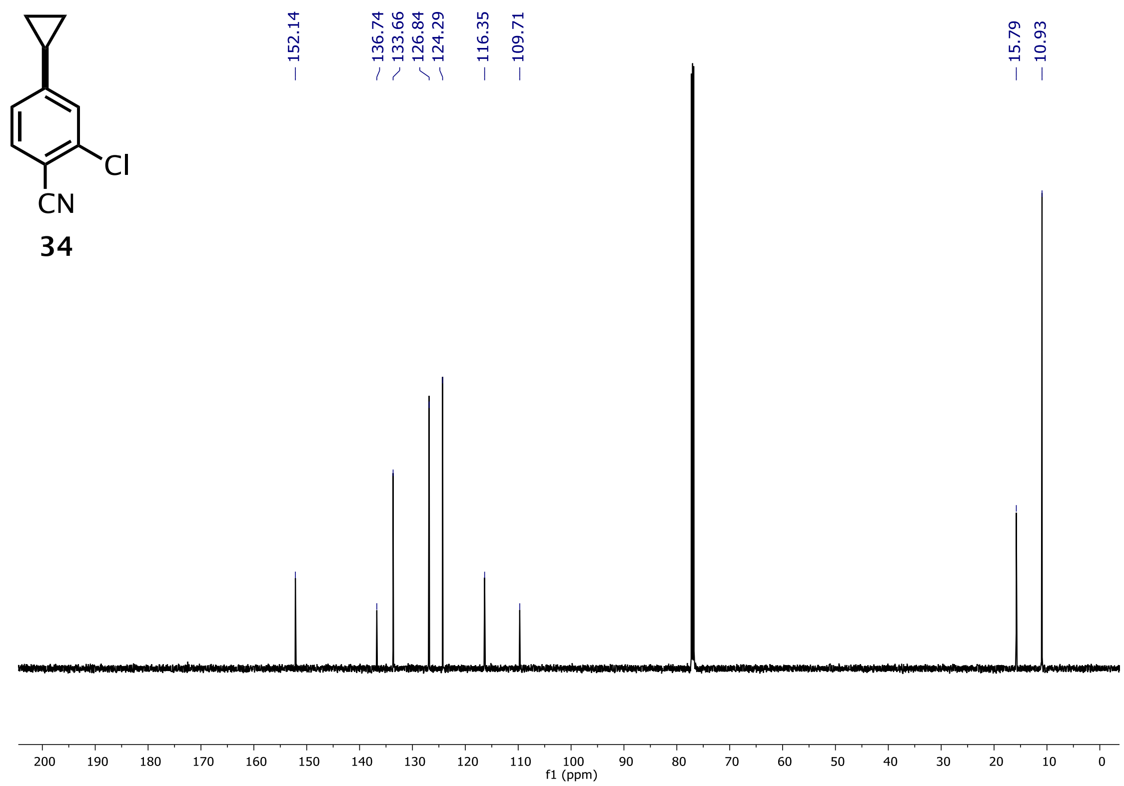
33

^{1}H (600 MHz, $CDCl_3$)



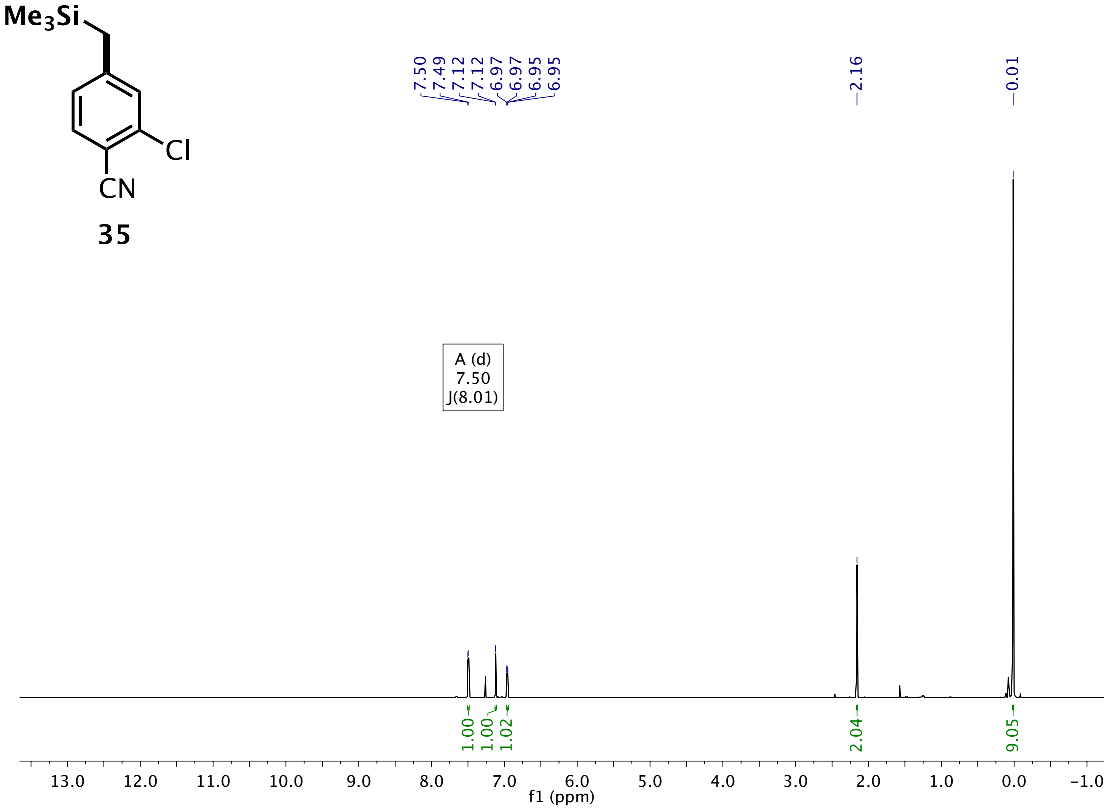
34

$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



34

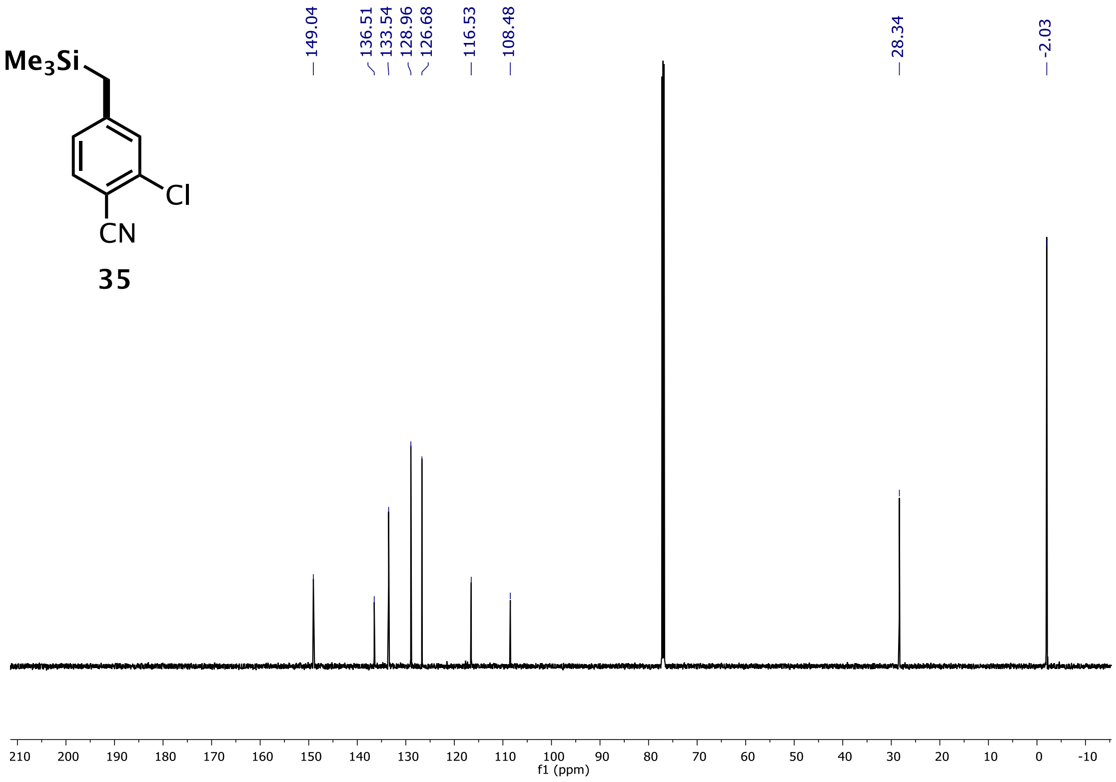
^1H (600 MHz, $CDCl_3$)



35

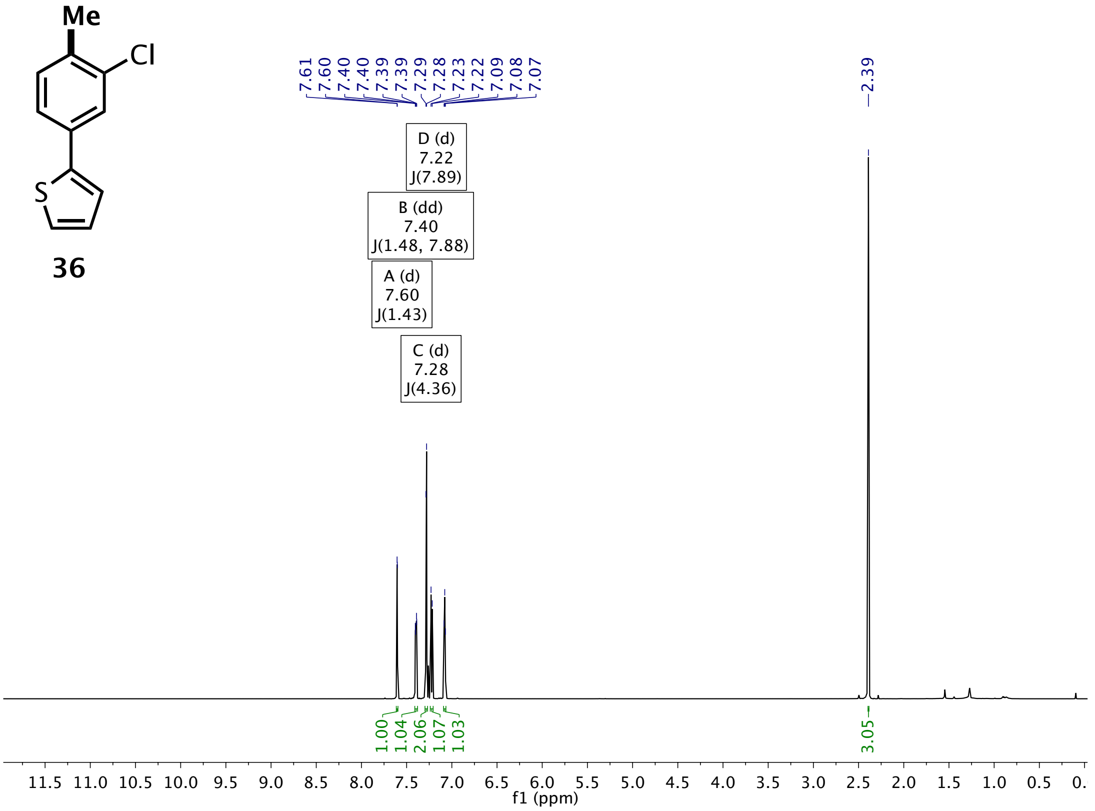
$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)

35

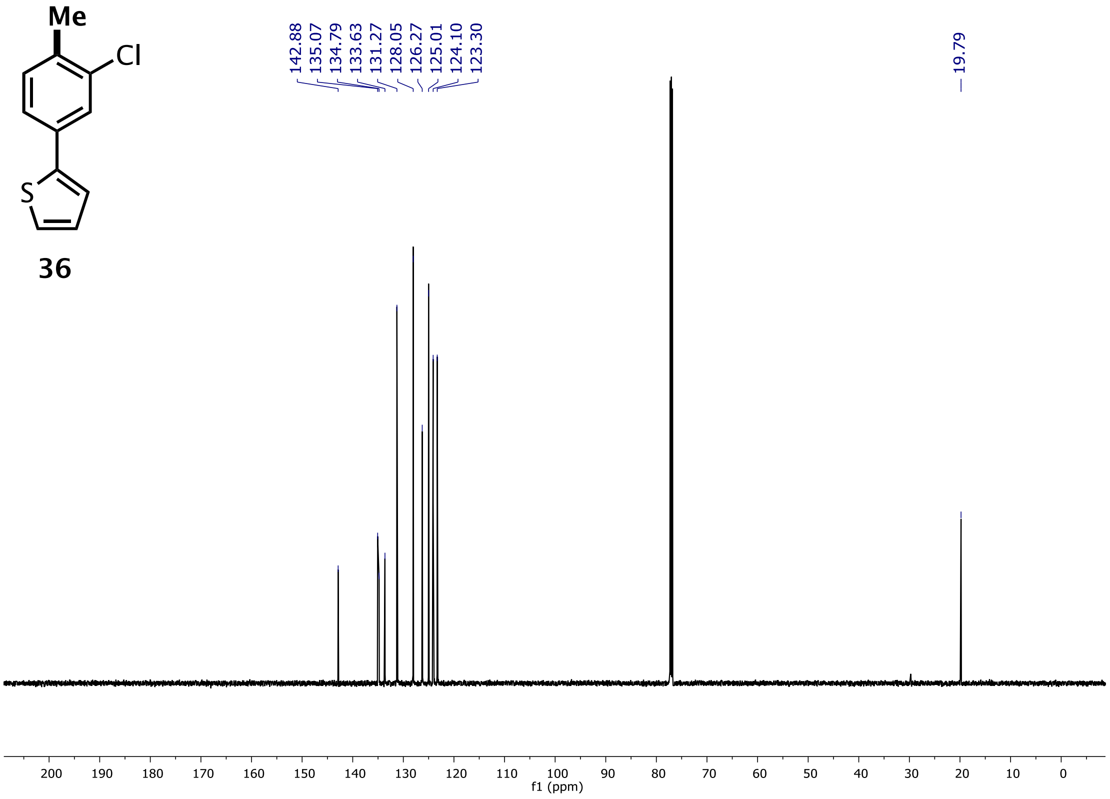


^{1}H (600 MHz, $CDCl_3$)

36

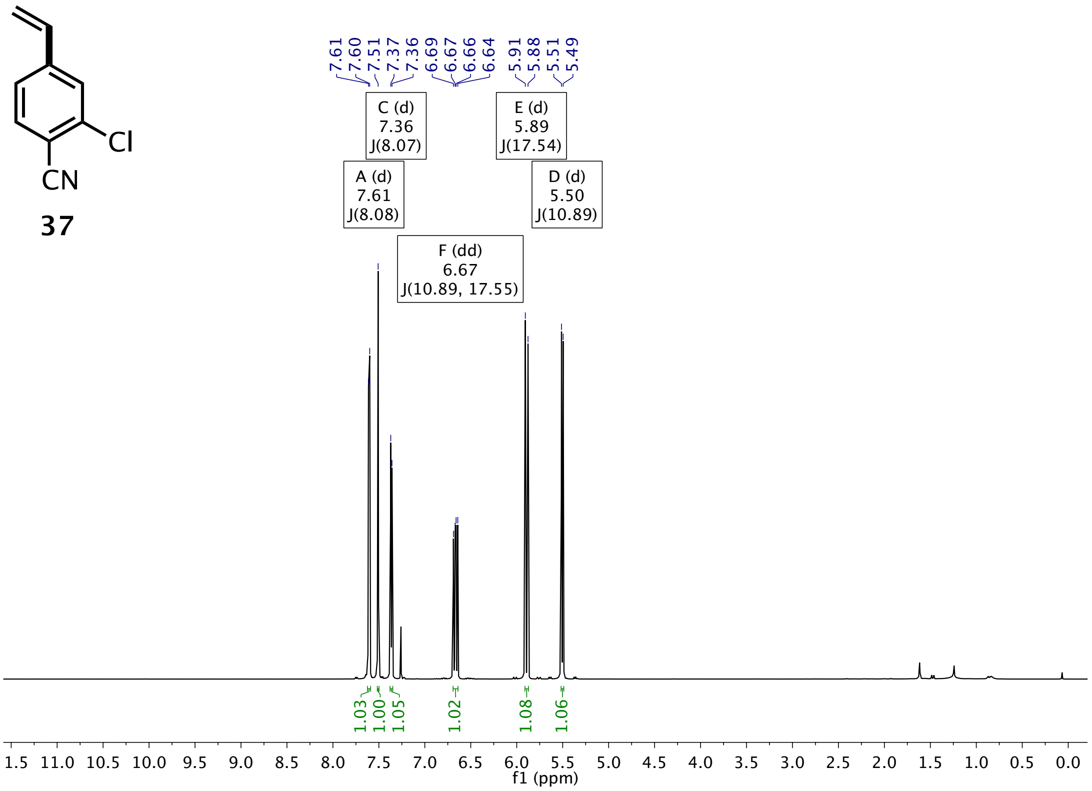


$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)



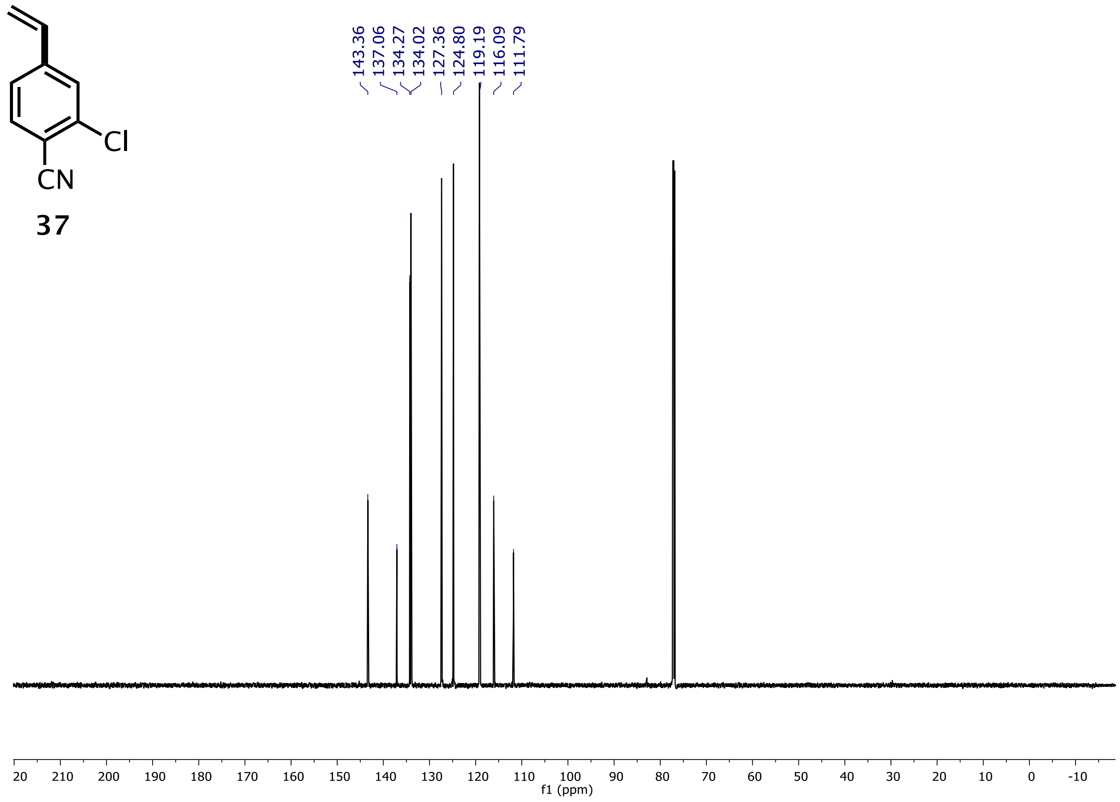
36

^{1}H (600 MHz, $CDCl_3$)



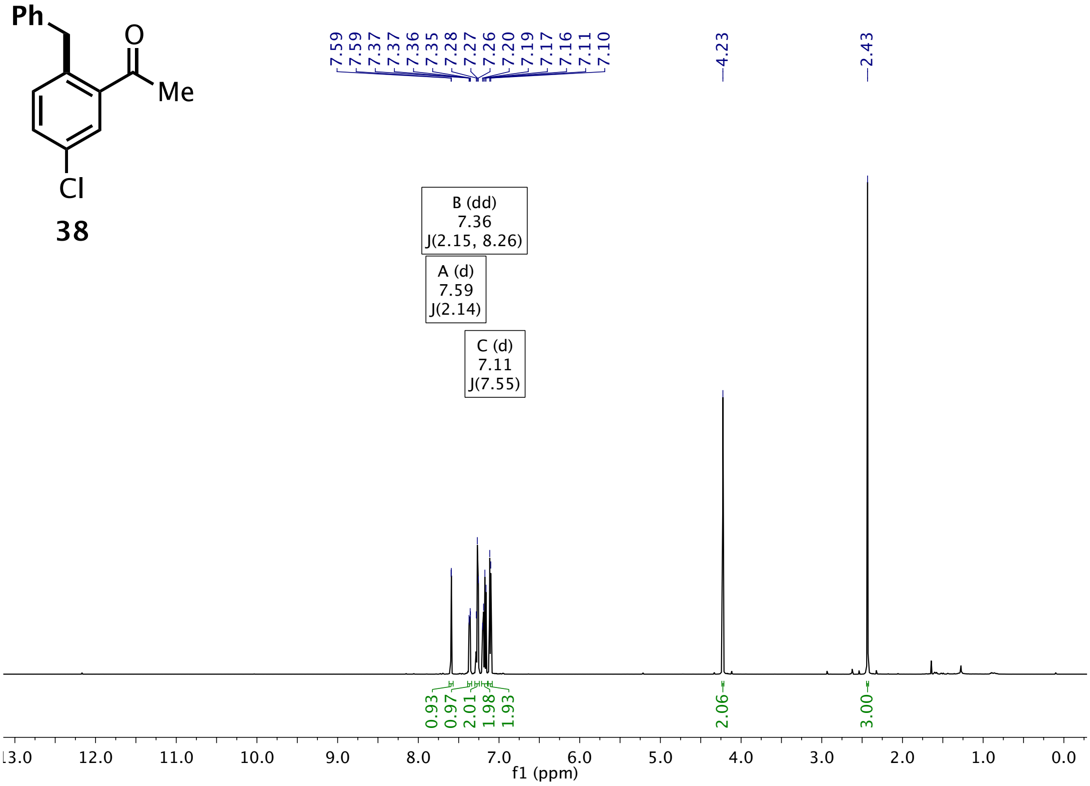
37

$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



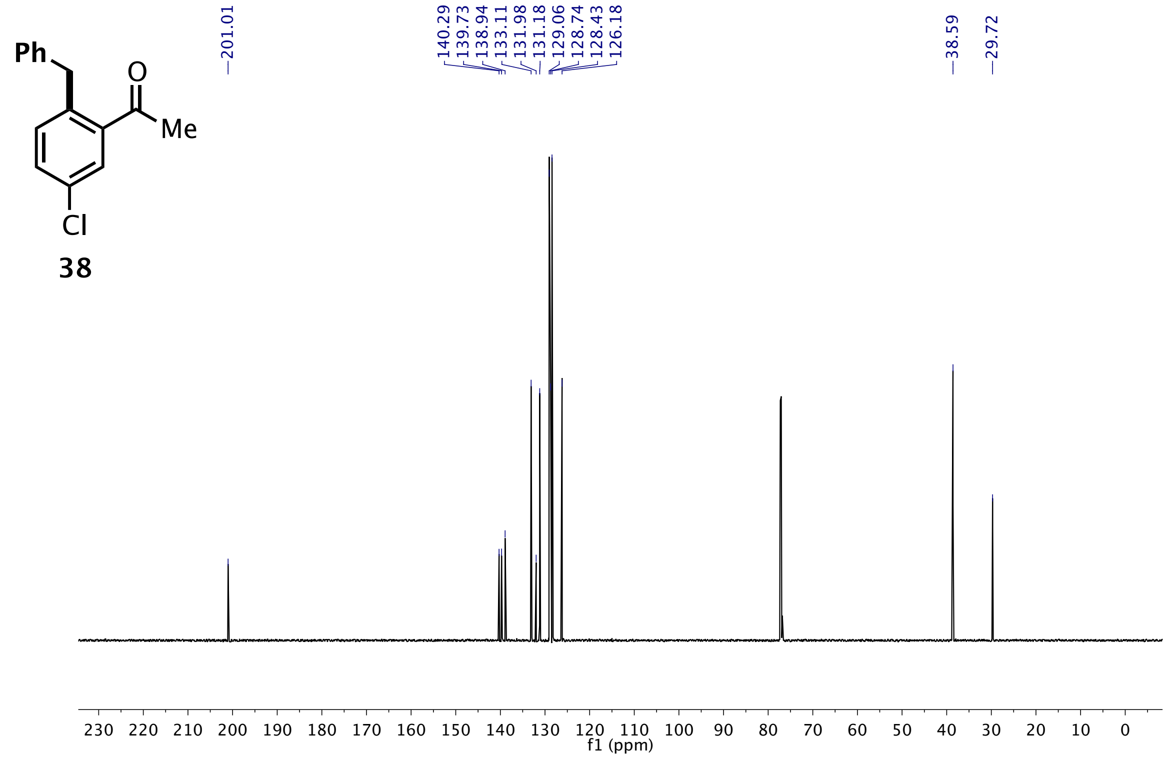
37

^1H (600 MHz, $CDCl_3$)



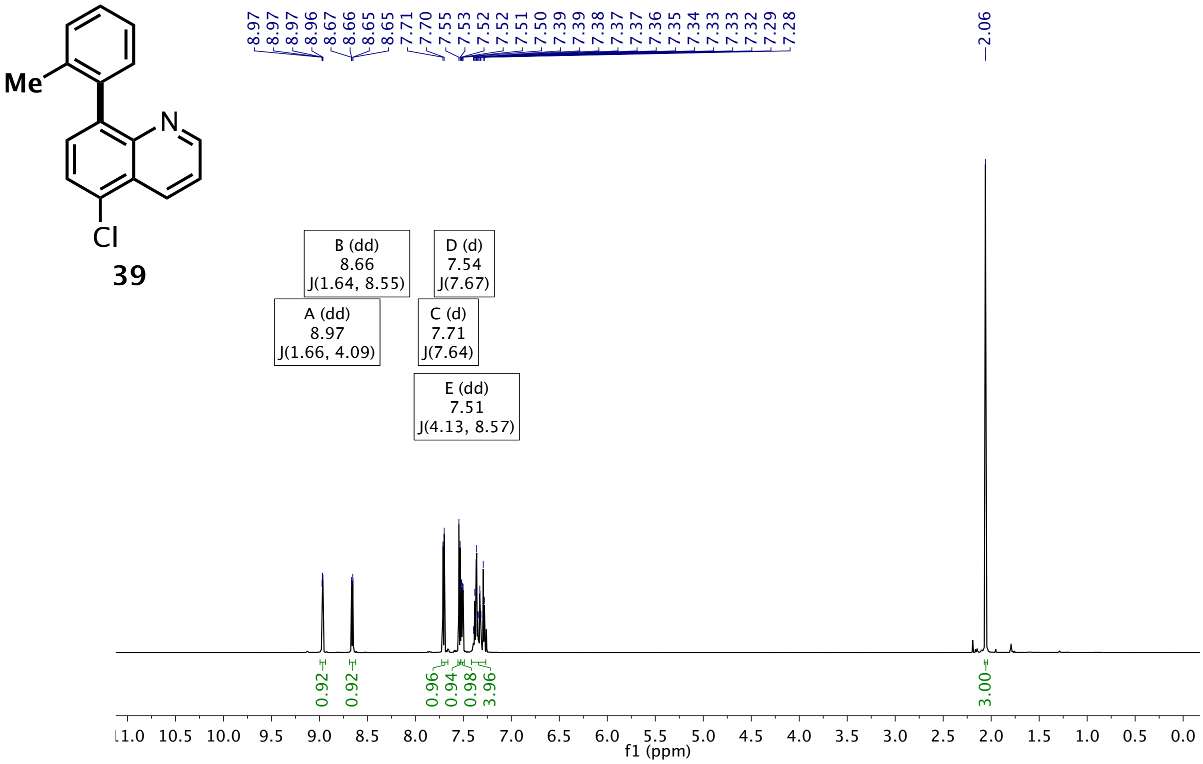
38

$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



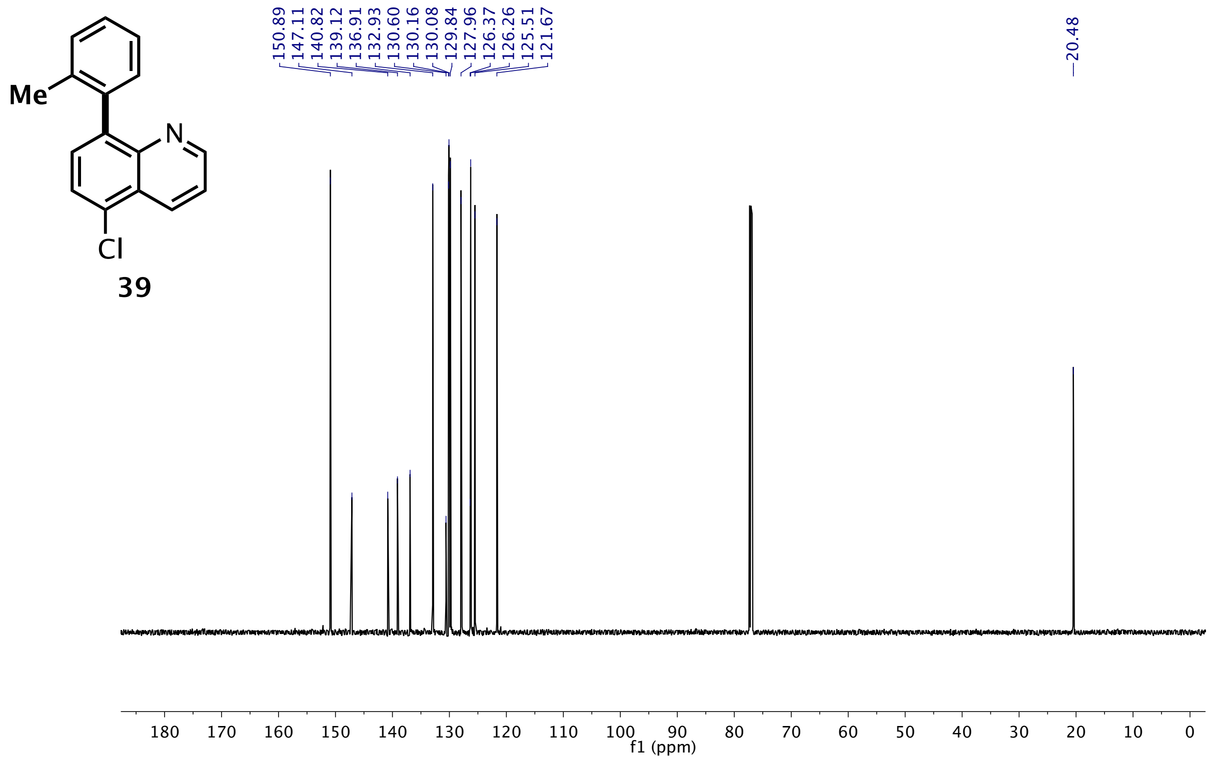
38

^1H (600 MHz, $CDCl_3$)

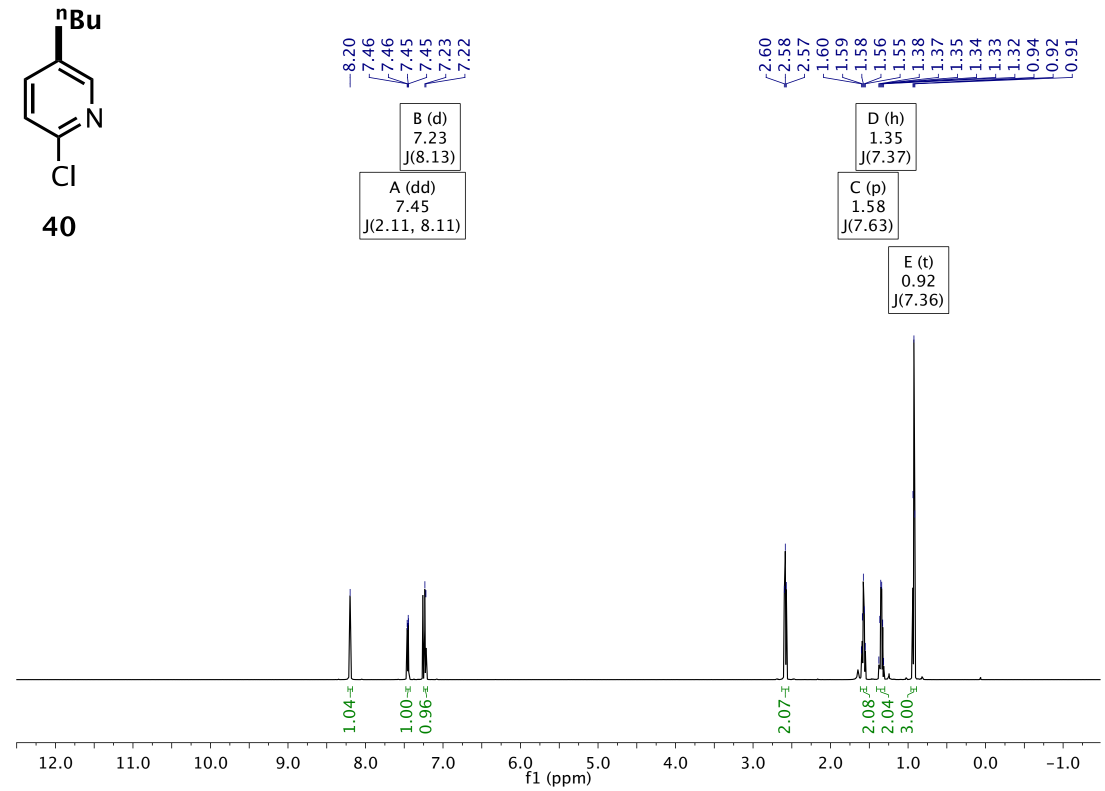


39

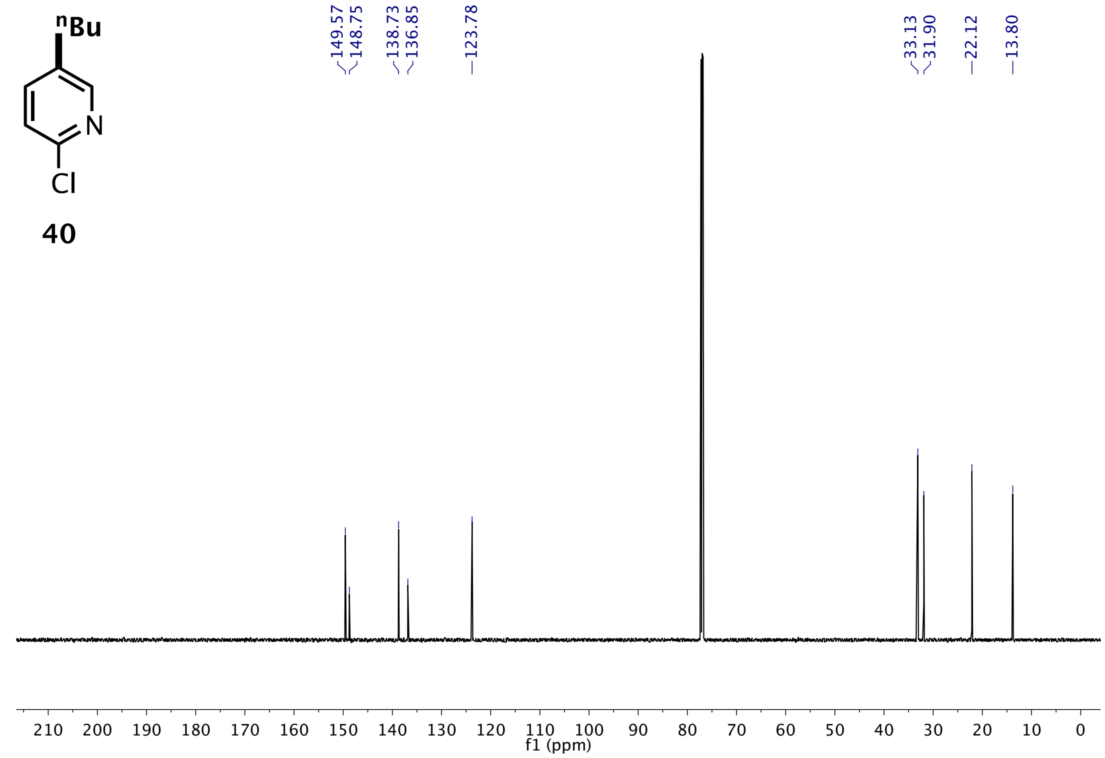
$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)



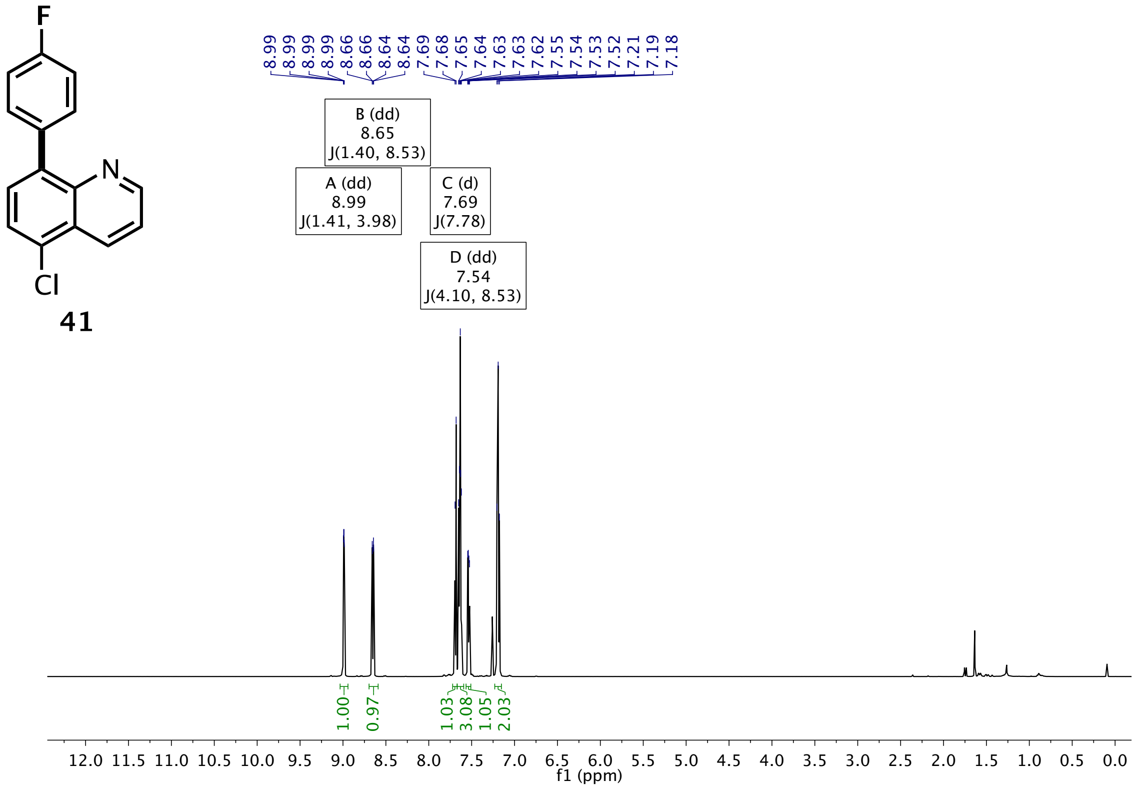
^{1}H (600 MHz, $CDCl_3$)



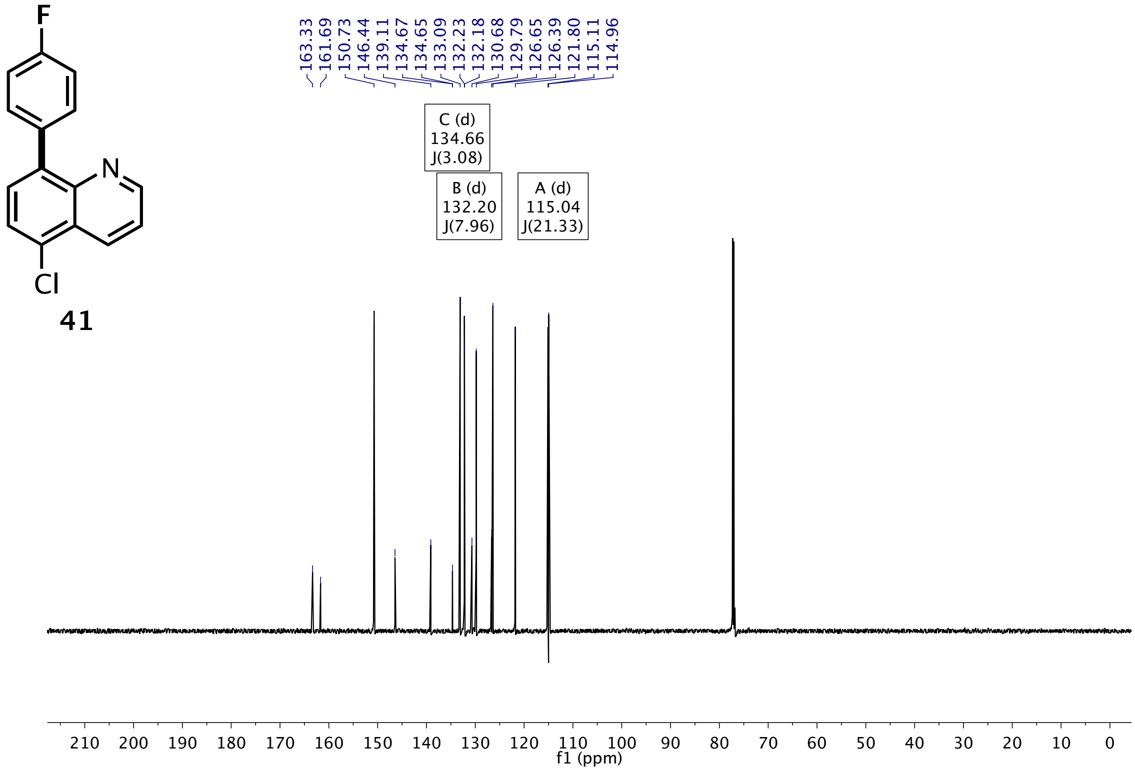
^{13}C{^{1}H} (151 MHz, CDCl$_3$)



^{1}H (600 MHz, CDCl$_3$)

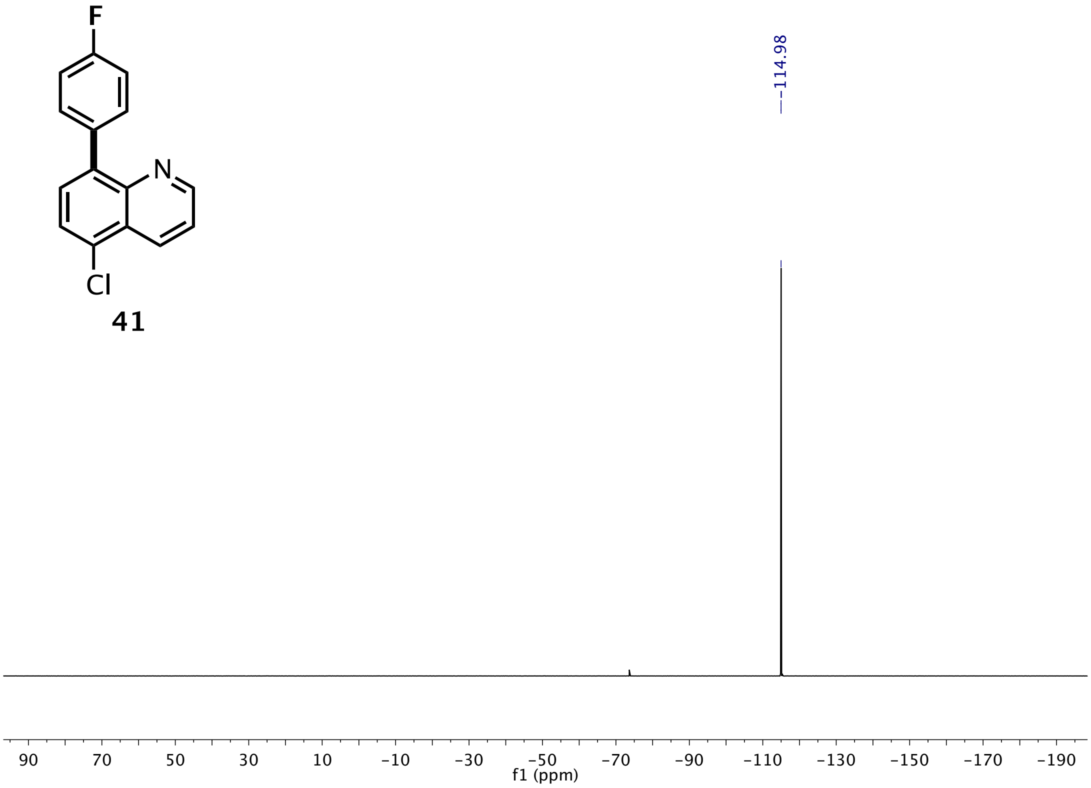


$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)



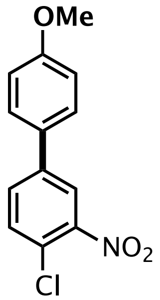
41

$^{19}F\{^{1}H\}$ (564 MHz, $CDCl_3$)

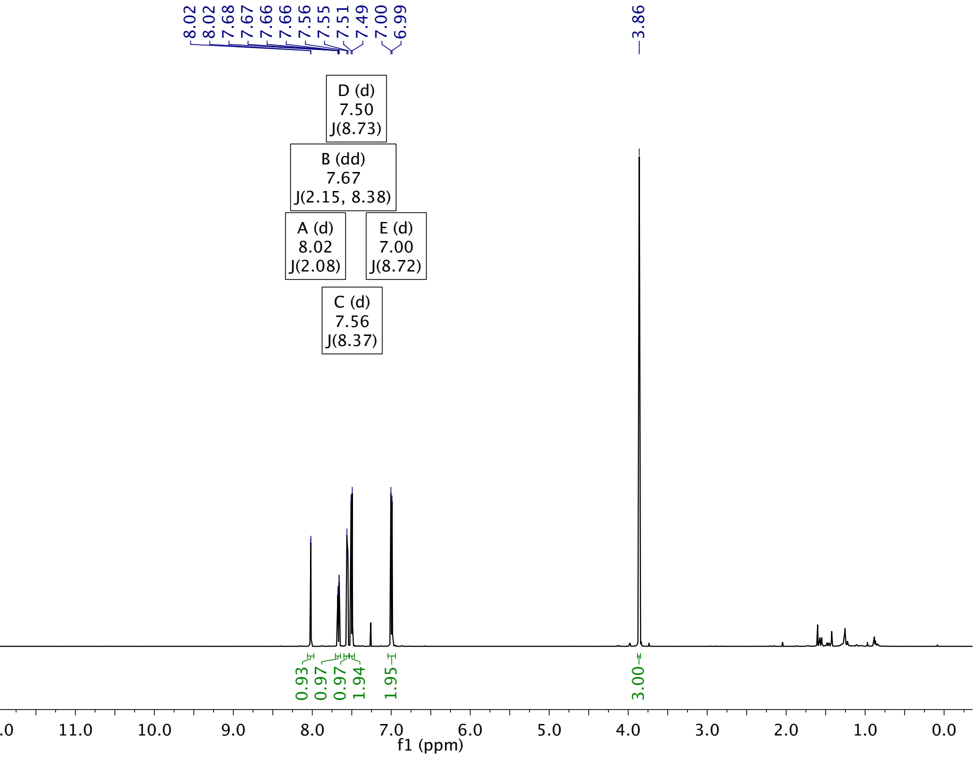


41

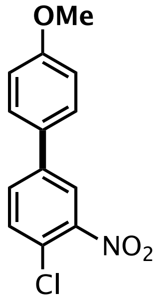
^{1}H (600 MHz, CDCl$_3$)



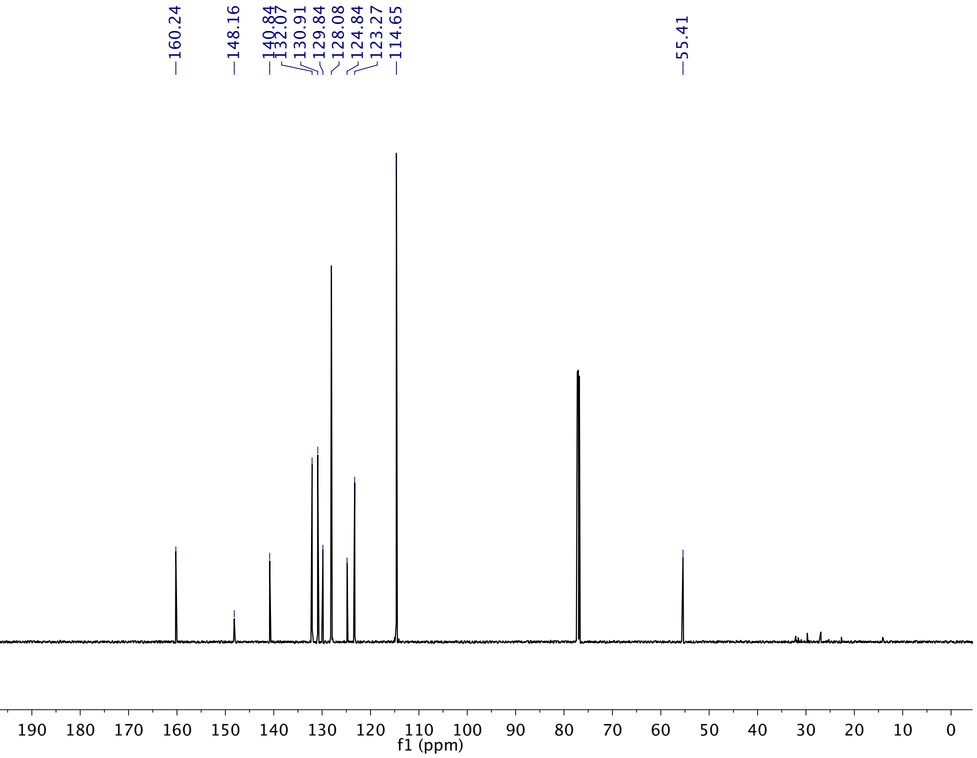
42



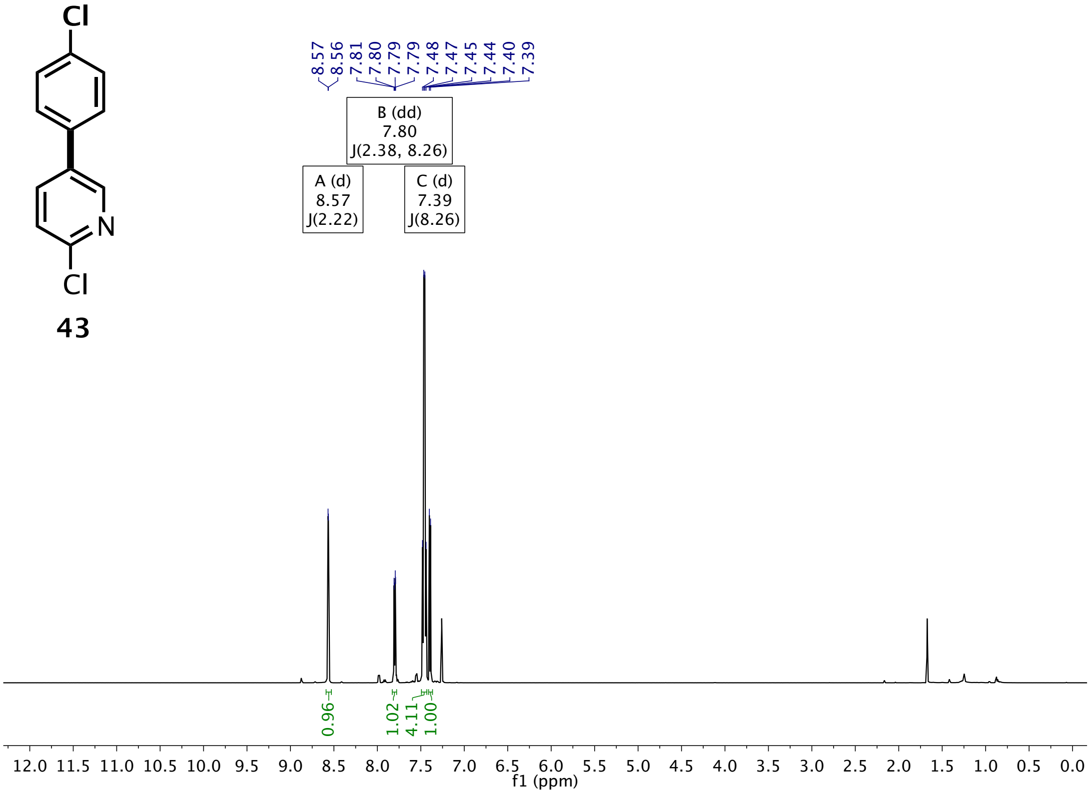
^{13}C{^{1}H} (151 MHz, CDCl$_3$)



42

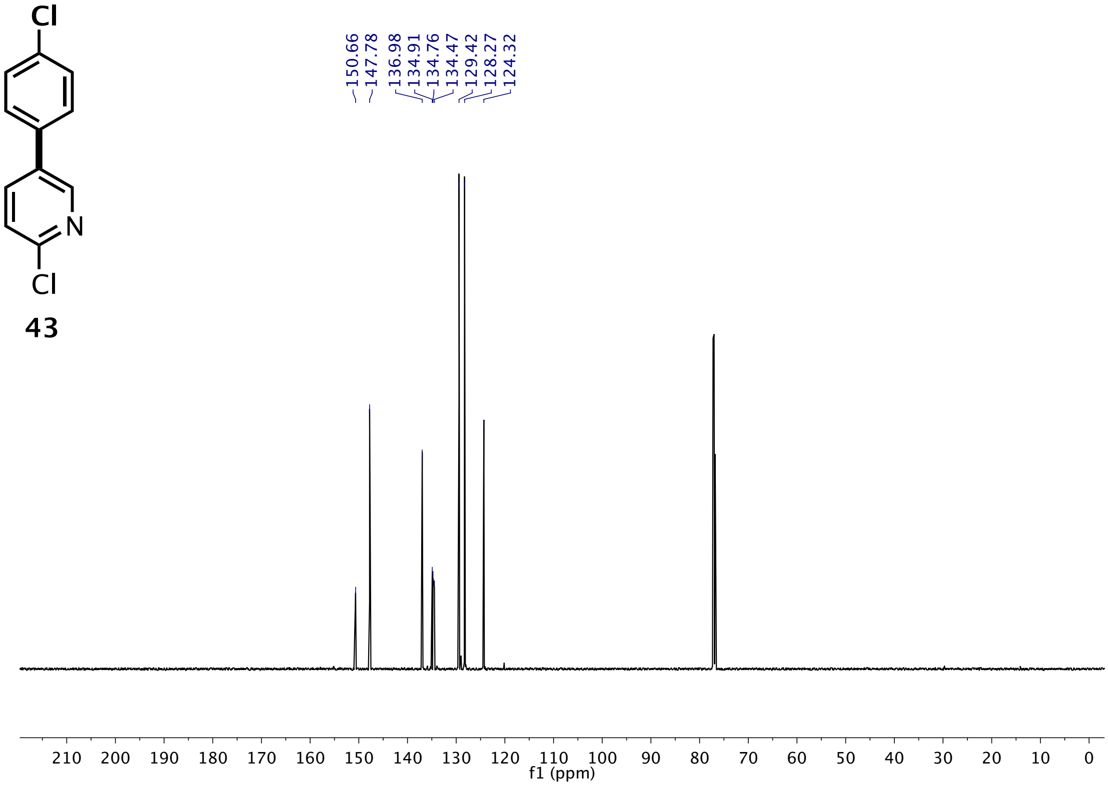


^{1}H (600 MHz, $CDCl_3$)



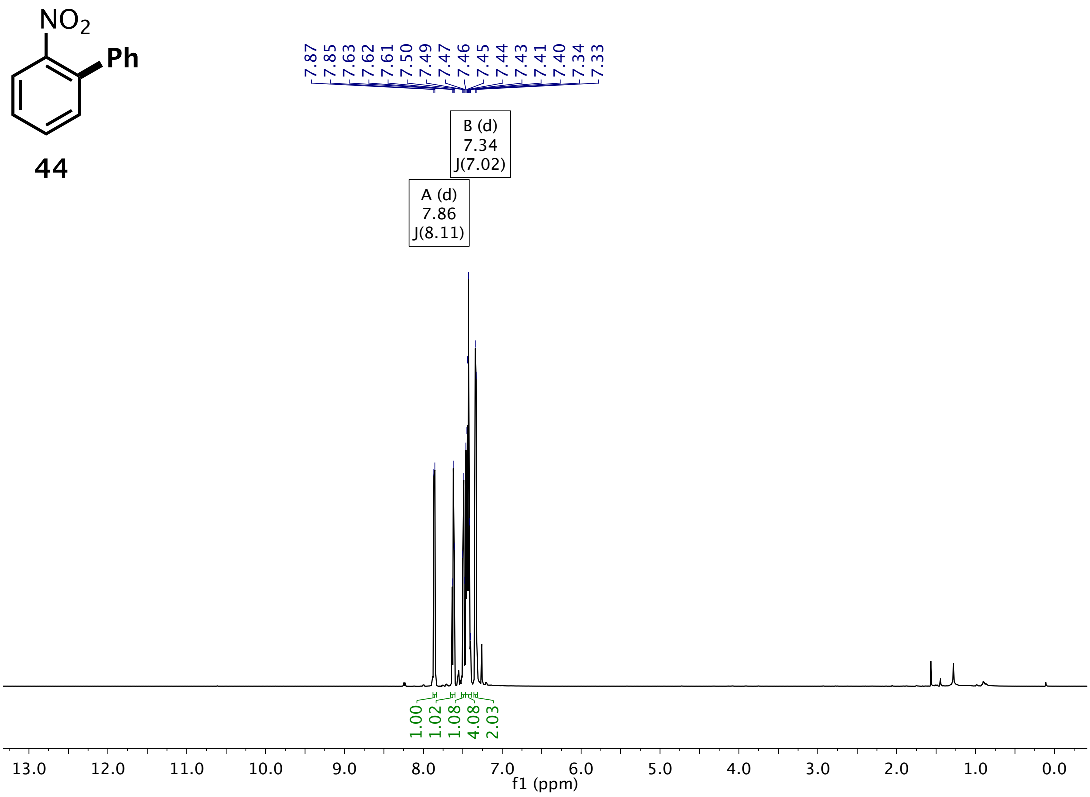
43

^{13}C{^{1}H} (151 MHz, $CDCl_3$)

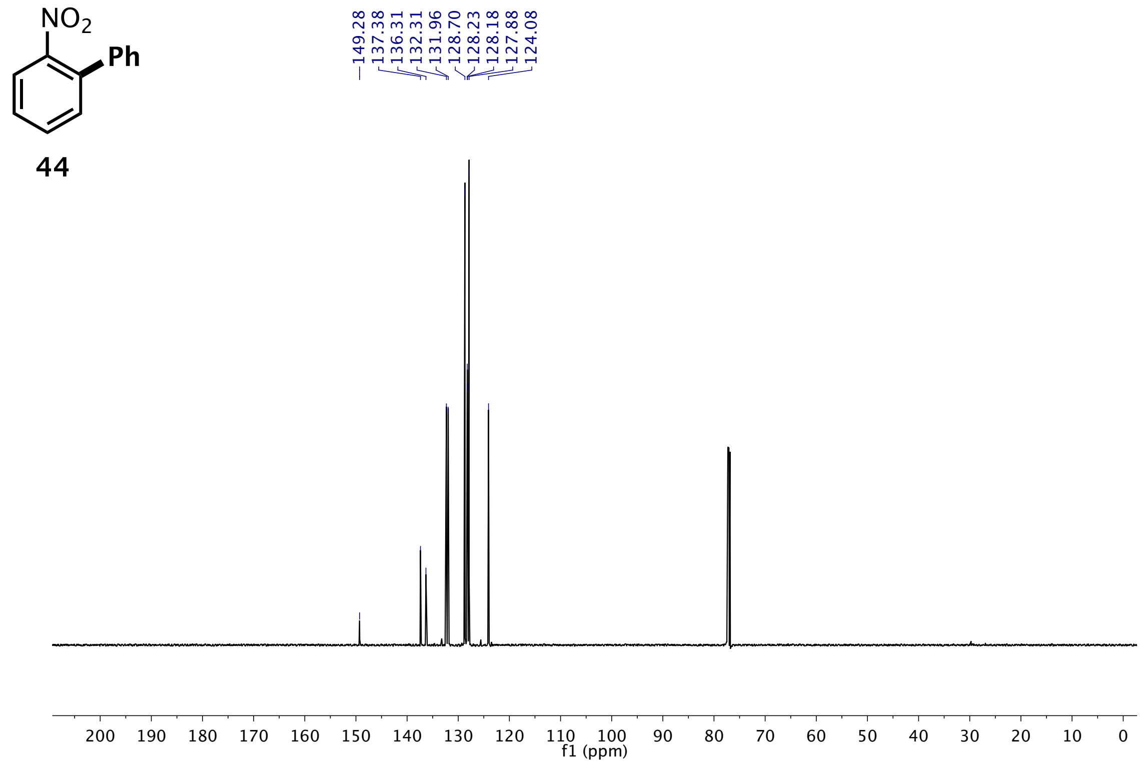


43

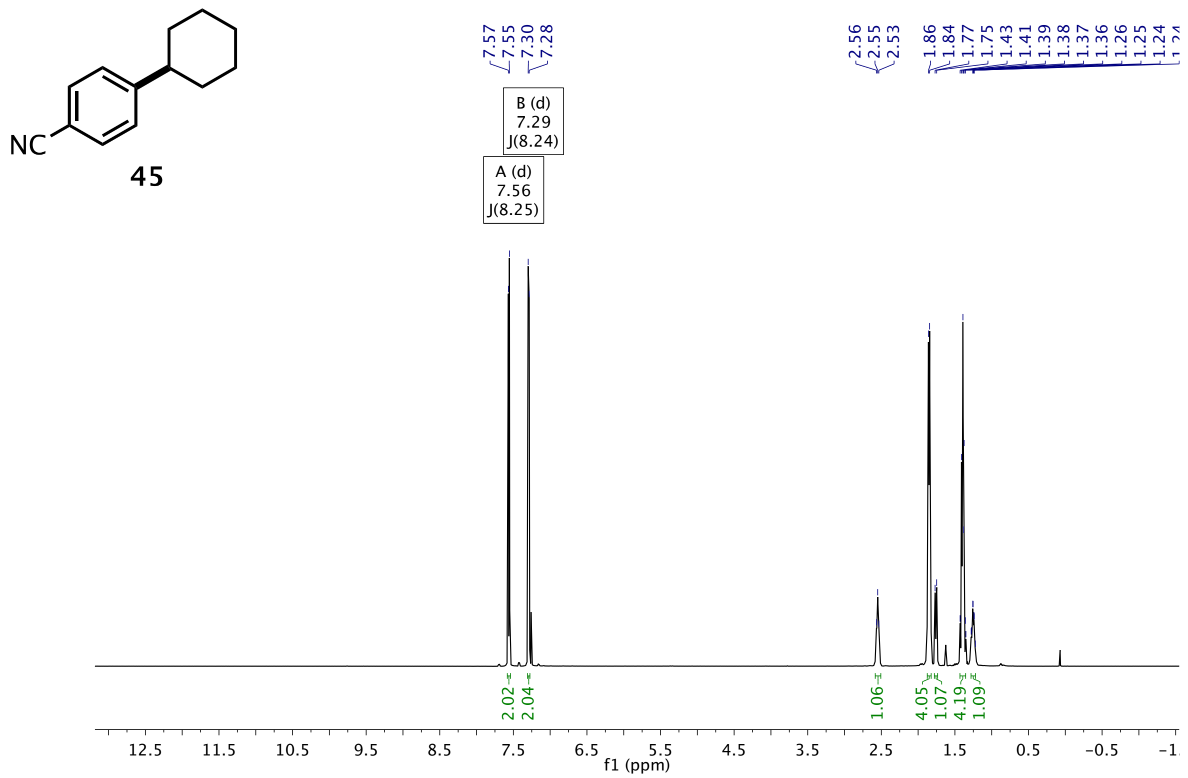
^{1}H (600 MHz, $CDCl_3$)



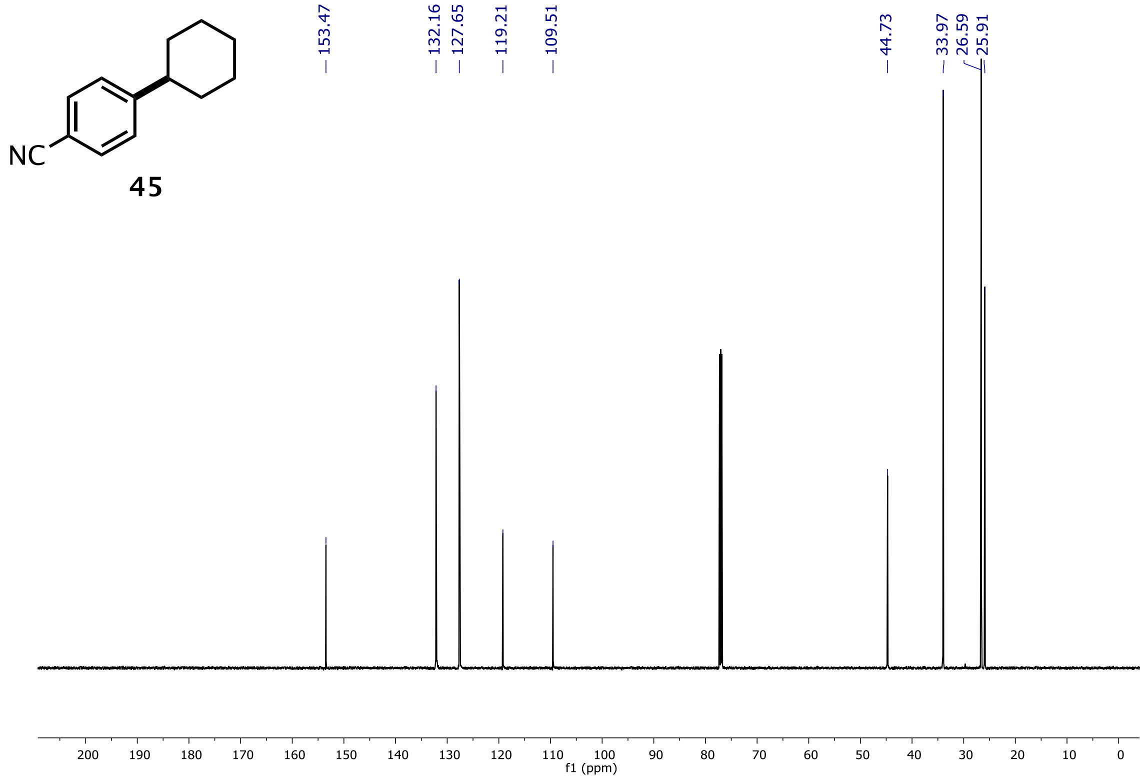
$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)



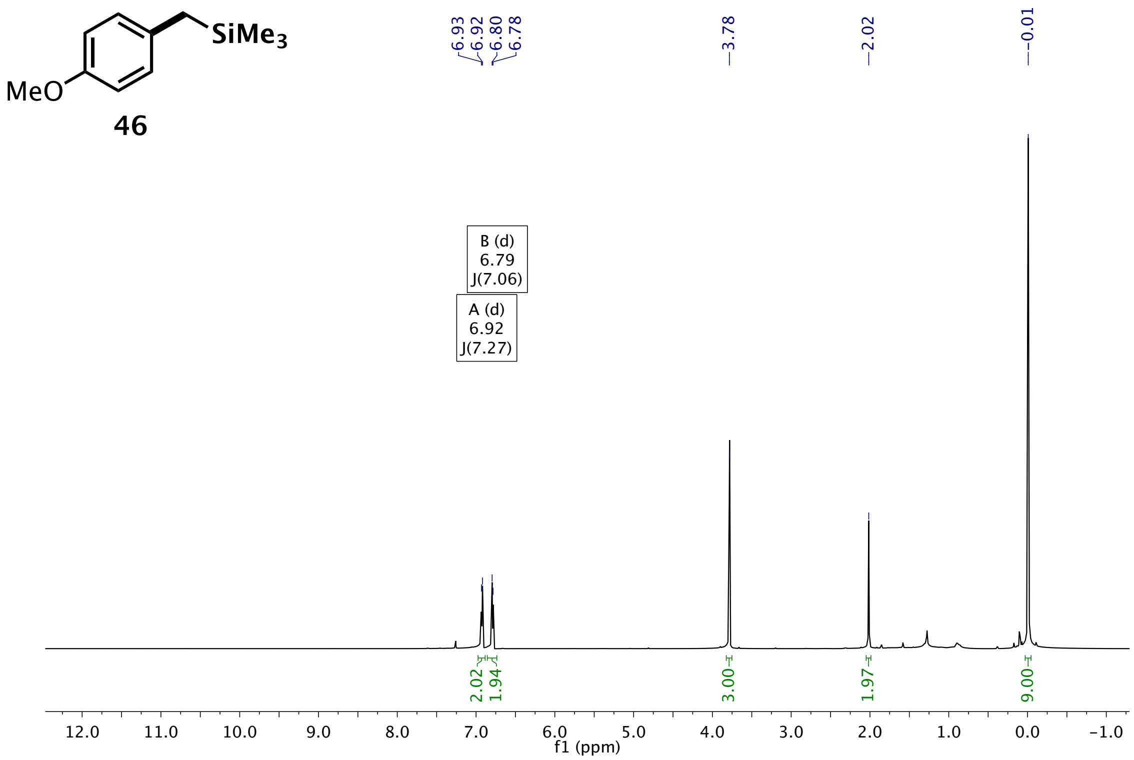
^{1}H (600 MHz, CDCl$_3$)



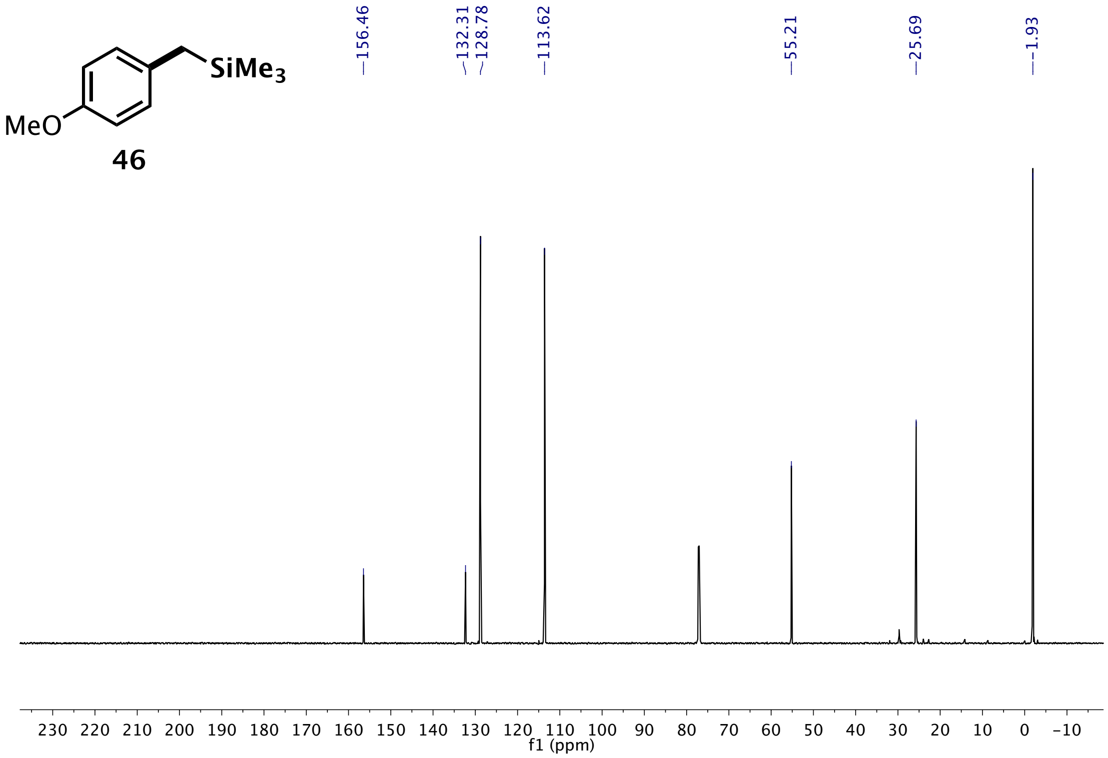
^{13}C{^{1}H} (151 MHz, CDCl$_3$)



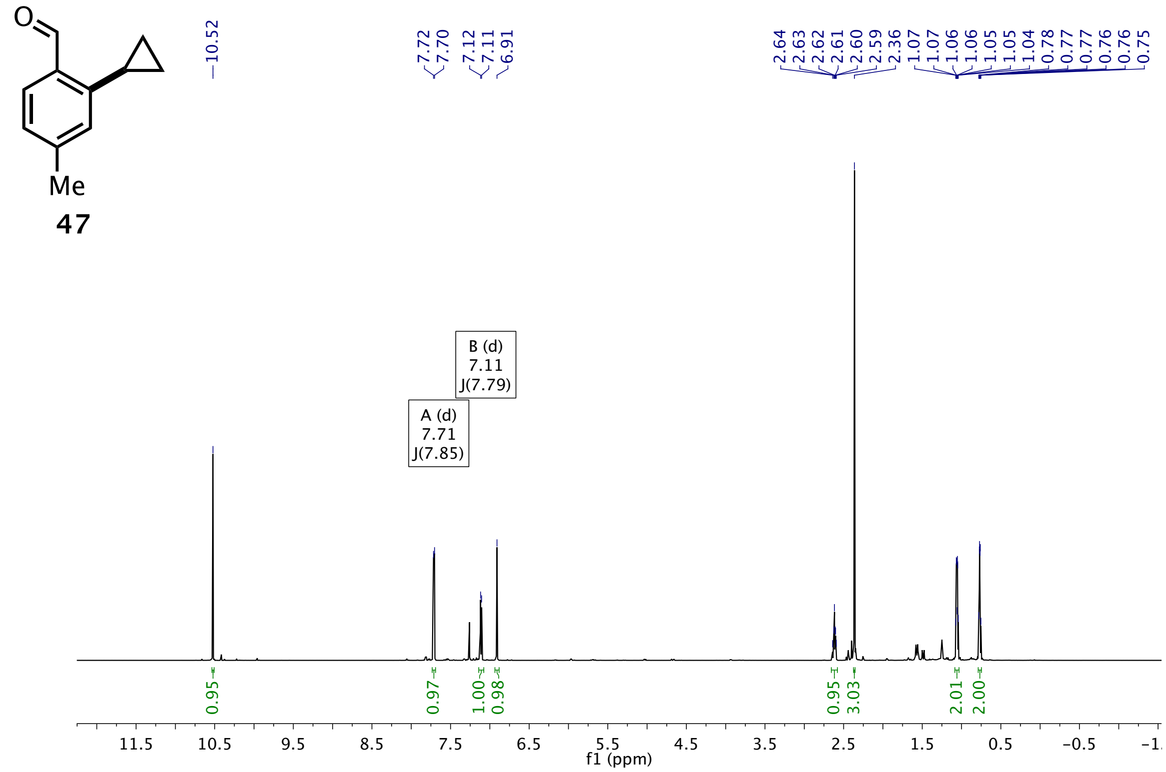
^{1}H (600 MHz, $CDCl_3$)


46

$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)

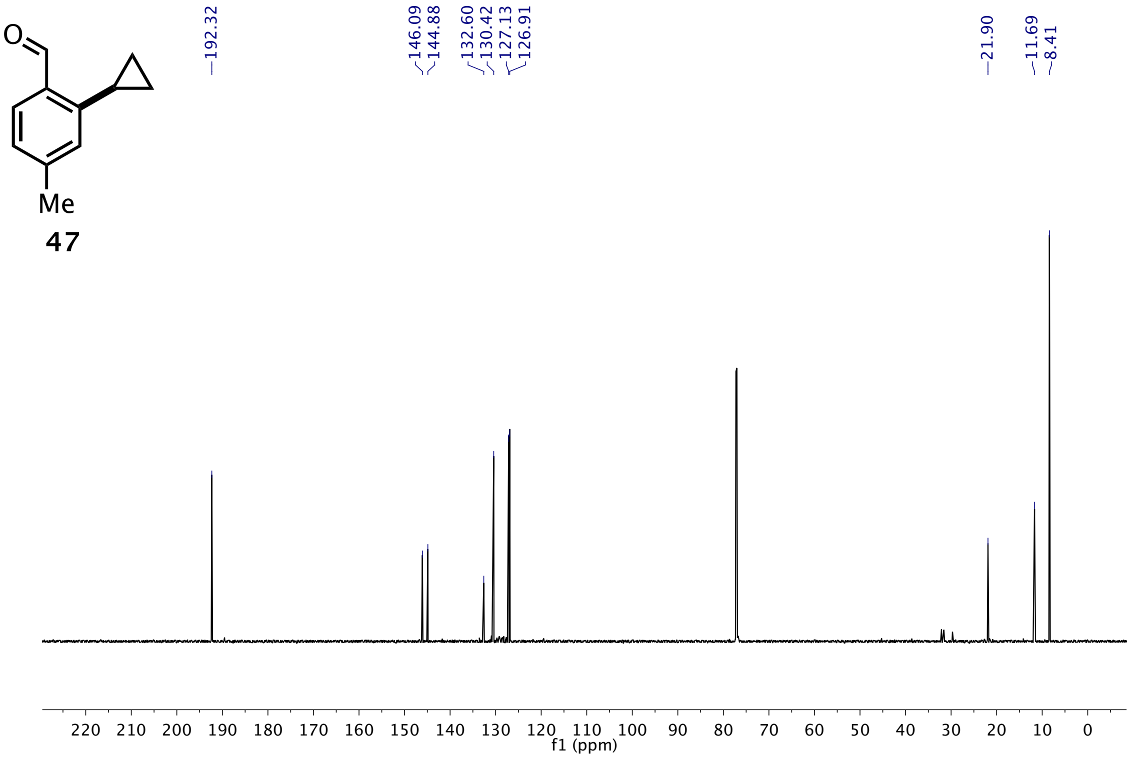

46

^1H (600 MHz, $CDCl_3$)



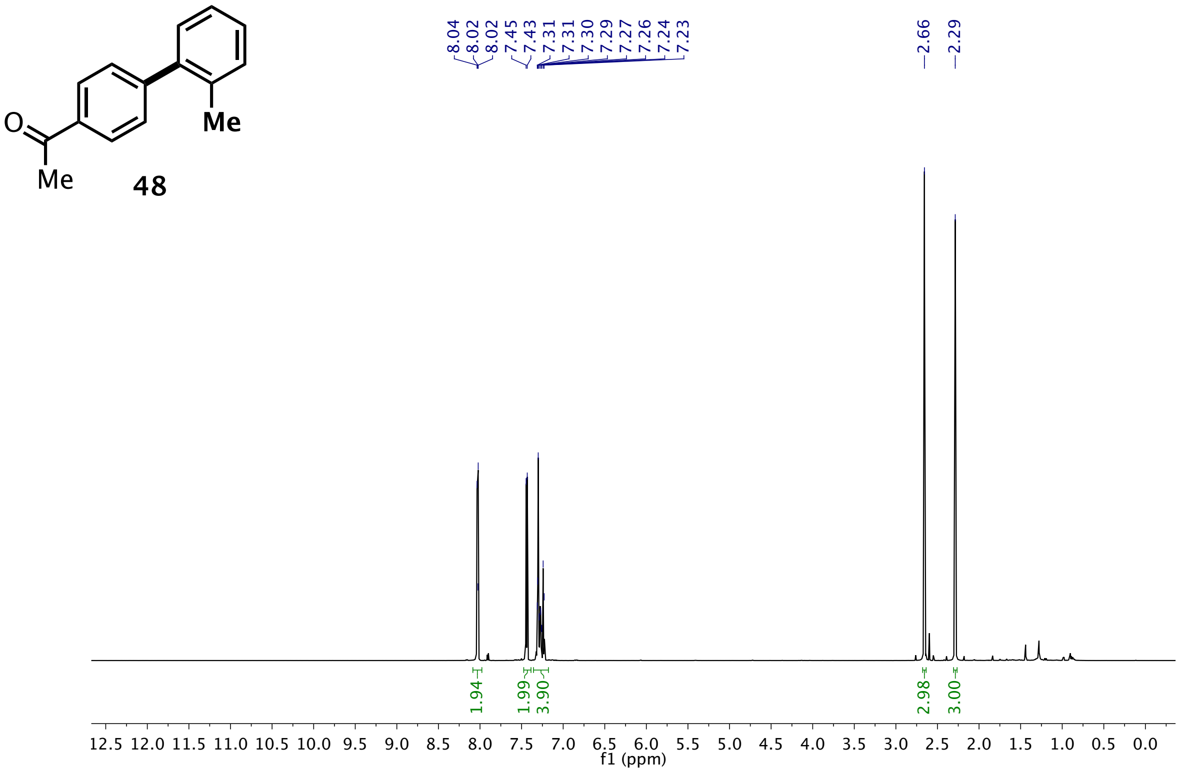
47

$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)

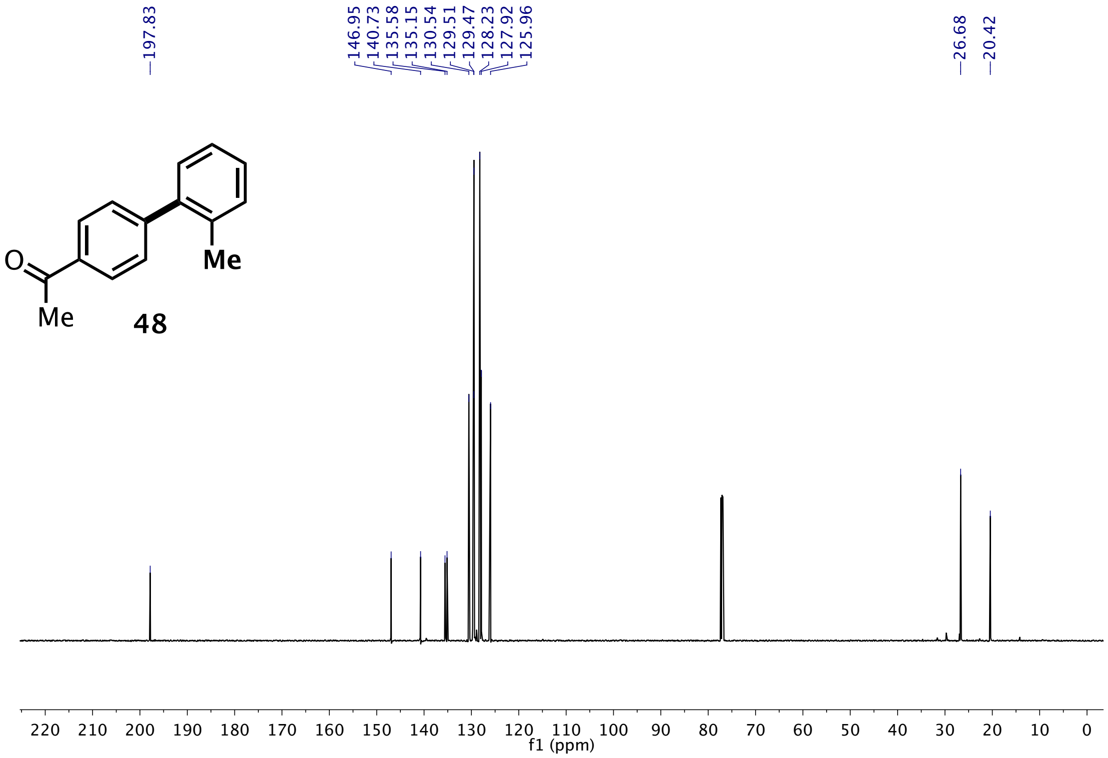


47

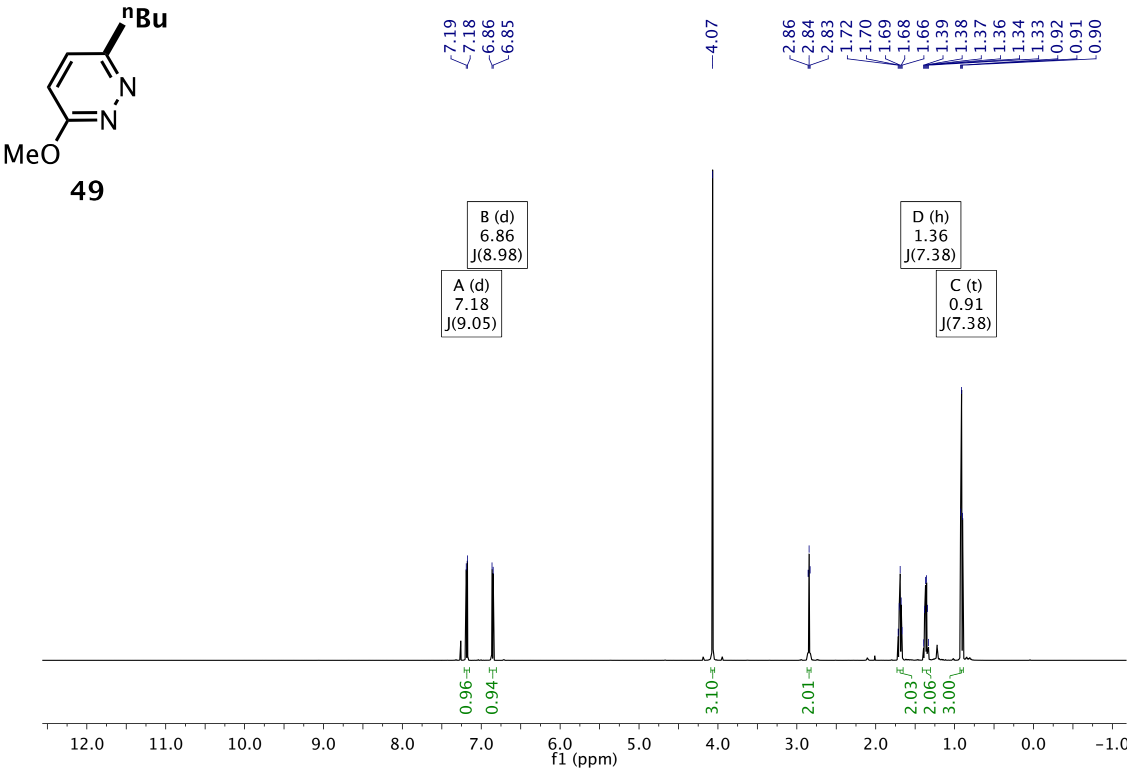
^{1}H (600 MHz, CDCl$_3$)



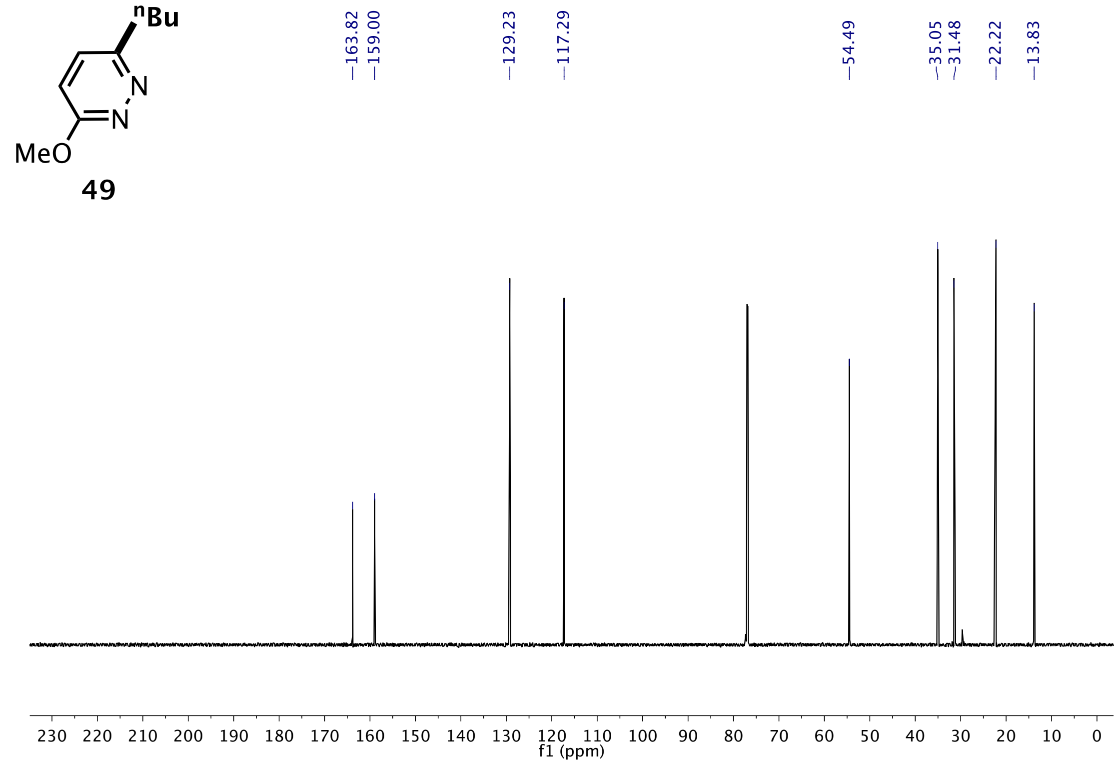
^{13}C{^{1}H} (151 MHz, CDCl$_3$)



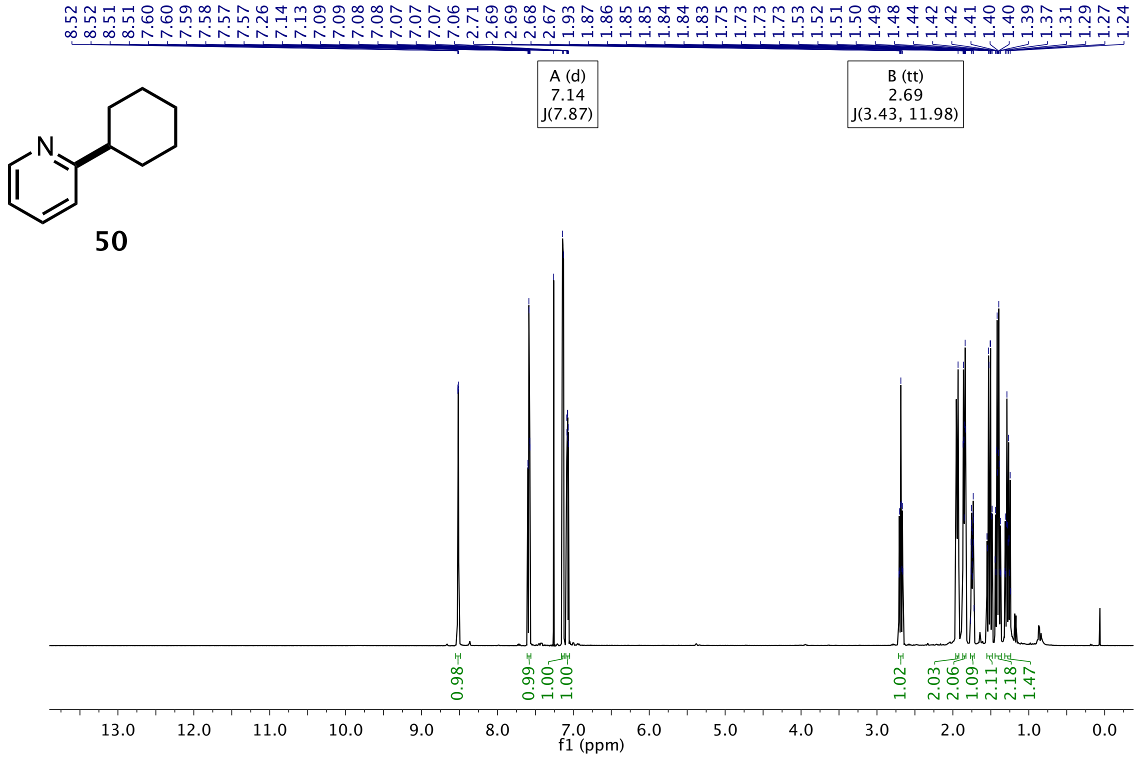
^{1}H (600 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)

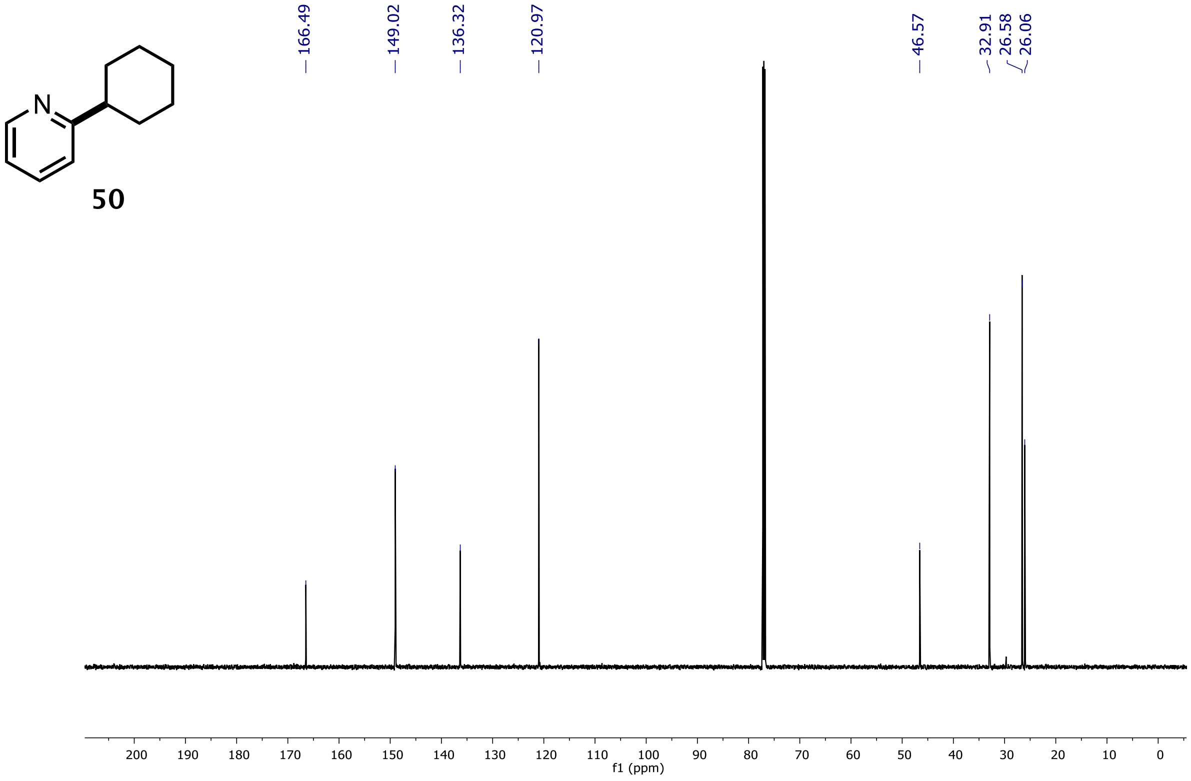


^{1}H (600 MHz, $CDCl_3$)



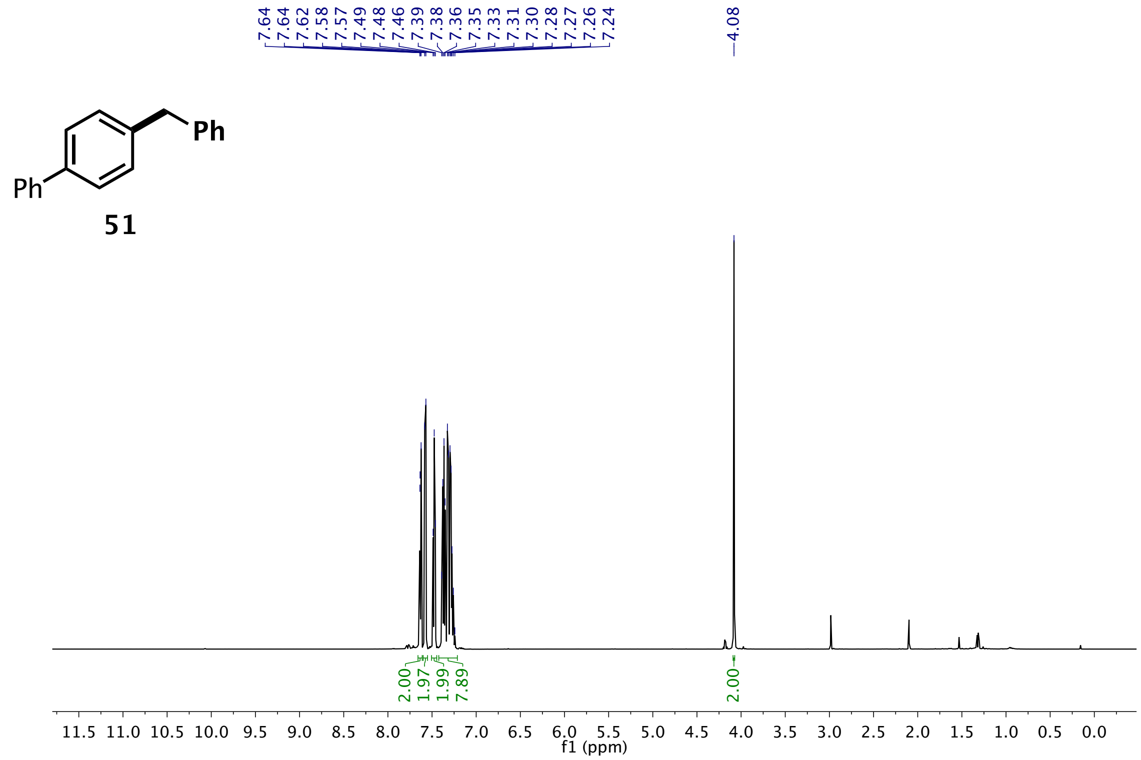
50

$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)

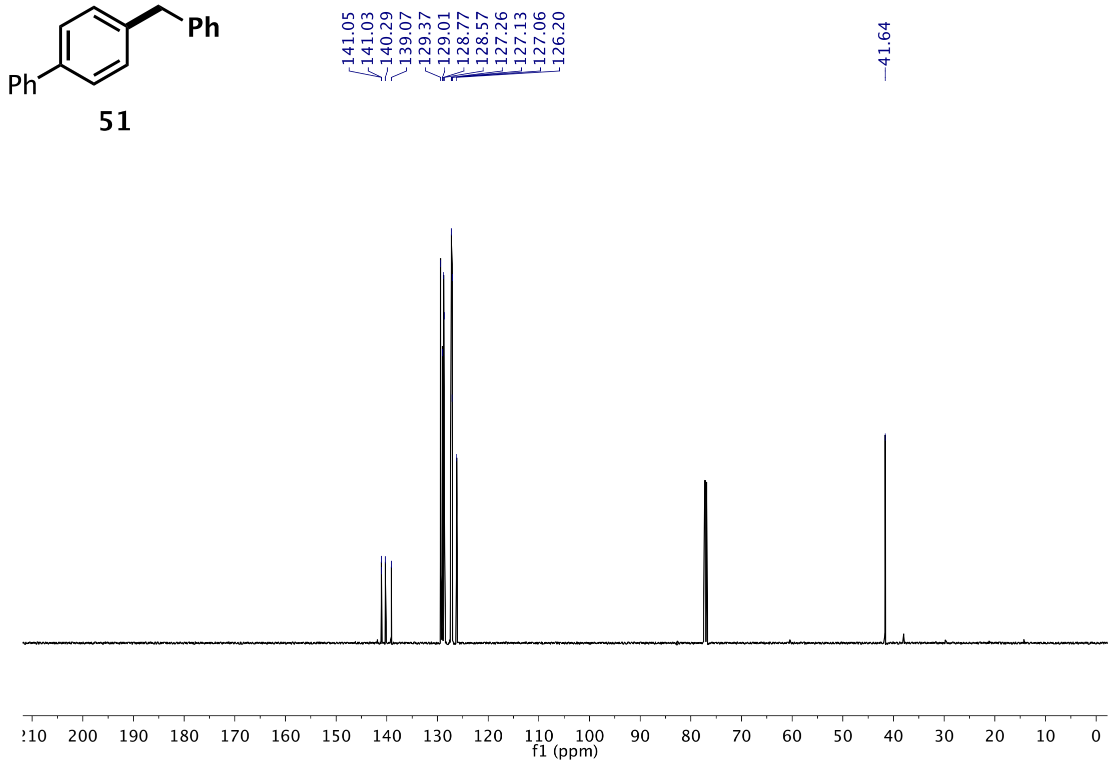


50

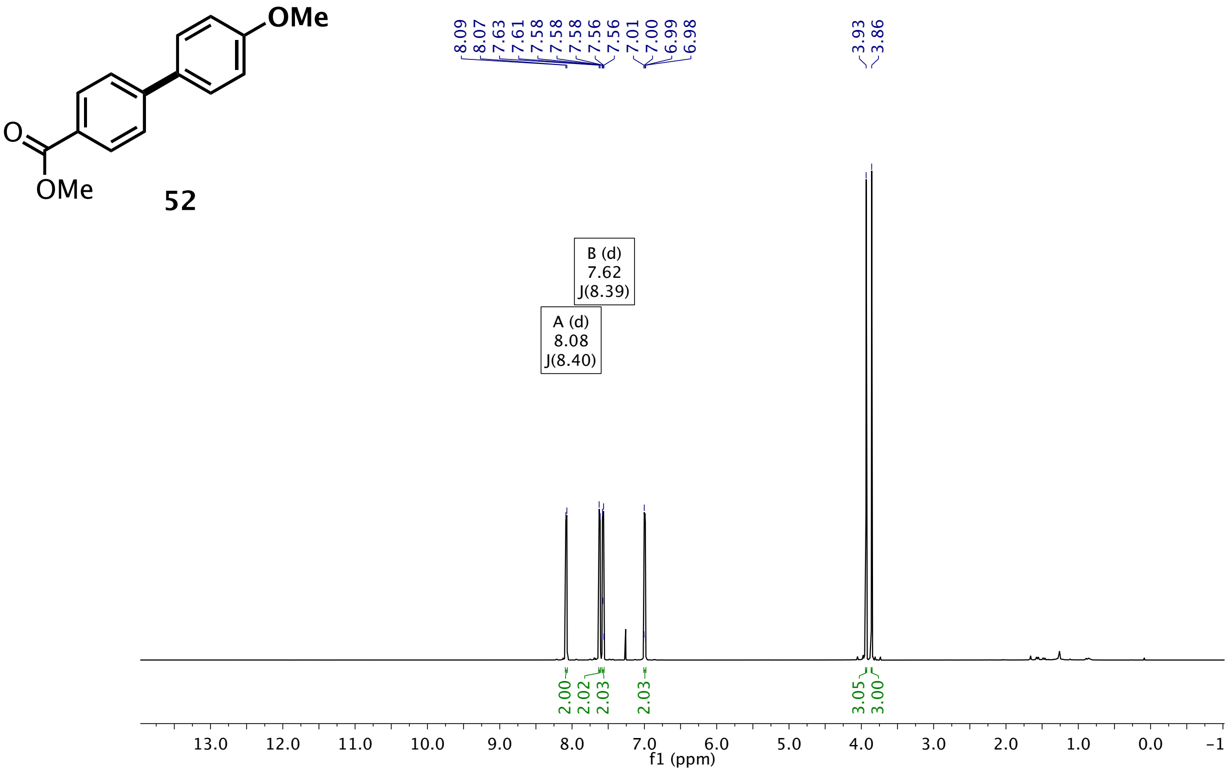
^{1}H (600 MHz, CDCl$_3$)



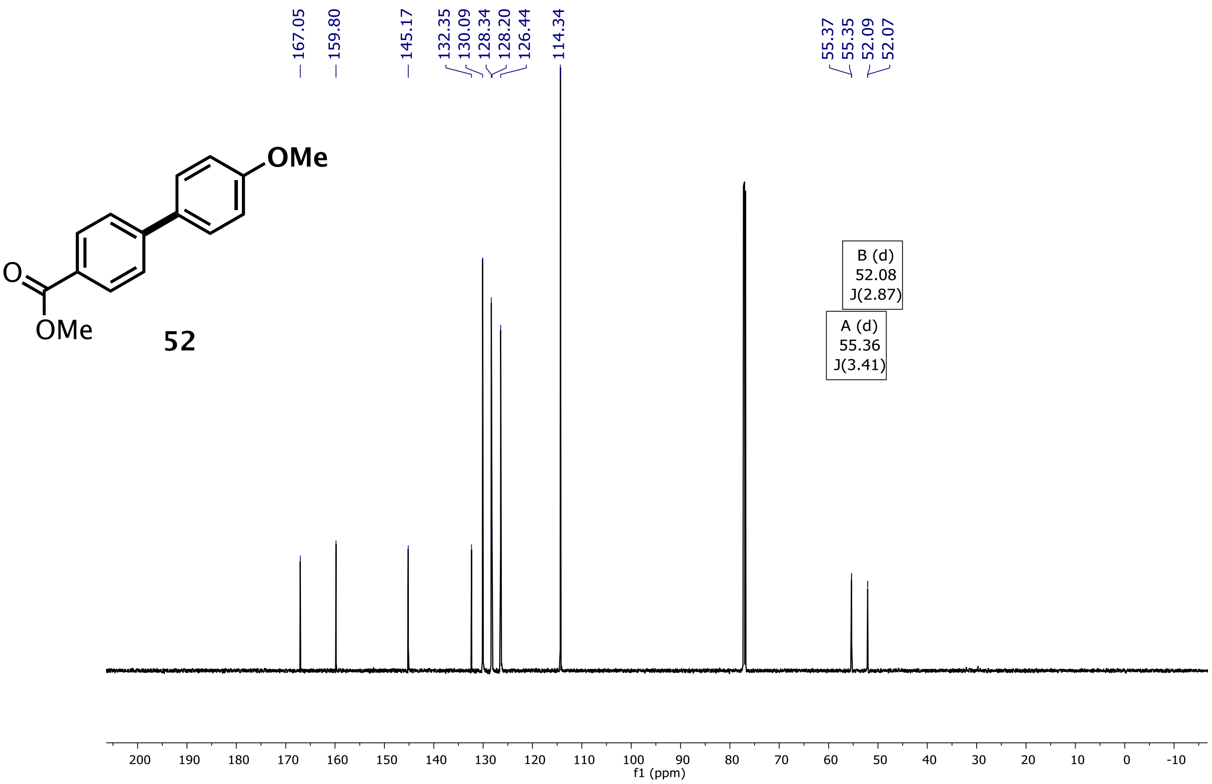
^{13}C{^{1}H} (151 MHz, CDCl$_3$)



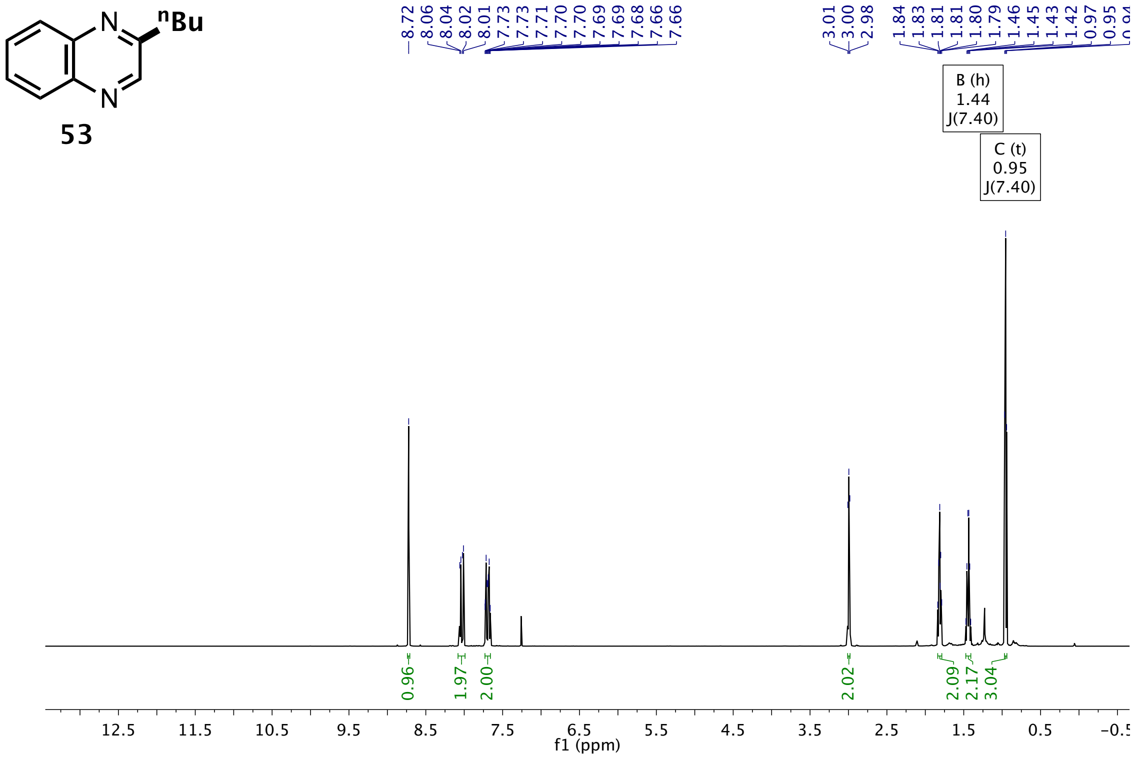
^{1}H (600 MHz, CDCl$_3$)



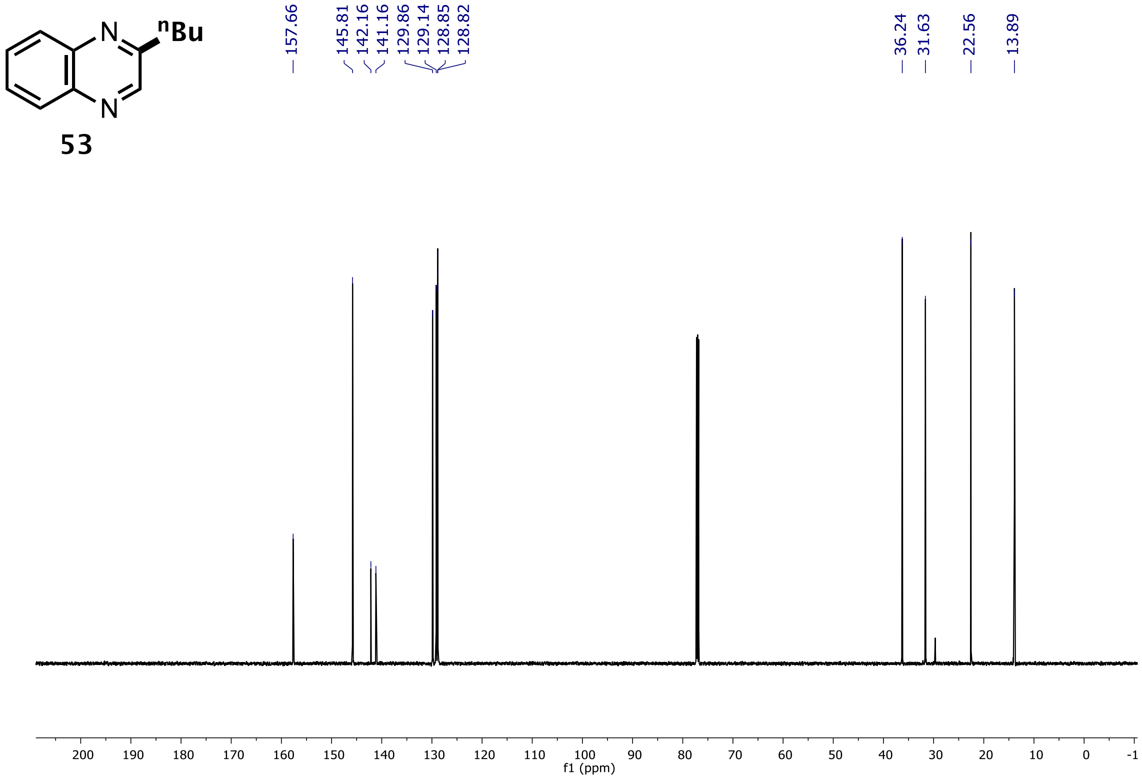
^{13}C{^{1}H} (151 MHz, CDCl$_3$)



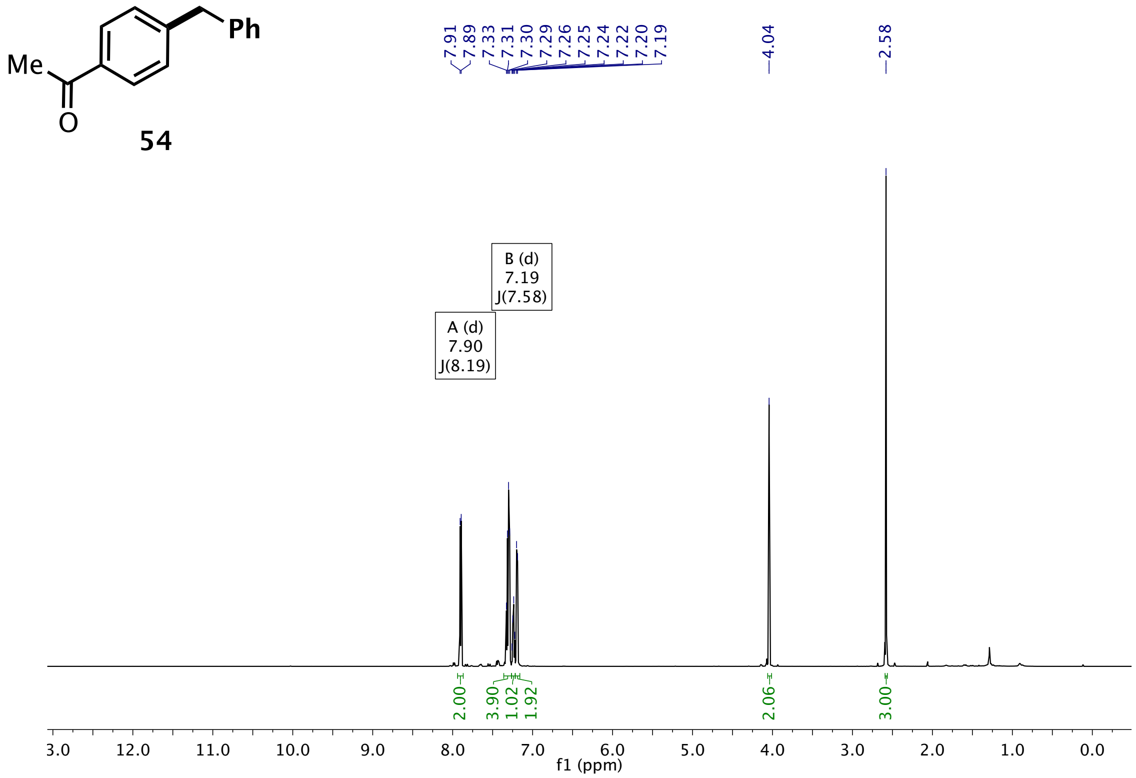
^{1}H (600 MHz, CDCl$_3$)



^{13}C{^{1}H} (151 MHz, CDCl$_3$)

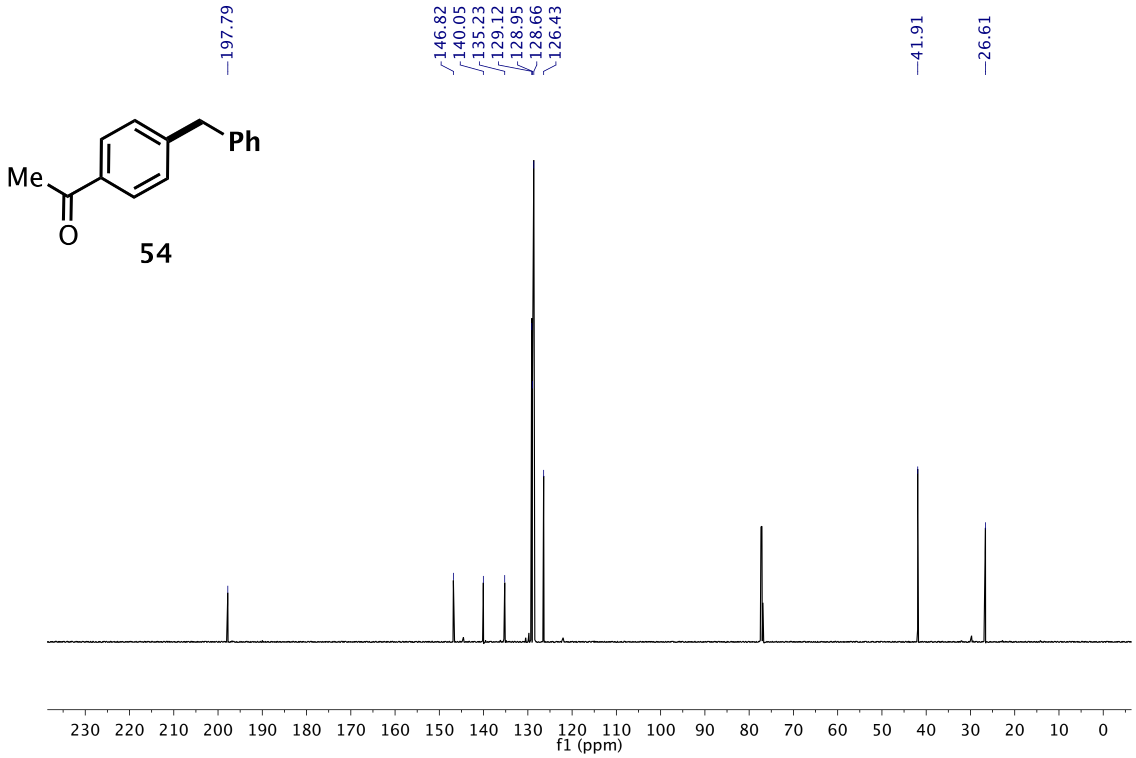


^{1}H (600 MHz, CDCl$_3$)



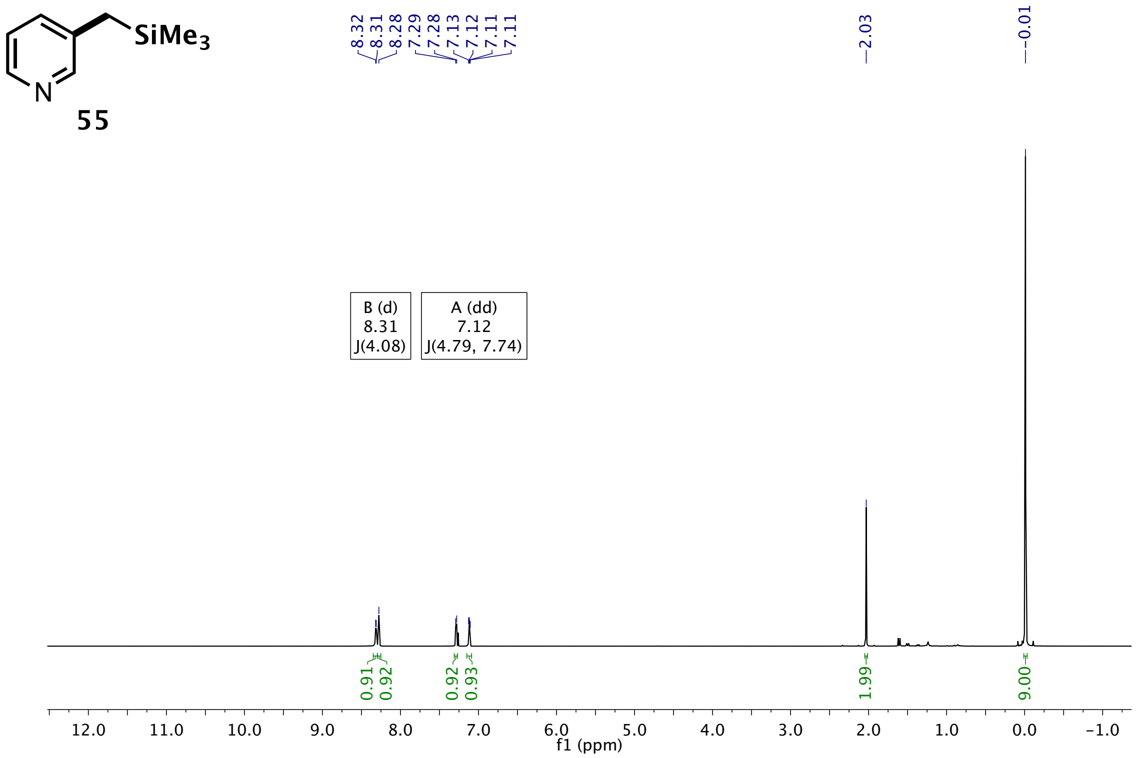
54

^{13}C{^{1}H} (151 MHz, CDCl$_3$)

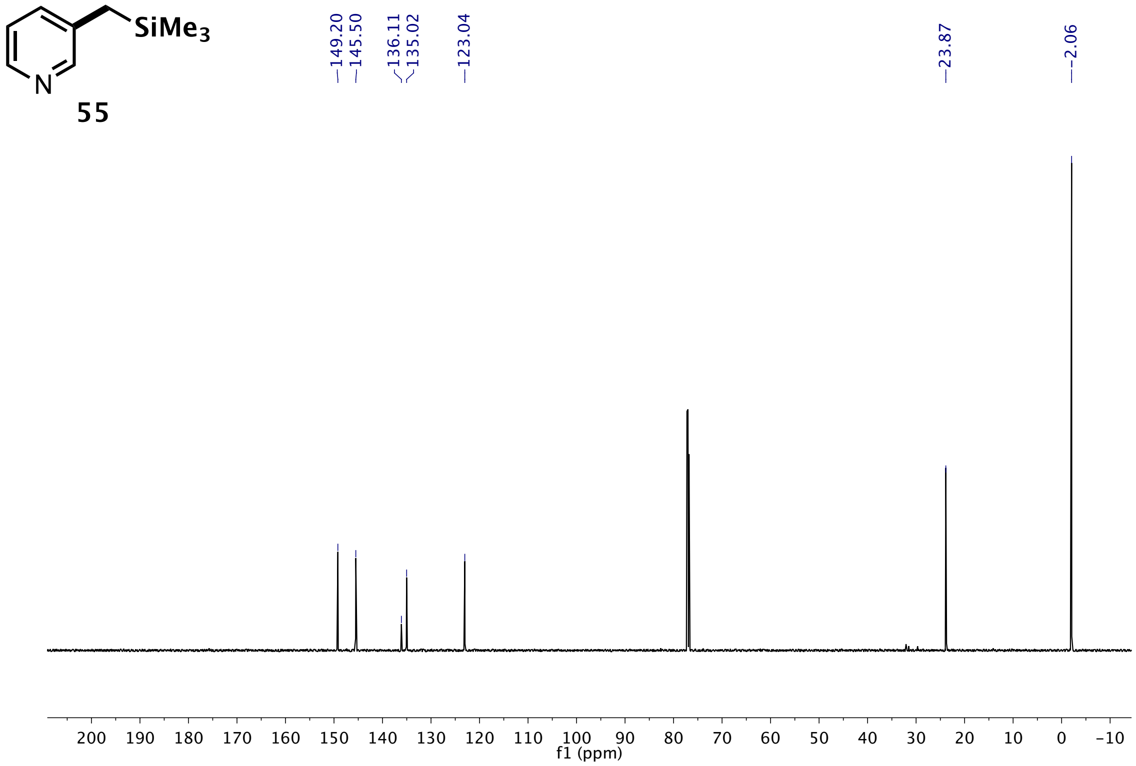


54

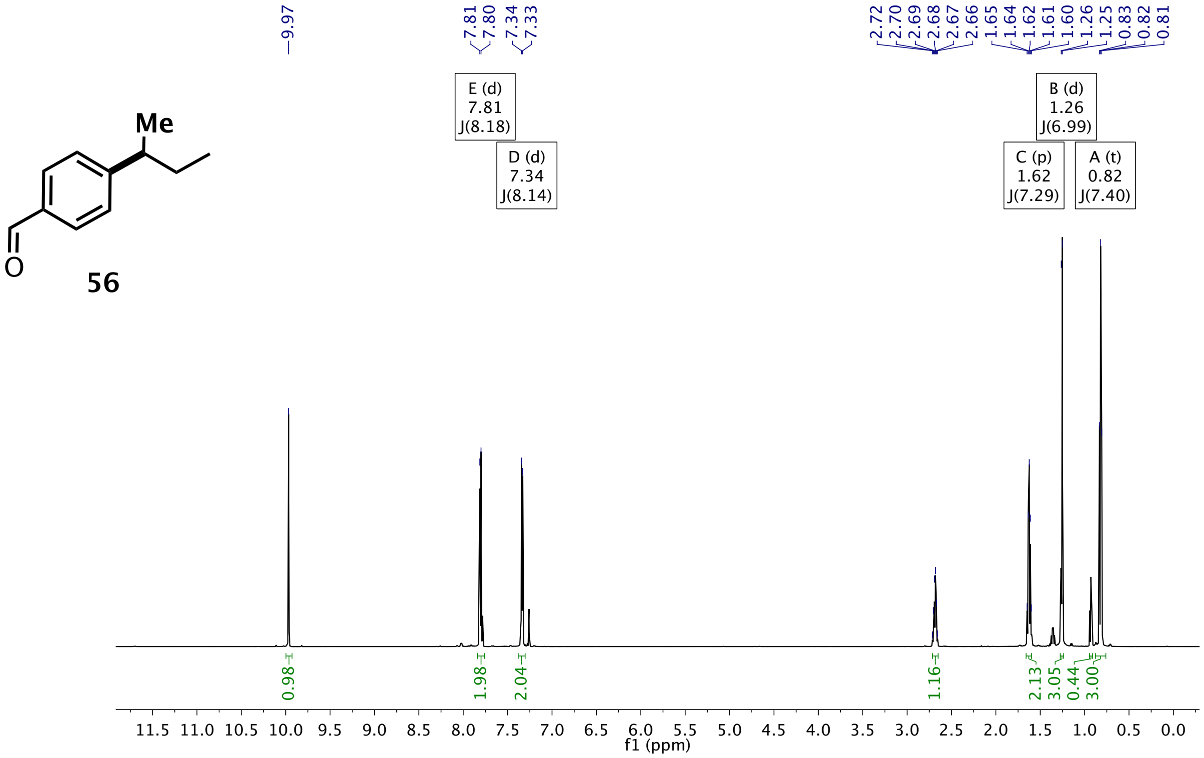
^{1}H (600 MHz, CDCl$_3$)



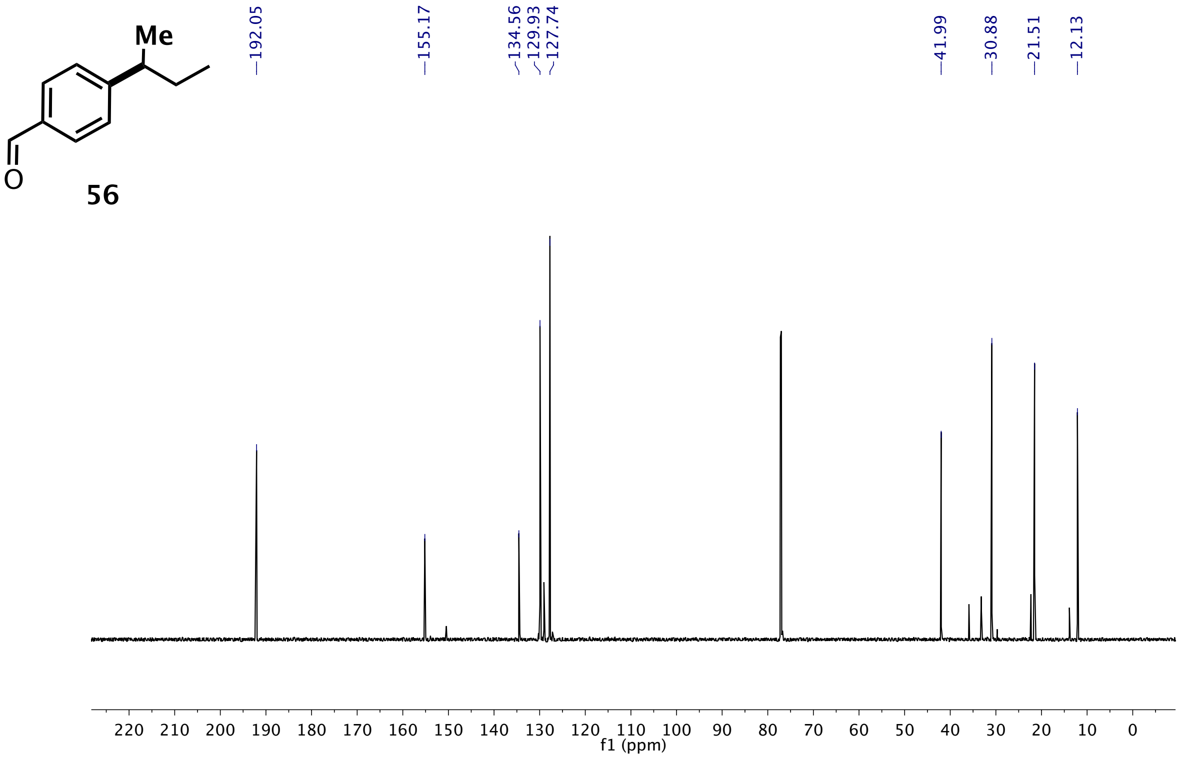
^{13}C{^{1}H} (151 MHz, CDCl$_3$)



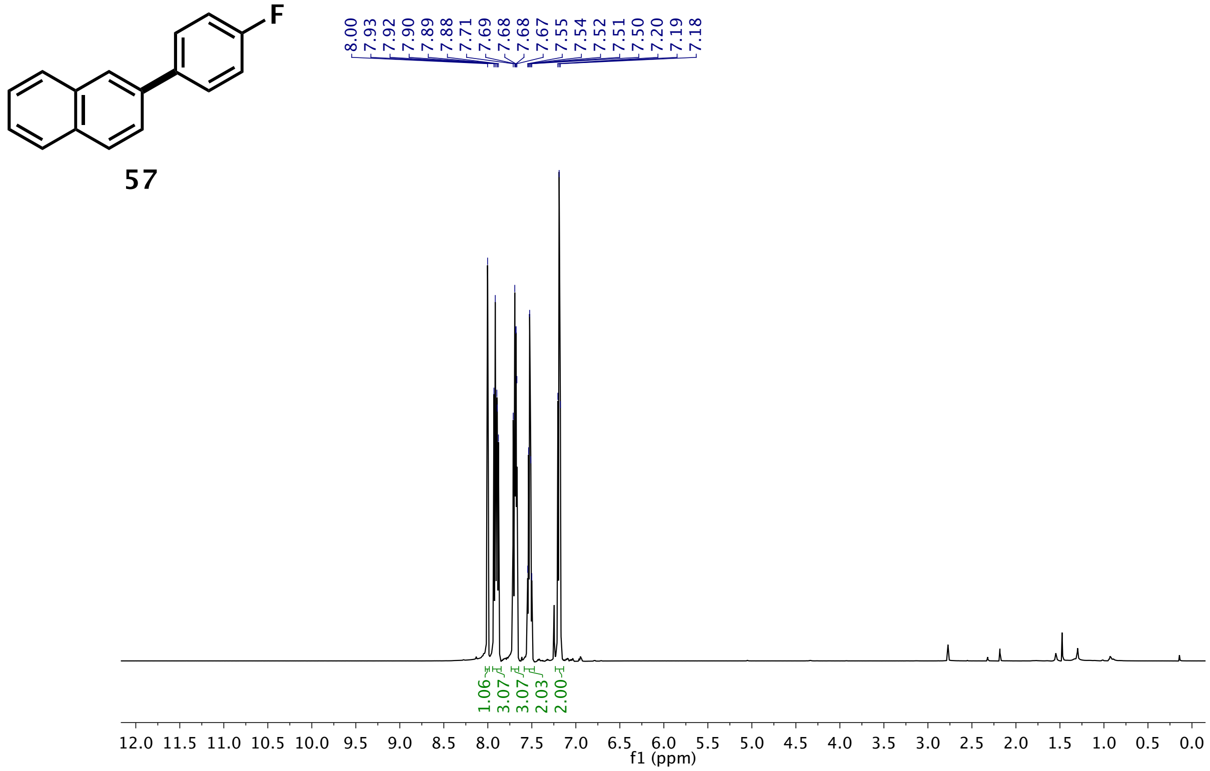
^{1}H (600 MHz, CDCl$_3$)



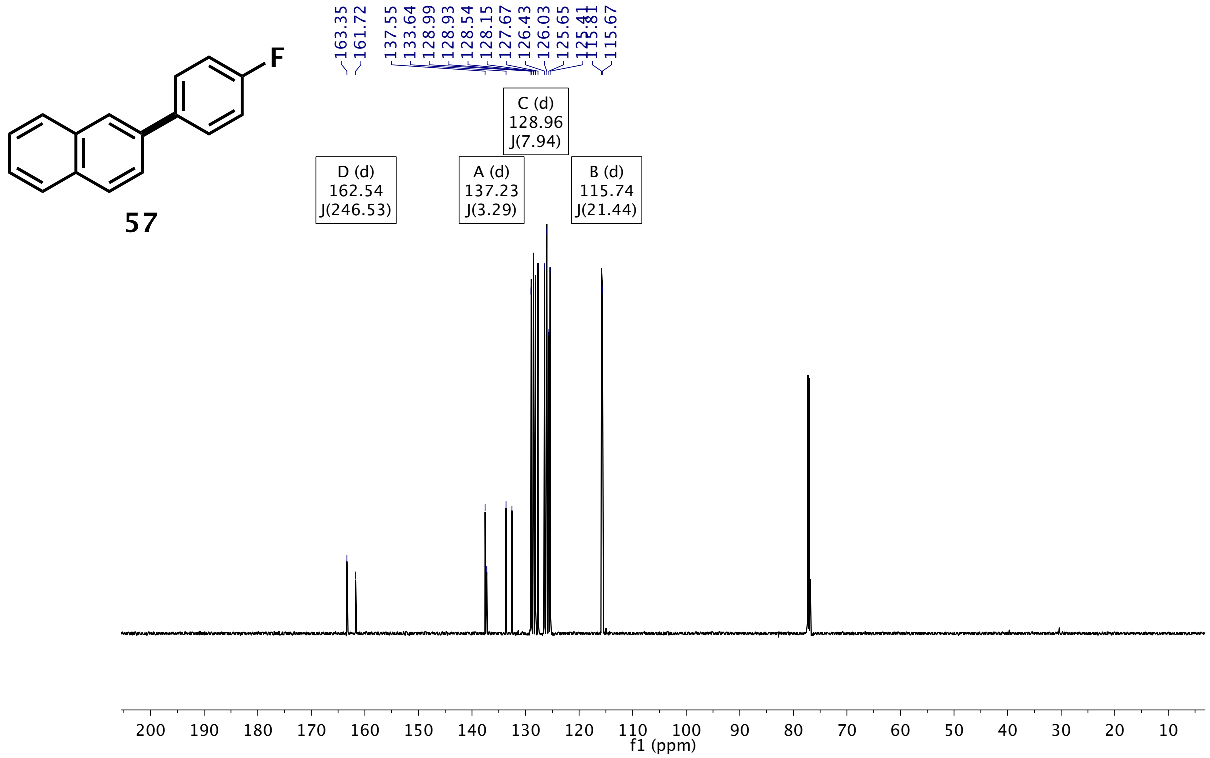
^{13}C{^{1}H} (151 MHz, CDCl$_3$)



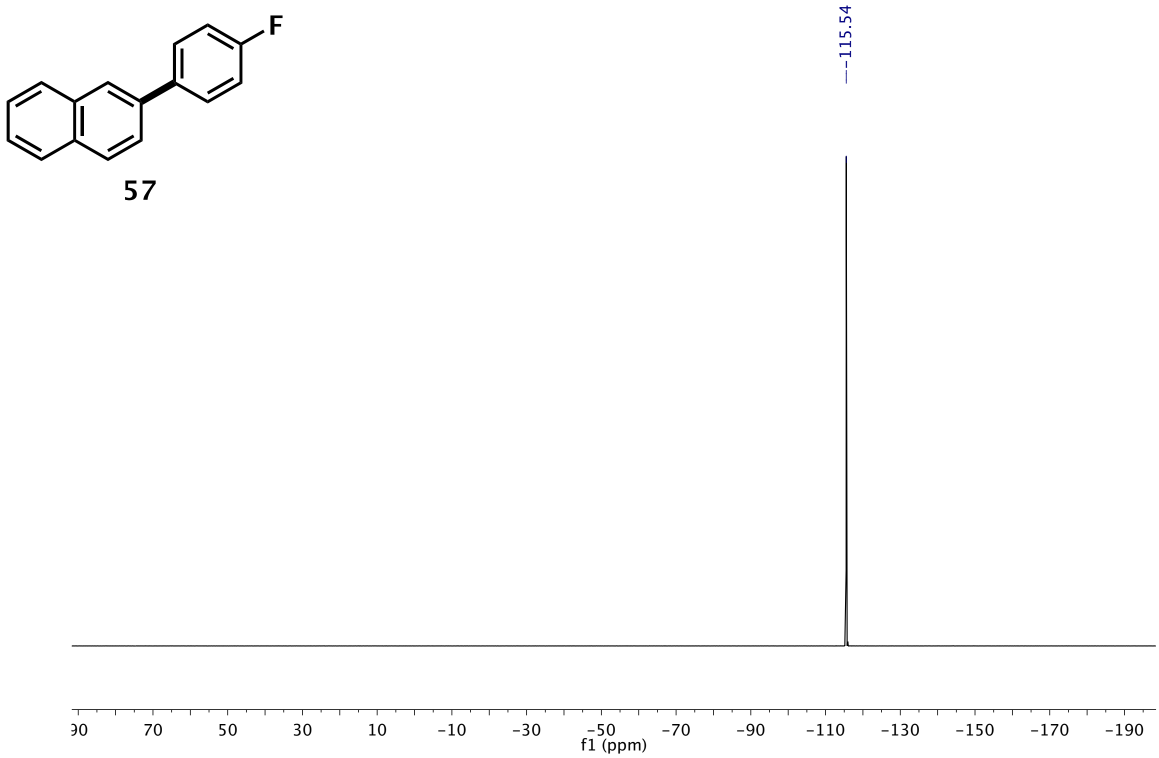
^{1}H (600 MHz, CDCl$_3$)



^{13}C{^{1}H} (151 MHz, CDCl$_3$)

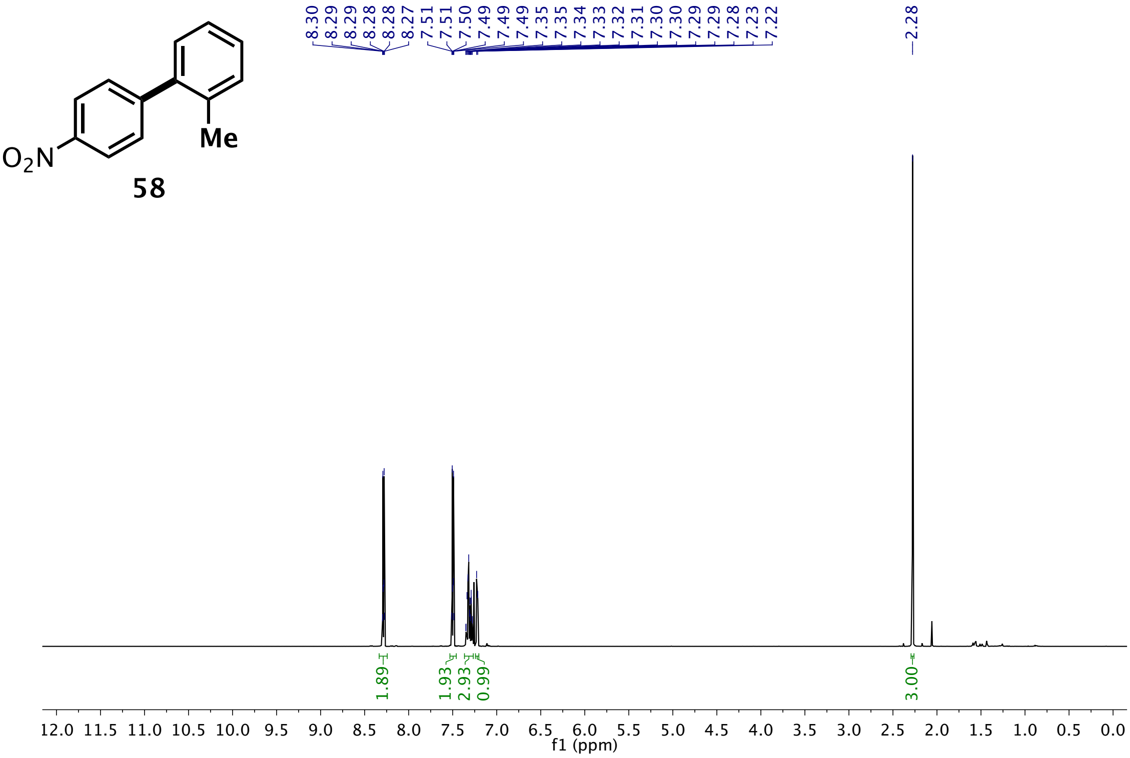


$^{19}F\{^{1}H\}$ (564 MHz, $CDCl_3$)



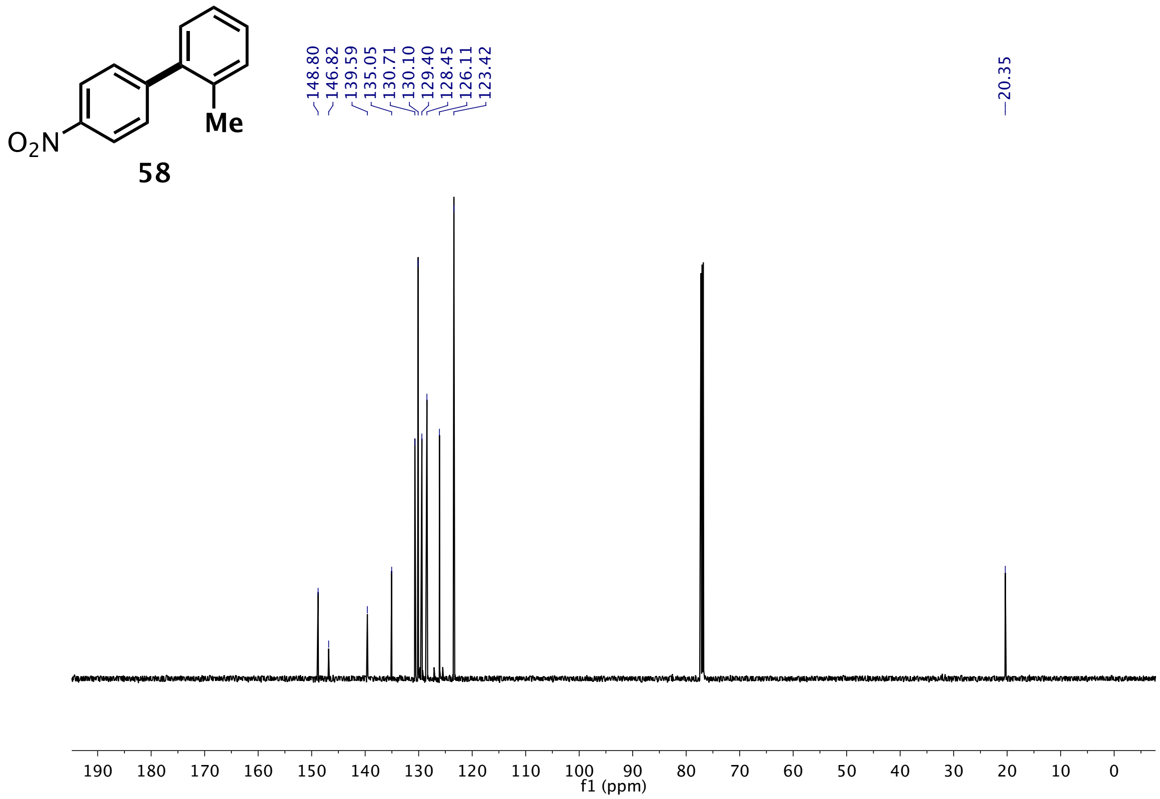
57

^{1}H (600 MHz, $CDCl_3$)



58

$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



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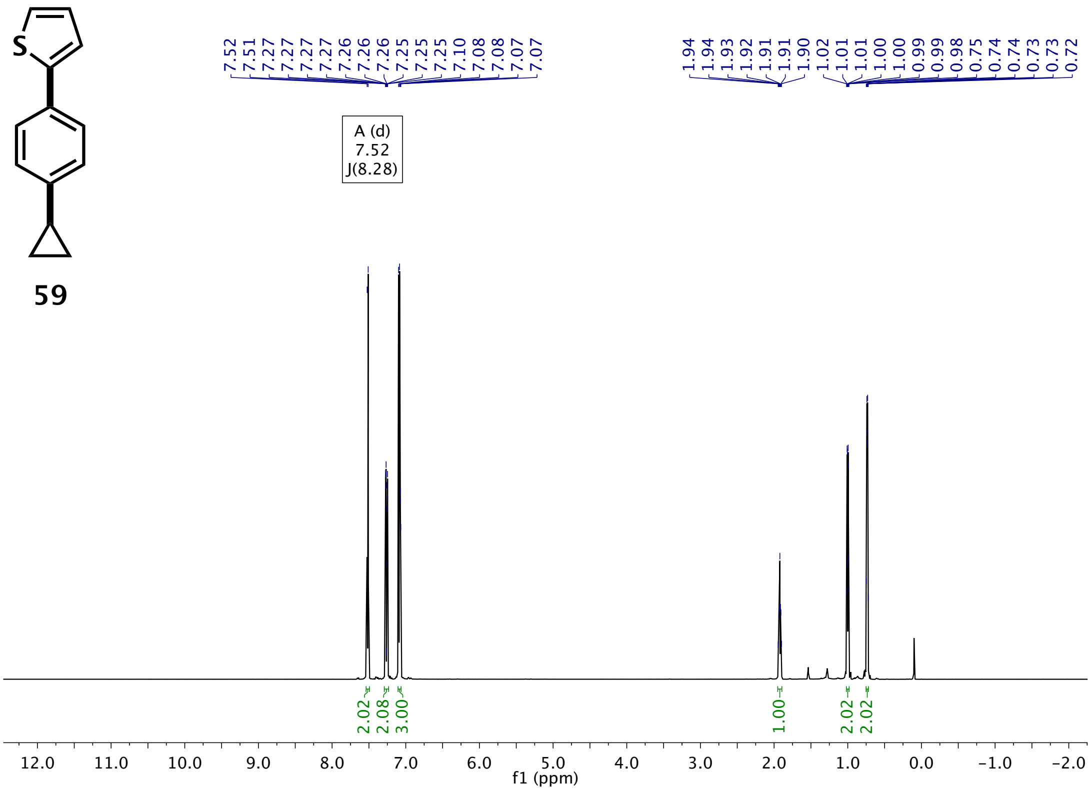
^1H (600 MHz, $CDCl_3$)



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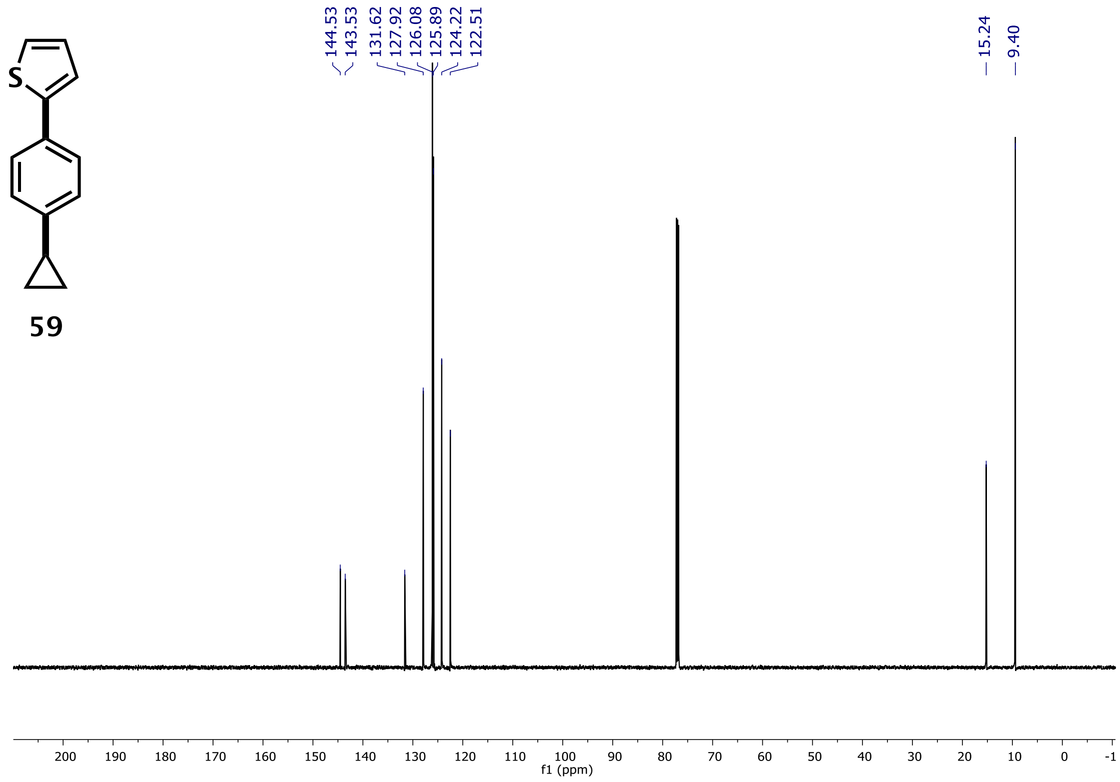
$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)



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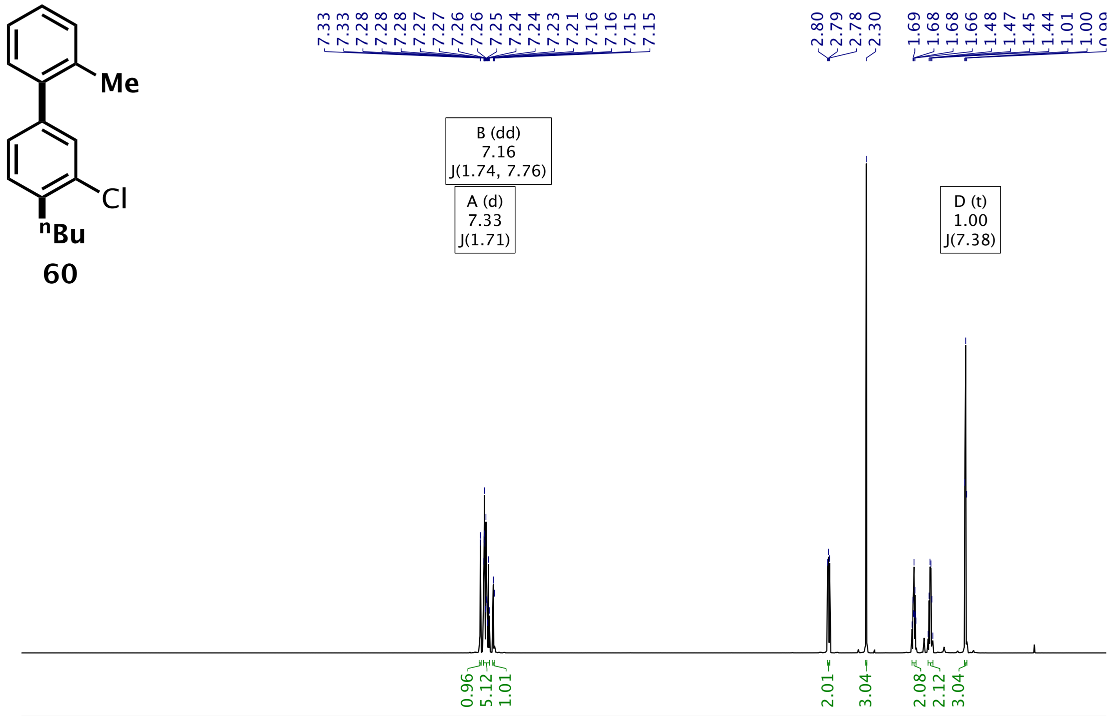
^{1}H (600 MHz, $CDCl_3$)



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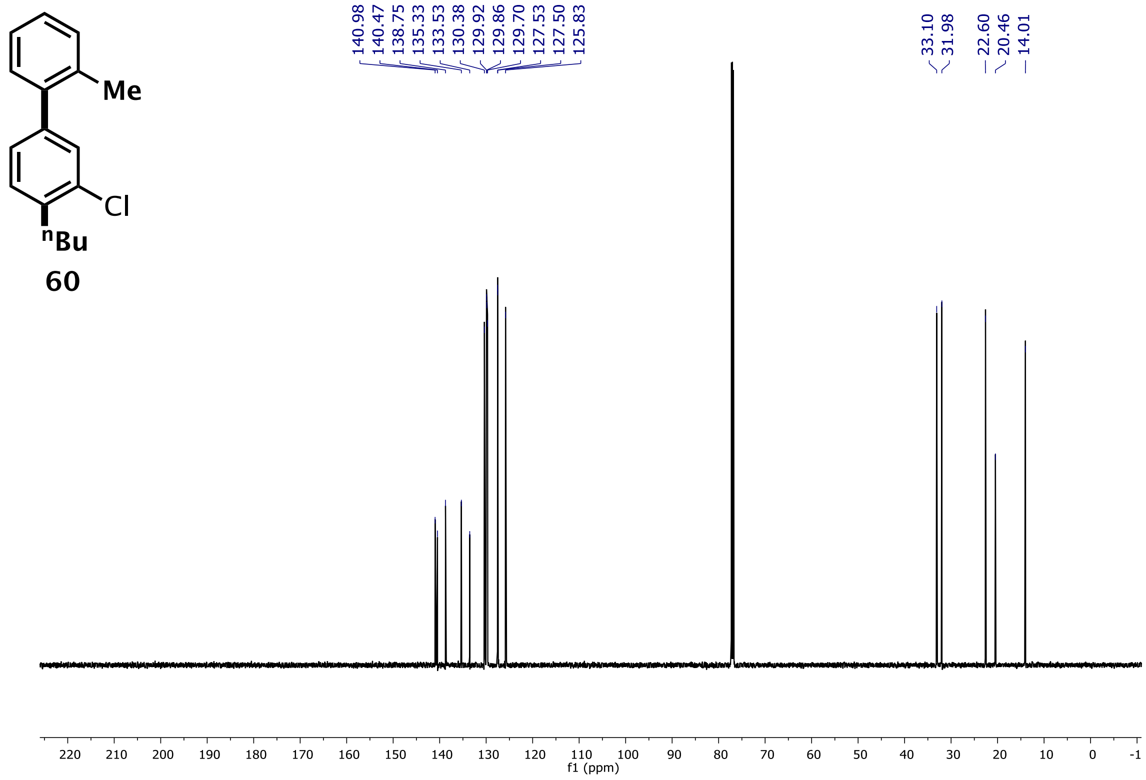
$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



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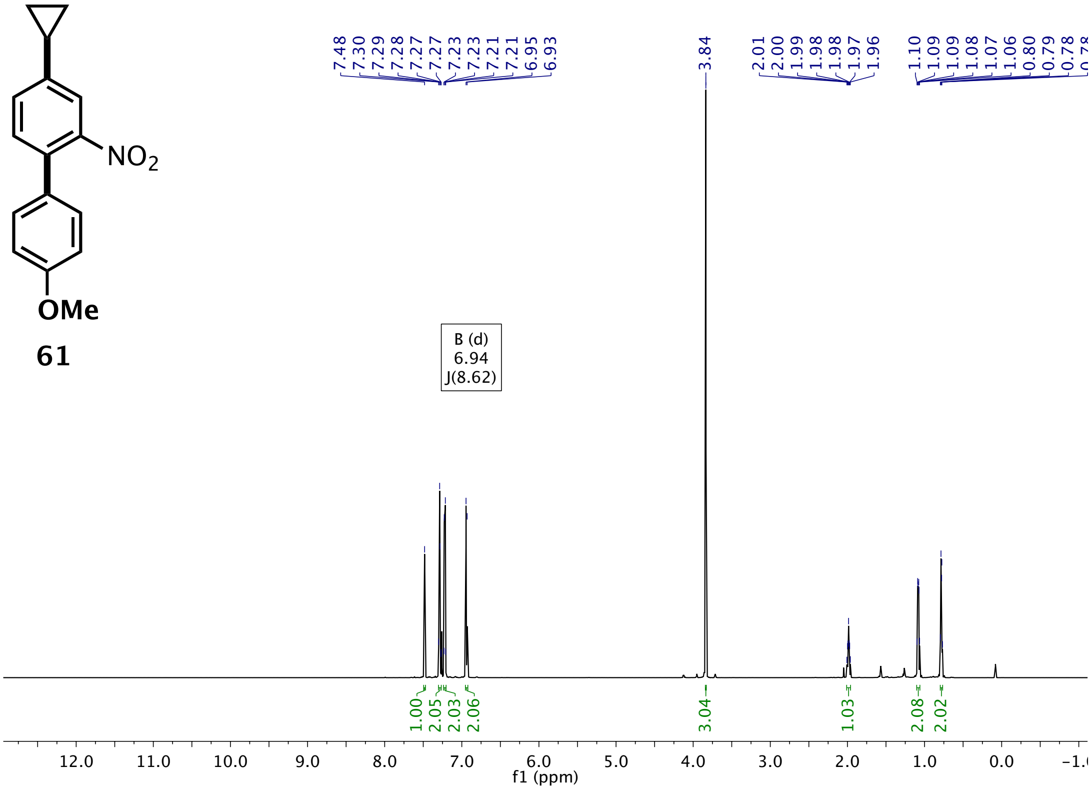
^1H (600 MHz, $CDCl_3$)



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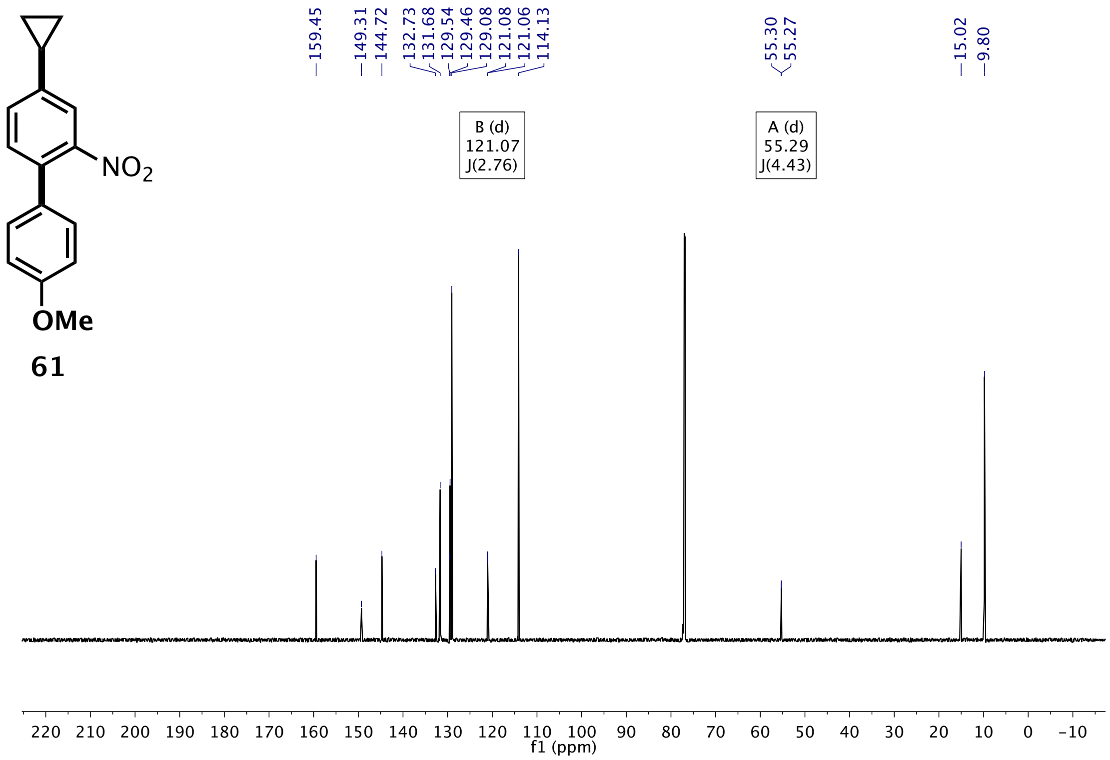
$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



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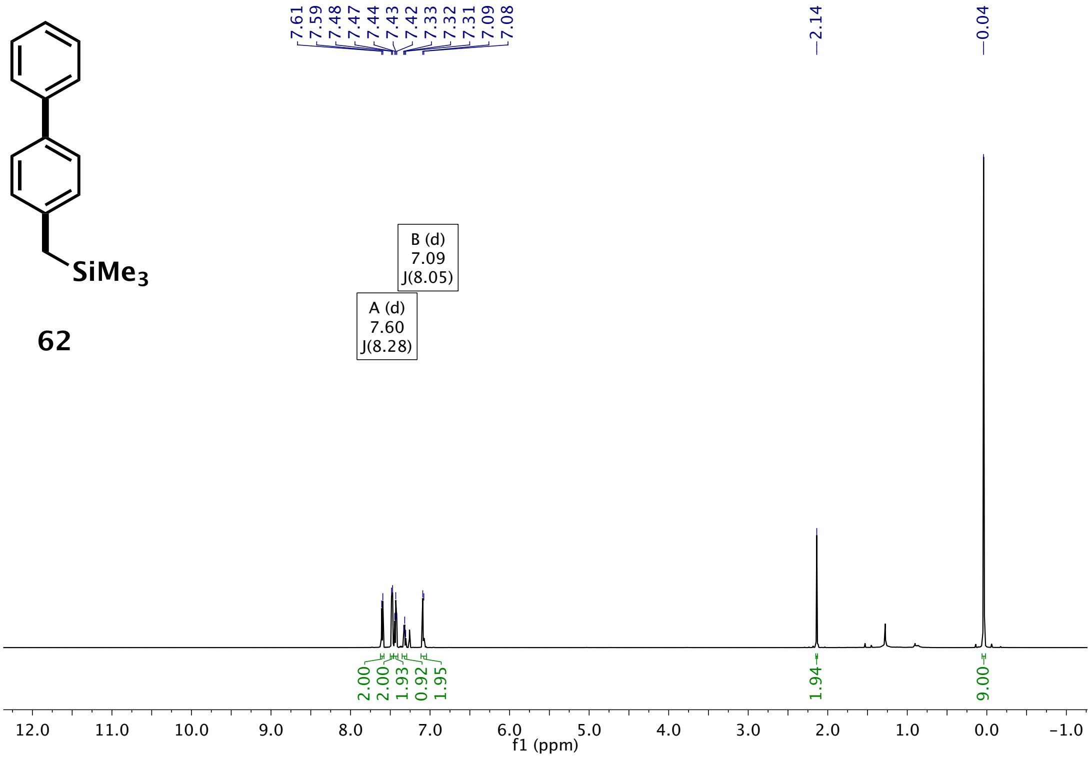
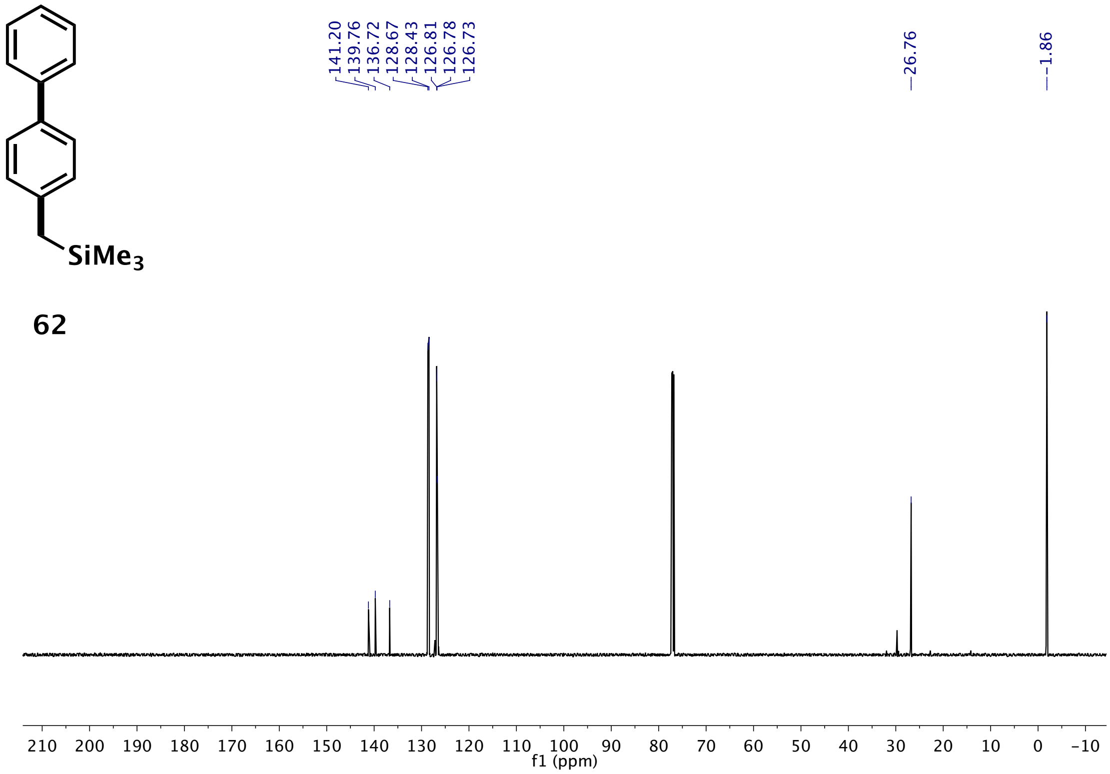
^1H (600 MHz, $CDCl_3$)



62

$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)



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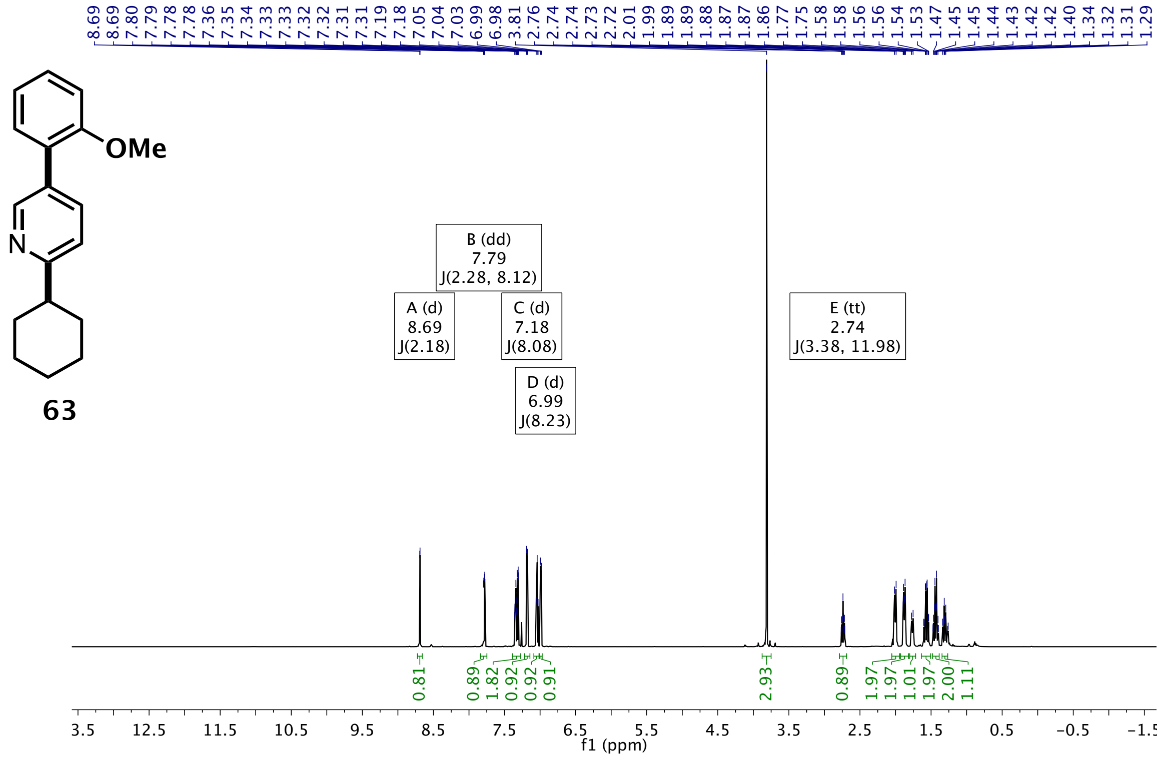
^{1}H (600 MHz, $CDCl_3$)



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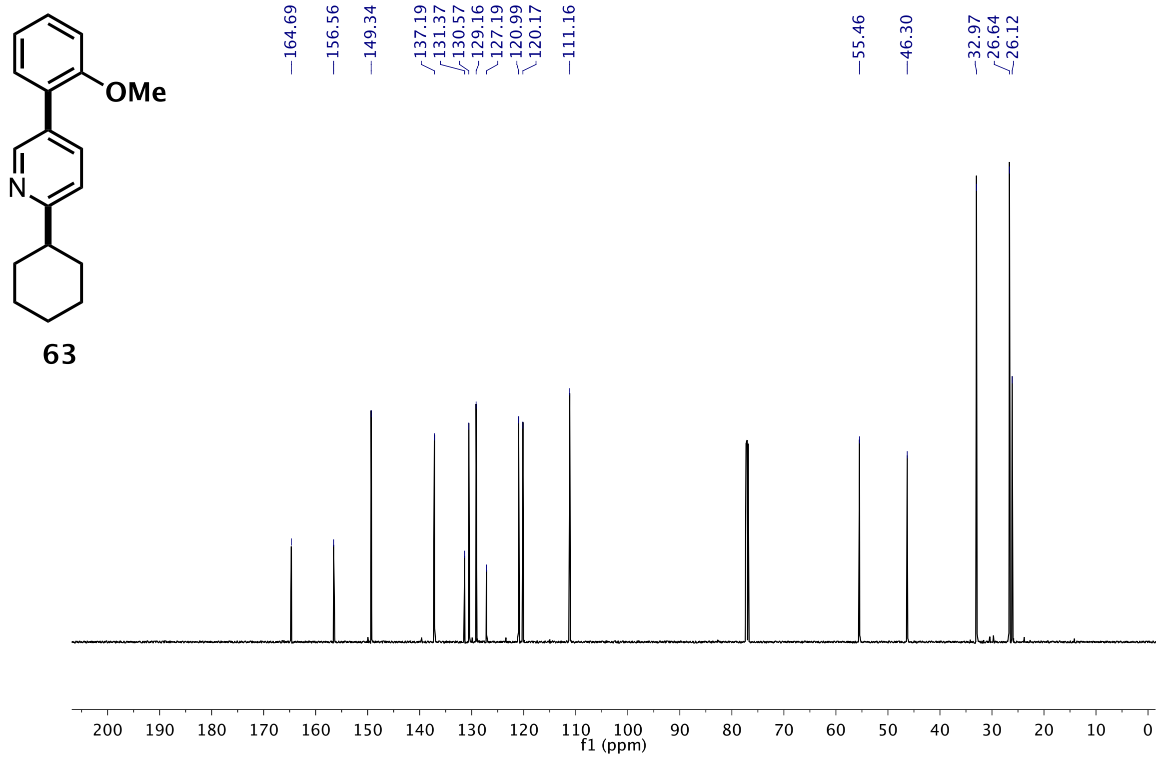
$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



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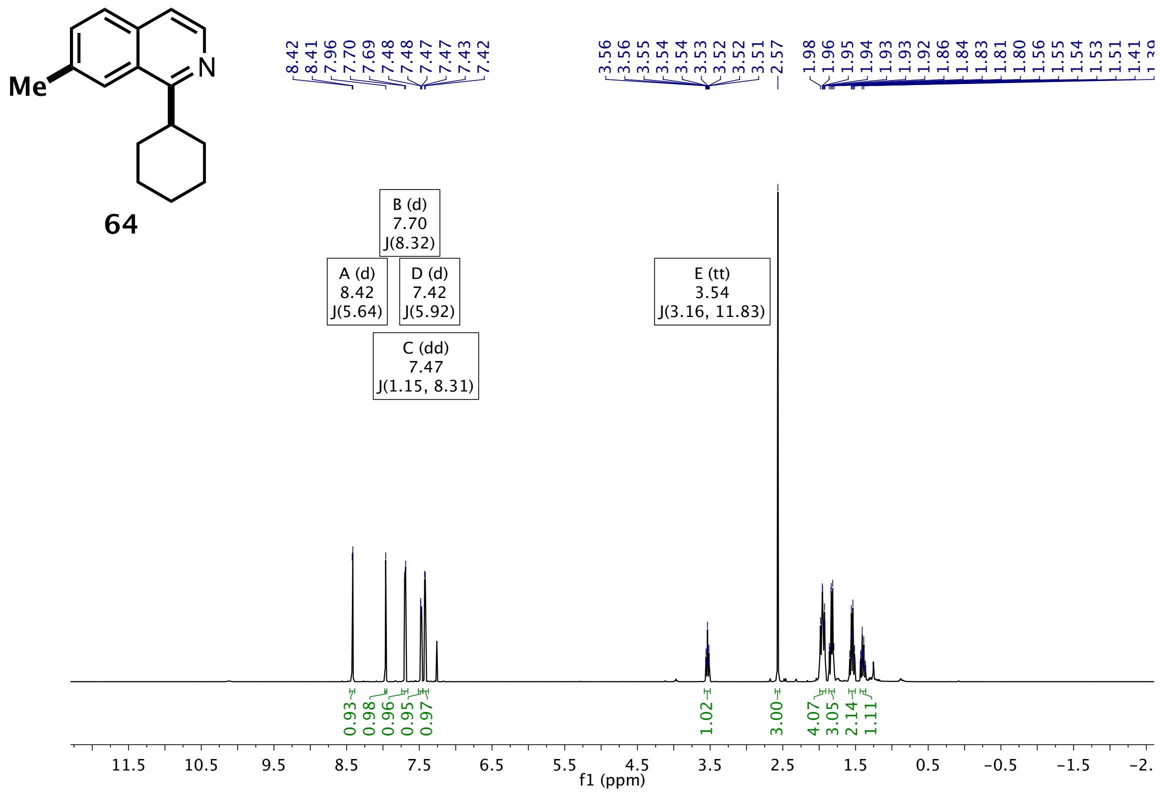
^1H (600 MHz, $CDCl_3$)



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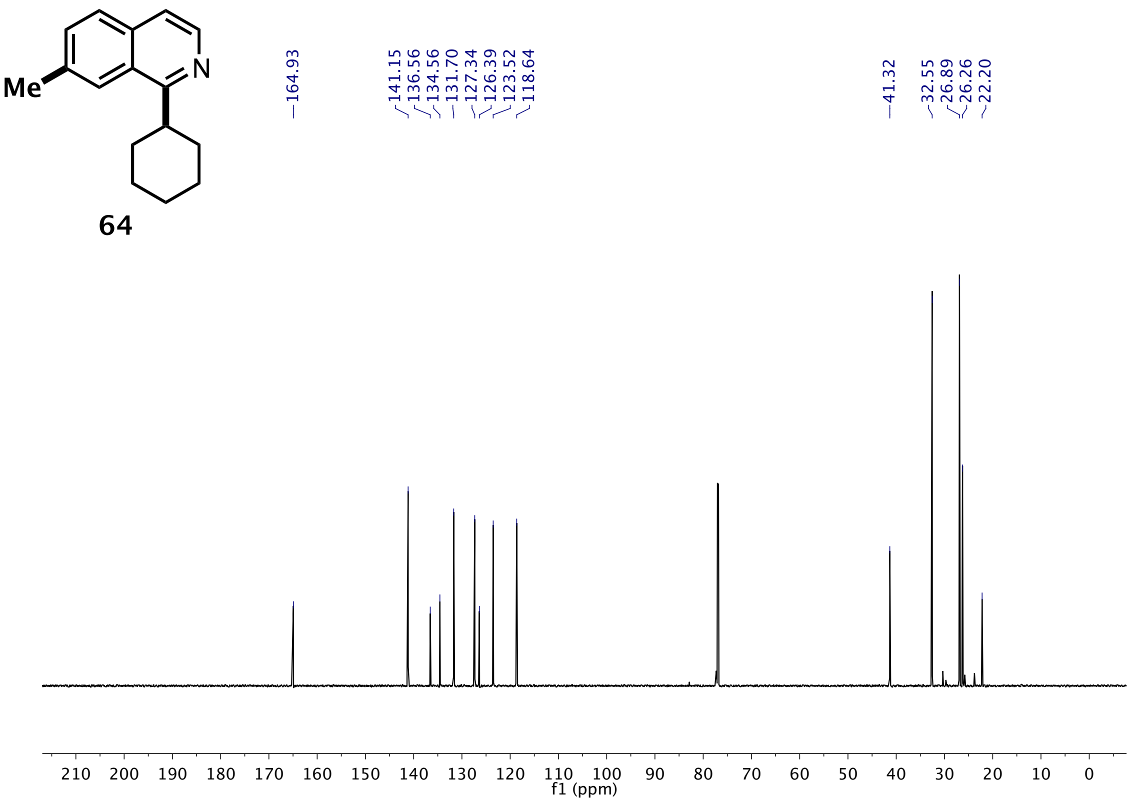
$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)



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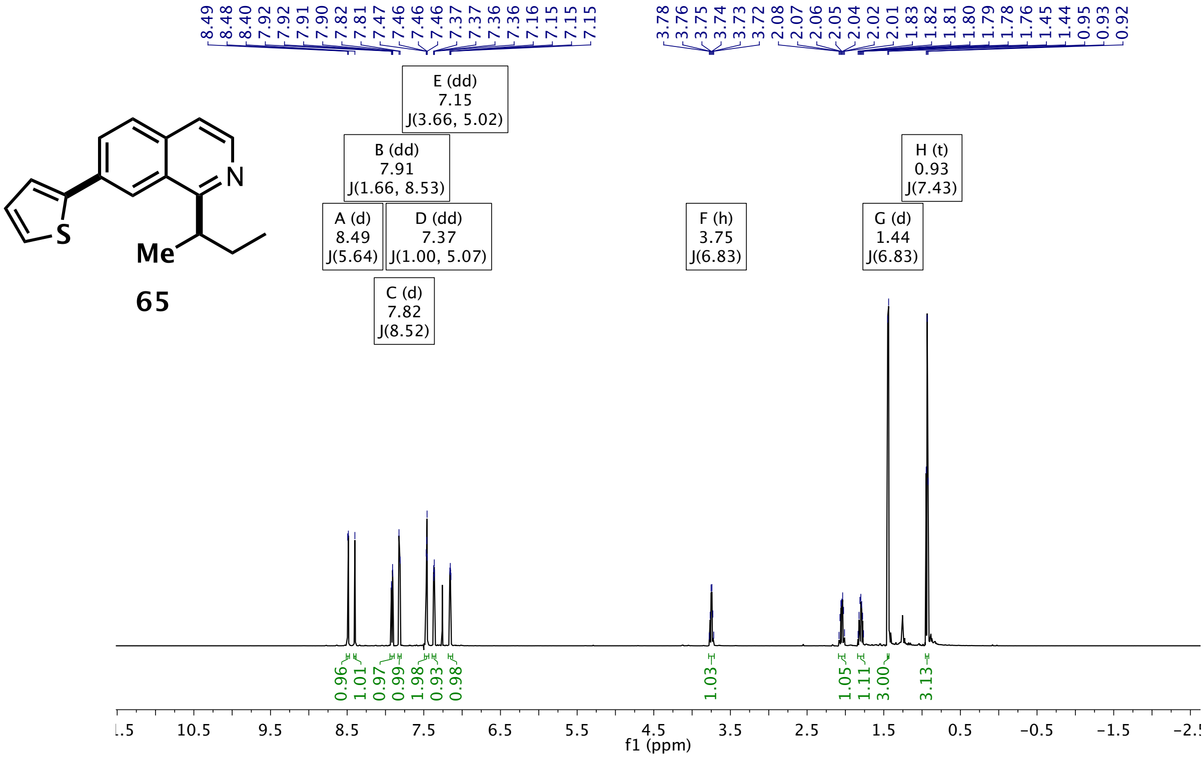
^{1}H (600 MHz, $CDCl_3$)



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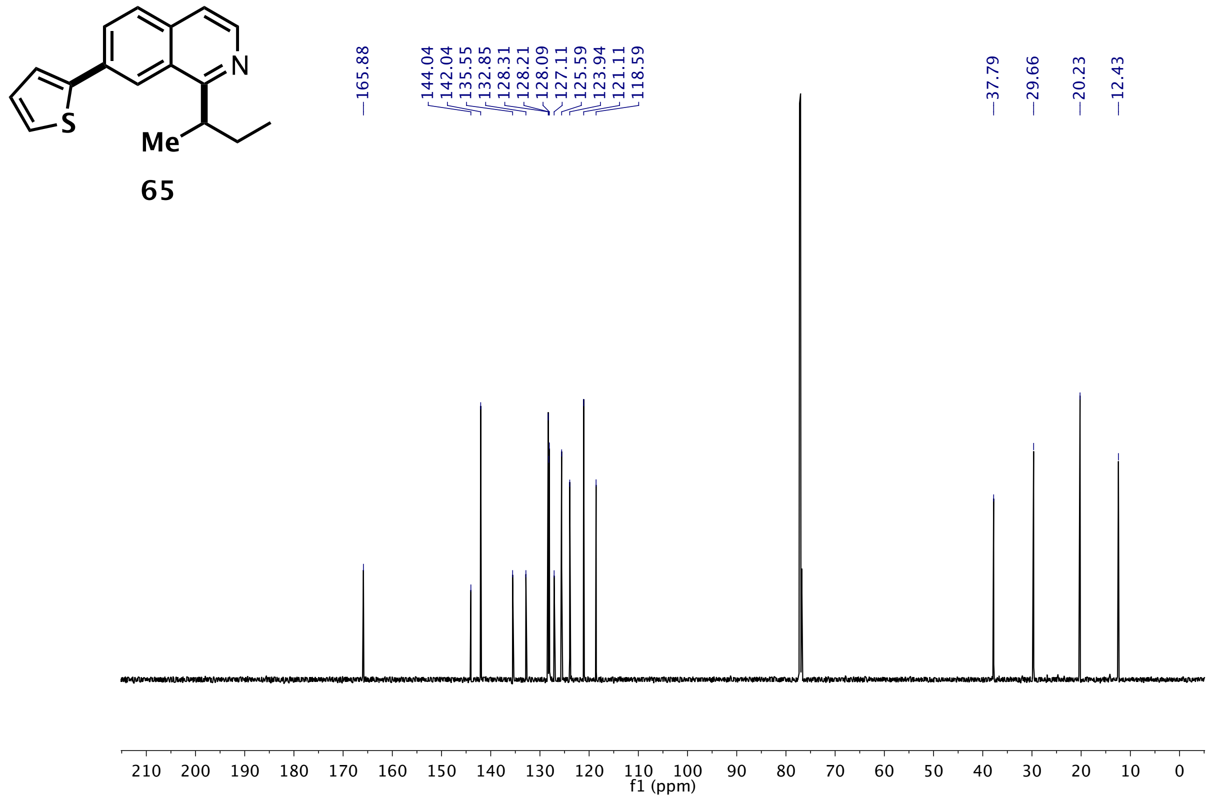
^{13}C{^{1}H} (151 MHz, CDCl$_3$)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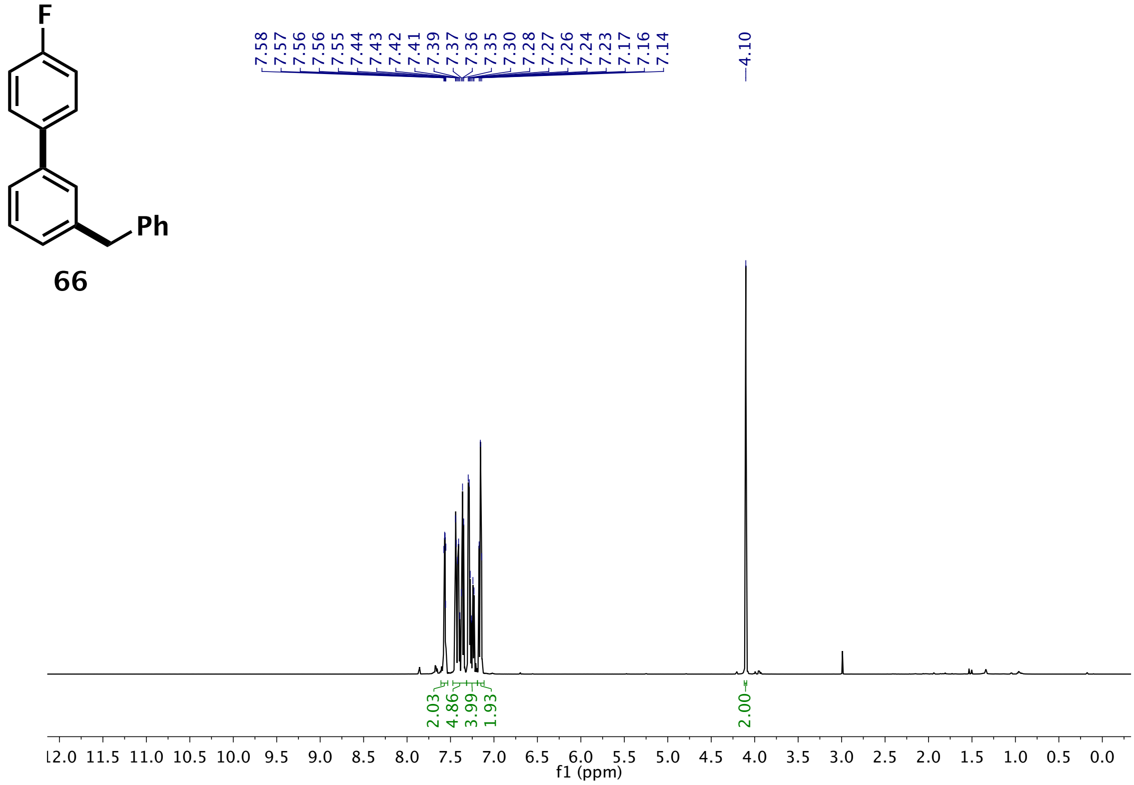
^{1}H (600 MHz, CDCl$_3$)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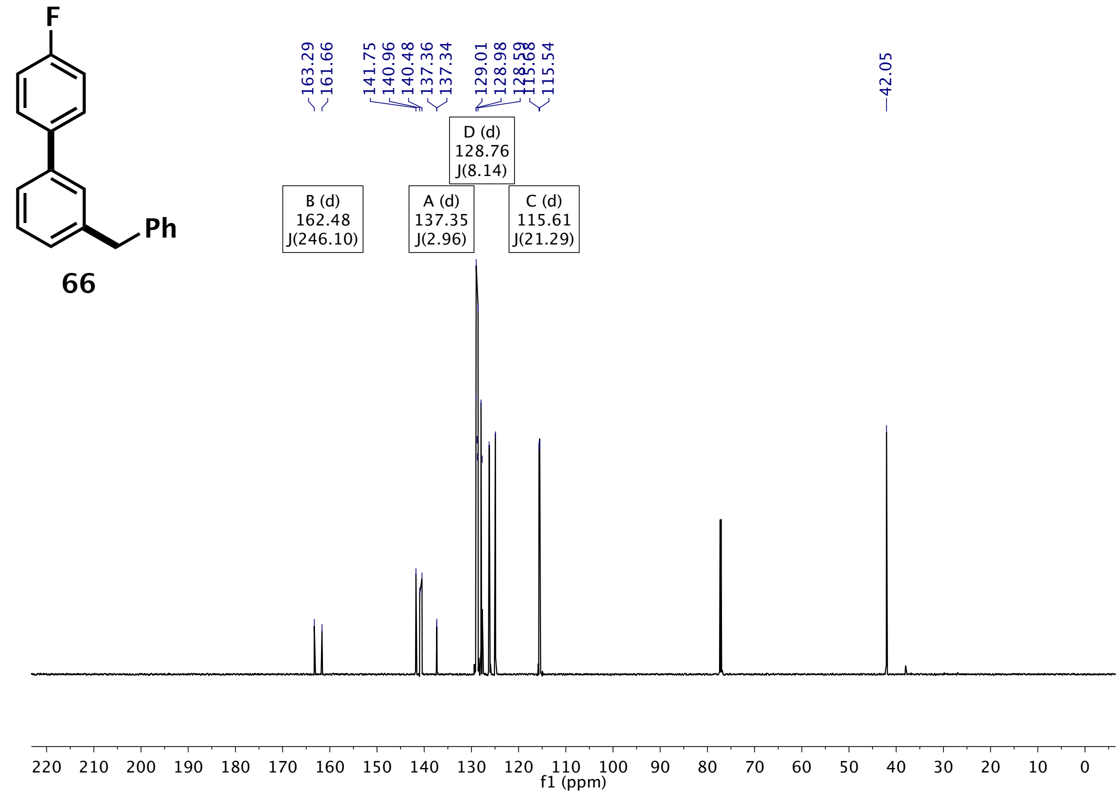
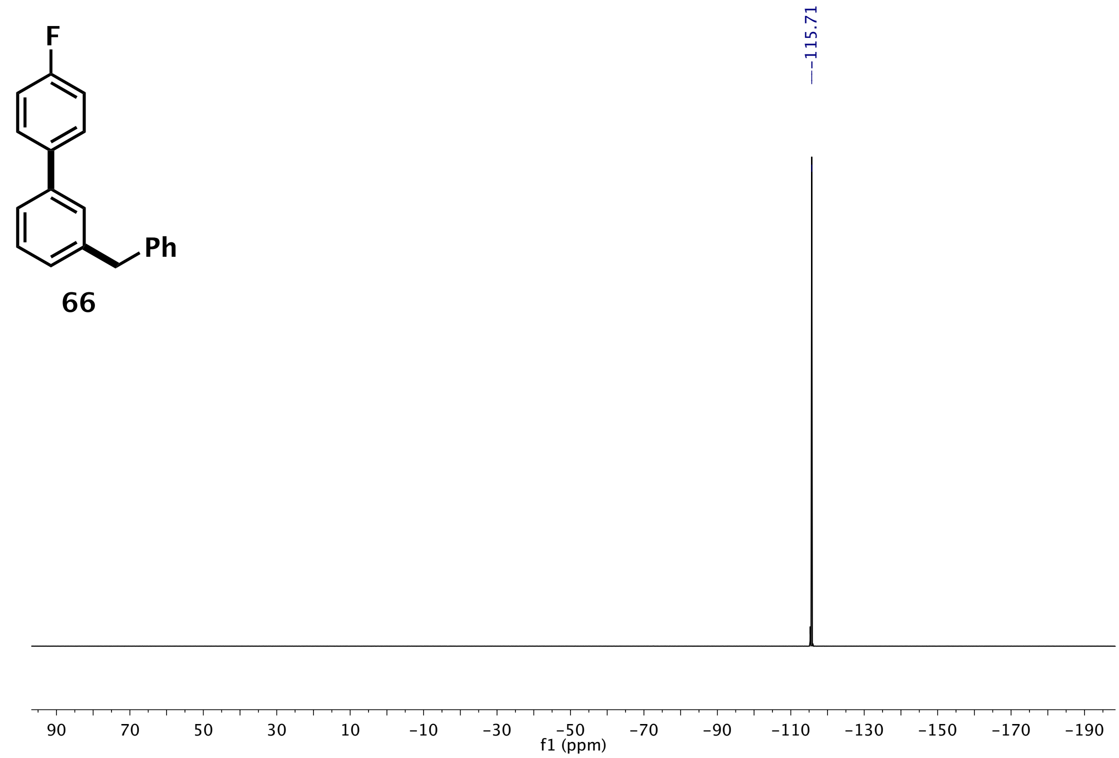
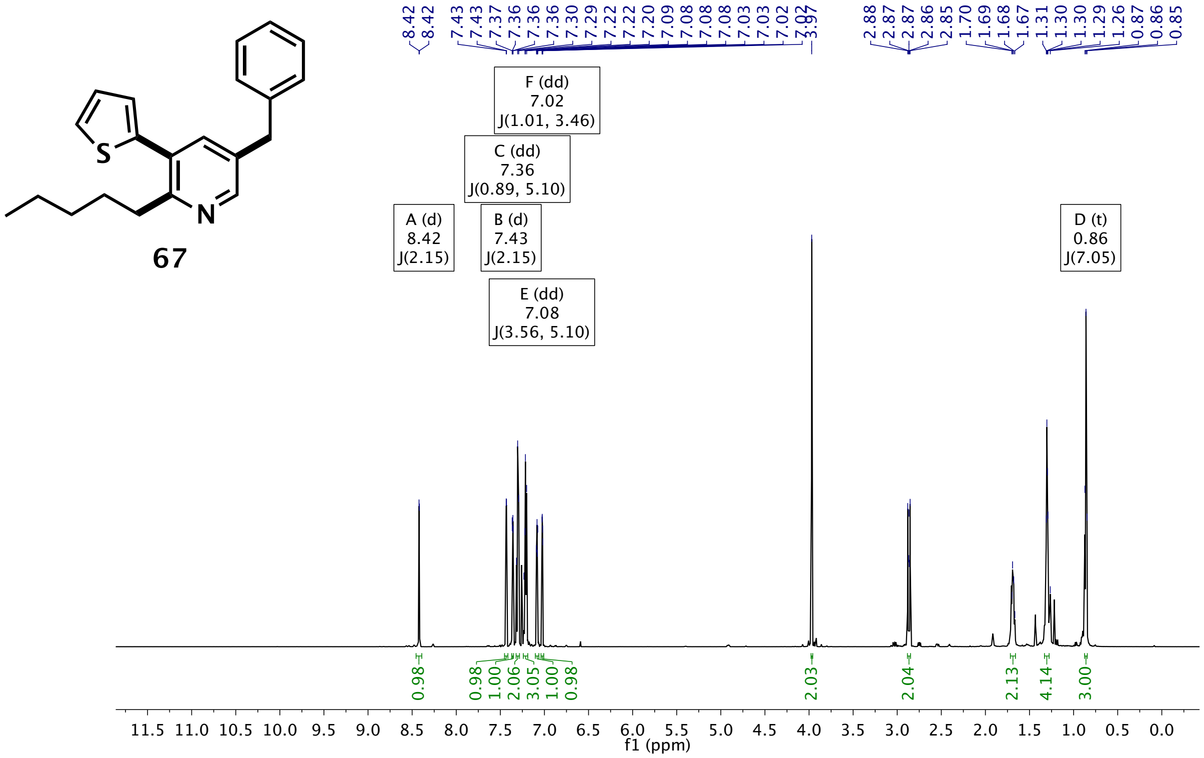
$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



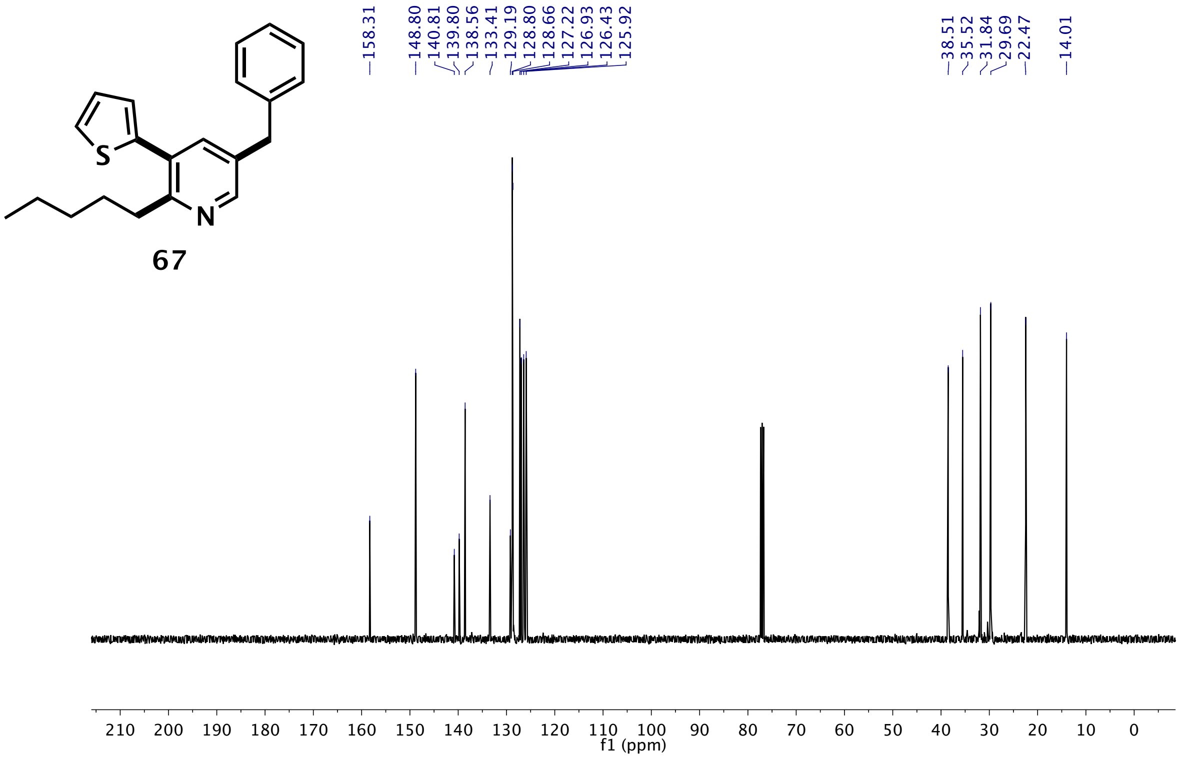
$^{19}F\{^1H\}$ (564 MHz, $CDCl_3$)



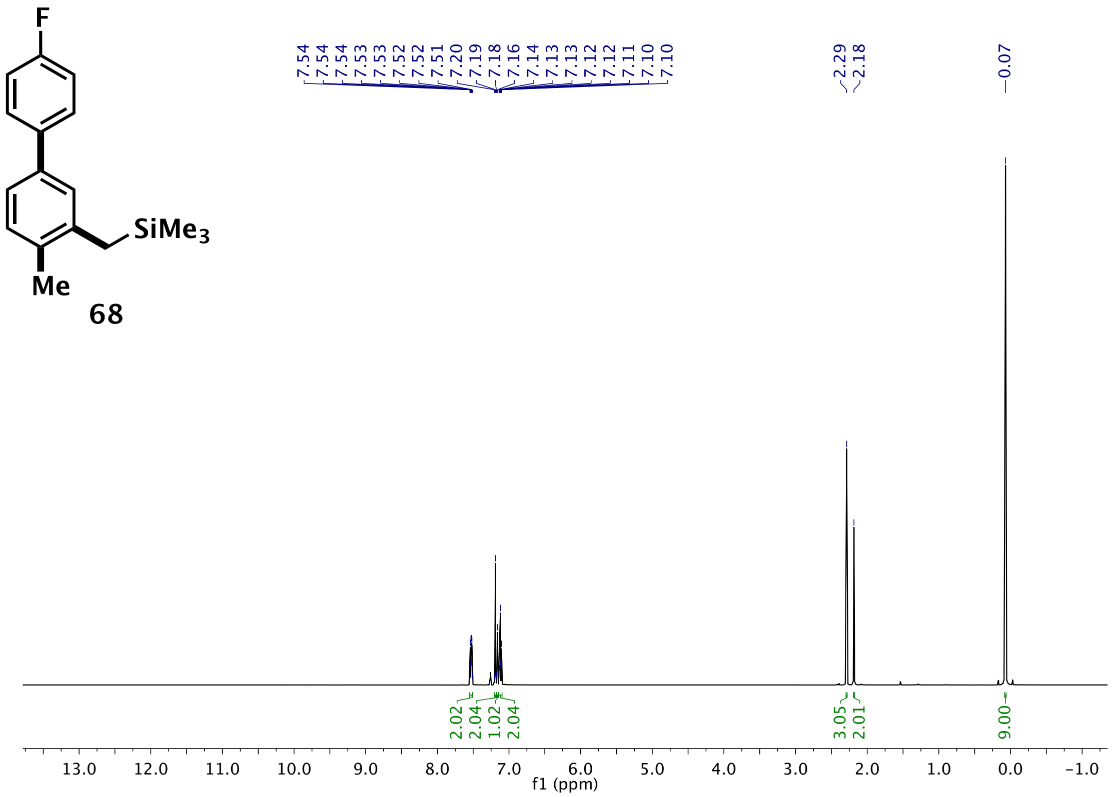
^{1}H (600 MHz, CDCl$_3$)



^{13}C{^{1}H} (151 MHz, CDCl$_3$)

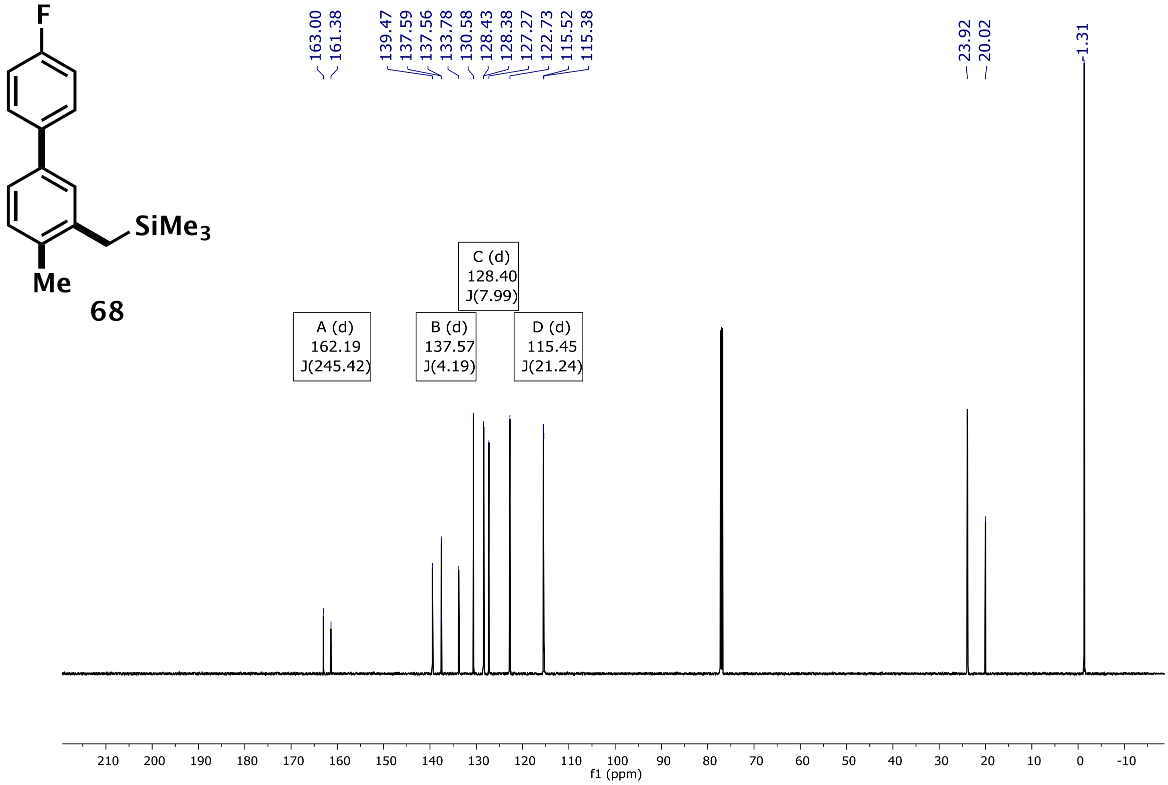


^{1}H (600 MHz, CDCl$_3$)



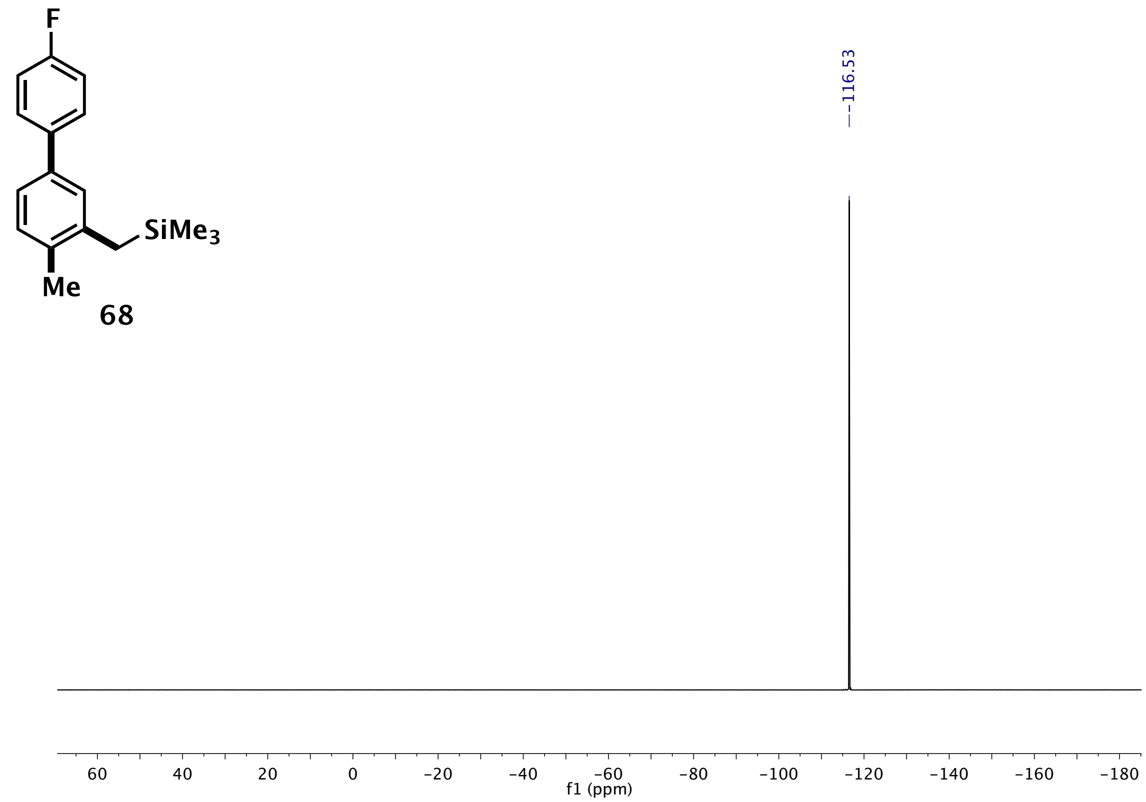
68

^{13}C{^{1}H} (151 MHz, CDCl$_3$)



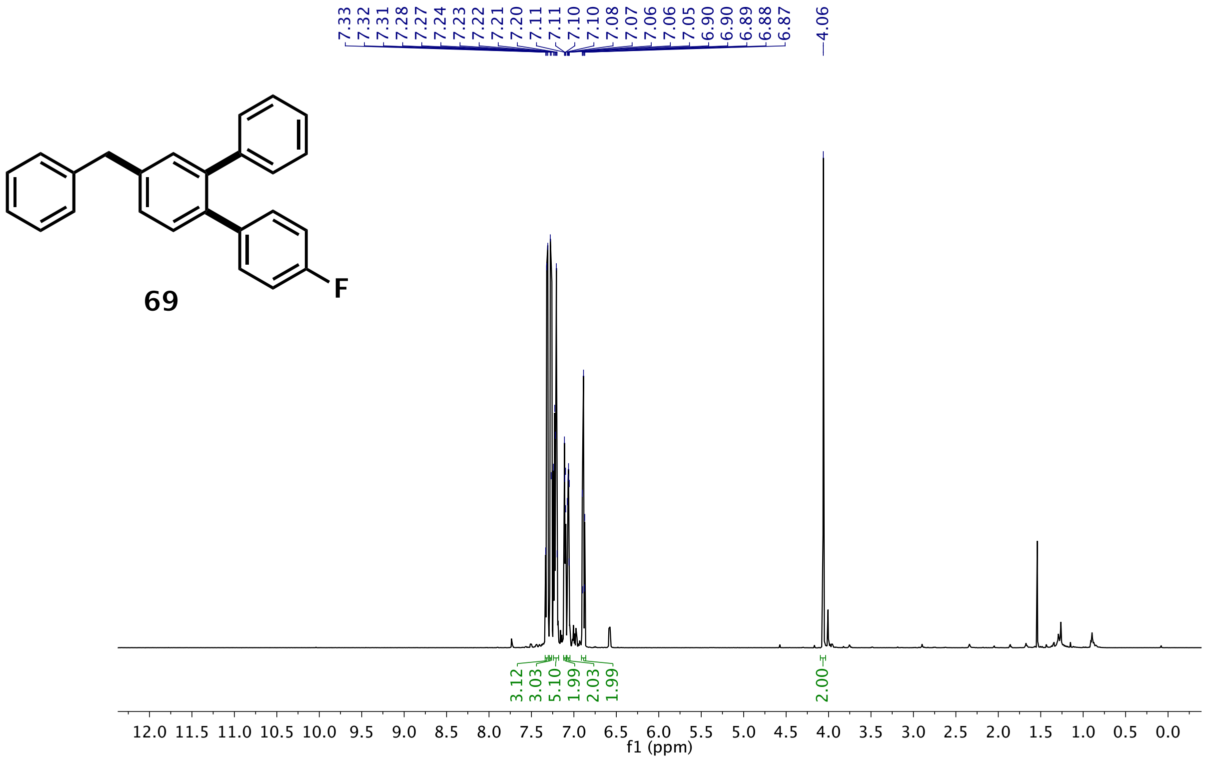
68

$^{19}F\{^1H\}$ (564 MHz, $CDCl_3$)



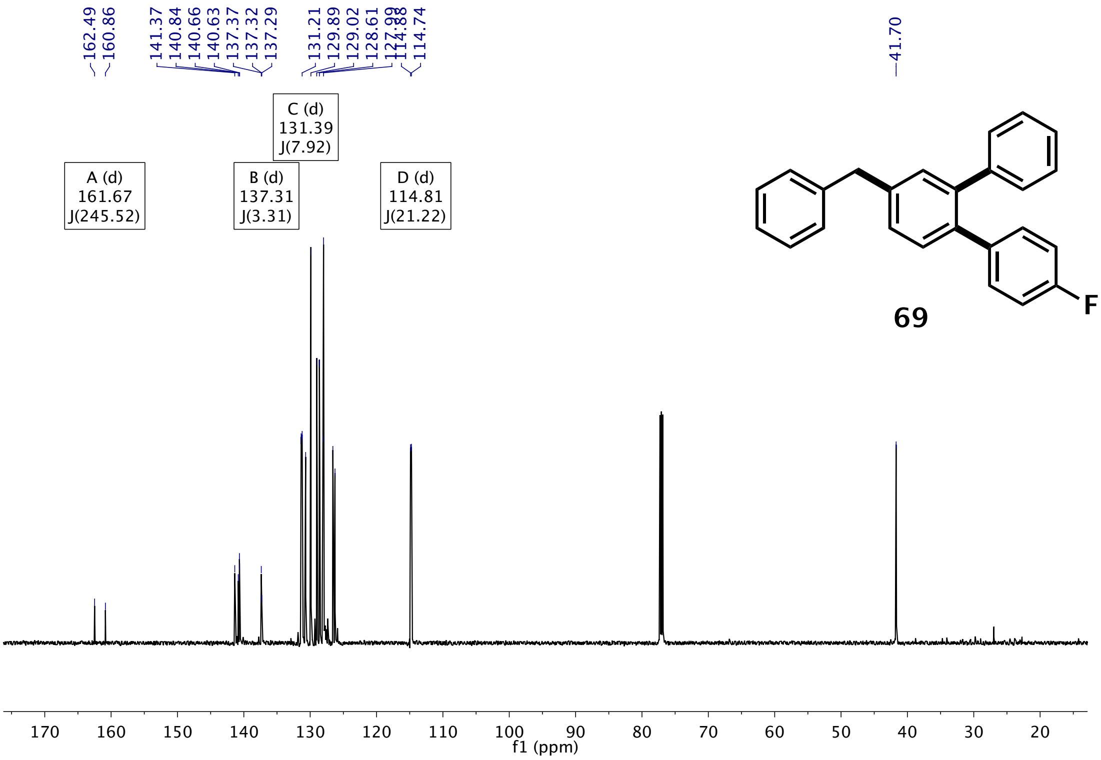
68

^1H (600 MHz, $CDCl_3$)

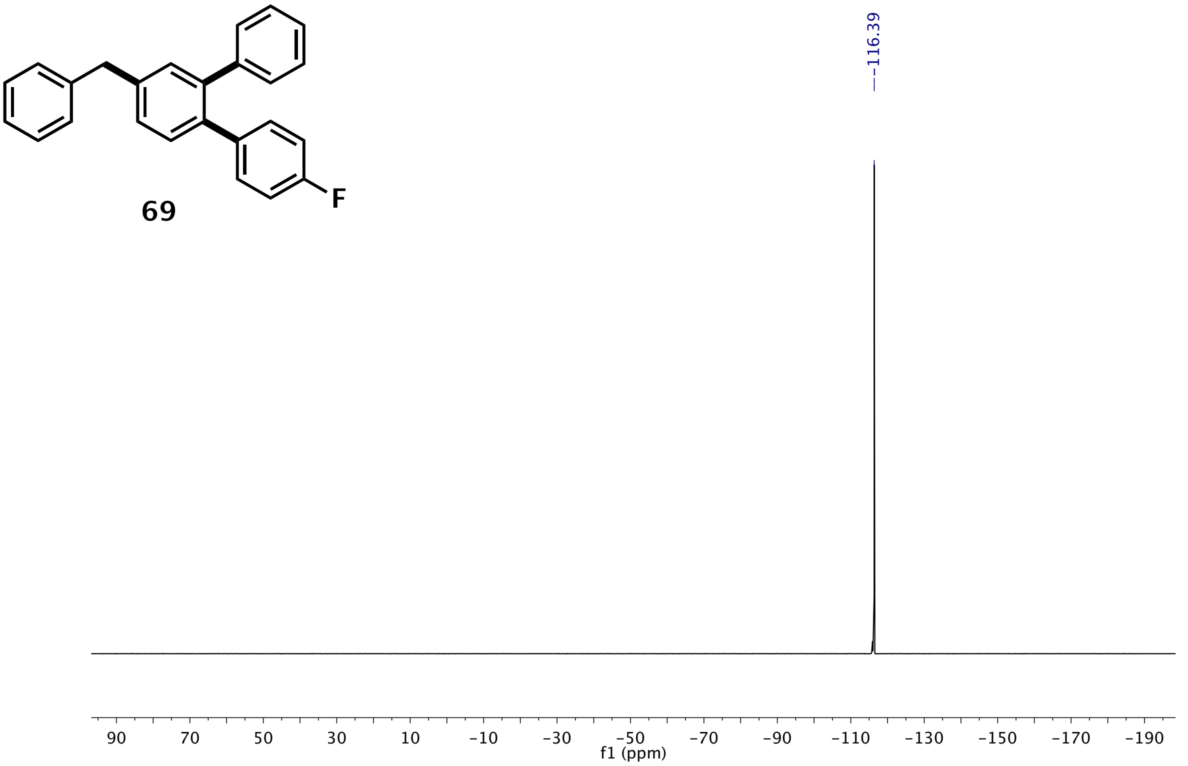


69

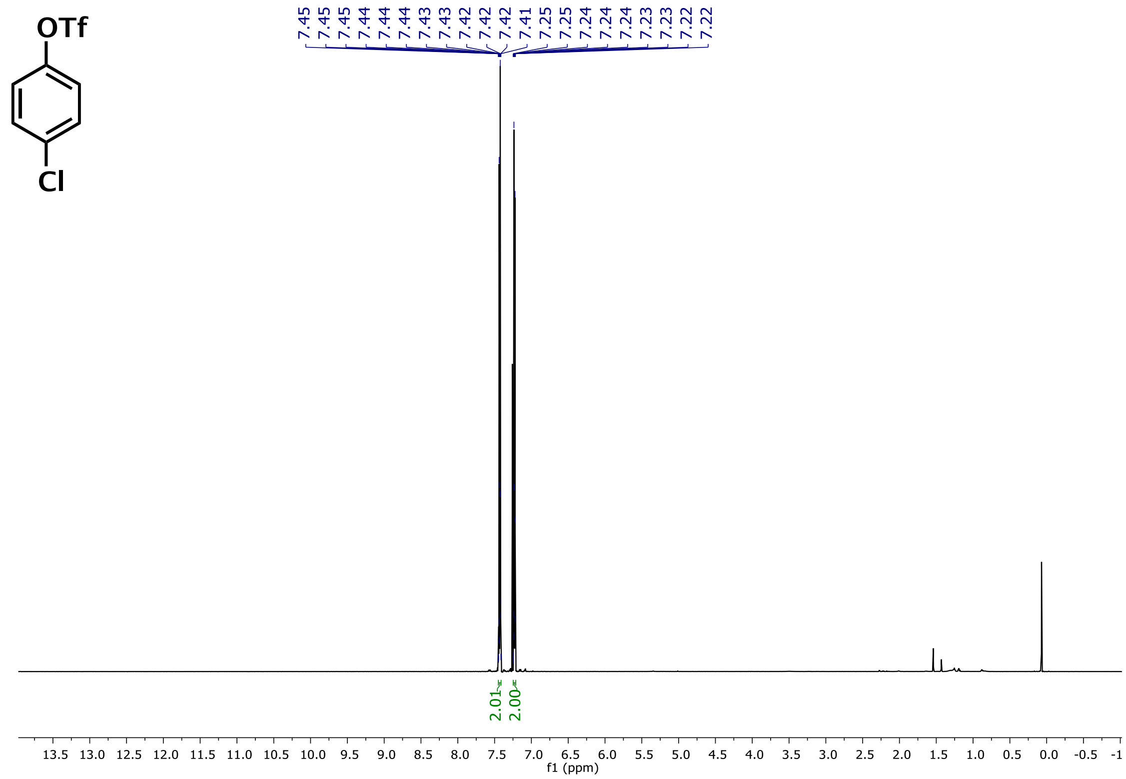
$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



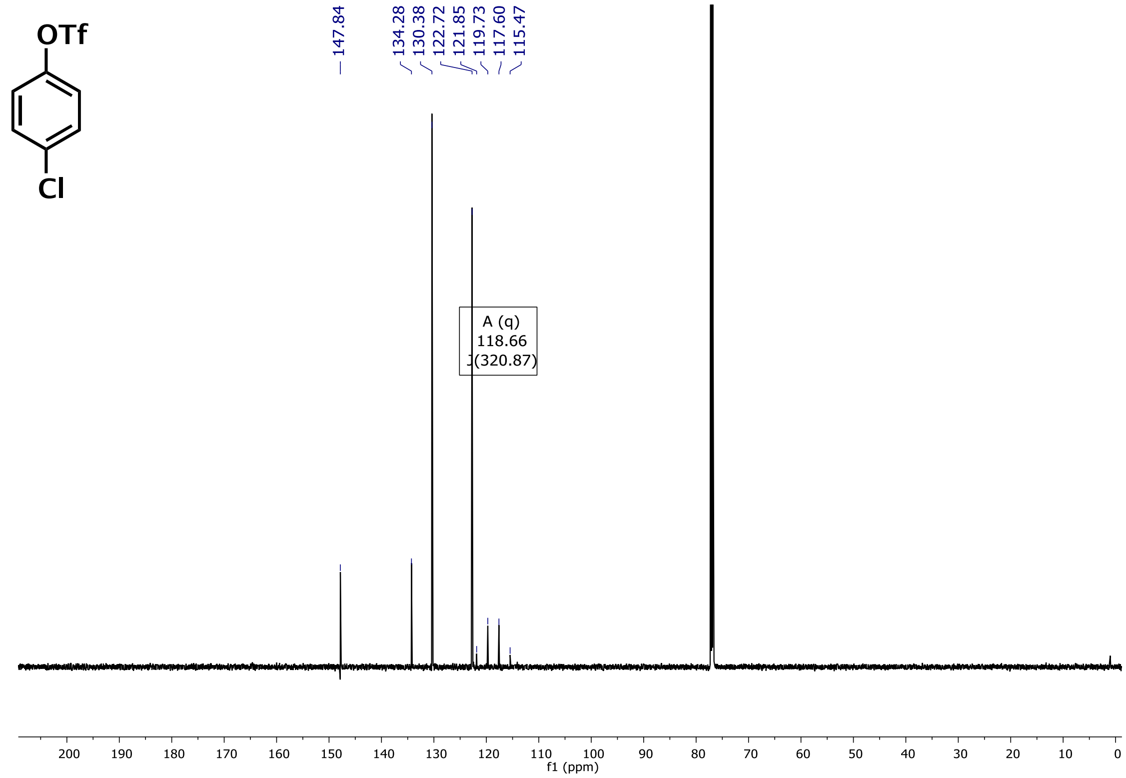
$^{19}F\{^1H\}$ (564 MHz, $CDCl_3$)



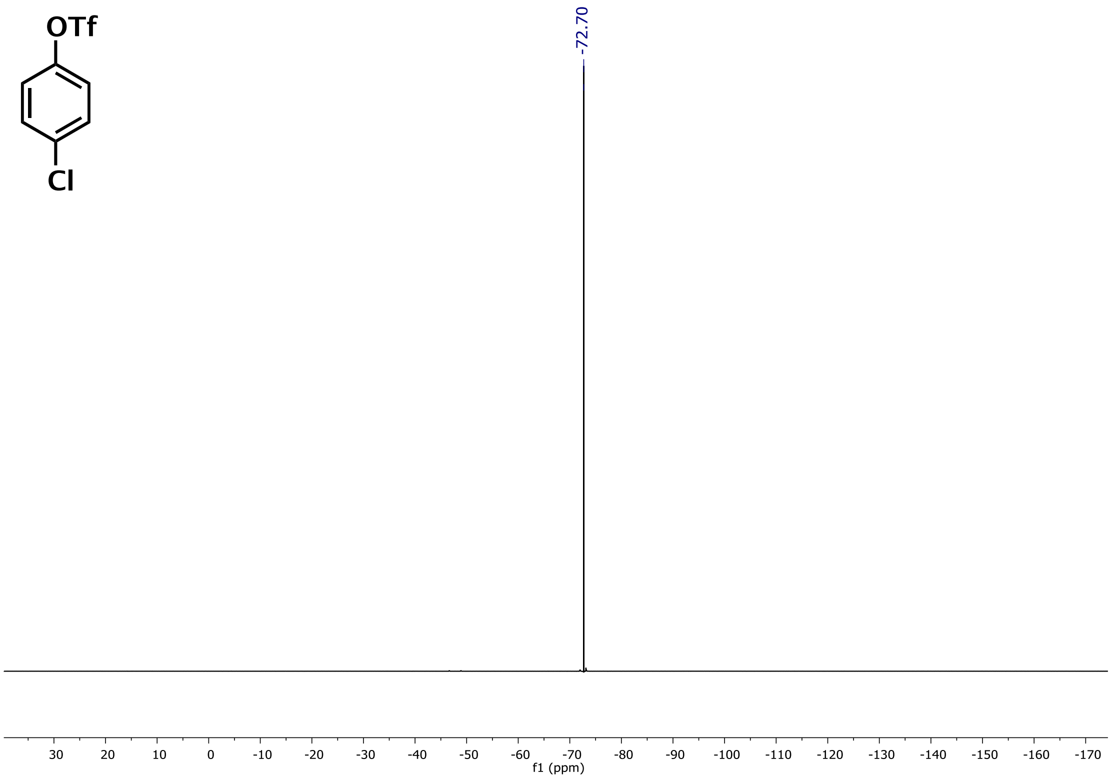
^{1}H (600 MHz, CDCl$_3$)



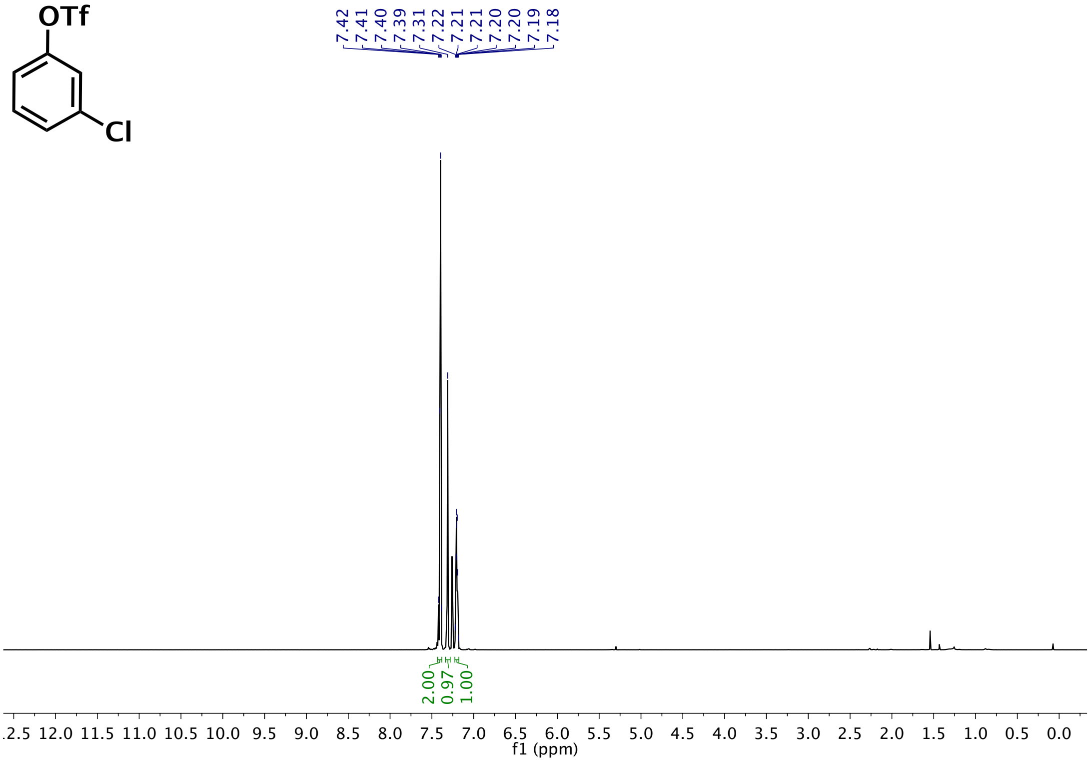
^{13}C{^{1}H} (151 MHz, CDCl$_3$)



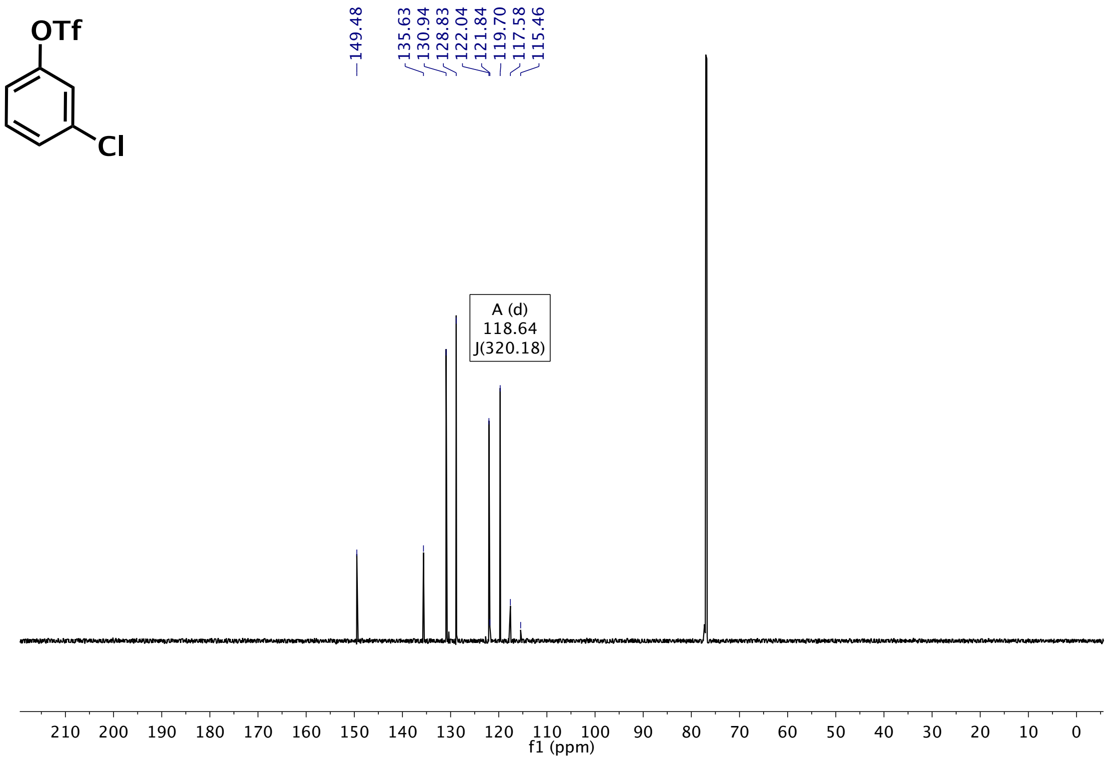
$^{19}F\{^1H\}$ (564 MHz, $CDCl_3$)



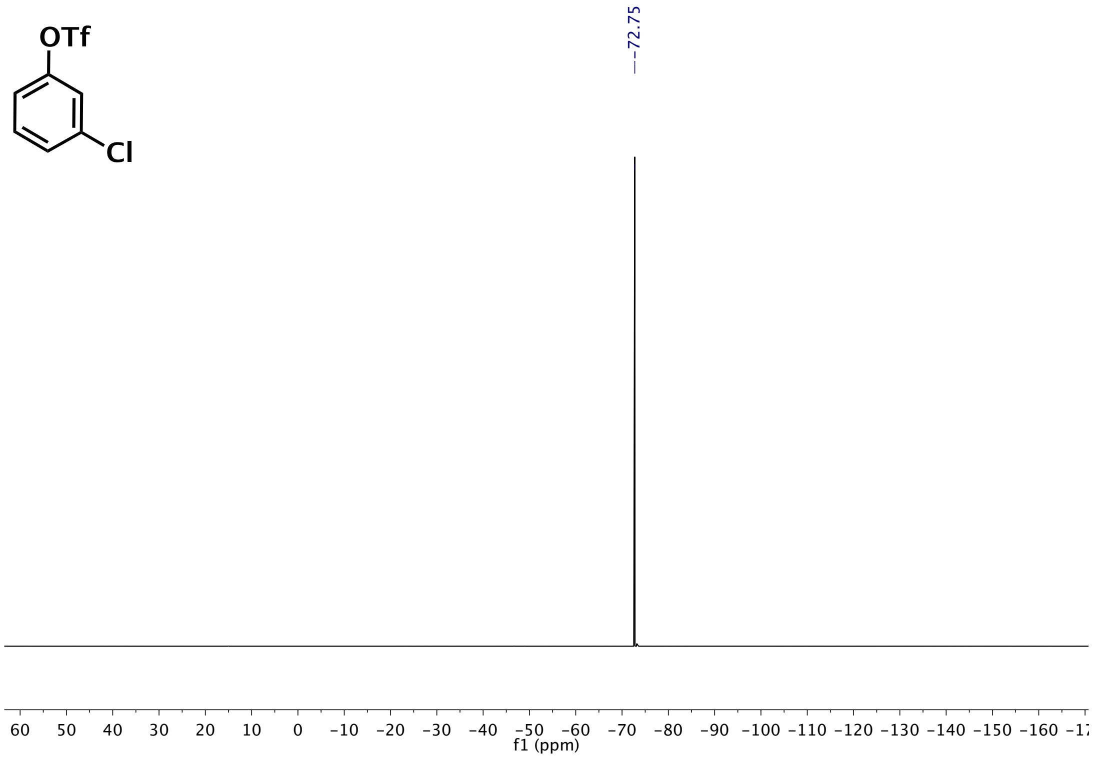
^1H (600 MHz, $CDCl_3$)



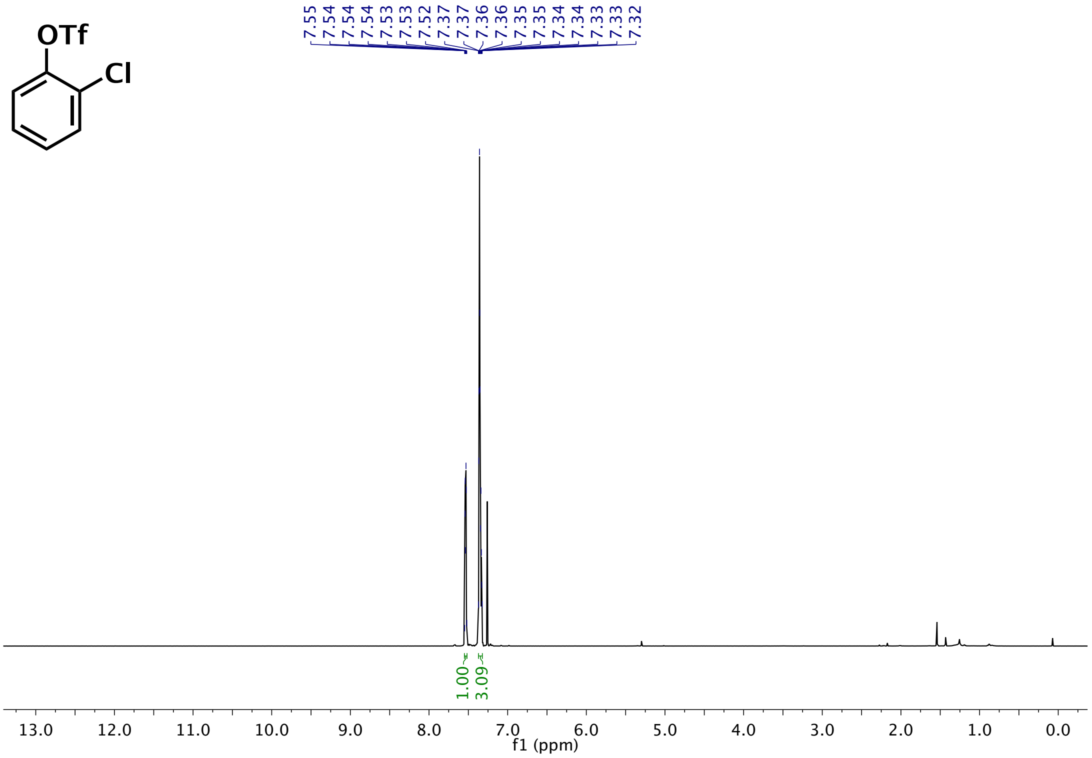
$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)



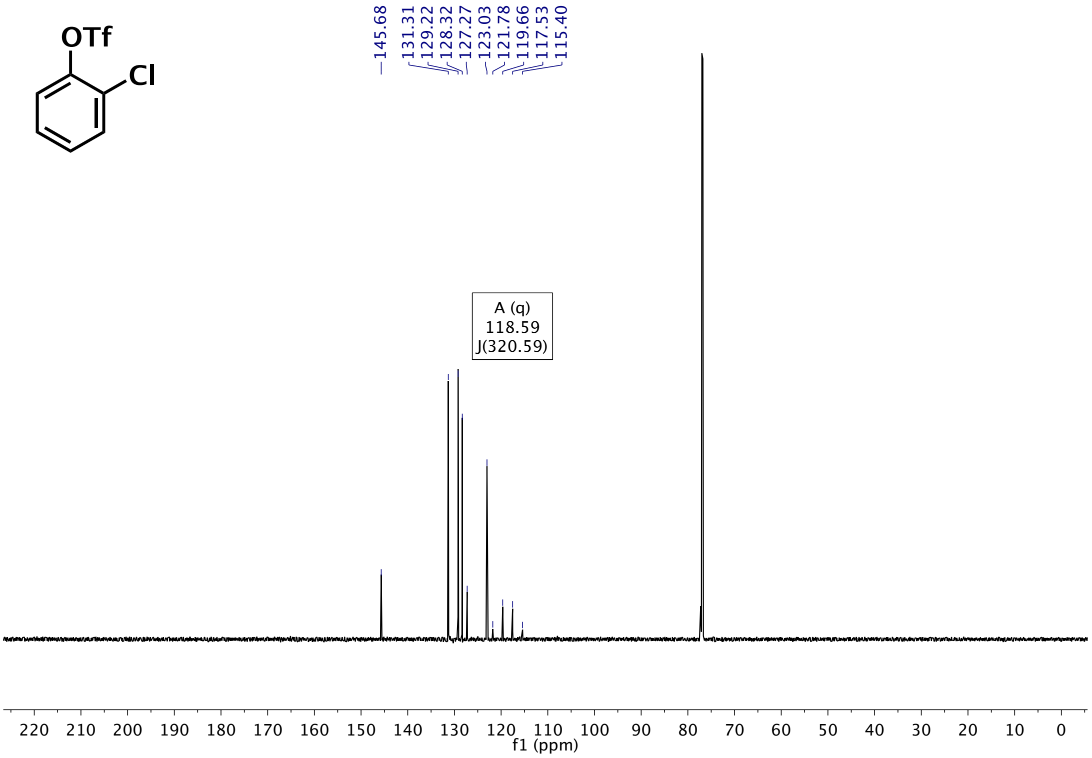
$^{19}F\{^{1}H\}$ (564 MHz, $CDCl_3$)



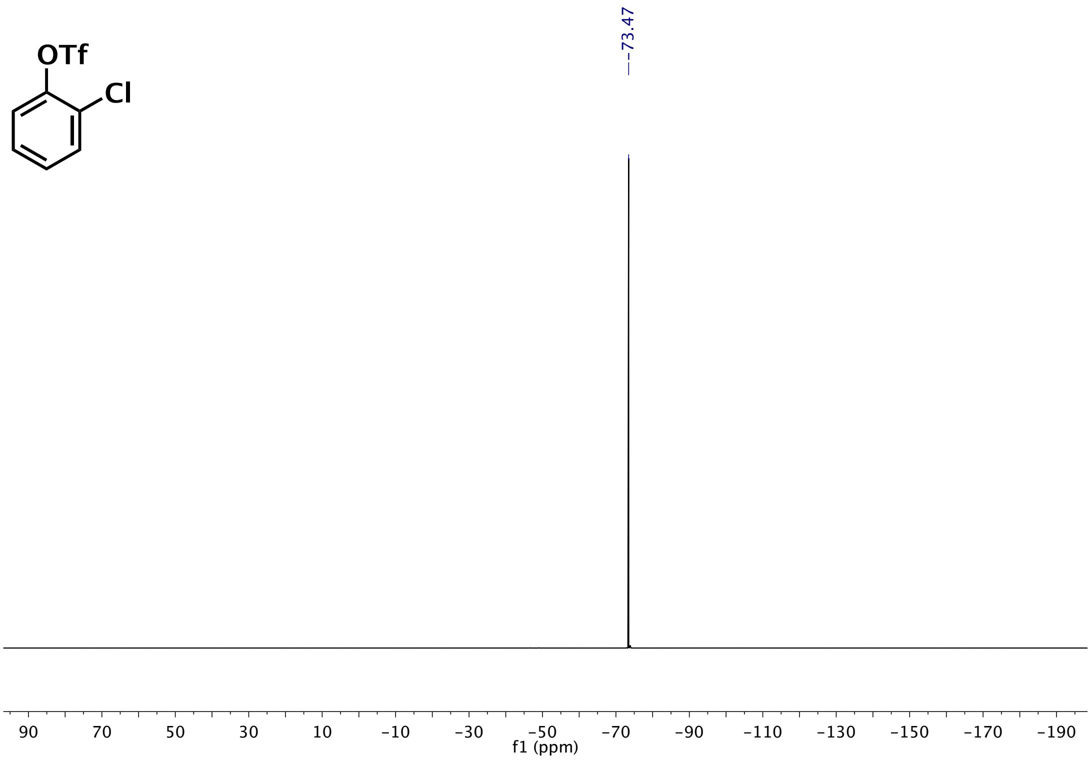
^{1}H (600 MHz, CDCl$_3$)



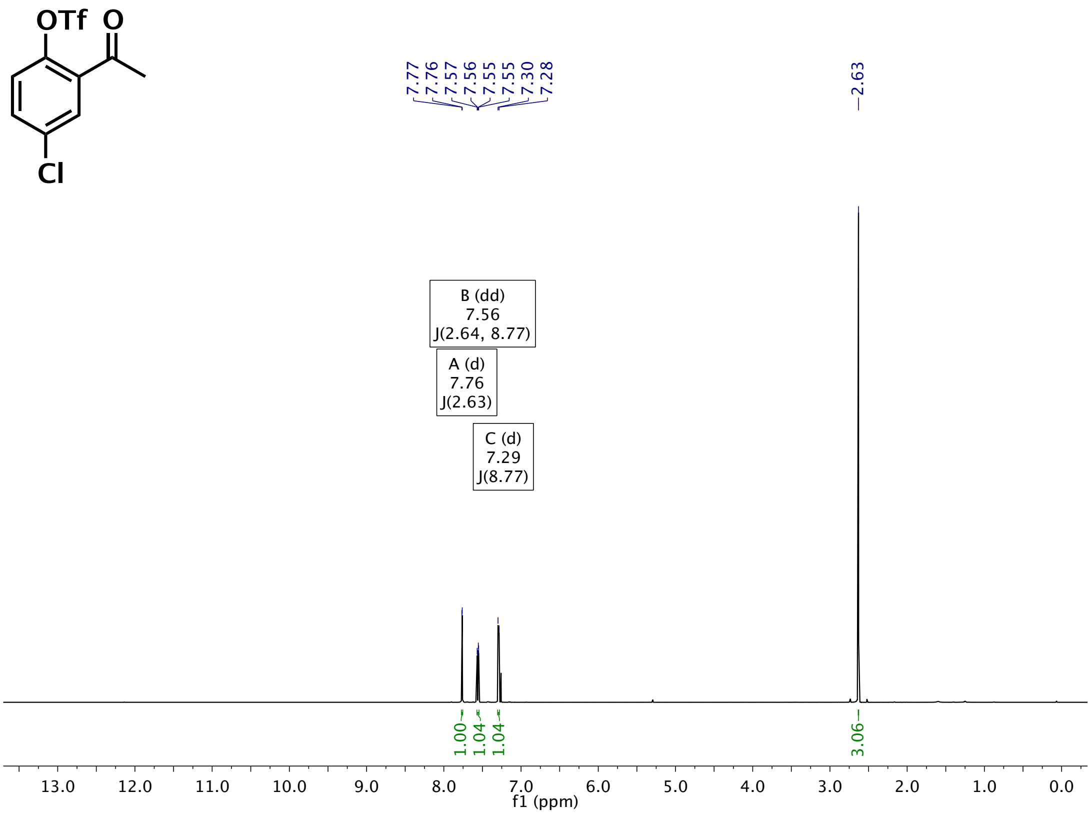
^{13}C{^{1}H} (151 MHz, CDCl$_3$)



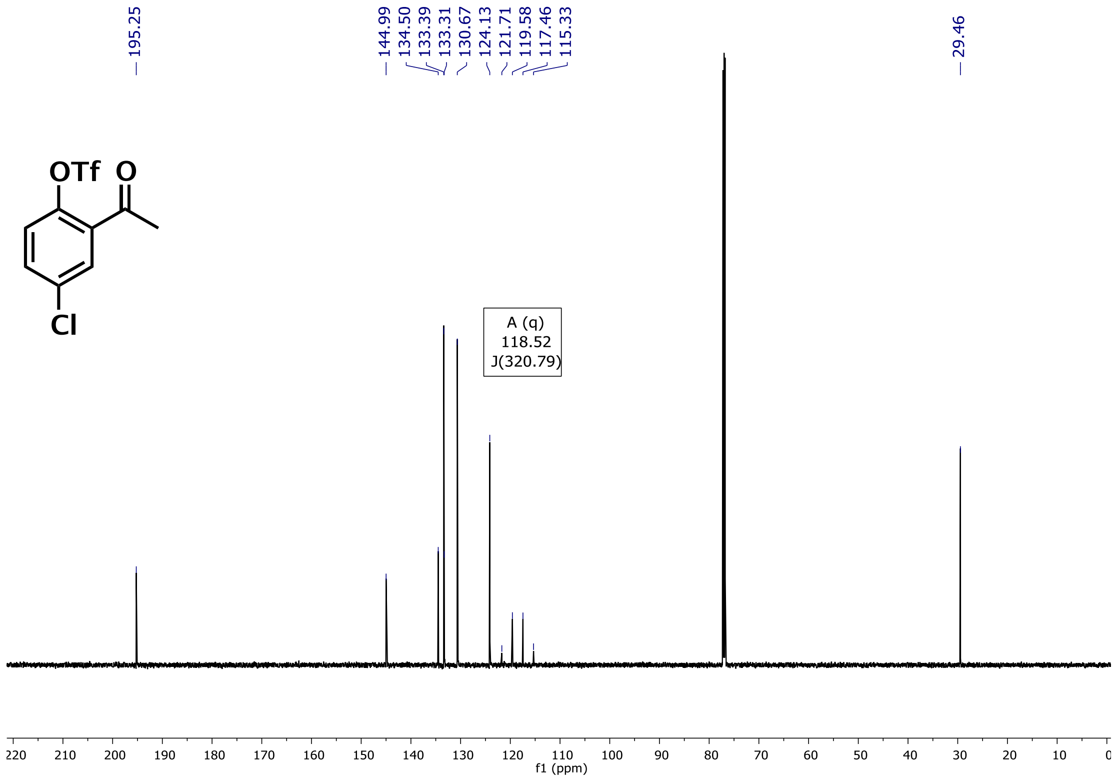
$^{19}F\{^{1}H\}$ (564 MHz, $CDCl_3$)



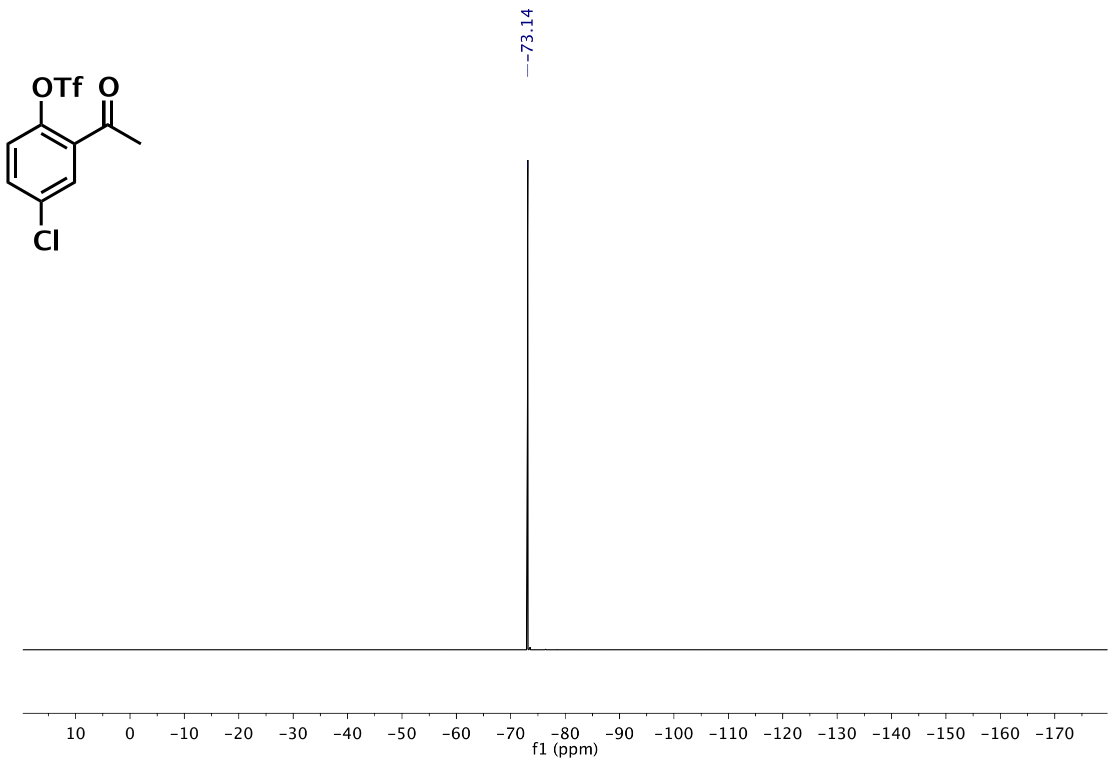
^{1}H (600 MHz, $CDCl_3$)



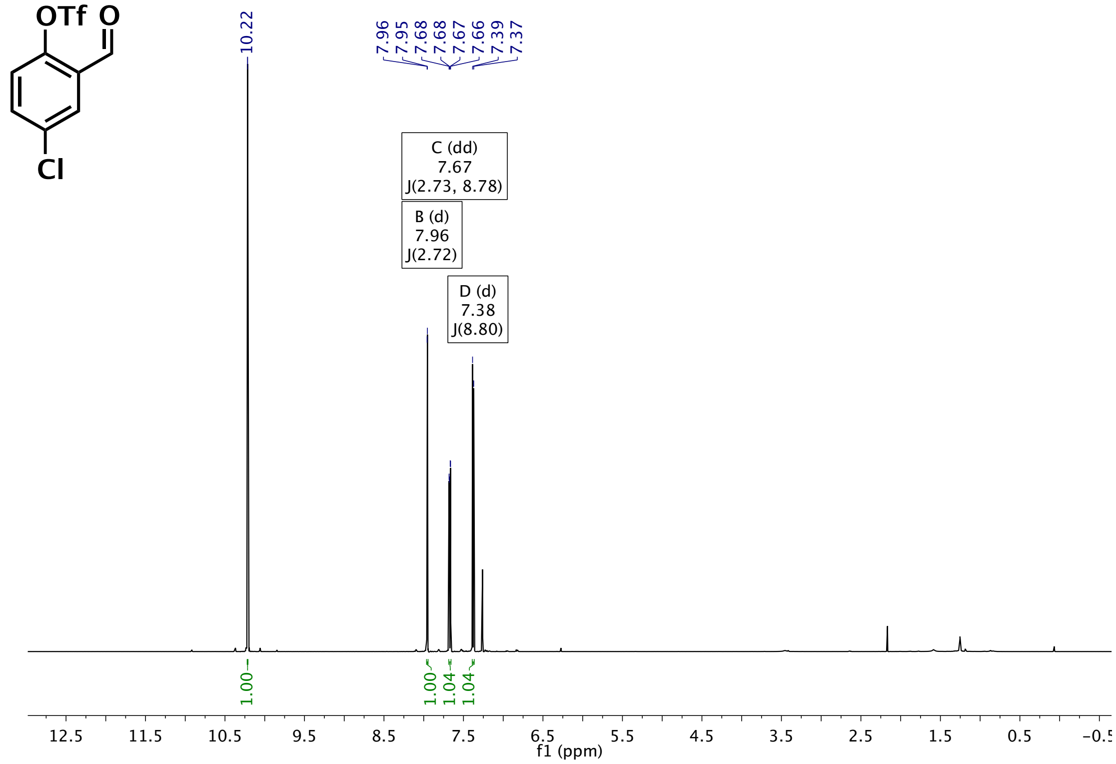
$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



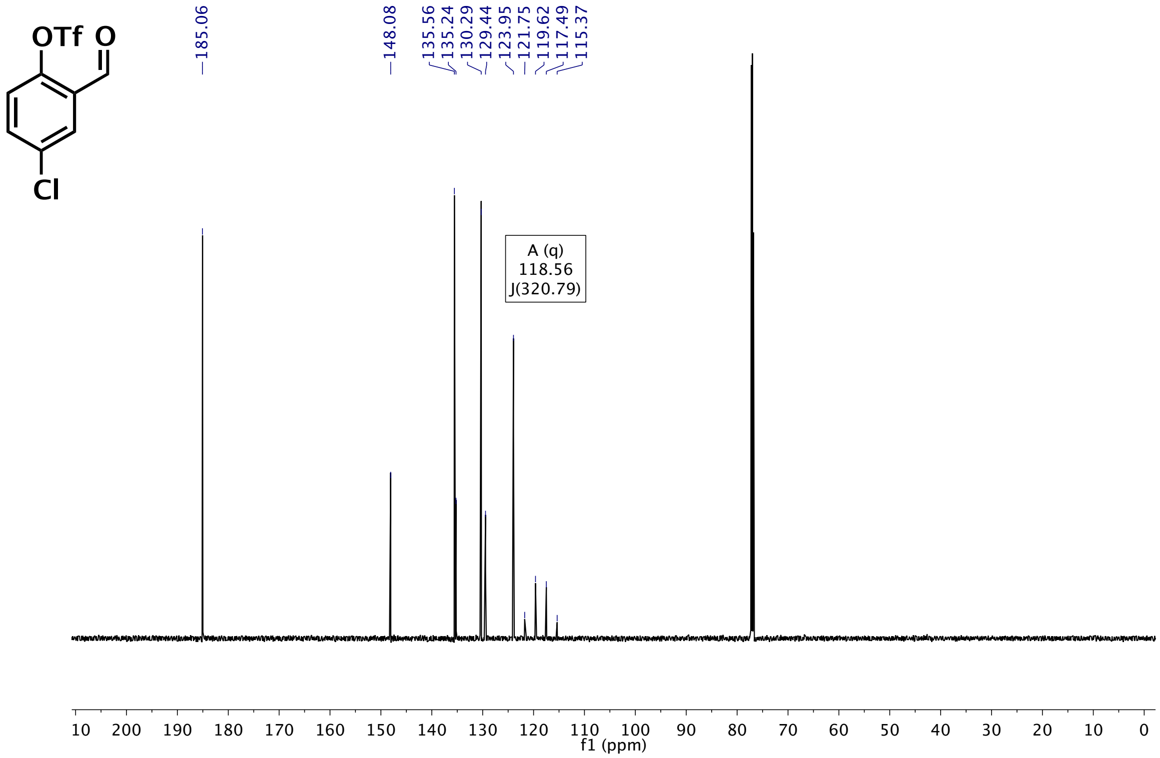
$^{19}F\{^1H\}$ (564 MHz, $CDCl_3$)



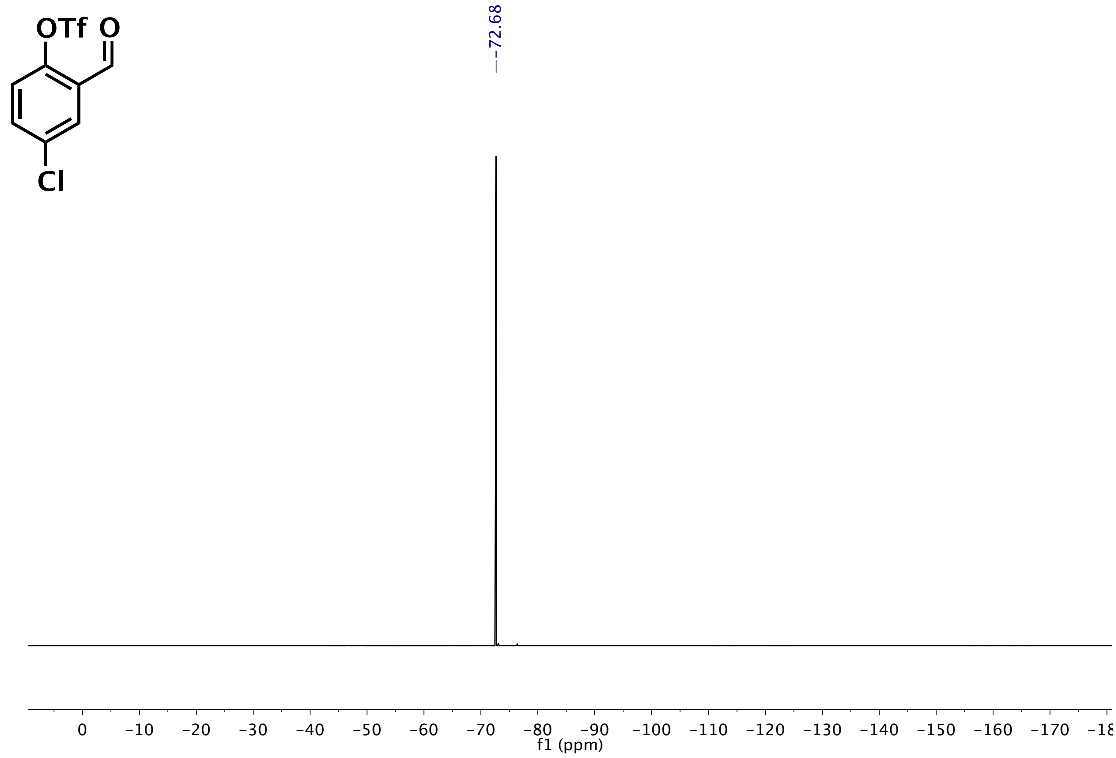
^{1}H (600 MHz, $CDCl_3$)



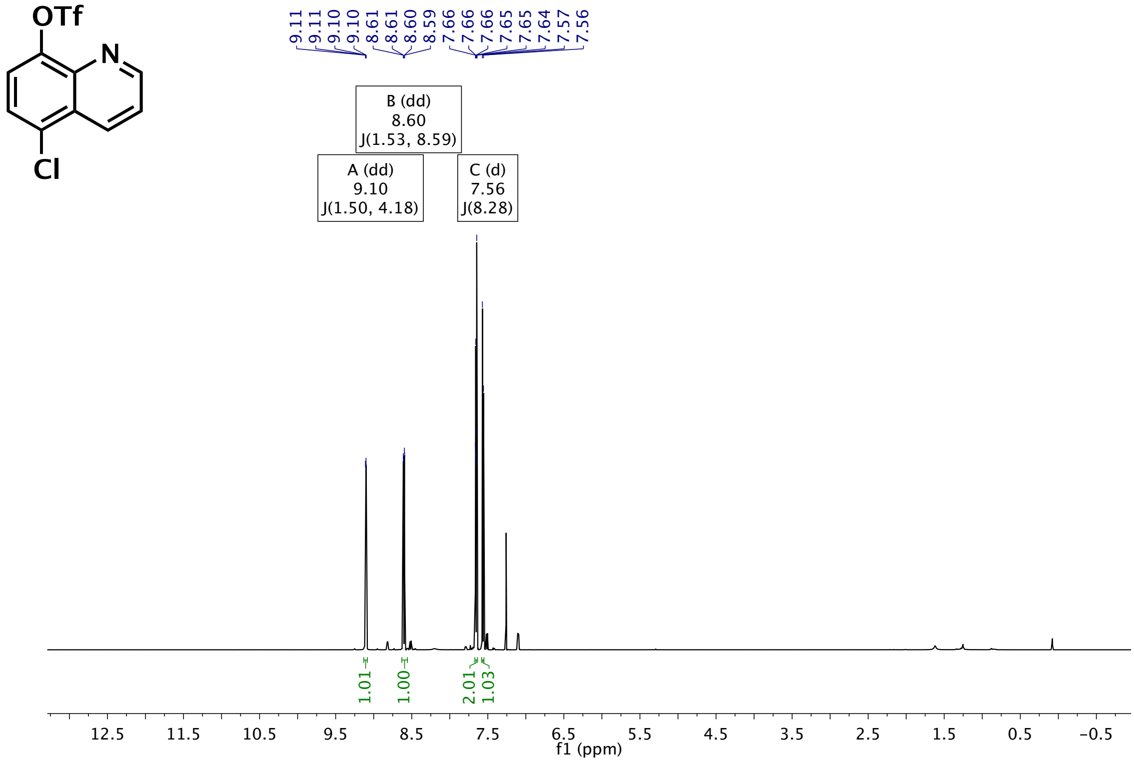
$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



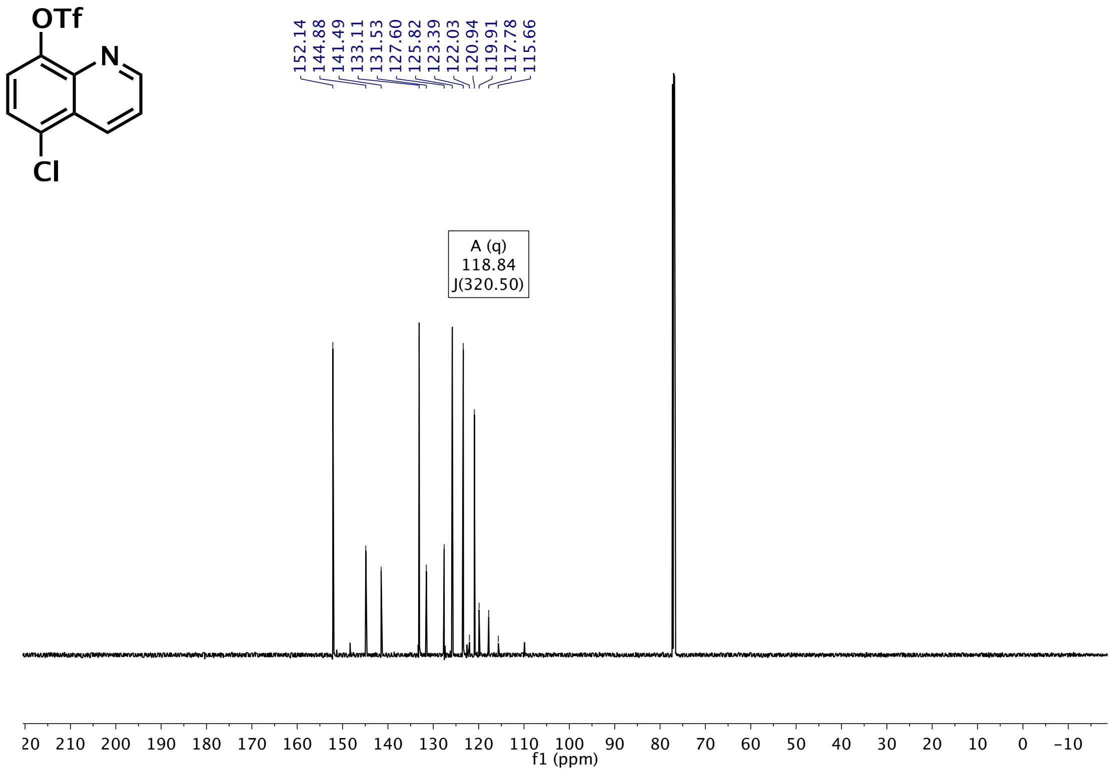
$^{19}F\{^{1}H\}$ (564 MHz, $CDCl_3$)



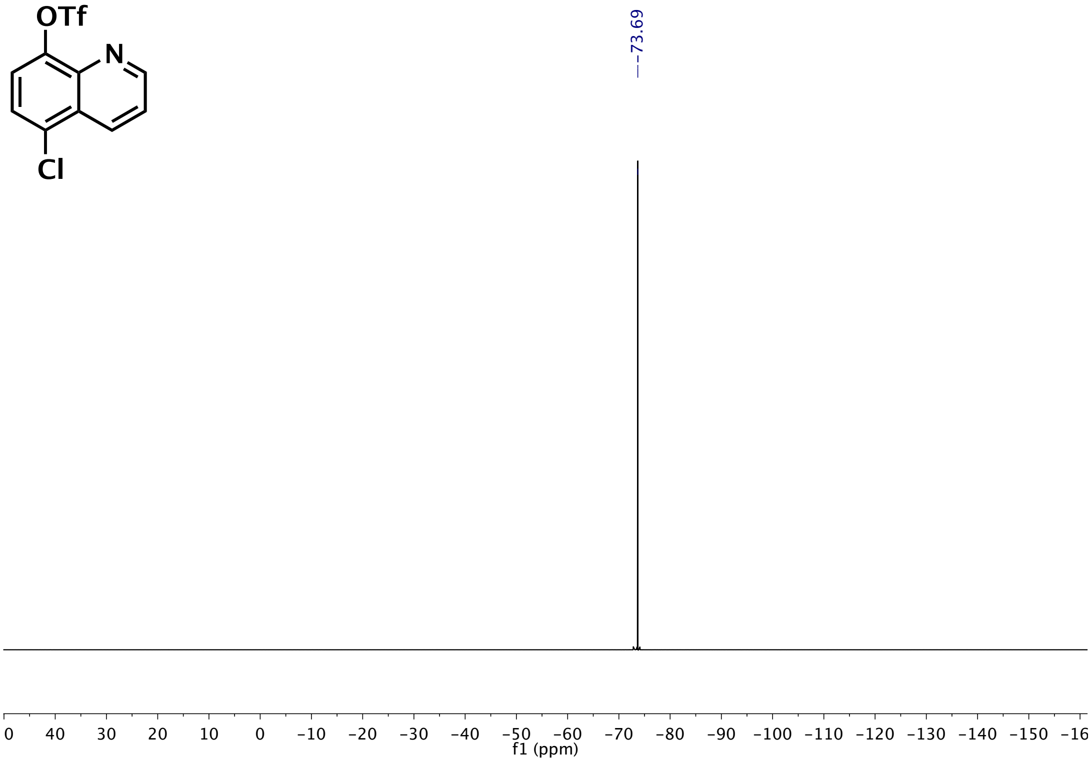
^{1}H (600 MHz, $CDCl_3$)



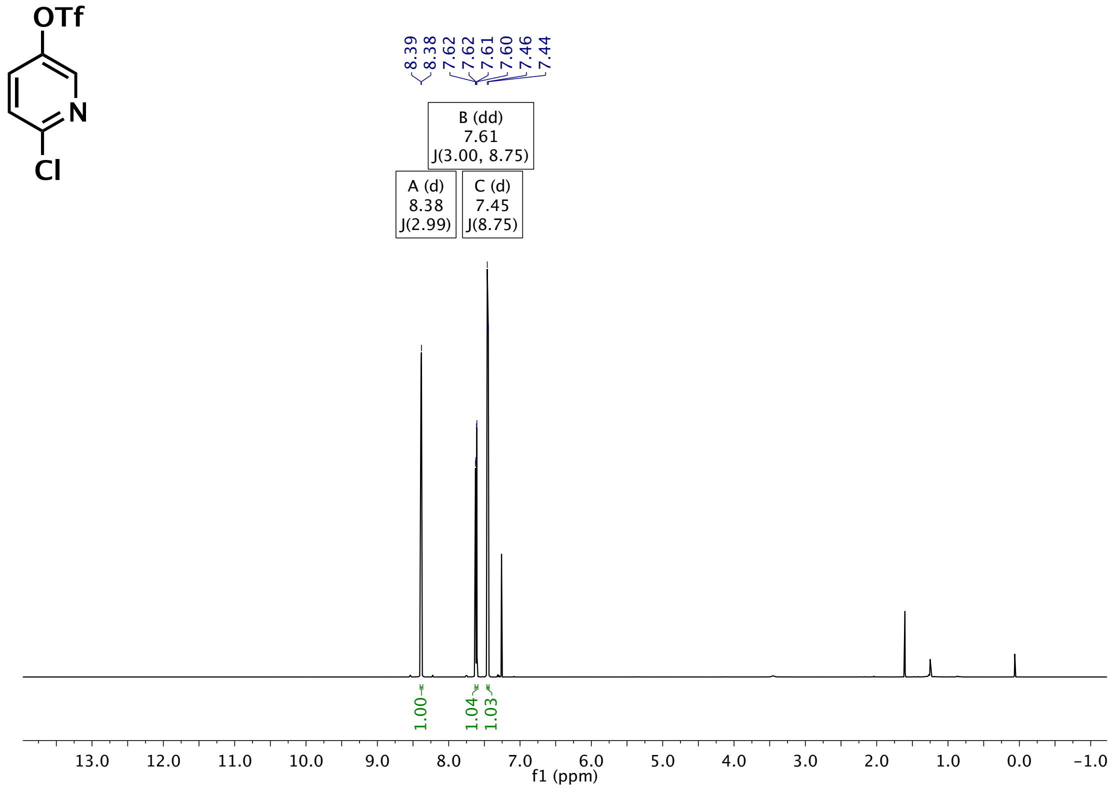
$^{13}C\{^1H\}$ (151 MHz, $CDCl_3$)



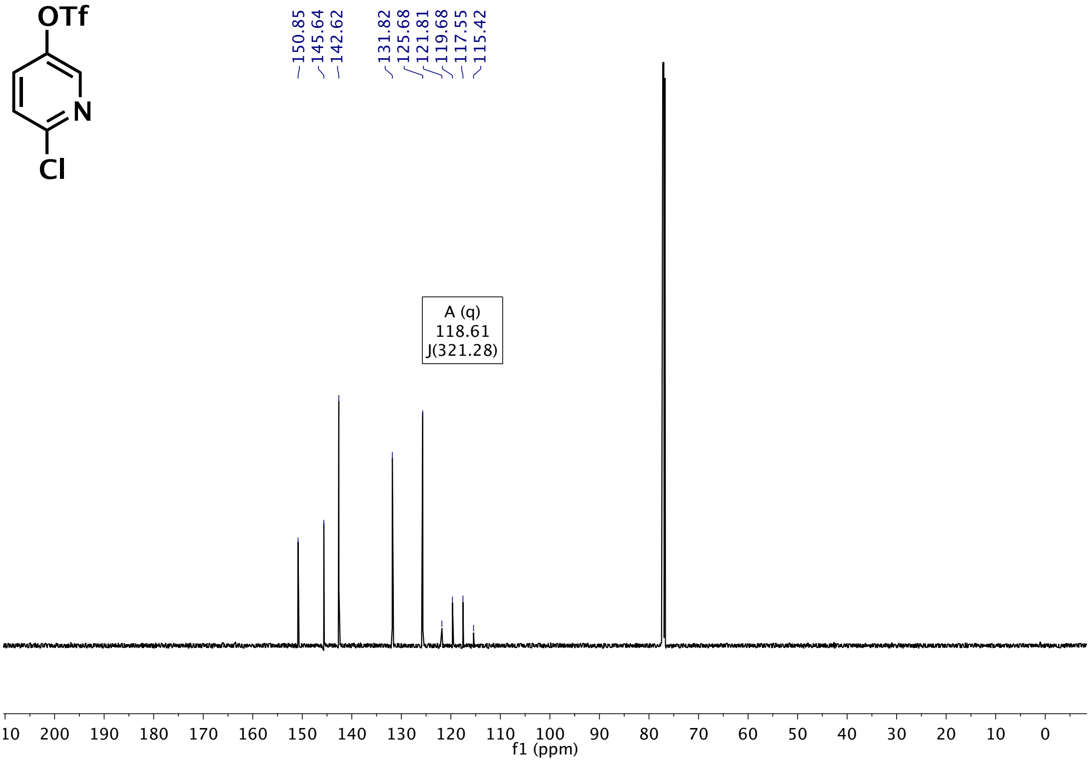
$^{19}F\{^1H\}$ (564 MHz, $CDCl_3$)



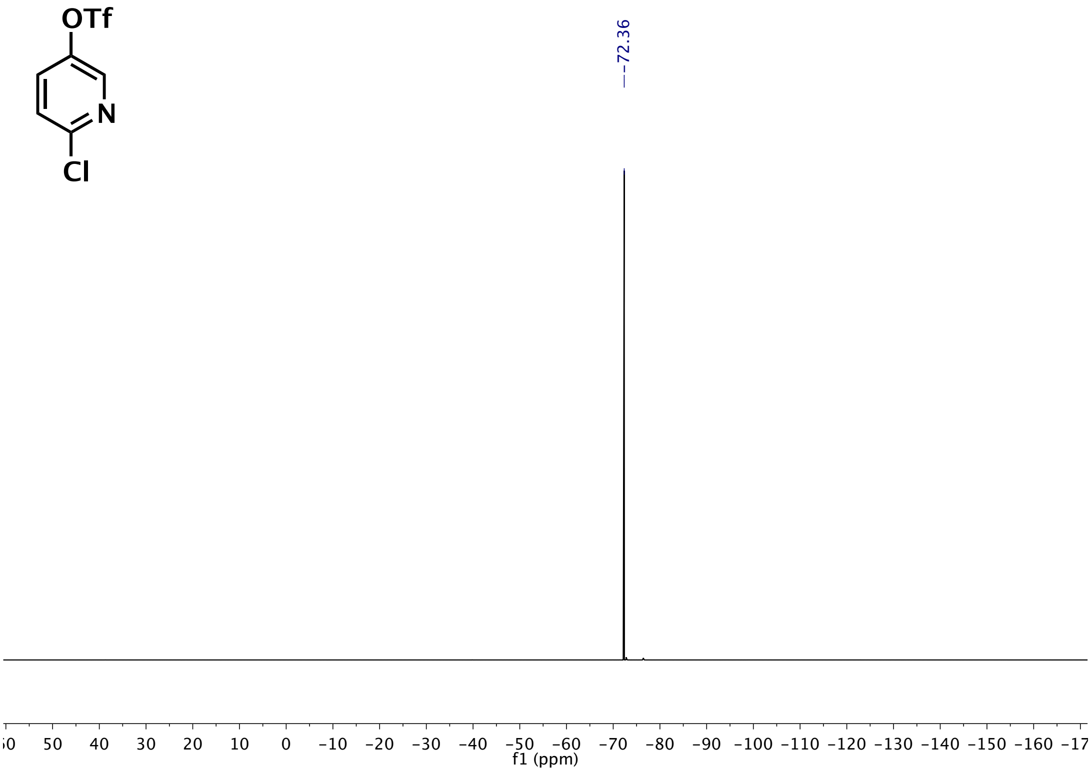
^{1}H (600 MHz, CDCl$_3$)



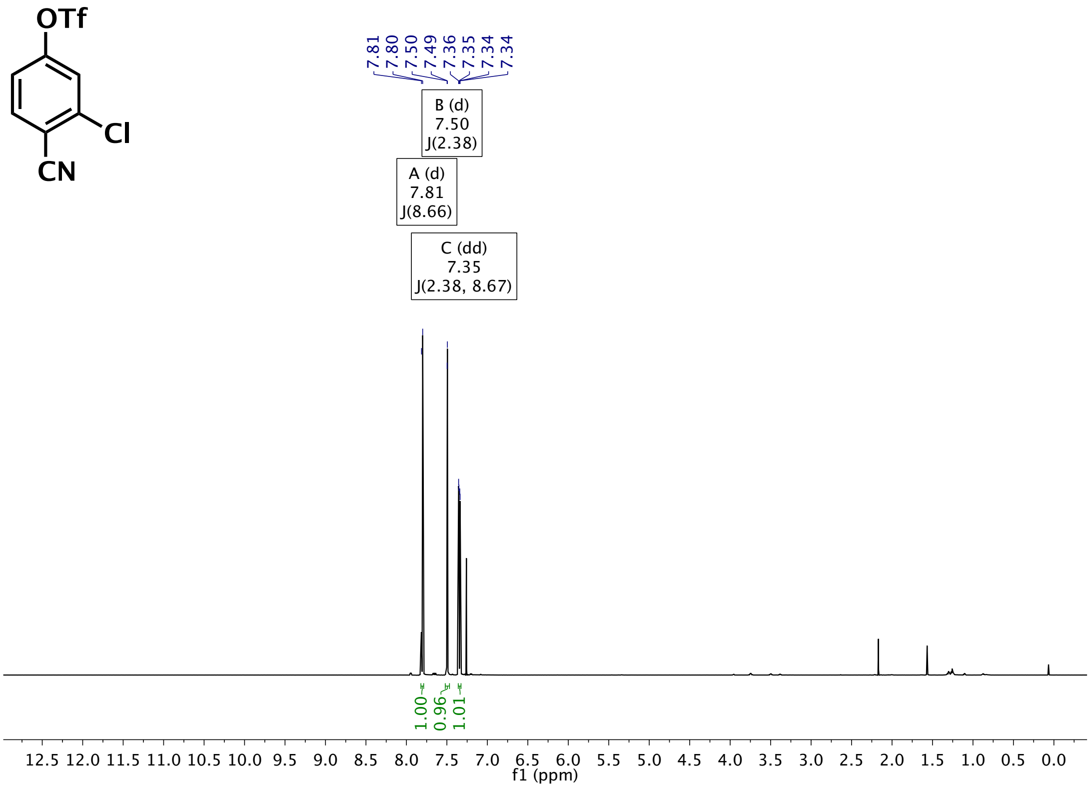
^{13}C{^{1}H} (151 MHz, CDCl$_3$)



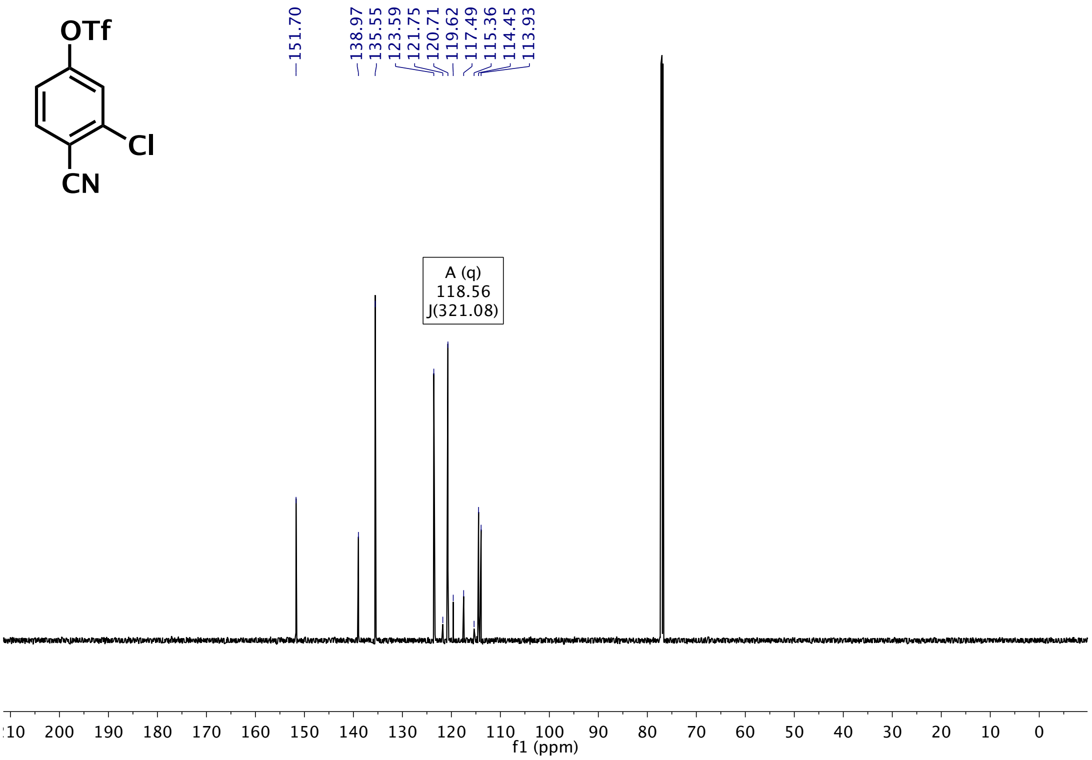
$^{19}F\{^1H\}$ (564 MHz, $CDCl_3$)



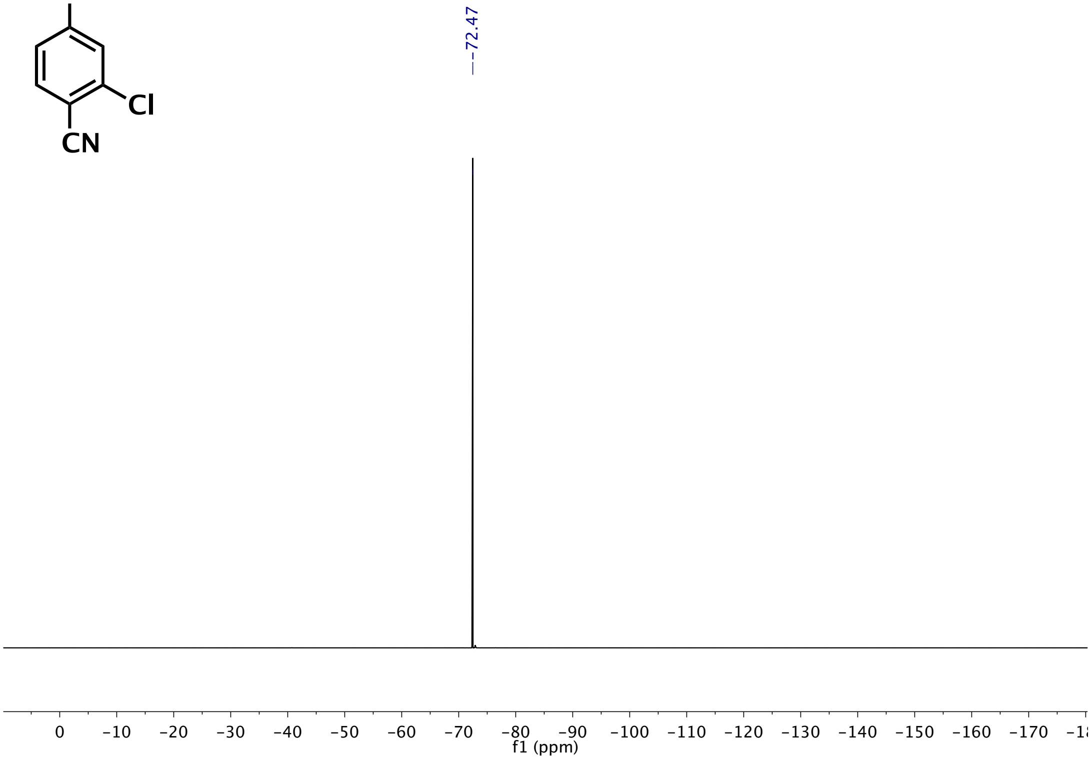
^1H (600 MHz, $CDCl_3$)



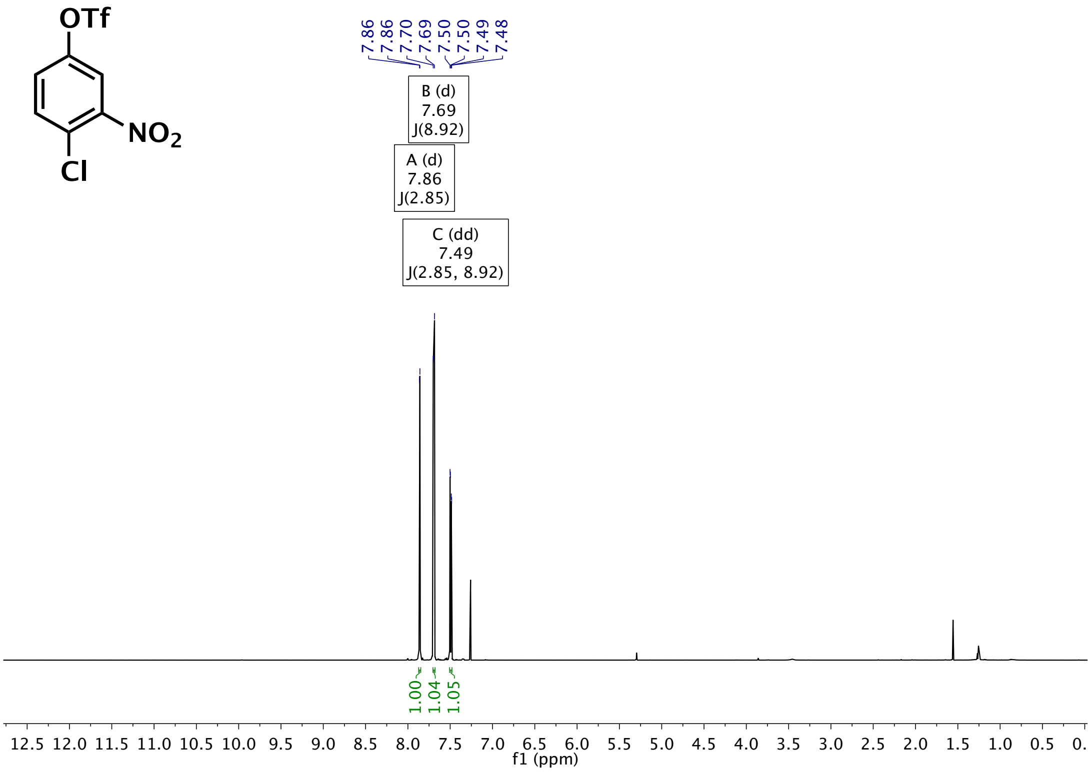
$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)



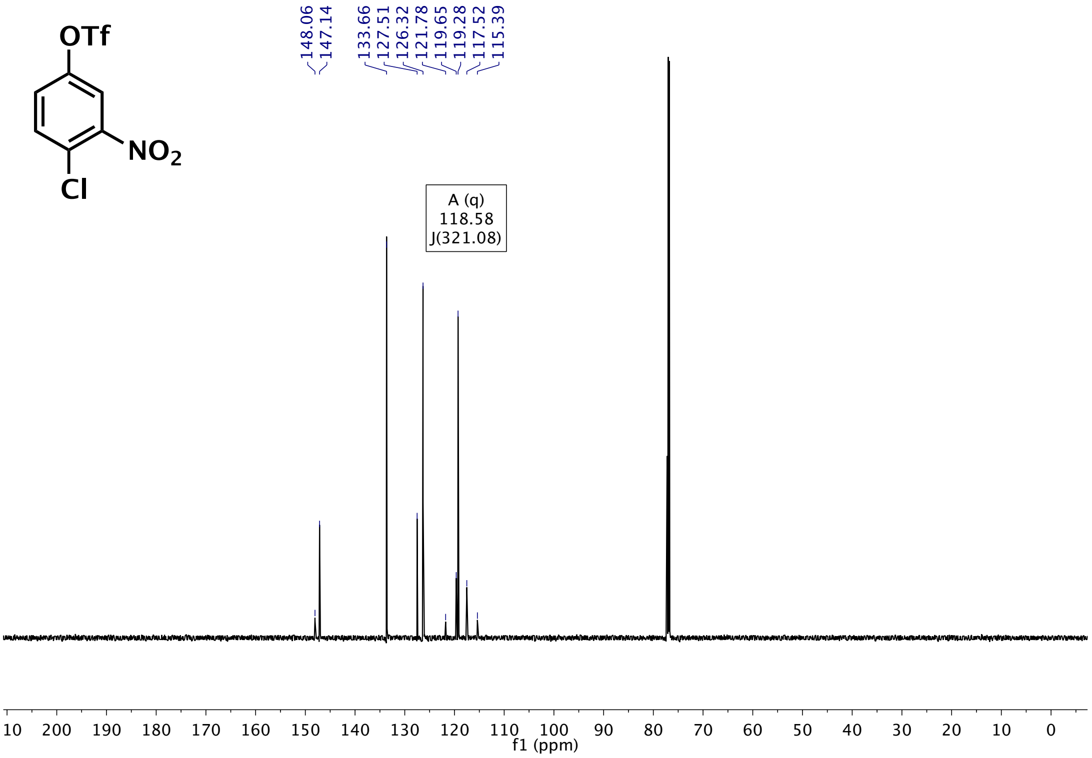
$^{19}F\{^{1}H\}$ (564 MHz, $CDCl_3$)



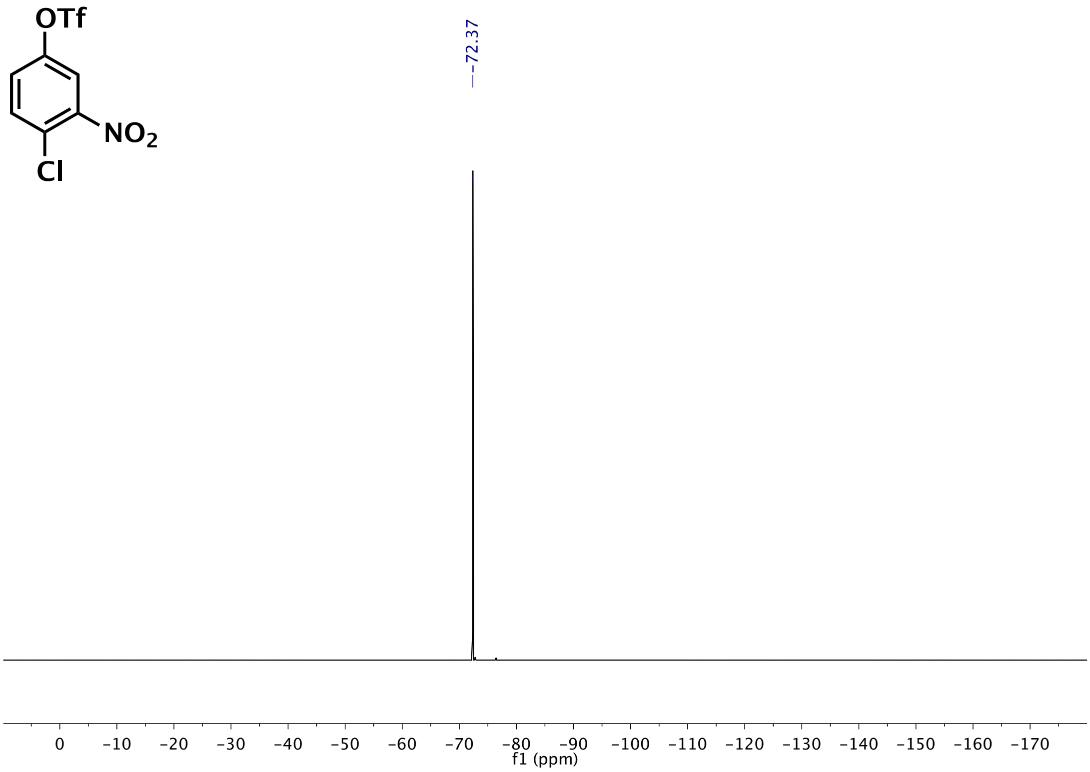
^{1}H (600 MHz, $CDCl_3$)



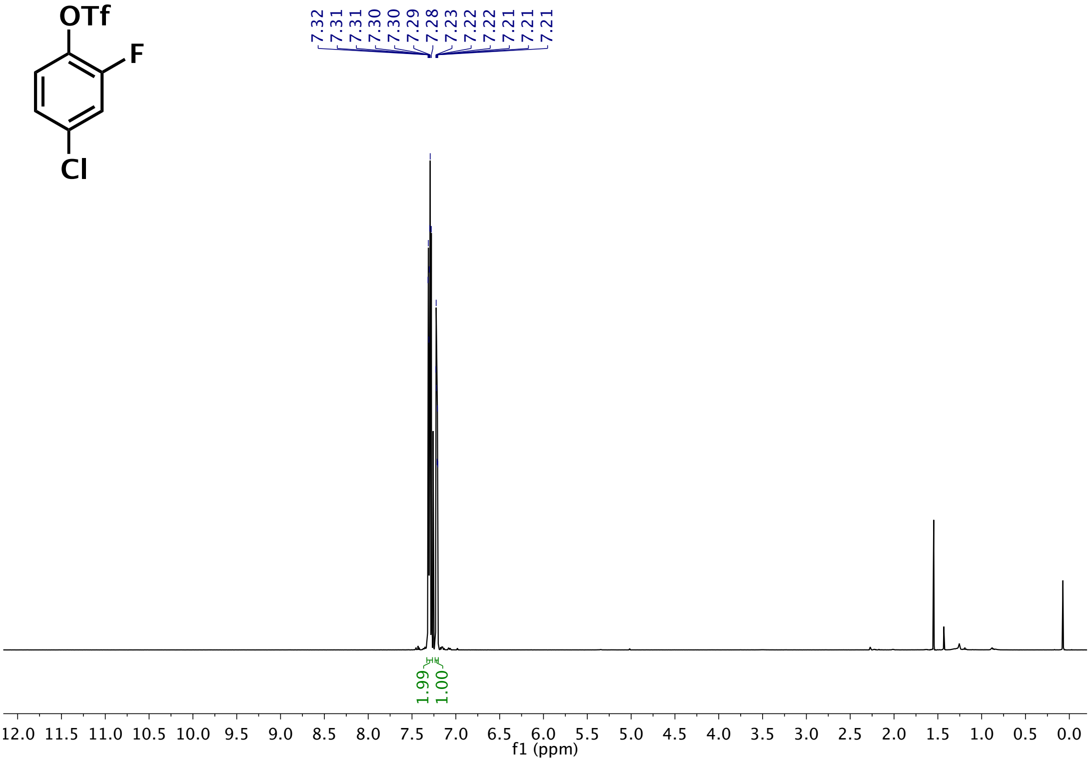
$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)



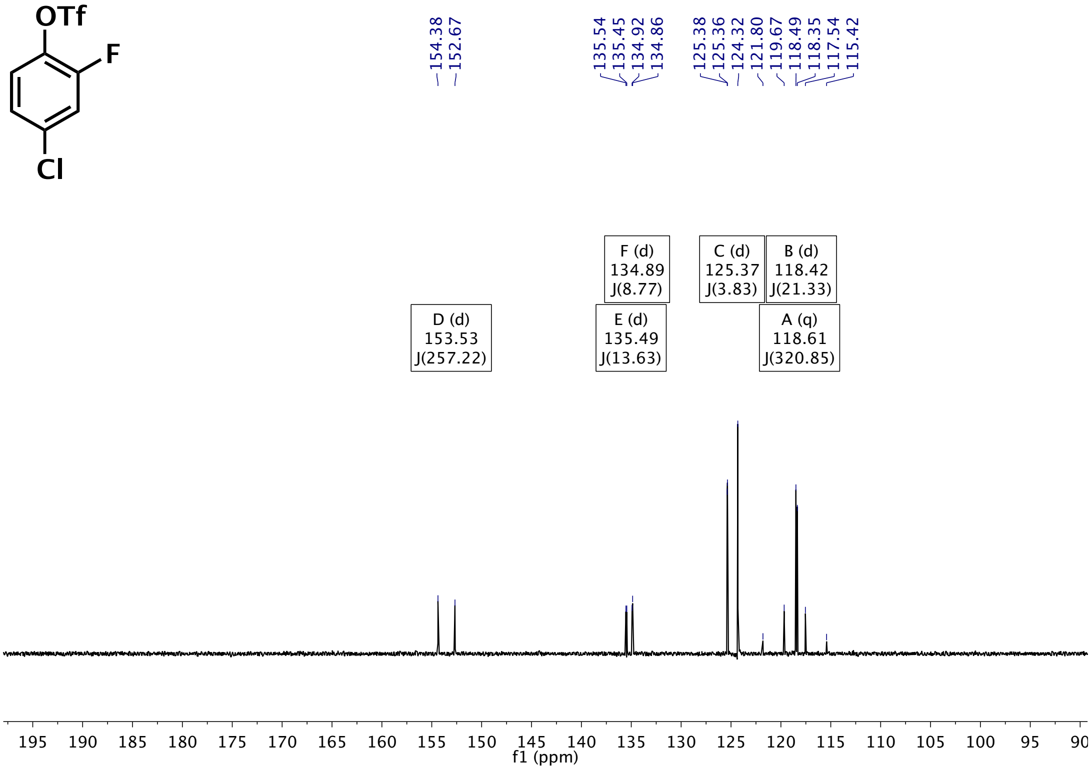
$^{19}F\{^{1}H\}$ (564 MHz, CDCl$_3$)



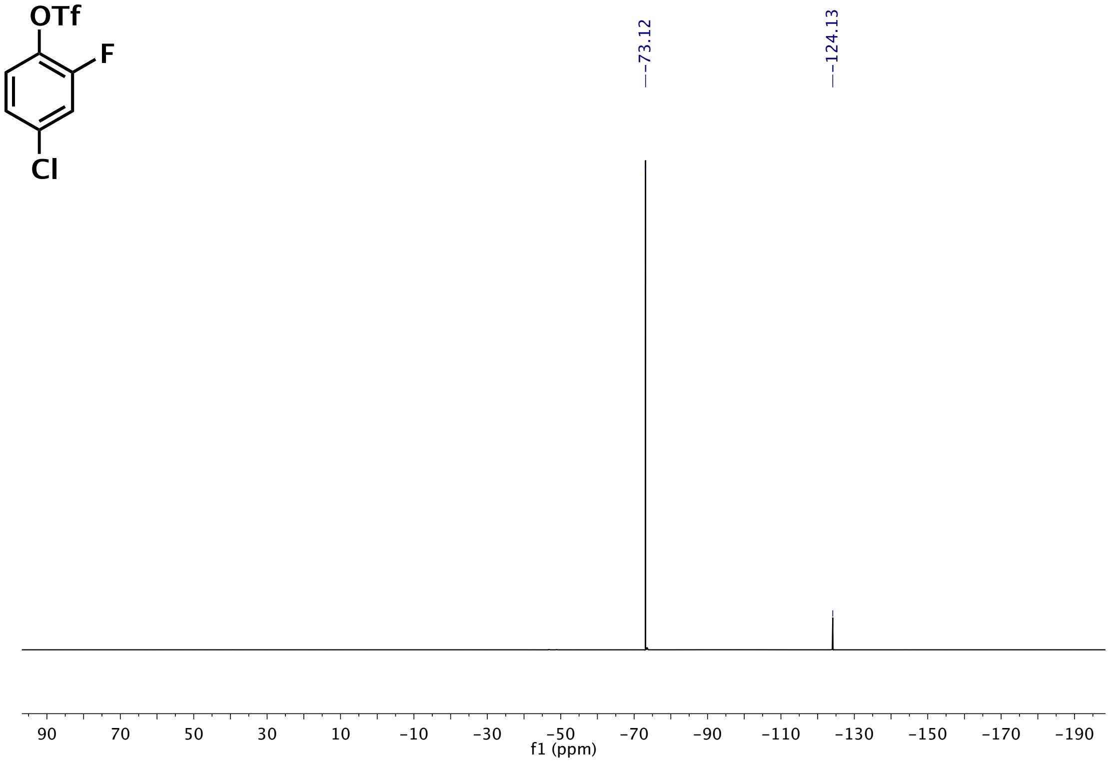
^{1}H (600 MHz, CDCl$_3$)



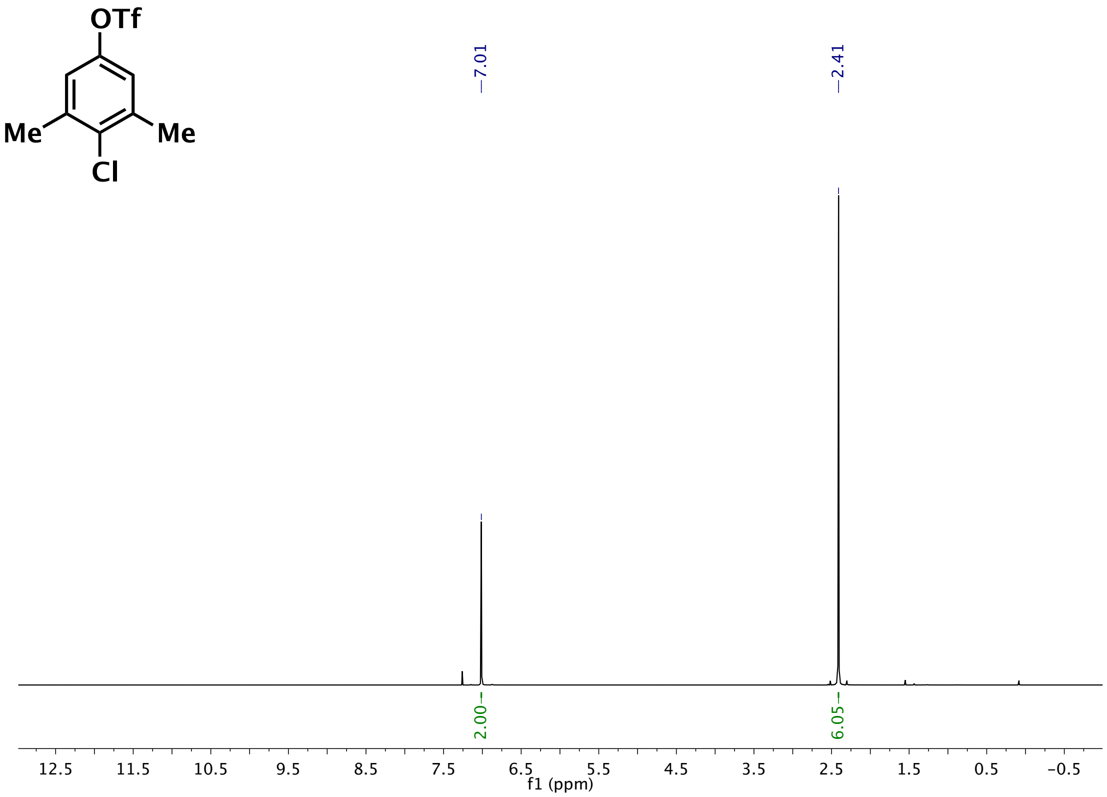
^{13}C{^{1}H} (151 MHz, CDCl$_3$)



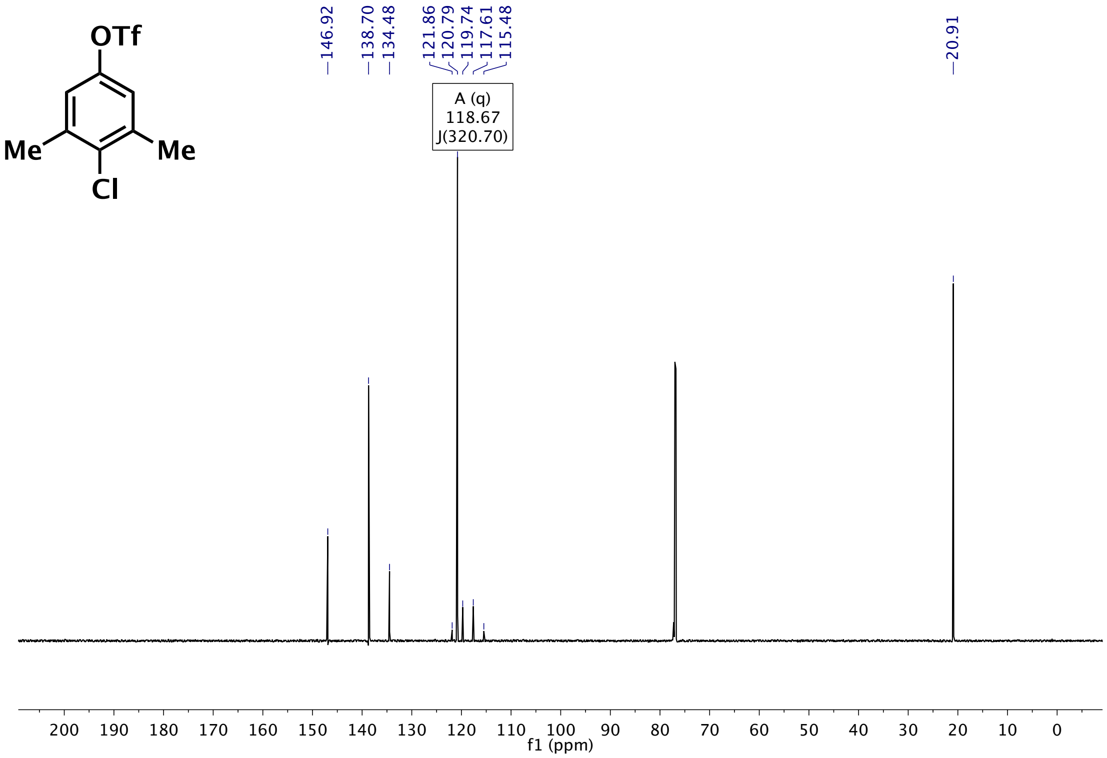
^{19}F{^{1}H} (564 MHz, CDCl$_3$)



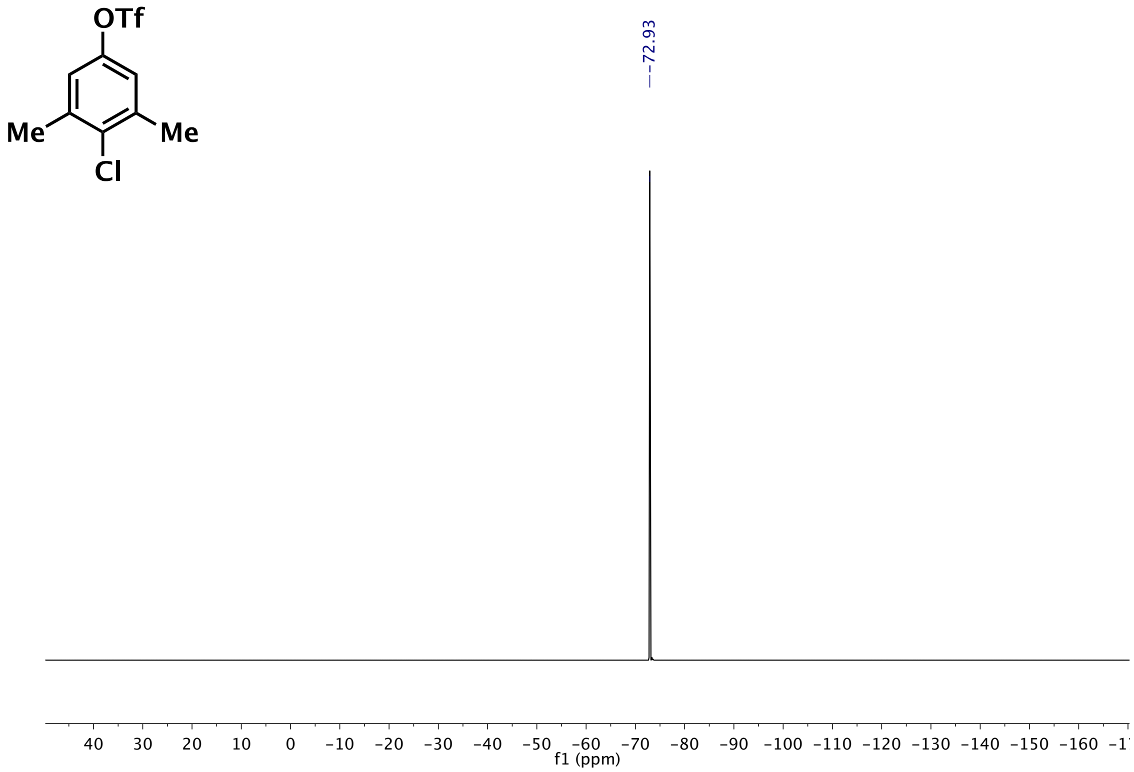
^{1}H (600 MHz, CDCl$_3$)



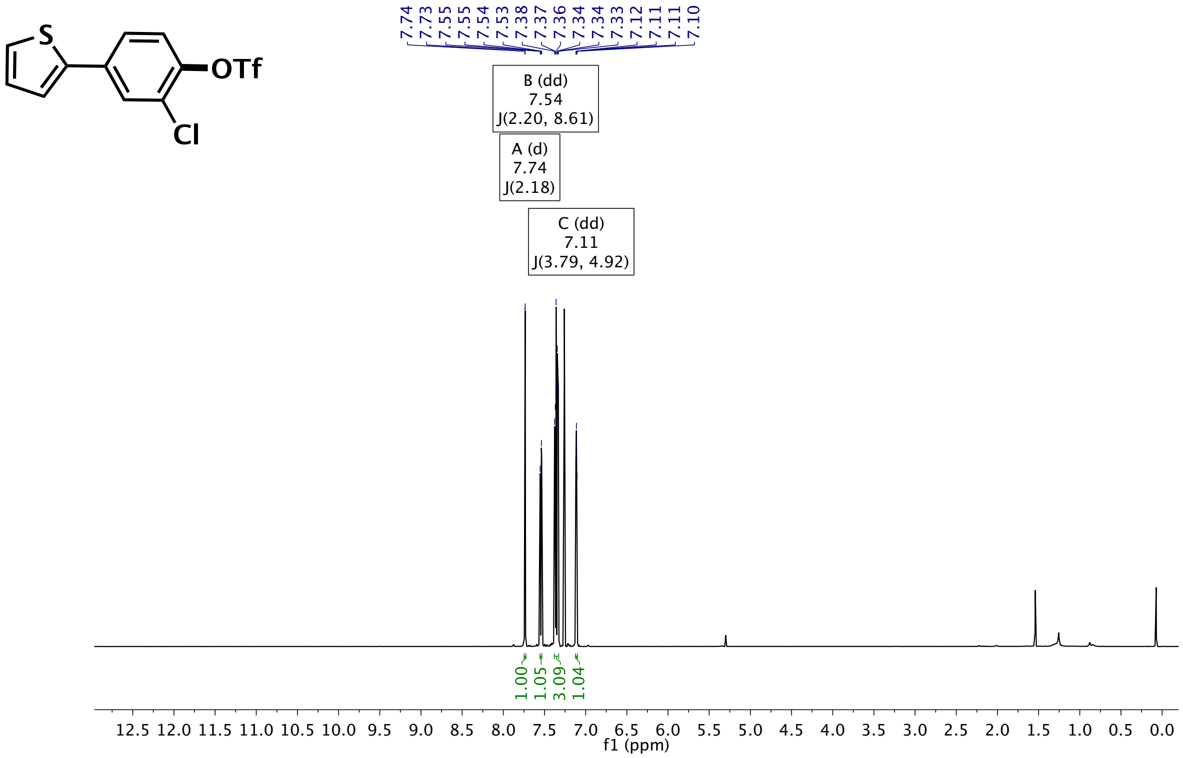
^{13}C{^{1}H} (151 MHz, CDCl$_3$)



$^{19}F\{^1H\}$ (564 MHz, $CDCl_3$)



^1H (600 MHz, $CDCl_3$)



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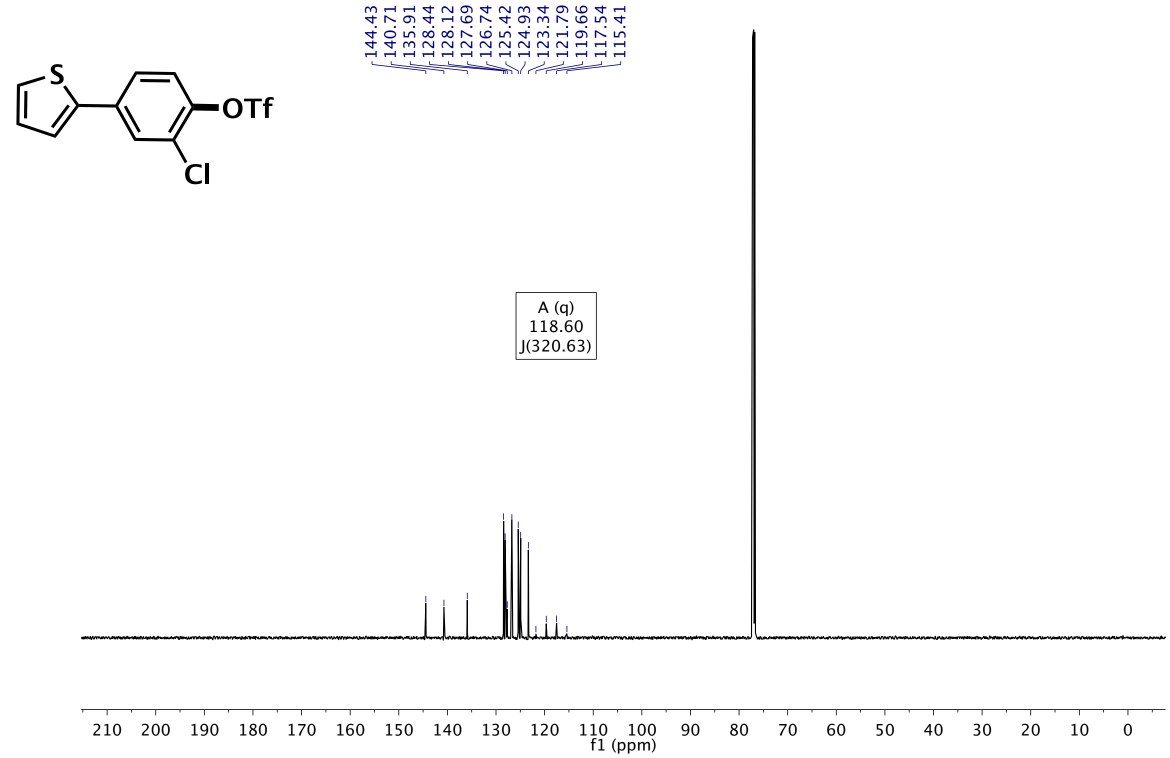

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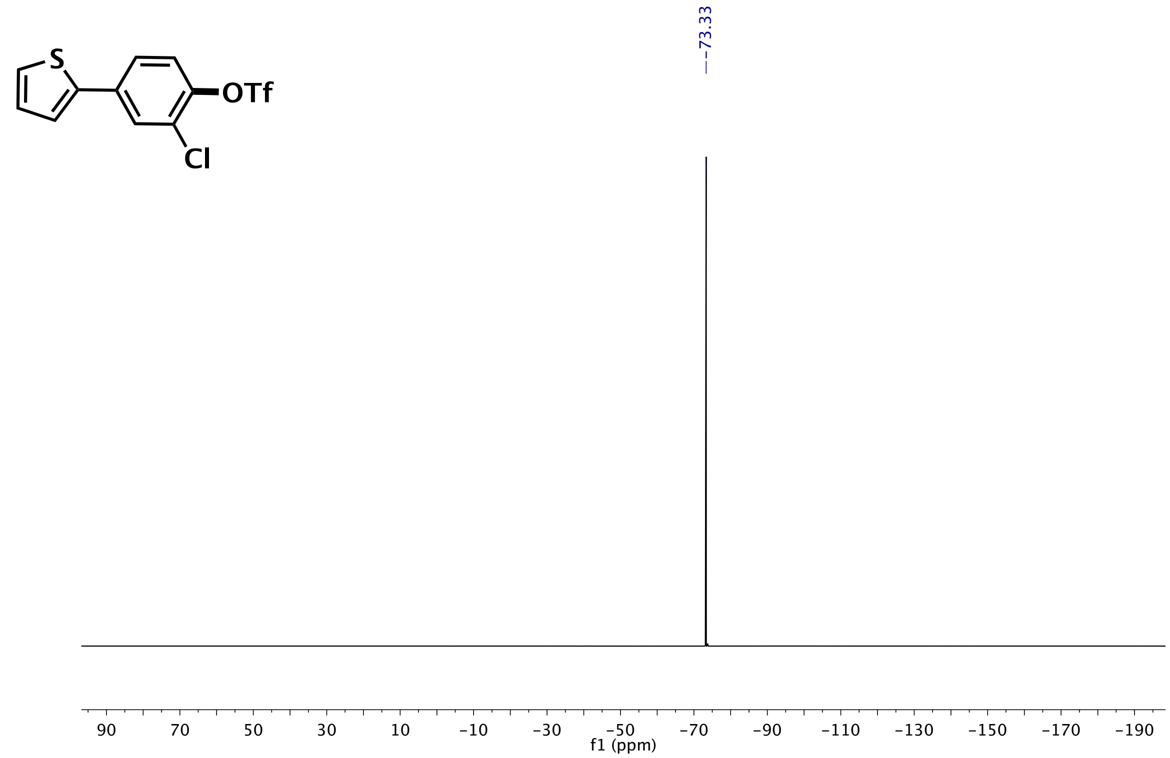
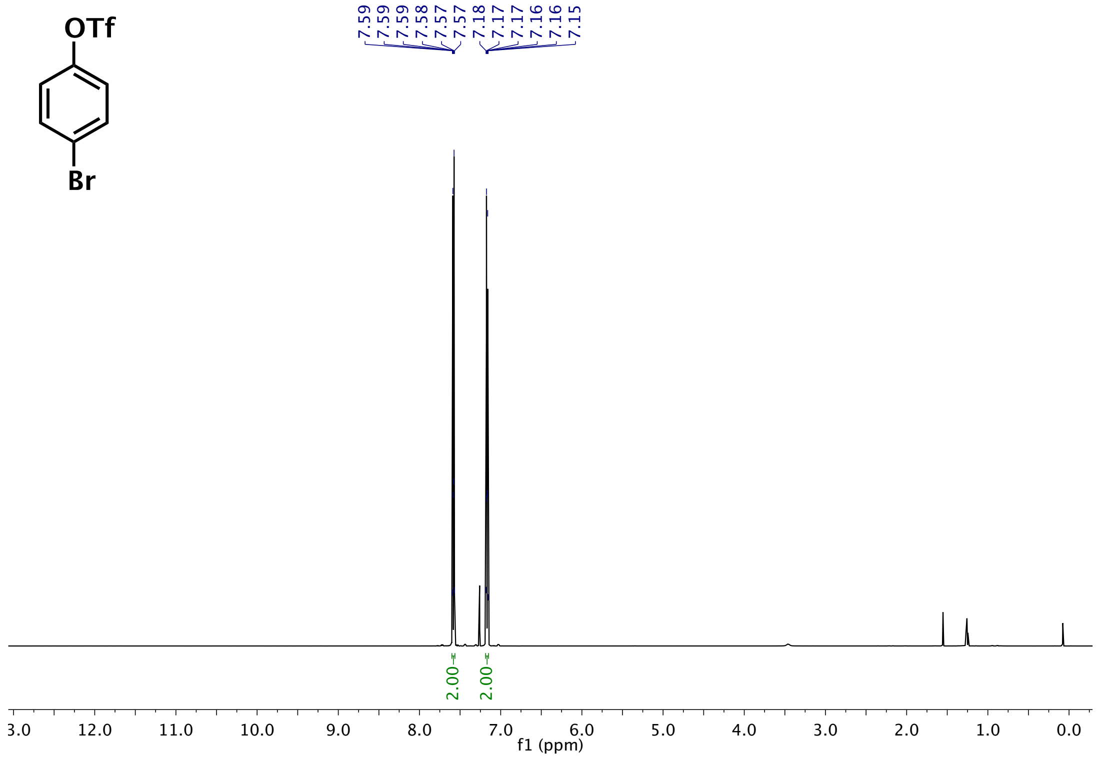


^{1}H (600 MHz, CDCl$_3$)



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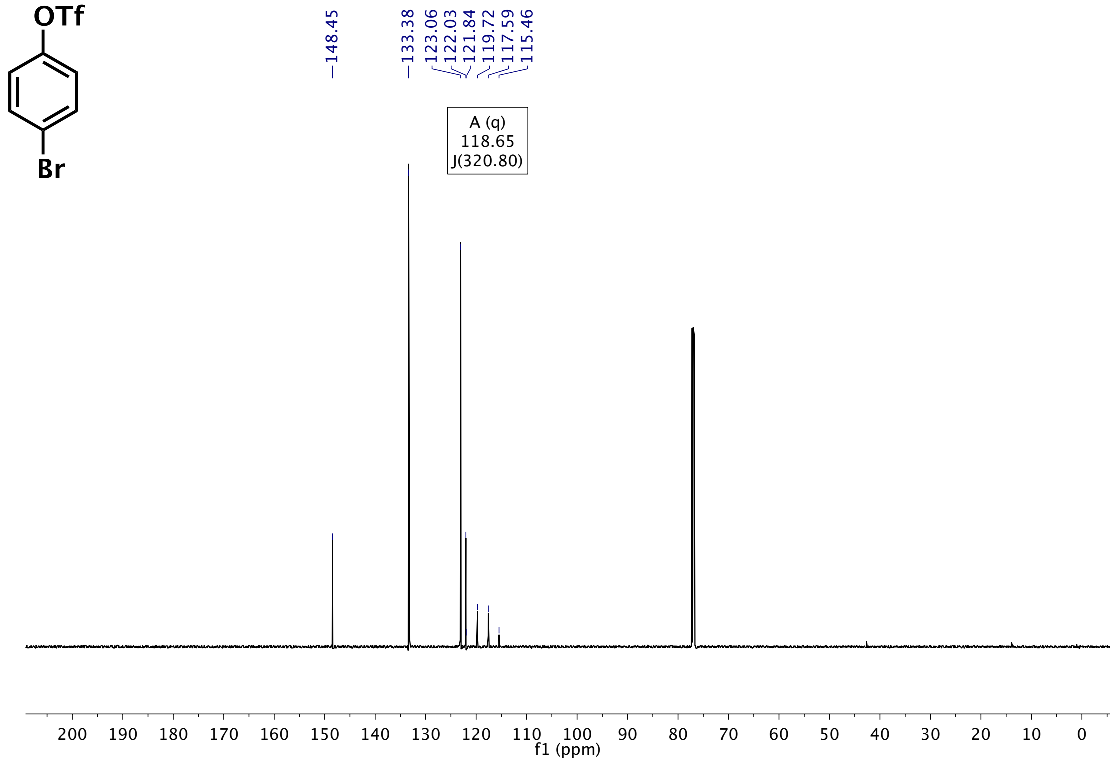
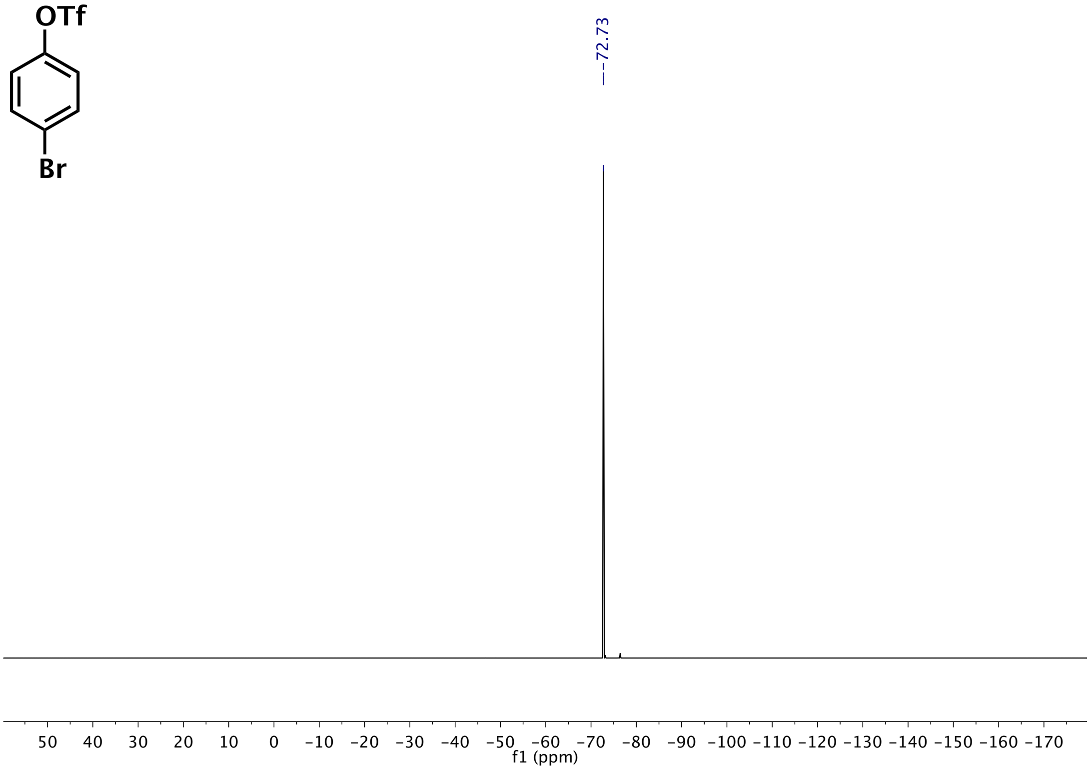
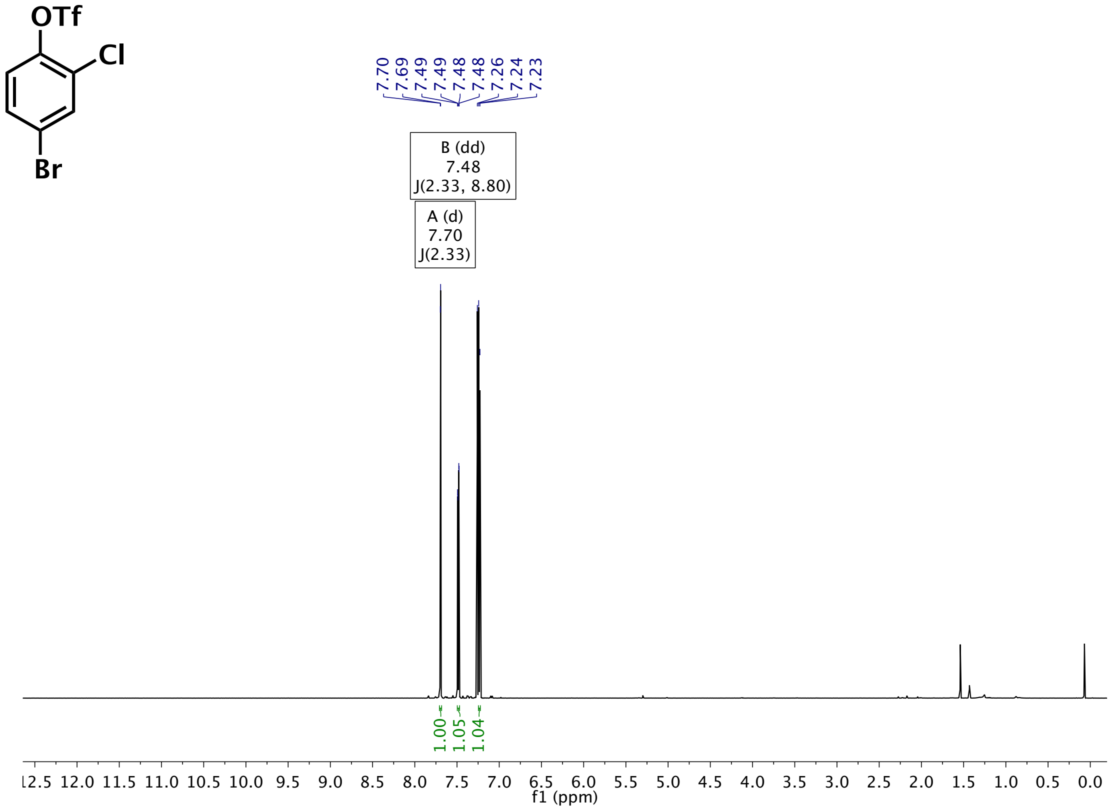


$^{19}F\{^1H\}$ (564 MHz, $CDCl_3$)



^1H (600 MHz, $CDCl_3$)



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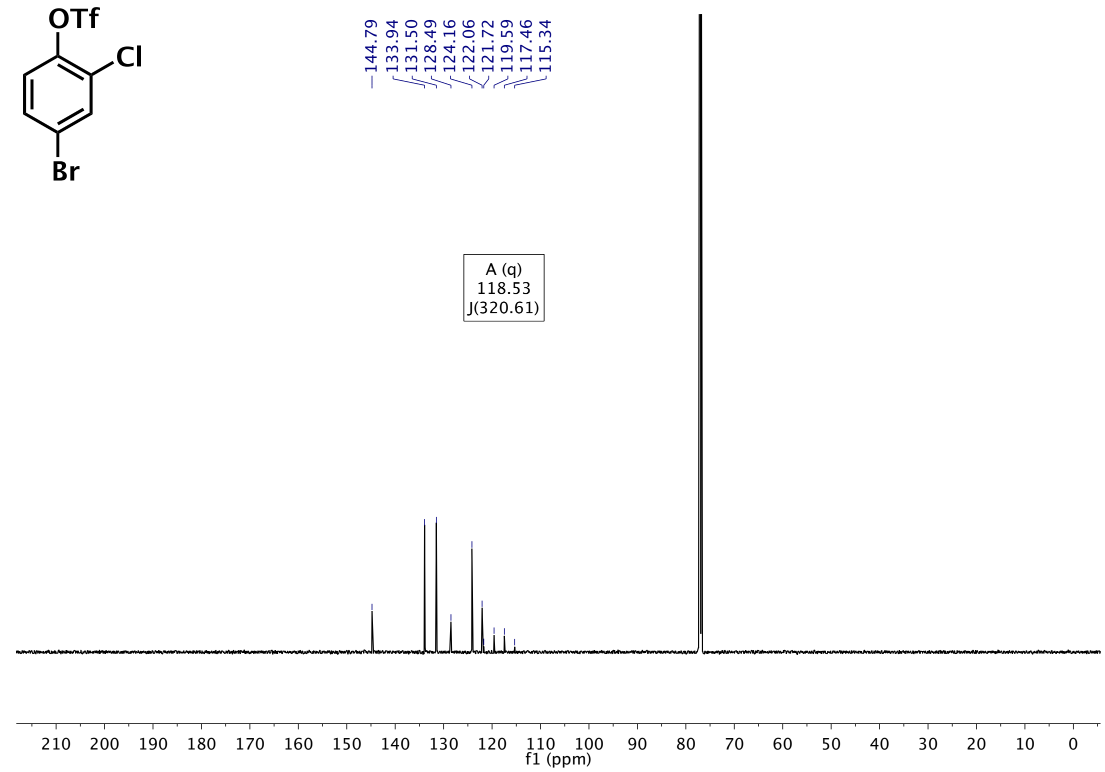
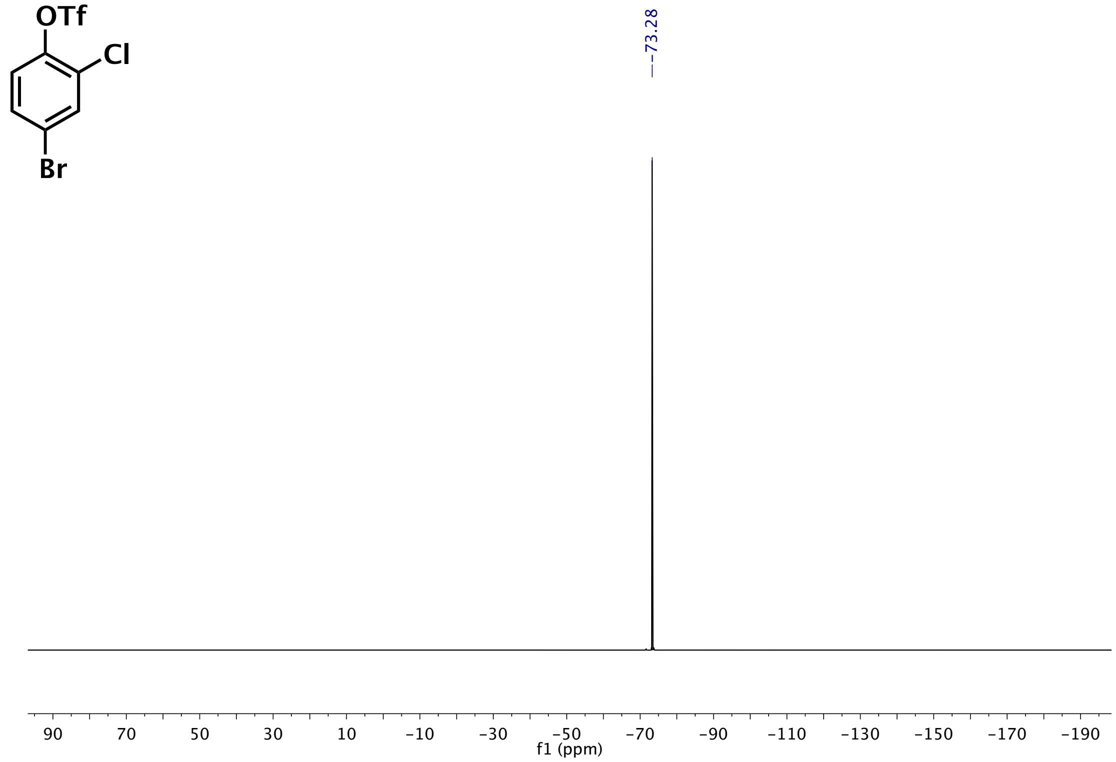
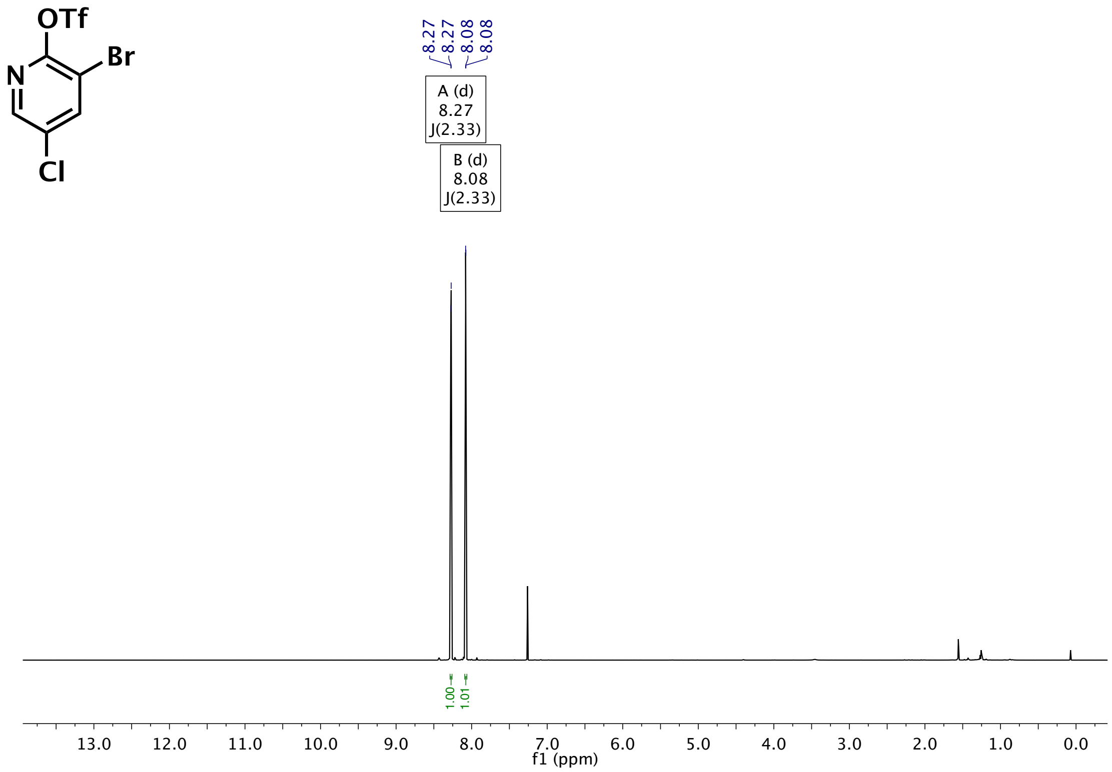


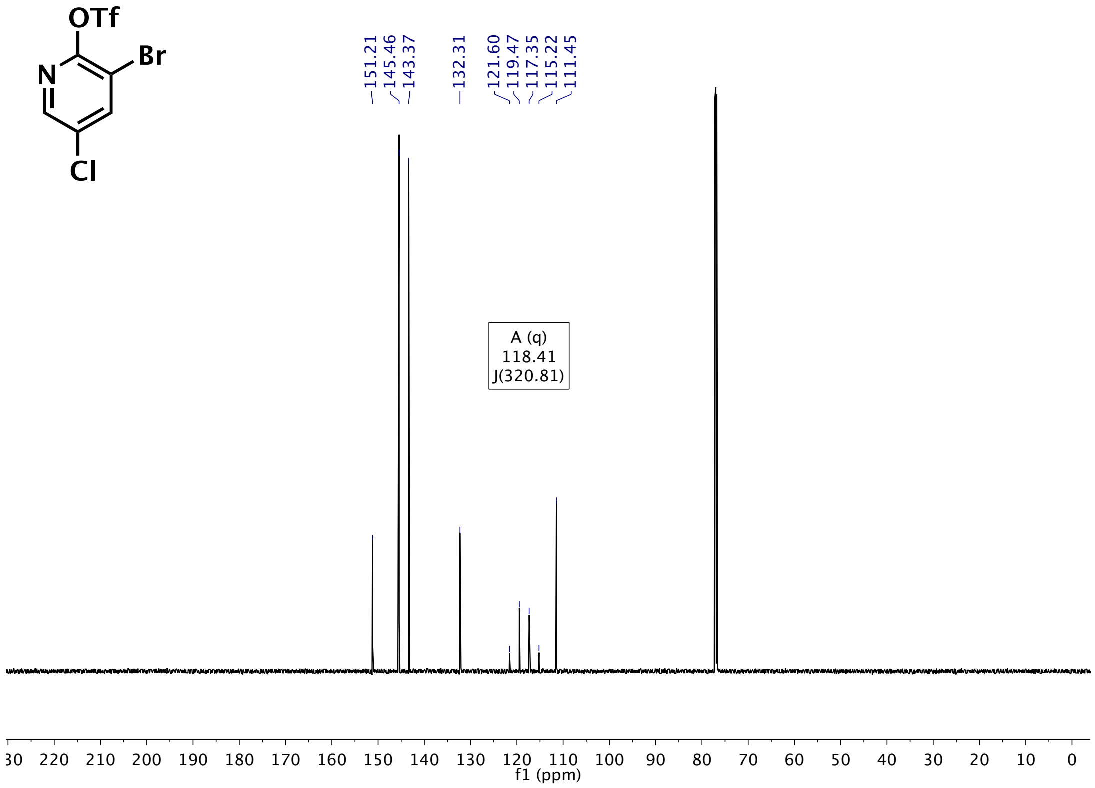
^{19}F{^{1}H} (564 MHz, CDCl$_3$)



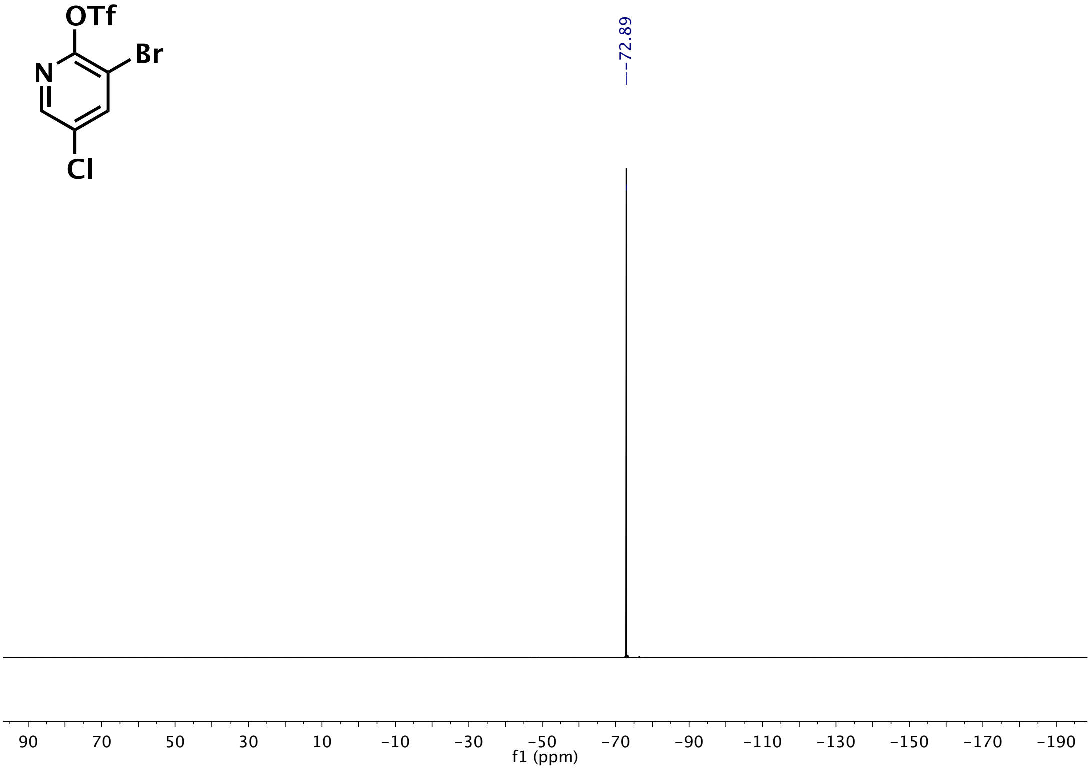
^{1}H (600 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ (151 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ (564 MHz, $CDCl_3$)



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