Iron-Catalyzed Cross-Coupling Reactions of Arylmagnesium Reagents with Aryl Chlorides and Tosylates: Influence of Ligand Structural Parameters and Identification of a General N-Heterocyclic Carbene Ligand

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Supporting Information

General information. All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. THF was dried over alumina under N_2 using a Grubbs-type solvent purification system. All arylmagnesium bromides were prepared from the corresponding aryl bromides and magnesium (turnings) using diisobutylaluminum hydride for activation.[1] All aryl tosylates[2] and aryl chlorides[3] were prepared according to the literature procedures. **L1**, **L2**, **L8**, **L15**, **L16**, **L17** and **L18** were purchased from Sigma Aldrich and used as received. **L9** and **L10** were purchased from Alfa Aesar and used as received. **L3**, **L4**, **L11** and **L12** were purchased from Strem Chemicals and used as received. **L5**,[4] **L6**,[5] **L7**,[6] **L13**,[7] **L14**[6], **L19**,[8] **L20**,[9] **L21**,[10] **L22-24**[11] were prepared according to literature procedures.

Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by Agilent GC Series 6890N and GCMS 7890A. Merck silica gel plates (60F-254) using UV light as visualizing agent. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. NMR spectra were recorded on Bruker DRX-400, ACF 300 and AMX 500 or Jeol JNM-ECZ500R/S1 spectrometer calibrated using residual deuterated solvent as an internal reference. The following

abbreviations were used to designate the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad.

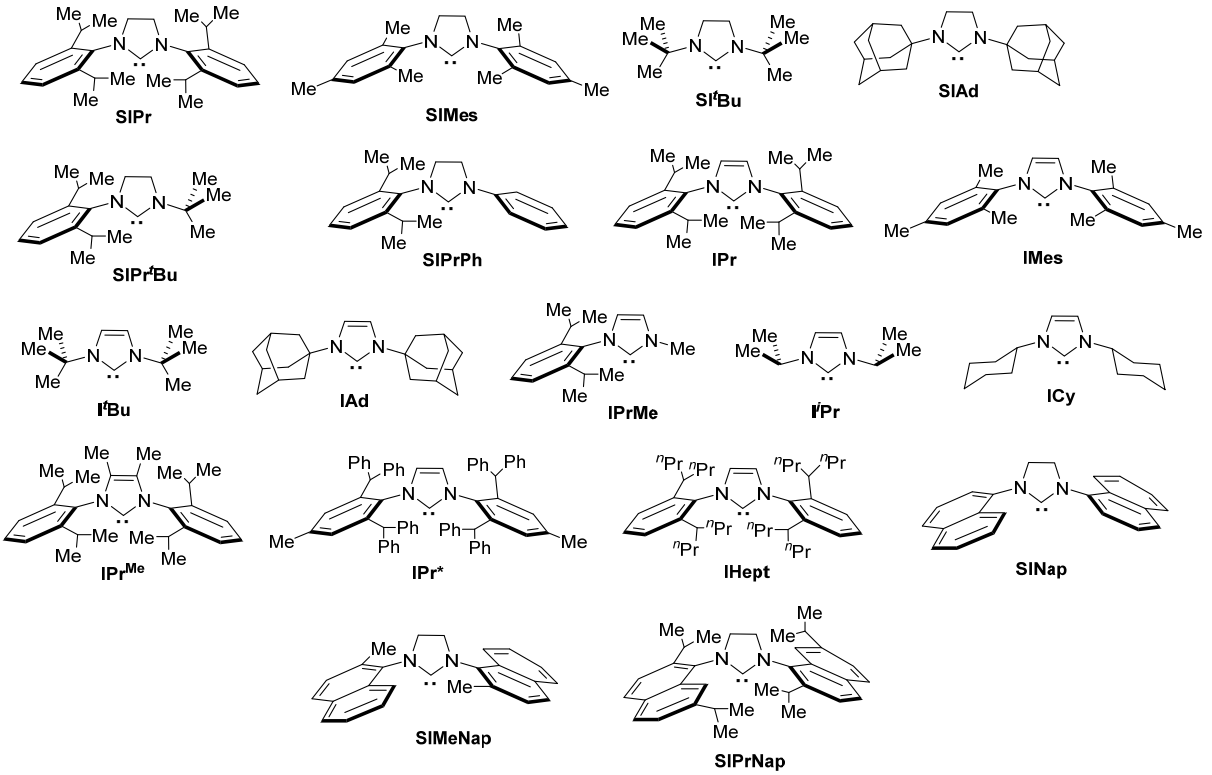


Figure S1. NHCs used in this study.

General procedure for the synthesis of *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(NHC)] complexes.

All azolium chloride salts NHC·HCl were converted into NHC·HBr salts by stirring with 3 equiv. LiBr in CH_3CN to prevent halide scrambling. The respective *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(NHC)] complexes were then prepared according to **Method A**. All azolium iodides NHC·HI were reacted with equimolar $AgBF_4$ in CH_3CN to afford the NHC·HBF$_4$ salts and the *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(NHC)] complexes were prepared following **Method B**. Notably, salts with saturated backbone are more prone to undergo base-promoted hydrolytic ring opening reaction. These side reactions could be suppressed by using dry solvents and inert atmosphere with the addition of molecular sieves.

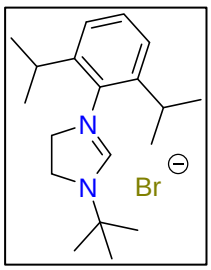
Method A. The $[PdBr_2(^iPr_2\text{-bimy})]_2$ dimer (94 mg, 0.10 mmol), NHC·HBr salt (0.20 mmol) and Ag_2O (28 mg, 0.12 mmol) were suspended in CH_2Cl_2 (30 mL, dry solvent for saturated azolium salts) and stirred overnight shielded from light. In the case of SIAd, the mixture was heated under reflux in order to get satisfactory yields. The resulting suspension was filtered through Celite. The filtrate was dried or subjected to column chromatography to afford the products as pale yellow solids.

Method B. A mixture of the $[PdBr_2(^iPr_2\text{-bimy})]_2$ dimer (94 mg, 0.10 mmol) and tetrabutylammonium bromide (64 mg, 0.20 mmol) was heated in $CHCl_3$ (10 mL) under reflux for 3 h. All the volatiles were removed in vacuo to give an orange solid of $(N^nBu_4)[PdBr_3(^iPr_2\text{-bimy})]$ which was then re-dissolved in CH_2Cl_2 (15 mL, dry solvent for saturated azolium salts). The NHC·HBF_4 salt (0.20 mmol) and Ag_2O (28 mg, 0.12 mmol) were added to the solution, and the resulting suspension was stirred overnight shielded from light. In the case of SI^{t}Bu and IAd, the mixture was heated under reflux in order to get satisfactory yields. The suspension was filtered through Celite and the filtrate was dried or subjected to column chromatography to afford the products as pale yellow solids.

X-ray Diffraction Studies.

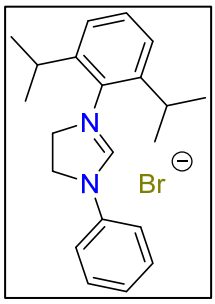
X-ray data were collected with a Bruker AXS SMART APEX diffractometer, using Mo- or Cu-K_α radiation with the SMART suite of Programs.[12] Data were processed and corrected for Lorentz and polarization effects with SAINT,[13] and for absorption effect with SADABS.[14] Structural solution and refinement were carried out with the SHELXTL suite of programs.[15] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. All H-atoms were put at calculated positions. A summary of the most important crystallographic data is given in Table S1.

SIPr^{t}Bu·HBr



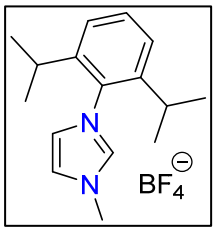
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.69 (s, 1 H, NCHN), 7.31 (t, ^3J(H,H) = 8 Hz, 1 H, Ar–H), 7.12 (d, ^3J(H,H) = 8 Hz, 2 H, Ar–H), 4.38 (t, ^3J(H,H) = 8 Hz, 2 H, NCH_2), 4.25 (t, ^3J(H,H) = 8 Hz, 2 H, NCH_2), 2.83–2.79 (m, 2 H, C*H*$(CH_3)_2$), 1.49 (s, 9 H, $C(CH_3)_3$), 1.19 (d, ^3J(H,H) = 7 Hz, 6 H, $CH(CH_3)_2$), 1.17 (d, ^3J(H,H) = 7 Hz, 6 H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 157.0 (NCHN), 146.9, 131.4, 130.9, 125.2 (Ar–C), 58.2, 54.4 (NCH_2), 47.5 ($NC(CH_3)_3$), 29.2 ($CH(CH_3)_2$), 29.1 ($C(CH_3)_3$), 25.5, 24.6 ($CH(CH_3)_2$). Anal. Calcd. for $C_{19}H_{31}BrN_2$: C, 62.12; H, 8.51; N, 7.63. Found: C, 62.02; H, 8.08; N, 8.02.[16] MS (ESI) *m/z* calcd. for $C_{19}H_{31}N_2$ $[M - Br]^+$ 287; found, 287.

SIPrPh·HBr



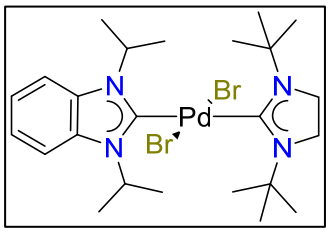
^{1}H NMR (300 MHz, $CDCl_3$): δ 10.46 (s, 1 H, NCHN), 7.65 (d, ^3J(H,H) = 8 Hz, 2 H, Ar–H), 7.35–7.28 (m, 3 H, Ar–H), 7.20 (d, ^3J(H,H) = 8 Hz, 1 H, Ar–H), 7.13 (d, ^3J(H,H) = 8 Hz, 2 H, Ar–H), 4.79 (t, ^3J(H,H) = 8 Hz, 2 H, NCH_2), 4.37 (t, ^3J(H,H) = 8 Hz, 2 H, NCH_2), 2.83 (m, ^3J(H,H) = 7 Hz, 2 H, C*H*$(CH_3)_2$), 1.19 (d, ^3J(H,H) = 7 Hz, 12 H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 156.1 (NCHN), 146.4, 135.8, 131.6, 130.4, 127.9, 125.2, 119.2 (Ar–C, 2 are coincident), 54.7, 50.1 (NCH_2), 29.3 ($CH(CH_3)_2$), 25.5, 24.6 ($CH(CH_3)_2$). Anal. Calcd. for $C_{21}H_{27}BrN_2$: C, 65.11; H, 7.03; N, 7.23. Found: C, 65.32; H, 7.09; N, 7.34. MS (ESI) *m/z* calcd. for $C_{21}H_{27}N_2$ $[M - Br]^+$ 307; found, 307.

IPrMe·HBF_4



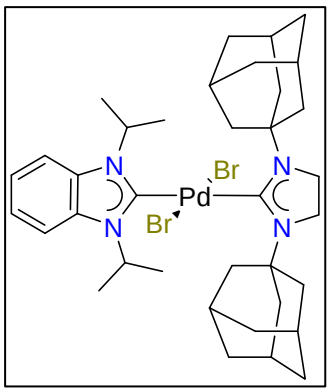
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.85 (s, 1 H, NCHN), 7.80 (t, ^{3}J(H,H) = 2 Hz, 1 H, Imi–H), 7.55 (t, ^{3}J(H,H) = 8 Hz, 1 H, Ar–H), 7.31 (d, ^{3}J(H,H) = 8 Hz, 2 H, Ar–H), 7.24 (t, ^{3}J(H,H) = 2 Hz, 1 H, Imi–H), 4.14 (s, 3 H, NCH_3), 2.29 (m, ^{3}J(H,H) = 7 Hz, 2 H, C*H*(CH_3)$_2$), 1.18–1.14 (m, 12 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 146.1 (Ar–C), 138.0 (NCHN), 132.5, 130.6, 125.4, 125.2 (Ar–C, 2 are coincident), 37.4 (NCH_3), 29.1 (*C*H(CH_3)$_2$), 24.8, 24.6 (CH(*C*H$_3$)$_2$). ^{19}F NMR (282 MHz, $CDCl_3$): δ -75.0, -75.1 (BF_4). Anal. Calcd. for $C_{16}H_{23}BF_4N_2$: C, 58.20; H, 7.02; N, 8.48. Found: C, 58.32; H, 7.14; N, 8.49. MS (ESI) *m/z* calcd. for $C_{16}H_{23}N_2$ [M – BF_4]$^+$ 243; found, 243.

trans-[$PdBr_2$(^{i}Pr$_2$-bimy)(**SI^{t}Bu**)] (**L3/8**)



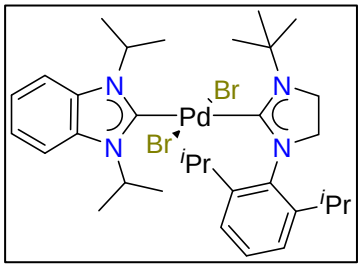
Method **B**. Column chromatography (SiO_2, hexane/CH_2Cl_2, 5:1). Yield: 60 mg, 0.09 mmol, 46%. Crystals were obtained by slow evaporation of a saturated solution in CH_2Cl_2/ether. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59–7.56 (dd, 2 H, Ar–H), 7.18–7.15 (dd, 2 H, Ar–H), 6.29 (m, ^{3}J(H,H) = 7 Hz, 2 H, NCH), 3.61 (s, 4 H, NCH_2), 1.99 (s, 18 H, C(CH_3)$_3$), 1.71 (d, ^{3}J(H,H) = 7 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 196.6 ($C_{SItBu\text{-}carbene}$), 178.6 ($C_{probe\text{-}carbene}$), 134.2, 122.4, 113.5 (Ar–C), 57.7, 54.0 (NCH and NCH_2), 46.5 (*C*(CH_3)$_3$), 32.2 (C(*C*H$_3$)$_3$), 21.5 (CH_3). Anal. Calcd. for $C_{24}H_{40}Br_2N_4Pd$: C, 44.29; H, 6.20; N, 8.61. Found: C, 44.38; H, 6.28; N, 8.38. MS (ESI) *m/z* calcd. for $C_{24}H_{40}BrN_4Pd$ [M – Br]$^+$ 571; found, 571.

trans-[$PdBr_2$(^{i}Pr_2-bimy)(**SIAd**)] (**L4**)



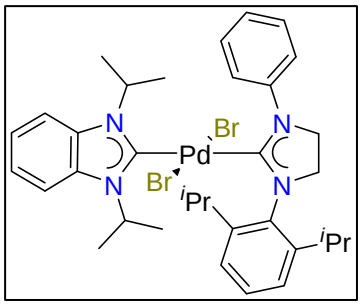
Method **A**. Column chromatography (SiO_2, hexane/ethyl acetate, 10:1). Yield: 90 mg, 0.11 mmol, 56%. Crystals were obtained by slow evaporation of a saturated solution in CH_2Cl_2/CH_3CN. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.59 (dd, 2 H, Ar–H), 7.18–7.16 (dd, 2 H, Ar–H), 6.29 (m, ^3J(H,H) = 7 Hz, 2 H, NCH), 3.59 (s, 4 H, NCH_2), 2.81 (d, ^3J(H,H) = 3 Hz, 12 H, CH_2), 2.27 (br-s, 6 H, CH), 1.79–1.76 (m, 12 H, CH_2), 1.73 (d, ^3J(H,H) = 7 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 194.7 ($C_{SIAd\text{-}carbene}$), 177.8 ($C_{probe\text{-}carbene}$), 134.1, 122.4, 113.7 (Ar–C), 58.7 ($C(CH_2)_3$), 53.9 (NCH), 44.6 (NCH_2), 43.9, 36.8, 30.7 (CH_2 and CH), 21.5 (CH_3). Anal. Calcd. for $C_{36}H_{52}Br_2N_4Pd$: C, 53.58; H, 6.49; N, 6.94. Found: C, 53.68; H, 6.86; N, 6.92. MS (ESI) *m/z* calcd. for $C_{36}H_{53}Br_2N_4Pd$ $[M + H]^+$ 807; found, 807.

trans-[$PdBr_2$(^{i}Pr_2-bimy)(**SIPr^{t}Bu**)] (**L5**)



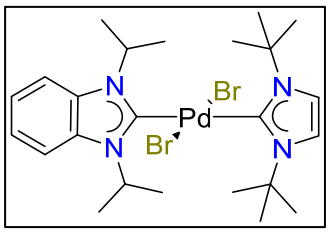
Method **A**. Column chromatography (SiO_2, hexane/CH_2Cl_2, 3:1). Yield: 36 mg, 0.05 mmol, 24%. Crystals were obtained by slow evaporation of a saturated solution in $CHCl_3$/hexane. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48–7.42 (m, 2 H, Ar–H), 7.36–7.32 (m, 3 H, Ar–H), 7.08–7.04 (m, 2 H, Ar–H), 5.98 (m, ^3J(H,H) = 7 Hz, 1 H, NCH), 4.84 (m, ^3J(H,H) = 7 Hz, 1 H, NCH), 3.88–3.83 (m, 4 H, NCH_2), 3.53 (m, ^3J(H,H) = 7 Hz, 2 H, CH(CH_3)$_2$), 1.99 (s, 9 H, C(CH_3)$_3$), 1.67 (d, ^3J(H,H) = 7 Hz, 6 H, NCH(CH_3)$_2$), 1.42 (d, ^3J(H,H) = 7 Hz, 6 H, NCH(CH_3)$_2$), 1.23 (d, ^3J(H,H) = 7 Hz, 6 H, CH(CH_3)$_2$), 1.13 (d, ^3J(H,H) = 7 Hz, 6 H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 200.3 ($C_{SIPrtBu\text{-}carbene}$), 178.2 ($C_{probe\text{-}carbene}$), 149.7, 137.6, 134.2, 134.0, 129.6, 124.8, 122.11, 122.08, 113.19, 113.18 (Ar–C), 57.7, 54.1, 53.7, 53.4 (NCH and NCH_2), 47.0 ($C(CH_3)_3$), 31.5 (C(CH_3)$_3$), 29.5 ($CH(CH_3)_2$), 27.9, 24.5 (CH(CH_3)$_2$), 21.4, 21.3 (NCH(CH_3)$_2$). Anal. Calcd. for $C_{32}H_{48}Br_2N_4Pd$: C, 50.91; H, 6.41; N, 7.42. Found: C, 51.30; H, 6.28; N, 7.25.[16] MS (ESI) *m/z* calcd. for $C_{32}H_{48}Br_2N_4NaPd$ $[M + Na]^+$ 777; found, 777.

trans-[$PdBr_2$(^{i}Pr_2-bimy)(**SIPrPh**)] (**L6**)



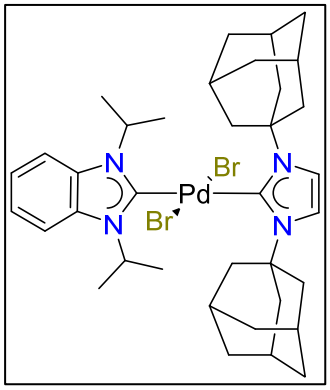
Method **A**. Column chromatography (SiO_2, hexane/CH_2Cl_2/ethyl acetate, 16:1:1). Yield: 31 mg, 0.04 mmol, 20%. Crystals were obtained by slow evaporation of a saturated solution in CH_3CN. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25–8.22 (m, 2 H, Ar–H), 7.51–7.41 (m, 4 H, Ar–H), 7.36–7.32 (m, 4 H, Ar–H), 7.08–7.04 (m, 2 H, Ar–H), 5.67 (m, ^3J(H,H) = 7 Hz, 1 H, NCH), 5.05 (m, ^3J(H,H) = 7 Hz, 1 H, NCH), 4.33–4.27 (m, 2 H, NCH_2), 4.18–4.11 (m, 2 H, NCH_2), 3.59 (m, ^3J(H,H) = 7 Hz, 2 H, C*H*(CH_3)$_2$), 1.54 (d, ^3J(H,H) = 7 Hz, 6 H, NCH(C*H*$_3$)$_2$), 1.46 (d, ^3J(H,H) = 7 Hz, 6 H, NCH(C*H*$_3$)$_2$), 1.29 (d, ^3J(H,H) = 7 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.20 (d, ^3J(H,H) = 7 Hz, 6 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 203.1 ($C_{SIPrtPh\text{-}carbene}$), 178.7 ($C_{probe\text{-}carbene}$), 149.3, 142.8, 136.2, 134.3, 134.0, 129.8, 129.0, 126.7, 125.3, 124.6, 122.2, 113.1, 112.9 (Ar–C, 2 are coincident), 54.3, 54.2, 53.6, 51.8 (NCH and NCH_2), 29.4 (*C*H(CH_3)$_2$), 28.2, 24.3 (CH(*C*H_3)$_2$), 21.4, 21.3 (NCH(*C*H_3)$_2$). Anal. Calcd. for $C_{34}H_{44}Br_2N_4Pd$: C, 52.69; H, 5.72; N, 7.23. Found: C, 52.95; H, 5.82; N, 6.67.[16] MS (ESI) *m/z* calcd. for $C_{34}H_{44}Br_2N_4NaPd$ $[M + Na]^+$ 797; found, 797.

trans-[$PdBr_2$(^{i}Pr_2-bimy)(**I^{t}Bu**)] (**L11/15**)



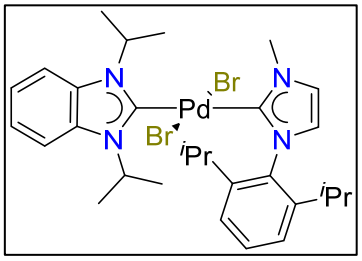
Method **A**. Recrystallization from CH_2Cl_2/$CHCl_3$. Yield: 86 mg, 0.13 mmol, 66%. Crystals were grown via slow evaporation of a saturated solution in THF. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59–7.57 (dd, 2 H, Ar–H), 7.19–7.17 (dd, 2 H, Ar–H), 7.16 (s, 2 H, Imi–H), 6.42 (m, ^3J(H,H) = 7 Hz, 2 H, NCH), 2.17 (s, 18 H, C(CH_3)$_3$), 1.76 (d, ^3J(H,H) = 7 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 177.6 ($C_{probe\text{-}carbene}$), 166.9 ($C_{ItBu\text{-}carbene}$), 134.2, 122.4, 119.6, 113.4 (Ar–C), 59.9 (*C*(CH_3)$_3$), 54.2 (NCH), 33.5 (C(*C*H_3)$_3$), 21.4 (CH_3). Anal. Calcd. for $C_{24}H_{38}Br_2N_4Pd$: C, 44.43; H, 5.90; N, 8.64. Found: C, 44.17; H, 5.86; N, 8.41. MS (ESI) *m/z* calcd. for $C_{24}H_{38}Br_2N_4NaPd$ $[M + Na]^+$ 671; found, 671.

trans-[$PdBr_2$(^{i}Pr_2-bimy)(**IAd**)] (**L12/16**)



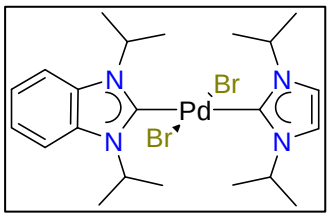
Method **B**. Yield: 66 mg, 0.08 mmol, 41%. Crystals were obtained by slow evaporation of a saturated solution in $CHCl_3$/hexane. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52–7.49 (dd, 2 H, Ar–H), 7.16 (s, 2 H, Imi–H), 7.09–7.07 (dd, 2 H, Ar–H), 6.32 (m, ^3J(H,H) = 7 Hz, 2 H, NCH), 2.85 (d, ^3J(H,H) = 3 Hz, 12 H, CH_2), 2.54 (br-s, 6 H, CH), 1.79–1.71 (m, 12 H, CH_2), 1.67 (d, ^3J(H,H) = 7 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 177.1 ($C_{probe\text{-}carbene}$), 164.8 ($C_{IAd\text{-}carbene}$), 134.2, 122.4, 118.7, 113.6 (Ar–C), 60.7 ($C(CH_2)_3$), 54.1 (NCH), 45.6, 36.6, 30.8 (CH_2 and CH), 21.4 (CH_3). Anal. Calcd. for $C_{36}H_{50}Br_2N_4Pd$: C, 53.71; H, 6.26; N, 6.96. Found: C, 54.00; H, 6.43; N, 7.10. MS (ESI) *m/z* calcd. for $C_{36}H_{50}BrN_4Pd$ $[M - Br]^+$ 723; found, 723.

trans-[$PdBr_2$(^{i}Pr_2-bimy)(**IPrMe**)] (**L13**)



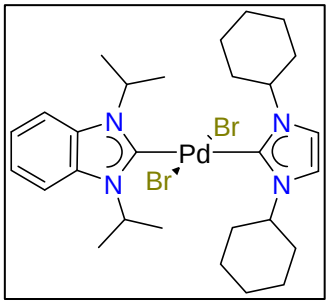
Method **B**. Colum chromatography (SiO_2, hexane/CH_2Cl_2/ethyl acetate, 16:1:1). Yield: 127 mg, 0.18 mmol, 89%. Crystals were obtained by slow evaporation of a saturated solution in $CHCl_3$/hexane. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52–7.48 (m, 2 H, Ar–H), 7.39–7.34 (m, 3 H, Ar–H), 7.12–7.10 (m, 2 H, Ar–H), 7.05 (br–s, 1 H, Imi–H), 6.96 (br–s, 1 H, Imi–H), 6.03 (m, ^3J(H,H) = 7 Hz, 1 H, NCH), 5.35 (m, ^3J(H,H) = 7 Hz, 1 H, NCH), 4.25 (s, 3 H, NCH_3), 3.00 (m, ^3J(H,H) = 7 Hz, 2 H, $CH(CH_3)_2$), 1.76 (d, ^3J(H,H) = 7 Hz, 6 H, $NCH(CH_3)_2$), 1.36–1.34 (m, 12 H, $NCH(CH_3)_2$ and $CH(CH_3)_2$), 1.02 (d, ^3J(H,H) = 7 Hz, 6 H, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 178.9 ($C_{probe\text{-}carbene}$), 173.6 ($C_{IPrMe\text{-}carbene}$), 148.2, 136.1, 134.4, 134.0, 130.4, 125.4, 124.1, 122.3, 122.0, 113.1, 112.9 (Ar–C, 2 are coincident), 54.4, 53.6 (NCH), 39.2 (NCH_3), 29.2 ($CH(CH_3)_2$), 27.5, 23.3 ($CH(CH_3)_2$), 21.7, 21.5 ($NCH(CH_3)_2$). Anal. Calcd. for $C_{29}H_{40}Br_2N_4Pd$: C, 49.00; H, 5.67; N, 7.88. Found: C, 49.08; H, 5.63; N, 7.70. MS (ESI) *m/z* calcd. for $C_{29}H_{40}BrN_4Pd$ $[M - Br]^+$ 629; found, 629.

trans-[$PdBr_2$(^{i}Pr_2-bimy)(**I^{i}Pr**)] (**L17**)



Method **A**. Yield: 87 mg, 0.14 mmol, 70%. Single crystals of the complex for $\%V_{bur}$ determination could not be obtained. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55–7.54 (dd, 2 H, Ar–H), 7.18–7.17 (dd, 2 H, Ar–H), 6.94 (s, 2 H, Imi–H), 6.22 (m, ^3J(H,H) = 7 Hz, 2 H, NCH), 5.63 (m, ^3J(H,H) = 7 Hz, 2 H, NCH), 1.82 (d, ^3J(H,H) = 7 Hz, 12 H, CH_3), 1.59 (d, ^3J(H,H) = 7 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 180.6 ($C_{carbene\text{-}probe}$), 168.1 ($C_{carbene\text{-}imi}$), 134.2, 122.5, 117.3, 113.1 (Ar–C), 54.3, 53.0 (NCH), 23.8, 21.7 (CH_3). Anal. Calcd. for $C_{22}H_{34}Br_2N_4Pd$: C, 42.57; H, 5.52; N, 9.03. Found: C, 42.56; H, 5.08; N, 9.26. MS (ESI) *m/z* calcd. for $C_{24}H_{37}BrN_5Pd$ [M – Br + CH_3CN]$^+$ 580; found, 580.

trans-[$PdBr_2$(^{i}Pr_2-bimy)(**ICy**)] (**L18**)



Method **B**. Yield: 84 mg, 0.12 mmol, 60%. Crystals were obtained by slow evaporation of a saturated solution in CH_3CN. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57–7.54 (dd, 2 H, Ar–H), 7.21–7.18 (dd, 2 H, Ar–H), 6.91 (s, 2 H, Imi–H), 6.26 (m, ^3J(H,H) = 7 Hz, 2 H, NCH), 5.25 (m, 2 H, NCH), 2.48–2.46 (m, 4 H, Cy–H), 2.01–1.97 (m, 4 H, Cy–H), 1.88–1.79 (m, 14 H, CH_3 and Cy–H), 1.60–1.44 (m, 8 H, Cy–H), 1.29–1.26 (m, 2 H, Cy–H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 181.2 ($C_{probe\text{-}carbene}$), 168.3 ($C_{ICy\text{-}carbene}$), 134.3, 122.6, 117.8, 113.0 (Ar–C), 60.9, 54.4 (NCH), 34.3, 26.7, 26.2 (Cy–C), 21.9 (CH_3). Anal. Calcd. for $C_{28}H_{42}Br_2N_4Pd$: C, 47.98; H, 6.04; N, 7.99. Found: C, 47.90; H, 6.06; N, 7.83. MS (ESI) *m/z* calcd. for $C_{28}H_{42}BrN_4Pd$ [M – Br]$^+$ 619; found, 619.

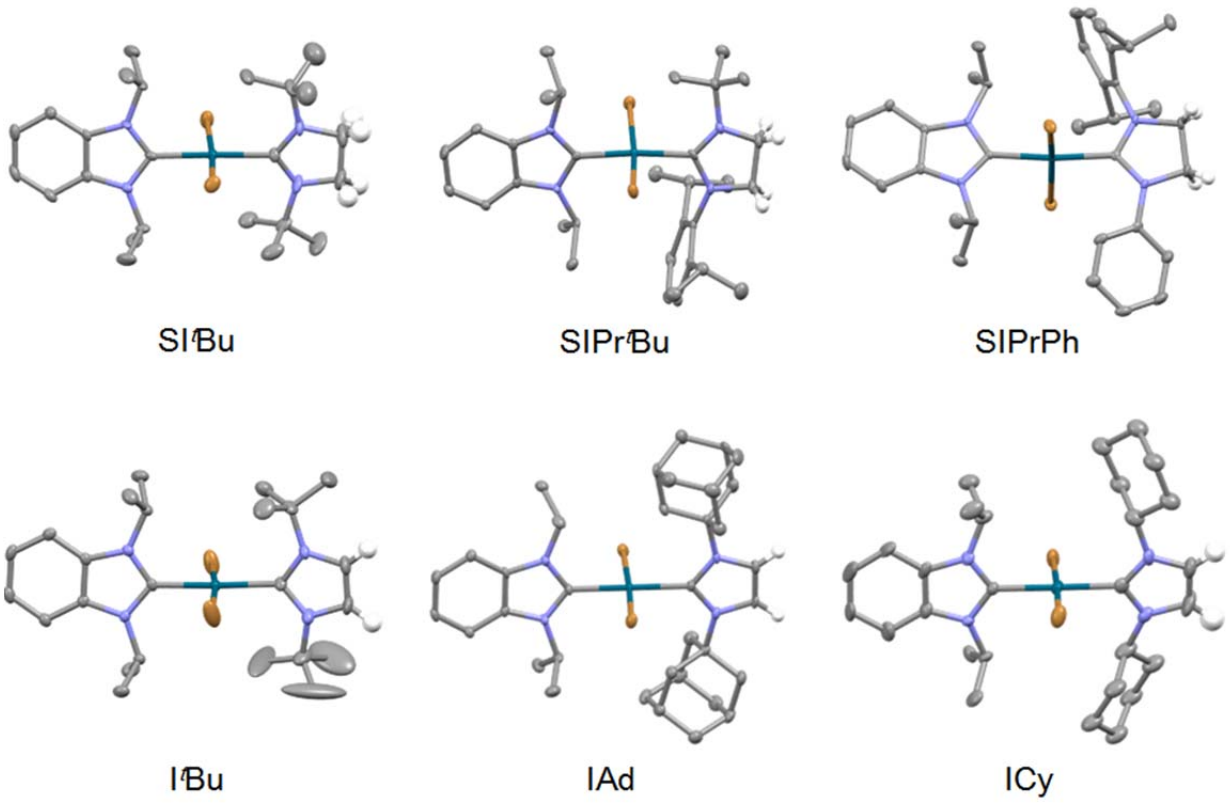


Figure S2. Molecular structures of *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(**NHC**)] complexes. Hydrogen atoms and solvent molecules have been omitted for clarity.

Table S1. Selected X-ray crystallographic data for the [$PdBr_2$(^{i}Pr_2-bimy)(NHC)] complexes.[a]

	SI^{t}Bu·0.5CH_2Cl_2	**SIAd**	**SIPr^{t}Bu**·0.5C_6H_{12}·0.5H_2O	**SIPrPh**·2CH_3CN
formula	$C_{24}H_{40}Br_2N_4Pd$·0.5CH_2Cl_2	$C_{36}H_{52}Br_2N_4Pd$	$C_{32}H_{48}Br_2N_4Pd$·0.5C_6H_{12}·0.5H_2O	$C_{34}H_{44}Br_2N_4Pd$·2CH_3CN
fw	693.28	807.03	798.99	857.06
color, habit	orange, block	yellow, plate	colourless, rod	colourless, block
cryst size [mm]	0.18×0.18×0.14	0.32×0.22×0.09	0.28×0.14×0.14	0.19×0.17×0.15
temp [K]	100(2)	100(2)	100(2)	100(2)
crystsyst	monoclinic	monoclinic	tetragonal	orthorhombic
space group	*P*21/c	*P*21/c	*I*-4	*P*bca
a[Å]	17.6275(8)	25.2070(16)	26.7002(16)	18.7633(5)
b [Å]	35.0719(17)	14.5000(9)	26.7002(16)	9.6729(3)
c [Å]	9.5562(4)	19.9484(12)	11.3817(6)	42.3969(11)
α [deg]	90.00	90.00	90.00	90.00
β [deg]	92.772(2)	111.217(2)	90.00	90.00
γ [deg]	90.00	90.00	90.00	90.00
V [Å^3]	5901.0(5)	6796.9(7)	8114.0(11)	7694.8(4)
Z	8	8	8	8
D_c [g cm^{-3}]	1.561	1.577	1.308	1.480
radiation used	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ [mm^{-1}]	3.447	2.929	2.454	2.594
θ range [deg]	2.385–28.282	2.043–25.027	2.412–28.281	2.207–28.281
no. of unique data	54965	11683	34118	90150
max., min. transmn	0.7459, 0.6818	0.7459, 0.6490	0.7457, 0.6178	0.7459, 0.6831
final R indices	R1 = 0.0469,	R1 = 0.0596,	R_1 = 0.0364,	R_1 = 0.0342,
[I> 2σ(I)]	wR2 = 0.0867	wR2 = 0.1066	wR_2 = 0.0893	wR_2 = 0.0690
R indices (all data)	R1 = 0.0771,	R1 = 0.1061,	R_1 = 0.0468,	R_1 = 0.0453,
	wR2 = 0.0948	wR2 = 0.1168	wR_2 = 0.0925	wR_2 = 0.0716
goodness-of-fit	1.078	1.102	1.066	1.188
peak/hole [e Å^{-3}]	2.813/–1.464	1.044/–1.243	1.178/–0.460	0.653/–1.358

[a] The complex was labelled with only the varying NHC ligand for clarity.

Continued…

	I^{t}Bu·0.5C_4H_8O	**IAd**·$CHCl_3$	**IPrMe**	**ICy**
formula	$C_{24}H_{38}Br_2N_4Pd$·0.5C_4H_8O	$C_{36}H_{50}Br_2N_4Pd$·$CHCl_3$	$C_{29}H_{40}Br_2N_4Pd$	$C_{28}H_{42}Br_2N_4Pd$
fw	684.85	924.39	710.87	700.87
color, habit	Yellow, plate	colourless, prism frag	colourless, rod	colourless, block
cryst size [mm]	0.32×0.30×0.12	0.11×0.11×0.14	0.18×0.09×0.09	0.19×0.18×0.15
temp [K]	100(2)	100(2)	100(2)	100(2)
crystsyst	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	*P*bca	*P*12(1)/c1	*P*21/c	*P*212121
a[Å]	9.6081(4)	13.3077(5)	19.111(3)	8.8887(10)
b [Å]	17.6273(7)	13.9107(5)	8.2634(10)	10.0752(9)
c [Å]	34.7082(14)	42.1427(14)	38.653(5)	66.400(7)
α [deg]	90.00	90.00	90.00	90.00
β [deg]	90.00	97.0150(10)	90.896(5)	90.00
γ [deg]	90.00	90.00	90.00	90.00
V [Å^3]	5878.4(4)	7743.0(5)	6103.2(15)	5946.4(11)
Z	8	8	8	8
D_c [g cm^{-3}]	1.548	1.586	1.547	1.566
radiation used	Mo Kα	Cu Kα	Mo Kα	Mo Kα
μ [mm^{-1}]	3.372	8.428	3.250	3.335
θ range [deg]	2.31–27.51	2.11–72.49	2.363–28.282	2.112–28.347
no. of unique data	39770	136770	132642	236734
max., min. transmn	0.6877, 0.4116	0.4058, 0.2407	0.7457, 0.6727	0.7457, 0.6824
final R indices	R_1 = 0.0411,	R_1 = 0.0474,	R1 = 0.0289,	R_1 = 0.0708,
[I> 2σ(I)]	wR_2 = 0.0948	wR_2 = 0.1084	wR2 = 0.0515	wR_2 = 0.1348
R indices (all data)	R_1 = 0.0555,	R_1 = 0.0516,	R1 = 0.0433,	R_1 = 0.0898,
	wR_2 = 0.1015	wR_2 = 0.1102	wR2 = 0.0550	wR_2 = 0.1401
goodness-of-fit	1.051	1.152	1.036	1.214
peak/hole [e Å^{-3}]	1.545/–1.685	1.320/–1.680	0.587/–0.945	3.161/–1.996

Fe-catalyzed Biaryl Cross-coupling Reaction

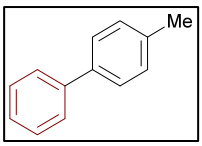
General Procedure for Iron-catalyzed Biaryl Cross-coupling Reaction of Aryl Chlorides:

In a glovebox, $Fe(OTf)_2$ (5.3 mg, 0.015 mmol, 3 mol%), SINap•HCl (7.9 mg, 0.015 mmol, 3 mol%) and NaO*t*Bu (1.4 mg, 0.015 mmol, 3 mol%) in THF (0.5 mL) were charged to a dried reaction tube. The mixture was allowed to stir at rt for 1 h before a solution of aryl chloride (0.5 mmol, 1.0 eq) and Grignard reagent (0.6 mmol, 1.2 eq) was added. The tube was sealed, taken out of the glovebox and stirred at 60 °C for 16h. The reaction progress was monitored by GC using dodecane as the internal standard. Once completed, the reaction mixture was quenched with saturated NH_4Cl and extracted with CH_2Cl_2 several times. The combined organic layers were dried over anhydrous $MgSO_4$, concentrated in vacuo and the resulting crude mixture was purified by silica gel column chromatography.

General Procedure for Iron-catalyzed Biaryl Cross-coupling Reaction of Aryl Tosylates:

In a glovebox, $Fe(OTf)_2$ (5.3 mg, 0.015 mmol, 3 mol%), SINap•HCl (23.7 mg, 0.045 mmol, 9 mol%) and NaO*t*Bu (4.2 mg, 0.045 mmol, 9 mol%) in THF (0.5 mL) were charged to a dried reaction tube. The mixture was allowed to stir at rt for 1 h before it was diluted with THF (6.5 mL). A solution of aryl chloride (0.5 mmol, 1.0 eq) and Grignard reagent (0.6 mmol, 1.2 eq) was added subsequently. The tube was sealed, taken out of the glovebox and stirred at 60 °C for 16h. The reaction progress was monitored by GC using dodecane as the internal standard. Once completed, the reaction mixture was quenched with saturated NH_4Cl and extracted with CH_2Cl_2 several times. The combined organic layers were dried over anhydrous $MgSO_4$, concentrated in vacuo and the resulting crude mixture was purified by silica gel column chromatography.

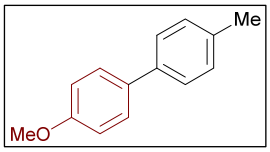
4-Methyl-1,1'-biphenyl (**3a**)[17]



3a was prepared from chlorobenzene (56 mg, 0.5 mmol) and *p*-tolylmagnesium bromide (0.79 mL, 0.6 mmol, 0.76 M in THF). The crude mixture was purified by flash column chromatography (pentane) to afford the desired product as white solid (83 mg, 98%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.58 – 7.51 (m, 2H), 7.47 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 141.3, 138.5, 137.1, 129.6, 128.8, 127.1, 127.1, 127.0, 21.2.

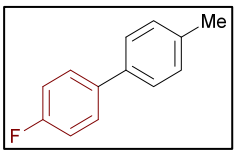
4-Methoxy-4'-methyl-1,1'-biphenyl (**3b**)[17]



3b was prepared from 1-chloro-4-methoxybenzene (71 mg, 0.5 mmol) and *p*-tolylmagnesium (0.79 mL, 0.6 mmol, 0.76 M in THF). The crude mixture was purified by flash column chromatography (5% Et_2O/petroleum ether) to afford the desired product as a white solid (96 mg, 97%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 23.8, 8.5 Hz, 4H), 7.12 (dd, *J* = 7.0, 1.4 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H), 2.28 (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.0, 138.1, 136.4, 133.8, 129.5, 128.0, 126.6, 114.3, 55.4, 21.1.

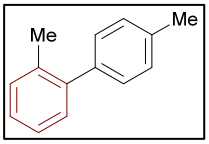
4-Fluoro-4'-methyl-1,1'-biphenyl (**3c**, Table 5) [17]



3c was prepared from 1-chloro-4-fluorobenzene (65 mg, 0.5 mmol) and *p*-tolylmagnesium bromide (0.79 mL, 0.6 mmol, 0.76 M in THF). The crude mixture was purified by flash column chromatography (pentane) to afford the desired product as white solid (85 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.55 (m, 2H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.17 (t, *J* = 8.7 Hz, 2H), 2.46 (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 246.7 Hz), 137.5, 137.4 (d, *J* = 3.0 Hz), 137.1, 129.6, 129.5, 128.5 (d, *J* = 3.0 Hz), 126.9, 115.6 (d, *J* = 21.2 Hz), 21.12.

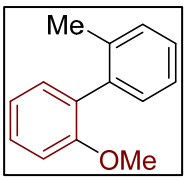
2,4'-Dimethyl-1,1'-biphenyl (**3d**) [17]



3d was prepared from 1-chloro-2-methylbenzene (63 mg, 0.5 mmol) and *p*-tolylmagnesium bromide (0.79 mL, 0.6 mmol, 0.76 M in THF). The crude mixture was purified by flash column chromatography (pentane) to afford the desired product as a colourless oil (80 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 8H), 2.45 (d, *J* = 2.3 Hz, 3H), 2.32 (d, *J* = 2.5 Hz, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.0, 139.2, 136.4, 135.5, 130.4, 129.9, 129.2, 128.9, 127.1, 125.8, 21.2, 20.6.

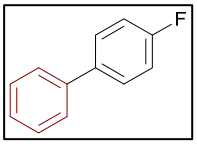
2-Methoxy-2'-methyl-1,1'-biphenyl **(3f)**



3f was prepared from 1-chloro-2-methoxybenzene (71.3 mg, 0.5 mmol) and *o*-tolylmagnesium bromide (0.86 mL, 0.6 mmol, 0.70 M in THF). The crude mixture was purified by flash column chromatography (1% Et2O/ petroleum ether) to afford the desired product as colourless oil (78mg, 79%).

^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.35 (ddd, *J* = 8.2, 7.4, 1.9 Hz, 1H), 7.25 – 7.15 (m, 3H), 7.13 – 7.05 (m, 3H), 7.01 (td, *J* = 7.4, 1.1 Hz, 1H), 3.74 (s, 3H), 2.08 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $(CD_3)_2CO$) δ 157.6, 139.9, 137.4, 131.7, 131.5, 130.7, 130.3, 129.6, 127.9, 126.2, 121.2, 111.8, 55.6, 20.1.

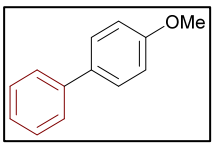
4-Fluoro-1,1'-biphenyl (**3h**) [17]



3h was prepared from chlorobenzene (56 mg, 0.5 mmol) and (4-fluorophenyl)magnesium bromide (0.71 mL, 0.6 mmol, 0.85 M in THF). The crude mixture was purified by flash column chromatography (pentane) to afford the desired product as a white solid (64 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 4H), 7.47 – 7.40 (m, 2H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.18 – 7.07 (m, 2H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 246.4 Hz), 140.4, 137.5, 137.4 (d, *J* = 3.0 Hz), 137.1, 128.9, 128.8 (d, *J* = 3.0 Hz), 127.3, 127.1, 115.7 (d, *J* = 21.2 Hz).

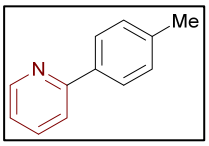
4-Methoxy-1,1'-biphenyl (**3i**, Table 5) [17]



3i prepared from chlorobenzene (56 mg, 0.5 mmol) and (4-methoxyphenyl)magnesium bromide (0.68 mL, 0.6 mmol, 0.88 M in THF). The crude mixture was purified by flash column chromatography (20% CH_2Cl_2/petroleum ether) to afford the desired product as white solid (80 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 4H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 1H), 6.94 – 6.87 (m, 2H), 3.78 (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.3, 140.9, 133.9, 128.8, 128.2, 126.8, 126.7, 114.3, 55.4.

2-(p-Tolyl)pyridine (**3j**) [17]

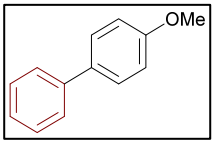


3j was prepared from 2-chloropyridine (57 mg, 0.5 mmol) and *p*-tolylmagnesium bromide (0.79 mL, 0.6 mmol, 0.76 M in THF). The crude mixture was purified by flash column chromatography (20% ether/petroleum ether) to afford the desired product as colourless oil (45mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dt, *J* = 4.9, 1.6 Hz, 1H), 8.00 – 7.85 (m, 2H), 7.80 – 7.64 (m, 2H), 7.38 – 7.24 (m, 2H), 7.19 (ddd, *J* = 6.2, 4.8, 2.3 Hz, 1H), 2.41 (s, 3H). ^{13}C {^{1}H}

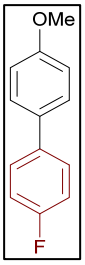
NMR (101 MHz, $CDCl_3$) δ 157.4, 149.4, 139.0, 136.8, 136.4, 129.5, 126.8, 121.8, 120.3, 21.3.

4-Methoxy-1,1'-biphenyl (**3i**, Table 6) [17]



3i was prepared from phenyl 4-methylbenzenesulfonate (124 mg, 0.5 mmol) and (4-methoxyphenyl)magnesium bromide (1.05 mL, 0.75 mmol, 0.72 M in THF). The crude mixture was purified by flash column chromatography (20% CH_2Cl_2/petroleum ether) to afford the desired product as white solid (86 mg, 93%).

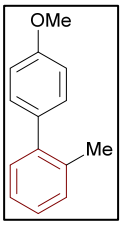
4-Fluoro-4'-methoxy-1,1'-biphenyl (**3k**) [17]



3h was prepared from 4-fluorophenyl 4-methylbenzenesulfonate (133 mg, 0.5 mmol), (4-methoxyphenyl)magnesium bromide (0.68 ml, 0.6 mmol,0.88 M in THF). The crude mixture was purified by flash column chromatography (20% CH_2Cl_2/petroleum ether) to afford the desired product as colourless oil (89 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (tt, J = 9.7, 2.6 Hz, 4H), 7.10 (t, J = 8.8 Hz, 2H), 7.01 – 6.93 (m, 2H), 3.85 (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.2(d, J = 246.4 Hz), 159.3, 137.1(d, J = 3.0 Hz), 133.0, 128.3 (d, J = 7.1 Hz), 128.1, 115.6 (d, J = 21.2 Hz), 114.4, 55.5.

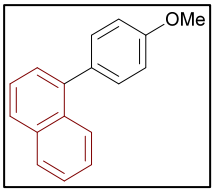
4'-Methoxy-2-methyl-1,1'-biphenyl (**3l**) [17]



3l was prepared from *o*-tolyl 4-methylbenzenesulfonate (131 mg, 0.5 mmol), (4-methoxyphenyl)magnesium bromide (0.68 ml, 0.6 mmol, 0.88 M in THF). The crude mixture was purified by flash column chromatography (20% CH_2Cl_2/petroleum ether) to afford the desired product as colourless oil (88 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.20 (m, 6H), 7.06 – 6.92 (m, 2H), 3.90 (d, J = 0.7 Hz, 3H), 2.33 (d, J = 2.0 Hz, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.6, 141.7, 135.6, 134.5, 130.4, 130.3, 129.9, 127.0, 125.8, 113.6, 55.4, 20.6.

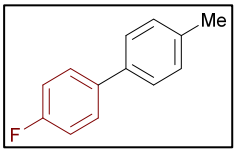
1-(4-Methoxyphenyl)naphthalene (**3m**) [17]



3m was prepared from naphthalen-1-yl 4-methylbenzenesulfonate (149 mg, 0.5 mmol) and (4-methoxyphenyl)magnesium bromide (0.68 ml, 0.6 mmol,0.88 M in THF). The crude mixture was purified by flash column chromatography (20% CH_2Cl_2/petroleum ether) to afford the desired product as off white solid (48 mg, 41%).

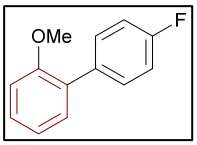
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.67 (m, 3H), 7.47 – 7.26 (m, 6H), 7.01 – 6.84 (m, 2H), 3.77 (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.1, 140.0, 134.0, 133.2, 132.0, 131.2, 128.3, 127.4, 127.0, 126.2, 126.0, 125.8, 125.5, 113.8, 55.4.

4-Fluoro-4'-methyl-1,1'-biphenyl (**3c**, Table 6) [17]



3c was prepared from 4-fluorophenyl 4-methylbenzenesulfonate (133 mg, 0.5 mmol) and *p*-tolylmagnesium bromide (0.45 mL, 0.6 mmol, 1.32 M in THF). The crude mixture was purified by flash column chromatography (pentane) to afford the desired product as white solid (62 mg, 66%).

4'-Fluoro-2-methoxy-1,1'-biphenyl (**3n**) [17]



3n was prepared from 2-methoxyphenyl 4-methylbenzenesulfonate (120 mg, 0.43 mmol) and (4-fluorophenyl)magnesium bromide (0.62 ml, 0.52 mmol,0.84 M in THF). The crude mixture was purified by flash column chromatography (5% ether/petroleum ether) to afford the desired product as brown solid (76 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.44 (m, 2H), 7.39 – 7.28 (m, 2H), 7.18 – 7.07 (m, 2H), 7.07 – 6.97 (m, 2H), 3.83 (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.1 (d, J = 246.4 Hz), 156.5, 134.5 (d, J = 3.0 Hz), 131.2(d, J = 8.1 Hz), 130.8, 129.8, 128.8, 121.0, 114.9(d, J = 21.2 Hz), 111.4, 55.6.

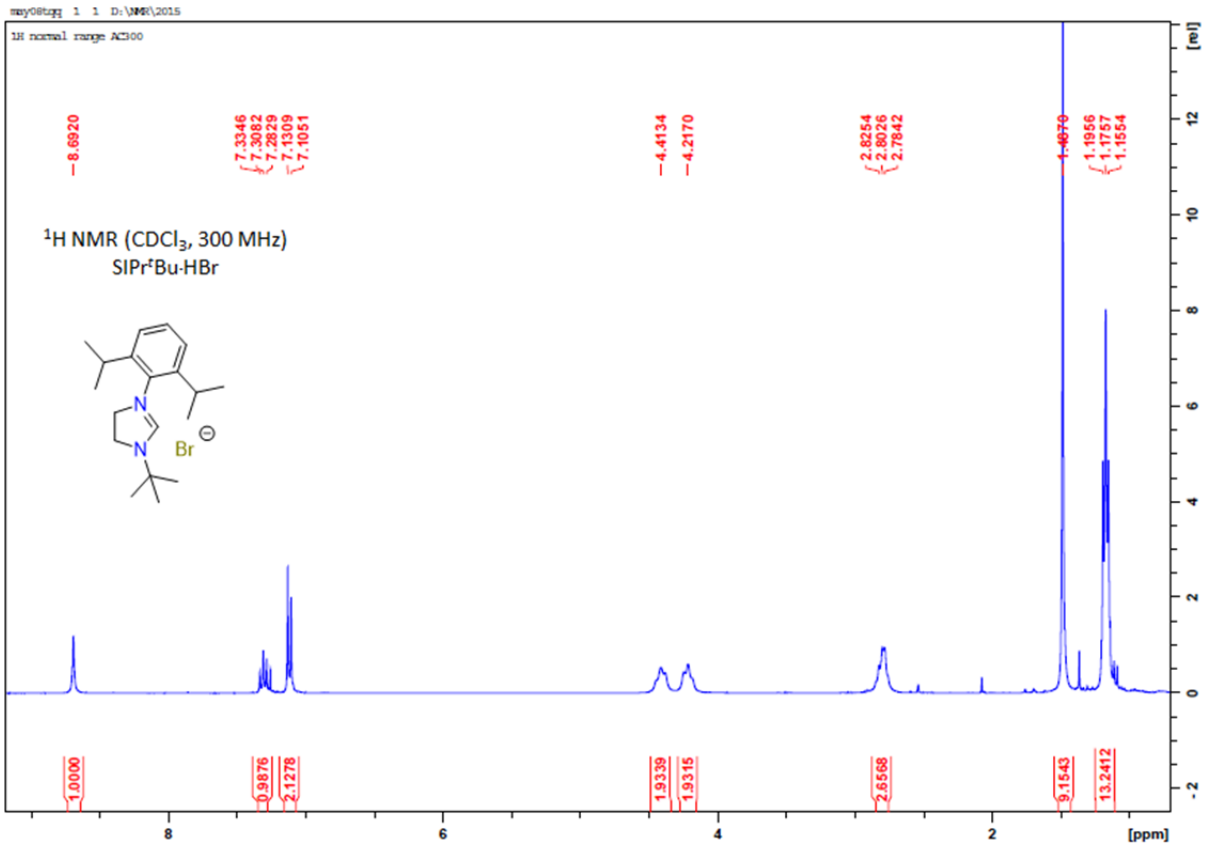


Figure S3. ^{1}H Spectra of SIPr^{t}Bu.HBr.

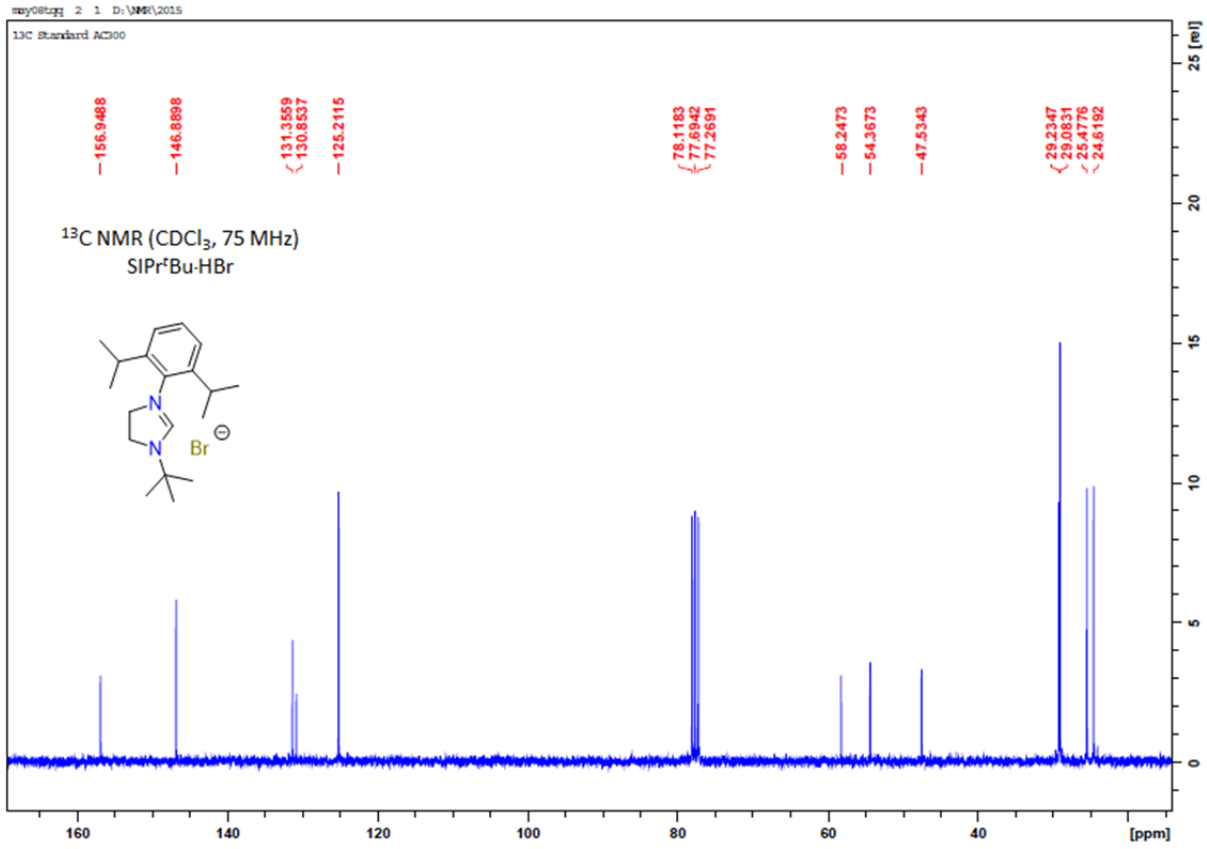


Figure S4. ^{13}C Spectra of SIPr^{t}Bu.HBr.

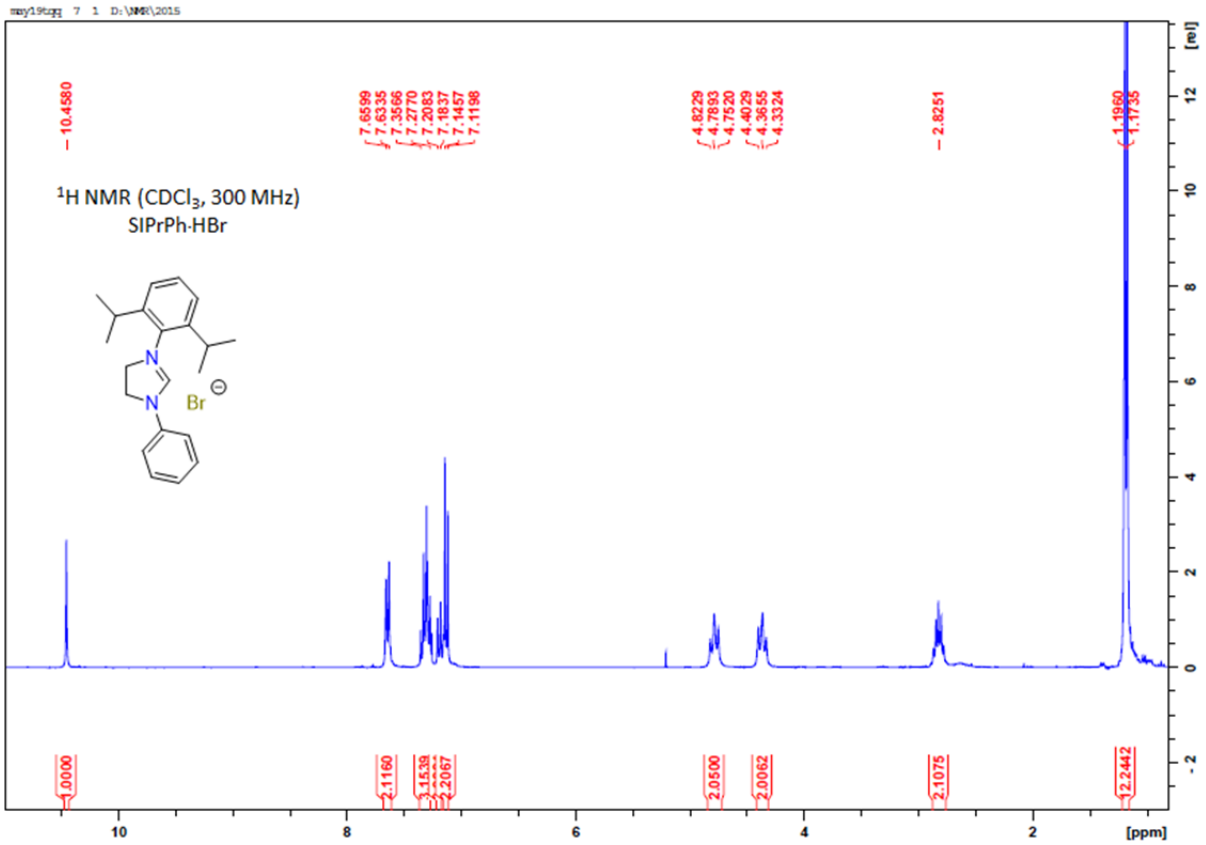


Figure S5. ^{1}H Spectra of SIPrPh.HBr.

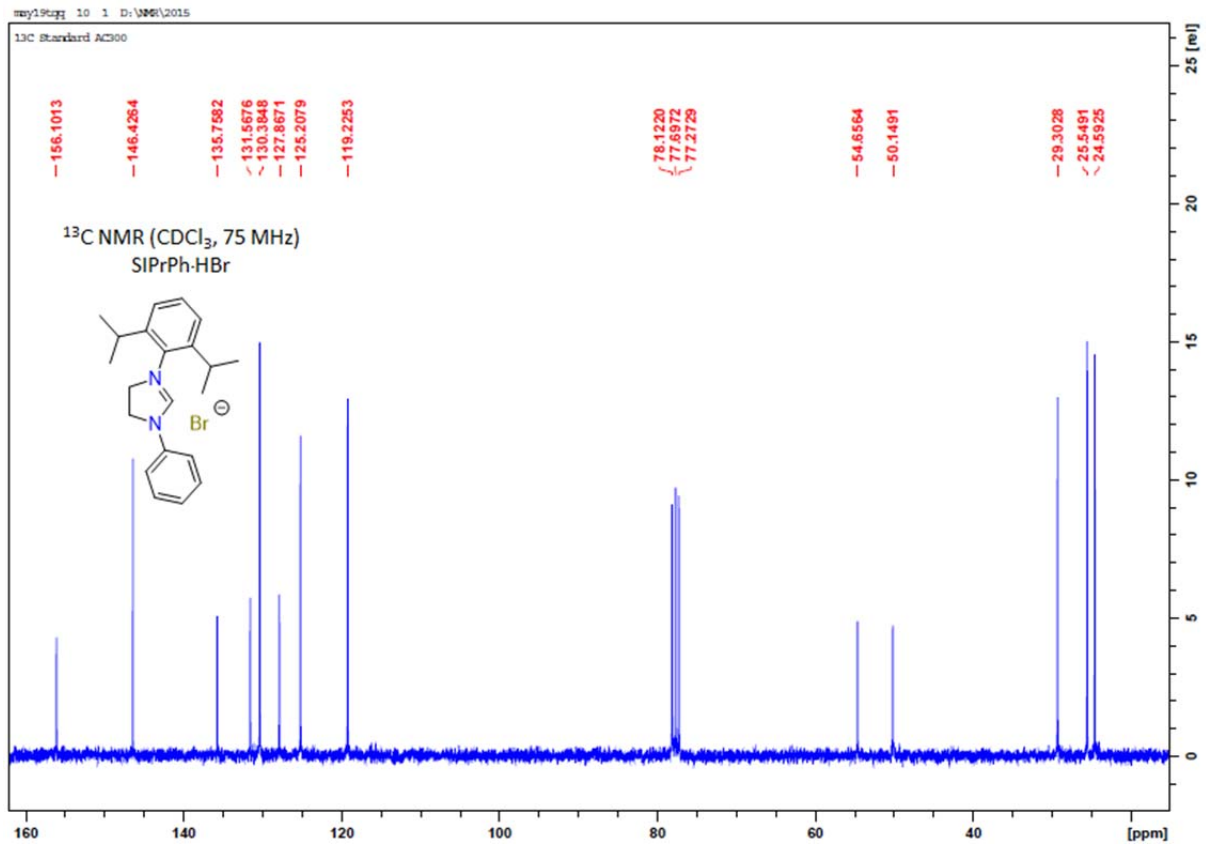


Figure S6. ^{13}C Spectra of SIPrPh.HBr.

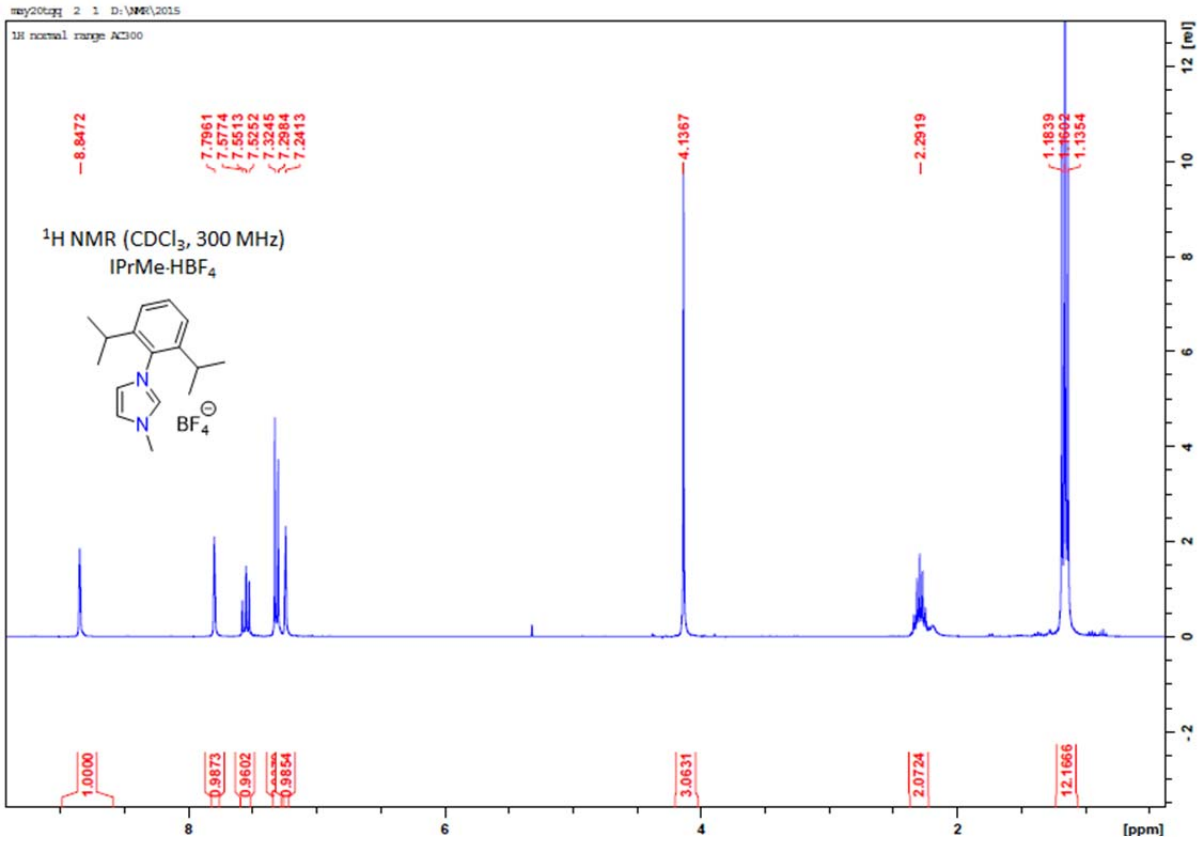


Figure S7. ^{1}H Spectra of IPrMe.HBF$_4$.

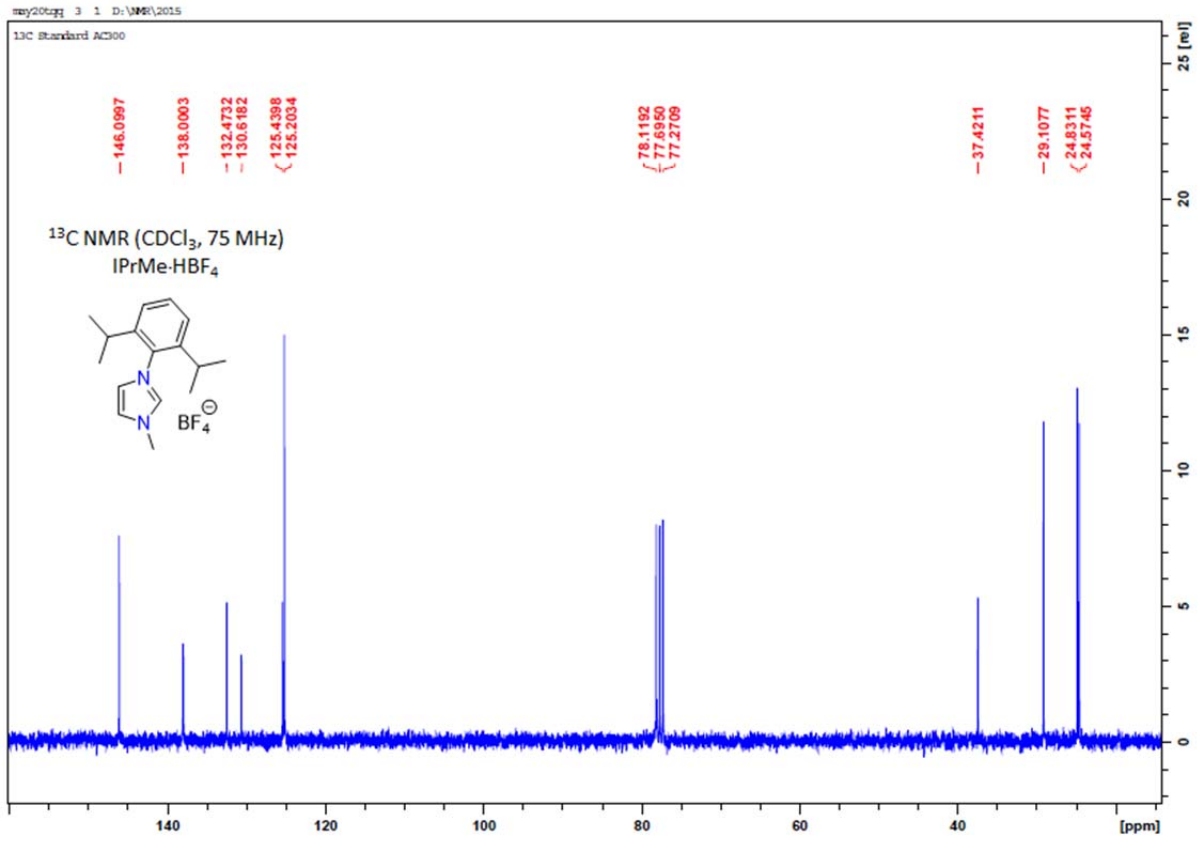


Figure S8. ^{13}C Spectra of IPrMe.HBF$_4$.

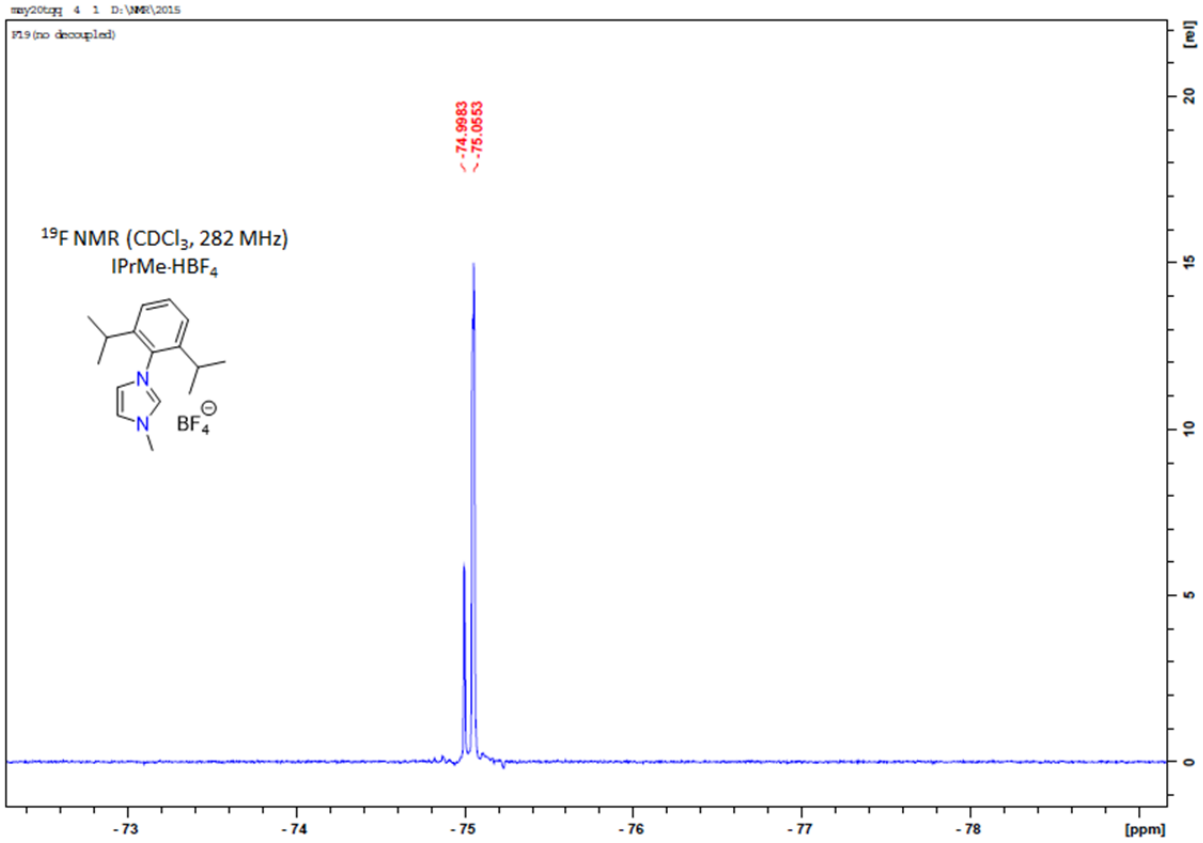


Figure S9. ^{19}F Spectra of IPrMe.HBF_4.

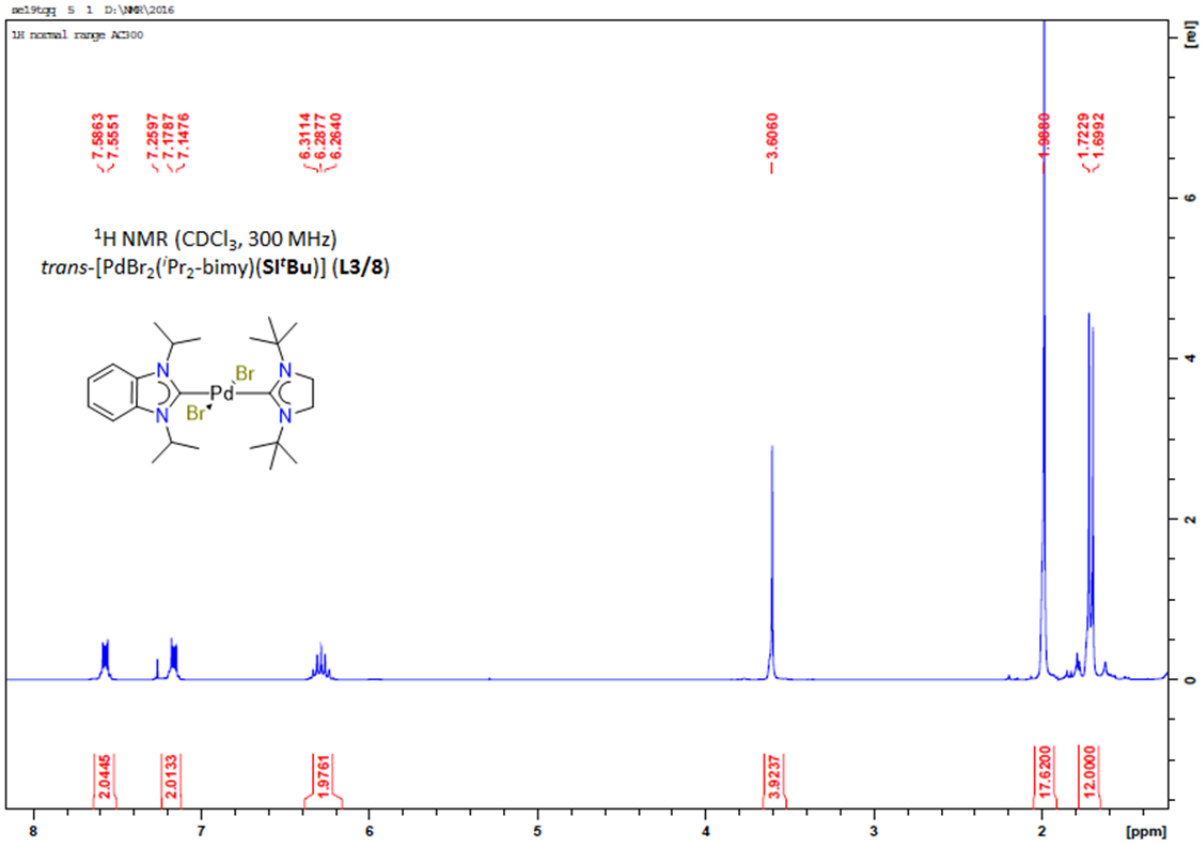


Figure S10. ^{19}H Spectra of *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(SI^{t}Bu)].

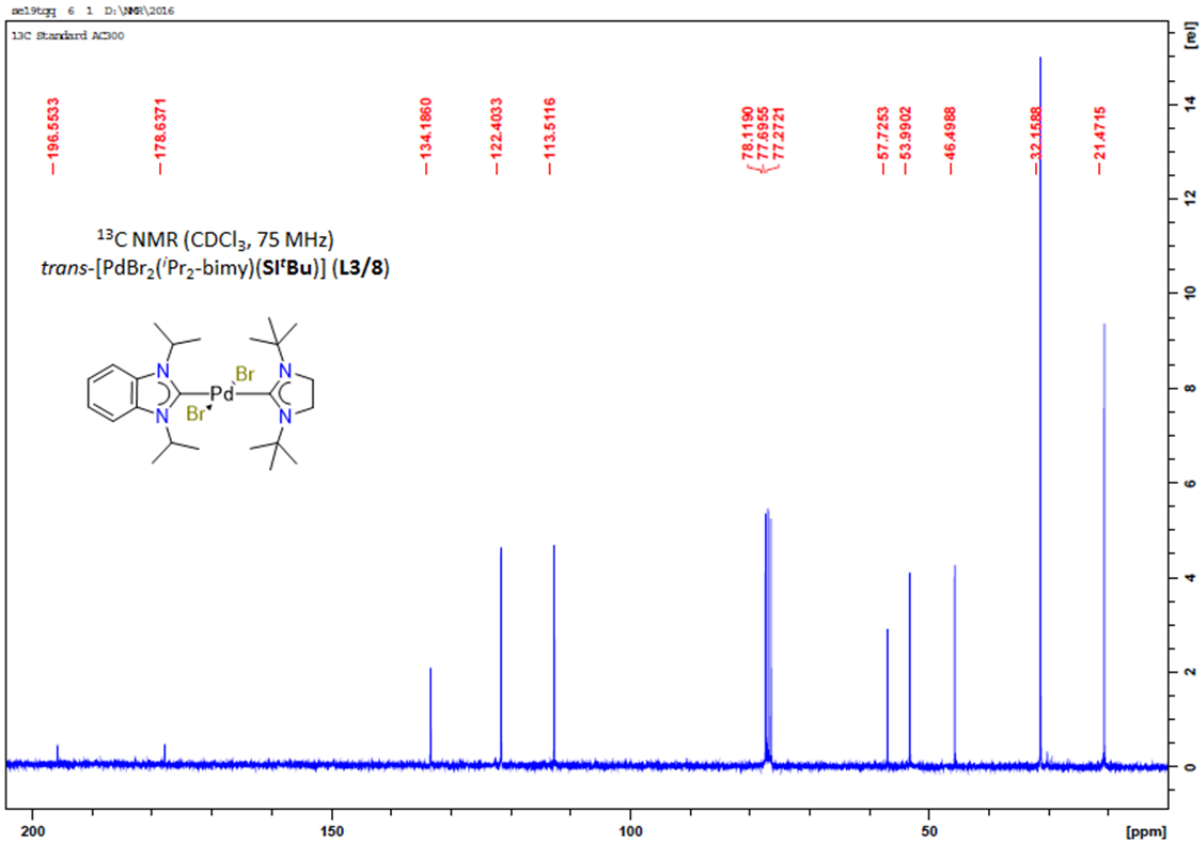


Figure S11. ^{13}C Spectra of *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(SI^{t}Bu)].

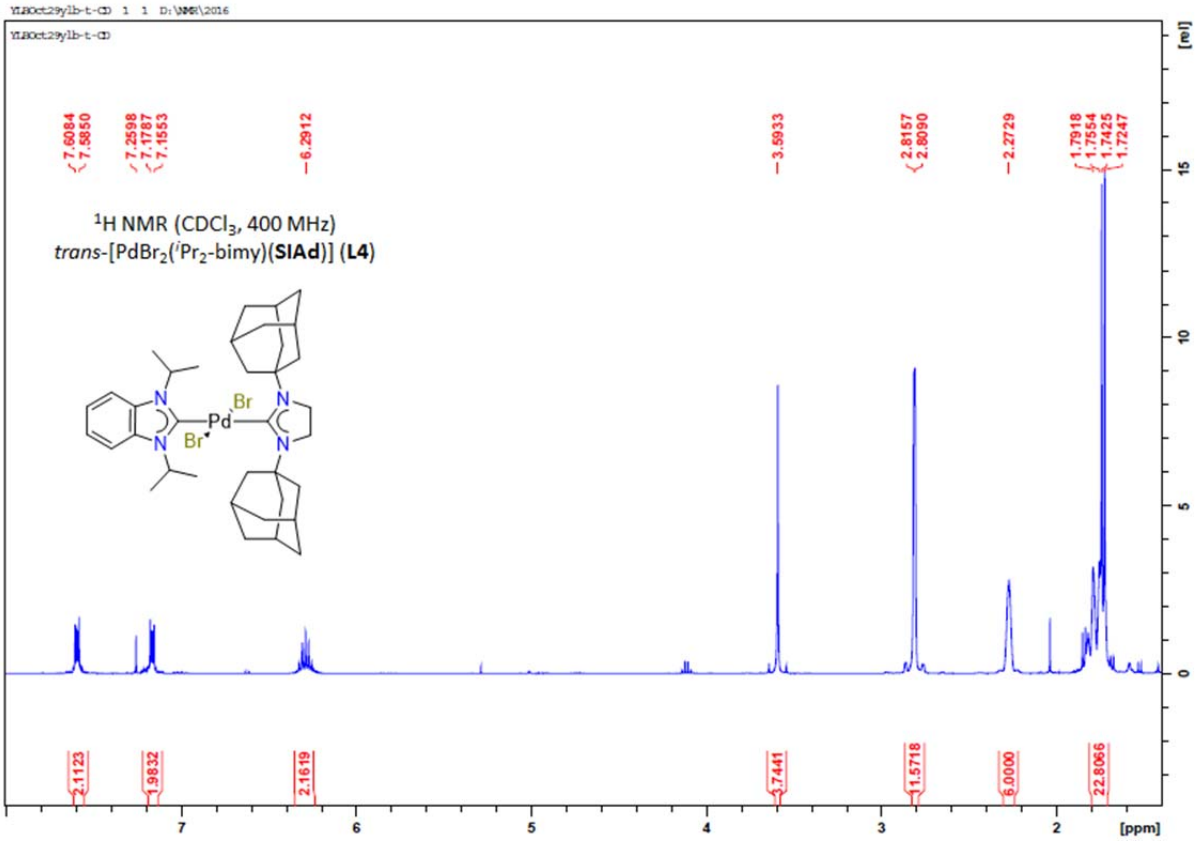


Figure S12. ^{1}H Spectra of *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(SIAd)]].

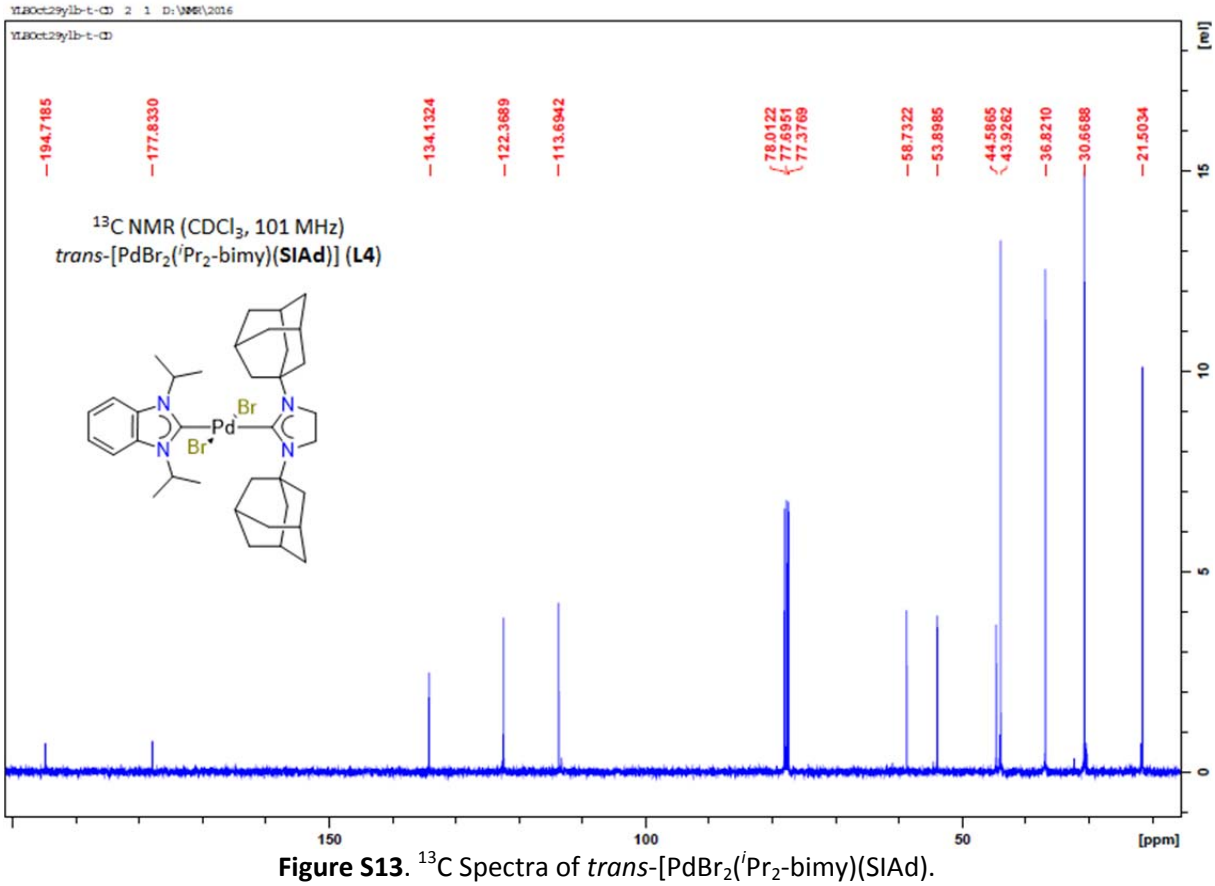


Figure S13. ^{13}C Spectra of *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(SIAd).

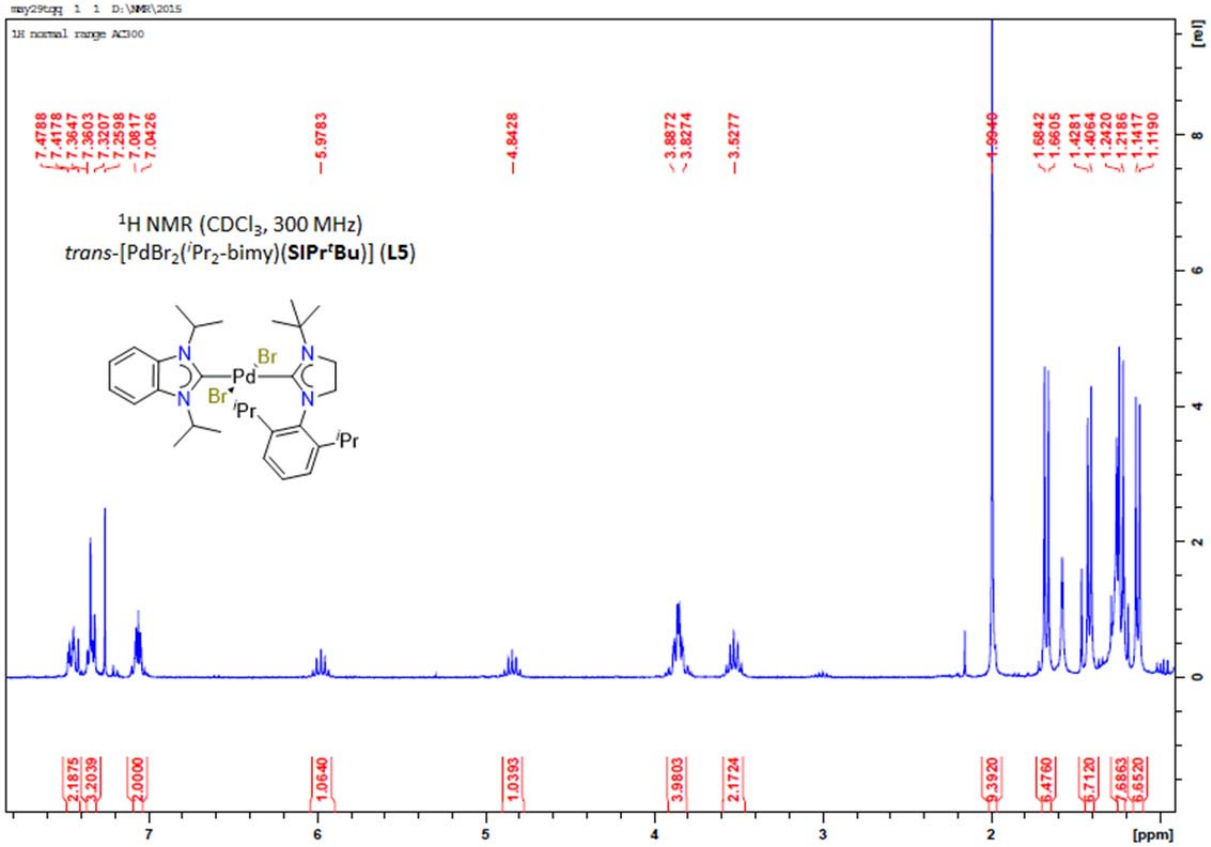


Figure S14. ^{1}H Spectra of *trans*-[$PdBr_2$(^{i}Pr$_2$-bimy)(SIPr^{t}Bu)].

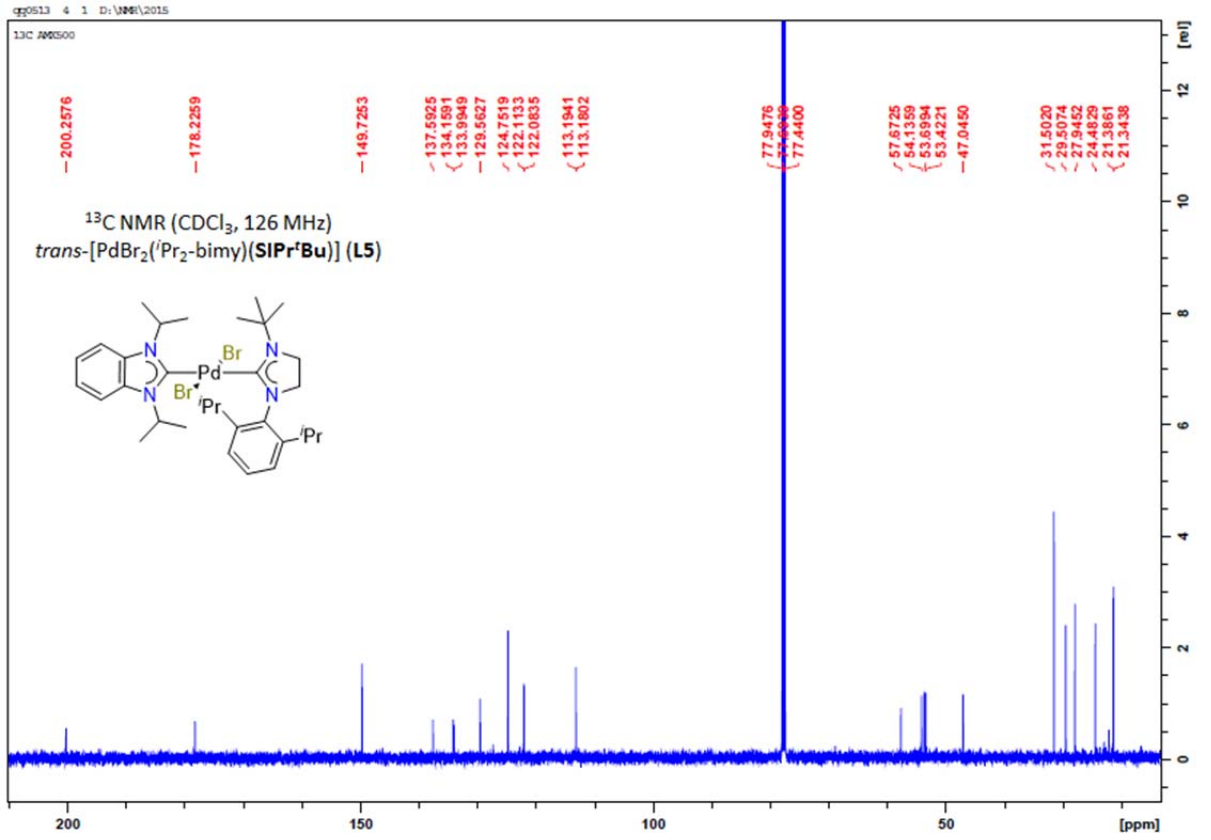


Figure S15. ^{13}C Spectra of *trans*-[$PdBr_2$(^{i}Pr$_2$-bimy)(SIPr^{t}Bu)].

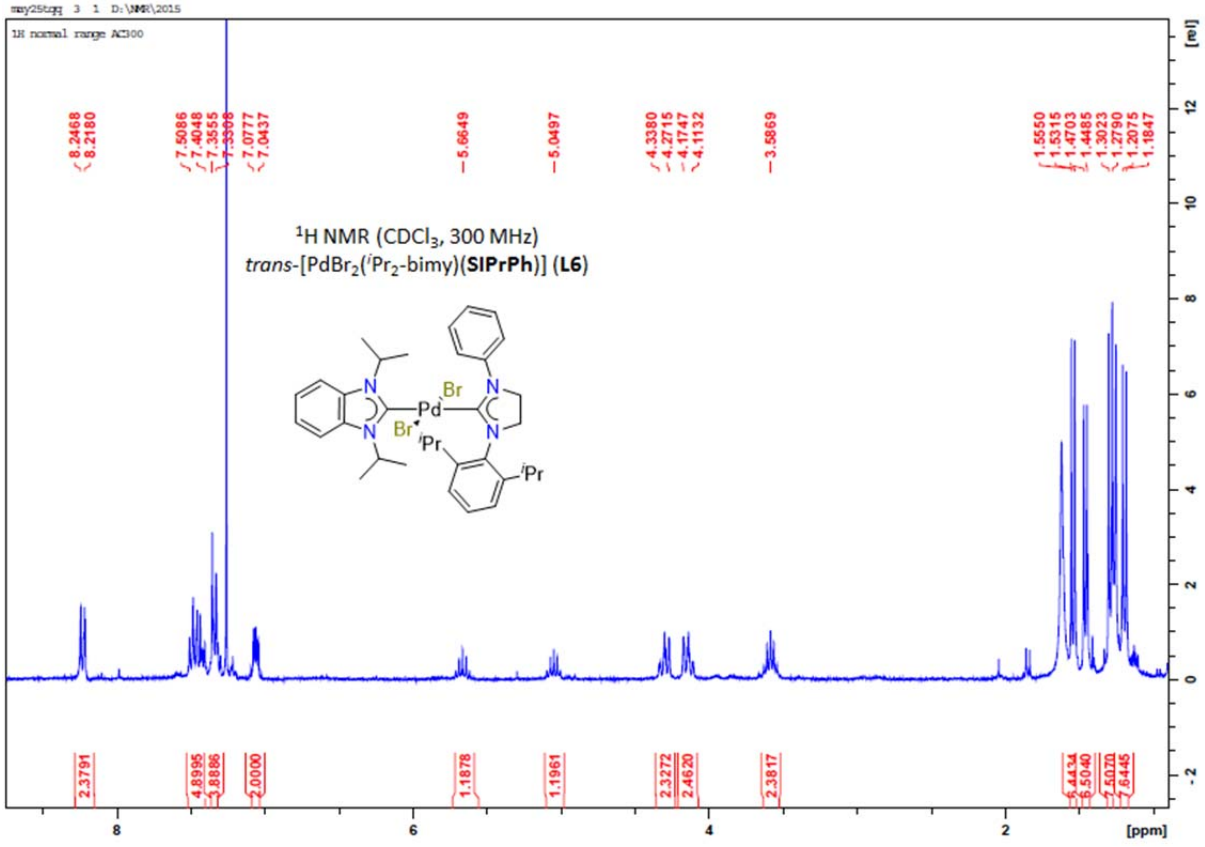


Figure S16. ^{1}H Spectra of *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(SIPrPh)].

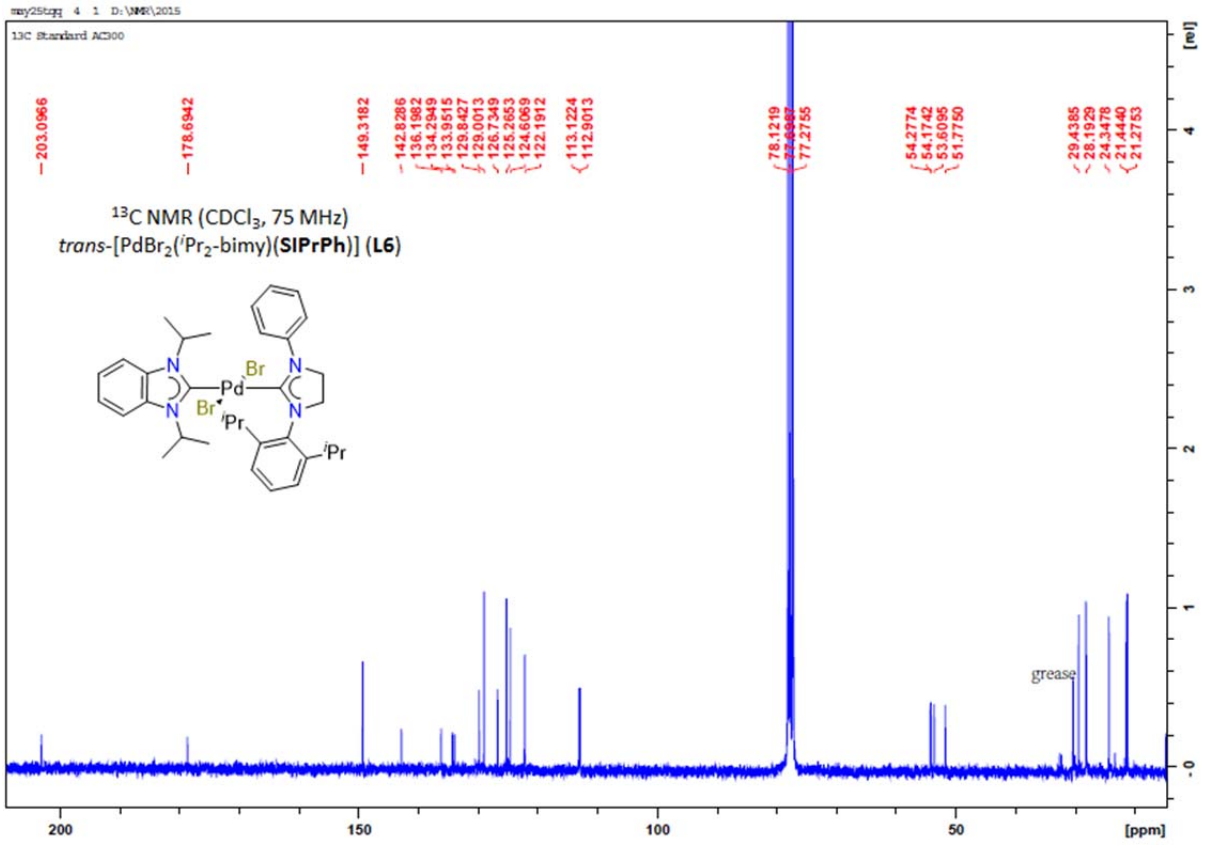


Figure S17. ^{13}C Spectra of *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(SIPrPh)].

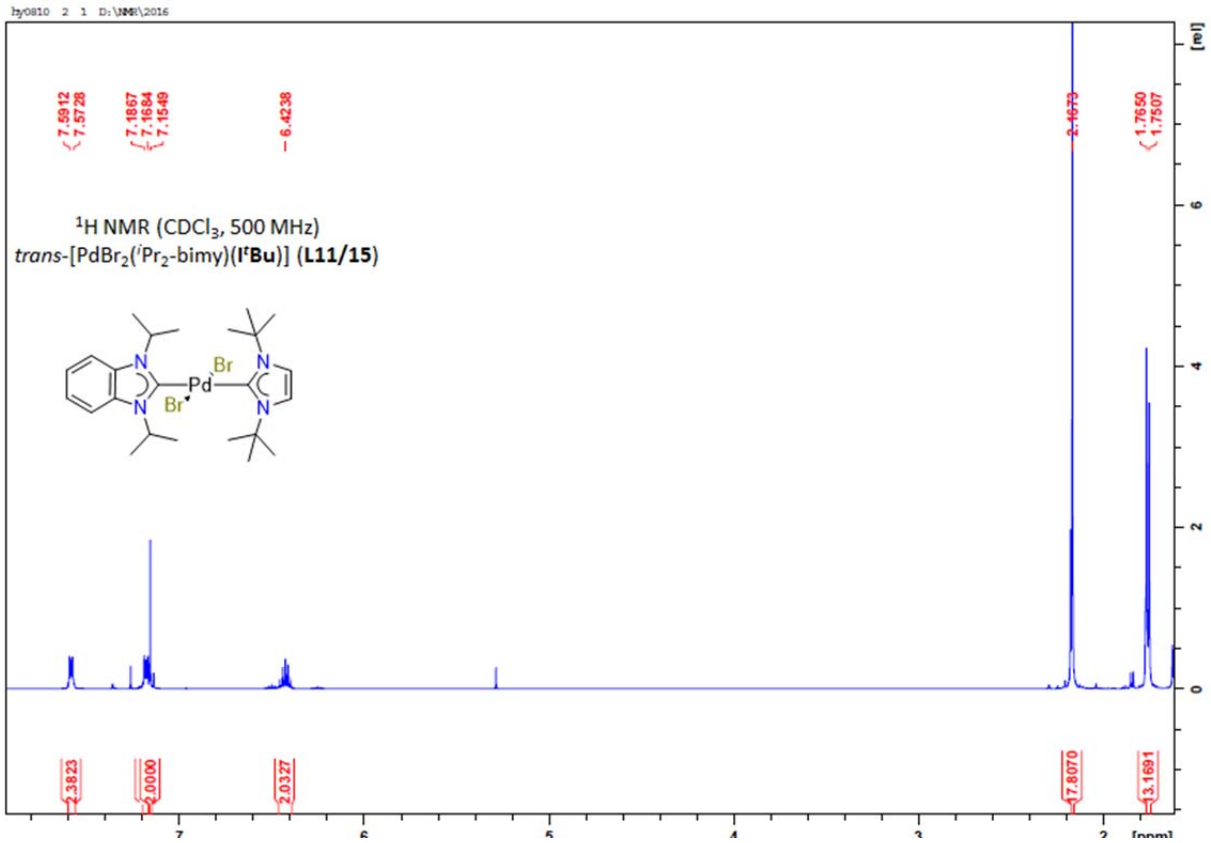


Figure S18. ^{1}H Spectra of *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(I^{t}Bu)].

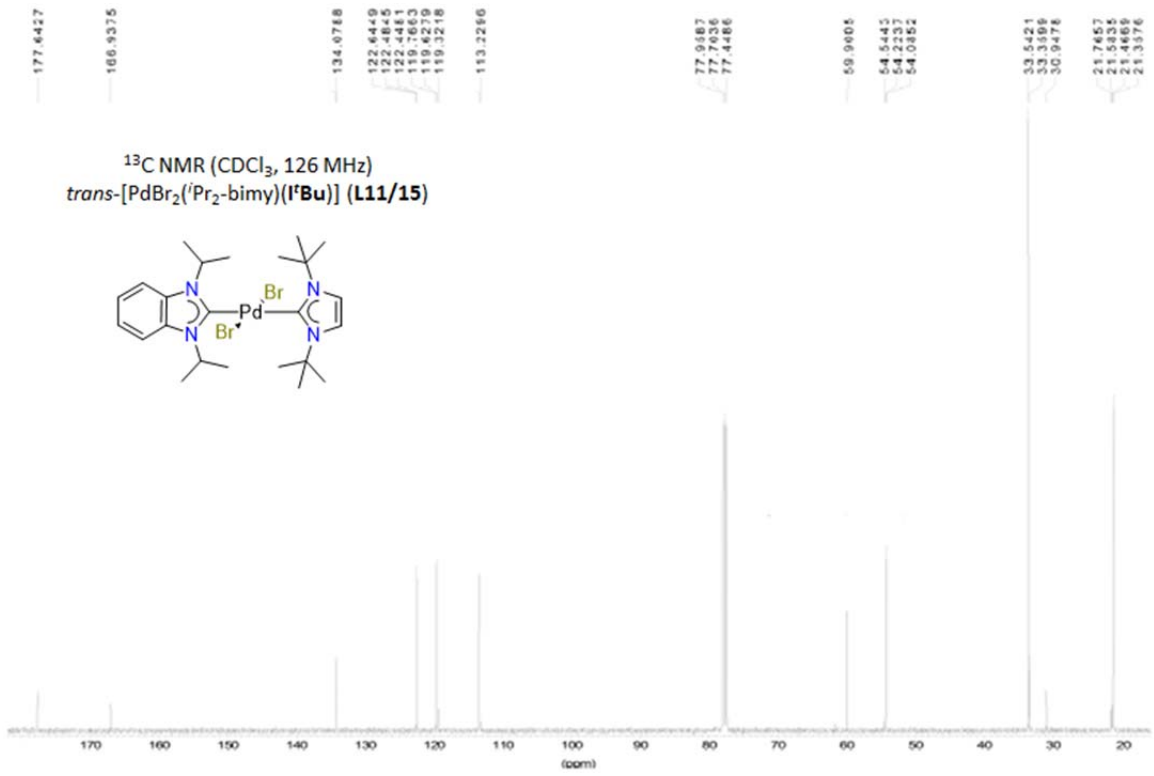


Figure S19. ^{13}C Spectra of *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(I^{t}Bu)].

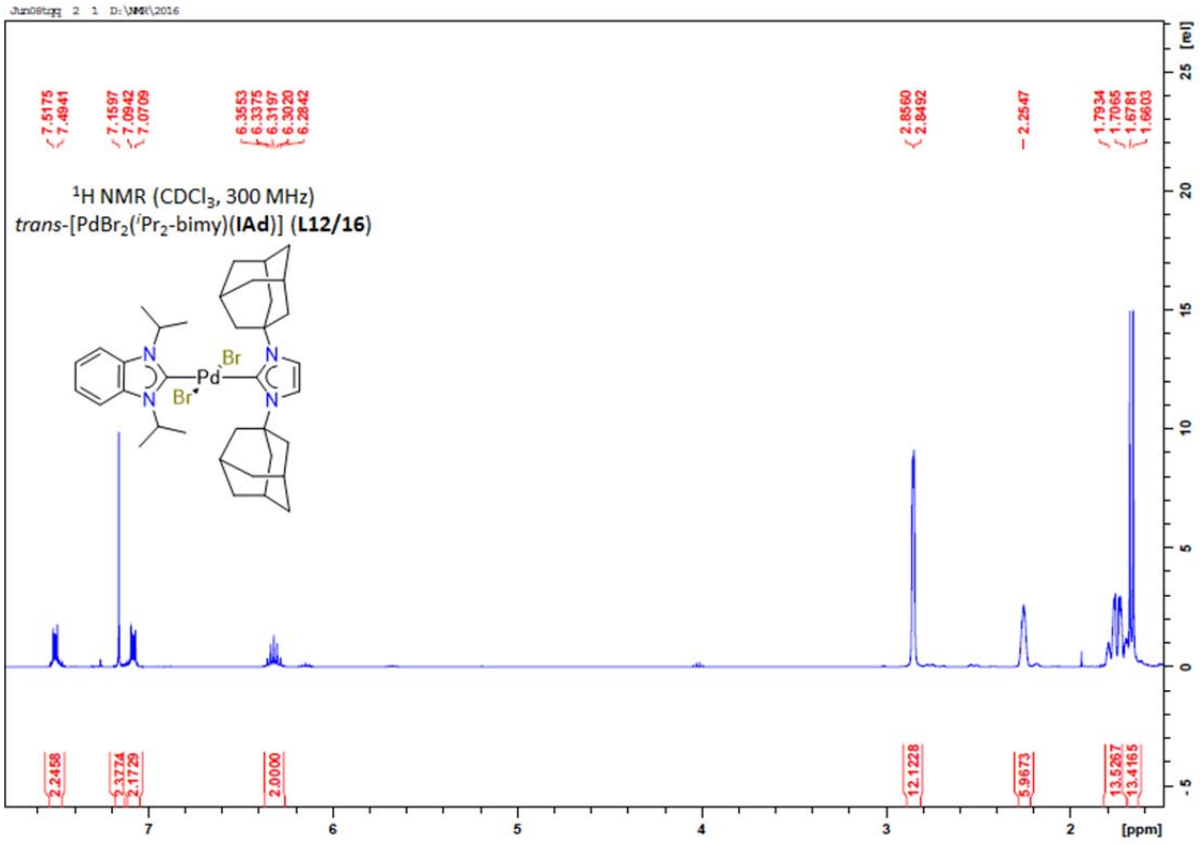


Figure S20. ^{1}H Spectra of *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(IAd)].

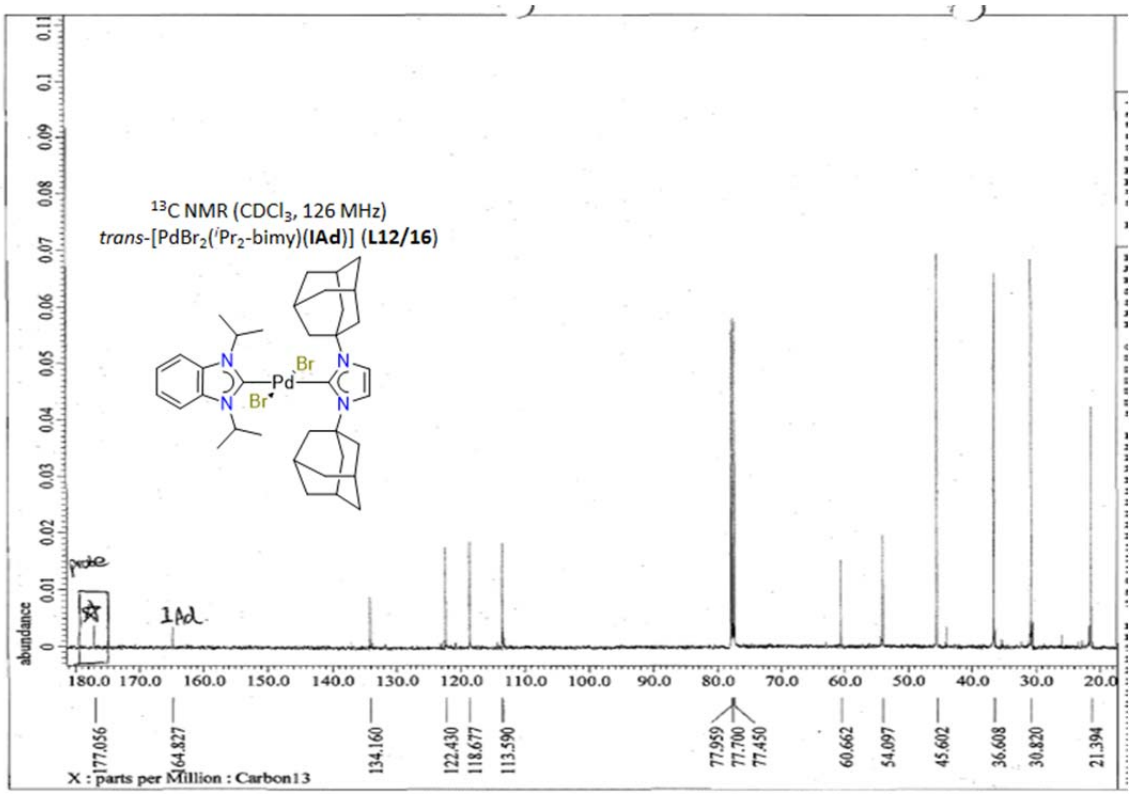


Figure S21. ^{13}C Spectra of *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(IAd)].

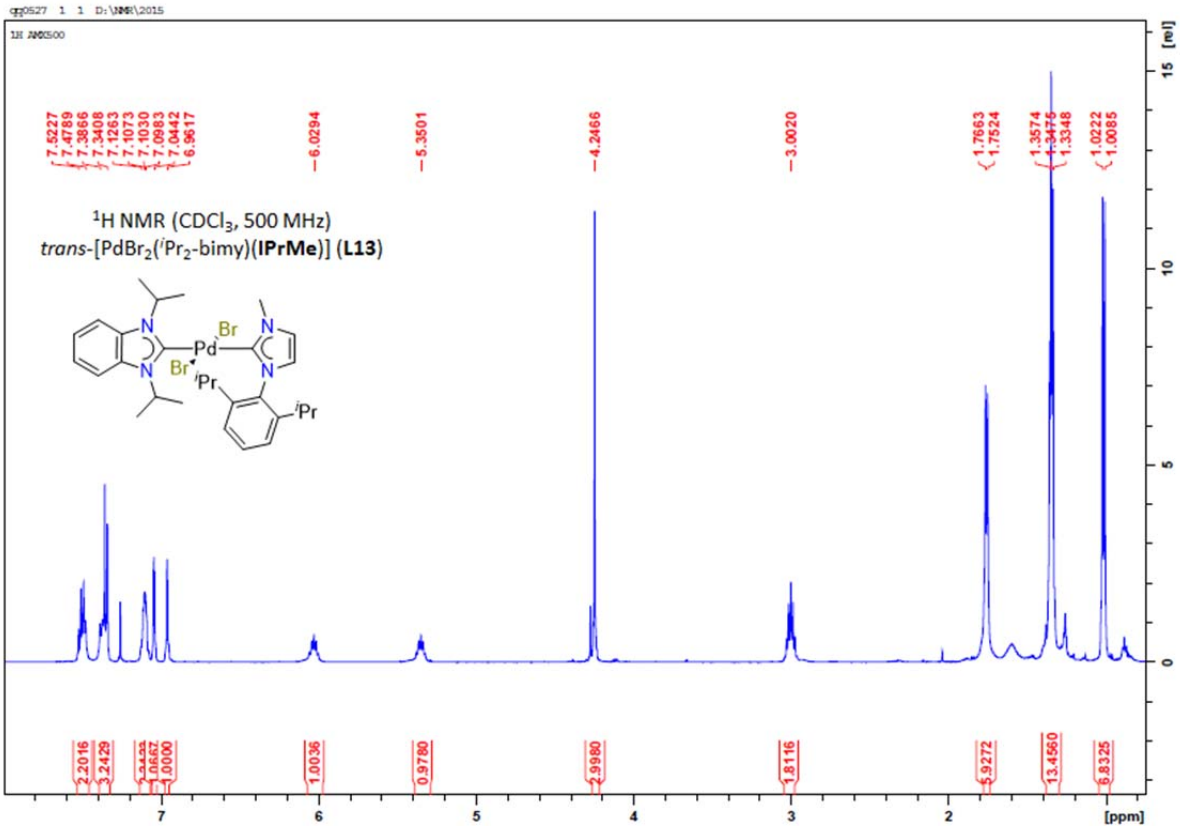


Figure S22. ^{1}H Spectra of *trans*-[$PdBr_2$(^{i}Pr$_2$-bimy)(IPrMe)].

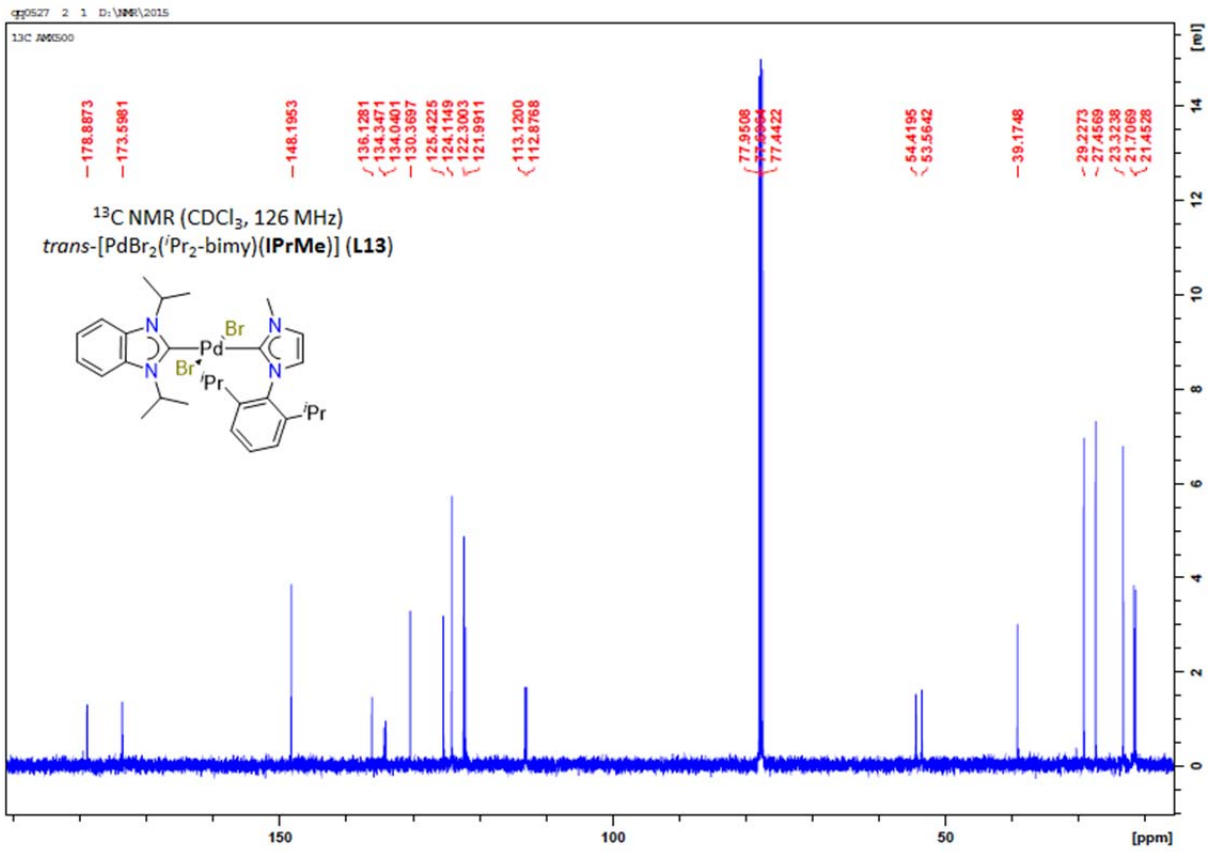


Figure S23. ^{13}C Spectra of *trans*-[$PdBr_2$(^{i}Pr$_2$-bimy)(IPrMe)].

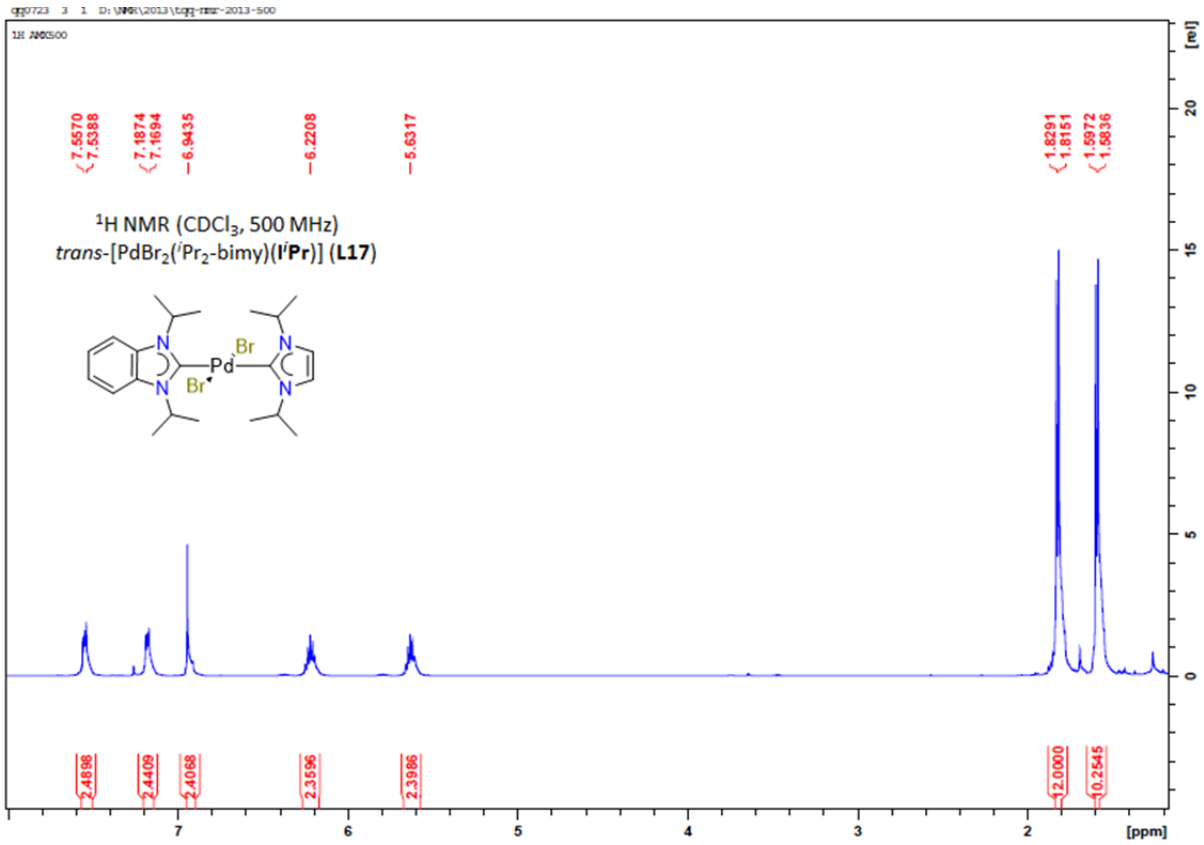


Figure S24. ^{1}H Spectra of *trans*-[$PdBr_2$(^{i}Pr$_2$-bimy)(I^{i}Pr)].

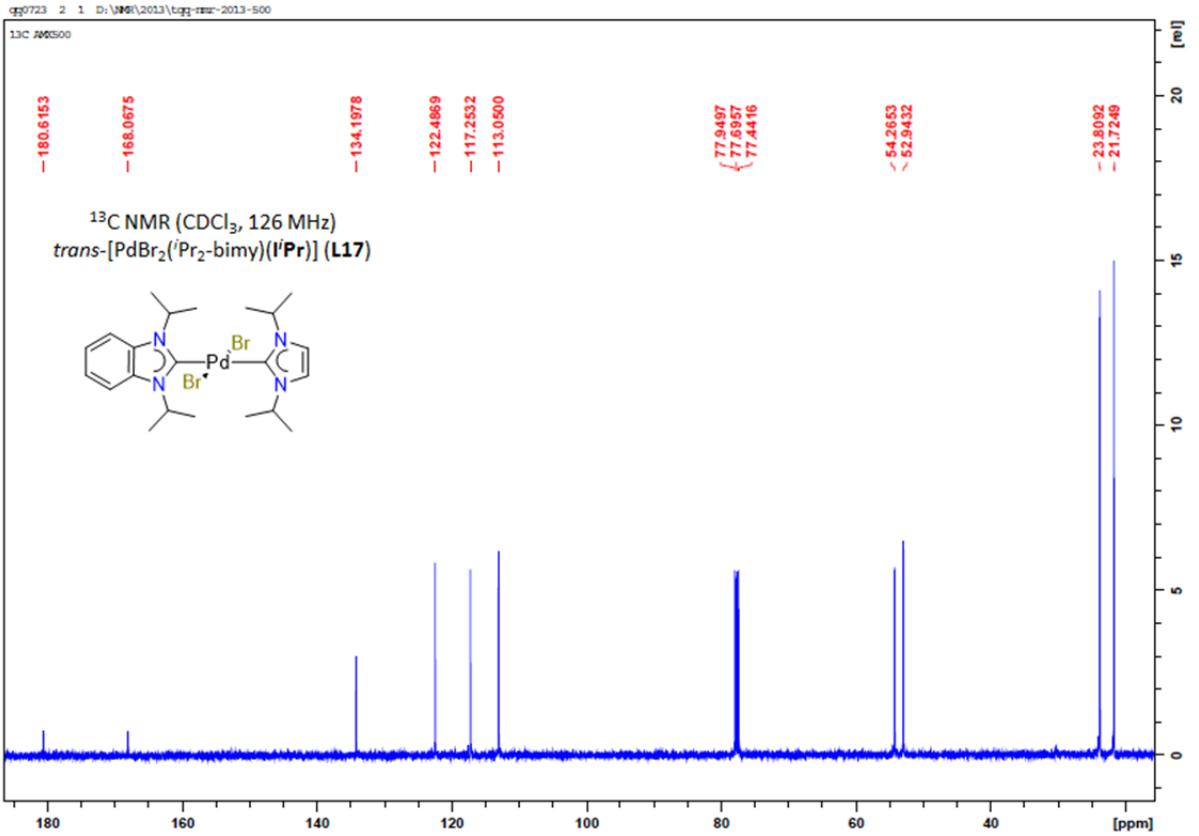


Figure S25. ^{13}C Spectra of *trans*-[$PdBr_2$(^{i}Pr$_2$-bimy)(I^{i}Pr)].

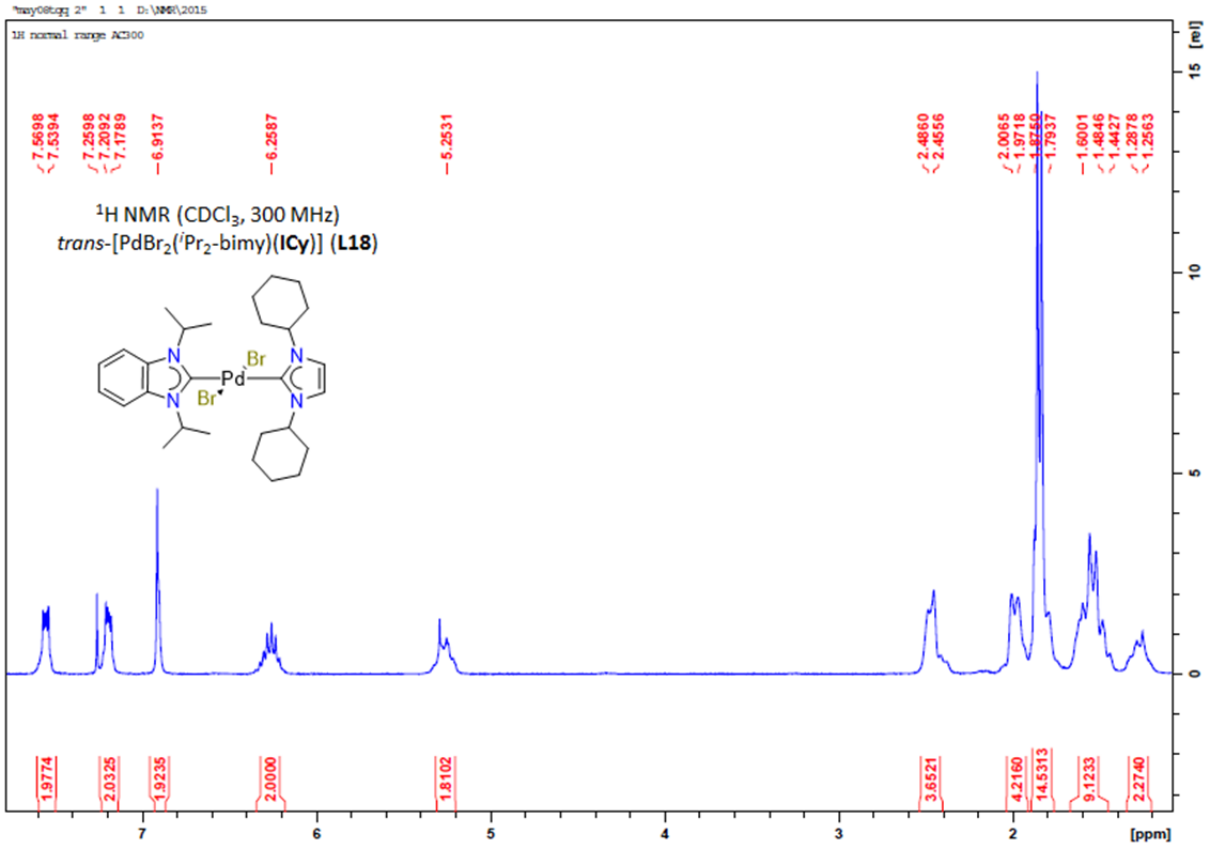


Figure S26. ^{1}H Spectra of *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(ICy)].

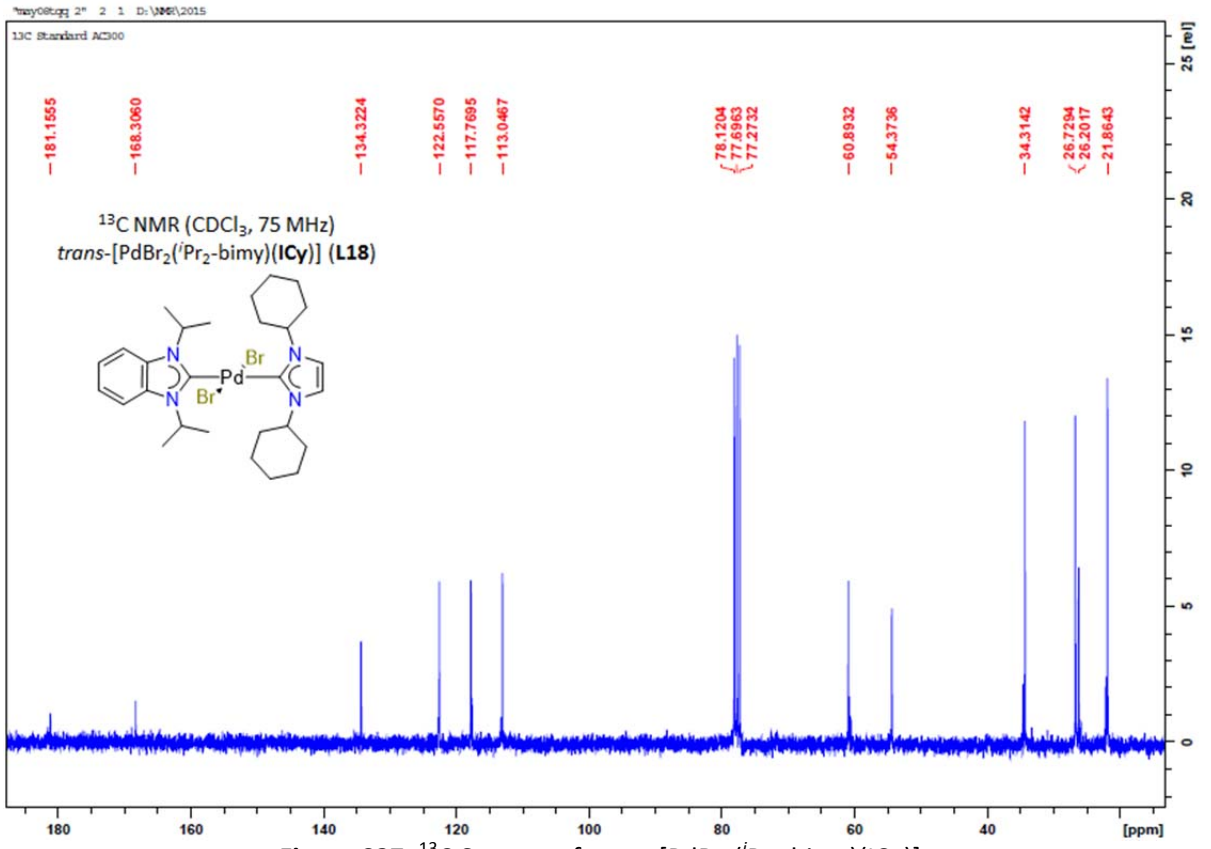


Figure S27. ^{13}C Spectra of *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(ICy)].

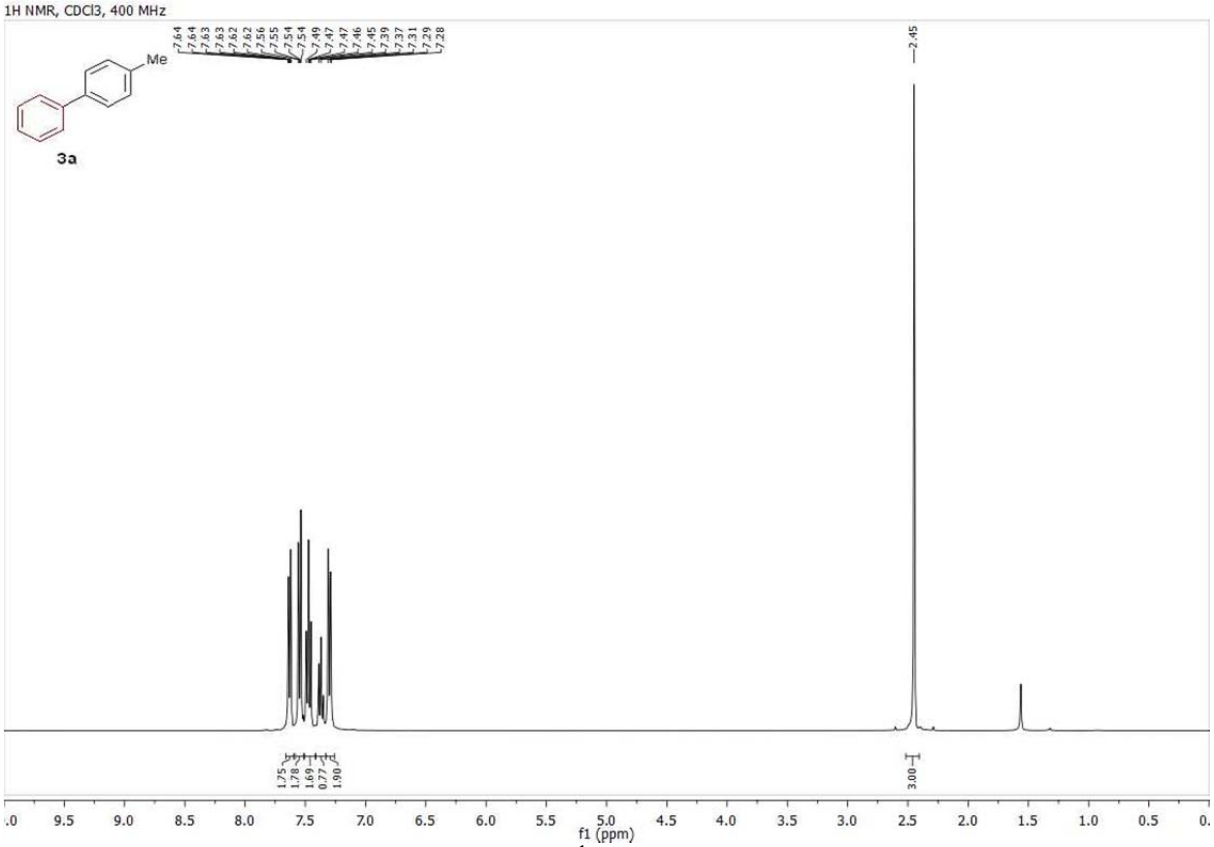


Figure S28. ^{1}H Spectra of **3a**.

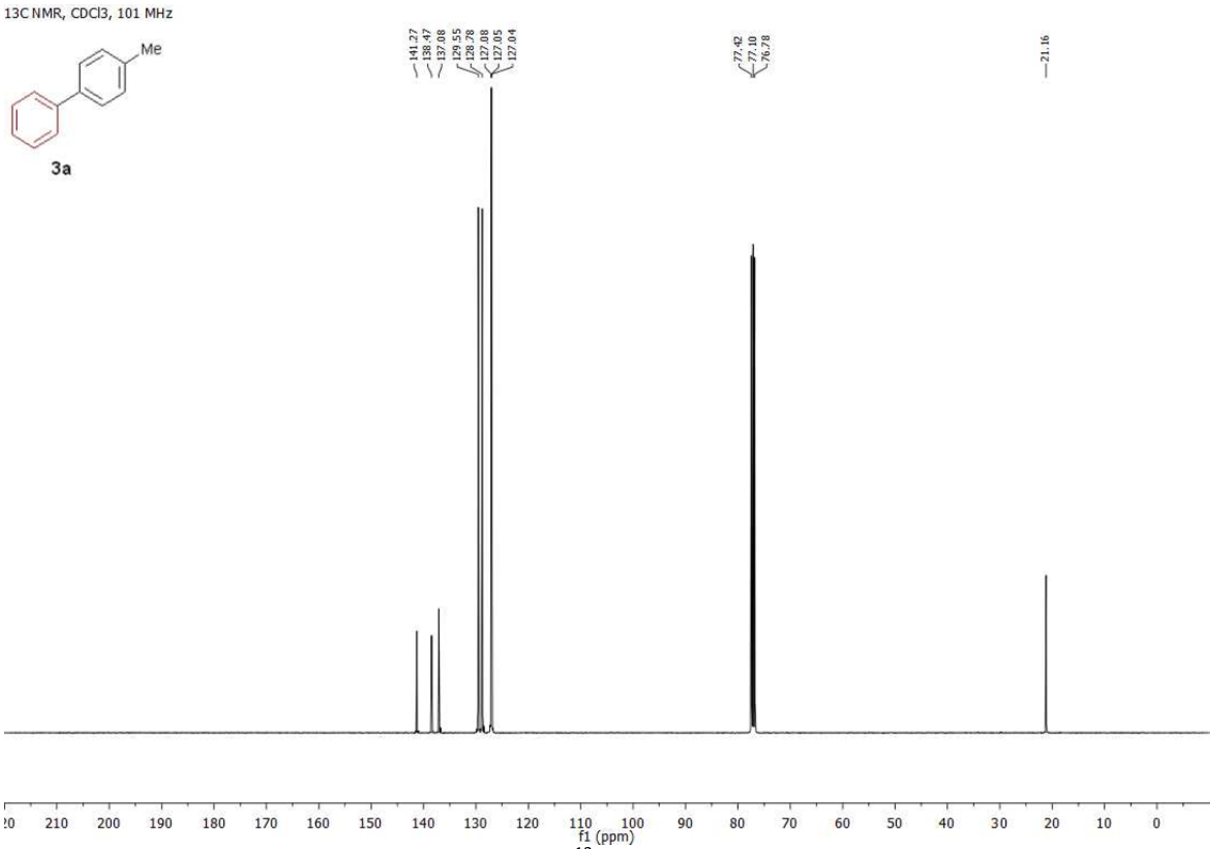


Figure S29. ^{13}C Spectra of **3a**.

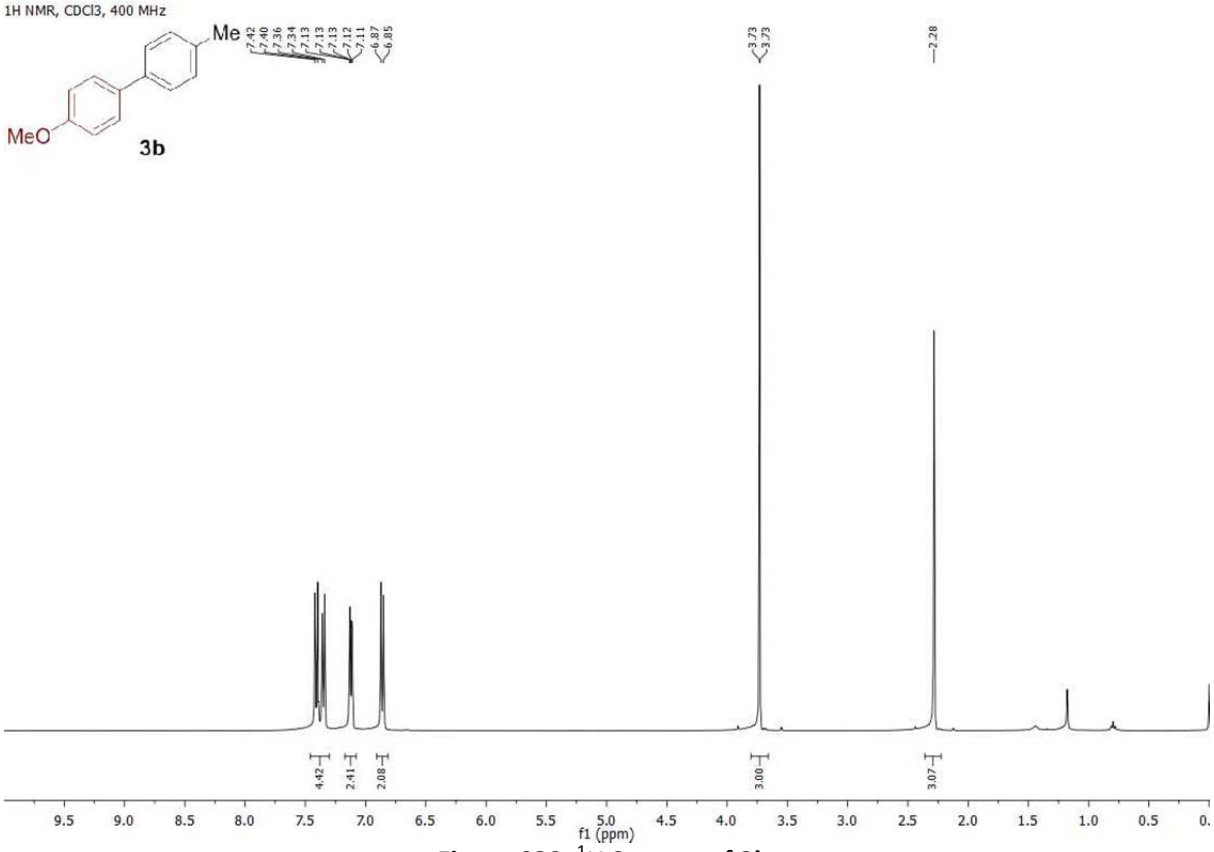


Figure S30. ^{1}H Spectra of **3b**.

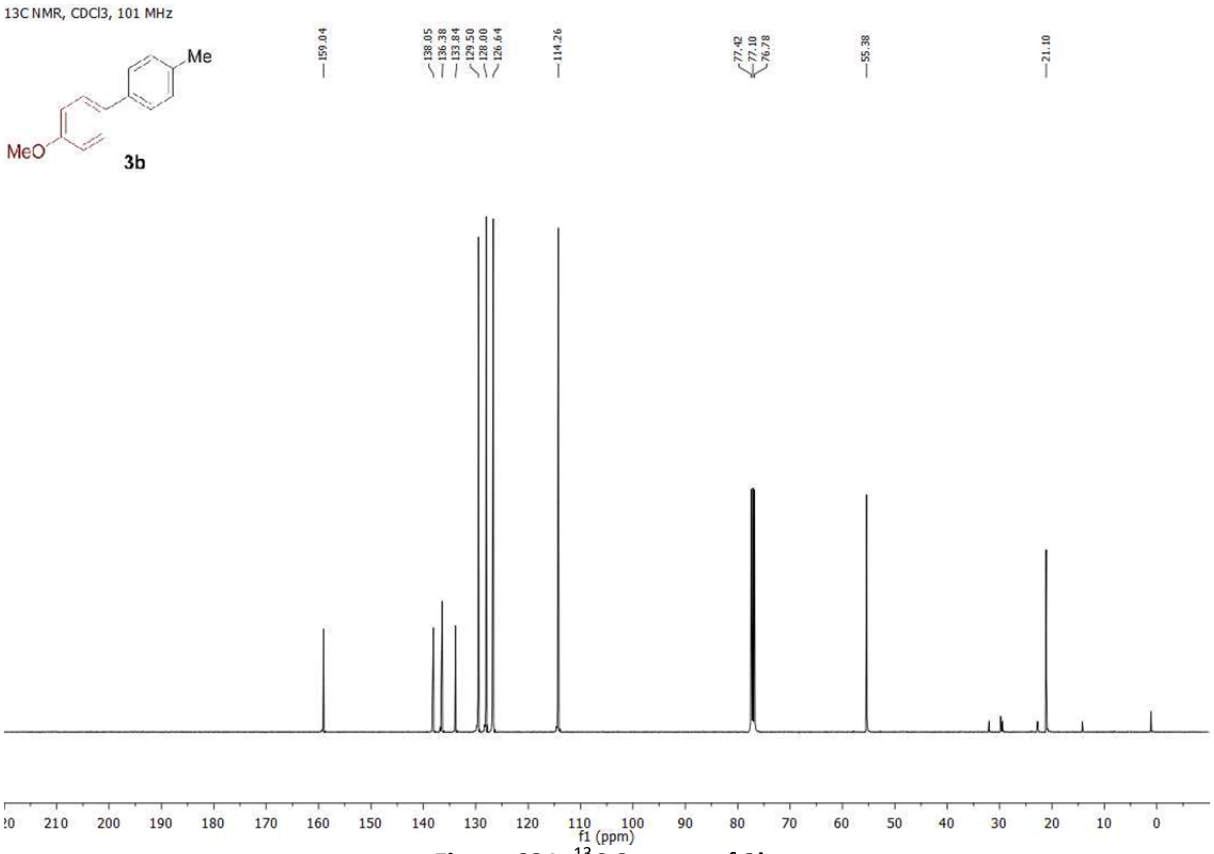


Figure S31. ^{13}C Spectra of **3b**.

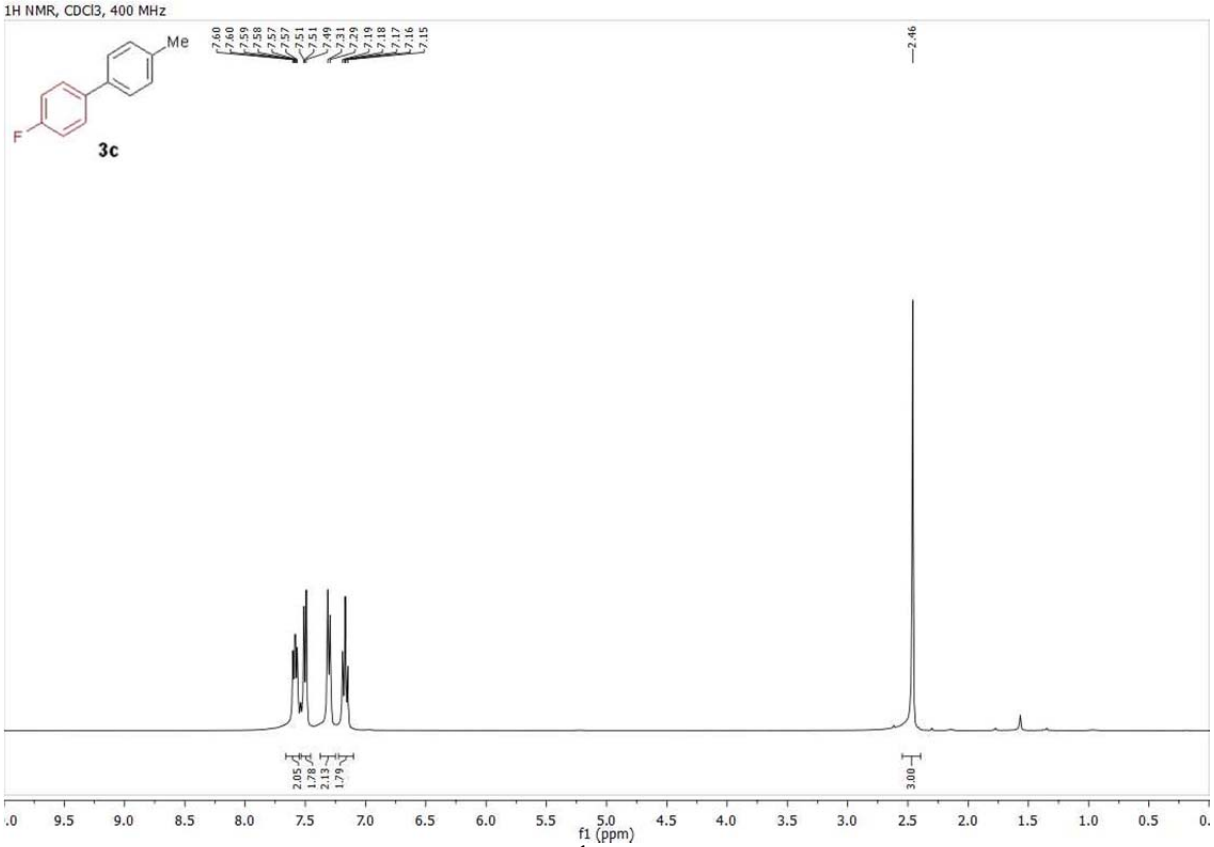


Figure S32. ^{1}H Spectra of **3c**.

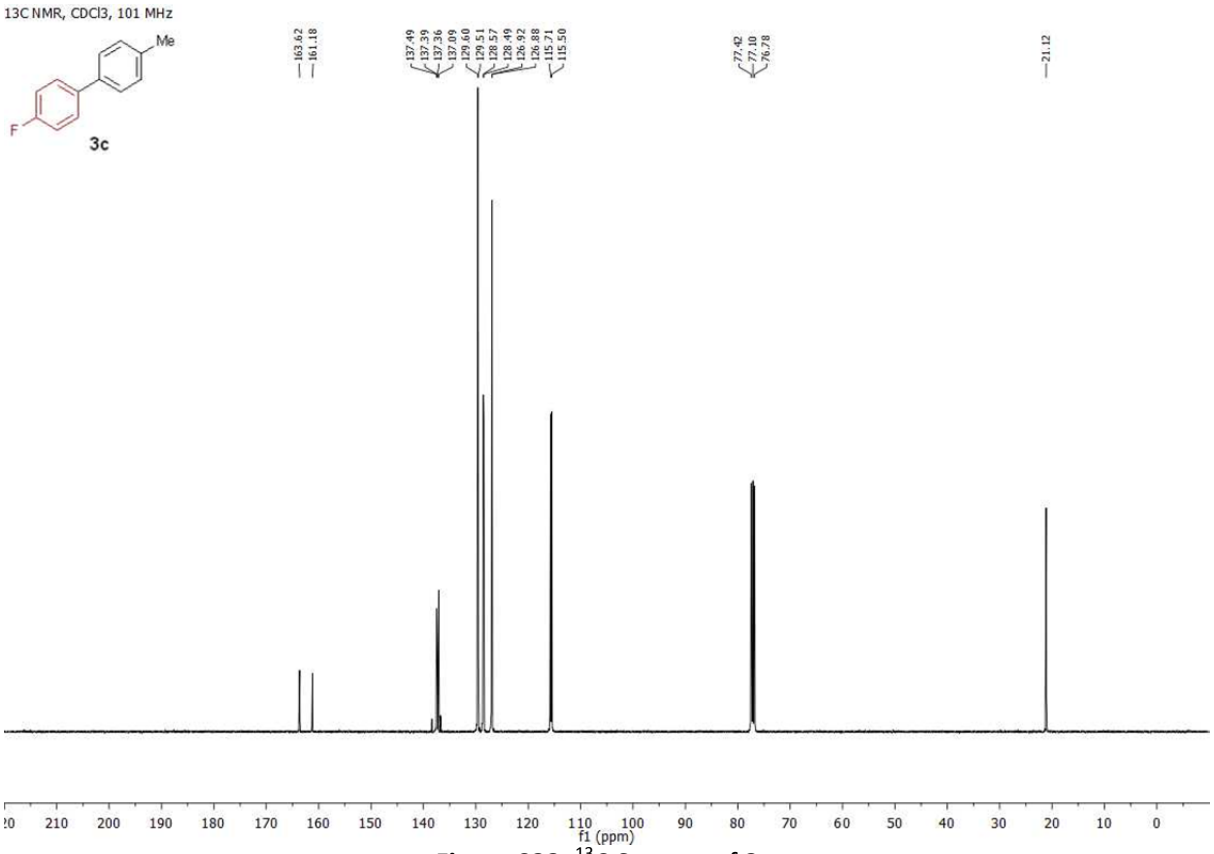


Figure S33. ^{13}C Spectra of **3c**.

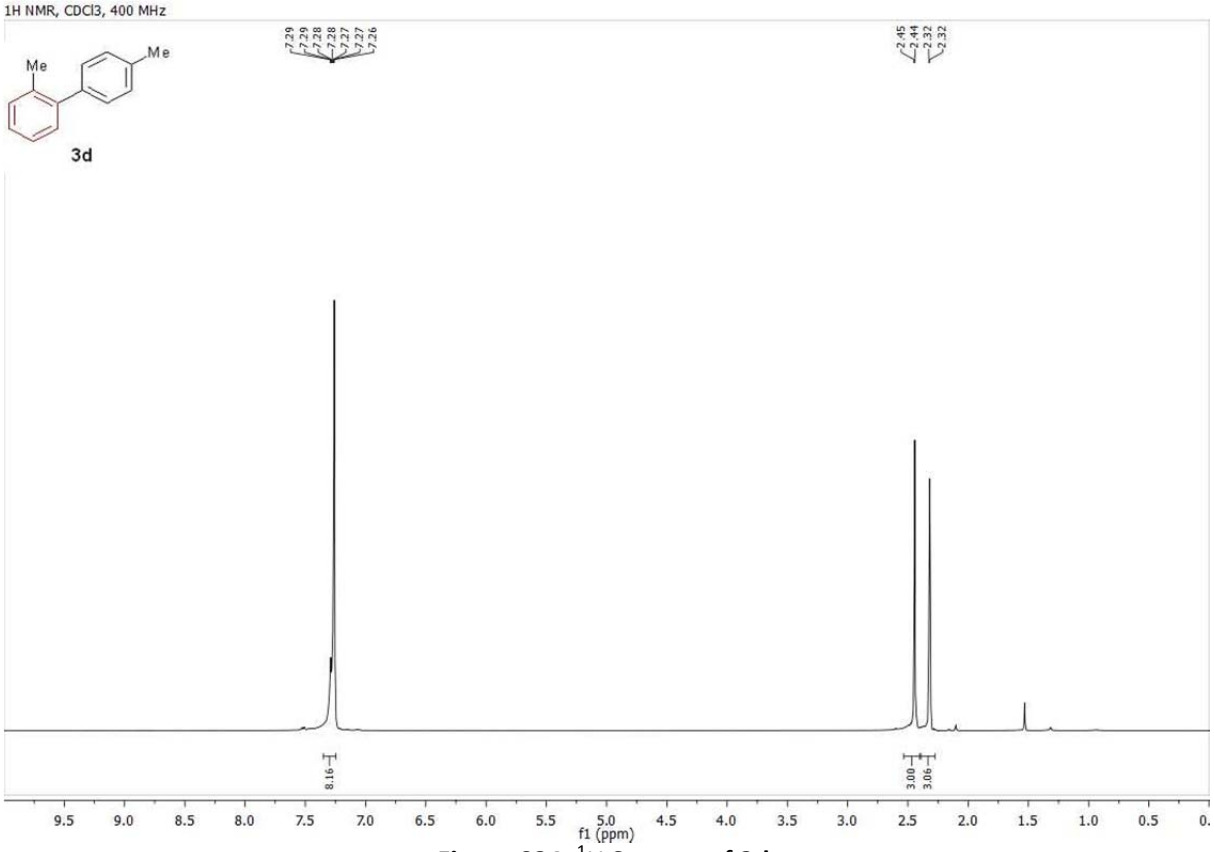


Figure S34. ^{1}H Spectra of **3d**.

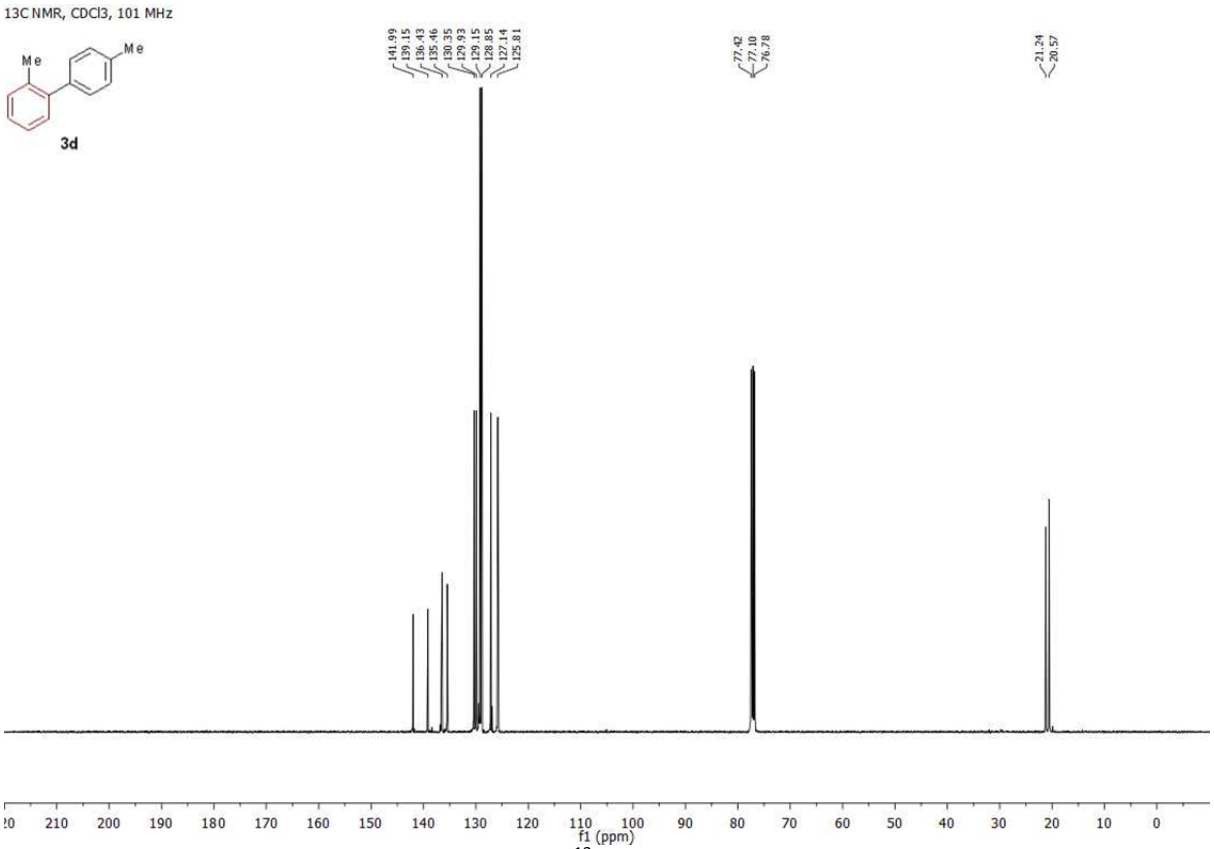


Figure S35. ^{13}C Spectra of **3d**.

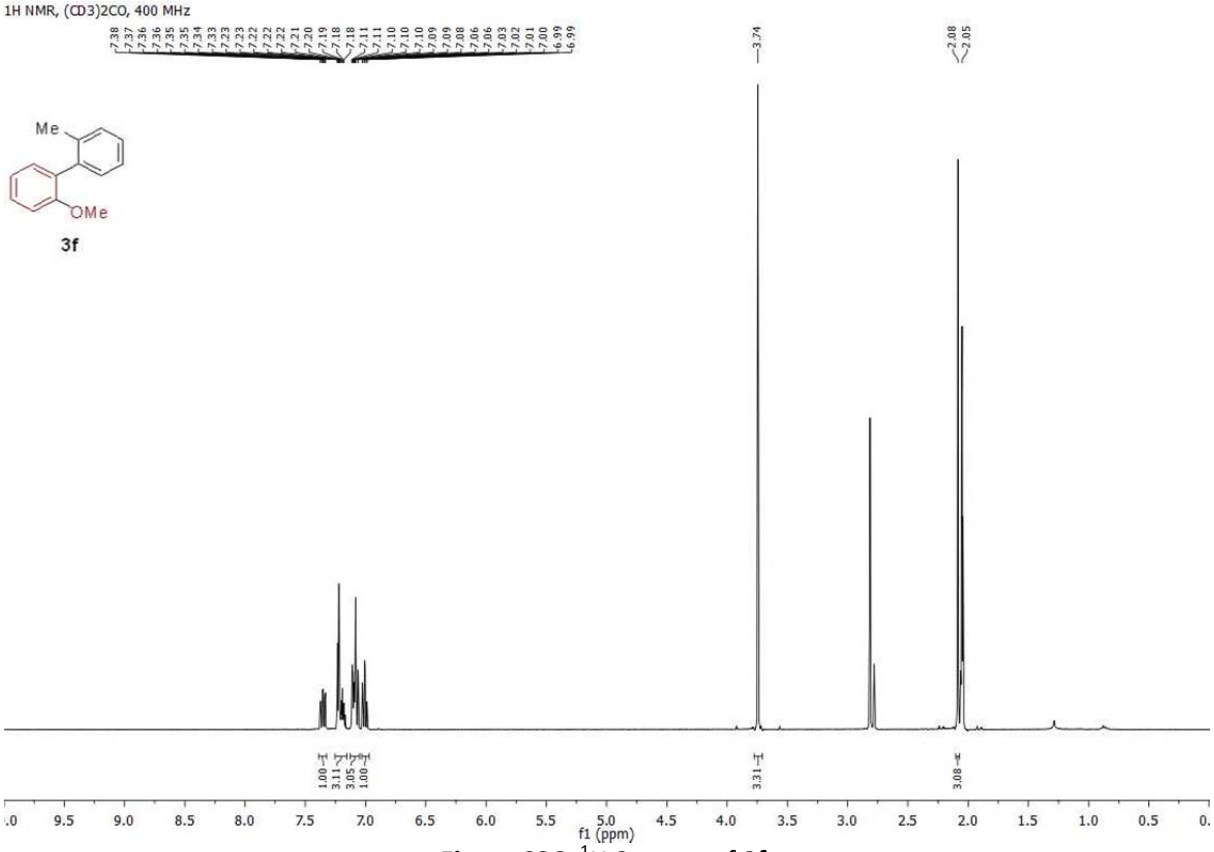


Figure S36. ^{1}H Spectra of **3f**.

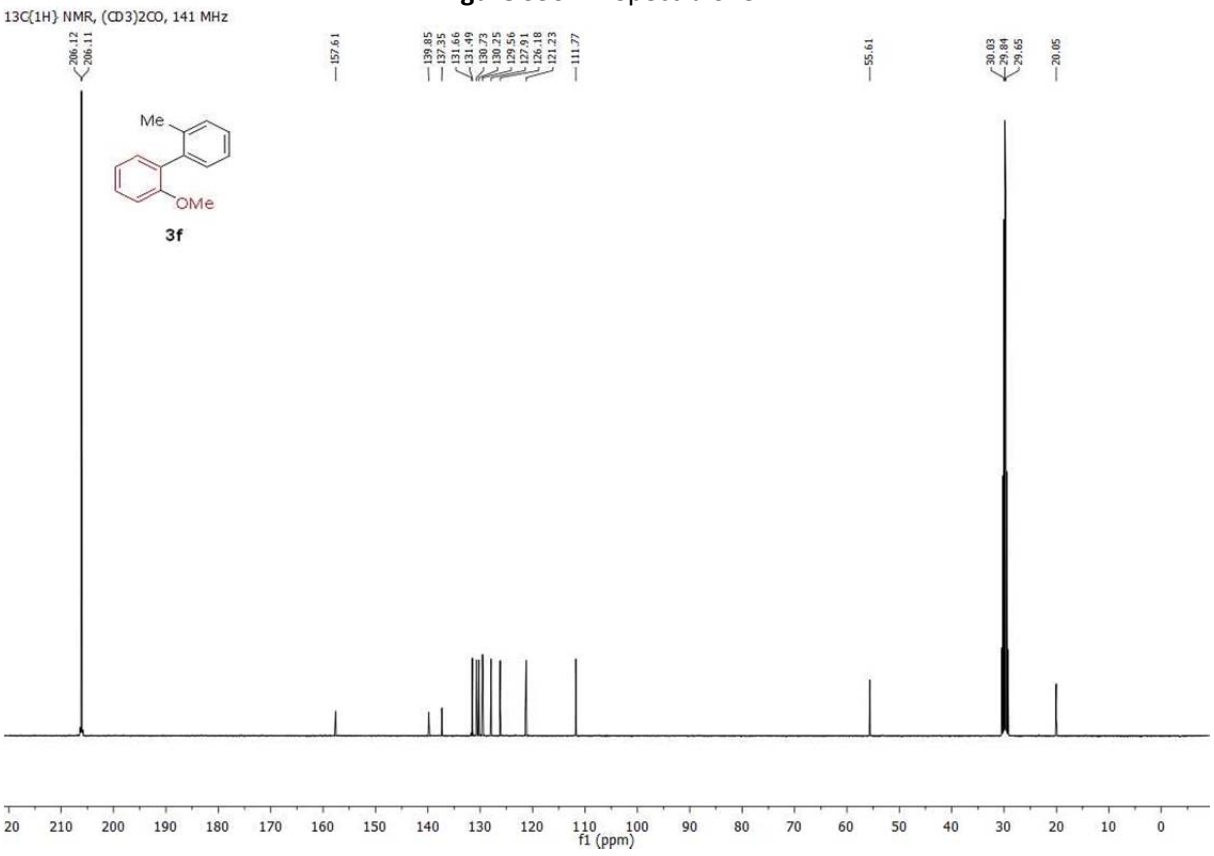


Figure S37. ^{13}C Spectra of **3f**.

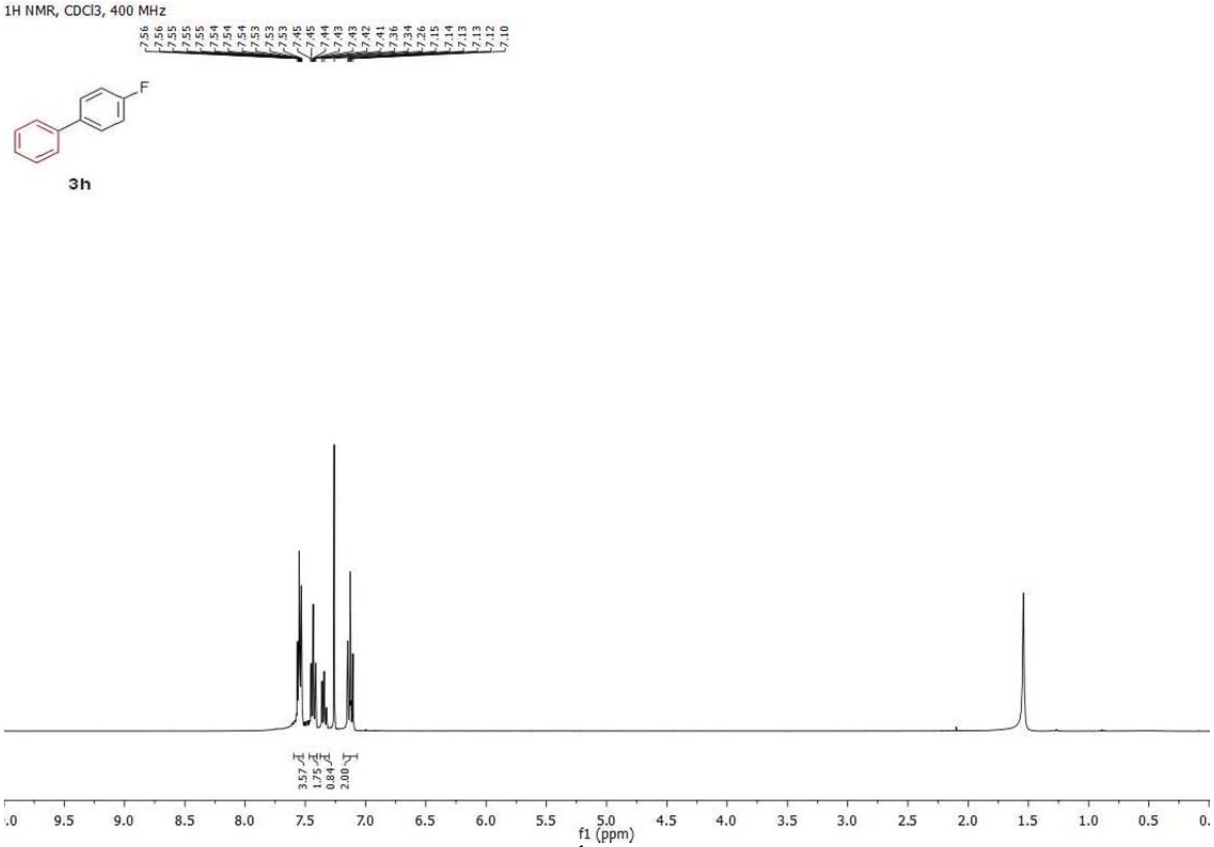


Figure S38. ^{1}H Spectra of **3h**.

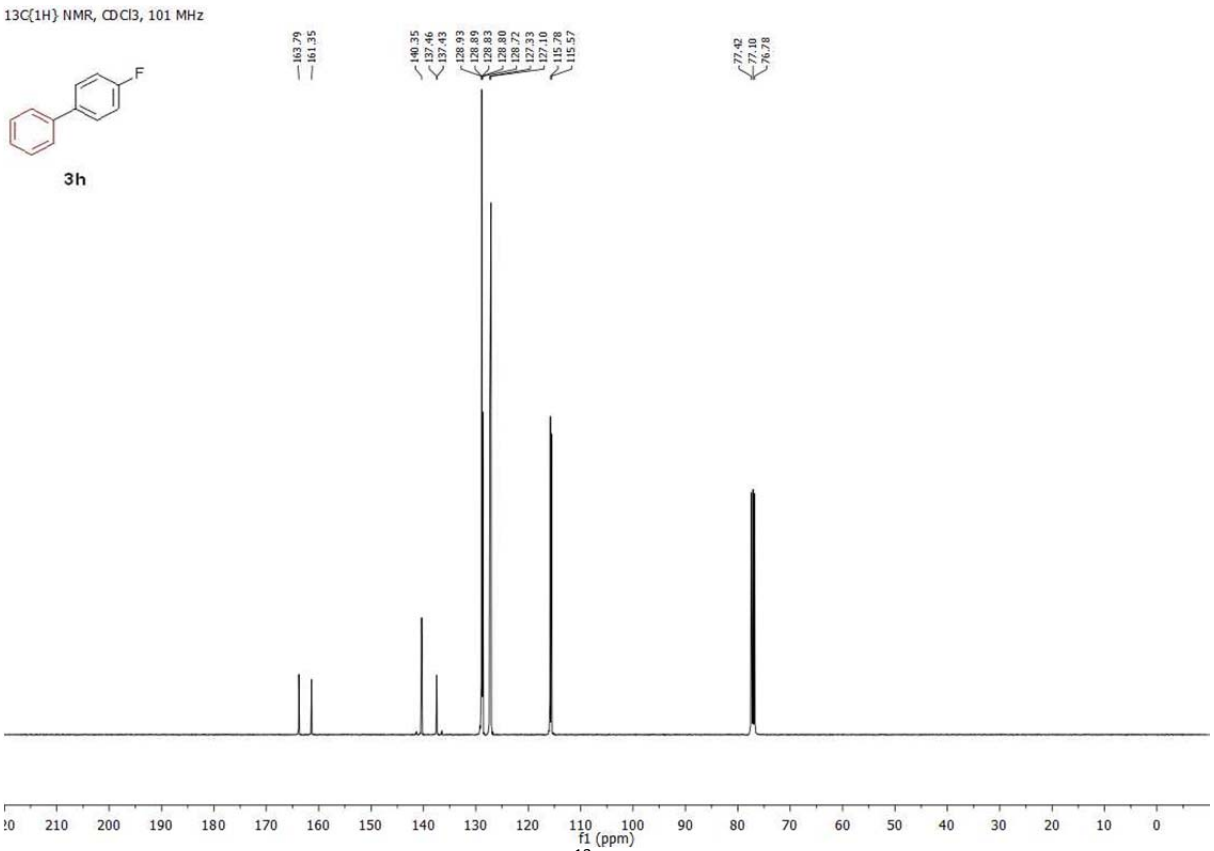


Figure S39. ^{13}C Spectra of **3h**.

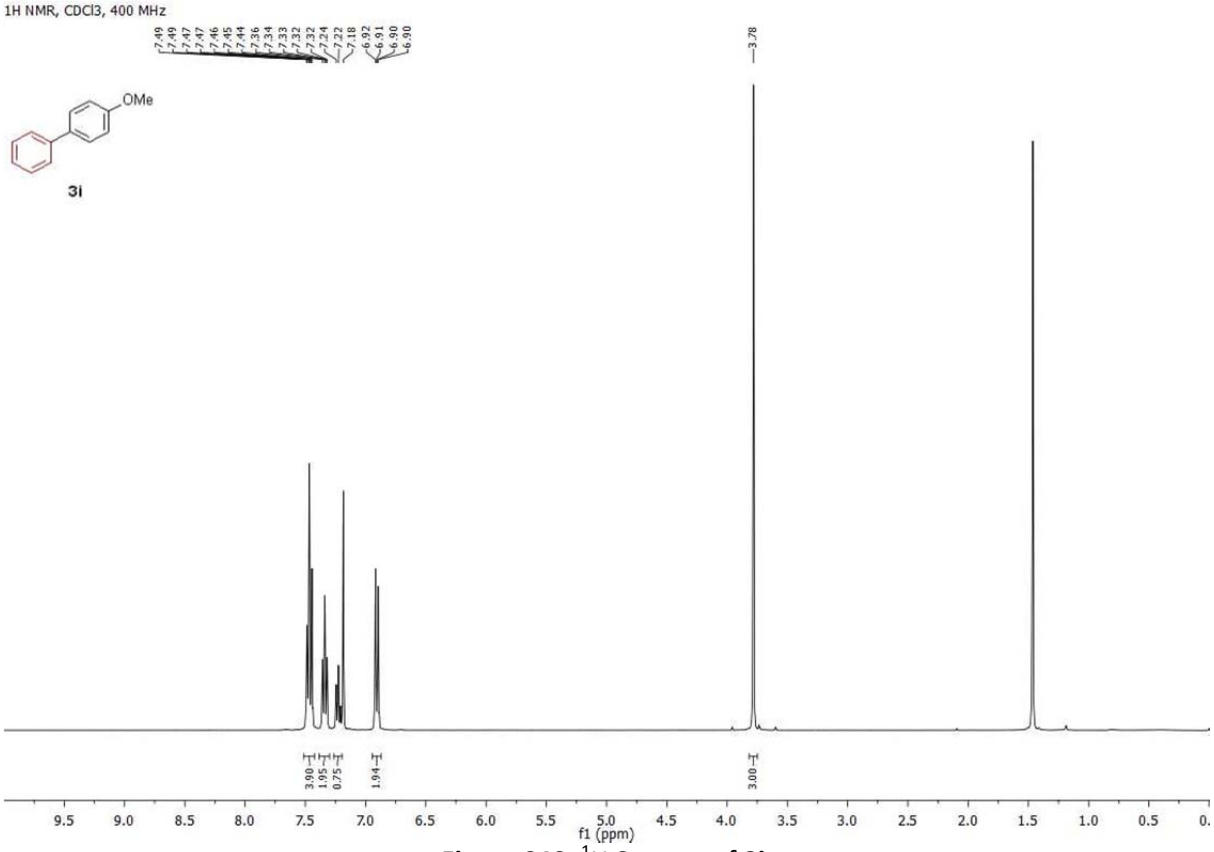


Figure S40. ^{1}H Spectra of **3i**.

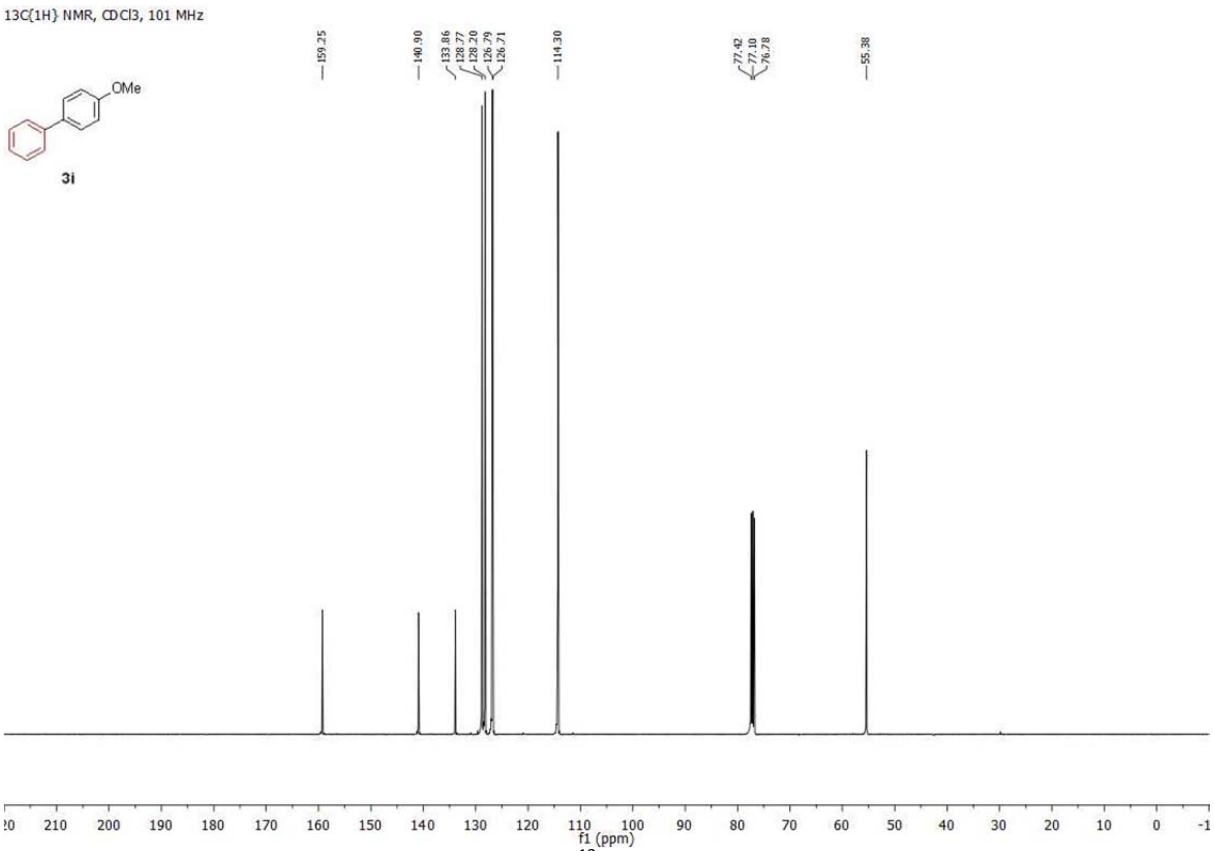


Figure S41. ^{13}C Spectra of **3i**.

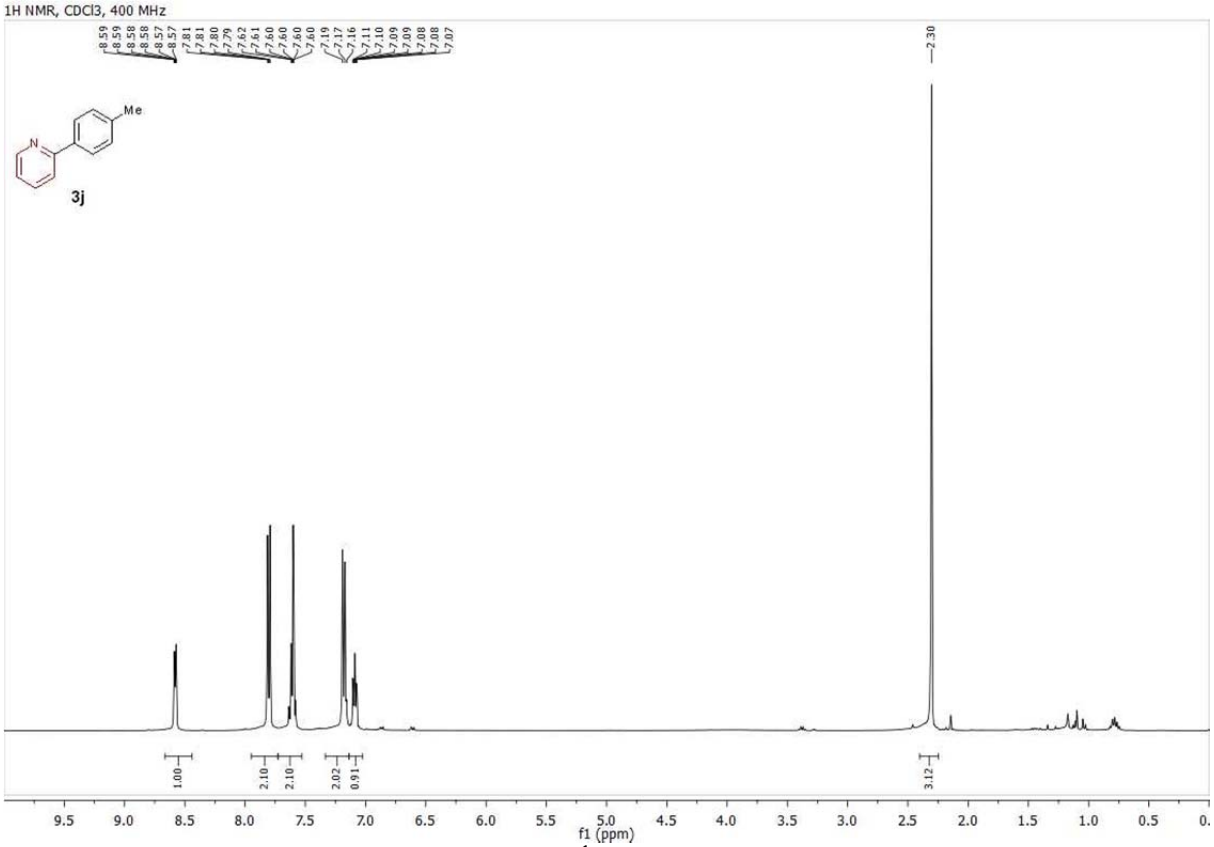


Figure S42. ^{1}H Spectra of **3j**.

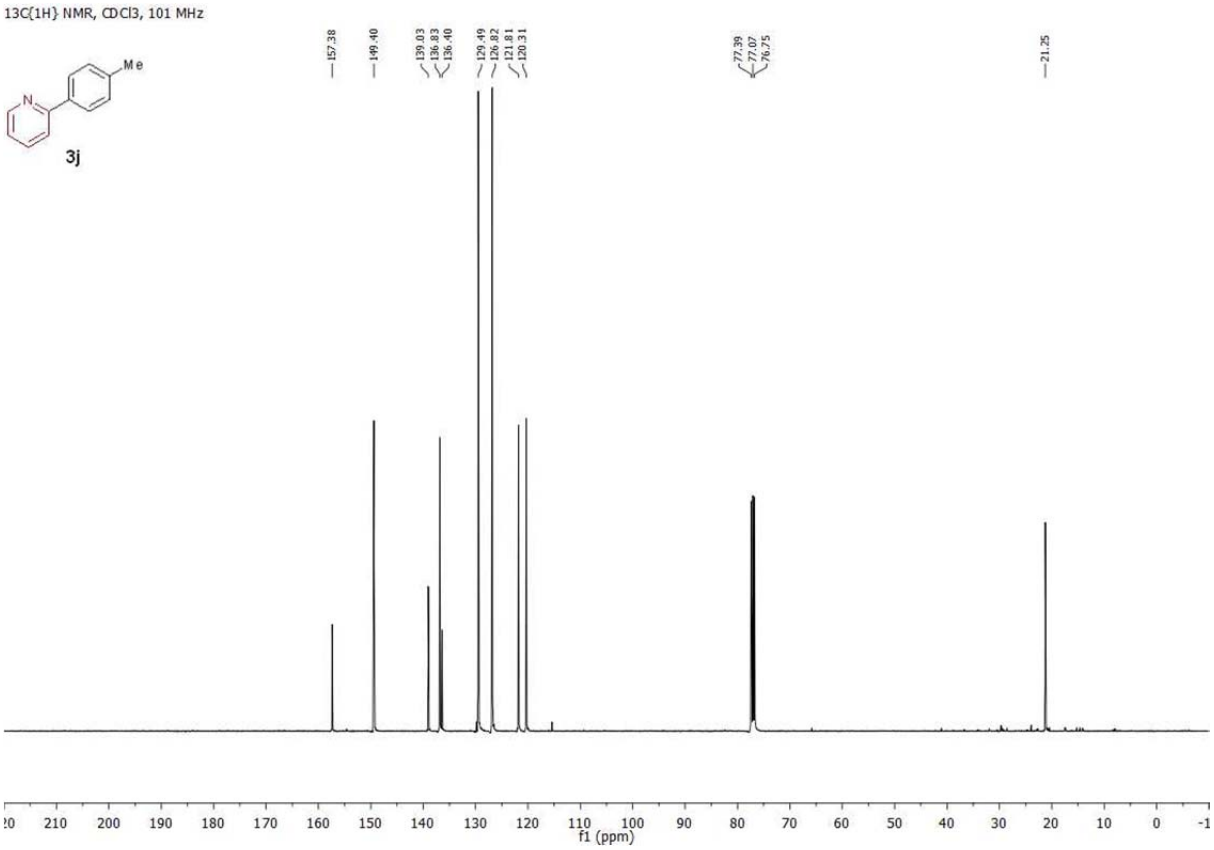


Figure S43. ^{13}C Spectra of **3j**.

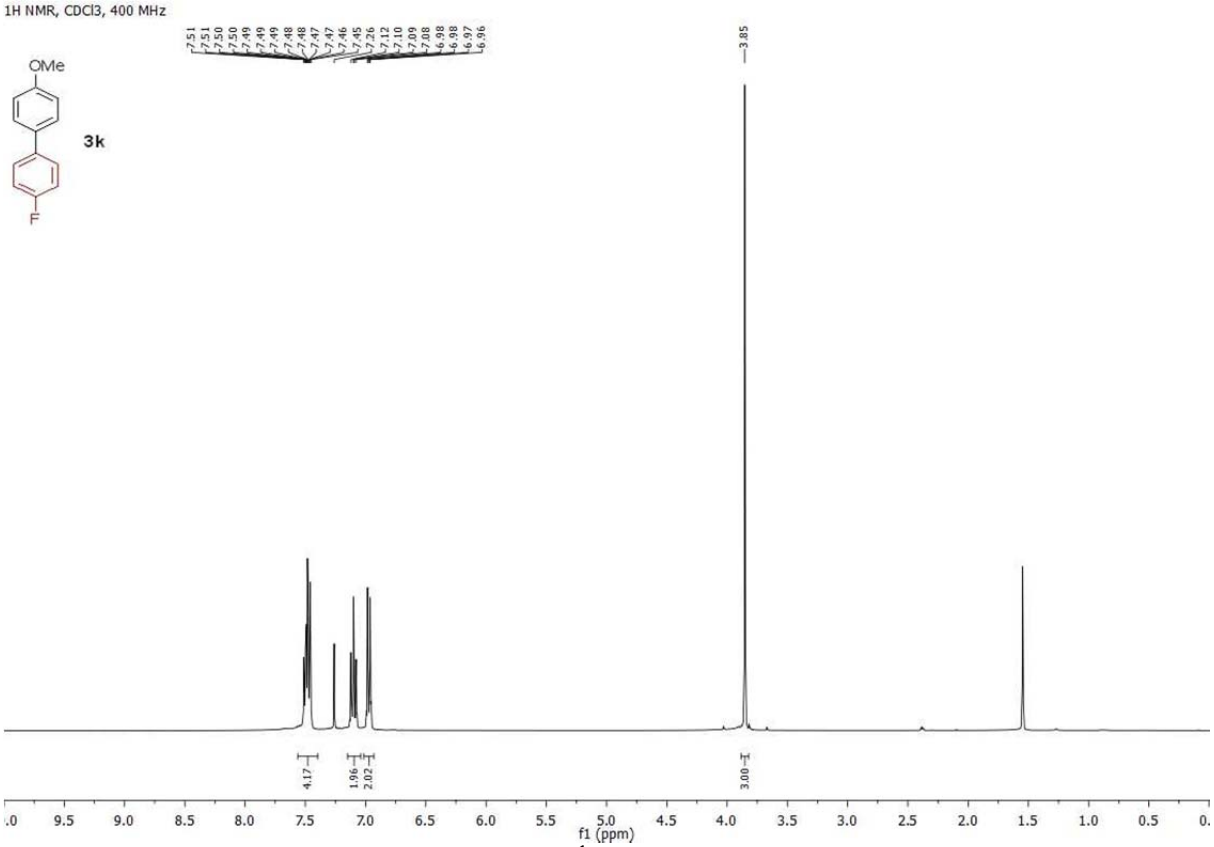


Figure S44. ^{1}H Spectra of **3k**.

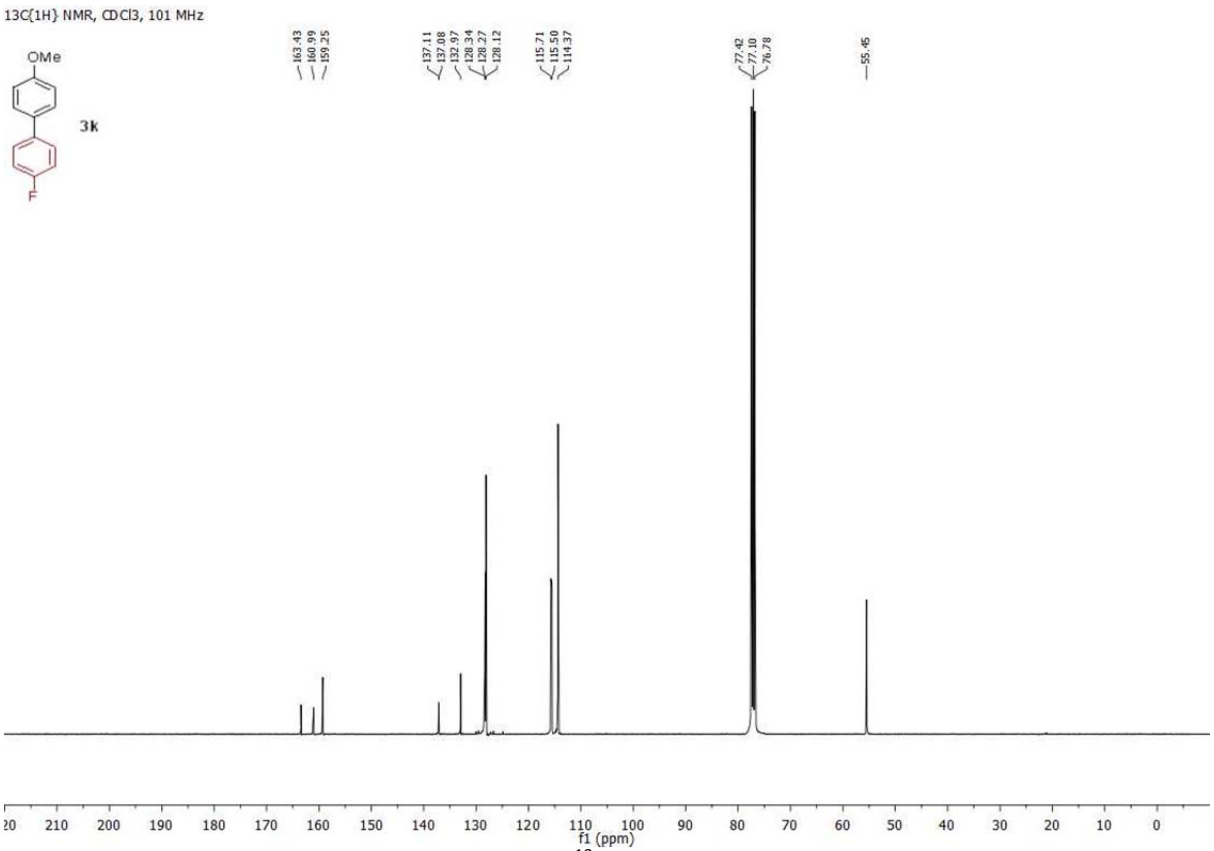


Figure S45. ^{13}C Spectra of **3k**.

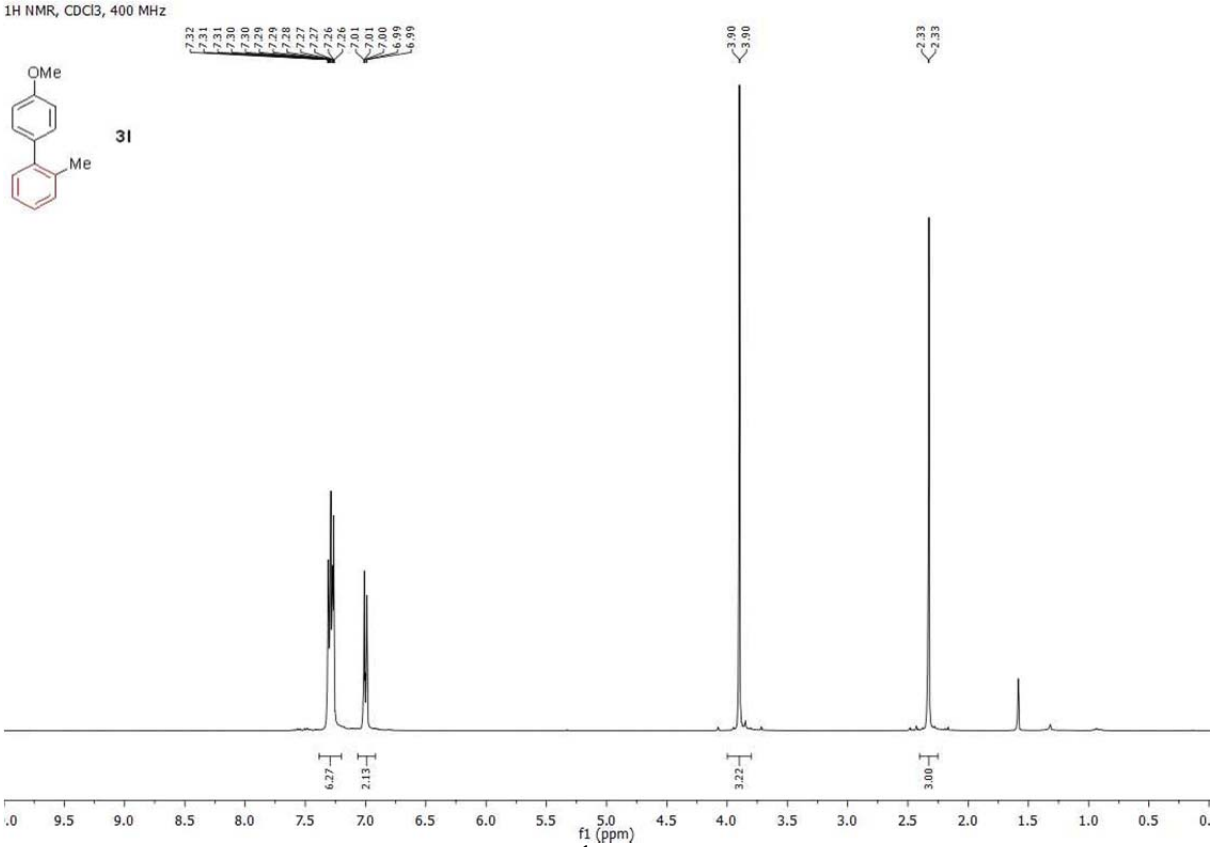


Figure S46. ^{1}H Spectra of **3l**.

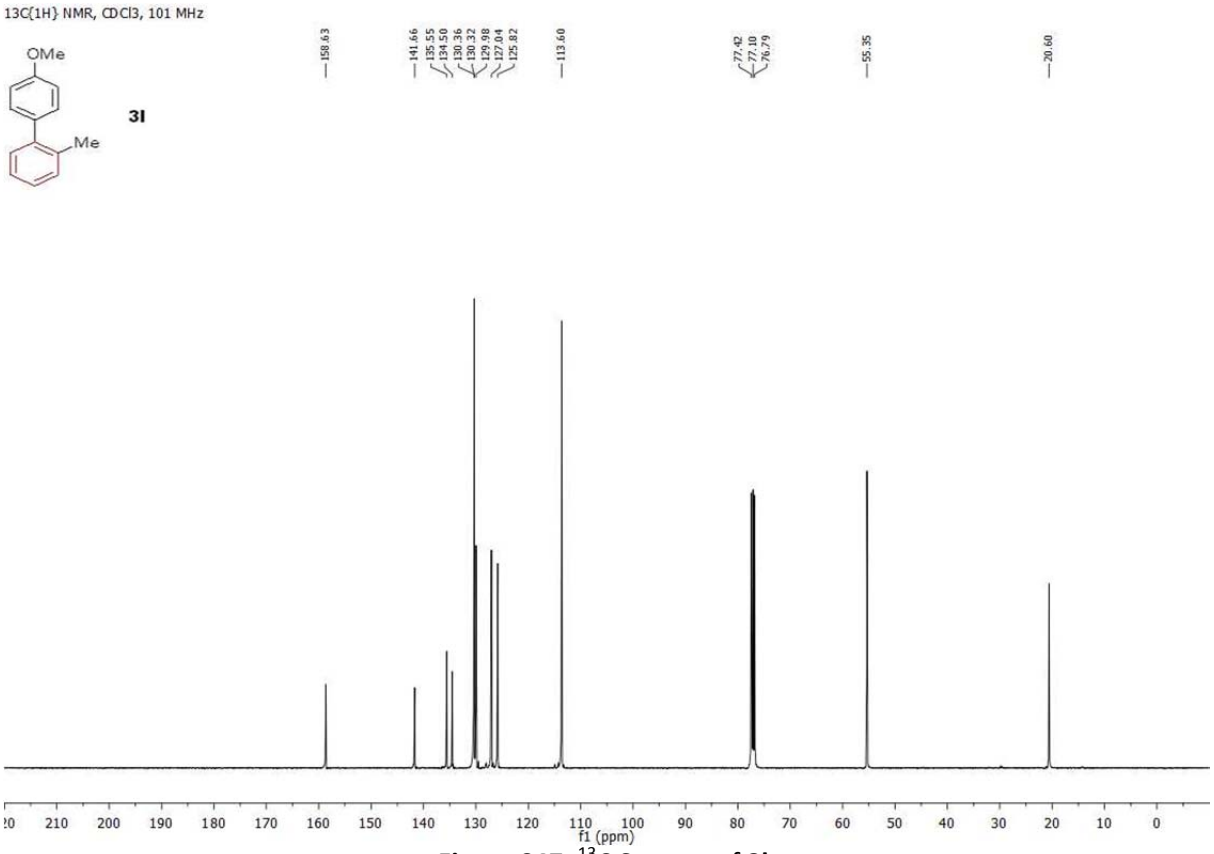


Figure S47. ^{13}C Spectra of **3l**.

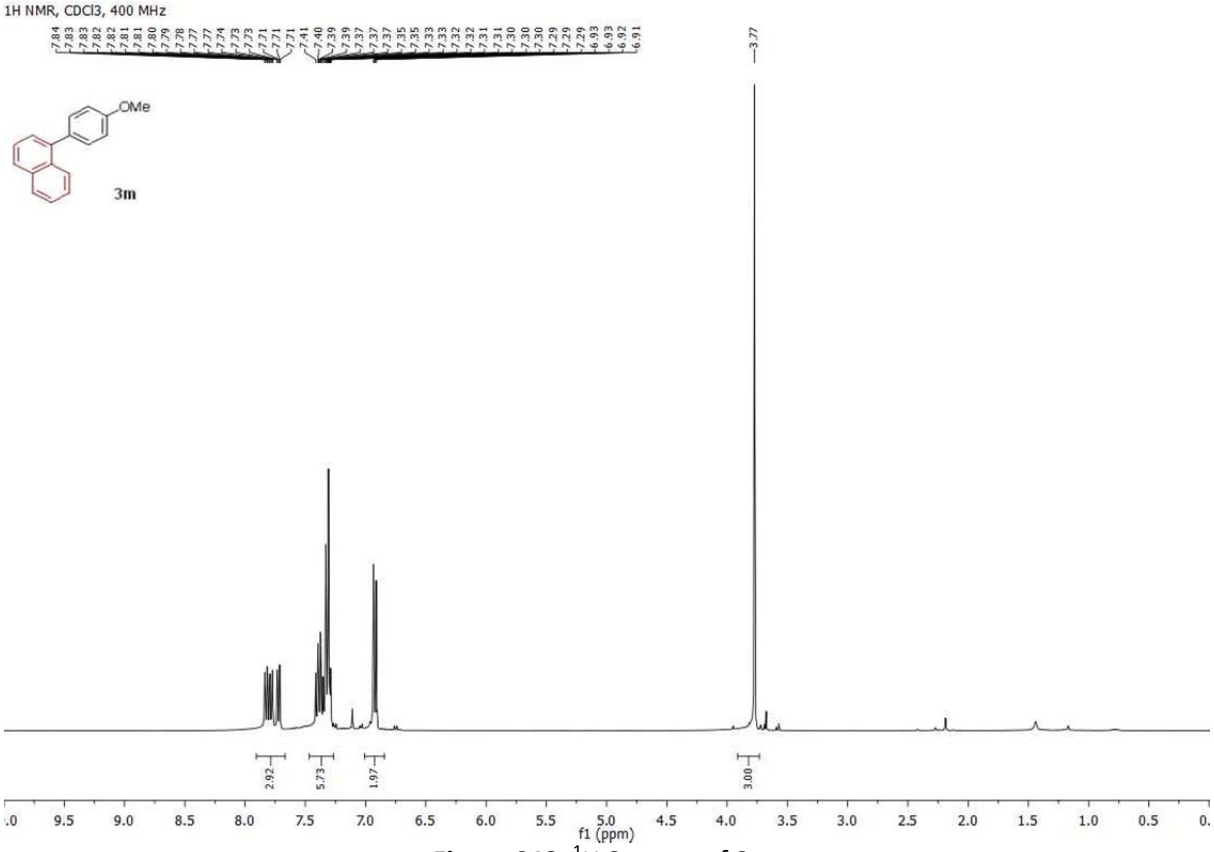


Figure S48. ^{1}H Spectra of **3m**.

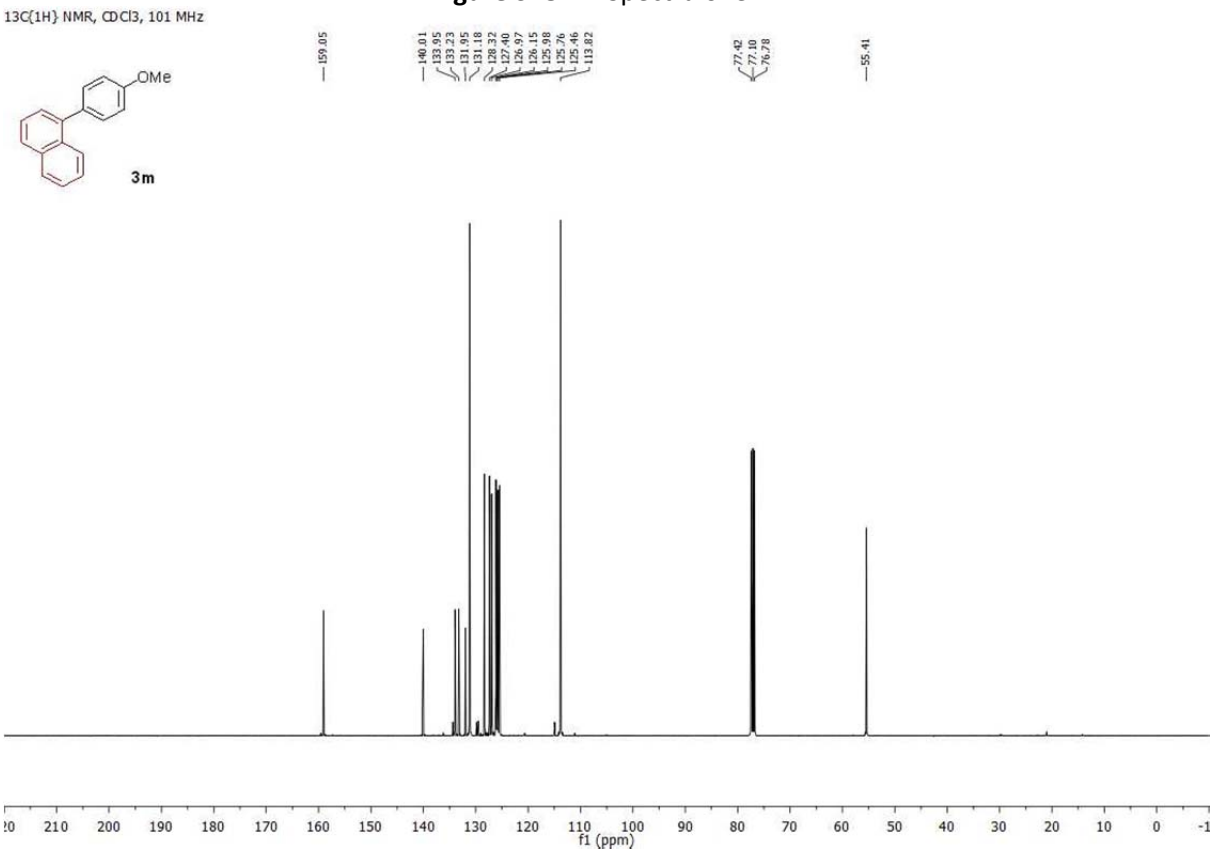


Figure S49. ^{13}C Spectra of **3m**.

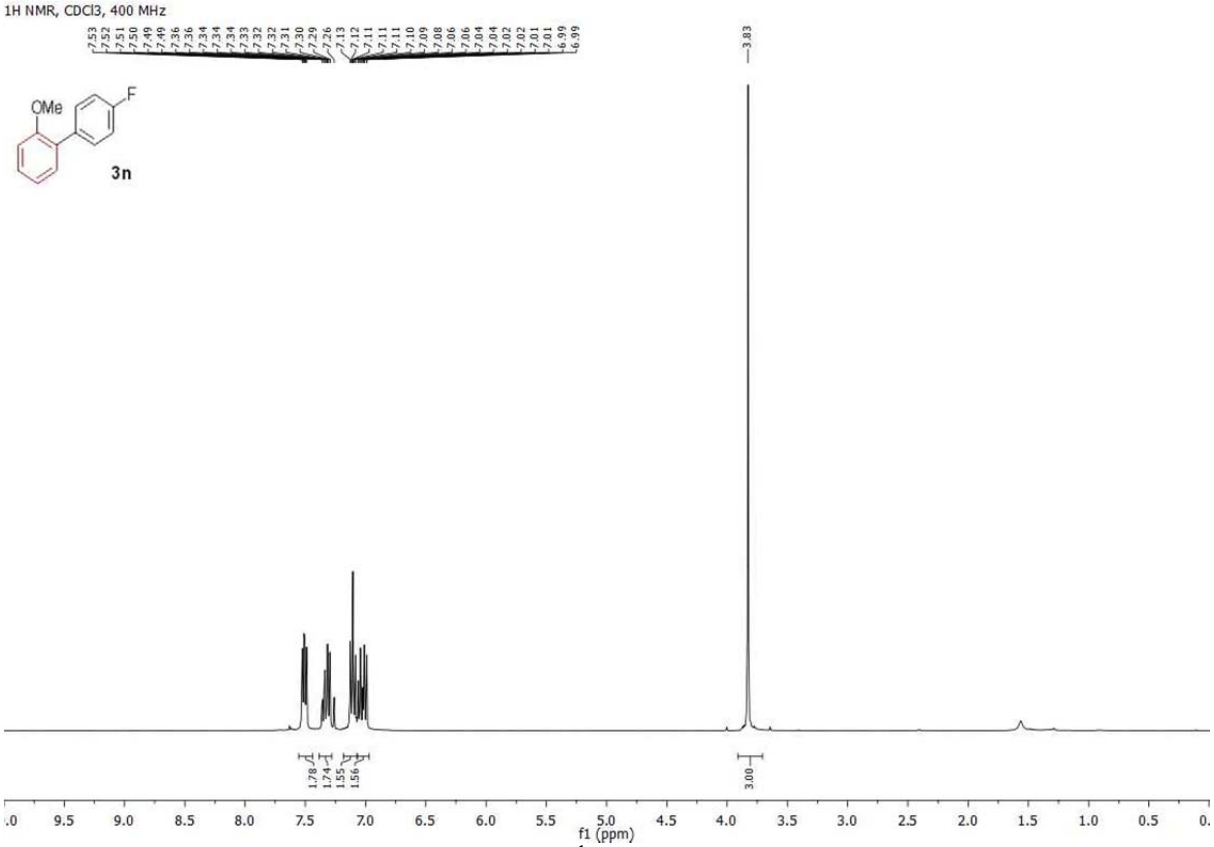


Figure S50. ^{1}H Spectra of **3n**.

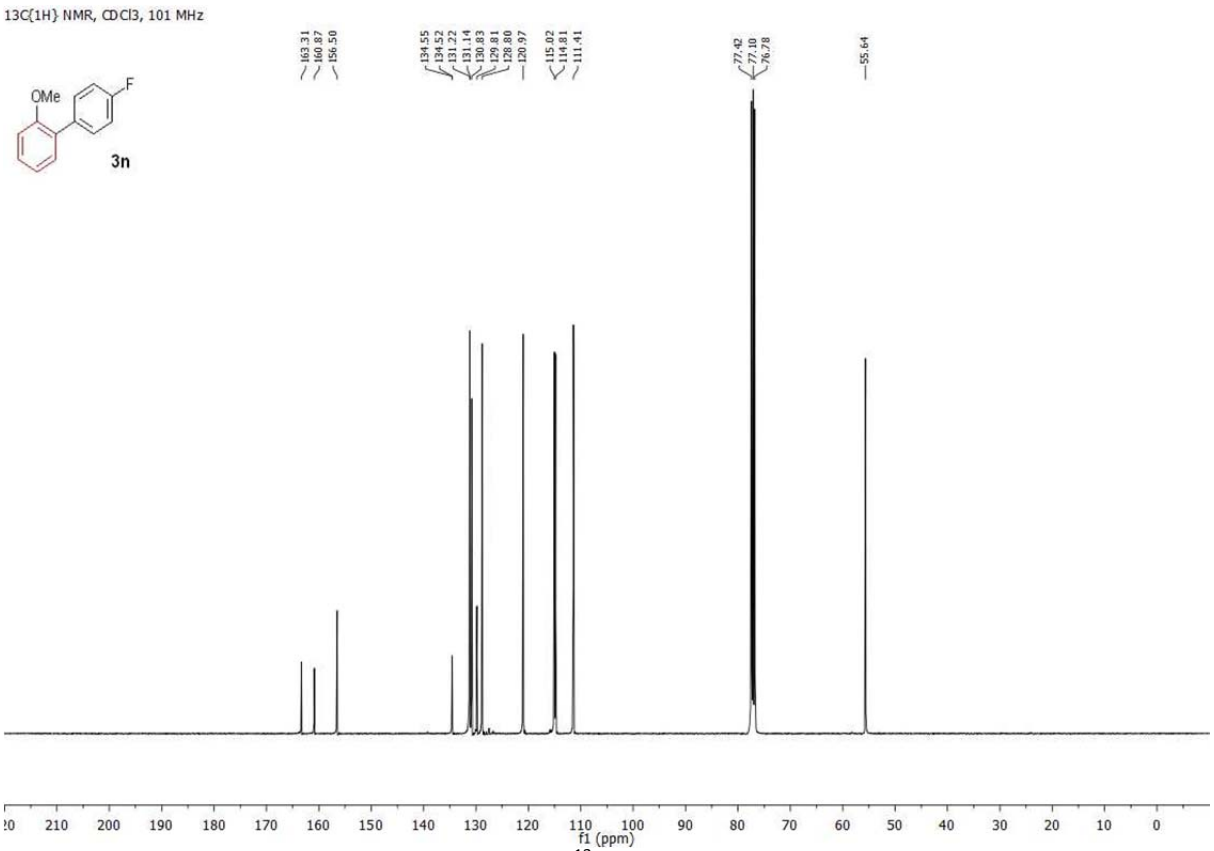


Figure S51. ^{13}C Spectra of **3n**.

References

(1) Tilstam, U.; Weinmann, H. *Org. Process Res. Dev.* **2002**, *6*, 906–910.
(2) Agrawal, T.; Cook, S. P. *Org. Lett.* **2014**, *16*, 5080–5083.
(3) Chua, Y.-Y.; Duong, H. A. *Chem. Comm.* **2014**, *50*, 8424–8427.
(4) Thomas, R. M.; Fedorov, A.; Keitz, B. K.; Grubbs, R. H. *Organometallics* **2011**, *30*, 6713–6717.
(5) Yamamoto, T.; Zhumagazin, A.; Furusawa, T.; Tanaka, T.; Yamakawa, T.; Oe, Y.; Ohta, T. *Adv. Synth. Cat.* **2014**, *356*, 3525–3529.
(6) Wei, S.; Wei, X.-G.; Su, X.; You, J.; Ren, Y. *Chem. Eur. J.* **2011**, *17*, 5965–5971.
(7) Dible, B. R.; Sigman, M. S. *Inorg. Chem.* **2006**, *45*, 8430–8441.
(8) Van Ausdall, B. R.; Glass, J. L.; Wiggins, K. M.; Aarif, A. M.; Louie, J. *J. Org. Chem.* **2009**, *74*, 7935–7942.
(9) Bertho-Gelloz, G.; Siegler, M. A.; Spek, A. L.; Tinant, B.; Reek, J. N. H.; Marko, I. E. *Dalton Trans.* **2010**, *39*, 1444–1446.
(10) Meiries, S.; Duc, G. L.; Chartoire, A.; Collado, A.; Speck, K.; Arachchige, K. S. A.; Slawin, A. M. Z.; Nolan, S. P. *Chem. Eur. J.* **2013**, *19*, 17358–17368.
(11) Luan, X.; Mariz, R.; Gatti, M.; Costabile, C.; Poater, A.; Cavallo, L.; Linden, A.; Dorta, R. *J. Am. Chem. Soc.* **2008**, *130*, 6848–6858.
(12) SMART, version 5.628; Bruker AXS Inc.: Madison, WI, 2001.
(13) SAINT+, version 6.22a; Bruker AXS Inc.: Madison, WI, 2001.
(14) G. W. Sheldrick, SADABS version 2.10; University of Göttingen: Göttingen, Germany, 2001.
(15) *SHELXTL,*version 6.14; Bruker AXS Inc.: Madison, WI, 2000.
(16) Although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date.
(17) Chua, Y.-Y.; Duong, H. A. *Chem. Comm.* **2016**, *52*, 1466–1469.