Supporting Information

2-Aryl-Indenylphosphine Ligands: Design, Synthesis and Application in Pd-Catalyzed Suzuki-Miyaura Coupling Reactions

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1. General experimental information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. Toluene and THF was degassed by sparging with nitrogen for at least 15 min before use. All reactions were performed in a resealable screw cap Schlenk flask (approx. 10 mL volume) in the presence of a Teflon coated magnetic stirrer bar (3 mm × 50 mm). Silica gel (70-230 and 230-400 mesh) was used for column chromatography. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR spectra were recorded on a Mercury-Plus (400 MHz) spectrometer. HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource. Compounds described in the literature were characterized by comparison of their ^{1}H NMR spectra to the previously reported.

Synthesis of 3-dicyclohexyphosphine-2-iodo-1,1-dimethylindene (1). $Pd(OAc)_2$ (114 mg, 0.5 mmol), DPPF (334 mg, 0.6 mmol), 2,3-diiodo-1, 1-dimethylindene (3.96 g, 10 mmol) and *t*BuONa (1.16 g, 12 mmol) were combined in a Schlenk flask (100 mL volume). Under an argon atmosphere toluene (50 mL) was added. After the mixture was stirred for 15 min, dicyclohexyphosphine (1.98 g, 10 mmol) was added. The vial was sealed with a cap containing a PTFE septum. The vial was then heated to 110 ℃ with vigorous stirring for 17 h. The cooled reaction mixture was then filtered through a bed of silica and washed down with CH_2Cl_2 (50 mL). The solution was concentrated, and the resulting crude material was purified by flash chromatography, giving the product as a white solid in 49% yield (2.28 g, 4.9 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 8.0 Hz, 1 H, Ar), 7.40 (d, J = 8.0 Hz, 1 H, Ar), 7.25-7.17 (m, 2 H, Ar), 2.41 (s, 2 H, Cy), 1.96 (s, 2 H, Cy), 1.81 (s, 2 H, Cy), 1.61 (t, J = 8.0 Hz, 5 H, Cy), 1.47 (s, 3 H, Cy), 1.38-1.31 (m, 6 H, Cy), 1.22 (s, 6 H, $(CH_3)_2$-C), 1.19-1.11 (m, 5 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0 (s, *C*-PCy_2), 142.9 (s, Ar), 126.3 (s, Ar), 125.0 (s, Ar), 122.1 (s, Ar), 121.1 (s, *C*-I), 54.9 (d, $J_{C\text{-}P}$ = 5.0 Hz, *C*-$(CH_3)_2$), 34.1 (s, Cy), 32.1 (s, Cy), 31.9 (s, Cy), 30.1 (d, $J_{C\text{-}P}$ = 9.0 Hz, $(CH_3)_2$-C), 26.9 (d, $J_{C\text{-}P}$ = 6.0 Hz, Cy), 26.7 (s, Cy), 26.2 (s, Cy), 25.9 (s, Cy). ^{31}P NMR (162 MHz, $CDCl_3$): δ 0.5 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{23}H_{32}IP$: 467.1359, found: 467.1354.

General procedure for preparation of indenylphosphine ligands.

Method A

To a mixture of 3-dicyclohexyphosphine-2-iodo-1, 1-dimethylindene (1.0 mmol), arylboronic acid (1.2 mmol), $K_3PO_4 \cdot 3H_2O$ (3.0 mmol), $Pd(OAc)_2$ (1 mol %) was charged degassed THF. The mixture was pumped and refilled with nitrogen three times. The resulting mixture was stirred at 110 ℃ under nitrogen for 24 h, and then cooled to room temperature, partioned with water (10 mL) and dichloromethane (10 mL). The organic layer was separated, dried over sodium sulfate, concentrated, and purified by silica gel column chromatography to provide phosphine ligands.

Method B

Step 1: $Pd(dba)_2$ (0.009 mmol), a phosphine ligand (0.018 mmol), KOAc (3.0 mmol) and bis(pinacolato)diboron (0.54 mmol) was loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar. aryl bromide (0.45 mmol) and dioxane (1.5 mL) were added. The tube was evacuated and flushed with nitrogen three times, and then placed in a preheated oil bath with the temperature indicated in the table and stirred for 12 h. After completion of the reaction, the reaction tube was allowed to cool to room temperature. partioned with water (10 mL) and dichloromethane (10 mL). The organic layer was separated, dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by column chromatography on silica gel to afford the desired arylboronic ester.

Step 2: To a mixture of 3-dicyclohexyphosphine-2-iodo-1, 1-dimethylindene (1.0 mmol), arylboronic ester (1.5 mmol), K_3PO_4 $3H_2O$ (3.0 mmol), $Pd(OAc)_2$ (3 mol %) was charged degassed dioxane (1.5 mL). The mixture was pumped and refilled with nitrogen three times. The resulting mixture was stirred at 110 ℃ under nitrogen for 24 h, and then cooled to room temperature, partioned with water (10 mL) and dichloromethane (10 mL). The organic layer was separated, dried over sodium sulfate,

concentrated, and purified by silica gel column chromatography to provide phosphorous ligands.

General procedure for Suzuki-Miyaura cross-coupling reaction. To a mixture of aryl chloride or heteroaryl chloride (1.0 mmol), arylboronic acid (1.2 mmol), K_3PO_4 (3 mmol), $Pd(OAc)_2$ (0.5 mol %), ligand (1 mol %) was charged degassed THF. The mixture was pumped and refilled with nitrogen three times. The resulting mixture was stirred at 110 ℃ under nitrogen for 3 h, and then cooled to room temperature, partioned with water (10 mL) and dichloromethane (10 mL). The organic layer was separated, dried over sodium sulfate, concentrated, and purified by silica gel column chromatography to provide biaryl compounds.

3-dicyclohexyphosphine-2-phenyl-1,1-dimethylindene (2). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.0 Hz, 1 H, Ar), 7.41-7.32 (m, 4 H, Ar, Ph), 7.28 (t, *J* = 8.0 Hz, 1 H, Ar), 7.24 (t, *J* = 4.0 Hz, 1 H, Ph), 7.10 (d, *J* = 8.0 Hz, 2 H, Ph), 2.25 (s, 2 H, Cy), 1.83 (d, *J* = 8.0 Hz, 2 H, Cy), 1.73 (d, *J* = 12.0 Hz, 2 H, Cy), 1.61 (d, *J* = 8.0 Hz, 5 H, Cy), 1.24 (s, 8 H, Cy, (C*H*$_3$)$_2$-C), 1.22-1.09 (m, 8 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0 (s, Ar), 143.8 (s, *C*-Ph), 137.4 (d, $J_{C\text{-}P}$ = 6.0 Hz, Ph), 132.6 (s, *C*-PCy_2), 132.4 (s, Ar), 129.5 (s, Ph), 127.6 (s, Ph), 127.0 (s, Ar), 126.3 (s, Ph), 124.9 (s, Ar), 122.2 (s, Ar), 121.5 (s, Ar), 52.4 (d, $J_{C\text{-}P}$ = 5.0 Hz, *C*-$(CH_3)_2$), 33.8 (s, Cy), 33.7 (s, Cy), 32.3 (s, Cy), 32.1 (s, Cy), 30.5 (d, $J_{C\text{-}P}$ = 10.0 Hz, (*C*H$_3$)$_2$-C), 27.1 (d, $J_{C\text{-}P}$ = 8.0 Hz, Cy), 26.9 (s, Cy), 26.8 (s, Cy), 26.2 (s, Cy), 24.3 (s, Cy) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ -18.9 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{29}H_{37}P$: 417.2706, found: 417.2706.

3-dicyclohexyphosphine-2-(2-methylphenyl)-1,1-dimethylindene (3). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1 H, Ar), 7.35 (d, *J* = 8.0 Hz, 1 H, Ph), 7.23-7.15 (m, 5 H, Ar, Ph), 6.94 (d, *J* = 8.0 Hz, 1 H, Ph), 2.50 (s, 1 H, Cy), 2.21 (s, 3 H, C*H*$_3$-Ph), 2.06 (s, 1 H, Cy), 1.84-1.66 (m, 10 H, Cy), 1.29-1.09 (m, 16 H, Cy, (C*H*$_3$)$_2$-C).^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3 (s, Ar), 143.7 (s, *C*-Ph), 136.1 (s, Ph), 136.0 (s, Ph), 133.3 (s, *C*-PCy_2), 133.1 (s, Ar), 130.1 (s, Ph), 129.9 ,(s, Ph) 127.1

(s, Ar), 126.2 (s, Ph), 124.6 (s, Ph), 124.3 (s, Ar), 122.3 (s, Ar), 121.3 (s, Ar), 53.6 (d, $J_{C\text{-}P}$ = 6.0 Hz, *C*-$(CH_3)_2$), 35.4 (s, Cy), 35.3 (s, Cy), 33.5 (d, $J_{C\text{-}P}$ = 9.0 Hz, $(CH_3)_2$-C), 33.1 (s, Cy), 32.8 (s, Cy), 32.2 (s, Cy), 32.0 (s, Cy), 30.8 (s, Cy), 27.4 (s, Cy), 27.3 (s, Cy), 26.5 (s, Cy), 26.4 (s, Cy), 26.0 (s, Cy), 23.8 (s, Cy), 21.1 (s, *CH*$_3$-Ph). ^{31}P NMR (162 MHz, $CDCl_3$): δ -16.6 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{30}H_{39}P$: 431.2873, found: 431.2878.

3-dicyclohexyphosphine-2-(3-methylphenyl)-1,1-dimethylindene (4). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 4.0 Hz, 1 H, Ar), 7.38 (d, *J* = 8.0 Hz, 1 H, Ph), 7.29 (d, *J* = 4.0 Hz, 2 H, Ar), 7.26-7.20 (m, 1 H, Ph), 7.16 (d, *J* = 8.0 Hz, 1 H, Ar), 6.88 (s, 2 H, Ph), 2.39 (s, 3 H, C*H*$_3$-Ph), 2.24 (s, 2 H, Cy), 1.83 (d, *J* = 8.0 Hz, 2 H, Cy), 1.73 (d, *J* = 12.0 Hz, 2 H, Cy), 1.60 (s, 5 H, Cy), 1.33 (d, *J* = 12.0 Hz, 2 H, Cy), 1.24 (s, 6 H, $(CH_3)_2$-C), 1.17-1.09 (m, 9 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1 (s, Ar), 144.0 (s, *C*-Ph), 137.4 (s, Ph), 137.0 (s, Ph), 132.4 (s, *C*-PCy_2), 132.2 (s, Ar), 130.1 (s, Ph), 127.9 (s, Ph), 127.5 (s, Ar), 126.7 (s, Ar), 126.3 (s, Ph), 124.9 (s, Ph), 122.2 (s, Ar), 121.5 (s, Ar), 52.4 (d, $J_{C\text{-}P}$ = 5.0 Hz, *C*-$(CH_3)_2$), 33.9 (d, $J_{C\text{-}P}$ = 10.0 Hz, $(CH_3)_2$-C), 32.4 (s, Cy), 32.2 (s, Cy), 30.5 (s, Cy), 30.4 (s, Cy), 27.2 (s, Cy), 27.1 (s, Cy), 27.0 (s, Cy), 26.9 (s, Cy), 26.3 (s, Cy), 24.4 (s, Cy), 21.7 (s, *C*H_3-Ph). ^{31}P NMR (162 MHz, $CDCl_3$): δ -18.93 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{30}H_{39}P$: 431.2873, found: 431.2879.

3-dicyclohexyphosphine-2-(3-methoxyphenyl)-1,1-dimethylindene (5). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1 H, Ar), 7.35-7.33 (m, 1 H, Ar), 7.30 (d, *J* = 8.0 Hz, 1 H, Ar), 7.23 (d, *J* = 4.0 Hz, 1 H, Ar), 7.21 (s, 1 H, Ph), 6.87-6.84 (m, 1 H, Ph), .6.67 (d, *J* = 8.0 Hz, 1 H, Ph), 6.61-6.60 (m, 1 H, Ph), 3.81 (s, 3 H, C*H*$_3$O-Ph), 2.25 (s, 2 H, Cy), 1.84 (d, *J* = 8.0 Hz, 2 H, Cy), 1.72 (d, *J* = 8.0 Hz, 2 H, Cy), 1.60 (d, *J* = 4.0 Hz, 5 H, Cy), 1.24 (s, 10 H, Cy, $(CH_3)_2$-C), 1.19-1.09 (m, 8 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8 (s, Ph), 151.0 (s, Ar), 141.7 (s, *C*-Ph), 136.8 (s, Ph), 130.6 (s, *C*-PCy_2), 130.4 (s, Ar), 126.7 (s, Ar), 124.4 (s, Ph), 123.0 (s, Ar), 120.3 (s, Ar), 120.2 (s, Ar), 119.6 (s, Ph), 113.9 (s, Ph), 110.1 (s, Ph), 53.3 (s, *C*H_3O-Ph), 50.7 (d, $J_{C\text{-}P}$ = 6.0 Hz, *C*-$(CH_3)_2$), 32.2 (s, Cy), 32.1 (s, Cy), 30.8 (s, Cy),

30.6 (s, Cy), 28.9 (d, $J_{C\text{-}P}$ = 10.0 Hz, (CH$_3$)$_2$-C), 25.5 (s, Cy), 25.4 (s, Cy), 25.4 (s, Cy), 25.2 (s, Cy), 24.6 (s, Cy), 22.8 (s, Cy). ^{31}P NMR (162 MHz, CDCl$_3$): δ -18.89 (s). HRMS (ESI/ [M+H]$^+$) Cacld. for $C_{30}H_{39}OP$: 447.2817, found: 447.2824.

3-dicyclohexyphosphine-2-(4-ethylphenyl)-1,1-dimethylindene (6). White solid, ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.64 (d, J = 8.0 Hz, 1 H, Ar), 7.37 (d, J = 4.0 Hz, 1 H, Ar), 7.29 (d, J = 8.0 Hz, 1 H, Ar), 7.22 (d, J = 8.0 Hz, 3 H, Ar, Ph), 7.01 (d, J = 8.0 Hz, 2 H, Ph), 2.73-2.67 (m, 2 H, CH_2-Ph), 2.25 (s, 2 H, Cy), 1.84 (d, J = 8.0 Hz, 2 H, Cy), 1.73 (d, J = 12.0 Hz, 2 H, Cy), 1.59 (s, 5 H, Cy), 1.29 (t, J = 8.0 Hz, 4 H, Cy, CH_3CH$_2$-Ph), 1.23 (s, 6 H, (CH_3)$_2$-C), 1.21-1.09 (m, 9 H, Cy). ^{13}C NMR(100 MHz, CDCl$_3$): δ 153.2 (s, Ar), 144.0 (s, C-Ph), 144.0 (s, Ph), 142.6 (s, Ph), 134.6 (s, C-PCy$_2$), 134.5 (s, Ar), 132.4 (s, Ar), 132.2 (s, Ph), 129.4 (s, Ph), 127.2 (s, Ph), 126.3 (s, Ar), 124.8 (s, Ph), 122.2 (s, Ar), 121.6 (s, Ar), 52.5 (d, $J_{C\text{-}P}$ = 5.0 Hz, C-(CH$_3$)$_2$), 33.9 (d, $J_{C\text{-}P}$ = 10.0 Hz, (CH$_3$)$_2$-C), 30.6 (s, Cy), 30.5 (s, Cy), 28.5 (s, Cy), 27.2 (s, Cy), 27.1 (s, Cy), 27.1 (s, Cy), 27.0 (s, Cy), 26.3 (s, CH$_2$-Ph), 24.4 (s, Cy), 15.0 (s, CH$_3$-CH$_2$Ph). ^{31}P NMR (162 MHz, CDCl$_3$): δ -17.8 (s). HRMS (ESI/ [M+H]$^+$) Cacld. for $C_{31}H_{41}P$: 445.3024, found: 445.3025.

3-dicyclohexyphosphine-2-(4-tert-butylphenyl)-1,1-dimethylindene (7). White solid, ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.65 (d, J = 8.0 Hz, 1 H, Ar), 7.37 (t, J = 8.0 Hz, 3 H, Ar), 7.28 (d, J = 4.0 Hz, 1 H, Ph), 7.23 (d, J = 8.0 Hz, 1 H, Ph), 7.03 (d, J = 8.0 Hz, 2 H, Ph), 2.20 (s, 2 H, Cy), 1.84 (s, 2 H, Cy), 1.71 (s, 2 H, Cy), 1.59 (s, 5 H, Cy), 1.36 (s, 9 H, (CH_3)$_3$C-Ph), 1.22 (s, 9 H, Cy, (CH_3)$_2$-C), 1.18-1.09 (m, 7 H, Cy). ^{13}C NMR (100 MHz, CDCl$_3$): δ 153.1 (s, Ar), 149.3 (s, C-CPh), 144.1 (s, Ph), 134.1 (s, C-PCy$_2$), 131.9 (s, Ar), 131.7 (s, Ar), 129.0 (s, Ar), 126.2 (s, Ph), 124.7 (s, Ph), 124.5 (s, Ph), 122.1 (s, Ar), 121.4 (s, Ar), 52.5 (d, $J_{C\text{-}P}$ = 5.0 Hz, C-(CH$_3$)$_2$), 34.4 (s, Cy), 33.7 (d, $J_{C\text{-}P}$ = 10.0 Hz, (CH$_3$)$_2$-C), 32.4 (s, Cy), 32.2 (s, C-Ph), 31.3 (s, (CH$_3$)$_3$-CPh), 30.5 (s, Cy), 30.4 (s, Cy), 27.1 (s, Cy), 27.0 (s, Cy), 26.9 (s, Cy), 26.2 (s, Cy), 24.3 (s, Cy). ^{31}P NMR (162 MHz, CDCl$_3$): δ -19.0 (s). HRMS (ESI/ [M+H]$^+$) Cacld. for $C_{33}H_{45}P$: 473.3332, found: 473.3333.

3-dicyclohexyphosphine-2-(4-methoxyphenyl)-1,1-dimethylindene (8). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 4.0 Hz, 1 H, Ar), 7.38 (d, *J* = 8.0 Hz, 1 H, Ar), 7.29 (d, *J* = 8.0 Hz, 1 H, Ar), 7.24 (d, *J* = 8.0 Hz, 1 H, Ar), 7.03 (d, *J* = 8.0 Hz, 2 H, Ph), 6.94 (d, *J* = 8.0 Hz, 2 H, Ph), 3.84 (s, 3 H, C*H*$_3$O-Ph), 2.28 (s, 2 H, Cy), 1.85 (s, 2 H, Cy), 1.74 (d, *J* = 12.0 Hz, 2 H, Cy), 1.60 (s, 5 H, Cy), 1.26 (s, 5 H, Cy), 1.23 (s, 6 H, (C*H*$_3$)$_2$-C), 1.21-1.12 (m, 6 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6 (s, Ph), 153.2 (s, Ar), 143.9 (d, $J_{C\text{-}P}$ = 5.0 Hz, *C*-Ph), 130.6 (s, *C*-PCy$_2$), 129.6 (d, $J_{C\text{-}P}$ = 6.0 Hz, Ar), 126.3 (s, Ph), 124.9 (s, Ph), 122.2 (s, Ar), 121.6 (s, Ar), 113.3 (s, Ph), 55.0 (d, $J_{C\text{-}P}$ = 2.0 Hz, *C*H$_3$O-Ph), 52.4 (d, $J_{C\text{-}P}$ = 5.0 Hz, *C*-(CH$_3$)$_2$), 33.9 (s, Cy), 33.8 (s, Cy), 32.5 (s, Cy), 32.3 (s, Cy), 30.6 (d, $J_{C\text{-}P}$ = 9.0 Hz, (*C*H$_3$)$_2$-C), 27.2 (s, Cy), 27.1 (s, Cy), 27.1 (s, Cy), 26.9 (s, Cy), 26.3 (s, Cy), 24.4 (s, Cy) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ -19.0 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{30}H_{39}OP$: 447.2817, found: 447.2823.

3-dicyclohexyphosphine-2-(4-ethoxyphenyl)-1,1-dimethylindene (9). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 4.0 Hz, 1 H, Ar), 7.36 (t, *J* = 4.0 Hz, 1 H, Ar), 7.28 (d, *J* = 4.0 Hz, 1 H, Ar), 7.24 (d, *J* = 8.0 Hz, 1 H, Ar), 7.01 (d, *J* = 8.0 Hz, 2 H, Ph), 6.93 (d, *J* = 12.0 Hz, 2 H, Ph), 4.09-4.04 (m, 2 H, C*H*$_2$O-Ph), 2.27 (s, 2 H, Cy), 1.85 (s, 2 H, Cy), 1.71 (s, 2 H, Cy), 1.59 (s, 5 H, Cy), 1.44 (t, *J* = 4.0 Hz, 3 H, C*H*$_3$CH$_2$O-Ph), 1.23 (s, 10 H, Cy, (C*H*$_3$)$_2$-C), 1.17-1.09 (m, 7 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0 (s, Ph), 151.1 (s, Ar), 142.0 (s, *C*-Ph), 128.6 (s, *C*-PCy$_2$), 127.5 (d, $J_{C\text{-}P}$ = 6.0 Hz, Ar), 124.3 (s, Ph), 122.9 (s, Ar), 120.2 (s, Ph), 119.6 (s, Ar), 111.8 (s, Ph), 61.4 (s, *CH*$_2$-OPh), 50.6 (d, $J_{C\text{-}P}$ = 6.0 Hz, *C*-(CH$_3$)$_2$), 32.1 (s, Cy), 28.8 (s, (*C*H$_3$)$_2$-C), 25.5 (s, Cy), 25.4 (s, Cy), 25.4 (s, Cy), 25.2 (s, Cy), 24.6 (s, Cy), 22.7 (s, Cy), 13.3 (s, *C*H$_3$-CH$_2$OPh). ^{31}P NMR (162 MHz, $CDCl_3$): δ -19.0 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{31}H_{41}OP$: 461.2979, found: 461.2987.

3-dicyclohexyphosphine-2-(3,4,5-trimethoxyphenyl)-1,1-dimethyl indene (10). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.0 Hz, 1 H, Ar), 7.38 (d, *J* = 8.0 Hz, 1 H, Ar), 7.30 (d, *J* = 8.0 Hz, 1 H, Ar), 7.25 (d, *J* = 8.0 Hz, 1 H, Ar), 6.30 (s, 2 H, Ph), 3.92 (s, 3 H, (C*H*$_3$O)$_3$-Ph), 3.85 (s, 6 H, (C*H*$_3$O)$_3$-Ph), 2.26 (s, 2 H, Cy), 1.88

(s, 2 H, Cy), 1.75 (d, *J* = 8.0 Hz, 2 H, Cy), 1.65-1.51 (m, 5 H, Cy), 1.26 (s, 8 H, Cy, (CH_3)$_2$-C), 1.18-1.10 (m, 8 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9 (s, Ph), 152.5 (s, Ar), 143.7 (s, *C*-Ph), 137.1 (s, Ph), 132.8 (s, *C*-PCy_2), 132.4 (s, Ph), 132.2 (s, Ar), 126.3 (s, Ar), 125.0 (s, Ar), 122.2 (s, Ar), 121.5 (s, Ar), 106.8 (s, Ph), 60.8 (s, *C*H_3-OPh), 56.0 (s, *C*H_3-OPh), 52.4 (d, J_{C-P} = 5.0 Hz, *C*-(CH_3)$_2$), 33.7 (s, Cy), 33.6 (s, Cy), 32.4 (s, Cy), 32.2 (s, Cy), 30.6 (d, J_{C-P} = 10.0 Hz, (*C*H_3)$_2$-C), 27.1 (s, Cy), 27.0 (s, Cy), 26.9 (s, Cy), 26.8 (s, Cy), 26.2 (s, Cy), 24.5 (s, Cy). ^{31}P NMR (162 MHz, $CDCl_3$): δ -18.7 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{32}H_{43}O_3P$: 507.3023, found: 507.3021.

3-dicyclohexyphosphine-2-indenyl-1,1-dimethylindene (11). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1 H, Ar), 7.48 (d, *J* = 4.0 Hz, 1 H, Ar), 7.43 (d, *J* = 8.0 Hz, 1 H, Ar), 7.37 (d, *J* = 8.0 Hz, 1 H, Ar), 7.29 (d, *J* = 4.0 Hz, 2 H, Ar), 7.25 (d, *J* = 8.0 Hz, 1 H, Ar), 7.18 (t, *J* = 8.0 Hz, 1 H, Ar), 6.87 (s, 1 H, Ar), 3.89 (s, 2 H, C*H*$_2$-Ar), 2.37 (s, 2 H, Cy), 1.93 (s, 2 H, Cy), 1.77 (s, 2 H, Cy), 1.61 (s, 5 H, Cy), 1.37 (s, 6 H, (CH_3)$_2$-C), 1.33-1.26 (m, 4 H, Cy), 1.21-1.10 (m, 7 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6 (s, Ar), 144.8 (s, Ar), 143.5 (s, Ar), 143.4 (s, *C*-Ar), 133.5 (s, *C*-PCy_2), 133.2 (s, *C*-Ar), 133.0 (s, Ar), 131.4 (s, Ar), 126.2 (s, Ar), 126.1 (s, Ar), 124.9 (s, Ar), 124.3 (s, Ar), 123.3 (s, Ar), 122.0 (s, Ar), 121.3 (s, Ar), 120.7 (s, *C*H=C), 52.6 (d, J_{C-P} = 6.0 Hz, *C*-(CH_3)$_2$), 45.3 (d, J_{C-P} = 14.0 Hz, *C*H_2-Ar), 34.2 (s, Cy), 34.1 (s, Cy), 32.9 (s, Cy), 32.7 (s, Cy), 30.6 (d, J_{C-P} = 9.0 Hz, (*C*H_3)$_2$-C), 27.3 (s, Cy), 27.2 (s, Cy), 27.1 (s, Cy), 27.0 (s, Cy), 26.4 (s, Cy), 25.2 (s, Cy). ^{31}P NMR (162 MHz, $CDCl_3$): δ -17.8 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{32}H_{39}P$: 455.2862, found: 455.2862.

3-dicyclohexyphosphine-2-(4-biphenyl)-1,1-dimethylindene (12). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.58 (m, 4 H, Ph), 7.42 (t, *J* = 4.0 Hz, 2 H, Ph), 7.37-7.28 (m, 2 H, Ph), 7.25-7.22 (m, 2 H, Ar), 7.15 (d, *J* = 8.0 Hz, 2 H, Ar), 2.28 (s, 2 H, Cy), 1.85 (s, 2 H, Cy), 1.73 (d, *J* = 8.0 Hz, 2 H, Cy), 1.60 (s, 5 H, Cy), 1.27 (d, *J* = 8.0 Hz, 10 H, Cy, (CH_3)$_2$-C), 1.18-1.11 (m, 7 H, Cy), 0.92-0.86 (m, 2 H, Cy). ^{13}C

NMR (100 MHz, $CDCl_3$): δ 153.0 (s, Ar), 143.7 (s, *C*-Ph), 140.8 (s, Ph), 139.5 (s, Ph), 136.4 (d, $J_{C\text{-}P}$ = 7.0 Hz, Ph), 129.9 (s, *C*-PCy_2), 128.5 (s, Ar), 126.9 (s, Ph), 126.3 (s, Ph), 124.9 (s, Ph), 122.2 (s, Ar), 121.5 (s, Ar), 52.7 (d, $J_{C\text{-}P}$ = 5.0 Hz, *C*-$(CH_3)_2$), 34.1 (s, Cy), 34.0 (s, Cy), 32.6 (s, Cy), 32.4 (s, Cy), 30.8 (d, $J_{C\text{-}P}$ = 9.0 Hz, $(CH_3)_2$-C), 29.8 (s, Cy), 27.4 (s, Cy), 27.3 (s, Cy), 27.2 (s, Cy), 27.1 (s, Cy) , 26.5 (s, Cy), 24.6 (s, Cy). ^{31}P NMR (162 MHz, $CDCl_3$): δ -18.9 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{35}H_{41}P$: 493.3019, found: 493.3015.

3-dicyclohexyphosphine-2-(4-chlorophenyl)-1,1-dimethylindene (13). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1 H, Ar), 7.35 (d, *J* = 8.0 Hz, 2 H, Ar), 7.24 (t, *J* = 4.0 Hz, 2 H, Ph), 7.01 (d, *J* = 8.0 Hz, 2 H, Ph), 2.27 (s, 2 H, Cy), 1.82 (s, 2 H, Cy), 1.70 (s, 2 H, Cy), 1.59 (s, 3 H, Cy), 1.52 (s, 2 H, Cy), 1.22 (s, 9 H, Cy, $(CH_3)_2$-C), 1.17-1.06 (m, 8 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8 (s, Ar), 143.3 (d, $J_{C\text{-}P}$ = 10.0 Hz, *C*-Ph), 135.8 (s, Ph), 133.0 (s, Ph), 130.8 (s, *C*-PCy_2), 128.0 (s, Ph), 126.3 (s, Ph), 125.1 (s, Ar), 122.3 (s, Ar), 121.5 (s, Ar), 52.5 (d, $J_{C\text{-}P}$ = 6.0 Hz, *C*-$(CH_3)_2$), 34.0 (s, Cy), 33.9 (s, Cy), 32.6 (s, Cy), 32.4 (s, Cy), 30.7 (d, $J_{C\text{-}P}$ = 9.0 Hz, $(CH_3)_2$-C), 27.3 (s, Cy), 27.2 (s, Cy), 27.1 (s, Cy), 27.0 (s, Cy), 26.4 (s, Cy), 24.5 (s, Cy). ^{31}P NMR (162 MHz, $CDCl_3$): δ -19.0 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{29}H_{36}ClP$: 451.2316, found: 451.2312.

3-dicyclohexyphosphine-2-(3-methyl-4-fluorophenyl)-1,1-dimethyl indene (14). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 4.0 Hz, 1 H, Ar), 7.34 (d, *J* = 4.0 Hz, 1 H, Ar), 7.22 (s, 2 H, Ar), 6.99 (t, *J* = 8.0 Hz, 1 H, Ph), 6.83 (s, 2 H, Ph), 2.30 (s, 4 H, Cy, CH_3-Ph), 1.81 (s, 2 H, Cy), 1.70 (s, 2 H, Cy), 1.59-1.50 (m, 6 H, Cy), 1.22 (s, 10 H, Cy, $(CH_3)_2$-C), 1.15-1.00 (m, 6 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8 (d, $J_{C\text{-}P}$ = 3.0 Hz, Ph), 143.4 (s, Ar), 143.4 (s, *C*-Ph), 132.2 (s, *C*-PCy_2), 128.3 (s, Ar), 126.2 (s, Ar), 124.9 (s, Ph), 122.1 (s, Ph), 121.5 (s, Ar), 114.4 (s, Ph), 114.2 (s, Ph), 52.4 (d, $J_{C\text{-}P}$ = 3.0 Hz, *C*-$(CH_3)_2$), 33.9, 30.7 (d, $J_{C\text{-}P}$ = 10.0 Hz, $(CH_3)_2$-C), 27.3 (s, Cy), 27.2 (s, Cy), 27.2 (s, Cy), 27.0 (s, Cy), 26.4 (s, Cy), 24.5 (s, Cy), 15.0 (s, *C*H_3-Ph). ^{31}P NMR (162 MHz, $CDCl_3$): δ -19.0 (s). ^{19}F NMR ($CDCl_3$): δ -124.32 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{30}H_{38}FP$: 449.2779, found: 449.2785.

3-dicyclohexyphosphine-2-(naphthalen-1-yl)-1,1-dimethylindene (15). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.80 (m, 2 H, Ph), 7.67 (t, *J* = 8.0 Hz, 2 H, Ar), 7.48 (t, *J* = 8.0 Hz, 1 H, Ph), 7.39 (t, *J* = 8.0 Hz, 2 H, Ar), 7.33-7.25 (m, 3 H, Ph), 7.16 (d, *J* = 8.0 Hz, 1 H, Ph), 2.45 (d, *J* = 8.0 Hz, 1 H, Cy), 2.10 (s, 1 H, Cy), 1.75-1.58 (m, 10 H, Cy), 1.34 (s, 3 H, $(CH_3)_2$-C), 1.29-1.19 (m, 3 H, $(CH_3)_2$-C), 1.14 (s, 6 H, Cy), 1.10-0.99 (m, 7 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7 (s, Ar), 141.8 (d, $J_{C\text{-}P}$ = 6.0 Hz, *C*-Ph), 133.5 (s, Ph), 133.0 (s, Ph), 133.0 (s, *C*-PCy_2), 131.5 (s, Ar), 130.7 (s, Ph), 126.3 (s, Ph), 125.7 (s, Ph), 125.4 (s, Ar), 125.2 (s, Ph), 124.5 (s, Ph), 123.6 (s, Ar), 123.1, 123.1 (s, Ar), 122.7 (s, Ph), 120.6 (s, Ph), 119.7 (s, Ar), 51.9 (d, $J_{C\text{-}P}$ = 6.0 Hz, *C*-$(CH_3)_2$), 33.2 (s, Cy), 33.1 (s, Cy), 31.7 (d, $J_{C\text{-}P}$ = 10.0 Hz, $(CH_3)_2$-C), 31.0 (s, Cy), 30.8 (s, Cy), 30.4 (s, Cy), 30.2 (s, Cy), 29.1 (s, Cy), 29.0 (d, $J_{C\text{-}P}$ = 9.0 Hz, Cy), 25.7 (d, $J_{C\text{-}P}$ = 6.0 Hz, Cy), 25.6 (d, $J_{C\text{-}P}$ = 3.0 Hz, Cy), 25.4 (s, Cy), 25.3 (s, Cy), 24.6 (s, Cy), 24.3 (s, Cy), 22.6 (s, Cy). ^{31}P NMR (162 MHz, $CDCl_3$): δ -17.0 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{33}H_{39}P$: 467.2868, found: 467.2869.

3-dicyclohexyphosphine-2-(naphthalen-2-yl)-1,1-dimethylindene (16). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (t, *J* = 4.0 Hz, 3 H, Ph), 7.64 (d, *J* = 4.0 Hz, 1 H, Ar), 7.52 (s, 1 H, Ph), 7.45 (t, *J* = 4.0 Hz, 2 H, Ar), 7.37 (d, *J* = 4.0 Hz, 1 H, Ar), 7.29 (d, *J* = 8.0 Hz, 1 H, Ph), 7.24-7.19 (m, 2 H, Ph), 2.27 (s, 2 H, Cy), 1.79 (s, 2 H, Cy), 1.68 (s, 3 H, Cy), 1.62 (s, 6 H, Cy), 1.28 (s, 9 H, Cy, $(CH_3)_2$-C), 1.25-1.13 (m, 10 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0 (s, Ar), 143.7 (s, *C*-Ph), 135.0 (s, Ph), 132.9 (s, *C*-PCy_2), 132.4 (s, Ph), 128.1 (d, $J_{C\text{-}P}$ = 4.0 Hz, Ph), 127.9 (s, Ar), 127.7 (s, Ph), 127.1 (s, Ph), 126.3 (s, Ar), 125.8 (s, Ph), 125.6 (s, Ph), 124.9 (s, Ph), 122.2 (s, Ph), 121.5 (s, Ar), 52.8 (s, *C*-$(CH_3)_2$), 34.1 (s, Cy), 34.0 (s, Cy), 32.6 (s, Cy), 32.4 (s, Cy), 30.7 (d, $J_{C\text{-}P}$ = 9.0 Hz, $(CH_3)_2$-C), 27.4 (s, Cy), 27.3 (s, Cy), 27.2 (s, Cy), 27.0 (s, Cy), 26.4 (s, Cy), 24.6 (s, Cy). ^{31}P NMR (162 MHz, $CDCl_3$): δ -18.9 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{33}H_{39}P$: 467.2868, found: 467.2875.

3-dicyclohexyphosphine-2-(2-biphenyl)-1,1-dimethylindene (17). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.51 (m, 3 H, Ar), 7.39 (s, 2 H, Ph), 7.32 (s, 1 H, Ar), 7.22-7.06 (m, 7 H, Ph), 2.52 (s, 1 H, Cy), 2.14 (s, 1 H, Cy), 1.90-1.53 (m, 10 H,

Cy), 1.25 (s, 11 H, Cy, (C*H*$_3$)$_2$-C), 1.04 (s, 3 H, Cy), 0.55 (s, 3 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0 (s, Ar), 143.7 (s, *C*-Ph), 142.3 (s, Ph), 140.5 (s, Ph), 135.1 (s, Ph), 134.7 (s, Ph), 132.2 (s, *C*-PCy$_2$), 130.3 (s, Ph), 129.6 (s, Ph), 127.5 (s, Ar), 127.2 (s, Ph), 126.3 (s, Ar), 126.0 (s, Ph), 125.7 (s, Ar), 124.6 (s, Ar), 122.2 (s, Ar), 121.0 (s, Ph), 53.9 (d, $J_{C\text{-}P}$ = 6.0 Hz, *C*-(CH$_3$)$_2$), 36.9 (s, Cy), 35.2 (d, $J_{C\text{-}P}$ = 10.0 Hz, Cy), 32.7 (s, Cy), 32.5 (s, Cy), 31.6 (d, $J_{C\text{-}P}$ = 8.0 Hz, (*C*H$_3$)$_2$-C), 31.1 (s, Cy), 27.9 (d, $J_{C\text{-}P}$ = 7.0 Hz, Cy), 27.8 (d, $J_{C\text{-}P}$ = 8.0 Hz, Cy), 27.5 (s, Cy), 27.3 (s, Cy), 26.6 (s, Cy), 26.4 (s, Cy), 23.2 (s, Cy). ^{31}P NMR (162 MHz, $CDCl_3$): δ -17.2 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{35}H_{41}P$: 493.3019, found: 493.3014.

3-dicyclohexyphosphine-2-(4-*n*-butylphenyl)-1,1-dimethylindene (18). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1 H, Ar), 7.34 (d, *J* = 8.0 Hz, 1 H, Ar), 7.22 (t, *J* = 8.0 Hz, 2 H, Ar), 7.17 (d, *J* = 8.0 Hz, 2 H, Ph), 6.97 (d, *J* = 8.0 Hz, 2 H, Ph), 2.64 (t, *J* = 8.0 Hz, 2 H, C*H*$_2$-Ph), 2.22 (s, 2 H, Cy), 1.82 (d, *J* = 8.0 Hz, 2 H, Cy), 1.72-1.58 (m, 9 H, Cy, CH$_3$(C*H*$_2$)$_2$CH$_2$-Ph), 1.43-1.38 (m, 2 H, Cy), 1.22 (s, 10 H, Cy, (C*H*$_3$)$_2$-C), 1.17-1.08 (m, 8 H, Cy), 0.96 (t, *J* = 8.0 Hz, 3 H, C*H*$_3$(CH$_2$)$_2$CH$_2$-Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9 (s, Ar), 143.9 (s, *C*-Ph), 143.8 (s, Ph), 141.2 (s, Ph), 134.4 (s, Ar), 134.3 (s, Ph), 132.1 (s, *C*-PCy$_2$), 131.9 (s, Ar), 129.2 (s, Ph), 127.5 (s, Ph), 126.1 (s, Ar), 124.7 (s, Ph), 122.1 (s, Ar), 121.4 (s, Ar), 52.6 (d, $J_{C\text{-}P}$ = 6.0 Hz, *C*-(CH$_3$)$_2$), 35.6 (s, *C*H$_2$-Ph), 33.9 (s, Cy), 33.5 (s, *C*H$_2$-CH$_2$Ph), 27.4 (d, $J_{C\text{-}P}$ = 8.0 Hz, (*C*H$_3$)$_2$-C), 27.2 (s, Cy), 26.4 (s, Cy), 24.5 (s, Cy), 22.8 (s, *C*H$_2$-(CH$_2$)$_2$Ph), 14.2 (s, *C*H$_3$-(CH$_2$)$_3$Ph). ^{31}P NMR (162 MHz, $CDCl_3$): δ -19.0 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{33}H_{45}P$: 473.3332, found: 473.3336.

3-dicyclohexyphosphine-2-(3,4-dimethylphenyl)-1,1-dimethylindene (19). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1 H, Ar), 7.34 (d, *J* = 8.0 Hz, 1 H, Ar), 7.22 (t, *J* = 8.0 Hz, 2 H, Ar), 6.94 (s, 1 H, Ph), 6.65 (s, 2 H, Ph), 2.34 (s, 6 H, C*H*$_3$-Ph), 2.23 (s, 2 H, Cy), 1.83 (s, 2 H, Cy), 1.70 (s, 2 H, Cy), 1.60 (s, 5 H, Cy), 1.22 (s, 10 H, Cy, (C*H*$_3$)$_2$-C), 1.17-1.09 (m, 5 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2 (s, Ar), 144.0 (s, *C*-Ph), 135.7 (s, Ph), 135.2 (s, Ph), 134.9 (d, $J_{C\text{-}P}$ = 6.0 Hz, Ph), 132.3 (s, *C*-PCy$_2$), 132.1 (s, Ar), 130.6 (s, Ph), 129.1 (s, Ph), 127.0 (s, Ar), 126.3 (s,

Ar), 124.8 (s, Ph), 122.2 (s, Ar), 121.5 (s, Ar), 52.4 (d, $J_{C\text{-}P}$ = 5.0 Hz, *C*-$(CH_3)_2$), 34.0 (s, Cy), 33.9 (s, Cy), 32.5 (s, Cy), 32.3 (s, Cy), 30.6 (d, $J_{C\text{-}P}$ = 10.0 Hz, $(CH_3)_2$-C), 27.2 (s, Cy), 27.2 (s, Cy), 27.1 (s, Cy), 27.0 (s, Cy), 26.3 (s, Cy), 24.4 (s, Cy), 20.0 (s, CH_3-Ph), 19.7 (s, CH_3-Ph). ^{31}P NMR (162 MHz, $CDCl_3$): δ -19.2 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{31}H_{41}P$: 445.3030, found: 445.3031.

3-dicyclohexyphosphine-2-(3,5-dimethylphenyl)-1,1-dimethylindene (20). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 4.0 Hz, 1 H, Ar), 7.38 (d, *J* = 8.0 Hz, 1 H, Ar), 7.29 (d, *J* = 4.0 Hz, 1 H, Ar), 7.20 (s, 1 H, Ar), 7.16 (d, *J* = 8.0 Hz, 1 H, Ph), 6.88 (s, 2 H, Ph), 2.39 (s, 3 H, C*H*$_3$-Ph), 2.24 (s, 2 H, Cy), 1.83 (s, 2 H, Cy), 1.70 (s, 2 H, Cy), 1.60 (s, 5 H, Cy), 1.54 (s, 3 H, C*H*$_3$-Ph), 1.33 (d, *J* = 12.0 Hz, 2 H, Cy), 1.24 (s, 6 H, $(CH_3)_2$-C), 1.17-1.09 (m, 9 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1 (s, Ar), 142.1 (s, *C*-Ph), 135.3 (s, Ph), 134.8 (s, Ph), 130.2 (s, *C*-PCy_2), 130.0 (s, Ph), 126.9 (s, Ar), 125.3 (s, Ar), 124.3 (s, Ar), 122.8 (s, Ar), 120.3 (s, Ph), 119.6 (s, Ar), 50.6 (d, $J_{C\text{-}P}$ = 6.0 Hz, *C*-$(CH_3)_2$), 32.3 (d, $J_{C\text{-}P}$ = 10.0 Hz, $(CH_3)_2$-C), 30.8 (s, Cy), 30.5 (s, Cy), 28.9 (s, Cy), 28.8 (s, Cy), 25.5 (s, Cy), 25.4 (s, Cy), 25.4 (s, Cy), 25.3 (s, Cy), 24.6 (s, Cy), 22.7 (s, Cy), 19.9 (s, CH_3-Ph). ^{31}P NMR (162 MHz, $CDCl_3$): δ -19.2 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{31}H_{41}P$: 445.3030, found: 445.3027.

3-dicyclohexyphosphine-2-(4-acetylphenyl)-1,1-dimethylindene (21). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.0 Hz, 2 H, Ph), 7.65 (d, *J* = 8.0 Hz, 1 H, Ar), 7.39 (d, *J* = 4.0 Hz, 1 H, Ar), 7.31-7.27 (m, 2 H, Ar), 7.21 (d, *J* = 8.0 Hz, 2 H, Ph), 2.63 (s, 3 H, C*H*$_3$CO-Ph), 2.31 (s, 2 H, Cy), 1.85 (d, *J* = 12.0 Hz, 2 H, Cy), 1.74 (d, *J* = 12.0 Hz, 2 H, Cy), 1.62 (d, *J* = 4.0 Hz, 5 H, Cy), 1.25 (s, 6 H, $(CH_3)_2$-C), 1.21-1.09 (m, 11 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8 (s, *C*O-Ph), 153.0 (s, Ar), 143.4 (d, $J_{C\text{-}P}$ = 5.0 Hz, *C*-Ph), 143.1 (d, $J_{C\text{-}P}$ = 6.0 Hz, Ph), 135.8 (s, Ph), 133.6 (s, *C*-PCy_2), 133.4 (s, Ph), 130.0 (s, Ph), 127.9 (s, Ph), 126.6 (s, Ar), 125.3 (s, Ph), 122.5 (s, Ar), 121.7 (s, Ar), 52.7 (d, $J_{C\text{-}P}$ = 6.0 Hz, *C*-$(CH_3)_2$), 33.9 (s, Cy), 33.8 (s, Cy), 32.4 (s, Cy), 32.2 (s, Cy), 30.6 (d, $J_{C\text{-}P}$ = 9.0 Hz, $(CH_3)_2$-C), 27.2 (s, Cy), 27.1 (s, Cy), 27.0 (s, Cy), 26.8 (s, Cy), 26.6 (s, CH_3-COPh), 26.3 (s, Cy), 24.4 (s, Cy). ^{31}P NMR (162

MHz, $CDCl_3$): δ -18.7 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{31}H_{39}OP$: 459.2817, found: 459.2827.

3-dicyclohexyphosphine-2-(4-cyanophenyl)-1,1-dimethylindene (22). White solid, ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.0 Hz, 2 H, Ph), 7.64 (t, *J* = 4.0 Hz, 1 H, Ar), 7.40-7.38 (m, 1 H, Ar), 7.32-7.28 (m, 2 H, Ar), 7.23 (d, *J* = 12.0 Hz, 2 H, Ph), 2.30 (t, *J* = 4.0 Hz, 2 H, Cy), 1.85 (d, *J* = 12.0 Hz, 2 H, Cy), 1.74 (d, *J* = 12.0 Hz, 2 H, Cy), 1.61 (s, 4 H, Cy), 1.53 (s, 1 H, Cy), 1.27 (s, 3 H, Cy), 1.24 (s, 6 H, $(CH_3)_2$-C), 1.22-1.05 (m, 8 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8 (s, Ar), 143.0 (d, J_{C-P} = 6.0 Hz, *C*-Ph), 131.5 (s, Ph), 130.5 (s, *C*-PCy_2), 126.6 (s, Ar), 125.5 (s, Ph), 122.5 (s, Ar), 121.6 (s, Ar), 118.9 (s, *C*N-Ph), 111.0 (s, Ph), 52.6 (d, J_{C-P} = 5.0 Hz, *C*-$(CH_3)_2$), 33.8 (s, Cy), 33.7 (s, Cy), 32.3 (s, Cy), 32.1 (s, Cy), 30.5 (d, J_{C-P} = 9.0 Hz, $(CH_3)_2$-C), 27.0 (s, Cy), 27.0 (s, Cy), 26.9 (s, Cy), 26.7 (s, Cy), 26.1 (s, Cy), 24.3 (s, Cy). ^{31}P NMR (162 MHz, $CDCl_3$): δ -18.9 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{30}H_{36}NP$: 442.2664, found: 442.2658.

3-dicyclohexyphosphine-2-(3-cyanophenyl)-1,1-dimethylindene (23). White solid, ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.0 Hz, 2 H, Ar), 7.52 (t, *J* = 4.0 Hz, 1 H, Ph), 7.38 (s, 2 H, Ar), 7.34-7.28 (m, 3 H, Ph), 2.30 (t, *J* = 4.0 Hz, 2 H, Cy), 1.84 (d, *J* = 8.0 Hz, 2 H, Cy), 1.75 (d, *J* = 12.0 Hz, 2 H, Cy), 1.63 (s, 4 H, Cy), 1.52 (s, 1 H, Cy), 1.24 (s, 9 H, Cy, $(CH_3)_2$-C), 1.19-1.05 (m, 8 H, Cy), 0.94-0.90 (m, 1 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7 (s, Ar), 143.0 (d, J_{C-P} = 5.0 Hz, *C*-Ph), 139.0 (s, Ph), 139.0 (s, Ph), 134.3 (s, Ph), 133.1 (s, *C*-PCy_2), 130.8 (s, *C*-PCy_2), 128.6 (s, Ph), 126.6 (s, Ar), 125.5 (s, Ph), 122.5 (s, Ar), 121.7 (s, Ar), 119.0 (s, *C*N-Ph), 112.0 (s, Ph), 52.4 (d, J_{C-P} = 5.0 Hz, *C*-$(CH_3)_2$), 38.7 (s, Cy), 33.8 (s, Cy), 33.7 (s, Cy), 32.3 (s, Cy), 32.1 (s, Cy), 30.5 (d, J_{C-P} = 9.0 Hz, $(CH_3)_2$-C), 27.0 (s, Cy), 26.9 (s, Cy), 26.9 (s, Cy), 26.7 (s, Cy), 26.1 (s, Cy), 24.2 (s, Cy). ^{31}P NMR (162 MHz, $CDCl_3$): δ -18.9 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{30}H_{36}NP$: 442.2664, found: 442.2667.

3-dicyclohexyphosphine-2-(4-aminophenyl)-1,1-dimethylindene (24). White solid, ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 4.0 Hz, 1 H, Ar), 7.36 (d, *J* = 8.0 Hz, 1 H,

Ar), 7.27 (d, *J* = 4.0 Hz, 1 H, Ar), 7.22 (t, *J* = 8.0 Hz, 1 H, Ar), 6.90 (d, *J* = 8.0 Hz, 2 H, Ph), 6.72 (d, *J* = 8.0 Hz, 2 H, Ph), 2.25 (s, 2 H, Cy), 1.84 (d, *J* = 8.0 Hz, 2 H, Cy), 1.73 (d, *J* = 12.0 Hz, 2 H, Cy), 1.58 (s, 5 H, Cy), 1.34-1.25 (m, 3 H, Cy), 1.22 (s, 6 H, $(CH_3)_2$-C), 1.20-1.08 (m, 8 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1 (s, Ar), 145.3 (s, Ph), 144.0 (d, $J_{C\text{-}P}$ = 4.0 Hz, *C*-Ph), 130.4 (s, Ph), 127.5 (s, *C*-PCy_2), 127.4 (s, Ph), 126.2 (s, Ph), 124.6 (s, Ar), 122.1 (s, Ar), 121.5 (s, Ar), 114.6 (s, Ph), 52.3 (d, $J_{C\text{-}P}$ = 6.0 Hz, *C*-$(CH_3)_2$), 33.8 (s, Cy), 33.7 (s, Cy), 32.4 (s, Cy), 32.2 (s, Cy), 30.5 (d, $J_{C\text{-}P}$ = 9.0 Hz, $(CH_3)_2$-C), 27.1 (s, Cy), 27.1 (s, Cy), 27.0 (s, Cy), 26.9 (s, Cy), 26.3 (s, Cy), 24.8 (s, Cy), 24.3 (s, Cy). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{29}H_{38}NP$: 432.2820, found: 432.2824.

3-dicyclohexyphosphine-2-(3-pyridyl)-1,1-dimethylindene (25). White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, *J* = 4.0 Hz, 1 H, Py), 8.38 (d, *J* = 4.0 Hz, 1 H, Py), 7.65 (t, *J* = 4.0 Hz, 1 H, Ar), 7.46-7.43 (m, 1 H, Ar), 7.40-7.38 (m, 1 H, Ar), 7.36-7.32 (m, 1 H, Ar), 7.30-7.27 (m, 2 H, Py), 2.30 (s, 2 H, Cy), 1.85 (d, *J* = 12.0 Hz, 3 H, Cy), 1.74 (d, *J* = 12.0 Hz, 2 H, Cy), 1.61 (s, 6 H, Cy), 1.26 (s, 9 H, Cy, $(CH_3)_2$-C), 1.17-1.10 (m, 8 H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9 (s, Py), 150.1 (s, Ar), 148.3 (s, Py), 143.2 (d, $J_{C\text{-}P}$ = 4.0 Hz, *C*-Ph), 137.0 (s, Py), 135.1 (s, Py), 134.9 (s, Ar), 133.4 (s, *C*-PCy_2), 133.3 (s, Ar), 126.5 (s, Ar), 125.4 (s, Ar), 122.7 (s, Py), 122.4 (s, Py), 121.6 (s, Ar), 52.5 (d, $J_{C\text{-}P}$ = 5.0 Hz, *C*-$(CH_3)_2$), 33.8 (s, Cy), 33.7 (s, Cy), 32.3 (s, Cy), 32.1 (s, Cy), 30.5 (d, $J_{C\text{-}P}$ = 9.0 Hz, $(CH_3)_2$-C), 27.0 (s, Cy), 26.9 (s, Cy), 26.9 (s, Cy), 26.7 (s, Cy), 26.1 (s, Cy), 24.1 (s, Cy). ^{31}P NMR (162 MHz, $CDCl_3$): δ -19.0 (s). HRMS (ESI/ $[M+H]^+$) Cacld. for $C_{28}H_{36}NP$: 418.2664, found: 418.2662.

1,1′-biphenyl. White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.0 Hz, 4 H, Ar), 7.40 (t, *J* = 8.0 Hz, 4 H, Ar), 7.33 (d, *J* = 8.0 Hz, 2 H, Ar) ppm. Data is consistent with that reported in the literature.[1]

3-methyl-1,1′-biphenyl. Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (t, *J* = 4.0 Hz, 2 H, Ar), 7.41-7.35 (m, 4 H, Ar), 7.32-7.28 (m, 2 H, Ar), 7.14 (d, *J* = 8.0 Hz, 1 H, Ar), 2.41 (s, 3 H, CH_3). Data is consistent with that reported in the literature.[2]

3, 3'-dimethyl-1,1'-biphenyl. Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.0 Hz, 4 H, Ar), 7.28 (t, *J* = 8.0 Hz, 2 H, Ar), 7.13 (d, *J* = 8.0 Hz, 2 H, Ar), 2.40 (s, 6 H, C*H*$_3$). Data is consistent with that reported in the literature.[1]

3, 4'-dimethyl-1,1'-biphenyl. Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.0 Hz, 2 H, Ar), 7.36 (d, *J* = 12.0 Hz, 2 H, Ar), 7.28 (t, *J* = 8.0 Hz, 1 H, Ar), 7.21 (d, *J* = 8.0 Hz, 2 H, Ar), 7.12 (d, *J* = 8.0 Hz, 1 H, Ar), 2.40 (d, *J* = 8.0 Hz, 6 H, C*H*$_3$-Ar). Data is consistent with that reported in the literature.[3]

3-methyl-2'-methyl-1,1'-biphenyl. Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.19 (m, 5 H, Ar), 7.11 (t, *J* = 8.0 Hz, 3 H, Ar), 2.39 (s, 3 H, C*H*$_3$), 2.26 (s, 3 H, C*H*$_3$). Data is consistent with that reported in the literature.[4]

3-methyl-4'-methoxy-1,1'-biphenyl. White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.47 (m, 2 H, Ar), 7.33-7.25 (m, 3 H, Ar), 7.10 (d, *J* = 8.0 Hz, 1 H, Ar), 6.95-6.92 (m, 2 H, Ar), 3.83 (s, 3 H, OC*H*$_3$), 2.40 (s, 3 H, C*H*$_3$). Data is consistent with that reported in the literature.[5]

3-methyl-2',6'-dimethyl-1,1'-biphenyl. Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (t, *J* = 8.0 Hz, 1 H, Ar), 7.12-7.06 (m, 4 H, Ar), 6.93 (d, *J* = 12.0 Hz, 2 H, Ar), 2.37 (s, 3 H, C*H*$_3$), 2.02 (s, 6 H, C*H*$_3$) ppm. Data is consistent with that reported in the literature.[6]

3-methyl-3'-nitro-1,1'-biphenyl. White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 4.0 Hz, 1 H, Ar), 8.16 (d, *J* = 8.0 Hz, 1 H, Ar), 7.87 (d, *J* = 8.0 Hz, 1 H, Ar), 7.56 (t, *J* = 8.0 Hz, 1 H, Ar), 7.40-7.33 (m, 3 H, Ar), 7.22 (d, *J* = 8.0 Hz, 1 H, Ar), 2.43 (s, 3 H, C*H*$_3$) ppm. Data is consistent with that reported in the literature.[7]

3-methyl-4'-trifluoromethyl-1,1'-biphenyl. White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (s, 3 H, Ar), 7.37-7.30 (m, 3 H, Ar), 7.20 (d, *J* = 8.0 Hz, 1 H, Ar), 2.42 (s, 3 H, C*H*$_3$). ^{19}F NMR (376 MHz, $CDCl_3$): δ -67.5 (s). Data is consistent with that reported in the literature.[8]

3-methyl-4'-cyano-1,1'-biphenyl. Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69-7.63 (m, 4 H, Ar), 7.35 (t, *J* = 8.0 Hz, 3 H, Ar), 7.22 (d, *J* = 8.0 Hz, 1 H, Ar), 2.42 (s, 3 H, C*H*$_3$) ppm. Data is consistent with that reported in the literature.[9]

3-methyl-2'-cyano-1,1'-biphenyl. White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.0 Hz, 1 H, Ar), 7.37-7.17 (m, 5 H, Ar), 7.06 (d, *J* = 8.0 Hz, 2 H, Ar), 3.62 (s, 2 H, C*H*$_2$-Ar), 2.40 (s, 3 H, C*H*$_3$-Ar). Data is consistent with that reported in the literature.[10]

2-(3-methylphenyl)pyridine. Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (t, *J* = 4.0 Hz, 1 H, Ar), 7.80 (s, 1 H, Ar), 7.73-7.67 (m, 3 H, Ar), 7.33 (t, *J* = 8.0 Hz, 1 H, Ar), 7.22-7.17 (m, 2 H, Ar), 2.43 (s, 3 H, C*H*$_3$). Data is consistent with that reported in the literature.[11]

3-(3-methylphenyl)pyridine. Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 4.0 Hz, 1 H, Ar), 8.55 (d, *J* = 4.0 Hz, 1 H, Ar), 7.85-7.82 (m, 1 H, Ar), 7.36-7.31 (m, 4 H, Ar), 7.20 (d, *J* = 4.0 Hz, 1 H, Ar), 2.43 (s, 3 H, C*H*$_3$). Data is consistent with that reported in the literature.[12]

2-(3-methylphenyl)pyrazine. Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (s, 1 H, Ar), 8.60 (d, *J* = 4.0 Hz, 1 H, Ar), 8.47 (d, *J* = 4.0 Hz, 1 H, Ar), 7.77 (t, *J* = 4.0 Hz, 2 H, Ar), 7.38 (t, *J* = 8.0 Hz, 1 H, Ar), 7.28 (d, *J* = 8.0 Hz, 1 H, Ar), 2.45 (s, 3 H, C*H*$_3$). Data is consistent with that reported in the literature.[13]

9-(3-methylphenyl)quinoline. White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (d, *J* = 4.0 Hz, 1 H, Ar), 8.17 (d, *J* = 8.0 Hz, 1 H, Ar), 7.79 (d, *J* = 8.0 Hz, 1 H, Ar), 7.69 (d, *J* = 8.0 Hz, 1 H, Ar), 7.56 (t, *J* = 8.0 Hz, 1 H, Ar), 7.46-7.33 (m, 4 H, Ar), 7.20 (d, *J* = 8.0 Hz, 1 H, Ar), 2.44 (s, 3 H, C*H*$_3$). Data is consistent with that reported in the literature.[14]

2-(3-methylphenyl)thiophene. Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.0 Hz, 2 H, Ar), 7.27-7.22 (m, 3 H, Ar), 7.07-7.03 (m, 2 H, Ar), 2.38 (s, 3 H, CH_3). Data is consistent with that reported in the literature.[4]

2-phenylthiophene. Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.0 Hz, 2 H, Ar), 7.34 (t, *J* = 8.0 Hz, 2 H, Ar), 7.27 (d, *J* = 12.0 Hz, 2 H, Ar), 7.05 (s, 1 H, Ar). Data is consistent with that reported in the literature.[15]

2-(naphthalen-1-yl)thiophene. White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (t, *J* = 8.0 Hz, 1 H, Ar), 7.87-7.81 (m, 2 H, Ar), 7.55-7.39 (m, 5 H, Ar), 7.22-7.14 (m, 2 H, Ar). Data is consistent with that reported in the literature.[16]

2-(4-methoxyphenyl)thiophene. Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.0 Hz, 2 H, Ar), 7.17 (t, *J* = 4.0 Hz, 2 H, Ar), 7.02 (t, *J* = 4.0 Hz, 1 H, Ar), 6.90 (d, *J* = 12.0 Hz, 2 H, Ar), 3.82 (s, 3 H, OCH_3) ppm. Data is consistent with that reported in the literature.[17]

2-(4-tert-butylphenyl)thiophene. White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.0 Hz, 2 H, Ar), 7.38 (d, *J* = 8.0 Hz, 2 H, Ar), 7.25-7.20 (m, 2 H, Ar), 7.03 (t, *J* = 4.0 Hz, 1 H, Ar), 1.33 (s, 9 H, CMe_3). Data is consistent with that reported in the literature.[18]

2-(2-methylphenyl)thiophene. Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (t, *J* = 4.0 Hz, 1 H, Ar), 7.30 (t, *J* = 4.0 Hz, 1 H, Ar), 7.23-7.18 (m, 3 H, Ar), 7.07-7.02 (m, 2 H, Ar), 2.41 (s, 3 H, CH_3). Data is consistent with that reported in the literature.[19]

2-(2-methoxyphenyl)thiophene. Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.0 Hz, 1 H, Ar), 7.46 (s, 1 H, Ar), 7.29-7.22 (m, 2 H, Ar), 7.06 (s, 1 H, Ar), 6.96 (t, *J* = 8.0 Hz, 2 H, Ar), 3.91 (s, 3 H, OCH_3). Data is consistent with that reported in the literature.[20]

2-(2-biphenyl)thiophene. White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.50 (m, 1 H, Ar), 7.36-7.13 (m, 9 H, Ar), 6.83 (t, *J* = 4.0 Hz, 1 H, Ar), 6.67 (d, *J* = 8.0 Hz, 1 H, Ar). Data is consistent with that reported in the literature.[21]

2-(4-fluorophenyl)thiophene. White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.51 (m, 2 H, Ar), 7.22 (t, *J* = 4.0 Hz, 2 H, Ar), 7.06-7.01 (m, 3 H, Ar). ^{19}F NMR (376 MHz, $CDCl_3$): δ -67.7 (s). Data is consistent with that reported in the literature.[22]

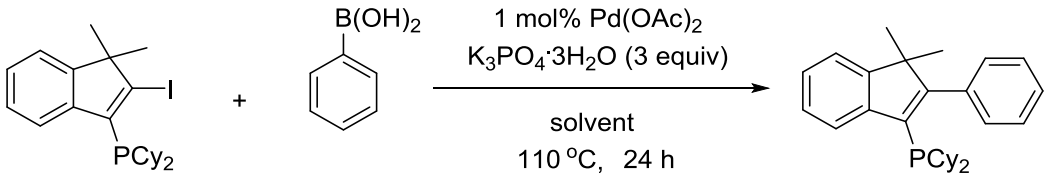
2-(4-trifluoromethylphenyl)thiophene. White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69-7.58 (m, 4 H, Ar), 7.37-7.32 (m, 2 H, Ar), 7.09 (t, *J* = 4.0 Hz, 1 H, Ar). ^{19}F NMR (376 MHz, $CDCl_3$): δ -67.69 (s). Data is consistent with that reported in the literature.[23]

1-(3'-methyl-[1,1'-biphenyl]-4-yl)ethanone. White solid,: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 2.63 (s, 3H), 2.43 (s, 3H) ppm. Data is consistent with that reported in the literature.[24]

3'-methyl-[1,1'-biphenyl]-2-carbaldehyde. Colourless liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.62-7.58 (m, 2H), 7.48-7.41 (m, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 2H), 2.42 (s, 2H), 2.32 (s, 1H) ppm. Data is consistent with that reported in the literature.[25]

3'-methyl-[1,1'-biphenyl]-4-carbaldehyde. White solid,: ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 4.0 Hz, 1H), 2.43 (s, 3H) ppm. Data is consistent with that reported in the literature.[26]

Table S1. Optimization of the Pd-catalyzed Suzuki-Miyaura cross-coupling reaction of compound **1** with phenylboronic acid

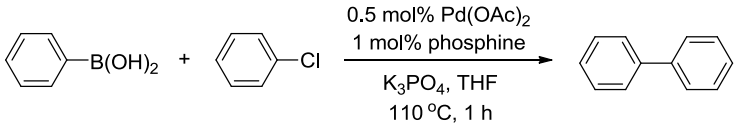


1 **2**

Entry[a]	Pd	Ligand	Solvent	Conv. [%][c]
1	$Pd(OAc)_2$	DPPF	toluene/H_2O 1:1	41
2	$Pd(OAc)_2$	PPh_3	toluene/H_2O 1:1	42
3	$Pd(OAc)_2$	xphos	toluene/H_2O 1:1	53[b]
4	$Pd(OAc)_2$	-	toluene/H_2O 1:1	57
5	$Pd(OAc)_2$	-	DMAC	52
6	$Pd(OAc)_2$	-	THF	99

[a] Reaction conditions: compound **1** (1 mmol), phenylboronic acid (1.2 mmol), $Pd(OAc)_2$ (1 mol%), Ligand (1.2 mol%), K_3PO_4 $3H_2O$ (3 equiv) and solvent at 110 ℃ in 24 h. [b] ligand (2 mol%). [c] Based on ^{31}P NMR.

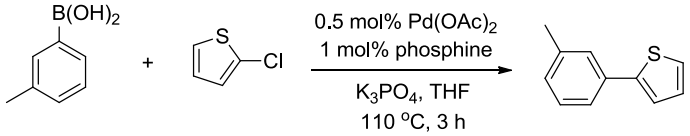
Table S2. Pd-catalyzed Suzuki-Miyaura cross-coupling reaction of chlorobenzene with phenylboronic acid by different phosphines.



Entry[a]	Phosphine Ligand	Yield (%)[b]
1	**1**	39
2	**2**	47
3	**3**	16
4	**4**	80
5	**5**	21
6	**6**	79
7	**7**	51
8	**8**	83
9	**9**	59
10	**10**	70
11	**11**	10
12	**12**	36
13	**13**	29
14	**14**	41
15	**15**	87
16	**16**	60
17	**17**	22
18	**18**	67
19	**19**	80
20	**20**	73
21	**21**	65
22	**22**	41
23	**23**	20
24	**24**	36
25	**25**	10
26	**P(*o*-tolyl)$_3$**	5
27	**PCy$_3$**	73
28	**CyJohnPhos**	58

[a] Reaction conditions: chlorobenzene (1 mmol), phenylboronic acid (1.2 mmol), $Pd(OAc)_2$ (0.5 mol%), indenylphosphine (1 mol%), K_3PO_4 (3 equiv) and THF (2 ml) at 110 ℃ in 1 h. [b] Isolated yield.

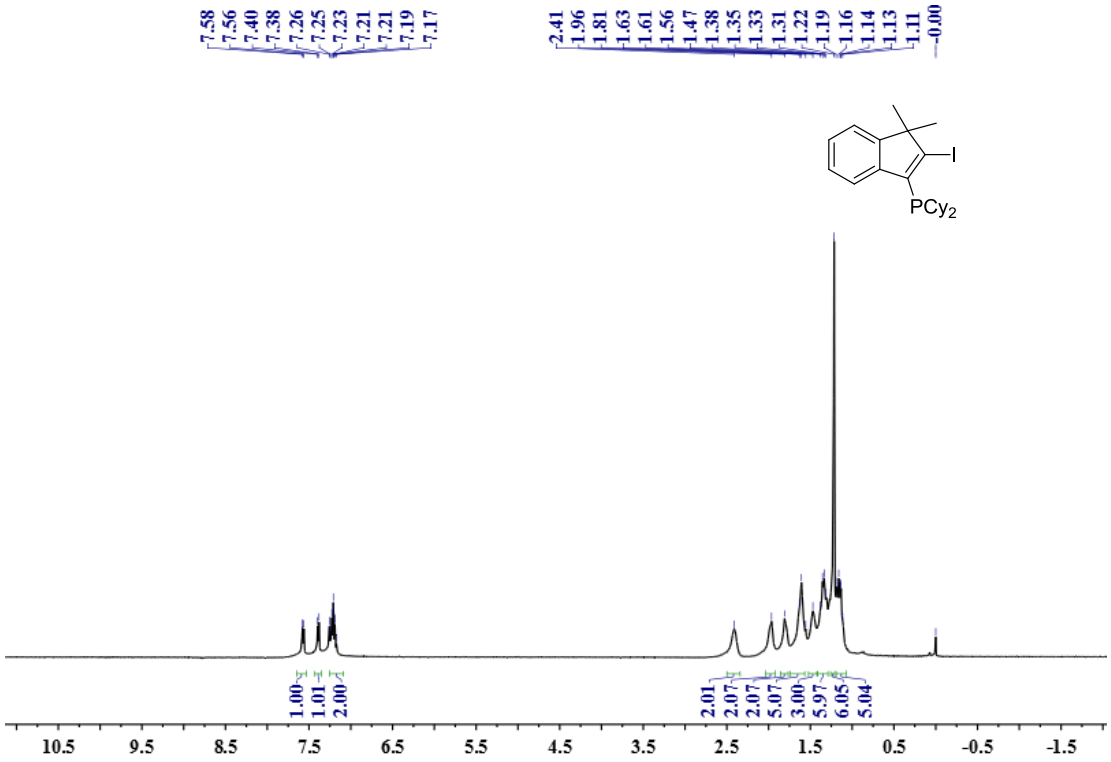
Table S3. Pd-catalyzed Suzuki-Miyaura cross-coupling reaction of 2-chlorothiophene with 3-tolylboronic acid by different phosphines.



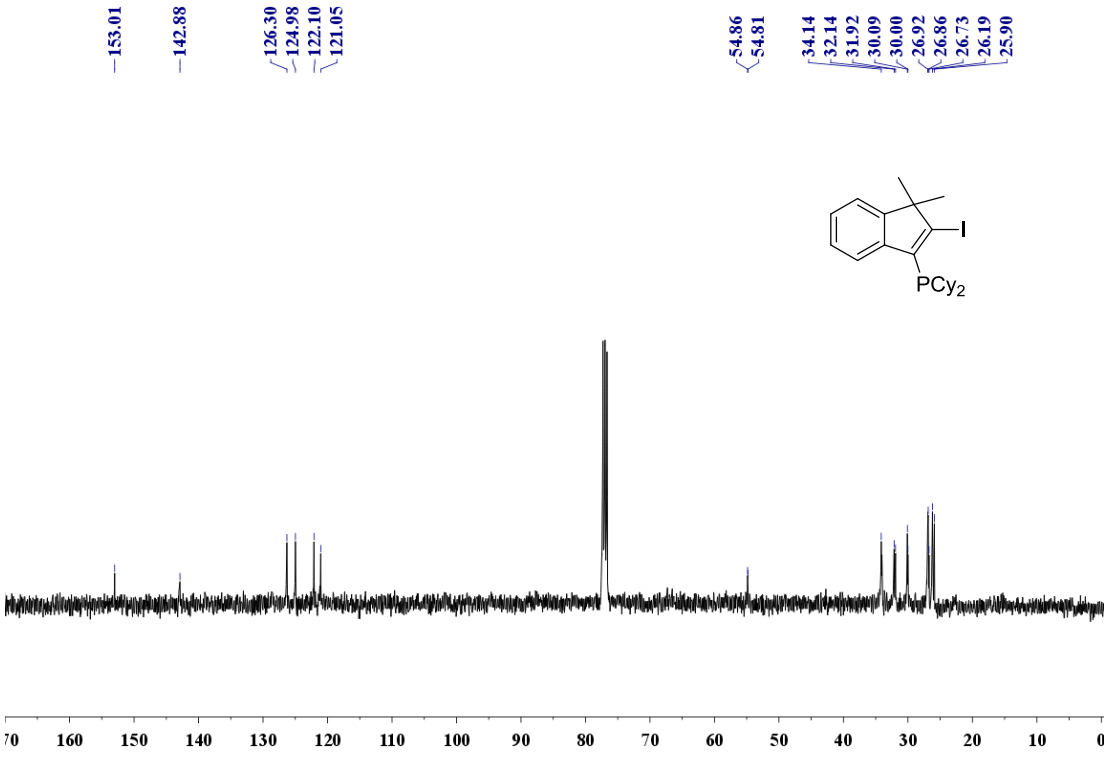
Entry[a]	Phosphine Ligand	Yield (%)[b]
1	**1**	37
2	**2**	40
3	**3**	48
4	**4**	44
5	**5**	26
6	**6**	55
7	**7**	45
8	**8**	18
9	**9**	58
10	**10**	83
11	**11**	51
12	**12**	49
13	**13**	21
14	**14**	56
15	**15**	53
16	**16**	31
17	**17**	40
18	**18**	19
19	**19**	85
20	**20**	81
21	**21**	58
22	**22**	52
23	**23**	21
24	**24**	50
25	**25**	21
26	**P(*o*-tolyl)$_3$**	4
27	**PCy$_3$**	45
28	**CyJohnPhos**	58

[a] Reaction conditions: 2-chlorothiophene (1 mmol), 3-tolylboronic acid (1.2 mmol), $Pd(OAc)_2$ (0.5 mol%), Ligand (1 mol%), K_3PO_4 (3 equiv) and THF (2 ml) at 110 ℃ in 3 h. [b] Isolated yield.

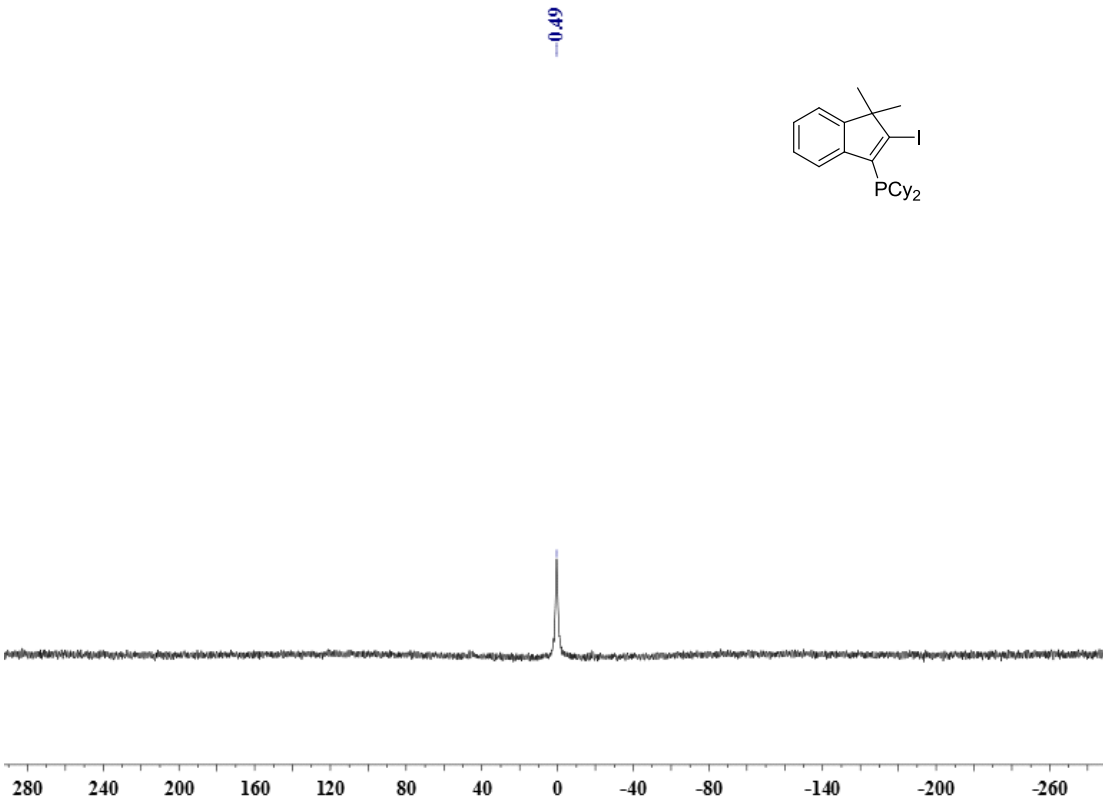
Spectrum Copies



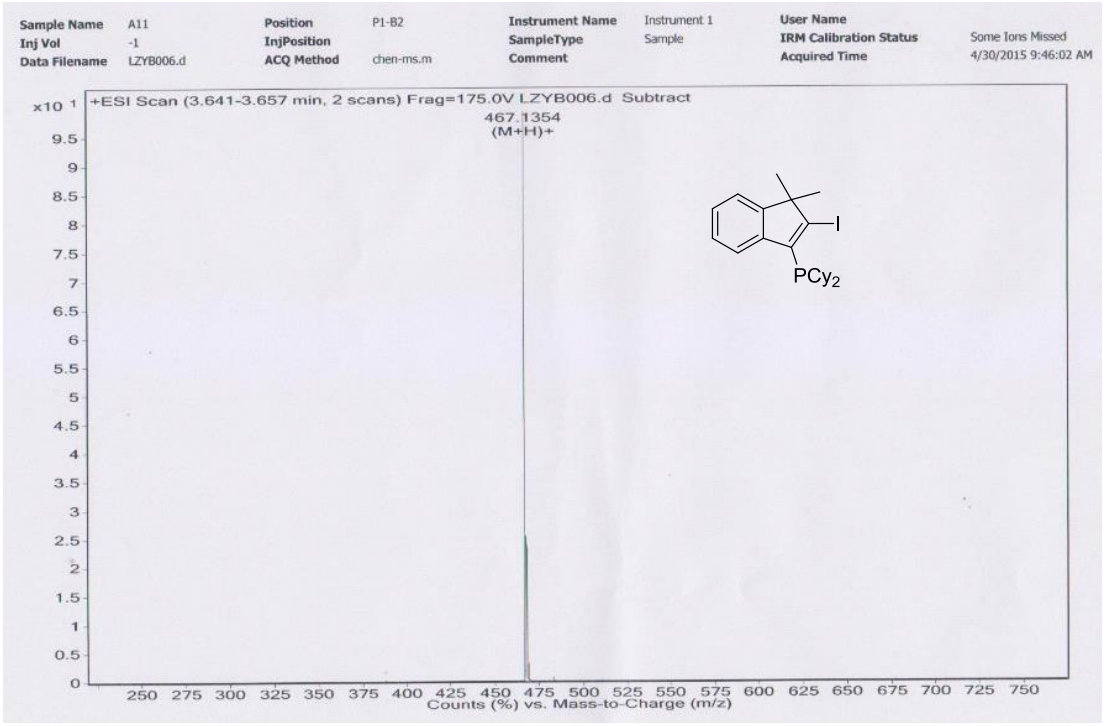
^{1}H NMR



^{13}C NMR


-0.49
I
PCy2
280
240
200
160
120
80
40
0
-40
-80
-140
-200
-260

^{31}P NMR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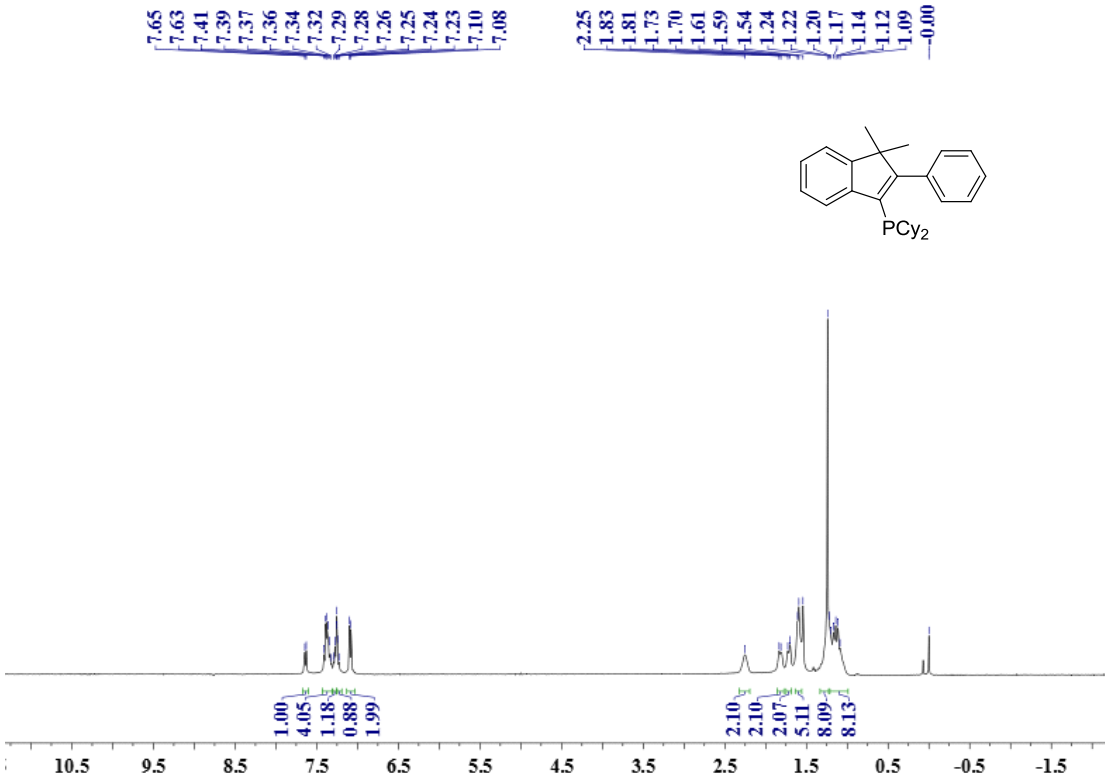
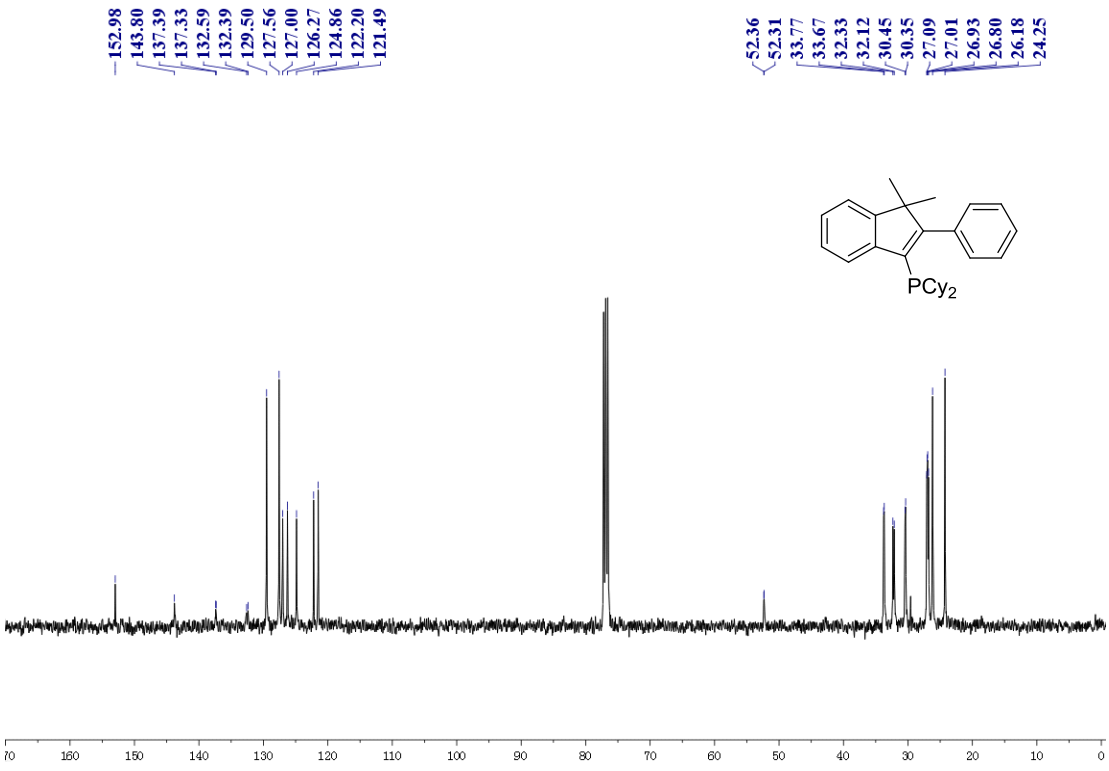
Data Filename LZYB006.d
Position P1-B2
InjPosition
ACQ Method chen-ms.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Some Ions Missed
Acquired Time 4/30/2015 9:46:02 AM
+ESI Scan (3.641-3.657 min, 2 scans) Frag=175.0V LZYB006.d Subtract
467.1354
(M+H)+
x10 1
9.5
9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
I
PCy2
250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 625 650 675 700 725 750
Counts (%) vs. Mass-to-Charge (m/z)

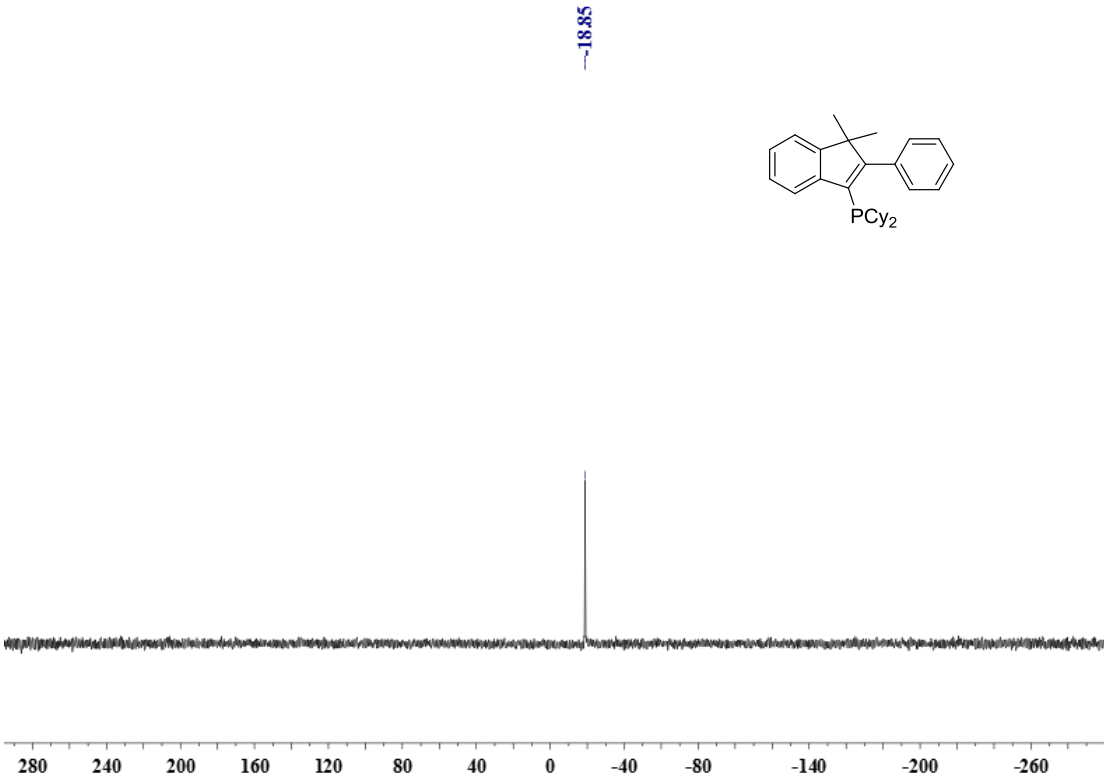
HRMS



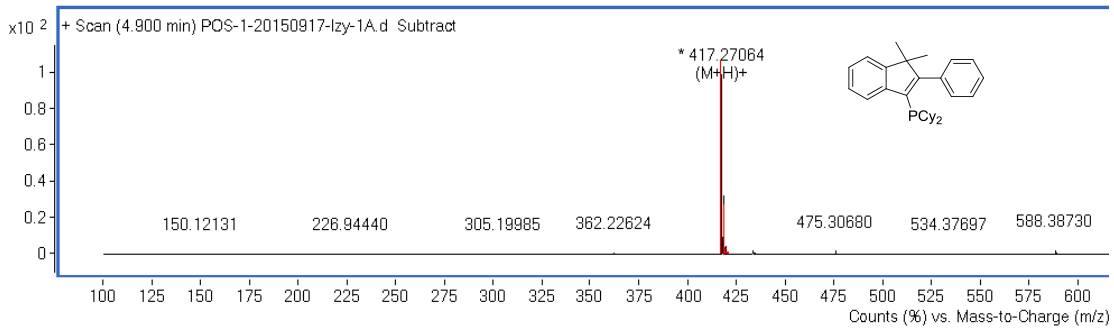
^{1}H NMR



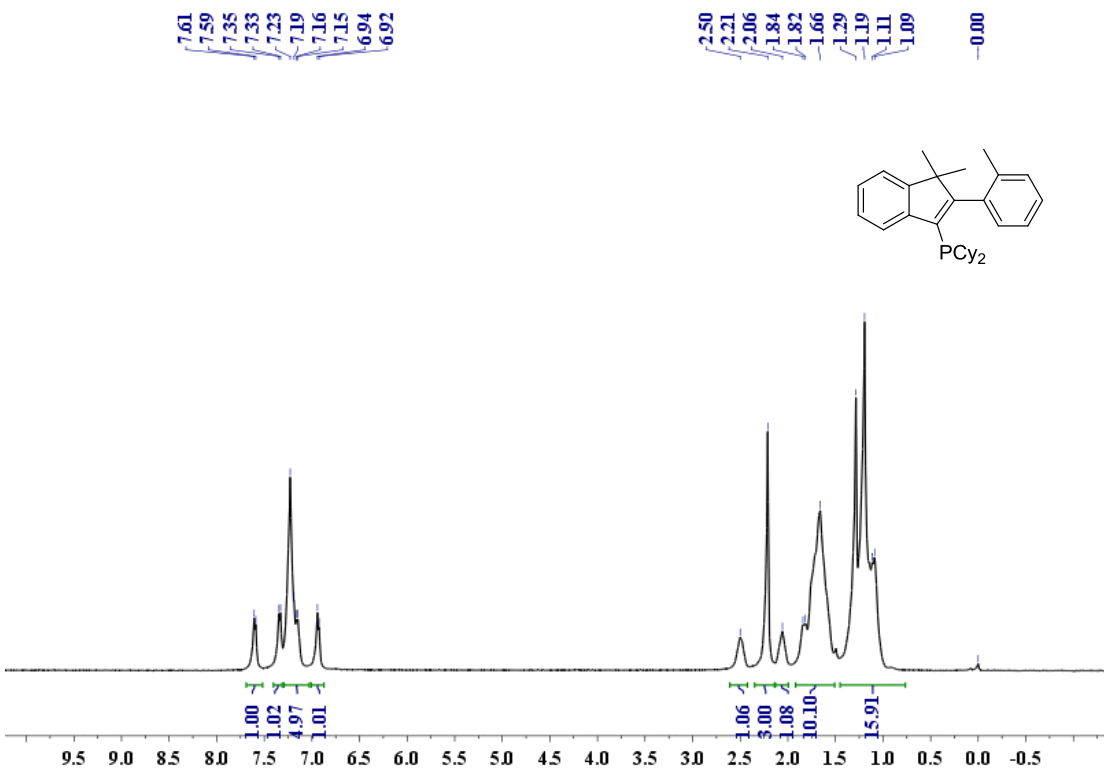
^{13}C NMR


-18.85
PCy2
280
240
200
160
120
80
40
0
-40
-80
-140
-200
-260

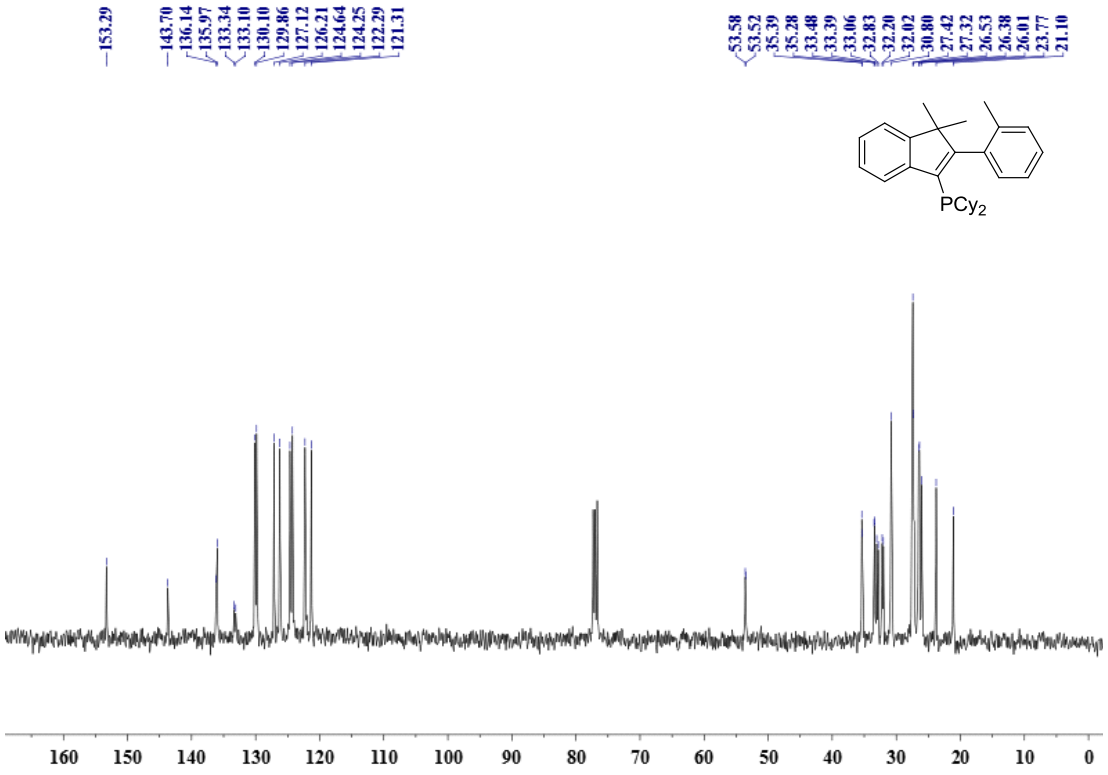
^{13}P NMR


x10 2
+ Scan (4.900 min) POS-1-20150917-lzy-1A.d Subtract
* 417.27064
(M+H)+
PCy2
150.12131
226.94440
305.19985
362.22624
475.30680
534.37697
588.38730
Counts (%) vs. Mass-to-Charge (m/z)

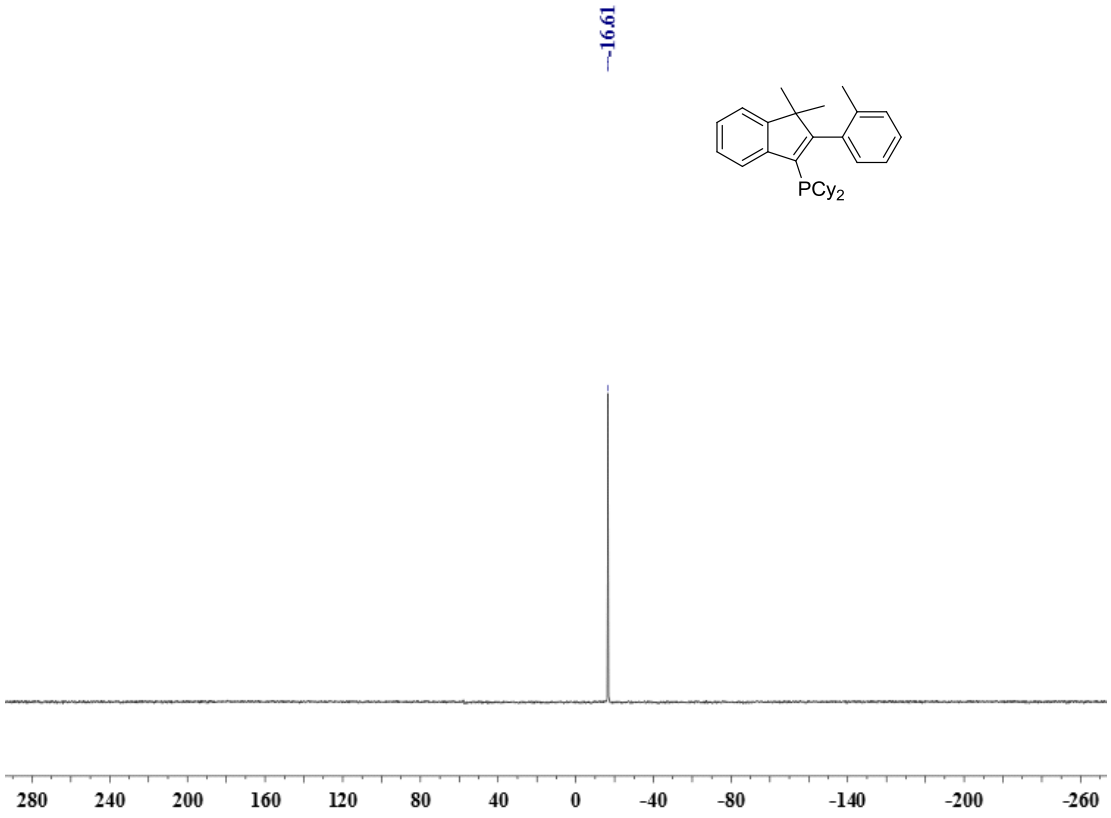
HRMS



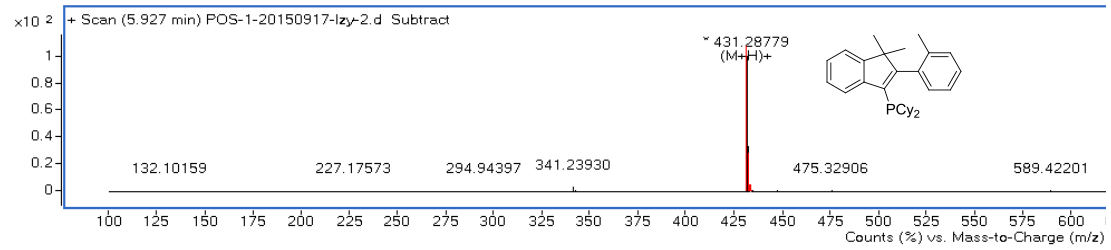
^{1}H NMR



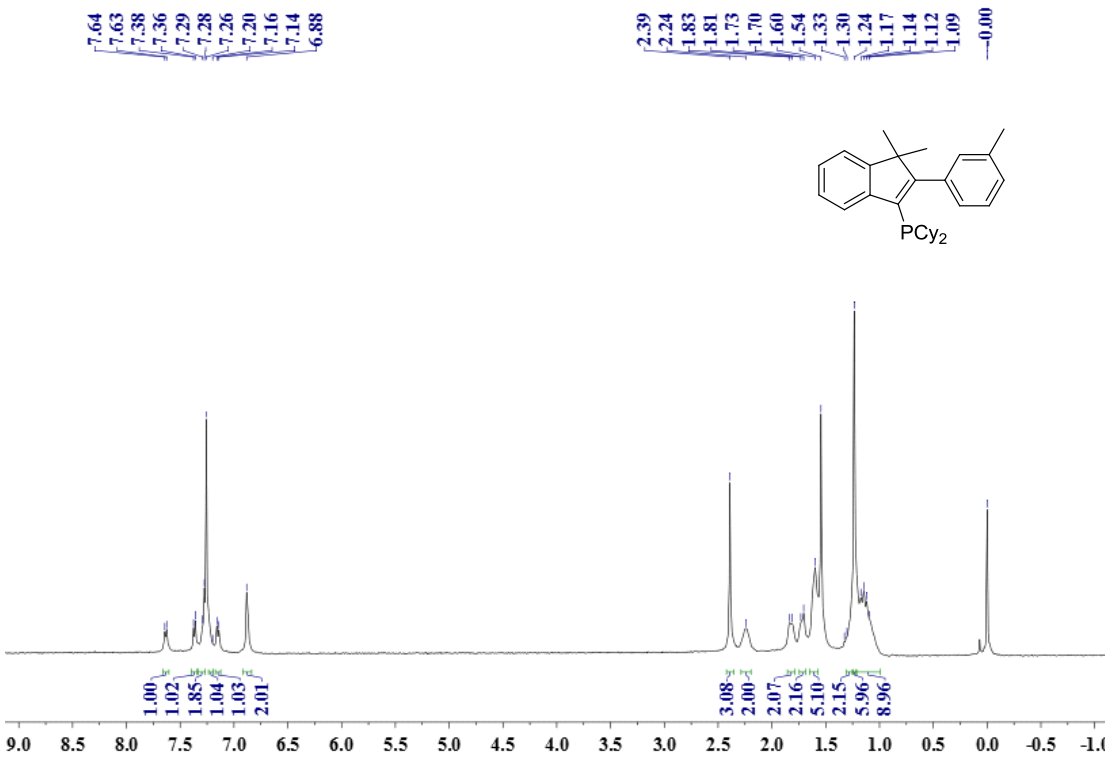
^{13}C NMR


16.61
PCy2
280
240
200
160
120
80
40
0
-40
-80
-140
-200
-260

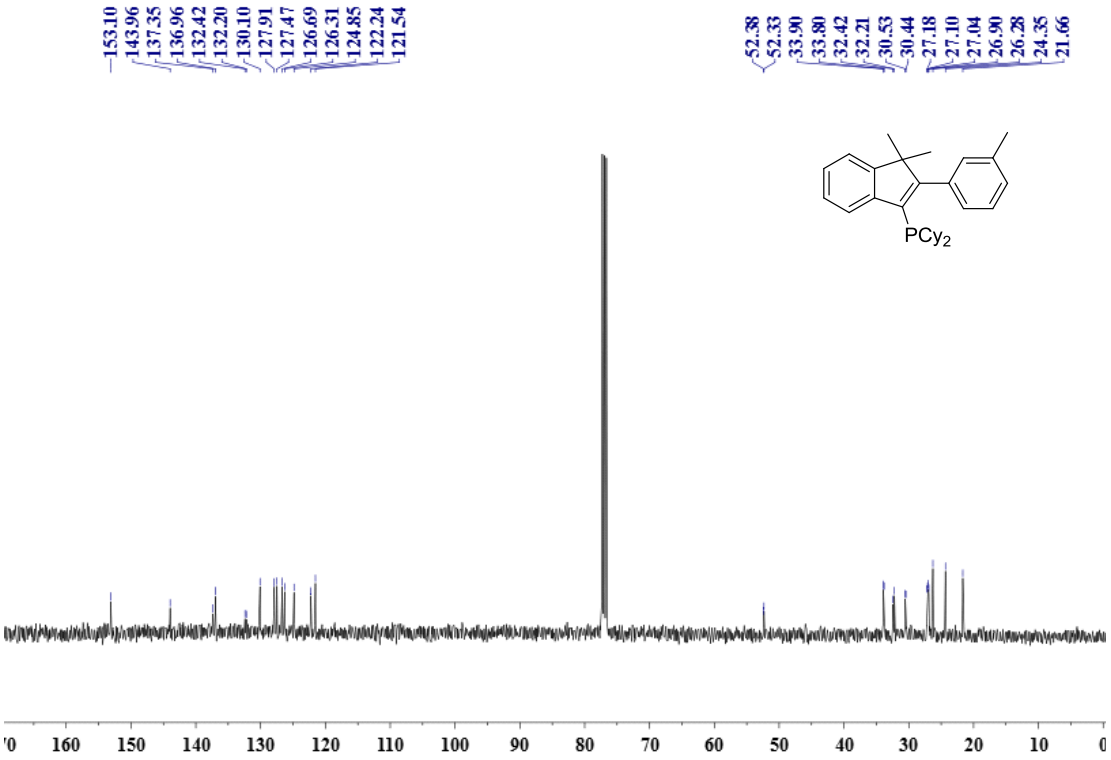
^{13}P NMR


x10 2
+ Scan (5.927 min) POS-1-20150917-lzy-2.d Subtract
431.28779
(M+H)+
PCy2
132.10159
227.17573
294.94397
341.23930
475.32906
589.42201
Counts (%) vs. Mass-to-Charge (m/z)

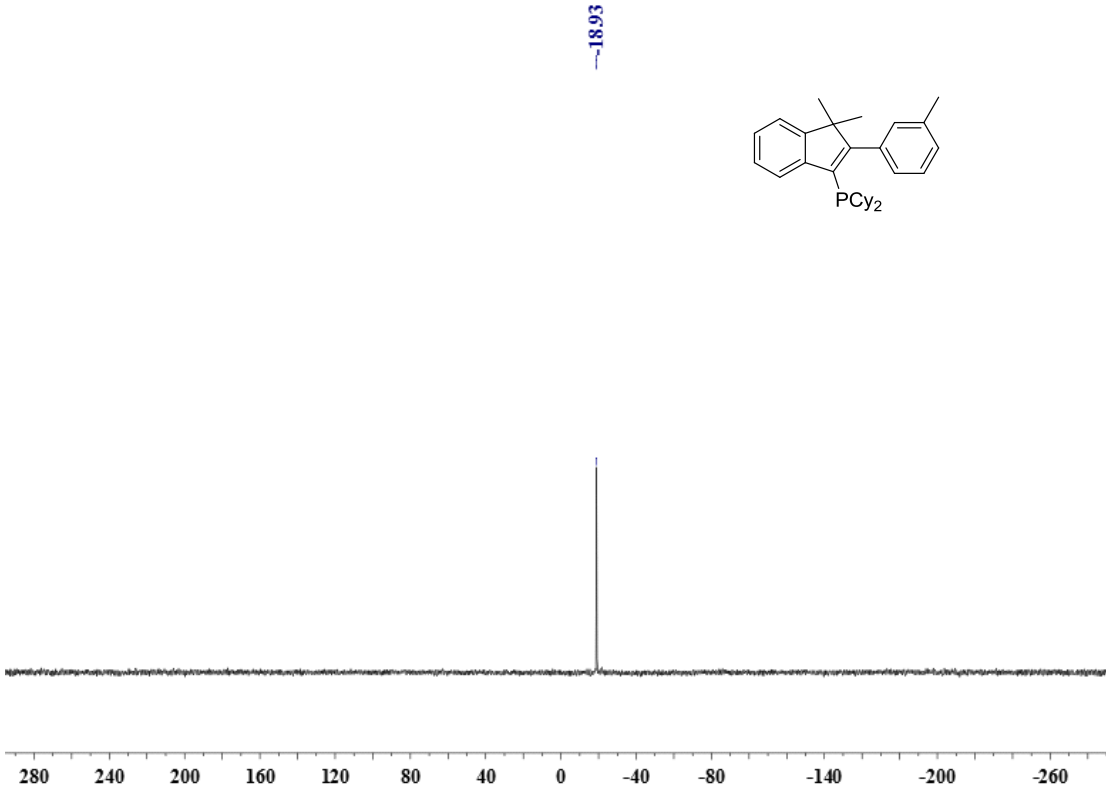
HRMS



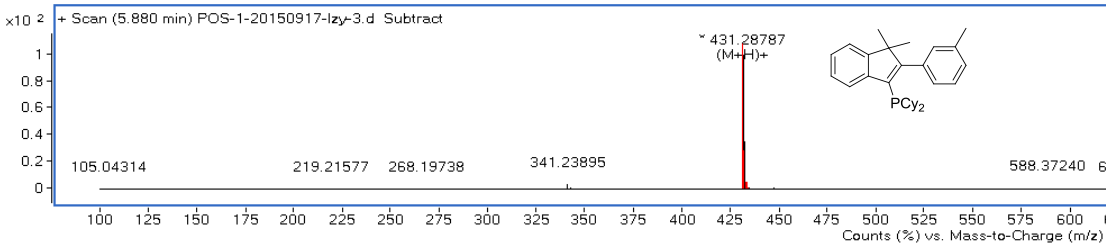
^{1}H NMR



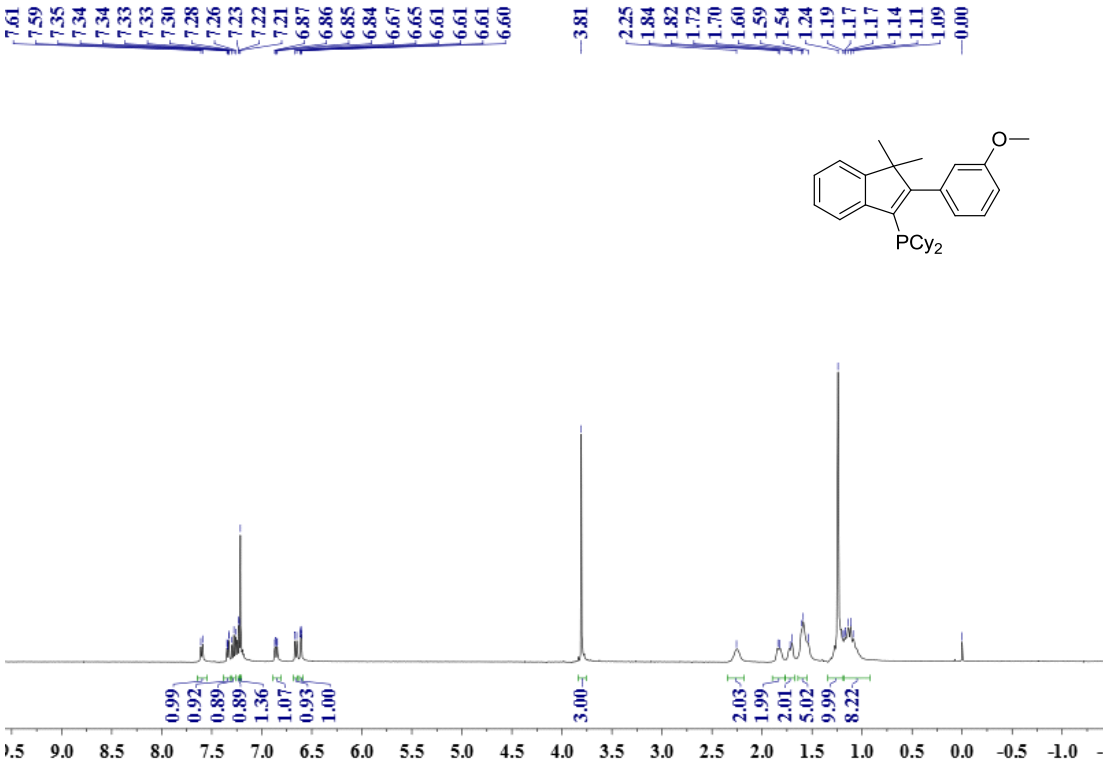
^{13}C NMR


-18.93
PCy2
280
240
200
160
120
80
40
0
-40
-80
-140
-200
-260

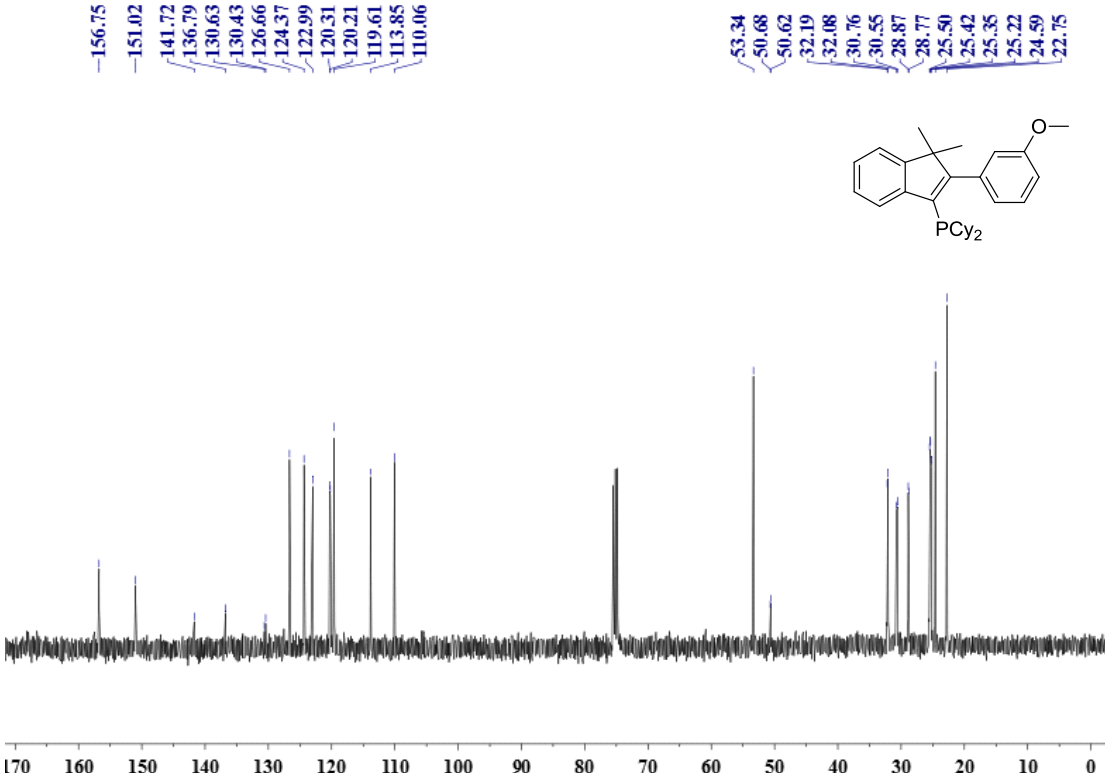
^{31}P NMR


+ Scan (5.880 min) POS-1-20150917-lzy-3.d Subtract
431.28787
(M+H)+
PCy2
105.04314
219.21577
268.19738
341.23895
588.37240
Counts (%) vs. Mass-to-Charge (m/z)

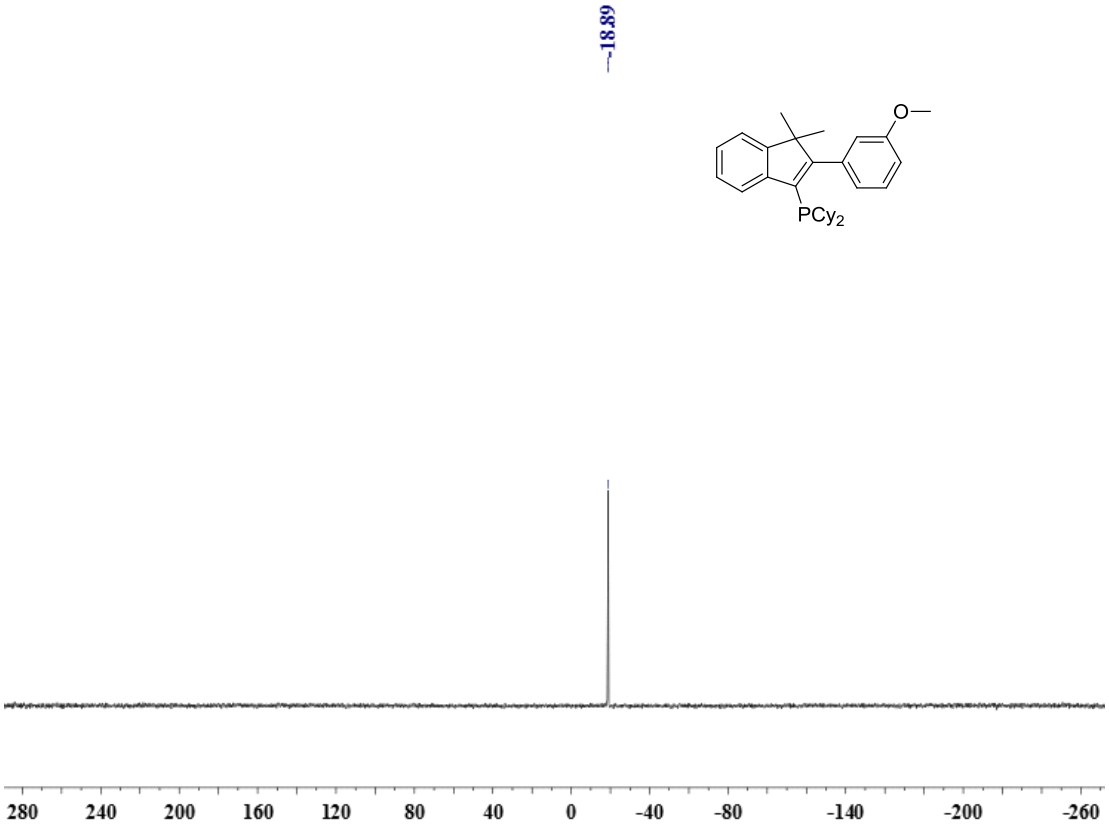
HRMS



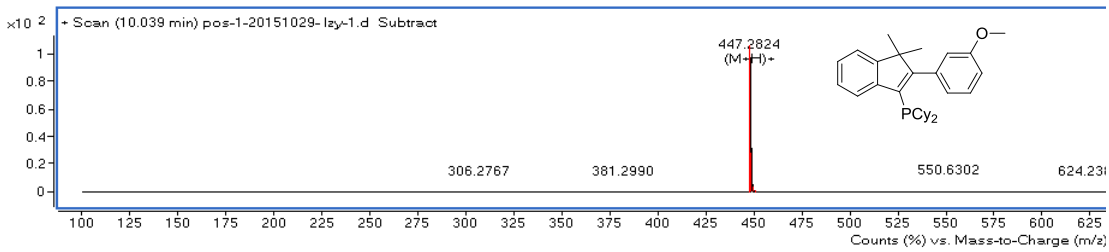
^{1}H NMR



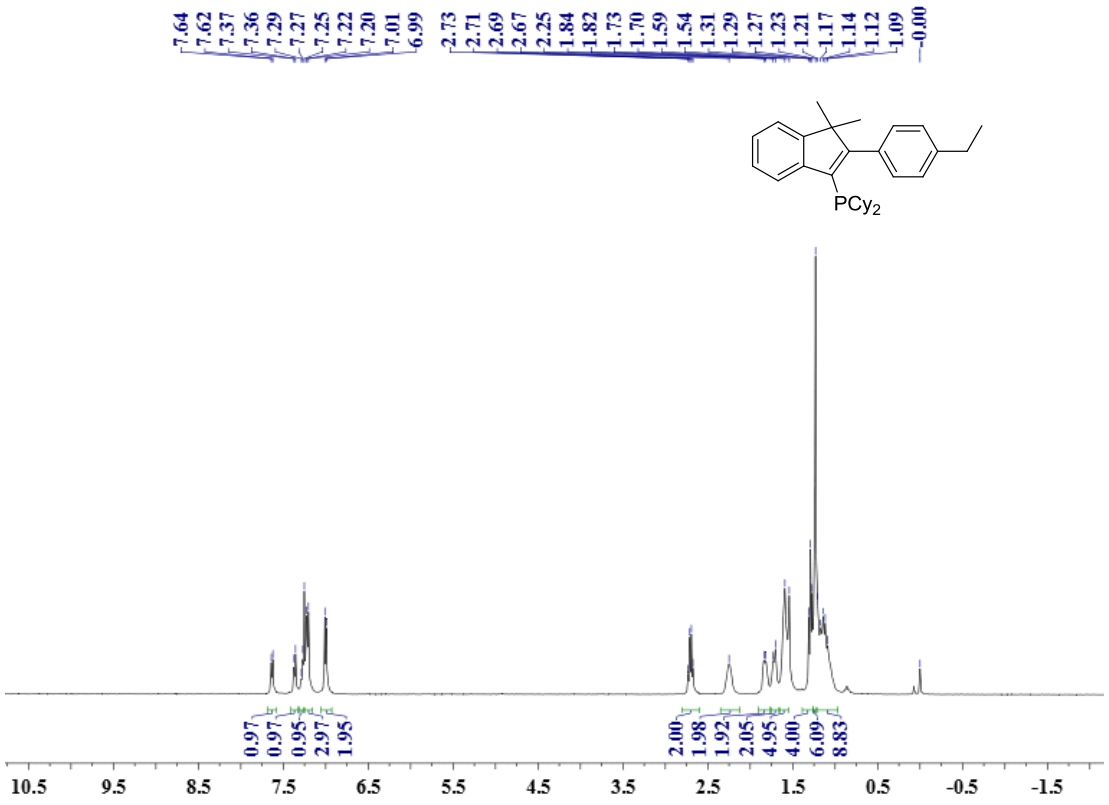
^{13}C NMR


18.89
O
PCy2
280
240
200
160
120
80
40
0
-40
-80
-140
-200
-260

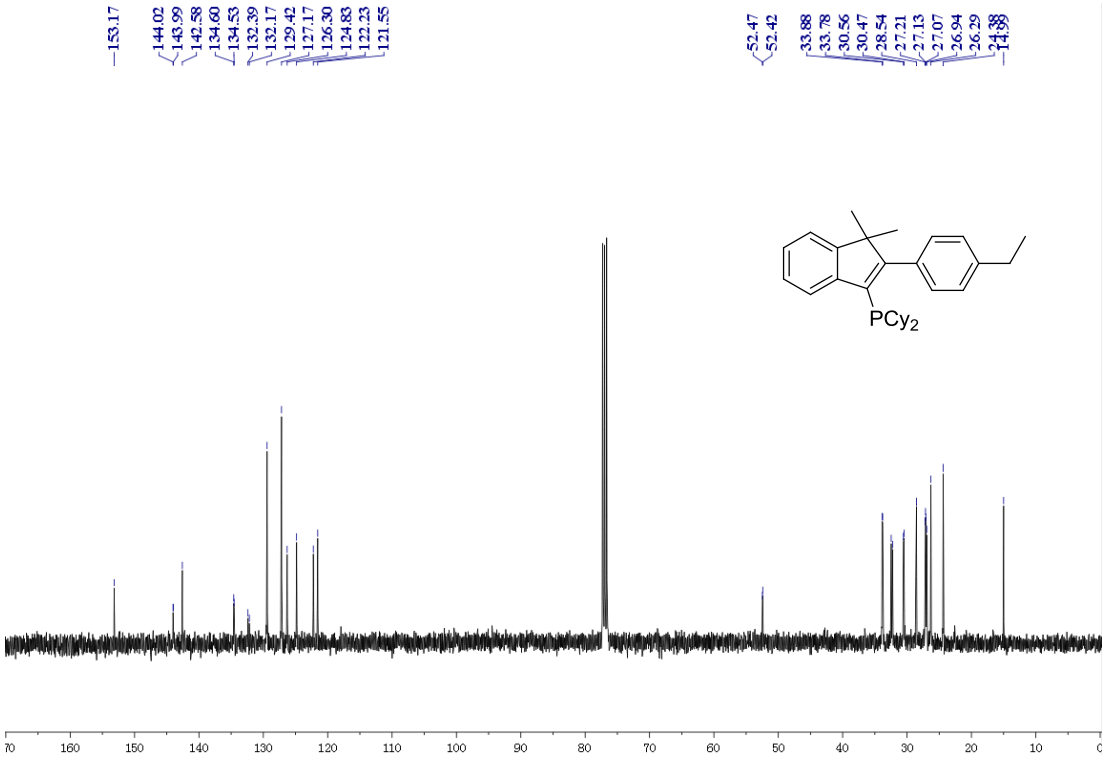
^{31}P NMR


x10 2
+ Scan (10.039 min) pos-1-20151029-lzy-1.d Subtract
447.2824
(M+H)+
O
PCy2
306.2767
381.2990
550.6302
624.23
Counts (%) vs. Mass-to-Charge (m/z)

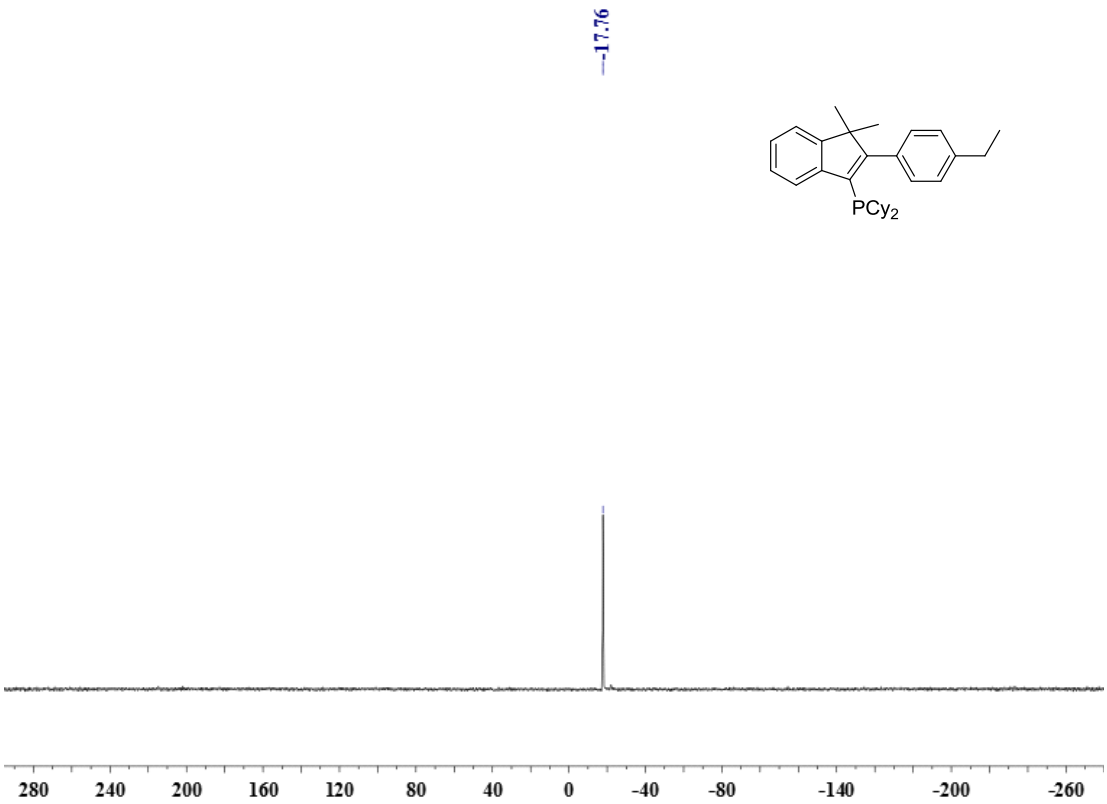
HRMS



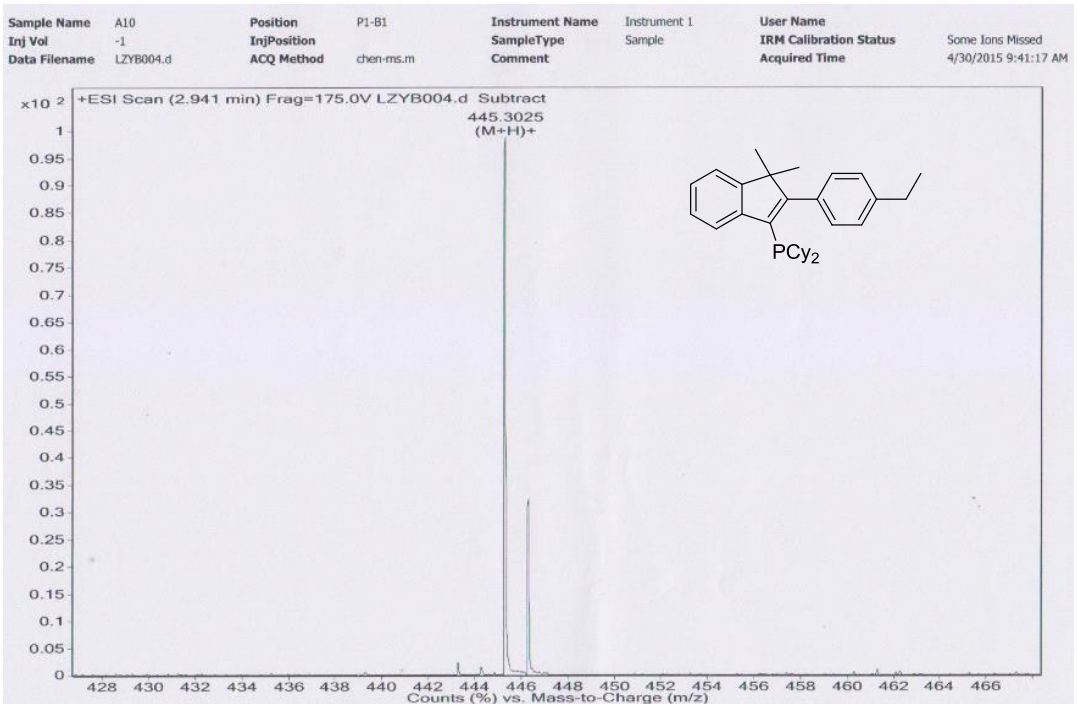
^{1}H NMR



^{13}C NMR


-17.76
PCy2
280
240
200
160
120
80
40
0
-40
-80
-140
-200
-260

^{31}P NMR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User Name
Inj Vol -1
InjPosition
SampleType Sample
IRM Calibration Status Some Ions Missed
Data Filename LZYB004.d
ACQ Method chen-ms.m
Comment
Acquired Time 4/30/2015 9:41:17 AM
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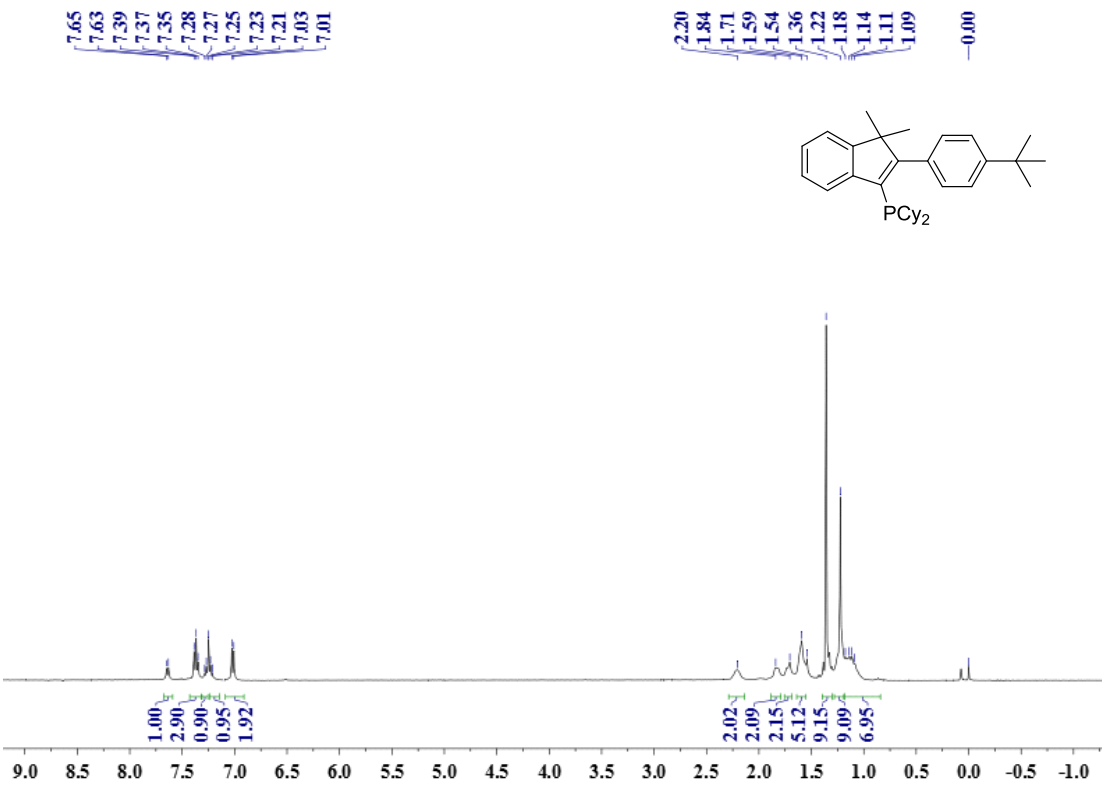
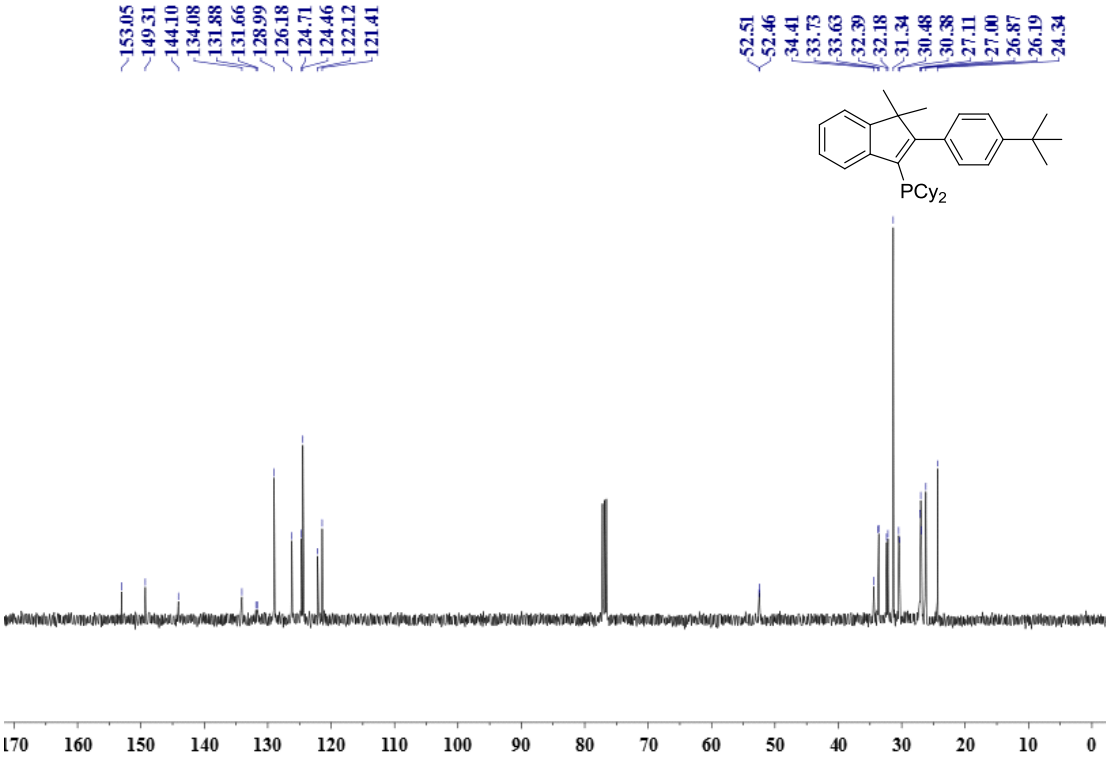
445.3025
(M+H)+
PCy2
x10 2
Counts (%) vs. Mass-to-Charge (m/z)

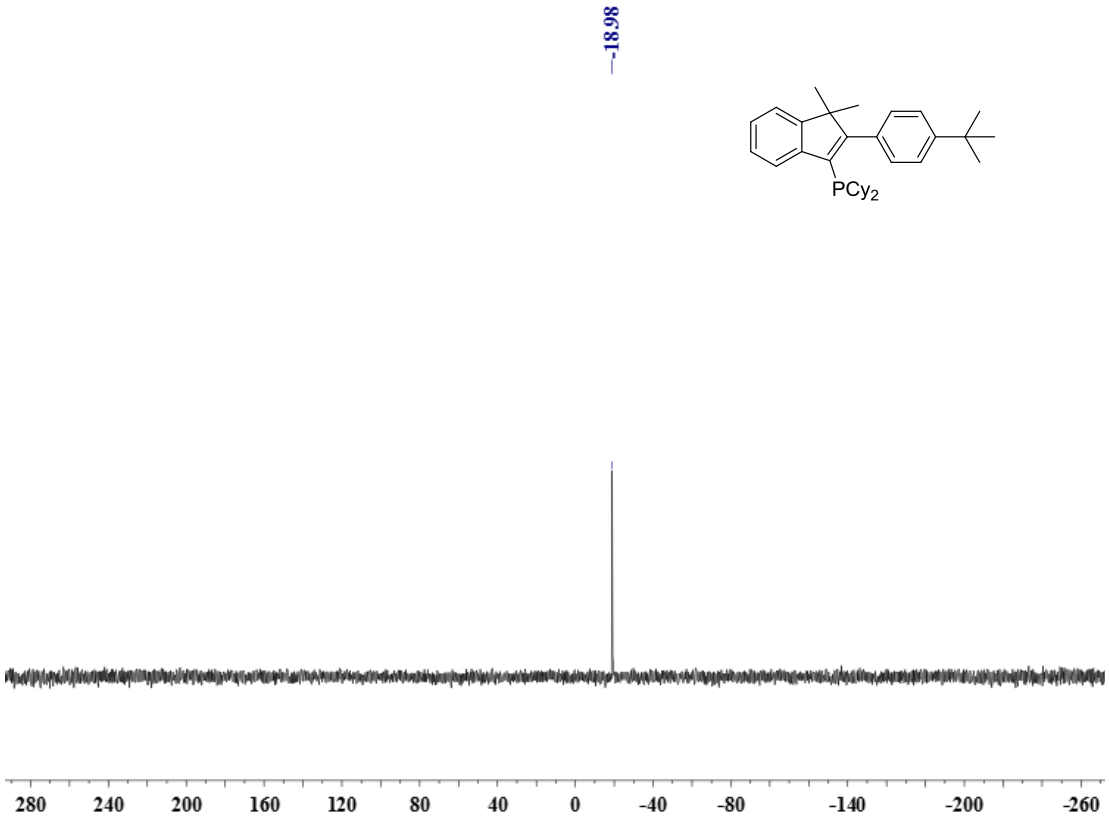
HRMS



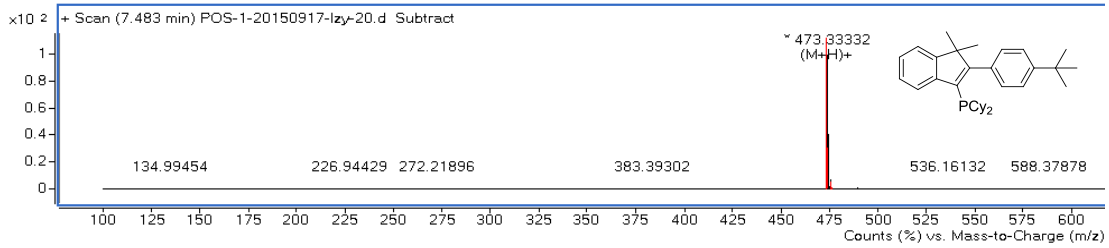
^{1}H NMR



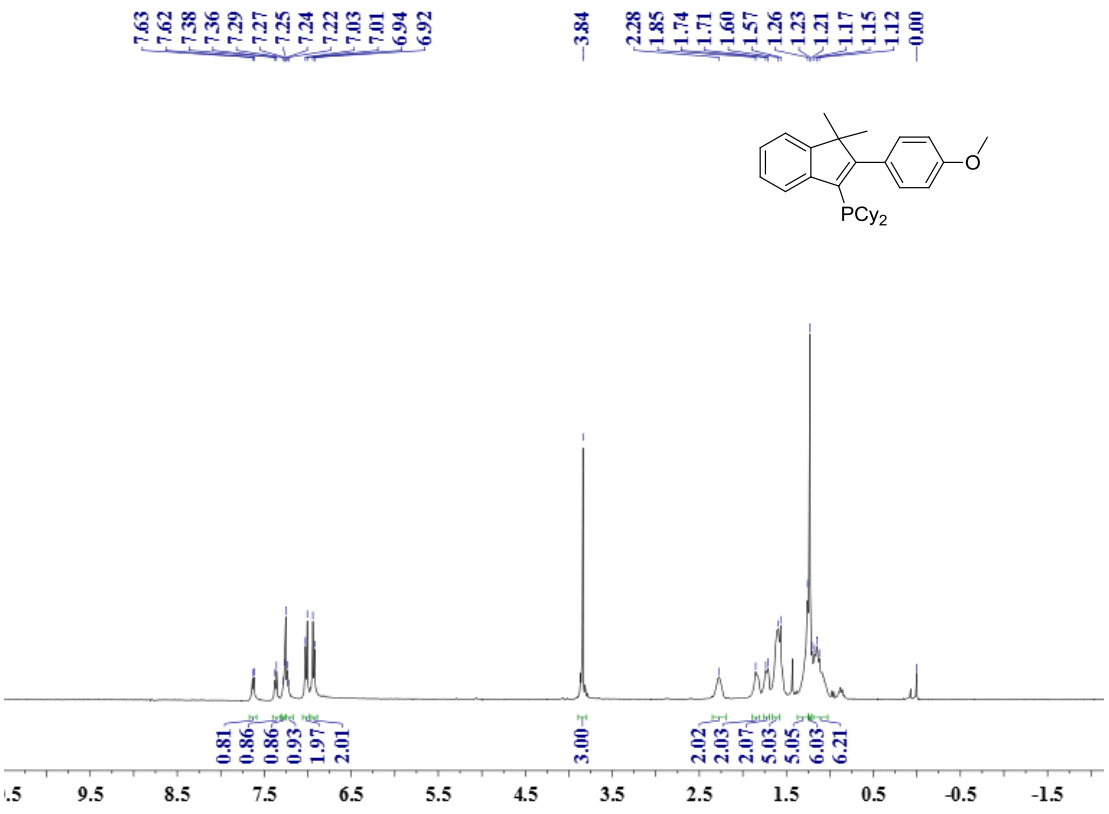
^{13}C NMR


-18.98
PCy2
280
240
200
160
120
80
40
0
-40
-80
-140
-200
-260

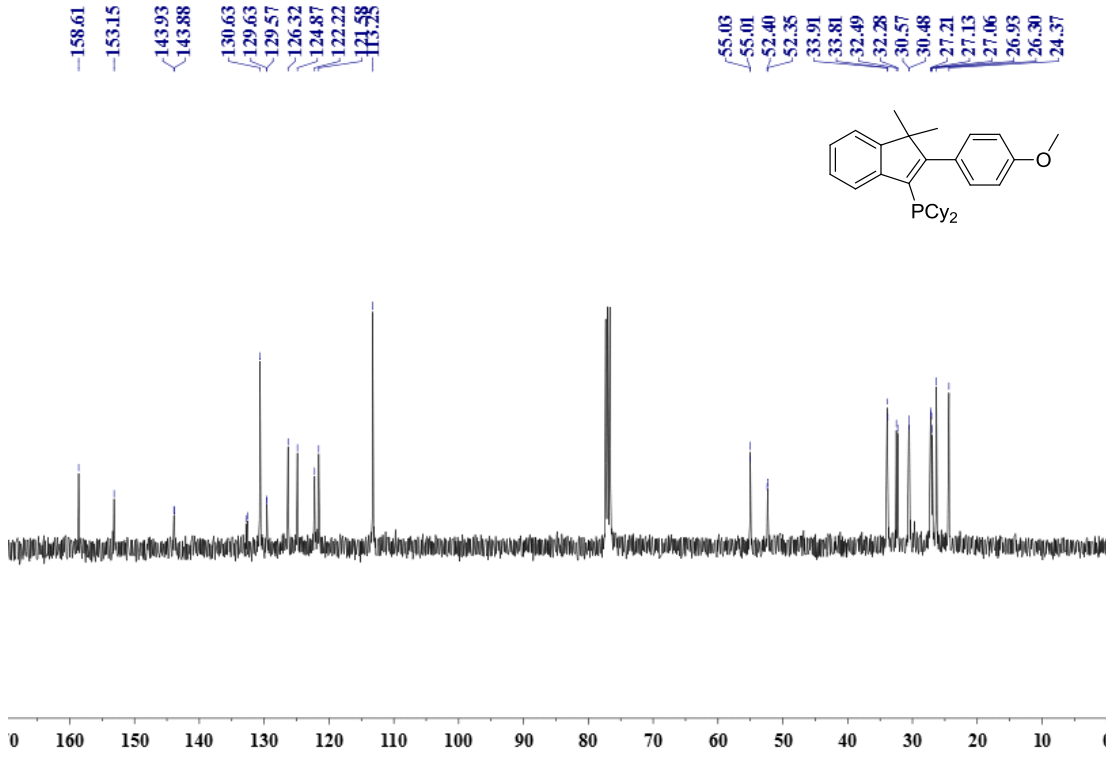
^{31}P NMR


x10 2
+ Scan (7.483 min) POS-1-20150917-lzy-20.d Subtract
473.33332
(M+H)+
PCy2
134.99454
226.94429
272.21896
383.39302
536.16132
588.37878
Counts (%) vs. Mass-to-Charge (m/z)

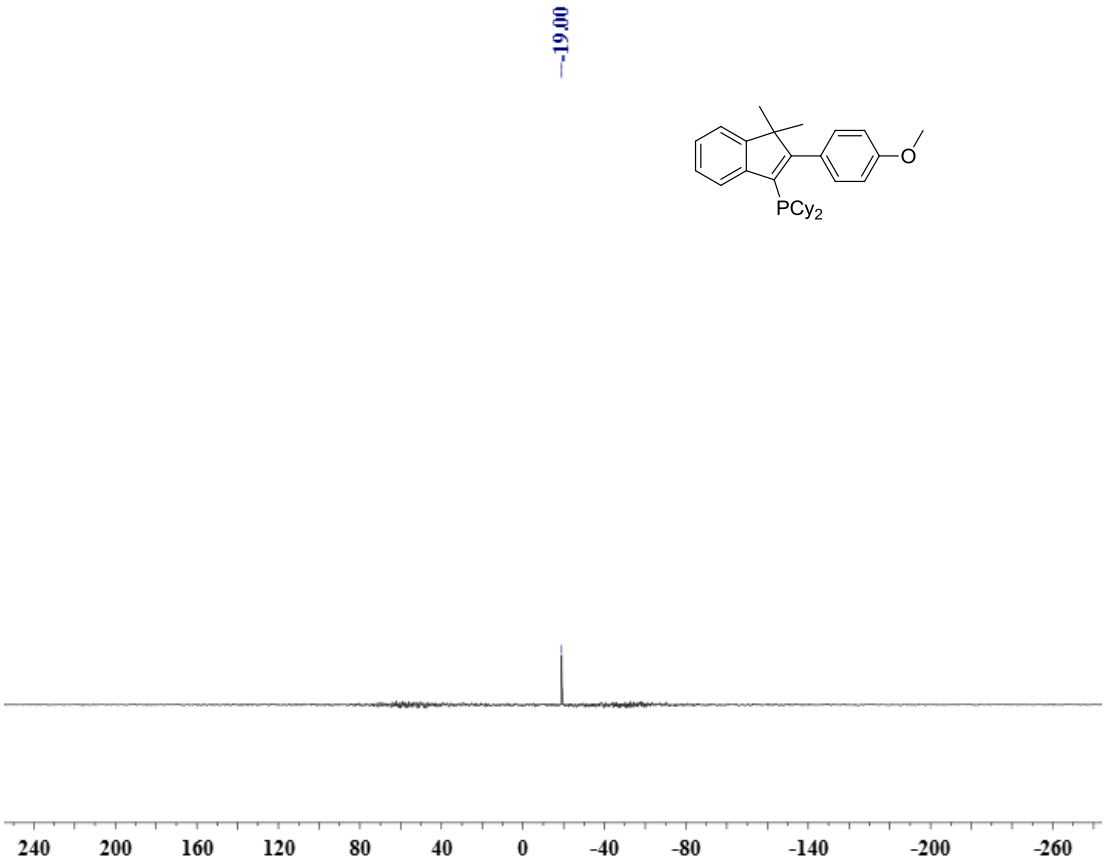
HRMS



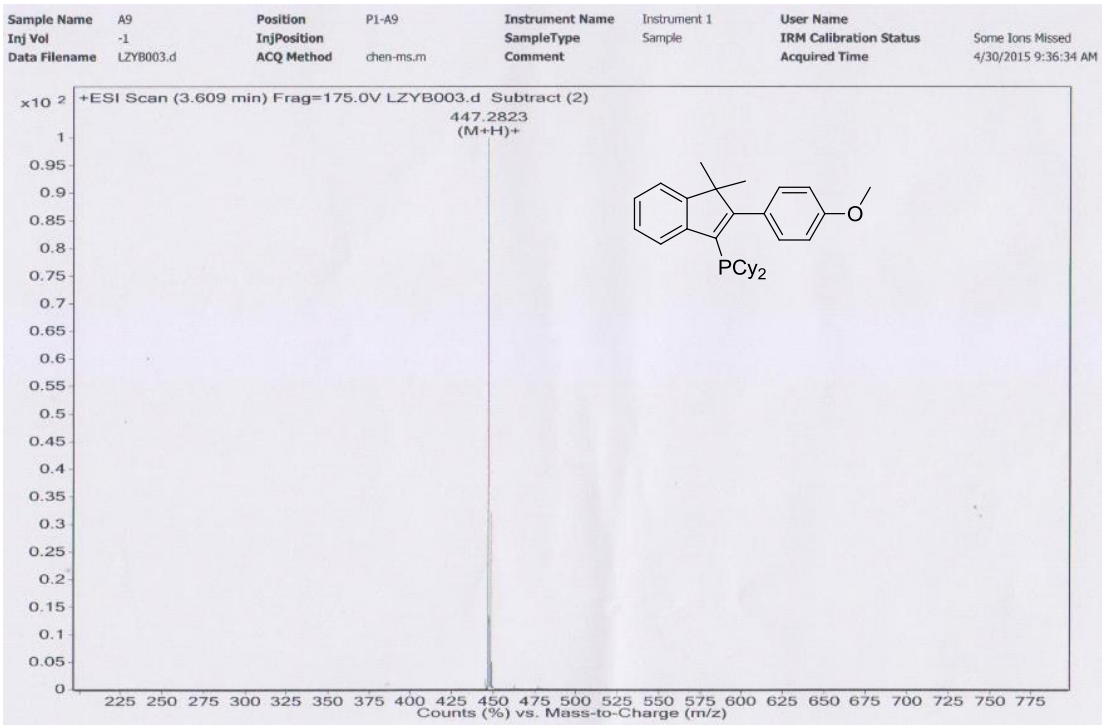
^{1}H NMR



^{13}C NMR


-19.00
O
PCy2
240
200
160
120
80
40
0
-40
-80
-140
-200
-260

^{31}P NMR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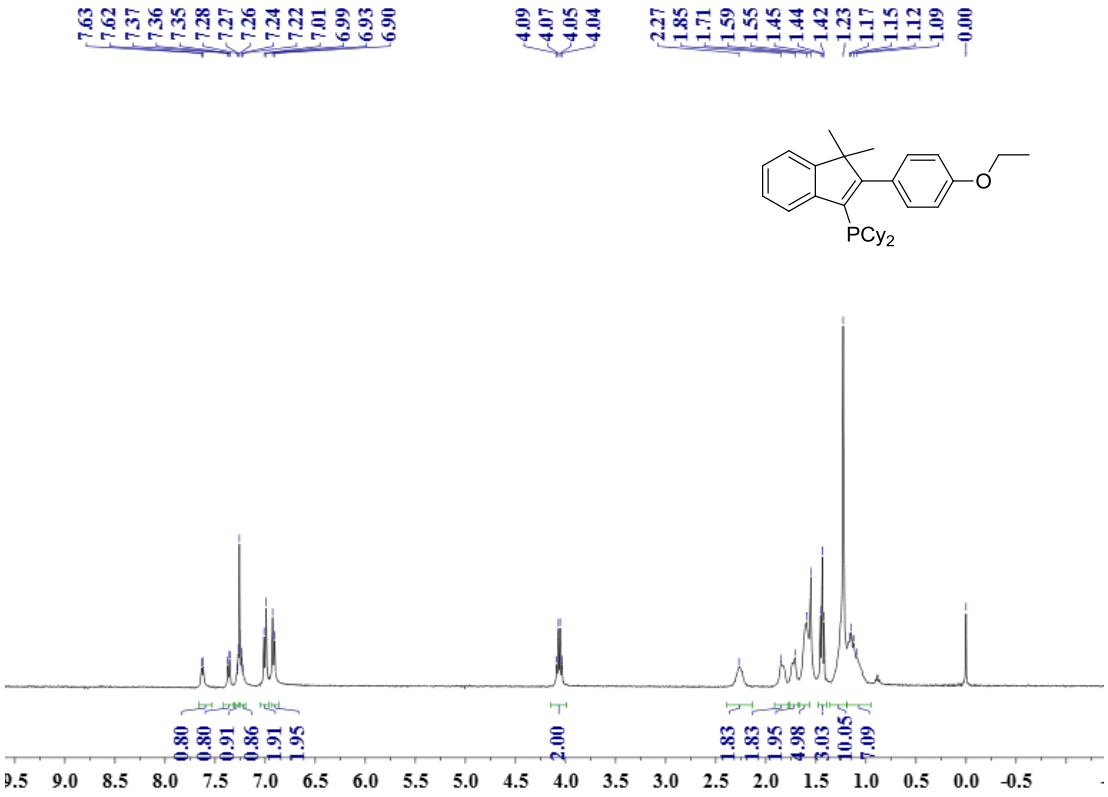
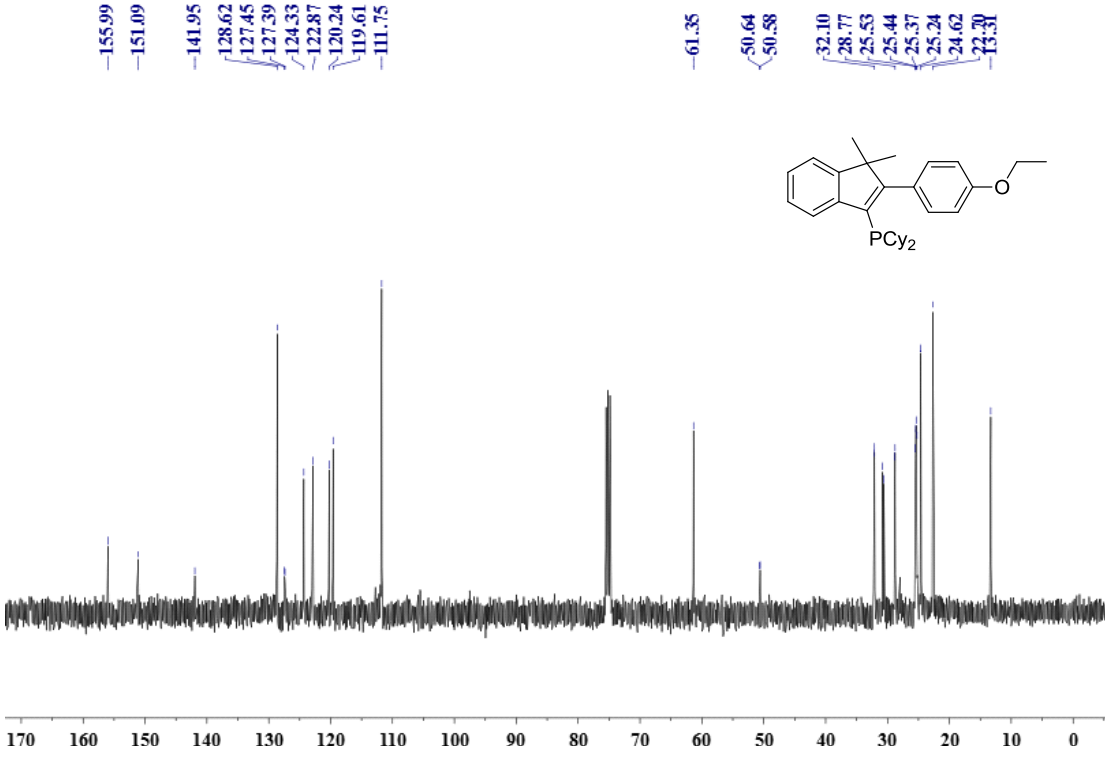
Position P1-A9
Instrument Name Instrument 1
User Name
Inj Vol -1
InjPosition
SampleType Sample
IRM Calibration Status Some Ions Missed
Data Filename LZYB003.d
ACQ Method chen-ms.m
Comment
Acquired Time 4/30/2015 9:36:34 AM
+ESI Scan (3.609 min) Frag=175.0V LZYB003.d Subtract (2)
447.2823
(M+H)+
O
PCy2
Counts (%) vs. Mass-to-Charge (m/z)

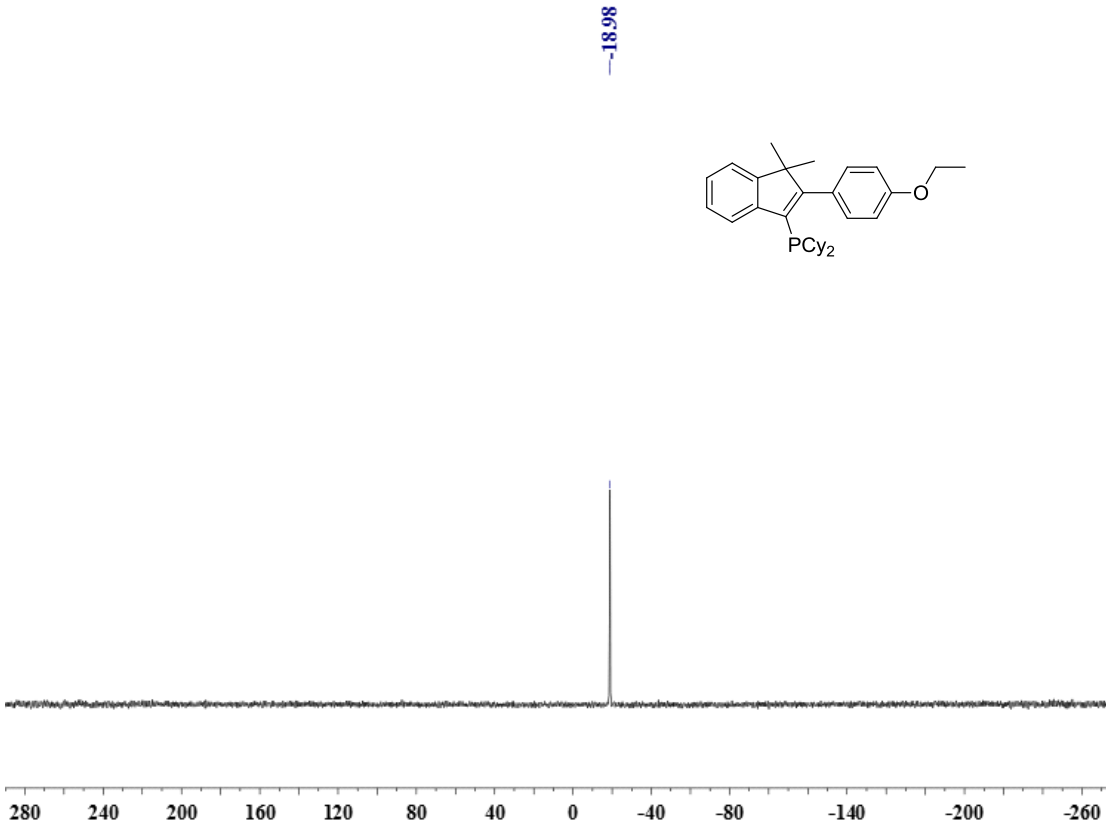
HRMS



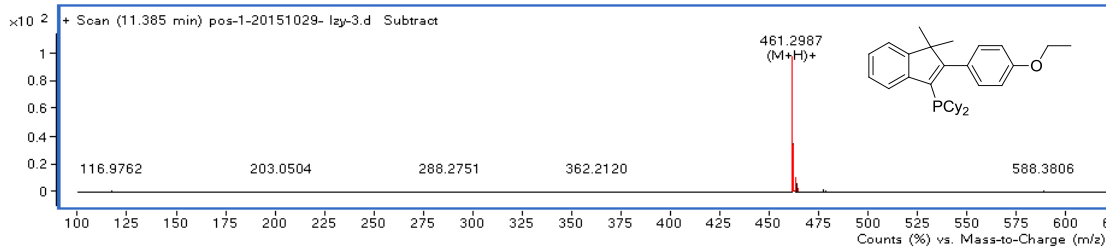
^{1}H NMR



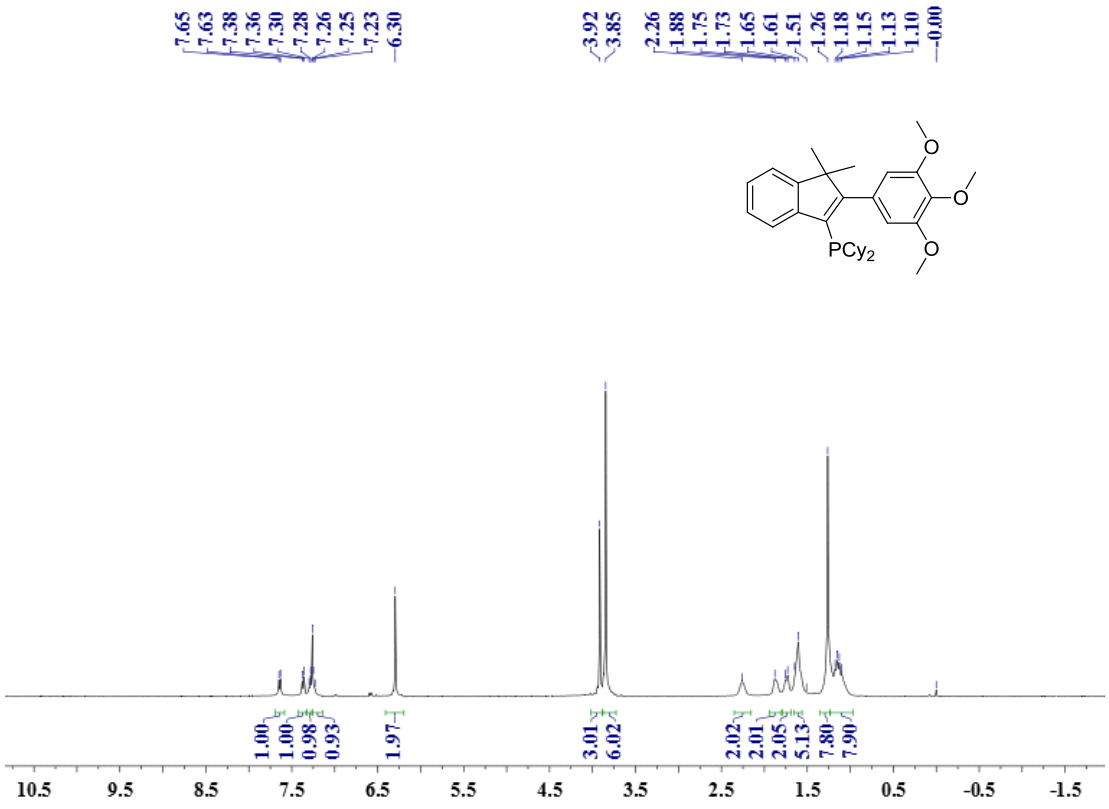
^{13}C NMR


-18.98
O
PCy2
280
240
200
160
120
80
40
0
-40
-80
-140
-200
-260

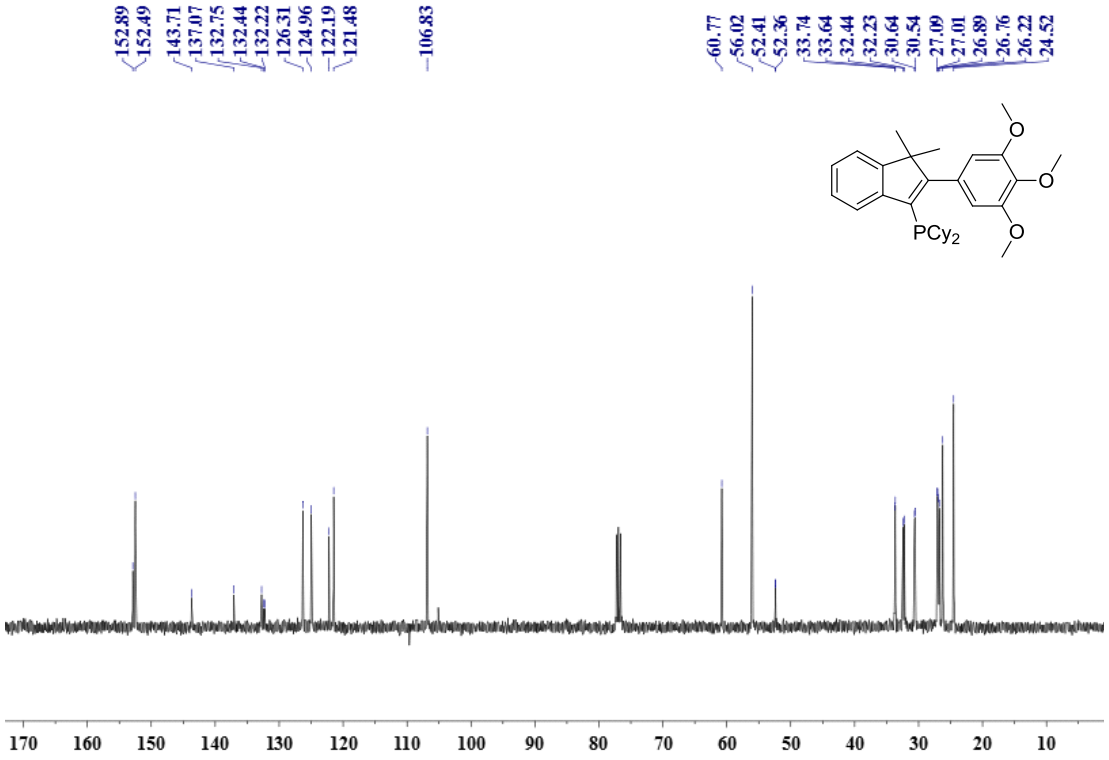
^{31}P NMR


x10 2
+ Scan (11.385 min) pos-1-20151029- lzy-3.d Subtract
461.2987
(M+H)+
O
PCy2
116.9762
203.0504
288.2751
362.2120
588.3806
Counts (%) vs. Mass-to-Charge (m/z)

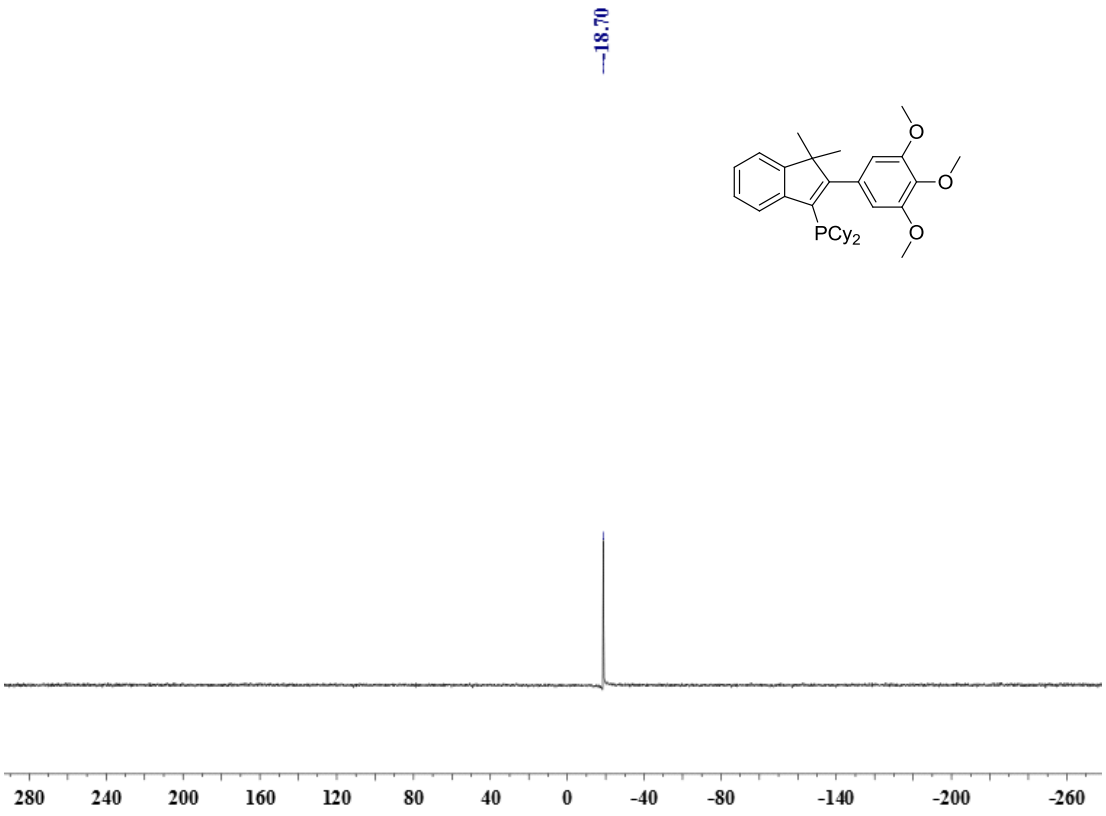
HRMS



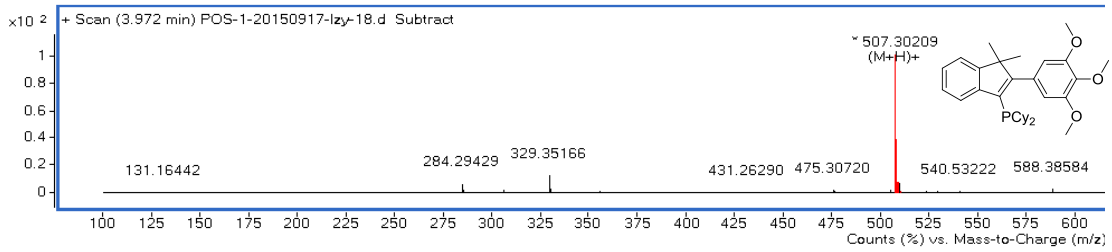
^{1}H NMR



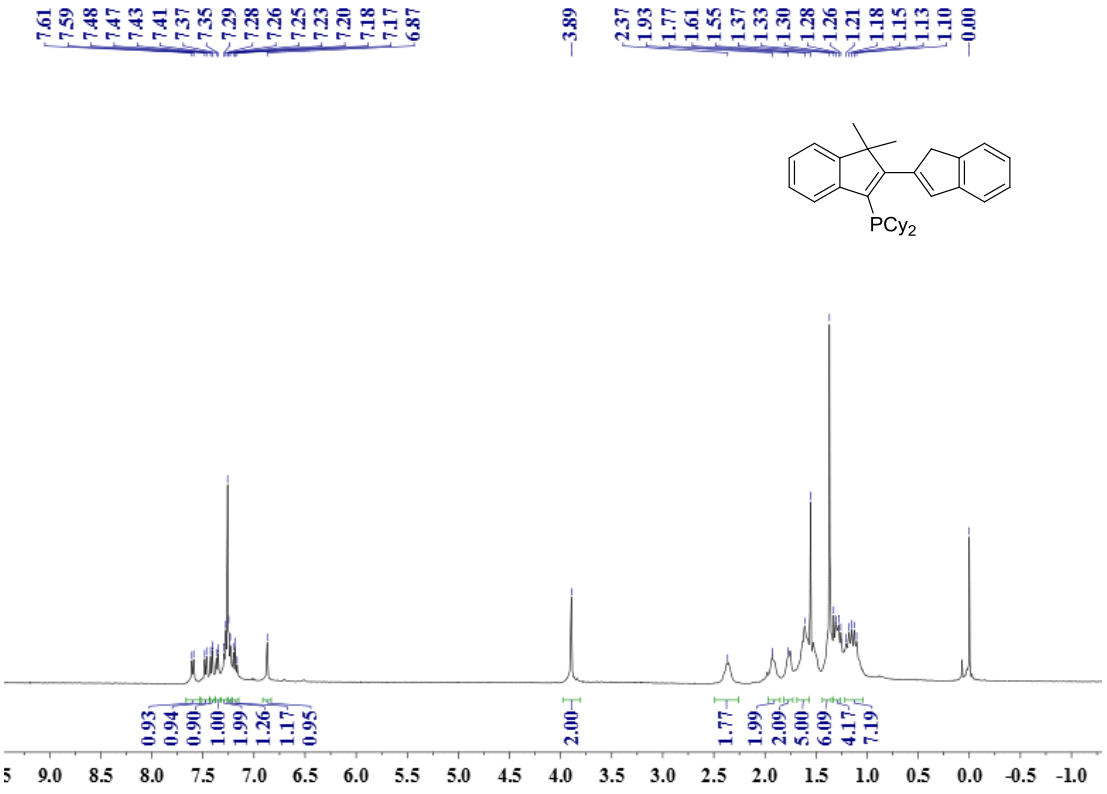
^{13}C NMR


18.70
O
O
O
PCy2
280
240
200
160
120
80
40
0
-40
-80
-140
-200
-260

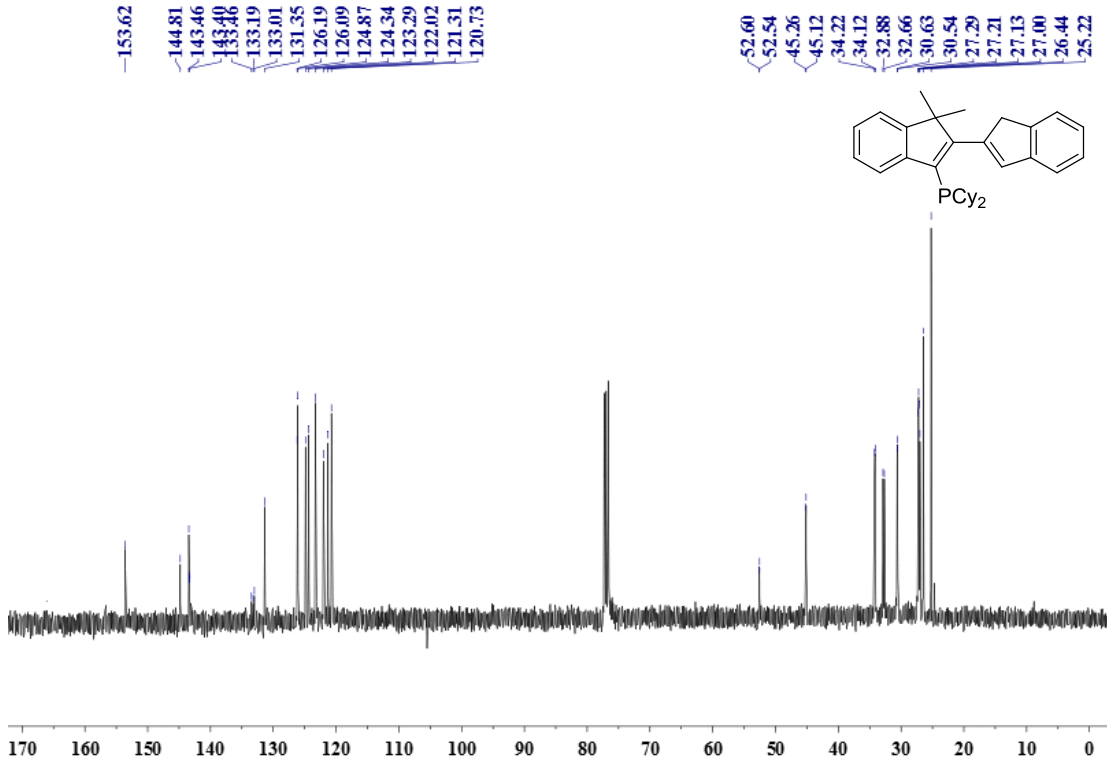
^{31}P NMR


x10 2
+ Scan (3.972 min) POS-1-20150917-lzy-18.d Subtract
507.30209
(M+H)+
O
O
O
PCy2
131.16442
284.29429
329.35166
431.26290
475.30720
540.53222
588.38584
Counts (%) vs. Mass-to-Charge (m/z)

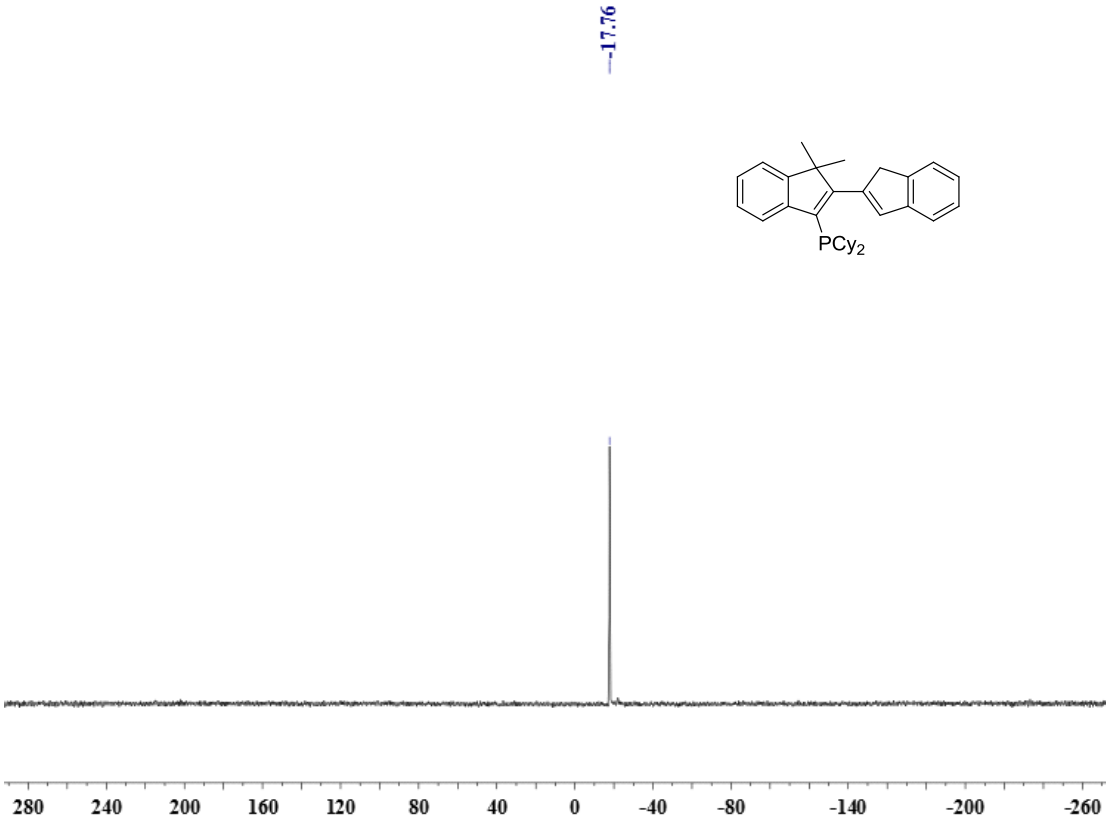
HRMS



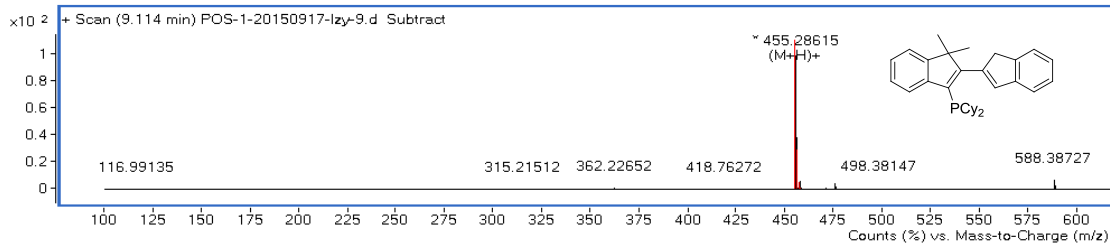
^{1}H NMR



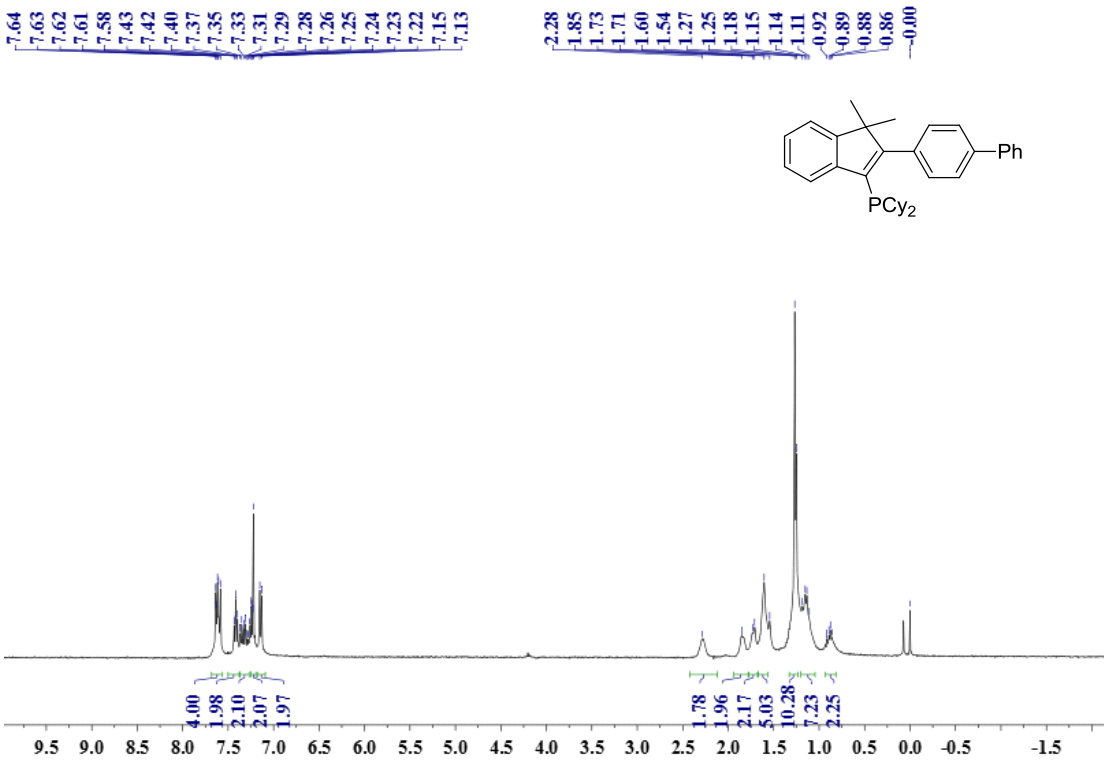
^{13}C NMR


-17.76
PCy2
280
240
200
160
120
80
40
0
-40
-80
-140
-200
-260

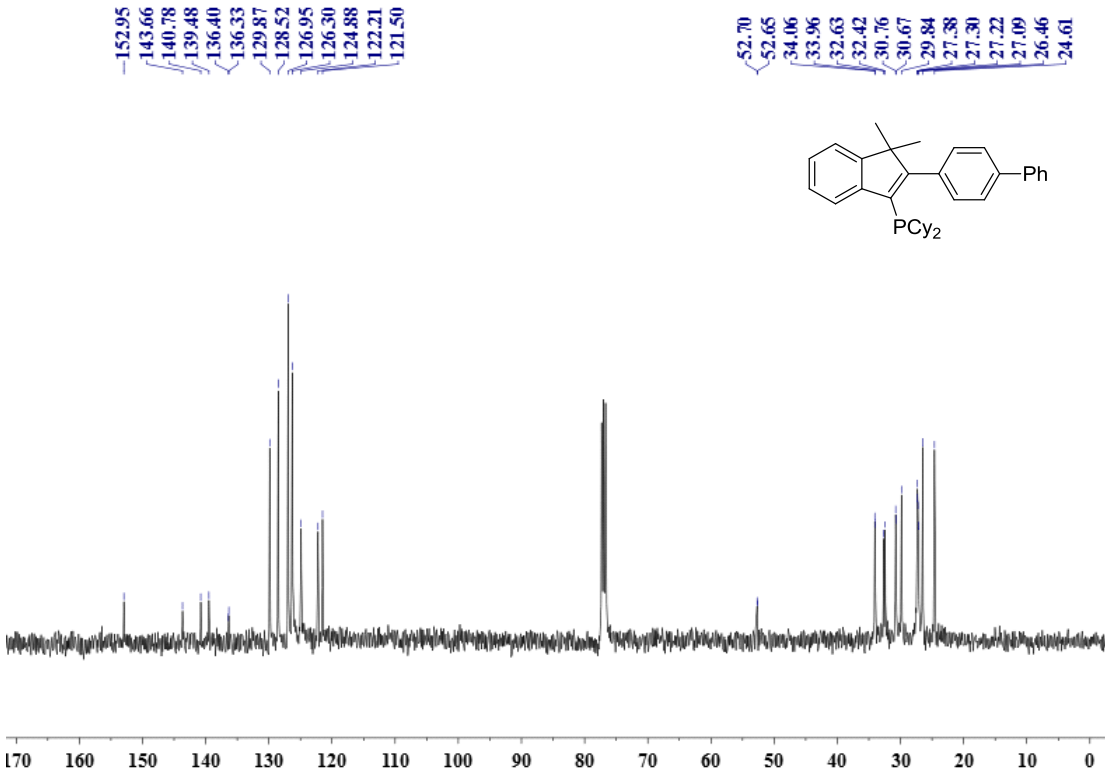
^{31}P NMR


x10 2
+ Scan (9.114 min) POS-1-20150917-lzy-9.d Subtract
455.28615
(M+H)+
PCy2
116.99135
315.21512
362.22652
418.76272
498.38147
588.38727
Counts (%) vs. Mass-to-Charge (m/z)

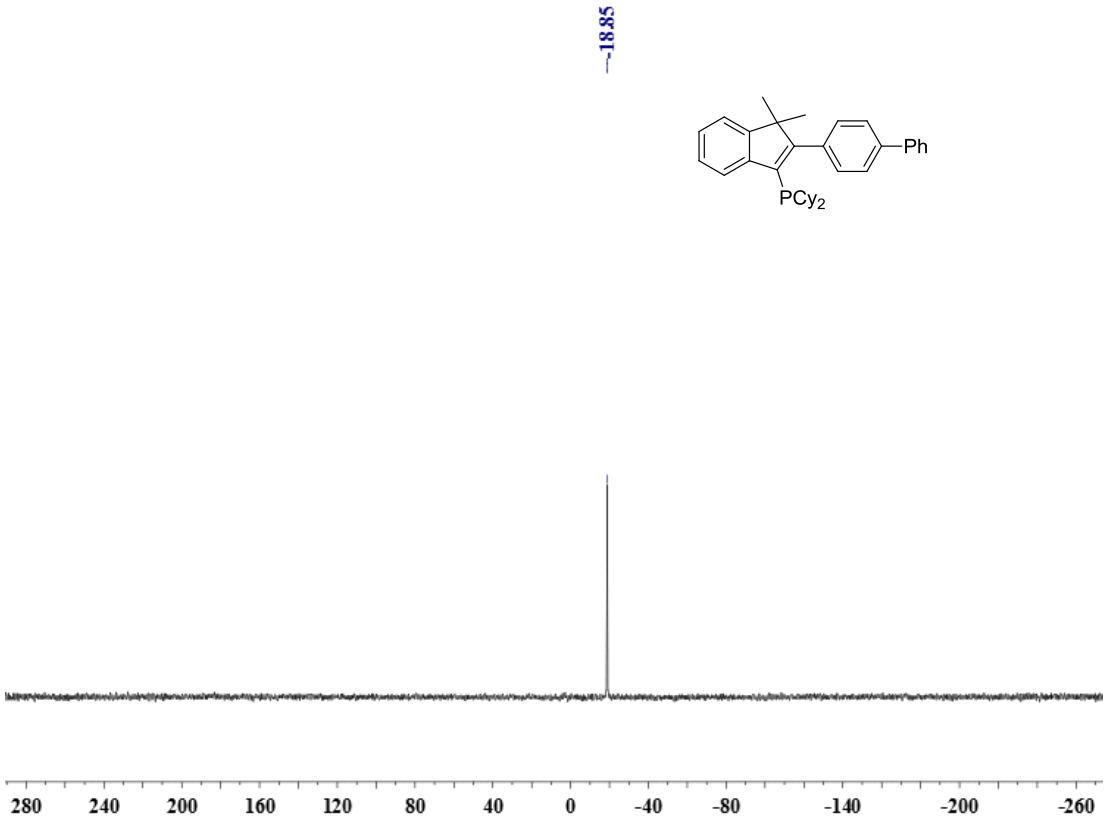
HRMS



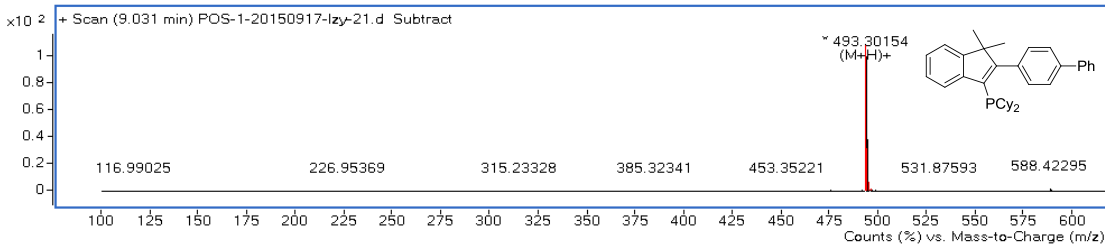
^{1}H NMR



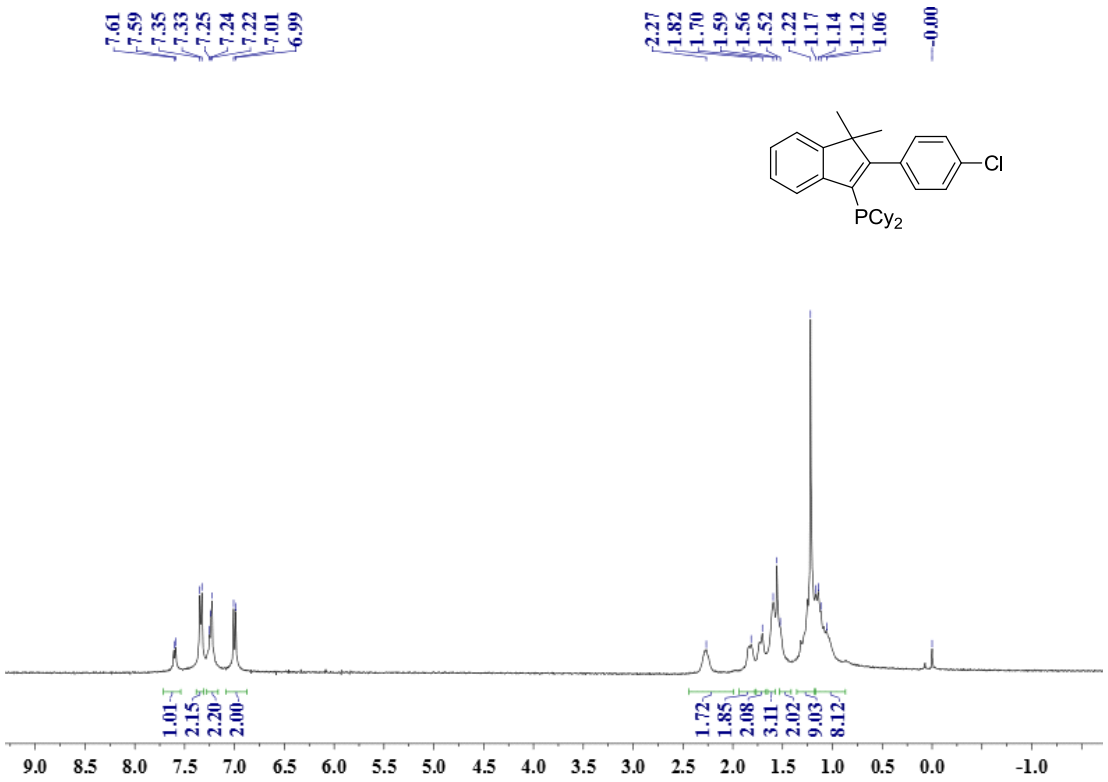
^{13}C NMR


18.85
Ph
PCy2
280
240
200
160
120
80
40
0
-40
-80
-140
-200
-260

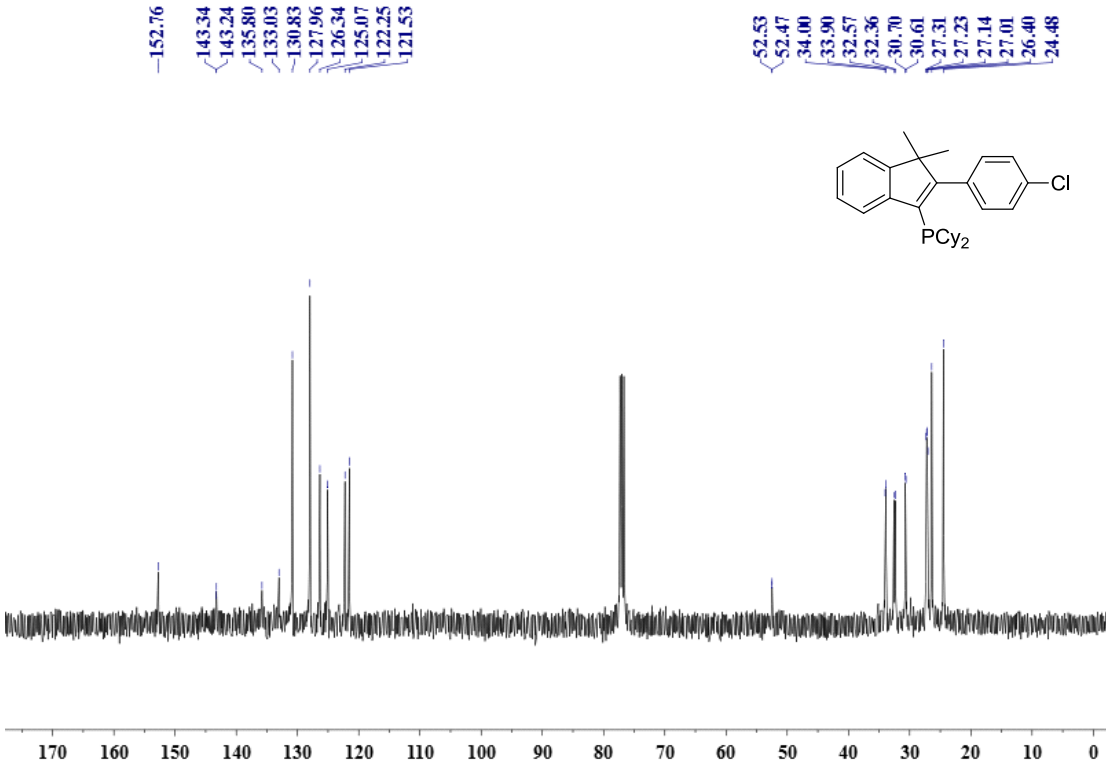
^{31}P NMR


×10 2
+ Scan (9.031 min) POS-1-20150917-lzy-21.d Subtract
493.30154
(M+H)+
Ph
PCy2
116.99025
226.95369
315.23328
385.32341
453.35221
531.87593
588.42295
Counts (%) vs. Mass-to-Charge (m/z)

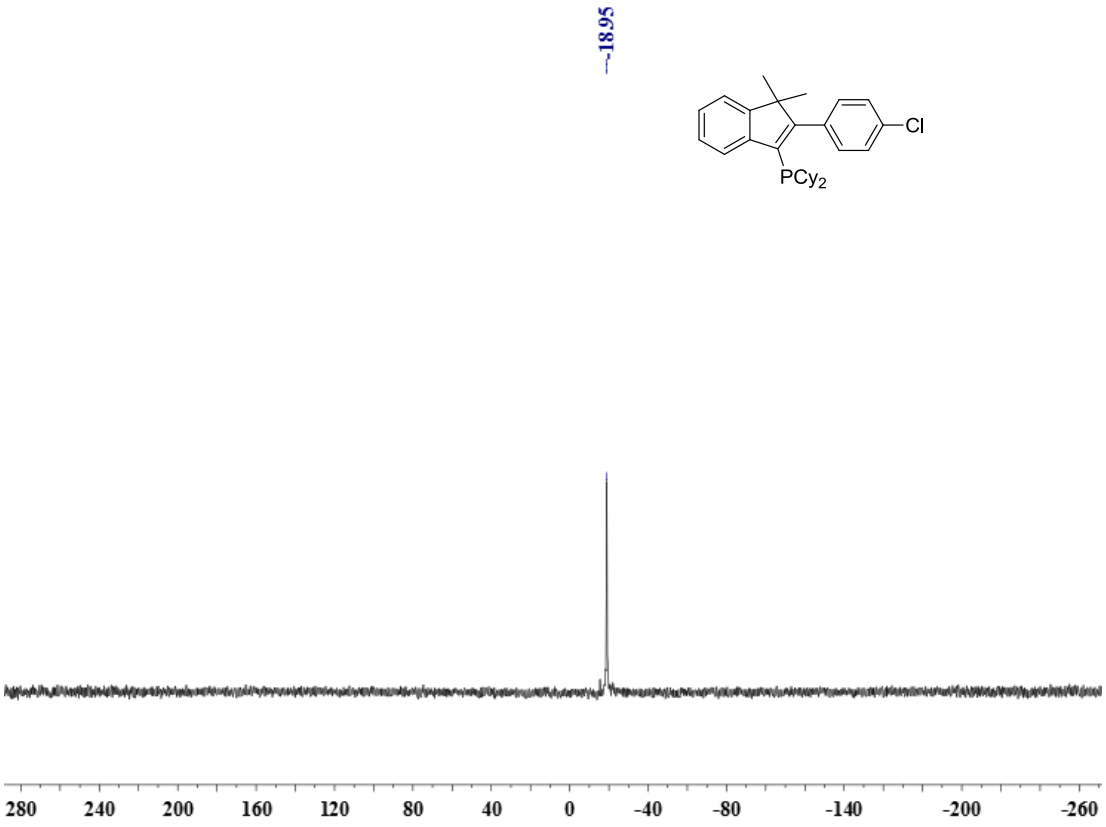
HRMS



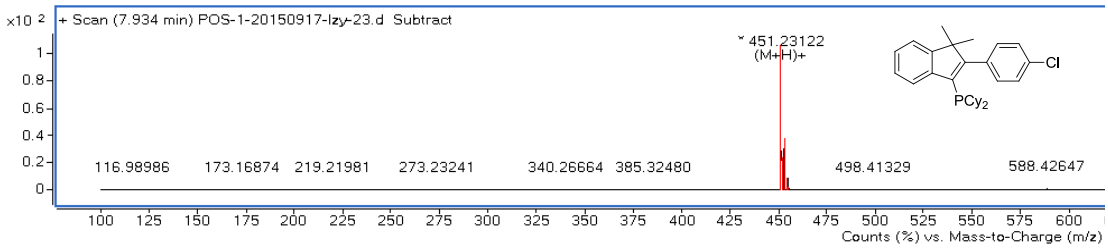
^{1}H NMR



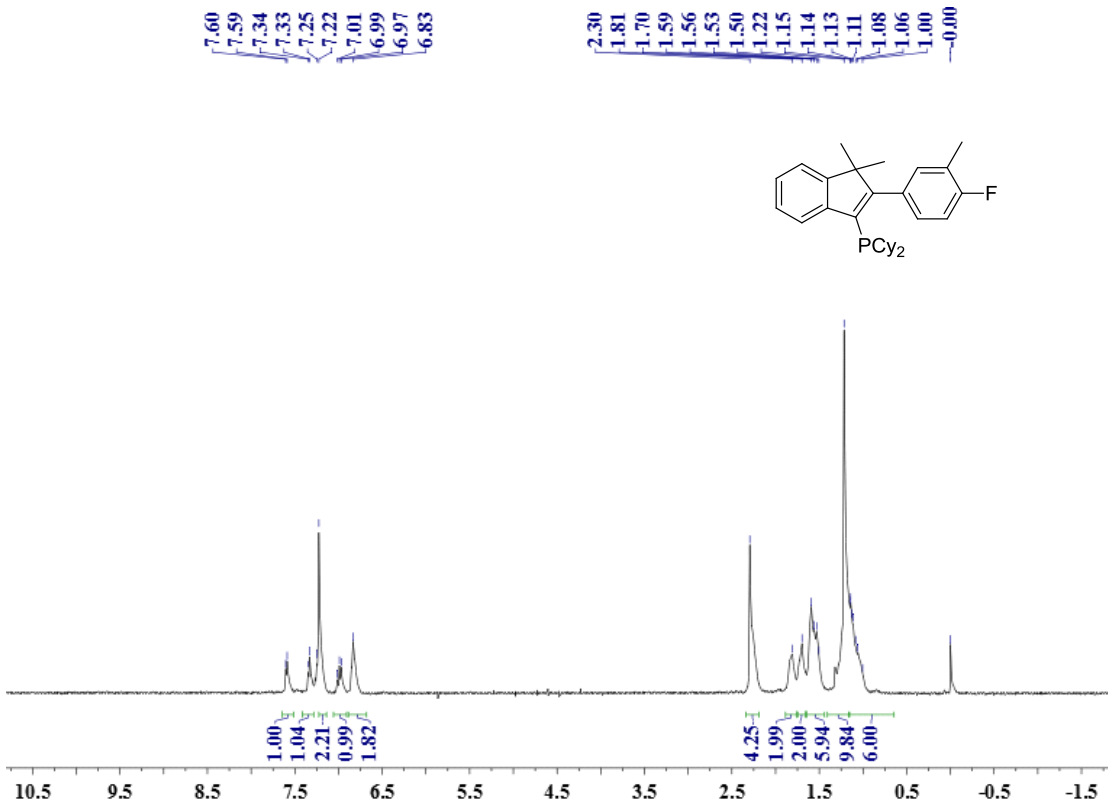
^{13}C NMR


18.95
Cl
PCy2
280
240
200
160
120
80
40
0
-40
-80
-140
-200
-260

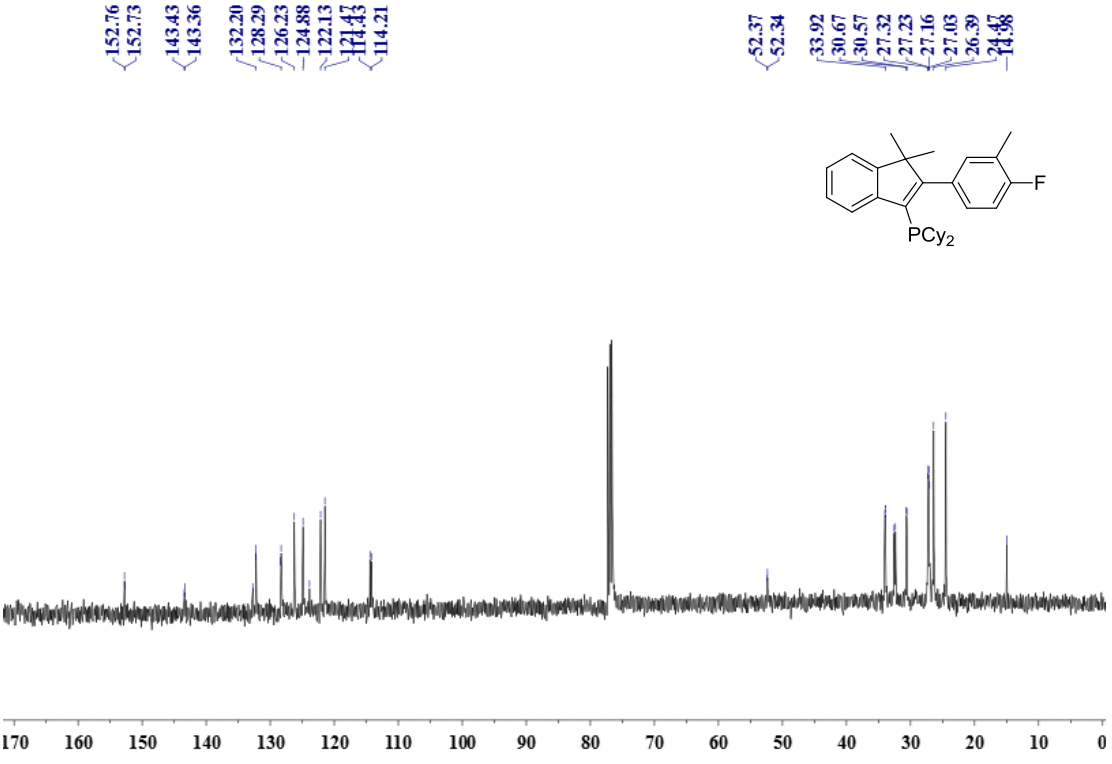
^{31}P NMR


x10 2
+ Scan (7.934 min) POS-1-20150917-lzy-23.d Subtract
451.23122
(M+H)+
Cl
PCy2
116.98986
173.16874
219.21981
273.23241
340.26664
385.32480
498.41329
588.42647
Counts (%) vs. Mass-to-Charge (m/z)

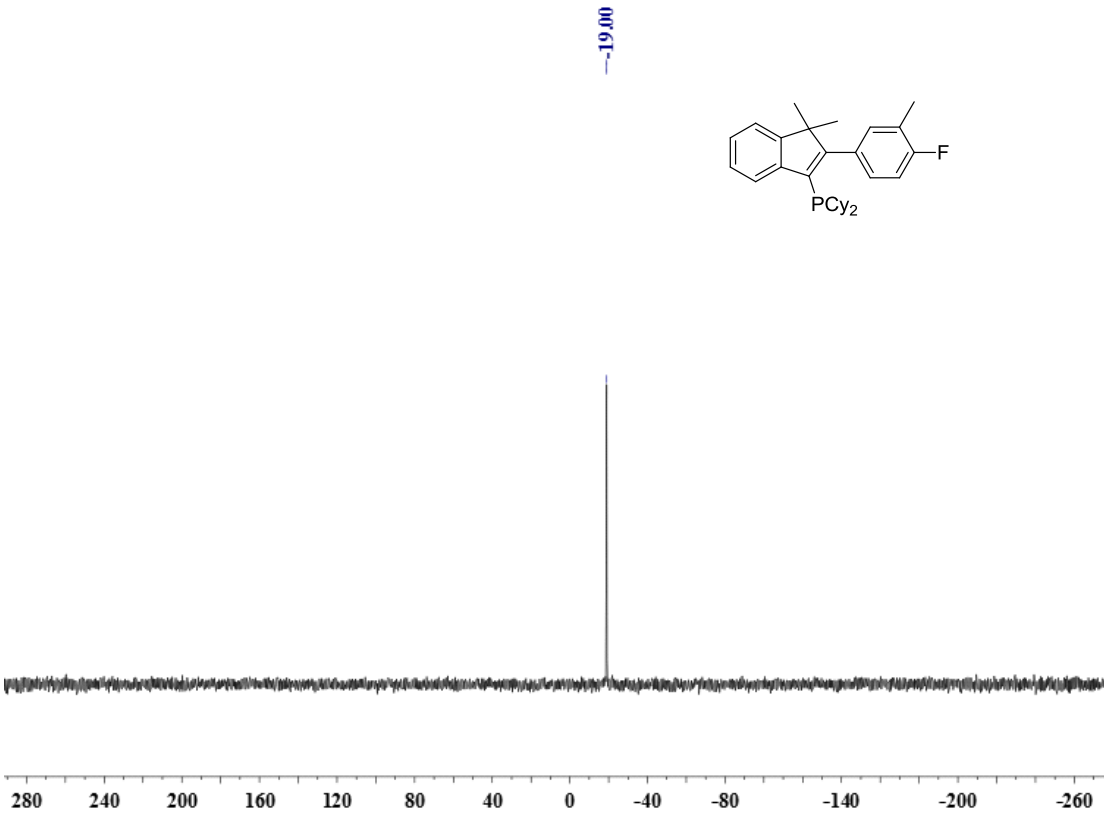
HRMS



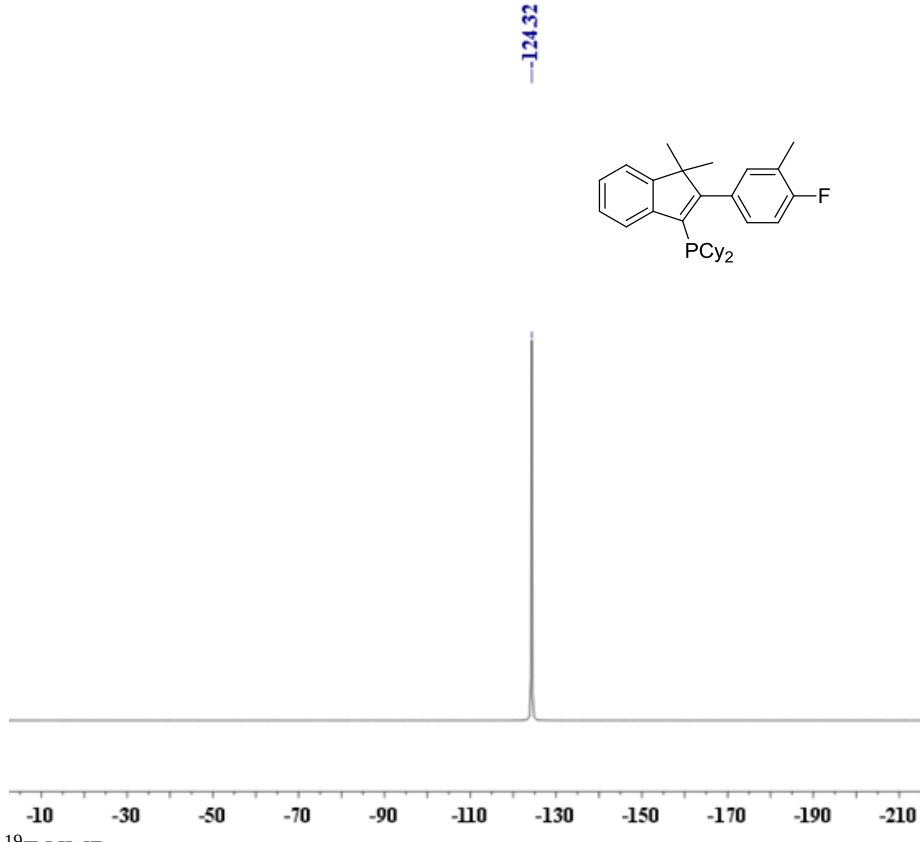
^{1}H NMR



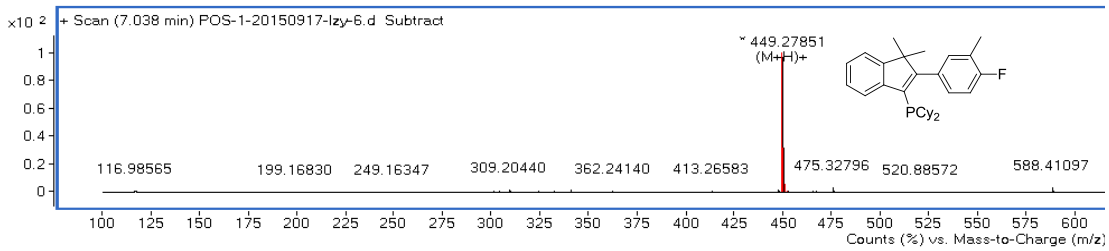
^{13}C NMR



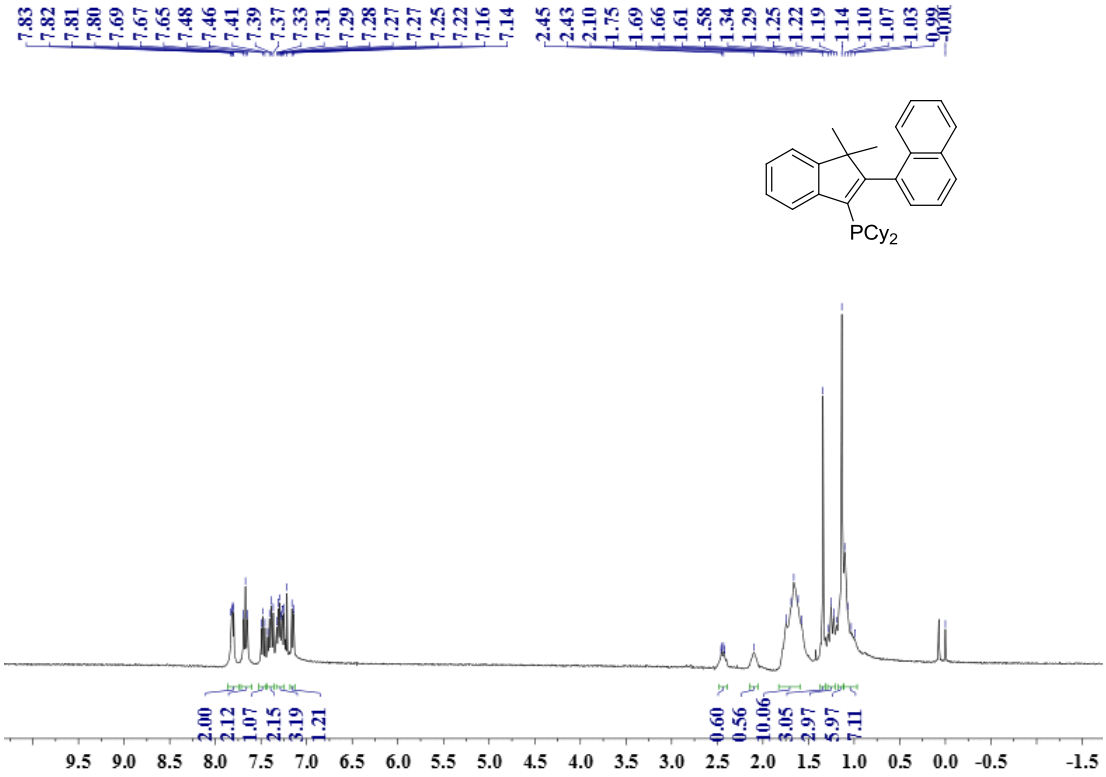
^{31}P NMR



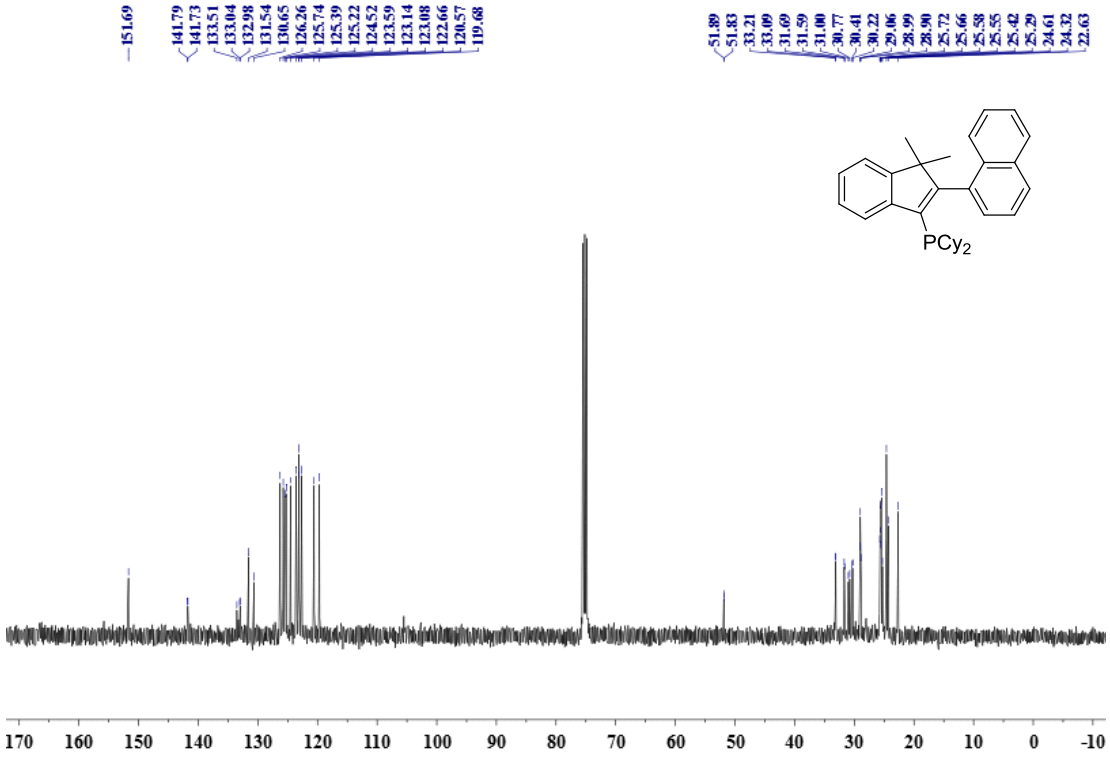
^{19}F NMR


x10 2
+ Scan (7.038 min) POS-1-20150917-lzy-6.d Subtract
449.27851
(M+H)+
F
PCy2
116.98565
199.16830
249.16347
309.20440
362.24140
413.26583
475.32796
520.88572
588.41097
Counts (%) vs. Mass-to-Charge (m/z)

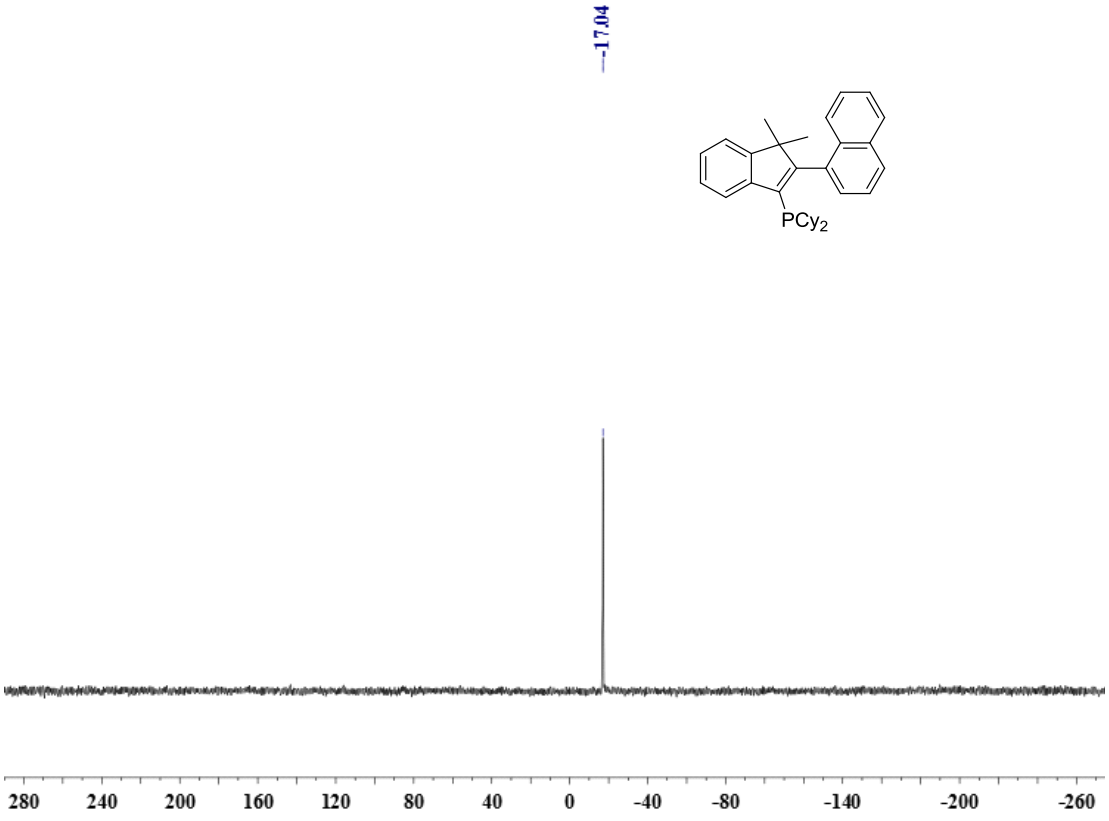
HRMS


PCy2

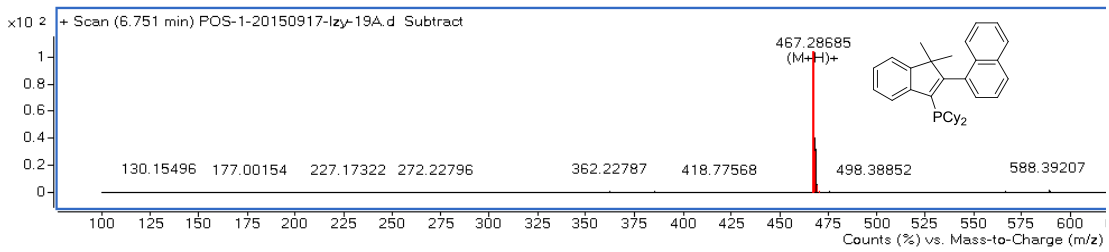
^{1}H NMR



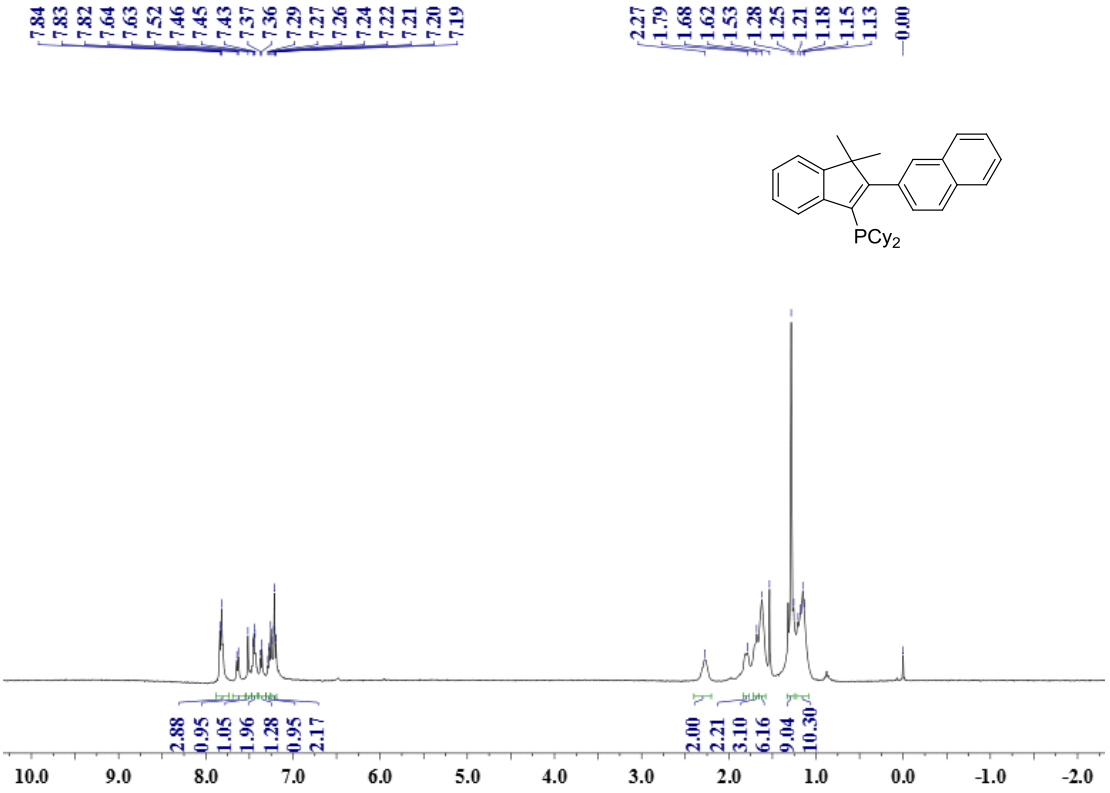
^{13}C NMR



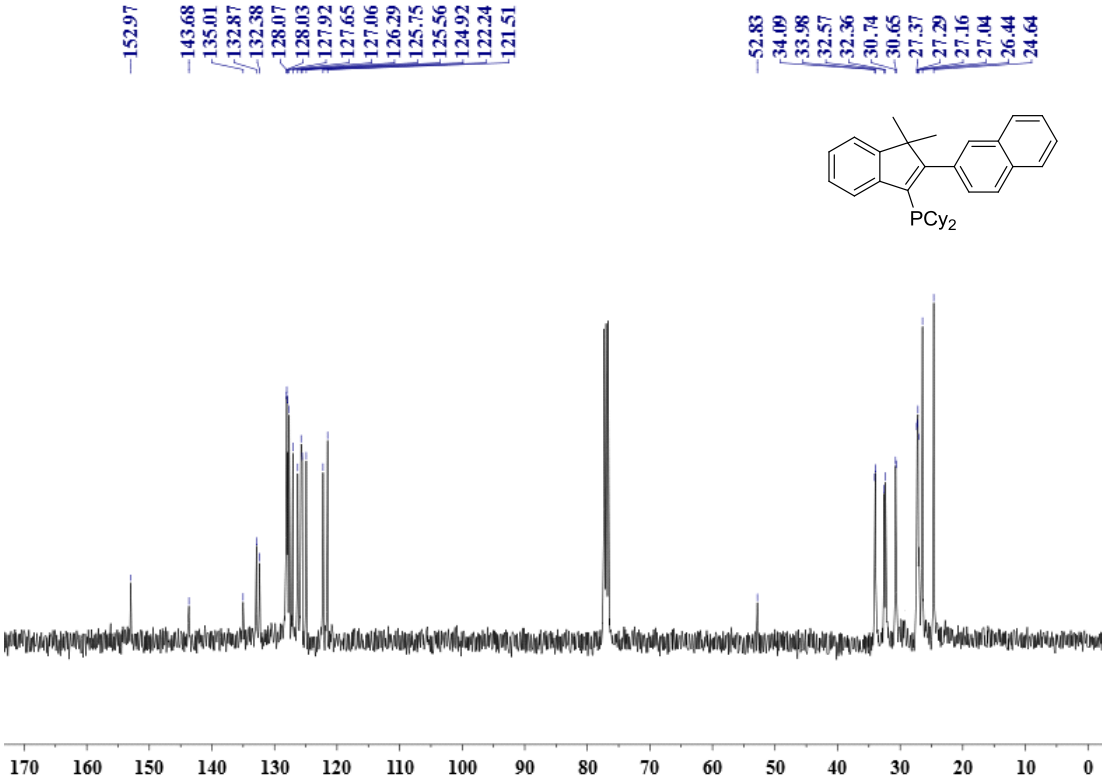
^{31}P NMR


x10 2
+ Scan (6.751 min) POS-1-20150917-lzy-19A.d Subtract
467.28685
(M+H)+
PCy2
130.15496
177.00154
227.17322
272.22796
362.22787
418.77568
498.38852
588.39207
Counts (%) vs. Mass-to-Charge (m/z)

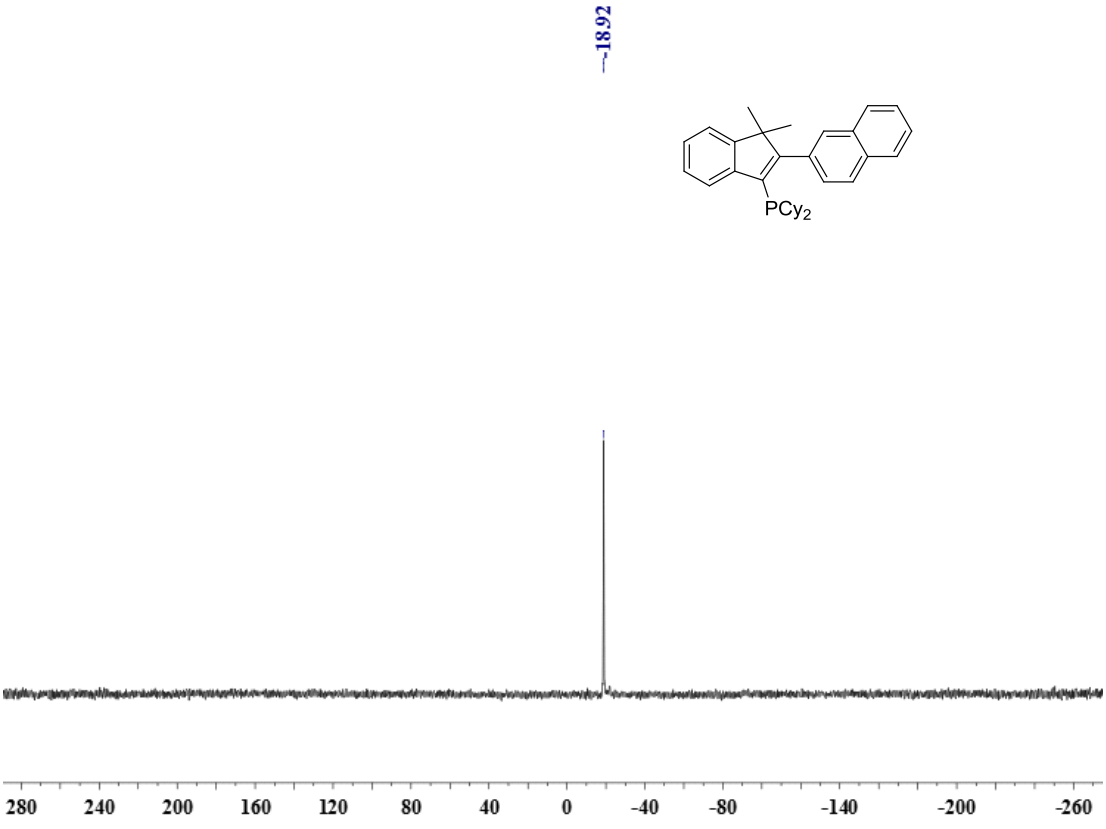
HRMS


7.84
7.83
7.82
7.64
7.63
7.52
7.46
7.45
7.43
7.37
7.36
7.29
7.27
7.26
7.24
7.22
7.21
7.20
7.19
2.27
1.79
1.68
1.62
1.53
1.28
1.25
1.21
1.18
1.15
1.13
0.00
PCy2
2.88
0.95
1.05
1.96
1.28
0.95
2.17
2.00
2.21
3.10
6.16
9.04
10.30
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0

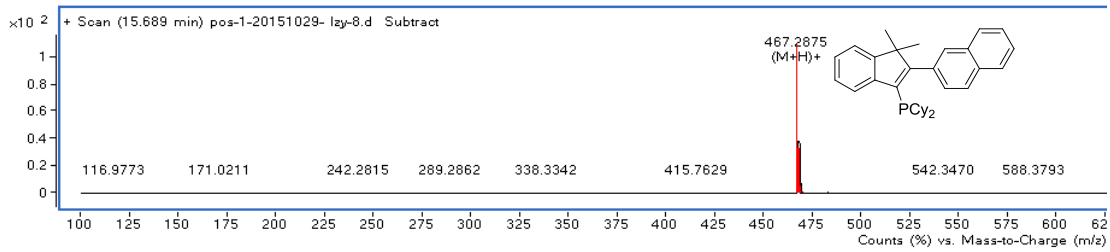
^{1}H NMR



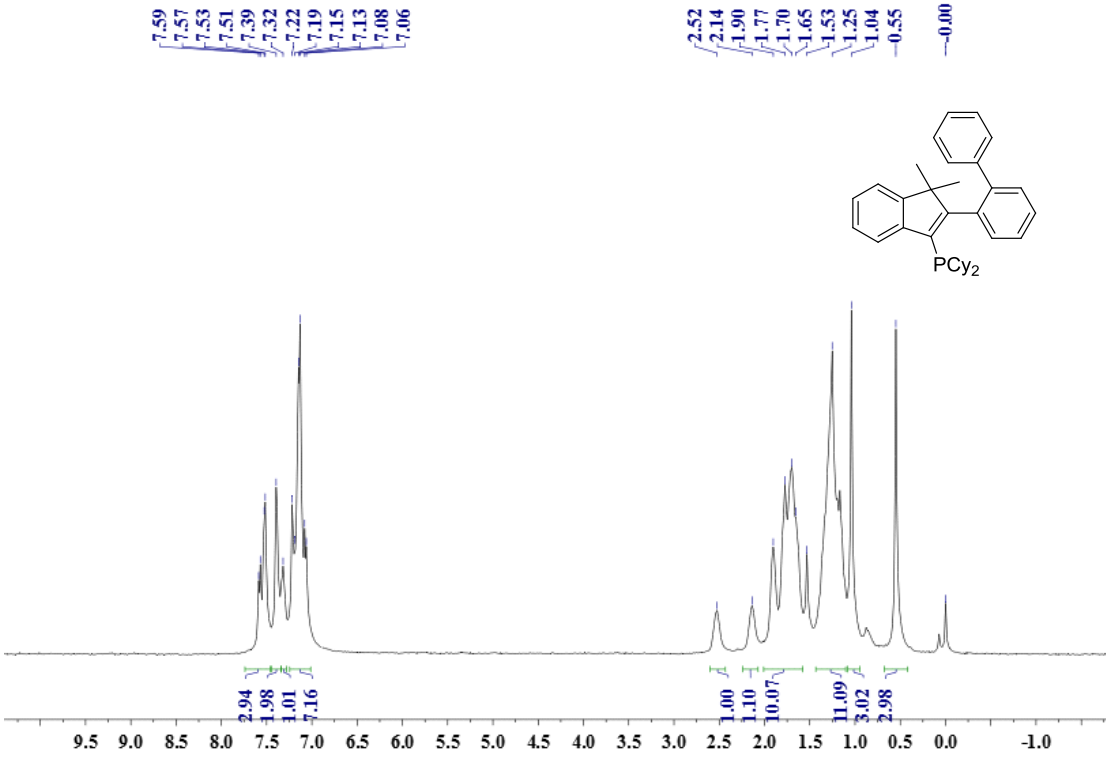
^{13}C NMR



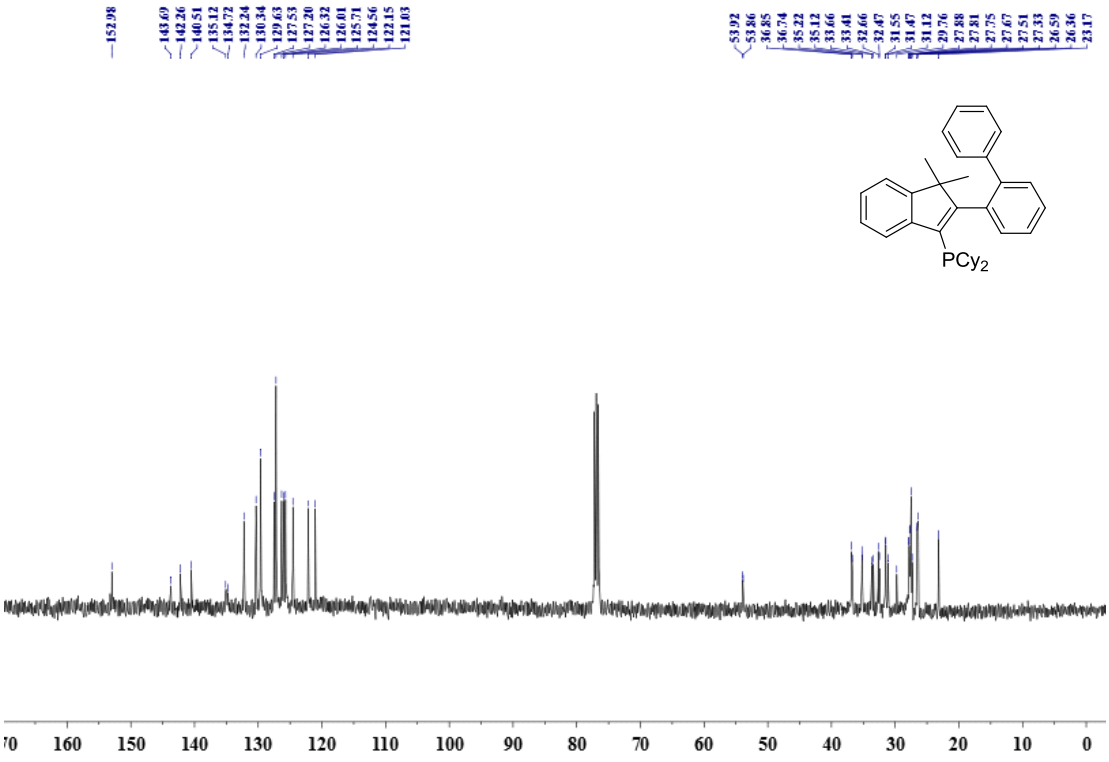
^{31}P NMR


+ Scan (15.689 min) pos-1-20151029- lzy-8.d Subtract
467.2875
(M+H)+
PCy2
116.9773
171.0211
242.2815
289.2862
338.3342
415.7629
542.3470
588.3793
Counts (%) vs. Mass-to-Charge (m/z)

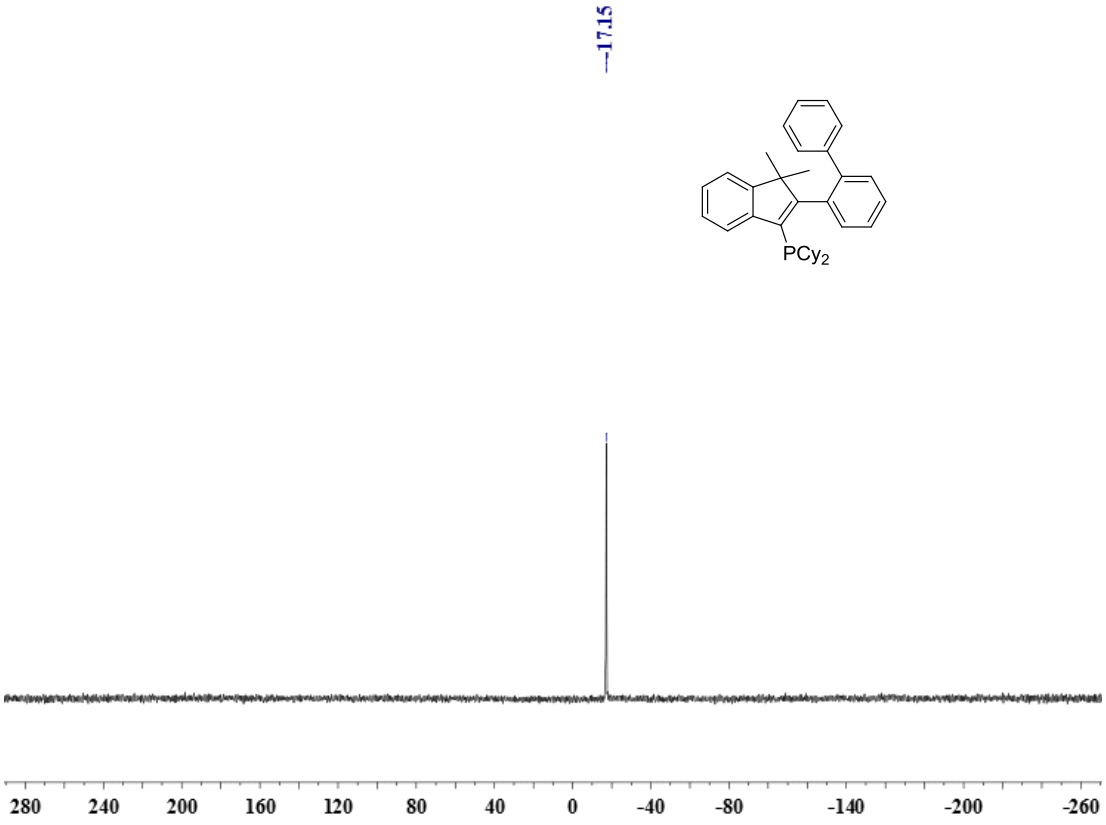
HRMS


7.59
7.57
7.53
7.51
7.39
7.32
7.22
7.19
7.15
7.13
7.08
7.06
2.52
2.14
1.90
1.77
1.70
1.65
1.53
1.25
1.04
0.55
0.00
PCy2
2.94
1.98
1.01
7.16
1.00
1.10
10.07
11.09
3.02
2.98

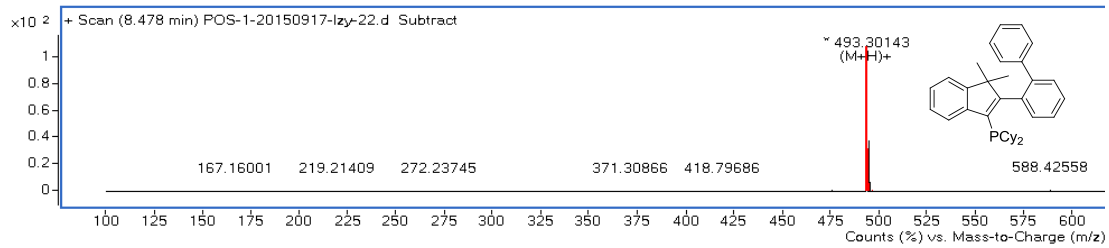
^{1}H NMR



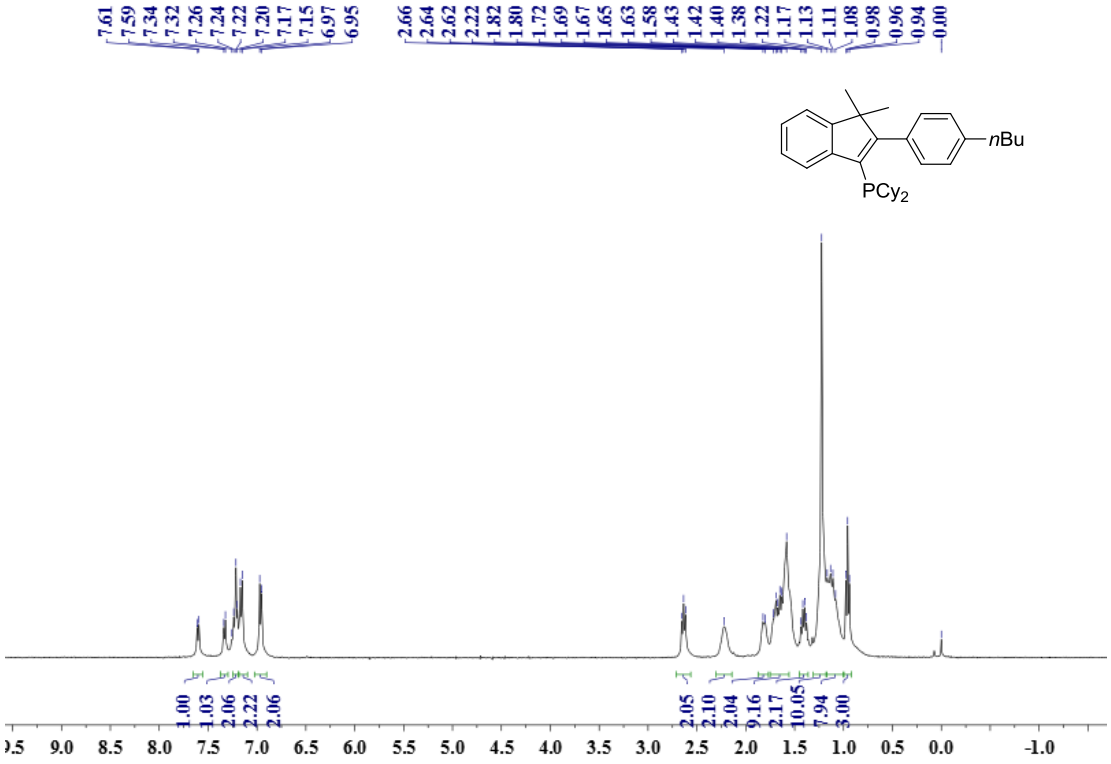
^{13}C NMR



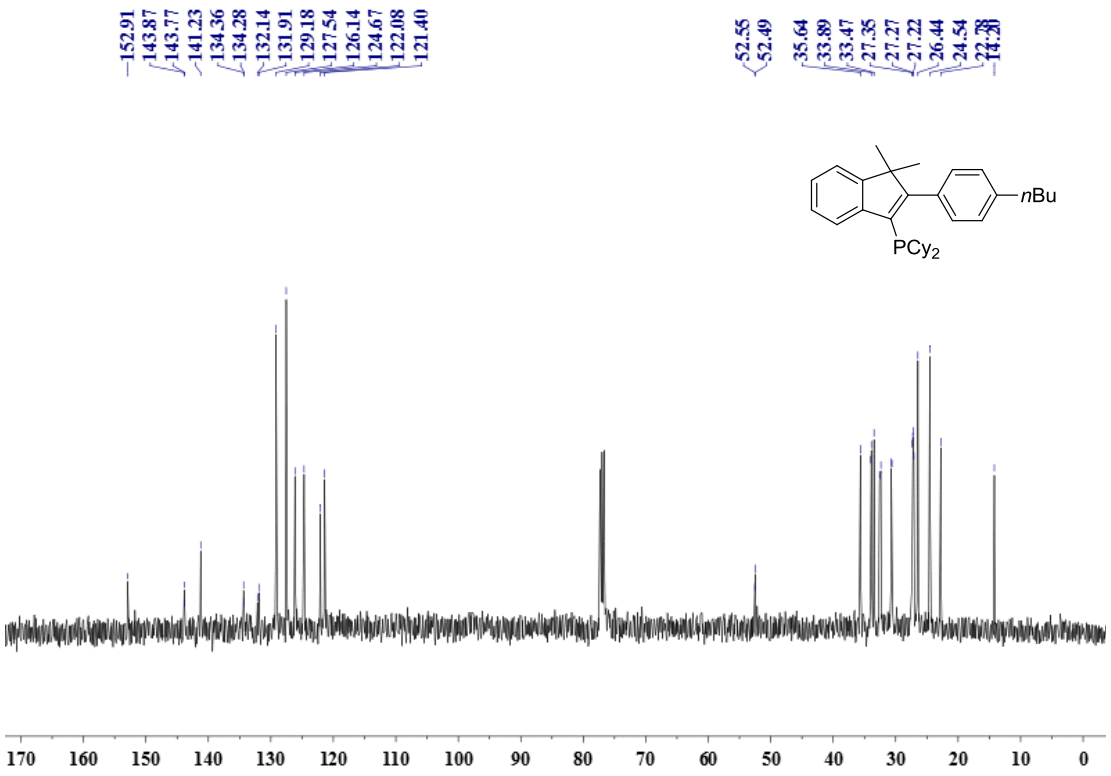
^{31}P NMR


x10 2
+ Scan (8.478 min) POS-1-20150917-lzy-22.d Subtract
493.30143
(M+H)+
PCy2
167.16001
219.21409
272.23745
371.30866
418.79686
588.42558
Counts (%) vs. Mass-to-Charge (m/z)

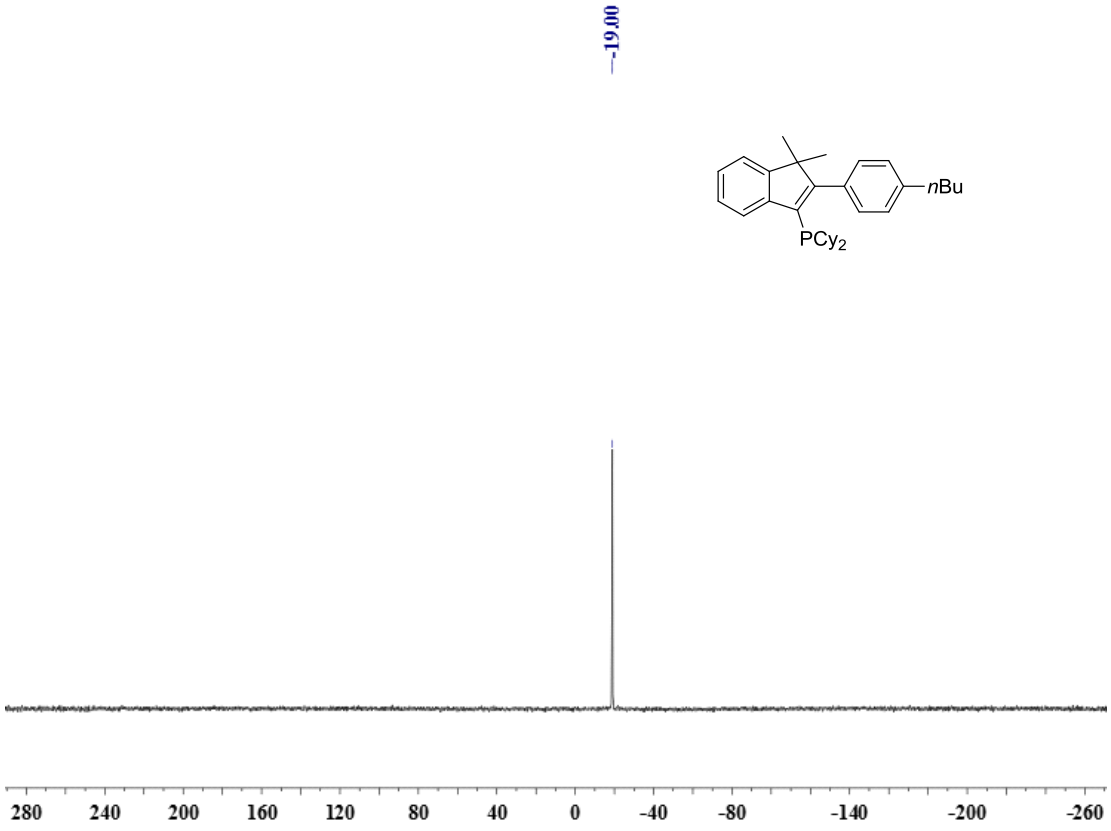
HRMS


nBu
PCy2

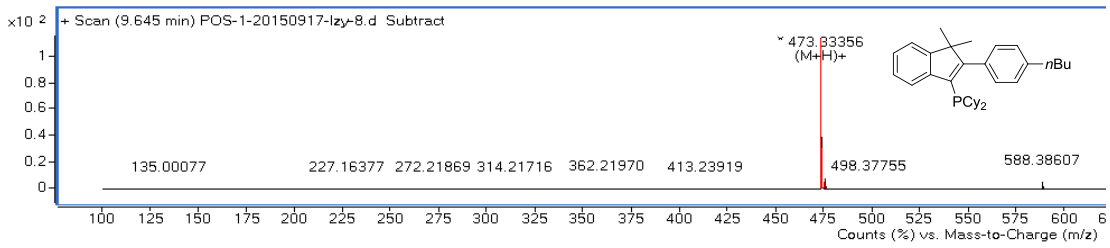
^{1}H NMR



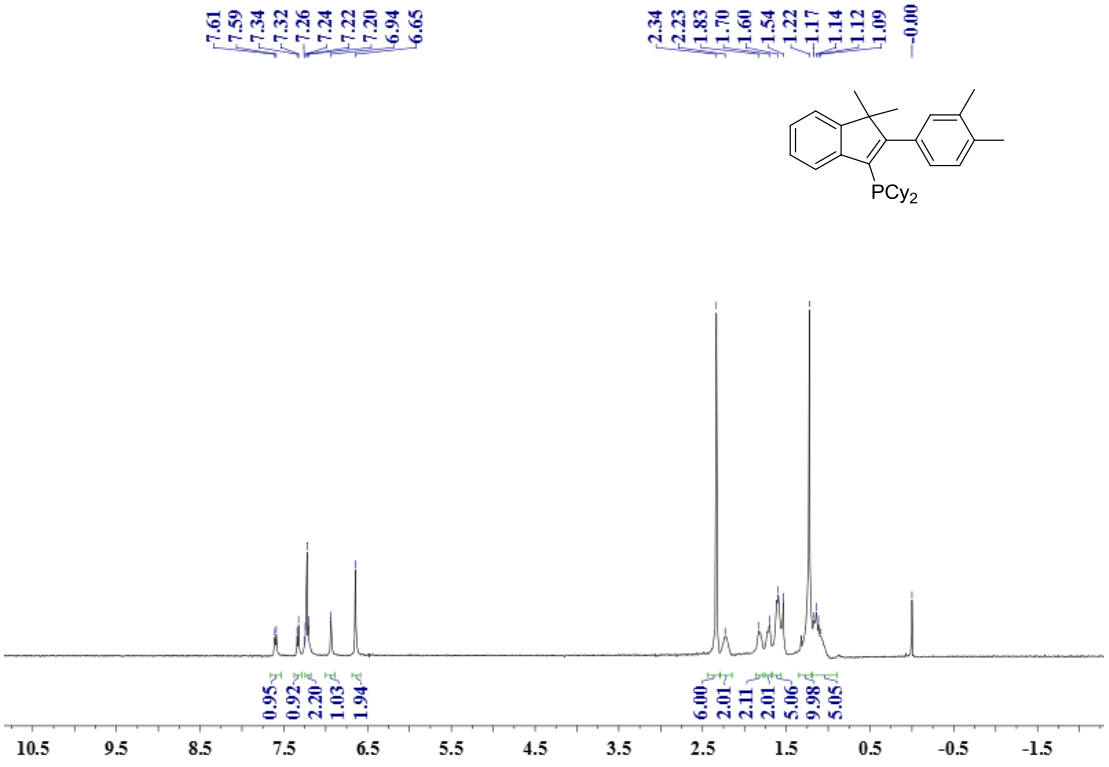
^{13}C NMR



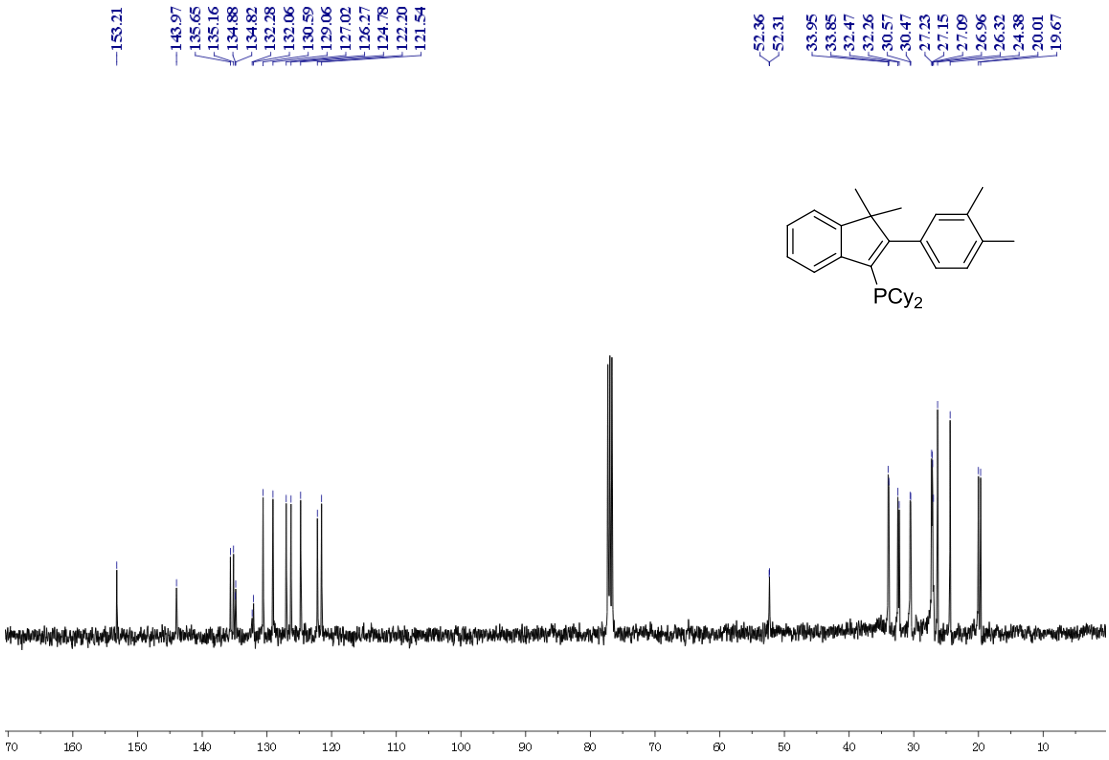
^{31}P NMR


x10 2
+ Scan (9.645 min) POS-1-20150917-lzy-8.d Subtract
473.33356
(M+H)+
nBu
PCy2
135.00077
227.16377
272.21869
314.21716
362.21970
413.23919
498.37755
588.38607
Counts (%) vs. Mass-to-Charge (m/z)

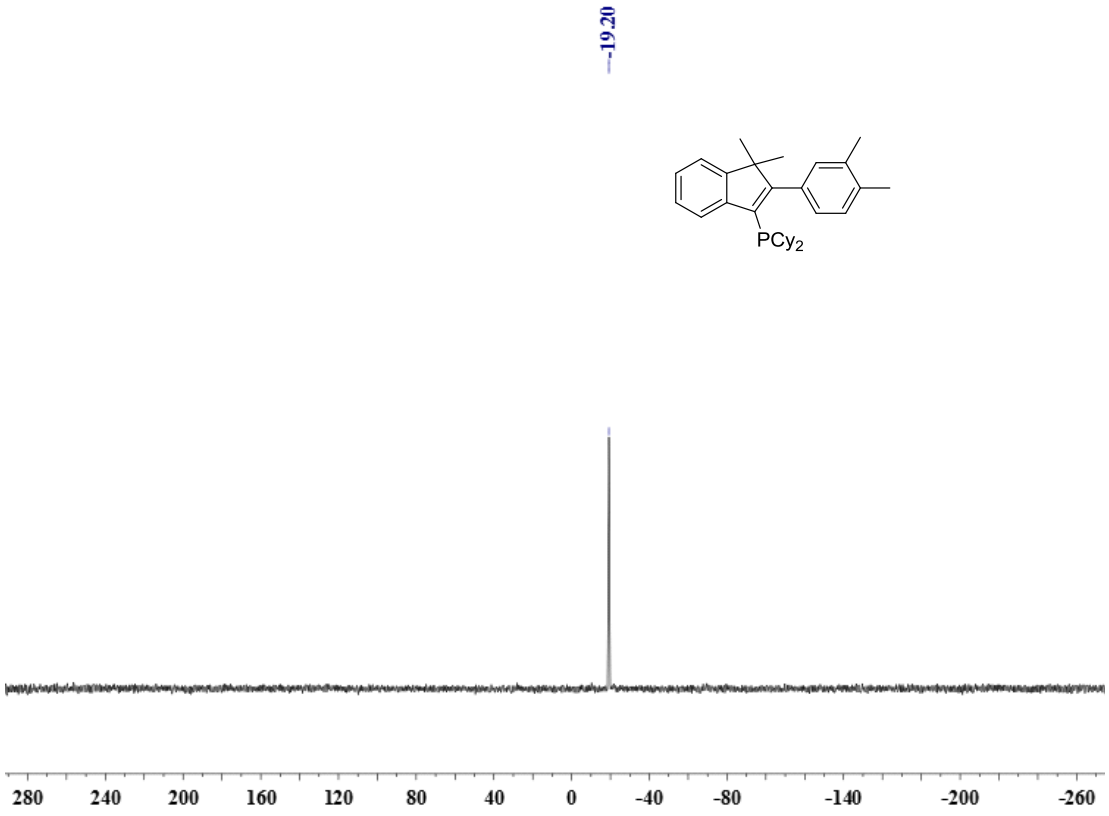
HRMS


7.61
7.59
7.34
7.32
7.26
7.24
7.22
7.20
6.94
6.65
2.34
2.23
1.83
1.70
1.60
1.54
1.22
1.17
1.14
1.12
1.09
0.00
PCy2
0.95
0.92
2.20
1.03
1.94
6.00
2.01
2.11
2.01
5.06
9.98
5.05

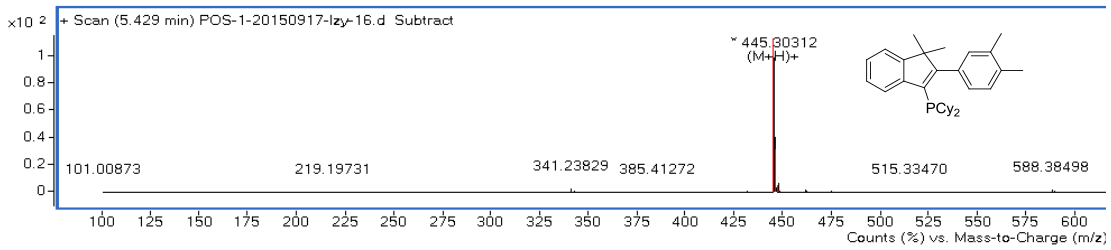
^{1}H NMR



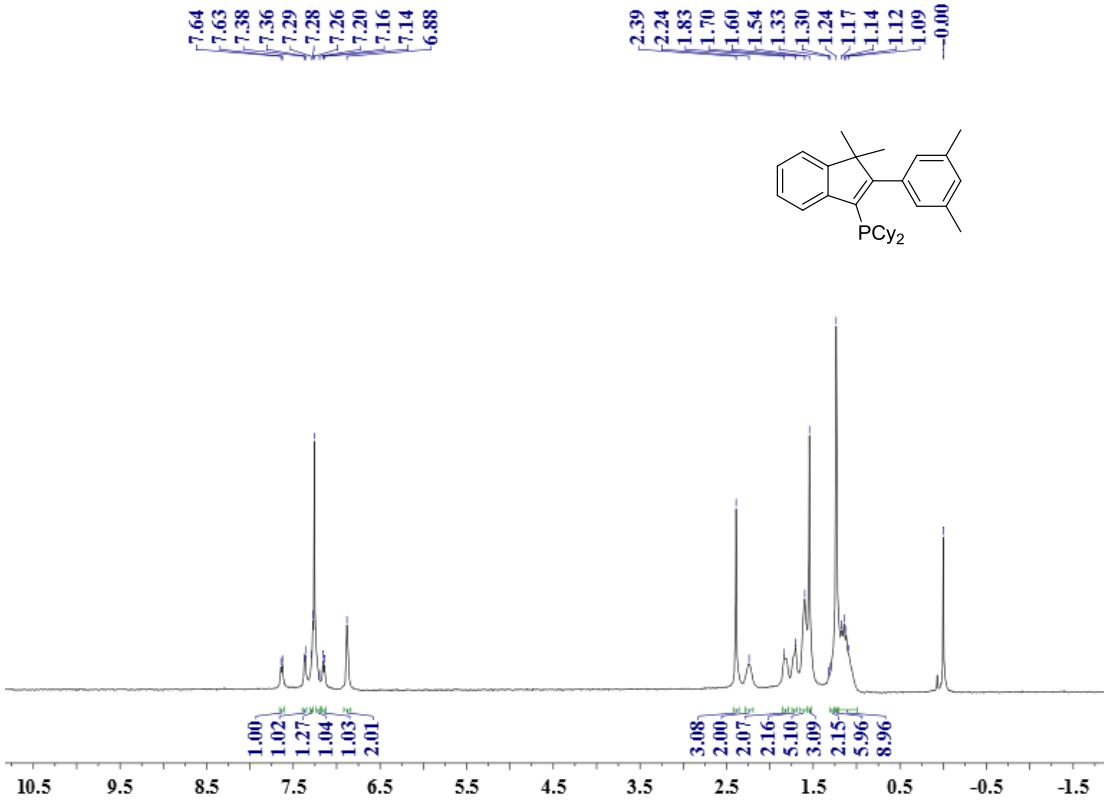
^{13}C NMR



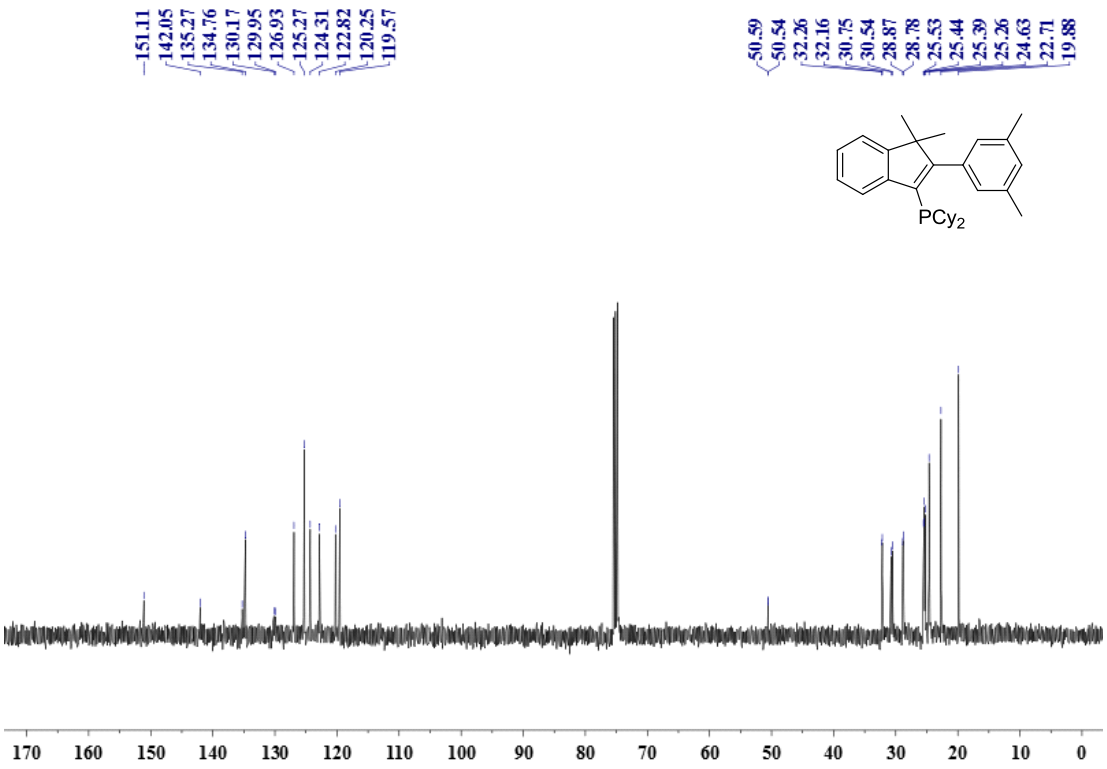
^{31}P NMR


x10 2
+ Scan (5.429 min) POS-1-20150917-lzy-16.d Subtract
445.30312
(M+H)+
PCy2
101.00873
219.19731
341.23829
385.41272
515.33470
588.38498
Counts (%) vs. Mass-to-Charge (m/z)

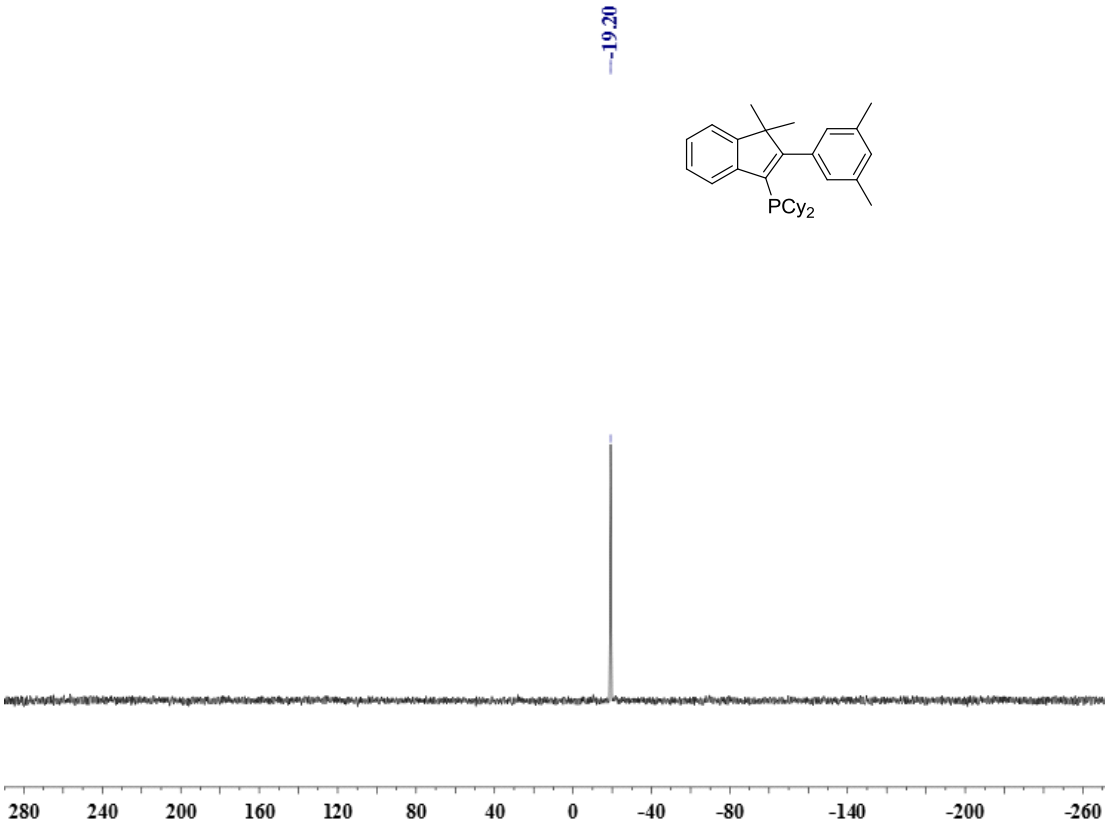
HRMS


7.64
7.63
7.38
7.36
7.29
7.28
7.26
7.20
7.16
7.14
6.88
2.39
2.24
1.83
1.70
1.60
1.54
1.33
1.30
1.24
1.17
1.14
1.12
1.09
0.00
PCy2
1.00
1.02
1.27
1.04
1.03
2.01
3.08
2.00
2.07
2.16
5.10
3.09
2.15
5.96
8.96
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5

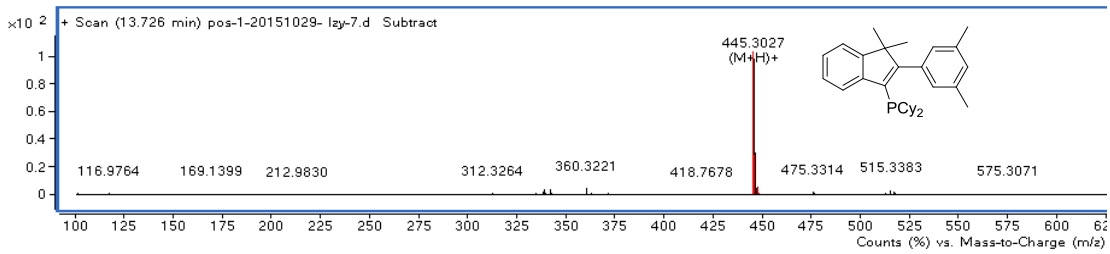
^{1}H NMR



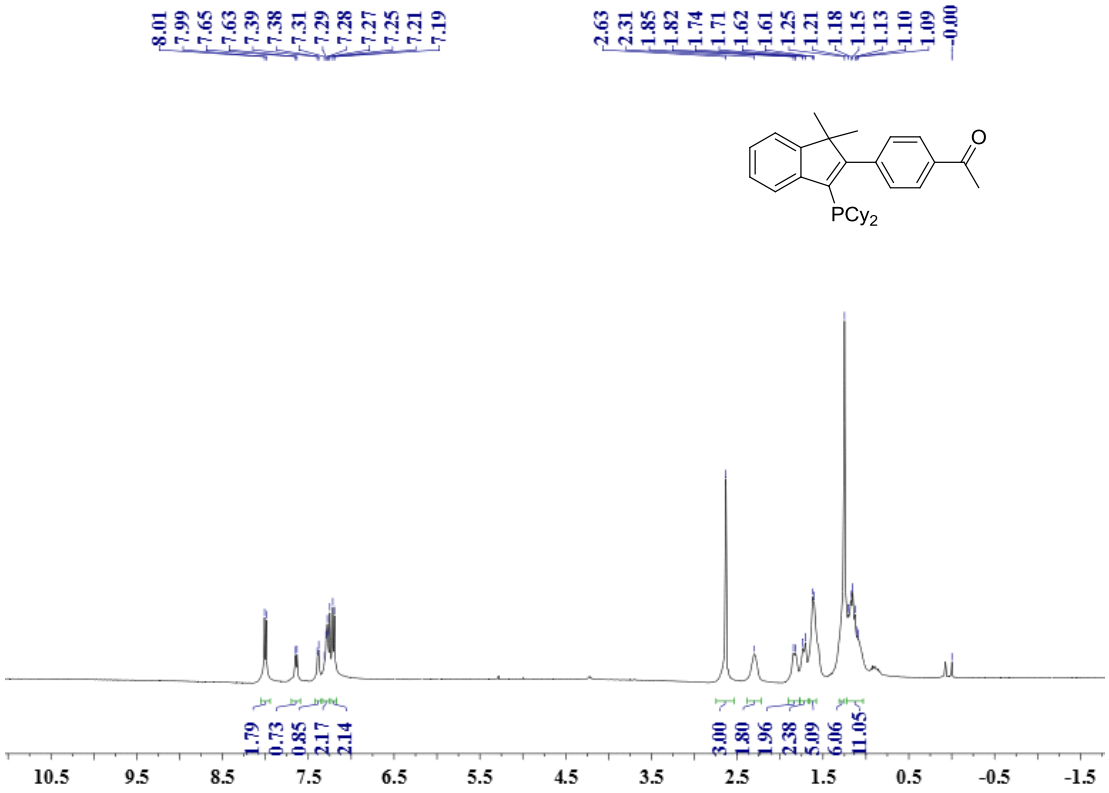
^{13}C NMR



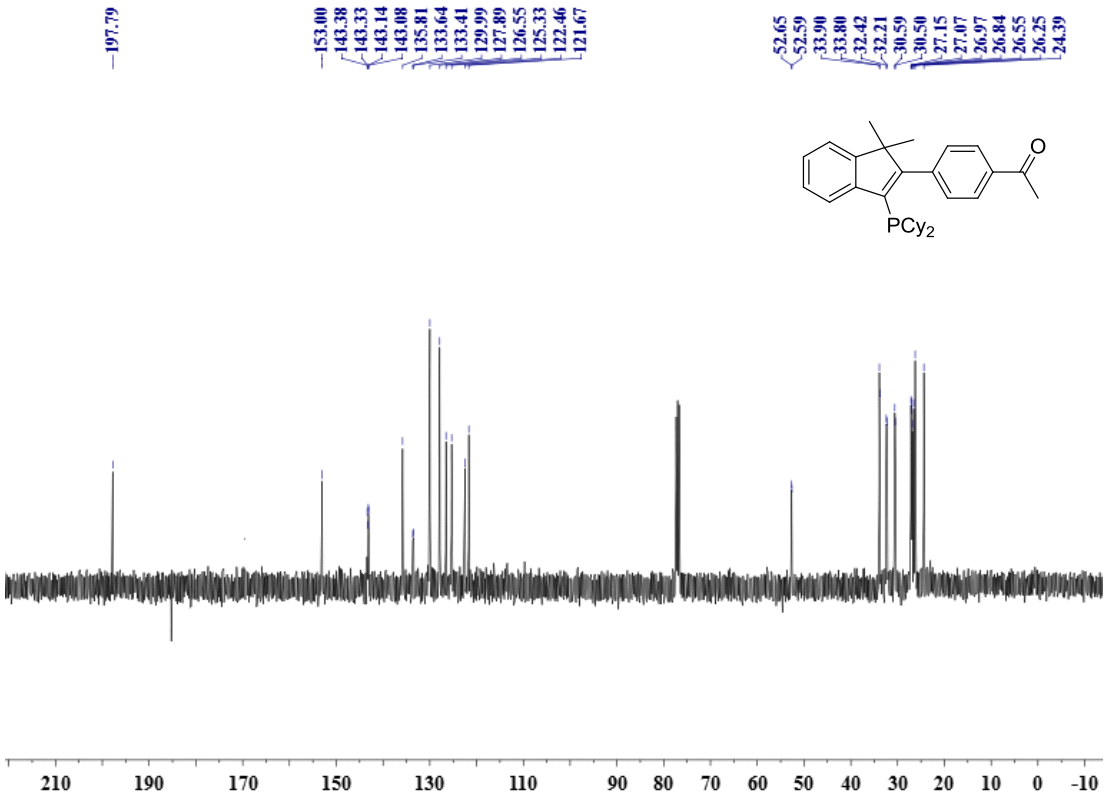
^{31}P NMR


×10 2
+ Scan (13.726 min) pos-1-20151029- lzy-7.d Subtract
445.3027
(M+H)+
PCy2
116.9764
169.1399
212.9830
312.3264
360.3221
418.7678
475.3314
515.3383
575.3071
Counts (%) vs. Mass-to-Charge (m/z)

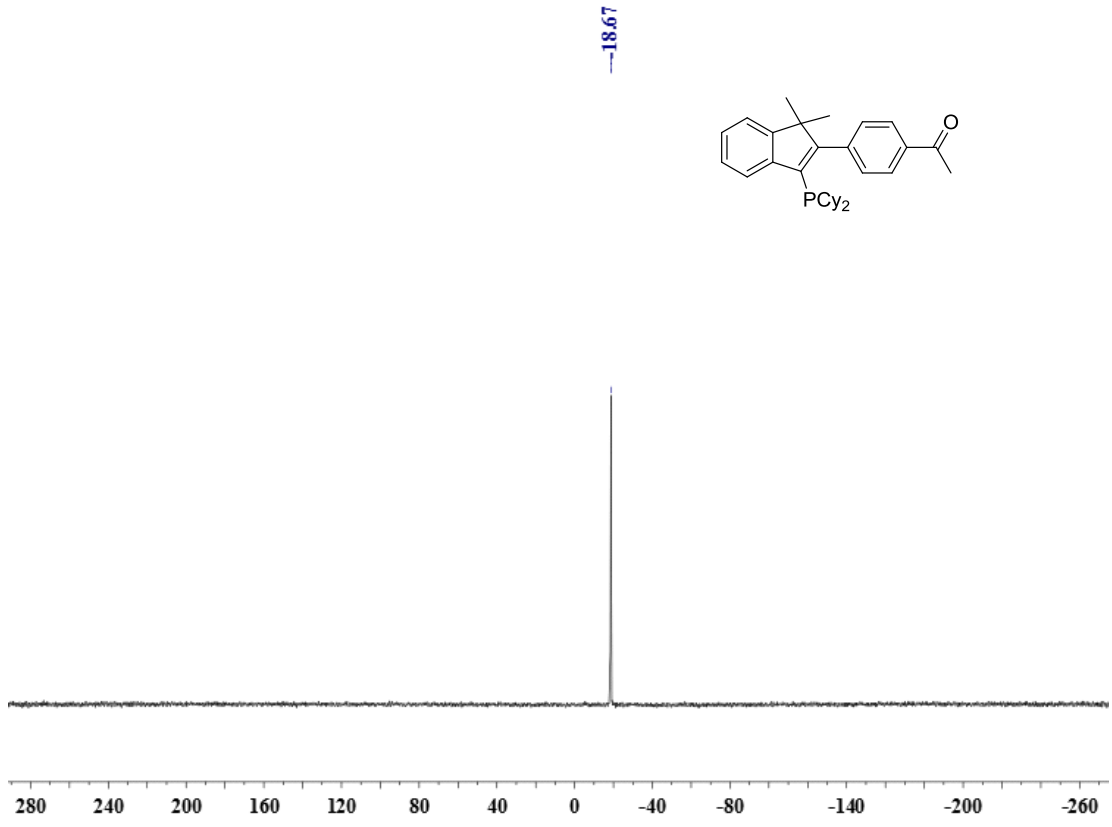
HRMS


8.01
7.99
7.65
7.63
7.39
7.38
7.31
7.29
7.28
7.27
7.25
7.21
7.19
2.63
2.31
1.85
1.82
1.74
1.71
1.62
1.61
1.25
1.21
1.18
1.15
1.13
1.10
1.09
0.00
O
PCy2
1.79
0.73
0.85
2.17
2.14
3.00
1.80
1.96
2.38
5.09
6.06
11.05
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5

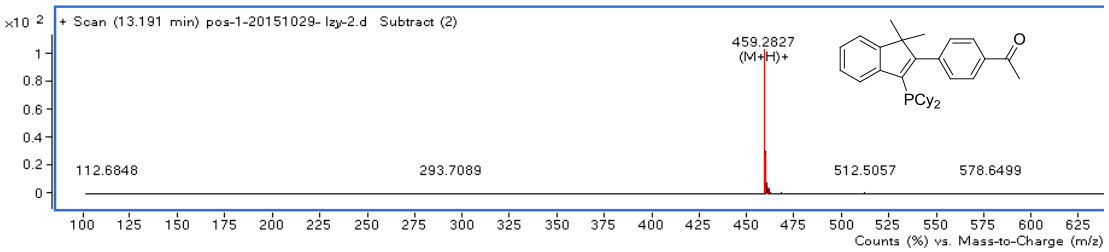
^{1}H NMR



^{13}C NMR



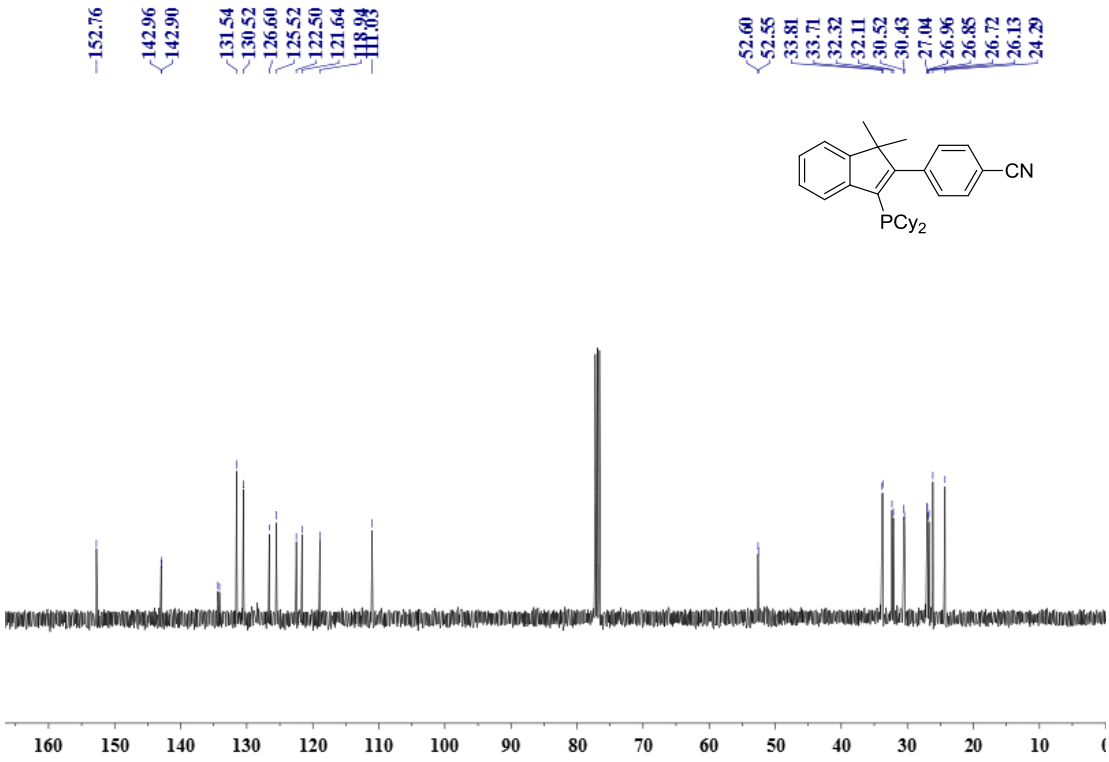
^{31}P NMR


x10 2
+ Scan (13.191 min) pos-1-20151029- lzy-2.d Subtract (2)
459.2827
(M+H)+
O
PCy2
112.6848
293.7089
512.5057
578.6499
Counts (%) vs. Mass-to-Charge (m/z)

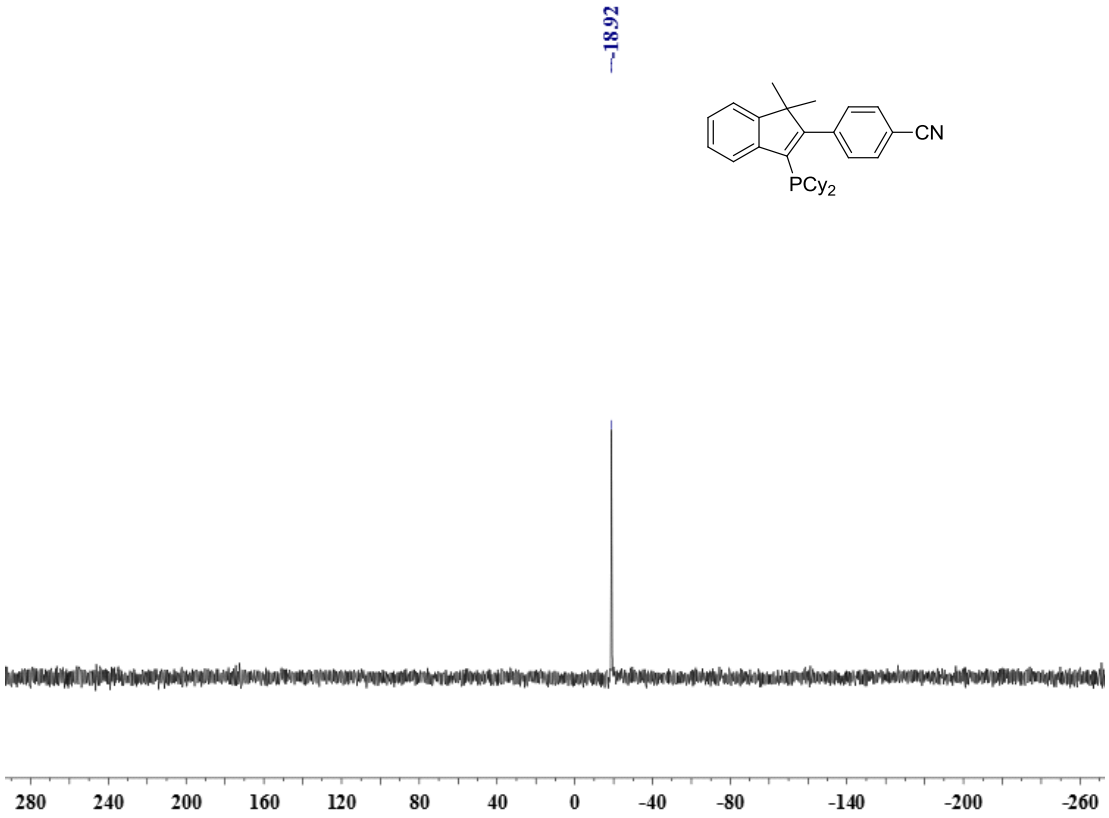
HRMS


7.70
7.68
7.65
7.64
7.63
7.40
7.39
7.38
7.38
7.32
7.30
7.30
7.29
7.28
7.25
7.23
7.20
2.31
2.30
2.29
1.85
1.82
1.74
1.71
1.61
1.56
1.53
1.27
1.24
1.22
1.20
1.18
1.15
1.13
1.09
1.05
0.00
CN
PCy2
1.92
1.02
0.97
2.03
2.07
2.00
2.05
2.11
4.01
1.09
2.99
6.07
8.07
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5

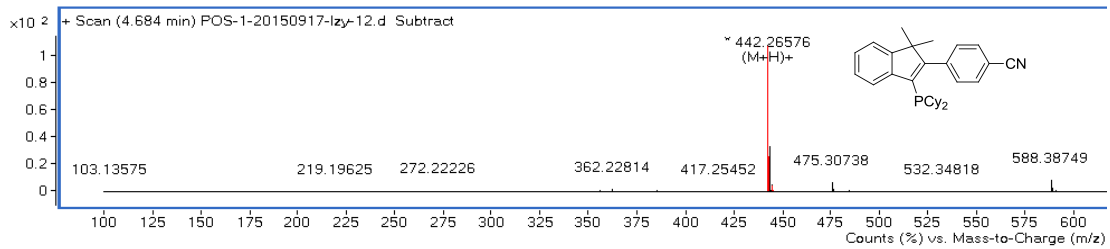
^{1}H NMR



^{13}C NMR

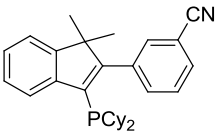


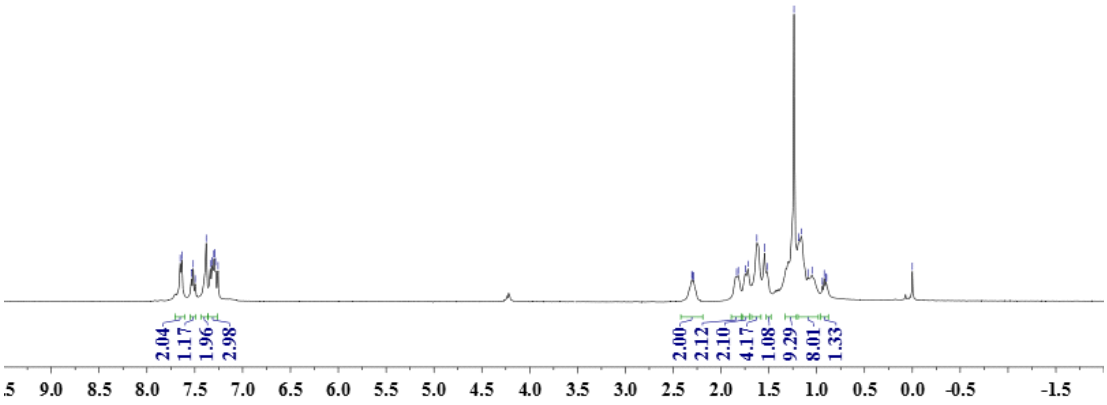
^{31}P NMR


x10 2
+ Scan (4.684 min) POS-1-20150917-lzy-12.d Subtract
442.26576
(M+H)+
CN
PCy2
103.13575
219.19625
272.22226
362.22814
417.25452
475.30738
532.34818
588.38749
Counts (%) vs. Mass-to-Charge (m/z)

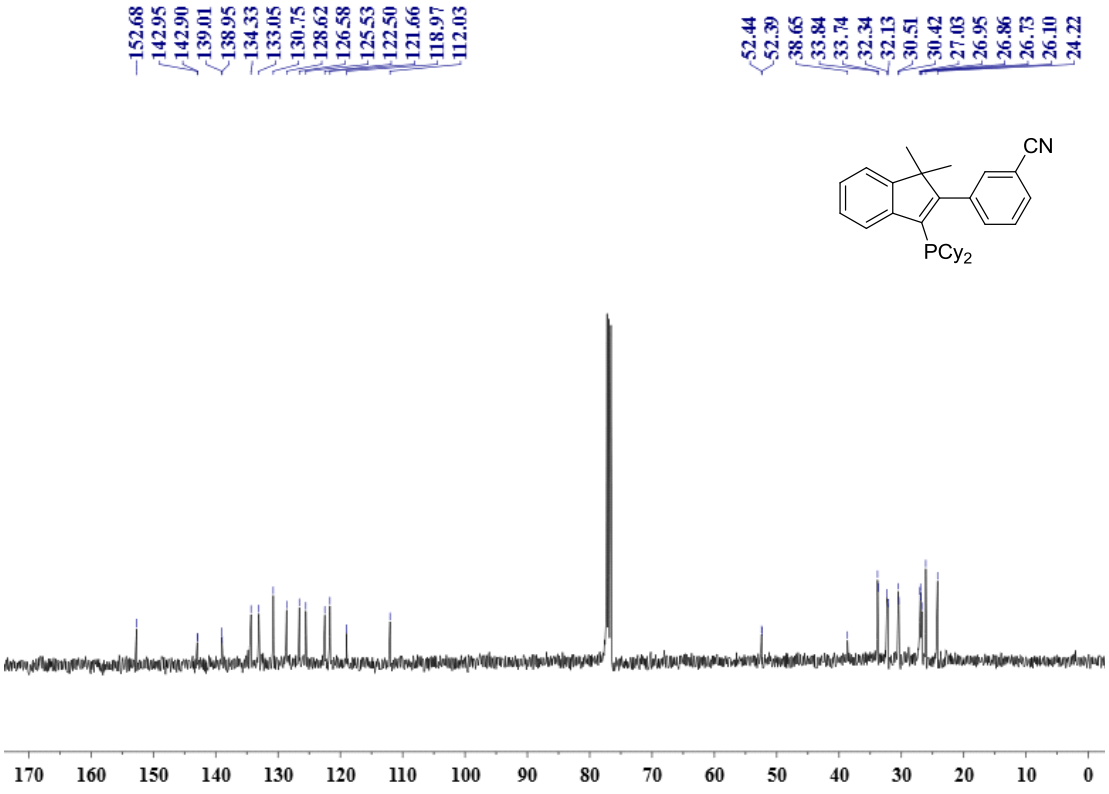
HRMS


7.65
7.63
7.53
7.52
7.50
7.38
7.34
7.32
7.30
7.29
7.28
7.26
2.31
2.30
2.29
1.84
1.82
1.75
1.72
1.63
1.55
1.52
1.24
1.19
1.16
1.09
1.05
0.94
0.92
0.90
0.90
0.00

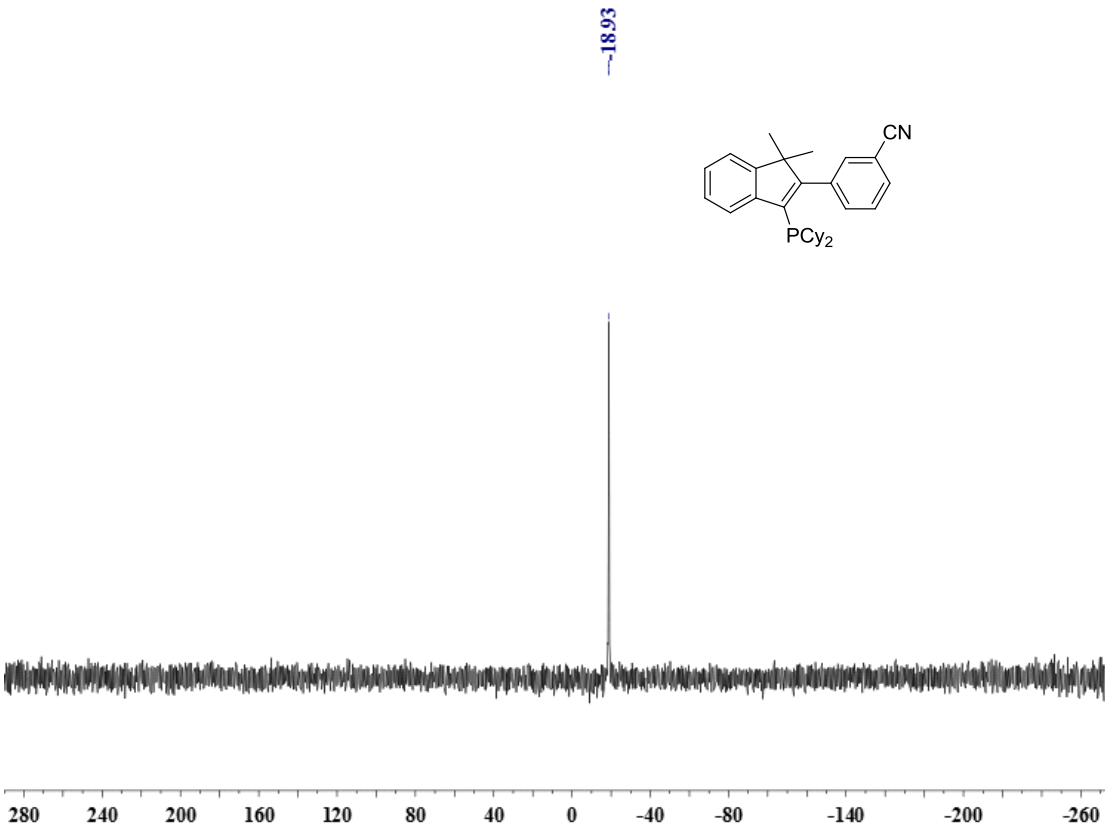

CN
PCy2


2.04
1.17
1.96
2.98
2.00
2.12
2.10
4.17
1.08
9.29
8.01
1.33

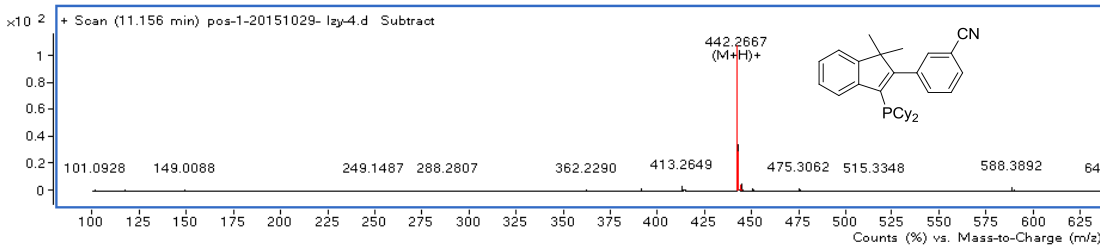
^{1}H NMR



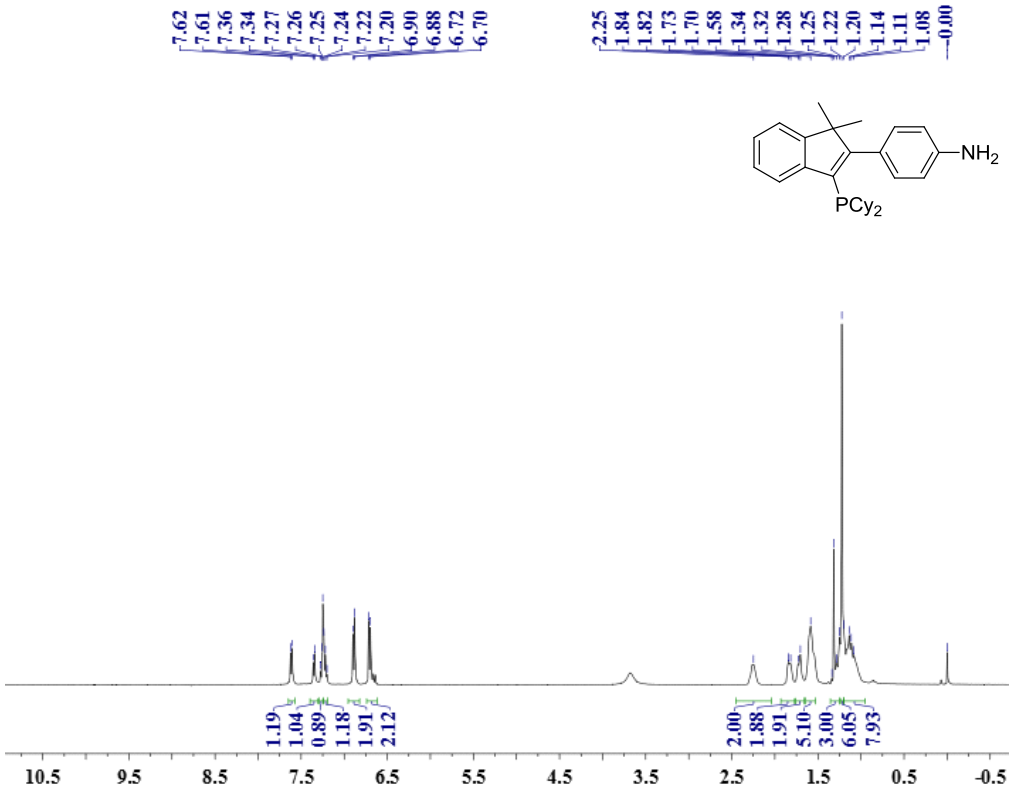
^{13}C NMR



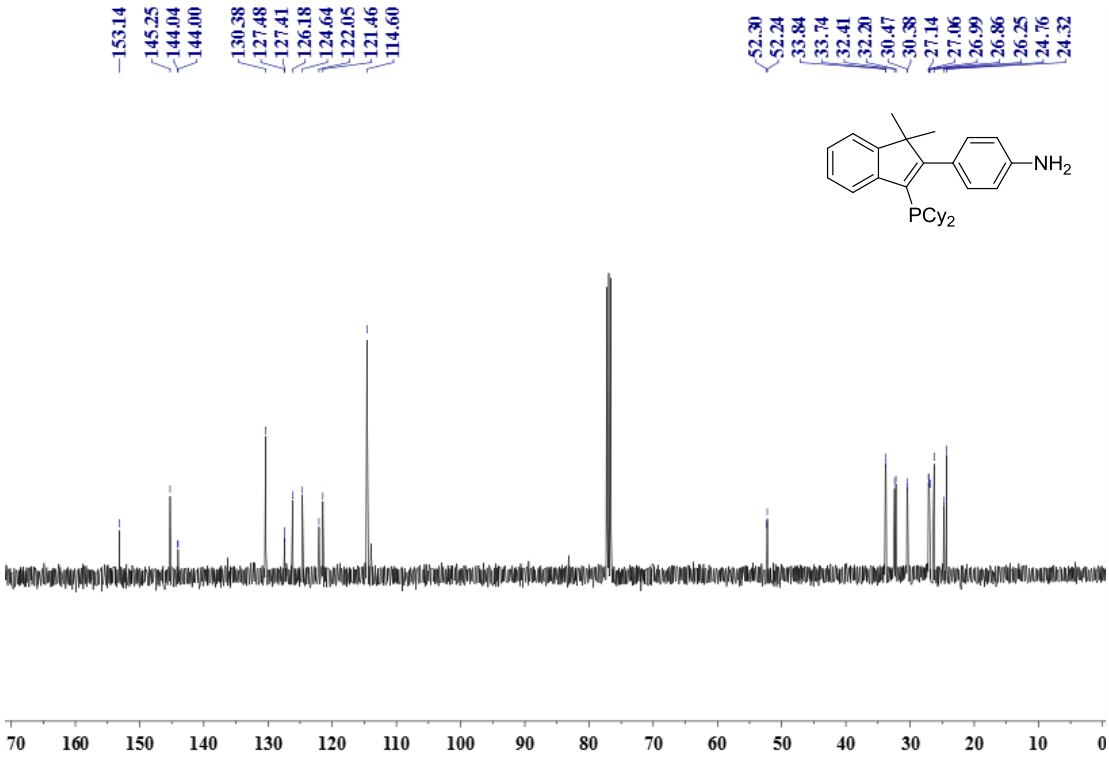
^{31}P NMR


x10 2
+ Scan (11.156 min) pos-1-20151029- lzy-4.d Subtract
442.2667
(M+H)+
CN
PCy2
101.0928
149.0088
249.1487
288.2807
362.2290
413.2649
475.3062
515.3348
588.3892
Counts (%) vs. Mass-to-Charge (m/z)

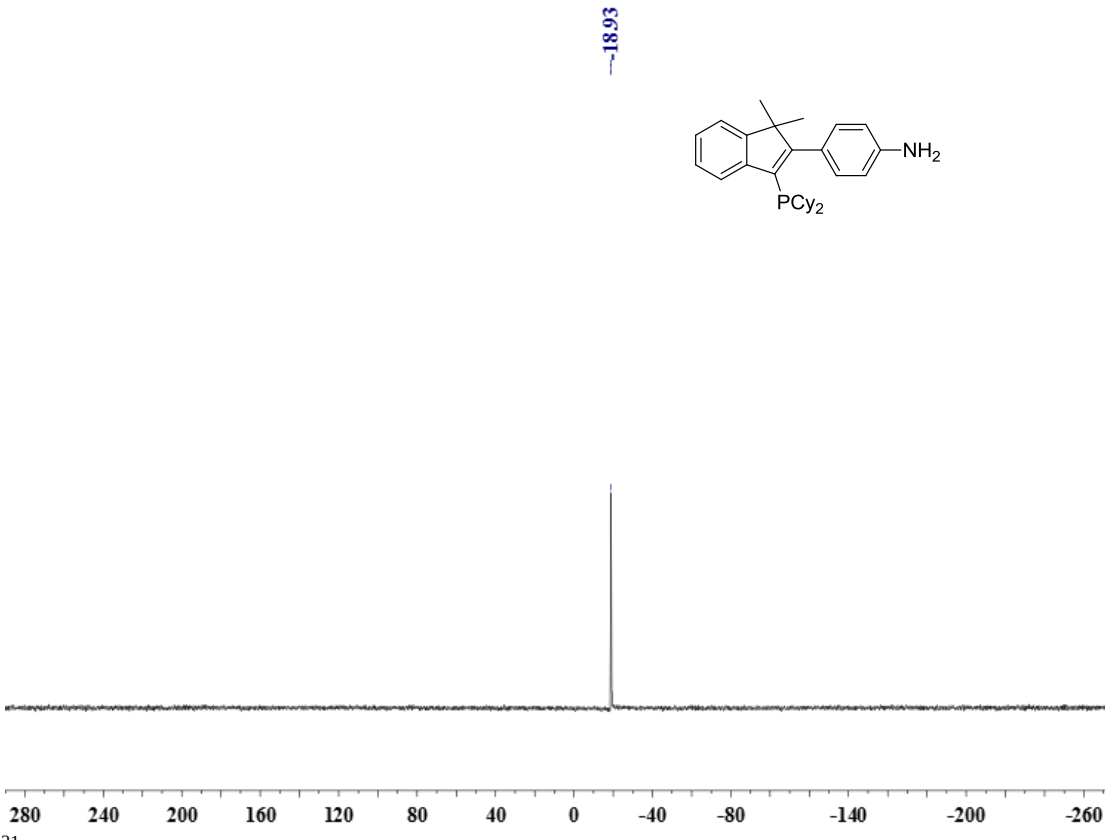
HRMS


7.62
7.61
7.36
7.34
7.27
7.26
7.25
7.24
7.22
7.20
6.90
6.88
6.72
6.70
2.25
1.84
1.82
1.73
1.70
1.58
1.34
1.32
1.28
1.25
1.22
1.20
1.14
1.11
1.08
0.00
NH2
PCy2
1.19
1.04
0.89
1.18
1.91
2.12
2.00
1.88
1.91
5.10
3.00
6.05
7.93
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5

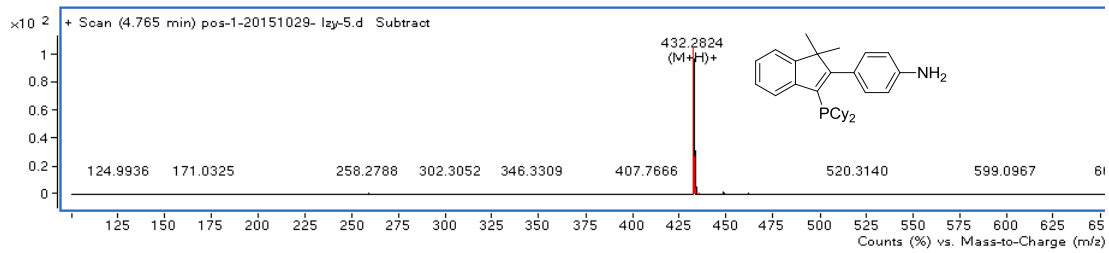
^{1}H NMR



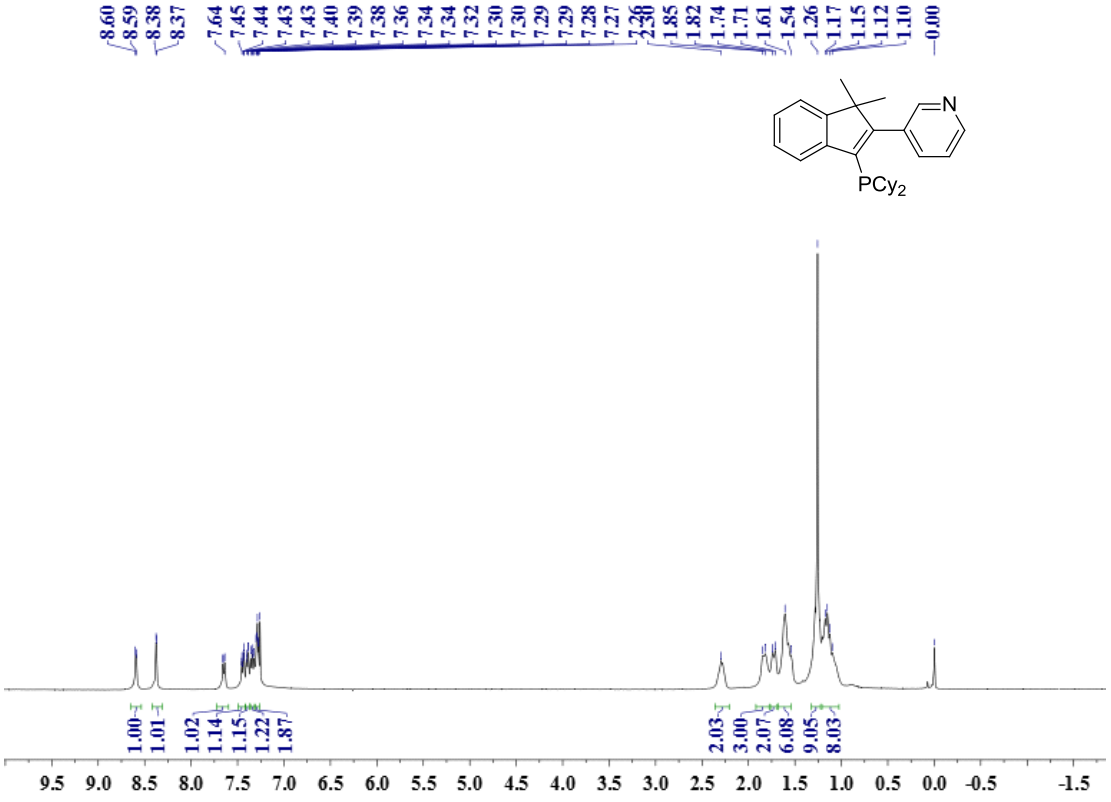
^{13}C NMR



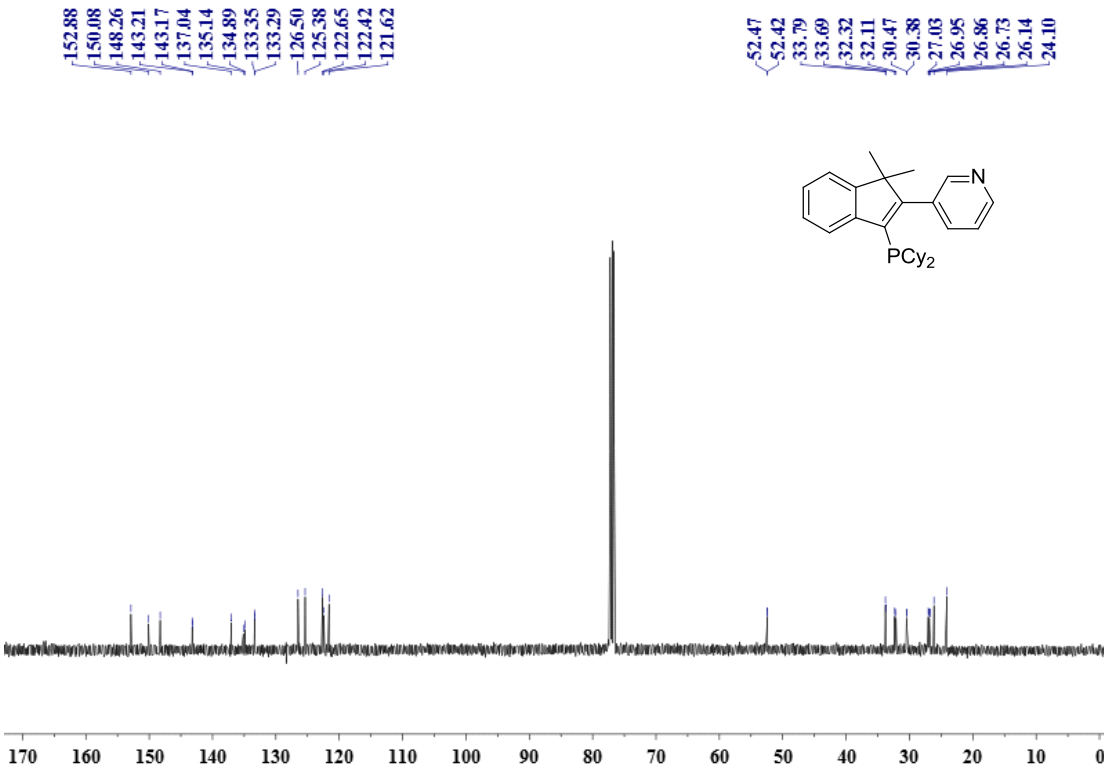
^{31}P NMR


+ Scan (4.765 min) pos-1-20151029- lzy-5.d Subtract
432.2824
(M+H)+
NH2
PCy2
124.9936
171.0325
258.2788
302.3052
346.3309
407.7666
520.3140
599.0967
Counts (%) vs. Mass-to-Charge (m/z)

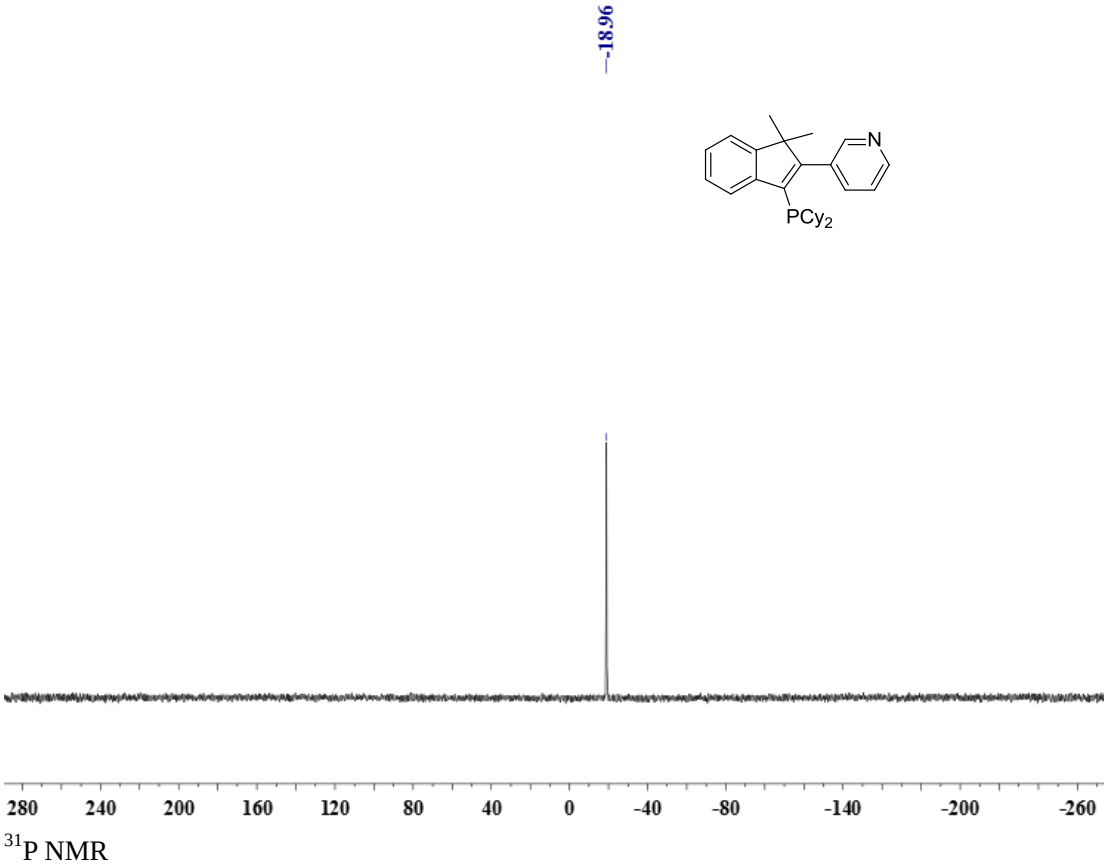
HRMS


N
PCy2

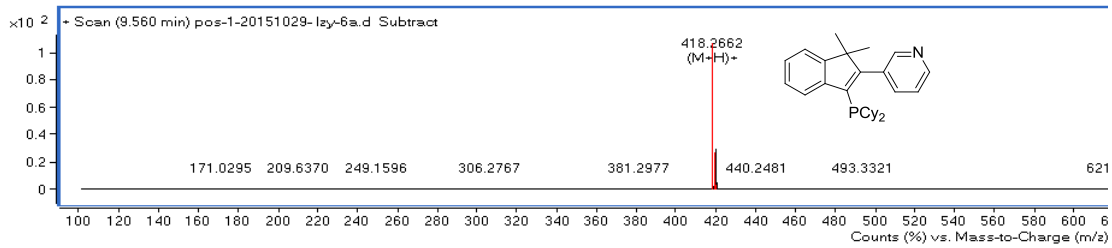
^{1}H NMR



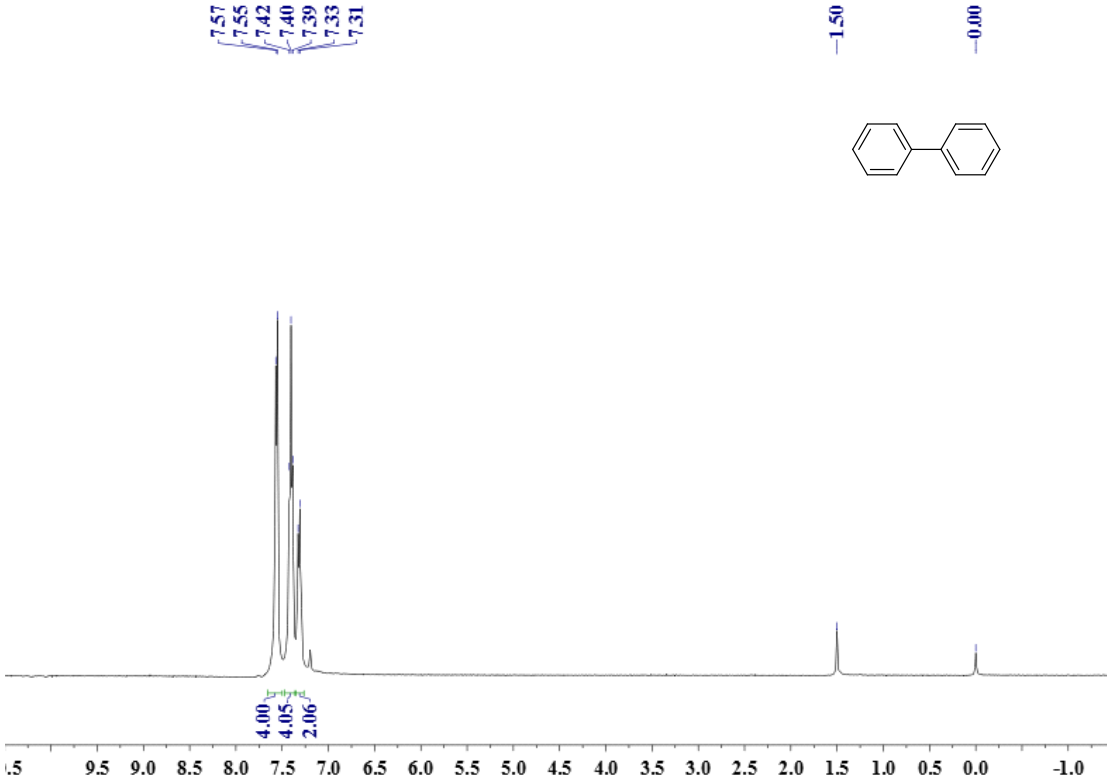
^{13}C NMR



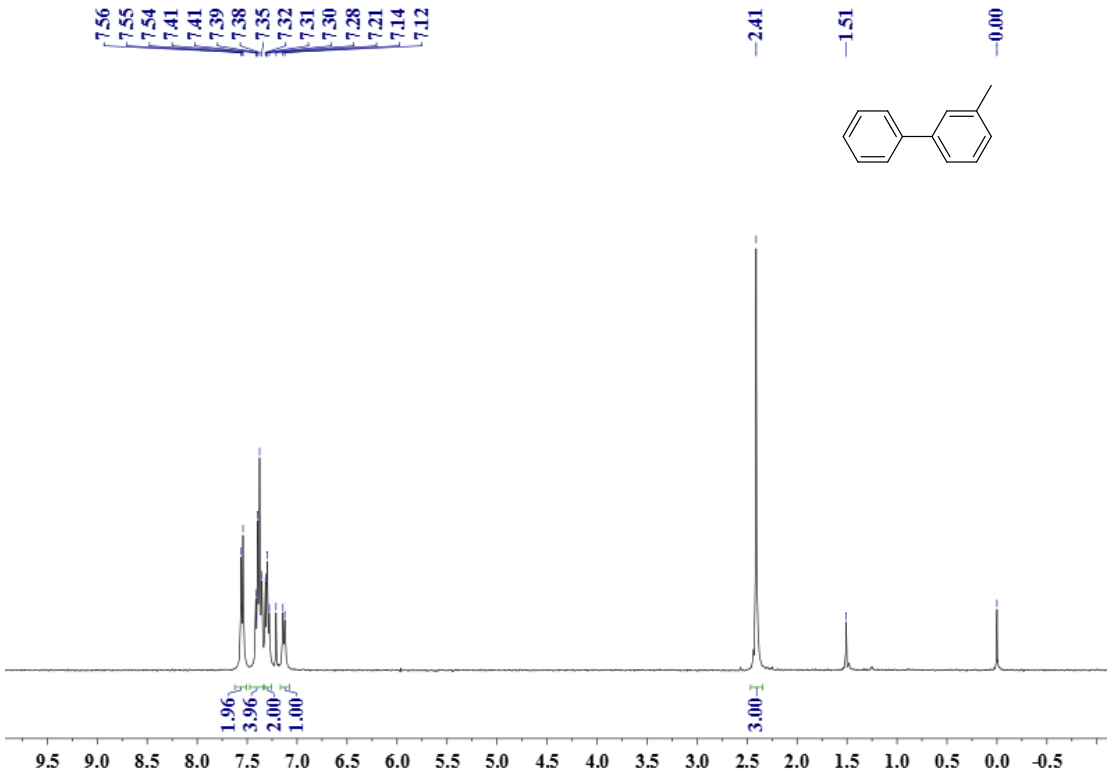
^{31}P NMR


x10 2
+ Scan (9.560 min) pos-1-20151029-lzy-6a.d Subtract
418.2662
(M+H)+
PCy2
N
171.0295
209.6370
249.1596
306.2767
381.2977
440.2481
493.3321
621
Counts (%) vs. Mass-to-Charge (m/z)

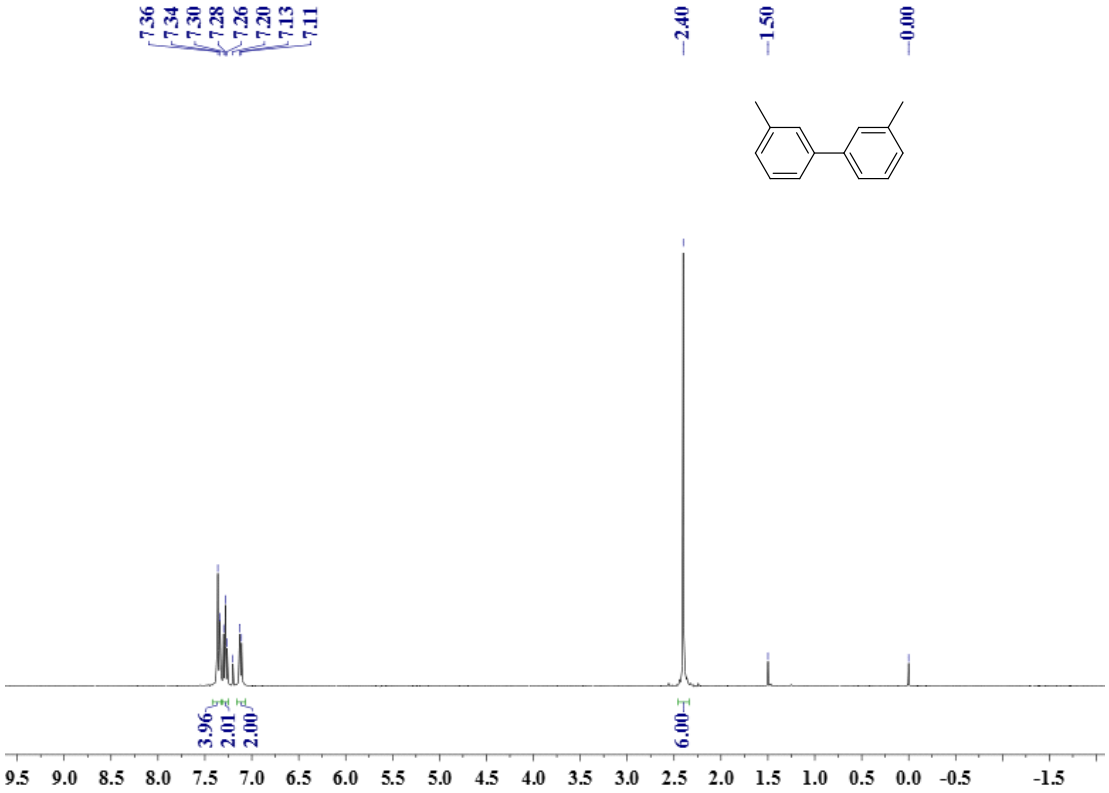
HRMS


7.57
7.55
7.42
7.40
7.39
7.33
7.31
1.50
0.00
4.00
4.05
2.06

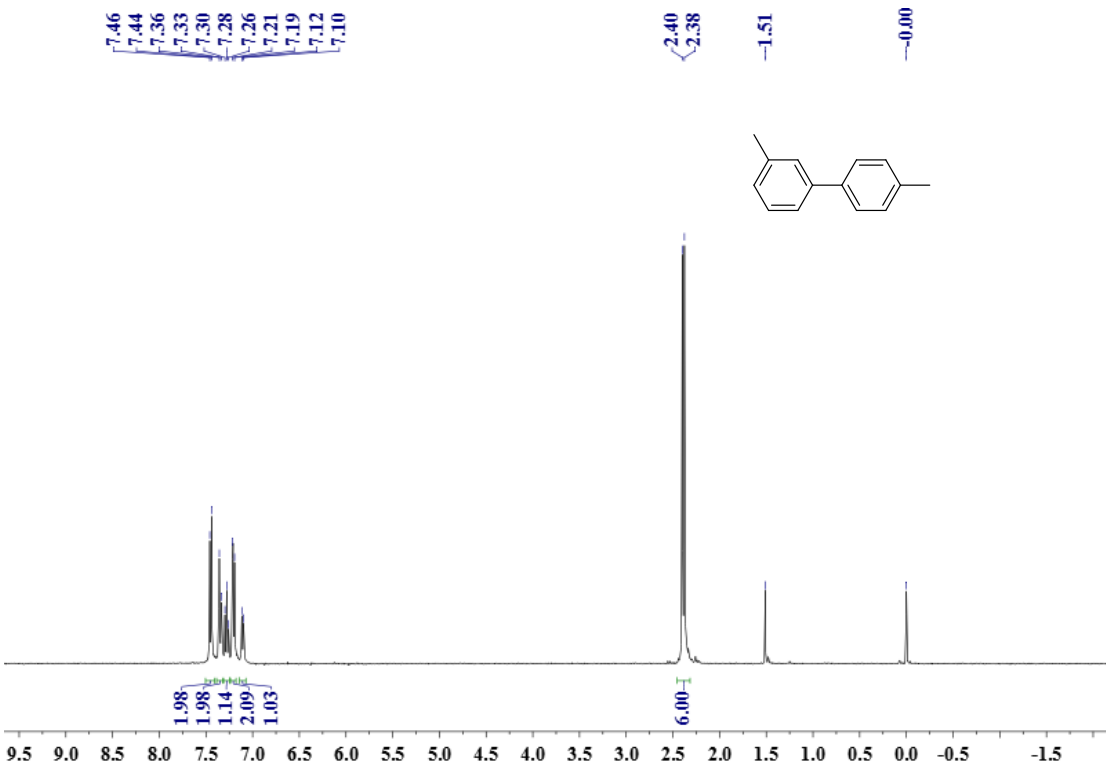
^{1}H NMR


7.56
7.55
7.54
7.41
7.41
7.39
7.38
7.35
7.32
7.31
7.30
7.28
7.21
7.14
7.12
2.41
1.51
0.00
1.96
3.96
2.00
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

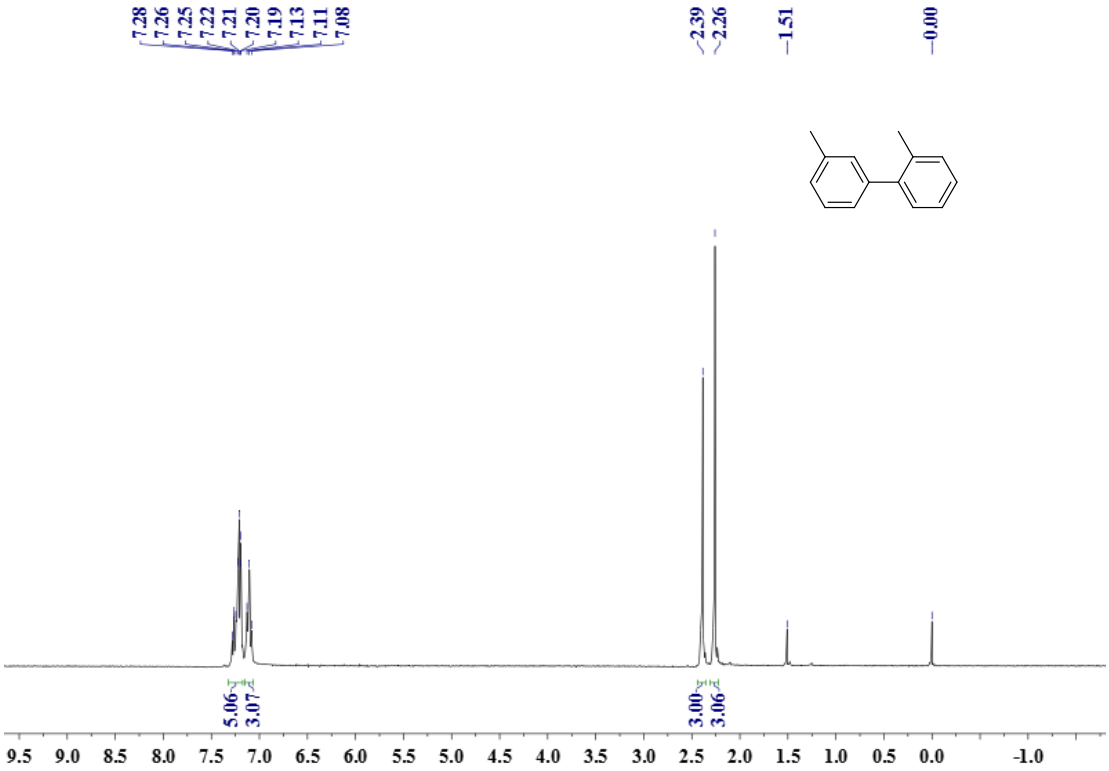
^{1}H NMR


7.36
7.34
7.30
7.28
7.26
7.20
7.13
7.11
2.40
1.50
0.00
3.96
2.01
2.00
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.5

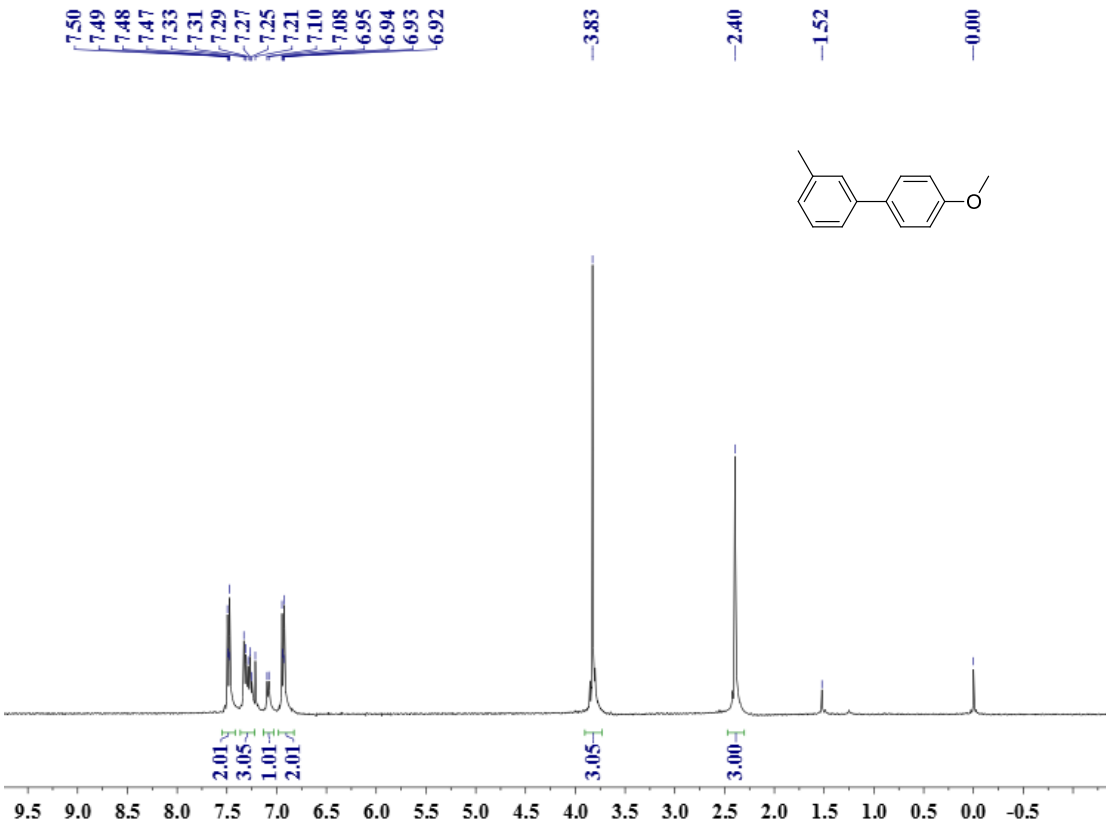
^{1}H NMR


7.46
7.44
7.36
7.33
7.30
7.28
7.26
7.21
7.19
7.12
7.10
2.40
2.38
1.51
0.00
1.98
1.98
1.14
2.09
1.03
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.5

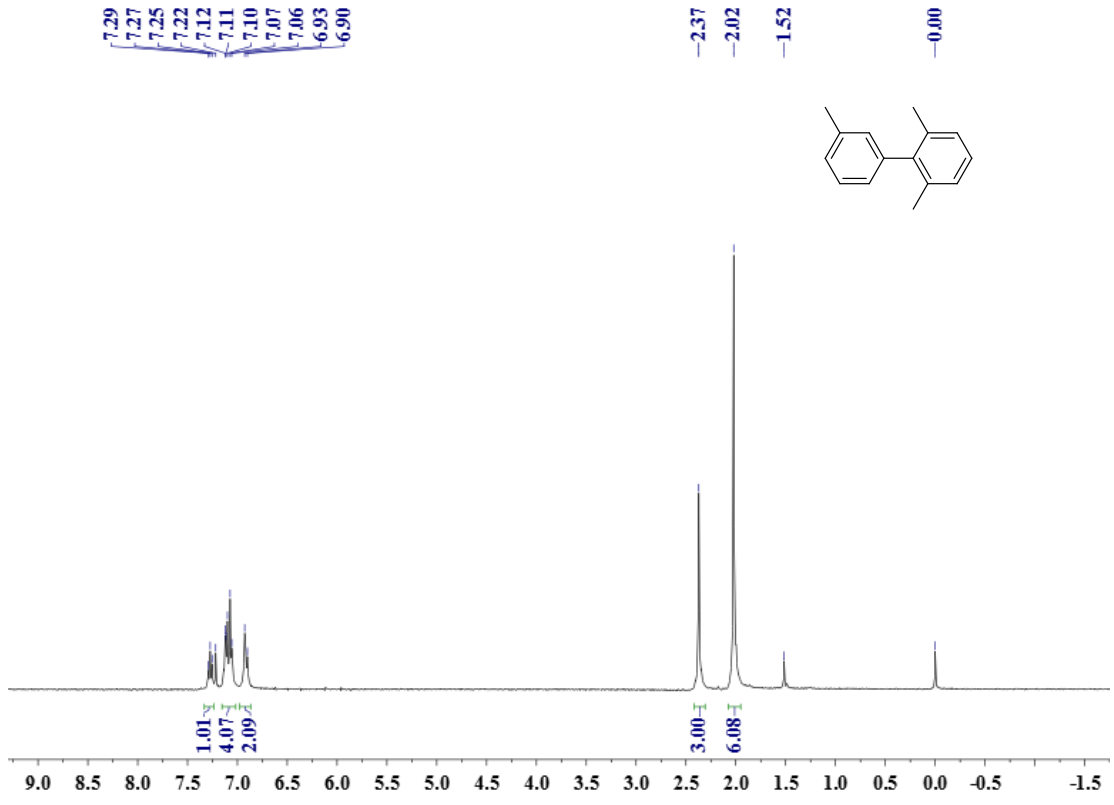
^{1}H NMR


7.28
7.26
7.25
7.22
7.21
7.20
7.19
7.13
7.11
7.08
2.39
2.26
1.51
0.00
5.06
3.07
3.00
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0

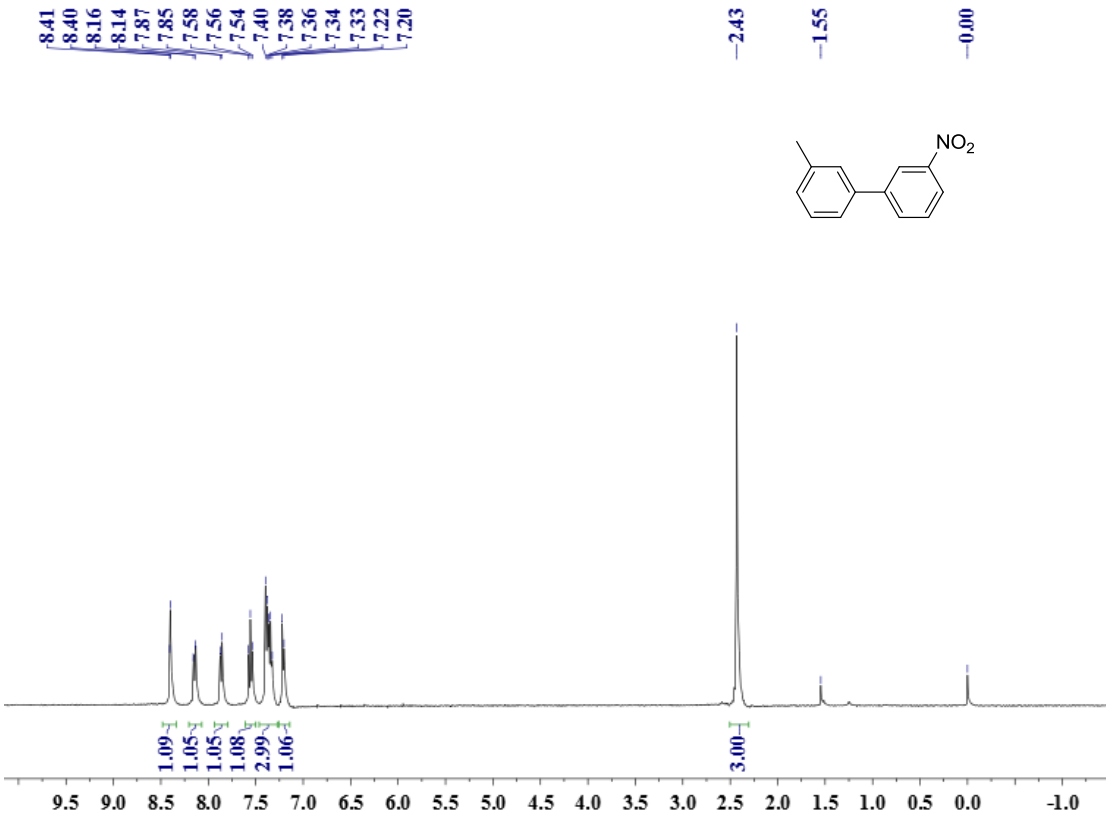
^{1}H NMR


7.50
7.49
7.48
7.47
7.33
7.31
7.29
7.27
7.25
7.21
7.10
7.08
6.95
6.94
6.93
6.92
3.83
2.40
1.52
0.00
O
2.01
3.05
1.01
2.01
3.05
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

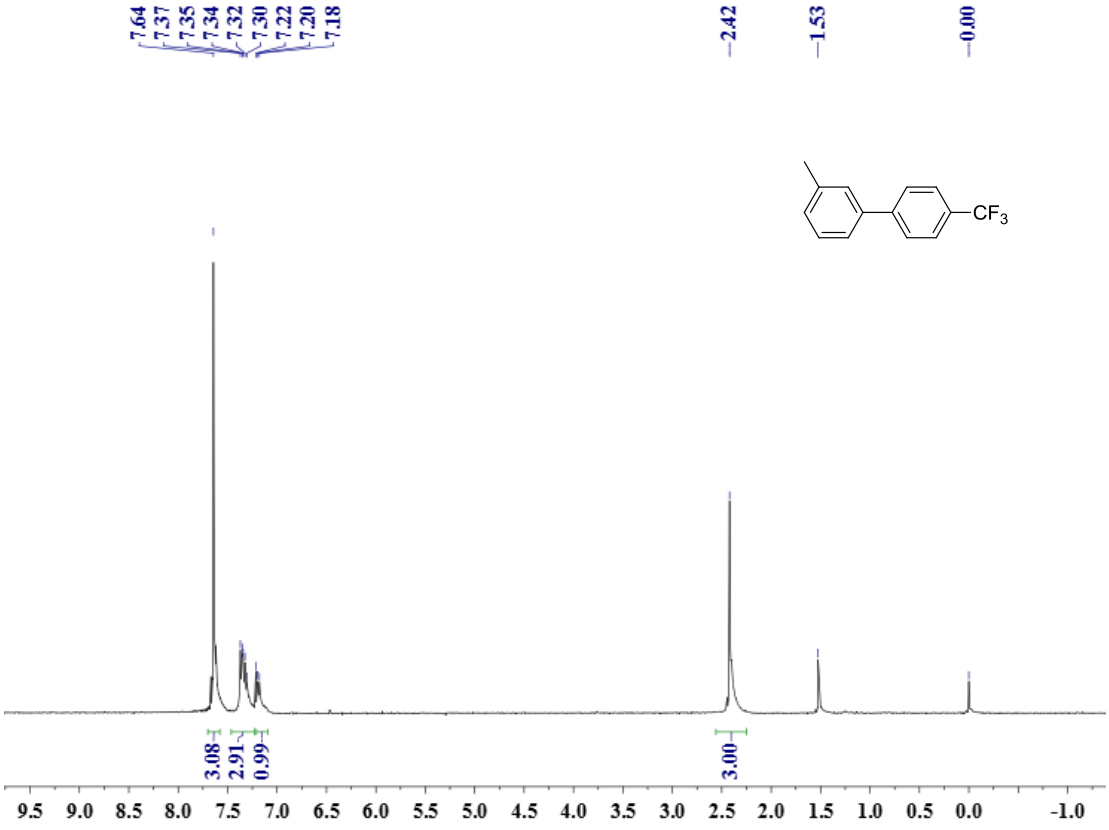
^{1}H NMR


7.29
7.27
7.25
7.22
7.12
7.11
7.10
7.07
7.06
6.93
6.90
2.37
2.02
1.52
0.00
1.01
4.07
2.09
3.00
6.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.5

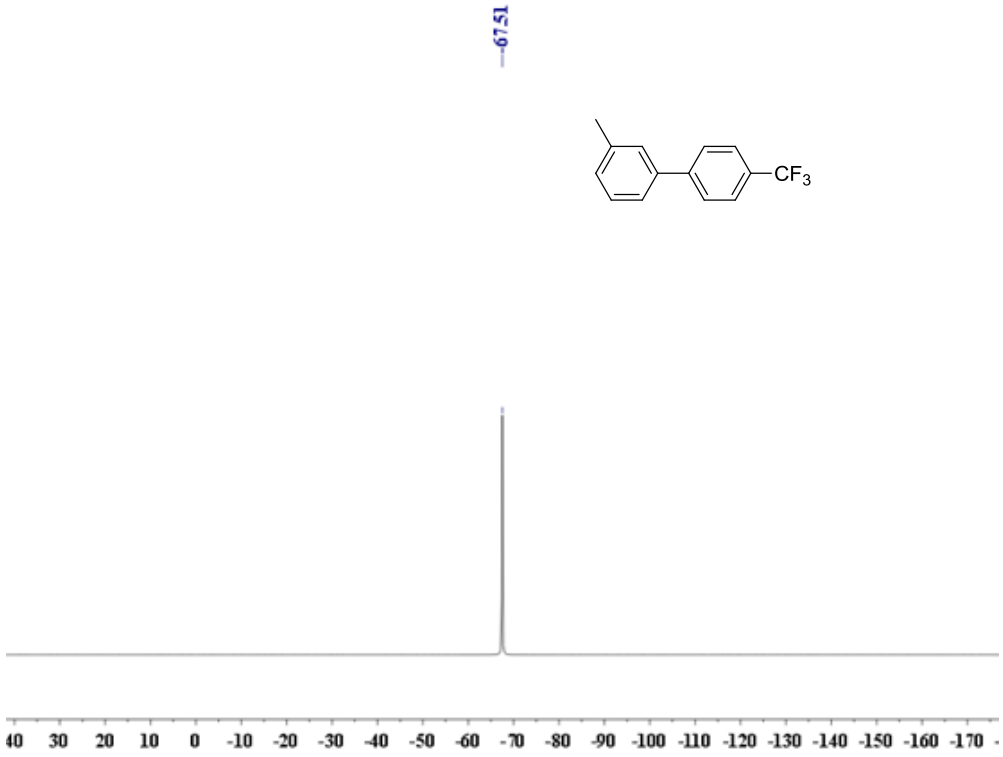
^{1}H NMR


8.41
8.40
8.16
8.14
7.87
7.85
7.58
7.56
7.54
7.40
7.38
7.36
7.34
7.33
7.22
7.20
2.43
1.55
0.00
NO2
1.09
1.05
1.05
1.08
2.99
1.06
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0

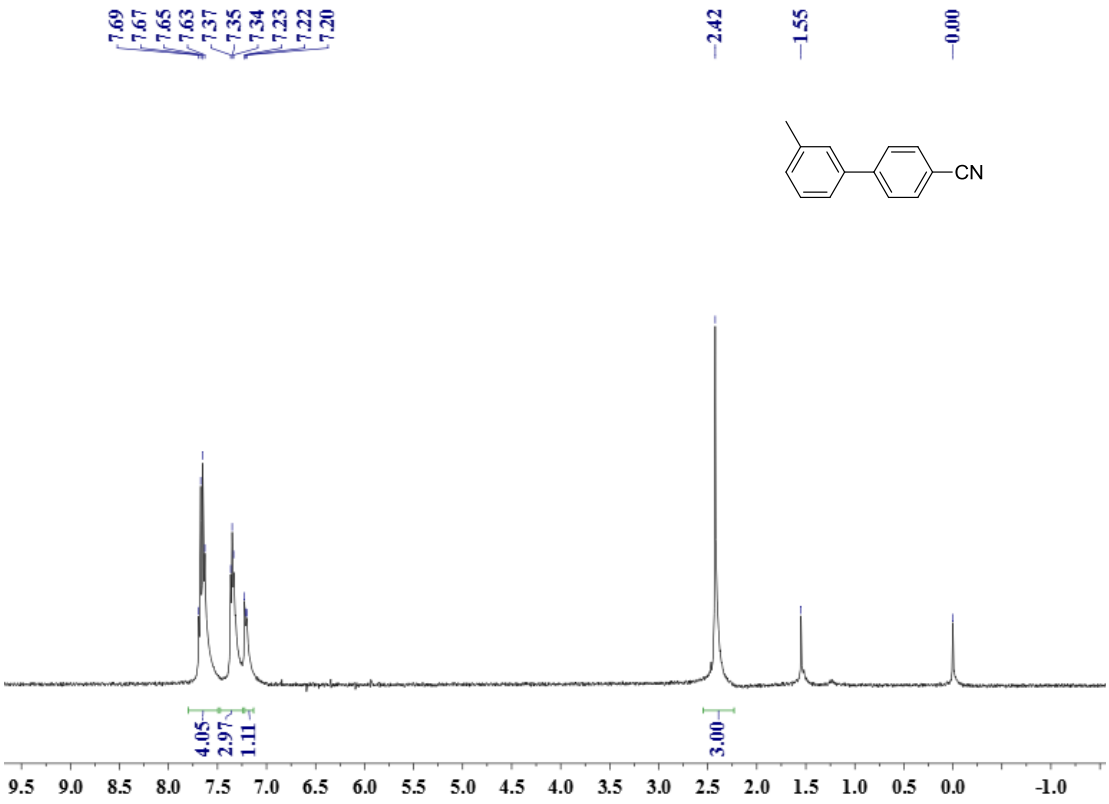
^{1}H NMR


7.64
7.37
7.35
7.34
7.32
7.30
7.22
7.20
7.18
2.42
1.53
0.00
CF3
3.08
2.91
0.99
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0

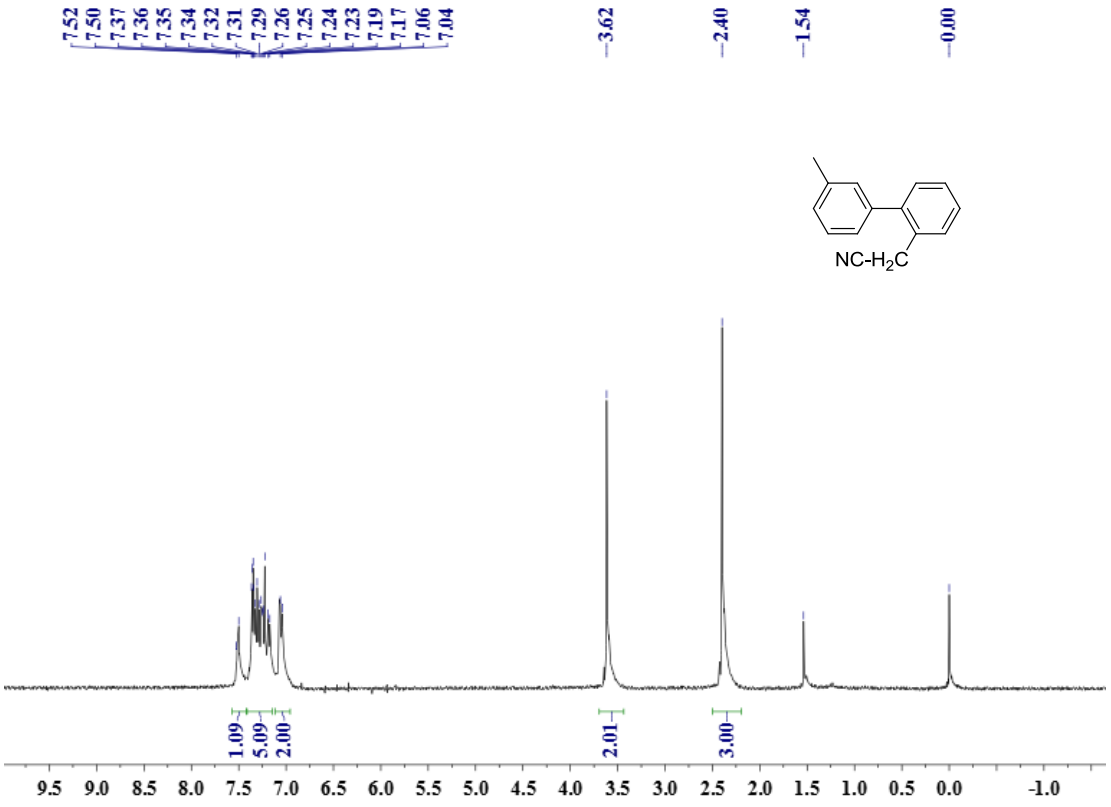
^{1}H NMR



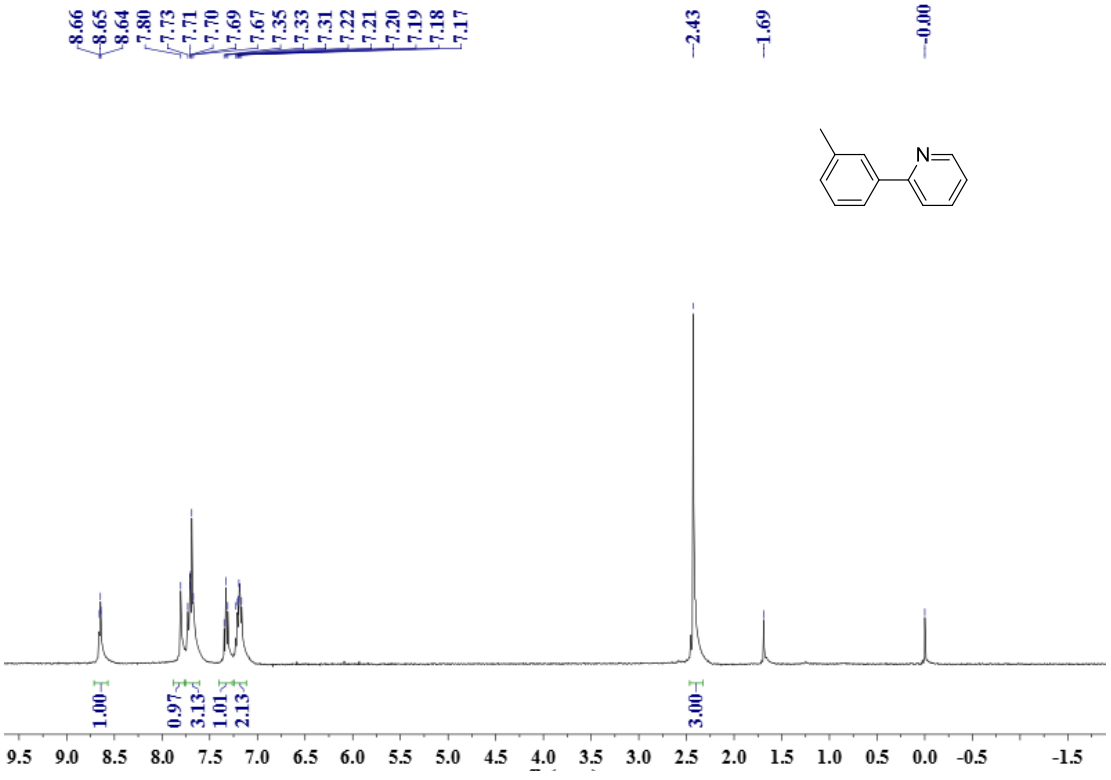
^{19}F NMR



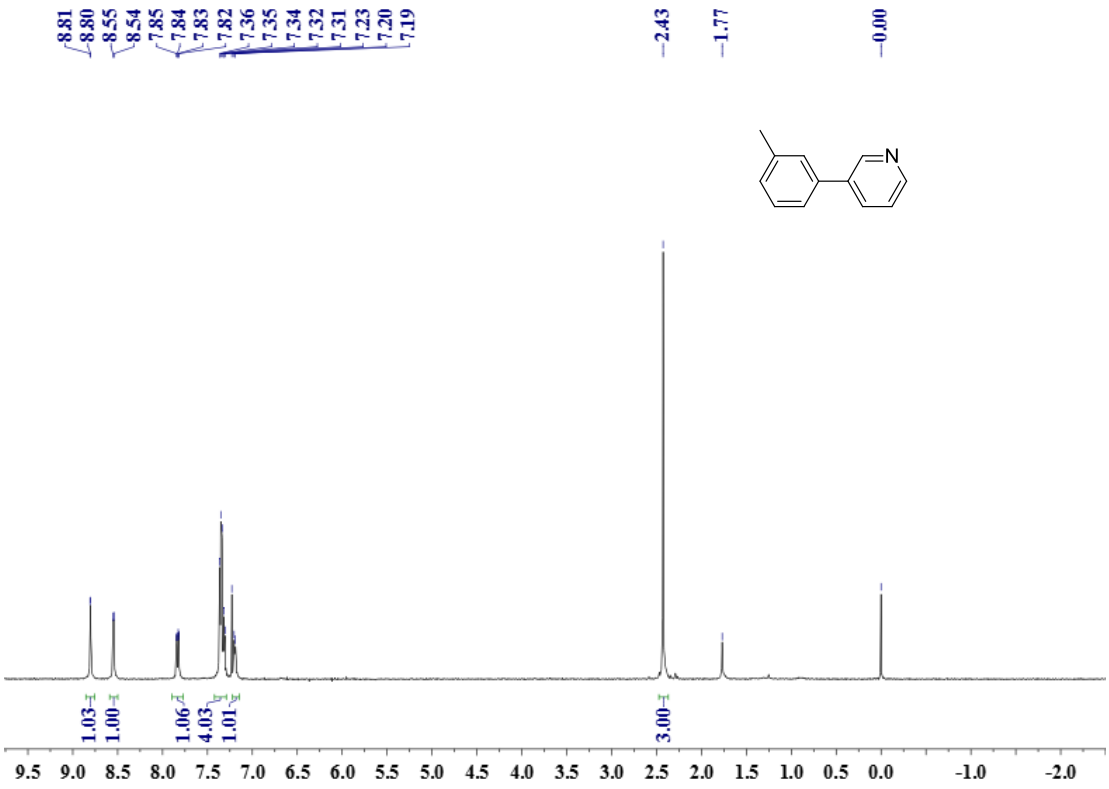
^{1}H NMR


7.52
7.50
7.37
7.36
7.35
7.34
7.32
7.31
7.29
7.26
7.25
7.24
7.23
7.19
7.17
7.06
7.04
3.62
2.40
1.54
0.00
NC-H2C
1.09
5.09
2.00
2.01
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0

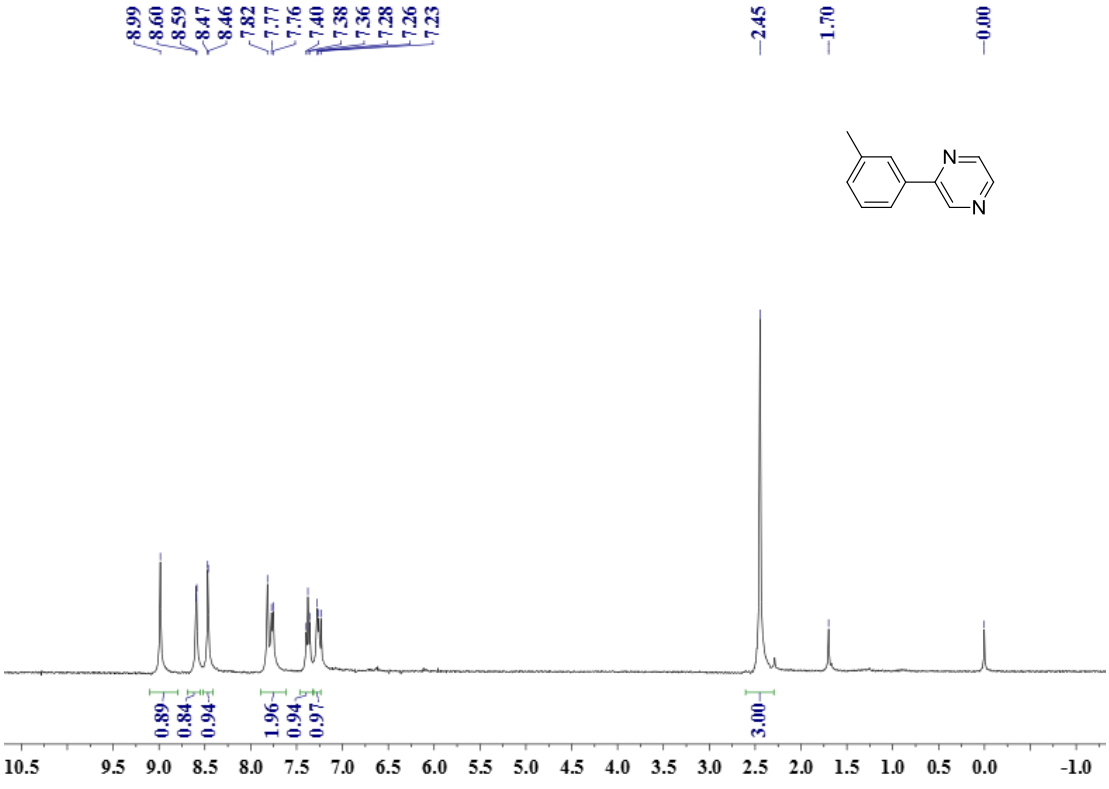
^{1}H NMR


8.66
8.65
8.64
7.80
7.73
7.71
7.70
7.69
7.67
7.35
7.33
7.31
7.22
7.21
7.20
7.19
7.18
7.17
2.43
1.69
0.00
N
1.00
0.97
3.13
1.01
2.13
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.5

^{1}H NMR


8.81
8.80
8.55
8.54
7.85
7.84
7.83
7.82
7.36
7.35
7.34
7.32
7.31
7.23
7.20
7.19
2.43
1.77
0.00
N
1.03
1.00
1.06
4.03
1.01
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0 -2.0

^{1}H NMR


8.99
8.60
8.59
8.47
8.46
7.82
7.77
7.76
7.40
7.38
7.36
7.28
7.26
7.23
2.45
1.70
0.00
N
N
0.89
0.84
0.94
1.96
0.94
0.97
3.00
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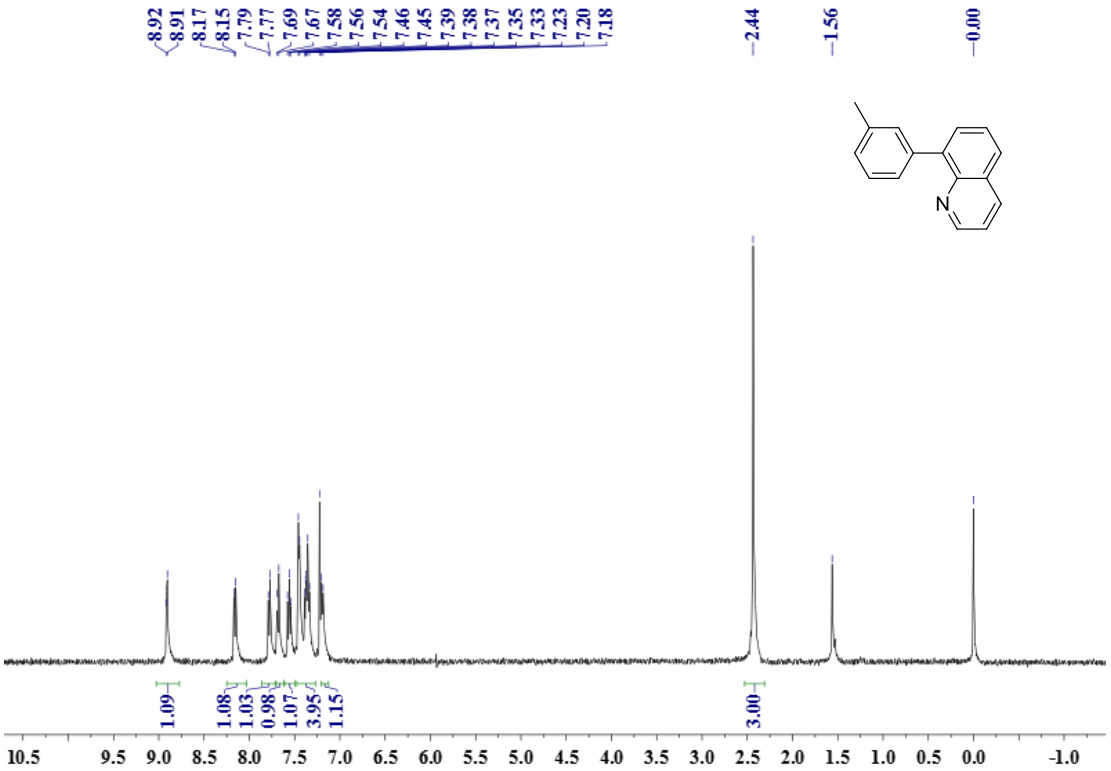
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N
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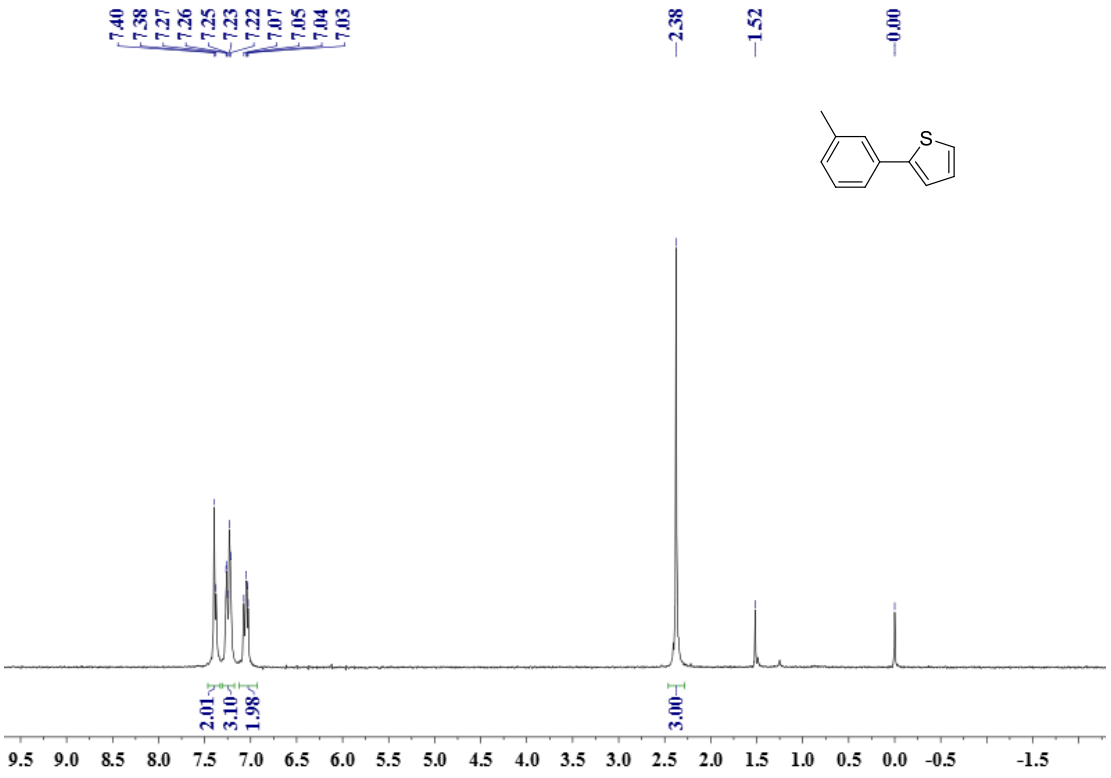
^{1}H NMR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0.00
S
2.01
3.10
1.98
3.00
9.5
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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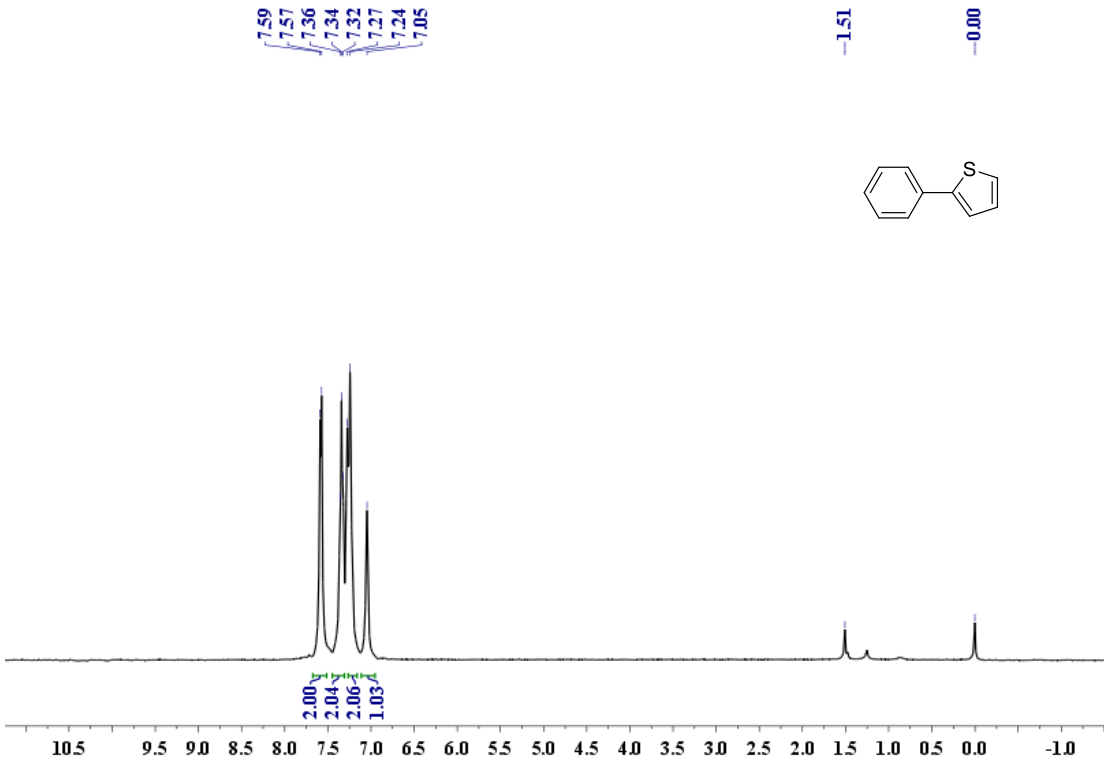
0.0
-0.5
-1.5

^{1}H NMR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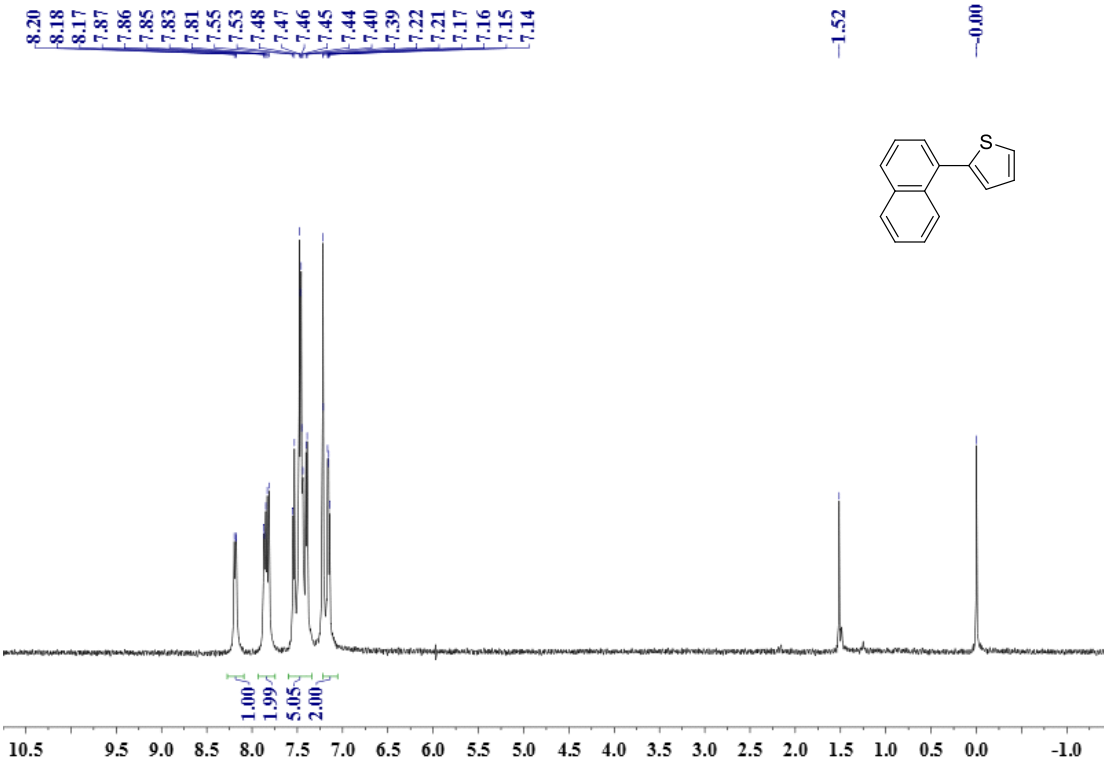
2.06
1.03
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0

^{1}H NMR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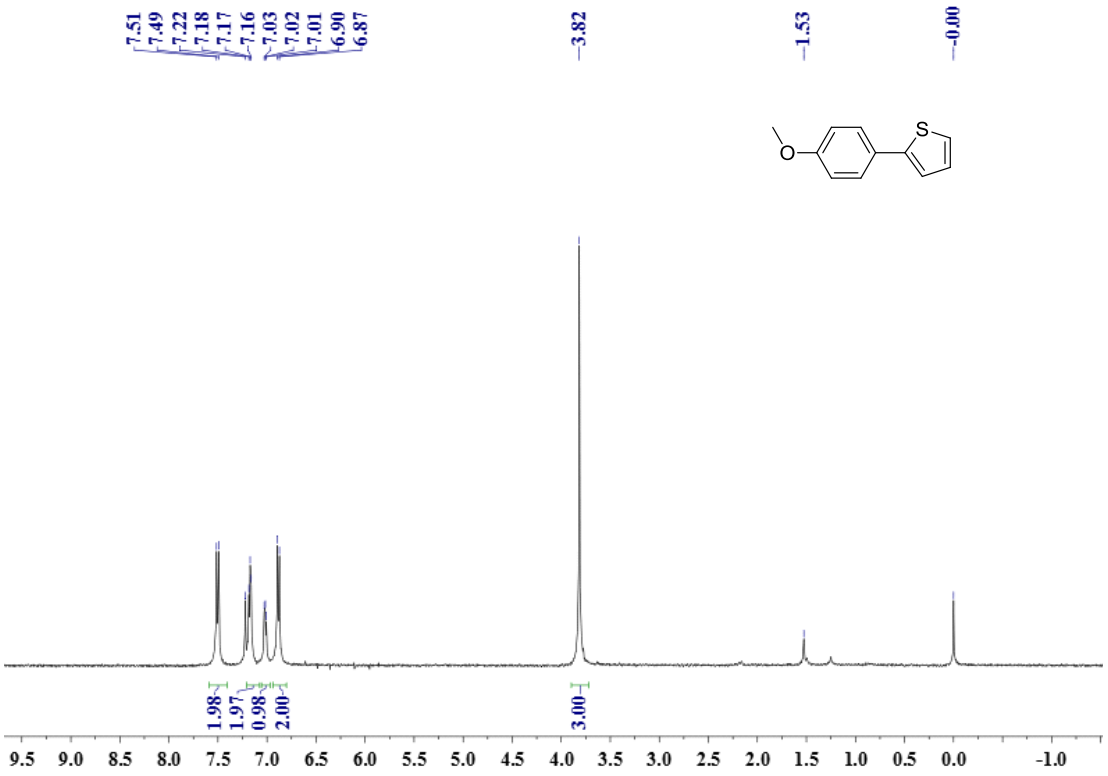
7.15
7.14
1.52
0.00
S
1.00
1.99
5.05
2.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0

^{1}H NMR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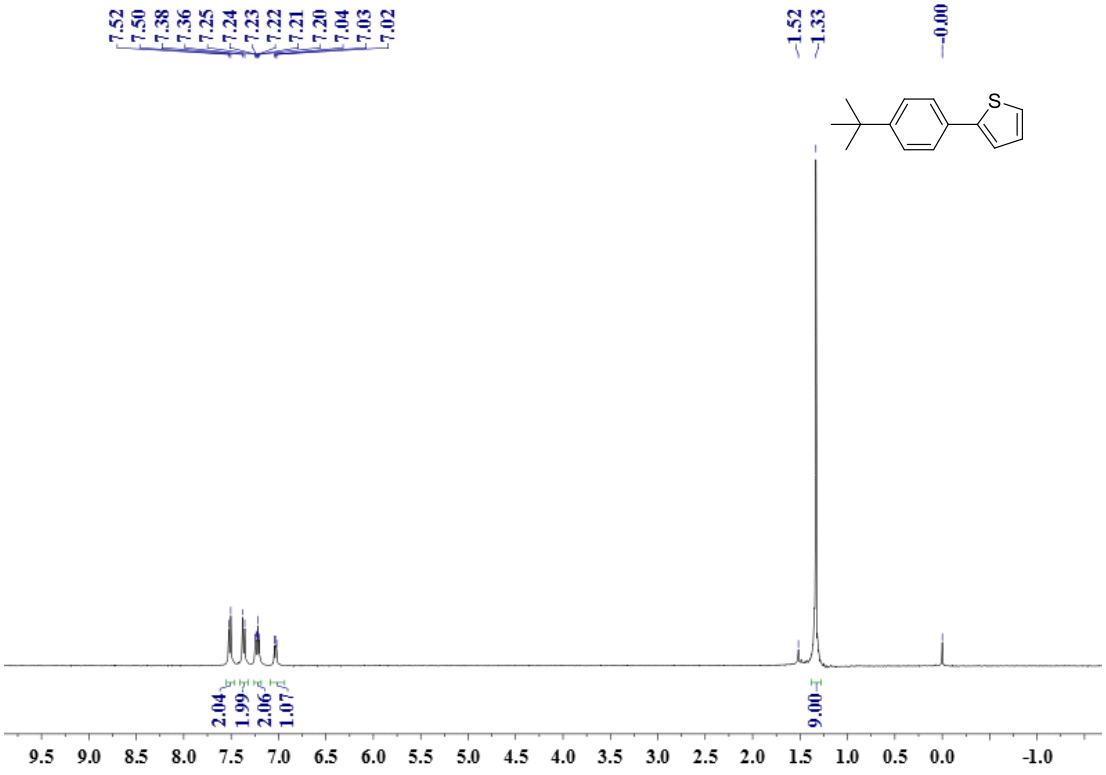
0.00
O
S
1.98
1.97
0.98
2.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0

^{1}H NMR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1.33
0.00
S
2.04
1.99
2.06
1.07
9.00
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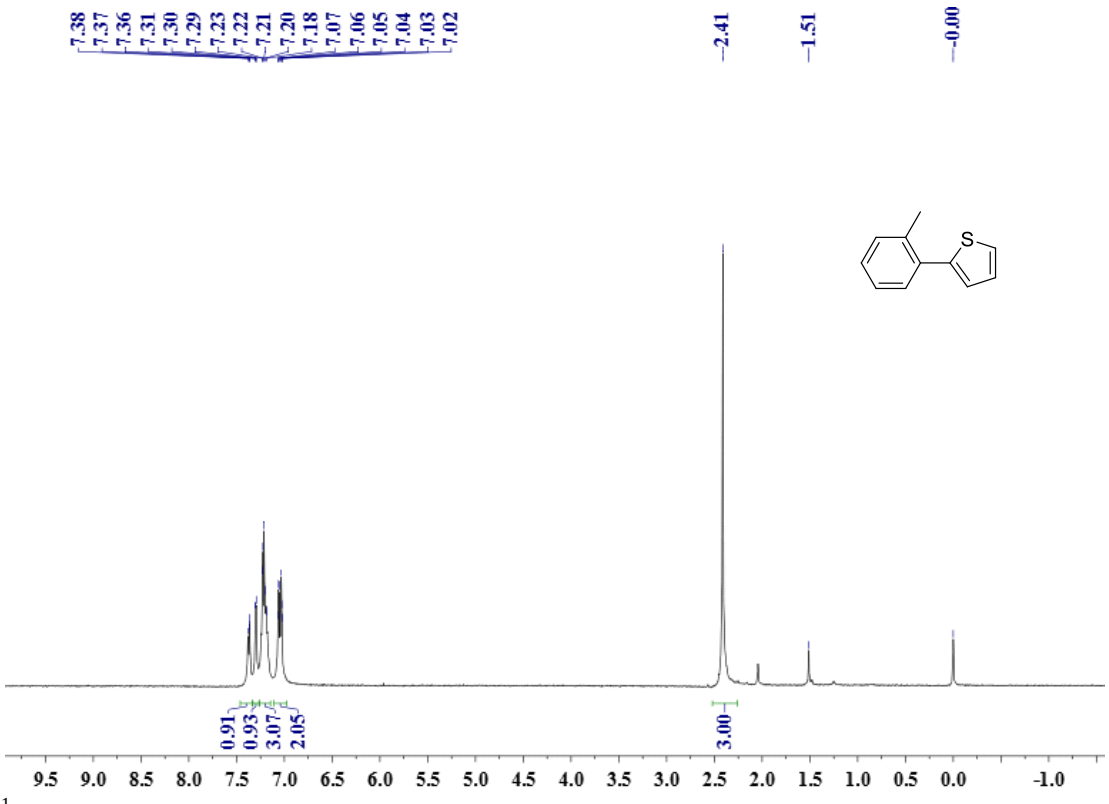
^{1}H NMR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7.04
7.03
7.02
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1.51
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S
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0.93
3.07
2.05
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0

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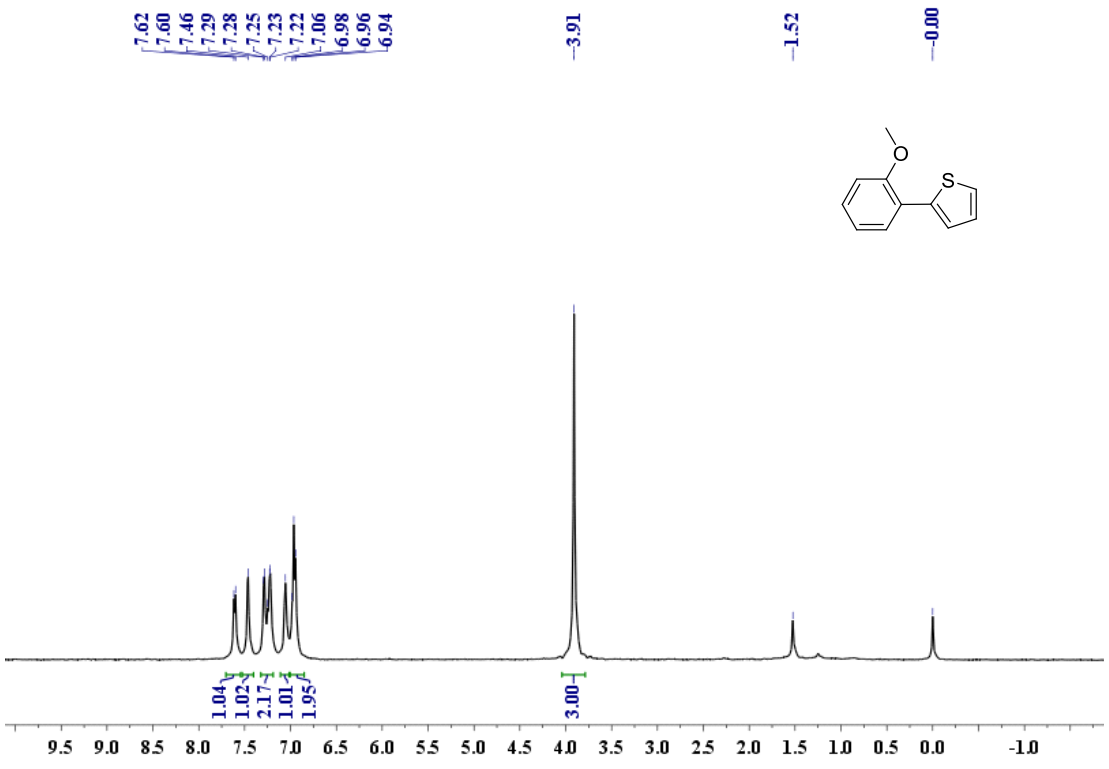
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1.02
2.17
1.01
1.95
3.00
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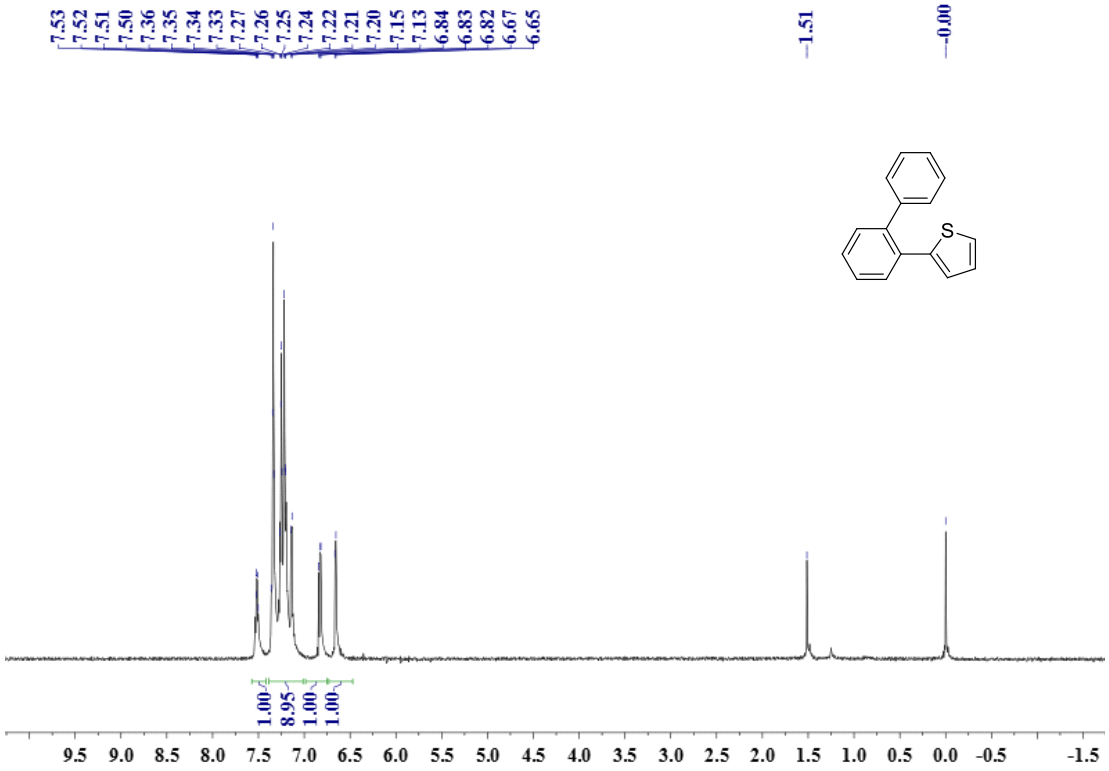
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7.20
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7.13
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6.83
6.82
6.67
6.65
1.51
0.00
S
1.00
8.95
1.00
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.5

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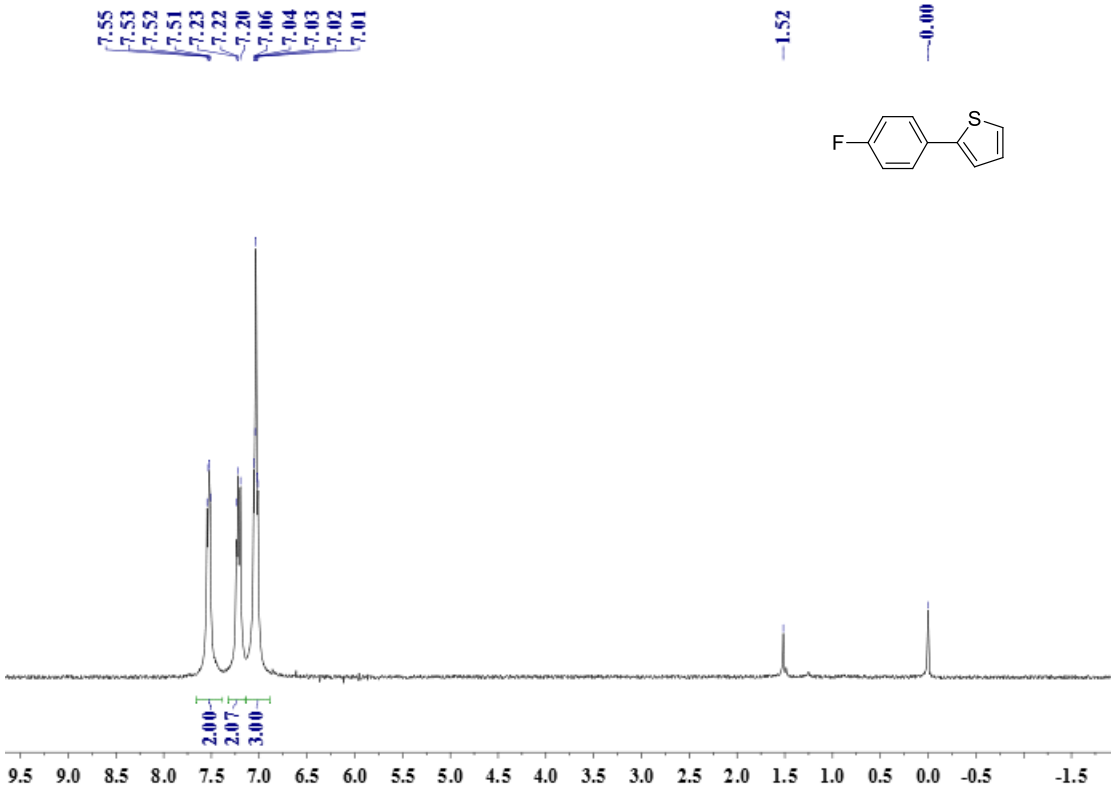
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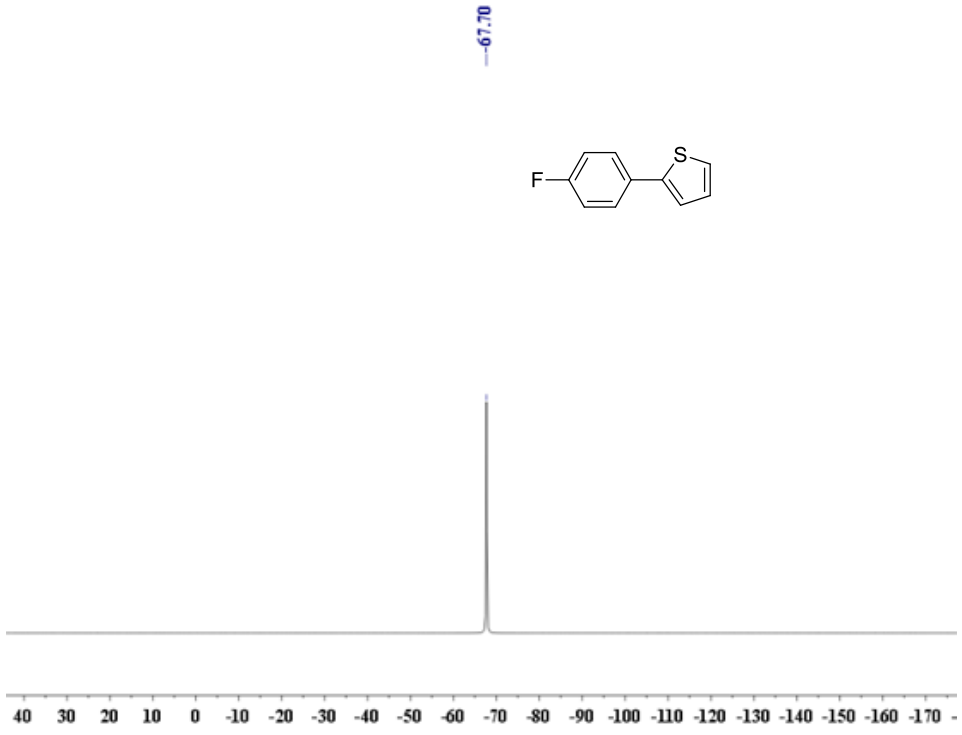
F
S
2.00
2.07
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.5

^{1}H NMR



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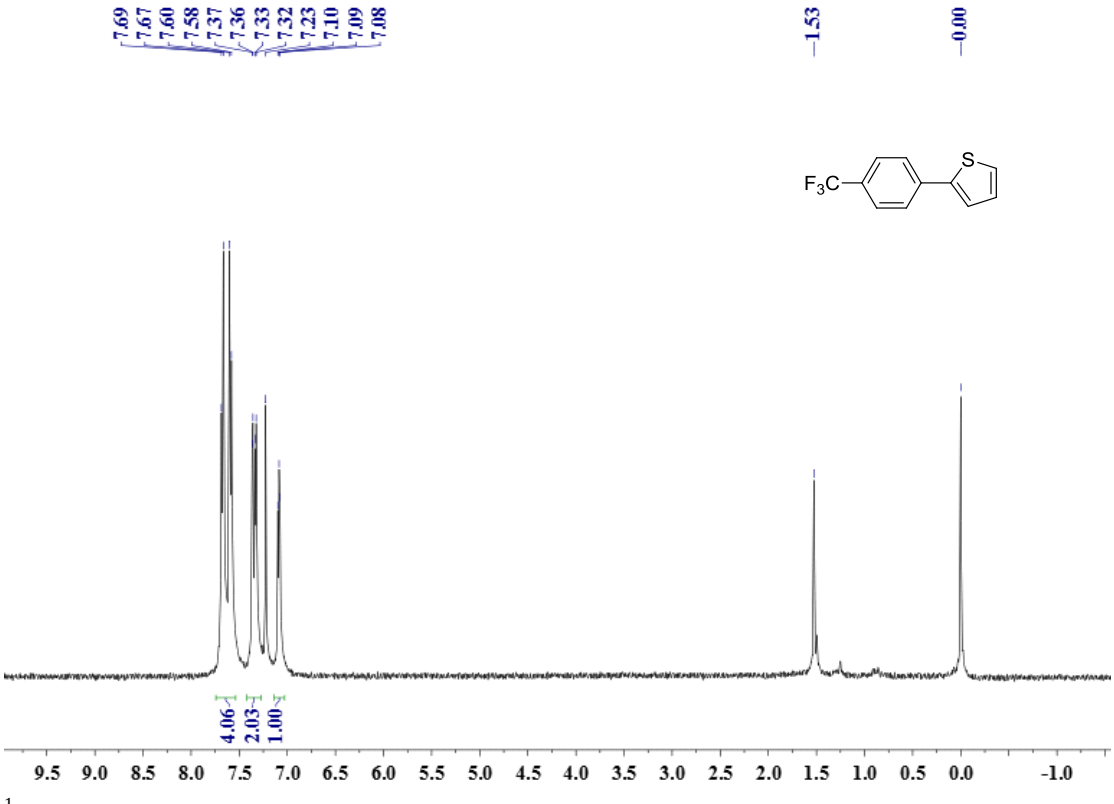

^{1}H NMR

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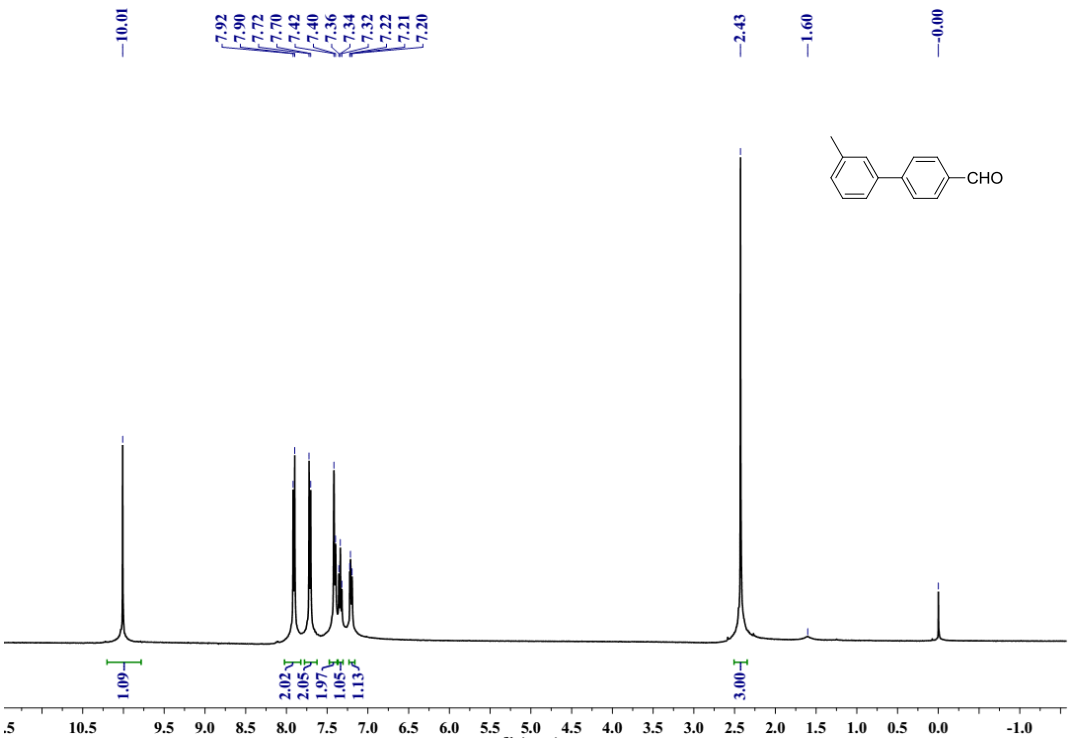

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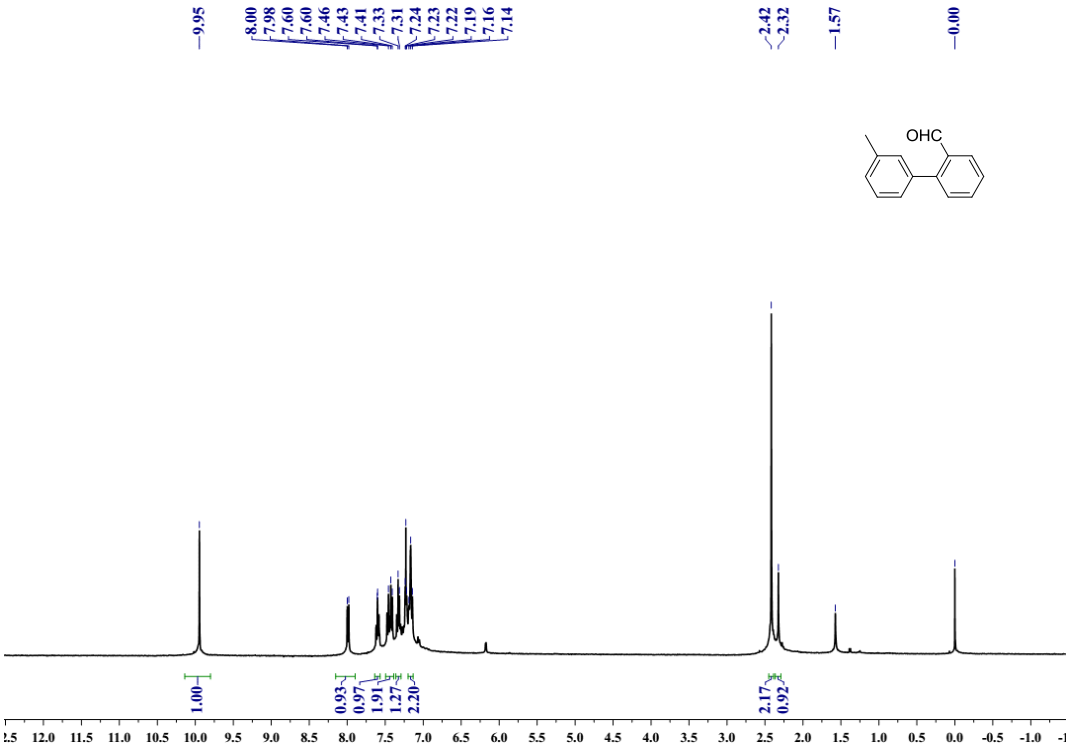
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7.19
7.16
7.14
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2.32
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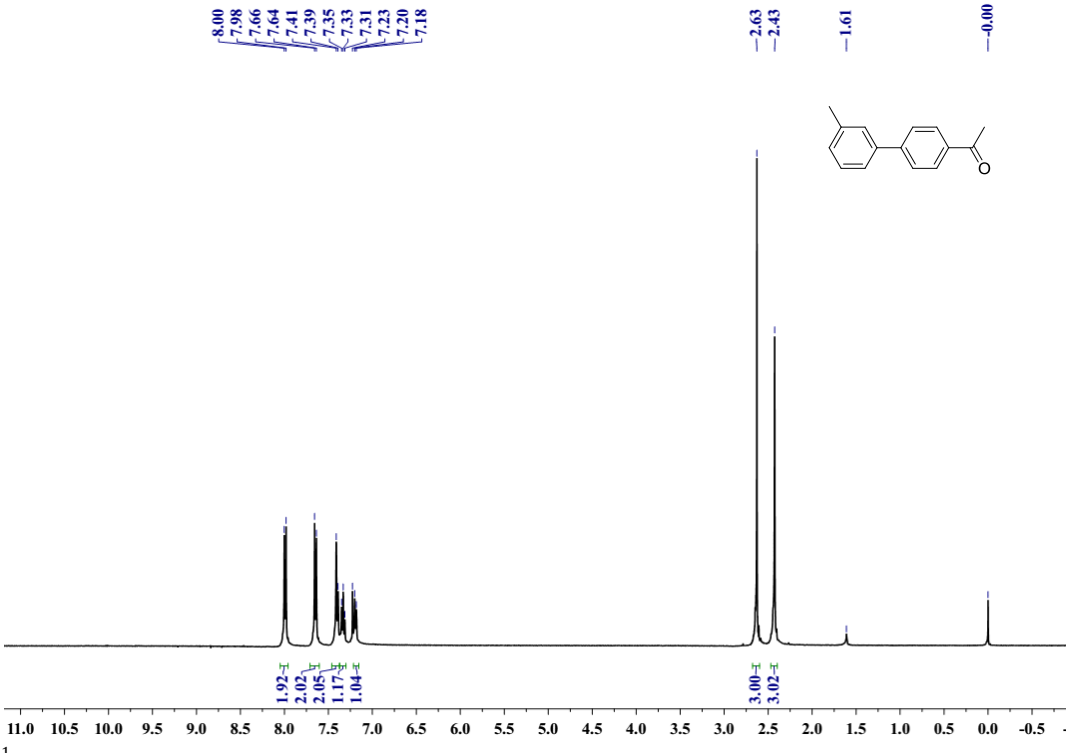
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O
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1.17
1.04
3.00
3.02

^{1}H NMR

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