Late-Stage Diversification of Biarylphosphines through Rhodium(I)-Catalyzed C–H Bond Alkenylation with Internal Alkynes

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1. General information

All reactions were carried out under argon atmosphere with standard Schlenk techniques. All reagents were obtained from commercial sources and used as supplied. All reactions were performed using dry and degassed solvents unless stated otherwise. Toluene was purified by passage through activated alumina using a Glass Contour Solvent Dispensing System. Technical grade heptane and diethyl ether were used for column chromatography.

^{1}H NMR spectra were recorded on Bruker GPX (300, 400 or 500 MHz) spectrometer. Chemical shifts (δ) were reported in parts per million relative to residual chloroform (7.28 ppm for ^{1}H; 77.23 ppm for ^{13}C), constants were reported in Hertz. ^{1}H NMR assignment abbreviations were the following: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). ^{13}C NMR spectra were recorded at 100 MHz on the same spectrometer and reported in ppm.

GC-MS analyses were performed with a GCMS-QP2010S (Shimadzu) instrument with a GC-2010 equipped with a 30 m capillary column (Supelco, SLBTM- 5ms, fused silica capillary column, 30 m x 0.25 mm x 0.25 mm film thickness), which was used with helium as the vector gas. The following GC conditions were used: initial temperature 80 ºC for 5 minutes, then rate 20 ºC/min until 280 ºC and 280 ºC for 28 minutes.

HRMS were recorded on a Waters Q-Tof 2 mass spectrometer at the corresponding facilities of the CRMPO, Centre Régional de Mesures Physiques de l'Ouest, Université de Rennes 1.

$[Rh(OAc)(COD)]_2$ was prepared according to literature procedures.[1]

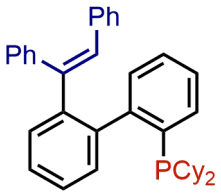
Diphenylacetylene and Bis(4-bromophenyl)acetylene were purchased and used as received. Other diaryl alkynes were prepared according to literature procedures.[2]

2. Rh(I)-Catalyzed C–H Bond Alkenylation: Procedure and Compound Characterizations

General Procedure A (monoalkenylation): To a 15 mL oven dried Schlenk tube, KOAc (4.92 mg, 0.05 mmol, 0.25 equiv.), biarylphosphine derivative (0.2 mmol, 1 equiv.), toluene (1 mL), alkyne (0.2 mmol, 1 equiv) and $[Rh(OAc)(COD)]_2$ (2.3 mg, 0.004mmol, 2 mol%) were successively added. The reaction mixture was evacuated by vacuum-argon cycles (5 times) and stirred at 120 °C (oil bath temperature) for 24 hours. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography to afford the desired alkenylated phosphines.

General Procedure B (symmetrical dialkenylaion): To a 15 mL oven dried Schlenk tube, KOAc (9.84 mg, 0.1 mmol, 0.5 equiv.), biarylphosphine derivative (0.2 mmol, 1 equiv.), toluene (1 mL), alkyne (0.6

mmol, 3 equiv.) and $[Rh(OAc)(COD)]_2$ (4.6mg, 0.008mmol, 4 mol%) were successively added. The reaction mixture was evacuated by vacuum-argon cycles (5 times) and stirred at 120 °C (oil bath temperature) for 24 hours. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography to afford the desired alkenylated phosphines.



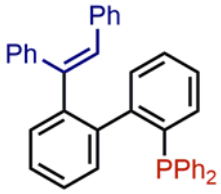
(*E*)-Dicyclohexyl(2'-(1,2-diphenylvinyl)-[1,1'-biphenyl]-2-yl)phosphane (3aa). Following the general procedure **A** using 2-(dicyclohexylphosphino)biphenyl (70.1 mg, 0.2 mmol) and diphenylacetylene (36.1 mg, 0.2 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **3aa** (90.8 mg, 86%) as a white solid; mp= 170-172 °C. Crystallization by diffusion method from CH_2Cl_2 solution with *n*-hexane has afforded single crystal to analyze by X-ray diffraction.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 – 7.33 (m, 4H), 7.23 – 7.05 (m, 8H), 7.05 – 6.95 (m, 3H), 6.92 (d, *J* = 7.5 Hz, 2H), 6.75 (dd, *J* = 7.8, 3.8 Hz, 1H), 6.68 (s, 1H), 1.89 (d, *J* = 13.0 Hz, 2H), 1.80 – 1.61 (m, 7H), 1.52 (d, *J* = 8.1 Hz, 2H), 1.47 – 1.34 (m, 3H), 1.28 – 0.92 (m, 8H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 149.4 (d, *J* = 30.7 Hz), 144.0 (d, *J* = 1.9 Hz), 142.7, 141.9 (d, *J* = 5.4 Hz), 141.1, 137.4 , 134.3 (d, *J* = 19.8 Hz), 132.2 (d, *J* = 3.2 Hz), 132.1 (d, *J* = 2.3 Hz), 131.6 , 130.6 (d, *J* = 5.7 Hz), 130.4 , 130.0 (d, *J* = 1.7 Hz), 129.4 , 127.7 (d, *J* = 17.0 Hz), 127.4 , 127.2 , 126.6 (d, *J* = 12.4 Hz), 126.3 , 125.8 , 36.7 (d, *J* = 16.2 Hz), 32.8 (d, *J* = 12.8 Hz), 31.0 (d, *J* = 13.9 Hz), 30.5 (d, *J* = 19.8 Hz), 30.2 (d, *J* = 13.3 Hz), 29.1 (d, *J* = 3.8 Hz), 27.8 (d, *J* = 6.6 Hz), 27.7 , 27.3 , 27.1 (d, *J* = 4.2 Hz), 27.0 , 26.5 (d, *J* = 11.9 Hz).

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -10.5 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{38}H_{42}P$ 529.3018; Found 529.3022.



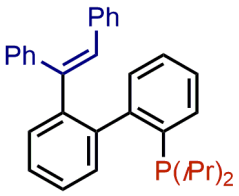
(*E*)-(2'-(1,2-Diphenylvinyl)-[1,1'-biphenyl]-2-yl)diphenylphosphane (3ba). Following the general procedure **A** using 2-(diphenylphosphino)biphenyl (67.7 mg, 0.2 mmol) and diphenylacetylene (36.1 mg, 0.2 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **3ba** (78.5 mg, 76%) as a white solid; mp= 173-175 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.43 – 7.16 (m, 10H), 7.15 – 6.88 (m, 14H), 6.85 – 6.81 (m, 2H), 6.80 (s, 1H), 6.73 (d, *J* = 7.6 Hz, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 147.5 (d, *J* = 31.7 Hz), 143.5 , 143.1 , 140.6 (d, *J* = 6.6 Hz), 140.5 , 138.6 (d, *J* = 13.1 Hz), 137.4 , 136.1 (d, *J* = 11.7 Hz), 134.1 , 133.9 , 133.7 (d, *J* = 1.9 Hz), 133.4 , 133.2 , 131.7 (d, *J* = 2.5 Hz), 131.3 (d, *J* = 3.9 Hz), 130.3 (d, *J* = 2.3 Hz), 129.7 , 129.4 , 128.5 , 128.3 (d, *J* = 7.0 Hz), 128.1 (d, *J* = 6.0 Hz), 127.8 (d, *J* = 5.3 Hz), 127.5 , 126.91 , 126.5 (d, *J* = 3.1 Hz), 126.5 .

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz): δ -13.2 (s).

HRMS (ESI) Calcd for: $C_{38}H_{30}P$: 517.2079; Found: 517.2080 $[M+H]^+$



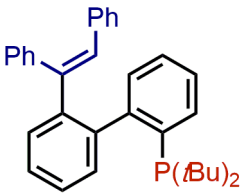
(*E*)-(2'-(1,2-Diphenylvinyl)-[1,1'-biphenyl]-2-yl)diisopropylphosphane (3ca). Following the general procedure **A** using 2-(di-(iso-propyl)phosphino)biphenyl (54.1 mg, 0.2 mmol) and diphenylacetylene (36.1 mg, 0.2 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **3ca** (72.6 mg, 81%) as a white solid; mp= 148-150 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 – 7.31 (m, 4H), 7.18 – 6.91 (m, 11H), 6.84 (s, 1H), 6.82 (s, 1H), 6.67 (ddd, *J* = 7.7, 3.8, 1.3 Hz, 2H), 2.36 – 1.73 (m, 2H), 1.22 (dd, *J* = 14.8, 6.7 Hz, 3H), 1.04 – 0.86 (m, 9H).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz): δ 148.9 (d, *J* = 29.1 Hz), 144.0 (d, *J* = 1.9 Hz), 142.9 , 141.0 , 137.4 , 132.1 (d, *J* = 2.1 Hz), 131.8 , 131.5 , 130.6 , 130.5 , 130.5 , 129.8 (d, *J* = 1.7 Hz), 129.4 , 127.7 (d, *J* = 8.2 Hz), 127.5 , 127.4 , 127.3 , 126.6 , 126.4 (d, *J* = 7.4 Hz), 125.9 , 26.2 (d, *J* = 17.3 Hz), 22.6 (d, *J* = 10.6 Hz), 21.0 (d, *J* = 15.7 Hz), 20.3 (d, *J* = 14.5 Hz), 20.0 , 19.1 (d, *J* = 6.1 Hz).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz): δ -2.9 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{34}P$: 449.2392; Found 449.2396.



(*E*)-Di-tert-butyl(2'-(1,2-diphenylvinyl)-[1,1'-biphenyl]-2-yl)phosphane (3da). Following the general procedure **A** using 2-(di-(tert-butyl)phosphino)biphenyl (60.4 mg, 0.2 mmol) and diphenylacetylene (36.1 mg, 0.2 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **3da** (51.5 mg, 54%) as a white solid; mp= 166-168 °C.

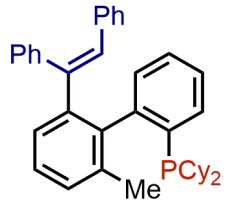
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (dt, *J* = 7.8, 1.6 Hz, 1H), 7.39 – 7.28 (m, 3H), 7.14 – 7.02 (m, 8H), 6.94 (dd, *J* = 6.9, 2.9 Hz, 2H), 6.91 – 6.84 (m, 3H), 6.65 (s, 1H), 6.62 – 6.54 (m, 1H), 1.29 (d, *J* = 11.6 Hz, 9H), 1.05 (d, *J* = 11.2 Hz, 9H).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz): δ 149.7 (d, *J* = 33.8 Hz), 143.8 (d, *J* = 2.4 Hz), 143.1, 142.4 (d, *J* = 5.7 Hz), 141.1, 137.3, 135.7 (d, *J* = 27.9 Hz), 135.0 (d, *J* = 2.8 Hz), 132.7 (d, *J* = 1.7 Hz), 131.3 (d, *J* = 6.6 Hz), 131.2, 130.5, 129.9 (d, *J* = 1.8 Hz), 129.5, 127.7 (d, *J* = 11.4 Hz), 127.3, 126.9, 126.7, 126.4, 126.0, 125.1, 33.5 (d, *J* = 23.5 Hz), 32.0 (d, *J* = 25.3 Hz), 31.9 (d, *J* = 15.5 Hz), 30.3 (d, *J* = 14.2 Hz), .

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz): δ 21.9 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{38}P$ 477.2705; Found 477.2710.

(*E*)-Dicyclohexyl(2'-(1,2-diphenylvinyl)-6'-methyl-[1,1'-biphenyl]-2-yl)phosphane (3ea). Following the general procedure **A** using 2-(dicyclohexylphosphino)-2'-methyl-biphenyl (MePhos) (72.8 mg, 0.2 mmol) and diphenylacetylene (36.1 mg, 0.2 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **3ea** (73.8 mg, 68%) as pale yellow oil.

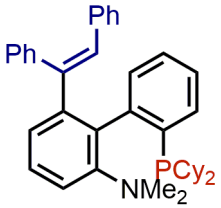


^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 – 7.15 (m, 6H), 7.11 – 7.00 (m, 6H), 6.96 (t, *J* = 7.5 Hz, 2H), 6.83 – 6.59 (m, 3H), 6.32 (dd, *J* = 7.9, 3.8 Hz, 1H), 1.97 (s, 3H), 1.88 – 1.43 (m, 11H), 1.36 – 0.95 (m, 11H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 146.8 (d, *J* = 31.6 Hz), 144.5 , 143.8 , 141.3 , 137.4 , 136.6 , 132.1 , 131.0 , 129.5 , 129.5 , 129.2 , 129.2 , 128.7 , 128.5 (d, *J* = 2.9 Hz), 128.3 , 127.7 , 127.6 , 127.2 , 126.4 (d, *J* = 7.1 Hz), 125.5 (d, *J* = 3.6 Hz), 35.9 (d, *J* = 8.8 Hz), 32.4 (d, *J* = 8.5 Hz), 31.9 , 31.0 , 30.3 , 30.2 (d, *J* = 2.9 Hz), 29.1 , 28.9 (d, *J* = 6.2 Hz), 27.8 (d, *J* = 7.3 Hz), 27.1 , 26.4, 22.7 , 21.2 .

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -7.8 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{39}H_{44}P$ 543.3175; Found 543.3176.



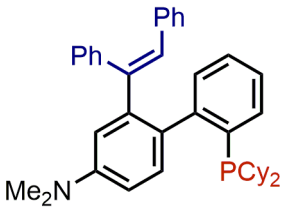
(*E*)-2'-(Dicyclohexylphosphanyl)-6-(1,2-diphenylvinyl)-N,N-dimethyl-[1,1'-biphenyl]-2-amine (3fa). Following the general procedure **A** using 2-(dicyclohexylphosphino)-2'-dimethylamimo-biphenyl (DavePhos) (78.8 mg, 0.2 mmol) and diphenylacetylene (36.1 mg, 0.2 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **3fa** (91.4 mg, 80%) as a pale yellow solid; mp= 86-88 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49 (d, *J* = 6.9 Hz, 1H), 7.42 – 7.35 (m, 1H), 7.15 – 7.04 (m, 9H), 6.92 – 6.81 (m, 5H), 6.72 – 6.65 (m, 1H), 6.47 (s, 1H), 2.51 (s, 6H), 2.08 – 1.61 (m, 11H), 1.36 – 1.16 (m, 11H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 152.9 , 145.8 (d, *J* = 31.3 Hz), 144.9 , 143.2 , 141.3 , 137.7 , 136.9 (d, *J* = 16.8 Hz), 136.3 , 132.7 , 131.9 , 131.4 , 130.0 , 129.2 , 127.9 , 127.7 , 127.6 , 126.6 (d, *J* = 8.3 Hz), 126.2 , 125.5 , 117.7 , 44.9 , 35.9 (d, *J* = 16.1 Hz), 33.4 (d, *J* = 14.5 Hz), 32.7 (d, *J* = 21.5 Hz), 31.9 , 30.8 (d, *J* = 14.6 Hz), 30.6 (d, *J* = 18.0 Hz), 29.0 , 28.3 (d, *J* = 14.4 Hz), 28.0 (d, *J* = 4.2 Hz), 27.9 , 27.2 (d, *J* = 10.8 Hz), 26.6 (d, *J* = 7.1 Hz).

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -8.2(s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{40}H_{47}NP$ 572.3440; Found 572.3441.



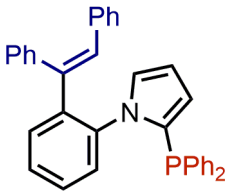
(*E*)-2'-(Dicyclohexylphosphanyl)-2-(1,2-diphenylvinyl)-N,N-dimethyl-[1,1'-biphenyl]-4-amine (3ga). Following the general procedure **A** using 2-(dicyclohexylphosphino)-4'-dimethylamimo-biphenyl (78.8 mg, 0.2 mmol) and diphenylacetylene (36.1 mg, 0.2 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **3ga** (90.3 mg, 79%) as a pale yellow solid; mp= 101-103 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (d, *J* = 7.6 Hz, 1H), 7.11 – 6.97 (m, 10H), 6.88 (dd, *J* = 19.8, 7.5 Hz, 3H), 6.76 (s, 2H), 6.68 (dd, *J* = 8.0, 3.9 Hz, 1H), 6.65 (s, 1H), 3.02 (s, 6H), 1.91 – 1.52 (m, 10H), 1.47 – 0.97 (m, 12H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 149.7 , 149.3 (d, *J* = 14.5 Hz), 144.4 , 143.76 , 141.0 , 137.6 , 134.9 , 134.7 , 132.8 , 132.2 , 131.3 (d, *J* = 5.6 Hz), 131.0 , 129.9 , 129.4 , 127.6 (d, *J* = 4.3 Hz), 127.2 , 126.4 (d, *J* = 11.1 Hz), 125.3 , 114.6 , 110.2 , 40.6 , 36.6 (d, *J* = 16.2 Hz), 32.9 (d, *J* = 12.8 Hz), 31.0 (d, *J* = 13.9 Hz), 30.5 (d, *J* = 19.6 Hz), 30.1 (d, *J* = 13.4 Hz), 29.0 (d, *J* = 5.1 Hz), 27.8 , 27.8 (d, *J* = 3.6 Hz), 27.3, 27.1 (d, *J* = 5.2 Hz), 27.0 , 26.5 (d, *J* = 10.6 Hz).

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -10.7 (s) [presence of **1g** phosphine oxide at 45.4 ppm (<5%)].

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{40}H_{47}NP$ 572.3440; Found 572.3433.



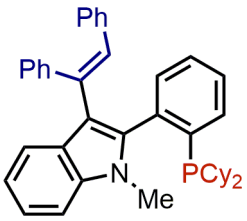
(*E*)-2-(Diphenylphosphanyl)-1-(2-(1,2-diphenylvinyl)phenyl)-1H-pyrrole (3ha). Following the general procedure **A** using N-phenylpyrrol-2-yldiphenylphosphine (65.6 mg, 0.2 mmol) and diphenylacetylene (36.1 mg, 0.2 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **3ha** (77.8 mg, 77%) as a white solid; mp= 82-84 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.41 (ddd, *J* = 16.6, 6.9, 2.5 Hz, 6H), 7.27 – 7.13 (m, 11H), 7.11 – 7.01 (m, 5H), 7.00 – 6.93 (m, 1H), 6.84 (td, *J* = 2.9, 1.6 Hz, 1H), 6.76 (s, 1H), 6.19 – 6.14 (m, 1H), 6.02 (dd, *J* = 3.6, 1.6 Hz, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 142.1 , 140.4 , 139.5 , 138.6 (d, *J* = 2.3 Hz), 138.1 , 137.2 , 133.3 (d, *J* = 19.5 Hz), 131.4 , 131.3 (d, *J* = 2.1 Hz), 129.7 (d, *J* = 6.1 Hz), 129.5 (d, *J* = 2.0 Hz), 129.4 (d, *J* = 3.9 Hz), 129.1 (d, *J* = 2.5 Hz), 128.2 , 128.0 (d, *J* = 11.3 Hz), 127.7 , 127.2 (d, *J* = 2.5 Hz), 127.2 , 126.9 , 118.9 , 109.6 .

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -30.7 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{36}H_{29}NP$ 506.2032; Found 506.2036.



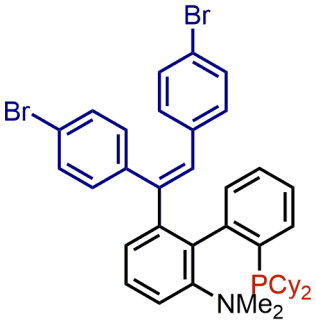
(*E*)-2-(2-(Dicyclohexylphosphanyl)phenyl)-3-(1,2-diphenylvinyl)-1-methyl-1H-indole (3ia). Following the general procedure **A** using 2-[2-(dicyclohexylphosphino)phenyl]-1-methyl-1H-indole (CM-Phos) (80.8 mg, 0.2mmol) and diphenylacetylene (36.1 mg, 0.2 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **3ia** (46.5 mg, 40%) as pale yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (dd, *J* = 8.0, 4.4 Hz, 2H), 7.28 – 7.19 (m, 5H), 7.19 – 7.10 (m, 4H), 7.08 – 7.00 (m, 5H), 6.96 – 6.90 (m, 2H), 6.60 (s, 1H), 3.46 (s, 3H), 1.90 – 1.55 (m, 11H), 1.35 – 1.04 (m, 11H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 141.7 , 137.9 , 136.5 (d, *J* = 4.9 Hz), 136.4 , 132.7, 132.7 (d, *J* = 5.7 Hz), 130.6 (d, *J* = 2.1 Hz), 130.4 (d, *J* = 10.0 Hz), 129.2 , 128.6 , 127.9 , 127.7 (d, *J* = 4.5 Hz), 127.6 , 127.5 , 127.4 , 126.9 , 125.7 (d, *J* = 5.5 Hz), 121.4 (d, *J* = 7.2 Hz), 120.5 , 119.6 , 117.9 , 109.3 , 35.3 (d, *J* = 14.9 Hz), 34.9 (d, *J* = 15.1 Hz), 31.0 (d, *J* = 3.1 Hz), 30.7 (d, *J* = 6.9 Hz), 30.5 , 30.1 (d, *J* = 13.3 Hz), 29.9 , 29.7 , 27.5 (d, *J* = 10.0 Hz), 27.3 (d, *J* = 11.0 Hz), 27.2 (d, *J* = 10.0 Hz), 26.7 (d, *J* = 6.1 Hz), 26.4 (d, *J* = 7.8 Hz).

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -9.81 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{41}H_{45}NP$ 582.3284; Found 582.3287.



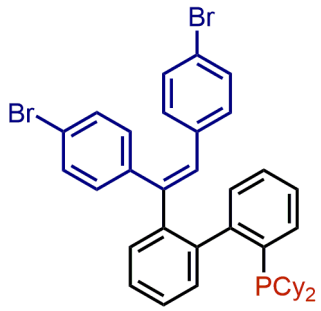
(*E*)-6-(1,2-Bis(4-bromophenyl)vinyl)-2'-(dicyclohexylphosphanyl)-N,N-dimethyl-[1,1'-biphenyl]-2-amine (3fb). Following the general procedure **A** using 2-(dicyclohexylphosphino)-2'-dimethylamimo-biphenyl (DavePhos) (78.8 mg, 0.2 mmol), and Bis(4-bromophenyl)acetylene (67.2 mg, 0.2 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **3fb** (111.9 mg, 77%) as a pale yellow solid; mp= 111-113 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (d, *J* = 7.1 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.22 – 7.02 (m, 8H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 2H), 6.63 (d, *J* = 8.1 Hz, 2H), 6.40 (s, 1H), 2.50 (s, 6H), 1.99 – 1.65 (m, 11H), 1.36 – 1.10 (m, 11H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 153.1 , 145.5 (d, *J* = 31.0 Hz), 144.1 , 142.8 , 139.9 , 136.9 (d, *J* = 17.8 Hz), 136.2 , 132.6 , 131.9 , 131.5 , 131.0 (d, *J* = 15.4 Hz), 130.7 , 130.6 , 128.1 , 126.7 , 125.5 (d, *J* = 48.0 Hz), 120.6 (d, *J* = 51.8 Hz), 118.2 , 45.0 , 35.9 (d, *J* = 16.3 Hz), 33.1 , 32.9 (d, *J* = 14.1 Hz), 32.6 , 31.9 , 30.9 (d, *J* = 14.2 Hz), 30.5 (d, *J* = 18.2 Hz), 28.3 (d, *J* = 14.9 Hz), 27.8 , 27.7 (d, *J* = 3.4 Hz), 27.05(d, *J* = 10.2 Hz), 26.5 .

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 8.0 (s) [presence of **1f** phosphine oxide at 44.5 ppm (<5%)].

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{40}H_{45}Br_2NP$ 728.1651; Found 728.1653.



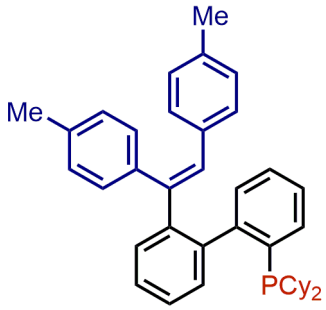
(*E*)-(2'-(1,2-Bis(4-bromophenyl)vinyl)-[1,1'-biphenyl]-2-yl)dicyclohexylphosphane (3ab). Following the general procedure **A** using 2-(dicyclohexylphosphino)biphenyl (70.1 mg, 0.2 mmol), and Bis(4-bromophenyl)acetylene (67.2 mg, 0.2 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **3ab** (111.1 mg, 81%) as white solid; mp= 179-181 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.42 – 7.30 (m, 5H), 7.23 – 7.12 (m, 6H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 2H), 6.68 (dd, *J* = 7.4, 2.4 Hz, 2H), 6.56 (s, 1H), 1.85 – 1.43 (m, 11H), 1.32 – 0.90 (m, 11H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 148.9 (d, *J* = 29.7 Hz), 143.1 (d, *J* = 2.0 Hz), 142.4 , 139.6 , 135.9 , 132.1 (d, *J* = 3.1 Hz), 131.5 (d, *J* = 1.8 Hz), 131.1 , 130.9 (d, *J* = 8.0 Hz), 130.6 (d, *J* = 15.0 Hz), 130.2 , 127.4 , 126.8 , 126.1 , 120.9 , 120.6 , 36.4 , 32.3 , 30.8 (d, *J* = 5.3 Hz), 30.7 , 30.4 , 30.3 , 28.9 , 27.7 (d, *J* = 10.0 Hz), 27.1 , 26.9 (d, *J* = 9.1 Hz), 26.5 , 26.3 .

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -10.5 (s) [presence of **1a** phosphine at -13.4 ppm (<5%)].

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{38}H_{40}Br_2P$ 685.1228; Found 685.1228.



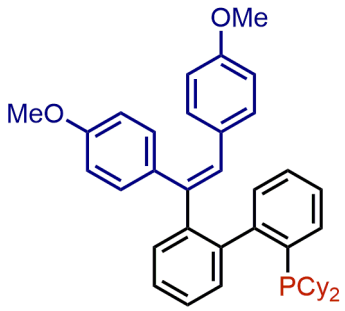
(*E*)-Dicyclohexyl(2'-(1,2-di-p-tolylvinyl)-[1,1'-biphenyl]-2-yl)phosphane (3ac). Following the general procedure **A** using 2-(dicyclohexylphosphino)biphenyl (70.1 mg, 0.2 mmol), and 1,2-di-*p*-tolylethyne (41.5 mg, 0.2 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **3ac** (91.3mg, 82%) as white solid; mp= 103-105 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 – 7.30 (m, 4H), 7.15 (t, *J* = 6.2 Hz, 2H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.93 – 6.84 (m, 6H), 6.80 (dd, *J* = 13.1, 6.2 Hz, 3H), 6.52 (s, 1H), 2.33 (s, 3H), 2.25 (s, 3H), 1.90 – 1.47 (m, 11H), 1.40 – 0.96 (m, 11H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 149.5 (d, *J* = 30.5 Hz), 144.1 (d, *J* = 1.9 Hz), 141.7 (d, *J* = 35.2 Hz), 138.3 , 136.0 (d, *J* = 13.8 Hz), 134.7 , 134.3 (d, *J* = 20.0 Hz), 132.1 (d, *J* = 16.9 Hz), 131.3 , 130.6 , 130.3 , 129.9 , 129.2 , 128.4 (d, *J* = 23.2 Hz), 127.2 (d, *J* = 29.5 Hz), 125.8 (d, *J* = 27.6 Hz), 36.6 (d, *J* = 16.4 Hz), 32.9 (d, *J* = 12.8 Hz), 30.9 (d, *J* = 13.6 Hz), 30.5 , 30.4 , 30.2 (d, *J* = 13.2 Hz), 29.1 , 27.7 , 27.2 , 27.1 (d, *J* = 11.5 Hz), 26.6 , 26.4 , 21.3 , 21.2.

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -10.9 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{40}H_{46}P$ 557.3331; Found 557.3328.



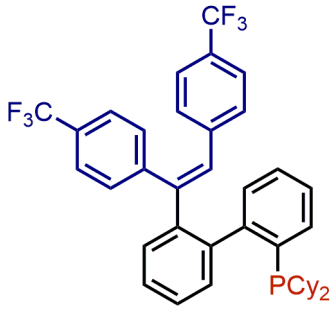
(*E*)-(2'-(1,2-Bis(4-methoxyphenyl)vinyl)-[1,1'-biphenyl]-2-yl)dicyclohexylphosphane (3ad). Following the general procedure **A** using 2-(dicyclohexylphosphino)biphenyl (70.1 mg, 0.2 mmol), and 1,2-bis(3-methoxyphenyl)ethyne (47.8 mg, 0.2mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **3ad** (100.1 mg, 85%) as a white solid; mp= 164-166°C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 – 7.30 (m, 4H), 7.16 (d, *J* = 7.4 Hz, 2H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.82 – 6.76 (m, 1H), 6.65 (d, *J* = 8.3 Hz, 4H), 6.52 (s, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 1.93 – 1.49 (m, 11H), 1.44 – 0.97 (m, 11H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 158.2 (d, *J* = 28.4 Hz), 149.6 (d, *J* = 30.8 Hz), 144.4 (d, *J* = 2.0 Hz), 141.8 (d, *J* = 5.6 Hz), 140.3 , 134.3, 134.1 , 133.9 , 132.2 (d, *J* = 3.3 Hz), 132.0 (d, *J* = 2.4 Hz), 131.2 (d, *J* = 2.0 Hz), 130.7 , 130.6 , 130.5 , 130.4 , 130.2 , 127.2 (d, *J* = 23.5 Hz), 125.9 (d, *J* = 23.2 Hz), 113.2 (d, *J* = 23.5 Hz) , 55.2 , 55.1 , 36.7 (d, *J* = 16.5 Hz), 32.8 (d, *J* = 12.7 Hz), 31.0 (d, *J* = 14.0 Hz), 30.5 (d, *J* = 19.9 Hz), 30.2 (d, *J* = 13.0 Hz), 29.1 (d, *J* = 4.8 Hz), 27.8 , 27.7 (d, *J* = 5.3 Hz), 27.3 , 27.1 , 27.0 , 26.5 (d, *J* = 15.1 Hz).

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -10.9 (s)

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{40}H_{46}O_2P$ 589.3230; Found 589.3231.



(*E*)-(2'-(1,2-Bis(4-(trifluoromethyl)phenyl)vinyl)-[1,1'-biphenyl]-2-yl)dicyclohexylphosphane (3ae). Following the general procedure **A** using 2-(dicyclohexylphosphino)biphenyl (70.1 mg, 0.2 mmol), and 1,2-bis(4-(trifluoromethyl)phenyl)ethyne (63.2 mg, 0.2 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **3ae** (110.3 mg, 83%) as a white solid; mp= 124-126 °C.

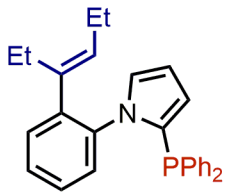
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49 – 7.31 (m, 7H), 7.29 (s, 1H), 7.27 (s, 1H), 7.19 – 7.11 (m, 2H), 7.10 – 7.02 (m, 2H), 6.88 (t, *J* = 6.3 Hz, 3H), 6.54 (ddd, *J* = 7.7, 3.9, 1.3 Hz, 1H), 1.88 – 1.53 (m, 11H), 1.35 – 0.88 (m, 11H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 148.6 (d, *J* = 28.4 Hz), 144.2, 143.8, 142.8 (d, *J* = 1.9 Hz), 140.2, 132.1 (d, *J* = 2.6 Hz), 131.1, 130.4, 129.9, 129.5, 129.1, 128.9, 128.8 (d, *J* = 3.8 Hz), 128.6 (d, *J* = 3.7 Hz), 127.9, 127.2, 126.2, 125.2 (d, *J* = 11.3 Hz), 124.8 (q, *J* = 271.1 Hz), 124.7 (q, *J* = 271.5 Hz), 123.0 (d, *J* = 11.1 Hz), 120.8 (d, *J* = 11.1 Hz), 36.3 (d, *J* = 17.6 Hz), 31.9 (d, *J* = 9.6 Hz), 30.6, 30.1, 28.8, 28.7, 27.5, 27.0, 26.9, 26.8, 26.4 (d, *J* = 5.1 Hz), 26.2.

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -9.6 (s).

^{19} F{^{1}H} NMR ($CDCl_3$, 282 MHz): δ -62.5 (s), -62.6 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{40}H_{40}F_6P$ 665.2766; Found 665.2772.



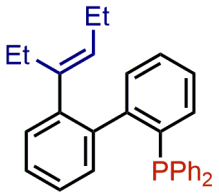
(*E*)-2-(Diphenylphosphanyl)-1-(2-(hex-3-en-3-yl)phenyl)-1H-pyrrole (3hf). Following the general procedure **A** using N-phenylpyrrol-2-yldiphenylphosphine (65.6 mg, 0.2 mmol), and 3-hexyne (23 µL, 0.2 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **3hf** (55.7 mg, 68%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 – 7.29 (m, 11H), 7.21 – 7.10 (m, 2H), 6.95 – 6.91 (m, 2H), 6.33 – 6.27 (m, 1H), 6.18 (dd, *J* = 3.6, 1.7 Hz, 1H), 5.43 (t, *J* = 7.2 Hz, 1H), 2.21 – 1.84 (m, 4H), 0.96 (t, *J* = 7.5 Hz, 3H), 0.81 (t, *J* = 7.6 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 141.4, 140.5, 138.2 (d, *J* = 7.0 Hz), 137.7 (d, *J* = 2.7 Hz), 133.3 (d, *J* = 19.7 Hz), 132.6, 131.0, 129.1 (d, *J* = 2.0 Hz), 128.6 (d, *J* = 5.2 Hz), 128.2 (d, *J* = 6.4 Hz), 127.9, 127.7 (d, *J* = 2.5 Hz), 126.6, 119.1 (d, *J* = 2.6 Hz), 109.3 (d, *J* = 1.4 Hz), 22.1, 21.3, 14.2, 13.6 (d, *J* = 2.3 Hz).

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -33.2 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{29}NP$ 410.2032; Found 410.2026.



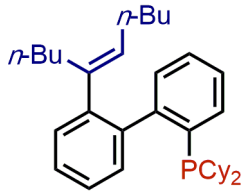
(*E*)-(2'-(Hex-3-en-3-yl)-[1,1'-biphenyl]-2-yl)diphenylphosphane (3bf). Following the general procedure **A** using 2-(diphenylphosphino)biphenyl (67.7 mg, 0.2 mmol), and 3-hexyne (23 µL, 0.2 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **3bf** (62.2mg, 72%) as colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 – 7.29 (m, 13H), 7.24 – 7.16 (m, 3H), 7.06 (ddd, *J* = 7.5, 5.8, 3.0 Hz, 1H), 6.81 (dt, *J* = 6.8, 1.3 Hz, 1H), 5.44 (t, *J* = 7.2 Hz, 1H), 2.15 – 1.95 (m, 4H), 0.91 (td, *J* = 7.5, 4.2 Hz, 6H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 148.5 (d, *J* = 32.7 Hz), 143.0, 141.6, 139.5 (d, *J* = 7.2 Hz), 139.0 (d, *J* = 13.8 Hz), 138.0 (d, *J* = 12.2 Hz), 136.3 (d, *J* = 12.2 Hz), 134.7 (d, *J* = 2.3 Hz), 133.9 (d, *J* = 19.9 Hz), 133.3 (d, *J* = 19.1 Hz), 132.9 (d, *J* = 1.9 Hz), 131.2 (d, *J* = 4.9 Hz), 130.7 (d, *J* = 5.8 Hz), 129.8, 128.4 (d, *J* = 1.8 Hz), 128.3 (d, *J* = 3.3 Hz), 128.2 (d, *J* = 4.9 Hz), 128.0, 127.2 (d, *J* = 21.0 Hz), 125.3, 23.8, 21.3, 14.2, 13.5 (d, *J* = 2.0 Hz).

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -14.9 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{42}P$ 433.3024; Found 433.3025.



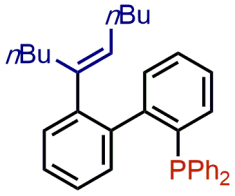
(*E*)-Dicyclohexyl(2'-(dec-5-en-5-yl)-[1,1'-biphenyl]-2-yl)phosphane (3ag). Following the general procedure **A** using 2-(dicyclohexylphosphino)biphenyl (70.1 mg, 0.2 mmol), and 5-decyne (36 µL, 0.2 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **3ag** (63.4 mg, 65%) as colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (d, *J* = 7.0 Hz, 1H), 7.34 – 7.22 (m, 6H), 7.12 (d, *J* = 7.4 Hz, 1H), 5.40 (t, *J* = 7.2 Hz, 1H), 2.13 – 1.61 (m, 17H), 1.35 – 1.10 (m, 17H), 0.91 (t, *J* = 6.9 Hz, 3H), 0.82 (t, *J* = 6.9 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 149.9 (d, *J* = 31.4 Hz), 143.6 , 141.4 , 140.1 , 135.0 (d, *J* = 22.3 Hz), 132.7 , 132.1 , 131.8 (d, *J* = 3.9 Hz), 131.0 , 129.9 , 127.5 , 127.0 , 126.1 , 125.1 , 37.0 (d, *J* = 15.8 Hz), 34.0 (d, *J* = 14.8 Hz), 31.9 , 30.9 , 30.7 (d, *J* = 13.4 Hz), 30.5 (d, *J* = 17.8 Hz), 30.1 , 29.9 , 28.0 , 27.7 (d, *J* = 15.0 Hz), 27.2 , 26.5 (d, *J* = 12.6 Hz), 22.5 (d, *J* = 7.2 Hz), 14.0 .

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -11.4 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{50}P$ 489.3645; Found 489.3645.



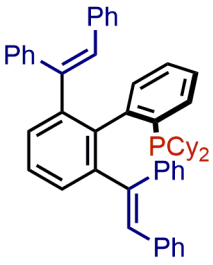
(*E*)-(2'-(Dec-5-en-5-yl)-[1,1'-biphenyl]-2-yl)diphenylphosphane (3bg). Following the general procedure **A** using 2-(diphenylphosphino)biphenyl (67.7 mg, 0.2 mmol) and 5-decyne (36 µL, 0.2 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **3bg** (62.6 mg, 67%) as colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 – 7.25 (m, 13H), 7.19 (ddd, *J* = 9.6, 7.0, 3.6 Hz, 3H), 7.11 – 6.98 (m, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 5.47 (t, *J* = 7.3 Hz, 1H), 2.13 – 1.92 (m, 4H), 1.36 – 1.10 (m, 8H), 0.96 – 0.81 (m, 6H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 148.5 (d, *J* = 32.8 Hz), 143.4, 140.8, 139.4 (d, *J* = 7.2 Hz), 139.0 (d, *J* = 13.5 Hz), 138.0 (d, *J* = 12.3 Hz), 136.2 (d, *J* = 12.2 Hz), 134.7 (d, *J* = 2.3 Hz), 133.9 (d, *J* = 19.9 Hz), 133.3 (d, *J* = 19.0 Hz), 132.1 (d, *J* = 1.8 Hz), 131.2 (d, *J* = 4.8 Hz), 130.8 (d, *J* = 5.8 Hz), 129.7, 128.4 (d, *J* = 3.4 Hz), 128.3, 128.2, 128.1 (d, *J* = 3.3 Hz), 127.9, 127.3, 127.0, 125.2, 31.9, 30.8 (d, *J* = 1.4 Hz), 30.6, 27.9, 22.7, 22.3, 14.1.

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -14.8 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{38}P$ 477.2706; Found 477.2706.



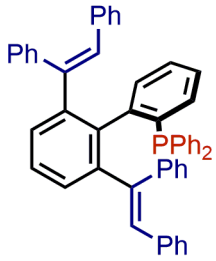
(2',6'-Bis((*E*)-1,2-diphenylvinyl)-[1,1'-biphenyl]-2-yl)dicyclohexylphosphane (4aa). Following the general procedure **B** using 2-(dicyclohexylphosphino)biphenyl (70.1 mg, 0.2 mmol) and diphenylacetylene (108.3 mg, 0.6 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **4aa** (110.2 mg, 78%) as white solid; mp= 208-210 °C. Recrystallization by diffusion method from CH_2Cl_2 solution with *n*-hexane has afforded single crystal to analyze by X-ray diffraction.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (s, 3H), 7.28 (d, *J* = 3.4 Hz, 1H), 7.10 – 6.93 (m, 17H), 6.86 – 6.76 (m, 1H), 6.70 (d, *J* = 7.5 Hz, 4H), 6.63 (s, 1H), 6.10 (t, *J* = 7.6 Hz, 1H), 5.53 (dd, *J* = 7.9, 3.8 Hz, 1H), 2.00 – 1.56 (m, 11H), 1.42 – 1.14 (m, 11H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 145.1 (d, *J* = 30.6 Hz), 144.6 (d, *J* = 1.9 Hz), 143.8, 141.5, 141.0, 137.3, 135.6 (d, *J* = 17.7 Hz), 132.2 (d, *J* = 5.9 Hz), 131.6, 131.0, 129.6, 129.5, 127.8, 127.6, 127.2, 126.5 (d, *J* = 4.2 Hz), 125.5, 124.9, 34.5 (d, *J* = 15.8 Hz), 31.8 (d, *J* = 17.6 Hz), 29.4 (d, *J* = 10.9 Hz), 27.6 (d, *J* = 12.0 Hz), 27.4 (d, *J* = 7.9 Hz), 26.4.

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -7.7 (s) [presence of **1a** phosphine oxide at 45.4 ppm (<5%)]..

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{52}H_{52}P$ 707.3801; Found 707.3803.



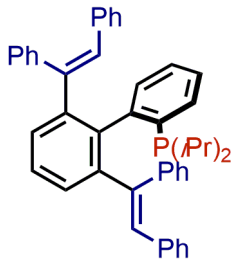
(2',6'-Bis((*E*)-1,2-diphenylvinyl)-[1,1'-biphenyl]-2-yl)diphenylphosphane (4ba). Following the general procedure **B** using 2-(diphenylphosphino)biphenyl (67.7 mg, 0.2 mmol) and diphenylacetylene (108.3 mg, 0.6 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **4ba** (83.3 mg, 60%) as white solid; mp= 213-215 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 – 7.45 (m, 3H), 7.32 – 7.27 (m, 6H), 7.21 (td, *J* = 7.4, 1.6 Hz, 4H), 7.14 – 7.11 (m, 1H), 7.09 – 6.97 (m, 12H), 6.83 (td, *J* = 7.6, 1.3 Hz, 1H), 6.73 – 6.69 (m, 4H), 6.67 – 6.64 (m, 4H), 6.35 (s, 2H), 6.27 (t, *J* = 7.5 Hz, 1H), 5.74 (ddd, *J* = 7.9, 4.7, 1.3 Hz, 1H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 146.1, 145.8, 145.0 (d, *J* = 1.9 Hz), 142.9, 141.2, 140.4 (d, *J* = 5.8 Hz), 139.1 (d, *J* = 13.4 Hz), 137.1, 135.5 (d, *J* = 10.0 Hz), 134.8 (d, *J* = 2.8 Hz), 133.4 (d, *J* = 18.9 Hz), 131.7, 131.2 (d, *J* = 6.7 Hz), 130.6, 129.6 (d, *J* = 5.5 Hz), 128.3 (d, *J* = 6.2 Hz), 128.0, 127.7, 127.5, 127.4, 126.9, 126.5, 126.4, 126.0.

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -15.0 (s) [presence of **1b** phosphine oxide at 47.4 ppm (<5%)].

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{52}H_{40}P$ 695.2862; Found 695.2860.



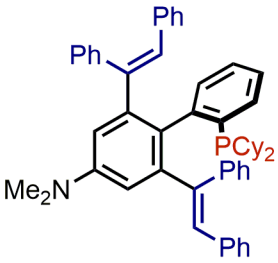
(2',6'-Bis((*E*)-1,2-diphenylvinyl)-[1,1'-biphenyl]-2-yl)diisopropylphosphane (4ca). Following the general procedure **B** using 2-(di-(iso-propyl)phosphino)biphenyl (54.1 mg, 0.2 mmol) and diphenylacetylene (108.3 mg, 0.6 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **4ca** (92.7 mg, 74%) as white solid; mp= 188-190 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (brs, 3H), 7.09 – 7.01 (m, 9H), 6.93 (t, *J* = 7.7 Hz, 9H), 6.73 – 6.63 (m, 2H), 6.62 – 6.58 (m, 4H), 6.05 (s, 1H), 5.44 (dd, *J* = 8.0, 3.9 Hz, 1H), 1.22 – 1.04 (m, 14H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ\ 144.7 (d, *J* = 1.6 Hz), 144.5, 144.2, 144.1, 144.0, 137.3, 132.1, 131.7, 131.5, 130.9, 130.6 (d, *J* = 5.9 Hz), 129.6, 129.4 (d, *J* = 2.3 Hz), 129.3, 127.7, 126.5, 125.5, 125.1, 23.1 (d, *J* = 13.2 Hz), 22.6, 18.5 (d, *J* = 9.1 Hz).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ -1.1 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{46}H_{44}P$ 627.3175; Found 627.3181.



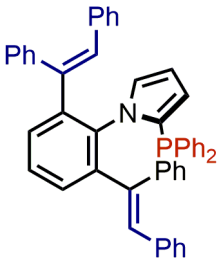
2'-(Dicyclohexylphosphanyl)-2,6-bis((*E*)-1,2-diphenylvinyl)-N,N-dimethyl-[1,1'-biphenyl]-4-amine (4ga). Following the general procedure **B** using 2-(dicyclohexylphosphino)-4'-dimethylamimo-biphenyl (78.8 mg, 0.2 mmol) and diphenylacetylene (108.3 mg, 0.6 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 97:3) to afford **4ga** (105.1mg, 70%) as pale yellow solid; mp= 141-143 °C.

^1H NMR ($CDCl_3$, 400 MHz): δ 7.23 (d, *J* = 7.7 Hz, 1H), 7.06 – 6.92 (m, 17H), 6.83 (s, 2H), 6.75 – 6.66 (m, 6H), 5.98 (t, *J* = 7.6 Hz, 1H), 5.39 (dd, *J* = 7.9, 4.0 Hz, 1H), 3.06 (s, 6H), 1.96 – 1.54 (m, 11H), 1.46 – 1.10 (m, 11H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 148.9, 145.6, 145.1 (d, *J* = 14.0 Hz), 141.4, 137.5, 136.3 (d, *J* = 19.0 Hz), 133.3 (d, *J* = 4.4 Hz), 133.2, 131.4, 130.8, 129.8, 129.5, 129.4, 127.6 (d, *J* = 4.2 Hz), 126.4, 125.3, 124.4, 115.1, 40.6, 34.7 (d, *J* = 15.8 Hz), 31.7 (d, *J* = 17.5 Hz), 29.6 (d, *J* = 11.5 Hz), 27.6 (d, *J* = 12.0 Hz), 27.4 (d, *J* = 8.1 Hz), 26.4.

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ -8.1 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{54}H_{57}NP$ 750.4223; Found 750.4228.



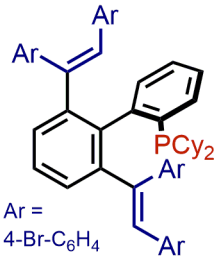
1-(2,6-Bis((*E*)-1,2-diphenylvinyl)phenyl)-2-(diphenylphosphanyl)-1H-pyrrole (4ha). Following the general procedure **B** using N-phenylpyrrol-2-yldiphenylphosphine (65.6 mg, 0.2 mmol), and diphenylacetylene (108.3 mg, 0.6 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 97:3) to afford **4ha** (102.5 mg, 75%) as pale yellow solid; mp= 203-205°C.

^1H NMR ($CDCl_3$, 400 MHz): δ 7.51 – 7.39 (m, 7H), 7.29 – 7.23 (m, 2H), 7.22 – 7.11 (m, 10H), 7.10 – 7.00 (m, 6H), 6.96 (dt, *J* = 6.8, 1.5 Hz, 4H), 6.70 – 6.60 (m, 4H), 6.37 (s, 2H), 6.24 (dd, *J* = 3.6, 1.5 Hz, 1H), 5.82 (ddd, *J* = 4.1, 2.6, 1.4 Hz, 1H), 5.71 – 5.68 (m, 1H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 144.4 (d, *J* = 2.0 Hz), 140.2, 139.5, 139.1 (d, *J* = 6.0 Hz), 137.3 (d, *J* = 1.8 Hz), 137.0, 133.4, 133.1, 131.1 (d, *J* = 1.6 Hz), 130.9, 129.7, 129.6, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6 (d, *J* = 2.8 Hz), 127.5, 127.0, 126.6, 119.4 (d, *J* = 3.4 Hz), 109.0.

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ -33.9 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{50}H_{39}NP$: 684.2814; Found 684.2811.



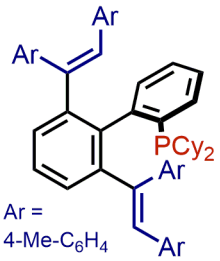
(2',6'-Bis((*E*)-1,2-bis(4-bromophenyl)vinyl)-[1,1'-biphenyl]-2-yl)dicyclohexylphosphane (4ab). Following the general procedure **B** using 2-(dicyclohexylphosphino)biphenyl (70.1 mg, 0.2 mmol), and Bis(4-bromophenyl)acetylene (201.6 mg, 0.6 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **4ab** (149.2 mg, 73%) as white solid; mp= 220-222 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 (s, 3H), 7.29 – 7.24 (m, 1H), 7.19 (d, *J* = 8.5 Hz, 4H), 7.16 – 7.11 (m, 4H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 4H), 6.52 (d, *J* = 8.2 Hz, 6H), 6.23 (t, *J* = 7.6 Hz, 1H), 5.57 (ddd, *J* = 7.9, 3.8, 1.3 Hz, 1H), 1.96 – 1.54 (m, 11H), 1.37 – 1.12 (m, 11H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 144.8, 144.5, 143.8 (d, *J* = 1.8 Hz), 143.1, 140.8, 139.9, 135.7, 132.2, 131.8 (d, *J* = 2.6 Hz), 131.2, 131.1, 131.0, 130.9, 127.6, 125.7, 125.5, 121.0, 120.8, 34.2 (d, *J* = 15.8 Hz), 31.9, 31.7 (d, *J* = 17.5 Hz), 29.2 (d, *J* = 10.3 Hz), 27.6 (d, *J* = 12.3 Hz), 27.3 (d, *J* = 8.0 Hz), 26.4.

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -7.3(s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{52}H_{48}Br_4P$ 1019.0222; Found 1019.0222.



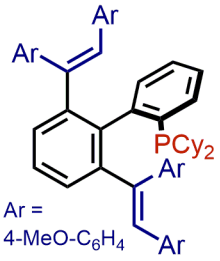
(2',6'-Bis((*E*)-1,2-di-p-tolylvinyl)-[1,1'-biphenyl]-2-yl)dicyclohexylphosphane (4ac). Following the general procedure **B** using 2-(dicyclohexylphosphino)biphenyl (70.1 mg, 0.2 mmol), and 1,2-di-*p*-tolylethyne (124.5 mg, 0.6 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **4ac** (111.3 mg, 73%) as white solid; mp= 169-171 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38 (s, 3H), 7.27 (s, 1H), 6.89 – 6.81 (m, 13H), 6.64 (d, *J* = 7.7 Hz, 4H), 6.53 (s, 2H), 6.17 (t, *J* = 7.5 Hz, 1H), 5.75 (dd, *J* = 8.0, 3.8 Hz, 1H), 2.30 (s, 6H), 2.24 (s, 6H), 1.97 – 1.55 (m, 11H), 1.41 – 1.11 (m, 11H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 145.6, 145.4, 144.7 (d, *J* = 1.9 Hz), 142.6, 140.8 (d, *J* = 4.7 Hz), 138.7, 136.0 (d, *J* = 4.8 Hz), 135.4 (d, *J* = 17.7 Hz), 134.7, 132.5 (d, *J* = 5.8 Hz), 131.5, 131.2, 130.7, 129.6, 129.3, 128.4, 128.3, 126.9, 125.4, 124.9, 34.4 (d, *J* = 15.6 Hz), 31.9, 31.7 (d, *J* = 17.5 Hz), 29.4 (d, *J* = 11.0 Hz), 27.6 (d, *J* = 12.2 Hz), 27.4 (d, *J* = 7.7 Hz), 26.5, 21.3, 21.1.

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -8.2 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{56}H_{60}P$ 763.4427; Found 763.4426.



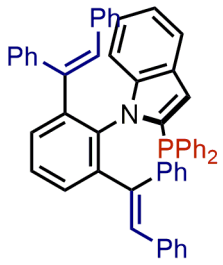
(2',6'-Bis((*E*)-1,2-bis(4-methoxyphenyl)vinyl)-[1,1'-biphenyl]-2-yl)dicyclohexylphosphane (4ad). Following the general procedure **B** using 2-(dicyclohexylphosphino)biphenyl (70.1 mg, 0.2 mmol), and 1,2-bis(3-methoxyphenyl)ethyne (143.4 mg, 0.6mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **4ad** (124.1 mg, 75%) as white solid; mp= 189-191 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (s, 3H), 7.28 (d, *J* = 8.7 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 4H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.64 – 6.53 (m, 12H), 6.50 (s, 2H), 6.21 (t, *J* = 7.5 Hz, 1H), 5.62 (dd, *J* = 7.5, 3.6 Hz, 1H), 3.78 (s, 6H), 3.73 (s, 6H), 1.99 – 1.53 (m, 11H), 1.45 – 1.01 (m, 11H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 158.3, 158.0, 145.7, 145.4, 144.9 (d, *J* = 1.8 Hz), 141.5, 140.8, 135.5, 135.3, 134.3, 132.4 (d, *J* = 6.0 Hz), 131.5, 130.8, 130.6, 130.3, 127.0, 125.2, 124.8, 113.3, 113.0, 55.2, 55.1, 34.5 (d, *J* = 15.7 Hz), 31.8 (d, *J* = 17.3 Hz), 29.4 (d, *J* = 10.8 Hz), 27.6 (d, *J* = 12.1 Hz), 27.4 (d, *J* = 7.8 Hz), 26.5.

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -8.1 (s).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{56}H_{60}O_4P$ 827.4223; Found 827.4219.



1-(2,6-Bis((*E*)-1,2-diphenylvinyl)phenyl)-2-(diphenylphosphanyl)-1H-indole (4ja). Following the general procedure **B** using N-phenylindolo-2-yldiphenylphosphine (75.6 mg, 0.20 mmol) and diphenylacetylene (108.3 mg, 0.6 mmol), the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 97:3) to afford **4ja** (114.3 mg, 78%) as a white solid; mp= 199-201 °C.

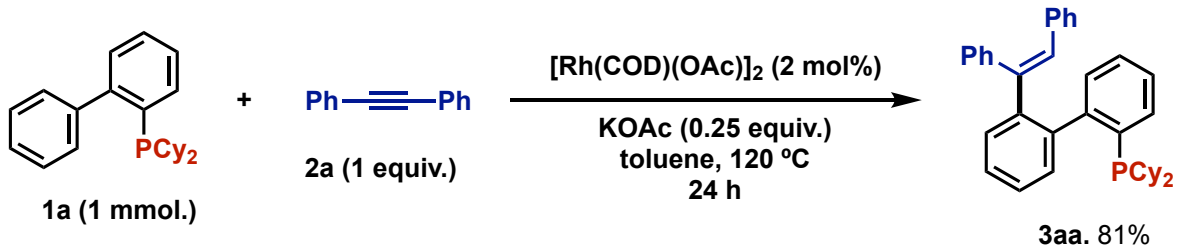
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 – 7.38 (m, 8H), 7.30 – 7.23 (m, 3H), 7.53 – 7.38 (m, 8H), 7.21 – 7.16 (m, 5H), 6.74 – 6.69 (m, 4H), 6.60 (s, 1H), 6.38 – 6.29 (m, 5H), 6.24 (s, 2H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 145.1 (d, *J* = 1.8 Hz), 139.9 (d, *J* = 3.5 Hz), 139.7, 139.6, 137.9 (d, *J* = 7.3 Hz), 136.8, 134.6 (d, *J* = 1.8 Hz), 133.7, 133.5, 131.2 (d, *J* = 1.9 Hz), 131.1, 129.4, 129.2, 128.5, 128.4, 128.3 (d, *J* = 1.6 Hz), 127.8, 127.4 (d, *J* = 1.4 Hz), 127.3, 126.8, 126.4, 122.2, 119.7, 118.9, 113.4 (d, *J* = 3.5 Hz), 111.7 (d, *J* = 1.9 Hz).

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -31.7 (s).

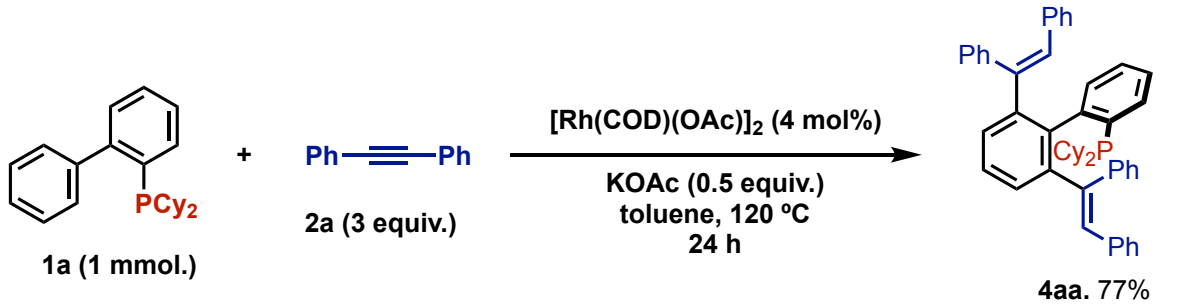
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{54}H_{41}NP$ 734.2972; Found 734.2976.\

3. Rh(I)-Catalyzed C–H Bond Alkenylation: Reaction on 1 mmol Scale



Scheme S1. Rhodium(I)-Catalyzed *Ortho'* C–H Bond Alkenylation of JPhos (1 mmol scale)

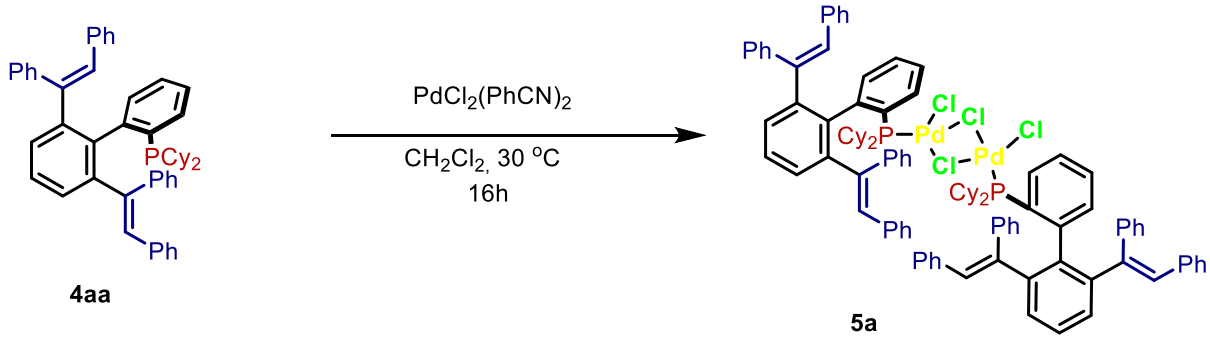
To a 15 mL oven dried Schlenk tube, KOAc (24 mg, 0.25 mmol, 0.25 equiv.), JPhos (250 mg, 1 mmol, 1 equiv.), toluene (5 mL), diphenylacetylene (178 mg, 1 mmol, 1 equiv) and $[Rh(OAc)(COD)]_2$ (11.5 mg, 0.02 mmol, 2 mol%) were successively added. The reaction mixture was evacuated by vacuum-argon cycles (5 times) and stirred at 120 °C (oil bath temperature) for 24 hours. After cooling the reaction at room temperature and concentration, the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **3aa** (420 mg, 81%).



Scheme S2. Rhodium(I)-Catalyzed Two-Fold *ortho', ortho'* C–H Bonds Alkenylation JPhos (1 mmol scale)

To a 15 mL oven dried Schlenk tube, KOAc (48 mg, 0.5 mmol, 0.5 equiv.), JPhos (250 mg, 1 mmol, 1 equiv.),toluene (5mL), diphenylacetylene (534 mg, 3 mmol, 3 equiv) and $[Rh(OAc)(COD)]_2$ (23 mg, 0.04 mmol, 4 mol%) were successively added. The reaction mixture was evacuated by vacuum-argon cycles (5 times) and stirred at 120 °C (oil bath temperature) for 24 hours. After cooling the reaction at room temperature and concentration, the residue was purified by flash chromatography on silica gel (heptane-Et_2O = 99:1) to afford **4aa** (540 mg, 77%).

4. Preparation and Characterization of the Palladium Complex 5a



Scheme S3. Preparation of Pd Complex **5a**

General Procedure C: To a 15 mL oven dried Schlenk tube, (2',6'-bis((E)-1,2-diphenylvinyl)-[1,1'-biphenyl]-2-yl)dicyclohexylphosphane (**4aa**) (70.7 mg, 0.1 mmol, 1 equiv) and $PdCl_2(PhCN)_2$ (38.4 mg, 0.1mmol, 1 equiv) were dissolved in degassed CH_2Cl_2. The reaction mixture was stirred at 30 °C (oil bath temperature) for 16 hours. Then the solvent was removed and the residue was washed with pentane to get the orange powder **5a** (70.7 mg, 78%). Recrystallization by diffusion method from CH_2Cl_2 solution with n-hexane has afforded single crystal to analyze by X-ray diffraction.

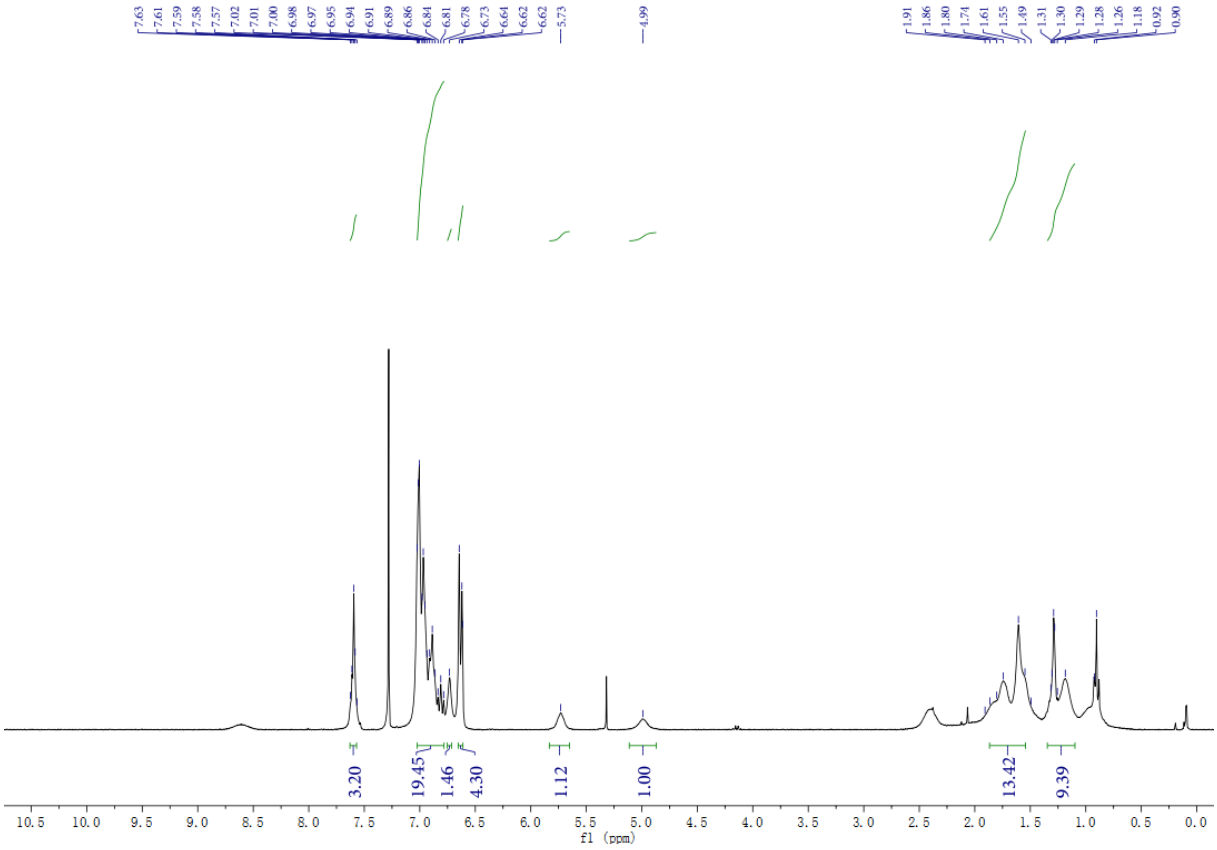
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (q, *J* = 4.0 Hz, 3H), 7.02 – 6.78 (m, 19H), 6.73 (s, 1H), 6.63 (d, *J* = 7.3 Hz, 4H), 5.73 (s, 1H), 4.99 (s, 1H), 1.90 – 1.61 (s, 13H), 1.35 – 1.10 (m, 9H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 145.1 (d, *J* = 5.0 Hz), 143.3 , 141.9 , 140.6 , 139.9 , 139.1 , 137.9 , 136.9 , 134.1 (d, *J* = 7.5 Hz), 132.8 , 132.2 , 129.7 (d, *J* = 28.7 Hz), 129.1 , 129.0 , 128.5 , 128.2 , 127.7 (d, *J* = 18.8 Hz), 126.7 (d, *J* = 9.2 Hz), 125.9 (d, *J* = 5.8 Hz), 125.3 , 124.0 (d, *J* = 13.8 Hz), 34.2 (d, *J* = 11.0 Hz), 31.2 (d, *J* = 2.4 Hz), 30.6 (d, *J* = 8.7 Hz), 27.5 , 27.4 (d, *J* = 1.8 Hz), 27.4 , 25.7 .

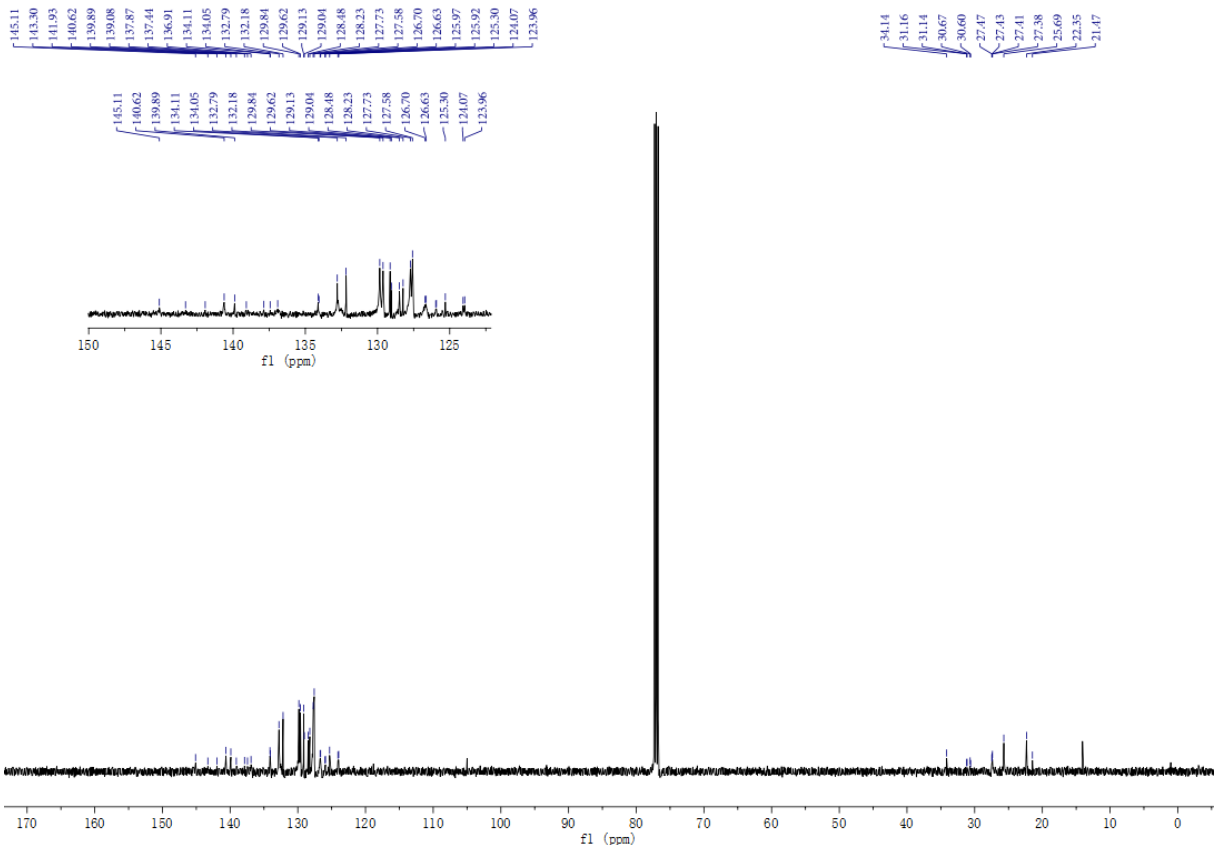
^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 67.0 (s).

Elemental analysis: calcd (%) for $C_{104}H_{102}Cl_4P_2Pd_2$ (1768.54): C 70.63, H 5.81; found: C 70.45, H 5.67.

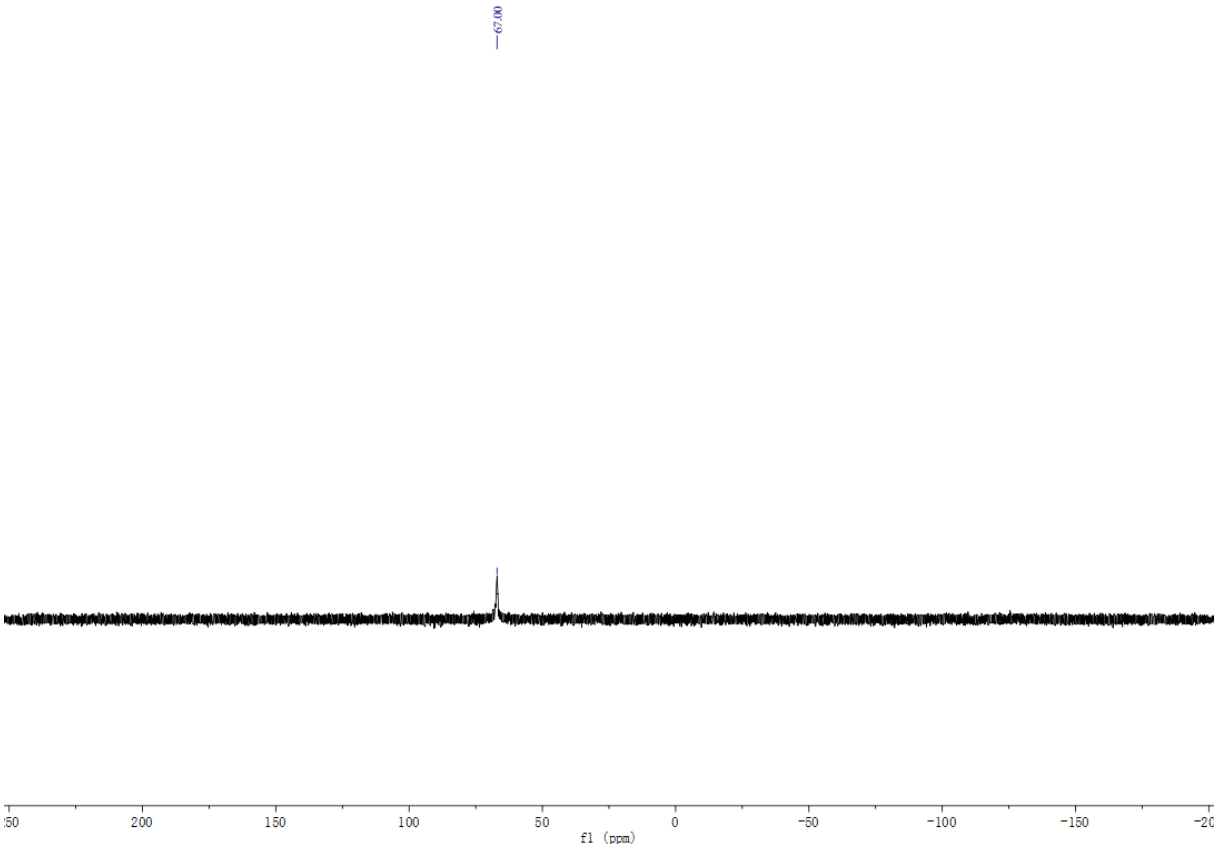
5a ^{1}H NMR ($CDCl_3$, 400 MHz)



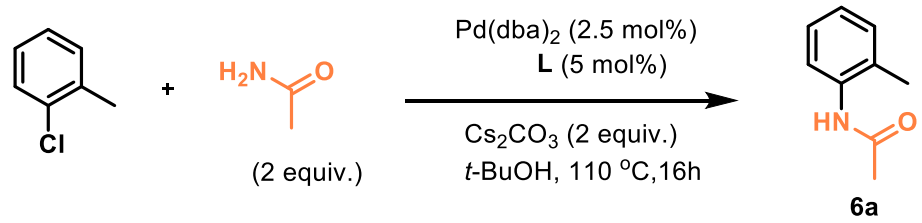
5a ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



5a $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



4. Catalytic Evaluation of Phosphine in Pd-Catalyzed Amidation: Procedure and Compound Characterizations



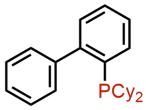
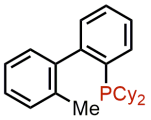
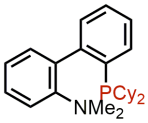
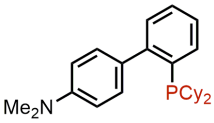
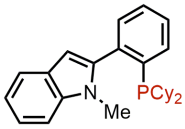
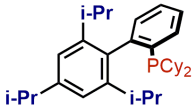
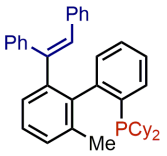
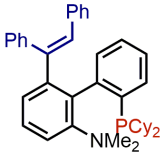
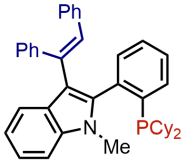
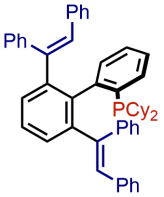
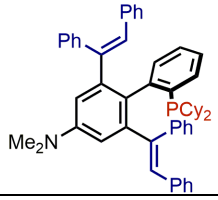
6a

General Procedure D: In oven-dried 15 mL Schlenk tube, which was equipped with a magnetic stir bar, $Pd(dba)_2$ (4.3 mg, 0.0075 mmol, 2.5 mol%), biarylphosphine phosphine (0.015 mmol, 5 mol%.), amide (0.6 mmol), aryl chloride (0.3 mmol) Cs_2CO_3 (195 mg, 0.6 mmol) and t-BuOH (1.5 mL) were successfully added under argon. The solution was heated to 110 °C for 16 h. The reaction was cold done and *n*-dodecane (38 µL, 0.3 mmol) was added to analyze and calculate the yields by GC-analysis.

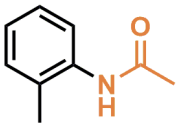
GC analysis: Performed on a Shimadzu GC-2010 apparatus (Column: INTERCHIM, UPTIBOND 1 PREMIUM, 0.25 mm ID, 0.25 mm, 30.0 m; Gas pressure: 81.7 kPa ; Total flow: 30.8 mL.min $^{-1}$; Column flow : 1.07 mL.min -1 ; Velocity: 27.4 cm/sec; Purge flow: 3.0 mL.min^{-1} ; Sprit ratio: 46.0; Injector: 250ºC, FID: 280ºC; Column program: starting from 50°C, 2 min hold, 10°C/min to 240°C, 5 min hold).

t_R (min) = 11.0 (internal standard), 14.4 (product)

Table S1. Evaluation of Biarylphosphine in Pd-Catalyzed Amidation of 2-Chlorotoluene with Acetamide

Entry	L structure	L	MM (g/mol)	m Ligand (mg)	Yield of 6a (%)[a]
1		**1a**	350.48	5.3	0
2		**1e**	364.50	5.5	0
3		**1f**	393.55	5.9	0
4		**1g**	393.55	5.9	0
5		**1i**	403.53	6.1	0
6		**CyXPhos**	476.72	7.2	8
7		**3ea**	542.31	8.2	37
8		**3fa**	571.34	8.6	23
9		**3ia**	581.32	8.7	15
10		**4aa**	706.38	10.6	95
11		**4ga**	749.42	11.2	82

[a] Determined by GC-analysis using *n*-dodecane as internal standard.

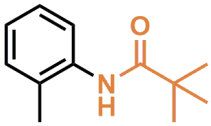


***N*-(o-tolyl)acetamide (6a)**: Reaction was performed using acetamide (35.4 mg, 0.6 mmol), 2-chlorotoluene (35 µL, 0.3 mmol) and Cs_2CO_3 (195 mg, 0.6 mmol), $Pd(dba)_2$ (4.3 mg, 0.0075 mmol, 2.5 mol%), ligand **4aa** (10.6 mg, 0.015 mmol, 5 mol%) and *t*-BuOH (1.5 mL), the residue was purified by flash chromatography on silica gel (heptane-EtOAc = 70:30) to afford **6a** (40.7 mg, 91%) as a white solid; mp= 108-110 °C; GC: t_R = 8.4 min. **MS (EI)**: m/z: 149 (M^+).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 2H), 7.11 – 7.04 (m, 1H), 2.20 (s, 3H), 2.12 (s, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 169.0, 135.7, 130.6, 130.5, 126.5, 125.6, 124.3, 23.9, 17.8.

The NMR spectra are identical with those reported in the literature.[3]

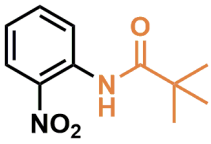


***N*-(o-tolyl)pivalamide (6b)**: Reaction was performed using pivalamide (60.7 mg, 0.6 mmol), 2-chlorotoluene (35 µL, 0.3 mmol) and Cs_2CO_3 (195 mg, 0.6 mmol), $Pd(dba)_2$ (4.3 mg, 0.0075 mmol, 2.5 mol%), ligand **4aa** (10.6 mg, 0.015 mmol, 5 mol%) and t-BuOH (1.5 mL), the residue was purified by flash chromatography on silica gel (heptane-EtOAc = 70:30) to afford **6b** (51.6 mg, 90%) as a white solid; mp= 111-113 °C; GC: t_R = 9.3 min. **MS (EI)**: m/z: 191 (M^+).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.27 – 7.18 (m, 3H), 7.08 (td, *J* = 7.4, 1.3 Hz, 1H), 2.28 (s, 3H), 1.36 (s, 9H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 176.5, 135.9, 130.4, 128.7, 126.8, 124.9, 122.8, 39.7, 27.7, 17.6.

The NMR spectra are identical with those reported in the literature.[4]

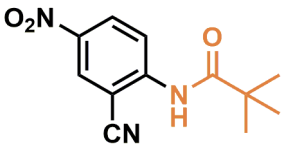


***N*-(2-nitrophenyl)pivalamide (6c)**: Reaction was performed using pivalamide (60.7 mg, 0.6 mmol), 2-nitrochlorobenzene (47.3 mg, 0.3 mmol) and Cs_2CO_3 (195 mg, 0.6 mmol), $Pd(dba)_2$ (4.3 mg, 0.0075 mmol, 2.5 mol%), ligand **4aa** (10.6 mg, 0.015 mmol, 5 mol%) and t-BuOH (1.5 mL), the residue was purified by flash chromatography on silica gel (heptane-EtOAc = 70:30) to afford **6c** (53.2 mg, 80%) as yellow oil; GC: t_R = 10.3 min. **MS (EI)**: m/z: 222 (M^+).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.70 (s, 1H), 8.80 (dd, *J* = 8.6, 1.4 Hz, 1H), 8.18 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.69 – 7.54 (m, 1H), 7.20 – 7.06 (m, 1H), 1.34 (s, 9H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 177.8, 136.3, 136.0, 135.4, 125.7, 122.9, 122.0, 40.5, 27.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{14}N_2O_3$ 223.1077; Found 223.1077.

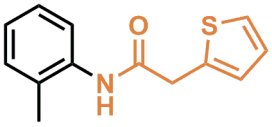


***N*-(2-cyano-4-nitrophenyl)pivalamide (6d)**: Reaction was performed using pivalamide (60.7 mg, 0.6 mmol), 2-chloro-5-nitrobenzonitrile (54.8 mg, 0.3 mmol) and Cs_2CO_3 (195 mg, 0.6 mmol), $Pd(dba)_2$ (4.3 mg, 0.0075 mmol, 2.5 mol%), ligand **4aa** (10.6 mg, 0.015 mmol, 5 mol%) and t-BuOH (1.5 mL), the residue was purified by flash chromatography on silica gel (heptane-EtOAc = 70:30) to afford **6d** (61.5 mg, 83%) as a white solid; mp= 230-232 °C; GC: t_R = 13.6 min. **MS (EI)**: m/z: 247 (M^+).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.38 (s, 1H), 9.13 (d, *J* = 2.6 Hz, 1H), 8.56 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 1.55 (s, 9H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 166.0, 162.9, 153.2, 145.4, 129.4, 128.6, 122.8, 120.6, 38.0, 28.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{13}N_3O_3$ 248.1030; Found 248.1029.

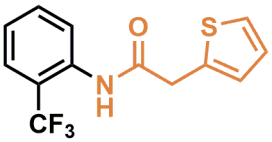


2-(Thiophen-2-yl)-*N*-(o-tolyl)acetamide (6e): Reaction was performed using 2-(thiophen-2-yl)acetamide (84.7 mg, 0.6 mmol), 2-chlorotoluene (35 µL, 0.3 mmol) and Cs_2CO_3 (195 mg, 0.6 mmol), $Pd(dba)_2$ (4.3 mg, 0.0075 mmol, 2.5 mol%), ligand **4aa** (10.6 mg, 0.015 mmol, 5 mol%) and t-BuOH (1.5 mL), the residue was purified by flash chromatography on silica gel (heptane-EtOAc = 70:30) to afford **6e** (58.2 mg, 84%) as a white solid; mp= 146-148 °C; GC: t_R = 12.5 min. **MS (EI)**: m/z: 231 (M^+).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 – 7.86 (m, 1H), 7.37 – 7.32 (m, 1H), 7.28 (s, 1H), 7.22 (td, *J* = 7.7, 1.7 Hz, 1H), 7.14 (d, *J* = 6.6 Hz, 1H), 7.08 (dd, *J* = 9.9, 2.4 Hz, 3H), 4.00 (s, 2H), 2.02 (s, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 167.9, 136.0, 135.4, 130.4, 128.4, 128.1, 127.7, 126.8, 126.2, 125.2, 122.3, 38.4, 17.2.

The NMR spectra are identical with those reported in the literature.[5]



2-(Thiophen-2-yl)-*N*-(2-(trifluoromethyl)phenyl)acetamide (6f): Reaction was performed using 2-(thiophen-2-yl)acetamide (84.7 mg, 0.6 mmol), 2-chlorobenzotrifluoride (40 µL, 0.3 mmol) and Cs_2CO_3 (195 mg, 0.6 mmol), $Pd(dba)_2$ (4.3 mg, 0.0075 mmol, 2.5 mol%), ligand **4aa** (10.6 mg, 0.015 mmol, 5 mol%) and t-BuOH (1.5 mL), the residue was purified by flash chromatography on silica gel (heptane-EtOAc = 70:30) to afford **6f** (68.4 mg, 80%) as a yellow solid; mp= 109-111 °C; GC: t_R = 11.0 min. **MS (EI)**: m/z: 285 (M^+).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28 (d, *J* = 8.3 Hz, 1H), 7.78 – 7.68 (m, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.36 (dd, *J* = 4.9, 1.5 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.12 – 7.08 (m, 2H), 4.02 (s, 2H).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 168.1, 135.1, 134.6, 132.9, 128.3, 127.8, 126.5, 126.0 (q, *J* = 5.2 Hz), 124.5, 123.8, 123.7 (q, *J* = 273.6 Hz), 38.5.

$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 471 MHz): δ3 -61.2 (s).

The NMR spectra are identical with those reported in the literature.[5]

5. Solid-State Structures

Crystal measurement for 3aa:

Crystallization by diffusion method from CH_2Cl_2 solution with *n*-hexane has afforded single crystal to analyze by X-ray diffraction.

The single crystal X-ray diffraction studies were carried out on D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, [*], Mo-Kα radiation (λ = 0.71073 Å, multilayer monochromator), T = 150 K; monoclinic P $2_1/c$ (I.T.#14), a = 9.7682(18), b = 15.168(3), c = 20.187(4) Å, β = 90.385(8) °, V = 2990.9(10) $Å^3$. Z = 4, d = 1.174 $g.cm^{-3}$, μ = 0.117 mm^{-1}. The structure was solved by dual-space algorithm using the SHELXT program [1], and then refined with full-matrix least-squares methods based on F^2 (SHELXL) [2]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 6853 unique intensities and 352 parameters converged at ωR_F^2 = 0.1375 (R_F = 0.0527) for 4937 observed reflections with I > 2σ(I).

[1] G. M. Sheldrick, Acta Cryst. A71 (2015) 3-8

[2] Sheldrick G.M., Acta Cryst. C71 (2015) 3-8

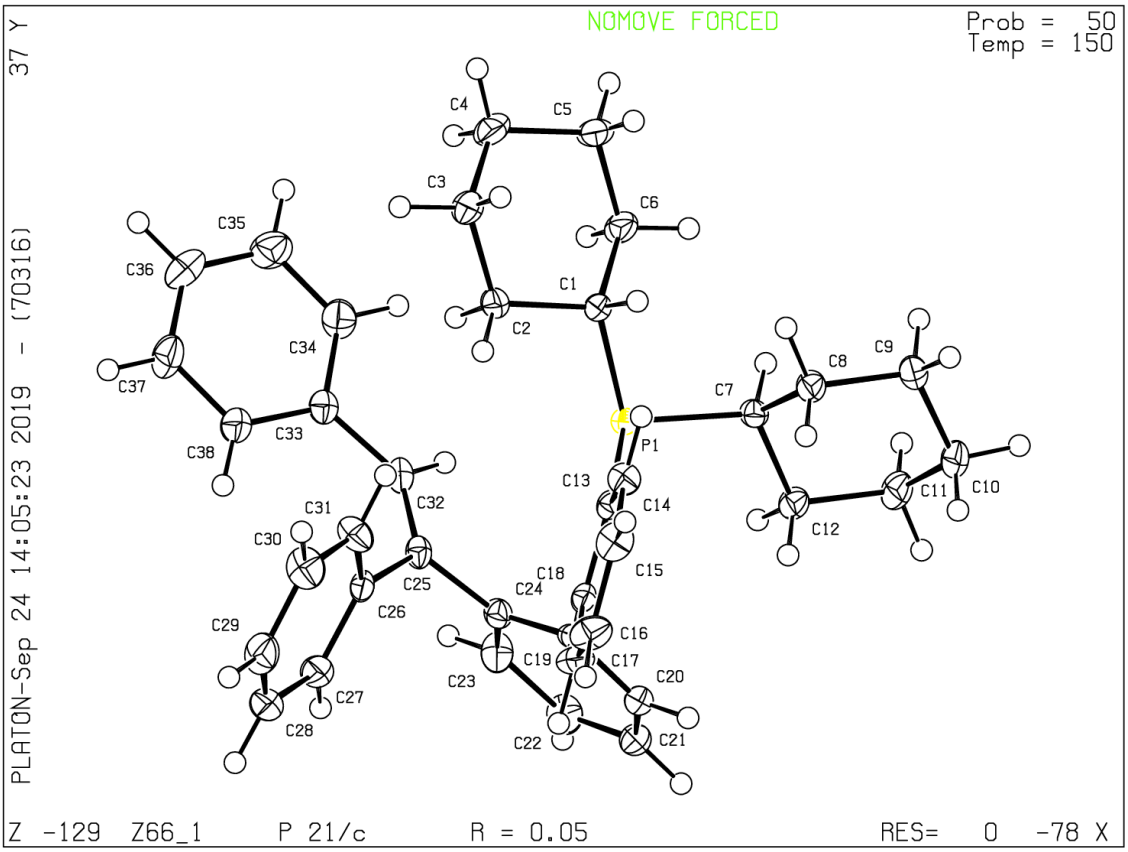


Figure S1. ORTEP diagram of the solid-state molecular structure of **3aa**. Thermal ellipsoids are at the 50% probability level. (CCDC 968419).

Table S1. Crystal data and structure refinement for **3aa**.

Empirical formula	C38H41P
Formula weight	528.68 g/mol
Temperature	150 K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P 21/c
Unit cell dimensions	a = 9.7682(18) Å
	b = 15.168(3) Å
	c = 20.187(4) Å
	α = 90 °
	β = 90.385(8) °
	γ = 90 °
Volume	2990.9(10) Å3
Z, Calculated density	4, 1.174 g.cm-3
Absorption coefficient	0.117 mm-1
F(000)	1136
Crystal size	0.400 x 0.300 x 0.220 mm
Crystal color	colourless
Theta range for data collection	2.424 to 27.528 °
h_min, h_max	-12, 12
k_min, k_max	-19, 17
l_min, l_max	-26, 26
Reflections collected / unique	25185 / 6853 [R(int)a = 0.0884]
Reflections [I>2σ]	4937
Completeness to theta_max	0.993
Absorption correction type	multi-scan
Max. and min. transmission	0.975, 0.765
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	6853 / 0 / 352
bS (Goodness-of-fit)	0.988
Final R indices [I>2σ]	R1c = 0.0527, wR2d = 0.1375
R indices (all data)	R1c = 0.0876, wR2d = 0.1597
Largest diff. peak and hole	0.278 and -0.385 e-.Å-3

Table S2. **Fractional atomic coordinates, site occupancy (%) and equivalent isotropic displacement parameters (Å^2)** for **2aa**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	U11	U22	U33	U23	U13	U12
P1	0.0144(2)	0.0154(2)	0.0161(3)	0.00092(17)	0.00038(17)	-0.00100(17)
C1	0.0155(9)	0.0188(8)	0.0167(10)	0.0004(7)	0.0008(7)	0.0011(7)
C2	0.0195(9)	0.0259(9)	0.0180(10)	0.0032(8)	0.0025(8)	0.0015(7)
C3	0.0167(10)	0.0387(12)	0.0272(12)	0.0061(9)	0.0055(8)	0.0040(8)
C4	0.0244(11)	0.0405(12)	0.0396(14)	0.0124(10)	0.0103(10)	0.0146(9)
C5	0.0259(11)	0.0421(13)	0.0350(13)	0.0196(10)	0.0086(9)	0.0156(9)
C6	0.0211(10)	0.0266(10)	0.0315(12)	0.0096(8)	0.0085(9)	0.0055(8)
C7	0.0153(9)	0.0213(9)	0.0179(10)	0.0044(7)	0.0016(7)	-0.0005(7)
C8	0.0167(9)	0.0318(11)	0.0193(11)	-0.0003(8)	0.0006(8)	0.0012(8)

C9	0.0245(10)	0.0414(12)	0.0175(11)	0.0007(9)	0.0022(8)	0.0065(9)
C10	0.0227(10)	0.0409(12)	0.0236(12)	0.0014(9)	0.0085(9)	0.0049(9)
C11	0.0175(10)	0.0384(12)	0.0301(12)	0.0004(9)	0.0069(8)	0.0006(8)
C12	0.0154(9)	0.0286(10)	0.0225(11)	-0.0005(8)	0.0012(8)	0.0006(7)
C13	0.0148(8)	0.0157(8)	0.0184(10)	0.0000(7)	0.0039(7)	-0.0003(7)
C14	0.0204(10)	0.0222(9)	0.0227(11)	-0.0003(8)	-0.0008(8)	-0.0018(7)
C15	0.0240(10)	0.0202(9)	0.0351(13)	-0.0024(8)	0.0025(9)	-0.0068(8)
C16	0.0271(11)	0.0150(9)	0.0422(14)	0.0055(8)	0.0016(9)	-0.0017(8)
C17	0.0211(10)	0.0224(10)	0.0316(12)	0.0071(8)	-0.0014(8)	0.0036(8)
C18	0.0150(9)	0.0191(9)	0.0175(10)	-0.0009(7)	0.0037(7)	0.0019(7)
C19	0.0154(9)	0.0208(9)	0.0160(10)	0.0056(7)	-0.0004(7)	0.0014(7)
C20	0.0193(9)	0.0257(10)	0.0188(10)	0.0020(8)	0.0015(8)	0.0037(7)
C21	0.0159(9)	0.0386(12)	0.0238(11)	0.0041(9)	0.0017(8)	0.0039(8)
C22	0.0166(10)	0.0428(12)	0.0279(12)	-0.0026(9)	-0.0013(8)	-0.0077(8)
C23	0.0211(10)	0.0338(11)	0.0244(11)	-0.0068(8)	0.0014(8)	-0.0060(8)
C24	0.0167(9)	0.0231(9)	0.0175(10)	0.0024(7)	0.0018(7)	-0.0010(7)
C25	0.0158(9)	0.0226(9)	0.0156(10)	-0.0036(7)	0.0012(7)	-0.0033(7)
C26	0.0165(9)	0.0214(9)	0.0168(10)	-0.0030(7)	0.0039(7)	0.0014(7)
C27	0.0214(10)	0.0333(11)	0.0249(12)	0.0044(8)	0.0017(8)	0.0040(8)
C28	0.0330(12)	0.0391(12)	0.0253(12)	0.0108(9)	0.0060(9)	0.0108(9)
C29	0.0330(12)	0.0274(11)	0.0360(13)	0.0074(9)	0.0147(10)	-0.0011(9)
C30	0.0260(11)	0.0348(12)	0.0328(13)	0.0018(9)	0.0025(9)	-0.0101(9)
C31	0.0263(10)	0.0317(11)	0.0205(11)	0.0032(8)	-0.0029(8)	-0.0064(8)
C32	0.0198(9)	0.0246(10)	0.0171(10)	-0.0037(8)	0.0036(7)	-0.0030(7)
C33	0.0196(9)	0.0198(9)	0.0185(10)	-0.0049(7)	-0.0003(7)	-0.0039(7)
C34	0.0350(12)	0.0234(10)	0.0288(12)	0.0003(9)	0.0064(9)	-0.0008(8)
C35	0.0380(13)	0.0234(10)	0.0416(14)	0.0020(9)	0.0008(11)	0.0044(9)
C36	0.0232(11)	0.0302(11)	0.0471(15)	-0.0080(10)	0.0015(10)	0.0064(8)
C37	0.0279(11)	0.0370(12)	0.0356(13)	-0.0022(10)	0.0128(10)	0.0017(9)
C38	0.0252(10)	0.0302(11)	0.0250(11)	0.0025(8)	0.0056(9)	0.0033(8)

Table S3. Bond lengths [Å] for **3aa**.

P1	- C13	= 1.8531(18)
P1	- C1	= 1.8619(18)
P1	- C7	= 1.8675(19)
C1	- C6	= 1.530(3)
C1	- C2	= 1.535(2)
C1	- H1	= 1.0000
C2	- C3	= 1.527(3)
C2	- H2A	= 0.9900
C2	- H2B	= 0.9900
C3	- C4	= 1.517(3)
C3	- H3A	= 0.9900
C3	- H3B	= 0.9900
C4	- C5	= 1.532(3)
C4	- H4A	= 0.9900
C4	- H4B	= 0.9900
C5	- C6	= 1.526(3)
C5	- H5A	= 0.9900
C5	- H5B	= 0.9900
C6	- H6A	= 0.9900

C6 - H6B = 0.9900
C7 - C8 = 1.524(3)
C7 - C12 = 1.537(2)
C7 - H7 = 1.0000
C8 - C9 = 1.531(3)
C8 - H8A = 0.9900
C8 - H8B = 0.9900
C9 - C10 = 1.524(3)
C9 - H9A = 0.9900
C9 - H9B = 0.9900
C10 - C11 = 1.524(3)
C10 - H10A = 0.9900
C10 - H10B = 0.9900
C11 - C12 = 1.535(3)
C11 - H11A = 0.9900
C11 - H11B = 0.9900
C12 - H12A = 0.9900
C12 - H12B = 0.9900
C13 - C14 = 1.405(3)
C13 - C18 = 1.407(3)
C14 - C15 = 1.380(3)
C14 - H14 = 0.9500
C15 - C16 = 1.381(3)
C15 - H15 = 0.9500
C16 - C17 = 1.382(3)
C16 - H16 = 0.9500
C17 - C18 = 1.401(3)
C17 - H17 = 0.9500
C18 - C19 = 1.499(2)
C19 - C20 = 1.401(2)
C19 - C24 = 1.406(3)
C20 - C21 = 1.381(3)
C20 - H20 = 0.9500
C21 - C22 = 1.382(3)
C21 - H21 = 0.9500
C22 - C23 = 1.384(3)
C22 - H22 = 0.9500
C23 - C24 = 1.399(3)
C23 - H23 = 0.9500
C24 - C25 = 1.497(2)
C25 - C32 = 1.335(3)
C25 - C26 = 1.504(2)
C26 - C31 = 1.388(3)
C26 - C27 = 1.388(3)
C27 - C28 = 1.388(3)
C27 - H27 = 0.9500
C28 - C29 = 1.376(3)
C28 - H28 = 0.9500
C29 - C30 = 1.381(3)
C29 - H29 = 0.9500
C30 - C31 = 1.382(3)
C30 - H30 = 0.9500

C31	- H31	= 0.9500	
C32	- C33	= 1.479(2)	
C32	- H32	= 0.9500	
C33	- C34	= 1.391(3)	
C33	- C38	= 1.393(3)	
C34	- C35	= 1.391(3)	
C34	- H34	= 0.9500	
C35	- C36	= 1.375(3)	
C35	- H35	= 0.9500	
C36	- C37	= 1.377(3)	
C36	- H36	= 0.9500	
C37	- C38	= 1.394(3)	
C37	- H37	= 0.9500	
C38	- H38	= 0.9500	

Table S4. Angles [°]for **3aa**.

C13	- P1	- C1	= 102.34(8)
C13	- P1	- C7	= 102.89(8)
C1	- P1	- C7	= 101.03(8)
C6	- C1	- C2	= 110.23(15)
C6	- C1	- P1	= 109.90(12)
C2	- C1	- P1	= 110.67(13)
C6	- C1	- H1	= 108.70
C2	- C1	- H1	= 108.70
P1	- C1	- H1	= 108.70
C3	- C2	- C1	= 112.58(16)
C3	- C2	- H2A	= 109.10
C1	- C2	- H2A	= 109.10
C3	- C2	- H2B	= 109.10
C1	- C2	- H2B	= 109.10
H2A	- C2	- H2B	= 107.80
C4	- C3	- C2	= 111.78(16)
C4	- C3	- H3A	= 109.30
C2	- C3	- H3A	= 109.30
C4	- C3	- H3B	= 109.30
C2	- C3	- H3B	= 109.30
H3A	- C3	- H3B	= 107.90
C3	- C4	- C5	= 110.68(17)
C3	- C4	- H4A	= 109.50
C5	- C4	- H4A	= 109.50
C3	- C4	- H4B	= 109.50
C5	- C4	- H4B	= 109.50
H4A	- C4	- H4B	= 108.10
C6	- C5	- C4	= 110.85(18)
C6	- C5	- H5A	= 109.50
C4	- C5	- H5A	= 109.50
C6	- C5	- H5B	= 109.50
C4	- C5	- H5B	= 109.50
H5A	- C5	- H5B	= 108.10
C5	- C6	- C1	= 111.87(16)
C5	- C6	- H6A	= 109.20

C1 - C6 - H6A = 109.20
C5 - C6 - H6B = 109.20
C1 - C6 - H6B = 109.20
H6A - C6 - H6B = 107.90
C8 - C7 - C12 = 109.63(15)
C8 - C7 - P1 = 118.51(12)
C12 - C7 - P1 = 110.83(13)
C8 - C7 - H7 = 105.60
C12 - C7 - H7 = 105.60
P1 - C7 - H7 = 105.60
C7 - C8 - C9 = 110.63(15)
C7 - C8 - H8A = 109.50
C9 - C8 - H8A = 109.50
C7 - C8 - H8B = 109.50
C9 - C8 - H8B = 109.50
H8A - C8 - H8B = 108.10
C10 - C9 - C8 = 111.95(17)
C10 - C9 - H9A = 109.20
C8 - C9 - H9A = 109.20
C10 - C9 - H9B = 109.20
C8 - C9 - H9B = 109.20
H9A - C9 - H9B = 107.90
C11 - C10 - C9 = 111.18(17)
C11 - C10 - H10A = 109.40
C9 - C10 - H10A = 109.40
C11 - C10 - H10B = 109.40
C9 - C10 - H10B = 109.40
H10A - C10 - H10B = 108.00
C10 - C11 - C12 = 111.62(16)
C10 - C11 - H11A = 109.30
C12 - C11 - H11A = 109.30
C10 - C11 - H11B = 109.30
C12 - C11 - H11B = 109.30
H11A - C11 - H11B = 108.00
C11 - C12 - C7 = 110.92(16)
C11 - C12 - H12A = 109.50
C7 - C12 - H12A = 109.50
C11 - C12 - H12B = 109.50
C7 - C12 - H12B = 109.50
H12A - C12 - H12B = 108.00
C14 - C13 - C18 = 117.85(16)
C14 - C13 - P1 = 122.07(14)
C18 - C13 - P1 = 120.06(13)
C15 - C14 - C13 = 122.23(19)
C15 - C14 - H14 = 118.90
C13 - C14 - H14 = 118.90
C14 - C15 - C16 = 119.61(18)
C14 - C15 - H15 = 120.20
C16 - C15 - H15 = 120.20
C15 - C16 - C17 = 119.53(18)
C15 - C16 - H16 = 120.20
C17 - C16 - H16 = 120.20

C16	- C17	- C18	= 121.73(19)
C16	- C17	- H17	= 119.10
C18	- C17	- H17	= 119.10
C17	- C18	- C13	= 119.04(17)
C17	- C18	- C19	= 117.25(16)
C13	- C18	- C19	= 123.50(16)
C20	- C19	- C24	= 118.43(17)
C20	- C19	- C18	= 117.32(16)
C24	- C19	- C18	= 124.24(16)
C21	- C20	- C19	= 122.01(18)
C21	- C20	- H20	= 119.00
C19	- C20	- H20	= 119.00
C20	- C21	- C22	= 119.59(18)
C20	- C21	- H21	= 120.20
C22	- C21	- H21	= 120.20
C21	- C22	- C23	= 119.27(19)
C21	- C22	- H22	= 120.40
C23	- C22	- H22	= 120.40
C22	- C23	- C24	= 122.12(19)
C22	- C23	- H23	= 118.90
C24	- C23	- H23	= 118.90
C23	- C24	- C19	= 118.50(17)
C23	- C24	- C25	= 118.60(17)
C19	- C24	- C25	= 122.85(16)
C32	- C25	- C24	= 119.03(16)
C32	- C25	- C26	= 125.03(16)
C24	- C25	- C26	= 115.88(15)
C31	- C26	- C27	= 118.54(18)
C31	- C26	- C25	= 121.39(17)
C27	- C26	- C25	= 120.05(17)
C28	- C27	- C26	= 120.57(19)
C28	- C27	- H27	= 119.70
C26	- C27	- H27	= 119.70
C29	- C28	- C27	= 120.50(2)
C29	- C28	- H28	= 119.80
C27	- C28	- H28	= 119.80
C28	- C29	- C30	= 119.11(19)
C28	- C29	- H29	= 120.40
C30	- C29	- H29	= 120.40
C29	- C30	- C31	= 120.80(2)
C29	- C30	- H30	= 119.60
C31	- C30	- H30	= 119.60
C30	- C31	- C26	= 120.47(19)
C30	- C31	- H31	= 119.80
C26	- C31	- H31	= 119.80
C25	- C32	- C33	= 131.38(17)
C25	- C32	- H32	= 114.30
C33	- C32	- H32	= 114.30
C34	- C33	- C38	= 117.76(18)
C34	- C33	- C32	= 117.37(17)
C38	- C33	- C32	= 124.83(17)
C33	- C34	- C35	= 121.70(2)

C33	- C34	- H34	= 119.20
C35	- C34	- H34	= 119.20
C36	- C35	- C34	= 119.70(2)
C36	- C35	- H35	= 120.10
C34	- C35	- H35	= 120.10
C35	- C36	- C37	= 119.57(19)
C35	- C36	- H36	= 120.20
C37	- C36	- H36	= 120.20
C36	- C37	- C38	= 120.90(2)
C36	- C37	- H37	= 119.60
C38	- C37	- H37	= 119.60
C33	- C38	- C37	= 120.33(19)
C33	- C38	- H38	= 119.80
C37	- C38	- H38	= 119.80

Table S5. Torsion angles [°] for **3aa**.

C13	- P1	- C1	- C6	= 171.49(13)
C7	- P1	- C1	- C6	= 65.51(15)
C13	- P1	- C1	- C2	= -66.54(13)
C7	- P1	- C1	- C2	= -172.52(12)
C6	- C1	- C2	- C3	= -53.00(2)
P1	- C1	- C2	- C3	= -174.79(13)
C1	- C2	- C3	- C4	= 54.10(2)
C2	- C3	- C4	- C5	= -55.20(3)
C3	- C4	- C5	- C6	= 56.60(3)
C4	- C5	- C6	- C1	= -57.00(2)
C2	- C1	- C6	- C5	= 54.60(2)
P1	- C1	- C6	- C5	= 176.85(15)
C13	- P1	- C7	- C8	= -55.55(15)
C1	- P1	- C7	- C8	= 50.00(15)
C13	- P1	- C7	- C12	= 72.46(14)
C1	- P1	- C7	- C12	= 178.01(12)
C12	- C7	- C8	- C9	= 58.10(2)
P1	- C7	- C8	- C9	= -173.33(13)
C7	- C8	- C9	- C10	= -56.80(2)
C8	- C9	- C10	- C11	= 54.00(2)
C9	- C10	- C11	- C12	= -53.40(2)
C10	- C11	- C12	- C7	= 55.90(2)
C8	- C7	- C12	- C11	= -57.90(2)
P1	- C7	- C12	- C11	= 169.45(13)
C1	- P1	- C13	- C14	= -28.45(17)
C7	- P1	- C13	- C14	= 76.09(16)
C1	- P1	- C13	- C18	= 152.41(14)
C7	- P1	- C13	- C18	= -103.05(15)
C18	- C13	- C14	- C15	= 0.60(3)
P1	- C13	- C14	- C15	= -178.57(15)
C13	- C14	- C15	- C16	= 0.50(3)
C14	- C15	- C16	- C17	= -0.90(3)
C15	- C16	- C17	- C18	= 0.40(3)
C16	- C17	- C18	- C13	= 0.70(3)
C16	- C17	- C18	- C19	= 175.56(18)

C14 - C13 - C18 - C17 = -1.10(3)
P1 - C13 - C18 - C17 = 178.05(13)
C14 - C13 - C18 - C19 = -175.68(16)
P1 - C13 - C18 - C19 = 3.50(2)
C17 - C18 - C19 - C20 = -65.10(2)
C13 - C18 - C19 - C20 = 109.60(2)
C17 - C18 - C19 - C24 = 113.70(2)
C13 - C18 - C19 - C24 = -71.70(3)
C24 - C19 - C20 - C21 = 1.80(3)
C18 - C19 - C20 - C21 = -179.30(17)
C19 - C20 - C21 - C22 = 0.70(3)
C20 - C21 - C22 - C23 = -1.90(3)
C21 - C22 - C23 - C24 = 0.60(3)
C22 - C23 - C24 - C19 = 1.90(3)
C22 - C23 - C24 - C25 = -175.73(19)
C20 - C19 - C24 - C23 = -3.10(3)
C18 - C19 - C24 - C23 = 178.14(17)
C20 - C19 - C24 - C25 = 174.47(17)
C18 - C19 - C24 - C25 = -4.30(3)
C23 - C24 - C25 - C32 = -59.30(3)
C19 - C24 - C25 - C32 = 123.10(2)
C23 - C24 - C25 - C26 = 117.97(19)
C19 - C24 - C25 - C26 = -59.60(2)
C32 - C25 - C26 - C31 = -64.00(3)
C24 - C25 - C26 - C31 = 119.00(2)
C32 - C25 - C26 - C27 = 117.20(2)
C24 - C25 - C26 - C27 = -59.80(2)
C31 - C26 - C27 - C28 = -0.40(3)
C25 - C26 - C27 - C28 = 178.49(18)
C26 - C27 - C28 - C29 = -1.00(3)
C27 - C28 - C29 - C30 = 2.00(3)
C28 - C29 - C30 - C31 = -1.50(3)
C29 - C30 - C31 - C26 = 0.10(3)
C27 - C26 - C31 - C30 = 0.80(3)
C25 - C26 - C31 - C30 = -178.02(19)
C24 - C25 - C32 - C33 = 174.11(19)
C26 - C25 - C32 - C33 = -2.90(3)
C25 - C32 - C33 - C34 = 158.30(2)
C25 - C32 - C33 - C38 = -24.00(3)
C38 - C33 - C34 - C35 = 1.70(3)
C32 - C33 - C34 - C35 = 179.62(19)
C33 - C34 - C35 - C36 = -1.40(3)
C34 - C35 - C36 - C37 = 0.20(3)
C35 - C36 - C37 - C38 = 0.60(4)
C34 - C33 - C38 - C37 = -1.00(3)
C32 - C33 - C38 - C37 = -178.68(19)
C36 - C37 - C38 - C33 = -0.20(3)

Crystal measurement for 4aa:

Crystallization by diffusion method from CH_2Cl_2 solution with *n*-hexane has afforded single crystal to analyze by X-ray diffraction.

The single crystal X-ray diffraction studies were carried out on D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, [*], Mo-*Kα* radiation (*λ* = 0.71073 , multilayer monochromator), *T* = 150 K; triclinic *P* -1 (I.T.#2), *a* = 15.0306(13), *b* = 16.0708(13), *c* = 19.4591(16) , *α* = 95.629(3), *β* = 105.254(3), *γ* = 108.810(3) , *V* = 4205.6(6) ^{3}. *Z* = 2, *d* = 1.183 g.cm^{-3}, *μ* = 0.164 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program [1], and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*) [2]. The contribution of the disordered solvents to the calculated structure factors was estimated following the *BYPASS* algorithm [3], implemented as the *SQUEEZE* option in *PLATON* [4]. A new data set, free of solvent contribution, was then used in the final refinement. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 19092 unique intensities and 982 parameters converged at ωR_F^2 = 0.1172 (R_F = 0.0490) for 13976 observed reflections with $I > 2\sigma(I)$.

[1] G. M. Sheldrick, Acta Cryst. A71 (2015) 3-8
[2] Sheldrick G.M., Acta Cryst. C71 (2015) 3-8

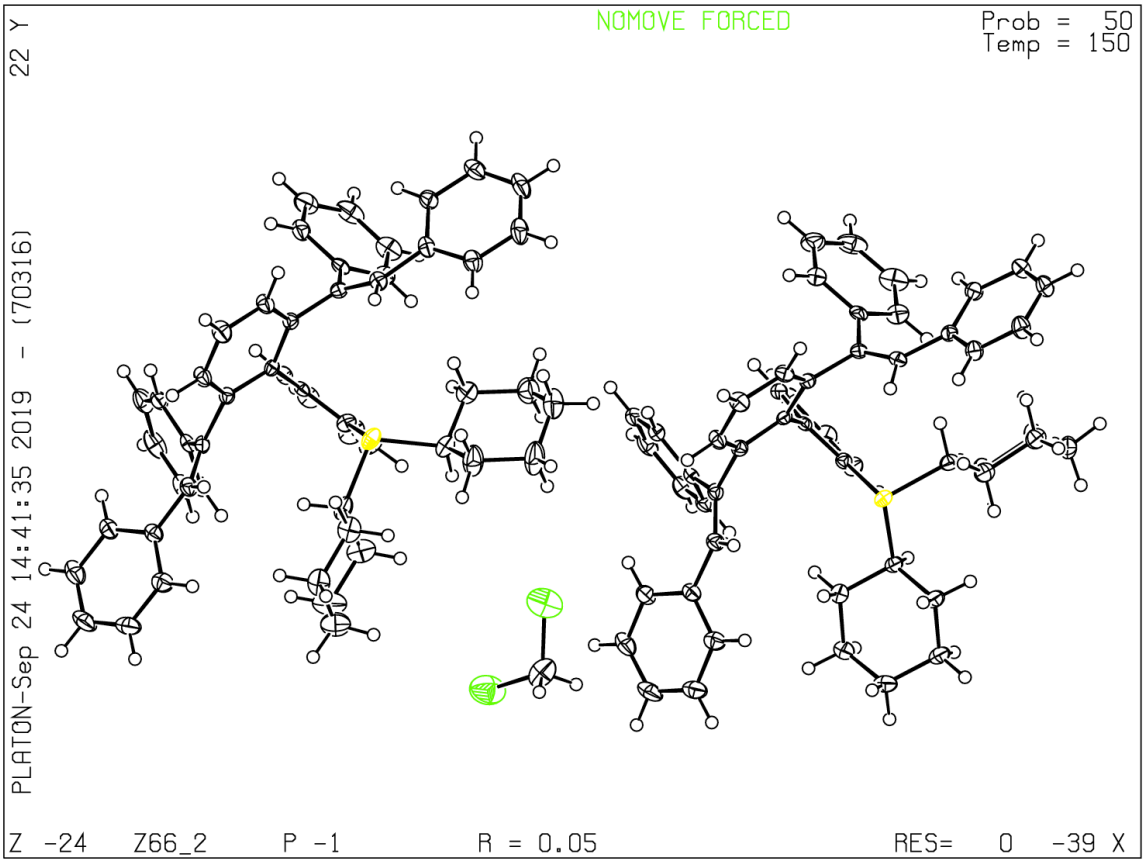


Figure S2. ORTEP diagram of the solid-state molecular structure of **4aa**. Thermal ellipsoids are at the 50% probability level. (CCDC 1968421).

Table S6. Crystal data and structure refinement for **4aa**.

Empirical formula	$C_{105}H_{104}Cl_2P_2$
Formula weight	1498.72 g/mol
Temperature	150 *K*
Wavelength	0.71073 Å
Crystal system, space group	triclinic, *P* -1
Unit cell dimensions	a = 15.0306(13) Å
	b = 16.0708(13) Å
	c = 19.4591(16) Å
	α = 95.629(3) °
	β = 105.254(3) °
	γ = 108.810(3) °
Volume	4205.6(6) $Å^3$
Z, Calculated density	2, 1.183 $g.cm^{-3}$
Absorption coefficient	0.164 mm^{-1}
F(000)	1596
Crystal size	0.580 x 0.320 x 0.180 mm
Crystal color	colourless
Theta range for data collection	2.215 to 27.527 °
h_min, h_max	-19, 19
k_min, k_max	-20, 20
l_min, l_max	-24, 25
Reflections collected / unique	79668 / 19092 [R(int)[a] = 0.0683]
Reflections [I>2σ]	13976
Completeness to theta_max	0.986
Absorption correction type	multi-scan
Max. and min. transmission	0.971, 0.874
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	19092 / 0 / 982
[b]S (Goodness-of-fit)	1.011
Final *R* indices [I>2σ]	$R1^c$ = 0.0490, $wR2^d$ = 0.1172
R indices (all data)	$R1^c$ = 0.0779, $wR2^d$ = 0.1339
Largest diff. peak and hole	1.058 and -0.545 $e^-.Å^{-3}$

Table S7. **Fractional atomic coordinates, site occupancy (%) and equivalent isotropic displacement parameters (Å²)** for **4aa**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	occ.	U(eq)	adp
P1	0.16644(4)	0.83103(3)	0.29726(3)	1	0.02289(11)	Uani
C1	0.22780(15)	0.74712(13)	0.29264(11)	1	0.0262(4)	Uani
H1	0.181477	0.686630	0.293241	1	0.031	Uiso
C2	0.25363(16)	0.74405(14)	0.22142(11)	1	0.0307(4)	Uani
H2A	0.191570	0.718118	0.180057	1	0.037	Uiso
H2B	0.288433	0.806094	0.216946	1	0.037	Uiso
C3	0.31849(17)	0.68908(16)	0.21650(13)	1	0.0383(5)	Uani
H3A	0.280487	0.625178	0.213939	1	0.046	Uiso
H3B	0.336908	0.693747	0.171392	1	0.046	Uiso
C4	0.41182(17)	0.72128(17)	0.28156(14)	1	0.0429(6)	Uani
H4A	0.450804	0.682700	0.277954	1	0.051	Uiso
H4B	0.452988	0.783511	0.281956	1	0.051	Uiso
C5	0.3850(2)	0.71800(19)	0.35109(14)	1	0.0497(7)	Uani

H5A	0.446245	0.740331	0.393188	1	0.060	Uiso
H5B	0.347711	0.655055	0.351940	1	0.060	Uiso
C6	0.32210(18)	0.77501(18)	0.35782(13)	1	0.0434(6)	Uani
H6A	0.362072	0.838837	0.362003	1	0.052	Uiso
H6B	0.303609	0.769278	0.402827	1	0.052	Uiso
C7	0.10494(14)	0.81011(12)	0.36880(10)	1	0.0255(4)	Uani
H7	0.056149	0.841031	0.359795	1	0.031	Uiso
C8	0.04472(17)	0.71340(14)	0.36904(12)	1	0.0364(5)	Uani
H8A	0.089434	0.679434	0.380267	1	0.044	Uiso
H8B	-0.003720	0.684625	0.320189	1	0.044	Uiso
C9	-0.01012(19)	0.71002(17)	0.42543(12)	1	0.0459(6)	Uani
H9A	-0.058643	0.739874	0.412027	1	0.055	Uiso
H9B	-0.046886	0.646700	0.425623	1	0.055	Uiso
C10	0.06178(19)	0.75627(16)	0.50105(12)	1	0.0429(6)	Uani
H10A	0.024294	0.756143	0.535967	1	0.051	Uiso
H10B	0.105864	0.722623	0.516520	1	0.051	Uiso
C11	0.12377(16)	0.85227(14)	0.50210(11)	1	0.0344(5)	Uani
H11A	0.173128	0.879135	0.550868	1	0.041	Uiso
H11B	0.080456	0.887779	0.492773	1	0.041	Uiso
C12	0.17712(15)	0.85686(14)	0.44508(11)	1	0.0315(5)	Uani
H12A	0.226670	0.828003	0.458005	1	0.038	Uiso
H12B	0.212730	0.920479	0.444958	1	0.038	Uiso
C13	0.05575(13)	0.78358(11)	0.21542(10)	1	0.0201(4)	Uani
C14	0.00725(15)	0.69097(12)	0.18858(11)	1	0.0294(4)	Uani
H14	0.032216	0.650722	0.212683	1	0.035	Uiso
C15	-0.07604(16)	0.65668(13)	0.12787(11)	1	0.0328(5)	Uani
H15	-0.109336	0.593646	0.111996	1	0.039	Uiso
C16	-0.11057(14)	0.71463(13)	0.09041(10)	1	0.0254(4)	Uani
H16	-0.166889	0.691578	0.048121	1	0.031	Uiso
C17	-0.06273(13)	0.80618(12)	0.11482(10)	1	0.0198(4)	Uani
H17	-0.085487	0.845737	0.088128	1	0.024	Uiso
C18	0.01853(12)	0.84170(11)	0.17806(9)	1	0.0153(3)	Uani
C19	0.06346(12)	0.94133(11)	0.20577(9)	1	0.0154(3)	Uani
C20	0.02623(12)	0.98397(11)	0.25241(9)	1	0.0167(3)	Uani
C21	0.07513(13)	1.07622(12)	0.28155(10)	1	0.0227(4)	Uani
H21	0.050520	1.105210	0.312998	1	0.027	Uiso
C22	0.15832(14)	1.12562(12)	0.26538(11)	1	0.0271(4)	Uani
H22	0.191145	1.187743	0.286244	1	0.033	Uiso
C23	0.19362(13)	1.08413(12)	0.21860(11)	1	0.0230(4)	Uani
H23	0.250195	1.118467	0.206944	1	0.028	Uiso
C24	0.14740(12)	0.99275(11)	0.18836(9)	1	0.0169(3)	Uani
C25	-0.06323(12)	0.93805(11)	0.27362(10)	1	0.0176(3)	Uani
C26	-0.15711(12)	0.88287(11)	0.21563(10)	1	0.0179(3)	Uani
C27	-0.19199(13)	0.91584(13)	0.15501(10)	1	0.0227(4)	Uani
H27	-0.153817	0.972896	0.148881	1	0.027	Uiso
C28	-0.28267(15)	0.86565(15)	0.10319(11)	1	0.0318(5)	Uani
H28	-0.305978	0.888575	0.061722	1	0.038	Uiso
C29	-0.33901(14)	0.78288(15)	0.11152(12)	1	0.0344(5)	Uani
H29	-0.401397	0.749400	0.076300	1	0.041	Uiso
C30	-0.30463(15)	0.74877(14)	0.17108(12)	1	0.0317(5)	Uani
H30	-0.343154	0.691580	0.176744	1	0.038	Uiso
C31	-0.21376(14)	0.79800(12)	0.22272(11)	1	0.0238(4)	Uani

H31	-0.189866	0.773818	0.263227	1	0.029	Uiso
C32	-0.06050(13)	0.95411(12)	0.34358(10)	1	0.0205(4)	Uani
H32	0.003657	0.982630	0.377933	1	0.025	Uiso
C33	-0.14343(13)	0.93352(12)	0.37431(10)	1	0.0212(4)	Uani
C34	-0.23604(14)	0.93572(12)	0.33731(11)	1	0.0247(4)	Uani
H34	-0.248433	0.946880	0.289303	1	0.030	Uiso
C35	-0.30968(15)	0.92177(14)	0.37008(12)	1	0.0326(5)	Uani
H35	-0.372307	0.922791	0.344153	1	0.039	Uiso
C36	-0.29269(17)	0.90638(14)	0.44027(13)	1	0.0358(5)	Uani
H36	-0.343403	0.896911	0.462485	1	0.043	Uiso
C37	-0.20180(17)	0.90486(13)	0.47777(12)	1	0.0331(5)	Uani
H37	-0.189784	0.894540	0.526027	1	0.040	Uiso
C38	-0.12780(15)	0.91837(13)	0.44529(11)	1	0.0268(4)	Uani
H38	-0.065421	0.917291	0.471745	1	0.032	Uiso
C39	0.19405(13)	0.95313(11)	0.14154(10)	1	0.0180(3)	Uani
C40	0.13501(12)	0.90457(12)	0.06538(10)	1	0.0187(4)	Uani
C41	0.09047(14)	0.94722(14)	0.01562(11)	1	0.0279(4)	Uani
H41	0.091087	1.005251	0.031600	1	0.033	Uiso
C42	0.04500(15)	0.90548(16)	-0.05743(11)	1	0.0350(5)	Uani
H42	0.014743	0.935143	-0.090879	1	0.042	Uiso
C43	0.04375(15)	0.82131(16)	-0.08135(11)	1	0.0354(5)	Uani
H43	0.013859	0.793343	-0.131290	1	0.043	Uiso
C44	0.08627(15)	0.77809(14)	-0.03215(11)	1	0.0324(5)	Uani
H44	0.084824	0.719800	-0.048335	1	0.039	Uiso
C45	0.13115(14)	0.81887(12)	0.04078(11)	1	0.0255(4)	Uani
H45	0.159446	0.787996	0.074140	1	0.031	Uiso
C46	0.29140(13)	0.96843(11)	0.16820(10)	1	0.0202(4)	Uani
H46	0.321809	0.997308	0.217913	1	0.024	Uiso
C47	0.35751(13)	0.94683(11)	0.13137(10)	1	0.0216(4)	Uani
C48	0.34584(14)	0.94524(12)	0.05730(11)	1	0.0241(4)	Uani
H48	0.292977	0.959112	0.028296	1	0.029	Uiso
C49	0.41009(15)	0.92379(14)	0.02586(12)	1	0.0307(4)	Uani
H49	0.400919	0.922668	-0.024476	1	0.037	Uiso
C50	0.48781(15)	0.90394(14)	0.06756(13)	1	0.0332(5)	Uani
H50	0.530948	0.887860	0.045582	1	0.040	Uiso
C51	0.50263(14)	0.90748(14)	0.14085(12)	1	0.0317(5)	Uani
H51	0.556641	0.894907	0.169648	1	0.038	Uiso
C52	0.43849(13)	0.92945(13)	0.17251(11)	1	0.0262(4)	Uani
H52	0.449867	0.932751	0.223263	1	0.031	Uiso
P2	0.62284(3)	0.27673(3)	0.29955(2)	1	0.01755(10)	Uani
C53	0.54882(13)	0.17549(11)	0.32691(10)	1	0.0191(4)	Uani
H53	0.517214	0.124320	0.284152	1	0.023	Uiso
C54	0.61474(14)	0.14949(13)	0.38915(11)	1	0.0267(4)	Uani
H54A	0.663354	0.131385	0.371810	1	0.032	Uiso
H54B	0.651815	0.202181	0.429545	1	0.032	Uiso
C55	0.55328(16)	0.07226(14)	0.41698(12)	1	0.0316(5)	Uani
H55A	0.520994	0.017991	0.377765	1	0.038	Uiso
H55B	0.597571	0.058626	0.458124	1	0.038	Uiso
C56	0.47453(16)	0.09517(15)	0.44184(11)	1	0.0325(5)	Uani
H56A	0.506870	0.145811	0.484181	1	0.039	Uiso
H56B	0.434281	0.042855	0.457263	1	0.039	Uiso
C57	0.40746(15)	0.12061(13)	0.38086(11)	1	0.0274(4)	Uani

H57A	0.360376	0.139809	0.399419	1	0.033	Uiso
H57B	0.368715	0.067486	0.341059	1	0.033	Uiso
C58	0.46757(14)	0.19644(13)	0.35122(11)	1	0.0242(4)	Uani
H58A	0.498582	0.251823	0.389310	1	0.029	Uiso
H58B	0.422293	0.207921	0.309331	1	0.029	Uiso
C59	0.70840(13)	0.24040(12)	0.25994(10)	1	0.0203(4)	Uani
H59	0.722914	0.280160	0.224732	1	0.024	Uiso
C60	0.66980(14)	0.14414(13)	0.21606(11)	1	0.0277(4)	Uani
H60A	0.652857	0.101264	0.248001	1	0.033	Uiso
H60B	0.608676	0.134148	0.176039	1	0.033	Uiso
C61	0.74605(16)	0.12607(14)	0.18429(12)	1	0.0335(5)	Uani
H61A	0.719937	0.062544	0.158976	1	0.040	Uiso
H61B	0.757394	0.164130	0.148086	1	0.040	Uiso
C62	0.84400(15)	0.14558(13)	0.24333(12)	1	0.0317(5)	Uani
H62A	0.834114	0.103549	0.276971	1	0.038	Uiso
H62B	0.892766	0.136169	0.220794	1	0.038	Uiso
C63	0.88373(14)	0.24142(13)	0.28559(12)	1	0.0284(4)	Uani
H63A	0.900182	0.283299	0.252840	1	0.034	Uiso
H63B	0.945307	0.251591	0.325216	1	0.034	Uiso
C64	0.80864(13)	0.26118(13)	0.31803(11)	1	0.0247(4)	Uani
H64A	0.835333	0.325218	0.342134	1	0.030	Uiso
H64B	0.798739	0.224714	0.355443	1	0.030	Uiso
C65	0.53332(12)	0.28073(11)	0.21561(9)	1	0.0164(3)	Uani
C66	0.53454(12)	0.36374(11)	0.19749(9)	1	0.0141(3)	Uani
C67	0.47331(12)	0.36503(12)	0.12975(9)	1	0.0185(4)	Uani
H67	0.477149	0.421077	0.116390	1	0.022	Uiso
C68	0.40748(13)	0.28679(13)	0.08191(10)	1	0.0228(4)	Uani
H68	0.366289	0.289039	0.036352	1	0.027	Uiso
C69	0.40228(14)	0.20501(12)	0.10121(10)	1	0.0243(4)	Uani
H69	0.355572	0.150845	0.069612	1	0.029	Uiso
C70	0.46488(13)	0.20226(12)	0.16624(10)	1	0.0219(4)	Uani
H70	0.461685	0.145620	0.178060	1	0.026	Uiso
C71	0.59345(12)	0.45366(11)	0.24788(9)	1	0.0149(3)	Uani
C72	0.68981(12)	0.50480(11)	0.24919(9)	1	0.0164(3)	Uani
C73	0.73790(13)	0.59134(12)	0.29230(10)	1	0.0203(4)	Uani
H73	0.802580	0.625846	0.292504	1	0.024	Uiso
C74	0.69347(14)	0.62753(12)	0.33442(10)	1	0.0233(4)	Uani
H74	0.726251	0.686965	0.362215	1	0.028	Uiso
C75	0.60032(13)	0.57599(12)	0.33564(10)	1	0.0211(4)	Uani
H75	0.570184	0.599847	0.365727	1	0.025	Uiso
C76	0.55000(12)	0.48944(11)	0.29330(9)	1	0.0174(3)	Uani
C77	0.45232(12)	0.43680(11)	0.30123(9)	1	0.0169(3)	Uani
C78	0.36409(12)	0.40755(11)	0.23513(9)	1	0.0174(3)	Uani
C79	0.29874(13)	0.31888(12)	0.21388(10)	1	0.0209(4)	Uani
H79	0.310012	0.276358	0.242361	1	0.025	Uiso
C80	0.21751(14)	0.29170(13)	0.15183(11)	1	0.0269(4)	Uani
H80	0.173334	0.230968	0.138118	1	0.032	Uiso
C81	0.20068(14)	0.35312(15)	0.10974(11)	1	0.0295(4)	Uani
H81	0.144611	0.334756	0.067413	1	0.035	Uiso
C82	0.26562(15)	0.44106(15)	0.12950(11)	1	0.0287(4)	Uani
H82	0.254287	0.483077	0.100474	1	0.034	Uiso
C83	0.34754(14)	0.46857(12)	0.19162(10)	1	0.0224(4)	Uani

H83	0.392375	0.529046	0.204484	1	0.027	Uiso
C84	0.45086(13)	0.42274(12)	0.36808(10)	1	0.0203(4)	Uani
H84	0.514179	0.443761	0.403852	1	0.024	Uiso
C85	0.36767(13)	0.38024(12)	0.39521(10)	1	0.0208(4)	Uani
C86	0.38664(15)	0.34175(13)	0.45606(10)	1	0.0257(4)	Uani
H86	0.451904	0.344006	0.478472	1	0.031	Uiso
C87	0.31215(16)	0.30029(13)	0.48443(11)	1	0.0311(5)	Uani
H87	0.326216	0.273122	0.525150	1	0.037	Uiso
C88	0.21712(16)	0.29843(14)	0.45346(12)	1	0.0330(5)	Uani
H88	0.165811	0.269618	0.472598	1	0.040	Uiso
C89	0.19744(15)	0.33862(13)	0.39471(12)	1	0.0306(5)	Uani
H89	0.132606	0.338278	0.373818	1	0.037	Uiso
C90	0.27209(14)	0.37965(13)	0.36592(11)	1	0.0254(4)	Uani
H90	0.257833	0.407660	0.325752	1	0.030	Uiso
C91	0.74812(12)	0.46987(11)	0.21002(9)	1	0.0169(3)	Uani
C92	0.70665(12)	0.44399(12)	0.12922(10)	1	0.0183(4)	Uani
C93	0.67510(15)	0.50338(14)	0.09049(11)	1	0.0274(4)	Uani
H93	0.683109	0.560225	0.115874	1	0.033	Uiso
C94	0.63236(16)	0.48082(16)	0.01574(12)	1	0.0363(5)	Uani
H94	0.611380	0.522081	-0.009769	1	0.044	Uiso
C95	0.62018(16)	0.39830(16)	-0.02179(11)	1	0.0377(5)	Uani
H95	0.590916	0.382744	-0.073116	1	0.045	Uiso
C96	0.65050(16)	0.33886(15)	0.01530(11)	1	0.0359(5)	Uani
H96	0.641756	0.281996	-0.010505	1	0.043	Uiso
C97	0.69391(14)	0.36127(13)	0.09039(10)	1	0.0263(4)	Uani
H97	0.715057	0.319749	0.115409	1	0.032	Uiso
C98	0.83623(12)	0.47338(11)	0.25361(10)	1	0.0178(3)	Uani
H98	0.842243	0.485049	0.303761	1	0.021	Uiso
C99	0.92468(12)	0.46330(11)	0.24121(10)	1	0.0175(3)	Uani
C100	0.93737(13)	0.44026(12)	0.17409(10)	1	0.0209(4)	Uani
H100	0.883742	0.425704	0.130543	1	0.025	Uiso
C101	1.02785(14)	0.43861(13)	0.17093(11)	1	0.0253(4)	Uani
H101	1.035355	0.422214	0.125124	1	0.030	Uiso
C102	1.10734(14)	0.46046(13)	0.23343(11)	1	0.0267(4)	Uani
H102	1.169100	0.459409	0.230541	1	0.032	Uiso
C103	1.09635(14)	0.48389(13)	0.30029(11)	1	0.0261(4)	Uani
H103	1.150766	0.499510	0.343469	1	0.031	Uiso
C104	1.00631(13)	0.48446(12)	0.30395(10)	1	0.0215(4)	Uani
H104	0.999205	0.499568	0.350139	1	0.026	Uiso
Cl1	0.12663(5)	0.51763(6)	0.51564(4)	1	0.0669(2)	Uani
Cl2	0.31188(5)	0.59780(5)	0.48622(4)	1	0.05756(18)	Uani
C105	0.25238(18)	0.53179(15)	0.53956(13)	1	0.0430(6)	Uani
H10C	0.258706	0.472315	0.532885	1	0.052	Uiso
H10D	0.285038	0.560912	0.591522	1	0.052	Uiso

Table S8. Bond lengths [Å] for **4aa**.

P1	- C13	= 1.8534(18)
P1	- C7	= 1.864(2)
P1	- C1	= 1.8705(19)
C1	- C6	= 1.533(3)

C1 - C2 = 1.535(3)
C1 - H1 = 1.0000
C2 - C3 = 1.526(3)
C2 - H2A = 0.9900
C2 - H2B = 0.9900
C3 - C4 = 1.519(3)
C3 - H3A = 0.9900
C3 - H3B = 0.9900
C4 - C5 = 1.511(4)
C4 - H4A = 0.9900
C4 - H4B = 0.9900
C5 - C6 = 1.533(3)
C5 - H5A = 0.9900
C5 - H5B = 0.9900
C6 - H6A = 0.9900
C6 - H6B = 0.9900
C7 - C8 = 1.527(3)
C7 - C12 = 1.534(3)
C7 - H7 = 1.0000
C8 - C9 = 1.531(3)
C8 - H8A = 0.9900
C8 - H8B = 0.9900
C9 - C10 = 1.522(3)
C9 - H9A = 0.9900
C9 - H9B = 0.9900
C10 - C11 = 1.518(3)
C10 - H10A = 0.9900
C10 - H10B = 0.9900
C11 - C12 = 1.525(3)
C11 - H11A = 0.9900
C11 - H11B = 0.9900
C12 - H12A = 0.9900
C12 - H12B = 0.9900
C13 - C14 = 1.402(2)
C13 - C18 = 1.404(2)
C14 - C15 = 1.384(3)
C14 - H14 = 0.9500
C15 - C16 = 1.383(3)
C15 - H15 = 0.9500
C16 - C17 = 1.381(3)
C16 - H16 = 0.9500
C17 - C18 = 1.398(2)
C17 - H17 = 0.9500
C18 - C19 = 1.501(2)
C19 - C24 = 1.413(2)
C19 - C20 = 1.414(2)
C20 - C21 = 1.405(2)
C20 - C25 = 1.495(2)
C21 - C22 = 1.382(3)
C21 - H21 = 0.9500
C22 - C23 = 1.385(3)
C22 - H22 = 0.9500

C23 - C24 = 1.394(2)
C23 - H23 = 0.9500
C24 - C39 = 1.496(2)
C25 - C32 = 1.348(3)
C25 - C26 = 1.487(2)
C26 - C27 = 1.387(3)
C26 - C31 = 1.398(2)
C27 - C28 = 1.390(3)
C27 - H27 = 0.9500
C28 - C29 = 1.379(3)
C28 - H28 = 0.9500
C29 - C30 = 1.379(3)
C29 - H29 = 0.9500
C30 - C31 = 1.388(3)
C30 - H30 = 0.9500
C31 - H31 = 0.9500
C32 - C33 = 1.479(2)
C32 - H32 = 0.9500
C33 - C38 = 1.398(3)
C33 - C34 = 1.402(3)
C34 - C35 = 1.386(3)
C34 - H34 = 0.9500
C35 - C36 = 1.384(3)
C35 - H35 = 0.9500
C36 - C37 = 1.378(3)
C36 - H36 = 0.9500
C37 - C38 = 1.387(3)
C37 - H37 = 0.9500
C38 - H38 = 0.9500
C39 - C46 = 1.347(2)
C39 - C40 = 1.492(2)
C40 - C45 = 1.391(3)
C40 - C41 = 1.393(3)
C41 - C42 = 1.394(3)
C41 - H41 = 0.9500
C42 - C43 = 1.379(3)
C42 - H42 = 0.9500
C43 - C44 = 1.379(3)
C43 - H43 = 0.9500
C44 - C45 = 1.388(3)
C44 - H44 = 0.9500
C45 - H45 = 0.9500
C46 - C47 = 1.473(2)
C46 - H46 = 0.9500
C47 - C52 = 1.397(3)
C47 - C48 = 1.402(3)
C48 - C49 = 1.382(3)
C48 - H48 = 0.9500
C49 - C50 = 1.385(3)
C49 - H49 = 0.9500
C50 - C51 = 1.377(3)
C50 - H50 = 0.9500

C51 - C52 = 1.387(3)
C51 - H51 = 0.9500
C52 - H52 = 0.9500
P2 - C65 = 1.8445(17)
P2 - C53 = 1.8662(18)
P2 - C59 = 1.8724(19)
C53 - C54 = 1.536(2)
C53 - C58 = 1.538(3)
C53 - H53 = 1.0000
C54 - C55 = 1.531(3)
C54 - H54A = 0.9900
C54 - H54B = 0.9900
C55 - C56 = 1.522(3)
C55 - H55A = 0.9900
C55 - H55B = 0.9900
C56 - C57 = 1.524(3)
C56 - H56A = 0.9900
C56 - H56B = 0.9900
C57 - C58 = 1.528(3)
C57 - H57A = 0.9900
C57 - H57B = 0.9900
C58 - H58A = 0.9900
C58 - H58B = 0.9900
C59 - C60 = 1.536(3)
C59 - C64 = 1.538(2)
C59 - H59 = 1.0000
C60 - C61 = 1.527(3)
C60 - H60A = 0.9900
C60 - H60B = 0.9900
C61 - C62 = 1.526(3)
C61 - H61A = 0.9900
C61 - H61B = 0.9900
C62 - C63 = 1.518(3)
C62 - H62A = 0.9900
C62 - H62B = 0.9900
C63 - C64 = 1.530(3)
C63 - H63A = 0.9900
C63 - H63B = 0.9900
C64 - H64A = 0.9900
C64 - H64B = 0.9900
C65 - C70 = 1.406(2)
C65 - C66 = 1.409(2)
C66 - C67 = 1.401(2)
C66 - C71 = 1.508(2)
C67 - C68 = 1.382(2)
C67 - H67 = 0.9500
C68 - C69 = 1.386(3)
C68 - H68 = 0.9500
C69 - C70 = 1.378(3)
C69 - H69 = 0.9500
C70 - H70 = 0.9500
C71 - C72 = 1.408(2)

C71 - C76 = 1.409(2)
C72 - C73 = 1.402(2)
C72 - C91 = 1.500(2)
C73 - C74 = 1.379(3)
C73 - H73 = 0.9500
C74 - C75 = 1.386(3)
C74 - H74 = 0.9500
C75 - C76 = 1.398(2)
C75 - H75 = 0.9500
C76 - C77 = 1.496(2)
C77 - C84 = 1.347(2)
C77 - C78 = 1.489(2)
C78 - C79 = 1.391(2)
C78 - C83 = 1.396(2)
C79 - C80 = 1.384(3)
C79 - H79 = 0.9500
C80 - C81 = 1.386(3)
C80 - H80 = 0.9500
C81 - C82 = 1.380(3)
C81 - H81 = 0.9500
C82 - C83 = 1.391(3)
C82 - H82 = 0.9500
C83 - H83 = 0.9500
C84 - C85 = 1.475(2)
C84 - H84 = 0.9500
C85 - C86 = 1.395(3)
C85 - C90 = 1.396(3)
C86 - C87 = 1.385(3)
C86 - H86 = 0.9500
C87 - C88 = 1.386(3)
C87 - H87 = 0.9500
C88 - C89 = 1.379(3)
C88 - H88 = 0.9500
C89 - C90 = 1.391(3)
C89 - H89 = 0.9500
C90 - H90 = 0.9500
C91 - C98 = 1.352(2)
C91 - C92 = 1.491(2)
C92 - C97 = 1.392(3)
C92 - C93 = 1.396(3)
C93 - C94 = 1.384(3)
C93 - H93 = 0.9500
C94 - C95 = 1.382(3)
C94 - H94 = 0.9500
C95 - C96 = 1.373(3)
C95 - H95 = 0.9500
C96 - C97 = 1.391(3)
C96 - H96 = 0.9500
C97 - H97 = 0.9500
C98 - C99 = 1.467(2)
C98 - H98 = 0.9500
C99 - C100 = 1.401(3)

C99 - C104 = 1.405(2)
C100 - C101 = 1.386(3)
C100 - H100 = 0.9500
C101 - C102 = 1.382(3)
C101 - H101 = 0.9500
C102 - C103 = 1.385(3)
C102 - H102 = 0.9500
C103 - C104 = 1.377(3)
C103 - H103 = 0.9500
C104 - H104 = 0.9500
Cl1 - C105 = 1.755(3)
Cl2 - C105 = 1.759(3)
C105 - H10C = 0.9900
C105 - H10D = 0.9900

Table S9. Angles [°] for **4aa**.

C13 - P1 - C7 = 99.27(8)
C13 - P1 - C1 = 102.15(8)
C7 - P1 - C1 = 106.75(9)
C6 - C1 - C2 = 110.10(18)
C6 - C1 - P1 = 109.75(14)
C2 - C1 - P1 = 108.15(13)
C6 - C1 - H1 = 109.60
C2 - C1 - H1 = 109.60
P1 - C1 - H1 = 109.60
C3 - C2 - C1 = 113.28(17)
C3 - C2 - H2A = 108.90
C1 - C2 - H2A = 108.90
C3 - C2 - H2B = 108.90
C1 - C2 - H2B = 108.90
H2A - C2 - H2B = 107.70
C4 - C3 - C2 = 111.55(18)
C4 - C3 - H3A = 109.30
C2 - C3 - H3A = 109.30
C4 - C3 - H3B = 109.30
C2 - C3 - H3B = 109.30
H3A - C3 - H3B = 108.00
C5 - C4 - C3 = 110.00(2)
C5 - C4 - H4A = 109.70
C3 - C4 - H4A = 109.70
C5 - C4 - H4B = 109.70
C3 - C4 - H4B = 109.70
H4A - C4 - H4B = 108.20
C4 - C5 - C6 = 111.30(2)
C4 - C5 - H5A = 109.40
C6 - C5 - H5A = 109.40
C4 - C5 - H5B = 109.40
C6 - C5 - H5B = 109.40
H5A - C5 - H5B = 108.00
C5 - C6 - C1 = 112.46(19)
C5 - C6 - H6A = 109.10

C1 - C6 - H6A = 109.10
C5 - C6 - H6B = 109.10
C1 - C6 - H6B = 109.10
H6A - C6 - H6B = 107.80
C8 - C7 - C12 = 110.02(17)
C8 - C7 - P1 = 118.31(14)
C12 - C7 - P1 = 111.81(14)
C8 - C7 - H7 = 105.20
C12 - C7 - H7 = 105.20
P1 - C7 - H7 = 105.20
C7 - C8 - C9 = 110.96(18)
C7 - C8 - H8A = 109.40
C9 - C8 - H8A = 109.40
C7 - C8 - H8B = 109.40
C9 - C8 - H8B = 109.40
H8A - C8 - H8B = 108.00
C10 - C9 - C8 = 111.00(2)
C10 - C9 - H9A = 109.40
C8 - C9 - H9A = 109.40
C10 - C9 - H9B = 109.40
C8 - C9 - H9B = 109.40
H9A - C9 - H9B = 108.00
C11 - C10 - C9 = 111.10(19)
C11 - C10 - H10A = 109.40
C9 - C10 - H10A = 109.40
C11 - C10 - H10B = 109.40
C9 - C10 - H10B = 109.40
H10A - C10 - H10B = 108.00
C10 - C11 - C12 = 111.61(18)
C10 - C11 - H11A = 109.30
C12 - C11 - H11A = 109.30
C10 - C11 - H11B = 109.30
C12 - C11 - H11B = 109.30
H11A - C11 - H11B = 108.00
C11 - C12 - C7 = 111.76(17)
C11 - C12 - H12A = 109.30
C7 - C12 - H12A = 109.30
C11 - C12 - H12B = 109.30
C7 - C12 - H12B = 109.30
H12A - C12 - H12B = 107.90
C14 - C13 - C18 = 118.07(16)
C14 - C13 - P1 = 122.50(14)
C18 - C13 - P1 = 119.44(13)
C15 - C14 - C13 = 121.71(18)
C15 - C14 - H14 = 119.10
C13 - C14 - H14 = 119.10
C16 - C15 - C14 = 119.70(17)
C16 - C15 - H15 = 120.20
C14 - C15 - H15 = 120.20
C17 - C16 - C15 = 119.66(17)
C17 - C16 - H16 = 120.20
C15 - C16 - H16 = 120.20

C16	- C17	- C18	=	121.24(17)
C16	- C17	- H17	=	119.40
C18	- C17	- H17	=	119.40
C17	- C18	- C13	=	119.52(15)
C17	- C18	- C19	=	119.47(15)
C13	- C18	- C19	=	120.99(15)
C24	- C19	- C20	=	119.34(15)
C24	- C19	- C18	=	119.73(15)
C20	- C19	- C18	=	120.84(15)
C21	- C20	- C19	=	118.99(16)
C21	- C20	- C25	=	116.25(15)
C19	- C20	- C25	=	124.76(15)
C22	- C21	- C20	=	121.28(17)
C22	- C21	- H21	=	119.40
C20	- C21	- H21	=	119.40
C21	- C22	- C23	=	119.68(17)
C21	- C22	- H22	=	120.20
C23	- C22	- H22	=	120.20
C22	- C23	- C24	=	121.00(17)
C22	- C23	- H23	=	119.50
C24	- C23	- H23	=	119.50
C23	- C24	- C19	=	119.70(16)
C23	- C24	- C39	=	117.03(15)
C19	- C24	- C39	=	123.18(15)
C32	- C25	- C26	=	120.92(16)
C32	- C25	- C20	=	119.86(16)
C26	- C25	- C20	=	118.90(15)
C27	- C26	- C31	=	118.81(17)
C27	- C26	- C25	=	120.77(16)
C31	- C26	- C25	=	120.38(16)
C26	- C27	- C28	=	120.21(18)
C26	- C27	- H27	=	119.90
C28	- C27	- H27	=	119.90
C29	- C28	- C27	=	120.50(2)
C29	- C28	- H28	=	119.70
C27	- C28	- H28	=	119.70
C28	- C29	- C30	=	119.87(18)
C28	- C29	- H29	=	120.10
C30	- C29	- H29	=	120.10
C29	- C30	- C31	=	120.01(19)
C29	- C30	- H30	=	120.00
C31	- C30	- H30	=	120.00
C30	- C31	- C26	=	120.56(19)
C30	- C31	- H31	=	119.70
C26	- C31	- H31	=	119.70
C25	- C32	- C33	=	129.02(17)
C25	- C32	- H32	=	115.50
C33	- C32	- H32	=	115.50
C38	- C33	- C34	=	117.78(17)
C38	- C33	- C32	=	119.44(17)
C34	- C33	- C32	=	122.57(17)
C35	- C34	- C33	=	120.68(19)

C35 - C34 - H34 = 119.70
C33 - C34 - H34 = 119.70
C36 - C35 - C34 = 120.50(2)
C36 - C35 - H35 = 119.70
C34 - C35 - H35 = 119.70
C37 - C36 - C35 = 119.65(19)
C37 - C36 - H36 = 120.20
C35 - C36 - H36 = 120.20
C36 - C37 - C38 = 120.20(2)
C36 - C37 - H37 = 119.90
C38 - C37 - H37 = 119.90
C37 - C38 - C33 = 121.14(19)
C37 - C38 - H38 = 119.40
C33 - C38 - H38 = 119.40
C46 - C39 - C40 = 121.61(16)
C46 - C39 - C24 = 118.17(16)
C40 - C39 - C24 = 120.04(15)
C45 - C40 - C41 = 118.48(17)
C45 - C40 - C39 = 120.58(16)
C41 - C40 - C39 = 120.66(16)
C40 - C41 - C42 = 120.57(19)
C40 - C41 - H41 = 119.70
C42 - C41 - H41 = 119.70
C43 - C42 - C41 = 120.30(2)
C43 - C42 - H42 = 119.90
C41 - C42 - H42 = 119.90
C42 - C43 - C44 = 119.43(19)
C42 - C43 - H43 = 120.30
C44 - C43 - H43 = 120.30
C43 - C44 - C45 = 120.70(2)
C43 - C44 - H44 = 119.70
C45 - C44 - H44 = 119.70
C44 - C45 - C40 = 120.52(19)
C44 - C45 - H45 = 119.70
C40 - C45 - H45 = 119.70
C39 - C46 - C47 = 129.31(17)
C39 - C46 - H46 = 115.30
C47 - C46 - H46 = 115.30
C52 - C47 - C48 = 117.53(17)
C52 - C47 - C46 = 118.64(18)
C48 - C47 - C46 = 123.80(17)
C49 - C48 - C47 = 120.98(18)
C49 - C48 - H48 = 119.50
C47 - C48 - H48 = 119.50
C48 - C49 - C50 = 120.10(2)
C48 - C49 - H49 = 119.90
C50 - C49 - H49 = 119.90
C51 - C50 - C49 = 120.07(19)
C51 - C50 - H50 = 120.00
C49 - C50 - H50 = 120.00
C50 - C51 - C52 = 119.80(19)
C50 - C51 - H51 = 120.10

C52 - C51 - H51 = 120.10
C51 - C52 - C47 = 121.40(2)
C51 - C52 - H52 = 119.30
C47 - C52 - H52 = 119.30
C65 - P2 - C53 = 101.96(8)
C65 - P2 - C59 = 99.97(8)
C53 - P2 - C59 = 105.34(8)
C54 - C53 - C58 = 109.91(15)
C54 - C53 - P2 = 110.92(12)
C58 - C53 - P2 = 108.49(12)
C54 - C53 - H53 = 109.20
C58 - C53 - H53 = 109.20
P2 - C53 - H53 = 109.20
C55 - C54 - C53 = 111.32(16)
C55 - C54 - H54A = 109.40
C53 - C54 - H54A = 109.40
C55 - C54 - H54B = 109.40
C53 - C54 - H54B = 109.40
H54A - C54 - H54B = 108.00
C56 - C55 - C54 = 111.65(17)
C56 - C55 - H55A = 109.30
C54 - C55 - H55A = 109.30
C56 - C55 - H55B = 109.30
C54 - C55 - H55B = 109.30
H55A - C55 - H55B = 108.00
C55 - C56 - C57 = 110.90(16)
C55 - C56 - H56A = 109.50
C57 - C56 - H56A = 109.50
C55 - C56 - H56B = 109.50
C57 - C56 - H56B = 109.50
H56A - C56 - H56B = 108.00
C56 - C57 - C58 = 111.21(16)
C56 - C57 - H57A = 109.40
C58 - C57 - H57A = 109.40
C56 - C57 - H57B = 109.40
C58 - C57 - H57B = 109.40
H57A - C57 - H57B = 108.00
C57 - C58 - C53 = 113.02(15)
C57 - C58 - H58A = 109.00
C53 - C58 - H58A = 109.00
C57 - C58 - H58B = 109.00
C53 - C58 - H58B = 109.00
H58A - C58 - H58B = 107.80
C60 - C59 - C64 = 110.61(15)
C60 - C59 - P2 = 118.05(13)
C64 - C59 - P2 = 110.95(13)
C60 - C59 - H59 = 105.40
C64 - C59 - H59 = 105.40
P2 - C59 - H59 = 105.40
C61 - C60 - C59 = 111.88(16)
C61 - C60 - H60A = 109.20
C59 - C60 - H60A = 109.20

C61 - C60 - H60B = 109.20
C59 - C60 - H60B = 109.20
H60A - C60 - H60B = 107.90
C62 - C61 - C60 = 111.47(18)
C62 - C61 - H61A = 109.30
C60 - C61 - H61A = 109.30
C62 - C61 - H61B = 109.30
C60 - C61 - H61B = 109.30
H61A - C61 - H61B = 108.00
C63 - C62 - C61 = 110.67(16)
C63 - C62 - H62A = 109.50
C61 - C62 - H62A = 109.50
C63 - C62 - H62B = 109.50
C61 - C62 - H62B = 109.50
H62A - C62 - H62B = 108.10
C62 - C63 - C64 = 111.67(16)
C62 - C63 - H63A = 109.30
C64 - C63 - H63A = 109.30
C62 - C63 - H63B = 109.30
C64 - C63 - H63B = 109.30
H63A - C63 - H63B = 107.90
C63 - C64 - C59 = 112.08(16)
C63 - C64 - H64A = 109.20
C59 - C64 - H64A = 109.20
C63 - C64 - H64B = 109.20
C59 - C64 - H64B = 109.20
H64A - C64 - H64B = 107.90
C70 - C65 - C66 = 117.71(16)
C70 - C65 - P2 = 121.84(13)
C66 - C65 - P2 = 120.39(13)
C67 - C66 - C65 = 119.28(15)
C67 - C66 - C71 = 115.97(14)
C65 - C66 - C71 = 124.65(15)
C68 - C67 - C66 = 121.63(16)
C68 - C67 - H67 = 119.20
C66 - C67 - H67 = 119.20
C67 - C68 - C69 = 119.20(17)
C67 - C68 - H68 = 120.40
C69 - C68 - H68 = 120.40
C70 - C69 - C68 = 120.01(17)
C70 - C69 - H69 = 120.00
C68 - C69 - H69 = 120.00
C69 - C70 - C65 = 122.01(17)
C69 - C70 - H70 = 119.00
C65 - C70 - H70 = 119.00
C72 - C71 - C76 = 118.66(15)
C72 - C71 - C66 = 121.94(15)
C76 - C71 - C66 = 119.36(14)
C73 - C72 - C71 = 119.60(16)
C73 - C72 - C91 = 116.78(15)
C71 - C72 - C91 = 123.52(15)
C74 - C73 - C72 = 121.50(16)

C74 - C73 - H73 = 119.30
C72 - C73 - H73 = 119.30
C73 - C74 - C75 = 119.06(16)
C73 - C74 - H74 = 120.50
C75 - C74 - H74 = 120.50
C74 - C75 - C76 = 121.05(17)
C74 - C75 - H75 = 119.50
C76 - C75 - H75 = 119.50
C75 - C76 - C71 = 120.02(16)
C75 - C76 - C77 = 117.33(15)
C71 - C76 - C77 = 122.59(15)
C84 - C77 - C78 = 125.36(16)
C84 - C77 - C76 = 117.35(16)
C78 - C77 - C76 = 117.24(15)
C79 - C78 - C83 = 118.65(16)
C79 - C78 - C77 = 121.14(15)
C83 - C78 - C77 = 120.17(16)
C80 - C79 - C78 = 120.96(17)
C80 - C79 - H79 = 119.50
C78 - C79 - H79 = 119.50
C79 - C80 - C81 = 119.96(18)
C79 - C80 - H80 = 120.00
C81 - C80 - H80 = 120.00
C82 - C81 - C80 = 119.79(18)
C82 - C81 - H81 = 120.10
C80 - C81 - H81 = 120.10
C81 - C82 - C83 = 120.44(18)
C81 - C82 - H82 = 119.80
C83 - C82 - H82 = 119.80
C82 - C83 - C78 = 120.18(18)
C82 - C83 - H83 = 119.90
C78 - C83 - H83 = 119.90
C77 - C84 - C85 = 130.98(17)
C77 - C84 - H84 = 114.50
C85 - C84 - H84 = 114.50
C86 - C85 - C90 = 117.79(17)
C86 - C85 - C84 = 117.99(17)
C90 - C85 - C84 = 124.15(17)
C87 - C86 - C85 = 121.26(19)
C87 - C86 - H86 = 119.40
C85 - C86 - H86 = 119.40
C86 - C87 - C88 = 120.10(2)
C86 - C87 - H87 = 120.00
C88 - C87 - H87 = 120.00
C89 - C88 - C87 = 119.64(18)
C89 - C88 - H88 = 120.20
C87 - C88 - H88 = 120.20
C88 - C89 - C90 = 120.28(19)
C88 - C89 - H89 = 119.90
C90 - C89 - H89 = 119.90
C89 - C90 - C85 = 120.91(19)
C89 - C90 - H90 = 119.50

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C85    - C90    - H90    =  119.50
C98    - C91    - C92    =  128.81(16)
C98    - C91    - C72    =  114.08(15)
C92    - C91    - C72    =  116.86(14)
C97    - C92    - C93    =  118.01(17)
C97    - C92    - C91    =  122.95(16)
C93    - C92    - C91    =  118.98(16)
C94    - C93    - C92    =  121.10(19)
C94    - C93    - H93    =  119.40
C92    - C93    - H93    =  119.40
C95    - C94    - C93    =  120.00(2)
C95    - C94    - H94    =  120.00
C93    - C94    - H94    =  120.00
C96    - C95    - C94    =  119.80(19)
C96    - C95    - H95    =  120.10
C94    - C95    - H95    =  120.10
C95    - C96    - C97    =  120.50(2)
C95    - C96    - H96    =  119.80
C97    - C96    - H96    =  119.80
C96    - C97    - C92    =  120.60(19)
C96    - C97    - H97    =  119.70
C92    - C97    - H97    =  119.70
C91    - C98    - C99    =  134.66(17)
C91    - C98    - H98    =  112.70
C99    - C98    - H98    =  112.70
C100   - C99    - C104   =  117.65(16)
C100   - C99    - C98    =  127.01(16)
C104   - C99    - C98    =  115.23(16)
C101   - C100   - C99    =  120.26(17)
C101   - C100   - H100   =  119.90
C99    - C100   - H100   =  119.90
C102   - C101   - C100   =  120.99(18)
C102   - C101   - H101   =  119.50
C100   - C101   - H101   =  119.50
C101   - C102   - C103   =  119.57(17)
C101   - C102   - H102   =  120.20
C103   - C102   - H102   =  120.20
C104   - C103   - C102   =  119.77(18)
C104   - C103   - H103   =  120.10
C102   - C103   - H103   =  120.10
C103   - C104   - C99    =  121.74(17)
C103   - C104   - H104   =  119.10
C99    - C104   - H104   =  119.10
Cl1    - C105   - Cl2    =  111.22(13)
Cl1    - C105   - H10C   =  109.40
Cl2    - C105   - H10C   =  109.40
Cl1    - C105   - H10D   =  109.40
Cl2    - C105   - H10D   =  109.40
H10C   - C105   - H10D   =  108.00
```

Table S10. Torsion angles [°] for **4aa**.

C13	- P1	- C1	- C6	= -179.31(16)
C7	- P1	- C1	- C6	= -75.61(17)
C13	- P1	- C1	- C2	= 60.56(15)
C7	- P1	- C1	- C2	= 164.26(13)
C6	- C1	- C2	- C3	= 51.00(2)
P1	- C1	- C2	- C3	= 170.93(15)
C1	- C2	- C3	- C4	= -54.50(3)
C2	- C3	- C4	- C5	= 56.80(3)
C3	- C4	- C5	- C6	= -57.80(3)
C4	- C5	- C6	- C1	= 56.50(3)
C2	- C1	- C6	- C5	= -51.70(3)
P1	- C1	- C6	- C5	= -170.65(19)
C13	- P1	- C7	- C8	= 60.15(16)
C1	- P1	- C7	- C8	= -45.63(17)
C13	- P1	- C7	- C12	= -170.48(13)
C1	- P1	- C7	- C12	= 83.75(15)
C12	- C7	- C8	- C9	= 56.60(2)
P1	- C7	- C8	- C9	= -173.24(16)
C7	- C8	- C9	- C10	= -57.40(3)
C8	- C9	- C10	- C11	= 56.00(3)
C9	- C10	- C11	- C12	= -54.80(3)
C10	- C11	- C12	- C7	= 54.90(2)
C8	- C7	- C12	- C11	= -55.50(2)
P1	- C7	- C12	- C11	= 170.96(14)
C7	- P1	- C13	- C14	= -77.35(18)
C1	- P1	- C13	- C14	= 32.15(19)
C7	- P1	- C13	- C18	= 103.04(15)
C1	- P1	- C13	- C18	= -147.45(15)
C18	- C13	- C14	- C15	= -1.20(3)
P1	- C13	- C14	- C15	= 179.22(17)
C13	- C14	- C15	- C16	= 2.80(3)
C14	- C15	- C16	- C17	= -1.30(3)
C15	- C16	- C17	- C18	= -1.90(3)
C16	- C17	- C18	- C13	= 3.50(3)
C16	- C17	- C18	- C19	= -175.34(16)
C14	- C13	- C18	- C17	= -2.00(3)
P1	- C13	- C18	- C17	= 177.67(13)
C14	- C13	- C18	- C19	= 176.87(17)
P1	- C13	- C18	- C19	= -3.50(2)
C17	- C18	- C19	- C24	= -96.76(19)
C13	- C18	- C19	- C24	= 84.40(2)
C17	- C18	- C19	- C20	= 86.70(2)
C13	- C18	- C19	- C20	= -92.10(2)
C24	- C19	- C20	- C21	= -1.40(2)
C18	- C19	- C20	- C21	= 175.16(15)
C24	- C19	- C20	- C25	= 178.38(16)
C18	- C19	- C20	- C25	= -5.10(3)
C19	- C20	- C21	- C22	= 0.10(3)
C25	- C20	- C21	- C22	= -179.67(17)

C20	- C21	- C22	- C23	= 1.10(3)
C21	- C22	- C23	- C24	= -1.00(3)
C22	- C23	- C24	- C19	= -0.30(3)
C22	- C23	- C24	- C39	= -176.93(17)
C20	- C19	- C24	- C23	= 1.50(2)
C18	- C19	- C24	- C23	= -175.12(16)
C20	- C19	- C24	- C39	= 177.92(15)
C18	- C19	- C24	- C39	= 1.30(2)
C21	- C20	- C25	- C32	= -45.10(2)
C19	- C20	- C25	- C32	= 135.13(18)
C21	- C20	- C25	- C26	= 128.41(17)
C19	- C20	- C25	- C26	= -51.40(2)
C32	- C25	- C26	- C27	= 125.64(19)
C20	- C25	- C26	- C27	= -47.80(2)
C32	- C25	- C26	- C31	= -51.90(2)
C20	- C25	- C26	- C31	= 134.71(17)
C31	- C26	- C27	- C28	= 1.20(3)
C25	- C26	- C27	- C28	= -176.32(17)
C26	- C27	- C28	- C29	= 0.20(3)
C27	- C28	- C29	- C30	= -1.00(3)
C28	- C29	- C30	- C31	= 0.40(3)
C29	- C30	- C31	- C26	= 1.10(3)
C27	- C26	- C31	- C30	= -1.80(3)
C25	- C26	- C31	- C30	= 175.69(17)
C26	- C25	- C32	- C33	= -8.50(3)
C20	- C25	- C32	- C33	= 164.89(17)
C25	- C32	- C33	- C38	= 152.06(19)
C25	- C32	- C33	- C34	= -33.40(3)
C38	- C33	- C34	- C35	= -1.00(3)
C32	- C33	- C34	- C35	= -175.71(17)
C33	- C34	- C35	- C36	= 0.70(3)
C34	- C35	- C36	- C37	= 0.00(3)
C35	- C36	- C37	- C38	= -0.20(3)
C36	- C37	- C38	- C33	= -0.10(3)
C34	- C33	- C38	- C37	= 0.80(3)
C32	- C33	- C38	- C37	= 175.60(17)
C23	- C24	- C39	- C46	= 51.00(2)
C19	- C24	- C39	- C46	= -125.54(18)
C23	- C24	- C39	- C40	= -124.11(18)
C19	- C24	- C39	- C40	= 59.30(2)
C46	- C39	- C40	- C45	= 56.60(2)
C24	- C39	- C40	- C45	= -128.43(18)
C46	- C39	- C40	- C41	= -117.30(2)
C24	- C39	- C40	- C41	= 57.70(2)
C45	- C40	- C41	- C42	= -1.40(3)
C39	- C40	- C41	- C42	= 172.64(17)
C40	- C41	- C42	- C43	= -0.10(3)
C41	- C42	- C43	- C44	= 1.20(3)
C42	- C43	- C44	- C45	= -0.80(3)
C43	- C44	- C45	- C40	= -0.70(3)
C41	- C40	- C45	- C44	= 1.80(3)
C39	- C40	- C45	- C44	= -172.22(17)

C40 - C39 - C46 - C47 = 2.90(3)
C24 - C39 - C46 - C47 = -172.17(17)
C39 - C46 - C47 - C52 = -150.53(19)
C39 - C46 - C47 - C48 = 31.50(3)
C52 - C47 - C48 - C49 = 2.50(3)
C46 - C47 - C48 - C49 = -179.53(17)
C47 - C48 - C49 - C50 = -0.40(3)
C48 - C49 - C50 - C51 = -1.50(3)
C49 - C50 - C51 - C52 = 1.10(3)
C50 - C51 - C52 - C47 = 1.10(3)
C48 - C47 - C52 - C51 = -2.80(3)
C46 - C47 - C52 - C51 = 179.07(17)
C65 - P2 - C53 - C54 = 170.20(13)
C59 - P2 - C53 - C54 = 66.21(14)
C65 - P2 - C53 - C58 = -68.99(13)
C59 - P2 - C53 - C58 = -172.98(12)
C58 - C53 - C54 - C55 = 54.50(2)
P2 - C53 - C54 - C55 = 174.45(14)
C53 - C54 - C55 - C56 = -56.90(2)
C54 - C55 - C56 - C57 = 56.50(2)
C55 - C56 - C57 - C58 = -54.60(2)
C56 - C57 - C58 - C53 = 54.30(2)
C54 - C53 - C58 - C57 = -53.80(2)
P2 - C53 - C58 - C57 = -175.26(13)
C65 - P2 - C59 - C60 = -69.73(15)
C53 - P2 - C59 - C60 = 35.73(16)
C65 - P2 - C59 - C64 = 161.14(12)
C53 - P2 - C59 - C64 = -93.41(13)
C64 - C59 - C60 - C61 = -53.50(2)
P2 - C59 - C60 - C61 = 177.21(14)
C59 - C60 - C61 - C62 = 55.70(2)
C60 - C61 - C62 - C63 = -56.40(2)
C61 - C62 - C63 - C64 = 55.90(2)
C62 - C63 - C64 - C59 = -55.00(2)
C60 - C59 - C64 - C63 = 53.10(2)
P2 - C59 - C64 - C63 = -173.93(12)
C53 - P2 - C65 - C70 = -36.41(16)
C59 - P2 - C65 - C70 = 71.75(16)
C53 - P2 - C65 - C66 = 146.35(14)
C59 - P2 - C65 - C66 = -105.49(14)
C70 - C65 - C66 - C67 = -4.30(2)
P2 - C65 - C66 - C67 = 173.01(13)
C70 - C65 - C66 - C71 = 171.87(16)
P2 - C65 - C66 - C71 = -10.80(2)
C65 - C66 - C67 - C68 = 3.80(3)
C71 - C66 - C67 - C68 = -172.72(16)
C66 - C67 - C68 - C69 = -0.40(3)
C67 - C68 - C69 - C70 = -2.40(3)
C68 - C69 - C70 - C65 = 1.80(3)
C66 - C65 - C70 - C69 = 1.70(3)
P2 - C65 - C70 - C69 = -175.66(15)
C67 - C66 - C71 - C72 = -91.65(19)

C65 - C66 - C71 - C72 = 92.00(2)
C67 - C66 - C71 - C76 = 86.03(19)
C65 - C66 - C71 - C76 = -90.30(2)
C76 - C71 - C72 - C73 = -3.40(2)
C66 - C71 - C72 - C73 = 174.32(15)
C76 - C71 - C72 - C91 = 172.73(15)
C66 - C71 - C72 - C91 = -9.60(2)
C71 - C72 - C73 - C74 = 0.80(3)
C91 - C72 - C73 - C74 = -175.58(16)
C72 - C73 - C74 - C75 = 1.90(3)
C73 - C74 - C75 - C76 = -2.00(3)
C74 - C75 - C76 - C71 = -0.70(3)
C74 - C75 - C76 - C77 = 176.65(17)
C72 - C71 - C76 - C75 = 3.30(2)
C66 - C71 - C76 - C75 = -174.43(15)
C72 - C71 - C76 - C77 = -173.84(15)
C66 - C71 - C76 - C77 = 8.40(2)
C75 - C76 - C77 - C84 = -57.90(2)
C71 - C76 - C77 - C84 = 119.35(19)
C75 - C76 - C77 - C78 = 119.64(18)
C71 - C76 - C77 - C78 = -63.10(2)
C84 - C77 - C78 - C79 = -52.80(3)
C76 - C77 - C78 - C79 = 129.91(17)
C84 - C77 - C78 - C83 = 129.64(19)
C76 - C77 - C78 - C83 = -47.70(2)
C83 - C78 - C79 - C80 = -1.50(3)
C77 - C78 - C79 - C80 = -179.12(17)
C78 - C79 - C80 - C81 = 0.30(3)
C79 - C80 - C81 - C82 = 0.60(3)
C80 - C81 - C82 - C83 = -0.40(3)
C81 - C82 - C83 - C78 = -0.80(3)
C79 - C78 - C83 - C82 = 1.80(3)
C77 - C78 - C83 - C82 = 179.40(16)
C78 - C77 - C84 - C85 = -2.40(3)
C76 - C77 - C84 - C85 = 174.96(17)
C77 - C84 - C85 - C86 = 154.11(19)
C77 - C84 - C85 - C90 = -28.90(3)
C90 - C85 - C86 - C87 = 3.20(3)
C84 - C85 - C86 - C87 = -179.71(17)
C85 - C86 - C87 - C88 = -1.60(3)
C86 - C87 - C88 - C89 = -0.50(3)
C87 - C88 - C89 - C90 = 1.00(3)
C88 - C89 - C90 - C85 = 0.60(3)
C86 - C85 - C90 - C89 = -2.70(3)
C84 - C85 - C90 - C89 = -179.61(18)
C73 - C72 - C91 - C98 = 53.70(2)
C71 - C72 - C91 - C98 = -122.53(18)
C73 - C72 - C91 - C92 = -121.16(17)
C71 - C72 - C91 - C92 = 62.60(2)
C98 - C91 - C92 - C97 = 57.30(3)
C72 - C91 - C92 - C97 = -128.70(18)
C98 - C91 - C92 - C93 = -125.40(2)

C72 - C91 - C92 - C93 = 48.50(2)
C97 - C92 - C93 - C94 = 0.00(3)
C91 - C92 - C93 - C94 = -177.30(18)
C92 - C93 - C94 - C95 = 0.10(3)
C93 - C94 - C95 - C96 = 0.10(3)
C94 - C95 - C96 - C97 = -0.40(3)
C95 - C96 - C97 - C92 = 0.50(3)
C93 - C92 - C97 - C96 = -0.30(3)
C91 - C92 - C97 - C96 = 176.91(18)
C92 - C91 - C98 - C99 = 7.00(3)
C72 - C91 - C98 - C99 = -167.07(17)
C91 - C98 - C99 - C100 = -4.40(3)
C91 - C98 - C99 - C104 = 171.66(19)
C104 - C99 - C100 - C101 = 0.20(3)
C98 - C99 - C100 - C101 = 176.09(17)
C99 - C100 - C101 - C102 = -0.70(3)
C100 - C101 - C102 - C103 = 0.40(3)
C101 - C102 - C103 - C104 = 0.60(3)
C102 - C103 - C104 - C99 = -1.10(3)
C100 - C99 - C104 - C103 = 0.80(3)
C98 - C99 - C104 - C103 = -175.64(16)

Crystal measurement for 5a:

Crystallization by diffusion method from CH_2Cl_2 solution with *n*-hexane has afforded single crystal to analyze by X-ray diffraction.

The single crystal X-ray diffraction studies were carried out on D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector [*], Mo-*Kα* radiation (*λ* = 0.71073 , multilayer monochromator) , *T* = 150 K; triclinic *P* -1 (I.T.#2), *a* = 11.1775(11), *b* = 14.2939(14), *c* = 15.4307(16) , *α* = 90.257(3), *β* = 97.380(4), *γ* = 91.255(4) , *V* = 2444.3(4) ^{3}. *Z* = 1, *d* = 1.432 g.cm^{-3}, *μ* = 0.777 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program [1], and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*) [2]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 11239 unique intensities and 559 parameters converged at ωR_F^2 = 0.1633 (R_F = 0.0647) for 7972 observed reflections with $I > 2\sigma(I)$.

[1] G. M. Sheldrick, Acta Cryst. A71 (2015) 3-8
[2] Sheldrick G.M., Acta Cryst. C71 (2015) 3-8

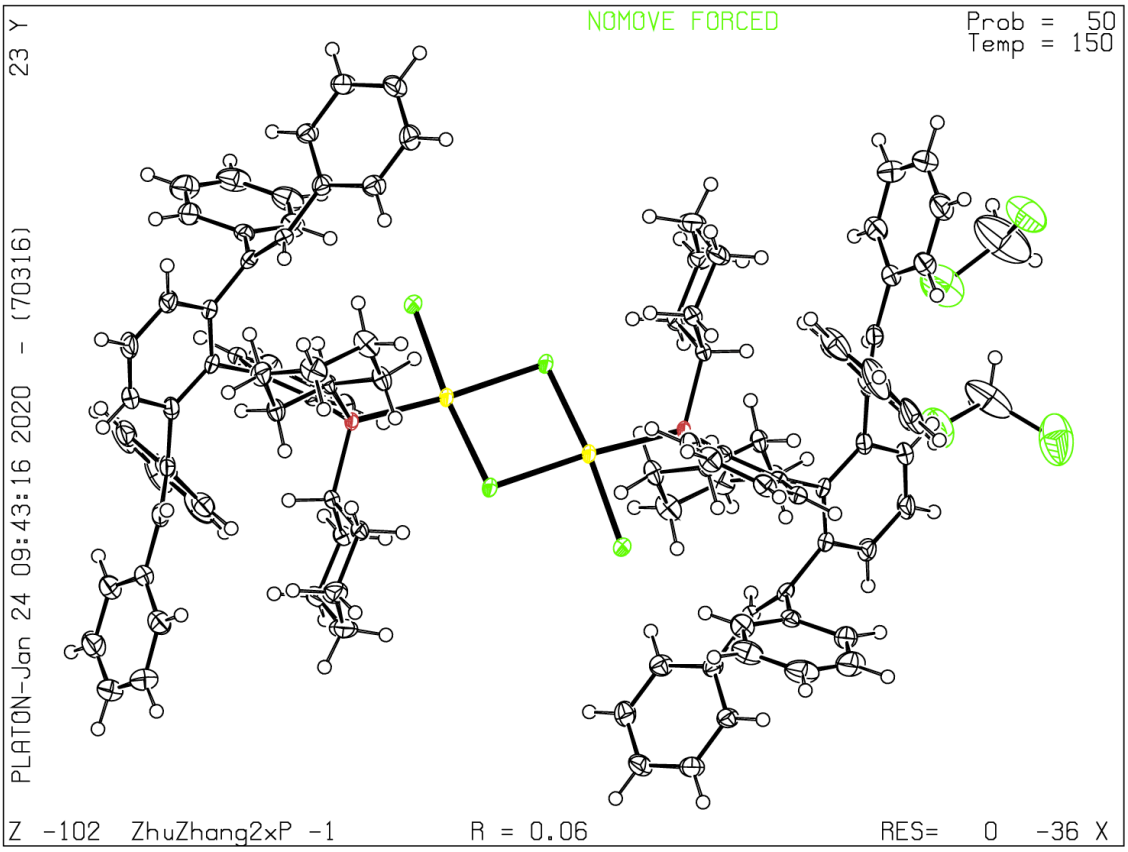


Figure S3. ORTEP diagram of the solid-state molecular structure of **5a**. Thermal ellipsoids are at the 50% probability level. (CCDC 1982983).

Table S11. Crystal data and structure refinement for **50**.

Empirical formula	$C_{108}H_{110}Cl_{12}P_2Pd_2$
Formula weight	2108.09 g/mol
Temperature	150 *K*
Wavelength	0.71073 Å
Crystal system, space group	triclinic, *P* -1
Unit cell dimensions	a = 11.1775(11) Å
	b = 14.2939(14) Å
	c = 15.4307(16) Å
	α = 90.257(3) °
	β = 97.380(4) °
	γ = 91.255(4) °
Volume	2444.3(4) $Å^3$
Z, Calculated density	1, 1.432 $g.cm^{-3}$
Absorption coefficient	0.777 mm^{-1}
F(000)	1084
Crystal size	0.330 x 0.220 x 0.130 mm
Crystal color	orange
Crystal description	pism
Theta range for data collection	2.300 to 27.588 °
$(\sin\theta/\lambda)_{max}$ ($Å^{-1}$)	0.652
h_min, h_max	-14, 14

k_min, k_max	-18, 18
l_min, l_max	-20, 20
Reflections collected / unique	40084 / 11239 [R(int)[a] = 0.0838]
Reflections [I>2σ]	7972
Completeness to theta_max	0.991
Absorption correction type	multi-scan
Max. and min. transmission	0.904, 0.771
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11239 / 0 / 559
[b]S (Goodness-of-fit)	1.005
Final *R* indices [I>2σ]	$R1^c$ = 0.0647, $wR2^d$ = 0.1633
R indices (all data)	$R1^c$ = 0.1025, $wR2^d$ = 0.1904
Largest diff. peak and hole	1.809 and -1.631 $e^-.Å^{-3}$

Table S11. **Fractional atomic coordinates, site occupancy (%) and equivalent isotropic displacement parameters (Å²)** for **5a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	occ.	U(eq)	adp
Pd1	0.43031(3)	0.93359(2)	0.07514(2)	1	0.01642(12)	Uani
Cl1	0.58505(11)	0.91291(8)	-0.00867(8)	1	0.0214(3)	Uani
Cl2	0.26966(11)	0.96535(9)	0.14673(8)	1	0.0249(3)	Uani
P1	0.43226(11)	0.79354(8)	0.14286(7)	1	0.0141(2)	Uani
C1	0.5575(4)	0.7142(3)	0.1322(3)	1	0.0188(10)	Uani
H1	0.540859	0.656989	0.166205	1	0.023	Uiso
C2	0.5658(5)	0.6800(3)	0.0385(3)	1	0.0223(10)	Uani
H2A	0.486699	0.653102	0.012758	1	0.027	Uiso
H2B	0.585626	0.733680	0.002176	1	0.027	Uiso
C3	0.6626(5)	0.6060(4)	0.0381(4)	1	0.0337(13)	Uani
H3A	0.638113	0.549615	0.069107	1	0.040	Uiso
H3B	0.669512	0.587622	-0.022991	1	0.040	Uiso
C4	0.7852(5)	0.6422(4)	0.0820(5)	1	0.0404(15)	Uani
H4A	0.814636	0.693588	0.046897	1	0.048	Uiso
H4B	0.844064	0.591254	0.084746	1	0.048	Uiso
C5	0.7757(5)	0.6779(4)	0.1743(4)	1	0.0326(13)	Uani
H5A	0.754208	0.624977	0.210920	1	0.039	Uiso
H5B	0.855099	0.703945	0.200385	1	0.039	Uiso
C6	0.6813(5)	0.7529(4)	0.1739(4)	1	0.0241(11)	Uani
H6A	0.705167	0.807626	0.140410	1	0.029	Uiso
H6B	0.676063	0.773688	0.234517	1	0.029	Uiso
C7	0.2906(4)	0.7301(3)	0.0990(3)	1	0.0171(9)	Uani
H7	0.226912	0.752861	0.133376	1	0.021	Uiso
C8	0.2511(5)	0.7585(4)	0.0032(3)	1	0.0246(11)	Uani
H8A	0.245919	0.827476	-0.000028	1	0.030	Uiso
H8B	0.313000	0.738930	-0.033252	1	0.030	Uiso
C9	0.1302(5)	0.7148(4)	-0.0333(4)	1	0.0312(12)	Uani
H9A	0.111657	0.731276	-0.095802	1	0.037	Uiso
H9B	0.066369	0.740622	-0.001879	1	0.037	Uiso
C10	0.1298(5)	0.6081(4)	-0.0245(4)	1	0.0321(13)	Uani
H10A	0.048095	0.582181	-0.044998	1	0.039	Uiso
H10B	0.186825	0.581276	-0.061386	1	0.039	Uiso

C11	0.1661(5)	0.5809(4)	0.0704(4)	1	0.0266(11) Uani
H11A	0.168617	0.511866	0.074665	1	0.032 Uiso
H11B	0.104671	0.602862	0.106174	1	0.032 Uiso
C12	0.2891(5)	0.6227(3)	0.1068(3)	1	0.0220(10) Uani
H12A	0.351824	0.596696	0.074422	1	0.026 Uiso
H12B	0.308236	0.605335	0.169016	1	0.026 Uiso
C13	0.4471(4)	0.8209(3)	0.2609(3)	1	0.0157(9) Uani
C14	0.5236(5)	0.8997(4)	0.2827(3)	1	0.0239(11) Uani
H14	0.559052	0.930652	0.237634	1	0.029 Uiso
C15	0.5485(5)	0.9333(4)	0.3671(4)	1	0.0271(11) Uani
H15	0.602894	0.984942	0.379958	1	0.033 Uiso
C16	0.4940(5)	0.8914(4)	0.4332(3)	1	0.0263(11) Uani
H16	0.508704	0.914935	0.491307	1	0.032 Uiso
C17	0.4183(4)	0.8153(3)	0.4131(3)	1	0.0202(10) Uani
H17	0.380001	0.787420	0.458434	1	0.024 Uiso
C18	0.3950(4)	0.7767(3)	0.3286(3)	1	0.0159(9) Uani
C19	0.3185(4)	0.6885(3)	0.3202(3)	1	0.0187(10) Uani
C20	0.3726(5)	0.6002(4)	0.3322(3)	1	0.0221(10) Uani
C21	0.2981(5)	0.5201(4)	0.3254(4)	1	0.0289(12) Uani
H21	0.333655	0.460425	0.333262	1	0.035 Uiso
C22	0.1744(5)	0.5253(4)	0.3076(4)	1	0.0307(12) Uani
H22	0.125760	0.469743	0.302334	1	0.037 Uiso
C23	0.1215(5)	0.6115(4)	0.2974(4)	1	0.0265(11) Uani
H23	0.036229	0.614823	0.285271	1	0.032 Uiso
C24	0.1917(5)	0.6940(4)	0.3048(3)	1	0.0209(10) Uani
C25	0.5056(5)	0.5857(4)	0.3534(3)	1	0.0227(10) Uani
C26	0.5569(5)	0.5176(4)	0.3110(3)	1	0.0246(11) Uani
H26	0.508549	0.492106	0.261020	1	0.030 Uiso
C27	0.6794(5)	0.4764(4)	0.3315(4)	1	0.0288(12) Uani
C28	0.7298(6)	0.4331(4)	0.2647(4)	1	0.0373(14) Uani
H28	0.686899	0.432441	0.207355	1	0.045 Uiso
C29	0.8411(7)	0.3907(5)	0.2791(5)	1	0.0506(19) Uani
H29	0.875737	0.364109	0.231799	1	0.061 Uiso
C30	0.9011(6)	0.3879(5)	0.3635(5)	1	0.0487(18) Uani
H30	0.975872	0.356991	0.374570	1	0.058 Uiso
C31	0.8526(6)	0.4296(5)	0.4313(5)	1	0.0434(16) Uani
H31	0.894870	0.428558	0.488780	1	0.052 Uiso
C32	0.7418(5)	0.4734(4)	0.4159(4)	1	0.0333(13) Uani
H32	0.708424	0.501340	0.463119	1	0.040 Uiso
C33	0.5747(5)	0.6404(4)	0.4259(3)	1	0.0253(11) Uani
C34	0.6819(5)	0.6886(4)	0.4158(4)	1	0.0315(12) Uani
H34	0.710810	0.688752	0.360530	1	0.038 Uiso
C35	0.7467(7)	0.7362(4)	0.4858(5)	1	0.0483(18) Uani
H35	0.819938	0.768364	0.478397	1	0.058 Uiso
C36	0.7047(8)	0.7370(5)	0.5669(5)	1	0.054(2) Uani
H36	0.749595	0.769325	0.614780	1	0.065 Uiso
C37	0.5988(8)	0.6914(5)	0.5776(4)	1	0.0487(19) Uani
H37	0.569423	0.692855	0.632646	1	0.058 Uiso
C38	0.5344(6)	0.6428(4)	0.5080(4)	1	0.0338(13) Uani
H38	0.461550	0.610580	0.516237	1	0.041 Uiso
C39	0.1280(4)	0.7855(4)	0.2956(3)	1	0.0205(10) Uani
C40	0.0552(4)	0.8031(4)	0.2217(3)	1	0.0205(10) Uani

H40	0.056219	0.758075	0.176321	1	0.025	Uiso
C41	-0.0266(5)	0.8821(4)	0.2002(3)	1	0.0228(10)	Uani
C42	-0.0450(5)	0.9130(4)	0.1137(3)	1	0.0263(11)	Uani
H42	-0.002936	0.884672	0.071120	1	0.032	Uiso
C43	-0.1235(5)	0.9841(4)	0.0896(4)	1	0.0321(13)	Uani
H43	-0.132487	1.005937	0.031152	1	0.039	Uiso
C44	-0.1892(5)	1.0240(4)	0.1496(4)	1	0.0320(13)	Uani
H44	-0.244229	1.072262	0.132427	1	0.038	Uiso
C45	-0.1739(5)	0.9928(4)	0.2350(4)	1	0.0298(12)	Uani
H45	-0.219222	1.019359	0.276590	1	0.036	Uiso
C46	-0.0926(5)	0.9228(4)	0.2603(3)	1	0.0248(11)	Uani
H46	-0.082041	0.902497	0.319267	1	0.030	Uiso
C47	0.1402(4)	0.8487(4)	0.3733(3)	1	0.0218(10)	Uani
C48	0.1754(5)	0.9414(4)	0.3674(4)	1	0.0294(12)	Uani
H48	0.194631	0.965010	0.313267	1	0.035	Uiso
C49	0.1831(6)	1.0006(5)	0.4399(4)	1	0.0379(14)	Uani
H49	0.207968	1.064237	0.435503	1	0.045	Uiso
C50	0.1543(6)	0.9660(5)	0.5185(4)	1	0.0428(16)	Uani
H50	0.157957	1.006455	0.567787	1	0.051	Uiso
C51	0.1205(6)	0.8740(5)	0.5258(4)	1	0.0438(17)	Uani
H51	0.102168	0.850862	0.580285	1	0.053	Uiso
C52	0.1129(5)	0.8145(4)	0.4539(4)	1	0.0314(13)	Uani
H52	0.089309	0.750685	0.459178	1	0.038	Uiso
Cl4	0.1624(3)	0.31712(16)	0.16303(19)	1	0.0831(7)	Uani
Cl3	0.0748(3)	0.1532(2)	0.2416(2)	1	0.0999(10)	Uani
Cl5	0.4704(3)	0.2695(2)	0.19084(15)	1	0.0903(9)	Uani
Cl6	0.6388(2)	0.18056(17)	0.32189(19)	1	0.0791(7)	Uani
C53	0.1559(10)	0.1994(7)	0.1564(7)	1	0.087(3)	Uani
H53A	0.238616	0.174682	0.163040	1	0.104	Uiso
H53B	0.114410	0.179501	0.098503	1	0.104	Uiso
C54	0.5343(14)	0.1669(9)	0.2337(8)	1	0.125(6)	Uani
H54A	0.468814	0.125165	0.249547	1	0.150	Uiso
H54B	0.571893	0.134979	0.187311	1	0.150	Uiso

Table S12. Bond lengths [Å] for **5a**.

Pd1	- P1 = 2.2615(12)
Pd1	- Cl2 = 2.2785(12)
Pd1	- Cl1 = 2.3120(12)
Pd1	- Cl1_#1 = 2.4263(12)
P1	- C1 = 1.844(5)
P1	- C13 = 1.847(5)
P1	- C7 = 1.856(5)
C1	- C2 = 1.539(7)
C1	- C6 = 1.539(7)
C2	- C3 = 1.531(7)
C3	- C4 = 1.527(9)
C4	- C5 = 1.527(9)
C5	- C6 = 1.520(7)
C7	- C12 = 1.540(6)
C7	- C8 = 1.546(7)
C8	- C9 = 1.516(8)

C9 - C10 = 1.532(8)
C10 - C11 = 1.523(8)
C11 - C12 = 1.525(7)
C13 - C18 = 1.404(6)
C13 - C14 = 1.412(7)
C14 - C15 = 1.379(7)
C15 - C16 = 1.384(8)
C16 - C17 = 1.373(7)
C17 - C18 = 1.404(7)
C18 - C19 = 1.504(7)
C19 - C24 = 1.411(7)
C19 - C20 = 1.414(7)
C20 - C21 = 1.397(8)
C20 - C25 = 1.499(7)
C21 - C22 = 1.379(8)
C22 - C23 = 1.378(8)
C23 - C24 = 1.398(7)
C24 - C39 = 1.501(7)
C25 - C26 = 1.349(7)
C25 - C33 = 1.485(7)
C26 - C27 = 1.499(8)
C27 - C28 = 1.387(8)
C27 - C32 = 1.397(8)
C28 - C29 = 1.389(9)
C29 - C30 = 1.388(11)
C30 - C31 = 1.379(10)
C31 - C32 = 1.393(8)
C33 - C34 = 1.395(8)
C33 - C38 = 1.398(8)
C34 - C35 = 1.388(9)
C35 - C36 = 1.391(11)
C36 - C37 = 1.368(12)
C37 - C38 = 1.388(9)
C39 - C40 = 1.342(7)
C39 - C47 = 1.489(7)
C40 - C41 = 1.481(7)
C41 - C46 = 1.389(7)
C41 - C42 = 1.399(7)
C42 - C43 = 1.378(8)
C43 - C44 = 1.382(8)
C44 - C45 = 1.384(8)
C45 - C46 = 1.390(7)
C47 - C48 = 1.381(8)
C47 - C52 = 1.406(7)
C48 - C49 = 1.393(8)
C49 - C50 = 1.385(9)
C50 - C51 = 1.369(10)
C51 - C52 = 1.388(9)
Cl4 - C53 = 1.685(10)
Cl3 - C53 = 1.809(13)
Cl5 - C54 = 1.740(12)
Cl6 - C54 = 1.683(12)

Table S13. Angles [°] for **5a**.

P1	- Pd1	- Cl2	=	85.85(4)
P1	- Pd1	- Cl1	=	99.74(4)
Cl2	- Pd1	- Cl1	=	173.81(4)
P1	- Pd1	- Cl1_#1	=	175.44(4)
Cl2	- Pd1	- Cl1_#1	=	89.60(4)
Cl1	- Pd1	- Cl1_#1	=	84.81(4)
Pd1	- Cl1	- Pd1_#1	=	95.19(4)
C1	- P1	- C13	=	104.2(2)
C1	- P1	- C7	=	107.1(2)
C13	- P1	- C7	=	114.8(2)
C1	- P1	- Pd1	=	118.79(16)
C13	- P1	- Pd1	=	105.55(15)
C7	- P1	- Pd1	=	106.85(15)
C2	- C1	- C6	=	109.8(4)
C2	- C1	- P1	=	114.9(3)
C6	- C1	- P1	=	113.7(3)
C3	- C2	- C1	=	110.7(4)
C4	- C3	- C2	=	111.6(5)
C3	- C4	- C5	=	110.7(5)
C6	- C5	- C4	=	111.4(5)
C5	- C6	- C1	=	110.2(4)
C12	- C7	- C8	=	110.0(4)
C12	- C7	- P1	=	117.1(3)
C8	- C7	- P1	=	110.3(3)
C9	- C8	- C7	=	112.3(4)
C8	- C9	- C10	=	111.7(5)
C11	- C10	- C9	=	110.3(4)
C10	- C11	- C12	=	111.9(4)
C11	- C12	- C7	=	111.0(4)
C18	- C13	- C14	=	117.8(4)
C18	- C13	- P1	=	130.5(4)
C14	- C13	- P1	=	111.7(3)
C15	- C14	- C13	=	122.2(5)
C14	- C15	- C16	=	119.8(5)
C17	- C16	- C15	=	118.8(5)
C16	- C17	- C18	=	122.9(5)
C17	- C18	- C13	=	118.4(4)
C17	- C18	- C19	=	115.6(4)
C13	- C18	- C19	=	125.9(4)
C24	- C19	- C20	=	119.7(5)
C24	- C19	- C18	=	119.8(4)
C20	- C19	- C18	=	120.4(4)
C21	- C20	- C19	=	118.5(5)
C21	- C20	- C25	=	116.8(5)
C19	- C20	- C25	=	124.7(5)
C22	- C21	- C20	=	121.7(5)
C23	- C22	- C21	=	119.8(5)
C22	- C23	- C24	=	120.9(5)
C23	- C24	- C19	=	119.3(5)
C23	- C24	- C39	=	118.1(5)

C19	- C24	- C39	= 122.6(5)
C26	- C25	- C33	= 121.7(5)
C26	- C25	- C20	= 118.9(5)
C33	- C25	- C20	= 119.1(5)
C25	- C26	- C27	= 129.3(5)
C28	- C27	- C32	= 118.1(5)
C28	- C27	- C26	= 118.5(5)
C32	- C27	- C26	= 123.3(5)
C27	- C28	- C29	= 121.9(6)
C30	- C29	- C28	= 119.0(6)
C31	- C30	- C29	= 120.3(6)
C30	- C31	- C32	= 120.3(7)
C31	- C32	- C27	= 120.4(6)
C34	- C33	- C38	= 118.0(5)
C34	- C33	- C25	= 122.0(5)
C38	- C33	- C25	= 120.0(5)
C35	- C34	- C33	= 120.6(6)
C34	- C35	- C36	= 120.2(7)
C37	- C36	- C35	= 120.0(6)
C36	- C37	- C38	= 120.0(7)
C37	- C38	- C33	= 121.3(6)
C40	- C39	- C47	= 123.0(5)
C40	- C39	- C24	= 119.3(5)
C47	- C39	- C24	= 117.5(4)
C39	- C40	- C41	= 129.7(5)
C46	- C41	- C42	= 118.2(5)
C46	- C41	- C40	= 123.2(4)
C42	- C41	- C40	= 118.4(5)
C43	- C42	- C41	= 120.7(5)
C42	- C43	- C44	= 120.7(5)
C43	- C44	- C45	= 119.2(5)
C44	- C45	- C46	= 120.4(5)
C41	- C46	- C45	= 120.7(5)
C48	- C47	- C52	= 119.1(5)
C48	- C47	- C39	= 121.2(5)
C52	- C47	- C39	= 119.7(5)
C47	- C48	- C49	= 120.7(6)
C50	- C49	- C48	= 119.4(6)
C51	- C50	- C49	= 120.7(6)
C50	- C51	- C52	= 120.3(6)
C51	- C52	- C47	= 119.8(6)
Cl4	- C53	- Cl3	= 109.5(6)
Cl6	- C54	- Cl5	= 115.6(7)

Table S11. Torsion angles [°] for **5a**.

C13	- P1	- C1	- C2	= 179.9(3)
C7	- P1	- C1	- C2	= 57.8(4)
Pd1	- P1	- C1	- C2	= -63.1(4)
C13	- P1	- C1	- C6	= -52.5(4)
C7	- P1	- C1	- C6	= -174.5(3)
Pd1	- P1	- C1	- C6	= 64.5(4)

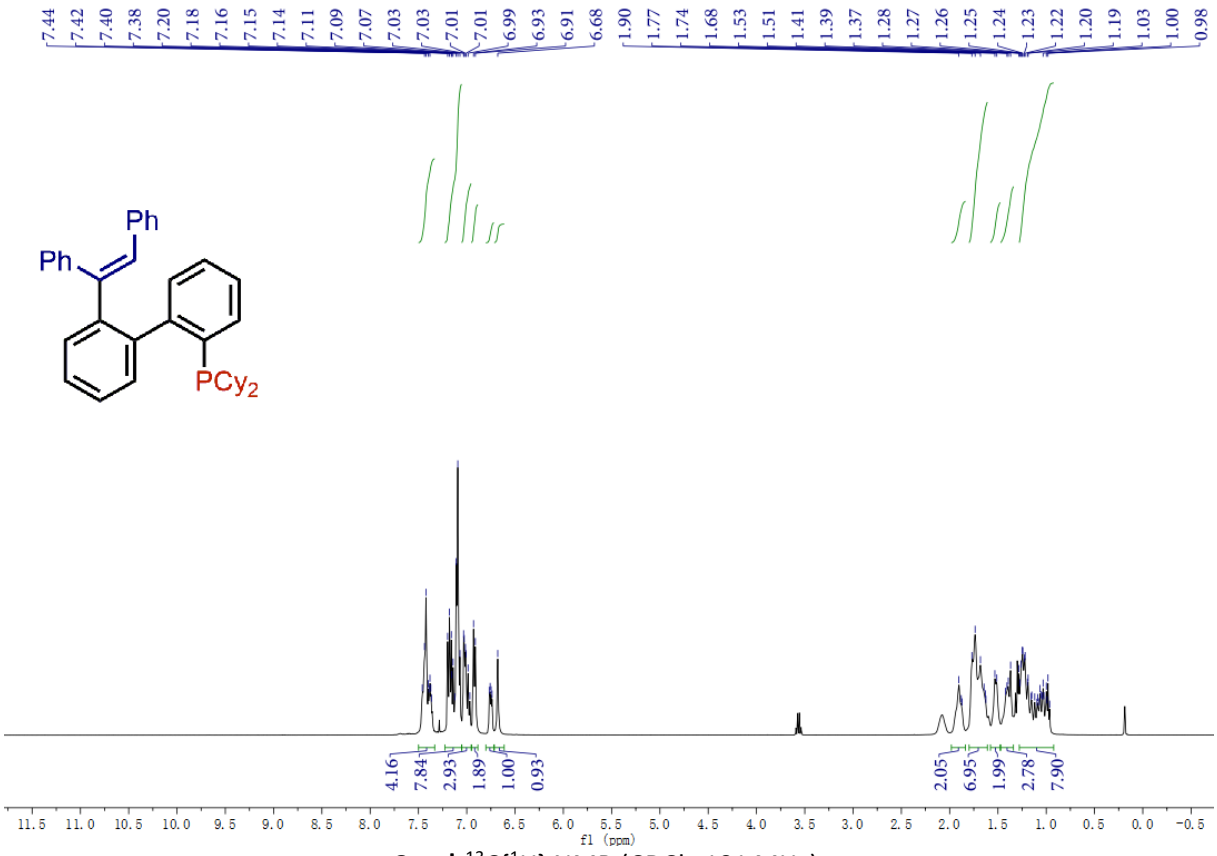
C6 - C1 - C2 - C3 = 57.1(5)
P1 - C1 - C2 - C3 = -173.3(4)
C1 - C2 - C3 - C4 = -55.8(6)
C2 - C3 - C4 - C5 = 54.8(7)
C3 - C4 - C5 - C6 = -56.2(6)
C4 - C5 - C6 - C1 = 58.1(6)
C2 - C1 - C6 - C5 = -58.2(5)
P1 - C1 - C6 - C5 = 171.6(4)
C1 - P1 - C7 - C12 = 29.6(4)
C13 - P1 - C7 - C12 = -85.5(4)
Pd1 - P1 - C7 - C12 = 157.9(3)
C1 - P1 - C7 - C8 = -97.2(4)
C13 - P1 - C7 - C8 = 147.7(3)
Pd1 - P1 - C7 - C8 = 31.1(4)
C12 - C7 - C8 - C9 = 54.2(6)
P1 - C7 - C8 - C9 = -175.2(4)
C7 - C8 - C9 - C10 = -54.9(6)
C8 - C9 - C10 - C11 = 55.3(7)
C9 - C10 - C11 - C12 = -56.7(6)
C10 - C11 - C12 - C7 = 57.2(6)
C8 - C7 - C12 - C11 = -54.7(5)
P1 - C7 - C12 - C11 = 178.4(3)
C1 - P1 - C13 - C18 = -91.5(5)
C7 - P1 - C13 - C18 = 25.2(5)
Pd1 - P1 - C13 - C18 = 142.6(4)
C1 - P1 - C13 - C14 = 88.9(4)
C7 - P1 - C13 - C14 = -154.4(3)
Pd1 - P1 - C13 - C14 = -37.0(4)
C18 - C13 - C14 - C15 = 0.5(7)
P1 - C13 - C14 - C15 = -179.9(4)
C13 - C14 - C15 - C16 = -2.5(8)
C14 - C15 - C16 - C17 = 1.7(8)
C15 - C16 - C17 - C18 = 1.1(8)
C16 - C17 - C18 - C13 = -3.1(7)
C16 - C17 - C18 - C19 = 174.9(5)
C14 - C13 - C18 - C17 = 2.2(6)
P1 - C13 - C18 - C17 = -177.3(4)
C14 - C13 - C18 - C19 = -175.5(4)
P1 - C13 - C18 - C19 = 4.9(7)
C17 - C18 - C19 - C24 = 88.0(5)
C13 - C18 - C19 - C24 = -94.2(6)
C17 - C18 - C19 - C20 = -88.6(5)
C13 - C18 - C19 - C20 = 89.2(6)
C24 - C19 - C20 - C21 = 2.2(7)
C18 - C19 - C20 - C21 = 178.8(5)
C24 - C19 - C20 - C25 = -176.8(5)
C18 - C19 - C20 - C25 = -0.2(7)
C19 - C20 - C21 - C22 = -0.1(8)
C25 - C20 - C21 - C22 = 178.9(5)
C20 - C21 - C22 - C23 = -1.0(9)
C21 - C22 - C23 - C24 = 0.1(9)
C22 - C23 - C24 - C19 = 2.0(8)

C22 - C23 - C24 - C39 = -178.2(5)
C20 - C19 - C24 - C23 = -3.2(7)
C18 - C19 - C24 - C23 = -179.8(4)
C20 - C19 - C24 - C39 = 177.1(4)
C18 - C19 - C24 - C39 = 0.5(7)
C21 - C20 - C25 - C26 = 44.7(7)
C19 - C20 - C25 - C26 = -136.3(5)
C21 - C20 - C25 - C33 = -129.6(5)
C19 - C20 - C25 - C33 = 49.4(7)
C33 - C25 - C26 - C27 = 7.6(8)
C20 - C25 - C26 - C27 = -166.5(5)
C25 - C26 - C27 - C28 = -157.0(6)
C25 - C26 - C27 - C32 = 27.7(9)
C32 - C27 - C28 - C29 = -2.5(9)
C26 - C27 - C28 - C29 = -178.0(6)
C27 - C28 - C29 - C30 = 3.0(11)
C28 - C29 - C30 - C31 = -2.4(11)
C29 - C30 - C31 - C32 = 1.3(10)
C30 - C31 - C32 - C27 = -0.8(10)
C28 - C27 - C32 - C31 = 1.3(9)
C26 - C27 - C32 - C31 = 176.6(5)
C26 - C25 - C33 - C34 = 55.2(7)
C20 - C25 - C33 - C34 = -130.6(5)
C26 - C25 - C33 - C38 = -123.1(6)
C20 - C25 - C33 - C38 = 51.0(7)
C38 - C33 - C34 - C35 = 0.8(8)
C25 - C33 - C34 - C35 = -177.6(5)
C33 - C34 - C35 - C36 = -0.5(9)
C34 - C35 - C36 - C37 = -0.5(10)
C35 - C36 - C37 - C38 = 1.1(10)
C36 - C37 - C38 - C33 = -0.9(9)
C34 - C33 - C38 - C37 = -0.1(8)
C25 - C33 - C38 - C37 = 178.3(5)
C23 - C24 - C39 - C40 = -58.5(6)
C19 - C24 - C39 - C40 = 121.3(5)
C23 - C24 - C39 - C47 = 115.8(5)
C19 - C24 - C39 - C47 = -64.4(6)
C47 - C39 - C40 - C41 = -1.1(8)
C24 - C39 - C40 - C41 = 172.9(5)
C39 - C40 - C41 - C46 = -37.1(8)
C39 - C40 - C41 - C42 = 147.7(5)
C46 - C41 - C42 - C43 = 2.2(8)
C40 - C41 - C42 - C43 = 177.7(5)
C41 - C42 - C43 - C44 = -2.5(9)
C42 - C43 - C44 - C45 = 1.1(9)
C43 - C44 - C45 - C46 = 0.6(9)
C42 - C41 - C46 - C45 = -0.5(8)
C40 - C41 - C46 - C45 = -175.8(5)
C44 - C45 - C46 - C41 = -0.8(9)
C40 - C39 - C47 - C48 = -57.4(7)
C24 - C39 - C47 - C48 = 128.5(5)
C40 - C39 - C47 - C52 = 121.1(6)

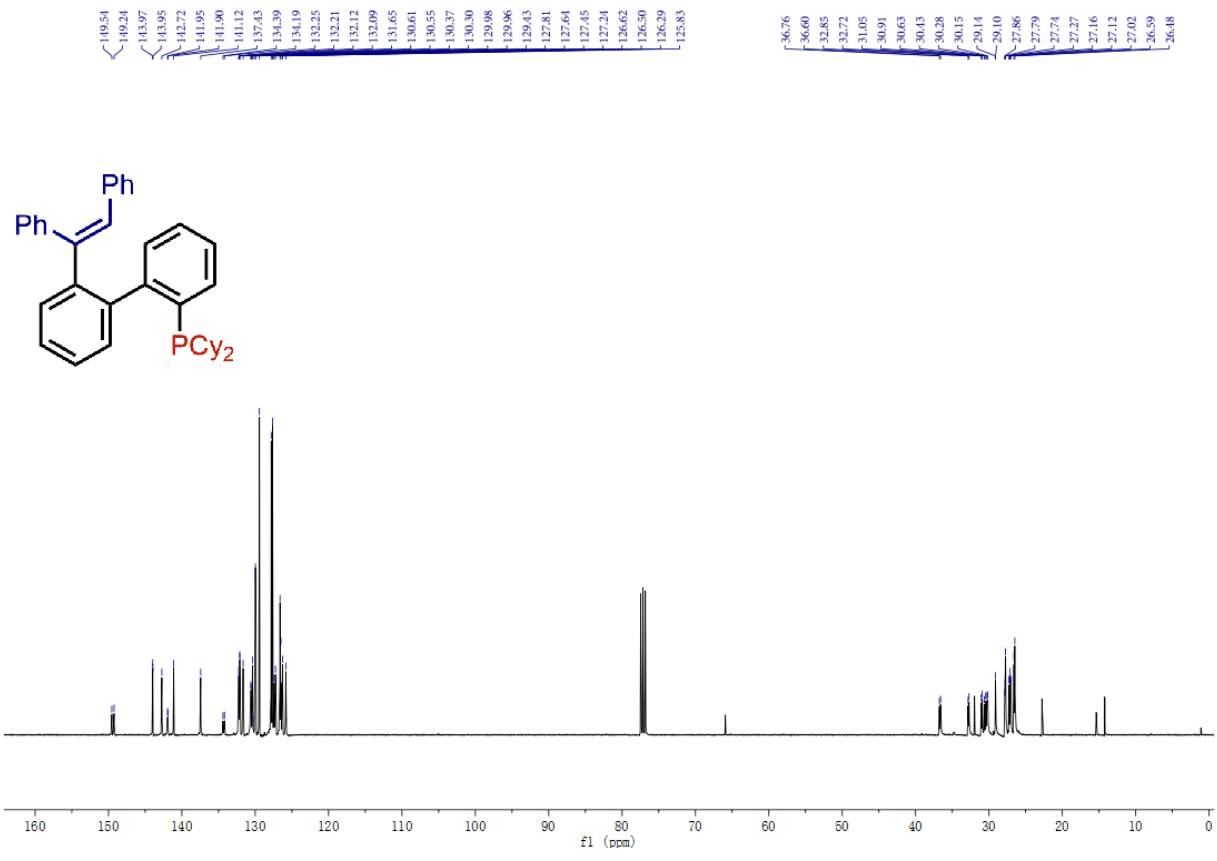
C24	- C39	- C47	- C52	= -52.9(6)
C52	- C47	- C48	- C49	= -0.5(8)
C39	- C47	- C48	- C49	= 178.1(5)
C47	- C48	- C49	- C50	= -0.4(9)
C48	- C49	- C50	- C51	= 1.2(9)
C49	- C50	- C51	- C52	= -1.0(10)
C50	- C51	- C52	- C47	= 0.1(9)
C48	- C47	- C52	- C51	= 0.6(8)
C39	- C47	- C52	- C51	= -178.0(5)

6. NMR Charts

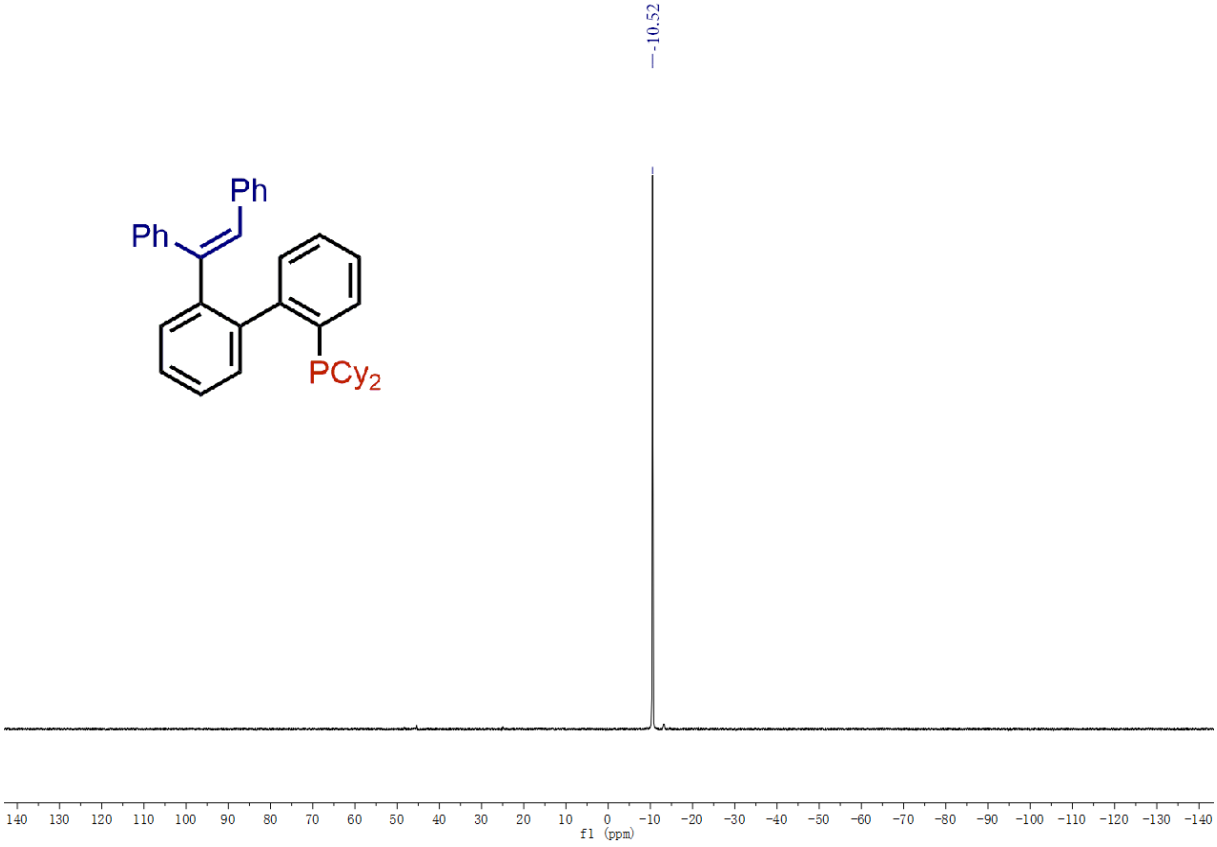
3aa | ^{1}H NMR ($CDCl_3$, 400 MHz)



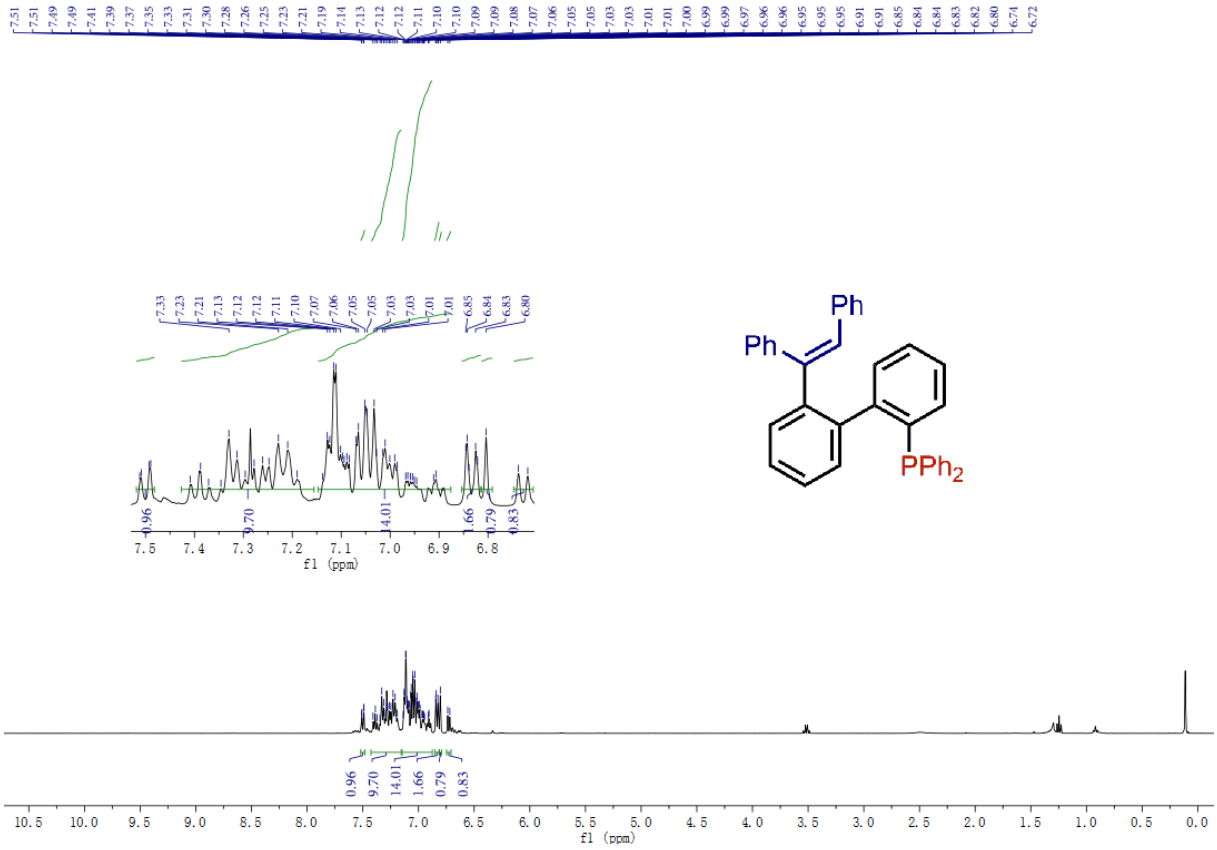
3aa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



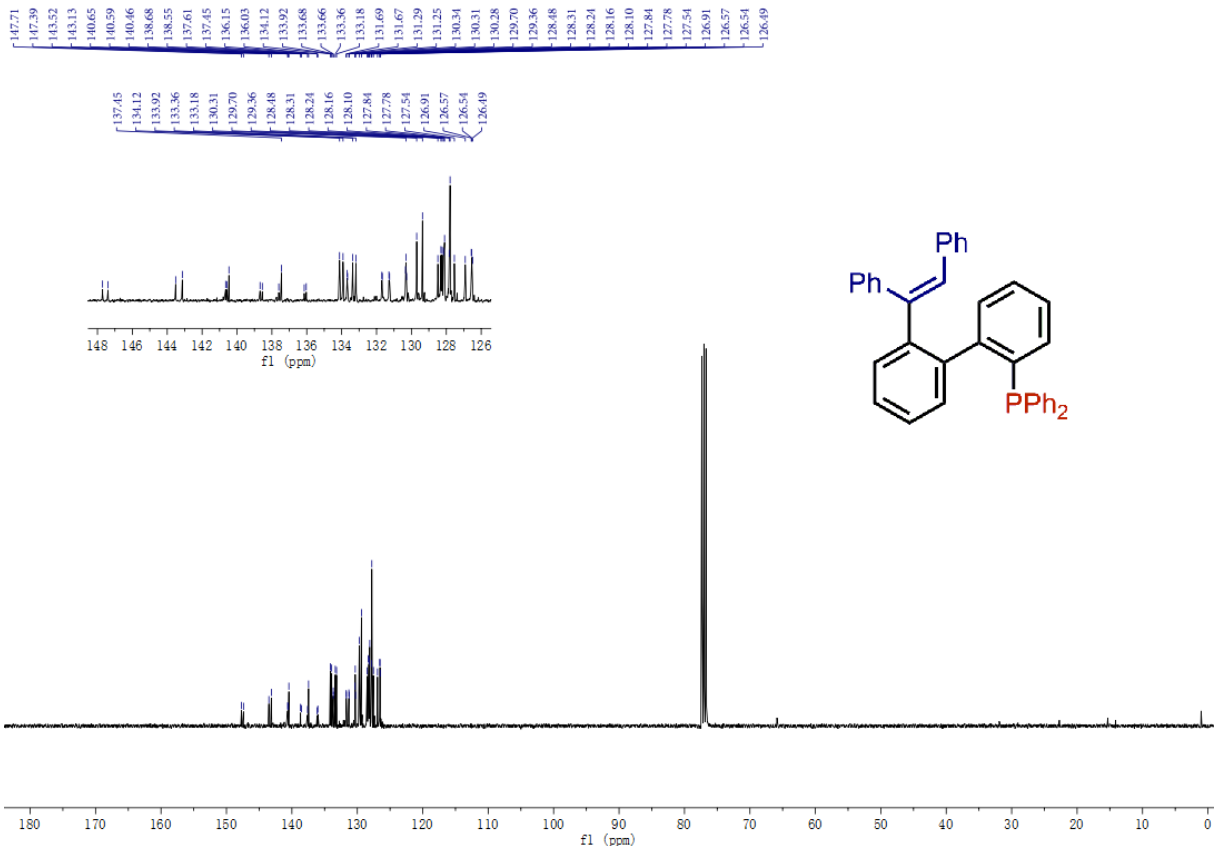
3aa | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



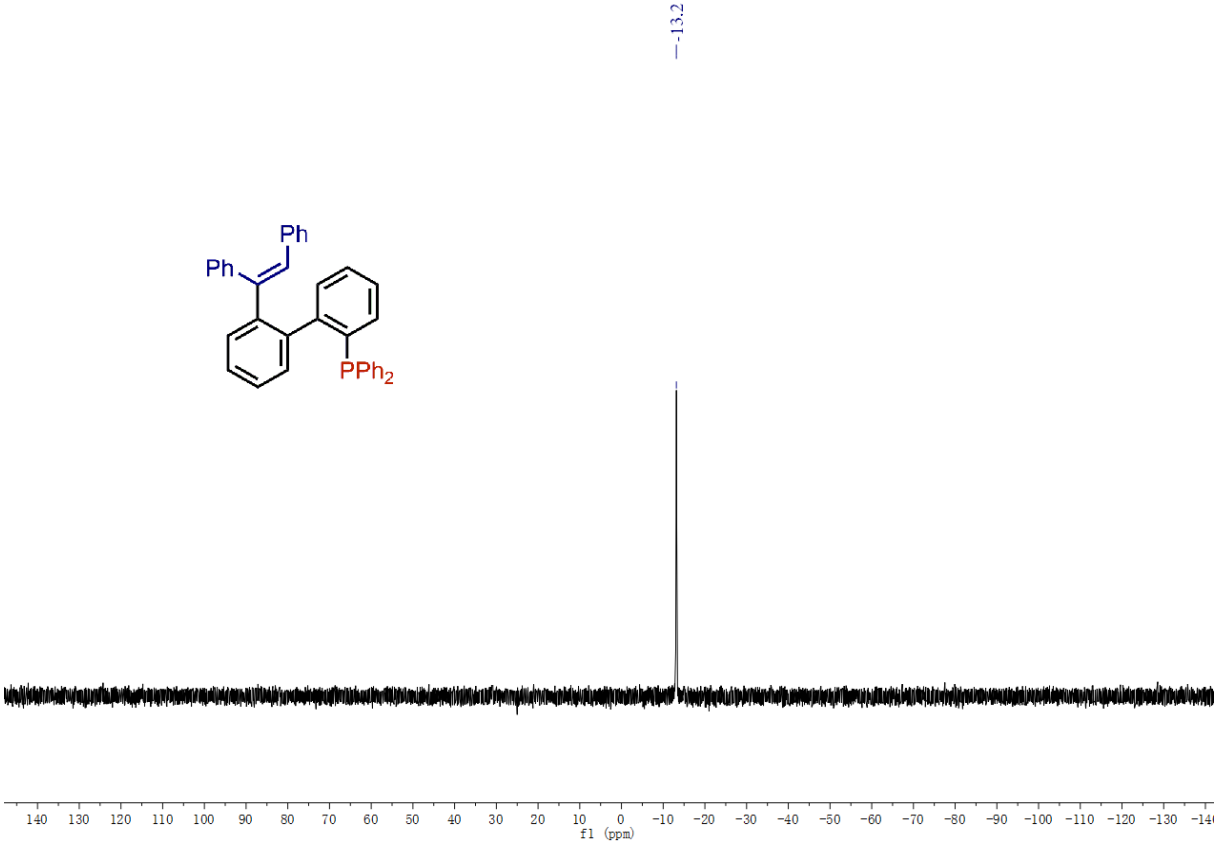
3ba | ^{1}H NMR ($CDCl_3$, 400 MHz)



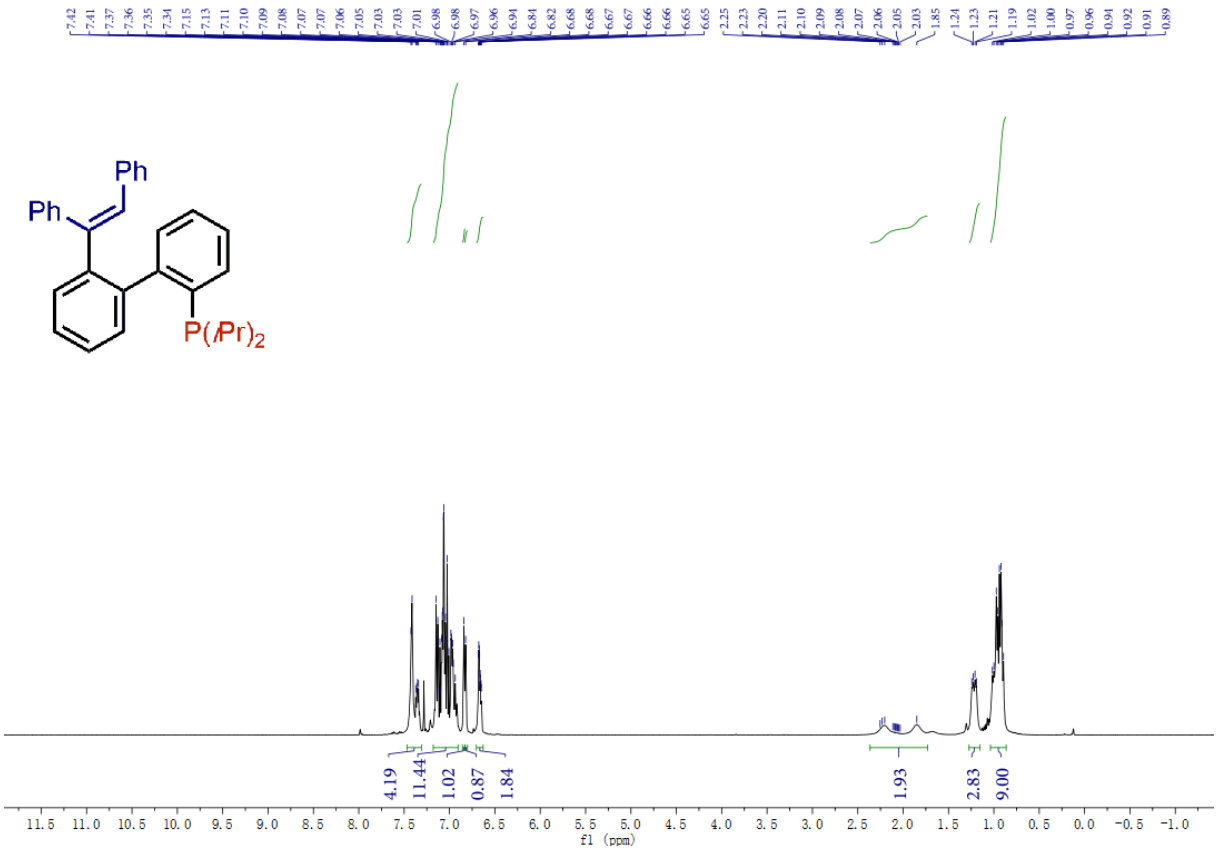
3ba | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



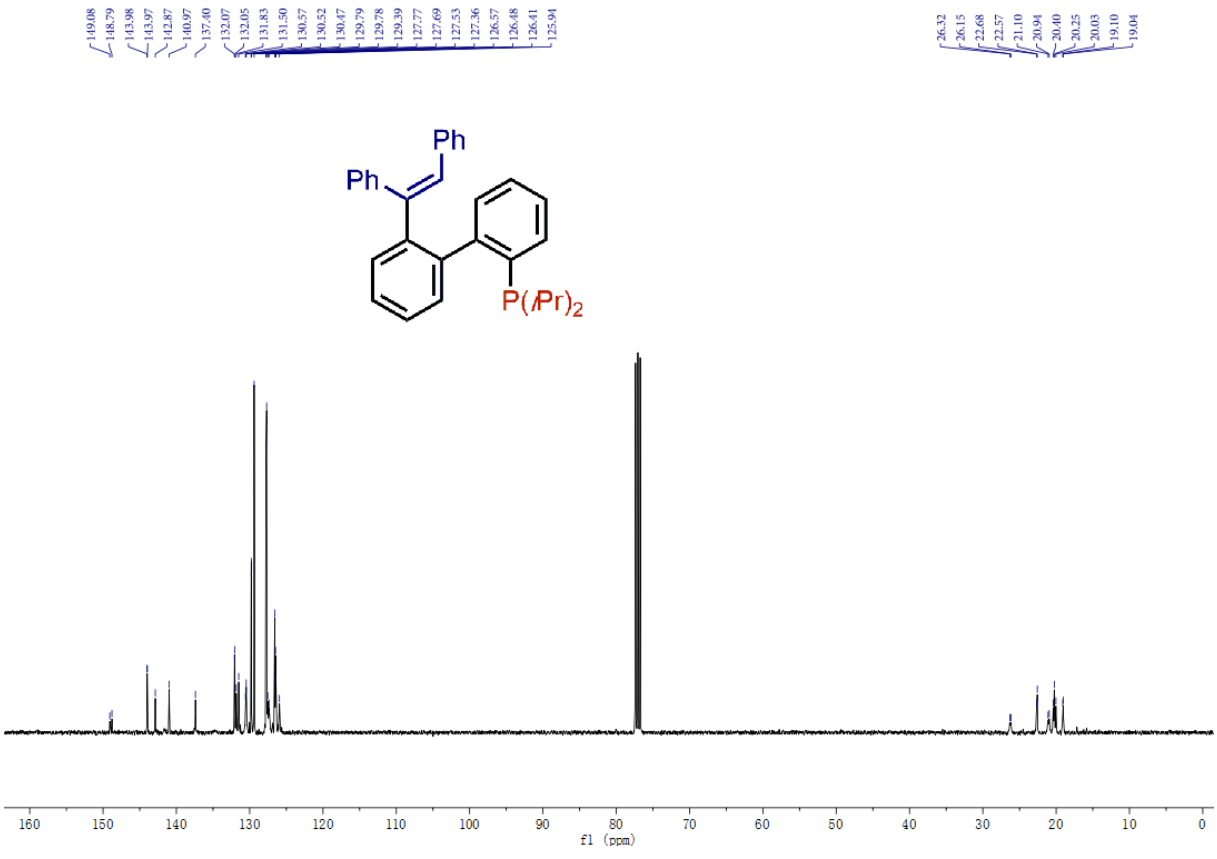
3ba | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



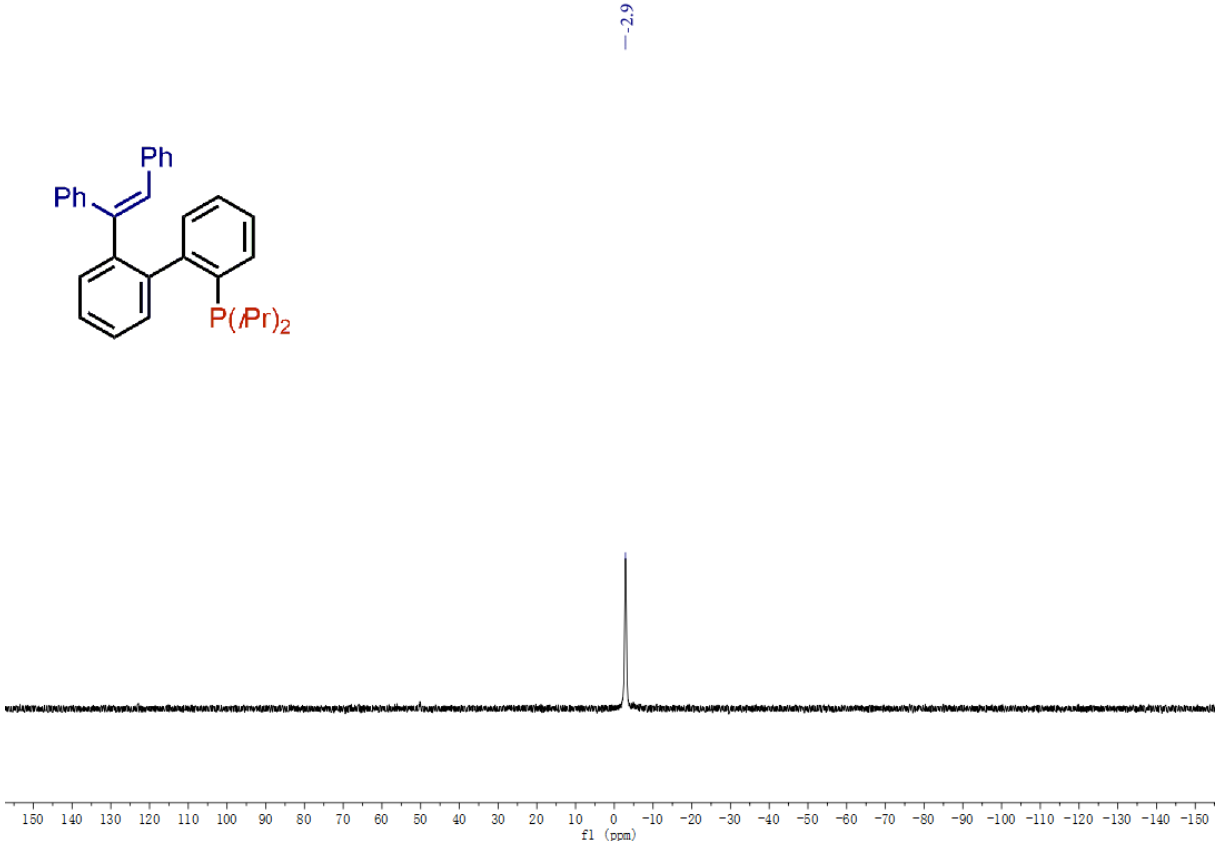
3ca | ^{1}H NMR ($CDCl_3$, 400 MHz)



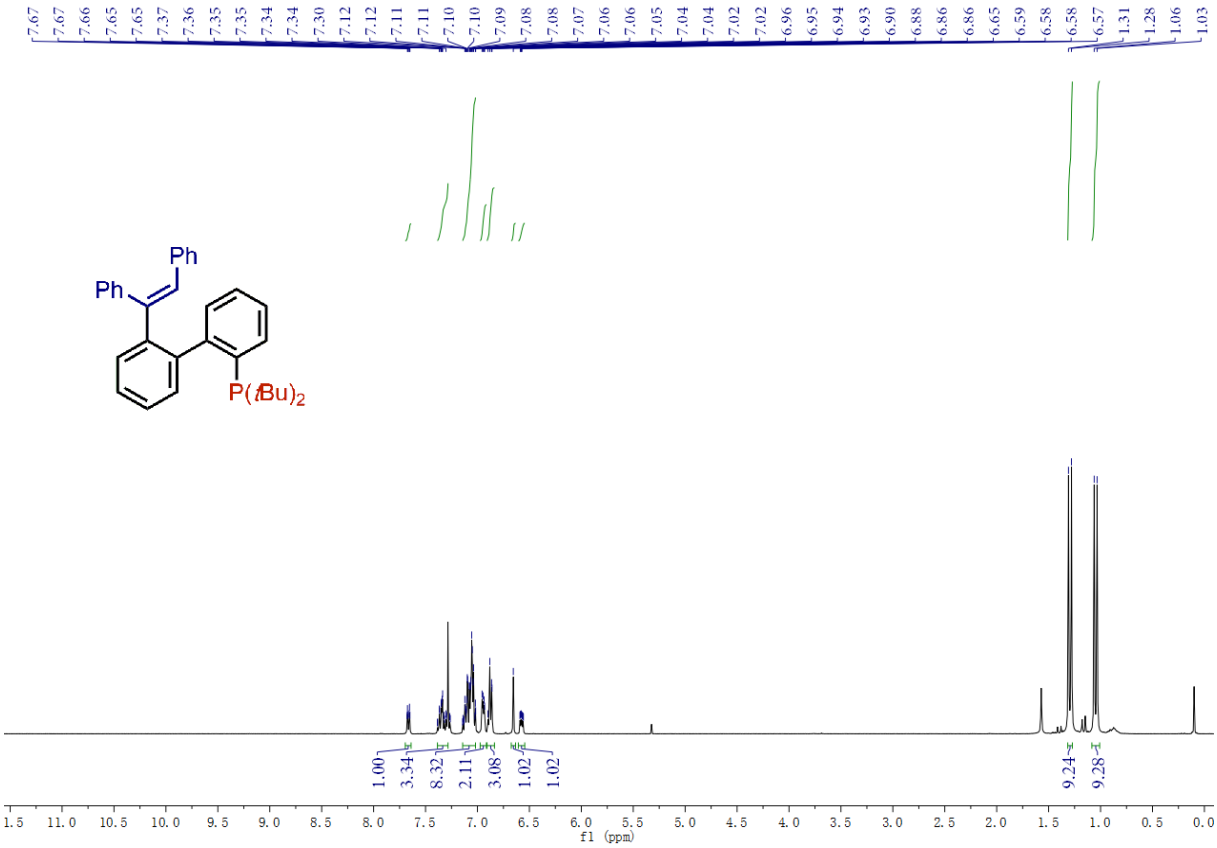
3ca | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



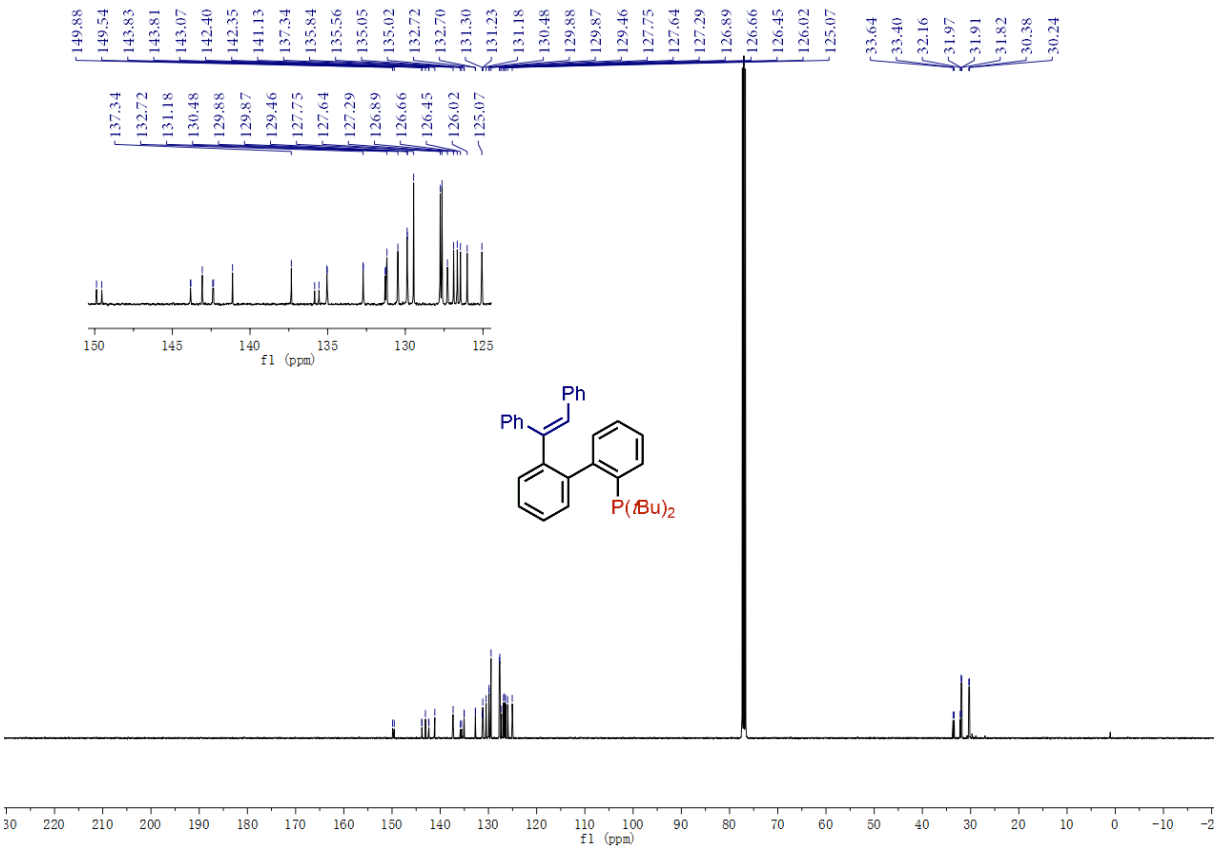
3ca | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



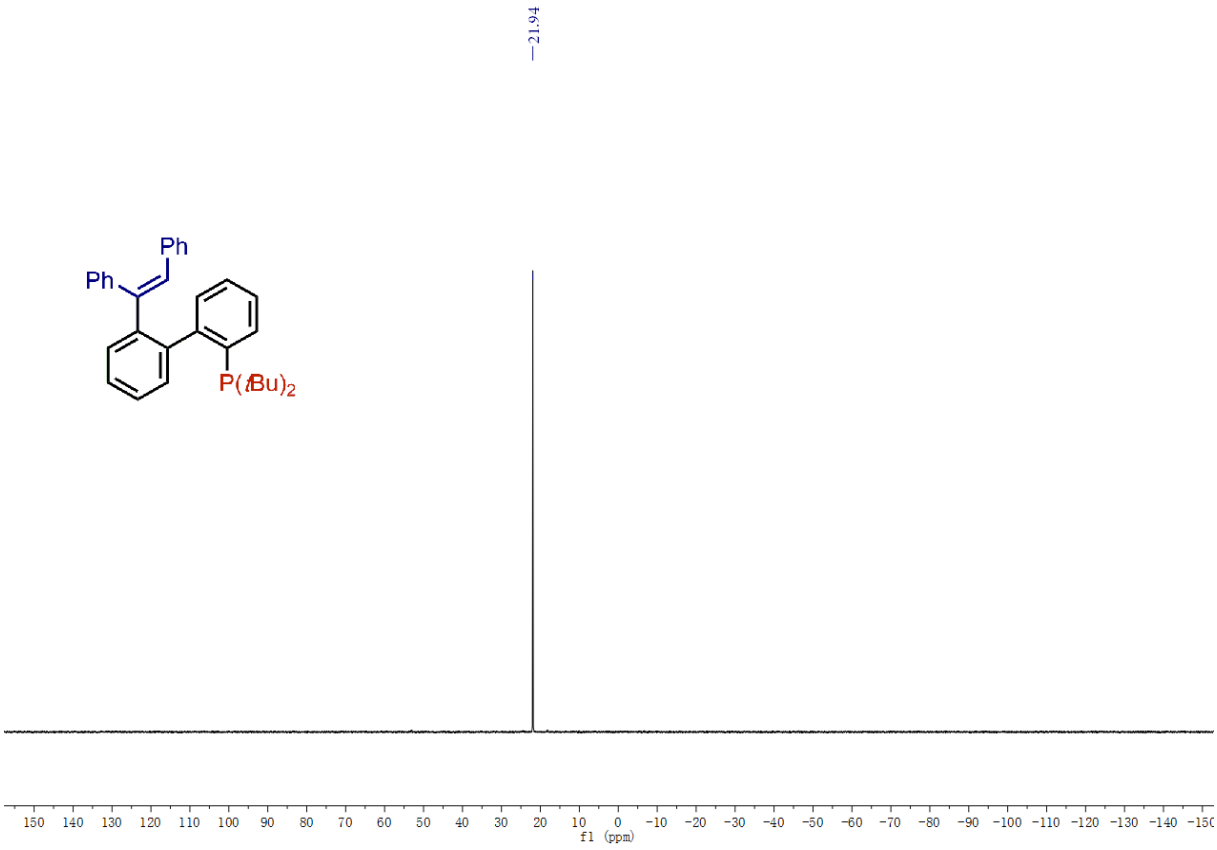
3da| ^{1}H NMR ($CDCl_3$, 400 MHz)



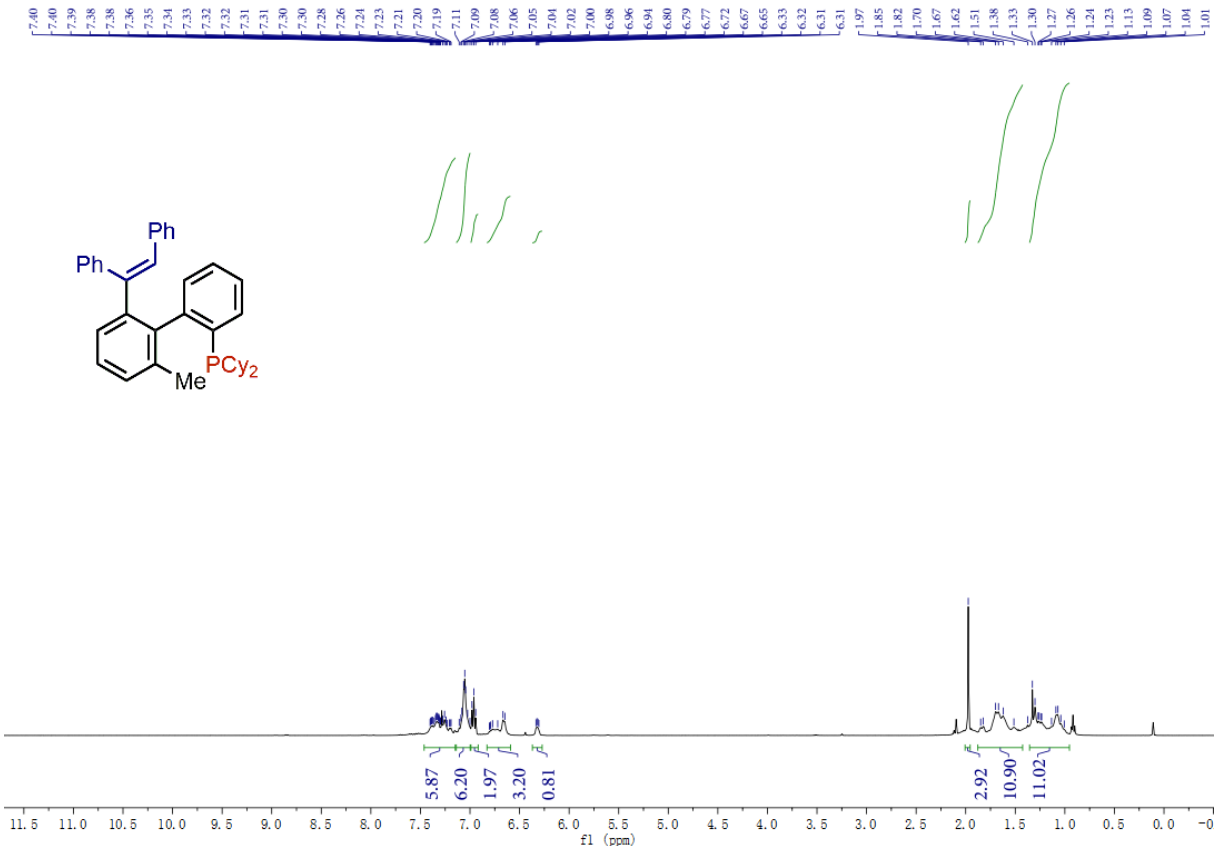
3da | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



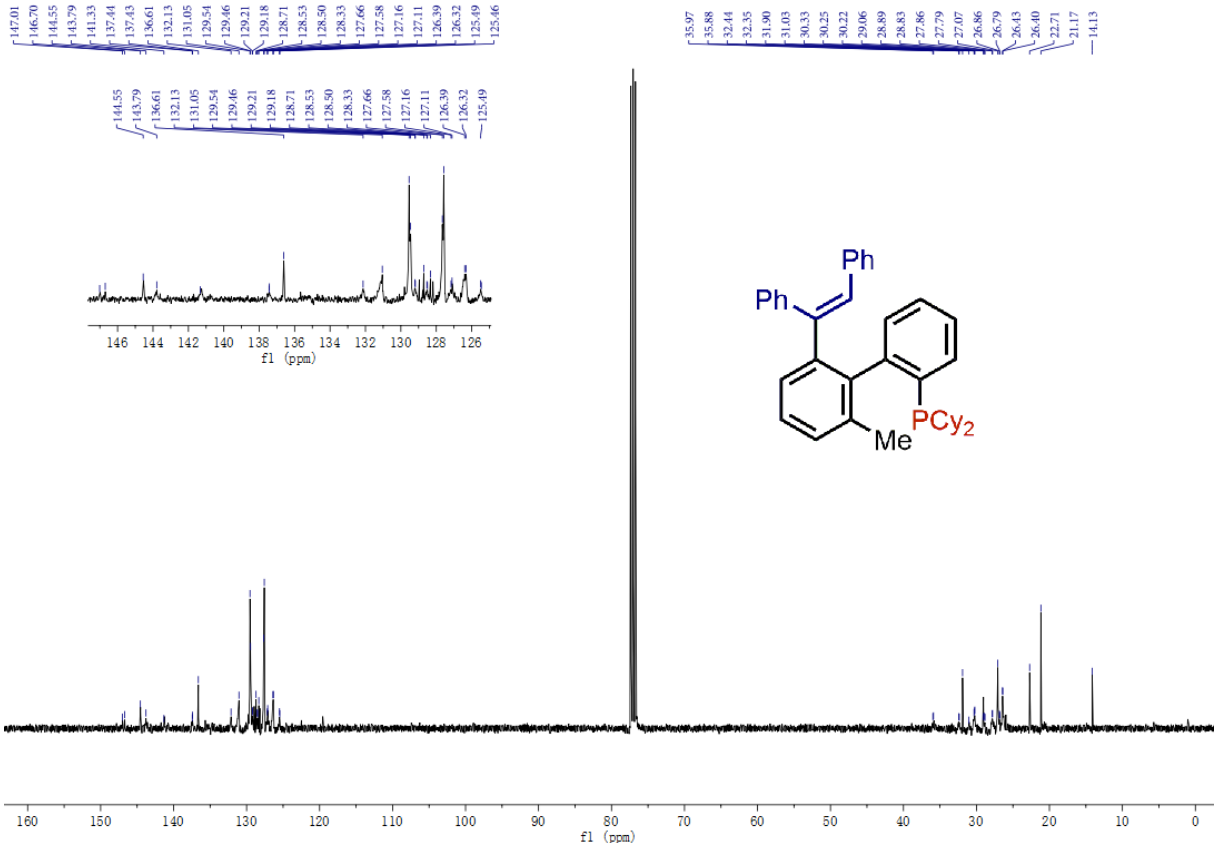
3da | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



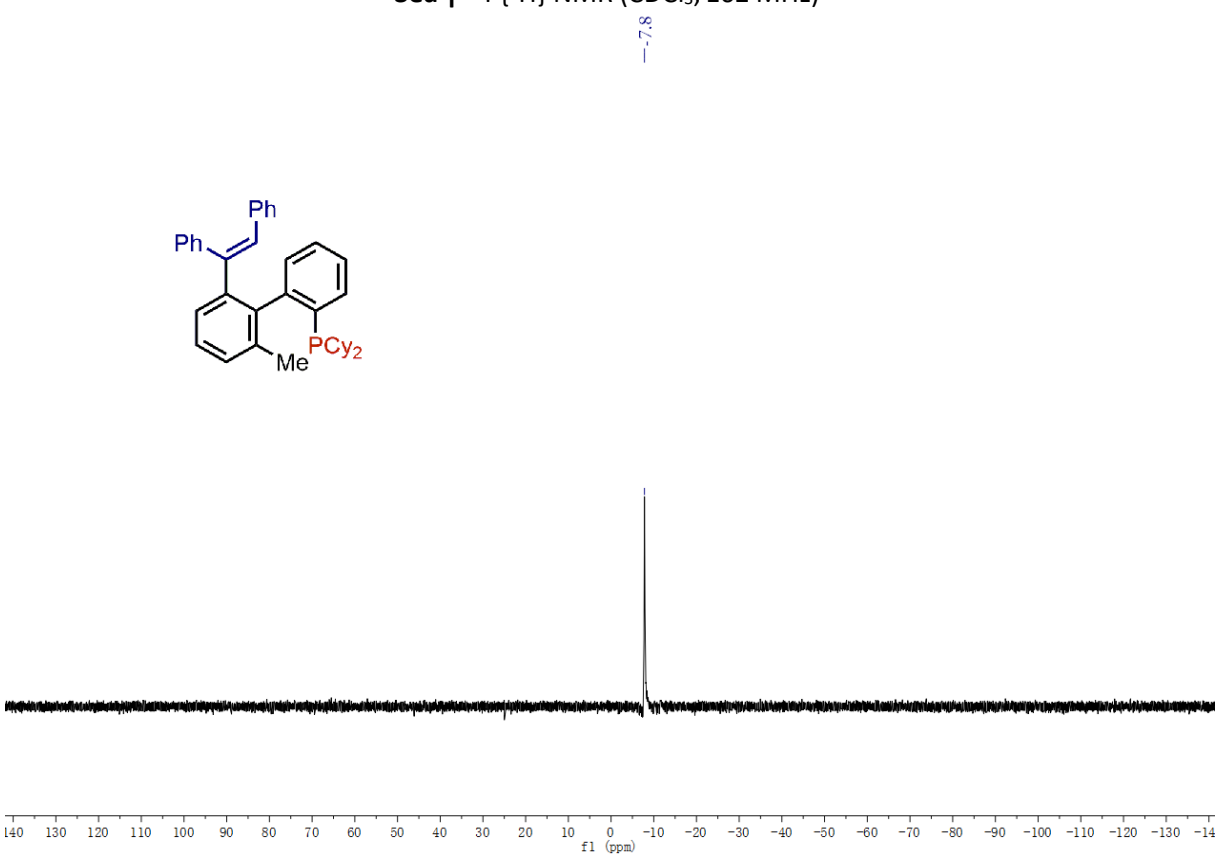
3ea| ^{1}H NMR ($CDCl_3$, 400 MHz)



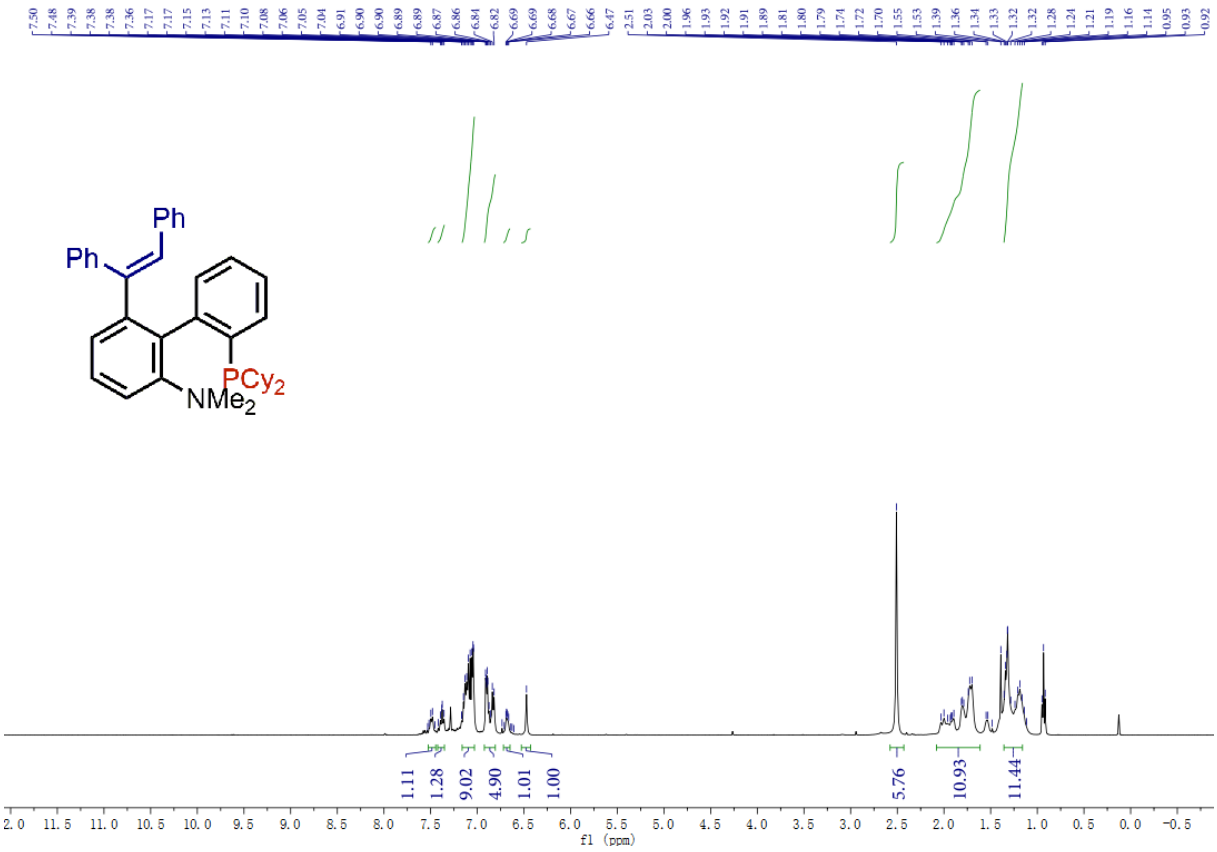
3ea | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



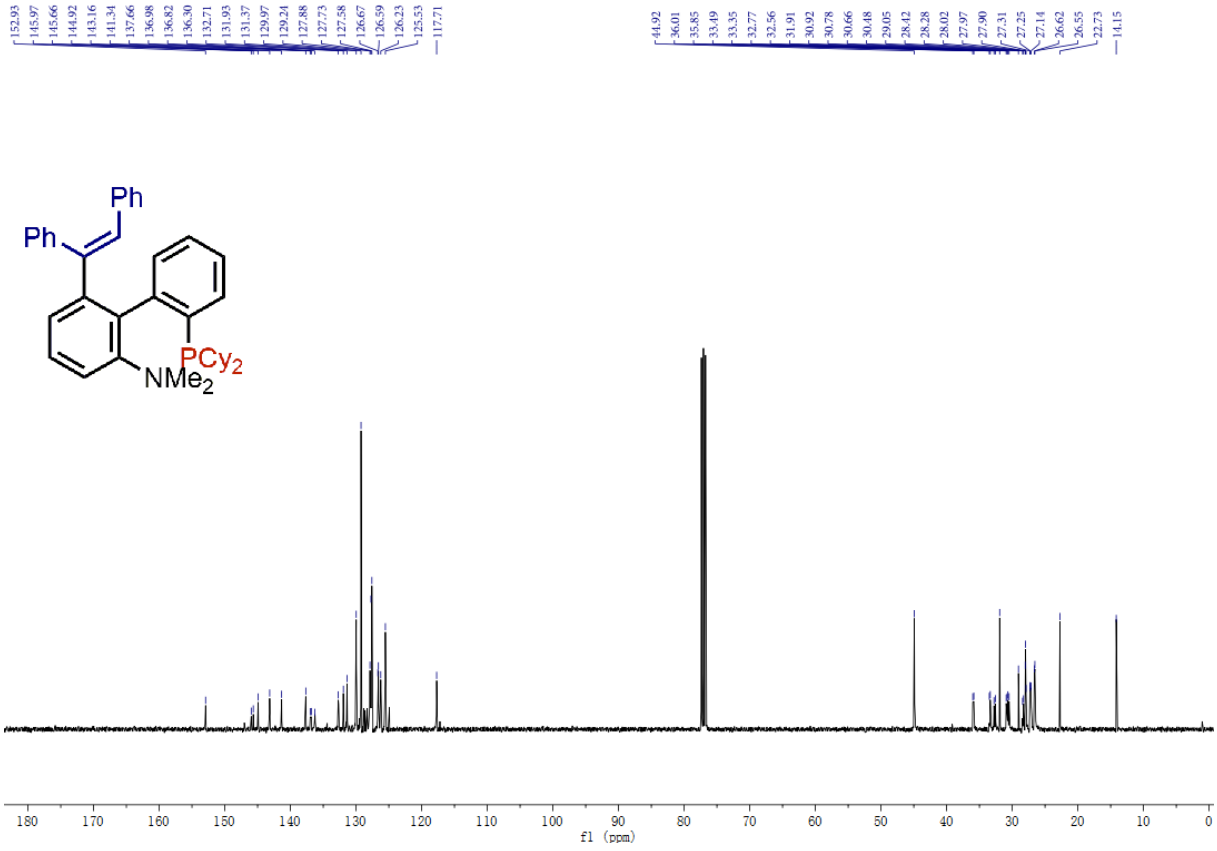
3ea | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



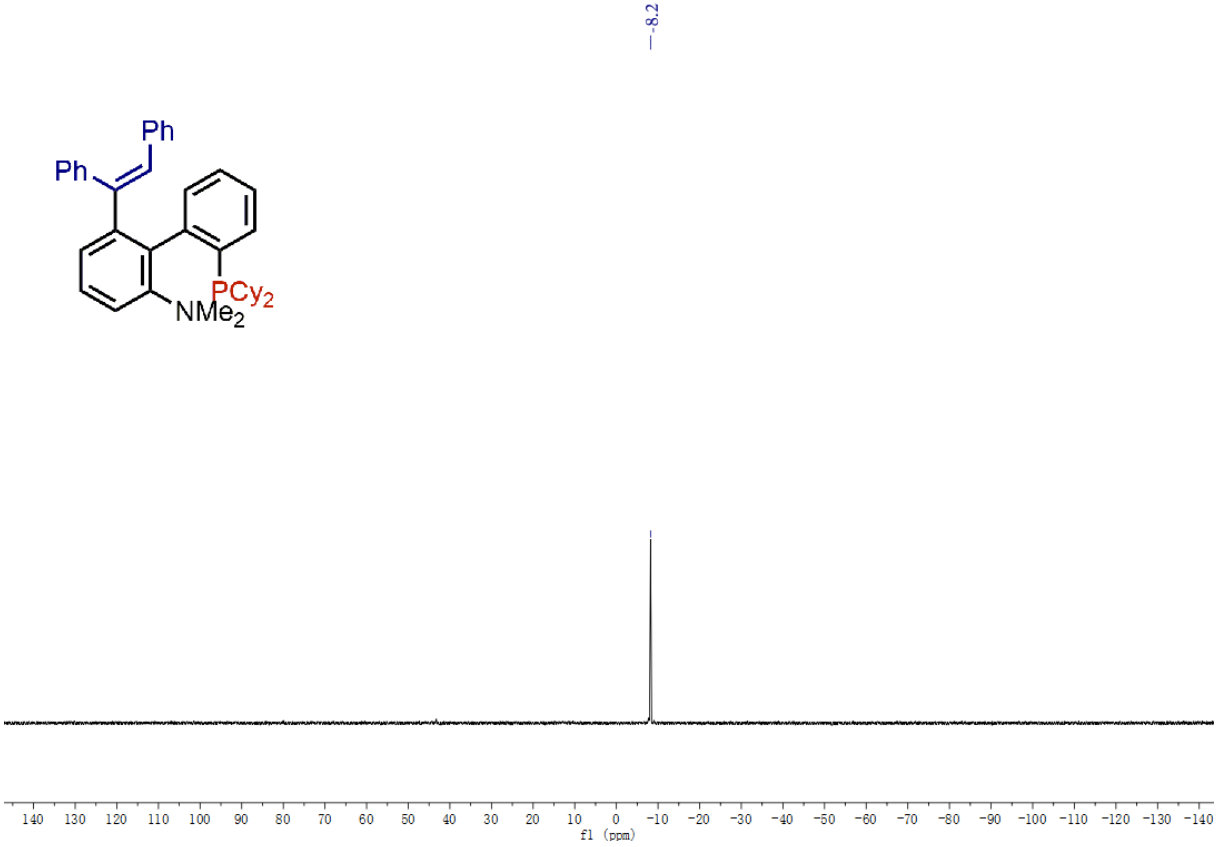
3fa | ^{1}H NMR ($CDCl_3$, 400 MHz)



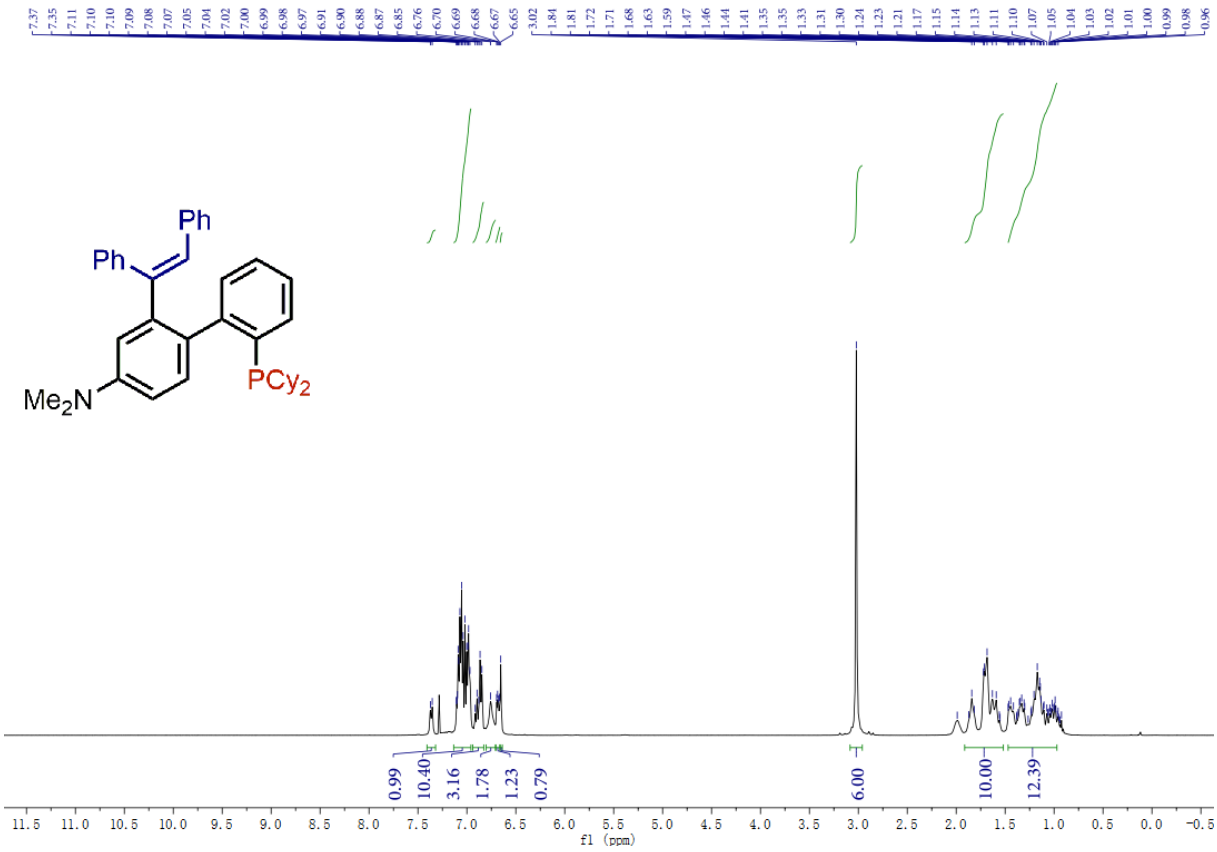
3fa | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



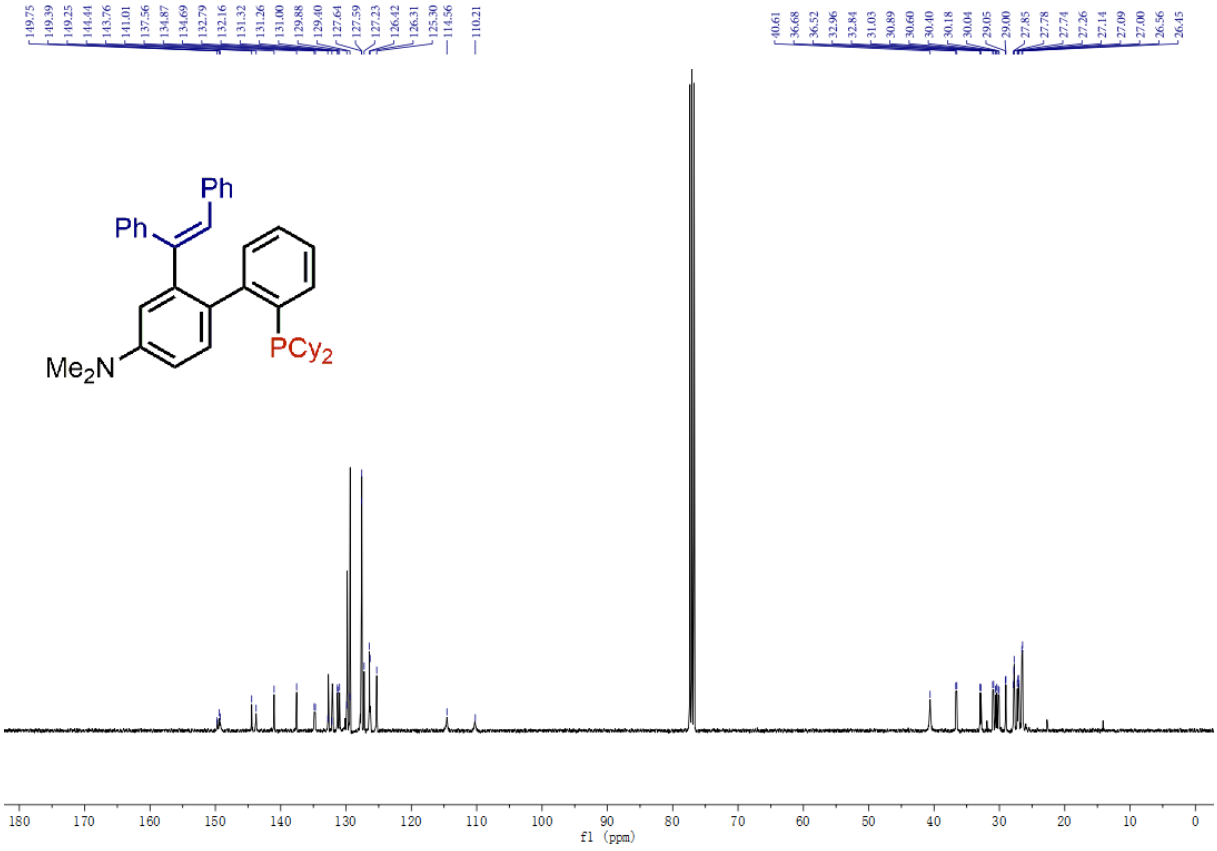
3fa | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



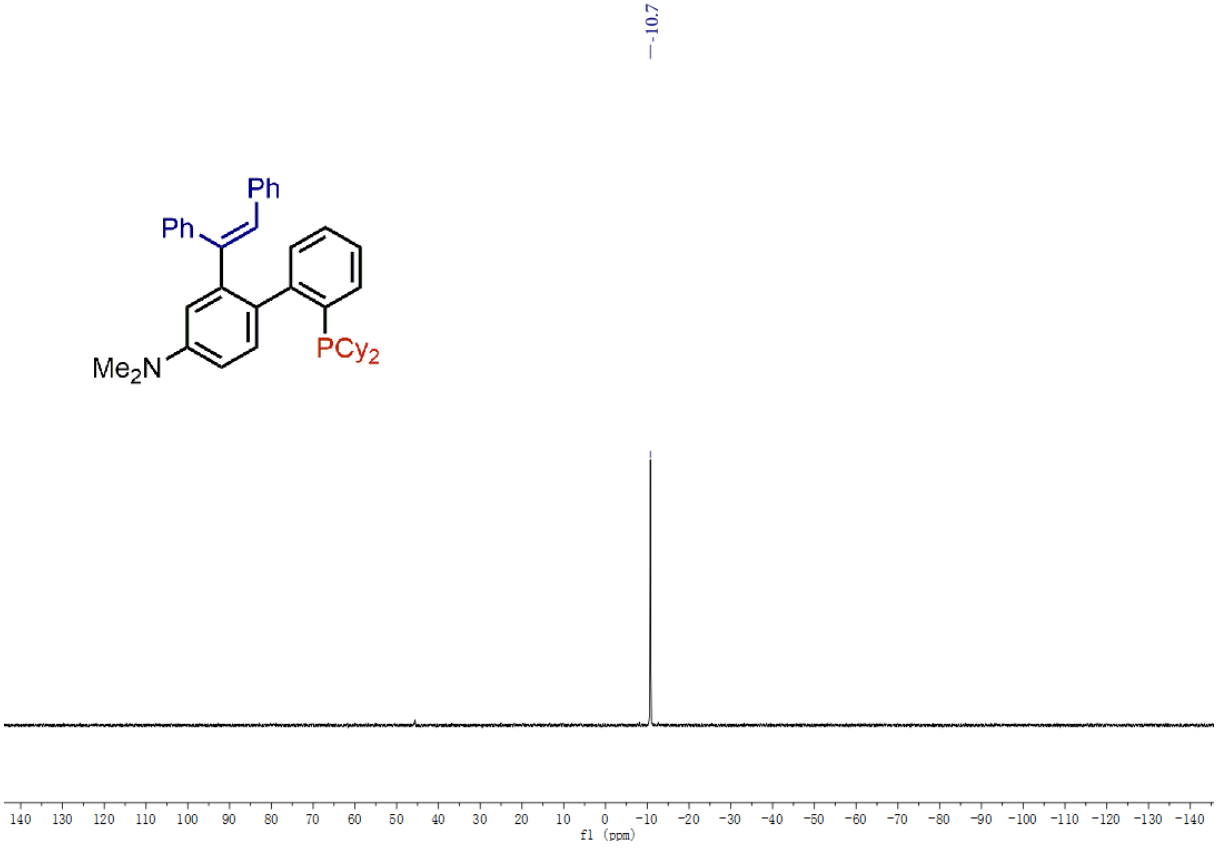
3ga | ^{1}H NMR ($CDCl_3$, 400 MHz)



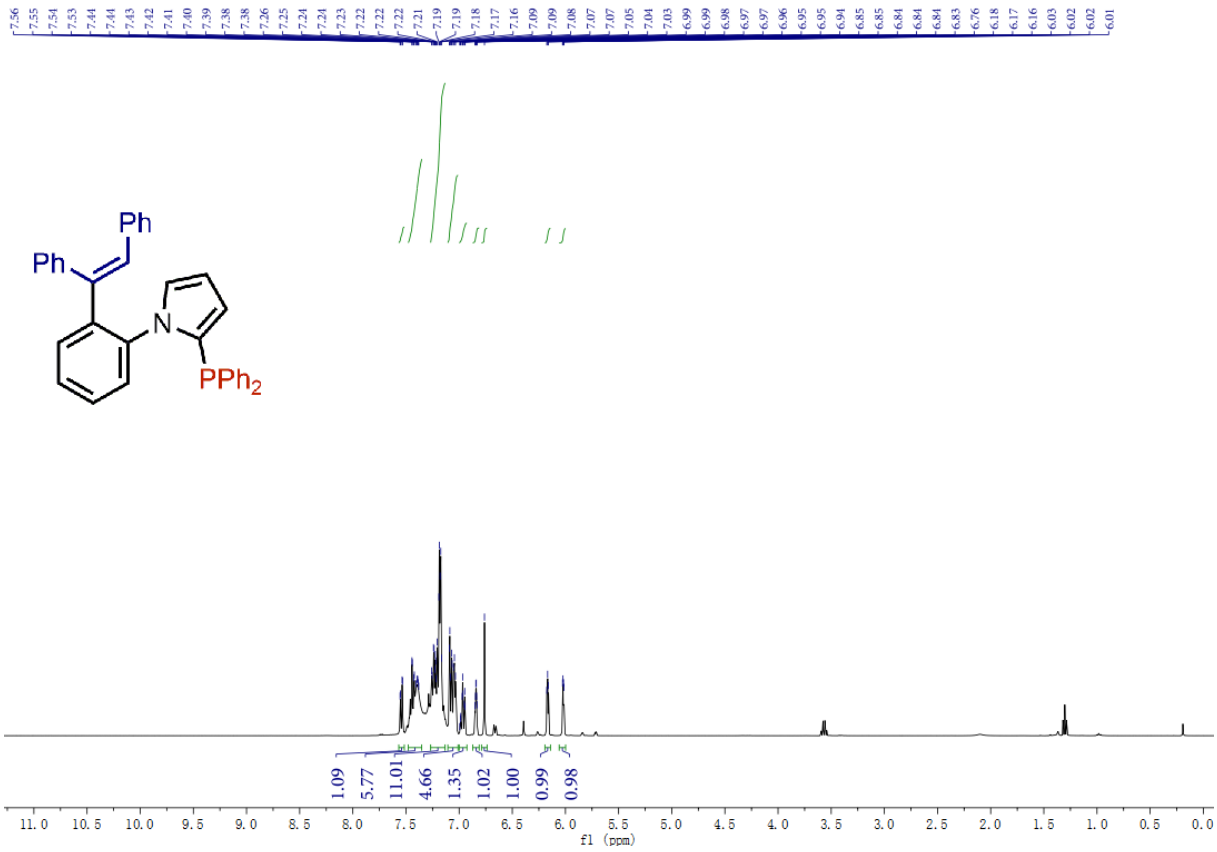
3ga | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



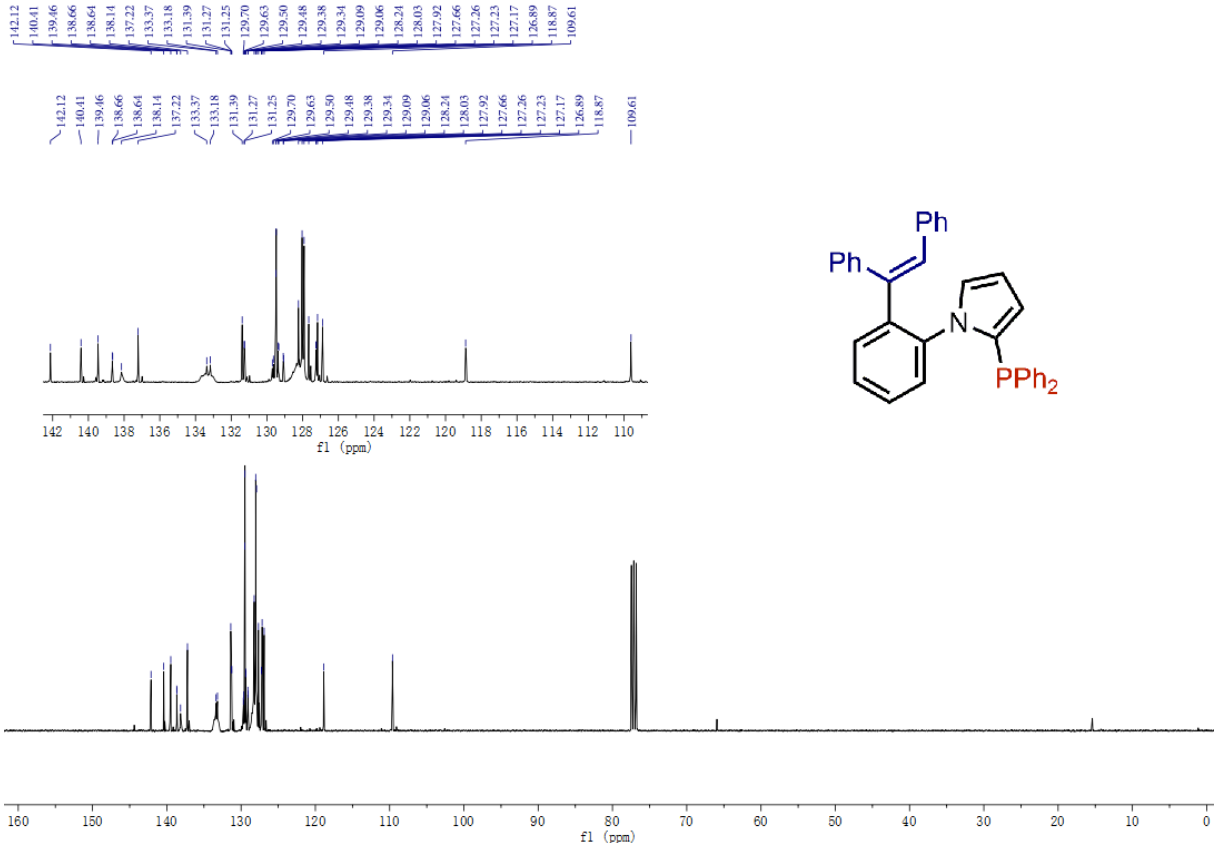
3ga | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



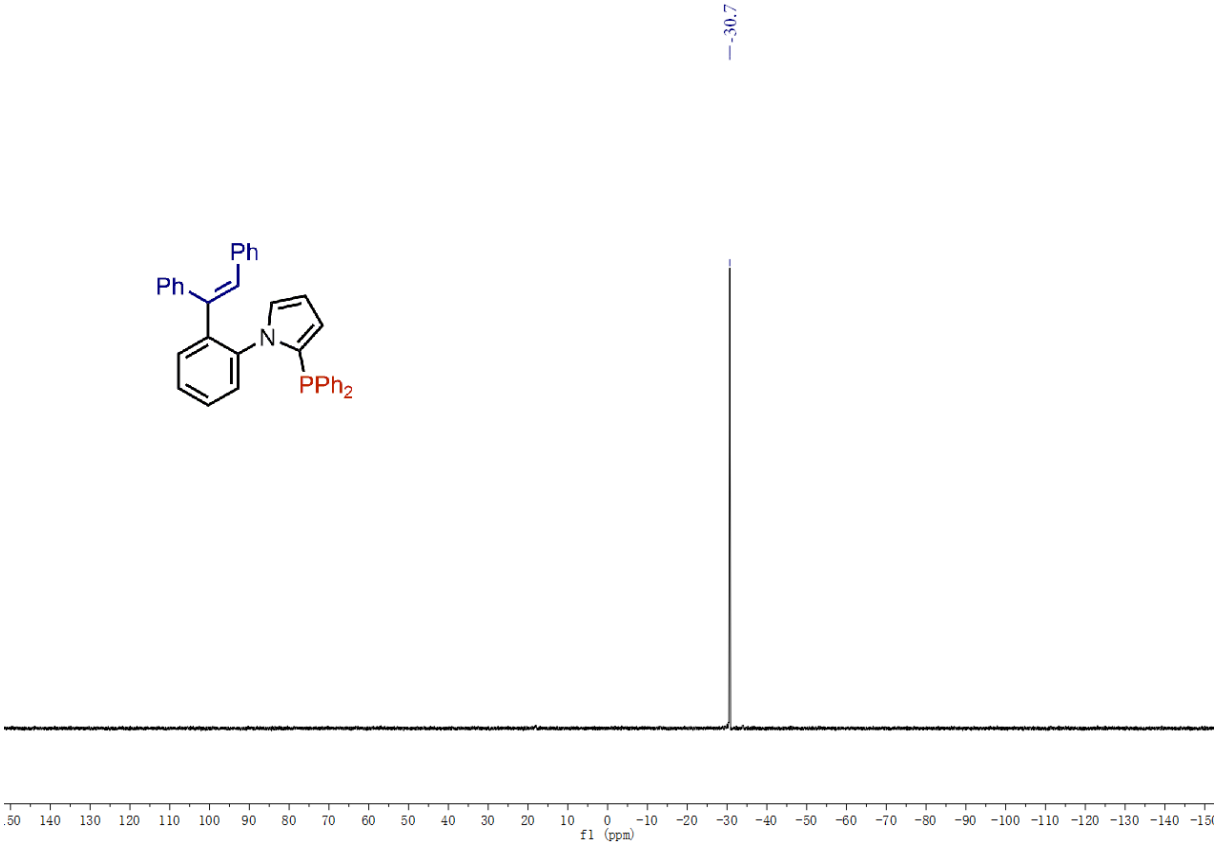
3ha | ^{1}H NMR ($CDCl_3$, 400 MHz)



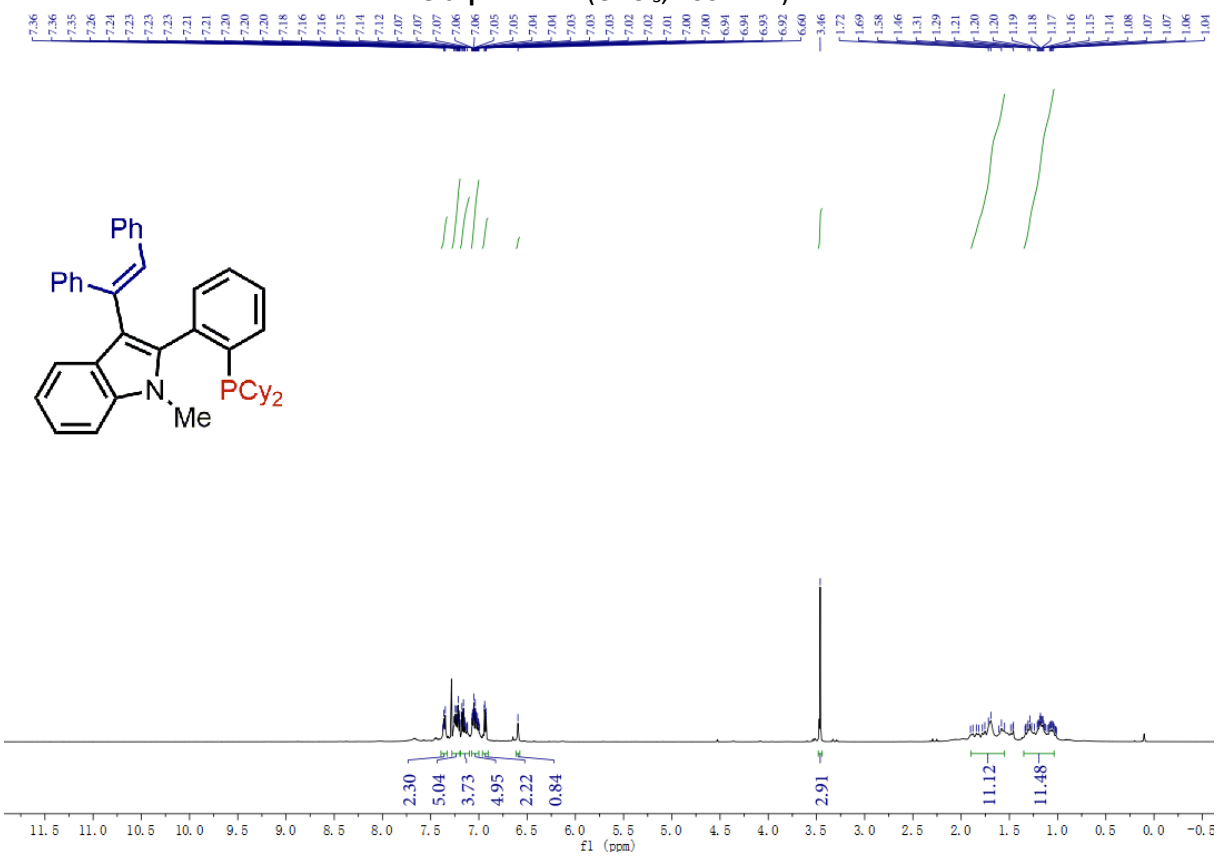
3ha | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



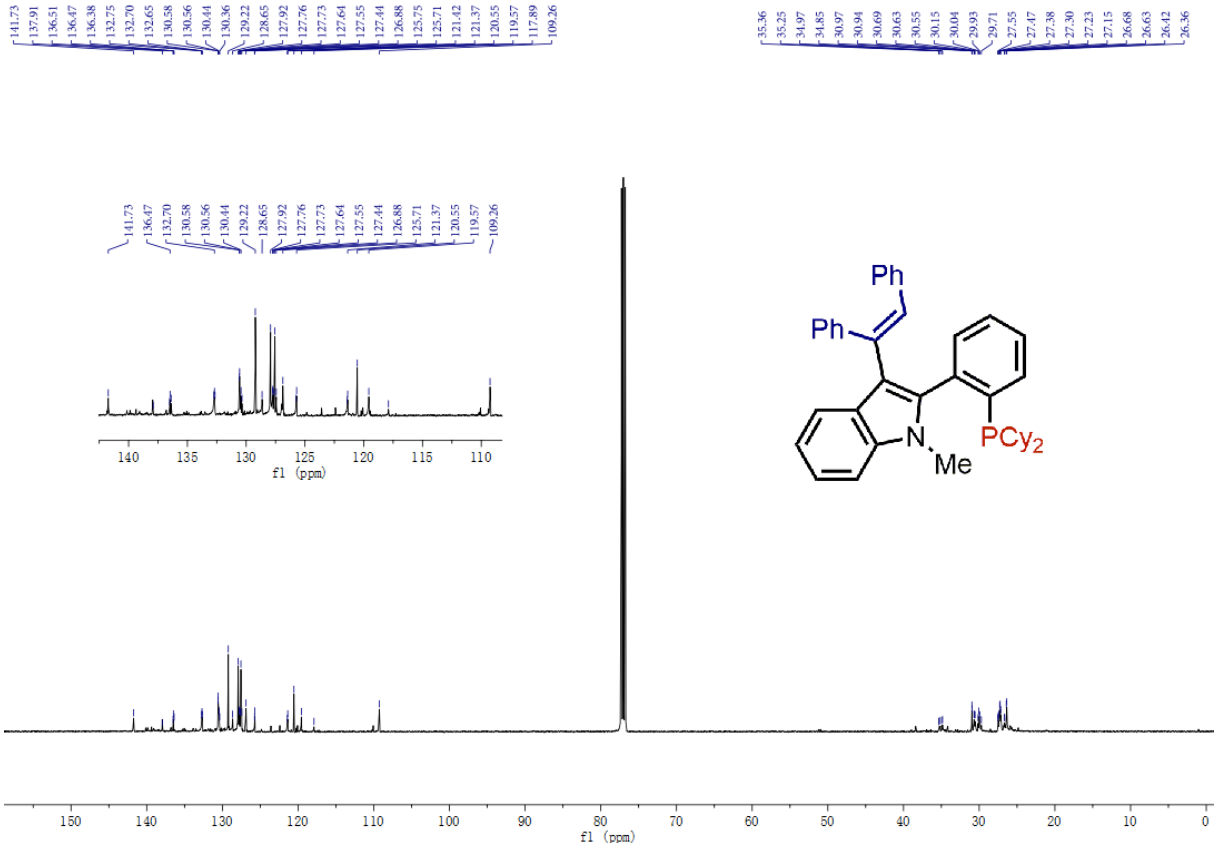
3ha | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



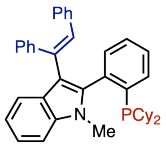
3ia | ^{1}H NMR ($CDCl_3$, 400 MHz)



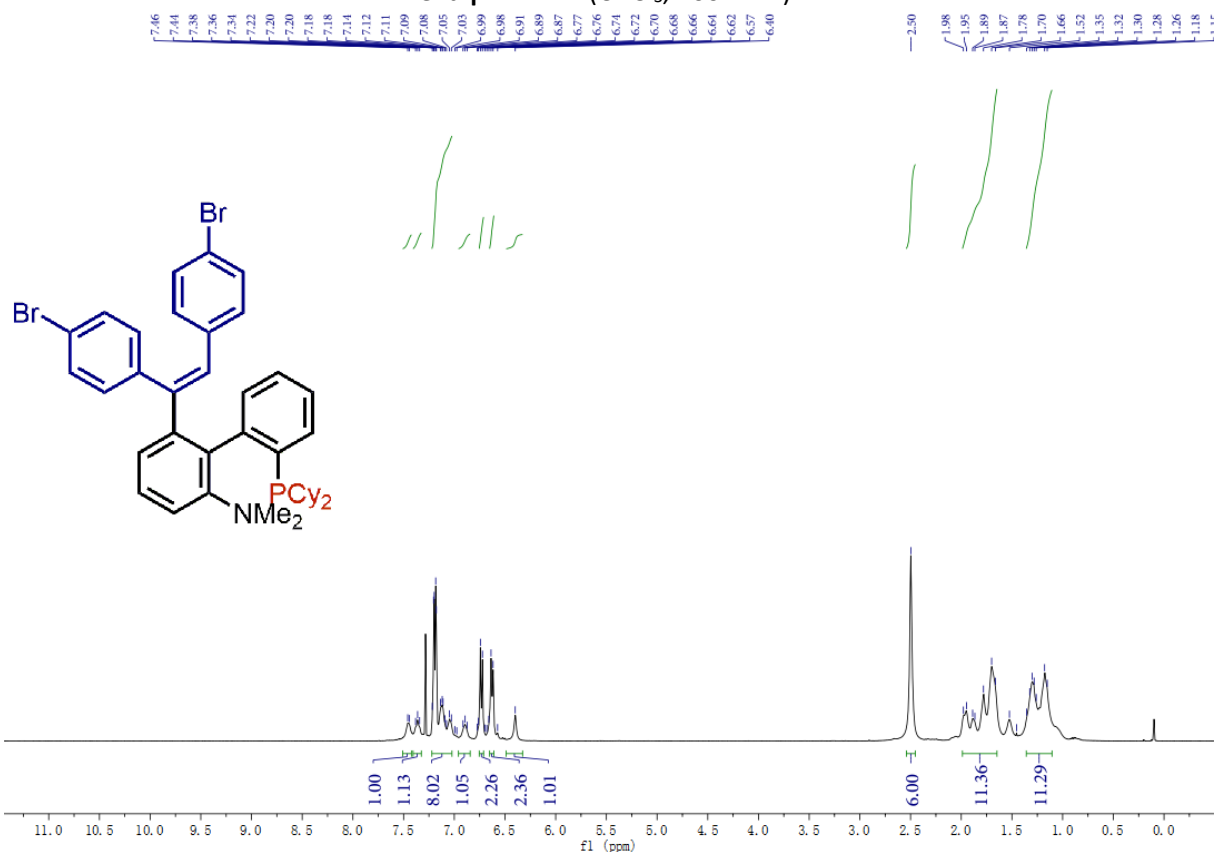
3ia | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



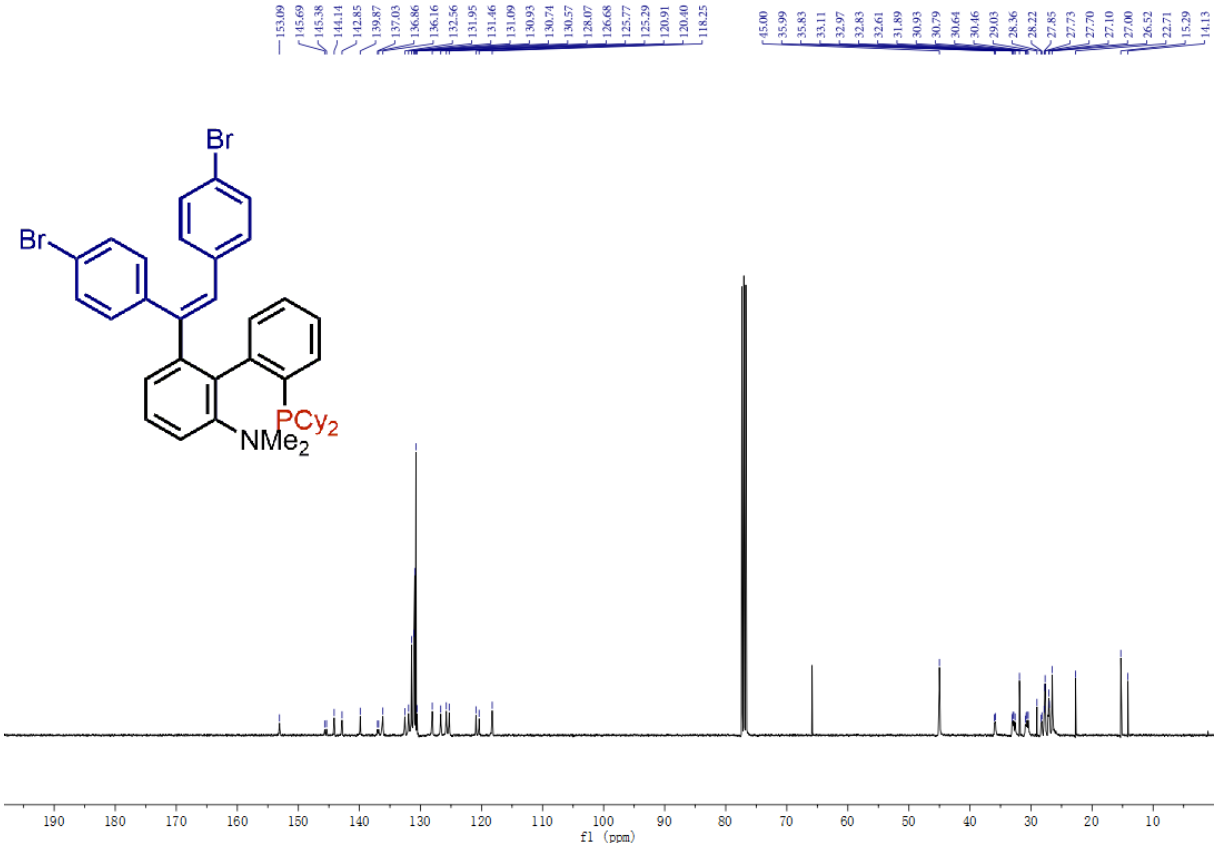
3ia | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



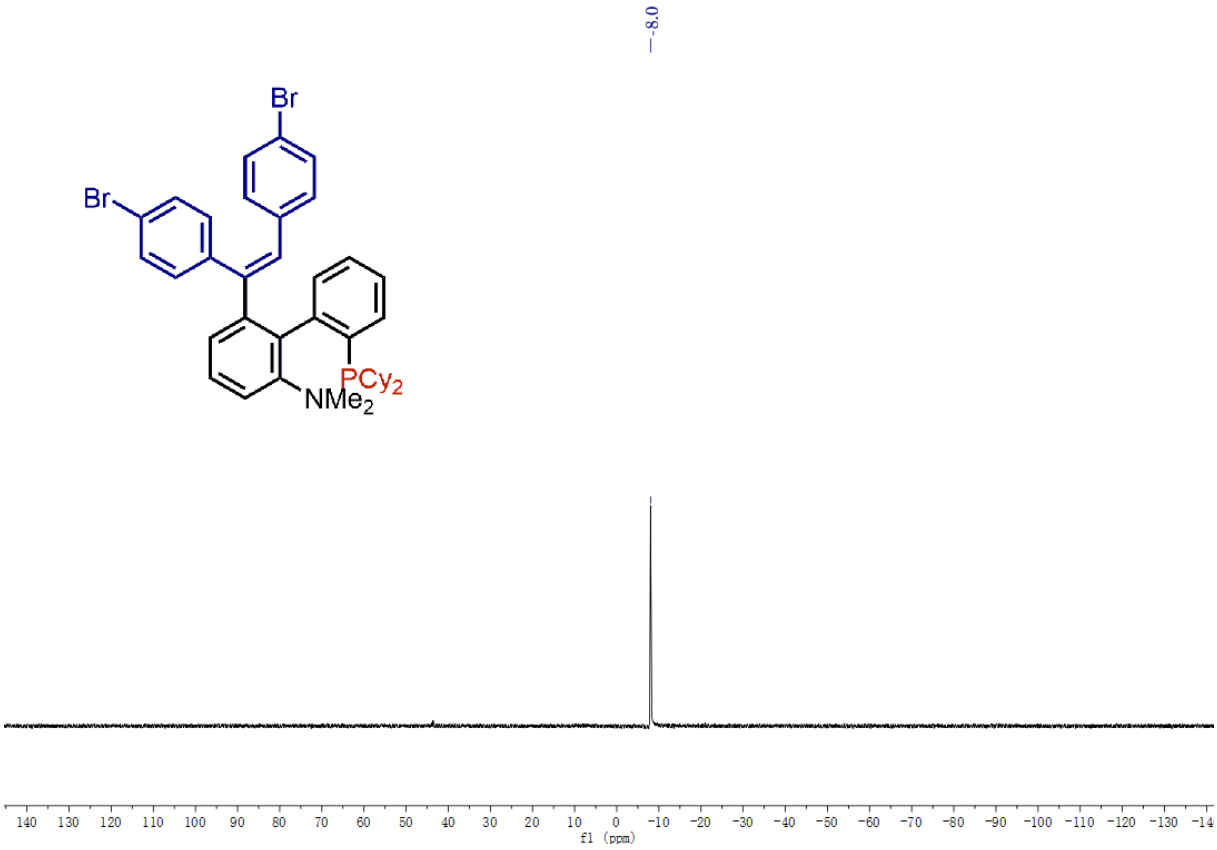
3fb | ^{1}H NMR ($CDCl_3$, 400 MHz)



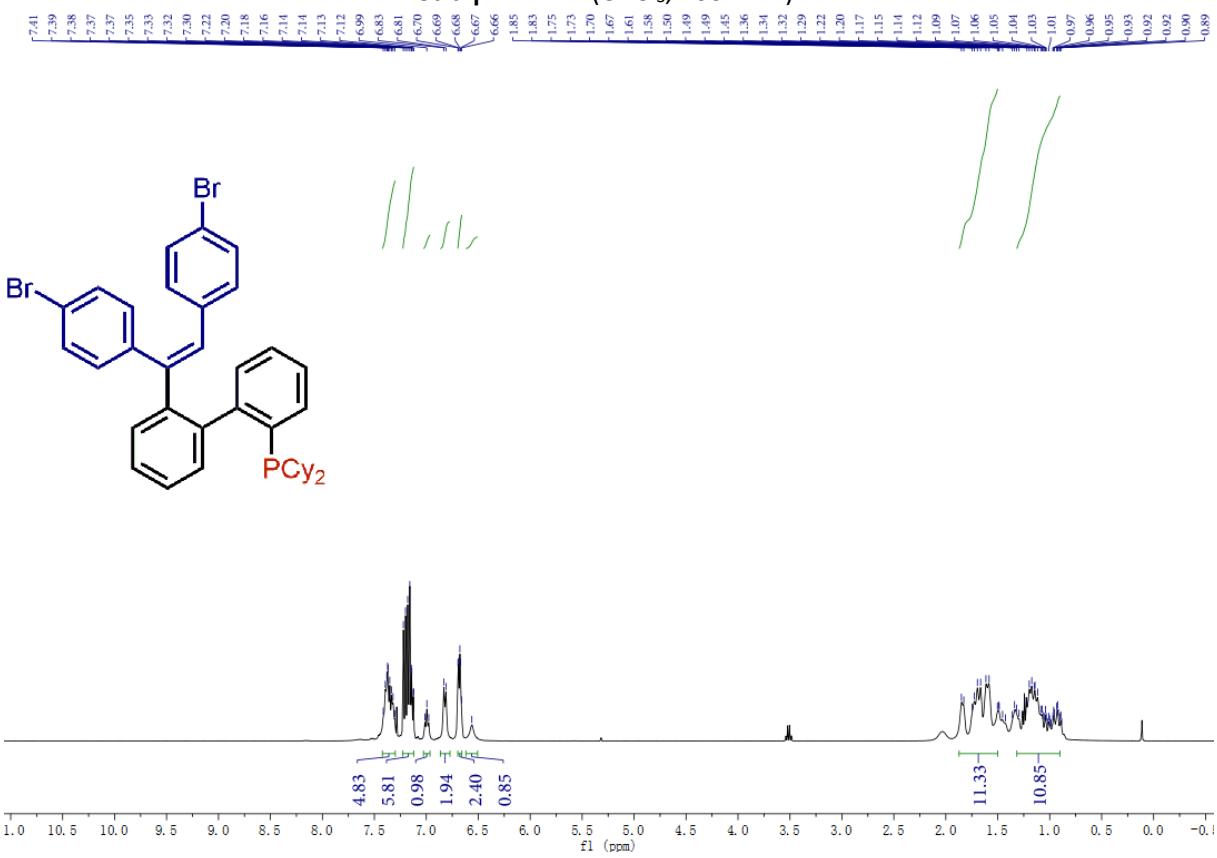
3fb | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



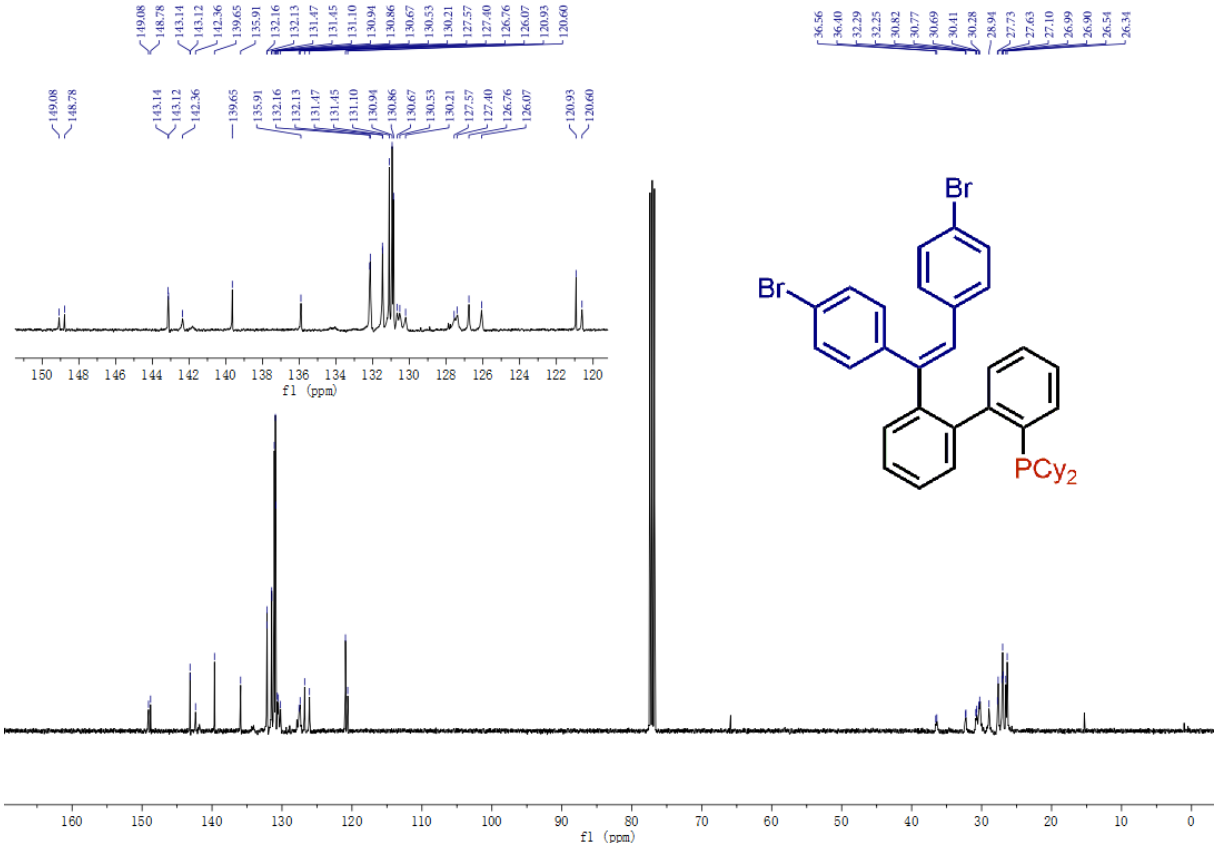
3fb | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



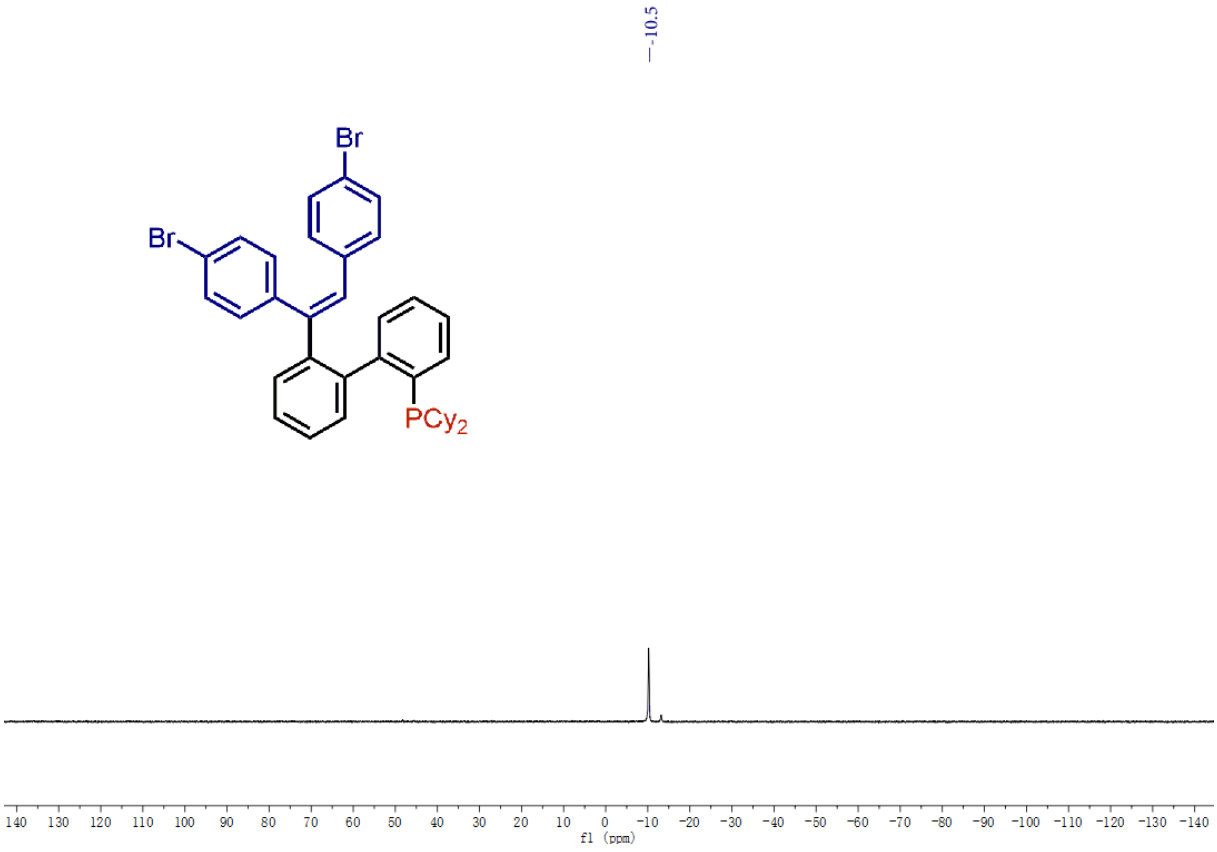
3ab | ^{1}H NMR ($CDCl_3$, 400 MHz)



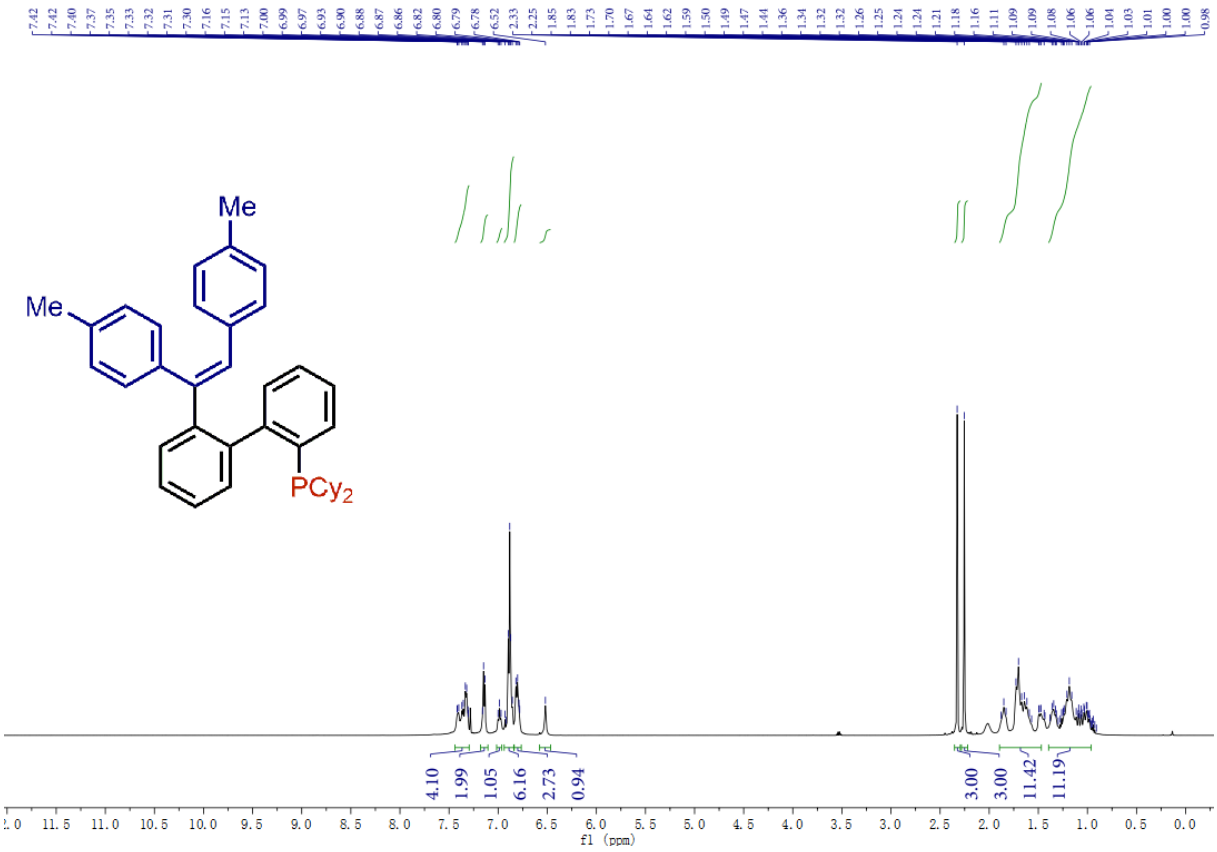
3ab | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



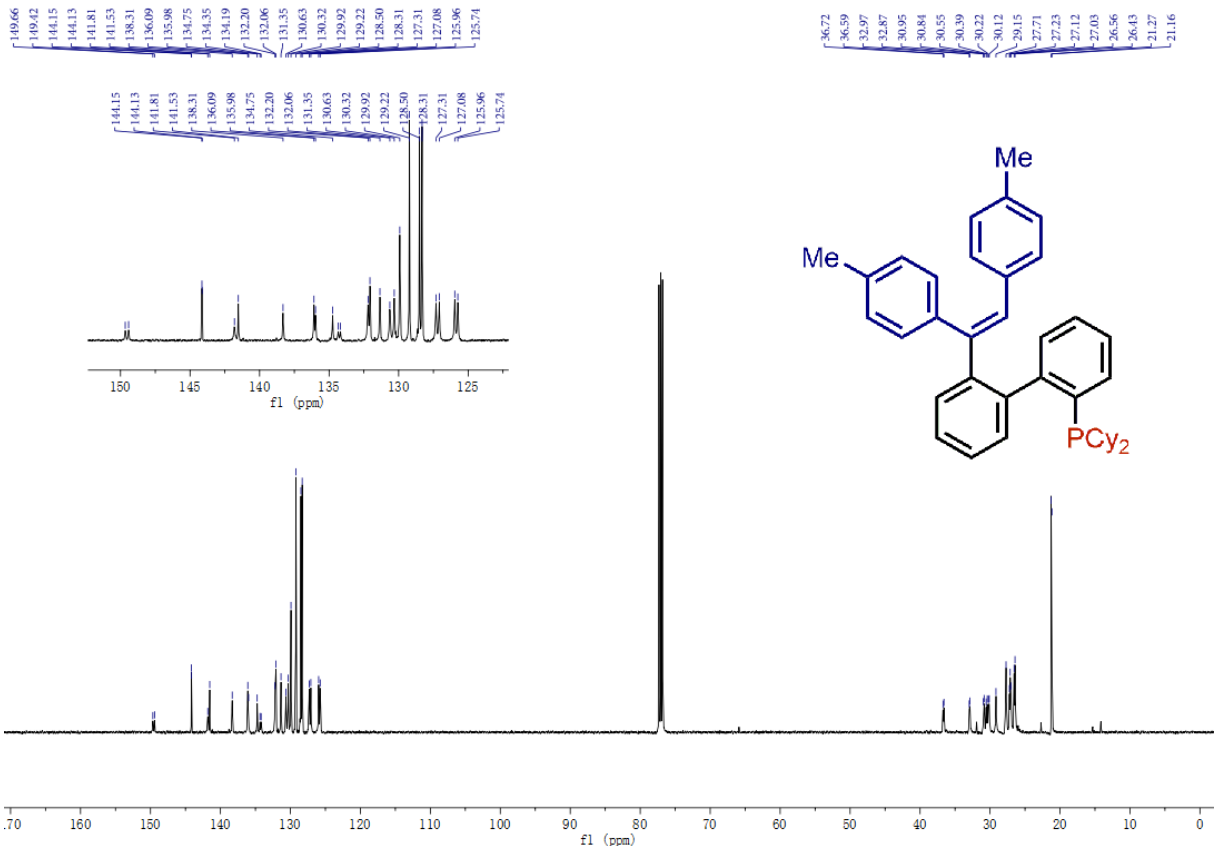
3ab | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



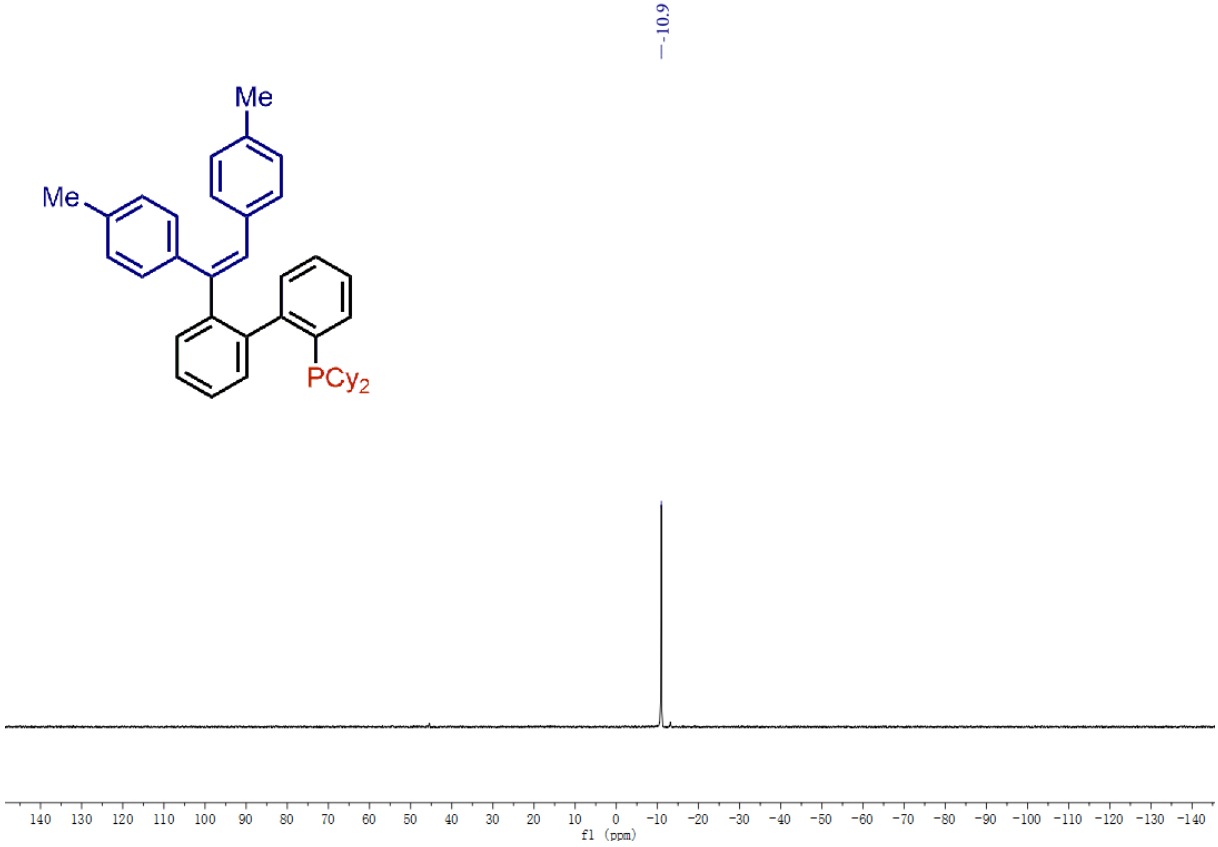
3ac | ^{1}H NMR ($CDCl_3$, 400 MHz)



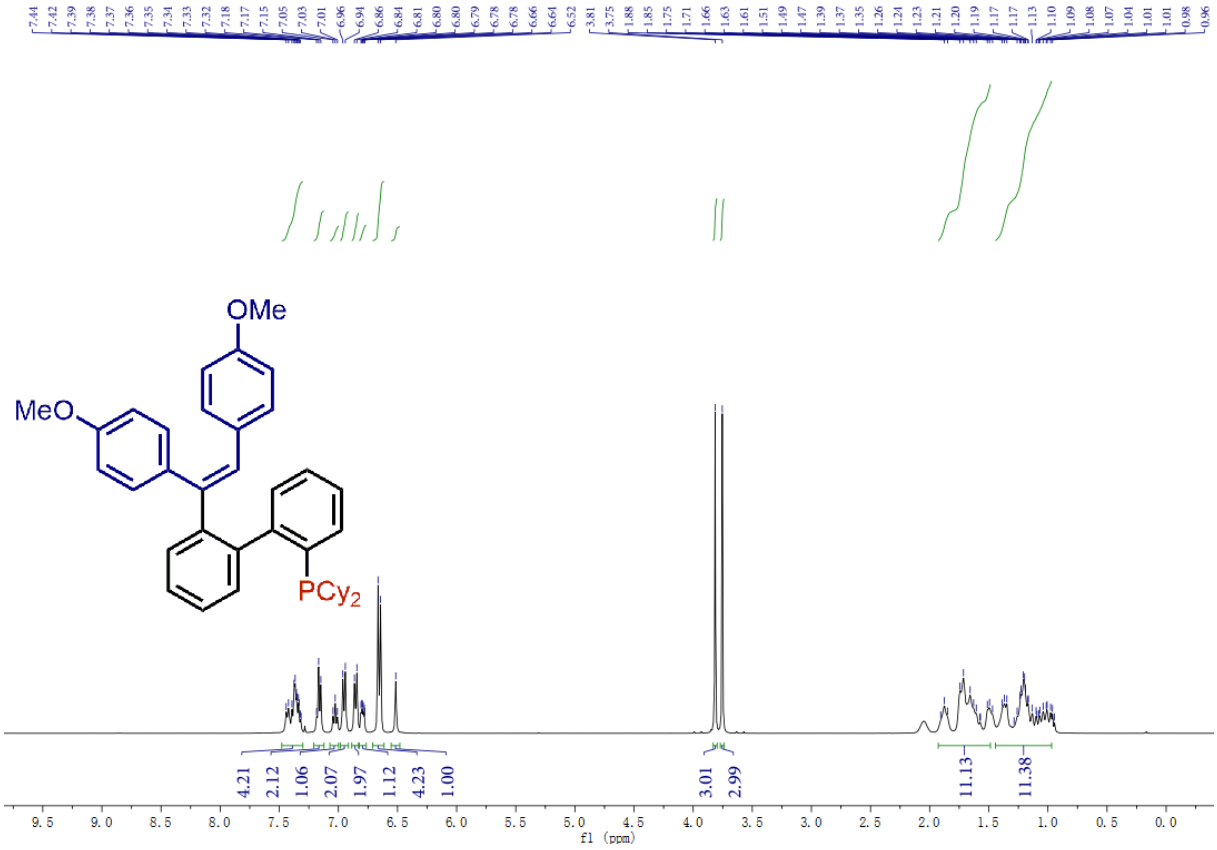
3ac | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



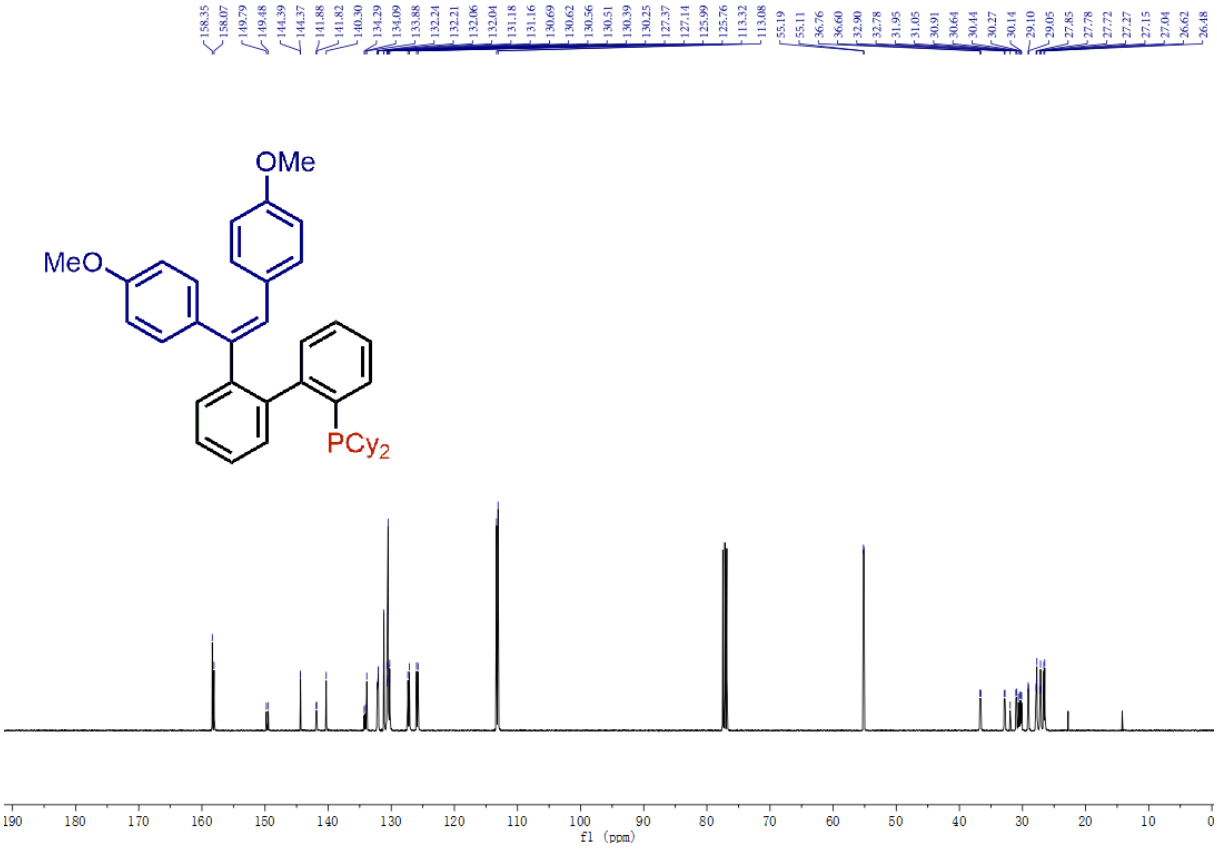
3ac | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



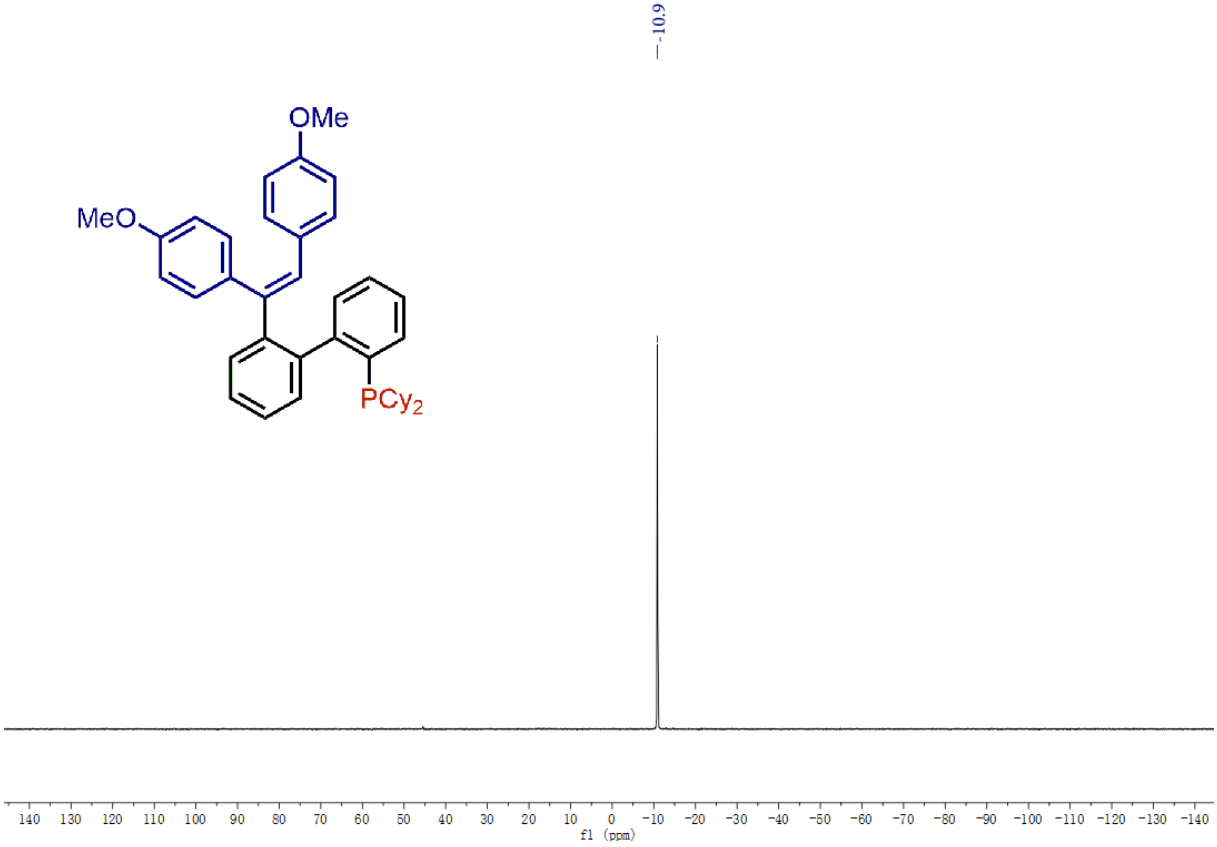
3ad | ^{1}H NMR ($CDCl_3$, 400 MHz)



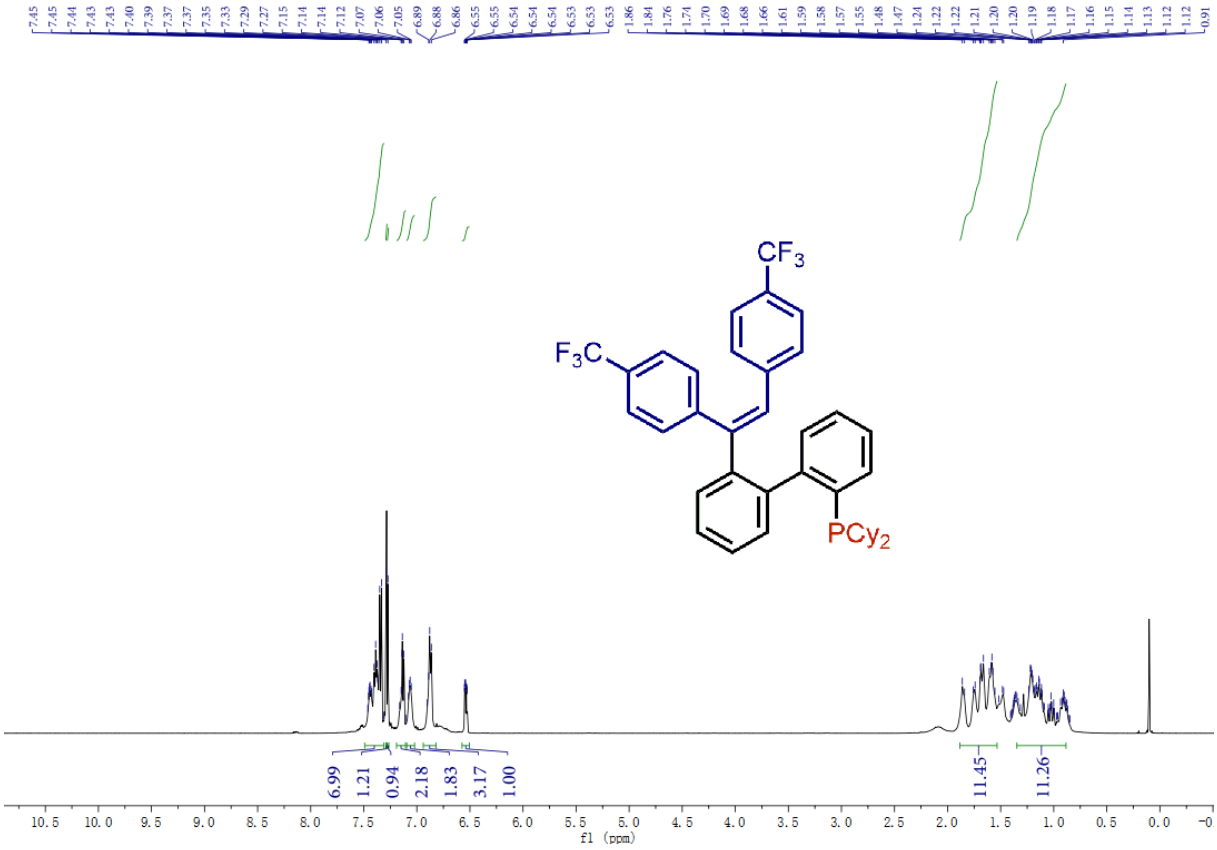
3ad | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



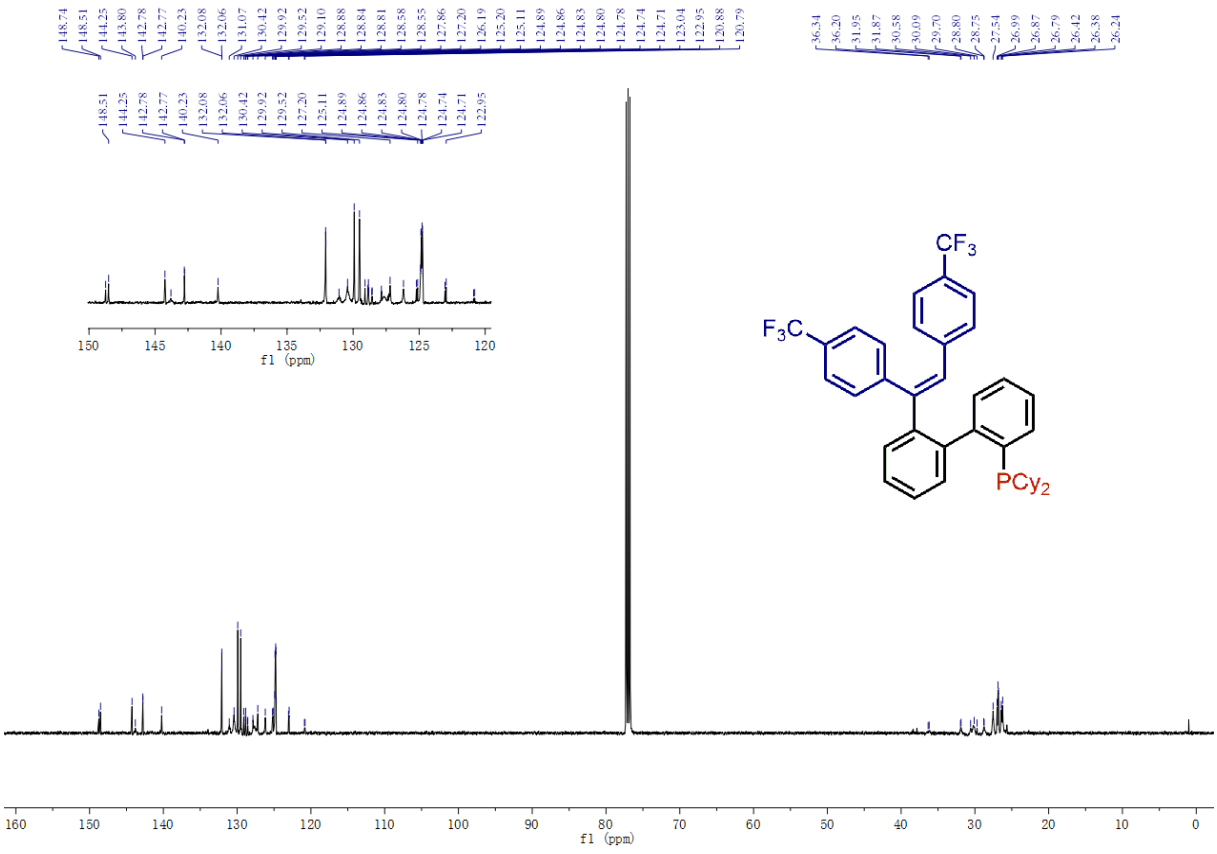
3ad | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



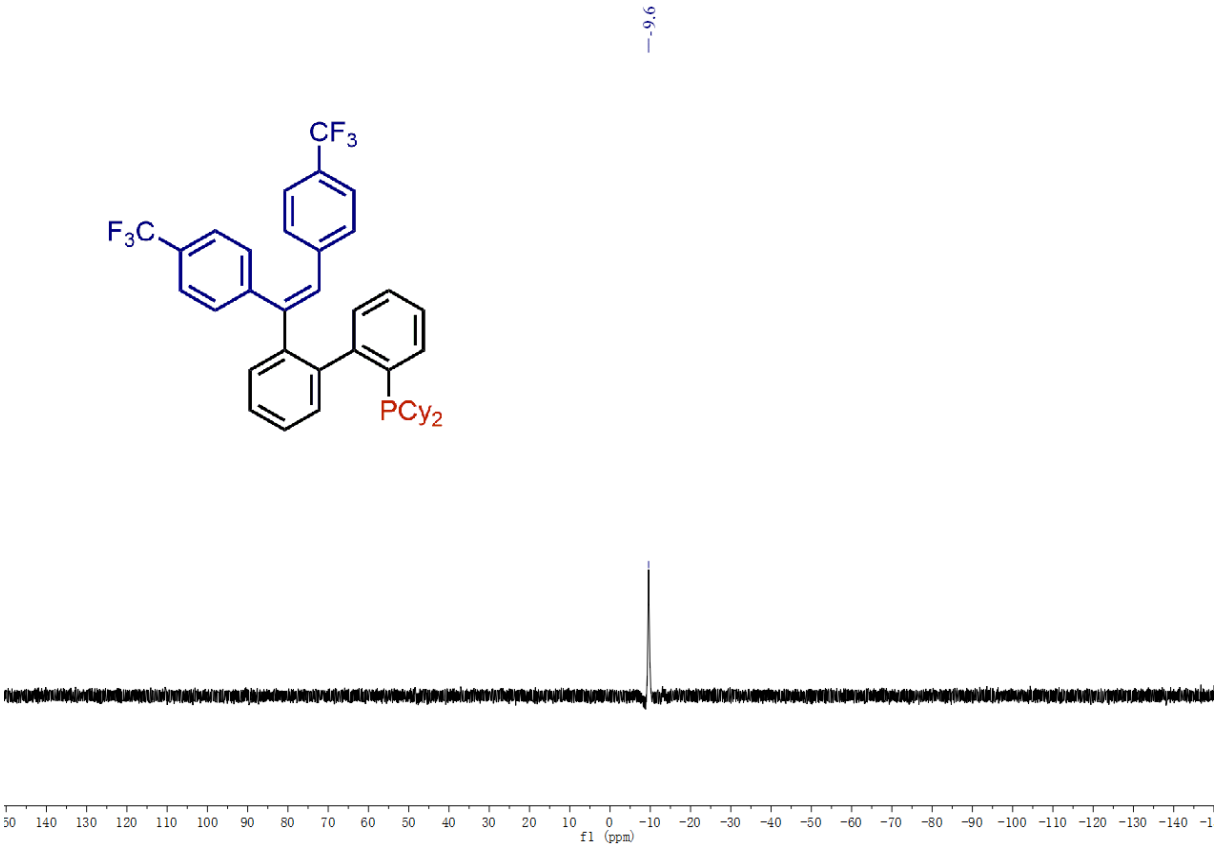
3ae | ^{1}H NMR ($CDCl_3$, 400 MHz)



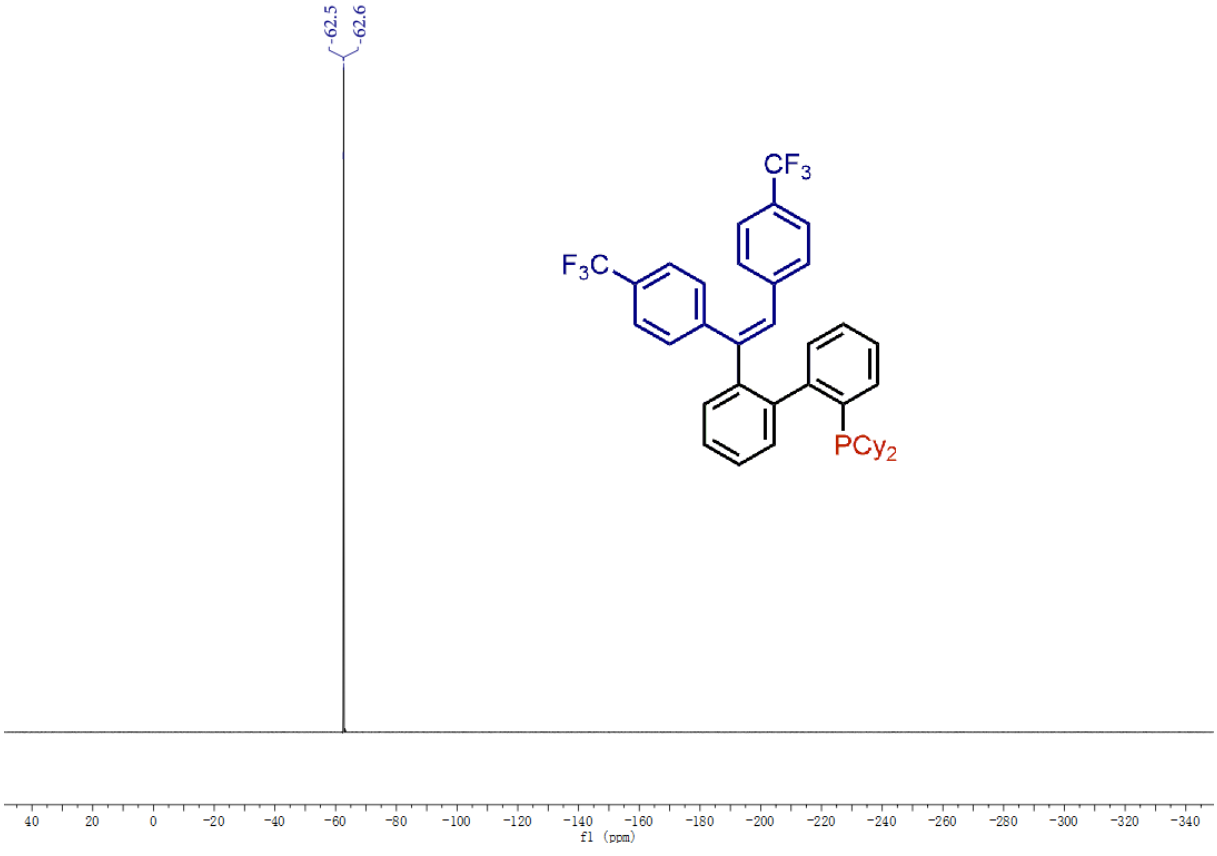
3ae | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



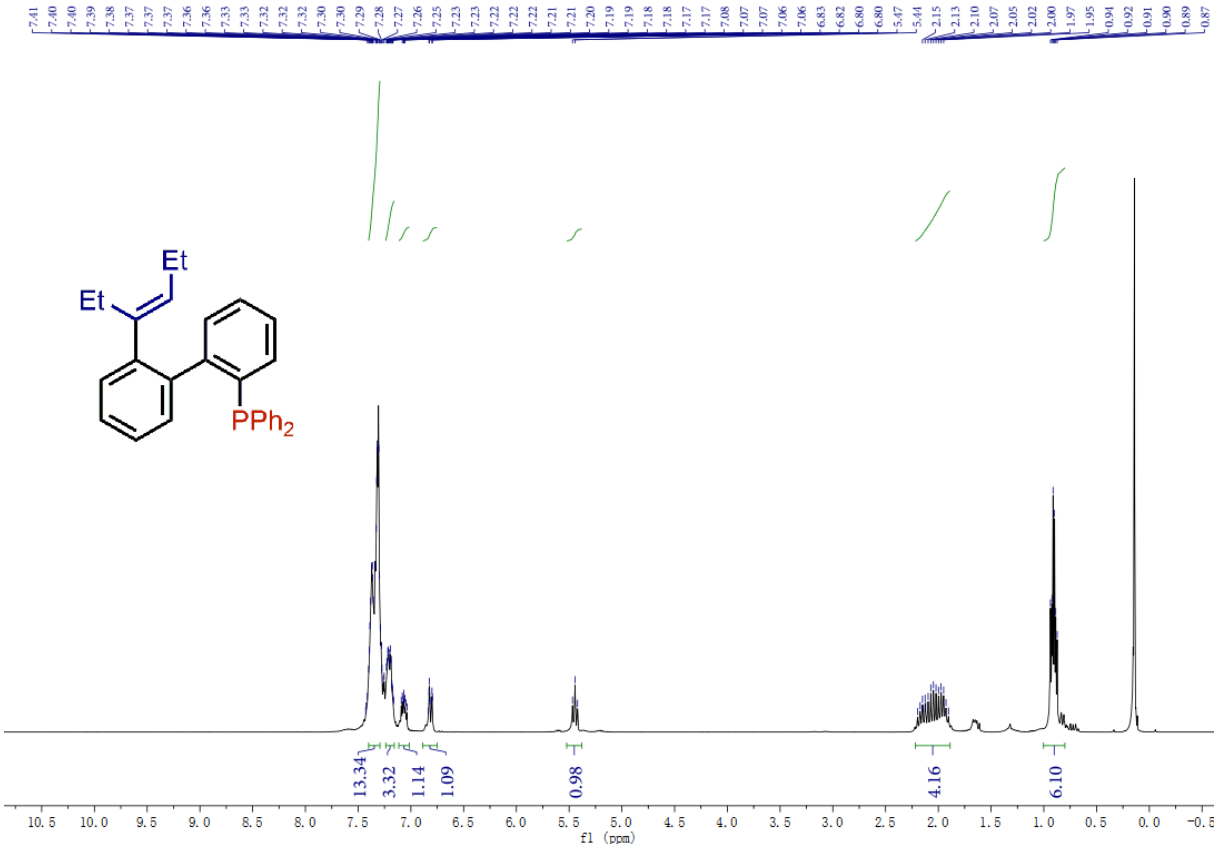
3ae | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



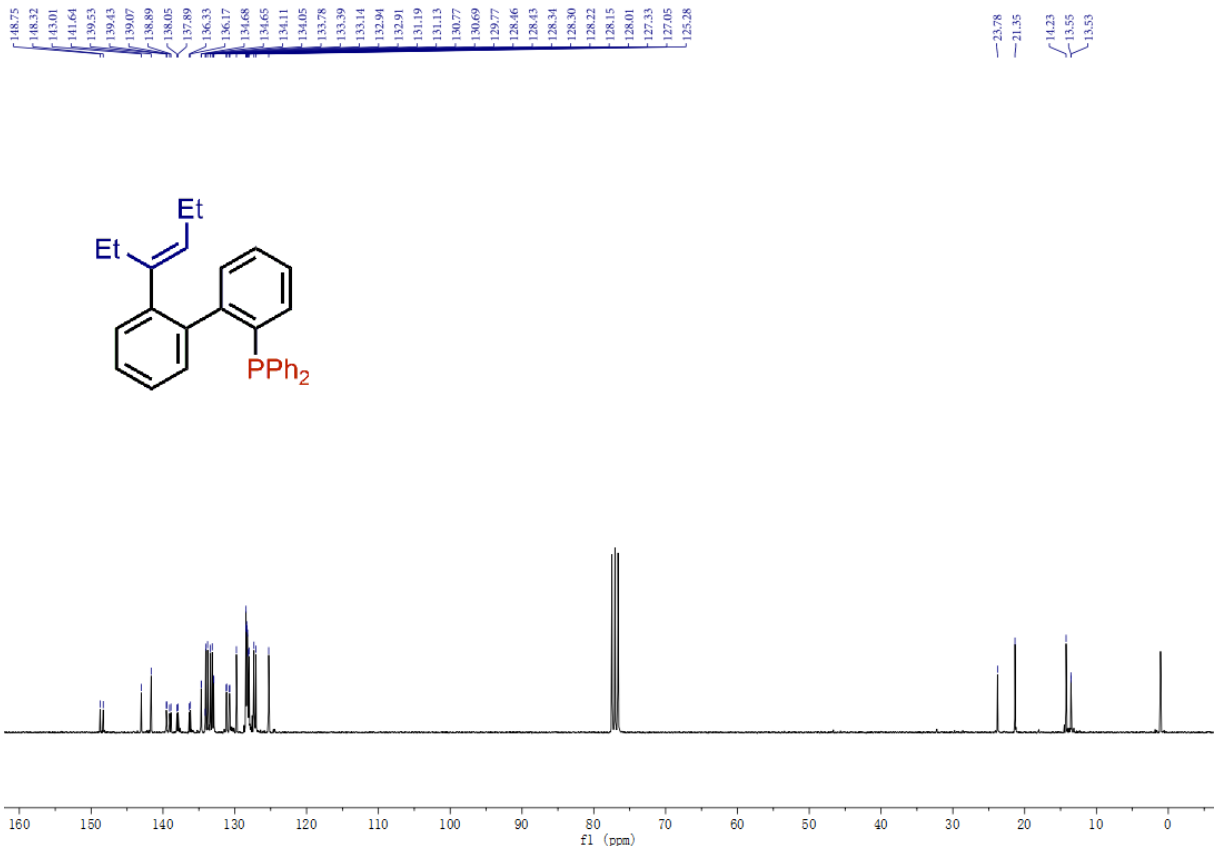
3ae | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 471 MHz)



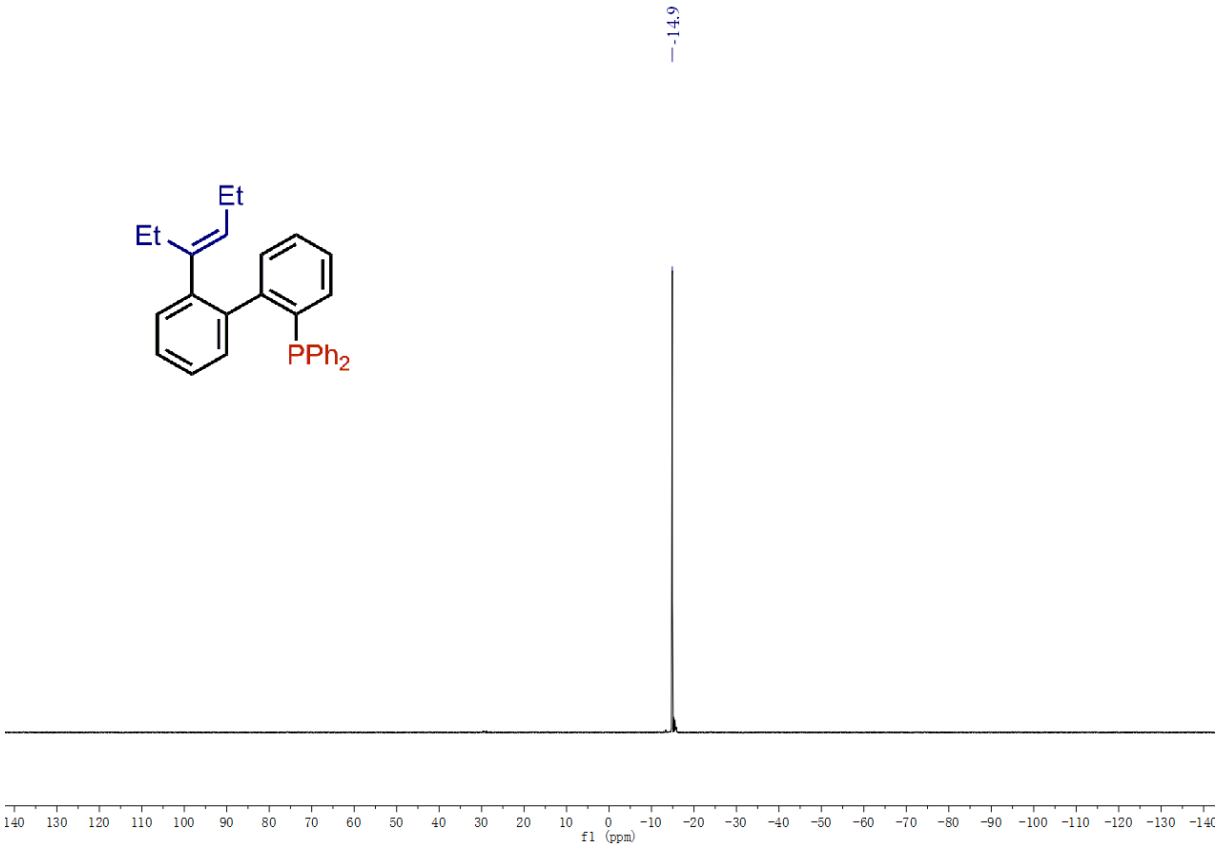
3bf | ^{1}H NMR ($CDCl_3$, 400 MHz)



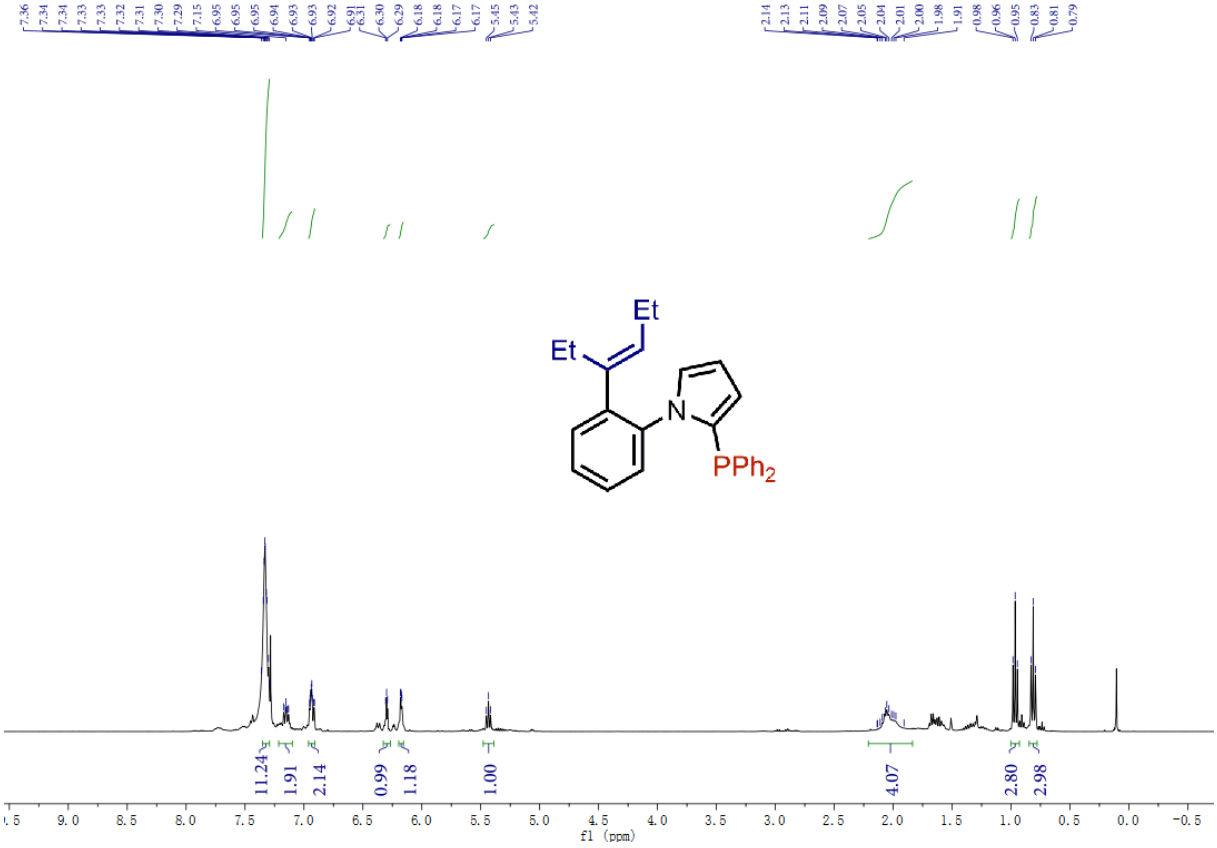
3bf | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



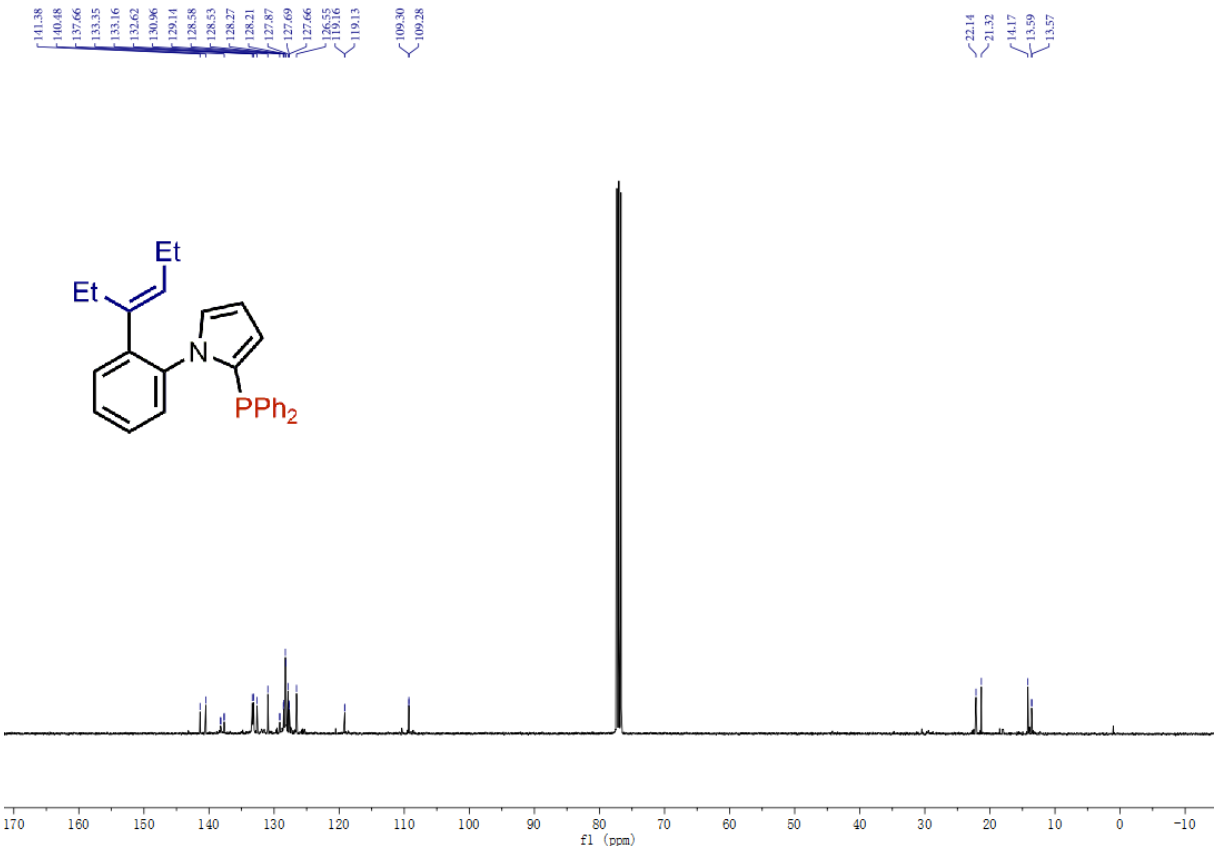
3bf | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



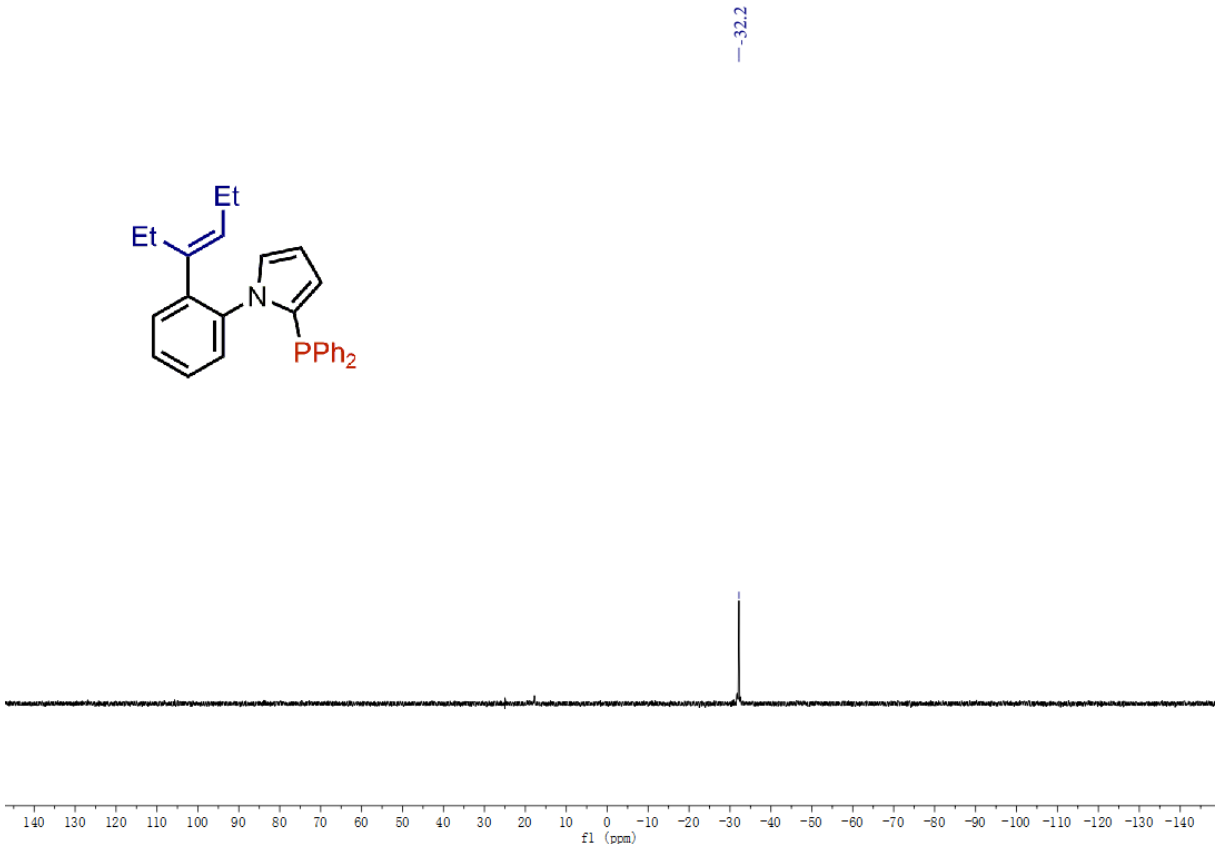
3hf | ^{1}H NMR ($CDCl_3$, 400 MHz)



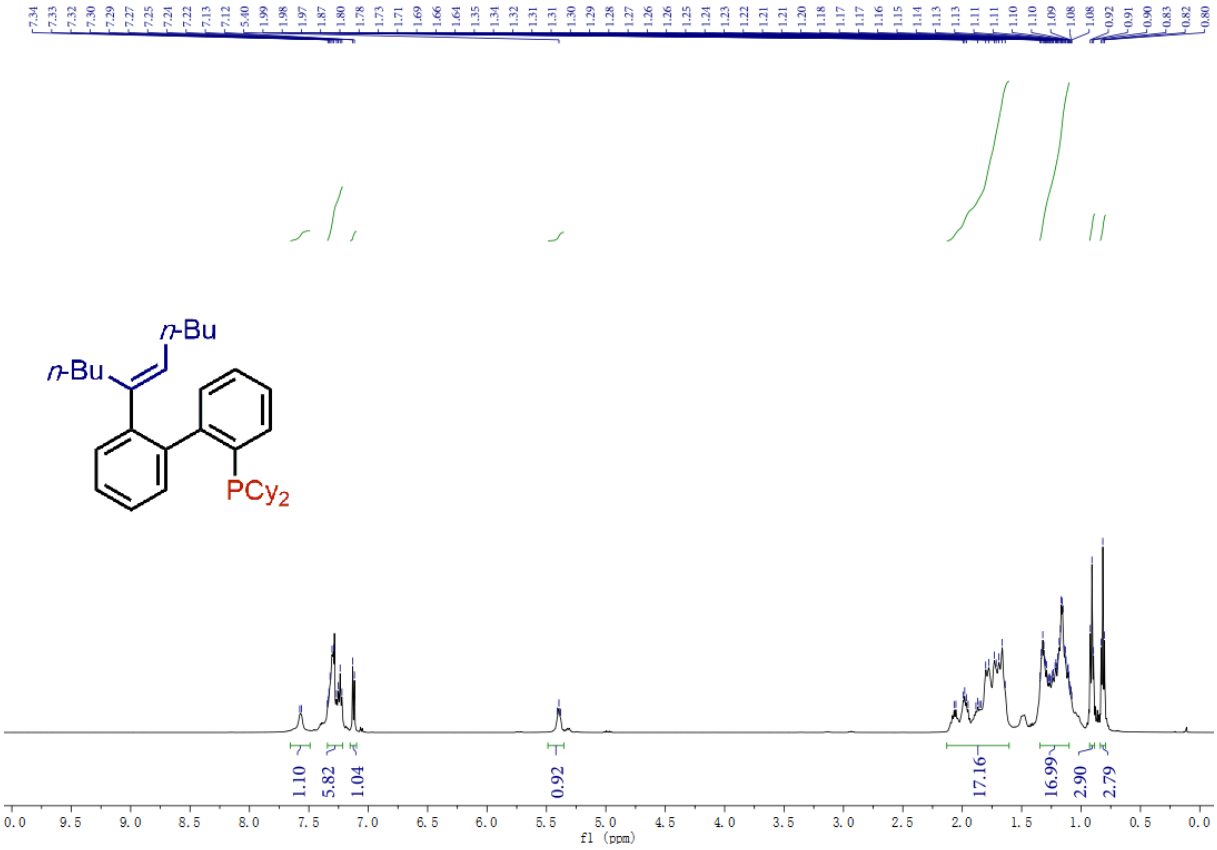
3hf | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



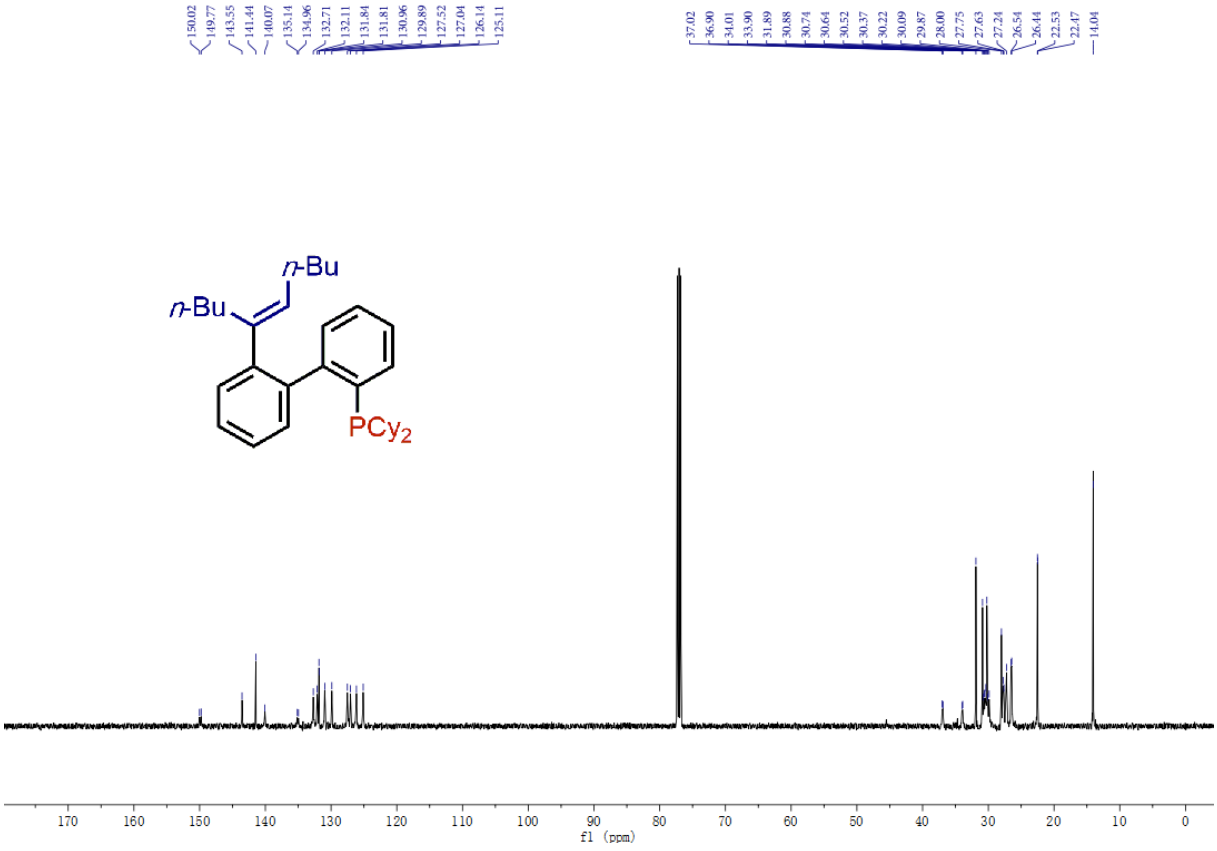
3hf | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



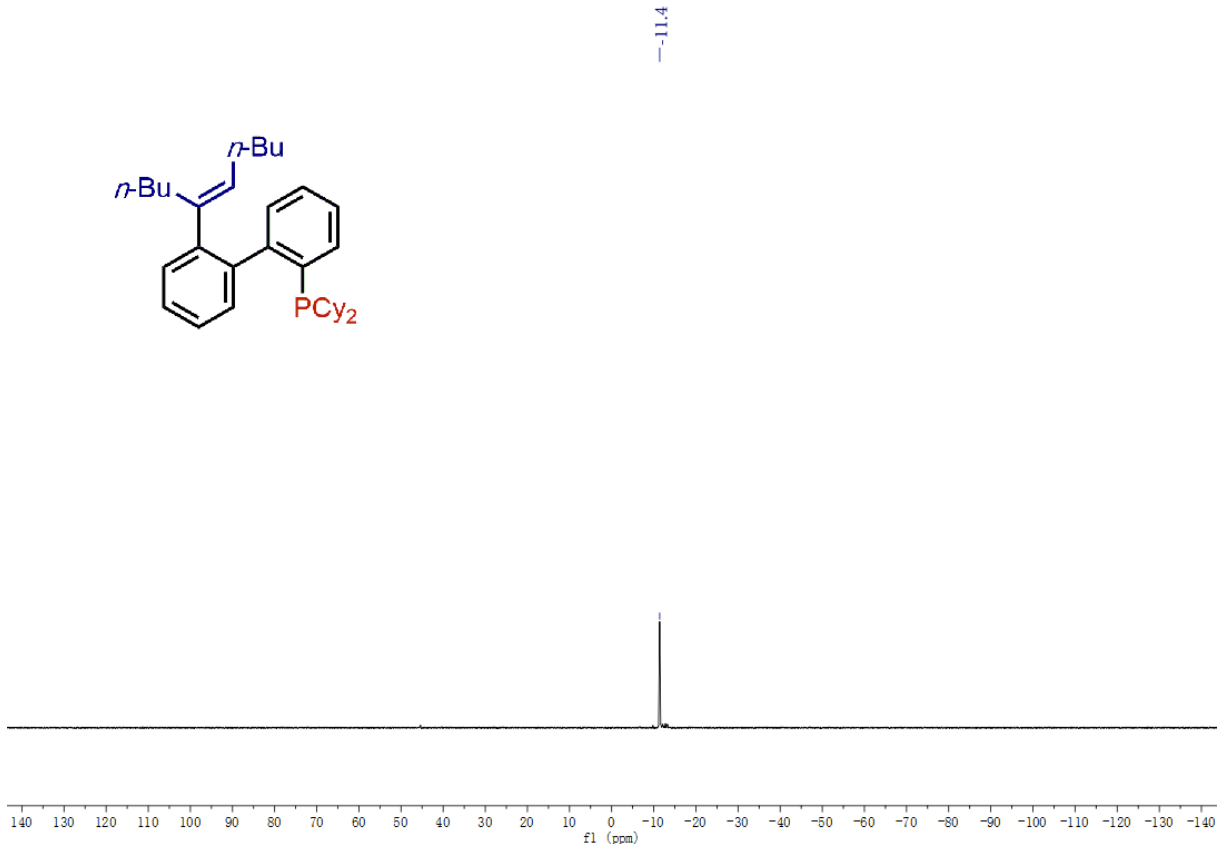
3ag | ^{1}H NMR ($CDCl_3$, 400 MHz)



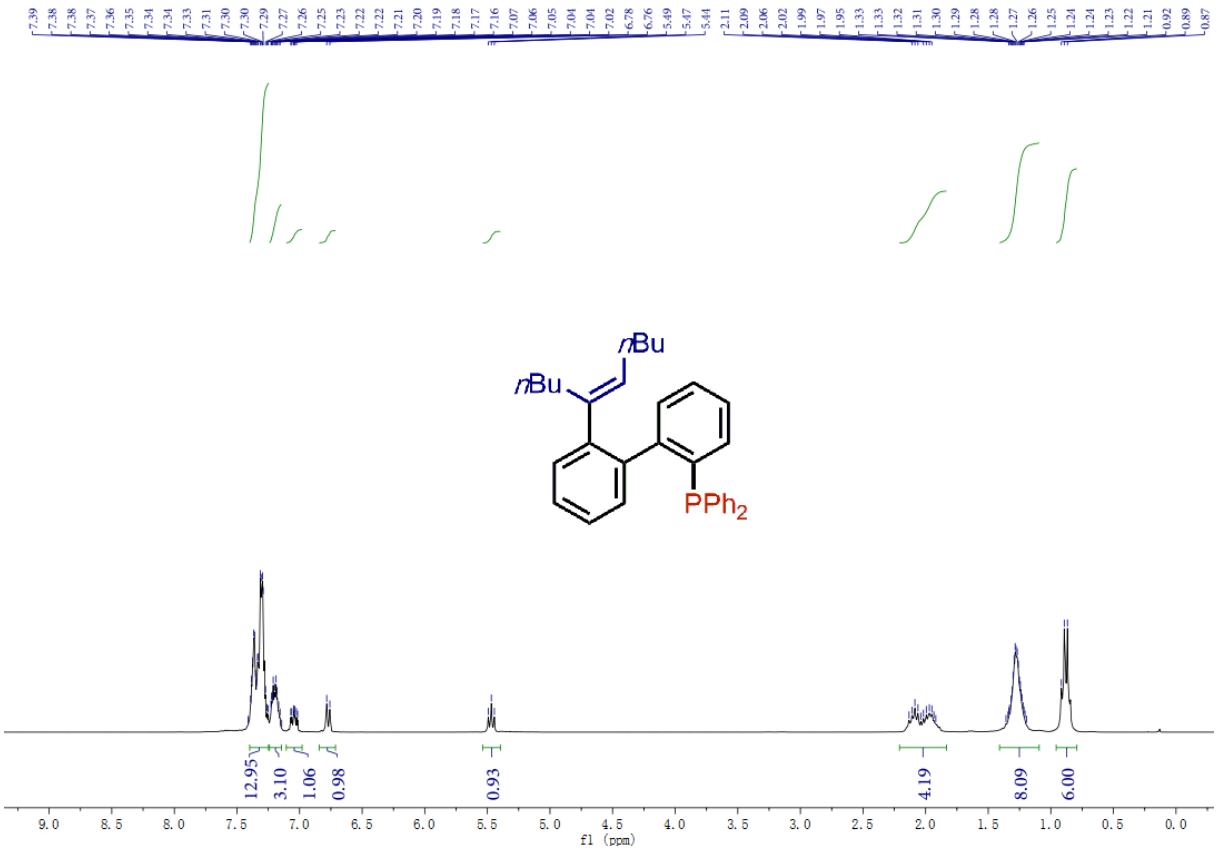
3ag | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



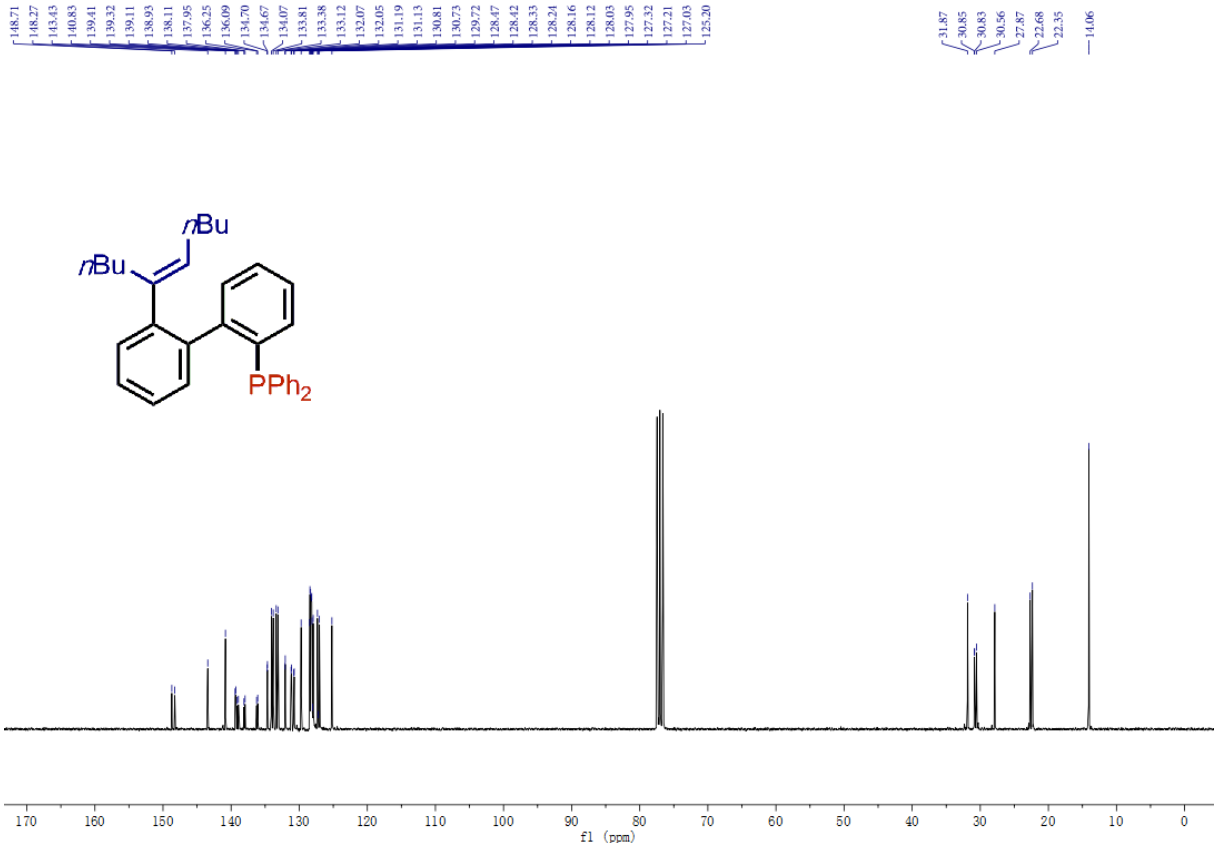
3ag | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



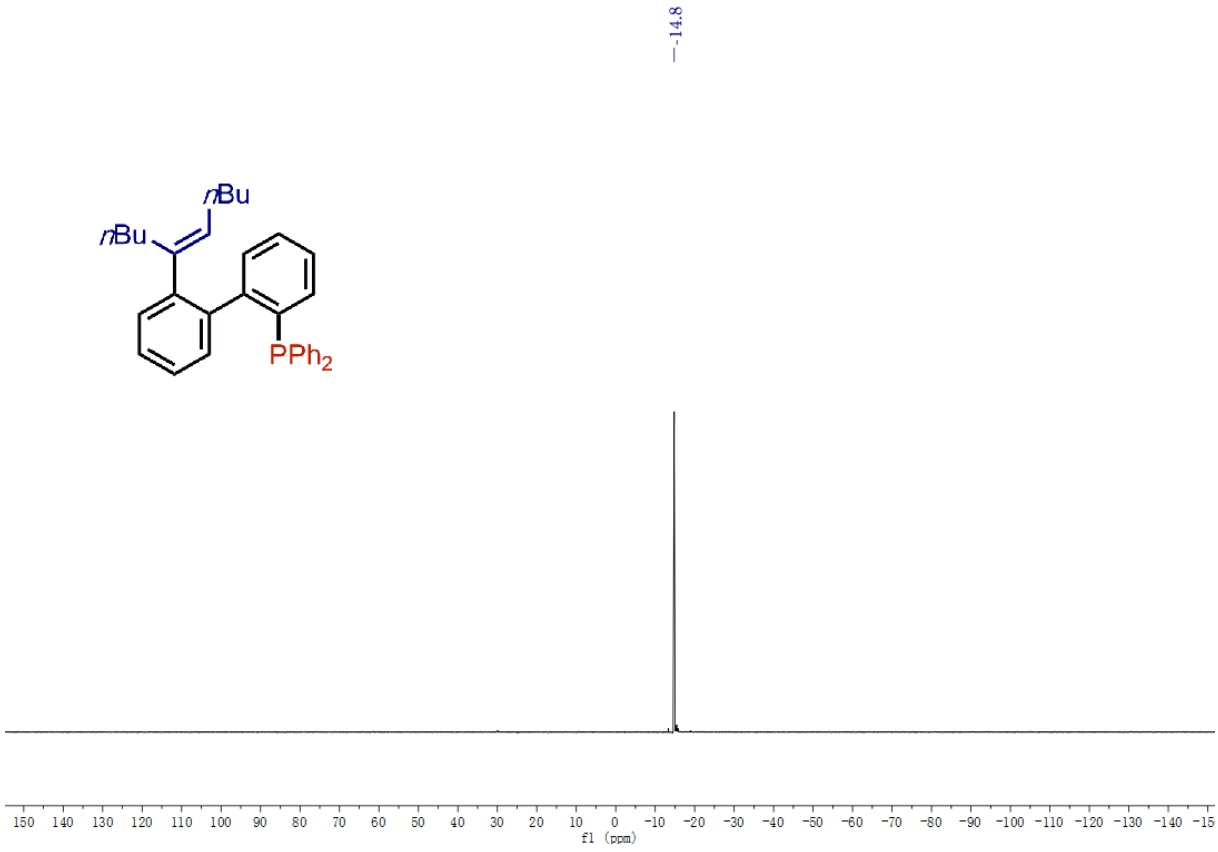
3bg | ^{1}H NMR ($CDCl_3$, 400 MHz)



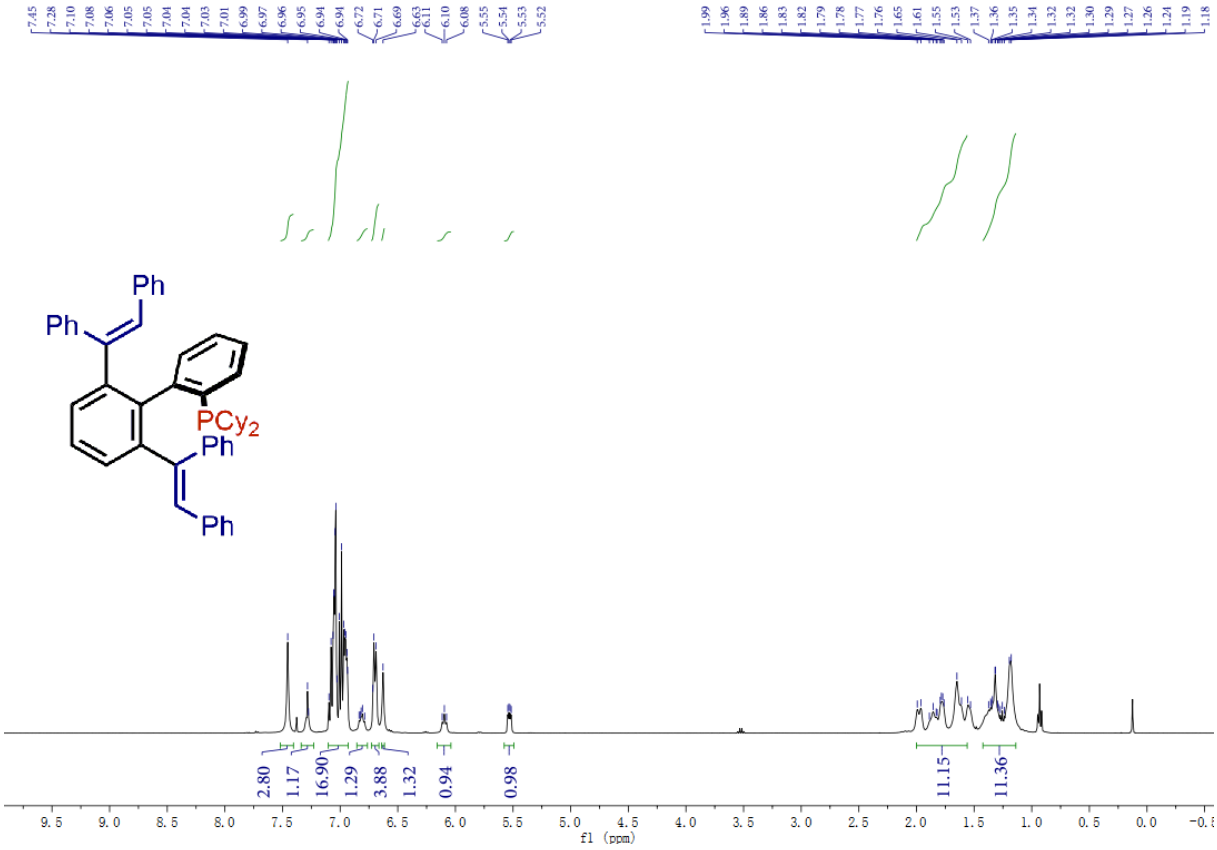
3bg | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



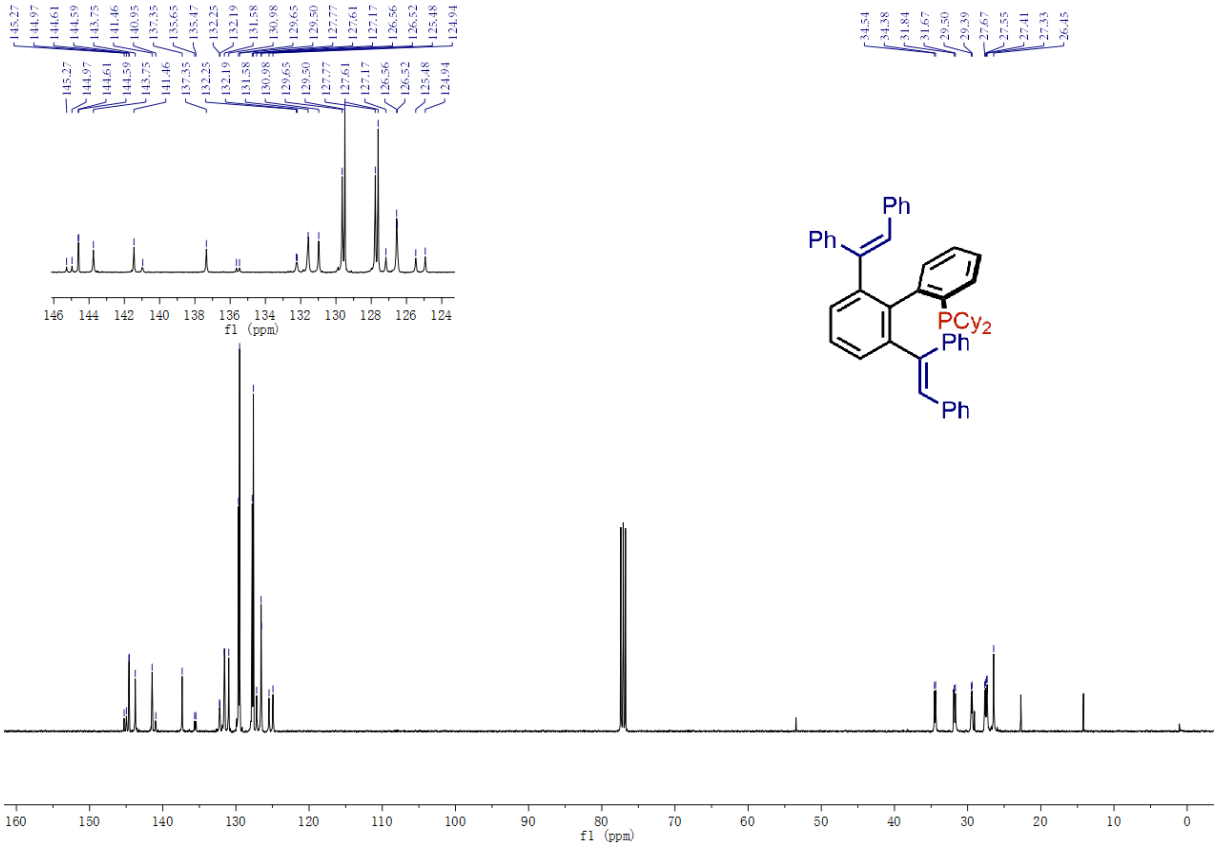
3bg | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



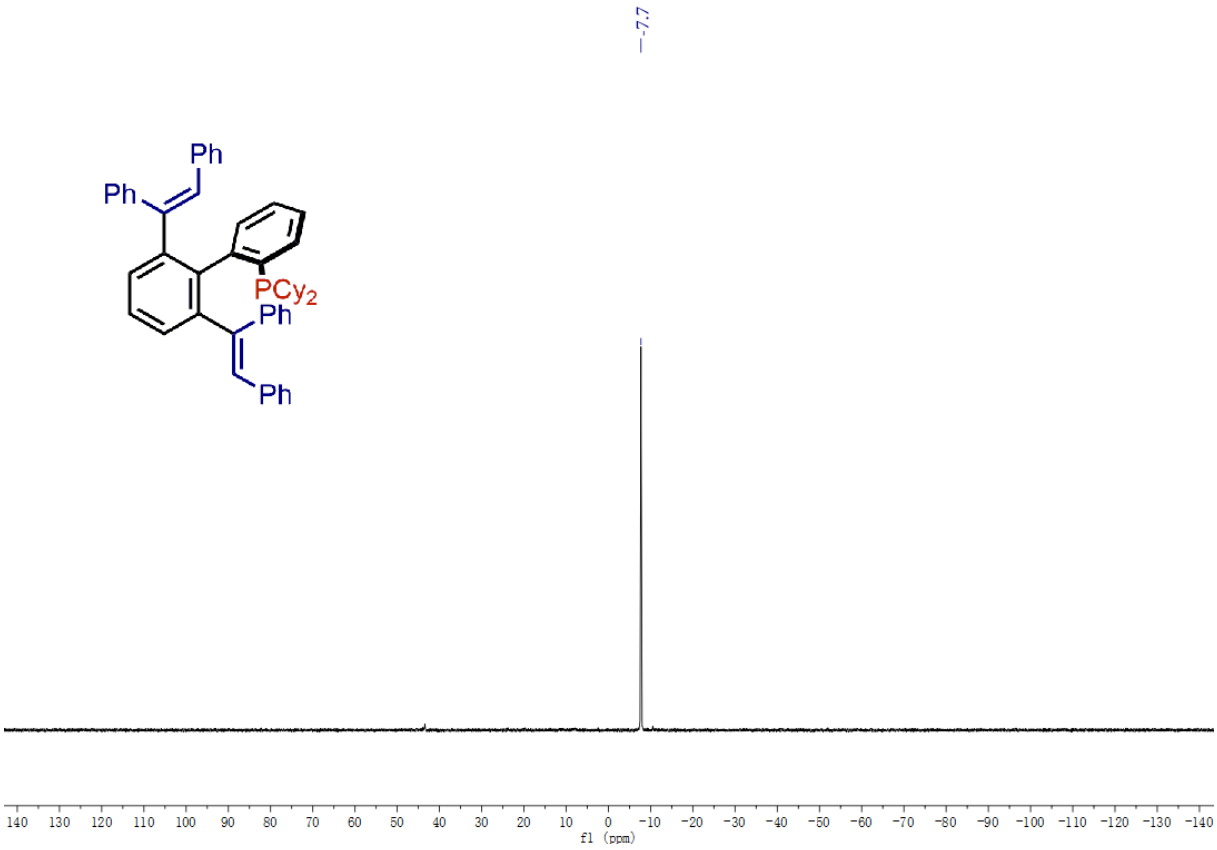
4aa | ^{1}H NMR ($CDCl_3$, 400 MHz)



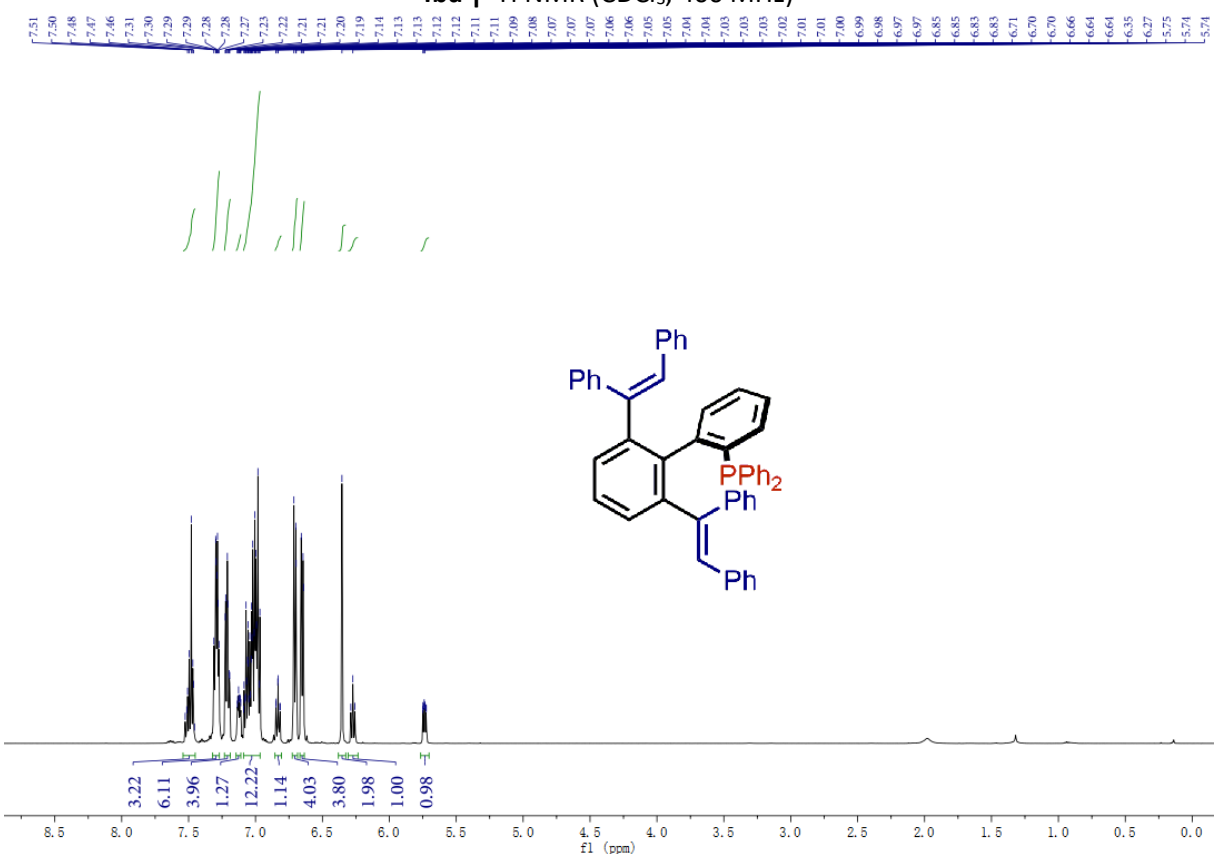
4aa | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



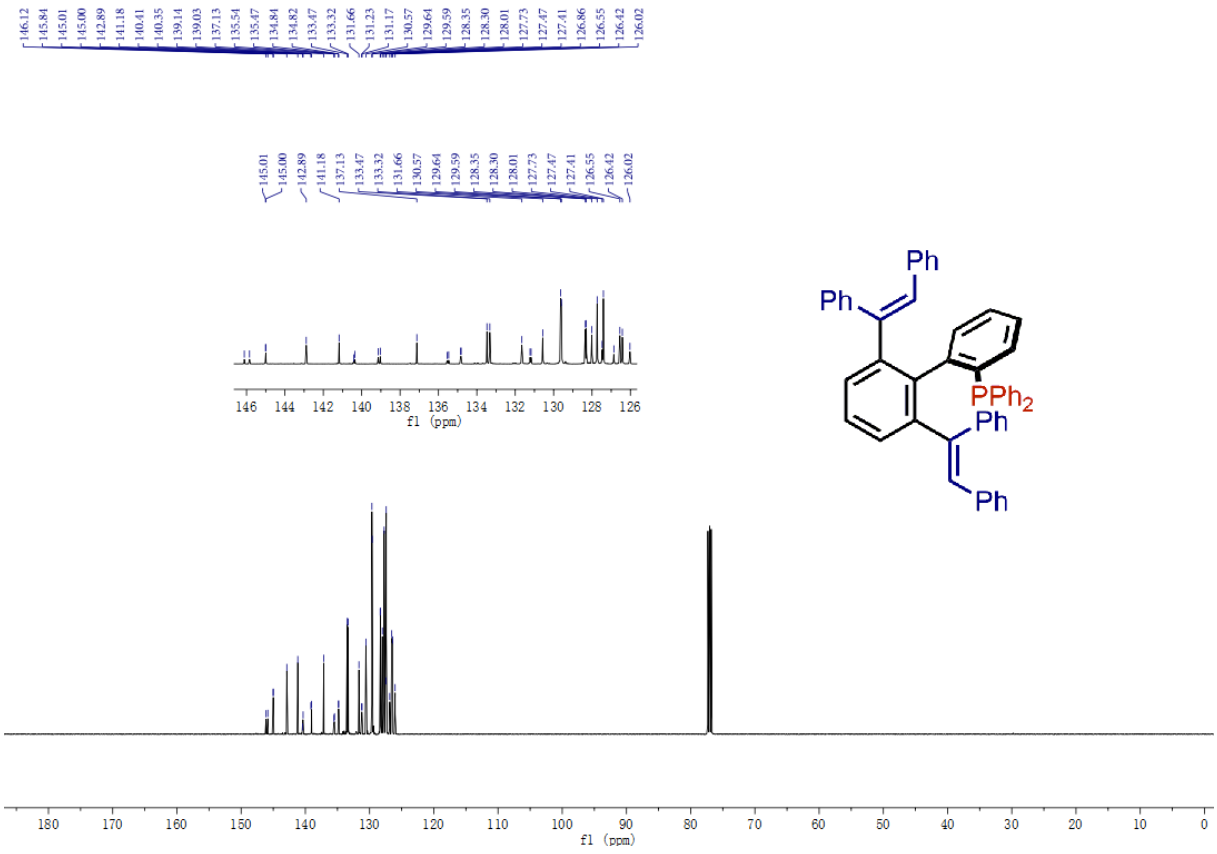
4aa | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



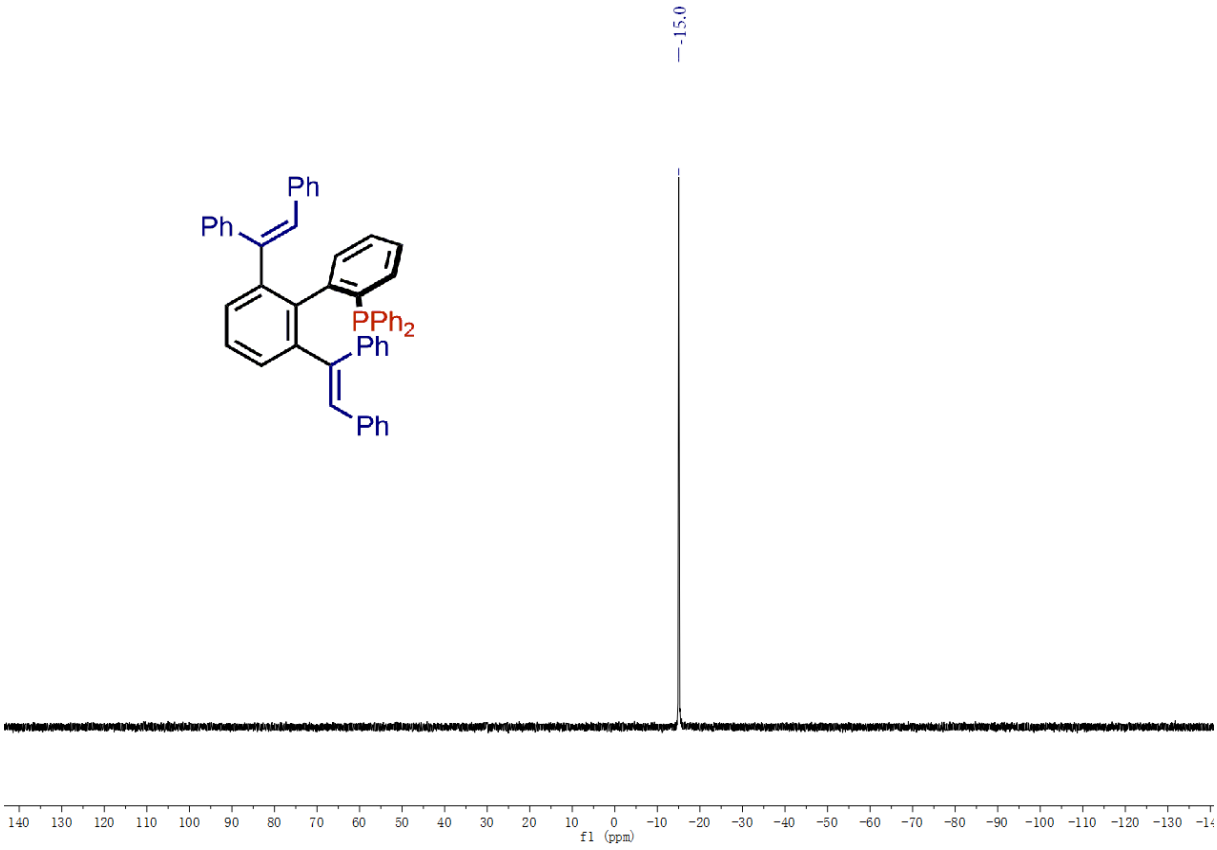
4ba | ^{1}H NMR ($CDCl_3$, 400 MHz)



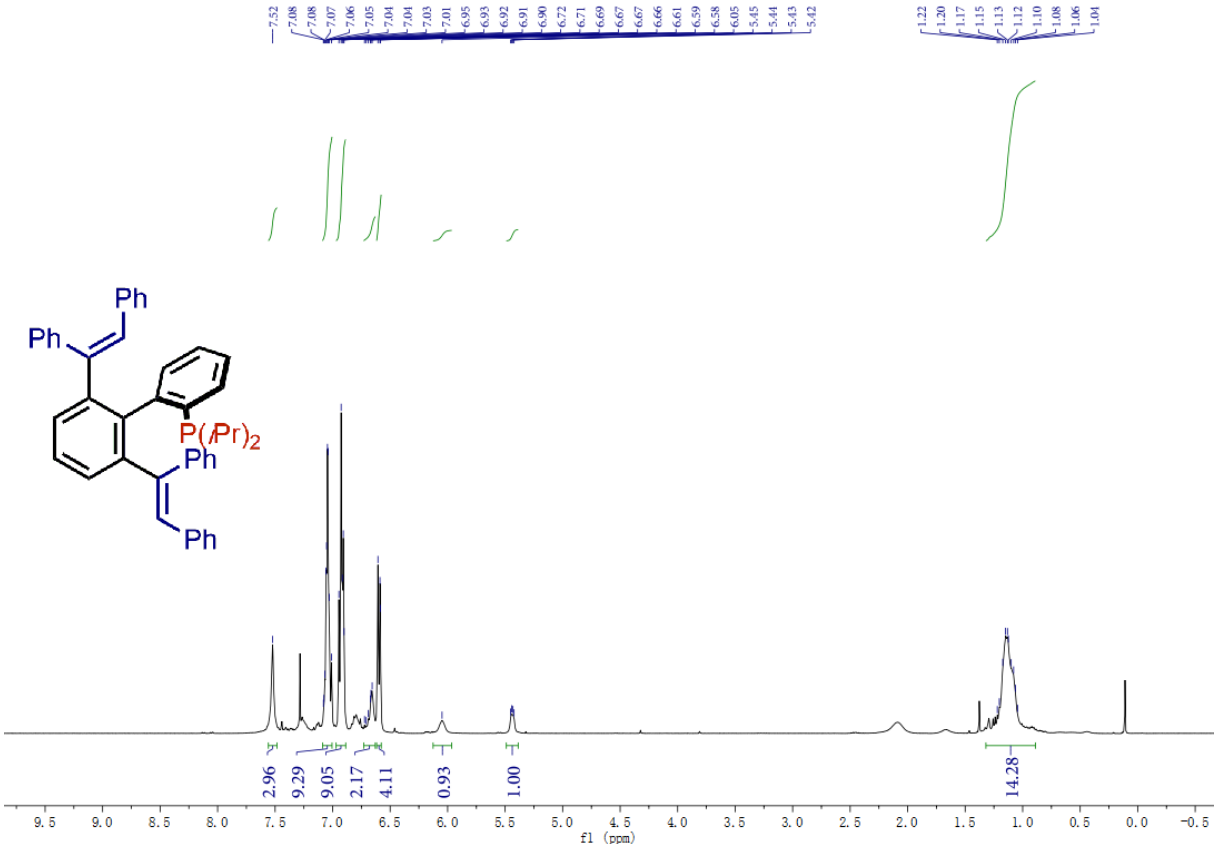
4ba | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



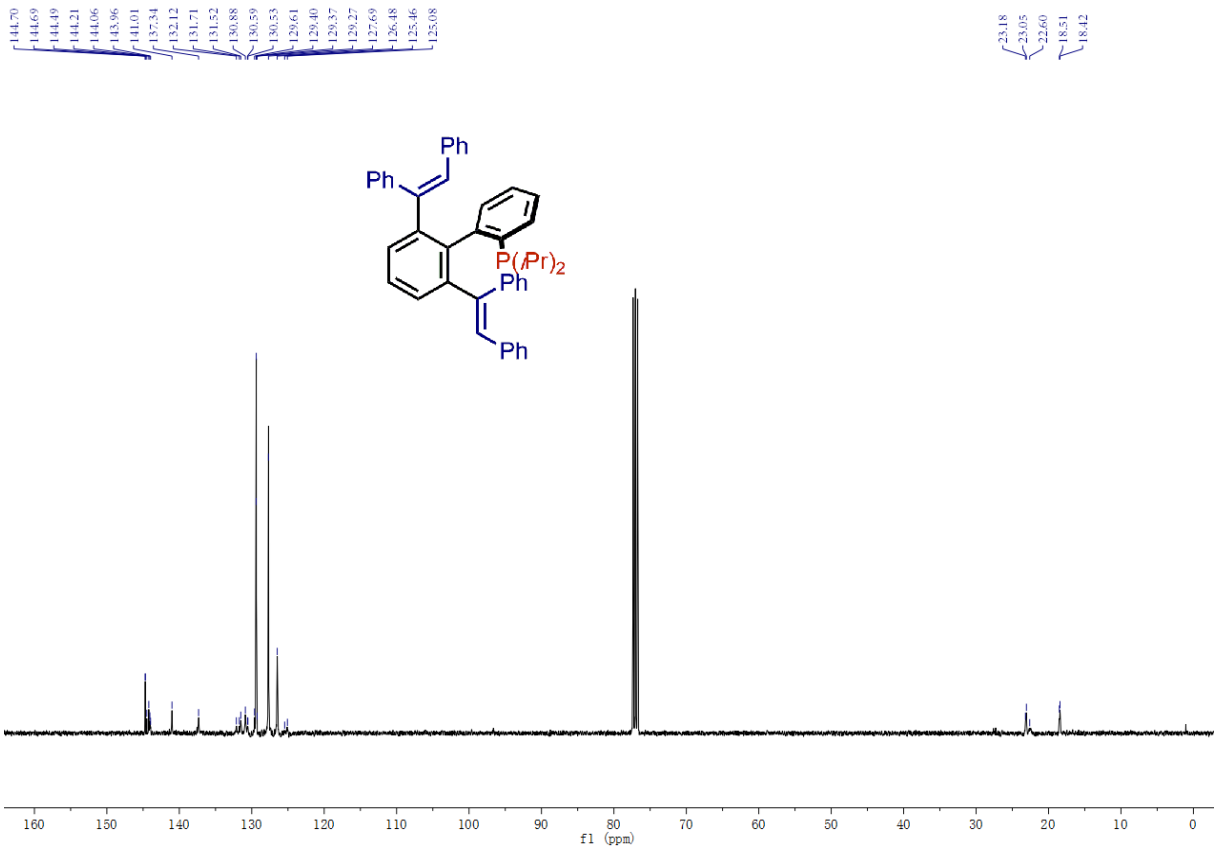
4ba | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



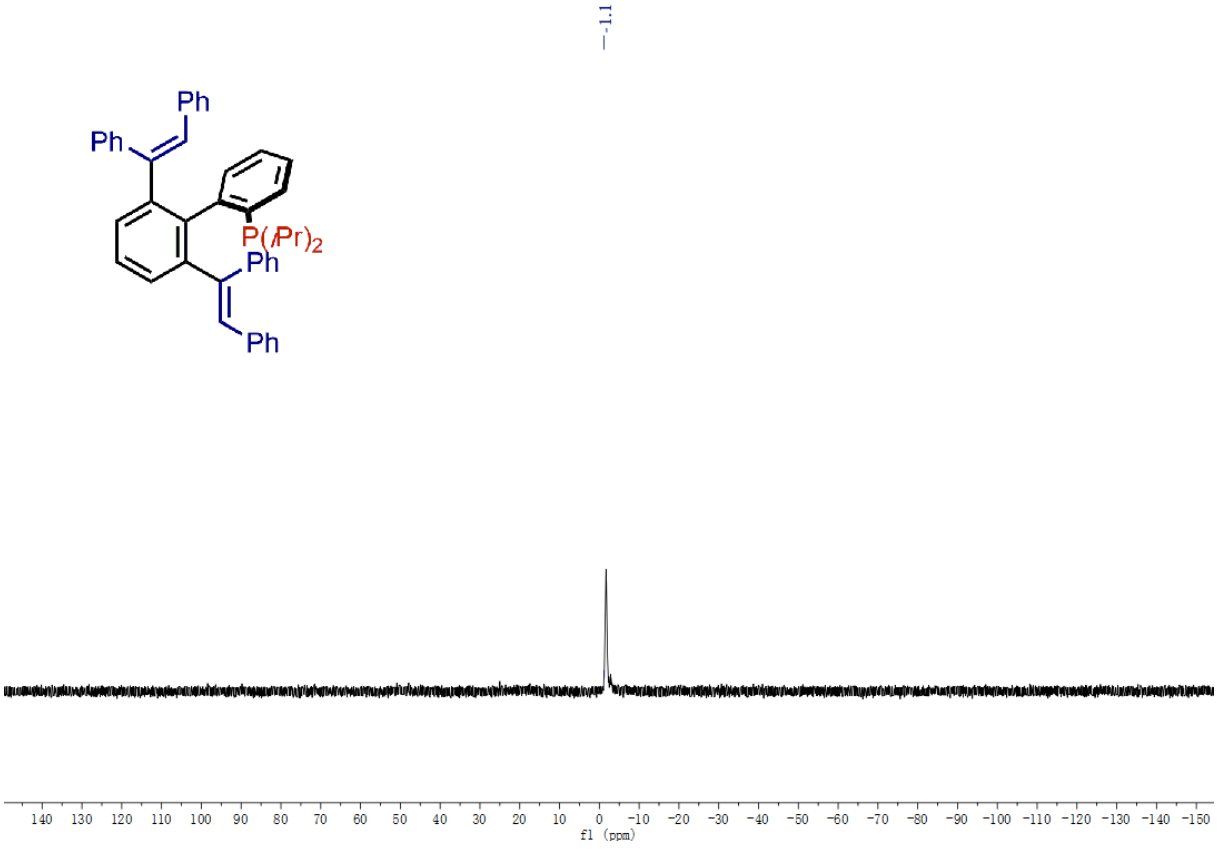
4ca | ^{1}H NMR ($CDCl_3$, 400 MHz)



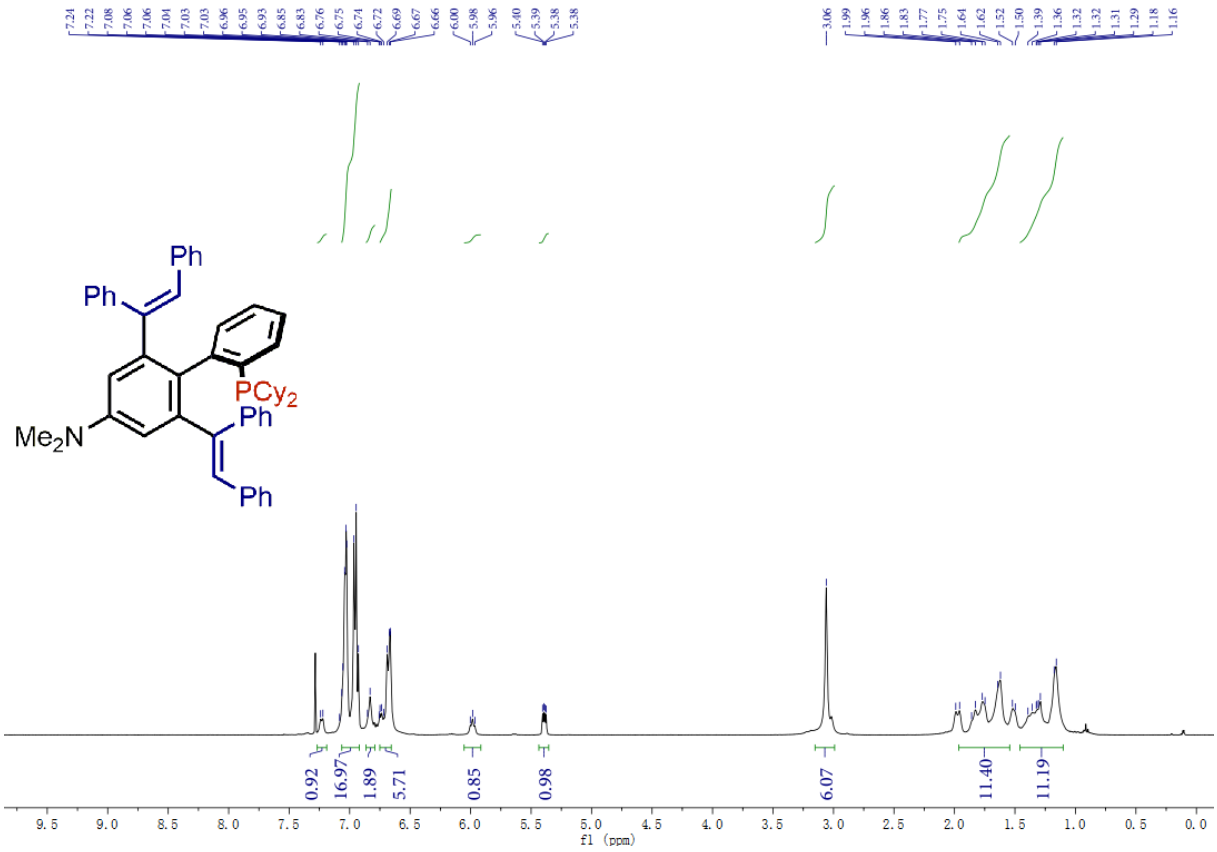
4ca | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



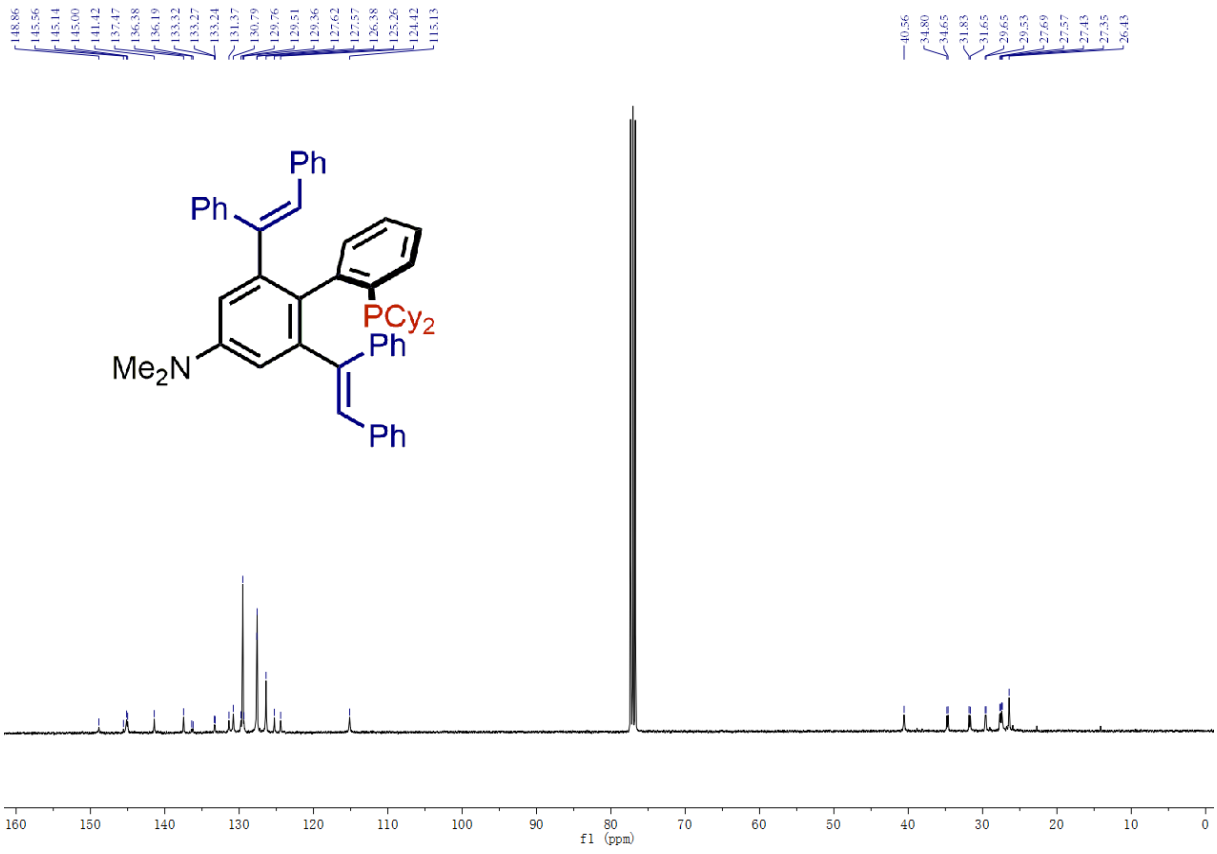
4ca | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



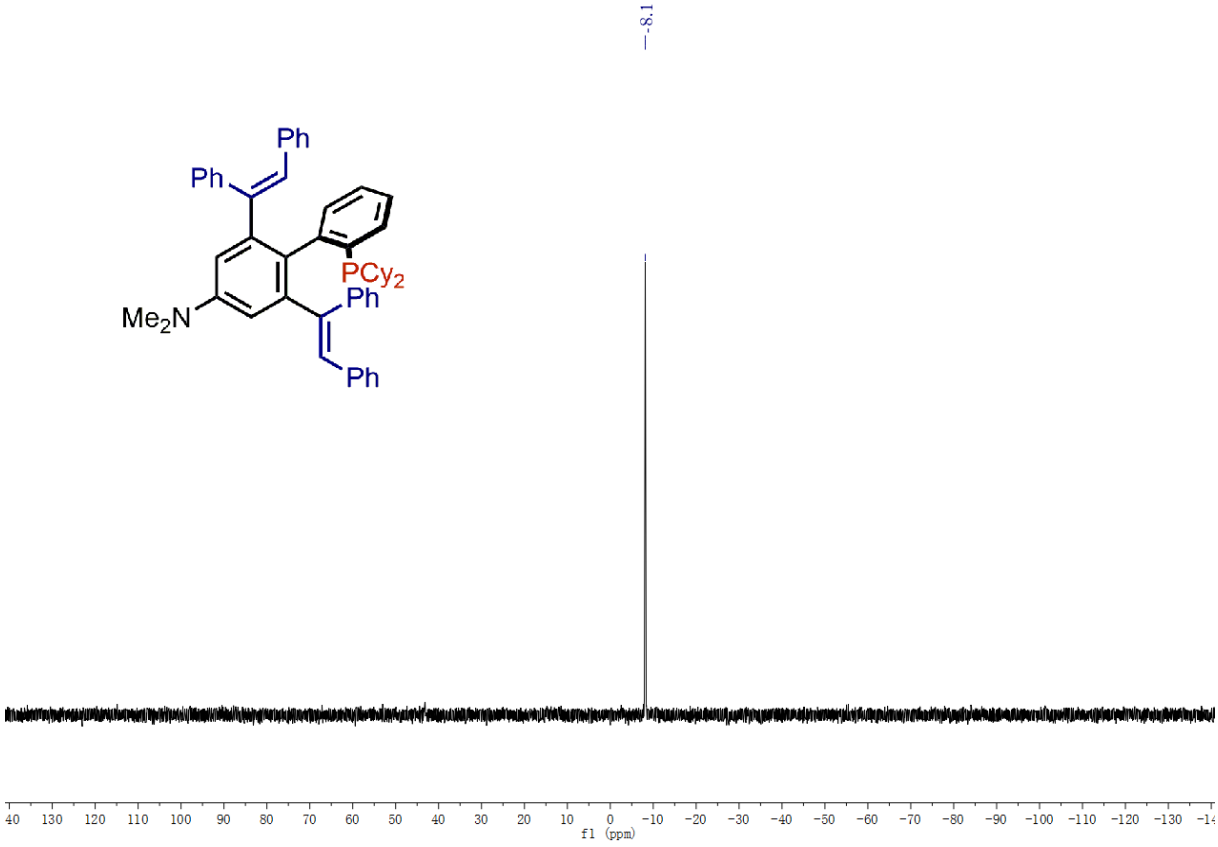
4ga | ^{1}H NMR ($CDCl_3$, 400 MHz)



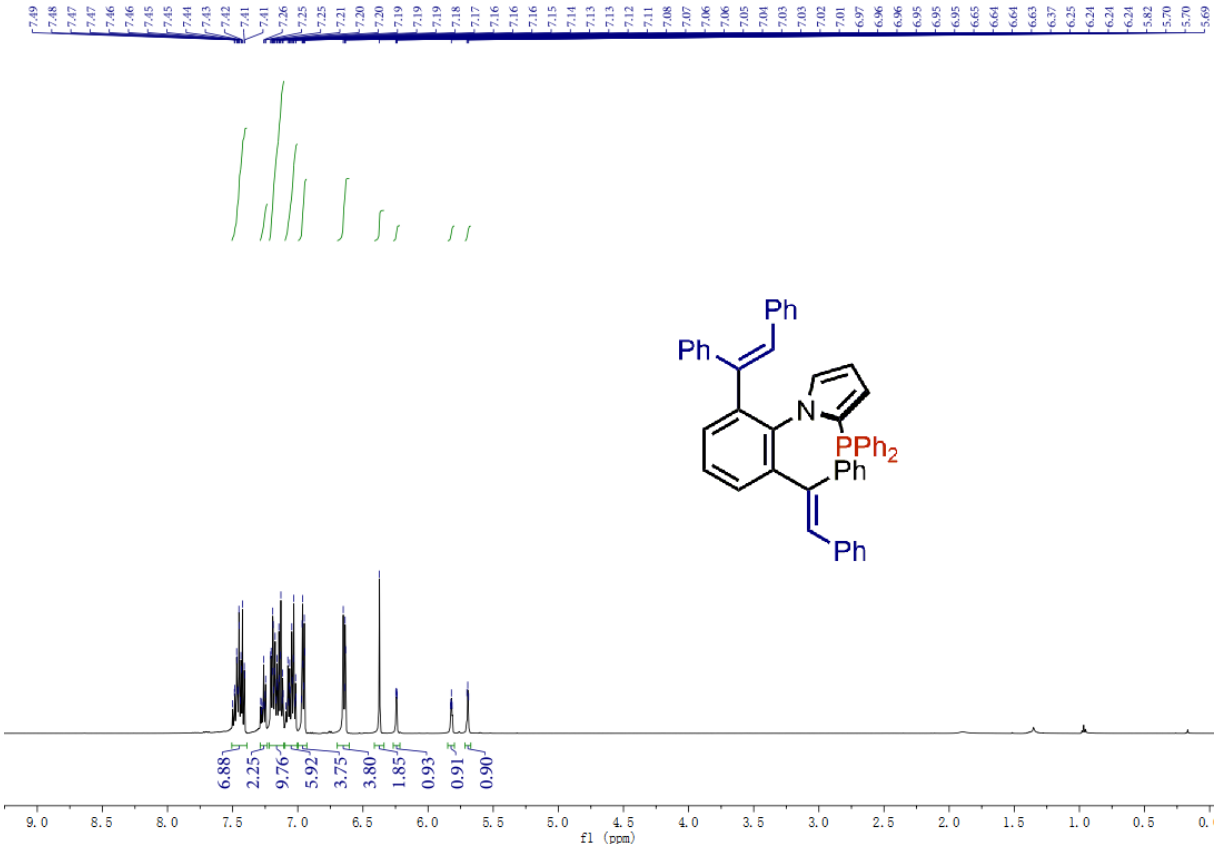
4ga | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



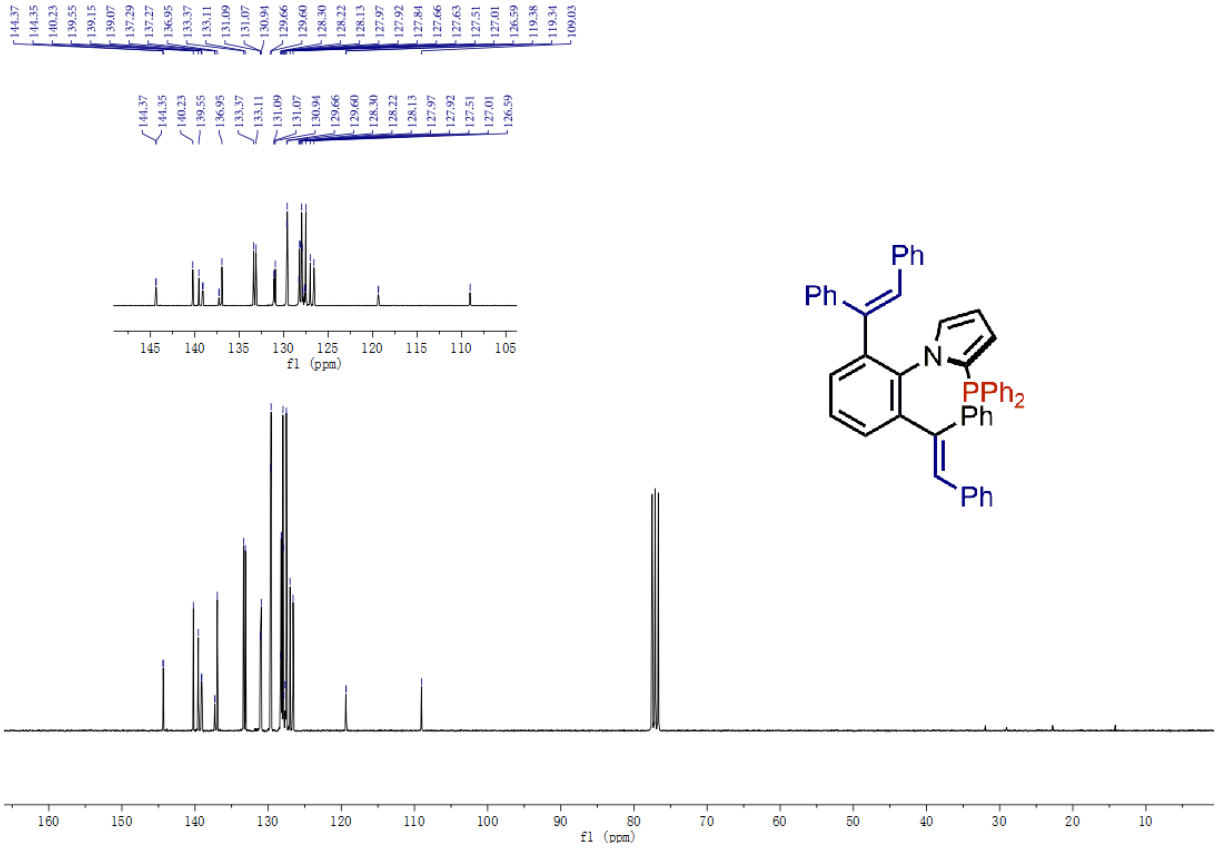
4ga | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



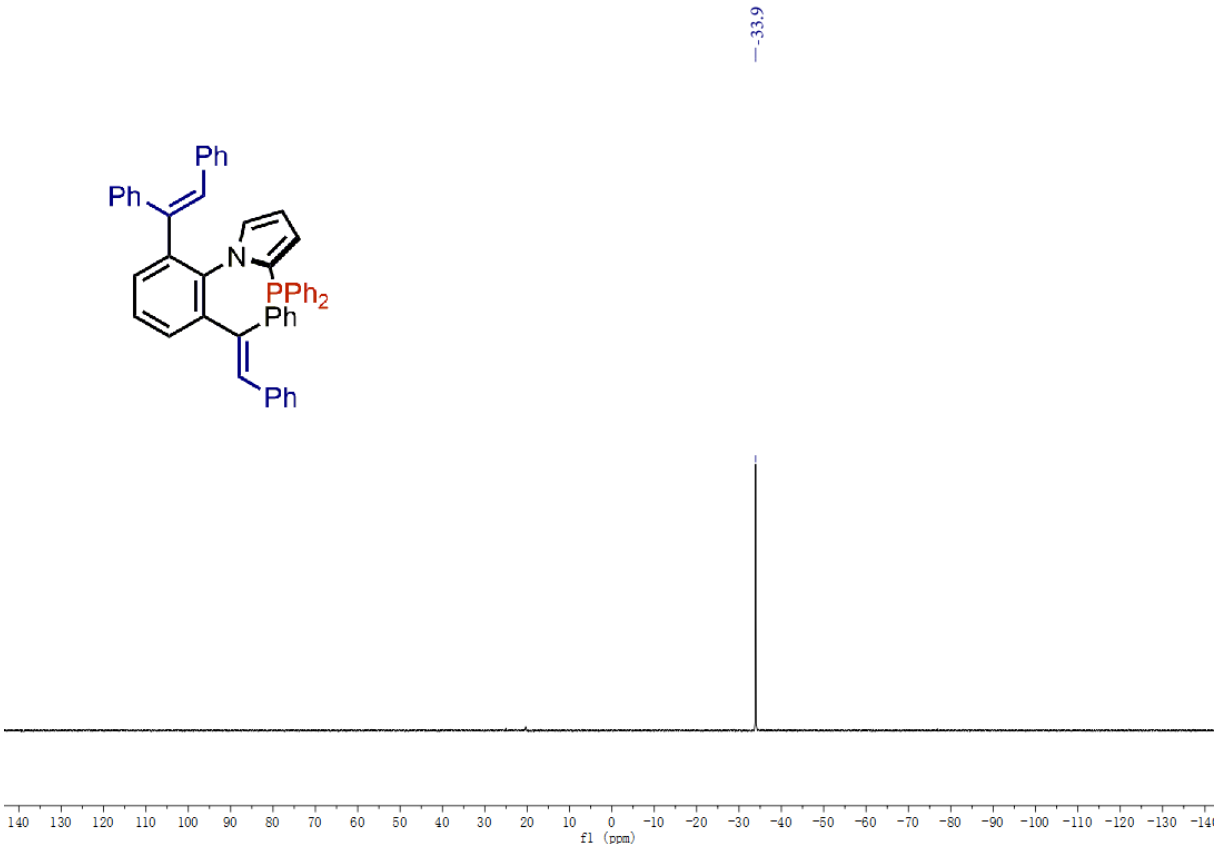
4ha | ^{1}H NMR ($CDCl_3$, 400 MHz)



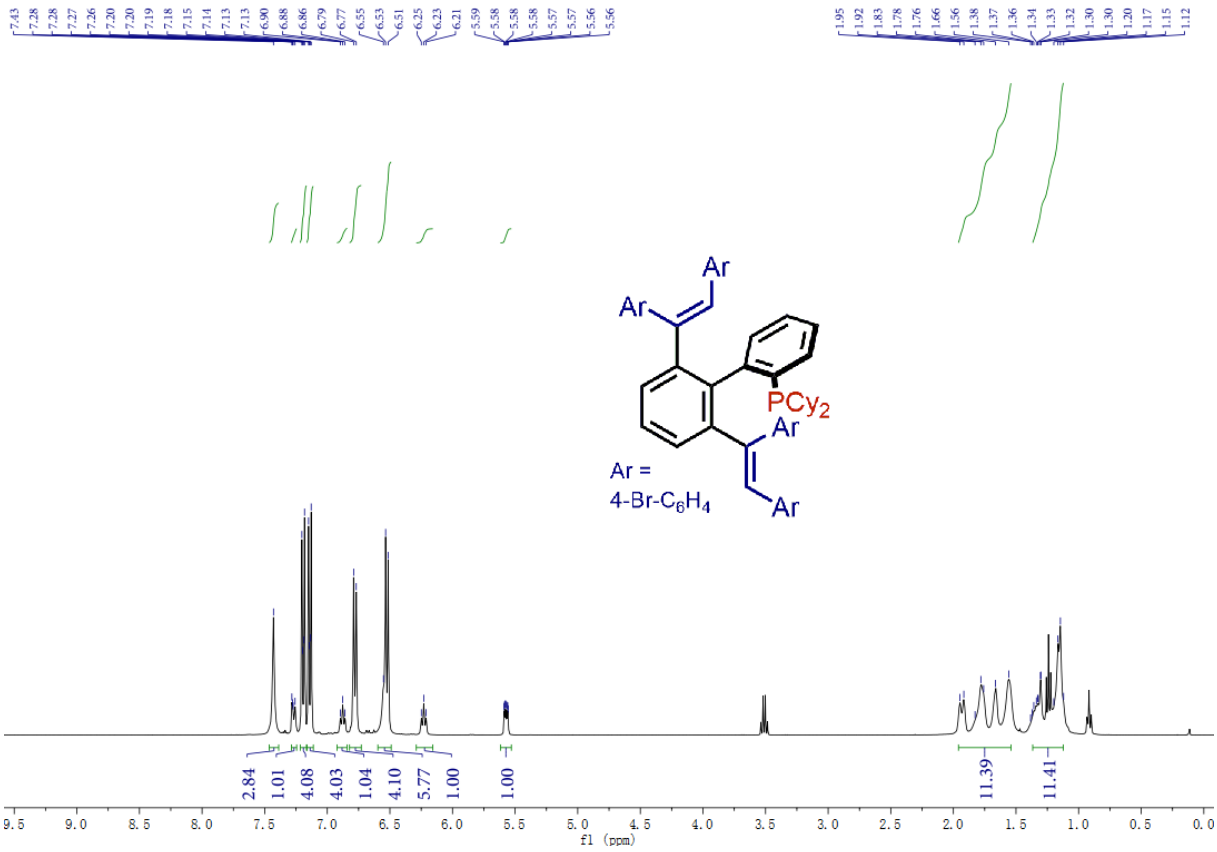
4ha | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



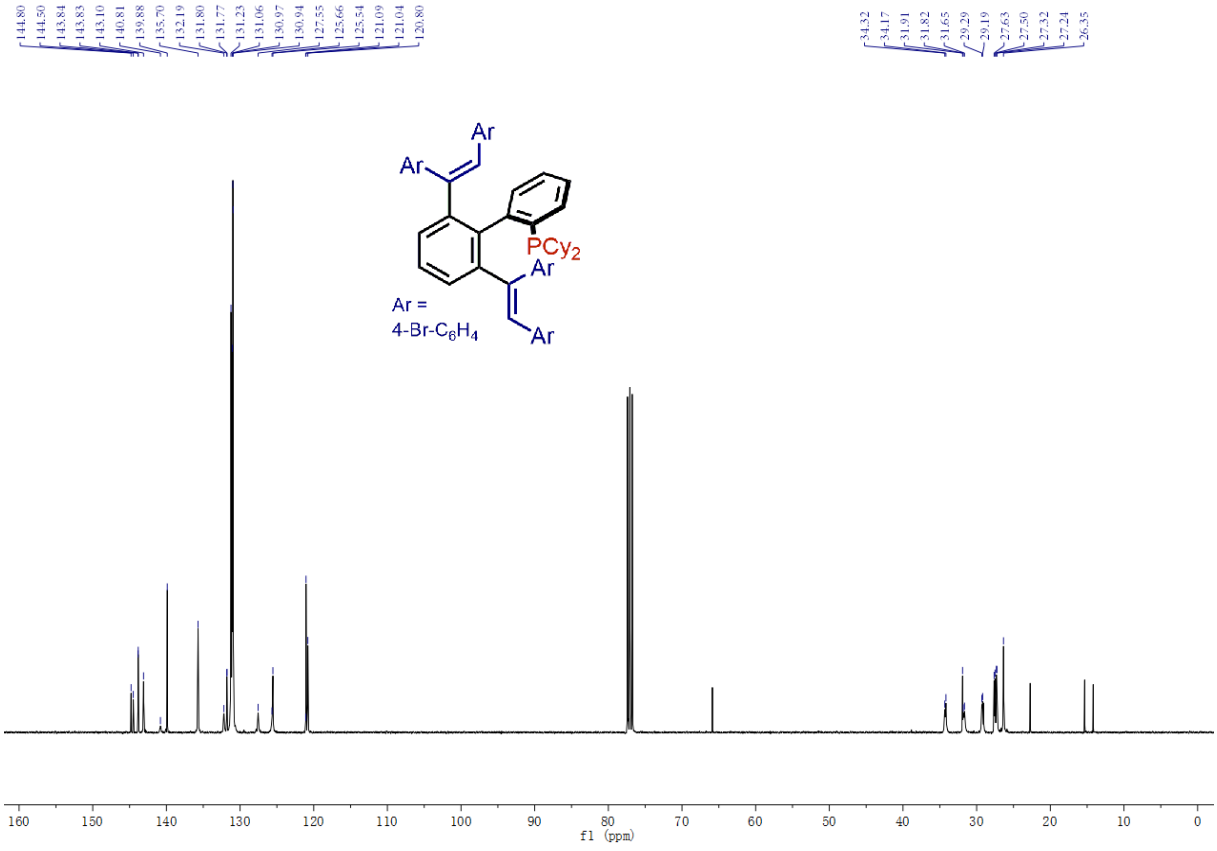
4ha | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



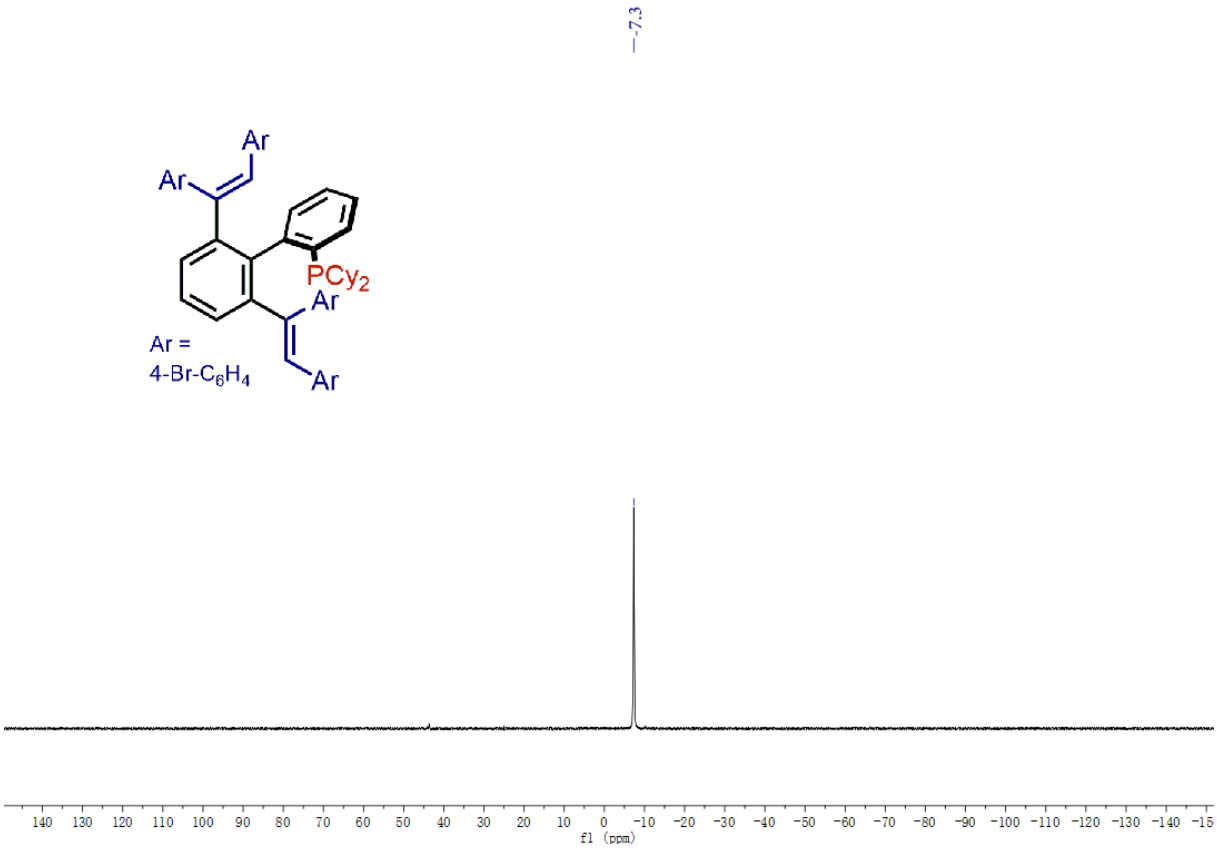
4ab | ^{1}H NMR ($CDCl_3$, 400 MHz)



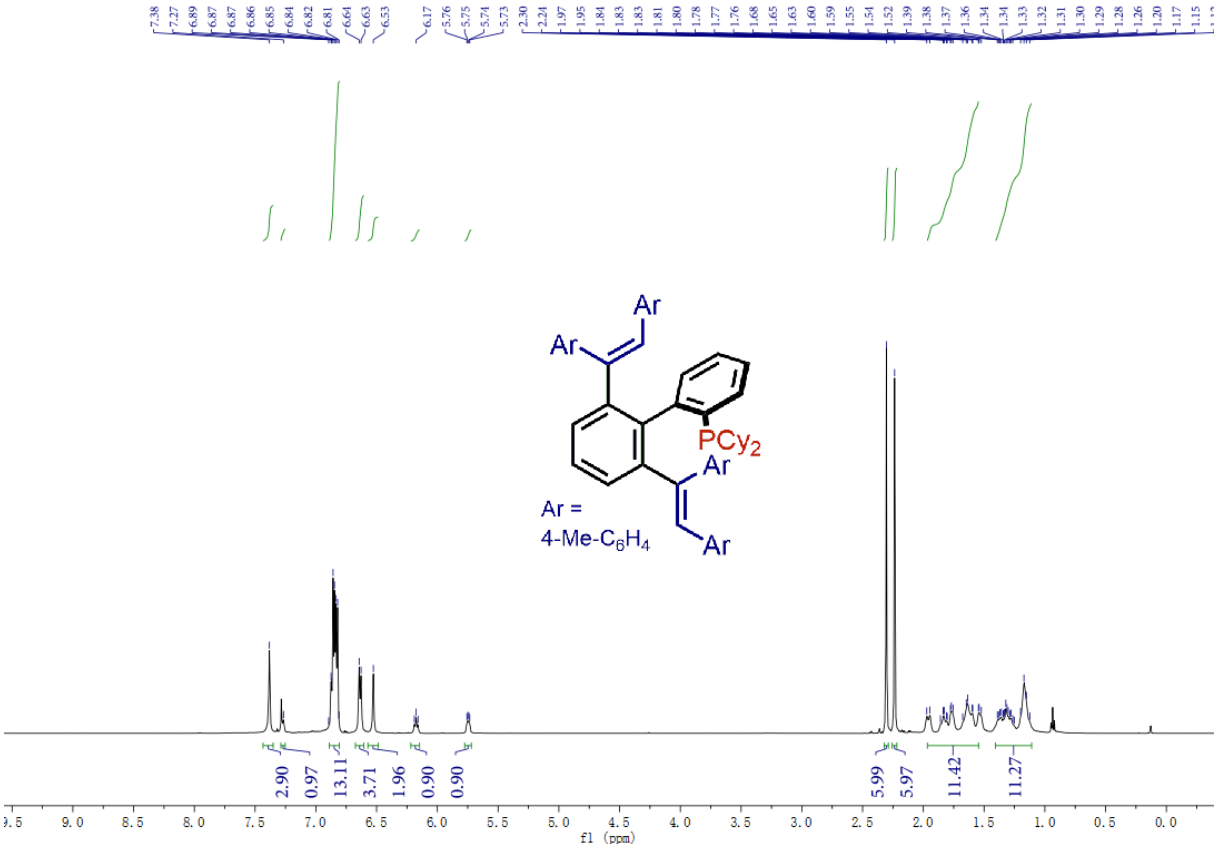
4ab | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



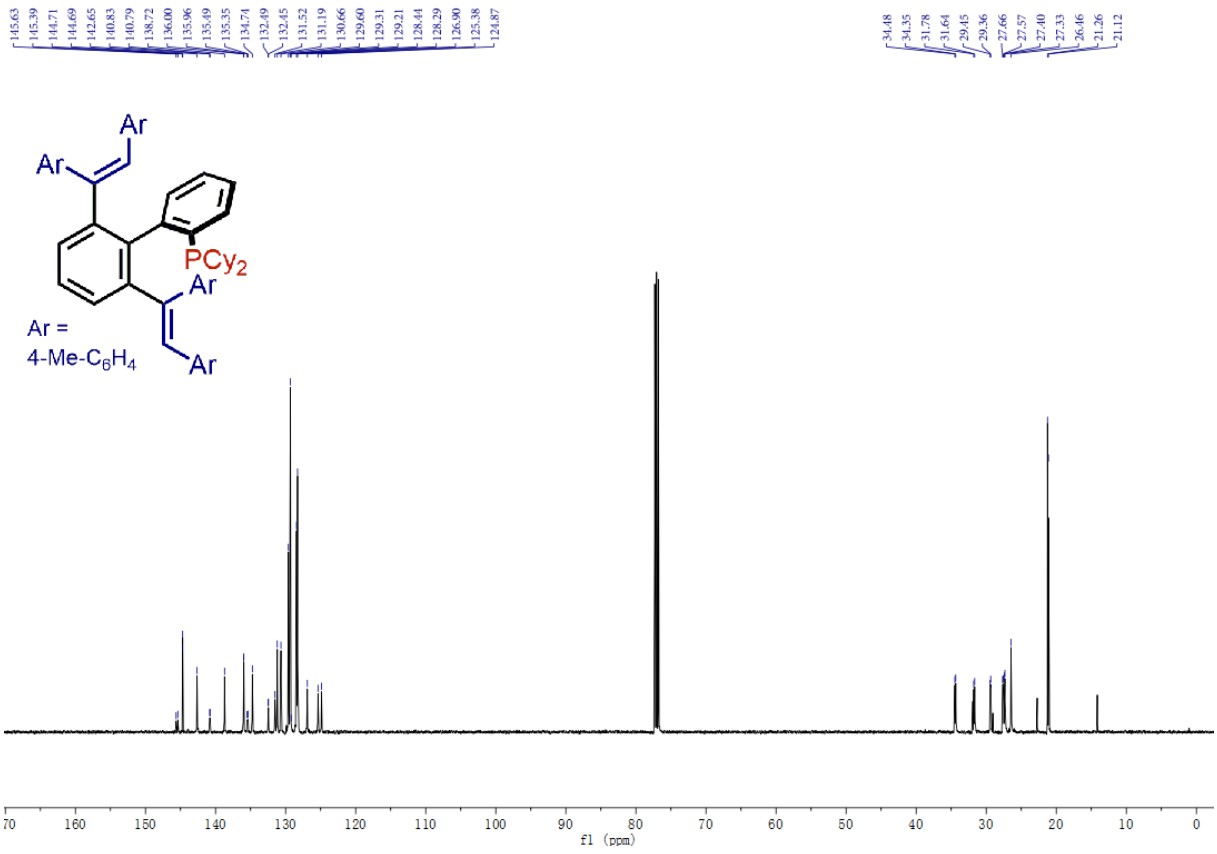
4ab | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



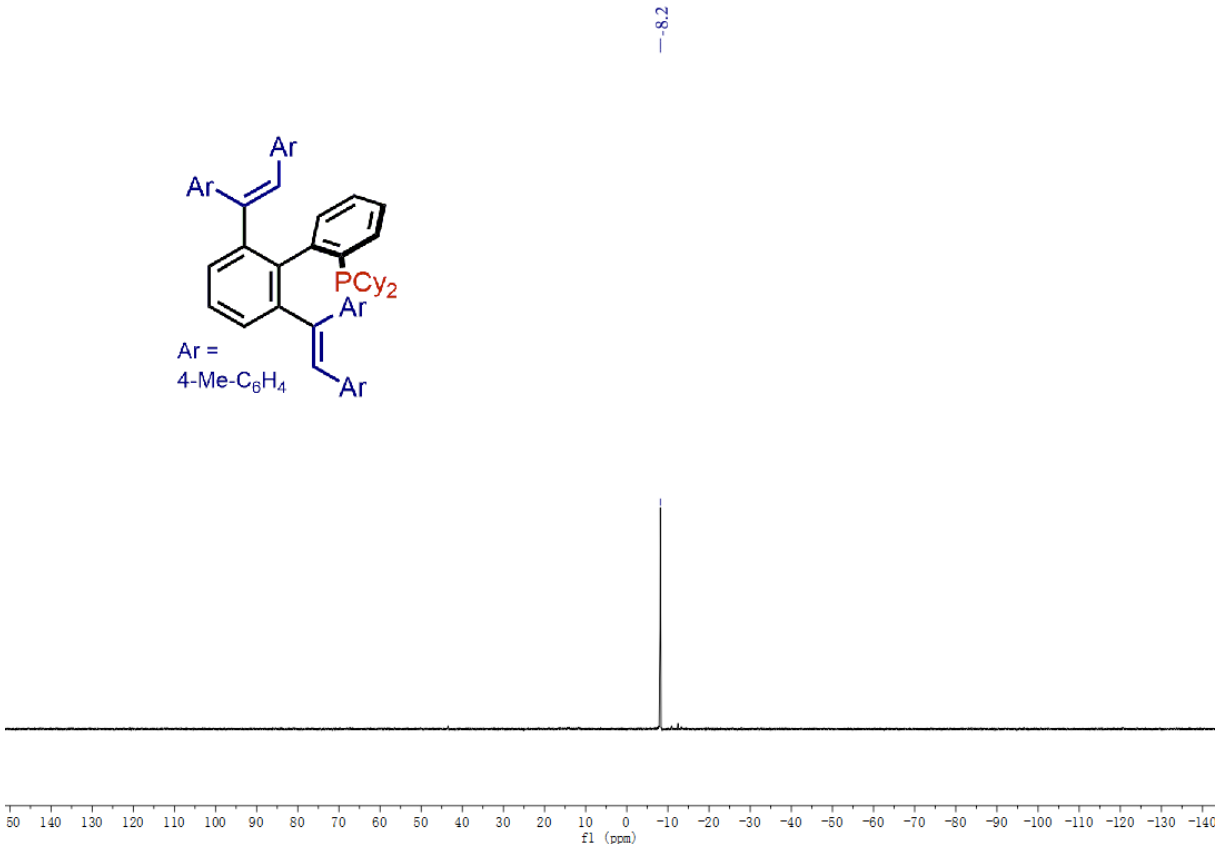
4ac | ^{1}H NMR ($CDCl_3$, 400 MHz)



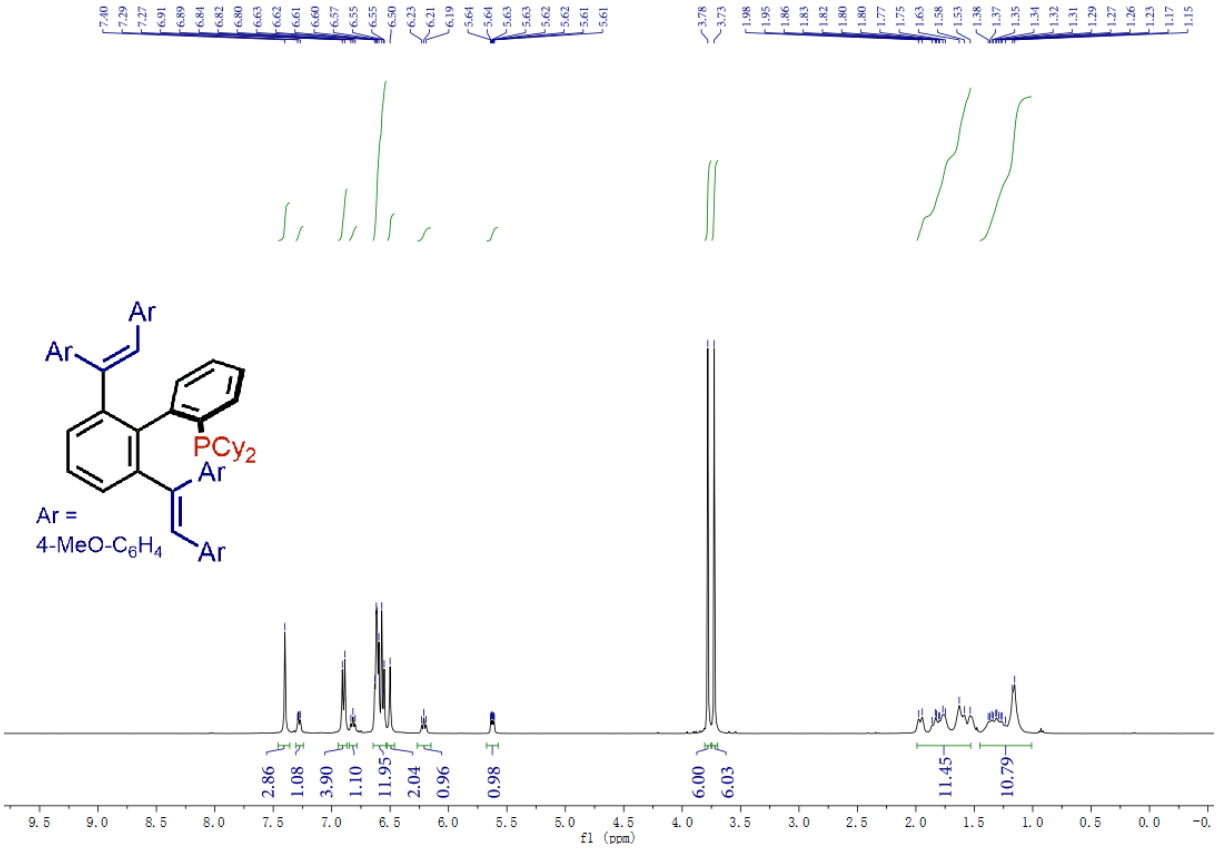
4ac | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



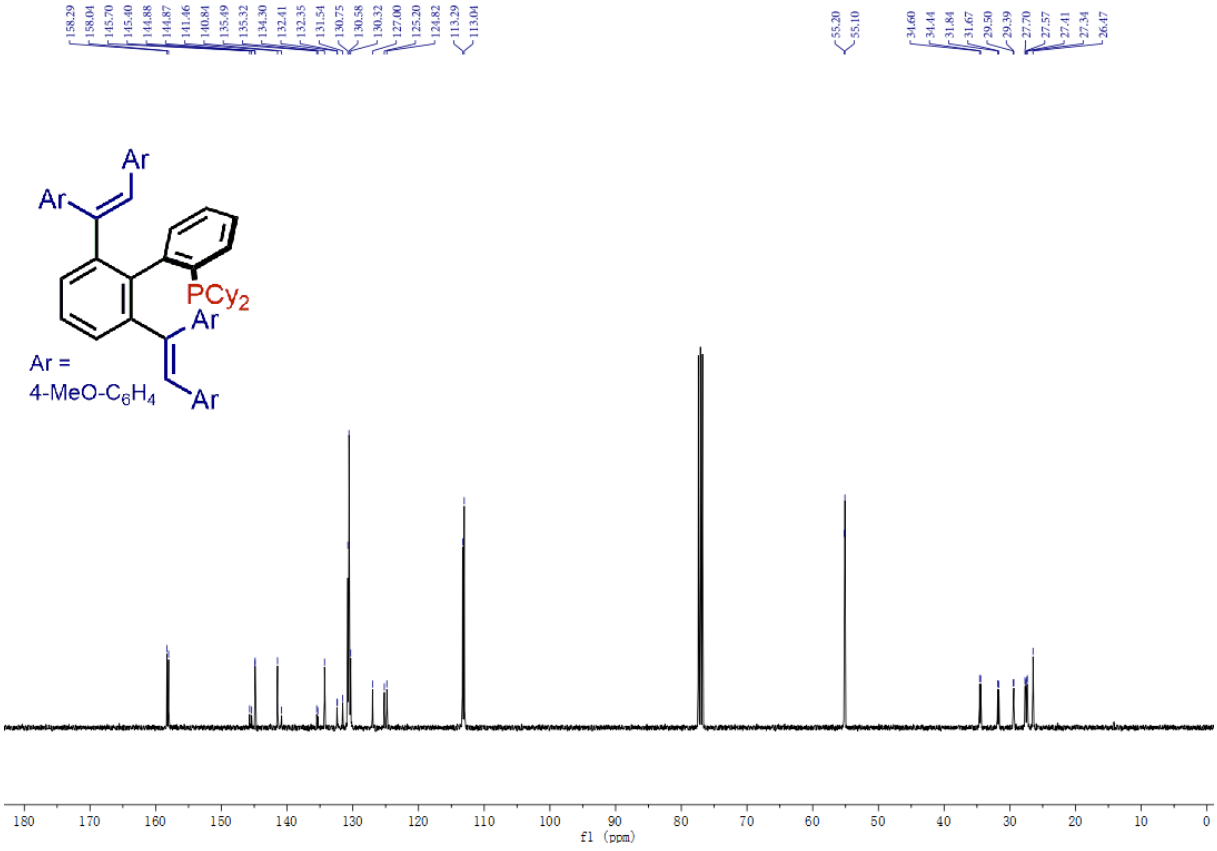
4ac | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



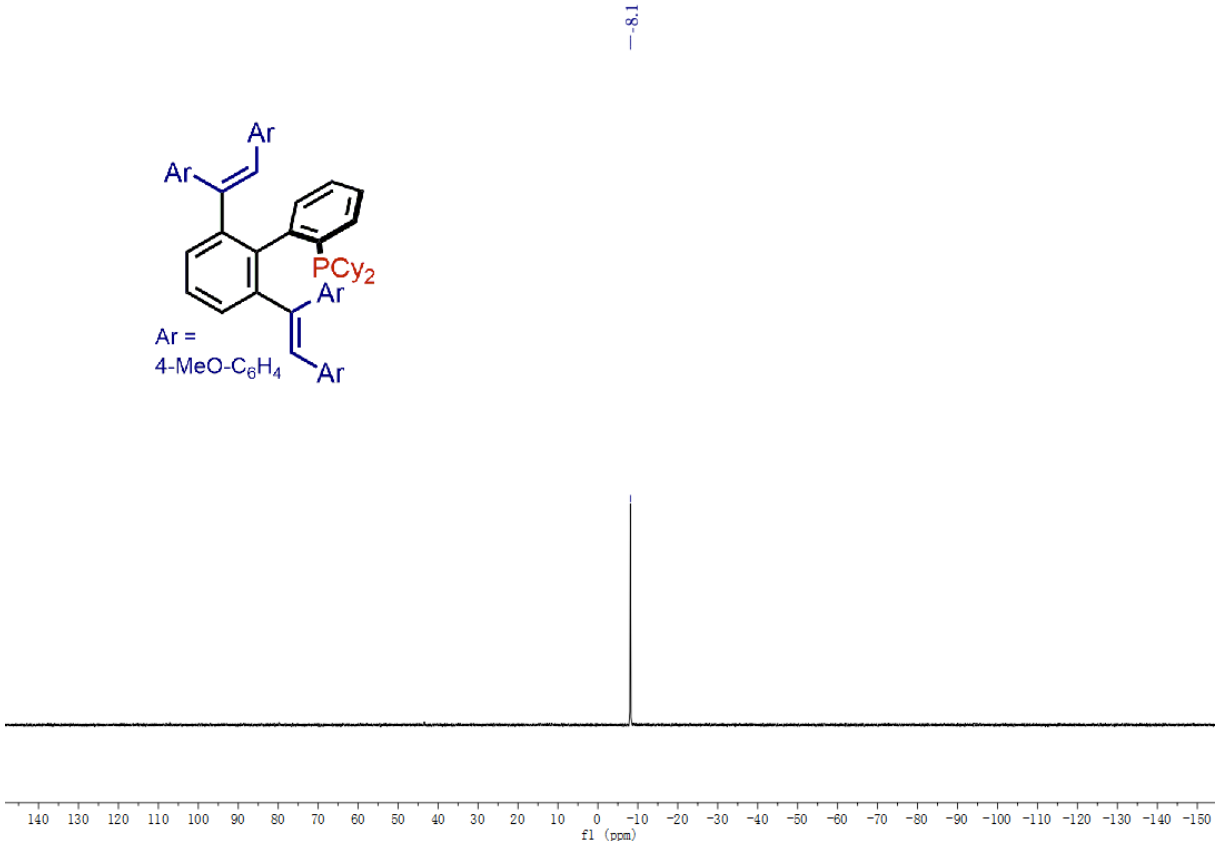
4ad | ^{1}H NMR ($CDCl_3$, 400 MHz)



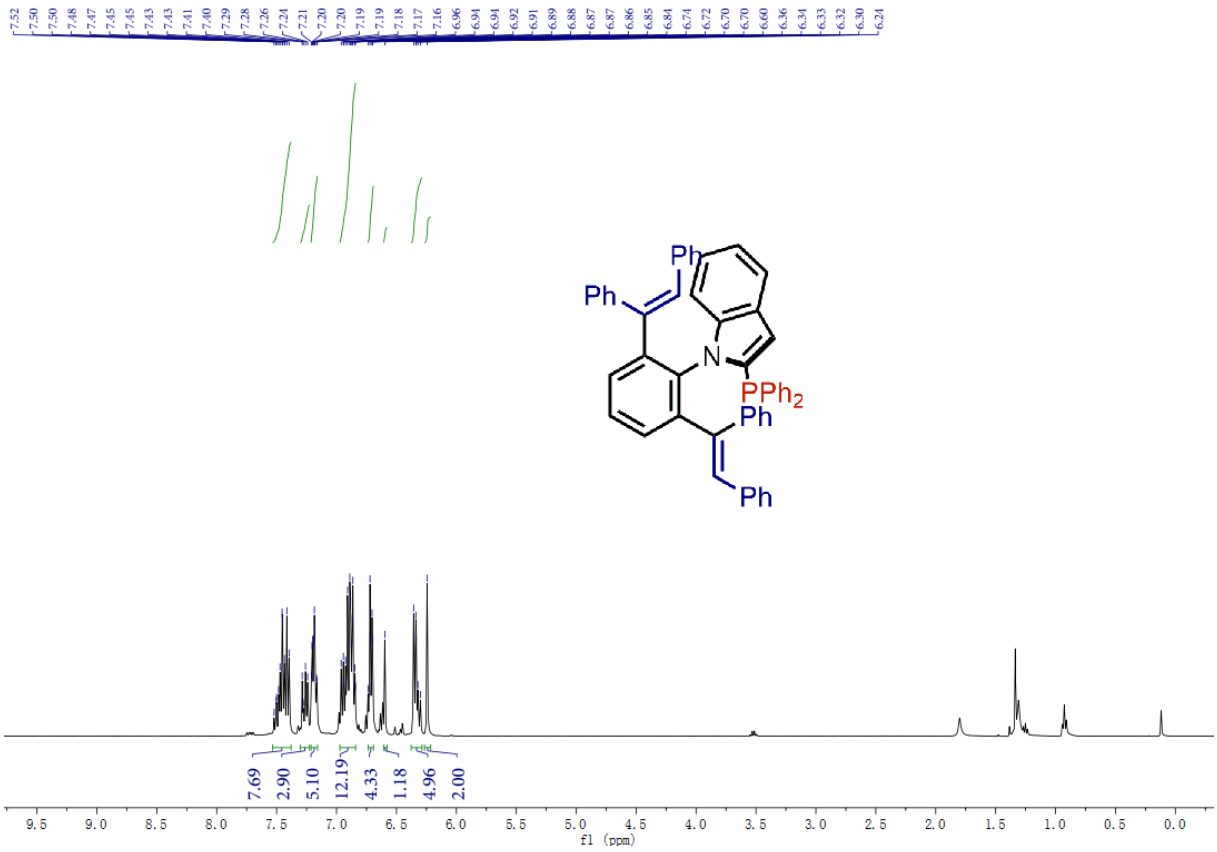
4ad | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



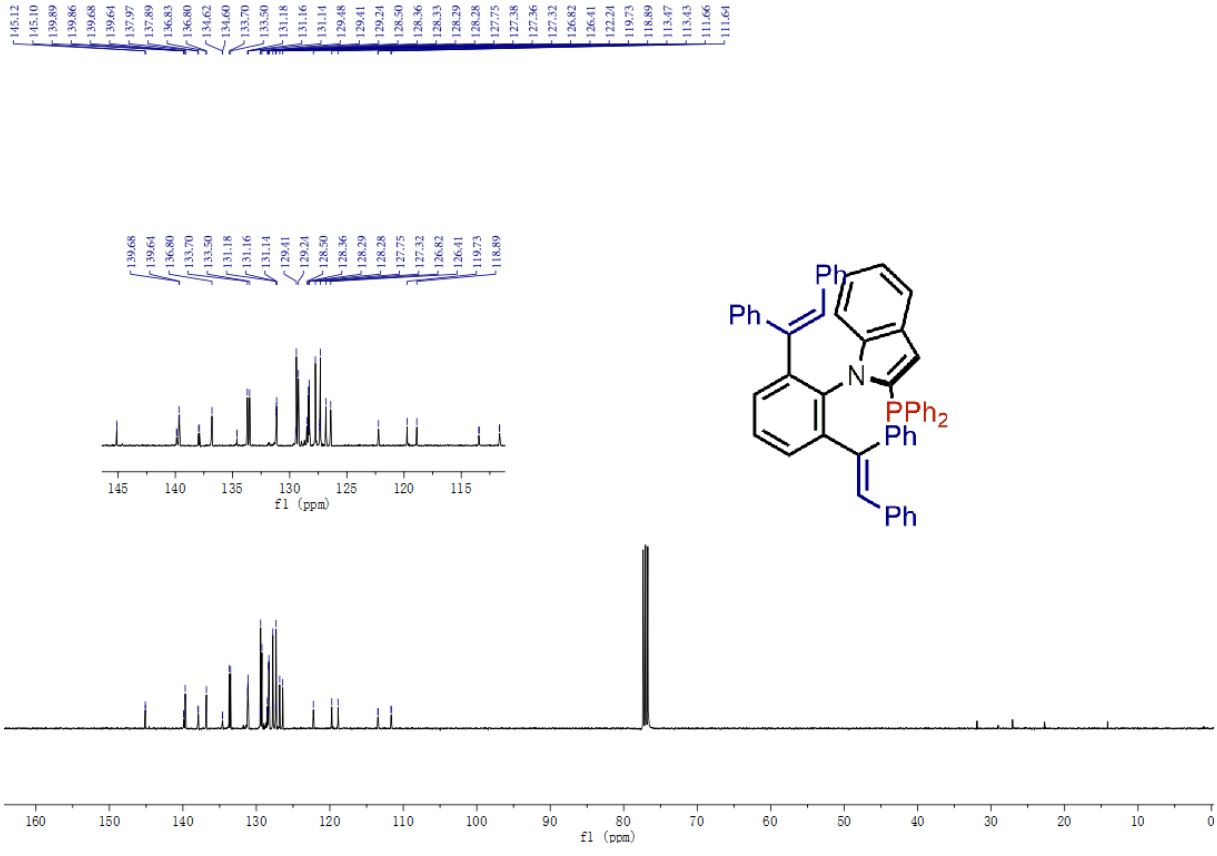
4ad | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



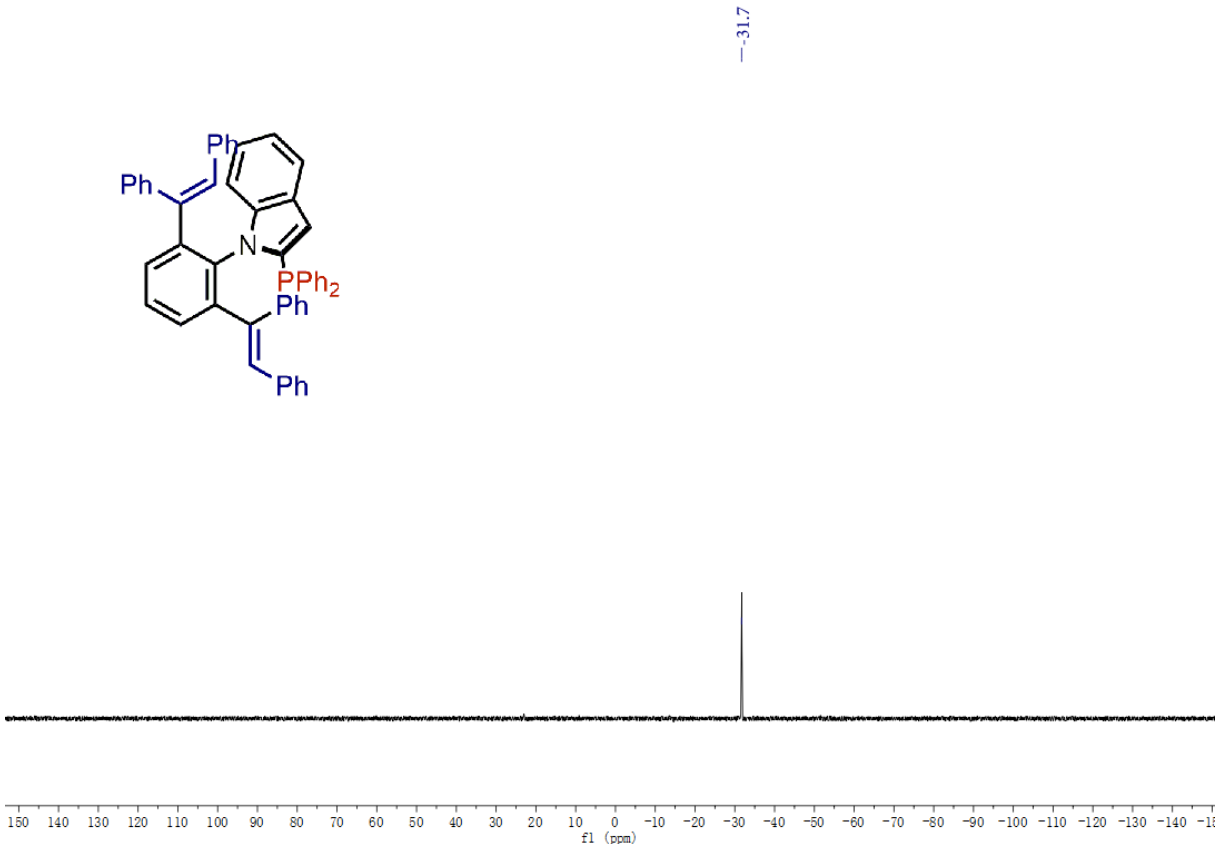
4ja | ^{1}H NMR ($CDCl_3$, 400 MHz)



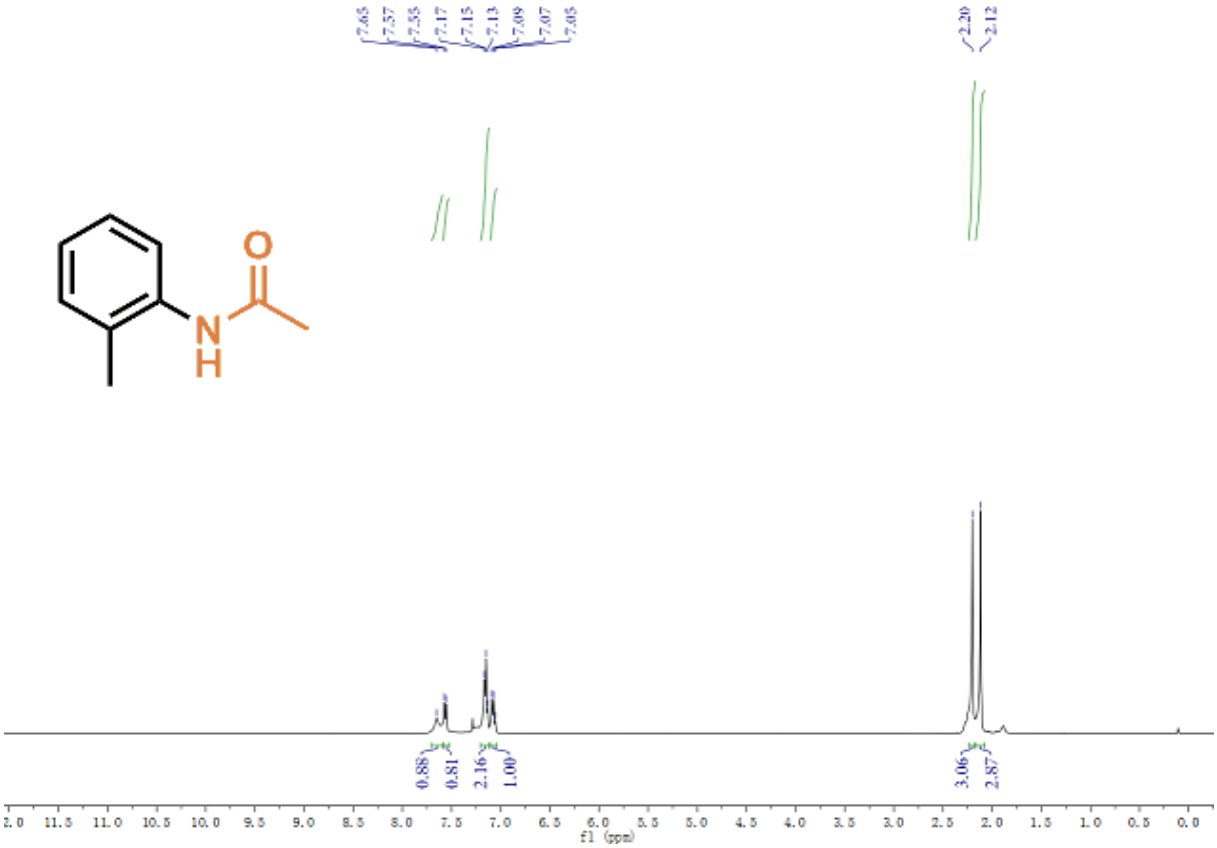
4ja | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



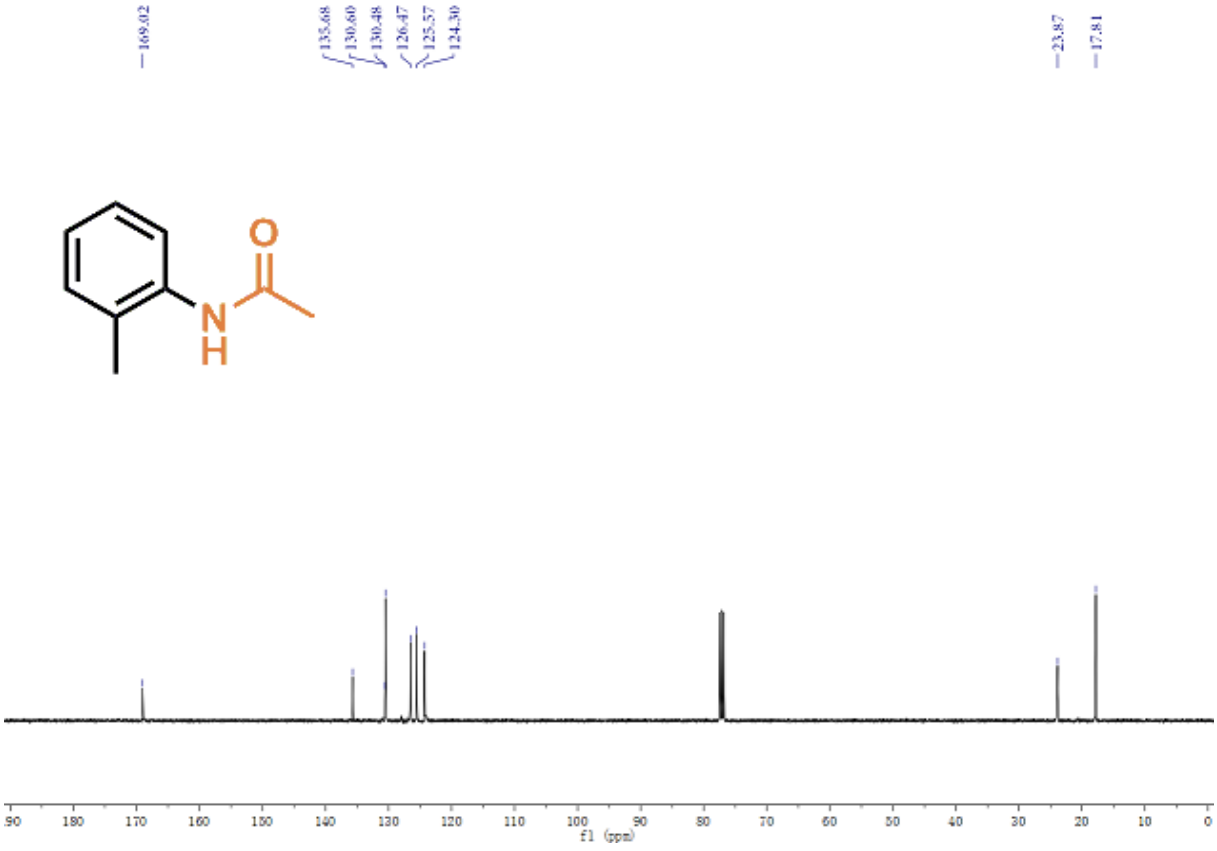
4ja | $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz)



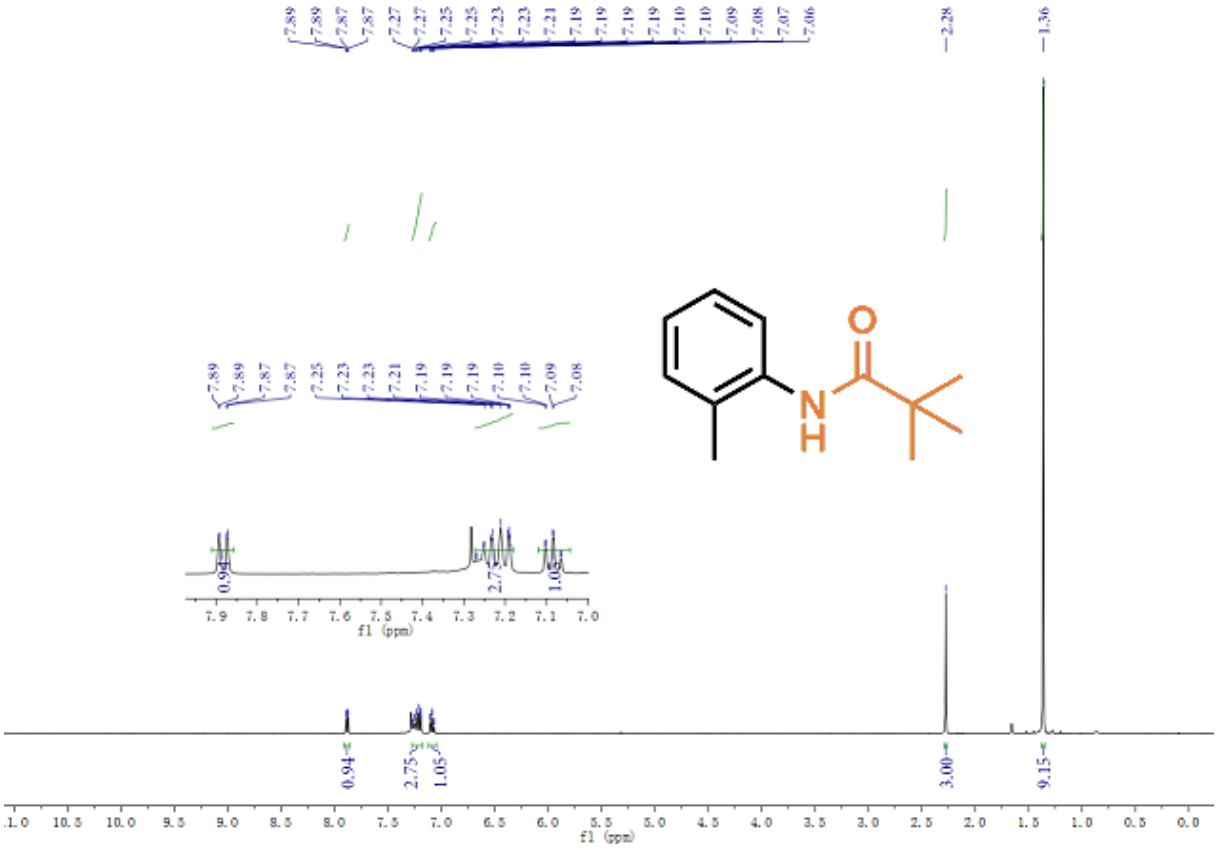
6a | ^{1}H NMR ($CDCl_3$, 400 MHz)



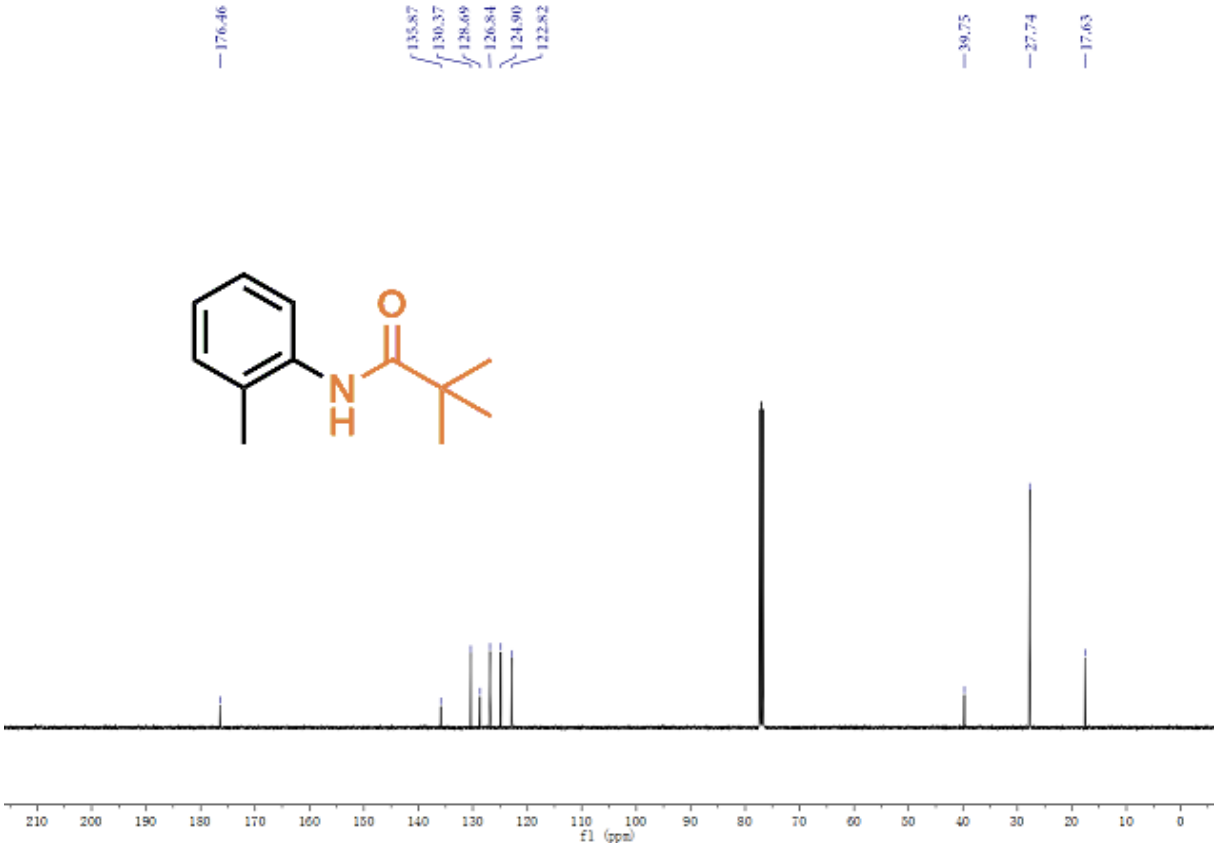
6a | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



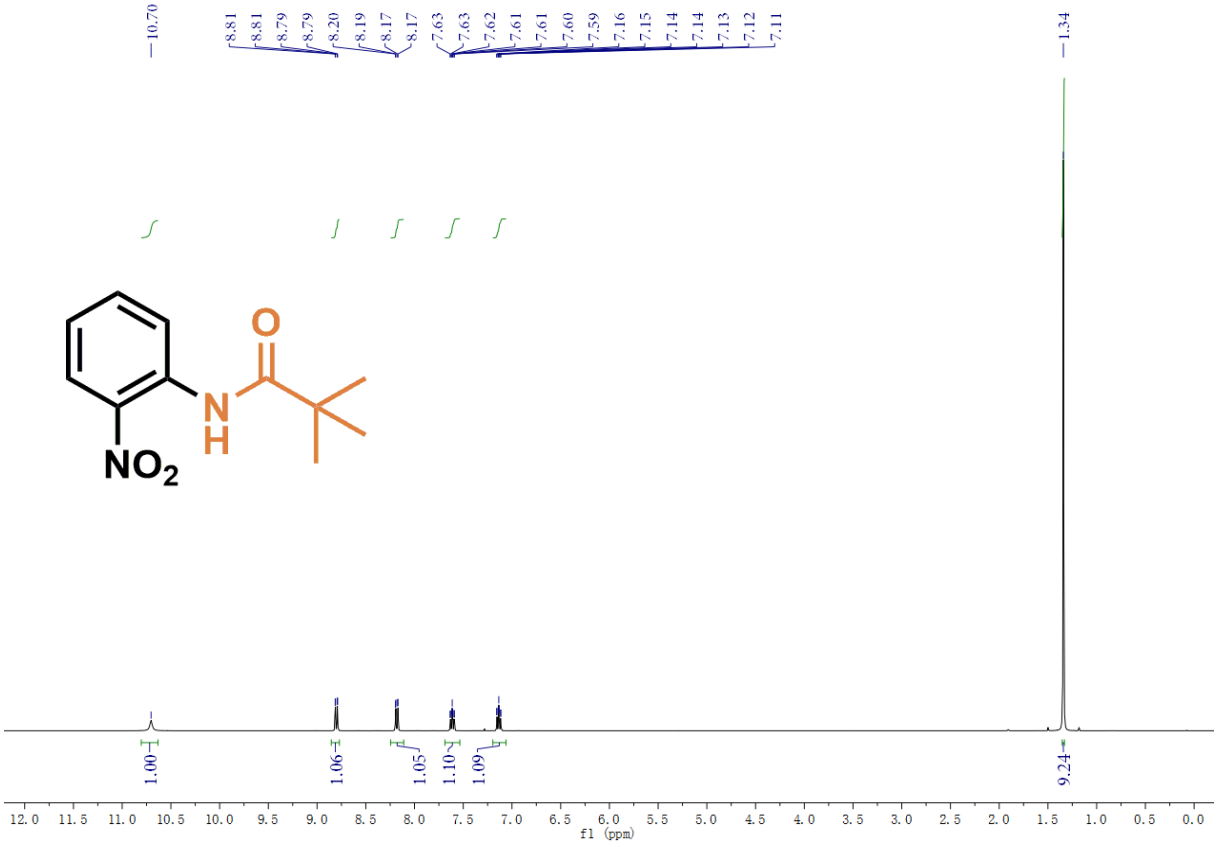
6b | ^{1}H NMR ($CDCl_3$, 400 MHz)



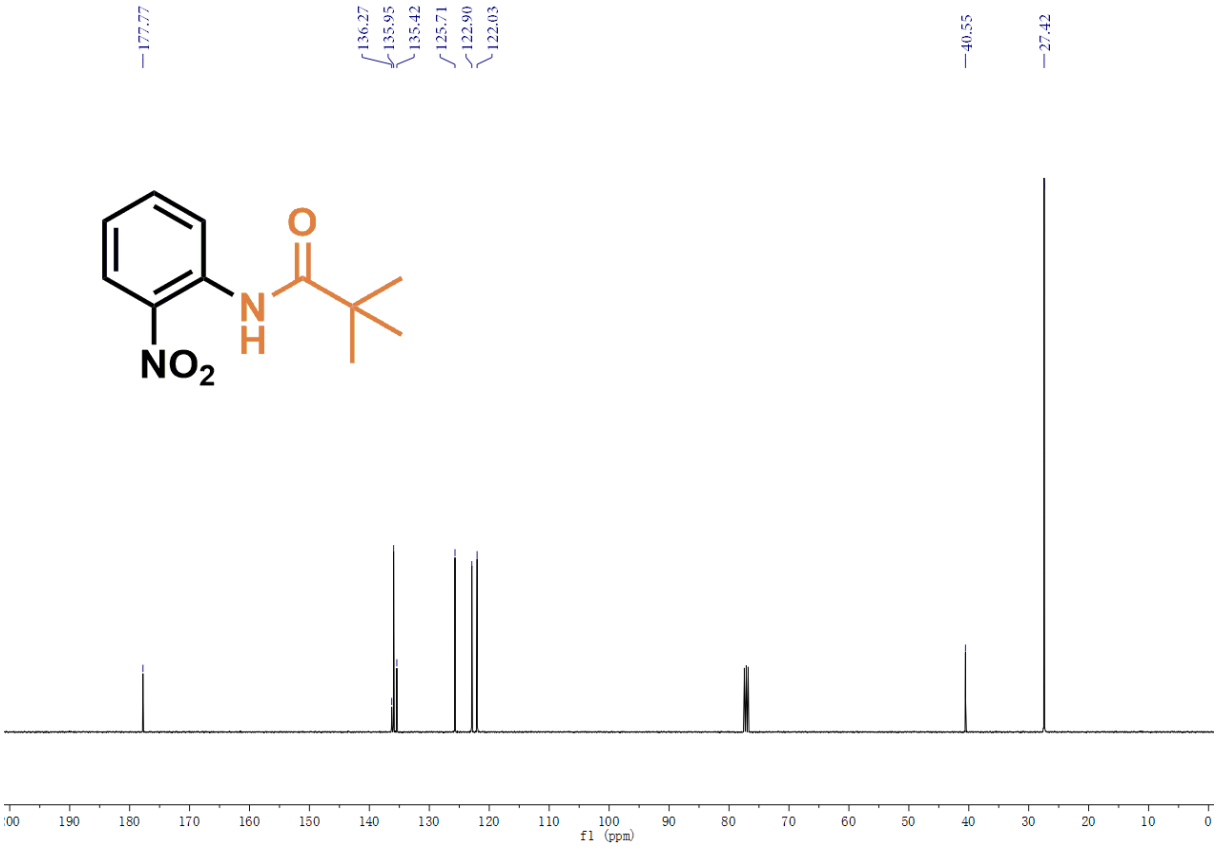
6b | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



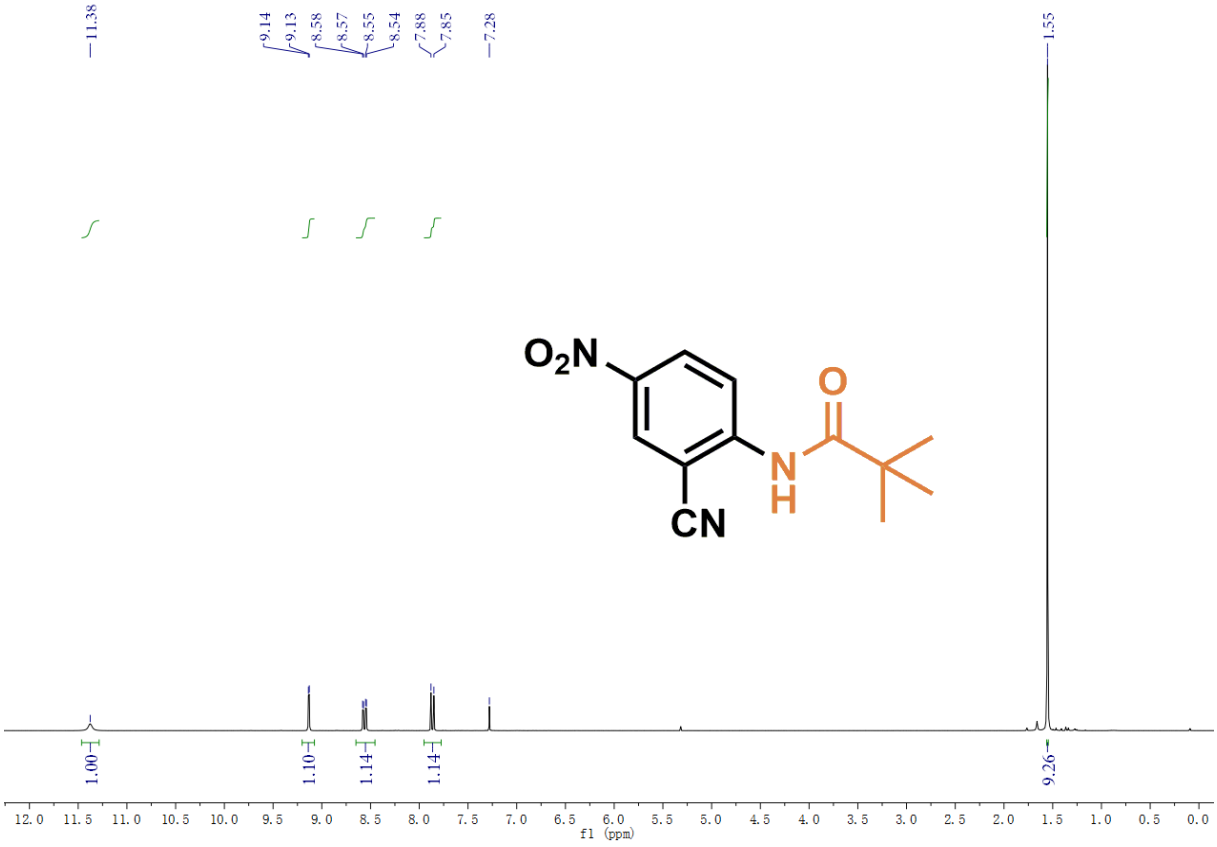
6c | ^{1}H NMR ($CDCl_3$, 400 MHz)



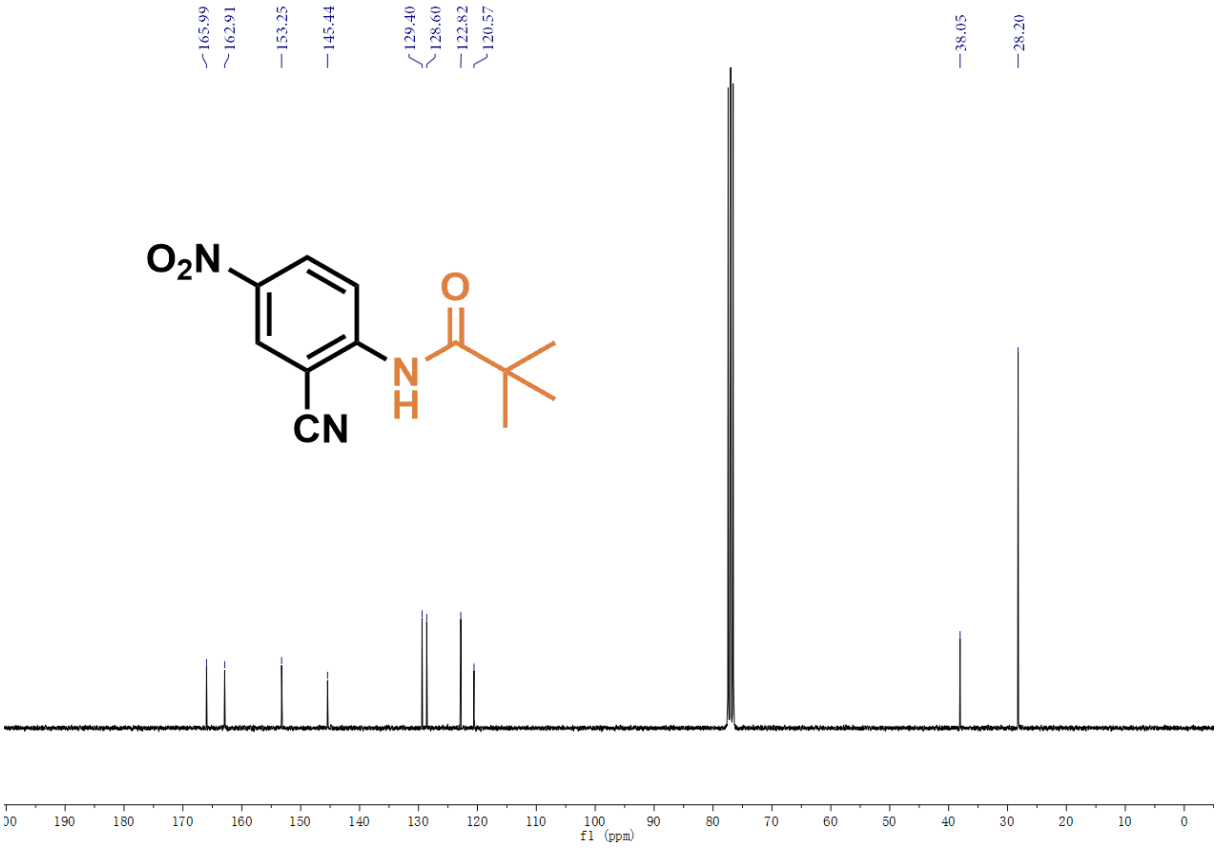
6c | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



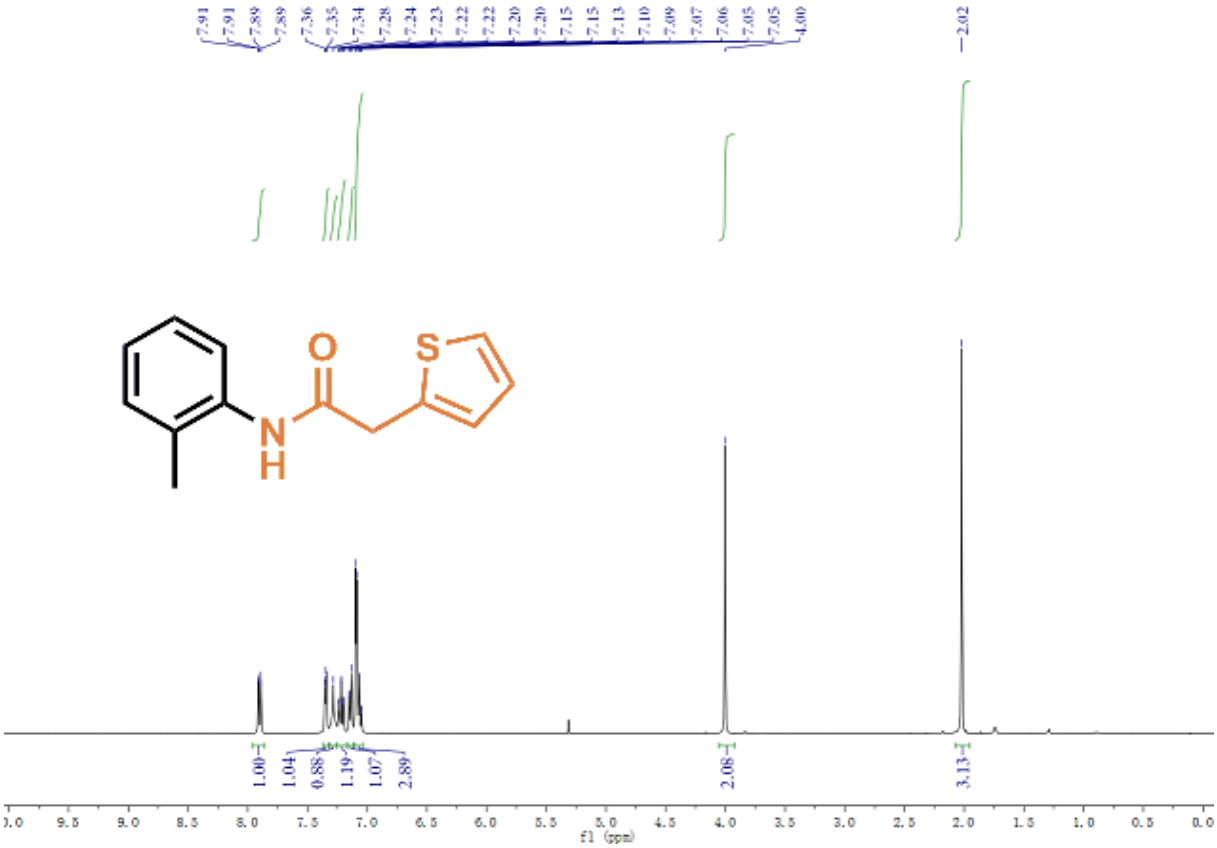
6d | ^{1}H NMR ($CDCl_3$, 400 MHz)



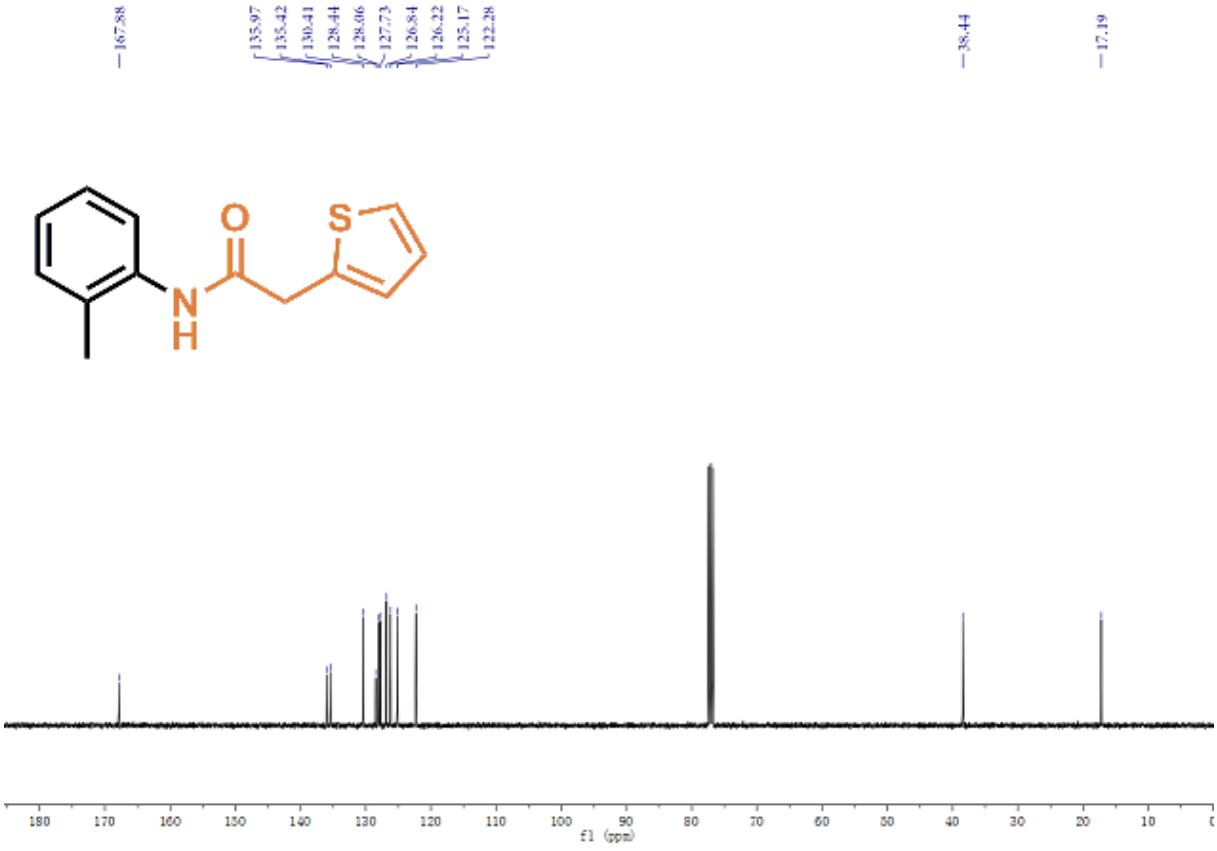
6d | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



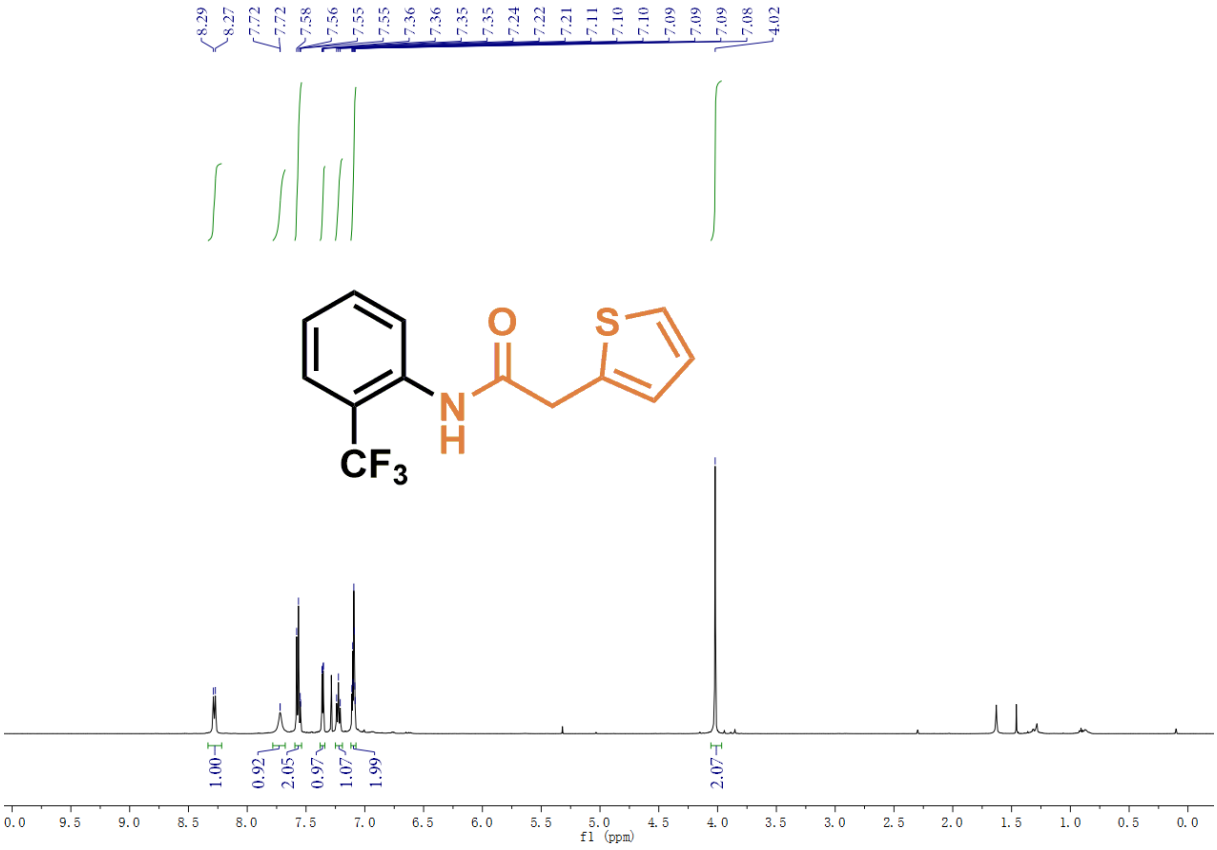
6e | ^{1}H NMR ($CDCl_3$, 400 MHz)



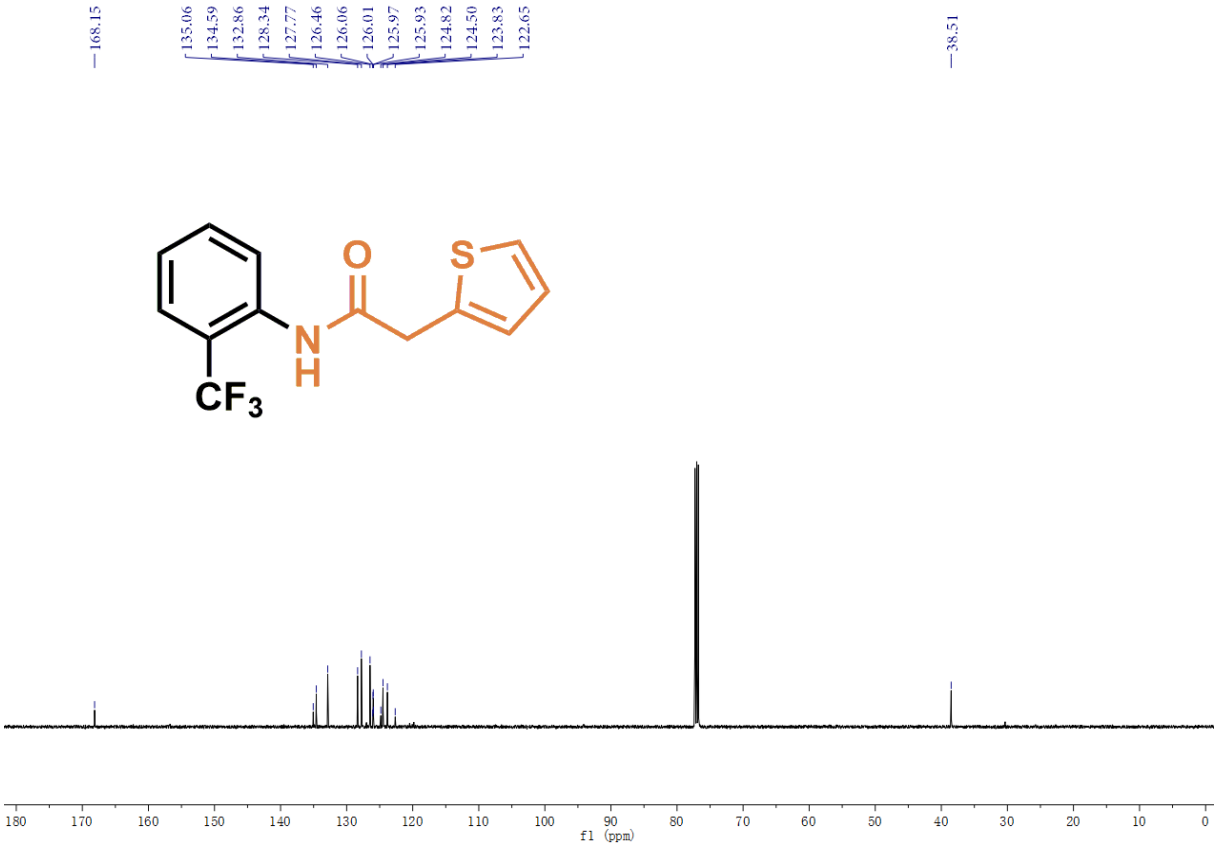
6e | ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



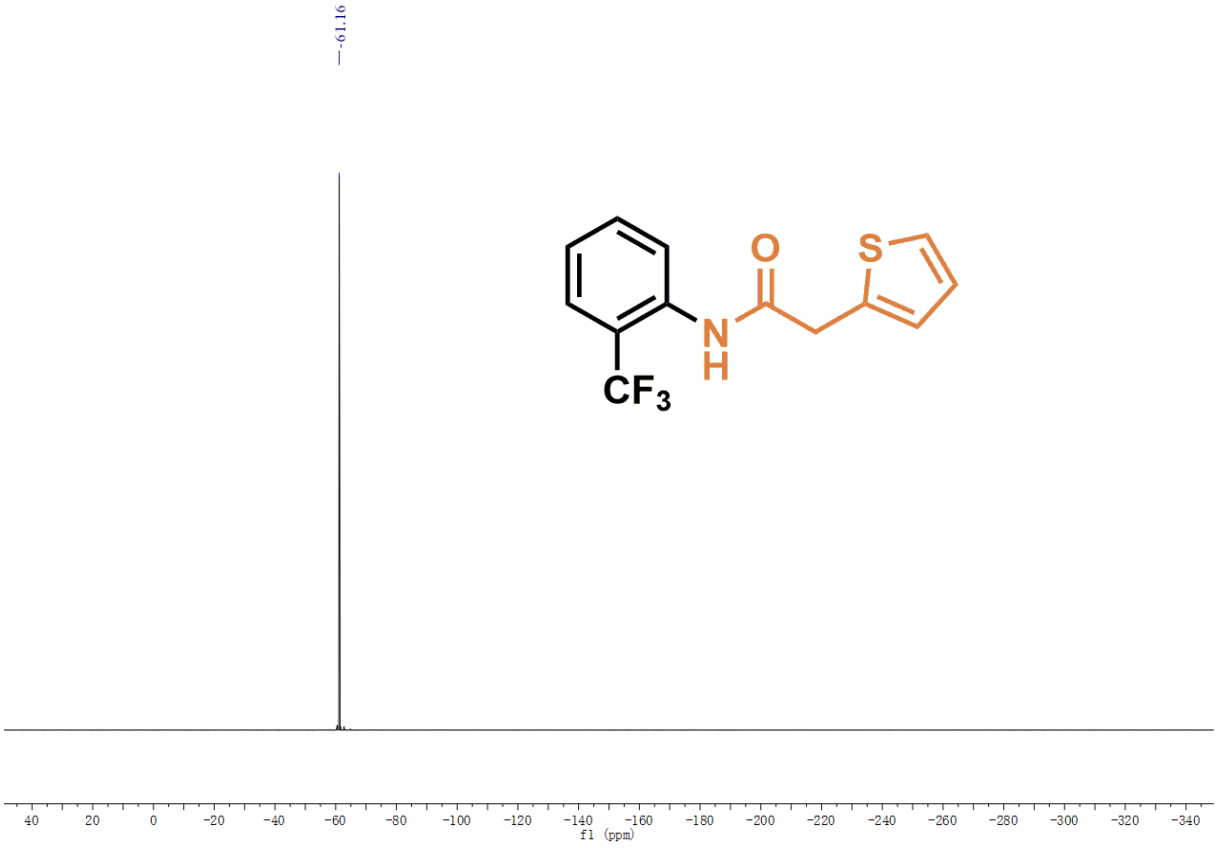
6f | ^{1}H NMR ($CDCl_3$, 400 MHz)



6f | $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



6f | $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 471 MHz)



7. References

[1] J. Chatt, L. M. Venanzi, *Journal of the Chemical Society (Resumed)* **1957**, 4735-4741.

[2] Martinez, A. M.; Echavarren, J.; Alonso, I.; Rodriguez, N.; Gomez Arrayas, R.; Carretero, J. C., *Chemical science* **2015,** *6* (10), 5802-5814.

[3] Fors, B. P.; Dooleweerdt, K.; Zeng, Q.; Buchwald, S. L., *Tetrahedron* 2009, 65 (33), 6576-6583.

[4] Brasche, G.; Garcia-Fortanet, J.; Buchwald, S. L., *Organic letters* 2008, 10 (11), 2207-2210.

[5] Lourenço, M. C. S.; Vicente, F. R.; de Oliveira, M. d. G. M.; Candéa, A. L. P.; Gonçalves, R. S. B.; Nogueira, T. C. M.; de Lima Ferreira, M.; de Souza, M. V. N., *Bioorganic & medicinal chemistry letters* 2007, 17 (24), 6895-6898.