Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

for

Borane as an Efficient Directing Group. Stereoselective 1,2-Addition of Organometallic Reagents to Borane P-Stereogenic *N*-Phosphanylimines.

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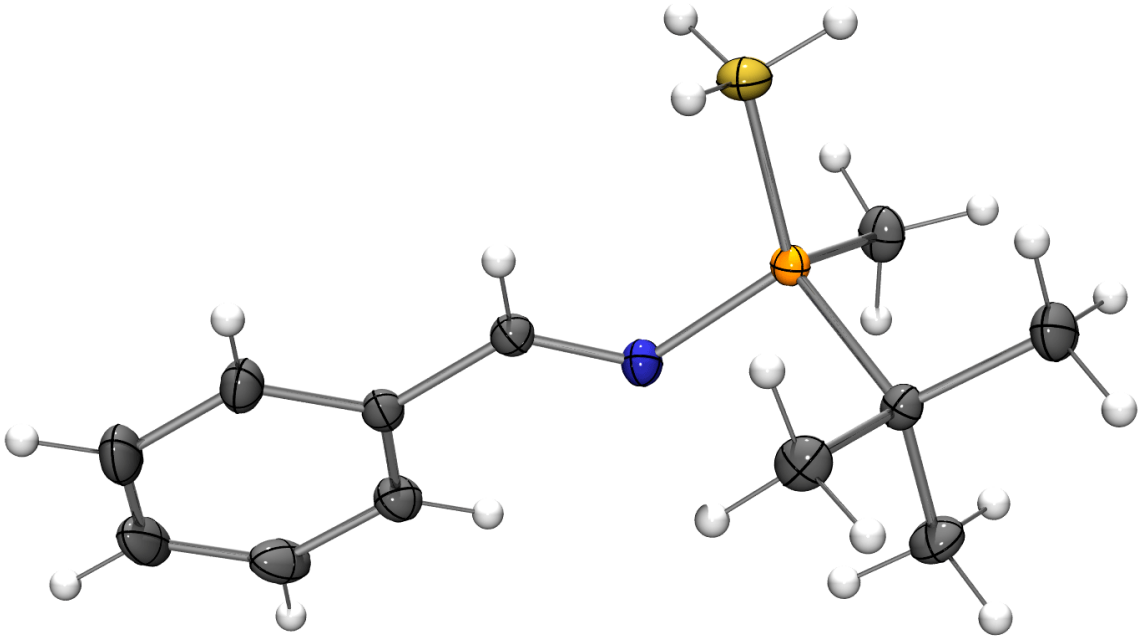
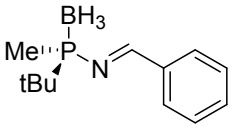
X-Ray structure of (R_P)-(–)-2: Ortep drawing with 50% probability ellipsoids is displayed. CCDC deposit # 1037633.



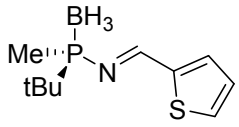
General Methods. All reactions were carried out under nitrogen atmosphere in dried solvents. THF, Et_2O and CH_2Cl_2 were dried in a PureSolv purification system from Innovative Technology, Inc. Toluene was purchased from Aldrich and used without further purification. Thin layer chromatography was carried out using TLC-aluminum sheets with silica gel (Merk 60 F254). Chromatography purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 35-70 μm). NMR spectra were recorded at 23°C on a Varian Mercury 400 or Varian 500 apparatus. ^{1}H NMR and ^{13}C NMR spectra were referenced either to relative internal TMS or to residual solvent peaks. ^{31}P NMR spectra were referenced to phosphoric acid. Optical rotations were recorded on a Perkin Elmer polarimeter at the sodium D line at room temperature concentration in g/mL). Melting points were determined using a Büchi melting point apparatus and were not corrected. IR spectra were recorded in a FT-IR apparatus. HRMS were recorded using an electrospray ionization spectrometer. HPLC chromatography was performed on an Agilent Technologies Series 1100 chromatograph with UV detector.

Microwave irradiation experiments were performed using a CEM X under open vessel method; reaction time refers to the hold time at the set temperature and not to the total irradiation time. Reaction cooling is performed by nitrogen automatically after the heated period has elapsed.

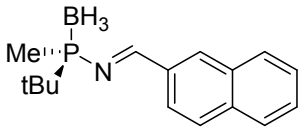
General procedure A for the synthesis of P*-phosphanimines-borane: A round bottom flask was charged with (*S*)-*tert*-butyl(methyl)phosphanamine-borane. The flask was flushed with nitrogen and then $Ti(OEt)_4$ and the corresponding aldehyde were added via syringe. The reaction flask was placed into the microwave reactor (under open vessel conditions) and heated at 80ºC for 35 min. After cooling to room temperature, the mixture was diluted with ethyl acetate and 0.5 mL of water was added while being rapidly stirred. The resulting suspension was filtered through a plug of Celite® plug, eluting with additional ethyl acetate. The filtrate was concentrated and purified by column chromatography on silica gel (eluting with hexane/ethyl acetate mixtures).



(*S,E*) – *N* -(*tert*-butyl(methyl)phosphanyl)-1-phenylmethanimine-borane, 2. Following general procedure A, (*S*)-*tert*-butyl(methyl)phosphanamine-borane (3.75 mmol, 500 mg), benzaldehyde (4.13 mmol, 413 µL), $Ti(OEt)_4$ (13.5 mmol, 3mL), neat. Column chromatography: silica gel, 4:1 hexane/ethyl acetate. White solid; yield: 477 mg (57% yield). Mp: 97-99 ºC. $[\alpha]_D$(+) 106.0 (c=1.2, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.03 (d, *J* = 28 Hz, 1H), 7.91 – 7.88 (m, 2H), 7.60 – 7.51 (m, 1H), 7.52 – 7.43 (m, 2H), 1.48 (d, *J* = 10 Hz, 2H), 1.21 (d, *J* = 14 Hz, 10H), 0.97 – 0.11 (m, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 176.4, 136.3 (d, J_P = 21 Hz), 133.2, 129.8, 129.0, 29.9 (d, J_P = 42 Hz), 24.6 (d, J_P = 3 Hz), 9.3 (d, J_P = 41 Hz) ppm.^{31}P NMR (162 MHz, Chloroform-*d*) δ 81.8 (q, J_B = 60 Hz) ppm. IR (film, cm^{-1}) 2943, 2866, 2354, 1630, 1448, 1367, 885, 692. HRMS calcd for $[C_{12}H_{22}NBP+H^+]^+$: 222.1577, found: 222.1578.

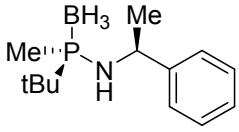


(*S,E*)-*N*-(*tert*-butyl(methyl)phosphanyl)-1-(thiophen-2-yl) methanimine-borane, 3. Following general procedure A, (*S*)-*tert*-butyl(methyl)phosphanamine-borane (3.75 mmol, 500 mg), thiophene-2-carbaldehyde (4.13 mmol, 390 µL), $Ti(OEt)_4$ (13.5 mmol, 3mL), neat. Column chromatography: silica gel, 4:1 hexane/ethyl acetate. Yellow pale solid; yield: 490 mg (58% yield). Mp: 104-105 ºC. $[\alpha]_D$: (+)150.6 (c=1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.06 (d, *J* = 26 Hz, 1H), 7.60 (d, *J* = 4 Hz, 2H), 7.16 (t, *J* = 4 Hz, 1H), 1.46 (d, *J* = 9 Hz, 3H), 1.19 (d, *J* = 14 Hz, 9H), 0.96 – 0.14 (m, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.4, 135.2, 133.1, 128.4, 30.0 (d, J_P = 42 Hz), 24.6 (d, J_P = 3 Hz), 9.5 (d, J_P = 41 Hz) ppm. ^{31} P NMR (202 MHz, Chloroform-*d*) δ 82.2 (q, J_B =60 Hz) ppm. IR (film, cm^{-1}) 3090, 2968, 2866, 2366, 1591, 1418, 1213, 1066, 886, 713. HRMS calcd for $[C_{10}H_{20}NBPS+H^+]^+$: 228.1141, found: 228.1141.

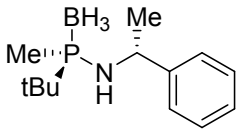


(S,*E*)- *N* -(*tert*-butyl (methyl) phosphanyl) -1- (naphthalen-2-yl) methanimine-borane, 4. Following general procedure A, (*S*)-*tert*-butyl(methyl)phosphanamine-borane (1.51 mmol, 200 mg), benzaldehyde (1.6 mmol, 250 mg), $Ti(OEt)_4$ (5.6 mmol, 1.2 mL), neat. Column chromatography: silica gel, 4:1 hexane/ethyl acetate. White solid; yield: 208 mg (51% yield). Mp:108-109 ºC. $[\alpha]_D$: (+) 90.7 (c=1.1, $CHCl_3$). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.19 (d, J = 28 Hz, 1H), 8.26 (s, 1H), 8.07 (d, J = 7 Hz, 1H), 7.96 (d, J = 8 Hz, 1H), 7.89 (d, J = 12 Hz, 2H), 7.65 – 7.49 (m, 2H), 1.52 (d, J = 9 Hz, 3H), 1.24 (d, J = 14 Hz, 9H), 1.01 – 0.17 (m, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 176.4 , 136.0 , 134.0 (d, J_P = 22 Hz) , 133.8 , 133.0 , 129.4 , 128.9 , 128.6 , 128.1 , 127.0 , 123.6 , 30.0 (d, J_P = 42 Hz), 24.7 (d, J_P = 3 Hz), 9.4 (d, J_P = 41 Hz) ppm. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 81.2 (q, J_B = 61 Hz) ppm. IR (film, cm^{-1}) 2967, 2392, 2360, 1614, 1469, 1367, 1059, 904, 829, 754. HRMS calcd for $[C_{16}H_{23}NBP+H^+]^+$: 272.1734, found: 272.1731.

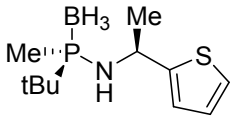
General procedure B for stereoselective 1,2-addition of organometallic reagents to borane-P-stereogenic phosphanimines: A solution of phosphanimine-borane (1 equiv.) in the corresponding solvent was placed at -78ºC . The organometallic reagent was added dropwise via syringe at the same temperature under stirring. The reaction progress was followed by TLC until completion. The reaction mixture was diluted with ethyl acetate and 0.5 mL of water was added while being rapidly stirred. The organic phase was washed twice with brine, dried over magnesium sulfate and concentrated. The crude was then purify by column chromatography on silica gel (eluting with hexane/ethyl acetate mixtures). ^1H, ^{13}C and ^{31}P-NMR are described for the major diastereomer.



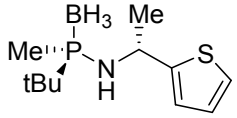
***(S)* – 1 – *tert* – butyl - 1 - methyl -N- (*(S)*-1-phenylethyl) phosphanamine-borane, 5a.** Following general procedure B, ((*S,E*)-*N*-(*tert*-butyl(methyl)phosphanyl)-1-phenylmethanimine-borane (0.1 mmol, 22.1 mg), MeLi (1.6 M) (0.5 mmol, 313µL), CH_2Cl_2 (2 mL). Column chromatography: silica gel, 9:1 hexane/ethyl acetate. White solid; 22.5 mg (95% yield, *dr* (5a:5b) = 98:2). Mp: 102-104 ºC. $[\alpha]_D$: (+) 8.41 (c=0.9, $CHCl_3$). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.27 (m, 4H), 7.28 – 7.19 (m, 1H), 4.52 – 4.37 (m, 1H), 1.74 (br d, J = 8 Hz, 1H), 1.44 (d, J = 7 Hz, 3H), 1.20 (d, J = 9 Hz, 3H), 1.11 (d, J = 14 Hz, 9H), 0.91 – 0.08 (m, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.3 (d, J_P = 3 Hz), 128.7, 127.1, 125.9, 52.8, 30.7 (d, J_P = 42 Hz), 26.8 (d, J_P = 5 Hz), 24.8 (d, J_P = 3 Hz), 10.1 (d, J_P = 36 Hz) ppm. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 69.2 (q, J_B=69 Hz) ppm. IR (film, cm^{-1}) 3336, 2973, 2348, 1450, 1123, 1067, 889, 703, 636. HRMS calcd for $[C_{13}H_{25}NBP+H^+]^+$: 238.1890, found 238.1892.



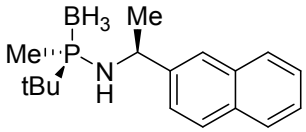
***(S)* – 1 – *tert* – butyl - 1 - methyl -N- (*(R)*-1-phenylethyl) phosphanamine-borane, 5b.** Following general procedure B, ((*S,E*)-*N*-(*tert*-butyl(methyl)phosphanyl)-1-phenylmethanimine-borane (0.2 mmol, 44.2 mg), MeLi (1.6 M) (1 mmol, 616 µL), THF (4 mL). Column chromatography: silica gel, 9:1 hexane/ethyl acetate. White solid; 43.5 mg (90% yield, *dr* (5a:5b) = 29:71). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.25 (m, 4H), 7.28 – 7.19 (m, 1H), 4.52 – 4.37 (m, 1H), 1.80 (br d, *J* = 10 Hz, 1H), 1.46 (d, *J* = 7 Hz, 3H), 1.24 (d, *J* = 9 Hz, 3H), 1.07 (d, *J* = 14 Hz, 1H), 0.92 – 0.11 (m, 3H) ppm.



***(S)*-1- *tert* - butyl - 1 - methyl - *N* - (*(S)*-1-(thiophen-2-yl)ethyl) phosphanamine-Borane, 6a.** Following general procedure B, *(S,E)*-*N*-(*tert*-butyl(methyl)phosphanyl)-1-(thiophen-2-yl)methanimine-borane (0.1 mmol, 22.1 mg), MeLi (1.6 M) (0.5 mmol, 313µL), CH_2Cl_2 (2 mL). Column chromatography: silica gel, 9:1 hexane/ethyl acetate. Yellow oil; 20.9 mg (86% yield, *dr*= 98:2). $[\alpha]_D$: (+) 11.9 (c=0.7, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.13 (m, 1H), 6.97 – 6.90 (m, 2H), 4.84 – 4.68 (m, 1H), 1.73 (br d, *J* = 11 Hz, 1H), 1.55 (d, *J* = 7 Hz, 3H), 1.30 (d, *J* = 9 Hz, 3H), 1.14 (d, *J* = 14 Hz, 9H), 0.95 – 0.12 (m, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.4 (d, J_P = 3 Hz), 127.0, 124.0, 123.3, 48.9 (d, J_P = 2 Hz), 30.7 (d, J_P = 42 Hz), 26.6 (d, J_P = 4 Hz), 24.7 (d, J_P = 3 Hz), 10.4 (d, J_P = 36 Hz) ppm. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 70.1 (q, J_B = 68 Hz) ppm. IR (film, cm^{-1}) 3334, 2969, 2379, 1470, 1297, 1066, 887, 701. HRMS calcd for $[C_{11}H_{23}BNPS+NH_4^+]^+$: 261.1720, found 261.1722.

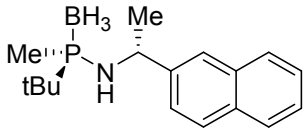


***(S)*-1- *tert* - butyl - 1 - methyl - *N* - (*(R)*-1-(thiophen-2-yl)ethyl) phosphanamine-Borane, 6b.** Following general procedure B, *(S,E)*-*N*-(*tert*-butyl(methyl)phosphanyl)-1-(thiophen-2-yl)methanimine-borane (0.1 mmol, 22.7 mg), MeLi (1.6 M) (0.5 mmol, 313µL), THF (2 mL). Column chromatography: silica gel, 9:1 hexane/ethyl acetate. Yellow oil; 20.3 mg (83% yield, *dr*= (6a:6b) 37:63). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.16 (m, 1H), 7.00 – 6.88 (m, 2H), 4.86 – 4.64 (m, 1H), 1.78 (br d, *J* = 11 Hz 1H) 1.57 (d, *J* = 7 Hz, 3H), 1.34 (d, *J* = 9 Hz, 3H), 1.13 (d, *J* = 14 Hz, 9H), 0.91 – 0.16 (m, 3H) ppm.

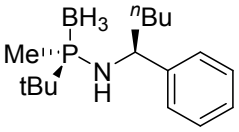


***(S)* - 1- *tert* – butyl - 1- methyl - *N*- (*(S)*-1- (naphthalen-2-yl)ethyl) phosphanamine-Borane, 7a.** Following general procedure B, *(S,E)*-*N*-(*tert* – butyl (methyl) phosphanyl)-1 - (naphthalen-2-yl) methanimine–borane (0.1 mmol, 27.1 mg), MeLi (1.6 M) (0.5 mmol, 313µL), CH_2Cl_2 (2 mL). Column

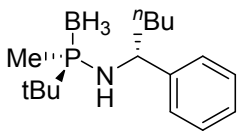
chromatography: silica gel, 9:1 hexane/ethyl acetate. White solid; yield: 28.4 mg (99% yield, *dr* (7a:7b)= 97:3). Mp: 137-139 ºC. $[\alpha]_D$: (–) 22.28 (c=0.4, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.81 (m, 3H), 7.78 7.71 (m, 1H), 7.53 – 7.40 (m, 3H), 4.67 – 4.58 (m, 1H), 1.84 (br d, J = 10 Hz, 1H), 1.53 (d, J = 7 Hz, 3H), 1.22 (d, J = 9 Hz, 3H), 1.12 (d, J = 14 Hz, 9H), 0.93 – 0.15 (m, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.7 (d, J_P = 2 Hz), 133.5 , 132.7 , 128.6 , 128.0 , 127.8 , 126.3 , 125.9 , 124.5 , 124.3 , 52.9 , 30.7 (d, J_P = 42 Hz), 26.7 (d, J_P = 5 Hz), 24.8 (d, J_P = 3 Hz), 10.1 (d, J_P = 36 Hz) ppm. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 69.4 (q, J_B = 68 Hz) ppm. IR (film, cm^{-1}): 3334, 2962, 2366, 1514, 1450, 1380, 1021, 887, 745, 470. HRMS calcd for $[C_{17}H_{27}BNP+H^+]^+$: 288.2047, found 288.2047.



***(S)* - 1- *tert* – butyl - 1- methyl - *N*- (*(R)*-1- (naphthalen-2-yl)ethyl) phosphanamine-Borane, 7b.** Following general procedure B, *(S,E)*-*N*-(*tert*-butyl (methyl) phosphanyl)-1-(naphthalen-2-yl) methanimine–borane (0.1 mmol, 27.1 mg), MeLi (1.6 M) (0.5 mmol, 313µL), THF (2 mL). Column chromatography: silica gel, 9:1 hexane/ethyl acetate. White solid; yield: 28.5 mg (99% yield, *dr* (7a:7b) = 25:75). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.79 (m, 3H), 7.77 – 7.71 (m, 1H), 7.54 – 7.41 (m, 3H), 4.78 – 4.55 (m, 1H), 1.92 (br d, J = 11 Hz, 1H), 1.55 (d, J = 7 Hz, 3H), 1.26 (d, J = 9 Hz, 3H), 1.08 (d, J = 14 Hz, 9H), 1.01 – 0.15 (m, 3H) ppm.

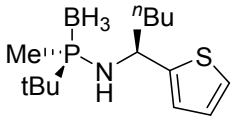


***(S)*-1-*tert*-butyl-1-methyl-*N*- (*(S)*-1-phenylpentyl) phosphanamine-borane, 8a**. Following general procedure B, ((*S,E*)-*N*-(*tert*-butyl(methyl)phosphanyl)-1-phenylmethanimine-borane (0.2 mmol, 44.2 mg), ^{n}BuLi (2.5 M) (0.6 mmol, 240 µL), CH_2Cl_2 (2 mL). Column chromatography: silica gel, 9:1 hexane/ethyl acetate. White solid; 51.1 mg (92% yield, *dr* (8a:8b)= 98:2). Mp: 102-104 ºC. $[\alpha]_D$: (-) 8.2 (c=0.8, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.29 (m, 2H), 7.26 – 7.19 (m, 3H), 4.23-4.15 (m, 1H), 1.75 (d, J = 10 Hz, 1H), 1.74 – 1.60 (m, 2H), 1.38 – 1.23 (m, 4H), 1.14 (d, J = 9 Hz, 3H), 1.08 (d, J = 14 Hz, 9H), 0.86 (t, J = 7 Hz, 3H), 0.72 – 0.09 (m, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.6 (d, J_P = 1 Hz), 128.6, 126.4, 57.4 (d, J_P = 1 Hz), 40.4 (d, J_P = 6 Hz), 30.6 (d, J_P = 44 Hz), 28.7, 24.8 (d, J_P = 3 Hz), 22.6, 14.1, 10.0 (d, J_P = 34 Hz) ppm. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 69.2 (q, J_B = 68 Hz) ppm. IR (film, cm^{-1}) 3335, 2973, 2408, 2370, 2348, 1444, 1123, 1066, 880, 707. HRMS calcd for $[C_{16}H_{31}NBP+H^+]^+$: 280.2360, found 280.2358.

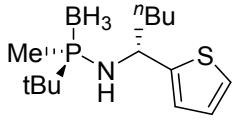


***(S)*-1-*tert*-butyl-1-methyl-*N*- (*(R)*-1-phenylpentyl) phosphanamine-borane, 8b**. Following general procedure B, ((*S,E*)-*N*-(*tert*-

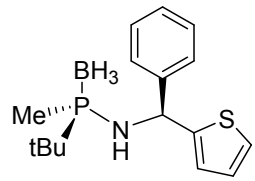
butyl(methyl)phosphanyl)-1-phenylmethanimine-borane (0.2 mmol, 44.2 mg), *n*-BuLi (2.5 M) (0.6 mmol, 240 µL), THF (2 mL). Column chromatography: silica gel, 9:1 hexane/ethyl acetate. White solid; 49.7 mg (89% yield, *dr* (8a:8b) = 12:88). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.27 (m, 2H), 7.25 – 7.20 (m, 3H), 4.34 – 4.07 (m, 1H), 1.83 (br d, *J* = 10 Hz, 1H), 1.74 – 1.63 (m, 2H), 1.36 – 1.24 (m, 4H), 1.20 (d, *J* = 9 Hz, 3H), 1.01 (d, *J* = 14 Hz, 9H), 0.86 (t, *J* = 7 Hz, 3H) ppm.



***(S)* -1- *tert*- butyl-1- methyl-*N*- (*(S)*-1-(thiophen-2-yl) pentyl) phosphanamine, 9a**. Following general procedure B, *(S,E)-N*-(*tert*-butyl(methyl)phosphanyl)-1-(thiophen-2-yl)methanimine-Borane (0.1 mmol, 22.1 mg), ^{n}BuLi (0.3 mmol, 120 µL), CH_2Cl_2 (2 mL). Column chromatography: silica gel, 9:1 hexane/ethyl acetate. Yellow oil; 25.9 mg (91% yield, *dr* (9a:9b) = 90:10). $[\alpha]_D$: (-) 17.2 (c=0.6, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 (dd, *J* = 5, 2 Hz, 1H), 7.01 – 6.84 (m, 2H), 4.62 – 4.54 (m, 1H), 1.89 – 1.68 (m, 2H), 1.64 (d, *J* = 10 Hz, 1H), 1.39 – 1.26 (m, 4H), 1.15 (d, *J* = 9 Hz, 3H) 1.13 (d, *J* = 14 Hz, 9H), 0.88 (t, *J* = 7 Hz, 3H), 0.72 – 0.14 (m, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.4, 126.8, 124.1, 123.7, 53.1, 40.5 (d, J_P = 6 Hz), 30.5 (d, J_P = 44 Hz), 28.4, 24.7 (d, J_P = 3 Hz), 22.5, 14.1, 10.3 (d, J_P = 33 Hz) ppm. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 70.2 (q, J_B= 67 Hz) ppm. IR (film, cm^{-1}) 3335, 2957, 2379, 1464, 1417, 1292, 1071, 891, 701. HRMS calcd for $[C_{14}H_{29}BNPS+H^+]^+$: 286.1924, found 286.1924.

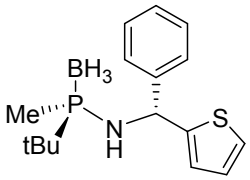


***(S)* -1- *tert*- butyl-1- methyl-*N*- (*(R)*-1-(thiophen-2-yl) pentyl) phosphanamine, 9b**. Following general procedure B, *(S,E)-N*-(*tert*-butyl(methyl)phosphanyl)-1-(thiophen-2-yl)methanimine-Borane (0.1 mmol, 22.1 mg), *n*-BuLi (0.3 mmol, 120 µL), THF (2 mL). Column chromatography: silica gel, 9:1 hexane/ethyl acetate. Yellow oil; 27.6 mg (97% yield, *dr* (9a:9b) = 10:90). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 (dd, *J* = 5, 2 Hz, 1H), 6.97 – 6.86 (m, 2H), 4.67 – 4.53 (m, 1H), 1.89 – 1.70 (m, 3H), 1.36 – 1.23 (m, 4H), 1.30 (d, *J* = 9 Hz, 3H), 1.04 (d, *J* = 14 Hz, 9H), 0.88 (t, *J* = 7 Hz, 3H), 0.72 – 0.14 (m, 3H) ppm

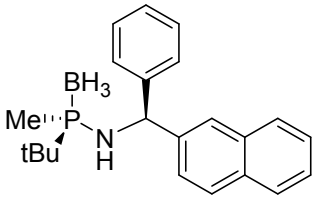


(*S*) – 1 –*tert* –butyl -1- methyl- *N*-((*S*)-phenyl (thiophen-2-yl) methyl) phosphanamine, 10a. Following general procedure B, *(S,E)-N*-(tert-butyl(methyl)phosphanyl)-1-(thiophen-2-yl)methanimine-borane (0.1 mmol, 22.1 mg), PhLi (1.8 M) (0.5 mmol, 278 µL), CH_2Cl_2 (2 mL). Column chromatography: silica gel, 9:1 hexane/ethyl acetate. White solid; 30.2 mg (99% yield, *dr* (10a:10b)>

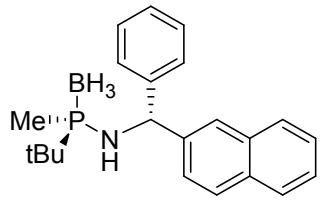
99:1). Mp: 99-101 ºC. $[\alpha]_D$: (+) 20.9 (c=0.7, $CHCl_3$). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.25 (m, 5H), 7.22 (dd, *J* = 5, 1 Hz, 1H), 6.90 (dd, *J* = 5, 4 Hz, 1H), 6.66 (dt, *J* = 4, 1 Hz, 1H), 5.77 (dd, *J* = 11, 9 Hz, 1H), 2.36 (br d, *J* = 11 Hz, 1H), 1.31 (d, *J* = 9 Hz, 3H), 1.07 (d, *J* = 14 Hz, 9H), 0.75 – 0.17 (m, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.9 (d, J_P = 4 Hz), 143.8 (d, J_P = 3 Hz), 128.8, 127.8, 127.1, 127.0, 125.5, 125.1, 57.2 (d, J_P = 2 Hz), 31.2 (d, J_P = 40 Hz), 24.8 (d, J_P = 3 Hz), 10.1 (d, J_P = 38 Hz) ppm. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 72.3 (q, J_B = 67 Hz) ppm. IR (film, cm^{-1}). 3348, 2981, 2377, 1454, 1407, 1246, 1073, 940,702. HRMS calcd for $[C_{16}H_{25}BNPS+H^+]^+$: 306.1611, found 306.1610.



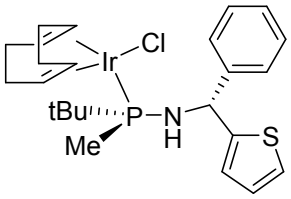
(*S*) – 1 –*tert* –butyl -1- methyl- *N*-((*R*)-phenyl (thiophen-2-yl) methyl) phosphanamine, 10b. Following general procedure B, *(S,E)-N*-(tert-butyl(methyl)phosphanyl)-1-(thiophen-2-yl)methanimine-borane (0.1 mmol, 22.1 mg), PhLi (1.8 M) (0.5 mmol, 278 µL), THF (2 mL). Column chromatography: silica gel, 9:1 hexane/ethyl acetate. White solid; 28.0 mg (93% yield, *dr* (10a:10b) = 60:40). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.25 (m, 5H), 7.25 – 7.18 (m, 1H), 6.89 (dd, *J* = 5, 4 Hz, 1H), 6.69 – 6.60 (m, 1H), 5.82 – 5.70 (m, 1H), 2.36 (br d, *J* = 11 Hz, 1H), 1.19 (d, *J* = 9 Hz, 3H), 1.15 (d, *J* = 14 Hz, 9H), 0.75 – 0.17 (m, 3H) ppm.



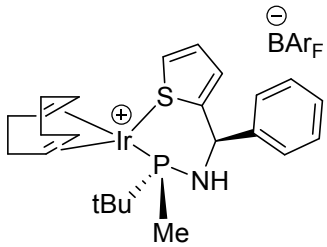
***(S)*-1-*tert*-butyl-1-methyl-*N*-*((S)*-naphthalen-2-yl (phenyl)methyl) phosphanamin*e*-borane, 11a.** Following general procedure B, *(S,E)-N*-(*tert*-butyl(methyl)phosphanyl)-1-(naphthalen-2-yl)methanimine–borane (0.1 mmol, 27.1 mg), PhLi (1.8 M) (0.5 mmol, 278µL), CH_2Cl_2 (2 mL). Column chromatography: silica gel, 9:1 hexane/ethyl acetate. Yellow pale solid; yield: 34.5 mg (99% yield, *dr* (11a:11b)> 99:1). Mp: 143-145 ºC. $[\alpha]_D$: (–) 15.0 (c=0.9, $CHCl_3$). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.77 (m, 3H), 7.76 – 7.68 (m, 1H), 7.63 – 7.56 (m, 1H), 7.53 – 7.39 (m, 3H), 7.38 – 7.26 (m, 4H), 5.84 – 5.59 (m, 1H), 2.28 (d, *J* = 11 Hz, 1H), 1.25 (d, *J* = 9 Hz, 3H), 1.12 (d, *J* = 14 Hz, 8H), 0.92 – 0.20 (m, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.1 , 141.8 , 133.4 , 132.7 , 128.9 , 128.7 , 128.6 , 128.2 , 127.8 , 127.5 , 127.4 , 126.4 , 126.2 , 126.0 , 125.7 , 60.8 , 31.1 (d, J_P = 41 Hz), 24.9 (d, J_P = 3 Hz), 10.2 (d, J_P = 36 Hz) ppm. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 71.9 (q, J_B = 66 Hz) ppm. IR (film, cm^{-1}): 3341, 3057, 2927, 2378, 1600, 1450, 1068, 906, 699. HRMS calcd for $[C_{23}H_{31}BNP\text{-}BH_3+O]^+$: 352.1825, found 352.1820.



***(S)*-1-*tert*-butyl-1-methyl-*N*-*((R)*-naphthalen-2-yl (phenyl)methyl) phosphanamin*e*-borane, 11b.** Following general procedure B, *(S,E)*-*N*-(*tert*-butyl(methyl)phosphanyl)-1-(naphthalen-2-yl)methanimine–borane (0.1 mmol, 27.1 mg), PhLi (1.8 M) (0.5 mmol, 278µL), THF (2 mL). Column chromatography: silica gel, 9:1 hexane/ethyl acetate. Yellow pale solid; yield: 32.5 mg (93% yield, *dr* (11a:11b) = 47:53). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.77 (m, 3H), 7.76 – 7.68 (m, 1H), 7.63 – 7.56 (m, 1H), 7.53 – 7.39 (m, 3H), 7.38 – 7.26 (m, 4H), 5.84 – 5.59 (m, 1H), 2.30 (d, *J* = 11 Hz, 1H), 1.28 (d, *J* = 9 Hz, 3H), 1.11 (d, *J* = 14 Hz, 9H), 0.92 – 0.20 (m, 3H) ppm.



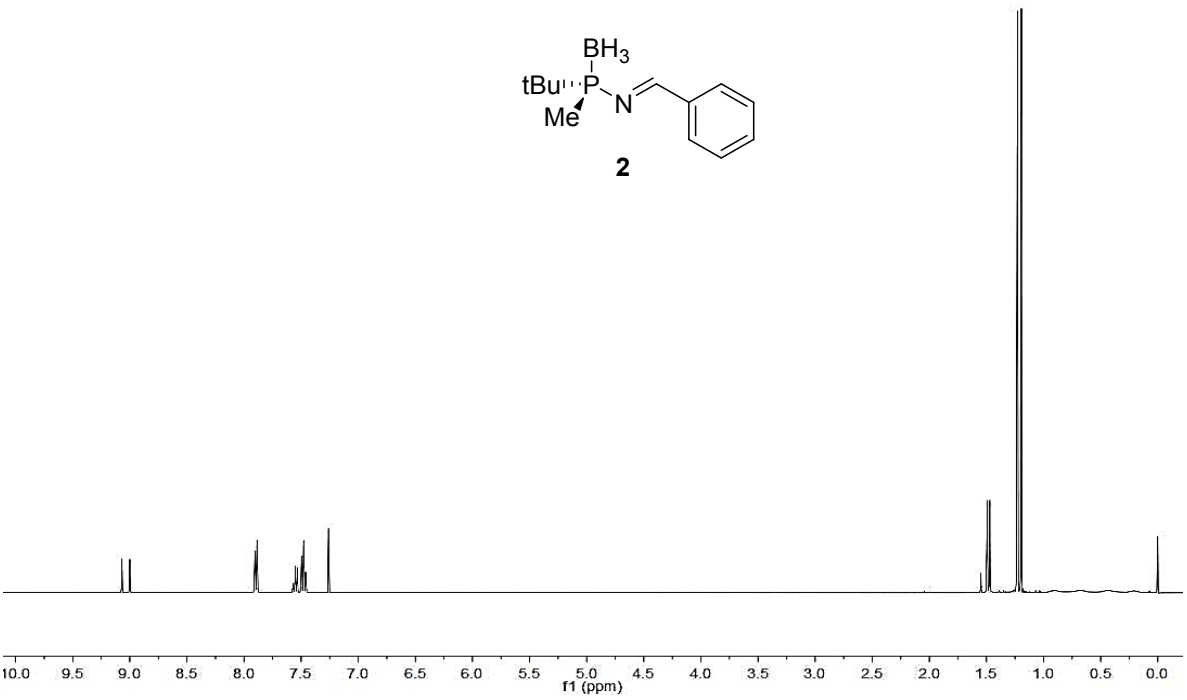
[Ir(COD)(η^1-10a)Cl], 12. (*R*)-1-*tert*-butyl-1-methyl-*N*-((*R*)-phenyl(thiophen-2-yl)methyl)phosphanamine, (*R$_P$, R*)-**10a** (0.16 mmol, 50 mg) and 1,4-diazabicyclo[2.2.2]octane (1.44 mmol, 162 mg) were dissolved in freshly distilled toluene (3mL) and the solution was stirred at 100 ºC for 16h. Consumption of the starting phosphine-borane was followed by TLC. The resulting solution was transferred via canula to a shlenck containing 1,5-cyclooctadiene-iridium(I) chloride dimer (0.09 mmol, 59 mg) and the solution was allowed to stir overnight at rt. The solvent was removed and the resulting crude was then purified by column chromatography on silica gel (eluting with dichloromethane) to obtain 68 mg (63%) of the desired compound as an orange solid. $[\alpha]_D$: (+) 2.6 (c = 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7 Hz, 2H), 7.37 (t, *J* = 7 Hz, 2H), 7.30 (d, *J* = 7 Hz, 1H), 7.20 (dd, *J* = 5, 1 Hz, 1H), 6.88 (dd, *J* = 5, 3 Hz, 1H), 6.80 – 6.70 (m, 1H), 5.65 (dd, *J* = 10, 6 Hz, 1H), 5.11-5.05 (m, 1H), 4.93-4.87 (m, 1H), 3.64 (t, *J* = 10 Hz, 1H), 3.09-3.03 (m, 1H), 2.94-2.89 (m, 1H), 2.22 – 2.10 (m, 4H), 1.81 – 1.54 (m, 4H), 1.31 (d, *J* = 15 Hz, 9H), 1.07 (d, *J* = 8 Hz, 3H) ppm.^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.3 (d, J_P = 5 Hz), 144.4 (d, J_P = 3 Hz), 128.6, 127.6, 127.2, 126.7, 125.4, 125.1, 94.0 (d, J_P = 12 Hz), 92.8 (d, J_P = 17 Hz), 58.1 (d, J_P = 5 Hz), 53.5, 49.9, 38.0 (d, J_P = 33 Hz), 34.1 (d, J_P = 4 Hz), 33.6 (d, J_P = 3 Hz), 29.7 (d, J_P = 2 Hz), 28.5 (d, J_P = 3 Hz), 27.2 (d, J_P = 5 Hz), 3.5 (d, J_P = 32 Hz) ppm.^{31}P NMR (162 MHz, Chloroform-*d*) δ 57.1 ppm. IR (film, cm^{-1}): 2911, 2847, 1720, 1450, 1284, 887, 695. HRMS calcd for $[C_{24}H_{34}IrNPS\text{-}Cl]^+$: 592.1773, found 592.1781.



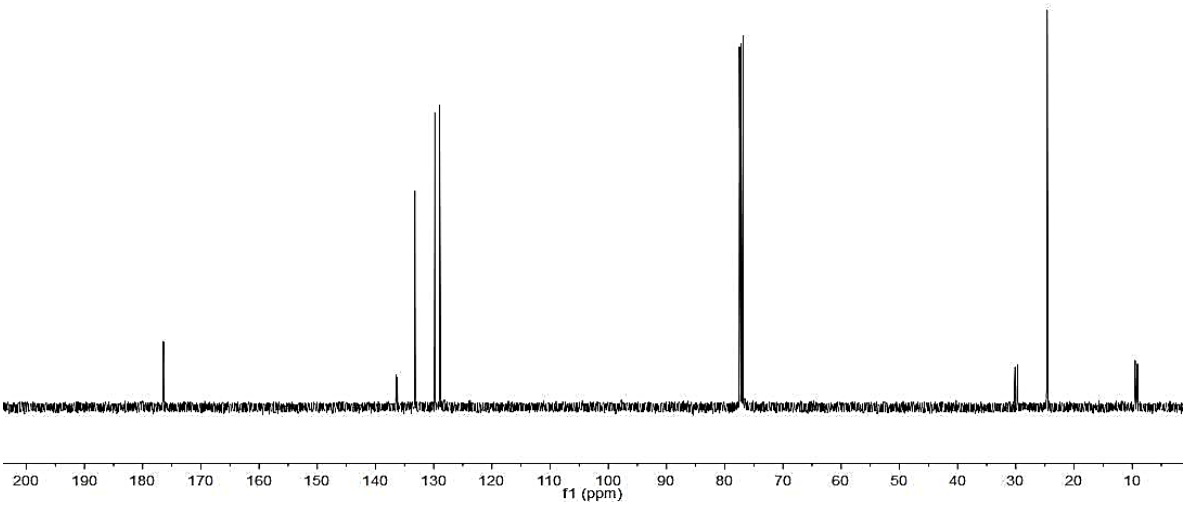
[Ir(COD)(10a)][B(Ar$_F$)$_4$], 13. A flask was charged with [Ir(COD)(η^1-**10a**)Cl] (**12**) (0.16 mmol, 100mg) and NaB(ArF)$_4$ (0.17 mmol, 149 mg) and the solids were dissolved in CH_2Cl_2 (5mL). The solution was stirred for 1h at rt. The resulting crude was then purified by column chromatography on silica gel (eluting with dichloromethane: hexane 7:3) to obtain 142 mg (61%) of the desired compound as an orange solid. $[\alpha]_D$: (+) 19.6 (c=0.5,

$CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (br s, 8H), 7.52 (br s, 4H), 7.49 (dd, J = 8, 2 Hz, 2H), 7.40 – 7.29 (m, 5H), 6.75 (dd, J = 3, 2 Hz, 1H), 5.65 (dd, J = 25, 6 Hz, 1H), 5.42 – 5.36 (m, 1H), 3.98-3.87 (m, 2H), 3.68 – 3.61 (m, 1H), 3.21 (t, J = 5 Hz, 1H), 2.26 – 1.82 (m, 8H), 1.24 (d, J = 16 Hz, 9H), 0.63 (d, J = 8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.9 (q, J_B = 50 Hz), 145.2, 142.2 (d, J_P = 4 Hz), 137.6, 134.9, 129.9, 129.3, 129.1 (qq, ^2J_F= 31, ^4J_F= 3 Hz), 127.7, 126.4, 124.7 (q, J_F = 273 Hz, 8xCF_3), 124.3 (d, J_P = 3 Hz), 117.6 (sept, J_F = 4 Hz,), 98.0 (d, J_P = 13 Hz), 93.2 (d, J_P = 10 Hz), 72.5, 68.2, 57.5, 37.2 (d, J_P = 43 Hz), 33.4 (d, J_P = 4 Hz), 32.3 (d, J_P = 3 Hz), 30.3 (d, J_P = 2 Hz), 28.8 (d, J_P = 2 Hz), 27.0 (d, J_P = 4 Hz), 9.2 (d, J_P = 25 Hz) ppm. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 55.2 ppm. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.36 ppm. IR (film, cm^{-1}): 2936, 2040, 1713, 1611, 1348, 1277, 1130, 836, 720. HRMS calcd for $[C_{24}H_{34}IrNPS]^+$: 592.1773 found 592.1770. Calc for $[C_{32}H_{12}BF_{24}]^-$: 863.0643, found 863.0628.

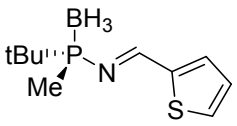
^{1}H NMR (400 MHz, $CDCl_3$)



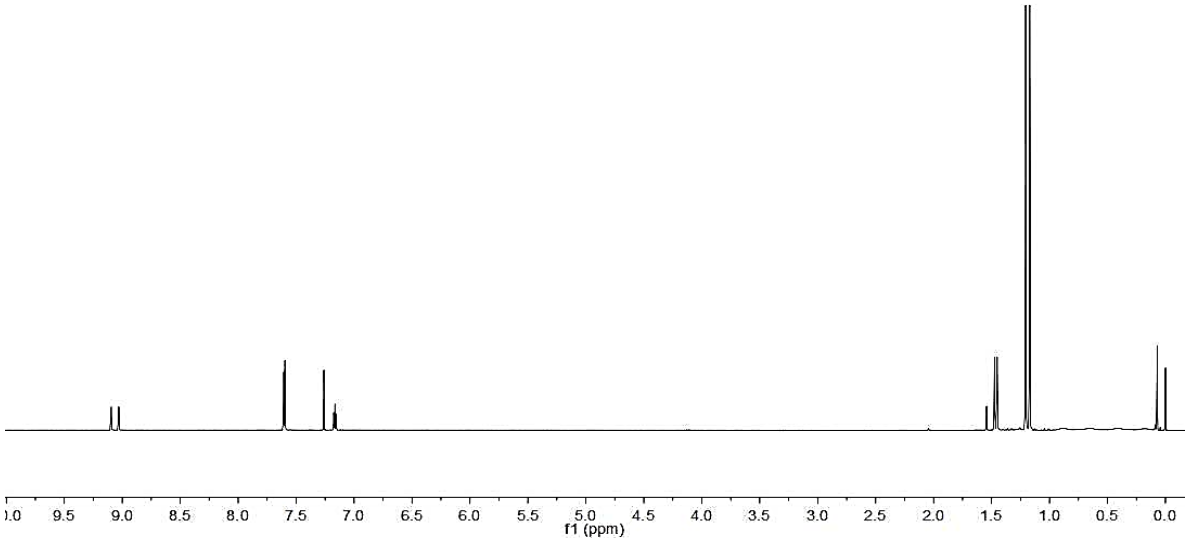
^{13}C NMR (100 MHz, $CDCl_3$)



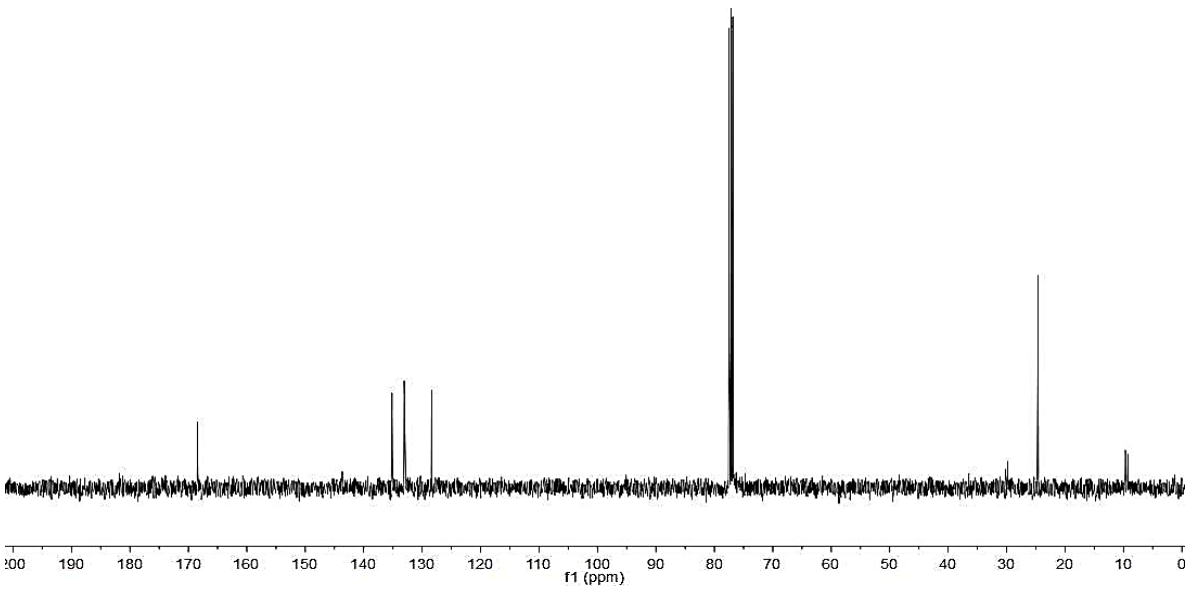
^{1}H NMR (400 MHz, $CDCl_3$)



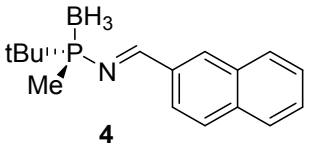
3



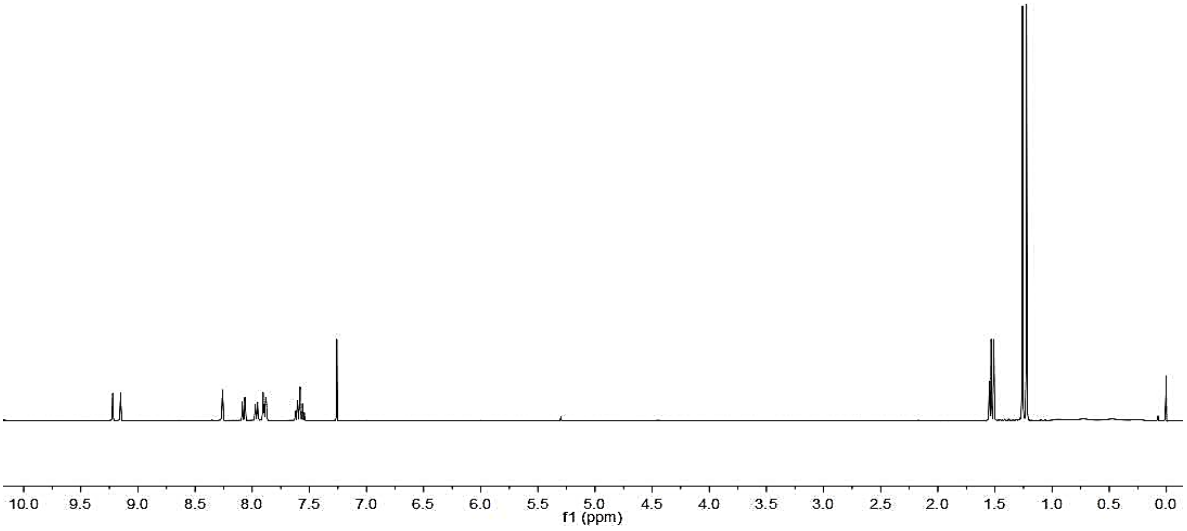
^{13}C NMR (100 MHz, $CDCl_3$)



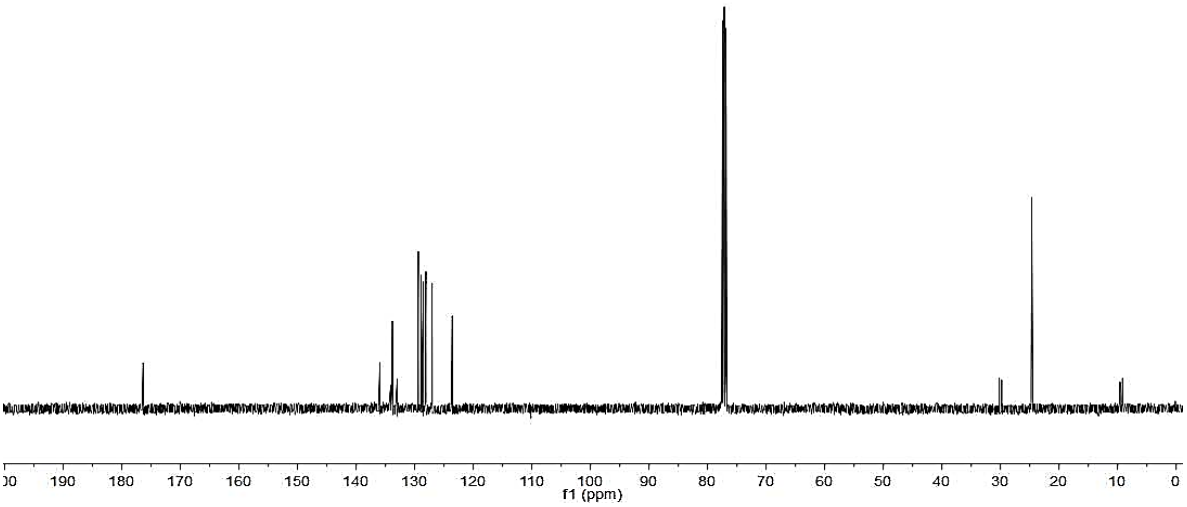
^{1}H NMR (400 MHz, $CDCl_3$)



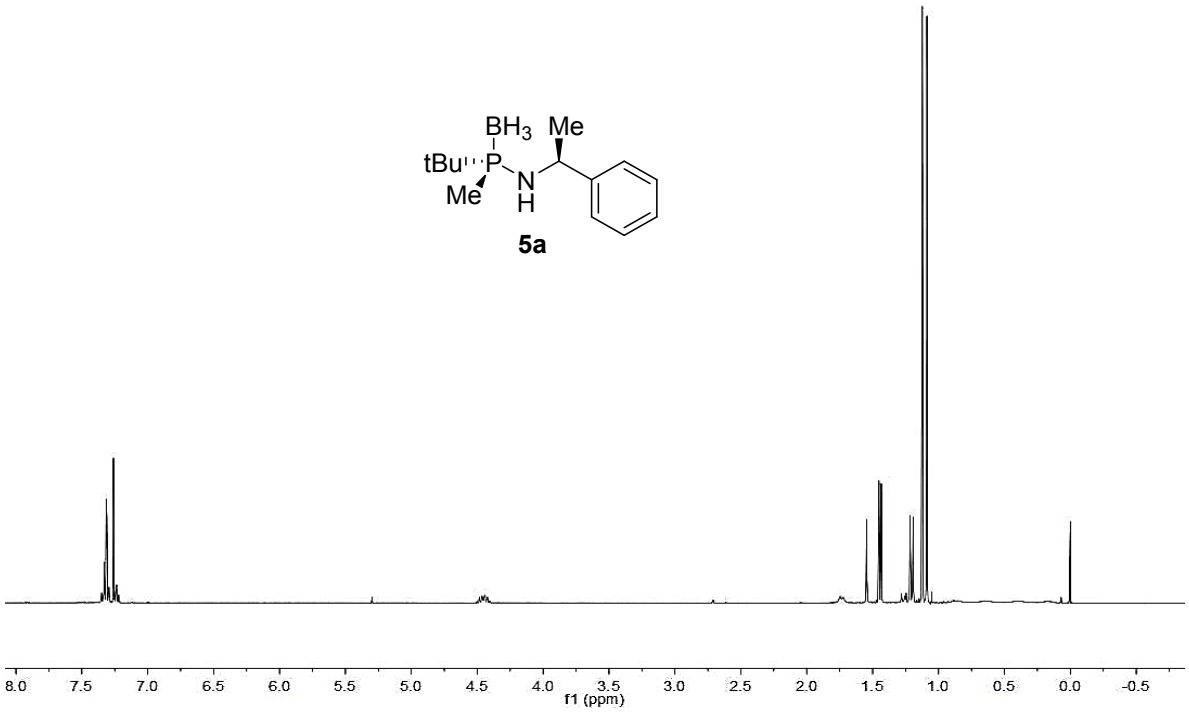
4



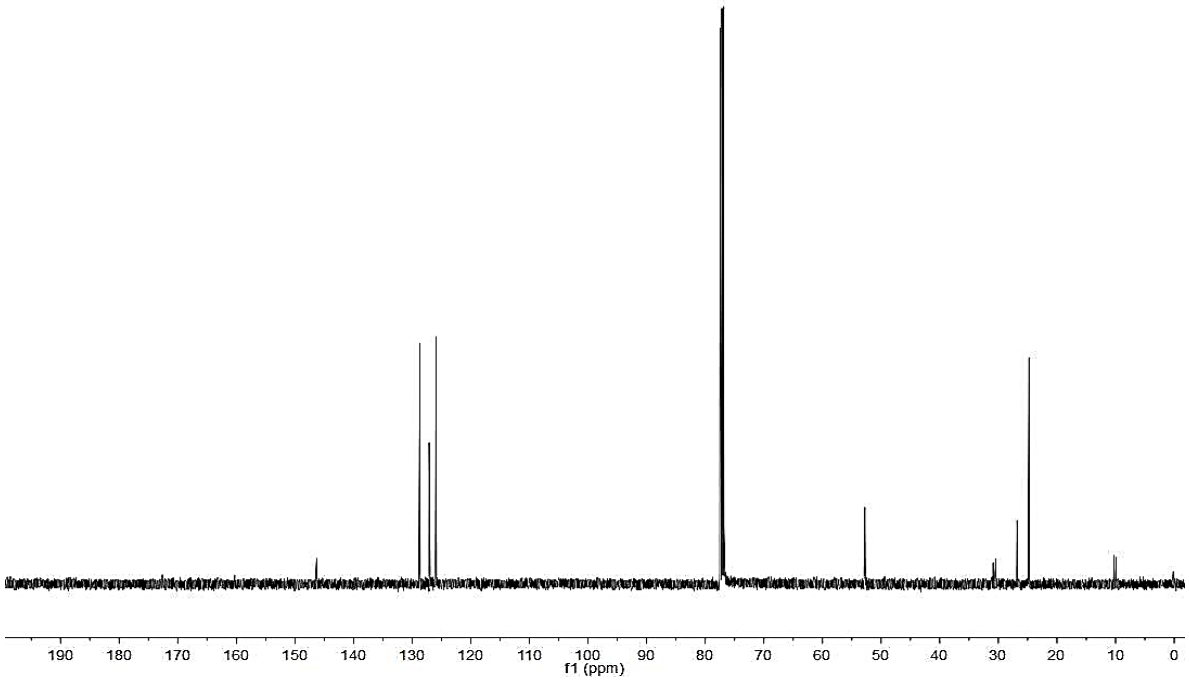
^{13}C NMR (100 MHz, $CDCl_3$)



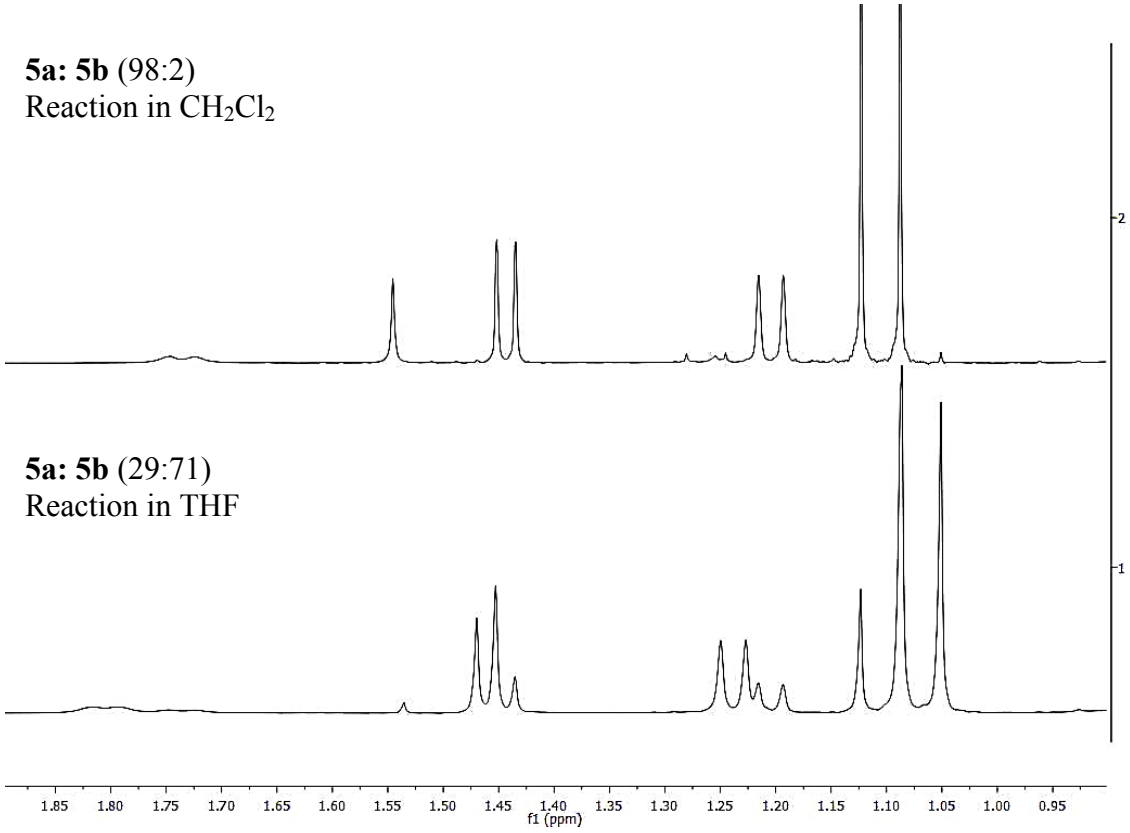
^{1}H NMR (400 MHz, $CDCl_3$)



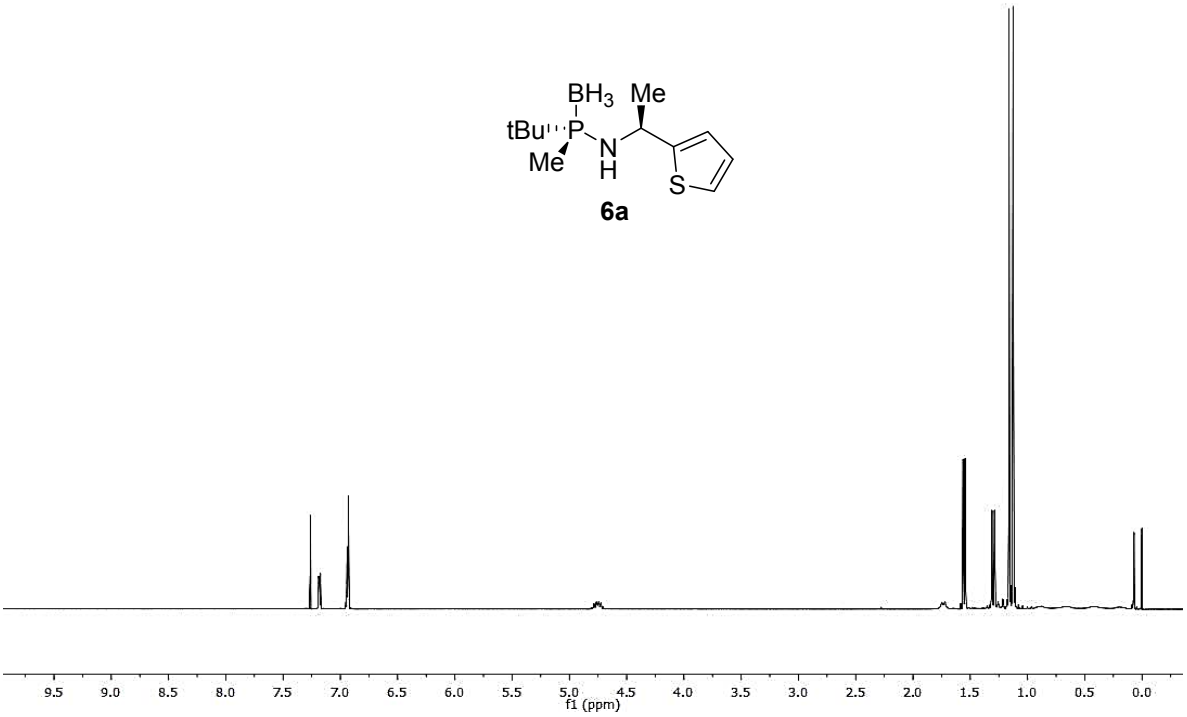
^{13}C NMR (100 MHz, $CDCl_3$)



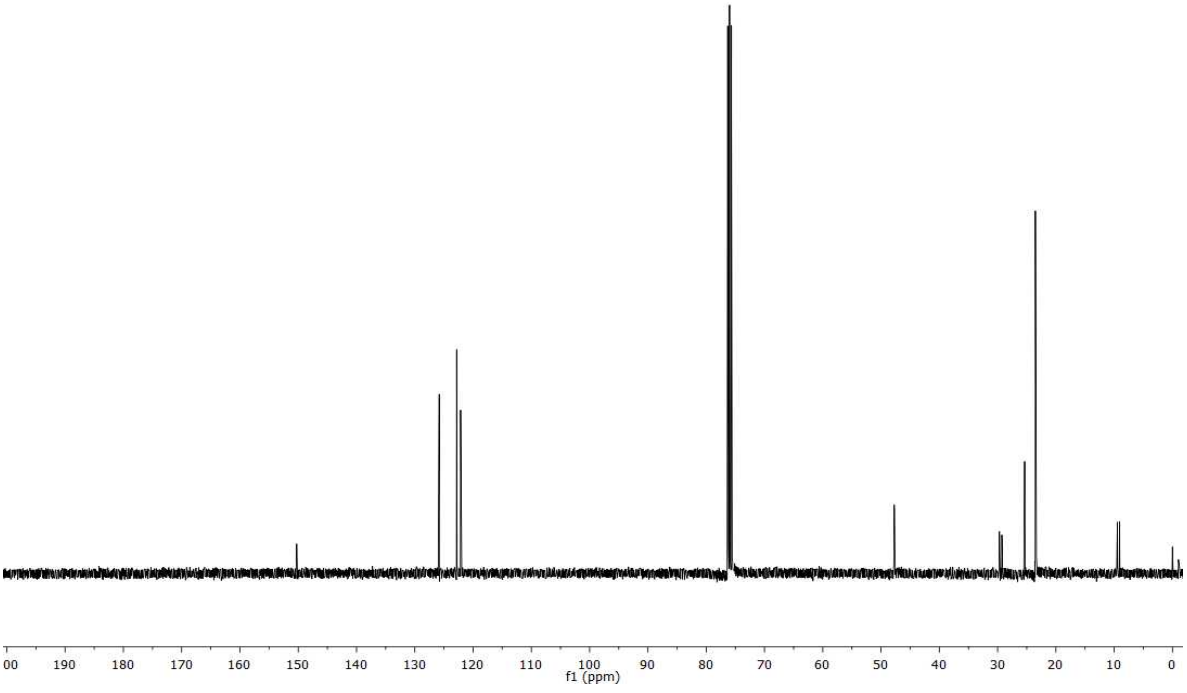
^{1}H NMR (400 MHz, $CDCl_3$)



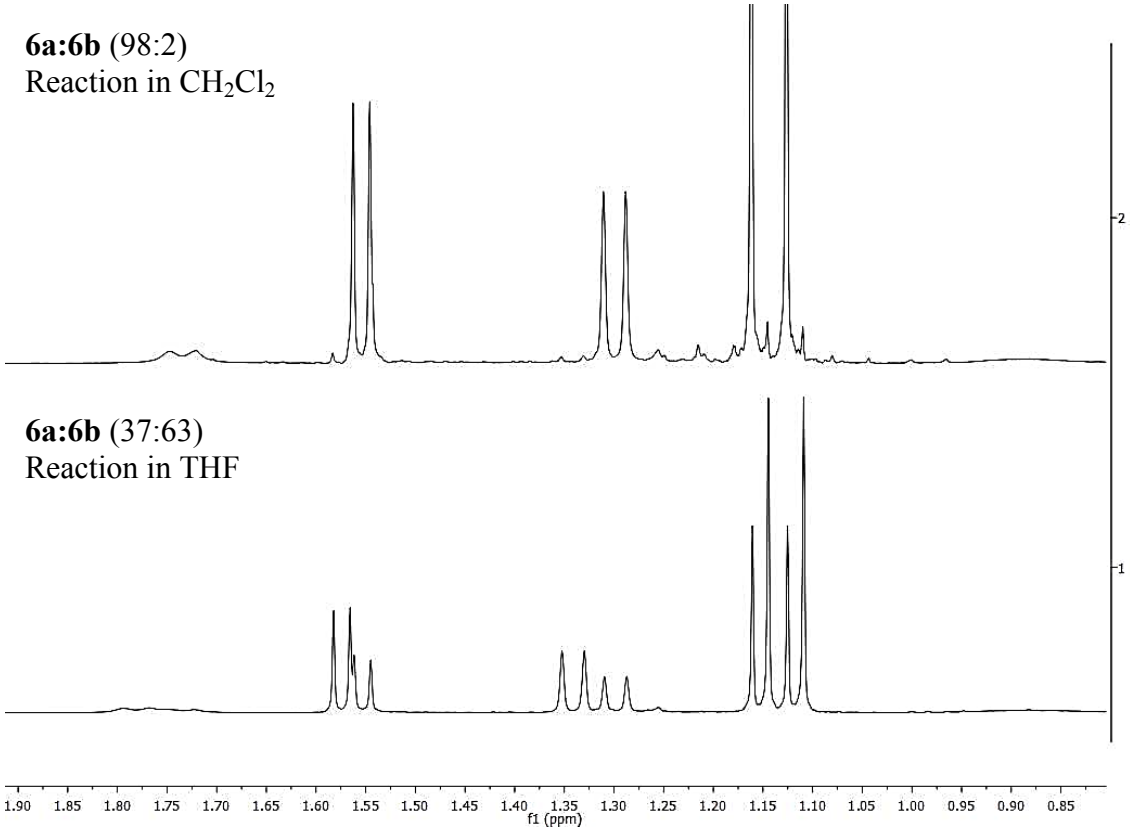
^{1}H NMR (400 MHz, $CDCl_3$)



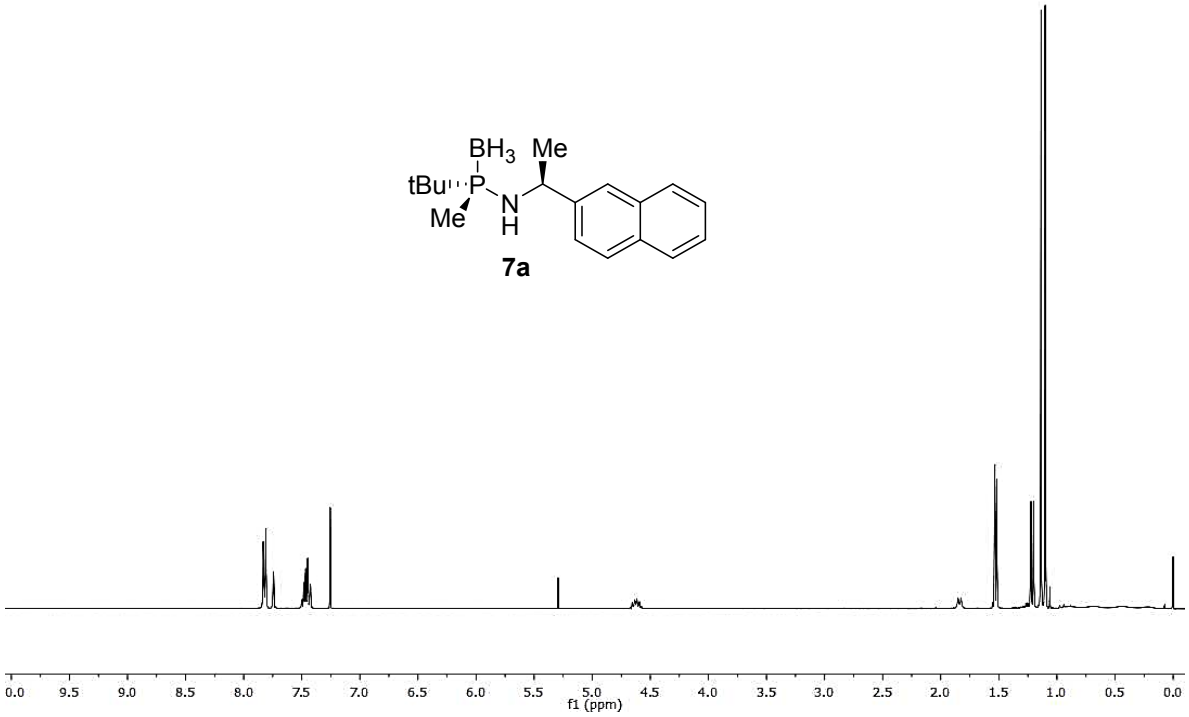
^{13}C NMR (100 MHz, $CDCl_3$)



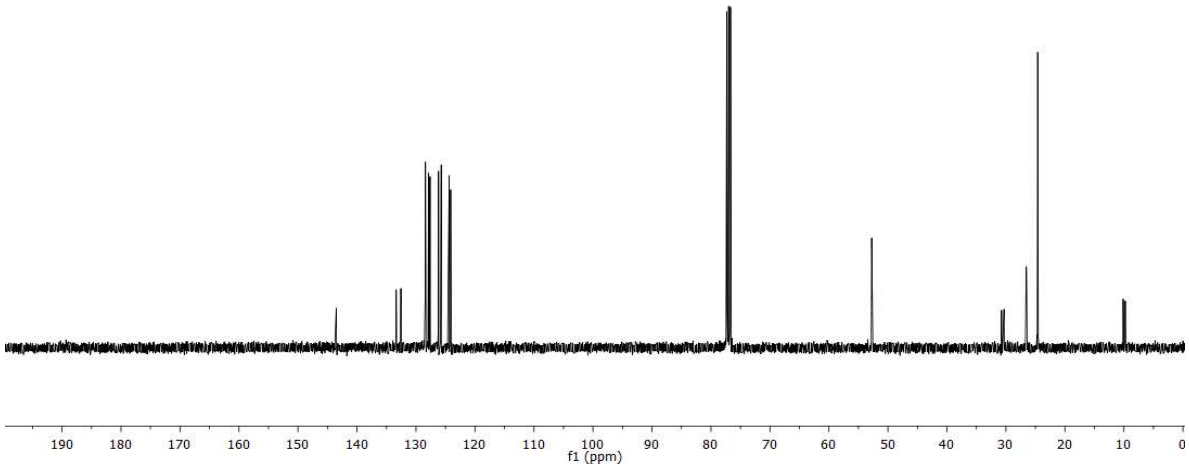
^{1}H NMR (400 MHz, $CDCl_3$)



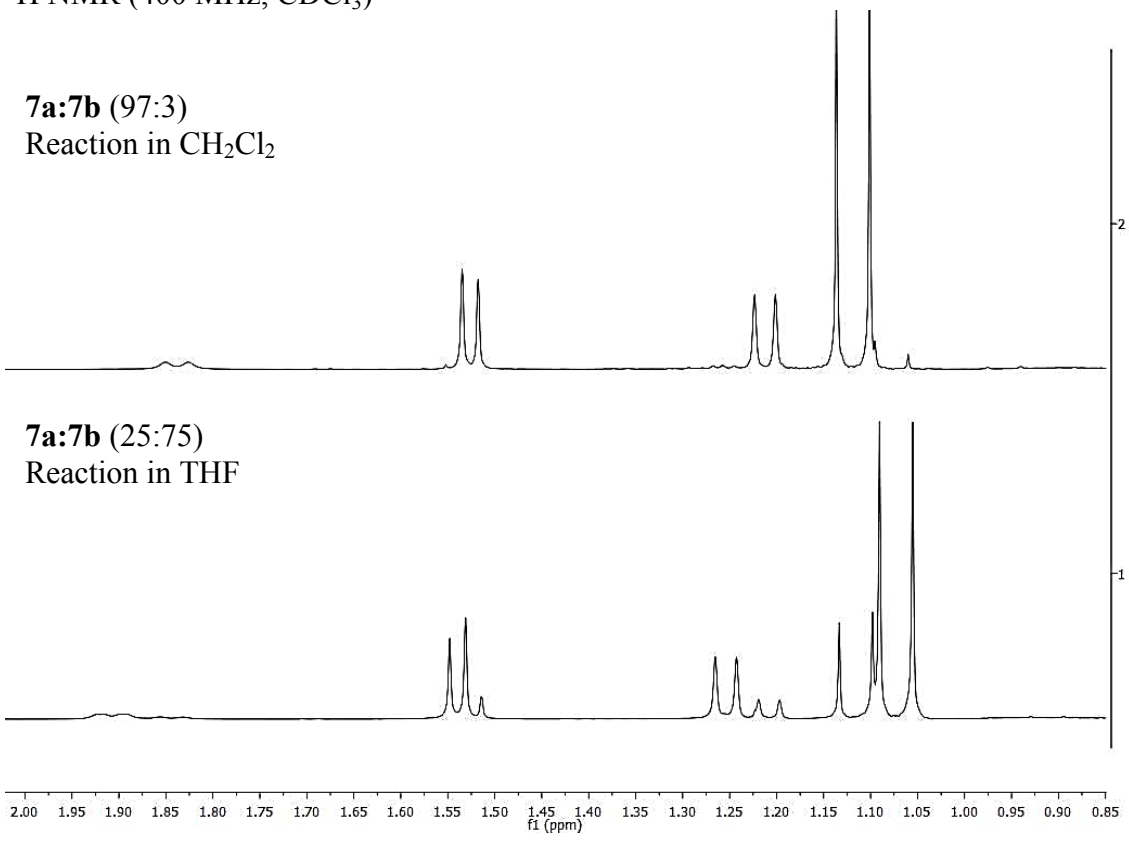
^{1}H NMR (400 MHz, $CDCl_3$)



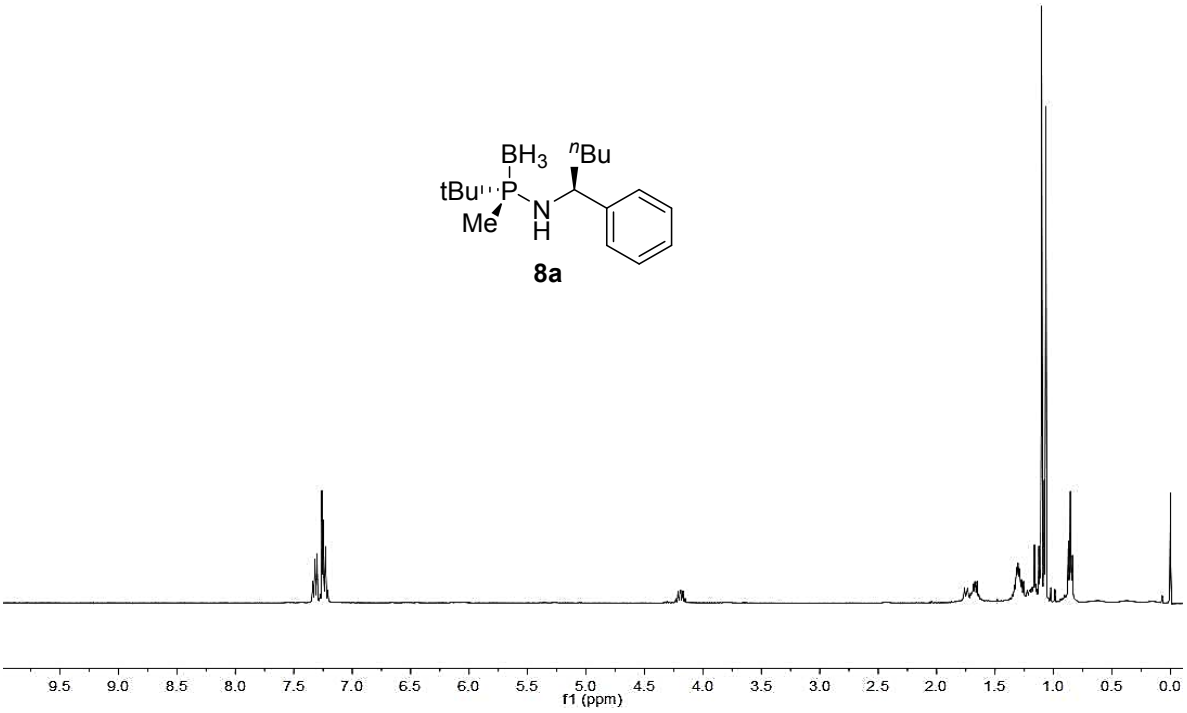
^{13}C NMR (100 MHz, $CDCl_3$)



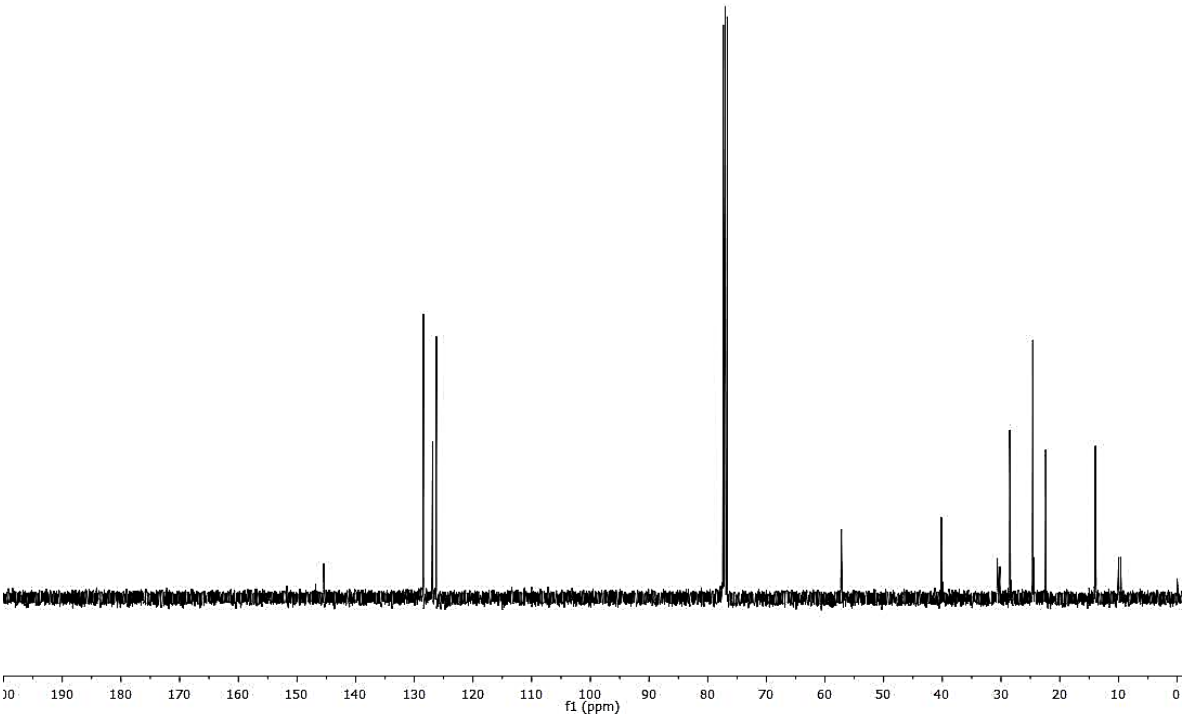
^{1}H NMR (400 MHz, $CDCl_3$)



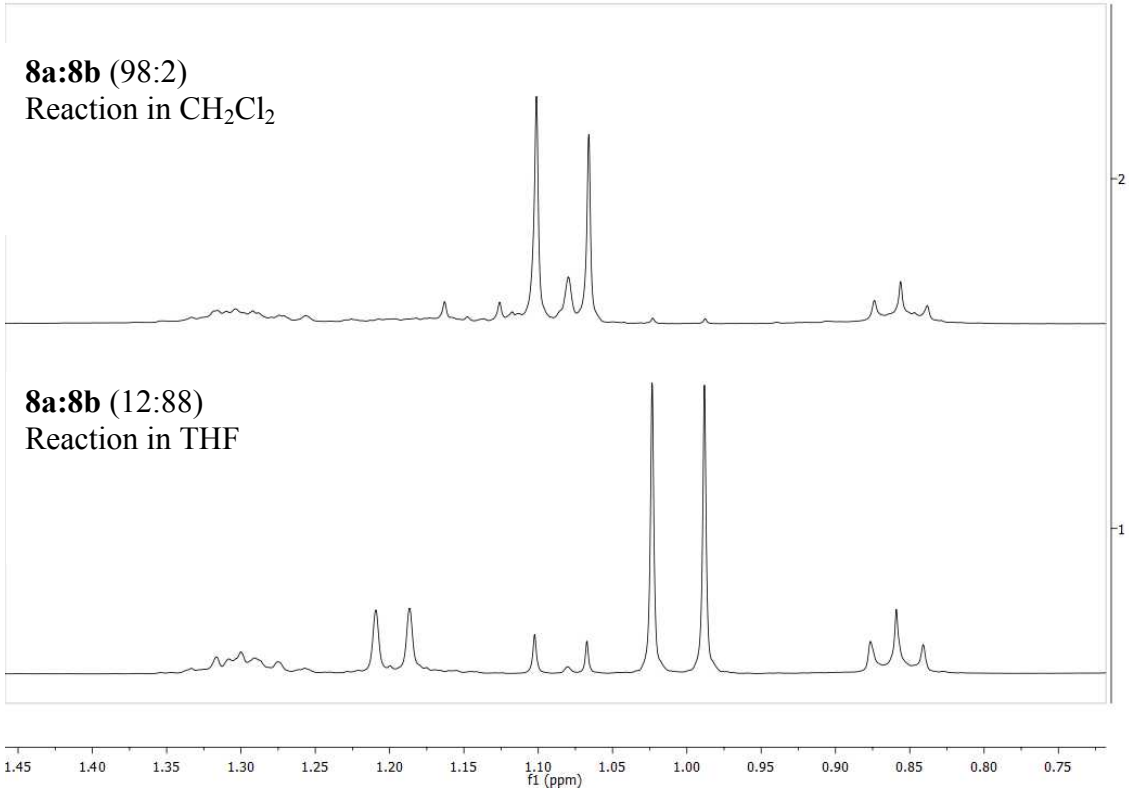
^{1}H NMR (400 MHz, $CDCl_3$)



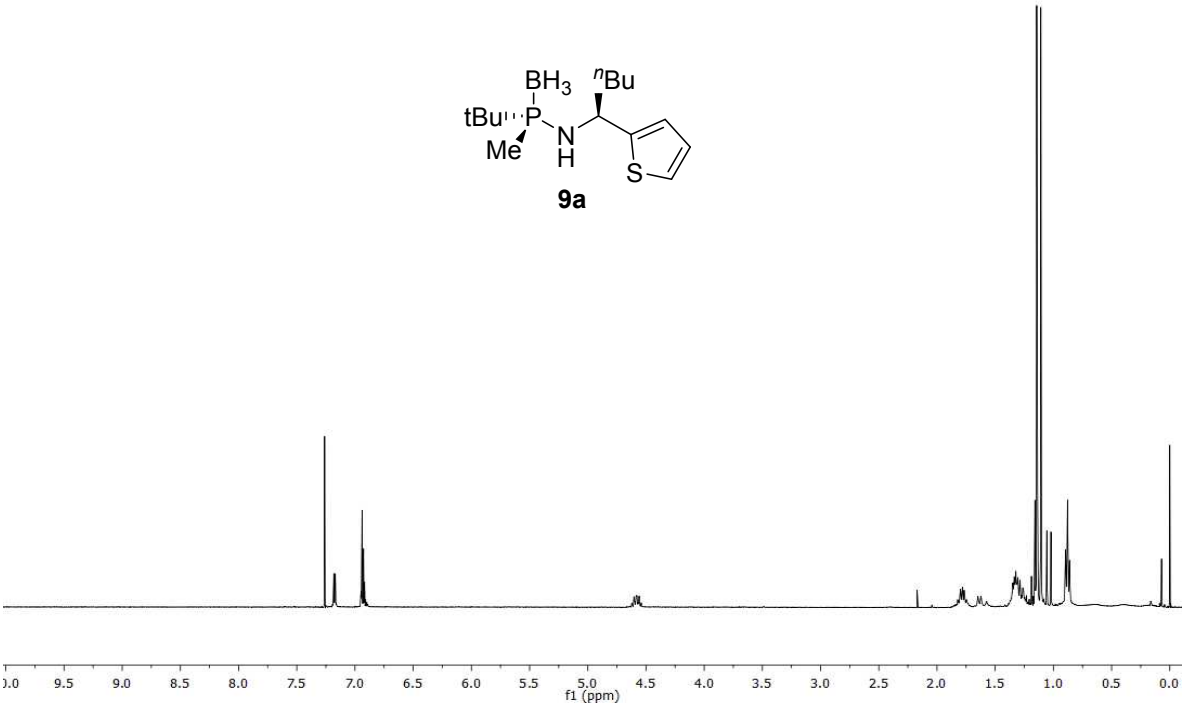
^{13}C NMR (100 MHz, $CDCl_3$)



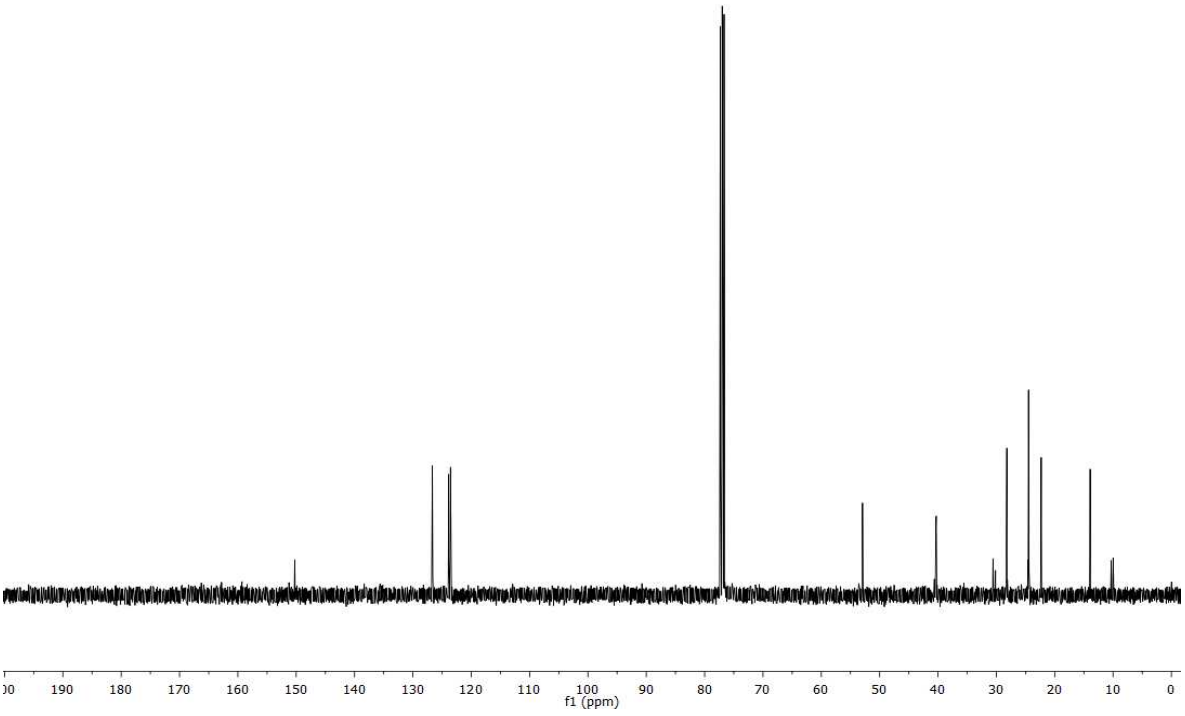
^{1}H NMR (400 MHz, $CDCl_3$)



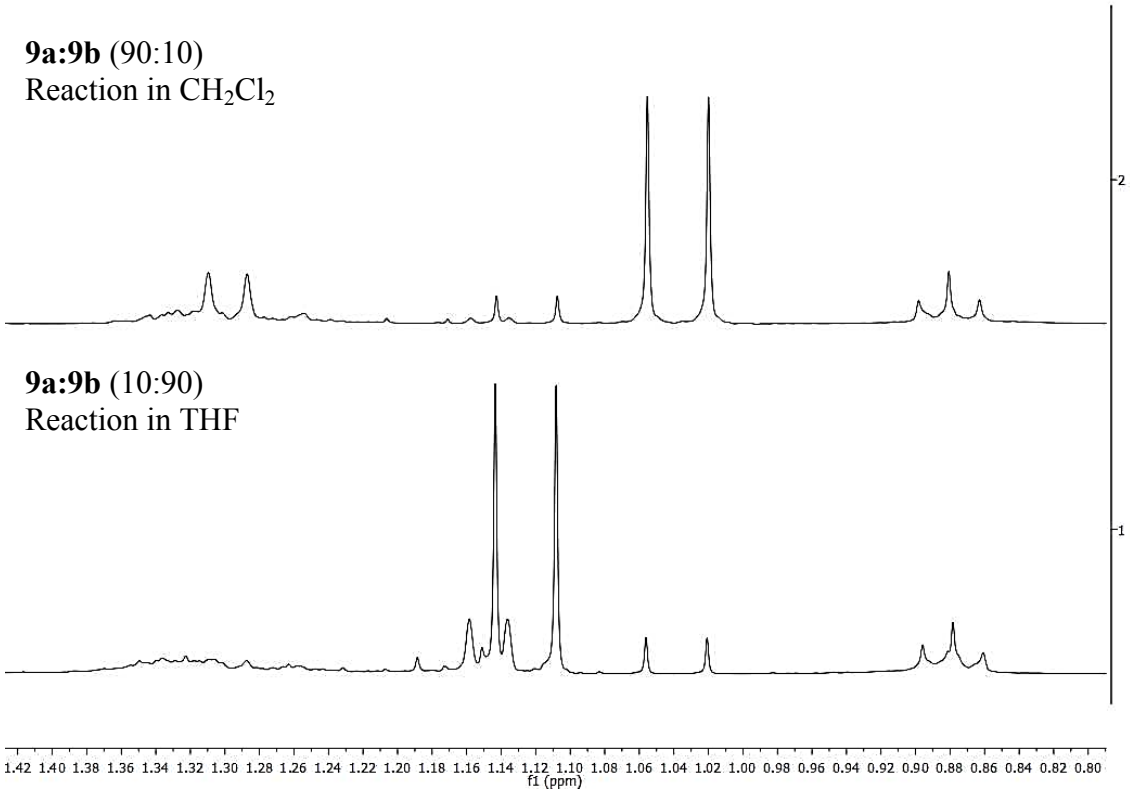
^{1}H NMR (400 MHz, $CDCl_3$)



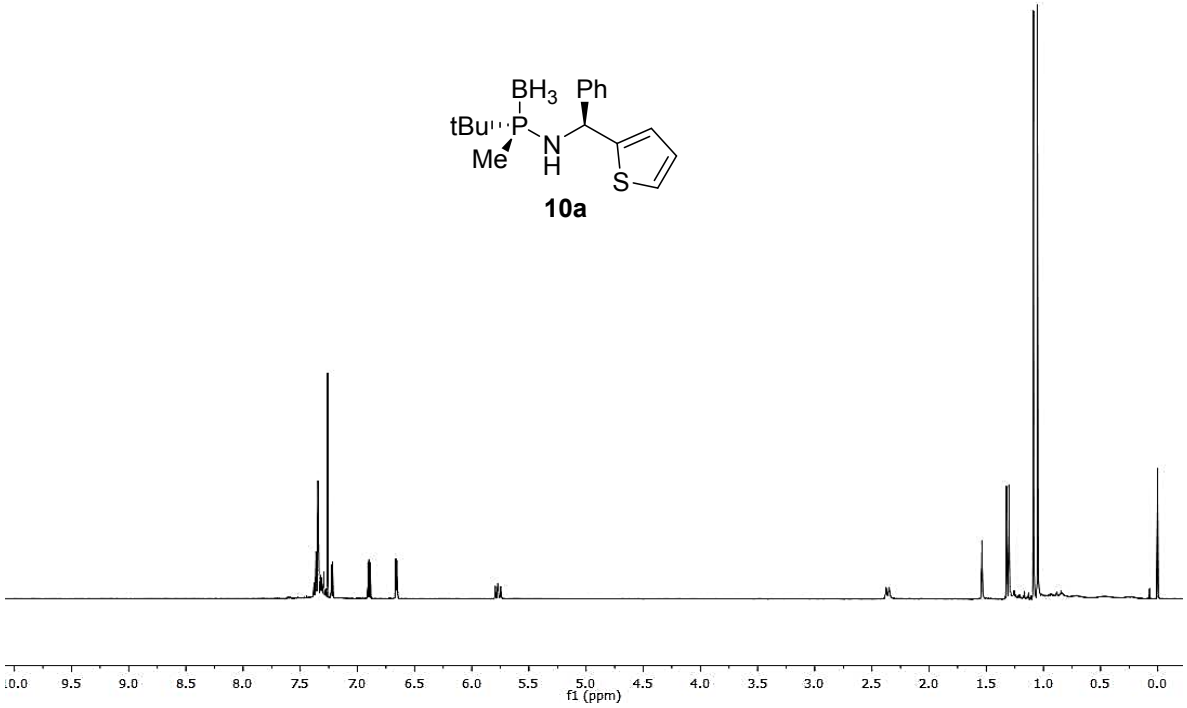
^{13}C NMR (100 MHz, $CDCl_3$)



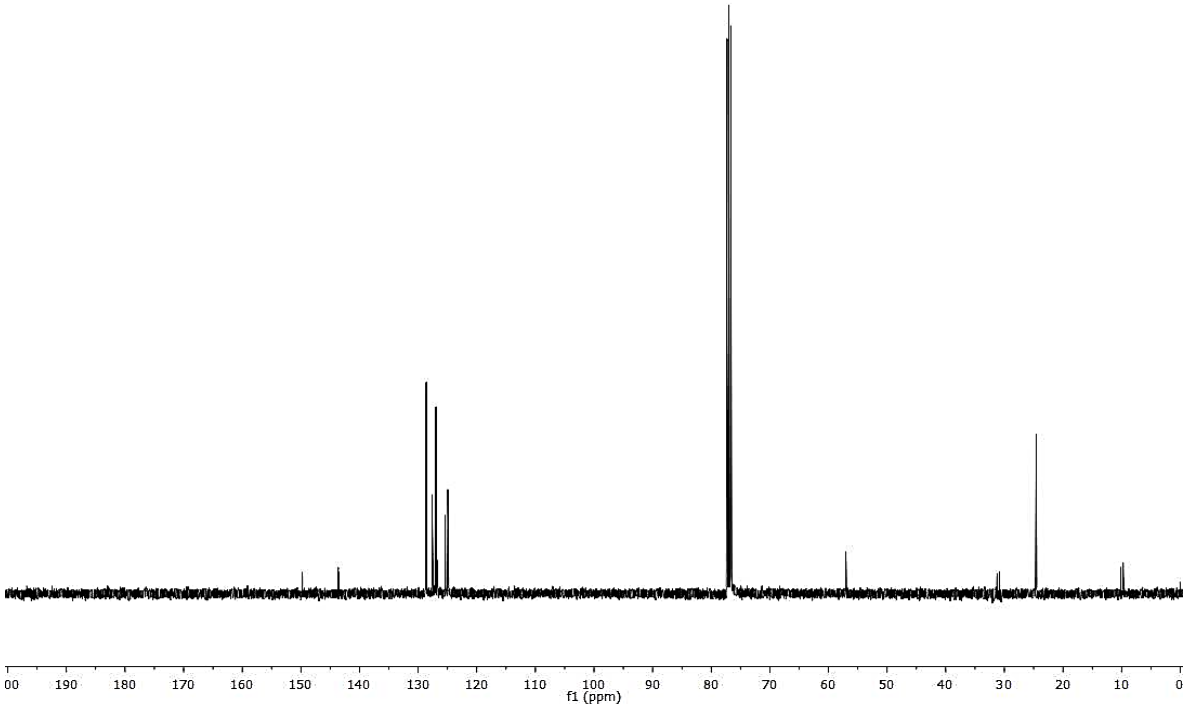
^{1}H NMR (400 MHz, $CDCl_3$)



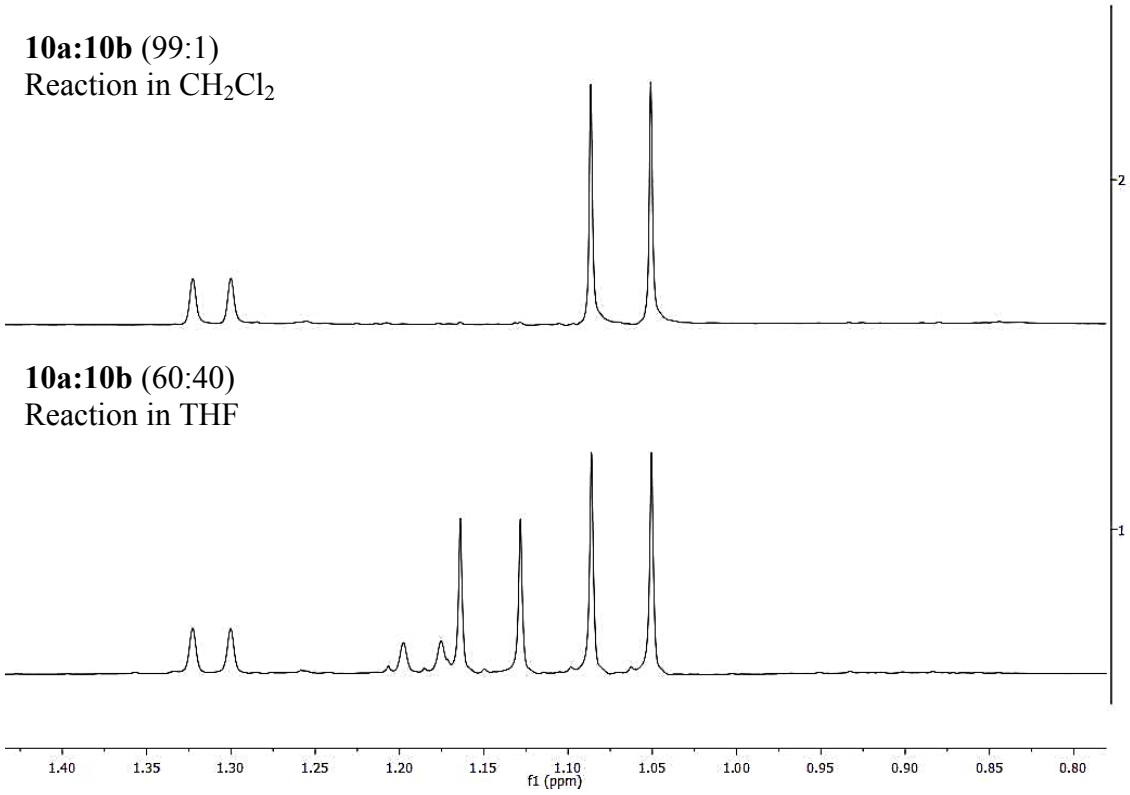
^{1}H NMR (400 MHz, $CDCl_3$)



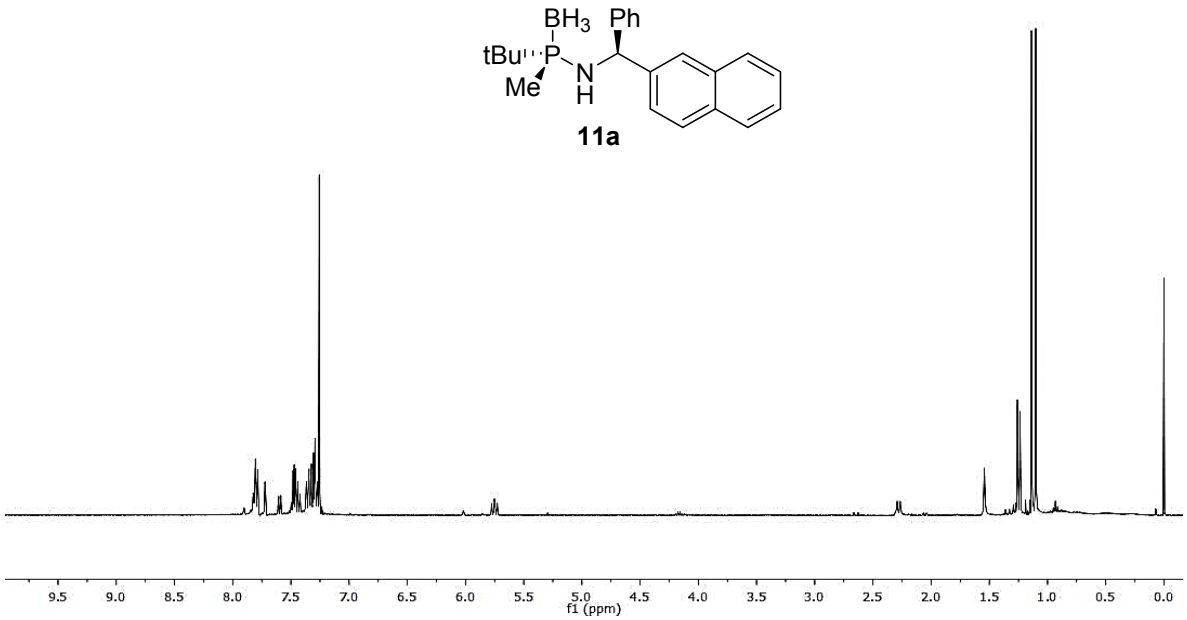
^{13}C NMR (100 MHz, $CDCl_3$)



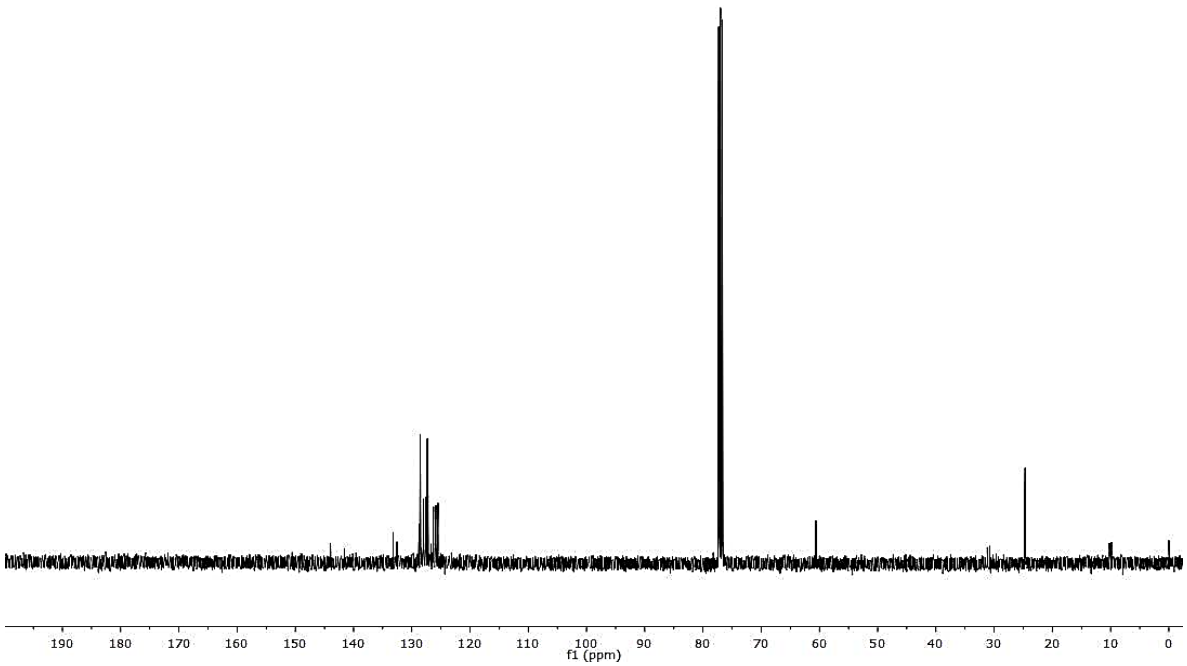
^{1}H NMR (400 MHz, $CDCl_3$)



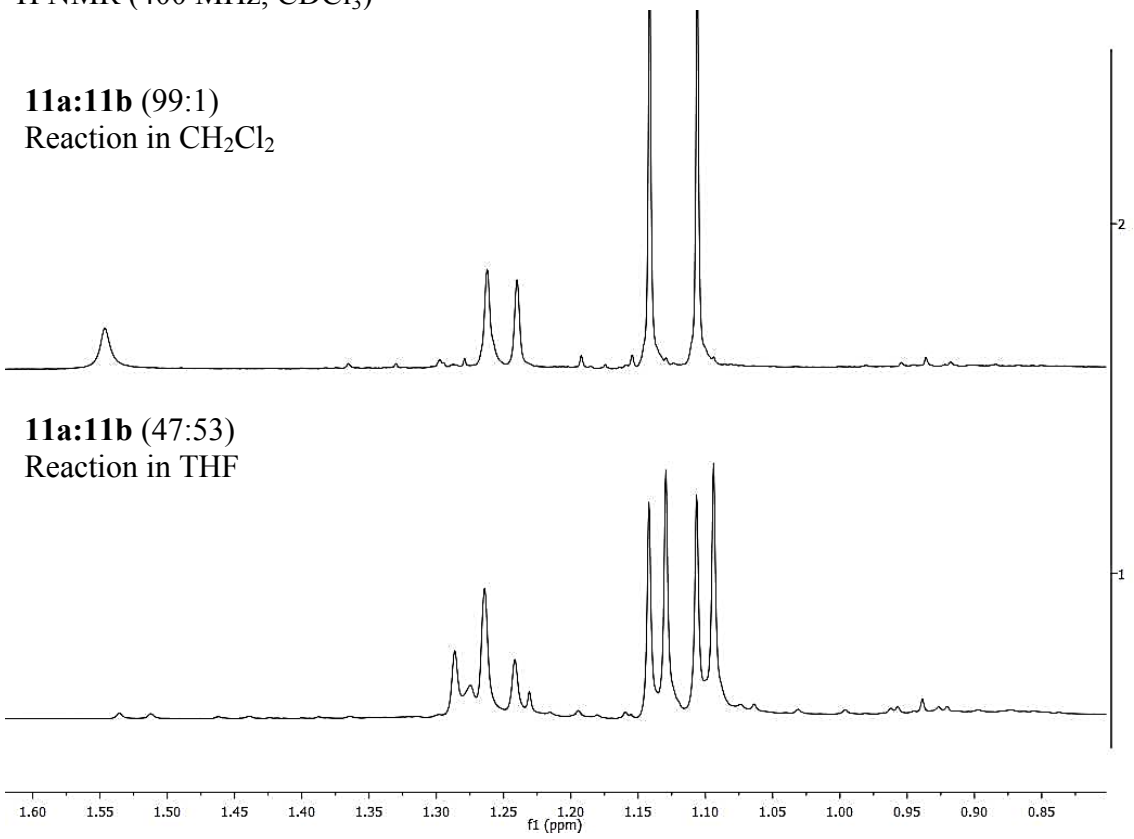
^{1}H NMR (400 MHz, $CDCl_3$)



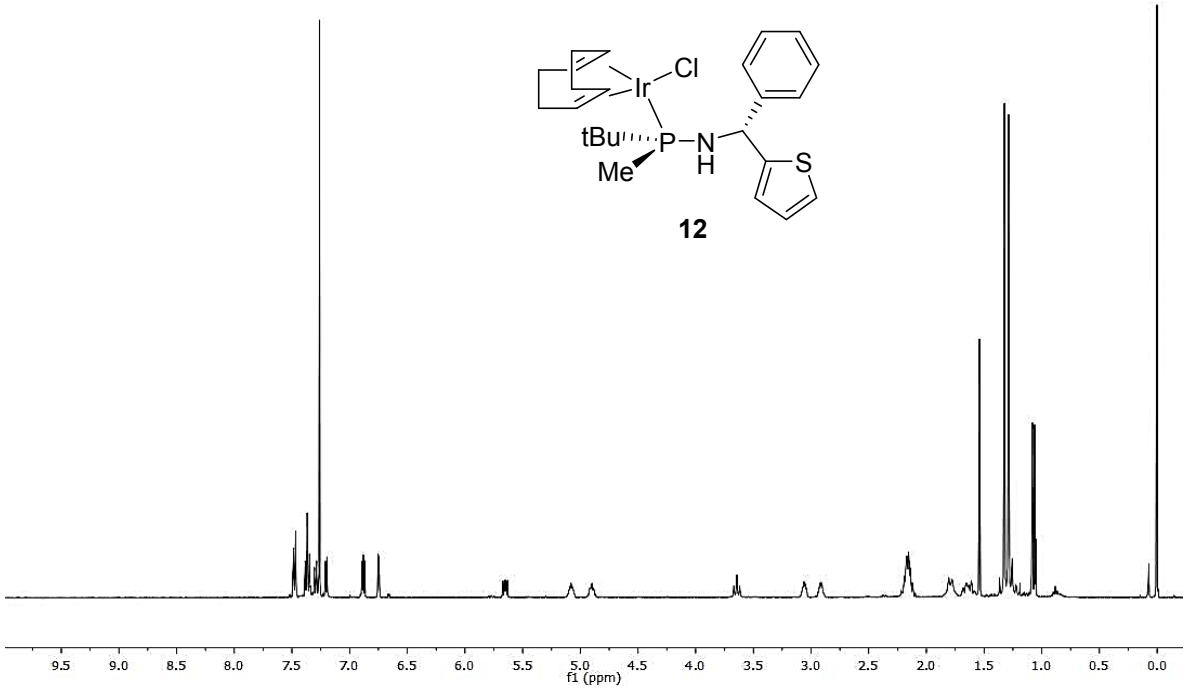
^{13}C NMR (100 MHz, $CDCl_3$)



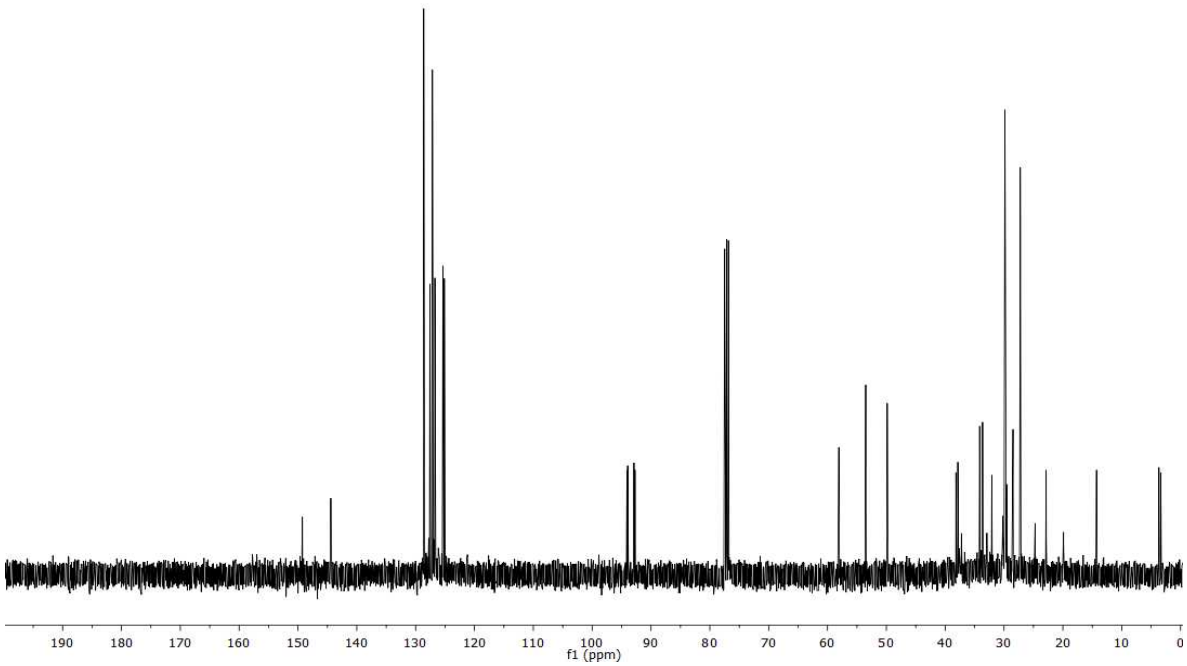
^{1}H NMR (400 MHz, $CDCl_3$)



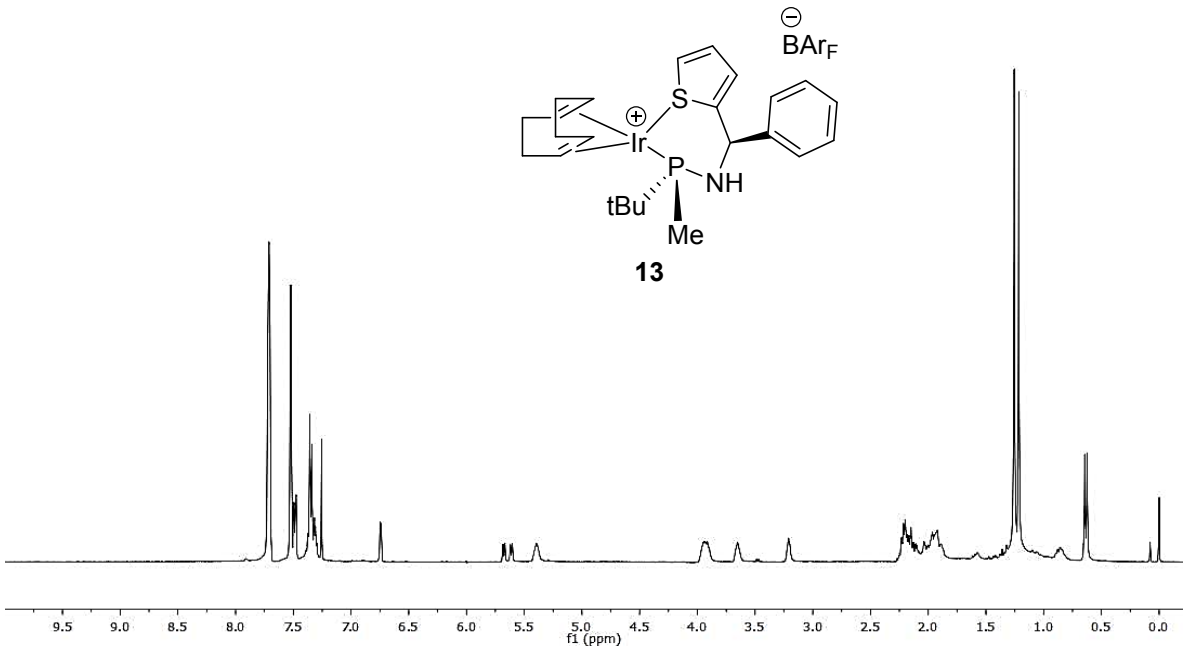
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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



^{13}C NMR (100 MHz, $CDCl_3$)