Electronic Supplementary Information

Rhodium-Catalyzed Regioselective Hydroaminomethylation of Terminal Olefins with Pyrrole-based Tetraphosphorus Ligands

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Contents

I. General Instrument

All reactions and manipulations were performed in a nitrogen-filled glove box or using standard Schlenk techniques, unless otherwise noted. Anhydrous solvents were purchased from EMD chemicals Inc. $Rh(acac)(CO)_2$ was purchased from Strem chemicals. All reagents were purchased from either Aldrich or VWR and were used without further purification. All olefins, amines and catalysts were stored in the nitrogen-filled glove box before using. Tetrabi was prepared according to the literature procedure. (Yu, Shichao; Zhang, Xiaowei; Yan, Yongjun; Cai, Chaoxian; Dai, Liyan; Zhang, Xumu. *Chem. Eur. J.* **2010**, *16*, 4938-4943.). ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Mercury 400 MHz FT-NMR spectrometer. All chemical shifts were reported in ppm. A positive ion mass spectrum of sample was acquired on a Thermo LTQ-FT mass spectrometer with an electrospray ionization source. Gas chromatography (GC) was performed on an Agilent 7890 series system using a *β*-Dex 225 column from Supelco (30m × 0.25mm ID).

II. General Methods

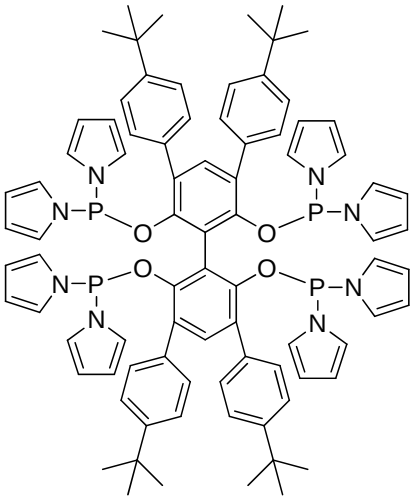
The products were isolated from the reaction mixture by solvent evaporation and further purified using column chromatography on 200-400 mesh silica gel supplied by Sorbent technologies. All yields reported refer to GC using 2-methoxyethyl ether as an internal standard. The purity of isolated compound was confirmed >98% by GC and NMR. The linear to branched ratios were determined by GC analysis of the crude reaction mixtures prior to flash chromatography. Compounds known in the literature were characterized by comparing their ^{1}H NMR, ^{13}C NMR data to the previously reported data. New products were further characterized by HRMS.

III. General Procedure for the Regioselective Hydroaminomethylation

All hydroaminomethylation experiments were performed in the nitrogen-filled glove box. In a typical experiment, a 10-mL long neck vial with a magnetic stirring bar was charged with ligand (4 μmol, 3.5 mg) and $Rh(acac)(CO)_2$ (1 μmol, 0.1 mL of 10 mmol solution in toluene), which was stirred for 10 min. 1-Hexene (1 mmol, 0.125 mL) and piperidine (1 mmol, 0.098 mL) was then added, followed by 2-methoxyethyl ether (0.1 mL), which was internal standard, and 2-propanol (3 mL). The reaction mixture was transfered to an autoclave after the vial was covered with a simple lid. The autoclave was purged with H_2 three times and subsequently charged with CO (5 bar) and H_2 (35 bar). The reaction was carried out at 125 ℃ for 6 h, then the autoclave was cooled to room temperature and depressurized carefully in a well-ventilated hood. The reaction mixture was immediately analyzed by GC to determine the conversion and regioselectivity.

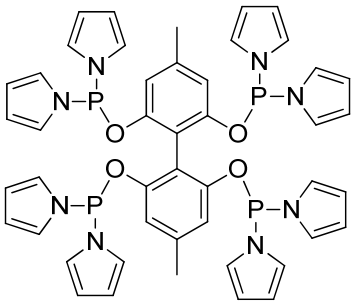
IV. NMR Data of New Pyrrole-based Ligands

Ligand L1



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18 (d, *J* = 8.3 Hz, 4H), 7.09 (d, *J* = 8.2 Hz, 8H), 6.46 (s, 16H), 6.04 (t, *J* = 1.8 Hz, 16H), 1.34 (s, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.25, 135.11, 133.79, 129.21, 125.29, 120.79, 111.66, 34.56, 31.36; ^{31}P NMR (161 MHz, $CDCl_3$) δ = 105.6. HRMS (ES^+) calcd for $C_{84}H_{87}N_8O_4P_4^+$ $[M+H]^+$ 1395.5795, found 1395.5798.

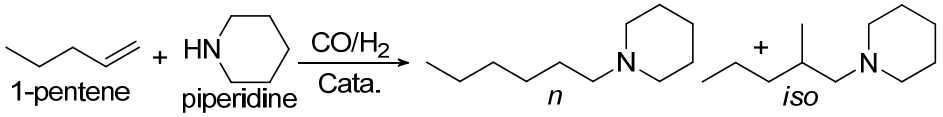
Ligand L2



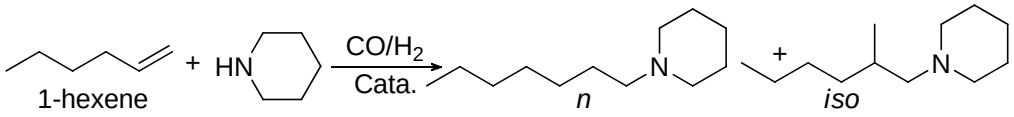
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.65 (s, 16H), 6.41 (s, 4H), 6.20 (t, *J* = 2.0 Hz, 16H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.26, 141.32, 121.12, 116.02, 115.90, 112.22, 21.37; ^{31}P NMR (161 MHz, $CDCl_3$) δ = 107.9. HRMS (ES^+) calcd for $C_{46}H_{43}N_8O_4P_4^+$ $[M+H]^+$ 895.2352, found 895.2347.

V. GC Analysis Conditions for Determination of Linear to Branch Ratio

All the solvents have been ignored by comparing to their standard GC spectra. All the RF (response factor) of substrate and product to 2-methoxylethyl ether has been calculated by the commercially available or isolated standard chemicals.

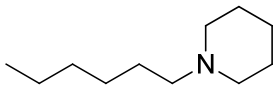


GC: *β*-Dex 225, 70 ℃ for 5 min, then 140 ℃ for 45 min (rate: 20 ℃/min), t_{iso} = 11.2 min, t_n = 12.2 min.



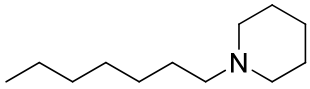
GC: β-Dex 225, 70 ℃ for 5 min, then 140 ℃ for 45 min (rate: 20 ℃/min), t_{iso} = 13.1 min, t_n = 14.8 min.

1-hexylpiperidine



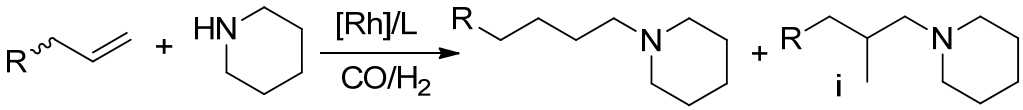
The crude product was purified by flash chromatography (n-hexane/EtOAc = 30:1, yield 98% by GC), clear liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.29 (s, br, 4H), 2.20 (t, J = 7.90 Hz, 2H), 1.51 (quintet, J = 4.05 Hz, 4H), 1.31-1.47 (m, 4H), 1.21 (s, 6H), 0.81 (t, J = 6.72 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 58.73, 53.68, 30.85, 26.48, 25.96, 25.02, 23.54, 21.62, 13.03.

1-heptylpiperidine



The crude product was purified by flash chromatography (n-hexane/EtOAc = 30:1, yield 98% by GC), clear liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.29 (s, br, 4H), 2.19 (t, J = 7.92 Hz, 2H), 1.51 (quintet, J = 5.63 Hz, 4H), 1.30-1.48 (m, 4H), 1.20 (s, 8H), 0.81 (t, J = 6.90 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 58.73, 53.69, 30.82, 28.29, 26.76, 26.00, 24.98, 23.55, 21.62, 13.06.

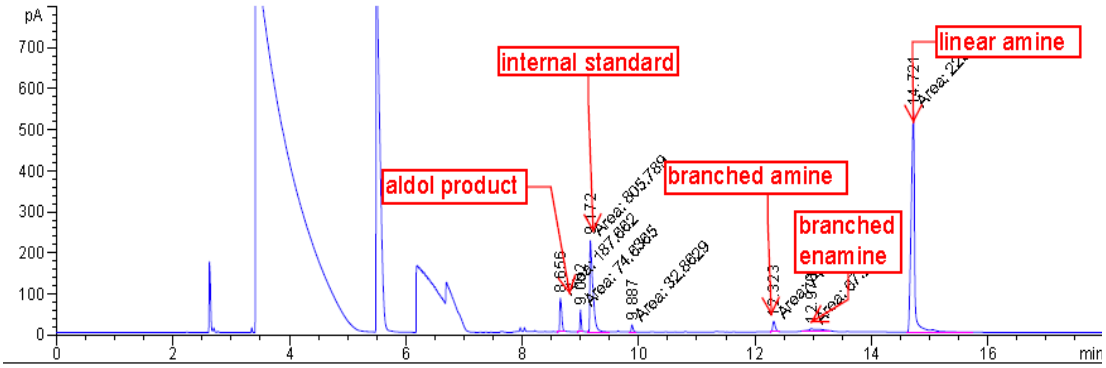
VI. Representative Gas Chromatogram Spectrum



Crude reaction mixture, Table 1, Entry 15:

Reaction conditions: 1 μmol $Rh(acac)(CO)_2$ and 4 μmol **L3** ligand, 1 mmol 1-hexene, 1 mmol piperidine, 0.1 mL 2-methoxylethyl ether, 3 mL 2-PrOH; CO/H_2 = 5/35 bar, 125 ℃, 8 h.

GC analysis conditions: β-Dex 225, 65 ℃, 5 min, 20 ℃/min, 130℃, 20 min.

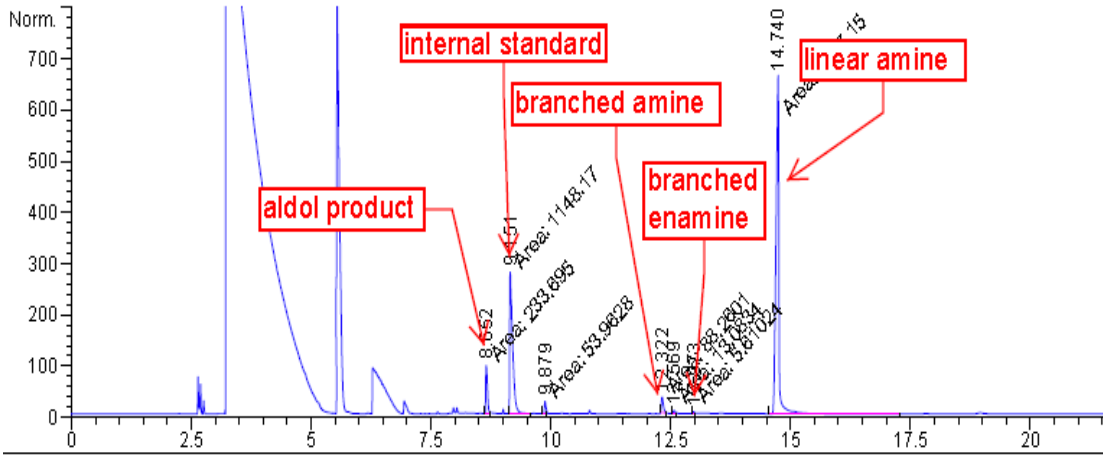


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.656	MM	0.0381	187.66183	81.99955	5.37167
2	9.002	MM	0.0235	74.63646	52.99867	2.13641
3	9.172	MM	0.0597	805.78912	224.83630	23.06509
4	9.887	MM	0.0327	32.86289	16.74984	0.94067
5	12.323	MM	0.0503	74.80370	24.79881	2.14120
6	12.970	MM	0.1955	67.26746	5.73546	1.92548
7	14.721	MM	0.0694	2250.52295	540.19672	64.41947
Totals :				3493.54441	947.31534	

Crude reaction mixture, Table 2, Entry 3:

Reaction conditions: 1 μmol Rh(acac)$(CO)_2$ and 4 μmol **L5** ligand, 1 mmol 1-hexene, 1 mmol piperidine, 0.1 mL 2-methoxylethyl ether, 3 mL 2-PrOH; CO/H_2 = 5/35 bar, 125 ℃, 8 h.

GC analysis conditions: *β*-Dex 225, 65 °C, 5 min, 20 ℃/min, 130 ℃, 20 min.



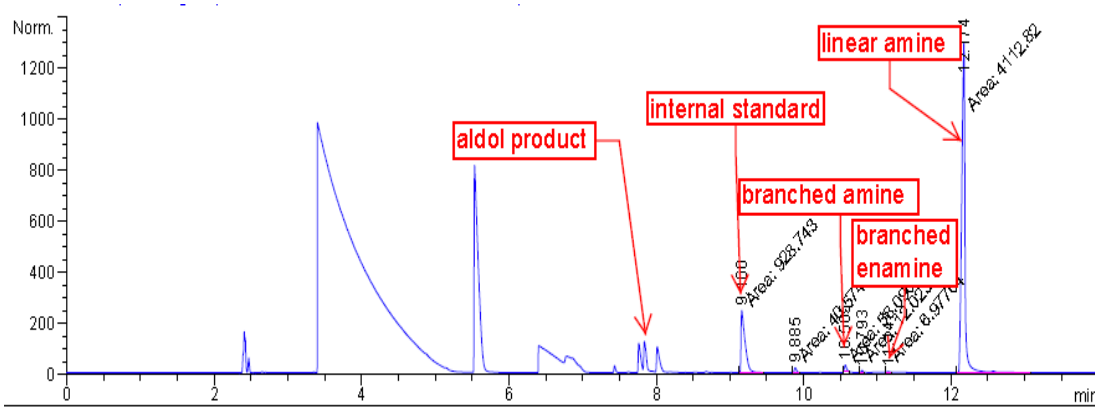
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.652	MM	0.0418	233.69470	93.26238	5.27535
2	9.151	MM	0.0692	1148.17493	276.51462	25.91855
3	9.879	MM	0.0369	53.96277	24.39432	1.21814
4	12.322	MM	0.0487	88.26006	30.19220	1.99236
5	12.569	MM	0.0429	13.08341	5.08403	0.29534
6	12.973	MM	0.0332	5.61024	2.81773	0.12664
7	14.740	MM	0.0728	2887.14941	661.23798	65.17362
Totals :				4429.93552	1093.50326	

Crude reaction mixture, Table 3, Entry 3:

Reaction conditions: 1 μmol Rh(acac)$(CO)_2$ and 4 μmol **L5** ligand, 1 mmol 1-pentene, 1 mmol piperidine, 0.1 mL 2-methoxylethyl ether, 3 mL 2-PrOH;

CO/H_2 = 5/35 bar, 125 ℃, 8 h.

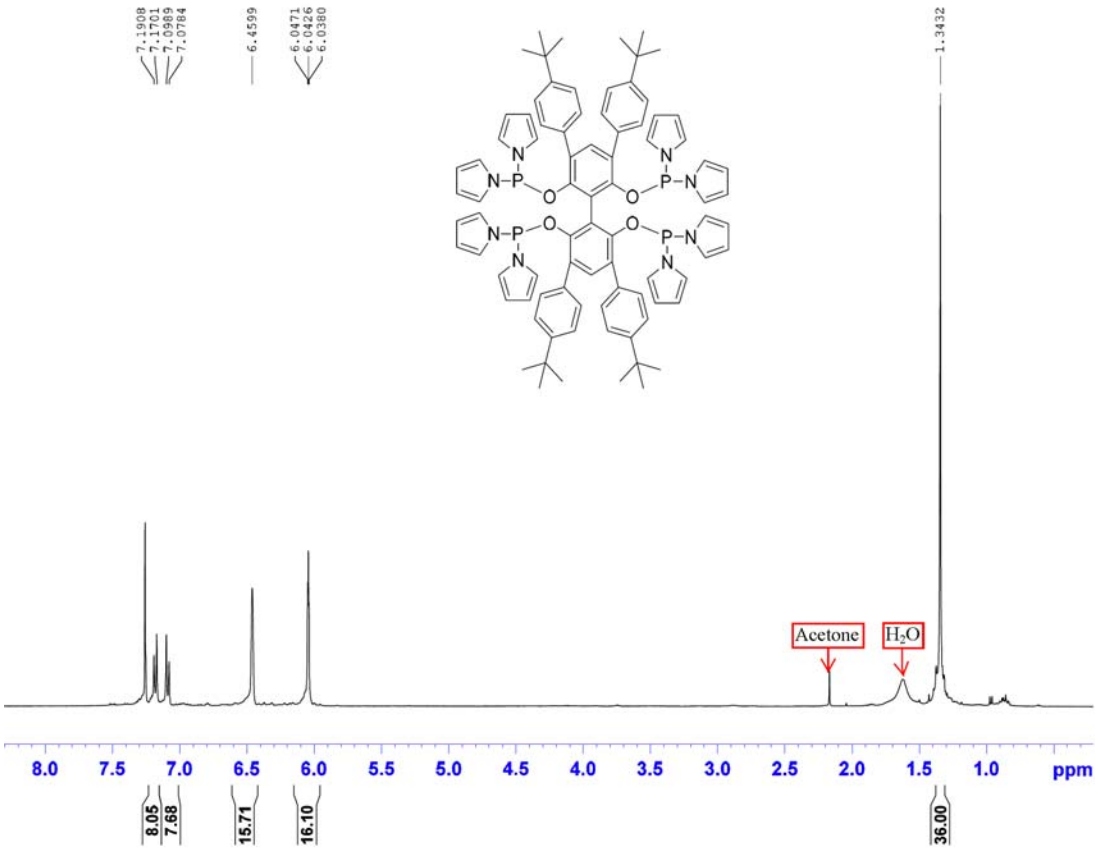
GC analysis conditions: β-Dex 225, 65 ℃, 5 min, 20 ℃/min, 130 ℃, 20 min.



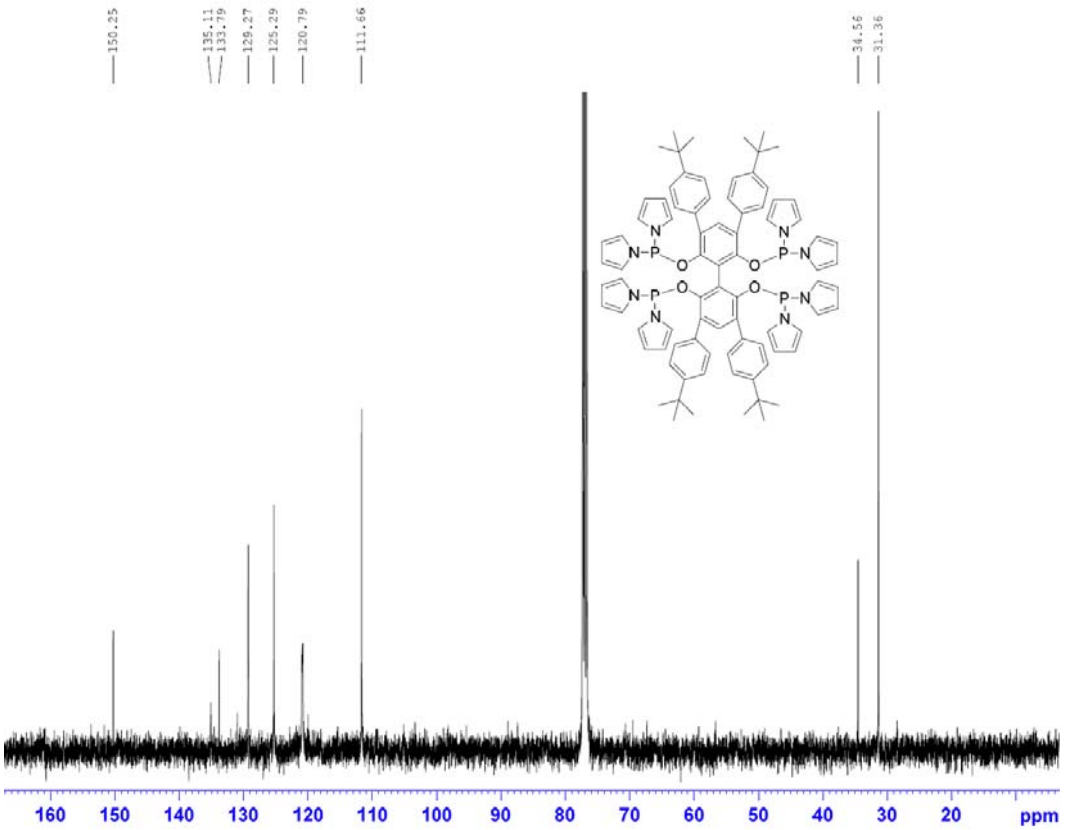
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	9.160	MM	0.0634	928.74286	244.33740	18.00160
2	9.885	MM	0.0353	40.57473	19.13181	0.78645
3	10.565	MM	0.0367	58.09059	26.40832	1.12596
4	10.793	MM	0.0247	12.02297	8.12722	0.23304
5	11.147	MM	0.0390	6.97704	2.98270	0.13523
6	12.174	MM	0.0527	4112.81592	1300.03821	79.71772
Totals :				5159.22411	1601.02565	

VII. NMR Spectrum

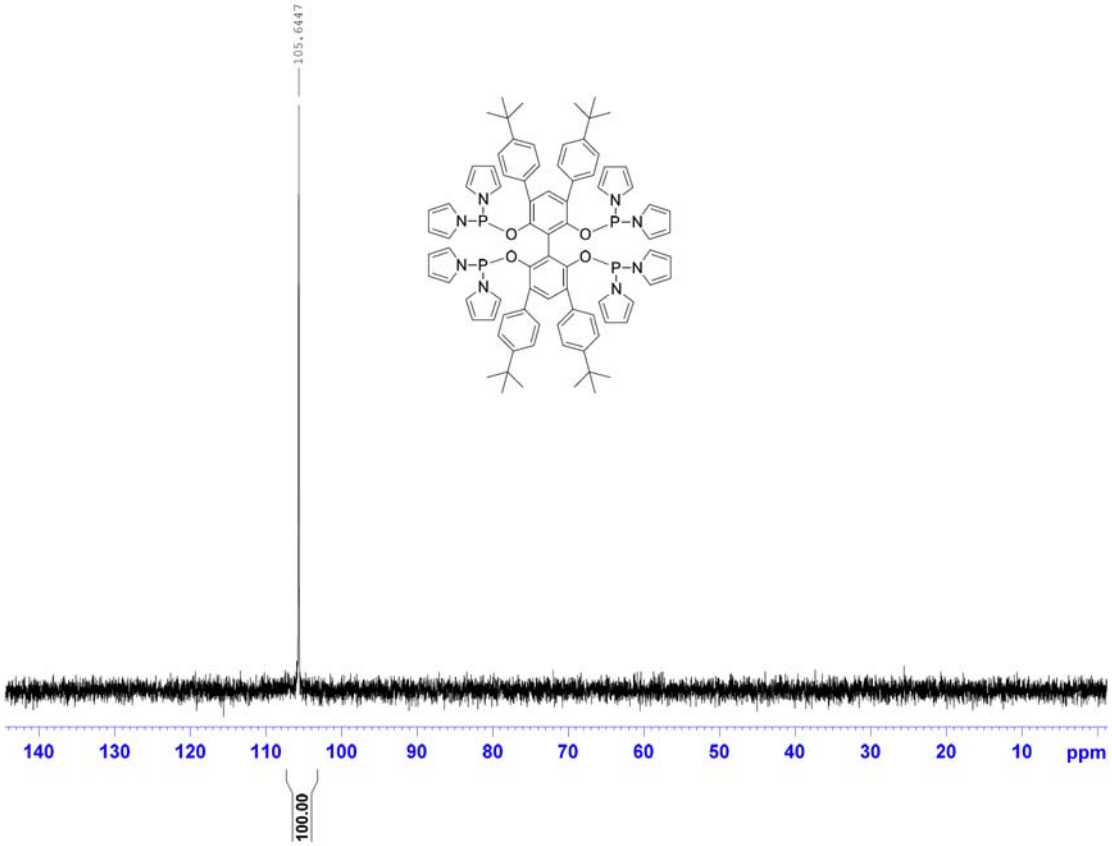
^{1}H NMR of Ligand L1



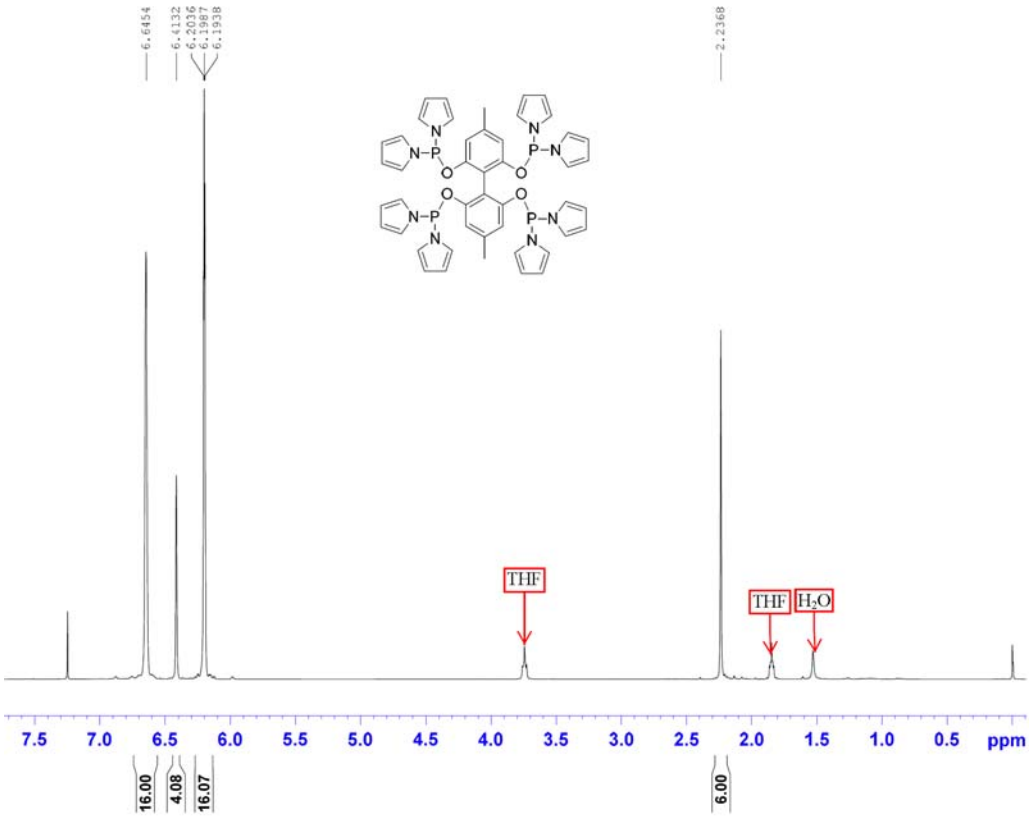
^{13}C NMR of Ligand L1



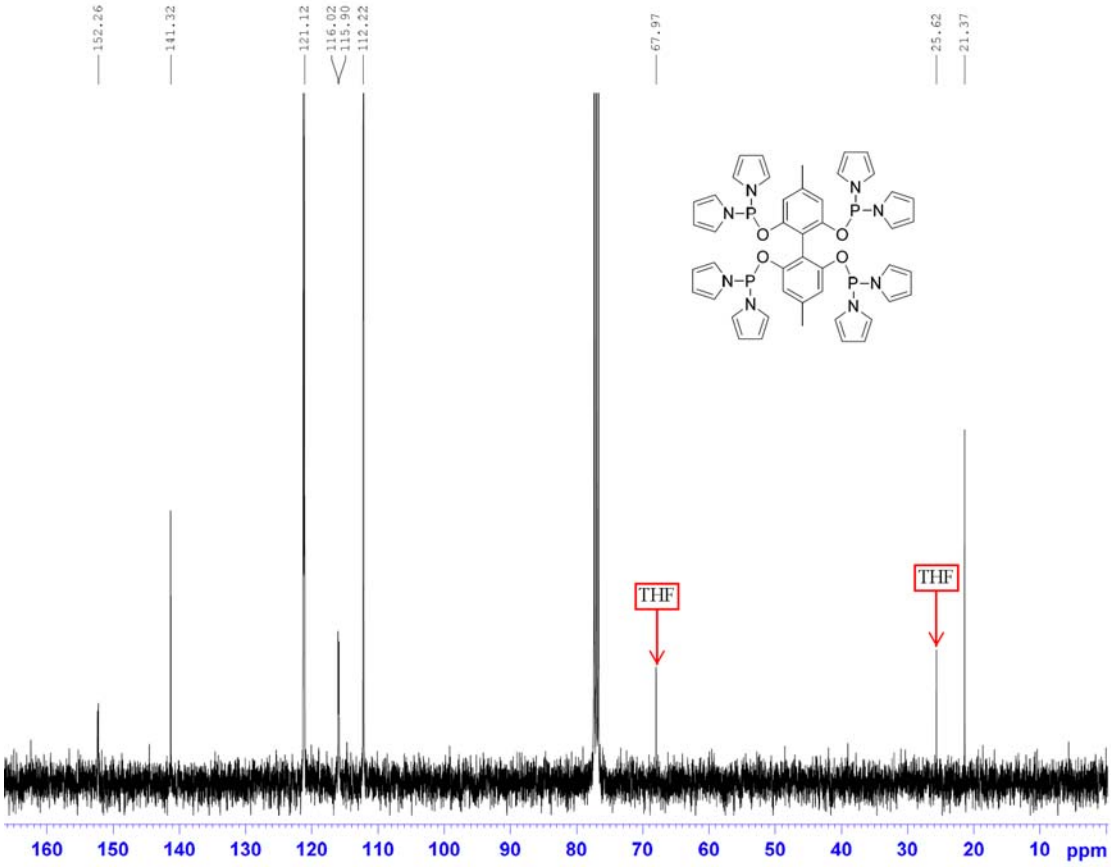
^{31}P NMR of Ligand L1



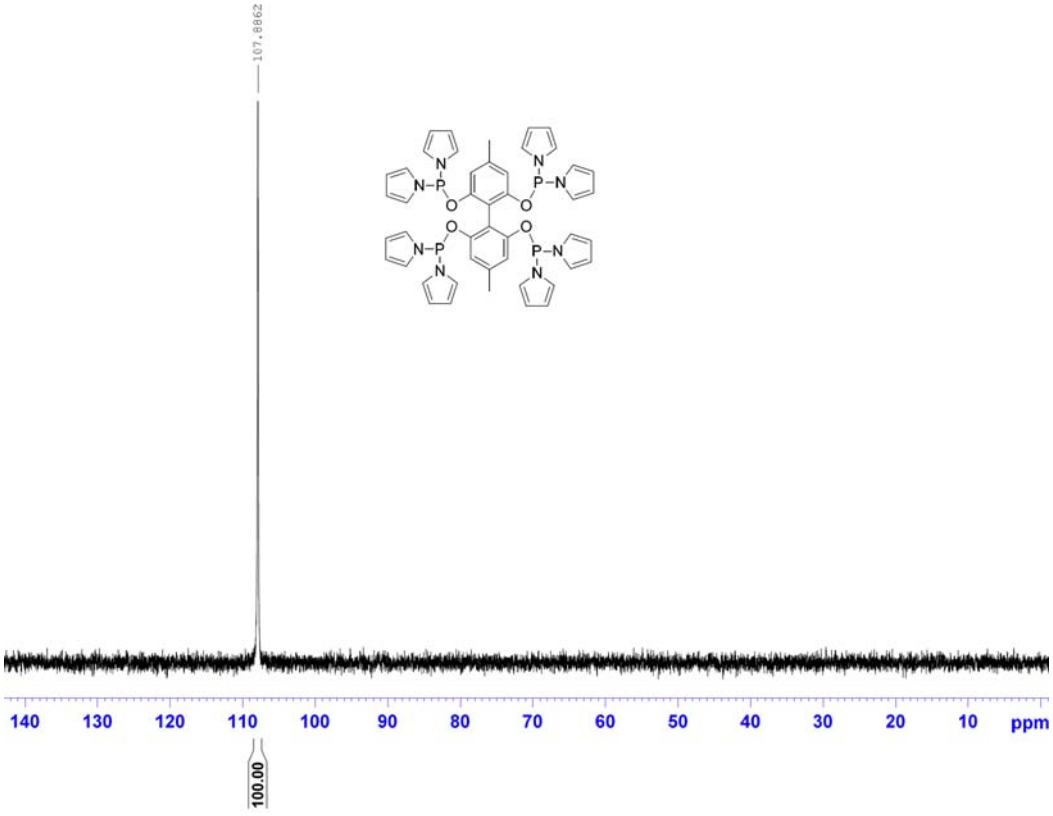
^{1}H NMR of Ligand L2



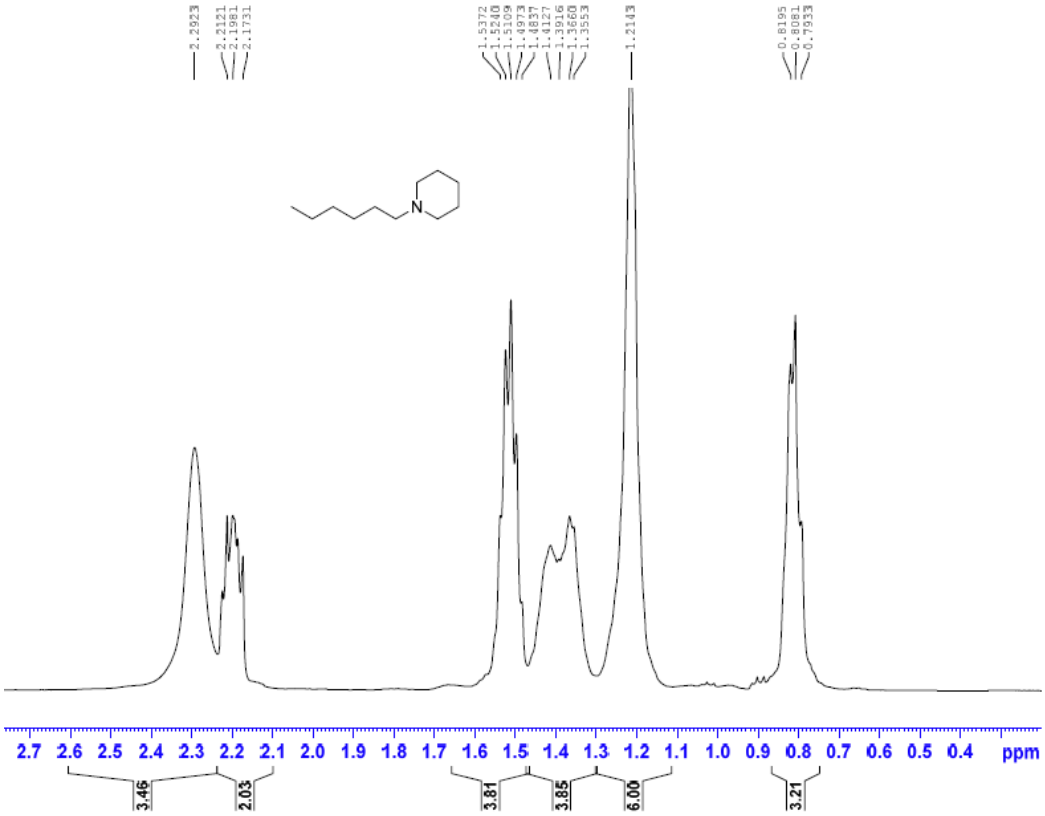
^{13}C NMR of Ligand L2



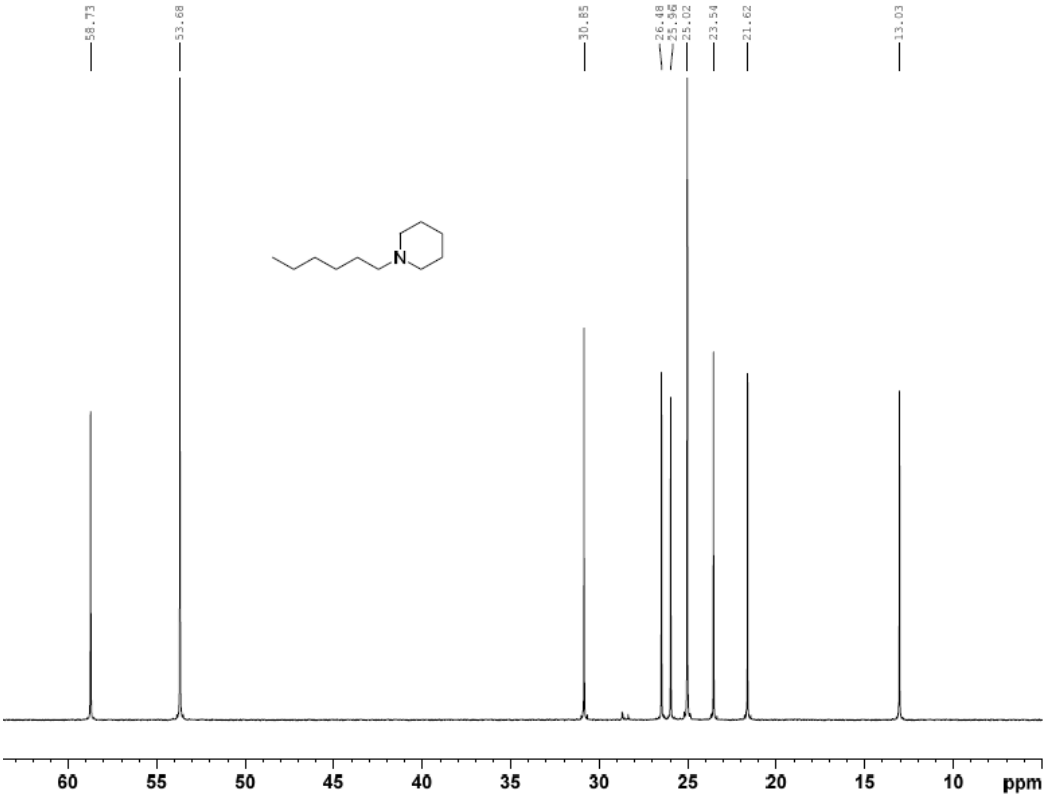
^{31}P NMR of Ligand L2



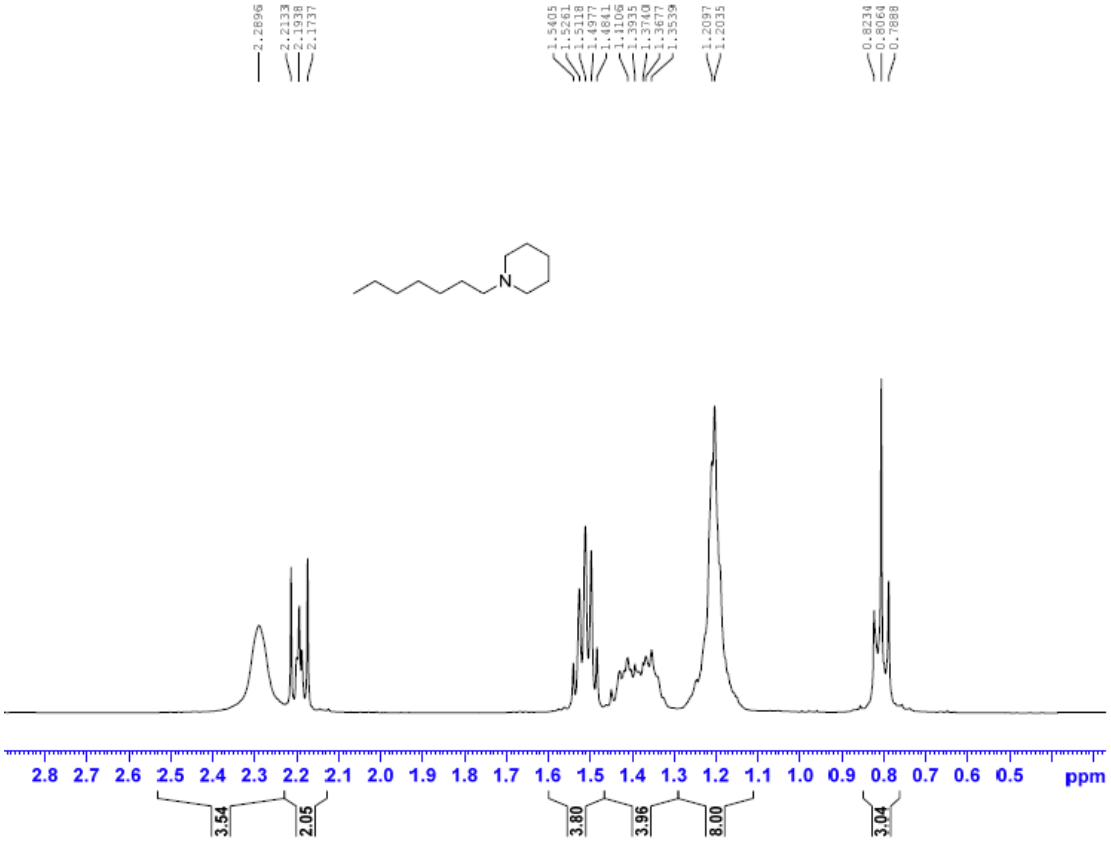
^{1}H NMR of 1-hexylpiperidine



^{13}C NMR of 1-hexylpiperidine



^{1}H NMR of 1-heptylpiperidine



^{13}C NMR of 1-heptylpiperidine