Supporting Information

Chromium Catalysts Based on Unsymmetrical PNP Ligands for Selective Ethylene Tri-/Tetramerization: Effect of Electron-Withdrawing/Donating Substituents on Catalytic Performance

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1. Experimental

1.1 General information

All the anhydrous and oxygen-free operations involved in the experiment were carried out in an N_2 atmosphere using a glove box. All solvents used in the synthesis of ligands are soaked in an activated 4Å molecular sieve for more than four days or subjected to distillation treatment and then passed through the solvent drying system (containing alumina or molecular sieve purification column) to remove water and oxygen. Other reagents were used directly without further treatment. NMR spectra were recorded by Bruker AscendIII−400 (400 MHz for ^{1}H, 162 MHz for ^{31}P, and 101 MHz for ^{13}C in $CDCl_3$) at 300K. The hydrogen spectrum and carbon spectrum are based on the non-aqueous solvent tetramethylsilane (TMS), and the phosphine spectrum is based on 85% phosphoric acid (H_3PO_4). Lithium salts of diphenylphosphanamine were prepared by simple lithiation of the corresponding diphenylphosphanamine [1].

1.2 Ligand synthesis

The L1-L6 ligands were prepared by the simple salt metathesis method, the detailed synthesis procedure is given below.

N-(bis(4-fluorophenyl)phosphanyl)-N-cyclopentyl-1,1-diphenylphosphanamine（L1）

Lithium cyclopentyl(diphenylphosphaneyl)amide was prepared through the lithiation of the *N*-cyclopentyl-1,1-diphenylphosphanamine [13]. To a solution of lithium cyclopentyl(diphenylphosphaneyl)amide (0.53 g, 1.9 mmol) in n-hexane at

−35°C, the hexane solution (10 mL) of chlorobis(4-fluorophenyl)phosphane (0.50 g, 1.9 mmol) was added under stirring. Stirring was carried out constantly overnight at room temperature and then the reaction mixture was filtered to remove lithium chloride salt. The solution was vacuum dried, washed with n-hexane (3x10 mL) and dried again under vacuum to obtain a yellow oily product. The colorless solid ligand L1 was isolated after recrystallization in hexane at −35 °C in 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.39 (Br, 2H, N-CH-C***H***$_2$), 1.52 (Br, 2H, N-CH-C***H***$_2$), 1.73 (Br, 2H, N-CH-CH_2-C***H***$_2$), 1.87 (Br, 2H, N-CH-CH_2-C***H***$_2$), 3.79 (m, 1H, N-C***H***), 7.01-7.06 (m, 4H, Ph-***H***), 7.29-7.35 (br, 14H, Ph-***H***). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K):δ 24.03, 34.07, 62.57 (Cyclopentyl, 5C); 162.09, 164.58 (-***C***-F, 2C);.115.24, 128.12, 128.75, 132.62, 132.84, 134.62, 135.60, 139.75(-Ph-***C***, 24C) ^{31}P NMR (162 MHz, $CDCl_3$, 298 K): δ 48.45 (Br), 50.07 (Br). Anal. Calcd for $C_{29}H_{27}F_2NP_2$ (found): C, 71.16 (71.34); H, 5.56 (5.72); N, 2.86 (2.69).

N-(bis(4-(trifluoromethyl)phenyl)phosphanyl)-N-cyclopentyl-1,1-diphenylphosphanamine（L2）

The synthesis procedure for L2 was similar to that followed for L1 except that chlorobis(4-(trifluoromethyl)phenyl)phosphine (0.80 g,2.2 mmol) was treated with lithium cyclopentyl(diphenylphosphaneyl)amide (0.61 g,2.2 mmol). The product was obtained as a white solid in 38% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.37 (Br, 2H, N-CH-C***H***$_2$), 1.55 (Br, 2H, N-CH-C***H***$_2$), 1.76 (Br, 2H, N-CH-CH_2-C***H***$_2$), 1.83 (Br, 2H, N-CH-CH_2-C***H***$_2$), 3.78 (m, 1H, N-C***H***), 7.32-7.43 (m, 14H, Ph-***H***), 7.54-7.56 (m, 4H, CF_3--C-C***H***$_2$). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K):δ 24.04, 34.21, 62.97

(Cyclopentyl, 5C); 122.72 (-***C***F_3, 2C);. 124.94, 125.43, 128.26, 129.01, 130.73, 131.05, 132.87, 139.20, 144.33 (-Ph-***C***, 24C).^{31}P NMR (162 MHz, $CDCl_3$, 298 K): δ 48.90-51.56 (d). Anal. Calcd for $C_{31}H_{27}F_6NP_2$ (found): C, 63.16 (63.35); H, 4.62 (4.88); N, 2.38 (2.19).

N-(bis(3,5-bis(trifluoromethyl)phenyl)phosphanyl)-N-cyclopentyl-1,1-diphenylphosphanamine（L3）

The synthesis procedure for L3 was similar to that followed for L1 except that bis(3,5-bis(trifluoromethyl)phenyl)chlorophosphane (0.50 g, 1.0 mmol) was treated with lithium cyclopentyl(diphenylphosphaneyl)amide (0.27 g,1.0 mmol). The product was obtained as a white solid in 32% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.39 (Br, 2H, N-CH-C***H***$_2$), 1.53 (Br, 2H, N-CH-C***H***$_2$), 1.73 (Br, 2H, N-CH-CH_2-C***H***$_2$), 1.85 (Br, 2H, N-CH-CH_2-C***H***$_2$), 3.69 (m, 1H, N-C***H***), 7.35 (m, 10H, Ph-***H***), 7.72 (m, 4H, CF_3--C-C***H-C-P***),7.86 (m, 2H, CF_3--C-C***H-C***-CF_3). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K):δ 23.84, 34.14, 63.11(Cyclopentyl, 5C); 124.47(-***C***F_3, 4C);. 123.07, , 128.55, 129.46, 132.42, 132.64, 142.01, 142.25.(-Ph-***C***, 24C). ^{31}P NMR (162 MHz, $CDCl_3$, 298 K): δ 51.04 (s). Anal. Calcd for $C_{33}H_{25}F_{12}NP_2$ (found): C, 54.63 (54.77); H, 3.47 (3.62); N, 1.93 (1.82).

N-cyclopentyl-N-(di-p-tolylphosphanyl)-1,1-diphenylphosphanamine（L4）

The synthesis procedure for L4 was similar to that followed for L1 except that chlorobis(*p*-tolyl)phosphine (0.50 g, 2.0 mmol) was treated with lithium cyclopentyl(diphenylphosphaneyl)amide (0.55 g, 2.0 mmol). The product was obtained as a white solid in 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.33 (Br,

2H, N-CH-C***H***$_2$), 1.47 (Br, 2H, N-CH-C***H***$_2$), 1.67 (Br, 2H, N-CH-CH$_2$-C***H***$_2$), 1.84 (Br, 2H, N-CH-CH$_2$-C***H***$_2$), 2.35 (s, 6H, -C***H***$_3$), 3.78 (m, 1H, N-C***H***), 7.09-7.11 (m, 8H, CH$_3$-Ph-***H***), 7.25-7.36 (br, 10H, Ph-***H***). ^{13}C NMR (100 MHz, CDCl$_3$, 298 K):δ21.37 (2C, -***C***H$_3$), 24.05, 34.02, 62.60 (Cyclopentyl, 5C); 127.98, 128.49, 128.80, 132.75, 132.97, 136.71, 136.83, 138.43, 140.16, 140.29 (-Ph-***C***, 24C) ^{31}P NMR (162 MHz, CDCl$_3$, 298 K): δ 48.89-49.28 (d). Anal. Calcd for $C_{31}H_{33}NP_2$ (found): C, 77.32 (77.57); H, 6.91 (7.03); N, 2.91 (2.69).

N-(bis(3,5-dimethylphenyl)phosphanyl)-N-cyclopentyl-1,1-diphenylphosphanamine（L5）

The synthesis procedure for L5 was similar to that followed for L1 except that chlorobis(3,5-dimethylphenyl)phosphine (0.50 g, 1.8 mmol) was treated with lithium cyclopentyl(diphenylphosphaneyl)amide (0.49 g, 1.8 mmol). The product was obtained as a white solid in 39% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 1.33 (Br, 2H, N-CH-C***H***$_2$), 1.50 (Br, 2H, N-CH-C***H***$_2$), 1.67 (Br, 2H, N-CH-CH$_2$-C***H***$_2$), 1.84 (Br, 2H, N-CH-CH$_2$-C***H***$_2$), 2.23 (s, 12H, -C***H***$_3$), 3.79 (m, 1H, N-C***H***), 6.94 (s, 6H, (CH$_3$)$_2$-Ph-***H***), 7.30-7.37(m, 10H, Ph-***H***). ^{13}C NMR (100 MHz, CDCl$_3$, 298 K): δ21.34 (4C, -***C***H$_3$), 24.05, 34.05, 62.80 (Cyclopentyl, 5C); 162.09, 164.58 (-***C***-F, 2C); 127.92, 128.46, 130.26, 130.38, 130.60, 132.83, 133.05, 137.40, 139.66, 140.20. (-Ph-***C***, 24C) ^{31}P NMR (162 MHz, CDCl$_3$, 298 K): δ −22.75 (s). Anal. Calcd for $C_{33}H_{37}NP_2$ (found): C, 77.78 (77.92); H, 7.32 (7.89); N, 2.75 (2.56).

N-(bis(3,5-dimethylphenyl)phosphanyl)-N-cyclopentyl-1,1-diphenylphosphana

mine（L6）

The synthesis procedure for L6 was similar to that followed for L1 except that chlorobis(4-methoxyphenyl)phosphine (0.50 g, 1.8 mmol) was treated with lithium cyclopentyl(diphenylphosphaneyl)amide (0.49 g, 1.8 mmol). The product was obtained as a colorless oil in 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.32 (Br, 2H, N-CH-C***H***$_2$), 1.49 (Br, 2H, N-CH-C***H***$_2$), 1.68 (Br, 2H, N-CH-CH_2-C***H***$_2$), 1.83 (Br, 2H, N-CH-CH_2-C***H***$_2$), 3.79 (m, 1H, N-C***H***), 3.82 (s, 6H, O-C***H***$_3$), 6.58-6.87 (Br, 4H, CH_3O-C-C***H-***), 7.26-7.35 (m, 14H, Ph-***H***). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K):δ 24.01, 33.91, 55.19 (Cyclopentyl, 5C); 55.19(-O***C***H_3, 2C); 113.63, 128.01, 128.45, 132.71, 134.34, 140.11(-Ph-***C***, 24C); 160.05(-***C***-OCH_3, 1C) ^{31}P NMR (162 MHz, $CDCl_3$, 298 K): δ 49.17 (s). Anal. Calcd for $C_{31}H_{33}NO_2P_2$ (found): C, 72.50 (72.47); H, 6.48 (6.49); N, 2.73 (2.66).

NMR Spectra of Ligands L1-L6

^{1}H NMR of *N*-(bis(4-fluorophenyl)phosphanyl)-*N*-cyclopentyl-1,1-diphenylphosphanamine

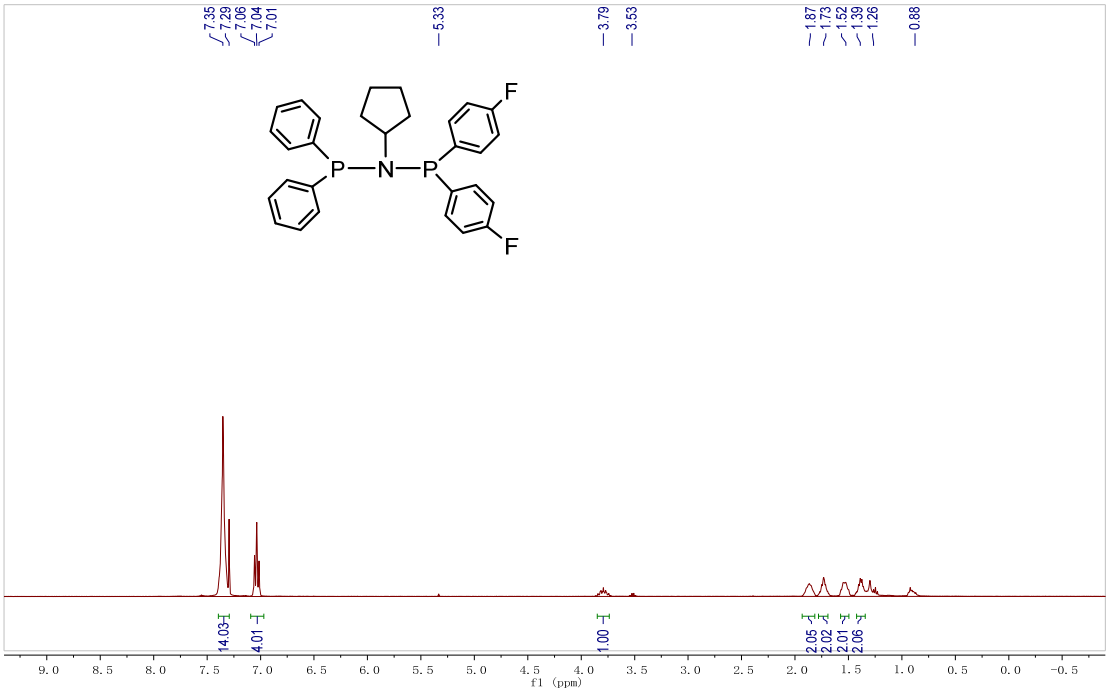

Figure S1. ^{1}H NMR Spectrum of L1

^{31}P NMR of *N*-(bis(4-fluorophenyl)phosphanyl)-*N*-cyclopentyl-1,1-diphenylphosphanamine

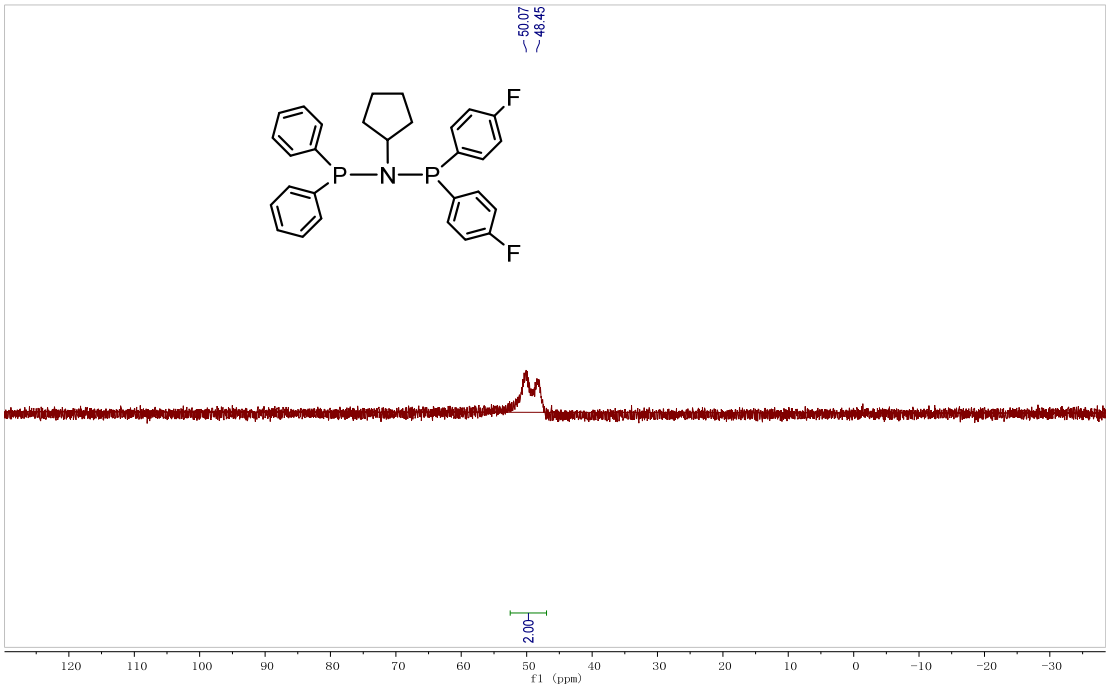

Figure S2. ^{31}P NMR Spectrum of L1

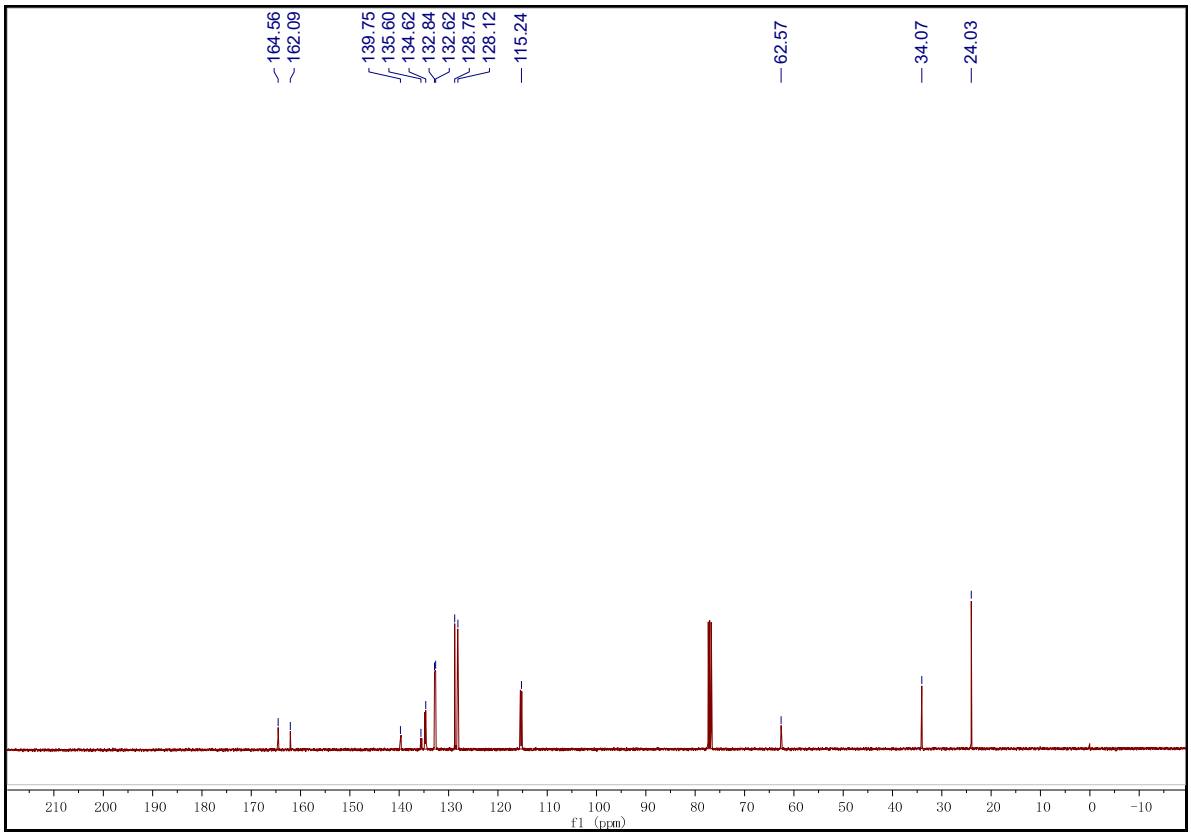

Figure S3. ^{13}C NMR Spectrum of L1

^{1}H NMR of *N*-(bis(4-(trifluoromethyl)phenyl)phosphanyl)-*N*-cyclopentyl-1,1-diphenylphosphanamine

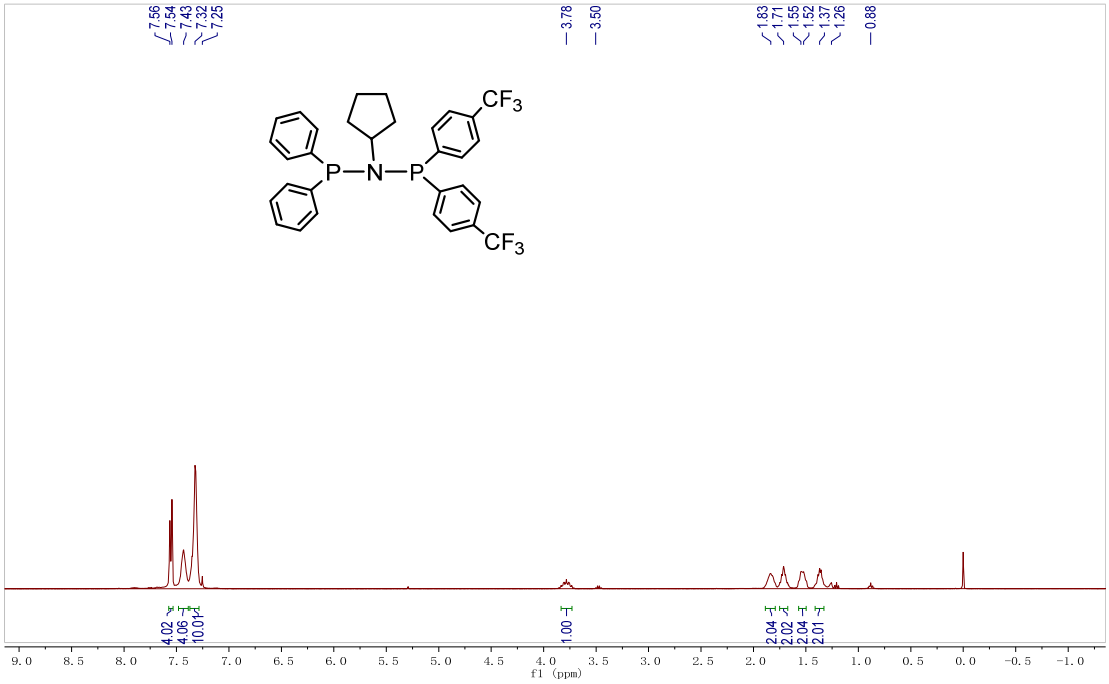

Figure S4. ^{1}H NMR Spectrum of L2

^{31}P NMR of *N*-(bis(4-(trifluoromethyl)phenyl)phosphanyl)-*N*-cyclopentyl-1,1-diphenylphosphanamine

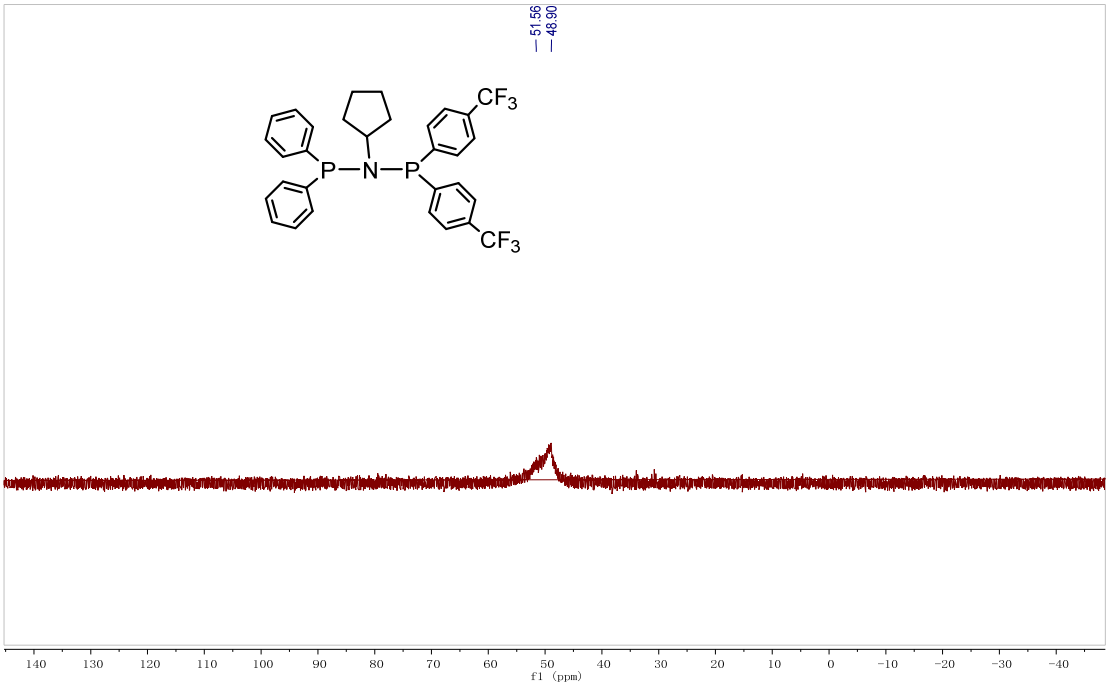

Figure S5. ^{31}P NMR Spectrum of L2

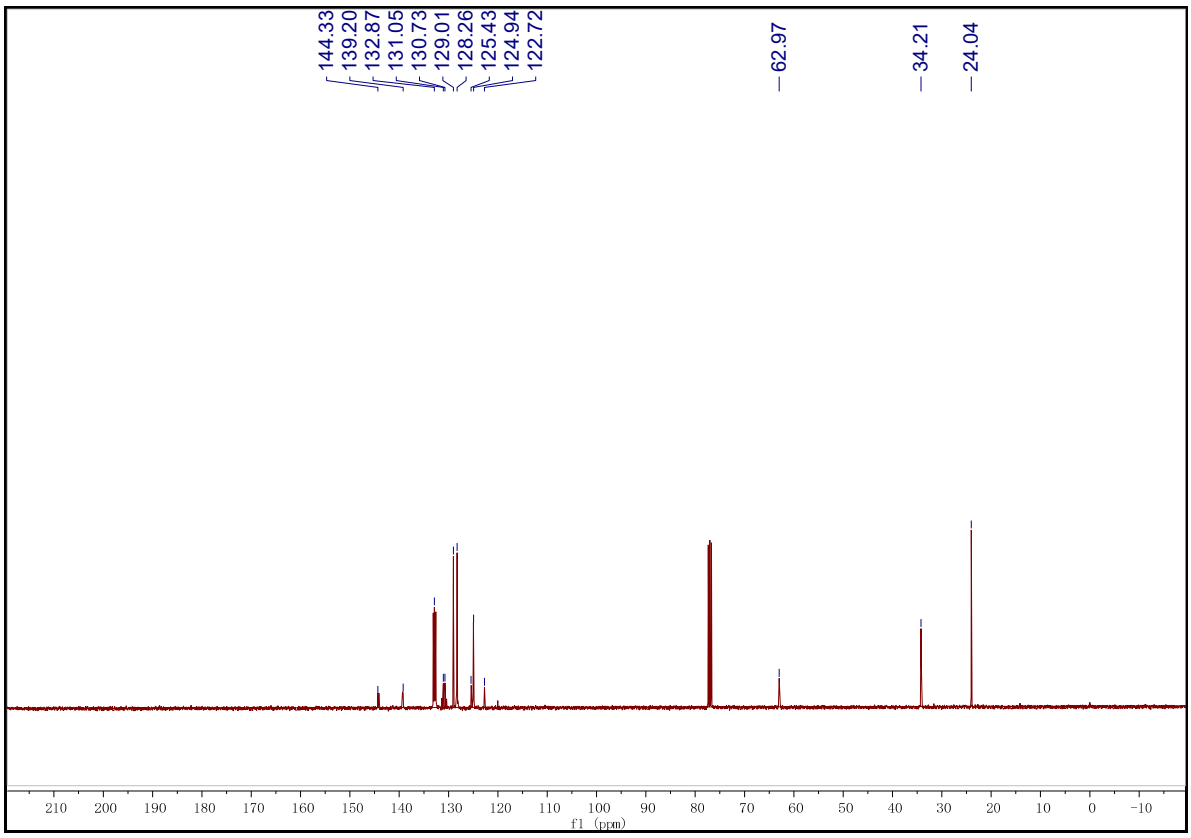

Figure S6. ^{13}C NMR Spectrum of L2

^{1}H NMR of *N*-(bis(3,5-bis(trifluoromethyl)phenyl)phosphanyl)-*N*-cyclopentyl-1,1-diphenylphosphanamine

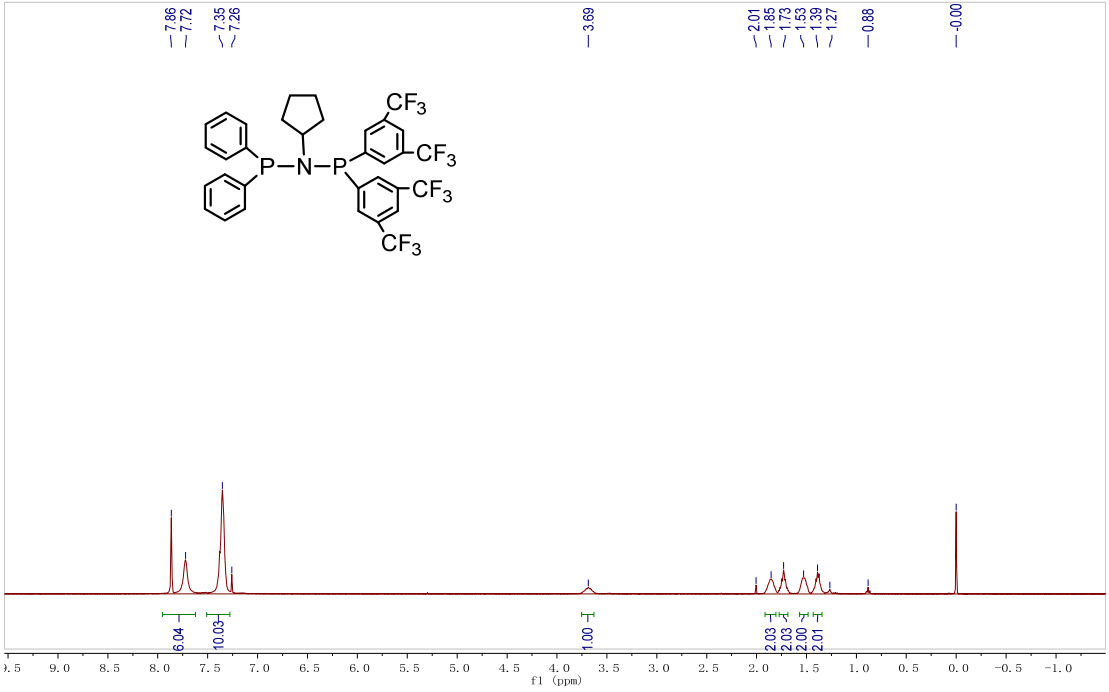

Figure S7. ^{1}H NMR Spectrum of L3

^{31}P NMR of *N*-(bis(3,5-bis(trifluoromethyl)phenyl)phosphanyl)-*N*-cyclopentyl-1,1-diphenylphosphanamine

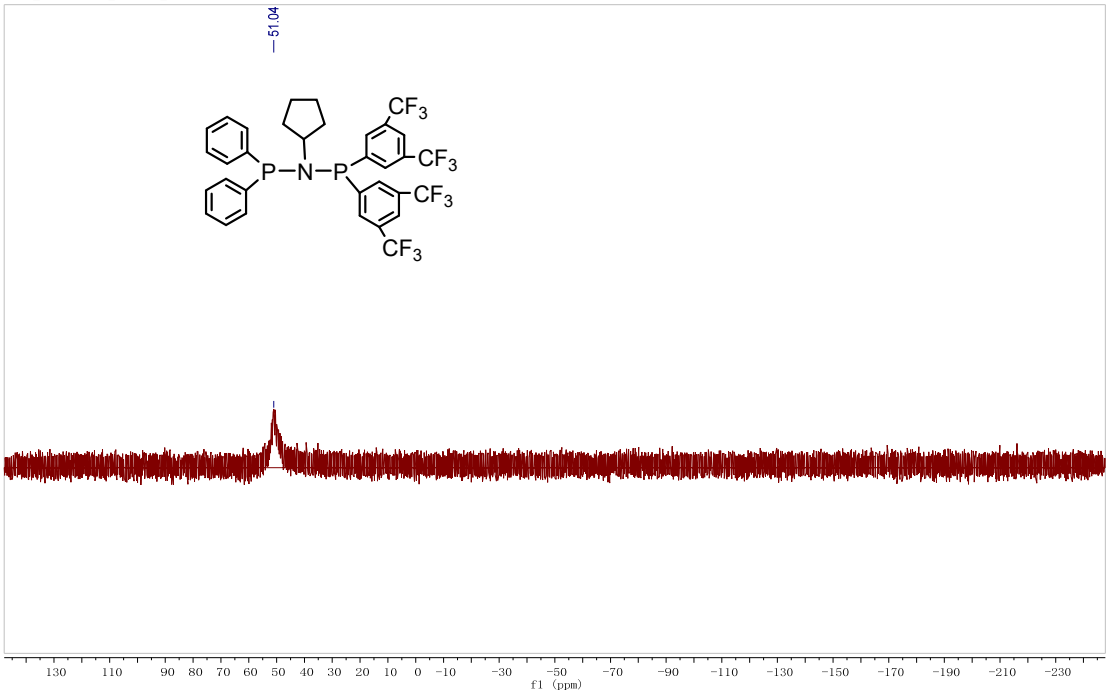

Figure S8. ^{31}P NMR Spectrum of L3

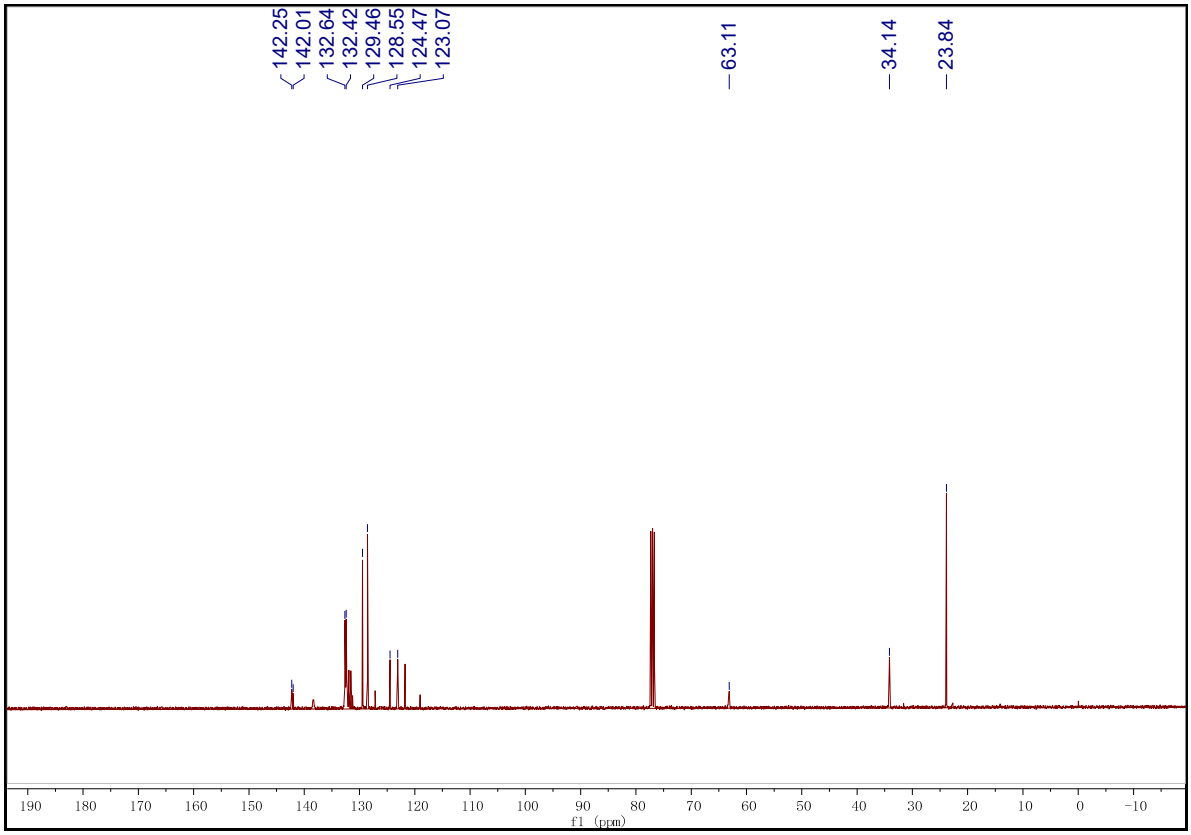

Figure S9. ^{13}C NMR Spectrum of L3

^{1}H NMR of *N*-cyclopentyl-*N*-(di-*p*-tolylphosphanyl)-1,1-diphenylphosphanamine

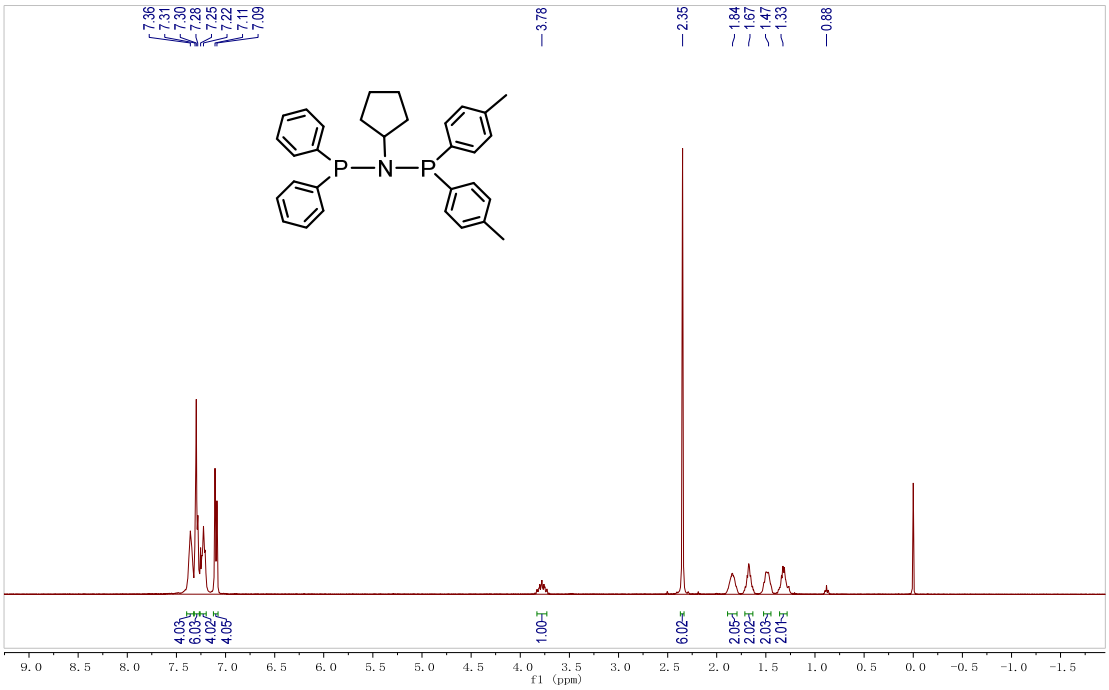

Figure S10. ^{1}H NMR Spectrum of L4

^{31}P NMR of *N*-cyclopentyl-*N*-(di-*p*-tolylphosphanyl)-1,1-diphenylphosphanamine

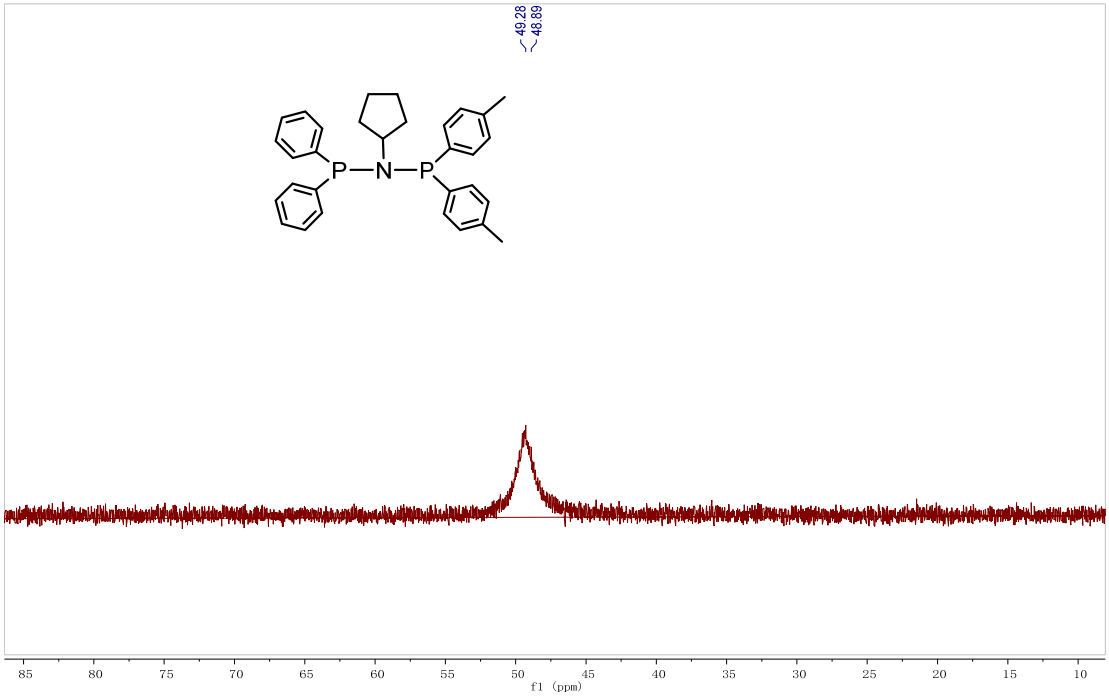

Figure S11. ^{31}P NMR Spectrum of L4

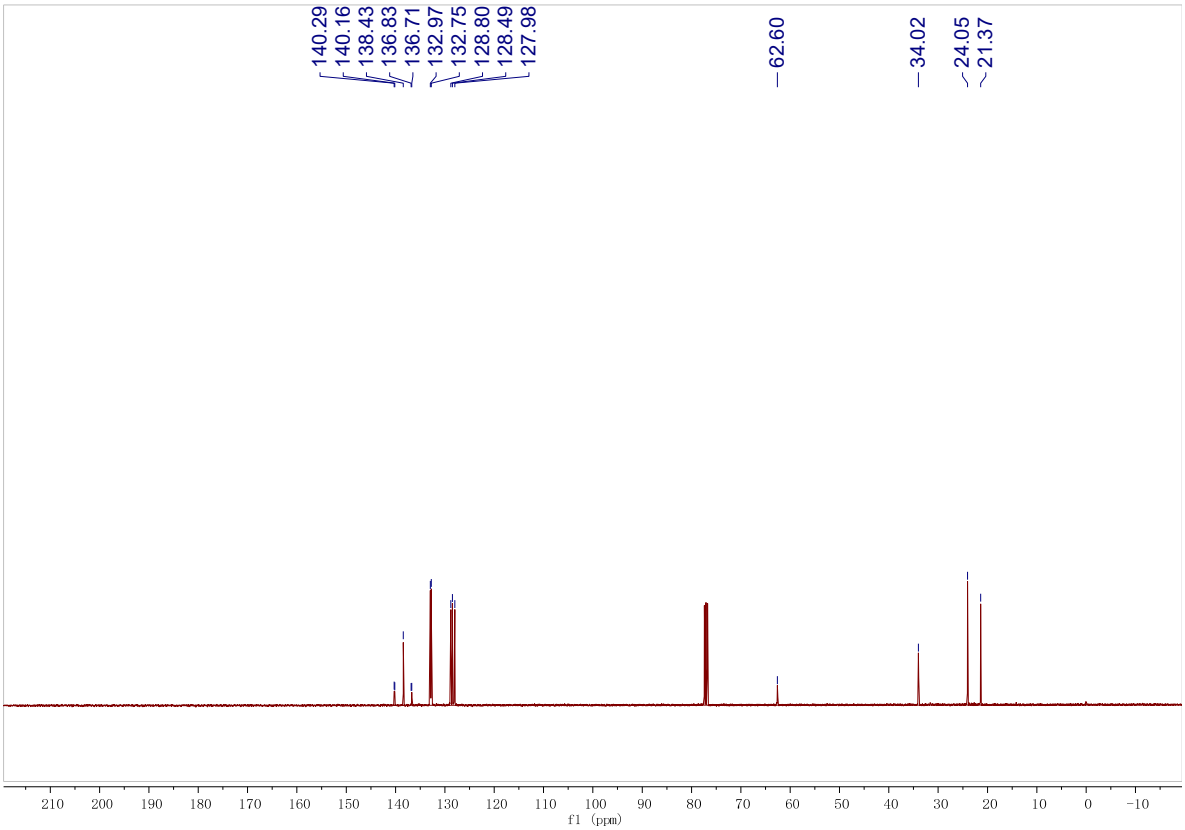

Figure S12. ^{13}C NMR Spectrum of L4

^{1}H NMR of *N*-(bis(3,5-dimethylphenyl)phosphanyl)-*N*-cyclopentyl-1,1-diphenylphosphanamine

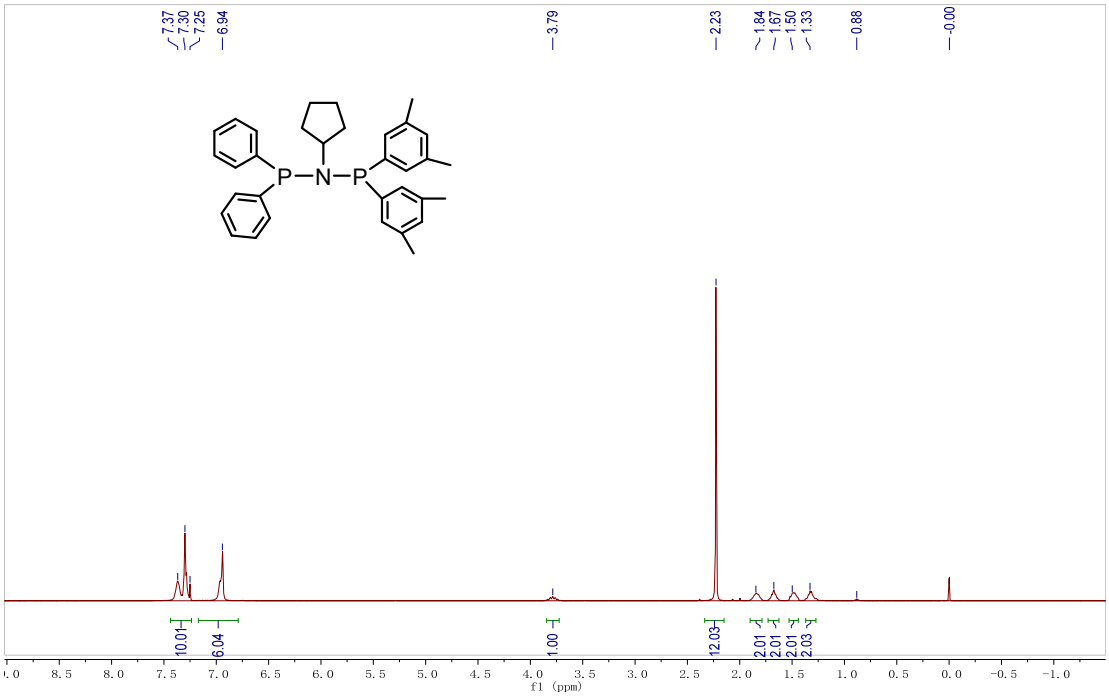

Figure S13. ^{1}H NMR Spectrum of L5

^{31}P NMR of *N*-(bis(3,5-dimethylphenyl)phosphanyl)-*N*-cyclopentyl-1,1-diphenylphosphanamine

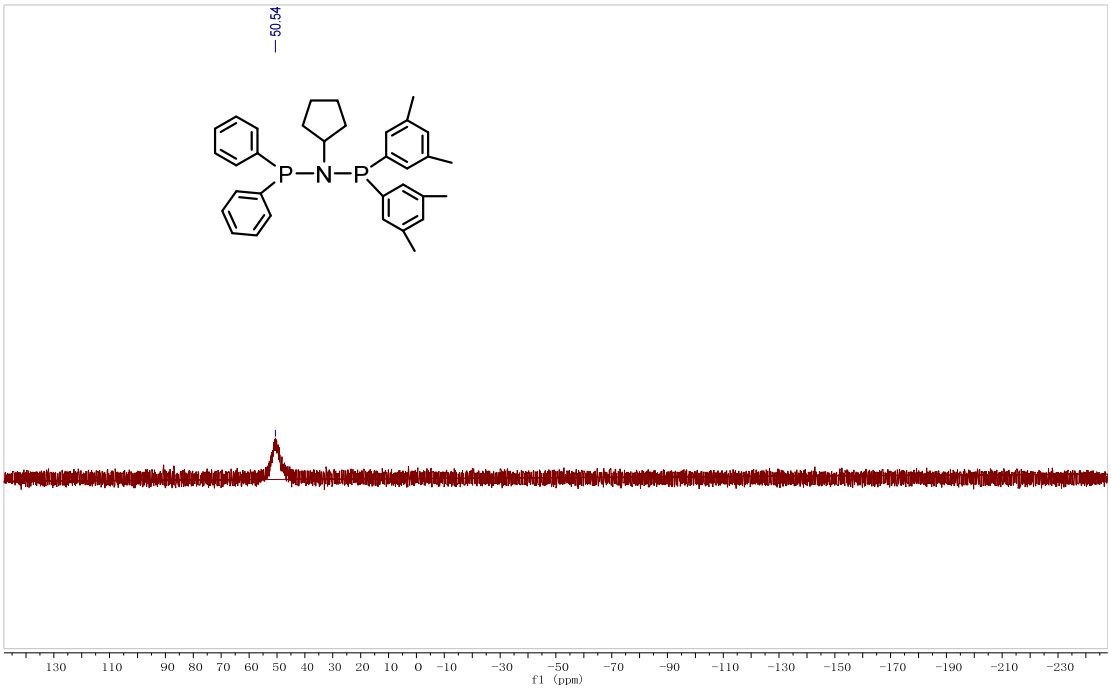

Figure S14. ^{31}P NMR Spectrum of L5

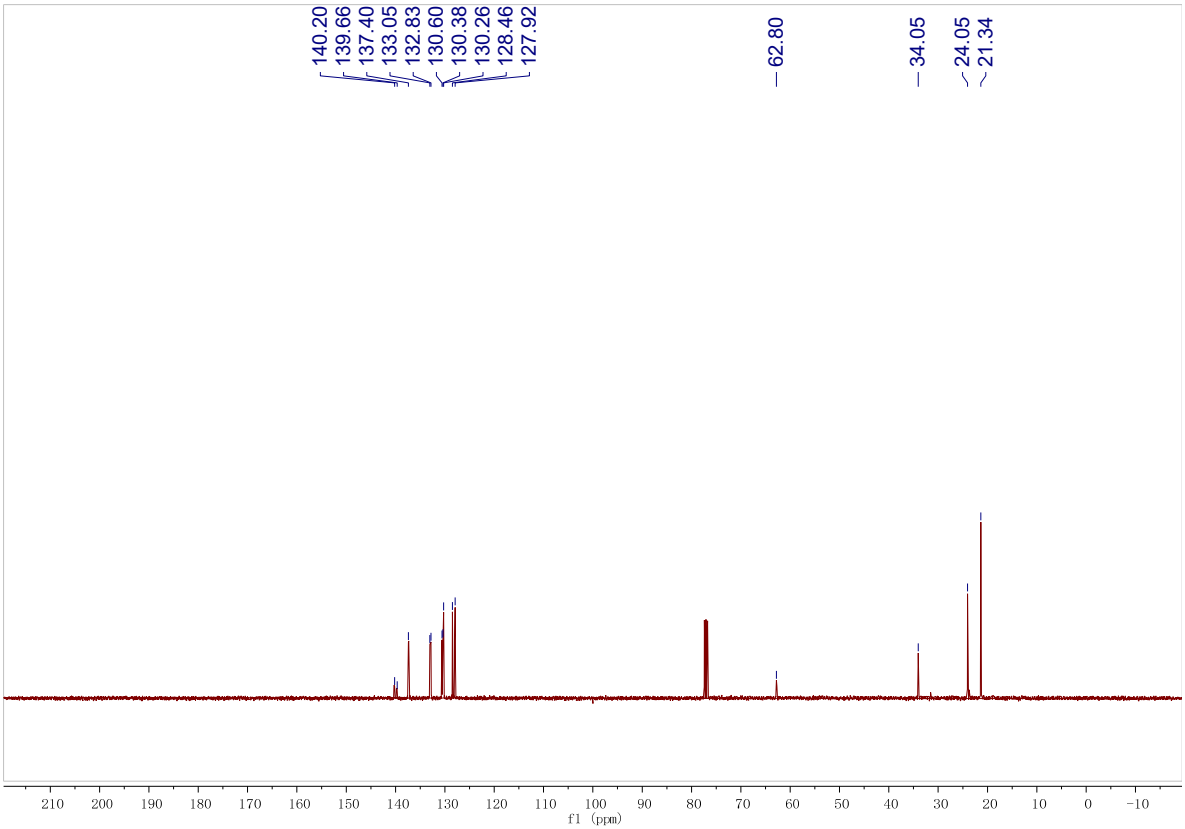

Figure S15. ^{13}C NMR Spectrum of L5

^{1}H *N*-(bis(4-methoxyphenyl)phosphanyl)-*N*-cyclopentyl-1,1-diphenylphosphanamine

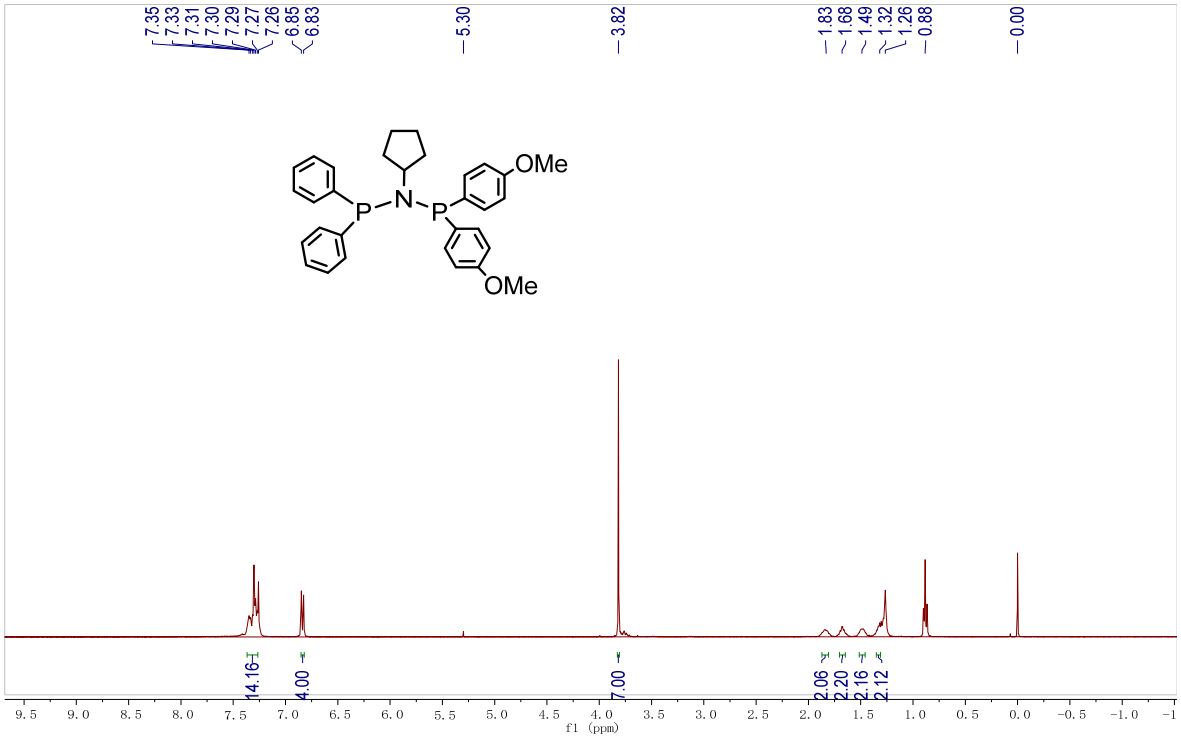

Figure S16. ^{1}H NMR Spectrum of L6

^{31}P *N*-(bis(4-methoxyphenyl)phosphanyl)-*N*-cyclopentyl-1,1-diphenylphosphanamine

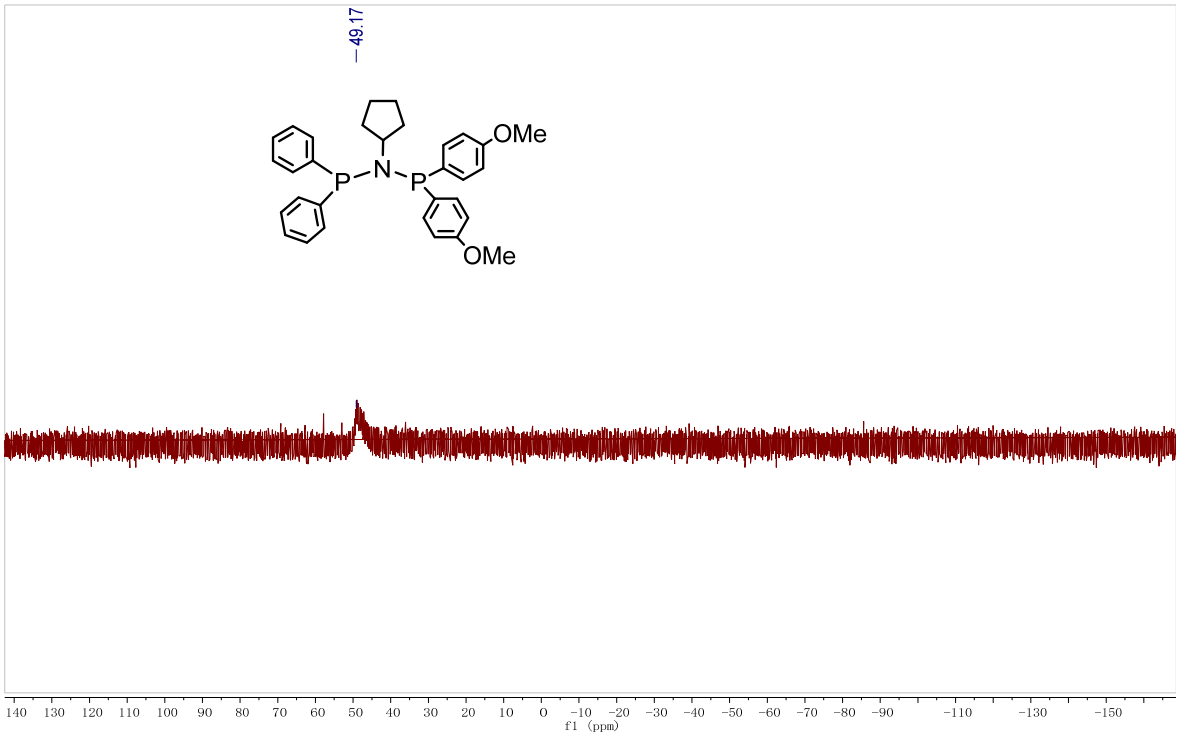

Figure S17. ^{31}P NMR Spectrum of L6

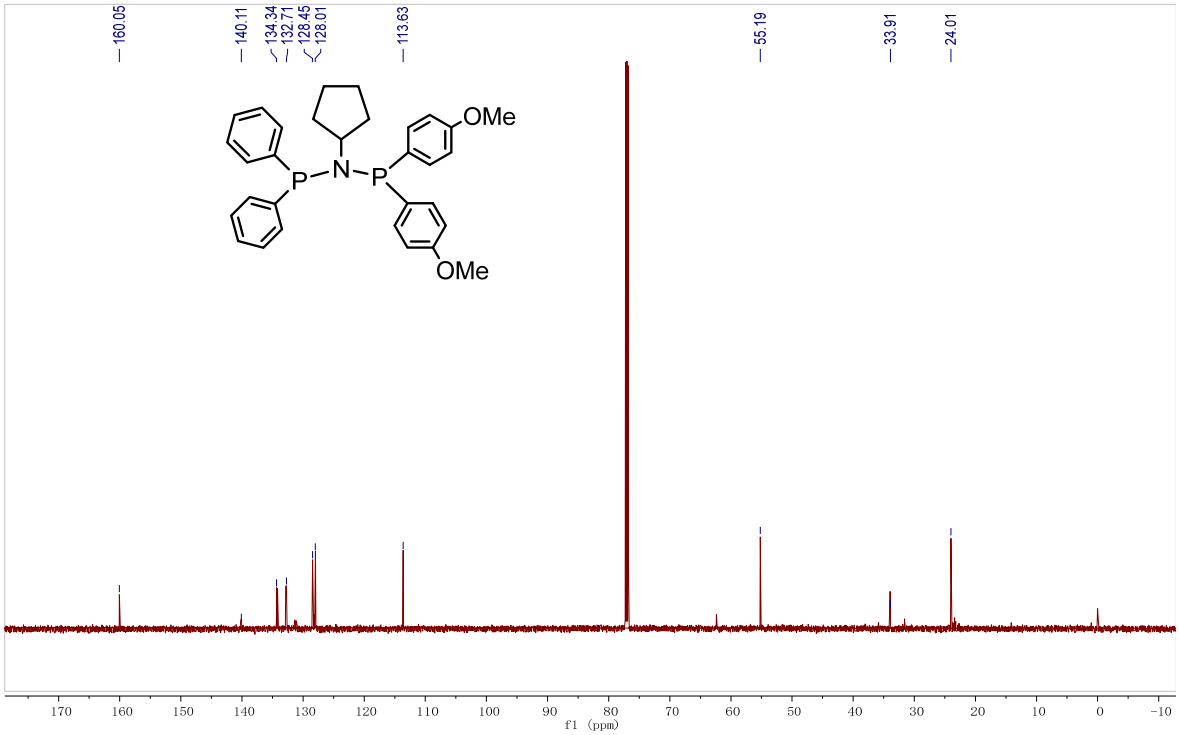

Figure S18. ^{13}C NMR Spectrum of L6

References

1. Boulens, P.; Pellier, E.; Jeanneau, E.; Reek, J.N.; Olivier-Bourbigou, H.; Breuil, P.A.R. Self-assembled organometallic Nickel complexes as catalysts for selective dimerization of ethylene into 1-butene. *Organometallics* **2015**, *34*, 1139–1142.