Supporting Information for the Paper "Synthesis of Calcium and Ytterbium Complexes Supported by a Tridentate Imino-Amidinate Ligand and the Application for Intermolecular Hydrophosphination of Alkenes and Alkynes"

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Experimental Procedures

Materials and Methods

All manipulations of air-sensitive materials were carried out under an atmosphere of dry argon or nitrogen by using modified Schlenck line and glovebox techniques. All solvents were freshly distilled from Na/benzophenone and degassed immediately prior to use. Chloroform-d and benzene-d_6 was purchased from Cambridge Isototope Laboratories and was stored over Na/K alloy. Alkenes and alkynes were purchased from Alfa-Aesar and J&K Scientific Ltd. All the liquid alkenes and alkynes were dried over CaH_2, freshly distilled and freeze-thaw degassed prior to use.

2-(CHNAr)$C_6H_4NH_2$ (Ar = 2,6-*i*$Pr_2C_6H_3$)[1], ArNC(Ph)Cl (Ar = 2,6-*i*$Pr_2C_6H_3$)[2], diphenylphosphine[3], Ca[N($SiMe_3$)$_2$]$_2$·2THF[4] and Yb[N($SiMe_3$)$_2$]$_2$·2THF[5] were prepared according to literature procedures.

Physical and Analytical Measurement

Elemental analyses were carried out on an Elemental Vario EL analyzer. Infrared spectra were recorded on a Bio-Rad FTS 6000 spectrometer. The ^{1}H, ^{13}C and ^{31}P NMR spectroscopic data were recorded on Bruker Mercury Plus 400 MHz NMR spectrometers. Chemical shifts (δ) for ^{1}H and ^{13}C are referenced to internal solvent resonances and reported relative to $SiMe_4$. Chemical shifts for ^{31}P are reported relative to an external 85% H_3PO_4 standard.

NMR-Scale Catalytic Reactions

In a glovebox, diphenylphosphine (43μL, 0.25mmol) was added to a solution of catalyst (0.012mmol, 5mol %) in C_6D_6, the alkene/alkyne (0.3mmol, 1.2equiv) was added either as a solid or a solution in the same solvent. The solution was then loaded into a Young's tap NMR tube. The mixture gradually turned into a dark yellow color, which indicates the formation of calcium phosphide. The reaction was monitored by ^{1}H and ^{31}P spectroscopy.

Preparative-scale Catalytic Reactions

This process was designed for the reactions with unknown products whose oxidation or sulfidation derivatives were previously reported. The catalyst (0.10mmol)

was dissolved in 5mL of toluene and then diphenylphosphine (0.37g, 2mmol) and the alkene/alkyne (2.2mmol, 1.1equiv.) was added as a solution in the same solvent (5mL). The reaction was then heated to the required temperature. After the reaction was complete, elemental sulfur (70mg, 2.1mmol) or H_2O_2 (30%, 2mL) was added at 0℃ to the mixture and stirred for 30min. For the sulfidation process, the solvent was removed in vacuum and the residue was tested by ^{1}H and ^{31}P spectroscopy to determine the regioselectivity. While for the oxidation process, the product was extracted with diethyl ether and dried over $MgSO_4$. After the solvent was removed, the residue was determined by ^{1}H and ^{31}P spectroscopy.

Preparation of Catalysts

*Synthesis of LH (**1**)*: N-(2-aminobenzylidene)-2,6-diisopropylaniline (5.0g, 17.85mmol) was dissolved in 30mL of toluene and cooled to -78 °C, then *n*-BuLi (2.4M, 7.4mL) was added dropwise to the solution. The mixture slowly warmed to room temperature and stirred for 2 h. After the solvent was removed, the solid was washed once with hexane and dried in vacuum for 2 h. The lithium salt was then dissolved in 30mL of THF and added to a solution of N-(2,6-diisopropyl)phenylbenzimidoylchloride (5.35g, 17.85mmol) in THF at 0 °C. The mixture slowly warmed to room temperature and stirred overnight. After the solvent was removed in vacuum, the residue was extracted with hexane (2×100mL). The resulting yellow solution was concentrated to 20mL and stored at -40 °C. A large amount of pale yellow crystals was gained (6.65g, 69%). M.p. 147-150°C. ^{1}H NMR ($CDCl_3$, 400MHz): δ 0.94 (m, 6H), 1.06 (d, 12H, 6.4Hz), 1.16 (m, 6H), 2.92 (m, 2H),

3.11 (m, 2H), 6.93-7.41 (m, 15H), 8.30 (s, 1H), 9.43 (m, 0.5H), 12.24 (m, 0.5H). ^{13}C NMR ($CDCl_3$, 100MHz): 23.4, 24.3, 27.9, 28.2 ($CHMe_2$), 119.2, 119.9, 120.4, 122.4, 122.7, 123.0, 124.7, 127.9, 128.1, 129.3, 132.4, 134.4, 135.3, 137.5, 138.1, 143.3, 144.6, 148.1 (ArC), 152.0, 166.2 (C=N). IR (KBr, cm^{-1}): 3371-3192(N–H), 1621(N-C-N). MS (ESI); m/z(%) = 544[M^+] (100). Anal. Calcd for $C_{38}H_{45}N_3$(534.78): C, 83.93; H, 8.34; N, 7.73. Found: C, 84.17; H, 8.25; N, 7.83.

*Synthesis of LCaN(SiMe$_3$)$_2$·THF (**2**)*: A solution of LH (1.63g, 3mmol) in 30mL of hexane was added to the solution of Ca[N(SiMe$_3$)$_2$]$_2$·2THF (1.52g, 3mmol) in the same solvent. The mixture was stirred for 36 h at room temperature and then filtered. The filtrate was concentrated and recrystallization at -40 °C to yield the product as light yellow crystals (1.90g, 78%). M.p. 151-154°C. ^{1}H NMR (C_6D_6, 400MHz): δ 0.24 (s, 18H), 0.97 (d, 6H, 6.4Hz), 1.10 (m, 4H), 1.27 (m, 6H), 1.31 (d, 12H, 6.4Hz), 3.26 (sept, 2H, 6.8Hz), 3.35 (m, 4H), 3.50 (sept, 2H, 6.8Hz), 6.21 (d, 1H, 8.4Hz), 6.44 (t, 1H, 7.2Hz), 6.66 (t, 1H, 8.4Hz), 6.81 (m, 3H), 6.97 (d, 1H, 7.6Hz), 7.08 (m, 8H), 8.06 (s, 1H). ^{13}C NMR (C_6D_6, 100MHz): 6.1 ($SiMe_3$), 24.0, 25.0, 25.5, 28.4 ($CHMe_2$), 29.0, 68.9 (THF), 117.6, 123.6, 123.9, 124.0, 124.1, 124.4, 126.0, 128.2, 128.5, 130.3, 132.2, 134.5, 135.7, 139.7, 141.3, 144.7, 150.7, 151.8(ArC), 169.2, 171.8 (C=N). IR (KBr, cm^{-1}): 3689, 3646, 3372, 3061, 2960, 2868, 1916, 1800, 1621, 1576, 1456, 1316, 1249, 1213, 1128, 1058, 932, 842, 697, 617, 531, 419. Anal. Calcd for $C_{48}H_{70}CaN_4OSi_2$(815.34): C, 70.71; H, 8.65; N, 6.87. Found: C, 70.16; H, 8.14; N, 6.33.

*Synthesis of LYbN(SiMe$_3$)$_2$·THF (**3**)*: A solution of LH (0.54g, 1mmol) in 20mL of hexane was added to the solution of Yb[N(SiMe$_3$)$_2$]$_2$·2THF (0.64g, 1mmol) in the same solvent at 0 °C. The mixture was stirred for 36 h at room temperature and then filtered. The filtrate was concentrated and recrystallization at -40 °C to yield the product as dark brown crystals (0.67g, 71%). M.p. 160-163°C. ^{1}H NMR (C$_6$D$_6$, 400MHz): δ 0.30 (s, 18H), 0.98 (d, 6H, 5.2Hz), 1.17 (d, 6H, 6.0Hz), 1.23 (m, 4H), 1.29 (d, 6H, 6.4Hz), 1.35 (d, 6H, 5.6Hz), 3.19 (br, 4H), 3.37 (sept, 2H, 6.4Hz), 3.56 (sept, 2H, 5.6Hz), 6.24 (d, 1H, 8.4Hz), 6.44 (t, 1H, 7.2Hz), 6.72 (t, 1H, 7.6Hz), 6.81 (m, 3H), 7.07 (m, 9H), 8.21 (s, 1H). ^{13}C NMR (C$_6$D$_6$, 100MHz): 6.0 (SiMe$_3$), 24.1, 25.4, 25.7, 28.2 (CHMe$_2$), 28.8, 68.8 (THF), 118.1, 123.7, 124.1, 124.3, 125.0, 126.0, 128.0, 128.2, 128.6, 130.0, 132.3, 134.8, 135.8, 139.9, 141.6, 144.7, 150.2, 151.0(ArC), 168.3, 170.8 (C=N). IR (KBr, cm^{-1}): 3645, 3060, 3025, 2960, 2868, 1917, 1620, 1534, 1440, 1402, 1362, 1317, 1248, 1214, 1162, 1128, 1044, 932, 898, 842, 754, 696, 619, 531, 468, 415. Anal. Calcd for C$_{48}$H$_{70}$YbN$_4$OSi$_2$(948.31): C, 60.79; H, 7.44; N, 5.91. Found: C, 60.51; H, 7.18; N, 5.63.

Reference

1. Li J.; Song H.; Cui C.; Cheng J. *Inorg. Chem.* **2008**, *47*, 3468.

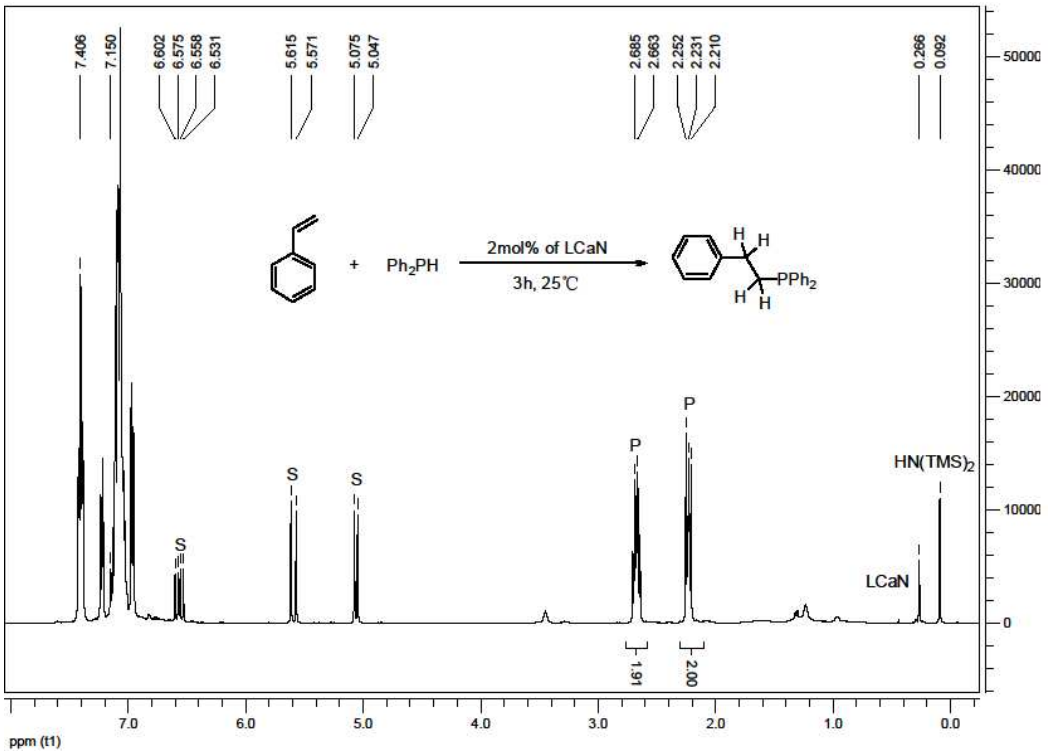
2. Bambirra S.; Otten E.; Leusen D.; Meetsma A.; Hessen B. *Z. Anorg. Allg. Chem.* **2006**, *632*, 1950.

3. Gulyas H.; Benet-Buchholz J.; Escudero-Adan E.; Freixa Z.; Leeuwen P. *Chem. Eur. J.* **2007**, *13*, 3424.

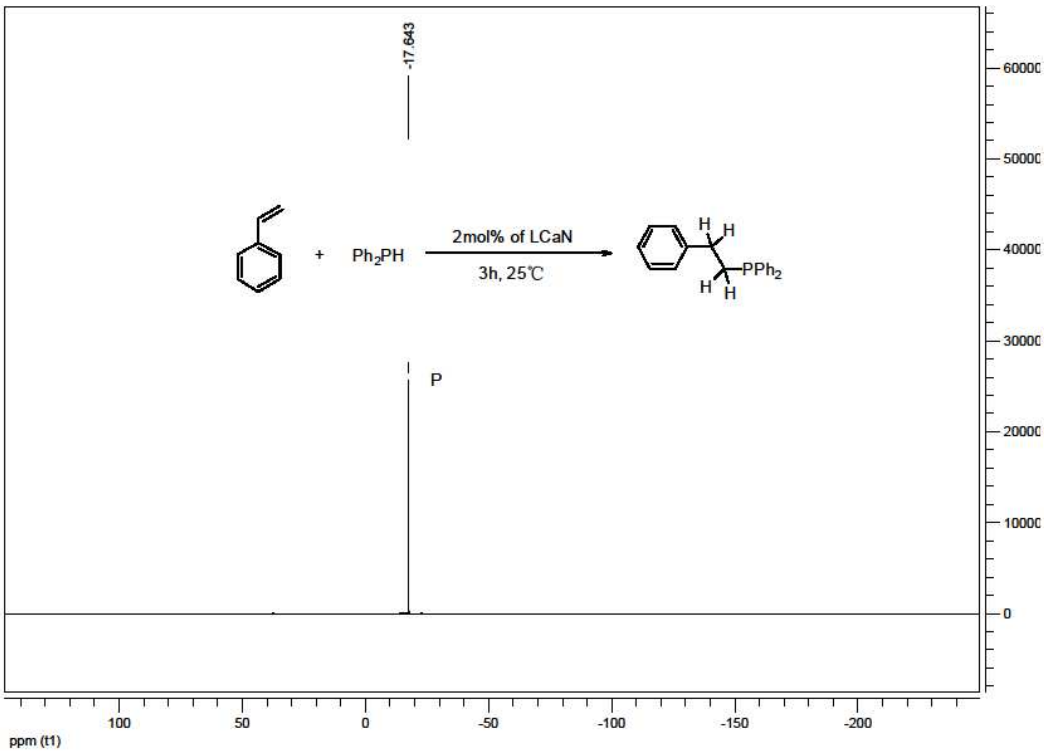
4. Sarazin Y.; Howard R.; Hughes D.; Humphreyb S.; Bochmanna M. *Dalton Trans*. **2006**, 340.

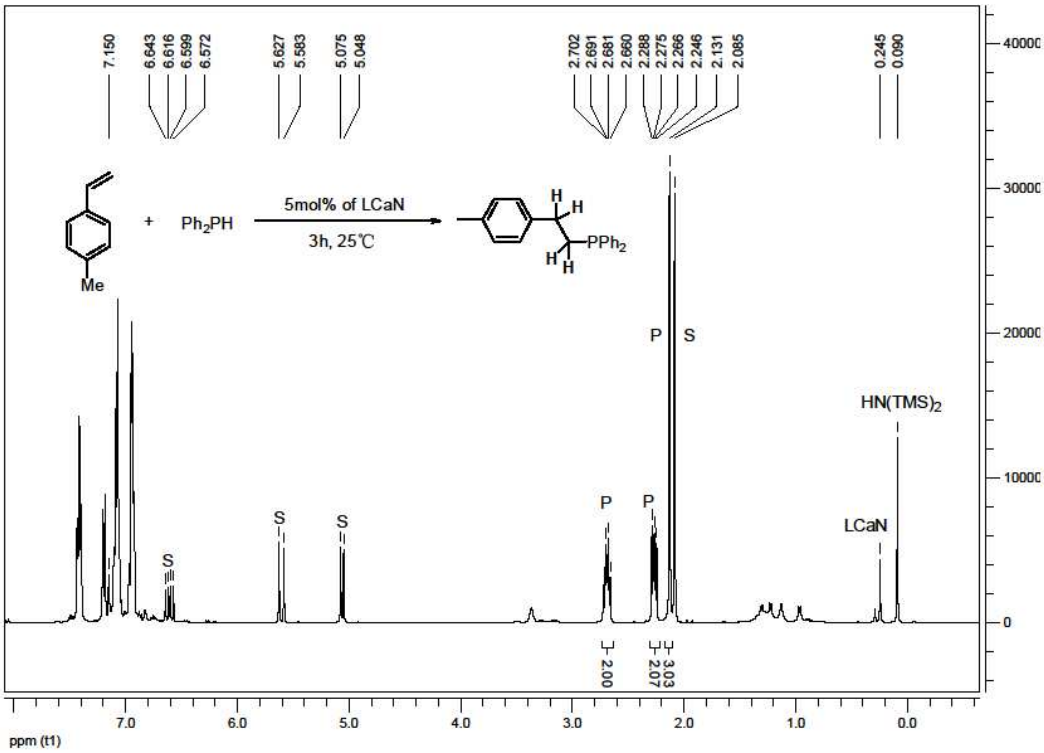
5. Hitchcock P.; Khvostov A.; Lappert M.; Protchenko A. *Journal of Organometallic Chemistry* **2002**, *647*,198.

Spectral data for NMR-scale reactions

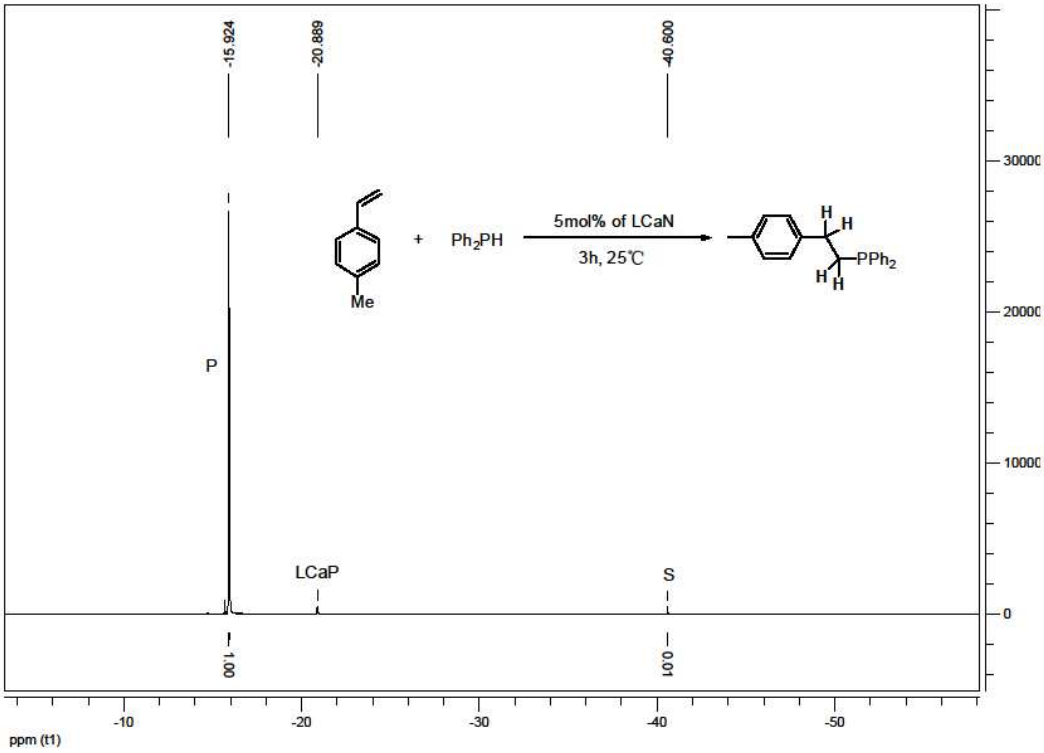


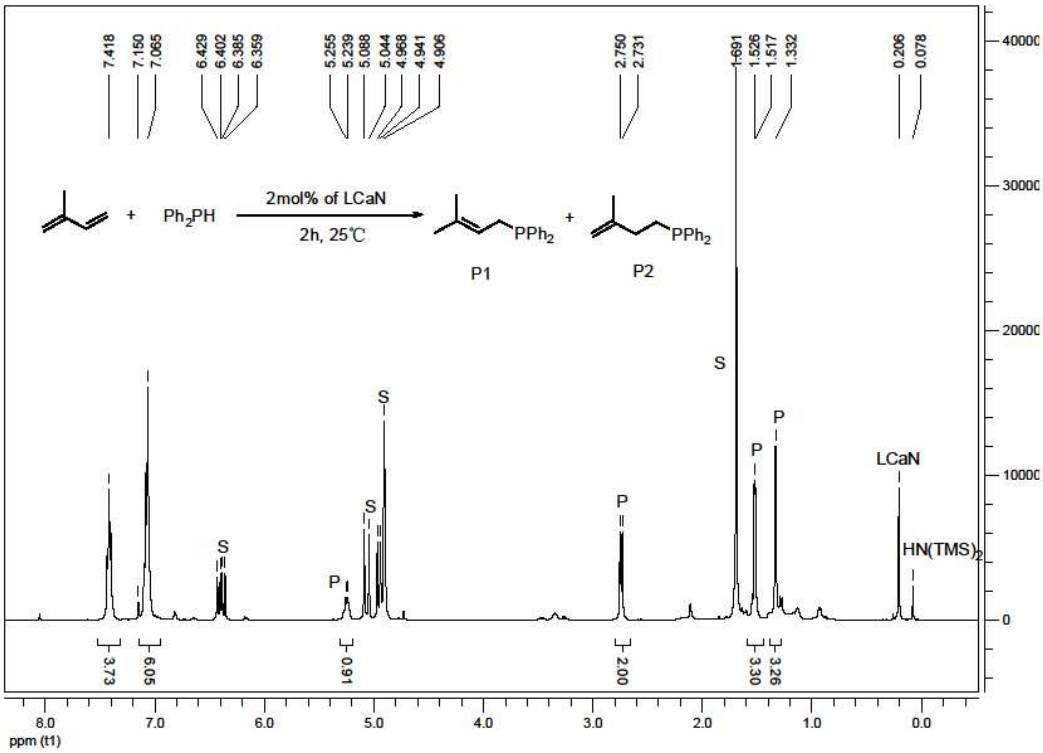
^{1}H NMR for Product (C_6D_6, 400 MHz): 2.23 (m, 2H), 2.67 (m, 2H), 6.96 (d, 2H, 7.2 Hz), 7.07-7.13 (m, 9H), 7.22 (d, 1H, 7.2 Hz), 7.41 (t, 3H, 7.6 Hz).



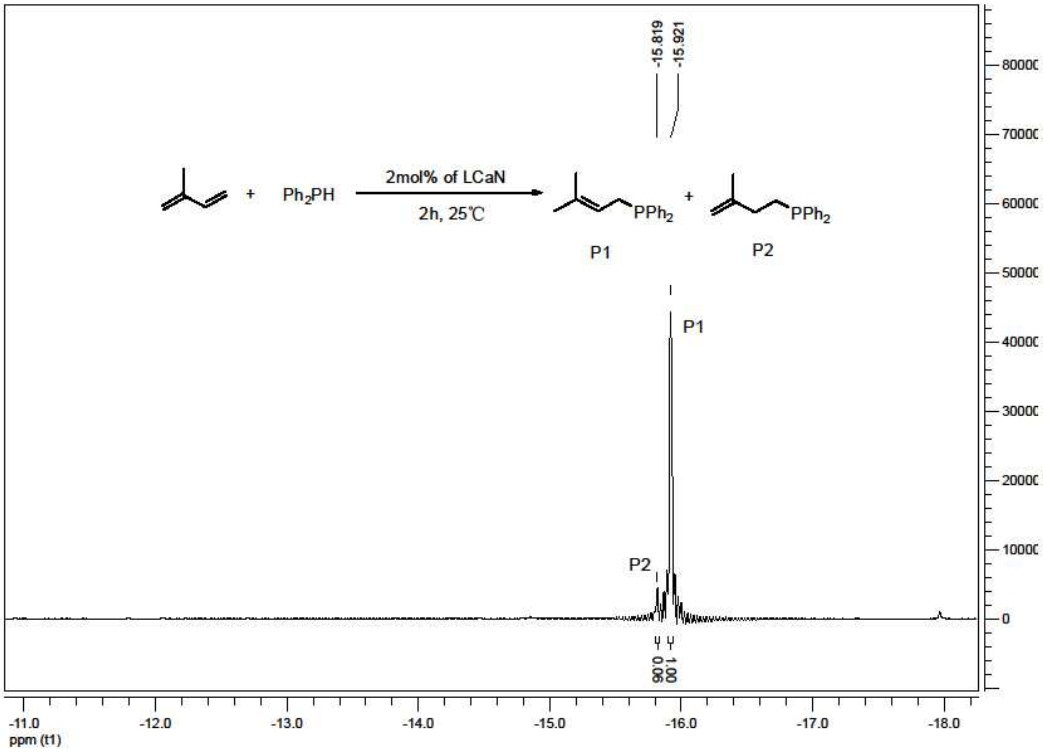


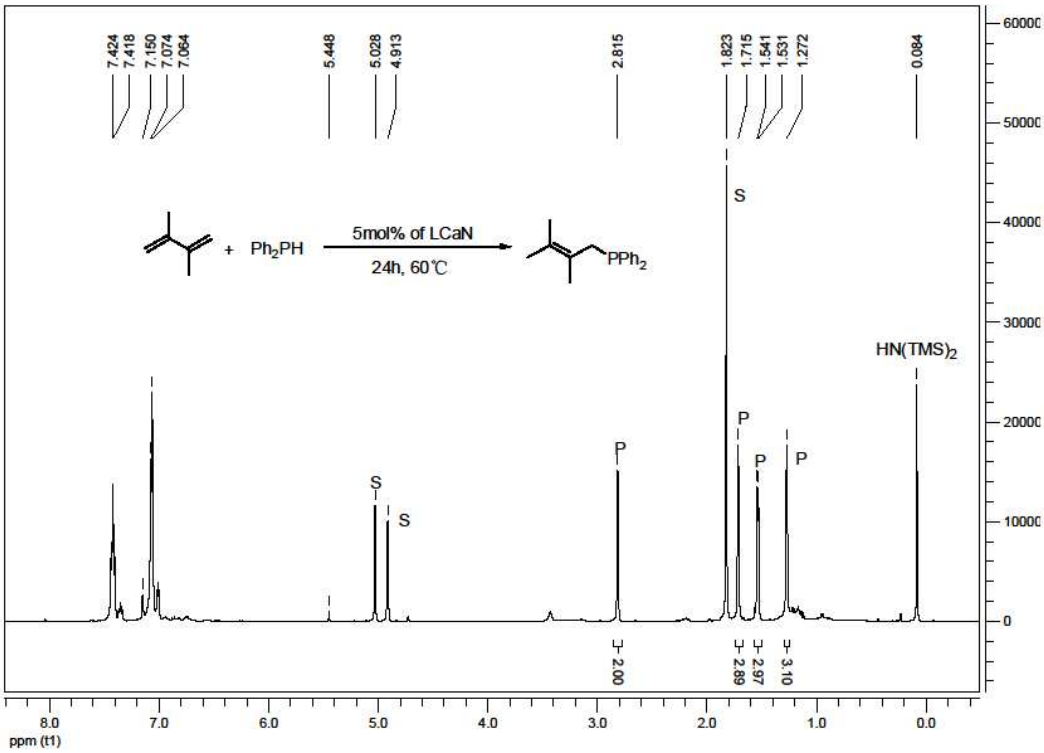
^{1}H NMR for Product (C_6D_6, 400 MHz): 2.13 (s, 3H), 2.27 (m, 2H), 2.69 (m, 2H), 6.93 (m, 5H), 7.08 (m, 5H), 7.19 (d, 2H, 8.0 Hz), 7.42 (t, 3H, 7.6 Hz).



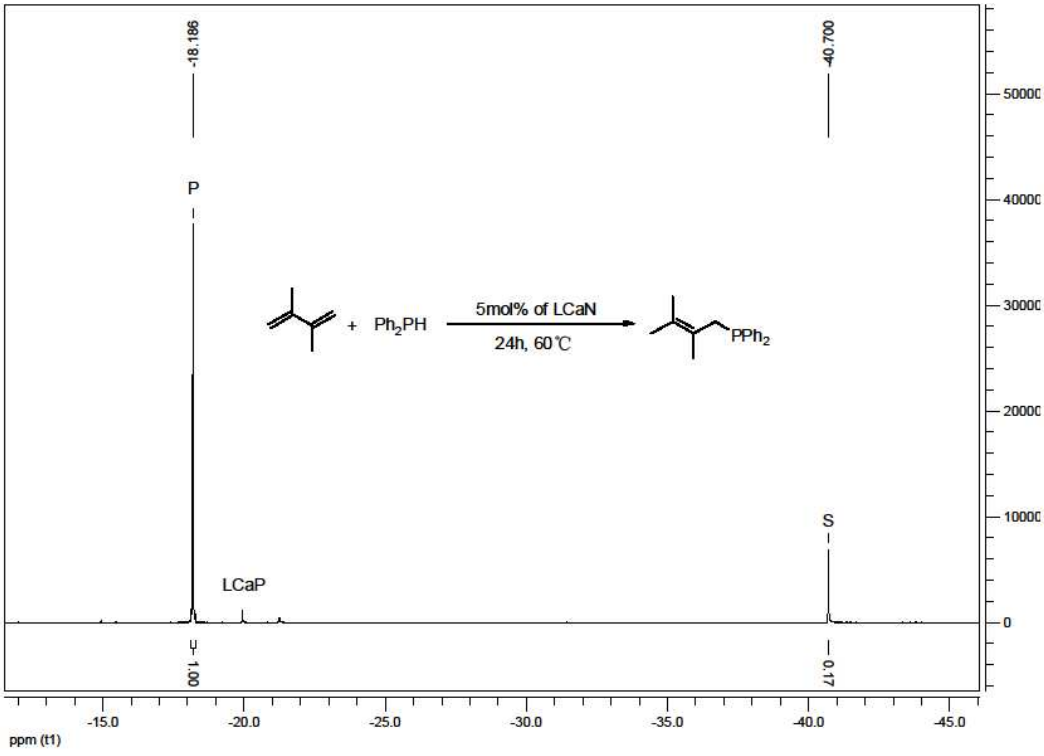


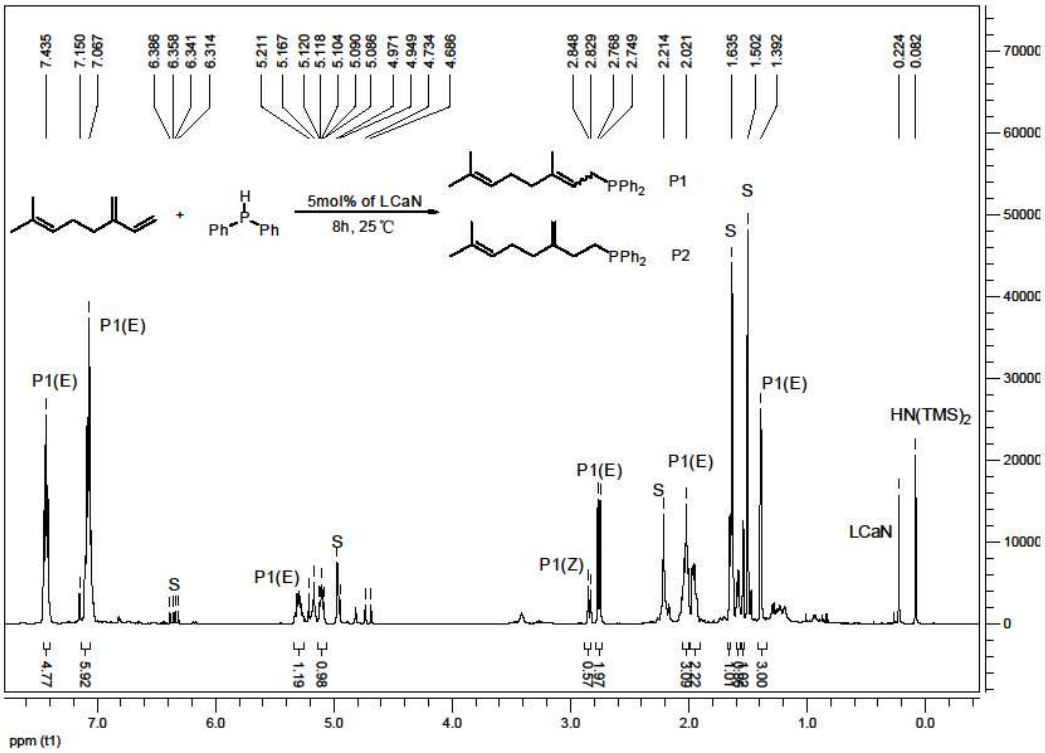
^{1}H NMR for P1 (C_6D_6, 400 MHz): 1.33 (s, 3H), 1.52 (d, 3H, 3.6 Hz), 2.74 (d, 2H, 7.6 Hz), 5.24 (m, 1H), 7.07 (m, 6H), 7.42 (m, 4H).



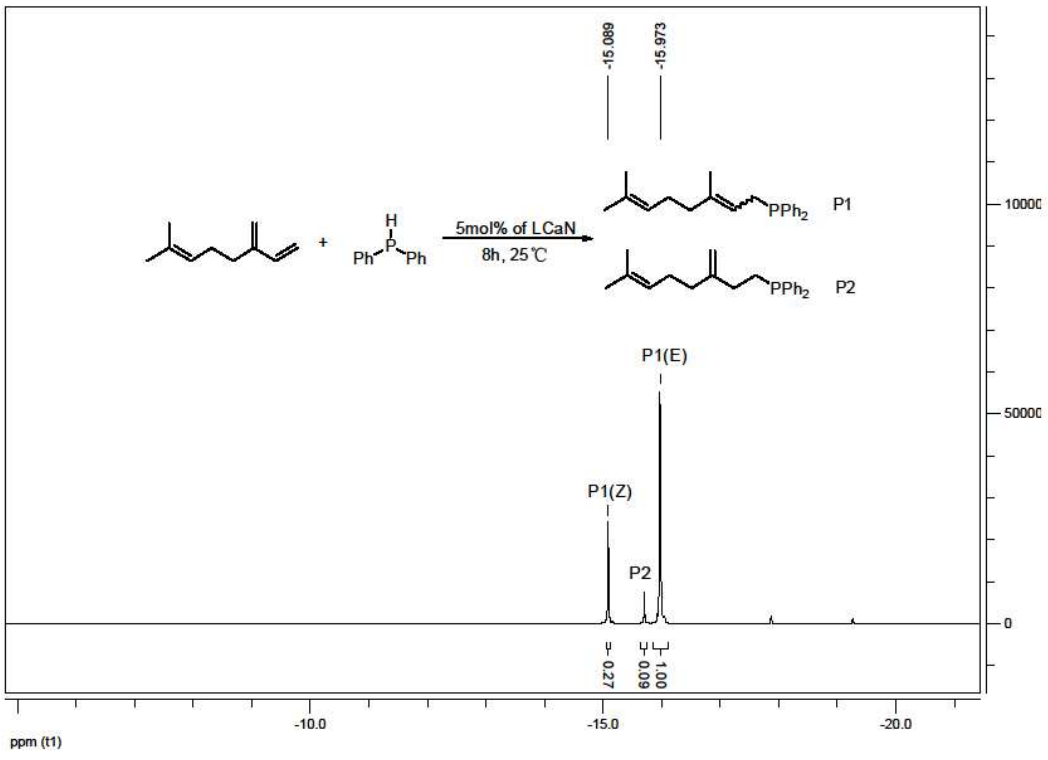


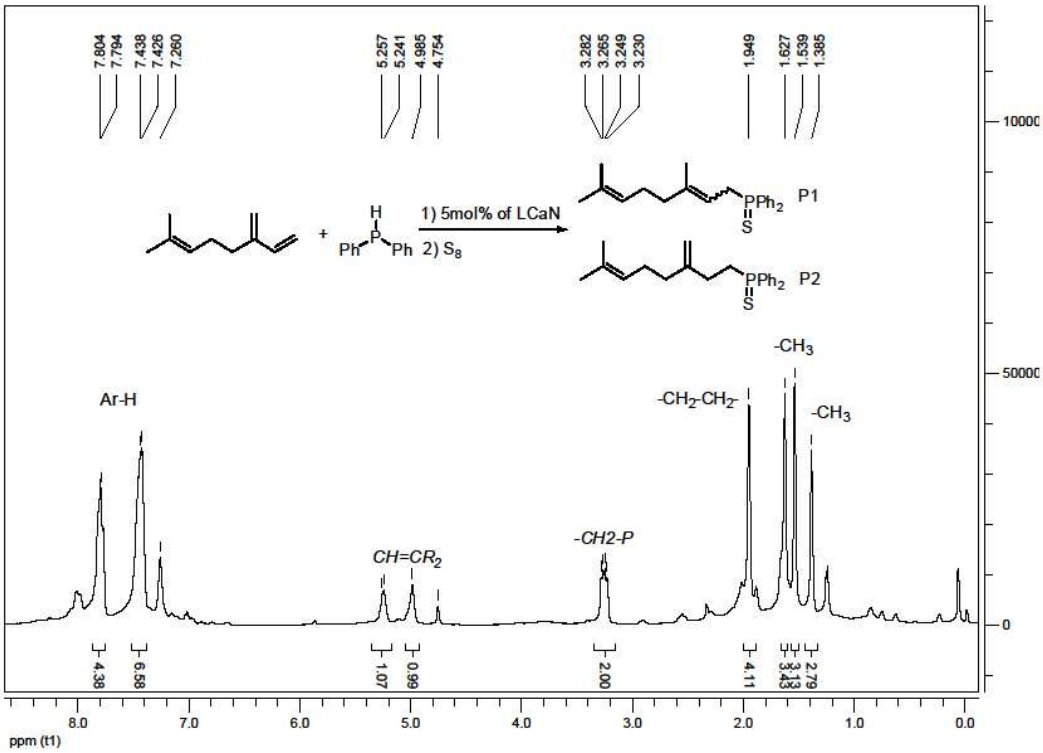
^{1}H NMR for Product (C_6D_6, 400 MHz): 1.27 (s, 3H), 1.54 (d, 3H, 4.0 Hz), 1.72 (s, 3H), 2.82 (s, 2H), 7.07 (m, 6H), 7.42 (m, 4H).

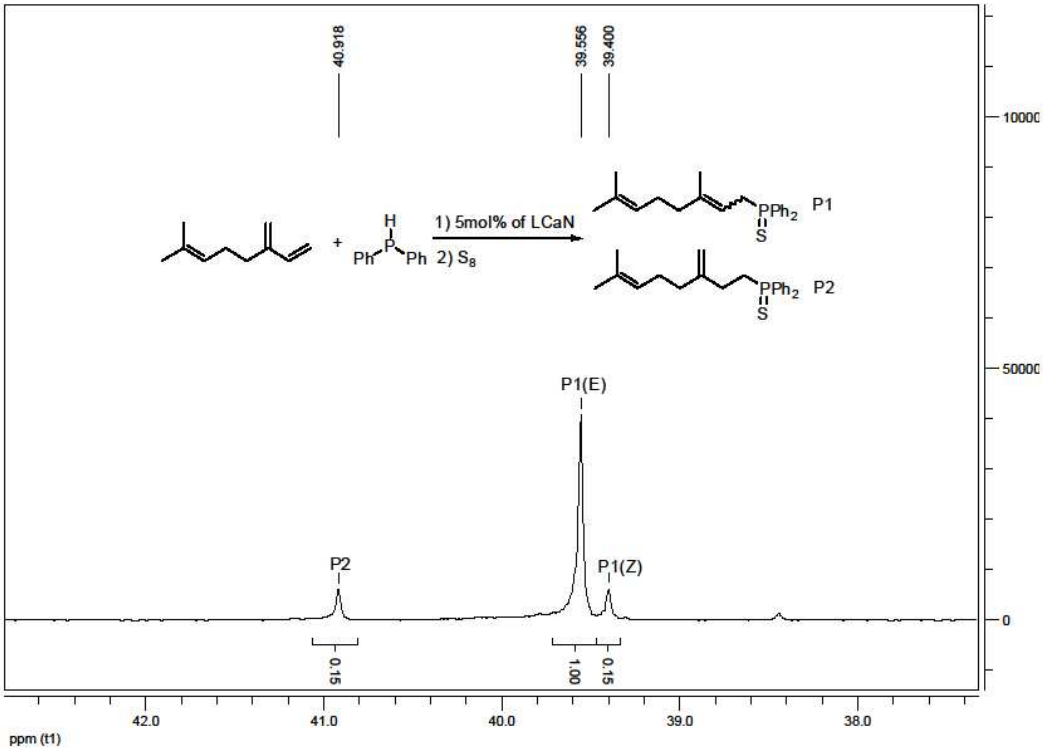


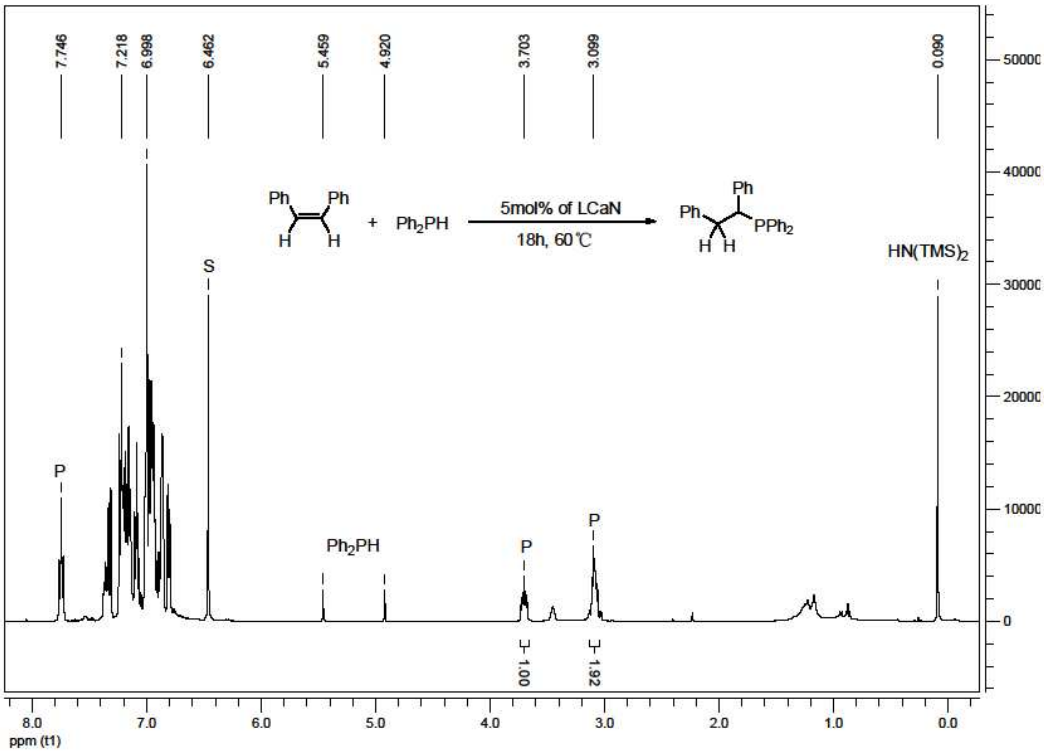


^{1}H NMR for P1(E) (C_6D_6, 400 MHz): 1.39 (s, 3H), 1.54 (s, 1H), 1.58 (m, 1H), 1.65 (m, 1H), 1.96 (m, 2H), 2.02 (m, 3H), 2.76 (d, 2H, 7.6 Hz), 5.10 (m, 1H), 5.30 (m, 1H), 7.08 (m, 6H), 7.44 (m, 4H).

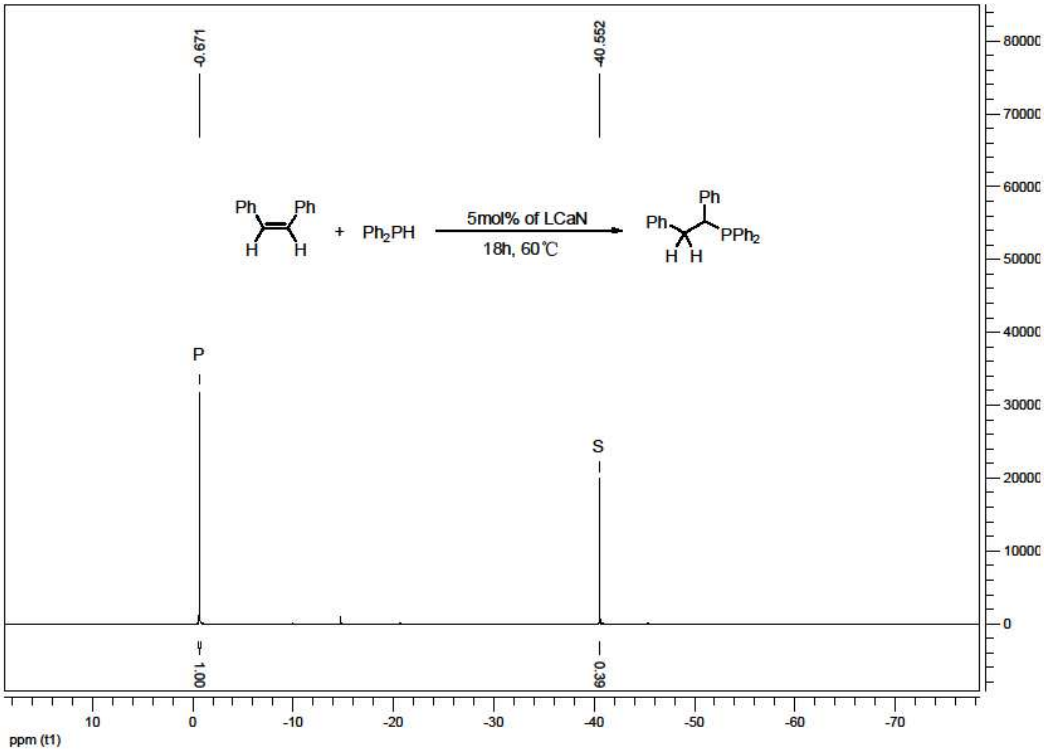


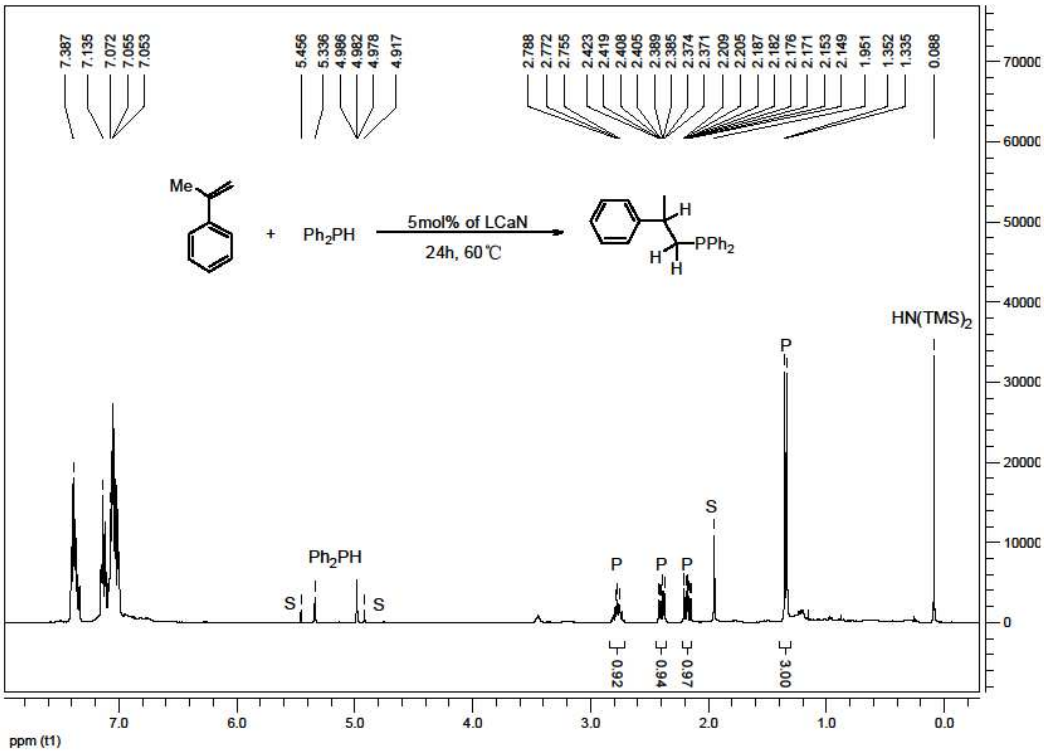

7.804
7.794
7.438
7.426
7.260
5.257
5.241
4.985
4.754
3.282
3.265
3.249
3.230
1.949
1.627
1.539
1.385
1) 5mol% of LCaN
2) S8
P1
P2
Ar-H
CH=CR2
-CH2-P
-CH2-CH2-
-CH3
-CH3
4.38
6.58
1.07
0.99
2.00
4.11
3.33
3.13
2.79
ppm (t1)


40.918
39.556
39.400
1) 5mol% of LCaN
2) S8
P1
P2
P1(E)
P2
P1(Z)
0.15
1.00
0.15
ppm (t1)

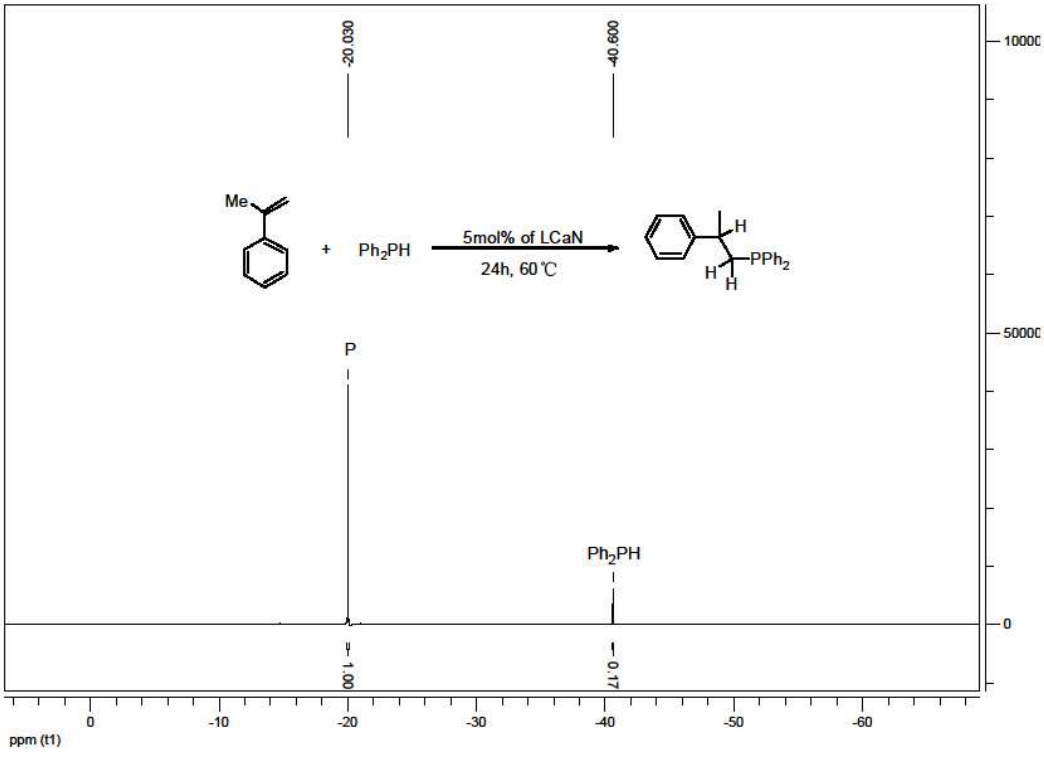


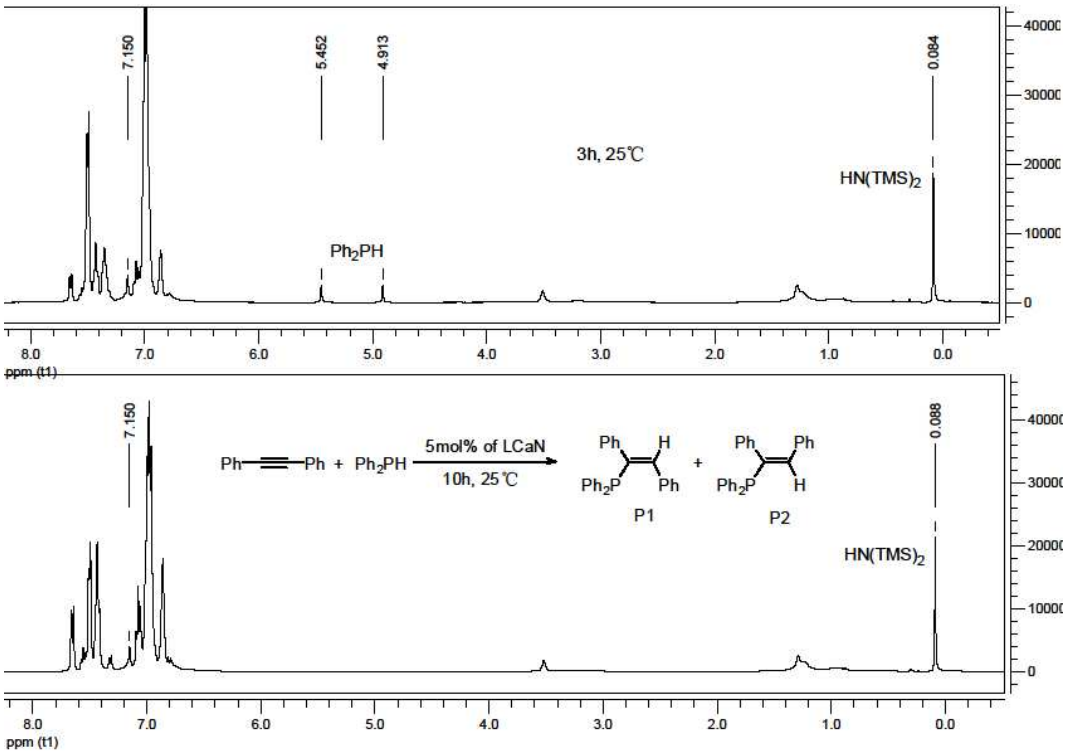
^{1}H NMR for Product (C_6D_6, 400 MHz): 3.10 (m, 2H), 3.70 (m, 1H), 6.81 (m, 2H), 6.86-7.24 (m, 13H), 7.33 (m, 3H), 7.75 (t, 2H, 7.6 Hz).



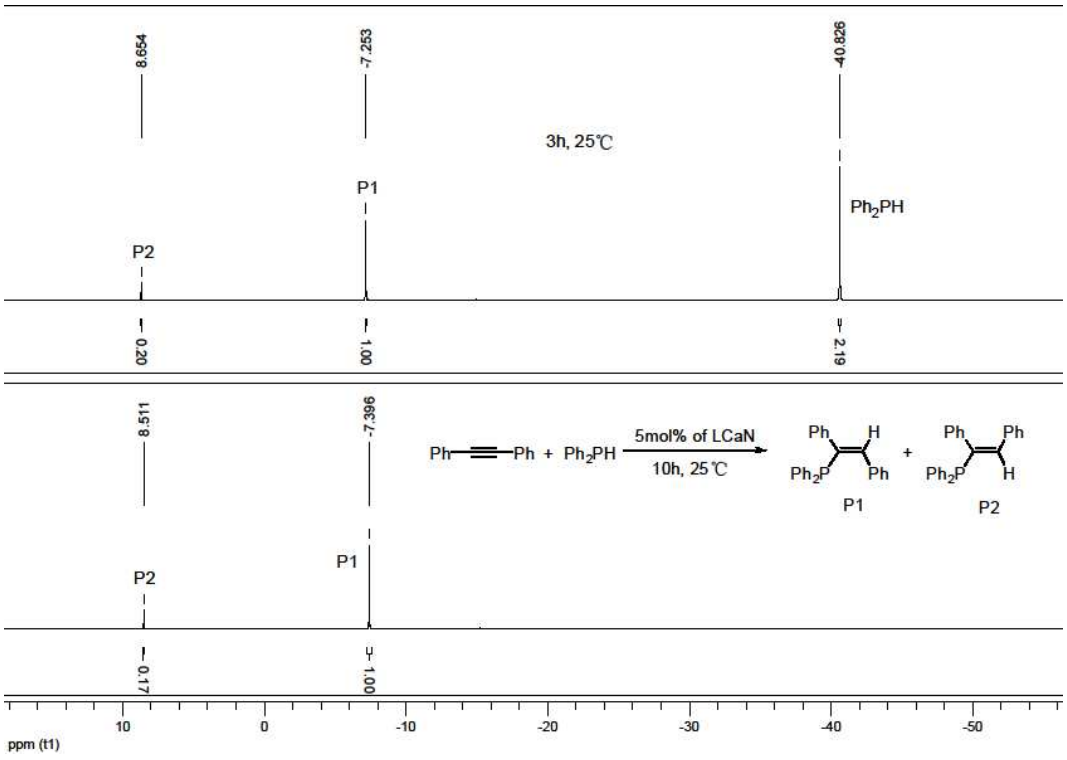


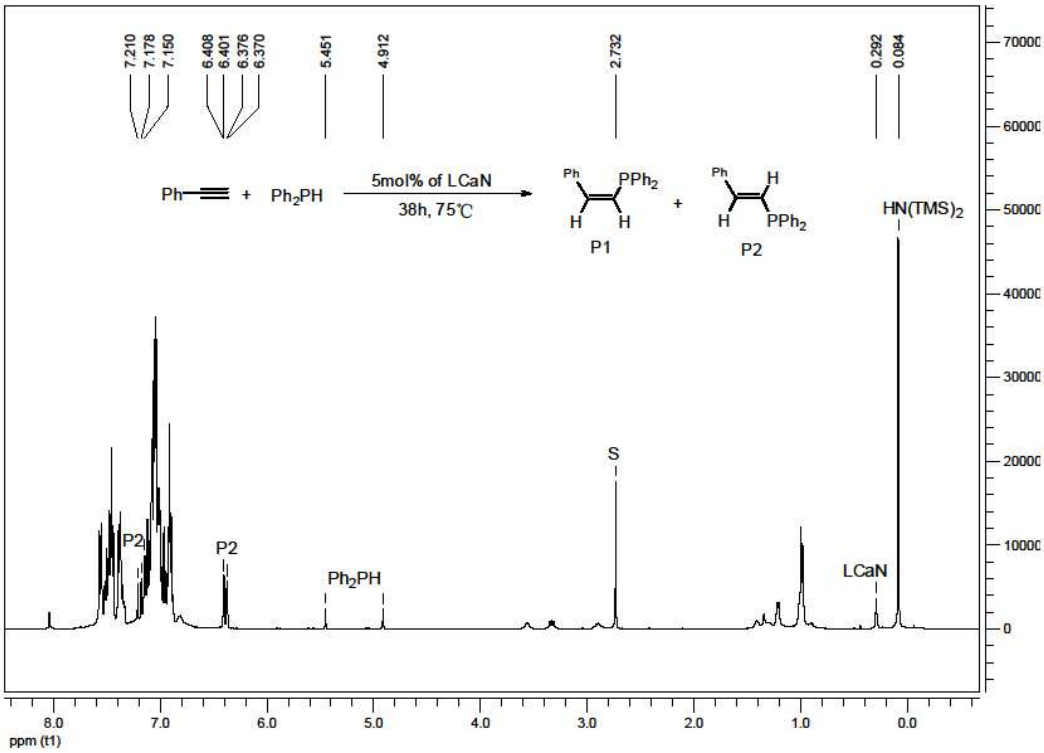
^{1}H NMR for Product (C_6D_6, 400 MHz): 1.34 (d, 3H, 6.8 Hz), 2.18 (m, 1H), 2.39 (m, 1H), 2.77 (sept, 1H, 6.4 Hz), 7.05 (m, 8H), 7.14 (m, 3H), 7.39 (m, 4H).



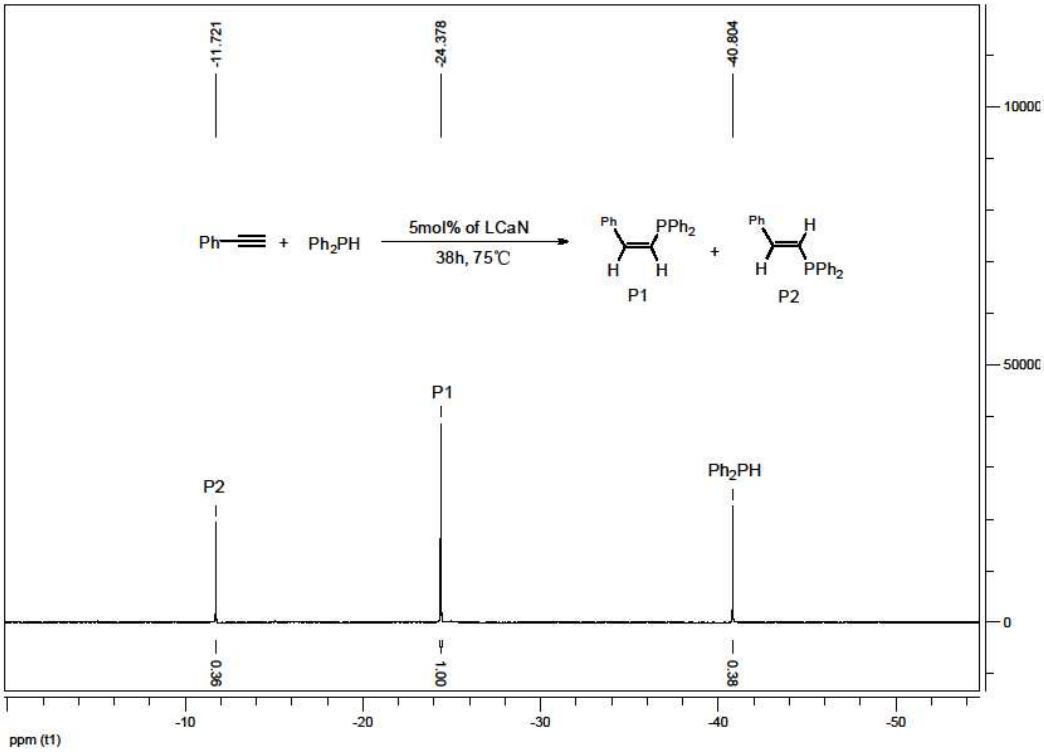


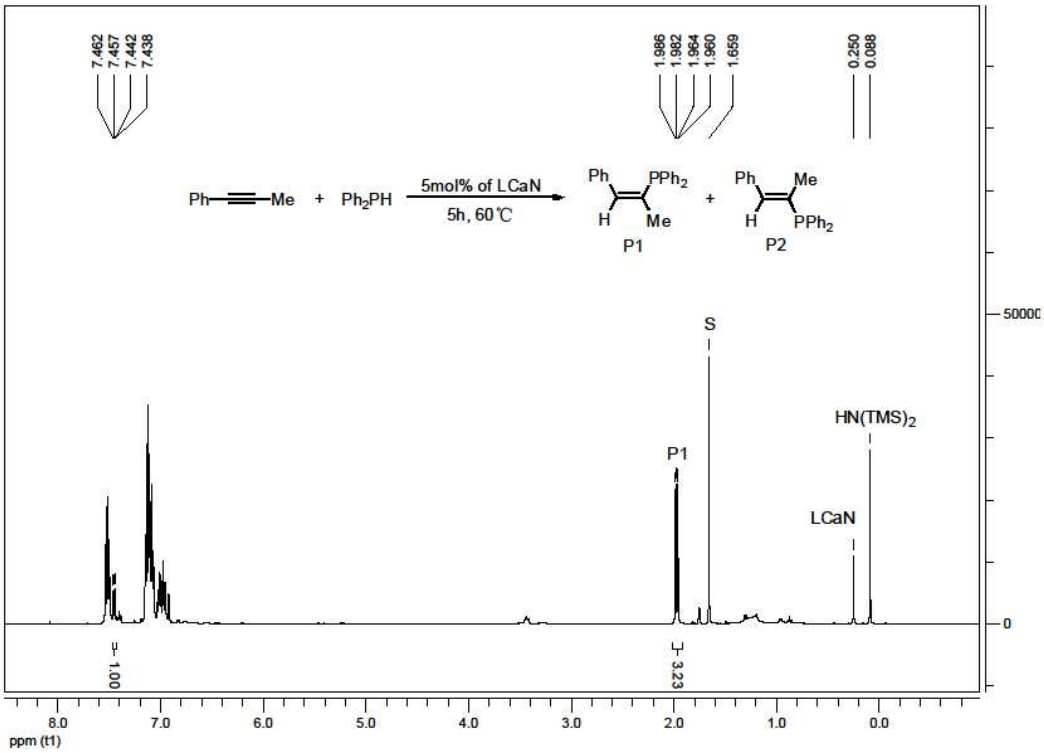
^{1}H NMR for P1 (C_6D_6, 400 MHz): 6.87 (m, 3H), 6.98 (m, 9H), 7.08 (t, 2H, 7.6 Hz), 7.44 (m, 3H), 7.50 (m, 3H), 7.65 (d, 1H, 7.6 Hz).



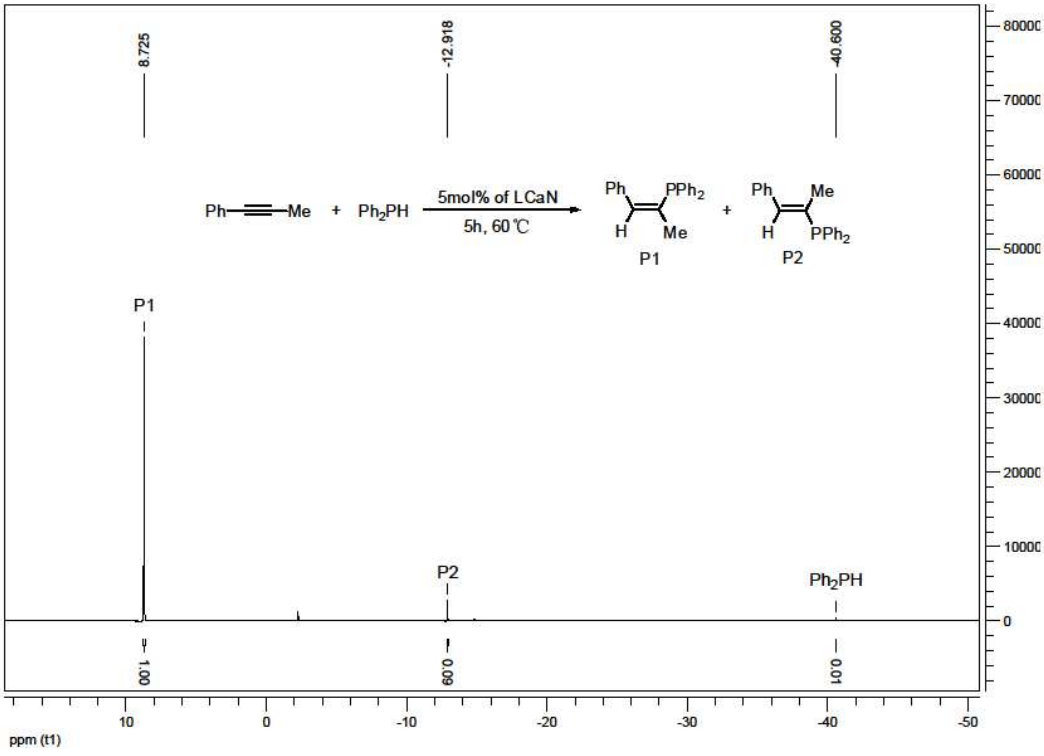


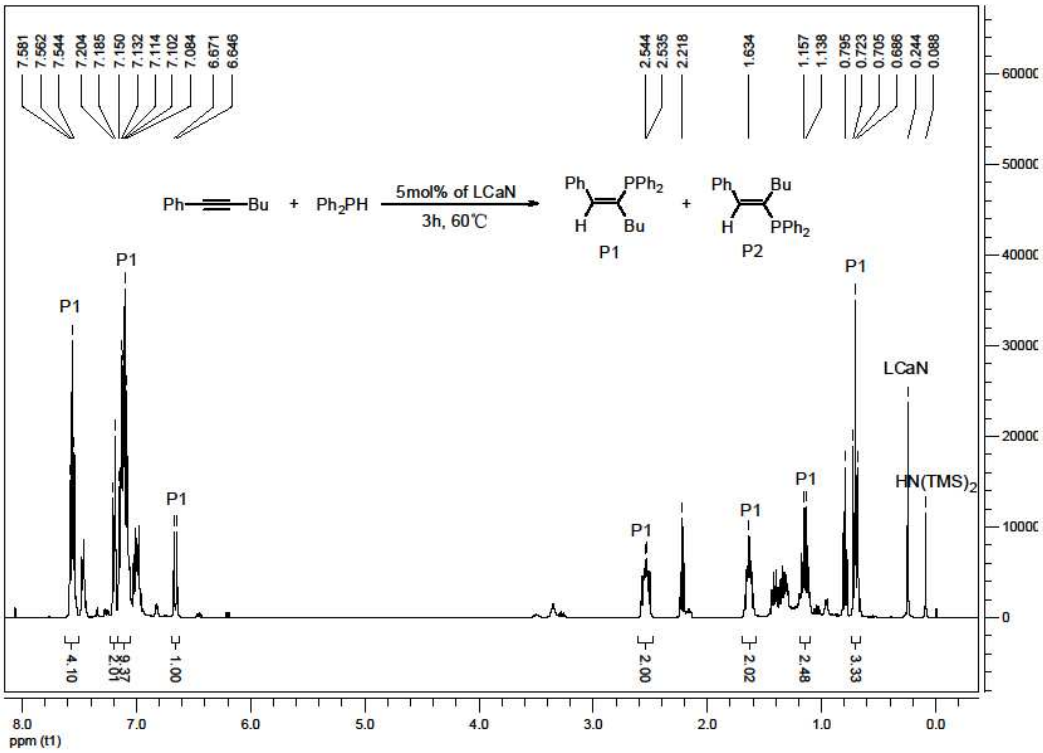
^{1}H NMR for P1 (C_6D_6, 400 MHz): 6.39 (dd, 1H, 8.8 Hz, 2.4 Hz), 7.00-7.12 (m, 9H), 7.19 (d, 1H, 8.8 Hz), 7.45 (m, 4H), 7.56 (d, 2H, 8.0 Hz).



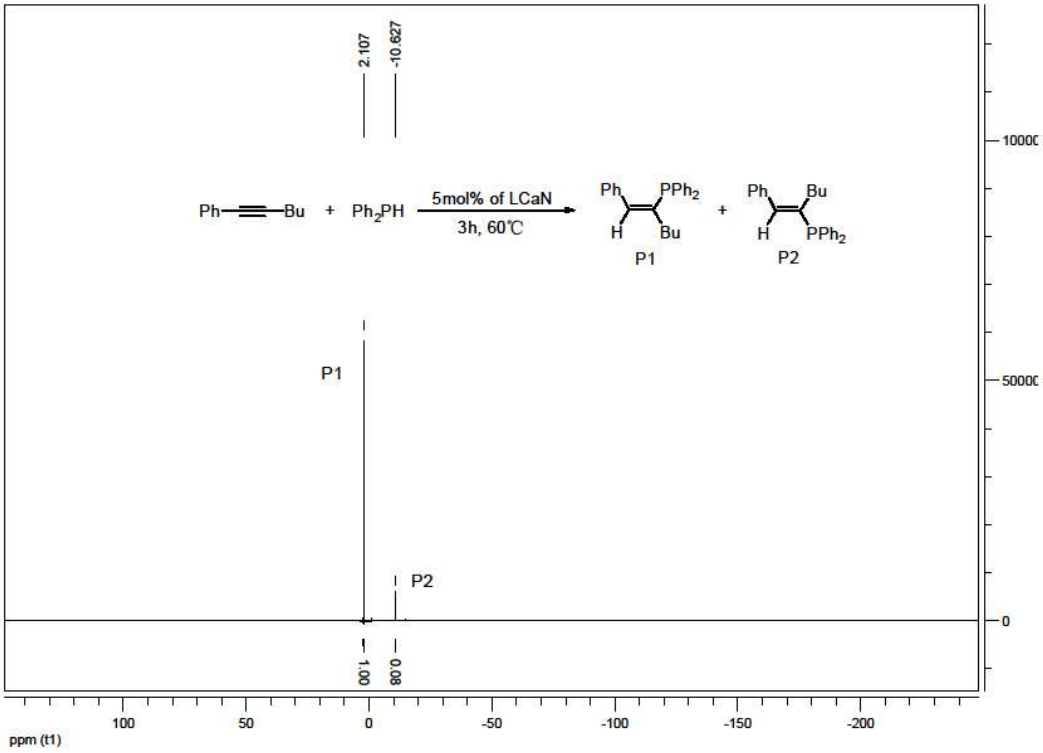


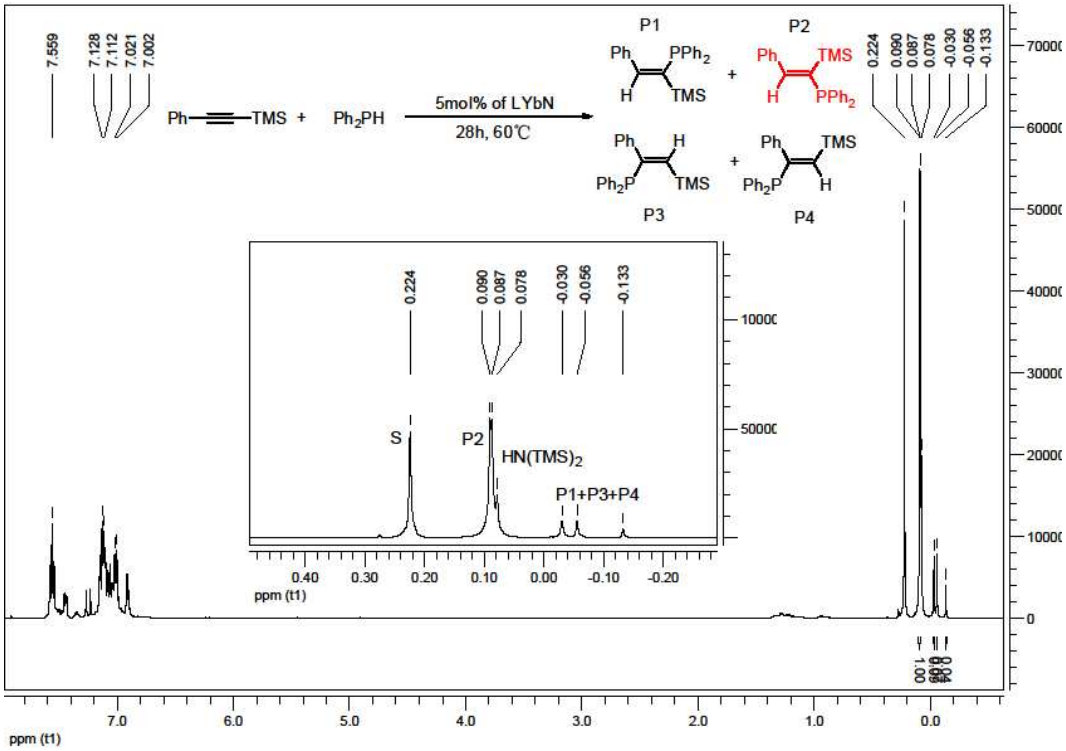
^{1}H NMR for P1 (C_6D_6, 400 MHz): 1.97 (dd, 3H, 8.8 Hz, 0.8 Hz), 7.07-7.15 (m, 12H), 7.52 (m, 3H).



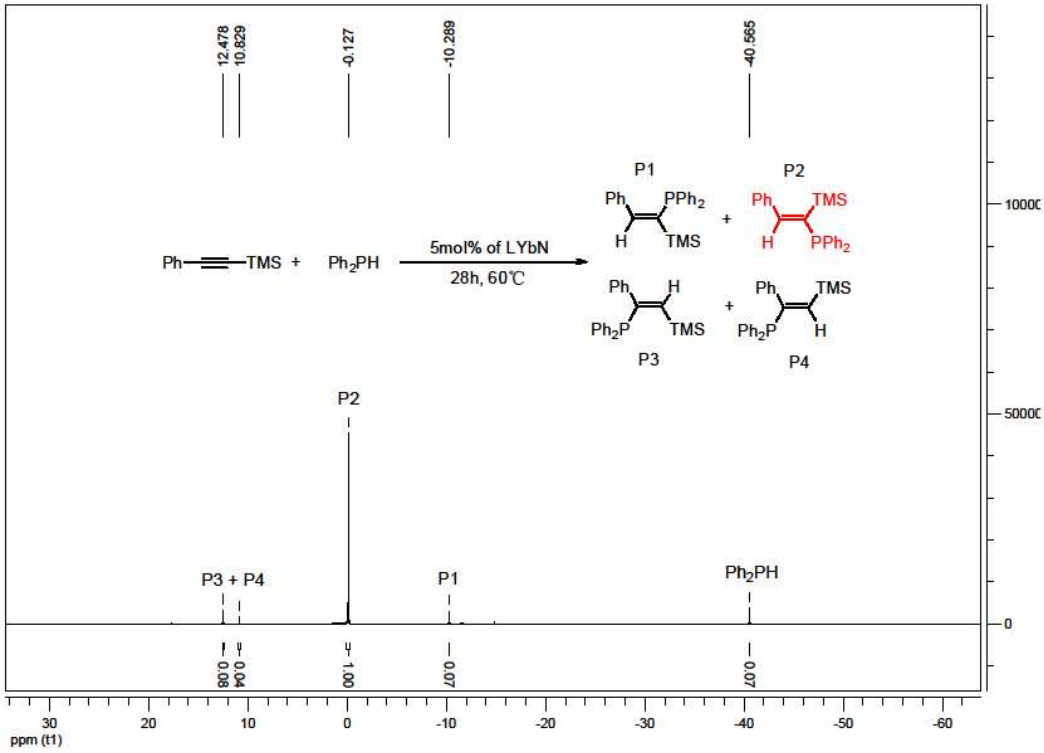


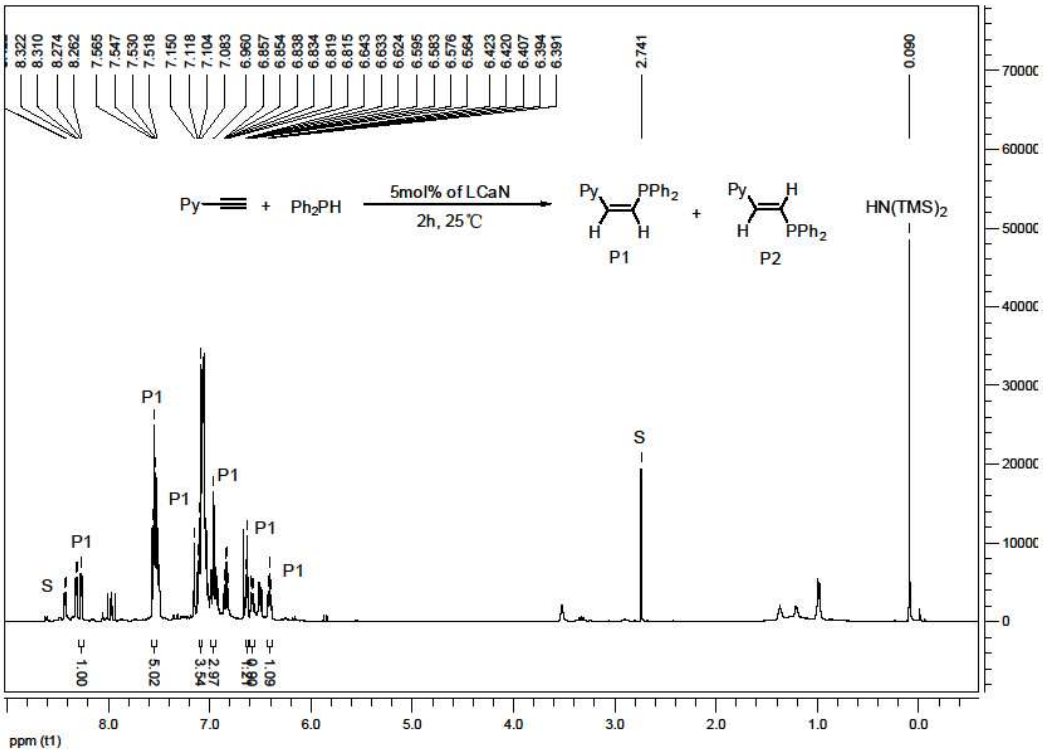
^{1}H NMR for P1 (C_6D_6, 400 MHz): 0.71 (t, 3H, 7.6 Hz), 1.15 (m, 2H), 1.63 (m, 2H), 2.54 (m, 2H), 6.66 (d, 1H, 10.0 Hz), 7.08-7.13 (m, 9H), 7.19 (d, 2H, 7.6 Hz), 7.56 (t, 4H, 7.6 Hz).



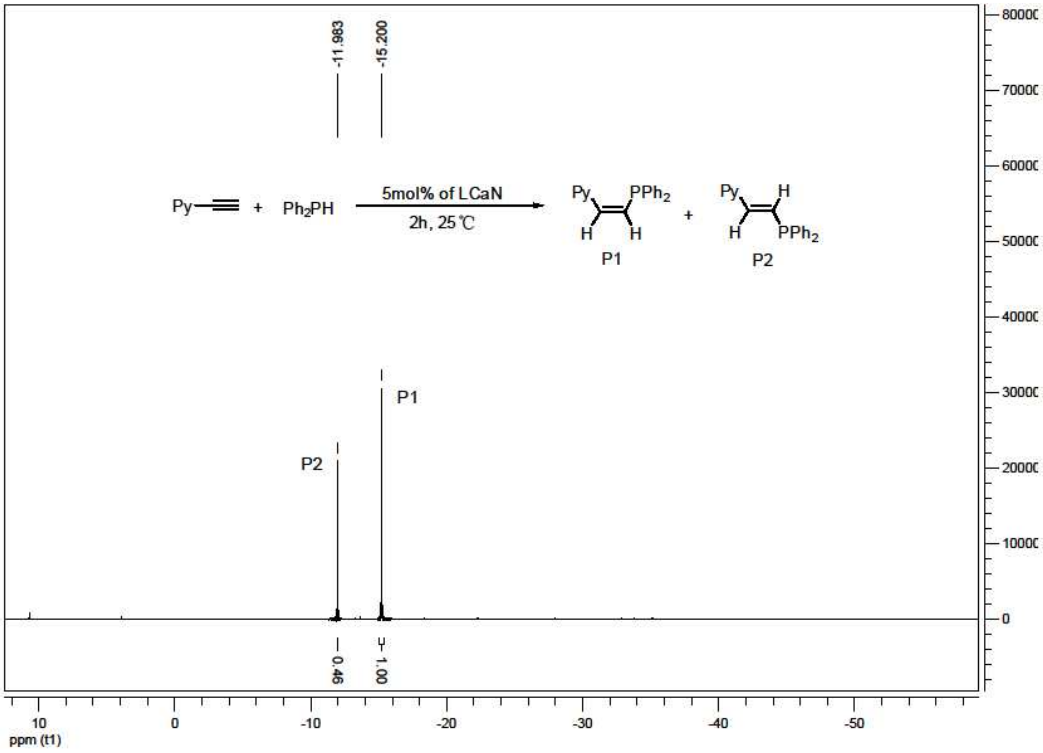


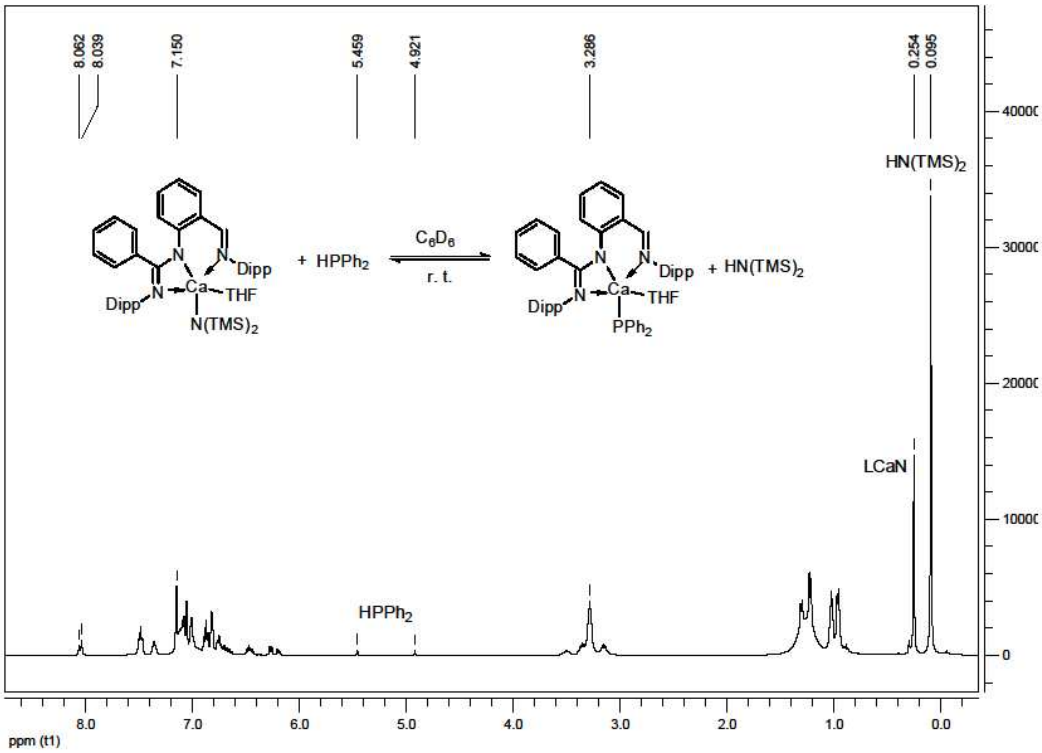
^{1}H NMR for P2 (C_6D_6, 400 MHz): 0.09 (d, 9H, 1.2 Hz), 7.01 (m, 5H), 7.12 (m, 5H), 7.25 (d, 1H, 14.4 Hz), 7.56 (m, 5H).

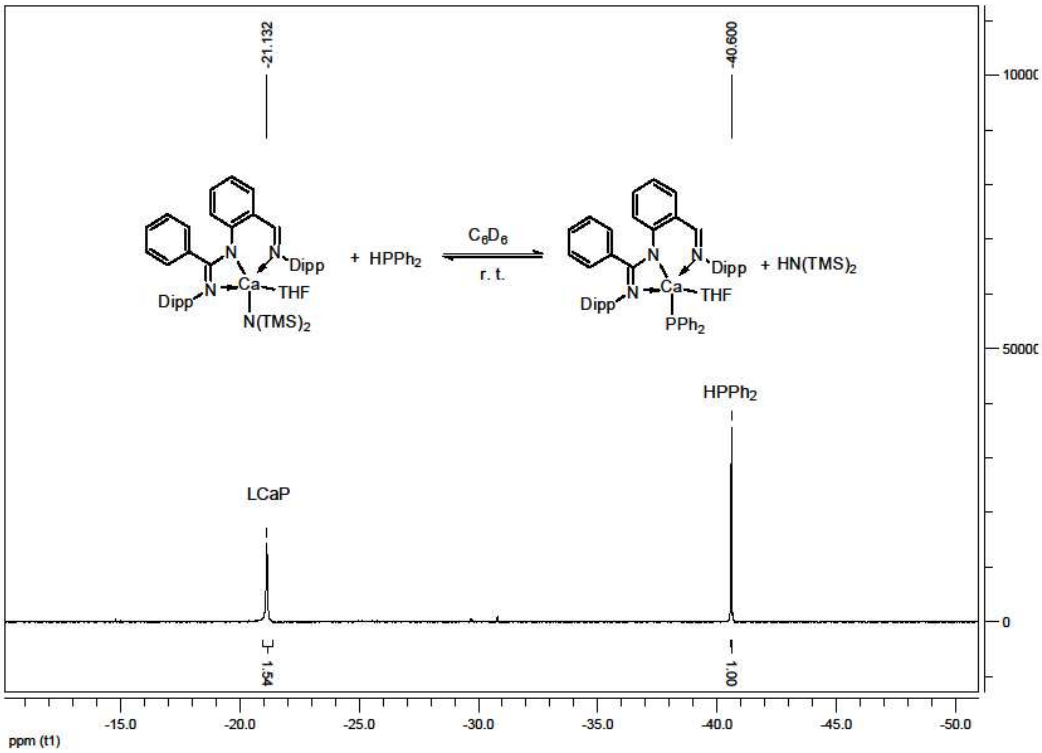




^{1}H NMR for P1 (C_6D_6, 400 MHz): 6.41 (m, 1H), 6.58 (m, 1H), 6.63 (t, 1H, 3.6 Hz), 6.96 (m, 3H), 7.09 (m, 4H), 7.54 (m, 5H), 8.27 (d, 1H, 4.8 Hz).




8.062
8.039
7.150
5.459
4.921
3.286
0.254
0.095
HN(TMS)2
LCaN
HPPh2
+ HPPh2
C6D6
r. t.
+ HN(TMS)2
Dipp
THF
N(TMS)2
PPh2
ppm (t1)


-21.132
-40.600
HPPh2
LCaP
1.54
1.00
+ HPPh2
C6D6
r. t.
+ HN(TMS)2
Dipp
THF
N(TMS)2
PPh2
ppm (t1)