

**Homoleptic Iron(II) and Cobalt(II) Bis (phosphoranimide)
Complexes for Selective Hydrofunctionalization of Unsaturated
Molecules**

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I. General Methods

Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates, glass.

Visualization on TLC was achieved by the use of UV light (254 nm).

Flash column chromatography was undertaken on silica gel (300-400 mesh).

The purity of nitrogen gas is 99.999%.

Air sensitive liquid and solutions were manipulated by using glove box and dry solvents. The catalytic reactions were performed under glove box (Delix, China) or sealed thick glass tube purchased from Synthware Company (BeiJing) under nitrogen atmosphere.

THF, benzene and deuterated benzene were distilled from Na metal under nitrogen protected solvent purification system obtained from Synthware Company. Pentane and Hexane was dried by the sodium-potassium alloy method using the same drying system above. Concentration of solution was carried out by using a rotary evaporator and generally followed by removal of residual solvents on a vacuum line held at 0.1–1 torr. Unless otherwise stated, all commercial reagents were used without additional purification. Alkyne, boron compounds and deuterated solvents were purchased from Aldrich chemical company, Strem or Aladdin.

Proton nuclear magnetic resonance spectra were recorded on Bruker Avance 400MHz or 600MHz, Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak (CHCl_3 in CDCl_3 : 7.24 ppm; C_6H_6 in C_6D_6 : 7.16 ppm). Mesitylene was used in the reaction condition optimization step for the clarification of product yield. The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet. Coupling constants, J , were reported in Hertz unit (Hz).

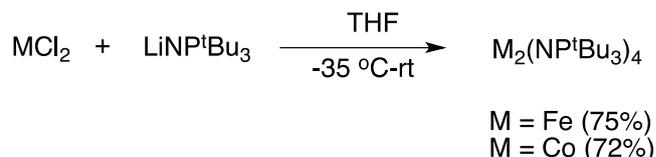
Carbon 13 nuclear magnetic resonance spectroscopy (^{13}C NMR) was recorded on Bruker Avance (100MHz) or 150MHz and was fully decoupled by broad band decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.23 ppm of chloroform-d and 128.39 ppm of C_6D_6 .

Phosphorus 31 nuclear magnetic resonance spectroscopy (^{31}P NMR) was recorded on Bruker Avance 243MHz and phosphoric acid was used as external standard.

Infrared (IR) spectra were recorded on Thermo Scientific Nicolet iS50. Frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance is reported.

High Resolution mass spectra were obtained by using Thermo Scientific Q Exactive (API or ESI as ion source) Melting points was measured using RD-II manufactured by Tianjin optical instrument factory. The diffraction data of X-ray crystal were collected on a Bruker APEX-II CCD diffractometer. A suitable size and quality of crystal was coated with Paratone-N oil and mounted on a glass top purchased from Bruker. The data were collected with graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Cell parameters were determined and refined by SHELXL-2014/7 (Sheldrick, 2014) program. Data reduction was performed using Bruker SAINT software.

II. Procedure of making iron and cobalt complexes A and B



Procedure of making iron complex A

In glove box with O₂ and H₂O level <0.1 ppm, FeCl₂ (76.2 mg, 0.60 mmol) was suspended in THF (6 mL) and put into fridge at (-35°C) around 30 mins, then the suspension of LiNP^tBu₃ (261.2 mg, 1.95 eq., 1.17 mmol) in THF (6 mL) was added. The color immediately changed to brown then to deep green. After 13 hours of stirring at room temperature, the THF was removed under reduced pressure. The deep green residue was extracted with hexane, filtered through celite, concentrated, cooled to -35°C for another 13 hours, then filtered through celite again. The solvent was removed under reduced pressure to afford complex **A** (219.8 mg, 75%, yellow-green powder). X-ray quality crystals were grown from a concentrated pentane or hexane solution at -35°C. Anal. Calcd for C₄₈H₁₀₈Fe₂N₄P₄: C, 59.01; H, 11.14; N, 5.73. Found: C, 58.55; H, 11.11; N, 5.43; ¹H NMR (600 MHz, C₆D₆) δ 5.59 (br s); 3.88 (br s); 1.41-0.49 (br m); there is no obvious peak on ³¹P NMR spectrum.

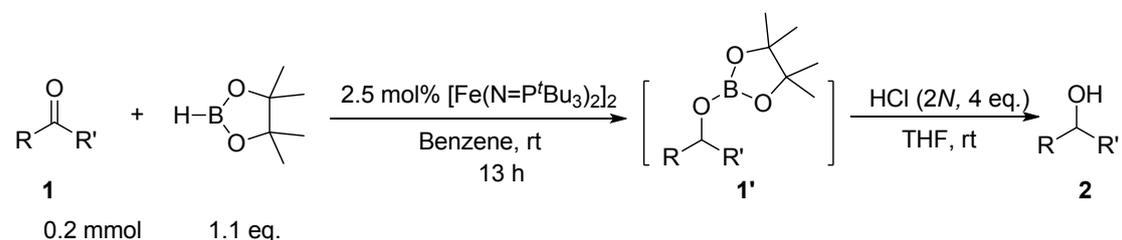
Procedure of making cobalt complex B

The procedure was similar with making iron complex.

CoCl₂ (77.9 mg, 0.6 mmol), LiNP^tBu₃ (261.2 mg, 1.95 eq., 1.17 mmol) to afford complex **B** as deep green powder (212.3 mg, 72%); Anal. Calcd for C₄₈H₁₀₈Co₂N₄P₄: C, 58.64; H, 11.07; N, 5.70. Found: C, 58.58; H, 11.12; N, 5.33; ¹H NMR (600 MHz, C₆D₆) δ 3.67 (br s); 1.32-0.25 (br m); there is no obvious peak on ³¹P NMR spectrum.

III. Procedure of Fe(bis-phosphoranimide) catalyzed hydroboration

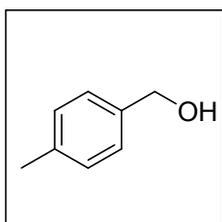
reaction of aldehydes and ketones.



In an N₂ charged glove box with oxygen and water levels ≤0.1 ppm, to an oven-dried screwed vial were added [Fe(N=P^tBu₃)₂]₂ (4.9 mg, 2.5 mol%) and dry benzene (2 mL) to give a light yellow solution, then HB(pin) (28 mg, 1.1 eq.) was added to form the dark solution immediately followed by the addition of Aldehyde or Ketone substrates (0.2 mmol). The resulting mixture was kept stirring under room temperature in glove box for 13 hours to form the intermediate **1'**. After the

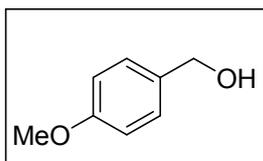
first step was completed, the volatile was removed directly by rotary evaporation and THF (2 mL) and diluted HCl (2*N*, 4 eq.) were added into the residue. The formed mixture was stirred for another 10 hours (for Aldehyde substrates) or 30 mins (for Ketone substrates) under room temperature. After the second step was accomplished, the reaction mixture was diluted with water (5 mL) and extracted with ether (5 mL×3 times). The organic phase was combined and washed 2 times with Brine. Then the ether solution was collected and the product was isolated and purified by short column chromatography (Hexane/Ethyl acetate) to get pure product of **2**.

4-Methyl benzyl alcohol (**2a**, Table 2).^{S1}



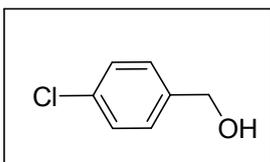
Eluent Hexane/Ethyl acetate. Colorless Oil (18 mg, 74%), ¹H NMR (600 MHz, CDCl₃) δ 7.31 (2H, d, *J* = 6 Hz), 7.23 (2H, d, *J* = 6 Hz), 4.69 (2H, s), 2.42 (3H, s), 1.88 (1H, br s); ¹³C NMR (150 MHz, CDCl₃) δ 138.11, 137.58, 129.43, 127.31, 65.43, 21.34.

4-Methoxy benzyl alcohol (**2b**, Table 2).^{S1}



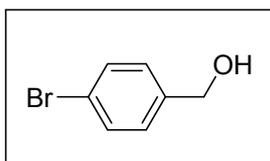
Eluent Hexane/Ethyl acetate. Colorless Oil (18 mg, 79%), ¹H NMR (600 MHz, CDCl₃) δ 7.27 (2H, d, *J* = 6 Hz), 6.87 (2H, d, *J* = 6 Hz), 4.58 (2H, s), 3.78 (3H, s), 1.86 (1H, br s); ¹³C NMR (150 MHz, CDCl₃) δ 159.37, 133.32, 128.83, 114.13, 65.18, 55.48.

4-Chloride benzyl alcohol (**2c**, Table 2).^{S1}



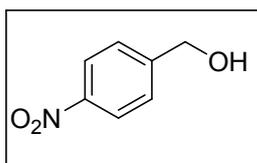
Eluent Hexane/Ethyl acetate. White solid (22 mg, 77%), ¹H NMR (600 MHz, CDCl₃) δ 7.30 (2H, d, *J* = 6 Hz), 7.26 (2H, d, *J* = 6 Hz), 4.62 (2H, s), 1.98 (1H, br s); ¹³C NMR (150 MHz, CDCl₃) δ 139.43, 133.53, 128.86, 128.46, 64.69.

4-Bromide benzyl alcohol (**2d**, Table 2).^{S1}



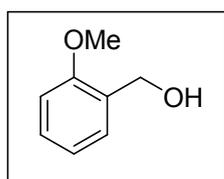
Eluent Hexane/Ethyl acetate. White solid (32 mg, 85%), ¹H NMR (600 MHz, CDCl₃) δ 7.46 (2H, d, *J* = 6 Hz), 7.21 (2H, d, *J* = 6 Hz), 4.62 (2H, s), 1.79 (1H, br s); ¹³C NMR (150 MHz, CDCl₃) δ 139.97, 131.83, 128.79, 121.66, 64.77.

4-Nitro benzyl alcohol (**2e**, Table 2).^{S1}



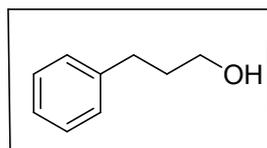
Eluent Hexane/Ethyl acetate. White solid (23 mg, 75%), ^1H NMR (600 MHz, CD_2Cl_2) δ 8.19 (2H, d, $J = 6$ Hz), 7.53 (2H, d, $J = 6$ Hz), 4.81 (2H, s), 2.12 (1H, br s); ^{13}C NMR (150 MHz, CDCl_3) δ 149.21, 147.80, 127.51, 124.12, 64.38.

2-Methoxybenzyl alcohol (2f, Table 2).^{S1}



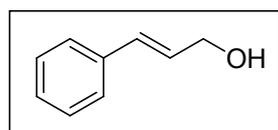
Eluent Hexane/Ethyl acetate. Colorless oil (23 mg, 83%), ^1H NMR (600 MHz, C_6D_6) δ 7.30 (1H, d, $J = 6$ Hz), 7.07 (1H, t, $J = 6$ Hz), 6.86 (1H, t, $J = 6$ Hz), 6.47 (1H, d, $J = 6$ Hz), 4.70 (2H, s), 3.20 (3H, s), 2.18 (1H, br s); ^{13}C NMR (150 MHz, C_6D_6) δ 157.76, 130.59, 128.86, 128.81, 121.20, 110.52, 61.76, 54.99.

3-Phenylpropan-1-ol (2g, Table 2).^{S1}



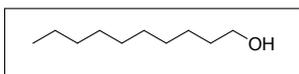
Eluent Hexane/Ethyl acetate. Colorless oil (26 mg, 95%), ^1H NMR (600 MHz, CDCl_3) δ 7.28 (2H, d, $J = 6$ Hz), 7.19 (3H, t, $J = 6$ Hz), 3.66 (2H, t, $J = 6$ Hz), 2.70 (2H, t, $J = 6$ Hz), 1.89 (2H, quint, $J = 6$ Hz), 1.50 (1H, br s); ^{13}C NMR (150 MHz, CDCl_3) δ 142.01, 128.62, 128.59, 126.06, 62.45, 34.41, 32.26.

(E)-3-Phenylprop-2-en-1-ol (2h, Table 2).^{S1}



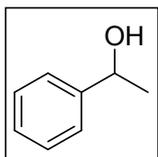
Eluent Hexane/Ethyl acetate. Colorless oil (23.6 mg, 88%), ^1H NMR (600 MHz, C_6D_6) δ 7.22 (2H, d, $J = 6$ Hz), 7.13 (2H, t, $J = 6$ Hz), 7.05 (1H, t, $J = 6$ Hz), 6.42 (1H, d, $J = 18$ Hz), 6.08 (1H, td, $J = 18, 6$ Hz), 3.92 (2H, d, $J = 6$ Hz), 1.36 (1H, br s); ^{13}C NMR (150 MHz, C_6D_6) δ 137.81, 130.79, 129.84, 129.18, 128.04, 127.11, 63.75.

Decan-1-ol (2i, Table 2).^{S1}



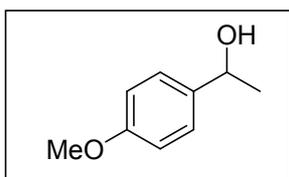
Eluent Hexane/Ethyl acetate. Colorless oil (26 mg, 82%), ^1H NMR (600 MHz, CDCl_3) δ 3.61 (2H, t, $J = 6$ Hz), 1.54 (2H, quint, $J = 6$ Hz), 1.45 (1H, br s), 1.35-1.19 (14H, m), 0.85 (3H, t, $J = 6$ Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 63.30, 33.01, 32.11, 29.83, 29.77, 29.65, 29.53, 25.95, 22.89, 14.31.

1-phenylethanol (2j, Table 2).^{S1}



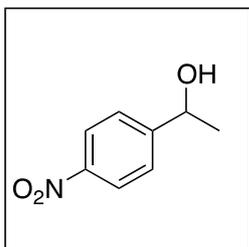
Eluent Hexane/Ethyl acetate. Colorless oil (16 mg, 65%), ^1H NMR (600 MHz, CDCl_3) δ 7.36 (2H, d, $J = 6$ Hz), 7.32 (2H, d, $J = 6$ Hz), 7.25 (1H, t, $J = 6$ Hz), 4.88 (1H, q, $J = 6$ Hz), 1.85 (1H, br s), 1.49 (3H, d, $J = 6$ Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 146.01, 128.70, 127.67, 125.58, 70.61, 25.35.

1-(4-Methoxyphenyl)ethanol (2k, Table 2).^{S1}



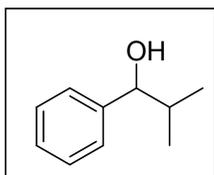
Eluent Hexane/Ethyl acetate. Colorless oil (26 mg, 85%), ^1H NMR (600 MHz, CDCl_3) δ 7.28 (2H, d, $J = 6$ Hz), 6.86 (2H, d, $J = 6$ Hz), 4.82 (1H, q, $J = 6$ Hz), 3.78 (3H, s), 1.96 (1H, br s), 1.45 (3H, d, $J = 6$ Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 159.13, 138.21, 126.84, 114.01, 70.11, 55.46, 25.19.

1-(4-nitrophenyl)ethanol (2l, Table 2).^{S1}



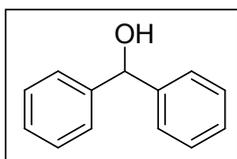
Eluent Hexane/Ethyl acetate. Colorless oil (23 mg, 69%), ^1H NMR (600 MHz, CDCl_3) δ 8.17 (2H, d, $J = 6$ Hz), 7.51 (2H, d, $J = 6$ Hz), 5.00 (1H, q, $J = 6$ Hz), 2.07 (1H, br s), 1.49 (3H, d, $J = 6$ Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 153.27, 147.38, 126.32, 123.96, 69.71, 25.71.

2-Methyl-1-phenylpropan-1-ol (2m, Table 2).^{S1}



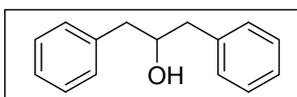
Eluent Hexane/Ethyl acetate. Colorless oil (24 mg, 79%), ^1H NMR (600 MHz, C_6D_6) δ 7.19 (2H, d, $J = 6$ Hz), 7.18 (2H, d, $J = 6$ Hz), 7.09 (1H, t, $J = 6$ Hz), 4.06 (1H, d, $J = 6$ Hz), 1.85-1.78 (1H, m), 1.25 (1H, br s), 0.97 (3H, d, $J = 6$ Hz), 0.75 (3H, d, $J = 6$ Hz); ^{13}C NMR (150 MHz, C_6D_6) δ 144.94, 128.61, 127.73, 127.23, 80.04, 36.06, 19.54, 18.52.

Diphenylmethanol (2n, Table 2).^{S1}



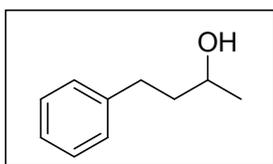
Eluent Hexane/Ethyl acetate. White solid (35 mg, 95%), ^1H NMR (600 MHz, CDCl_3) δ 7.26 (4H, d, $J = 6$ Hz), 7.23 (4H, t, $J = 6$ Hz), 7.16 (2H, d, $J = 6$ Hz), 5.72 (1H, s), 2.23 (1H, br s); ^{13}C NMR (150 MHz, CDCl_3) δ 143.99, 128.69, 127.77, 126.74, 76.44.

1,3-Diphenylpropan-2-ol (2o, Table 2).^{S1}



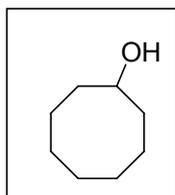
Eluent Hexane/Ethyl acetate. Colorless oil (32 mg, 75%), ^1H NMR (600 MHz, C_6D_6) δ 7.15 (5H, t, $J = 6$ Hz), 7.07 (5H, t, $J = 6$ Hz), 3.85-3.77 (1H, m), 2.66-2.55 (4H, m), 1.32 (1H, br s); ^{13}C NMR (150 MHz, C_6D_6) δ 139.57, 130.19, 128.99, 126.89, 73.98, 44.12.

4-Phenylbutan-2-ol (2p, Table 2).^{S1}



Eluent Hexane/Ethyl acetate. Colorless oil (25 mg, 83%), ^1H NMR (600 MHz, CDCl_3) δ 7.28 (2H, t, $J = 6$ Hz), 7.19 (2H, d, $J = 6$ Hz), 7.17 (1H, d, $J = 6$ Hz), 3.81 (1H, sext., $J = 6$ Hz), 2.78-2.63 (2H, m), 1.82-1.71 (2H, m), 1.50 (1H, br s), 1.21 (3H, d, $J = 6$ Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 140.25, 128.59, 126.00, 67.68, 41.04, 32.33, 23.81.

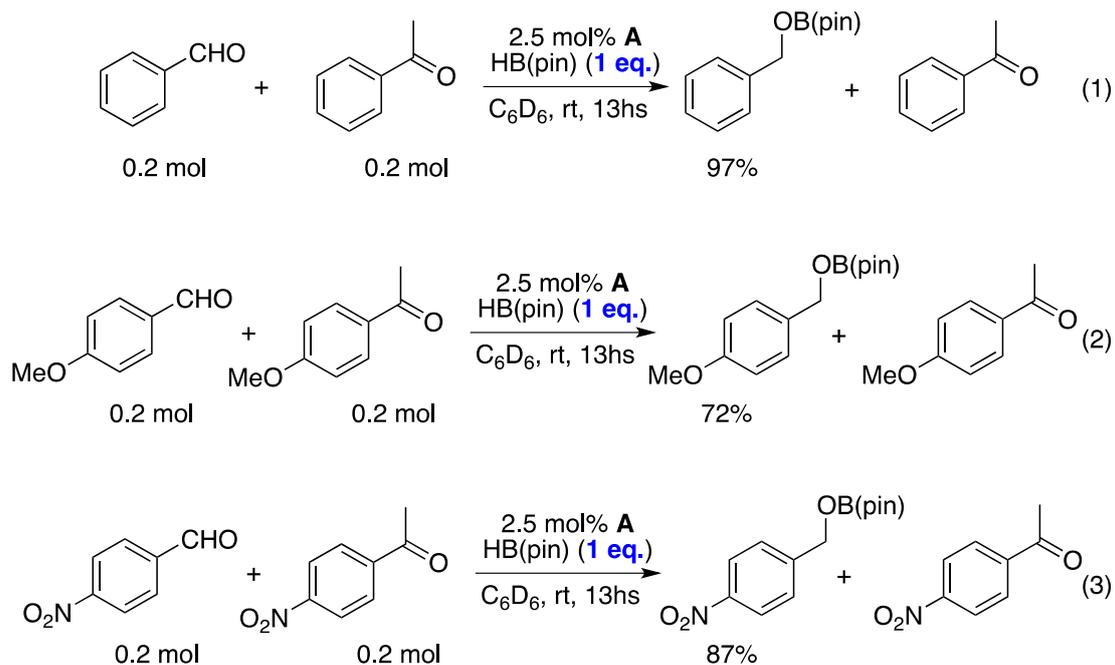
Cyclooctanol (2q, Table 2).^{S1}



Eluent Hexane/Ethyl acetate. Colorless oil (15 mg, 59%), ^1H NMR (600 MHz, C_6D_6) δ 3.63-3.58 (1H, m), 1.69-1.62 (2H, m), 1.61-1.51 (4H, m), 1.47-1.26 (8H, m), 0.87 (1H, br s); ^{13}C NMR (150 MHz, C_6D_6) δ 72.07, 35.32, 28.16, 25.81, 23.30.

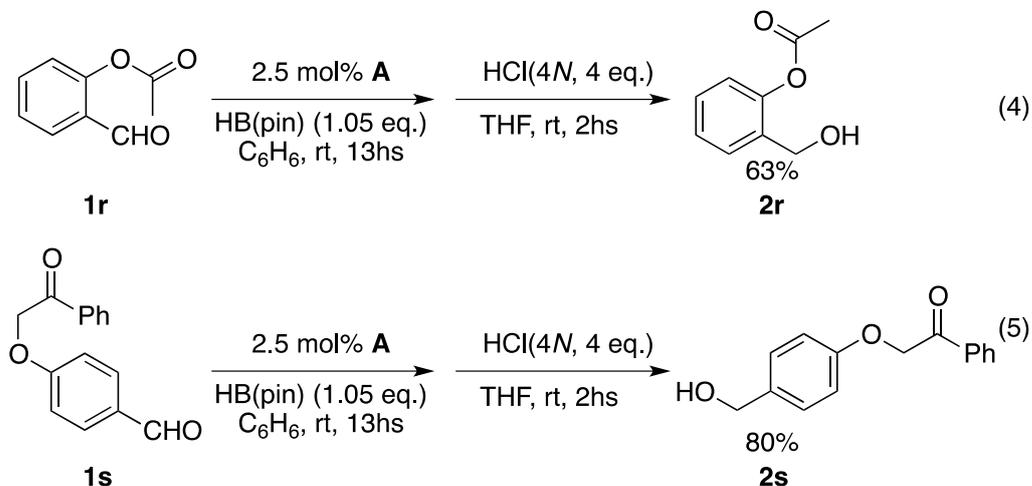
IV. Intermolecular and Intramolecular competing hydroboration reactions of aldehydes and ketones (Scheme 2).

Intermolecular comparison (eqs. 1-3, Scheme 2):



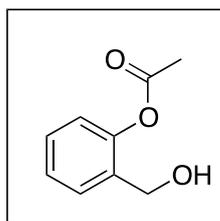
In an N_2 charged glove box with oxygen and water levels ≤ 0.1 ppm, to an oven-dried screwed vial were added $[Fe(N=P^tBu_3)_2]_2$ **A** (4.9 mg, 2.5 mol%) and dry C_6D_6 (2 mL) to give a light yellow solution, then HB(pin) (26 mg, 1.0 eq.) was added to form the dark solution immediately followed by the addition of Aldehyde and Ketone (0.2 mmol/each) into the vial. The resulting mixture was kept stirring under room temperature in glove box for 13 hours. Then the reaction mixture was filtered through short column using celite to get clear filtrate before the NMR test. The NMR yields of borates were determined by the integral of characteristic peaks ($ArCH_2OB(pin)$ and $ArC(O)CH_3$).

Intramolecular comparison (eqs. 4-5, Scheme 2):



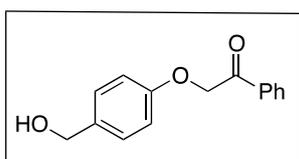
The procedure was same as above (section III). The reaction scale is 0.2 mmol.

2-(Hydroxymethyl)phenyl acetate (2r, Scheme 2).^{S1}



Eluent Hexane/Ethyl acetate. Colorless oil (21 mg, 63%), ¹H NMR (600 MHz, CDCl₃) δ 7.77 (1H, br s), 7.27-7.23 (2H, m), 6.87-6.94 (2H, m), 5.11 (2H, s), 2.09 (3H, s); ¹³C NMR (150 MHz, CDCl₃) δ 173.74, 155.57, 132.17, 131.17, 121.85, 120.68, 117.70, 63.33, 21.05.

2-[4-(Hydroxymethyl)phenoxy]-1-phenylethan-1-one (2s, Scheme 2).^{S1}

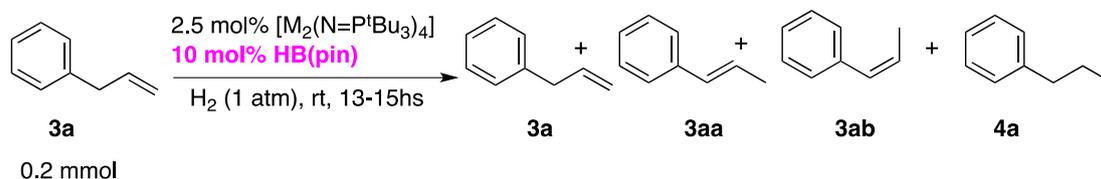


Eluent Hexane/Ethyl acetate. White solid (38 mg, 80%), ¹H NMR (600 MHz, CDCl₃) δ 7.97 (2H, d, *J* = 6 Hz), 7.60 (1H, t, *J* = 6 Hz), 7.48 (2H, t, *J* = 6 Hz), 7.25 (2H, t, *J* = 6 Hz), 6.90 (2H, d, *J* = 6 Hz), 5.25 (2H, s), 4.58 (2H, s), 1.74 (1H, br s); ¹³C NMR (150 MHz, CDCl₃) δ 194.66, 157.77, 134.70, 134.35, 134.12, 129.05, 128.86, 128.31, 115.04, 70.99, 65.08.

V. Procedure of Co(bis-phosphoranimide) catalyzed hydrogenation reaction of alkene and alkyne.

i. Comparison the catalytic activity of Fe and Co(bis-

phosphoranimide) in the hydrogenation reaction of allylbenzene

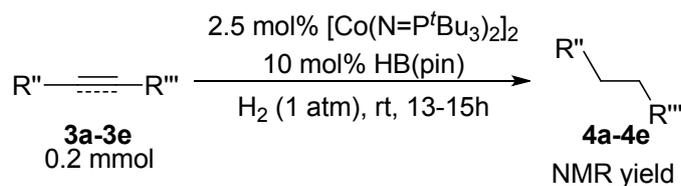


Entry	Metal	NMR yield of products (%) ^a			
		3a	3aa	3ab	4a
1	Fe	14.5	43	4	8
2	Co	0	0	0	82
3	Co ^b	71	0	0	0

^aMesitylene was used as the internal standard; ^bthere is no reaction occur without the participation of HB(pin) at room temperature.

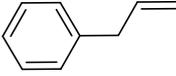
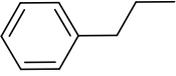
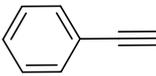
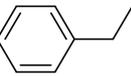
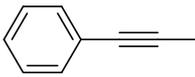
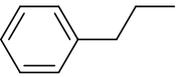
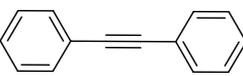
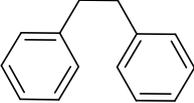
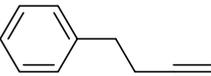
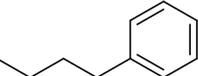
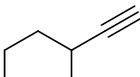
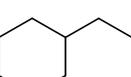
ii. Procedure of Co(bis-phosphoranimide) catalyzed hydrogenation

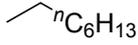
reaction of alkene and alkyne.



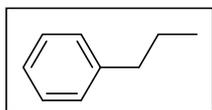
Mesitylene (1 eq.) as internal standard

In an N₂ charged glove box with oxygen and water levels ≤0.1 ppm, to an oven-dried thick wall Schlenk tube with screwed Teflon cap were added [Co(N=P^tBu₃)₂]₂ (4.9 mg, 2.5 mol%) and dry C₆D₆ (2 mL) to give a deep green solution, then HB(pin) (2.5 mg, 10 mol%) was added to form the dark solution immediately followed by the addition of alkene or alkyne substrates (0.2 mmol). The resulting mixture was taken out of the box and purged with hydrogen (purity 99.99%) under Schlenk vacuum line cooling with liquid nitrogen for 3 times. The screwed Teflon cap was closed under 1atm of H₂. The formed mixture was stirred for another 13 hours under room temperature. Then, the mesitylene (27μL, 0.8637 g/cm³, 0.2 mmol) was added into the mixture. The metal residue was filtrated off through the short silica gel column and washed with C₆D₆ (0.1 mL×2) at the same time. The organic filtrate was combined and the yield was measured by the analysis of ¹H NMR.

entry	Substrates 3	Products 4	NMR Yield of 4 (%)
1	 3a	 4a	82
2	 3b	 4b	81
3	 3c	 4a	83
4	 3d	 4c	>99%
5	 3e	 4d	83
6	 3f	 4e	92

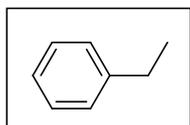
7	\equiv ⁿ C ₆ H ₁₃ 3g	 ⁿ C ₆ H ₁₃ 4f	80
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Propylbenzene (4a, Table 3).^{S2}



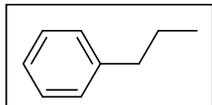
NMR yield 82%; ¹H NMR (600 MHz, C₆D₆) δ 7.17 (1.59 H, *t*, *J* = 6 Hz), 7.08 (0.59 H, *d*, *J* = 6 Hz), 7.05 (1.67 H, *d*, *J* = 6 Hz), 6.72 (3 H, *s*, Ph-*H* of Mesitylene), 2.42 (1.58 H, *t*, *J* = 6 Hz), 2.16 (9 H, *s*, CH₃ of Mesitylene), 1.51 (1.60 H, *sext.*, *J* = 6 Hz), 0.83 (2.46 H, *t*, *J* = 6 Hz).

Ethylbenzene (4b, Table 3).^{S2}



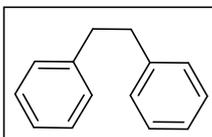
NMR yield 81%; ¹H NMR (600 MHz, C₆D₆) δ 7.17-7.13 (3H, *m*), 7.05 (1 H, *d*, *J* = 6 Hz), 7.04 (1 H, *d*, *J* = 6 Hz), 6.72 (3 H, *s*, Ph-*H* of Mesitylene), 2.42 (1.53 H, *q*, *J* = 6 Hz), 2.16 (9 H, *s*, CH₃ of Mesitylene), 1.06 (2.21 H, *t*, *J* = 6 Hz).

Propylbenzene (4a, Table 3).^{S2}



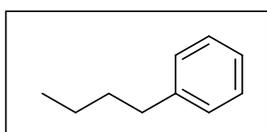
NMR yield 83%; ¹H NMR (600 MHz, C₆D₆) δ 7.17 (3 H, *t*, *J* = 6 Hz), 7.08 (0.57 H, *d*, *J* = 6 Hz), 7.05 (1.74 H, *d*, *J* = 6 Hz), 6.72 (3 H, *s*, Ph-*H* of Mesitylene), 2.41 (1.56 H, *t*, *J* = 6 Hz), 2.15 (9 H, *s*, CH₃ of Mesitylene), 1.51 (1.71 H, *sext.*, *J* = 6 Hz), 0.82 (2.48 H, *t*, *J* = 6 Hz).

1,2-Diphenylethane (4c, Table 3).^{S2}



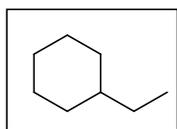
NMR yield >99%; ¹H NMR (600 MHz, C₆D₆) δ 7.15-7.11 (4 H, *m*), 7.07 (2 H, *t*, *J* = 6 Hz), 6.99 (4 H, *d*, *J* = 6 Hz), 6.72 (3 H, *s*, Ph-*H* of Mesitylene), 2.42 (1.58 H, *t*, *J* = 6 Hz), 2.74 (4 H, *s*), 2.16 (9 H, *s*, CH₃ of Mesitylene).

Butylbenzene (4d, Table 3).^{S2}



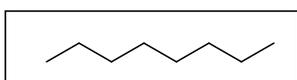
NMR yield 83%; ¹H NMR (600 MHz, C₆D₆) δ 7.20-7.15 (3 H, *m*), 7.10-7.05 (2 H, *m*), 6.72 (3 H, *s*, Ph-*H* of Mesitylene), 2.47 (1.85 H, *t*, *J* = 6 Hz), 2.16 (9 H, *s*, CH₃ of Mesitylene), 1.48 (1.72 H, *quint.* *J* = 6 Hz), 1.23 (1.76 H, *sext.* *J* = 6 Hz), 0.84 (2.5 H, *t*, *J* = 6 Hz).

Ethylcyclohexane (4e, Table 3).^{S2}



NMR yield 92%; ¹H NMR (600 MHz, C₆D₆) δ 6.72 (3 H, s, Ph-*H* of Mesitylene), 2.16 (9 H, s, CH₃ of Mesitylene), 1.71-1.61 (4.46 H, m), 1.24-1.10 (4.41 H, m), 1.08-1.00 (0.82 H, m), 0.87 (2.76 H, t, *J* = 6 Hz), 0.83 (1.52 H, d, *J* = 6 Hz).

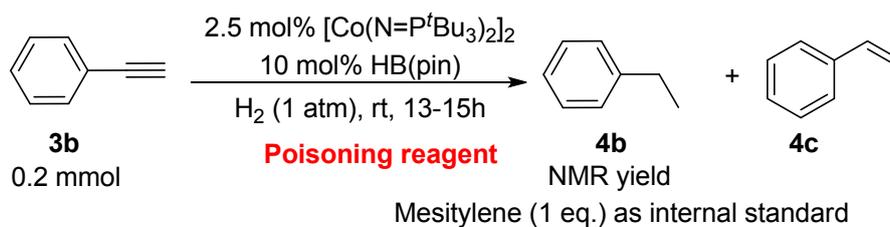
Octane (4f, Table 3).^{S2}



NMR yield 80%; ¹H NMR (600 MHz, C₆D₆) δ 6.72 (3 H, s, Ph-*H* of Mesitylene), 2.16 (9 H, s, CH₃ of Mesitylene), 1.33-1.23 (9.84 H, m), 0.91 (4.82 H, t, *J* = 6 Hz).

VI. Poisoning effect of Co(bis-phosphoranimide) catalyzed hydrogenation reaction.

The poisoning effect was measured using hydrogenation reaction of phenylacetylene as model.^{S3}



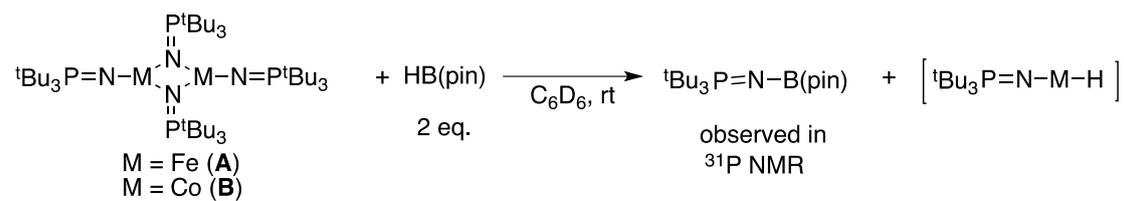
The procedure of poisoning effect experiments were same with above. The poisoning reagent was added into the reaction vial after the C₆D₆ solution of [Co(N=P^tBu₃)₂] and HB(pin) was obtained. The equivalent of poisoning reagent is relative to the *phenyl acetylene*. Mesitylene was used in NMR study as internal standard.

entry	Poisoning reagent	Equivalent (mol %)	NMR yield of 3b (%)	NMR yield of 4b (%)	NMR yield of 4c (%)
1	Hg	20	<1	80	<1
2	Hg	50	<1	75	<1

3	Hg	100	<1	63	<1
4	PPh ₃	5	<1	78	4
5	PMe ₃	5	<1	74	<1
6	dppe	5	<1	80	3
7	2,2'-bipyridine	5	<1	88	<1

NMR of Stoichiometric reaction of complexes A or B with 2 eq.

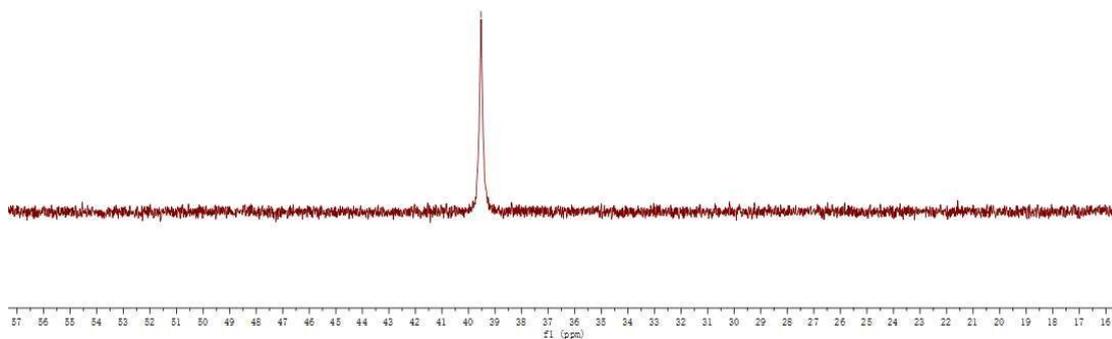
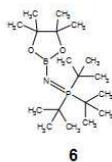
HB(pin)



M/HB(pin) = 1:2

³¹P NMR (243 MHz, C₆D₆)

— 31.532



VII. References:

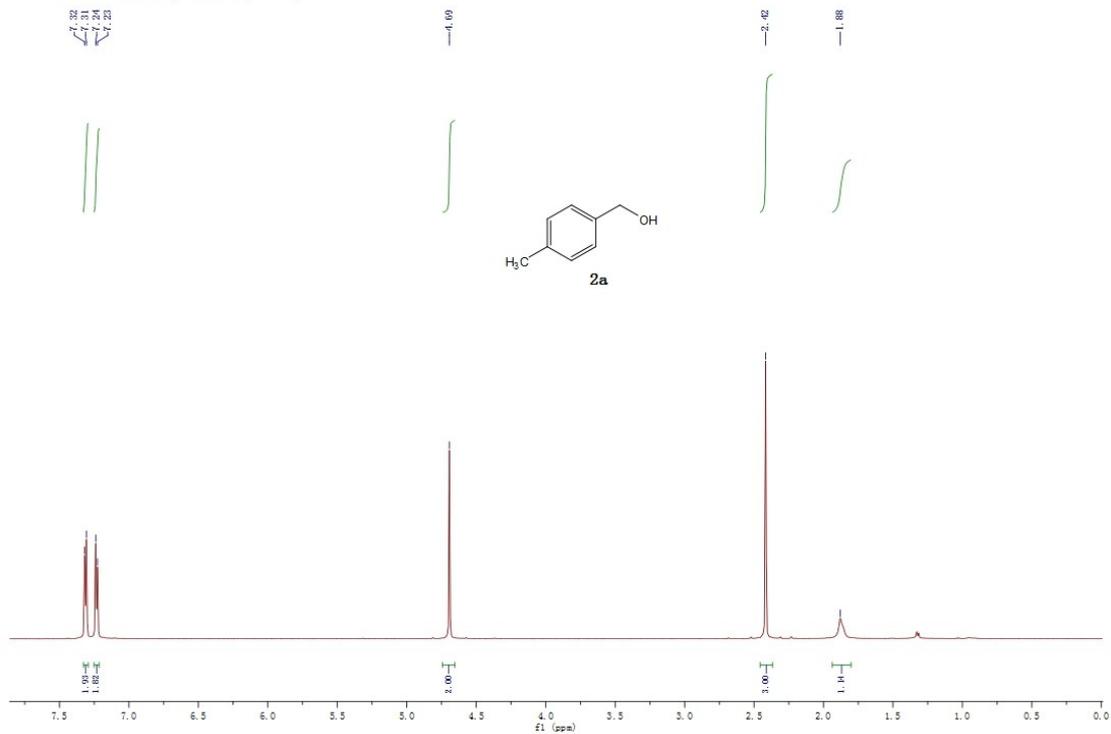
- S1. (a) V. K. Jakhar, M. Kr. Barman, S. Nembenna, *Org. Lett.*, 2016, **18**, 4710-4713; (b) C. Battilocchio, J. M. Hawkins, and S. V. Ley, *Org. Lett.*, 2013, **15**, 2278–2281; (c) Y. Wu, C. Shan, Y. Sun, P. Chen, J. Ying, J. Zhu, L. Liu, Y. Zhao, *Chem. Commun.* 2016, **52**, 13799-13802; (d) V. L. Weidner, C. J. Barger, M. Delferro, T. L. Lohr, T. J. Marks, *ACS Catal.*, **2017** **7**, 1244-1247.
- S2. (a) Y. Çetinkaya, O. Metin, M. Balci, *RSC Adv.*, 2016, **6**, 28538–28542; (b) V. Polshettiwar, M. N. Nadagouda, R. S. Varma, *Chem. Commun.*, 2008, 6318–6320; (c) C. Jun, Y. J. Park, Y. Yeon, J. Choi, W. Lee, S. Ko, J. Cheon, *Chem. Commun.* 2006, 1619-1621.
- S3. (a) D. Gärtner, A. Welther, B. R. Rad, R. Wolf, A. J. von Wangelin, *Angew. Chem. Int. Ed.*, 2014, **53**, 3722–3726; (b) Y. Li, S. Yu, X. Wu, J. Xiao, W. Shen, Z. Dong, J. Gao, *J. Am. Chem. Soc.*, 2014, **136**, 4031–4039.

APPENDIX

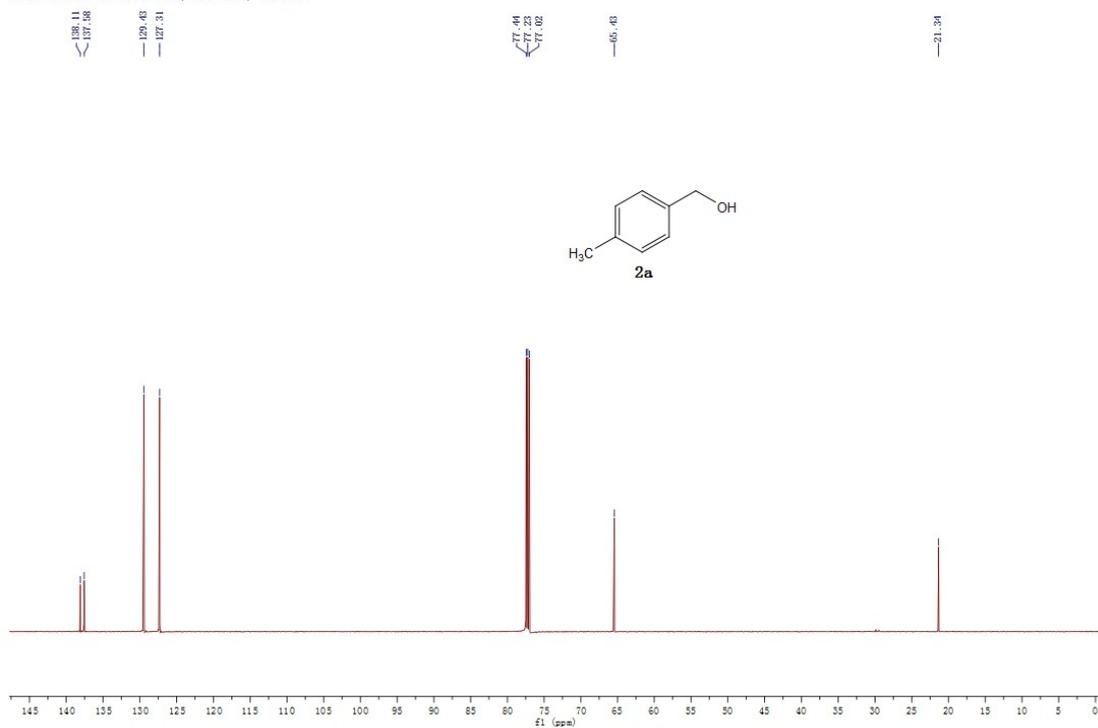
Appendix-1

^1H and ^{13}C Spectral Copies of hydroboration reaction of aldehydes and ketones catalyzed by Fe(bis-phosphoranimide)

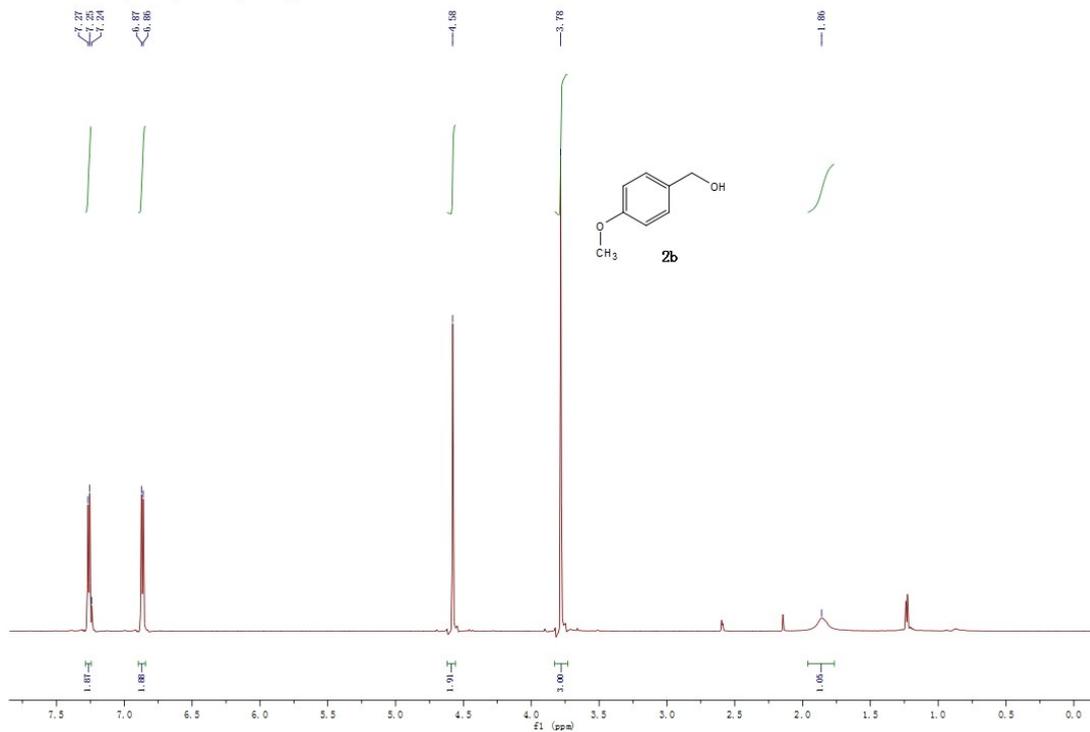
tbai-1-149-3 (^1H NMR, 600M Hz, CDCl_3)



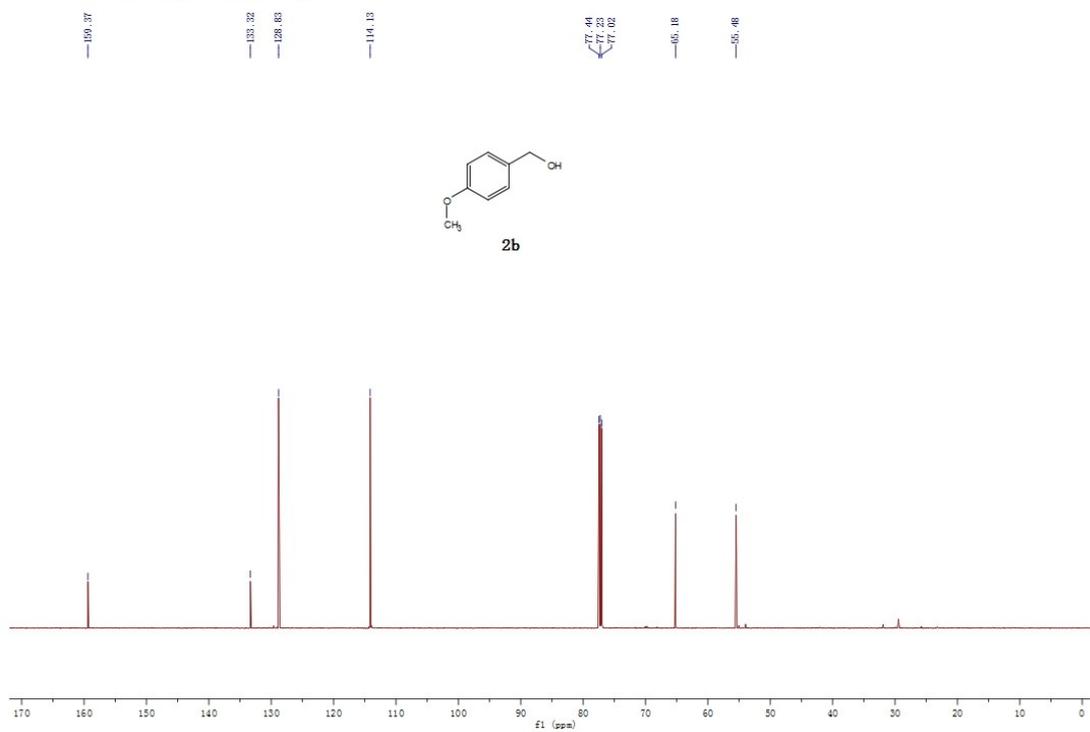
tbai-1-194-3 (^{13}C NMR, 150 MHz, CDCl_3)



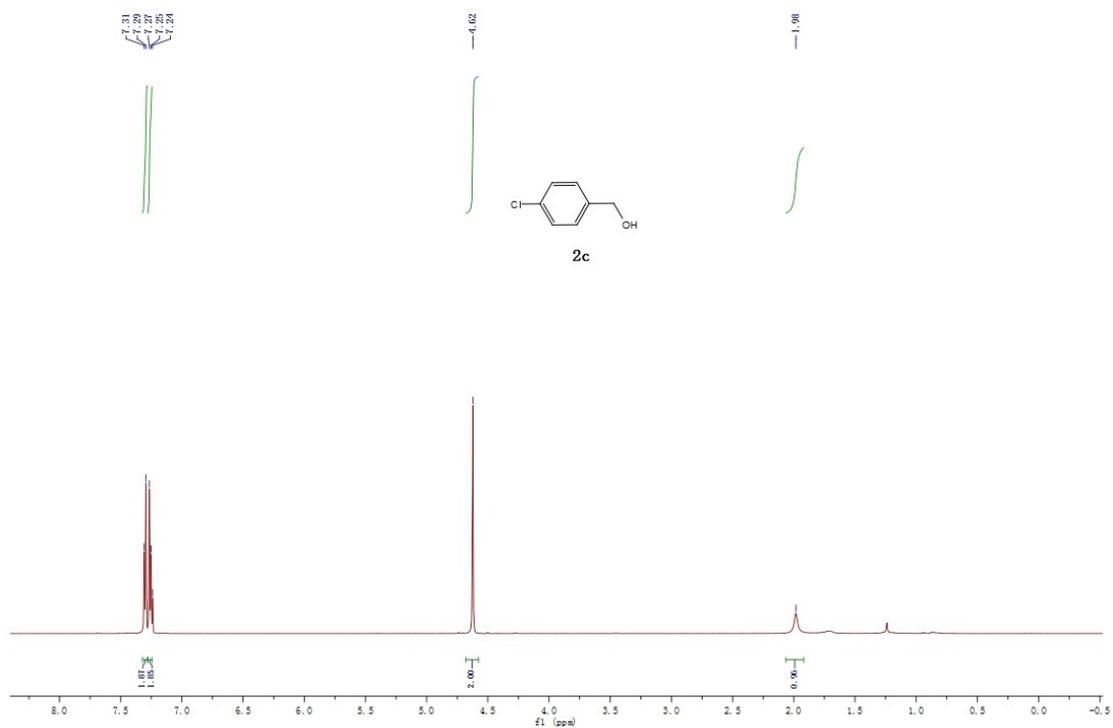
tbai-1-149-7 (^1H NMR, 600MHz, CDCl_3)



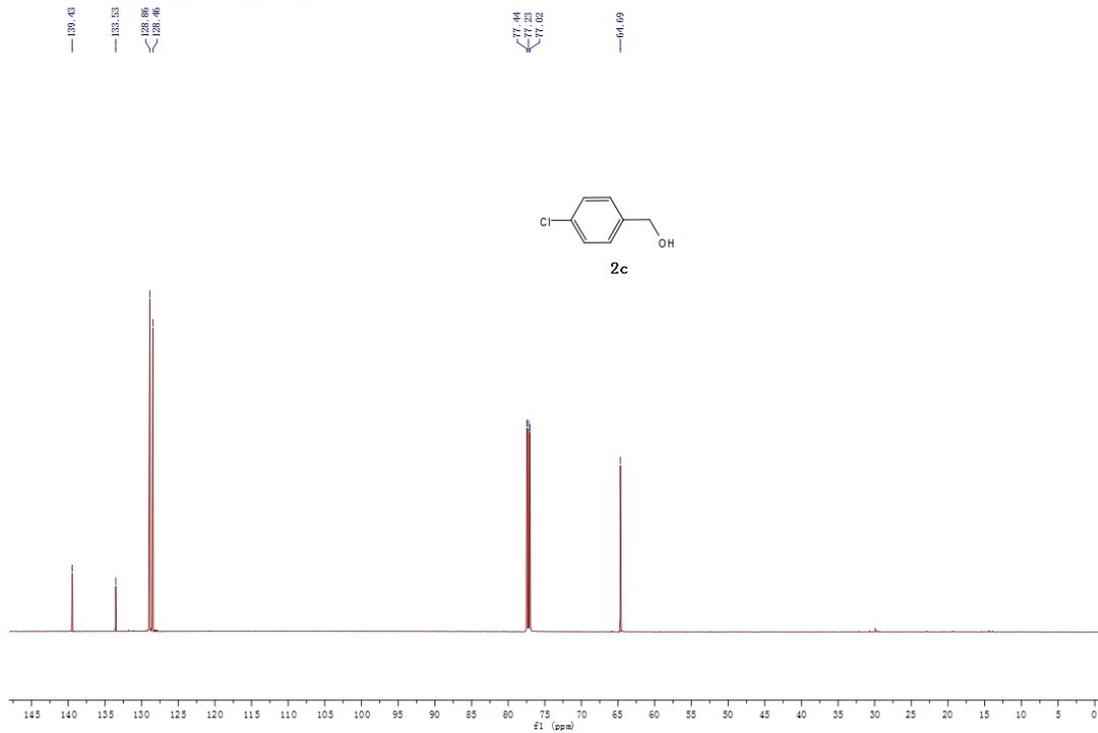
tbai-1-149-7 (^{13}C NMR, 151 MHz, CDCl_3)



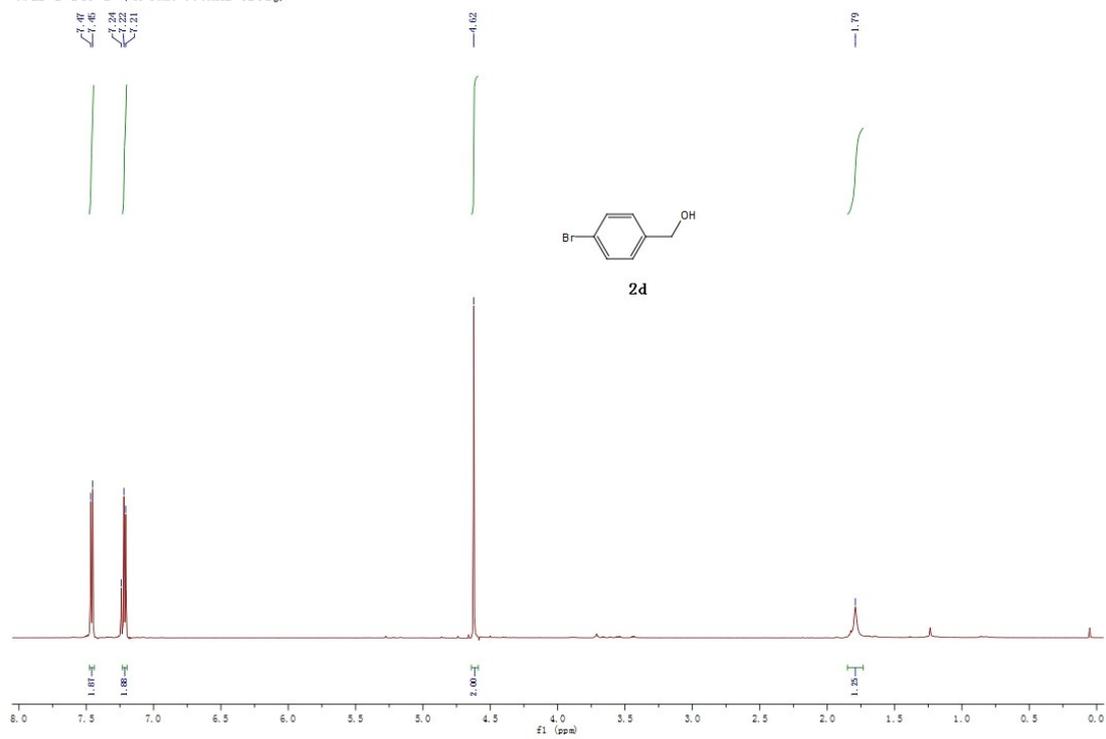
tbai-1-149-2 (^1H NMR, 600MHz, CDCl_3)



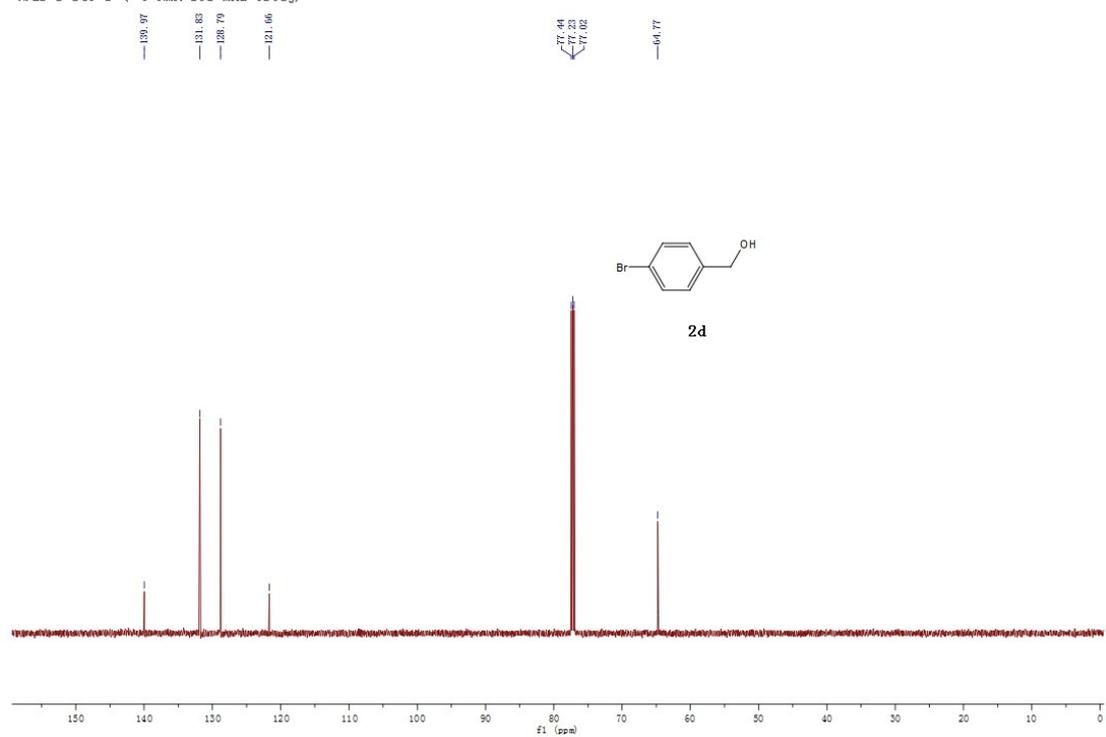
tbai-1-149-2 (^{13}C NMR, 151 MHz, CDCl_3)



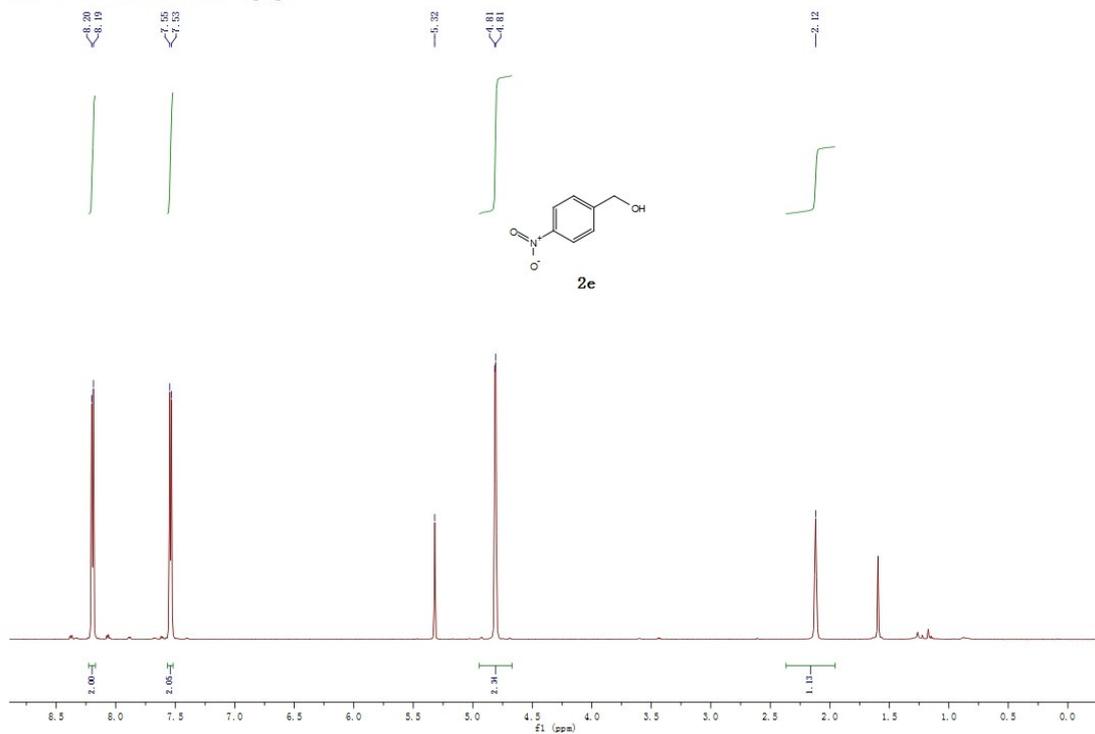
tbai-1-149-1 (¹H NMR 600MHz CDCl₃)



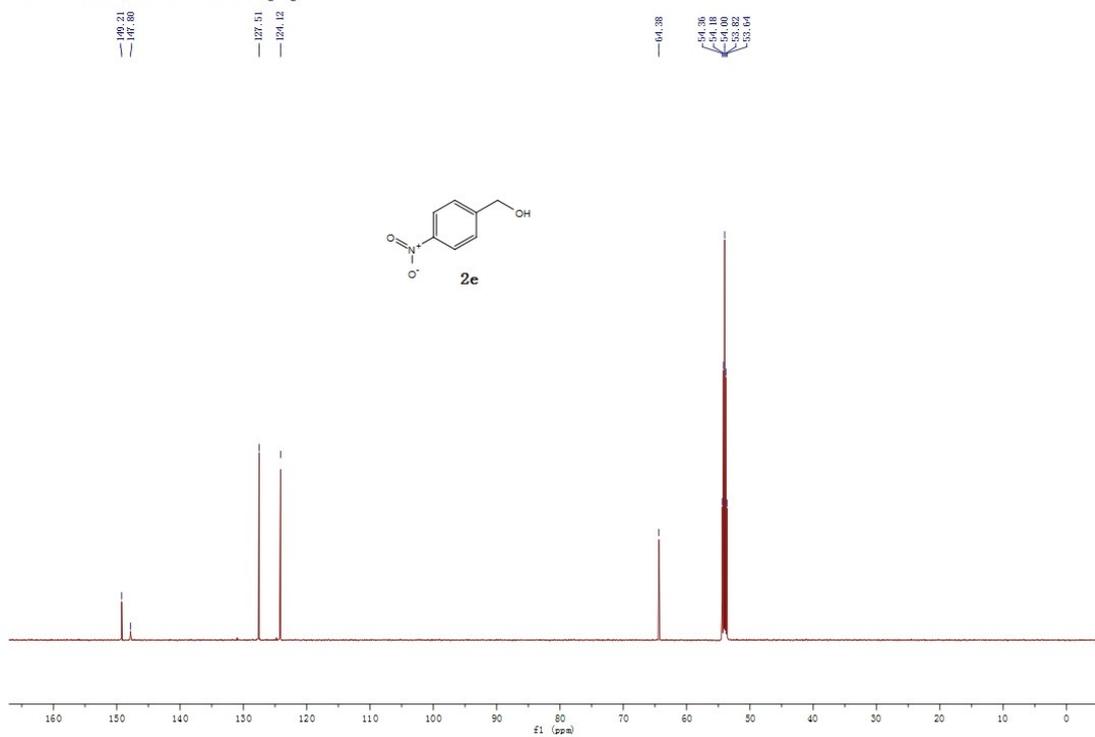
tbai-1-149-1 (¹³C NMR 151 MHz CDCl₃)



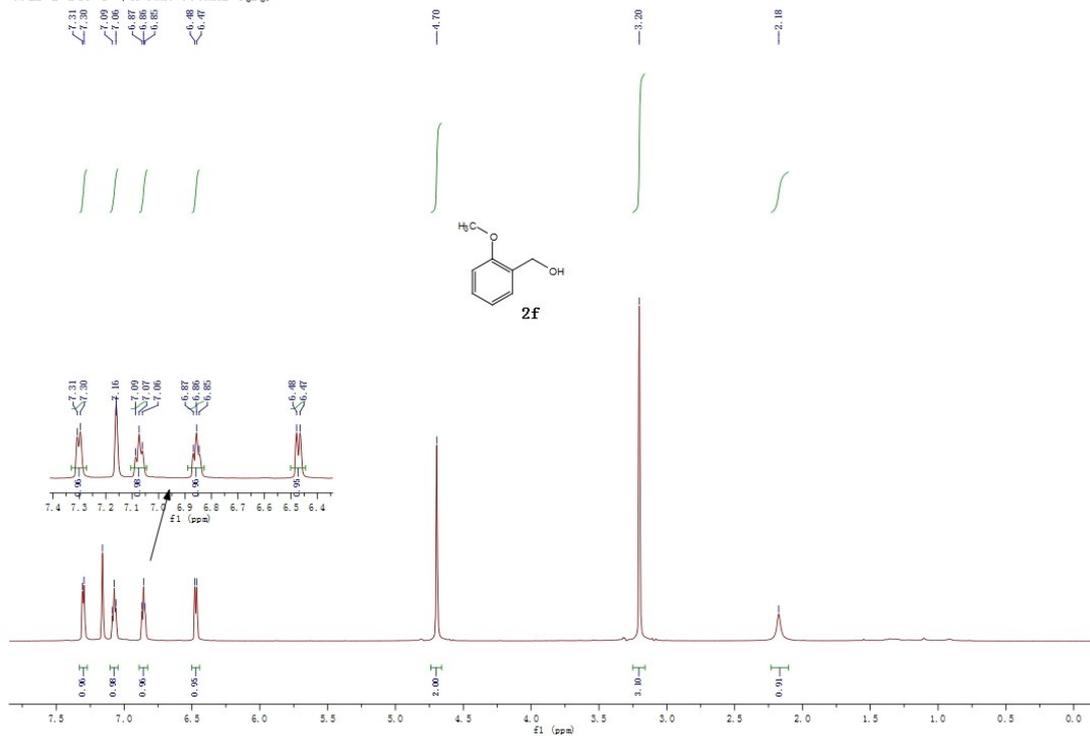
tbai-1-149-6 (¹H NMR 600MHz CD₂Cl₂)



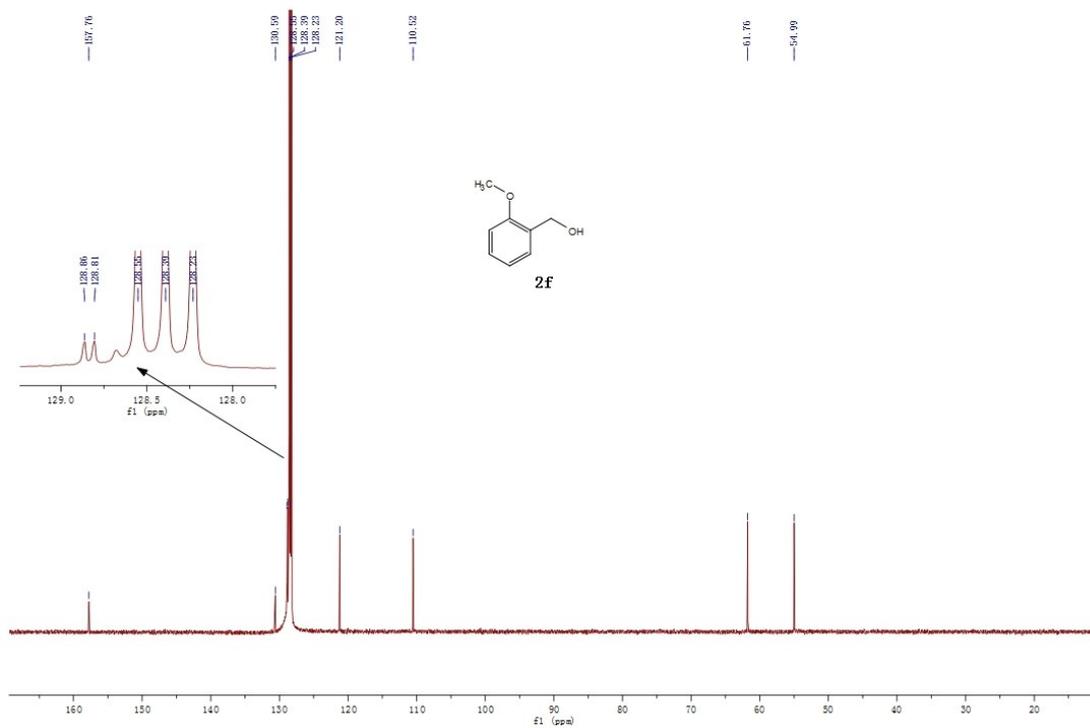
tbai-1-149-6 (¹³C NMR 151 MHz CD₂Cl₂)



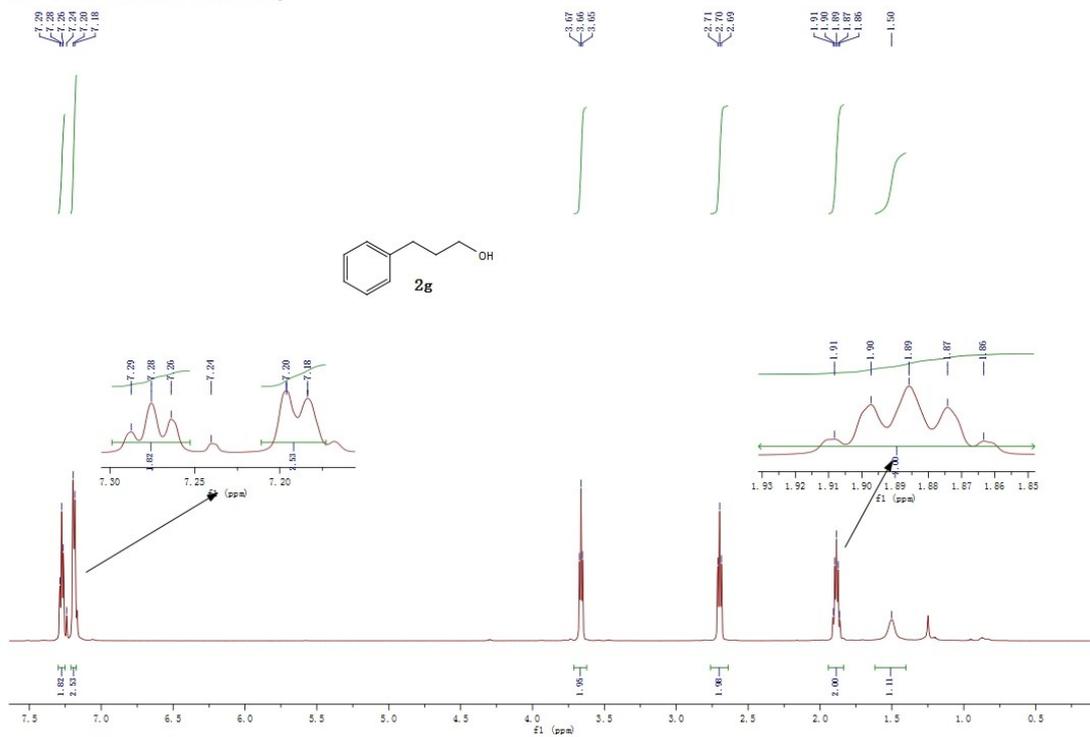
tbai-1-149-8 (¹H NMR 600MHz C₆D₆)



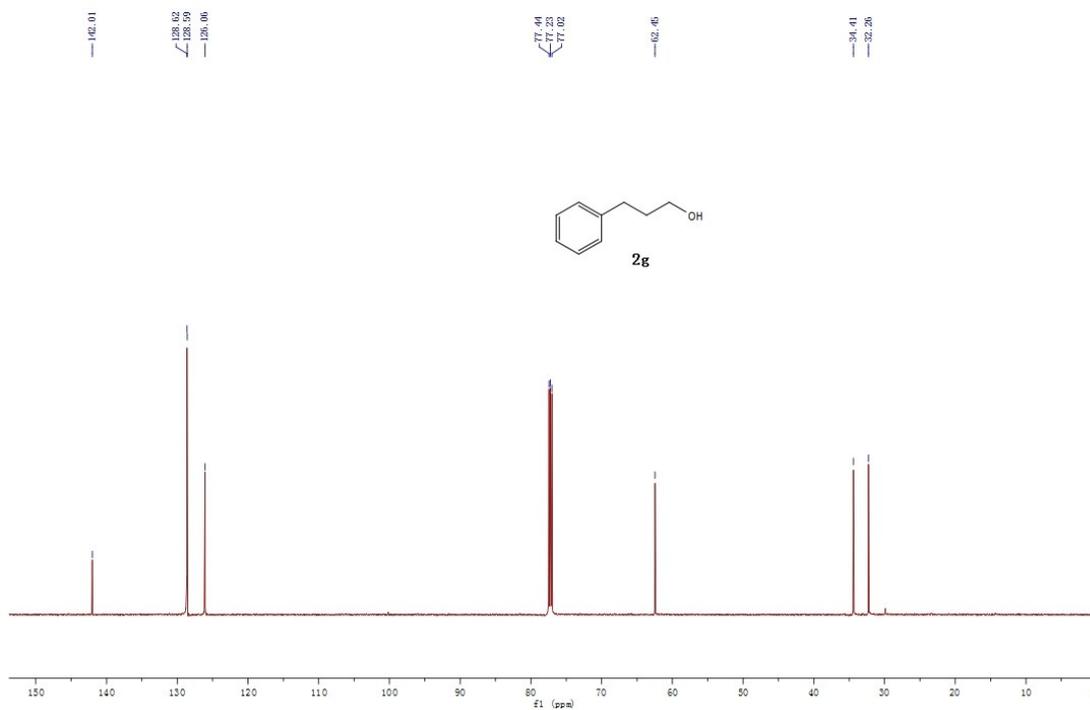
tbai-1-149-8 (¹³C NMR 151 MHz C₆D₆)



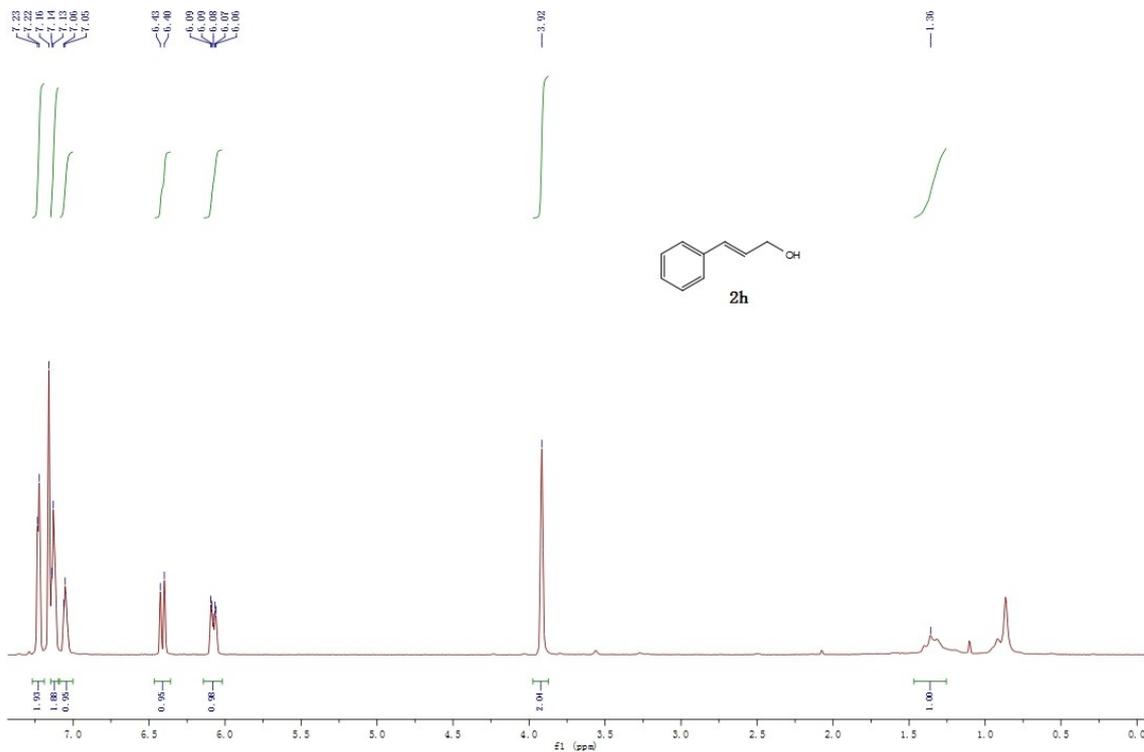
tbai-1-149-4 (¹H NMR 600 MHz CDCl₃)



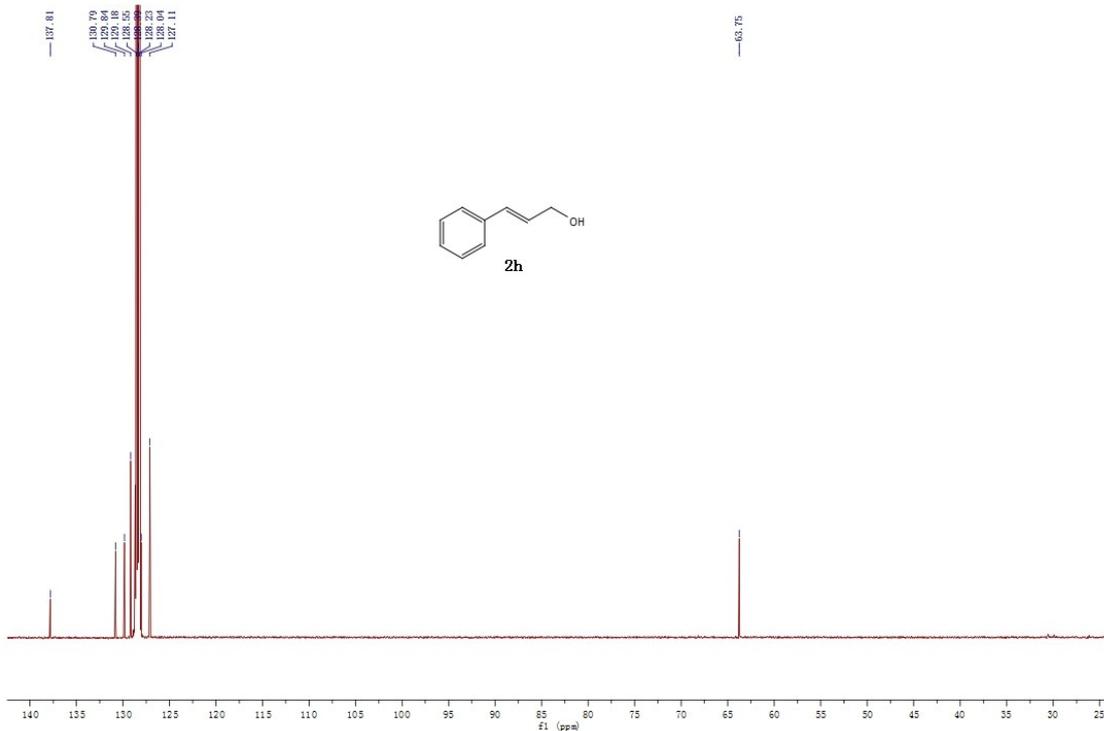
tbai-1-149-4 (¹³C NMR 151 MHz CDCl₃)



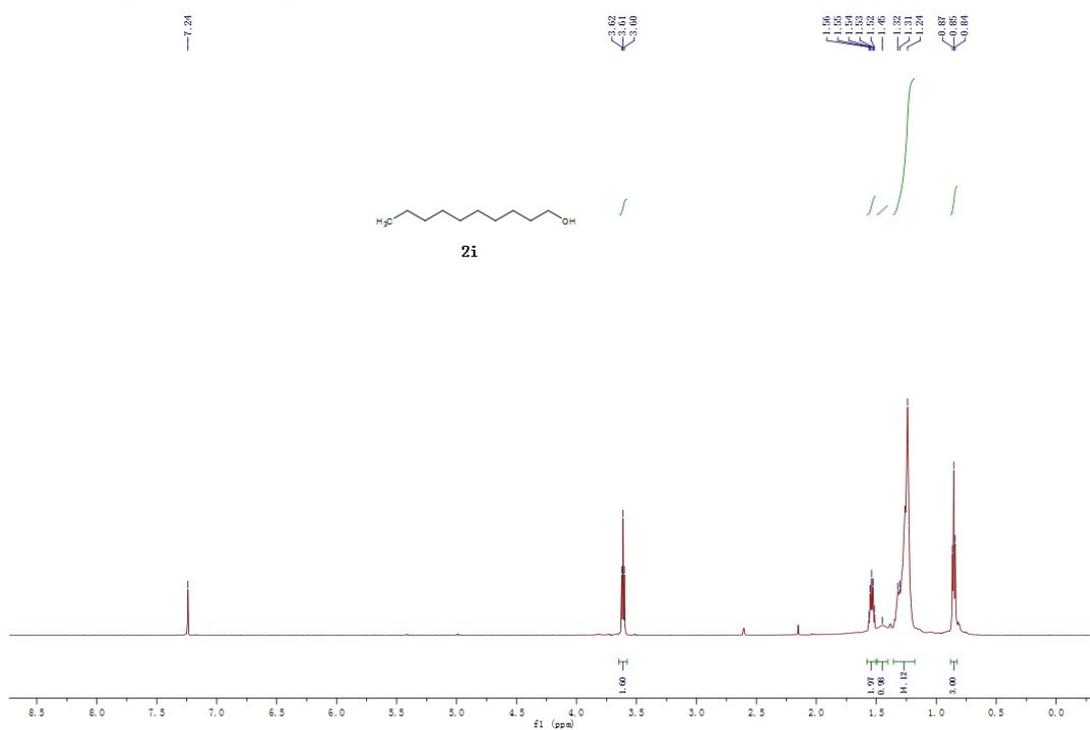
tbai-1-149-5 (¹H NMR 600MHz C₆D₆)



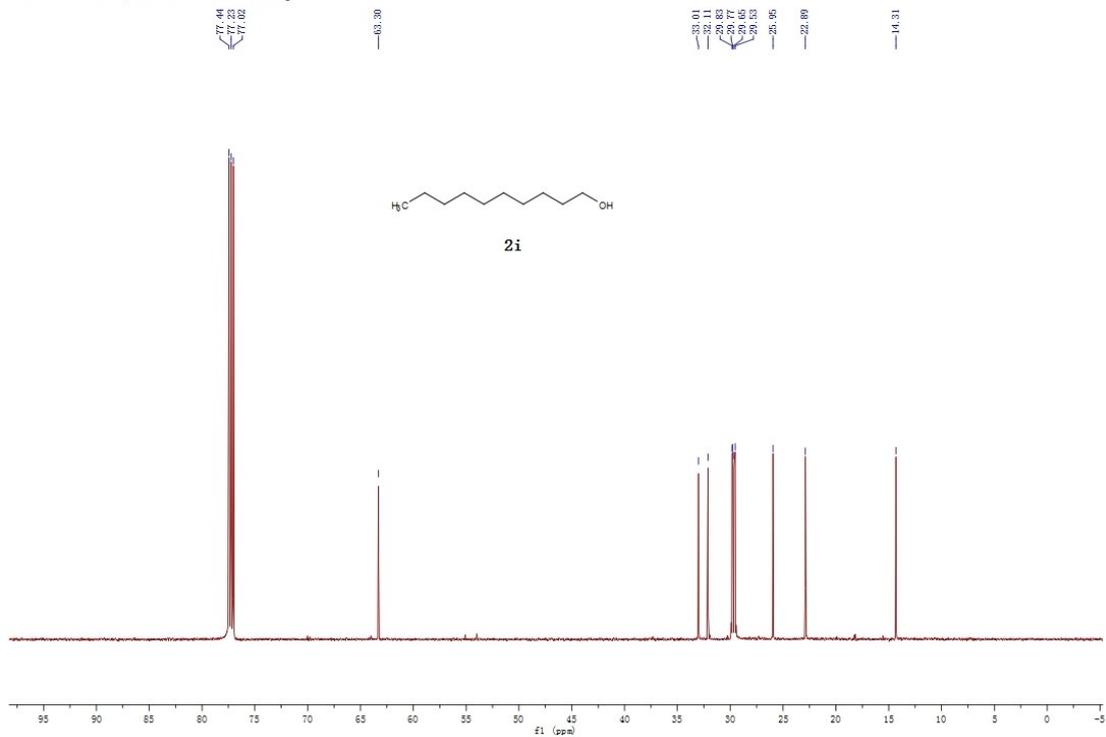
tbai-1-149-5 (¹³C NMR 151 MHz C₆D₆)



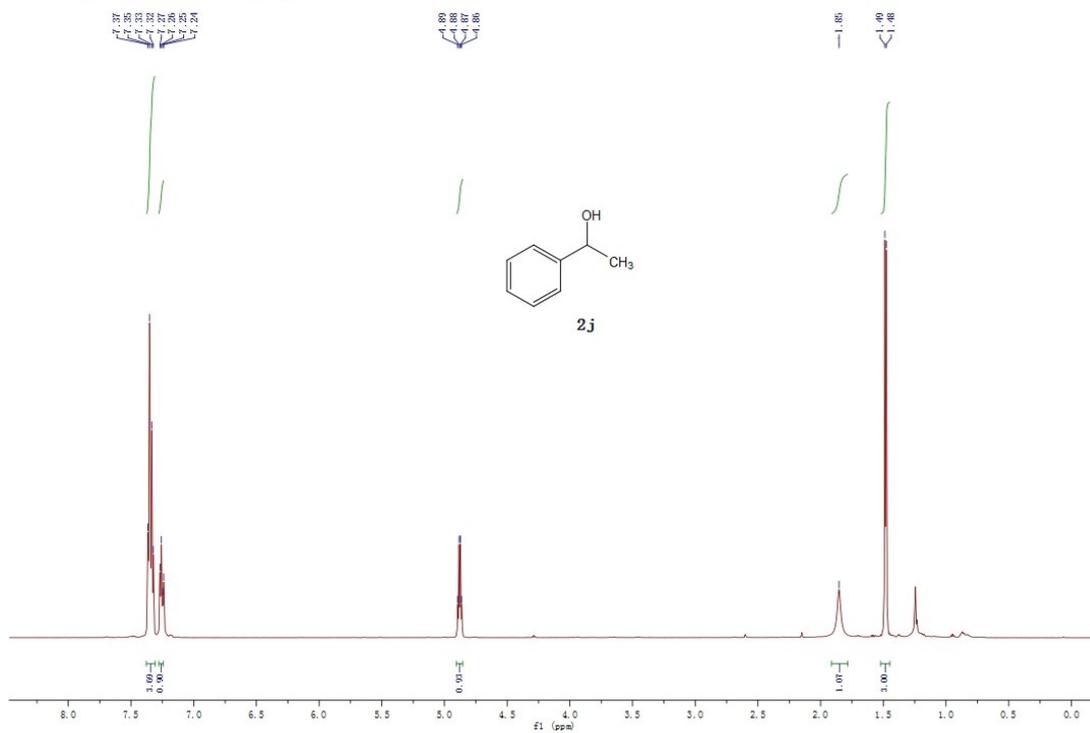
tbai-1-158-3 (^1H NMR 600 MHz CDCl_3)



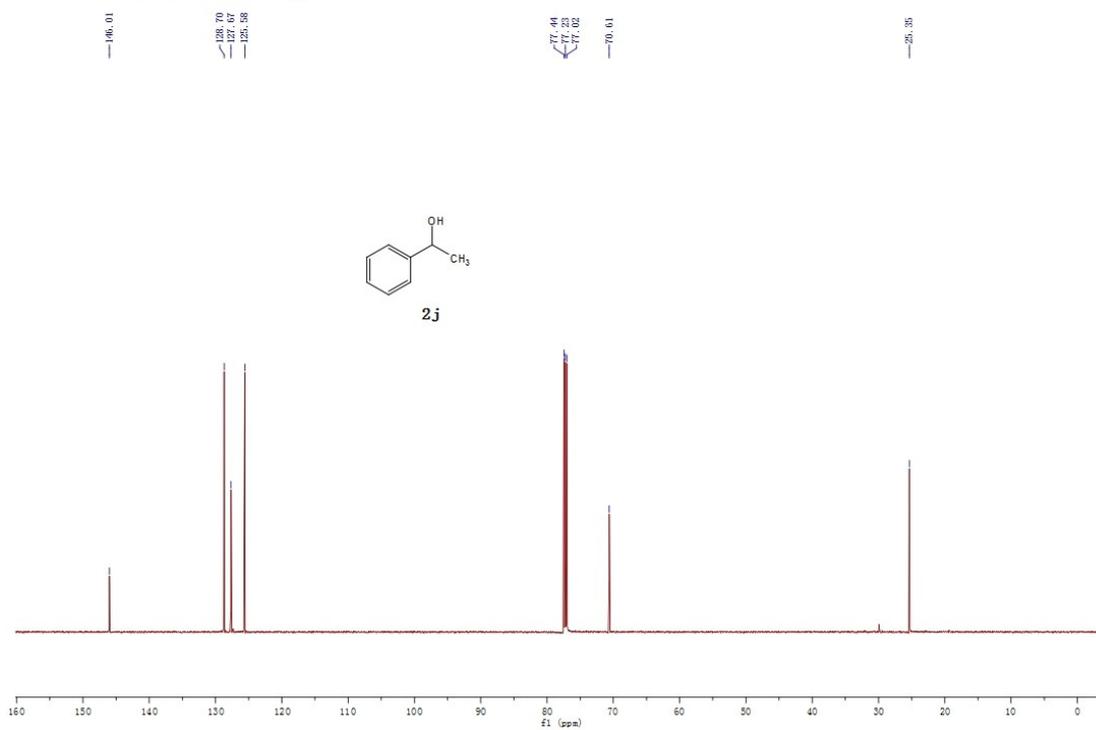
tbai-1-158-3 (^{13}C NMR 151 MHz CDCl_3)



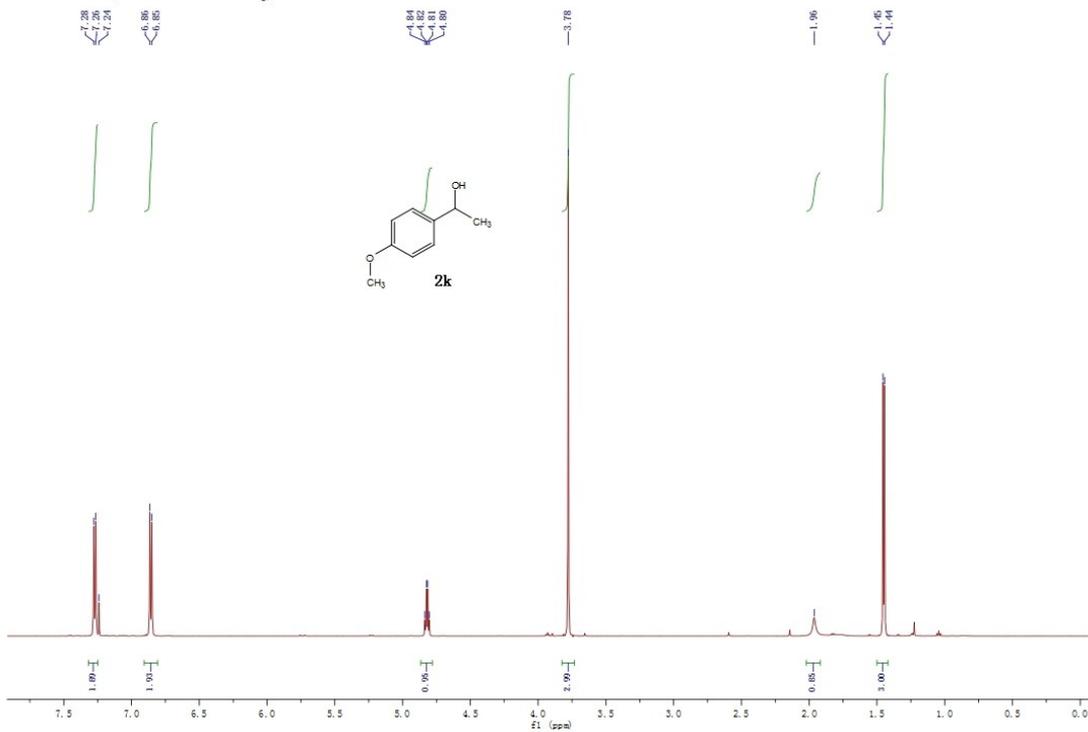
tbai-1-149-10 (¹H NMR 600MHz CDCl₃)



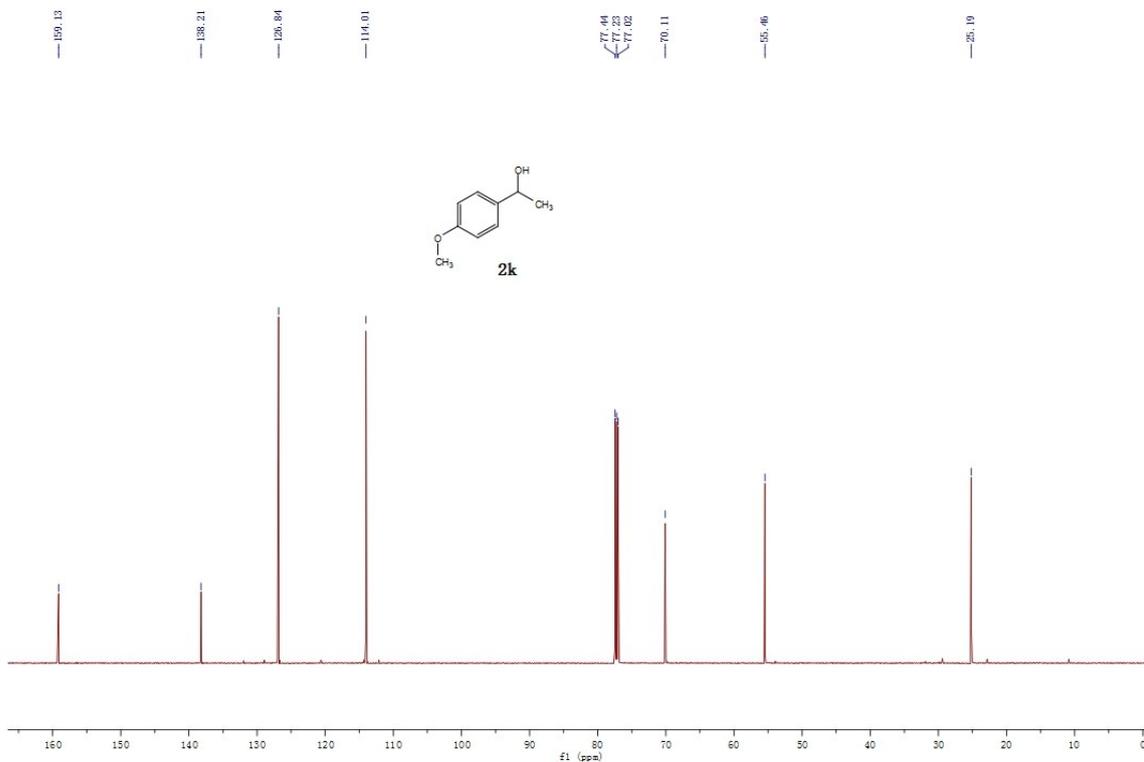
tbai-1-149-10 (¹³C NMR 151 MHz CDCl₃)



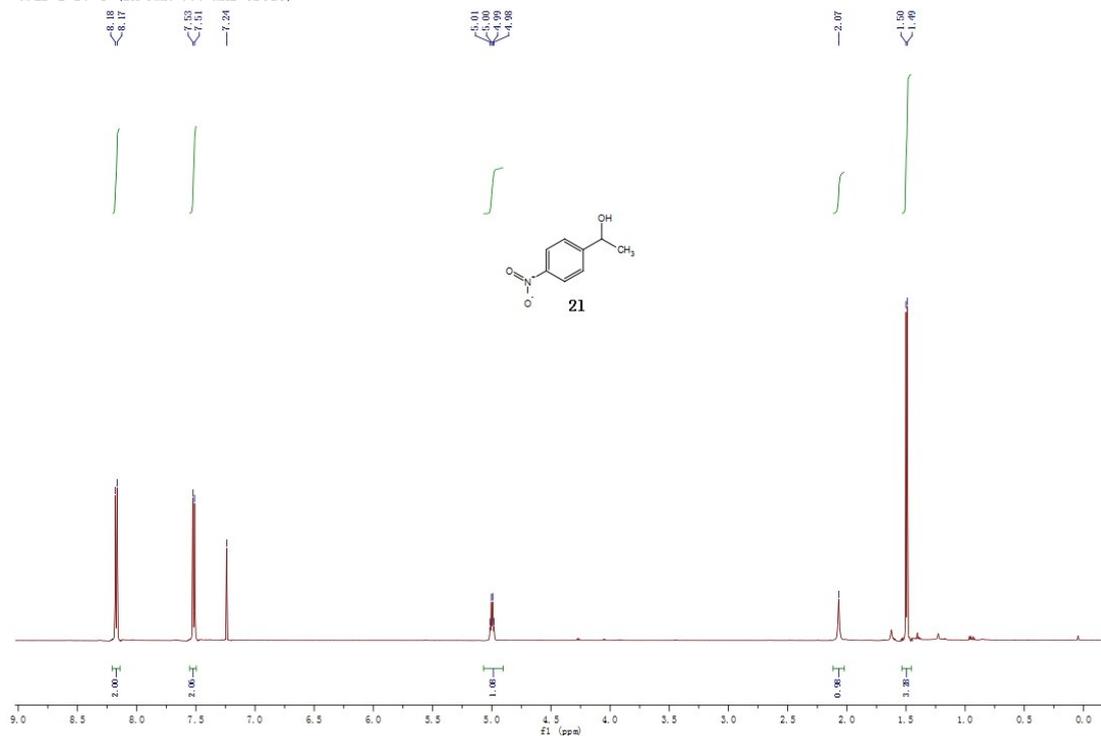
tbai-1-58-1 (¹H NMR 600MHz CDCl₃)



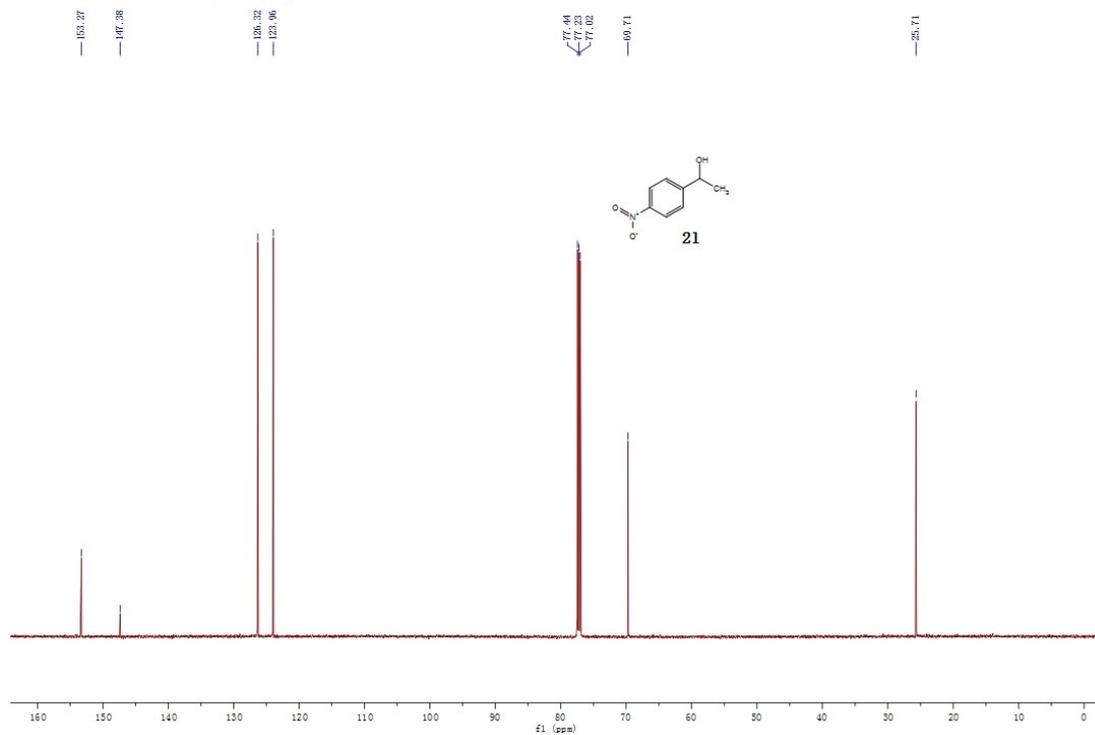
tbai-1-158-1 (¹³C NMR 151 MHz CDCl₃)



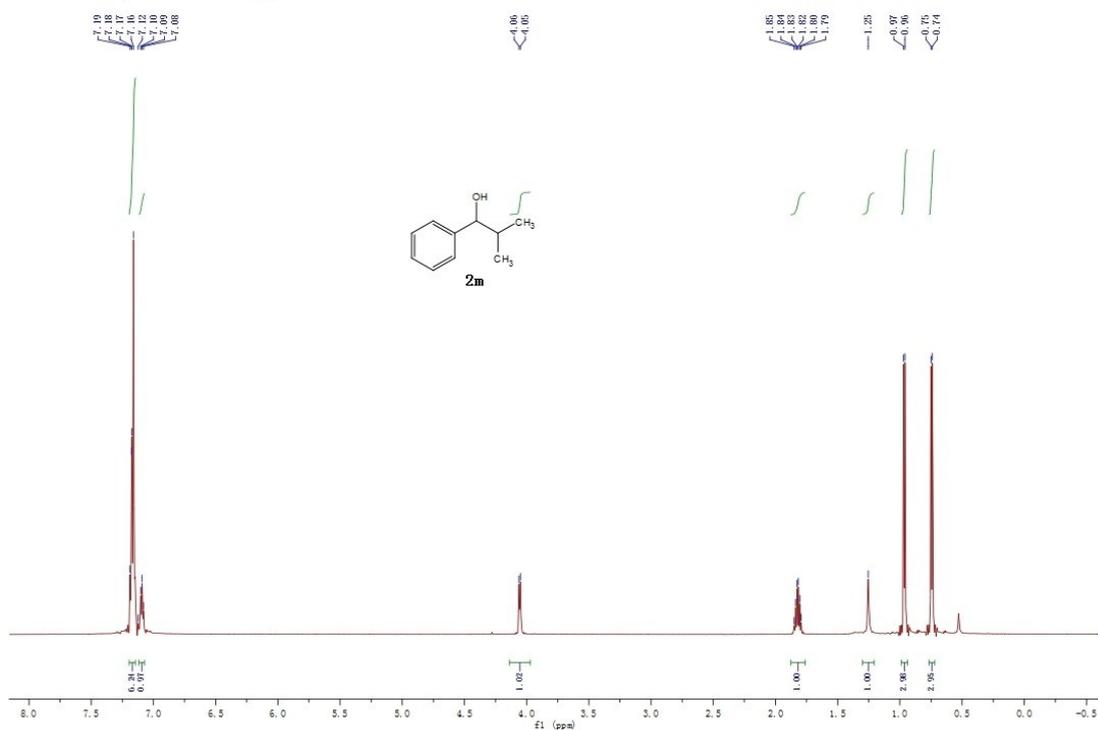
tbai-2-16-4 (1H NMR 600 MHz CDCl3)



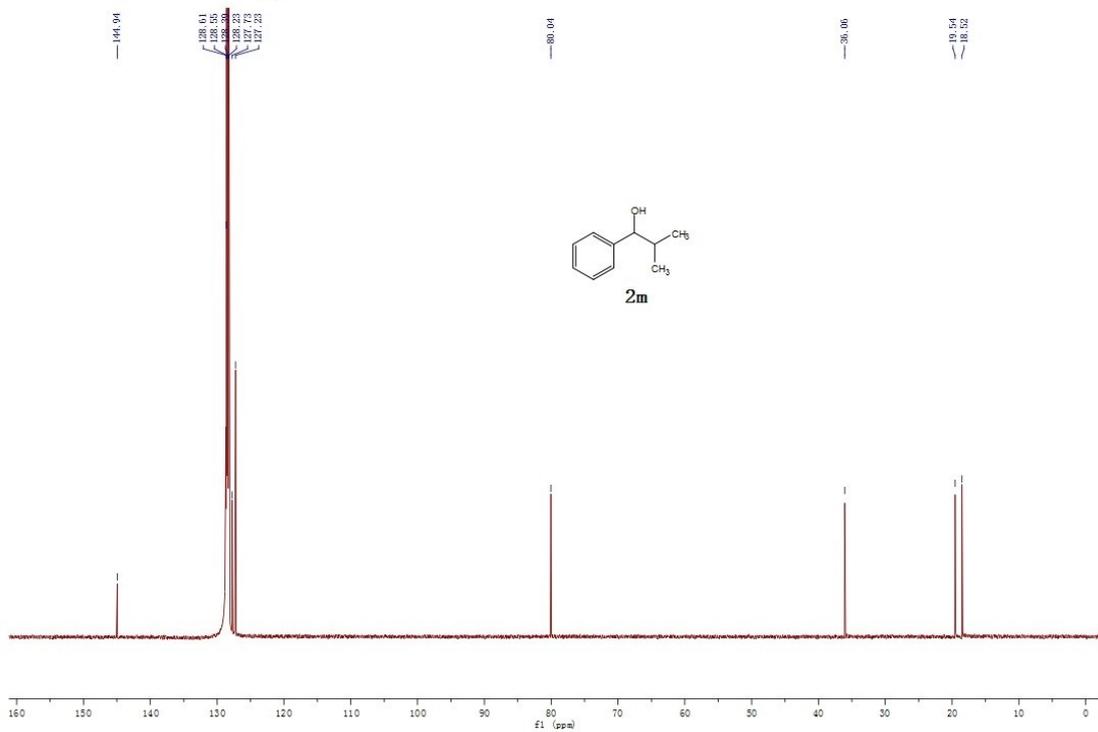
tbai-2-16-4 (13C NMR 151 MHz CDCl3)



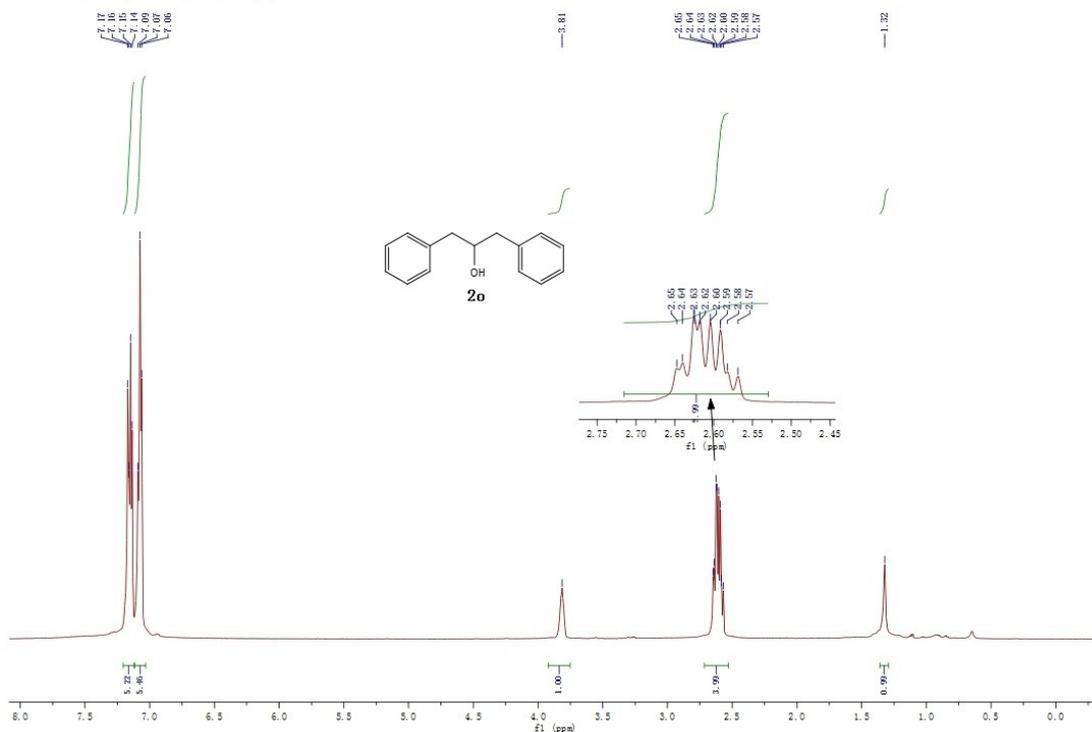
tbai-1-158-6 (¹H NMR 600 MHz C₆D₆)



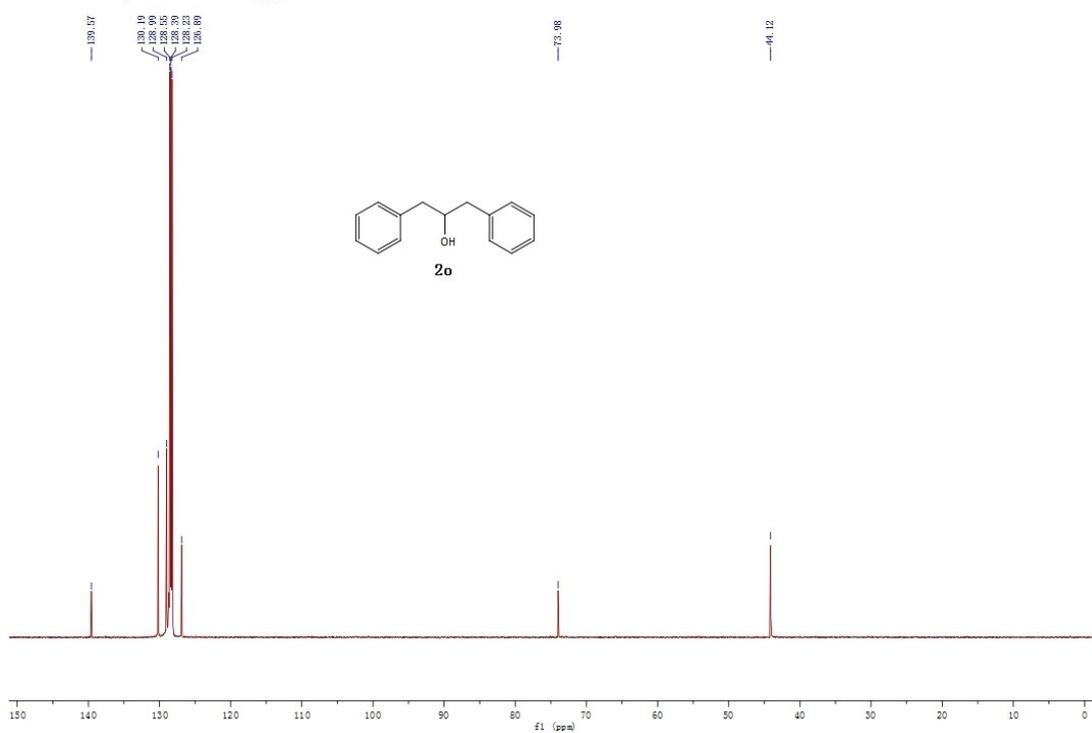
tbai-1-158-6 (¹³C NMR 151 MHz C₆D₆)



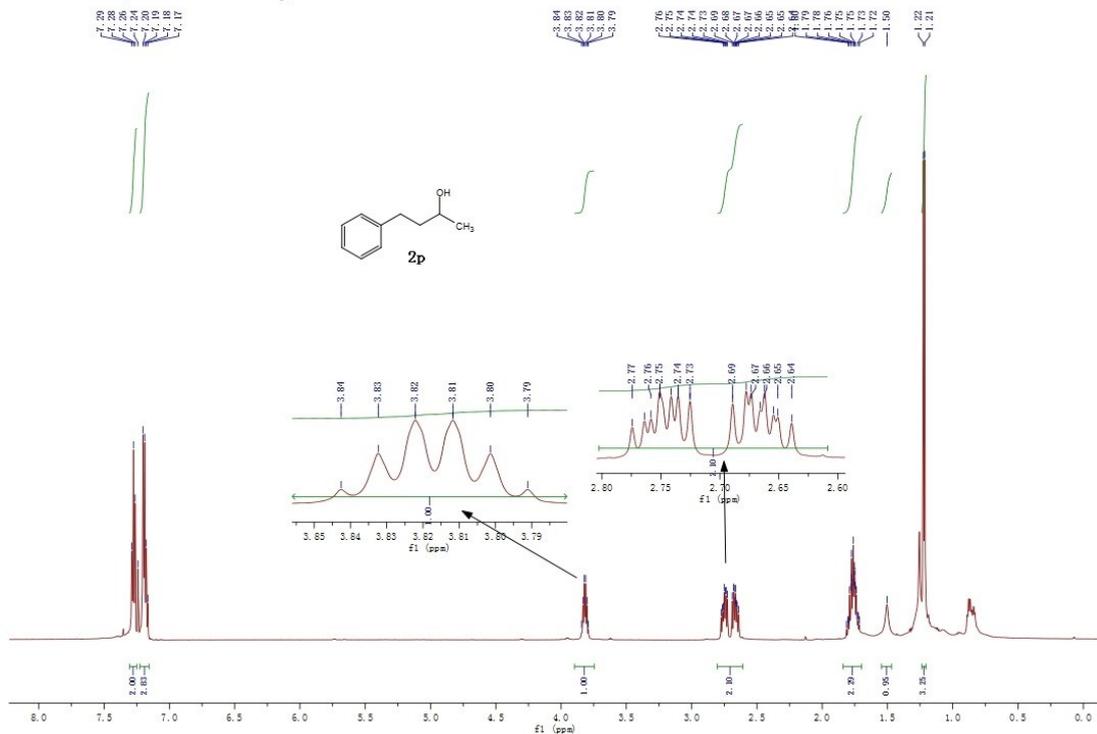
tbai-1-158-4 (^1H NMR 600 MHz C_6D_6)



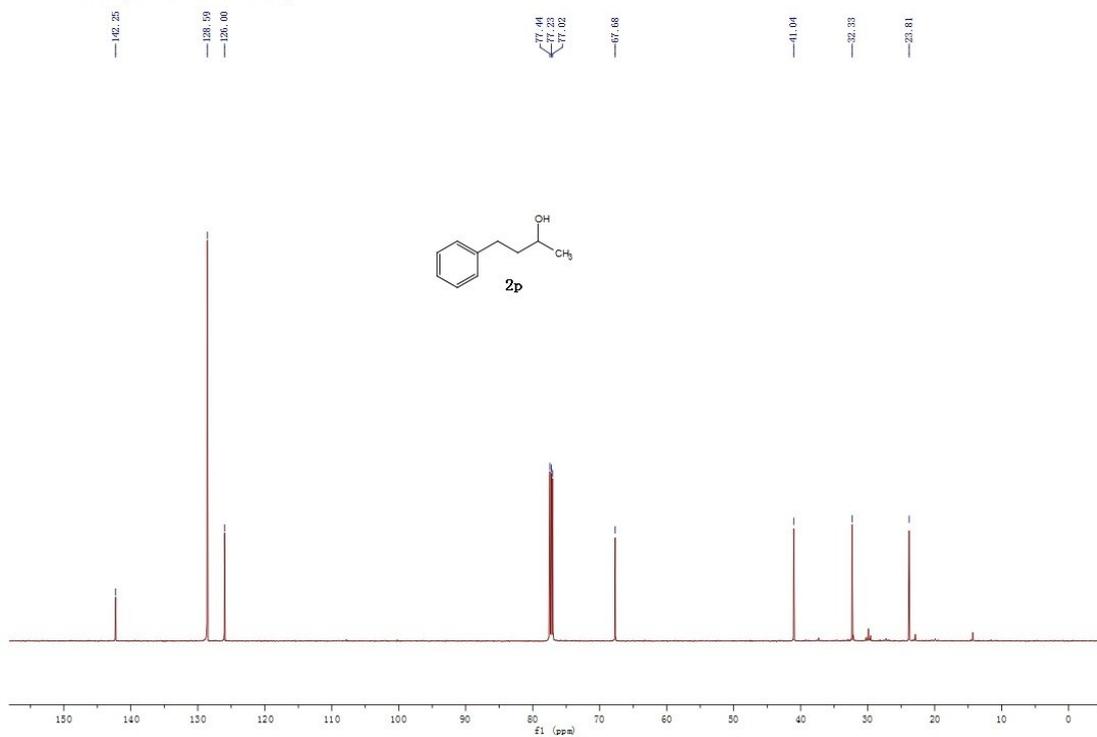
tbai-1-158-4 (^{13}C NMR 151 MHz C_6D_6)



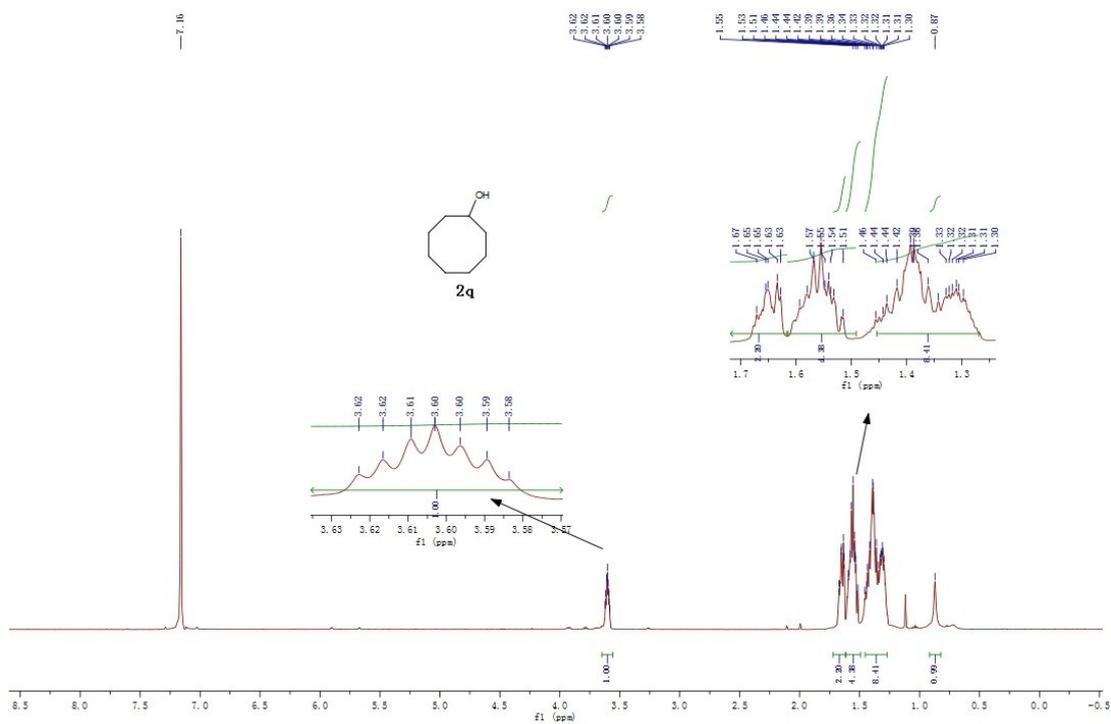
tbai-1-158-2 (¹H NMR 600 MHz CDCl₃)



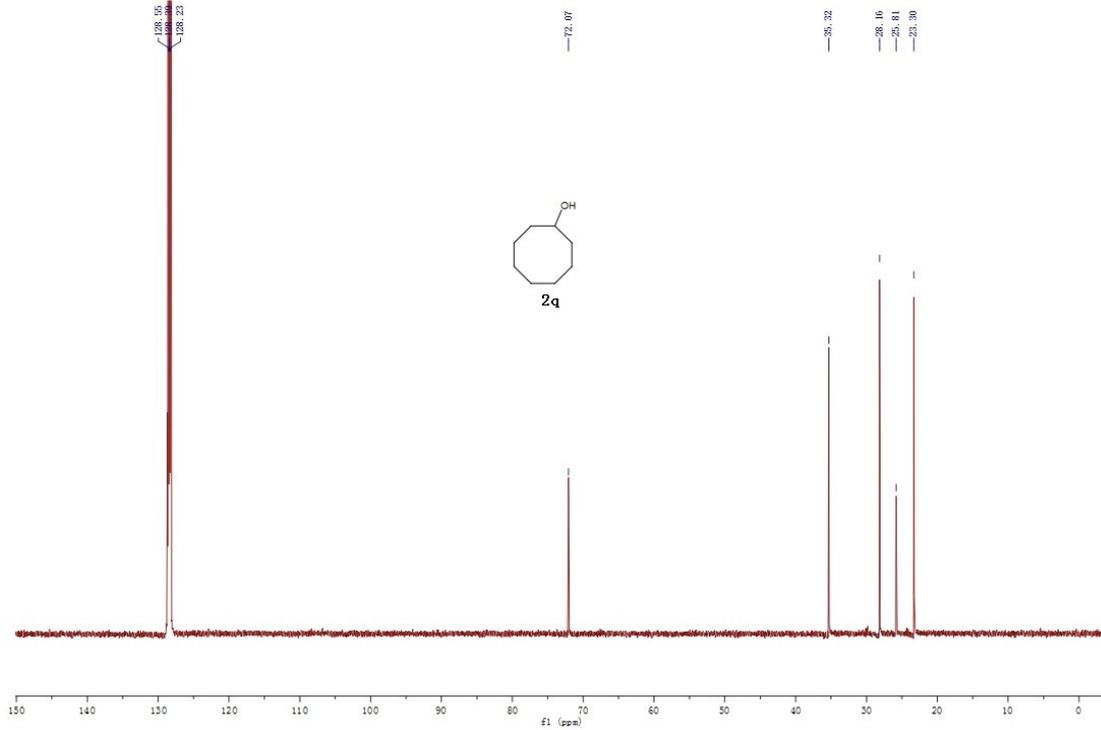
tbai-1-158-2 (¹³C NMR 151 MHz CDCl₃)



tbai-1-158-5 (¹H NMR 600 MHz C₆D₆)

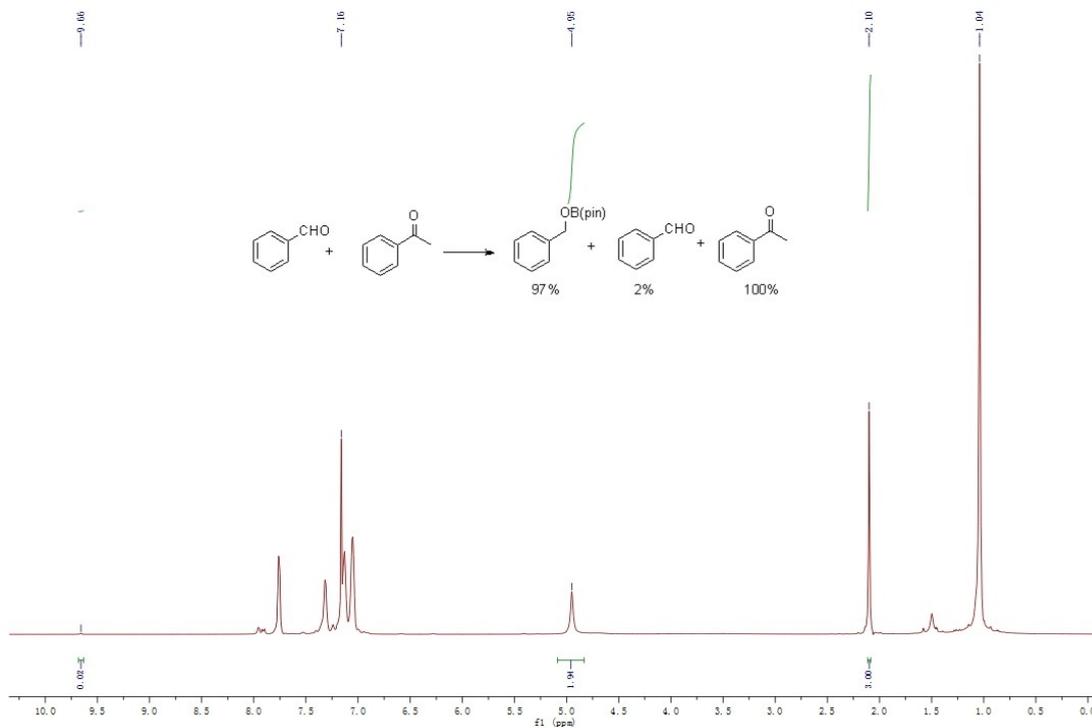


tbai-1-158-5 (¹³C NMR 151 MHz C₆D₆)

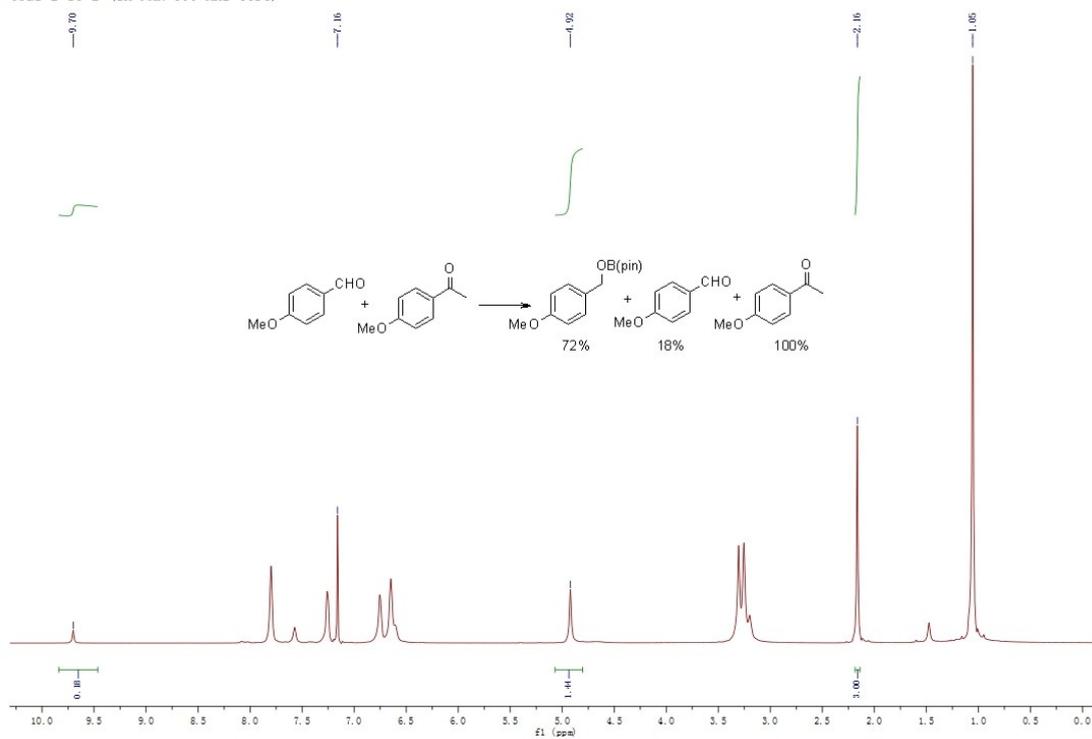


Appendix II. Competing hydroboration reaction of aldehydes and ketones.

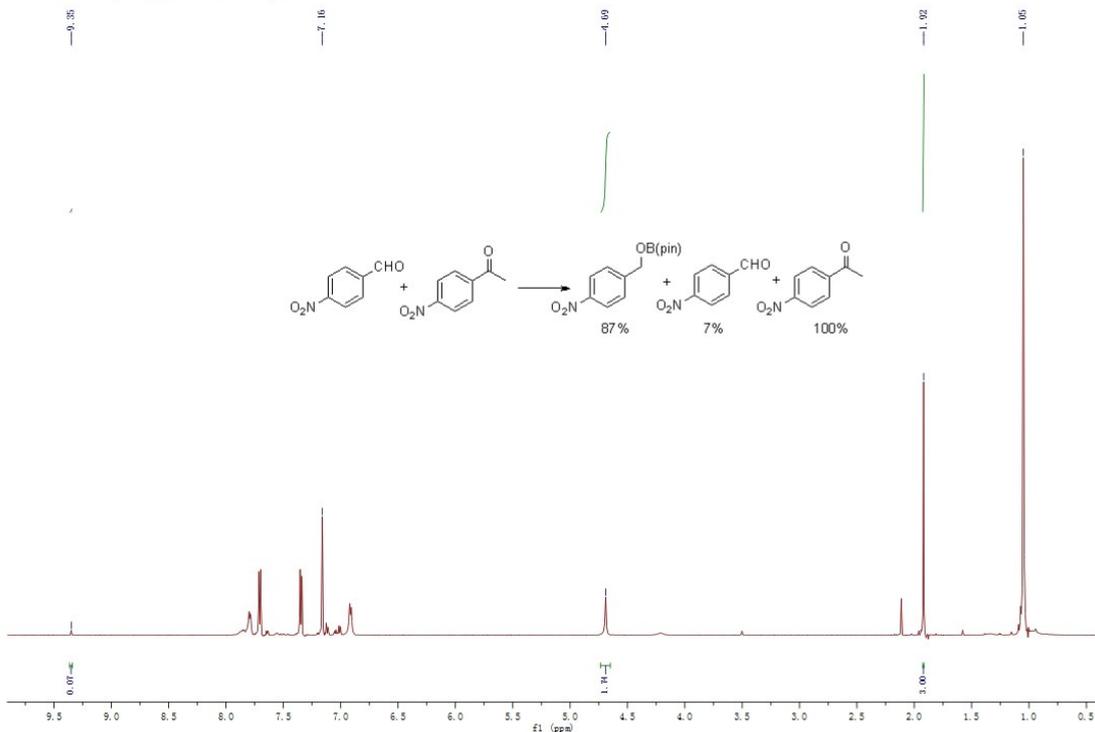
tbai-2-16-1 (1H NMR 600 MHz C6D6)



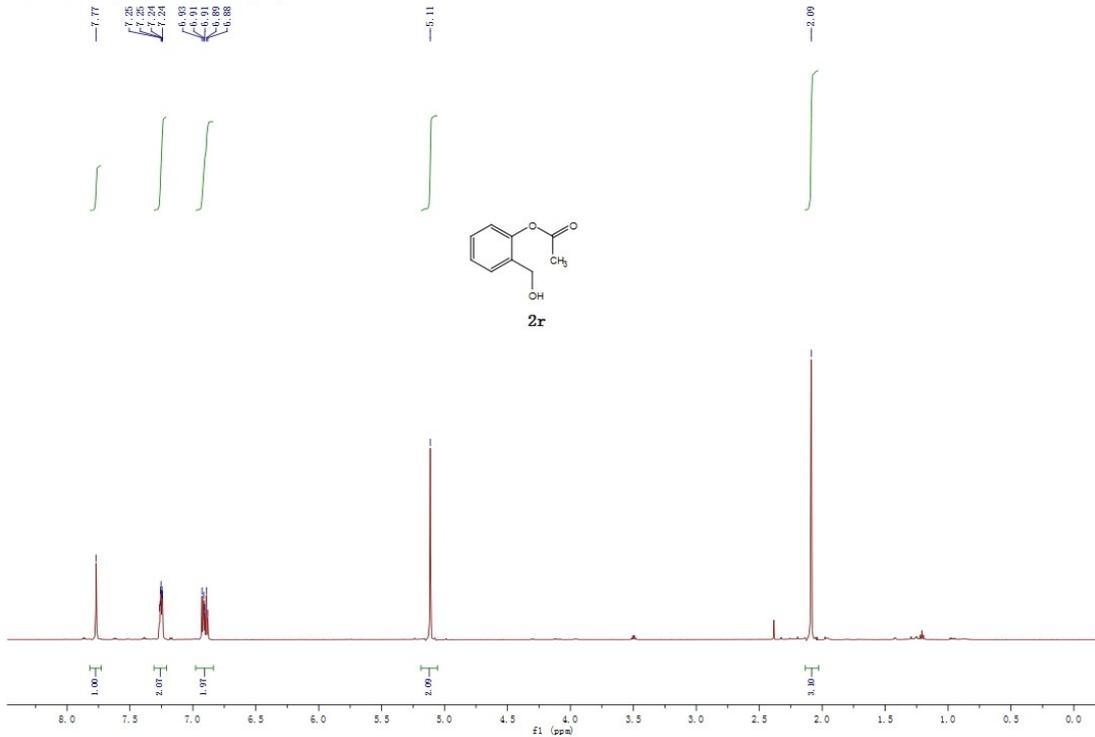
tbai-2-16-2 (1H NMR 600 MHz C6D6)



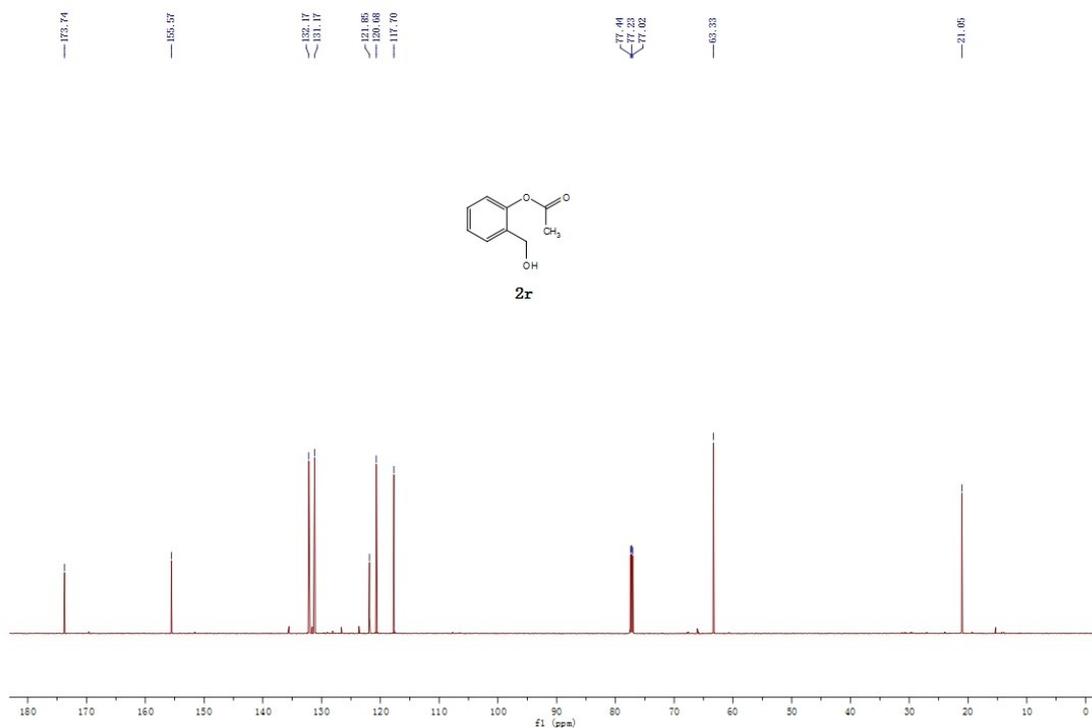
tbai-2-16-3 (1H NMR 600 MHz C6D6)



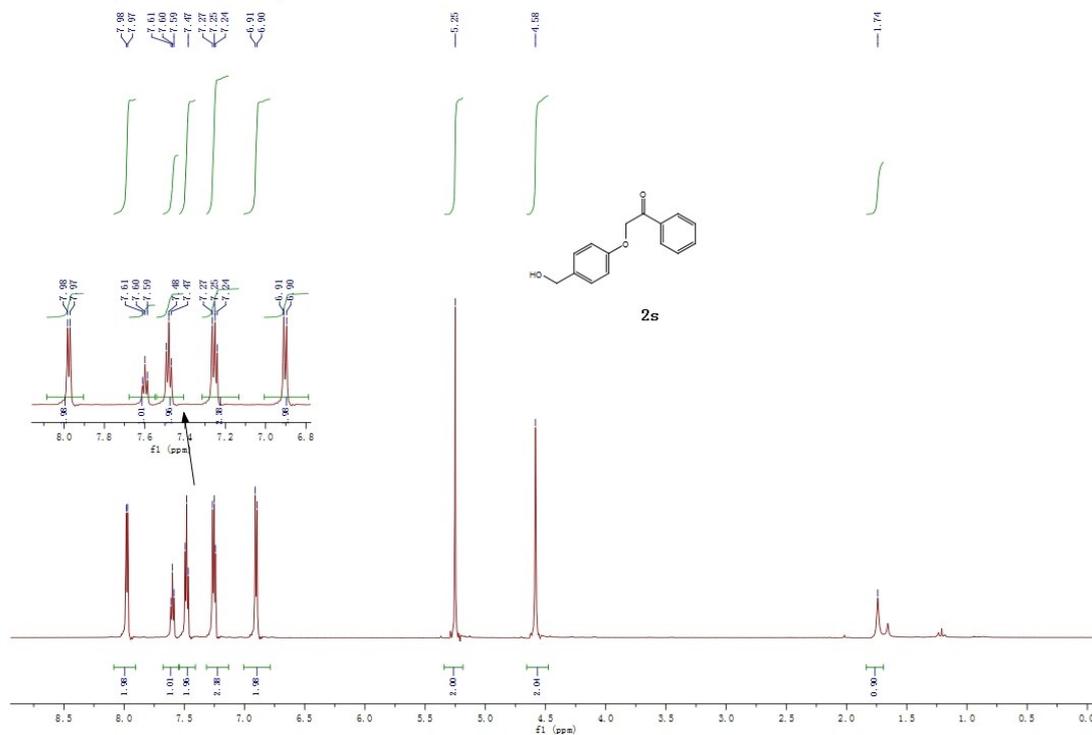
tbai-2-27-1 (1H NMR 600 MHz CDC13)



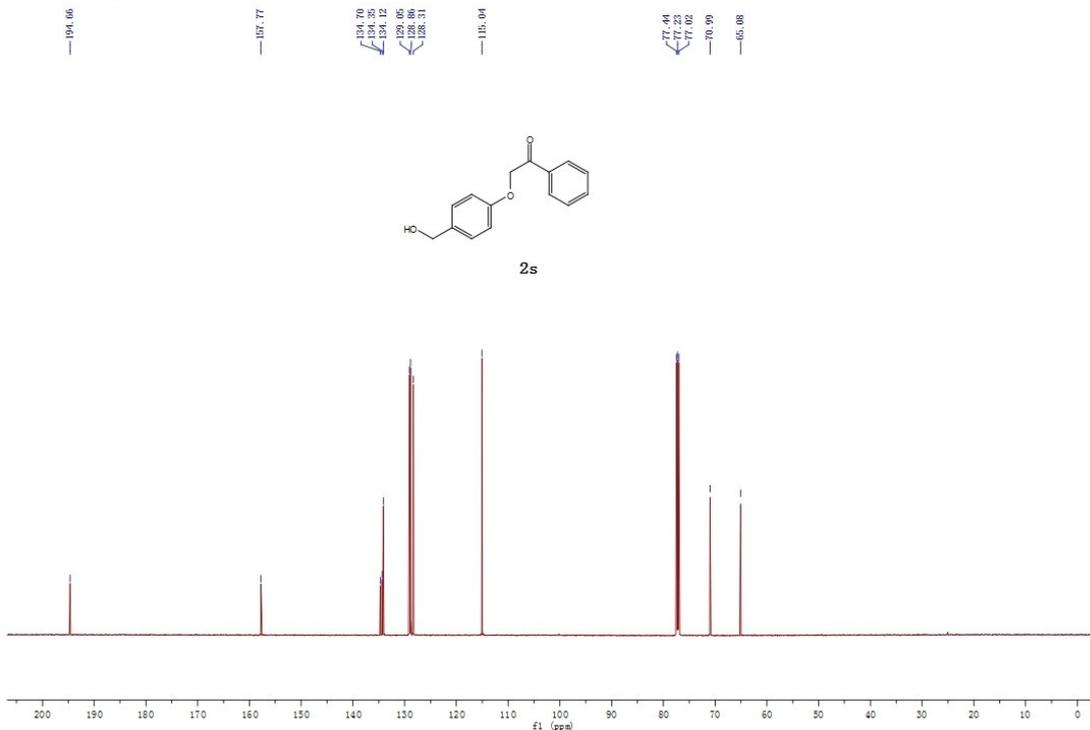
tbai-2-27-1 (13C NMR 151 MHz CDC13)



tbai-2-27-2 (1H NMR 600 MHz CDC13)



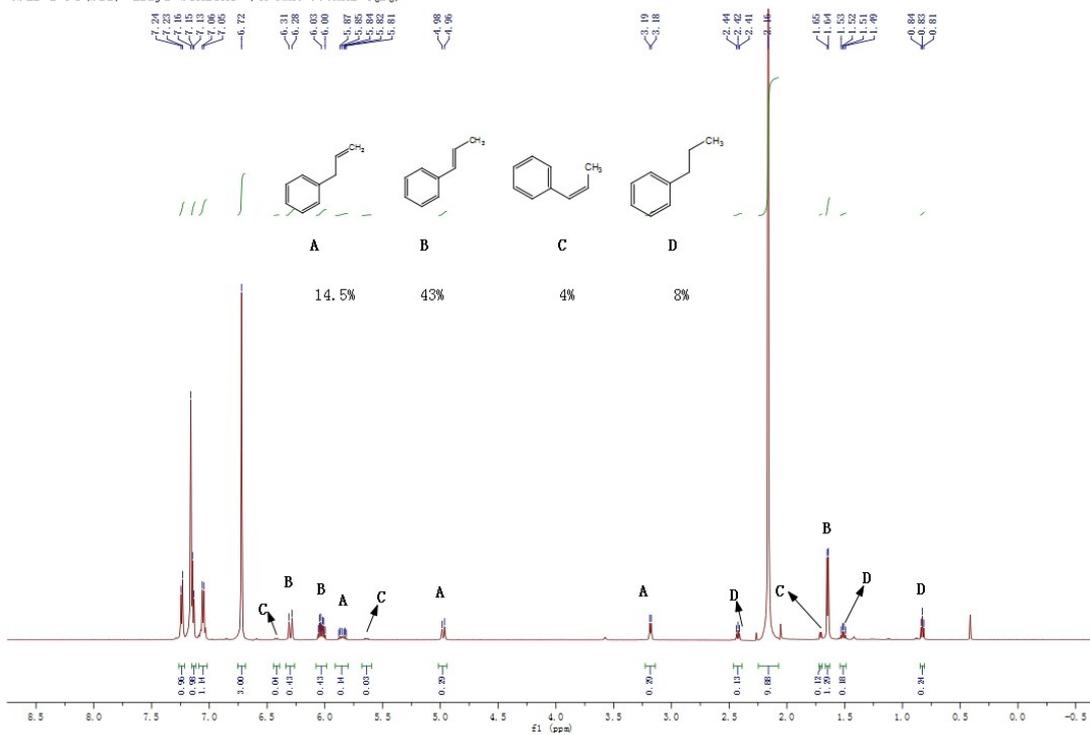
tbai-2-27-2 (13C NMR 151 MHz CDC13)



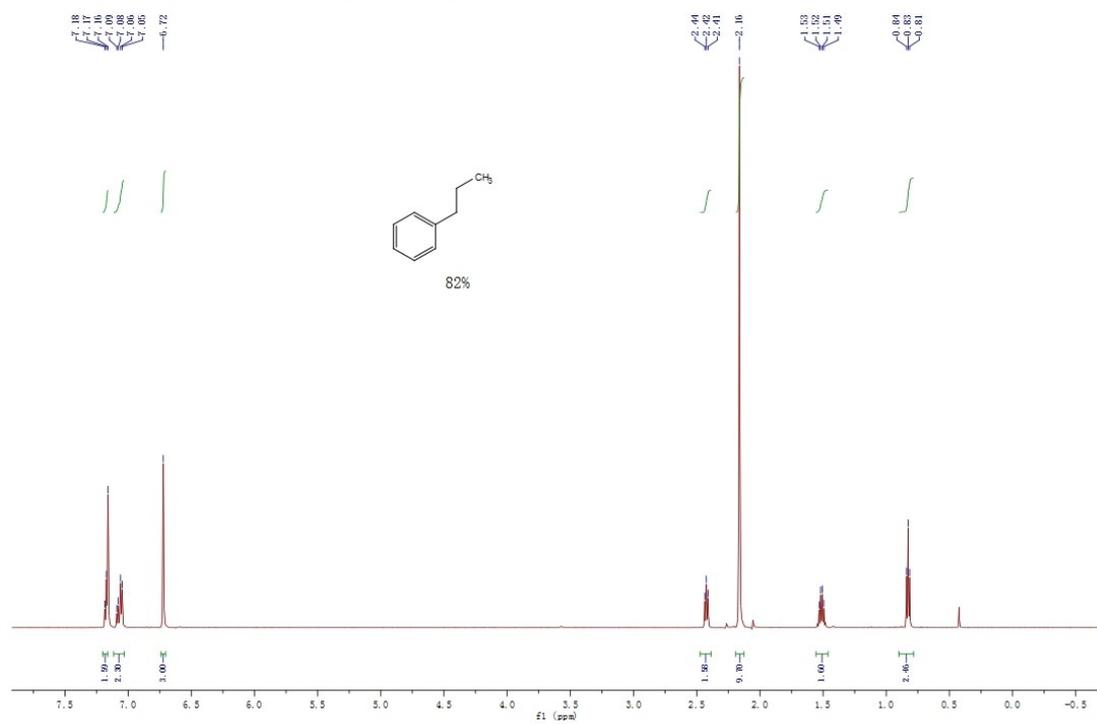
Appendix III.

Spectral Copies of ^1H NMR of hydrogenation reaction of alkenes and alkynes

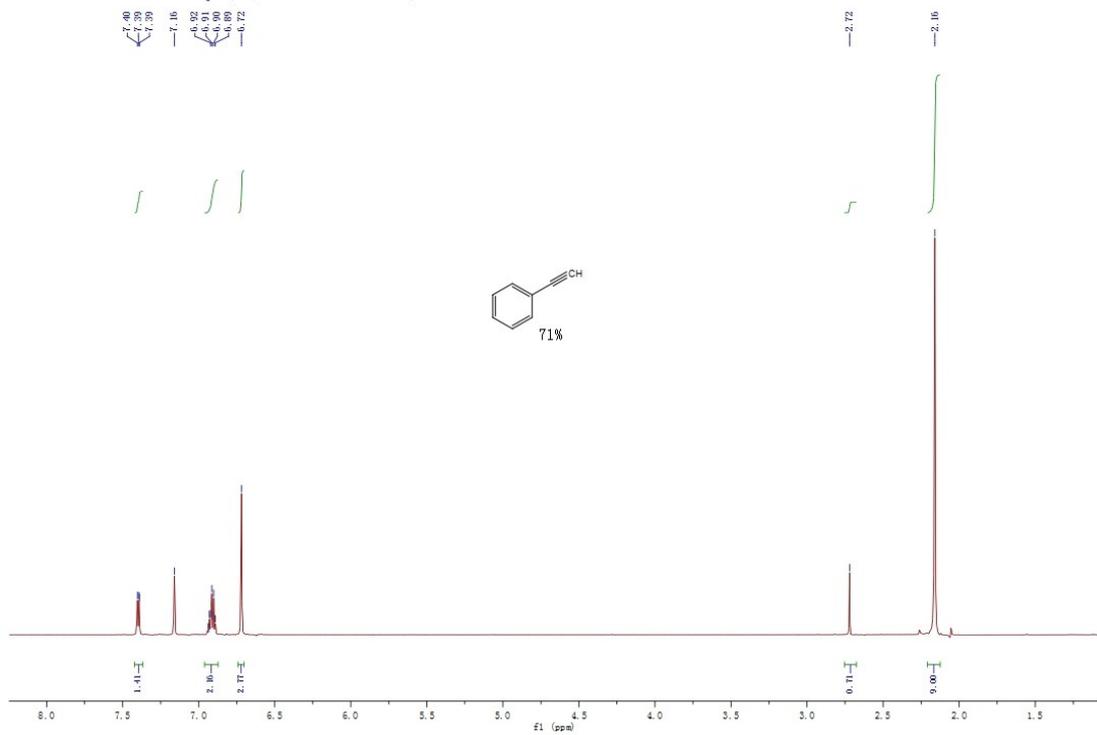
tbai-1-Fe(bis)+allyl benzene (^1H NMR 600MHz C_6D_6)



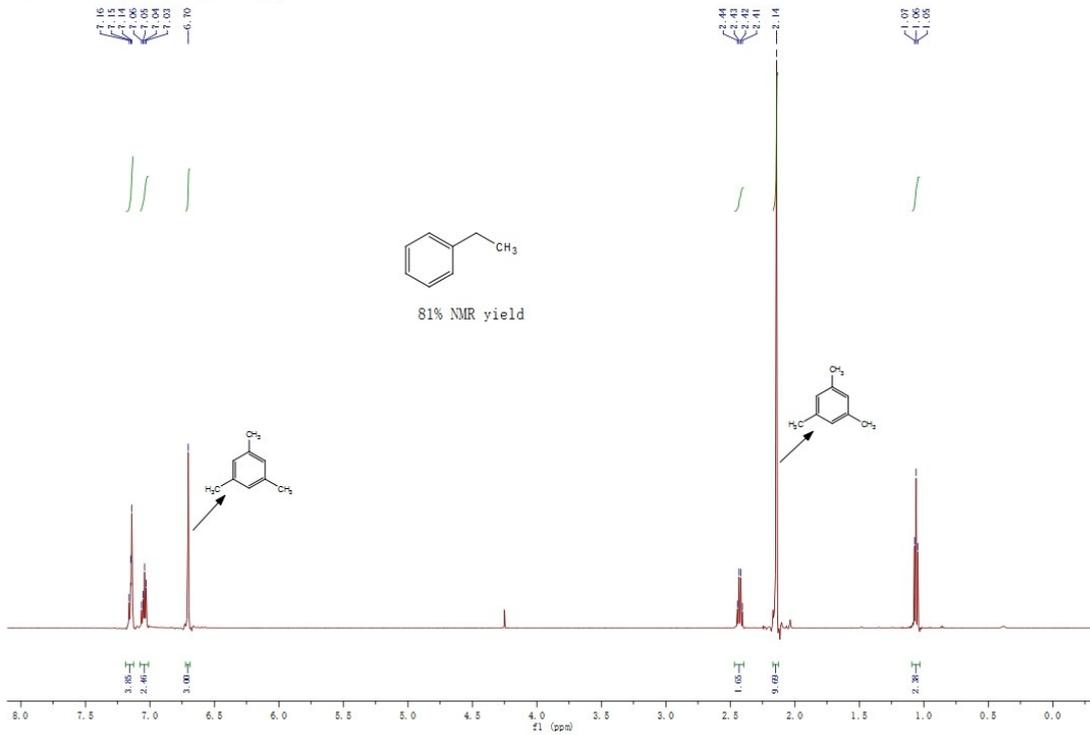
tbai-1-Co(bis)+allylbenzene+mesitylene (1H NMR 600MHz C6D6)



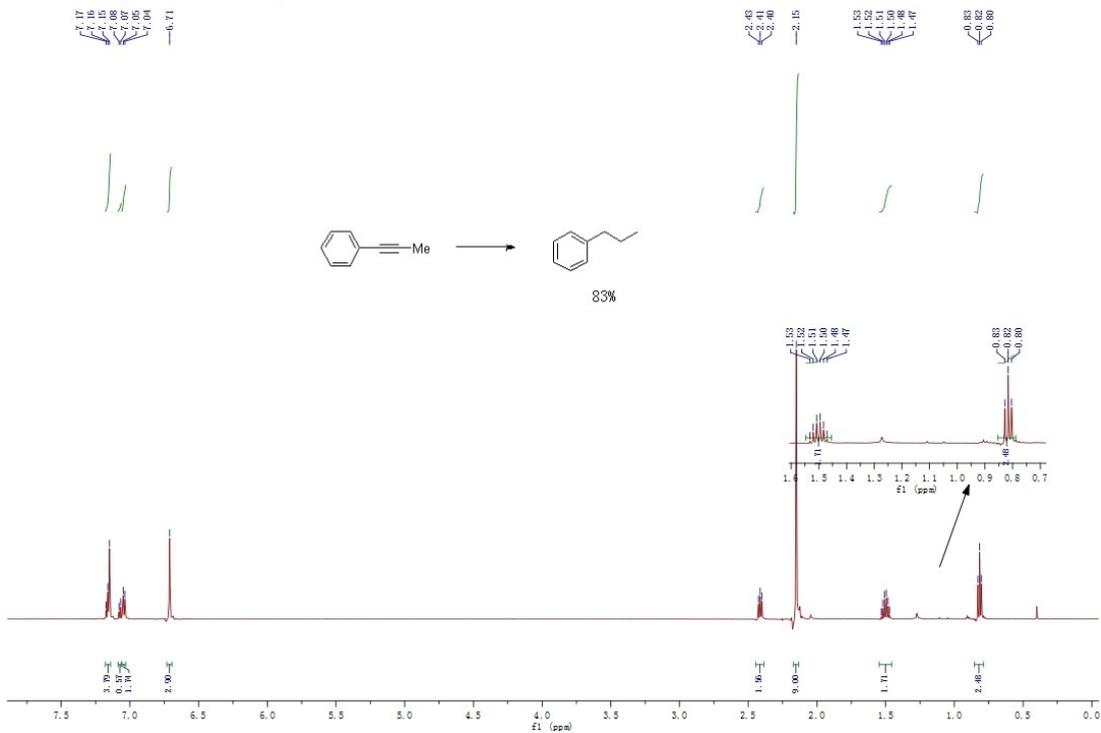
tbai-1-180-6-without HB(pin) (1H NMR 600 MHz C6D6)



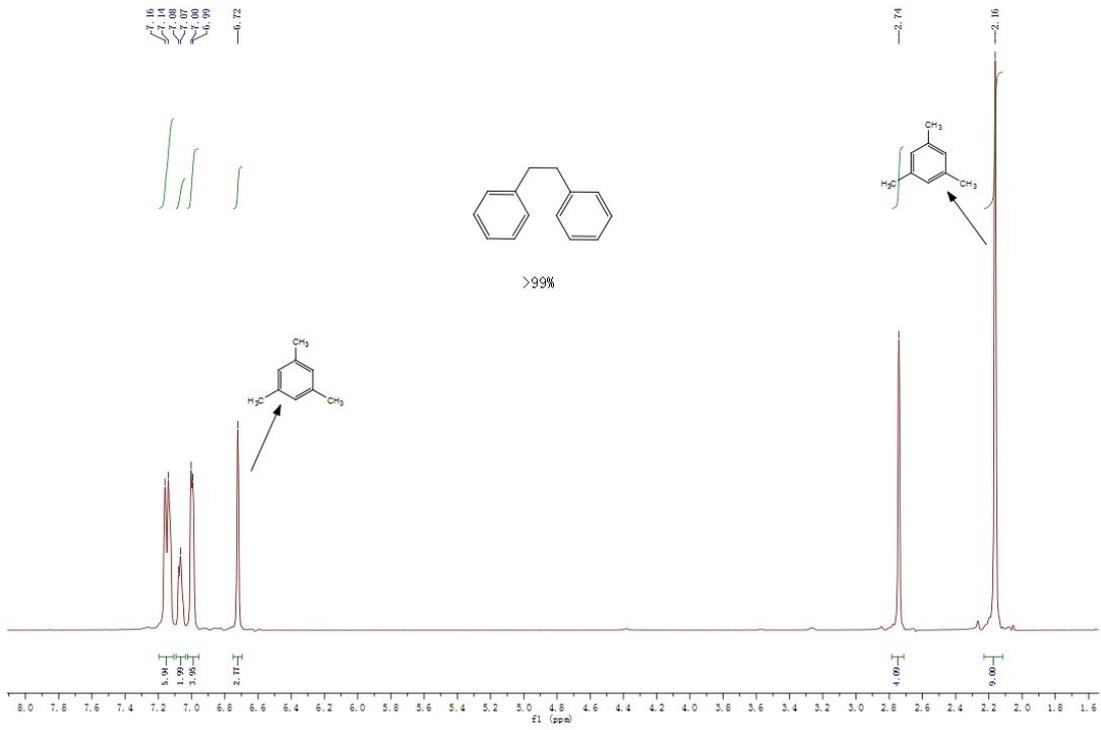
tbai-1-181-1 (1H NMR 600 MHz C6D6)



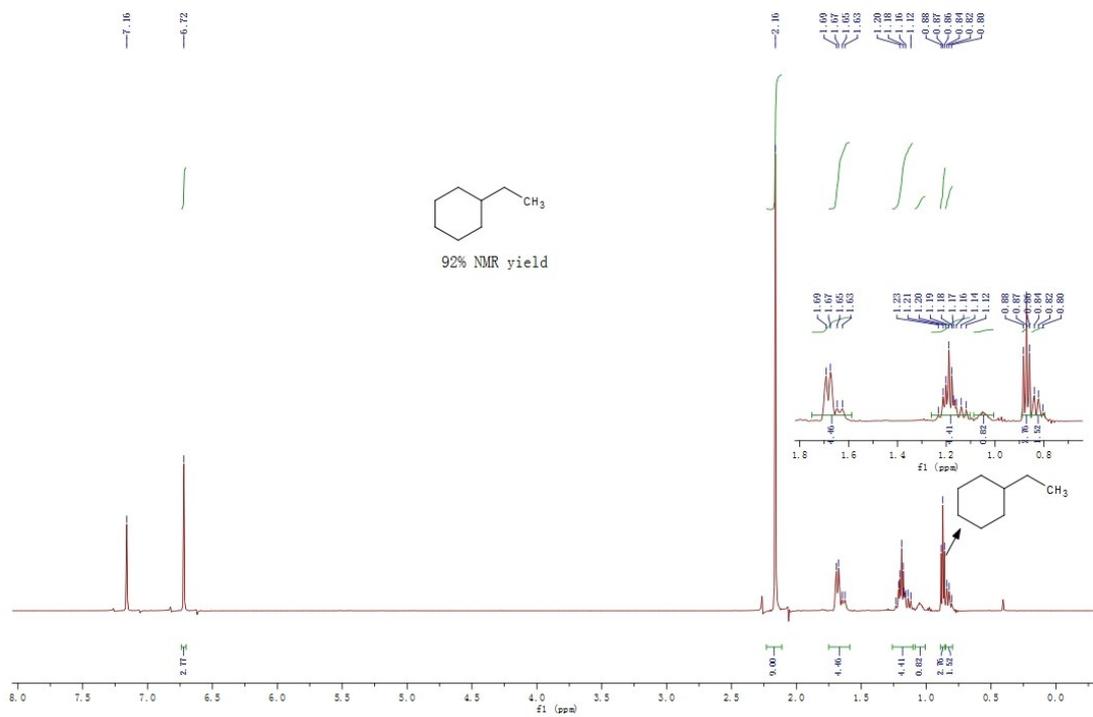
tbai-1-180-5 (1H NMR 600 MHz C6D6)



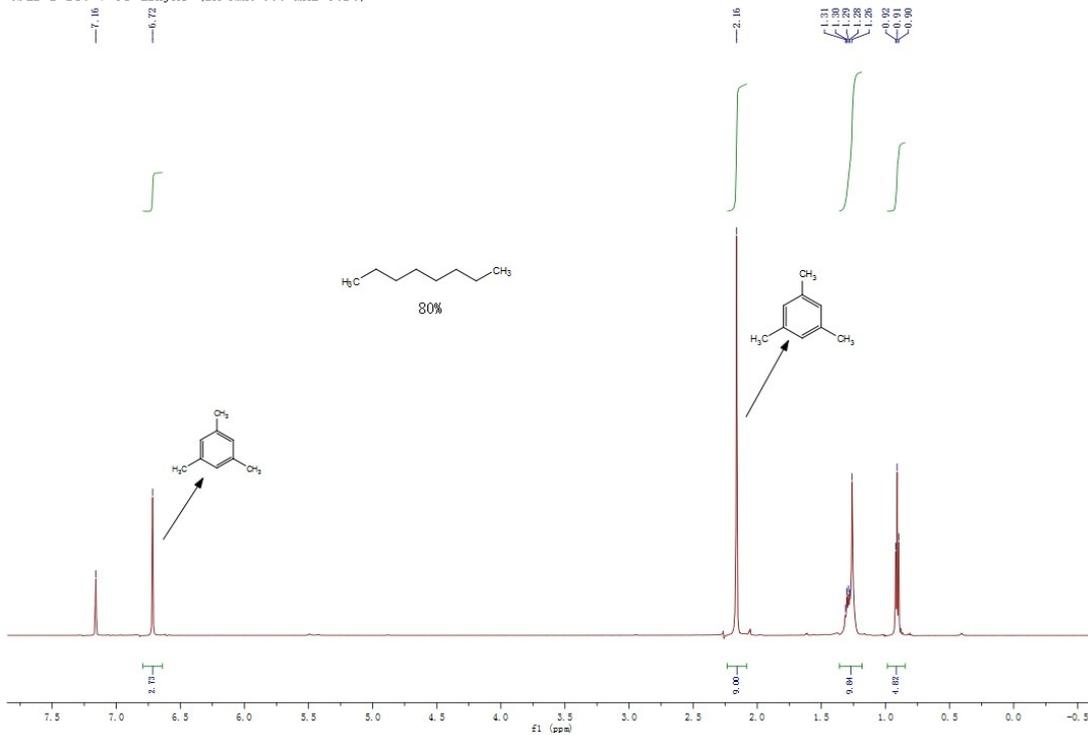
tbai-1-biphenylacetylene (1H NMR 600 MHz C6D6)



tbai-1-180-4 (1H NMR 600 MHz C6D6)



tbai-1-180-7-C8 alkyne (1H NMR 600 MHz C6D6)



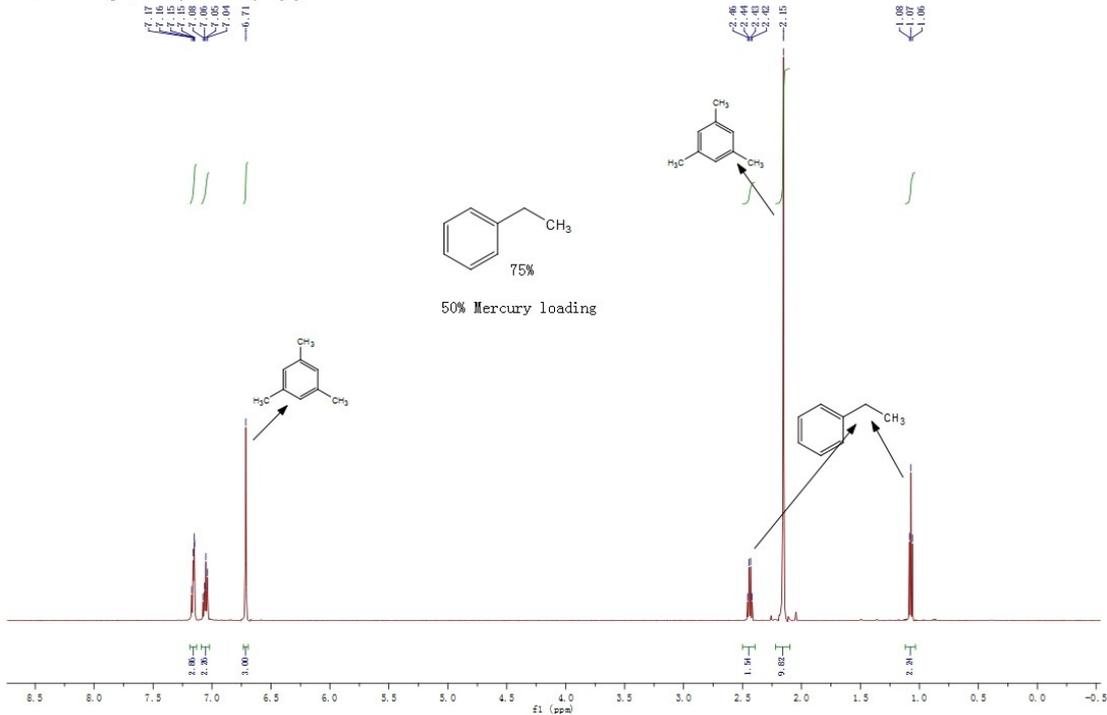
Appendix IV.

^1H NMR of Poisoning Effect experiments for Co(bis-phosphoramidate) B catalyzed hydrogenation reaction.

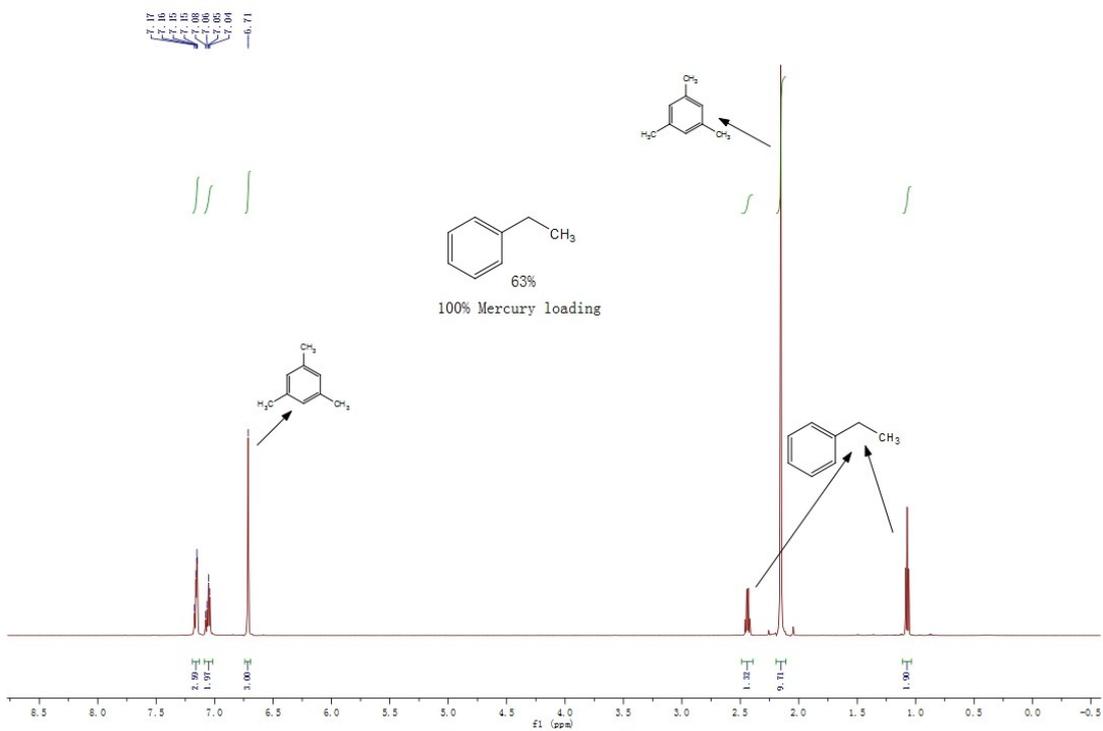
tbai-1-20% Hg (^1H NMR, 600 MHz, C_6D_6)



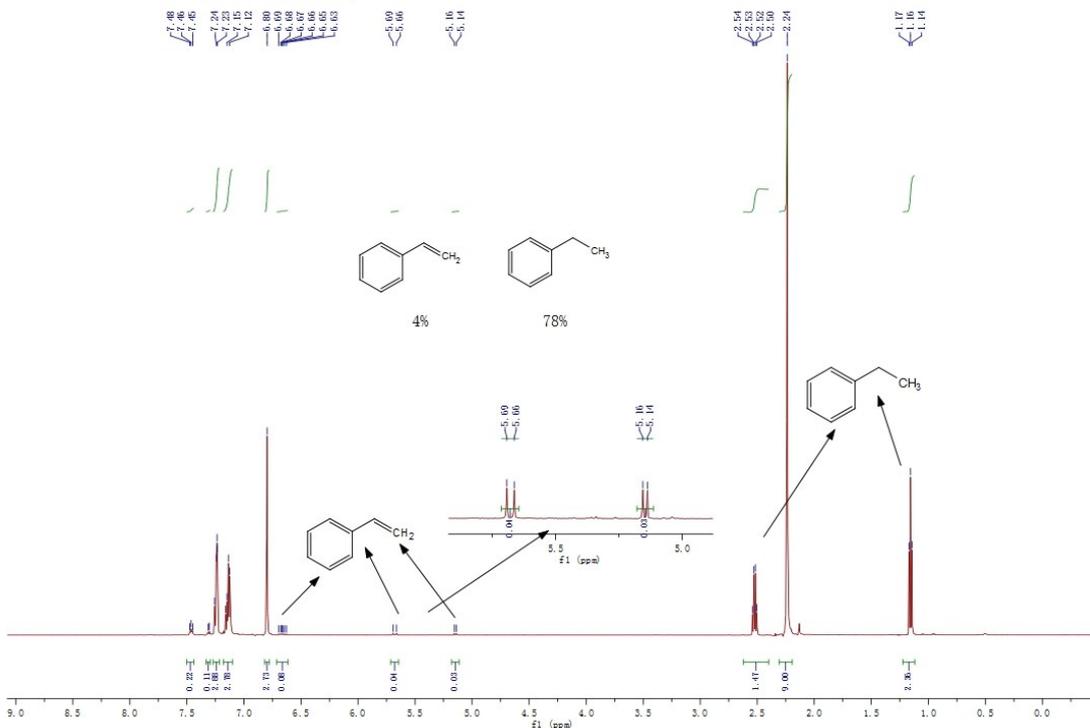
tbai-1-50% Hg (^1H NMR, 600 MHz, C_6D_6)



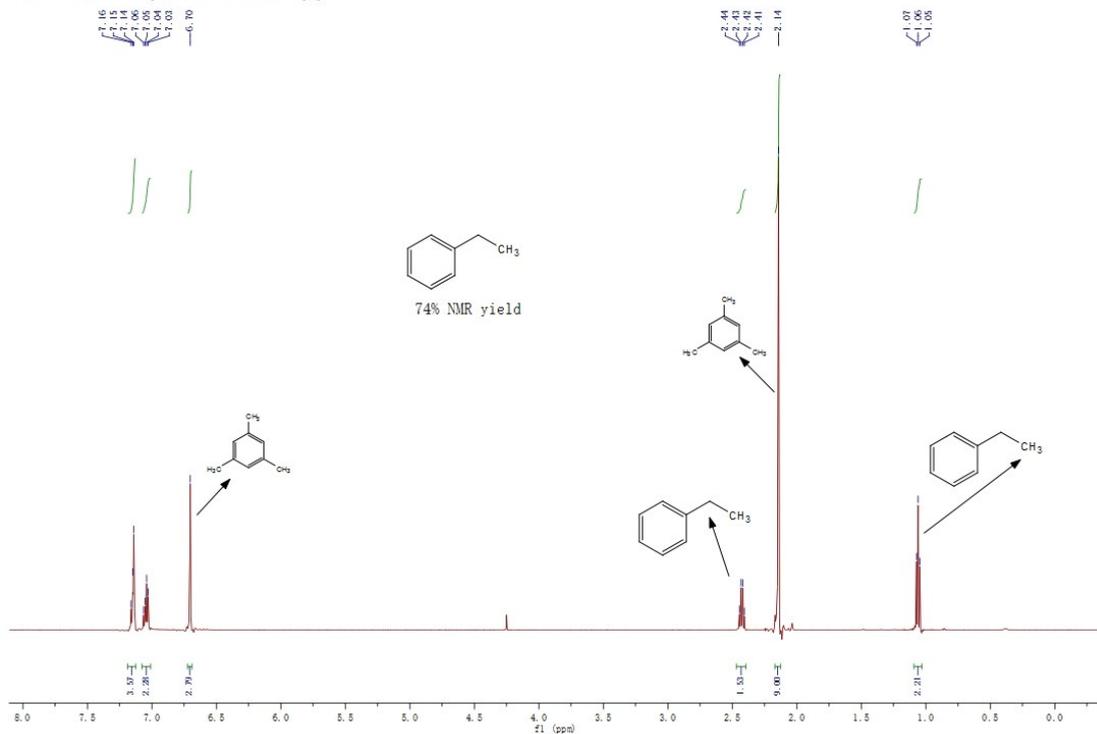
tbai-1-100% Hg (¹H NMR, 600 MHz, C₆D₆)



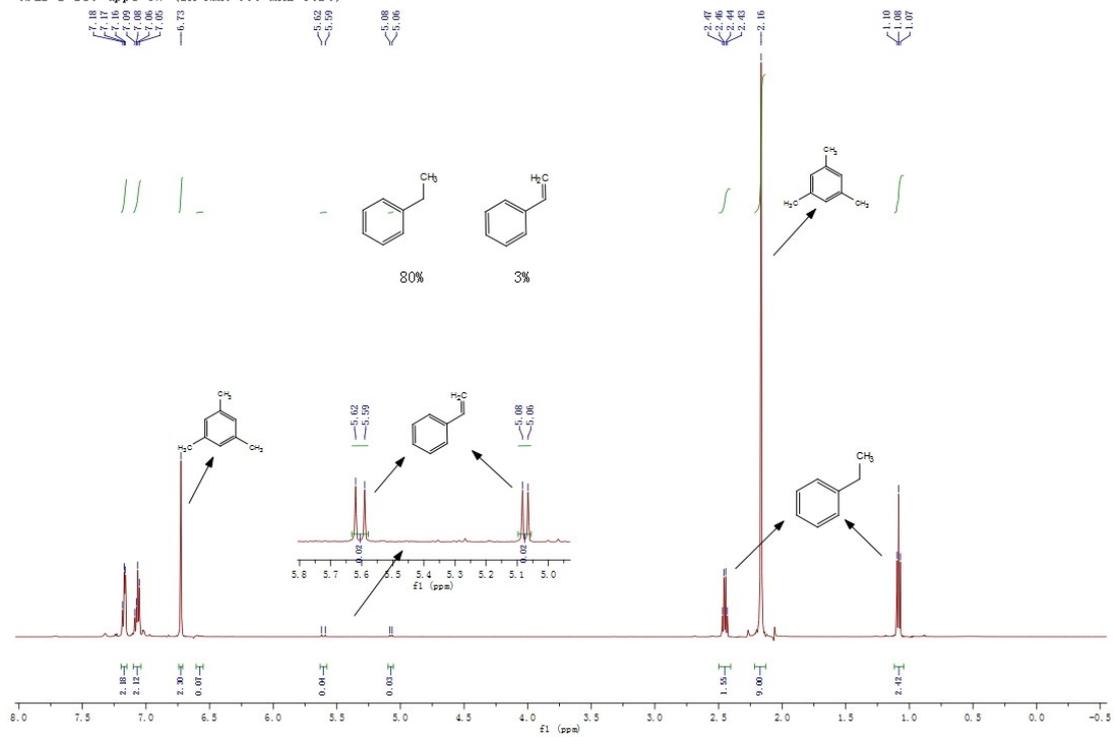
tbai-1-180-PPh3 5 mol% (¹H NMR 600MHz C6D6)



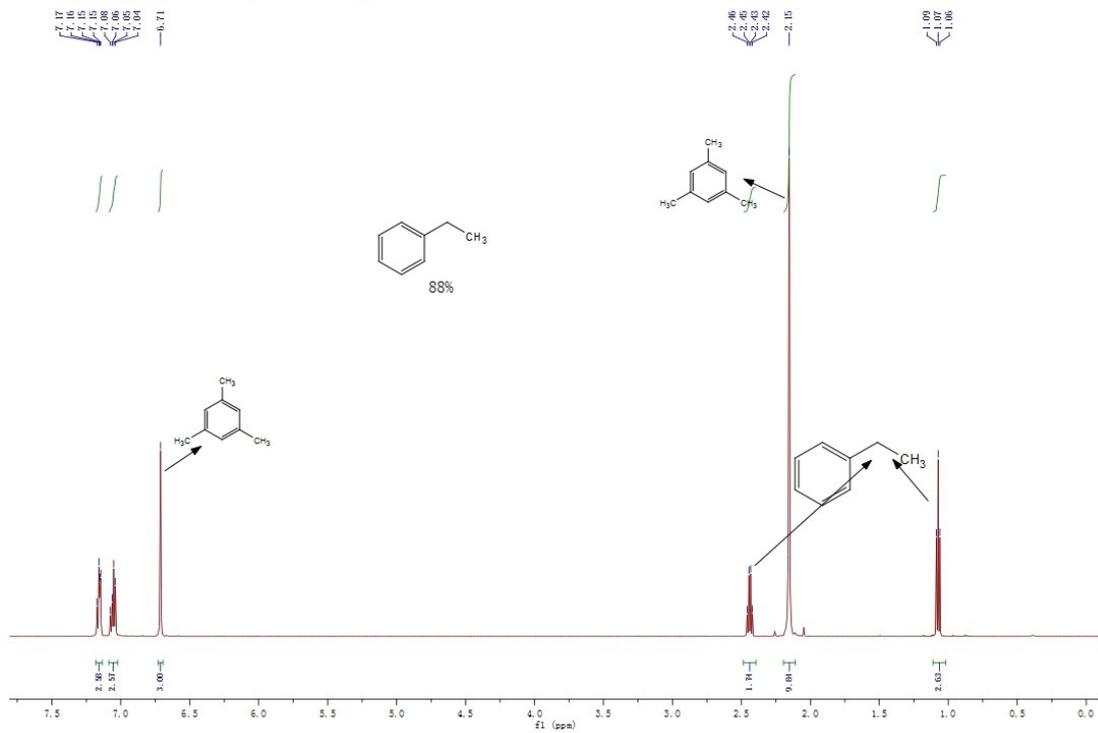
tbai-1-5 mol% PMe₃ (¹H NMR 600 MHz C₆D₆)



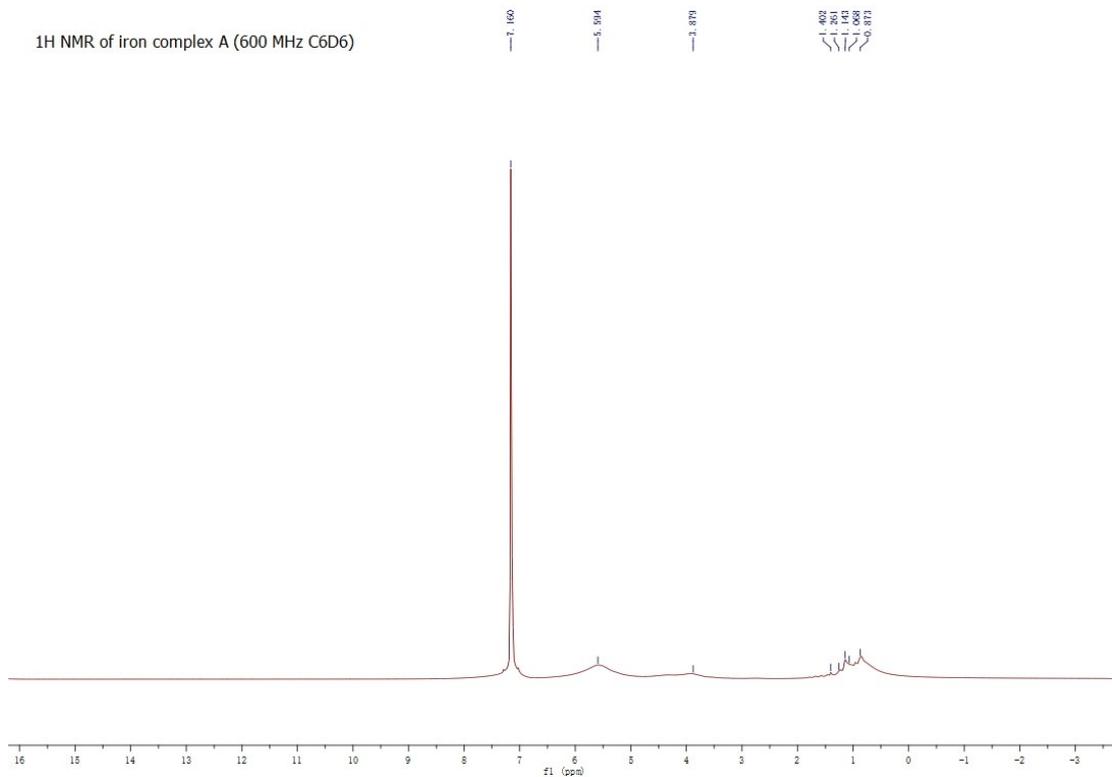
tbai-1-180-dppe 5% (¹H NMR 600 MHz C₆D₆)



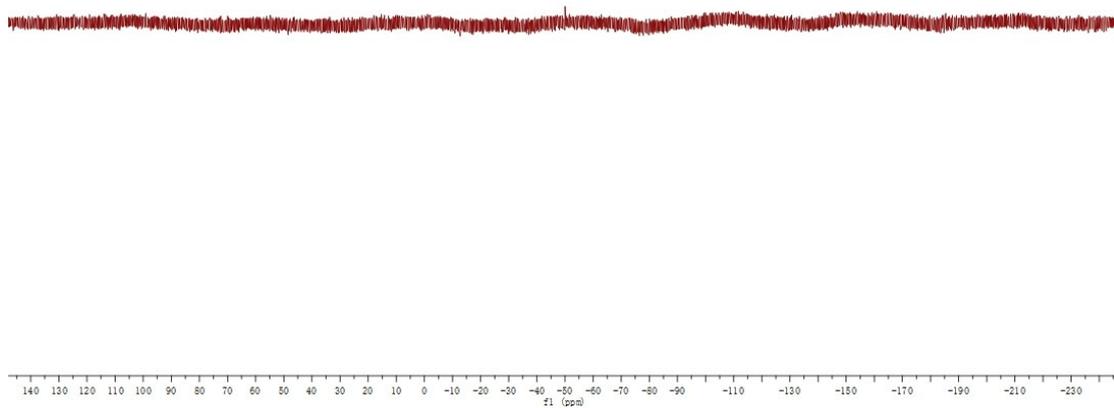
tbai-1-2,2'-Bipyridine (¹H NMR, 600 MHz, C₆D₆)



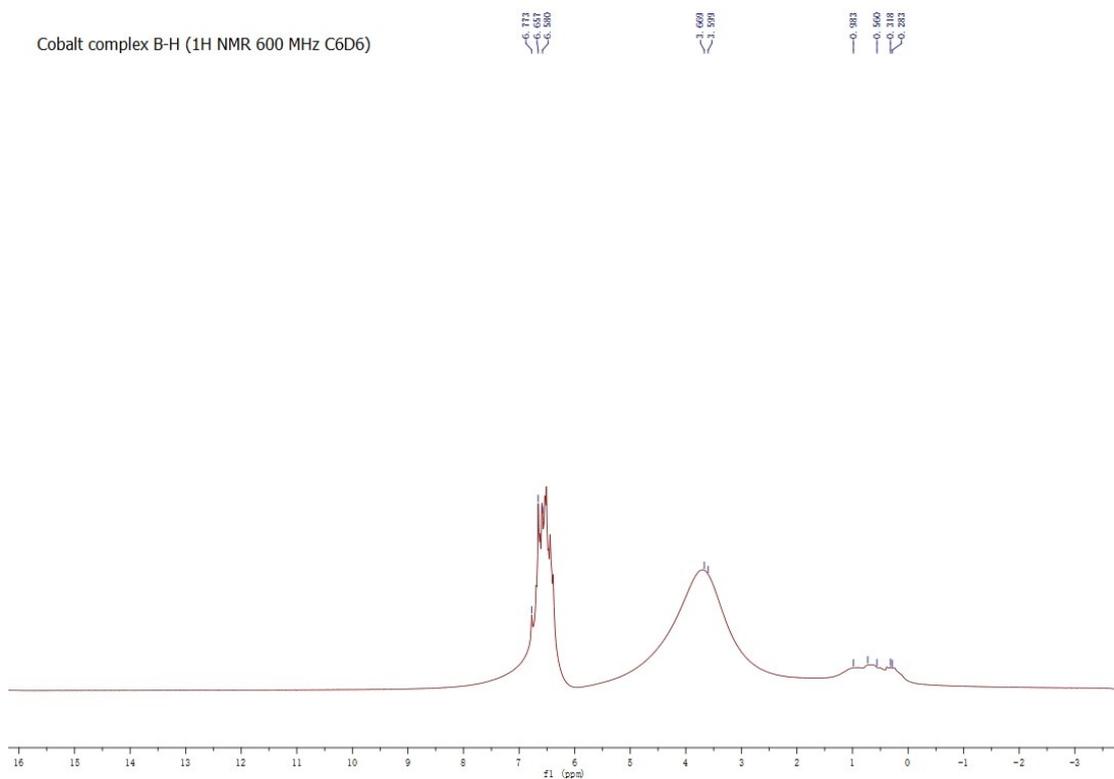
¹H NMR of iron complex A (600 MHz C₆D₆)



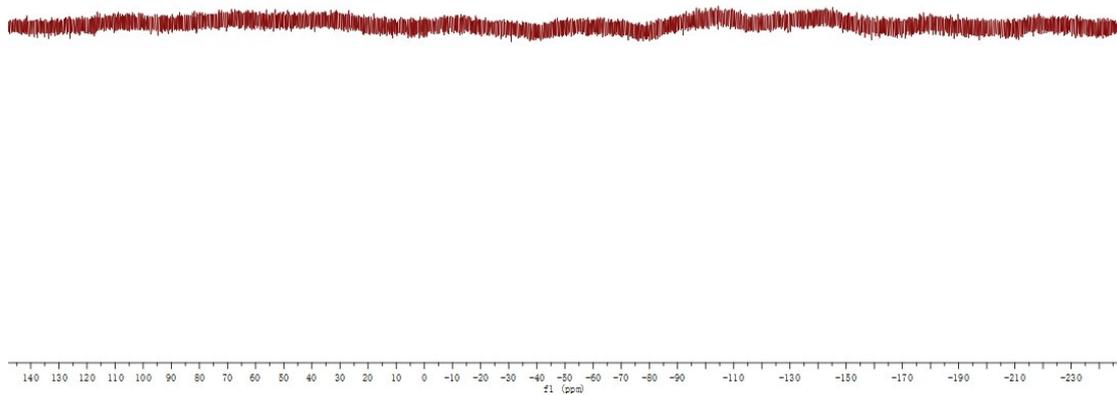
31P NMR of Iron complex A (C6D6, 243 MHz)



Cobalt complex B-H (1H NMR 600 MHz C6D6)

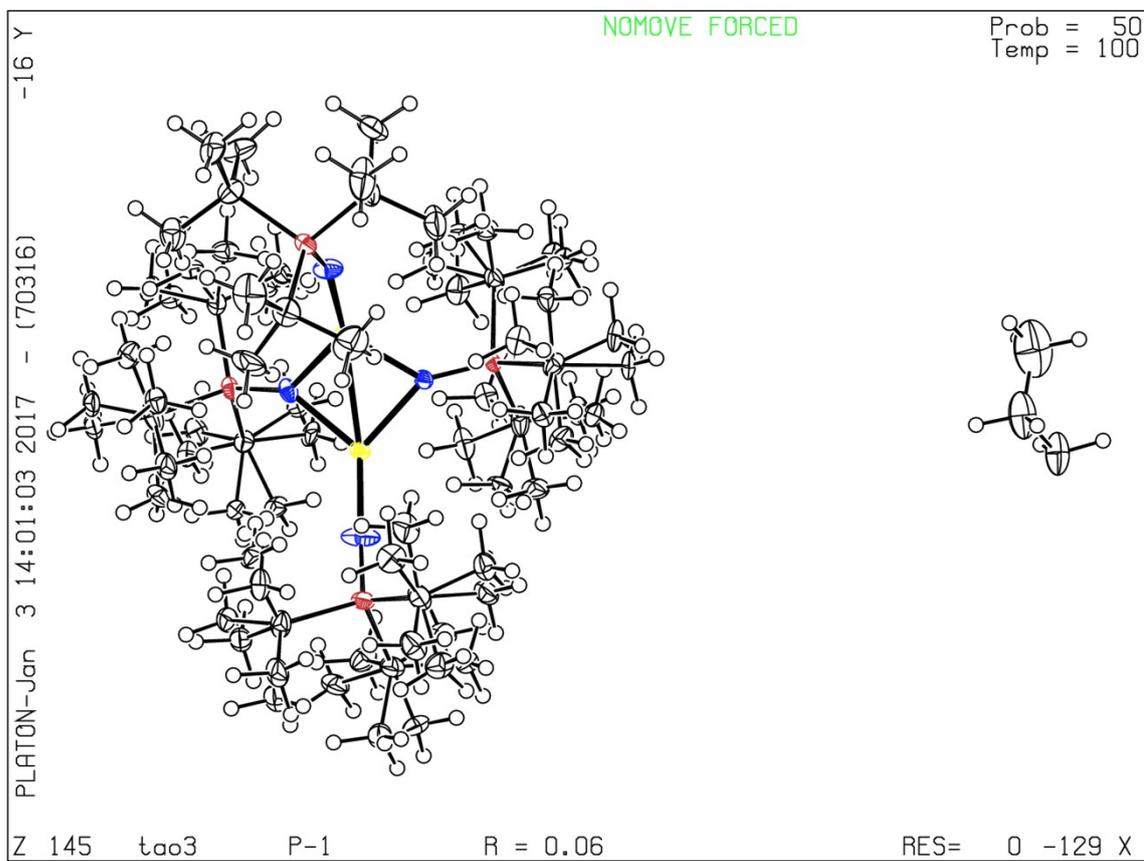


Cobalt complex B-P (31P NMR, 243 MHz, C6D6)



Appendix V. Crystallographic Data for X-ray.

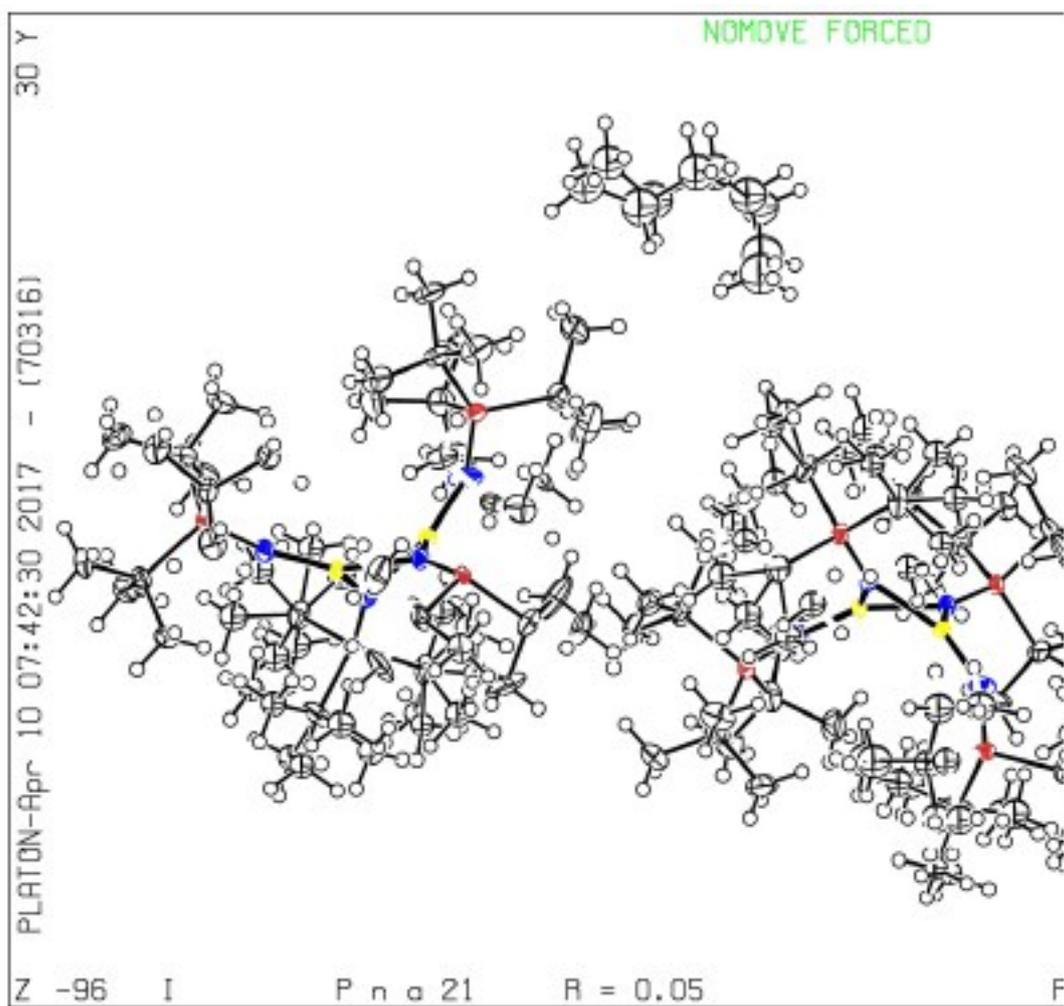
i. Crystal structure of iron complex A



Crystal data and structure refinement for A (CCDC: 1525454)

Identification code	Fe(bis-phosphoranimide)	
Empirical formula	C _{49.50} H _{111.50} Fe ₂ N ₄ P ₄	
Formula weight	998.51	
Temperature	100(2) K	
Wavelength	0.71073	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.448(2) Å	α = 83.232(5)°
	b = 13.300(2) Å	β = 80.779(5)°
	c = 19.898(3) Å	γ = 64.931(5)°
Volume	2940.8(9) Å ³	
Z	2	
Density (calculated)	1.128 g/cm ³	
Absorption coefficient	0.635 mm ⁻¹	
F(000)	1097	
Crystal size	0.25 x 0.23 x 0.11 mm ³	
Theta range for data collection	2.95-28.31°	
Index ranges	-14 ≤ h ≤ 16, -17 ≤ k ≤ 17, -26 ≤ l ≤ 26	
Reflections collected	38231	
Independent reflections	14386 [R(int) = 0.060]	
Completeness to theta = 30.41°	98.2%	
Absorption correction	Multi-scan; <i>SADABS</i>	
Max. and min. transmission	0.7457 and 0.5936	
Refinement method	difference Fourier map on F ²	
Data / restraints / parameters	14386 / 1 / 787	
Goodness-of-fit on F ²	1.035	
Final R indices [I > 2σ(I)]	R ₁ = 0.0622, wR ₂ = 0.1601	
R indices (all data)	R ₁ = 0.0836, wR ₂ = 0.1834	
Largest diff. peak and hole	0.912 and -0.949 e.Å ⁻³	

ii. Crystal structure of Cobalt complex B



Crystal data and structure refinement for A (CCDC: 1542180)

Identification code	Co(bis-phosphoranimide)	
Empirical formula	C ₅₃ H ₁₂₀ Co ₂ N ₄ P ₄	
Formula weight	1055.26	
Temperature	100(2) K	
Wavelength	0.71073	
Crystal system	Orthorhombic	
Space group	<i>Pna</i> 2 ₁	
Unit cell dimensions	a = 24.103 (1) Å	α = 90.000(0)°
	b = 22.7743 (10) Å	β = 90.000(0)°
	c = 22.3132 (9) Å	γ = 90.000(0)°
Volume	12248.4 (9) Å ³	
Z	8	
Density (calculated)	1.145 g/cm ³	
Absorption coefficient	0.681 mm ⁻¹	
F(000)	4640	
Crystal size	0.20 x 0.18 x 0.16 mm ³	
Theta range for data collection	2.83-27.53°	
Index ranges	-31 ≤ h ≤ 31, -29 ≤ k ≤ 29, -24 ≤ l ≤ 28	
Reflections collected	172361	
Independent reflections	25317 [R(int) = 0.044]	
Completeness to theta = 30.41°	99.8%	
Absorption correction	Multi-scan; <i>SADABS</i>	
Max. and min. transmission	0.7456 and 0.6874	
Refinement method	difference Fourier map on F ²	
Data / restraints / parameters	25317 / 13 / 1067	
Goodness-of-fit on F2	1.019	
Final R indices [I > 2σ(I)]	R1 = 0.0488, wR2 = 0.1200	
R indices (all data)	R1 = 0.0608, wR2 = 0.1117	
Largest diff. peak and hole	0.897 and -0.952 e.Å ⁻³	

