

**The Selective Activation of C-F Bond with the Auxiliary of Strong
Lewis Acid --- A Method to Change the Activation Preference of C-F
and C-H bond**

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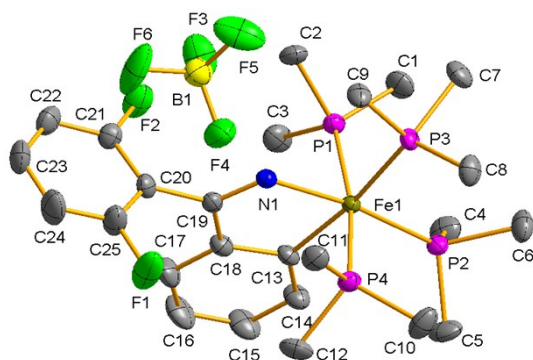
SI. Selected X-ray crystallographic data

	10*	11	12
formula	C ₂₅ H ₄₄ BF ₆ FeNP ₄	C ₂₃ H ₃₈ BrFFeNP ₃	C ₂₆ H ₄₄ FFeINP ₃
M_z	663.15	576.21	665.28
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	P2(1)/n	P2(1)/c	P2(1)/c
a [Å]	11.7534(1)	8.9625(3)	15.6776(12)
b [Å]	19.4894(2)	33.2859(13)	13.1670(11)
c [Å]	14.8134(1)	9.0190(3)	16.6228(17)
α [°]	90.00	90.00	90.00
β [°]	93.7660(1)	95.341(3)	118.742(5)
γ [°]	90.00	90.00	90.00
V [Å ³]	3385.9(5)	2678.91(2)	3008.6(5)
T [K]	296(2)	153(2)	296(2)
Z	4	4	4
μ [mm ⁻¹]	0.683	2.252	1.708
total reflns	25229	7826	42857
unique reflns	7774	4112	7226
R _{int}	0.0306	0.0487	0.0858
R ₁ [I>2 σ (I)]	0.0352	0.0533	0.0624
wR(F ²) [I>2 σ (I)]	0.1014	0.1477	0.1558
R ₁ (all data)	0.0456	0.0594	0.0957
wR(F ²)(all data)	0.1135	0.1544	0.1778
GOF on F ²	0.541	1.079	1.084

* The disorder solvent voids were squeezed. Based on the squeezed result, there are about 2.8 ethyl ether molecules in one cell.

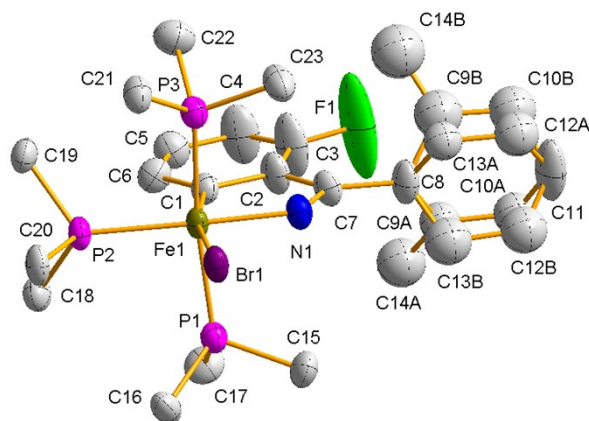
SII. The detailed crystal data of complex

Complex 10



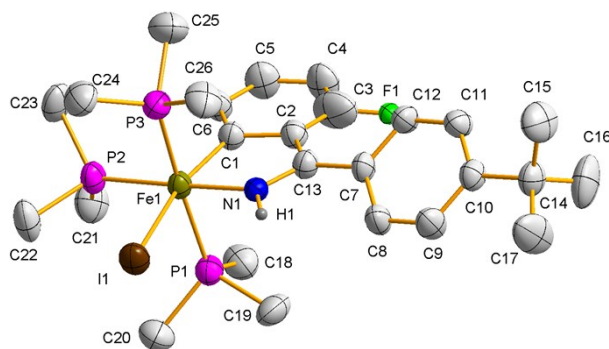
Fe(1)-C(13): 2.0164(2) Å, Fe(1)-N(1): 1.9858(2) Å, F(3)-B(1): 1.389(3) Å, F(4)-B(1): 1.370(3) Å, F(5)-B(1): 1.380(3) Å, F(6)-B(1): 1.367(3) Å. C(13)-Fe(1)-P(3): 171.72(6)°, P(1)-Fe(1)-P(3): 91.19(2)°

Complex 11



Fe(1)-Br(1): 2.5653(7) Å, Fe(1)-N(1): 1.945(4) Å, P(2)-Fe(1)-N(1): 175.45(1)°, P(1)-Fe(1)-C(1): 93.38(15)°

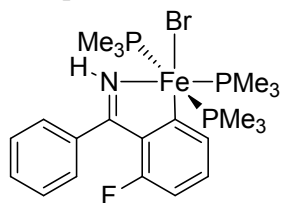
Complex 12



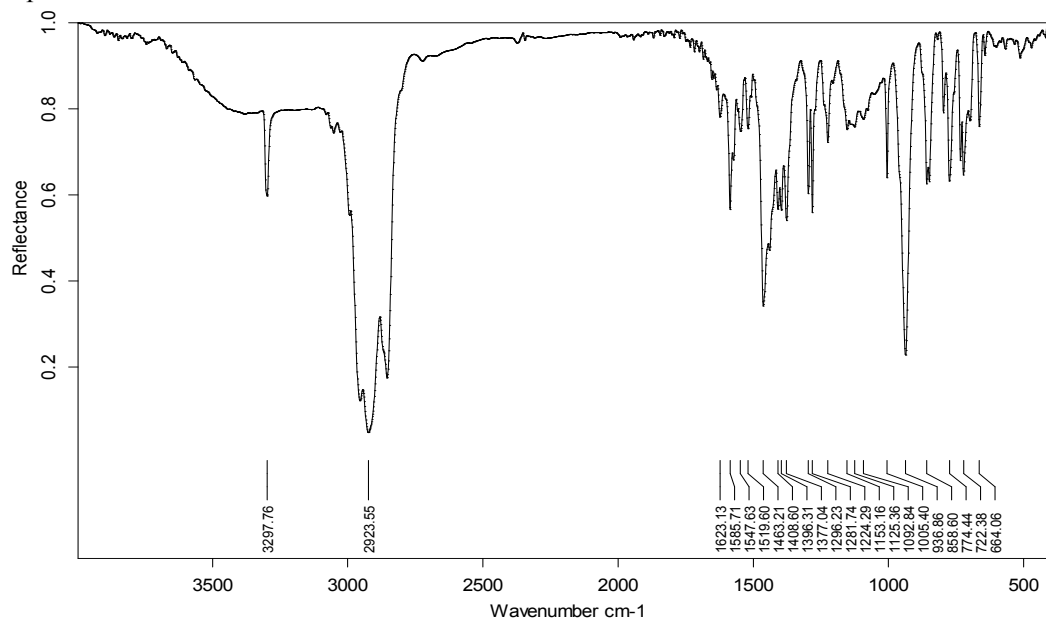
Fe(1)-I(1): 2.7478(9) Å, Fe(1)-N(1): 1.930(5) Å, P(2)-Fe(1)-P(3): 94.01(7)°, P(1)-Fe(1)-P(3): 172.69(7)°

SIII. The IR and NMR data of complexes

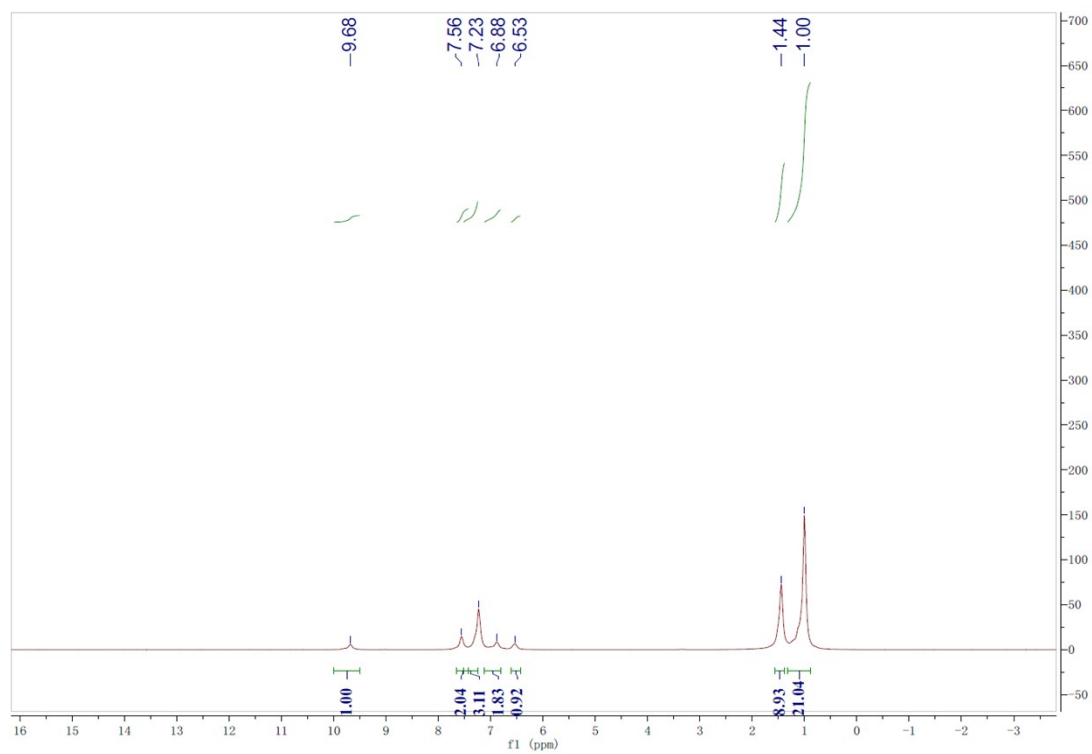
Complex 8



IR spectrum

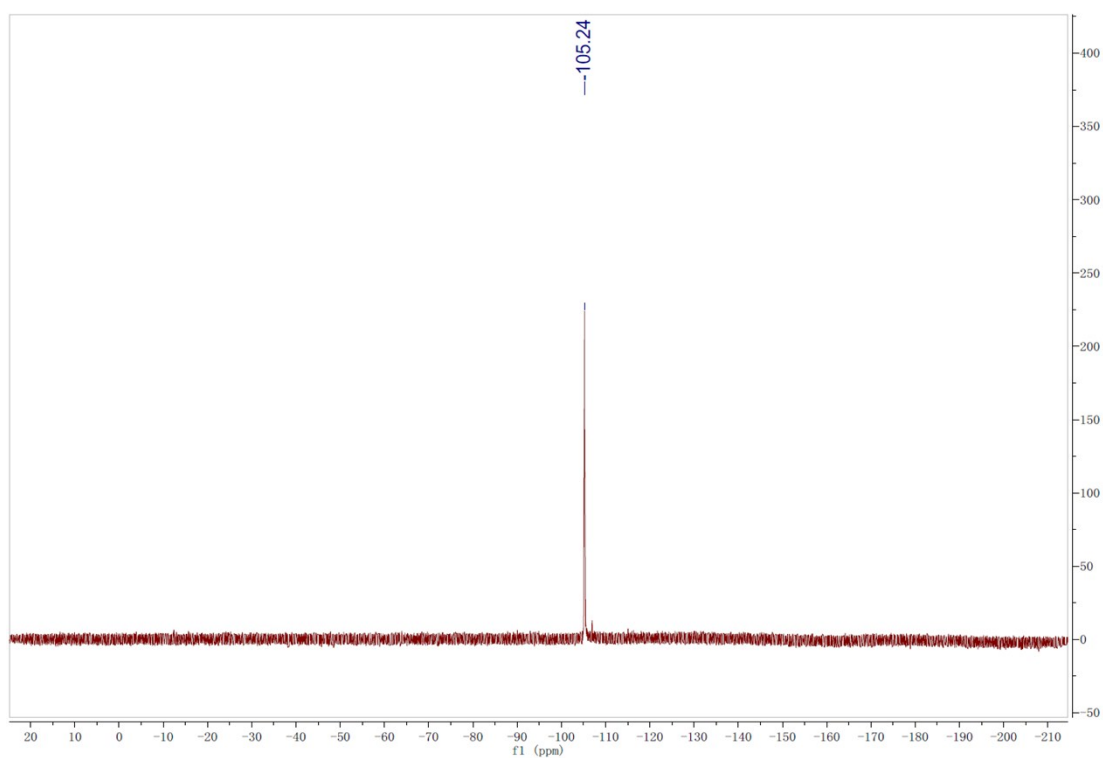


¹H NMR spectrum (C₆D₆)



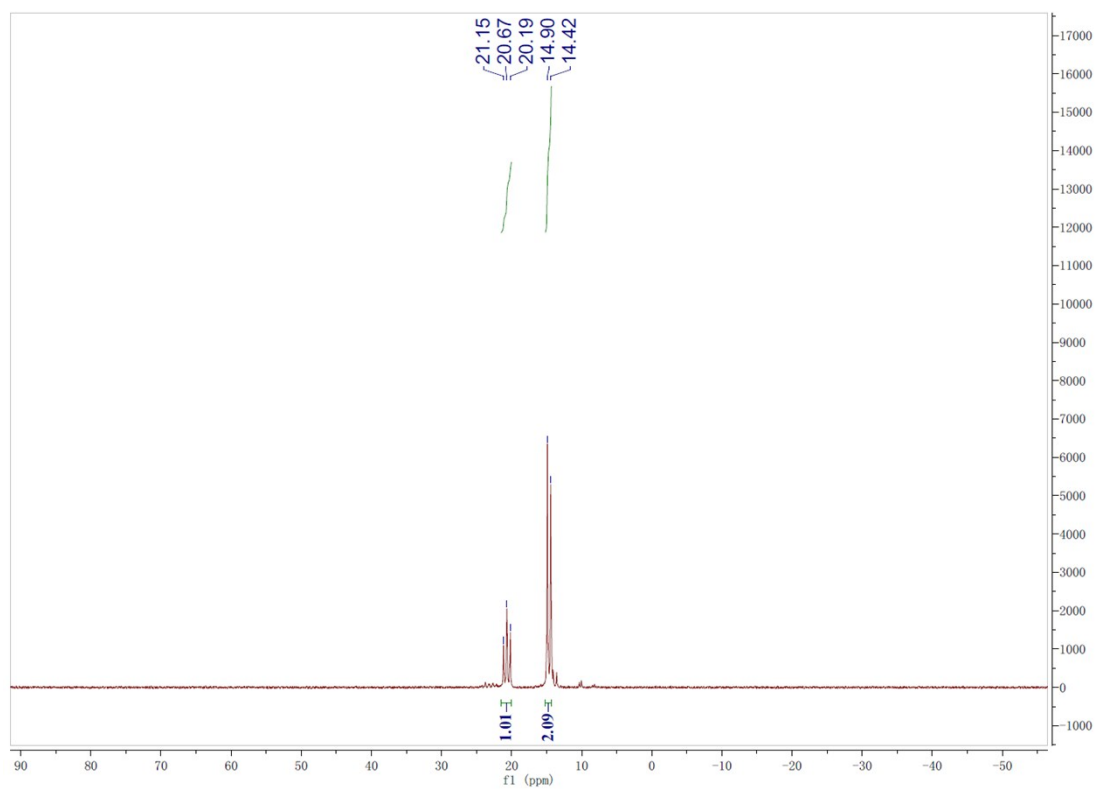
Note: Complex 8 was synthesized in diethyl ether.

^{19}F {H} NMR spectrum (C_6D_6)



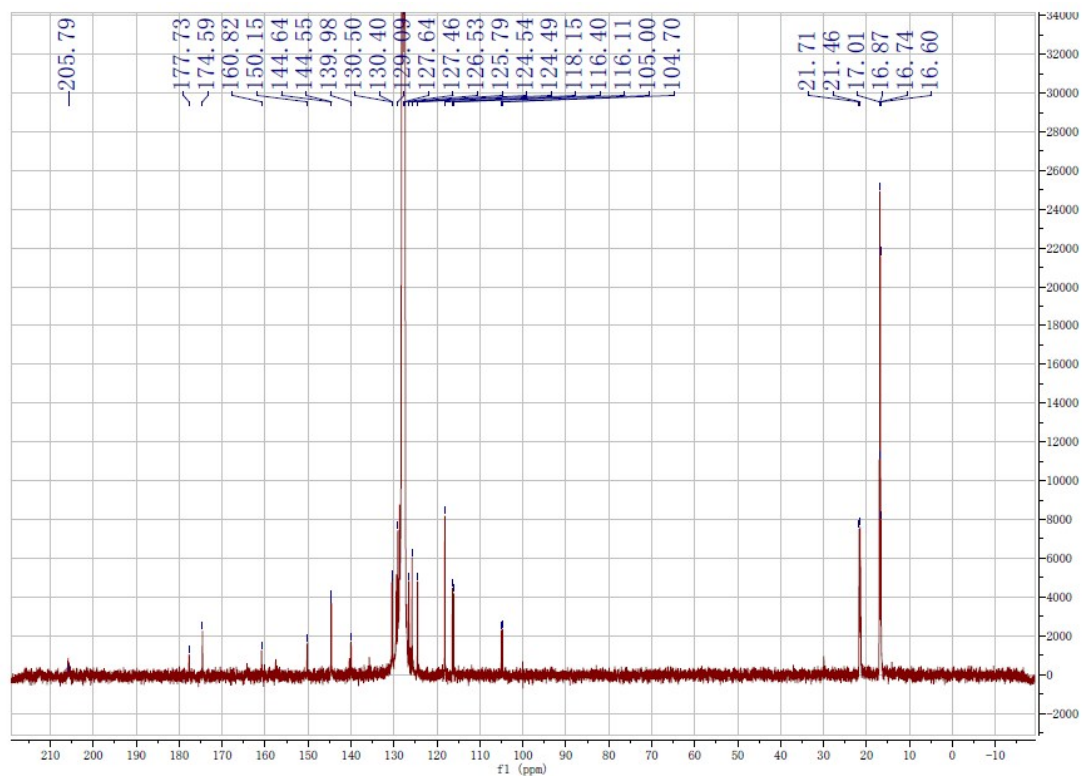
Note: Complex **8** was synthesized in ethyl ether.

^{31}P {H} NMR spectrum (C_6D_6)



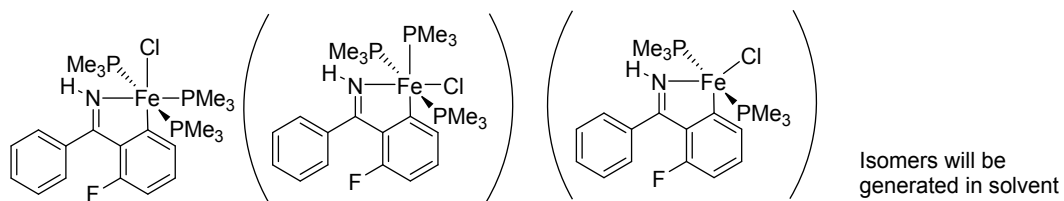
Note: Complex **8** was synthesized in diethyl ether

^{13}C {H} NMR spectrum (C_6D_6)

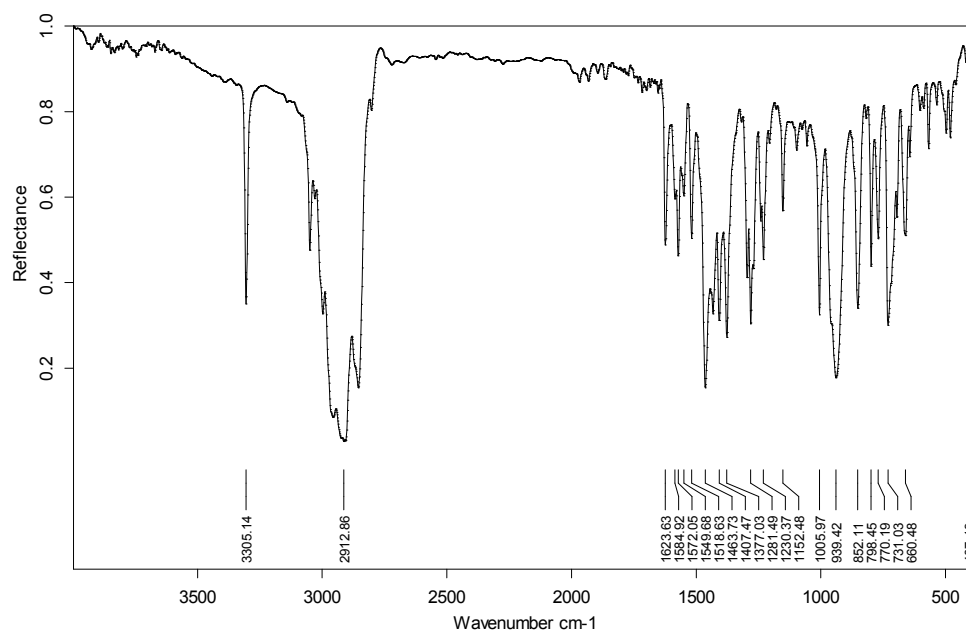


Note: Complex **8** was synthesized in diethyl ether.

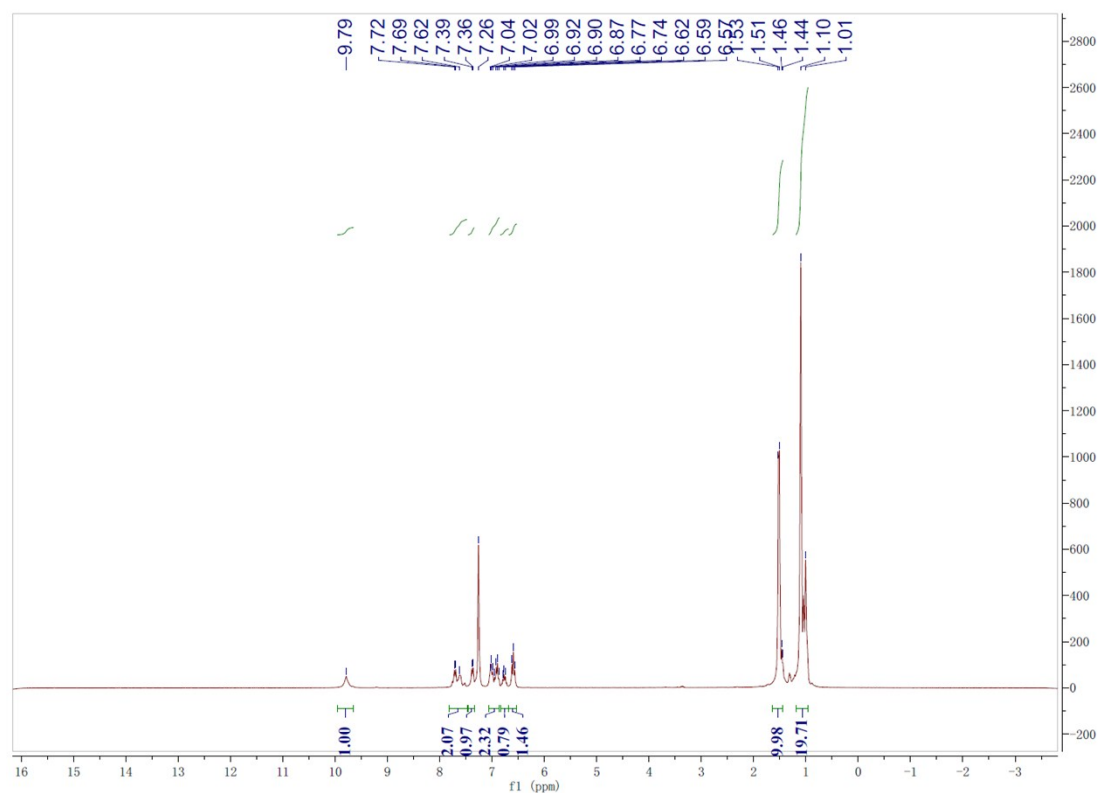
Complex 9



IR spectrum

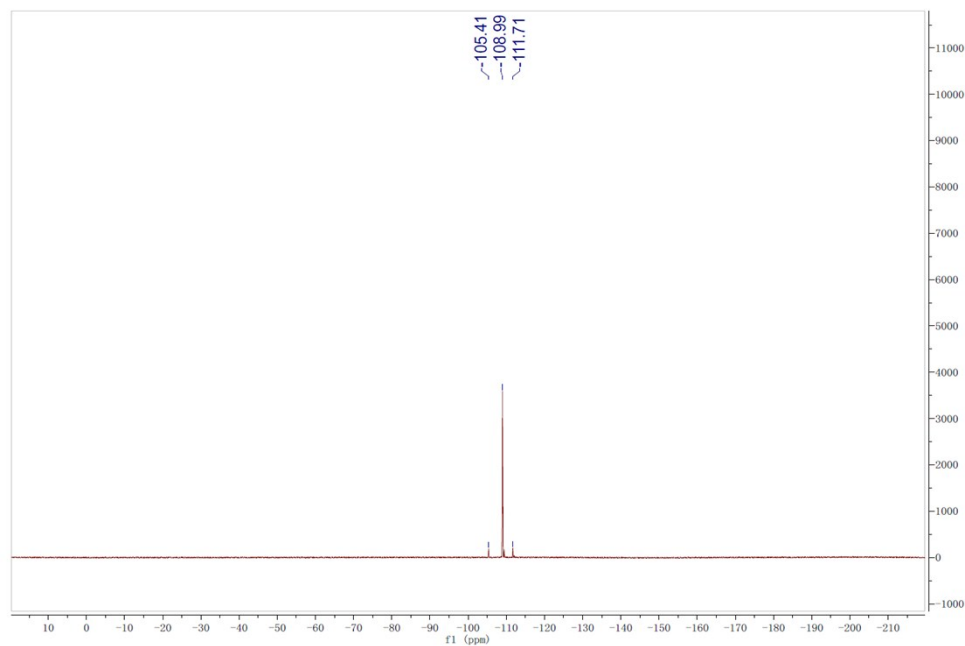


^1H NMR spectrum (C_6D_6)



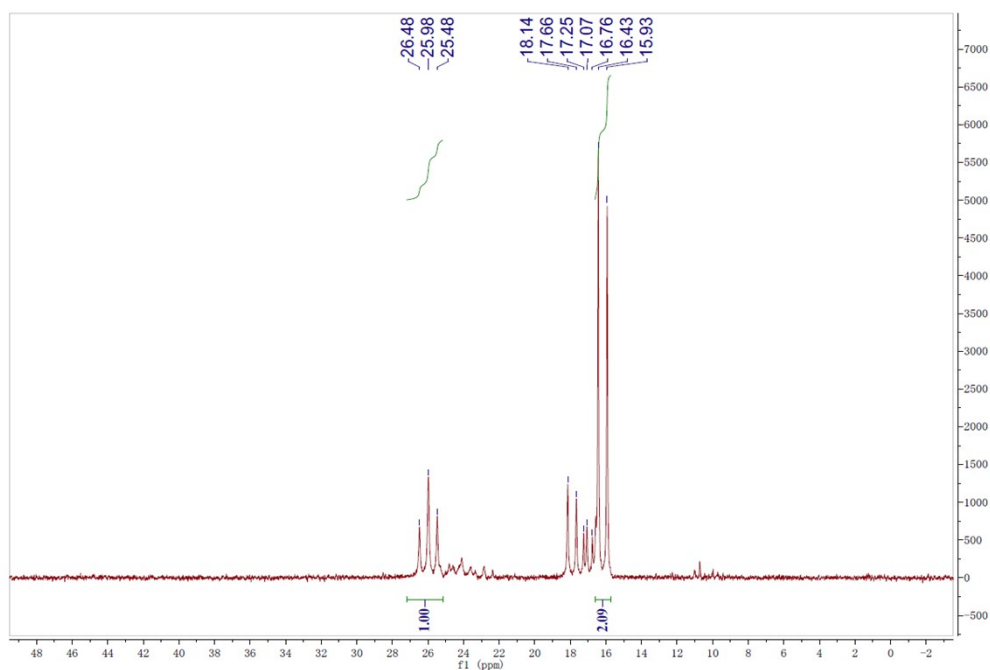
Note: Complex **9** was synthesized in diethyl ether. The signals at 1.01 and 1.05 ppm are the signals of PMe_3 contained by isomers.

^{19}F {H} NMR spectrum (C_6D_6)



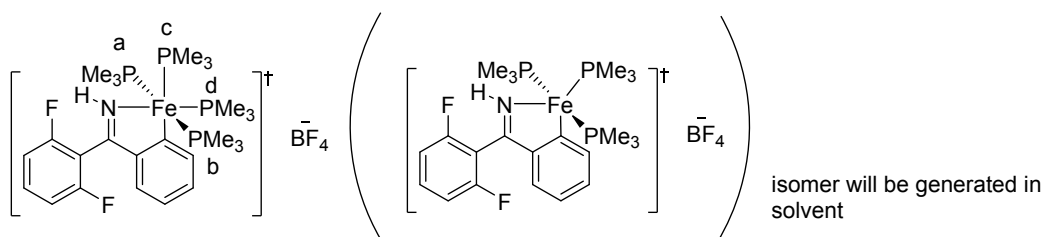
Note: Complex **9** was synthesized in diethyl ether. The signals at -111.7 and -105.4 ppm are the signals of isomers.

$^{31}\text{P} \{^1\text{H}\}$ NMR spectrum (C_6D_6)

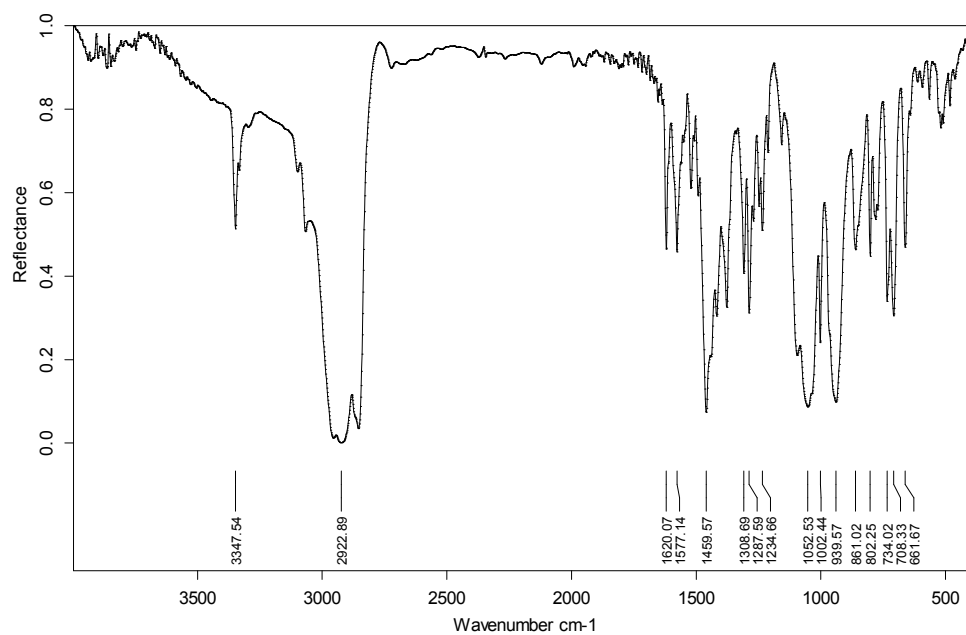


Note: Complex **9** was synthesized in diethyl ether. The signals at 17.9 ppm and 17.0 ppm are the signals of isomers.

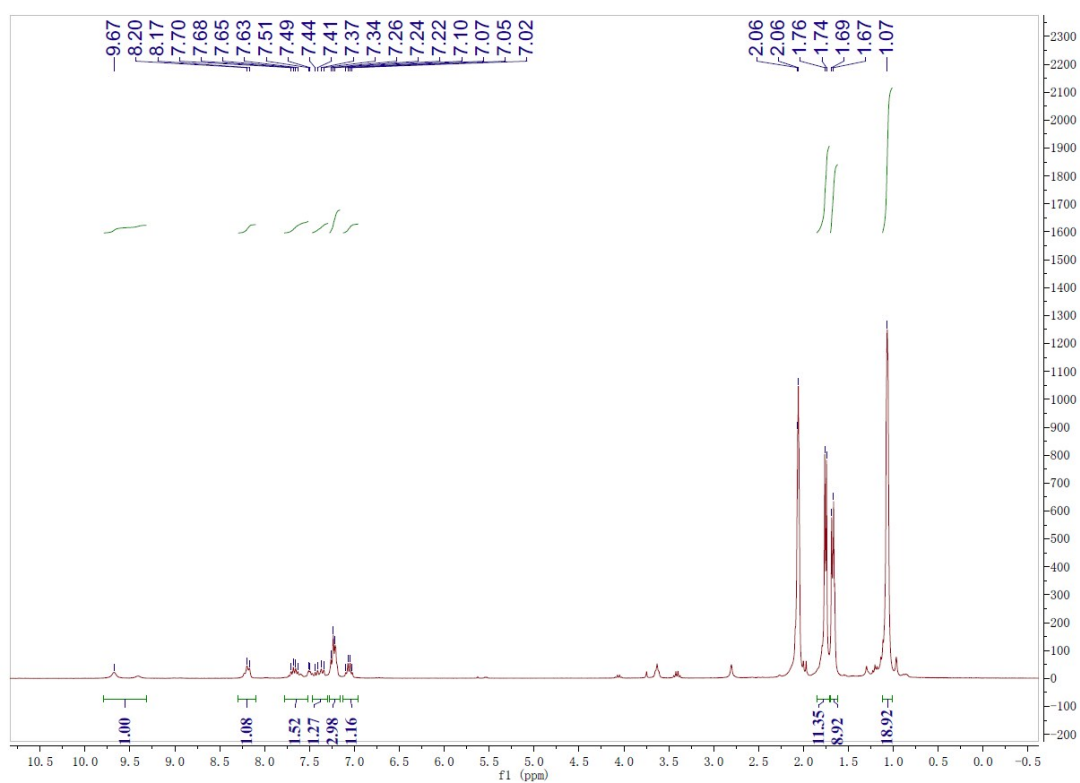
Complex 10



IR spectrum

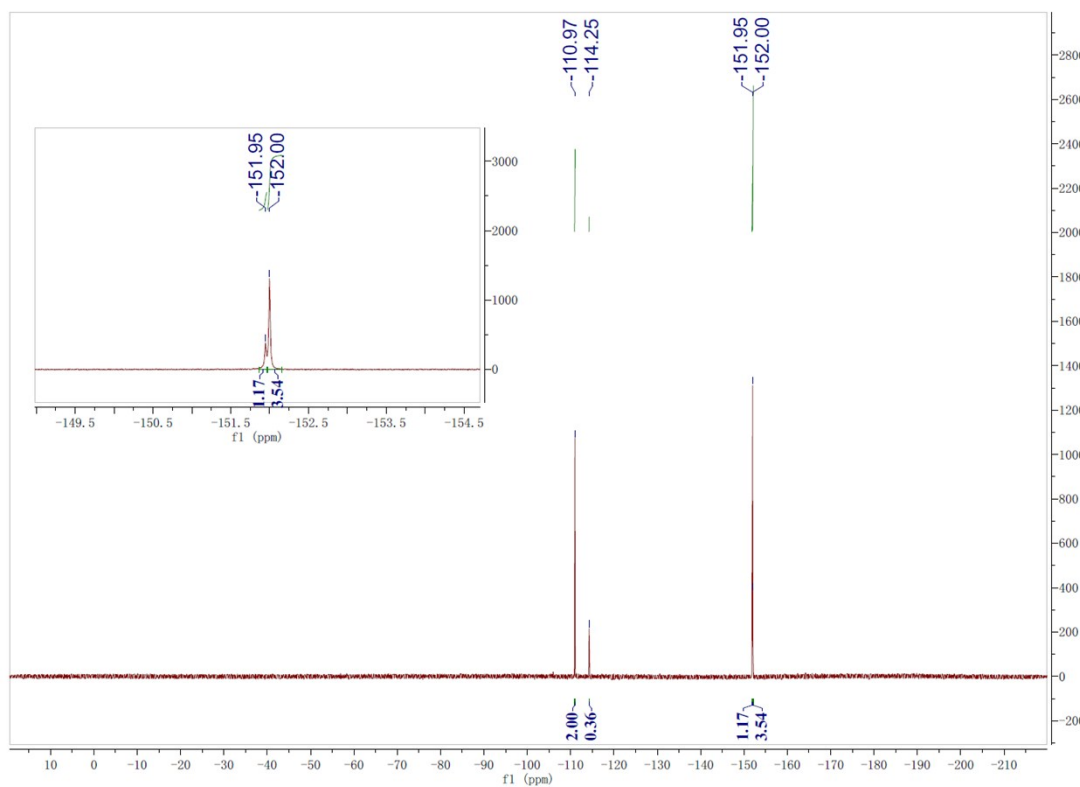


^1H NMR spectrum ($\text{C}_2\text{D}_6\text{CO}$)



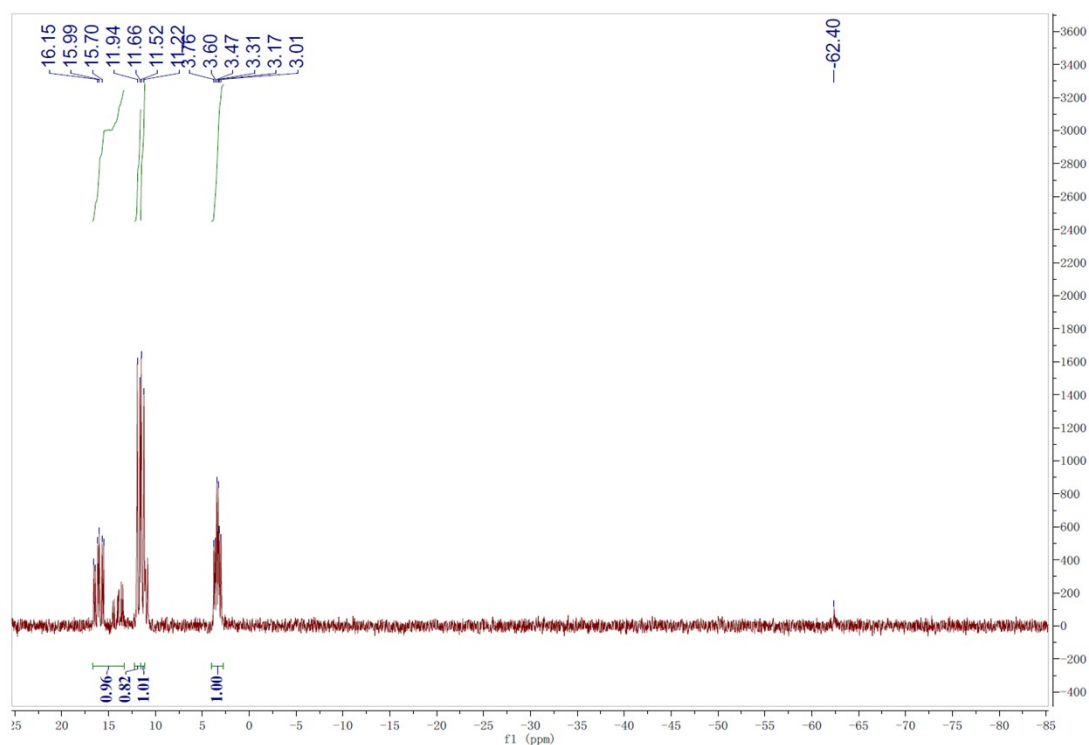
Note: Complex **10** was synthesized in THF and crystallized in THF/diethyl ether mix solvent.

^{19}F { ^1H } NMR spectrum ($\text{C}_2\text{D}_6\text{CO}$)



Note: Complex **10** was synthesized in THF and crystallized in THF/diethyl ether mix solvent. The signals at -114.2 and -152.0 ppm are the signal of isomer.

$^{31}\text{P} \{^1\text{H}\}$ NMR spectrum ($\text{C}_2\text{D}_6\text{CO}$)

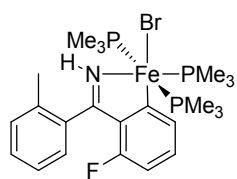


$^{31}\text{P} \{^1\text{H}\}$ NMR (121.5 MHz, C_6D_6 , 298 K, ppm): δ 3.4 (td, $^2J_{\text{P,P}} = 36.4$ Hz, $^2J_{\text{P,P}} = 7.3$ Hz, Pd(c)), 11.6 (dd, $^2J_{\text{P,P}} = 36.4$ Hz, $^2J_{\text{P,P}} = 51.0$ Hz, Pa & Pb), 16.1 (td, $^2J_{\text{P,P}} = 51.0$ Hz, $^2J_{\text{P,P}} = 7.3$ Hz, Pc(d)). The signals at 14 ppm are the signals of isomer produced by dissociation of PMe_3 ligand of complex **10** in solvent and the signal of dissociated PMe_3 ligand appears at -62.4 ppm.

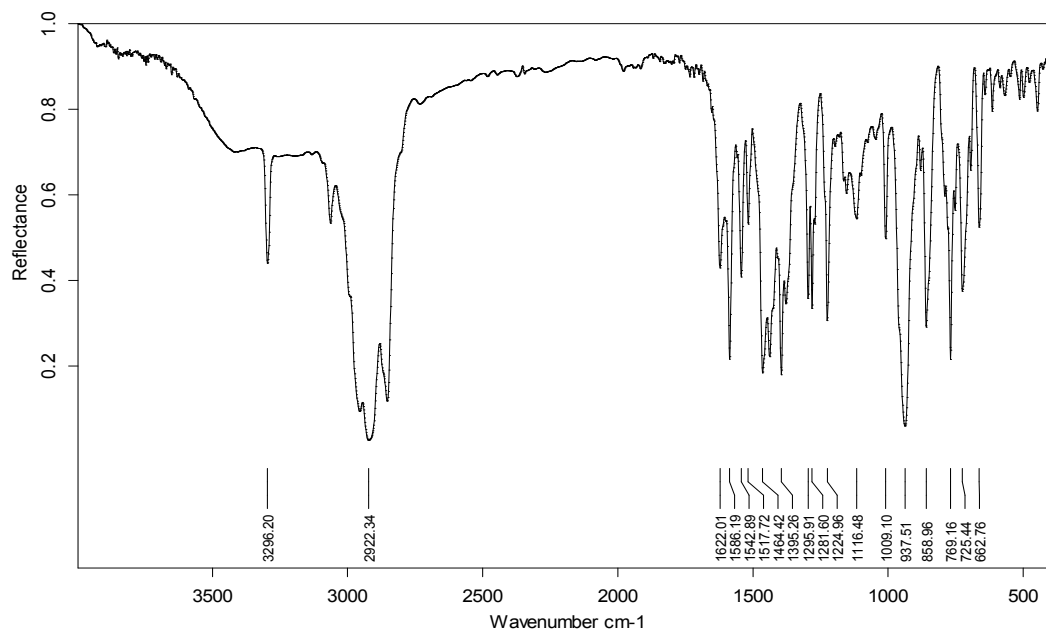
$^{13}\text{C} \{^1\text{H}\}$ NMR spectrum ($\text{C}_2\text{D}_6\text{CO}$)



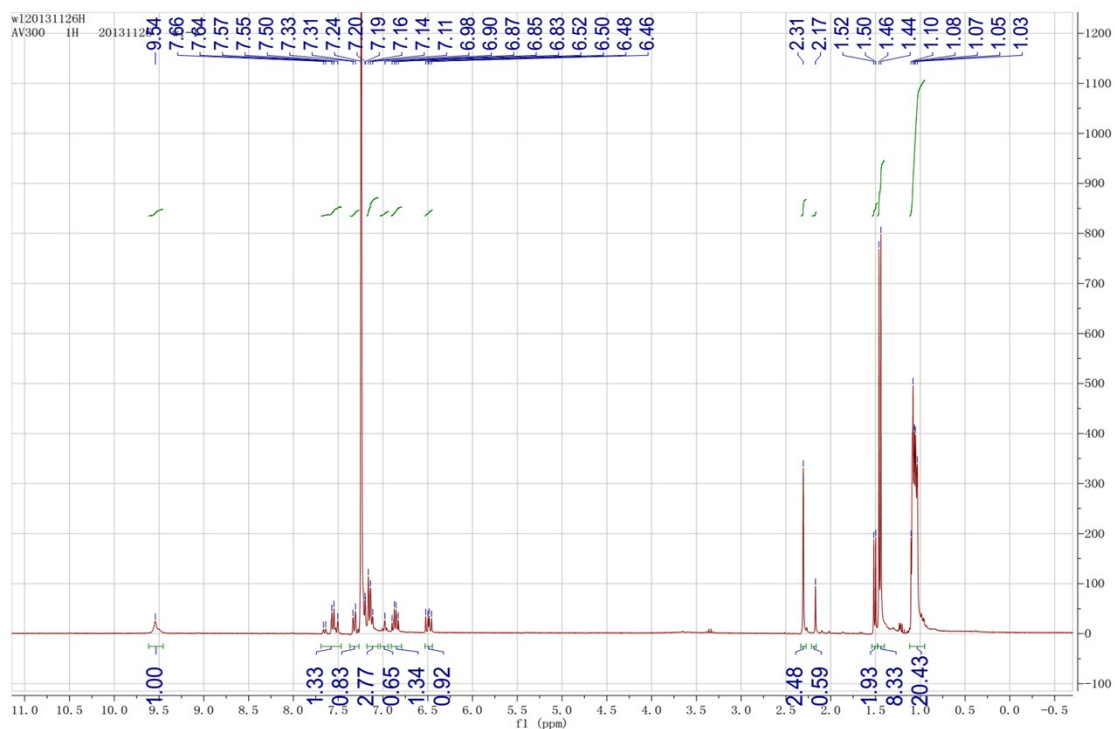
Complex 11



IR spectrum

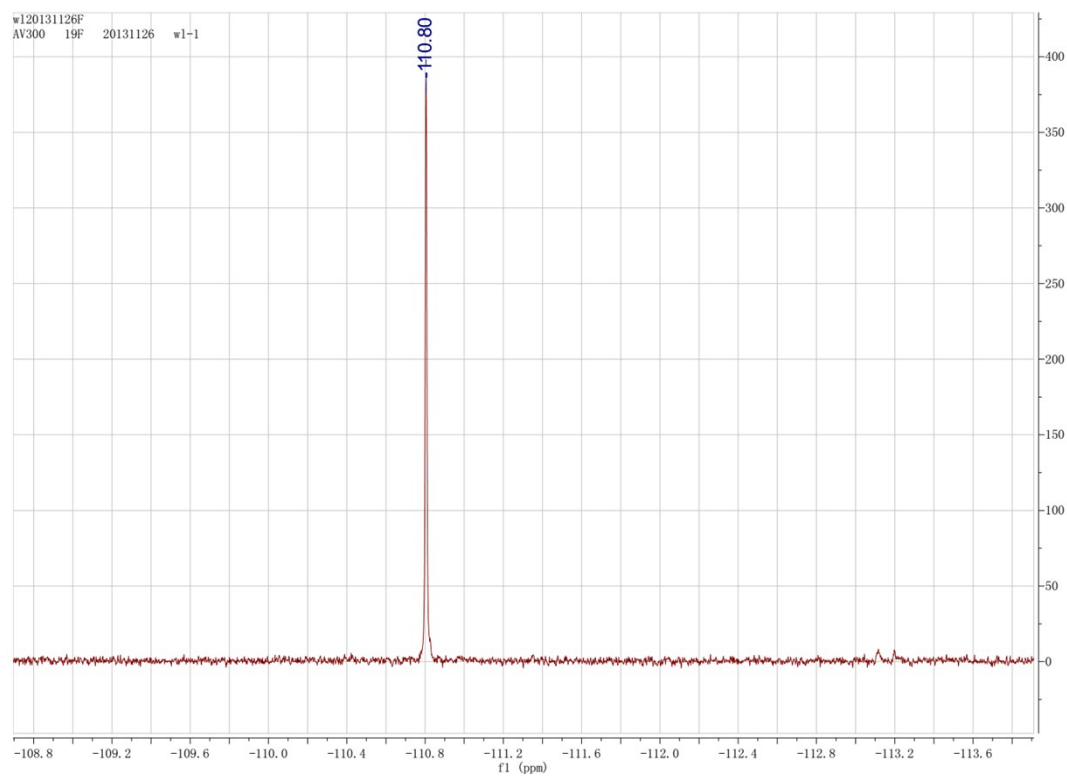


¹H NMR spectrum (C₆D₆)



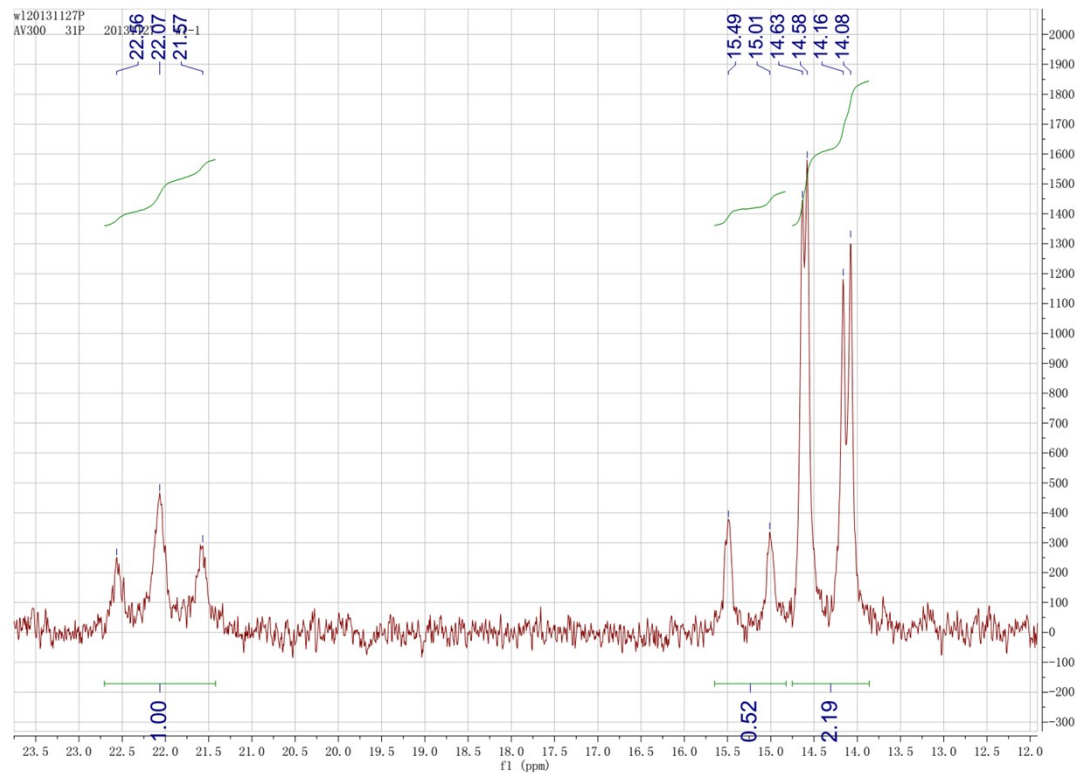
Note: Complex **11** was synthesized in diethyl ether. In solvent (C₆D₆), complex **11** would dissociate a PMe₃ ligand in some extent. The signals at 1.52, 1.27 ppm are the signal of this product.

^{19}F {H} NMR spectrum (C_6D_6)



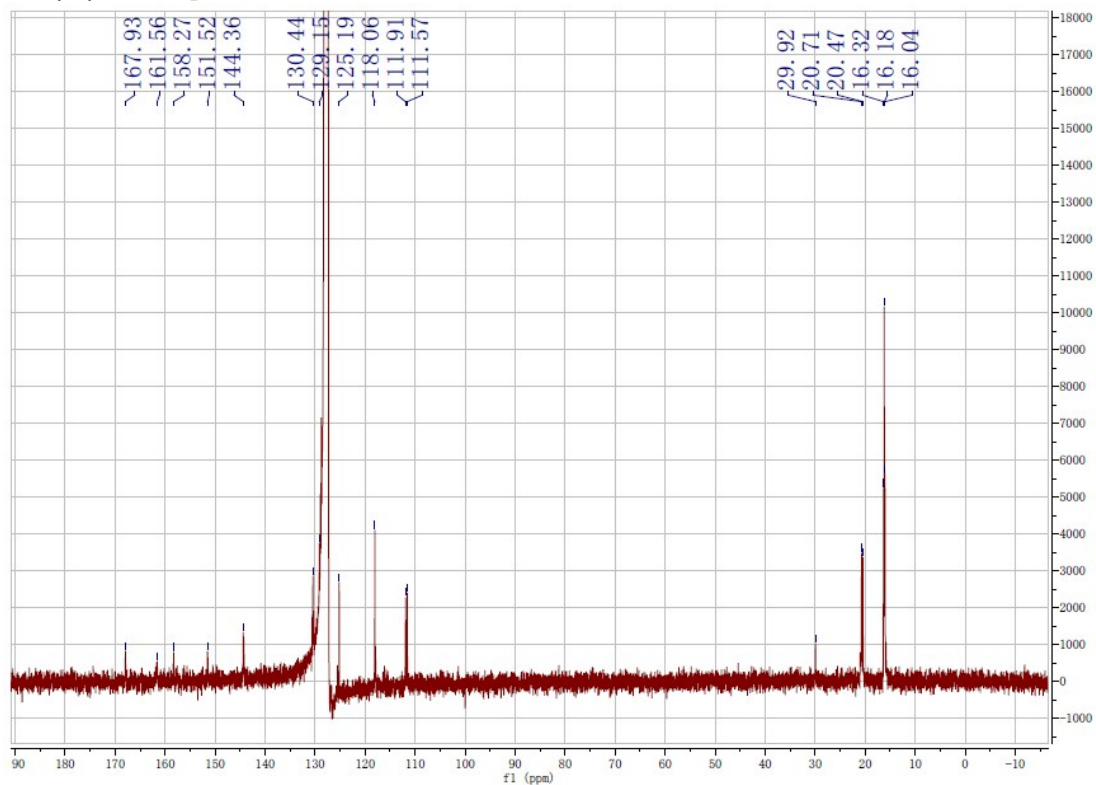
Note: Complex **11** was synthesized in diethyl ether.

^{31}P {H} NMR spectrum (C_6D_6)

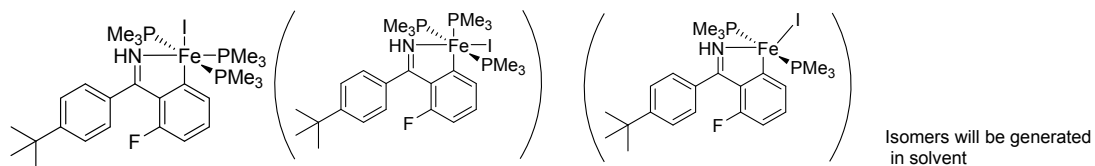


Note: Complex **11** was synthesized in diethyl ether. In solvent (C_6D_6), complex **11** would dissociate a PMe_3 ligand in some extent. The doublet at 15 ppm is the signal of this product.

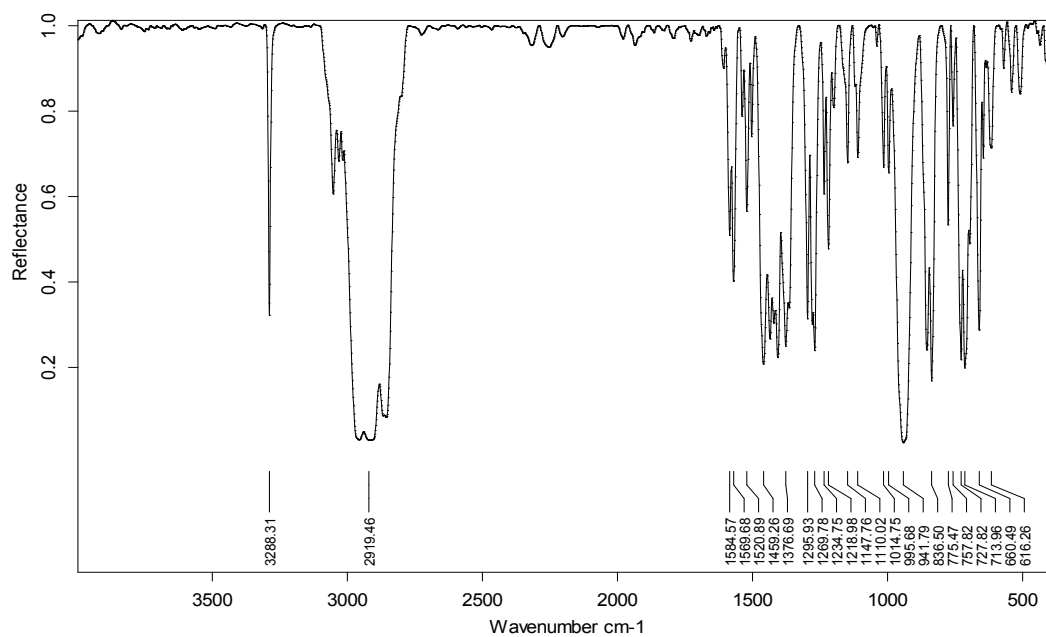
^{13}C {H} NMR spectrum (C_6D_6)



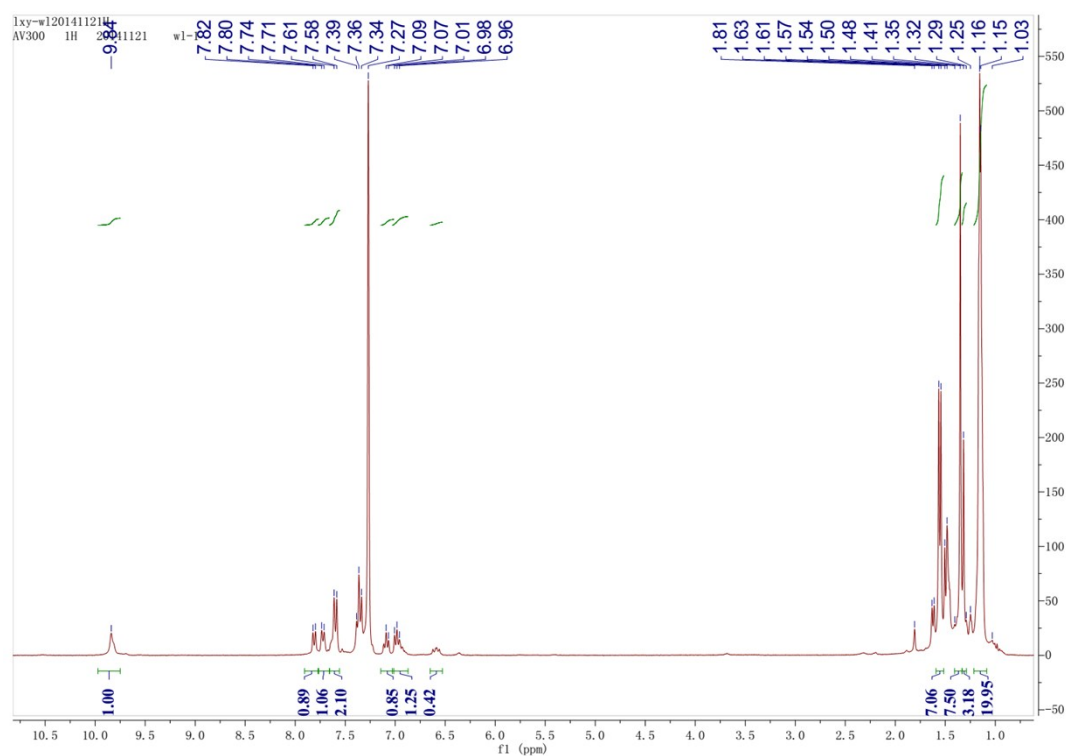
Complex 12



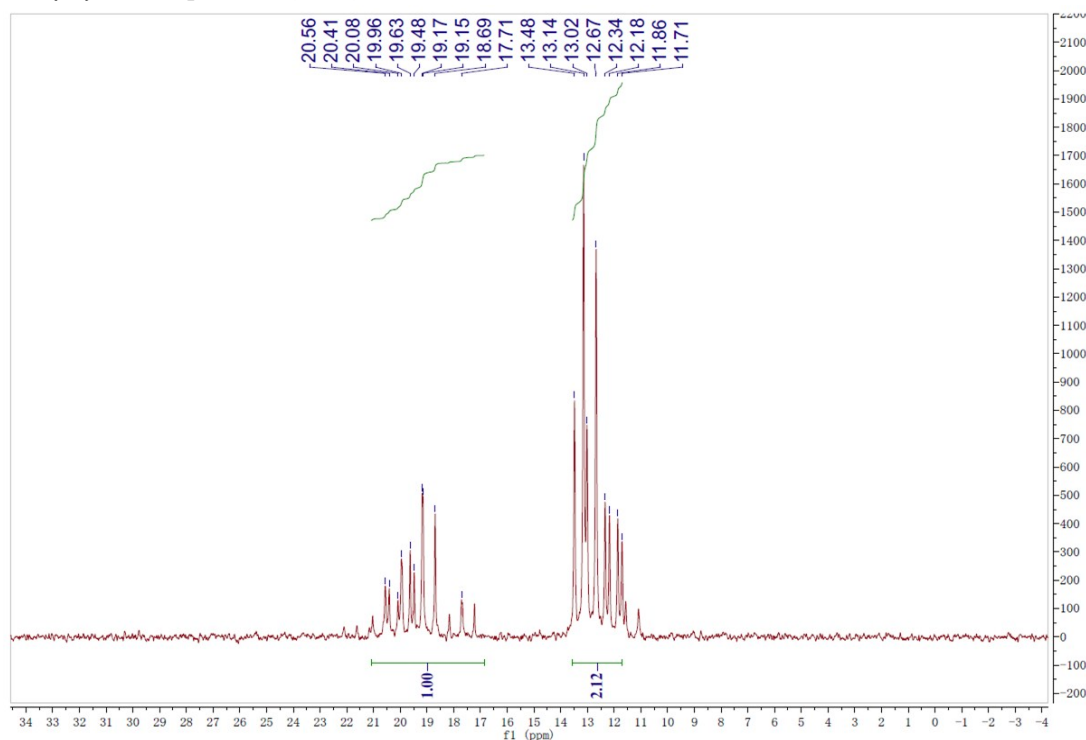
IR spectrum



^1H NMR spectrum (C_6D_6)

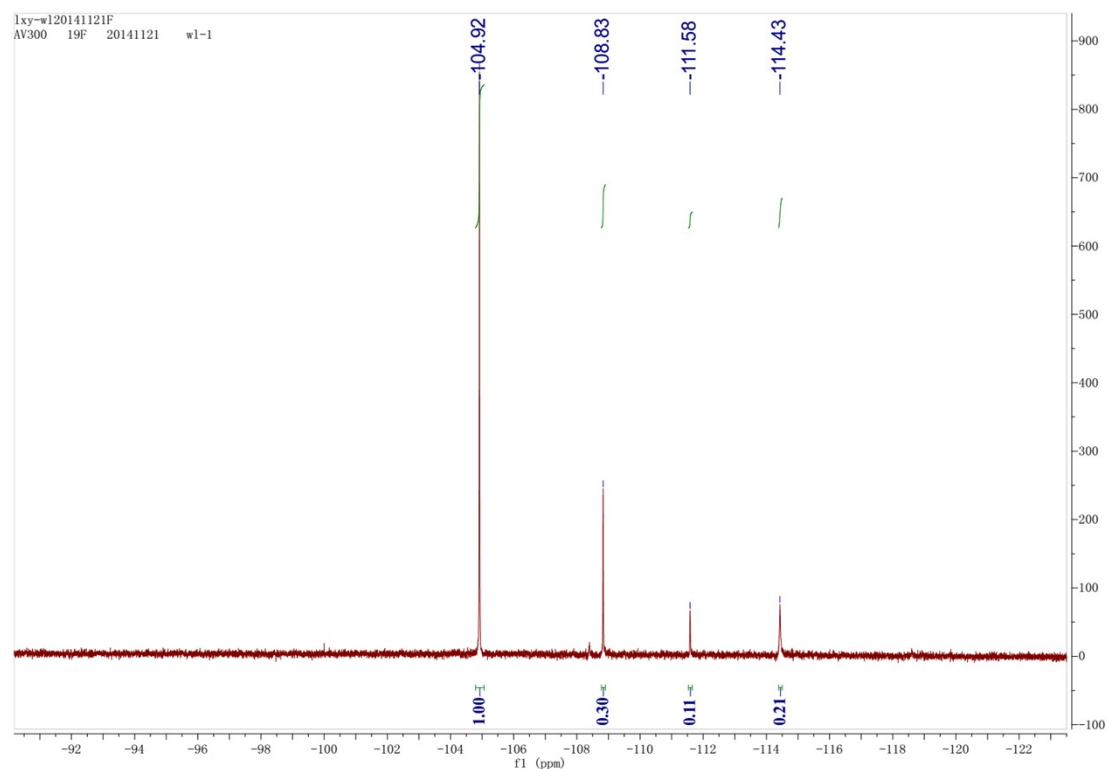


^{31}P {H} NMR spectrum (C_6D_6)



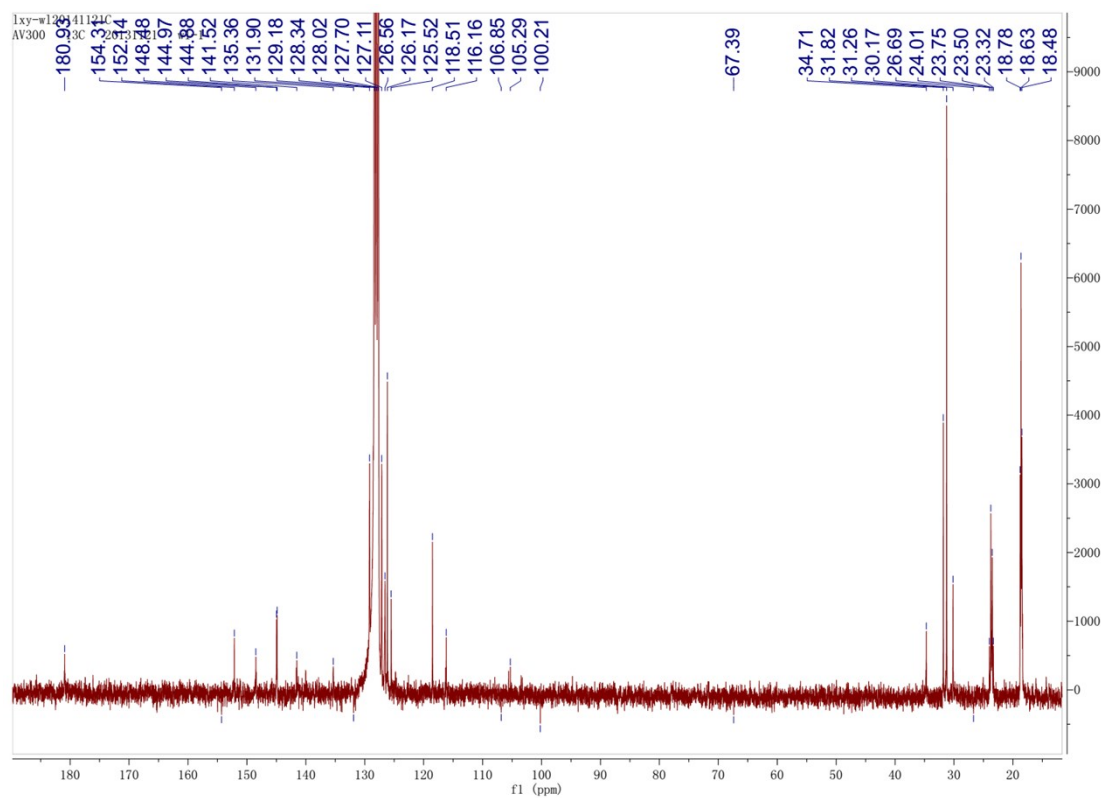
Note. In solvent (C_6D_6), the arrange of PMe_3 will occur. And In solvent (C_6D_6), complex **12** would dissociate a PMe_3 ligand in some extent. The signals of different isomers: 12.9 ppm (d, $^2J_{\text{P,P}} = 56.9$ Hz) and 19.2 ppm (d, $^2J_{\text{P,P}} = 56.9$ Hz); 13.1 ppm (d, $^2J_{\text{P,P}} = 55.9$ Hz) and 20.0 ppm (d, $^2J_{\text{P,P}} = 55.9$ Hz); 12.1 ppm (d, $^2J_{\text{P,P}} = 58.3$ Hz); 11.9 ppm (d, $^2J_{\text{P,P}} = 57.1$ Hz).

$^{19}\text{F} \{^1\text{H}\}$ NMR spectrum (C_6D_6)



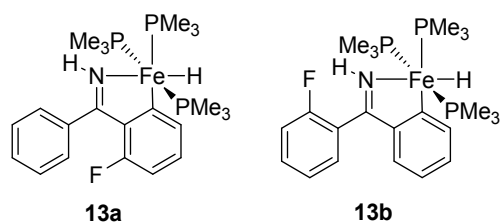
Note. The signals of different isomers: -104.9 ppm; -108.8 ppm; -111.6 ppm.

$^{13}\text{C} \{^1\text{H}\}$ NMR spectrum (C_6D_6)

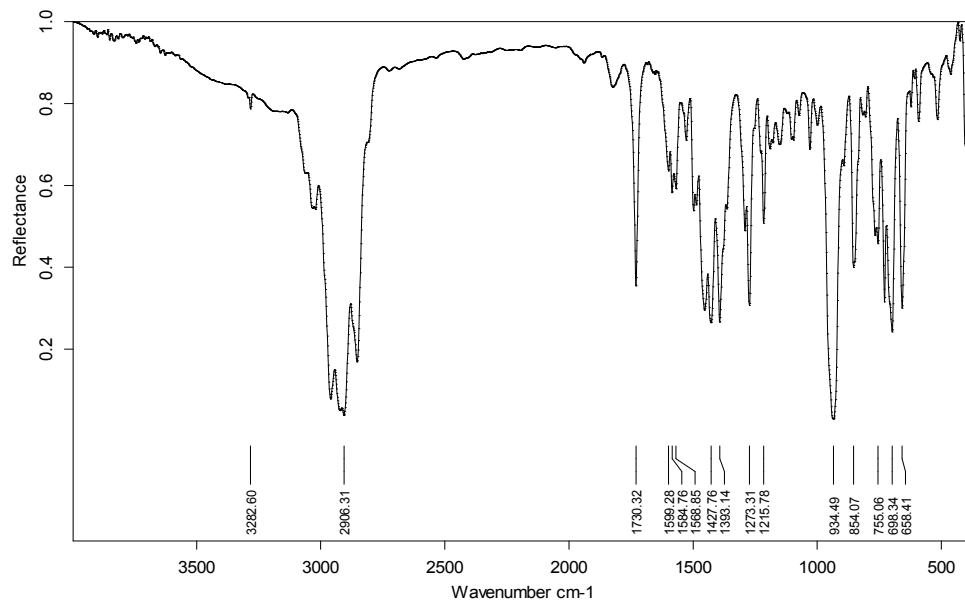


Note. Isomers exist.

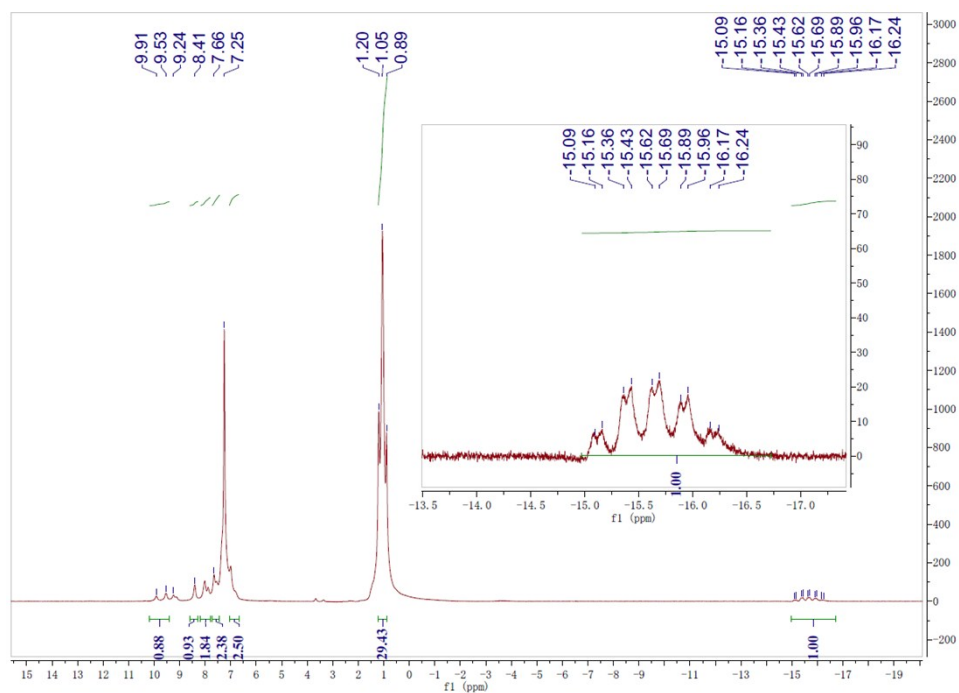
Complex 13



IR spectrum

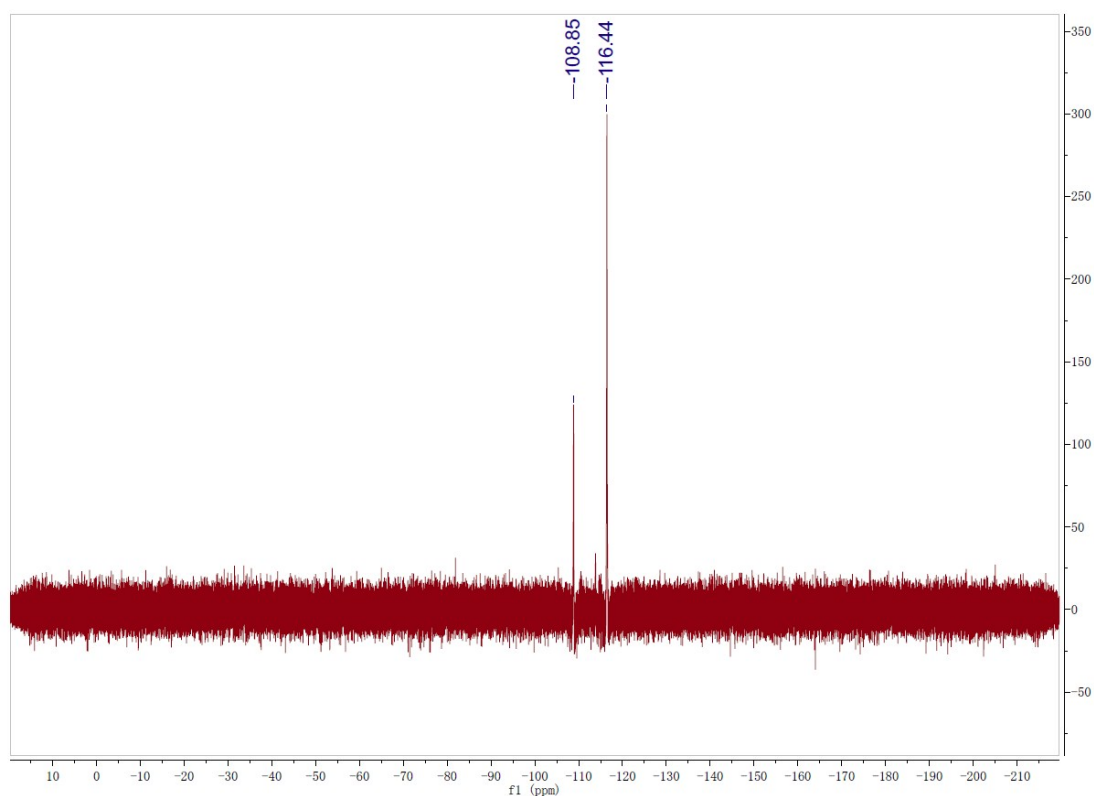


^1H NMR spectrum (C_6D_6)



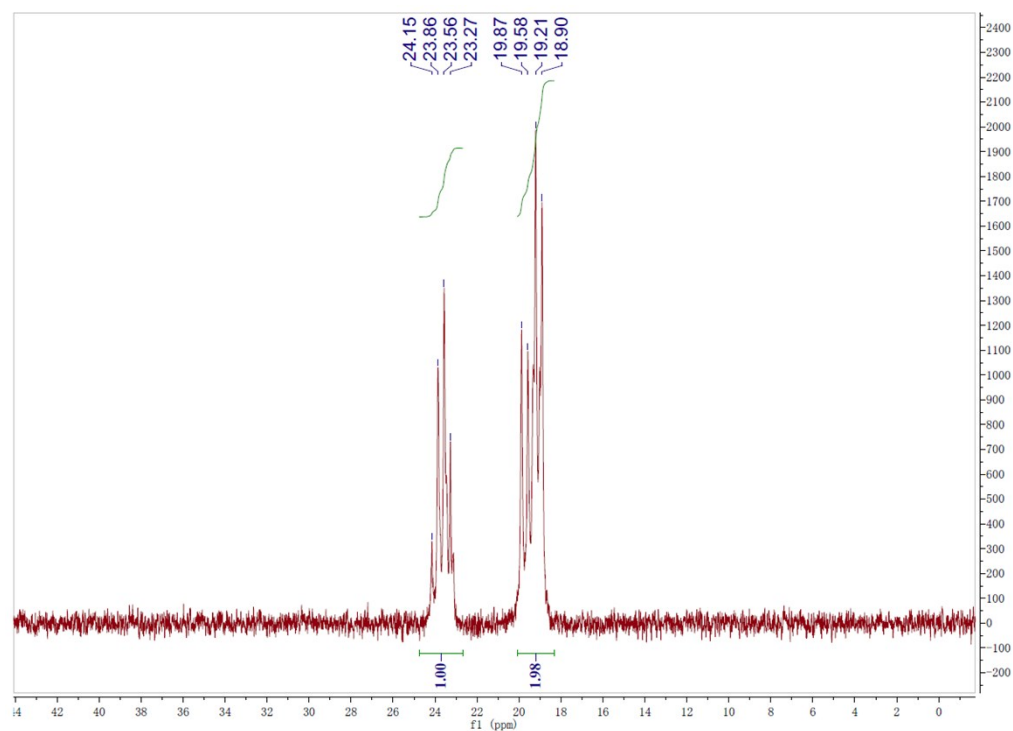
Note: Complexes **13a** and **13b** were synthesized in diethyl ether and crystallized in n-pentane. ^1H NMR (300 MHz, C_6D_6 , 298K, ppm): δ -15.92, -15.26 (td, $^2J_{\text{P,H}} = 21.0$ Hz, $^2J_{\text{P,H}} = 84.0$ Hz, 1 H, Fe-H), 1.05 (m, 27 H, $\text{P}(\text{CH}_3)_3$), 7.25 – 8.41 (m, 8H, Ar-H), 9.53, 9.91 (s, 1H, C=N-H).

^{19}F {H} NMR spectrum (C_6D_6)



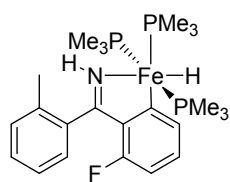
Note: Complexes **13a** and **13b** were synthesized in diethyl ether and crystallized in *n*-pentane. ^{19}F {H} NMR (282.4 MHz, C_6D_6 , 298 K, ppm): δ -108.8, 116.4 (s, F, Ar-F).

^{31}P {H} NMR spectrum (C_6D_6)

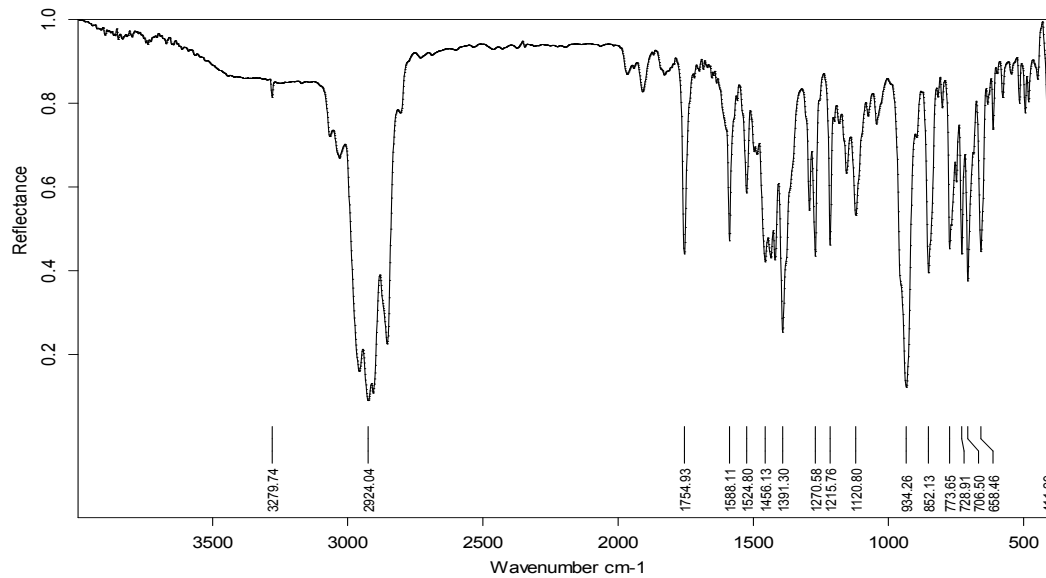


Note: **13a** and **13b**: ^{31}P NMR (121.5 MHz, C_6D_6 , 298 K, ppm): δ 24.1, 23.8 (t, $^2J_{\text{P,P}} = 36.4$ Hz, 1 P, $\text{P}(\text{CH}_3)_3$), 19.9, 19.2 (d, $^2J_{\text{P,P}} = 36.4$ Hz, 2 P, $\text{P}(\text{CH}_3)_3$).

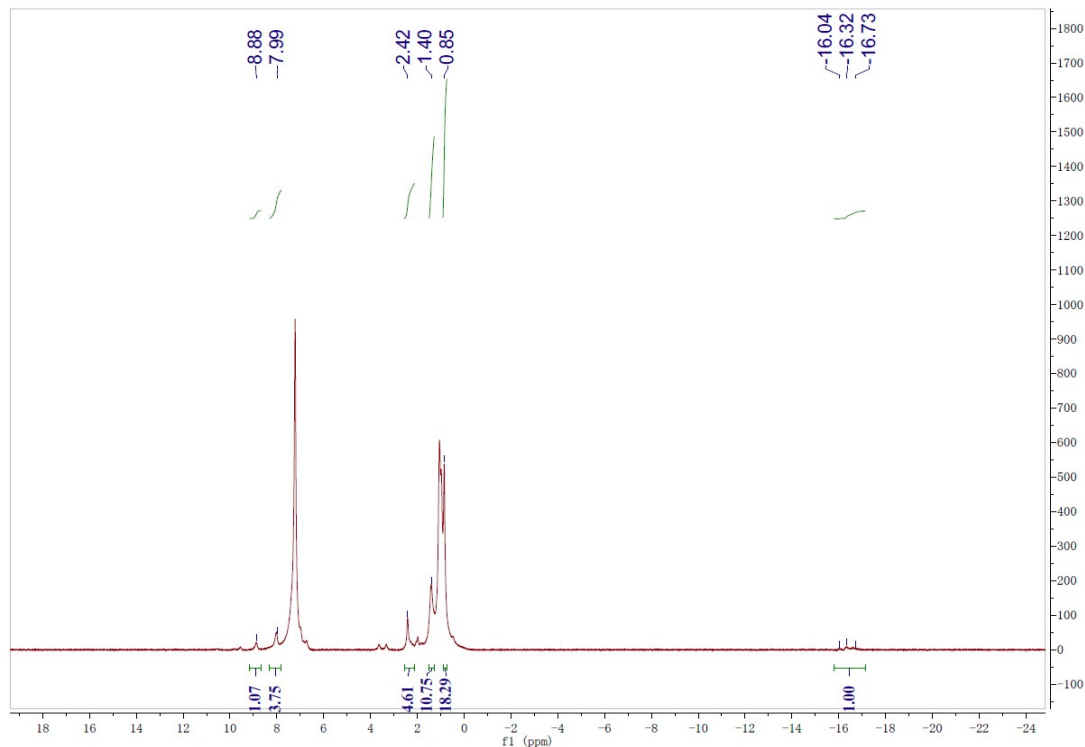
Complex 14



IR spectrum

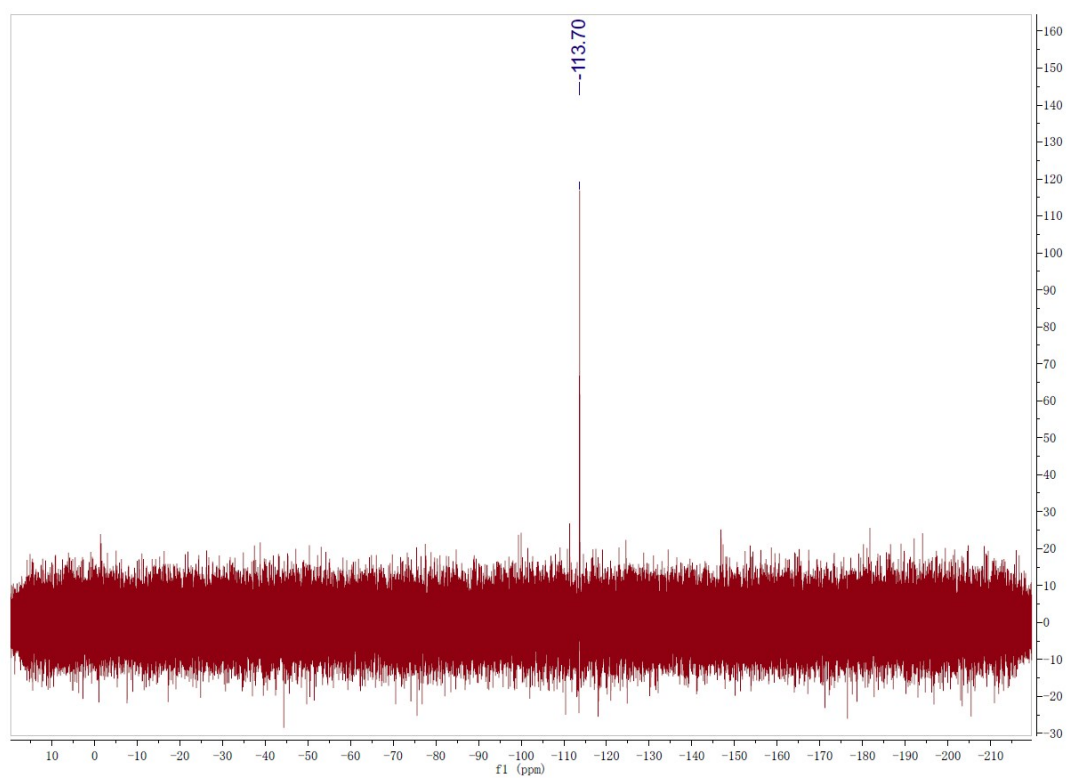


¹H NMR spectrum (C₆D₆)



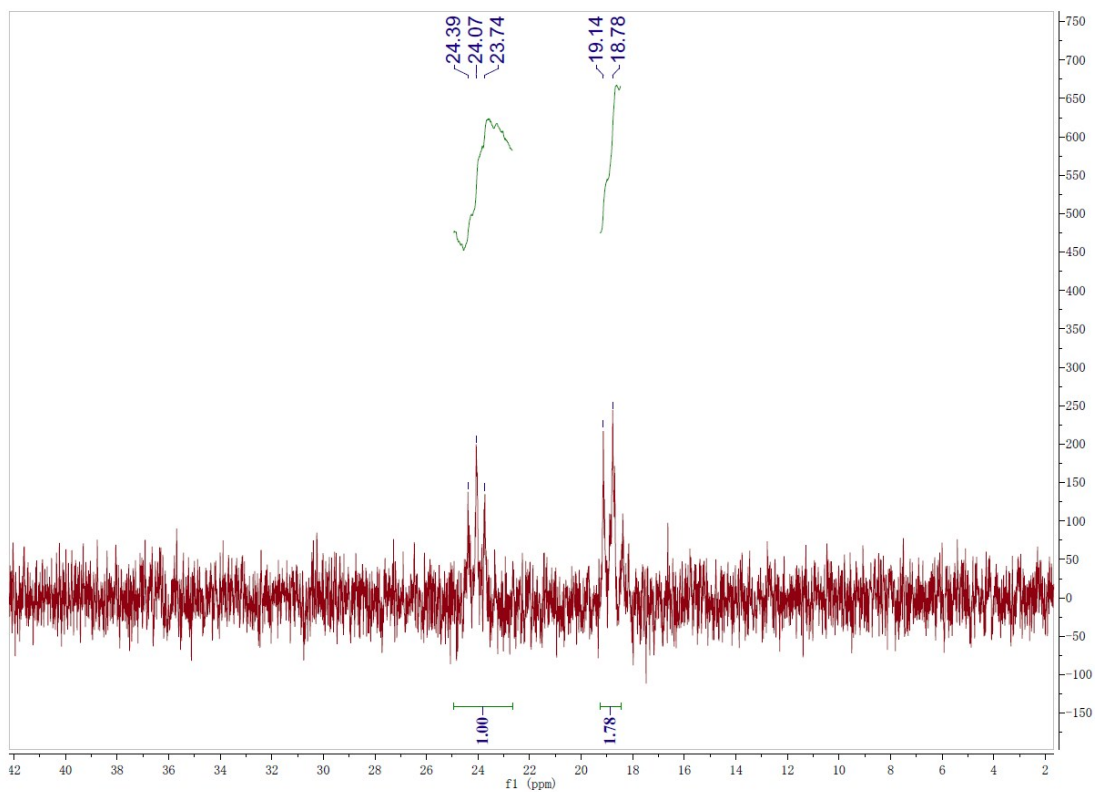
Note: Complex 14 was synthesized in diethyl ether and crystallized in n-pentane.

^{19}F {H} NMR spectrum (C_6D_6)



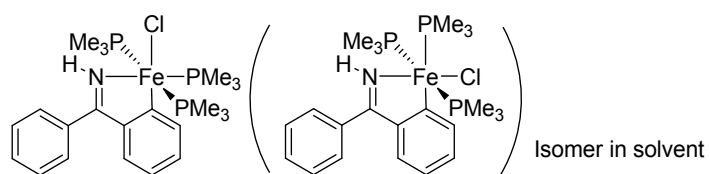
Note: Complex **14** was synthesized in diethyl ether and crystallized in *n*-pentane.

^{31}P {H} NMR spectrum (C_6D_6)

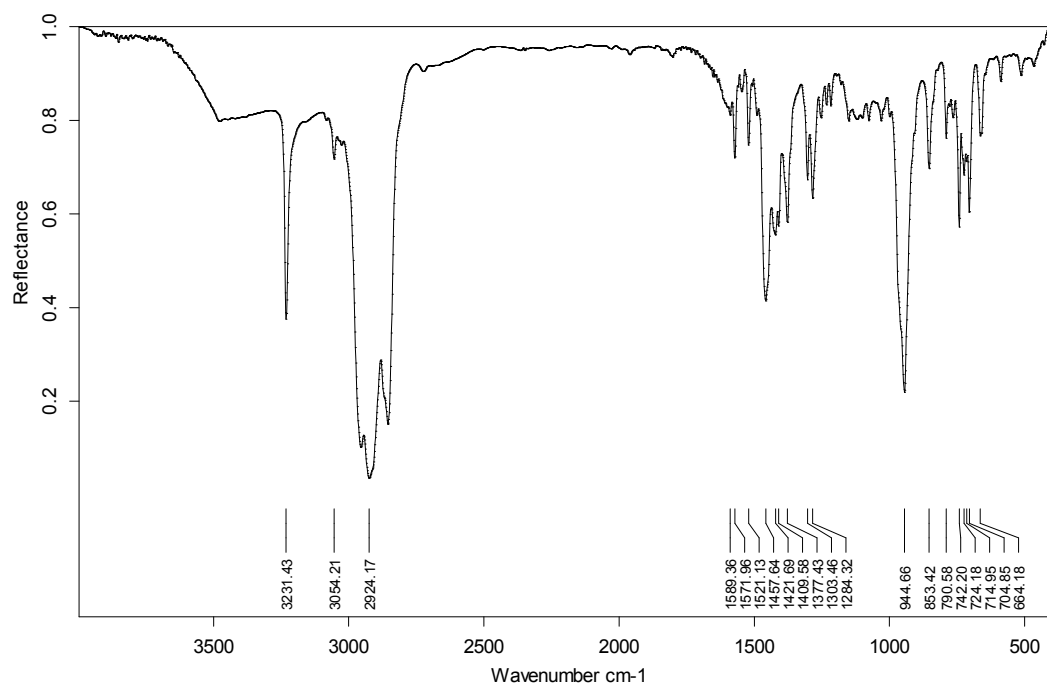


Note: Complex **14** was synthesized in diethyl ether and crystallized in *n*-pentane.

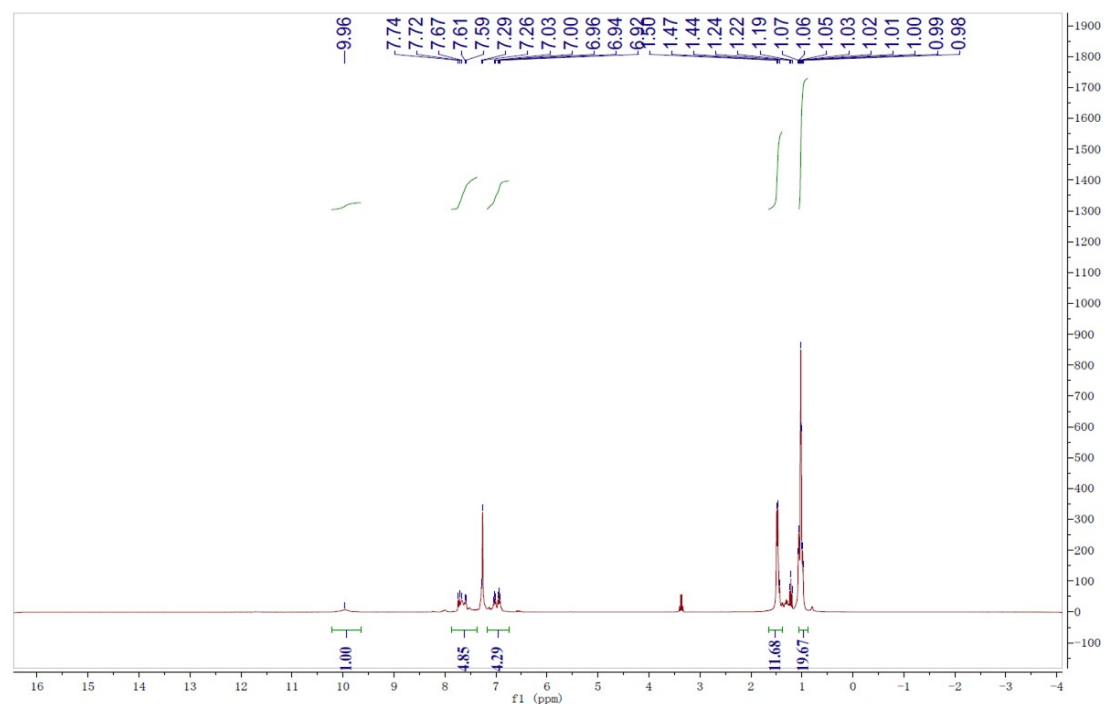
Complex 15



IR spectrum

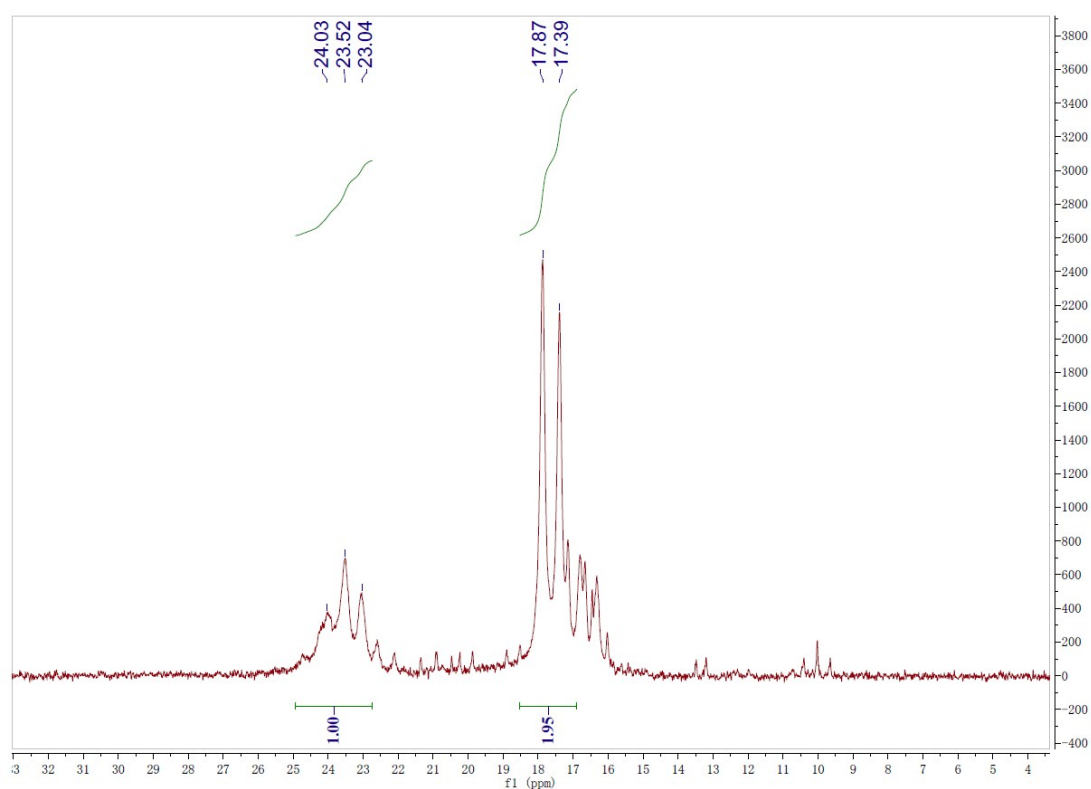


¹H NMR spectrum (C₆D₆)



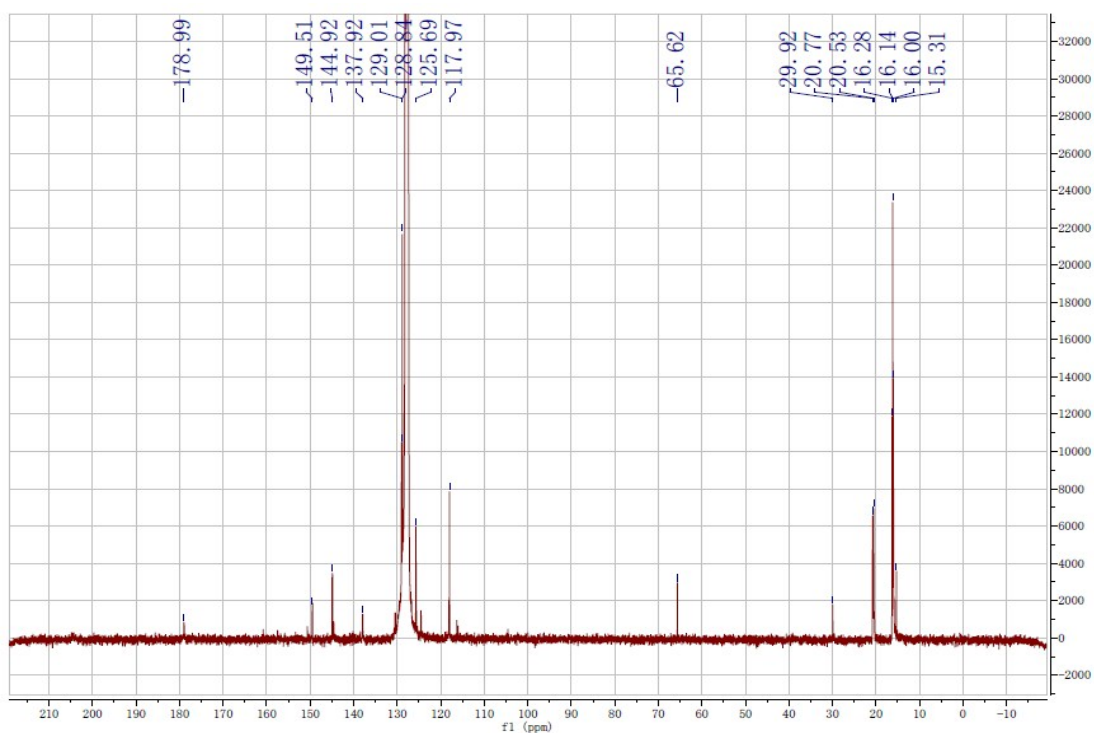
Note: Complex **15** was synthesized in diethyl ether. The signals at 3.4 ppm and 1.2 ppm are the typical signals of solvent.

$^{31}\text{P} \{^1\text{H}\}$ NMR spectrum (C_6D_6)



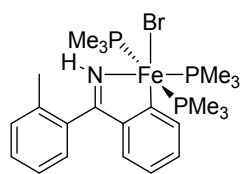
Note: Complex **15** was synthesized in diethyl ether. The signal at 16 ppm is the arrangement isomer of complex **15**.

$^{13}\text{C} \{^1\text{H}\}$ NMR spectrum (C_6D_6)

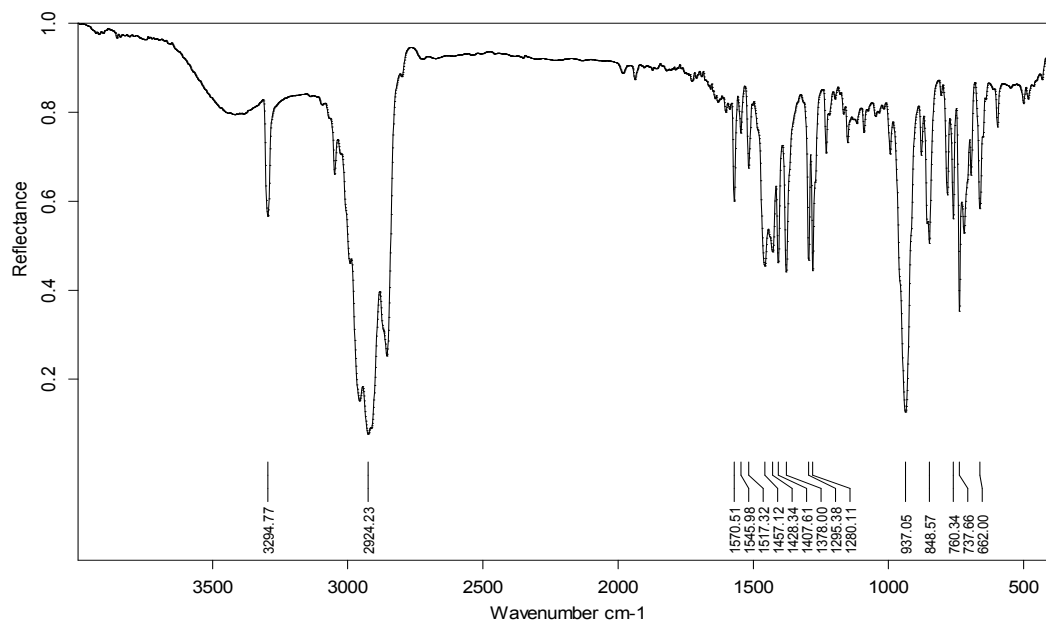


Note: Complex **15** was synthesized in diethyl ether. The signals at 3.4 ppm and 1.2 ppm are the typical signals of solvent. The signals of Et_2O appear at 15 and 65 ppm.

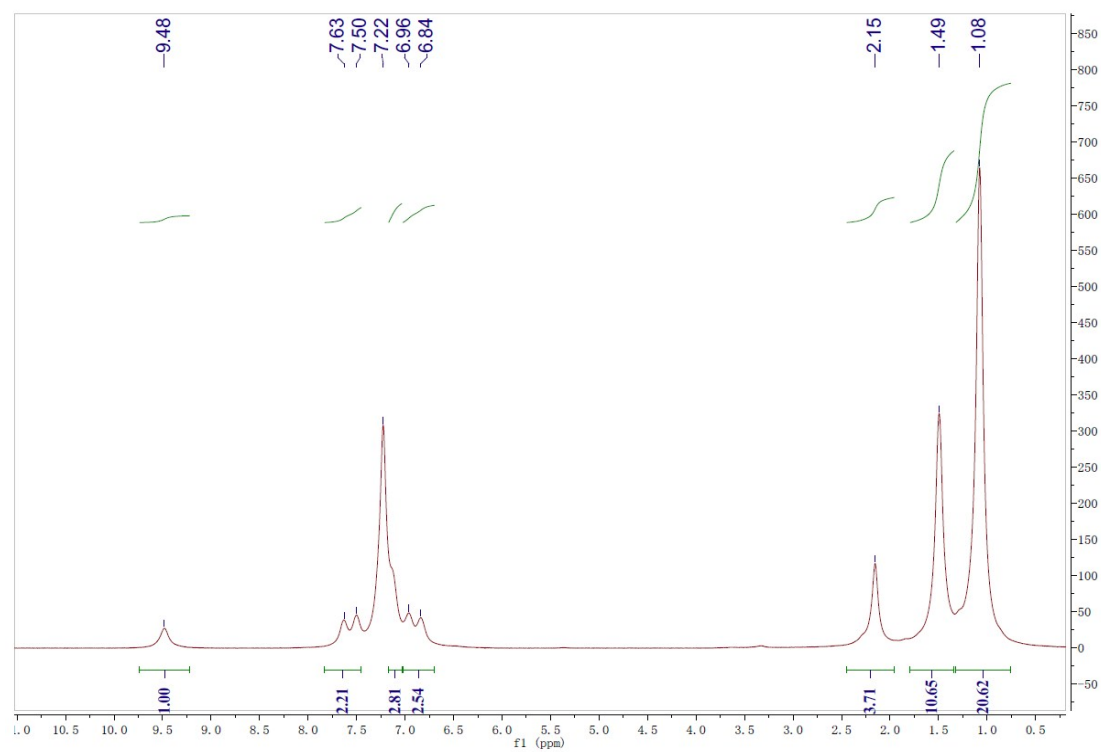
Complex 16



IR spectrum

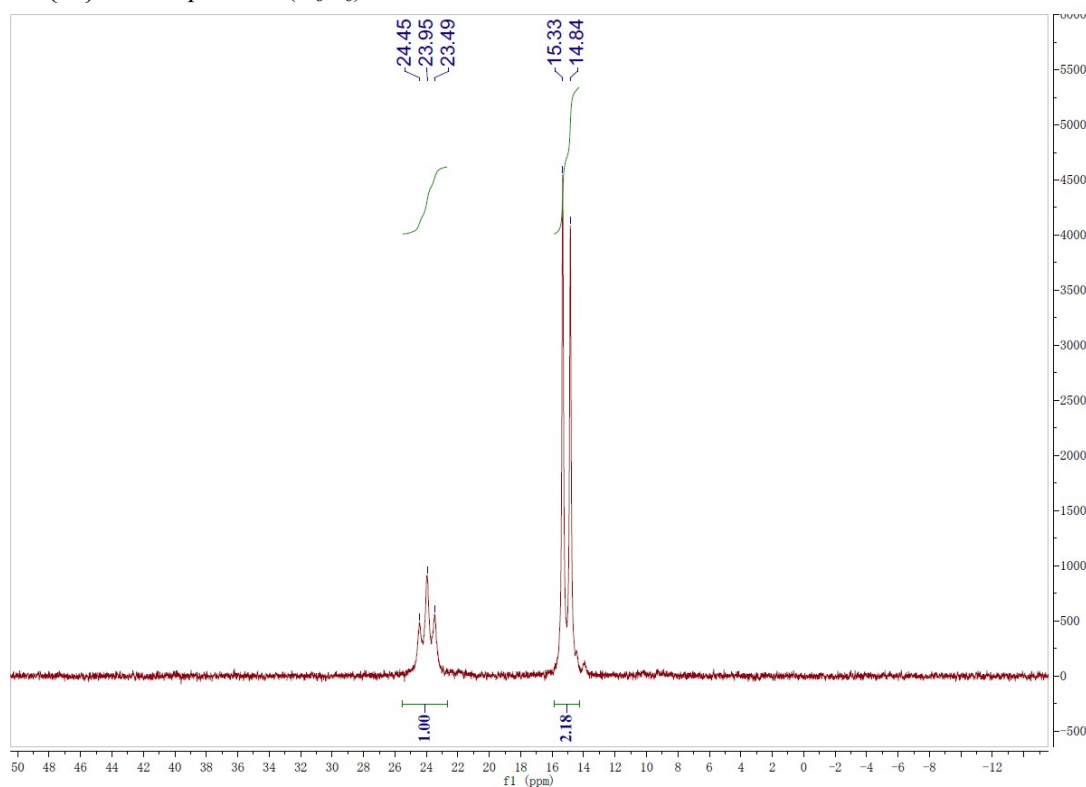


¹H NMR spectrum (C₆D₆)



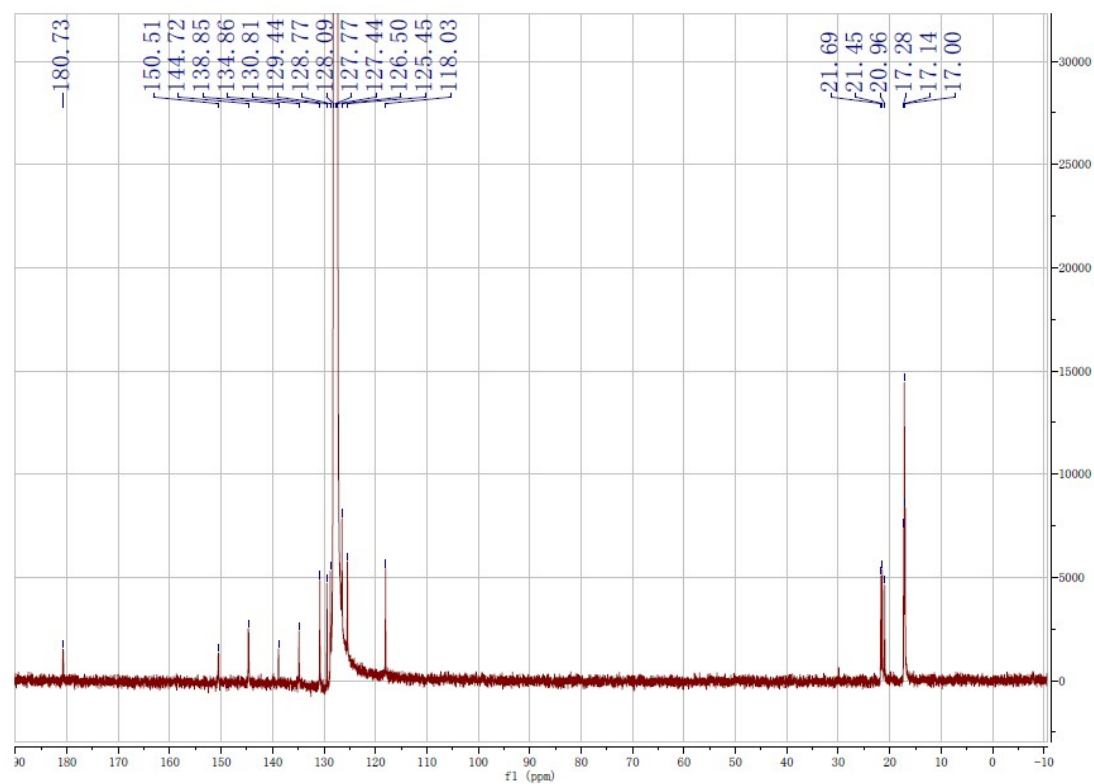
Note: Complex 16 was synthesized in diethyl ether.

$^{31}\text{P} \{^1\text{H}\}$ NMR spectrum (C_6D_6)



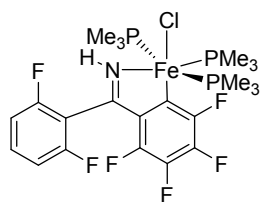
Note: Complex **16** was synthesized in diethyl ether.

$^{13}\text{C} \{^1\text{H}\}$ NMR spectrum (C_6D_6)

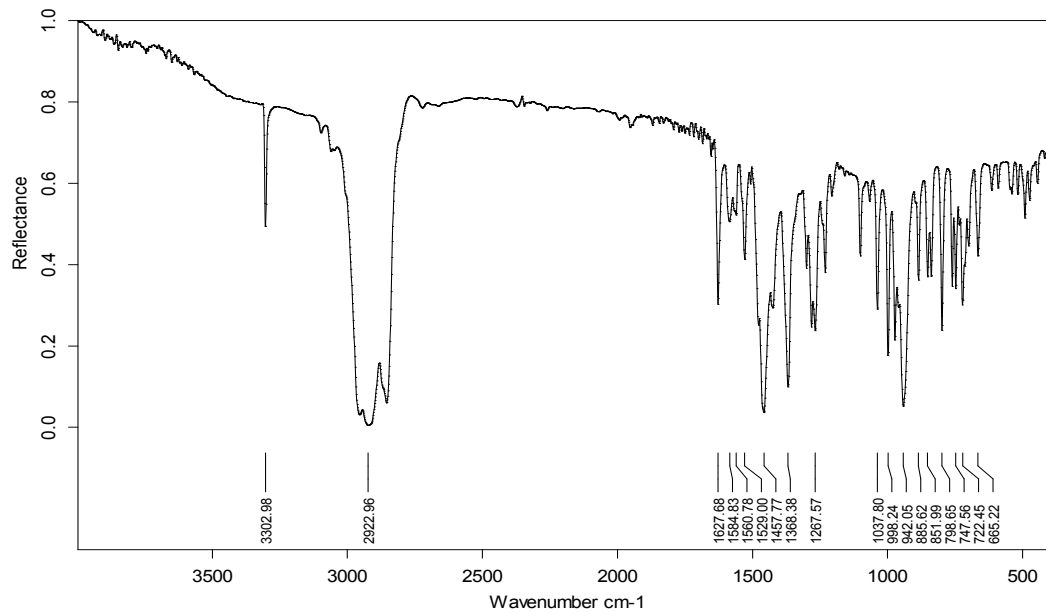


Note: Complex **16** was synthesized in diethyl ether.

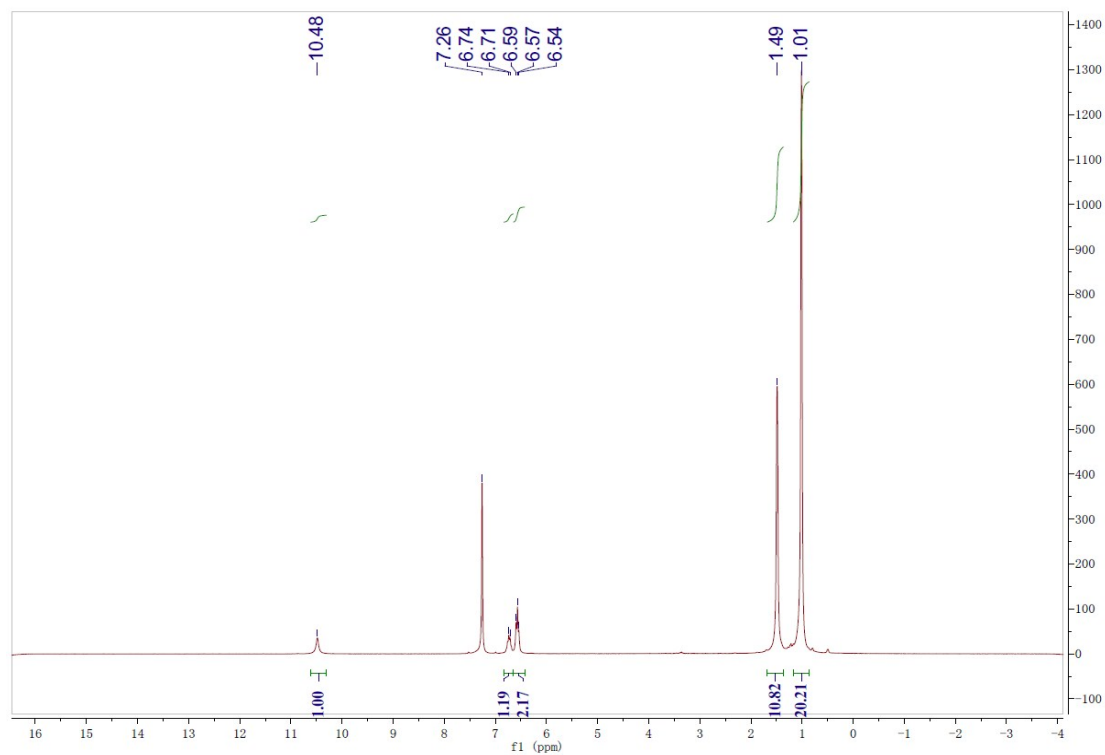
Complex 17



IR spectrum

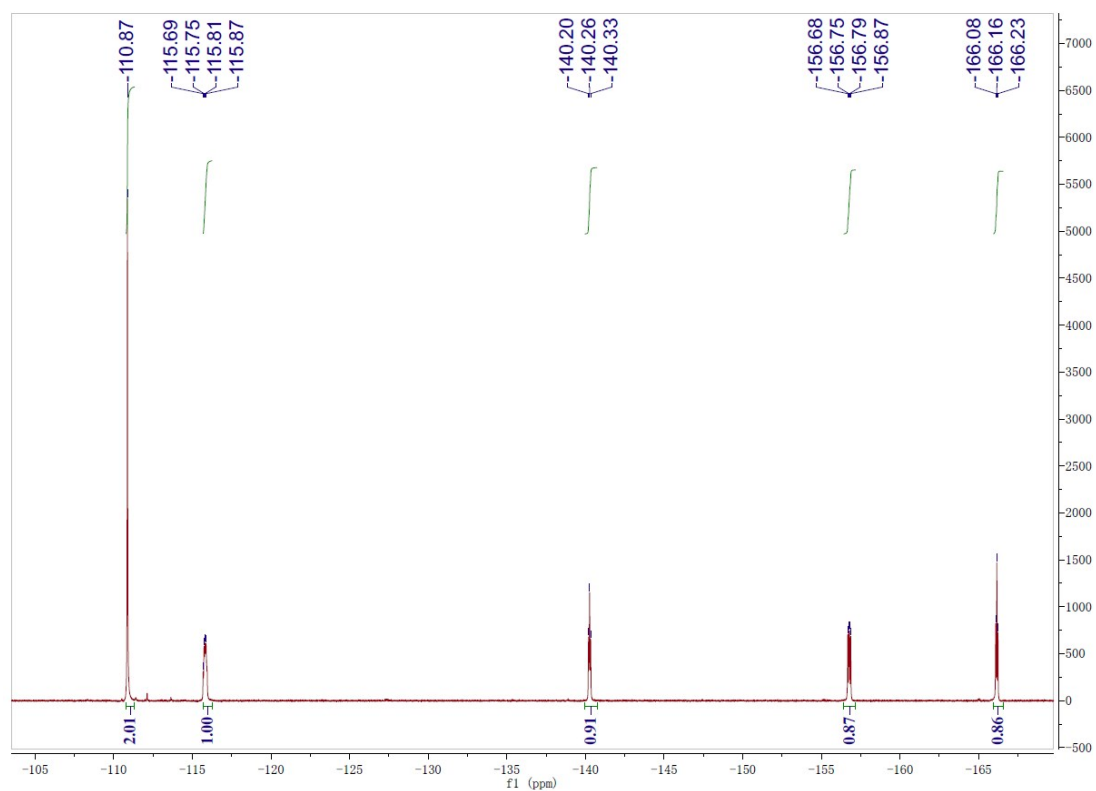


¹H NMR spectrum (C₆D₆)



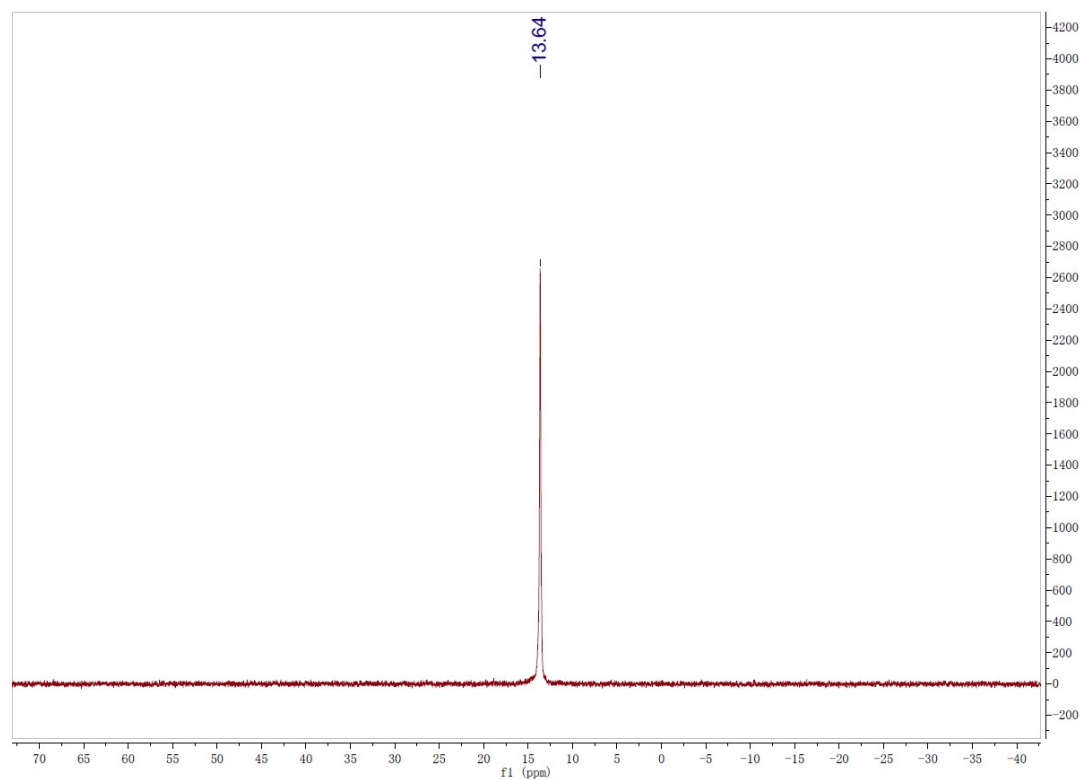
Note: Complex 17 was synthesized in diethyl ether.

^{19}F {H} NMR spectrum (C_6D_6)



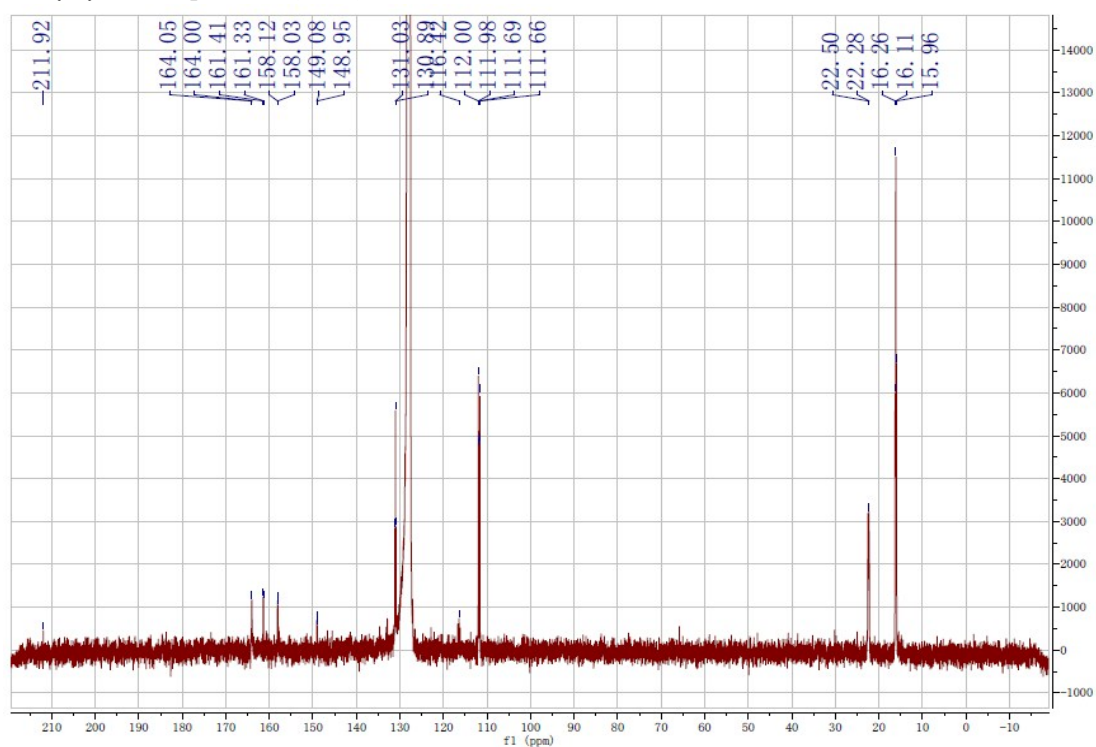
Note: Complex **17** was synthesized in diethyl ether.

^{31}P {H} NMR spectrum (C_6D_6)



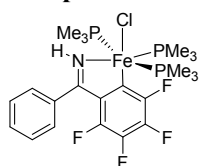
Note: Complex **17** was synthesized in diethyl ether.

^{13}C {H} NMR spectrum (C_6D_6)

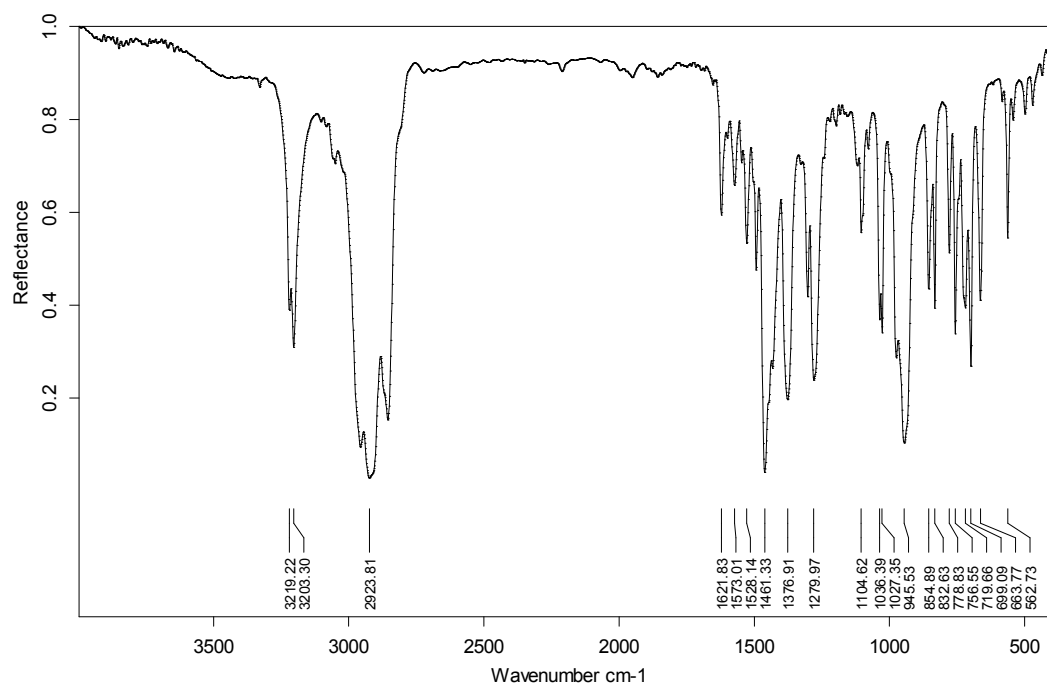


Note: Complex **17** was synthesized in diethyl ether.

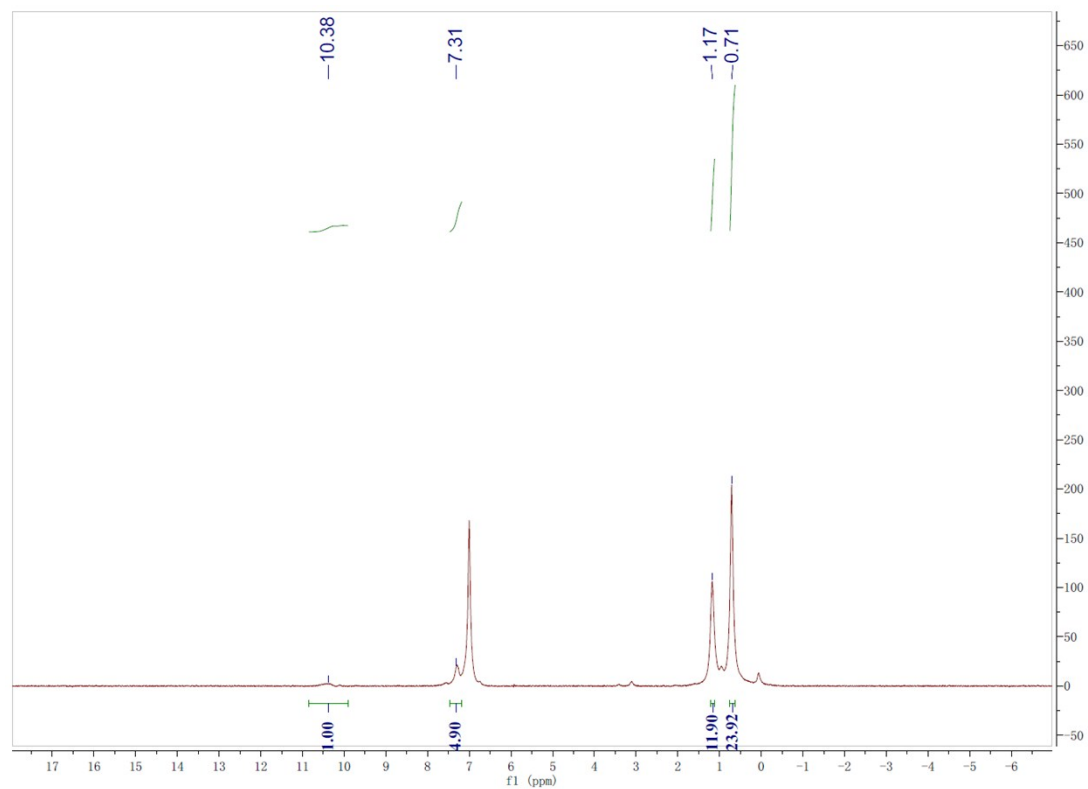
Complex 18



IR spectrum

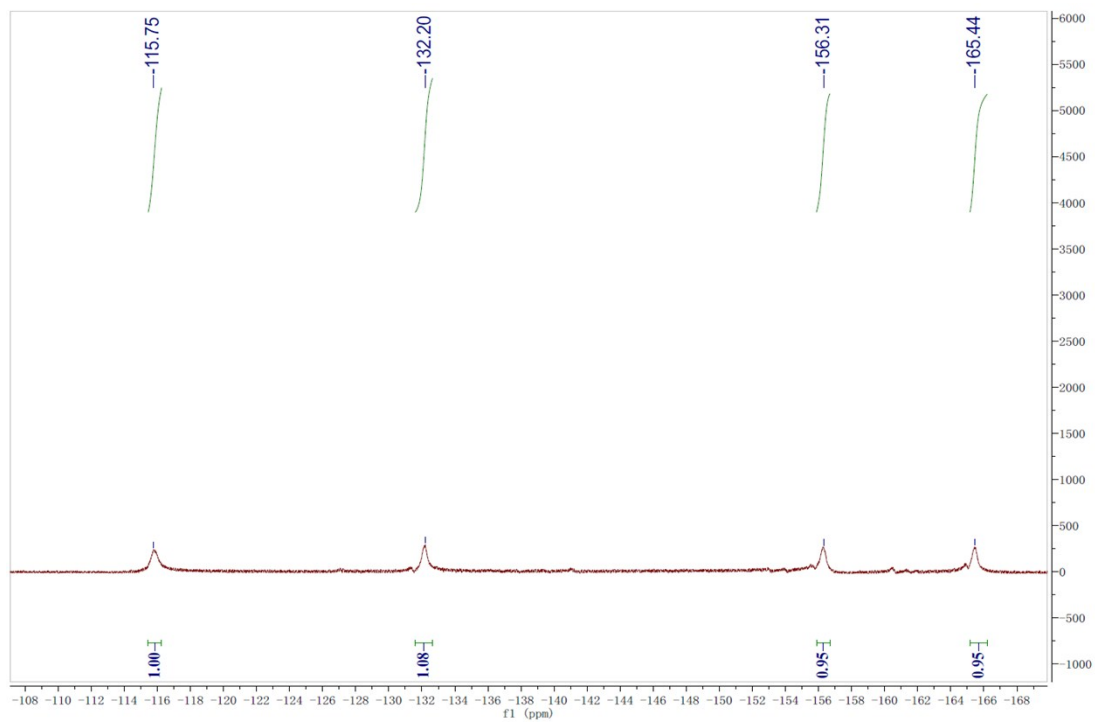


^1H NMR spectrum (C_6D_6)



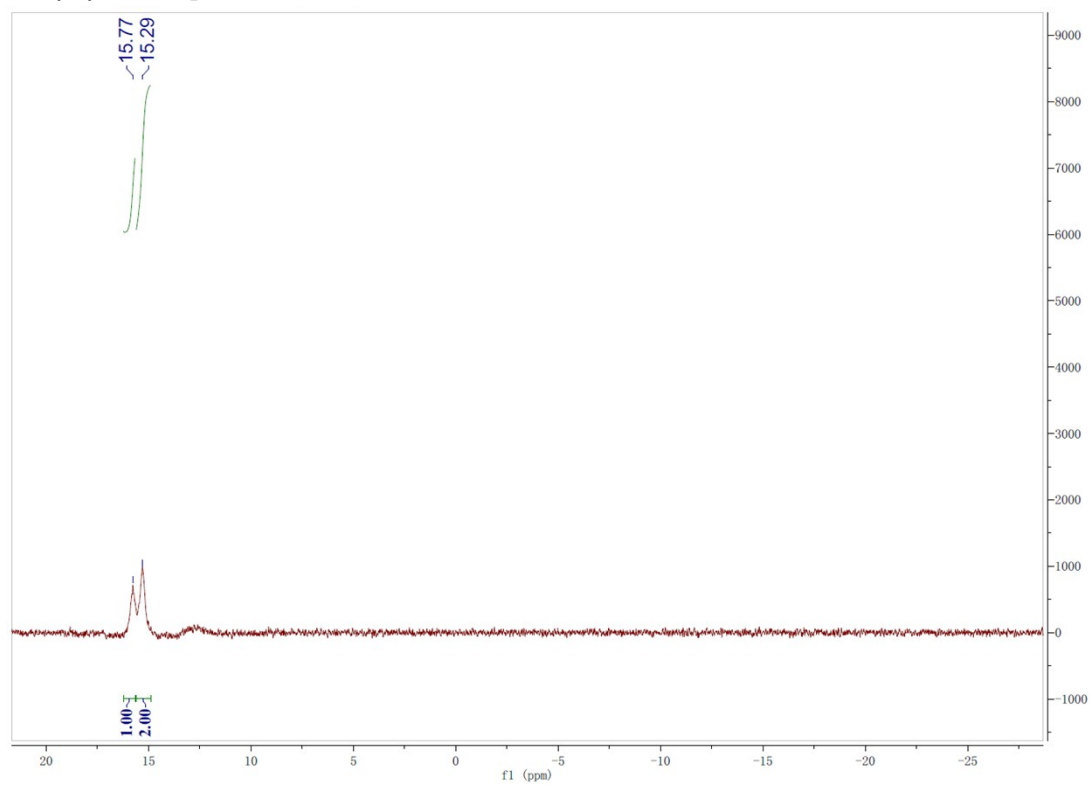
Note: Complex **18** was synthesized in diethyl ether.

^{19}F { ^1H } NMR spectrum (C_6D_6)



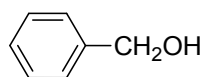
Note: Complex **18** was synthesized in diethyl ether.

$^{31}\text{P} \{^1\text{H}\}$ NMR spectrum (C_6D_6)

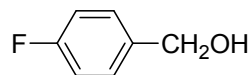
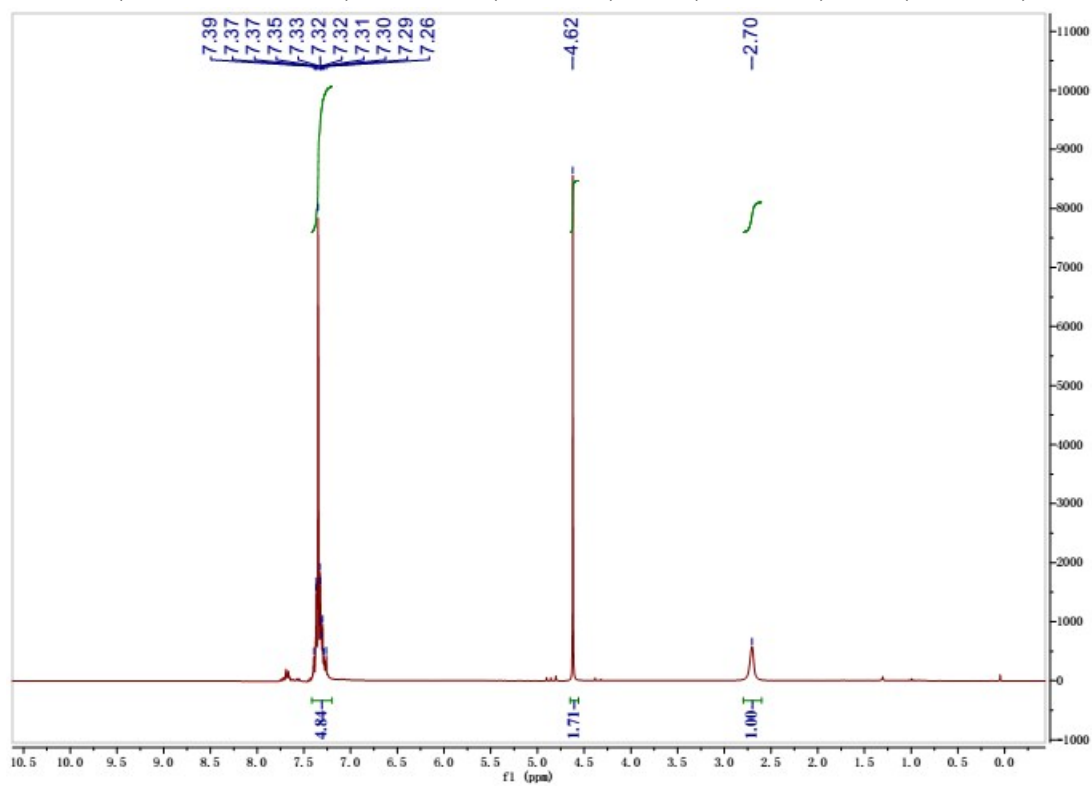


Note: Complex **18** was synthesized in diethyl ether.

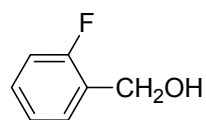
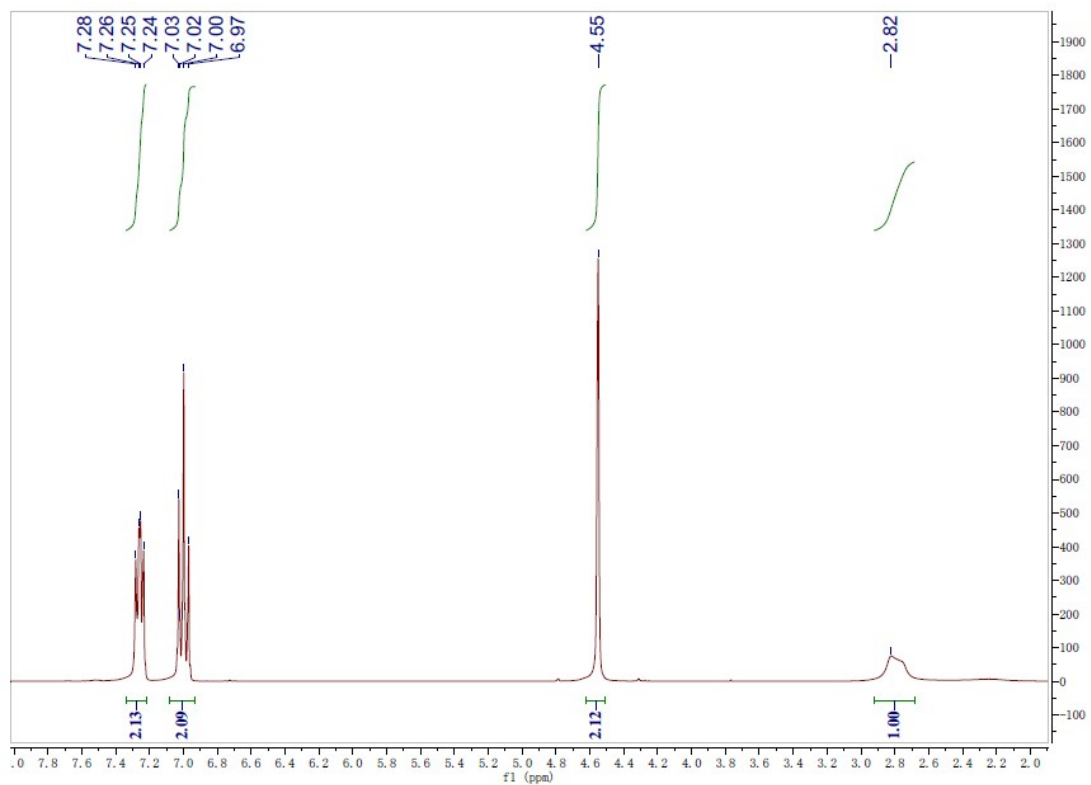
SIV. ^1H NMR spectra of Alcohol Products



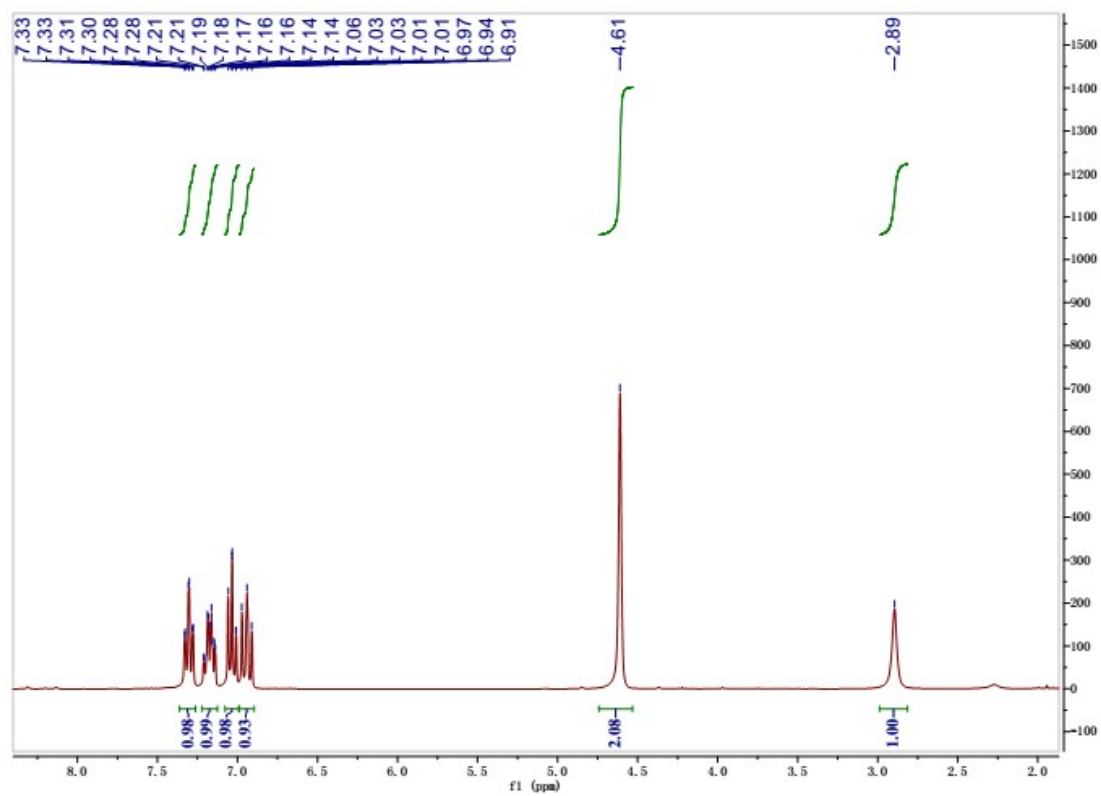
^1H NMR (300 MHz, CDCl_3 , δ): 7.26–7.39 (m, *Ar*, 5H), 4.62 (s, CH_2 , 2H), 2.70 (s, *OH*, 1H).

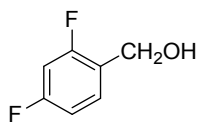


^1H NMR (300 MHz, CDCl_3 , δ): 6.97–7.28 (m, *Ar*, 4H), 4.55 (s, CH_2 , 2H), 2.82 (s, *OH*, 1H).

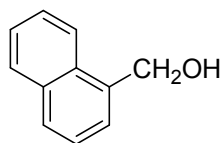
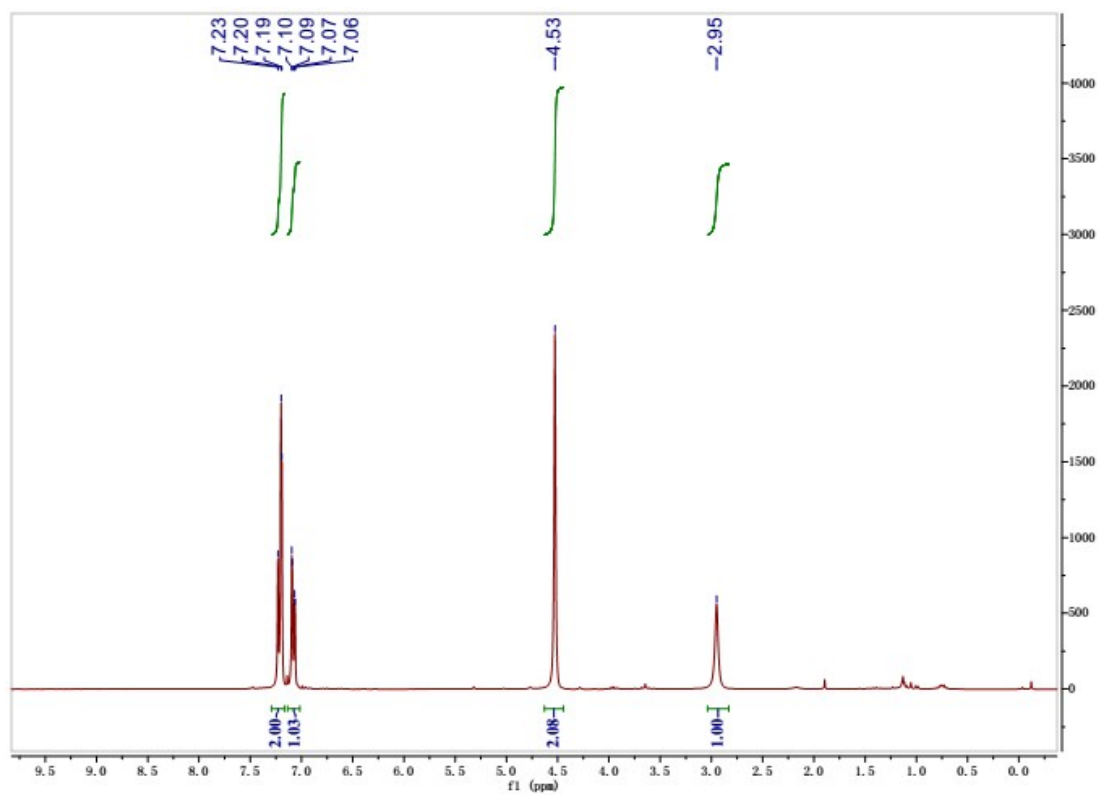


^1H NMR (300 MHz, CDCl₃, δ): 7.33–6.91 (m, *Ar*, 4H), 4.61 (s, CH₂, 2H), 2.89 (s, OH, 1H).

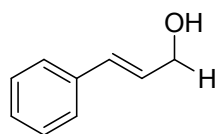
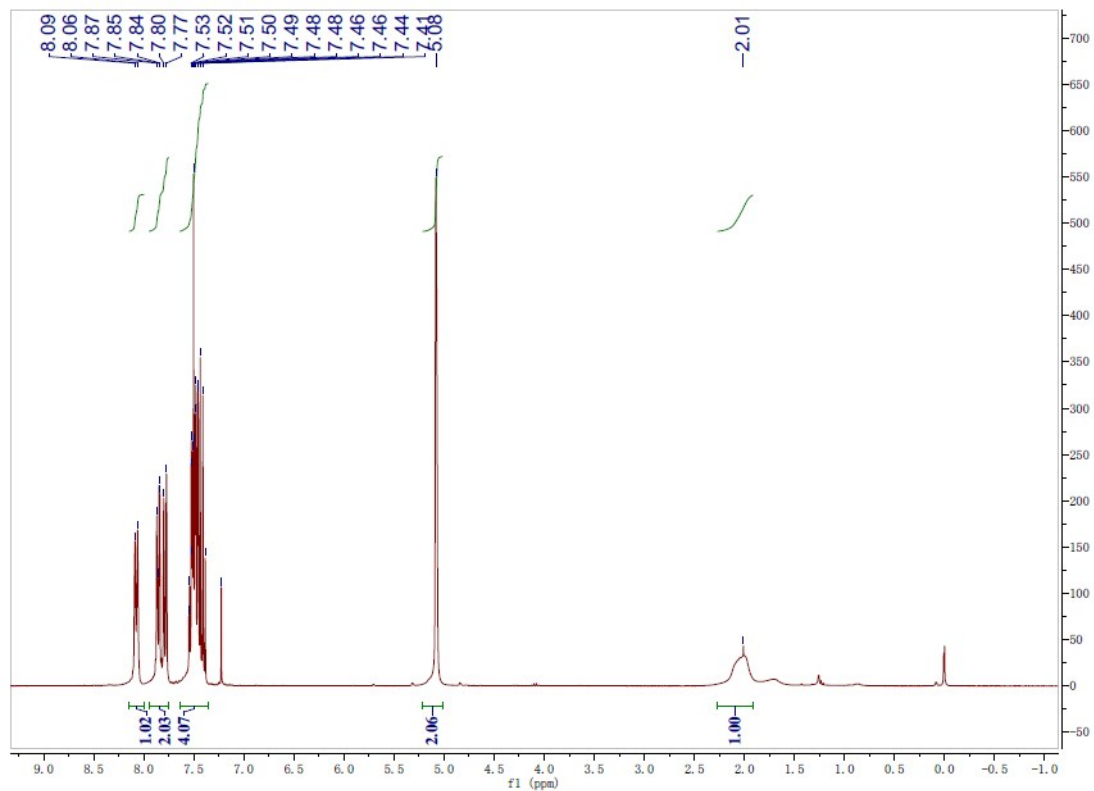




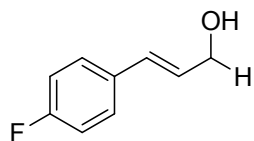
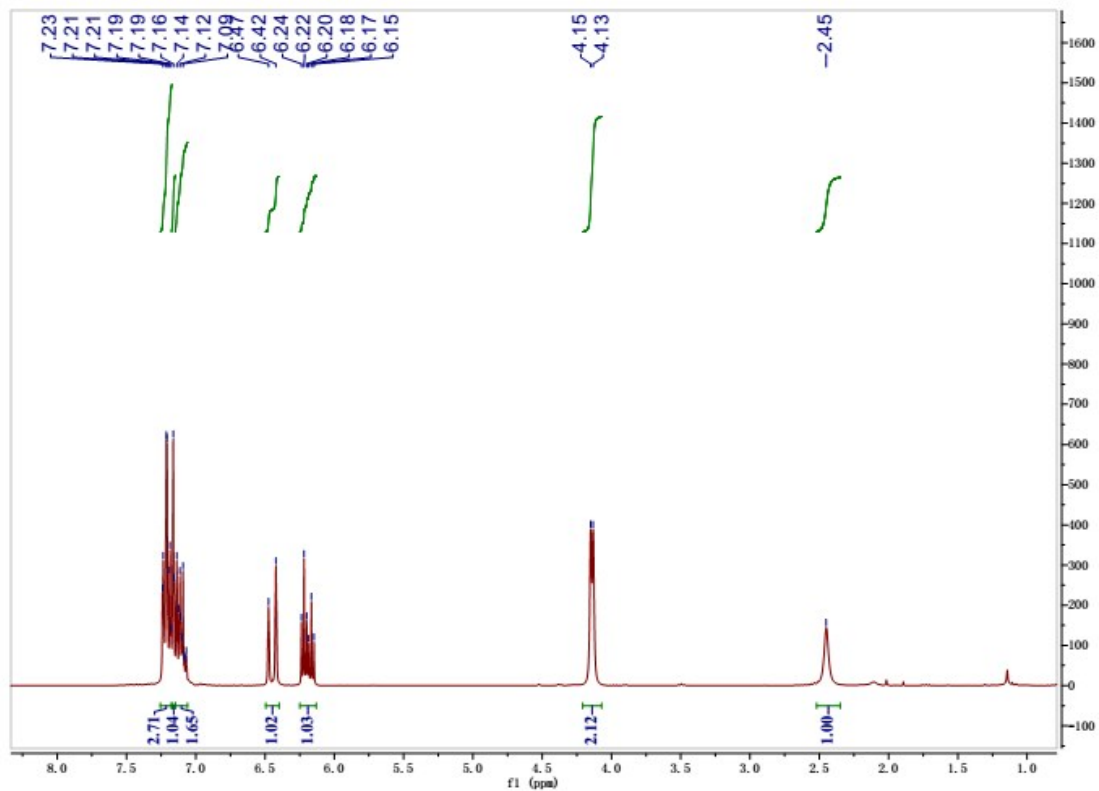
$^1\text{H NMR}$ (300 MHz, CDCl_3 , δ): 7.23–7.06 (m, *Ar*, 3H), 4.53 (s, CH_2 , 2H), 2.95 (s, *OH*, 1H).



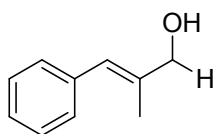
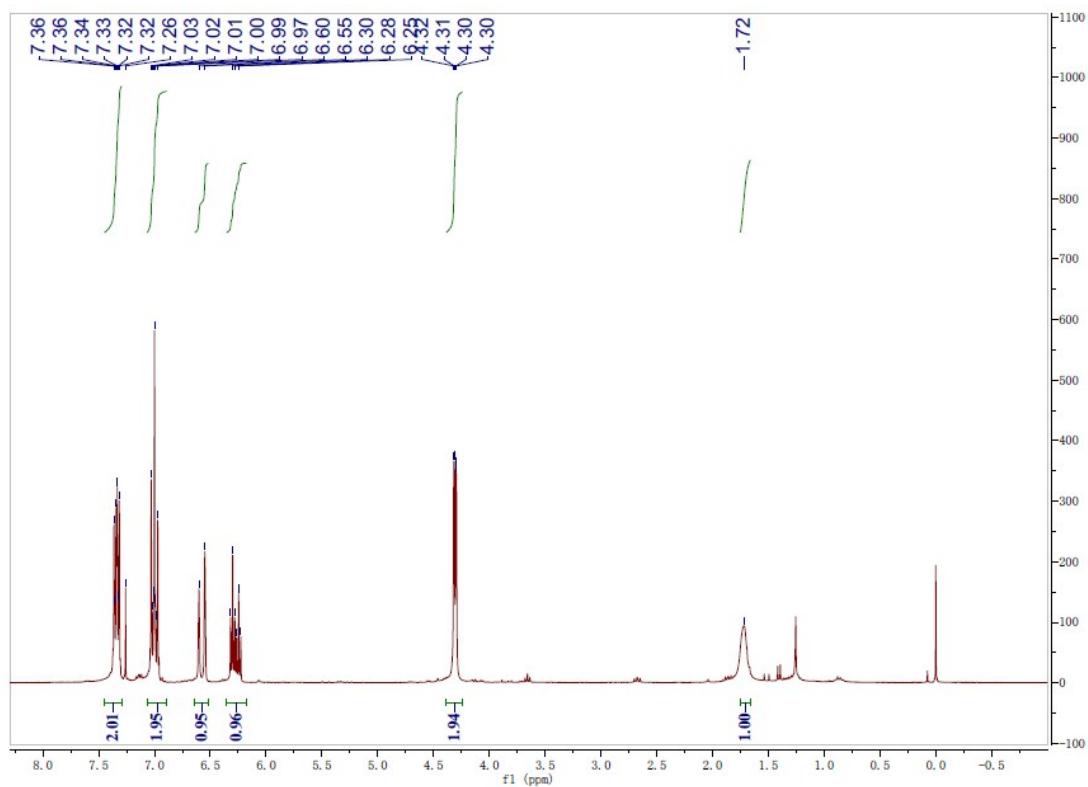
$^1\text{H NMR}$ (300 MHz, CDCl_3 , δ): 7.41–8.09 (m, *Ar*, 7H), 5.08 (s, CH_2 , 2H), 2.01 (s, *OH*, 1H).



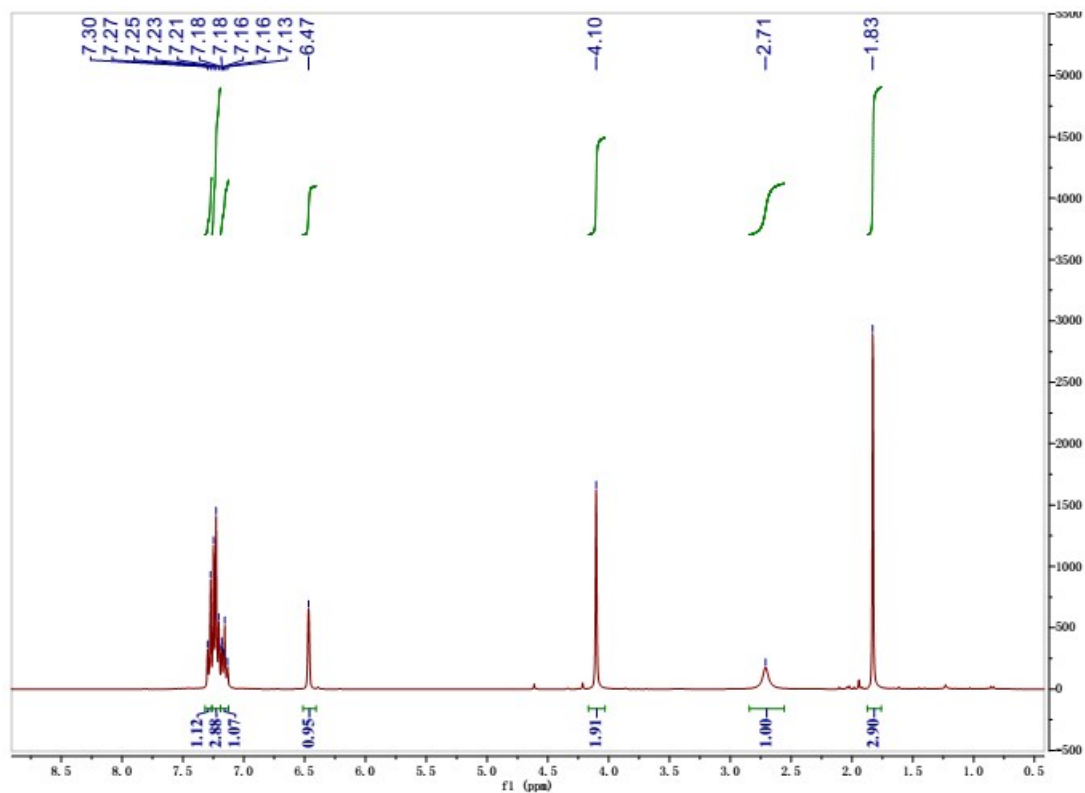
^1H NMR (300 MHz, CDCl_3 , δ): 7.23–7.09 (m, *Ar*, 5H), 6.44 (d, *HC=C*, 1H), 6.18 (m, *C=CH*, 1H), 4.14 (d, *CH₂*, 2H), 2.45 (s, *OH*, 1H).

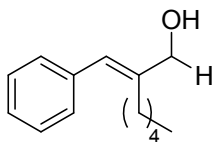


^1H NMR (300 MHz, CDCl_3 , δ): 7.34-6.97 (m, *Ar*, 4H), 6.55 (d, *HC=C*, 1H), 6.24 (m, *C=CH*, 1H), 4.30 (dd, *CH₂*, 2H), 1.72 (s, *OH*, 1H).

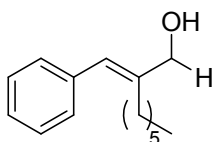
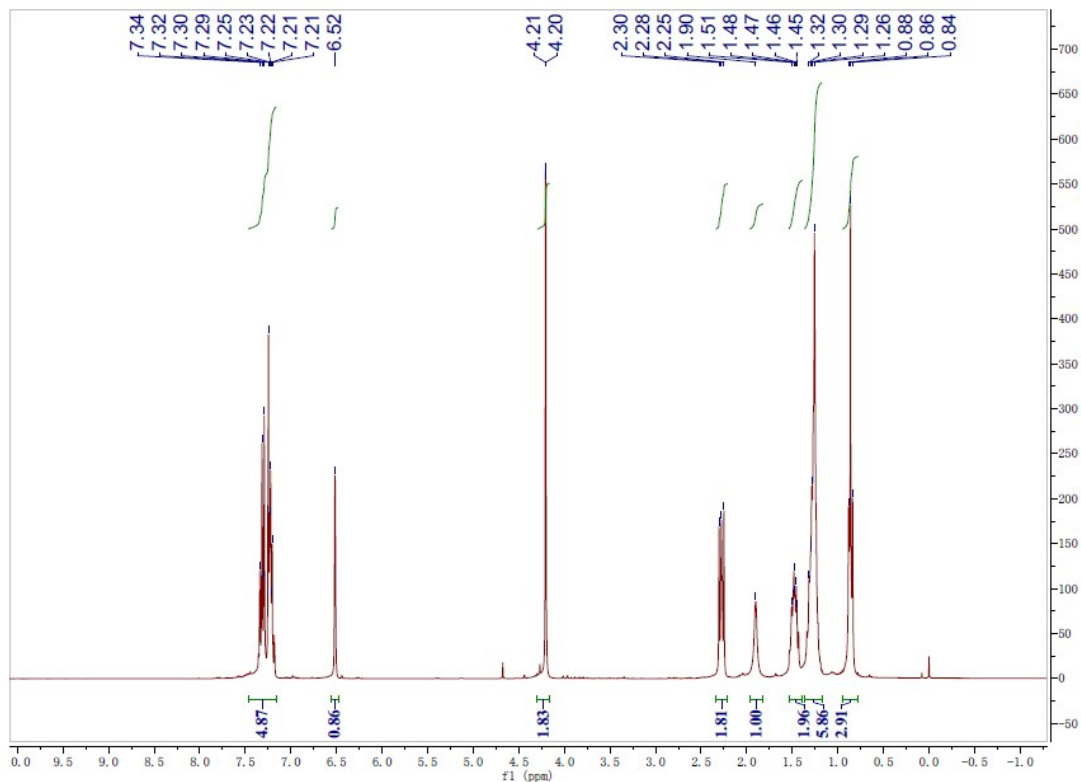


^1H NMR (300 MHz, CDCl_3 , δ): 7.30-7.13 (m, *Ar*, 5H), 6.47 (d, *HC=C*, 1H), 4.10 (s, CH_2 , 2H), 2.71 (s, *OH*, 1H), 1.83 (s, CH_3 , 3H)

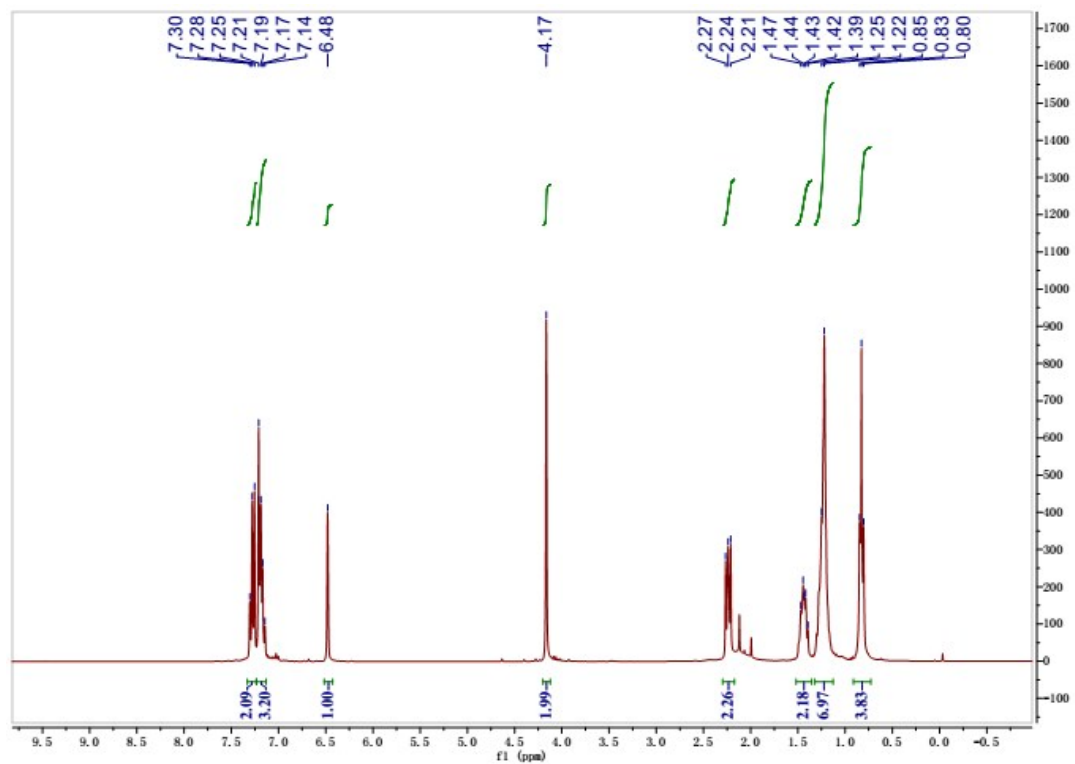




$^1\text{H NMR}$ (300 MHz, CDCl_3 , δ): 7.34-7.21 (m, *Ar*, 5H), 6.52 (d, *HC=C*, 1H), 4.21 (s, CH_2 , 2H), 2.28 (m, CH_2 , 2H), 1.90 (s, *OH*, 1H), 1.51 (m, CH_2 , 2H), 1.29 (m, CH_2 , 4H), 0.86 (t, CH_3 , 3H)

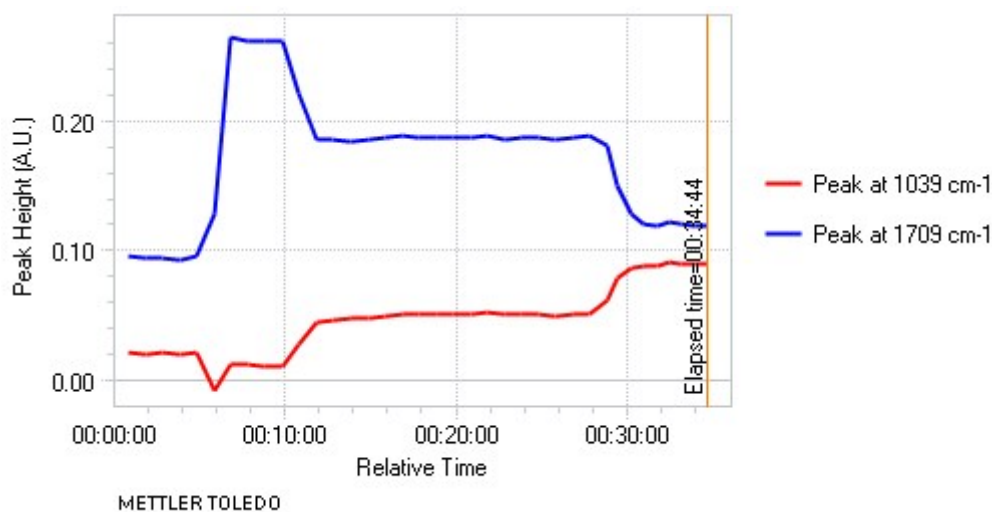


$^1\text{H NMR}$ (300 MHz, CDCl_3 , δ): 7.30-7.14 (m, *Ar*, 5H), 6.48 (d, *HC=C*, 1H), 4.17 (s, CH_2 , 2H), 2.24 (m, CH_2 , 2H), 1.43 (m, CH_2 , 2H), 1.24 (m, CH_2 , 6H), 0.83 (t, CH_3 , 3H)

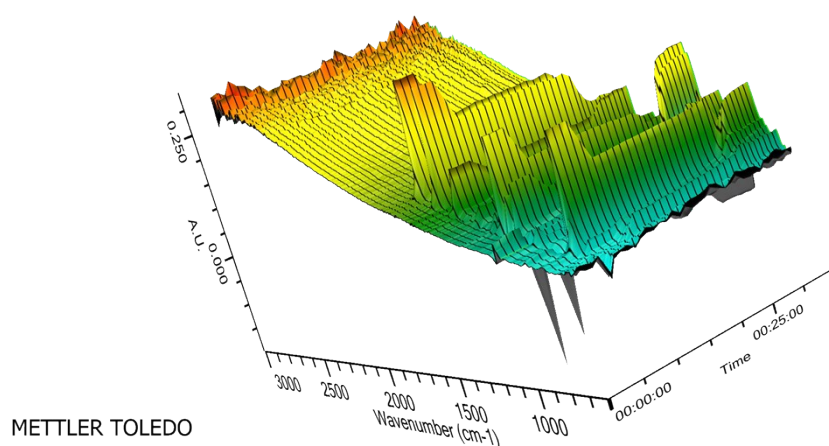


SV General Procedure of the Operando IR Experiment.

1 mL THF was charged into a two-necked Schlenk tube which had been connected with the Schlenk line. Through an adapter, the test probe was emerged into the solution. At the beginning, the operando IR spectrometer recorded the solvent signal for 10 min. After 5 min, 4-FC₆H₄CHO (0.17 g, 1.37 mmol) was added into the container. At the 10th minute, 1 mL THF solution of complex **15** (0.14 g, 0.27 mmol) was added into the mixture and the reaction container was heated to 55 °C. The mixture was kept stirring at this temperature for 15 min. During that period, the IR absorption (1709 cm⁻¹) for C=O bond of 4-FC₆H₄CHO maintained unchanged. At the 28th minute, the HSi(OCH₂CH₃)₃ (0.26 g, 1.6 mmol) was added. The operando IR spectra were continually recorded until the reaction was completed. The signal of C=O bond disappeared immediately and the one of C-O bond (1039 cm⁻¹) grew up.



(a)



(b)

Figure S1. Operando IR results for the cascade reaction with three components: (a) Kinetic Profiles; (b) Three-Dimensional Fourier Transform IR (3DFT-IR) Profiles.