Electronic Supplementary Information

Ferrocene and [3]ferrocenophane-based β-diketonato copper(II) and zinc(II) complexes: Synthesis, crystal structure, electrochemistry and catalytic effect on thermal decomposition of ammonium perchlorate

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Experimental

General procedure for the synthesis of β-diketone ligand

In a dry three-necked flask, NaH (0.108 g, 3mmol, 70% in oil), 1,2-dimethoxyethane (1 mL) and ethyl 4-alkoxybenzoate (0.5 mmol) were successively added and stirred for 5 min, then the solution of 2-acetyl[3]ferrocenophane[1] or acetylferrocenophane (0.5mmol) in 1,2-dimethoxyethane (1 mL) was added and refluxed for 5 h under N_2. After being cooled to room temperature, anhydrous ethanol was added to the suspensionin order to quench the reaction instantaneously. The solvent was distilled off, then benzene was added. The product was collected by filtration, acidified with HC1, washed with water, dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was subjected to flash column chromatography with petroleum ether / ethyl acetate (40:1, V:V) as eluent, and the second fraction was the desired product.

1-Ferrocenyl-3-(4-(octyloxy)phenyl)propane-1,3-dione (Fc8). Yield 43%, mp 79-80 ºC, R_f = 0.229 (petroleum ether:ethyl acetate = 30:1); IR (KBr, cm^{-1}): 3309, 3090, 2919, 2850, 1605, 1559, 1472, 1109, 843; ^{1}H NMR (500 MHz, $CDCl_3$) enol form>80%, (δ ppm): 16.74 (s, 1H, OH), 7.90 (d, J = 9.0 Hz, 2H, ArH), 6.96 (d, J =9.0 Hz, 2H, ArH), 6.33 (s, 1H, CH), 4.87 (s, 2H, FcH), 4.53 (s, 2H, FcH), 4.21 (s, 5H, FcH), 4.03 (t, J = 6.5 Hz, 2H, OCH_2), 1.84 – 1.78 (m, 2H, CH_2), 1.50 – 1.42 (m, 2H, CH_2), 1.28-1.26 (m, 8H, CH_2), 0.88 (t, J = 6.5 Hz, 3H, CH_3). Keto form (δ ppm): 8.10 (d, J = 9.0 Hz, 2H, ArH), 4.88 (s, 2H, FcH), 4.55 (s, 2H, FcH), 4.29 (s, 2H, $COCH_2CO$), 4.12 (s, 5H, FcH), 0.96 (t, J = 6.5 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) (δ ppm): 192.40, 180.62, 162.40, 131.59, 128.70, 127.51, 114.44, 92.59, 78.34, 72.82, 71.95, 70.30, 70.09, 68.58, 68.28, 31.93, 29.70, 29.68, 29.66, 29.60, 26.57, 29.36, 22.70, 14.12; ESI-MS *m/z*: calcd 459.16 for $[M-H]^-$; found: 459.14.

1-Ferrocenyl-3-(4-(dodecyloxy)phenyl)propane-1,3-dione (Fc12). Yield 43%, mp 73-76 ºC; R_f = 0.297 (petroleum ether: ethyl acetate = 30:1); IR (KBr, cm^{-1}): 3105, 2922, 2850, 1602, 1548, 1501, 1469, 1236, 1109, 1024, 999, 789, 504; ^{1}H NMR (500 MHz, $CDCl_3$) enol form>96% (δ ppm): 7.90 (d, J = 9.0 Hz, 2H, ArH), 6.96 (d, J = 9.0 Hz, 2H, ArH), 6.33 (s, 1H, CH), 4.87 (s, 2H, FcH), 4.53 (s, 2H, FcH), 4.21 (s, 5H, FcH), 4.03 (t, J = 6.5 Hz, 2H, OCH_2), 1.86 – 1.77 (m, 2H, CH_2), 1.48 – 1.42 (m, 2H, CH_2), 1.35-1.26 (m, 16H, CH_2), 0.88 (d, J = 6.5 Hz, 3H, CH_3). Keto form (δ ppm): 8.10 (d, J = 9.0 Hz, 2H, ArH), 4.30 (s, 2H,$COCH_2CO$), 4.12 (s, 5H, FcH); ^{13}C NMR (125 MHz, $CDCl_3$) (δ ppm): 196.50, 191.36, 190.49, 179.62, 162.63, 161.39, 130.56, 128.48, 127.68, 126.51, 113.42, 91.57, 77.38, 71.78, 70.92, 69.28, 69.07, 67.56, 67.30, 30.91, 28.64, 28.62, 28.60, 28.55, 28.36,

28.33, 21.67, 13.10; ESI-MS *m/z*: calcd 515.22 for $[M-H]^-$; found: 515.24.

1-Ferrocenyl-3-(4-(tetradecyloxy)phenyl)propane-1,3-dione (Fc14).Yield 47%, mp 69-71 ºC, R_f= 0.331 (petroleum ether:ethyl acetate = 30:1); IR (KBr, cm^{-1}): 3362, 3093, 2920, 2851, 1603, 1550, 1503, 1471, 1108, 839. ^1H NMR (500 MHz, $CDCl_3$) enol form>81% (δ ppm): 7.90 (d, J = 8.5 Hz, 2H, ArH), 6.96 (d, J = 8.5 Hz, 2H, ArH), 6.33 (s, 1H, CH), 4.88 (s, 2H, FcH), 4.54 (s, 2H, FcH), 4.22 (s, 5H, FcH), 4.03 (t, J = 6.5 Hz, 2H, OCH_2), 1.87 – 1.75 (m, 2H, CH_2), 1.49 – 1.44 (m, 2H, CH_2), 1.29 (d, J = 14.5 Hz, 20H, CH_2), 0.88 (t, J = 7.0 Hz, 3H, CH_3). Keto form (δ ppm): 8.10 (d, J = 8.5 Hz, 2H, ArH), 4.29 (s, 2H, $COCH_2CO$), 4.13 (s, 5H, FcH). ^{13}C NMR (125 MHz, $CDCl_3$) (δ ppm):192.39, 180.64, 162.41, 129.10, 128.70, 114.45, 92.60, 78.32, 72.91, 71.94, 70.30, 70.13, 69.74, 68.58, 68.28, 31.92, 29.95, 29.60, 29.56, 29.35, 29.15, 26.00, 22.69, 14.10.ESI-MS *m/z*: calcd 543.26 for $[M-H]^-$; found: 543.25.

1-Ferrocenyl-3-(4-(hexadecyloxy)phenyl)propane-1,3-dione (Fc16). Yield 47%, mp 65-67 ºC, R_f = 0.366 (petroleum ether:ethyl acetate = 30:1); IR (KBr, cm^{-1}): 3090, 2918, 2849, 1604, 1566, 1471, 1258, 1173, 931, 798, 498; ^1H NMR (500 MHz, $CDCl_3$) enol form>92% (δ ppm): 7.90 (d, J = 9.0 Hz, 2H, ArH), 6.96 (d, J = 9.0 Hz, 2H, ArH), 6.33 (s, 1H, CH), 4.87 (s, 2H, FcH), 4.54 (s, 2H, FcH), 4.21 (s, 5H, FcH), 4.03 (s, 2H, OCH_2), 1.84-1.78 (m, 2H, CH_2), 1.50-1.44 (m, 2H, CH_2), 1.36-1.26 (m, 24H, CH_2), 0.88 (t, J = 7.0 Hz, 3H). Keto form (δ ppm): 8.10(d, J = 9.0 Hz, 2H, ArH), 4.89 (s, 2H, FcH), 4.55 (s, 2H, FcH), 4.30(s, 2H, $COCH_2CO$), 4.12 (s, 5H, FcH); ^{13}C NMR (125 MHz, $CDCl_3$) (δ ppm): 191.38, 190.49, 179.61, 162.63, 161.39, 130.56, 127.68, 126.50, 113.42, 91.57,77.31, 71.78, 70.93, 69.28, 69.07, 67.57, 67.27, 30.91, 28.68, 28.65, 28.58, 28.55, 28.36, 28.34, 21.67, 24.99, 21.68, 13.10; ESI-MS *m/z*: calcd 573.30 for $[M+H]^+$; found: 573.05.

1-β-[3]Ferrocenophanyl-3-(4-(octyloxy)phenyl)propane-1,3-dione (Fp8). Yield 43%; mp 51-53ºC, R_f = 0.289 (petroleum ether:ethyl acetate = 20:1). IR (KBr, cm^{-1}): 3325, 3074, 2921, 2847, 1604, 1552, 1504, 1249, 1176, 844, 517. ^1H NMR (500 MHz, $CDCl_3$) enol form>69% (δ ppm): 7.87 (d, J = 8.0 Hz, 2H, ArH), 6.94 (d, J = 8.0 Hz, 2H, ArH), 6.24 (s, 1H, CH), 4.76 (s, 2H, FcH), 4.36- 4.35 (s, 2H, FcH), 4.31 (s, 1H, FcH), 4.02 (t, J = 6.5 Hz, 2H, OCH_2), 3.98 (s, 1H, FcH), 3.91 (s, 1H, FcH), 2.12 – 1.91 (m, 6H, CH_2), 1.81-1.79 (m, 2H, CH_2), 1.45-1.44 (m, 2H, CH_2), 1.33-1.25 (m, 8H, CH_2), 0.89 (t, J = 6.5 Hz, 3H, CH_3). Keto form (δ ppm): 8.12 (d, J = 9.0 Hz, 2H, ArH), 4.75 (s, 2H, FcH), 4.36 (s, 1H, FcH), 4.21(s, 2H, $COCH_2CO$), 4.13 (s, 1H, FcH), 4.10 (s, 1H, FcH), 3.86 (s, 1H, FcH), 3.51 (s, 1H, FcH). ^{13}C NMR (125 MHz, $CDCl_3$) (δ ppm): 193.07, 191.26, 179.19, 163.58, 162.20, 131.56, 128.58, 127.51, 114.41, 92.69, 90.72, 89.80, 87.19, 86.75, 74.56, 74.32, 73.78, 73.10, 71.09, 71.02, 71.00, 70.54, 70.25, 69.97, 69.88, 69.05, 68.37, 68.25, 34.86, 31.82, 29.35, 29.24, 29.15, 26.00, 24.48, 22.67, 14.12. ESI-MS *m/z*: calcd 500.2008 for M^+; found: 500.2025.

1-β-[3]Ferrocenophanyl-3-(4-(decanyloxy)phenyl)propane-1,3-dione (Fp10). Yield 45%; mp 50-53 ºC, R_f = 0.31 (petroleum ether:ethyl acetate = 20:1). IR (KBr, cm^{-1}): 3306.78, 3102.41, 2923.01, 2850.72, 1605.41, 1549.25, 1503.24, 1464.43, 1117.19, 844.67. ^1H NMR (500 MHz, $CDCl_3$) enol form>68.7%（δ ppm): 7.86 (d, J = 8.5 Hz, 1H, ArH), 6.94 (d, J = 8.5 Hz, 2H, ArH), 6.25 (s, 1H, CH), 4.74 (d, 2H, FcH), 4.35 (s, 1H, FcH), 4.32 (s, 1H, FcH), 4.29 (s, 1H, FcH), 4.02 (t, J = 6.5 Hz, 2H, OCH_2), 3.95 (s, 1H, FcH), 3.90 (s, 1H, FcH), 2.16 –1.76 (m, 8H CH_2), 1.51 – 1.40 (m, 2H CH_2), 1.40 – 1.18 (m, 14H, CH_2), 0.89 (t, J = 7.0 Hz, 3H, CH_3). Keto form (δ ppm): 8.12 (d, J = 9.0 Hz, 2H), 4.75 (s, 2H, FcH), 4.36 (s, 1H, FcH), 4.21 (s, 2H, $COCH_2CO$), 4.13 (s, 1H, FcH), 4.10 (s, 1H, FcH), 3.86 (s, 1H, FcH), 3.50 (s, 1H, FcH). ^{13}C NMR (125 MHz, $CDCl_3$) (δ ppm): 196.87, 193.09, 191.23, 179.18, 163.55, 162.17, 131.52, 129.42, 128.53, 127.48, 114.37, 92.51, 90.63 , 87.16, 86.59, 79.17, 73.06, 70.93,

70.49, 70.09, 69.83, 68.65, 31.89, 29.55, 29.38, 29.14, 26.00, 24.44, 24.08, 22.63, 14.13; ESI-MS *m/z*: calcd 529.24 for $[M+H]^+$; found: 529.24.

1-β-[3]Ferrocenophanyl-3-(4-(dodecyloxy)phenyl)propane-1,3-dione (Fp12). Yield 43%; mp 52-54ºC, R_f = 0. 33 (Petroleum ether: Ethyl acetate = 20:1). IR (KBr, cm^{-1}): 3306.78, 3078.68, 2922.15, 2851.24, 1603.11, 1554.38, 1505.67, 1118.38, 849.90. ^{1}H NMR (500 MHz, $CDCl_3$) enol form>69%（δ ppm): 16.59 (s, 1H, OH), 7.85 (d, J = 8.5 Hz, 2H, ArH), 6.95 (d, J = 8.5 Hz,2H, ArH), 6.19 (s, 1H, CH),4.86- 4.75 (m, 2H, FcH), 4.45-4.43 (m, 3H, FcH), 4.08 (s, 1H, FcH), 4.02 (t, J = 6.5 Hz, 2H, OCH_2), 3.99 (s, 1H, FcH), 2.05-1.79 (m, 8H, CH_2), 1.53 – 1.42 (m, 2H, CH_2), 1.40 – 1.24 (m, 16H, CH_2), 0.88 (t, J = 7.0 Hz, 3H, CH_3). Keto form (δ ppm): 8.12 (d, J = 8.5 Hz, 2H, ArH), 4.21 (s, 2H, $COCH_2CO$), 4.14 (s, 1H, FcH), 4.11 (s, 1H, FcH), 3.87 (s, 1H, FcH), 3.51 (s, 1H, FcH). ^{13}C NMR (125 MHz, $CDCl_3$) (δ ppm): 193.01, 191.29, 179.14, 162.21, 131.55, 128.62, 127.49, 114.40, 92.91, 90.75, 90.06, 87.20, 86.99, 74.58, 74.04, 73.12, 71.30, 71.05, 71.03, 70.56, 70.51, 70.07, 70.05, 69.99, 69.16, 68.34, 68.25, 34.70, 31.93, 29.62, 29.36, 29.16, 26.01, 24.49, 24.09 , 22.70, 14.13. ESI-MS *m/z*: calcd 557.27 for $[M+H]^+$; found: 557.12.

1-β-[3]Ferrocenophanyl-3-(4-(tetradecyloxy)phenyl)propane-1,3-dione (Fp14). Yield 47%; mp 52-54 ºC, R_f = 0.34 (petroleum ether:ethyl acetate = 20:1). IR (KBr, cm^{-1}): 3079.81, 2920.29, 2848.81, 1604.76, 1550.42, 1504.42, 1115.33, 841.81. ^{1}H NMR (500 MHz, $CDCl_3$) enol form>67%（δ ppm): 16.64 (s, 1H, OH), 7.86 (d, J = 8.5 Hz, 2H, ArH), 6.95 (d, J = 8.5 Hz, 2H, ArH), 6.25 (s, 1H, CH), , 4.74 (s, 1H, FcH), 4.36 (s, 1H, FcH), 4.33 (s, 1H, FcH), 4.30 (s, 1H, FcH), 4.02 (t, J = 6.5 Hz, 2H, OCH_2), 3.96 (s, 1H, FcH), 3.91 (s, 1H, FcH), 2.12-1.88 (m, 6H, CH_2), 1.84-1.78 (m, 2H, CH_2), 1.49-1.42 (m, 2H, CH_2), 1.36 – 1.21 (m, 20H, CH_2), 0.88 (t, J = 6.5 Hz, 3H, CH_2). Keto form (δ ppm): 8.12 (d, J = 9.0 Hz, 2H, ArH), 4.75 (s, 2H, FcH), 4.21(s, 2H, $COCH_2CO$), 4.13 (s, 1H, FcH), 4.11 (s, 1H, FcH), 3.86(s, 1H, FcH), 3.50 (s, 1H, FcH). ^{13}C NMR (125 MHz, $CDCl_3$) (δ ppm): 193.19, 191.81, 162.20, 131.57, 128.56, 114.40, 92.60, 90.73, 89.71, 87.20, 86.65, 75.08, 74.59, 74.10, 73.68, 73.11, 71.03, 71.01, 70.54, 70.50, 69.97, 68.76, 68.35, 68.26, 34.99, 31.95, 29.76,2 9.59, 29.48, 29.38, 29.17, 26.02, 24.48, 24.08, 22.72, 14.15. ESI-MS *m/z*: calcd 585.30 for $[M+H]^+$; found: 585.04.

1-β-[3]Ferrocenophanyl-3-(4-(hexadecyloxy)phenyl)propane-1,3-dione (Fp16). Yield 42%; mp 52-56 ºC, R_f = 0.35 (petroleum ether:ethyl acetate = 20:1); IR (KBr, cm^{-1}): 3306.78, 3078.68, 2922.15, 2851.24, 1603.11, 1554.38, 1505.67, 1299.50, 1118.38, 849.90; ^{1}H NMR (500 MHz, $CDCl_3$) enol form>68%（δ ppm): 7.86 (d, J = 6.5 Hz, 2H, ArH), 6.94 (d, J = 6.5 Hz, 2H, ArH), 6.20 (s, 1H, CH), 4.83-4.75 (m, 2H, FcH), 4.42-4.36 (m, 3H, FcH), 4.05 (s, 1H, FcH), 4.02 (t, J = 6.5 Hz, 2H, OCH_2), 3.97 (s, 1H, FcH), 2.06-1.85 (m,6H, CH_2), 1.83-1.75 (m,2H, CH_2), 1.46-1.43 (m, 2H, CH_2), 1.35 – 1.22 (m, 24H, CH_2), 0.88 (t, J = 7.0 Hz, 3H). Keto form (δ ppm): 8.12 (d, J = 6.5 Hz, 2H, ArH), 4.21 (s, 2H, $COCH_2CO$), 4.14 (s, 1H, FcH), 4.11 (s, 1H, FcH), 3.87 (s, 1H, FcH), 3.49 (s, 1H, FcH); ^{13}C NMR (125 MHz, $CDCl_3$) (δ ppm): 193.20, 191.33, 162.20, 131.57, 128.57, 114.40, 92.66, 90.90, 89.79, 88.67, 86.73, 74.29, 74.23, 74.20, 73.76, 73.31, 71.06, 70.23, 70.21, 69.86, 69.86, 69.00, 68.97, 68.29, 68.26, 53.45, 50.90, 34.92, 31.94, 29.64, 29.38, 29.15, 26.00, 24.47, 24.07, 22.71, 14.14; ESI-MS *m/z*: calcd 612.3284 for M^+; found: 612.3261.

References

[1] J.A. Winstead, R.R. Mcguire, R.E.Cochoy, A.D. Brown, JR., G.J. Gauthier, J. Org. Chem. 37 (1972) 2055-2060.

Table and Figures

Table S1 Crystal data and structure refinement for compound Fc8Cu.

Compd.	Fc8Cu
Empirical formula	$C_{54}H_{62}Cu\ Fe_2O_6$
Formula weight	982.29
T (K)	294(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	21.400(4)
b (Å)	9.7000(19)
c (Å)	25.900(5)
α (°)	90
β (°)	90(3)
γ (°)	90
Volume (Å^3)	5310.1(18)
Z, Calculated density (mg m^{-3})	4, 1.229
Absorption coefficient (mm^{-1})	0.980
F (000)	2060.0
Crystal size (mm^3)	0.2 × 0.2 × 0.2
θ range for data collection (°)	1.59-25.01
Reflections collected / unique	25721 / 9314 [R(int) = 0.0875]
Observed reflections [I> 2σ(I)]	4383
Completeness to θ = 25.01 (%)	99.4
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9314 / 0 / 570
Goodness-of-fit on F^2	1.002
Final R indices [I>2σ(I)]	R_1 = 0.0799, wR_2 = 0.2528
R indices (all data)	R_1 = 0.1398, wR_2 = 0.2809

Table S2 Selected bond distances (Å) and angles (°) of Fc8Cu.

Bond distances				Bond angles			
Cu(1)-O(5)	1.889(5)	C(32)-C(31)	1.381(10)	O(5)-Cu(1)-O(1)	179.2(2)	C(30)-O(5)-Cu(1)	128.4(5)
Cu(1)-O(1)	1.899(5)	C(7)-C(8)	1.373(10)	O(5)-Cu(1)-O(2)	87.6(2)	C(7)-O(1)-Cu(1)	127.4(5)
Cu(1)-O(2)	1.914(5)	C(9)-C(8)	1.399(10)	O(1)-Cu(1)-O(2)	92.9(2)	C(7)-C(8)-C(9)	125.7(7)
Cu(1)-O(6)	1.914(5)	C(30)-C(31)	1.379(10)	O(5)-Cu(1)-O(6)	93.0(2)	C(30)-C(31)-C(32)	125.9(7)
O(2)-C(9)	1.284(8)	C(27)-C(30)	1.473(10)	O(1)-Cu(1)-O(6)	86.4(2)	O(6)-C(32)-C(31)	125.7(7)
O(6)-C(32)	1.257(8)	C(32)-C(38)	1.478(10)	O(2)-Cu(1)-O(6)	179.1(2)	O(5)-C(30)-C(31)	122.0(7)
O(5)-C(30)	1.265(8)	C(7)-C(5)	1.490(10)	C(32)-O(6)-Cu(1)	124.5(5)	O(1)-C(7)-C(8)	123.7(7)
O(1)-C(7)	1.285(8)	C(9)-C(46)	1.444(10)	C(9)-O(2)-Cu(1)	126.4(5)	O(2)-C(9)-C(8)	123.8(7)

Table S3 UV-vis absorption data of selected ligands and complexes in CH_2Cl_2.

Compd.	Absorption λ_{max} / nm (log ε / L cm^{-1} mol^{-1})		
Fc8	277 (4.97)	351 (5.44)	482 (4.41)
Fc14	277 (4.98)	350 (5.45)	483 (4.43)
Fc8Cu	301 (5.68)	353 (5.88)	482 (4.90)
Fc14Cu	301 (5.72)	353 (5.92)	483 (4.94)
Fc14Zn	285 (5.66)	358 (5.94)	487 (4.95)
Fp8	267 (5.04)	349 (5.48)	490 (4.69)
Fp14	267 (5.04)	349 (5.43)	489 (4.65)
Fp8Cu	301 (5.73)	353 (5.88)	488 (5.17)
Fp8Zn	282 (5.61)	359 (5.97)	493 (5.22)
Fp14Cu	301 (5.77)	353 (5.93)	488 (5.21)
Fp14Zn	283 (5.60)	359 (5.97)	494 (5.23)

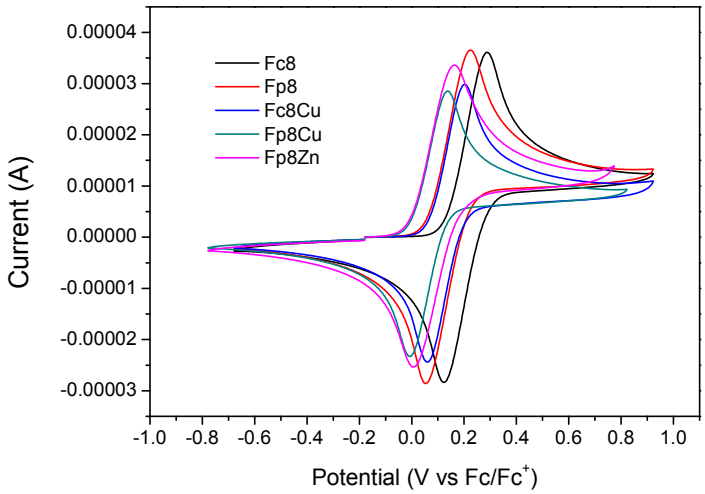

Fig. S1. CV curves of Fp8, Fc8Cu, Fp8Cu, Fp8Zn in CH_2Cl_2, 0.1 M $TBAPF_6$. Scan rate = 100 mV s^{-1}

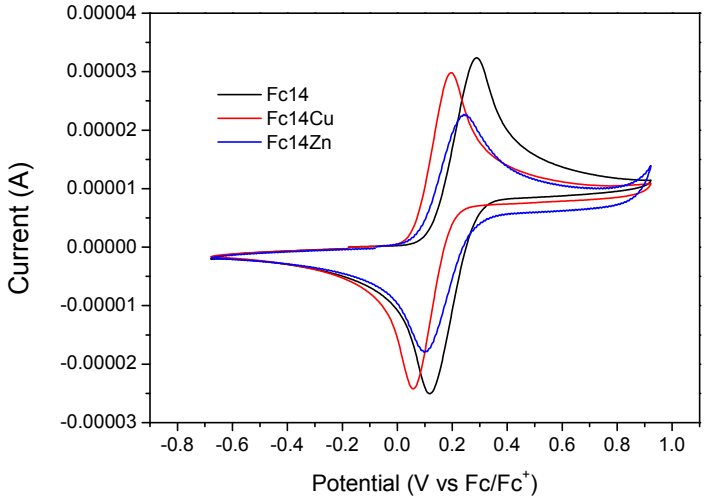

Fig. S2. CV curves of Fc14, Fc14Cu, Fc14Zn in CH_2Cl_2, 0.1 M $TBAPF_6$. Scan rate = 100 mV s^{-1}

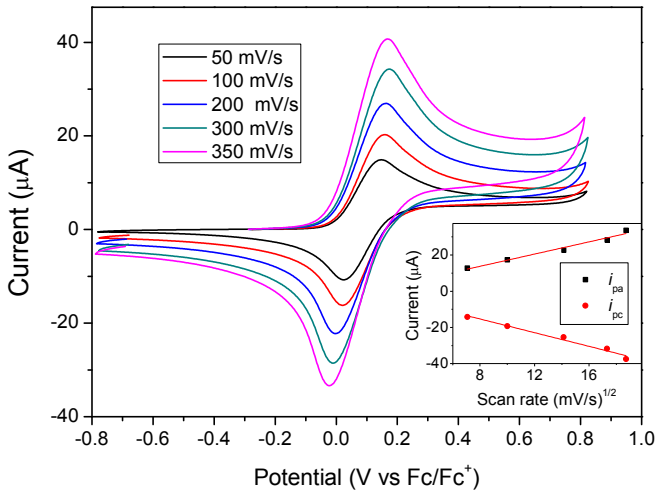

Fig. S3. CV curves and peak currents of Fp14Zn obtained at different scan rates in CH_2Cl_2.

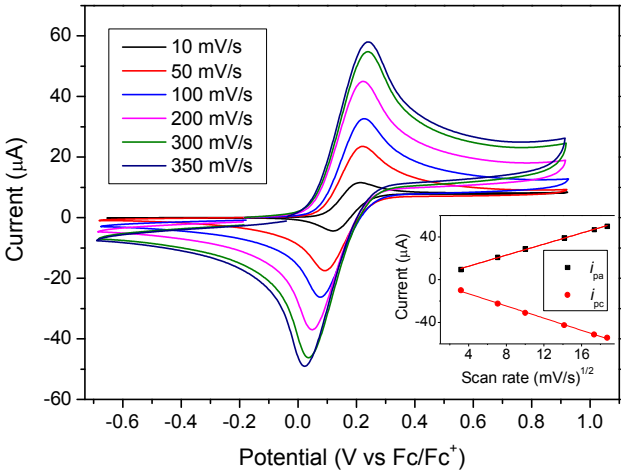

Fig. S4. CV curves and peak currents of Fp14 obtained at different scan rates in CH_2Cl_2.

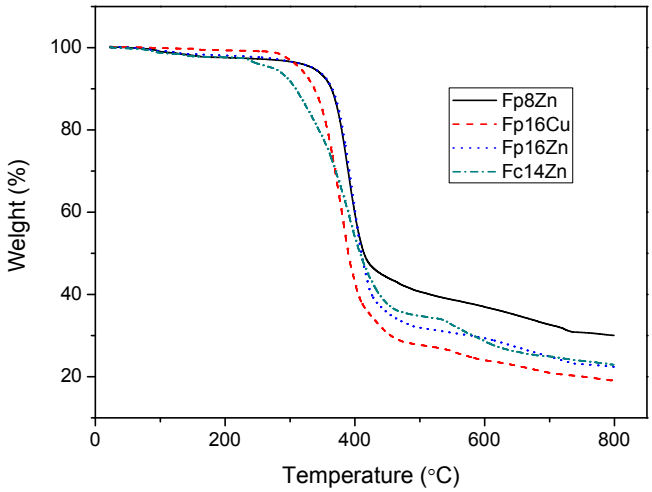

Fig. S5. TG curves of Fp8Zn, Fp16Cu, Fp16Zn and Fc14Zn.

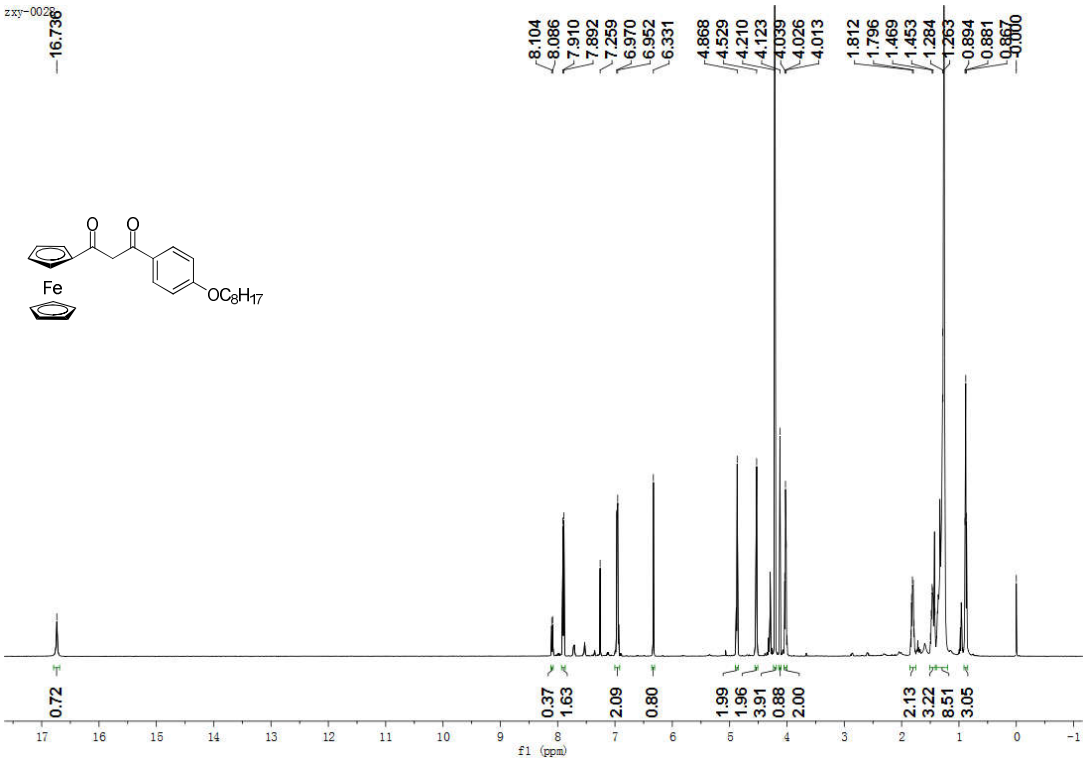

Fig. S6 ^{1}H NMR of compound Fc8

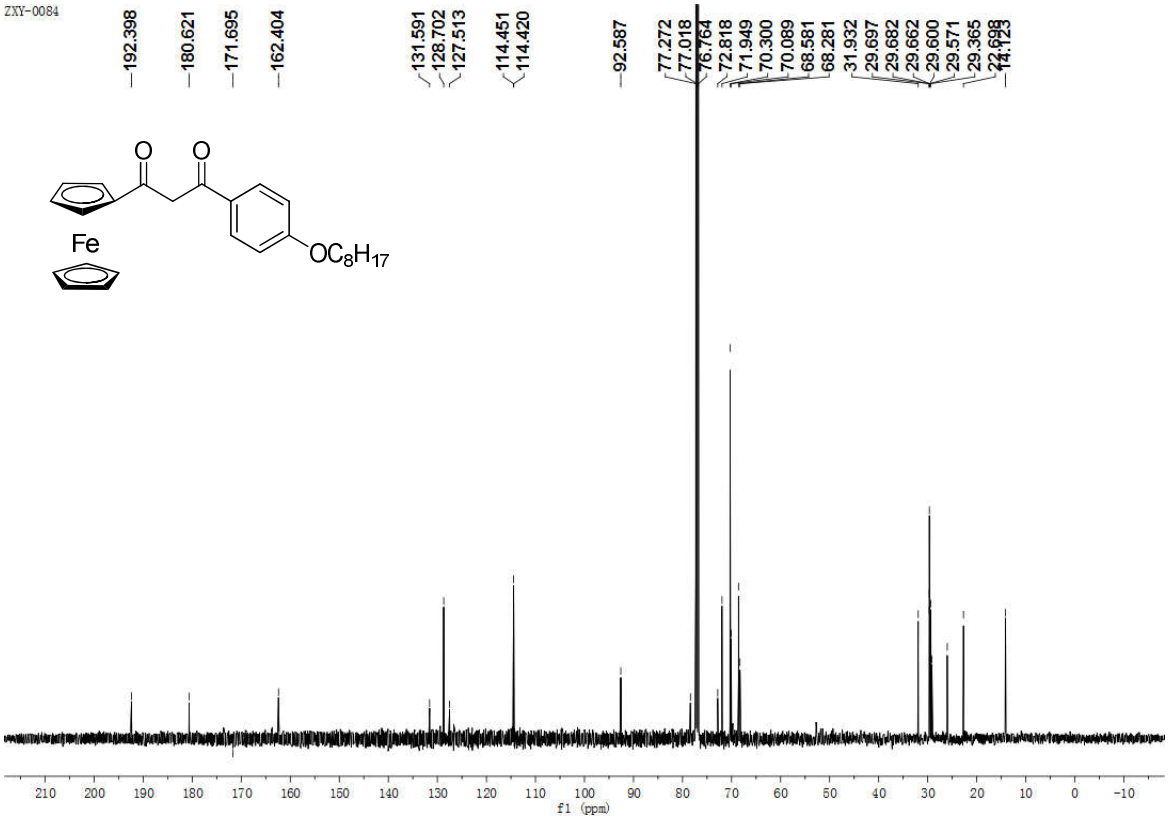

Fig. S7 ^{13}C NMR of compound Fc8

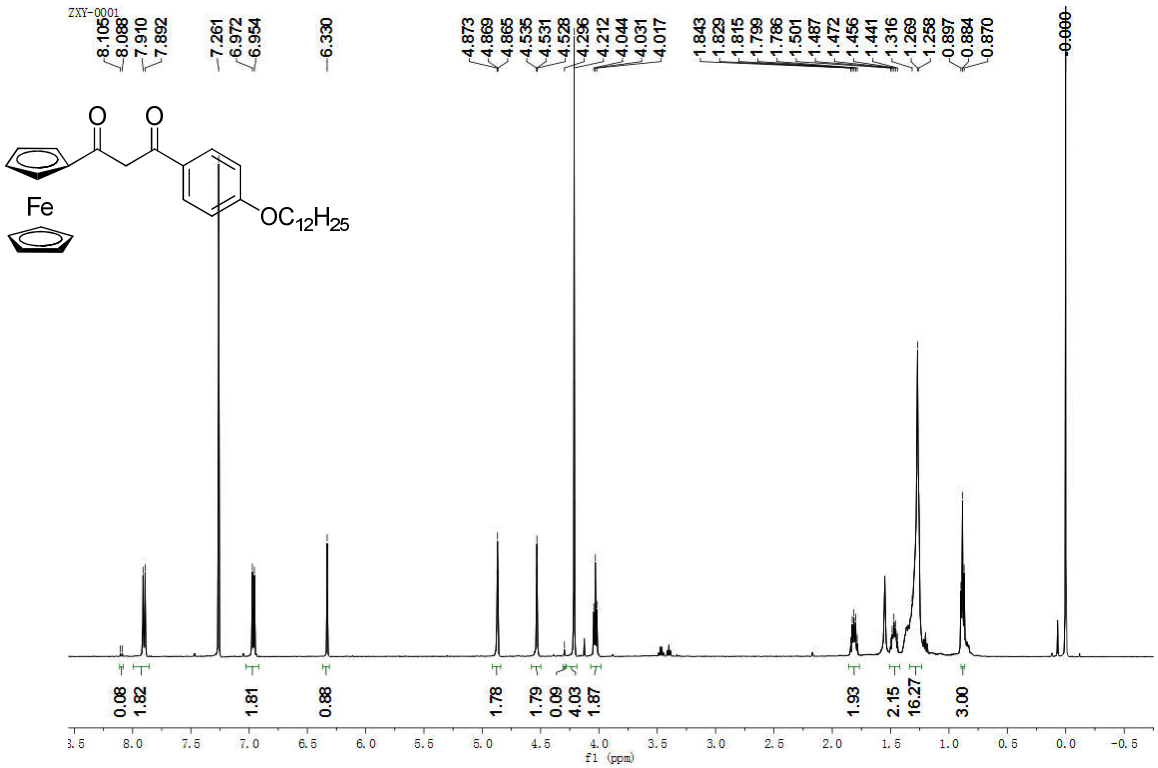

Fig. S8 ^{1}H NMR of compound Fc12

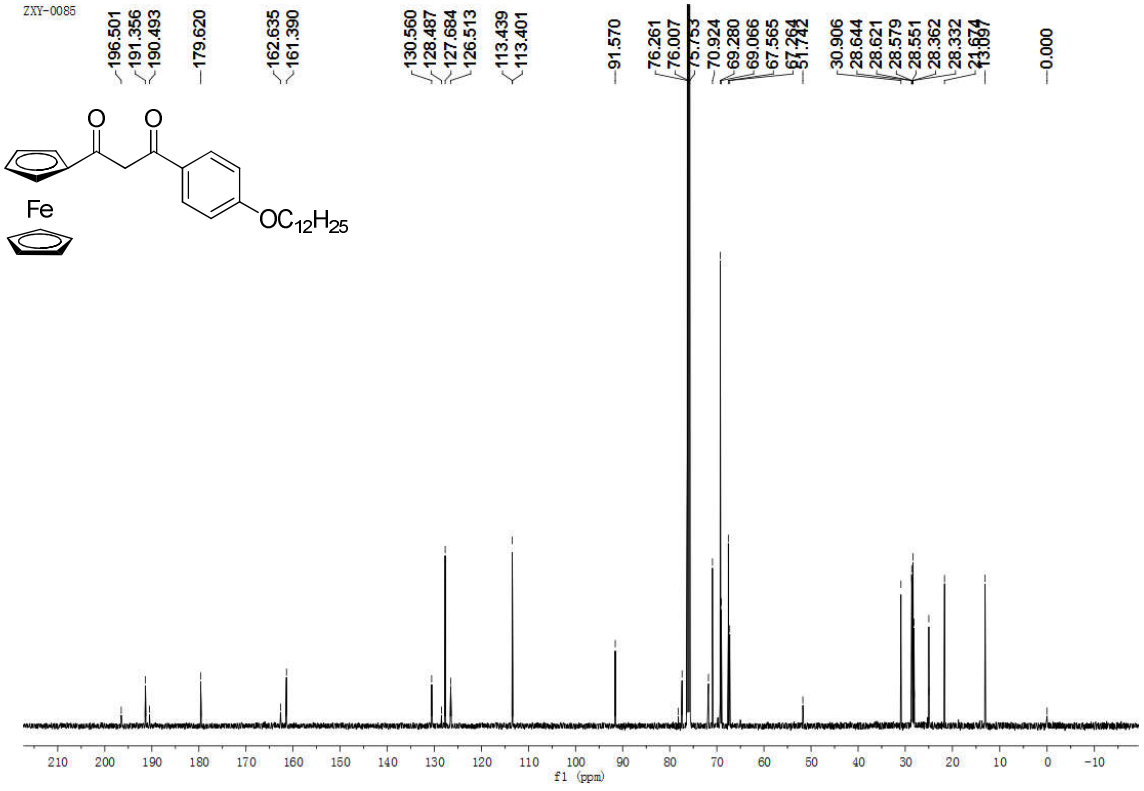

Fig. S9 ^{13}C NMR of compound Fc12

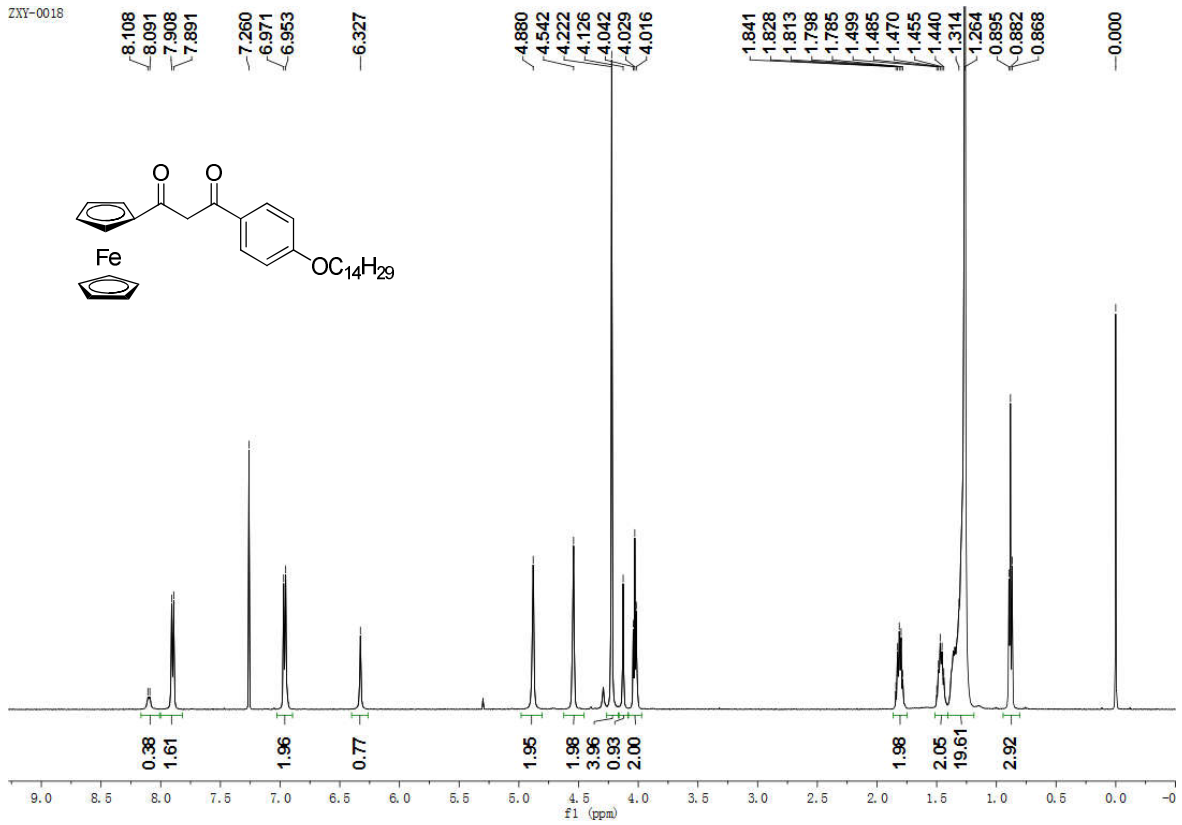

Fig. S10 ^{1}H NMR of compound Fc14

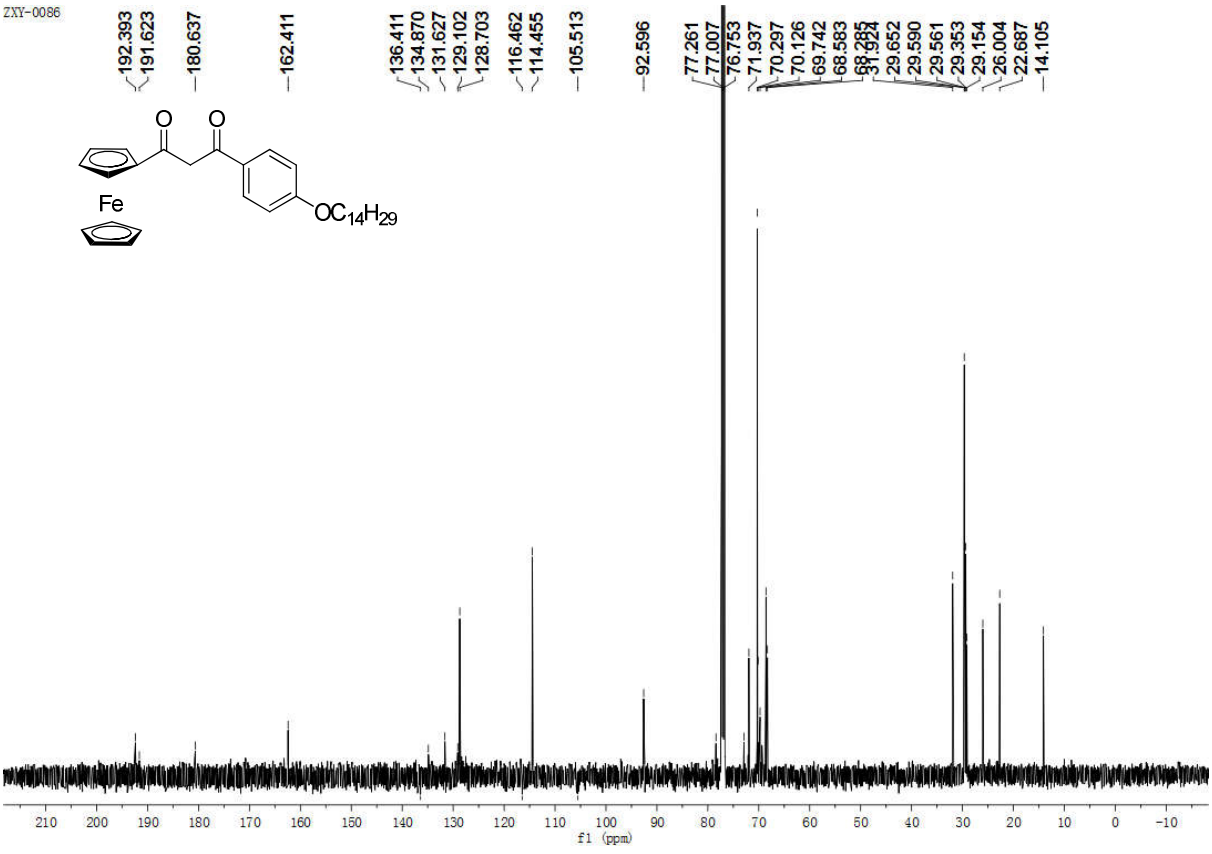

Fig. S11 ^{13}C NMR of compound Fc14

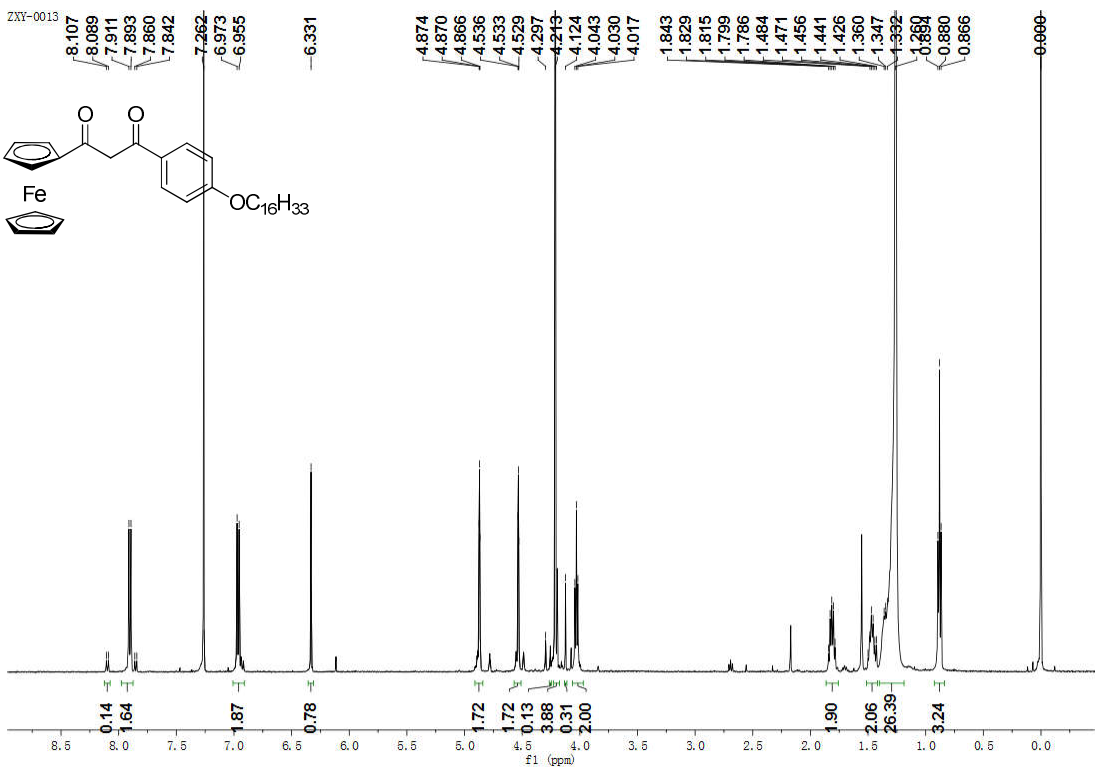

Fig.S12 ^{1}H NMR of compound Fc16

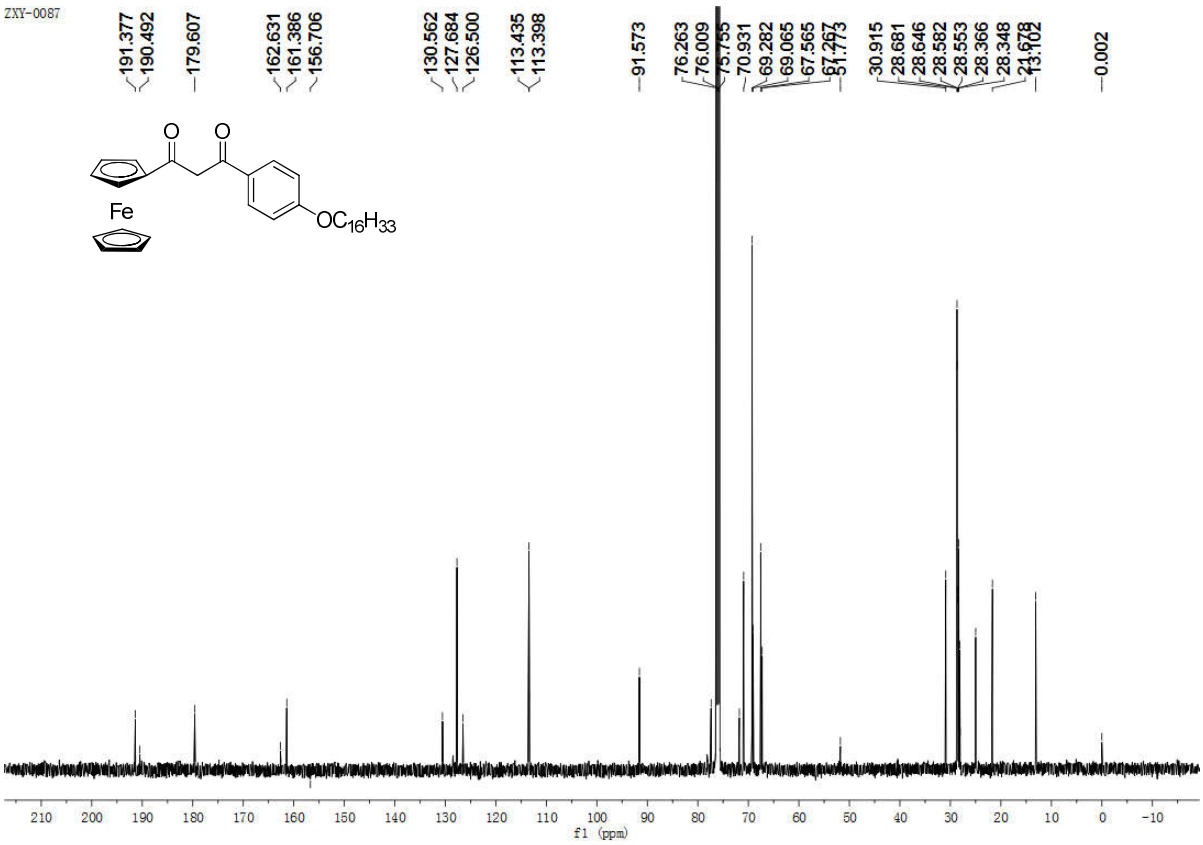

Fig. S13 ^{13}C NMR of compound Fc16

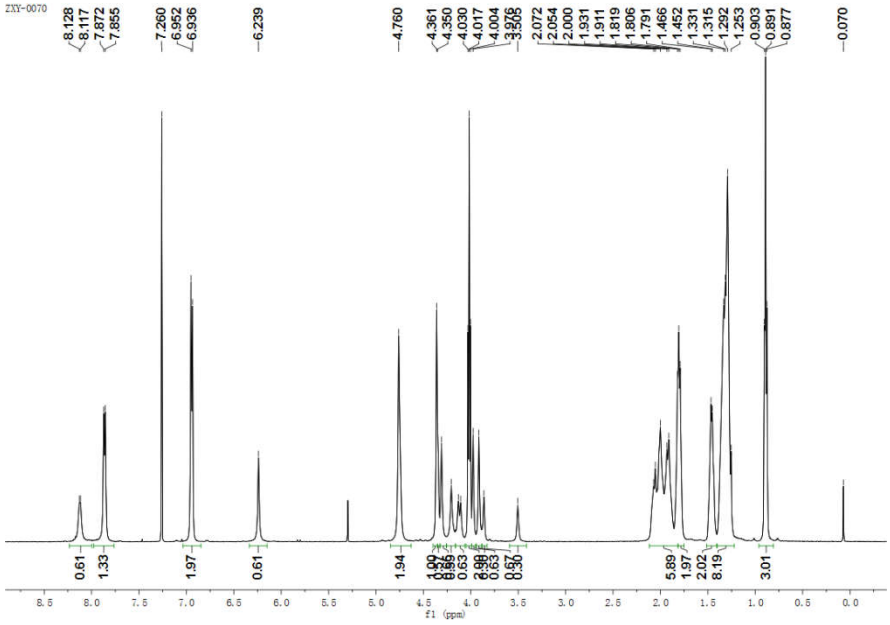

Fig. S14 ^{1}H NMR of compound Fp8

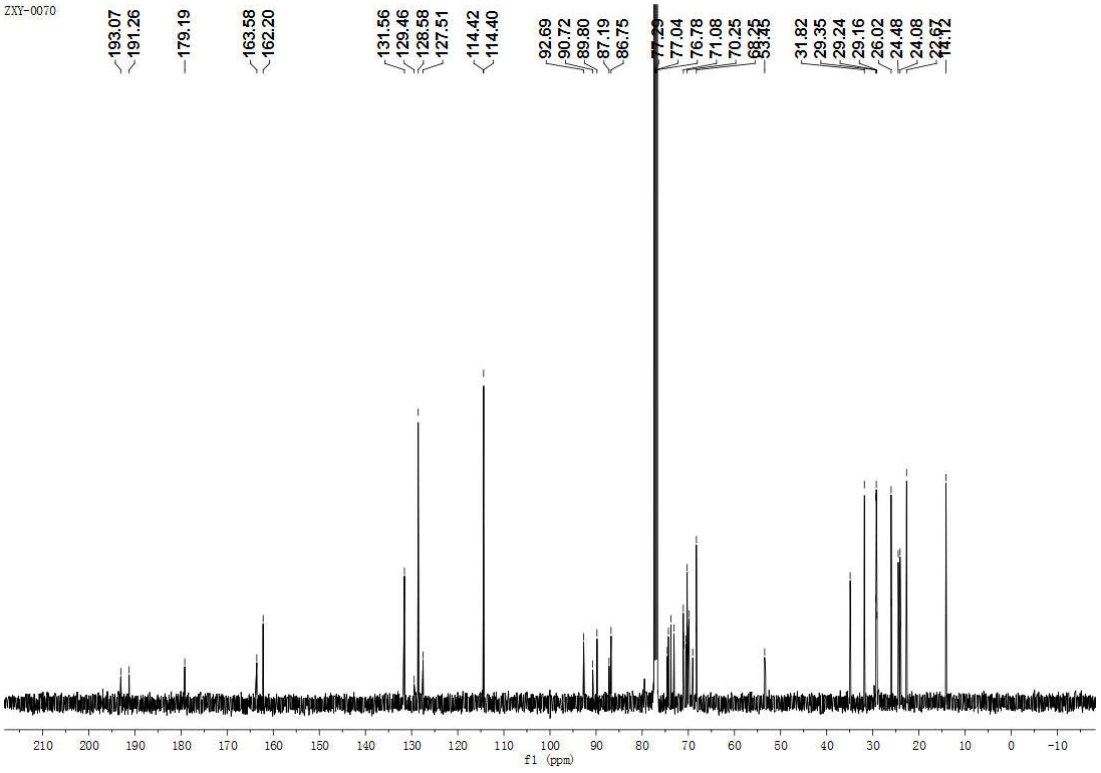

Fig. S15 ^{13}C NMR of compound Fp8

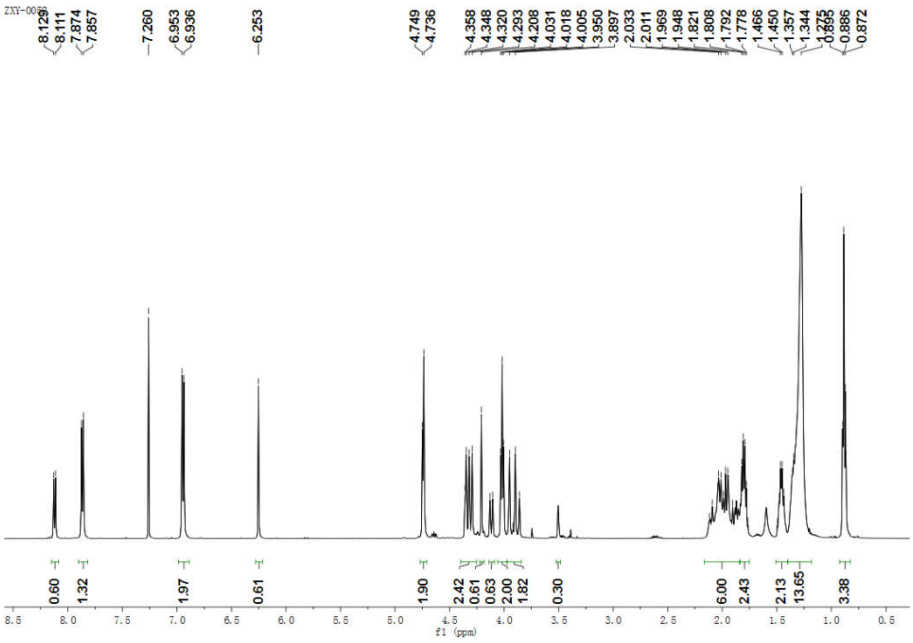

Fig. S16 ^{1}H NMR of compound Fp10

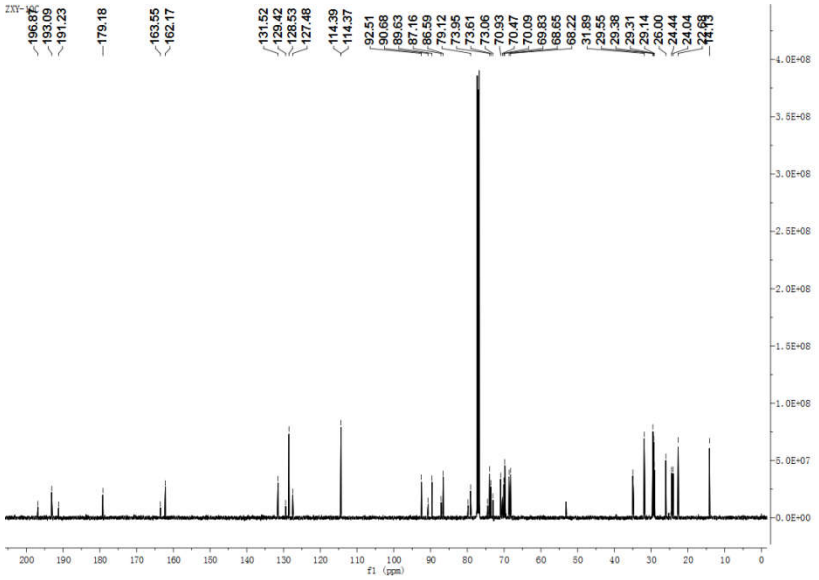

Fig. S17 ^{13}C NMR of compound Fp10

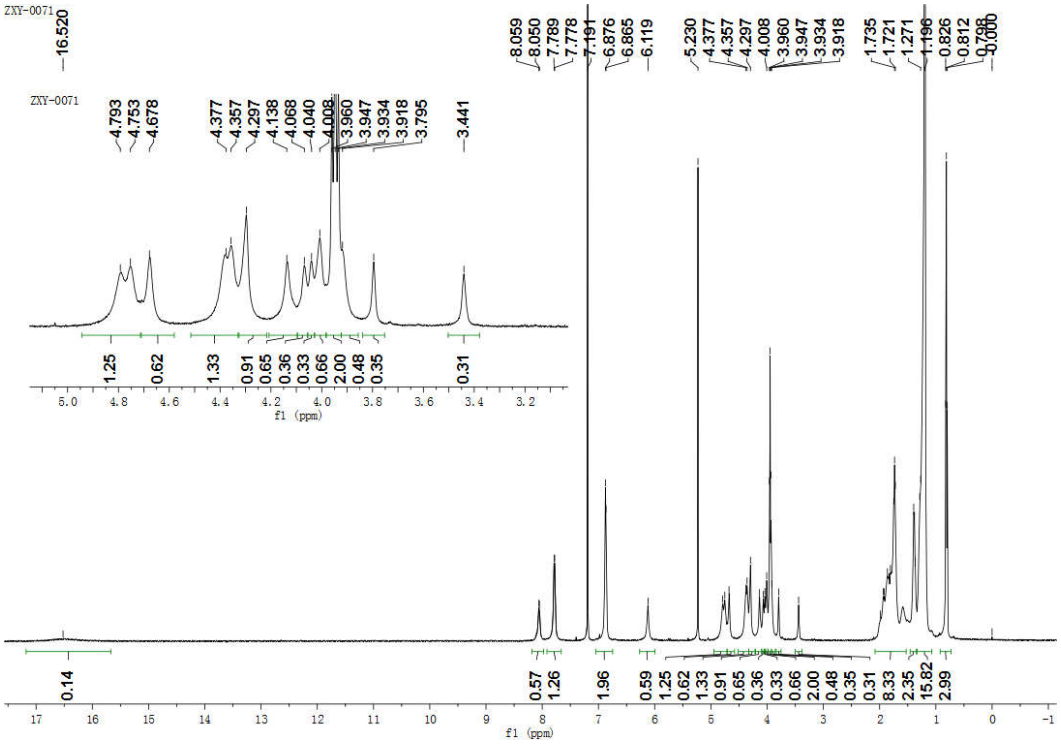

Fig. S18 ^{1}H NMR of compound Fp12

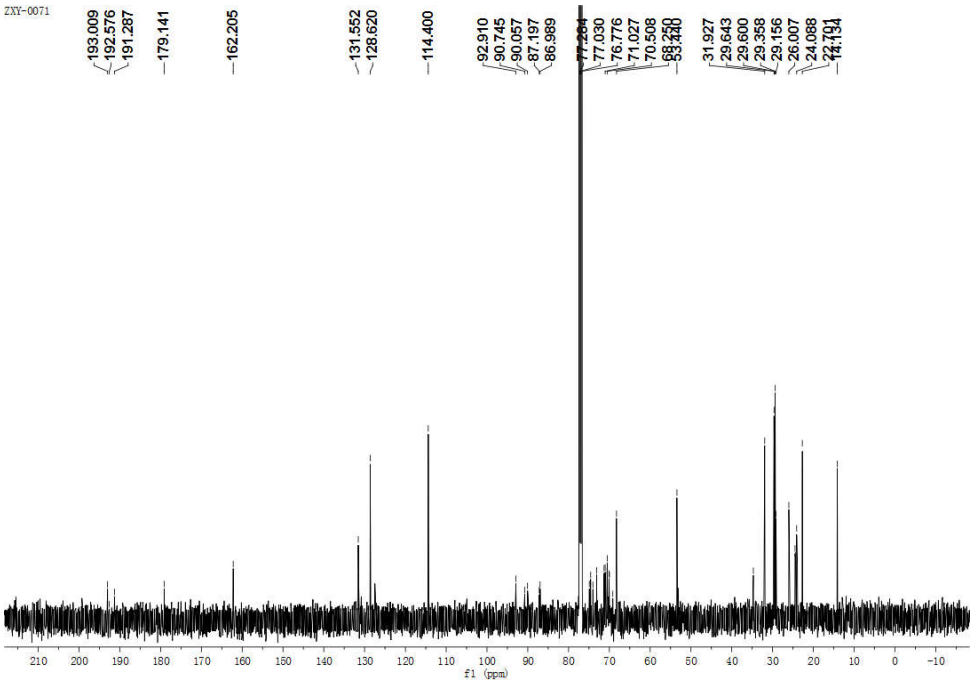

Fig. S19 ^{13}C NMR of compound Fp12

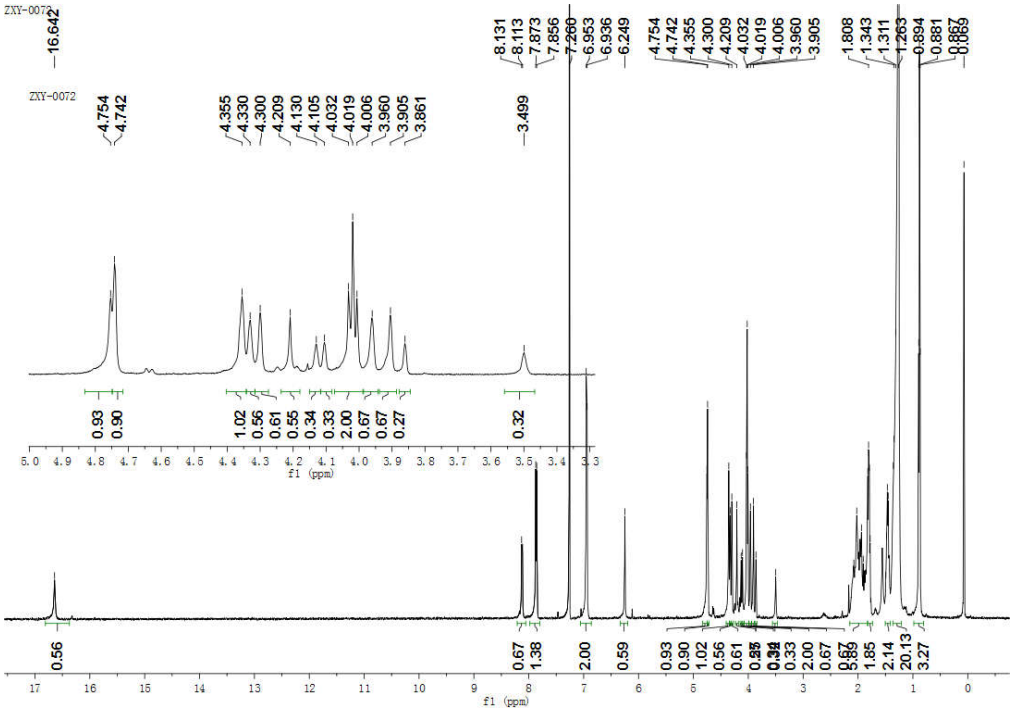

Fig. S20 ^{1}H NMR of compound Fp14

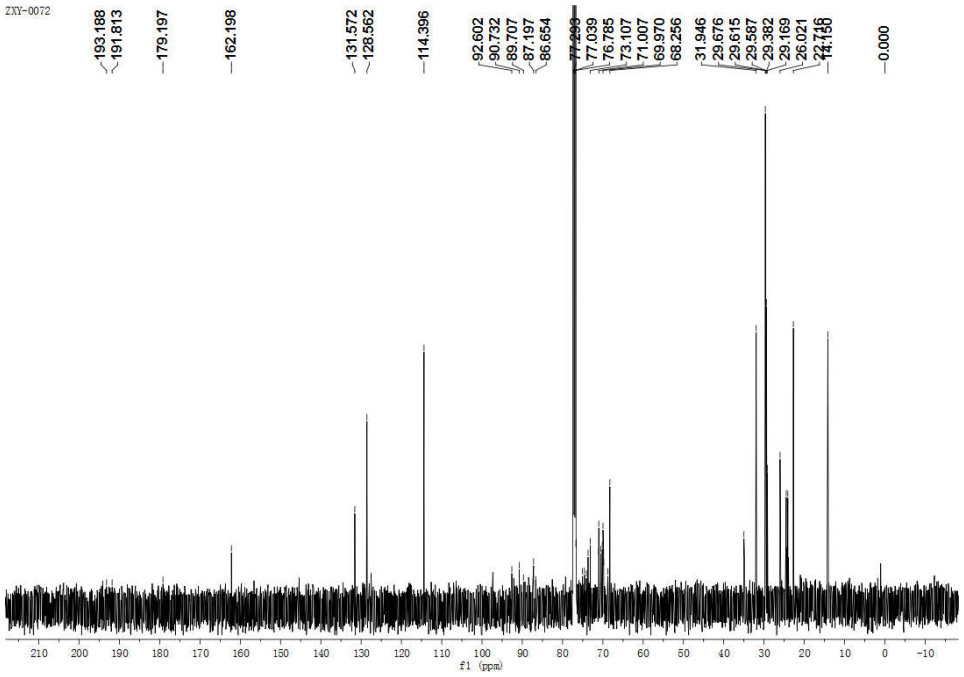

Fig. S21 ^{13}C NMR of compound Fp14

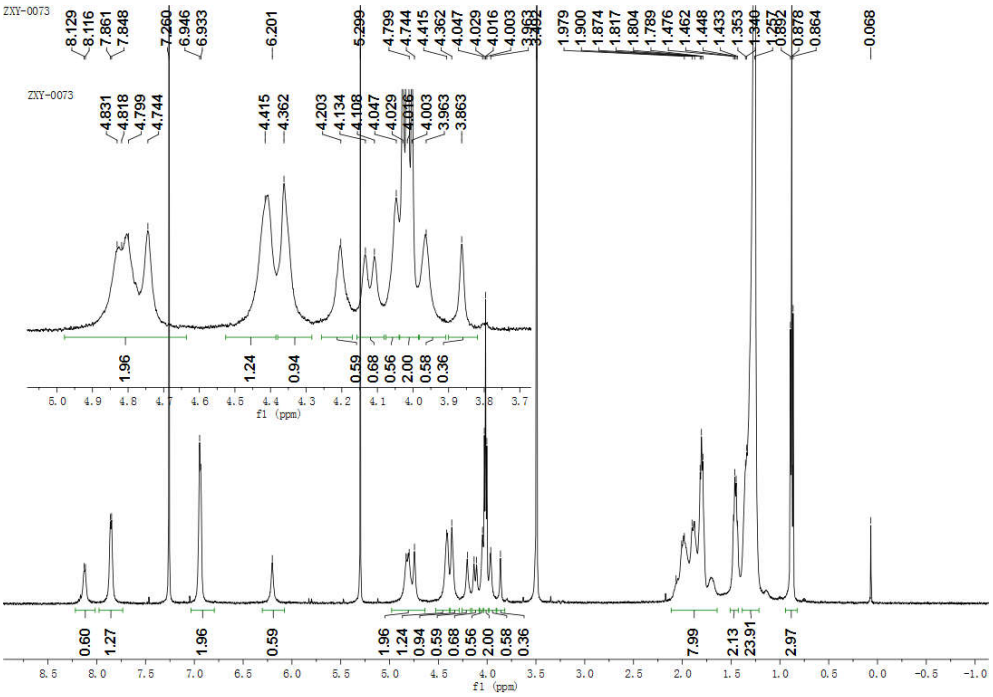

Fig. S22 ^{1}H NMR of compound Fp16

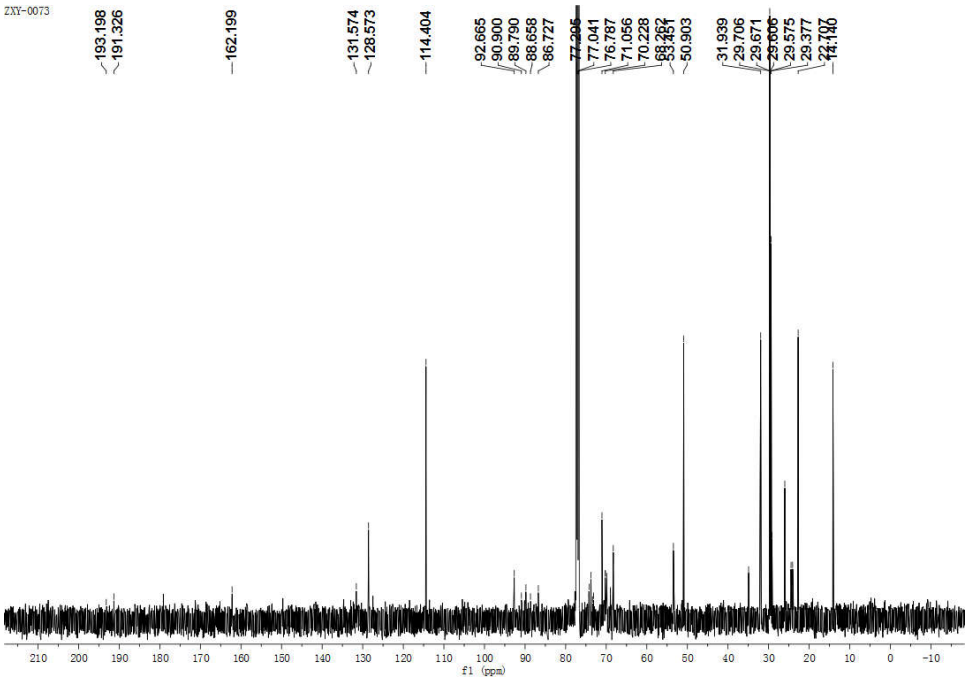

Fig. S23 ^{13}C NMR of compound Fp16

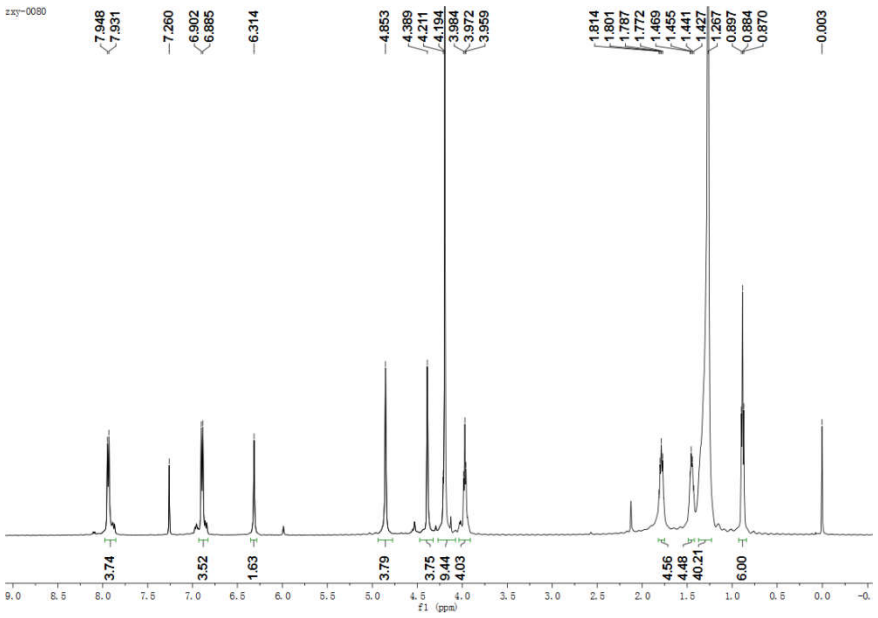

Fig.S24 ^{1}H NMR of compound Fc14Zn

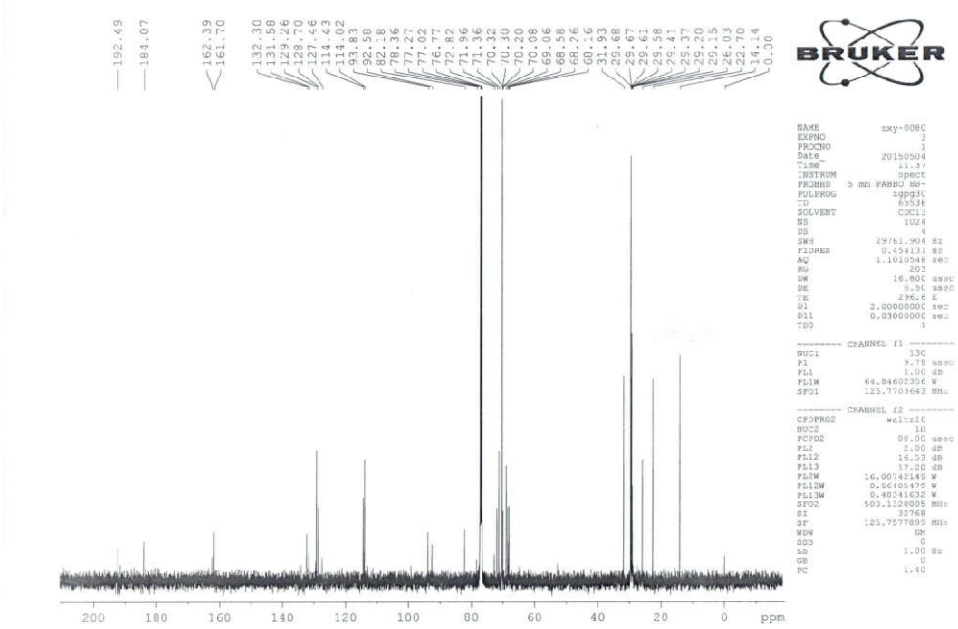

Fig.S25 ^{13}C NMR of compound Fc14Zn

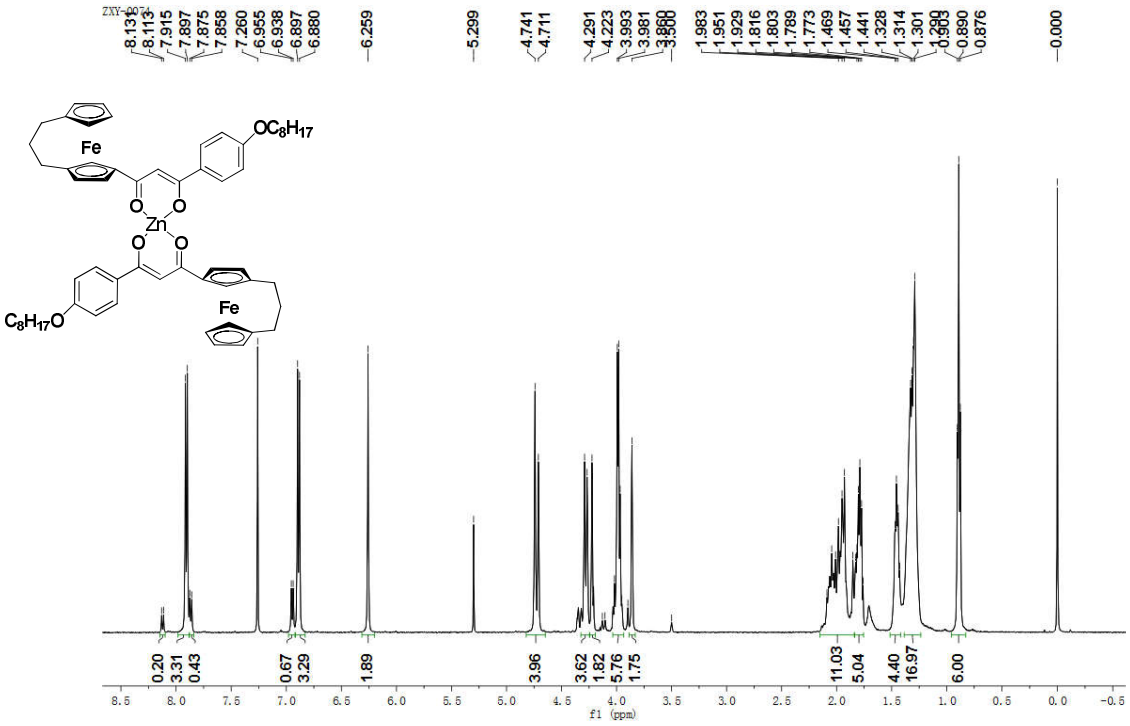

Fig. S26 ^{1}H NMR of compound Fp8Zn

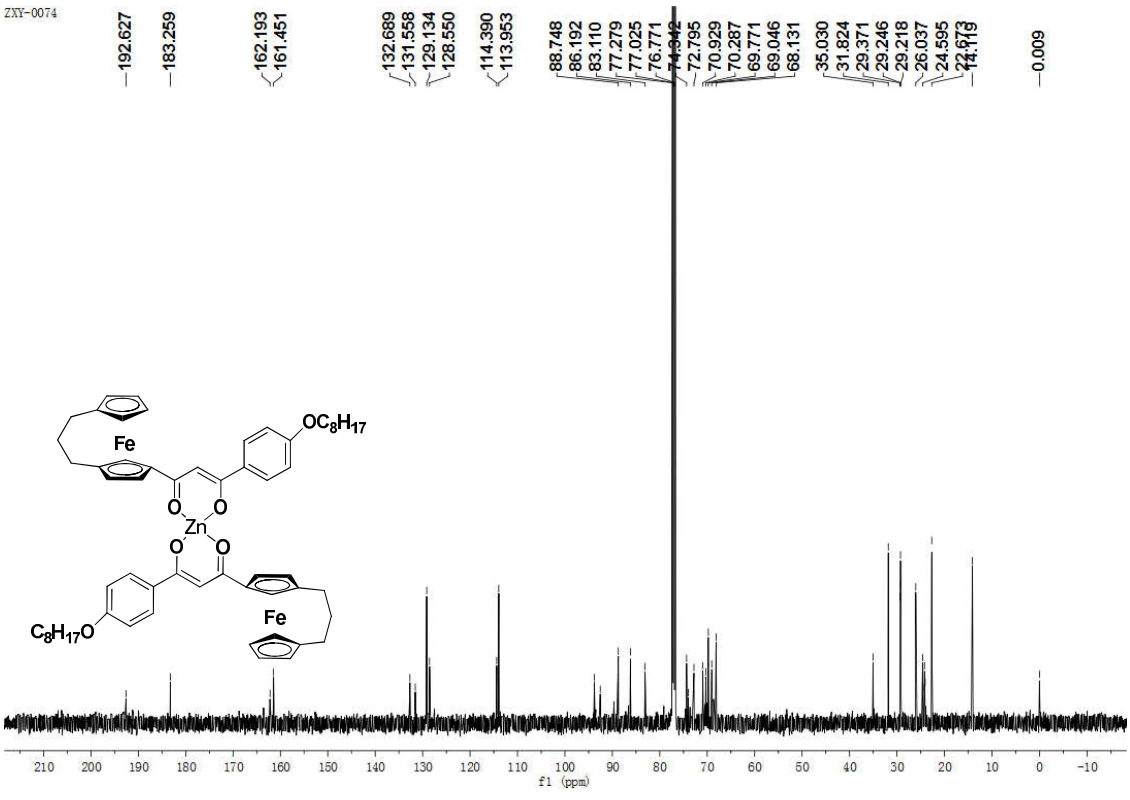

Fig. S27 ^{13}C NMR of compound Fp8Zn

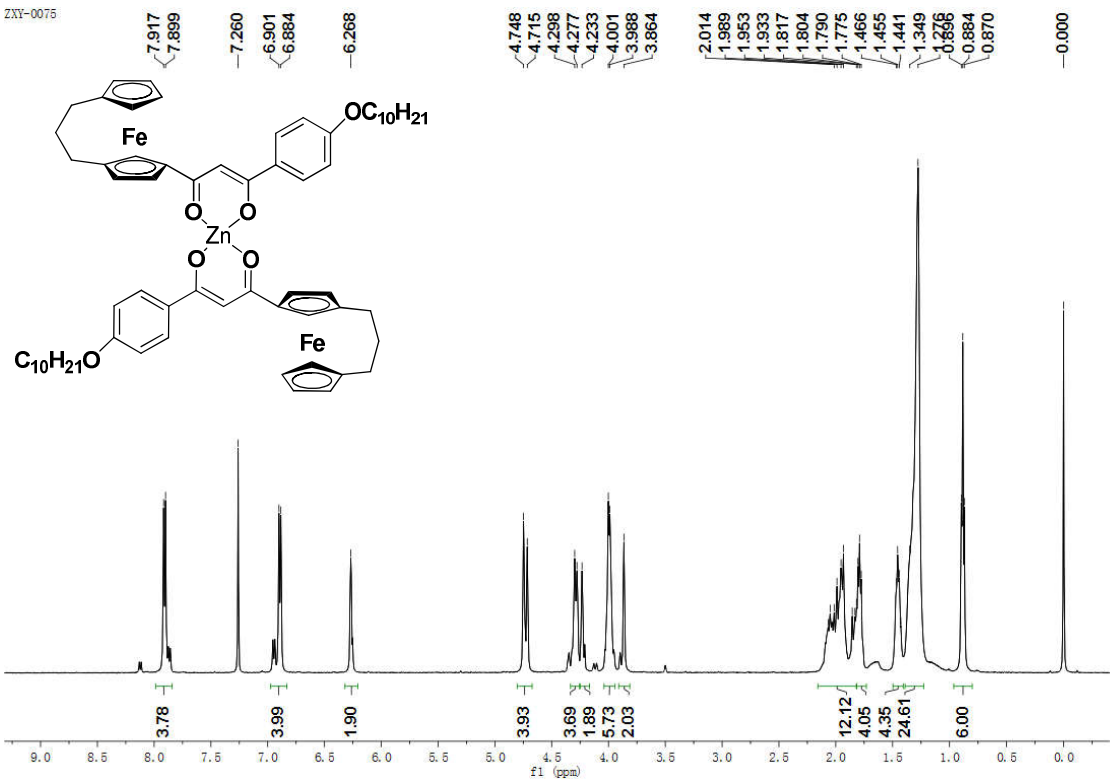

Fig. S28 ^{1}H NMR of compound Fp10Zn

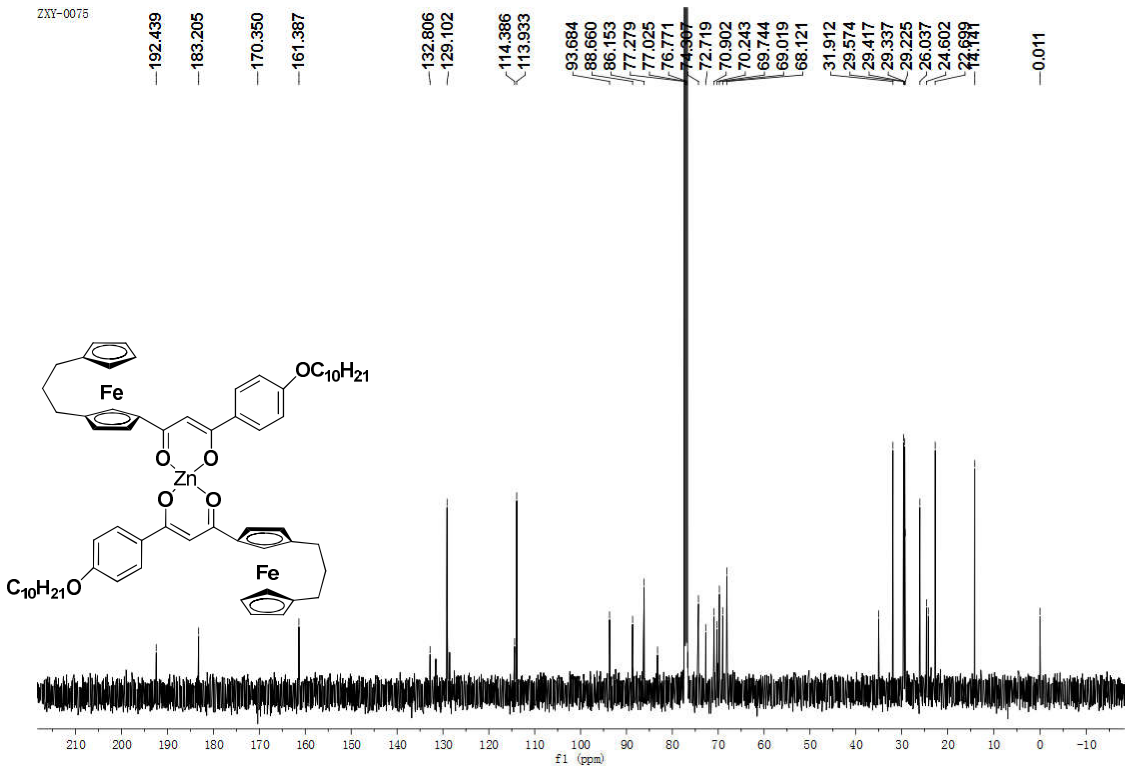

Fig. S29 ^{13}C NMR of compound Fp10Zn

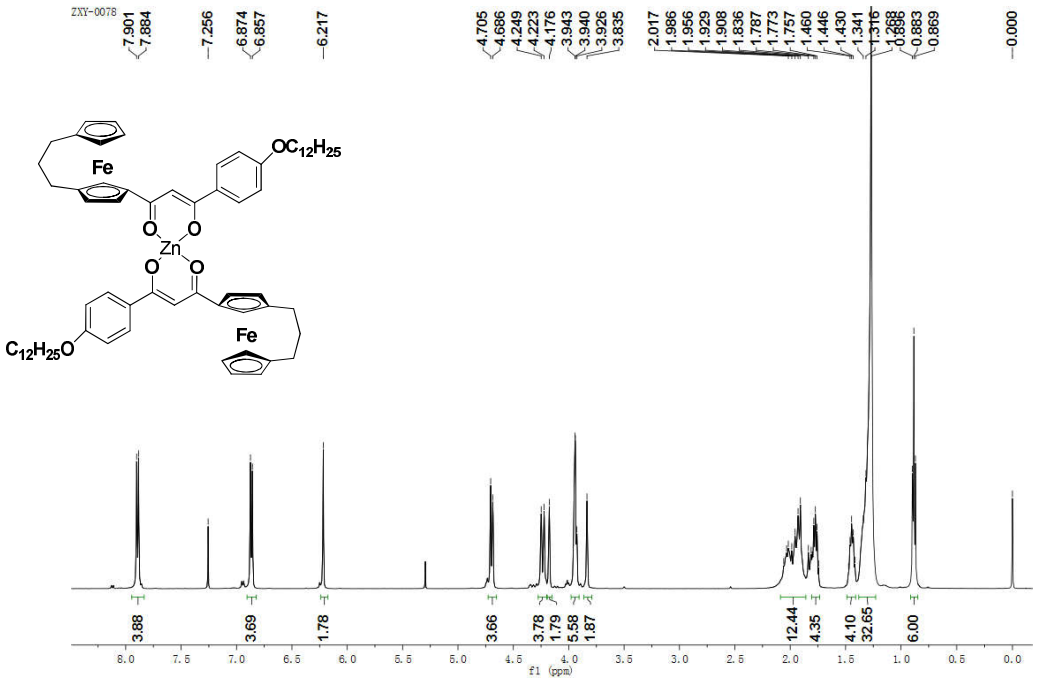

Fig. S30 ^{1}H NMR of compound Fp12Zn

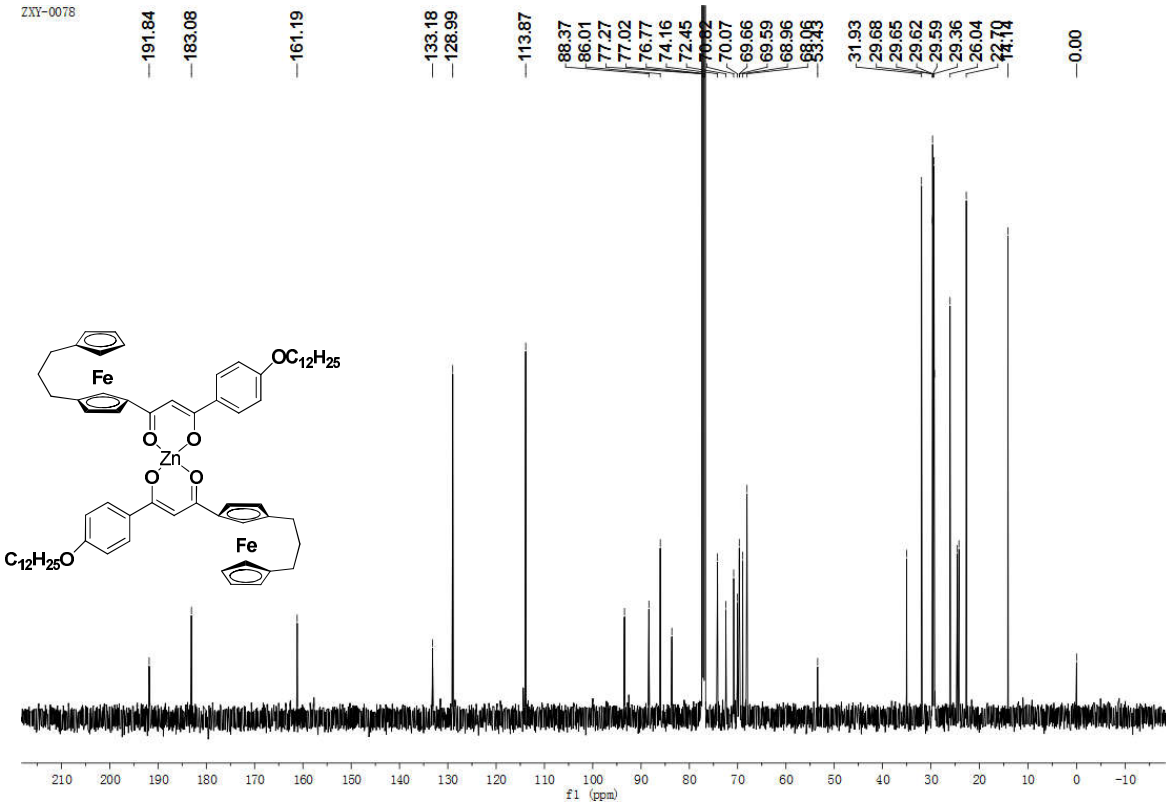

Fig. S31 ^{13}C NMR of compound Fp12Zn

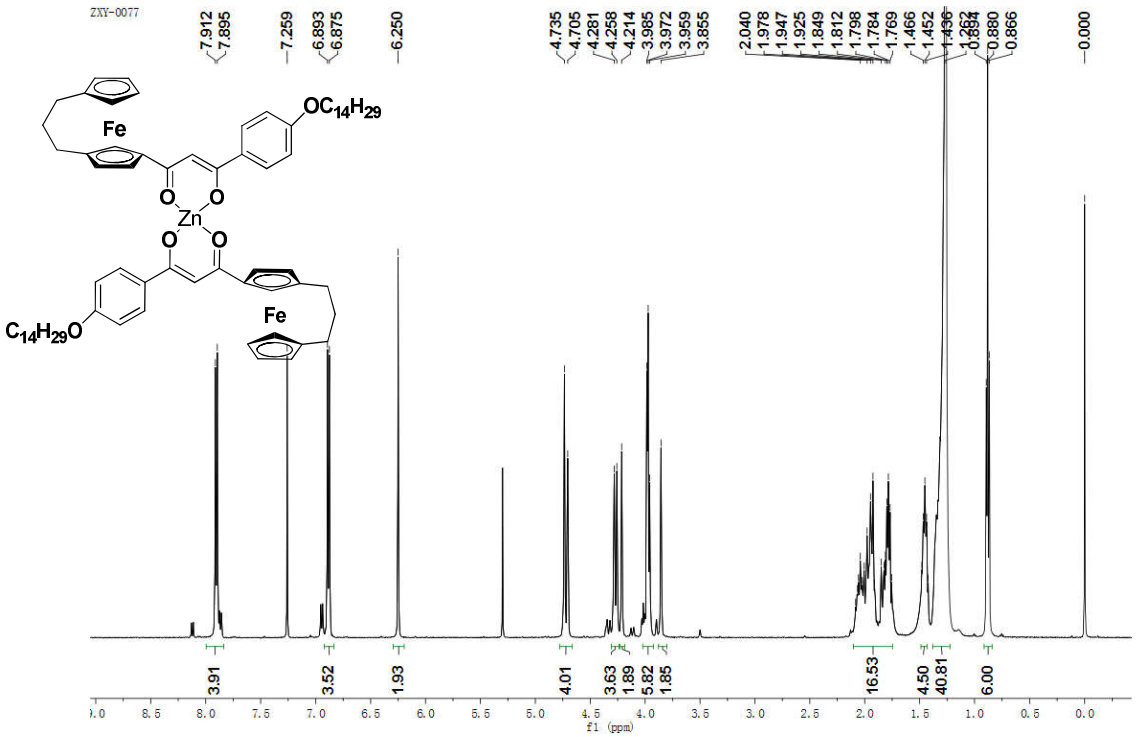

Fig. S32 ^{1}H NMR of compound Fp14Zn

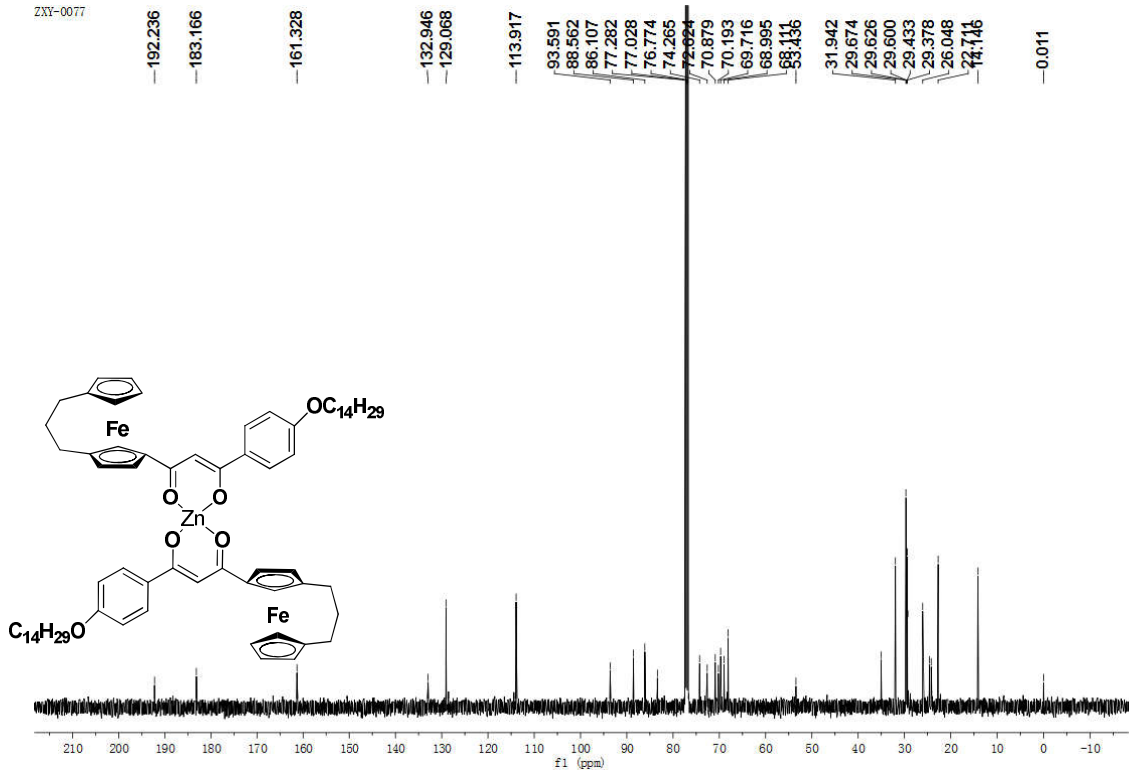

Fig. S33 ^{13}C NMR of compound Fp14Zn

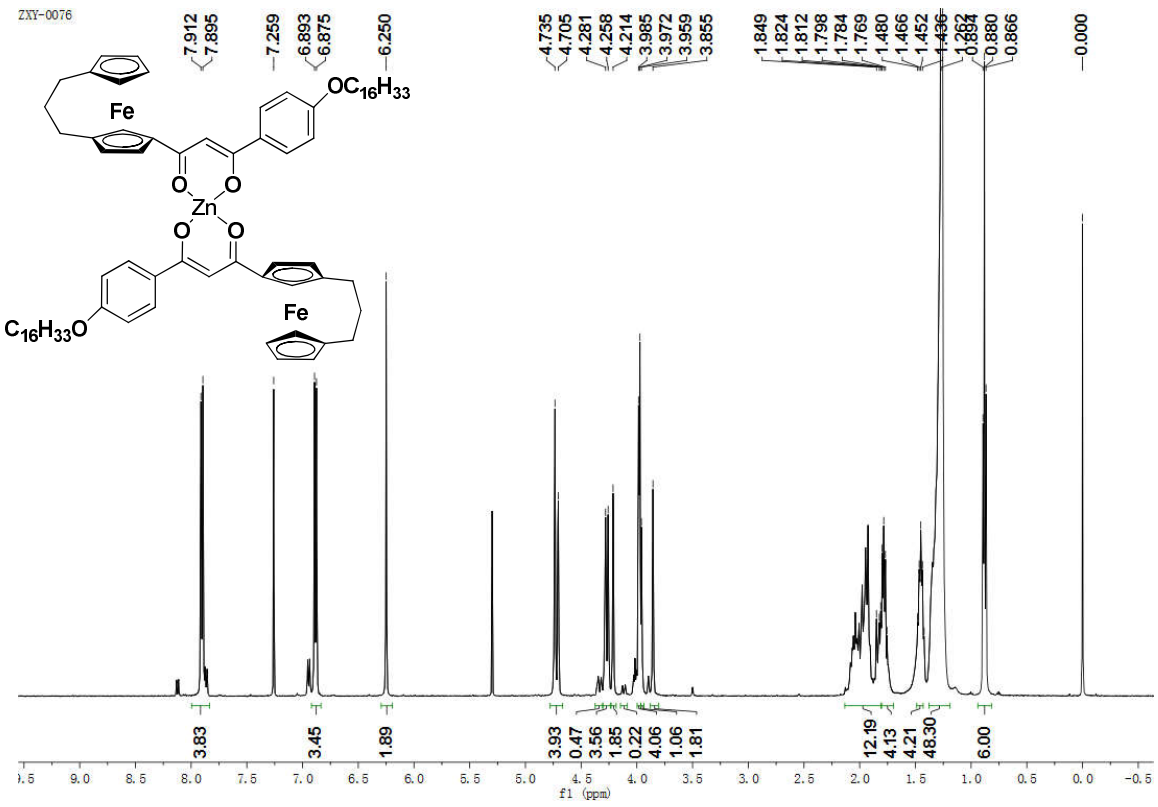

Fig. S34 ^{1}H NMR of compound Fp16Zn

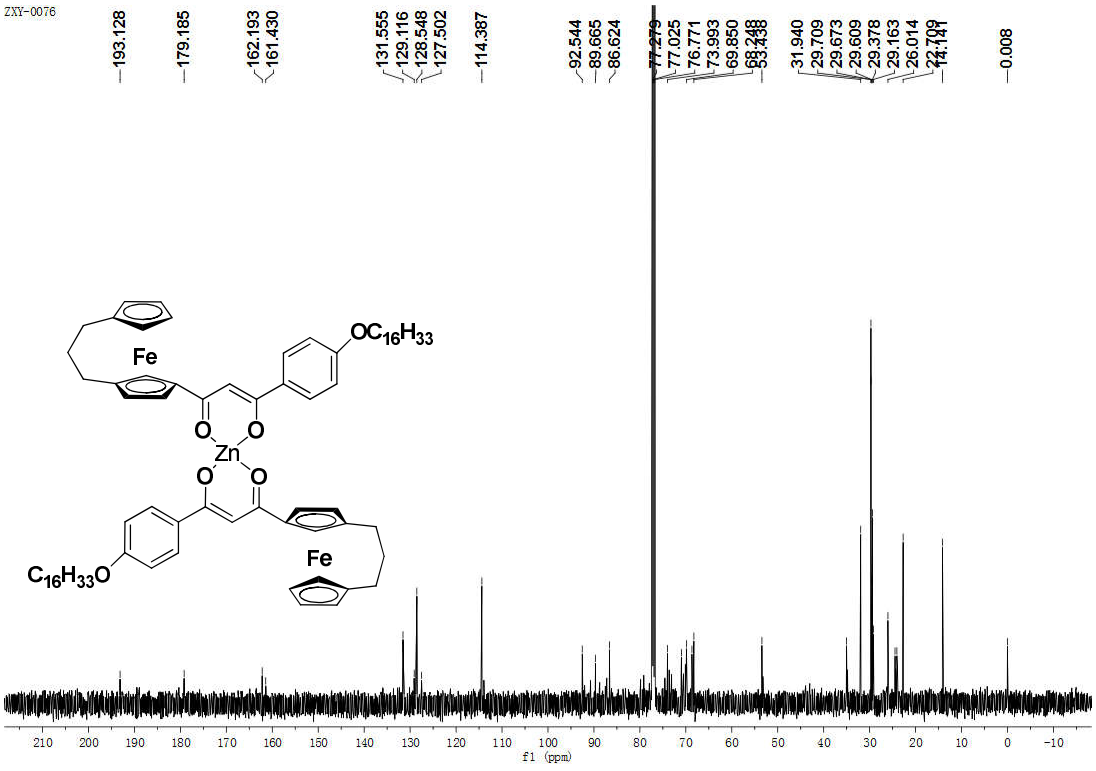

Fig. S35 ^{13}C NMR of compound Fp16Zn