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Supporting Information

New ferrocenyl-containing organic hole-transporting materials for perovskite solar cells in regular (n-i-p) and inverted (p-i-n) architectures

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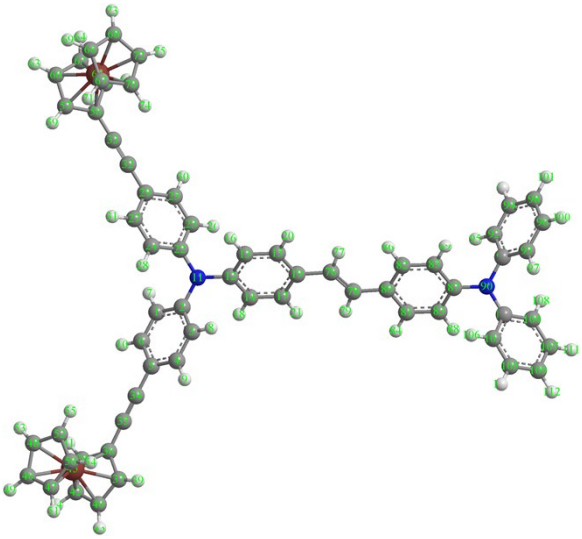
Characterization details for the synthesis of JW6, JW7 and JW8

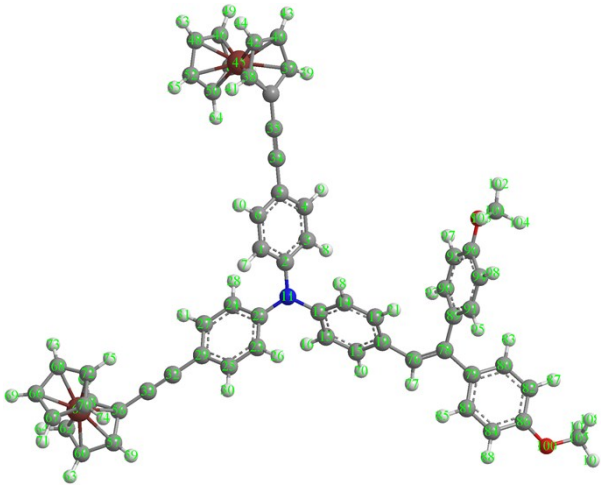
JW6, orange solid (63.2% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.39 (m, 8H), 7.30 (t, *J* = 7.8 Hz, 4H), 7.15 (d, *J* = 7.8 Hz, 4H), 7.12 (s, 2H), 7.08 (d, *J* = 8.6 Hz, 8H), 7.02-6.98 (m, 2H), 4.53 (s, 4H), 4.28 (s, 14H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.58, 146.55, 132.45, 129.92, 129.69, 129.28, 127.24, 124.57, 124.17, 123.72, 123.02, 122.91, 118.12, 87.82, 85.66, 71.34, 69.96, 68.74, 65.59. HRMS (ESI) (m/z): $[M]^+$ calcd. For $C_{62}H_{46}N_2Fe_2$, 931.2360; found: 931.2441.

JW7, orange solid (51.0% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.33 (m, 6H), 7.29 (d, *J* = 8.5 Hz, 4H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 4H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 6.3 Hz, 2H), 6.87 (d, *J* = 6.5 Hz, 2H), 4.51 (s, 4H), 4.27 (s, 14H), 3.87 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.22, 146.53, 144.96, 136.47, 132.40, 131.42, 130.35, 128.65, 125.48, 123.9, 123.72, 118.16, 114.17, 113.62, 87.80, 85.69, 71.34, 69.95, 68.71, 65.66, 55.23. HRMS (ESI) (m/z): $[M]^+$ calcd. For $C_{58}H_{46}NO_2Fe_2$, 900.4129; found: 900.4230.

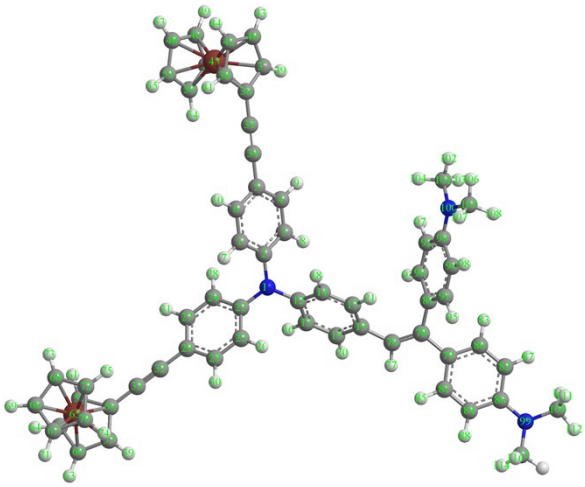
JW8, orange solid (59.3% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.42-7.37 (m, 6H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 4H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.74-6.69 (m, 3H), 4.51 (s, 4H), 4.26 (s, 14H), 3.01 (s, 6H), 2.99 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.61, 144.23, 142.04, 132.34, 131.14, 130.93, 130.15, 128.86, 128.52, 124.17, 123.53, 117.77, 112.38, 112.03, 87.63, 85.73, 71.32, 69.95, 68.71, 65.65, 40.50. HRMS (ESI) (m/z): $[M]^+$ calcd. For $C_{60}H_{51}N_3Fe_2$, 926.2782; found: 926.2863.



JW6



JW7



JW8

Fig.S1. The optimized structures of **JW6**, **JW7** and **JW8**.

Table S1. Representative bond lengths and dihedral angles of optimized structures of **JW6**, **JW7** and **JW8**.

Compounds	Bond lengths (Å)		dihedral angles (°)	
JW6	C(32)-C(29)	1.423	C(23)-C(22)-N(11)-C(12)	40.9
	C(22) -N(11)	1.419	C(78)-C(76)-C(19)C(17)	-5.1
	C(76)-C(19)	1.462	C(91)-N(90)-C(87)-C(85)	-39.2
	N(90)-C(87)	1.417		
JW7	C(34)-C(5)	1.423	C(78)-C(76)-C(19)C(17)	-26.9
	N(11)-C(2)	1.418	C(12)-N(11)-C(2)-C(3)	39.4
	C(76)-C(19)	1.468		
	C(89)-C(78)	1.491		
JW8	C(34)-C(5)	1.423	C(78)-C(76)-C(19)C(17)	-25.2
	N(11)-C(2)	1.416	C(12)-N(11)-C(2)-C(3)	37.9
	C(76)-C(19)	1.467		
	C(89)-C(78)	1.489		

Table S2. The photovoltaic parameters from eight cells of p-i-n type PSCs fabricated by **JW7**.

Cell	V_{OC} / mV	J_{SC} / mA cm^{-2}	*FF*	*PCE* / %
1	8.88	19.30	0.62	10.53
2	833	22.13	0.62	11.43
3	895	17.78	0.63	10.03
4	940	18.56	0.63	11.00
5	1050	18.07	0.53	10.06
6	852	18.30	0.63	9.82
7	810	20.66	0.59	9.87
8	907	19.49	0.56	9.90

Table S3. The photovoltaic parameters of hysteresis test for p-i-n type PSCs with various HTMs.

HTMs		V_{OC} / mV	J_{SC} / mA cm^{-2}	*FF*	*PCE* / %
JW6	Forward	850	19.73	0.61	10.23
	Reverse	1010	19.20	0.53	10.24
JW7	Forward	833	22.13	0.62	11.43
	Reverse	960	20.12	0.53	10.21
JW8	Forward	820	20.17	0.63	10.42
	Reverse	944	19.33	0.50	9.06
PEDOT	Forward	867	22.26	0.69	12.86
	Reverse	860	22.30	0.69	13.27

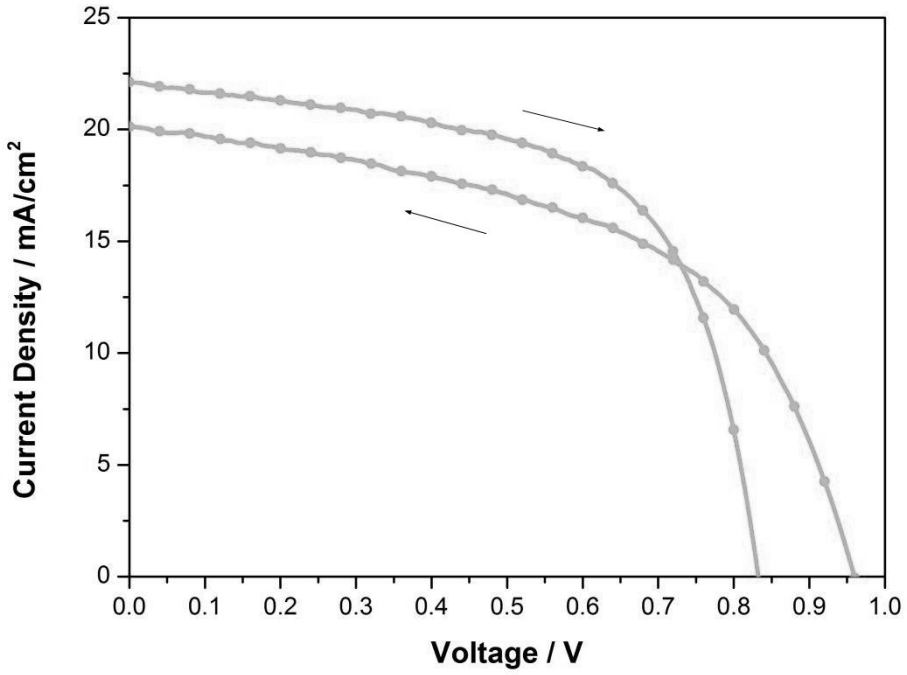
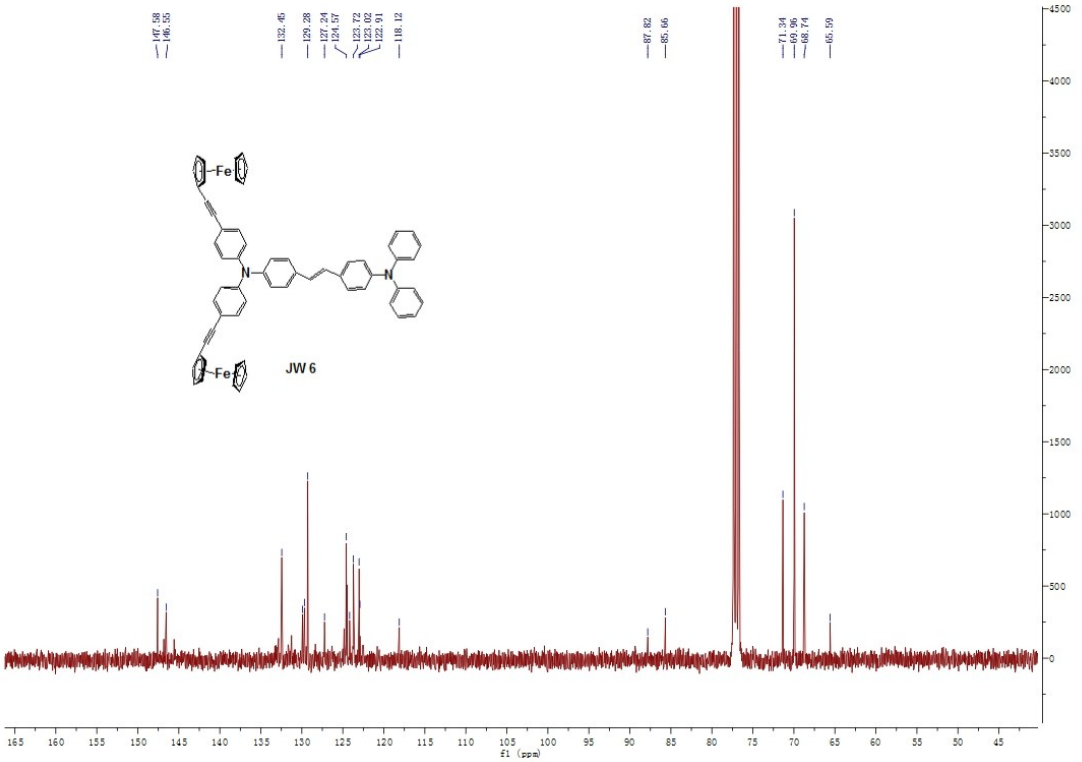
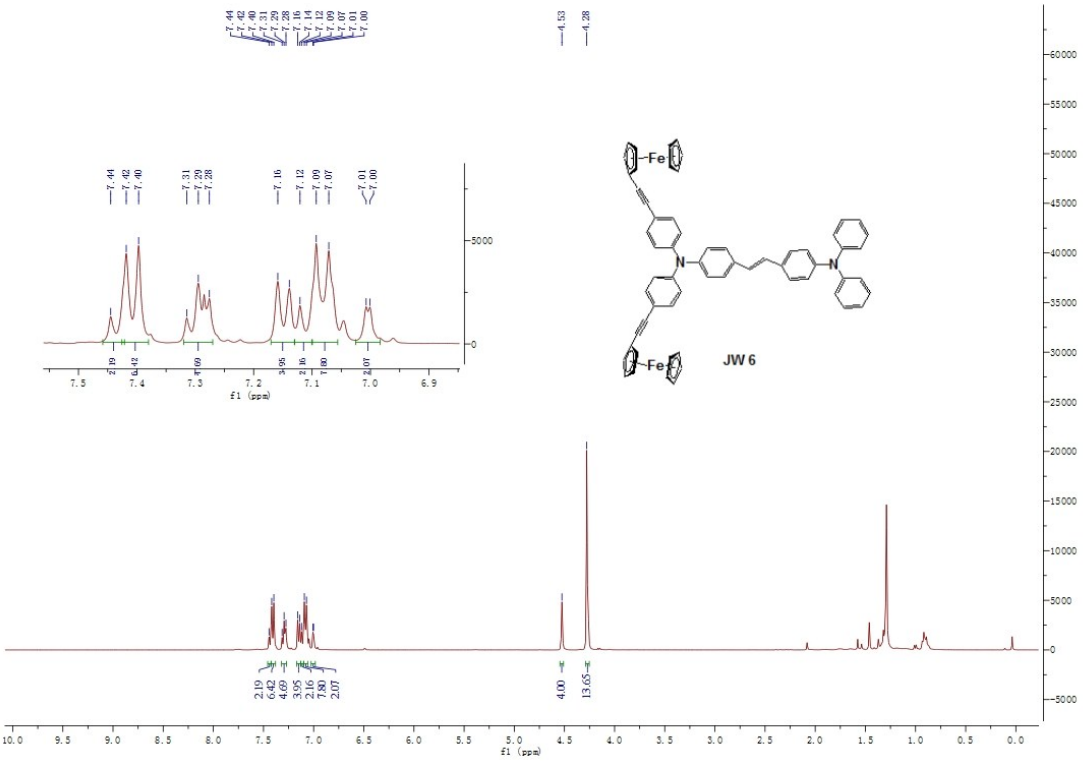


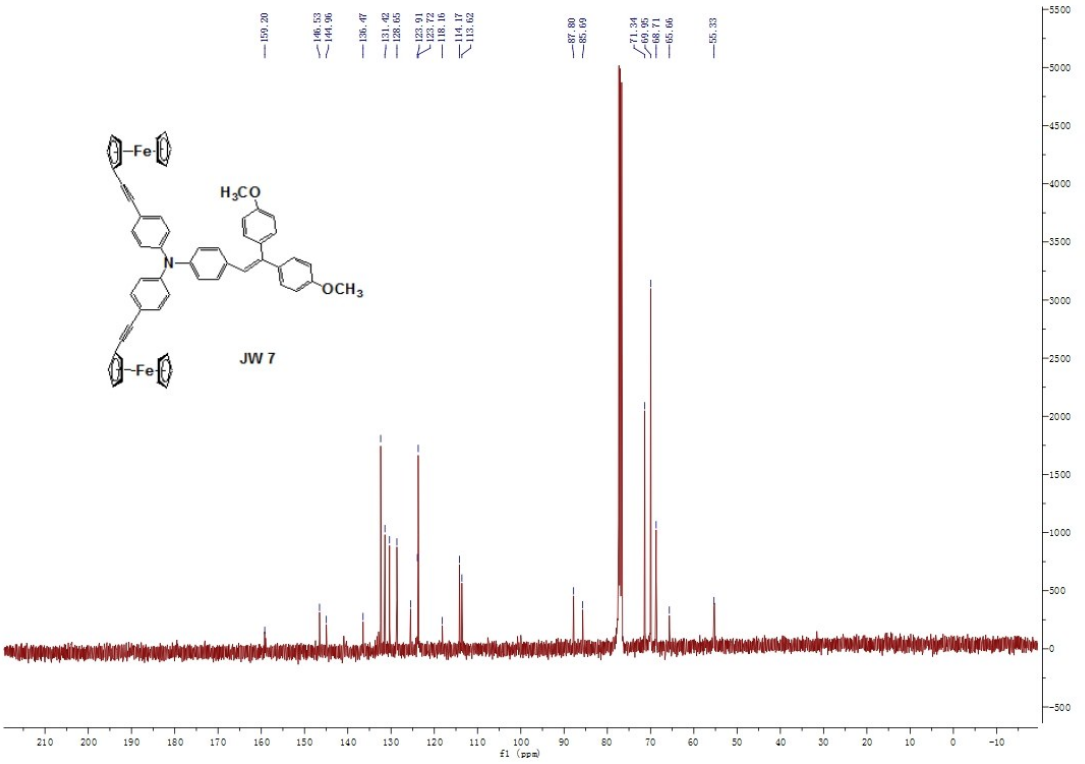
Fig. S2. J-V plots of p-i-n type PSCs based on **JW7** measured through reverse and forward bias at a scan rate of 0.1V/s.



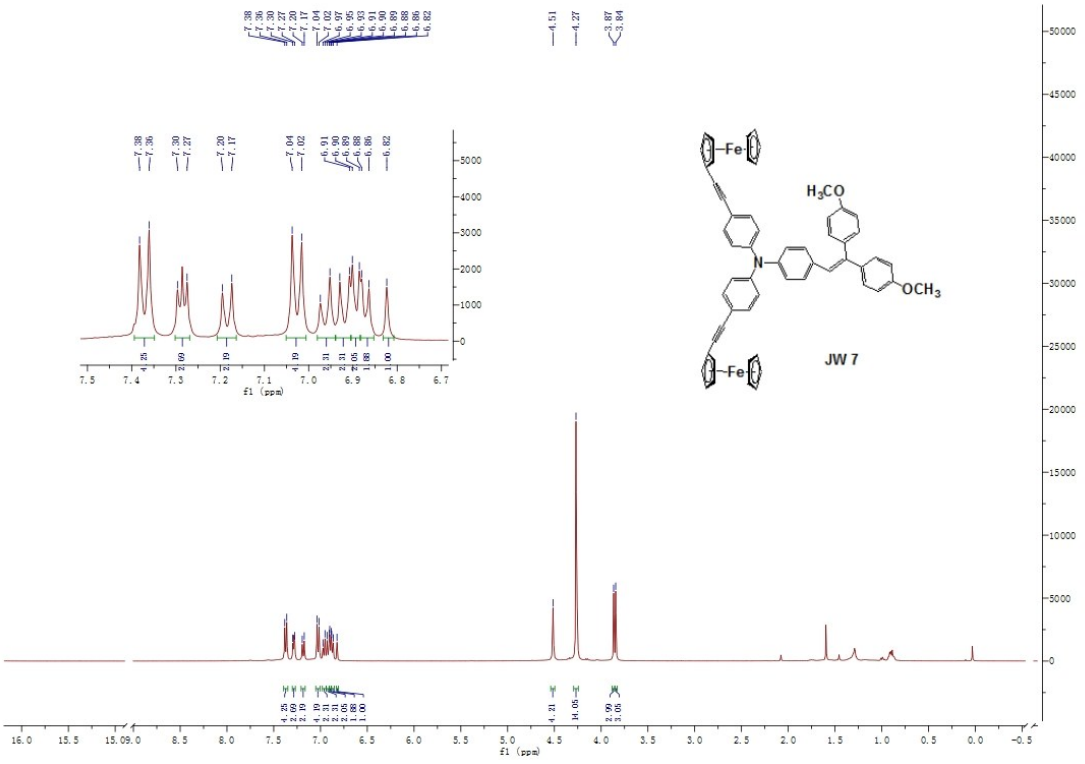
^{1}H NMR spectra of **JW6**



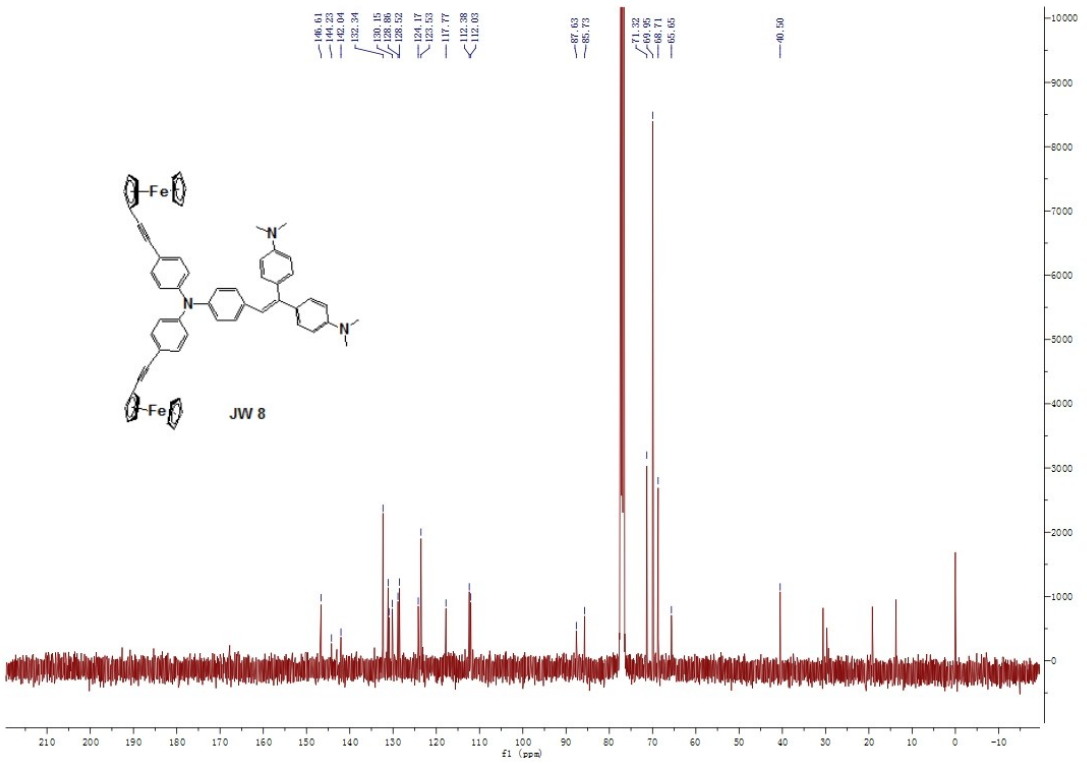
^{13}C NMR spectra of **JW6**



^{1}H NMR spectra of **JW7**



^{13}C NMR spectra of **JW7**



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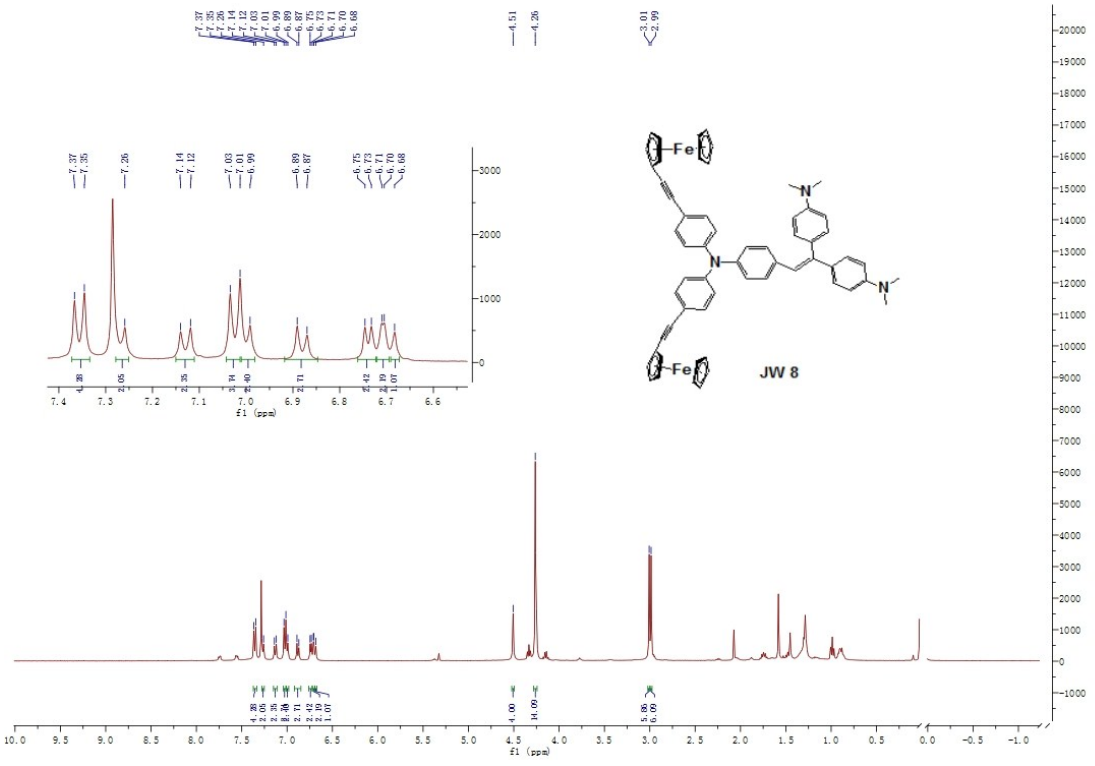

^{13}C NMR spectra of **JW8**