Electronic Supplementary Information

A new azobenzene liquid crystal involving chalcone and ester linkages

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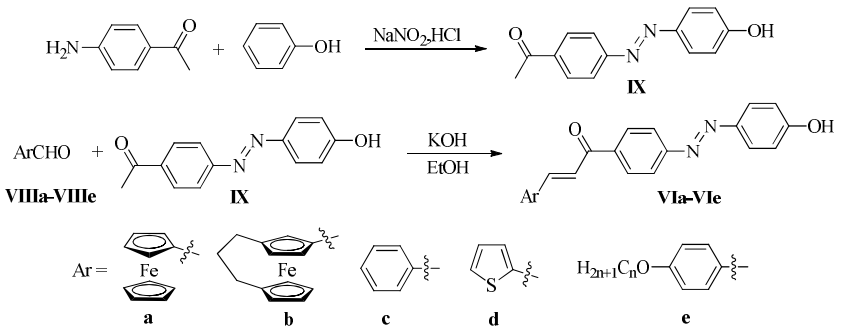

Scheme S1 Synthesis of compounds **VIa-VIe**

1-(4-((4-hydroxyphenyl)diazenyl)phenyl)ethanone **IX**: To 10 mmol of *p*-acetylphenylamine, 2.7 mL of concentrated hydrochloric acid and 20 mL of water were added. The mixture was placed in the ice bath. To the cooled mixture, a solution of 10 mmol of sodium nitrite in 3 mL of water was added dropwise and the resulting solution was stirred at a temperature between 0 and 5 ºC within 15 min. Subsequently, the solution containing 10 mmol of phenol in 6 mL of methanol was added dropwise. The reaction was stirred for 30 min and was neutralized with sodium acetate. After the temperature was raised to room temperature, the mixture was stirred for 1 h. The product was filtered, washed with large amount of water and dried under vacuum. Yield 80%, m.p. 191-192 ºC, R_f = 0.16 (petroleum ether:ethyl acetate = 5:1); ^{1}H NMR (500 MHz, DMSO) (δ ppm): 10.46 (s, 1H, OH), 8.13 (d, J = 8.5 Hz, 2H, C_6H_4), 7.91 (d, J = 8.5 Hz, 2H, C_6H_4), 7.86 (d, J = 9.0 Hz, 2H, C_6H_4), 6.97 (d, J = 9.0 Hz, 2H, C_6H_4), 2.64 (s, 3H, CH_3).

Aromatic aldehyde **IIIV** (0.1 mol) and **IX** (0.12 mol) were dissolved in 5 mL of anhydrous ethanol, to which the solution of KOH (0.4 g, 7.14 mmol) in 1 mL of H_2O was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 4 h, and then neutralized with dilute HC1. The aqueous phase was extracted with EtOAc, and the combined organic phases were washed with H_2O, 5% $NaHCO_3$ solution and H_2O, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was subjected to flash silica gel column chromatography with benzene / EtOAc (40:1, V:V) as eluent. The second fraction was the desired product **VI**.

VIa: yield 63%, m.p. 204-206 ºC, R_f = 0.43 (benzene:ethyl acetate = 10:1); ^{1}H NMR (500 MHz, DMSO) (δ ppm): 10.49 (s, 1H, OH), 8.25 (d, J = 7.0 Hz, 2H,C_6H_4), 7.94 (d, J = 7.0 Hz, 2H, C_6H_4), 7.88 (d, J = 7.0 Hz, 2H, C_6H_4), 7.73 (d, J = 15.0 Hz, 1H, CH), 7.51 (d, J = 15.0 Hz, 1H, CH), 6.98 (d, J = 7.0 Hz, 2H, C_6H_4), 4.90 (s, 2H, FcH), 4.59 (s, 2H, FcH), 4.22 (s, 5H, FcH).

VIb: yield 61.8%, m.p. 185-187 ºC, R_f = 0.39 (Benzene:Ethyl acetate = 10:1); ^{1}H NMR (500 MHz, DMSO) (δ

ppm): 10.48 (s, 1H, OH), 8.20 (d, *J* = 8.5 Hz, 2H, C_6H_4), 7.92 (d, *J* = 8.5 Hz, 2H, C_6H_4), 7.87 (d, *J* = 9.0 Hz, 2H, C_6H_4), 7.62 (d, *J* = 15.0 Hz, 1H, CH), 7.38 (d, *J* = 15.0 Hz, 1H, CH), 6.98 (d, *J* = 8.8 Hz, 2H, C_6H_4), 4.81 (s, 1H, FcH), 4.69 (s, 1H, FcH), 4.46 (s, 1H, FcH), 4.34 (s, 1H, FcH), 4.30 (s, 1H, FcH), 3.97 (s, 1H, FcH), 3.88 (s, 1H, FcH), 2.14 – 1.85 (m, 6H, CH_2).

VIc: yield 66%, m.p. 192-198 ºC, R_f = 0.167 (benzene:ethyl acetate = 40:1); ^{1}H NMR (500 MHz, DMSO) (δ ppm): 10.56 (s, 1H, OH), 8.41 (d, *J* = 8.5 Hz, 2H, C_6H_4), 8.09 (d, *J* = 15.5 Hz, 1H, CH), 8.04 – 7.96 (m, 4H C_6H_4, C_6H_5), 7.96 – 7.92 (m, 2H, C_6H_4), 7.86 (d, *J* = 15.5 Hz, 1H, CH), 7.57 – 7.52 (m, 3H, C_6H_5), 7.07 – 7.01 (m, 2H, C_6H_4).

VId: yield 65%, m.p. 203-208 ºC, R_f = 0.42 (benzene:ethyl acetate = 20:1); ^{1}H NMR (500 MHz, DMSO) (δ ppm): 10.49 (s, 1H, OH), 8.28 (d, *J* = 8.5 Hz, 2H, C_6H_4), 7.97 (d, *J* = 15.5 Hz, 1H, CH), 7.94 (d, *J* = 8.5 Hz, 2H, C_6H_4), 7.87 (d, *J* = 8.5 Hz, 2H, C_6H_4), 7.82 (d, *J* = 5.1 Hz, 1H, TpH), 7.74 (d, *J* = 4.0 Hz, 1H, TpH), 7.63 (d, *J* = 15.5 Hz, 1H, CH), 7.22 (m, 1H, TpH), 6.98 (d, *J* = 8.5 Hz, 2H, C_6H_4).

VIe-8: yield 55% ，m.p.159~160℃，R_f =0.32（Ethyl acetate: Petroleum ether =1：4）, ^{1}H NMR (500 MHz, DMSO) δ 10.50 (s, 1H), 8.32 (d, *J* = 8.5 Hz, 2H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.87 (t, *J* =9.0 Hz, 5H), 7.77 (d, *J* = 15.5 Hz, 1H), 7.00 (t, *J* = 9.5 Hz, 4H), 4.01 (t, *J* = 6.5 Hz, 2H), 1.75 ~ 1.66 (m, 2H), 1.43 ~ 1.35 (m, 2H), 1.29~1.25 (m, 8H), 0.86 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 188.66, 162.22, 161.43, 154.87, 145.88, 144.86, 139.17, 131.40, 130.22, 127.59, 125.84, 122.72, 119.78, 116.56, 115.30, 68.17, 40.16, 39.99, 39.83, 39.66, 39.49, 31.72, 29.32, 29.15, 29.07, 25.96, 22.56, 14.42.HRMS, m/z: Calcd for $C_{29}H_{32}N_2O_3$: 455.2329 $[M-H]^-$ found: 455.2340.

VIe-10, Yield 55% m.p.153~154℃，R_f =0.35（Ethyl acetate: Petroleum ether =1：4），^{1}H NMR (500 MHz, DMSO) δ 10.41 (s, 1H), 8.12 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.89 ~ 7.75 (m, 5H), 7.71 (d, *J* = 15.5 Hz, 1H), 4.02 (t, J = 6.5 Hz, 2H), 1.73 ~ 1.68(m, 2H), 1.40 (d, *J* = 7.5 Hz , 2H), 1.29~1.20 (m, 17H), 0.88 (t, *J* = 6.7 Hz .3H). HRMS, m/z: Calcd for $C_{31}H_{36}N_2O_3$:483.2642 $[M-H]^-$ found: 483.2641.

VIe-12, yield 55%，m.p. 149~150 ℃，R_f=0.36（Ethyl acetate: Petroleum ether =1：4）^{1}H NMR (500 MHz, DMSO) δ 10.49 (s, 1H), 8.32 (d, *J* = 8.5 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.90 ~ 7.85 (m, 5H), 7.76 (d, *J* = 15.5Hz, 1H), 4.04 (t, *J* = 6.5 Hz , 2H), 1.75 ~ 1.70 (m, 2H), 1.41(d ,*J* = 7.5 Hz , 2H), 1.32~1.25 (m, 17H), 0.85 (t, *J* = 6.5 Hz . 3H). HRMS, m/z: Calcd for $C_{33}H_{40}N_2O_3$: 511.2955 $[M-H]^-$ found: 511.2943.

VIe-14, yield 55%，m.p.148~149℃，R_f =0.38（Ethyl acetate: Petroleum ether =1：4），^{1}H NMR (500 MHz, DMSO) δ 10.56 (s, 1H), 8.39 (d, *J* = 8.5 Hz, 2H), 8.01 (d, *J* = 8.5 Hz, 2H), 7.98 ~ 7.88 (m, 5H), 7.83 (d, *J* = 15.5 Hz, 1H), 7.08 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 4.10 (t, *J* = 6.5 Hz, 2H), 1.78 (dd, *J* = 14.5, 6.8 Hz, 2H), 1.47 (d, *J* = 7.5 Hz, 2H), 1.41 ~ 1.27 (m, 20H), 0.91 (t, *J* = 7.0 Hz, 3H). HRMS, m/z: Calcd for $C_{35}H_{44}N_2O_3$: 539.3268 $[M-H]^-$ found: 539.3218.

Table S1 UV-vis absorption data of selected compounds in CH_2Cl_2.

Compd.	Absorption λ_{max} / nm (log ε / L cm^{-1} mol^{-1})		
Ia-8	261 (5.45)	347 (5.67)	523 (4.65)
Ib-8	261 (5.45)	346 (5.66)	535 (4.82)
Ic-8	263 (5.47)	345 (5.73)	-
Id-8	266 (5.41)	358 (5.70)	-
IIc-8	266 (4.44)	357 (4.51)	-
IId-8	282 (2.30)	357 (4.65)	-
III-8	266 (4.44)	356 (4.51)	-
IV-8	262 (4.42)	357 (4.67)	-
V	259 (4.71)	350 (4.69)	-

Table S2 Phase transition temperatures and associated enthalpies of compounds **I-III**.

Compd.	Phase transitions[a] °C (ΔH/kJ mol^{-1})		
	First heating	Second heating	First cooling
Ia-8	C_1 162.3 (11.2) C_2 187.8 (38.2) I	C_1 163.7 (-7.6) C_2 187.9 (39.7) I	I 167.2 (-30.9) C
Ia-10	C 183.6 (74.4) I	C_1 128.1 (-4.2) C_2 170.8 (27.8) I	I 147.4 (-4.0) C_2 139.8 (-4.8) C_1
Ia-12	C_1 105.8 (26.9) C_2 165.4 (6.1) C_3 175.6 (27.4) I	C_1 107.9 (1.4) C_2 173.5 (34.0) I	I 162.8 (-36.8) C_2 98.0 (-1.6) C_1
Ia-14	C_1 101.8 (4.7) C_2 126.7 (20.3) C_3 168.7 (28.3) I	C_1 105.2 (4.1) C_2 165.3 (9.2) C_3 172.5 (2.5) I	I 160.1 (-26.6) C_2 97.5 (-5.5) C_1
Ia-16	C_1 106.5 (15.3) C_2 174.9 (41.8) I	C_1 108.7 (5.6) C_2 168.7 (27.1) I	I 158.4 (28.5) C_2 102.4 (6.9) C_1
Ib-8	C_1 149.3 (38.2) C_2 154.3 (1.5) I	C 143.5 (36.3) I	I 80.4 (-6.2) Tg
Ib-12	C_1 99.6 (9.5) C_2 149.1 (44.2) I	C_1 108.9 (-5.5) C_2 148.1 (39.8) I	I 108.8 (-30.5) C
IIc-8	C 73.46 (35.1) I	C 113.89 (13.8) I	I 7.78 (-12.4) C
IIc-14	C_1 53.81 (7.1) C_2 72.68 (65.7) I	C_1 17.13 (11.6) C_2 68.09 (22.1) C_3 73.10 (41.7) I	I 57.25 (-60.6) C_1 11.02 (-10.5) C_2
IId-8	C_1 94.07 (50.6) I	C_1 26.12 (14.9) C_2 46.53 (-32.5) C_3 98.08 (49.4) I	I 20.82 (-15.7) C_1
III-8	C_1 135.24 (20.6) C_2 184.84 (45.1) I	C 185.03(42.3) I	171.02 (43.6) C
III-14	C_1 105.56 (14.7) C_2 136.22 (11.0) C_3 168.87 (35.2) C_4 173.58 (10.7) I	C_1 148.34 (2.5) C_2 170.09 (44.2) I	I 165.73(-42.6) C_1 147.49 (-2.0) C_2

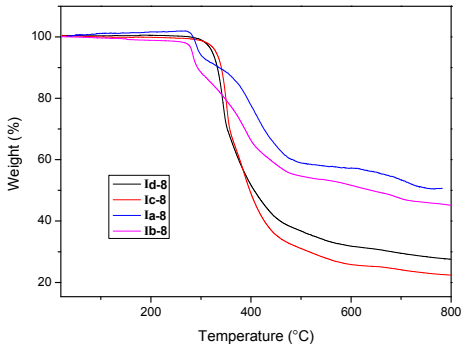

Fig. S1 TG curves of **Ia-Id**

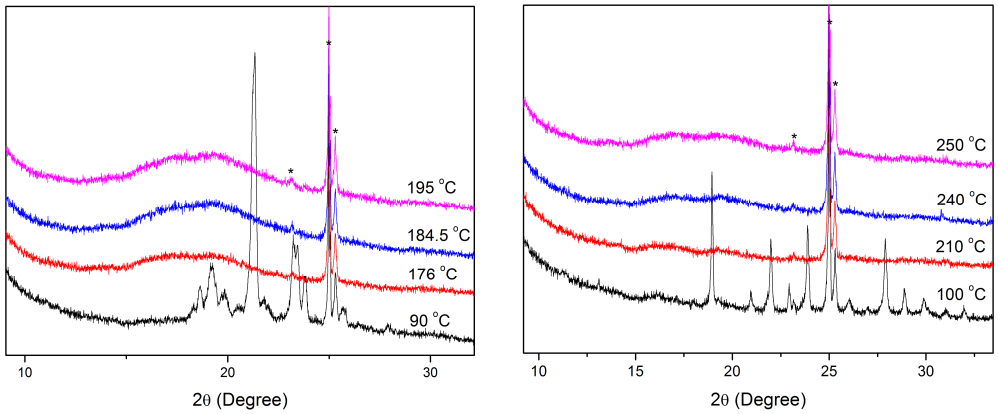

Fig. S2 XRD patterns of compound **IV-10** (left) and **V** (right) on cooling. Asterisks in the spectrum show the alumina from the sample cell holder.

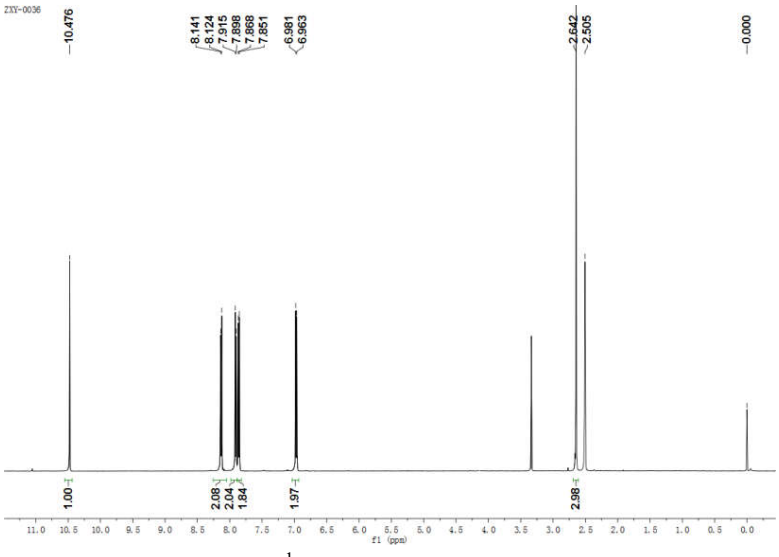

Fig. S3 ^{1}H NMR of compound **IX**

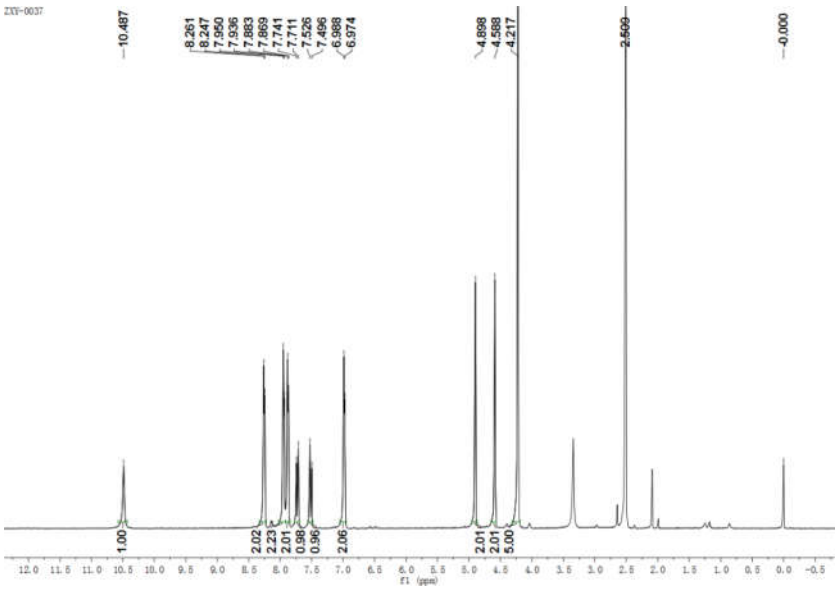

Fig. S4 ^{1}H NMR of compound **VIa**

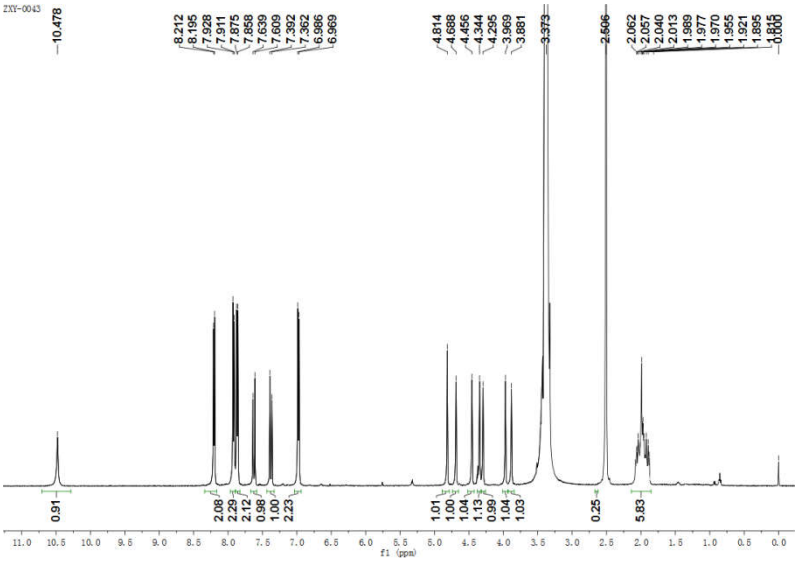

Fig. S5 ^{1}H NMR of compound **VIb**

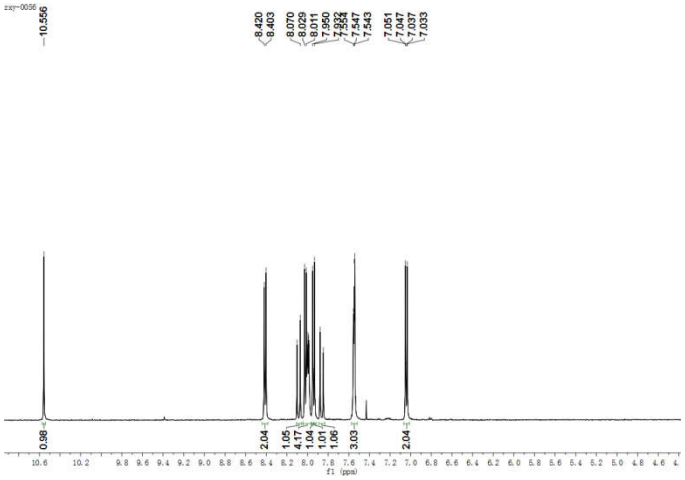

Fig. S6 ^{1}H NMR of compound **VIc**

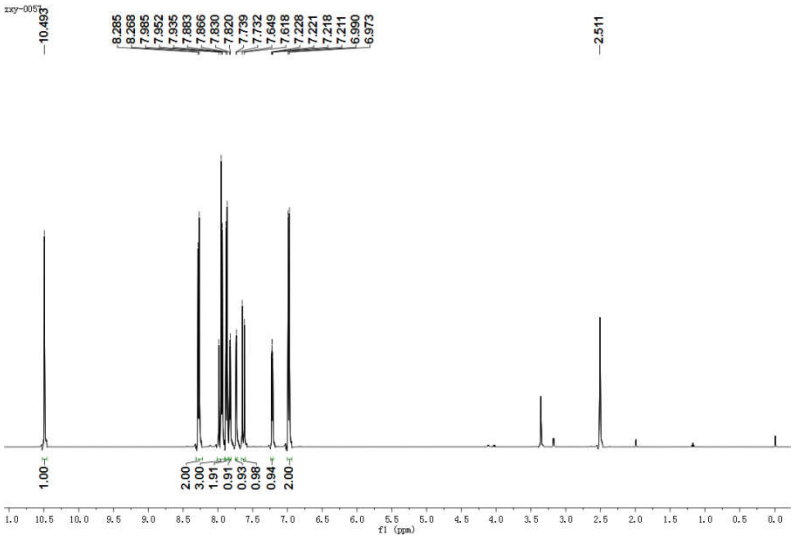

Fig. S7 ^{1}H NMR of compound **VId**

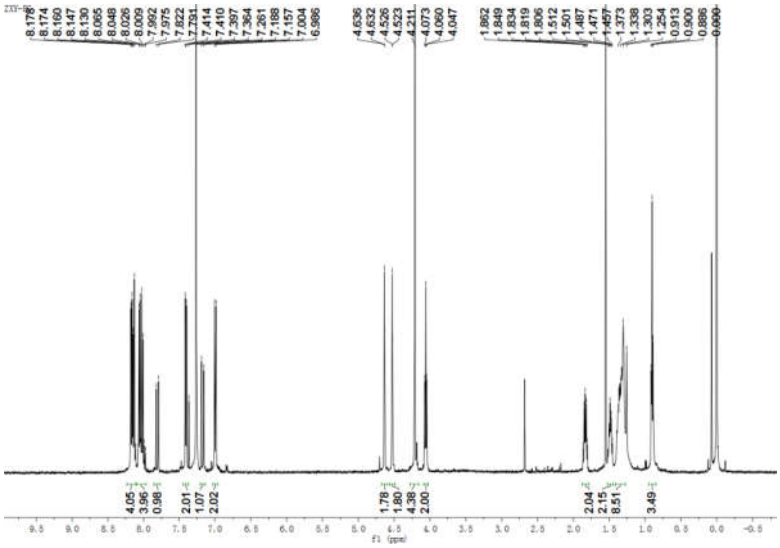

Fig. S8 ^{1}H NMR of compound **Ia-8**

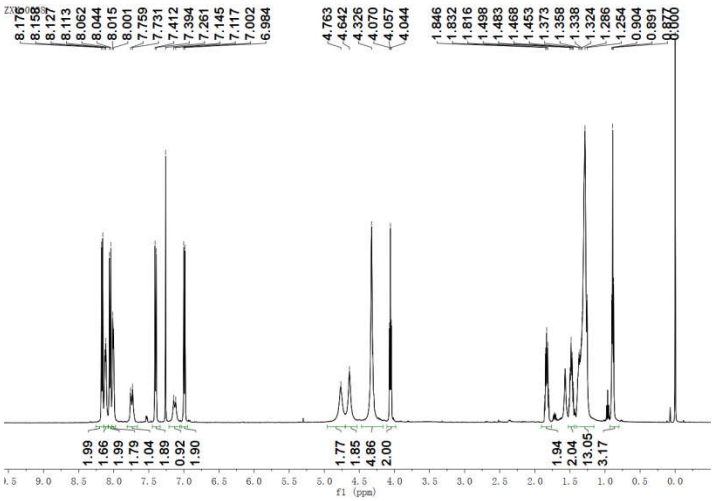

Fig. S9 ^{1}H NMR of compound **Ia-10**

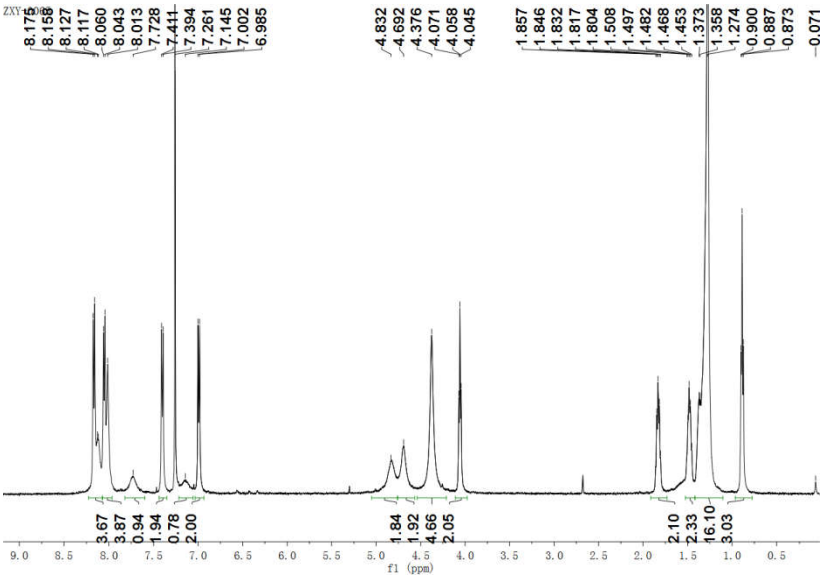

Fig. S10 ^{1}H NMR of compound **Ia-12**

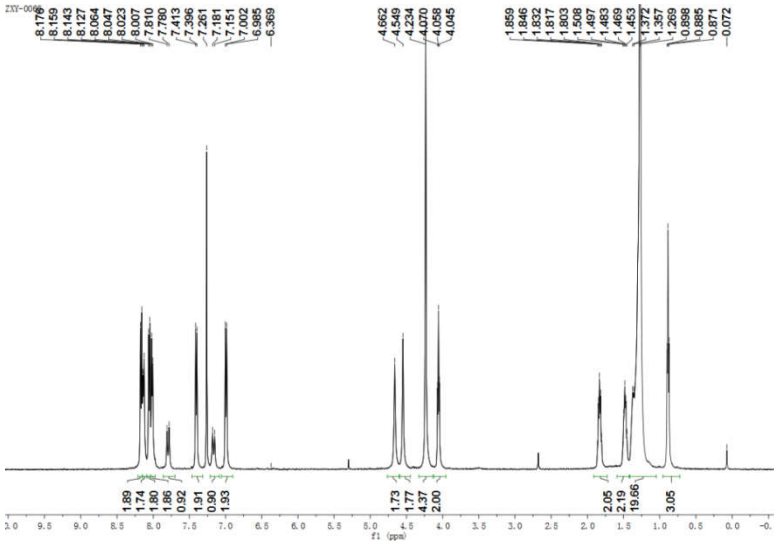

Fig. S11 ^{1}H NMR of compound **Ia-14**

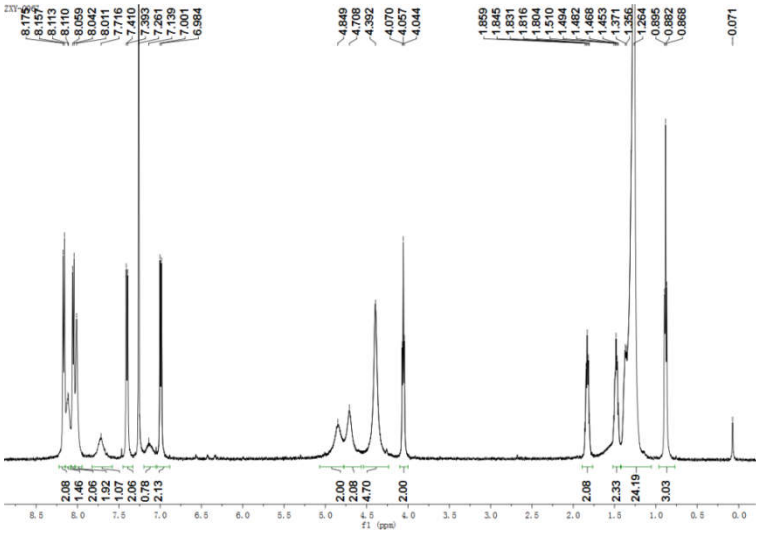

Fig. S12 ^{1}H NMR of compound **Ia-16**

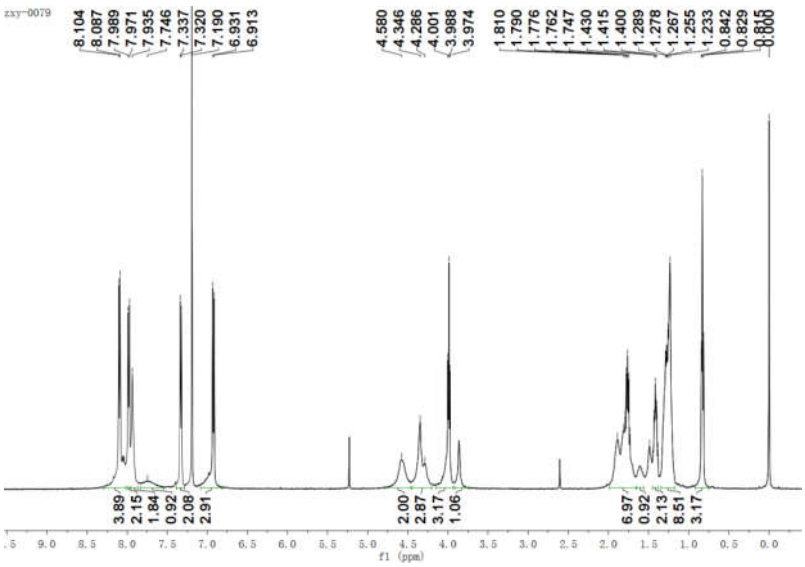

Fig. S13 ^{1}H NMR of compound **Ib-8**

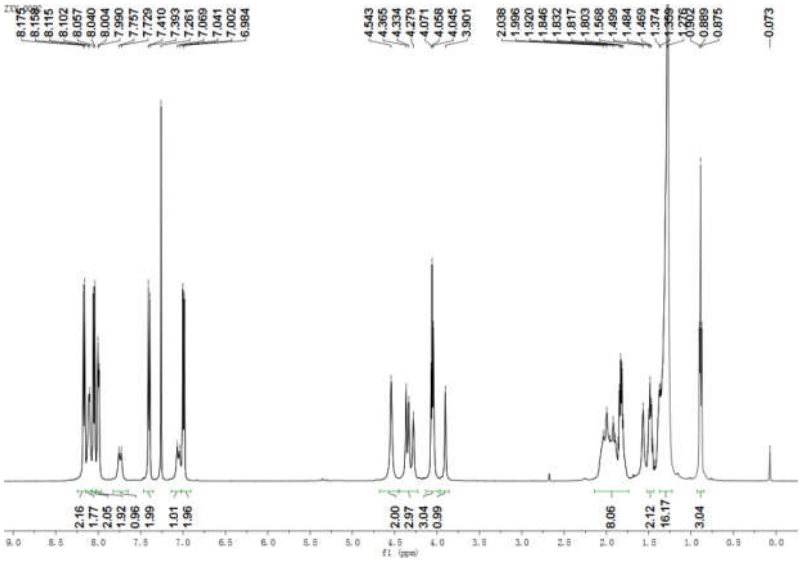

Fig. S14 ^{1}H NMR of compound **Ib-12**

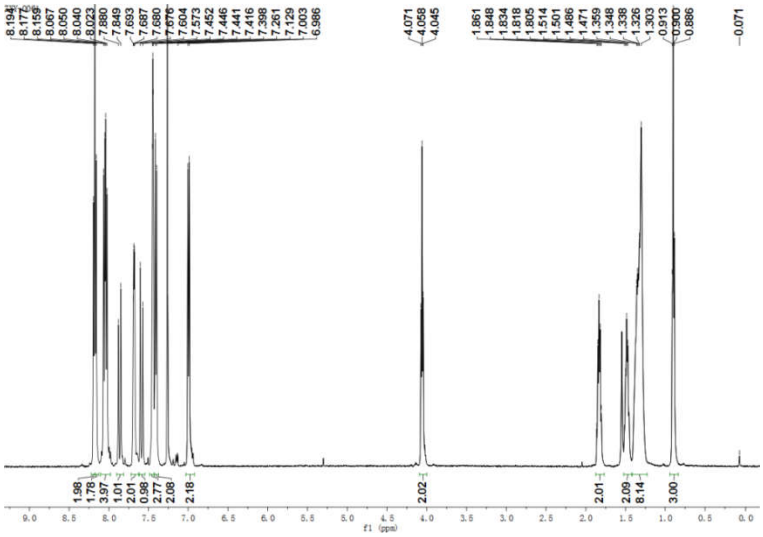

Fig. S15 ^{1}H NMR of compound **Ic-8**

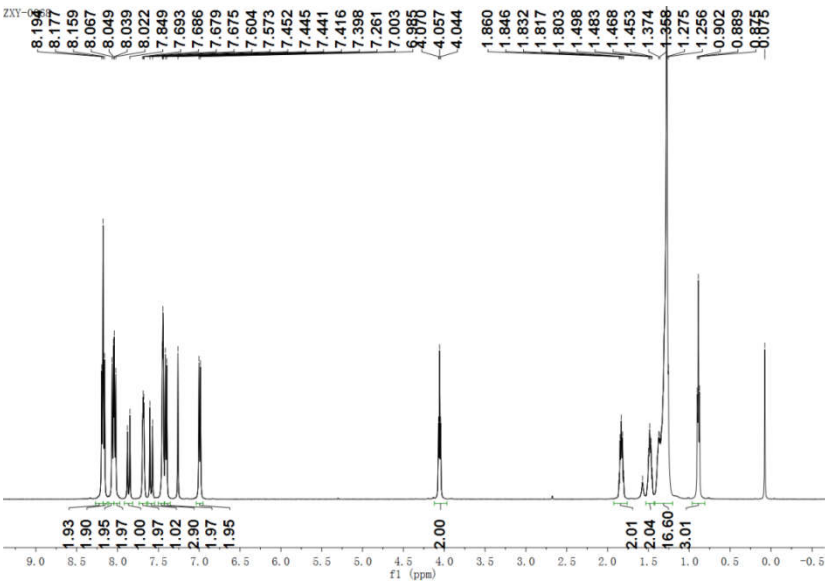

Fig. S16 ^{1}H NMR of compound **Ic-12**

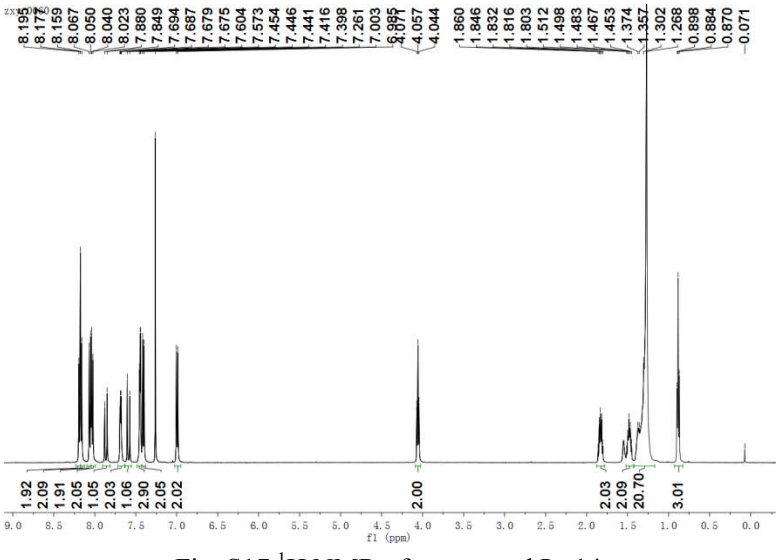

Fig. S17 ^{1}H NMR of compound **Ic-14**

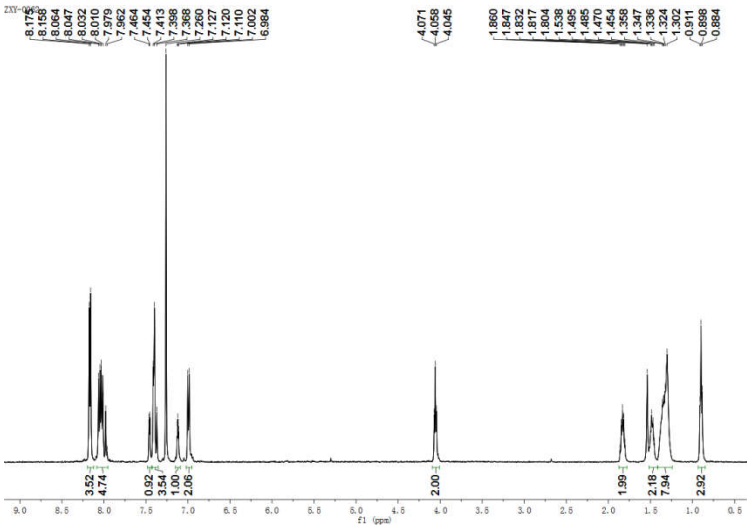

Fig. S18 ^{1}H NMR of compound **Id-8**

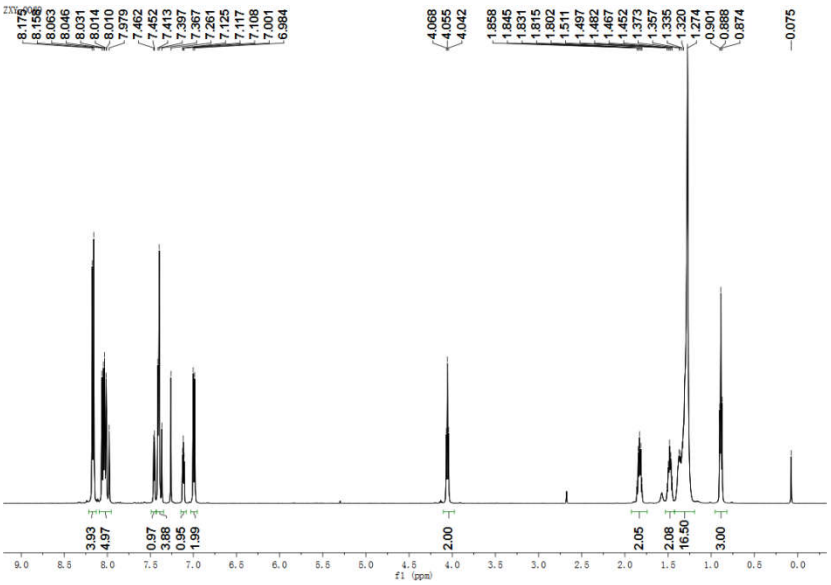

Fig. S19 ^{1}H NMR of compound **Id-12**

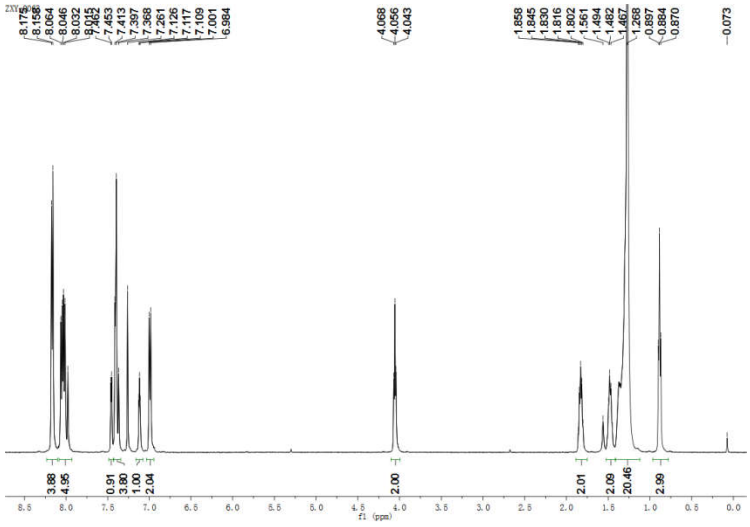

Fig. S20 ^{1}H NMR of compound **Id-14**

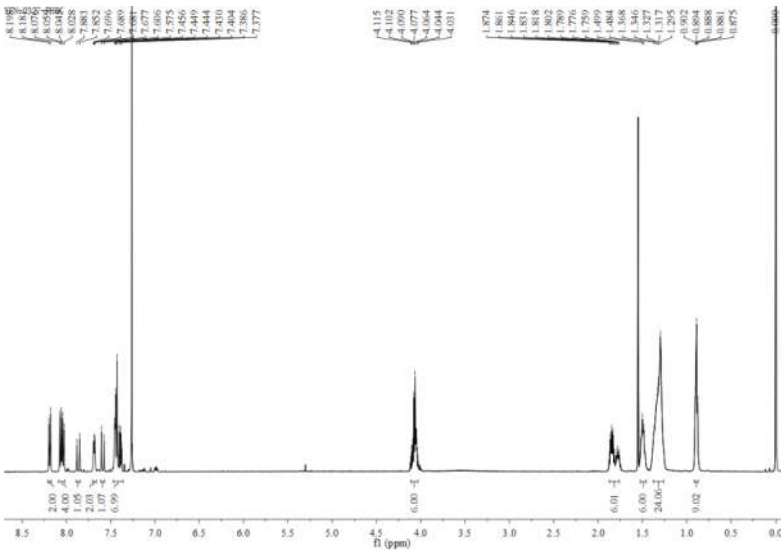

Fig. S21 ^{1}H NMR of compound **IIc-8**

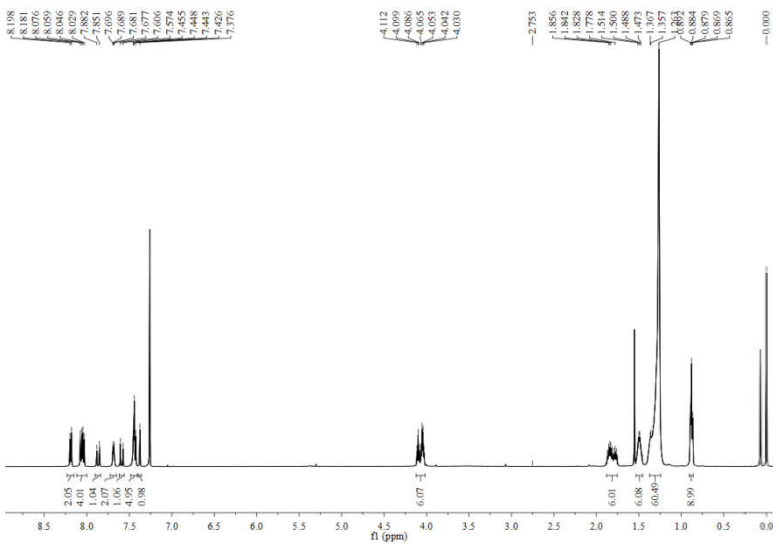

Fig. S22 ^{1}H NMR of compound **IIc-14**

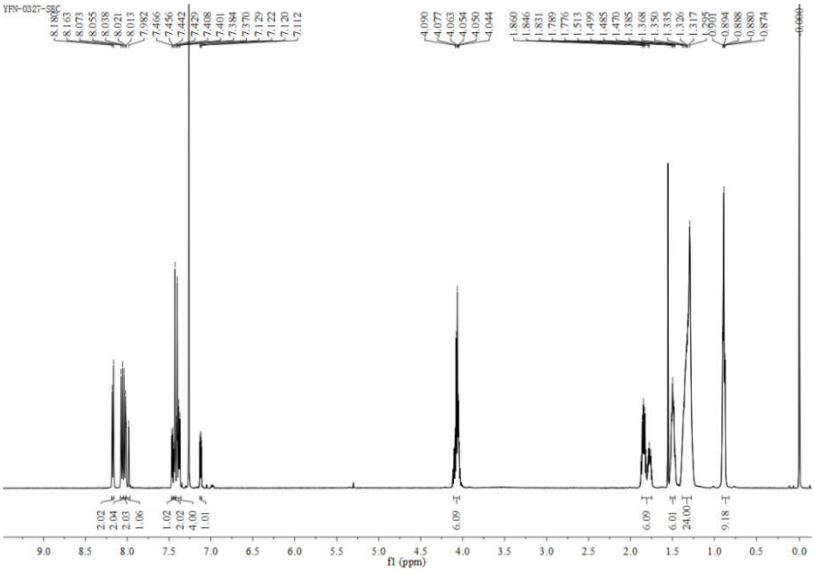

Fig. S23 ^{1}H NMR of compound **IId-8**

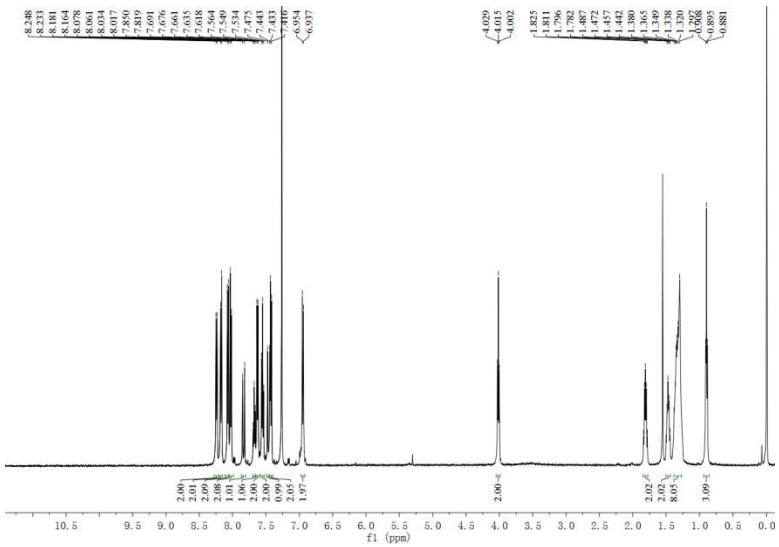

Fig. S24 ^{1}H NMR of compound **III-8**

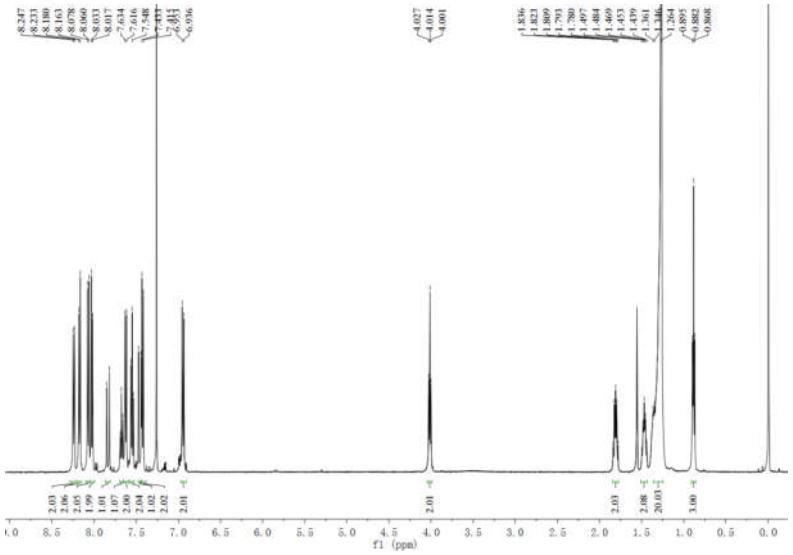

Fig. S25 ^{1}H NMR of compound **III-14**

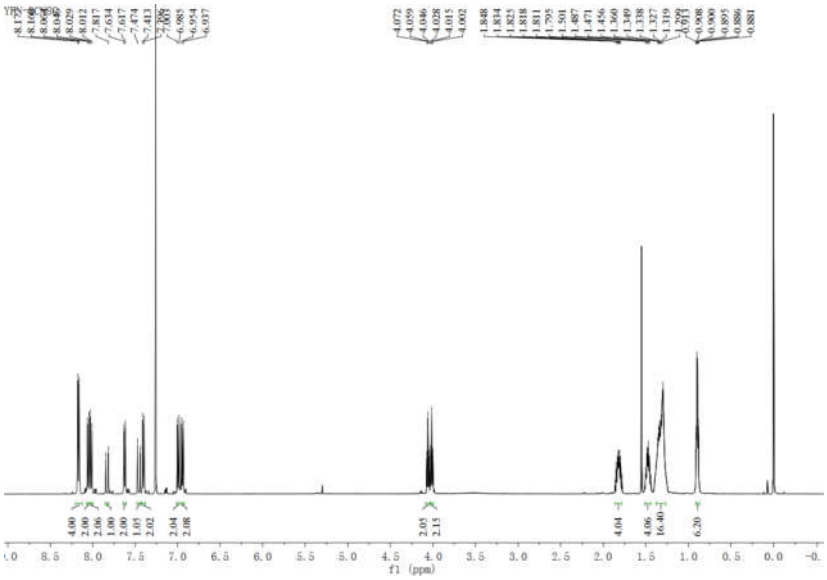

Fig. S26 ^{1}H NMR of compound **IV-8**

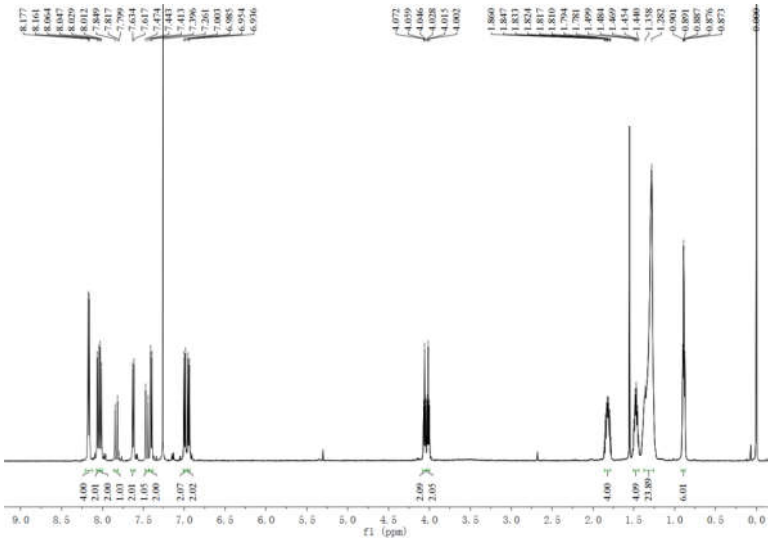

Fig. S27 ^{1}H NMR of compound **IV-10**

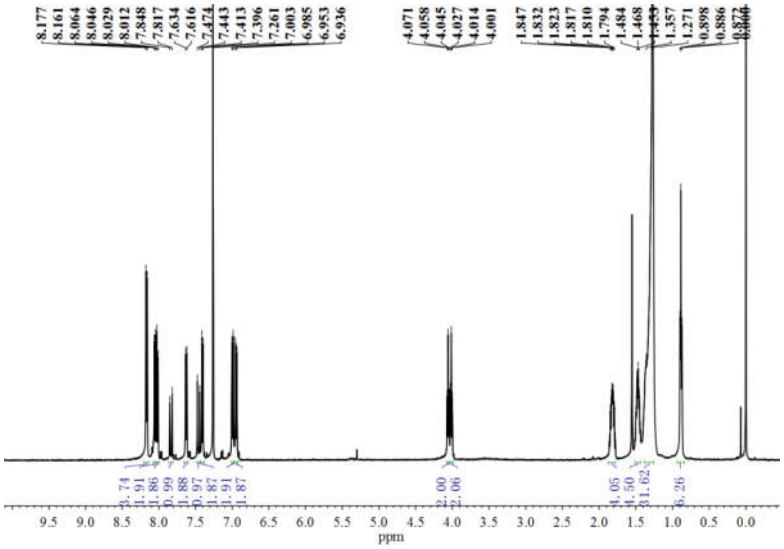

Fig. S28 ^{1}H NMR of compound **IV-12**

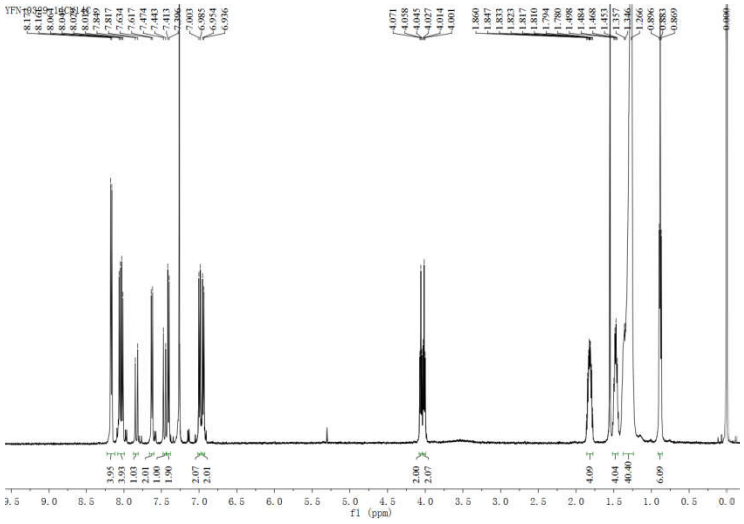

Fig. S29 ^{1}H NMR of compound **IV-14**

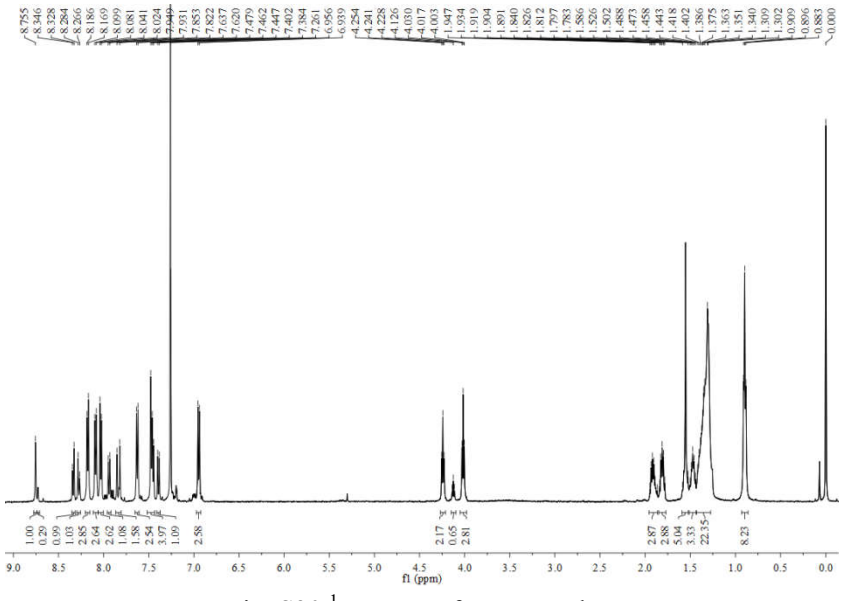

Fig. S30 ^{1}H NMR of compound **V**