Electronic Supplementary Information (ESI)

BINOL-based chiral aggregation-induced emission luminogens and application for detecting copper (II) ion in aqueous media

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Experimental section

Materials and Instrumentations

THF was refluxed with sodium and benzophenone and distilled prior to use. Petroleum ether and ethyl acetate for column chromatography were distilled before use. All starting materials were purchased from Acros, Alfa Aesar, Energy and used directly. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 300 and a Bruker AV 400 spectrometer using DMSO or $CDCl_3$ as solvent and tetramethylsilane (TMS; δ = 0) as the internal reference. High resolution mass spectra (HRMS) were recorded on a Bruker Maxis Spectrometer. UV-visible (UV-vis) absorption spectra were measured on a Hitachi U-3900 spectrophotometer. Fluorescence (FL) spectra were recorded on a Hitachi 7000 spectrofluorometer. Circular dichroism (CD) signal were measured on a Chirascan from Applied Photophysics. Scanning electron microscopy (SEM) images were obtained using Hitachi SU8020 field-emission SEM. The single crystal data was recorded with a Bruker SMART APEX-II CCD detector using graphite monochromated Cu-Kα radiation.

Preparation of Nanoaggregates

Stock DMSO solution of luminogens with a concentration of 1 mM was prepared. Aliquots of the stock solution were transferred to 5 mL volumetric flasks. After appropriate amounts of DMSO were added, water was added dropwise under vigorous stirring to furnish 10 μM solutions with different water contents (0–99 vol %). The PL measurements of the resulting solutions were then performed immediately.

Synthesis

2,2'-bis(methoxymethoxy)-1,1'-binaphthalene. (*R*)-1,1’-binaphthol (14.3 g, 50 mmol) was added slowly to a suspension of NaH (9.6 g, 400 mmol) in anhydrous DMF (50 mL) at 0 ℃ under N_2 atmosphere with stirring. The resulting solution was stirred at 0 ℃ for 1h. Then methoxymethyl chloride (19.5 mL, 150 mmol) was slowly added. The mixture was allowed to warm up to room temperature and stirred for

another 5 h. After reaction complete, quenched by water (50 mL). The aqueous layer was extracted with ethyl acetate (3×100 mL). Combined organic layers were washed with brine (3 x 60 mL) and dried over anhydrous Na_2SO_4. Then remove the solvent under reduced pressure, the resultant residue was recrystallized with methanol. Product was obtained as a pale yellow powder in 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.01 (d, *J* = 9 Hz, 2H, Ar H), 7.93 (d, *J* = 8 Hz, 2H, Ar H), 7.65 (d, *J* = 9 Hz, 2H, Ar H), 7.42-7.38 (m, 2H, Ar H), 7.31-7.24 (m, 4H, Ar H), 5.10 (d, *J* = 7 Hz, 2H; CH_2), 4.99 (d, *J* = 7 Hz, 2H; CH_2), 3.20 (s, 6H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 152.71, 134.09, 129.94, 129.47, 127.96, 126.38, 125.61, 124.13, 121.33, 117.29, 95.19, 55.86.

2,2'-bis(methoxymethoxy)-[1,1'-binaphthalene]-3,3'-dicarbaldehyde. *n*-BuLi (2.5 M in hexane, 9 mL, 22.5 mmol) was added to a solution of 2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (2.24 g, 6 mmol) in anhydrous THF (30 mL) at 0 ℃ under N_2 atmosphere. Then the mixture was allowed to warm up to room temperature and stirred for 2 h. Re-cooled the mixture to 0 ℃, and DMF (1.2 mL, 18 mmol) was added. The reaction was allowed to warm up to room temperature and stirred for another 4 h. After the reaction complete, quenched by saturated NH_4Cl (30 mL). The aqueous layer was extracted with ethyl acetate (2 x 30 mL). Combined organic phase and dried over anhydrous Na_2SO_4. Then remove the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (Petroleum ether/ethyl acetate (12:1) to afford the title compound in 39% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 10.54 (s, 2H, CHO), 8.61 (s, 2H, Ar H), 8.07 (d, *J* = 8.2 Hz, 2H, Ar H), 7.52-7.48 (m, 2H, Ar H), 7.42-7.38 (m, 2H, Ar H), 7.22 (d, *J* = 8.4 Hz, 2H, Ar H), 4.73 (d, *J* = 8.0 Hz, 2H; CH_2), 4.68 (d, *J* = 8.0 Hz, 2H; CH_2), 2.85 (s, 6H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 190.67, 154.06, 136.73, 132.39, 130.34, 130.10, 129.66, 128.91, 126.31, 126.13, 125.95, 100.63, 57.01. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{26}H_{22}O_6Na$, 453.1314, found, 453.1310.

2,2'-dihydroxy-[1,1'-binaphthalene]-3,3'-dicarbaldehyde. To an ice-cooled solution of 2,2'-bis(methoxymethoxy)-[1,1'-binaphthalene]-3,3'-dicarbaldehyde (430 mg, 0.698 mmol) in THF (6 mL) was slowly added conc. HCl (3 mL), and the

mixture was allowed to warm up to room temperature with stirring for another 3 hrs. After reaction complete, the mixture was extracted with ethyl ether (4 x 10 mL). Combined organic layers were washed with H_2O, $NaHCO_3$, brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to afford product which used directly for the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 10.60 (s, 2H, CHO), 10.18 (s, 2H, OH), 8.34 (s, 2H, Ar H), 8.00-7.98 (m, 2H, Ar H), 7.44-7.38 (m, 4H, Ar H), 7.22-7.20 (m, 2H, Ar H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 196.92, 153.78, 138.65, 137.57, 130.83, 130.15, 127.78, 124.99, 124.65, 122.24, 116.63. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{14}O_4Na$, 365.0790, found, 365.0790.

2,2'-bis(pyridin-2-ylmethoxy)-[1,1'-binaphthalene]-3,3'-dicarbaldehyde (BINOP-CHO). 2-Picolyl chloride hydrochloride (295.2 mg, 1.8 mmol) and K_2CO_3 (331.2 mg, 2.4 mmol) was suspended in 3ml DMF, then 2,2'-dihydroxy-[1,1'-binaphthalene]-3,3'-dicarbaldehyde (205.2 mg, 0.6 mmol) was added. The mixture was stirred at 80 ℃ overnight. After reaction complete, extracted with ethyl ether (3 x 5 mL) and washed with brine. The organic layers were combined and dried over anhydrous Na_2SO_4. Remove the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (Petroleum ether/ethyl acetate (1:1) to afford the title compound in 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 10.47 (s, 2H, CHO), 8.56 (s, 2H, Ar H), 8.31 (d, *J* = 4.6 Hz, 2H, Ar H), 8.02 (d, *J* = 8.0 Hz, 2H, Ar H), 7.50-7.35 (m, 6H, Ar H), 7.23 (d, *J* = 8.4 Hz, 2H, Ar H), 7.03-7.00 (m, 2H, Ar H), 6.78 (d, *J* = 7.8 Hz, 2H, Ar H), 4.98 (d, *J* = 12.0 Hz, 2H; CH_2), 4.73 (d, *J* = 12.0 Hz, 2H; CH_2); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 190.29, 156.31, 155.90, 148.91, 136.97, 136.49, 132.37, 130.53, 130.13, 129.97, 128.87, 126.38, 125.81, 125.33, 122.67, 121.08, 77.95. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{34}H_{24}N_2O_4Na$, 547.1634, found, 547.1639.

2,2'-((2,2'-bis(pyridin-2-ylmethoxy)-[1,1'-binaphthalene]-3,3'-diyl) bis(methanylylidene)) dimalononitrile (BINOP-CN). Compound BINOP-CHO (78.6 mg, 0.15 mmol) was dissolved in 6 mL ethanol, malononitrile (19.8 mg, 0.3 mmol) and one drop of NaOH (1N) were added, then stirred at room temperature for

2.5 h. After reaction complete, the solvent was evaporated under reduced pressure, the residue was purified by column chromatography on silica gel (Petroleum ether / ethyl acetate (1:1) to afford the title compound in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.87 (s, 2H, CH), 8.62 (s, 2H, Ar H), 8.48 (d, *J* = 4.5 Hz, 2H, Ar H), 8.05 (d, *J* = 8.0 Hz, 2H, Ar H), 7.57-7.46 (m, 6H, Ar H), 7.24 (d, *J* = 8.4 Hz, 2H, Ar H), 7.18-7.15 (m, 2H, Ar H), 6.78 (d, *J* = 7.8 Hz, 2H, Ar H), 4.65 (d, *J* = 12.0 Hz, 2H; CH_2), 4.52 (d, *J* = 12.0 Hz, 2H; CH_2); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 156.22, 155.19, 153.75, 149.70, 136.84, 136.56, 131.86, 130.73, 130.35, 130.11, 127.02, 125.71, 125.28, 125.01, 123.46, 122.10, 113.81, 112.89, 83.61, 77.92. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{40}H_{24}N_6O_2Na$, 643.1858, found, 643.1865.

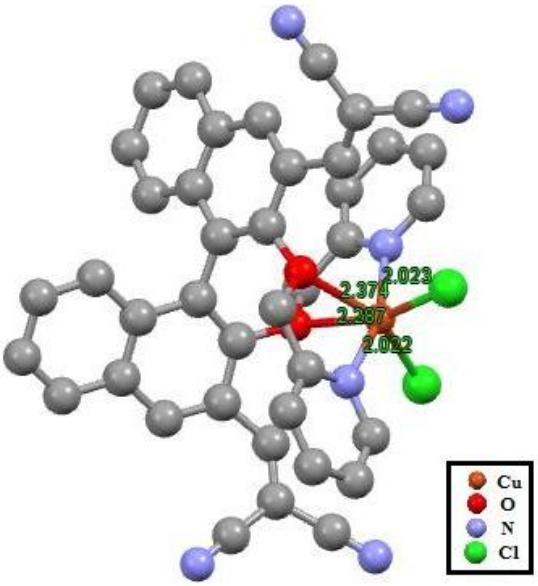
2,2'-((2,2'-bis(methoxymethoxy)-[1,1'-binaphthalene]-3,3'-diyl) bis (methanylylidene)) dimalononitrile (BINOM-CN). Compound 2,2'-bis(methoxymethoxy)-[1,1'-binaphthalene]-3,3'-dicarbaldehyde (129 mg, 0.3 mol) was dissolved in 5 mL ethanol, malononitrile (40.6 mg, 0.615 mmol) and one drop of NaOH (1N) were added, then stirred at room temperature for 2.5 h. After reaction completed, the mixture was filtered to afford the title compound in 46% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.94 (s, 2H, CH), 8.45 (s, 2H, Ar H), 8.08 (d, *J* = 8.0 Hz, 2H, Ar H), 7..60-7.55 (m, 2H, Ar H), 7.50-7.45 (m, 2H, Ar H), 7.16 (d, *J* = 8.4 Hz, 2H, Ar H), 4.56 (d, *J* = 8.0 Hz, 2H; CH_2), 4.50 (d, *J* = 8.0 Hz, 2H; CH_2), 3.09 (s, 6H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 156.49, 152.26, 136.39, 131.78, 130.66, 130.30, 130.19, 127.14, 125.93, 125.61, 125.38, 113.85, 112.79, 100.68, 83.94, 57.50. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{32}H_{22}N_4O_4Na$, 549.1539, found, 549.1508.

2,2'-((2,2'-dihydroxy-[1,1'-binaphthalene]-3,3'-diyl)bis(methanylylidene))dimalo nonitrile (BINOL-CN). Compound BINOM-CN (556 mg, 0.105 mmol) was dissolved in 4 mL ethanol and 8 mL $CHCl_3$. Then 6N HCl (8 mL) was added and stirred at 70^{o}C for 12 h. After reaction complete, the mixture was filtered off to obtain the title compound in 63% yield. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.24 (s, 2H, OH), 8.77 (s, 2H, Ar H), 8.33 (d, *J* = 8.2 Hz, 2H, Ar H), 7.68-7.64 (m, 2H, Ar H), 7.59-7.55 (m, 2H, Ar H), 7.22 (d, *J* = 8.5 Hz, 2H, Ar H); ^{13}C NMR (100 MHz, DMSO-d_6, δ): 156.45, 153.74, 147.45, 134.60, 133.08, 130.78, 130.09, 129.90, 126.72, 125.30,

117.53, 115.83, 114.46, 102.66. MS (MALDI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{28}H_{15}N_4O_2$, 438.1117, found, 439.133.

Table S1. Crystallographic data for complex of BINOP-CN-Cu.

Compound	BINOP-CN-Cu
Empirical formula	$C_{40}H_{24}Cl_2CuN_6O_2$
Formula weight	755.09
Crystal system	tetragonal
Space group	P 4_3 2_1 2
a [Å]	12.79416 (14)
b [Å]	12.79416 (14)
c [Å]	44.6986 (8)
b [^{o}]	90
V [Å^3]	7316.7 (2)
Z	8
T [K]	293
D_{calcd} [g cm^{-3}]	1.371
m [mm^{-1}]	2.537
q range [^{o}]	6.9830-72.0150
Total no. reflections	7214
R_1	0.0367
wR_2	0.0811
GOOF	0955



Scheme S1. The ORTEP drawing of complex BINOP-CN-Cu. All H atoms molecules are omitted for clarity.

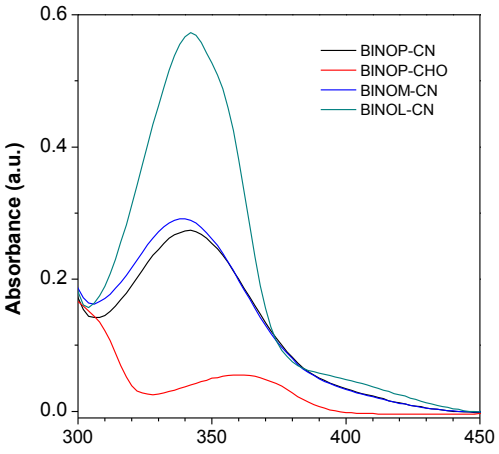


Fig. S1 (A) UV-vis and (B) emission spectra of BINOL derivatives (10 μM) in DMSO.

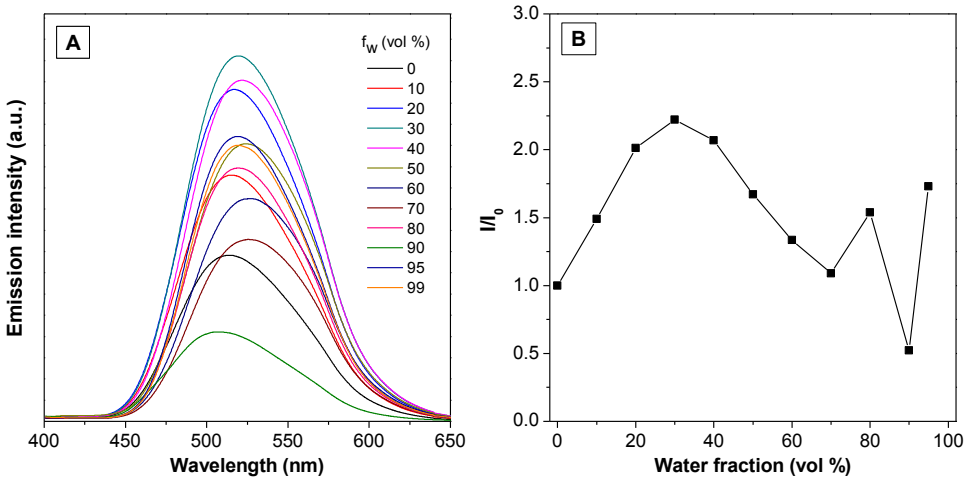


Fig. S2 (A) Emission spectra of BINOL-CN (10 μM) in DMSO and DMSO-water mixtures with different f_w. (B) Plots of emission intensity *versus* the composition of the aqueous mixtures of BINOL-CN.

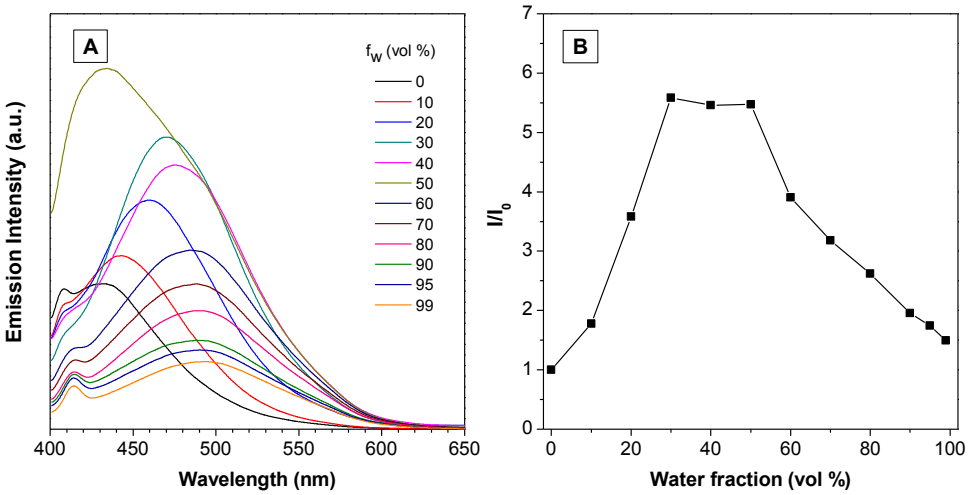


Fig. S3 (A) Emission spectra of BINOP-CHO (10 μM) in DMSO and DMSO-water mixtures with different f_w. (B) Plots of emission intensity *versus* the composition of the aqueous mixtures of BINOP-CHO.

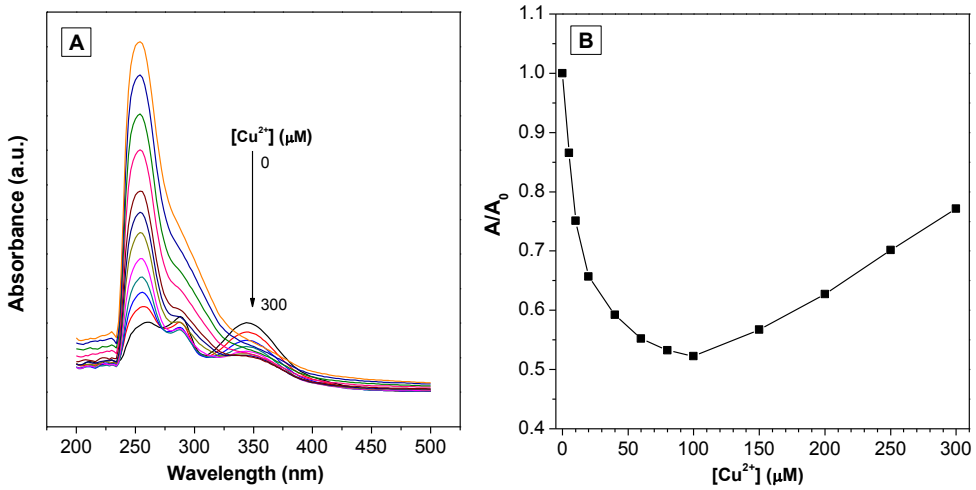


Fig. S4 UV-vis spectra of BINOP-CN (10 μM) in DMSO/PBS buffer (20 : 80 v/v, pH 7.4) with different concentration of Cu^{2+} (0-300 μM). (B) Plots of absorbance at 350 nm *versus* the concentration of Cu^{2+}.

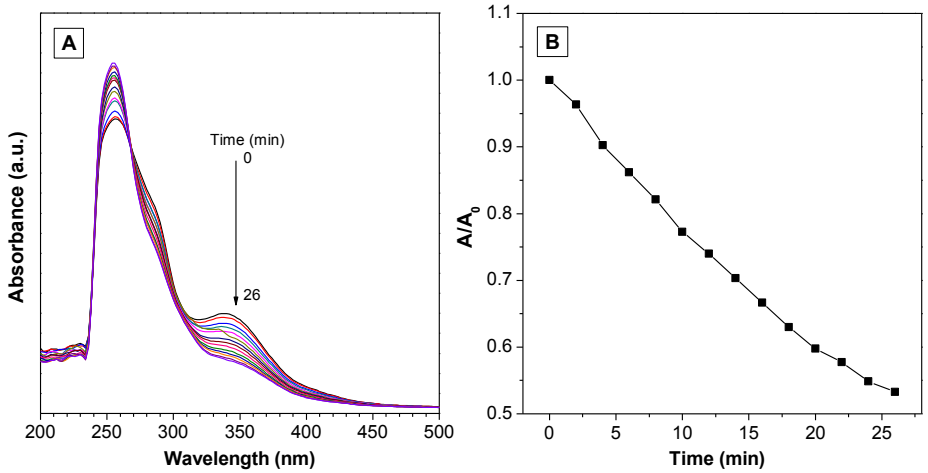


Fig. S5 The time–dependent UV-vis spectra for BINOP-CN (10 μM) with Cu^{2+} (200 μM) in DMSO/PBS buffer (20 : 80 v/v, pH 7.4). (B) Plots of absorbance at 350 nm *versus* the time.

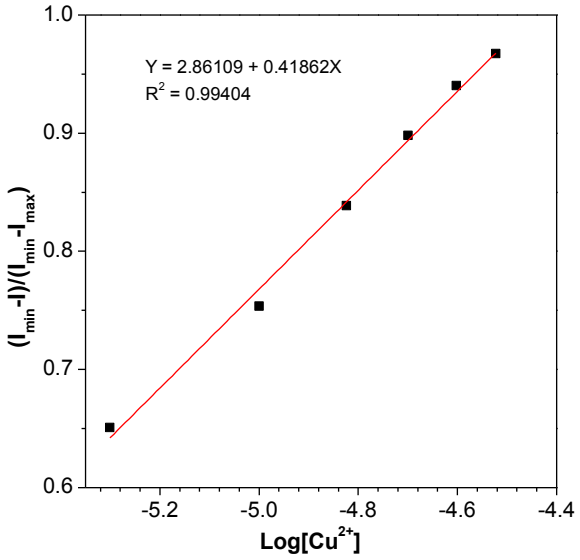


Fig. S6 Normalized fluorescence intensity of BINOP-CN (10 μM) to different Cu^{2+} concentrations (5.0, 10.0, 15.0, 20.0, 25.0, 30.0 μM) in DMSO/PBS buffer (20 : 80 v/v, pH 7.4). Detection limit = 1.48×10^{-7} M.

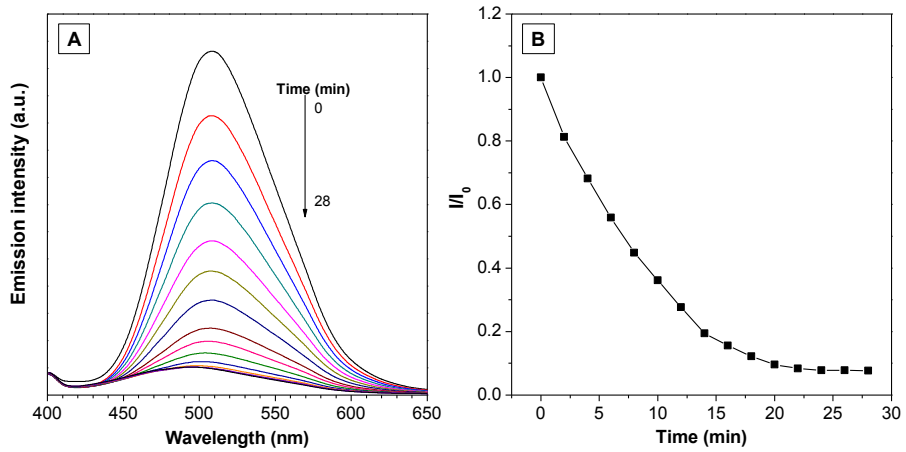


Fig. S7 The time–dependent emission spectra for BINOP-CN (10 μM) with Cu^{2+} (200 μM) in DMSO/PBS buffer (20 : 80 v/v, pH 7.4). (B) Plots of emission intensity 509 nm nm *versus* the time.

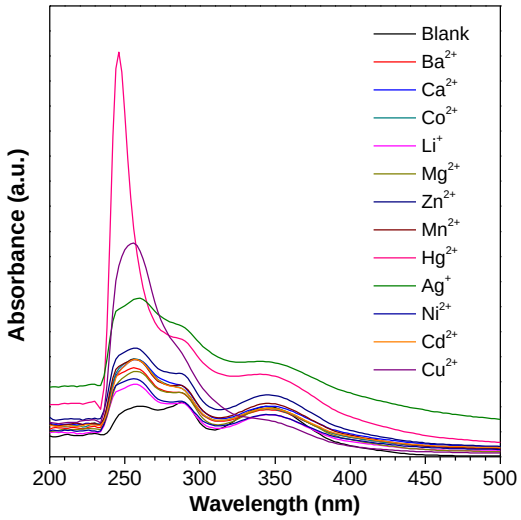


Fig. S8 UV-vis spectra of BINOP-CN (10 μM) with different metal ions (200 μM) in DMSO/PBS buffer (20 : 80 v/v, pH 7.4).

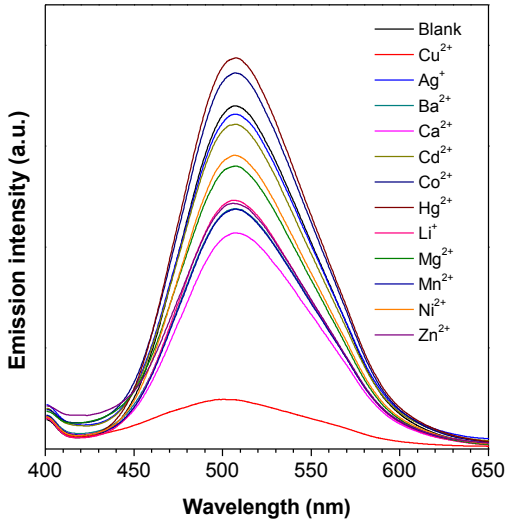
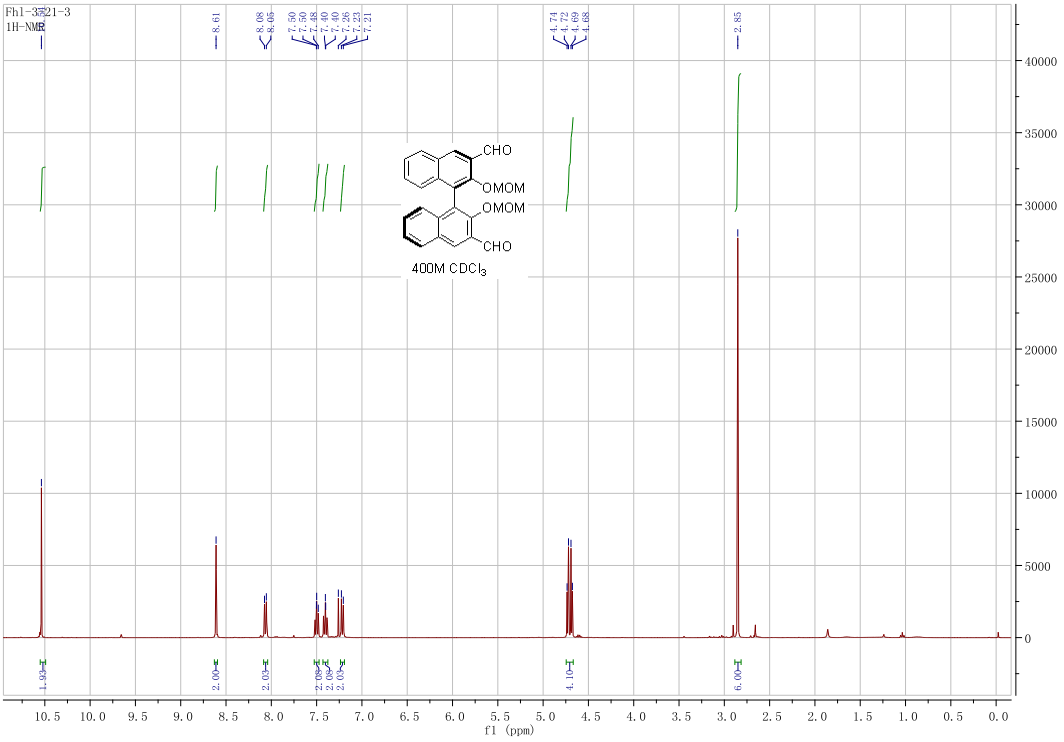


Fig. S9 Emission spectra of BINOP-CN (10 μM) with different metal ions (200 μM) in DMSO/PBS buffer (20 : 80 v/v, pH 7.4).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8.05
7.50
7.50
7.48
7.40
7.40
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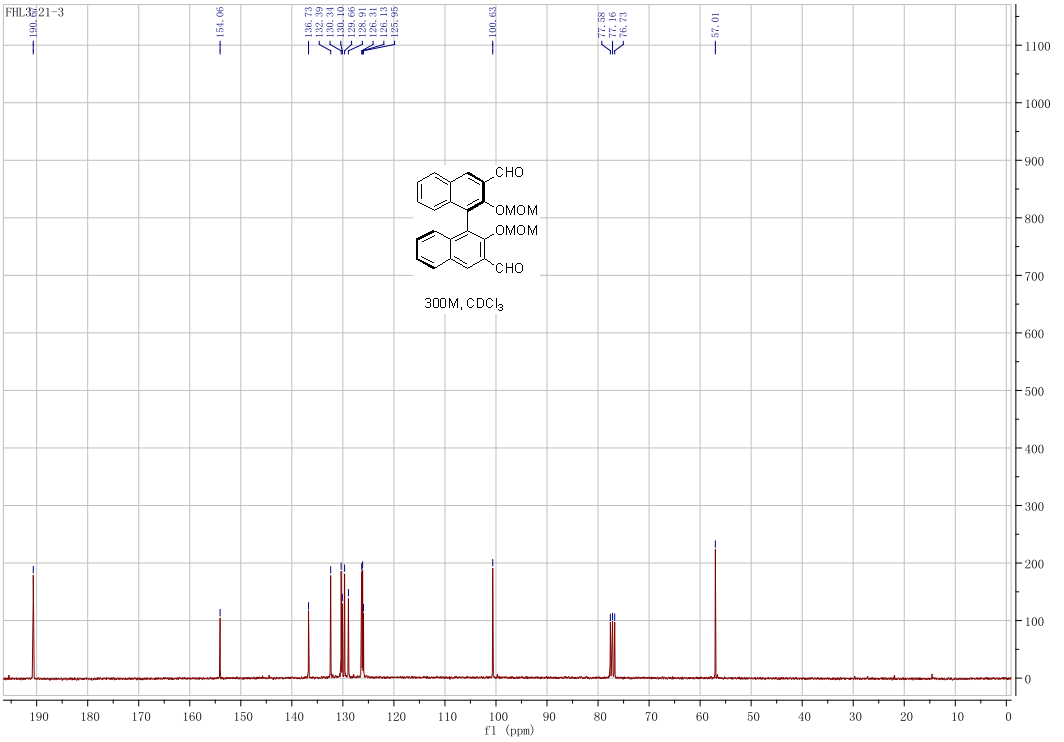
CHO
OMOM
OMOM
CHO
400M CDCl3
f1 (ppm)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132.39
130.34
130.16
129.66
128.91
126.31
126.13
125.96
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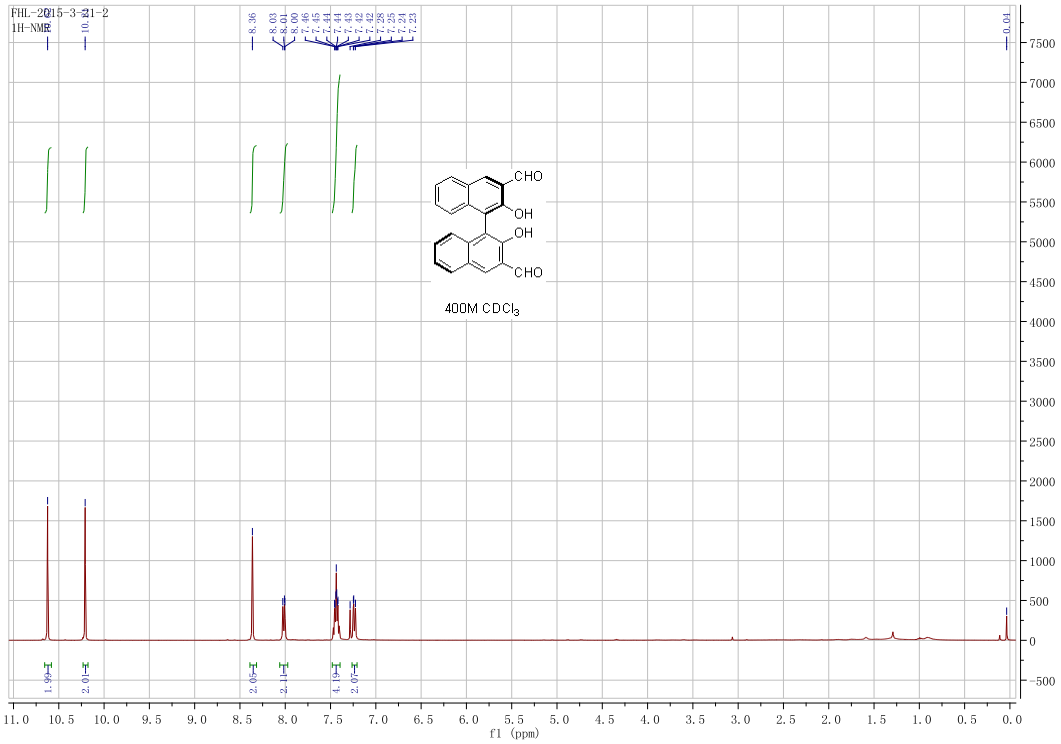
77.58
77.16
76.73
57.01
CHO
OMOM
OMOM
CHO
300M, CDCl3
f1 (ppm)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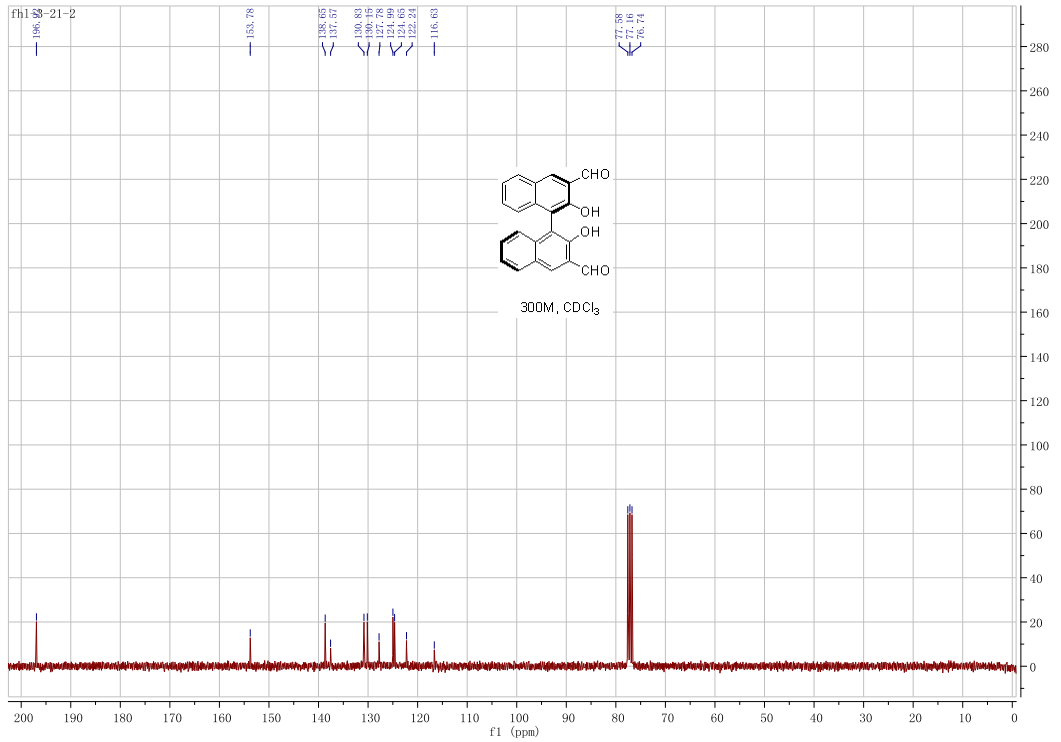
8.03
8.01
8.00
7.46
7.45
7.44
7.44
7.43
7.42
7.42
7.28
7.25
7.24
7.24
7.23
0.04
CHO
OH
OH
CHO
400M CDCl3
1.99
2.01
2.05
2.11
4.19
2.07
f1 (ppm)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137.57
130.83
130.45
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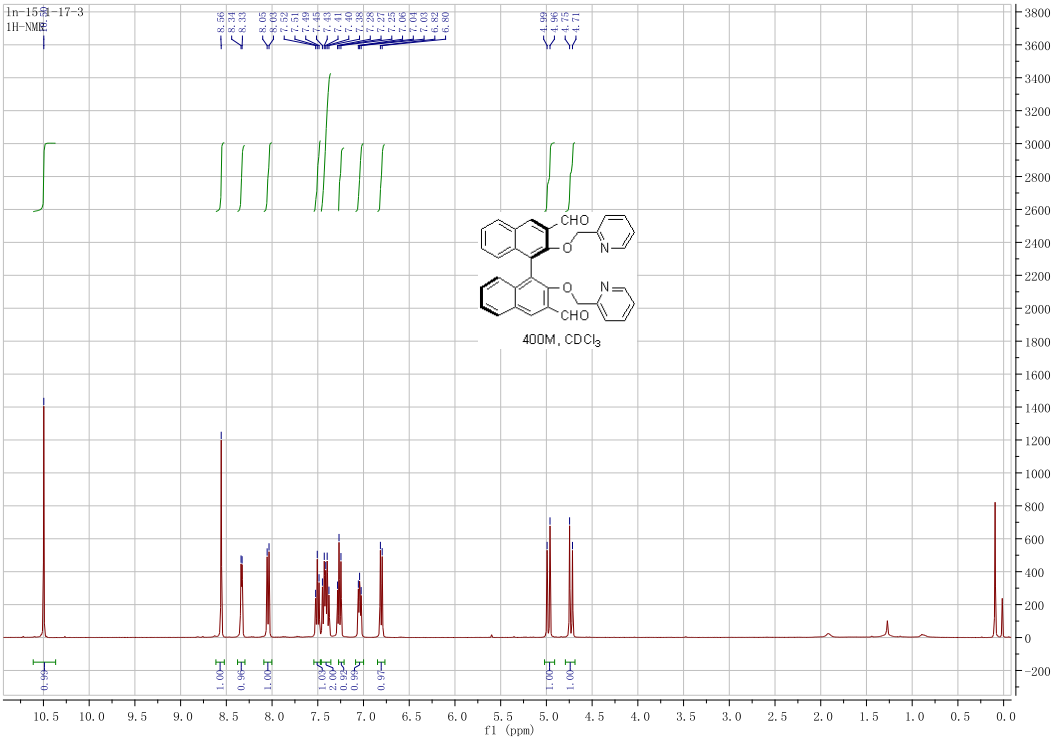
OH
OH
CHO
300M, CDCl3
f1 (ppm)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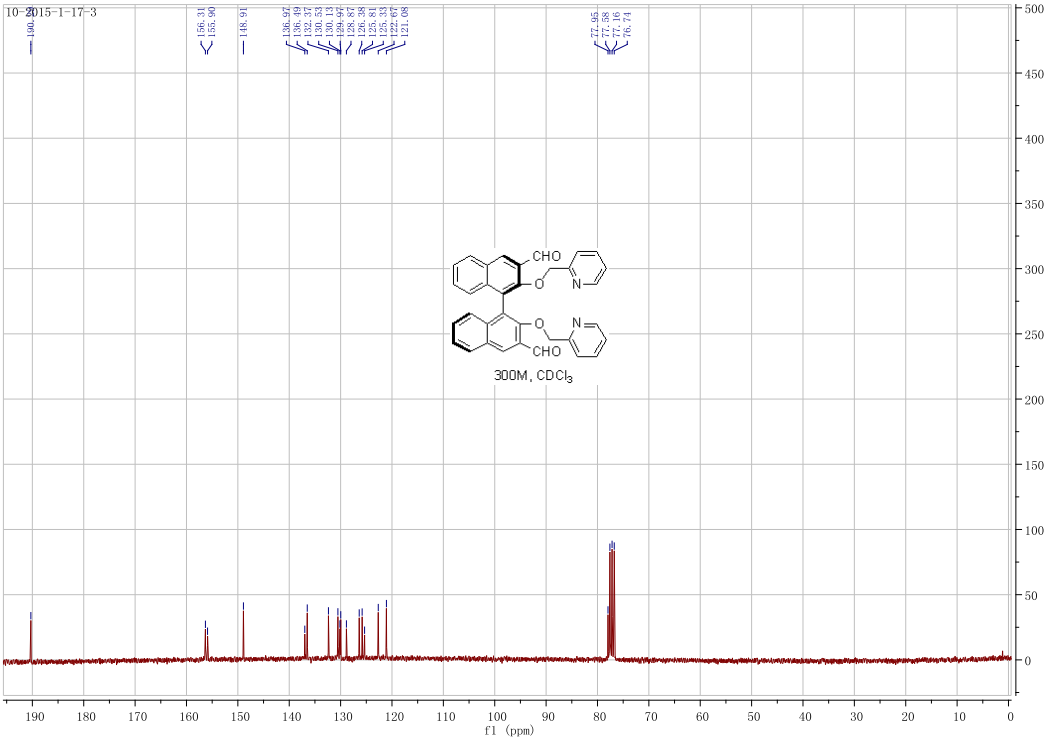
N
O
N
CHO
400M, CDCl3
f1 (ppm)


10-2015-1-17-3
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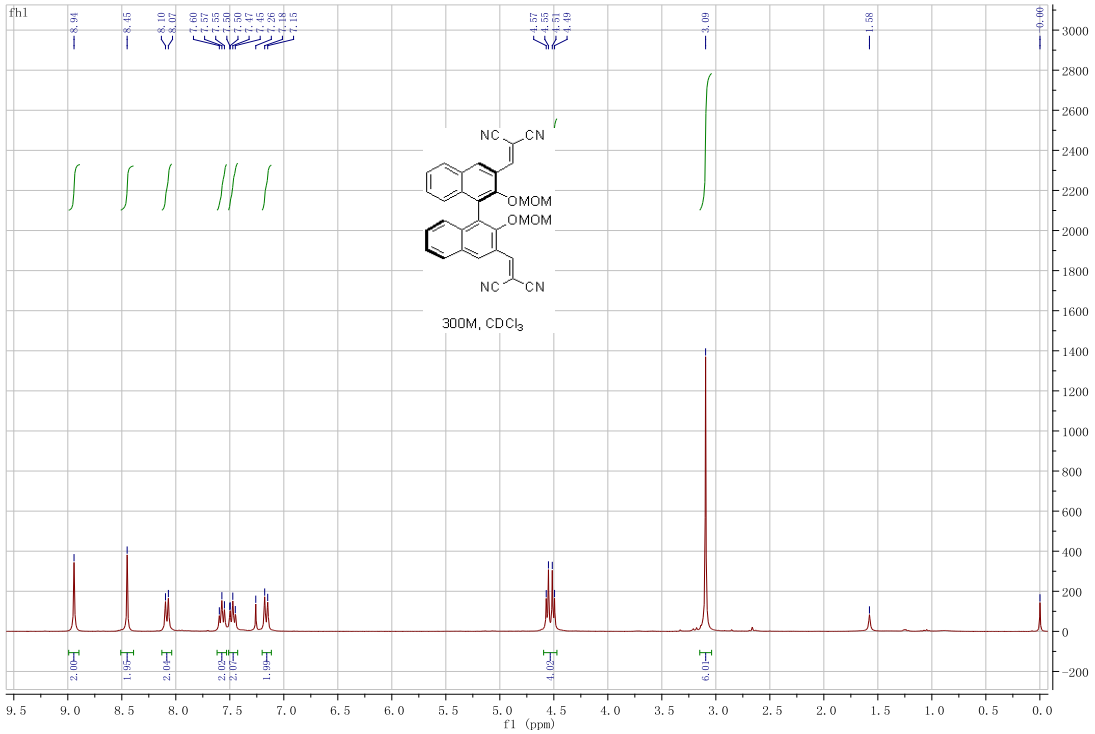
N
O
N
CHO
300M, CDCl3
f1 (ppm)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7.45
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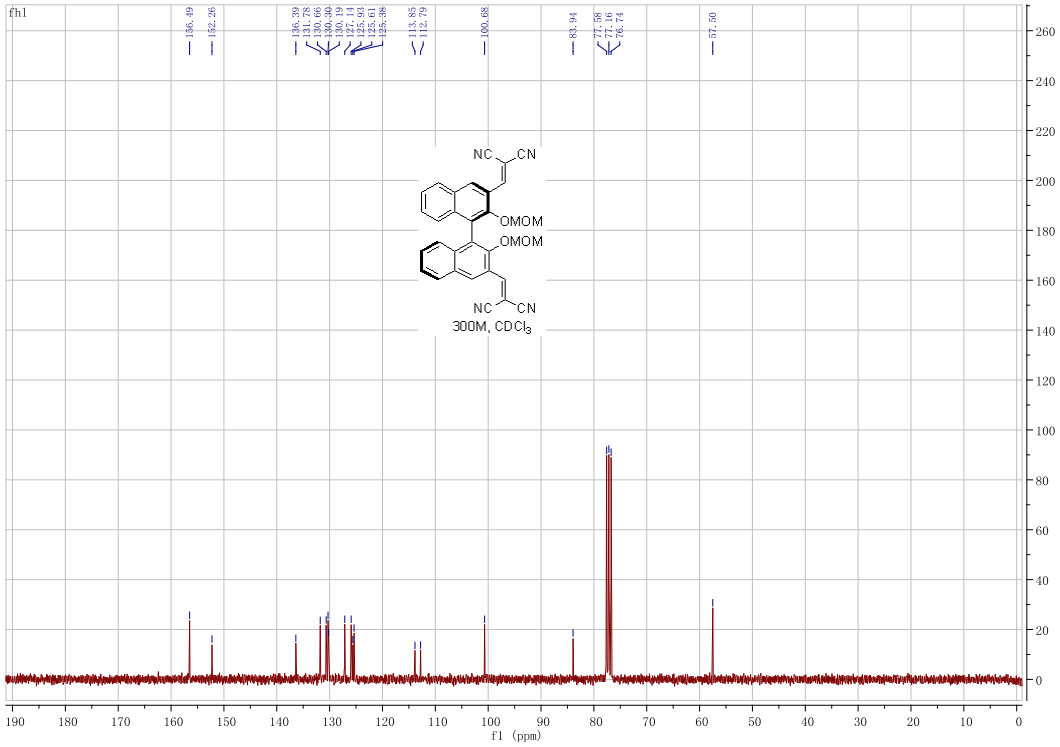
7.18
7.15
4.57
4.55
4.51
4.49
3.09
1.58
0.00
NC
CN
OMOM
OMOM
NC
CN
300M, CDCl3
2.00
1.95
2.04
2.02
2.07
1.99
4.02
6.01
f1 (ppm)


fh1
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152.26
136.39
131.78
130.66
130.30
130.19
127.14
125.93
125.61
125.38
113.85
112.79
100.68
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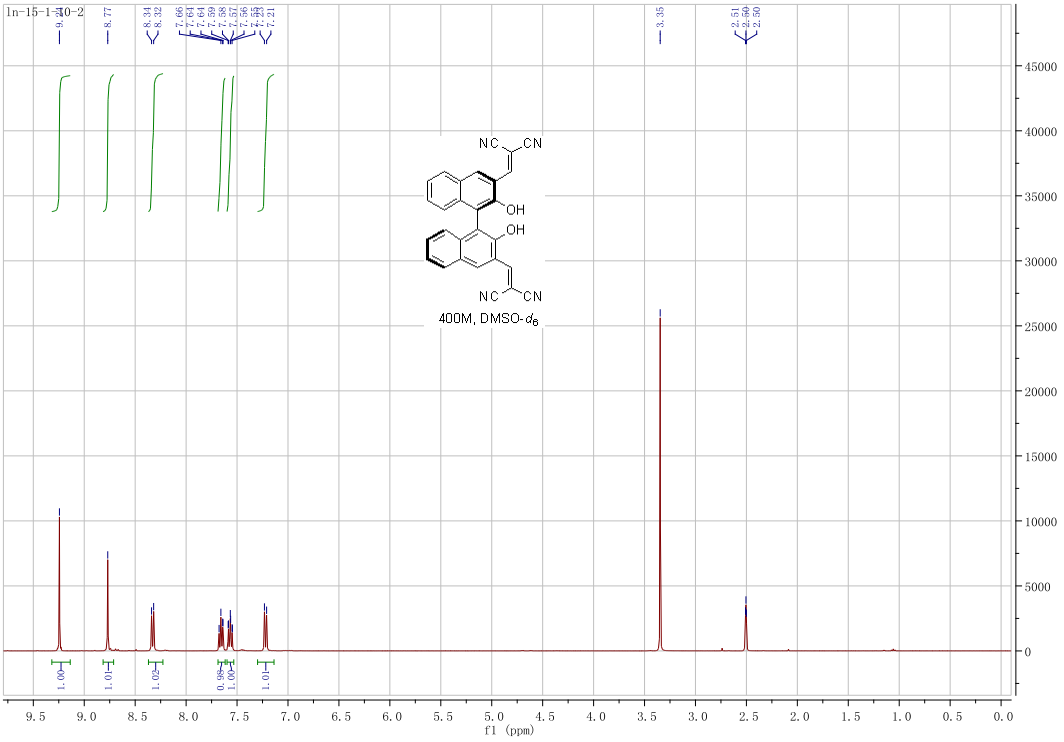
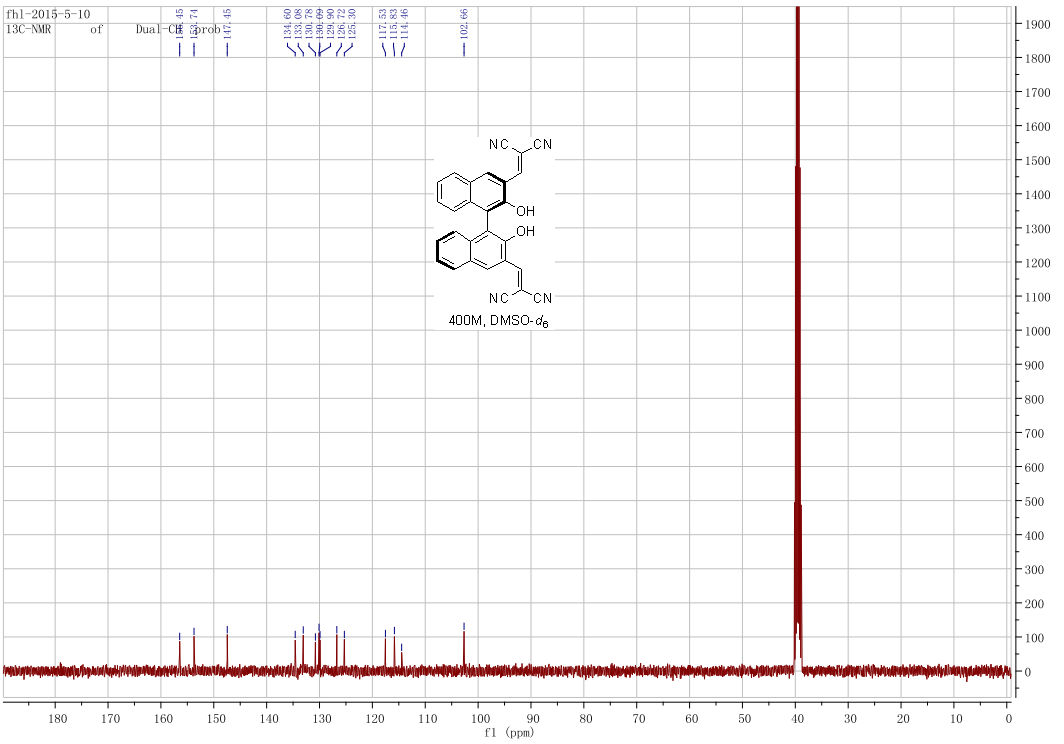
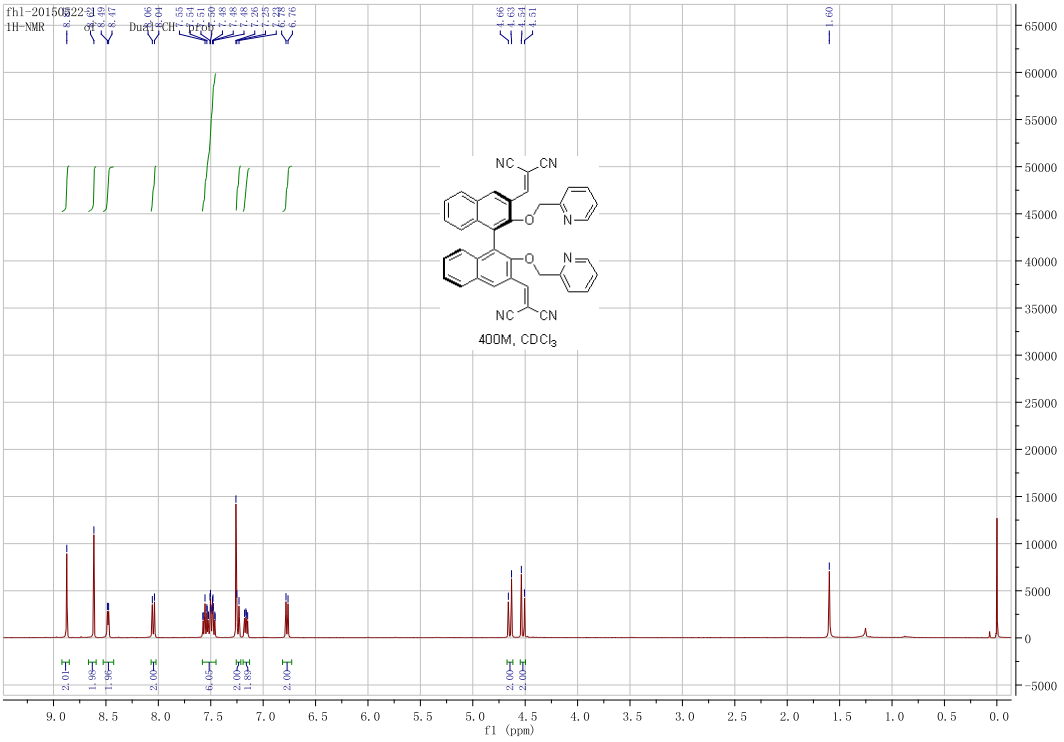
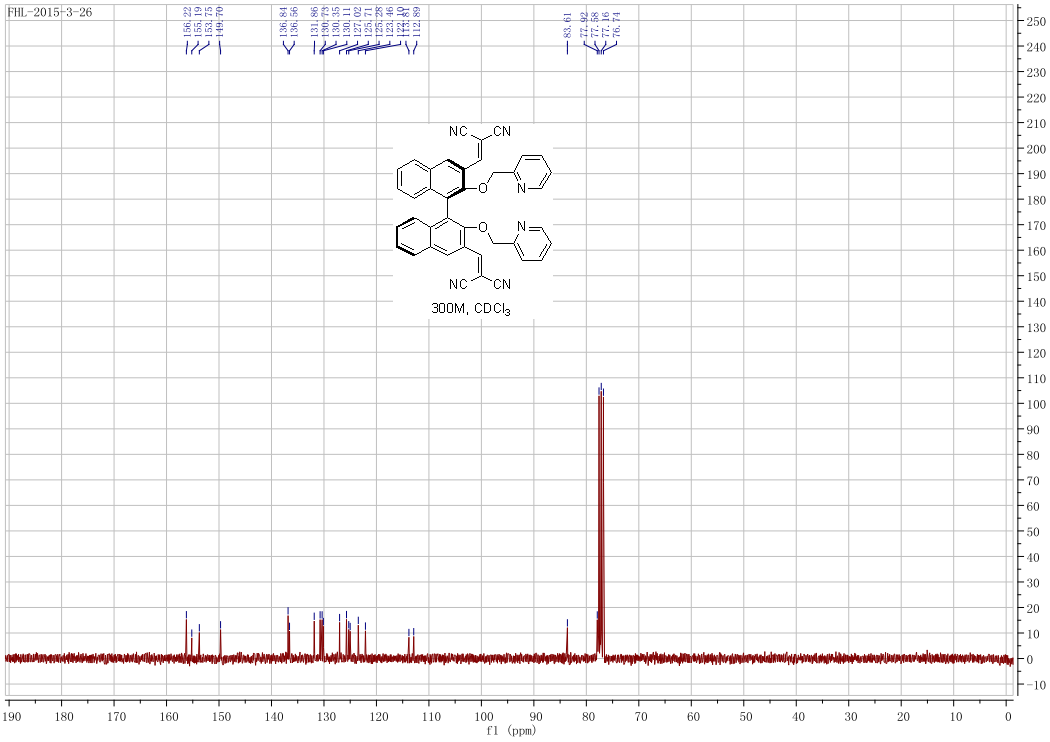
CN
OMOM
OMOM
NC
CN
300M, CDCl3
f1 (ppm)


ln-15-1-10-2
9.77
8.77
8.34
8.32
7.66
7.64
7.64
7.59
7.58
7.57
7.56
7.55
7.53
7.21
3.35
2.51
2.50
NC
CN
OH
OH
NC
CN
400M, DMSO-d_6
f1 (ppm)


fhl-2015-5-10
13C-NMR
of
Dual-CH
Prob
147.45
134.69
133.98
133.58
130.69
129.90
126.72
125.50
117.53
115.83
114.46
102.66
NC
CN
OH
OH
NC
CN
400M, DMSO-d_6
f1 (ppm)


fhl-20150322-02
1H-NMR
400M, CDCl3
f1 (ppm)


FHL-2015-3-26
300M, CDCl3
f1 (ppm)