Supporting Information

Selective Synthesis and (Chir)optical Properties of Binaphthyl-based Chiral Carbon Macrocycles

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1. General Information and Materials

All anhydrous solvents for syntheses and chemicals were purchased from commercial suppliers (Acros or Innochem). All the air-sensitive reactions were carried out using the standard Schlenk technique under nitrogen or argon atmosphere. The NMR spectra were recorded on a Bruker BioSpin (^{1}H 400 MHz, ^{13}C 100 MHz) spectrometer in $CDCl_3$ solution, and chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm) or $CHCl_3$ (δ 7.26 ppm). Chemical shifts for ^{13}C NMR are expressed ppm relative to $CDCl_3$ (δ 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, m = multiplet, br s = broad signal), coupling constant (Hz), and integration. High-resolution mass spectrometry (HR-MS) analyses were carried out using MALDI-TOF-MS techniques and *trans*-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile as the matrix. UV-vis spectra were obtained on a UNIC-3802 spectrophotometer in standard glass cuvettes. Fluorescence spectra were obtained on a FluoroMax-4 spectrofluorometer. Circular dichroism (CD) spectra were obtained on a spectropolarimeter (JASCO, Jasco-1500). Circularly polarized luminescence (CPL) spectra were obtained on a spectrometer (JASCO, CPL-300). Preparative thin-layer chromatography (PTLC) were performed using silica gel GF254 precoated plates and flash chromatography was performed on silica gel (200~300 mesh).

Single-Crystal XRD measurements of MBCM. Crystalline blocks of **MBCM** was obtained by slow evaporation of a mixed solution of dichloromethane (CH_2Cl_2) and methanol in a glass tube. After a two-week period, yellow block crystals suitable to crystal measurements formed. Single crystal XRD measurements of **MBCM** was conducted at 100 K at BL17B station of Shanghai Synchrotron Radiation Facility. The multi-scan method was used for absorption corrections. The crystal structures were solved with the ShelXT structure solution program using Intrinsic Phasing, later refined with the ShelXL refinement package embedded within OLEX2.[S1-S3] CCDC-2144375 contain the supplementary crystallographic data for this paper. These data can also be

obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Optical Characterization. The photoluminescence quantum yields for **MBCM** and **BBCM** were determined by using anthracene (ethanol) as standard and calculated according to the following equation:

$$\varphi_f = \varphi_{std} \times \frac{I_{unk}}{A_{unk}} \times \frac{A_{std}}{I_{std}} \times \frac{\eta_{unk}^2}{\eta_{std}^2}$$

where I_{unk} and I_{std} are the integrated emission intensities of the sample and the standard compound, respectively; A_{unk} and A_{std} are the absorbance of the sample and standard compound, respectively, at the desired wavelength λ_{ex}; and η_{unk} and η_{std} are the indexes of refraction of the sample and standard solutions, respectively.

2. Synthetic procedures of MBCM and BBCM

Synthesis of compound 1. The compound **1** was synthesized according to literature reports.[S4, S5]

Synthesis of compound 2. The compound **1** (1.5 g, 3.25 mmol) was arylated by Suzuki-Miyaura coupling reaction by using *p*-dibromobenzene (9.09 g, 38.95 mmol), $Pd(PPh_3)_4$ (187 mg, 0.1625 mmol), potassium carbonate (2.24 g, 16.21 mmol) in DMF/H_2O (40 mL : 5 mL), then, the solution was heated to 85 °C for 48 hours. Upon cooling to room temperature, the solvent was removed under reduced pressure, then the crude solid was purified on a silica column using hexane/CH_2Cl_2 (v/v, 2:1) to afford compound **2** as a white solid (1.6 g, 2.34 mmol, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.93 (s, 2H), 7.89 (d, J = 8 Hz, 2H), 7.64 (d, J = 8.4 Hz, 4H), 7.60 (d, J = 8.4 Hz, 4H), 7.43 (t, J = 14 Hz, 2H), 7.30 (t, J = 16 Hz, 4H), 4.39 (d, J = 6 Hz, 2H), 4.34 (d, J = 6 Hz, 2H), 2.36 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.21, 138.02, 134.36, 133.81, 131.63, 131.42, 130.92, 130.63, 128.06, 126.74, 126.69, 126.51, 125.55, 121.71, 98.77, 56.09 ppm. HR-MS (ESI) m/z calcd. for $C_{36}H_{28}NaBr_2O_4$ $[M + Na]^+$: 707.0232, found 707.0220.

Synthesis of compound 3. The compound **3** was synthesized according to literature reports.[S6] ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm) 7.77 (d, J = 8 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 6.12 (d, J = 10.4 Hz, 2H), 6.06 (d, J = 10.4 Hz, 2H), 3.43 (s, 6H), 1.25 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.28, 142.08, 135.07, 133.73, 133.5, 133.14, 128.59, 127.6, 124.38, 83.92, 74.98, 74.61, 52.11, 52.08, 24.98 ppm.

The analytical data is in accordance to the literature.[S6]

Synthesis of compound 4. To a mixture of compound **2** (1.0 g, 1.46 mmol), compound **3** (1.85 g, 4.08 mmol), $Pd(PPh_3)_4$ (168 mg, 0.145 mmol), and potassium carbonate (1.21 g, 8.76 mmol) in a round-bottom flask was added DMF (40 mL) and H_2O (6 mL), then, the solution was heated to 85 °C for 48 hours under nitrogen atmosphere. Upon cooling to room temperature, the solvent was removed under reduced pressure, then the crude reaction mixture was passed through a short silica gel column with CH_2Cl_2 to afford compound **4** as a white solid (1.29 g, 1.095 mmol, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm) 8.00 (s, 2H), 7.91 (d, *J* = 8 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 4H), 7.70 (d, *J* = 8.4 Hz, 4H), 7.63 (d, *J* = 8.4 Hz, 4H), 7.87 (d, *J* = 8.4 Hz, 4H), 7.37 (d, *J* = 8.4 Hz, 6H), 7.31-7.28 (m, 8H), 6.28 (d, *J* = 10 Hz, 4H), 6.09 (d, *J* = 10 Hz, 4H), 4.47 (d, *J* = 6 Hz, 2H),4.40 (d, *J* = 10 Hz, 4H), 3.46 (s, 6H), 3.44 (s, 6H), 2.40 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.50, 142.52, 142.16, 140.25, 139.67, 138.29, 133.85, 133.56, 133.25, 131.03, 130.68, 130.18, 128.67, 128.05, 127.64, 127.33, 127.25, 127.12, 126.75, 126.60, 125.39, 98.76, 74.79, 74.66, 56.06, 52.19 ppm. HR-MS (ESI) *m*/*z* calcd. for $C_{76}H_{64}NaCl_2O_8$ $[M + Na]^+$: 1197.3876, found 1197.3881.

Synthesis of compound 5. To a mixture of compound **4** (1.0 g, 0.85 mmol), K_3PO_4 (1.44 g, 6.8 mmol), $Pd(OAc)_2$ (9.65 mg, 0.043 mmol), S-Phos (45.36 mg, 0.111mmol) and bis(pinacolato)diboron (1.73 g, 6.8 mmol) in a round-bottom flask was added 1,4-dioxane (15 mL), then, the solution was heated to 95 °C for 36 hours under nitrogen atmosphere. Upon cooling to room temperature, the solvent was removed under reduced pressure, washed with methanol to afford **5** as a white solid (1.05 g, 0.774

mmol, 91%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm) 8.01 (s, 2H), 7.91 (d, *J* = 8 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 4H), 7.77 (d, *J* = 8.4 Hz, 4H), 7.70 (d, *J* = 8.4 Hz, 4H), 7.61 (d, *J* = 8.4 Hz, 4H), 7.50 (d, *J* = 8.4 Hz, 4H), 7.44 (d, *J* = 8.4 Hz, 6H), 7.30-7.32 (m, 4H), 6.15(d, *J* =4 Hz, 4H), 4.48 (d, *J* = 6 Hz, 2H), 6.12(d, *J* =6Hz, 4H), 4.44 (d, *J* = 6 Hz, 2H), 3.47 (s, 6H), 3.45 (s, 6H), 2.38 (s, 6H), 1.33 (s, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.58, 146.57, 140.15, 135.08, 133.82, 133.49, 131.04, 130.69, 130.16, 128.04, 127.22, 127.15, 126.66, 126.51, 125.50, 125.36, 98.79, 83.95, 77.48, 75.12, 74.89, 56.08, 52.17, 52.13, 25.00 ppm.HR-MS (ESI) *m*/*z* calcd. for $C_{88}H_{88}NaB_2O_{12}$ [*M* + Na]$^{+}$: 1381.6360, found 1381.6385.

Synthesis of compound 6. The compound **6** was synthesized according to literature reports.[S7] ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm) 7.43 (d, *J* = 8.4 Hz, 4H), 7.24 (d, *J* = 8.8 Hz, 4H), 6.07 (s, 4H), 3.41 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.45, 134.47, 131.66, 127.89, 121.87, 76.84, 74.58, 52.18 ppm.

The analytical data is in accordance to the literature.[S7]

Synthesis of MBCM. To a mixture of **5** (252.69 mg, 0.186 mmol), **6** (83.69 mg, 0.186 mmol), and KOH (208 mg, 3.718 mmol) in a round-bottom flask (500 mL) was added THF (250 mL) and H_2O (10 mL), then $Pd(PPh_3)_4$ (30.06 mg, 0.026 mmol) were added under argon atmosphere. Thereafter, the solution was heated at 75 °C for 48 hours. Upon cooling to room temperature, the solvent was removed under vacuum and the residue was extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous MgSO4, filtered, and concentrated under reduced pressure to afford the crude product as a gray solid for the next step without further purification.

To a round-bottom flask (50 mL, vessel A) containing a magnetic stirring bar were added sodium metal (274 mg, 11.9 mmol), dry THF (12 mL), and naphthalene (1.00 g, 7.82 mmol), and the resultant mixture was stirred at room temperature for 1 day. To another 250-mL round-bottom flask (vessel B) containing the above dry crude product and dry THF (30 mL) was added a solution of sodium naphthalide (2 mL, 2 mmol, 1.0 M in THF) in vessel A at -78 °C. This mixture was kept stirring at -78 °C for 2 hours. Then, 1.5 mL of I_2 solution (1 M in THF) was added. After warmed up to room temperature, the mixture was quenched with aqueous saturated sodium thiosulfate, extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography with hexane/CH_2Cl_2 as the eluent (v/v, 1:1). Further purification by recrystallization from MeOH and *n*-hexane afforded pure compound **MBCM** as a yellow solid (41 mg, 18.2% over two steps). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.02 (s, 2H), 7.92 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.4 Hz, 4H), 7.69-7.58 (m, 40H), 7.46-7.42 (m, 4H), 7.32 (t, J = 14 Hz, 2H), 4.36 (d, J = 6 Hz, 2H), 4.29 (d, J = 6 Hz, 2H), 2.38 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.52, 140.38, 140.34, 139.67, 139.56, 138.94, 138.92, 138.64, 138.60, 138.57, 138.45, 137.92, 135.20, 133.50, 130.99, 130.22, 130.05, 128.30, 128.07, 127.75, 127.63, 127.59, 127.54, 127.50, 127.43, 127.33, 126.25, 125.26, 99.20, 56.22 ppm. HR-MS (MALDI-TOF-MS) *m*/*z* calcd. for $C_{90}H_{64}NaO_4$ [M + Na]$^+$: 1231.4703, found 1231.4747. IR (KBr): 3467, 3024, 2920, 1653, 1482, 1427, 1384, 1156, 998, 812, 749, 521, 441 cm^{-1}.

Synthesis of BBCM. To a mixture of **5** (252.69 mg, 0.186 mmol), **2** (127.23 mg, 0.186

mmol), and KOH (208 mg, 3.718 mmol) in a round-bottom flask (500 mL) was added THF (250 mL) and H_2O (10 mL), then $Pd(PPh_3)_4$ (30.06 mg, 0.026 mmol) were added under argon atmosphere. Thereafter, the solution was heated at 75 °C for 48 hours. Upon cooling to room temperature, solvent was removed under vacuum and the residue was extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous MgSO4, filtered, and concentrated under reduced pressure to afford the crude product as a gray solid for the next step without further purification.

To a round-bottom flask (50 mL, vessel A) containing a magnetic stirring bar were added sodium metal (274 mg, 11.9 mmol), dry THF (12 mL), and naphthalene (1.00 g, 7.82 mmol), and the resultant mixture was stirred at room temperature for 1 day. To another 250-mL round-bottom flask (vessel B) containing the above dry crude product and dry THF (30 mL) was added a solution of sodium naphthalide (2 mL) in vessel A at -78 °C. This mixture was kept stirring at -78 °C for 2 hours. Then, 1.5 mL of I_2 solution (1 M in THF) was added. After warmed up to room temperature, the mixture was quenched with aqueous saturated sodium thiosulfate, extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography with hexane/CH_2Cl_2 as the eluent (v/v, 1:1). Further purification by recrystallization from

MeOH and *n*-hexane afforded pure compound **BBCM** as a pale-yellow solid (42 mg, 15.0 % over two steps). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.04 (s, 4H), 7.95 (d, J = 8 Hz, 4H), 7.76 (d, J = 8.4 Hz, 8H), 7.71-7.63 (m, 32H), 7.55 (d, J = 8.4 Hz, 4H), 7.46 (t, J = 14 Hz, 4H), 7.36 (t, J = 6 Hz, 4H), 4.31 (d, J = 6.4 Hz, 4H), 4.23 (d, J = 6.4

Hz, 4H), 2.46 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.13, 140.50, 140.19, 139.81, 139.65, 137.88, 135.44, 133.38, 131.04, 130.26, 129.76, 128.43, 128.09, 127.72, 127.63, 127.41, 126.65, 126.42, 125.90, 125.24, 99.37, 56.38 ppm. HR-MS (MALDI-TOF-MS) *m*/*z* calcd. for $C_{108}H_{80}NaO_8$ [*M* + Na]$^+$: 1528.5785, found 1528.5780. IR (KBr): 3443, 3027, 2923, 2855, 1623, 1485, 1384, 1155, 1081, 1000, 812, 749, 582, 518 cm^{-1}.

3. Physical characterizations and photophysical properties

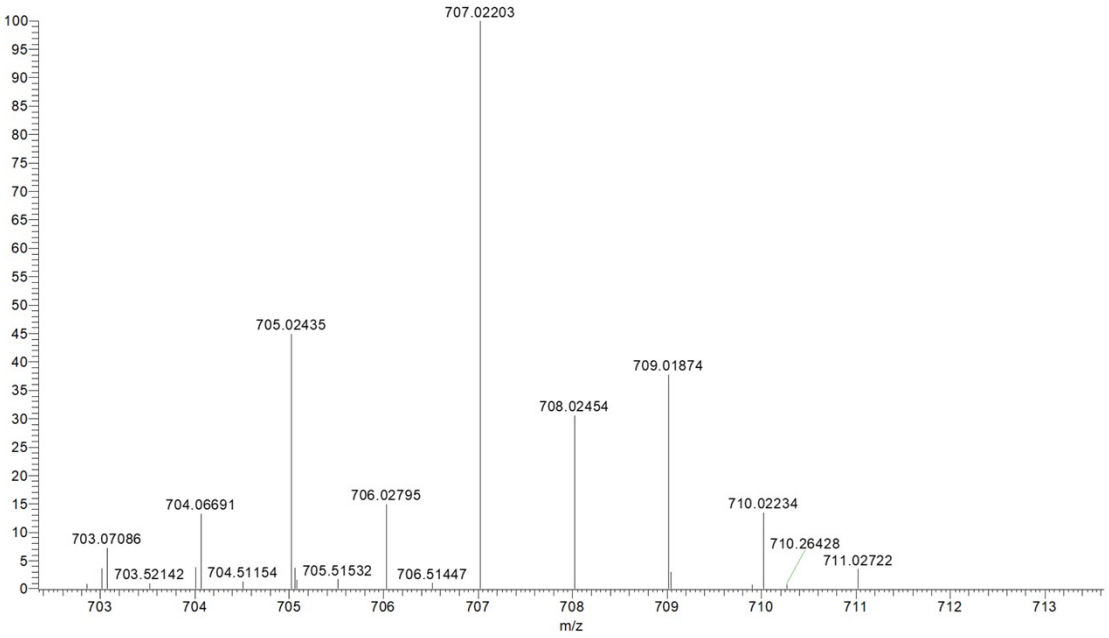

Figure S1. HR-MS (ESI) data for compound **2**.

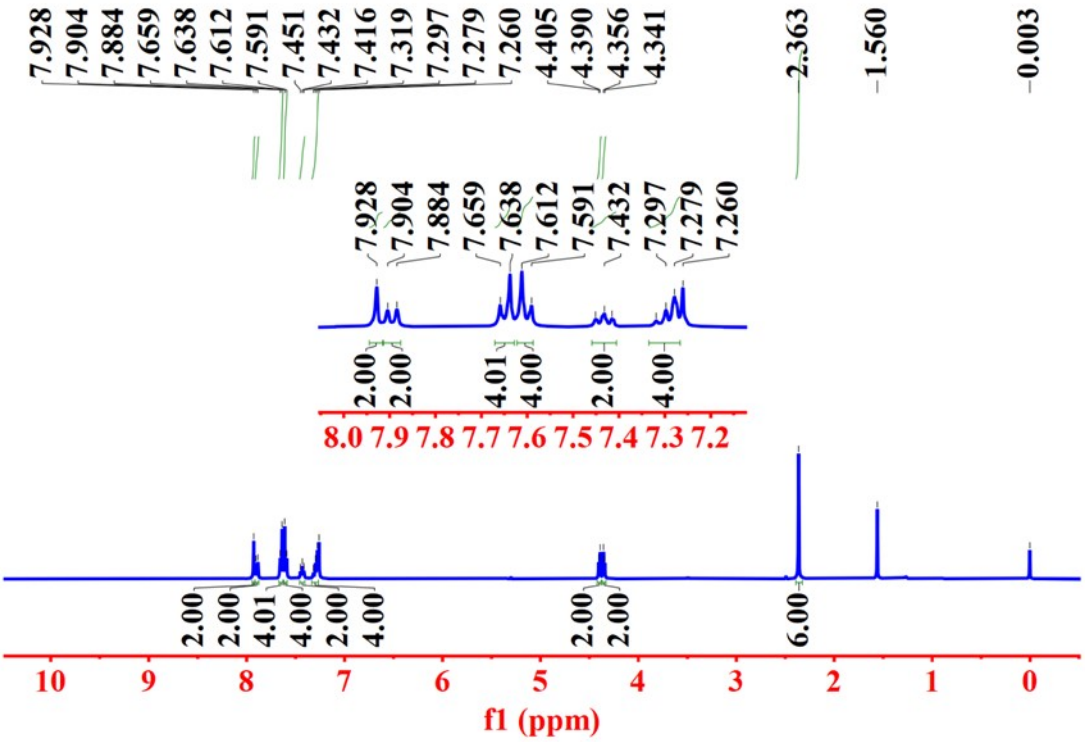

Figure S2. ^{1}H NMR spectrum (400 MHz) of compound **2** in $CDCl_3$.

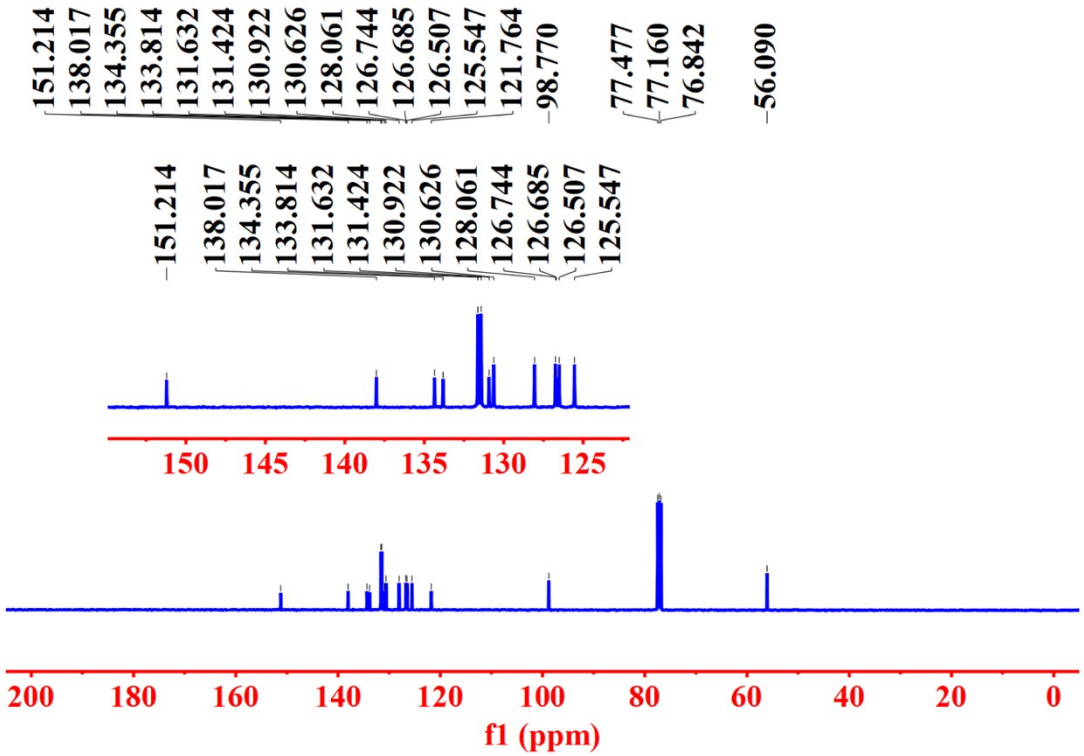

Figure S3. ^{13}C NMR spectrum of compound **2** in $CDCl_3$.

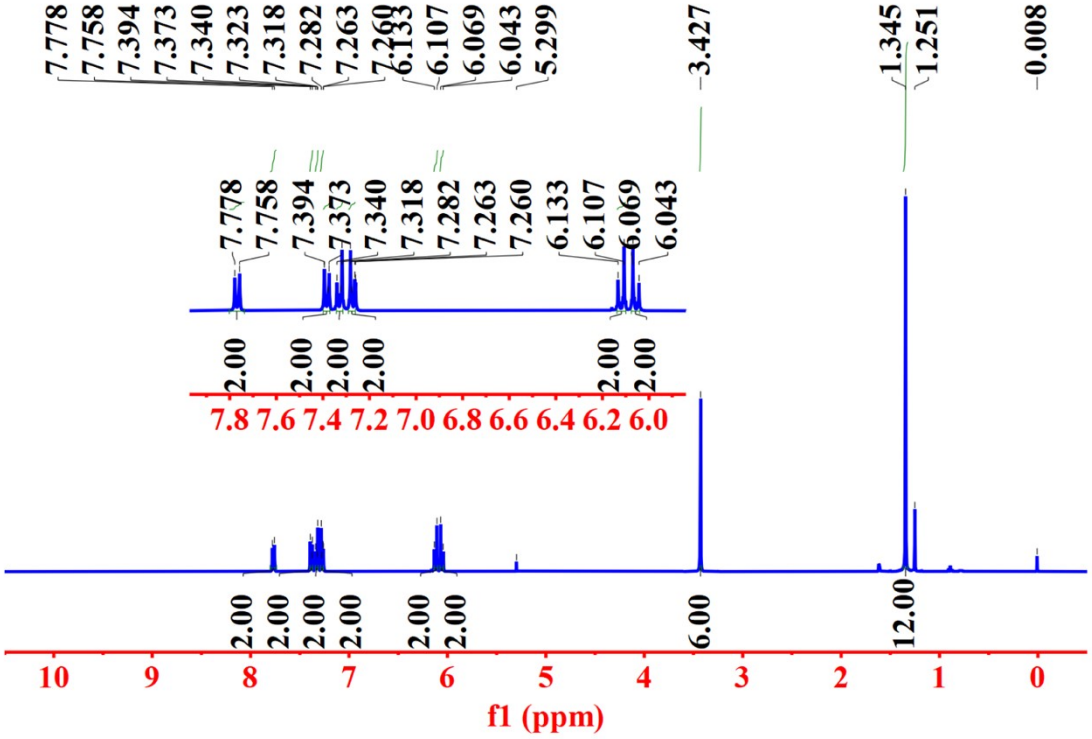

Figure S4. ^{1}H NMR spectrum (400 MHz) of compound **3** in $CDCl_3$.

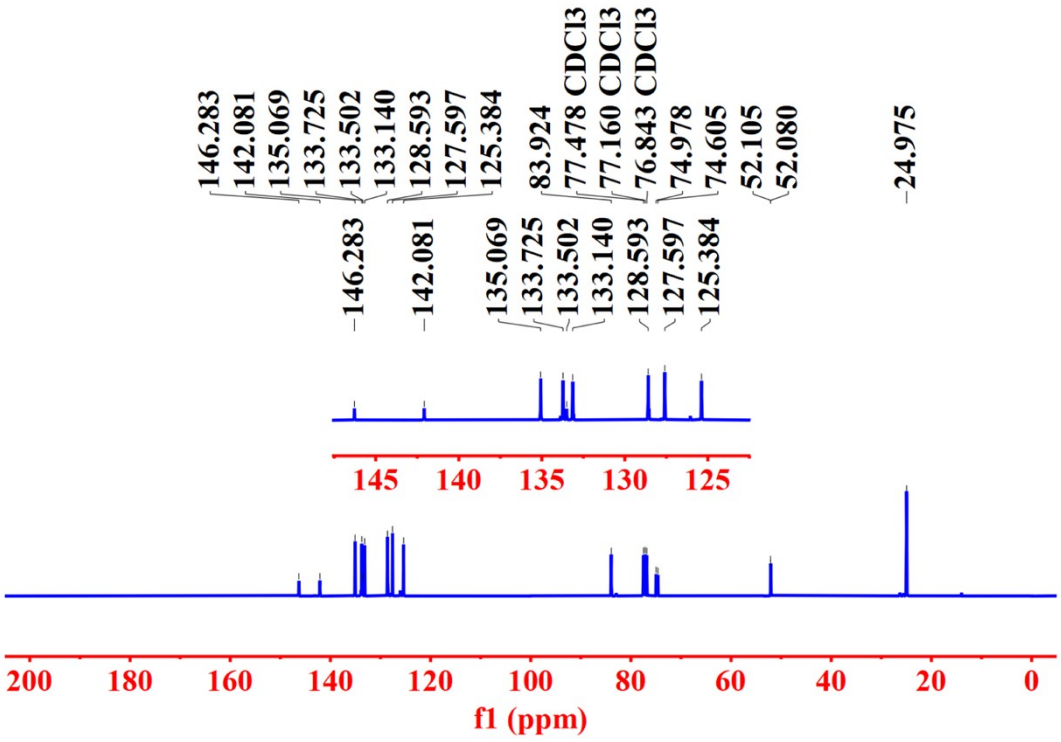

Figure S5. ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

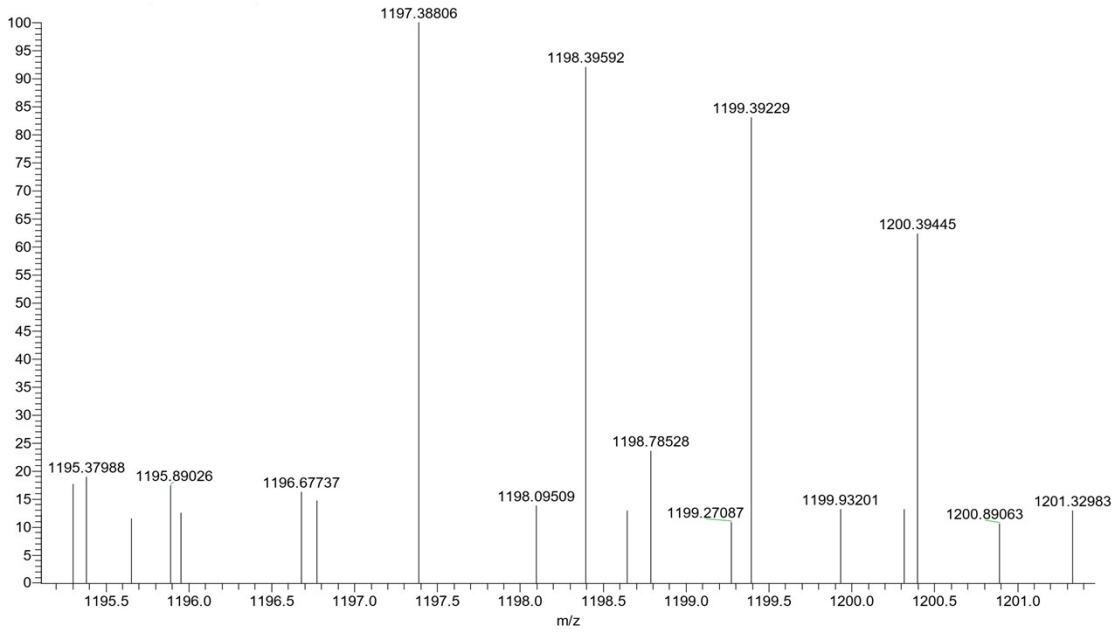

Figure S6. HR-MS (ESI) data for compound **4**.

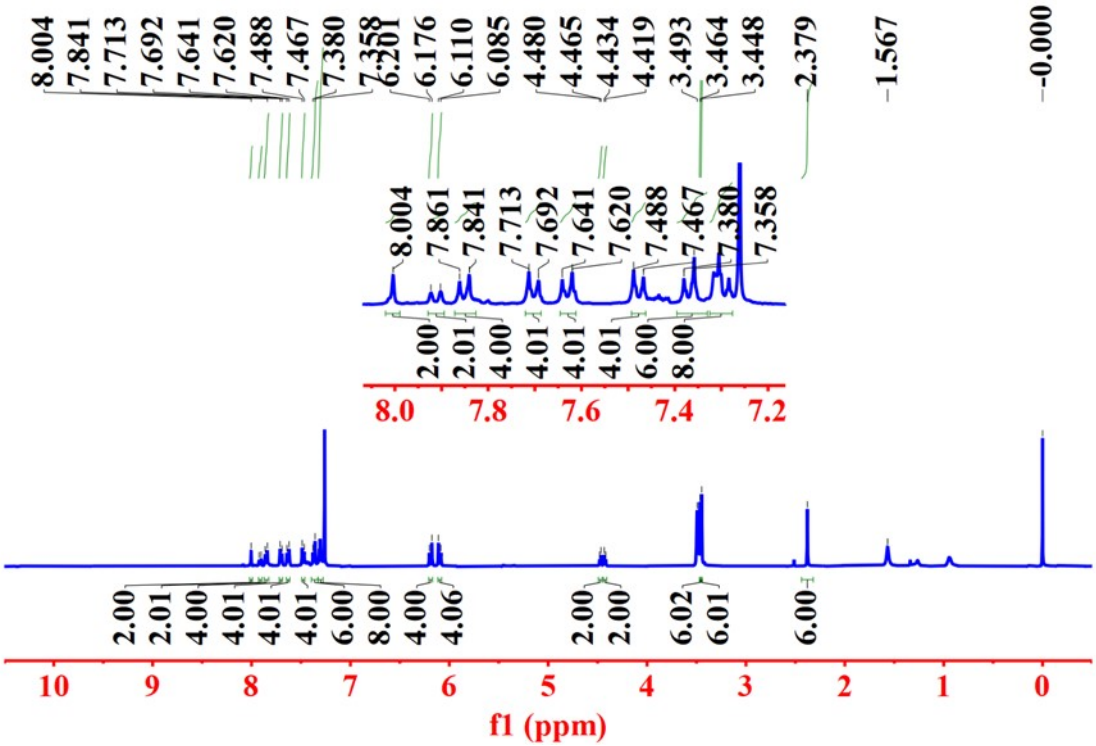

Figure S7. ^{1}H NMR spectrum (400 MHz) of compound **4** in $CDCl_3$.

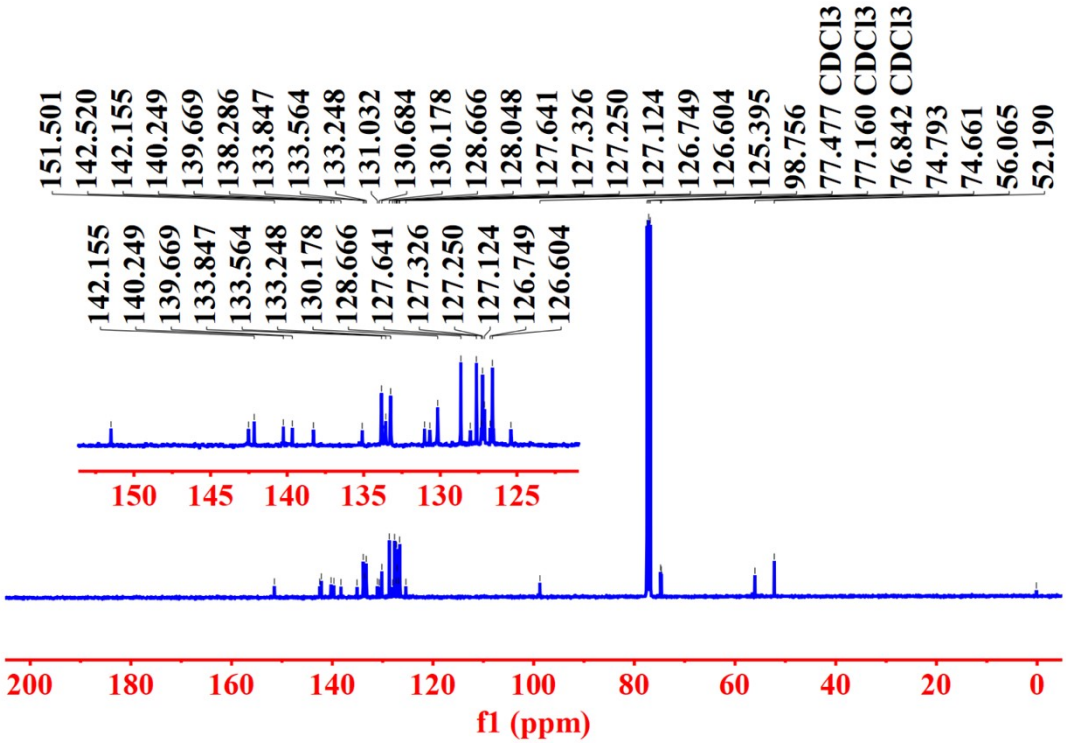

Figure S8. ^{13}C NMR spectrum of compound **4** in $CDCl_3$.

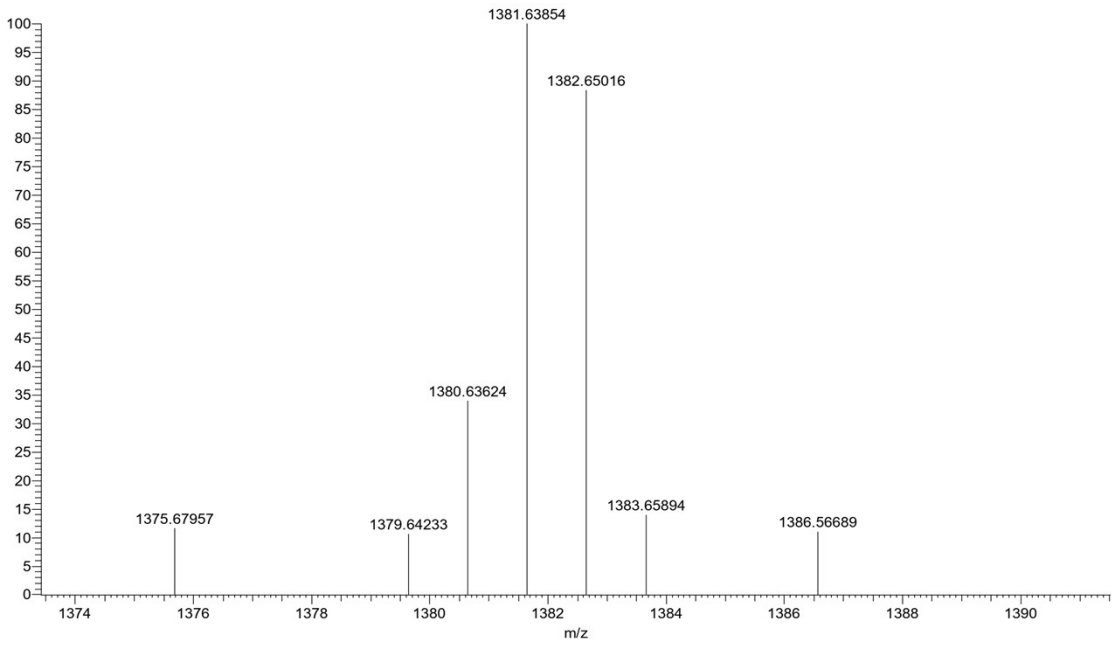

Figure S9. HR-MS (ESI) data for compound **5**.

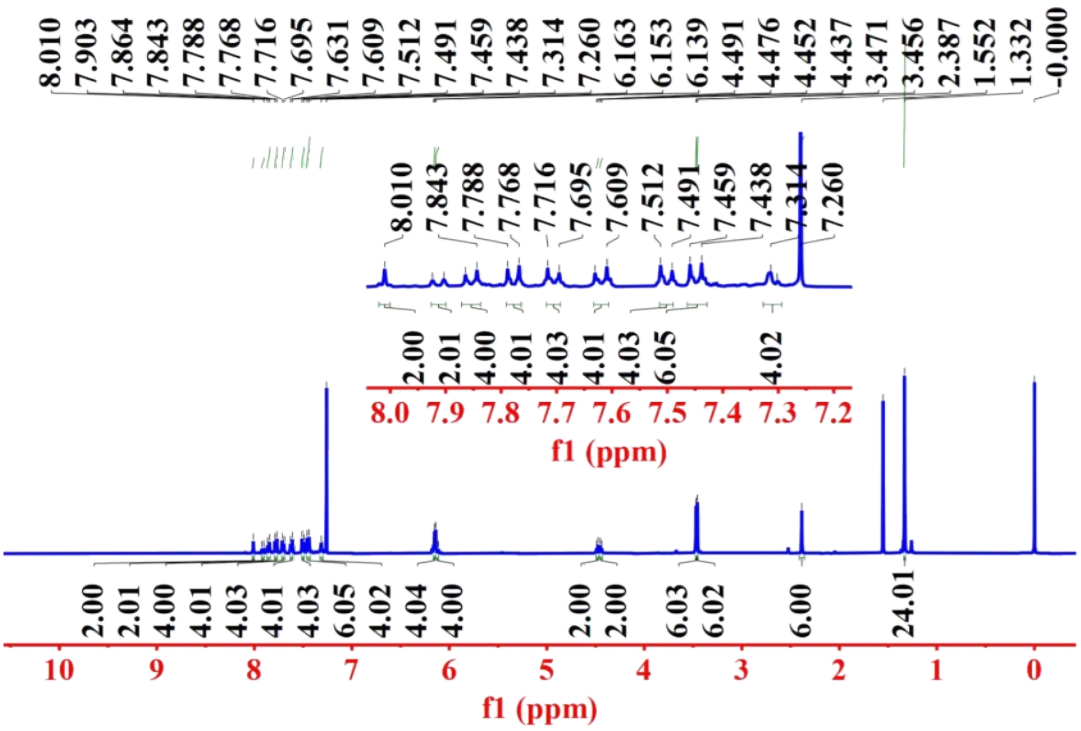

Figure S10. ^{1}H NMR spectrum (400 MHz) of compound **5** in $CDCl_3$.

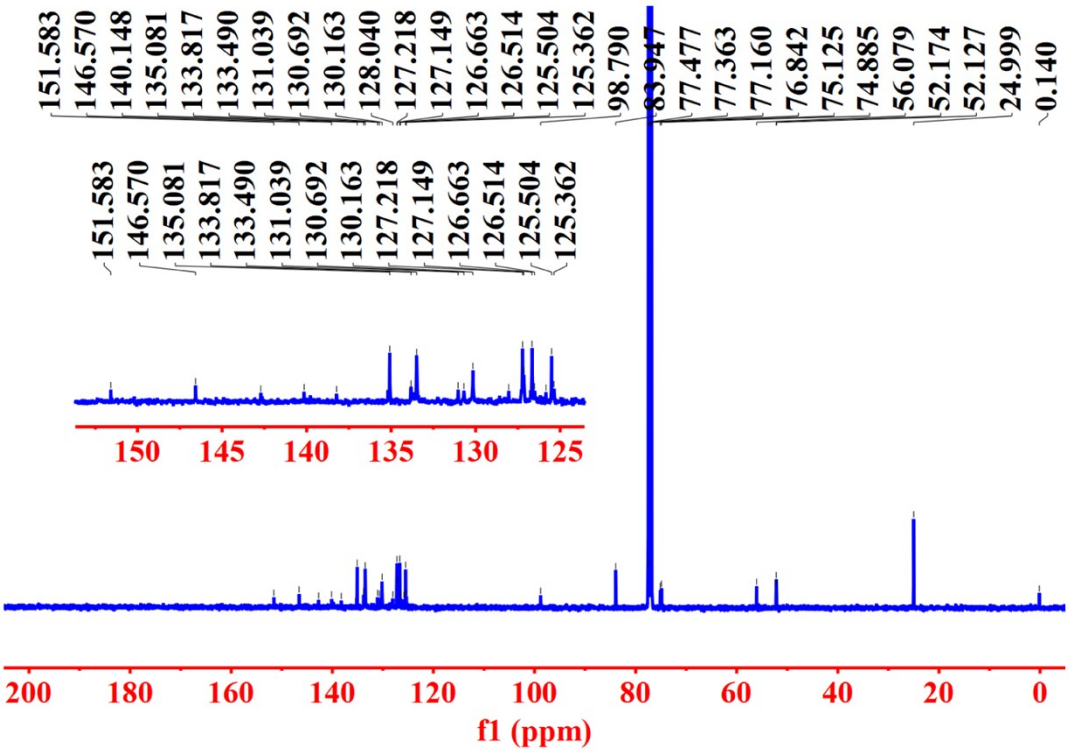

Figure S11. ^{13}C NMR spectrum of compound **5** in $CDCl_3$.

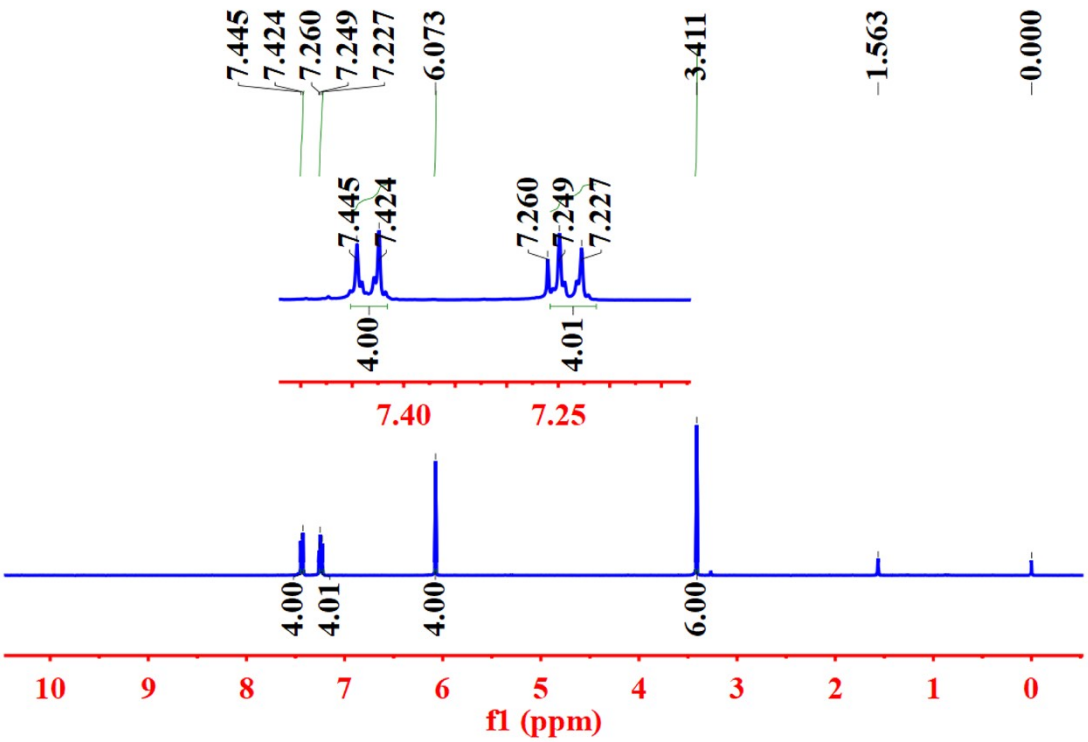

Figure S12. ^{1}H NMR spectrum (400 MHz) of compound **6** in $CDCl_3$.

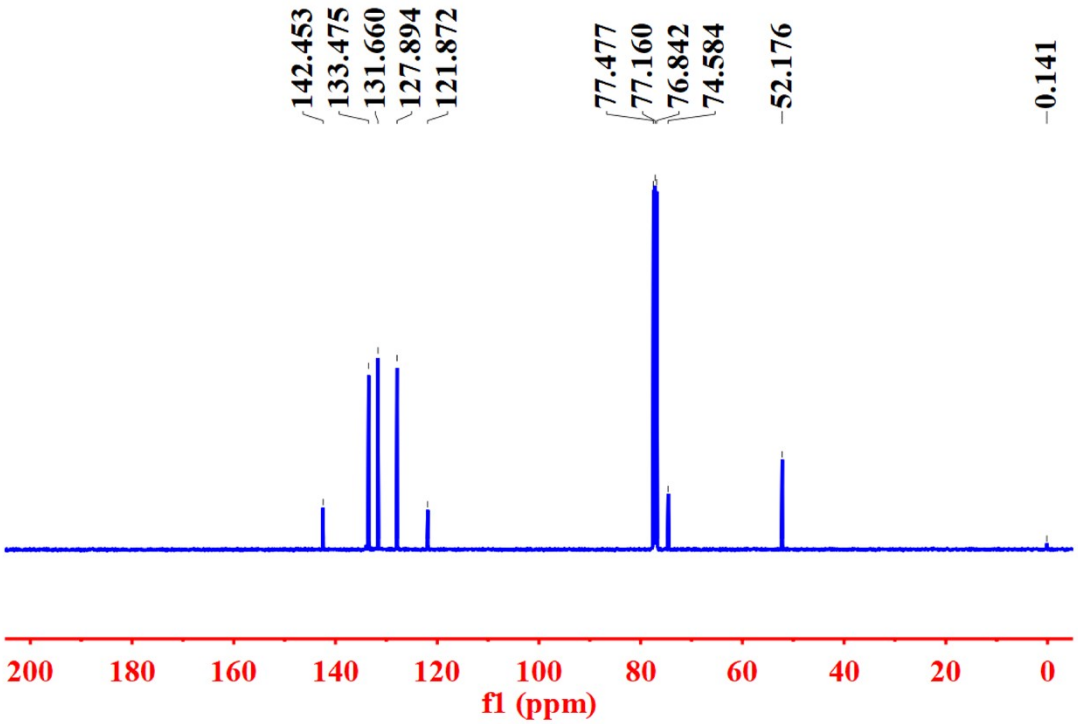

Figure S13. ^{13}C NMR spectrum of compound **6** in $CDCl_3$.

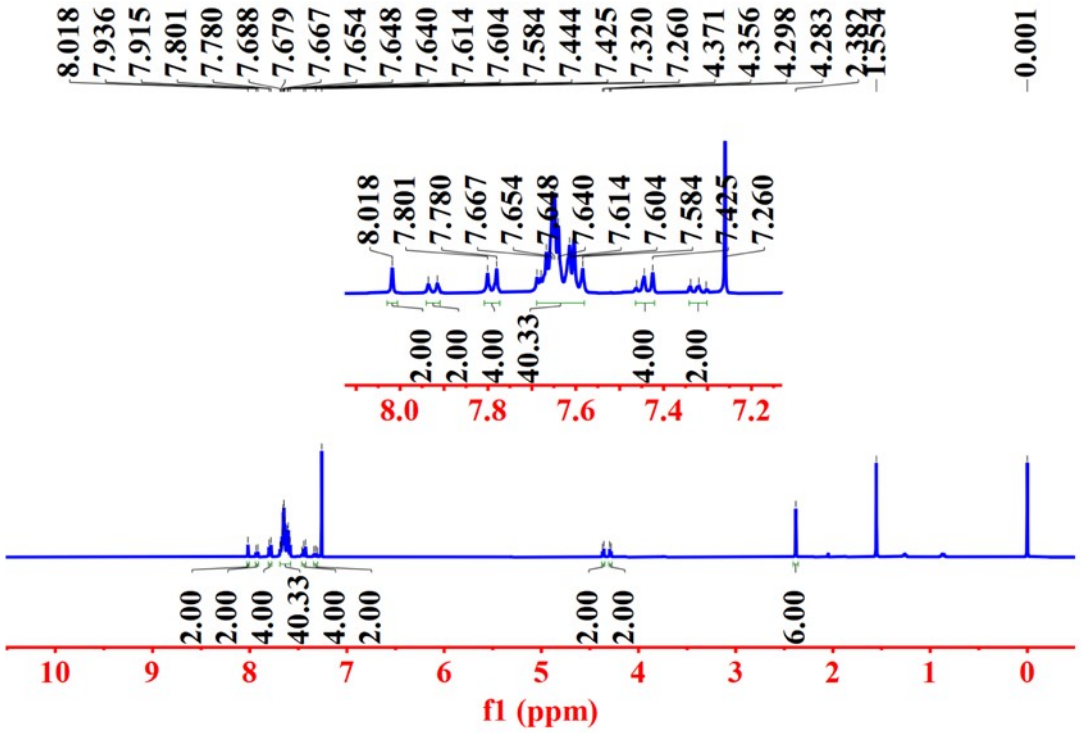

Figure S14. ^{1}H NMR spectrum (400 MHz) of **MBCM** in $CDCl_3$.

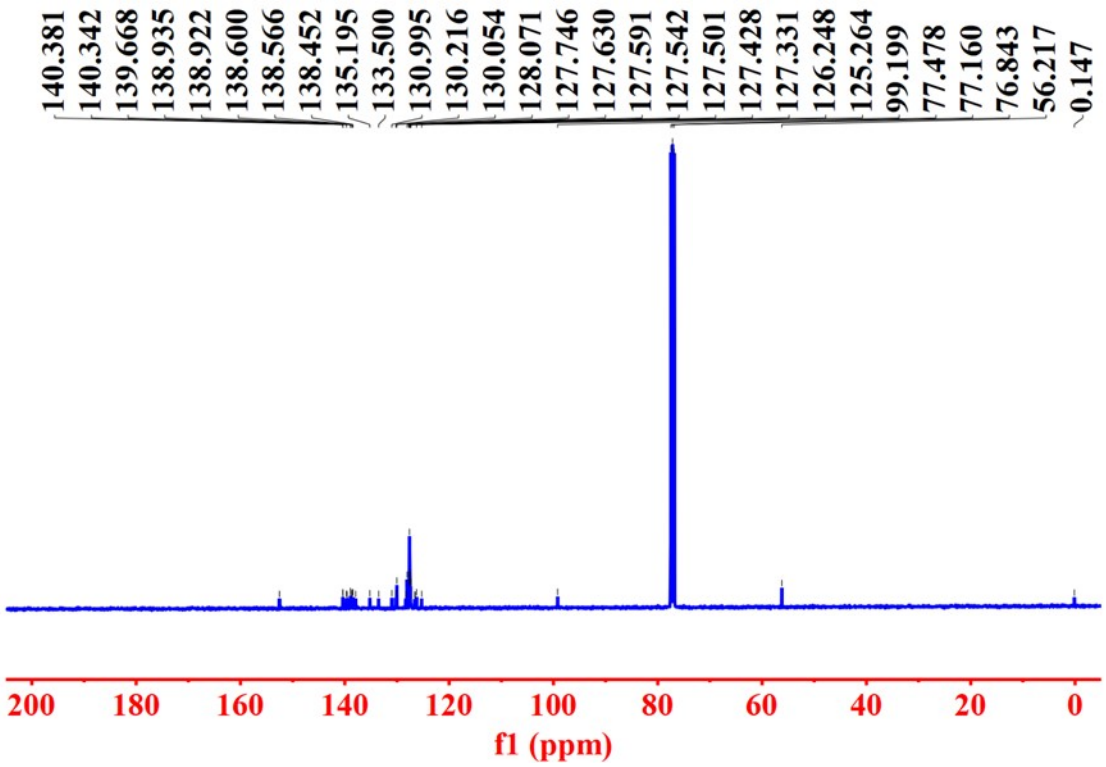

Figure S15. ^{13}C NMR spectrum of **MBCM** in $CDCl_3$.

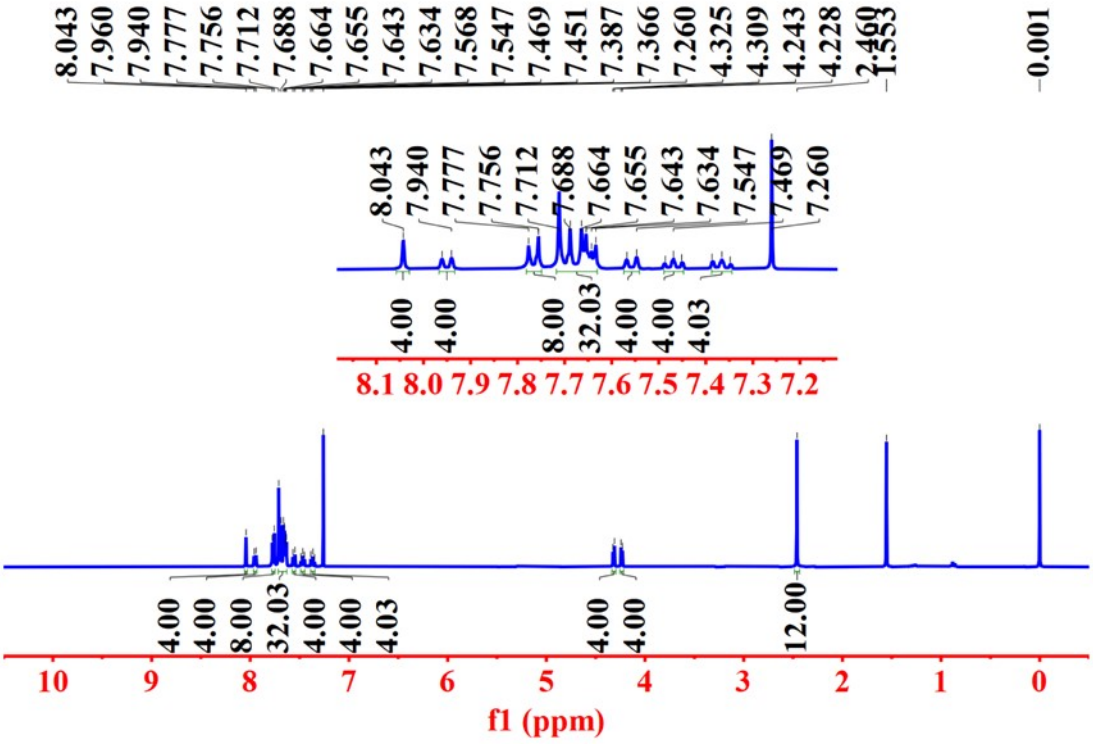

Figure S16. ^{1}H NMR spectrum (400 MHz) of **BBCM** in $CDCl_3$.

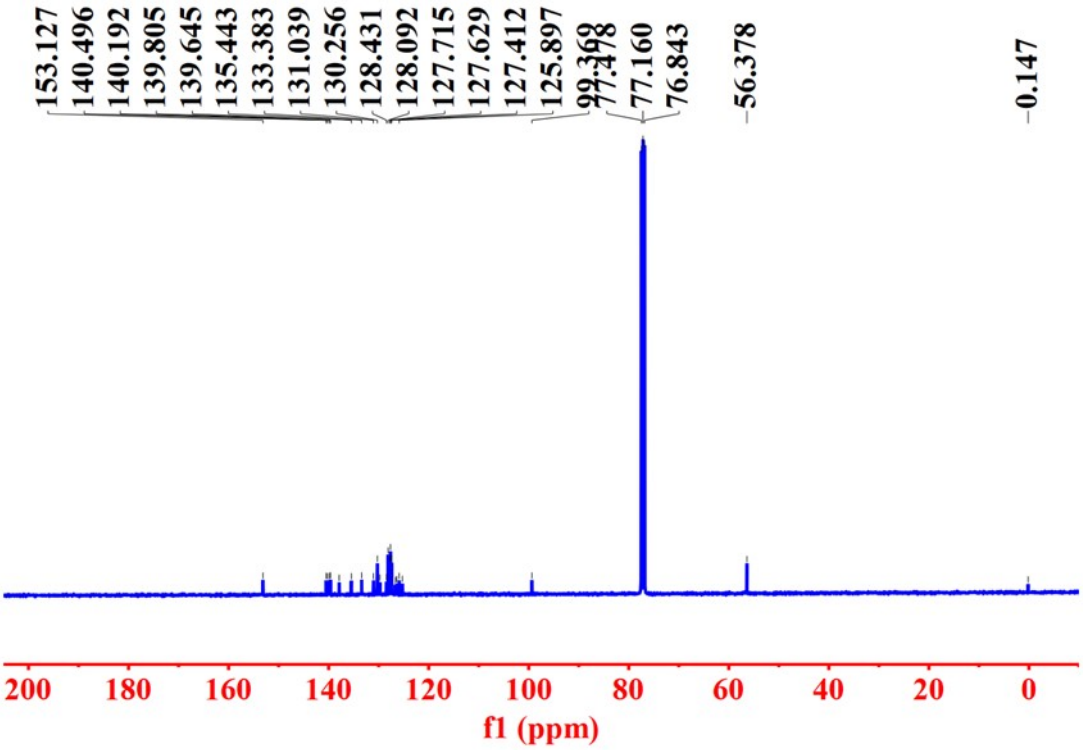

Figure S17. ^{13}C NMR spectrum of **BBCM** in $CDCl_3$.

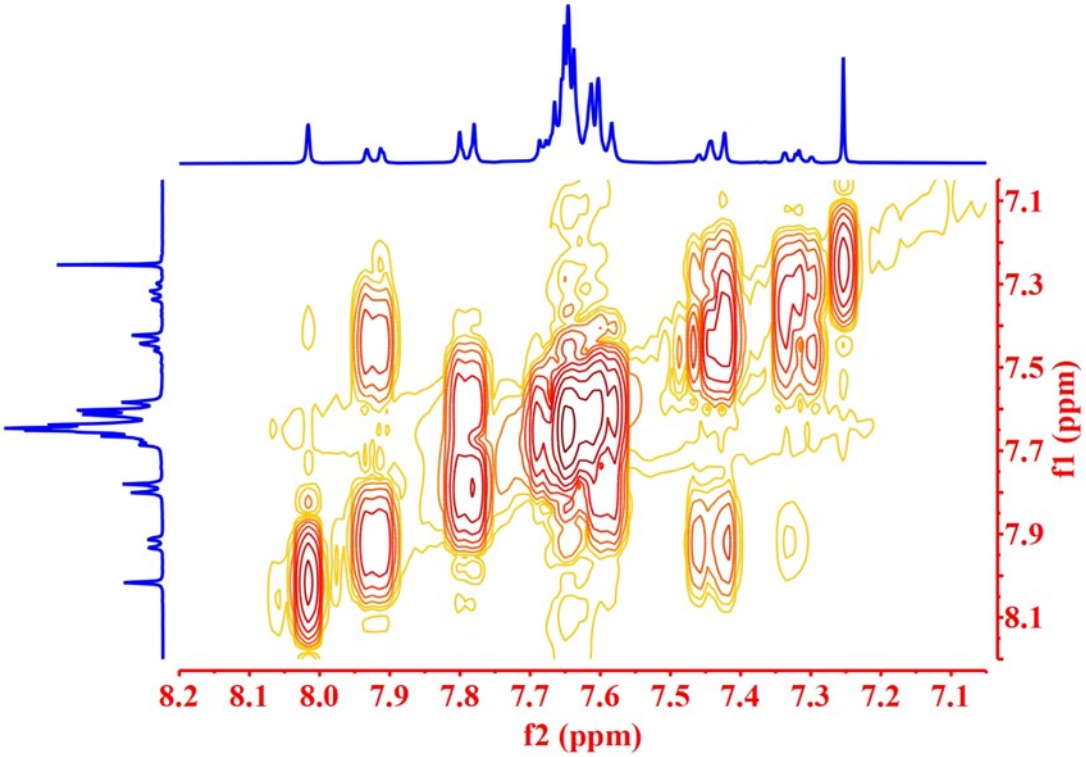

Figure S18. Expanded 2D ^{1}H-^{1}H COSY NMR spectrum (400 MHz) of **MBCM** in $CDCl_3$.

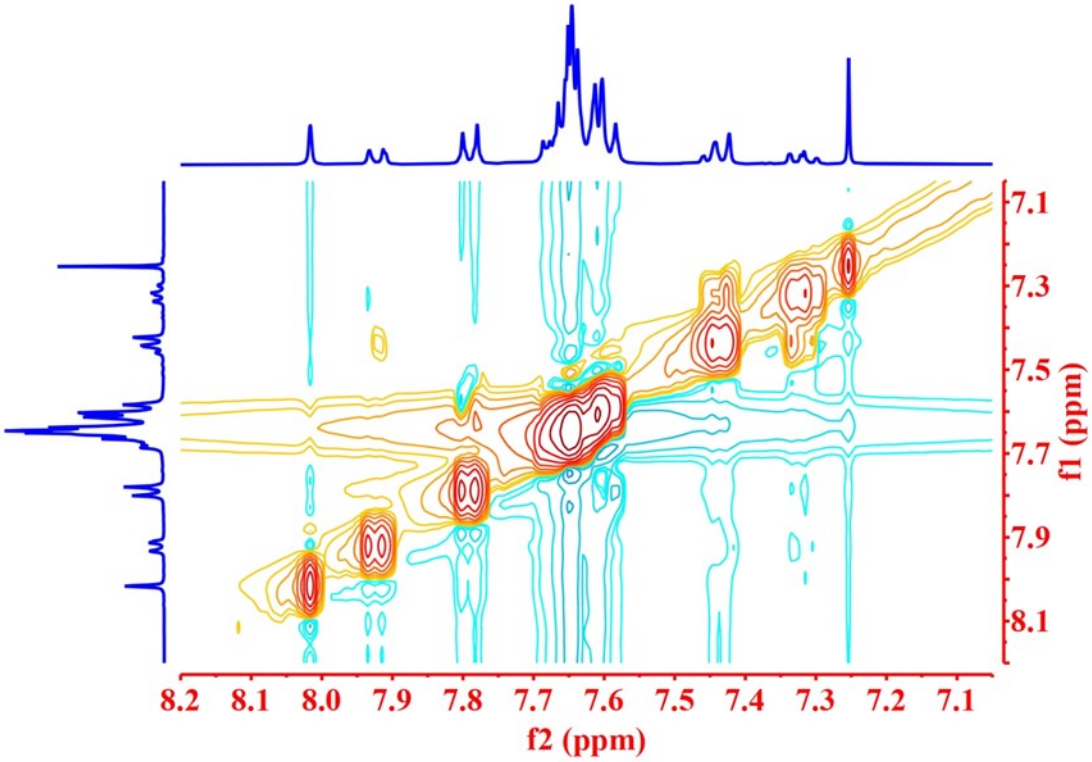

Figure S19. Expanded 2D ^{1}H-^{1}H NOESY NMR spectrum (400 MHz) of **MBCM** in $CDCl_3$.

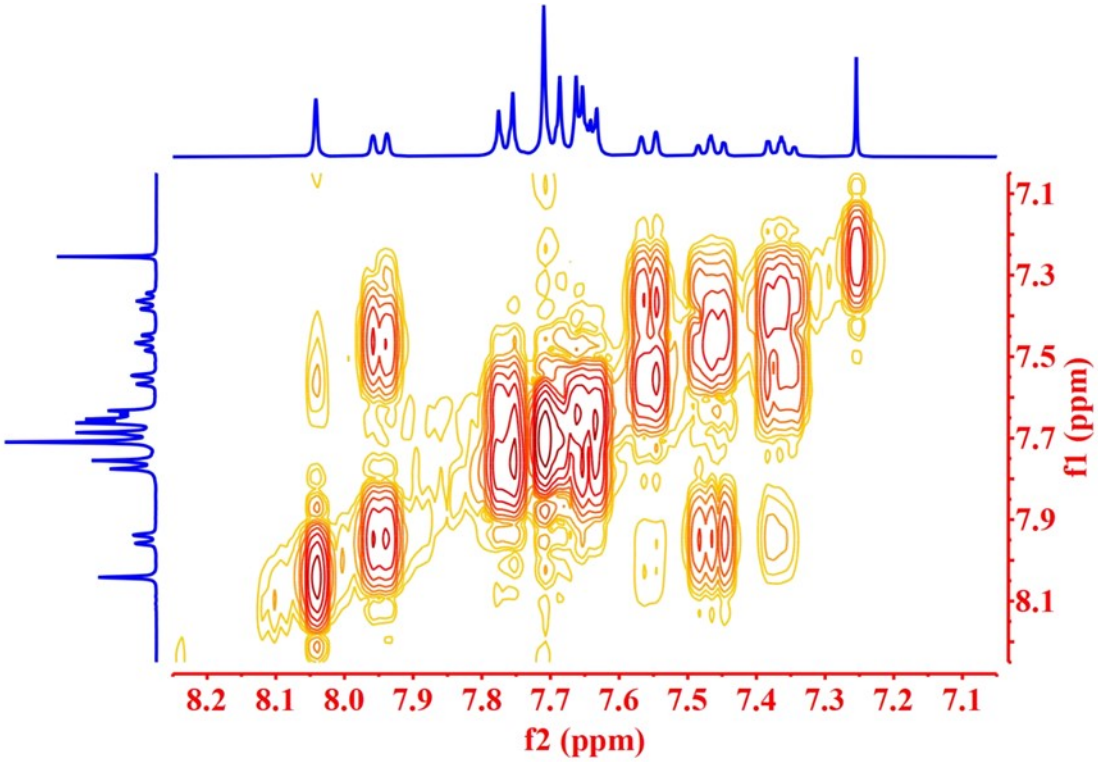

Figure S20. Expanded 2D ^{1}H-^{1}H COSY NMR spectrum (400 MHz) of **BBCM** in $CDCl_3$.

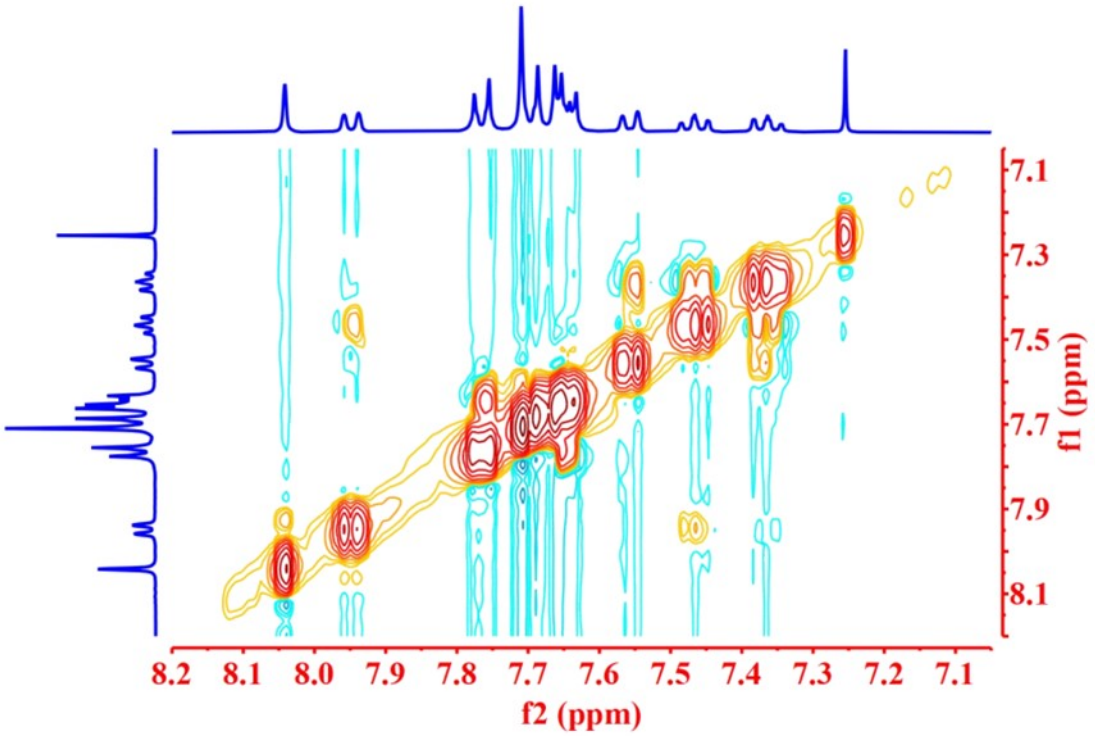

Figure S21. Expanded 2D ^{1}H-^{1}H NOESY NMR spectrum (400 MHz) of **BBCM** in $CDCl_3$.

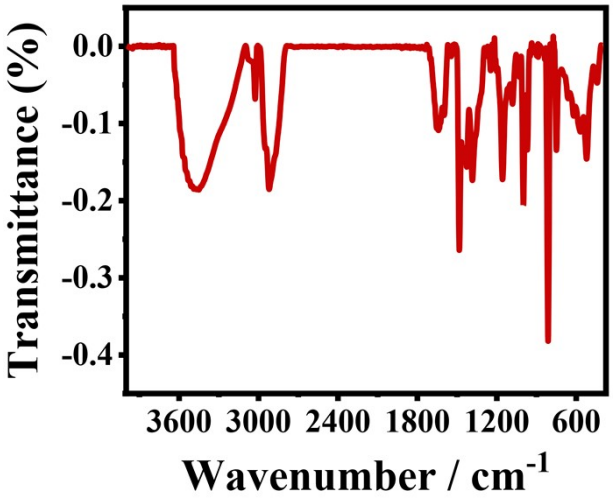

Figure S22. FTIR spectrum of **MBCM**.

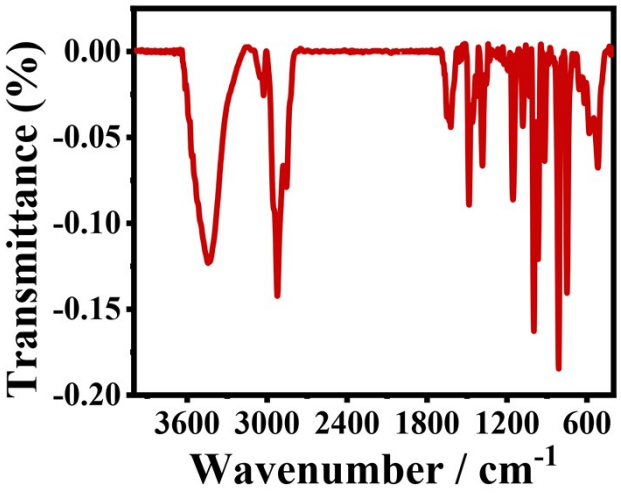

Figure S23. FTIR spectrum of **BBCM**.

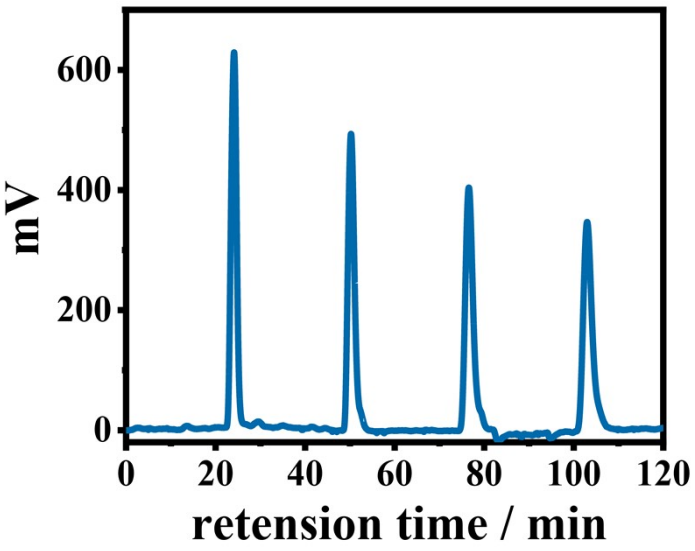

Figure S24. HPLC analysis for compound **3** with COSMOSIL Cholester column. Chromatographic conditions: flow rate = 1 mL/min, eluent = toluene/acetonitrile (1/1), UV detector = 280 nm.

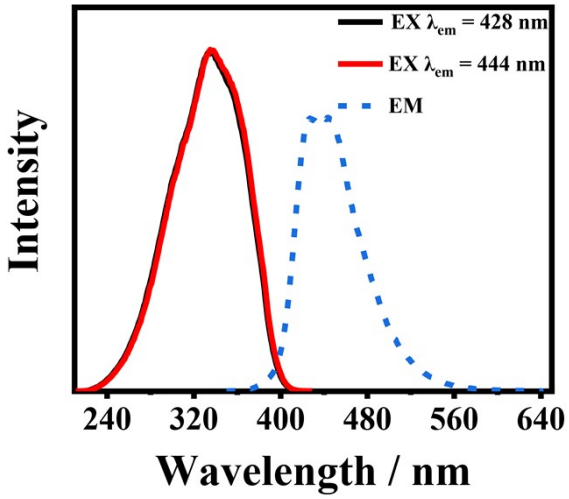

Figure S25. Emission spectrum (λ_{ex} = 330 nm) and excitation spectra ($\lambda_{em,\ black}$ = 428 nm; $\lambda_{em,\ red}$ = 444 nm) of **MBCM** (5.0×10^{-6} M).

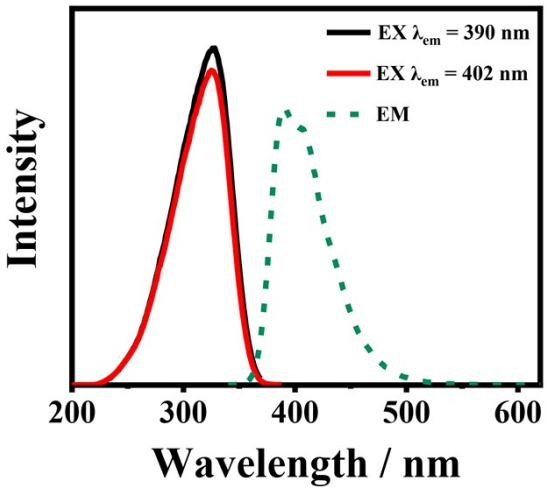

Figure S26. Emission spectrum (λ_{ex} = 320 nm) and excitation spectra ($\lambda_{em,\ black}$ = 390 nm; $\lambda_{em,\ red}$ = 402 nm) of **BBCM** (5.0×10^{-6} M).

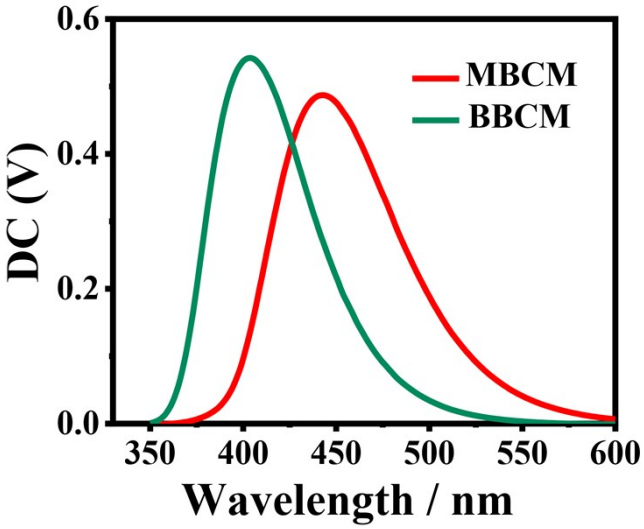

Figure S27. CPL emissions of **MBCM** (red) and **BBCM** (green) in CH_2Cl_2 (c = 1 × 10^{-5} M). Imaging condition: Excitation wavelength 300 nm, HT volt 443 V.

4. X-ray single crystal data of MBCM

Table S1. Crystal data, data collection and refinement of **MBCM**.

Complex	**MBCM + Solvent**
Formular	$C_{90}H_{64}O_4$ 1.5[CH_2Cl_2] 0.5[CH_2Cl_2]
Formular weight	1377.99
Temperature/K	100(2)
Crystal system	triclinic
Space group	P1
a / Å	12.816
b / Å	15.390
c / Å	20.122
α / deg	107.32
β / deg	108.42
γ / deg	92.58
Volume/$Å^3$	3552.1
Z	2
$\rho_{calc}g/cm^3$	1.131
μ/mm-1	0.068
F(000)	1272
Radiation	synchrotron
2Θ range for data collection/°	2.26 to 48.274
Reflections collected	10325
Data/restraints/parameters	10325/299/1770
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0593, wR_2 = 0.1610
Final R indexes [all data]	R_1 = 0.0612, wR_2 = 0.1641
Largest diff. peak/hole / e $Å^{-3}$	0.53/-0.34

5. References

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