Electronic Supplementary Information

Iridium(III)-Catalyzed One-Pot Synthesis of Planar Chiral Emissive Materials through C−H Activation

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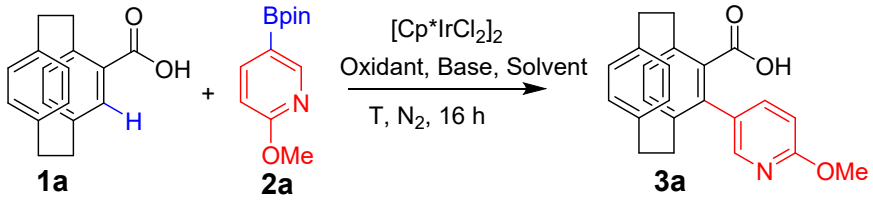
1. General Information

All solvents were used as received from commercial sources without further purification. Column flash chromatography was carried out on silica gel (200 – 400 mesh). Thin-layer chromatography (TLC) was performed on silica gel GF254. Reagents used to prepare the substrates and heteroaryl boron esters were purchased from Bidepharm and Energy Chemical without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-DRX (500 MHz and 126 MHz, respectively) instruments internally referenced to $SiMe_4$, chloroform signals. HRMS spectra were recorded on an Agilent 100 ABI-API4000 spectrometer. X-ray data were collected on Bruker Smart APEX II CCD diffractometer. The optical rotation measurements were recorded on an SGW®-2 automatic digital polarimeter (MA, China) at 589 nm wavelengths and at 28 °C by using DCM as the solvent (1 mg/mL). Chiral HPLC analysis of (R_p)/(S_p)-**1a**, **3a**, **3c**, **3h**, **3o**, and **3p** were performed using the Waters e2695 HPLC system with 2998PDA detector and CHIRALPAK IA column (250 × 4.6 mm, 5 μm) or CHIRALPAK IC column (250 × 4.6 mm, 5 μm); Mobile phase: mixed solvents of hexane and *iso*-propanol with the ratio of 95% : 5% as an eluent for **1a**, **3a**, and **3h**, 75% : 25% as an eluent for **3c**, 93% : 7% as an eluent for **3o**, and 98% : 2% as an eluent for **3p**; Flow rate: 1.0 mL/min for **1a**, **3a**, **3c**, **3h**, **3o**, and **3p**; Column temperature: 20 ℃ for **1a**; 35 ℃ for **3a**, **3c**, and **3h**; 30 ℃ for **3o** and **3p**. The absorbance spectra measurement was performed on a T9CS UV–vis spectrophotometer (Persee Instrument Co., Ltd. Beijing, China). The fluorescence spectra were measured on F-7100 (Hitachi, Japan) fluorescence spectrofluorometer (the pathlength of the quartz cell is 1 cm) with a xenon arc lamp as the light source. Circular dichroism (CD) spectra of (R_p)/(S_p)-**3a**, (R_p)/(S_p)-**3c**, (R_p)/(S_p)-**3h**, (R_p)/(S_p)-**3o**, and (R_p)/(S_p)-**3p** in THF solution (5.0×10^{-5} mol/L) were measured using a J-810-150s spectropolarimeter (JASCO J-1500·spectrophotometer, Japan), at room temperature (cell length: 10 mm, bandwidth: 1 nm, scanning speed: 100 nm/min, data pitch: 1 nm, accumulations: 2). The CD spectra were approximated using the simple moving average (SMA) method. Circularly polarized luminescence (CPL) spectra in THF solution (5.0×10^{-5} mol/L) and for (R_p)/(S_p)-**3a** and (R_p)/(S_p)-**3h** were recorded with a JASCO CPL-200 spectrofluoropolarimeter at room temperature. The CPL spectra were approximated using the SMA method. (λ_{ex} = 310 nm, cell length: 5 mm, E_x & E_m slit width: 3000 μm, scanning speed: 200 nm/min, data pitch: 1 nm, accumulations: 8).

2. Experimental Section

2.1 Optimization of Reaction Conditions

Table S1: Optimization of Reaction Conditions[a]



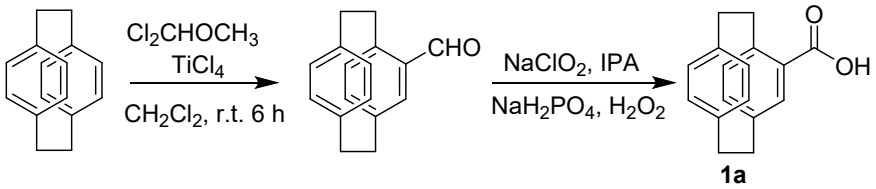
Entry	Oxidant	Base	Solvent	T (°C)	Yield (%)
1	Ag_2O	KH_2PO_4	THF	90	nr
2	Ag_2O	K_3PO_4	THF	90	nr
3	**Ag_2O**	**KOAc**	**THF**	**90**	**68**
4	Ag_2O	KF	THF	90	12
5	Ag_2O	K_2CO_3	THF	90	14
6	Ag_2O	$KHCO_3$	THF	90	10
7	Ag_2O	NaOAc	THF	90	45
8	Ag_2O	$NaHCO_3$	THF	90	14
9	Ag_2O	NaF	THF	90	13
10	Ag_2O	Li_2CO_3	THF	90	10
11	Ag_2O	LiOAc	THF	90	47
12	Ag_2O	LiF	THF	90	15
13	Ag_2O	Cs_2CO_3	THF	90	nr
14	Ag_2O	CsOAc	THF	90	50
15	PhCOOAg	KOAc	THF	90	nr
16	Ag_2CO_3	KOAc	THF	90	nr
17	AgOPiv	KOAc	THF	90	nr
18	AgOAc	KOAc	THF	90	nr
19	$AgNO_3$	KOAc	THF	90	nr
20	Ag_2SO_4	KOAc	THF	90	nr
21	AgF	KOAc	THF	90	nr
22	$AgNTf_2$	KOAc	THF	90	nr
23	Ag_2O	KOAc	Tol	90	35
24	Ag_2O	KOAc	1,4-Diox	90	57
25	Ag_2O	KOAc	DMSO	90	nr
26	Ag_2O	KOAc	DMF	90	nr
27	Ag_2O	KOAc	THF	130	67
28[b]	Ag_2O	KOAc	THF	90	41
29[c]	Ag_2O	KOAc	THF	90	nr
30[d]	-	KOAc	THF	90	nr

31[e]	Ag_2O	-	THF	90	nr
32[f]	Ag_2O	KOAc	THF	90	nr

[a]Reaction Conditions: **1a** (25.2 mg, 0.1 mmol), **2a** (47.0 mg, 0.2 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), Oxidant (0.2 mmol), Base (0.2 mmol), Solvent (2 mL), 90 °C, 16 h, Nitrogen atmosphere. Yields were analyzed by ^1H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard; [b]$[Cp^*Ir(MeCN)_3](SbF_6)_2$ (9.2 mg, 0.01 mmol) as the catalyst; [c]$[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol) as the catalyst; [d]Without Ag_2O; [e]Without KOAc; [f]Without the catalyst.

2.2 General Procedure for the Preparation of Substrates

I. The synthesis of the substrate 4-formyl[2.2]paracyclophane 1a.



Scheme S1. Synthetic routes for **1a**.

The synthesis of the substrate 4-formyl[2.2]paracyclophane.[1]

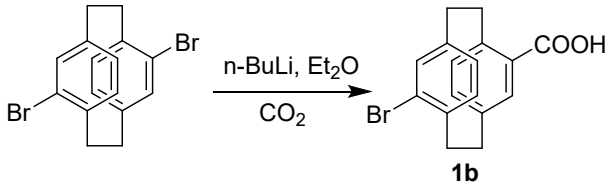
$TiCl_4$ (0.21 mL, 1.92 mmol) was added to a solution of [2.2]paracyclophane (0.20 g, 0.96 mmol) in dry DCM (20 mL). After the mixture was stirred at room temperature for 5 minutes, 1,1-dichlorodimethyl ether (93 μL, 1.06 mmol) was added, the resulting mixture was allowed to warm to room temperature. After stirring at r.t. for 6 h, the black solution was quenched by distilled water and stirred for 1 h until it became blue. The organic phase was separated and the aqueous phase was extracted with DCM (3 × 50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and gravity-filtered. The solvent was removed under reduced pressure and the crude product was purified via silica gel column chromatography using dichloromethane/petroleum ether (1:2) as the eluent. 4-Formyl[2.2]paracyclophane was isolated as amorphous white solid (0.22 g, 95% yield).

The synthesis of the substrate: 4-carboxy[2.2]paracyclophane 1a.[2]

4-Formyl[2.2]paracyclophane (0.17 g, 0.72 mmol) was dissolved in propan-2-ol (IPA) (10 mL). After the pH value of the mixed solution was adjusted to 4.5 by adding

sodium dihydrogen phosphate solution (8%), H_2O_2 (35%, 89 μL, 1.1 mmol) was added dropwise. Then, sodium chlorite solution (0.09 g, 2 mol/L) was added dropwise to the mixture over 30 min and the reaction mixture was stirred at room temperature for 12 h. The sodium sulfite was added to destroy the oxidant, then the organic solvent was removed under reduced pressure and the residuum was acidified with dilute sulfuric acid to pH = 3~4. The organic phase was separated, and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The organic solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (dichloromethane) to give the product **1a** (0.13 g, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.48 (s, 1H), 7.29 (d, J = 2.0 Hz, 1H), 6.72 (dd, J = 7.8, 2.0 Hz, 1H), 6.62 – 6.56 (m, 3H), 6.51 (ddt, J = 6.4, 4.6, 1.9 Hz, 2H), 4.21 (ddd, J = 12.9, 9.4, 2.3 Hz, 1H), 3.26 – 3.13 (m, 4H), 3.11 – 3.00 (m, 2H), 2.90 (ddd, J = 13.0, 10.0, 7.2 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 172.3, 143.8, 140.1, 140.0, 139.4, 137.4, 136.4, 136.2, 133.1, 132.8, 132.3, 131.8, 129.6, 36.3, 35.2, 35.1, 34.9. HRMS (ESI) m/z: Calcd for $C_{17}H_{16}O_2$: $[M+Na]^+$ 275.1043; Found: $[M+Na]^+$ 275.1038.

II. The synthesis of the substrate: 4-bromo-16-carboxy[2.2]paracyclophane 1b.[3]

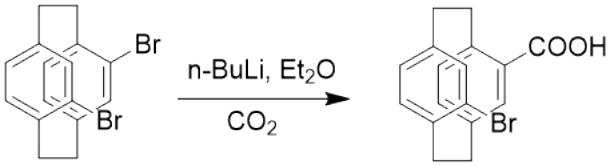


Scheme S2. Synthetic route for **1b**.

4,16-Dibromo-[2.2]paracyclophane (2.0 g, 5.5 mmol) was dissolved in Et_2O (30 mL), then at –78 ℃, n-butyllithium (3.3 mL, 2.8 M solution in hexane, 8.3 mmol) was added dropwise to the above-mixed solution under argon. The reaction mixture was stirred at room temperature for 2 h, then an excess of dry ice (10 g) was added. The resulting mixture was allowed to warm to room temperature, the organic solvent was removed under reduced pressure and the crude product was dissolved in H_2O (200 mL). The insoluble 4,16-dibromo-[2.2]paracyclophane was isolated by filtration and the aqueous phase was thoroughly washed with ether (3 × 50 mL) and CH_2Cl_2 (3 × 50 mL). The organic solvent was removed under reduced pressure to obtain final product **1b** (1.11 g, 61%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.60 (s, 1H), 7.21 (d, J = 7.6 Hz, 1H), 7.08 (d, J = 2.0 Hz, 1H), 6.63 (s, 1H), 6.51 (m, 3H), 4.02 (t, J = 11.2 Hz, 1H), 3.16 – 3.00 (m, 4H), 2.99 – 2.91 (m, 2H), 2.85 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, DMSO-

d_6): δ 168.7, 157.0, 142.4, 142.2, 139.3, 138.9, 137.0, 136.1, 135.2, 134.6, 132.0, 130.6, 127.1, 35.3, 34.8, 33.9, 33.0. HRMS (ESI) m/z: Calcd for $C_{17}H_{15}BrO_2$: $[M+K]^+$ 368.9887; Found: $[M+K]^+$ 368.9885.

III. The synthesis of the substrate: 4-bromo-12-carboxy[2.2]paracyclophane 1c.[3]

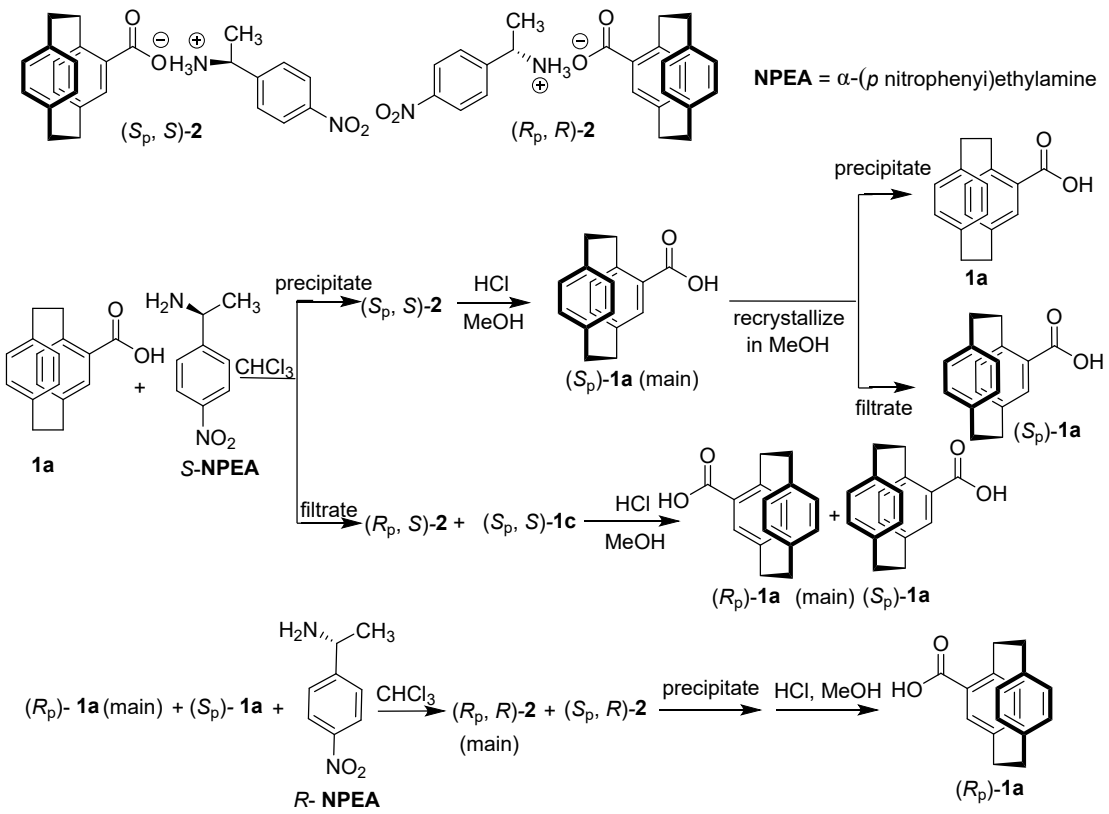


1c

Scheme S3. Synthetic route for **1c**.

White solid (0.93 g, 51%). The product **1c** was obtained by flash column chromatography on silica gel using petroleum ether/dichloromethane = 1:2 as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.60 (s, 1H), 7.93 (d, J = 1.9 Hz, 1H), 6.71 (dd, J = 7.9, 1.9 Hz, 1H), 6.69 – 6.63 (m, 2H), 6.61 (dd, J = 7.7, 1.8 Hz, 1H), 6.51 (d, J = 7.8 Hz, 1H), 4.23 – 4.15 (m, 1H), 3.54 – 3.47 (m, 1H), 3.27 (ddd, J = 13.2, 10.1, 6.8 Hz, 1H), 3.20 – 3.12 (m, 2H), 3.08 (m, 1H), 2.85 (dddd, J = 28.6, 13.4, 10.3, 7.1 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 171.5, 143.1, 142.1, 139.7, 139.0, 137.7, 136.2, 135.8, 135.0, 131.8, 131.1, 129.2, 126.8, 36.2, 35.8, 34.1, 32.5. HRMS (ESI) m/z: Calcd for $C_{17}H_{15}BrO_2$: $[M+H]^+$ 331.0328; Found: $[M+H]^+$ 331.0332.

IV. The synthesis of the substrate: (R_p)/(S_p)-4-carboxy[2.2]paracyclophane ((R_p)/(S_p)-1a).[4]



Scheme S4. Synthetic routes for (S_p)**-1a** and (R_p)**-1a**.

(*S*)-1-(4-Nitrophenyl)ethylamine hydrochloride ((*S*)-NPEA·HCl) (0.4 g, 1.9 mmol) was dissolved in ethanol and reacted with 30% sodium hydroxide solution and the reaction was monitored to be completed by TLC. The ethanol was removed under reduced pressure, and the aqueous phase was extracted with DCM (3 × 20 mL) and the combined organics was concentrated under reduced pressure to give (–)-(*S*)-NPEA (0.3 g, 80%). The (+)-(*R*)-NPEA (0.15g, 80%) was also synthesized following the above procedure.

The racemic **1a** (0.3 g, 1.2 mmol) and (–)-(*S*)-NPEA (0.2 g, 1.3 mmol) were dissolved in $CHCl_3$ (15 mL) and stirred at room temperature for 1 h. Then the reaction mixture was stirred at 50 ℃ for 2 h until the white solid precipitated from the solution. To complete sedimentation, the reaction mixture was stored overnight at –5 ℃. The precipitate was isolated by filtration and dried to obtain the main compound (S_p, *S*)**-2**. Then the main compound (S_p, *S*)**-2** was dissolved in methanol and hydrolyzed with 2 mol/L HCl. The precipitated solid was washed twice with H_2O (2 × 30 mL) to obtain the crude product and the crude product was recrystallized in methanol. The solid was

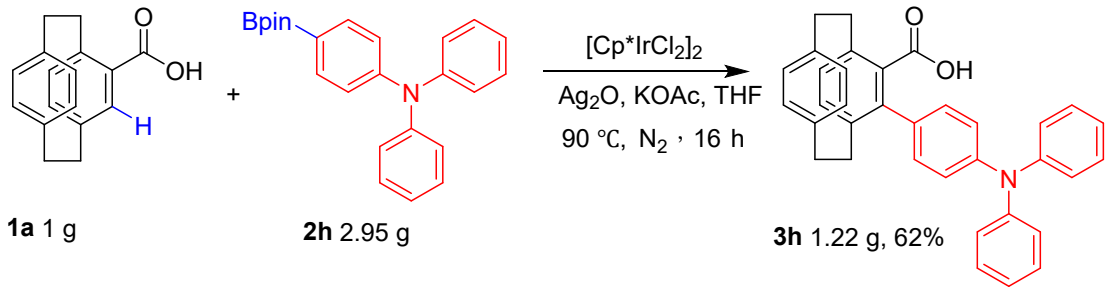
removed by suction filtration, and the filtrate was concentrated under reduced pressure to give pure (S_p)-**1a** (0.06 g, 20%), $[\alpha]_D^{25} = +147$ (c = 0.1, CH_2Cl_2).

The $CHCl_3$ filtrate was evaporated and hydrolyzed to obtain a partially resolved (R_p)-**1a**. The mixture of (R_p)-**1a** (main product) and (S_p)-**1a** (0.2 g, 0.8 mmol) and (+)-(*R*)-NPEA (0.15 g, 0.9 mmol) in $CHCl_3$ was stirred at room temperature for 1 h, then stirred at 50 ℃ for 2 h until the white optically pure diastereomers precipitated from the solution and stayed overnight at –5 ℃ to ensure enough diastereomer precipitation (R_p, *R*)-**2**. After recrystallization of (S_p, *S*)-**2** from ethanol and then hydrolysis, optically pure (R_p)-**1a** was obtained (0.09 g, 30%). $[\alpha]_D^{25} = -159$ (c = 0.1, CH_2Cl_2).

2.3 General Procedure for Ir(III)-Catalyzed C–H Arylation.[5]

To a 50 mL Schlenk-type sealed tube equipped with a magnetic stirring bar was added the substrate **1a** (0.1 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), 2-methoxypyridine boronic acid pinacol ester (0.2 mmol, 2 equiv), Ag_2O (46.0 mg, 0.2 mmol, 2 equiv), KOAc (19.6 mg, 0.2 mmol, 2 equiv) and dry THF (2.0 mL) under N_2 atmosphere. The tube was capped and subjected to a 90 °C preheated oil bath for 16 h. After cooling to room temperature, the reaction mixture was acidified with diluted hydrochloric acid (2 mol/L) to pH = 4~5. The filtrate was concentrated in vacuo to afford crude products, which was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the pure product **3a**.

2.4 Large-Scale Synthesis.

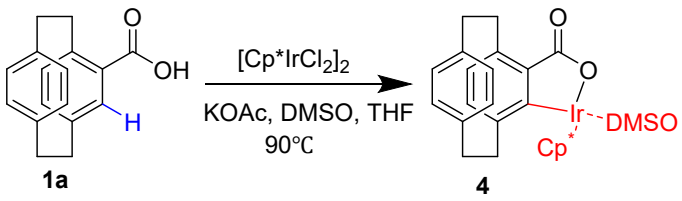


Scheme S5. Synthetic route for compound **3h**.

To a 50 mL three-necked flask with a magnetic stirring bar was added the substrate **1a** (1.0 g, 3.97 mmol), $[Cp^*IrCl_2]_2$ (0.16 g, 0.19 mmol, 0.05 equiv), **2h** (2.95 g, 7.94 mmol), Ag_2O (1.84 g, 7.94 mmol, 2 equiv), KOAc (0.78 g, 7.94 mmol, 2 equiv) and dry THF (40 mL) under N_2 atmosphere and subjected to a 90 °C preheated oil bath for

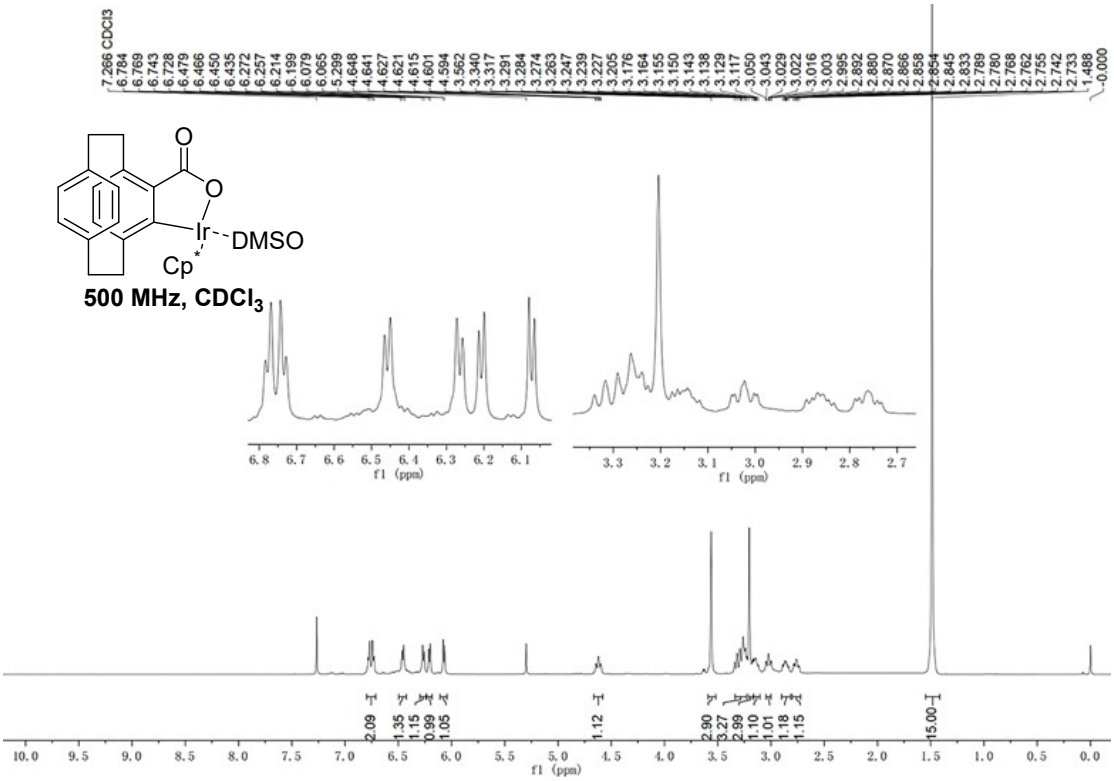
16 h. After cooling to room temperature, the reaction mixture was acidified with diluted hydrochloric acid (2 mol/L) to pH = 4~5, and then was filtered through a pad of Celite. The filtrate was concentrated in vacuo to afford crude products, which was purified by flash column chromatography on silica gel using dichloromethane/petroleum ether = 10:1 as the eluent to give the pure product **3h** (1.22 g, 62%).

3. Catalytic Activity of Intermediate 4



Scheme S6. Synthetic route for ntermediate **4**.

An oven-dried 25 mL Schlenk tube equipped with magnetic stirring bar was sequentially charged with **1a** (25.2 mg, 0.1 mmol), $[Cp^*IrCl_2]_2$ (40.0 mg, 0.05 mmol, 0.5 equiv), KOAc (19.6 mg, 0.2 mmol, 2 equiv), DMSO (14.2 μL, 0.2 mmol, 2 equiv) and THF (2 mL) in the air. The reaction mixture was stirred at 90 °C in oil bath for 2 h. A light yellow solid precipitate was formed, and the precipitate was isolated by filtration. The crude product was recrystallized in dichloromethane/petroleum ether and the intermediate **4** was collected as yellow solid (27 mg, 41%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.80 – 6.71 (m, 2H), 6.46 (d, J = 7.9 Hz, 1H), 6.26 (d, J = 7.8 Hz, 1H), 6.21 (d, J = 7.3 Hz, 1H), 6.07 (d, J = 7.3 Hz, 1H), 4.62 (m, 1H), 3.56 (s, 3H), 3.36 – 3.23 (m, 3H), 3.20 (s, 3H), 3.14 (m, 1H), 3.05 – 3.00 (m, 1H), 2.86 (ddd, J = 12.7, 10.5, 5.9 Hz, 1H), 2.80 – 2.72 (m, 1H), 1.49 (s, 15H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 184.3, 144.6, 144.4, 141.1, 140.6, 140.0, 134.8, 133.8, 133.3, 132.1, 132.0, 130.9, 130.6, 94.1, 49.9, 42.8, 36.1, 35.1, 34.9, 30.1, 8.9. HRMS (ESI) m/z: Calcd for $C_{27}H_{29}IrO_2$: $[M+K]^+$ 617.1428; Found: $[M+K]^+$ 617.1421.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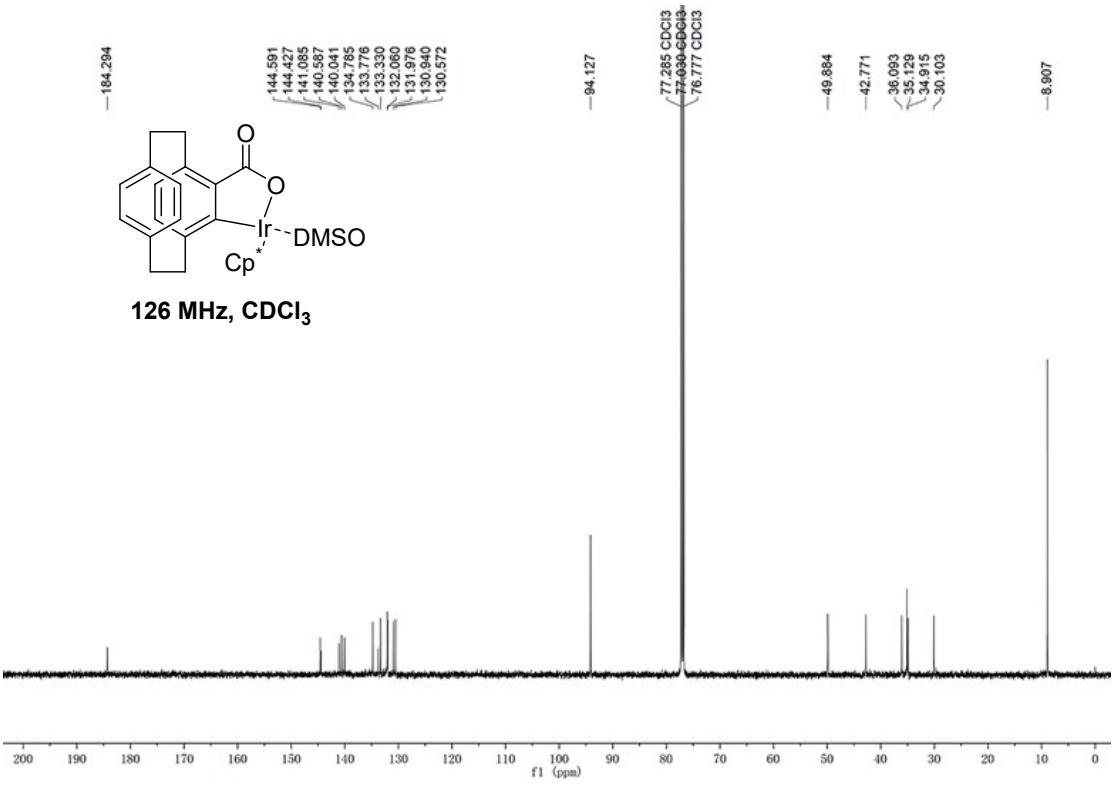
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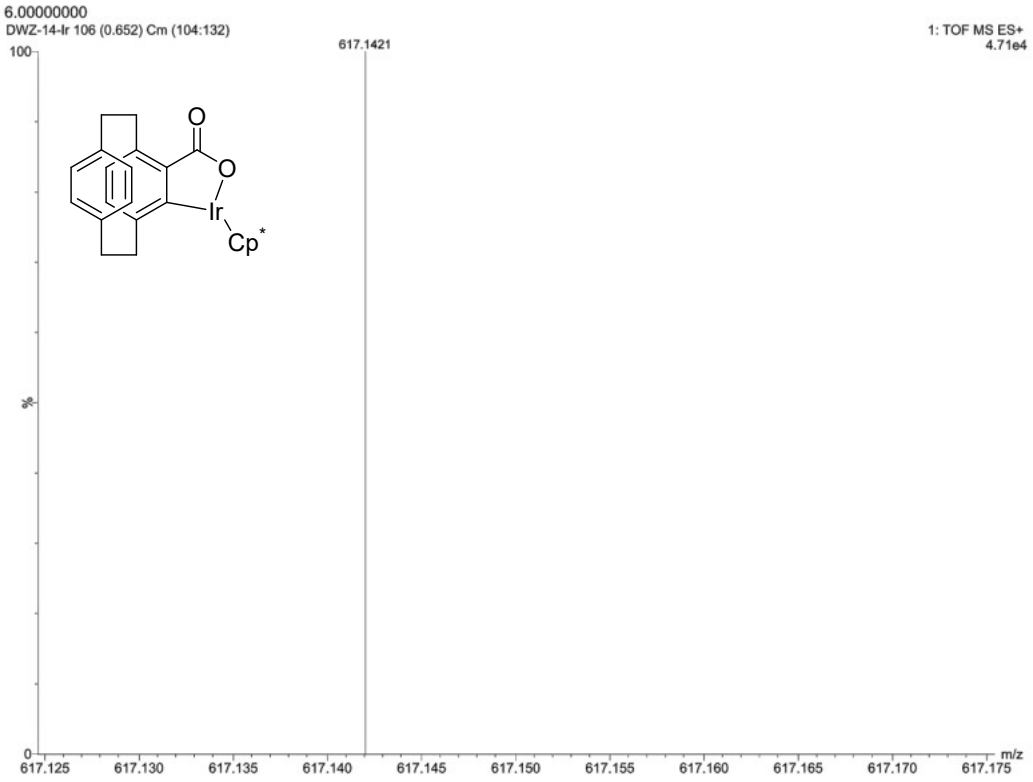
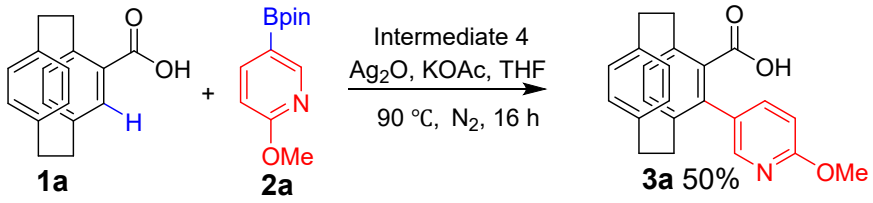


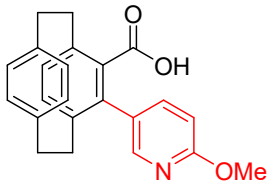
Intermediate 4 instead of $[Cp^*IrCl_2]_2$ was used in model reaction



Scheme S7. Synthetic route for **3a**.

To a 25 mL Schlenk-type sealed tube equipped with a magnetic stirring bar was added the substrate **1a** (25.2 mg, 0.1 mmol), intermediate **4** (6.6 mg, 0.01 mmol, 0.1 equiv), **2a** (47.0 mg, 0.2 mmol, 2 equiv), Ag_2O (46.4 mg, 0.2 mmol, 2 equiv), KOAc (19.6 mg, 0.2 mmol, 2 equiv), and dry THF (2 mL) under N_2 atmosphere. The tube was capped and subjected to a 90 °C preheated oil bath for 16 h. After cooling to room temperature, the reaction mixture was acidified with diluted hydrochloric acid (2 mol/L) to pH = 4~5, and then was filtered through a pad of Celite. The filtrate was concentrated in vacuo to afford crude products, which was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to obtain the desired product **3a** (18 mg, 50%).

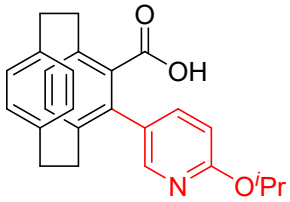
4. Characterization of New Compounds.



(R_p)/(S_p)-**3a**:

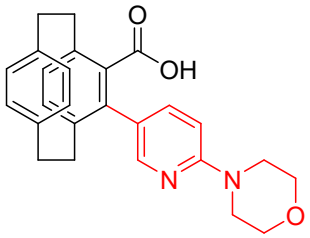
White solid (24.4 mg, 68%). The product **3a** was obtained by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 3:1 as the eluent. R_p $[\alpha]_D^{25}$ = +20.9 (c = 0.1, CH_2Cl_2), S_p $[\alpha]_D^{25}$ = −22.1 (c = 0.1, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.34 (s, 1H), 9.03 – 8.86 (m, 1H), 7.49 (d, J = 19.8 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 6.76 – 6.70 (m, 2H), 6.67 (dd, J = 7.8, 1.8 Hz, 1H), 6.59 (d, J = 7.8 Hz, 1H), 3.80 (s, 3H), 3.57 – 3.38 (m, 2H), 3.14 (t, J = 11.1 Hz, 1H), 3.05 – 2.80 (m, 5H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 171.2, 162.9, 145.7, 142.9, 140.4, 140.3, 139.2, 138.5, 136.9, 136.1, 134.9, 132.9, 132.1, 131.6, 130.6, 129.7, 129.4, 111.1, 54.2, 35.3, 34.8, 33.0, 29.7. HRMS (ESI) m/z: Calcd for $C_{23}H_{21}NO_3$: $[M+H]^+$ 360.1594; Found $[M+H]^+$ 360.1592.

The yields of the products (**3a**: 68%) was determined by ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as the internal standard.



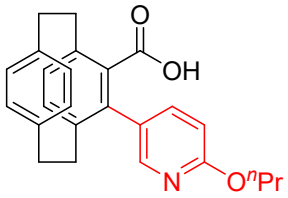
3b:

White solid (20.9 mg, 54%). The product **3b** was obtained by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 3:1 as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.97 (s, 1H), 8.95 (s, 1H), 7.55 – 7.34 (m, 2H), 6.76 (s, 1H), 6.64 (dd, J = 15.1, 7.8 Hz, 3H), 6.60 (d, J = 7.8 Hz, 1H), 6.51 (d, J = 7.9 Hz, 1H), 4.81 (s, 1H), 3.41 (s, 2H), 3.13 – 3.02 (m, 1H), 2.97 – 2.88 (m, 2H), 2.81 (m, 3H), 1.26 – 1.16 (m, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 171.1, 162.0, 145.9, 142.8, 140.9, 140.4, 139.2, 138.5, 136.9, 136.6, 134.8, 133.1, 132.9, 132.0, 131.7, 130.4, 129.9, 111.9, 68.9, 35.4, 34.8, 33.0, 29.7, 22.1. HRMS (ESI) m/z: Calcd for $C_{25}H_{25}NO_3$: $[M+H]^+$ 388.1907; Found: $[M+H]^+$ 388.1906.



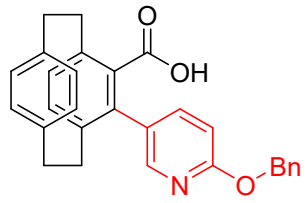
(R_p)/(S_p)-**3c**:

White solid (26.1 mg, 63%). The product **3c** was obtained by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 3:1 as the eluent. R_p $[\alpha]_D^{25}$ = 64.0 (c = 0.1, CH_2Cl_2), S_p $[\alpha]_D^{25}$ = −64.6 (c = 0.1, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (s, 1H), 7.40 (s, 2H), 6.82 – 6.67 (m, 4H), 6.65 (d, J = 7.8, 1H), 6.55 (d, J = 7.8 Hz, 1H), 3.74 (t, J = 5.0 Hz, 4H), 3.42 (m, 6H), 2.97 (t, J = 7.2 Hz, 2H), 2.87 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.5, 156.7, 145.8, 140.8, 139.2, 138.9, 138.2, 137.6, 135.7, 133.6, 131.8, 131.0, 130.6, 129.9, 128.9, 128.8, 125.2, 106.7, 65.5, 44.9, 41.0, 34.3, 33.8, 32.1, 28.7, 28.3. HRMS (ESI) m/z: Calcd for $C_{26}H_{26}N_2O_3$: $[M+H]^+$ 415.2016; Found: $[M+H]^+$ 415.2014.



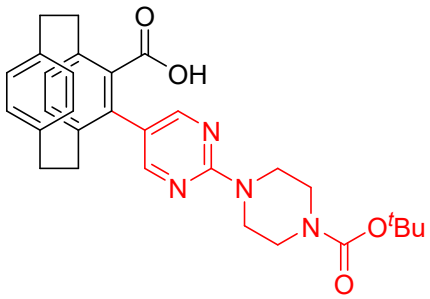
3d:

White solid (18.6 mg, 48%). The product **3d** was obtained by flash column chromatography on silica gel using dichloromethane/ethyl acetate = 10:1 as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.77 (s, 1H), 8.92 (s, 1H), 7.47 (s, 2H), 6.81 (d, J = 8.6 Hz, 2H), 6.76 – 6.69 (m, 2H), 6.66 (dd, J = 7.8, 1.9 Hz, 1H), 6.57 (d, J = 7.8 Hz, 1H), 4.12 (dt, J = 9.9, 6.5 Hz, 1H), 3.97 (s, 1H), 3.46 (t, J = 12.5Hz, 2H), 3.13 (t, J = 11.0 Hz, 1H), 3.05 – 2.95 (m, 2H), 2.89 (m, 3H), 1.34 – 1.23 (m, 2H), 0.93 (m, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 171.4, 162.8, 145.8, 142.8, 140.3, 140.3, 139.2, 138.5, 136.8, 136.3, 134.8, 132.9, 132.0, 131.6, 130.7, 129.8, 129.1, 111.2, 68.3, 35.4, 34.8, 33.0, 29.7, 22.2, 10.5. HRMS (ESI) m/z: Calcd for $C_{25}H_{25}NO_3$: $[M+H]^+$ 388.1907; Found: $[M+H]^+$ 388.1908.



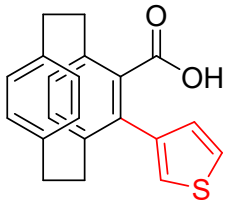
3e:

White solid (27.8 mg, 64%). The product **3e** was obtained by flash column chromatography on silica gel using petroleum ether/acetone = 8:1 as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.65 (s, 1H), 8.93 (s, 1H), 7.51 (s, 1H), 7.35 (m, 6H), 6.89 (d, J = 8.5 Hz, 1H), 6.81 (s, 1H), 6.75 – 6.69 (m, 2H), 6.66 (d, J = 7.8 Hz, 1H), 6.57 (d, J = 7.7 Hz, 1H), 5.29 (d, J = 11.2 Hz, 1H), 5.08 (s, 1H), 3.57 – 3.34 (m, 2H), 3.14 (t, J = 11.2 Hz, 1H), 2.94 (m, 5H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 171.7, 162.6, 145.7, 143.0, 140.1, 140.1, 139.3, 138.7, 137.0, 136.4, 136.1, 134.9, 133.0, 132.1, 131.6, 130.7, 130.6, 129.8, 128.5, 128.2, 128.1, 111.5, 68.8, 35.4, 34.9, 34.7, 33.1. HRMS (ESI) m/z: Calcd for $C_{29}H_{25}NO_3$: $[M+H]^+$ 436.1907; Found: $[M+H]^+$ 436.1911.



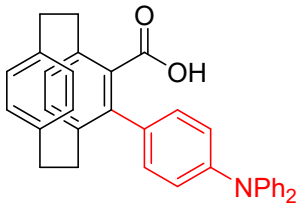
3f:

White solid (34.4 mg, 67%). The product **3f** was obtained by flash column chromatography on silica gel using petroleum ether/acetone = 8:1 as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.40 (s, 1H), 8.98 (s, 1H), 8.30 (m, 1H), 7.30 (dd, J = 7.9, 1.9 Hz, 1H), 6.76 (d, J = 7.8 Hz, 1H), 6.73 – 6.63 (m, 3H), 6.61 (d, J = 7.8 Hz, 1H), 3.74 (s, 4H), 3.53 – 3.37 (m, 6H), 3.14 (t, J = 11.2 Hz, 1H), 3.08 – 2.97 (m, 2H), 2.91 (m, 3H), 1.46 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 171.0, 159.5, 154.7, 140.5, 140.2, 139.2, 138.6, 137.0, 135.0, 133.4, 133.0, 132.3, 131.4, 130.6, 129.6, 122.5, 80.2, 43.9, 35.3, 34.8, 34.7, 33.1, 31.6, 28.4, 22.7, 14.1. HRMS (ESI) m/z: Calcd for $C_{30}H_{34}N_4O_4$: $[M+H]^+$ 515.2653; Found: $[M+H]^+$ 515.2654.



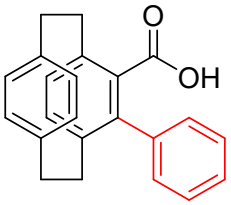
3g:

White solid (11.6 mg, 35%). The product **3g** was obtained by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 5:1 as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (dd, J = 5.0, 2.9 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.11 (d, J = 4.8 Hz, 1H), 6.94 (dd, J = 7.9, 1.9 Hz, 1H), 6.70 (dd, J = 7.8, 1.9 Hz, 1H), 6.68 – 6.62 (m, 2H), 6.57 (dd, J = 8.0, 1.9 Hz, 1H), 6.51 (d, J = 7.8 Hz, 1H), 3.31 (d, J = 9.1 Hz, 2H), 3.13 (t, J = 10.2 Hz, 1H), 3.03 (ddd, J = 14.9, 9.5, 5.9 Hz, 1H), 2.97 – 2.90 (m, 2H), 2.84 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.6, 147.6, 139.7, 139.7, 139.1, 138.7, 137.0, 134.1, 133.0, 132.9, 131.9, 131.5, 129.9, 129.3, 124.8, 123.2, 122.6, 35.2, 35.0, 34.4, 33.1. HRMS (ESI) m/z: Calcd for $C_{21}H_{18}O_2S$: $[M+H]^+$ 335.1100; Found: $[M+H]^+$ 335.1106.



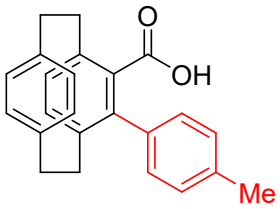
(R_p)/(S_p)-**3h**:

White solid (32.1 mg, 65%). The product **3h** was obtained by flash column chromatography on silica gel using dichloromethane/petroleum ether = 10:1 as the eluent. R_p $[\alpha]_D^{25}$ = 107 (c = 0.1, CH_2Cl_2), S_p $[\alpha]_D^{25}$ = −105 (c = 0.1, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.35 (m, 1H), 7.27 (m, 3H), 7.25 (s, 1H), 7.15 (d, J = 7.9 Hz, 4H), 7.09 (d, J = 8.1 Hz, 2H), 7.03 (t, J = 7.3 Hz, 3H), 6.88 (dd, J = 7.9, 1.8 Hz, 1H), 6.78 – 6.62 (m, 3H), 6.55 (dd, J = 7.9, 1.8 Hz, 1H), 6.48 (d, J = 7.8 Hz, 1H), 3.42 – 3.27 (m, 2H), 3.20 – 3.10 (m, 1H), 3.07 – 2.89 (m, 4H), 2.82 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.6, 147.6, 147.1, 147.1, 139.7, 139.7, 139.6, 139.1, 138.7, 138.7, 137.0, 134.1, 133.0, 132.9, 132.9, 131.9, 131.6, 131.5, 129.9, 129.5, 129.4, 129.3, 124.8, 123.2, 122.6, 35.2, 35.0, 34.4, 33.1. HRMS (ESI) m/z: Calcd for $C_{35}H_{29}NO_2$: $[M+H]^+$ 496.2271; Found: $[M+H]^+$ 496.2278.



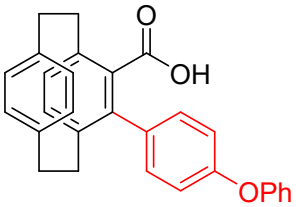
3i:

White solid (12.7 mg, 39%). The product **3i** was obtained by preparative thin-layer chromatography using dichloromethane/petroleum ether/triethylamine = 20:1:1 as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.49 – 7.25, (m, 3H), 7.07 (s, 1H), 6.86 (dd, J = 8.0, 1.8 Hz, 1H), 6.66 – 6.56 (m, 3H), 6.50 – 6.39 (m, 2H), 3.28 (m, 2H), 3.12 – 3.04 (m, 1H), 2.95 – 2.80 (m, 3H), 2.80 – 2.67 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 171.3, 138.8, 138.7, 138.6, 138.4, 138.1, 137.6, 137.2, 136.0, 133.3, 131.8, 130.9, 130.5, 128.9, 128.4, 127.4, 126.4, 34.2, 33.9, 33.3, 32.0. HRMS (ESI) m/z: Calcd for $C_{23}H_{20}O_2$: $[M+H]^+$ 329.1536; Found: $[M+H]^+$ 329.1544.



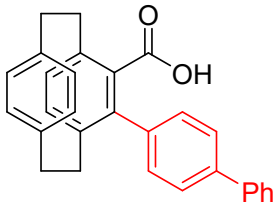
3j:

White solid (22.6 mg, 66%). The product **3j** was obtained by preparative thin-layer chromatography using dichloromethane/petroleum ether/triethylamine = 20:1:1 as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.19 (m, 2H), 6.98 (s, 1H), 6.84 (dd, J = 8.0, 1.0 Hz, 1H), 6.65 – 6.56 (m, 3H), 6.47 (d, J = 7.9 Hz, 1H), 6.43 (d, J =7.8 Hz, 1H), 3.31 – 3.22 (m, 2H), 3.07 (t, J = 10.6 Hz, 1H), 2.92 – 2.76 (m, 4H), 2.71 (ddd, J = 13.2, 9.8, 6.0 Hz, 1H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.3, 138.8, 138.7, 138.7, 138.0, 137.7, 136.1, 136.0, 135.4, 133.2, 131.8, 131.8, 130.8, 130.5, 128.9, 128.5, 128.1, 34.2, 33.9, 33.3, 32.0, 28.7. HRMS (ESI) m/z: Calcd for $C_{24}H_{22}O_2$: $[M+H]^+$ 343.1693; Found: $[M+H]^+$ 343.1692 .



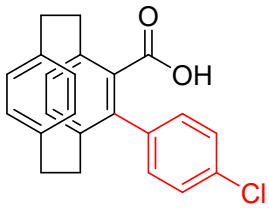
3k:

White solid (24.8 mg, 59%). The product **3k** was obtained by preparative thin-layer chromatography using dichloromethane/petroleum ether/triethylamine = 20:1:1 as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.29 (m, 1H), 7.26 (m, 1H), 7.18 (s, 1H), 7.03 (p, J = 11.4, 9.4 Hz, 5H), 6.83 (dd, J = 8.0, 1.8 Hz, 1H), 6.69 – 6.57 (m, 3H), 6.51 – 6.39 (m, 2H), 3.33 – 3.21 (m, 2H), 3.08 (q, J = 11.8, 11.1 Hz, 1H), 2.94 – 2.79 (m, 4H), 2.74 (ddd, J = 12.8, 9.4, 5.2 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 173.0, 155.9, 155.7, 138.7, 138.6, 138.3, 138.0, 137.7, 136.3, 136.1, 133.3, 133.2, 131.9, 130.9, 130.4, 128.8, 128.8, 128.5, 122.6, 118.4, 117.3, 34.2, 33.9, 33.3, 31.9. HRMS (ESI) m/z: Calcd for $C_{29}H_{24}O_3$: $[M+K]^+$ 459.1357; Found: $[M+K]^+$ 459.1352.



3l:

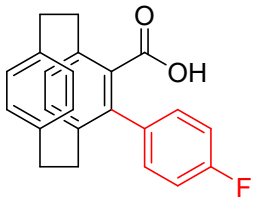
White solid (24.6 mg, 61%). The product **3l** was obtained by preparative thin-layer chromatography using dichloromethane/petroleum ether/triethylamine = 20:1:1 as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 7.8 Hz, 5H), 7.41 (s, 1H), 7.38 (s, 1H), 7.30 (t, J = 7.4 Hz, 1H), 7.18 (s, 1H), 6.85 (d, J = 7.5 Hz, 1H), 6.66 – 6.55 (m, 3H), 6.48 (d, J = 8.0 Hz, 1H), 6.42 (d, J = 7.8 Hz, 1H), 3.23 (m, 2H), 3.02 (t, J = 11.0 Hz, 1H), 2.95 – 2.87 (m, 2H), 2.81 (m, 2H), 2.76 – 2.68 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.6, 139.6, 139.0, 138.7, 138.6, 138.5, 138.2, 137.7, 137.6, 137.4, 136.1, 133.4, 131.8, 130.9, 130.5, 128.9, 128.4, 127.8, 126.4, 126.0, 126.0, 34.2, 33.9, 33.3, 32.0. HRMS (ESI) m/z: Calcd for $C_{29}H_{24}O_2$: $[M+K]^+$ 443.1408; Found: $[M+K]^+$ 443.1407.



3m:

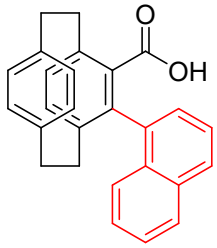
White solid (17.7 mg, 49%). The product **3m** was obtained by preparative thin-layer chromatography using dichloromethane/petroleum ether/triethylamine = 20:1:1 as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.25 (m, 3H), 7.02 (s, 1H), 6.81 (dd, J =

8.0, 1.9 Hz, 1H), 6.68 – 6.56 (m, 3H), 6.48 (dd, J = 8.0, 2 Hz, 1H), 6.43 (d, J = 7.5 Hz, 1H), 3.32 – 3.18 (m, 2H), 3.14 – 3.04 (m, 1H), 2.94 – 2.83 (m, 2H), 2.82 – 2.69 (m, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 172.9, 138.7, 138.5, 138.2, 137.6, 137.5, 136.9, 136.1, 133.6, 132.6, 131.9, 131.0, 130.4, 129.8, 128.7, 128.5, 127.6, 34.2, 33.9, 33.3, 31.9. HRMS (ESI) m/z: Calcd for $C_{23}H_{19}ClO_2$: $[M+H]^+$ 363.1146; Found: $[M+H]^+$ 363.1141.



3n:

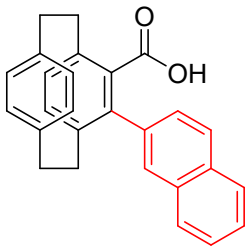
White solid (18.3 mg, 53%). The product **3n** was obtained by preparative thin-layer chromatography using dichloromethane/petroleum ether/triethylamine = 20:1:1 as the eluent. ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.05 (m, 3H), 6.83 (dd, J = 7.9, 1.8 Hz, 1H), 6.68 – 6.56 (m, 3H), 6.46 – 6.40 (m, 2H), 3.31 – 3.20 (m, 2H), 3.14 – 3.05 (m, 1H), 2.95 – 2.85 (m, 2H), 2.83 – 2.69 (m, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 172.3, 162.3, 160.3, 138.7, 138.6, 138.1, 137.7, 137.6, 136.1, 134.4, 134.4, 133.5, 131.9, 131.0, 130.4, 128.7, 128.6, 34.2, 33.9, 33.2, 31.9. HRMS (ESI) m/z: Calcd for $C_{23}H_{19}FO_2$: $[M+K]^+$ 385.1001; Found: $[M+K]^+$ 385.1005.



(R_p)/(S_p)-**3o**:

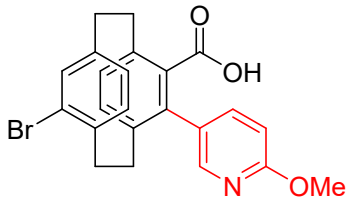
White solid (17.4 mg, 46%). The product **3o** was obtained by preparative thin-layer chromatography using dichloromethane/petroleum ether/triethylamine = 20:1:1 as the eluent. R_p $[\alpha]_D^{25}$ = 144 (c = 0.1, CH_2Cl_2), S_p $[\alpha]_D^{25}$ = −124 (c = 0.1, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (t, J = 7.2 Hz, 2H), 7.71 (d, J = 7.2 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 6.76 (d, J = 7.8 Hz, 1H), 6.69 (t, J = 7.2 Hz, 3H), 6.57 (d, J = 7.6 Hz, 1H), 3.40 – 3.25 (m, 2H), 3.13 (t, J = 11.0 Hz, 1H), 2.96 – 2.89 (m, 1H), 2.83 (m, 2H),

2.73 (m, 1H), 2.31 (ddd, J = 13.6, 9.7, 5.6 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 140.5, 140.0, 139.9, 135.8, 134.9, 134.8, 133.5, 132.9, 131.8, 131.5, 129.6, 128.1, 128.0, 126.9, 126.8, 126.2, 125.9, 125.8, 125.7, 125.3, 116.7, 113.9, 34.3, 33.0, 30.9, 29.7. HRMS (ESI) m/z: Calcd for $C_{27}H_{22}O_2$: $[M+H]^+$ 379.1693; Found: $[M+H]^+$ 379.1690.



(R_p)/(S_p)-**3p**:

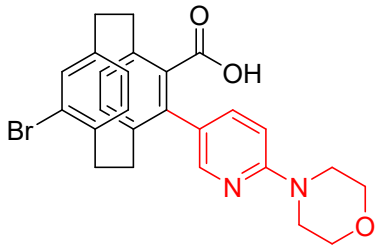
White solid (18.5 mg, 49%). The product **3p** was obtained by preparative thin-layer chromatography using dichloromethane/petroleum ether/triethylamine = 20:1:1 as the eluent. R_p $[\alpha]_D^{25}$ = 140 (c = 0.1, CH_2Cl_2), S_p $[\alpha]_D^{25}$ = −125 (c = 0.1, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03– 7.72 (m, 3H), 7.70– 7.18 (m, 4H), 6.89 (m, 1H), 6.64 (dd, J = 7.6, 2.0 Hz, 2H), 6.61– 6.38 (m, 3H), 3.20 (m, 2H), 3.04 (t, J = 10.3 Hz, 1H), 2.96 – 2.88 (m, 1H), 2.75 (ddd, J = 45.5, 12.9, 7.4 Hz, 4H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 172.9, 138.8, 138.6, 138.4, 138.0, 137.7, 136.2, 136.1, 136.0, 133.4, 132.4, 131.9, 131.5, 130.9, 130.5, 129.3, 128.7, 128.7, 127.3, 126.9, 126.7, 125.7, 125.2, 34.2, 33.9, 33.3, 32.1. HRMS (ESI) m/z: Calcd for $C_{27}H_{22}O_2$: $[M+H]^+$ 379.1693; Found: $[M+H]^+$ 379.1699.



3q:

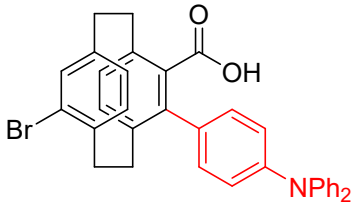
White solid (26.2 mg, 60%). The product **3q** was obtained by flash column chromatography on silica gel using petroleum ether/tetrahydrofuran = 3:1 as the eluent. ^{1}H NMR (500 MHz, THF-d_8) δ 8.24 – 7.20 (m, 2H), 7.21 (d, J = 7.8 Hz, 1H), 6.95 (dd, J = 7.8, 1.6 Hz, 1H), 6.68 (m, 2H), 6.42 (m, 2H), 3.82 (s, 3H), 3.25 – 3.19 (m, 1H), 3.16 (td, J = 11.2, 10.6, 3.9 Hz, 1H), 3.07 (ddd, J = 13.2, 9.8, 3.2 Hz, 1H), 2.98 – 2.92 (m, 2H), 2.90 (m, 1H), 2.82 (m, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, THF-d_8) δ 170.2, 163.2,

142.2, 138.5, 138.2, 138.2, 138.1, 138.0, 136.4, 136.0, 133.2, 132.7, 131.7, 131.3, 130.2, 128.4, 126.4, 109.9, 52.5, 34.0, 33.8, 33.2, 31.6. HRMS (ESI) m/z: Calcd for $C_{23}H_{20}BrNO_3$: $[M+H]^+$ 438.0699; Found: $[M+H]^+$ 438.0703.



3r:

White solid (28.5 mg, 58%). The product **3r** was obtained by flash column chromatography on silica gel using petroleum ether/ tetrahydrofuran = 3:1 as the eluent. ^{1}H NMR (500 MHz, THF-d_8) δ 10.86 (s, 1H), 7.01 (dd, J = 7.9, 1.8 Hz, 1H), 6.81 (d, J = 8.8 Hz, 1H), 6.70 (dd, J = 7.8, 2.9 Hz, 2H), 6.65 (dd, J = 7.8, 1.8 Hz, 1H), 6.49 (m, 2H), 5.79 (s, 1H), 3.78 (t, J = 4.8 Hz, 4H), 3.57 (m, 4H), 3.37–3.28 (m, 2H), 3.11 (m, 1H), 3.02 – 2.95 (m, 2H), 2.92 – 2.87 (m, 1H), 2.82 (dd, J = 10.4, 5.7 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, THF-d_8) δ 170.2, 158.2, 139.5, 139.3, 138.3, 138.2, 136.0, 135.9, 133.8, 132.6, 131.8, 131.7, 131.7, 131.6, 131.3, 129.5, 125.3, 105.4, 66.5, 45.4, 34.9, 34.6, 33.9, 32.8. HRMS (ESI) m/z: Calcd for $C_{26}H_{25}BrN_2O_3$: $[M+H]^+$ 493.1121; Found: $[M+H]^+$ 493.1118.

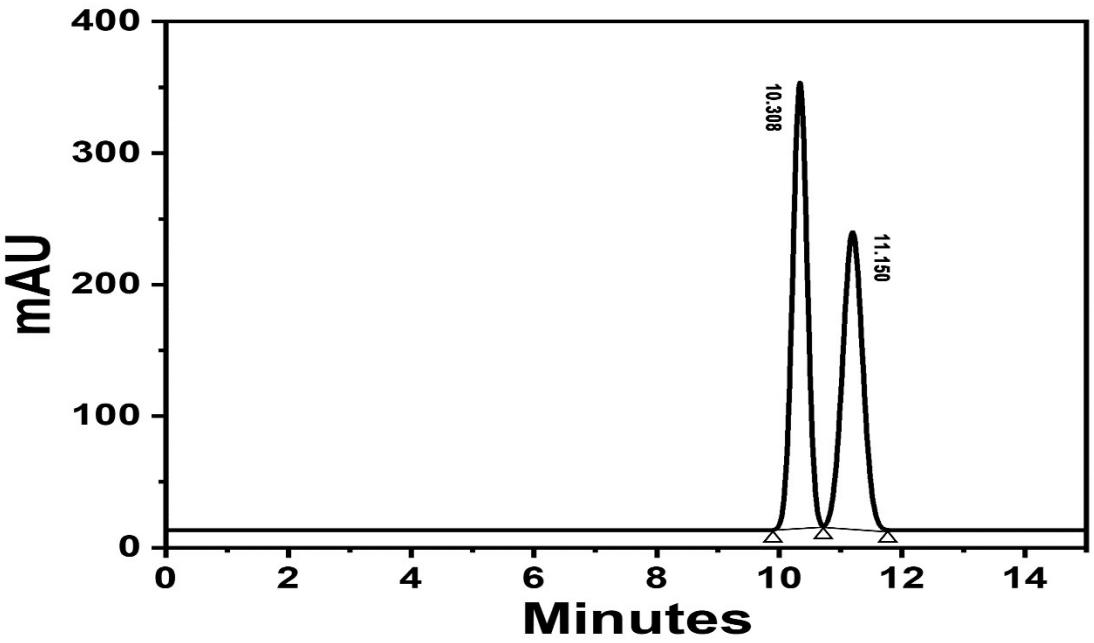


3s:

White solid (35.5 mg, 62%). The product **3s** was obtained by flash column chromatography on silica gel using petroleum ether/ tetrahydrofuran = 3:1 as the eluent. ^{1}H NMR (500 MHz, THF-d_8) δ 10.74 (s, 1H), 7.38 (s, 1H), 7.19 – 7.09 (m, 6H), 7.04 – 7.01 (m, 4H), 6.97 (d, J = 7.9 Hz, 2H), 6.94 – 6.88 (m, 3H), 6.67 (d, J = 1.7 Hz, 1H), 6.51 – 6.44 (m, 1H), 6.40 – 6.32 (m, 1H), 3.20 (td, J = 11.7, 11.0, 1.9 Hz, 1H), 3.17 – 3.07 (m, 2H), 3.06 – 2.96 (m, 2H), 2.95 – 2.91 (m, 1H), 2.90 – 2.86 (m, 1H), 2.80 (ddd, J = 11.9, 9.3, 4.0 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, THF-d_8) δ 170.4, 147.8, 146.8, 142.1, 139.2, 138.6, 137.9, 137.8, 136.8, 136.2, 136.0, 134.8, 134.1, 133.6, 132.7, 132.2, 131.6, 131.4, 130.2, 130.1, 129.1, 126.4, 124.5, 122.9, 122.4, 34.0, 33.9, 33.2,

31.9. HRMS (ESI) m/z: Calcd for $C_{35}H_{28}BrNO_2$: $[M+K]^+$ 612.0935; Found: $[M+K]^+$ 612.0931.

5. HPLC Chromatograms

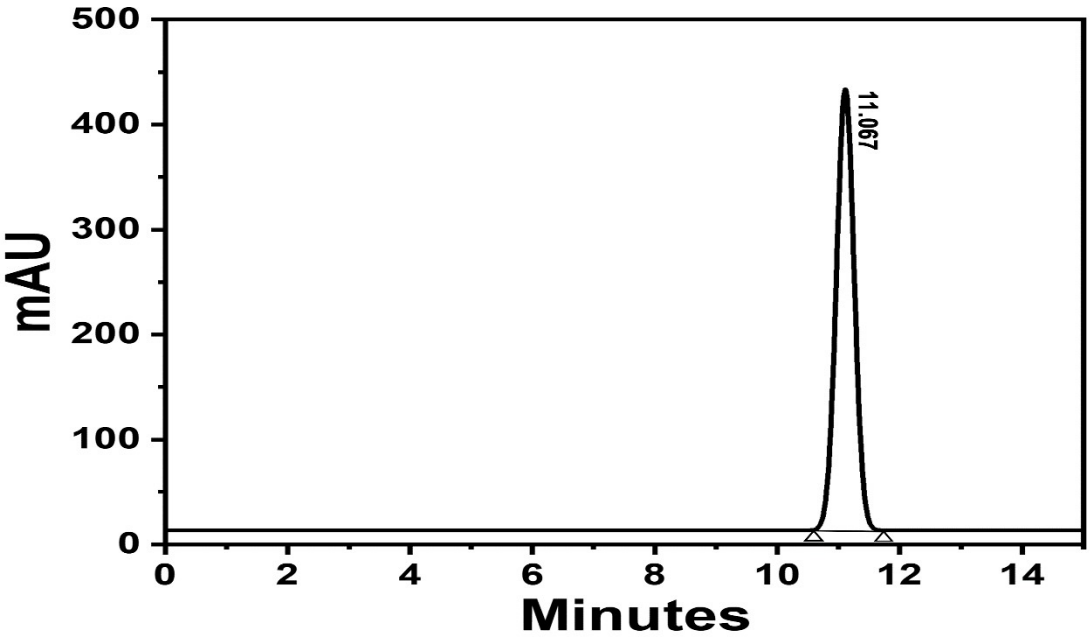


<Peak Table>

PDA Ch1 270 nm

Peak Name	Retention Time	Area	Peak Height	Area %
1	10.318	6218.754	358.413	51.017
2	11.150	5970.859	251.858	48.983
Total		12189.614	610.271	100.000

Figure S1. Chromatogram of the racemic of **1a**.

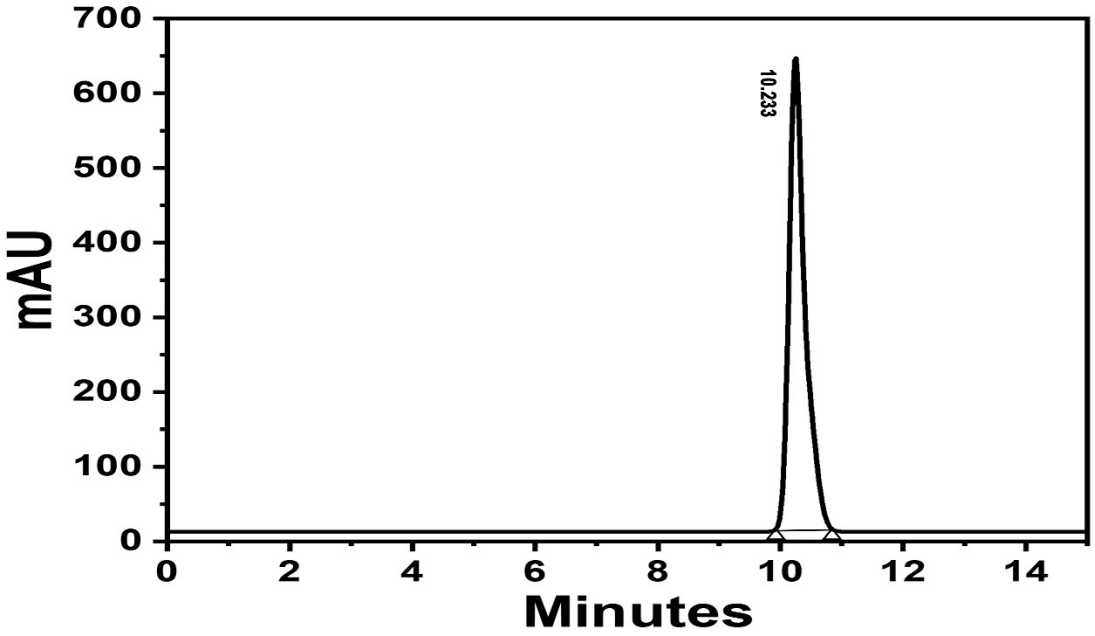


<Peak Table>

PDA Ch1 270 nm

Peak Name	Retention Time	Area	Peak Height	Area %
1	11.067	9714.872	445.415	100.000
Total		9714.872	445.415	100.000

Figure S2. Chromatogram of **(R_p)-1a**.

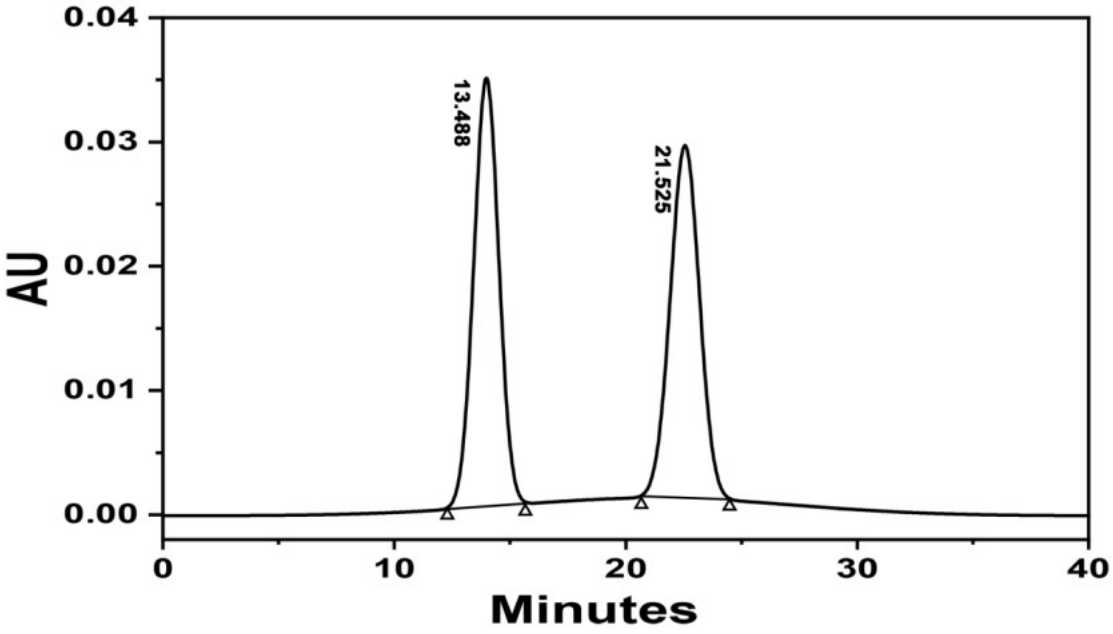


<Peak Table>

PDA Ch1 270 nm

Peak Name	Retention Time	Area	Peak Height	Area %
1	10.233	11455.167	626.811	100.000
Total		11455.167	626.811	100.000

Figure S3. Chromatogram of (S_p)**-1a**.

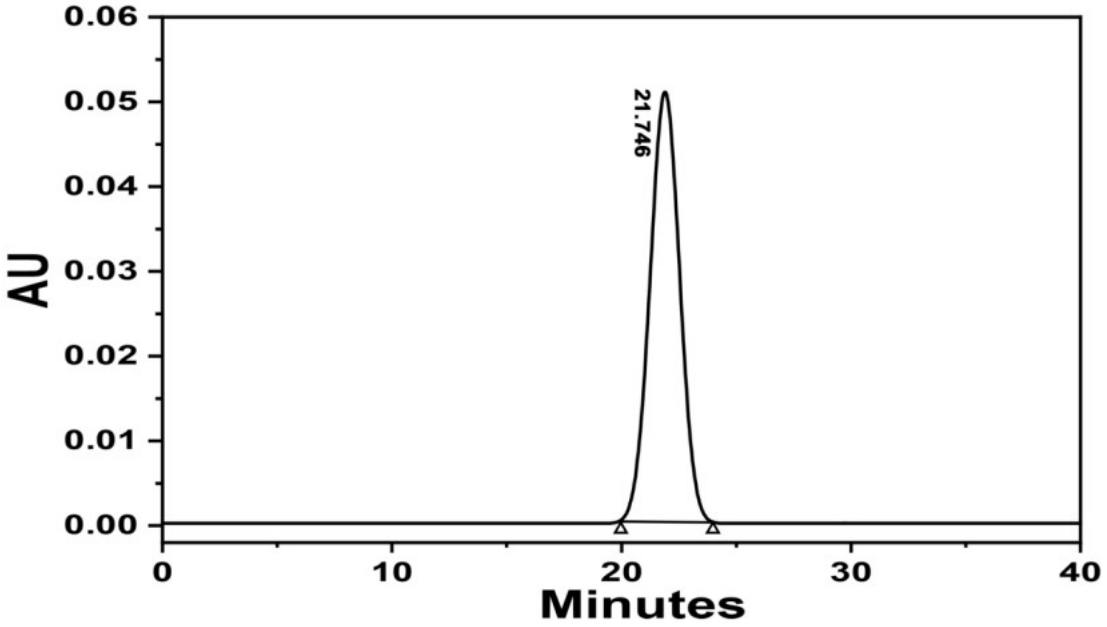


<Peak Table>

PDA Ch1 257 nm

Peak Name	Retention Time	Area	Peak Height	Area %
1	13.488	2973678	38090	49.90
2	21.525	2985988	32139	50.10
Total		5959666	70229	100.00

Figure S4. Chromatogram of the racemic of **3a**.

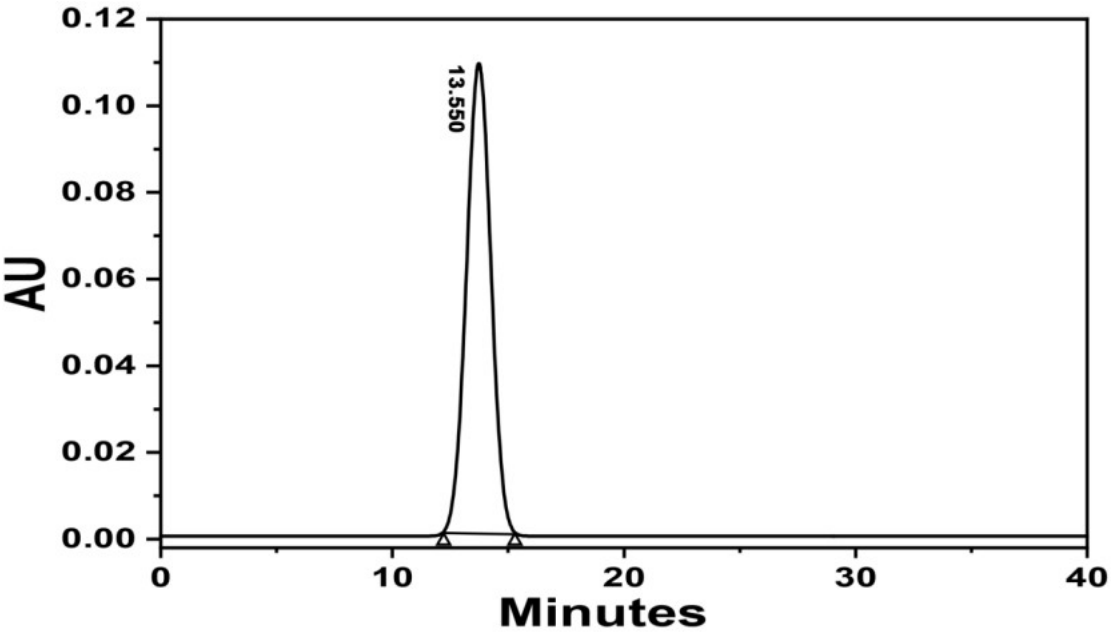


<Peak Table>

PDA Ch1 257 nm

Peak Name	Retention Time	Area	Peak Height	Area %
1	21.746	3890908	41194	100.00
Total		3890908	41194	100.00

Figure S5. Chromatogram of (R_p)**-3a**.



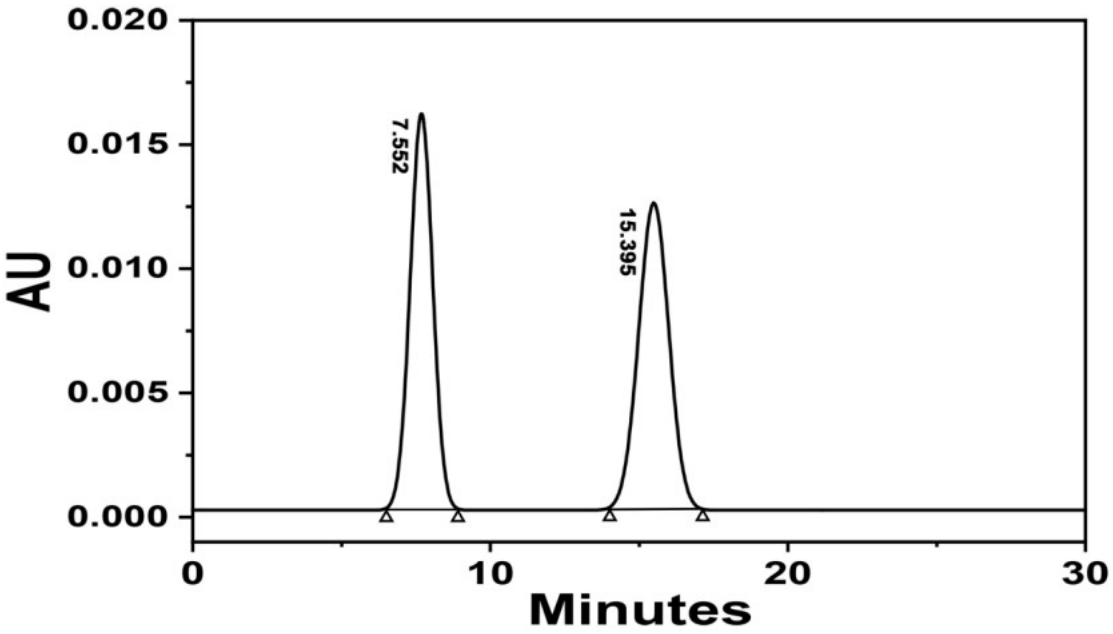
<Peak Table>

PDA Ch1 257 nm

Peak Name	Retention Time	Area	Peak Height	Area %

1	13.550	9389548	118039	100.00
Total		9389548	118039	100.00

Figure S6. Chromatogram of (S_p)**-3a**.

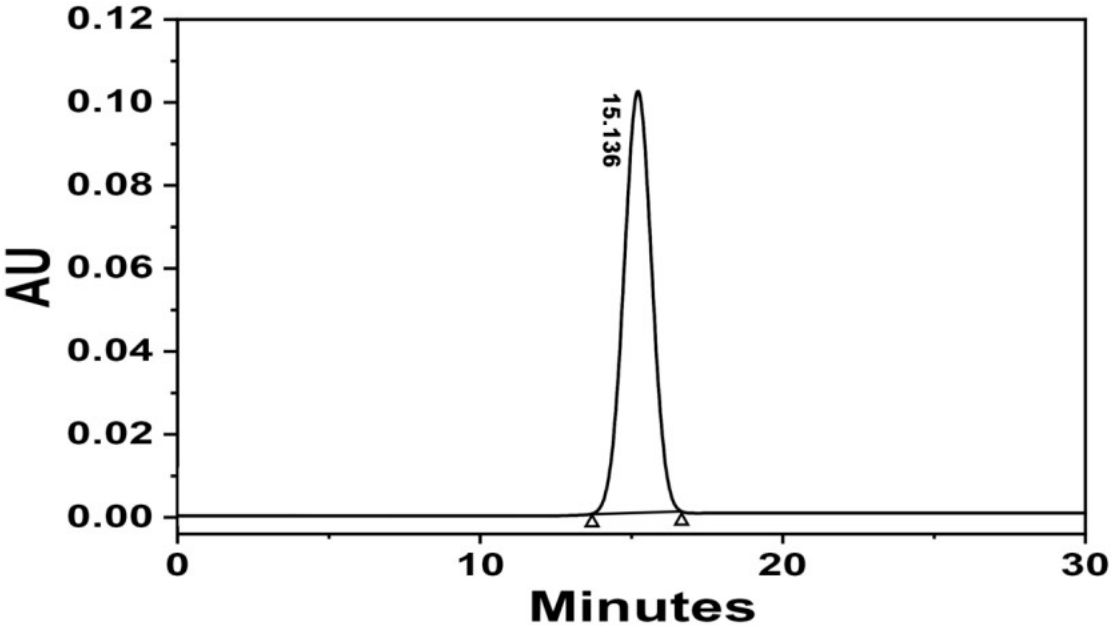


<Peak Table>

PDA Ch1 257 nm

Peak Name	Retention Time	Area	Peak Height	Area %
1	7.552	1052560	17116	50.57
2	15.395	1028980	13161	49.43
Total		2081540	30277	100.00

Figure S7. Chromatogram of the racemic of **3c**.

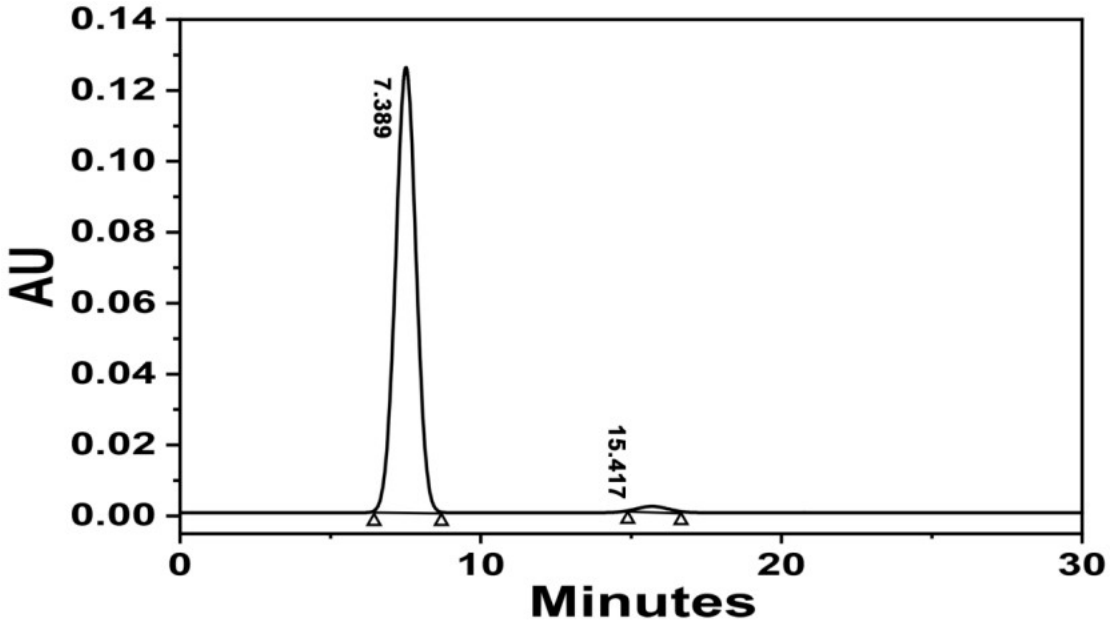


<Peak Table>

PDA Ch1 257 nm

Peak Name	Retention Time	Area	Peak Height	Area %
1	15.136	7569353	108559	100.00
Total		7569353	108559	100.00

Figure S8. Chromatogram of (R_p)**-3c**.

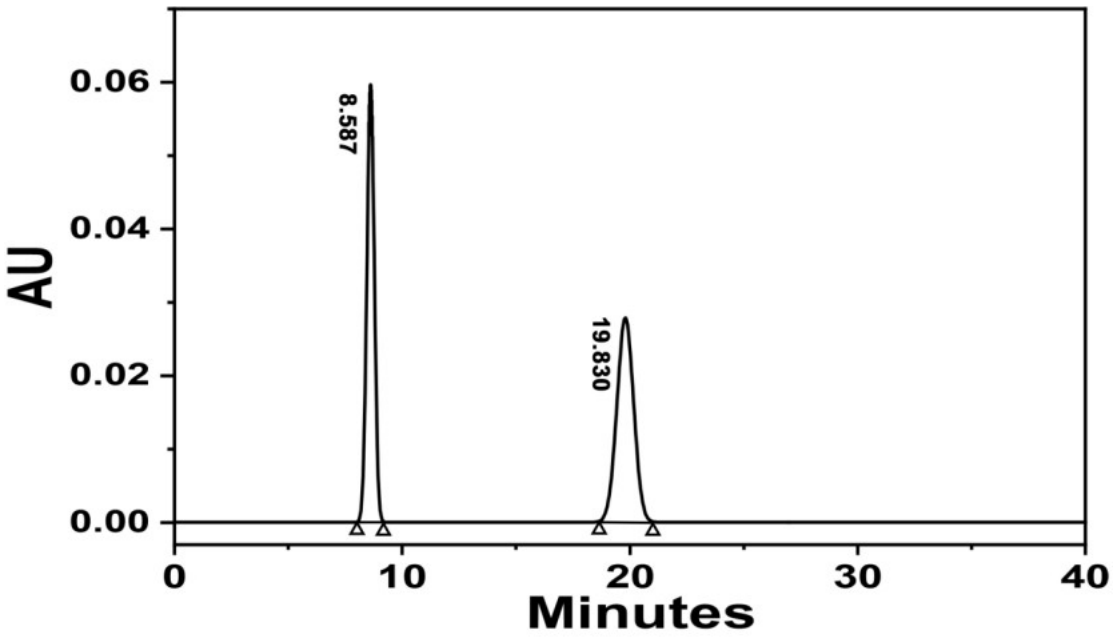


<Peak Table>

PDA Ch1 257 nm

Peak Name	Retention Time	Area	Peak Height	Area %
1	7.389	7283196	134442	99.71
2	15.417	51136	1349	0.29
Total		7334332	135791	100.00

Figure S9. Chromatogram of (S_p)**-3c**.

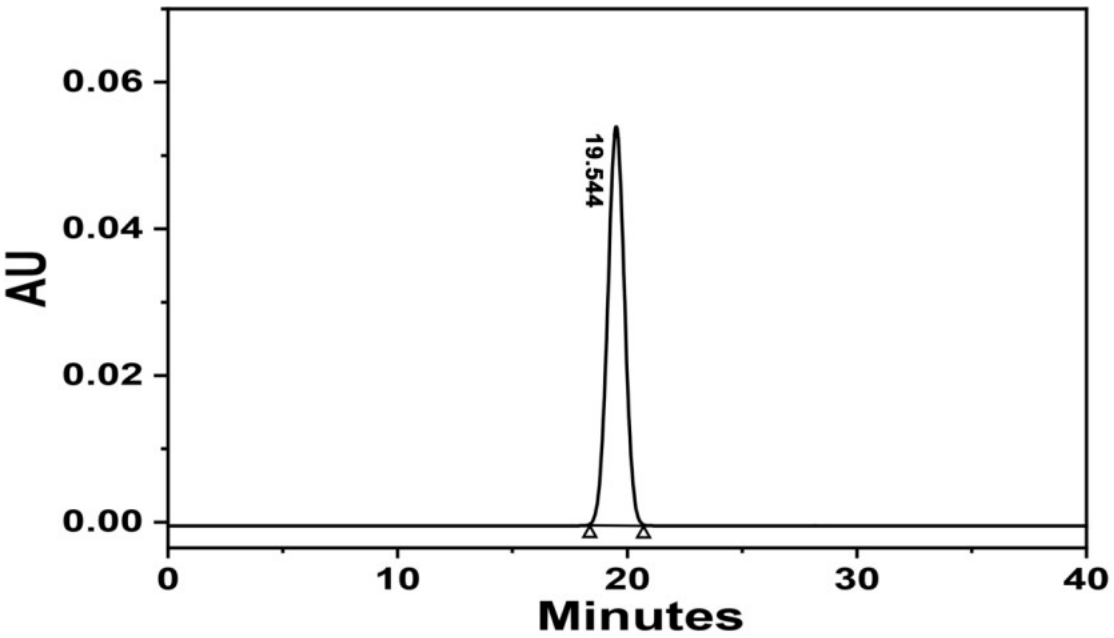


<Peak Table>

PDA Ch1 257 nm

Peak Name	Retention Time	Area	Peak Height	Area %
1	8.587	1535869	62766	50.07
2	19.830	1531705	29745	49.93
Total		3067574	92511	100.00

Figure S10. Chromatogram of the racemic of **3h**.

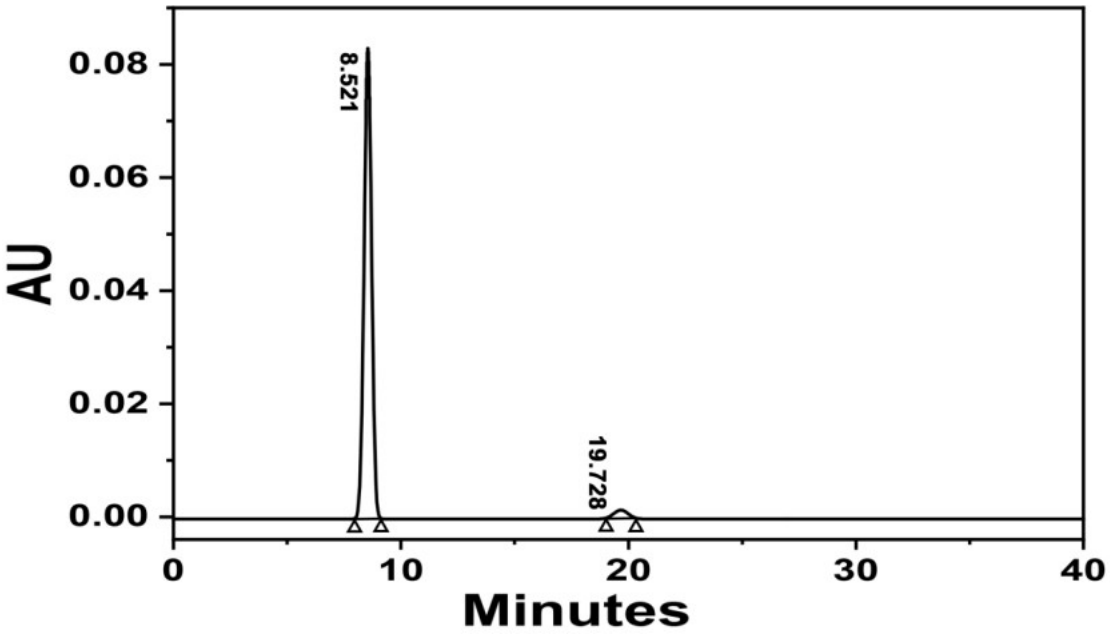


<Peak Table>

PDA Ch1 257 nm

Peak Name	Retention Time	Area	Peak Height	Area %
1	19.544	2922142	58309	100.00
Total		2922142	58309	100.00

Figure S11. Chromatogram of (R_p)**-3h**.

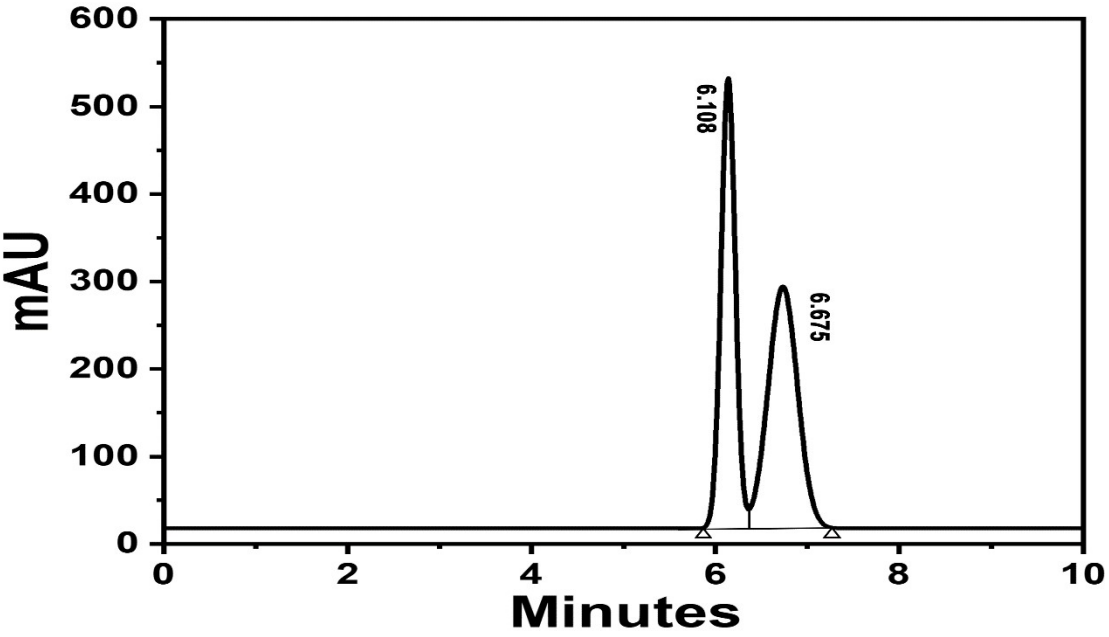


<Peak Table>

PDA Ch1 257 nm

Peak Name	Retention Time	Area	Peak Height	Area %
1	8.521	2122028	87848	99.68
2	19.728	16741	741	0.32
Total		2138769	88589	100.00

Figure S12. Chromatogram of (S_p)**-3h**.

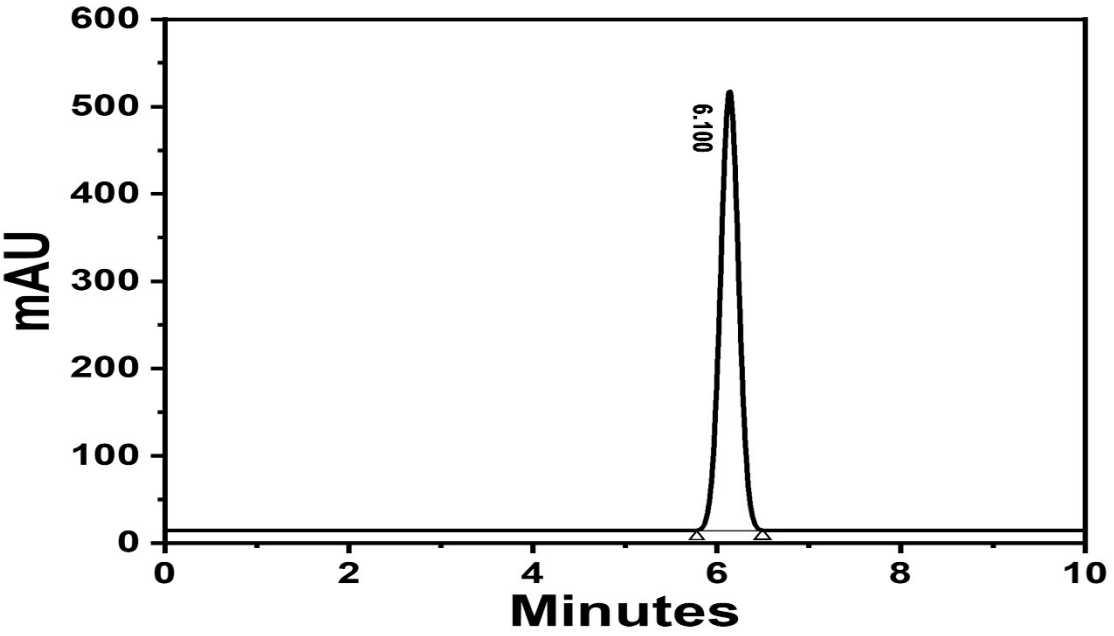


<Peak Table>

PDA Ch1 257 nm

Peak Name	Retention Time	Area	Peak Height	Area %
1	6.108	6651.650	549.790	49.697
2	6.675	6732.852	292.428	50.303
Total		13384.502	842.218	100.000

Figure S13. Chromatogram of the racemic of **3o**.

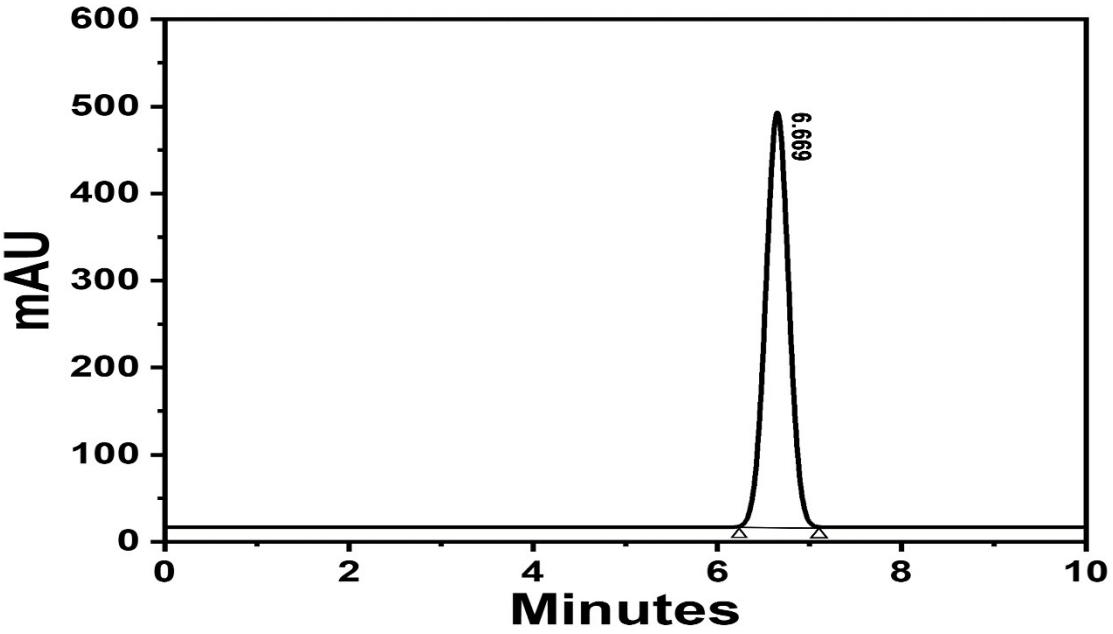


<Peak Table>

PDA Ch1 257 nm

Peak Name	Retention Time	Area	Peak Height	Area %
1	6.100	8919.920	525.104	100.000
Total		8919.920	555.104	100.000

Figure S14. Chromatogram of (R_p)**-3o**.

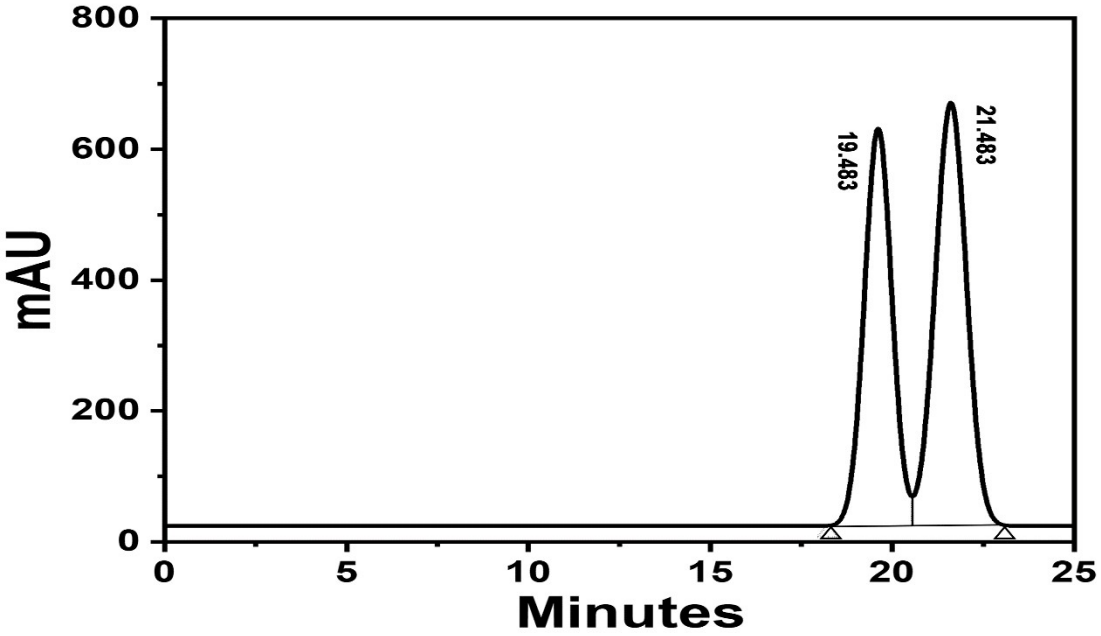


<Peak Table>

PDA Ch1 257 nm

Peak Name	Retention Time	Area	Peak Height	Area %
1	6.669	9557.340	495.047	100.000
Total		9557.340	495.047	100.000

Figure S15. Chromatogram of (S_p)**-3o**.

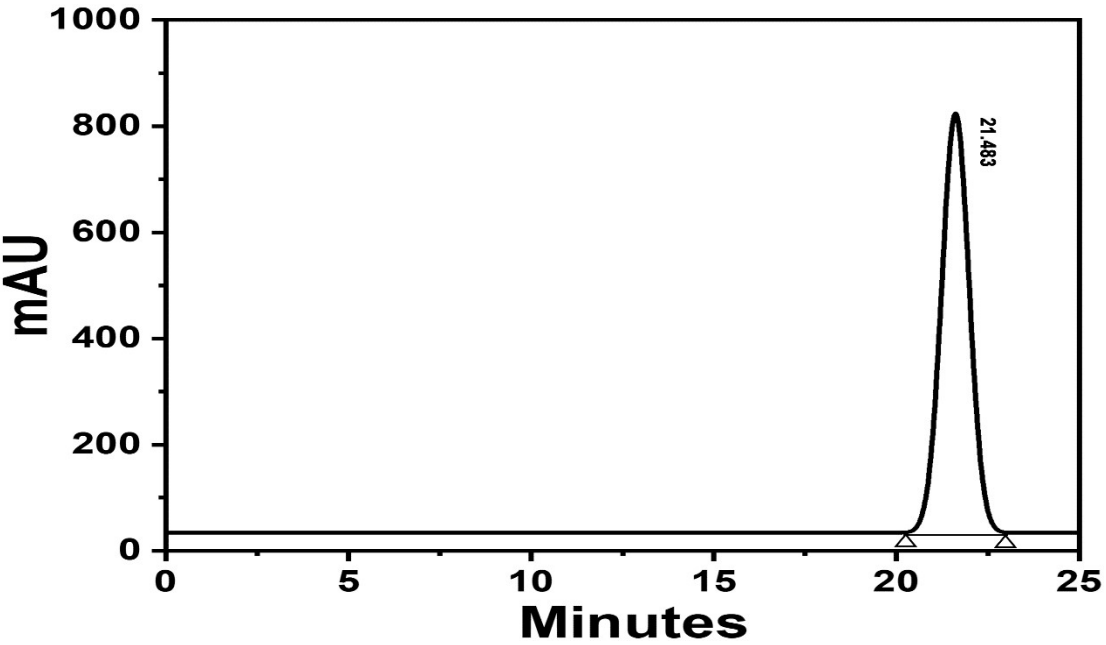


<Peak Table>

PDA Ch1 257 nm

Peak Name	Retention Time	Area	Peak Height	Area %
1	19.483	38157.742	652.737	48.942
2	21.483	39806.692	699.812	51.058
Total		77964.434	1352.549	100.000

Figure S16. Chromatogram of the racemic of **3p**.

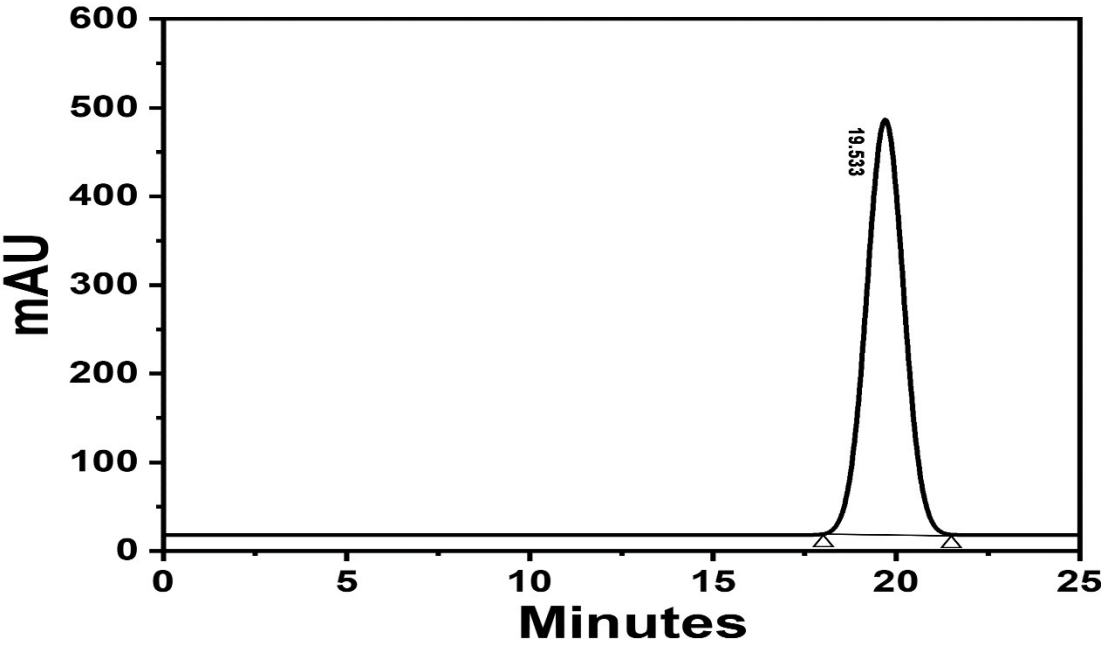


<Peak Table>

PDA Ch1 257 nm

Peak Name	Retention Time	Area	Peak Height	Area %
1	21.483	52398.164	848.223	100.000
Total		52398.164	848.223	100.000

Figure S17. Chromatogram of (R_p)**-3p**.



<Peak Table>

PDA Ch1 257 nm

Peak Name	Retention Time	Area	Peak Height	Area %
1	19.533	27820.675	464.756	100.000
Total		27820.675	464.756	100.000

Figure S18. Chromatogram of (S_p)**-3p**.

6. General Procedure for Crystal Preparation and Measurement.

The single crystal of compound **3a** was grown by slow evaporation of solvent at room temperature. Intensity data of **3a** was collected on a Rigaku Oxford Diffraction Synergy Custom DW system X-ray diffractometer with a Hypix detector using Cu-*K*α radiation (λ=1.54184 Å) at 140 K; The structure was solved by direct methods and refined by full-matrix least-squares methods with SHELX-2018 program. Displacement parameters were refined anisotropically, and the positions of the H-atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle

of refinement. Basic information pertaining to crystal parameters and structure refinement are summarized in Table S2, and hydrogen bonds are listed in Table S3. CCDC 2281238 contains the supplementary crystallographic data for this paper.

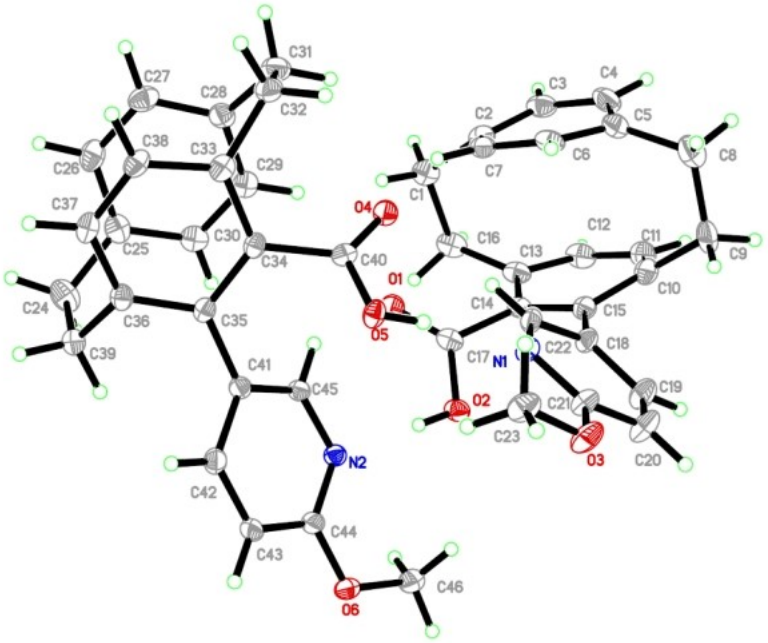


Figure S19. Single crystals of compound **3a** (Ellipsoids are drawn to 30% probability).

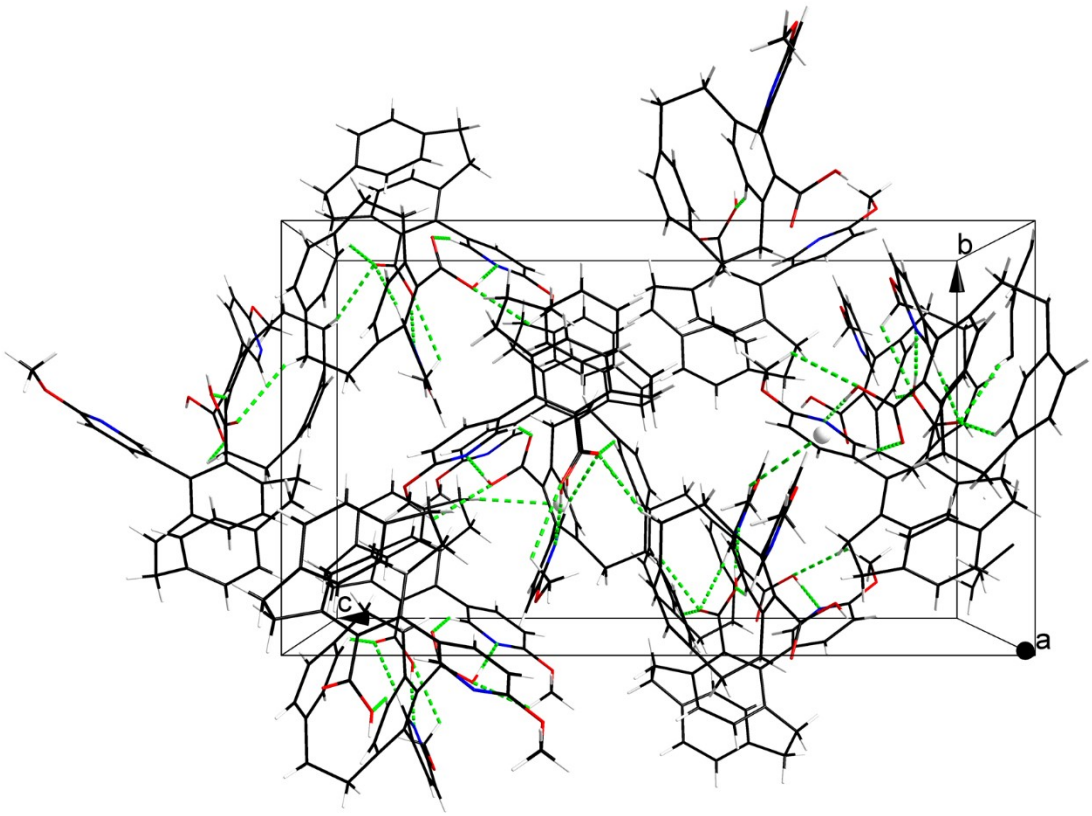


Figure S20. Molecular packing structure of **3a** along *a* axis. The green dotted lines show weak intermolecular interactions.

Table S2. Crystallographic data and structure refinement for **3a**.

Compound	**3a**
Empirical formula	$C_{46}H_{42}N_2O_6$
CCDC number	2281238
Formula weight	718.81
Temperature	140(2) K
Crystal system	Orthorhombic
space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 11.3401 (5) Å; α = 90° b = 13.7292 (5) Å; β = 90° c = 23.8310 (10) Å; γ = 90°
Volume	3710.3(3) Å^3
Z	4
Cal. Density	1.287 g/cm^3
Index ranges	-9 ≤ h ≤ 13 -13 ≤ k ≤ 16 -28 ≤ l ≤ 28
F（000）	1520
Crystal size	0.900 x 0.080 x 0.080 mm^3
GOF	1.070
R indices	R_1 = 0.0575, wR_2 = 0.1127

Table S3. Hydrogen bonds for **3a** [Å and °]

D–H···A	D(H···A)	∠(DHA)

O5–H5···N1	1.8845 (30) Å	174.120 (186)°
O2–H2···N2	1.9123 (33) Å	172.715 (186)°
C45–H45···O1	2.3660 (23) Å	137.766 (212)°
C46–H46C···O2	2.7078 (24) Å	114.020 (259)°
C7–H7···O4	2.6670 (23) Å	139.913 (212)°
C8–H8B···O4	2.4867 (24) Å	143.615 (306)°
C22–H22···O4	2.3787 (24) Å	137.440 (243)°
C12–H12···O5	2.4922 (23) Å	157.653 (214)°
C23–H23C···O5	2.6865 (25) Å	116.534 (245)°
C23–H23B···C42 (π)	2.8842 (38) Å	-
C24–H24A···C13 (π)	2.8836 (39) Å	-

7. Photophysical Properties.

Theoretical calculations

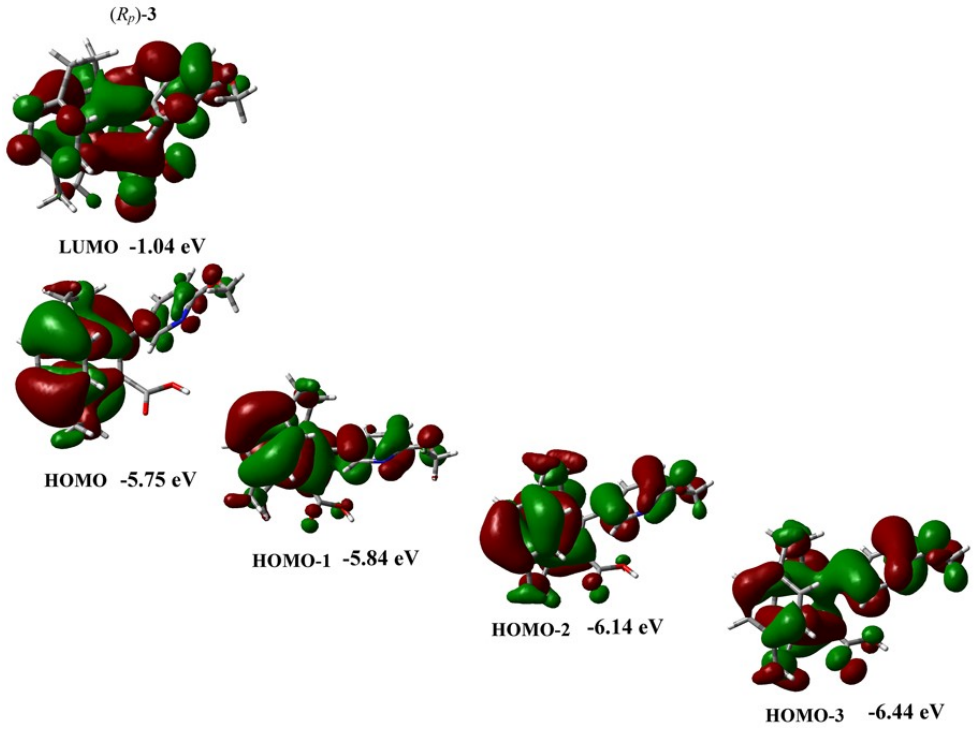


Figure S21. The angular nodal patterns of the LUMO, HOMO, HOMO-1, HOMO-2, and HOMO-3 of **3a**, calculated by using B3LYP/6-31G(d) basis set with the G09 program package.

Table S4. Related wave functions, oscillator strengths, and calculated electronic excitation energies of **3a**.

Compound	State[a] [b]	λ [nm]	f[c]	E_g (eV)	Orbital (coefficient)[d]
(R_p)-**3a**	S_1	313.71	0.0214	3.95	H-L (67.8 %)

	S_2	301.17	0.0425	4.12	H_{-1}-L (67.3 %)
	S_3	279.98	0.0170	4.43	H_{-2}-L (62.9 %)
	S_6	268.59	0.1482	4.62	H_{-3}-L (38.7 %)

[a]Only selected excited states were considered; [b]DCM was employed as the solvent for the DFT calculations; [c]Oscillator strength; [d]MOs involved in the transitions. H = HOMO, L = LUMO. Coefficient of the wavefunction for each excitation.

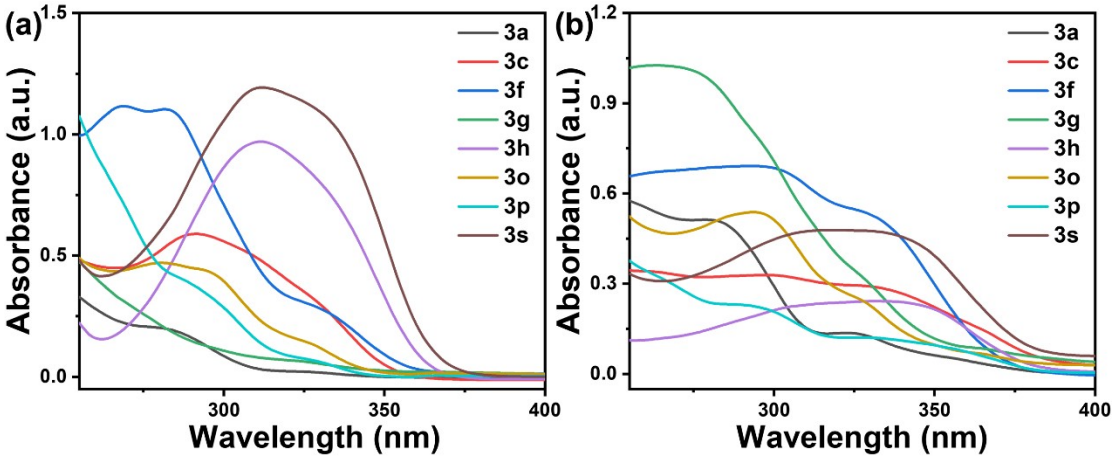


Figure S22. The absorption spectra of **3a**, **3c**, **3f**, **3g**, **3h**, **3o**, **3p**, and **3s** in (a) THF solutions (50 μM) and (b) PMMA films.

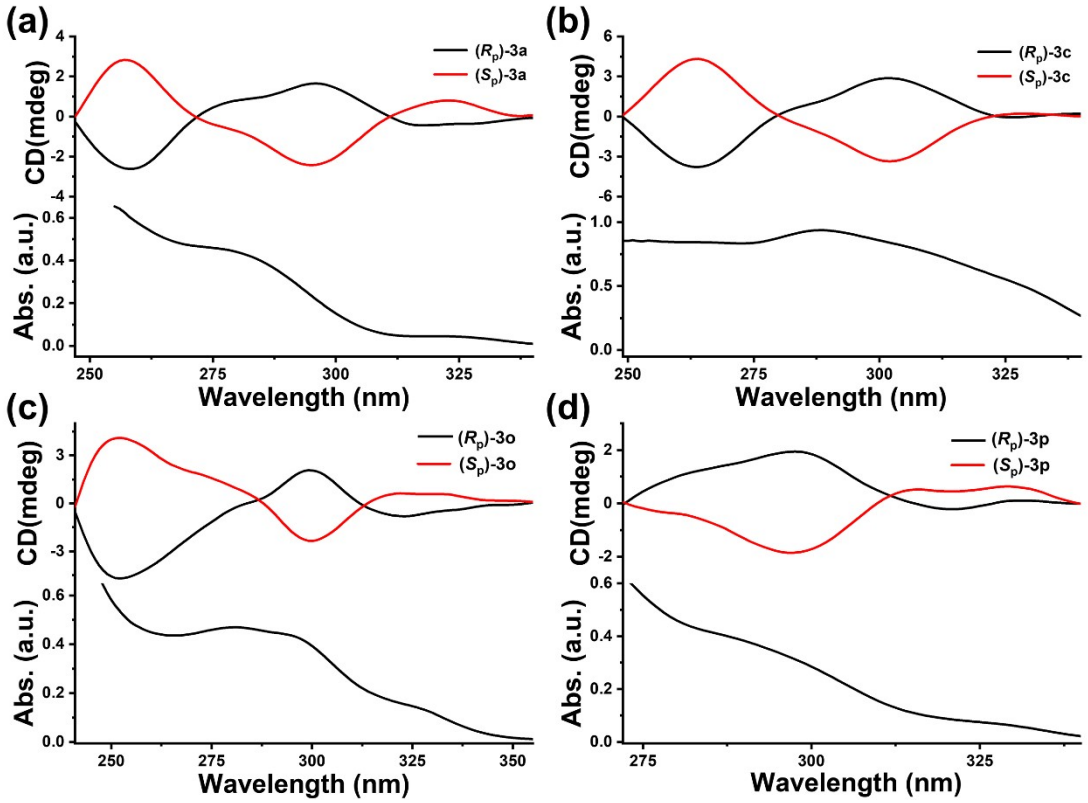


Figure S23. The CD and absorption spectra of (a) (R_p)/(S_p)-**3a**, (b) (R_p)/(S_p)-**3c**, (c)

(R_p)/(S_p)-**3o**, and (d) (R_p)/(S_p)-**3p** in THF solutions (50 μM).

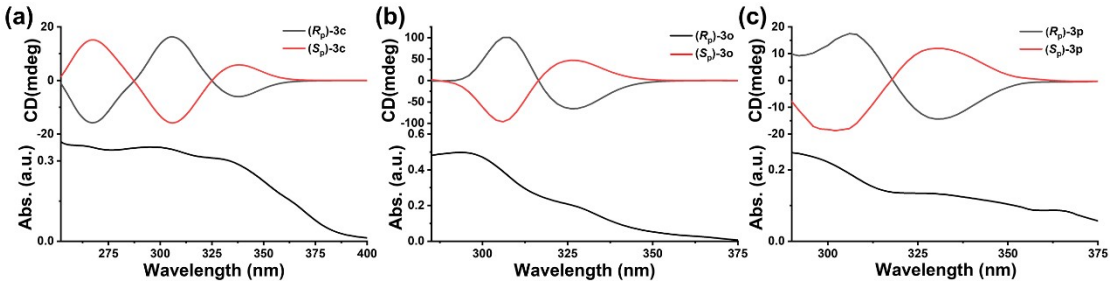
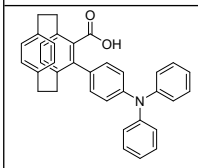
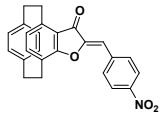
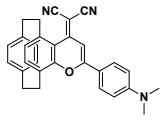
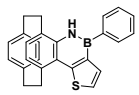
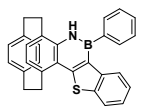
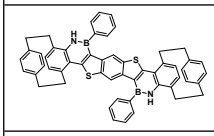
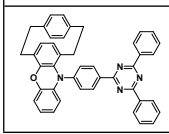
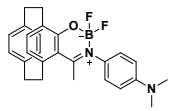
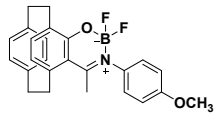
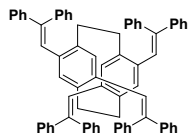
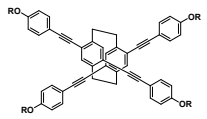


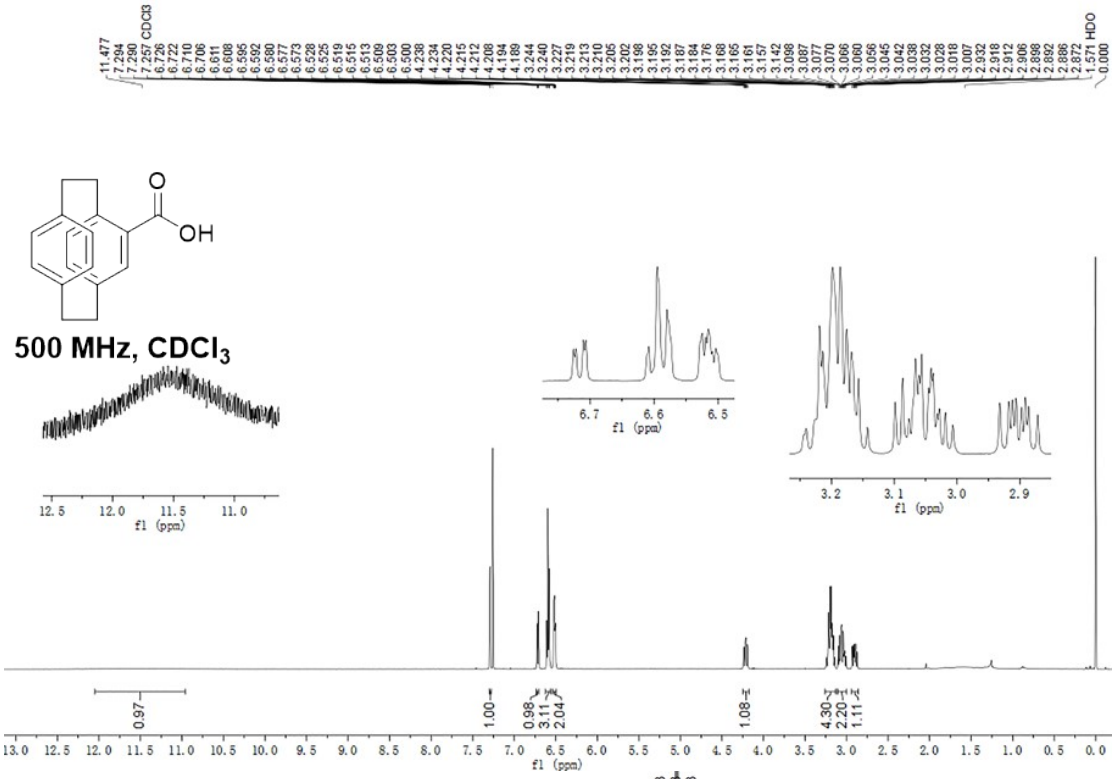
Figure S24. The CD and absorption spectra of (a) (R_p)/(S_p)-**3c**, (b) (R_p)/(S_p)-**3o**, and (c) (R_p)/(S_p)-**3p** in PMMA films.

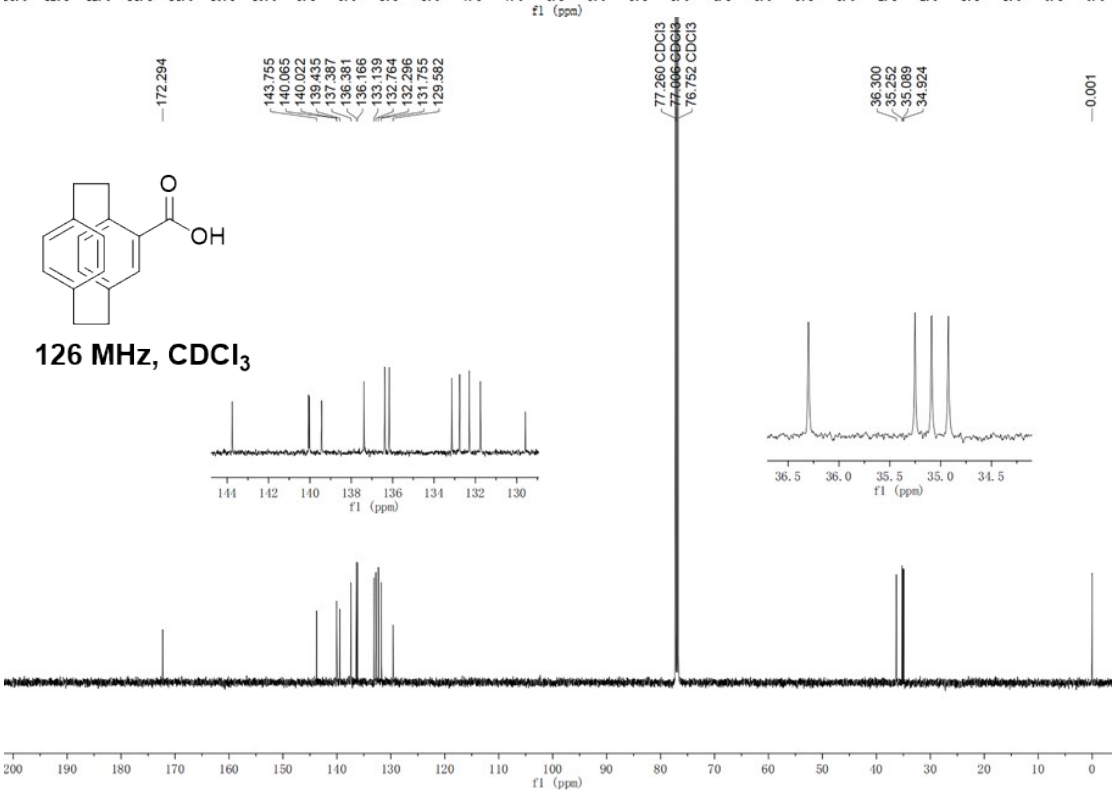
Table S5. Comparison of CPL performances of [2.2]paracyclophane derivatives.

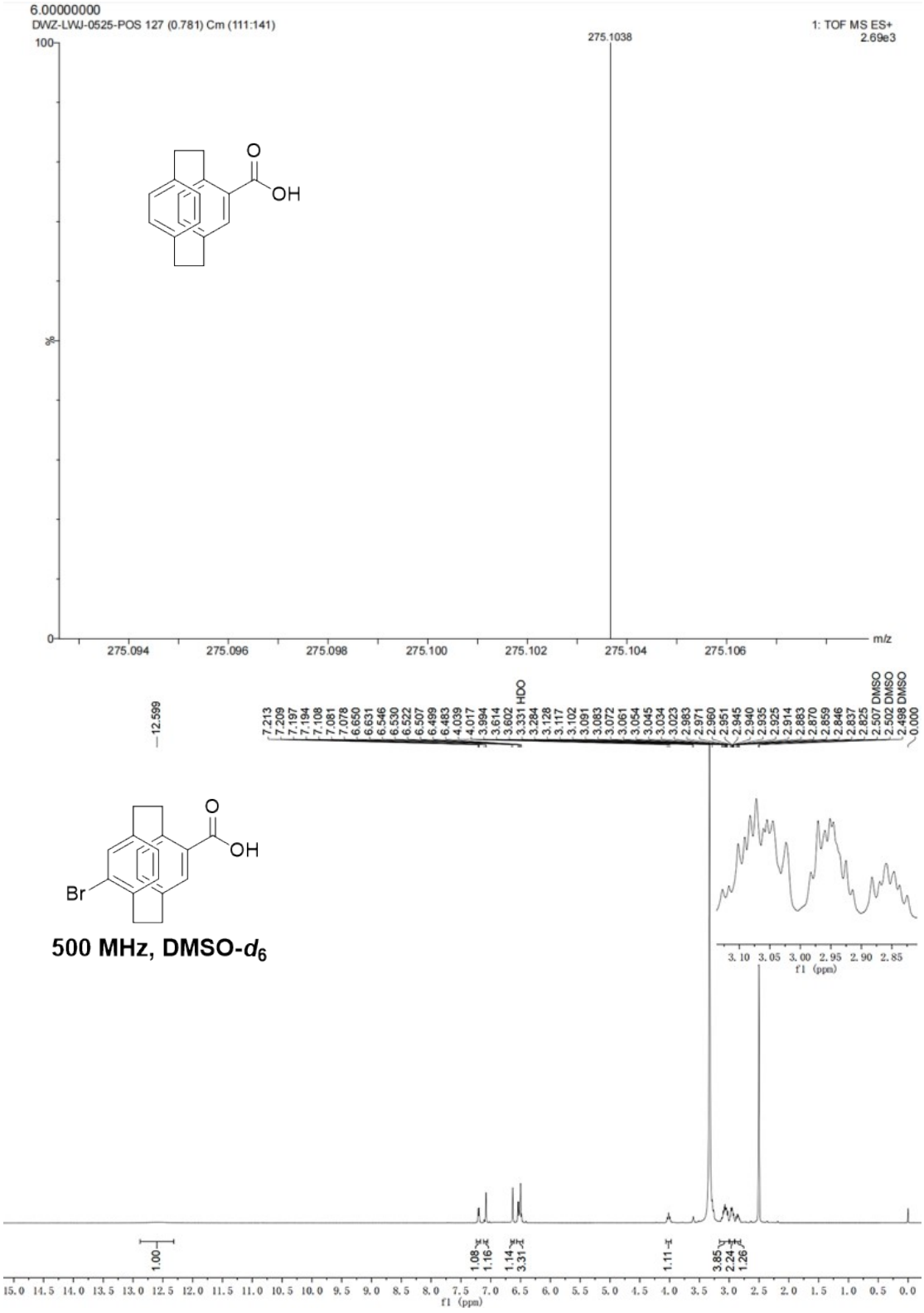
Structure	State	CPL emission wavelength (nm)	Φ_f (%)	$\|g_{lum}\|$	Ref.
	thin film	490	8	1.7×10^{-3}	This work
	solid	555	9	3.9×10^{-4}	Ref.6
	solid	662	97	1.9×10^{-3}	Ref.7
	doped in PMMA	393	75	4.8×10^{-3}	Ref.8
	doped in PMMA	395	70	2.9×10^{-3}	Ref.8
	doped in PMMA	404	70	5×10^{-4}	Ref.8
	thin film	548	47	2.7×10^{-3}	Ref.9

	solid	562	5	3.0×10^{-4}	Ref.10
	solid	488	8	1.8×10^{-3}	Ref.10
	in aggregation state	494	58	9.0×10^{-4}	Ref.11
	thin film	415	63	2.1×10^{-3}	Ref.12

8. Copies of NMR and HRMS Spectra.






6.00000000
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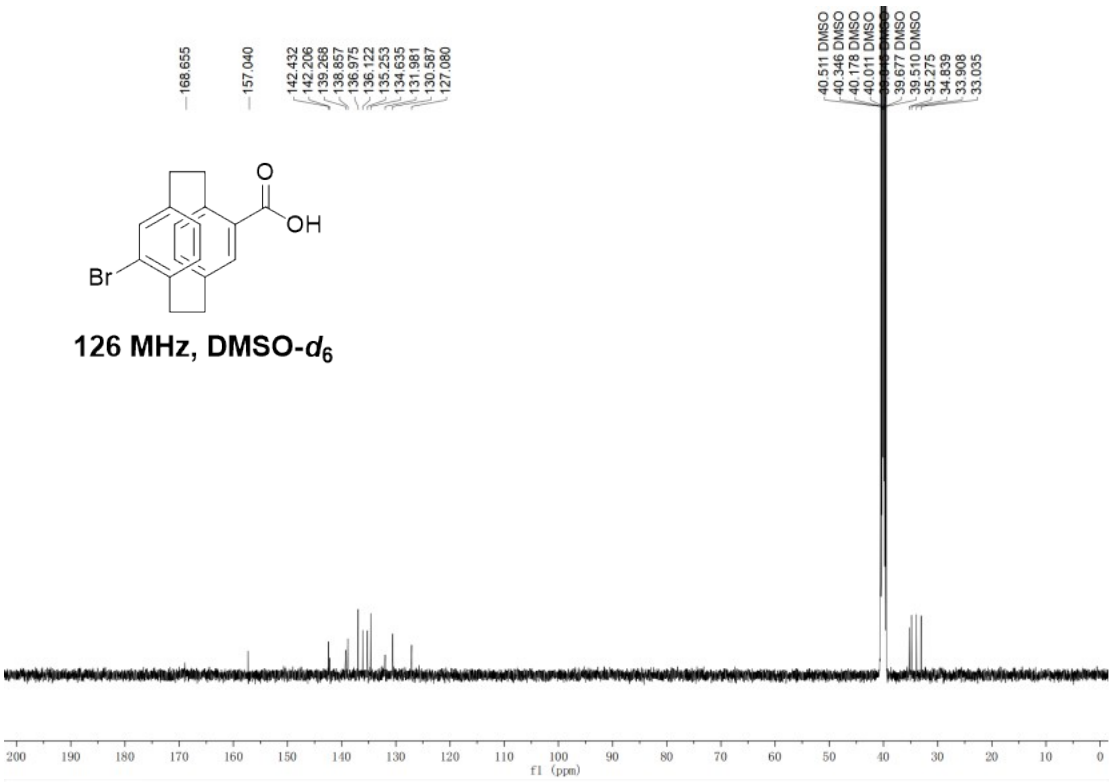
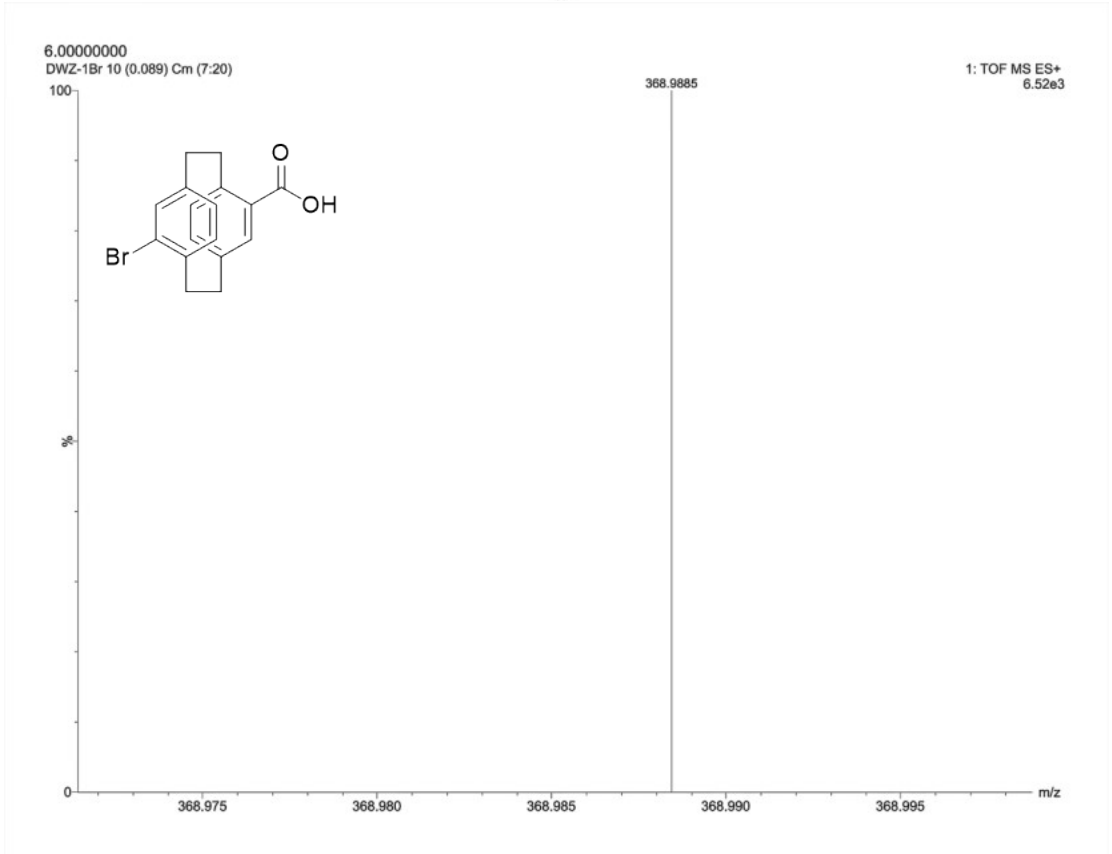
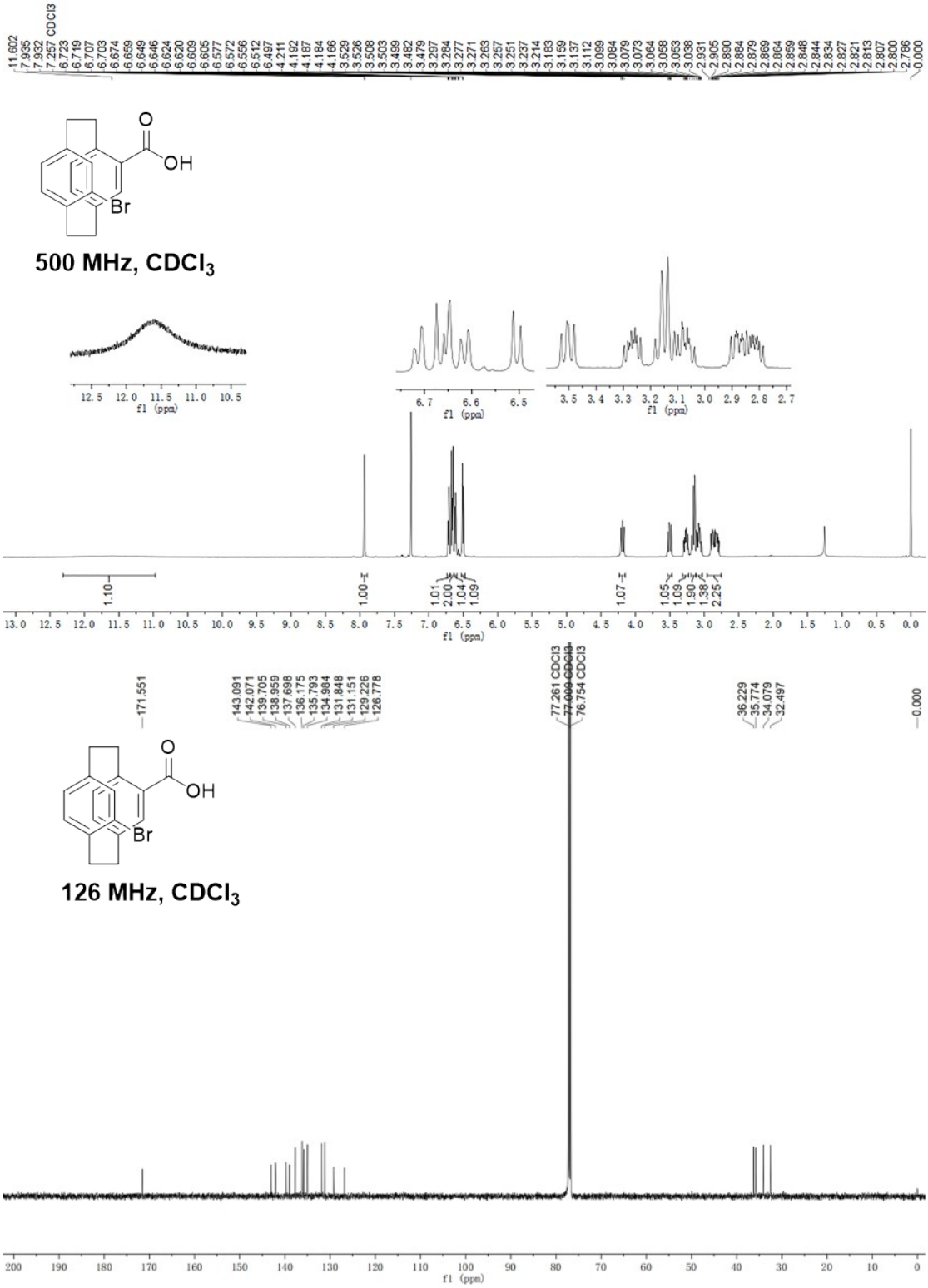
1: TOF MS ES+
2.69e3
275.1038
100
%
0
275.094
275.096
275.098
275.100
275.102
275.104
275.106
m/z
O
OH
12.599
7.213
7.209
7.197
7.194
7.108
7.081
7.078
6.650
6.631
6.546
6.530
6.522
6.507
6.499
6.483
4.039
4.017
3.994
3.614
3.602
3.331 HDO
3.284
3.128
3.117
3.102
3.091
3.083
3.072
3.061
3.054
3.045
3.034
3.023
2.983
2.971
2.960
2.951
2.945
2.940
2.935
2.925
2.914
2.883
2.870
2.859
2.846
2.837
2.825
2.507 DMSO
2.502 DMSO
2.498 DMSO
0.000
O
OH
Br
500 MHz, DMSO-d6
3.10 3.05 3.00 2.95 2.90 2.85
f1 (ppm)
1.00
1.08
1.16
1.14
3.31
1.11
3.85
2.24
1.26
15.0 14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.655
157.040
142.432
142.206
139.268
138.857
136.975
136.122
135.253
134.635
131.981
130.587
127.080
40.511 DMSO
40.346 DMSO
40.178 DMSO
40.011 DMSO
39.677 DMSO
39.510 DMSO
35.275
34.839
33.908
33.035
O
OH
Br
126 MHz, DMSO-d_6
f1 (ppm)


6.00000000
DWZ-1Br 10 (0.089) Cm (7:20)
1: TOF MS ES+
6.52e3
368.9885
100
%
0
O
OH
Br
368.975
368.980
368.985
368.990
368.995
m/z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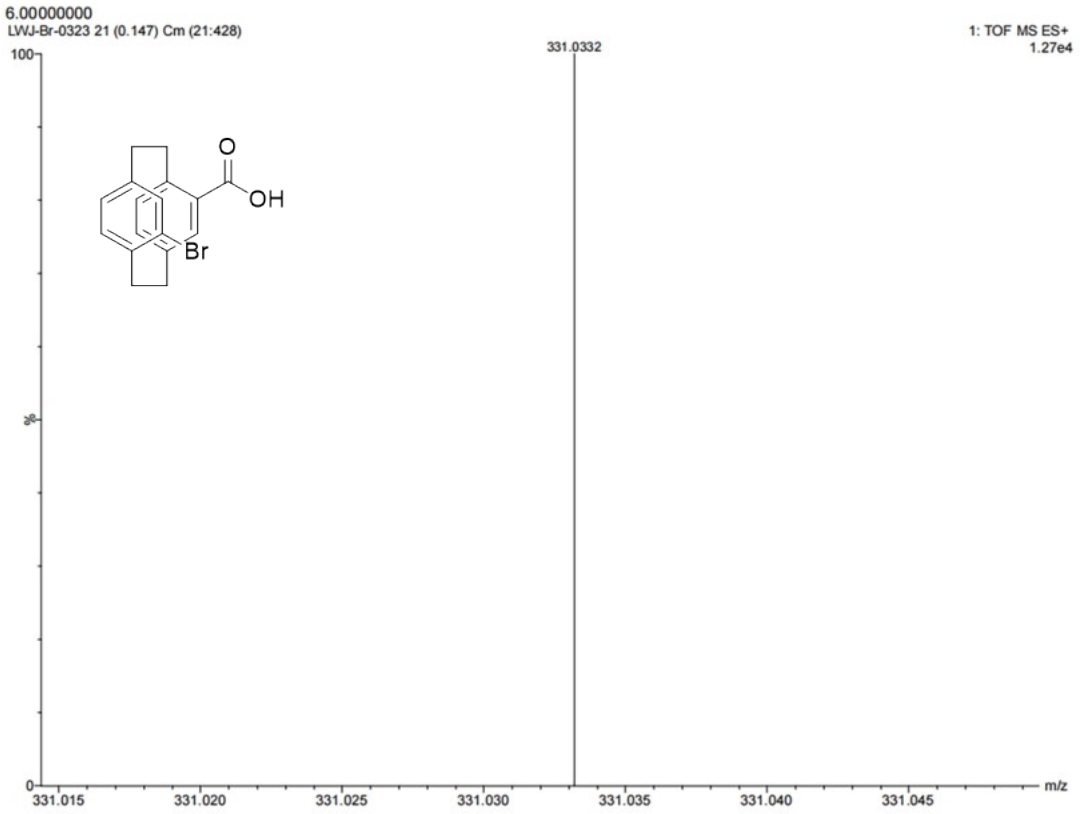
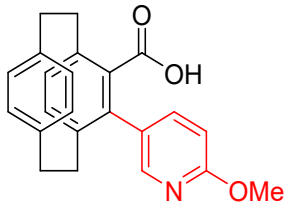
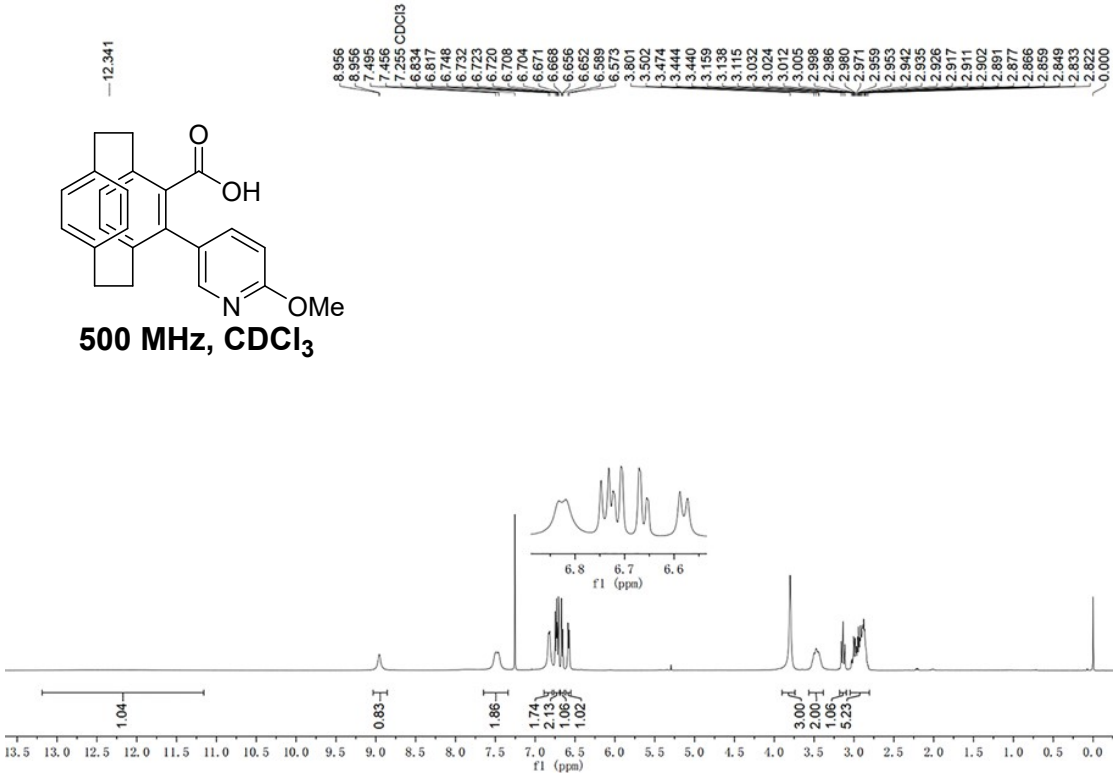
7.935
7.932
7.257 CDCl3
6.723
6.719
6.707
6.703
6.674
6.659
6.649
6.646
6.624
6.620
6.609
6.605
6.577
6.572
6.556
6.512
6.497
4.211
4.192
4.187
4.184
4.166
3.529
3.526
3.508
3.503
3.499
3.482
3.479
3.297
3.284
3.277
3.271
3.263
3.257
3.251
3.237
3.214
3.183
3.159
3.137
3.112
3.099
3.084
3.079
3.073
3.064
3.058
3.053
3.038
2.931
2.905
2.890
2.884
2.879
2.869
2.864
2.859
2.848
2.844
2.834
2.827
2.821
2.813
2.807
2.800
2.786
0.000
O
OH
Br
500 MHz, CDCl3
f1 (ppm)
1.10
1.00
1.01
2.00
1.04
1.09
1.07
1.05
1.09
1.90
1.38
2.25
171.551
143.091
142.071
139.705
138.959
137.698
136.175
135.793
134.984
131.848
131.151
129.226
126.778
77.261 CDCl3
77.009 CDCl3
76.754 CDCl3
36.229
35.774
34.079
32.497
0.000
126 MHz, CDCl3

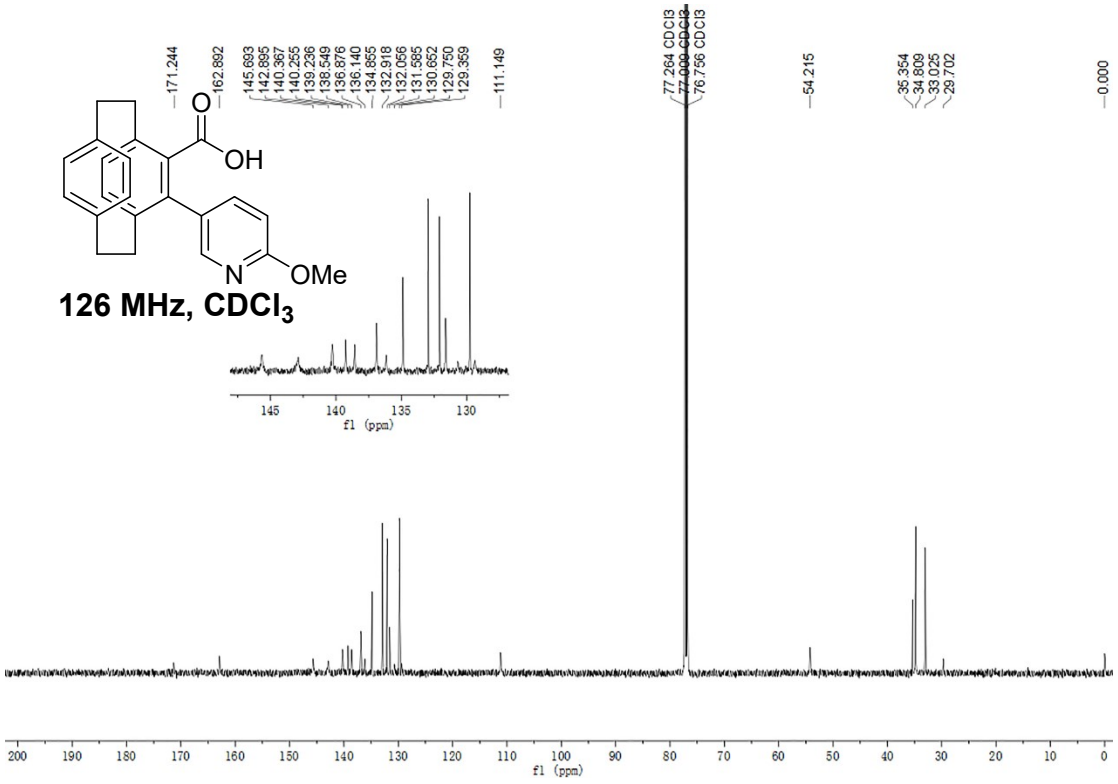

6.00000000
LWJ-Br-0323 21 (0.147) Cm (21:428)
1: TOF MS ES+
1.27e4
100
%
0
331.0332
O
OH
Br
331.015
331.020
331.025
331.030
331.035
331.040
331.045
m/z

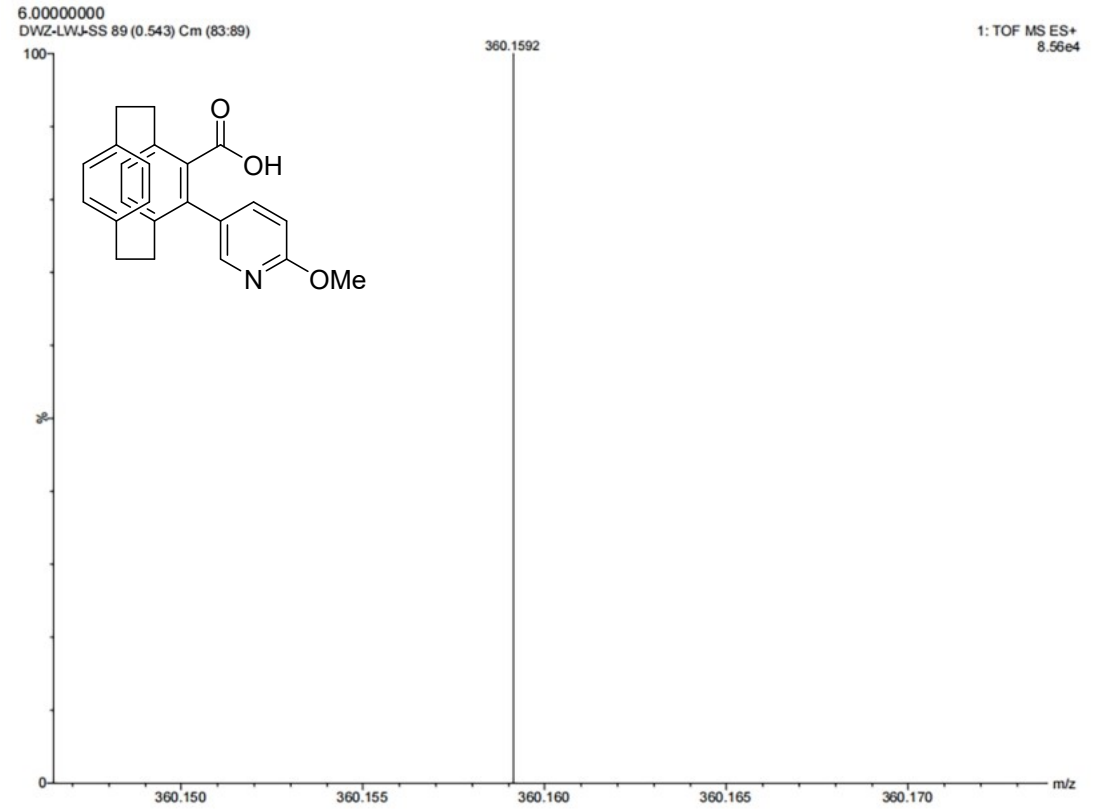

O
OH
N
OMe

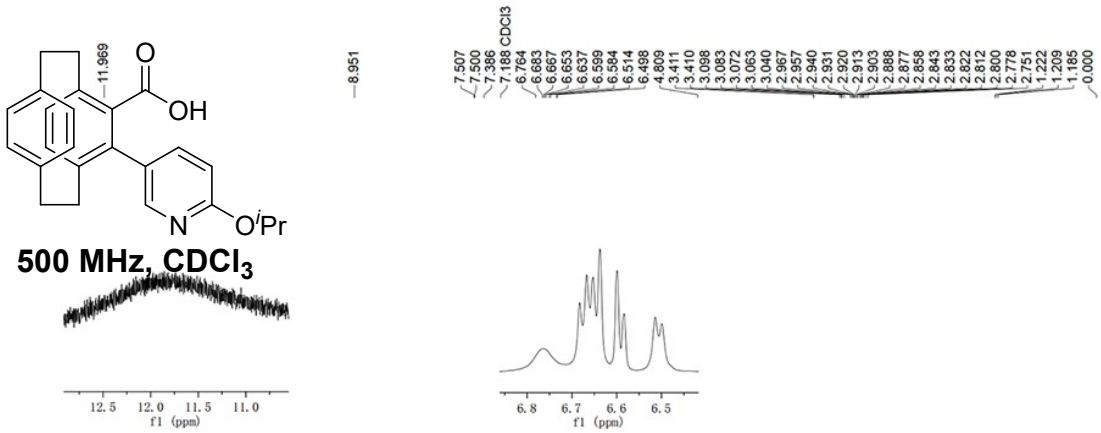
3a Yield: 68%

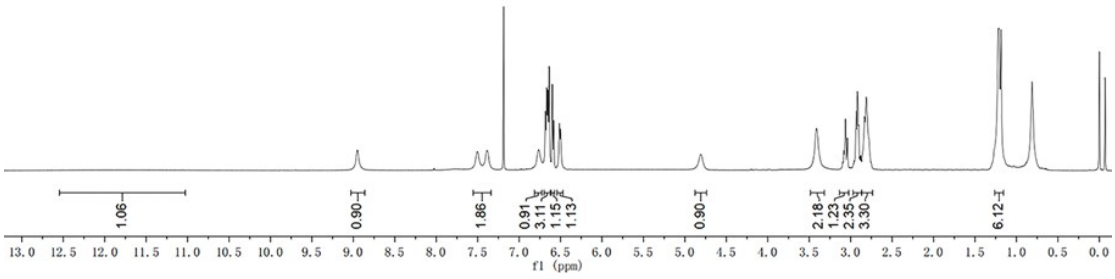
3.861
3.770
0.000
0.68
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

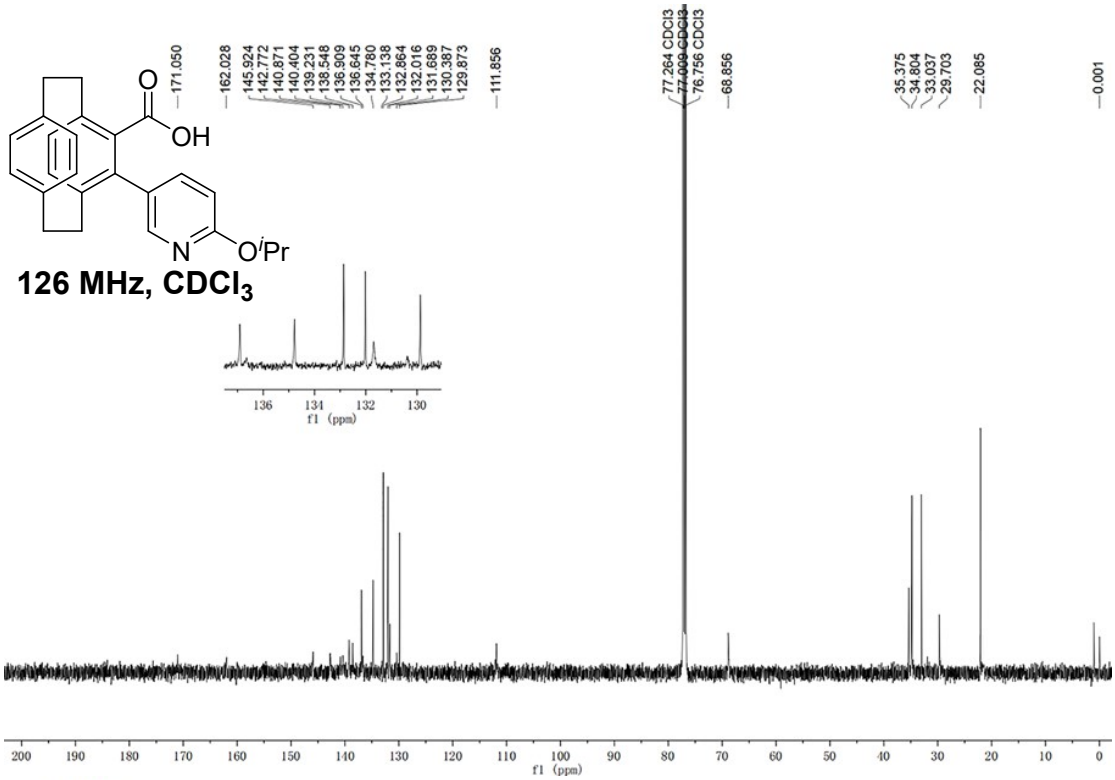

12.341
8.956
8.956
7.495
7.456
7.255 CDCl3
6.834
6.817
6.748
6.732
6.723
6.720
6.708
6.704
6.671
6.668
6.656
6.652
6.589
6.573
3.801
3.502
3.474
3.444
3.440
3.159
3.138
3.115
3.032
3.024
3.012
3.005
2.998
2.986
2.980
2.971
2.959
2.953
2.942
2.935
2.926
2.917
2.911
2.902
2.891
2.877
2.866
2.859
2.849
2.833
2.822
0.000
O
OH
N
OMe
500 MHz, CDCl3
6.8
6.7
6.6
f1 (ppm)
1.04
0.83
1.86
1.74
2.13
1.06
1.02
3.00
2.00
1.06
5.23
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

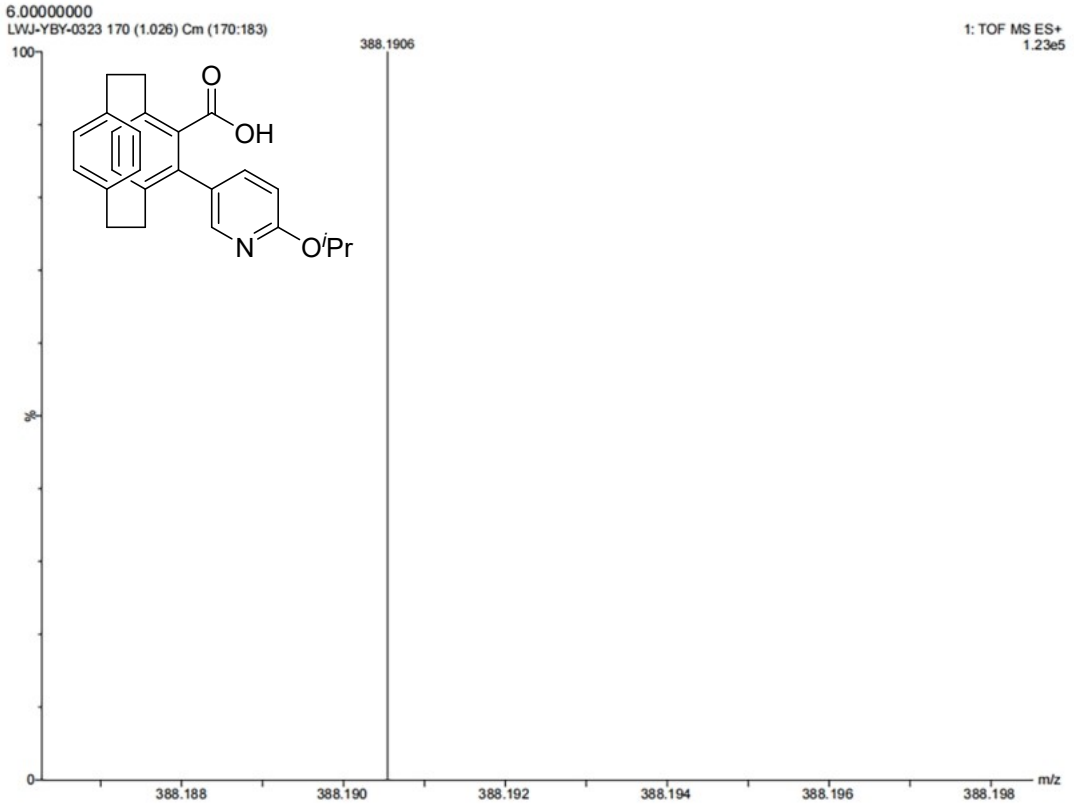

171.244
162.892
145.693
142.895
140.367
140.255
139.236
138.549
136.876
136.140
134.865
132.918
132.056
131.585
130.652
129.750
129.359
111.149
77.264 CDCl3
77.000 CDCl3
76.756 CDCl3
54.215
35.354
34.809
33.025
29.702
0.000
O
OH
N
OMe
126 MHz, CDCl3
145
140
135
130
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

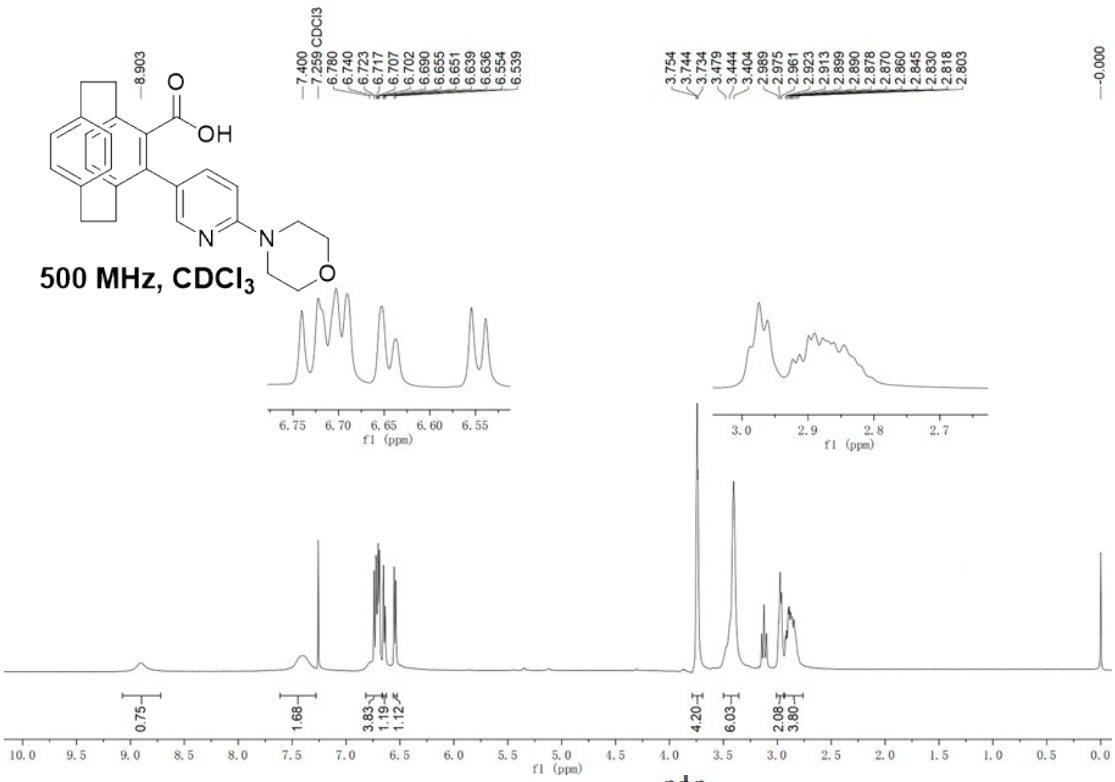

6.00000000
DWZ-LWJ-SS 89 (0.543) Cm (83:89)
1: TOF MS ES+
8.56e4
360.1592
100
%
0
O
OH
N
OMe
360.150
360.155
360.160
360.165
360.170
m/z

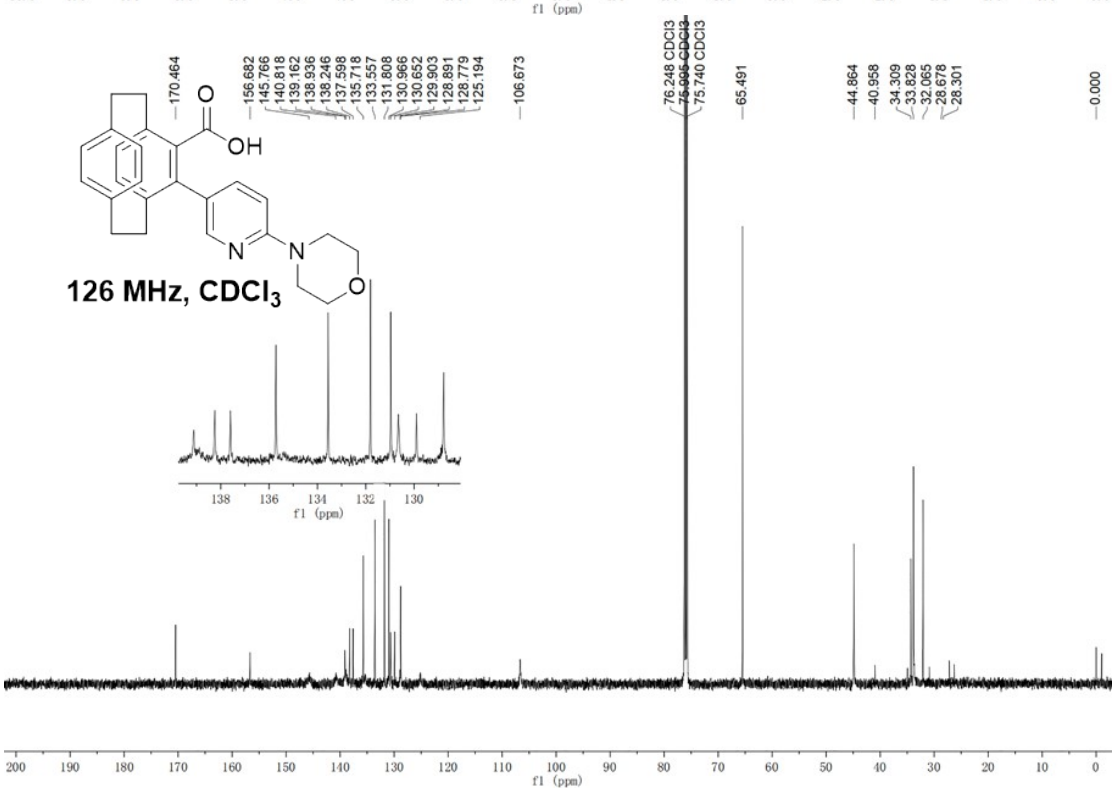

11.969
8.951
7.507
7.500
7.386
7.188 CDCl3
6.764
6.683
6.667
6.653
6.637
6.599
6.584
6.514
6.498
4.809
3.411
3.410
3.098
3.083
3.072
3.063
3.040
2.967
2.957
2.940
2.931
2.920
2.913
2.903
2.888
2.877
2.858
2.843
2.833
2.822
2.812
2.800
2.778
2.751
1.222
1.209
1.185
0.000
O
OH
N
O^{i}Pr
500 MHz, CDCl3
12.5
12.0
11.5
11.0
f1 (ppm)
6.8
6.7
6.6
6.5
f1 (ppm)

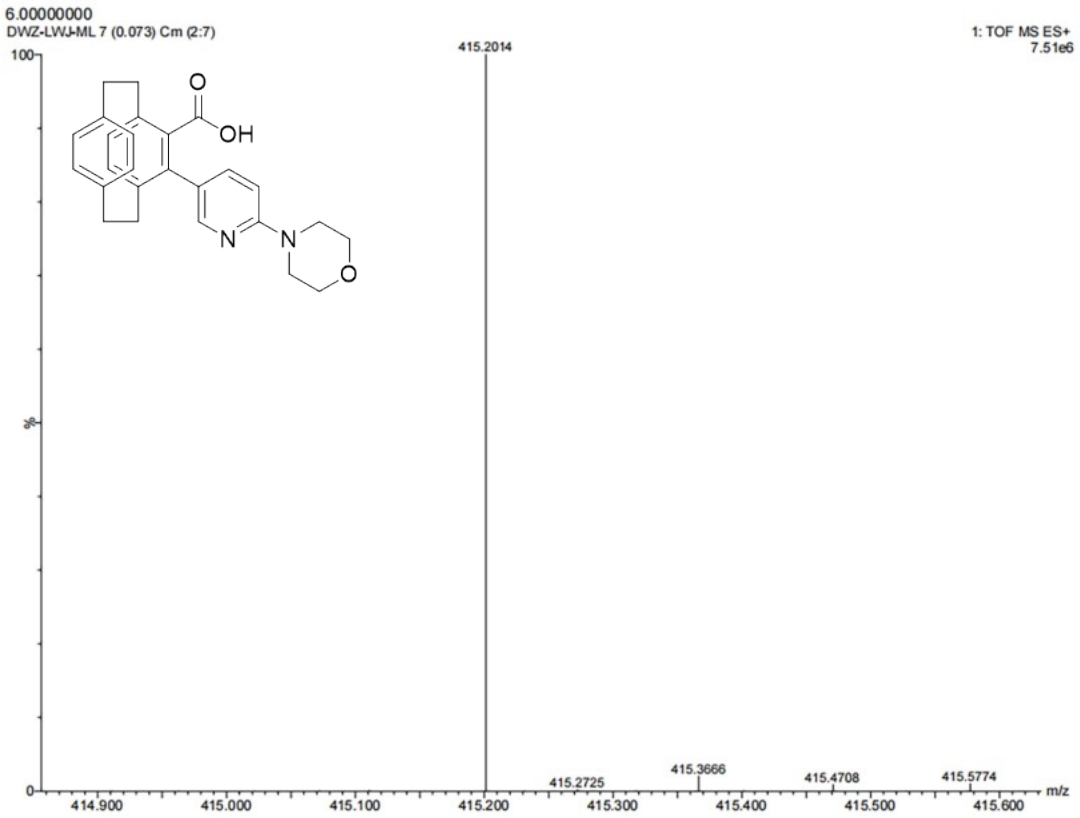

1.06
0.90
1.86
0.91
3.11
1.15
1.13
0.90
2.18
1.23
2.35
3.30
6.12
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

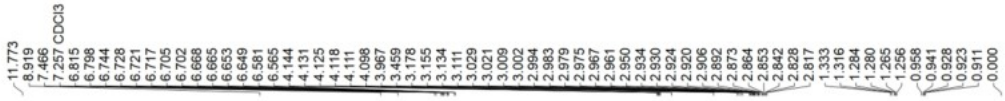

O
OH
N
O^{i}Pr
126 MHz, CDCl$_3$
171.050
162.028
145.924
142.772
140.871
140.404
139.231
138.548
136.809
136.645
134.780
133.138
132.864
132.016
131.689
130.387
129.873
111.856
77.264 CDCl3
77.009 CDCl3
76.756 CDCl3
68.856
35.375
34.804
33.037
29.703
22.085
0.001
136
134
132
130
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

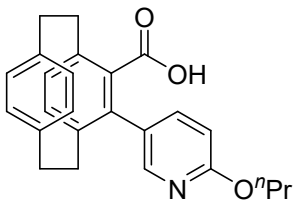

6.00000000
LWJ-YBY-0323 170 (1.026) Cm (170:183)
1: TOF MS ES+
1.23e5
388.1906
100
%
0
O
OH
N
O^{i}Pr
388.188
388.190
388.192
388.194
388.196
388.198
m/z


500 MHz, CDCl3
f1 (ppm)

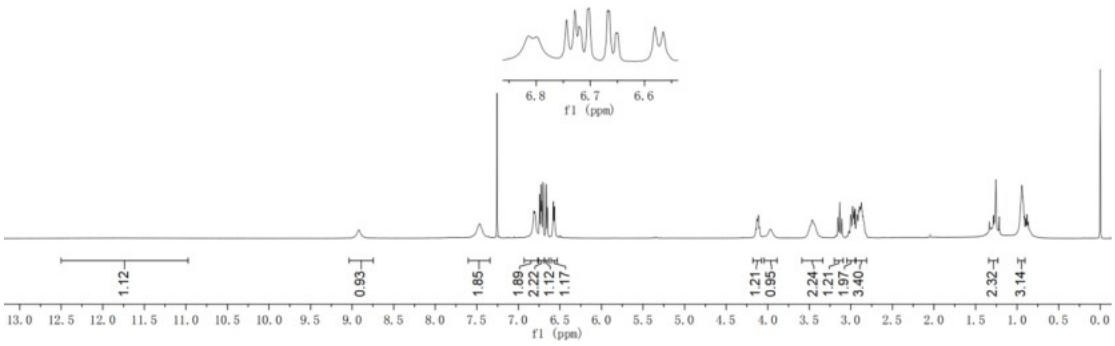

126 MHz, CDCl3
f1 (ppm)

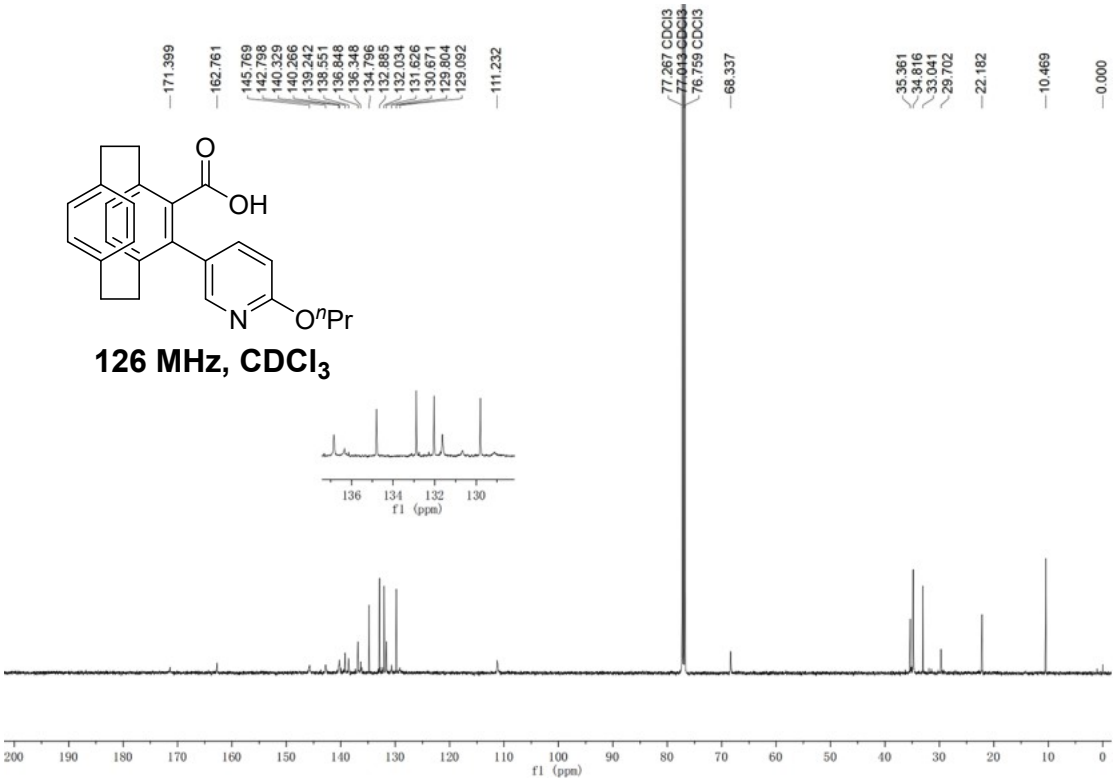


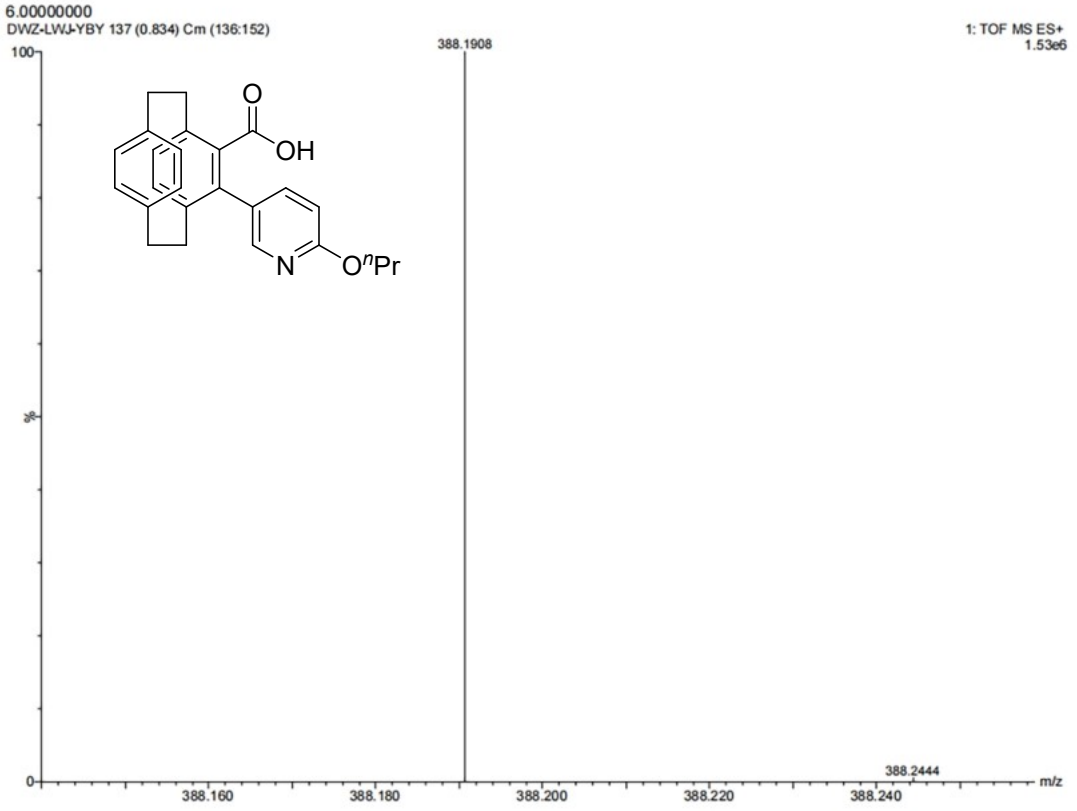


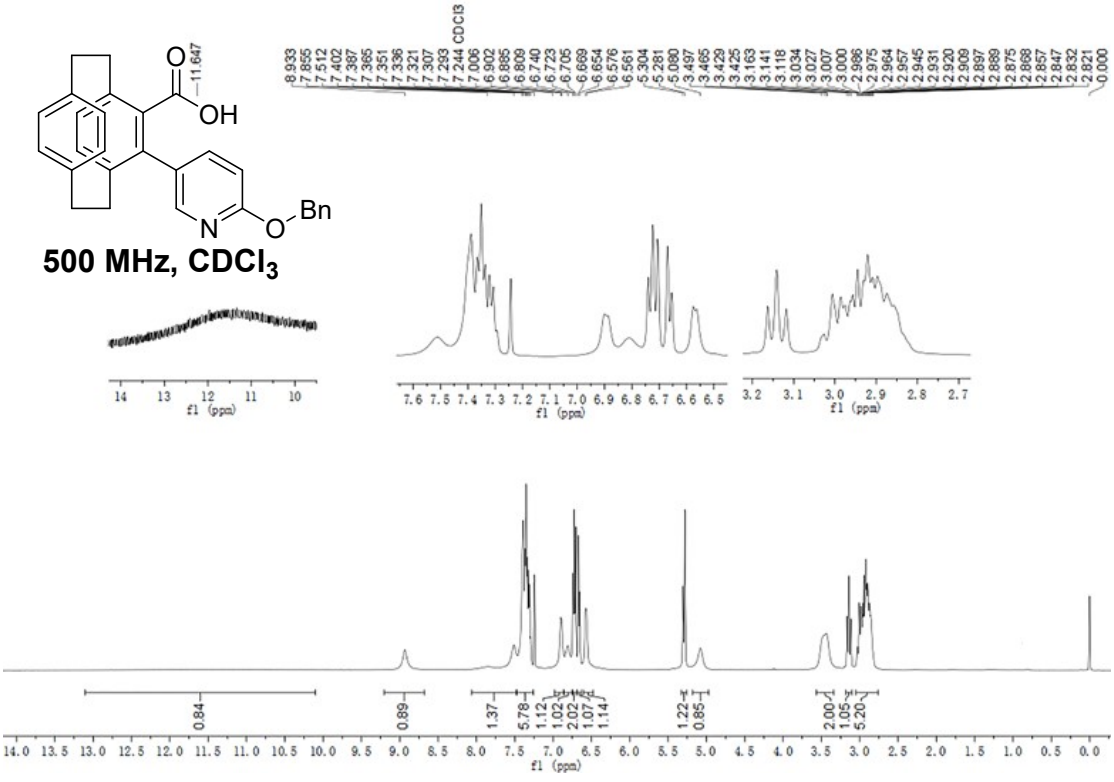


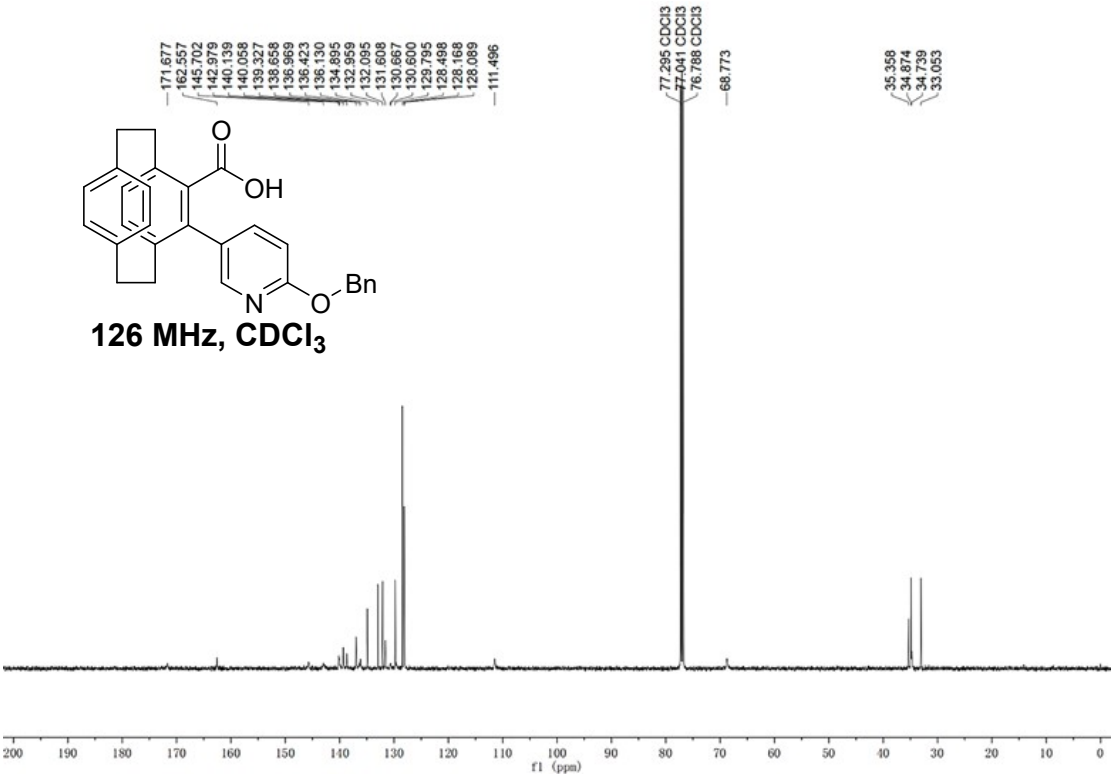
500 MHz, $CDCl_3$

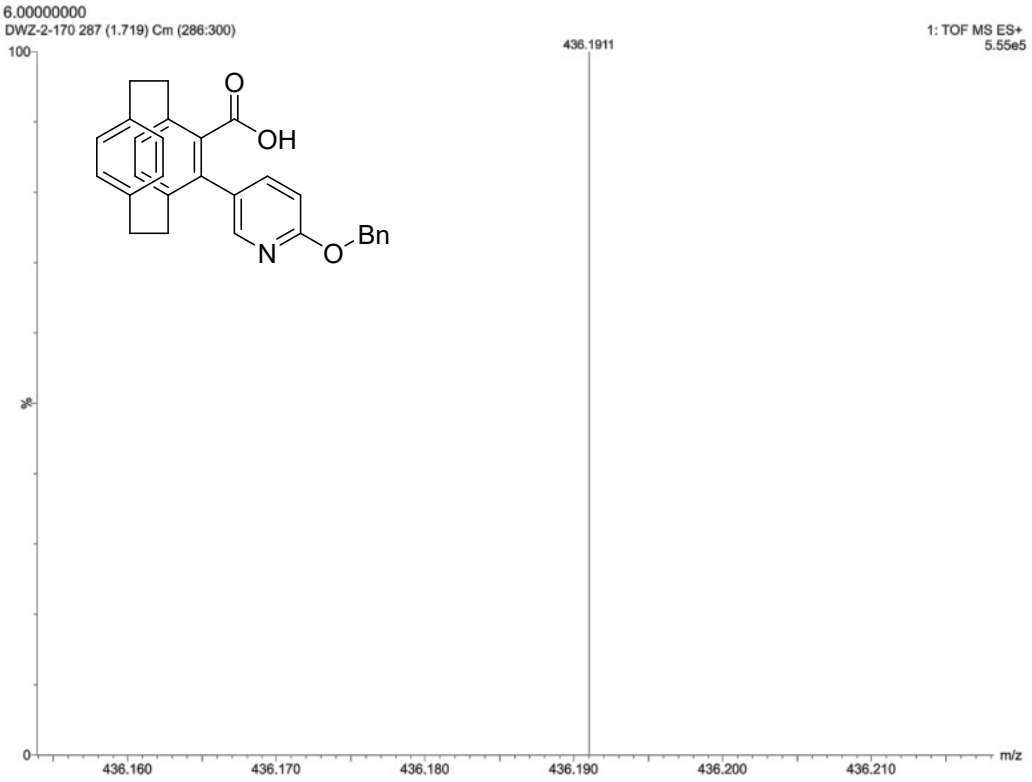


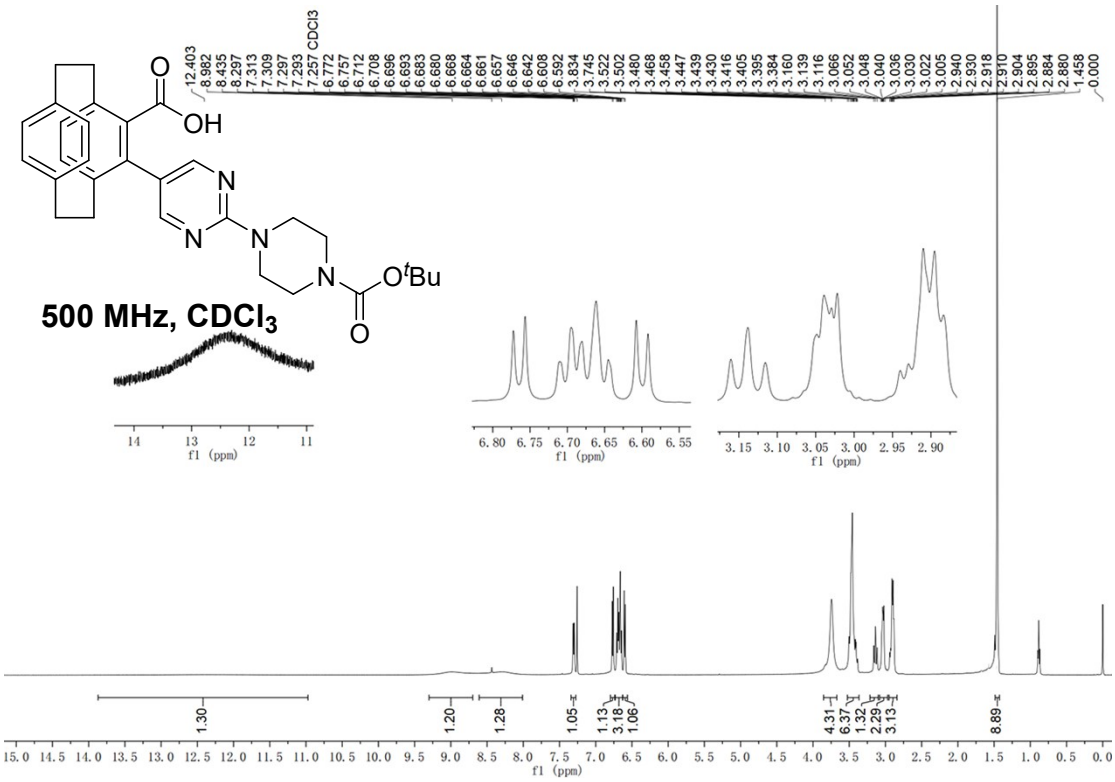

171.399
162.761
145.769
142.798
140.329
140.266
139.242
138.551
136.848
136.348
134.796
132.885
132.034
131.626
130.671
129.804
129.092
111.232
77.267 CDCl3
77.013 CDCl3
76.759 CDCl3
68.337
35.361
34.816
33.041
29.702
22.182
10.469
0.000
O
OH
N
O^{n}Pr
126 MHz, CDCl$_3$
136 134 132 130
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

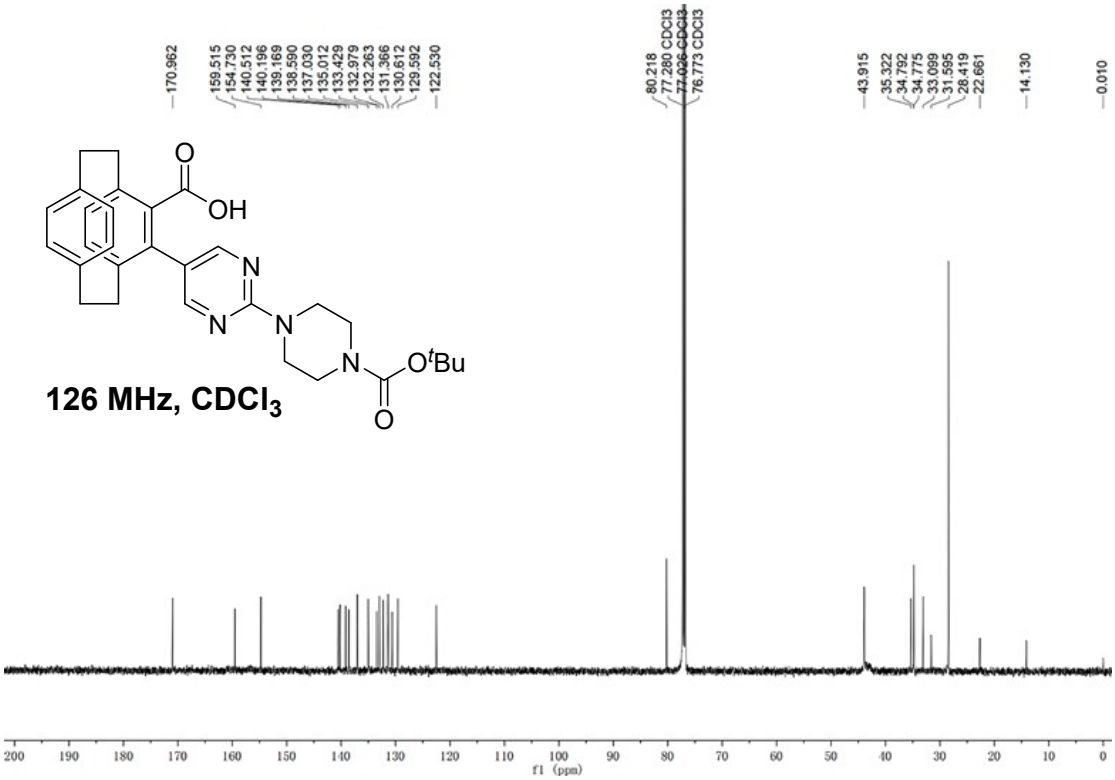

6.00000000
DWZ-LWJ-YBY 137 (0.834) Cm (136:152)
1: TOF MS ES+
1.53e6
388.1908
100
%
0
O
OH
N
O^{n}Pr
388.2444
m/z
388.160
388.180
388.200
388.220
388.240

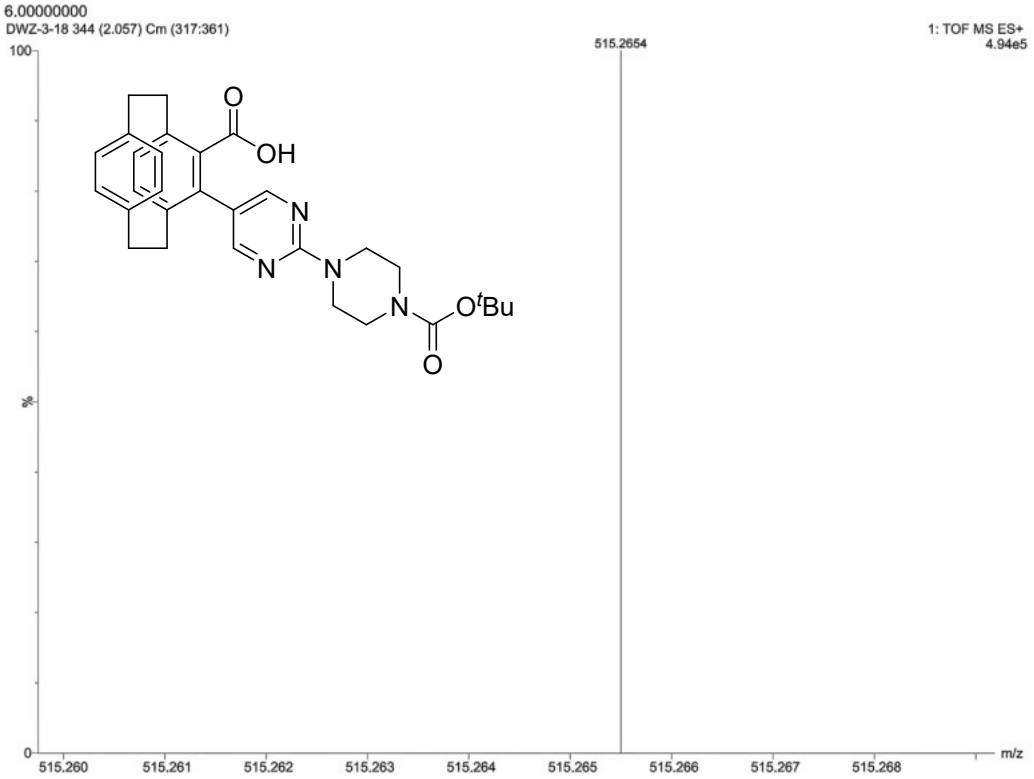

O
11.647
OH
N
O
Bn
500 MHz, CDCl3
CDCl3
f1 (ppm)
0.84
0.89
1.37
5.78
1.12
1.02
2.02
1.07
1.14
1.22
0.85
2.00
1.05
5.20

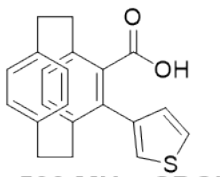

171.677
162.557
145.702
142.979
140.139
140.058
139.327
138.658
136.969
136.423
136.130
134.895
132.959
132.095
131.608
130.687
130.600
129.795
128.498
128.168
128.089
111.496
77.295 CDCl3
77.041 CDCl3
76.788 CDCl3
68.773
35.358
34.874
34.739
33.053
O
OH
N
O
Bn
126 MHz, CDCl3
f1 (ppm)


6.00000000
DWZ-2-170 287 (1.719) Cm (286:300)
1: TOF MS ES+
5.55e5
436.1911
100
%
0
436.160
436.170
436.180
436.190
436.200
436.210
m/z
O
OH
N
O
Bn

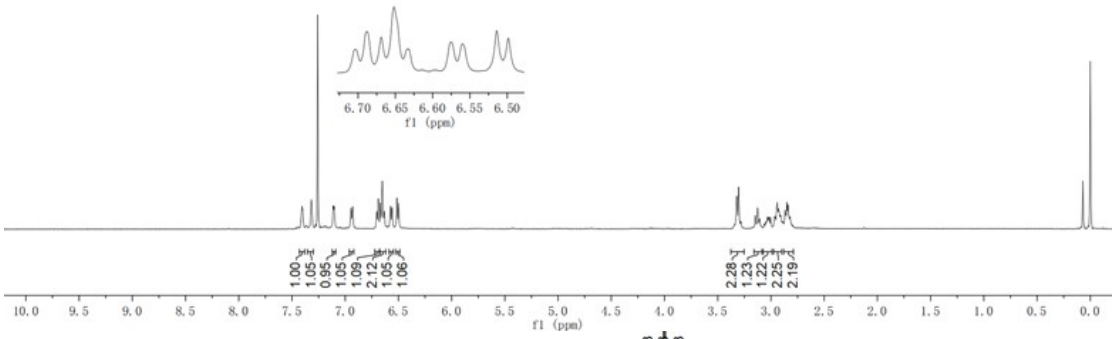

O
OH
N
N
N
N
O
O^{t}Bu
500 MHz, CDCl$_3$
CDCl3
f1 (ppm)
1.30
1.20
1.28
1.05
1.13
3.18
1.06
4.31
6.37
1.32
2.29
3.13
8.89

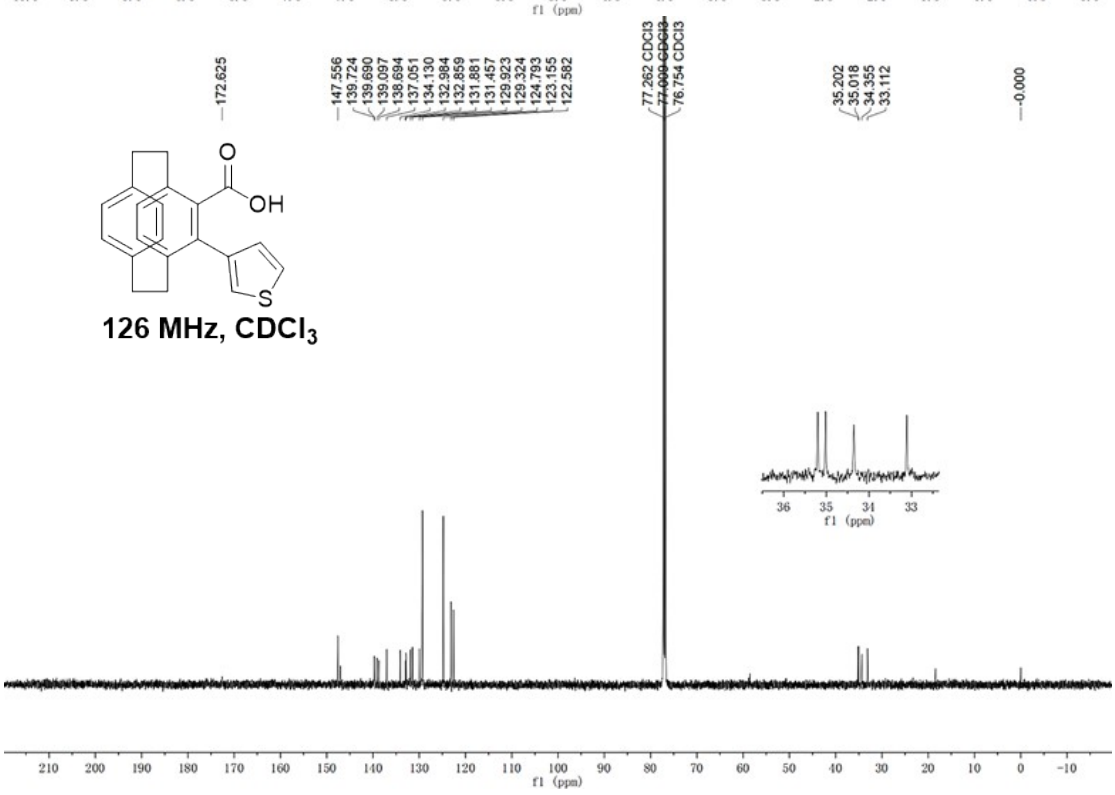

170.962
159.515
154.730
140.512
140.196
139.169
138.590
137.030
135.012
133.429
132.979
132.263
131.366
130.612
129.592
122.530
80.218
77.280 CDCl3
77.036 CDCl3
76.773 CDCl3
43.915
35.322
34.792
34.775
33.099
31.595
28.419
22.661
14.130
0.010
O
OH
N
N
N
N
O^{t}Bu
O
126 MHz, CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


6.00000000
DWZ-3-18 344 (2.057) Cm (317:361)
1: TOF MS ES+
4.94e5
515.2654
100
%
0
O
OH
N
N
N
N
O^{t}Bu
O
515.260 515.261 515.262 515.263 515.264 515.265 515.266 515.267 515.268
m/z

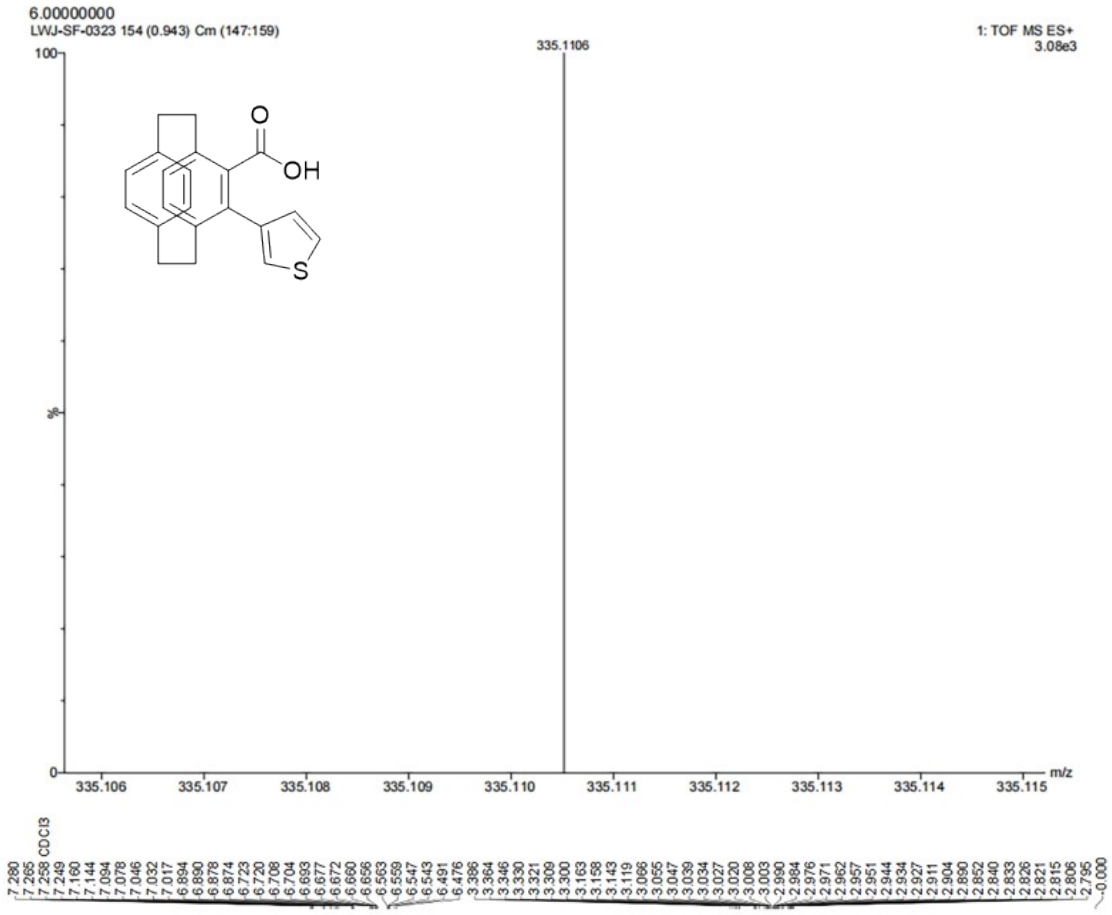


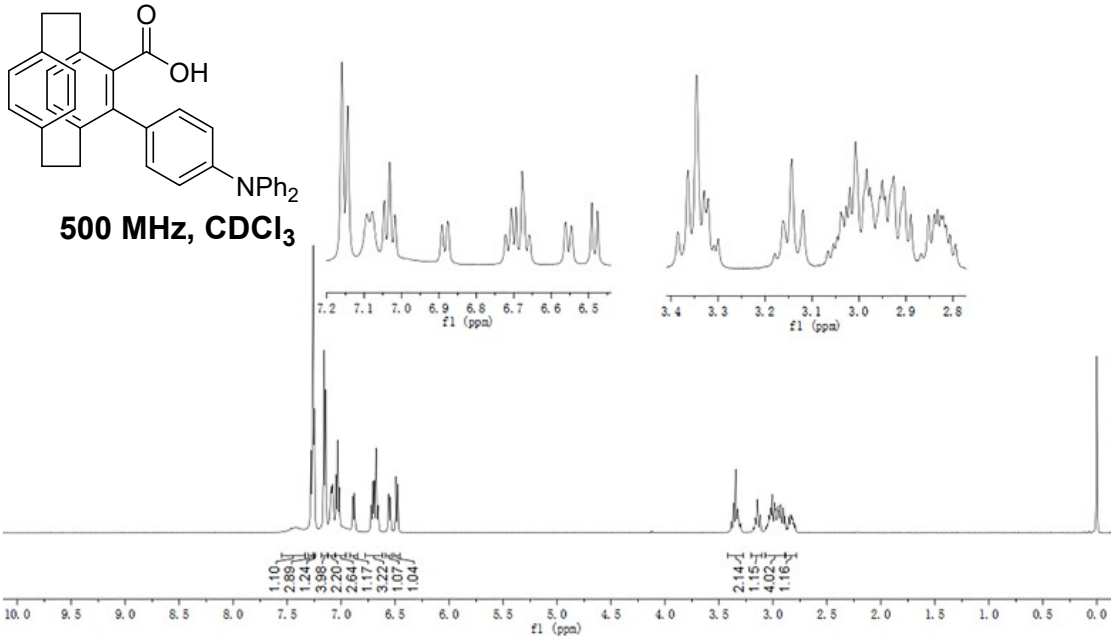
500 MHz, $CDCl_3$

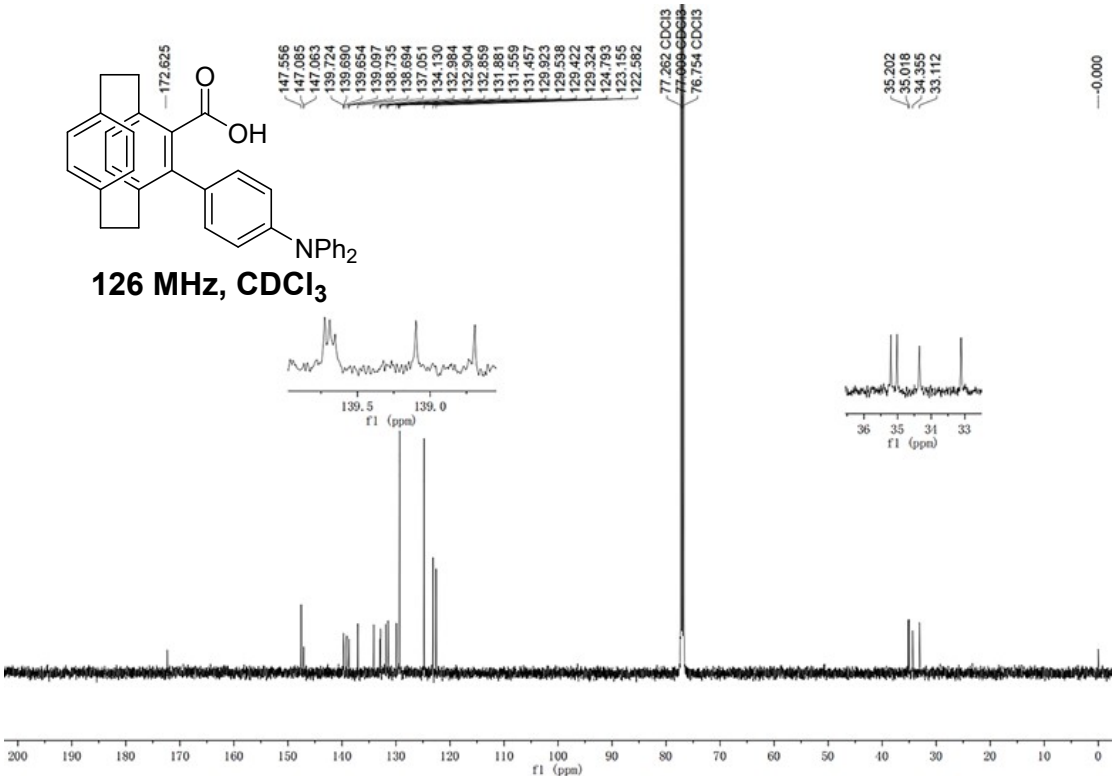


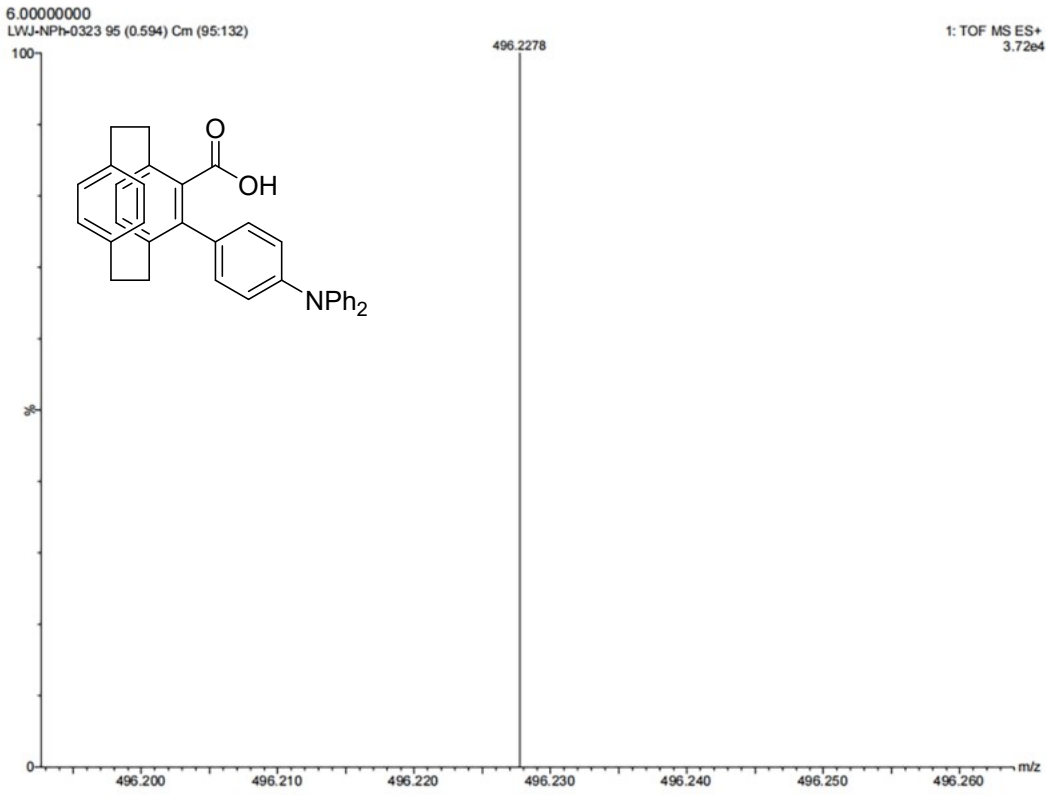


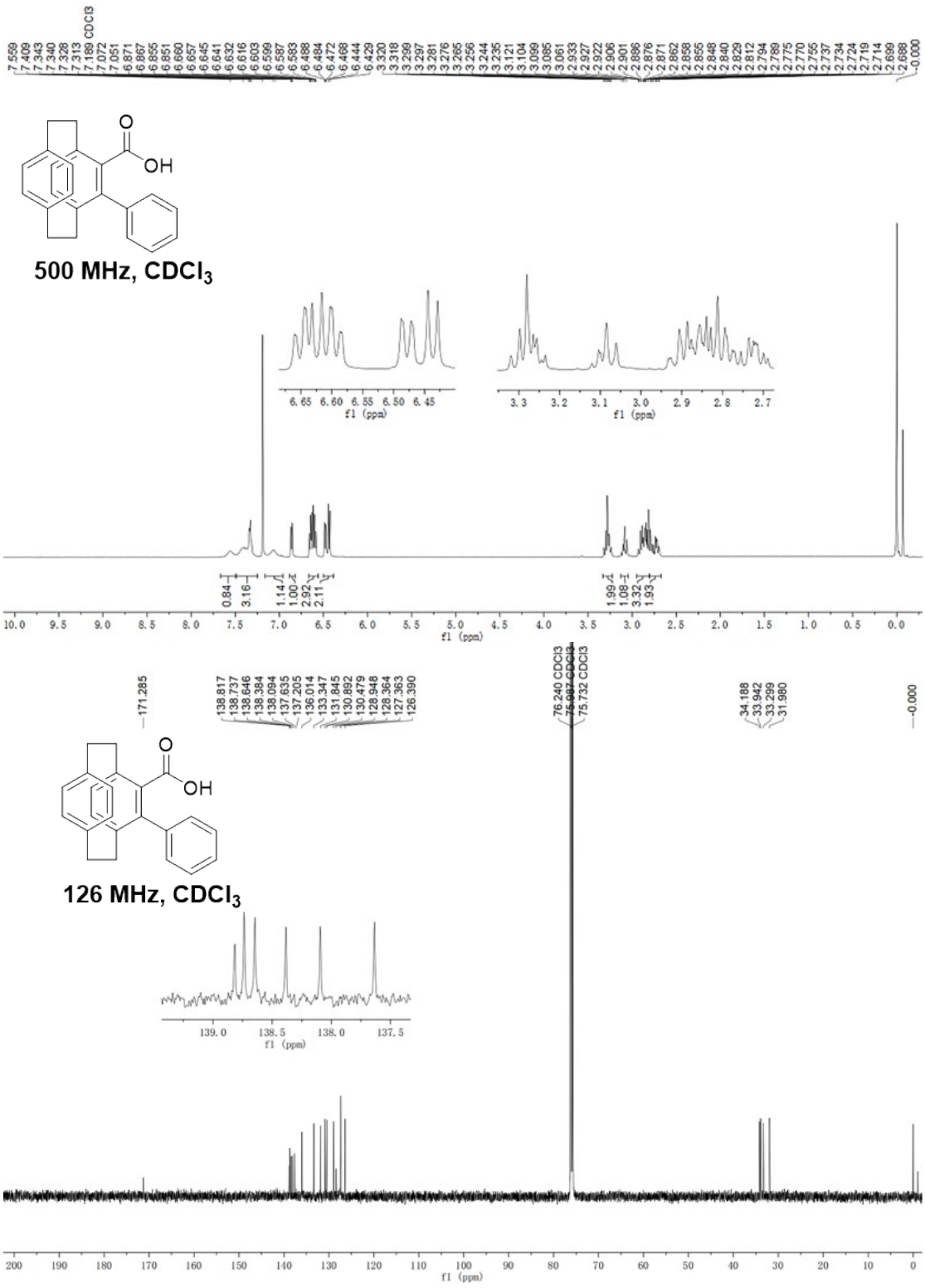
126 MHz, $CDCl_3$

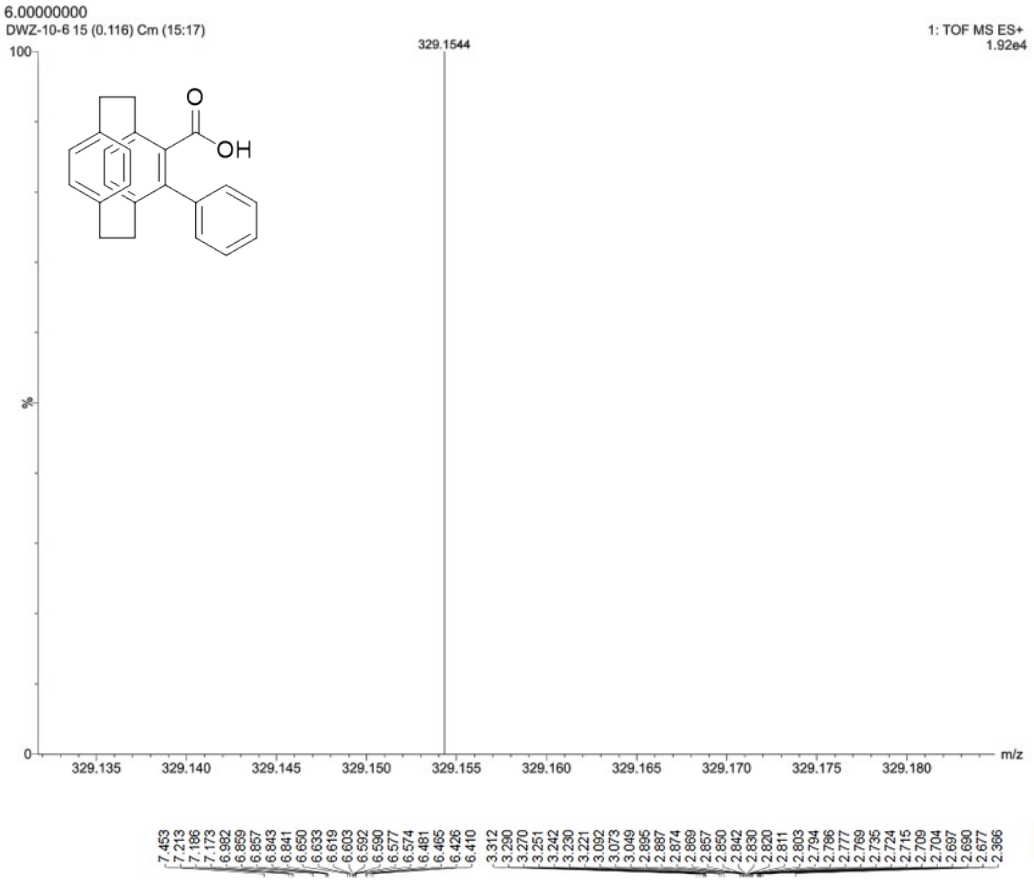

6.00000000
LWJ-SF-0323 154 (0.943) Cm (147:159)
1: TOF MS ES+
3.08e3
335.1106
100
%
0
O
OH
S
335.106
335.107
335.108
335.109
335.110
335.111
335.112
335.113
335.114
335.115
m/z
CDCl3

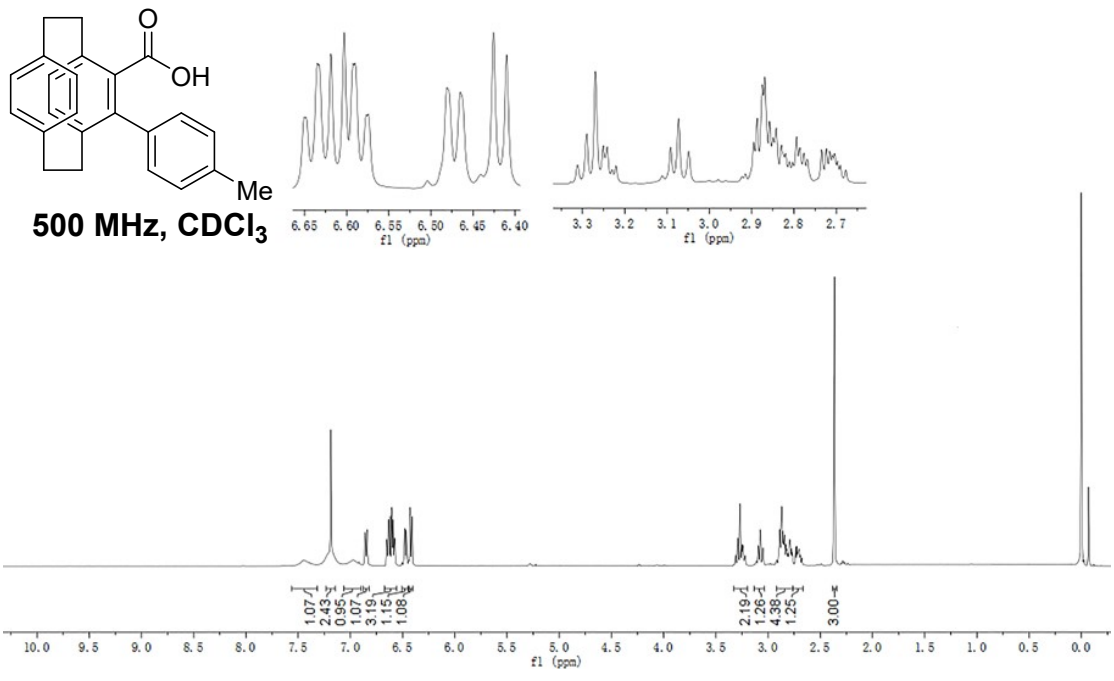

O
OH
NPh2
500 MHz, CDCl3
f1 (ppm)

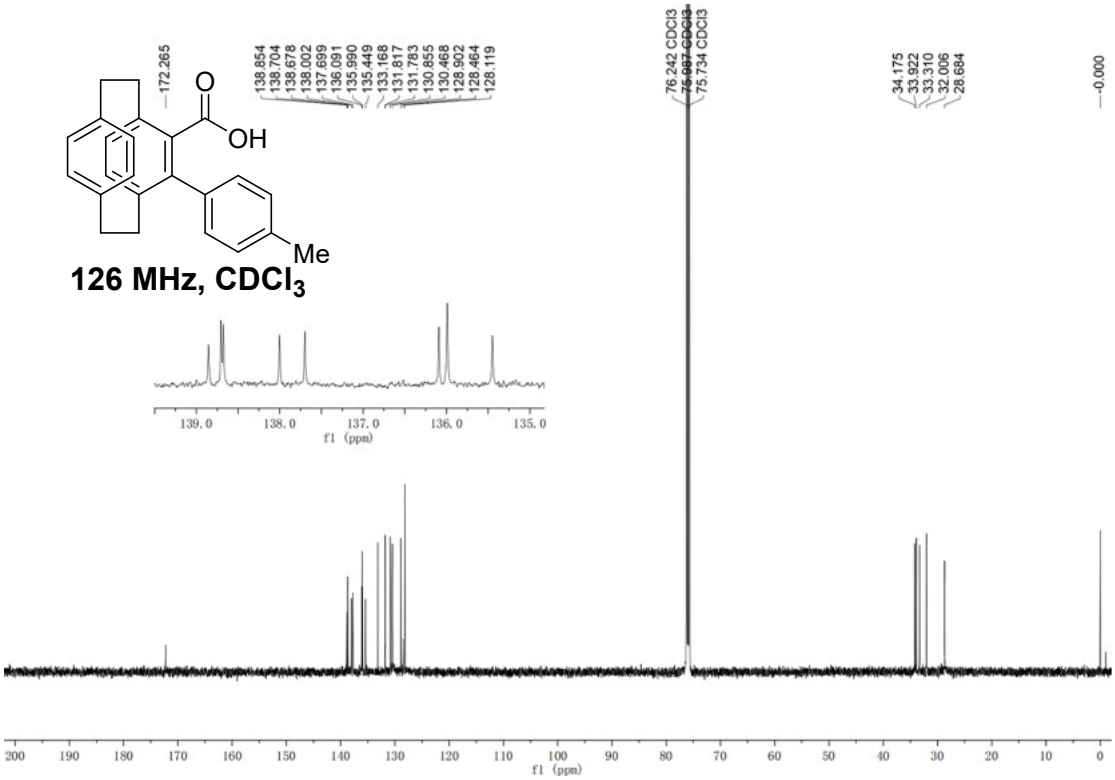

172.625
147.556
147.085
147.063
139.724
139.690
139.654
139.097
138.735
138.694
137.051
134.130
132.984
132.904
132.859
131.881
131.559
131.457
129.923
129.538
129.422
129.324
124.793
123.155
122.582
77.262 CDCl3
77.000 CDCl3
76.754 CDCl3
35.202
35.018
34.355
33.112
0.000
O
OH
NPh2
126 MHz, CDCl3
139.5
139.0
f1 (ppm)
36
35
34
33
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

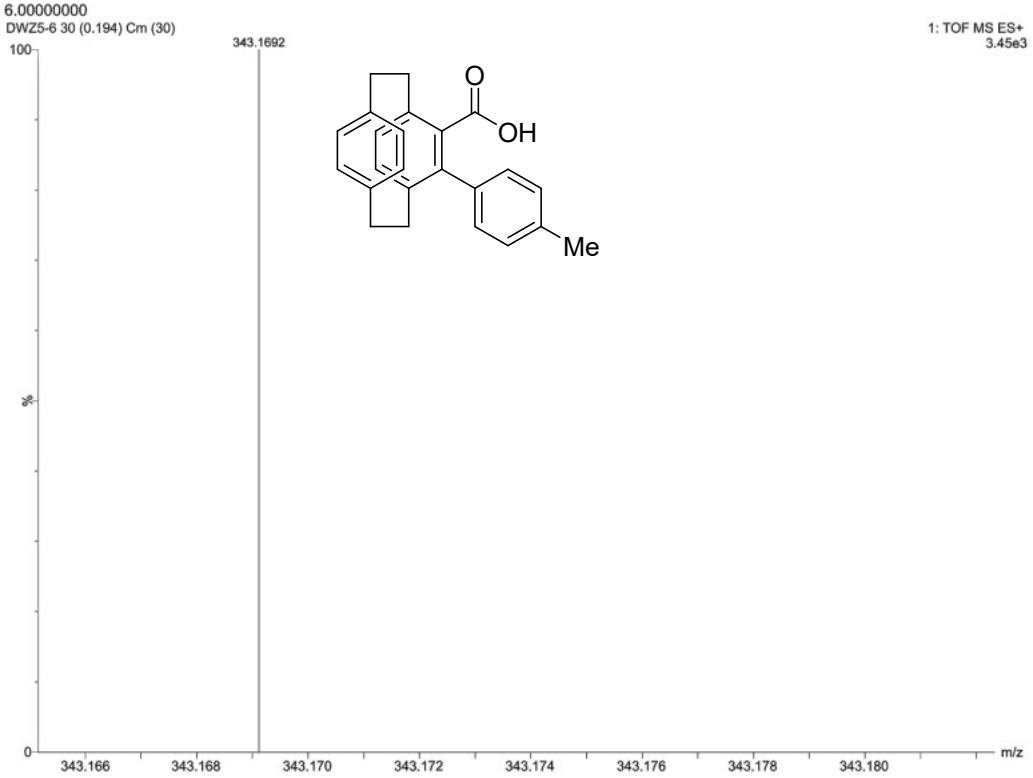

6.00000000
LWJ-NPh-0323 95 (0.594) Cm (95:132)
1: TOF MS ES+
3.72e4
496.2278
100
%
0
O
OH
NPh2
496.200
496.210
496.220
496.230
496.240
496.250
496.260
m/z

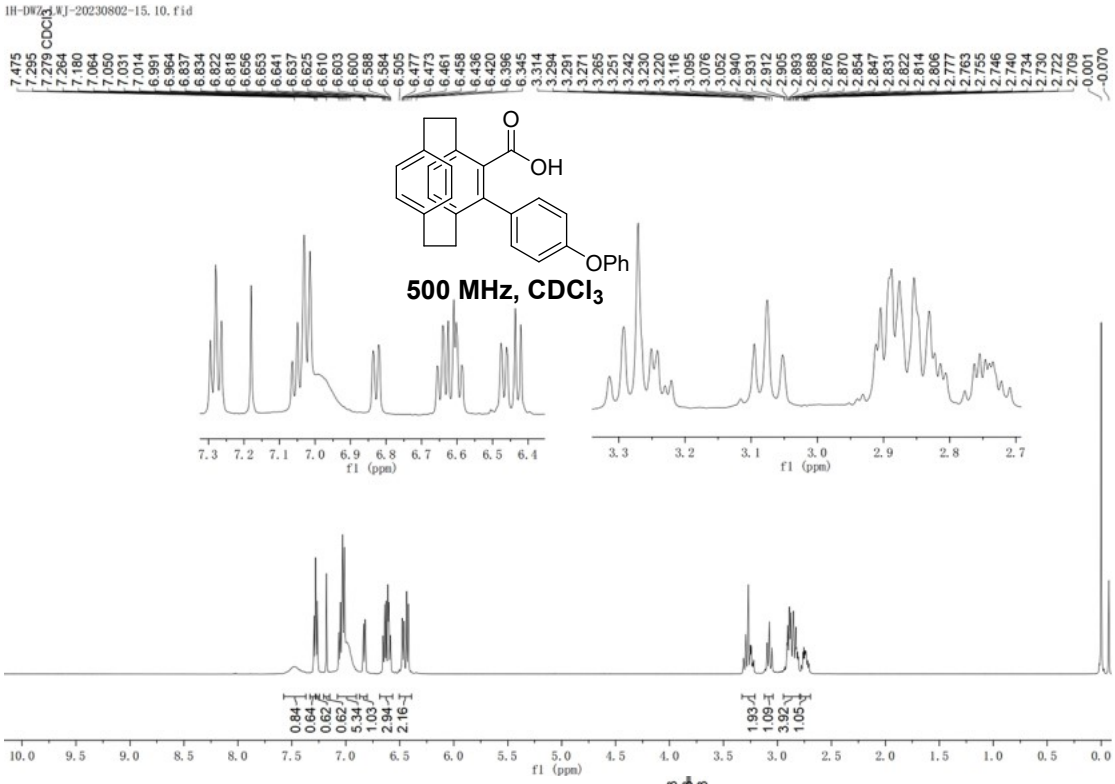

7.559
7.409
7.343
7.340
7.328
7.313
7.189 CDCl3
7.072
7.051
6.871
6.867
6.855
6.851
6.660
6.657
6.645
6.641
6.632
6.616
6.603
6.599
6.587
6.583
6.488
6.484
6.472
6.468
6.444
6.429
3.320
3.318
3.299
3.297
3.281
3.276
3.265
3.256
3.244
3.235
3.121
3.104
3.099
3.085
3.061
2.933
2.927
2.922
2.906
2.901
2.886
2.876
2.871
2.862
2.858
2.855
2.846
2.840
2.829
2.812
2.794
2.789
2.775
2.770
2.755
2.737
2.734
2.724
2.719
2.714
2.699
2.688
-0.000
O
OH
500 MHz, CDCl3
6.65 6.60 6.55 6.50 6.45
f1 (ppm)
3.3 3.2 3.1 3.0 2.9 2.8 2.7
f1 (ppm)
0.84
3.16
1.14
1.00
2.92
2.11
1.99
1.08
3.32
1.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
171.285
138.817
138.737
138.646
138.384
138.094
137.635
137.205
136.014
133.347
131.845
130.892
130.479
128.948
128.364
127.363
126.390
76.240 CDCl3
76.667 CDCl3
75.732 CDCl3
34.188
33.942
33.299
31.980
-0.000
O
OH
126 MHz, CDCl3
139.0 138.5 138.0 137.5
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

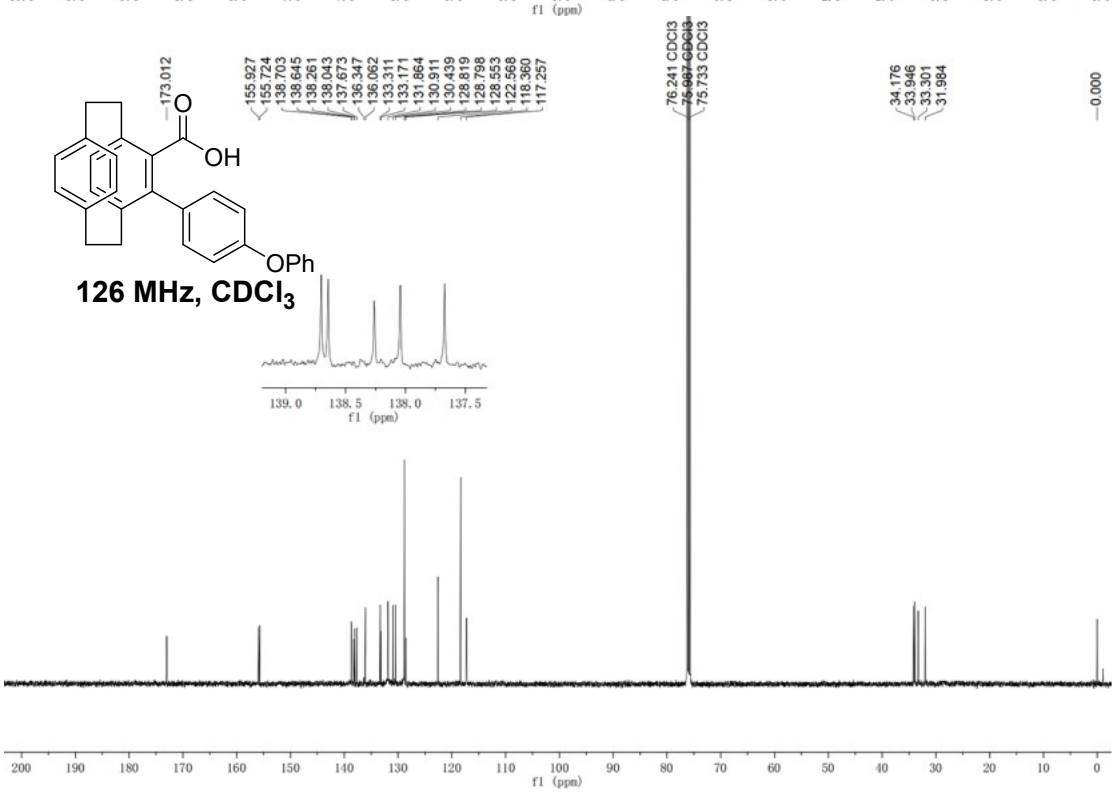

6.00000000
DWZ-10-6 15 (0.116) Cm (15:17)
1: TOF MS ES+
1.92e4
329.1544
100
%
0
O
OH
329.135
329.140
329.145
329.150
329.155
329.160
329.165
329.170
329.175
329.180
m/z

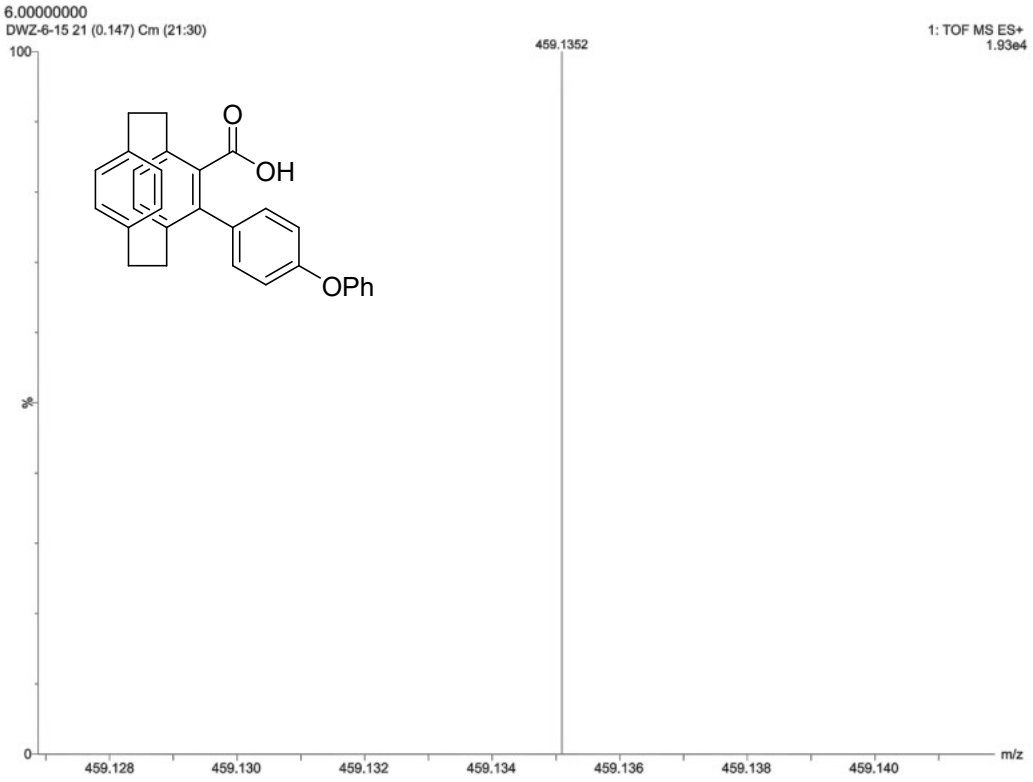

O
OH
Me
500 MHz, CDCl3
f1 (ppm)
1.07
2.43
0.95
1.07
3.19
1.15
1.08
2.19
1.26
4.38
1.25
3.00

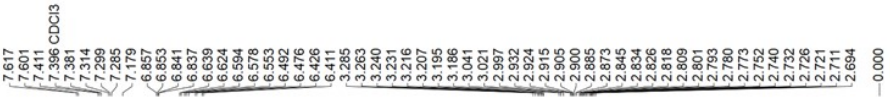

O
OH
Me
126 MHz, CDCl3
172.265
138.854
138.704
138.678
138.002
137.699
136.091
135.990
135.449
133.168
131.817
131.783
130.855
130.468
128.902
128.464
128.119
76.242 CDCl3
75.987 CDCl3
75.734 CDCl3
34.175
33.922
33.310
32.006
28.684
-0.000
f1 (ppm)

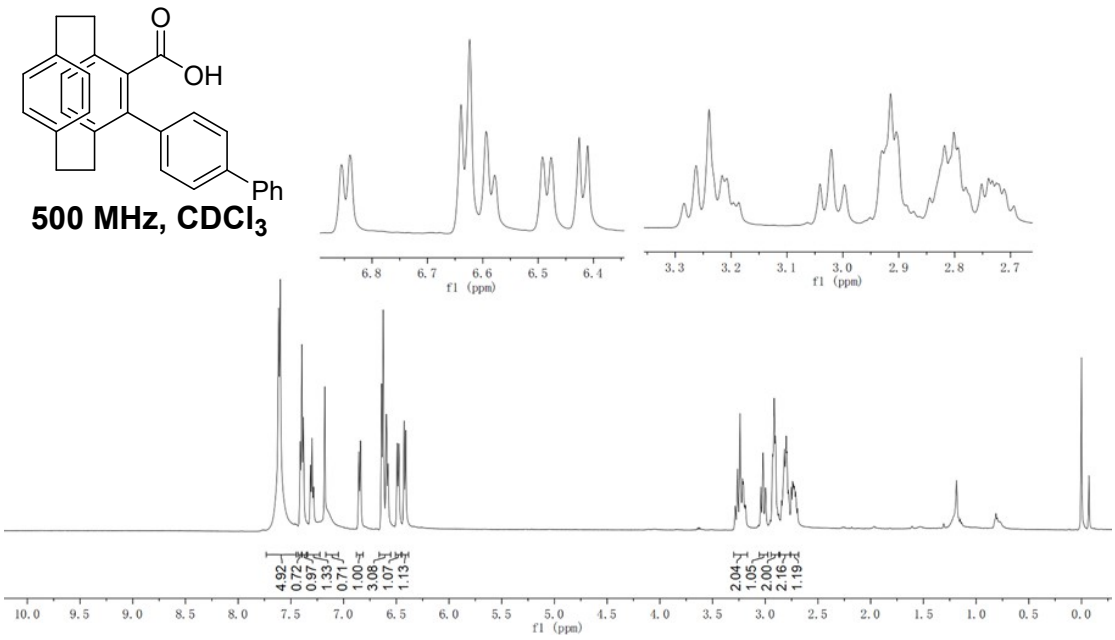

6.00000000
DWZ5-6 30 (0.194) Cm (30)
1: TOF MS ES+
3.45e3
343.1692
O
OH
Me
%
m/z

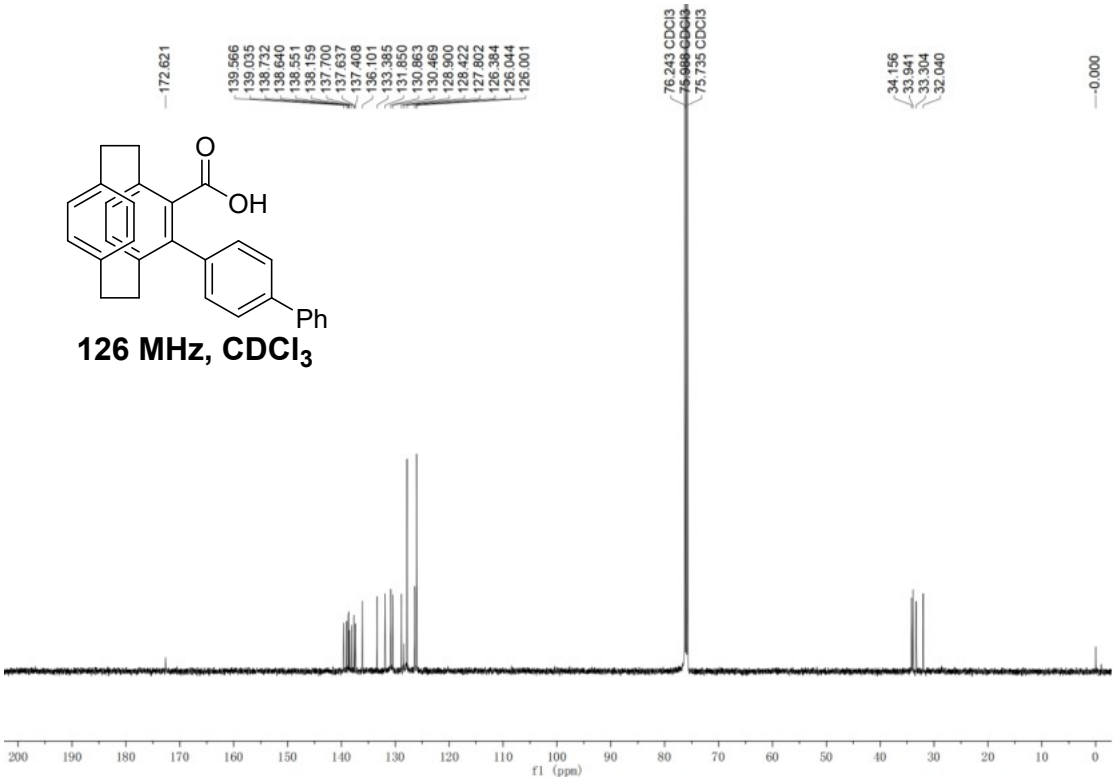

1H-DWZ-WJ-20230802-15.10.fid
O
OH
OPh
500 MHz, CDCl3
f1 (ppm)

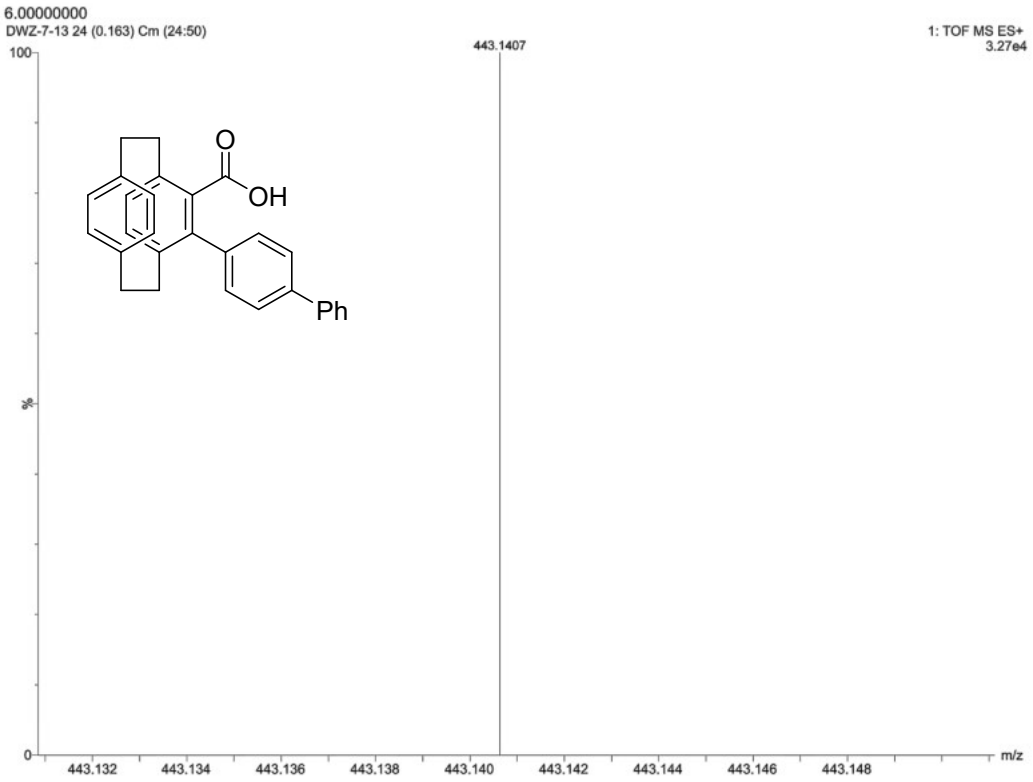

O
OH
OPh
126 MHz, CDCl3
f1 (ppm)

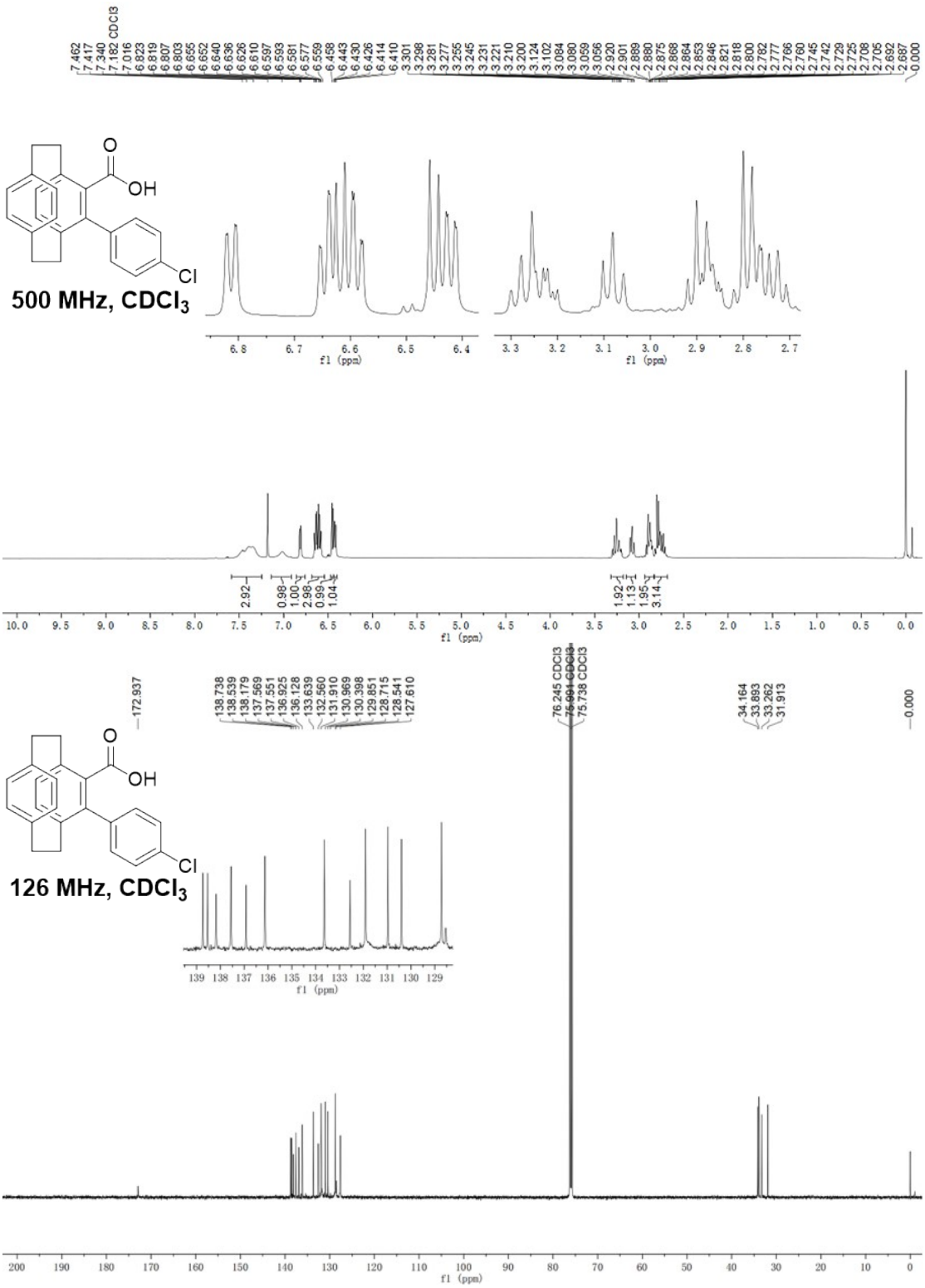

6.00000000
DWZ-6-15 21 (0.147) Cm (21:30)
1: TOF MS ES+
1.93e4
459.1352
100
%
0
O
OH
OPh
459.128
459.130
459.132
459.134
459.136
459.138
459.140
m/z

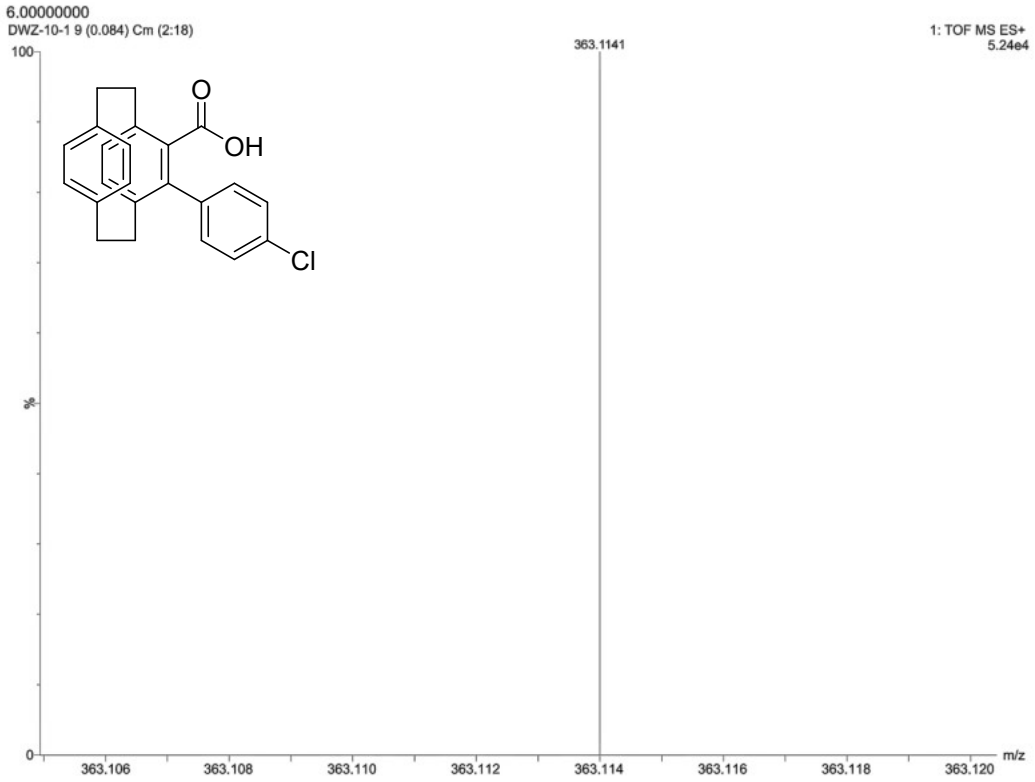

CDCl3
7.617
7.601
7.411
7.396
7.381
7.314
7.299
7.285
7.179
6.857
6.853
6.841
6.837
6.639
6.624
6.594
6.578
6.553
6.492
6.476
6.426
6.411
3.285
3.263
3.240
3.231
3.216
3.207
3.195
3.186
3.041
3.021
2.997
2.932
2.924
2.915
2.905
2.900
2.885
2.873
2.845
2.834
2.826
2.818
2.809
2.801
2.793
2.780
2.773
2.752
2.740
2.732
2.726
2.721
2.711
2.694
0.000

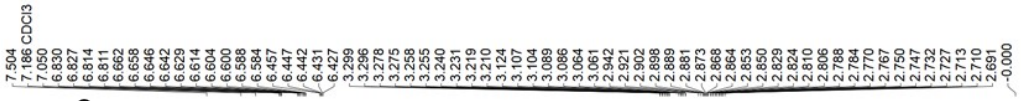

O
OH
Ph
500 MHz, CDCl3
6.8
6.7
6.6
6.5
6.4
f1 (ppm)
3.3
3.2
3.1
3.0
2.9
2.8
2.7
f1 (ppm)
4.92
0.72
0.97
1.33
0.71
1.00
3.08
1.07
1.13
2.04
1.05
2.00
2.16
1.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

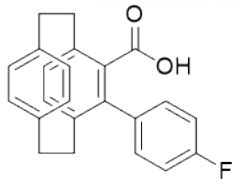

172.621
139.566
139.035
138.732
138.640
138.551
138.159
137.700
137.637
137.408
136.101
133.385
131.850
130.863
130.469
128.900
128.422
127.802
126.384
126.044
126.001
76.243 CDCl3
75.735 CDCl3
34.156
33.941
33.304
32.040
0.000
O
OH
Ph
126 MHz, CDCl3
f1 (ppm)


6.00000000
DWZ-7-13 24 (0.163) Cm (24:50)
1: TOF MS ES+
3.27e4
443.1407
100
%
0
O
OH
Ph
443.132
443.134
443.136
443.138
443.140
443.142
443.144
443.146
443.148
m/z

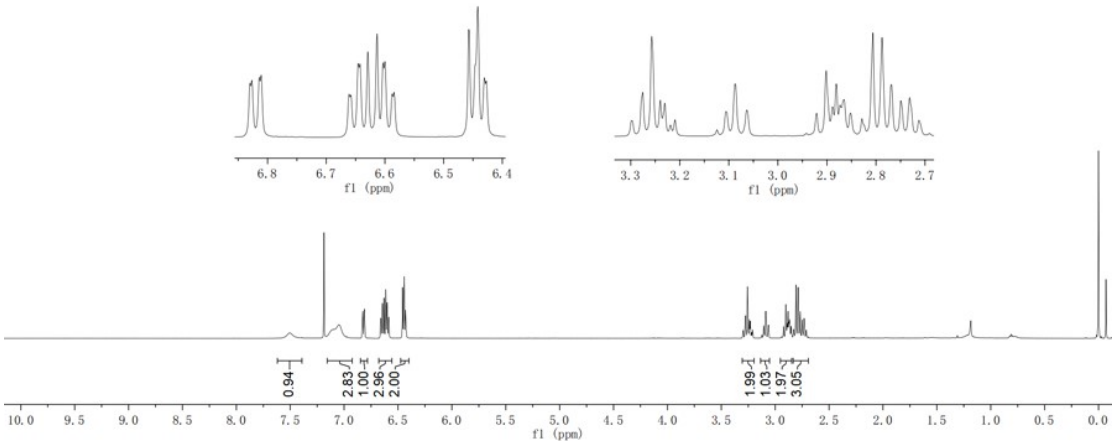

500 MHz, CDCl3
126 MHz, CDCl3
f1 (ppm)

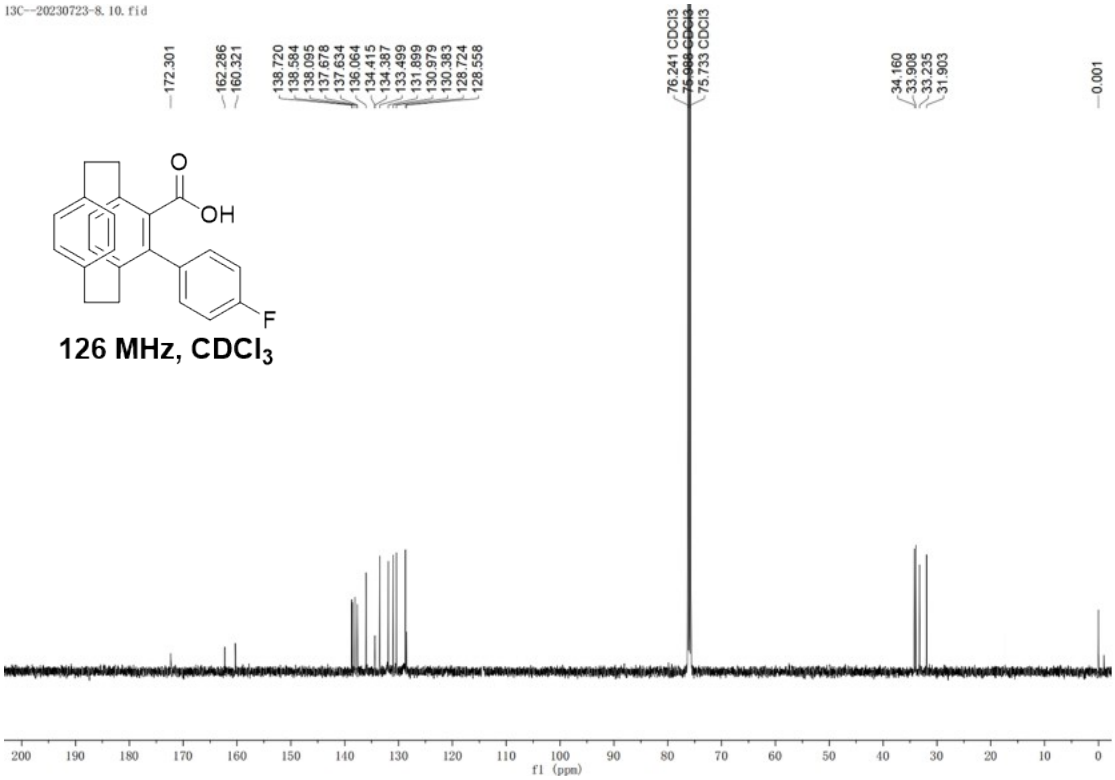


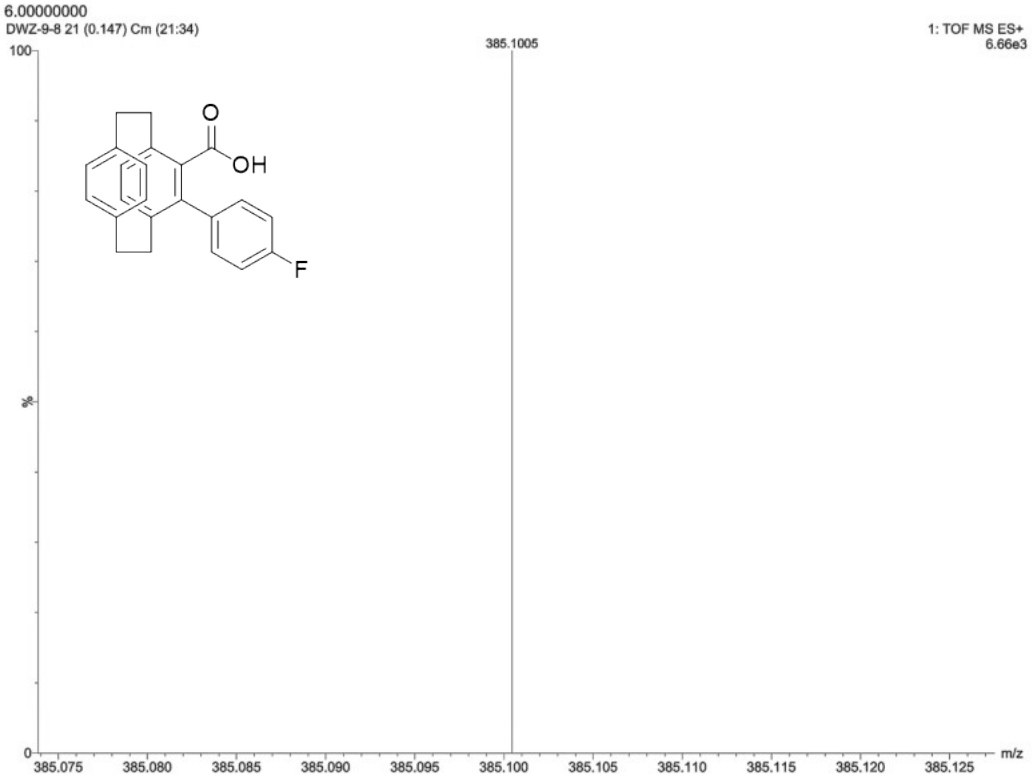


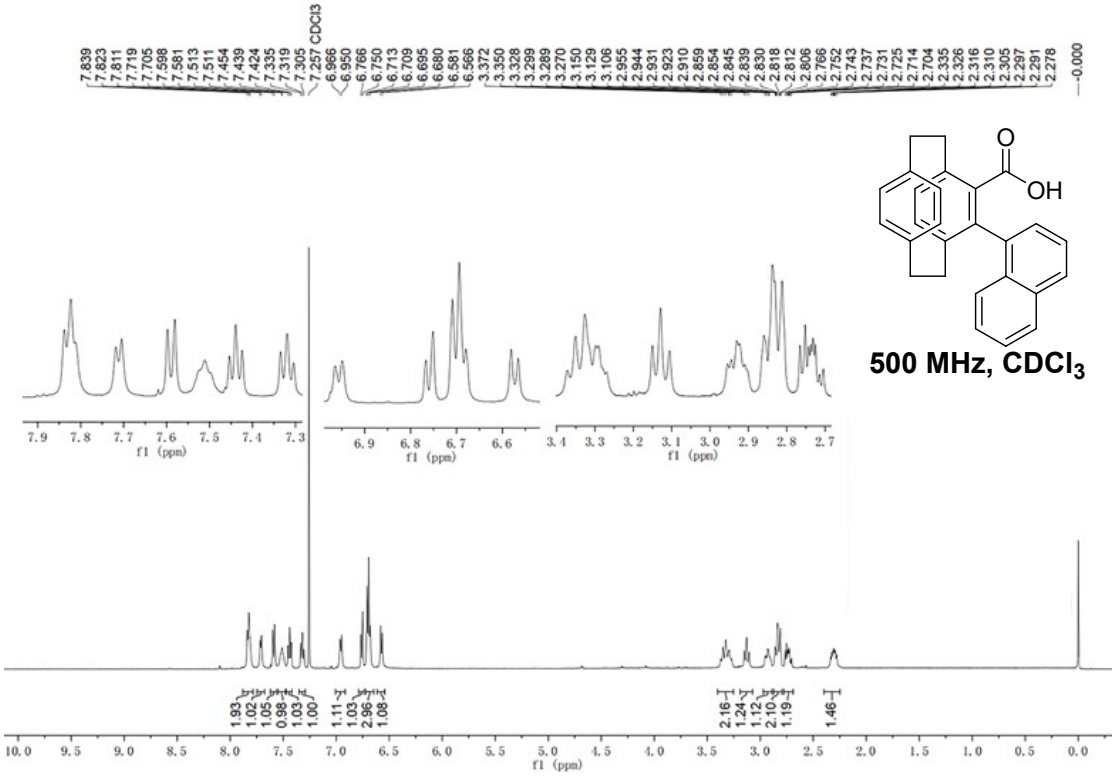


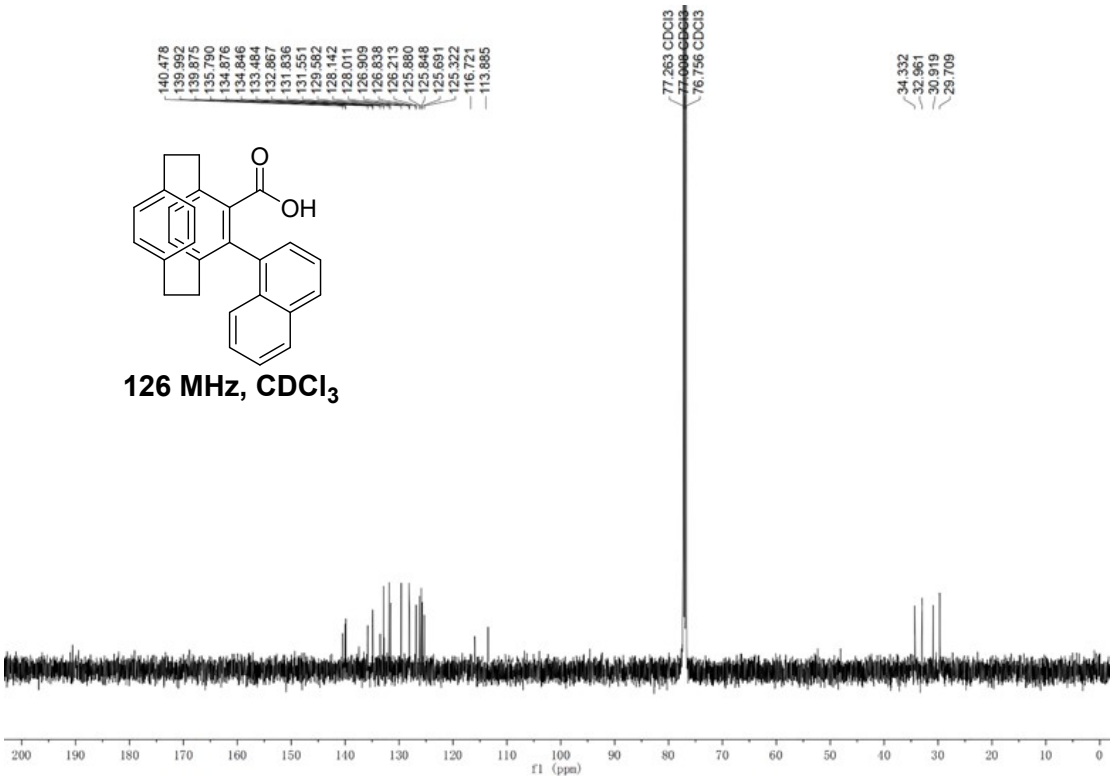
500 MHz, $CDCl_3$

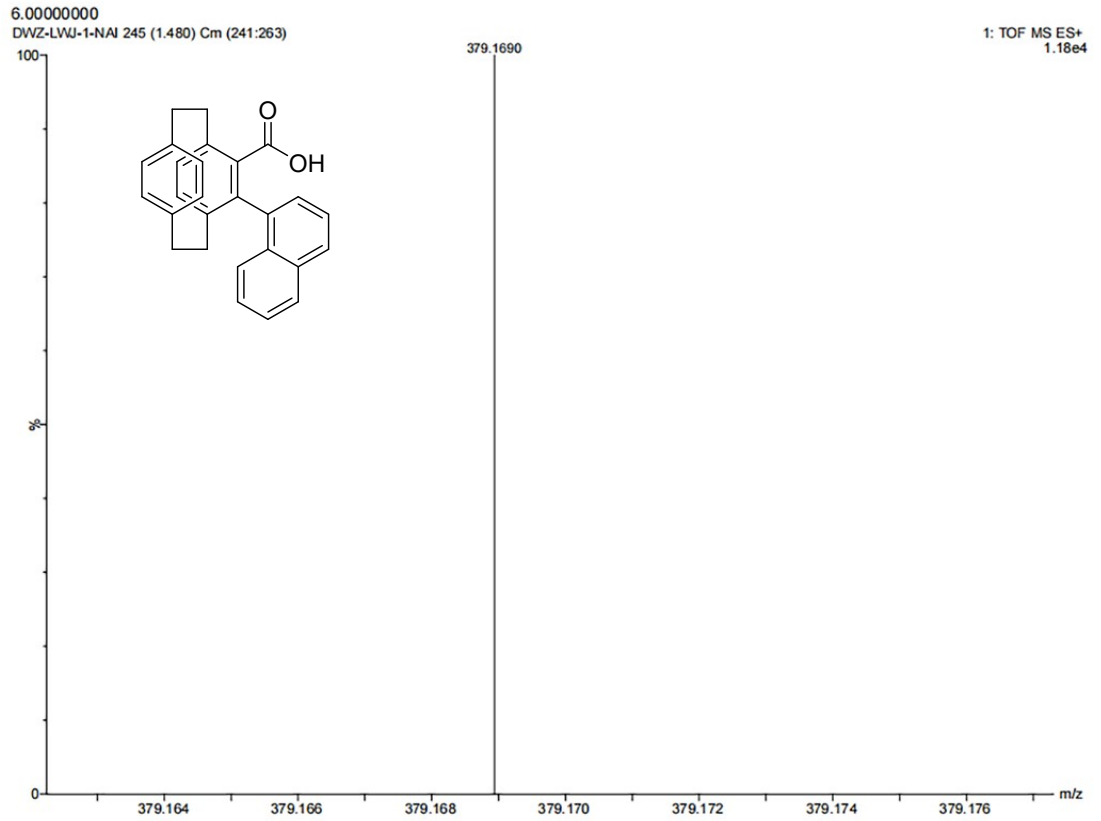


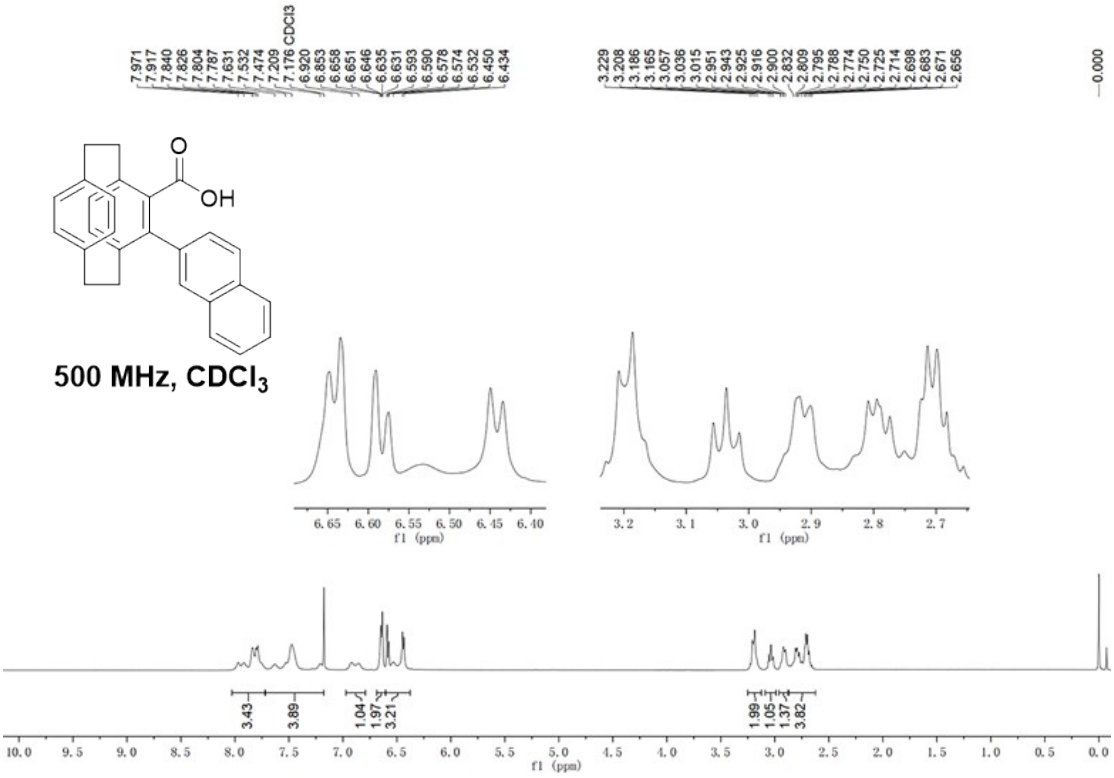

13C--20230723-8.10.fid
172.301
162.286
160.321
138.720
138.584
138.095
137.678
137.634
136.064
134.415
134.387
133.499
131.899
130.979
130.383
128.724
128.558
76.241 CDCl3
75.733 CDCl3
34.160
33.908
33.235
31.903
0.001
O
OH
F
126 MHz, CDCl3
f1 (ppm)

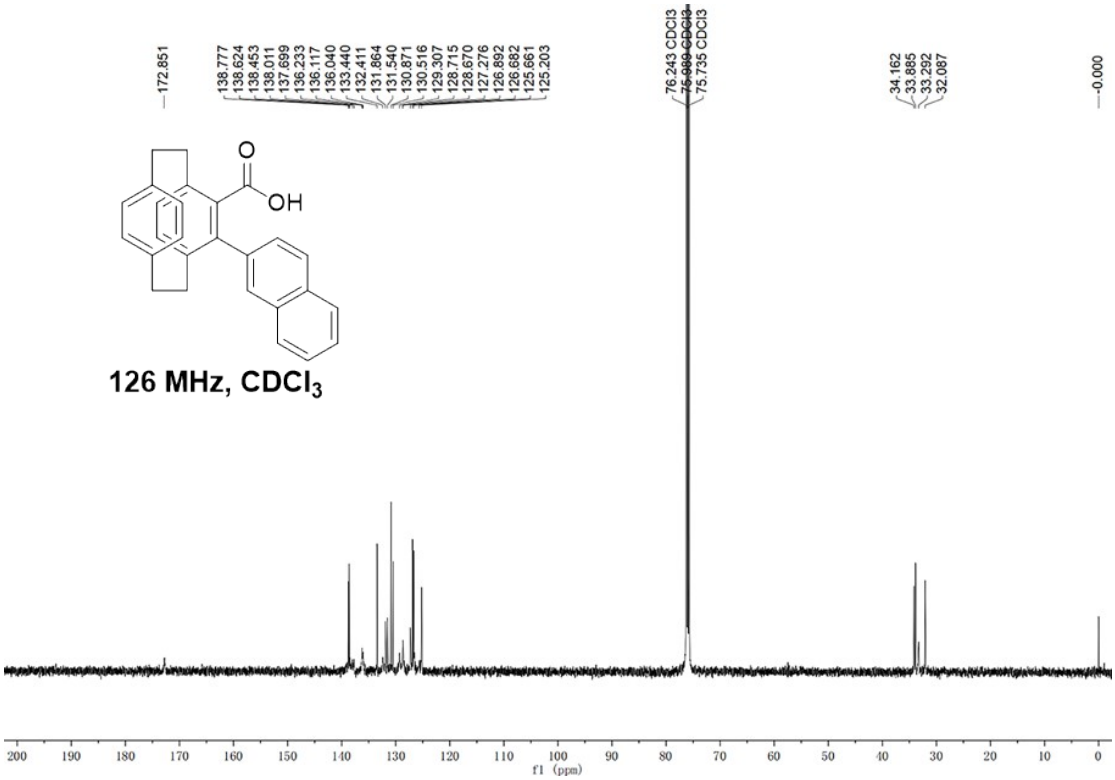

6.00000000
DWZ-9-8 21 (0.147) Cm (21:34)
1: TOF MS ES+
6.66e3
385.1005
100
%
0
O
OH
F
m/z
385.075
385.080
385.085
385.090
385.095
385.100
385.105
385.110
385.115
385.120
385.125


O
OH
500 MHz, CDCl3

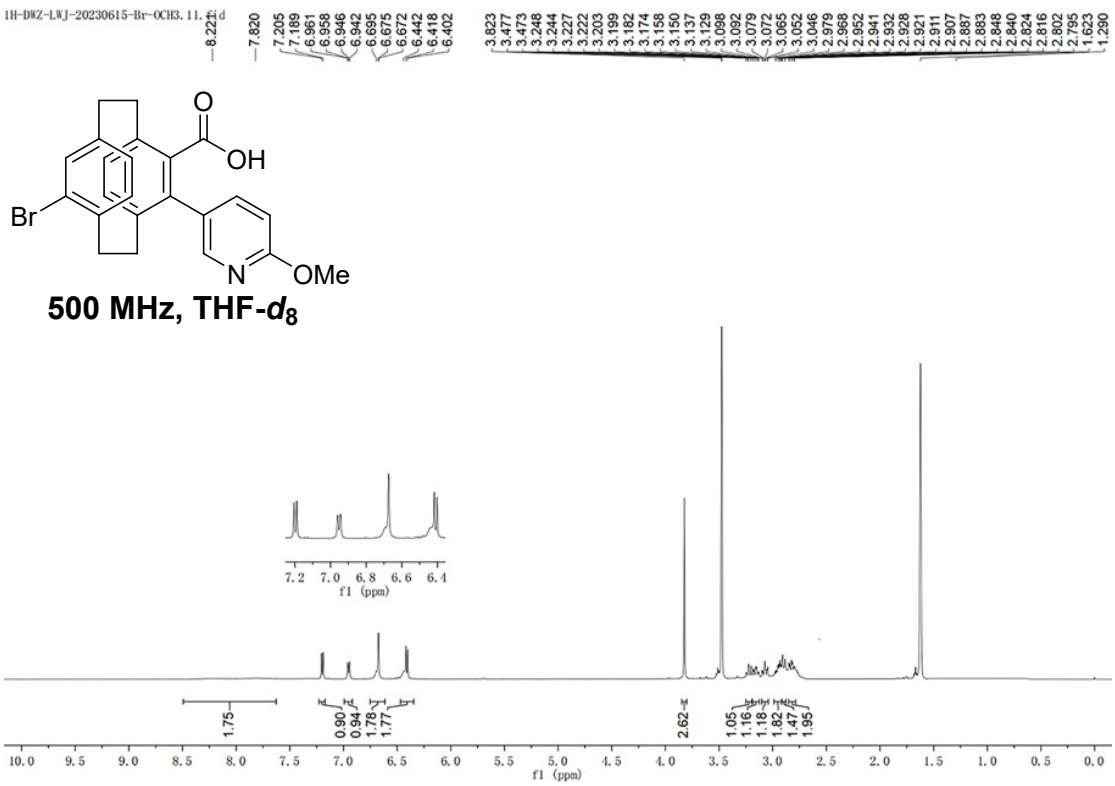

O
OH
126 MHz, CDCl3


6.00000000
DWZ-LWJ-1-NAI 245 (1.480) Cm (241:263)
1: TOF MS ES+
1.18e4
379.1690
100
%
0
O
OH
379.164
379.166
379.168
379.170
379.172
379.174
379.176
m/z

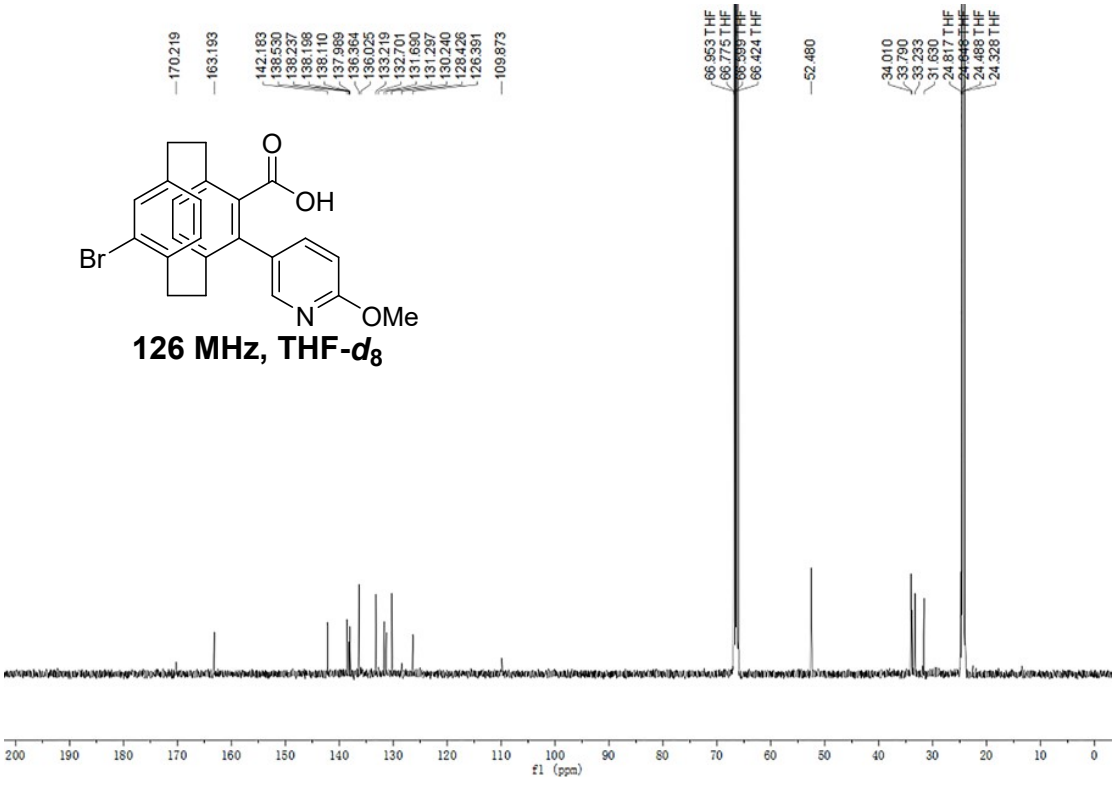

7.971
7.917
7.840
7.826
7.804
7.787
7.631
7.532
7.474
7.209
7.176 CDCl3
6.920
6.853
6.658
6.651
6.646
6.635
6.631
6.593
6.590
6.578
6.574
6.532
6.450
6.434
3.229
3.208
3.186
3.165
3.057
3.036
3.015
2.951
2.943
2.925
2.916
2.900
2.832
2.809
2.795
2.788
2.774
2.750
2.725
2.714
2.698
2.683
2.671
2.656
0.000
O
OH
500 MHz, CDCl3
6.65 6.60 6.55 6.50 6.45 6.40
f1 (ppm)
3.2 3.1 3.0 2.9 2.8 2.7
f1 (ppm)
3.43
3.89
1.04
1.97
3.21
1.99
1.05
1.37
3.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


172.851
138.777
138.624
138.453
138.011
137.699
136.233
136.117
136.040
133.440
132.411
131.864
131.540
130.871
130.516
129.307
128.715
128.670
127.276
126.892
126.682
125.661
125.203
76.243 CDCl3
75.735 CDCl3
34.162
33.885
33.292
32.087
0.000
O
OH
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

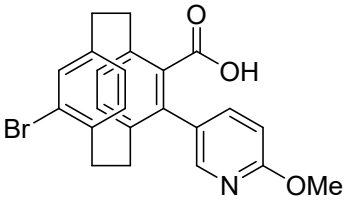

6.00000000
DWZ-8-5 298 (1.777) Cm (297:317)
1: TOF MS ES+
2.75e4
379.1699
100
%
0
O
OH
379.165 379.166 379.167 379.168 379.169 379.170 379.171 379.172 379.173
m/z

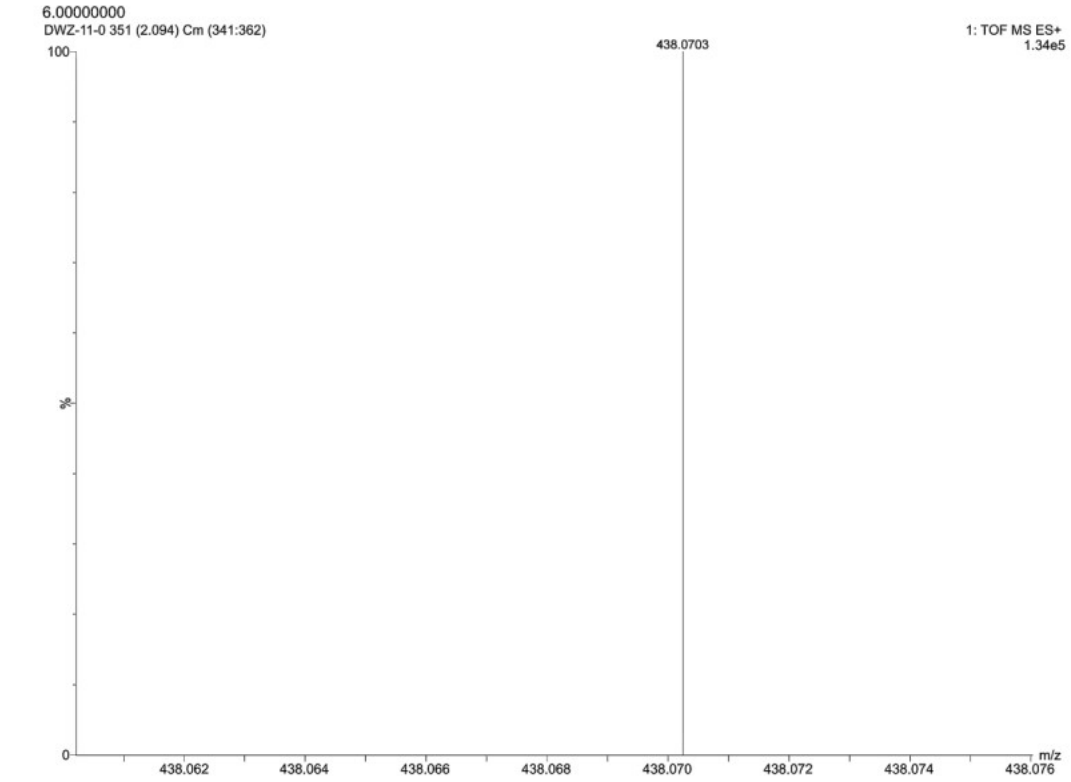


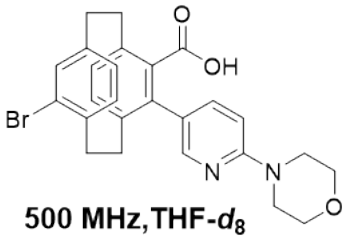
500 MHz, THF-d_8



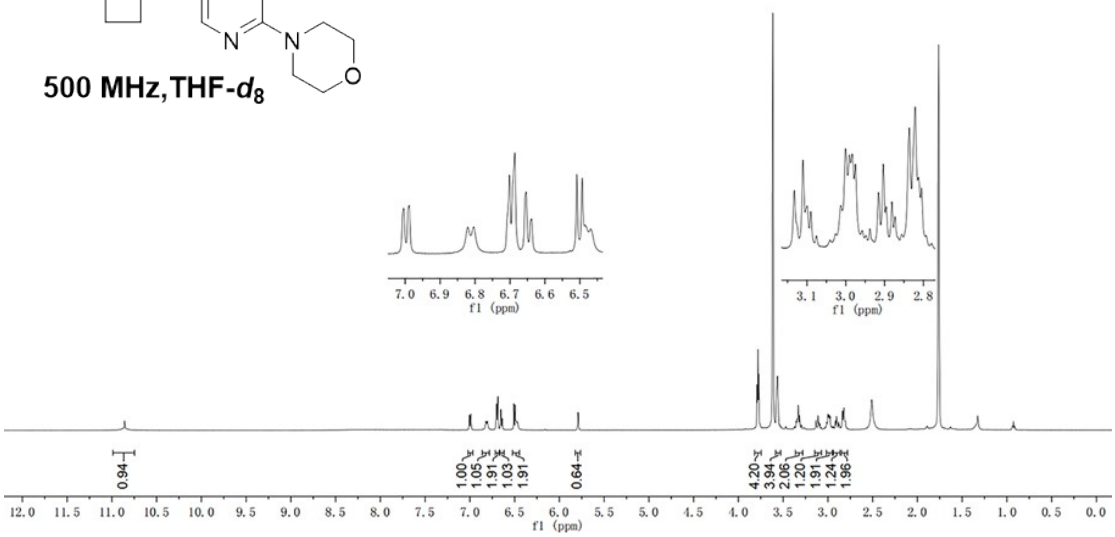
126 MHz, THF-d_8

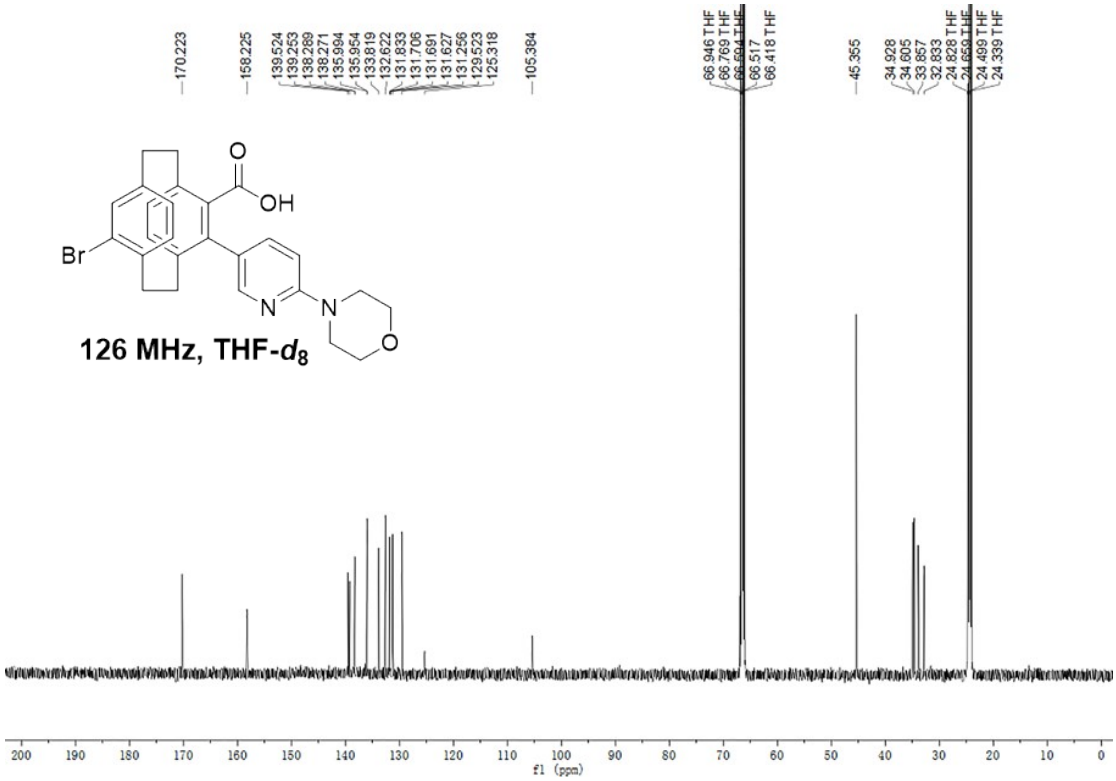


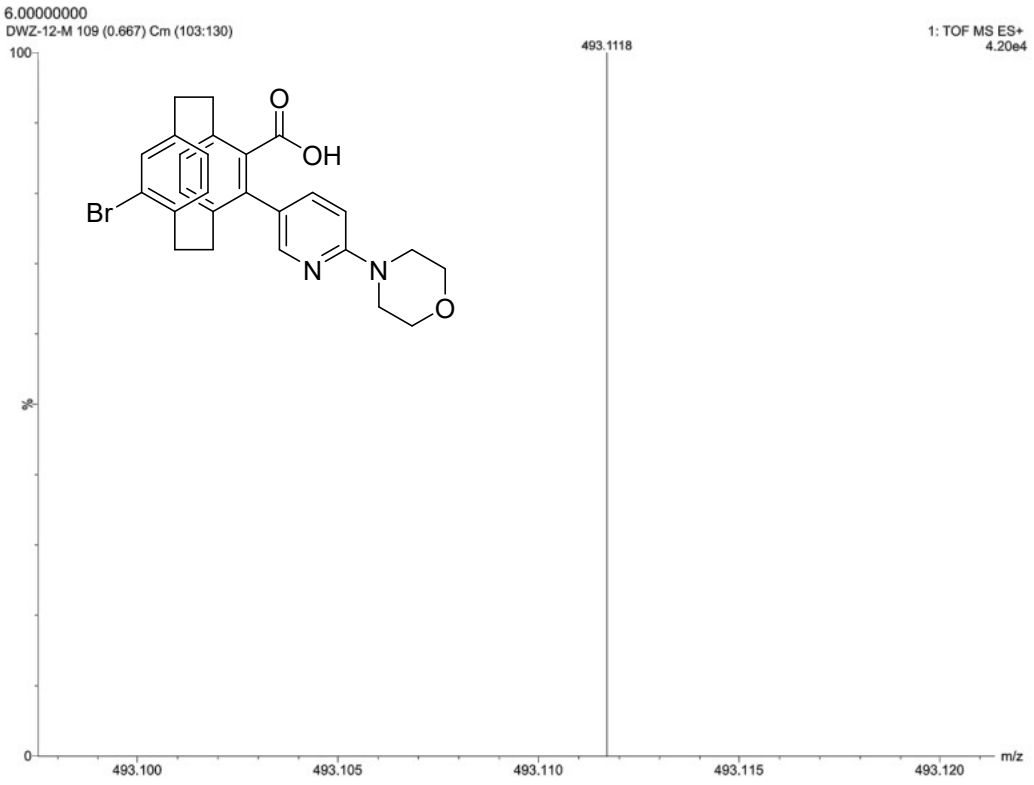


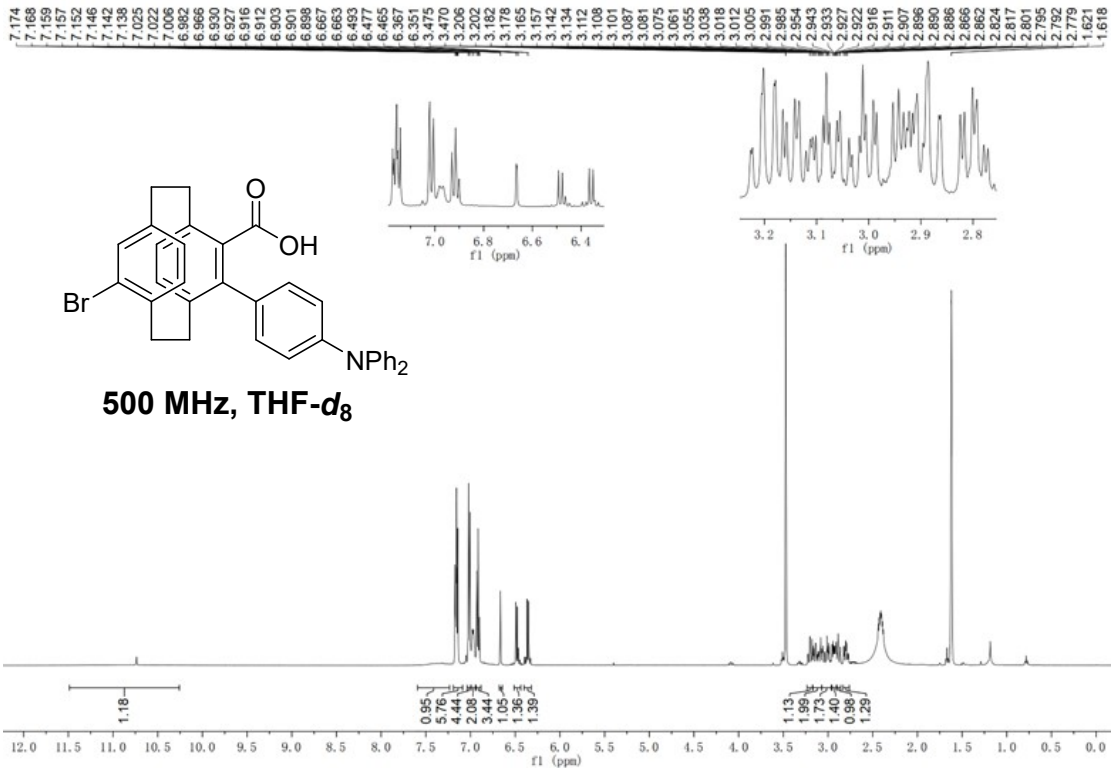


500 MHz,THF-d_8

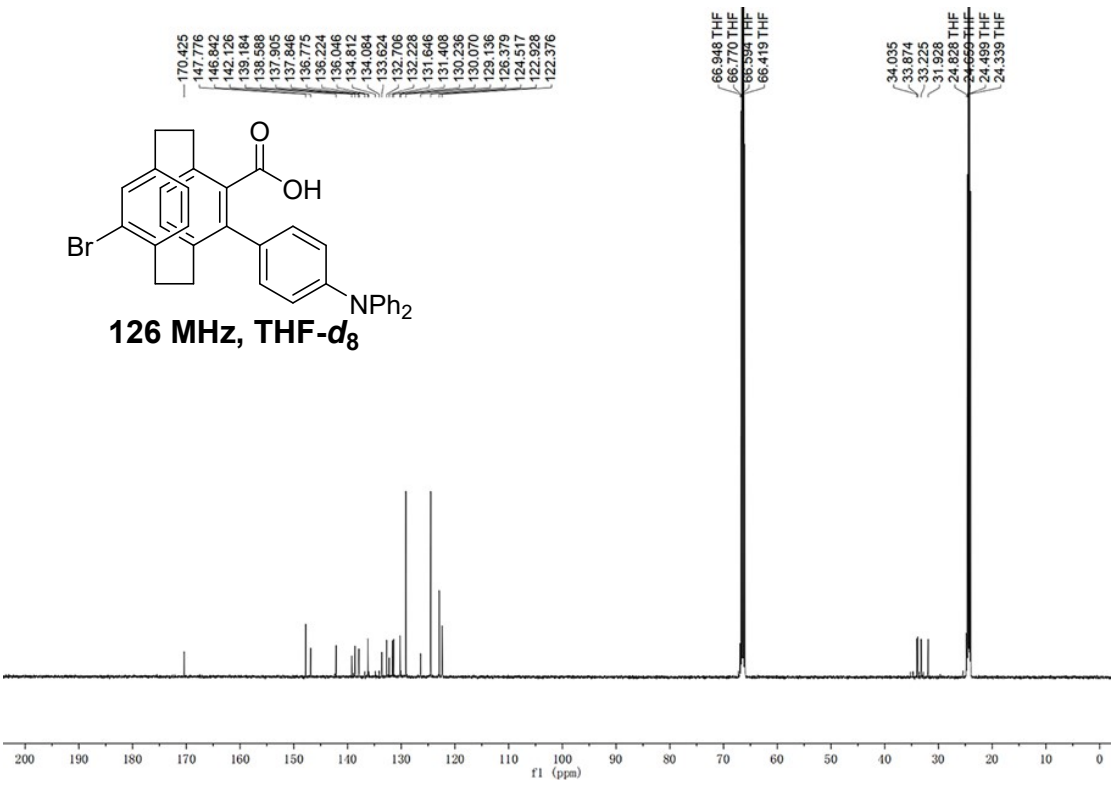



170.223
158.225
139.524
139.253
138.289
138.271
135.994
135.954
133.819
132.622
131.833
131.706
131.691
131.627
131.256
129.523
125.318
105.384
66.946 THF
66.769 THF
66.694 THF
66.517
66.418 THF
45.355
34.928
34.605
33.857
32.833
24.828 THF
24.659 THF
24.499 THF
24.339 THF
O
OH
Br
N
N
O
126 MHz, THF-d_8
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

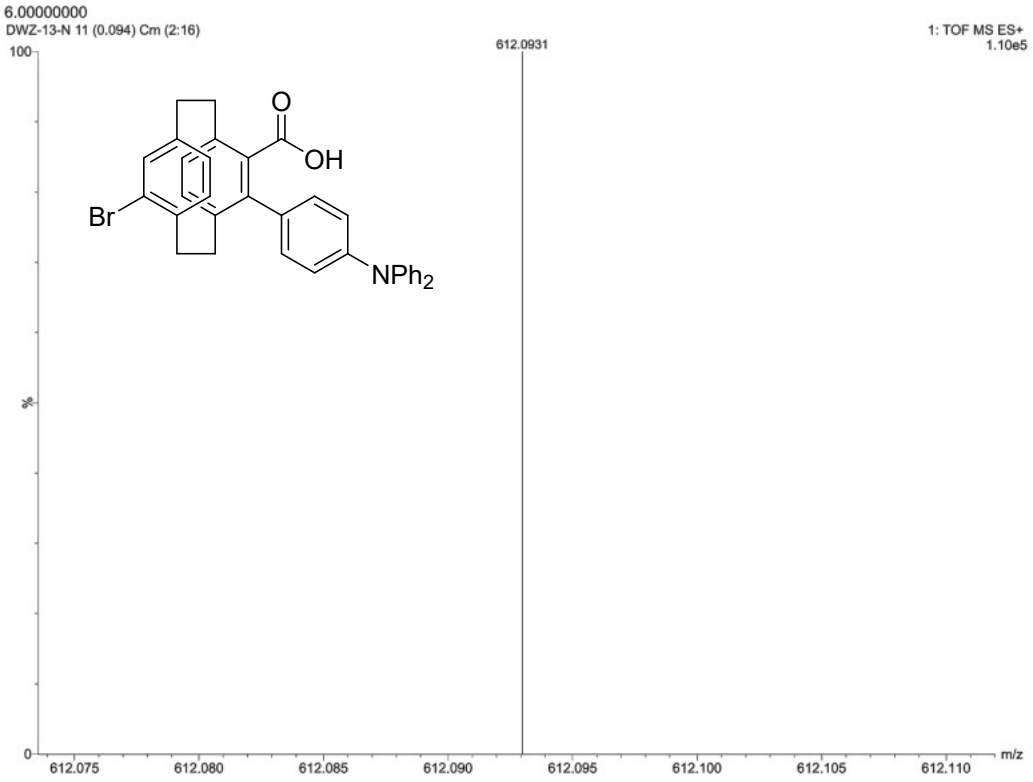

6.00000000
DWZ-12-M 109 (0.667) Cm (103:130)
1: TOF MS ES+
4.20e4
493.1118
100
%
0
O
OH
Br
N
N
O
493.100
493.105
493.110
493.115
493.120
m/z



500 MHz, THF-d_8



126 MHz, THF-d_8



9. Coordinates of Optimized Structures

Coordinates of **3a** in the S_0 state

Charge = 0 Multiplicity = 1

N	7.7995	3.3048	15.2587
O	5.3193	6.9979	16.1672
O	5.4026	5.2476	17.561
H	6.1124	5.6136	17.8213
O	9.1012	1.4877	15.8714
C	3.0943	7.942	14.1274
H	2.464	8.6203	13.777
H	3.9514	8.3963	14.3249
C	3.3232	6.8861	13.0744
C	2.2782	6.2849	12.395

H	1.4665	6.7623	12.2695
C	2.3952	5.0083	11.8988
H	1.6644	4.6114	11.4395
C	3.5827	4.291	12.0659
C	4.7066	5.0085	12.4645
H	5.5683	4.6157	12.3886
C	4.5781	6.2891	12.9703
H	5.3513	6.7655	13.2491
C	3.5963	2.7799	12.0952
H	4.469	2.4622	11.7524
H	2.893	2.4428	11.4854
C	3.3609	2.1686	13.5291
H	2.607	1.5285	13.4856
H	4.1691	1.6652	13.8003
C	3.059	3.2091	14.5755
C	1.7929	3.7739	14.6143
H	1.0515	3.2681	14.3028
C	1.5815	5.0466	15.0914
H	0.6982	5.3949	15.1239
C	2.6446	5.8293	15.5267
C	3.8479	5.1475	15.7952
C	4.0653	3.8397	15.332
C	2.5064	7.3262	15.4718
H	2.9801	7.724	16.2448
H	1.5488	7.5661	15.5466

C	4.9304	5.8994	16.5002
C	5.3979	3.1836	15.4822
C	5.5414	1.8943	16.0117
H	4.773	1.408	16.2867
C	6.7879	1.33	16.135
H	6.8937	0.4511	16.4797
C	7.8885	2.0793	15.7424
C	6.5604	3.8354	15.1377
H	6.488	4.7172	14.7918
C	10.2304	2.2243	15.3785
H	10.0499	2.5255	14.4636
H	11.0232	1.6482	15.3823
H	10.3892	3.0021	15.9532

10. References

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