Supporting Information

Pyrene-based conjugated porous polymers as a photocatalyst for oxidative cycloaddition of phenols

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Supporting Information

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1. General information

Materials.

Solvents and commercially available chemicals were obtained from were purchased from companies such as Alfa Aesar, Sigma-Aldrich, Aladdin, Macklin, etc., and employed without without further purification.

Methods.

Characterization. NMR spectra were recorded with a BrukerAvance III HD600 spectrometer at 600 MHz (^{1}H NMR), 151 MHz (^{13}C NMR). All ^{13}C, and ^{1}H NMR spectra were recorded using $CDCl_3$ as solvent. Solid-state cross-polarization along with magic angle spinning spectra (^{13}C CP/MAS) were recorded with an NMR spectrometer of Bruker Avance Neo 400WB. The Fourier transform infrared (FTIR) experiment was executed by a Thermo Fisher Scientific Nicolet iS20 (400–4000 cm^{-1}). Elemental analysis was carried out using elemental analyzer on a Vario-EL Cube. The scanning electron microscopic (SEM) investigation was recorded by ZEISS Sigma 300. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) images and element mapping were measured on a JEOL JEM-F200 microscope operated at 200 kV. Powder X-ray diffraction (PXRD) measurement was marched adopting a DX-2700A diffractometer with a filtered Cu Kα line, and the spectrum was gathered from 5° to 50° in 2° /min at room temperature. Inductively coupled plasma-mass spectrometry (ICP-MS) was executed by PerkinElmer ICP 2100. The solid-state UV−vis diffuse reflectance spectra were recorded with a Shimadzu UV-2600 UV−vis/NIR Spectrometer at ambient temperature. The N_2 adsorption/desorption isotherms and specific surface area were determined at 77 K using a Micromeritics ASAP 2460 Version 3.01 automated system with the Brunauer-Emmet-Teller (BET) method, while the pore size of the samples was determined using nonlocal density functional theory (NLDFT). The thermogravimetric analysis (TGA) curve was recorded on a RIGAKU, TG-DTA8122, thermo plus EVO2 thermogravimeter from 30 to 800 °C at a rate of 15 °C/min under an N_2 atmosphere. The transient luminescent spectra were performed on the FLS1000 laser flash photolysis instrument (Edinburgh, UK). Electron paramagnetic resonance (EPR) spectra were recorded with Bruker EMXplus-6/1 EPR spectrometer at room temperature. Information about the photochemical reactions: The light-promoted reactions were performed

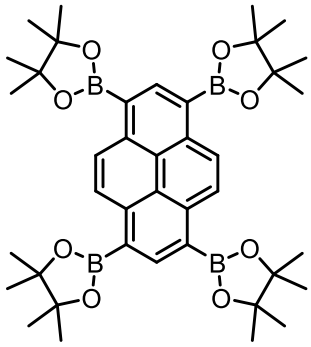
by blue LEDs (25 W 400-410 nm, purchased from Xuzhou Aijia Electronic Technology Co., Ltd, Jiangsu, China) approximately 4 cm away from the reaction tube with no filter, and with a fan to keep room temperature. The material of the irradiation vessel is borosilicate glass.

Photoelectrochemical measurement. To study the photoelectrochemical characteristics of the photocatalysts, we used a standard workstation with a three-electrode system (CHI 760E), which was prepared by adding 10 mg catalyst, Nafion (50 μL) in 1 mL of ethanol and sonicated for 30 min. Moreover, the mixture (100 μL) was dripped on an FTO glass (1×1 cm^2) and then dry at room temperature for photoelectric test. The Mott–Schottky analysis was executed by using a classical sample electrode with FTO conductive glass as an electrode, an electrode with platinum wire was used as a counter electrode while the Ag/AgCl was used as the reference electrode, measured at different frequencies. The photocurrent responses of the samples were recorded in 0.2 mol/L Na_2SO_4 under the radiation of a Xe lamp via 30 s light on-off cycles.

Computational details. All the calculations were performed using the Gaussian 16 software package[1]. Geometry optimization of the compounds was conducted at the B3LYP[2]-D3(BJ)[3]density functional theory level using the basis set 6-311g(d,p)[4] for all atoms. In addition, Hessian calculations for obtaining the vibrational frequencies were performed at the same level of theory as that for the geometry optimization to check whether the optimized geometrical structure is an energy minimum (with no imaginary frequency). The single-point energies calculations were performed by the M06-2X(D3)[5] density functional with the def2-TZVPP[6] for all atoms. For the Time-Dependent density functional theory (TD-DFT), CAM-B3LYP-D3(BJ)[7] is used for the corresponding excited state calculations. The electrostatic potential (ESP), three-dimensional parameters of substrate molecules, and holes-electrons maps were analyzed using the *Multiwfn 3.8* program[8]. Viewing of optimized structures and rendering of molecular orbitals and spin densities were performed using the program *VMD*[9].

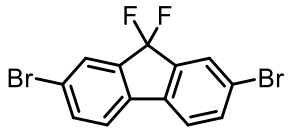
2. Synthetic procedures

Synthesis of 1,3,6,8-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (Py-$(Bpin)_4$) [10]



Bis(pinacolato)diboron (35.2g, 138.8 mmol) was added to a stirred solution of 1,3,6,8-tetrabromopyrene (12.0g, 23.0 mmol), Pd(dppf)Cl_2 (1.28 g, 2.0 mmol) and potassium acetate (14.0 g, 142.8 mmol) in anhydrous DMSO (240 mL) under nitrogen atmosphere. The reaction solution was heated to 80 ºC and stirred for 48 h. The reaction mixture was cooled to room temperature, and poured into water (1 L) and filtered. The product was purified by column chromatography on silica gel using dichloromethane and petroleum ether as the eluent to afford the product as a pale white solid (8.0 g, 48%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.16 (s, 4H), 8.99 (d, *J* = 2.0 Hz, 2H), 1.50 (s, 48H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 141.34, 137.98, 129.43, 124.65, 123.99, 83.84, 25.09.

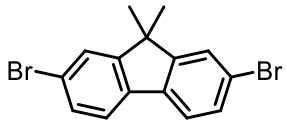
Synthesis of 2,7-dibromo-9,9-difluoro-9*H*-fluorene (2Br-FF) [11]



NFSI (*N*-fluorobis(benzenesulfon)imide, 3.8 g, 12.0 mmol) and 2,7-dibromo-9*H*-fluorene (972.0 mg, 3.0 mmol) were dissolved in THF (15 mL) and stirred for 10 min at -70 ℃. KHMDS (potassium hexamethylsilazane, 1.0 M in THF, 12 mL, 12.0 mmol) was added dropwise into the reaction over 20 min. Then the reaction mixture was stirred at this temperature for over 3 hours until the reaction was finished (detected by TLC, petroleum ether/ethyl acetate, 200:1). The excess of base (KHMDS) was quenched with 30 drops of CH_3OH, followed by addition of 20 mL of hexane. The suspension was filtered through a pad of silica gel and the filtrate was concentrated. Finally, the solid residue was recrystallized by petroleum ether/ethyl acetate (80:1) to provide 2,7-dibromo-9,9-difluoro-9*H*-fluorene as a pale yellow solid (860.0 mg, 79% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.74 (q, *J* = 1.7 Hz, 2H), 7.59 (dd, *J* = 8.1, 1.8 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 139.28 (t, *J* = 25.3 Hz), 137.39

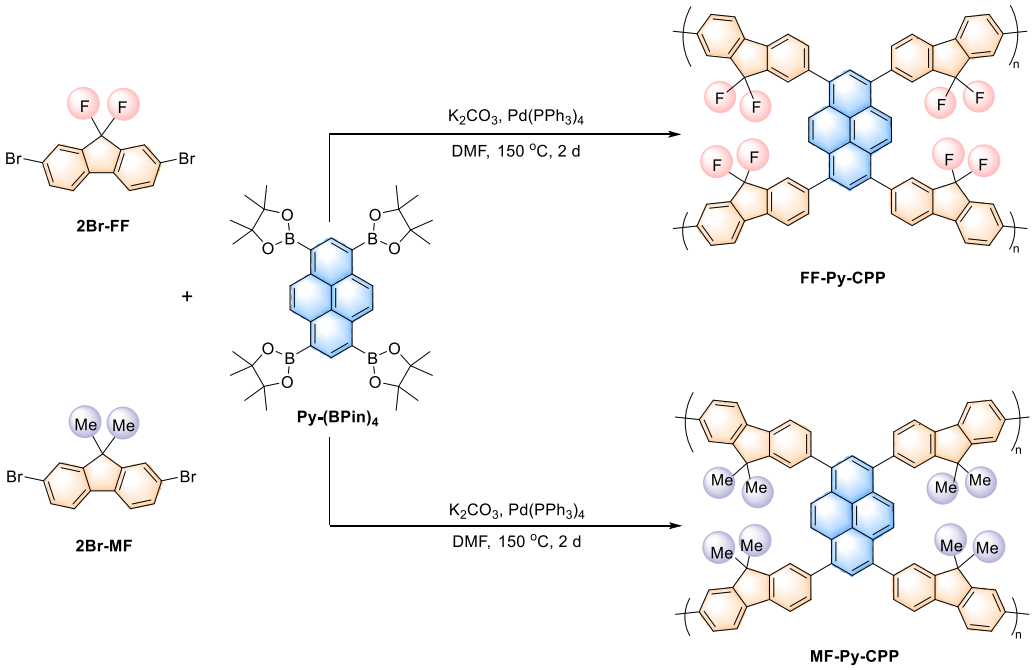
(t, *J* = 4.8 Hz), 135.30, 127.47, 123.36, 122.83, 121.83, 121.73, 120.11. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -111.02.

Synthesis of 2,7-dibromo-9,9-dimethyl-9*H*-fluorene (2Br-MF) [11]



2,7-dibromo-9*H*-fluorene (3.2 g, 10.0 mmol) and KI (166.0 mg, 1.0 mmol) were dispersed in dimethyl sulfoxide (DMSO, 20 mL) at room temperature. KOH pellets (2.2 g, 40.0 mmol) was added over 10 min. After addition, the mixture was stirred for 1 hour until the solution intense red. CH_3I (1.56 mL, 25.0 mmol) was added dropwise over 20 min, and the stirring was continued for 16 hours at room temperature. The reaction was quenched with CH_2Cl_2 (40 mL). The suspension was filtered through a pad of silica gel, and the filtrate was poured into water (200 mL). The mixture was then extracted with CH_2Cl_2 (20 mL × 3). The combined organic layers were dried by anhydrous Na_2SO_4, then concentrated by vacuum evaporator. The product was purified by column chromatography on silica gel using petroleum ether and ethyl acetate (100:1) as the eluent to afford the 2,7-dibromo-9,9-dimethyl-9*H*-fluorene as a white solid (2.9 g, 83% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 4.1, 2.2 Hz, 3H), 7.53 (s, 1H), 7.46 (dd, *J* = 8.1, 1.8 Hz, 2H), 1.47 (s, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.28, 137.19, 130.37, 126.23, 121.51 (d, *J* = 5.9 Hz), 47.34, 26.88.

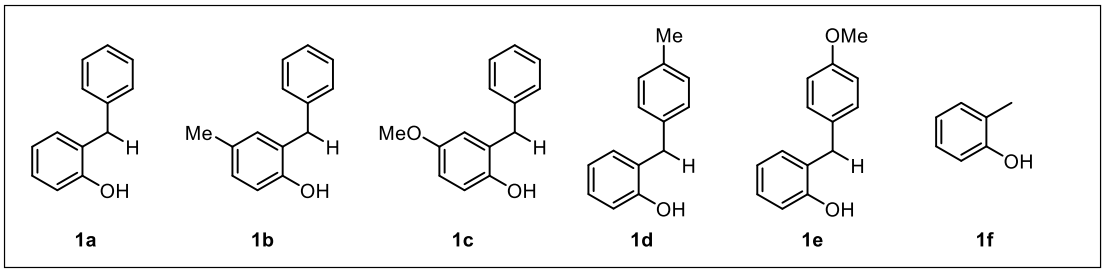
Synthesis of the FF-Py-CPP and MF-Py-CPP

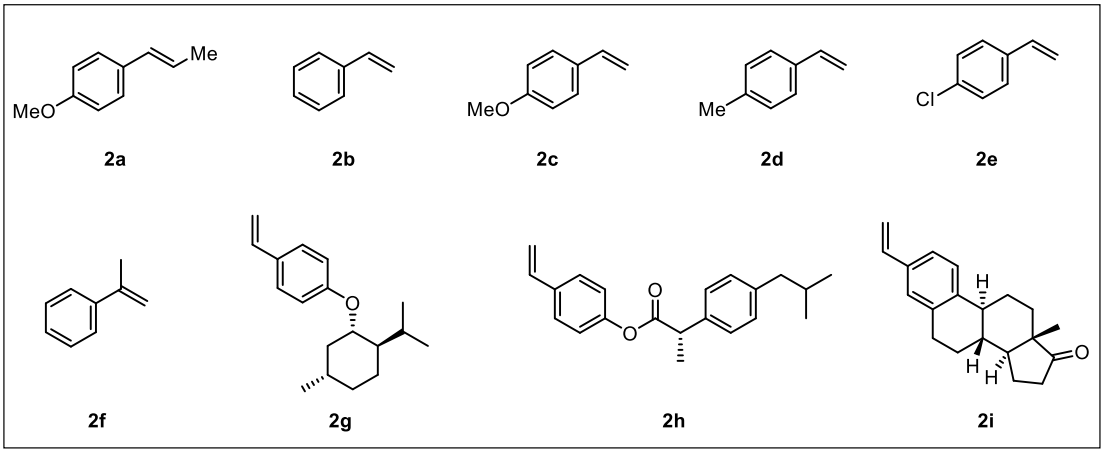


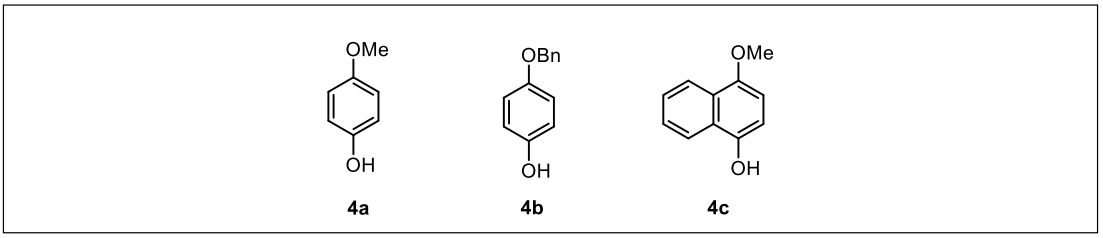
FF-Py-CPP was synthesized according to a literature procedure with modifications.[10] A mixture of 1,3,6,8-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (Py-$(Bpin)_4$, 353 mg, 0.5 mmol), 2,7-dibromo-9,9-difluoro-9*H*-fluorene (2Br-FF, 358 mg, 1.0 mmol), K_2CO_3 (2.0 M aqueous solution, 2 mL), $Pd(PPh_3)_4$ (10 mg, 0.63 mol%), and DMF (20 mL) was charged into a Schlenk tube. The reaction mixture was degassed via N_2 bubbling for 15 min, heated to 150 °C and stirred for 48 h. After cooling to ambient temperature, the precipitate was obtained by filtration. The crude polymer was sequentially washed with ethanol, deionized water, tetrahydrofuran and dichloromethane. Following vacuum drying at 70 °C for 24 h, FF-Py-CPP was obtained as a yellow solid powder in 80% yield. Elemental analysis (%) calcd. for $(C_{42}H_{18}F_4)_n$ (%): C 84.3; H 3.0. Found: C 71.5; H 4.2. Pd 0.00189 wt% was obtained from inductively coupled plasma atomic emission spectroscopy (ICP-MS).

The same procedure was applied to MF-Py-CPP, wherein 2,7-dibromo-9,9-dimethyl-9*H*-fluorene (2Br-MF, 350 mg, 1.00 mmol) instead of 2Br-FF. MF-Py-CPP was obtained as yellow solid powder in 75% yield. Elemental analysis (%) calcd. for $(C_{46}H_{30})_n$ (%): C 94.8; H 5.2. Found: C 80.1; H 5.8. Pd 0.00336 wt% was obtained from inductively coupled plasma atomic emission spectroscopy (ICP-MS).

3. Overview of Substrates







3. Characterizations

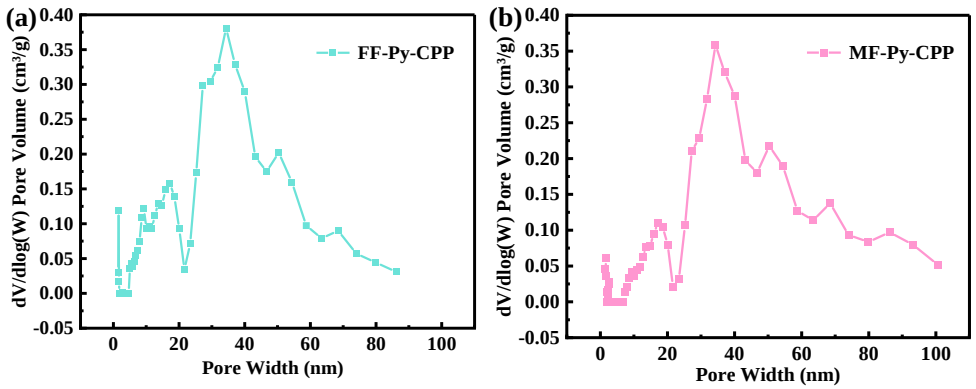


Fig. S1. Pore size distribution of (a) FF-Py-CPP and (b) MF-Py-CPP.

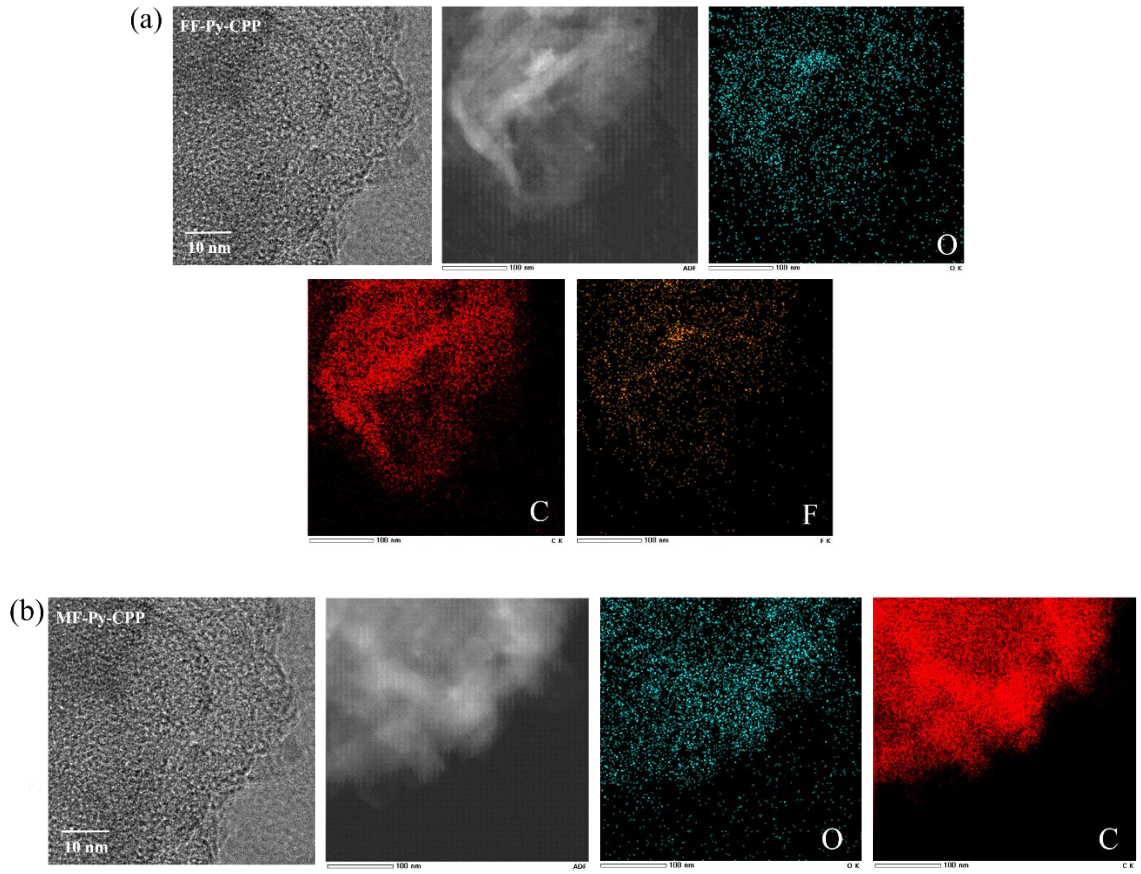


Fig. S2. (a) High-resolution TEM images and EDS mapping of FF-Py-CPP. (b) High-resolution TEM images and EDS mapping of MF-Py-CPP.

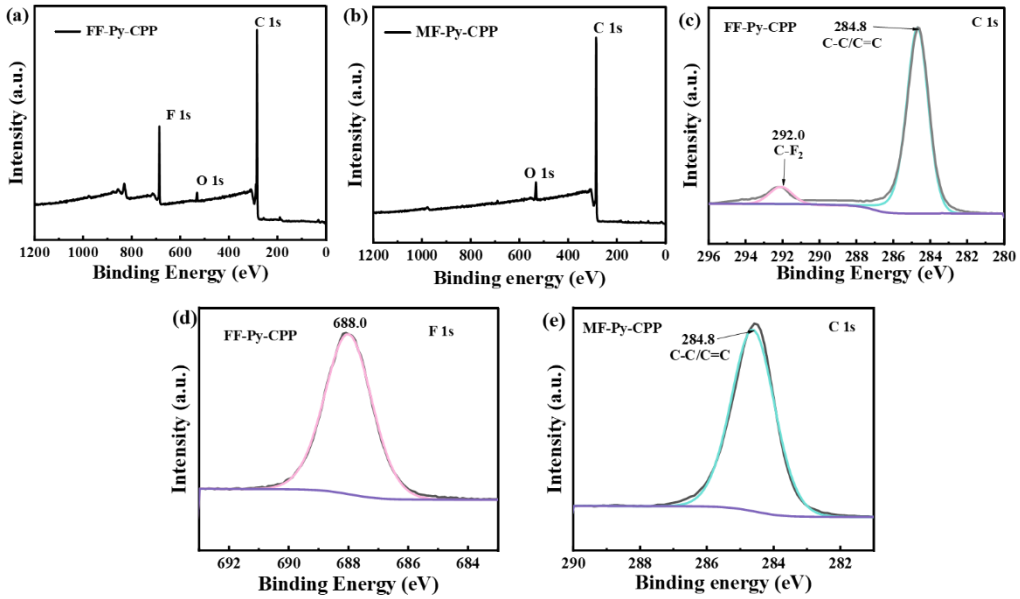


Fig. S3. (a) Wide-scan XPS spectrum of FF-Py-CPP. (b) Wide-scan XPS spectrum of MF-Py-CPP. (c) XPS C1s spectra of FF-Py-CPP (d) XPS F1s spectra of FF-Py-CPP (e) XPS C1s spectra of MF-Py-CPP.

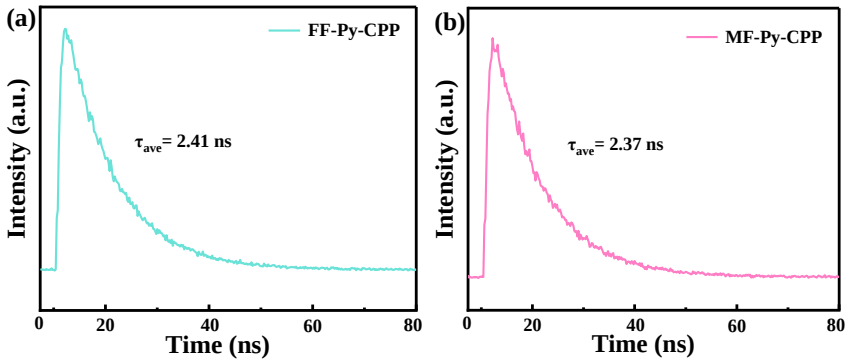


Fig. S4. Photoluminescence decay spectra of (a) FF-Py-CPP and (b) MF-Py-CPP.

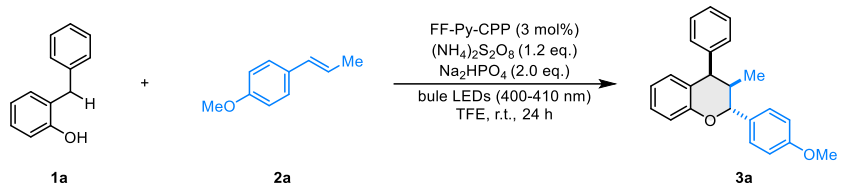
4. Photocatalytic cycloaddition reactions

4.1 [4+2] Cycloaddition reaction

General procedure of [4+2] cycloaddition reaction.

A 10 mL oven-dried reaction vessel with a stir bar was charged with FF-Py-CPP (3 mol%) and 2,2,2-trifluoroethanol (TFE, 1 mL). Subsequently, phenols **1** (0.20 mmol), olefins **2** (0.40 mmol), Na_2HPO_4 (0.40 mmol), and $(NH_4)_2S_2O_8$ (0.24 mmol) were added. The reaction mixture was stirred under the irradiation of a 25 W blue LED (400-410 nm) with fan cooling to maintain ambient temperature for 24 h. The FF-Py-CPP catalyst was recovered by centrifugation and washed with EtOAc three times. The residue was further purified by rapid column chromatography (SiO_2) using the suitable eluent (PE/EtOAc) to afford the desired products.

Table S1. Optimization of [4+2] cycloaddition reaction conditions.



Entry	Variation from the standard conditions	Yield (%)[b]
1	Standard condition[a]	74
2	No FF-Py-CPP	NR
3	No light (dark)	NR
4	No $(NH_4)_2S_2O_8$	NR
5	No Na_2HPO_4	65
6	Na_3PO_4 instead of Na_2HPO_4	32
7	^{t}BuOOH instead of $(NH_4)_2S_2O_8$	NR
8	BPO instead of $(NH_4)_2S_2O_8$	trace
9	TBHP instead of $(NH_4)_2S_2O_8$	24
10	MeOH instead of TFE	31

11	DCE instead of TFE	25
12	CH_3CN instead of TFE	trace
13	Under 360-370 nm 25 W LEDs	50
14	Under 460-470 nm 25 W LEDs	48
15	Under 520-530 nm 25 W LEDs	23
16	Under 400-410 nm 5 W LEDs	65
17	Under 400-410 nm 45 W LEDs	72
18	1 mol% of FF-Py-CPP instead of 3 mol%	34
19	1.5 mol% of FF-Py-CPP instead of 3 mol%	43
20	2 mol% of FF-Py-CPP instead of 3 mol%	50
21	2.5 mol% of FF-Py-CPP instead of 3 mol%	61
22	3.5 mol% of FF-Py-CPP instead of 3 mol%	74
23	4 mol% of FF-Py-CPP instead of 3 mol%	73
24	5 mol% of FF-Py-CPP instead of 3 mol%	73
25	10 mol% of FF-Py-CPP instead of 3 mol%	74
26	MF-Py-CPP instead of FF-Py-CPP	32
27	FF-2Br instead of FF-Py-CPP	NR
28	Py-$BPin_4$ instead of FF-Py-CPP	NR

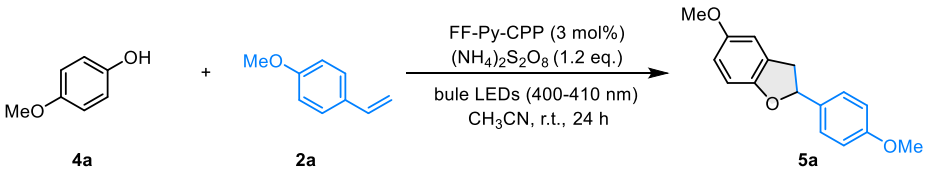
[a]Standard conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), FF-Py-CPP (3 mol%), $(NH_4)_2S_2O_8$ (0.24 mmol), Na_2HPO_4 (0.40 mmol), TFE (1 mL), 400-410 nm 25 W LEDs, room temperature, 24 h. [b]Isolated yields.

4.2 [3+2] Cycloaddition reaction

General procedure of [3+2] cycloaddition reaction.

A 10 mL oven-dried reaction vessel with a stir bar was charged with FF-Py-CPP (3 mol%) and CH_3CN (1 mL). Subsequently, phenols **4** (0.20 mmol), olefins **2** (0.40 mmol), and ammonium persulfate (0.24 mmol) were added. The reaction mixture was stirred under the irradiation of a 25 W blue LED (400-410 nm) with fan cooling to maintain ambient temperature for 24 h. The FF-Py-CPP catalyst was recovered by centrifugation and washed with EtOAc three times. The residue was further purified by rapid column chromatography (SiO_2) using the suitable eluent (PE/EtOAc) to afford the desired products.

Table S2. Optimization of [3+2] cycloaddition reaction conditions.



Entry	Variation from the standard conditions[a]	Yield (%)[b]
1	TFE	N.R.
2	CH_3CN	70

3	MeOH	N.R.
4	BPO instead of $(NH_4)_2S_2O_8$	45
5	TBHP instead of $(NH_4)_2S_2O_8$	N.R.

[a]Reaction conditions: **4** (0.20 mmol), **2** (0.40 mmol), FF-Py-CPP (3 mol%), $(NH_4)_2S_2O_8$ (0.24 mmol), CH_3CN (2.0 mL), 400-410 nm 25 W blue LEDs, room temperature, 24 h. [b]Isolated yields.

5. Light on/off experiment

This experiment was performed according to the general procedure using **1a** (0.20 mmol), **2a** (0.40 mmol), Na_2HPO_4 (0.40 mmol), $(NH_4)_2S_2O_8$ (0.24 mmol), and FF-Py-CPP (3 mol%) in TFE (1 mL). The light was switched on and off every 3 hours, and the samples taken after each time interval with light on and light off were analyzed by ^1H NMR analysis (Fig. S5).

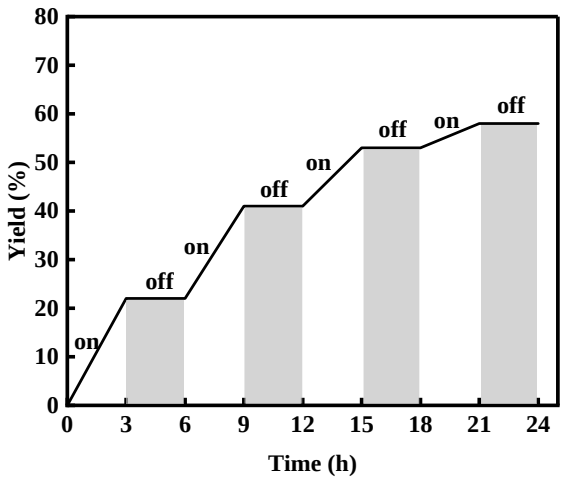


Fig. S5. Light-on/off experiment over time.

7. Substrate adsorption experiments

In order to investigate the adsorption performance of FF-Py-CPP in equimolar **1a**/**2a** solutions. 5 mg of FF-Py-CPP was added to 1 mL of **1a**/**2a** equimolar solution (0.1-1.0 mmol mL^{-1}), and the mixture was shaken in a thermostatic water bath at 150 rpm and 25 °C for 4 h. Afterward, take the supernatant and calculate the concentration by the internal standard method of nuclear magnetic resonance. The equilibrium adsorption capacity q_e (mmol · g^{-1}) was calculated by the following Eqs.

$q_e = V \times (C_0 - C_e)/m$

where C_0 (mmol L^{-1}) is the initial solute concentration of **1a** or **2a**, V (L) is the total volume of the solution, C_e (mmol L^{-1}) the equilibrium solute concentration, and m (g) is the mass of adsorbent.

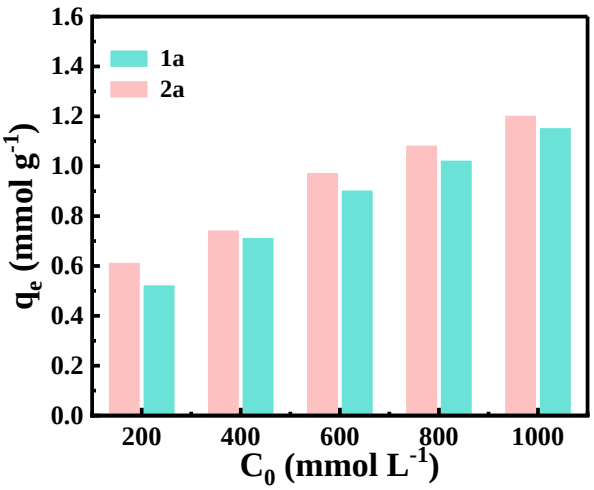


Fig. S6. Adsorption of **1a** and **2a** on FF-Py-CPP in equimolar solution.

8. Apparent quantum yield (AQY) measurement

The AQY was calculated by the following equation:

$$\text{AQY} = \frac{K \times M \times N_A \times h \times c}{A \times P \times t \times \lambda} \times 100\%$$

Where, K is number of transferred electrons in the reaction, M is the amount of product molecules (mol), N_A is Avogadro constant (6.022×10^{23} mol^{-1}), h is the Planck constant (6.626×10^{-34} J·s), c is the speed of light (3×10^{8} m s^{-1}), A is the irradiation area (1 cm^{-2}), P is the intensity of irradiation light (0.0025 W cm^{-2}), t is the photoreaction time (24 h), λ is the wavelength of the monochromatic light (410 nm).

The calculated apparent quantum yield (AQY = 19.8%) of the reaction underscores the good catalytic performance of the FF-Py-CPP.

9. Photocatalyst recyclability studies

The photocatalytic reaction was performed according to the general procedure using **1a** (0.20 mmol), **2a** (0.40 mmol), Na_2HPO_4 (0.40 mmol), $(NH_4)_2S_2O_8$ (0.24 mmol), and FF-Py-CPP (0.06 mmol) in TFE (1 mL). After the reaction was complete, FF-Py-CPP was recovered by centrifugation and washed with EA (10 mL), water (10 mL), THF (10 mL), and acetone (10 mL), dried under vacuum at room temperature overnight, and used for the next cycle. FF-Py-CPP was recycled over six consecutive catalytic runs. After each cycle, **3a** was isolated via rapid column chromatography (SiO_2) with a suitable eluent (PE/EtOAc) to afford the desired product.

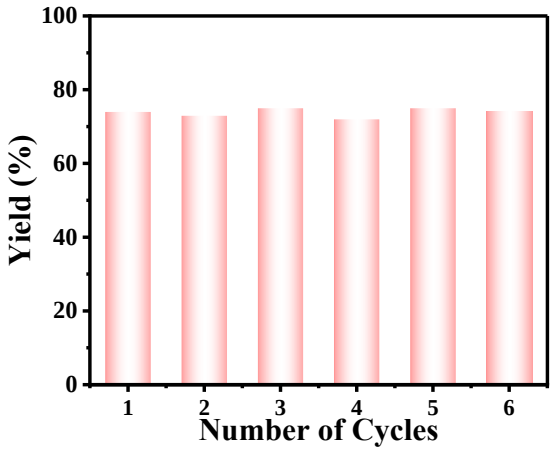


Fig. S7. Plot of number of cycles vs yield.

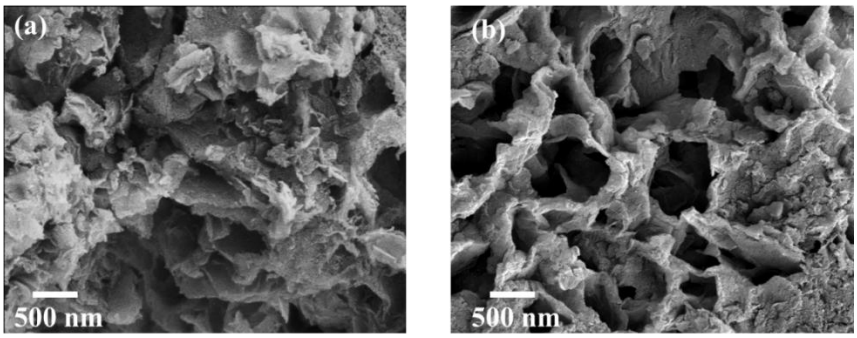


Fig. S8. Comparison of SEM images of FF-Py-CCP (a) before and (b) after catalysis.

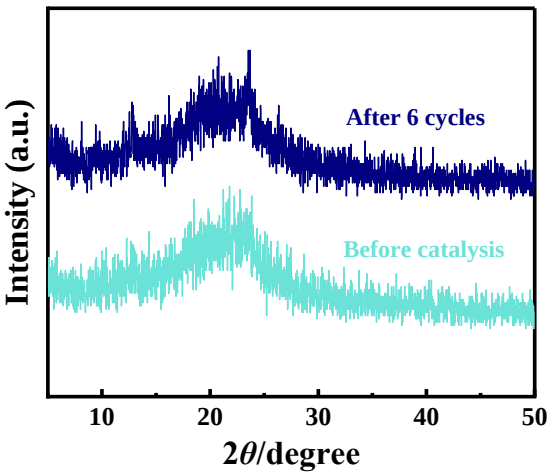


Fig. S9. Comparison of PXRD patterns of FF-Py-CCP before and after catalysis.

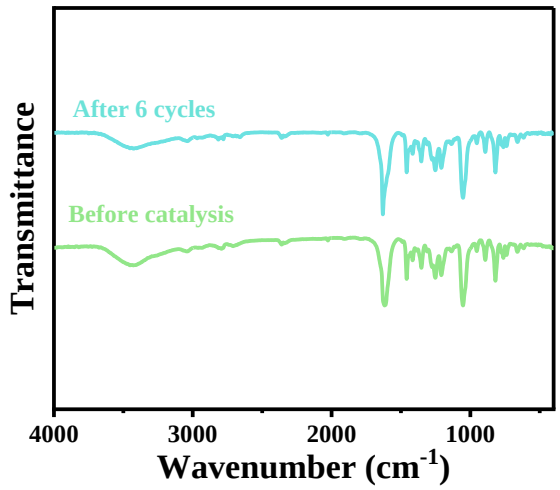


Fig. S10. FTIR analysis of FF-Py-CPP before and after six catalytic cycles.

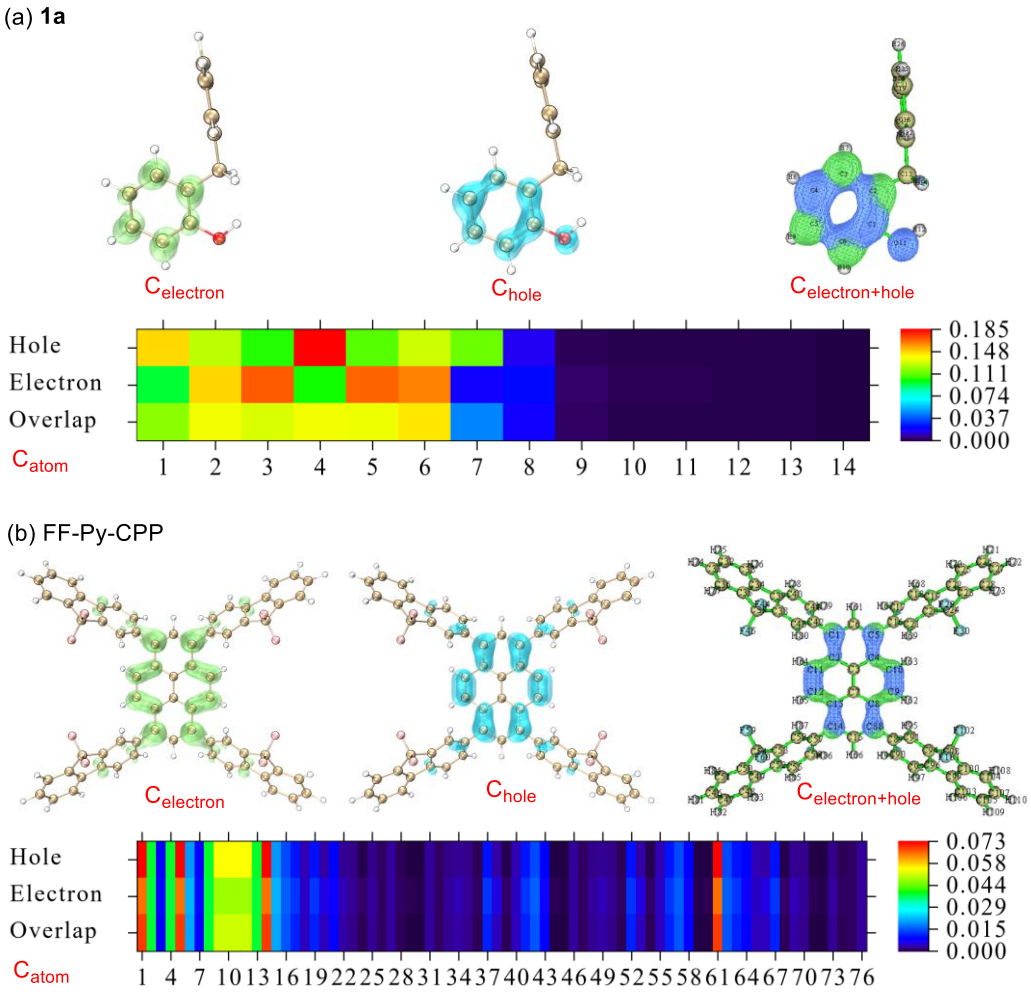


Fig. S11. Hole electron analysis based on electron excitation characteristics. (a) **1a**, and (b) FF-Py-CPP. Contribution maps of electron, hole, and "electron + hole" during the "$S_0 \rightarrow S_1$" excitation of these two model molecules, as well as the contribution heat maps of non-hydrogen

atoms to holes, electrons, and the overlap between holes and electrons, are presented respectively. The isosurface 0.01 a.u. is plotted.

Table S3. Contribution of each non-hydrogen atom/ the key molecular orbital (MO) to hole and electron in **1a** (a), and (b) FF-Py-CPP.

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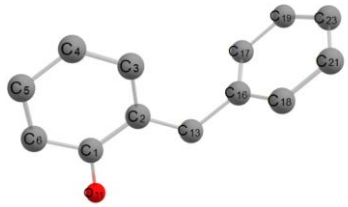
Note: contributions <= 0.50 % will not be printed

(a) **1a**



C_{atom}:

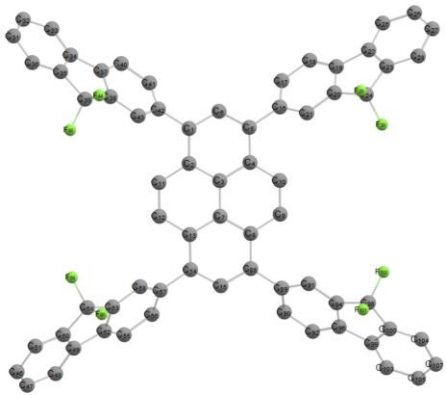
1(C)	Hole: 14.68 %	Electron: 9.62 %	Overlap: 11.88 %	Diff.: -5.05 %
2(C)	Hole: 12.70 %	Electron: 14.78 %	Overlap: 13.70 %	Diff.: 2.08 %
3(C)	Hole: 10.35 %	Electron: 16.86 %	Overlap: 13.21 %	Diff.: 6.52 %
4(C)	Hole: 18.54 %	Electron: 10.15 %	Overlap: 13.72 %	Diff.: -8.39 %
5(C)	Hole: 10.88 %	Electron: 16.76 %	Overlap: 13.51 %	Diff.: 5.88 %
6(C)	Hole: 12.98 %	Electron: 16.23 %	Overlap: 14.52 %	Diff.: 3.25 %
11(O)	Hole: 11.24 %	Electron: 1.86 %	Overlap: 4.57 %	Diff.: -9.39 %
13(C)	Hole: 1.55 %	Electron: 2.27 %	Overlap: 1.87 %	Diff.: 0.72 %
16(C)	Hole: 0.18 %	Electron: 0.33 %	Overlap: 0.24 %	Diff.: 0.14 %
17(C)	Hole: 0.09 %	Electron: 0.20 %	Overlap: 0.14 %	Diff.: 0.11 %
18(C)	Hole: 0.09 %	Electron: 0.20 %	Overlap: 0.14 %	Diff.: 0.11 %
19(C)	Hole: 0.07 %	Electron: 0.12 %	Overlap: 0.09 %	Diff.: 0.05 %
21(C)	Hole: 0.08 %	Electron: 0.12 %	Overlap: 0.10 %	Diff.: 0.05 %
23(C)	Hole: 0.06 %	Electron: 0.07 %	Overlap: 0.07 %	Diff.: 0.01 %

Sum of hole shown above: 93.51% Sum of electron shown above: 89.58%

C_{MO}:

MO 48, Occ:	2.00000	Hole: 22.783 %	Electron:	0.000 % (HOMO-1)
MO 49, Occ:	2.00000	Hole: 74.472 %	Electron:	0.000 % (HOMO)
MO 50, Occ:	0.00000	Hole: 0.000 %	Electron:	5.629 % (LUMO)
MO 52, Occ:	0.00000	Hole: 0.000 %	Electron:	74.163 % (LUMO+1)
MO 53, Occ:	0.00000	Hole: 0.000 %	Electron:	19.490 % (LUMO+2)

(b) FF-Py-CPP



C_{atom}:

1(C)	Hole:	7.30 %	Electron:	6.51 %	Overlap:	6.89 %	Diff.:	-0.79 %
2(C)	Hole:	3.80 %	Electron:	3.74 %	Overlap:	3.77 %	Diff.:	-0.07 %
3(C)	Hole:	0.79 %	Electron:	0.92 %	Overlap:	0.85 %	Diff.:	0.13 %
4(C)	Hole:	3.80 %	Electron:	3.74 %	Overlap:	3.77 %	Diff.:	-0.07 %
5(C)	Hole:	7.30 %	Electron:	6.51 %	Overlap:	6.89 %	Diff.:	-0.79 %
6(C)	Hole:	1.98 %	Electron:	2.18 %	Overlap:	2.07 %	Diff.:	0.20 %
7(C)	Hole:	0.79 %	Electron:	0.92 %	Overlap:	0.85 %	Diff.:	0.13 %
8(C)	Hole:	3.80 %	Electron:	3.74 %	Overlap:	3.77 %	Diff.:	-0.07 %
9(C)	Hole:	5.45 %	Electron:	4.79 %	Overlap:	5.11 %	Diff.:	-0.65 %
10(C)	Hole:	5.45 %	Electron:	4.79 %	Overlap:	5.11 %	Diff.:	-0.65 %
11(C)	Hole:	5.45 %	Electron:	4.79 %	Overlap:	5.11 %	Diff.:	-0.65 %
12(C)	Hole:	5.45 %	Electron:	4.79 %	Overlap:	5.11 %	Diff.:	-0.65 %
13(C)	Hole:	3.80 %	Electron:	3.74 %	Overlap:	3.77 %	Diff.:	-0.07 %
14(C)	Hole:	7.30 %	Electron:	6.51 %	Overlap:	6.89 %	Diff.:	-0.79 %
15(C)	Hole:	1.98 %	Electron:	2.18 %	Overlap:	2.07 %	Diff.:	0.20 %
16(C)	Hole:	1.40 %	Electron:	1.54 %	Overlap:	1.47 %	Diff.:	0.14 %
17(C)	Hole:	0.98 %	Electron:	1.21 %	Overlap:	1.09 %	Diff.:	0.23 %
18(C)	Hole:	0.40 %	Electron:	0.43 %	Overlap:	0.42 %	Diff.:	0.03 %
19(C)	Hole:	0.97 %	Electron:	1.21 %	Overlap:	1.08 %	Diff.:	0.25 %
20(C)	Hole:	0.32 %	Electron:	0.57 %	Overlap:	0.43 %	Diff.:	0.26 %
21(C)	Hole:	0.86 %	Electron:	0.76 %	Overlap:	0.81 %	Diff.:	-0.10 %
22(C)	Hole:	0.28 %	Electron:	0.38 %	Overlap:	0.32 %	Diff.:	0.10 %
23(C)	Hole:	0.25 %	Electron:	0.26 %	Overlap:	0.26 %	Diff.:	0.01 %
24(C)	Hole:	0.05 %	Electron:	0.13 %	Overlap:	0.08 %	Diff.:	0.08 %
25(C)	Hole:	0.23 %	Electron:	0.30 %	Overlap:	0.27 %	Diff.:	0.06 %
26(C)	Hole:	0.11 %	Electron:	0.11 %	Overlap:	0.11 %	Diff.:	0.01 %
27(C)	Hole:	0.31 %	Electron:	0.31 %	Overlap:	0.31 %	Diff.:	0.00 %
28(C)	Hole:	0.08 %	Electron:	0.09 %	Overlap:	0.09 %	Diff.:	0.01 %
29(F)	Hole:	0.01 %	Electron:	0.06 %	Overlap:	0.02 %	Diff.:	0.05 %
30(F)	Hole:	0.01 %	Electron:	0.06 %	Overlap:	0.03 %	Diff.:	0.04 %
31(C)	Hole:	0.31 %	Electron:	0.31 %	Overlap:	0.31 %	Diff.:	0.00 %
32(C)	Hole:	0.11 %	Electron:	0.11 %	Overlap:	0.11 %	Diff.:	0.01 %
33(C)	Hole:	0.23 %	Electron:	0.30 %	Overlap:	0.27 %	Diff.:	0.06 %

34(C)	Hole:	0.28 %	Electron:	0.38 %	Overlap:	0.32 %	Diff.:	0.10 %
35(C)	Hole:	0.25 %	Electron:	0.26 %	Overlap:	0.26 %	Diff.:	0.01 %
36(C)	Hole:	0.08 %	Electron:	0.09 %	Overlap:	0.09 %	Diff.:	0.01 %
37(C)	Hole:	0.97 %	Electron:	1.21 %	Overlap:	1.08 %	Diff.:	0.25 %
38(C)	Hole:	0.32 %	Electron:	0.57 %	Overlap:	0.43 %	Diff.:	0.26 %
39(C)	Hole:	0.05 %	Electron:	0.13 %	Overlap:	0.08 %	Diff.:	0.08 %
40(C)	Hole:	0.40 %	Electron:	0.43 %	Overlap:	0.42 %	Diff.:	0.03 %
41(C)	Hole:	0.98 %	Electron:	1.21 %	Overlap:	1.09 %	Diff.:	0.23 %
42(C)	Hole:	1.40 %	Electron:	1.54 %	Overlap:	1.47 %	Diff.:	0.14 %
43(C)	Hole:	0.86 %	Electron:	0.76 %	Overlap:	0.81 %	Diff.:	-0.10 %
44(F)	Hole:	0.01 %	Electron:	0.06 %	Overlap:	0.02 %	Diff.:	0.05 %
45(F)	Hole:	0.01 %	Electron:	0.06 %	Overlap:	0.03 %	Diff.:	0.04 %
46(C)	Hole:	0.31 %	Electron:	0.31 %	Overlap:	0.31 %	Diff.:	0.00 %
47(C)	Hole:	0.11 %	Electron:	0.11 %	Overlap:	0.11 %	Diff.:	0.01 %
48(C)	Hole:	0.23 %	Electron:	0.30 %	Overlap:	0.27 %	Diff.:	0.06 %
49(C)	Hole:	0.28 %	Electron:	0.38 %	Overlap:	0.32 %	Diff.:	0.10 %
50(C)	Hole:	0.25 %	Electron:	0.26 %	Overlap:	0.26 %	Diff.:	0.01 %
51(C)	Hole:	0.08 %	Electron:	0.09 %	Overlap:	0.09 %	Diff.:	0.01 %
52(C)	Hole:	0.97 %	Electron:	1.21 %	Overlap:	1.08 %	Diff.:	0.25 %
53(C)	Hole:	0.32 %	Electron:	0.57 %	Overlap:	0.43 %	Diff.:	0.26 %
54(C)	Hole:	0.05 %	Electron:	0.13 %	Overlap:	0.08 %	Diff.:	0.08 %
55(C)	Hole:	0.40 %	Electron:	0.43 %	Overlap:	0.42 %	Diff.:	0.03 %
56(C)	Hole:	0.98 %	Electron:	1.21 %	Overlap:	1.09 %	Diff.:	0.23 %
57(C)	Hole:	1.40 %	Electron:	1.54 %	Overlap:	1.47 %	Diff.:	0.14 %
58(C)	Hole:	0.86 %	Electron:	0.76 %	Overlap:	0.81 %	Diff.:	-0.10 %
59(F)	Hole:	0.01 %	Electron:	0.06 %	Overlap:	0.03 %	Diff.:	0.04 %
60(F)	Hole:	0.01 %	Electron:	0.06 %	Overlap:	0.02 %	Diff.:	0.05 %
88(C)	Hole:	7.30 %	Electron:	6.51 %	Overlap:	6.89 %	Diff.:	-0.79 %
89(C)	Hole:	1.40 %	Electron:	1.54 %	Overlap:	1.47 %	Diff.:	0.14 %
90(C)	Hole:	0.98 %	Electron:	1.21 %	Overlap:	1.09 %	Diff.:	0.23 %
91(C)	Hole:	0.86 %	Electron:	0.76 %	Overlap:	0.81 %	Diff.:	-0.10 %
92(C)	Hole:	0.40 %	Electron:	0.43 %	Overlap:	0.42 %	Diff.:	0.03 %
94(C)	Hole:	0.32 %	Electron:	0.57 %	Overlap:	0.43 %	Diff.:	0.26 %
96(C)	Hole:	0.97 %	Electron:	1.21 %	Overlap:	1.08 %	Diff.:	0.25 %
98(C)	Hole:	0.05 %	Electron:	0.13 %	Overlap:	0.08 %	Diff.:	0.08 %
99(C)	Hole:	0.28 %	Electron:	0.38 %	Overlap:	0.32 %	Diff.:	0.10 %
100(C)	Hole:	0.25 %	Electron:	0.26 %	Overlap:	0.26 %	Diff.:	0.01 %
101(F)	Hole:	0.01 %	Electron:	0.06 %	Overlap:	0.02 %	Diff.:	0.05 %
102(F)	Hole:	0.01 %	Electron:	0.06 %	Overlap:	0.03 %	Diff.:	0.04 %
103(C)	Hole:	0.23 %	Electron:	0.30 %	Overlap:	0.27 %	Diff.:	0.06 %
104(C)	Hole:	0.08 %	Electron:	0.09 %	Overlap:	0.09 %	Diff.:	0.01 %
105(C)	Hole:	0.11 %	Electron:	0.11 %	Overlap:	0.11 %	Diff.:	0.01 %
107(C)	Hole:	0.31 %	Electron:	0.31 %	Overlap:	0.31 %	Diff.:	0.00 %

Sum of hole shown above: 96.76% Sum of electron shown above: 96.12%

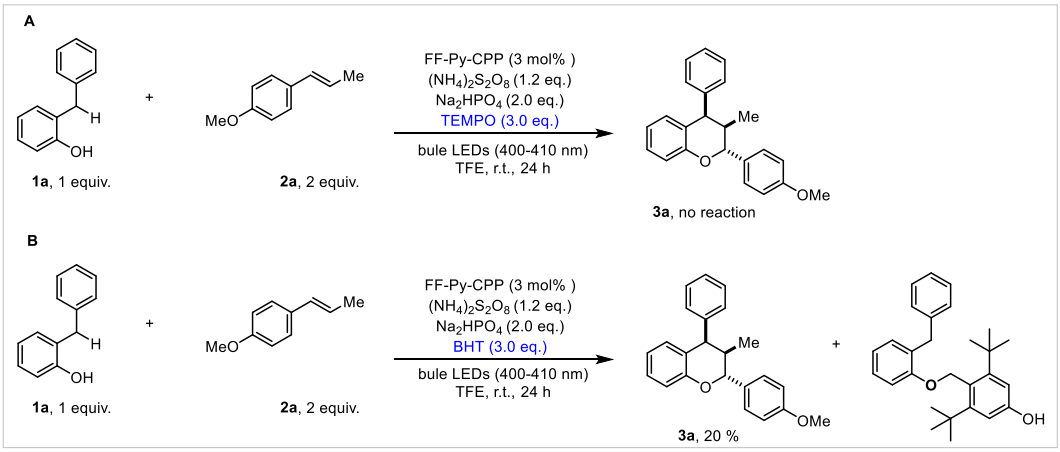
C_{MO}:

MO	257, Occ:	2.00000	Hole:	92.516 %	Electron:	0.000 % (HOMO)
MO	258, Occ:	0.00000	Hole:	0.000 %	Electron:	91.495 % (LUMO)

10. Radical capturing experiments

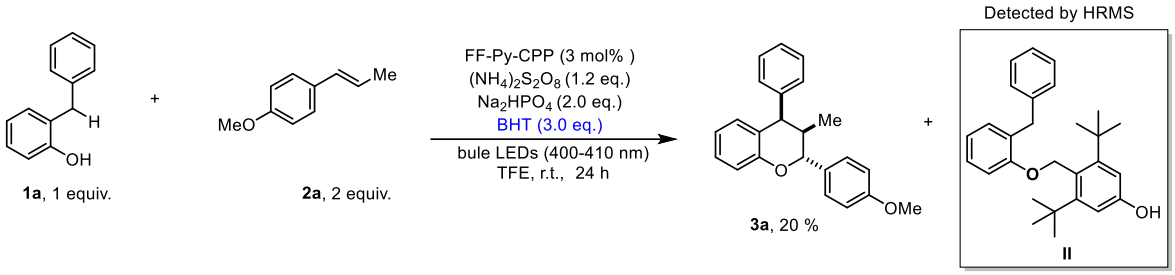
The photocatalytic reaction was performed according to the general procedure using **1a** (0.20 mmol), **2a** (0.40 mmol), Na_2HPO_4 (0.40 mmol), $(NH_4)_2S_2O_8$ (0.24 mmol), and FF-Py-CPP (0.06 mmol) in TFE (1 mL). Afterward, 2,2,6,6- tetramethylpiperidin-1-yl)oxidanyl (TEMPO, 3.0 equiv) was added to the mixture. The mixture was stirred under blue LED (400-410 nm) irradiation at room temperature for 24 h. (As shown in Scheme S1-A).

The photocatalytic reaction was performed according to the general procedure using **1a** (0.20 mmol), **2a** (0.40 mmol), Na_2HPO_4 (0.40 mmol), $(NH_4)_2S_2O_8$ (0.24 mmol), and FF-Py-CPP (0.06 mmol) in TFE (1 mL). Afterward, 2,6-di-*tert*-butyl-4-methylphenol (BHT, 3.0 equiv) was added to the mixture. The mixture was stirred under blue LED (400-410 nm) irradiation at room temperature for 24 h. (As shown in Scheme S1-B).



Scheme S1 Radical trapping experiments used TEMPO and BHT as radical scavengers.

11. HRMS of the intermediates



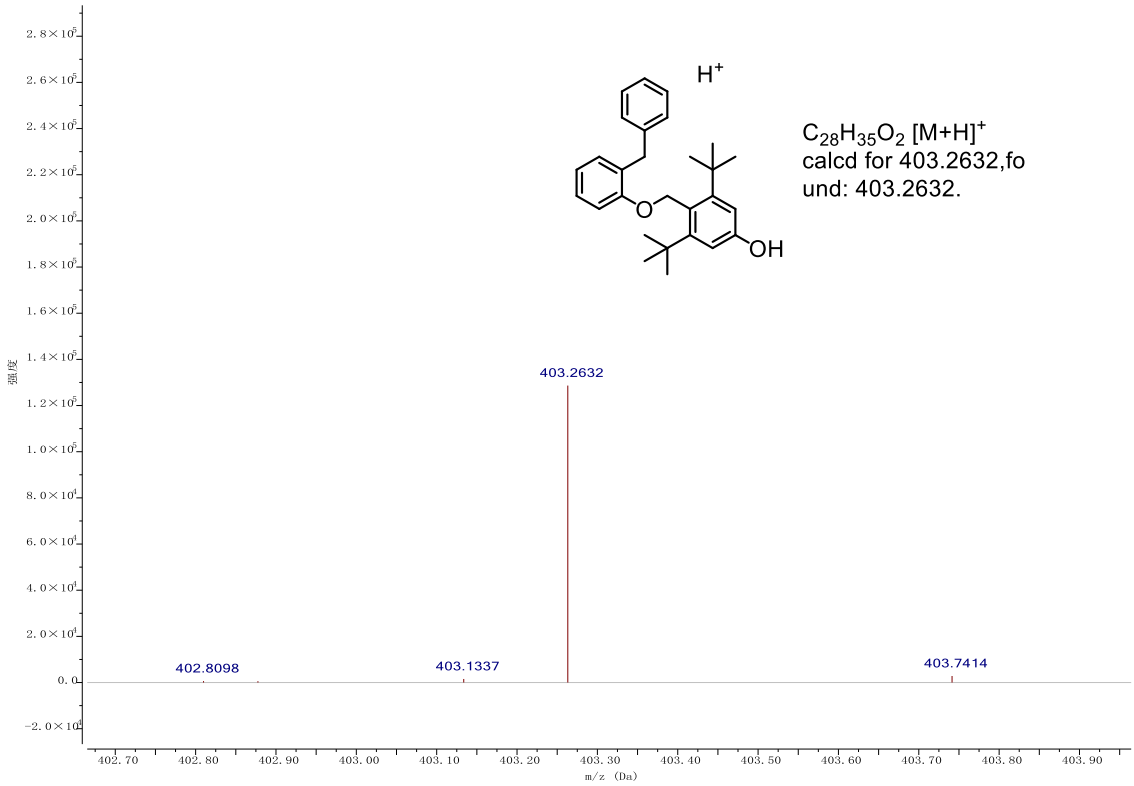


Fig. S12. HRMS spectra of intermediate II.

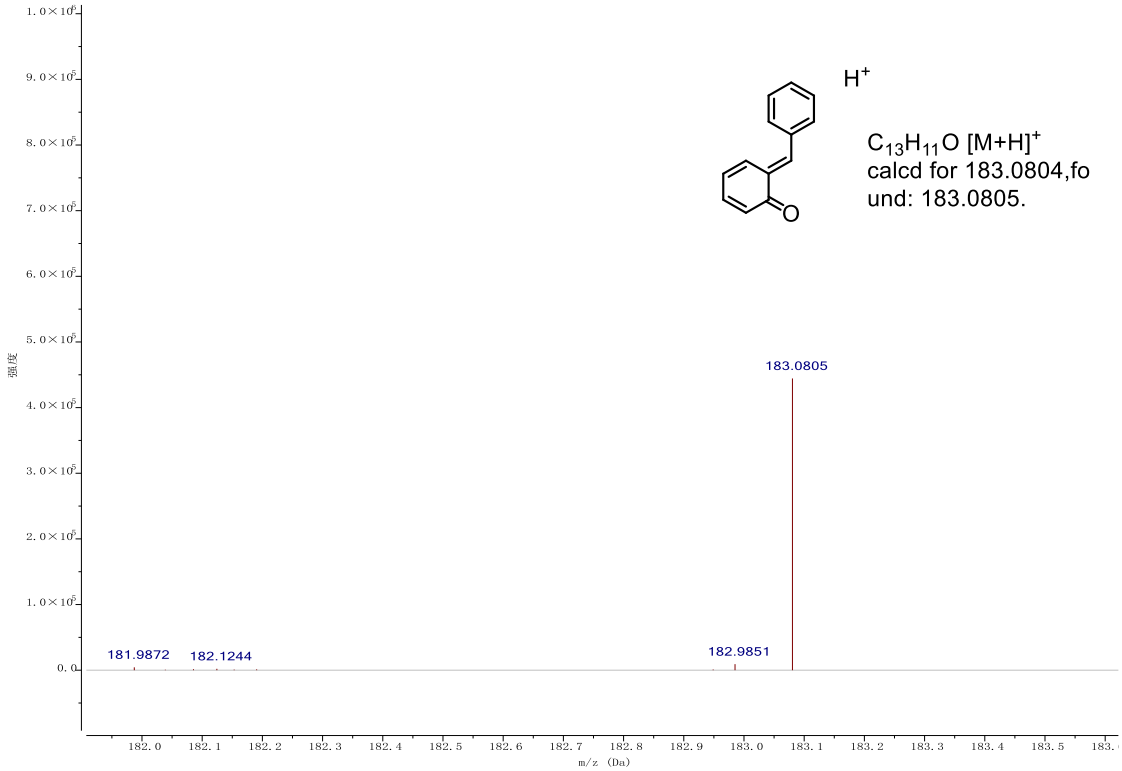
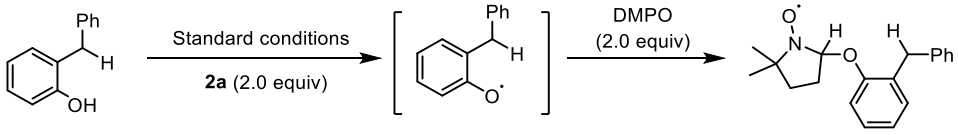


Fig. S13. HRMS spectra of *ortho*-quinone methide intermediate.

12. Procedure of EPR experiments



1a (1.0 equiv) **II** **6**

The photocatalytic reaction was performed according to the general procedure using **1a** (0.20 mmol), **2a** (0.40 mmol), Na_2HPO_4 (0.40 mmol), $(NH_4)_2S_2O_8$ (0.24 mmol), and FF-Py-CPP (0.06 mmol) in TFE (1 mL). Afterward, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) (2.0 equiv) was added to the mixture, and then the solution was excited under 300W xenon lamp of full spectrum at r.t. for 5 min. After reaction, drawing 30 μL resulting mixture was analyzed directly by EPR spectroscopy at room temperature, an obvious signal is detected. The EPR spectrum showed an e.p.r. quartet spectrum of **6** (gFactor = 2.00742, aN = 13.469 G), suggesting that radical intermediate II is generated in the reaction process.

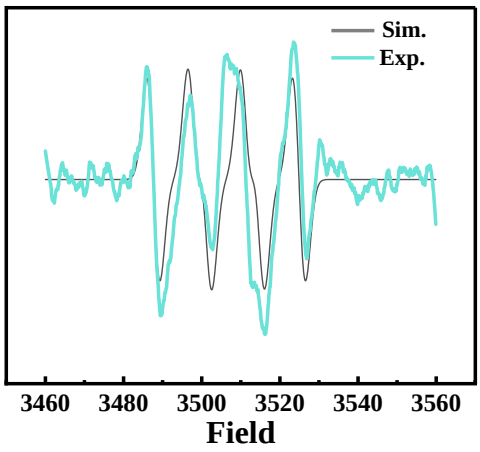


Fig. S14. EPR spectrum of **6**.

13. Stern–volmer analysis

Stern-Volmer fluorescence quenching experiments were conducted with freshly prepared solutions of 10^{-5} M FF-Py-CPP in TFE at room temperature. Solutions were irradiated at 340 nm, and fluorescence emission was measured from 450 nm to 650 nm. Control experiments showed that **1a** primarily quenched the excited state of FF-Py-CPP.

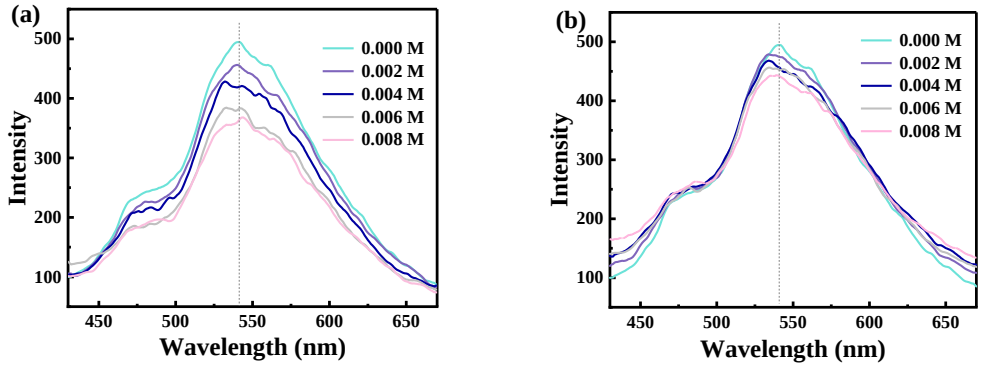


Fig. S15. Steady-state emission quenching of FF-Py-CPP with substrate (a) **1a** and (b) **2a** (Stern–Volmer analysis).

14. Cyclic voltammetry (CV) measurements of FF-Py-CPP and 1a.

Cyclic voltammetry (CV) measurement of FF-Py-CPP. Cyclic voltammetry (CV) measurement was performed using Chenhua CHI 760E potentiostat/galvanostat in a three-electrode system: as-prepared electrode film drop-casted with the polymers as the working

electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode, Bu_4NPF_6 (0.1 M in TFE) was used as electrolyte. For preparation of electrode film, 10 mg of catalyst were mixed with 1.0 mL of ethanol and 30 μL of Nafion solution to get a slurry. Then, 30 μL of this slurry was evenly dropped onto the FTO substrate and the solvent evaporate. The measurement was carried out in a 0.1 M of Bu_4NPF_6 solution as supporting electrolyte in TFE with a scan rate of 100 mV s^{-1}.

Cyclic voltammetry curves of **1a**: Cyclic voltammograms of **1a** were performed in a 5.0 mL three-electrode system. A steady glassy carbon disk electrode was used as the working electrode, while a platinum wire as the counter electrode. The reference was an SCE electrode. Bu_4NPF_6 was employed as the electrolyte. A mixed solvent of **1a** (0.5 mmol) containing Bu_4NPF_6 (0.1 M) in TFE was poured into the electrochemical cell in cyclic voltammetry experiments and the scan rate was 0.10 V/s, ranging from -2.5 V to 2.5 V.

15. References

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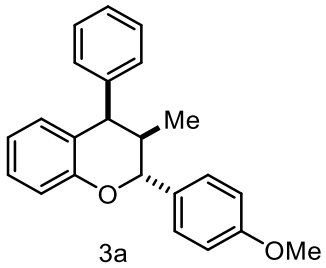
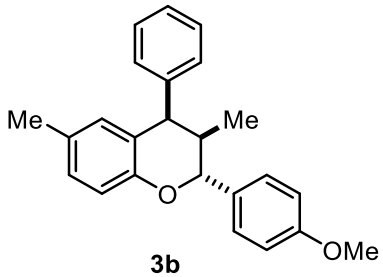
16. Characterization data for compounds



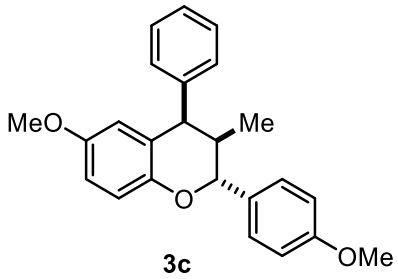
3a

3a (2*R*,3*R*,4*R*)-2-(4-methoxyphenyl)-3-methyl-4-phenylchromane ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31–7.26 (m, 2H), 7.25 – 7.20 (m, 3H), 7.18 – 7.14 (m, 1H), 7.14 – 7.10 (m, 2H), 6.98 – 6.94 (m, 2H), 6.89 – 6.85 (m, 2H), 6.85 – 6.80 (m, 1H), 4.82 (d, *J* = 10.3 Hz, 1H), 4.09 (d, *J* = 5.2 Hz, 1H), 3.79 (s, 3H), 2.50 – 2.42 (m, 1H), 0.55 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 159.49, 154.92, 142.18, 132.41, 130.39, 128.53, 127.95 (d, *J* = 2.3 Hz), 126.53, 124.95, 120.40, 116.62, 113.87, 78.75, 55.31, 46.85, 37.05, 15.46. **HRMS** (ESI) Calcd.for $C_{23}H_{22}KO_2$ $[M+K]^+$ 369.1251, Found: 369.1265.



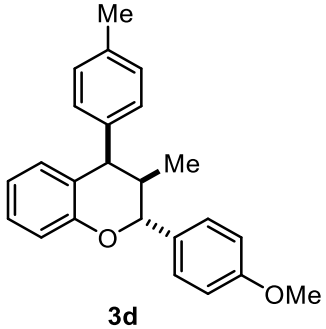
3b

3b (2*R*,3*R*,4*R*)-2-(4-methoxyphenyl)-3,6-dimethyl-4-phenylchromane ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.27 (m, 2H), 7.25 – 7.19 (m, 3H), 7.16 – 7.11 (m, 2H), 6.96 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.90 – 6.84 (m, 3H), 6.76 (d, *J* = 2.2 Hz, 1H), 4.79 (d, *J* = 10.2 Hz, 1H), 4.04 (d, *J* = 5.3 Hz, 1H), 3.78 (s, 3H), 2.48 – 2.39 (m, 1H), 2.19 (s, 3H), 0.53 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 159.47, 152.76, 142.32, 132.57, 130.60, 130.41, 129.49, 128.72, 128.54, 127.93, 126.52, 124.55, 116.34, 113.85, 78.66, 55.30, 46.94, 37.14, 20.50, 15.51. **HRMS** (ESI) Calcd.for $C_{24}H_{24}NaO_2$ $[M+Na]^+$ 367.1669, Found: 367.1672.



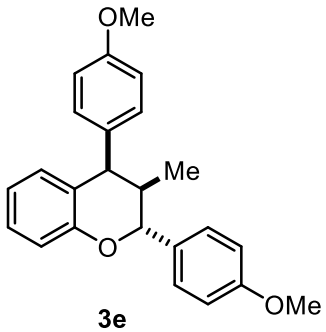
3c

3c (2*R*,3*R*,4*R*)-6-methoxy-2-(4-methoxyphenyl)-3-methyl-4-phenylchromane ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 – 7.29 (m, 2H), 7.28 – 7.21 (m, 3H), 7.18 – 7.13 (m, 2H), 6.92 (d, *J* = 8.9 Hz, 1H), 6.90 – 6.86 (m, 2H), 6.78 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.50 (d, *J* = 3.0 Hz, 1H), 4.80 (d, *J* = 10.2 Hz, 1H), 4.07 (d, *J* = 5.3 Hz, 1H), 3.81 (s, 3H), 3.68 (s, 3H), 2.50 – 2.43 (m, 1H), 0.55 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 159.44, 153.38, 149.08, 142.01, 132.56, 130.37, 128.49, 127.93, 126.55, 125.26, 117.22, 114.51, 114.46, 113.84, 78.61, 55.70, 55.29, 47.18, 37.10, 15.44. **HRMS** (ESI) Calcd.for $C_{24}H_{24}O_3$ $[M+H]^+$ 361.1798, Found: 361.1788.



3d

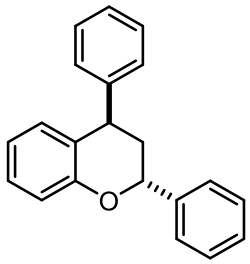
3d (2*R*,3*R*,4*R*)-2-(4-methoxyphenyl)-3-methyl-4-(p-tolyl)chromane ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 – 7.28 (m, 2H), 7.23 – 7.18 (m, 1H), 7.18 – 7.15 (m, 2H), 7.08 – 7.05 (m, 2H), 7.05 – 7.01 (m, 2H), 6.95 – 6.92 (m, 2H), 6.91 – 6.87 (m, 1H), 4.88 (d, *J* = 10.3 Hz, 1H), 4.12 (d, *J* = 5.2 Hz, 1H), 3.84 (s, 3H), 2.54 – 2.47 (m, 1H), 2.39 (s, 3H), 0.61 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 159.52, 154.95, 139.23, 136.10, 132.52, 130.43, 130.32, 128.71, 128.59, 127.90, 125.24, 120.43, 116.63, 113.89, 78.82, 55.32, 46.52, 37.13, 21.09, 15.52. **HRMS** (ESI) Calcd.for $C_{24}H_{24}NaO_2$ $[M+Na]^+$ 367.1669, Found:367.1670.



3e

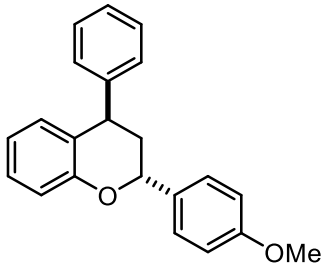
3e (2*R*,3*R*,4*R*)-2,4-bis(4-methoxyphenyl)-3-methylchromane ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 – 7.27 (m, 2H), 7.23 – 7.19 (m, 1H), 7.11 – 7.07 (m, 2H), 7.05 – 7.00 (m, 2H), 6.96 – 6.90 (m, 2H), 6.90 – 6.87 (m, 3H), 4.85 (d, *J* = 10.3 Hz, 1H), 4.10 (d, *J* = 5.1 Hz, 1H), 3.83 (d, *J* = 3.0 Hz, 6H), 2.52 – 2.44 (m, 1H), 0.61 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151

MHz, Chloroform-*d*) δ 159.46, 158.23, 154.84, 134.31, 132.44, 131.25, 130.35, 128.54, 127.84, 125.29, 120.37, 116.59, 113.84, 113.31, 78.75, 55.27 (d, *J* = 9.5 Hz), 46.03, 37.17, 15.46. **HRMS** (ESI) Calcd.for $C_{23}H_{22}ClO_2$ $[M+H]^+$ 361.1798, Found: 361.1782.



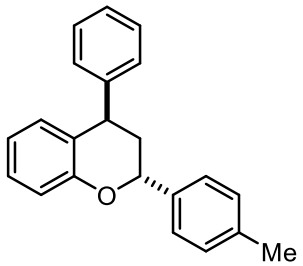
3f

3f (2*R*,4*R*)-2,4-diphenylchromane ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.53 – 7.49 (m, 2H), 7.41 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.37 – 7.32 (m, 3H), 7.30 – 7.22 (m, 3H), 7.18 – 7.14 (m, 1H), 6.98 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.84 – 6.78 (m, 2H), 5.24 (dd, *J* = 11.5, 1.9 Hz, 1H), 4.38 (dd, *J* = 12.2, 5.8 Hz, 1H), 2.46 – 2.41 (m, 1H), 2.30 (dt, *J* = 13.7, 11.9 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 155.53, 144.53, 141.22, 129.82, 128.69, 128.60 (d, *J* = 2.5 Hz), 128.08, 127.80, 126.81, 126.11, 125.72, 120.60, 117.03, 78.12, 43.52, 40.65. **HRMS** (ESI) Calcd.for $C_{21}H_{18}NaO$ $[M+Na]^+$ 309.1250, Found: 309.1250.



3g

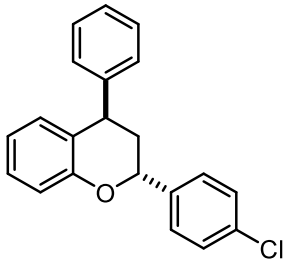
3g (2*R*,4*R*)-2-(4-methoxyphenyl)-4-phenylchromane ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.50 – 7.44 (m, 2H), 7.41 – 7.35 (m, 2H), 7.34 – 7.27 (m, 3H), 7.21 – 7.16 (m, 1H), 7.04 – 6.96 (m, 3H), 6.89 – 6.82 (m, 2H), 5.24 – 5.19 (m, 1H), 4.43 – 4.37 (m, 1H), 3.87 – 3.85 (m, 3H), 2.47 – 2.41 (m, 1H), 2.40 – 2.31 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 159.55, 155.73, 144.71, 133.41, 129.89, 128.75, 128.68, 127.82, 127.61, 126.84, 125.77, 120.60, 117.08, 114.05, 77.87, 55.39, 43.64, 40.48. **HRMS** (ESI) Calcd.for 317.1536 $C_{22}H_{21}O_2$ $[M+H]^+$, Found: 317.1522.



3h

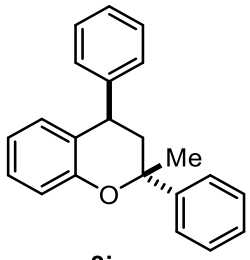
3h (2*R*,4*R*)-4-phenyl-2-(*p*-tolyl)chromane ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.26 – 7.16 (m, 5H), 7.15 – 7.10 (m, 1H), 6.95 – 6.92 (m, 1H), 6.80 – 6.74 (m, 2H), 5.16 (dd, *J* = 11.5, 2.1 Hz, 1H), 4.33 (dd, *J* = 12.2, 5.9 Hz, 1H), 2.40 –

2.35 (m, 1H), 2.35 (d, *J* = 1.6 Hz, 3H), 2.33 – 2.23 (m, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 155.67, 144.66, 138.27, 137.85, 129.84, 129.30, 128.71, 128.65, 127.79, 126.81, 126.17, 125.77, 120.56, 117.07, 78.06, 43.60, 40.52, 21.25. **HRMS** (ESI) Calcd.for $C_{22}H_{20}NaO$ $[M+Na]^+$ 323.1406, Found: 323.1412.



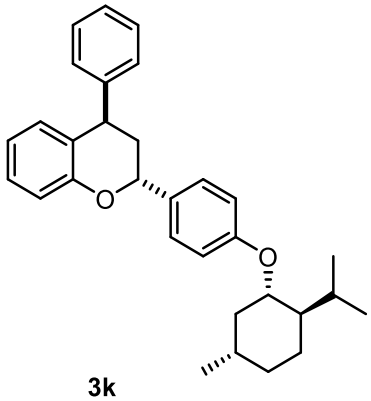
3i

3i (2*R*,4*R*)-2-(4-chlorophenyl)-4-phenylchromane ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.46 – 7.42 (m, 2H), 7.40 – 7.31 (m, 4H), 7.30 – 7.25 (m, 1H), 7.25 – 7.22 (m, 2H), 7.18 – 7.14 (m, 1H), 6.96 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.85 – 6.77 (m, 2H), 5.20 (dd, *J* = 11.5, 1.9 Hz, 1H), 4.37 (dd, *J* = 12.2, 5.8 Hz, 1H), 2.43 – 2.38 (m, 1H), 2.28 – 2.20 (m, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 155.27, 144.33, 139.77, 133.76, 129.84, 128.74 (d, *J* = 2.1 Hz), 128.59, 127.88, 127.49, 126.90, 125.60, 120.80, 116.98, 77.36, 43.40, 40.62. **HRMS** (ESI) Calcd.for $C_{21}H_{17}ClNaO$ $[M+Na]^+$ 343.0860, Found: 343.0842.



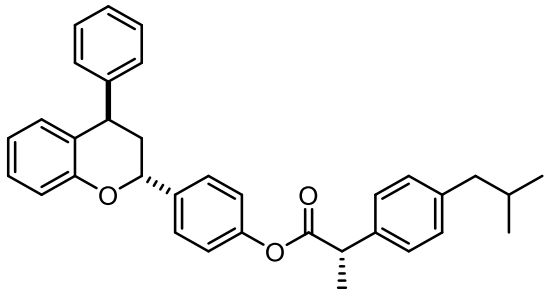
3j

3j (2*R*,4*R*)-2-methyl-2,4-diphenylchromane ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.69 – 7.66 (m, 2H) (mixture), 7.53 – 7.49 (m, 1H) (mixture), 7.48 – 7.31 (m, 10H) (mixture), 7.30 – 7.27 (m, 3H) (mixture), 7.28 – 7.22 (m, 1H) (mixture), 7.20 – 7.15 (m, 2H) (mixture), 6.95 – 6.90 (m, 2H) (mixture), 6.83 – 6.79 (m, 1H) (mixture), 6.71 – 6.68 (m, 1H) (mixture), 4.36 (dd, *J* = 12.1, 5.9 Hz, 1H) (major), 3.72 (dd, *J* = 12.8, 5.3 Hz, 1H) (minor), 2.81 (dd, *J* = 13.8, 5.3 Hz, 1H) (minor), 2.50 (dd, *J* = 13.8, 6.0 Hz, 1H) (major), 2.43 (dd, *J* = 13.8, 12.8 Hz, 1H) (minor), 2.34 (dd, *J* = 13.7, 12.1 Hz, 1H) (major), 1.84 – 1.82 (m, 3H) (major), 1.80 (s, 2H) (minor). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 154.45, 154.05, 147.04, 145.41, 144.65, 144.60, 129.95, 129.77, 128.93, 128.74, 128.71, 128.42, 128.08, 127.98, 127.12, 126.94, 126.84, 126.78, 125.60, 125.08, 124.76, 124.55, 120.37, 120.29, 117.78, 116.89, 79.12, 77.78, 44.59, 42.87, 40.24, 39.95, 32.36, 25.01. **HRMS** (ESI) Calcd.for $C_{22}H_{20}NaO$ $[M+Na]^+$ 323.1406, Found: 323.1418.



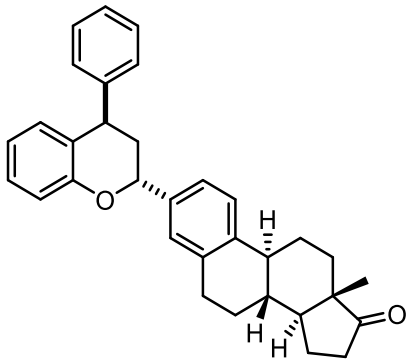
3k

3k ((2*S*,4*R*)-2-(4-(((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl)oxy)phenyl)-4-phenylchromane ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 – 7.42 (m, 2H), 7.40 – 7.35 (m, 2H), 7.33 – 7.27 (m, 3H), 7.22 – 7.16 (m, 1H), 7.03 – 6.97 (m, 2H), 6.84 (q, *J* = 3.3, 2.9 Hz, 1H), 5.21 (d, *J* = 11.4 Hz, 1H), 4.40 (dd, *J* = 12.2, 5.9 Hz, 1H), 4.15 – 4.07 (m, 1H), 2.49 – 2.18 (m, 3H), 1.83 – 1.74 (m, 2H), 1.63 – 1.48 (m, 2H), 1.22 – 1.05 (m, 2H), 1.04 – 0.96 (m, 6H), 0.87 – 0.82 (m, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 158.38, 155.77, 144.73, 133.05, 129.88, 128.73, 128.66, 127.80, 127.67, 126.81, 125.77, 120.57, 117.09, 115.89 (d, *J* = 2.5 Hz), 77.95 (d, *J* = 3.6 Hz), 77.61, 48.15, 43.66, 40.44, 40.36, 34.61, 31.50, 26.20, 23.85, 22.26, 20.86, 16.73. **HRMS** (ESI) Calcd.for $C_{31}H_{36}KO_2$ $[M+K]^+$ 479.2347, Found: 479.2359.



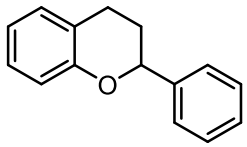
3l

3l 4-((2*S*,4*R*)-4-phenylchroman-2-yl)phenyl (*S*)-2-(4-isobutylphenyl)propanoate ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.50 – 7.45 (m, 2H), 7.36 – 7.30 (m, 4H), 7.30 – 7.24 (m, 1H), 7.25 – 7.22 (m, 2H), 7.19 – 7.12 (m, 3H), 7.07 – 7.03 (m, 2H), 6.95 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.83 – 6.77 (m, 2H), 5.21 (dd, *J* = 11.5, 1.9 Hz, 1H), 4.36 (dd, *J* = 12.2, 5.8 Hz, 1H), 3.96 (q, *J* = 7.2 Hz, 1H), 2.50 (d, *J* = 7.2 Hz, 2H), 2.43 – 2.38 (m, 1H), 2.29 – 2.21 (m, 1H), 1.94 – 1.85 (m, 1H), 1.63 (d, *J* = 7.2 Hz, 3H), 0.94 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 173.20, 155.38, 150.59, 144.41, 140.87, 138.69, 137.25, 129.81, 129.56, 128.71, 128.60, 127.82, 127.26, 127.13, 126.85, 125.67, 121.53, 120.68, 116.98, 77.53, 45.30, 45.09, 43.45, 40.55, 30.23, 22.44, 18.59. **HRMS** (ESI) Calcd.for $C_{34}H_{34}NaO_3$ $[M+Na]^+$ 513.2400, Found: 513.2417.



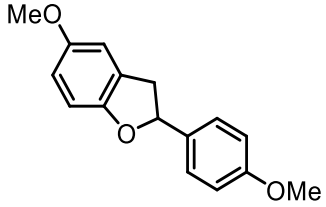
3m

3m (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-((2*R*,4*R*)-4-phenylchroman-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.39 – 7.35 (m, 3H) (mixture), 7.34 – 7.27 (m, 6H) (mixture), 7.21 – 7.13 (m, 2H) (mixture), 7.09 – 7.04 (m, 1H) (mixture), 7.01 (dd, *J* = 8.0, 1.1 Hz, 1H) (mixture), 6.86 – 6.81 (m, 2H) (mixture), 5.23 – 5.18 (m, 1H) (major), 4.39 (dd, *J* = 12.1, 5.9 Hz, 1H) (major), 3.04 – 2.98 (m, 2H) (major), 2.97 – 2.93 (m, 1H) (minor), 2.60 – 2.42 (m, 3H) (mixture), 2.40 – 2.27 (m, 3H) (mixture), 2.24 – 2.14 (m, 1H) (mixture), 2.14 – 1.99 (m, 4H) (mixture), 1.74 – 1.45 (m, 8H) (mixture), 0.96 (s, 3H) (major), 0.95 (s, 1H) (minor). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.68, 144.67, 139.78, 138.67 (d, *J* = 2.3 Hz), 136.83, 130.91, 129.89, 128.89 – 128.41 (m), 127.83, 126.87 (d, *J* = 7.5 Hz), 125.79 – 125.62 (m), 123.81 (d, *J* = 1.9 Hz), 120.62, 117.19, 117.09, 77.98 (d, *J* = 5.1 Hz), 73.06 (d, *J* = 8.7 Hz), 50.57, 48.04, 44.47 (d, *J* = 4.4 Hz), 43.58, 40.40 (d, *J* = 2.7 Hz), 38.22 – 38.10 (m), 35.94, 31.70, 29.62 – 29.48 (m), 26.59 (d, *J* = 2.7 Hz), 25.83 (d, *J* = 4.3 Hz), 21.69, 13.95. **HRMS** (ESI) Calcd.for $C_{33}H_{35}O_2$ $[M+H]^+$ 463.2632, Found: 463.2623.



3n

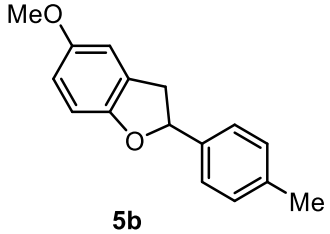
3n 2-phenylchromane ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 – 7.38 (m, 4H), 7.36 – 7.31 (m, 1H), 7.17 – 7.09 (m, 2H), 6.96 – 6.87 (m, 2H), 5.09 (dd, *J* = 10.2, 2.4 Hz, 1H), 3.07 – 2.96 (m, 1H), 2.86 – 2.77 (m, 1H), 2.26 – 2.20 (m, 1H), 2.16 – 2.07 (m, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 155.15, 141.77, 129.56, 128.55, 127.86, 127.37, 126.02, 121.86, 120.34, 116.96, 77.78, 29.99, 25.12. **HRMS** (ESI) Calcd.for $C_{15}H_{15}O$ $[M+H]^+$ 211.1117, Found: 211.1116.



5a

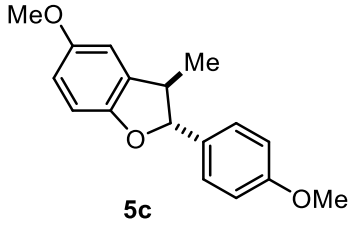
5a ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 – 7.33 (m, 2H), 6.92 – 6.89 (m, 2H), 6.79 (dq, *J* = 3.4, 2.3, 1.7 Hz, 1H), 6.75 (s, 1H), 6.72 – 6.69 (m, 1H), 5.69 (t, *J* = 8.8 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.55 (dd, *J* = 15.7, 9.2 Hz, 1H), 3.20 (ddt, *J* = 15.7, 8.4, 1.1 Hz, 1H). **^{13}C NMR**

(151 MHz, Chloroform-*d*) δ 159.48, 154.25, 153.75, 133.95, 127.75, 127.33, 114.03, 112.99, 111.21, 109.19, 84.21, 56.06, 55.33, 38.73. **HRMS** (ESI) Calcd.for $C_{16}H_{17}O_3$ $[M+H]^+$ 257.1172, Found: 257.1180.



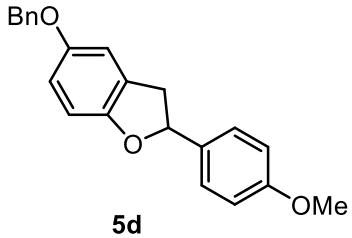
5b

5b ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 – 7.34 (m, 2H), 7.25 – 7.22 (m, 2H), 6.85 – 6.82 (m, 2H), 6.78 – 6.75 (m, 1H), 5.75 (t, *J* = 8.8 Hz, 1H), 3.82 (s, 3H), 3.64 – 3.57 (m, 1H), 3.27 – 3.21 (m, 1H), 2.41 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 154.35, 153.91, 139.08, 137.80, 129.37, 127.76, 125.91, 113.05, 111.29, 109.25, 84.34, 56.06, 38.90, 21.25. **HRMS** (ESI) Calcd.for $C_{16}H_{16}NaO_2$ $[M+Na]^+$ 263.1043, Found: 263.1042.



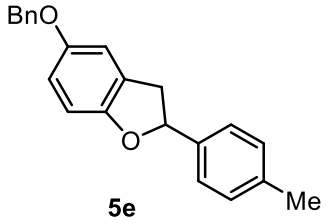
5c

5c (2*R*,3*R*)-5-methoxy-2-(4-methoxyphenyl)-3-methyl-2,3-dihydrobenzofuran ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 – 7.34 (m, 2H), 6.93 – 6.89 (m, 2H), 6.75 (d, *J* = 8.5 Hz, 1H), 6.73 – 6.69 (m, 2H), 5.08 (d, *J* = 9.1 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.44 – 3.38 (m, 1H), 1.38 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 159.65, 154.42, 153.28, 133.13, 132.71, 127.66, 114.01, 112.88, 110.10, 109.35, 92.61, 56.07, 55.33, 45.68, 17.59. **HRMS** (ESI) Calcd.for $C_{17}H_{19}O_3$ $[M+H]^+$ 271.1329, Found: 271.1323.



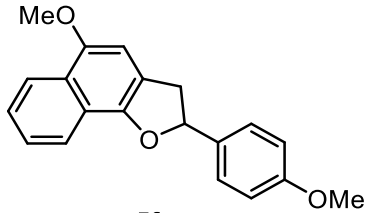
5d

5d 5-(benzyloxy)-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48 – 7.45 (m, 2H), 7.44 – 7.40 (m, 2H), 7.38 – 7.34 (m, 3H), 6.95 – 6.92 (m, 2H), 6.89 (dd, *J* = 2.7, 1.3 Hz, 1H), 6.82 – 6.77 (m, 2H), 5.71 (t, *J* = 8.8 Hz, 1H), 5.04 (s, 2H), 3.83 (s, 3H), 3.56 (dd, *J* = 15.7, 9.2 Hz, 1H), 3.22 (ddt, *J* = 15.7, 8.5, 1.0 Hz, 1H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 159.52, 154.02, 153.48, 137.48, 133.95, 128.61, 127.92, 127.80, 127.54, 127.37, 114.32, 114.06, 112.40, 109.25, 84.28, 71.10, 55.35, 38.74. **HRMS** (ESI) Calcd.for $C_{22}H_{20}O_3Na$ $[M+Na]^+$ 355.1305, Found: 355.1323.



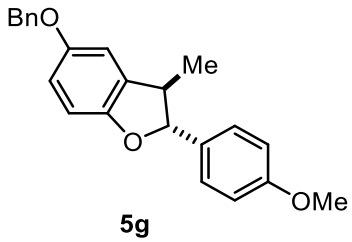
5e

5e 5-(benzyloxy)-2-(p-tolyl)-2,3-dihydrobenzofuran ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.49 – 7.45 (m, 2H), 7.42 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.22 (d, *J* = 7.9 Hz, 2H), 6.91 – 6.88 (m, 1H), 6.83 – 6.79 (m, 2H), 5.73 (t, *J* = 8.8 Hz, 1H), 5.05 (s, 2H), 3.59 (dd, *J* = 15.7, 9.3 Hz, 1H), 3.25 – 3.18 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.10, 153.50, 138.99, 137.82, 137.49, 129.35, 128.61, 127.92, 127.74, 127.54, 125.89, 114.33, 112.42, 109.27, 84.36, 71.11, 38.85, 21.23. **HRMS** (ESI) Calcd.for $C_{22}H_{20}O_2Na$ $[M+Na]^+$ 339.1356, Found: 339.1369.



5f

5f 5-methoxy-2-(4-methoxyphenyl)-2,3-dihydronaphtho[1,2-*b*]furan ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.23 – 8.19 (m, 1H), 7.98 – 7.94 (m, 1H), 7.51 – 7.42 (m, 2H), 7.42 – 7.37 (m, 2H), 6.93 – 6.89 (m, 2H), 6.74 (s, 1H), 5.88 (dd, *J* = 9.6, 8.0 Hz, 1H), 3.97 (s, 3H), 3.81 (s, 3H), 3.76 (dd, *J* = 15.3, 9.6 Hz, 1H), 3.36 (dd, *J* = 15.3, 8.0 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 159.43, 150.16, 148.46, 134.58, 127.31, 126.04, 125.42, 124.98, 122.49, 121.32, 120.83, 118.17, 114.03, 101.63, 84.10, 56.08, 55.34, 40.08. **HRMS** (ESI) Calcd.for $C_{20}H_{19}O_3$ $[M+H]^+$ 307.1329, Found: 307.1318.

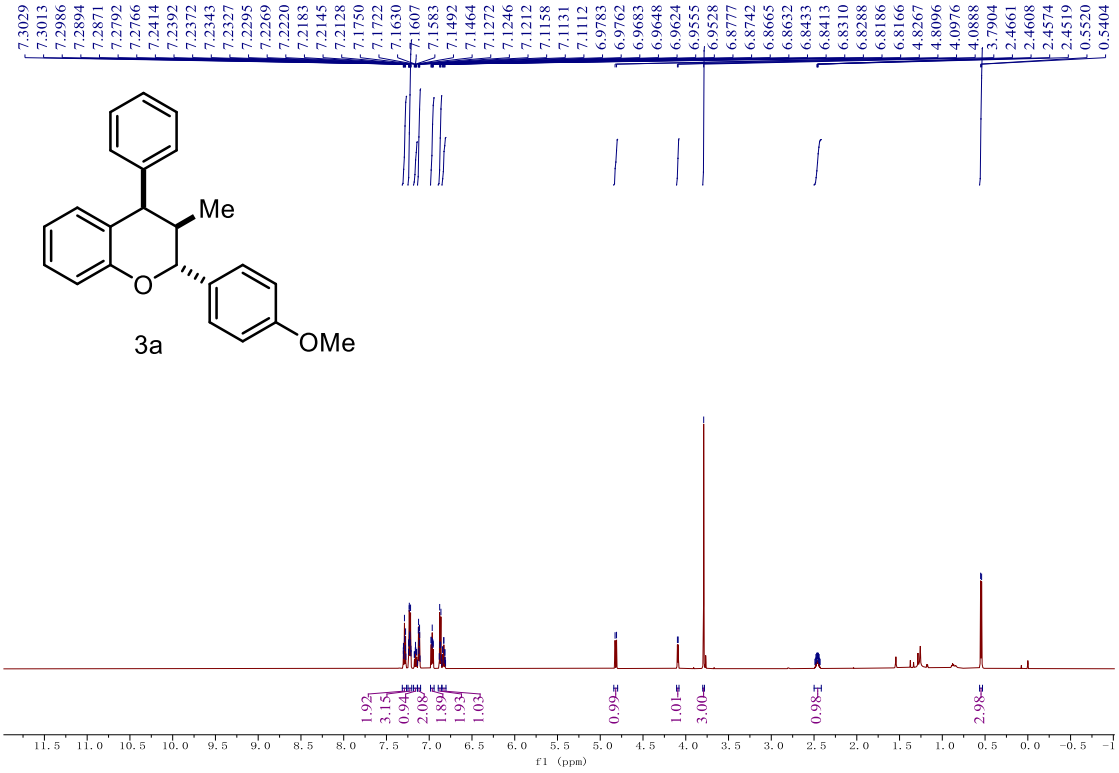


5g

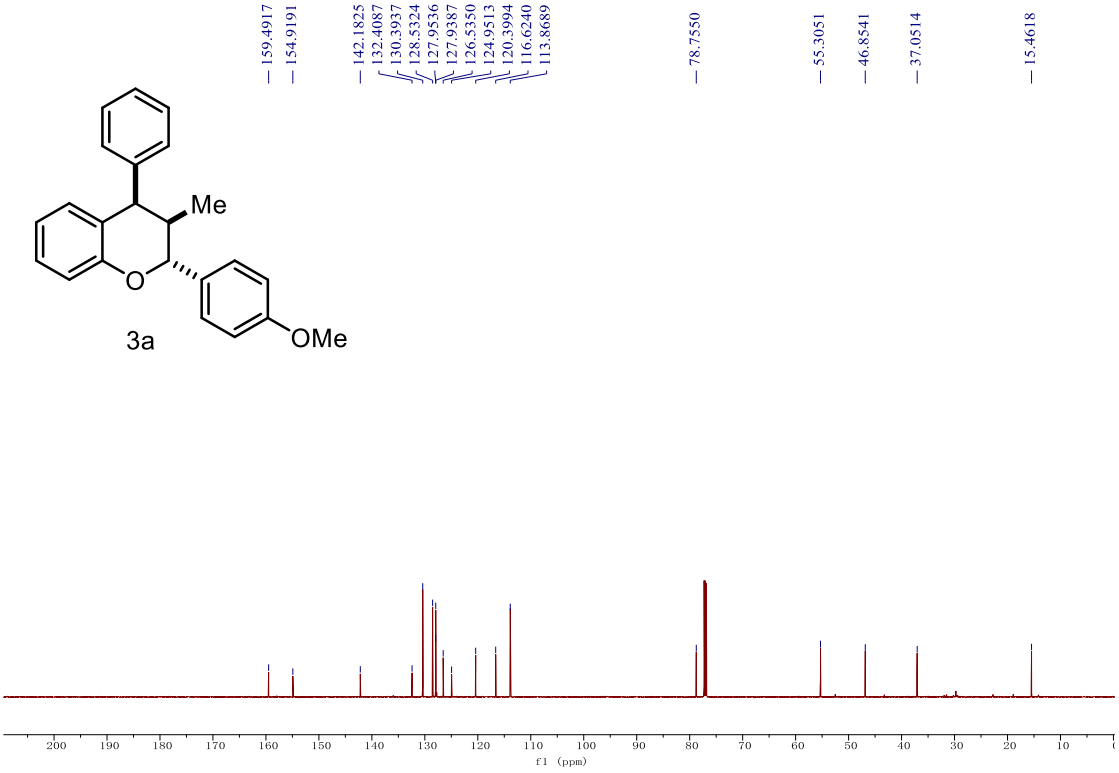
(2*R*,3*R*)-5-(benzyloxy)-2-(4-methoxyphenyl)-3-methyl-2,3-dihydrobenzofuran ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.2 Hz, 2H), 7.46 – 7.35 (m, 5H), 6.99 – 6.95 (m, 2H), 6.88 – 6.80 (m, 3H), 5.13 (d, *J* = 9.1 Hz, 1H), 5.07 (d, *J* = 2.3 Hz, 2H), 3.85 (s, 3H), 3.50 – 3.43 (m, 1H), 1.42 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 159.72, 153.70, 153.59, 137.48, 133.25, 132.74, 128.62, 127.96, 127.74, 127.61, 114.12, 114.08, 111.39, 109.42, 92.69, 71.13, 55.36, 45.73, 17.63. **HRMS** (ESI) Calcd.for $C_{23}H_{22}KO_3$ $[M+K]^+$ 385.1201, Found: 385.1209.

17. Copies of NMR spectra

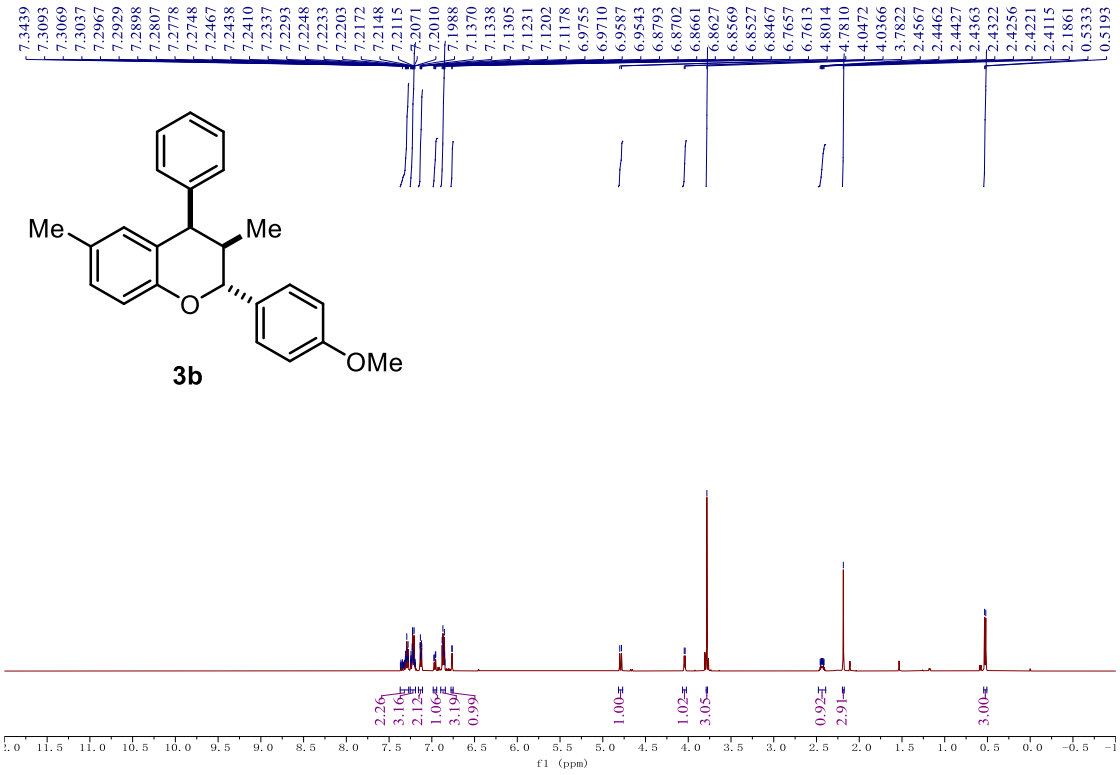
3a ^{1}H NMR (600 MHz, Chloroform-*d*)



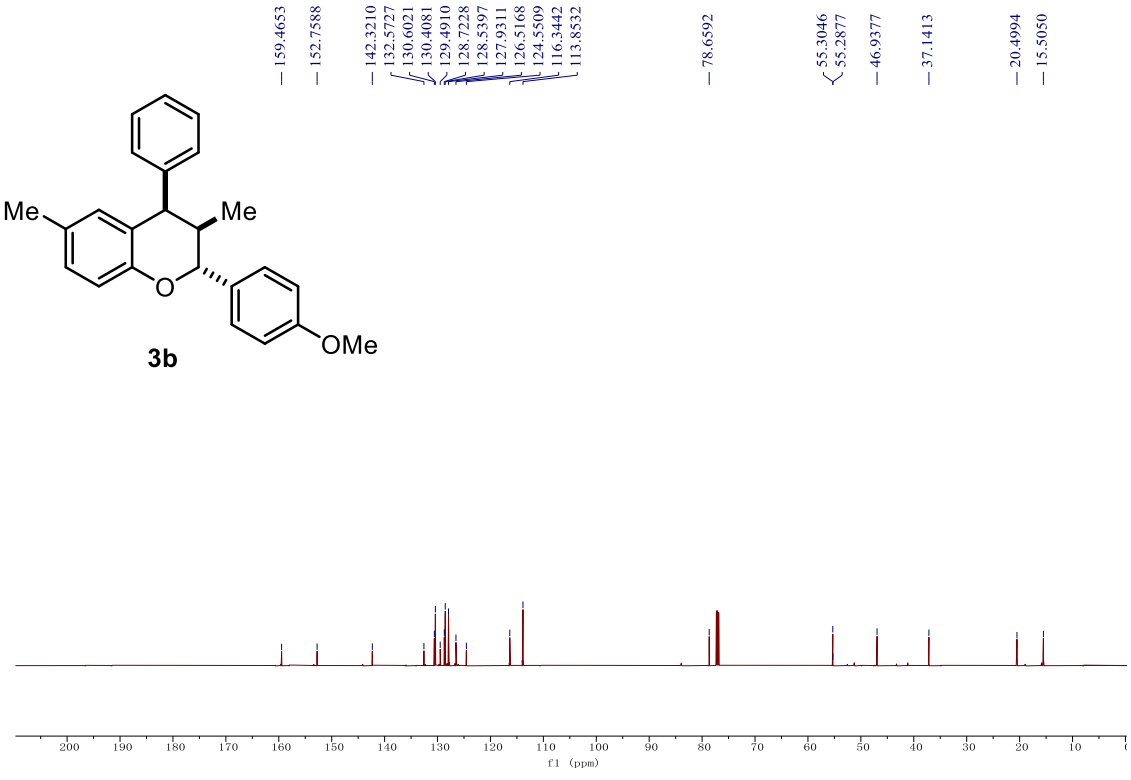
3a ^{13}C NMR (151 MHz, Chloroform-*d*)



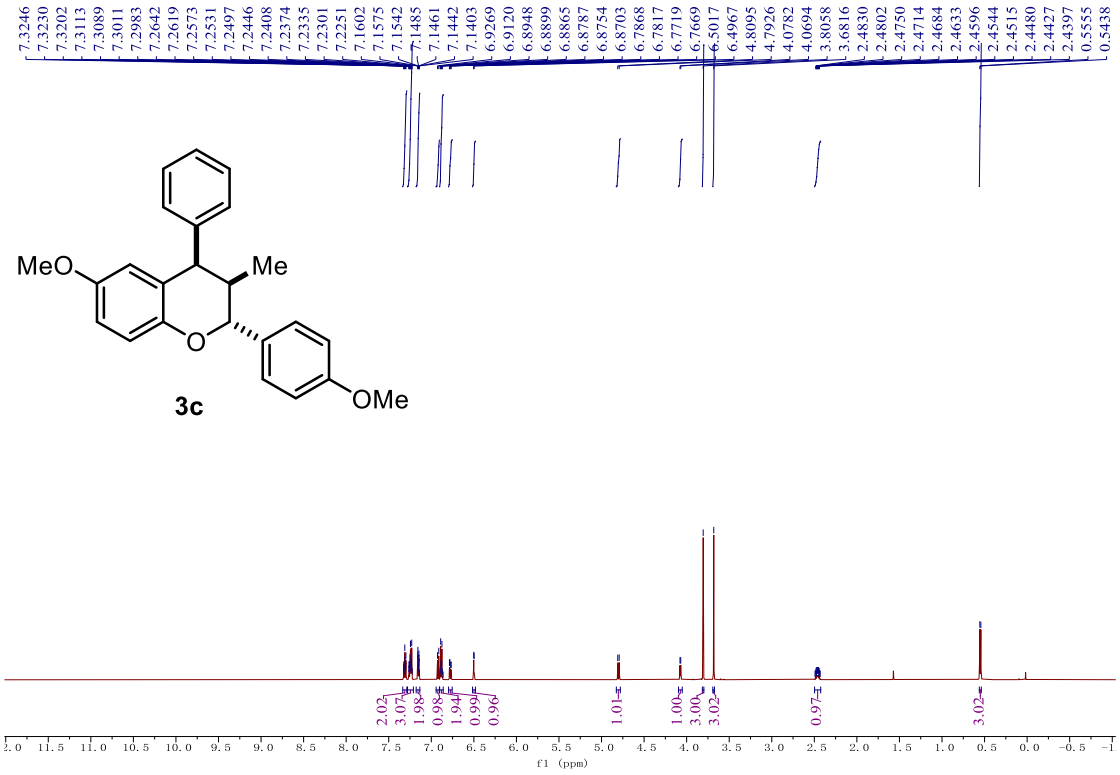
3b ^{1}H NMR (500 MHz, Chloroform-*d*)



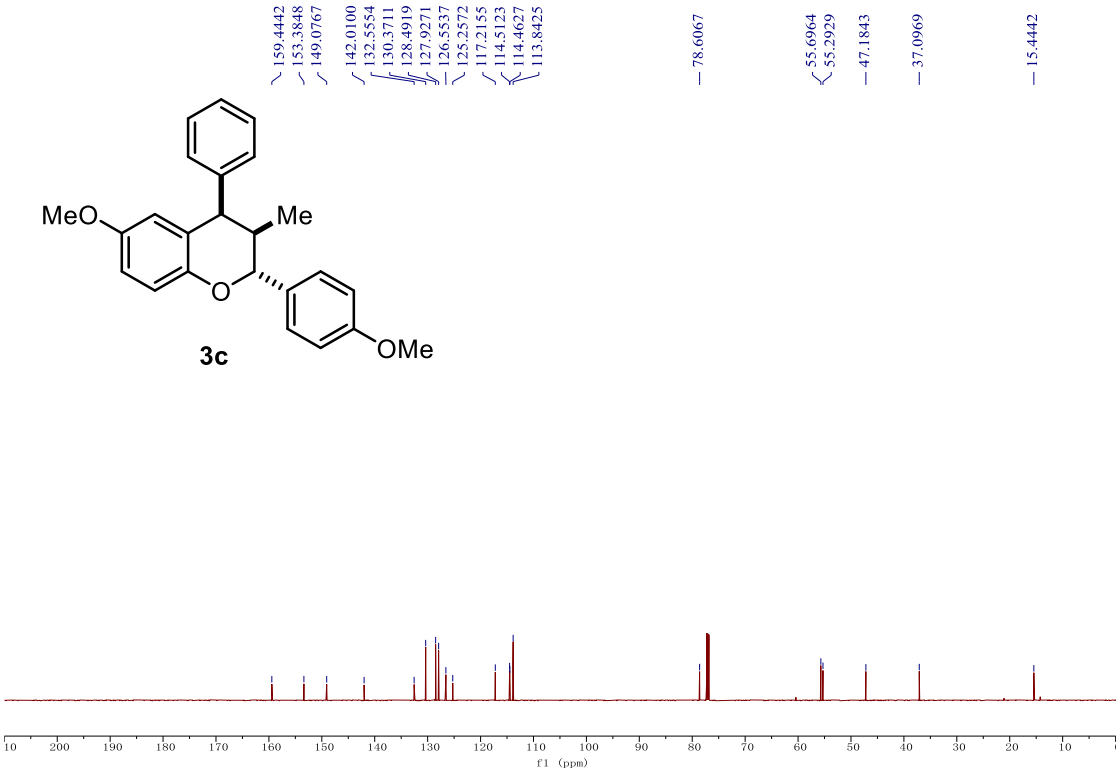
3b ^{13}C NMR (151 MHz, Chloroform-*d*)



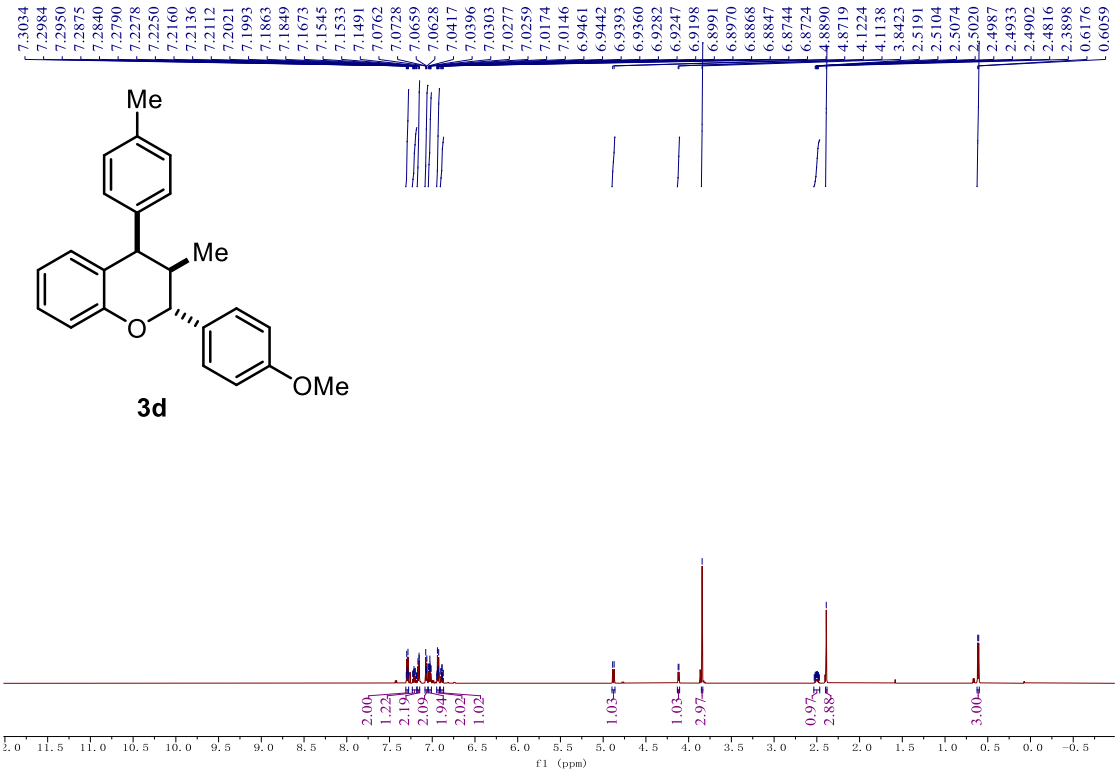
3c ^{1}H NMR (600 MHz, Chloroform-*d*)



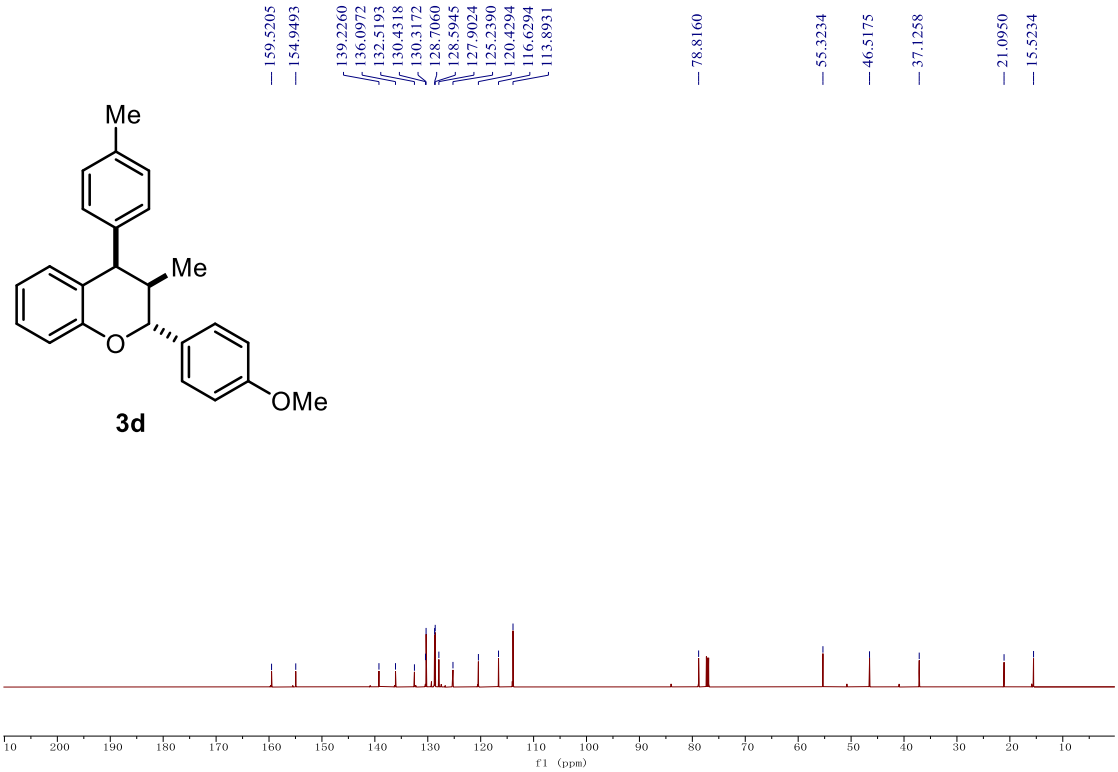
3c ^{13}C NMR (151 MHz, Chloroform-*d*)



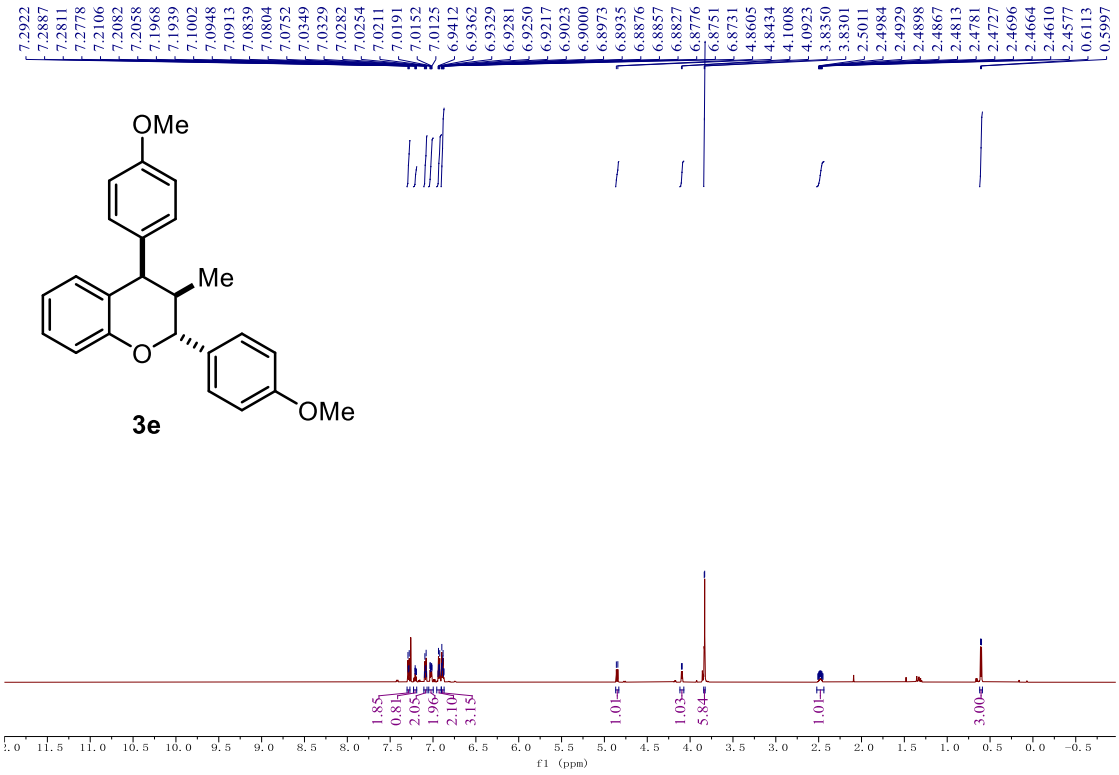
3d ^{1}H NMR (600 MHz, Chloroform-*d*)



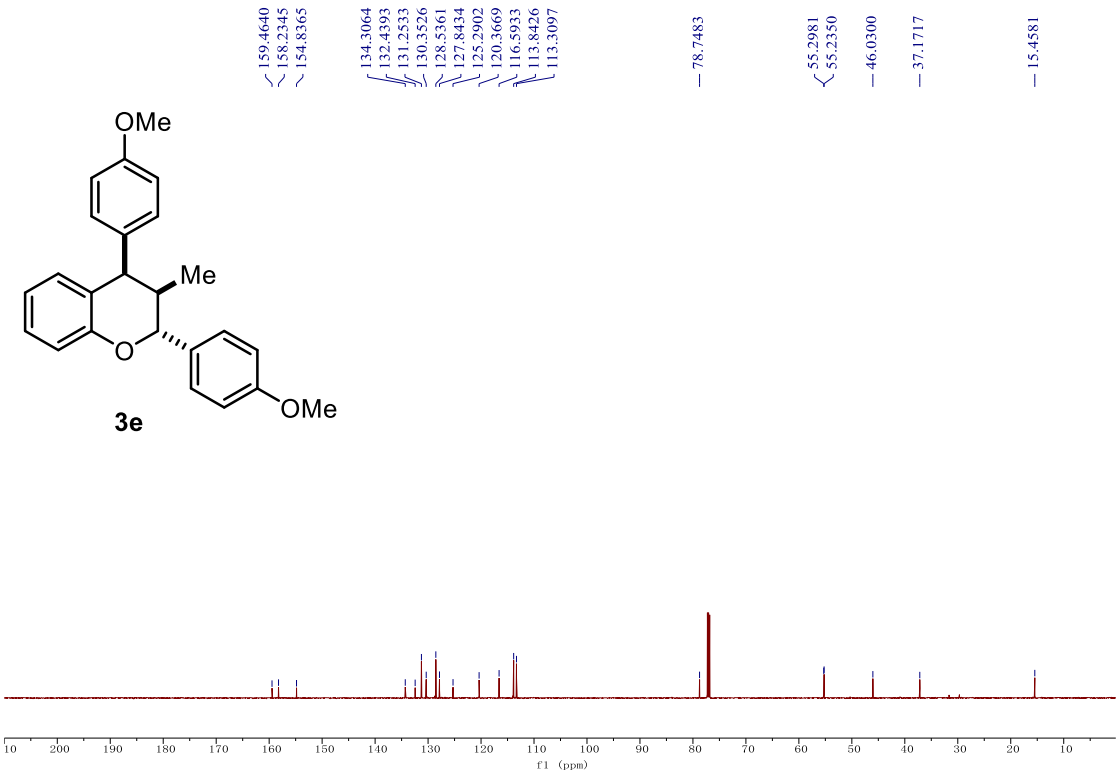
3d ^{13}C NMR (151 MHz, Chloroform-*d*)



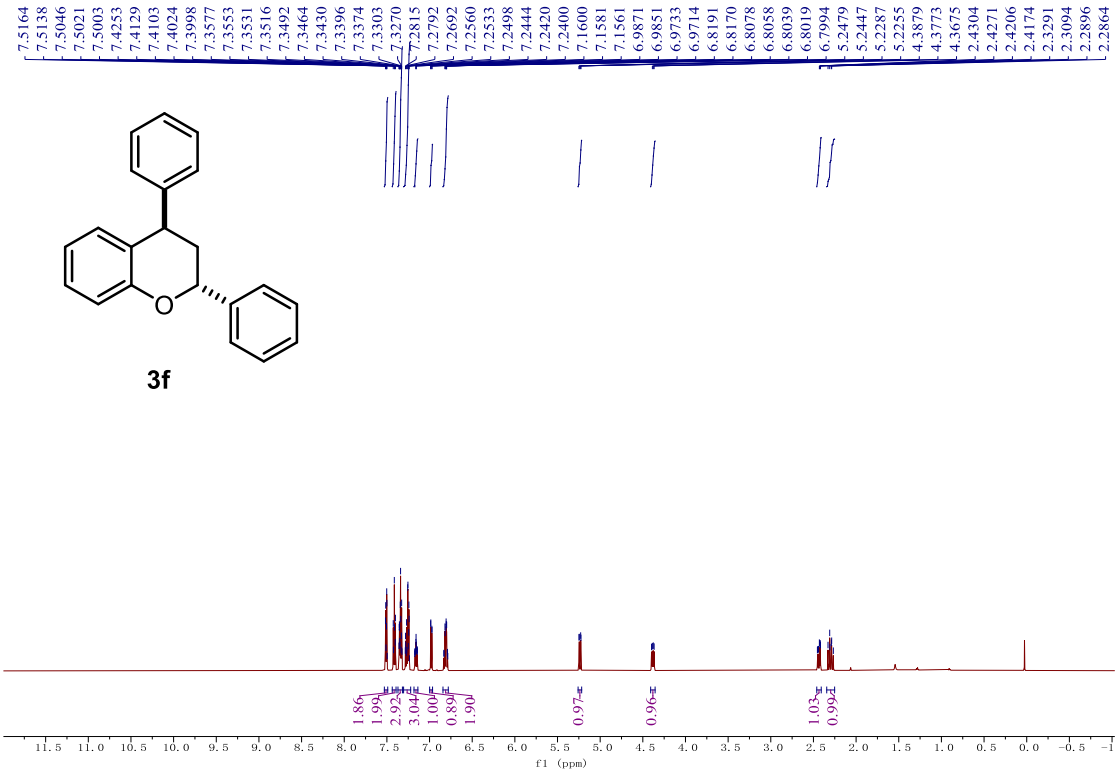
3e ^{1}H NMR (600 MHz, Chloroform-*d*)



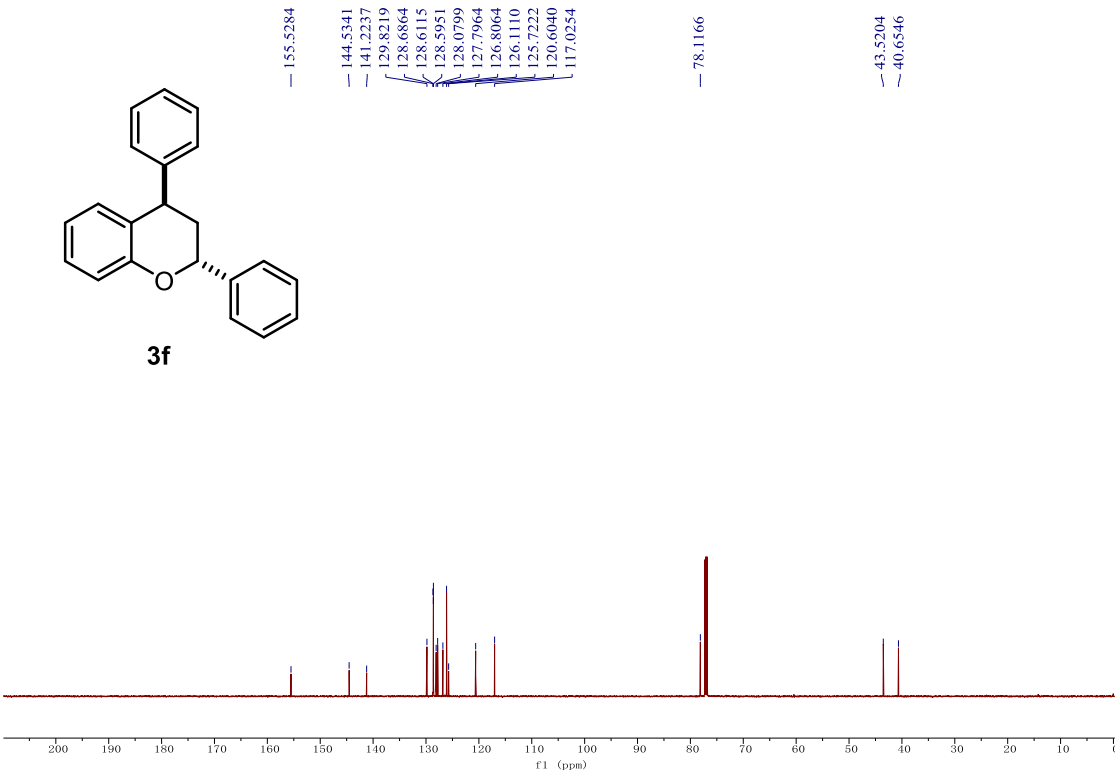
3e ^{13}C NMR (151 MHz, Chloroform-*d*)



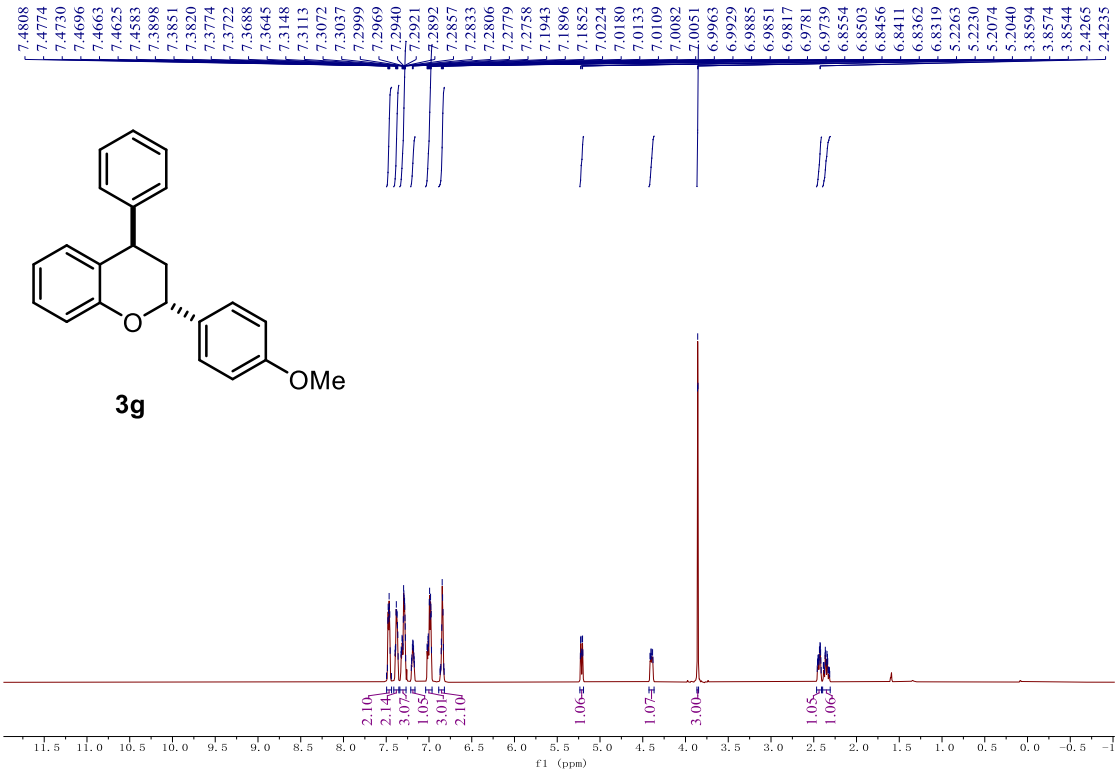
3f ^{1}H NMR (600 MHz, Chloroform-*d*)



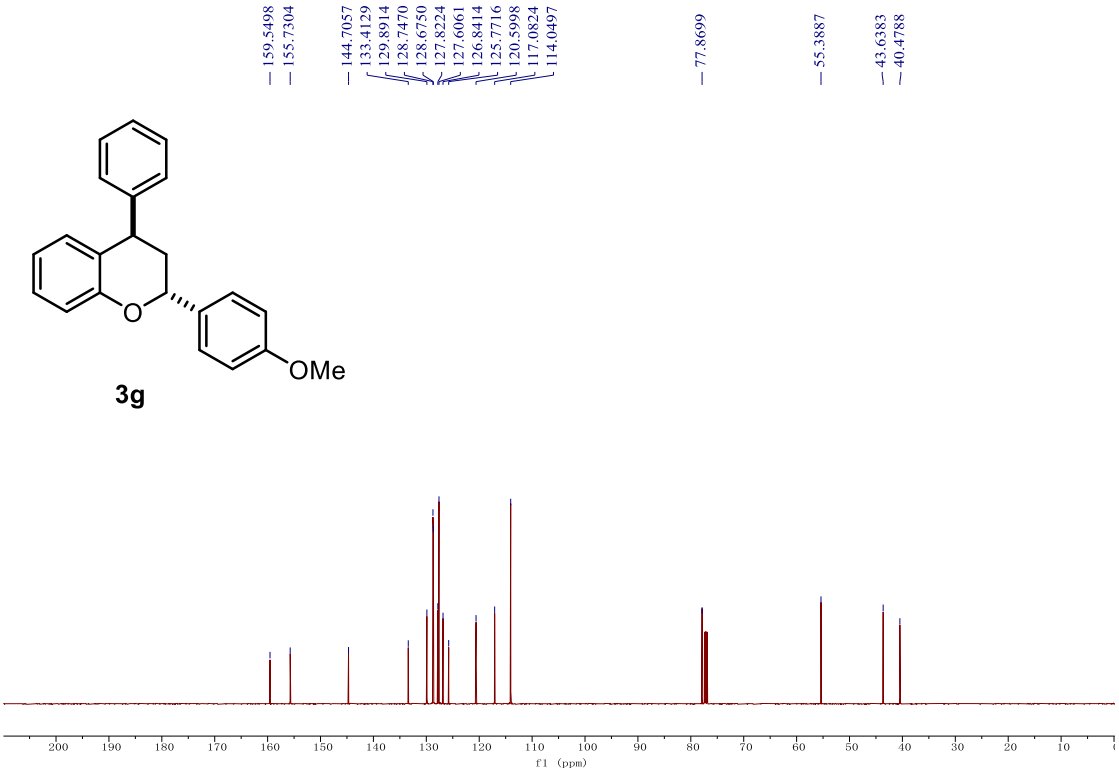
3f ^{13}C NMR (151 MHz, Chloroform-*d*)



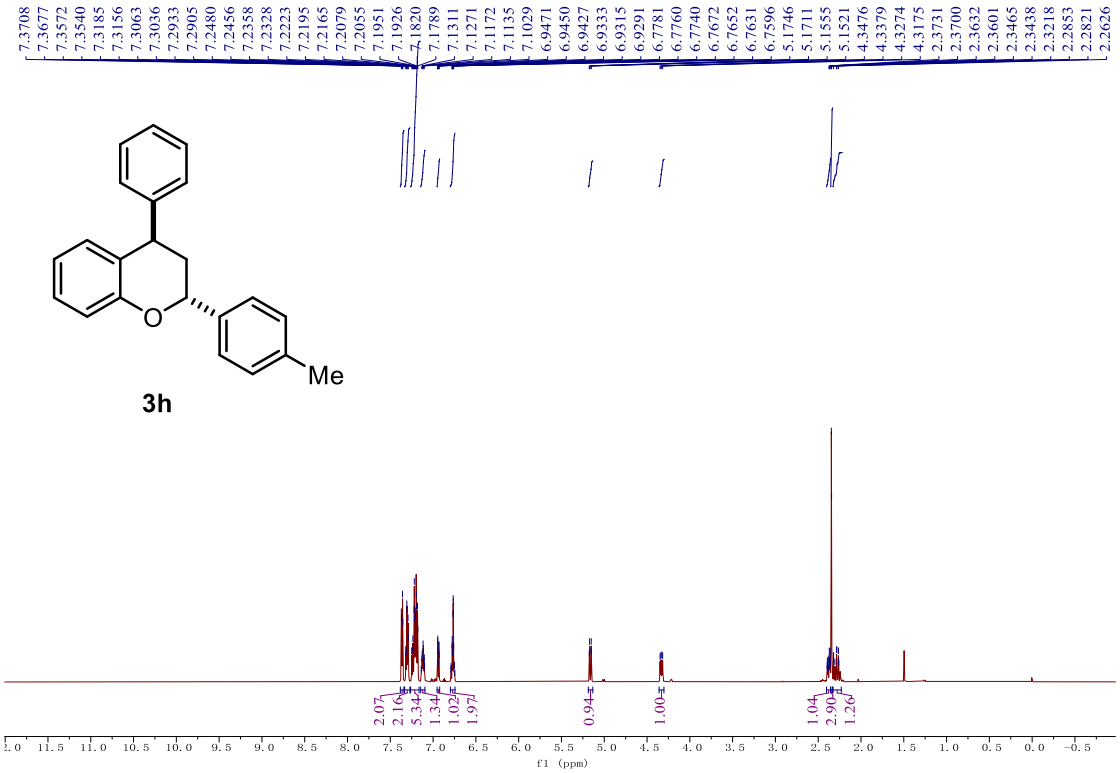
3g ^{1}H NMR (600 MHz, Chloroform-*d*



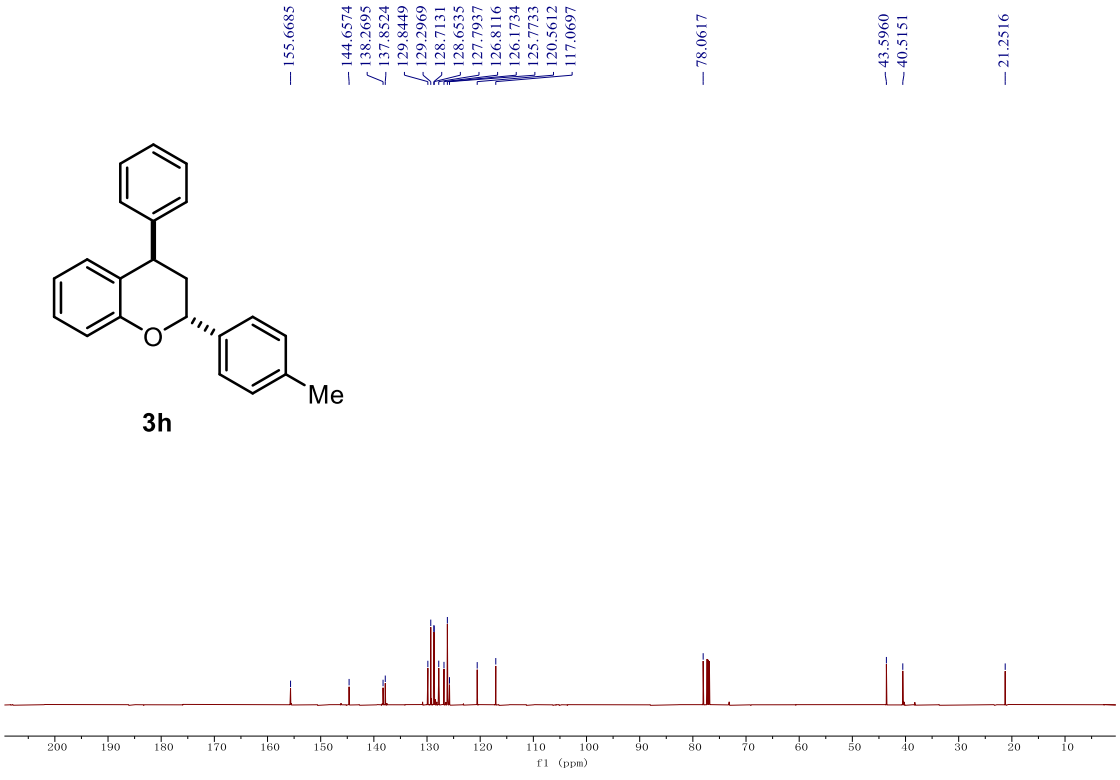
3g ^{13}C NMR (126 MHz, Chloroform-*d*)



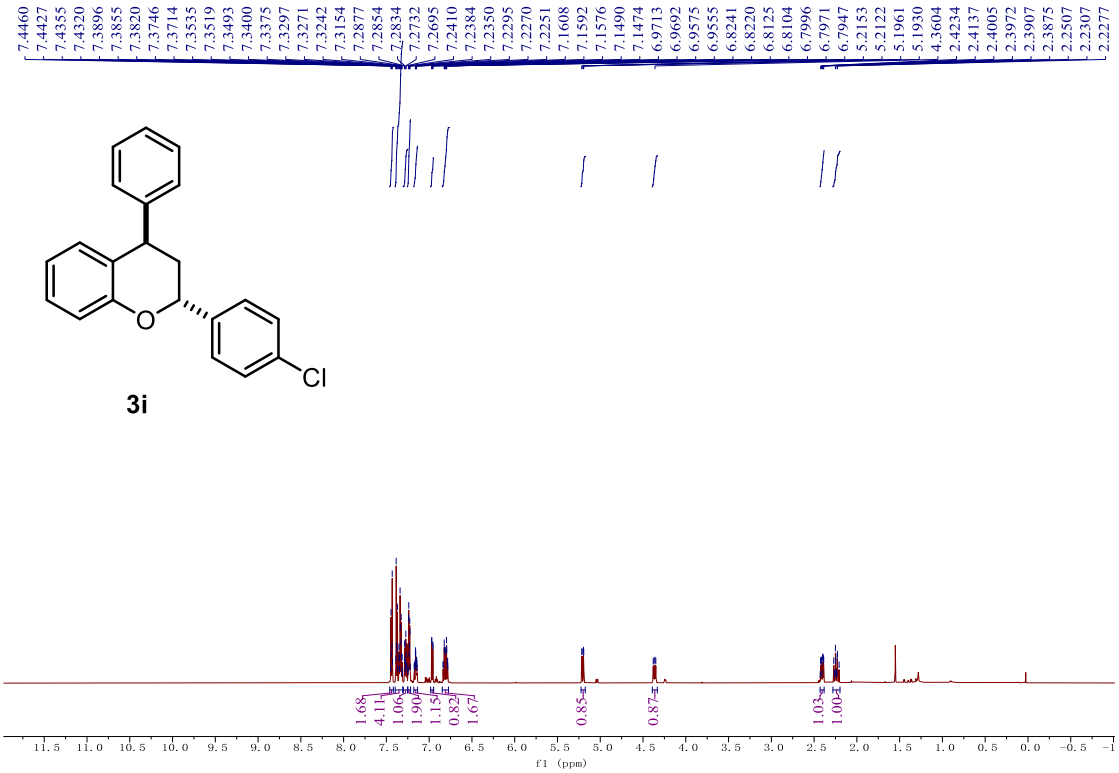
3h ^{1}H NMR (600 MHz, Chloroform-*d*)



3h ^{13}C NMR (151 MHz, Chloroform-*d*)

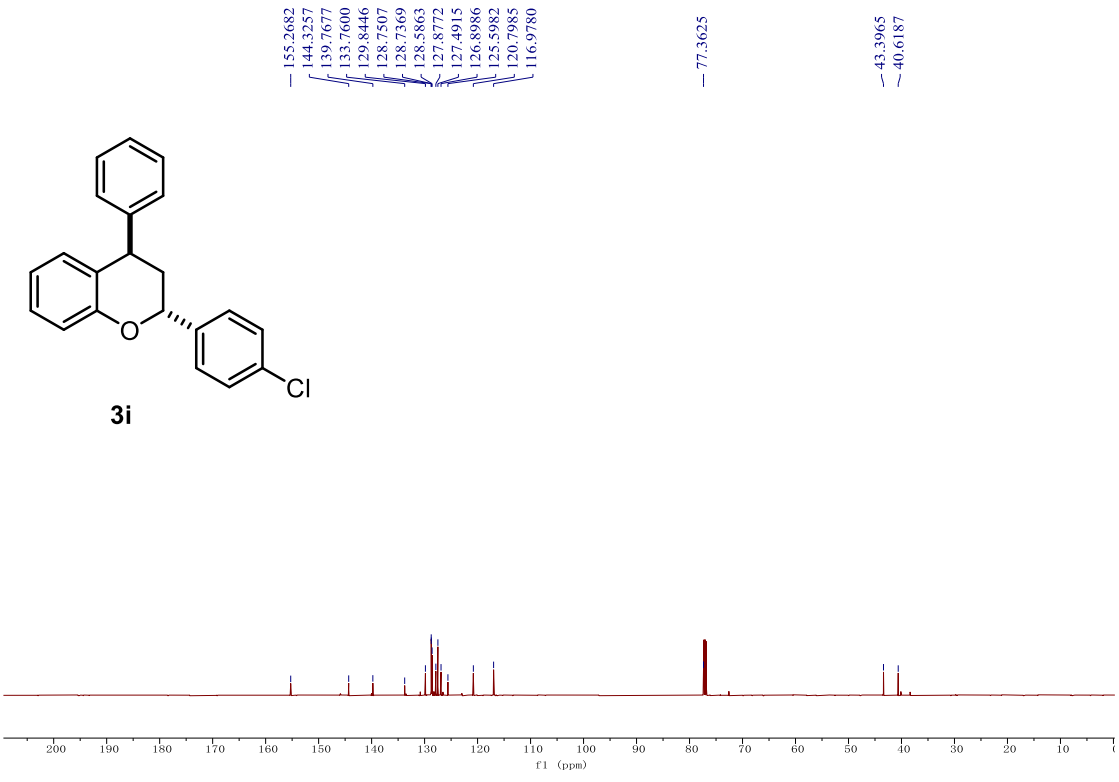


3i ^{1}H NMR (600 MHz, Chloroform-*d*)



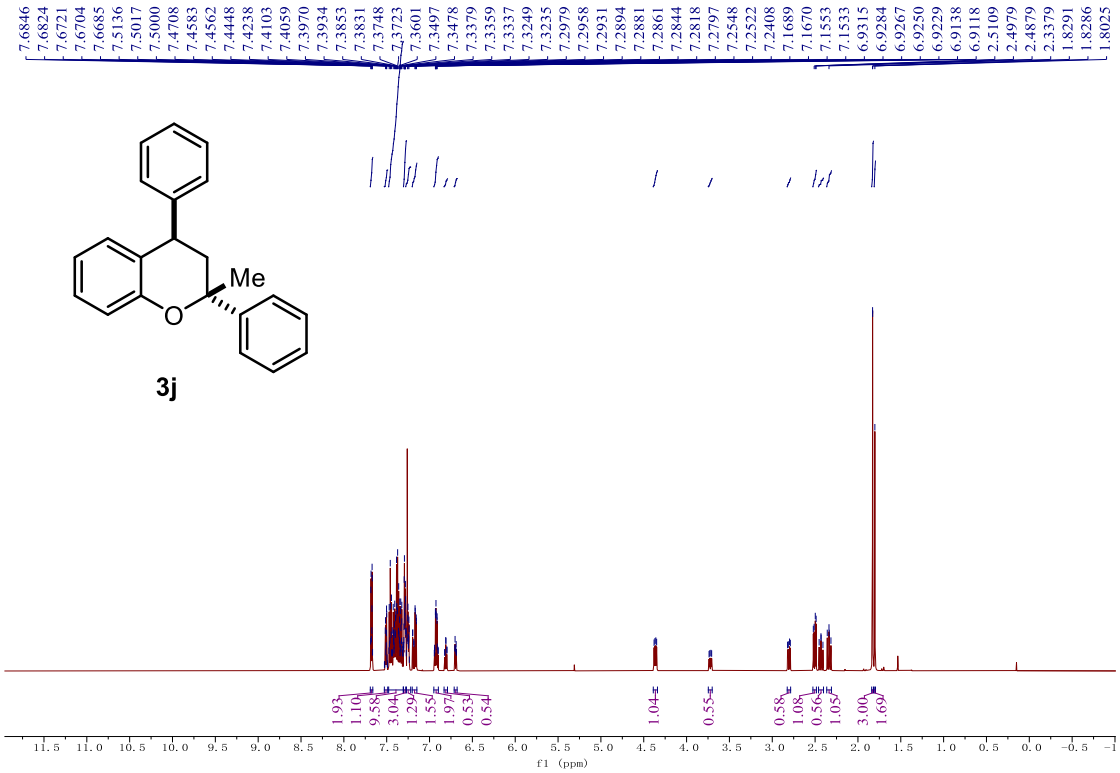
3i

3i ^{13}C NMR (151 MHz, Chloroform-*d*)

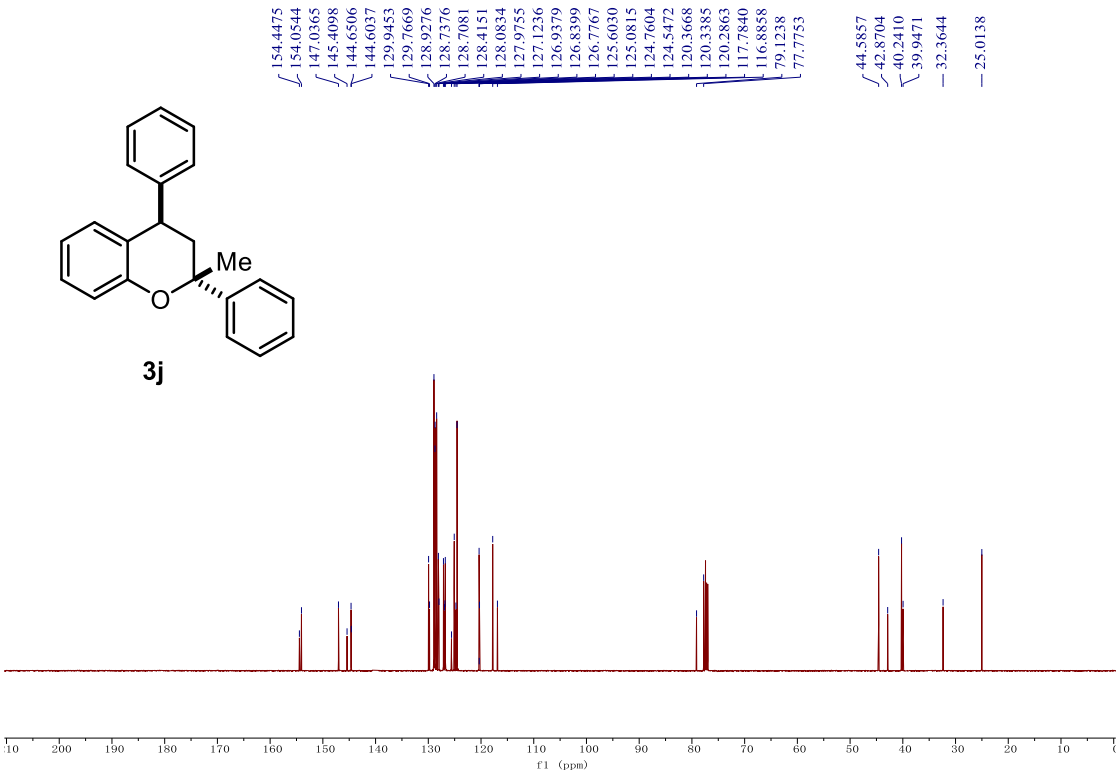


3i

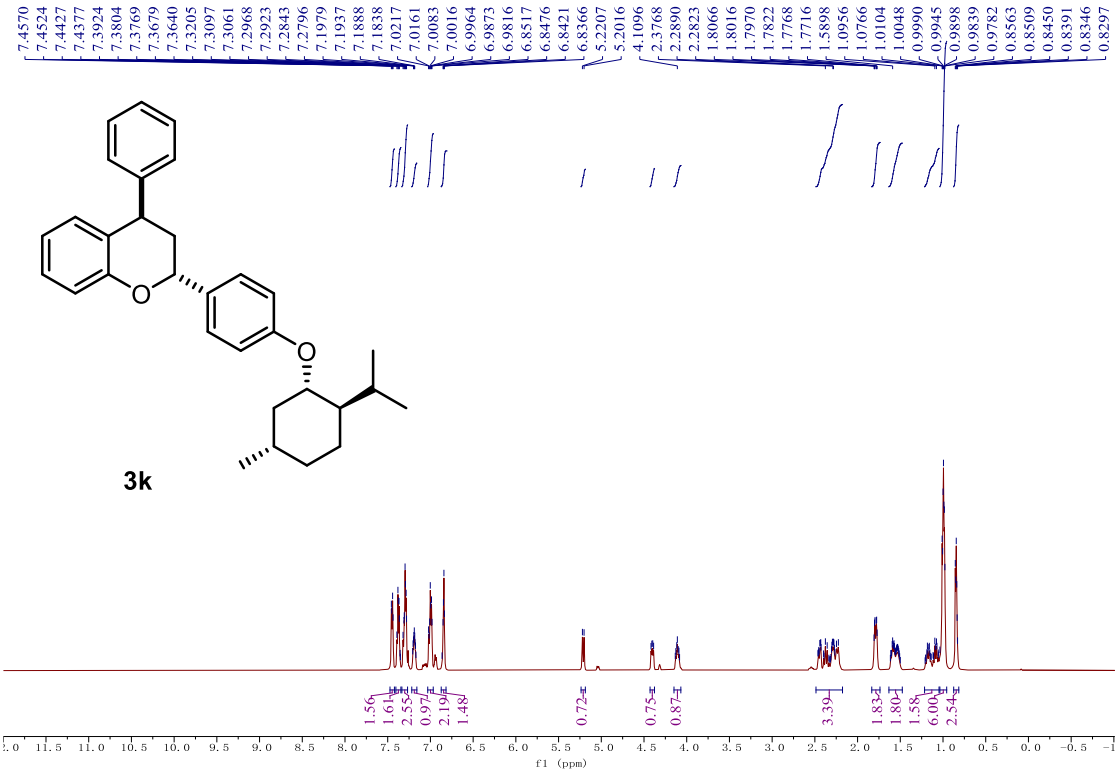
3j ^{1}H NMR (600 MHz, Chloroform-*d*)



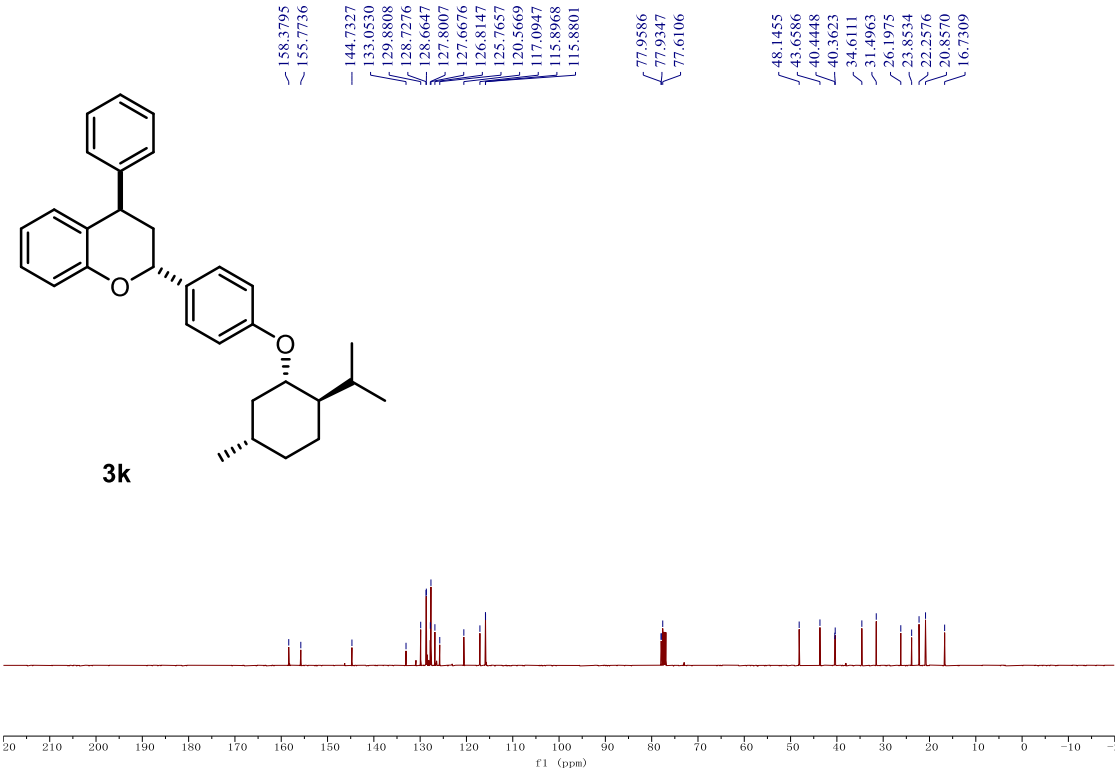
3j ^{13}C NMR (151 MHz, Chloroform-*d*)



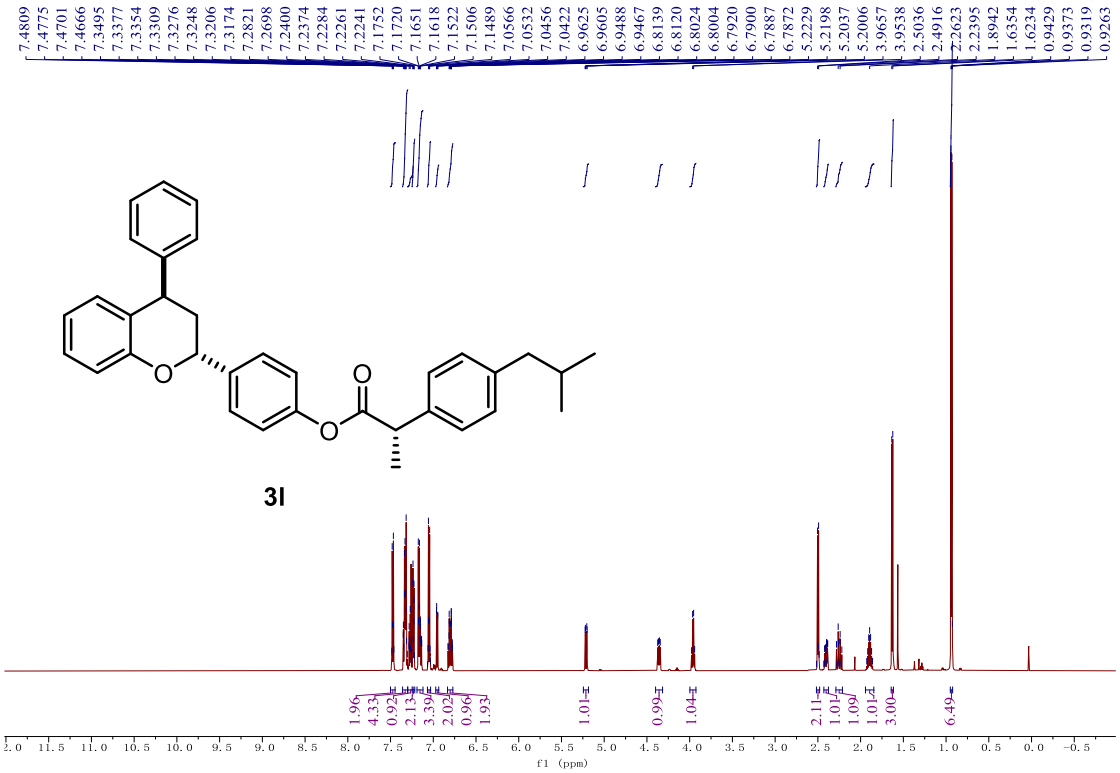
3k ^{1}H NMR (600 MHz, Chloroform-*d*)



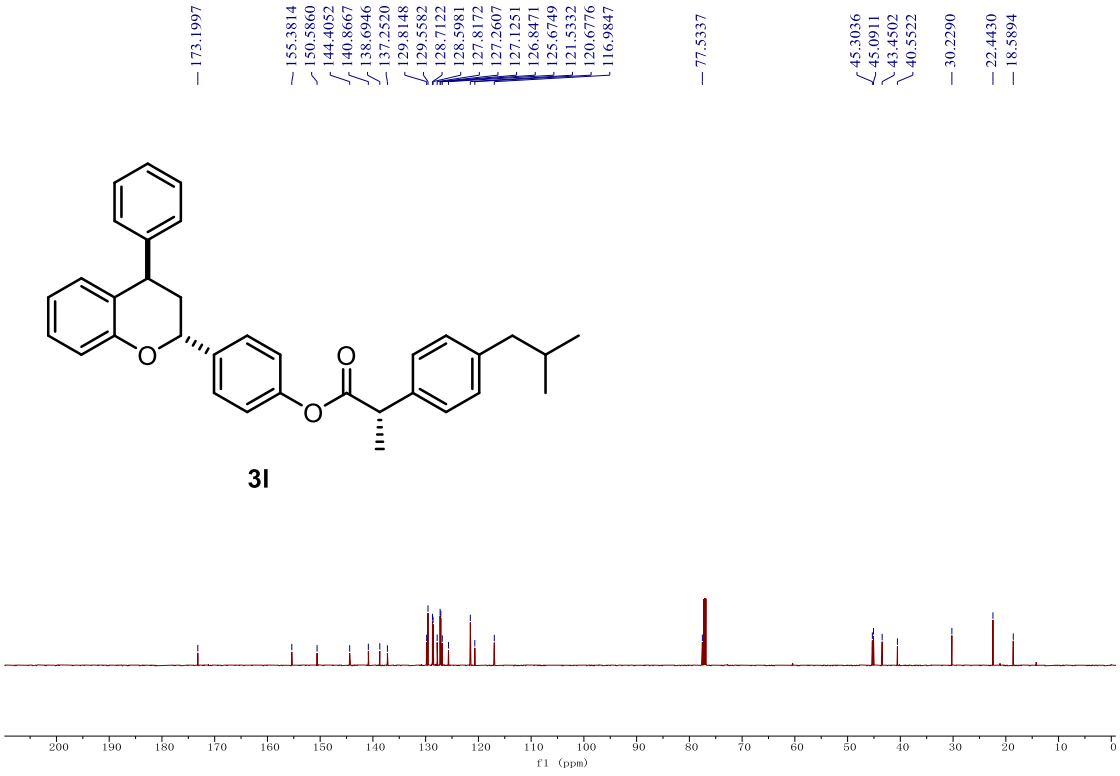
3k ^{13}C NMR (151 MHz, Chloroform-*d*)



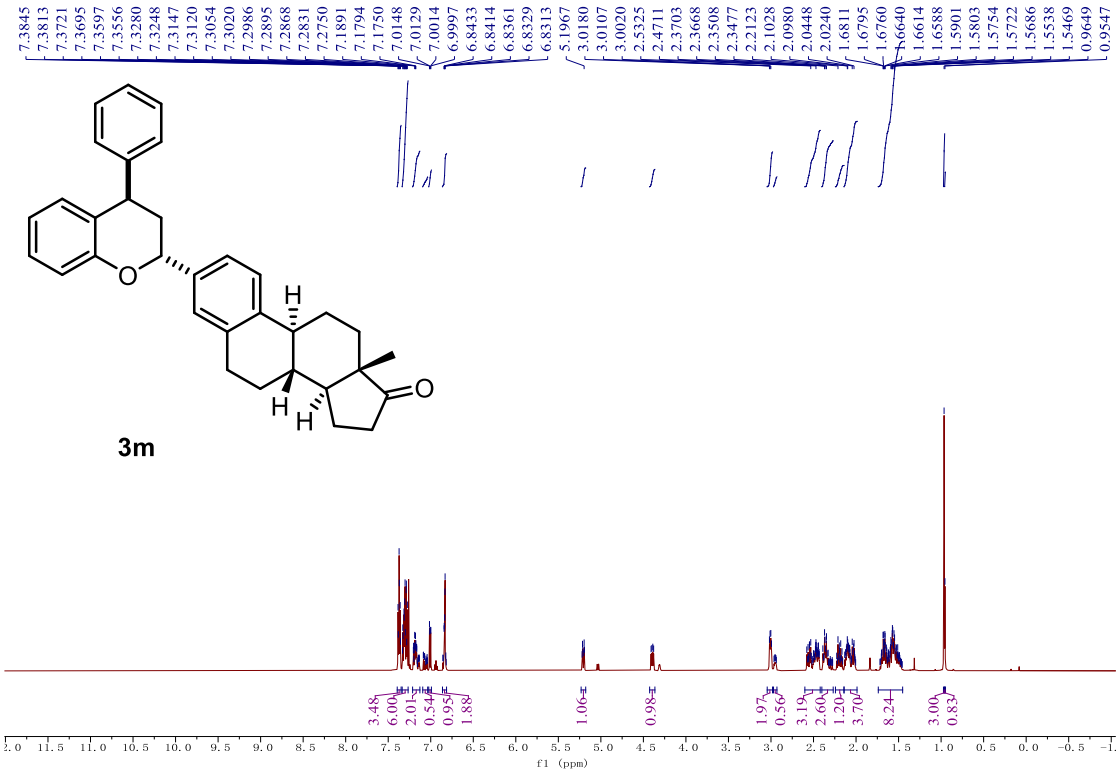
3l ^{1}H NMR (600 MHz, Chloroform-*d*)



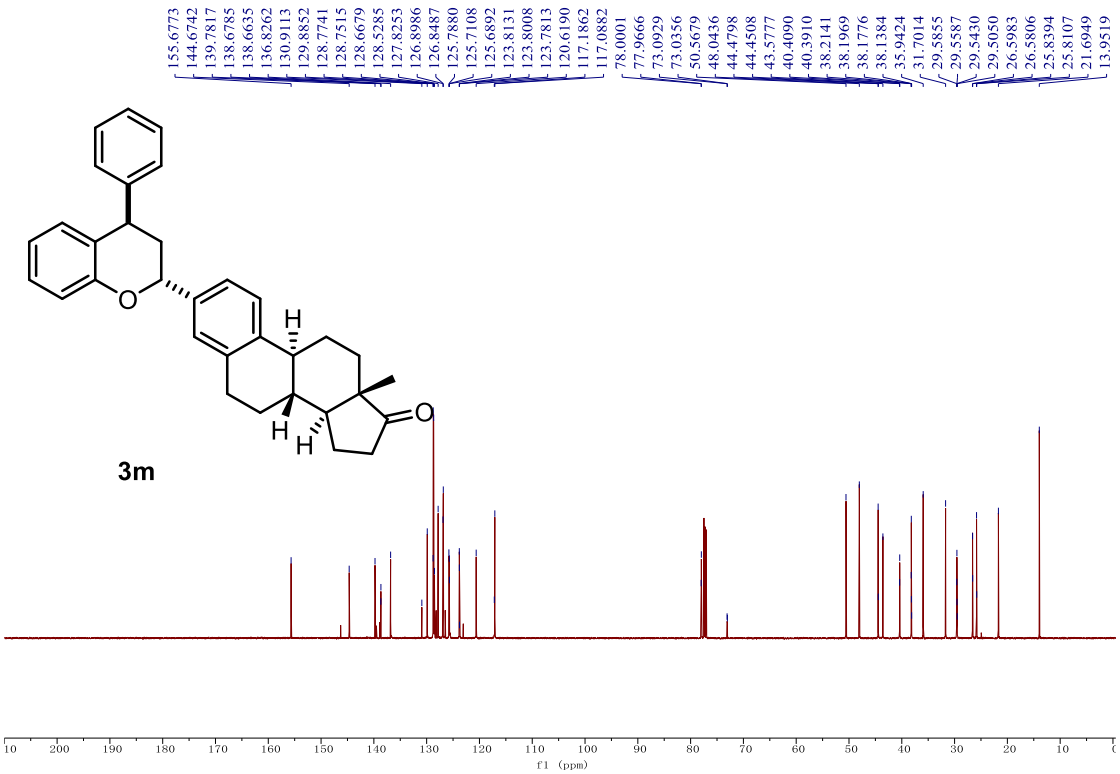
3l ^{13}C NMR (151 MHz, Chloroform-*d*)



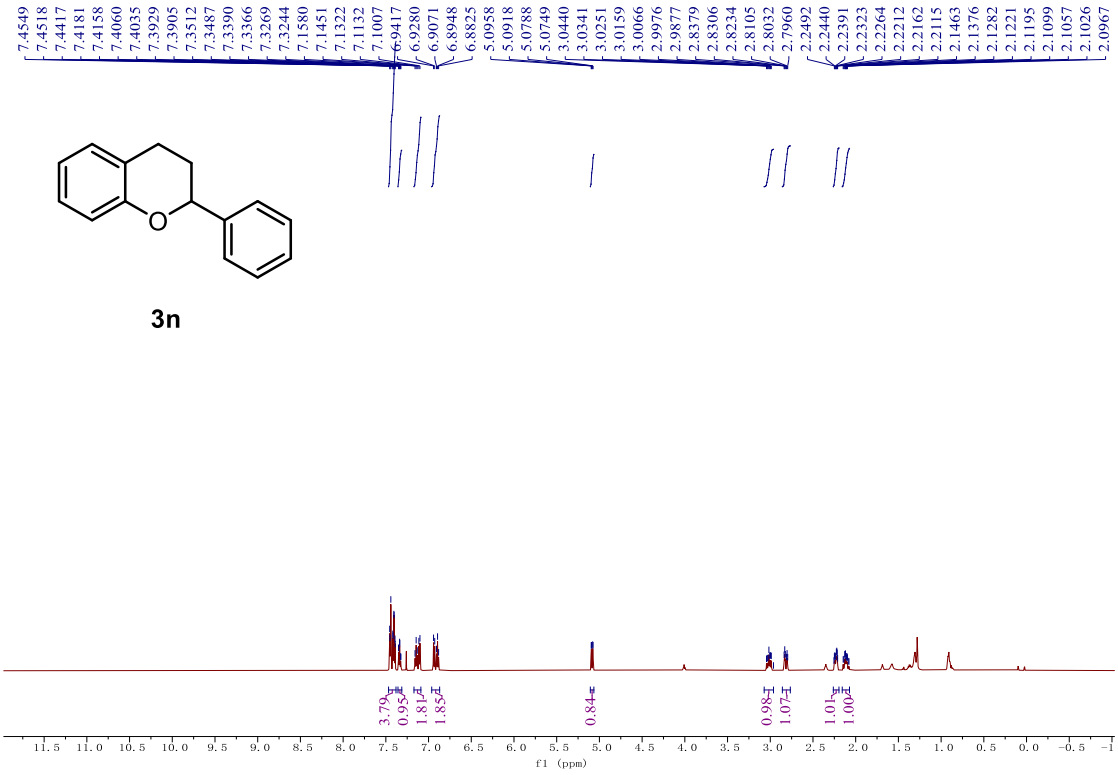
3m ^{1}H NMR (600 MHz, Chloroform-*d*)



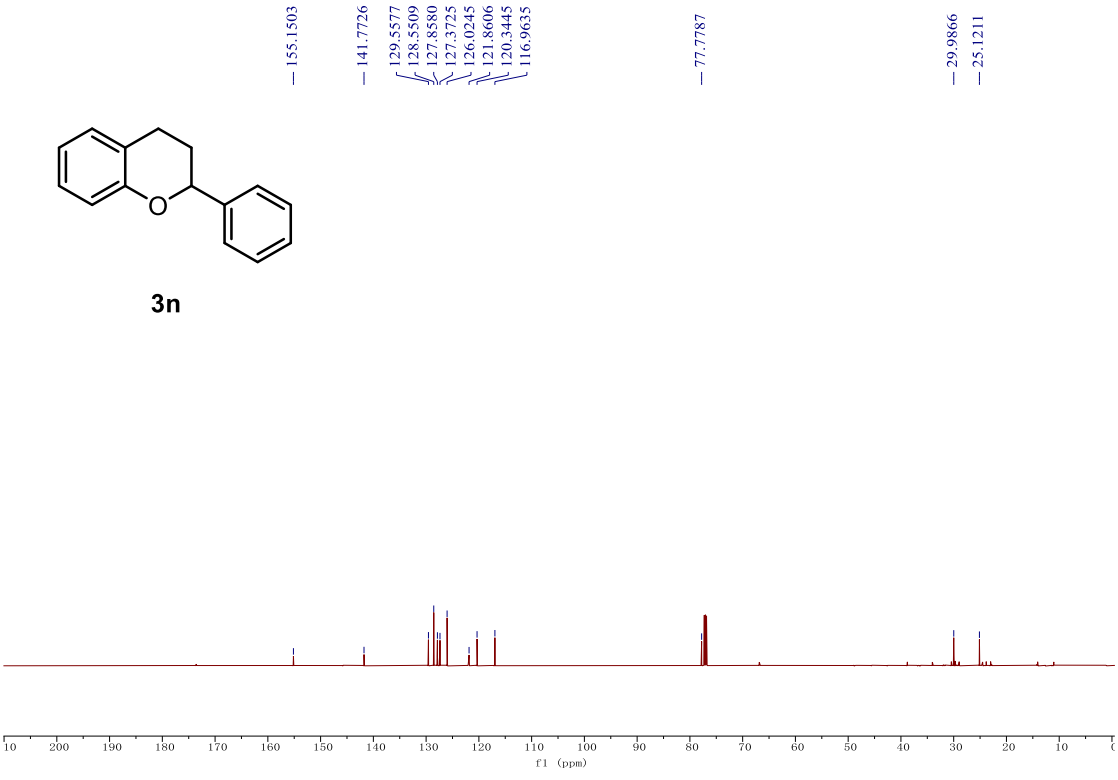
3m ^{13}C NMR (151 MHz, Chloroform-*d*)



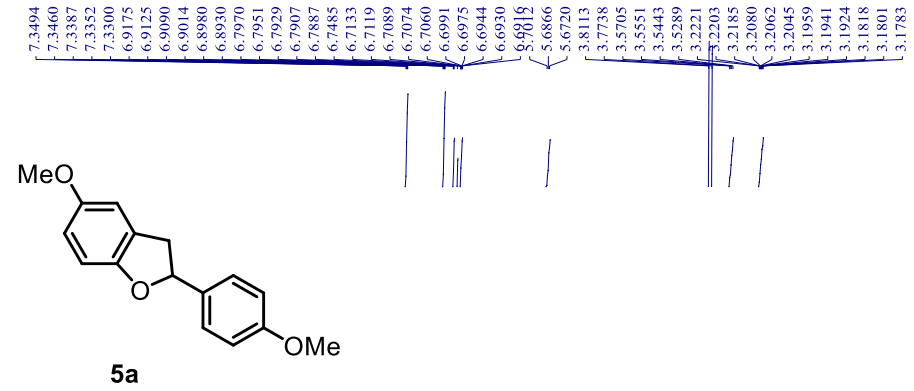
3n ^{1}H NMR (600 MHz, Chloroform-*d*)



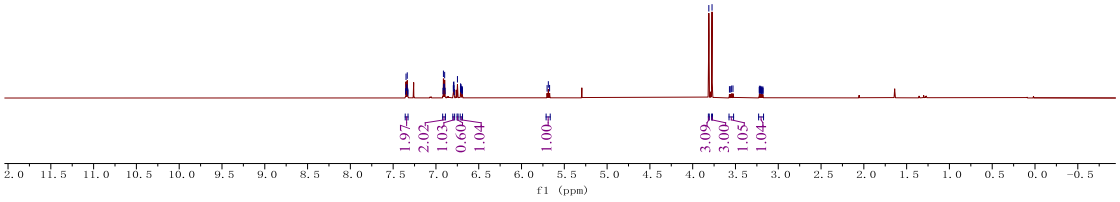
3n ^{13}C NMR (151 MHz, Chloroform-*d*)



5a ^{1}H NMR (600 MHz, Chloroform-*d*)

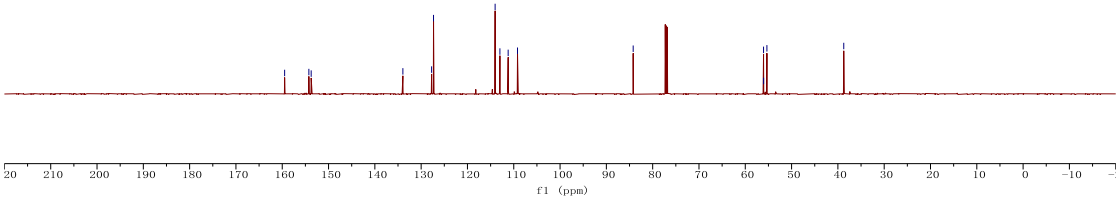


5a

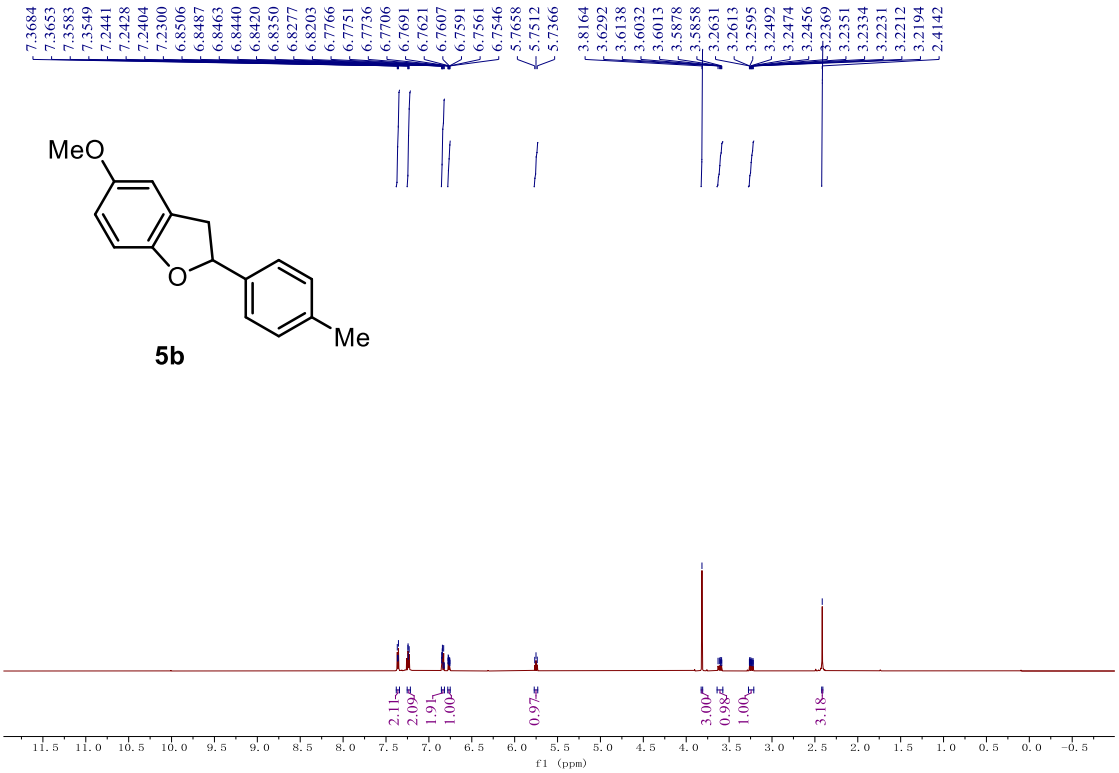


5a ^{13}C NMR (151 MHz, Chloroform-*d*)

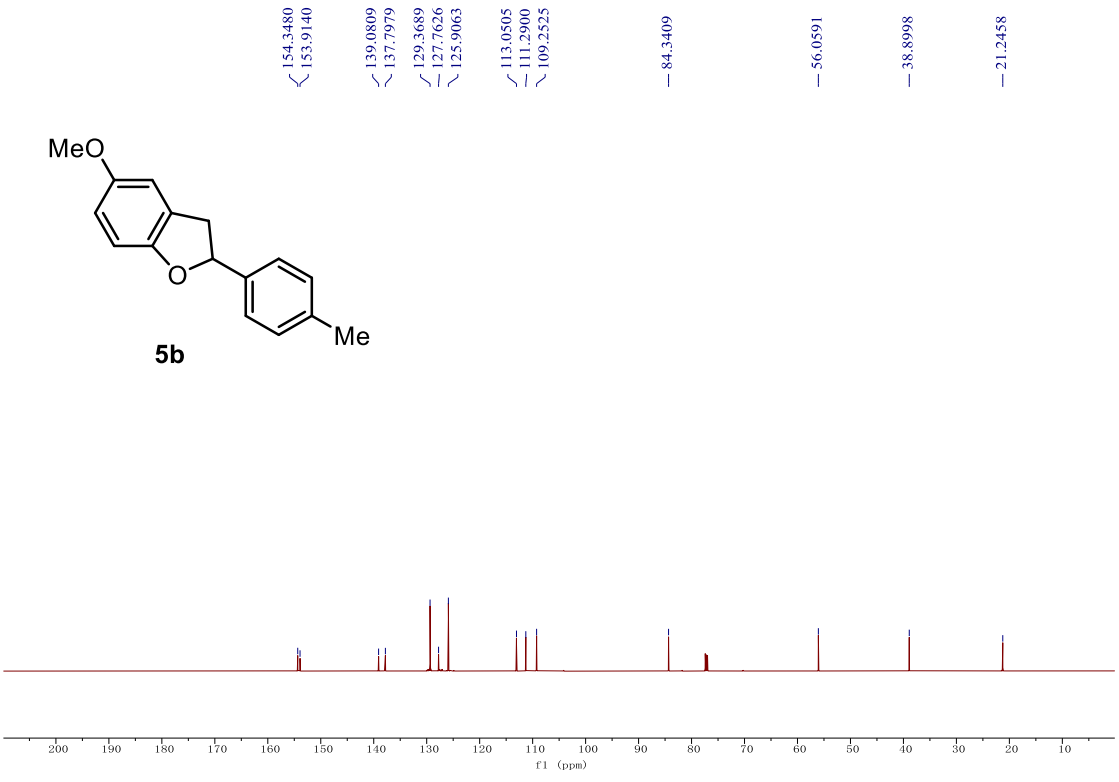
5a



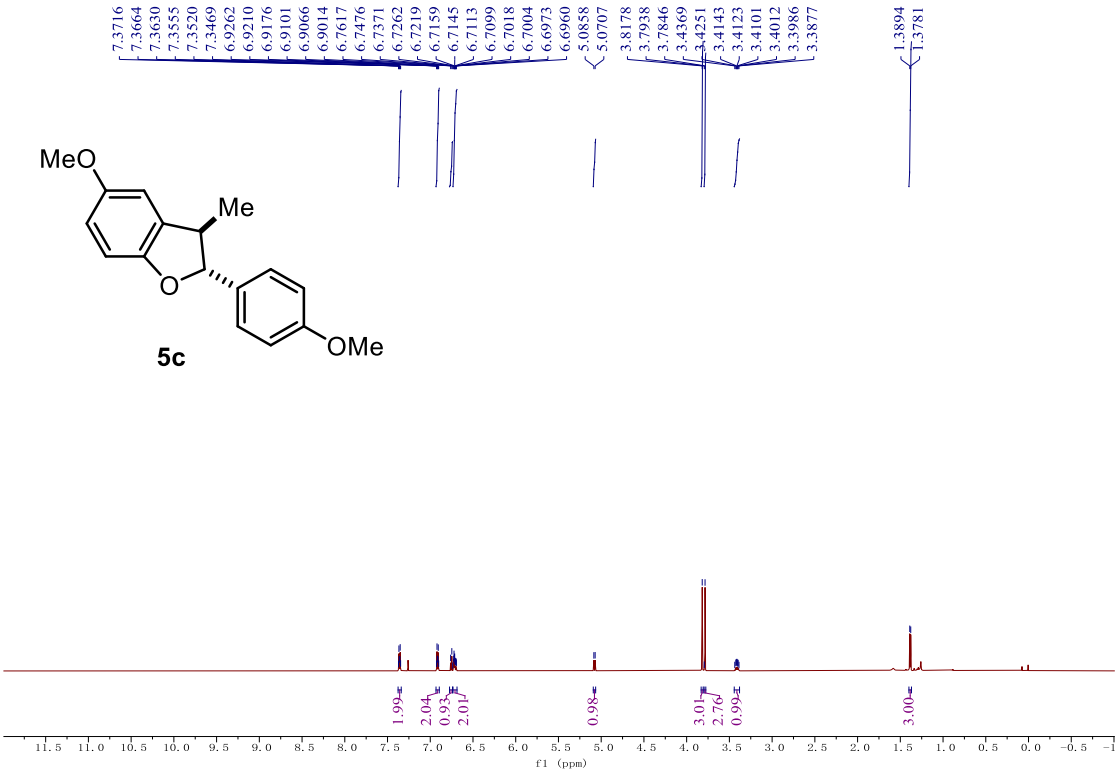
5b ^{1}H NMR (600 MHz, Chloroform-*d*)



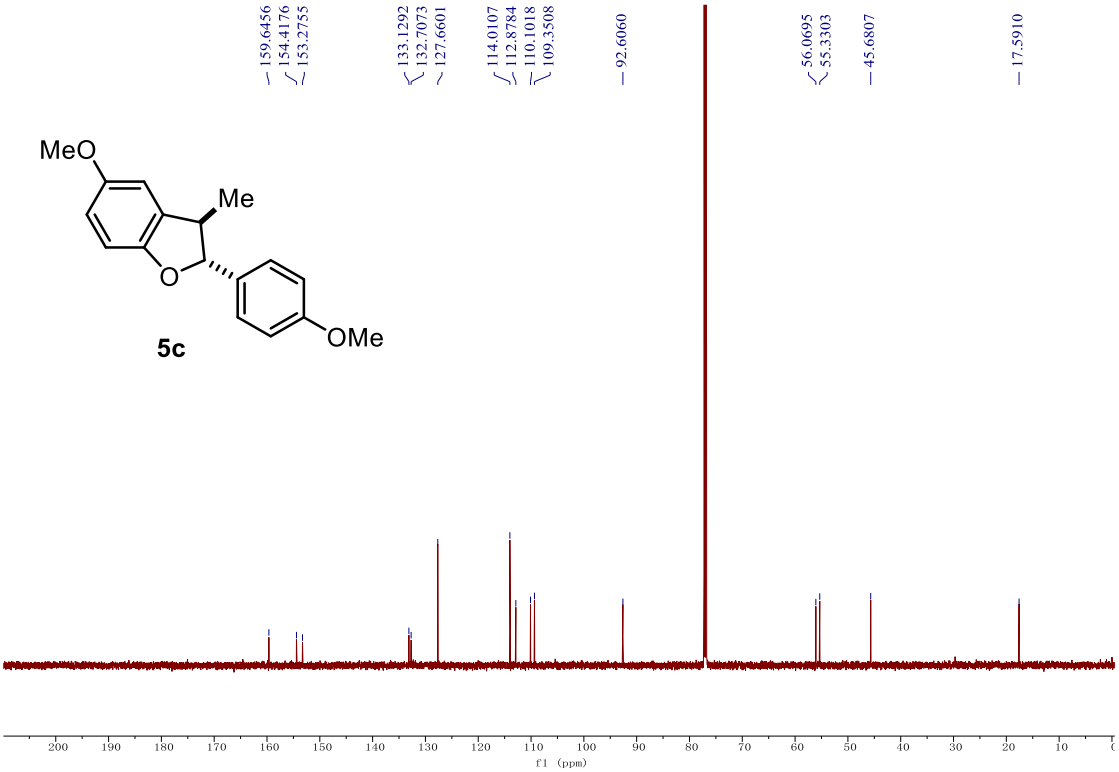
5b ^{13}C NMR (151 MHz, Chloroform-*d*)



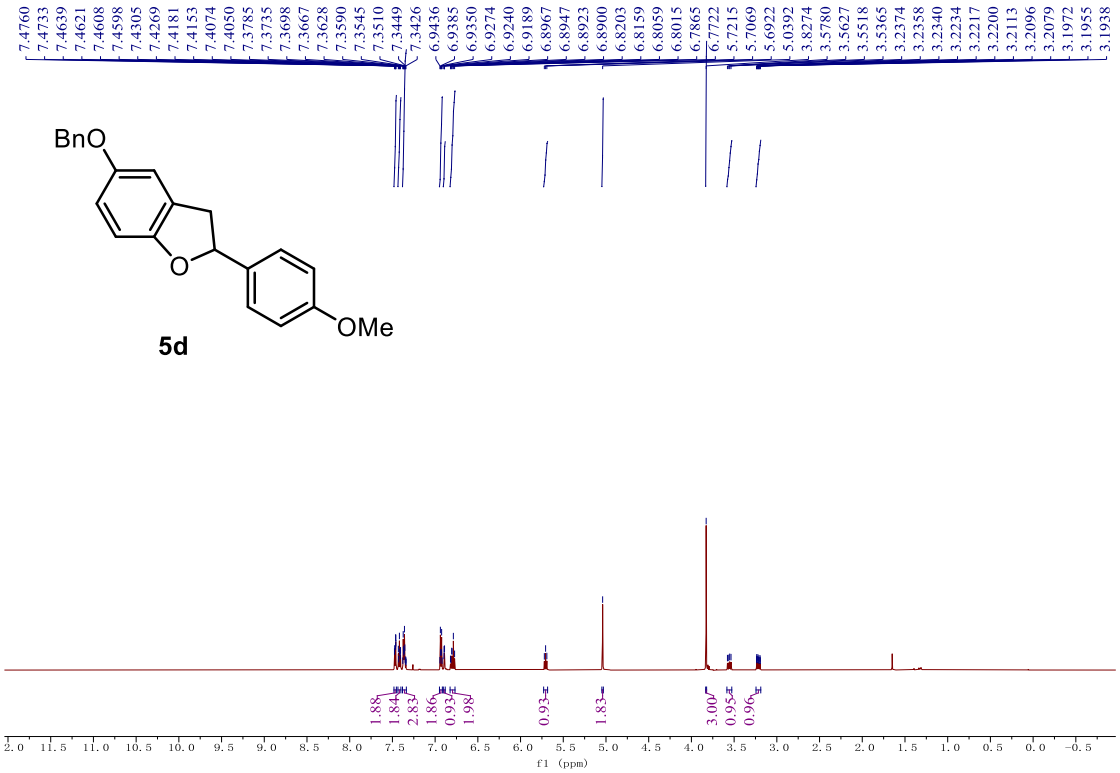
5c ^{1}H NMR (600 MHz, Chloroform-*d*)



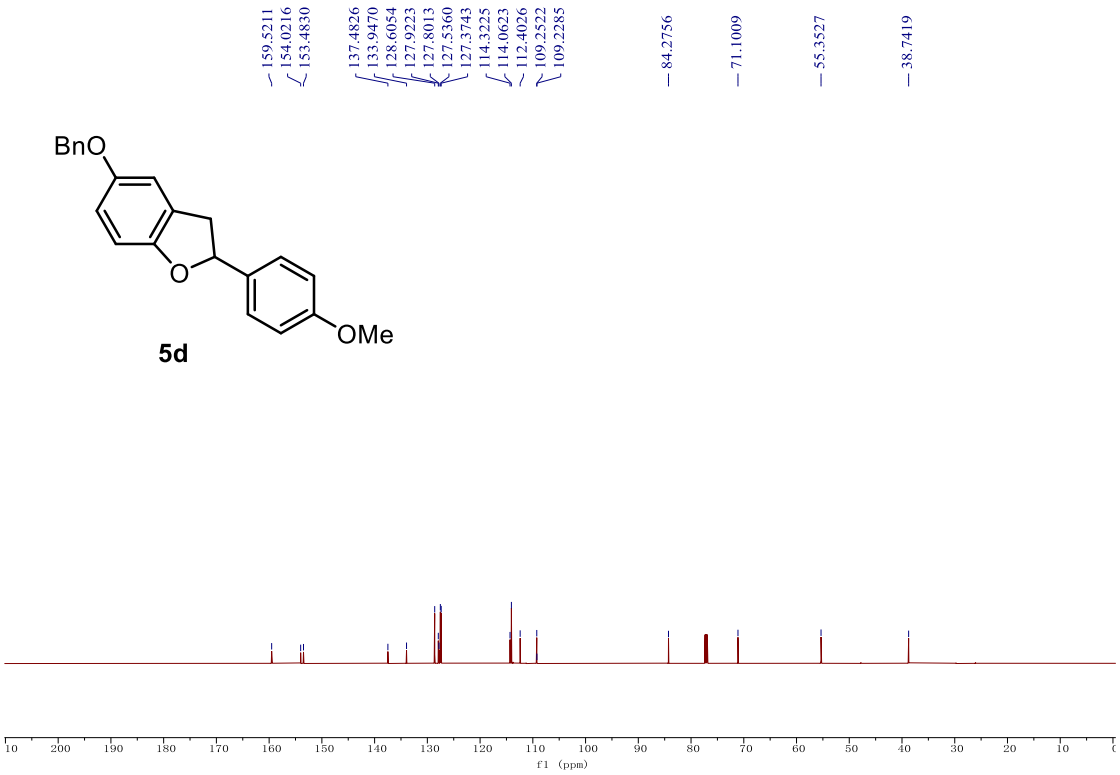
5c ^{13}C NMR (151 MHz, Chloroform-*d*)



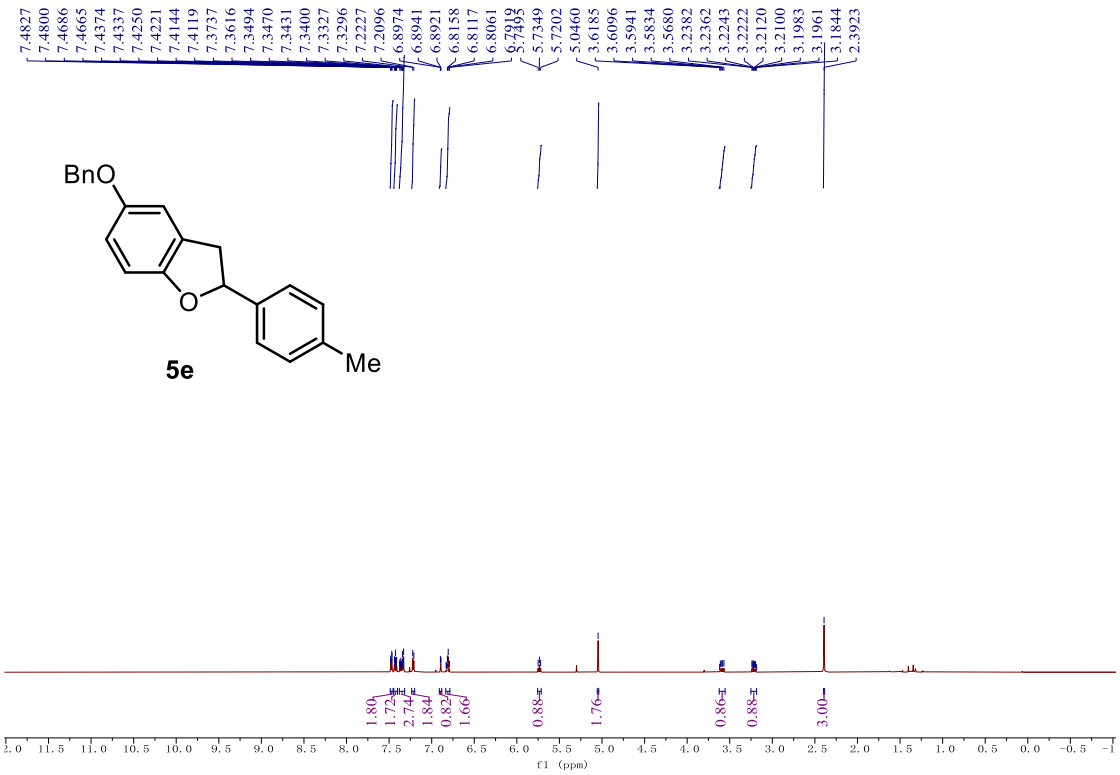
5d ^{1}H NMR (600 MHz, Chloroform-*d*)



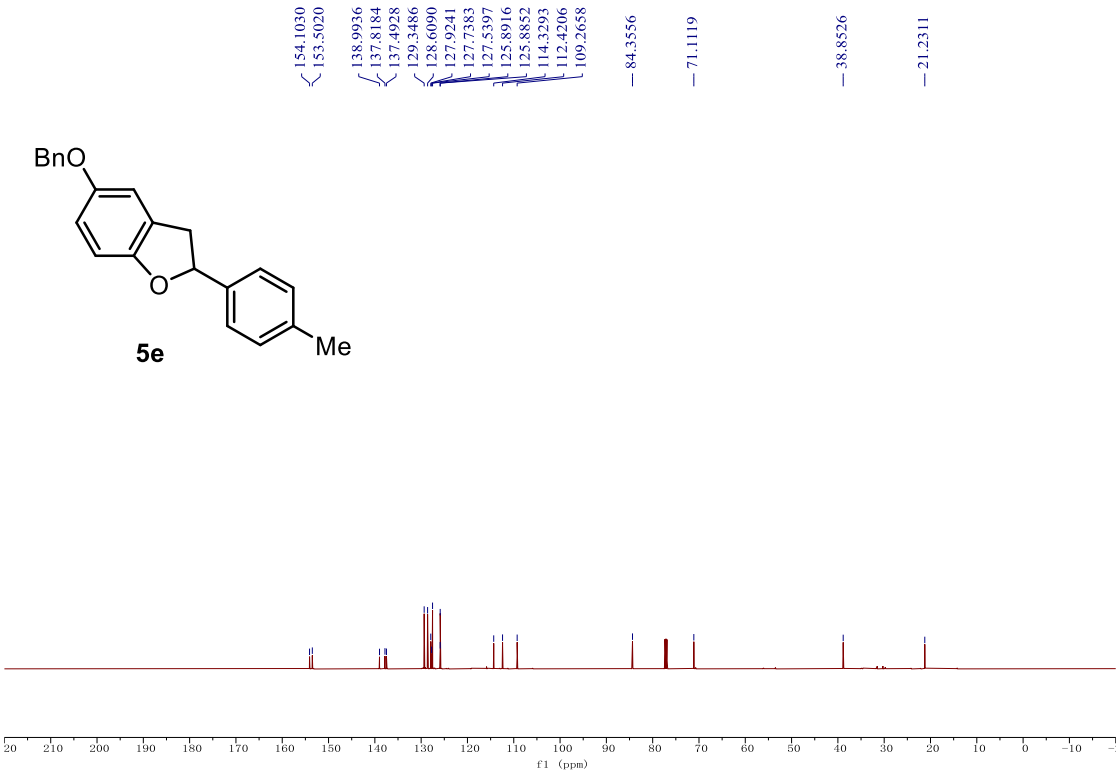
5d ^{13}C NMR (151 MHz, Chloroform-*d*)



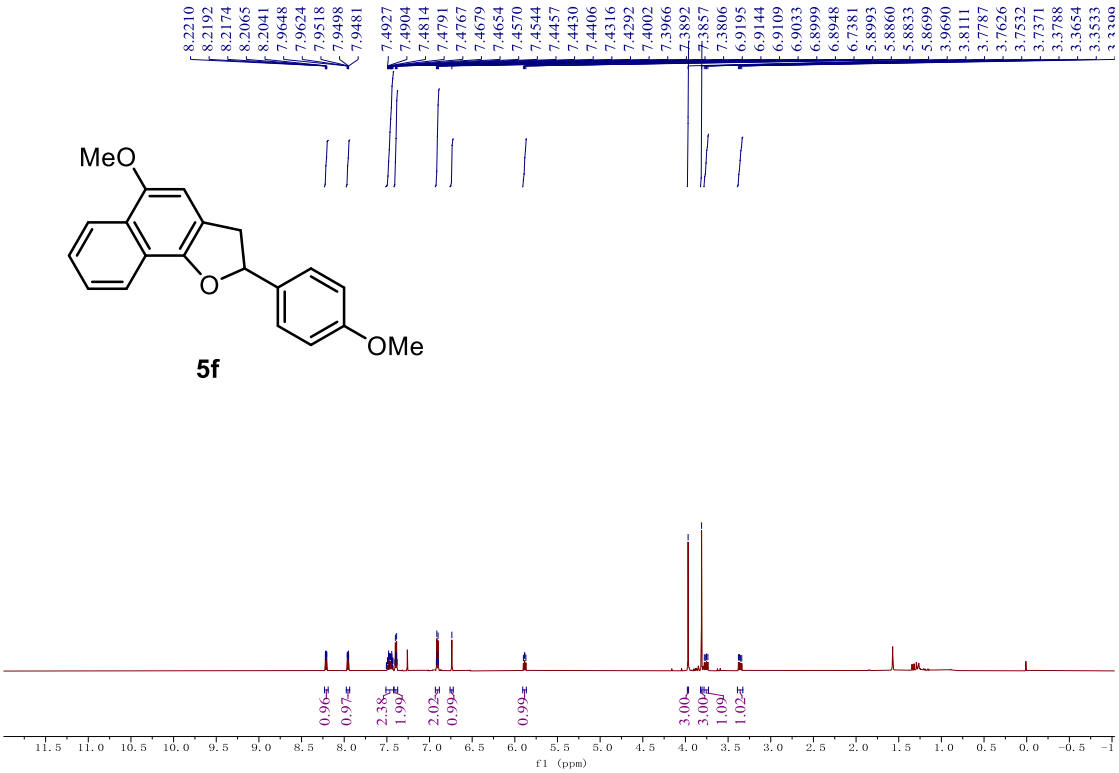
5e ^{1}H NMR (600 MHz, Chloroform-*d*)



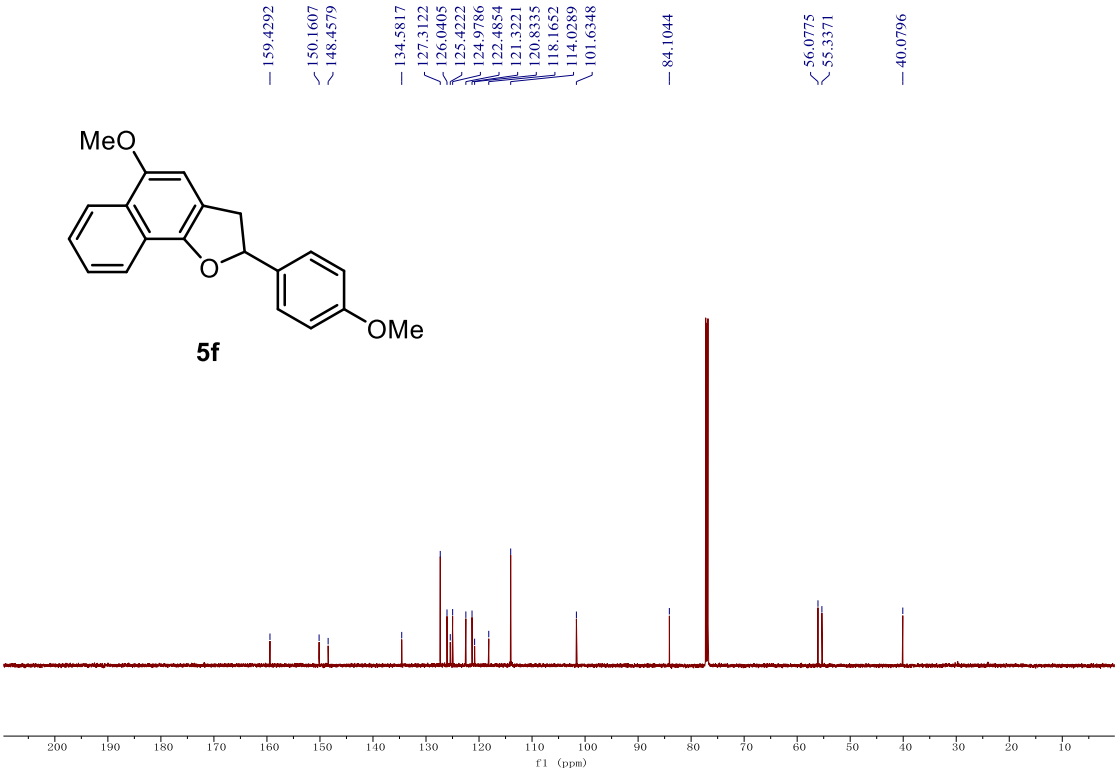
5e ^{13}C NMR (151 MHz, Chloroform-*d*)



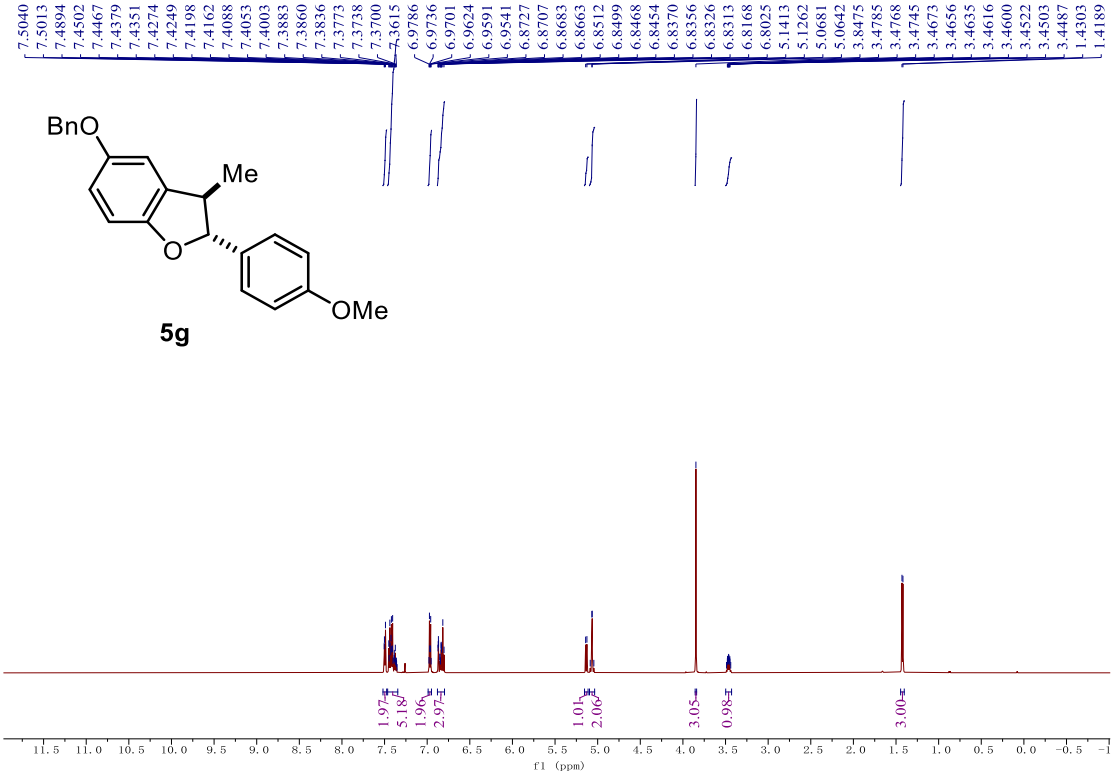
5f ^{1}H NMR (600 MHz, Chloroform-*d*)



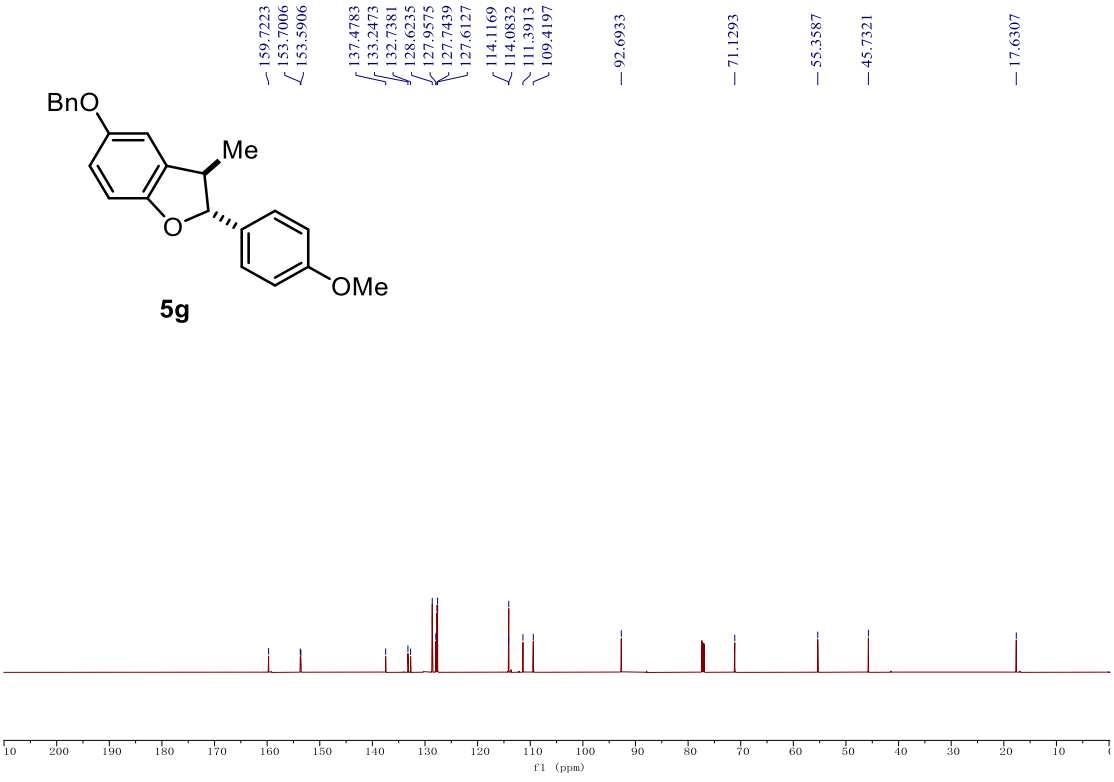
5f ^{13}C NMR (151 MHz, Chloroform-*d*)



5g ^{1}H NMR (600 MHz, Chloroform-*d*)



5g ^{13}C NMR (151 MHz, Chloroform-*d*)



18. Crystal Data and Structure

Crystal data and structure refinement for compound 3c.

Bond precision: C-C = 0.0030 A Wavelength=1.54178

Cell: a=9.8677(7) b=10.1558(7) c=10.8302(7)

alpha=112.405(6) beta=101.117(6) gamma=92.787(6)

Temperature: 293 K

	Calculated	Reported
Volume	975.62(13)	975.62(12)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C24 H24 O3	C24 H24 O3
Sum formula	C24 H24 O3	C24 H24 O3
Mr	360.43	360.43
Dx, g cm-3	1.227	1.227
Z	2	2
Mu (mm-1)	0.632	0.632
F000	384.0	384.0
F000'	385.12	
h, k, lmax	12,12,13	12,12,13
Nref	3770	3653
Tmin, Tmax	0.939,0.939	0.257,1.000
Tmin'	0.939	

Correction method= # Reported T Limits: Tmin=0.257 Tmax=1.000 AbsCorr = NONE

Data completeness= 0.969 Theta(max)= 70.917

R(reflections)= 0.0654(3013) wR2(reflections)= 0.1797(3653)

S = 1.053 Npar= 247

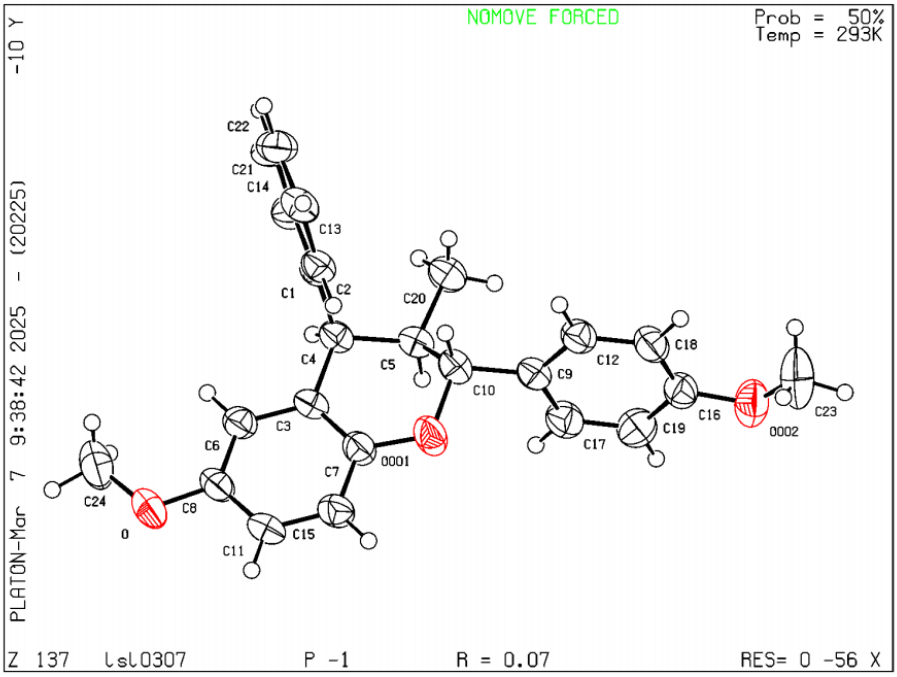


Fig. S16 X-crystal structure of **3c**, CCDC: 2488731.

19. Cartesian coordinates of the DFT-optimized structure

Table S4. Cartesian coordinates of the DFT-optimized structure of **1a** depicted.

1a

B3LYP-D3BJ/6-311g(d,p)

E = -578.034416 a.u.

C	2.42338900	-0.70223600	0.00016700
C	1.09951600	-0.23365500	-0.00025700
C	0.88931000	1.14546500	-0.00061700
C	1.95578800	2.04045800	-0.00051200
C	3.26089100	1.55579900	-0.00005000
C	3.49632700	0.18601400	0.00028100
H	-0.12666000	1.51919700	-0.00096300
H	1.76643000	3.10698400	-0.00075400
H	4.09967000	2.24219000	-0.00001800
H	4.50114900	-0.21798300	0.00053400
O	2.72462400	-2.03837100	0.00043800
H	1.91356700	-2.55469900	0.00041900
C	-0.03888000	-1.24261900	-0.00038200
H	0.05763500	-1.89348800	-0.87987100
H	0.05770900	-1.89390100	0.87881600
C	-1.42090100	-0.63910200	-0.00007800
C	-2.06322300	-0.33418100	1.20173800
C	-2.06400300	-0.33488000	-1.20167000
C	-3.32198400	0.26040300	1.20432400

H	-1.56922300	-0.55981400	2.14086800
C	-3.32275900	0.25970300	-1.20379800
H	-1.57060500	-0.56106700	-2.14098000
C	-3.95549200	0.55927200	0.00038200
H	-3.80850000	0.48880200	2.14563600
H	-3.80988100	0.48755400	-2.14493000
H	-4.93613600	1.02055500	0.00056600

Table S5. Cartesian coordinates of the DFT-optimized structure of intermediate **I** depicted.

Intermediate **II**

(U)B3LYP-D3BJ/6-311g(d,p)

E = -577.753534 a.u.

C	1.80111600	-0.87427000	-0.12662500
C	1.04298100	0.20516300	-0.69867200
C	1.38531000	1.51532000	-0.33159200
C	2.44165000	1.75911400	0.51980000
C	3.18273700	0.68035500	1.06584100
C	2.87081100	-0.62231700	0.74374400
H	0.82510600	2.33994900	-0.75356700
H	2.72030200	2.77538300	0.76667600
H	4.00316800	0.88449000	1.74238100
H	3.43529100	-1.44915200	1.15995300
O	1.44287600	-2.10742600	-0.49186000
H	2.03339400	-2.77409200	-0.11360800
C	-0.10172700	-0.07887700	-1.63241500
H	-0.17661900	0.69248200	-2.39759500
H	0.00443400	-1.04784700	-2.11508000
C	-1.29589600	-0.03902800	-0.70153600
C	-1.60761600	-1.15755100	0.10523500
C	-2.07841600	1.12774800	-0.59608600
C	-2.70990000	-1.12863800	0.94150900
H	-0.99082100	-2.04466000	0.04309200
C	-3.17664100	1.15321300	0.24207600
H	-1.84158900	1.98980300	-1.20809000
C	-3.49475000	0.02599000	1.01818100
H	-2.96299700	-1.99608800	1.53767400
H	-3.80014500	2.03684600	0.29482600
H	-4.35049100	0.05495700	1.68145200

Table S6. Cartesian coordinates of the DFT-optimized structure of intermediate **II** depicted.

Intermediate **II**

(U)B3LYP-D3BJ/6-311g(d,p)

E = -577.393581 a.u.

C	2.45453100	-0.81686100	0.00021500

C	1.09675200	-0.26549200	-0.00024100
C	0.92571100	1.10282400	-0.00063900
C	2.02913500	1.97114500	-0.00061600
C	3.34650800	1.47338000	-0.00017700
C	3.56296800	0.11926200	0.00023000
H	-0.07507200	1.51684700	-0.00097000
H	1.86153400	3.04191000	-0.00093900
H	4.18142100	2.16456000	-0.00016100
H	4.55757500	-0.30983100	0.00058400
O	2.64734100	-2.05094900	0.00060000
C	-0.03881600	-1.25790600	-0.00030900
H	0.08780900	-1.91511500	-0.86681100
H	0.08799400	-1.91544600	0.86590800
C	-1.41351600	-0.64209100	-0.00007600
C	-2.05521400	-0.33089500	1.20130100
C	-2.05587900	-0.33137500	-1.20121400
C	-3.30897900	0.27458500	1.20417900
H	-1.56626200	-0.56634100	2.14076700
C	-3.30965100	0.27410900	-1.20363700
H	-1.56745300	-0.56719800	-2.14085900
C	-3.93995600	0.57957900	0.00038300
H	-3.79472000	0.50470700	2.14555500
H	-3.79591300	0.50385800	-2.14483500
H	-4.91721000	1.04806100	0.00056300

Table S7. Cartesian coordinates of the DFT-optimized structure of FF-Py-CPP (C_{2V}) depicted.

FF-Py-CPP (C_{2V})

B3LYP-D3BJ/6-311g(d,p)

E = -3411.683333 a.u.

C	-1.22309200	2.84307900	-0.77762900
C	-1.23818300	1.42931600	-0.79754600
C	0.00000000	0.71641200	-0.79130300
C	1.23818300	1.42931600	-0.79754600
C	1.22309200	2.84307900	-0.77762900
C	0.00000000	3.51129000	-0.77990200
C	0.00000000	-0.71641200	-0.79130300
C	1.23818300	-1.42931600	-0.79754600
C	2.45424300	-0.67849100	-0.88563300
C	2.45424300	0.67849100	-0.88563300
C	-2.45424300	0.67849100	-0.88563300
C	-2.45424300	-0.67849100	-0.88563300
C	-1.23818300	-1.42931600	-0.79754600
C	-1.22309200	-2.84307900	-0.77762900
C	0.00000000	-3.51129000	-0.77990200

C	2.46832900	3.64685200	-0.72539800
C	2.68963500	4.66194800	-1.66685700
C	3.83317000	5.46091500	-1.63474400
C	4.77436600	5.23955700	-0.63795300
C	4.55228700	4.22906000	0.30966400
C	3.42416500	3.43783300	0.28571400
C	6.06096600	5.89769300	-0.33958300
C	6.62638700	5.29057800	0.79250700
C	5.71016900	4.19106100	1.28327100
C	6.72529000	6.94189100	-0.97112200
C	7.95332500	7.36232300	-0.45406800
C	8.50692500	6.75243000	0.67139400
C	7.83986600	5.70122000	1.30888600
F	5.30282700	4.39708500	2.57978800
F	6.33252300	2.96454700	1.28950300
C	-8.50692500	6.75243000	0.67139400
C	-7.95332500	7.36232300	-0.45406800
C	-6.72529000	6.94189100	-0.97112200
C	-6.06096600	5.89769300	-0.33958300
C	-6.62638700	5.29057800	0.79250700
C	-7.83986600	5.70122000	1.30888600
C	-4.77436600	5.23955700	-0.63795300
C	-4.55228700	4.22906000	0.30966400
C	-5.71016900	4.19106100	1.28327100
C	-3.83317000	5.46091500	-1.63474400
C	-2.68963500	4.66194800	-1.66685700
C	-2.46832900	3.64685200	-0.72539800
C	-3.42416500	3.43783300	0.28571400
F	-5.30282700	4.39708500	2.57978800
F	-6.33252300	2.96454700	1.28950300
C	-8.50692500	-6.75243000	0.67139400
C	-7.95332500	-7.36232300	-0.45406800
C	-6.72529000	-6.94189100	-0.97112200
C	-6.06096600	-5.89769300	-0.33958300
C	-6.62638700	-5.29057800	0.79250700
C	-7.83986600	-5.70122000	1.30888600
C	-4.77436600	-5.23955700	-0.63795300
C	-4.55228700	-4.22906000	0.30966400
C	-5.71016900	-4.19106100	1.28327100
C	-3.83317000	-5.46091500	-1.63474400
C	-2.68963500	-4.66194800	-1.66685700
C	-2.46832900	-3.64685200	-0.72539800
C	-3.42416500	-3.43783300	0.28571400
F	-6.33252300	-2.96454700	1.28950300

F	-5.30282700	-4.39708500	2.57978800
H	0.00000000	4.59325500	-0.72395200
H	3.39085100	-1.21041800	-0.97811000
H	3.39085100	1.21041800	-0.97811000
H	-3.39085100	1.21041800	-0.97811000
H	-3.39085100	-1.21041800	-0.97811000
H	0.00000000	-4.59325500	-0.72395200
H	1.95510300	4.81335300	-2.44911200
H	3.97893300	6.23233600	-2.38173900
H	3.26512600	2.67632100	1.03910700
H	6.30513900	7.42364600	-1.84617100
H	8.48426600	8.17547900	-0.93519300
H	9.46044400	7.09579900	1.05411700
H	8.26160600	5.22111300	2.18364700
H	-9.46044400	7.09579900	1.05411700
H	-8.48426600	8.17547900	-0.93519300
H	-6.30513900	7.42364600	-1.84617100
H	-8.26160600	5.22111300	2.18364700
H	-3.97893300	6.23233600	-2.38173900
H	-1.95510300	4.81335300	-2.44911200
H	-3.26512600	2.67632100	1.03910700
H	-9.46044400	-7.09579900	1.05411700
H	-8.48426600	-8.17547900	-0.93519300
H	-6.30513900	-7.42364600	-1.84617100
H	-8.26160600	-5.22111300	2.18364700
H	-3.97893300	-6.23233600	-2.38173900
H	-1.95510300	-4.81335300	-2.44911200
H	-3.26512600	-2.67632100	1.03910700
C	1.22309200	-2.84307900	-0.77762900
C	2.46832900	-3.64685200	-0.72539800
C	2.68963500	-4.66194800	-1.66685700
C	3.42416500	-3.43783300	0.28571400
C	3.83317000	-5.46091500	-1.63474400
H	1.95510300	-4.81335300	-2.44911200
C	4.55228700	-4.22906000	0.30966400
H	3.26512600	-2.67632100	1.03910700
C	4.77436600	-5.23955700	-0.63795300
H	3.97893300	-6.23233600	-2.38173900
C	5.71016900	-4.19106100	1.28327100
C	6.06096600	-5.89769300	-0.33958300
C	6.62638700	-5.29057800	0.79250700
F	5.30282700	-4.39708500	2.57978800
F	6.33252300	-2.96454700	1.28950300
C	6.72529000	-6.94189100	-0.97112200

C	7.83986600	-5.70122000	1.30888600
C	7.95332500	-7.36232300	-0.45406800
H	6.30513900	-7.42364600	-1.84617100
C	8.50692500	-6.75243000	0.67139400
H	8.26160600	-5.22111300	2.18364700
H	8.48426600	-8.17547900	-0.93519300
H	9.46044400	-7.09579900	1.05411700

Table S8. Cartesian coordinates of the DFT-optimized structure of FF-Py-CPP (C_2) depicted.

FF-Py-CPP (C_2)

B3LYP-D3BJ/6-311g(d,p)

E = -3411.683138 a.u.

C	0.01790600	2.84258200	-1.44553500
C	-0.00007700	1.42963900	-1.46097300
C	0.00007700	0.71643700	-0.22268500
C	0.00189100	1.42974600	1.01542000
C	0.02306100	2.84327300	0.99930800
C	0.05203500	3.51124700	-0.22332200
C	-0.00007700	-0.71643700	-0.22268500
C	-0.00189100	-1.42974600	1.01542000
C	-0.00802400	-0.67841000	2.23429700
C	0.00802400	0.67841000	2.23429700
C	0.00642100	0.67838500	-2.67980900
C	-0.00642100	-0.67838500	-2.67980900
C	0.00007700	-1.42963900	-1.46097300
C	-0.01790600	-2.84258200	-1.44553500
C	-0.05203500	-3.51124700	-0.22332200
C	-0.02306100	-2.84327300	0.99930800
C	-0.01363400	3.65089600	2.24380200
C	0.98561400	4.60129900	2.49384600
C	0.97089800	5.40199200	3.63683200
C	-0.06722200	5.24842200	4.54617400
C	-1.07318700	4.30365200	4.29361300
C	-1.06633600	3.51103900	3.16616300
C	-0.36098100	5.92601000	5.82388000
C	-1.54850800	5.39677700	6.35274000
C	-2.08300400	4.33251900	5.41989400
C	0.31859200	6.92531600	6.50935800
C	-0.20695200	7.38004900	7.72147600
C	-1.38773200	6.84777900	8.23869900
C	-2.07361200	5.84180800	7.55026600
F	-3.34972200	4.62486900	4.97190400
F	-2.19294100	3.10897700	6.03980700
C	-0.90452200	-8.15419900	-7.87803900

C	0.27477100	-7.44944500	-8.11772500
C	0.71994400	-6.46594700	-7.23056300
C	-0.03869800	-6.20122700	-6.09719400
C	-1.22409500	-6.91591100	-5.86489800
C	-1.67001200	-7.88907900	-6.73770100
C	0.16133800	-5.24282500	-4.99282300
C	-0.89859500	-5.37160400	-4.08400900
C	-1.85284600	-6.43869000	-4.57431900
C	1.16605100	-4.31542000	-4.74604700
C	1.08785100	-3.53043700	-3.59572600
C	0.02528000	-3.65311200	-2.68838600
C	-0.98146400	-4.59989500	-2.94385600
F	-3.12210700	-5.94559600	-4.76874900
F	-1.99817800	-7.45750200	-3.66131000
C	0.01363400	-3.65089600	2.24380200
C	-0.98561400	-4.60129900	2.49384600
C	-0.97089800	-5.40199200	3.63683200
C	0.06722200	-5.24842200	4.54617400
C	1.07318700	-4.30365200	4.29361300
C	1.06633600	-3.51103900	3.16616300
C	0.36098100	-5.92601000	5.82388000
C	1.54850800	-5.39677700	6.35274000
C	2.08300400	-4.33251900	5.41989400
C	-0.31859200	-6.92531600	6.50935800
C	0.20695200	-7.38004900	7.72147600
C	1.38773200	-6.84777900	8.23869900
C	2.07361200	-5.84180800	7.55026600
F	3.34972200	-4.62486900	4.97190400
F	2.19294100	-3.10897700	6.03980700
H	0.03784300	4.59468500	-0.22349800
H	-0.02674200	-1.20910300	3.17575900
H	0.02674200	1.20910300	3.17575900
H	0.02491900	1.21186500	-3.61983600
H	-0.02491900	-1.21186500	-3.61983600
H	-0.03784300	-4.59468500	-0.22349800
H	1.79741600	4.70089700	1.78294200
H	1.76229900	6.12262400	3.80581800
H	-1.86309300	2.80079100	2.98252200
H	1.23695600	7.34647000	6.11759700
H	0.31135800	8.15884300	8.26864400
H	-1.77580400	7.21641400	9.18055100
H	-2.99142600	5.42199500	7.94394400
H	-1.22942600	-8.91235900	-8.58031500
H	0.85539000	-7.66825000	-9.00629800

H	1.63807600	-5.92510700	-7.42747700
H	-2.58740600	-8.43130900	-6.54278300
H	2.00383400	-4.20316100	-5.42411700
H	1.87494500	-2.81723200	-3.38264100
H	-1.81366100	-4.70763900	-2.25863800
H	-1.79741600	-4.70089700	1.78294200
H	-1.76229900	-6.12262400	3.80581800
H	1.86309300	-2.80079100	2.98252200
H	-1.23695600	-7.34647000	6.11759700
H	-0.31135800	-8.15884300	8.26864400
H	1.77580400	-7.21641400	9.18055100
H	2.99142600	-5.42199500	7.94394400
C	-0.02528000	3.65311200	-2.68838600
C	-1.08785100	3.53043700	-3.59572600
C	0.98146400	4.59989500	-2.94385600
C	-1.16605100	4.31542000	-4.74604700
H	-1.87494500	2.81723200	-3.38264100
C	0.89859500	5.37160400	-4.08400900
H	1.81366100	4.70763900	-2.25863800
C	-0.16133800	5.24282500	-4.99282300
H	-2.00383400	4.20316100	-5.42411700
C	1.85284600	6.43869000	-4.57431900
C	0.03869800	6.20122700	-6.09719400
C	1.22409500	6.91591100	-5.86489800
F	3.12210700	5.94559600	-4.76874900
F	1.99817800	7.45750200	-3.66131000
C	-0.71994400	6.46594700	-7.23056300
C	1.67001200	7.88907900	-6.73770100
C	-0.27477100	7.44944500	-8.11772500
H	-1.63807600	5.92510700	-7.42747700
C	0.90452200	8.15419900	-7.87803900
H	2.58740600	8.43130900	-6.54278300
H	-0.85539000	7.66825000	-9.00629800
H	1.22942600	8.91235900	-8.58031500

Table S9. Cartesian coordinates of the DFT-optimized structure of FF-Py-CPP (C_s) depicted.

FF-Py-CPP (C_s)

B3LYP-D3BJ/6-311g(d,p)

E = -3411.682390 a.u.

C	0.66293500	-3.20957700	1.22256400
C	0.64513500	-1.79606900	1.23838100
C	0.64657200	-1.08285400	0.00000000
C	0.64513500	-1.79606900	-1.23838100
C	0.66293500	-3.20957700	-1.22256400

C	0.69236800	-3.87773600	0.00000000
C	0.65060300	0.35020400	0.00000000
C	0.65150600	1.06359600	-1.23797300
C	0.63784400	0.31235900	-2.45661200
C	0.64882400	-1.04445100	-2.45724600
C	0.64882400	-1.04445100	2.45724600
C	0.63784400	0.31235900	2.45661200
C	0.65150600	1.06359600	1.23797300
C	0.63900400	2.47694400	1.22247900
C	0.60984000	3.14544400	0.00000000
C	0.62332200	-4.01672100	-2.46728900
C	1.62057400	-4.96895600	-2.71872600
C	1.60450200	-5.76889900	-3.86227900
C	0.56729900	-5.61194400	-4.77208200
C	-0.43636400	-4.66487100	-4.51878700
C	-0.42887900	-3.87409800	-3.38998900
C	0.27247000	-6.28753300	-6.05059900
C	-0.91296700	-5.75407800	-6.57988900
C	-1.44419000	-4.68787400	-5.64720900
C	0.94884800	-7.28901900	-6.73612500
C	0.42222300	-7.74172100	-7.94855500
C	-0.75658900	-7.20534600	-8.46603400
C	-1.43923300	-6.19712900	-7.77764400
F	-2.71314500	-4.97255200	-5.20333200
F	-1.54371100	-3.46308400	-6.26700500
C	-0.75658900	-7.20534600	8.46603400
C	0.42222300	-7.74172100	7.94855500
C	0.94884800	-7.28901900	6.73612500
C	0.27247000	-6.28753300	6.05059900
C	-0.91296700	-5.75407800	6.57988900
C	-1.43923300	-6.19712900	7.77764400
C	0.56729900	-5.61194400	4.77208200
C	-0.43636400	-4.66487100	4.51878700
C	-1.44419000	-4.68787400	5.64720900
C	1.60450200	-5.76889900	3.86227900
C	1.62057400	-4.96895600	2.71872600
C	0.62332200	-4.01672100	2.46728900
C	-0.42887900	-3.87409800	3.38998900
F	-2.71314500	-4.97255200	5.20333200
F	-1.54371100	-3.46308400	6.26700500
C	-0.23458300	7.78648600	7.65824600
C	0.93523300	7.06836800	7.90473000
C	1.37648800	6.08287500	7.01790000
C	0.62359400	5.82983900	5.87801400

C	-0.55223700	6.55777500	5.63901200
C	-0.99425300	7.53307400	6.51140200
C	0.82124600	4.87222000	4.77265400
C	-0.23080400	5.01416800	3.85662200
C	-1.17680400	6.09120300	4.34227800
C	1.81771200	3.93464400	4.53121900
C	1.73867100	3.15225600	3.37932800
C	0.68324300	3.28721800	2.46540100
C	-0.31469700	4.24501100	2.71484600
F	-2.45240000	5.61233200	4.52601700
F	-1.30198300	7.11385000	3.43151100
H	0.67320100	-4.96106400	0.00000000
H	0.61288800	0.84527700	-3.39668100
H	0.65878500	-1.57531300	-3.39877500
H	0.65878500	-1.57531300	3.39877500
H	0.61288800	0.84527700	3.39668100
H	0.62651000	4.22888900	0.00000000
H	2.43223600	-5.07019600	-2.00779900
H	2.39421800	-6.49133700	-4.03192200
H	-1.22473900	-3.16309800	-3.20543700
H	1.86537600	-7.71385500	-6.34393300
H	0.93779200	-8.52246200	-8.49555700
H	-1.14591600	-7.57280700	-9.40781500
H	-2.35576000	-5.77445400	-8.17123100
H	-1.14591600	-7.57280700	9.40781500
H	0.93779200	-8.52246200	8.49555700
H	1.86537600	-7.71385500	6.34393300
H	-2.35576000	-5.77445400	8.17123100
H	2.39421800	-6.49133700	4.03192200
H	2.43223600	-5.07019600	2.00779900
H	-1.22473900	-3.16309800	3.20543700
H	-0.55685700	8.54575900	8.36054600
H	1.51112900	7.27794500	8.79860400
H	2.28690500	5.53110400	7.22034400
H	-1.90443200	8.08542800	6.31126300
H	2.64916400	3.81196200	5.21526000
H	2.51924000	2.43055000	3.17087400
H	-1.14132100	4.36298100	2.02460700
C	0.63900400	2.47694400	-1.22247900
C	0.68324300	3.28721800	-2.46540100
C	1.73867100	3.15225600	-3.37932800
C	-0.31469700	4.24501100	-2.71484600
C	1.81771200	3.93464400	-4.53121900
H	2.51924000	2.43055000	-3.17087400

C	-0.23080400	5.01416800	-3.85662200
H	-1.14132100	4.36298100	-2.02460700
C	0.82124600	4.87222000	-4.77265400
H	2.64916400	3.81196200	-5.21526000
C	-1.17680400	6.09120300	-4.34227800
C	0.62359400	5.82983900	-5.87801400
C	-0.55223700	6.55777500	-5.63901200
F	-1.30198300	7.11385000	-3.43151100
F	-2.45240000	5.61233200	-4.52601700
C	1.37648800	6.08287500	-7.01790000
C	-0.99425300	7.53307400	-6.51140200
C	0.93523300	7.06836800	-7.90473000
H	2.28690500	5.53110400	-7.22034400
C	-0.23458300	7.78648600	-7.65824600
H	-1.90443200	8.08542800	-6.31126300
H	1.51112900	7.27794500	-8.79860400
H	-0.55685700	8.54575900	-8.36054600

Table S10. Cartesian coordinates of the DFT-optimized structure of MF-Py-CPP (C_{2v}) depicted.

MF-Py-CPP (C_{2V})

B3LYP-D3BJ/6-311g(d,p)

E = -2932.221409 a.u.

C	-1.22393200	2.84395900	-0.83608300
C	-1.23749000	1.43016300	-0.88030000
C	0.00000000	0.71678300	-0.87707600
C	1.23749000	1.43016300	-0.88030000
C	1.22393200	2.84395900	-0.83608300
C	0.00000000	3.51151800	-0.82587400
C	0.00000000	-0.71678300	-0.87707600
C	1.23749000	-1.43016300	-0.88030000
C	2.45170100	-0.67853800	-0.99159700
C	2.45170100	0.67853800	-0.99159700
C	-2.45170100	0.67853800	-0.99159700
C	-2.45170100	-0.67853800	-0.99159700
C	-1.23749000	-1.43016300	-0.88030000
C	-1.22393200	-2.84395900	-0.83608300
C	0.00000000	-3.51151800	-0.82587400
C	2.47242200	3.64057600	-0.76020500
C	2.70009700	4.68772600	-1.66598600
C	3.85487100	5.46305800	-1.60389400
C	4.79981600	5.19026900	-0.61783300
C	4.57829800	4.15002500	0.30214800
C	3.42876700	3.38456100	0.23752800
C	6.08946300	5.81664400	-0.31126700

C	6.65324500	5.15769600	0.79680300
C	5.73816500	4.03930400	1.28629800
C	6.75852700	6.87607000	-0.92060300
C	7.99546300	7.27074300	-0.41354500
C	8.55485800	6.61680300	0.68553700
C	7.88371100	5.55440900	1.29687700
C	-8.55485800	6.61680300	0.68553700
C	-7.99546300	7.27074300	-0.41354500
C	-6.75852700	6.87607000	-0.92060300
C	-6.08946300	5.81664400	-0.31126700
C	-6.65324500	5.15769600	0.79680300
C	-7.88371100	5.55440900	1.29687700
C	-4.79981600	5.19026900	-0.61783300
C	-4.57829800	4.15002500	0.30214800
C	-5.73816500	4.03930400	1.28629800
C	-3.85487100	5.46305800	-1.60389400
C	-2.70009700	4.68772600	-1.66598600
C	-2.47242200	3.64057600	-0.76020500
C	-3.42876700	3.38456100	0.23752800
C	-8.55485800	-6.61680300	0.68553700
C	-7.99546300	-7.27074300	-0.41354500
C	-6.75852700	-6.87607000	-0.92060300
C	-6.08946300	-5.81664400	-0.31126700
C	-6.65324500	-5.15769600	0.79680300
C	-7.88371100	-5.55440900	1.29687700
C	-4.79981600	-5.19026900	-0.61783300
C	-4.57829800	-4.15002500	0.30214800
C	-5.73816500	-4.03930400	1.28629800
C	-3.85487100	-5.46305800	-1.60389400
C	-2.70009700	-4.68772600	-1.66598600
C	-2.47242200	-3.64057600	-0.76020500
C	-3.42876700	-3.38456100	0.23752800
H	0.00000000	4.59227500	-0.74982200
H	3.38413700	-1.21351300	-1.10608200
H	3.38413700	1.21351300	-1.10608200
H	-3.38413700	1.21351300	-1.10608200
H	-3.38413700	-1.21351300	-1.10608200
H	0.00000000	-4.59227500	-0.74982200
H	1.96561600	4.87748100	-2.43993400
H	4.01300700	6.26040200	-2.32128300
H	3.24713700	2.59328600	0.95574000
H	6.32819800	7.38697000	-1.77456500
H	8.52884100	8.09302300	-0.87635000
H	9.51763400	6.93626900	1.06728700

H	8.32530100	5.05177100	2.15066300
H	-9.51763400	6.93626900	1.06728700
H	-8.52884100	8.09302300	-0.87635000
H	-6.32819800	7.38697000	-1.77456500
H	-8.32530100	5.05177100	2.15066300
H	-4.01300700	6.26040200	-2.32128300
H	-1.96561600	4.87748100	-2.43993400
H	-3.24713700	2.59328600	0.95574000
H	-9.51763400	-6.93626900	1.06728700
H	-8.52884100	-8.09302300	-0.87635000
H	-6.32819800	-7.38697000	-1.77456500
H	-8.32530100	-5.05177100	2.15066300
H	-4.01300700	-6.26040200	-2.32128300
H	-1.96561600	-4.87748100	-2.43993400
H	-3.24713700	-2.59328600	0.95574000
C	1.22393200	-2.84395900	-0.83608300
C	2.47242200	-3.64057600	-0.76020500
C	2.70009700	-4.68772600	-1.66598600
C	3.42876700	-3.38456100	0.23752800
C	3.85487100	-5.46305800	-1.60389400
H	1.96561600	-4.87748100	-2.43993400
C	4.57829800	-4.15002500	0.30214800
H	3.24713700	-2.59328600	0.95574000
C	4.79981600	-5.19026900	-0.61783300
H	4.01300700	-6.26040200	-2.32128300
C	5.73816500	-4.03930400	1.28629800
C	6.08946300	-5.81664400	-0.31126700
C	6.65324500	-5.15769600	0.79680300
C	6.75852700	-6.87607000	-0.92060300
C	7.88371100	-5.55440900	1.29687700
C	7.99546300	-7.27074300	-0.41354500
H	6.32819800	-7.38697000	-1.77456500
C	8.55485800	-6.61680300	0.68553700
H	8.32530100	-5.05177100	2.15066300
H	8.52884100	-8.09302300	-0.87635000
H	9.51763400	-6.93626900	1.06728700
C	-5.27052600	4.29125700	2.73224500
H	-4.77950600	5.26258500	2.81631200
H	-6.12067200	4.27423800	3.41923800
H	-4.56339800	3.51939300	3.04716200
C	-6.42568600	2.66452000	1.17814500
H	-6.76222700	2.47950300	0.15615300
H	-5.73477000	1.86661900	1.46336100
H	-7.29393500	2.61528700	1.84044800

C	-6.42568600	-2.66452000	1.17814500
H	-5.73477000	-1.86661900	1.46336100
H	-6.76222700	-2.47950300	0.15615300
H	-7.29393500	-2.61528700	1.84044800
C	-5.27052600	-4.29125700	2.73224500
H	-6.12067200	-4.27423800	3.41923800
H	-4.77950600	-5.26258500	2.81631200
H	-4.56339800	-3.51939300	3.04716200
C	6.42568600	-2.66452000	1.17814500
H	6.76222700	-2.47950300	0.15615300
H	5.73477000	-1.86661900	1.46336100
H	7.29393500	-2.61528700	1.84044800
C	5.27052600	-4.29125700	2.73224500
H	4.77950600	-5.26258500	2.81631200
H	6.12067200	-4.27423800	3.41923800
H	4.56339800	-3.51939300	3.04716200
C	6.42568600	2.66452000	1.17814500
H	5.73477000	1.86661900	1.46336100
H	6.76222700	2.47950300	0.15615300
H	7.29393500	2.61528700	1.84044800
C	5.27052600	4.29125700	2.73224500
H	6.12067200	4.27423800	3.41923800
H	4.77950600	5.26258500	2.81631200
H	4.56339800	3.51939300	3.04716200

Table S11. Cartesian coordinates of the DFT-optimized structure of MF-Py-CPP (C_2) depicted.

MF-Py-CPP (C_2)

B3LYP-D3BJ/6-311g(d,p)

E = -2932.219605 a.u.

C	0.01848900	2.84386100	-1.45651800
C	0.00042000	1.43031700	-1.47114700
C	0.00007200	0.71678600	-0.23282500
C	0.00132600	1.43053400	1.00523800
C	0.01963200	2.84427800	0.99056100
C	0.04956600	3.51103200	-0.23293600
C	-0.00007200	-0.71678600	-0.23282500
C	-0.00132600	-1.43053400	1.00523800
C	-0.00798300	-0.67843900	2.22392200
C	0.00798300	0.67843900	2.22392200
C	0.00691900	0.67847600	-2.68981300
C	-0.00691900	-0.67847600	-2.68981300
C	-0.00042000	-1.43031700	-1.47114700
C	-0.01848900	-2.84386100	-1.45651800
C	-0.04956600	-3.51103200	-0.23293600

C	-0.01963200	-2.84427800	0.99056100
C	-0.02403700	3.65096200	2.23584200
C	0.97237600	4.60448000	2.49170700
C	0.94330800	5.39479300	3.63780000
C	-0.10209900	5.23284200	4.54334500
C	-1.11231200	4.28713200	4.29269300
C	-1.07871800	3.50481000	3.15264100
C	-0.39657500	5.90418600	5.81313600
C	-1.58837700	5.36852700	6.33484400
C	-2.15026500	4.29285000	5.41026800
C	0.28901500	6.90538800	6.49785800
C	-0.22642200	7.36620700	7.70818500
C	-1.40883700	6.83465700	8.22581100
C	-2.09654100	5.83066100	7.53891400
C	-0.91498700	-8.14865600	-7.88320300
C	0.25972700	-7.43462500	-8.12555500
C	0.69239300	-6.45540800	-7.23286200
C	-0.06829200	-6.20158800	-6.09348300
C	-1.25230000	-6.92113600	-5.84930900
C	-1.67799900	-7.89377900	-6.74052000
C	0.13182800	-5.25040500	-4.99588500
C	-0.92750300	-5.39079400	-4.08281700
C	-1.90467900	-6.46605100	-4.54735700
C	1.13943600	-4.31761100	-4.75992800
C	1.07568200	-3.52856600	-3.61544900
C	0.01963200	-3.65528300	-2.69921500
C	-0.98450300	-4.60550100	-2.94441300
C	0.02403700	-3.65096200	2.23584200
C	-0.97237600	-4.60448000	2.49170700
C	-0.94330800	-5.39479300	3.63780000
C	0.10209900	-5.23284200	4.54334500
C	1.11231200	-4.28713200	4.29269300
C	1.07871800	-3.50481000	3.15264100
C	0.39657500	-5.90418600	5.81313600
C	1.58837700	-5.36852700	6.33484400
C	2.15026500	-4.29285000	5.41026800
C	-0.28901500	-6.90538800	6.49785800
C	0.22642200	-7.36620700	7.70818500
C	1.40883700	-6.83465700	8.22581100
C	2.09654100	-5.83066100	7.53891400
H	0.03314400	4.59441400	-0.23297400
H	-0.02789100	-1.21239300	3.16356700
H	0.02789100	1.21239300	3.16356700
H	0.02446400	1.21326600	-3.62910500

H	-0.02446400	-1.21326600	-3.62910500
H	-0.03314400	-4.59441400	-0.23297400
H	1.78744800	4.70965900	1.78517600
H	1.72940600	6.11926100	3.81855600
H	-1.86469400	2.78693600	2.94731800
H	1.20775500	7.32129000	6.09979700
H	0.29495500	8.14458200	8.25329400
H	-1.79606700	7.20423800	9.16825800
H	-3.01475200	5.42313300	7.94802600
H	-1.23729800	-8.90677300	-8.58755900
H	0.84018300	-7.64436100	-9.01657700
H	1.60542300	-5.90335200	-7.42540900
H	-2.58964300	-8.45308400	-6.55975900
H	1.96918700	-4.20805200	-5.44908700
H	1.86293800	-2.81288900	-3.41135900
H	-1.80427200	-4.70199000	-2.24088400
H	-1.78744800	-4.70965900	1.78517600
H	-1.72940600	-6.11926100	3.81855600
H	1.86469400	-2.78693600	2.94731800
H	-1.20775500	-7.32129000	6.09979700
H	-0.29495500	-8.14458200	8.25329400
H	1.79606700	-7.20423800	9.16825800
H	3.01475200	-5.42313300	7.94802600
C	-0.01963200	3.65528300	-2.69921500
C	-1.07568200	3.52856600	-3.61544900
C	0.98450300	4.60550100	-2.94441300
C	-1.13943600	4.31761100	-4.75992800
H	-1.86293800	2.81288900	-3.41135900
C	0.92750300	5.39079400	-4.08281700
H	1.80427200	4.70199000	-2.24088400
C	-0.13182800	5.25040500	-4.99588500
H	-1.96918700	4.20805200	-5.44908700
C	1.90467900	6.46605100	-4.54735700
C	0.06829200	6.20158800	-6.09348300
C	1.25230000	6.92113600	-5.84930900
C	-0.69239300	6.45540800	-7.23286200
C	1.67799900	7.89377900	-6.74052000
C	-0.25972700	7.43462500	-8.12555500
H	-1.60542300	5.90335200	-7.42540900
C	0.91498700	8.14865600	-7.88320300
H	2.58964300	8.45308400	-6.55975900
H	-0.84018300	7.64436100	-9.01657700
H	1.23729800	8.90677300	-8.58755900
C	3.54189500	-4.68405000	4.87778900

H	4.26212800	-4.74897900	5.69753700
H	3.50545300	-5.65189900	4.37417300
H	3.90409700	-3.93828600	4.16541200
C	2.21249800	-2.92443500	6.11553200
H	2.54925500	-2.14980800	5.42152700
H	1.22981700	-2.64121200	6.49787700
H	2.91203400	-2.95582600	6.95489700
C	3.30457200	5.87495300	-4.80093300
H	3.73344000	5.49071800	-3.87173800
H	3.25409900	5.05593800	-5.52091600
H	3.97845600	6.63977100	-5.19580500
C	1.98722200	7.61989800	-3.52992200
H	0.99838300	8.04345300	-3.34410400
H	2.39451700	7.26523300	-2.57941400
H	2.63815300	8.41506400	-3.90268700
C	-1.98722200	-7.61989800	-3.52992200
H	-0.99838300	-8.04345300	-3.34410400
H	-2.39451700	-7.26523300	-2.57941400
H	-2.63815300	-8.41506400	-3.90268700
C	-3.30457200	-5.87495300	-4.80093300
H	-3.73344000	-5.49071800	-3.87173800
H	-3.25409900	-5.05593800	-5.52091600
H	-3.97845600	-6.63977100	-5.19580500
C	-2.21249800	2.92443500	6.11553200
H	-2.54925500	2.14980800	5.42152700
H	-1.22981700	2.64121200	6.49787700
H	-2.91203400	2.95582600	6.95489700
C	-3.54189500	4.68405000	4.87778900
H	-4.26212800	4.74897900	5.69753700
H	-3.50545300	5.65189900	4.37417300
H	-3.90409700	3.93828600	4.16541200

Table S12. Cartesian coordinates of the DFT-optimized structure of MF-Py-CPP (C_s) depicted.

MF-Py-CPP (C_s)

B3LYP-D3BJ/6-311g(d,p)

E = -2932.219632 a.u.

C	-0.71293700	-3.22790600	-1.22337700
C	-0.70043500	-1.81407800	-1.23807100
C	-0.70217800	-1.10039300	0.00000000
C	-0.70043500	-1.81407800	1.23807100
C	-0.71293700	-3.22790600	1.22337700
C	-0.74063300	-3.89523400	0.00000000
C	-0.70572700	0.33317400	0.00000000
C	-0.70604300	1.04663400	1.23836700

C	-0.69930400	0.29485800	2.45705300
C	-0.71059400	-1.06209400	2.45688400
C	-0.71059400	-1.06209400	-2.45688400
C	-0.69930400	0.29485800	-2.45705300
C	-0.70604300	1.04663400	-1.23836700
C	-0.68905500	2.46011100	-1.22372100
C	-0.65912400	3.12677600	0.00000000
C	-0.66331200	-4.03419900	2.46869300
C	-1.65518100	-4.99166200	2.72723900
C	-1.61908900	-5.78239300	3.87283600
C	-0.57110400	-5.61703500	4.77477900
C	0.43451300	-4.66716200	4.52143400
C	0.39372000	-3.88407300	3.38213800
C	-0.26928500	-6.28866500	6.04270100
C	0.92247600	-5.74914500	6.56050200
C	1.47670200	-4.67019500	5.63509800
C	-0.94847700	-7.29326300	6.72881500
C	-0.42664400	-7.75364900	7.93656100
C	0.75577600	-7.21832900	8.45028200
C	1.43703500	-6.21088800	7.76200900
C	0.75577600	-7.21832900	-8.45028200
C	-0.42664400	-7.75364900	-7.93656100
C	-0.94847700	-7.29326300	-6.72881500
C	-0.26928500	-6.28866500	-6.04270100
C	0.92247600	-5.74914500	-6.56050200
C	1.43703500	-6.21088800	-7.76200900
C	-0.57110400	-5.61703500	-4.77477900
C	0.43451300	-4.66716200	-4.52143400
C	1.47670200	-4.67019500	-5.63509800
C	-1.61908900	-5.78239300	-3.87283600
C	-1.65518100	-4.99166200	-2.72723900
C	-0.66331200	-4.03419900	-2.46869300
C	0.39372000	-3.88407300	-3.38213800
C	0.22139700	7.78000500	-7.63567600
C	-0.95148200	7.06492500	-7.88373200
C	-1.38572400	6.08279200	-6.99500800
C	-0.62846800	5.82709700	-5.85377500
C	0.55370000	6.54773500	-5.60385100
C	0.98097800	7.52327600	-6.49111800
C	-0.83089500	4.87278600	-4.75929500
C	0.22537400	5.01218400	-3.84256900
C	1.20246400	6.09008900	-4.30099800
C	-1.83820300	3.93833400	-4.52857500
C	-1.77742000	3.14691600	-3.38552300

C	-0.72442300	3.27265600	-2.46568400
C	0.27965400	4.22425500	-2.70595700
H	-0.71929300	-4.97850300	0.00000000
H	-0.68468500	0.82957700	3.39644000
H	-0.73035700	-1.59647400	3.39631600
H	-0.73035700	-1.59647400	-3.39631600
H	-0.68468500	0.82957700	-3.39644000
H	-0.67582600	4.21017200	0.00000000
H	-2.47197500	-5.09993100	2.02319900
H	-2.40170700	-6.51003900	4.05581300
H	1.17588400	-3.16261800	3.17469000
H	-1.86721700	-7.71205300	6.33381200
H	-0.94303100	-8.53460900	8.48272100
H	1.14802300	-7.58763100	9.39076500
H	2.35528000	-5.80043000	8.16812500
H	1.14802300	-7.58763100	-9.39076500
H	-0.94303100	-8.53460900	-8.48272100
H	-1.86721700	-7.71205300	-6.33381200
H	2.35528000	-5.80043000	-8.16812500
H	-2.40170700	-6.51003900	-4.05581300
H	-2.47197500	-5.09993100	-2.02319900
H	1.17588400	-3.16261800	-3.17469000
H	0.54492500	8.54040300	-8.33700200
H	-1.52931700	7.27616100	-8.77609600
H	-2.29735400	5.53000400	-7.19199300
H	1.89119600	8.08345200	-6.30588800
H	-2.66578200	3.82953200	-5.22044700
H	-2.56496300	2.43050000	-3.18521300
H	1.09719400	4.31994500	-1.99970600
C	-0.68905500	2.46011100	1.22372100
C	-0.72442300	3.27265600	2.46568400
C	-1.77742000	3.14691600	3.38552300
C	0.27965400	4.22425500	2.70595700
C	-1.83820300	3.93833400	4.52857500
H	-2.56496300	2.43050000	3.18521300
C	0.22537400	5.01218400	3.84256900
H	1.09719400	4.31994500	1.99970600
C	-0.83089500	4.87278600	4.75929500
H	-2.66578200	3.82953200	5.22044700
C	1.20246400	6.09008900	4.30099800
C	-0.62846800	5.82709700	5.85377500
C	0.55370000	6.54773500	5.60385100
C	-1.38572400	6.08279200	6.99500800
C	0.98097800	7.52327600	6.49111800

C	-0.95148200	7.06492500	7.88373200
H	-2.29735400	5.53000400	7.19199300
C	0.22139700	7.78000500	7.63567600
H	1.89119600	8.08345200	6.30588800
H	-1.52931700	7.27616100	8.77609600
H	0.54492500	8.54040300	8.33700200
C	2.86773300	-5.05554000	-5.09680500
H	3.22430300	-4.30754700	-4.38390100
H	2.83297800	-6.02293600	-4.59220500
H	3.59136600	-5.11869800	-5.91370900
C	1.53660900	-3.30246000	-6.34185600
H	0.55437600	-3.02332300	-6.72827200
H	1.86777900	-2.52568800	-5.64754600
H	2.23944500	-3.33233200	-7.17852300
C	2.60419300	5.50202700	-4.55140200
H	3.03046700	5.11579300	-3.62181800
H	2.55749800	4.68499200	-5.27389300
H	3.27823100	6.26900900	-4.94179100
C	1.27968200	7.24118900	-3.27996500
H	0.28951700	7.66253600	-3.09621700
H	1.68432100	6.88428200	-2.32911400
H	1.93057000	8.03851500	-3.64814900
C	2.60419300	5.50202700	4.55140200
H	2.55749800	4.68499200	5.27389300
H	3.03046700	5.11579300	3.62181800
H	3.27823100	6.26900900	4.94179100
C	1.27968200	7.24118900	3.27996500
H	1.68432100	6.88428200	2.32911400
H	0.28951700	7.66253600	3.09621700
H	1.93057000	8.03851500	3.64814900
C	2.86773300	-5.05554000	5.09680500
H	2.83297800	-6.02293600	4.59220500
H	3.22430300	-4.30754700	4.38390100
H	3.59136600	-5.11869800	5.91370900
C	1.53660900	-3.30246000	6.34185600
H	1.86777900	-2.52568800	5.64754600
H	0.55437600	-3.02332300	6.72827200
H	2.23944500	-3.33233200	7.17852300