Electronic Supplementary Information (ESI)

Tandem construction of flavone-bridged conjugated porous polymers for photosynthesis of 2,3-dihydrobenzofurans

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Table of Contents

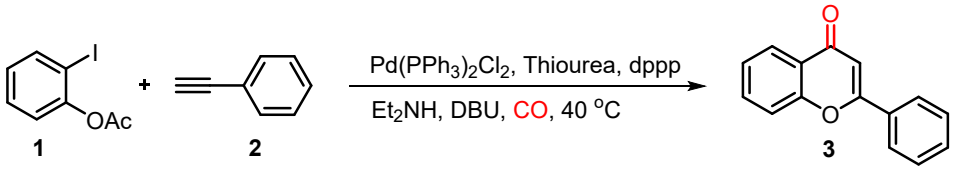
A. Summary of Figures and Tables

B. General Information

All reagents were purchased from commercial sources and used as received. All experiments were carried out under air atmosphere, unless otherwise indicated. 1,3,5-triethynylbenzene[1] and tris(4-ethynylphenyl)amine[2] were prepared according to the literature procedures. Irradiation of photochemical reactions was carried out using a 24 W blue LED bulb.

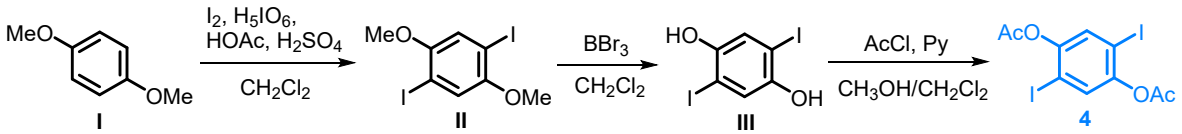
The liquid ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. The chemical shifts δ are given in ppm relative to tetramethylsilane and the coupling constants J are given in Hz. The spectra were recorded with $CDCl_3$ or DMSO-d_6 as solvent at room temperature. The morphology and size of the obtained samples were characterized by a JEOL-6701F field-emission scanning electron microscope (SEM, operated at 10 kV). The nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020M system. The samples were outgassed at 120 °C for 8 h before the measurements. Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) method. The pore size distribution curves were obtained from the adsorption branches using Barrett-Joyner-Halenda (BJH) models. Elemental analysis was carried out on an Elementar Analysensysteme GmbH Vario EL V3.00 elemental analyzer. Solid-state NMR spectra were obtained on a WB 400 MHz Bruker Avance II spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with the contact time of 2 ms (ramp 100) and the recycle delay of 2 s with a 4-mm double-resonance probe. FT-IR spectra were recorded on a Nicolet FT-170SX spectrometer. Samples were prepared by dispersing in anhydrous KBr. The diffuse reflectance spectra of the solids were collected at room temperature with a UV-Vis-NIR diffuse reflectance spectrometer (Agilent Technologies, Cary 5000) at a photometric range of 250–800 nm. The thermogravimetric analysis (TGA) was performed on a STA 449C Jupiter instrument, with the temperature from ambient to 1000 °C under nitrogen atmosphere (heating rate of 10 °C/min). Powder X-ray diffraction (PXRD) data were collected with a PANalytical X'Pert Pro diffractometer operated at 40 kV and 40 mA with Cu Kα radiation at a scan rate of 15°/min. The photoelectrochemical experiments, which included transient photocurrent measurement and Mott-Schottky analysis, were performed on a CHI660E workstation (CHI Instruments). The electrochemical experiments were carried out in a three-electrode beaker cell, which included an Ag/AgCl as reference electrode, a platinum plate as counter electrode, and 0.5N Na_2SO_4 aqueous electrolyte were used in this matter.

C. Synthesis of Functional Monomer



Scheme S1 Synthesis of **3**.

Synthesis of 2-phenyl-4H-chromen-4-one (3). A mixture of **1** (1 mmol, 230 μL), **2** (2 mmol, 220 μL), $Pd(PPh_3)_2Cl_2$ (0.05 mmol, 35.0 mg), thiourea (0.05 mmol, 3.8 mg), 1,3-bis(diphenylphosphino)propane (0.05 mmol, 20.6 mg) and DBU (5.0 mmol, 784 μL) in $HNEt_2$ (5 mL) was degassed with CO for 10 min, and then stirred at 40 °C for 48 h. The solvent was removed under vacuum and the residue was diluted with brine and adjusted to neutral with 3N HCl, extrated with CH_2Cl_2 (15 mL) and dried over anhydrous Na_2SO_4. The crude product was purified by flash chromatography through silica gel column (EtOAc/PE = 3/7) to give compound **3** (0.14 g, 62%).[3] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (dd, J = 7.9, 1.7 Hz, 1H), 7.96-7.89 (m, 2H), 7.70 (ddd, J = 8.7, 7.1, 1.7 Hz, 1H), 7.62-7.46 (m, 4H), 7.42 (ddd, J = 8.1, 7.1, 1.1 Hz, 1H), 6.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.6, 163.5, 156.4, 133.9, 131.9, 131.7, 129.1, 126.4, 125.8, 125.3, 124.1, 118.2, 107.7.



Scheme S2 Synthesis of **4**.

Synthesis of 1,4-diiodo-2,5-dimethoxybenzene (II). A mixture of 1,4-dimethoxybenzene **I** (9.11 g, 66 mmol), iodine (13.92 g, 54.8 mmol), H_5IO_6 (6.12 g, 27.1 mmol), acetic acid (120 mL), sulphuric acid (5.4 mL), water (27 mL) and CH_2Cl_2 (24 mL) was heated to 75 °C for 15 h. A precipitate formed. The suspension was cooled with an ice-bath and filtered. The isolated solid was washed with saturated aqueous Na_2SO_3 solution and finally with water and dried in vacuo. Compound **II** was obtained as pale solid (23.50 g, 91%).[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (s, 2H), 3.83 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.5, 121.8, 85.6, 57.3.

Synthesis of 2,5-diiodobenzene-1,4-diol (III). A solution of **II** (1 g, 2.56 mmol) in 30 mL of anhydrous CH_2Cl_2 was degassed by bubbling with argon and cooled to -78 °C. Subsequently,

BBr_3 (2.73 g, 10.9 mmol) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 16 h. Water (100 mL) was carefully added and the formed precipitate collected by filtration. Compound **III** was obtained as white solid (0.81 g, 87%).[5] ^{1}H NMR (400 MHz, DMSO-*d6*): δ 9.78 (s, 2H), 7.12 (s, 2H); ^{13}C NMR (100 MHz, DMSO-*d6*): δ 150.2, 123.4, 84.1.

Synthesis of 2,5-diiodo-1,4-phenylene diacetate (4). Pyridine (24.5 mL) was added to a solution of **III** (2.1g, 5.29 mmol) in dry CH_2Cl_2 (300 mL).The solution was cooled to 0 ºC and the nacetyl chloride (14.3 mL) was added. The reaction was stirred for 3 h at room temperature. MeOH (100 mL) was then added and the resulting mixture was stirred for another 5 min, and subsequently the solvent was removed. The residue was diluted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude was recrystallized with a mixture of ethyl acetate and petroleum ether to obtained compound **4** as brown solid (14.00 g, 63%).[6] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (s, 2H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 149.4, 132.5, 90.0, 21.1.

D. Synthesis of FL-CPPs

Synthesis of FL-CPP1. A mixture of **4** (0.23 g, 0.5 mmol), **5** (0.1 g, 0.67 mmol), $Pd(PPh_3)_2Cl_2$ (0.036 g, 0.05 mmol), thiourea (0.004 g, 0.05 mmol), 1,3-bis(diphenylphosphino)propane (0.036 g, 0.05 mmol) and DBU (0.75 mL) in DMF (1 mL) was degassed with CO for 10 min, then $HNEt_2$ (5 mL, degassed with CO) was added. The mixture was heated to 50 °C and stirred at this temperature for 72 h under CO atmosphere. After cooling to room temperature, the resulting precipitate was filtered and washed in turn (four times each) with water, DMF, CH_3OH, CH_2Cl_2 and acetone. Further purification of the precipitate was carried out by Soxhlet extraction with CH_2Cl_2 and THF (each for 24 h) to remove any unreacted monomers or catalyst residues. After drying at 80 °C for 24 h, FL-CPP1 was obtained as brown powder (0.11 g). Elemental analysis calcd (%) for $C_8H_3O_3$: C 65.32, H 2.06; found: C 66.26, H 5.61.

Synthesis of FL-CPP2. A mixture of **4** (0.23 g, 0.5 mmol), **6** (0.21 g, 0.67 mmol), $Pd(PPh_3)_2Cl_2$ (0.036 g, 0.05 mmol), thiourea (0.004 g, 0.05 mmol), 1,3-bis(diphenylphosphino)propane (0.021 g, 0.05 mmol) and DBU (0.75 mL) in DMF (1 mL) was degassed with CO for 10 min, then $HNEt_2$ (5 mL, degassed with CO) was added. The mixture was then heated to 50 °C and stirred at this temperature for 72 h under CO atmosphere. After cooling to room temperature, the resulting precipitate was filtered and washed in turn (four times each) with water, DMF, CH_3OH, CH_2Cl_2 and acetone. Further purification of the precipitate was carried out by Soxhlet extraction with CH_2Cl_2 and THF (each for 24 h) to remove any unreacted monomers or catalyst residues. After drying at 80 °C for 24 h, FL-CPP2 was obtained as reddish brown powder (0.14 g). Elemental analysis calcd (%) for $C_{36}H_{18}NO_6$: C 77.14, H 3.24, N 2.50; found: C 68.82, H 5.00, N 4.29.

E. Characterization of FL-CPPs

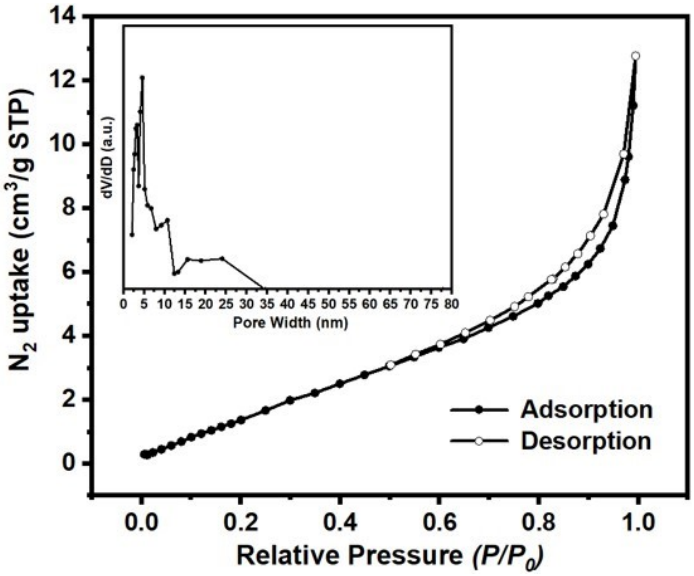


Fig. S1 N_2 adsorption (filled symbols) and desorption (empty symbols) isotherms of FL-CPP1, the insert is the BJH pore size distribution curve of FL-CPP1.

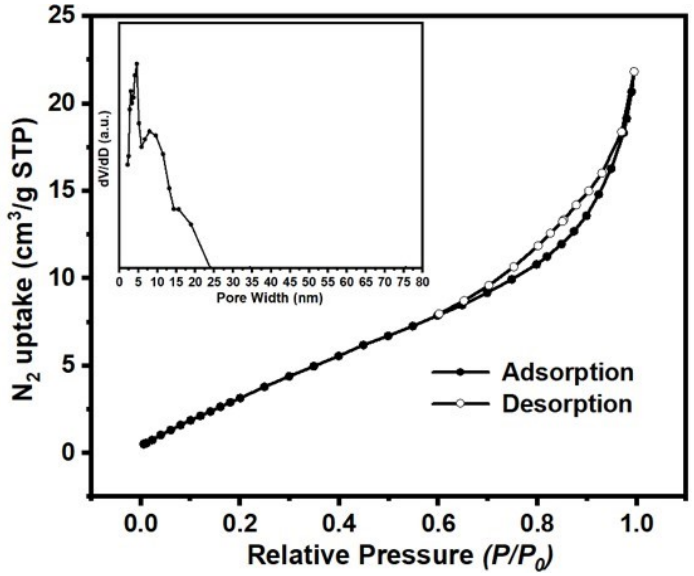


Fig. S2 N_2 adsorption (filled symbols) and desorption (empty symbols) isotherms of FL-CPP2, the insert is the BJH pore size distribution curve of FL-CPP2.

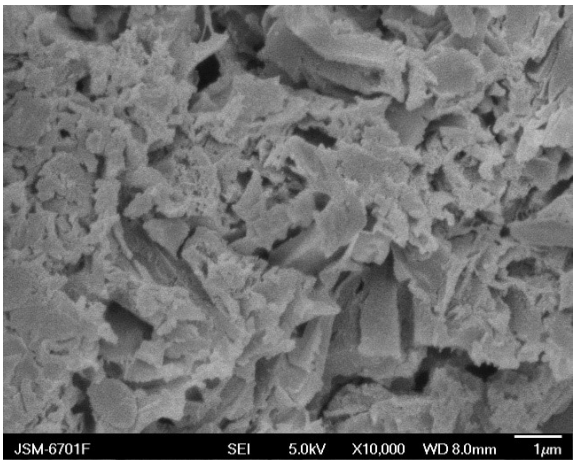


Fig. S3 SEM image of FL-CPP1.

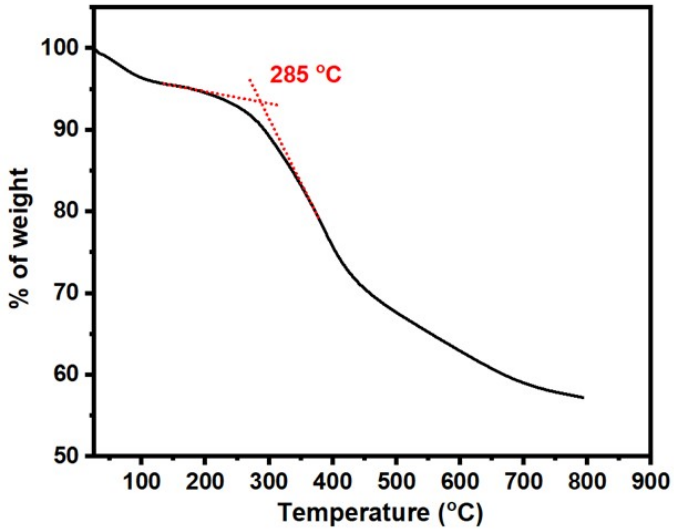


Fig. S4 TGA curve of FL-CPP1.

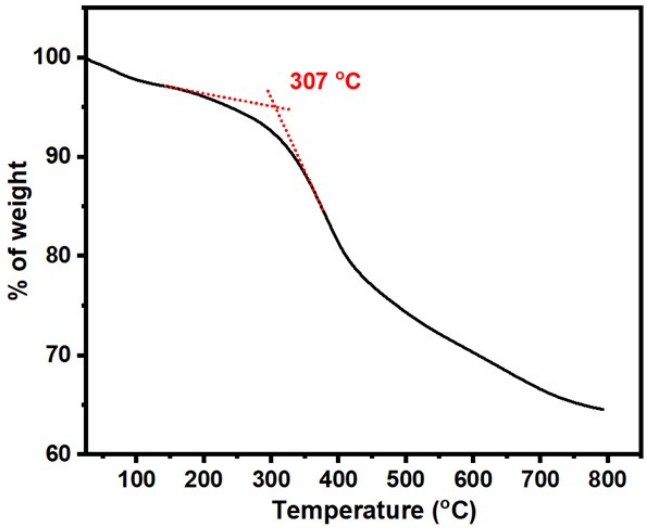


Fig. S5 TGA curve of FL-CPP2.

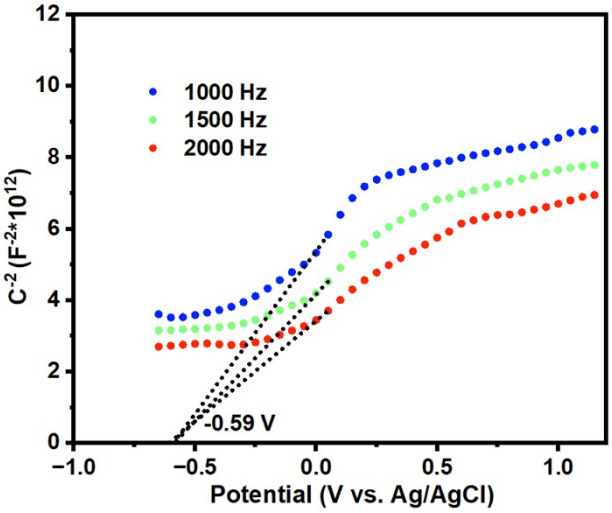


Fig. S6 Mott-Schottky plot of FL-CPP1.

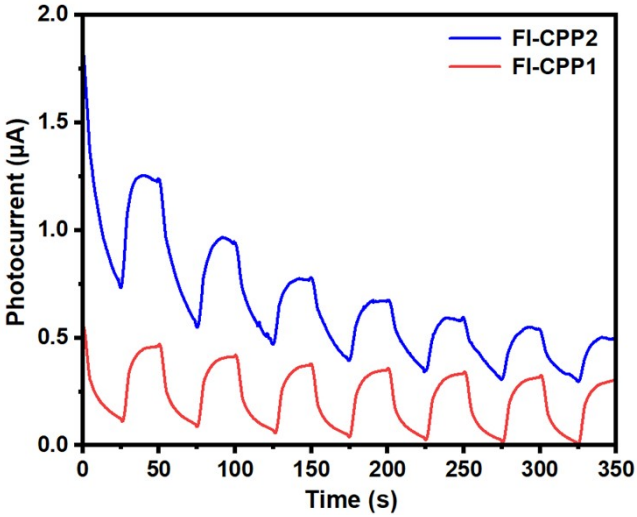


Fig. S7 Photocurrent measurements of FL-CPP1 and FL-CPP2.

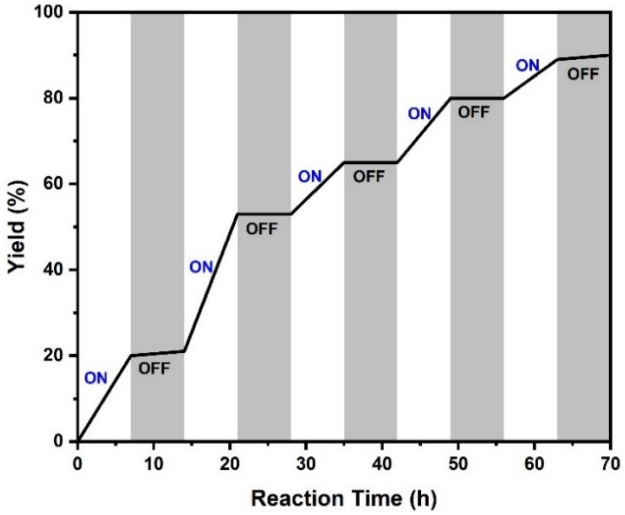


Fig. S8 Light-on/-off experiment.

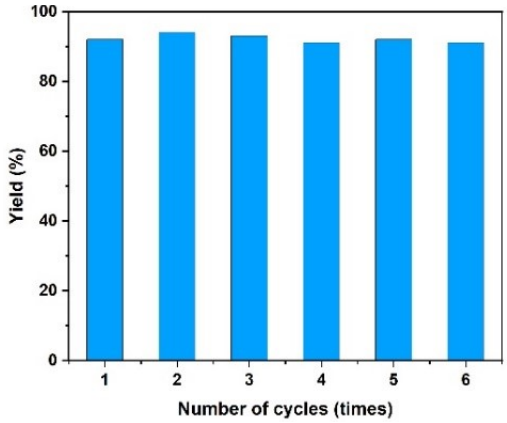


Fig. S9 Assessment of the reusability of FL-CPP2 in the visible-light induced [3+2] cycloaddition of **7a** with **8a**. The irregular trends of yields was caused by the errors during the product isolation process.

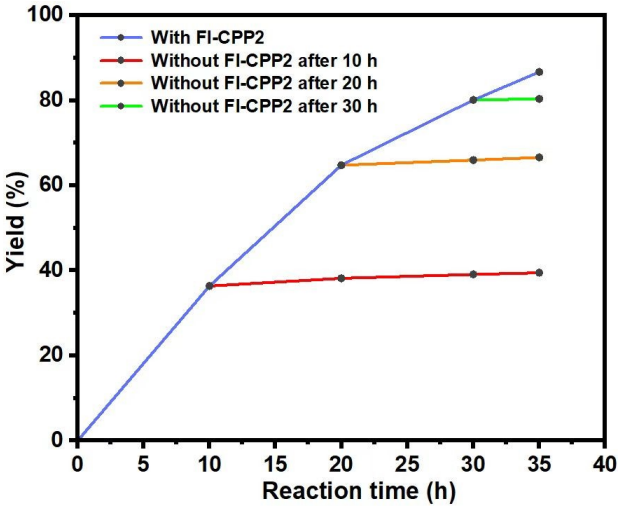


Fig. S10. Hot filtration experiment.

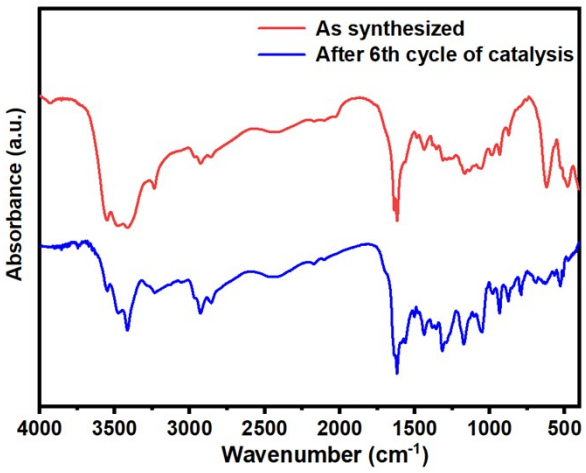


Fig. S11 FT-IR spectra of fresh (red) and recycled FL-CPP2 catalyst after 6 times of catalytic reactions (blue).

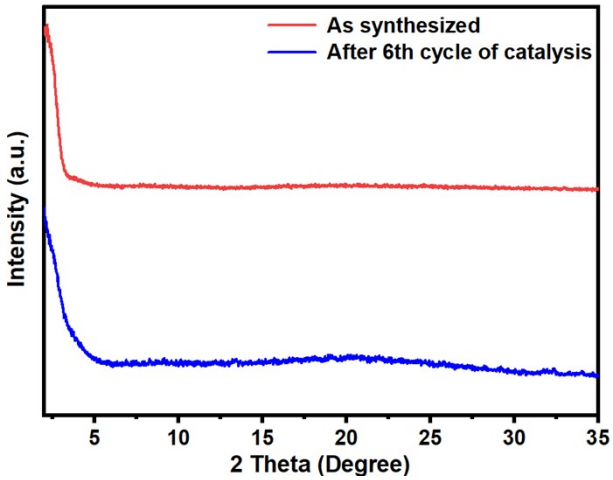
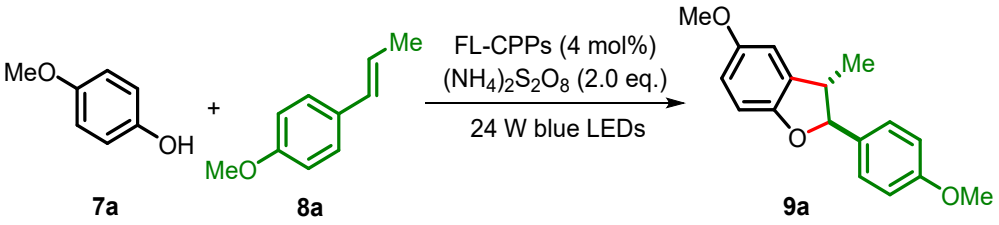


Fig. S12 PXRD patterns of fresh (red) and recycled FL-CPP2 catalyst after 6 times of catalytic reactions (blue).

F. Typical Procedure for Reaction

Table S1 Screening experiments of the visible-light induced [3+2] cycloaddition of phenol with olefin catalyzed by FL-CPPs.[a]



7a **8a** **9a**

Entry	Catalyst	Solvent	Yield (%)[b]
1	FL-CPP2	Toluene	19
2	FL-CPP2	1,4-Dioxane	48
3	FL-CPP2	DMF	12
4	FL-CPP2	THF	28
5	FL-CPP2	EtOH	45
6	FL-CPP2	MeOH	42
7	FL-CPP2	DCE	19
8	FL-CPP2	CH_3NO_2	50
9	FL-CPP2	CH_3CN	90
10	FL-CPP1	CH_3CN	74
11[c]	FL-CPP2	CH_3CN	63
12[d]	FL-CPP2	CH_3CN	99(93)[e]
13	**3**	CH_3CN	Trace
14		CH_3CN	NR
15[f]	FL-CPP2	CH_3CN	NR
16[g]	FL-CPP2	CH_3CN	NR
17[h]	FL-CPP2	CH_3CN	NR
18[i]	FL-CPP2	CH_3CN	41
19[j]	FL-CPP2	CH_3CN	NR
20[k]	FL-CPP2	CH_3CN	NR
21[l]	FL-CPP2	CH_3CN	NR
22[m]	FL-CPP2	CH_3CN	NR
23[n]	FL-CPP2	CH_3CN	NR

[a]Reaction conditions: **7a** (0.1 mmol), **8a** (0.3 mmol), FL-CPP (4 mol%), $(NH_4)_2S_2O_8$ (2.0 eq), solvent (2.0 mL), 24 W blue LED light at room temperature under argon. [b]Yield determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [c]0.2 mmol **8a**. [d]0.4 mmol **8a**. [e]Yield of isolated product. [f]No $(NH_4)_2S_2O_8$. [g]No light. [h]Addition of TEMPO. [i]Addition of $CuSO_4$. [j]Addition of KI. [k]Green LEDs was used. [l]Orange LEDs was used. [m]Red LEDs was used. [n]NIR LEDs (820 nm) was used.

General procedure for the visible-light induced oxidative [3+2] cycloaddition of phenols with olefins catalyzed by FL-CPPs.

A 20 mL vial equipped with a stir bar was charged with FL-CPPs (0.004 mmol) and CH_3CN (2 mL) under argon atmosphere. Subsequently, phenol **7** (0.1 mmol), olefin **8** (0.4 mmol) and $(NH_4)_2S_2O_8$ (0.2 mmol) were added. The reaction mixture was stirred at room temperature under 24 W blue LED irradiation. After the reaction was completed, the mixture was diluted with EtOAc, the catalyst was isolated via centrifugation, and thoroughly washed with EtOAc (6 times). The combined organic phase was concentrated under reduced pressure, and the residue was separated by silica gel column chromatography (petroleum ether/EtOAc) to obtain the product **9**.

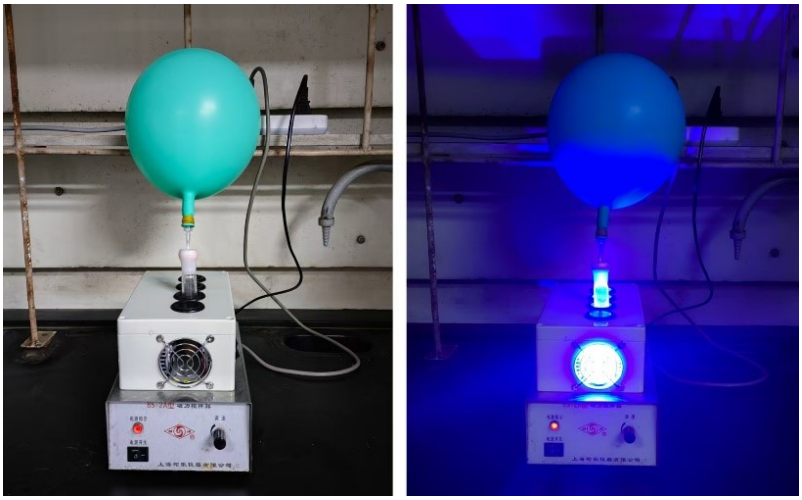
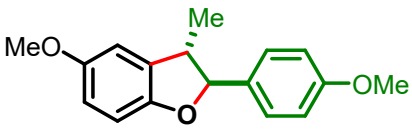
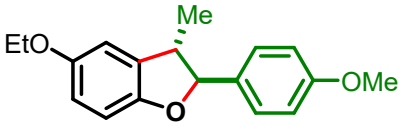


Fig. S13 Picture of photoreaction device.



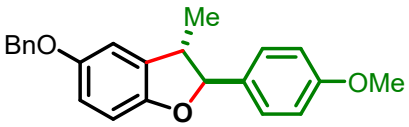
9a

5-**Methoxy-2-(4-methoxyphenyl)-3-methyl-2,3-dihydrobenzofuran (9a).**[7] Colorless oil (25.1 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 6.79-6.70 (m, 3H), 5.08 (d, J = 9.0 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.47-3.35 (m, 1H), 1.38 (d, J = 6.8, 1.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 154.5, 153.4, 133.2, 132.8, 127.8, 114.1, 113.0, 110.2, 109.5, 92.7, 56.2, 55.4, 45.8, 17.7.



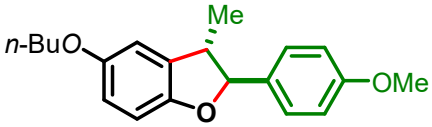
9b

5-Ethoxy-2-(4-methoxyphenyl)-3-methyl-2,3-dihydrobenzofuran (9b).[8] White solid (29.0 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 8.6 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 6.76-6.69 (m, 3H), 5.08 (dd, J = 9.1, 2.5 Hz, 1H), 3.99 (q, J = 7.0, 2H), 3.82 (s, 3H), 3.47-3.35 (m, 1H), 1.43-1.33 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 153.8, 153.4, 133.2, 132.9, 127.8, 114.1, 113.0, 110.2, 109.5, 92.7, 56.2, 55.4, 45.8, 17.7, 15.2.



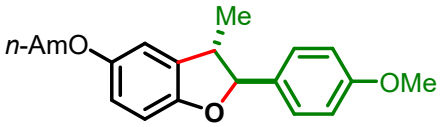
9c

5-(Benzyloxy)-2-(4-methoxyphenyl)-3-methyl-2,3-dihydrobenzofuran (9c).[7] White solid (26.0 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.33 (m, 7H), 6.91-6.89 (m, 2H), 6.82-6.73 (m, 3H), 5.07 (d, J = 9.1 Hz, 1H), 5.01 (s, 2H), 3.80 (s, 3H), 3.44-3.36 (m, 1H), 1.36 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 153.7, 153.6, 137.5, 133.2, 132.7, 128.6, 128.0, 127.7, 127.6, 114.1, 114.0, 111.4, 109.4, 92.7, 71.1, 55.4, 45.8, 17.7.



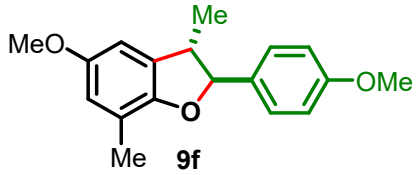
9d

5-Butyl-2-(4-methoxyphenyl)-3-methyl-2,3-dihydrobenzofuran (9d).[9] White solid (24.0 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.64 Hz, 2H), 6.91 (d, d, J = 8.72 Hz, 2H), 6.76-6.71 (m, 3H), 5.07 (d, J = 9.1 Hz, 1H), 3.92 (t, J = 6.5 Hz, 2H), 3.82 (s, 3H), 3.43-3.38 (m, 1H), 1.78-1.72 (m, 2H), 1.53-1.47 (m, 2H), 1.36 (d, J = 6.7 Hz, 3H), 0.97 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 154.1, 153.3, 133.2, 132.8, 127.7, 114.1, 113.8, 111.0, 109.4, 92.7, 68.8, 55.5, 45.8, 31.7, 19.4, 17.7, 14.0.



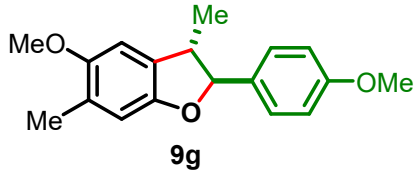
9e

2-(4-Methoxyphenyl)-3-methyl-5-(pentyloxy)-2,3-dihydrobenzofuran (9e).[9] White solid (23.8 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.32 (m, 2H), 6.96-6.87 (m, 2H), 6.78-6.66 (m, 3H), 5.07 (d, J = 9.2 Hz, 1H), 3.91 (t, J = 6.6 Hz,2H), 3.82 (s, 3H), 3.47-3.35 (m, 1H), 1.77 (p, J = 6.6 Hz, 2H), 1.51-1.34 (m, 7H), 0.94 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 153.9, 153.1, 133.1, 132.7, 127.7, 114.0, 113.6, 110.9, 109.3, 92.6, 68.9, 55.3, 45.7, 29.2, 28.3, 22.5, 17.5, 14.1.



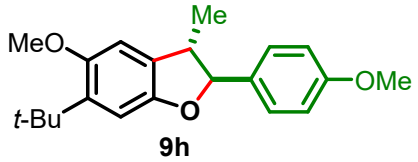
9f

5-Methoxy-2-(4-methoxyphenyl)-3,7-dimethyl-2,3-dihydrobenzofuran (9f).[7] White solid (27.3 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 6.56 (s, 2H), 5.06 (d, J = 9.1 Hz, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 3.43-3.36 (m, 1H), 2.23 (s, 3H), 1.36 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 154.4, 151.9, 133.2, 132.3, 127.8, 120.0, 114.7, 114.1, 107.2, 92.3, 56.2, 55.5, 46.2, 17.8, 15.6.



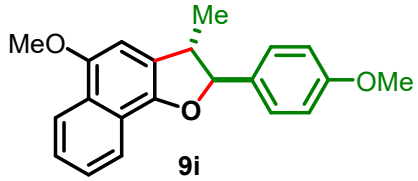
9g

5-Methoxy-2-(4-methoxyphenyl)-3,6-dimethyl-2,3-dihydrobenzofuran (9g).[7] White solid (21.0 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H), 6.57 (s, 2H), 5.06 (d, J = 9.1 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.42-3.37 (m, 1H), 2.24 (s, 3H), 1.37 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 154.4, 151.9, 133.1, 132.3, 127.8, 120.0, 114.7, 114.1, 107.2, 92.3, 56.2, 55.5, 46.2, 17.8, 15.6.



9h

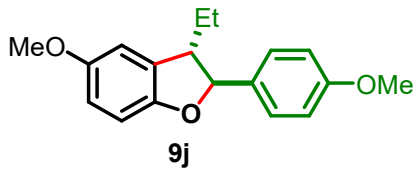
6-(*Tert*-butyl)-5-methoxy-2-(4-methoxyphenyl)-3-methyl-2,3-dihydrobenzofuran (9h).[7] White solid (27.7 mg, 85%).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.35 (m, 2H), 6.93-6.88 (m, 2H), 6.85 (s, 1H), 6.71 (s, 1H), 5.06 (d, J = 9.2 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.44-3.40 (m, 1H), 1.41-1.36 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 153.5, 153.0, 138.7, 133.1, 129.3, 127.8, 114.1, 108.1, 108.0, 92.7, 56.2, 55.5, 46.0, 35.1, 30.0, 17.7.



9i

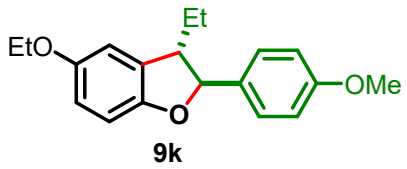
5-Methoxy-2-(4-methoxyphenyl)-3-methyl-2,3-dihydronaphtho[1,2-b]furan (9i).[7] Faint yellow solid (22.0 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (dd, J = 8.3, 1.6 Hz, 1H), 7.96 (dd, J = 7.3, 1.7 Hz, 1H), 7.51-7.38 (m, 4H), 6.97-6.87 (m, 2H), 6.68 (s, 1H), 5.29 (d, J = 8.5 Hz, 1H), 3.99 (s, 3H), 3.82 (s, 3H), 3.65-3.57 (m, 1H), 1.49 (d, J = 6.8 Hz, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$): δ 159.7, 150.5, 148.0, 133.6, 127.7, 126.1, 125.6, 125.1, 123.5, 122.6, 121.4, 121.0, 114.1, 100.7, 92.7, 56.2, 55.5, 47.2, 18.9.



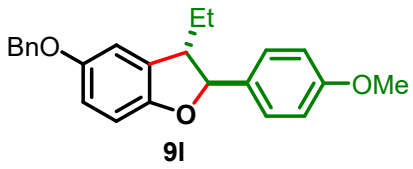
9j

3-Ethyl-5-methoxy-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran (9j).[7] White solid (26.0 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.78-6.71 (m, 3H), 5.27 (d, J = 6.8 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.36-3.31 (m, 1H), 1.86-1.76 (m, 2H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 154.3, 153.7, 134.3, 131.6, 127.6, 114.1, 113.1, 111.0, 109.3, 89.9, 56.2, 55.4, 52.3, 27.4, 11.4.



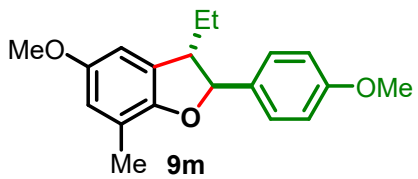
9k

5-Ethoxy-3-ethyl-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran (9k). White solid (25.4 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 6.79-6.68 (m, 3H), 5.26 (d, J = 6.8 Hz, 1H), 3.99 (q, J = 7.0 Hz, 2H), 3.80 (s, 3H), 3.35-3.30 (m, 1H), 1.85-1.74 (m, 2H), 1.40 (t, J = 7.0 Hz, 3H), 1.01 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 153.7, 153.6, 134.3, 131.6, 127.6, 114.1, 113.9, 111.8, 109.3, 89.9, 64.5, 55.4, 52.3, 27.3, 15.2, 11.4. HRMS (ESI) calcd for $C_{19}H_{22}O_3Na$ (M+Na$^+$) 321.1461, found 321.1451.



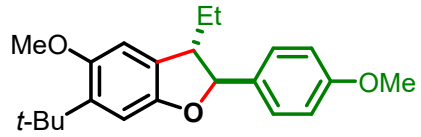
9l

5-(Benzyloxy)-3-ethyl-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran (9l). White solid (30.0mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.28 (m, 7H), 6.68-6.72 (m, 5H), 5.25 (d, J = 6.8 Hz, 1H), 5.00 (s, 2H), 3.80 (s, 3H), 3.34-3.29 (m, 1H), 1.89-1.70 (m, 2H), 0.98 (t, J = 12.8 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 153.9, 153.6, 137.5, 134.2, 131.7, 128.7, 128.0, 127.7, 127.6, 114.3, 114.1, 112.2, 109.3, 89.9, 71.3, 55.4, 52.3, 27.3, 11.4. HRMS (ESI) calcd for $C_{24}H_{24}O_3Na$ (M+Na$^+$) 383.1618, found: 383.1604.



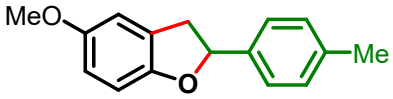
9m

3-Ethyl-5-methoxy-2-(4-methoxyphenyl)-7-methyl-2,3-dihydrobenzofuran (9m). White solid (22.0 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.60-6.55 (m, 2H), 5.25 (d, J = 6.8 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.33-3.26 (m, 1H), 2.24 (s, 3H), 1.86-1.73 (m, 2H), 1.02 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 154.2, 152.1, 134.6, 130.6, 127.5, 119.8, 114.8, 114.1, 107.9, 89.4, 56.1, 55.4, 52.8, 27.4, 15.7, 11.4. HRMS (ESI) calcd for $C_{19}H_{22}O_3Na$ ($M+Na^+$) 321.1461, found 321.1450.



9n

6-(*Tert*-butyl)-3-ethyl-5-methoxy-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran (9n). White solid (26.1 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.31 (m, 2H), 6.91-6.88 (m, 2H), 6.85 (s, 1H), 6.74 (s, 1H), 5.23 (d, J = 9.2 Hz, 1H), 3.81 (s, 3H), 3.82 (s, 3H), 3.36-3.31 (m, 1H), 1.91-1.71 (m, 2H) , 1.37 (s, 9H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 153.3, 153.2, 138.8, 134.4, 127.7, 127.6, 114.1, 108.8, 107.9, 90.0, 56.2, 55.4, 52.5, 35.1, 30.0, 27.5, 11.6. HRMS (ESI) calcd for $C_{22}H_{28}O_3Na$ ($M+Na^+$) 363.1931, found 363.1915.



9o

5-Methoxy-2-(p-tolyl)-2,3-dihydrobenzofuran (9o).[8] White solid (13.9 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 6.78-6.74 (m, 2H), 6.69 (dd, J = 8.6, 2.6 Hz, 1H), 5.70 (t, J = 8.8 Hz, 1H), 3.77 (s, 3H), 3.57 (dd, J = 15.7, 9.2 Hz, 1H), 3.19 (dd, J = 15.7, 8.3 Hz, 1H), 2.35 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 154.4, 154.0, 139.1, 137.9, 129.4, 127.8, 126.0, 113.1, 111.3, 109.3, 84.4, 56.2, 39.0, 21.3.

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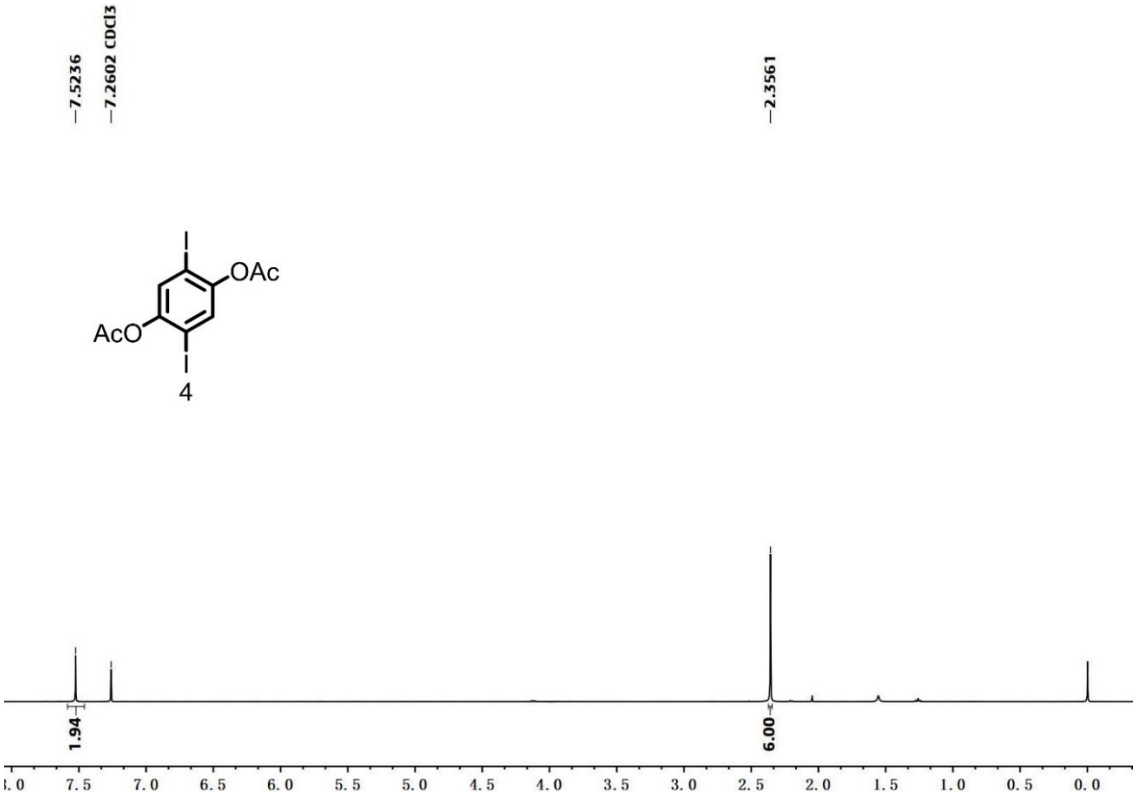
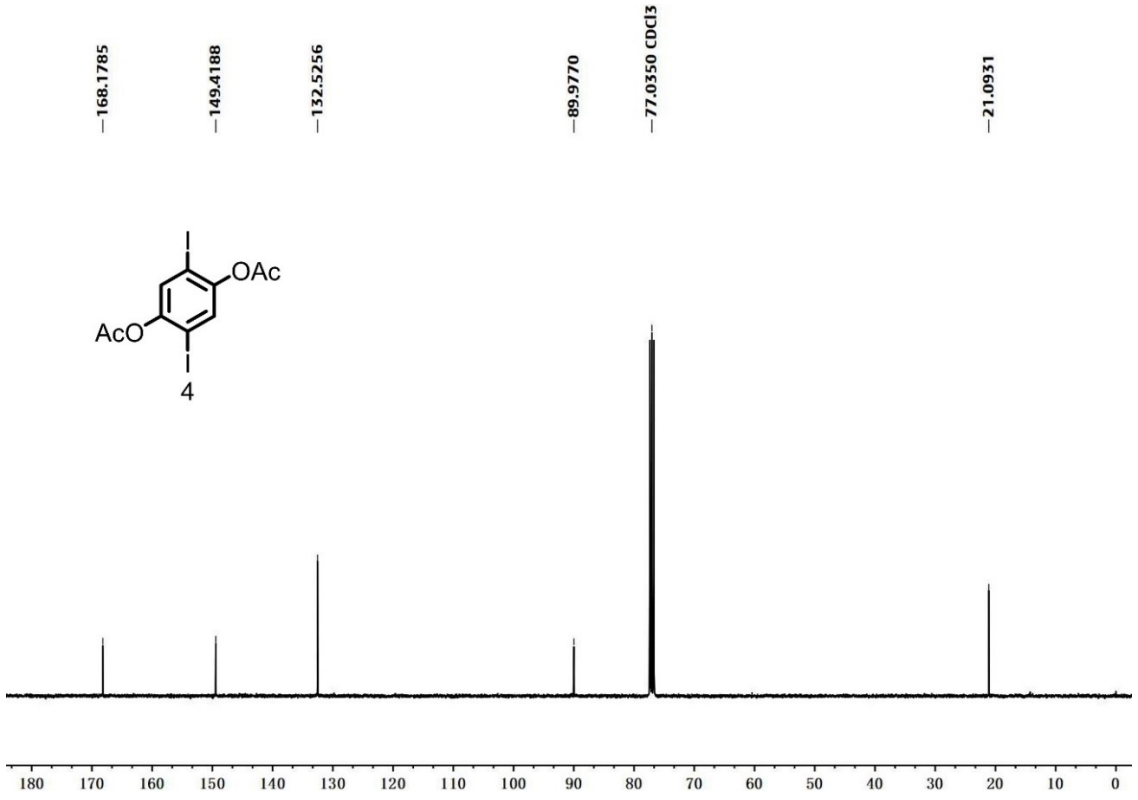
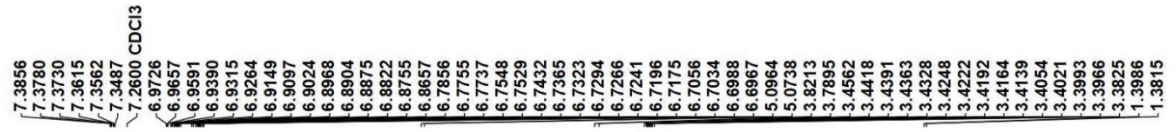
H. Copies of ^{1}H and ^{13}C NMR Spectra



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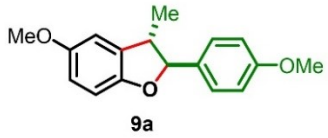
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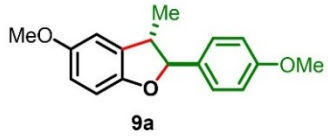
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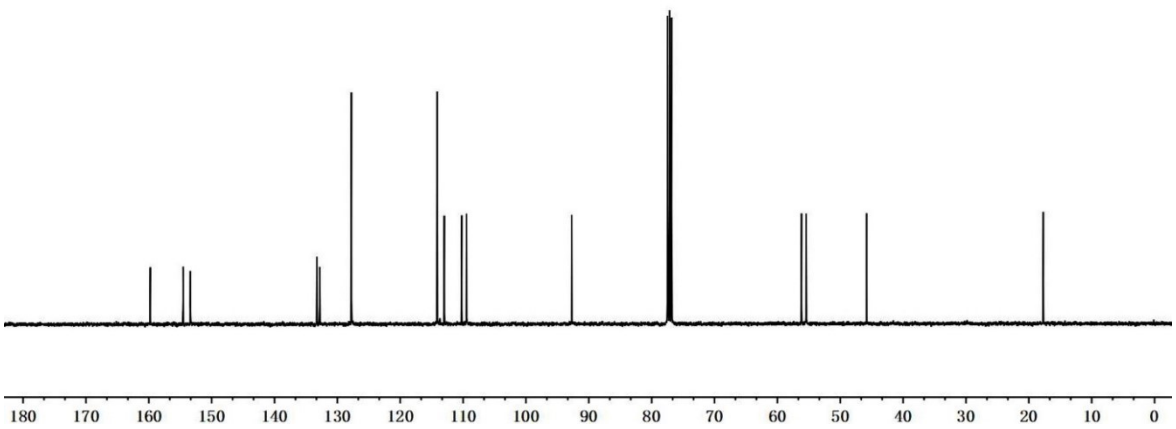
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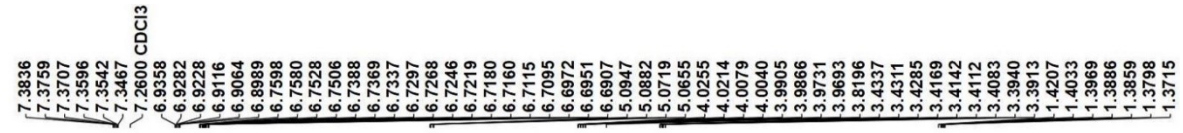
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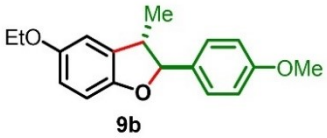
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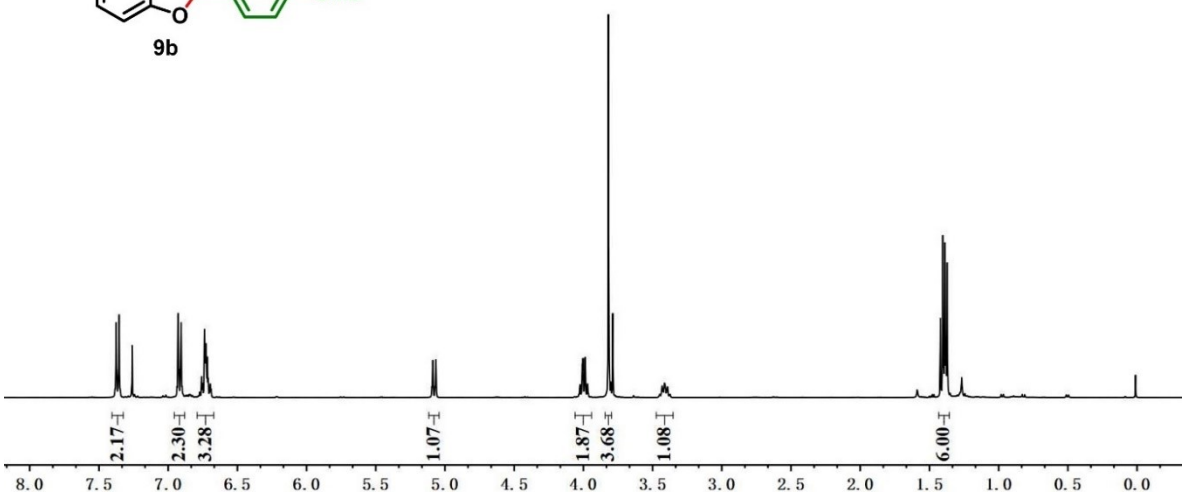
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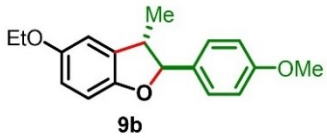
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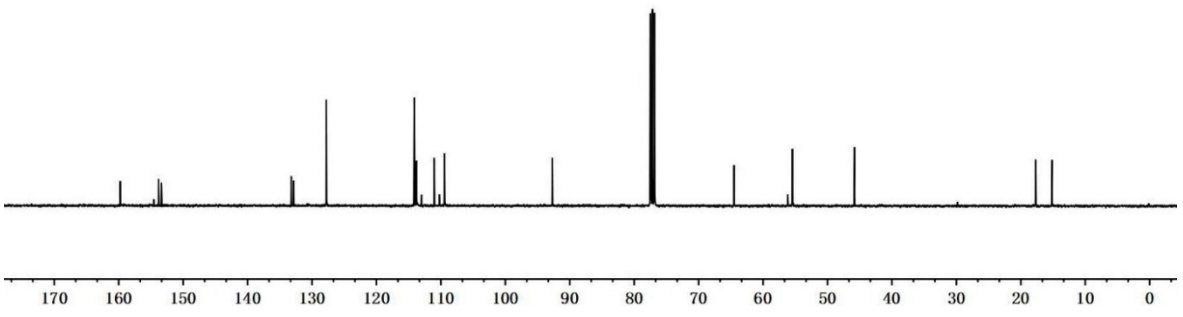
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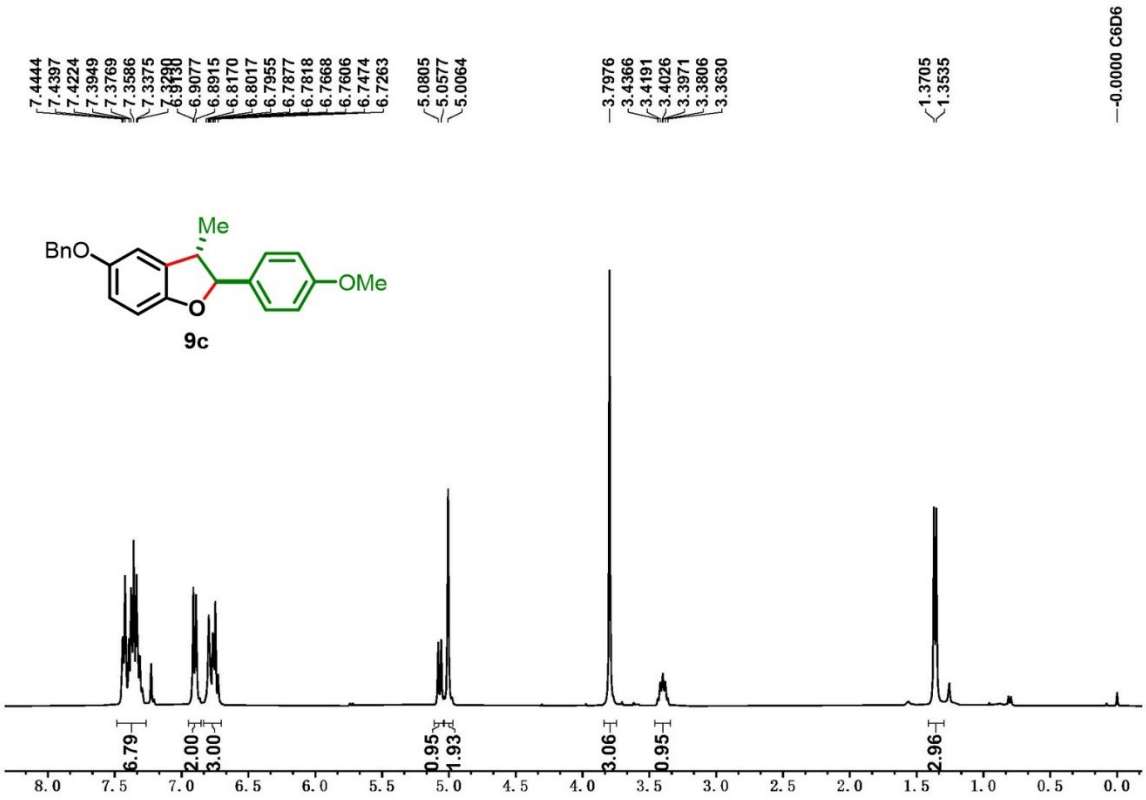
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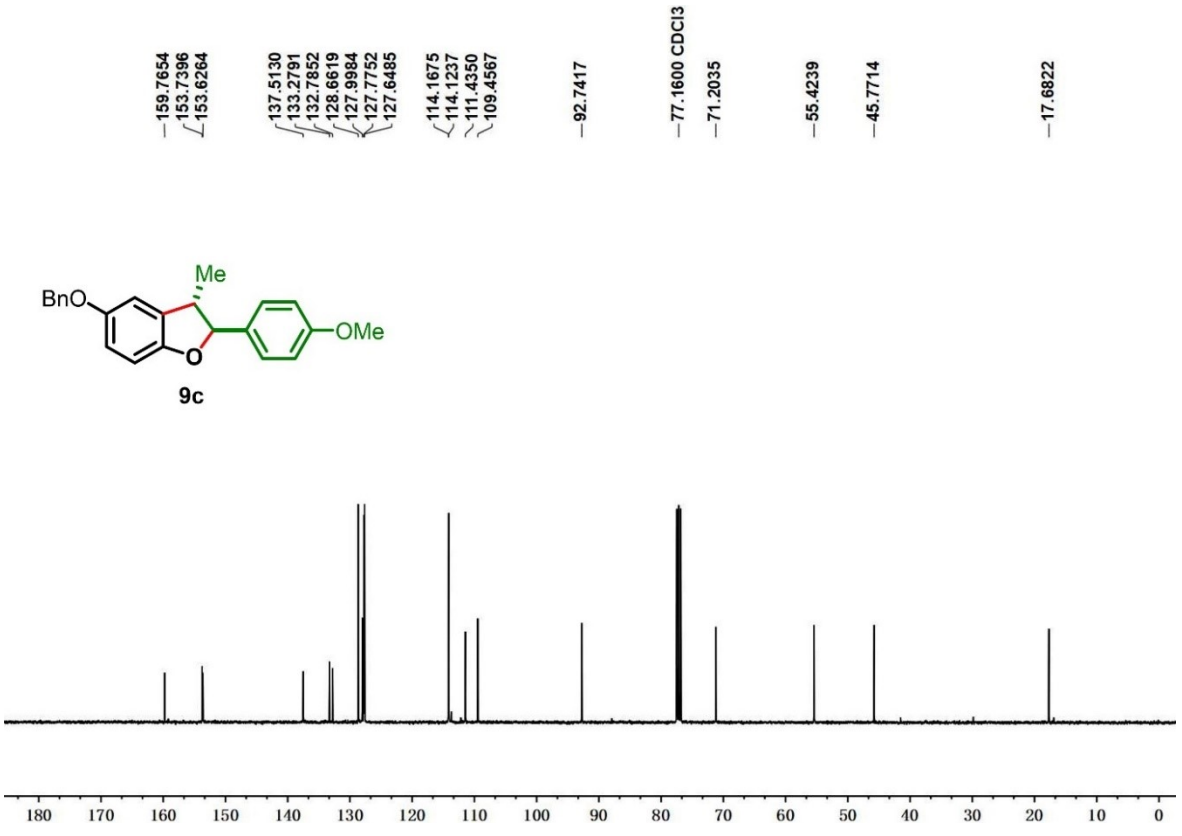
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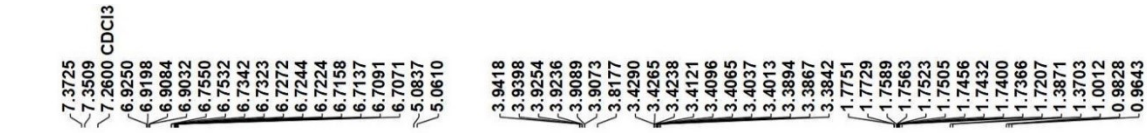
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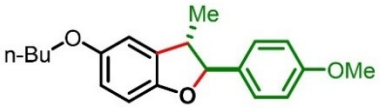
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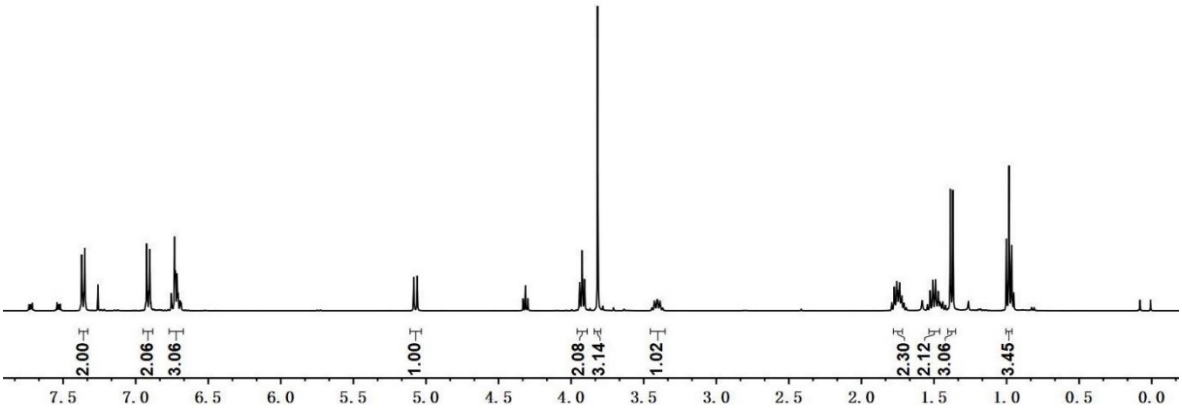
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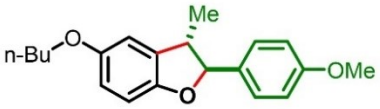
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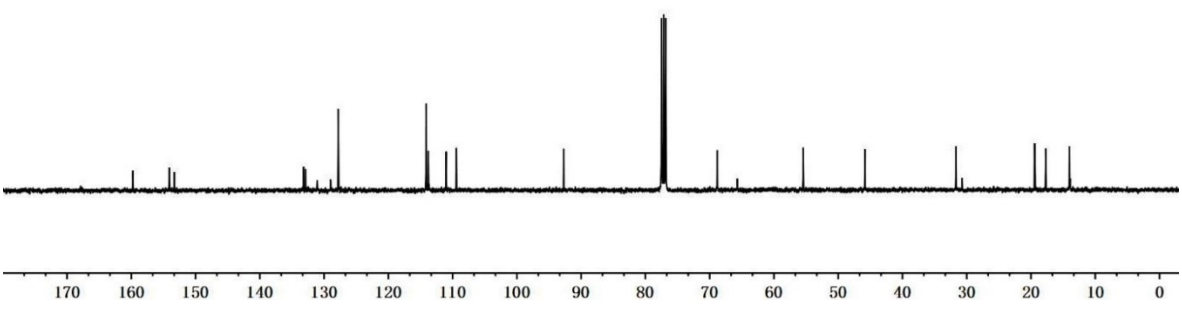
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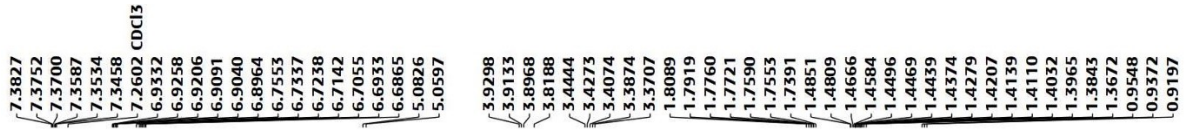
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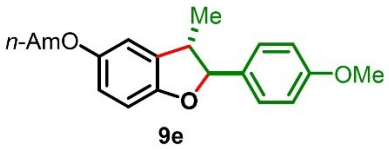
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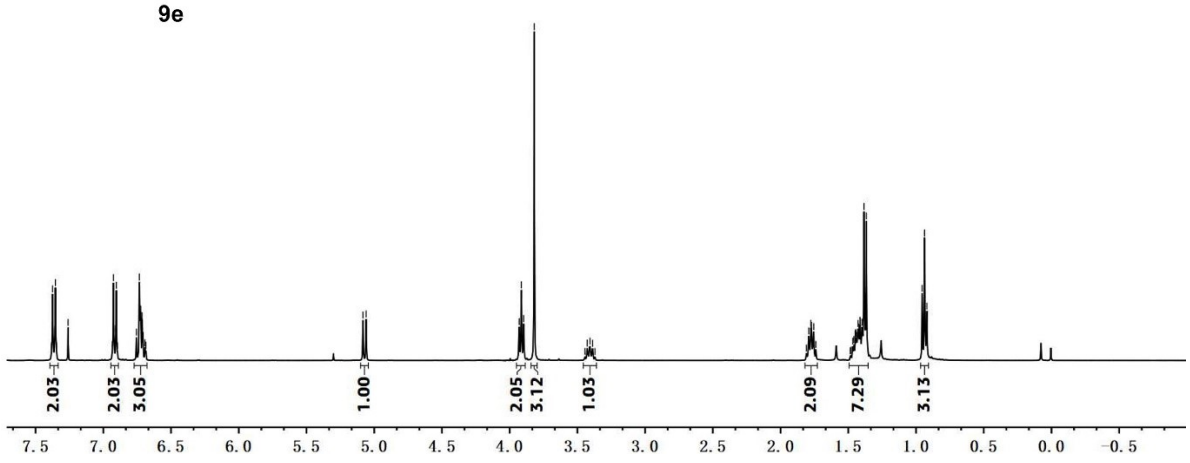
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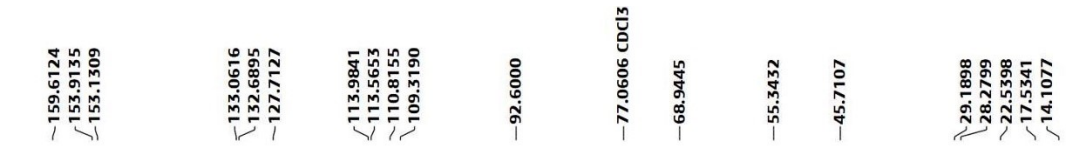
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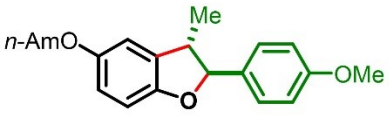
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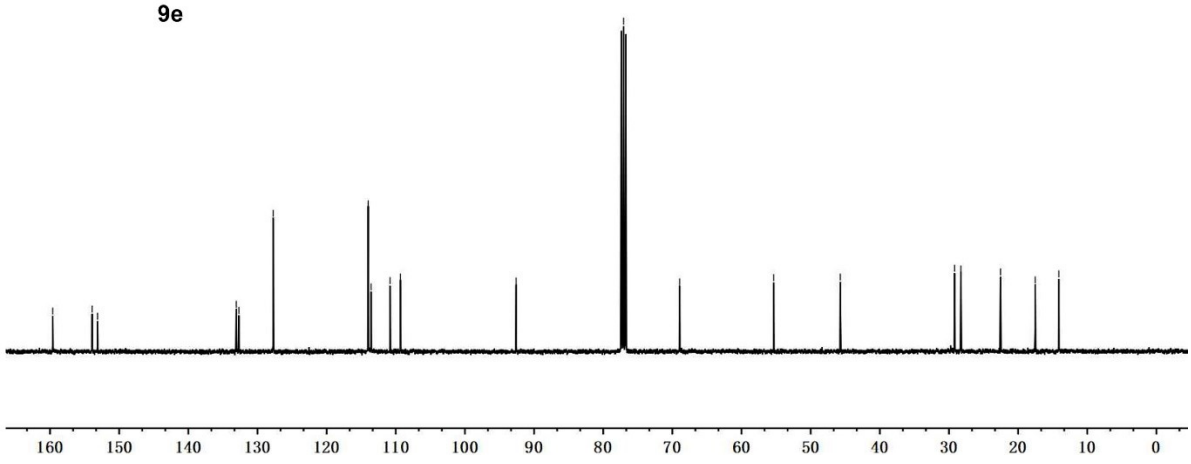
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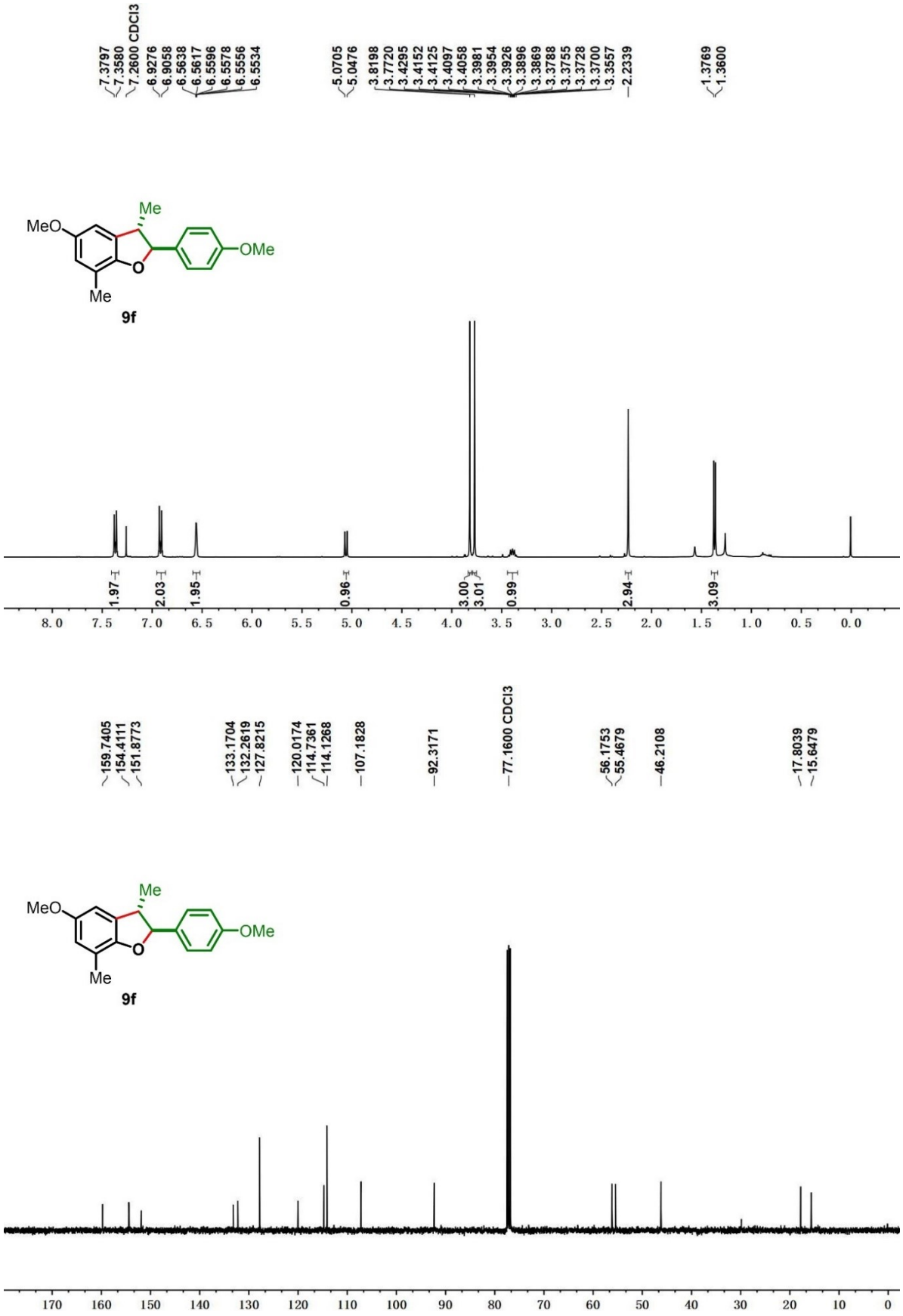
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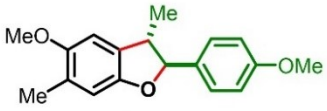
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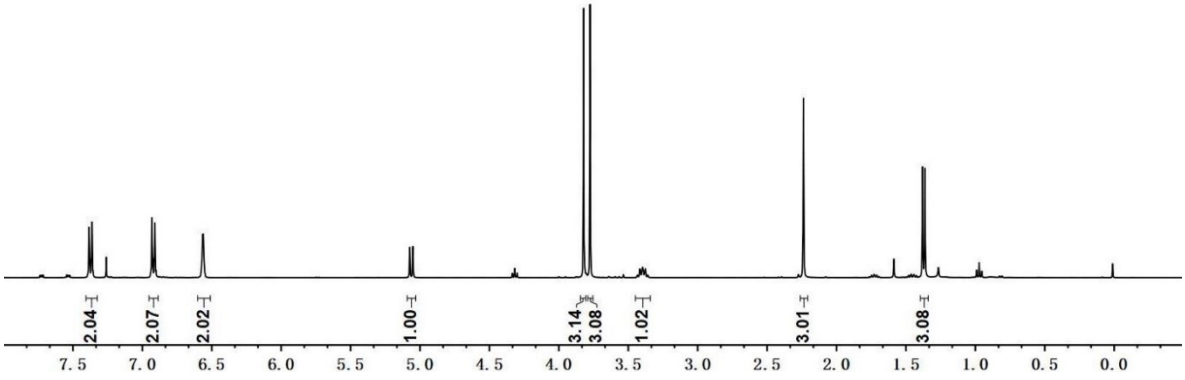
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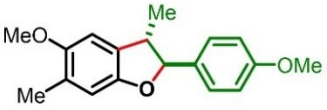
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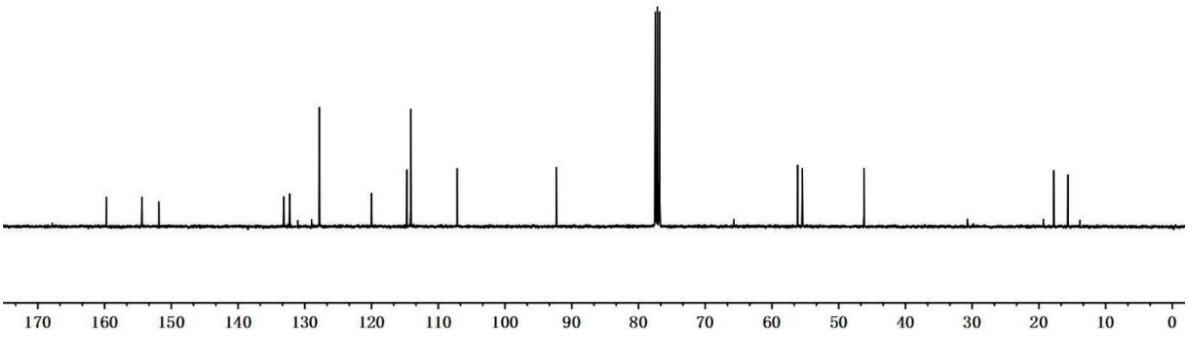
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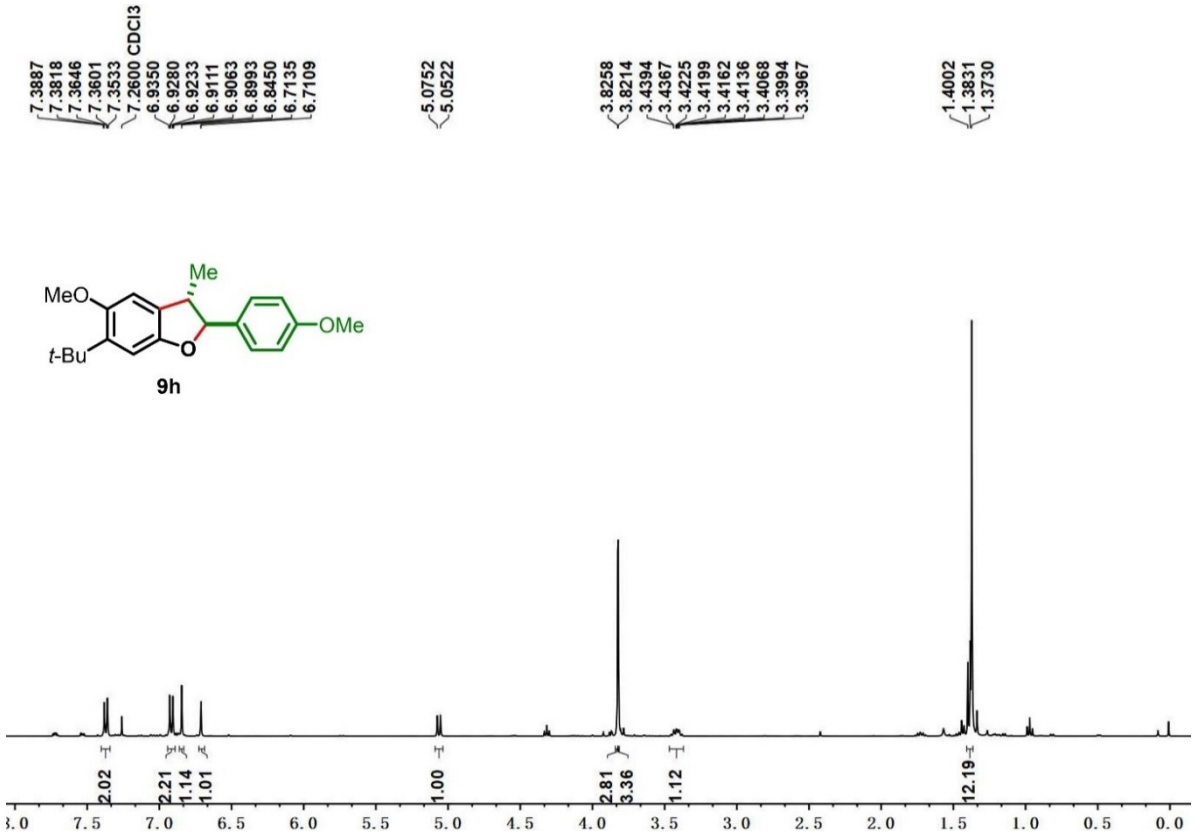
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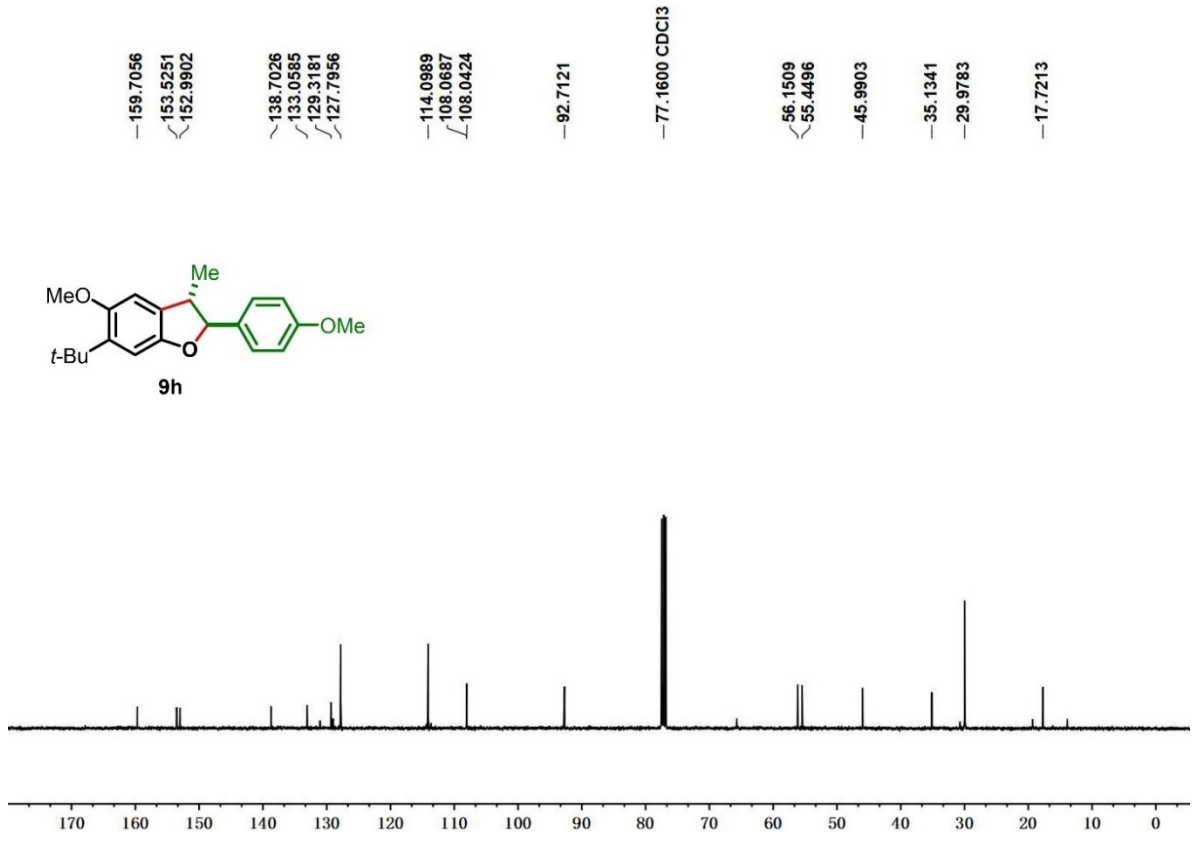
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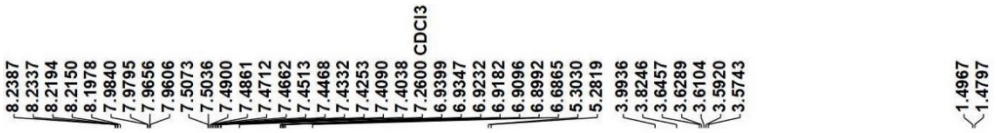
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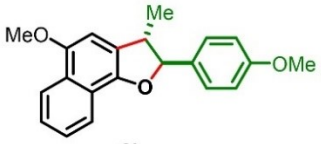
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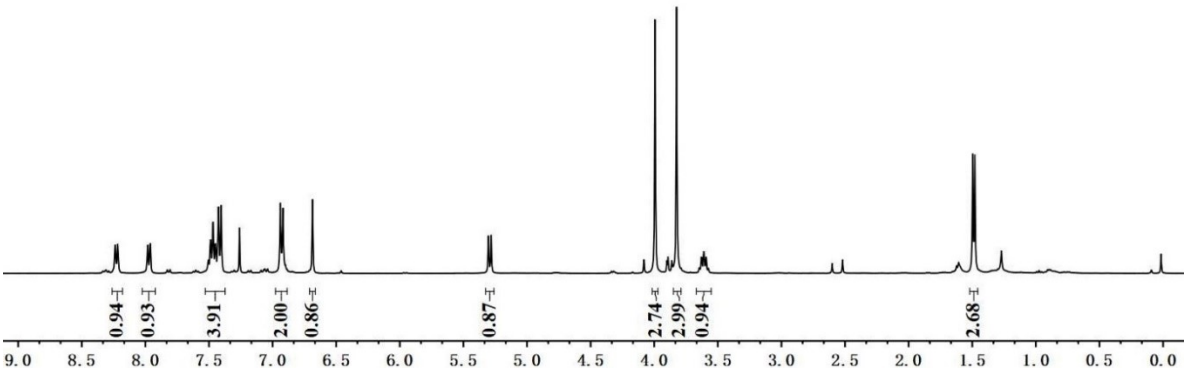
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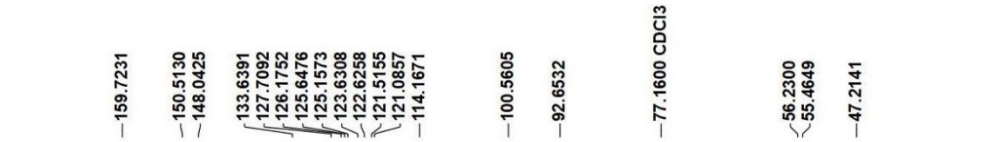
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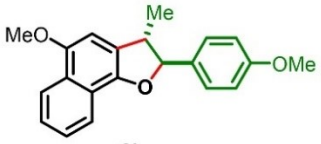
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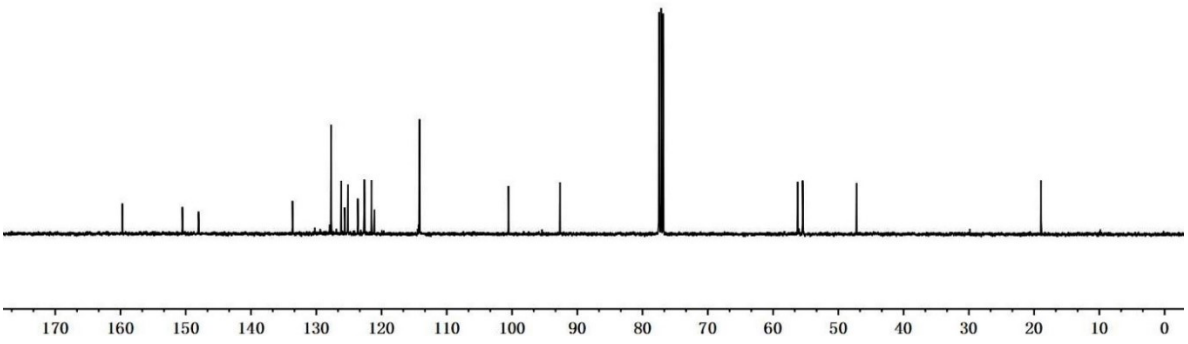
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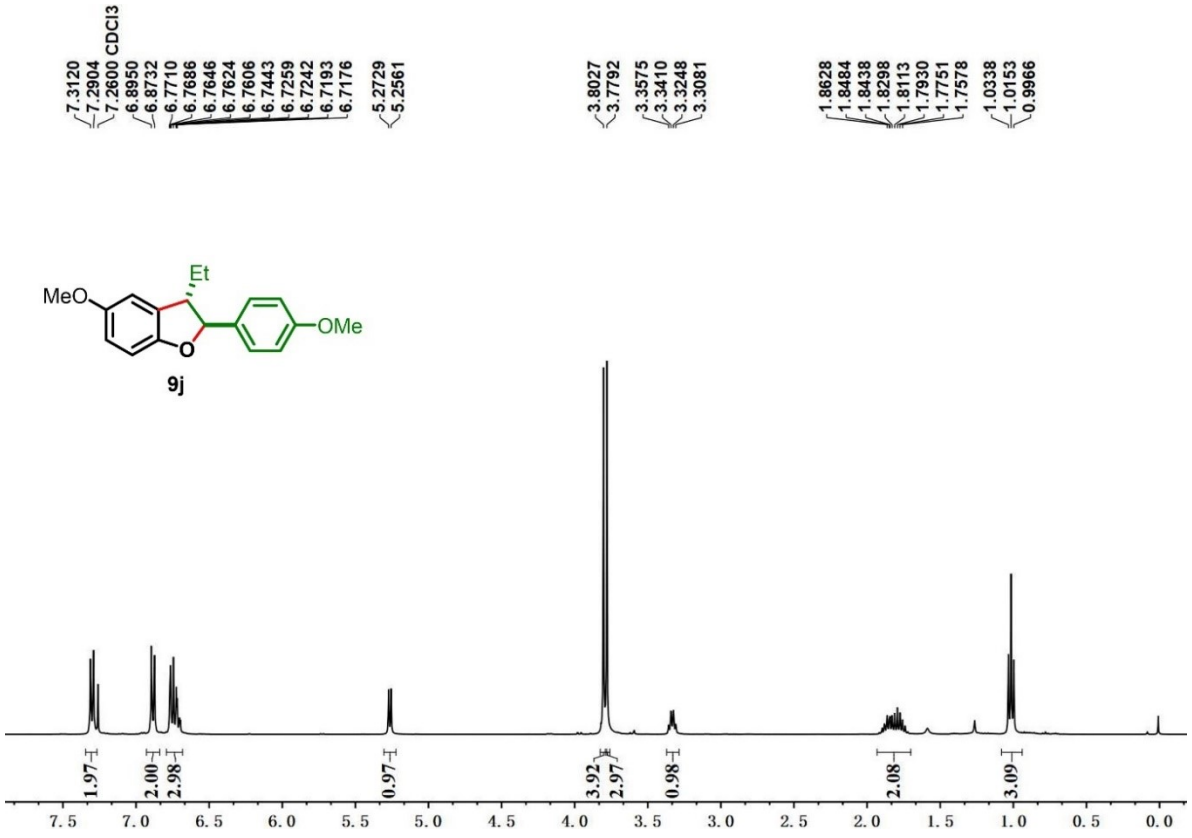
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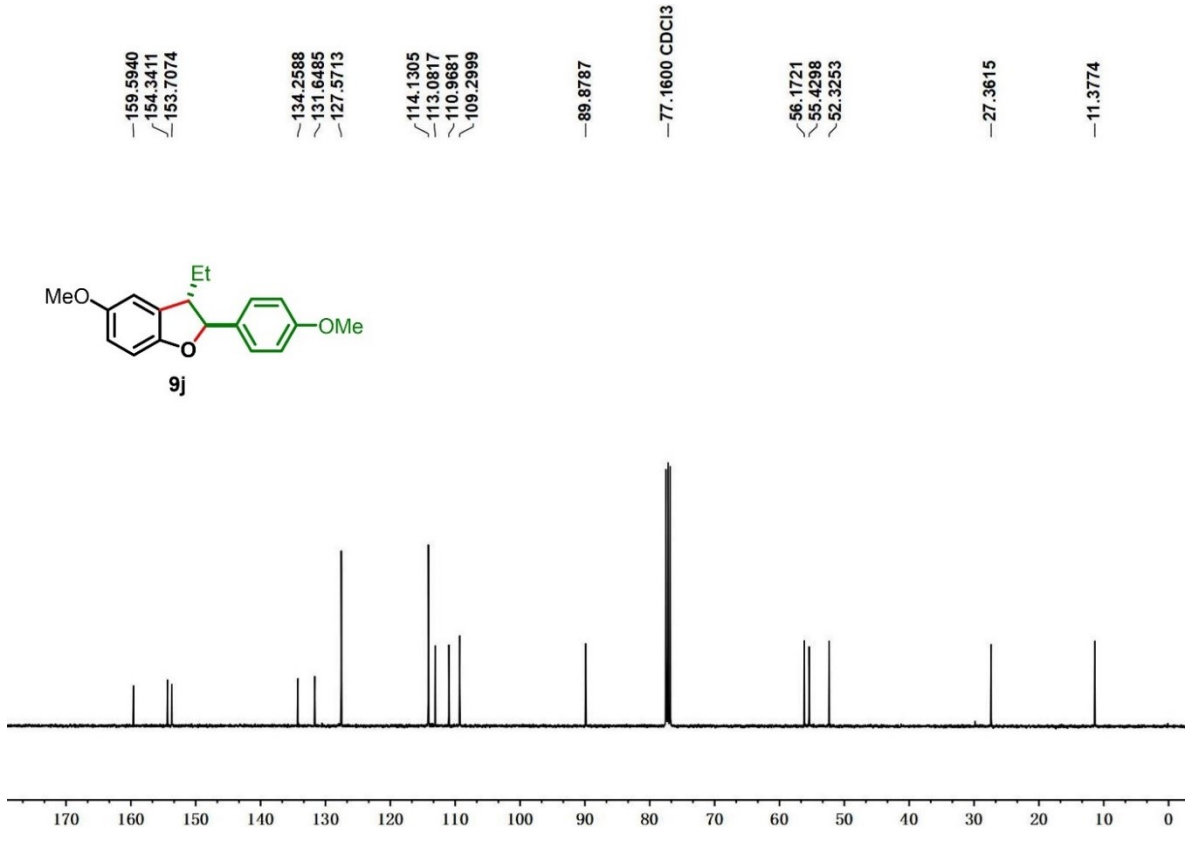
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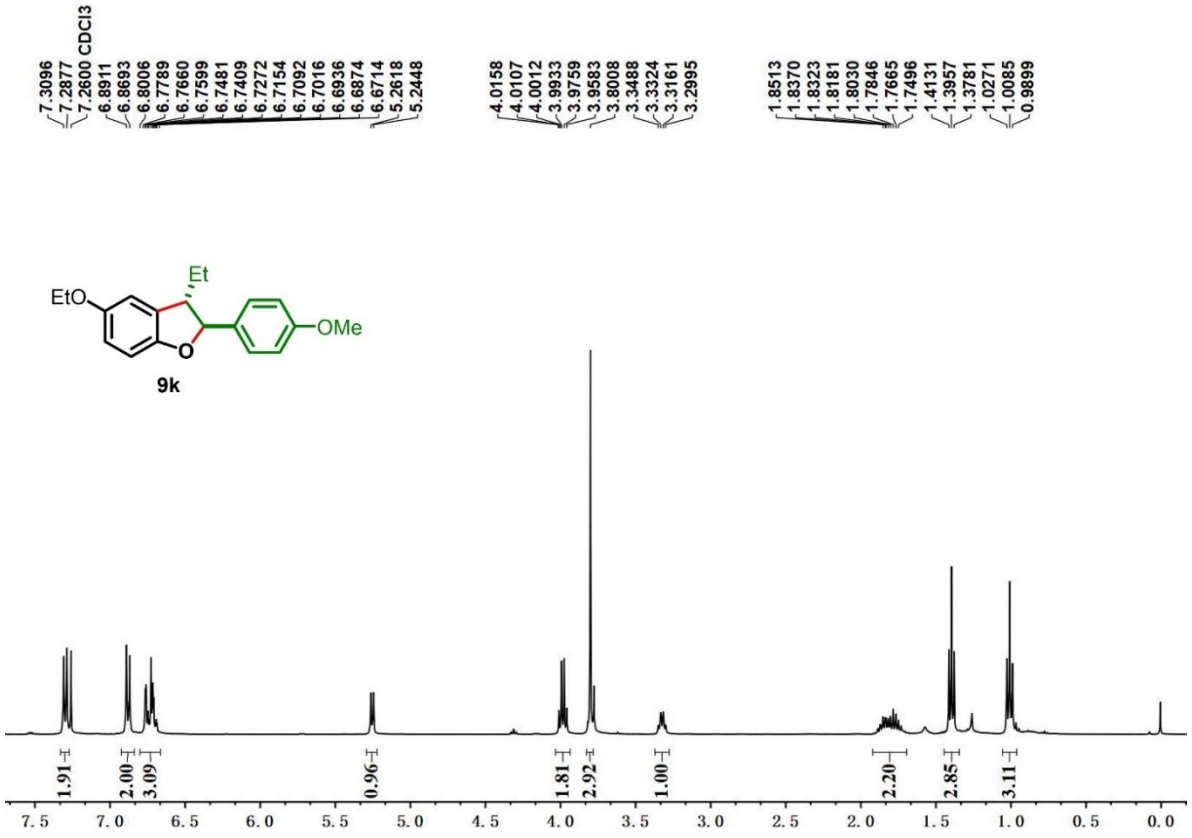
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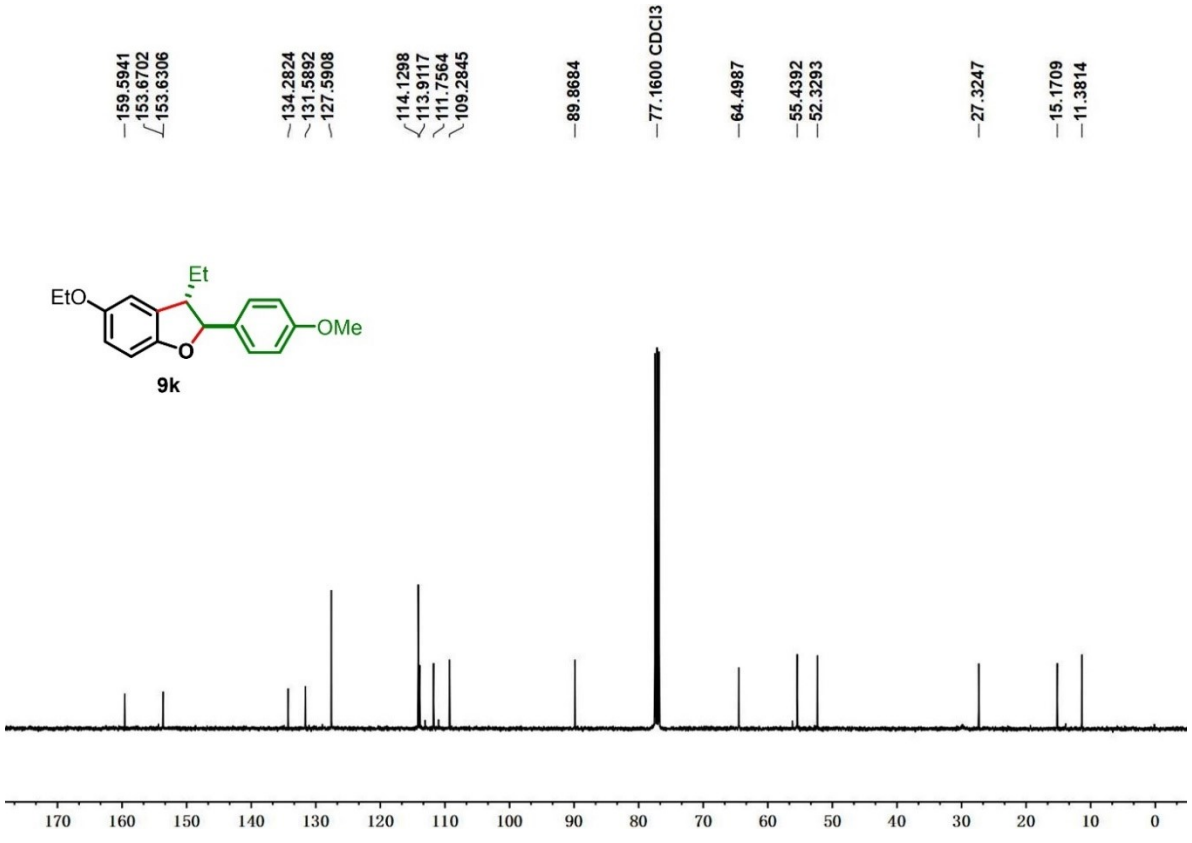
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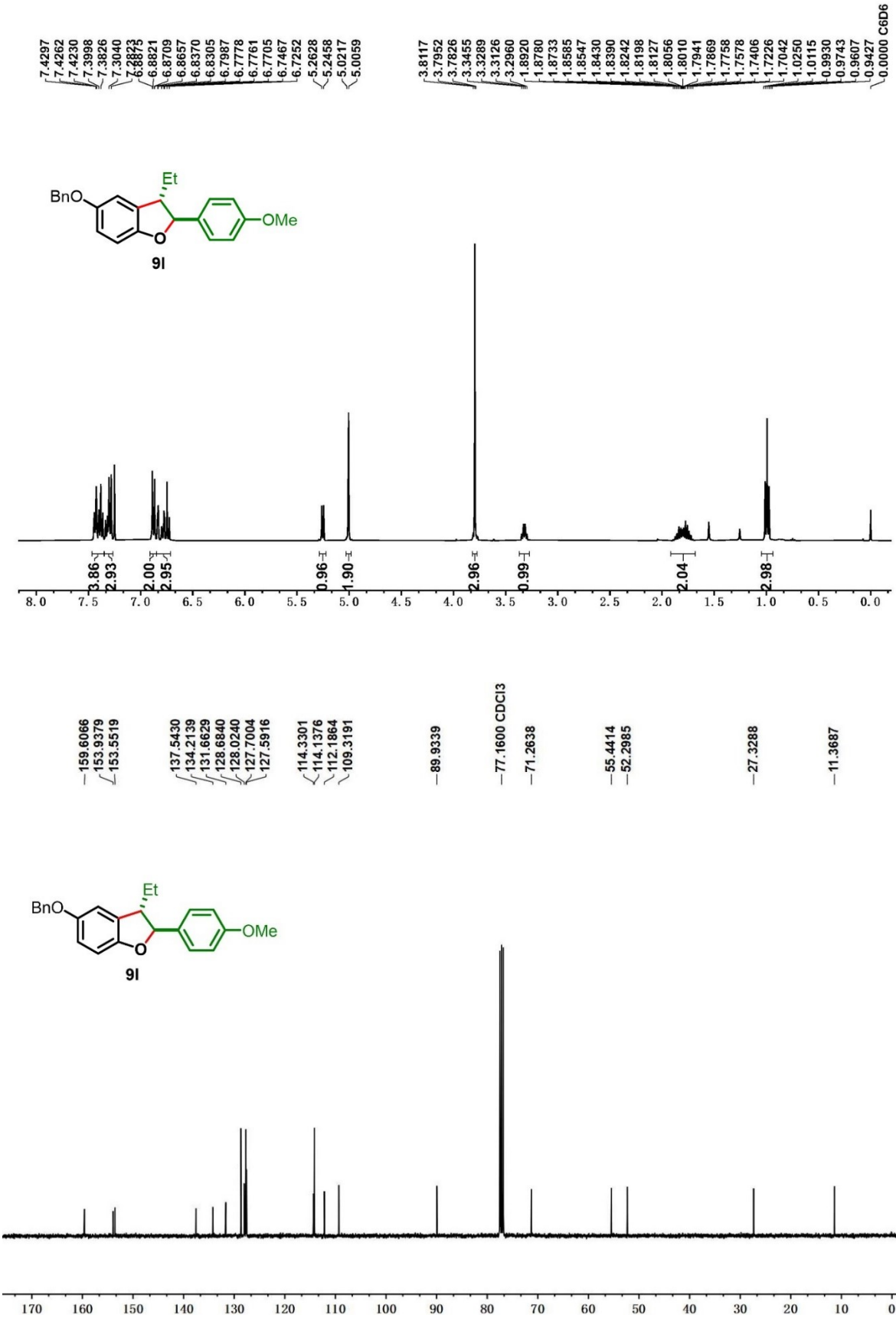
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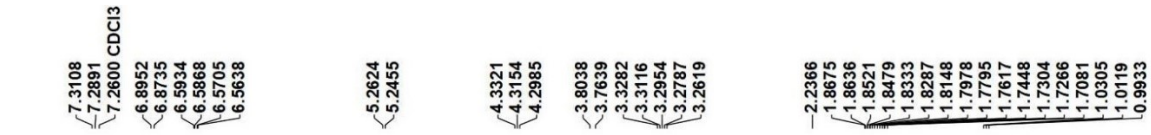
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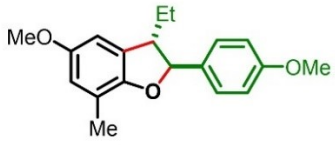
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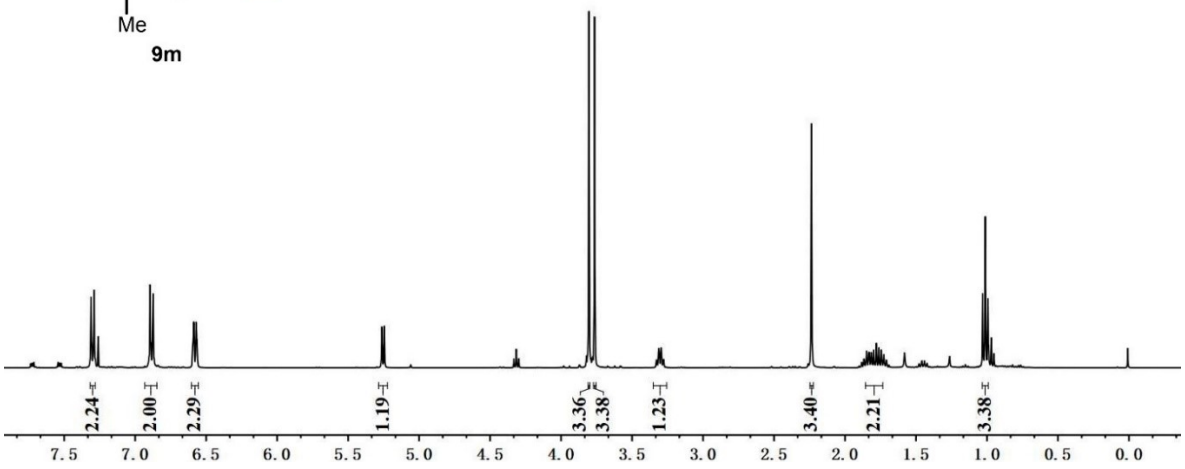
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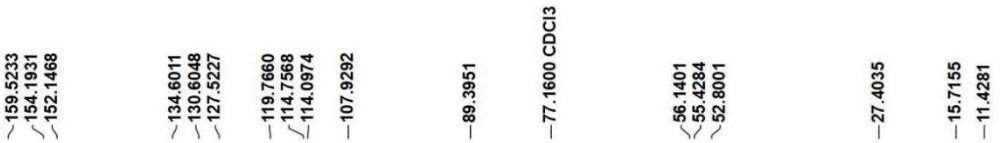
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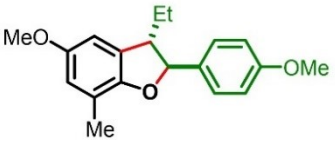
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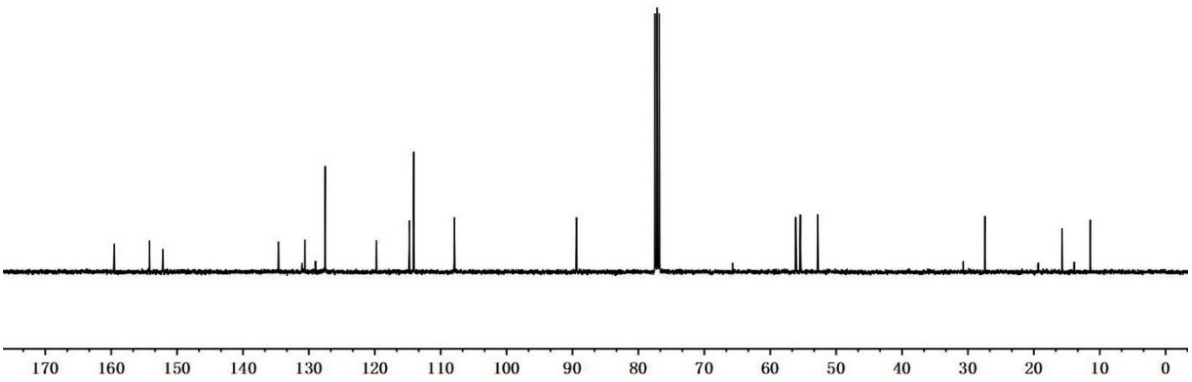
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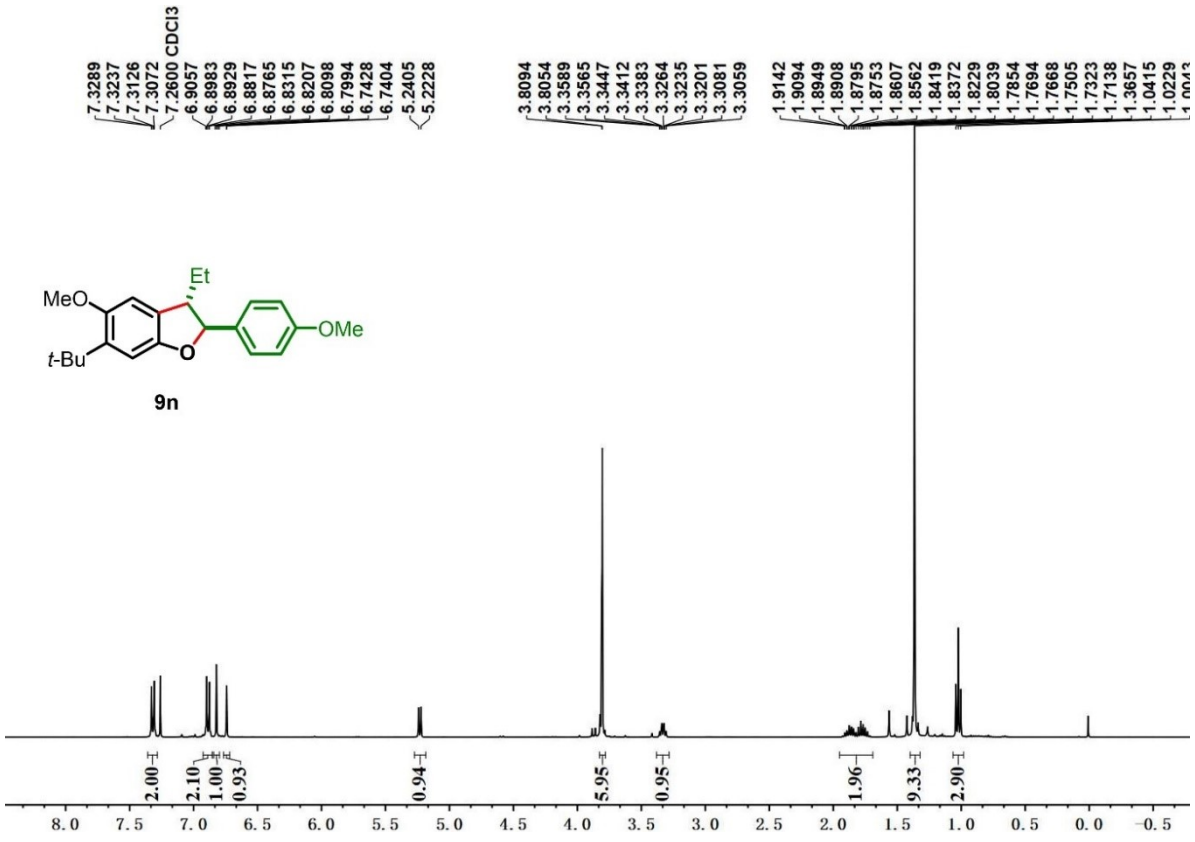
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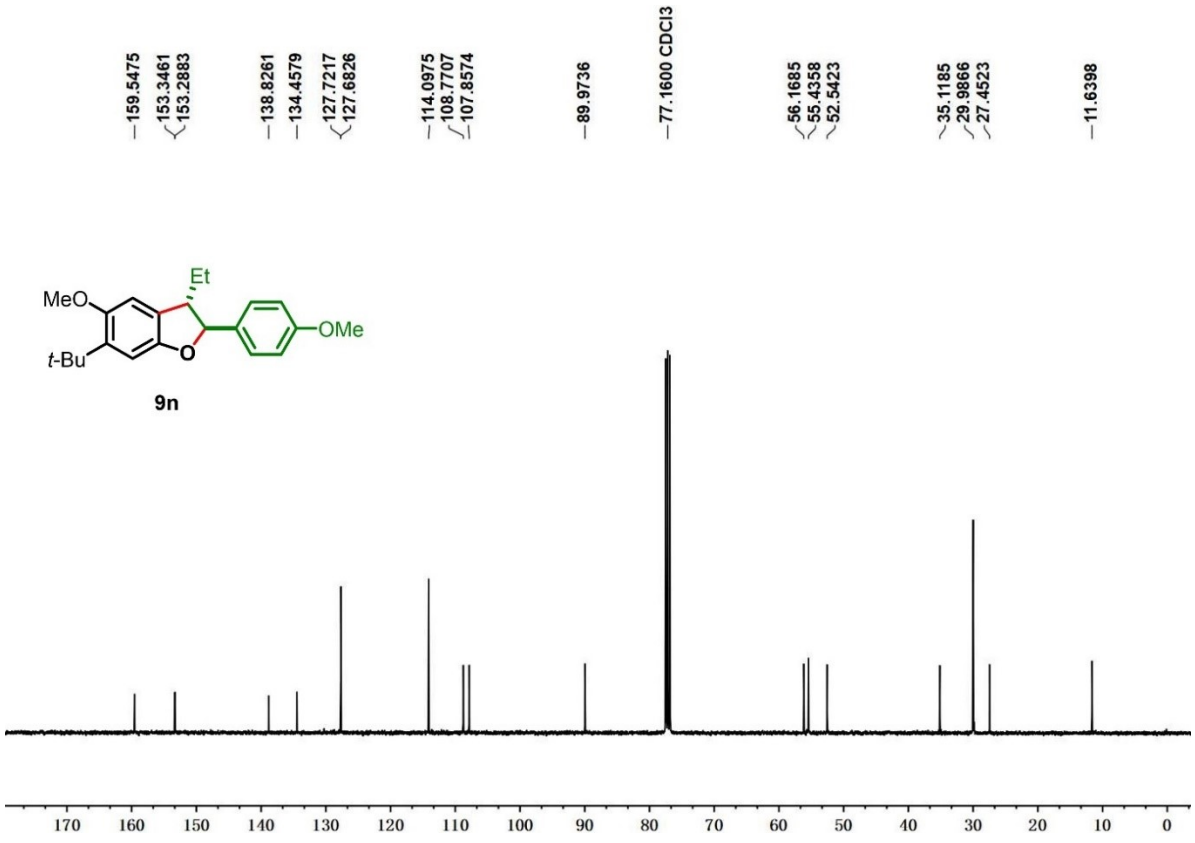
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t-Bu
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9n


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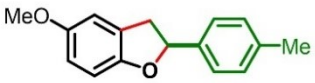
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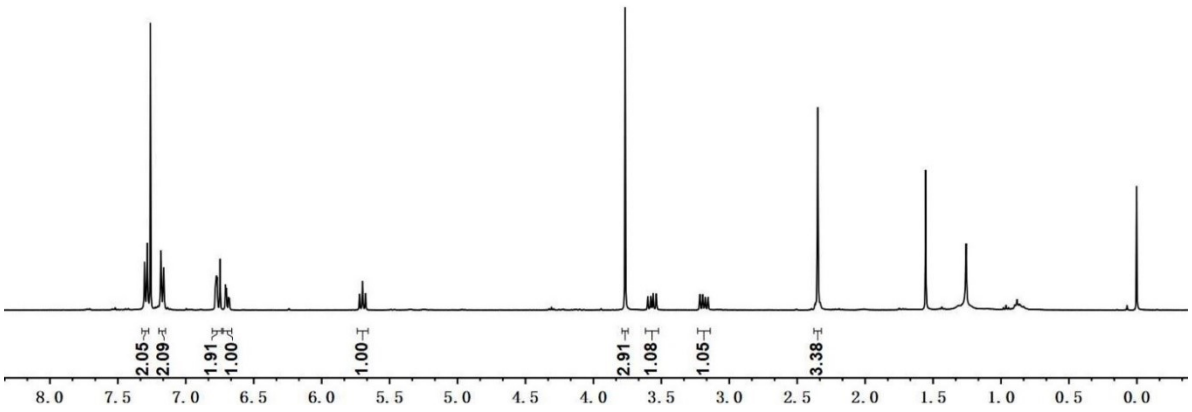
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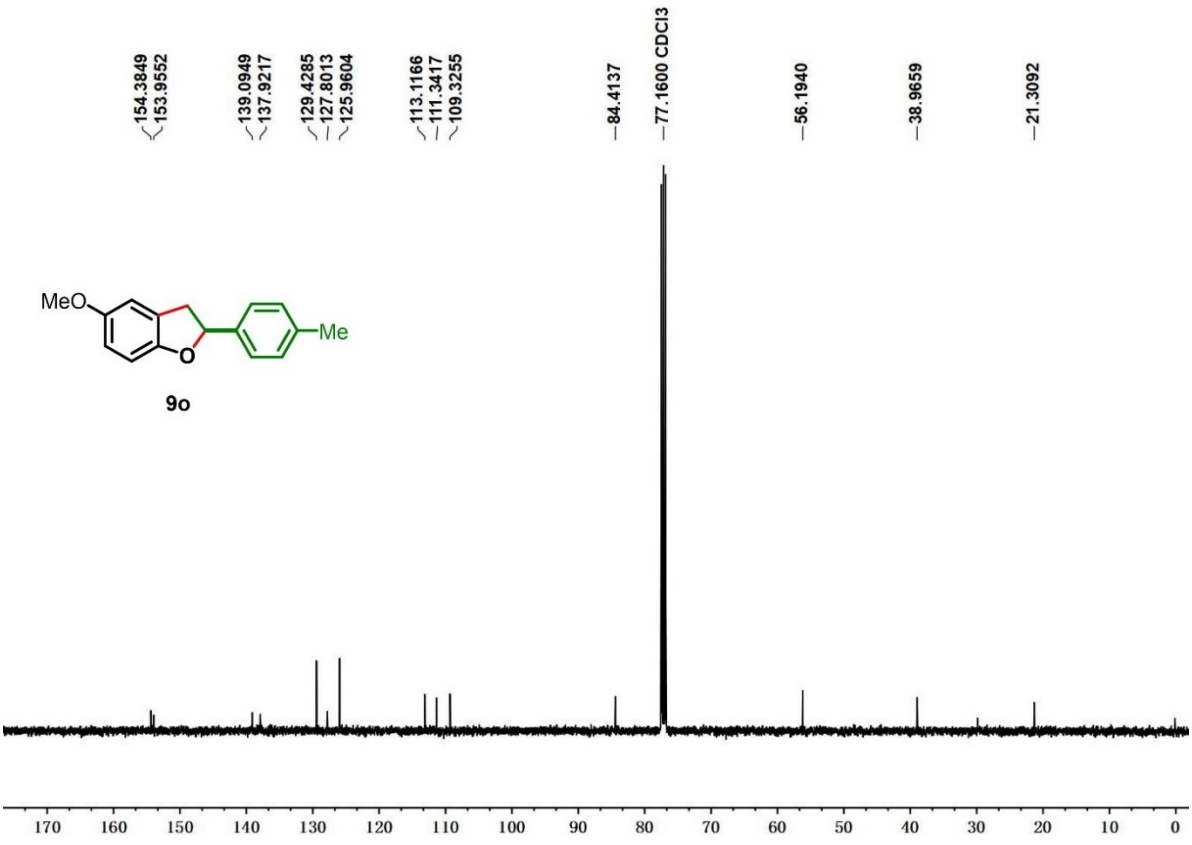
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MeO
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9o