

Supplementary information for

Augmentation of Pd-Catalysed Oxidative C-H/C-H Carbonylation through Alternating Current Electrosynthesis

Haoran Li,^{†,§} Jiaqi Peng,^{†,§} Li Zeng,^{*,†} Linpu Zhou,[†] Muhammad Shabbir,[†] Feiran Xiao,[‡] Jiaxin Yuan,[‡] Hong Yi,^{*,†} Aiwen Lei^{*,†,‡}

[†] College of Chemistry and Molecular Sciences, The Institute for Advanced Studies (IAS), Wuhan University, Wuhan 430072, P. R. China

[‡] State Key Laboratory of Power Grid Environmental Protection, School of Electrical Engineering and Automation, Wuhan University, P. R. China

[§] These authors contributed equally.

Table of Contents

1. General information	1
2. Experimental procedures for synthesis of diphenyl ethers	2
2.1 Synthesis of diphenyl ethers 1b-1l	2
2.2 Synthesis of diphenyl ethers 1m-1s	3
3. Experimental procedures for AC electrolysis	3
4. Experimental procedures for gram scale synthesis	5
5. Electrochemical procedures for cyclic voltammetry	6
6. Electrochemical procedures for constant potential experiment	7
7. Pd deposition on electrode surface	8
8. Monitoring the atmosphere	8
9. Determination of palladium by gravimetric method	9
10. Extension of AC-driven Pd-catalyzed electro-oxidative reactions	11
11. Control experiments	13
12. Detail descriptions for products	15
13. Spectral data	21
14. References	46

1. General information

All glassware was oven dried at 110 °C for hours and cooled down under vacuum. The instruments for AC electrolysis were the HSPY™ 120-01 DC stabilized power supply, which was connected to a self-designed alternating current device respectively (frequency range: 0 – 5 Hz, time resolution: 0.1 s, duty ratio range: 0 – 100%). All electrolytic cells were self-designed and purchased from Jiehengda™ limited liability company (WeChat: lovely03; patent: CN213041724U, CN306250840S, CN306250839S, CN306237711S). Cyclic voltammograms (CV) were obtained on a CHI 605E potentiostat. GC yields were recorded by SHIMADZU™ GC-2014 gas chromatography. Hydrogen gas content was analyzed by gas chromatography (GC9790 Plus, Fuli™, China, TCD, nitrogen as a carrier gas and 5 Å molecular sieve column, a thermal conductivity detector). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument and accurate masses were reported for the molecular ion Hydrogen $[M+H]^+$. Unless otherwise noted, materials and solvents were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I₂ chamber. Flash chromatography columns were packed with 200-300 silica gel in petroleum (bp. 60-90 °C). ¹H, ¹³C and ¹⁹F NMR data were recorded with Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform).

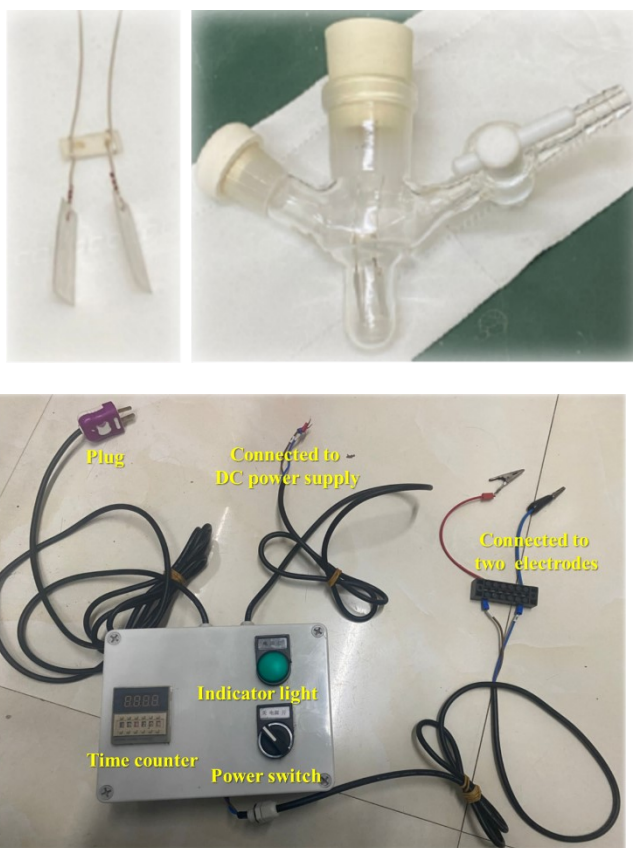
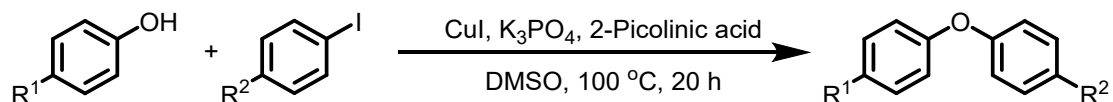


Fig. S1. Pt electrodes and AC electrolysis set-up.

2. Experimental procedures for synthesis of diphenyl ethers

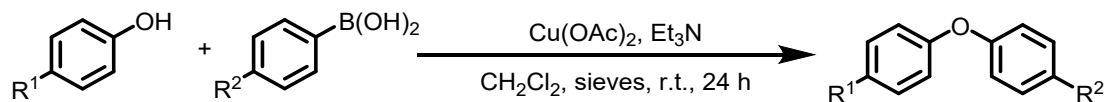
2.1 Synthesis of diphenyl ethers 1b-11



According to the literature,¹ a round-bottom Schlenk-flask (250 mL) was equipped with a magnetic stir bar, copper iodide (456 mg, 2.40 mmol, 10.0 mol%), picolinic acid (590 mg, 4.80 mmol, 20.0 mol%) and potassium phosphate (10.2 g, 48.0 mmol, 2 equiv.). A second Schlenk flask (100 mL) was charged with the aryl iodide (24.0 mmol, 1 equiv.), the phenol (28.8 mmol, 1.2 equiv.) and anhydrous DMSO (50 mL). The solution of flask 2 was transferred into flask 1 under flowing argon and the reaction mixture was stirred for 20 h at 100 °C, subsequently. After cooling down, the reaction mixture was diluted with 1:1 mixture of a saturated aqueous solution of NH₄Cl (200 mL) and H₂O (200 mL). After extraction with DCM (3 × 200 mL) the combined organic phases were washed with 5% aqueous solution of KOH (300 mL) and brine (300 mL).

After drying the mixture over Na_2SO_4 the solvent was removed and purification of the crude mixture was achieved over silica gel, respectively.

2.2 Synthesis of diphenyl ethers 1m-1s



According to the literature,² a 50 mL round-bottom flask is charged with phenol (1 equiv.), $\text{Cu}(\text{OAc})_2$ (1 equiv.), arylboronic acid (2 equiv.), and powdered 4Å molecular sieves. The reaction mixture is diluted with DCM to yield a solution approximately 0.1 M in phenol, and the amine base (5 equiv.) is added. After stirring the colored heterogeneous reaction mixture for 18 h at 25 °C under ambient atmosphere, the resulting slurry is filtered and the diaryl ether is isolated from the organic filtrate by flash chromatography.

3. Experimental procedures for AC electrolysis

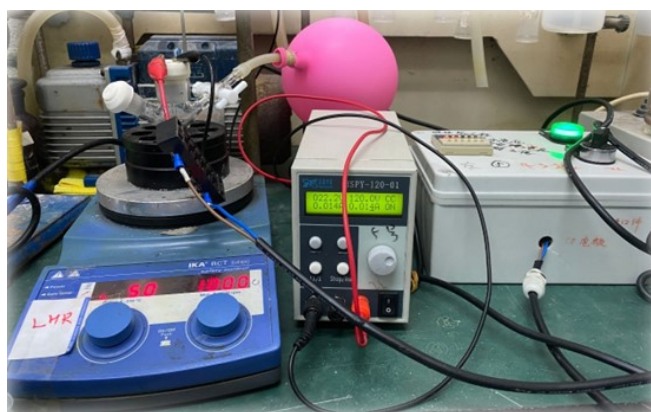
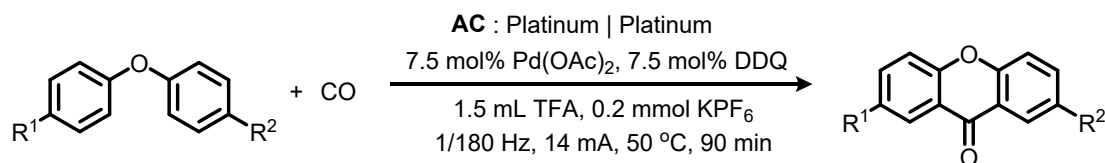
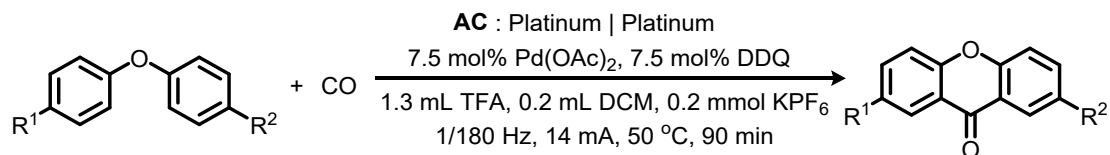


Fig. S2. Set-up of AC electrolysis.

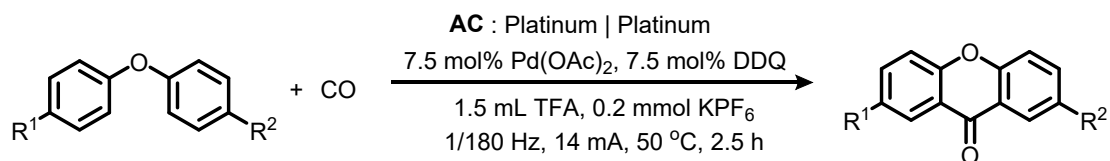


Method 1-A: **2a** to **2e**, **2g**, **2h**, **2j**, **2k**, **2m** to **2q**. In a 2.5 mL oven-dried two-necked undivided cell equipped with a stir bar, diphenyl ether (0.30 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 0.0225 mmol), DDQ (5.1 mg, 0.0225 mmol) and KPF_6 (36.8 mg, 0.20 mmol) were added into the undivided cell. The undivided cell was equipped with two platinum plate electrodes. A balloon filled CO (1.0 atm.) was connected to the undivided cell by the side tube and purged three times. TFA (1.5 mL) was added to the tube through a syringe. Mixtures were stirred and electrolyzed at alternating current of 14 mA (square wave, 1/180 Hz, duty ratio = 67%) at 50 °C for 1.5 h. At

the end of the reaction, the reaction was quenched by saturated NaHCO₃ aqueous solution and extracted with Ethyl acetate three times. The combined organic layer was dried over anhydrous Na₂SO₄ and was evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on 200-300 mesh silica gel (petroleum : Ethyl acetate= 40 : 1).



Method 1-B: 2i, 2s. In a 2.5 mL oven-dried two-necked undivided cell equipped with a stir bar, diphenyl ether (0.30 mmol), Pd(OAc)₂ (5.0 mg, 0.0225 mmol), DDQ (5.1 mg, 0.0225 mmol) and KPF₆ (36.8 mg, 0.20 mmol) were added into the undivided cell. The undivided cell was equipped with two platinum plate electrodes. A balloon filled CO (1.0 atm.) was connected to the undivided cell by the side tube and purged three times. CH₂Cl₂ (0.2 mL) and TFA (1.3 mL) was added to the tube through a syringe. Mixtures were stirred and electrolyzed at alternating current of 14 mA (square wave, 1/180 Hz, duty ratio = 67%) at 50 °C for 1.5 h. At the end of the reaction, the reaction was quenched by saturated NaHCO₃ aqueous solution and extracted with Ethyl acetate three times. The combined organic layer was dried over anhydrous Na₂SO₄ and was evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on 200-300 mesh silica gel (petroleum : Ethyl acetate= 40 : 1).



Method 1-C: 2f, 2l, 2r, 2t In a 2.5 mL oven-dried two-necked undivided cell equipped with a stir bar, diphenyl ether (0.30 mmol), Pd(OAc)₂ (5.0 mg, 0.0225 mmol), DDQ (5.1 mg, 0.0225 mmol) and KPF₆ (36.8 mg, 0.20 mmol) were added into the undivided cell. The undivided cell was equipped with two platinum plate electrodes. A balloon filled CO (1.0 atm.) was connected to the undivided cell by the side tube and purged three times. TFA (1.5 mL) was added to the tube through a syringe. Mixtures were stirred and electrolyzed at alternating current of 14 mA (square wave, 1/180 Hz, duty ratio = 67%) at 50 °C for 2.5 h. At the end of the reaction, the

reaction was quenched by saturated NaHCO₃ aqueous solution and extracted with Ethyl acetate three times. The combined organic layer was dried over anhydrous Na₂SO₄ and was evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on 200-300 mesh silica gel (petroleum : Ethyl acetate= 40 : 1).

4.Experimental procedures for gram scale synthesis

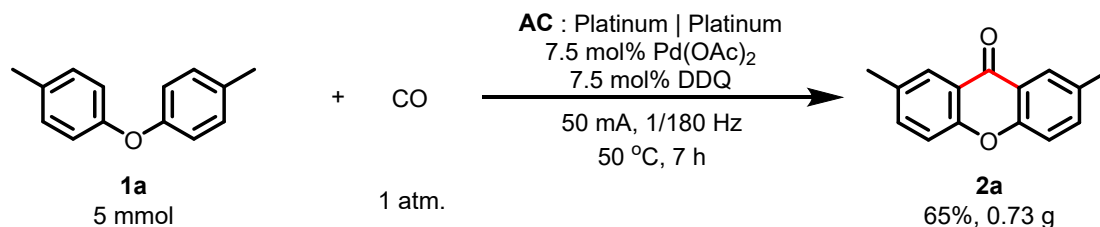


Fig. S3. Set-up of gram-scale AC electrocatalysis.

In a 50 mL oven-dried three-necked flask equipped with a stir bar, *p*-tolyl ether (990 mg, 5.0 mmol), Pd(OAc)₂ (84.0 mg, 0.375 mmol), DDQ (85.1 mg, 0.375 mmol) and KPF₆ (73.6 mg, 0.40 mmol) were added into the undivided cell. The three-necked flask was equipped with a glass Allihn condenser in the middle and two platinum plate electrodes on both sides. A balloon filled CO (1.0 atm.) was connected to the top of the glass Allihn condenser and purged three times. TFA (30 mL) was added to the tube through a syringe. Mixtures were stirred and electrolyzed at alternating current of 50 mA (square wave, 1/180 Hz, duty ratio = 67%) at 50 °C for 7 h. At the end of the reaction, the reaction was quenched by saturated NaHCO₃ aqueous solution and extracted with Ethyl acetate three times. The combined organic layer was dried

over anhydrous Na_2SO_4 and was evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on 200-300 mesh silica gel (petroleum : Ethyl acetate= 40 : 1).

5. Electrochemical procedures for cyclic voltammetry

Cyclic voltammograms were recorded with a CorrTest® CS2350H bipotentiostat at room temperature. Et_4NPF_6 (55.0 mg, 0.2 mmol) was used as the supporting electrolyte. The scan range is between -0.5 V to 1.5 V vs. Ag/AgCl. reference electrode (negative scan). The scan rate was 100 mV/s.

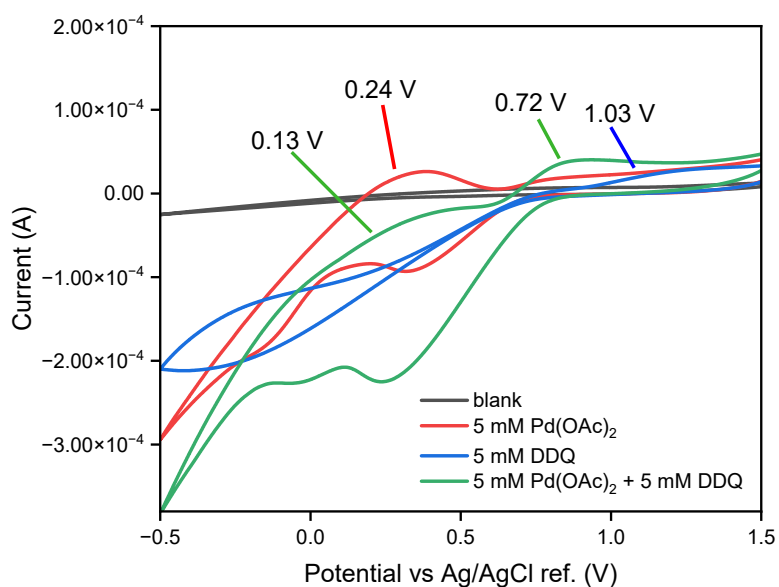
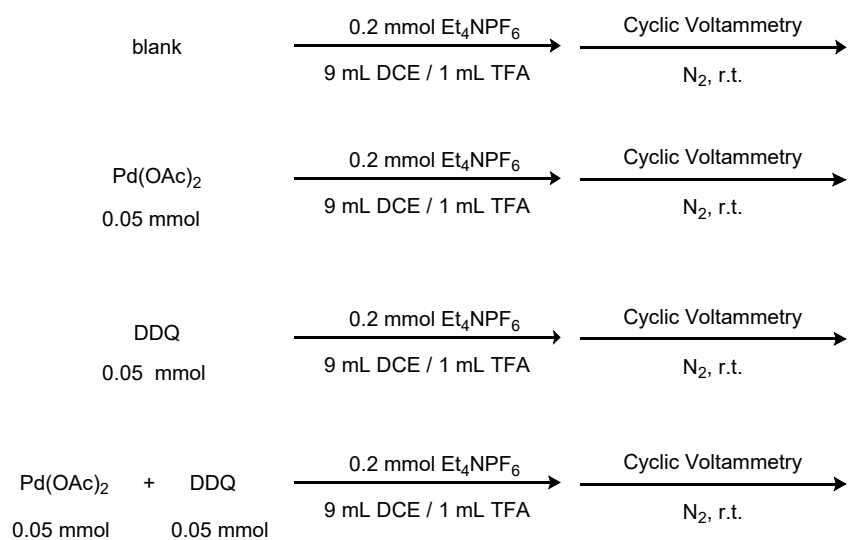


Fig. S4. CV for Pd(OAc)₂, DDQ and their mixture.

In a 10 mL oven-dried undivided cell equipped with a stir bar, Pd(OAc)₂ (11.2 mg, 0.05 mmol) and DDQ (11.4 mg, 0.05 mmol) were added respectively. A balloon filled N₂ (1.0 atm.) was connected to the Schlenk tube by the side tube and purged three times. Et₄NPF₆ (55.0 mg, 0.2 mmol), DCE (9.0 mL) and TFA (1.0 mL) were then added to the tube. The solution was stirred for 5 min. at room temperature. The undivided cell was equipped with Pt disc electrode as working electrode (diameter = 3.0 mm), and Pt wire auxiliary electrode as counter electrode. The scan range was -1.0 V to 1.0 V. The scan rate was 100 mV/s. All potentials were referenced against the Ag/AgCl reference electrode.

6. Electrochemical procedures for constant potential experiment

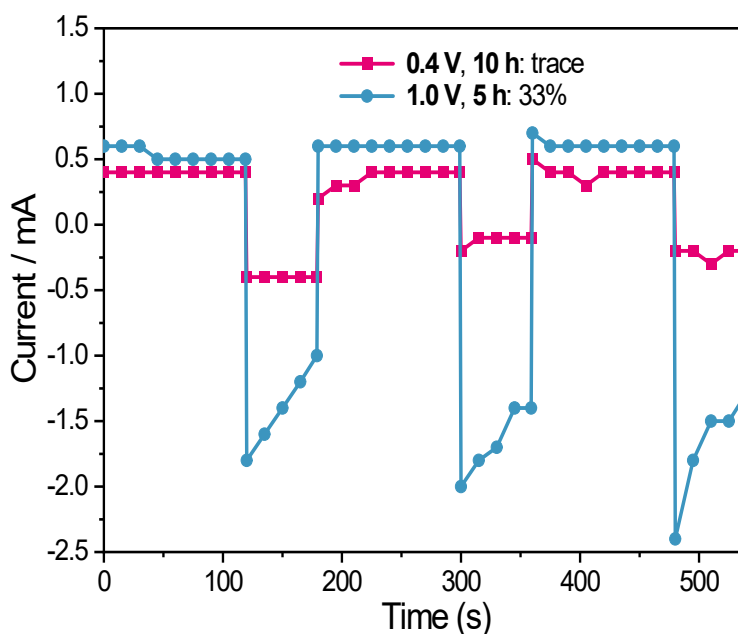
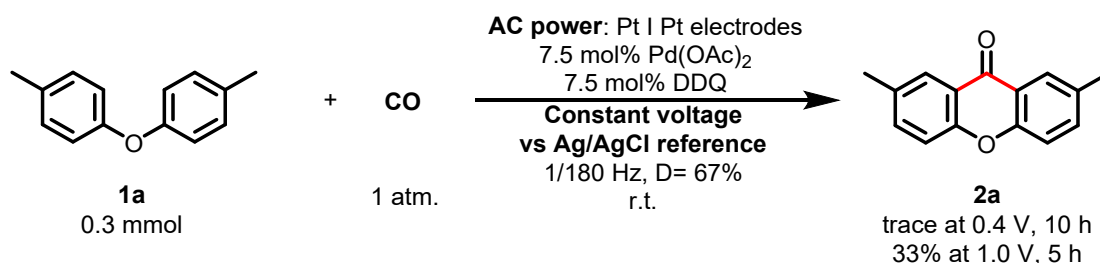


Fig. S5. Current variations under the constant-potential AC electrolysis with 0.4, 1.0 V working potentials and their product yields.

In a 2.5 mL oven-dried two-necked undivided cell equipped with a stir bar, p-tolyl ether (59.4 mg, 0.30 mmol), Pd(OAc)₂ (5.0 mg, 0.0225 mmol), DDQ (5.1 mg, 0.0225 mmol) and KPF₆

(36.8 mg, 0.20 mmol) were added into the undivided cell. The undivided cell was equipped with two platinum plate electrodes as working electrodes and Ag/AgCl electrode as reference electrode. A balloon filled CO (1.0 atm.) was connected to the undivided cell by the side tube and purged three times. TFA (1.5 mL) were added to the tube through a syringe. Mixtures were stirred and electrolyzed at constant potential of 0.4 V (10 h) and 1.0 V (5 h) respectively (square wave, 1/180 Hz, duty ratio = 67%) at room temperature. At the end of the reaction, the reaction was quenched by saturated NaHCO₃ aqueous solution and extracted with Ethyl acetate three times. The combined organic layer was dried over anhydrous Na₂SO₄ and was evaporated in vacuum. The yield was determined by GC analysis with biphenyl as the internal standard.

7. Pd deposition on electrode surface

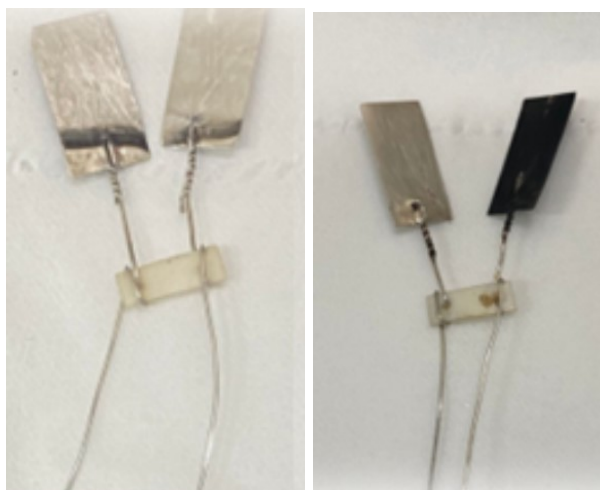


Fig. S6. The difference of deposition on electrodes between AC and DC electrolysis. left: The deposition electrodes for AC electrolysis. right: The deposition electrodes for DC electrolysis.

8. Monitoring the atmosphere

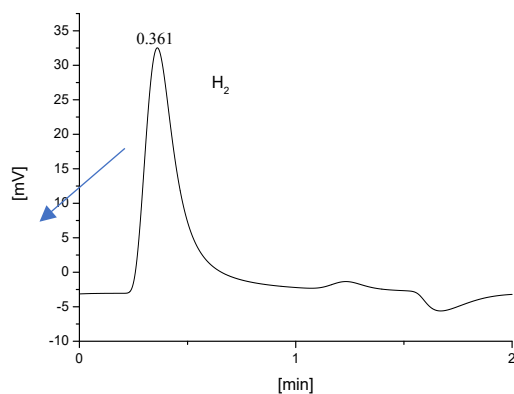


Fig. S7. Monitoring the atmosphere by GC.

9. Determination of palladium by gravimetric method

The content of palladium was determined by gravimetric method after precipitation of dimethylglyoxime.¹¹

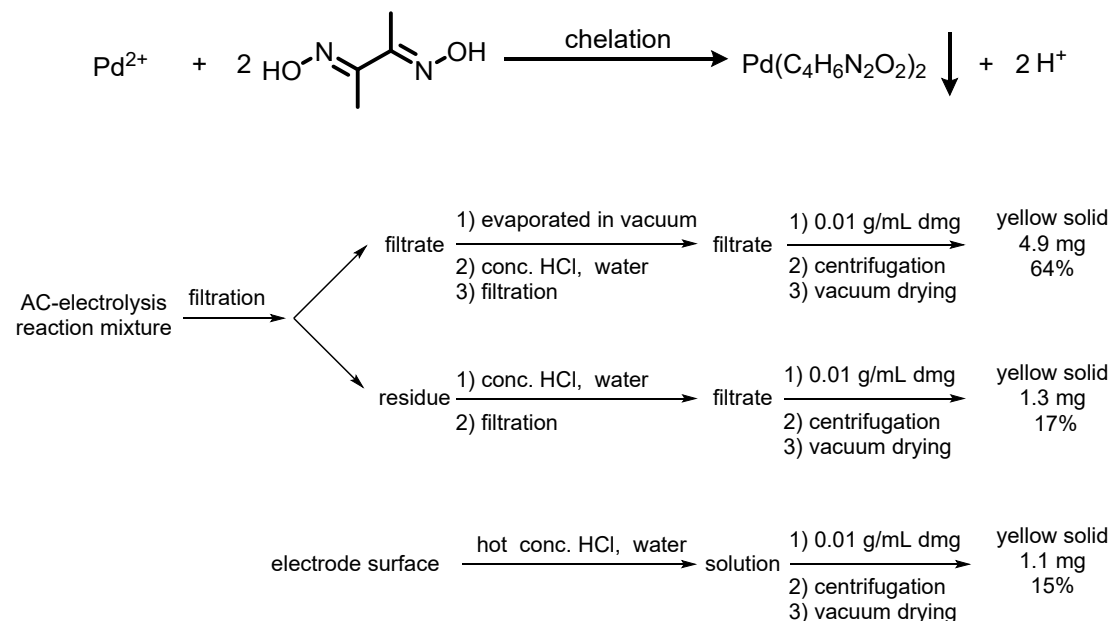


Fig. S8 Gravimetric determination of AC electrolysis reaction.

In a 2.5 mL oven-dried two-necked undivided cell equipped with a stir bar, 4-tolyl ether (59.4 mg, 0.30 mmol), Pd(OAc)₂ (5.0 mg, 0.0225 mmol), DDQ (5.1 mg, 0.0225 mmol) and KPF₆ (36.8 mg, 0.20 mmol) were added into the undivided cell. The undivided cell was equipped with two platinum plate electrodes. A balloon filled CO (1.0 atm.) was connected to the undivided cell by the side tube and purged three times. TFA (1.5 mL) was added to the tube through a syringe. Mixtures were stirred and electrolyzed at alternating current of 14 mA (square wave, 1/180 Hz, duty ratio = 67%) at 50 °C for 1.5 h. Then the reaction mixture was cooled to room temperature, paper-filtered and washed with ethyl acetate three times. The combined filtrate was then evaporated in vacuum, dissolved with 1 mL concentrated hydrochloric acid, diluted with 4 mL water and then stirred for 10 min at room temperature. The residue was dissolved with 1 mL concentrated hydrochloric acid, diluted with 4 mL water and then stirred for 10 min at room temperature. The two electrodes of reaction were both washed with 1 mL concentrated hydrochloric acid at 50 °C and then diluted with 4 mL water. All these solution samples were heated at 80 °C and treated subsequently with a 1 mL solution of 0.01 g/mL dimethylglyoxime in ethanol. After stirring for 10 min and standing for 10 min,

the solution was cooled down to room temperature, centrifuged and the residue was washed with 10 mL 1.2 mol/L hydrochloric acid solution for three times. The resulting solid was dried in vacuum drying oven at 80 °C for 1 day.

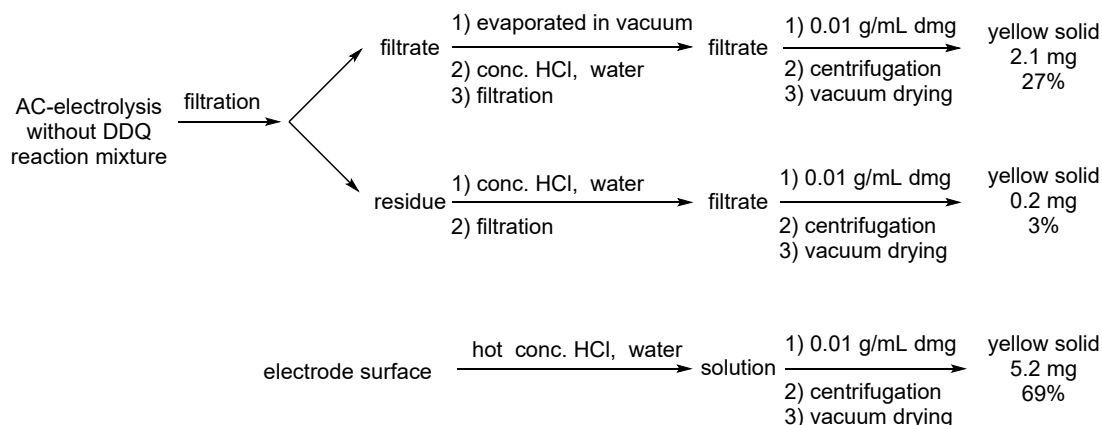


Fig. S9 Gravimetric determination of AC electrolysis reaction in absence of DDQ.

In a 2.5 mL oven-dried two-necked undivided cell equipped with a stir bar, 4-tolyl ether (59.4 mg, 0.30 mmol), Pd(OAc)₂ (5.0 mg, 0.0225 mmol) and KPF₆ (36.8 mg, 0.20 mmol) were added into the undivided cell. The undivided cell was equipped with two platinum plate electrodes. A balloon filled CO (1.0 atm.) was connected to the undivided cell by the side tube and purged three times. TFA (1.5 mL) was added to the tube through a syringe. Mixtures were stirred and electrolyzed at alternating current of 14 mA (square wave, 1/180 Hz, duty ratio = 67%) at 50 °C for 1.5 h. Then the reaction mixture was cooled to room temperature, paper-filtered and washed with Ethyl acetate three times. The combined filtrate was then evaporated in vacuum, dissolved with 1 mL concentrated hydrochloric acid, diluted with 4 mL water and then stirred for 10 min at room temperature. The residue was dissolved with 1 mL concentrated hydrochloric acid, diluted with 4 mL water and then stirred for 10 min at room temperature. The two electrodes of reaction were both washed with 1 mL concentrated hydrochloric acid at 50 °C and then diluted with 4 mL water. All these solution samples were heated at 80 °C and treated subsequently with a 1 mL solution of 0.01 g/mL dimethylglyoxime in ethanol. After stirring for 10 min and standing for 10 min, the solution was cooled down to room temperature, centrifuged and the residue was washed with 10 mL 1.2 mol/L hydrochloric acid solution for three times. The resulting solid was dried in vacuum drying oven at 80 °C for 1 day.

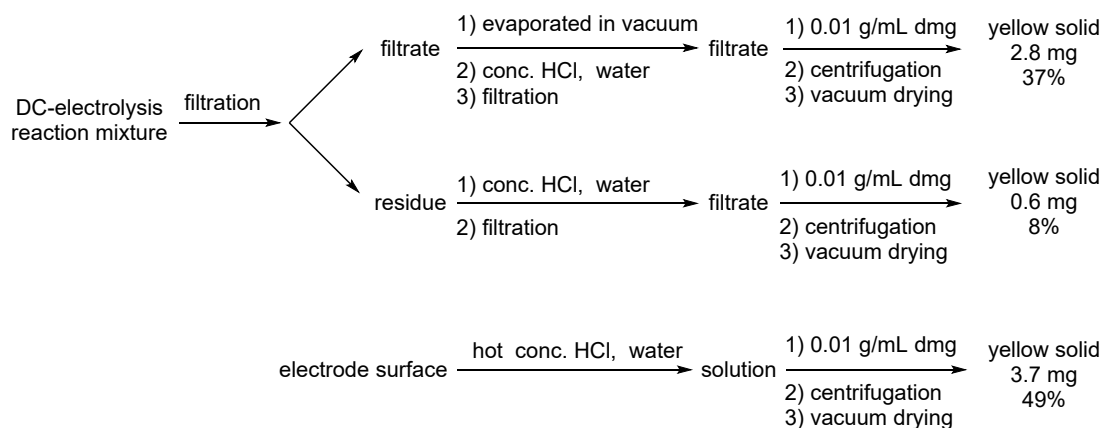


Fig. S10 Gravimetric determination of DC electrolysis reaction.

In a 2.5 mL oven-dried two-necked undivided cell equipped with a stir bar, 4-tolyl ether (59.4 mg, 0.30 mmol), Pd(OAc)₂ (5.0 mg, 0.0225 mmol), DDQ (5.1 mg, 0.0225 mmol) and KPF₆ (36.8 mg, 0.20 mmol) were added into the undivided cell. The undivided cell was equipped with two platinum plate electrodes. A balloon filled CO (1.0 atm.) was connected to the undivided cell by the side tube and purged three times. TFA (1.5 mL) was added to the tube through a syringe. Mixtures were stirred and electrolyzed at direct current of 14 mA at 50 °C for 1.5 h. Then the reaction mixture was cooled to room temperature, paper-filtered and washed with Ethyl acetate three times. The combined filtrate was then evaporated in vacuum, dissolved with 1 mL concentrated hydrochloric acid, diluted with 4 mL water and then stirred for 10 min at room temperature. The residue was dissolved with 1 mL concentrated hydrochloric acid, diluted with 4 mL water and then stirred for 10 min at room temperature. The two electrodes of reaction were both washed with 1 mL concentrated hydrochloric acid at 50 °C and then diluted with 4 mL water. All these solution samples were heated at 80 °C and treated subsequently with a 1 mL solution of 0.01 g/mL dimethylglyoxime in ethanol. After stirring for 10 min and standing for 10 min, the solution was cooled down to room temperature, centrifuged and the residue was washed with 10 mL 1.2 mol/L hydrochloric acid solution for three times. The resulting solid was dried in vacuum drying oven at 80 °C for 1 day.

10. Extension of AC-driven Pd-catalyzed electro-oxidative reactions

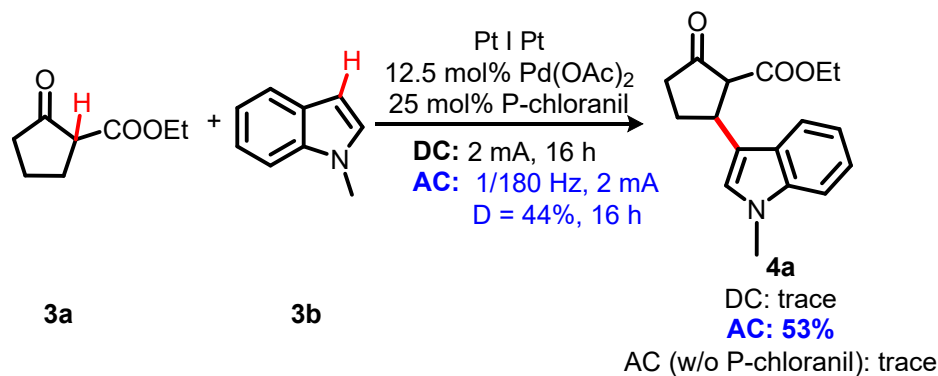


Fig. S11 C(sp²)-H/C(sp³)-H cross-coupling.

In a 2.5 mL oven-dried two-necked undivided cell equipped with a stir bar, ethyl 2-oxocyclopentane-1-carboxylate (0.40 mmol, 62.4 mg), 1-methyl-1*H*-indole (0.80 mmol, 104.8 mg), Pd(OAc)₂ (11.2 mg, 0.050 mmol), P-chloranil (24.6 mg, 0.10 mmol) and ⁿBu₄NClO₄ (85.3 mg, 0.25 mmol) were added into the undivided cell. The undivided cell was equipped with two platinum plate electrodes. A balloon filled N₂ was connected to the undivided cell by the side tube and purged three times. AcOH (2.0 mL) was added to the tube through a syringe. Mixtures were stirred and electrolyzed at alternating current of 2.0 mA (square wave, 1/180 Hz, duty ratio = 44%) at 50 °C for 16 h (3.0 F/mol). At the end of the reaction, the reaction was quenched by saturated NaHCO₃ aqueous solution and extracted with Ethyl acetate three times. The combined organic layer was dried over anhydrous Na₂SO₄ and was evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on 200-300 mesh silica gel (petroleum : Ethyl acetate= 20 : 1).

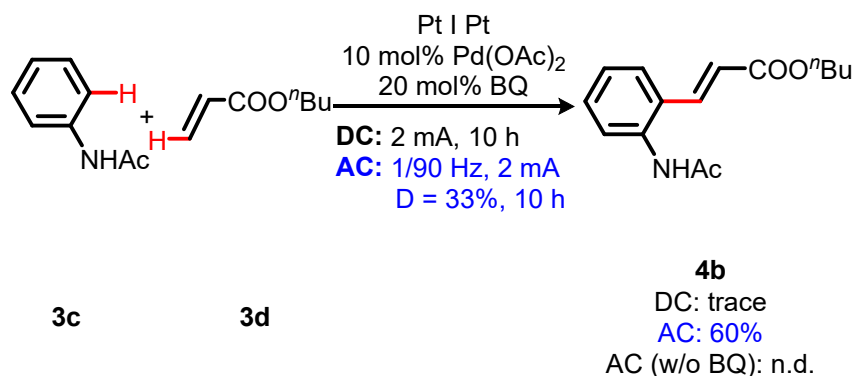


Fig. S12 C(sp²)-H/C(sp²)-H cross-coupling.

In a 2.0 mL oven-dried two-necked undivided cell equipped with a stir bar, acetanilide (0.50 mmol, 67.5 mg), Butyl Acrylate (0.20 mmol, 25.6 mg), Pd(OAc)₂ (4.5 mg, 0.020 mmol), BQ

(4.3 mg, 0.040 mmol) and $n\text{Bu}_4\text{NBF}_4$ (65.9 mg, 0.20 mmol) were added into the undivided cell. The undivided cell was equipped with a carbon plate electrode and a platinum plate electrode. A balloon filled N_2 was connected to the undivided cell by the side tube and purged three times. TFA/DCM (2.0/0.5 mL) was added to the tube through a syringe. Mixtures were stirred and electrolyzed at alternating current of 2 mA (square wave, 1/90 Hz, duty ratio = 33%) at room temperature for 10 h (3.7 F/mol). At the end of the reaction, the reaction was quenched by saturated NaHCO_3 aqueous solution and extracted with Ethyl acetate three times. The combined organic layer was dried over anhydrous Na_2SO_4 and was evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on 200-300 mesh silica gel (petroleum : Ethyl acetate= 10 : 1).

11. Control experiments

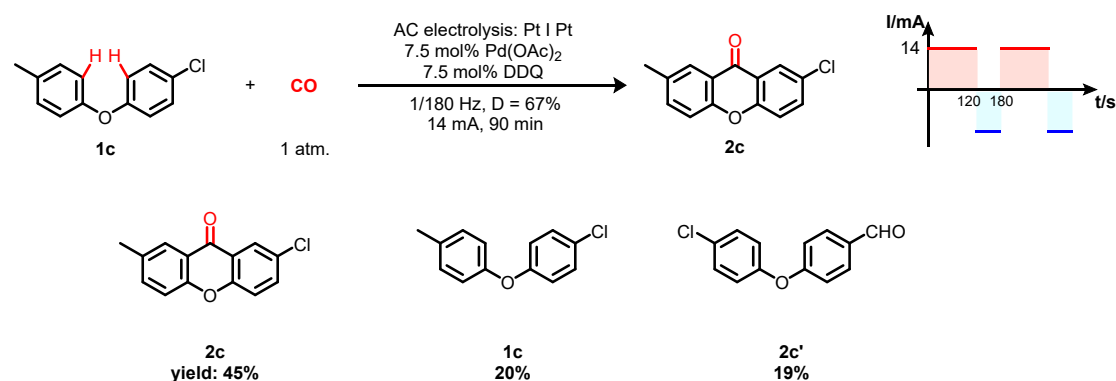


Fig. S13. The conversion of **1c** and their whereabouts under AC conditions.

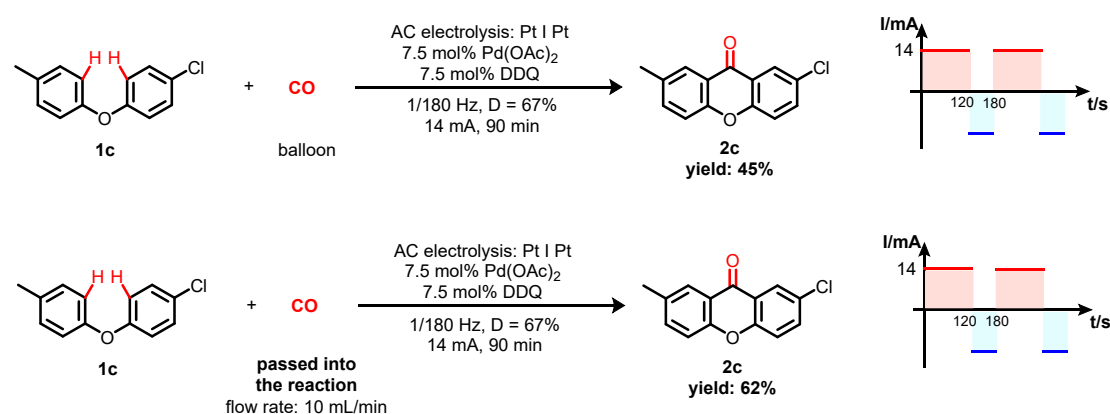


Fig. S14. The yield comparison for AC electrolysis between blowing CO and linking CO balloon.

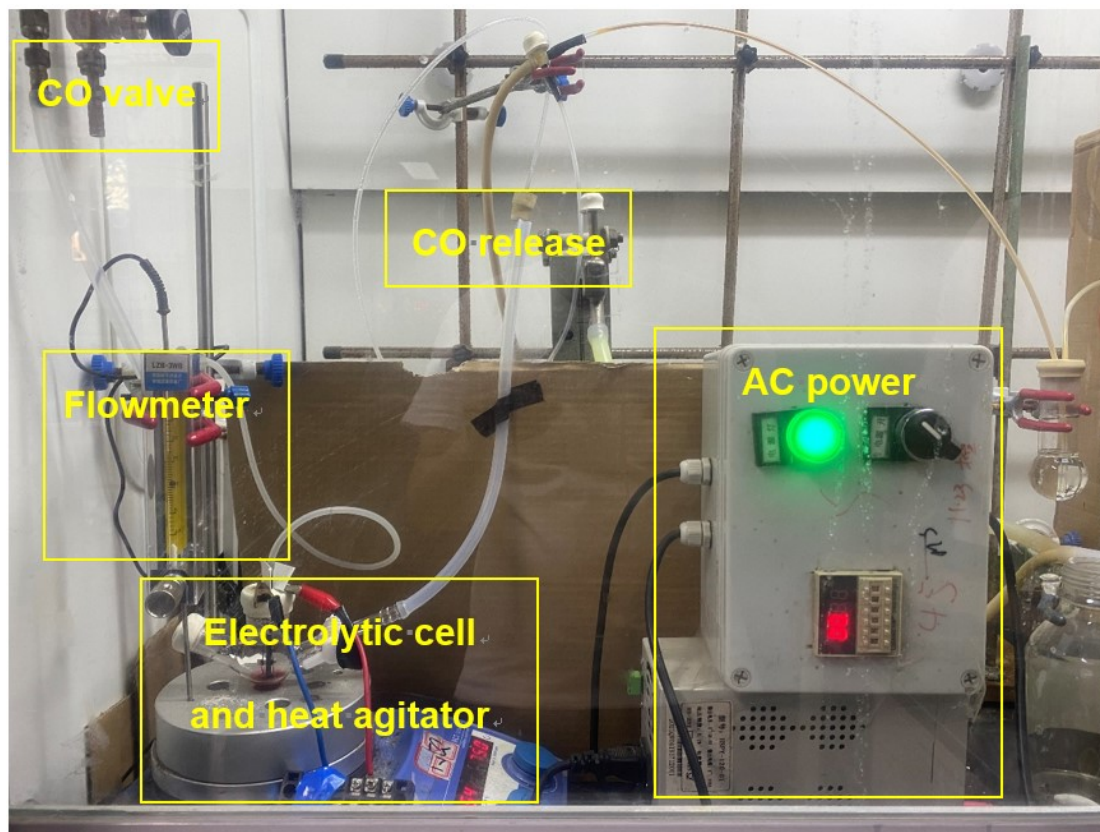


Fig. S15. The experimental set-up for AC electrolysis involving CO blowing.

In a 2.5 mL oven-dried two-necked undivided cell equipped with a stir bar, diphenyl ether **1c** (0.30 mmol), Pd(OAc)₂ (5.0 mg, 0.0225 mmol), DDQ (5.1 mg, 0.0225 mmol) and KPF₆ (36.8 mg, 0.20 mmol) were added into the undivided cell. The undivided cell was equipped with two platinum plate electrodes. A tube was connected to CO valve and the undivided cell. Flow rate of CO was 10 mL/min. TFA (1.5 mL) was added to the tube through a syringe. Mixtures were stirred and electrolyzed at alternating current of 14 mA (square wave, 1/180 Hz, duty ratio = 67%) at 50 °C for 1.5 h. At the end of the reaction, the reaction was quenched by saturated NaHCO₃ aqueous solution and extracted with Ethyl acetate three times. The combined organic layer was dried over anhydrous Na₂SO₄ and was evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on 200-300 mesh silica gel (petroleum : Ethyl acetate= 40 : 1).

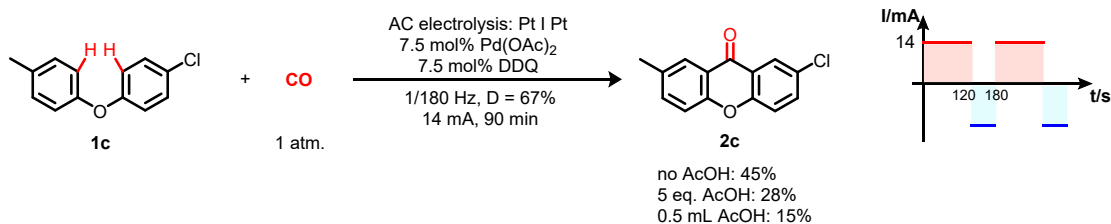
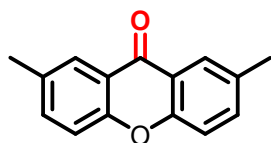


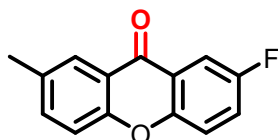
Fig. S16. The AC electrolytic result for diaryl ether 1u which has a substituent at the meta-position of phenyl ring.

In a 2.5 mL oven-dried two-necked undivided cell equipped with a stir bar, diphenyl ether **1c** (0.30 mmol), Pd(OAc)₂ (5.0 mg, 0.0225 mmol), DDQ (5.1 mg, 0.0225 mmol) and KPF₆ (36.8 mg, 0.20 mmol) were added into the undivided cell. The undivided cell was equipped with two platinum plate electrodes. A balloon filled CO (1.0 atm.) was connected to the undivided cell by the side tube and purged three times. TFA (1.5 mL), AcOH (5 eq. or 0.50 mL) were added to the tube through a syringe. Mixtures were stirred and electrolyzed at alternating current of 14 mA (square wave, 1/180 Hz, duty ratio = 67%) at 50 °C for 1.5 h. At the end of the reaction, the reaction was quenched by saturated NaHCO₃ aqueous solution and extracted with Ethyl acetate three times. The combined organic layer was dried over anhydrous Na₂SO₄ and was evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on 200-300 mesh silica gel (petroleum : Ethyl acetate = 40 : 1).

12. Detail descriptions for products

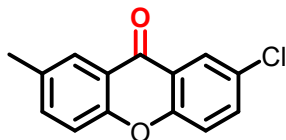


2,7-Dimethyl-9H-xanthene-9-one (2a)³: yellow solid was obtained with 82% isolated yield (**method 1-A**, 55.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 1.1 Hz, 2H), 7.51 (dd, *J* = 8.5, 2.1 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 2.46 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 177.38, 154.41, 135.91, 133.45, 126.00, 121.41, 117.70, 20.82.

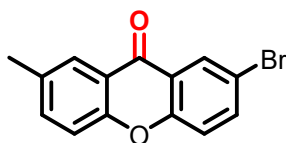


2-Fluoro-7-methyl-9H-xanthene-9-one (2b)⁴: yellow solid was obtained with 86% isolated yield (**method 1-A**, 58.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 0.9 Hz, 1H), 7.93 (dd, *J* = 8.3, 2.7 Hz, 1H), 7.52 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.44 (dt, *J* = 8.1, 3.7 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 1H), 2.46 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 176.43 (d, *J* = 2.22 Hz), 158.44 (d,

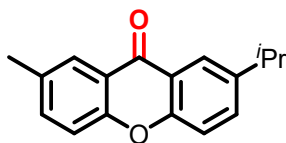
$J = 245.73$ Hz), 154.18, 152.19 (d, $J = 1.52$ Hz), 136.27, 133.85, 125.75, 122.66 (d, $J = 25.45$ Hz), 122.42 (d, $J = 7.07$ Hz), 120.42, 119.84 (d, $J = 7.88$ Hz), 117.64, 111.20 (d, $J = 23.63$ Hz), 20.76. ^{19}F NMR (377 MHz, CDCl_3) δ -117.41.



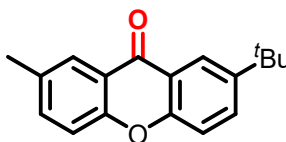
2-Chloro-7-methyl-9H-xanthen-9-one (2c)⁵: yellow oil was obtained with 45% isolated yield (**method 1-A**, 32.6 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.28 (d, $J = 2.6$ Hz, 1H), 8.10 (dd, $J = 6.7, 1.2$ Hz, 1H), 7.64 (dd, $J = 8.9, 2.6$ Hz, 1H), 7.54 (ddd, $J = 5.8, 3.9, 2.0$ Hz, 1H), 7.43 (d, $J = 8.9$ Hz, 1H), 7.38 (dd, $J = 8.5, 4.8$ Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 176.16, 154.45, 154.24, 136.42, 134.70, 134.11, 129.44, 126.02, 125.98, 122.58, 121.03, 119.68, 117.76, 20.82.



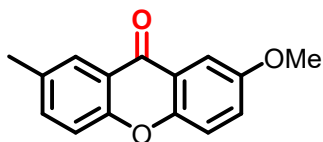
2-Bromo-7-methyl-9H-xanthen-9-one (2d)³: yellow oil was obtained with 41% isolated yield (**method 1-A**, 35.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.41 (d, $J = 2.5$ Hz, 1H), 8.06 (d, $J = 1.1$ Hz, 1H), 7.75 (dd, $J = 8.9, 2.5$ Hz, 1H), 7.52 (dd, $J = 8.5, 2.2$ Hz, 1H), 7.35 (dd, $J = 8.7, 4.0$ Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 175.89, 154.78, 154.12, 137.34, 136.36, 134.06, 129.08, 125.96, 122.92, 120.98, 119.88, 117.72, 116.72, 20.79.



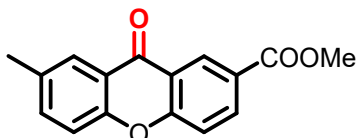
2-Isopropyl-7-methyl-9H-xanthen-9-one (2e): yellow oil was obtained with 62% isolated yield (**method 1-A**, 46.8 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, $J = 2.3$ Hz, 1H), 8.14 – 8.10 (m, 1H), 7.59 (dd, $J = 8.7, 2.3$ Hz, 1H), 7.53 – 7.48 (m, 1H), 7.39 (dd, $J = 14.2, 8.6$ Hz, 2H), 3.12 – 2.97 (m, 1H), 2.46 (s, 3H), 1.32 (d, $J = 6.9$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.43, 154.57, 154.38, 144.43, 135.86, 133.56, 133.41, 125.98, 123.38, 121.45, 121.39, 117.77, 117.65, 33.66, 23.96, 20.79. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$: 253.1223 found: 253.1220.



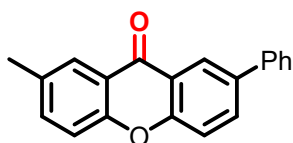
2-(Tert-butyl)-7-methyl-9H-xanthen-9-one (2f)⁶: colorless solid was obtained with 68% isolated yield (**method 1-C**, 54.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.31 (d, $J = 2.5$ Hz, 1H), 8.10 (d, $J = 1.0$ Hz, 1H), 7.74 (dd, $J = 8.8, 2.5$ Hz, 1H), 7.46 (dd, $J = 8.5, 1.9$ Hz, 1H), 7.34 (dd, $J = 20.6, 8.7$ Hz, 2H), 2.43 (s, 3H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.30, 154.23, 154.19, 146.68, 135.71, 133.28, 132.44, 126.36, 125.92, 122.24, 121.30, 120.96, 117.49, 34.63, 31.27, 20.71.



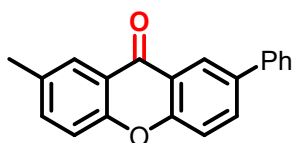
3-Methoxy-6-methyl-9H-xanthen-9-one (2g)³: colorless solid was obtained with 49% isolated yield (**method 1-A**, 35.3 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 1.3 Hz, 1H), 7.67 (d, *J* = 3.1 Hz, 1H), 7.49 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.32 (ddd, *J* = 12.7, 12.2, 6.1 Hz, 3H), 3.90 (s, 3H), 2.45 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 176.99, 155.71, 154.21, 150.88, 135.77, 133.35, 125.77, 124.66, 121.90, 120.72, 119.26, 117.61, 105.62, 55.81, 20.77.



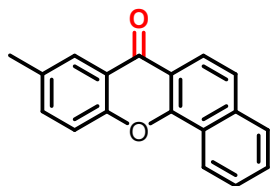
Methyl 7-methyl-9-oxo-9H-xanthene-2-carboxylate (2h): colorless solid was obtained with 31% isolated yield (**method 1-A**, 25.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 9.03 (d, *J* = 2.2 Hz, 1H), 8.36 (dd, *J* = 8.8, 2.2 Hz, 1H), 8.14 (d, *J* = 1.1 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.42 (d, *J* = 8.5 Hz, 1H), 3.98 (s, 3H), 2.49 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 176.68, 165.93, 158.74, 154.20, 136.51, 135.20, 134.47, 129.35, 126.18, 125.80, 121.40, 121.38, 118.40, 117.83, 52.37, 20.85. HRMS (ESI) calcd for C₁₆H₁₂O₄ [M+H]⁺: 269.0808 found: 269.0811.



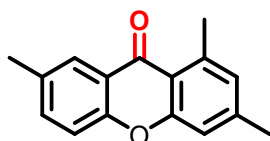
2-Methyl-7-phenyl-9H-xanthen-9-one (2i): white solid was obtained with 68% isolated yield (**method 1-B**, 58.5 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.57 (d, *J* = 2.3 Hz, 1H), 8.16 (d, *J* = 1.0 Hz, 1H), 7.97 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.74 – 7.64 (m, 2H), 7.61 – 7.53 (m, 2H), 7.44 (ddd, *J* = 19.6, 14.9, 7.3 Hz, 4H), 2.49 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 177.32, 155.61, 154.42, 139.49, 136.87, 136.12, 133.80, 133.50, 128.95, 127.65, 127.11, 126.11, 124.58, 121.91, 121.45, 118.48, 117.79, 20.86. HRMS (ESI) calcd for C₂₀H₁₅O₂ [M+H]⁺: 287.1067 found: 287.1058.



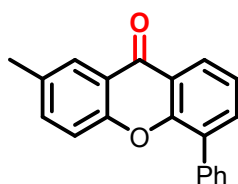
2,4,7-Trimethyl-9H-xanthen-9-one (2j)⁶: yellow solid was obtained with 67% isolated yield (**method 1-A**, 47.9 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 1.4 Hz, 1H), 7.94 (d, *J* = 0.7 Hz, 1H), 7.49 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.34 (d, *J* = 0.7 Hz, 1H), 2.49 (s, 3H), 2.45 (s, 3H), 2.40 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 177.57, 154.19, 152.70, 136.80, 135.66, 133.28, 132.72, 126.81, 125.84, 123.47, 121.15, 121.10, 117.69, 20.78, 20.72, 15.65.



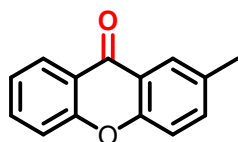
9-Methyl-7H-benzo[c]xanthen-7-one (2k)⁶: colorless oil was obtained with 69% isolated yield (**method 1-A**, 54.9 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.67 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.28 (d, *J* = 8.7 Hz, 1H), 8.19 (s, 1H), 7.93 (dd, *J* = 7.1, 1.9 Hz, 1H), 7.76 – 7.66 (m, 3H), 7.61 – 7.56 (m, 2H), 2.51 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 176.98, 154.01, 153.65, 136.47, 135.61, 134.28, 129.47, 128.06, 126.81, 125.87, 124.13, 123.81, 122.90, 122.05, 121.56, 117.82, 117.53, 20.94.



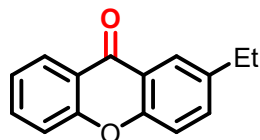
1,3,7-Trimethyl-9H-xanthen-9-one (2l): colorless solid was obtained with 67% isolated yield (**method 1-C**, 47.9 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 1.2 Hz, 1H), 7.46 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.09 (s, 1H), 6.90 (s, 1H), 2.88 (s, 3H), 2.43 (d, *J* = 10.8 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 178.70, 157.66, 153.45, 144.72, 141.64, 135.30, 133.17, 127.93, 125.96, 122.43, 117.96, 117.12, 115.83, 23.17, 21.66, 20.85. HRMS (ESI) calcd for C₁₆H₁₅O₂ [M+H]⁺: 239.1067 found: 239.1067.



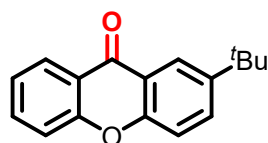
2-Methyl-5-phenyl-9H-xanthen-9-one (2m): colorless solid was obtained with 49% isolated yield (**method 1-A**, 42.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.36 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.12 (d, *J* = 1.3 Hz, 1H), 7.74 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.66 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.56 – 7.39 (m, 5H), 7.29 (d, *J* = 8.5 Hz, 1H), 2.46 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 177.36, 154.17, 152.92, 136.39, 136.01, 135.64, 133.77, 131.32, 129.63, 128.34, 127.82, 126.08, 125.88, 123.59, 122.18, 121.09, 117.88, 20.82. HRMS (ESI) calcd for C₂₀H₁₅O₂ [M+H]⁺: 287.1067 found: 287.1062.



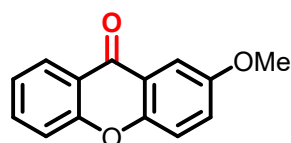
2-Methyl-9H-xanthen-9-one (2n)³: yellow oil was obtained with 60% isolated yield (**method 1-A**, 38.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.34 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.12 (s, 1H), 7.71 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.57 – 7.45 (m, 2H), 7.42 – 7.34 (m, 2H), 2.47 (d, *J* = 2.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 177.28, 156.17, 154.39, 136.06, 134.61, 133.68, 126.71, 126.01, 123.68, 121.80, 121.45, 117.92, 117.72, 20.82.



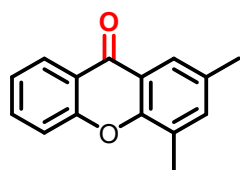
2-Ethyl-9H-xanthen-9-one (2o)⁷: yellow oil was obtained with 63% isolated yield (**method 1-A**, 42.3 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.35 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.21 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.73 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.54 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 3.01 (q, *J* = 7.5 Hz, 2H), 1.37 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 177.59, 156.03, 154.16, 134.64, 134.10, 133.11, 126.67, 124.30, 123.82, 123.58, 121.74, 121.63, 118.00, 22.95, 14.15.



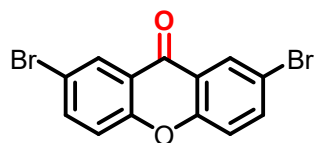
2-(Tert-butyl)-9H-xanthen-9-one (2p)⁸: yellow oil was obtained with 48% isolated yield (**method 1-A**, 36.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.42 – 8.27 (m, 2H), 7.77 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.69 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.43 (dd, *J* = 17.0, 8.6 Hz, 2H), 7.38 – 7.31 (m, 1H), 1.40 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 177.34, 156.06, 154.23, 146.96, 134.51, 132.68, 126.65, 123.61, 122.32, 121.74, 121.04, 117.82, 117.51, 34.68, 31.29.



2-Methoxy-9H-xanthen-9-one (2q)⁸: colorless solid was obtained with 58% isolated yield (**method 1-A**, 39.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.34 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.70 (dt, *J* = 5.9, 2.1 Hz, 2H), 7.52 – 7.28 (m, 4H), 3.91 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 177.01, 156.03, 155.90, 150.91, 134.52, 126.60, 124.84, 123.64, 122.02, 121.16, 119.35, 117.89, 105.73, 55.87.

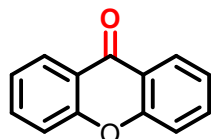


2,4-Dimethyl-9H-xanthen-9-one (2r)⁹: colorless oil was obtained with 55% isolated yield (**method 1-C**, 37.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.32 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.97 – 7.93 (m, 1H), 7.69 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.49 (dd, *J* = 8.4, 0.5 Hz, 1H), 7.38 – 7.31 (m, 2H), 2.51 (s, 3H), 2.41 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 177.54, 155.98, 152.71, 137.01, 134.41, 132.99, 126.87, 126.60, 123.58, 123.52, 121.53, 121.23, 117.95, 20.75, 15.67.

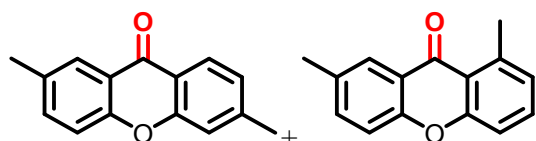


2,7-Dibromo-9H-xanthen-9-one (2s)¹⁰: brown solid was obtained with 49% isolated yield (**method 1-B**, 52.4 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.45 (d, *J* = 2.5 Hz, 2H), 7.83 (dd, *J* =

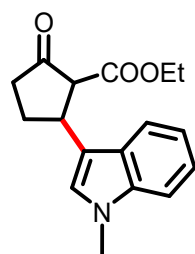
8.9, 2.5 Hz, 2H), 7.41 (d, $J = 8.9$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 174.82, 154.80, 138.06, 129.32, 122.77, 120.05, 117.49.



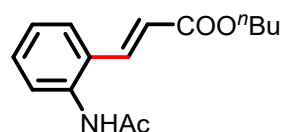
9H-Xanthen-9-one (2t)⁶: colorless solid was obtained with 31% isolated yield (**method 1-C**, 18.4 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.39 (dd, $J = 8.0, 1.6$ Hz, 2H), 7.77 (ddd, $J = 8.7, 7.1, 1.7$ Hz, 2H), 7.54 (dd, $J = 8.4, 0.6$ Hz, 2H), 7.42 (ddd, $J = 8.0, 7.2, 1.0$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.23, 156.17, 134.81, 126.73, 123.90, 121.85, 117.97.



2,6-Dimethyl-9H-xanthen-9-one (2u) + 1,7-Dimethyl-9H-xanthen-9-one (2u')¹⁴: colorless solids were obtained with 35% and 24% isolated yield, respectively. (**method 1-A**, 23.5 mg, 16.1 mg). **2,6-Dimethyl-9H-xanthen-9-one (2u)**: ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 8.1$ Hz, 1H), 8.11 (d, $J = 1.3$ Hz, 1H), 7.51 (dd, $J = 8.5, 2.2$ Hz, 1H), 7.37 (d, $J = 8.5$ Hz, 1H), 7.26 (s, 1H), 7.17 (d, $J = 8.1$ Hz, 1H), 2.50 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.08, 156.29, 154.35, 146.09, 135.80, 133.52, 126.50, 125.98, 125.24, 121.53, 119.59, 117.67, 117.66, 21.97, 20.82. **1,7-Dimethyl-9H-xanthen-9-one (2u')**: ^1H NMR (400 MHz, CDCl_3) δ 8.06 (s, 1H), 7.56 – 7.46 (m, 2H), 7.32 (t, $J = 8.1$ Hz, 2H), 7.10 (d, $J = 7.3$ Hz, 1H), 2.93 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 179.03, 157.62, 153.51, 142.07, 135.58, 133.51, 133.37, 126.49, 126.05, 122.44, 120.27, 117.21, 116.02, 23.31, 20.87.



Ethyl (2S)-2-(1-methyl-1H-indol-3-yl)-5-oxocyclopentane-1-carboxylate (4a)¹²: colorless oil was obtained with 53% isolated yield. ^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, $J = 8.0$ Hz, 1H), 7.29 (d, $J = 8.1$ Hz, 1H), 7.23 (t, $J = 7.6$ Hz, 1H), 7.10 (t, $J = 7.4$ Hz, 1H), 6.90 (s, 1H), 4.24 – 4.10 (m, 2H), 4.10 – 4.01 (m, 1H), 3.72 (s, 3H), 3.42 (d, $J = 11.2$ Hz, 1H), 2.62 – 2.42 (m, 3H), 2.15 – 2.02 (m, 1H), 1.21 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 211.54, 169.23, 137.27, 126.69, 125.19, 121.84, 119.23, 118.94, 115.05, 109.39, 62.05, 61.36, 38.60, 38.34, 32.60, 28.49, 14.03.



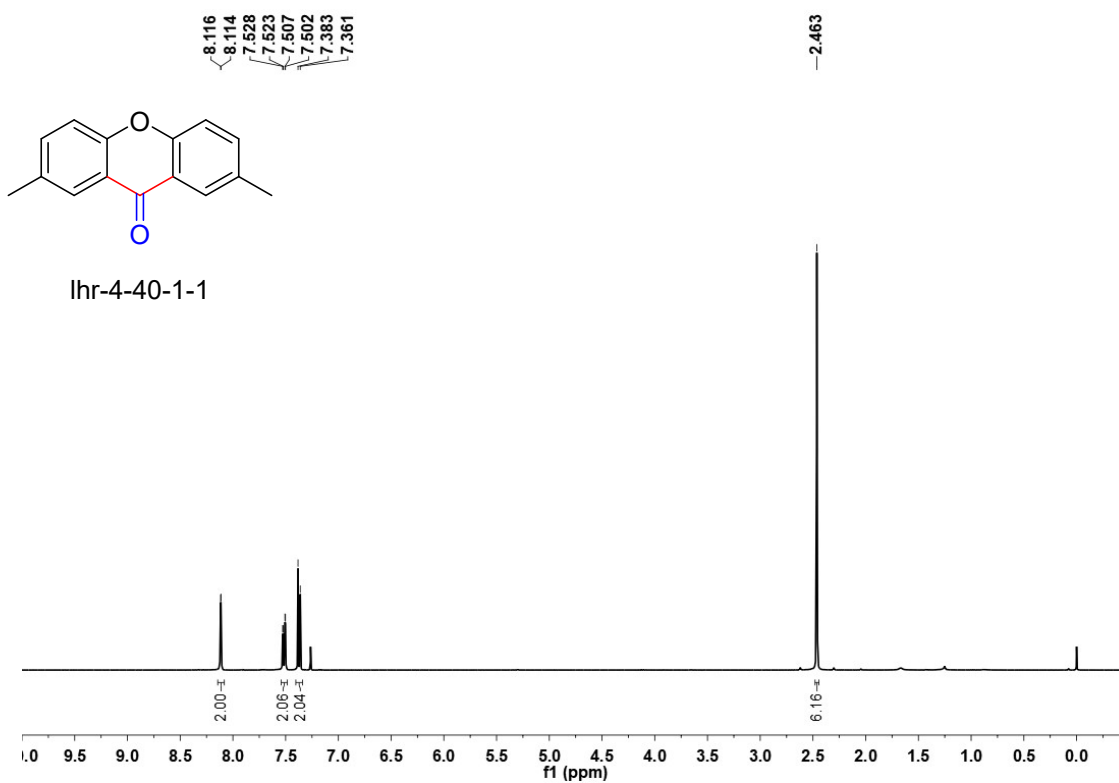
Butyl (E)-3-(2-acetamidophenyl)acrylate (4b)¹³: yellow solid was obtained with 60% isolated yield. ^1H NMR (400 MHz, CDCl_3) δ 7.94 (s, 1H), 7.81 (d, $J = 15.9$ Hz, 1H), 7.63 (d, J

= 8.1 Hz, 1H), 7.53 (d, $J = 7.7$ Hz, 1H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.28 – 7.15 (m, 1H), 6.36 (d, $J = 15.8$ Hz, 1H), 4.17 (t, $J = 6.7$ Hz, 2H), 2.19 (s, 3H), 1.72 – 1.60 (m, 2H), 1.47 – 1.35 (m, 2H), 0.95 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.27, 166.97, 139.49, 135.92, 130.61, 128.74, 126.83, 125.87, 125.55, 120.03, 64.54, 30.60, 23.83, 19.08, 13.64.

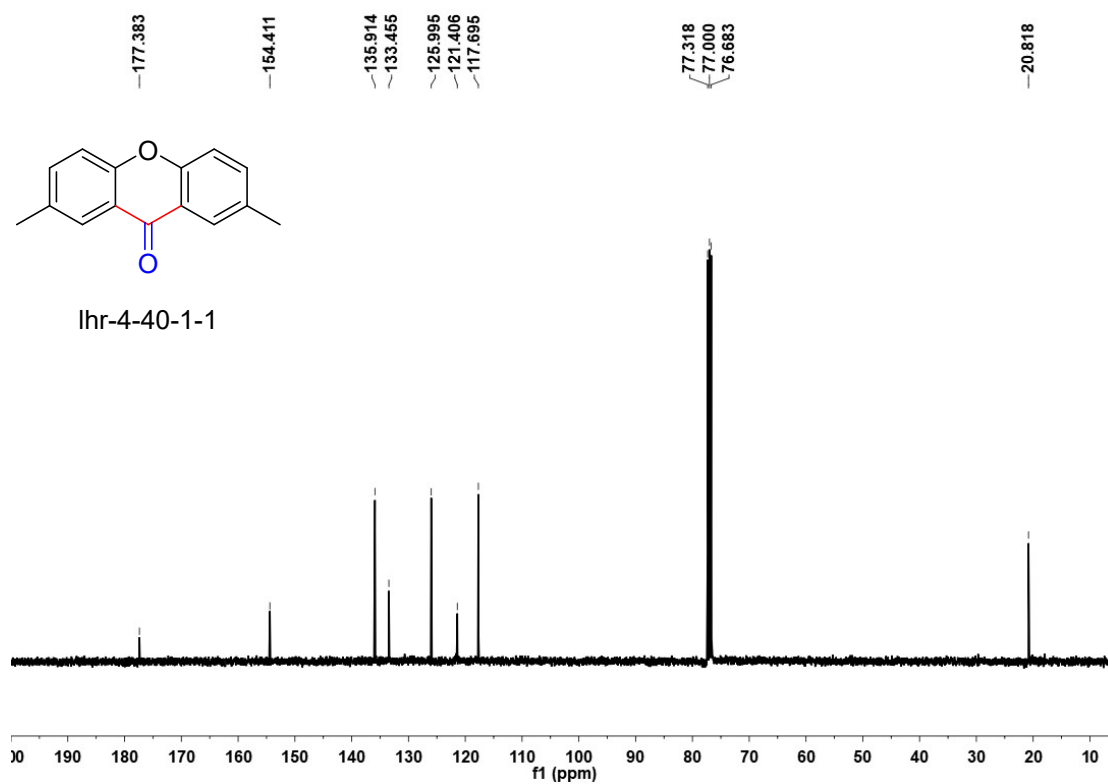
13. Spectral data

2a

¹H NMR

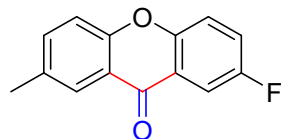
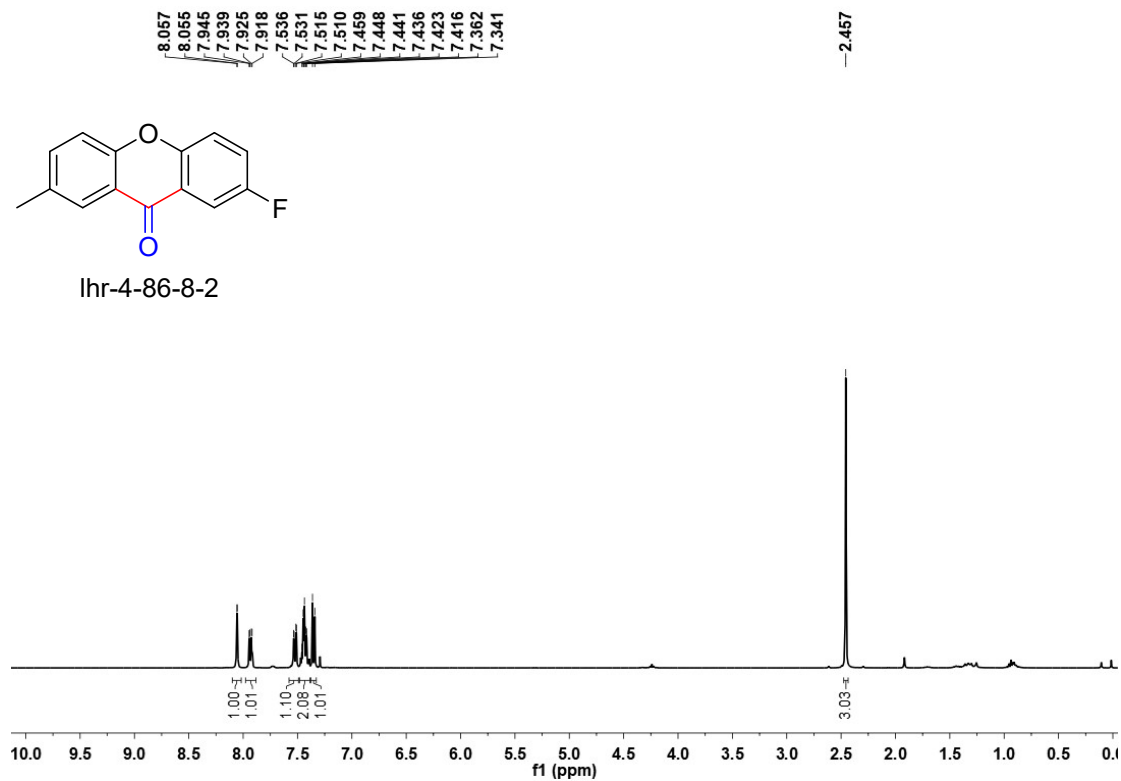


¹³C NMR



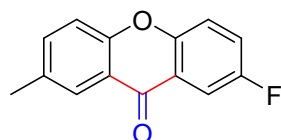
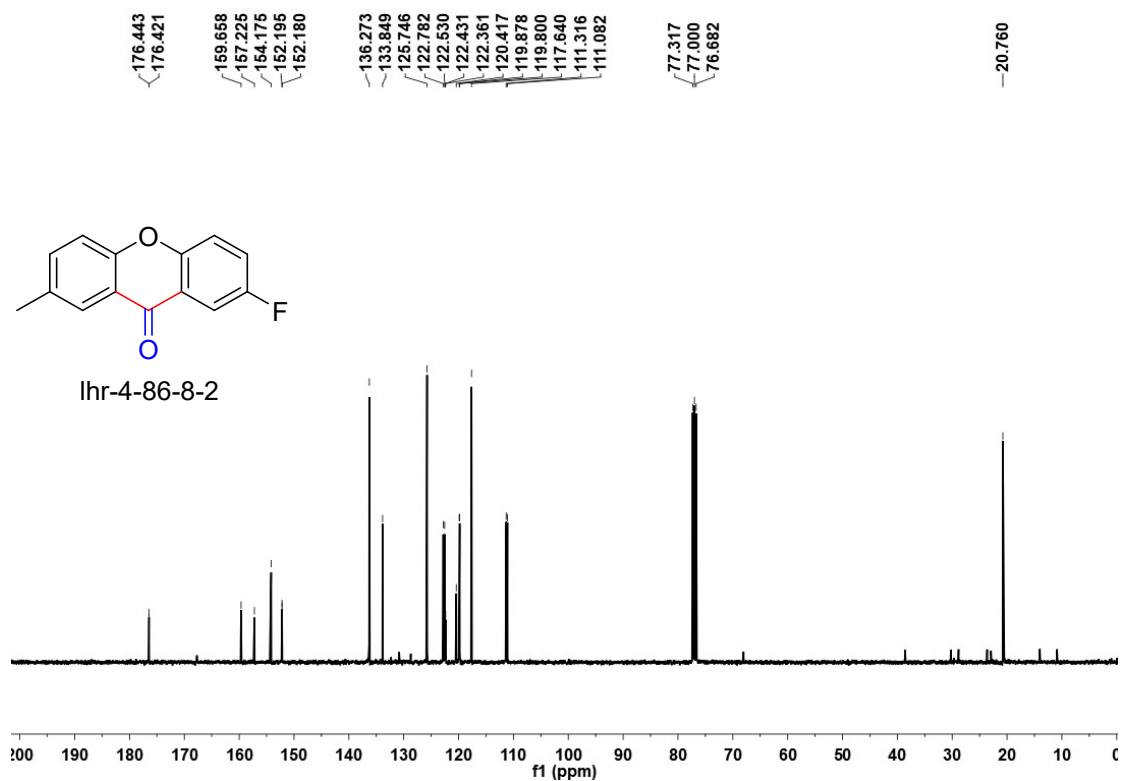
2b

¹H NMR



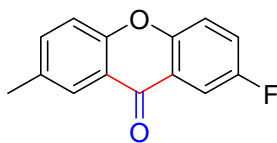
lhr-4-86-8-2

¹³C NMR

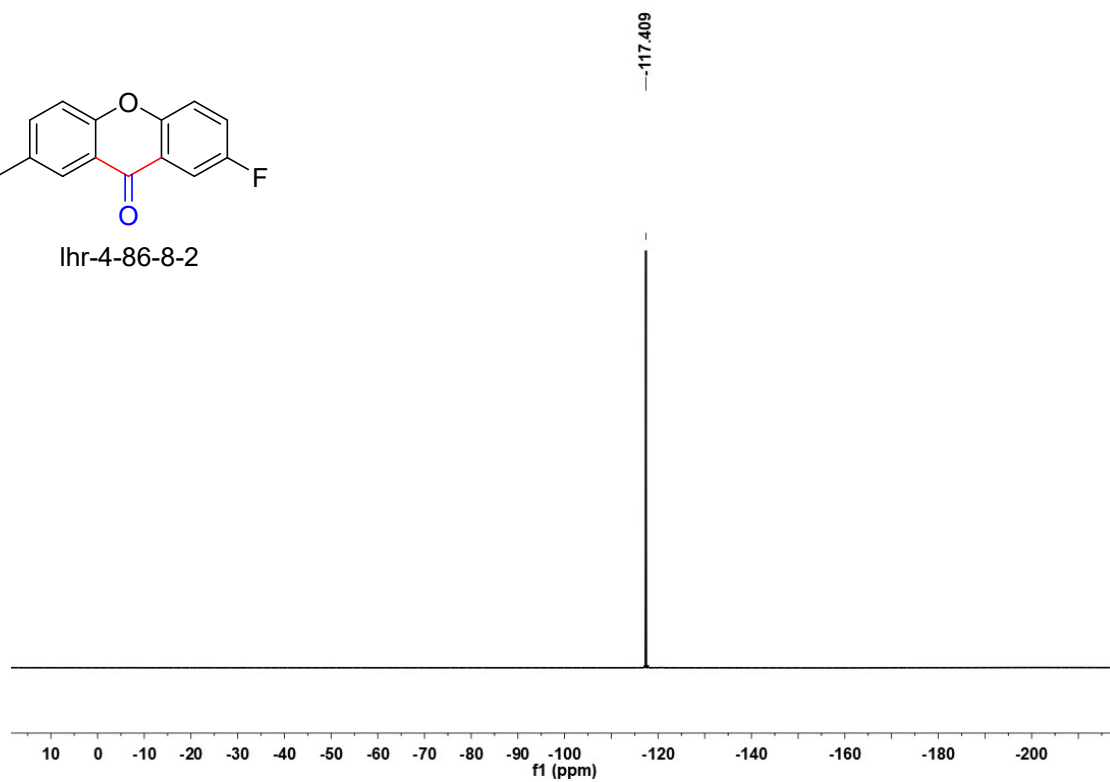


lhr-4-86-8-2

¹⁹F NMR

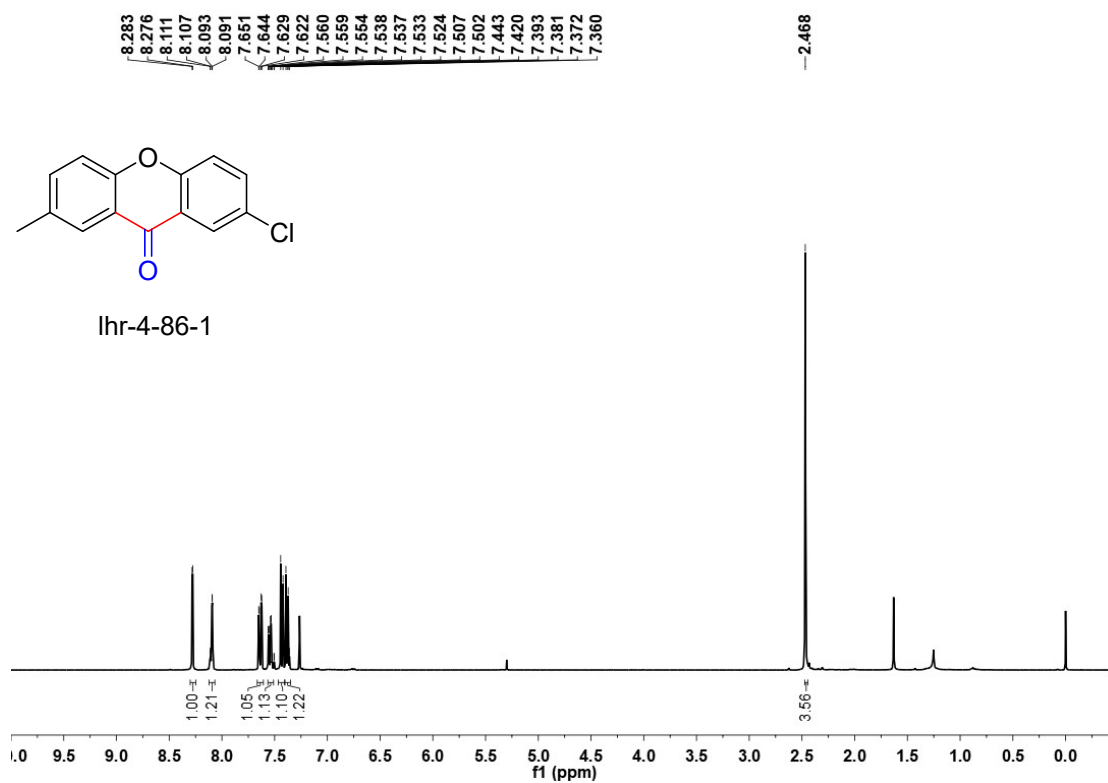


lhr-4-86-8-2

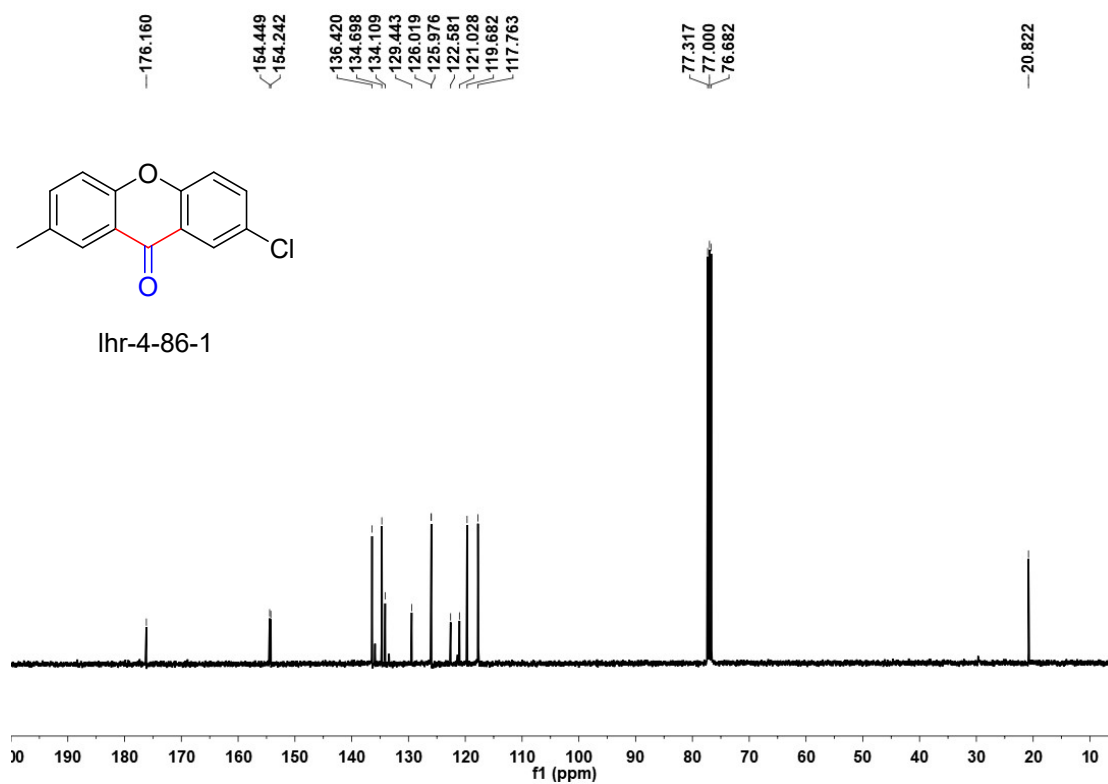


2c

¹H NMR

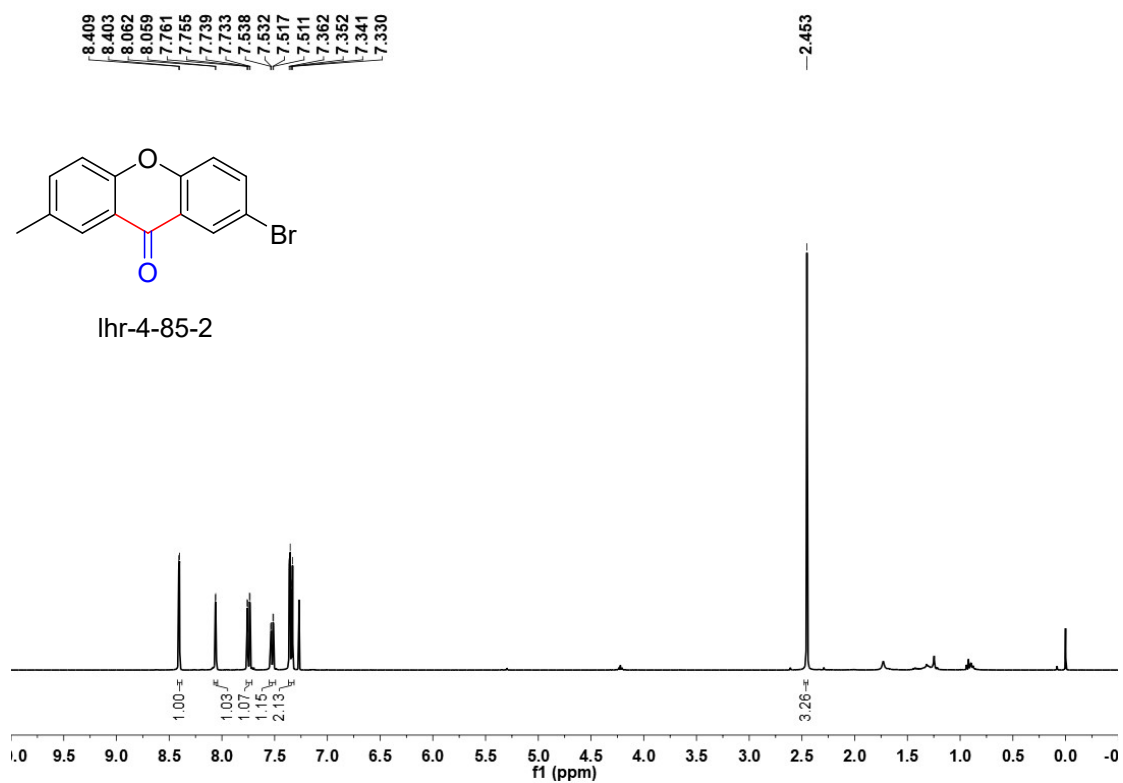


¹³C NMR

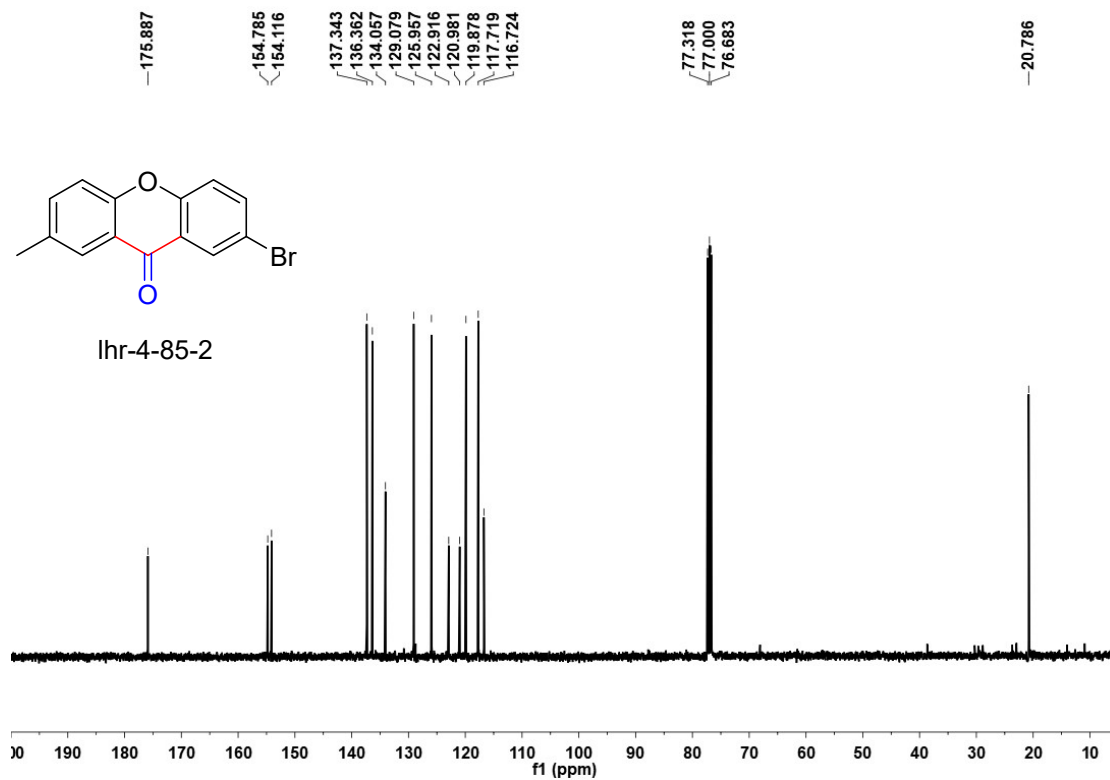


2d

¹H NMR

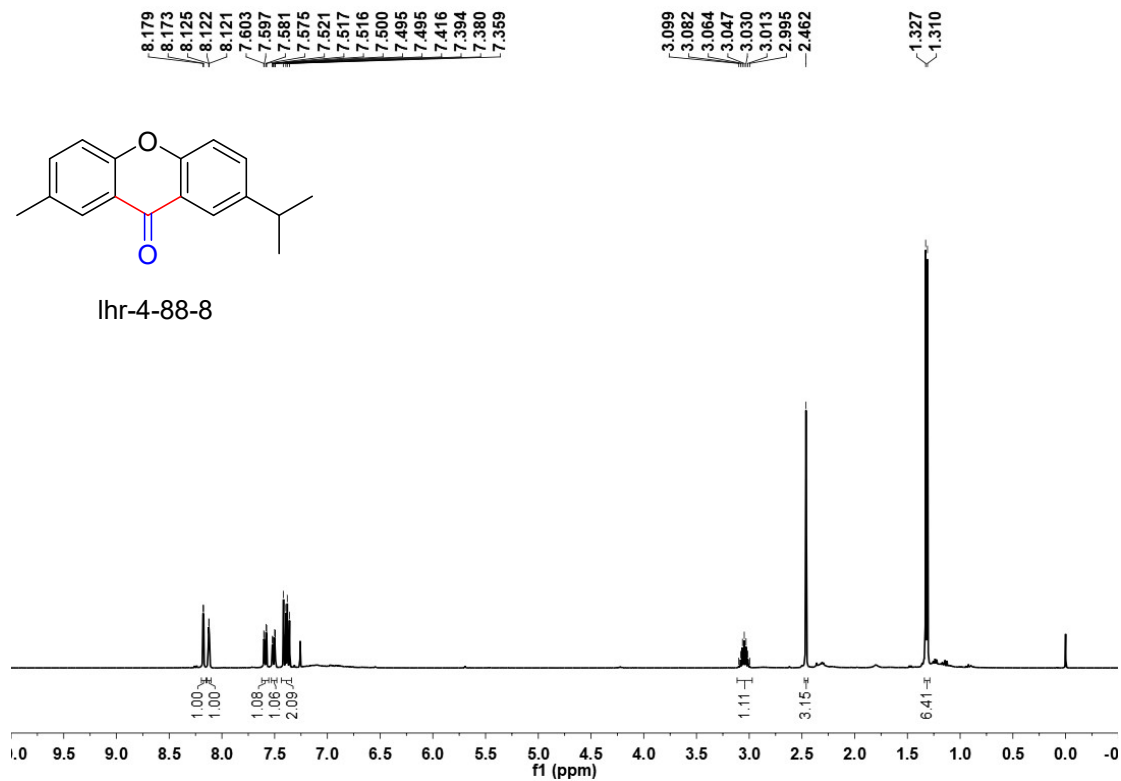


¹³C NMR

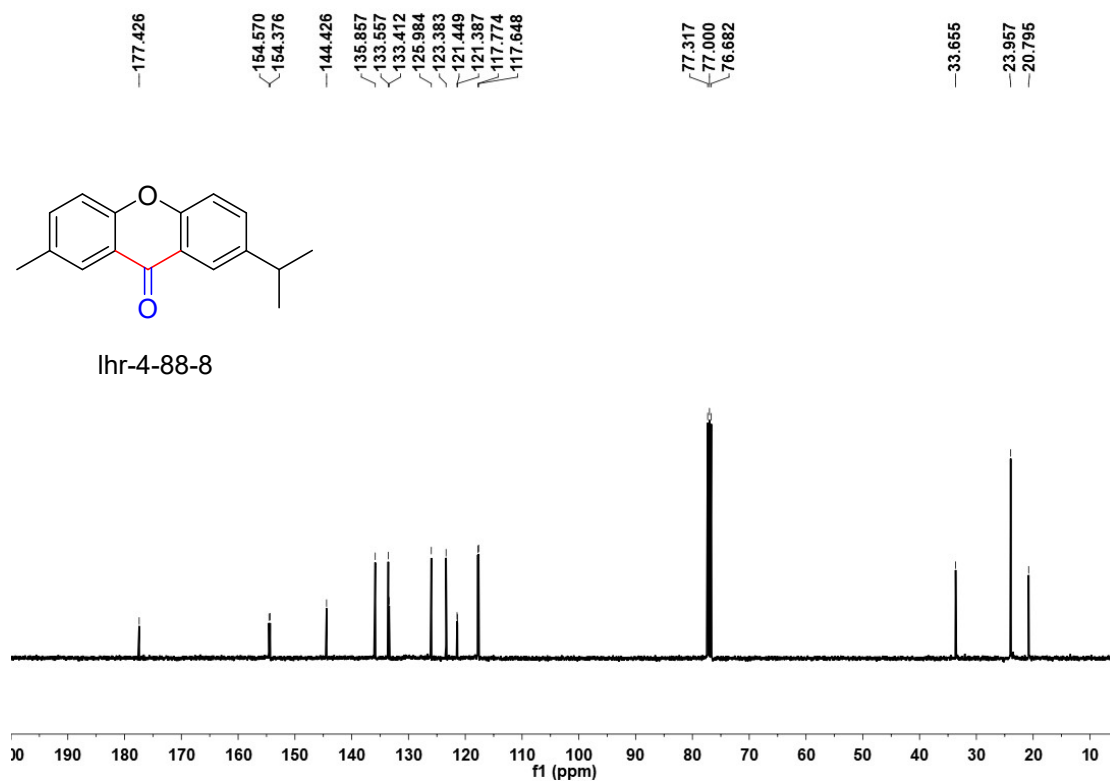


2e

¹H NMR

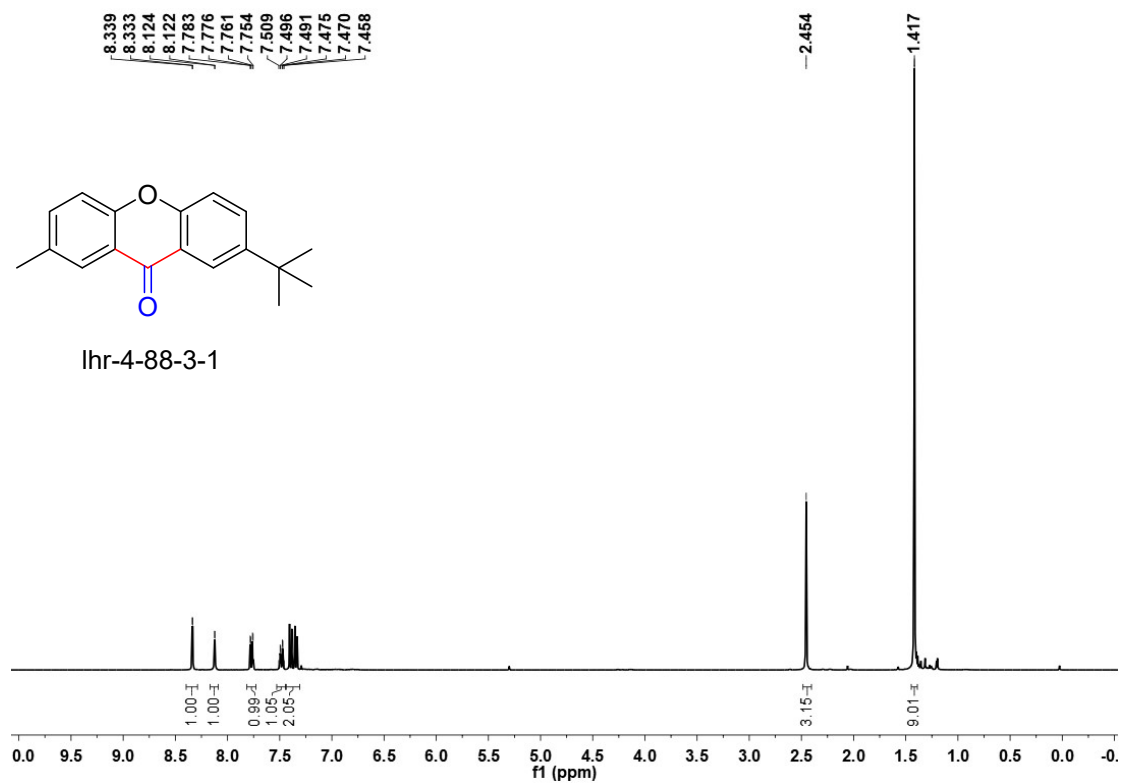


¹³C NMR

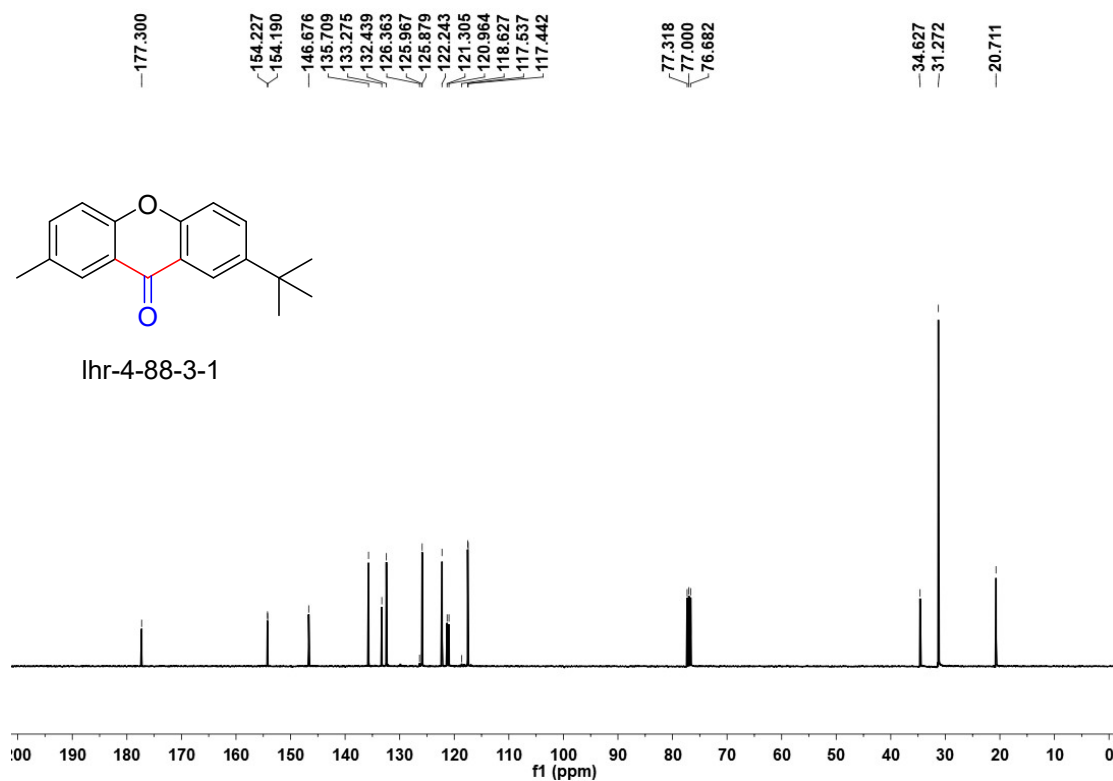


2f

¹H NMR

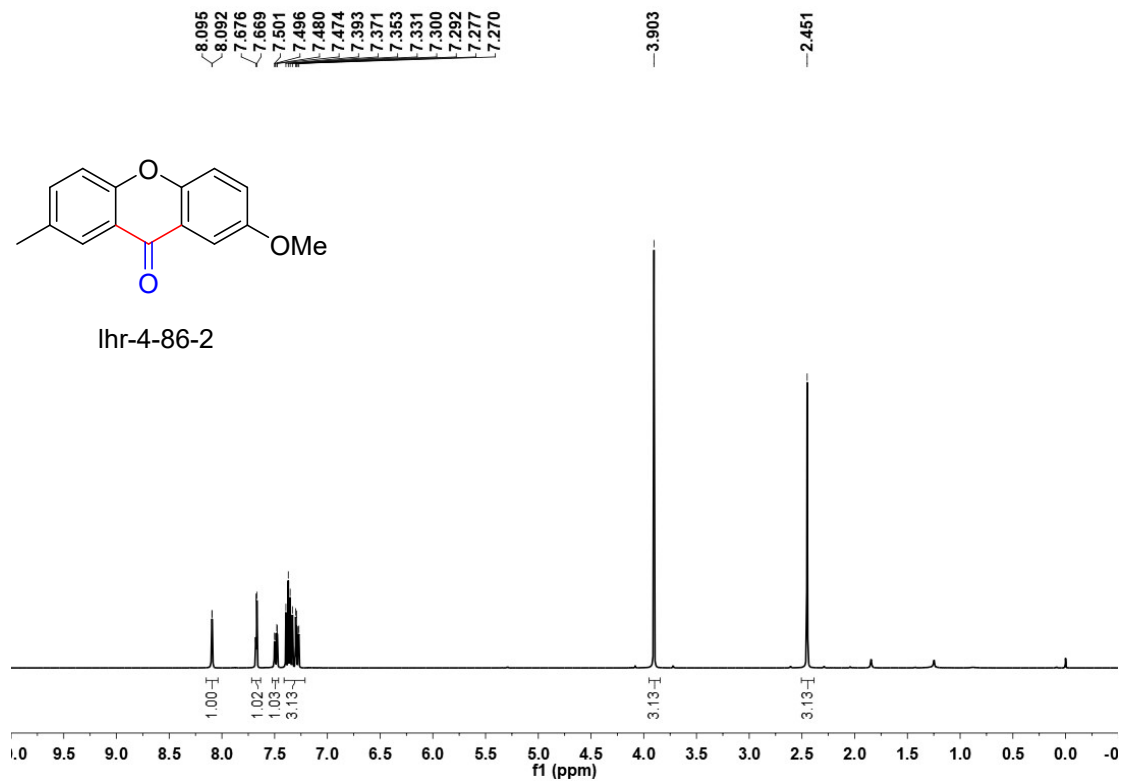


¹³C NMR

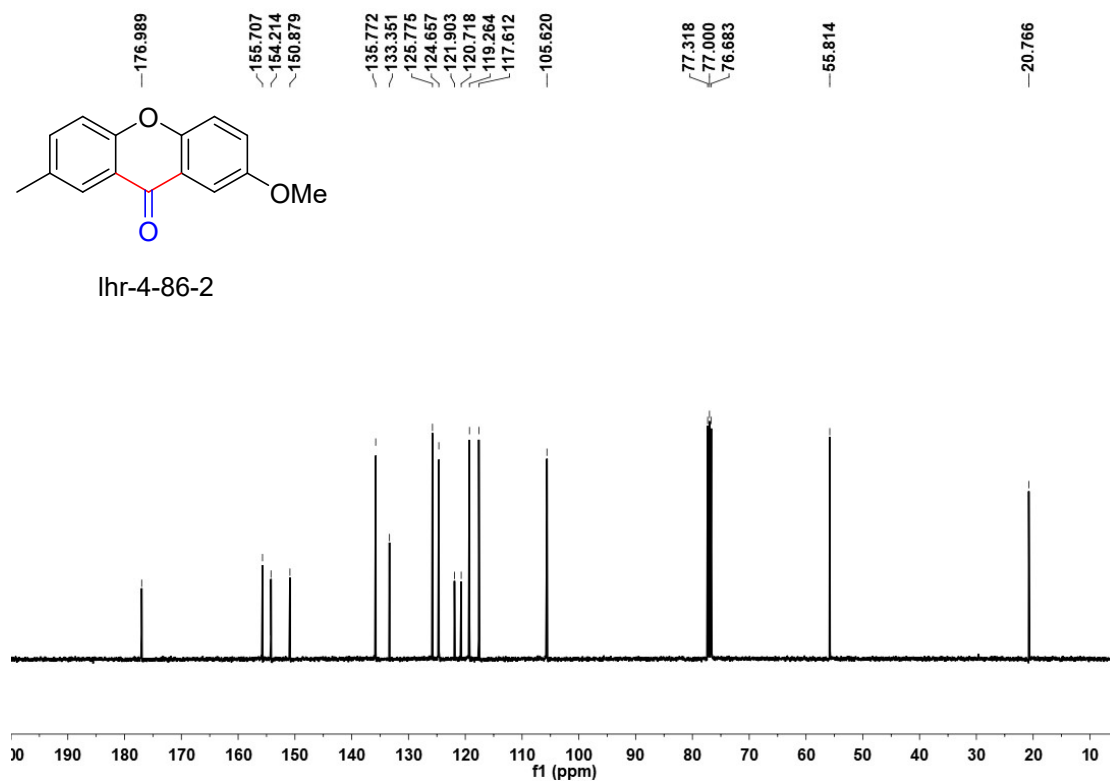


2g

¹H NMR

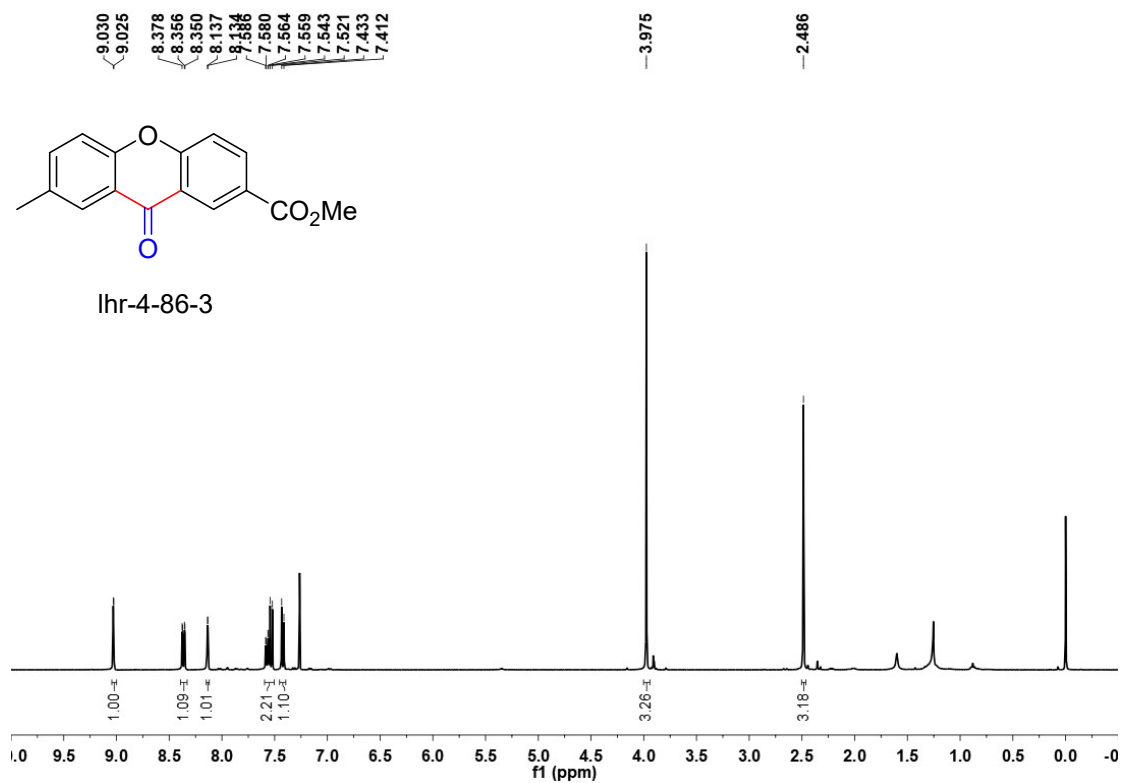


¹³C NMR

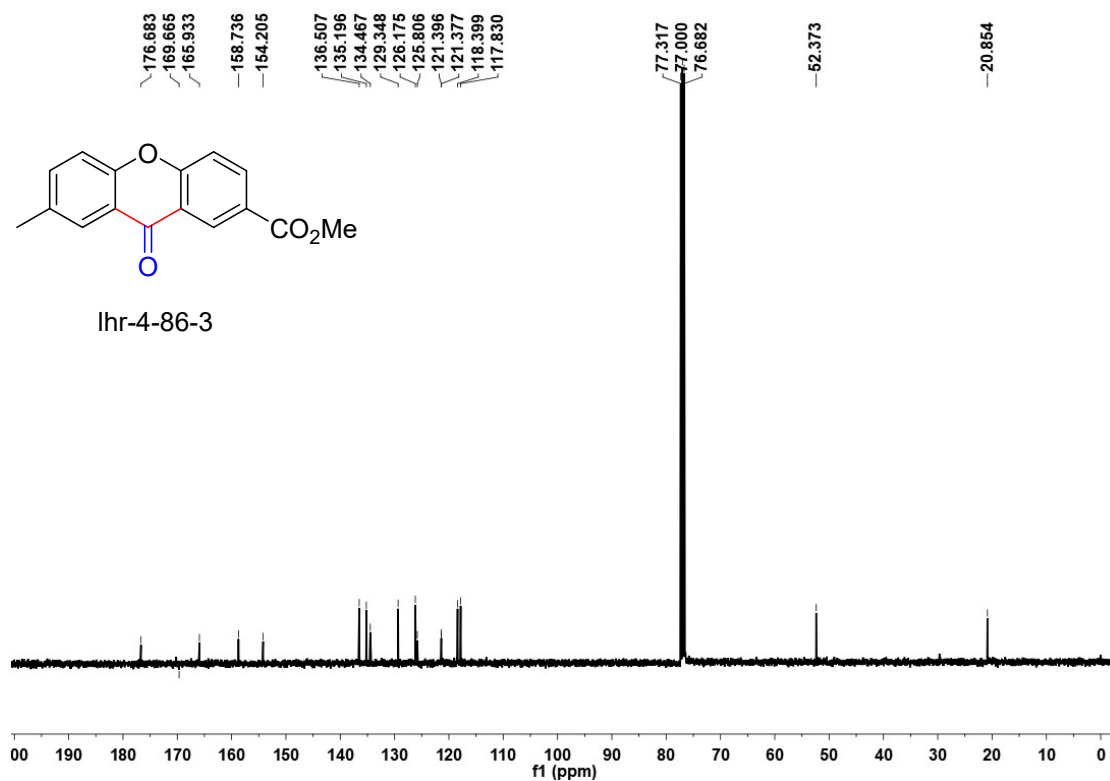


2h

¹H NMR



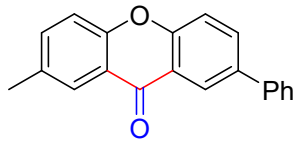
¹³C NMR



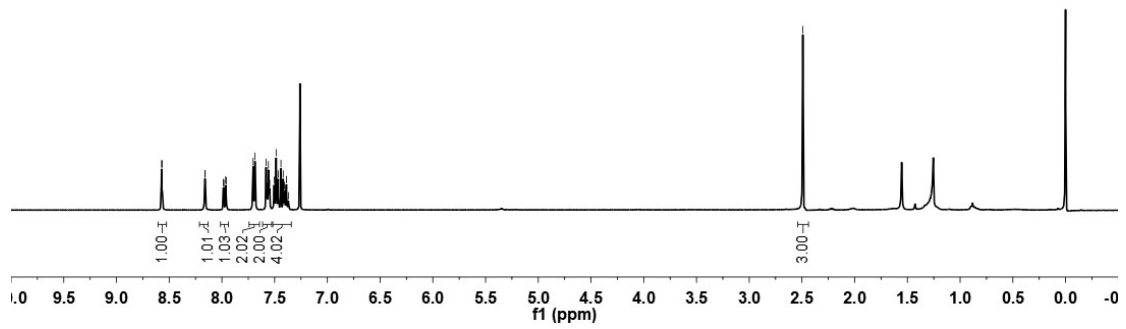
2i

¹H NMR

8.572
8.567
8.161
8.159
7.987
7.981
7.966
7.959
7.707
7.704
7.686
7.581
7.574
7.568
7.559
7.552
7.547
7.504
7.486
7.466
7.440
7.419
7.407
7.389
7.370
-2.492

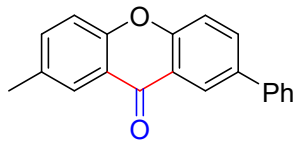


lhr-4-88-1

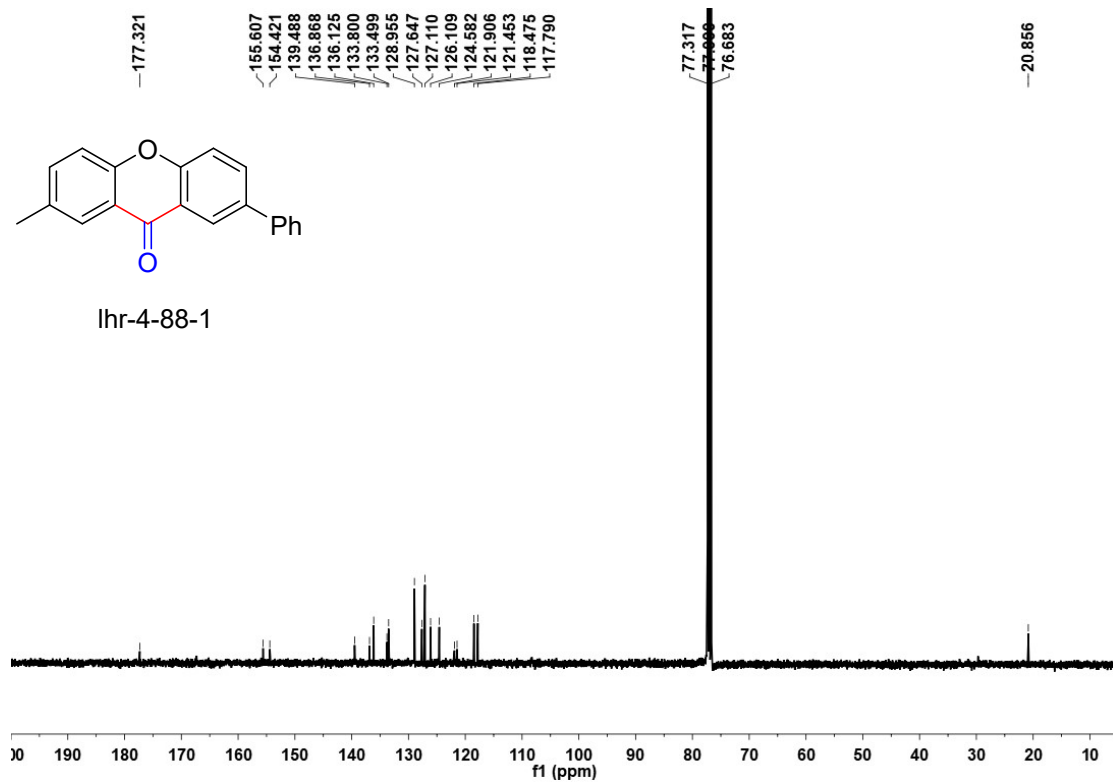


¹³C NMR

177.321
155.607
154.421
139.488
136.868
136.125
133.800
133.499
128.955
127.647
127.110
126.109
124.582
121.906
121.453
118.475
117.790
77.317
77.000
76.683
20.856

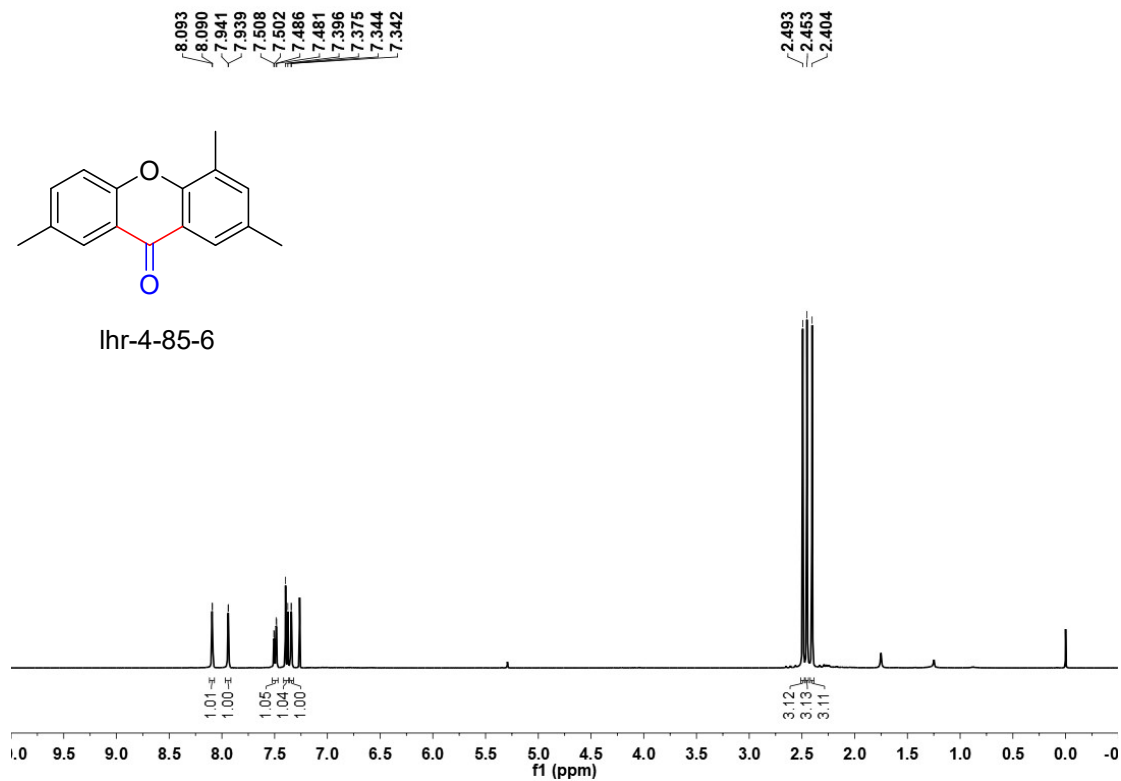


lhr-4-88-1

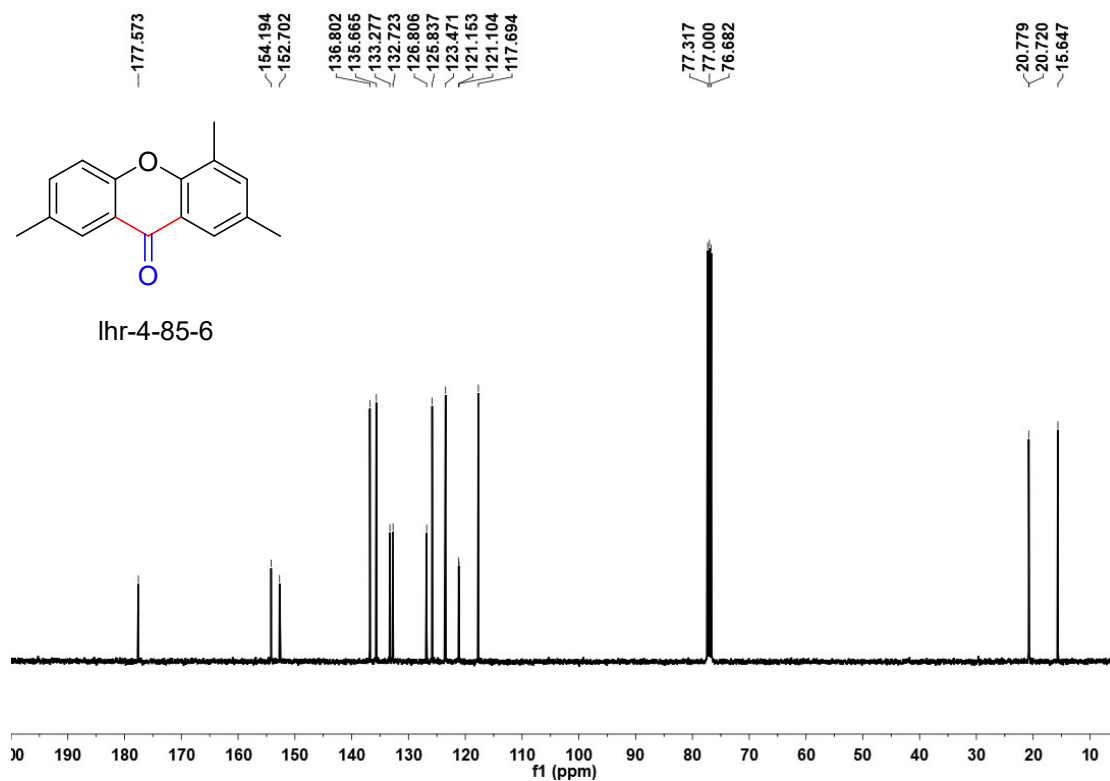


2j

¹H NMR



¹³C NMR

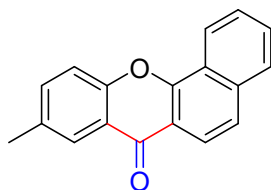


2k

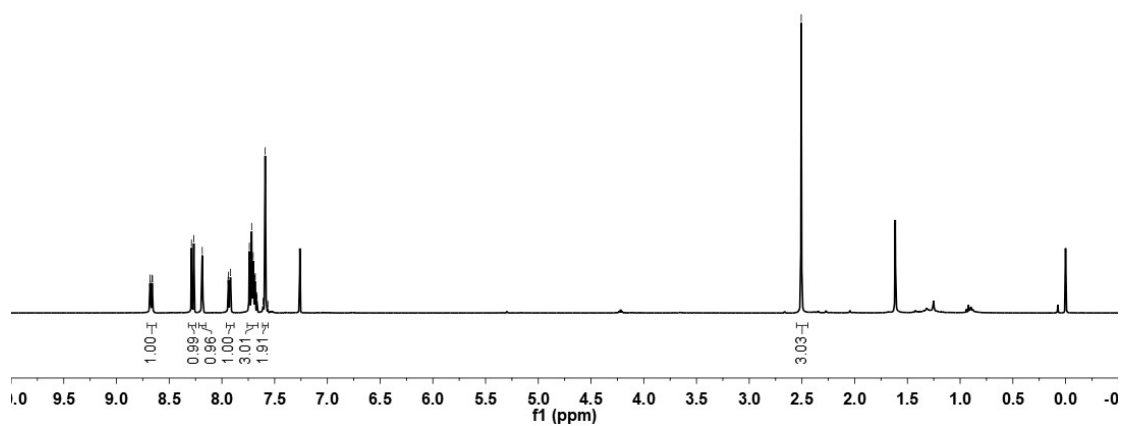
¹H NMR

8.681
8.678
8.662
8.658
8.289
8.267
8.186
7.941
7.937
7.924
7.919
7.740
7.718
7.707
7.703
7.698
7.687
7.684
7.670
7.666
7.609
7.590
7.564

2.507



lhr-4-89-2-1

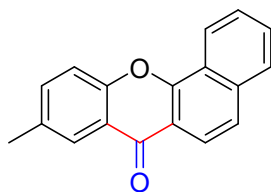


¹³C NMR

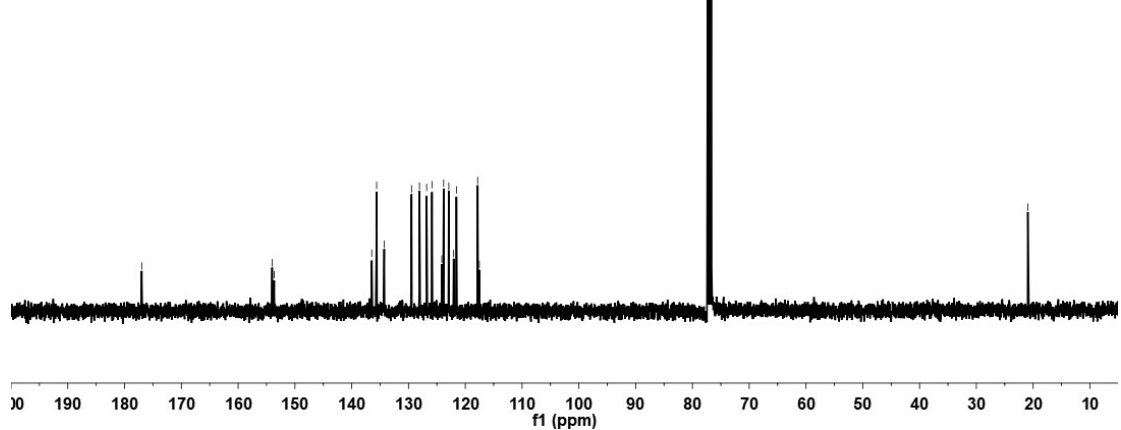
176.983
154.012
153.650
136.470
135.611
134.278
129.467
128.065
126.806
125.868
124.132
123.808
122.905
122.048
121.564
117.817
117.531

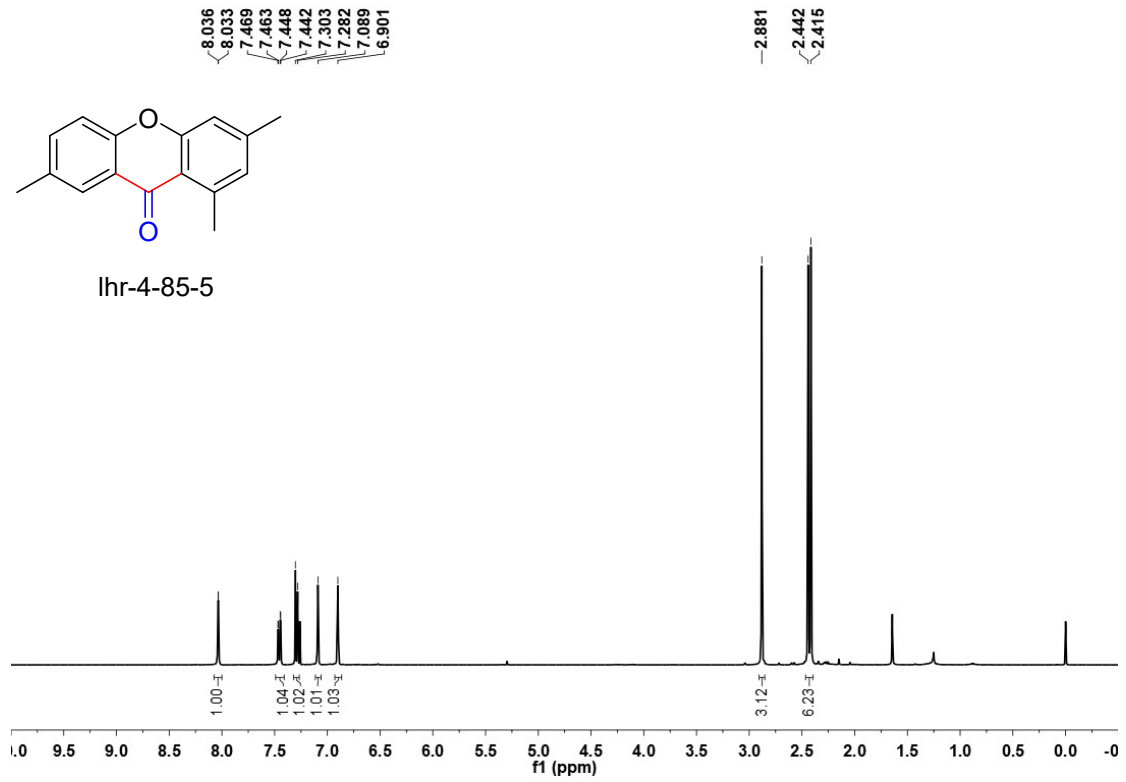
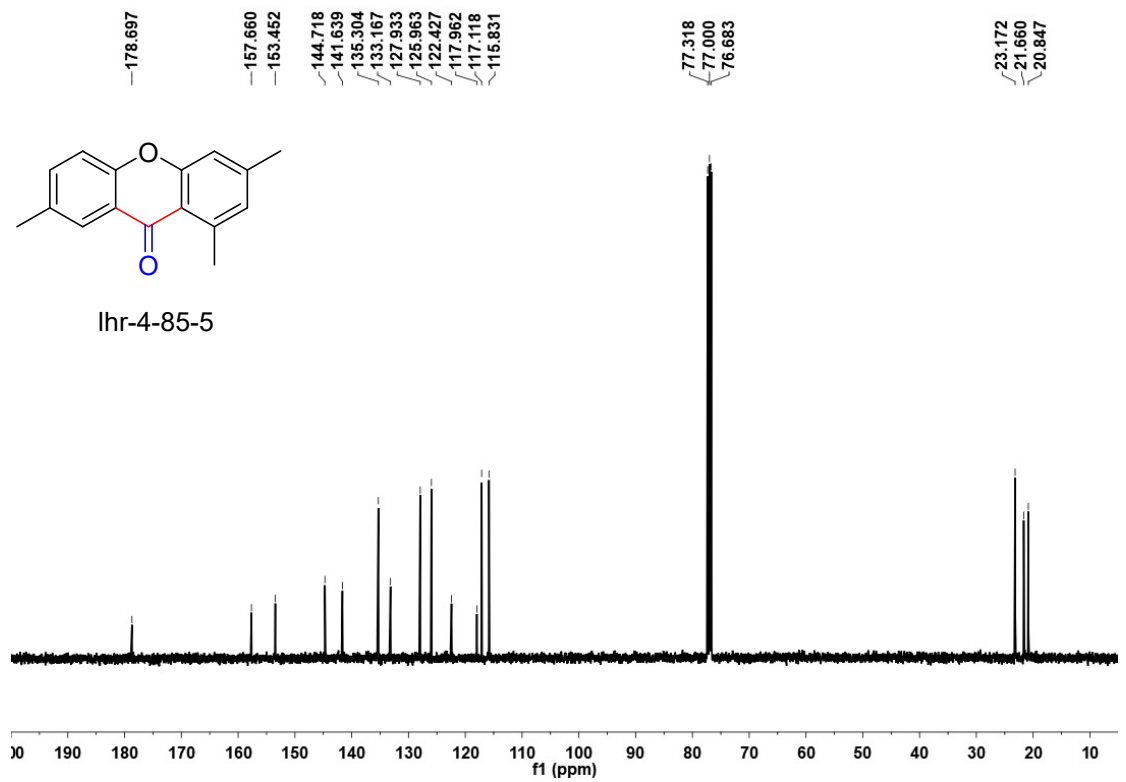
77.317
77.000
76.682

20.935



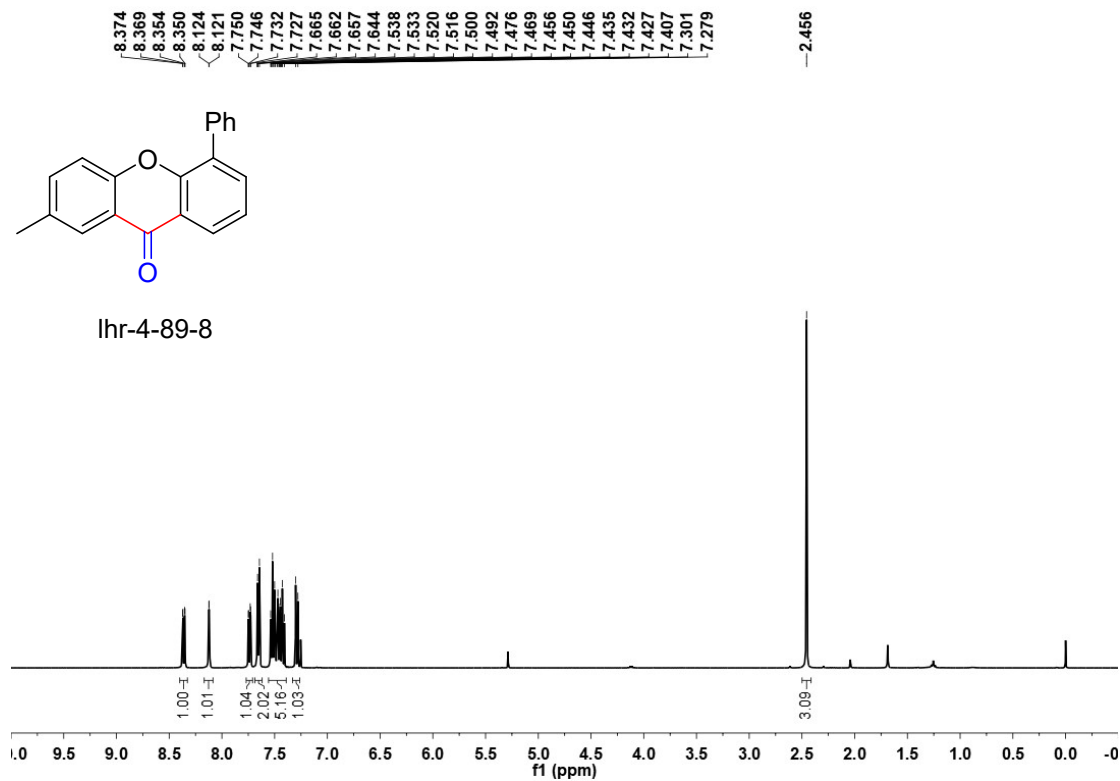
lhr-4-89-2-1



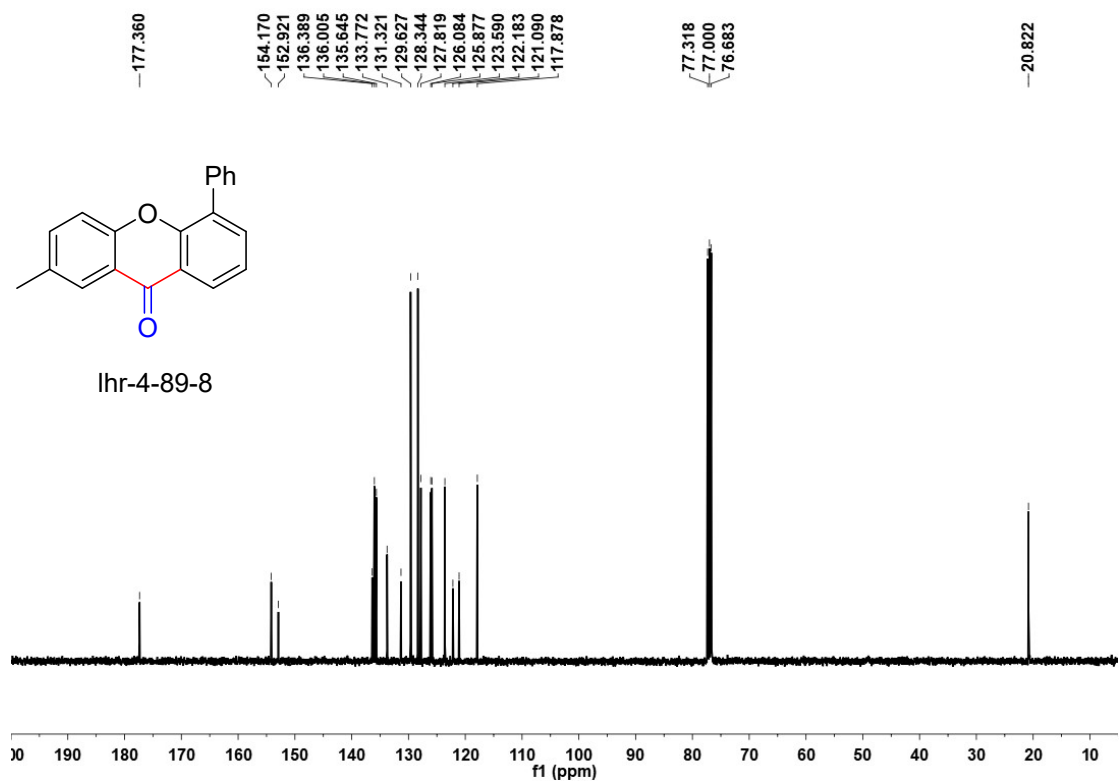
¹H NMR¹³C NMR

2m

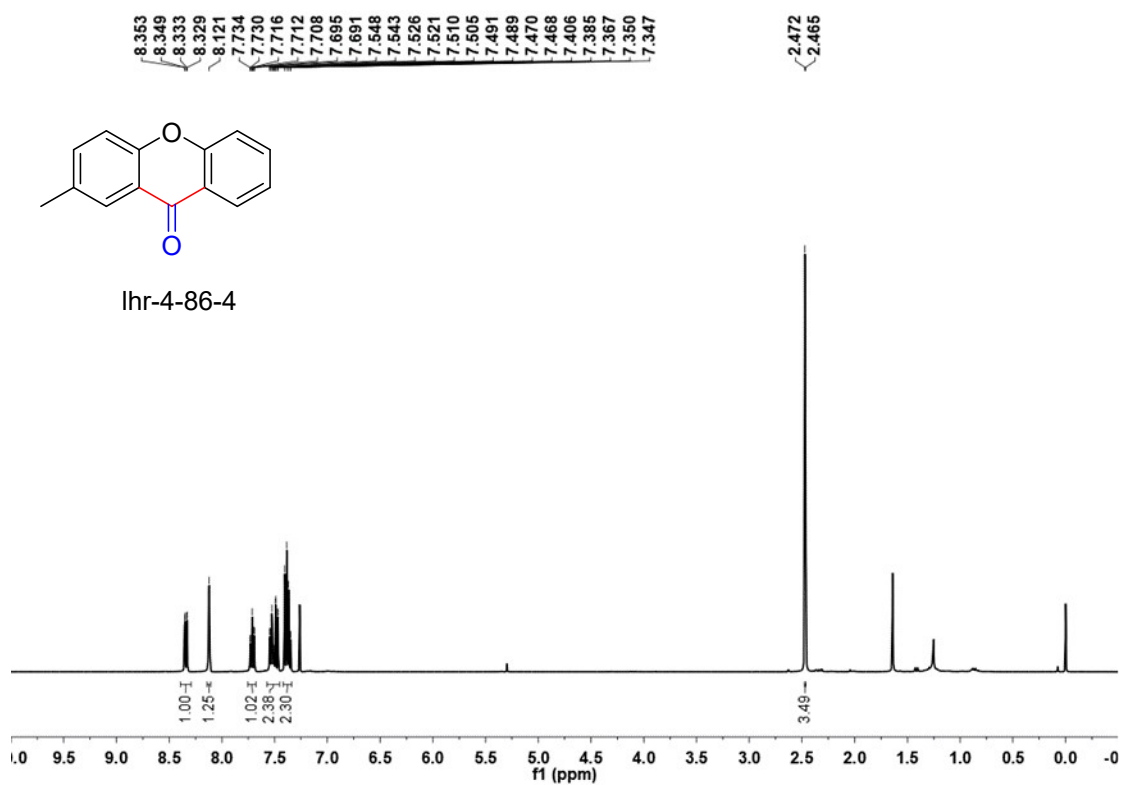
¹H NMR



¹³C NMR

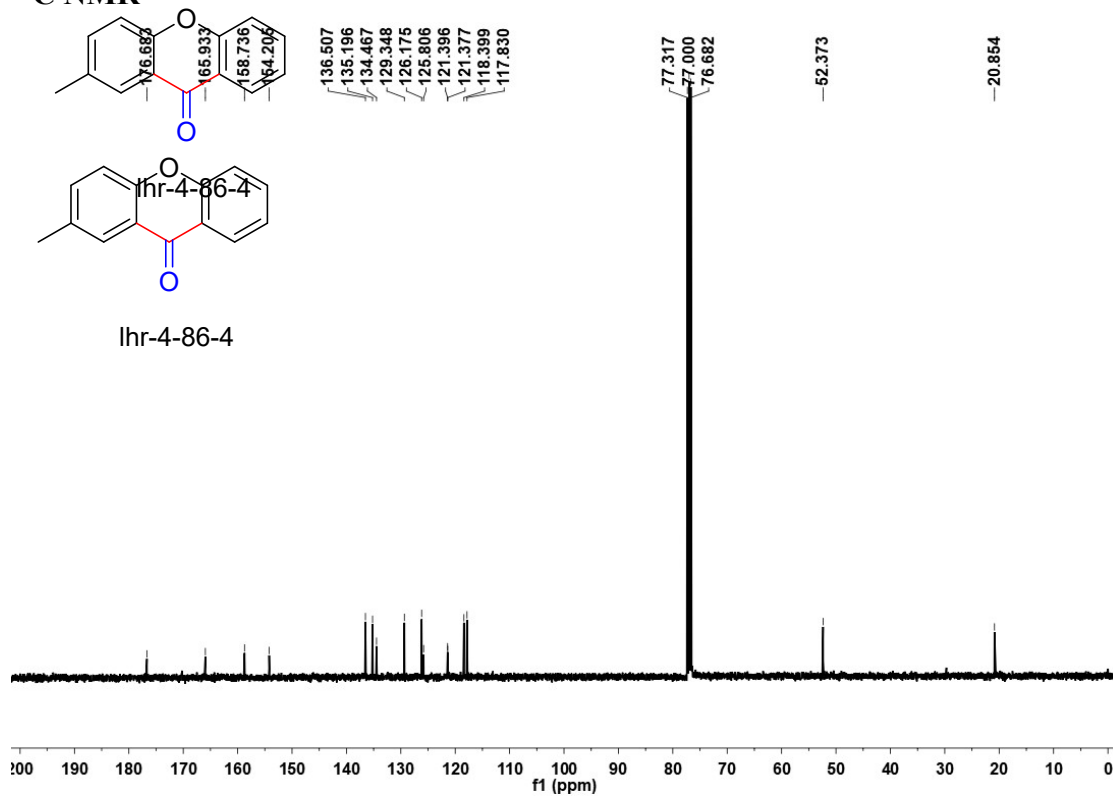


2n



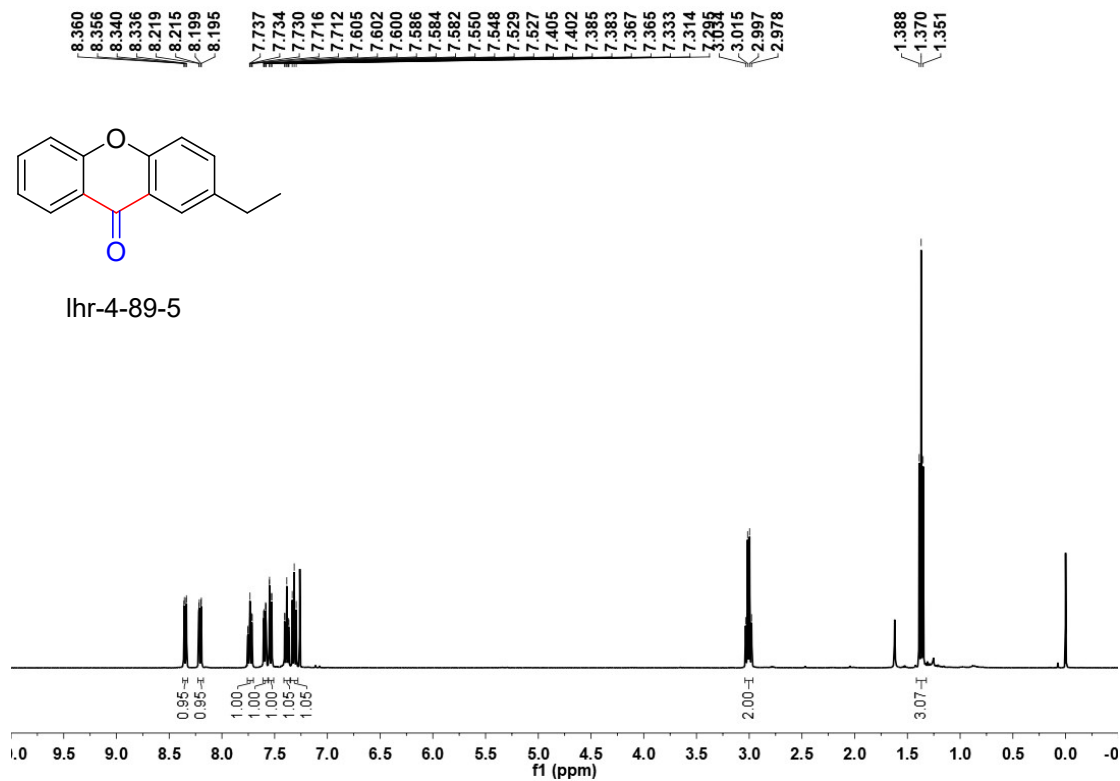
¹H NMR

¹³C NMR

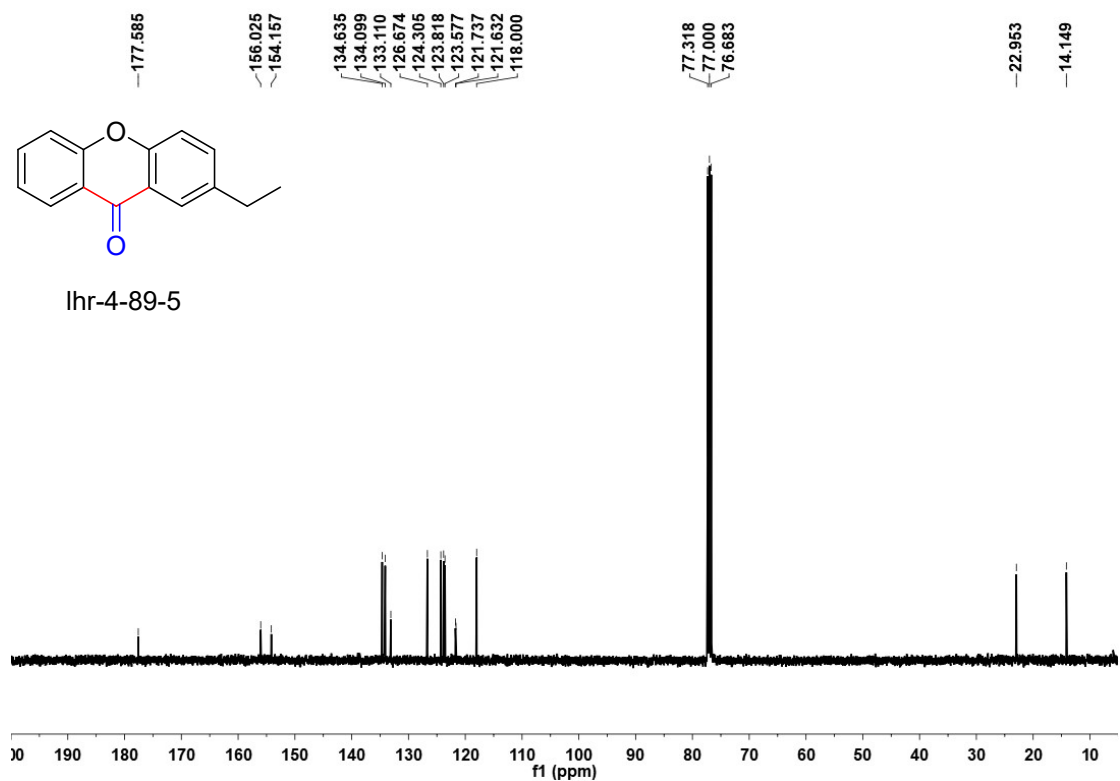


2o

¹H NMR

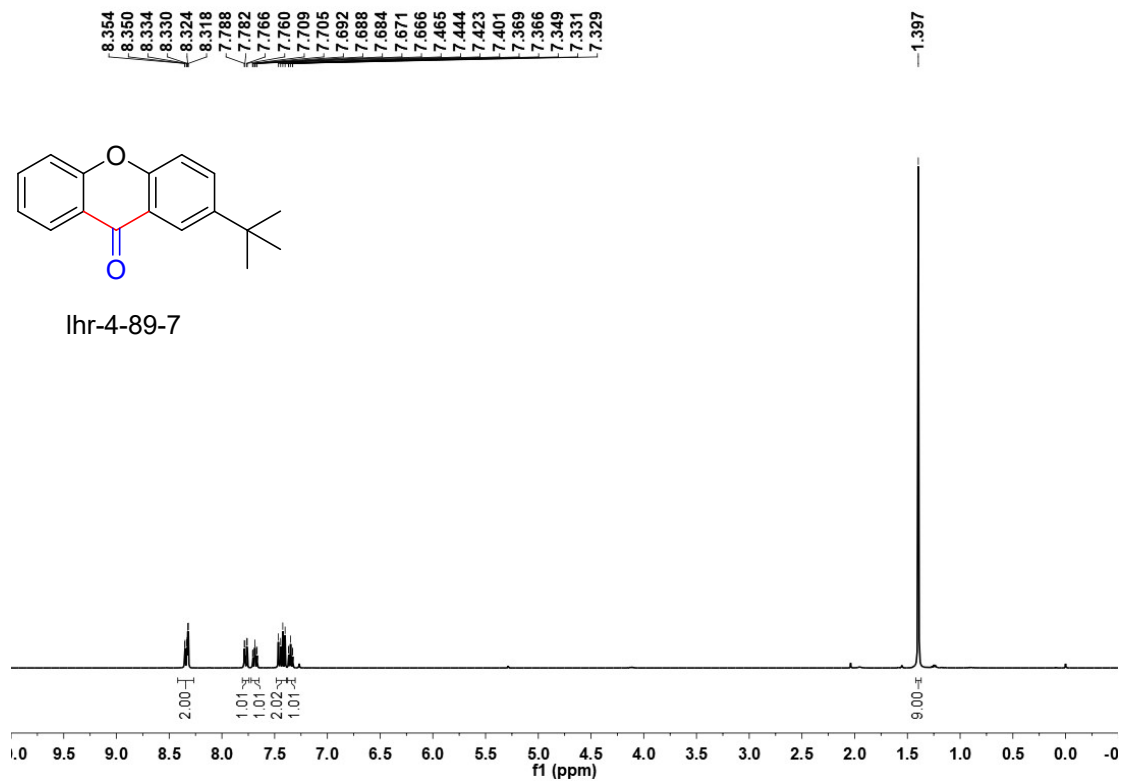


¹³C NMR

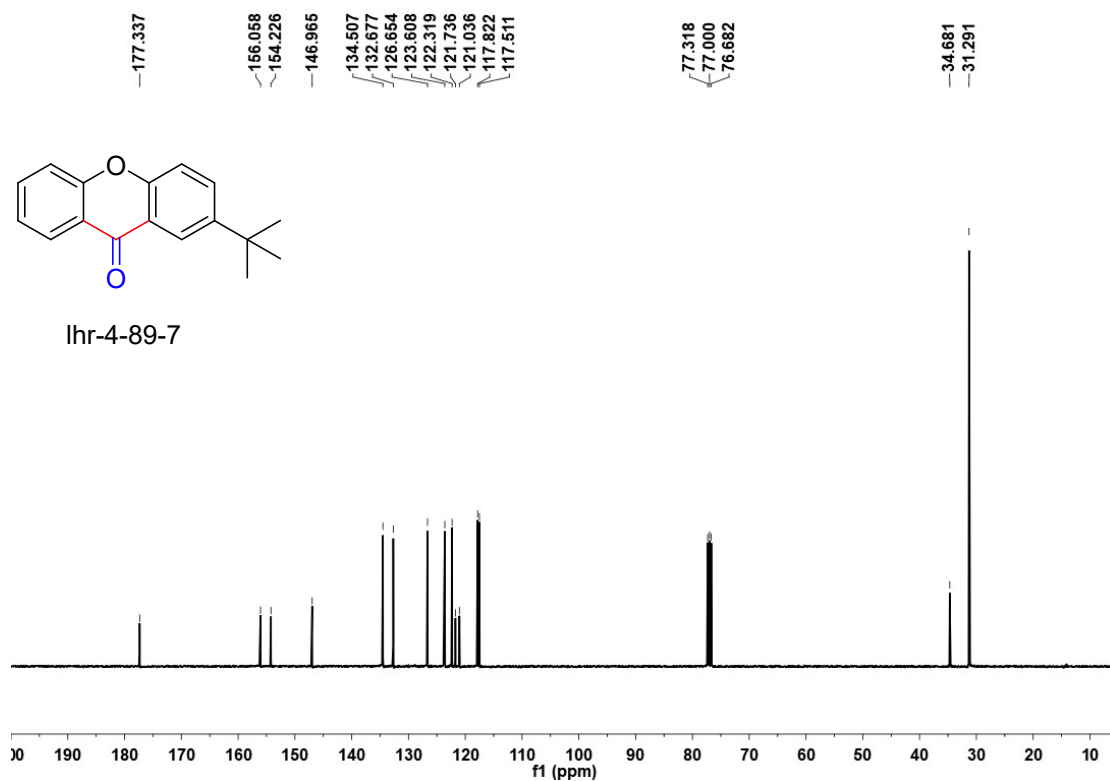


2p

¹H NMR

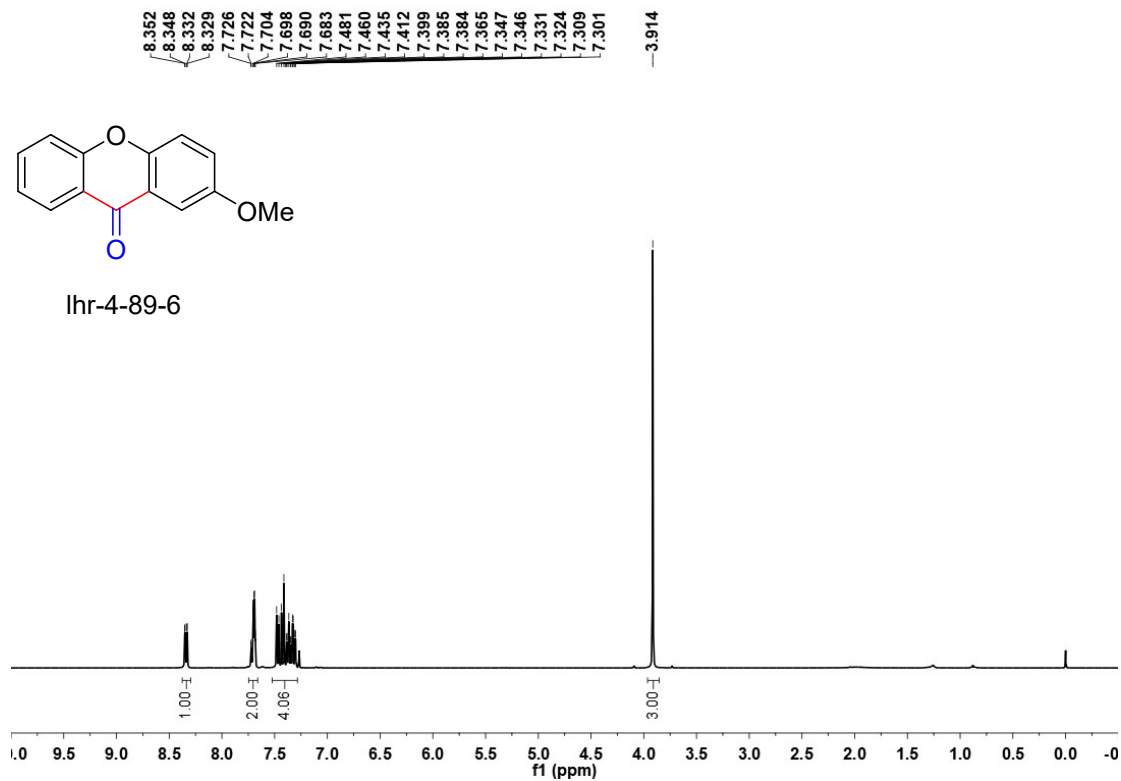


¹³C NMR

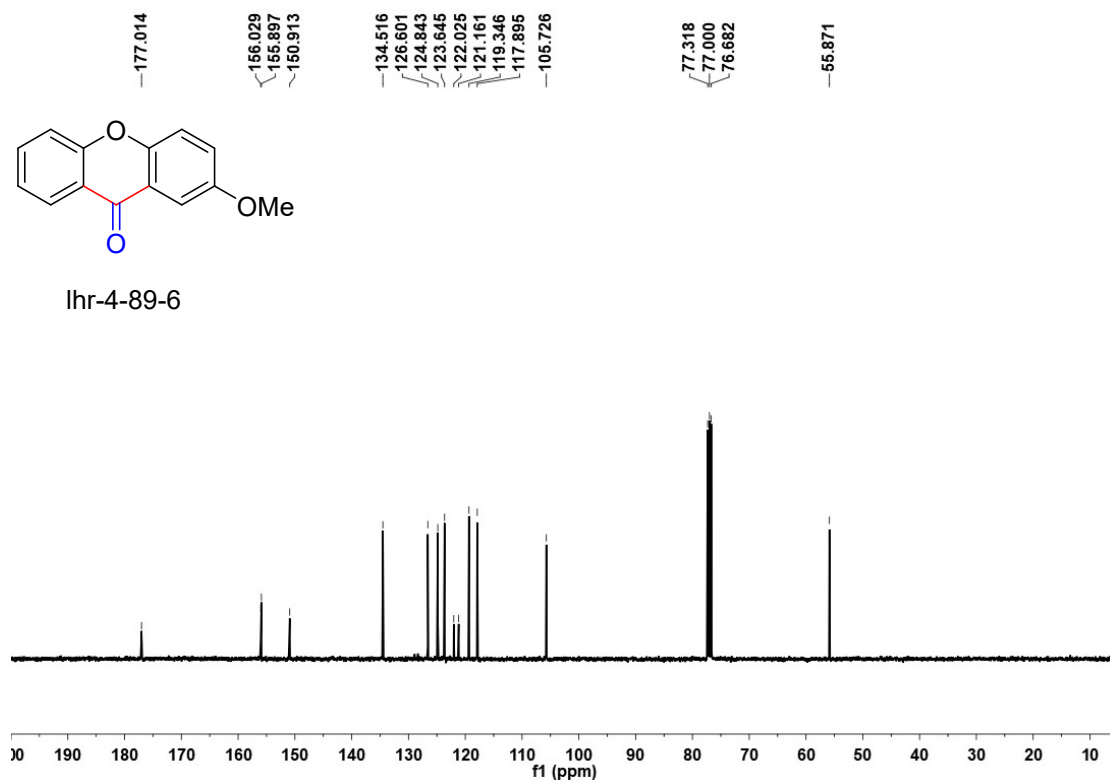


2q

¹H NMR

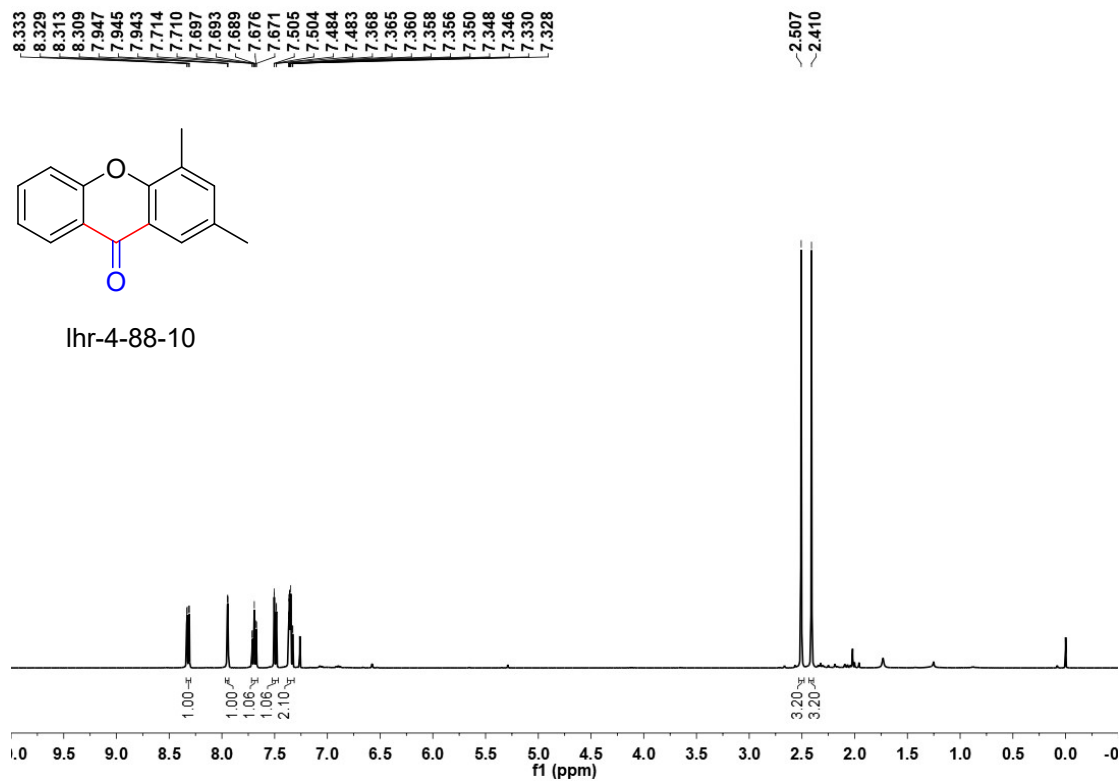


¹³C NMR

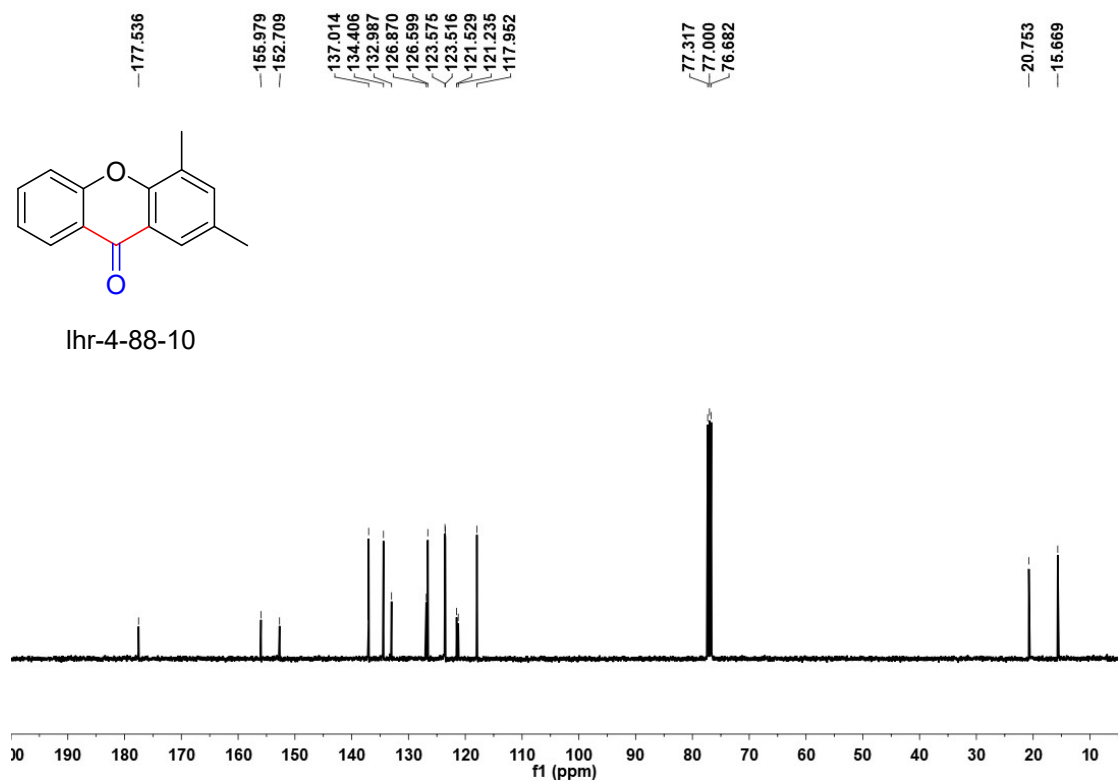


2r

¹H NMR

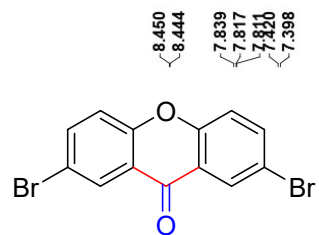


¹³C NMR

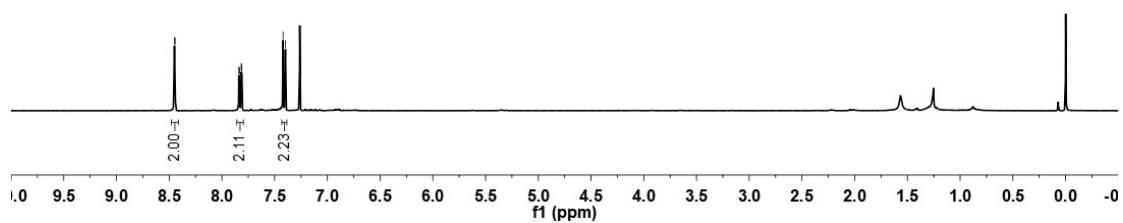


2s

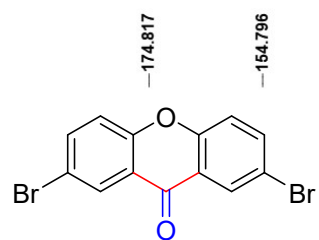
¹H NMR



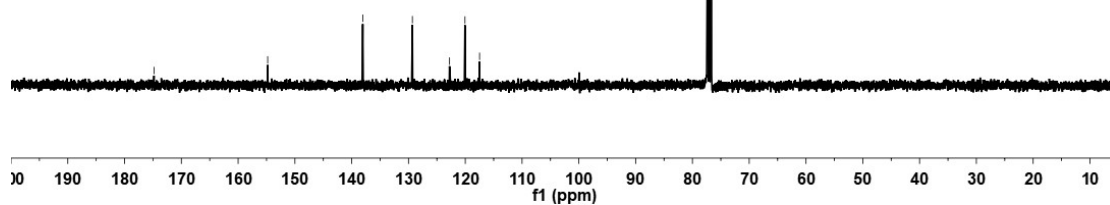
Ihr-4-89-4



¹³C NMR



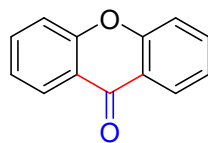
Ihr-4-89-4



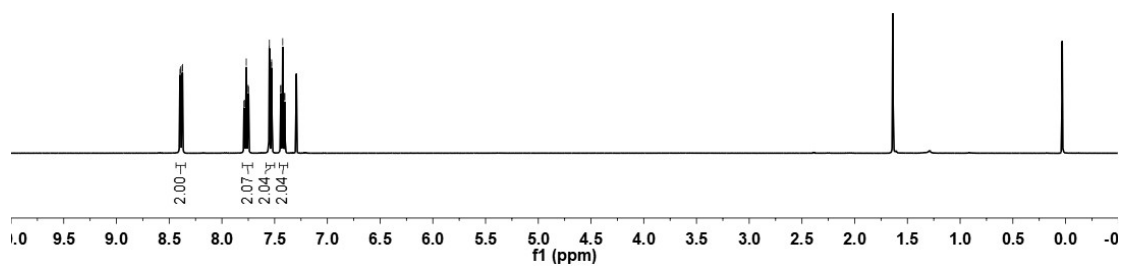
2t

¹H NMR

8.398
8.394
8.378
8.374
7.791
7.786
7.773
7.769
7.766
7.752
7.747
7.561
7.550
7.530
7.529
7.443
7.441
7.425
7.423
7.421
7.406
7.403

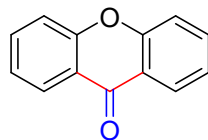


lhr-4-83-0-1

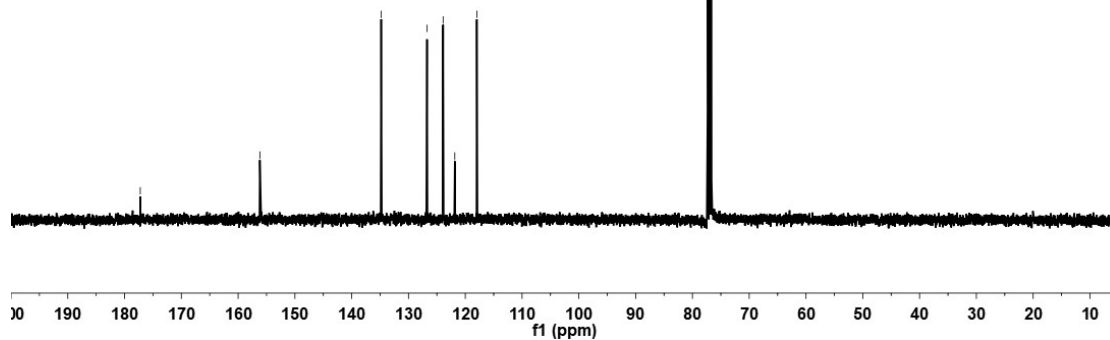


¹³C NMR

177.234
166.174
134.811
126.734
123.903
121.848
117.970
77.317
77.000
76.683

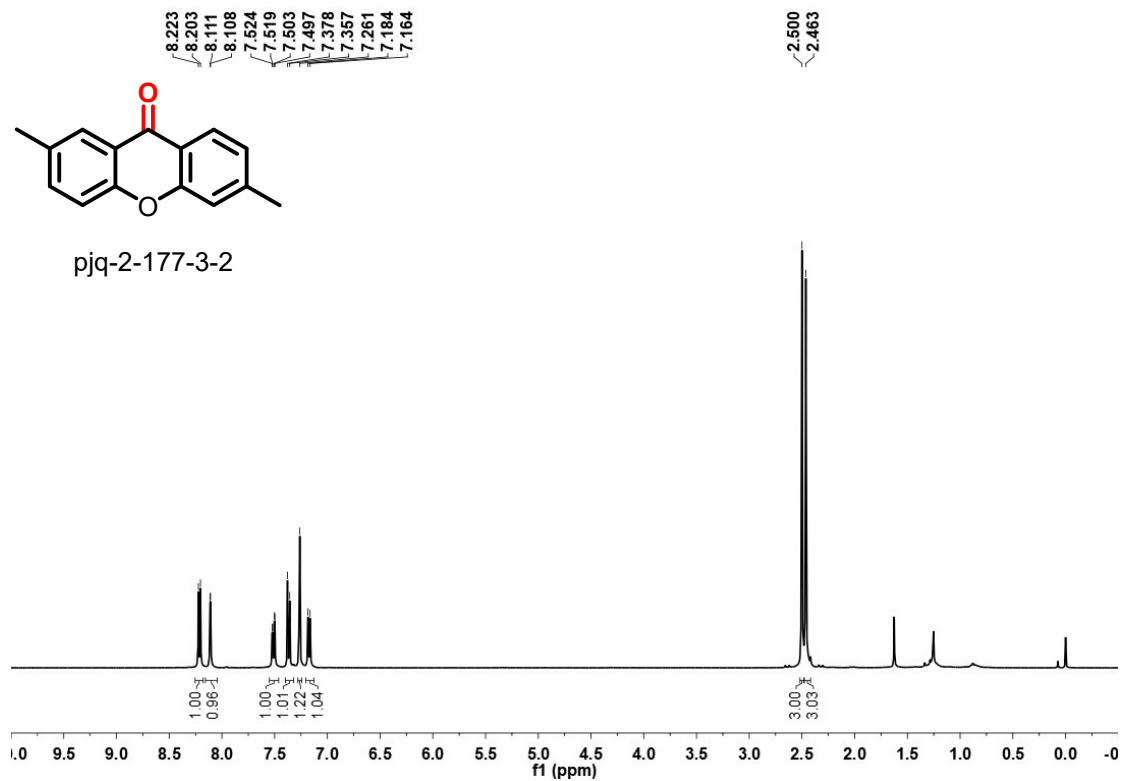


lhr-4-83-0-1

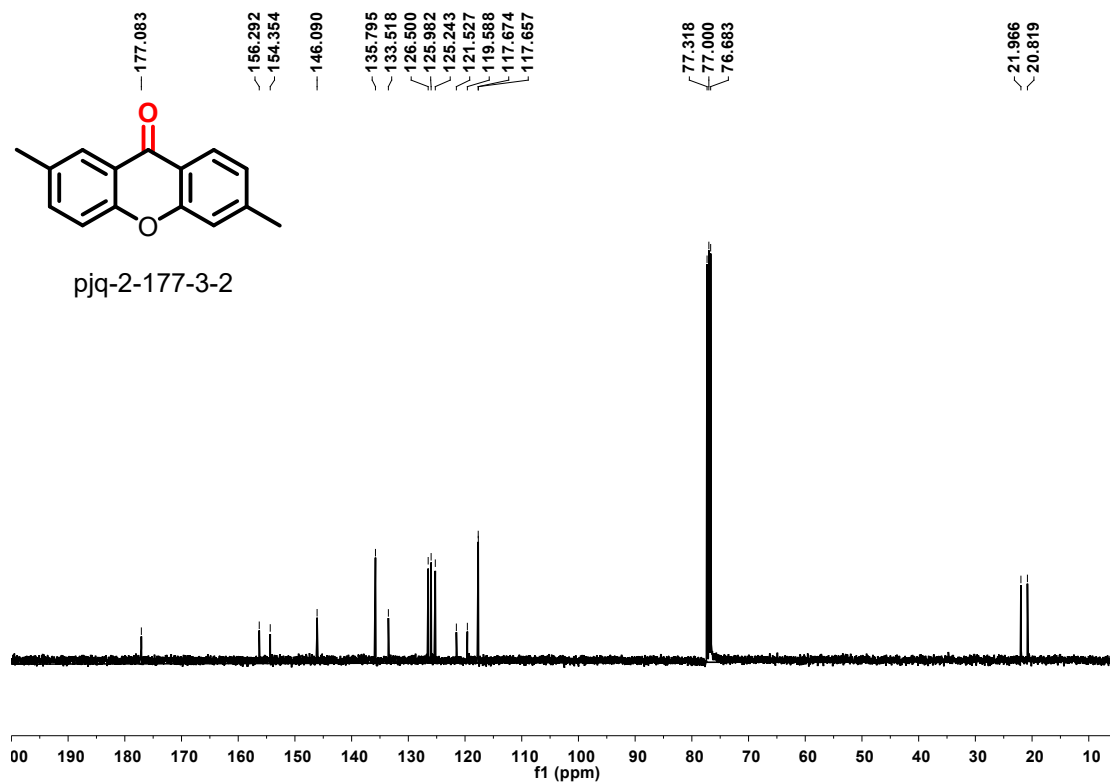


2u

¹H NMR

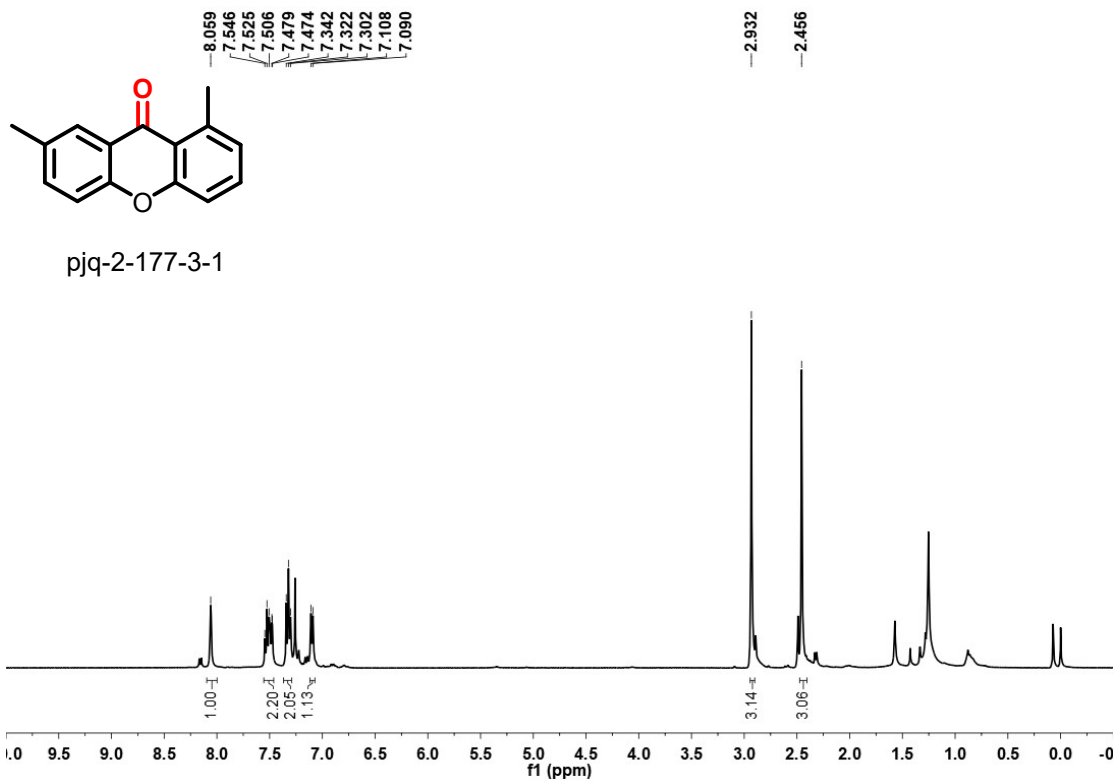


¹³C NMR

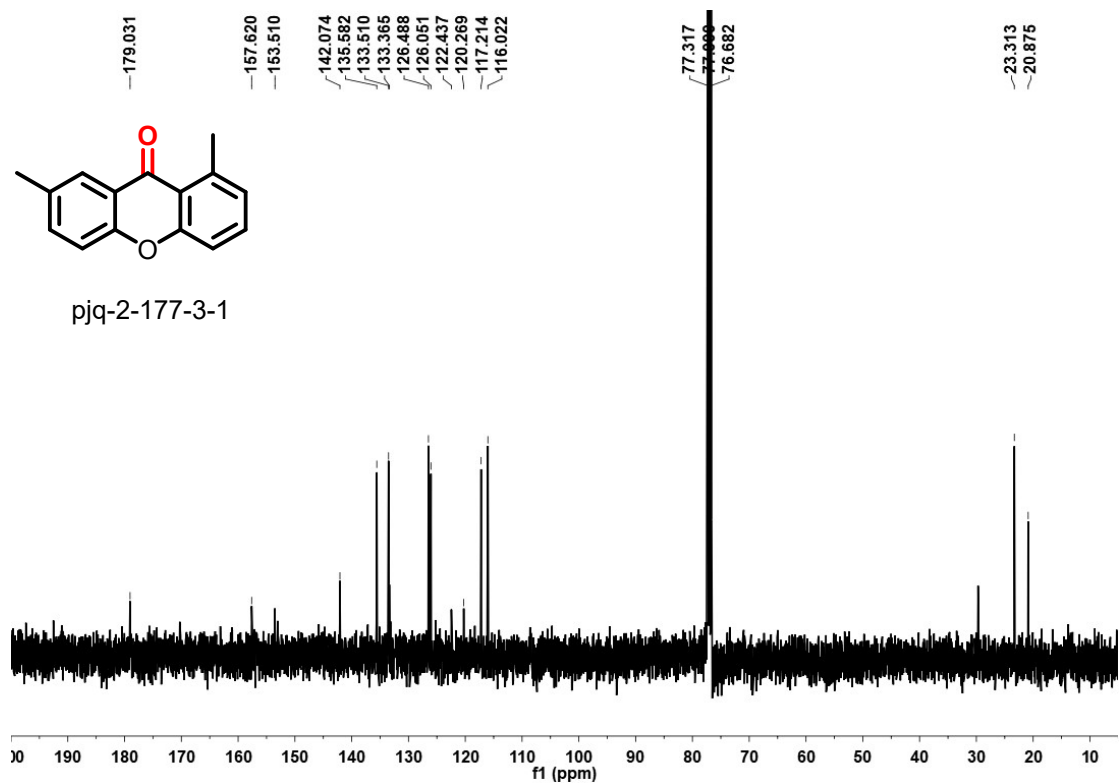


2u'

¹H NMR

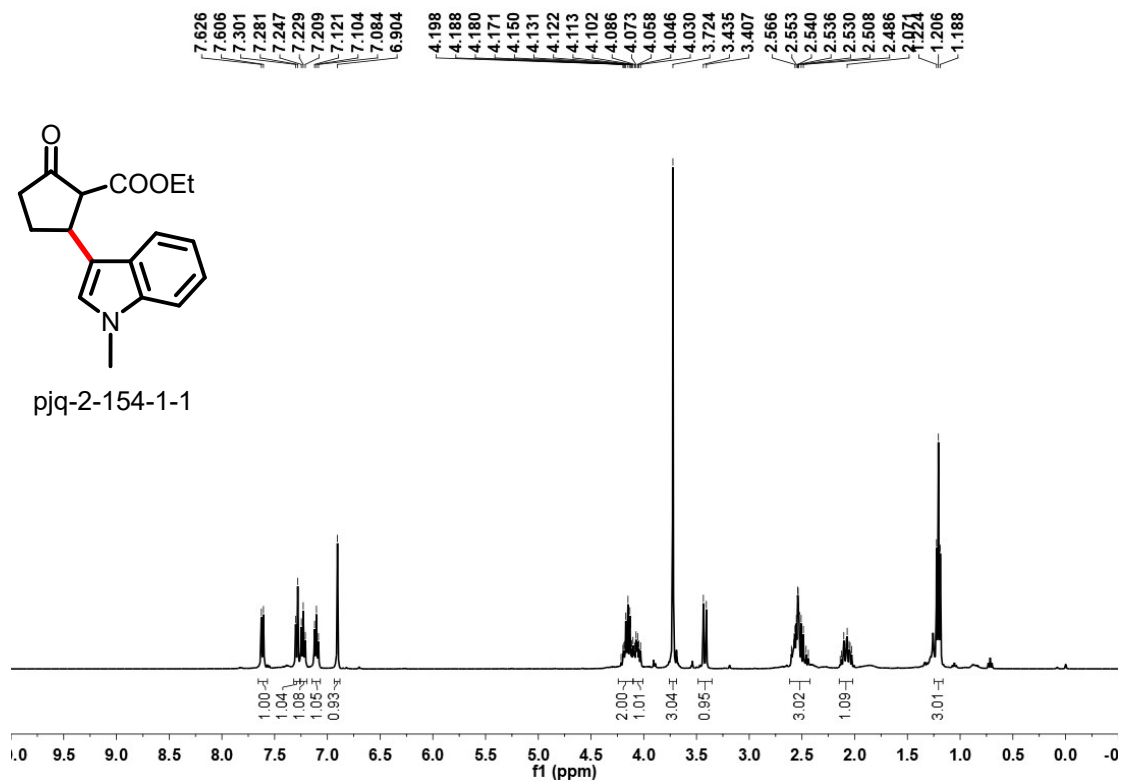


¹³C NMR

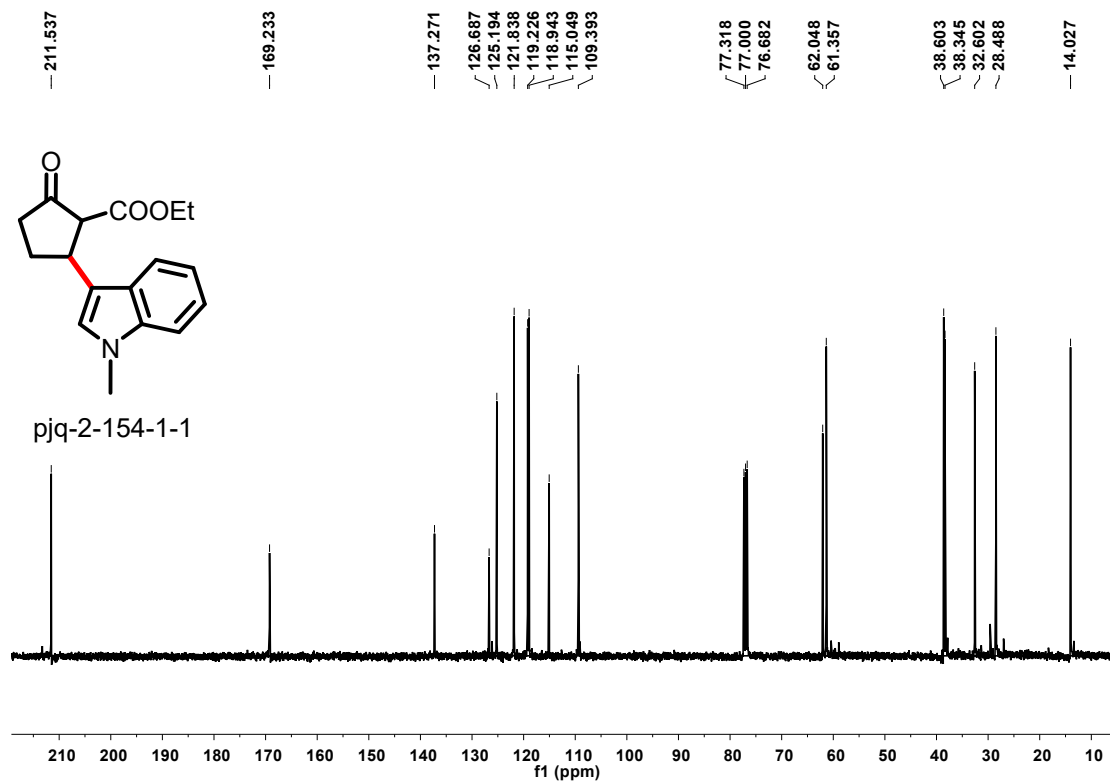


4a

¹H NMR

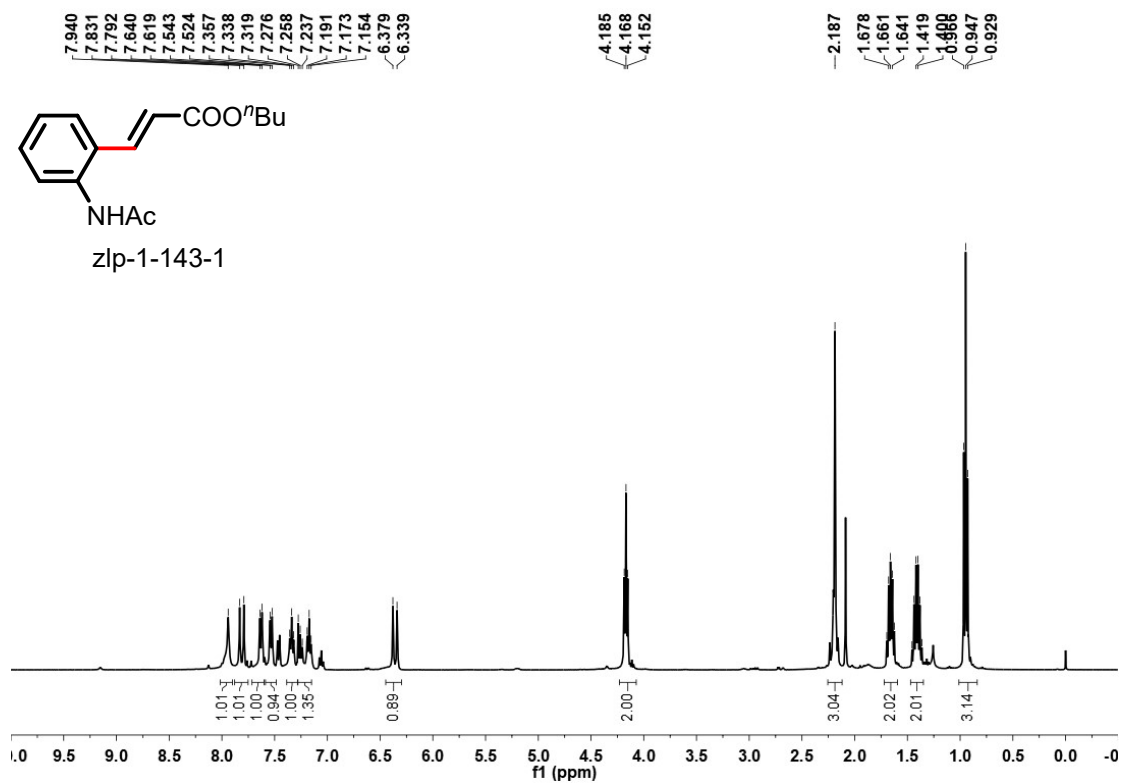


¹³C NMR

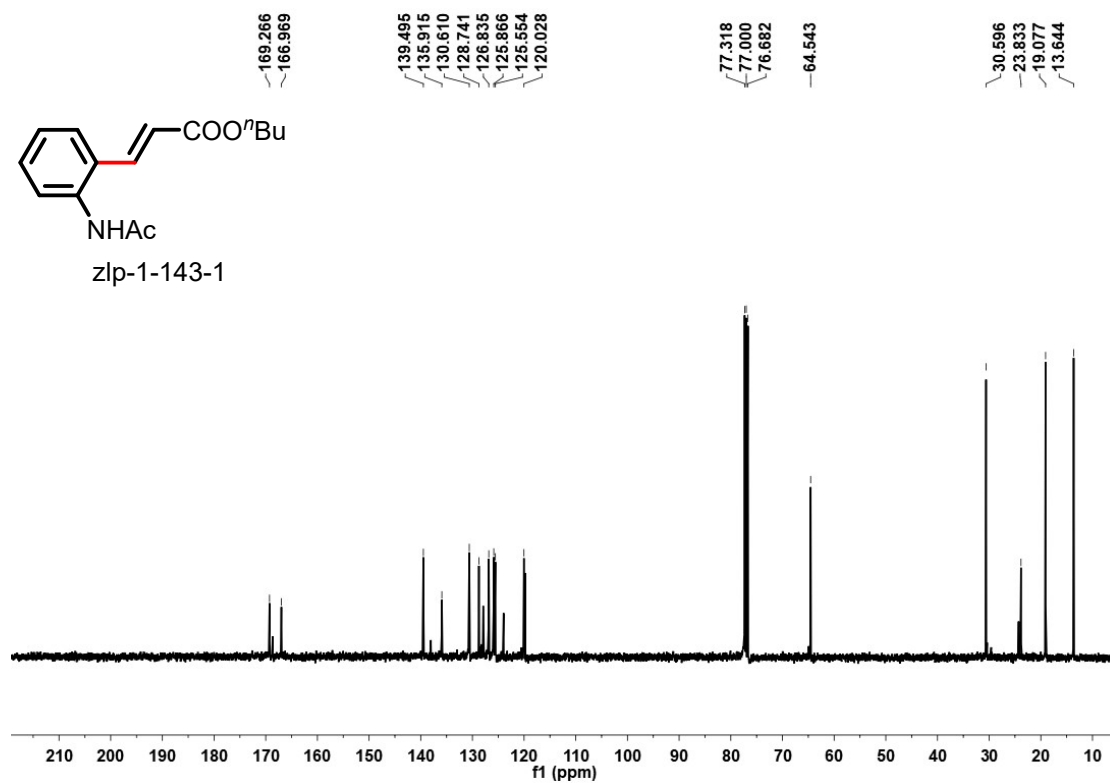


4b

¹H NMR



¹³C NMR



14. References

- 1 Simon Rengshausen, Fabian Etscheidt, Johannes Großkurth, Kylie L. Luska, Alexis Bordet and Walter Leitner *. Catalytic Hydrogenolysis of Substituted Diaryl Ethers by Using Ruthenium Nanoparticles on an Acidic Supported Ionic Liquid Phase (Ru@SILP-SO₃H). *Synlett*. **2019**, 30, 405-412.
- 2 David A Evans*, Jeffrey L Katz and Theodore R West. Synthesis of diaryl ethers through the copper-promoted arylation of phenols with arylboronic acids. An expedient synthesis of thyroxine. *Tetrahedron Lett* **1998**, 39, 2937-2940.
- 3 Sizhuo Wang, Kai Xie, Ze Tan,* Xiangyu An, Xingjian Zhou, Can-Cheng Guo and Zhihong Peng. One-step preparation of xanthenes via Pd-catalyzed annulation of 1,2-dibromoarenes and salicylaldehydes. *Chem Commun* **2009**, 42, 6469-6471.
- 4 Barbero, Nekane; SanMartin, Raul* and Dominguez, Esther*. An efficient copper-catalytic system for performing intramolecular O-arylation reactions in aqueous media. New synthesis of xanthenes. *Green Chem* **2009**, 11, 830-836.
- 5 Yingmeng Xu, Jing Zhou, Congcong Zhang, Tao Zhang* and Zhenting Du*. Synthesis of xanthenes through the palladium-catalyzed carbonylation/C–H activation sequence. *Tetrahedron Lett* **2014**, 55, 6432-6434.
- 6 Hua Zhang, Renyi Shi, Pei Gan, Chao Liu, Anxing Ding, Qiuyi Wang, and Aiwen Lei*. Palladium-Catalyzed Oxidative Double CH Functionalization/Carbonylation for the Synthesis of Xanthenes. *Angew. Chem. Int. Ed.* **2012**, 51, 5204-5207.
- 7 Mao, Mao; Wu, Qing-Qing; Ren, Ming-Guang and Song, Qin-Hua*. Highly efficient and regiospecific photocyclization of 2,2'-diacyl bixanthylenes. *Org. Biomol. Chem.* **2011**, 9, 3165-3169.
- 8 Zhao, Jian; Yue, Dawei; Campo, Marino A. and Larock, Richard C*. An Aryl to Imidoyl Palladium Migration Process Involving Intramolecular C–H Activation. *J. Am. Chem. Soc.* **2007**, 129, 5288–5295.
- 9 Martina Pickert and Wilhelm Frahm*. Substituted Xanthenes as Antimycobacterial Agents, Part 1: Synthesis and Assignment of ¹H/¹³C NMR Chemical Shifts. *Archiv der Pharmazie* **1998**, 331, 177–192.
- 10 Maddali L. N. Rao* and Boddu S. Ramakrishna. Rh-catalyzed direct synthesis of 2,2'-dihydroxybenzophenones and xanthenes. *RSC Adv* **2016**, 6, 75505-75511.
- 11 T. M. Malyutina, B. V. Shneider, T. Yu. Alekseeva and Yu. A. Karpov. Determination of high concentrations of palladium by combined use of gravimetric and spectral analysis. *Inorg Mater.* **2013**, 49, 1277–1282.
12. Leskinen, M. V., Yip, K.-T., Valkonen, A., Pihko, P. M. Palladium-Catalyzed Dehydrogenative β'-Functionalization of β-Keto Esters with Indoles at Room Temperature. *J. Am. Chem. Soc.*, **2012**, 134, 5750-5753.
13. Amatore, C., Cammoun, C., Jutand, A. Electrochemical Recycling of Benzoquinone in the Pd/Benzoquinone-Catalyzed Heck-Type Reactions from Arenes. *Adv. Synth. Catal.*, **2007**, 349, 292-296.
14. Xu, Y., Zhou, J., Zhang, C., Chen, K., Zhang, T., Du, Z.,. Synthesis of Xanthenes through the Palladium-Catalyzed Carbonylation/C–H Activation Sequence. *Tetrahedron Lett.*, **2014**, 55, 6432-6434.