Supporting Information

Non-Kolbe Oxidation Driven Electrochemical C(sp^2)-H Lactonization towards the Synthesis of Isocoumarins

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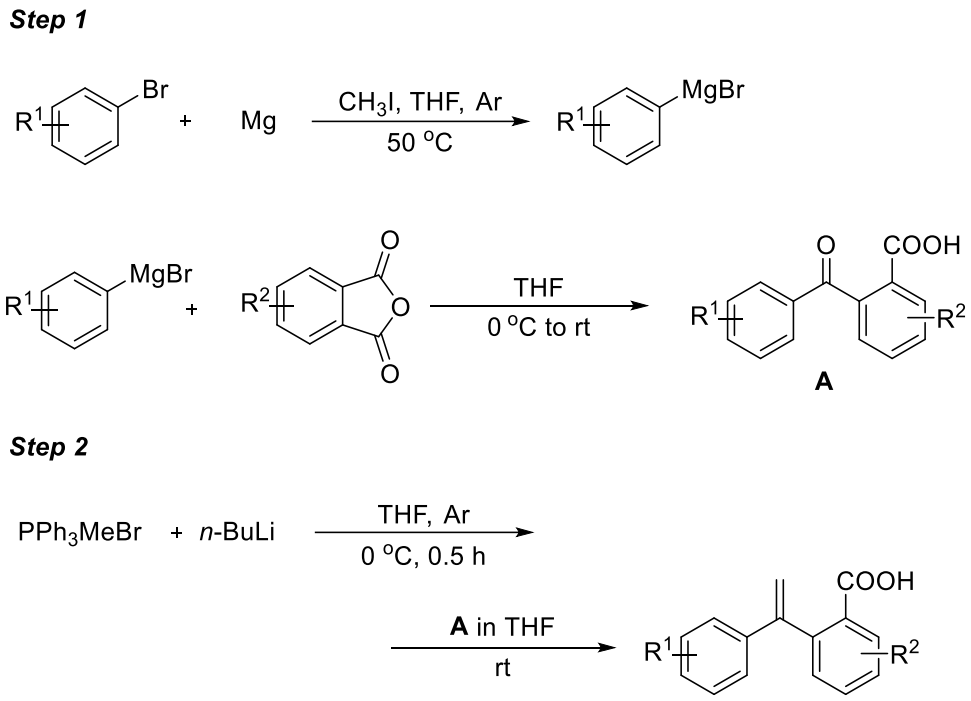
1. General Information

Electrochemical reactions were performed in customized undivided cells. Flash chromatography was performed using silica gel (300-400 mesh) from *Qingdao Ocean Chemical* (China). Commercial reagents were purchased from *Sigma Aldrich*, *J&K Scientific*, *Energy Chemical*, and *Heowns* and used as received. Proton nuclear magnetic resonance (^{1}H-NMR) spectra and carbon nuclear magnetic resonance (^{13}C-NMR) spectra were recorded on a *Bruker-500* (500 MHz) or a *Bruker-600* (600 MHz) spectrometers. Chemical shifts for protons are reported in parts per million downfield from TMS (tetramethylsilane) and are referenced to residual protium in the NMR solvent ($CDCl_3$ = δ 7.26, DMSO-d_6 = δ 2.50). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.2, DMSO-d_6 = δ 39.5). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. The mass spectral data were determined with a *Bruker SolariX XR* high-resolution mass spectrometer. Cyclic voltammetry measurements were carried out in a three-electrode cell by using glassy carbon as the working electrode, a Pt wire as auxiliary electrode, and an Ag/AgCl (saturated KCl) as reference electrode on a computer-controlled *CHI600E* instrument at room temperature.

2. General Procedures for Preparation of Substrates

2.1 Preparation of Substrates from Aryl Halides



Procedure **I**:

Step 1

In a 25 mL Schlenk flask equipped with a magnetic stirring bar, Mg (scrap, 12 mmol, 288 mg, 1.2 eq.) was added. The flask was evacuated and backfilled with argon for three times, after that, a solution of aryl halide (10 mmol, 1.0 eq.) in dried THF (20 mmol, 0.5 M) was added followed by CH_3I (0.1 mL). The mixture would be heated with an oil bath at 50 °C for 5 h. The corresponding Grignard reagent was obtained as yellow solution.

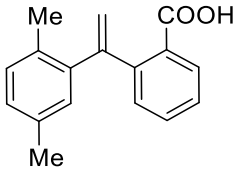
Another 100 mL round bottom flask with a solution of phthalic anhydride (10.0 mmol, 1.48 g, 1.0 eq.) in dried THF (10 mL) was cooled to 0 °C with ice-water bath, then above Grignard reagent was added dropwise. Once the addition was complete, the system was allowed to react overnight under room temperature. The final solution should be acidified with saturated NH_4Cl aq. (10 mL), extracted with EA (20 mL) for three times. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum to give a crude product, which was further purified by flash column chromatography on silica gel (PE: EA = 10:1 to 1:1) to deliver the desired carboxylic acid **A**.

Step 2

In a 50 mL Schlenk tube equipped with a magnetic stirring bar, PPh_3MeBr (9 mmol, 3.21 g, 3.0 eq.) was added. The tube was evacuated and backfilled with argon for three times, then dried THF (10 mL) was added to form a white suspension. After the mixture was cooled to 0 °C with ice-water bath, *n*-BuLi (1.6 M in hexane, 5.6 mL, 3.0 eq.) was added dropwise. The system would be stirred under 0 °C for another 0.5 h

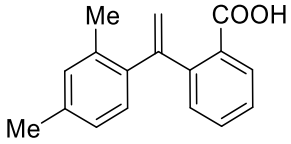
to deliver a red solution. A solution of the carboxylic acid **A** (3 mmol, 1.0 eq.) in THF (10 mL) was added, then the mixture was allowed to react overnight under room temperature after that. The final system should be acidified with HCl (1 M, 10 mL), extracted with EA (20 mL) for three times. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum to give a crude product, which was further purified by flash column chromatography on silica gel (PE: EA = 10:1 to 3:1) to deliver the desired substrate.

Substrate **1a-1n** were prepared according to procedure **I**.



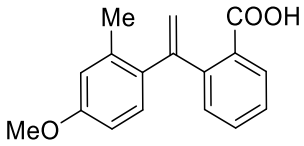
2-(1-(2,5-dimethylphenyl)vinyl)benzoic acid (1a)[1]

Prepared via the general procedure **I**. The product **1a** was furnished as a white solid in 70% yield (1.76 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.49 (td, *J* = 7.6, 1.4 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.03 – 7.00 (m, 1H), 6.98 – 6.92 (m, 2H), 5.50 (d, *J* = 1.3 Hz, 1H), 5.39 (d, *J* = 1.3 Hz, 1H), 2.23 (s, 3H), 2.14 (s, 3H). Melting point = 160-162 ^{o}C.



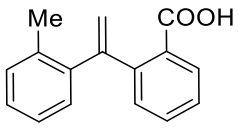
2-(1-(2,4-dimethylphenyl)vinyl)benzoic acid (1b)[2]

Prepared via the general procedure **I**. The product **1b** was furnished as a white solid in 62% yield (1.56 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.47 (td, *J* = 7.6, 1.4 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.01 – 6.93 (m, 2H), 6.89 (d, *J* = 7.9 Hz, 1H), 5.48 (d, *J* = 1.4 Hz, 1H), 5.38 (d, *J* = 1.3 Hz, 1H), 2.27 (s, 3H), 2.16 (s, 3H). Melting point = 188-190 ^{o}C.



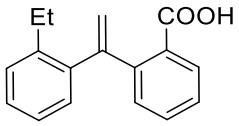
2-(1-(4-methoxy-2-methylphenyl)vinyl)benzoic acid (1c)[3]

Prepared via the general procedure **I**. The product **1c** was furnished as a white solid in 58% yield (1.58 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.48 (td, *J* = 7.6, 1.5 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.68 (d, *J* = 2.7 Hz, 1H), 6.62 (dd, *J* = 8.5, 2.7 Hz, 1H), 5.46 (d, *J* = 1.4 Hz, 1H), 5.34 (d, *J* = 1.4 Hz, 1H), 3.74 (s, 3H), 2.17 (s, 3H). Melting point = 191-193 ^{o}C.



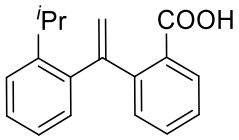
2-(1-(*o*-tolyl)vinyl)benzoic acid (1d)[4]

Prepared via the general procedure **I**. The product **1d** was furnished as a white solid in 69% yield (1.66 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.50 (td, *J* = 7.6, 1.5 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.16 – 7.06 (m, 4H), 5.53 (d, *J* = 1.3 Hz, 1H), 5.41 (d, *J* = 1.3 Hz, 1H), 2.21 (s, 3H). Melting point = 130-132 ^{o}C.



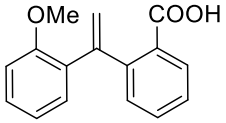
2-(1-(2-ethylphenyl)vinyl)benzoic acid (1e)[5]

Prepared via the general procedure **I**. The product **1e** was furnished as a white solid in 65% yield (1.64 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.49 (td, *J* = 7.5, 1.5 Hz, 1H), 7.37 (d, *J* = 2.7 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.17 – 7.14 (m, 1H), 7.12 – 7.08 (m, 1H), 5.53 (d, *J* = 1.4 Hz, 1H), 5.41 (d, *J* = 1.4 Hz, 1H), 2.57 (q, *J* = 7.5 Hz, 2H), 1.07 (t, *J* = 7.5 Hz, 3H). Melting point = 83-85 ^{o}C.



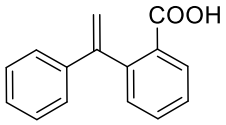
2-(1-(2-isopropylphenyl)vinyl)benzoic acid (1f)[6]

Prepared via the general procedure **I**. The product **1f** was furnished as a white solid in 49% yield (1.30 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.43 (td, *J* = 7.6, 1.5 Hz, 1H), 7.34 (td, *J* = 7.6, 1.3 Hz, 1H), 7.30 – 7.23 (m, 3H), 7.19 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.09 (td, *J* = 7.3, 1.6 Hz, 1H), 5.50 (d, *J* = 1.3 Hz, 1H), 5.38 (d, *J* = 1.3 Hz, 1H), 3.25 – 3.13 (m, 1H), 1.05 (d, *J* = 6.8 Hz, 6H). Melting point = 100-102 ^{o}C.



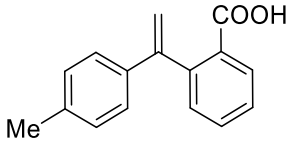
2-(1-(2-methoxyphenyl)vinyl)benzoic acid (1g)[7]

Prepared via the general procedure **I**. The product **1g** was furnished as a white solid in 80% yield (2.03 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.33 (td, *J* = 7.5, 1.5 Hz, 1H), 7.27 (td, *J* = 7.5, 1.4 Hz, 1H), 7.24 – 7.15 (m, 2H), 7.12 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.90 (td, *J* = 7.5, 1.1 Hz, 1H), 6.79 (dd, *J* = 8.2, 1.1 Hz, 1H), 5.55 (d, *J* = 1.4 Hz, 1H), 5.35 (d, *J* = 1.3 Hz, 1H), 3.54 (s, 3H). Melting point = 81-83 ^{o}C.



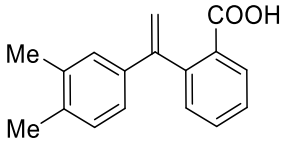
2-(1-phenylvinyl)benzoic acid (1h)[8]

Prepared via the general procedure **I**. The product **1h** was furnished as a white solid in 67% yield (1.50 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.57 (td, *J* = 7.5, 1.4 Hz, 1H), 7.43 (td, *J* = 7.6, 1.3 Hz, 1H), 7.38 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.26 – 7.20 (m, 5H), 5.67 (d, *J* = 1.0 Hz, 1H), 5.23 (d, *J* = 1.0 Hz, 1H).



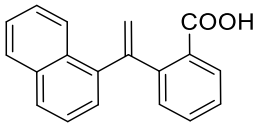
2-(1-(*p*-tolyl)vinyl)benzoic acid (1i)[1]

Prepared via the general procedure **I**. The product **1i** was furnished as a white solid in 58% yield (1.38 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.56 (td, *J* = 7.5, 1.4 Hz, 1H), 7.43 (td, *J* = 7.6, 1.3 Hz, 1H), 7.37 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.14 – 7.11 (m, 2H), 7.08 – 7.05 (m, 2H), 5.64 (d, *J* = 1.1 Hz, 1H), 5.17 (d, *J* = 1.1 Hz, 1H), 2.32 (s, 3H). Melting point = 124-126 ^{o}C.



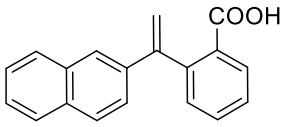
2-(1-(3,4-dimethylphenyl)vinyl)benzoic acid (1j)[1]

Prepared via the general procedure **I**. The product **1j** was furnished as a white solid in 82% yield (2.1 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.55 (td, *J* = 7.5, 1.4 Hz, 1H), 7.42 (td, *J* = 7.6, 1.3 Hz, 1H), 7.35 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.04 – 6.98 (m, 2H), 6.94 (dd, *J* = 7.8, 2.0 Hz, 1H), 5.63 (d, *J* = 1.1 Hz, 1H), 5.14 (d, *J* = 1.1 Hz, 1H), 2.20 (d, *J* = 9.6 Hz, 6H). Melting point = 169-171 ^{o}C.



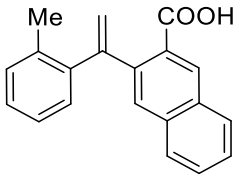
2-(1-(naphthalen-1-yl)vinyl)benzoic acid (1k)[2]

Prepared via the general procedure **I**. The product **1k** was furnished as a white solid in 53% yield (1.45 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.85 – 7.74 (m, 3H), 7.48 (td, *J* = 7.6, 1.5 Hz, 1H), 7.44 – 7.33 (m, 5H), 7.21 (dd, *J* = 7.2, 1.3 Hz, 1H), 5.68 (d, *J* = 1.3 Hz, 1H), 5.60 (d, *J* = 1.3 Hz, 1H). Melting point = 143-145 ^{o}C.



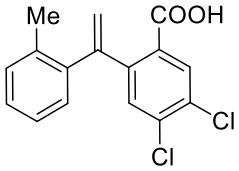
2-(1-(naphthalen-2-yl)vinyl)benzoic acid (1l)[1]

Prepared via the general procedure **I**. The product **1l** was furnished as a white solid in 71% yield (1.95 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.77 – 7.74 (m, 1H), 7.72 – 7.65 (m, 2H), 7.59 (td, *J* = 7.5, 1.4 Hz, 1H), 7.52 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.48 – 7.36 (m, 5H), 5.75 (s, 1H), 5.26 (s, 1H). Melting point = 158-160 ^{o}C.



3-(1-(*o*-tolyl)vinyl)-2-naphthoic acid (1m)[9]

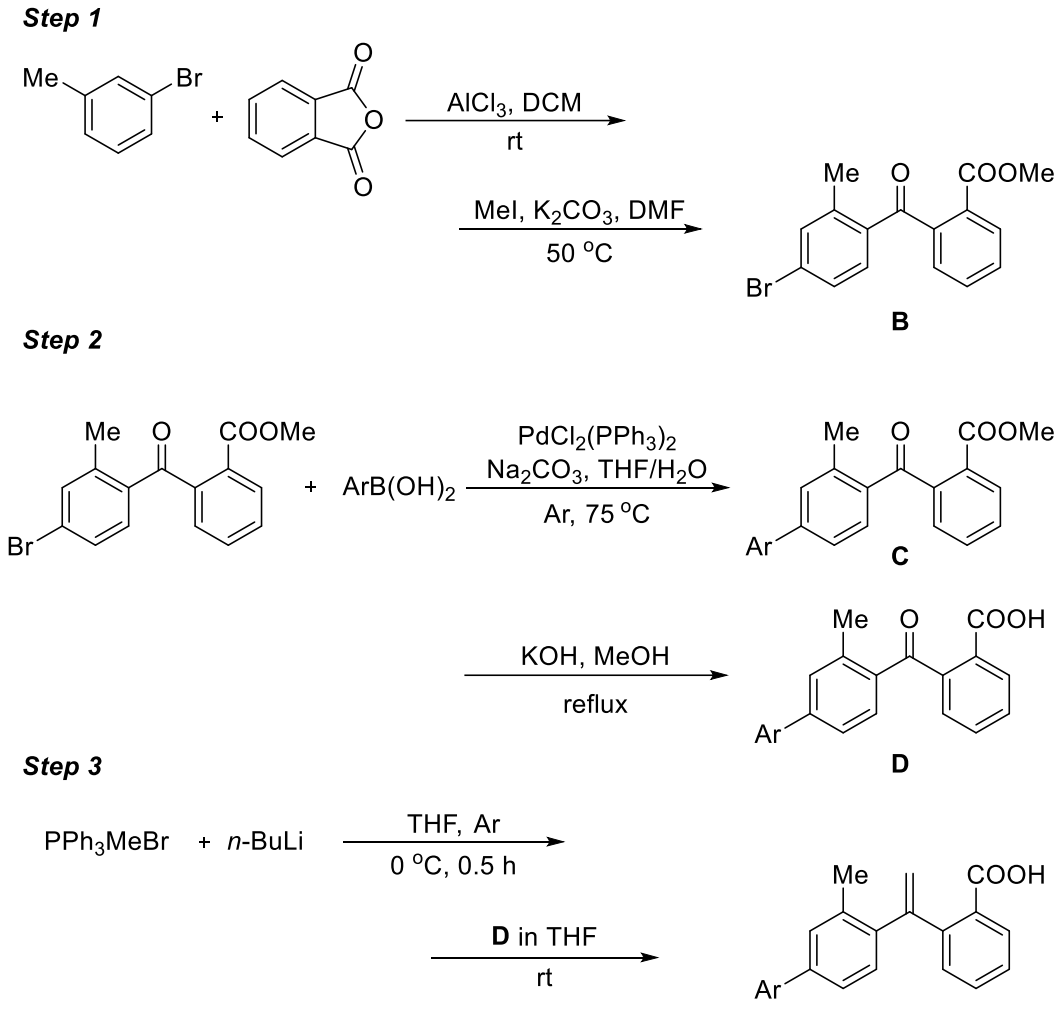
Prepared via the general procedure **I**. The product **1m** was furnished as a white solid in 41% yield (1.18 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 – 8.34 (m, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.87 – 7.81 (m, 2H), 7.63 – 7.58 (m, 1H), 7.57 – 7.53 (m, 1H), 7.18 – 7.13 (m, 2H), 7.12 – 7.04 (m, 2H), 5.65 (d, *J* = 1.4 Hz, 1H), 5.46 (d, *J* = 1.3 Hz, 1H), 2.26 (s, 3H). Melting point = 185-187 °C.



4,5-dichloro-2-(1-(*o*-tolyl)vinyl)benzoic acid (1n)[10]

Prepared via the general procedure **I**. The product **1n** was furnished as a white solid in 65% yield (1.99 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.44 (s, 1H), 7.17 – 7.13 (m, 2H), 7.09 (td, *J* = 7.1, 6.6, 2.1 Hz, 1H), 7.04 (d, *J* = 6.1 Hz, 1H), 5.53 (d, *J* = 1.0 Hz, 1H), 5.44 (d, *J* = 1.0 Hz, 1H), 2.22 (s, 3H). Melting point = 188-190 °C.

2.2 Preparation of Substrates from 3-Bromotoluene



Procedure **II**:

Step 1

In a 100 mL round bottom flask equipped with a magnetic stirring bar, phthalic anhydride (10.0 mmol, 1.48 g, 1.0 eq.) was added followed by DCM (20 mL, 0.5 M) to form a white suspension. Then $AlCl_3$ (20.0 mmol, 2.0 eq.) was added into above system slowly. The mixture would be stirred for 5 min. After that, 3-bromotoluene (15 mmol, 1.5 eq.) was added dropwise. Once the phthalic anhydride was consumed totally monitored by TLC, the mixture could be cooled with ice-water bath and dealt with HCl (2 M, 20 mL). DCM (20 mL) was used to extract above mixture for three times. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum to give a crude product as yellow oil, which was used without further purification.

The crude product was dissolved with DMF (20 mL, 0.5 M) in a 100 mL round bottom flask, then K_2CO_3 (20 mmol, 2.0 eq.) and iodomethane (15 mmol, 1.5 eq.) was added. The mixture was heated at 50 °C in an oil bath for 5 h. After that, a solution could be got by filtering. The solution was diluted with EA (50 mL), washed with water (100 mL) and brine (100 mL). The combined organic phase was dried over anhydrous

Na_2SO_4 and concentrated under vacuum to give a crude product, which was further purified by flash column chromatography on silica gel (PE: EA = 40:1) to deliver the desired ester **B**

Step 2

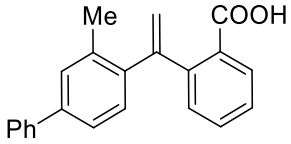
In a 50 mL Schlenk tube equipped with a magnetic stirring bar, corresponding phenylboronic acid (13.0 mmol, 1.3 eq.), $PdCl_2(PPh_3)_2$ (0.25 mmol, 0.025 eq.) and Na_2CO_3 (20 mmol, 2.0 eq.) were added. The tube was evacuated and backfilled with argon for three times, then THF/H_2O (1:1, 0.5 M) was added. The tube was evacuated upon slight boiling and backfilled with argon for three times. The mixture was stirred for 20 min at room temperature. Then the ester **B** (10 mmol, 1.0 eq.) was added, the mixture was heated at 80 ^oC and stirred for 14 h in an oil bath. After being cooling down to room temperature, the mixture was extracted with ethyl acetate (20 mL) for three times. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum to give a crude product, which was further purified by flash column chromatography on silica gel (PE: EA = 40:1) to obtain the product **C**.

The cross-coupling product **C** was dissolved in methanol (0.5 M), then KOH aq. (1 M, 2.0 eq.) was added dropwise. The mixture was heated at 70 ^oC in an oil bath overnight. After being cooling down to room temperature, methanol was removed under vacuum and HCl aq. (1 M) was added dropwise to release the product acid. The aqueous layer was extracted with ethyl acetate (15 mL) for three times. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum to give a crude product, which was further purified by flash column chromatography on silica gel (PE: EA = 10:1 to 1:1) to obtain the product **D**.

Step 3

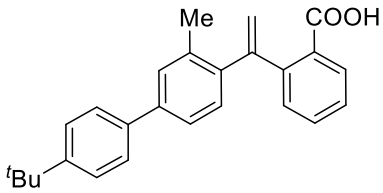
In a 50 mL Schlenk tube equipped with a magnetic stirring bar, PPh_3MeBr (9 mmol, 3.21 g, 3.0 eq.) was added. The tube was evacuated and backfilled with argon for three times, then dried THF (10 mL) was added to form a white suspension. After the mixture was cooled to 0 ^oC with ice-water bath, *n*-BuLi (1.6 M in hexane, 5.6 mL, 3.0 eq.) was added dropwise. The system would be stirred under 0 ^oC for another 0.5 h to deliver a red solution. A solution of the carboxylic acid **D** (3 mmol, 1.0 eq.) in THF (10 mL) was added, then the mixture was allowed to react overnight under room temperature after that. The final system should be acidified with HCl (1 M, 10 mL), extracted with EA (20 mL) for three times. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum to give a crude product, which was further purified by flash column chromatography on silica gel (PE: EA = 10:1 to 3:1) to deliver the desired substrate.

Substrate **3a**-**3j** were prepared according to procedure **II**.



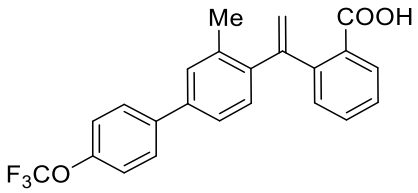
2-(1-(3-methyl-[1,1'-biphenyl]-4-yl)vinyl)benzoic acid (3a)

Prepared via the general procedure **II**. The product **3a** was furnished as a white solid in 41% yield (643 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.55 – 7.53 (m, 2H), 7.50 (td, *J* = 7.6, 1.4 Hz, 1H), 7.41 – 7.37 (m, 3H), 7.36 – 7.28 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 1H), 5.53 (d, *J* = 1.3 Hz, 1H), 5.41 (d, *J* = 1.3 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ173.3, 148.6, 143.8, 141.0, 140.2, 140.0, 136.6, 132.0, 130.9 (d, *J* = 4.3 Hz), 130.2, 129.8, 129.5, 128.8, 127.6, 127.3, 127.2, 124.2, 119.1, 21.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{18}NaO_2^+$ 337.1199; Found 333.1208. Melting point = 165-167 °C.



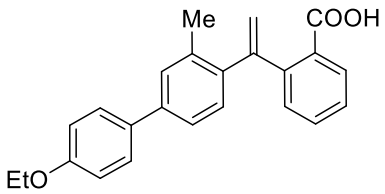
2-(1-(4'-(tert-butyl)-3-methyl-[1,1'-biphenyl]-4-yl)vinyl)benzoic acid (3b)

Prepared via the general procedure **II**. The product **3b** was furnished as a white solid in 38% yield (681 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.53 – 7.48 (m, 3H), 7.42 (t, *J* = 8.0 Hz, 3H), 7.37 – 7.29 (m, 3H), 7.14 (d, *J* = 7.9 Hz, 1H), 5.53 (d, *J* = 1.4 Hz, 1H), 5.42 (d, *J* = 1.4 Hz, 1H), 2.26 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 150.2, 148.6, 143.8, 140.1, 139.7, 138.0, 136.5, 131.9, 130.9 (d, *J* = 3.7 Hz), 130.2, 130.0, 129.4, 127.5, 126.8, 125.7, 124.0, 119.0, 34.7, 31.5, 21.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{26}NaO_2^+$ 393.1825; Found 393.1831. Melting point = 148-150 °C.



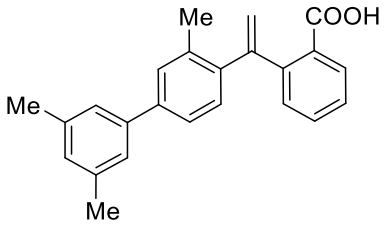
2-(1-(3-methyl-4'-(trifluoromethoxy)-[1,1'-biphenyl]-4-yl)vinyl)benzoic acid (3c)

Prepared via the general procedure **II**. The product **3c** was furnished as a white solid in 29% yield (577 mg). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.80 – 7.75 (m, 2H), 7.64 (d, *J* = 6.3 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.45 – 7.38 (m, 4H), 7.29 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 5.50 (s, 1H), 5.40 (s, 1H), 2.25 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 169.2, 148.2, 147.8, 141.9, 140.5, 139.1, 137.3, 136.3, 132.2, 130.8, 130.3, 130.2, 129.0, 128.9, 128.4, 127.6, 123.7, 121.4, 120.1 (q, *J* = 256.2 Hz), 118.4, 20.6. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{17}F_3NaO_3^+$ 421.1022; Found 421.1031. Melting point = 141-143 °C.



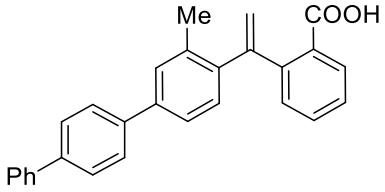
2-(1-(4'-ethoxy-3-methyl-[1,1'-biphenyl]-4-yl)vinyl)benzoic acid (3d)

Prepared via the general procedure **II**. The product **3d** was furnished as a white solid in 28% yield (501 mg). ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.69 (s, 1H), 7.62 (d, J = 8.3 Hz, 1H), 7.58 (d, J = 8.6 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.36 (dd, J = 8.0, 2.1 Hz, 1H), 7.29 (d, J = 7.6 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.99 (d, J = 8.6 Hz, 2H), 5.46 (s, 1H), 5.37 (s, 1H), 4.06 (q, J = 7.0 Hz, 2H), 2.22 (s, 3H), 1.34 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 169.2, 158.1, 148.3, 142.1, 139.2, 138.5, 135.9, 132.1, 131.9, 130.8, 130.2 (d, J = 2.6 Hz), 129.0, 128.2, 127.5 (d, J = 6.6 Hz), 123.0, 118.0, 114.7, 63.0, 20.6, 14.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{22}NaO_3^+$ 381.1461; Found 381.1470. Melting point = 182-184 ^{o}C.



2-(1-(3,3',5'-trimethyl-[1,1'-biphenyl]-4-yl)vinyl)benzoic acid (3e)

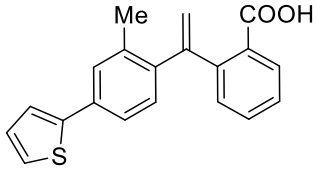
Prepared via the general procedure **II**. The product **3e** was furnished as a white solid in 44% yield (752 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, J = 7.8, 1.4 Hz, 1H), 7.42 (td, J = 7.6, 1.4 Hz, 1H), 7.32 (dd, J = 7.8, 1.2 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.19 – 7.15 (m, 2H), 7.10 – 7.07 (m, 2H), 7.04 (d, J = 7.9 Hz, 1H), 6.91 – 6.87 (m, 1H), 5.45 (d, J = 1.3 Hz, 1H), 5.33 (d, J = 1.3 Hz, 1H), 2.26 (s, 6H), 2.16 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 148.6, 143.9, 141.0, 140.5, 139.8, 138.2, 136.5, 131.9, 130.9, 130.8, 130.2, 130.0, 129.5, 128.9, 127.5, 125.1, 124.2, 119.0, 21.5, 21.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{22}NaO_2^+$ 365.1512; Found 365.1522. Melting point = 176-178 ^{o}C.



2-(1-(3-methyl-[1,1':4',1''-terphenyl]-4-yl)vinyl)benzoic acid (3f)

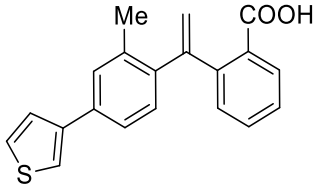
Prepared via the general procedure **II**. The product **3f** was furnished as a white solid in 49% yield (994 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 7.8 Hz, 1H), 7.68 – 7.61 (m, 6H), 7.52 – 7.49 (m, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.42 – 7.40 (m, 2H), 7.38 – 7.32 (m, 3H), 7.17 (d, J = 7.9 Hz, 1H), 5.55 (s, 1H), 5.44 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 148.6, 143.8, 140.9, 140.1 (d, J = 2.5 Hz), 139.8, 139.7,

136.7, 132.0, 131.0 (d, *J* = 5.5 Hz), 130.2, 129.8, 129.4, 129.0, 127.6, 127.5 (d, *J* = 5.7 Hz), 127.4, 127.2, 124.1, 119.1, 21.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{22}NaO_2^+$ 413.1512; Found 413.1520. Melting point = 198-202 °C.



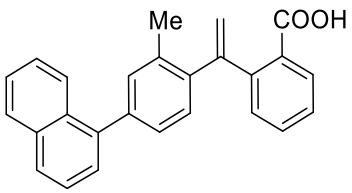
2-(1-(2-methyl-4-(thiophen-2-yl)phenyl)vinyl)benzoic acid (3g)

Prepared via the general procedure **II**. The product **3g** was furnished as a white solid in 37% yield (592 mg). ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 12.70 (s, 1H), 7.62 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.55 – 7.48 (m, 3H), 7.45 (d, *J* = 1.9 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.31 (d, *J* = 6.4 Hz, 1H), 7.13 (dd, *J* = 5.1, 3.6 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 5.49 (d, *J* = 1.3 Hz, 1H), 5.38 (d, *J* = 1.4 Hz, 1H), 2.19 (s, 3H). ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 169.2, 148.2, 143.1, 141.9, 140.1, 136.3, 132.5, 132.1, 130.8, 130.4, 130.2, 129.0, 128.4, 127.6, 127.4, 125.5, 123.5, 122.4, 118.3, 20.5. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{16}NaO_2S^+$ 343.0763; Found 343.0771. Melting point = 141-143 °C.



2-(1-(2-methyl-4-(thiophen-3-yl)phenyl)vinyl)benzoic acid (3h)

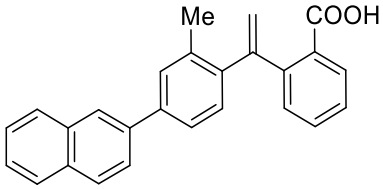
Prepared via the general procedure **II**. The product **3h** was furnished as a white solid in 33% yield (528 mg). ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 12.69 (s, 1H), 7.84 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.64 – 7.61 (m, 2H), 7.55 – 7.49 (m, 3H), 7.46 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 5.47 (d, *J* = 1.4 Hz, 1H), 5.38 (d, *J* = 1.4 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 169.2, 148.3, 142.0 141.1, 139.6, 136.0, 133.9, 132.1, 130.8, 130.2 (d, *J* = 7.3 Hz), 129.0, 128.2, 127.5, 127.0, 126.1, 123.1, 120.7, 118.1, 20.6. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{16}NaO_2S^+$ 343.0763; Found 343.0772. Melting point = 172-174 °C.



2-(1-(2-methyl-4-(naphthalen-1-yl)phenyl)vinyl)benzoic acid (3i)

Prepared via the general procedure **II**. The product **3i** was furnished as a white solid in 28% yield (510 mg). ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 12.80 (s, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.66 (dd, *J* = 7.7, 1.4 Hz,

1H), 7.59 – 7.48 (m, 4H), 7.43 (t, *J* = 6.8 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.23 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 5.53 (s, 1H), 5.46 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 169.3, 148.3, 142.0, 140.0, 139.2, 138.8, 135.7, 133.4, 132.2, 131.8, 130.8, 130.2, 129.7, 129.0, 128.3, 127.5 (d, *J* = 2.2 Hz), 126.8, 126.7, 126.3, 125.9, 125.5, 125.4, 118.4, 20.5. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{20}NaO_2^+$ 387.1356; Found 387.1359. Melting point = 248-250 ^{o}C.



2-(1-(2-methyl-4-(naphthalen-2-yl)phenyl)vinyl)benzoic acid (3j)

Prepared via the general procedure **II**. The product **3j** was furnished as a white solid in 42% yield (764 mg). ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.74 (s, 1H), 8.22 (d, *J* = 1.9 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 2H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.85 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.66 – 7.63 (m, 2H), 7.59 – 7.50 (m, 4H), 7.43 (td, *J* = 7.6, 1.3 Hz, 1H), 7.33 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 5.51 (d, *J* = 1.4 Hz, 1H), 5.43 (d, *J* = 1.3 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 169.3, 148.3, 142.0, 140.1, 138.6, 137.0, 136.2, 133.3, 132.2, 132.1, 130.9, 130.4, 130.3, 129.1, 128.4, 128.2, 127.6, 127.5, 126.4, 126.1, 125.0 (d, *J* = 5.5 Hz), 123.9, 118.3, 20.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{20}NaO_2^+$ 387.1356; Found 387.1363. Melting point = 175-177 ^{o}C.

3. Experimental Details for Electrochemical Reactions

3.1 Overview of Materials Involved

As shown in **Figure S1**, our electrochemical reactions were performed using a DC power supply (*MS-303DS*, *Mai Sheng* Company) and a magnetic stirrer (*85-2A*, *Heng Yan* Company). The undivided cell (customized from *Rui Jing* Company) was equipped with a magnetic stirring bar (length = 10 mm, Φ = 5 mm). The graphite electrodes of anode and cathode were both consisting of graphite rods (length = 90 mm, Φ = 2 mm) with graphite felts (10 mm x 10 mm x 3 mm). The reaction would be carried out under room temperature in air at a certain voltage with the distance of 5 mm between electrodes.

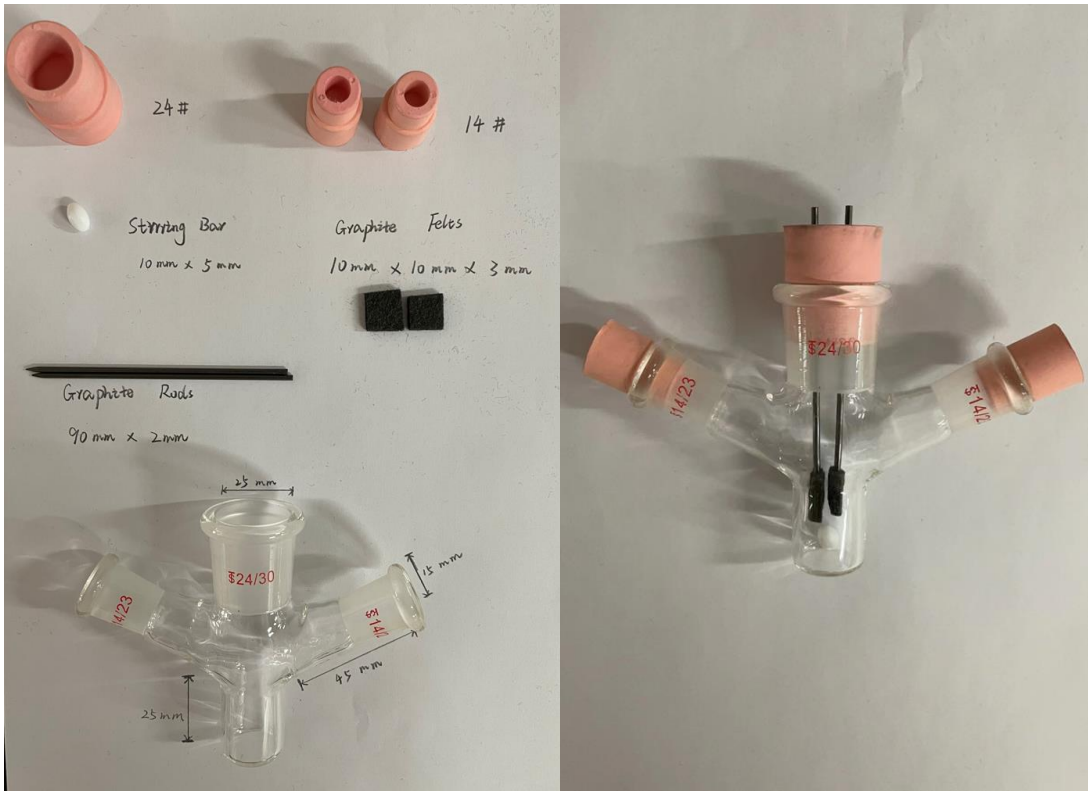
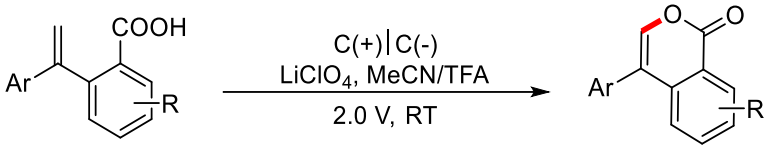


Figure S1. List and Assembly of Electrochemical Experimental Materials

3.2 General Procedure for Electrochemical Reactions



Procedure **III**:

As shown in **Figure S2**, in an undivided cell with graphite electrodes equipped with a magnetic stirring bar, substrate (0.2 mmol, 1.0 eq.), $LiClO_4$ (0.6 mmol, 3.0 eq.), and acetonitrile/trifluoroacetic acid (5.5:0.5, 6 mL, 0.033 M) were added. After fully stirring for 10 min, electrolysis was initiated under room temperature at a constant voltage of 2.0 V. The reaction was monitored by TLC to determine the end. The mixture was diluted with EA (20 mL), washed with saturated K_2CO_3 solution (20 mL) and brine (20 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum to give a crude product, and the residue was purified by flash chromatography on silica gel to afford the desired compound.

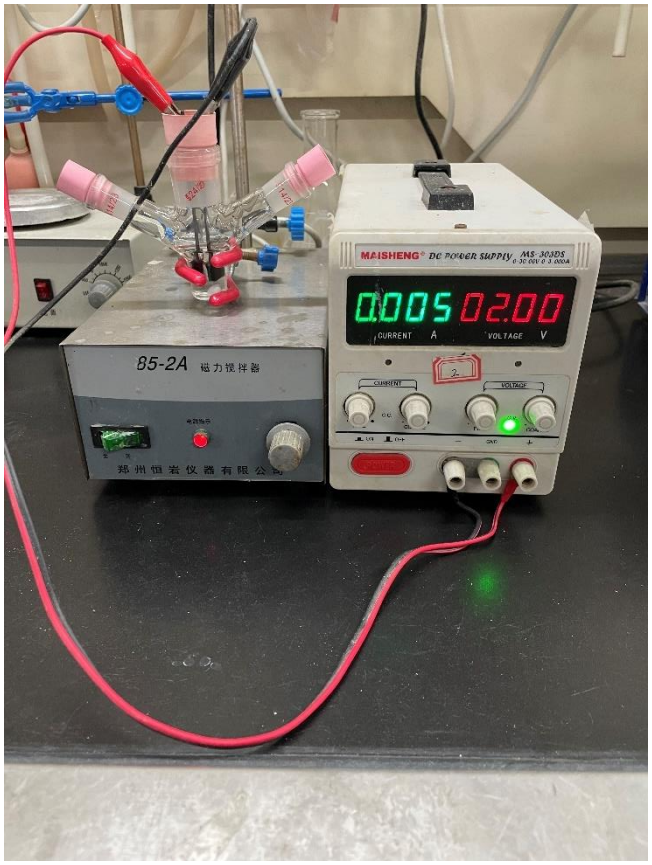
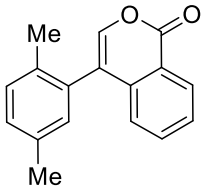
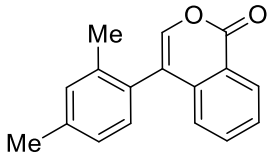


Figure S2. Schematic Diagram of the Experimental Set-up



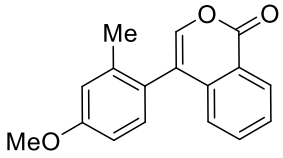
4-(2,5-dimethylphenyl)-1H-isochromen-1-one (2a)

Prepared via the general procedure **III**. The product **2a** was furnished as a yellow oil in 91% yield (45.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.65 (td, *J* = 7.6, 1.4 Hz, 1H), 7.54 (td, *J* = 7.6, 1.2 Hz, 1H), 7.20 (d, *J* = 9.3 Hz, 3H), 7.06 – 7.00 (m, 3H), 2.36 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4, 142.4, 137.2, 135.9, 134.8 (d, *J* = 9.0 Hz), 132.1, 131.7, 130.4, 130.0, 129.7, 128.6, 124.9, 121.4, 120.1, 21.0, 19.5. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{14}NaO_2^+$ 273.0886; Found 273.0896.



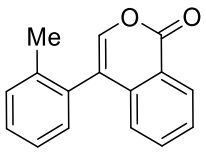
4-(2,4-dimethylphenyl)-1H-isochromen-1-one (2b)

Prepared via the general procedure **III**. The product **2b** was furnished as a yellow oil in 86% yield (43.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.64 (td, *J* = 7.6, 1.4 Hz, 1H), 7.53 (td, *J* = 7.6, 1.2 Hz, 1H), 7.17 (d, *J* = 12.5 Hz, 2H), 7.12 – 7.10 (m, 1H), 7.01 (d, *J* = 6.9 Hz, 1H), 2.40 (s, 3H), 2.11 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4, 142.5, 138.9, 137.8, 137.4, 134.8, 131.3, 131.0, 130.0, 129.3, 128.6, 127.0, 124.9, 121.4, 119.9, 21.3, 19.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{14}NaO_2^+$ 273.0886; Found 273.0896.



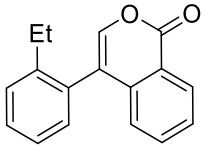
4-(4-methoxy-2-methylphenyl)-1H-isochromen-1-one (2c)

Prepared via the general procedure **III**. The product **2c** was furnished as a yellow oil in 66% yield (35.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.65 (td, *J* = 7.7, 1.4 Hz, 1H), 7.57 – 7.50 (m, 1H), 7.18 (s, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.88 (d, *J* = 2.7 Hz, 1H), 6.83 (dd, *J* = 8.3, 2.7 Hz, 1H), 3.86 (s, 3H), 2.12 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 142.7, 139.6, 137.6, 134.9, 132.2, 130.1, 128.6, 124.9, 124.6, 121.4, 119.6, 116.1, 111.5, 55.5, 20.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{14}NaO_3^+$ 289.0835; Found 289.0841.



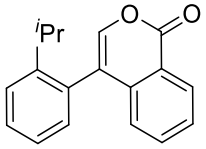
4-(*o*-tolyl)-1H-isochromen-1-one (2d)

Prepared via the general procedure **III**. The product **2d** was furnished as a yellow oil in 83% yield (39.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.65 (td, *J* = 7.6, 1.4 Hz, 1H), 7.54 (td, *J* = 7.6, 1.2 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.35 – 7.28 (m, 2H), 7.24 – 7.20 (m, 2H), 6.99 (dd, *J* = 8.0, 1.2 Hz, 1H), 2.16 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.3, 142.5, 138.0, 137.2, 134.9, 132.3, 131.1, 130.5, 130.1, 129.0, 128.7, 126.3, 124.8, 121.4, 119.9, 20.0. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{12}NaO_2^+$ 259.0730; Found 259.0739.



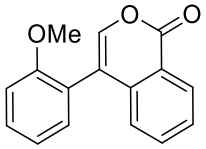
4-(2-ethylphenyl)-1H-isochromen-1-one (2e)

Prepared via the general procedure **III**. The product **2e** was furnished as a yellow oil in 72% yield (36 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.64 (td, *J* = 7.6, 1.4 Hz, 1H), 7.54 (td, *J* = 7.5, 1.2 Hz, 1H), 7.43 (td, *J* = 7.4, 1.5 Hz, 1H), 7.38 (d, *J* = 6.2 Hz, 1H), 7.29 (td, *J* = 7.3, 1.5 Hz, 1H), 7.23 – 7.18 (m, 2H), 6.99 (dd, *J* = 8.0, 1.2 Hz, 1H), 2.57 – 2.38 (m, 1H), 1.09 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.3, 144.1, 142.5, 137.7, 134.8, 131.6, 131.3, 130.0, 129.3, 128.8, 128.7, 126.3, 125.0, 121.4, 119.6, 26.4, 15.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{14}NaO_2^+$ 273.0886; Found 273.0896.



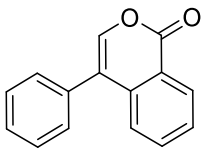
4-(2-isopropylphenyl)-1H-isochromen-1-one (2f)

Prepared via the general procedure **III**. The product **2f** was furnished as a yellow oil in 87% yield (46.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.64 (td, *J* = 7.6, 1.4 Hz, 1H), 7.54 (td, *J* = 7.6, 1.2 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.31 – 7.23 (m, 1H), 7.21 – 7.16 (m, 2H), 6.99 (d, *J* = 8.6 Hz, 1H), 2.86 – 2.74 (m, 1H), 1.14 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.3, 149.0, 142.4, 138.0, 134.8, 131.3, 130.9, 130.0, 129.5, 128.7, 126.2, 126.0, 125.0, 121.4, 119.7, 30.4, 25.3, 23.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{16}NaO_2^+$ 287.1043; Found 287.1051.



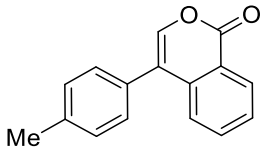
4-(2-methoxyphenyl)-1H-isochromen-1-one (2g)

Prepared via the general procedure **III**. The product **2g** was furnished as a yellow oil in 65% yield (33.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.57 – 7.53 (m, 1H), 7.49 (td, *J* = 7.8, 1.8 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.16 – 7.04 (m, 3H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.5, 158.0, 142.8, 137.2, 134.4, 132.0, 130.5, 129.7, 128.3, 125.3, 121.9, 121.3, 121.0, 117.8, 111.1, 55.6. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{13}O_3^+$ 253.0859; Found 253.0870.



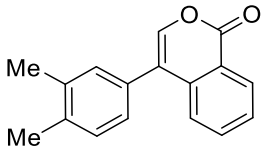
4-phenyl-1H-isochromen-1-one (2h)[11]

Prepared via the general procedure **III**. The product **2h** was furnished as a yellow oil in 55% yield (24.4mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.58 – 7.54 (m, 1H), 7.52 – 7.45 (m, 3H), 7.42 – 7.39 (m, 3H), 7.26 (s, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2, 142.4, 136.9, 134.8, 133.2, 130.2, 130.0, 129.0, 128.7, 128.6, 124.8, 121.5, 120.8.



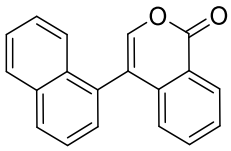
4-(p-tolyl)-1H-isochromen-1-one (2i)

Prepared via the general procedure **III**. The product **2i** was furnished as a yellow oil in 37% yield (17.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.72 – 7.65 (m, 1H), 7.55 (td, *J* = 7.7, 1.2 Hz, 1H), 7.42 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.31 – 7.26 (m, 4H), 7.24 (s, 1H), 2.44 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 162.3, 142.2, 138.5, 137.1, 134.8, 130.2, 129.8, 129.7, 128.6, 124.8, 121.5, 120.7, 21.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{13}O_2^+$ 237.0910; Found 237.0921.



4-(3,4-dimethylphenyl)-1H-isochromen-1-one (2j)

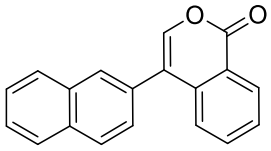
Prepared via the general procedure **III**. The product **2j** was furnished as a yellow oil in 35% yield (17.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.73 – 7.64 (m, 1H), 7.55 (td, *J* = 7.7, 1.2 Hz, 1H), 7.43 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.26 (d, *J* = 2.7 Hz, 1H), 7.24 (d, *J* = 3.2 Hz, 1H), 7.17 – 7.16 (m, 1H), 7.13 (dd, *J* = 7.6, 2.0 Hz, 1H), 2.34 (d, *J* = 5.9 Hz, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 162.3, 142.2, 137.3, 137.2, 137.1, 134.7, 131.1, 130.6, 130.2, 130.1, 128.6, 127.4, 124.9, 121.5, 120.8, 20.0, 19.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{15}O_2^+$ 251.1067; Found 251.1077.



4-(naphthalen-1-yl)-1H-isochromen-1-one (2k)

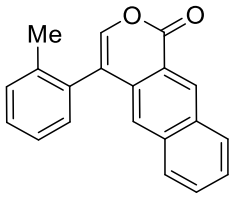
Prepared via the general procedure **III**. The product **2k** was furnished as a yellow oil in 95% yield (51.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 – 8.40 (m, 1H), 7.97 (dd, *J* = 17.1, 8.2 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.55 – 7.52 (m, 3H), 7.50 (td, *J* = 7.1, 1.2 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.36 (s, 1H), 6.94 – 6.87 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.3, 143.3, 137.7, 134.8, 133.8, 132.9, 130.5, 130.0,

129.5, 128.8, 128.7, 128.6, 126.7, 126.4, 125.7, 125.7, 125.4, 121.3, 119.0. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{12}NaO_2^+$ 295.0730; Found 295.0738.



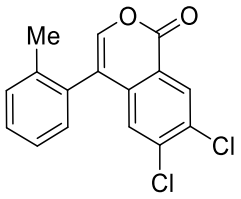
4-(naphthalen-2-yl)-1H-isochromen-1-one (2l)

Prepared via the general procedure **III**. The product **2l** was furnished as a yellow oil in 65% yield (35.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (d, *J* = 7.9 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.94 – 7.88 (m, 3H), 7.73 – 7.66 (m, 1H), 7.60 – 7.56 (m, 3H), 7.51 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.36 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2, 142.6, 137.1, 134.9, 133.6, 133.2, 130.7, 130.3, 129.0, 128.8, 128.6, 128.1, 128.0, 127.6, 126.9, 126.8, 124.9, 121.5, 120.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{12}NaO_2^+$ 295.0730; Found 295.0739.



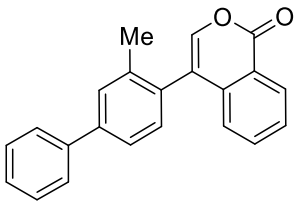
4-(o-tolyl)-1H-benzo[g]isochromen-1-one (2m)

Prepared via the general procedure **III**. The product **2m** was furnished as a yellow oil in 70% yield (40.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.51 (m, 2H), 7.44 (td, *J* = 7.3, 1.6 Hz, 1H), 7.39 (d, *J* = 9.2 Hz, 2H), 7.35 (td, *J* = 7.3, 1.5 Hz, 1H), 7.31 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.16 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6, 141.1, 138.2, 136.4, 132.8, 132.5, 132.1, 131.2, 130.6, 129.7, 129.5, 129.0, 128.2, 127.1, 126.4, 123.7, 119.9, 119.6, 20.0. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{14}NaO_2^+$ 309.0886; Found 309.0894.



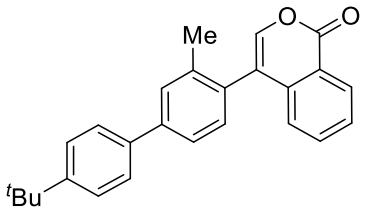
6,7-dichloro-4-(o-tolyl)-1H-isochromen-1-one (2n)

Prepared via the general procedure **III**. The product **2n** was furnished as a yellow oil in 65% yield (39.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.41 (td, *J* = 7.5, 1.5 Hz, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.32 (td, *J* = 7.6, 1.5 Hz, 1H), 7.22 – 7.19 (m, 2H), 7.06 (s, 1H), 2.16 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 143.8, 140.4, 137.8, 136.7, 133.2, 131.7, 131.2, 131.0, 130.8, 129.5, 126.7, 126.6, 120.8, 118.7, 20.0. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{10}Cl_2NaO2^+$ 326.9950; Found 326.9960.



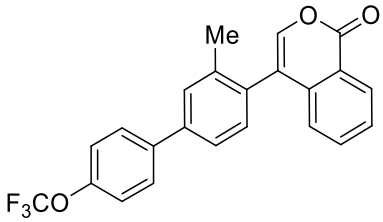
4-(3-methyl-[1,1'-biphenyl]-4-yl)-1H-isochromen-1-one (4a)

Prepared via the general procedure **III**. The product **4a** was furnished as a white solid in 94% yield (59.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 7.9 Hz, 1H), 7.71 – 7.63 (m, 3H), 7.58 – 7.47 (m, 5H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 4.2 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.3, 142.6, 142.0, 140.7, 138.5, 137.2, 135.0, 131.6, 131.4, 130.1, 129.3, 129.0, 128.7, 127.8, 127.3, 125.1, 124.9, 121.5, 119.7, 20.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{16}NaO_2^+$ 335.1043; Found 335.1053. Melting point = 122-124 ^{o}C.



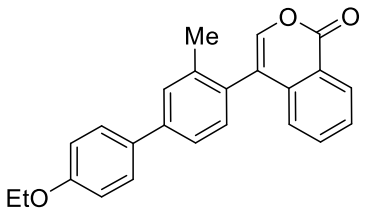
4-(4'-(tert-butyl)-3-methyl-[1,1'-biphenyl]-4-yl)-1H-isochromen-1-one (4b)

Prepared via the general procedure **III**. The product **4b** was furnished as a white solid in 75% yield (55.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 7.9 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.55 (d, *J* = 6.0 Hz, 2H), 7.52 – 7.49 (m, 3H), 7.30 – 7.24 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 2.21 (s, 3H), 1.39 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4, 142.6, 141.8, 138.4, 137.8, 137.3, 134.9, 131.5, 131.0, 130.1, 129.1, 128.7, 126.9, 126.0, 125.0, 124.9, 121.5, 119.8, 34.7, 31.5, 20.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{24}NaO_2^+$ 391.1669; Found 391.1678. Melting point = 128-130 ^{o}C.



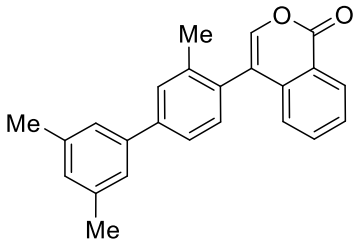
4-(3-methyl-4'-(trifluoromethoxy)-[1,1'-biphenyl]-4-yl)-1H-isochromen-1-one (4c)

Prepared via the general procedure **III**. The product **4c** was furnished as a white solid in 99% yield (78.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.3 Hz, 1H), 7.67 (dd, *J* = 13.7, 8.3 Hz, 3H), 7.59 – 7.52 (m, 2H), 7.49 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.32 (dd, *J* = 8.1, 3.6 Hz, 3H), 7.24 (s, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.3, 149.0, 142.6, 140.6, 139.4, 138.7, 137.1, 135.0, 131.9, 131.8, 130.2, 129.3, 129.0, 128.8, 128.6, 125.1, 124.8, 121.5, 120.7 (q, *J* = 257.3 Hz), 119.5, 20.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{16}F_3O_3^+$ 397.1046; Found 397.1057. Melting point = 90-92 ^{o}C.



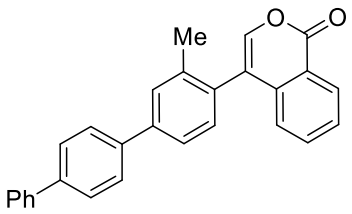
4-(4'-ethoxy-3-methyl-[1,1'-biphenyl]-4-yl)-1H-isochromen-1-one (4d)

Prepared via the general procedure **III**. The product **4d** was furnished as a white solid in 68% yield (48.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.70 – 7.63 (m, 1H), 7.60 – 7.51 (m, 4H), 7.48 (dd, *J* = 7.9, 2.0 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 2H), 4.10 (q, *J* = 7.0 Hz, 2H), 2.21 (s, 3H), 1.46 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4, 158.9, 142.6, 141.6, 138.4, 137.3, 134.9, 133.0, 131.6, 130.6, 130.1, 128.8, 128.7, 128.3, 125.0, 124.6, 121.5, 119.8, 115.0, 63.7, 20.3, 15.0. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{20}NaO_3^+$ 379.1305; Found 379.1314. Melting point = 118-120 ºC.



4-(3,3',5'-trimethyl-[1,1'-biphenyl]-4-yl)-1H-isochromen-1-one (4e)

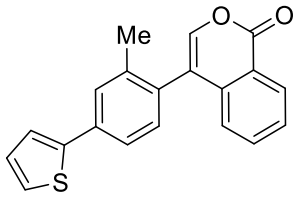
Prepared via the general procedure **III**. The product **4e** was furnished as a yellow oil in 64% yield (43.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.67 (td, *J* = 7.6, 1.4 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.50 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.29 – 7.26 (m, 4H), 7.24 (s, 1H), 7.08 (s, 1H), 7.04 – 7.03 (m, 1H), 2.41 (s, 6H), 2.21 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4, 142.6, 142.2, 140.7, 138.5, 138.3, 137.3, 134.9, 131.5, 131.1, 130.1, 129.4, 129.3, 128.7, 125.2, 125.1, 125.0, 121.5, 119.8, 21.6, 20.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{20}NaO_2^+$ 363.1356; Found 363.1362.



4-(3-methyl-[1,1':4',1''-terphenyl]-4-yl)-1H-isochromen-1-one (4f)

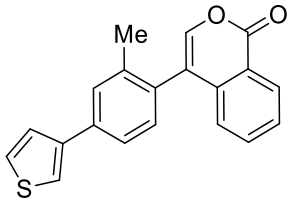
Prepared via the general procedure **III**. The product **4f** was furnished as a white solid in 90% yield (70 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 6.5 Hz, 1H), 7.76 – 7.66 (m, 7H), 7.62 (s, 1H), 7.57 (t, *J* = 7.0 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.26 (s, 1H), 7.10 (d, *J* = 8.3 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.3, 142.6, 141.5, 140.7, 140.6, 139.5, 138.6, 137.2, 135.0, 131.7, 131.5, 130.2, 129.2, 129.0, 128.8, 127.7, 127.6, 127.2, 125.0, 124.9,

121.48, 119.7, 20.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{20}NaO_2^+$ 411.1356; Found 411.1360. Melting point = 176-178 °C.



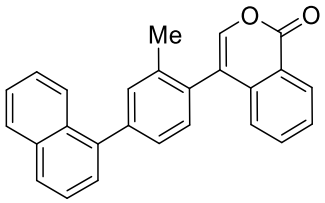
4-(2-methyl-4-(thiophen-2-yl)phenyl)-1H-isochromen-1-one (4g)

Prepared via the general procedure **III**. The product **4g** was furnished as a white solid in 62% yield (39.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.9 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.38 (d, *J* = 3.6 Hz, 1H), 7.33 (d, *J* = 5.1 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.12 (t, *J* = 4.4 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.3, 143.8, 142.6, 138.7, 137.1, 135.2, 135.0, 131.7, 131.5, 130.1, 128.8, 128.3, 128.0, 125.4, 124.8, 123.9, 123.6, 121.5, 120.0, 20.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{14}NaO_2S^+$ 341.0607; Found 341.0615. Melting point = 158-160 °C.



4-(2-methyl-4-(thiophen-3-yl)phenyl)-1H-isochromen-1-one (4h)

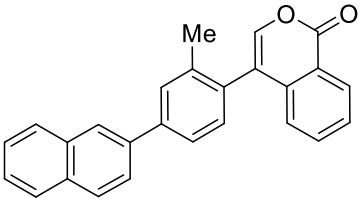
Prepared via the general procedure **III**. The product **4h** was furnished as a white solid in 65% yield (41.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.9 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.38 (d, *J* = 3.6 Hz, 1H), 7.33 (d, *J* = 5.1 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.12 (t, *J* = 4.4 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.3, 143.8, 142.6, 138.7, 137.1, 135.2, 135.0, 131.7, 131.5, 130.1, 128.8, 128.3, 128.0, 125.4, 124.8, 123.9, 123.6, 121.5, 120.0, 20.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{14}NaO_2S^+$ 341.0607; Found 341.0615. Melting point = 156-158 °C.



4-(2-methyl-4-(naphthalen-1-yl)phenyl)-1H-isochromen-1-one (4i)

Prepared via the general procedure **III**. The product **4i** was furnished as a white solid in 77% yield (56.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (d, *J* = 9.3 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.73 (td, *J* = 7.6, 1.4 Hz, 1H), 7.60 – 7.48 (m, 6H), 7.44 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.32 (s, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4, 142.7, 141.6, 139.8, 138.0, 137.2, 135.0, 134.0, 132.2, 131.7, 131.3, 131.0, 130.2, 128.8, 128.5, 128.1, 128.0, 127.1, 126.3, 126.0, 125.6, 125.0, 121.5, 119.8, 20.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{18}NaO_2^+$ 385.1199; Found 385.1208. Melting point = 182-184 ^oC.



4-(2-methyl-4-(naphthalen-2-yl)phenyl)-1H-isochromen-1-one (4j)

Prepared via the general procedure **III**. The product **4j** was furnished as a white solid in 60% yield (43.7 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 8.0, 1.4 Hz, 1H), 8.13 – 8.09 (m, 1H), 7.98 – 7.88 (m, 3H), 7.81 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.72 – 7.63 (m, 3H), 7.60 – 7.48 (m, 3H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 5.4 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.3, 142.6, 141.9, 138.6, 138.0, 137.2, 135.0, 133.8, 132.9, 131.7, 131.5, 130.2, 129.5, 128.8, 128.7, 128.4, 127.8, 126.6, 126.3, 126.0, 125.5, 125.4, 124.9, 121.5, 119.7, 20.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{18}NaO_2^+$ 385.1199; Found 385.1205. Melting point = 182-184 ^oC.

3.3 Gram Scale-up Reaction

Overview of Materials Used in Gram Scale-up Reaction

Electrodes: The home-made working electrode and counter electrode were made with graphite felts (50 mm x 25 mm x 3 mm) and graphite rods (length = 90 mm, Φ = 2 mm). The graphite felts were fixed with graphite rods to form the electrodes.
Electrochemical cell: A 100 mL beaker (length = 84 mm, Φ = 47 mm) was used as the home-made cell, and a paper bobbin with two pinholes (Φ = 2 mm) was used as a cap to seal the cell.
Stirring bar: A magnetic stirring bar (length = 30 mm, Φ = 10 mm) was applied.
Reaction conditions: The gram scale-up reaction was proceeded under room temperature (about 25 ℃) at a constant cell voltage of 2.0 V for 11 h. The distance between electrodes was 10 mm.

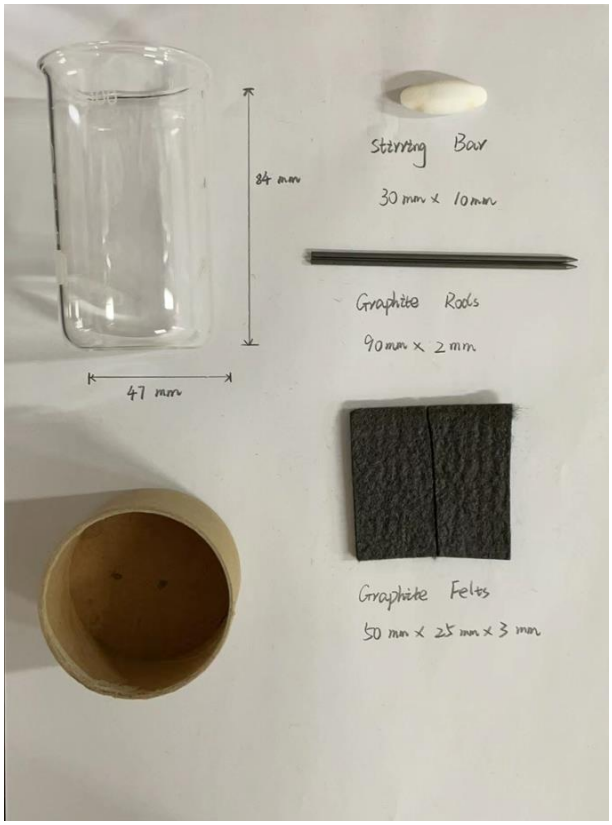
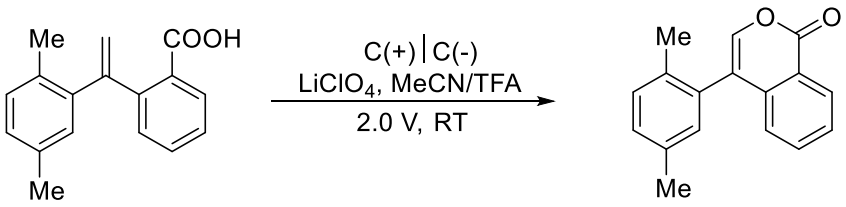


Figure S3. List of Electrochemical Experimental Materials for Scale-up

Gram Scale Reaction



4.0 mmol, 1.01 g 0.73 g, 73%

As shown in **Figure S4**, in a 100 mL beaker with graphite electrodes (graphite felts: 50 mm x 25 mm x 3 mm) equipped with a magnetic stirring bar (length = 30 mm, Φ = 10 mm), substrate **1a** (4.0 mmol, 1.01 g, 1.0 eq.), $LiClO_4$ (12.0 mmol, 3.0 eq.), acetonitrile/acetic acid (90:9, 99 mL, 0.04 M) were added. After fully stirring for 10 min, electrolysis was initiated under room temperature at a constant voltage of 2.0 V for 11 h. The reaction was monitored by TLC to determine the end. The mixture was diluted with EA (100 mL), washed with saturated K_2CO_3 solution (100 mL) and brine (100 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum to give a crude product, and the residue was purified by flash chromatography on silica gel to afford the desired compound **2a** (0.73 g, 73%).

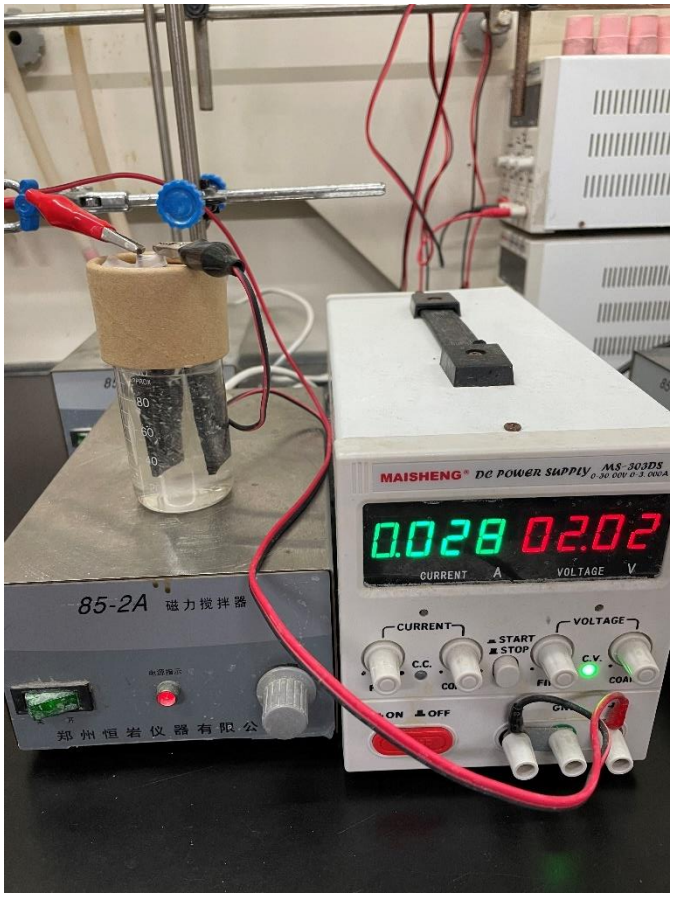
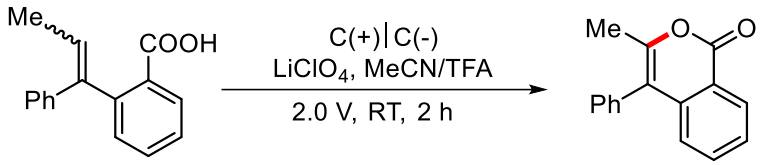


Figure S4. Gram Scaling-up Reaction

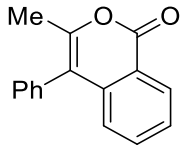
3.4 Additional Substrate with an Internal Olefin Moiety



R-1
E/Z isomers

R-2, 32%

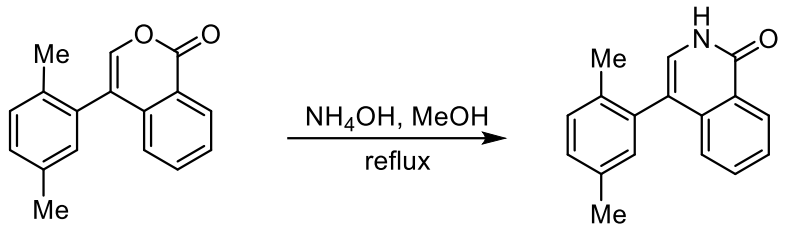
The product **R-1** was prepared as **E/Z** isomers via Wittig reaction in **Step 2** of the general procedure **I** with $EtPPh_3Br$.[12] The electrochemical reaction of **R-1** via the general procedure **III** could obtain the corresponding isocoumarin **R-2** in 32% yield. Thus, the substrates with internal olefin moieties might be available in the transformation.



3-methyl-4-phenyl-1H-isochromen-1-one (R-2)[13]

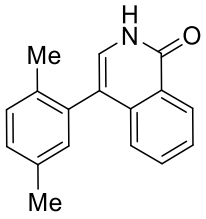
Prepared via the general procedure **III**. The product **R-2** was furnished as a yellow oil in 32% yield (15.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ8.33 (d, *J* = 7.9 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.29 – 7.26 (m, 2H), 7.00 (d, *J* = 8.1 Hz, 1H), 2.13 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.9, 151.8, 138.8, 134.7, 134.6, 130.7, 129.6, 129.1, 128.3, 127.5, 124.7, 120.1, 116.5, 18.2.

4. Derivatizations of Product 2a



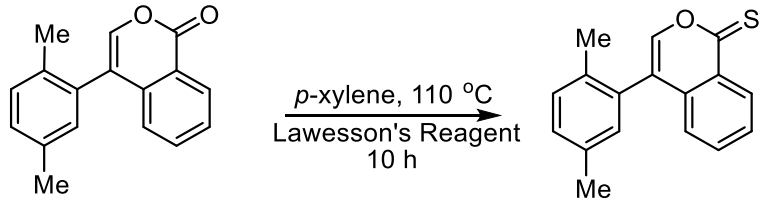
2a **D**-1

In a 25 mL sealing tube, **2a** (0.3 mmol, 75.1 mg) was dissolved with MeOH (0.1 M, 3 mL), followed by the addition of NH_4OH (0.5 mL). The above mixture was heated under 80 °C in an oil bath overnight. The final system should be acidified with HCl (1 M, 10 mL), extracted with EA (10 mL) for three times. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum to give a crude product, which was further purified by flash column chromatography on silica gel (PE: EA = 10:1 to 2:1) to deliver the desired substrate.



4-(2,5-dimethylphenyl)isoquinolin-1(2H)-one (D-1)

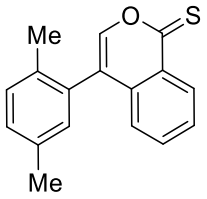
Prepared via the above procedure. The product **D-1** was furnished as a white solid in 82% yield (61.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.52 (s, 1H), 8.51 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.54 – 7.50 (m, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 16.9 Hz, 2H), 2.36 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 138.0, 135.6, 135.5, 134.8, 132.7, 131.9, 130.2, 129.1, 127.7, 126.9, 126.6, 125.9, 125.4, 119.7, 21.0, 19.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{16}NO^+$ 250.1226; Found 250.1237. Melting point = 144-146 °C.



2a **D**-2

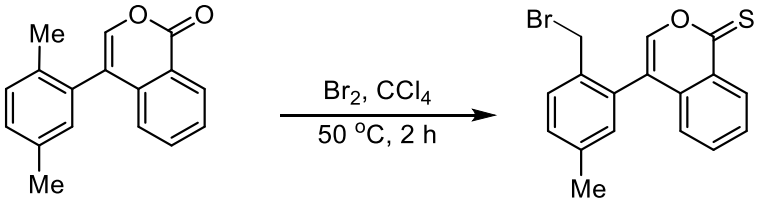
In a 25 mL Schlenk tube, **2a** (0.3 mmol, 75.1 mg) and Lawesson's Reagent (0.6 mmol, 2.0 eq.) were added. The tube was evacuated and backfilled with argon for three times, then dried *p*-xylene (0.1 M, 3 mL) was added to form a suspension. The above mixture was heated under 110 °C in an oil bath for 10 h. The final system should be filtered with Celite, washed with EA (5 mL) for three times. The combined organic phase was concentrated under vacuum to give a crude product, which was further

purified by flash column chromatography on silica gel (PE: EA =20:1) to deliver the desired substrate.



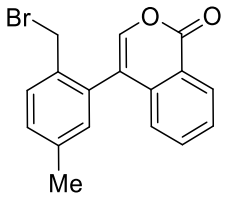
4-(2,5-dimethylphenyl)-1H-isochromene-1-thione (D-2)

Prepared via the above procedure. The product **D-2** was furnished as a yellow solid in 96% yield (76.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (d, *J* = 8.2 Hz, 1H), 7.70 – 7.63 (m, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.48 (s, 1H), 7.21 (q, *J* = 7.9 Hz, 2H), 7.06 – 7.02 (m, 2H), 2.37 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.4, 145.3, 136.0, 135.2, 134.6, 131.7, 131.6, 131.5, 130.8, 130.5, 130.0, 129.6, 125.1, 122.9, 21.0, 19.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{15}OS^+$ 267.0838; Found 267.0849. Melting point = 80-82 °C.



2a **D**-3

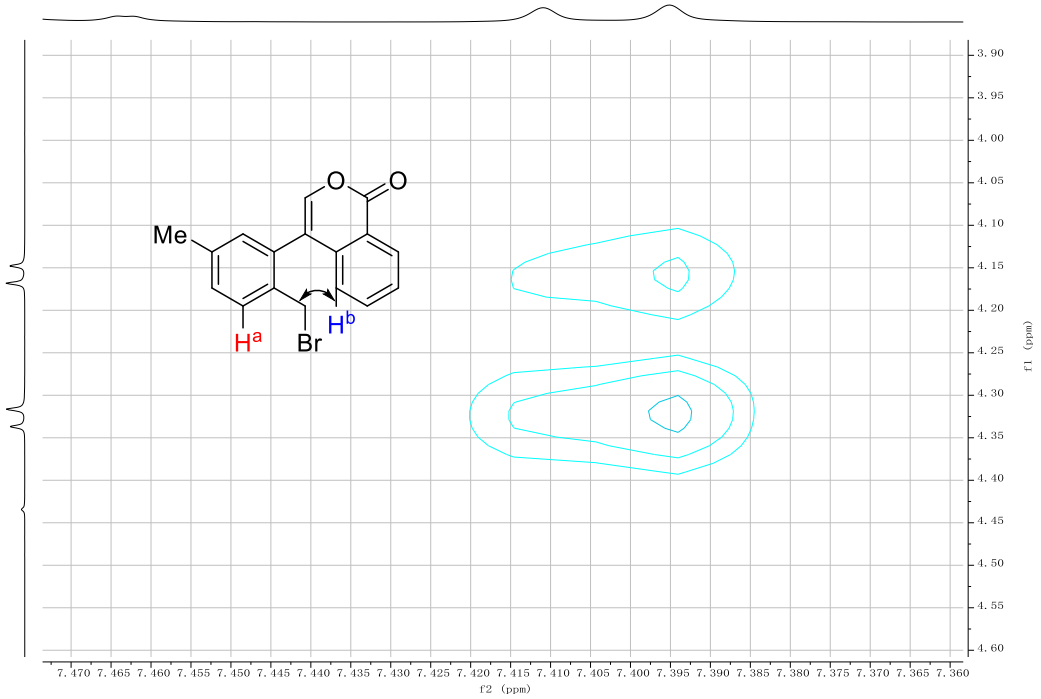
In a 25 mL tube, **2a** (0.3 mmol, 75.1 mg) was added, followed by a solution of Br_2 (0.25 mL) in CCl_4 (0.05 M, 6 mL). The above mixture was heated under 50 °C in an oil bath for 2 h. The final system should be concentrated under vacuum to give a crude product, which was further purified by flash column chromatography on silica gel (PE: EA = 20:1) to deliver the desired substrate. The structure of **D-3** was determined by NOESY spectra.

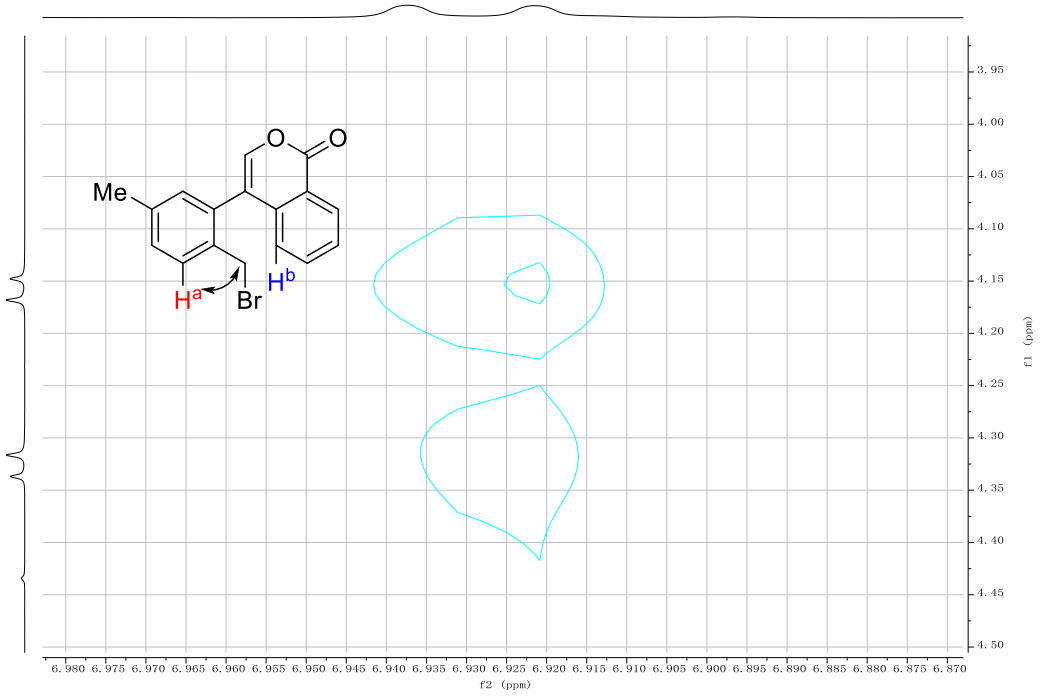


4-(2-(bromomethyl)-5-methylphenyl)-1H-isochromene-1-thione (D-3)

Prepared via the above procedure. The product **D-3** was furnished as a white solid in 85% yield (83.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 6.6 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.02 (s, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 4.34 (d, *J* = 10.2 Hz, 1H), 4.17 (d, *J* = 10.2 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.0, 143.0, 139.3, 134.9, 134.8, 132.6, 132.3, 131.1, 130.5, 130.1, 128.9, 124.9, 121.43, 117.85, 31.19, 21.27. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{13}BrNaO_2^+$ 350.9991; Found 351.0002. Melting point = 140-142 °C.

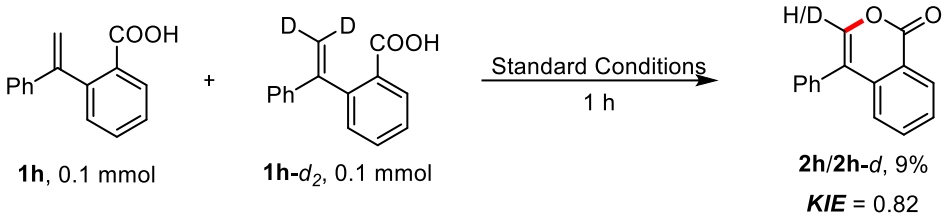
^{1}H-^{1}H NOESY Spectra of ***D-3***





5. Primary Mechanism Explorations

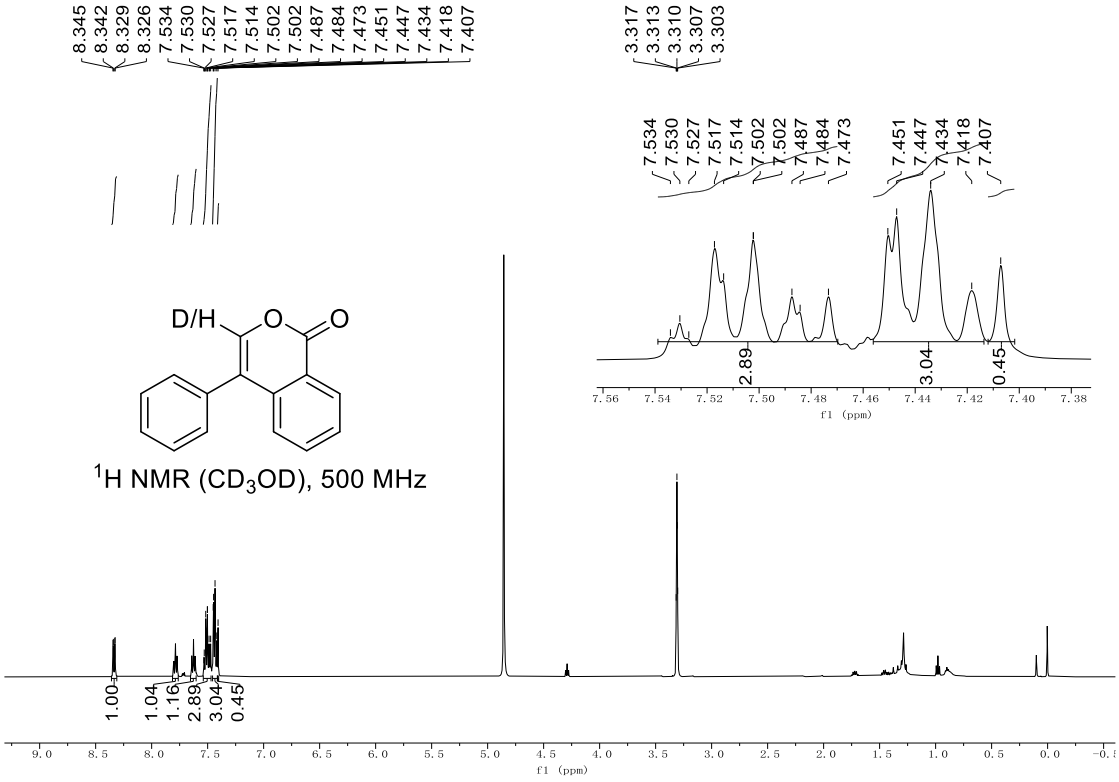
5.1 KIE Experiments



1h, 0.1 mmol **1h**-d_2, 0.1 mmol **2h**/**2h**-*d*, 9%

KIE = 0.82

According to procedure **III**, in an undivided cell with graphite electrodes equipped with a magnetic stirring bar, **1h** (0.1 mmol, 0.5 eq.) and **1h**-d_2 (0.1 mmol, 0.5 eq.), $LiClO_4$ (0.6 mmol, 3.0 eq.), and acetonitrile/trifluoroacetic acid (5.5:0.5, 6 mL, 0.033 M) were added. After fully stirring for 10 min, electrolysis was initiated under room temperature at a constant voltage of 2.0 V for 1h. The mixture was diluted with EA (20 mL), washed with saturated K_2CO_3 solution (20 mL) and brine (20 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum to give a crude product, and the residue was purified by flash chromatography on silica gel to afford the desired compound with the yield of 9%. The KIE value was determined by ^{1}H-NMR of crude product [KIE = 0.45/(1-0.45) = 0.82].



5.2 Chronopotentiometry Experiment

As shown in **Figure S5**, in an undivided cell with graphite electrodes (graphite rods length = 90 mm, Φ = 2 mm, graphite felts 10 mm x 10 mm x 3 mm) equipped with a magnetic stirring bar (length = 18 mm, Φ = 8 mm), substrate **1h** (0.6 mmol, 1.0 eq.), $LiClO_4$ (1.8 mmol, 3.0 eq.), and acetonitrile/trifluoroacetic acid (16.5:1.5, 18 mL, 0.033 M) were added. After fully stirring for 10 min, electrolysis was initiated under room temperature at a constant voltage of 2.0 V for 4 h. A saturated calomel electrode (0.2412 V) was used as a reference electrode to determine the actual potential. Measurements were taken every half hour using a multimeter and potential-time curves were plotted.

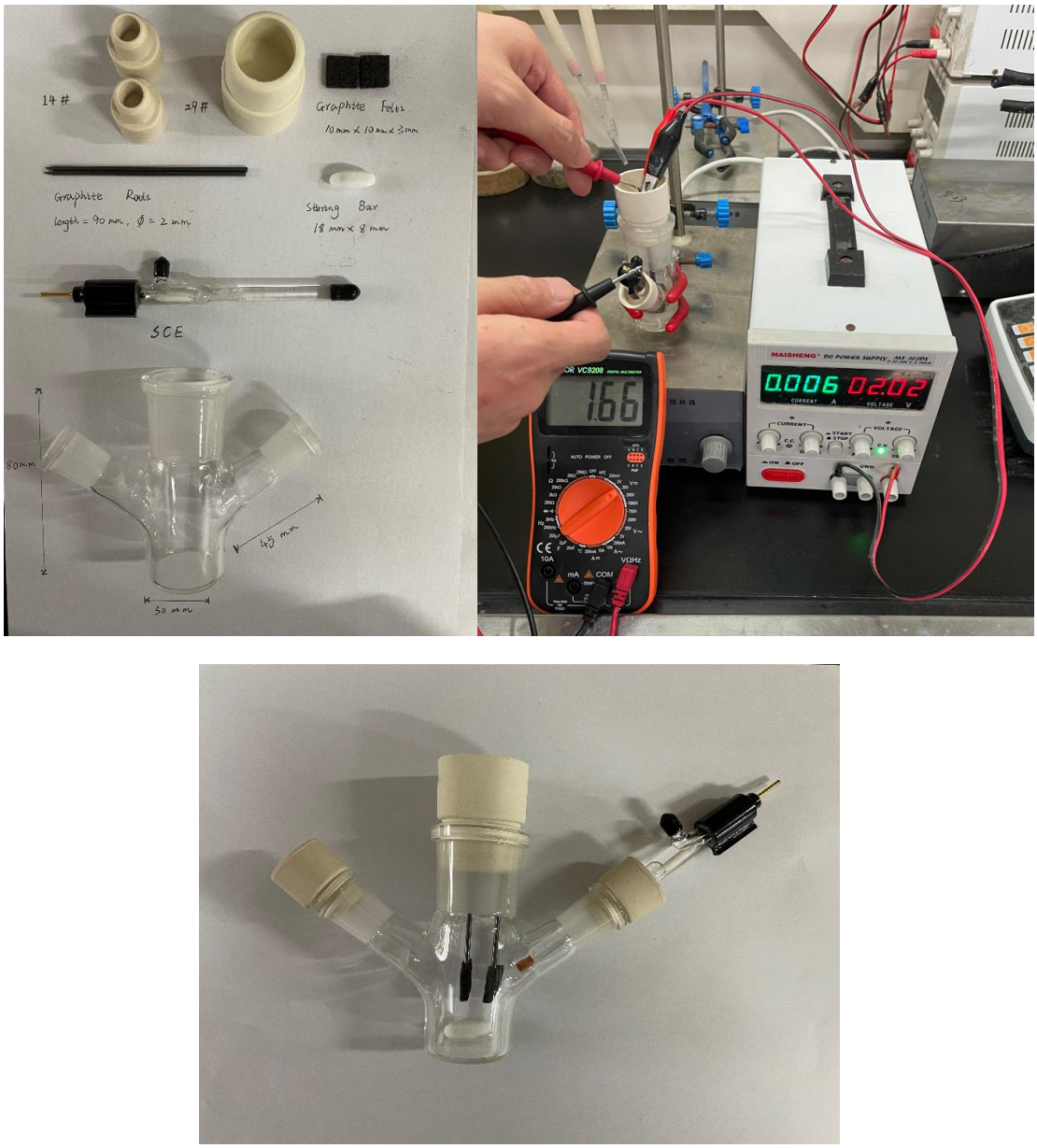


Figure S5. Schematic Diagram of Chronopotentiometry Experiment

Table S1: Potentials Measured with a Multimeter

Reaction Time/h	0	0.5	1	1.5	2	2.5	3	3.5	4
Anode/V	1.68	1.66	1.65	1.63	1.64	1.64	1.82	1.92	1.97
Cathode/V	-0.33	-0.35	-0.35	-0.38	-0.37	-0.36	-0.17	-0.1	-0.06

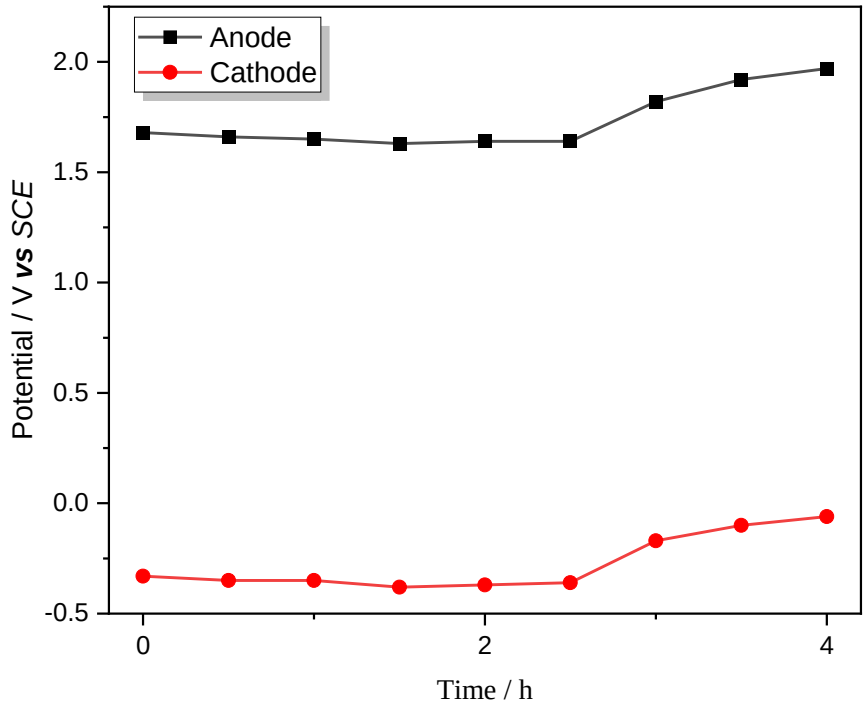


Figure S6. Potential-time Curves

5.3 Cyclic Voltammetry Studies

For the cyclic voltametric measurement, IUPAC convention was followed. The CV curves were recorded on a computer-controlled *CHI600E* instrument using an electrolyte of $LiClO_4$ in acetonitrile with a three-electrode cell (beaker-type cell) at room temperature (about 25 ºC). For the CV experiments, the initial potential was 0.0 V, switching potential was 2.0 V and the scan rate was 100 mV/s in the positive direction. The mixtures were stirred for 5 mins, and then all solutions used for the voltametric experiments were deoxygenated by purging with high-purity argon gas up to 5 mins, all the measured current had been normalized to mA/cm^2. All of cyclic voltammograms were obtained using glass carbon as the working electrode, Pt wire and an Ag/AgCl (saturated KCl solution) electrode as the counter and reference electrode, respectively. All the instruments and materials were purchased from *Chen Hua Company* (Shanghai, China).

Working electrode: The working electrode is a glassy carbon electrode (length = 60 mm, Φ = 3 mm, 0.07 cm^2). Polished with 0.05 μm Al_2O_3 and then sonicated in distilled water before drying.
Reference electrode: An Ag/AgCl (saturated KCl solution) electrode (length = 70 mm, Φ = 4 mm) as the reference electrode.
Counter electrode: The counter electrode is a Pt wire (length = 30 mm, Φ = 0.5 mm).
Electrochemical Cell: A beaker-type cell (length = 40 mm, Φ = 25 mm) with a teflon cap was used.

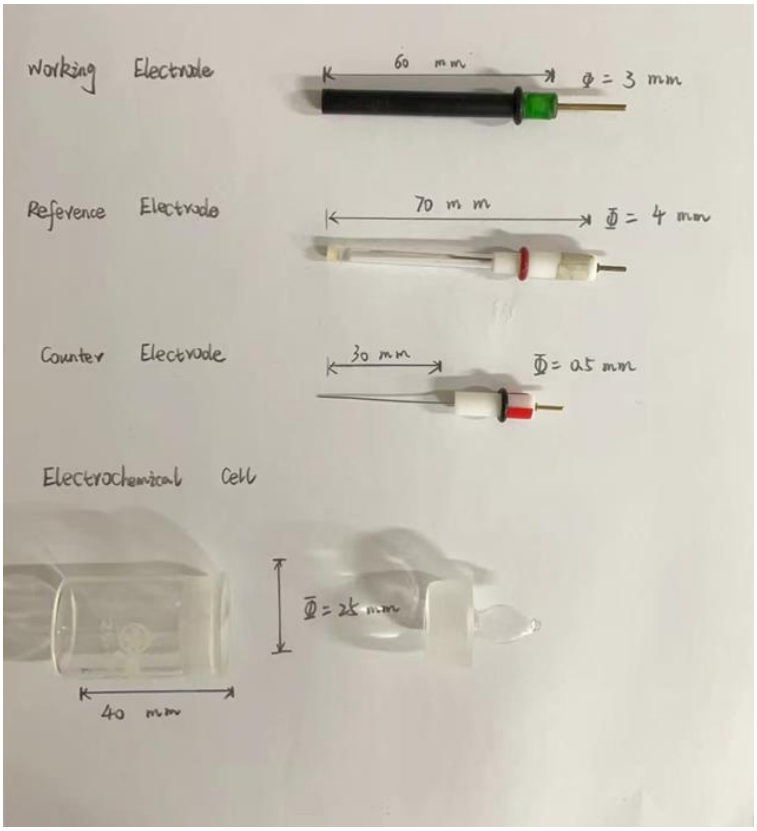


Figure S7. List of Materials for CV Experiments

Compounds Involved in CV Experiments

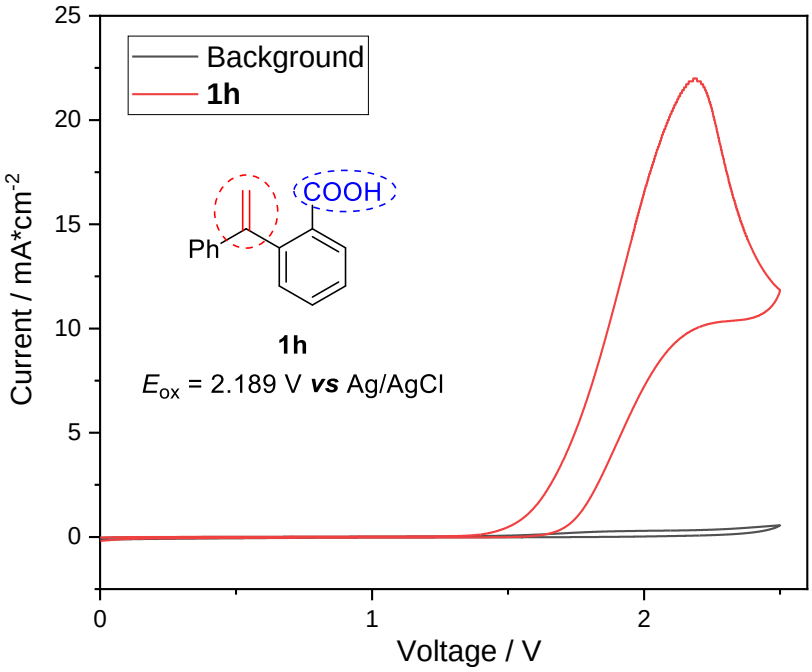


Figure S8-1. CV Curve of **1h**

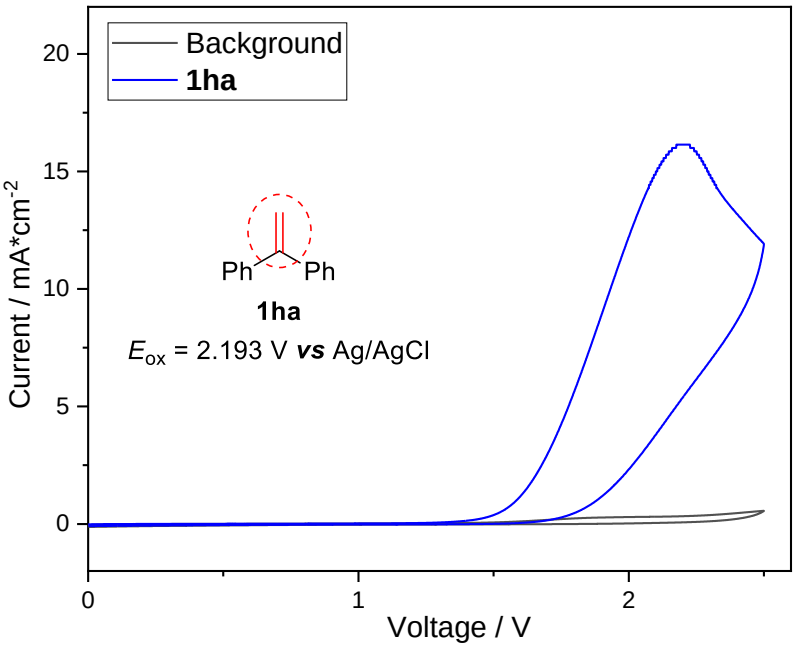


Figure S8-2. CV Curve of **1ha**

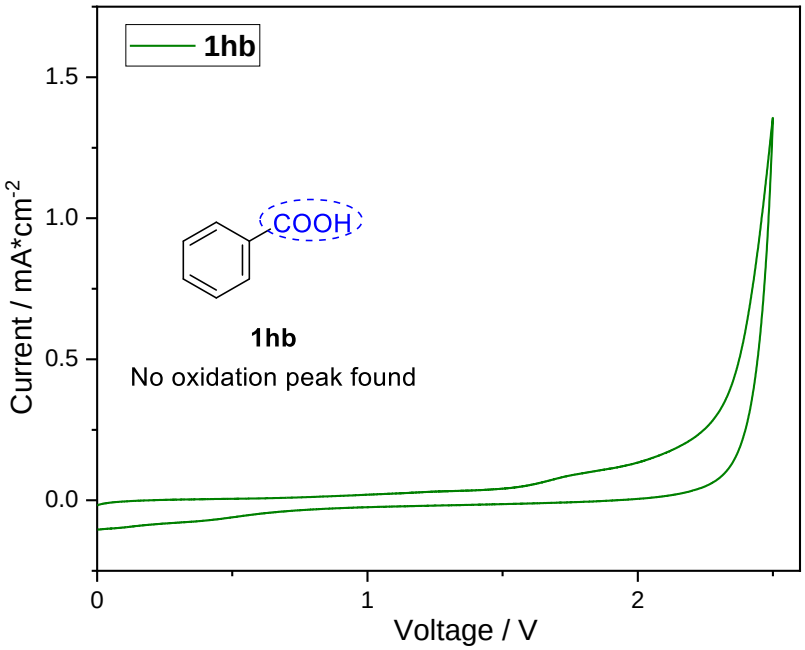


Figure S8-3. CV Curve of **1hb**

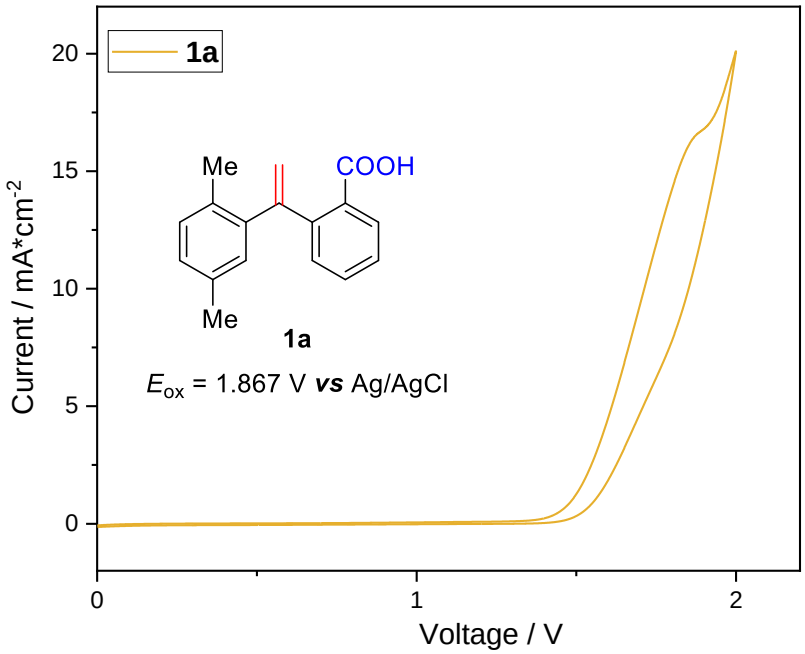


Figure S8-4. CV Curve of **1a**

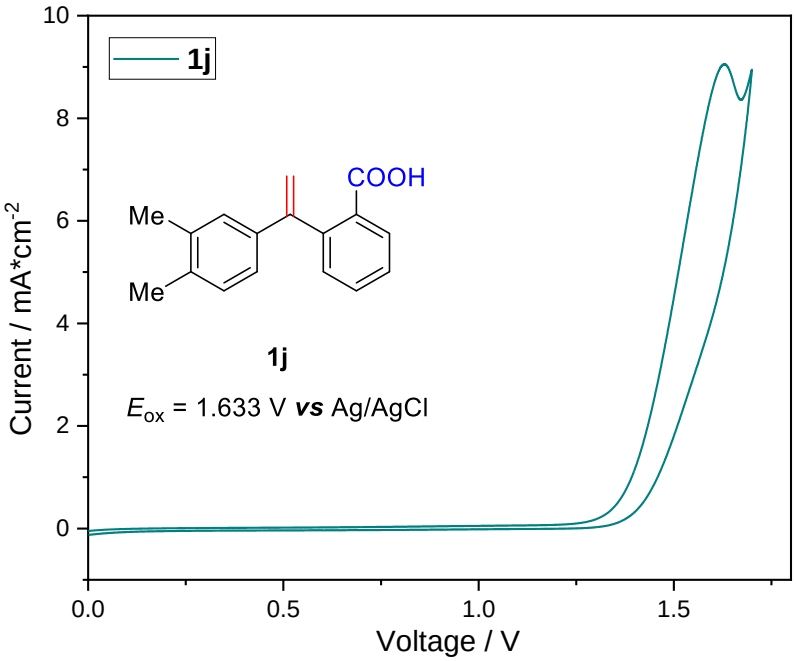
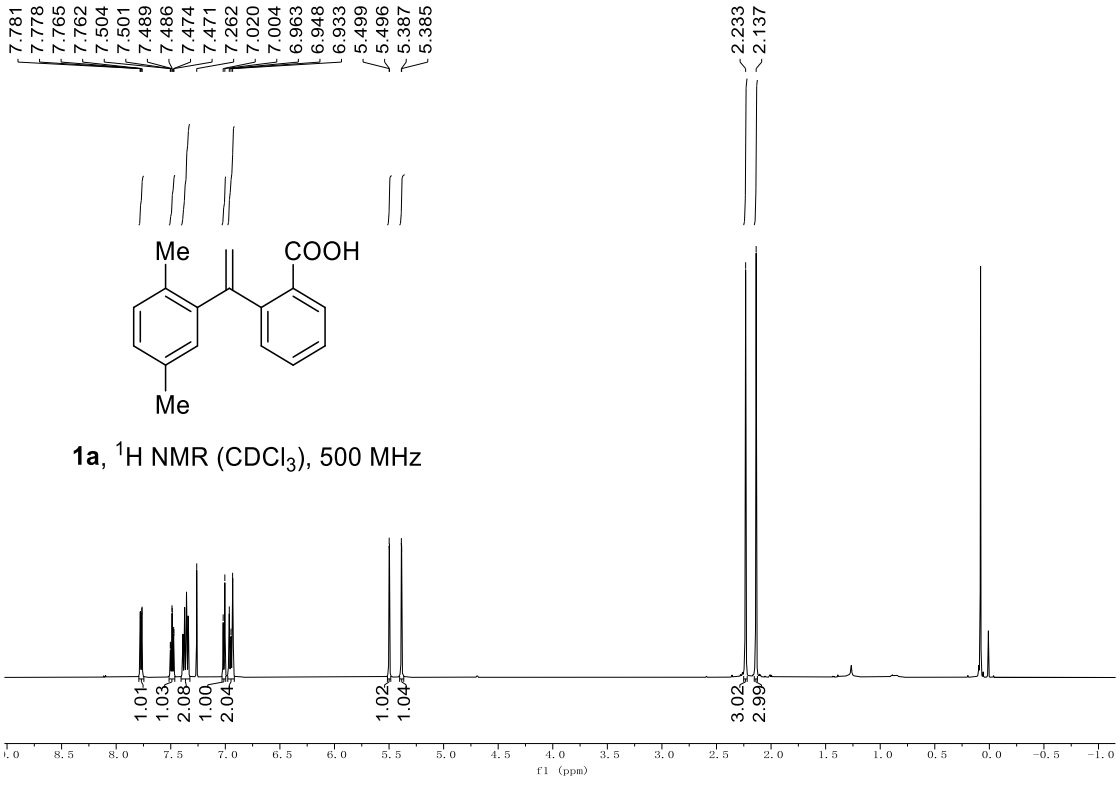


Figure S8-5. CV Curve of **1j**

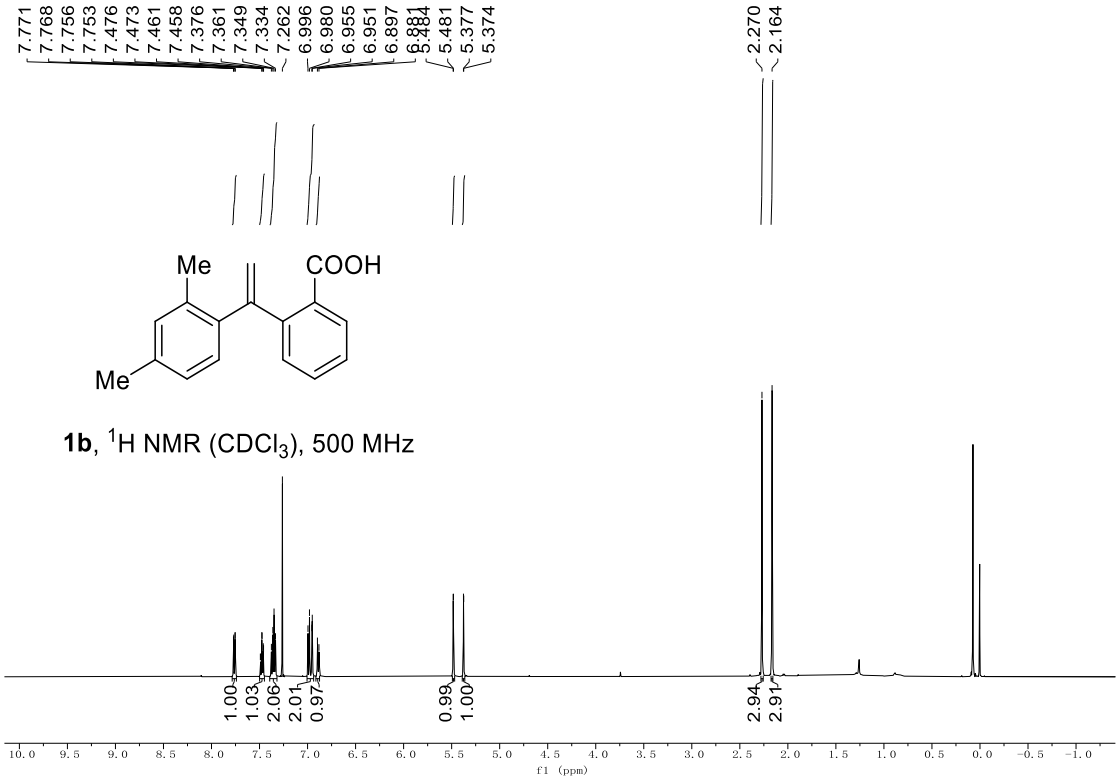
Background: MeCN (2.75 mL), $LiClO_4$ (0.3 mmol), TFA (0.25 mL); **1h**: **1h** (0.1 mmol) under background; **1ha**: **1ha** (0.1 mmol) under background; **1hb**: **1hb** (0.1 mmol) under background; **1a**: **1a** (0.1 mmol) under background; **1j**: **1j** (0.1 mmol) under background.

6. NMR Spectra

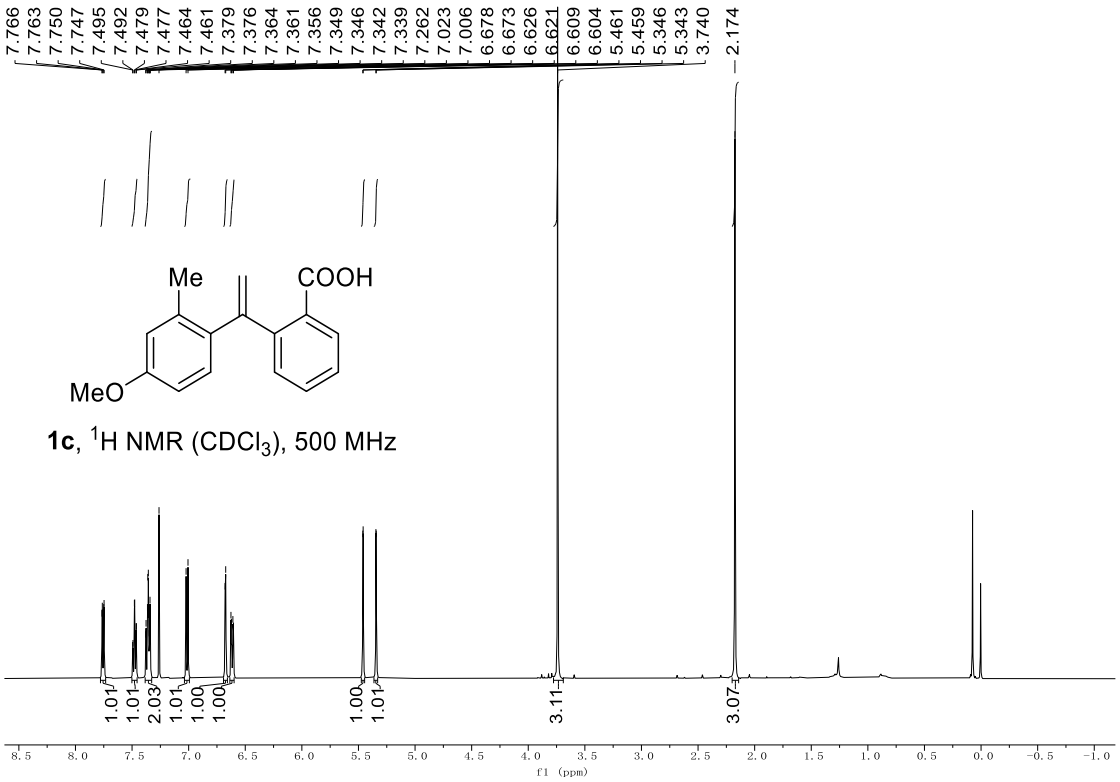
6.1 NMR Spectra of Substrates



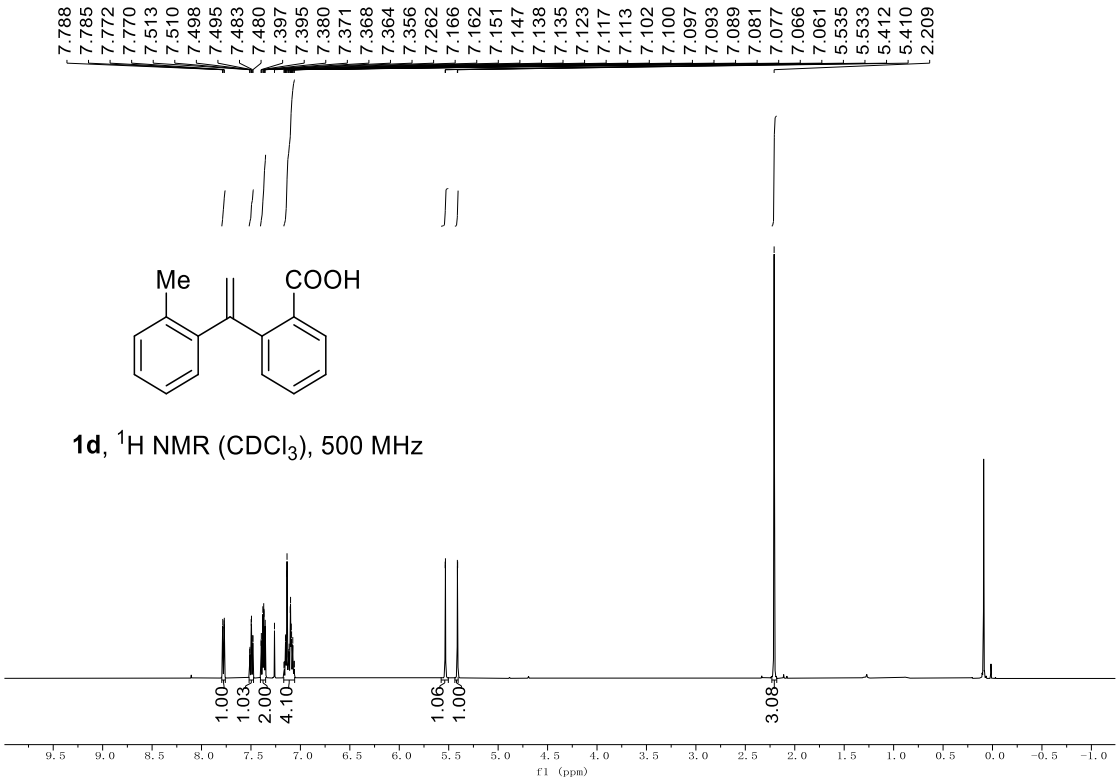
1a, ^{1}H NMR ($CDCl_3$), 500 MHz



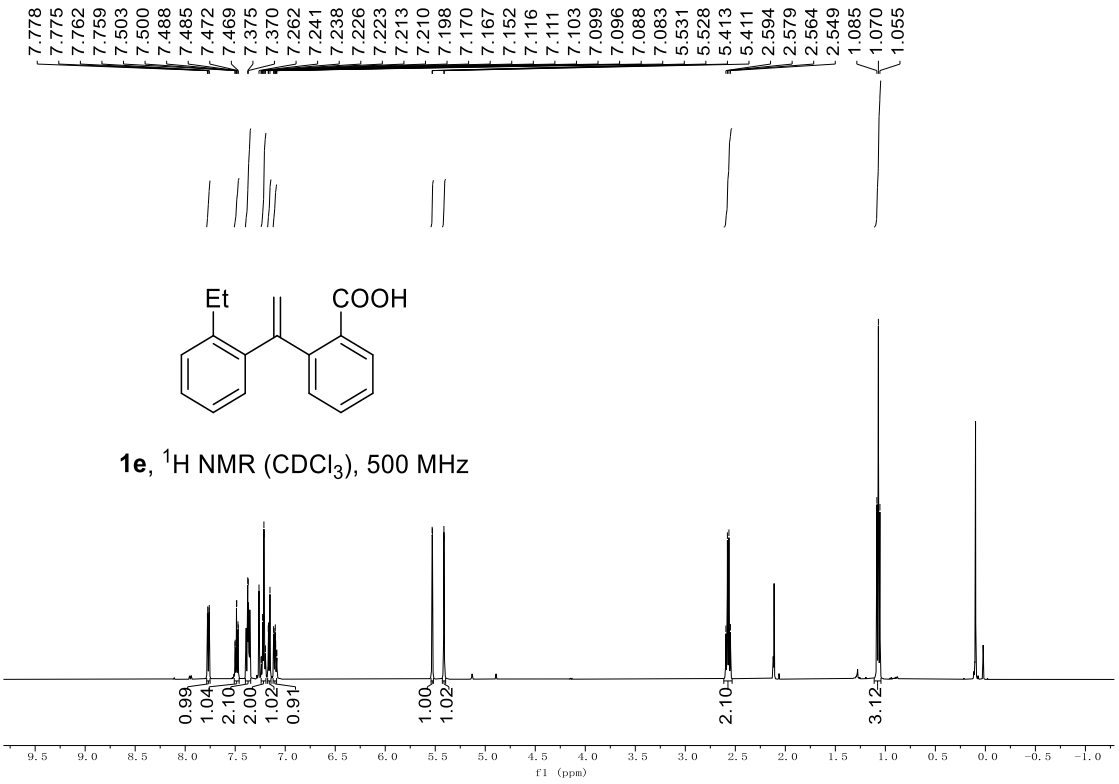
1b, ^{1}H NMR ($CDCl_3$), 500 MHz



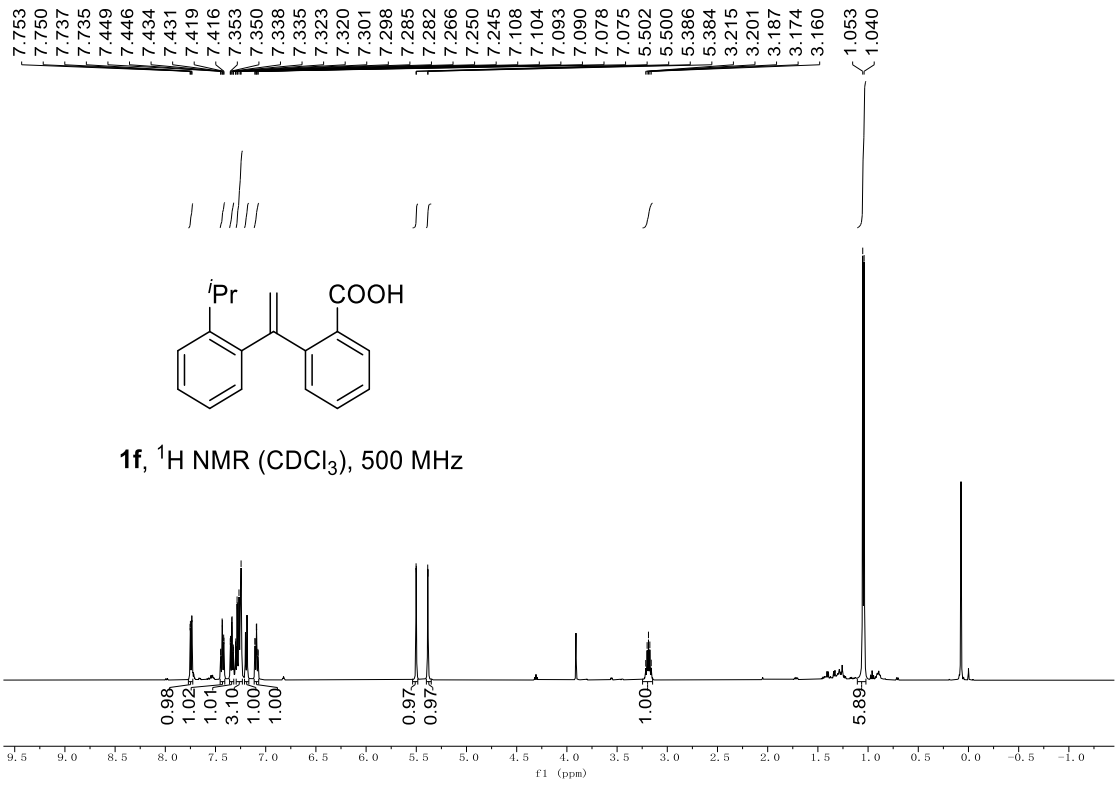
1c, ^{1}H NMR ($CDCl_3$), 500 MHz



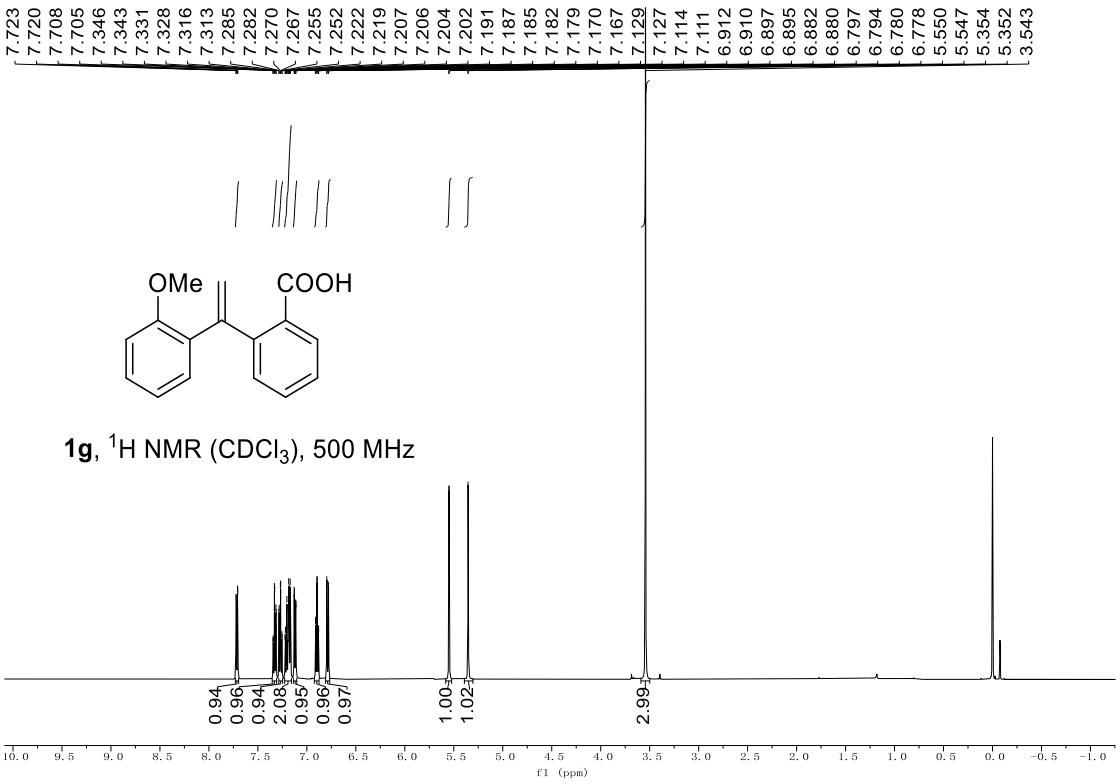
1d, ^{1}H NMR ($CDCl_3$), 500 MHz



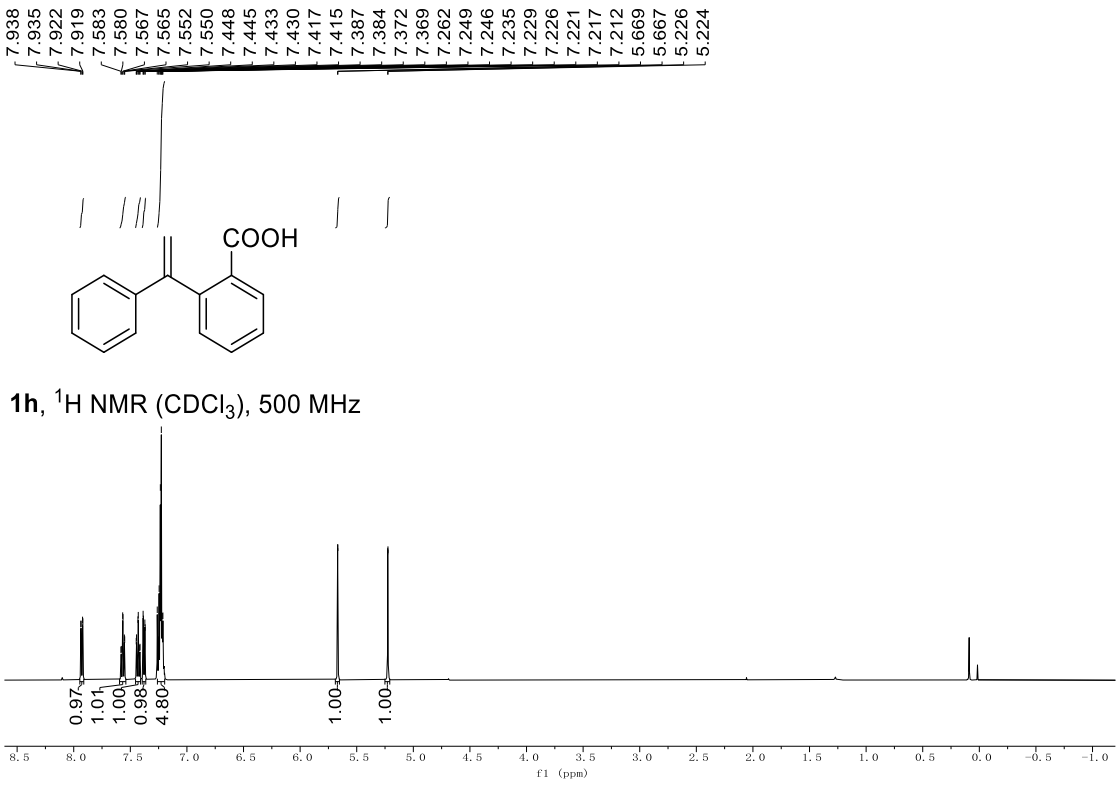
1e, ^{1}H NMR ($CDCl_3$), 500 MHz



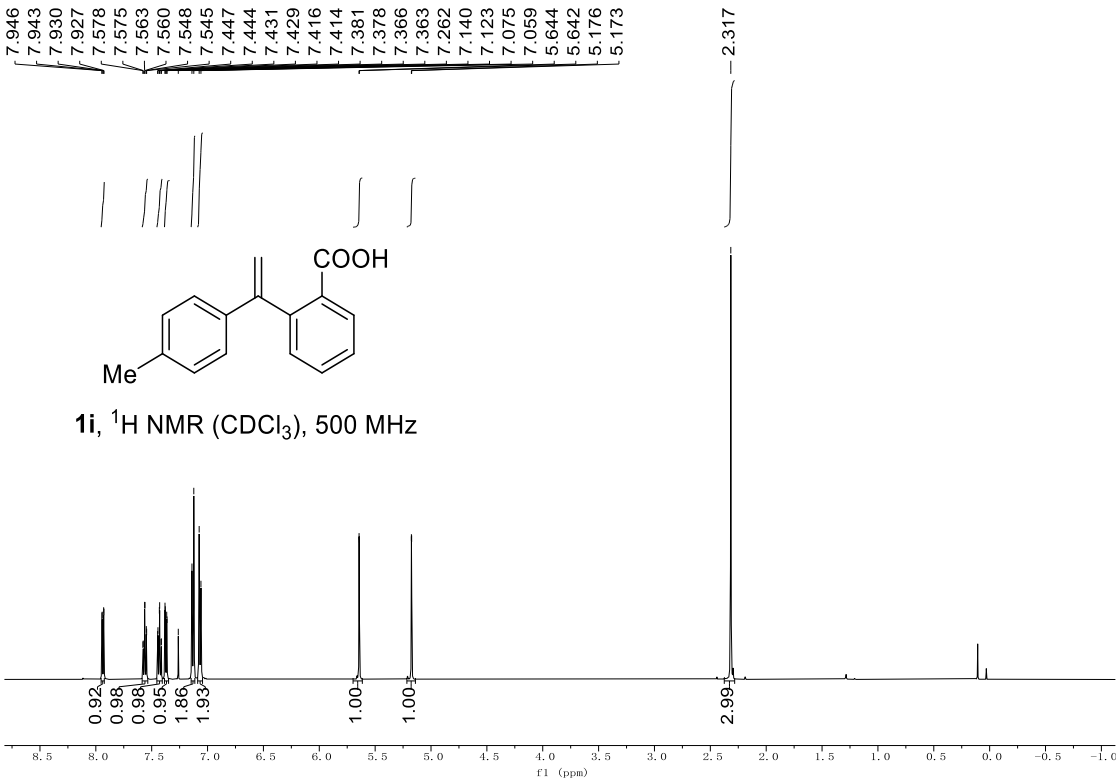
1f, ^{1}H NMR ($CDCl_3$), 500 MHz



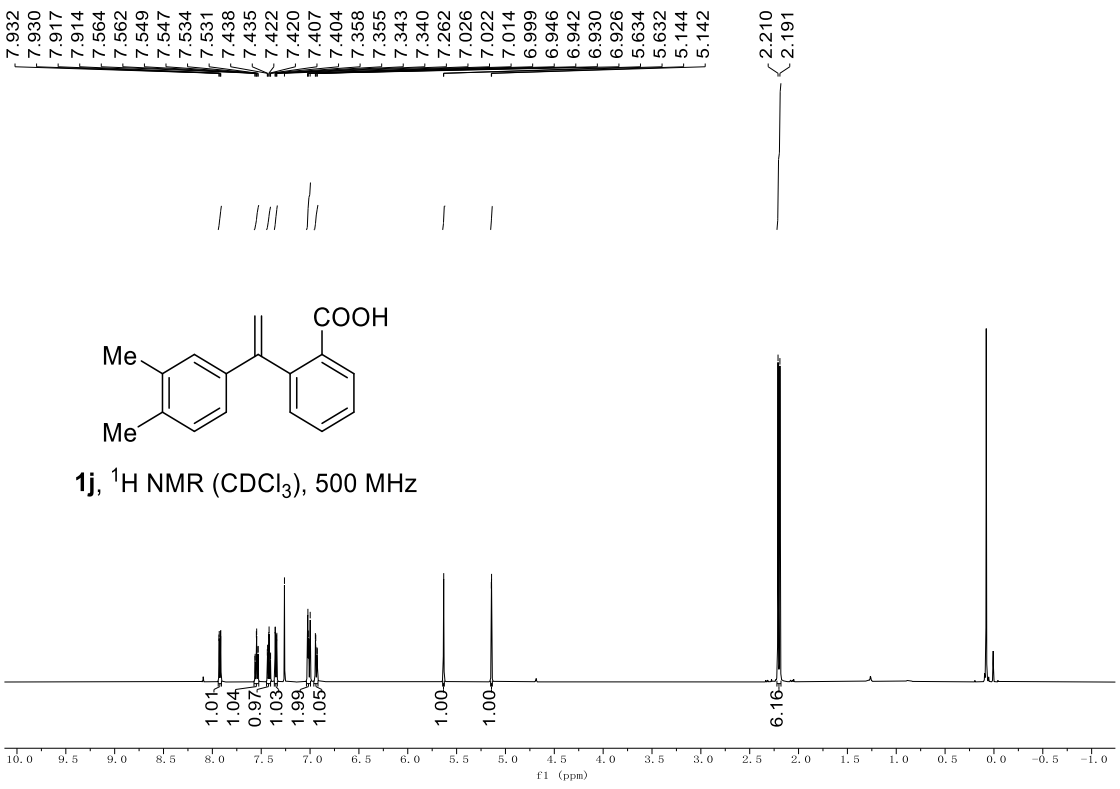
1g, ^{1}H NMR ($CDCl_3$), 500 MHz



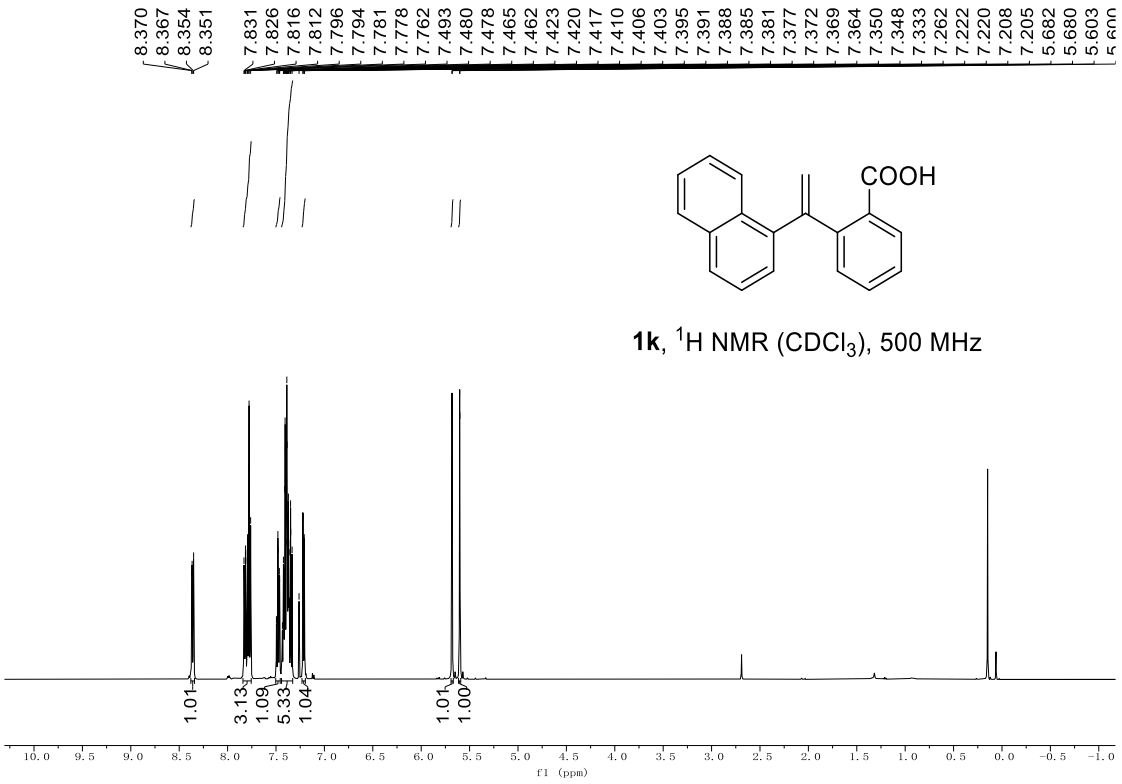
1h, ^{1}H NMR ($CDCl_3$), 500 MHz



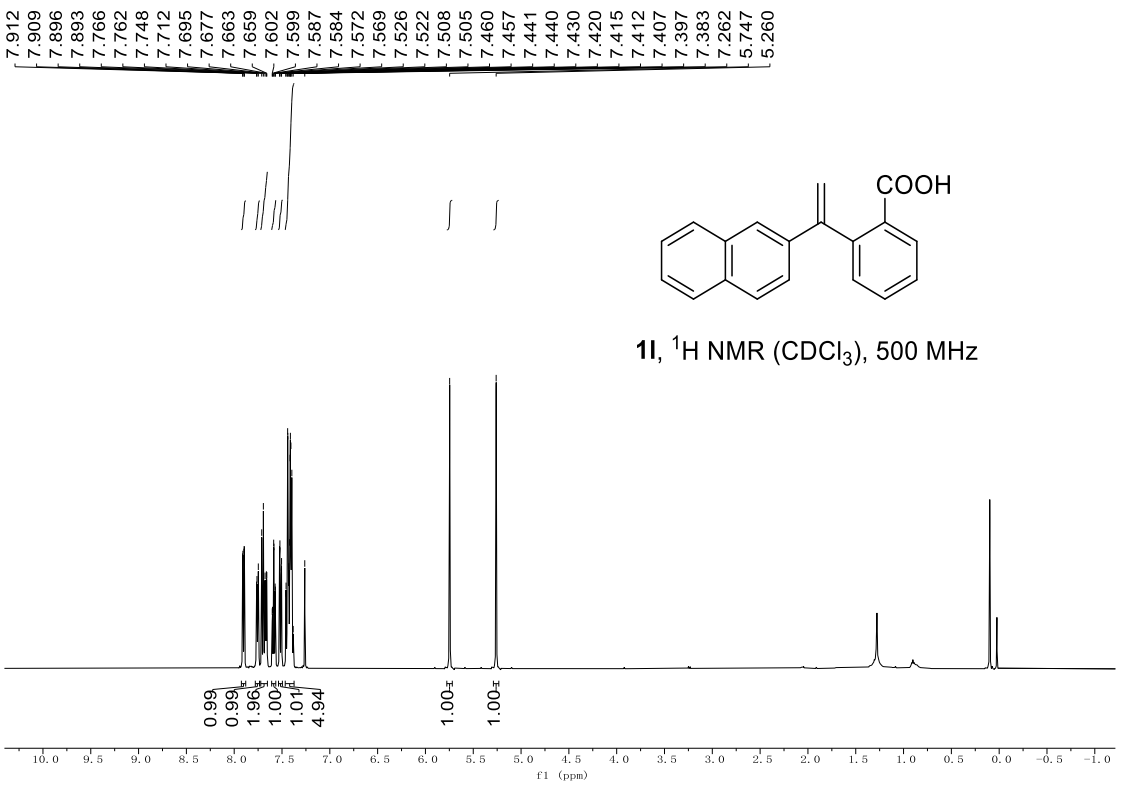
1i, ^{1}H NMR ($CDCl_3$), 500 MHz



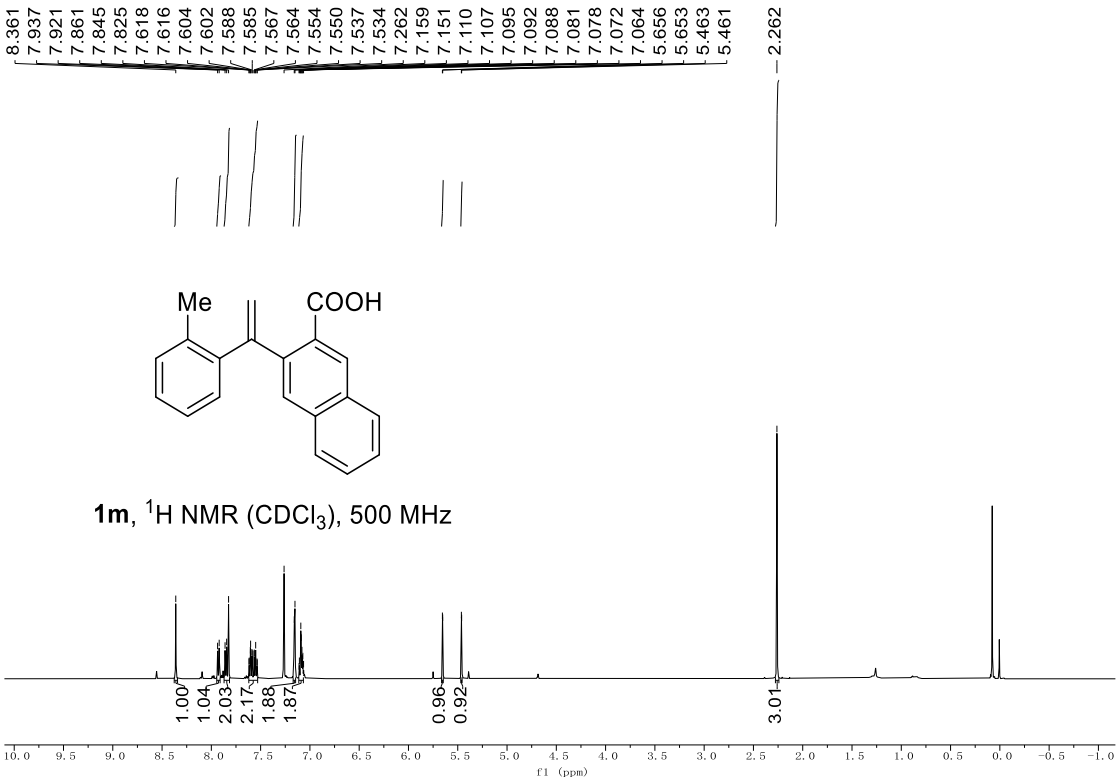
1j, ^{1}H NMR ($CDCl_3$), 500 MHz



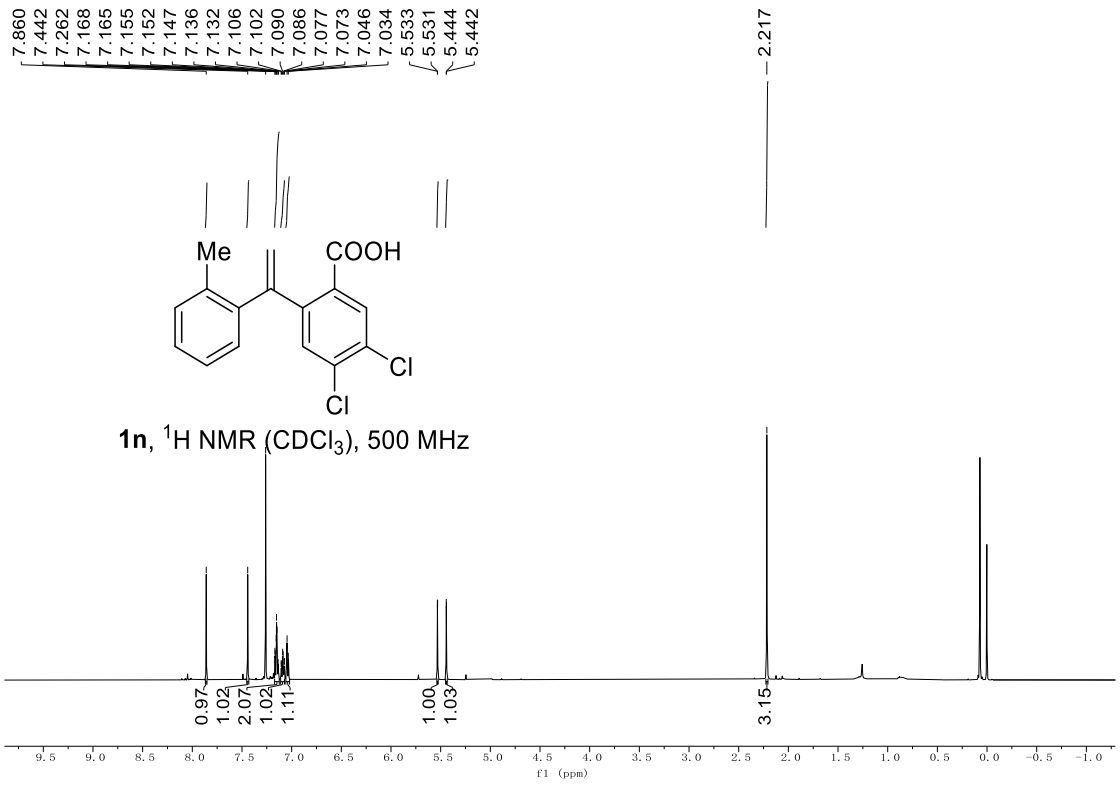
1k, ^{1}H NMR ($CDCl_3$), 500 MHz



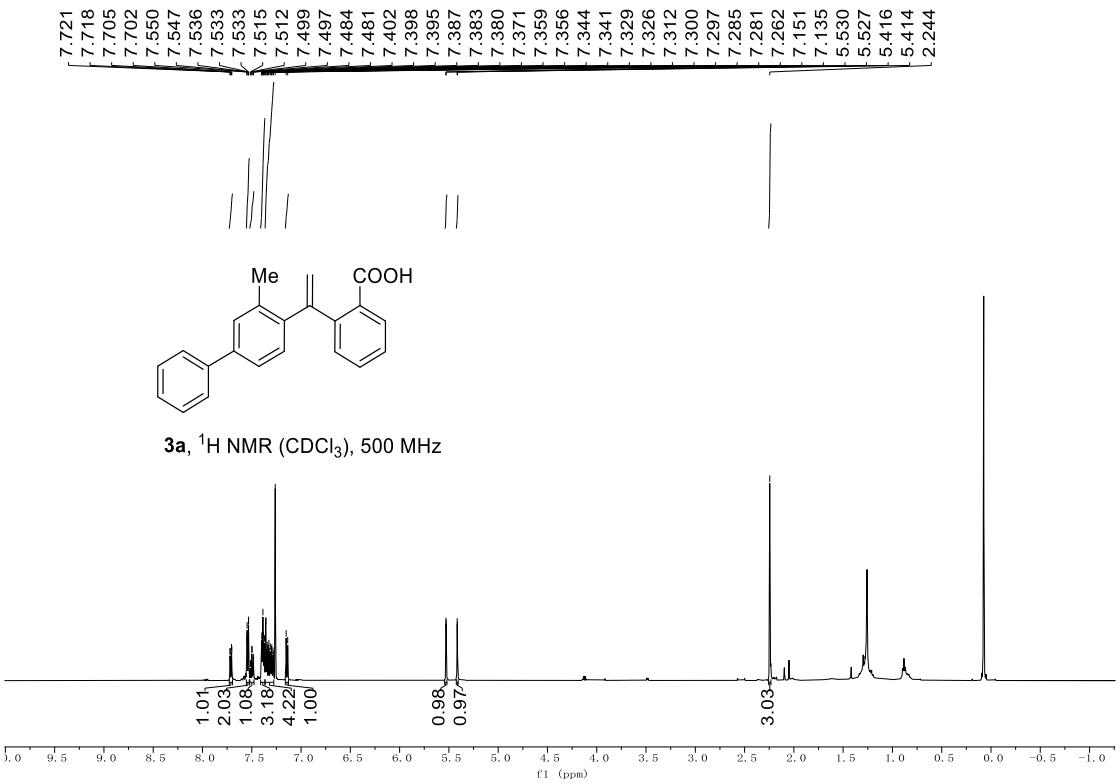
1l, ^{1}H NMR ($CDCl_3$), 500 MHz



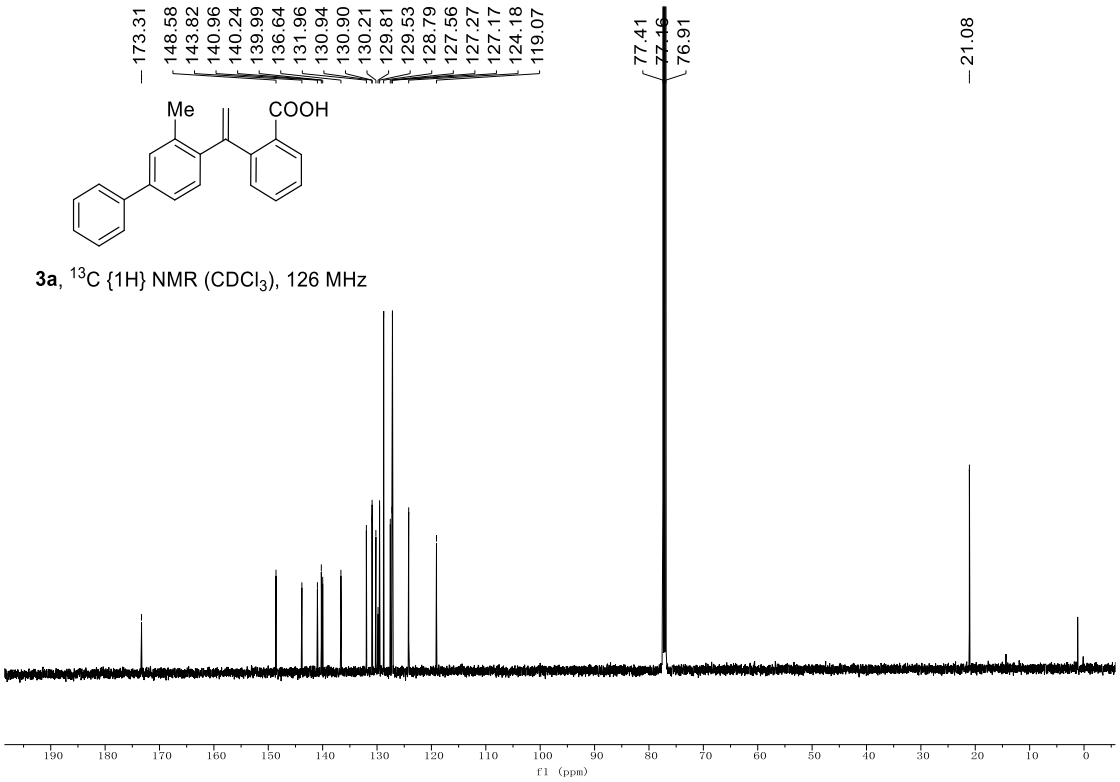
1m, ^{1}H NMR ($CDCl_3$), 500 MHz



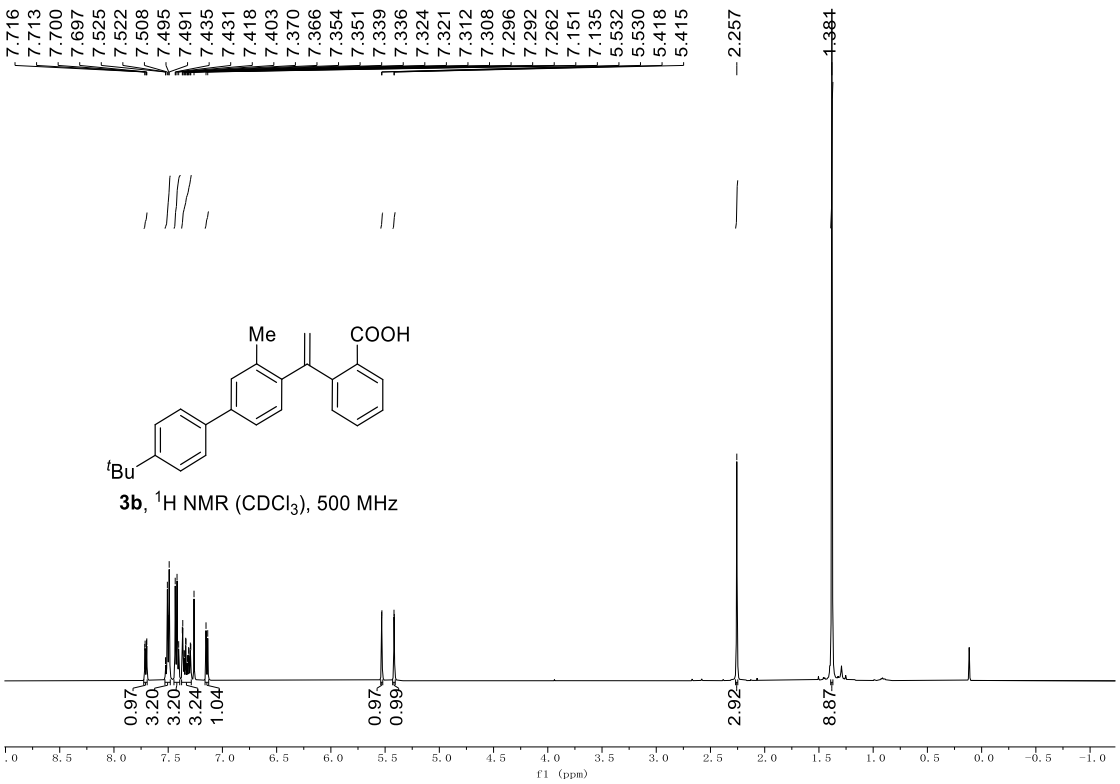
1n, ^{1}H NMR ($CDCl_3$), 500 MHz



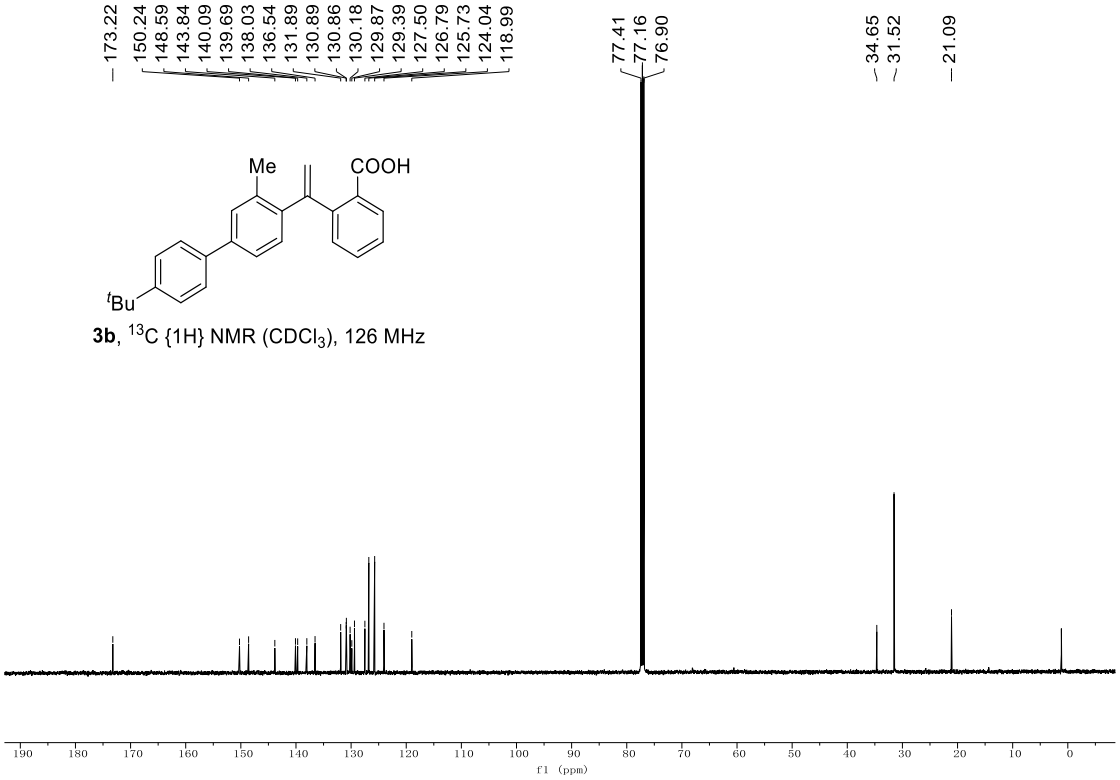
3a, ^{1}H NMR ($CDCl_3$), 500 MHz



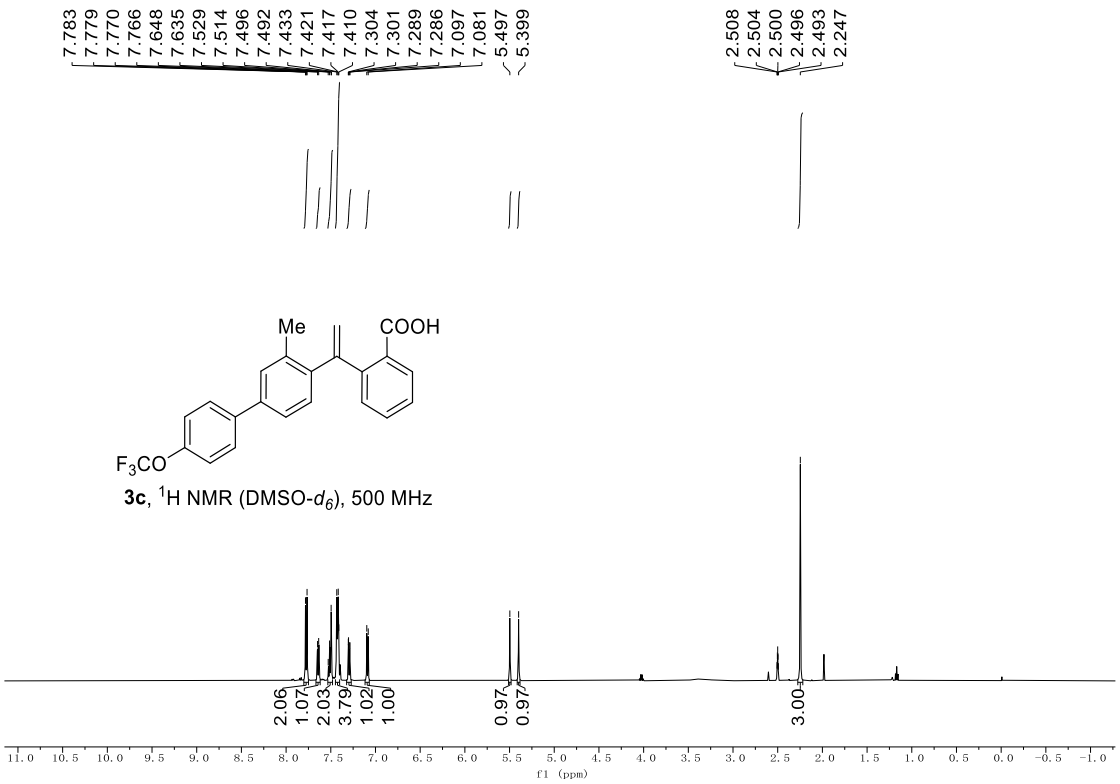
3a, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



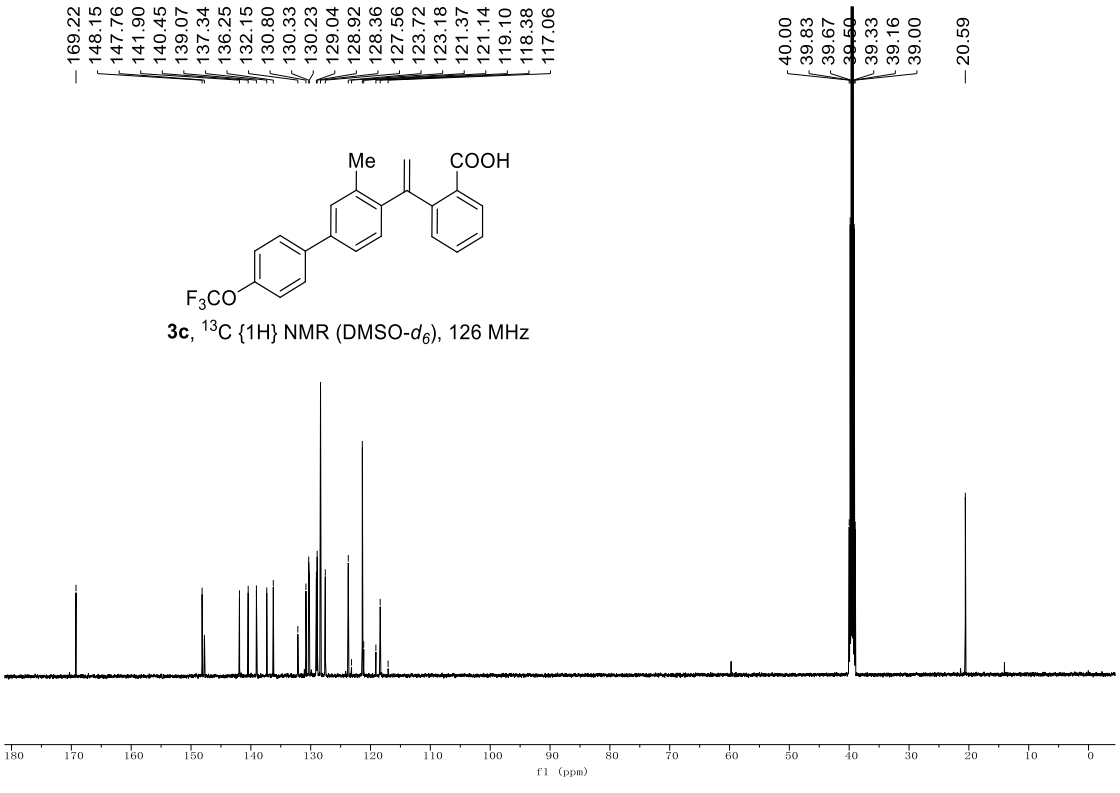
3b, ^{1}H NMR ($CDCl_3$), 500 MHz



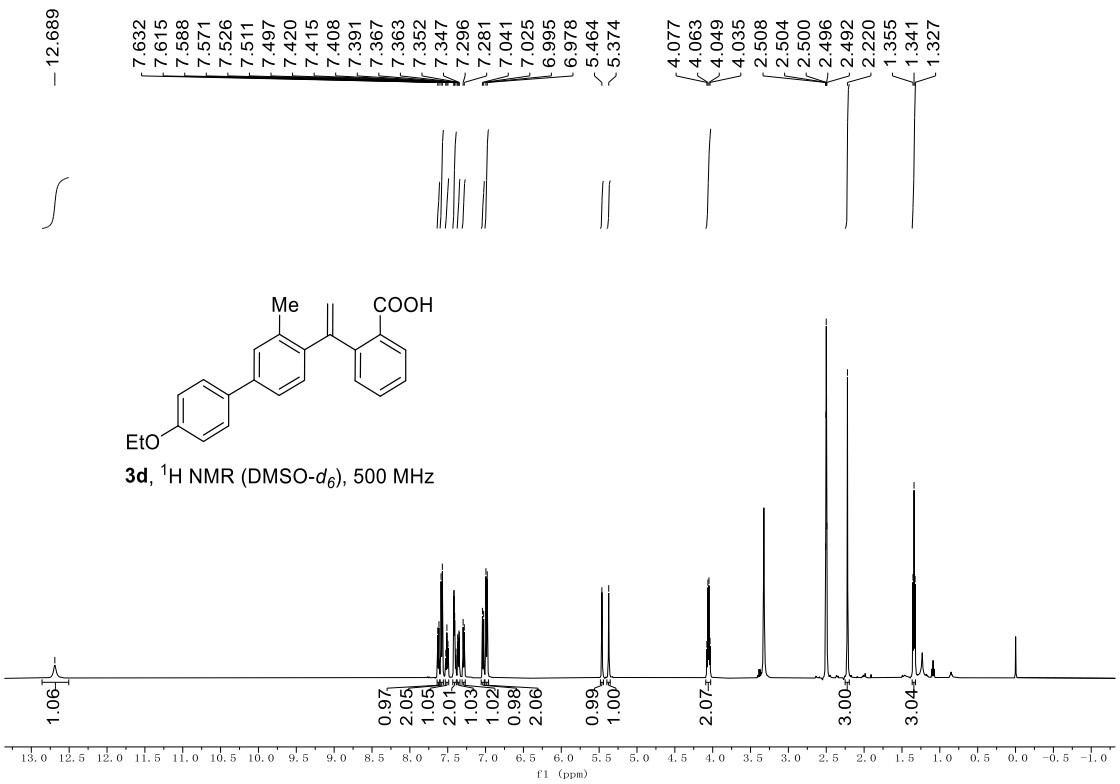
3b, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



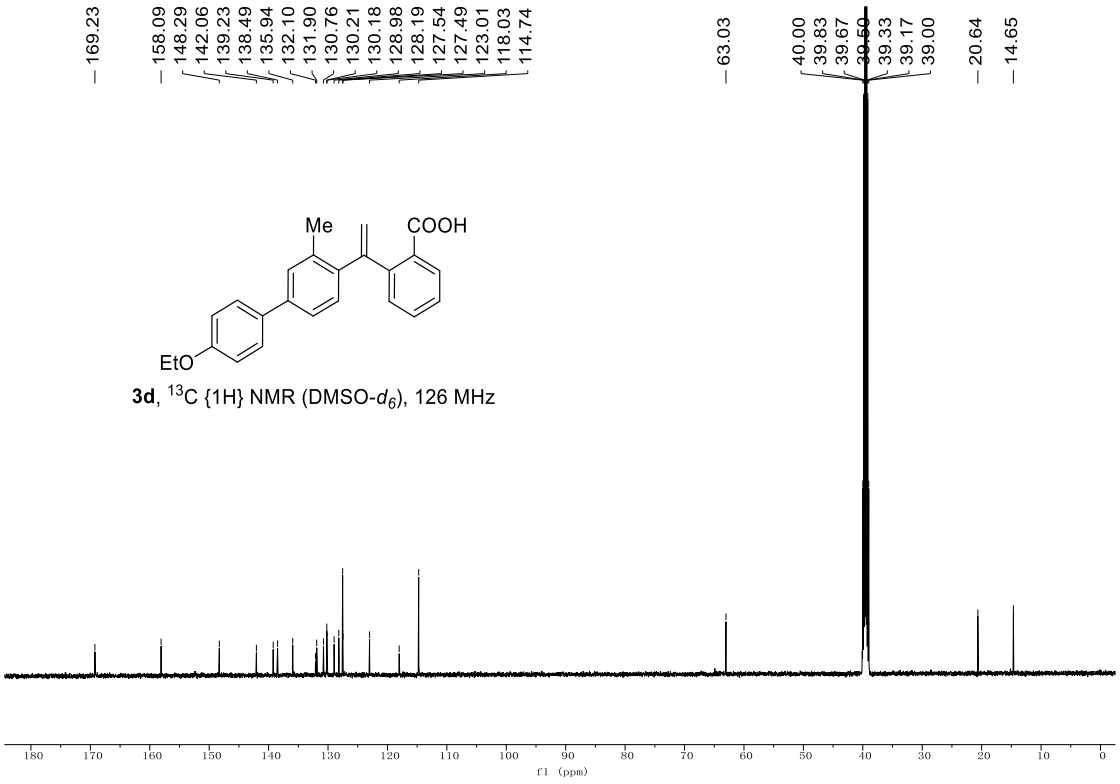
3c, ^{1}H NMR (DMSO-d_6), 500 MHz



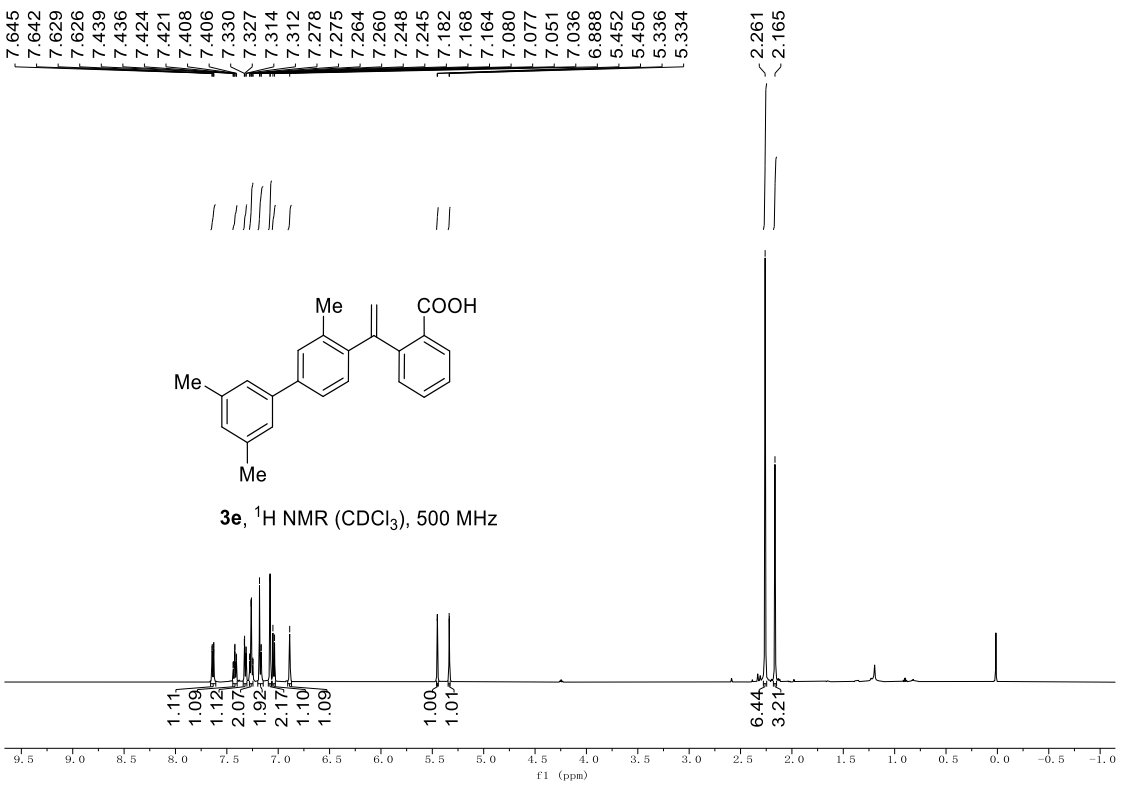
3c, ^{13}C {1H} NMR (DMSO-d_6), 126 MHz



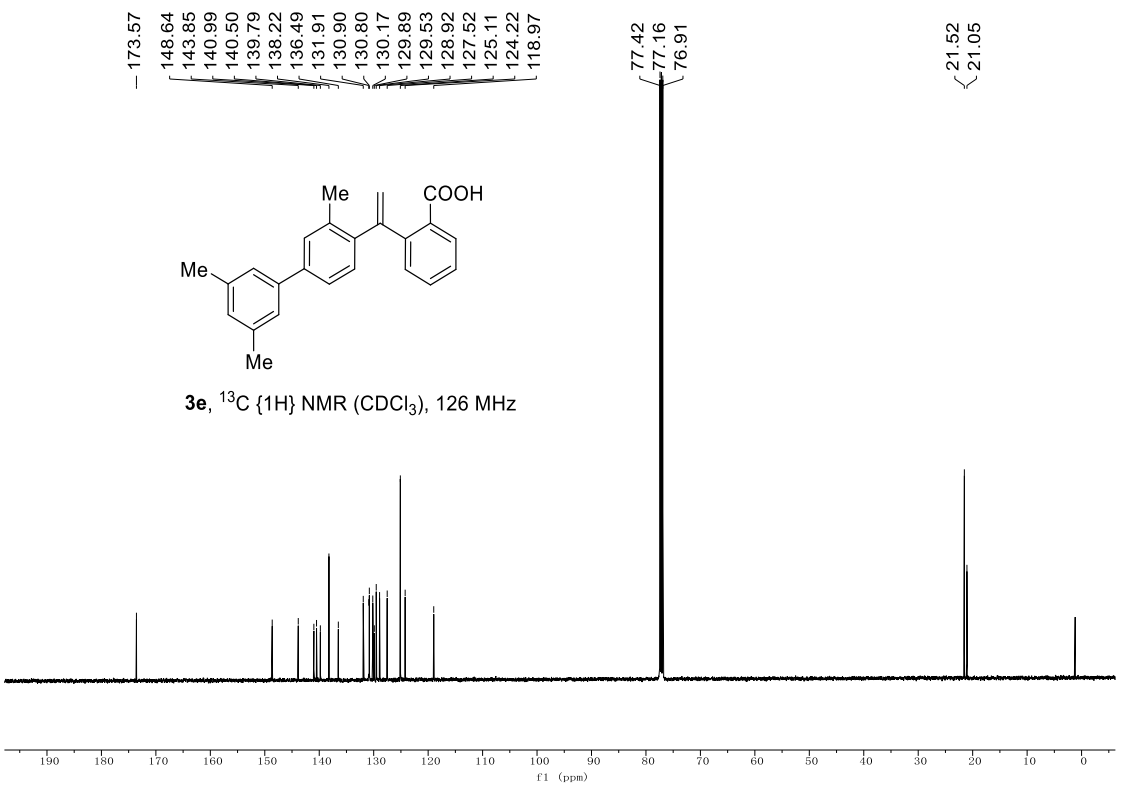
3d, ^{1}H NMR (DMSO-d_6), 500 MHz



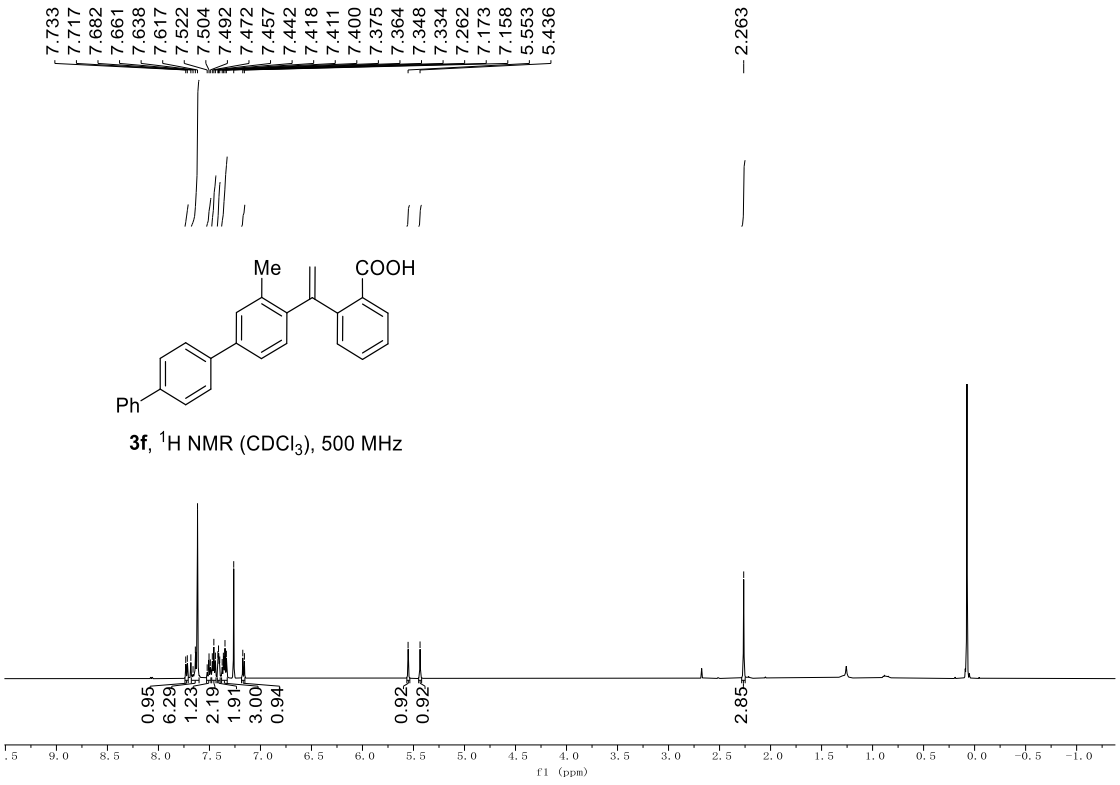
3d, ^{13}C {1H} NMR (DMSO-d_6), 126 MHz



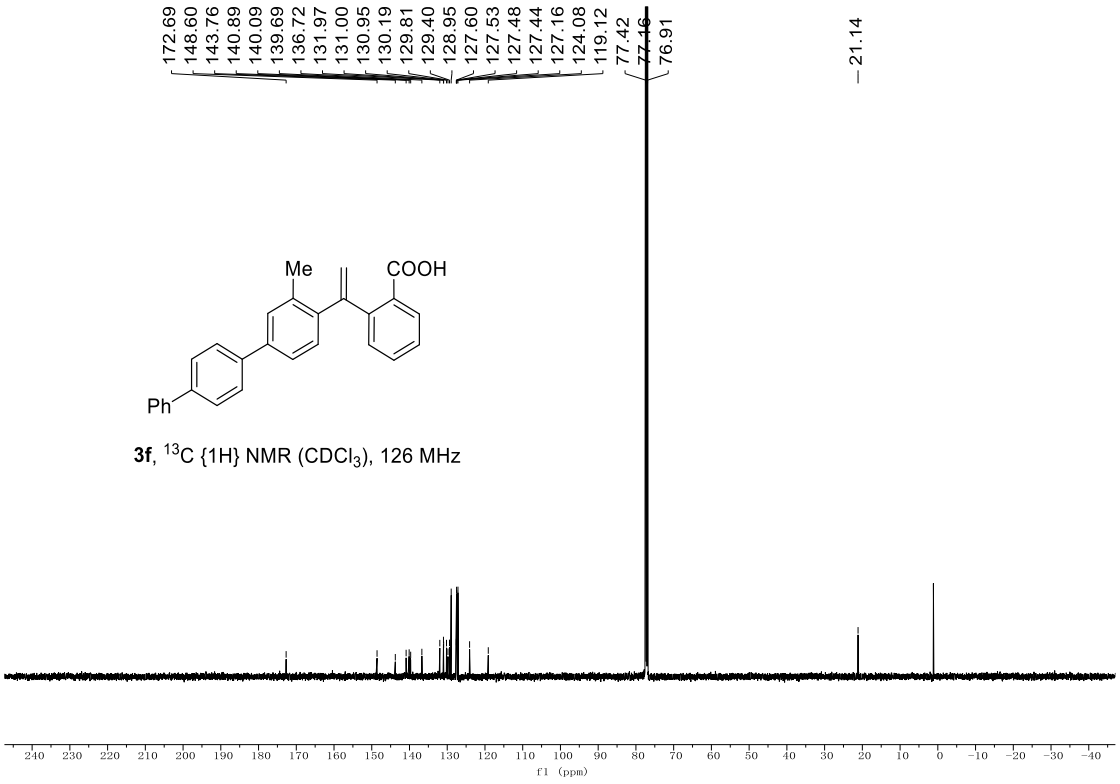
3e, ^{1}H NMR ($CDCl_3$), 500 MHz



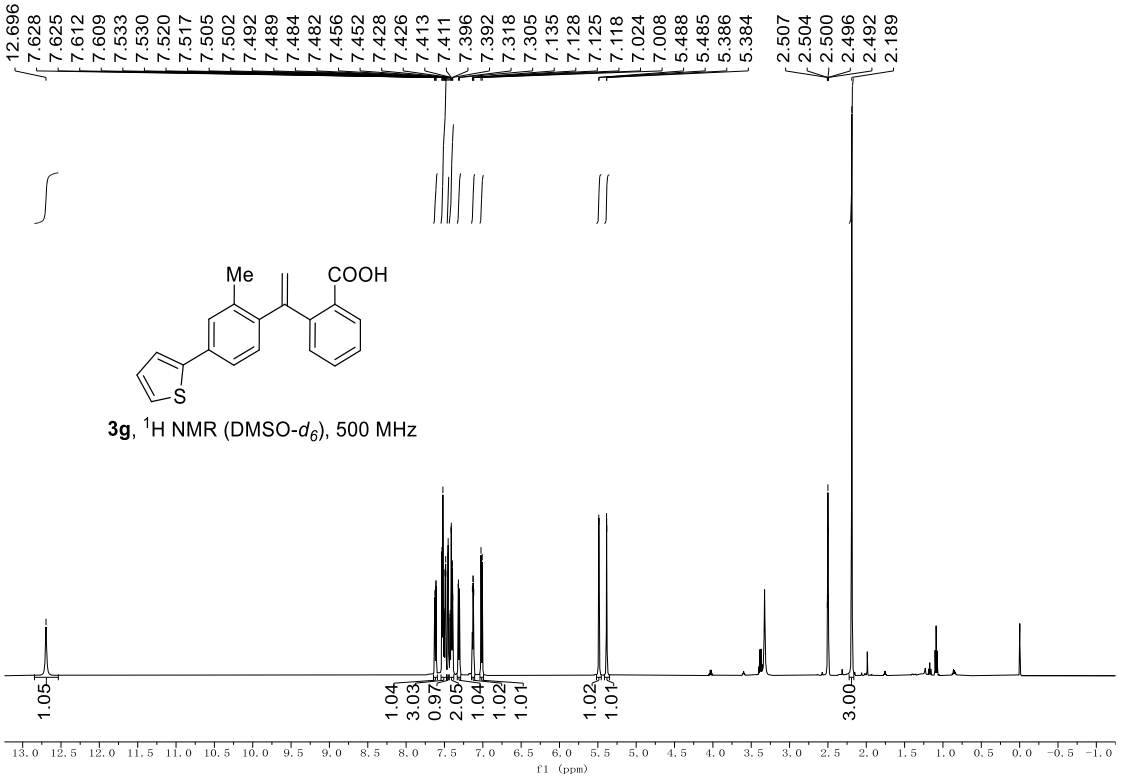
3e, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



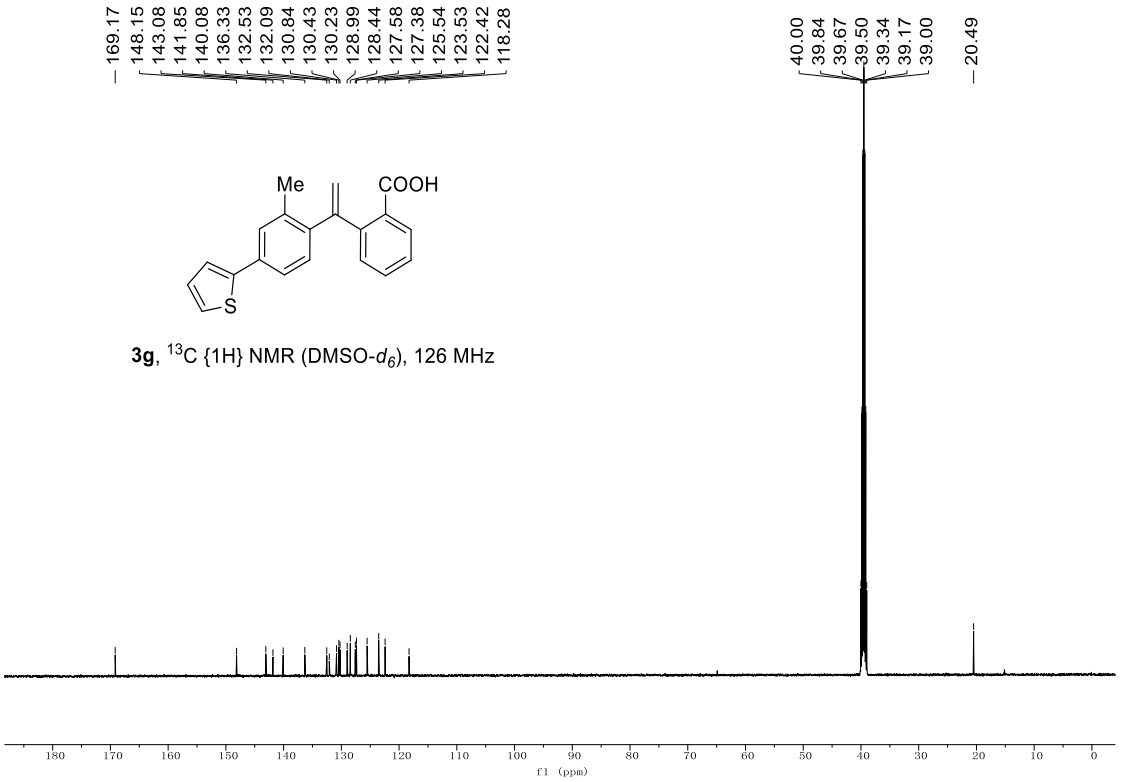
3f, ^{1}H NMR ($CDCl_3$), 500 MHz



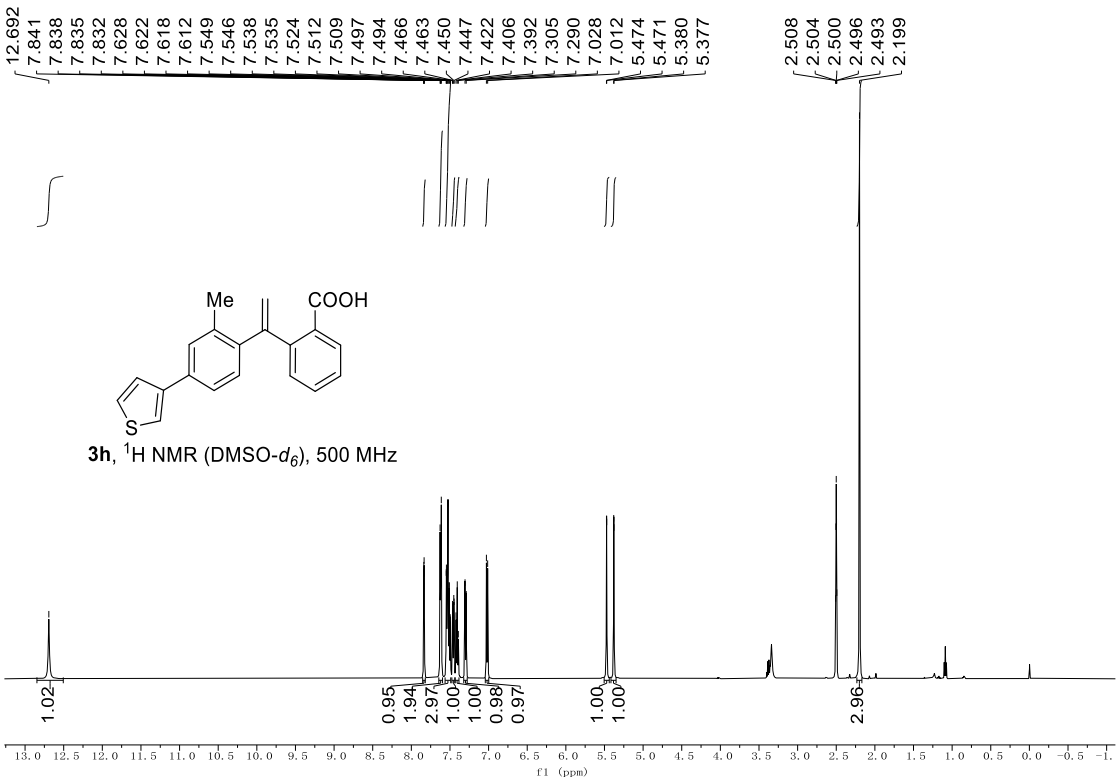
3f, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



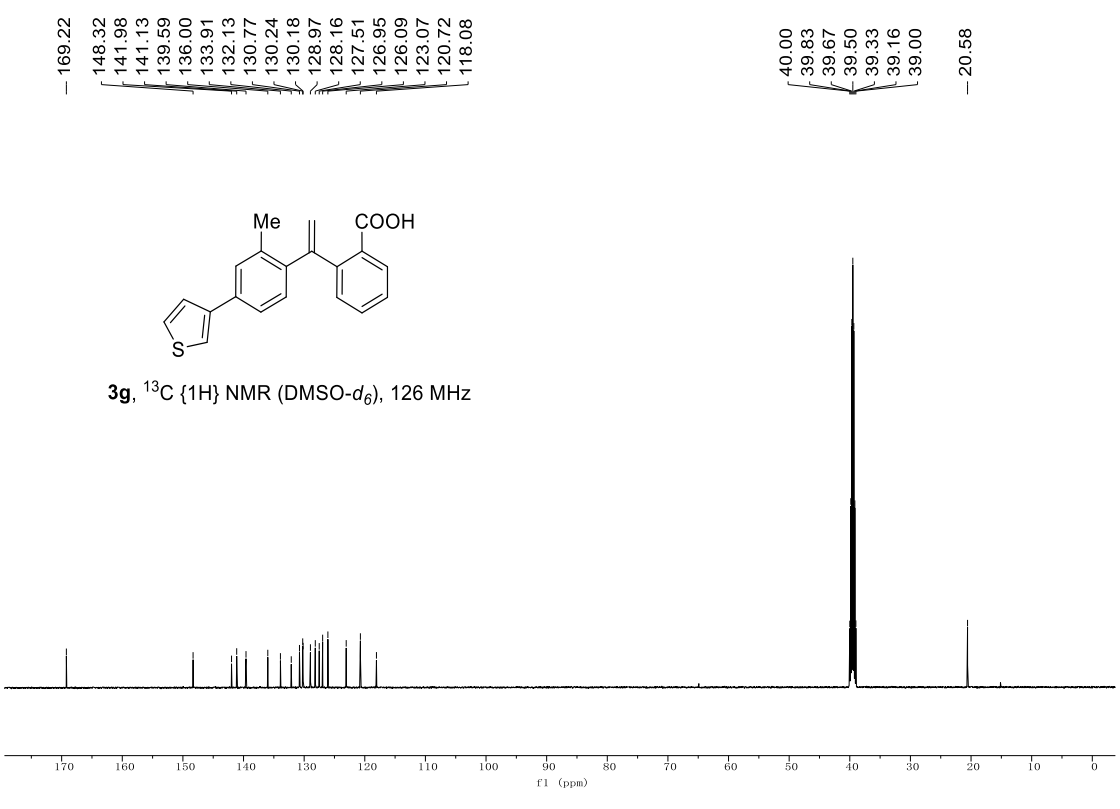
3g, ^{1}H NMR (DMSO-d_6), 500 MHz



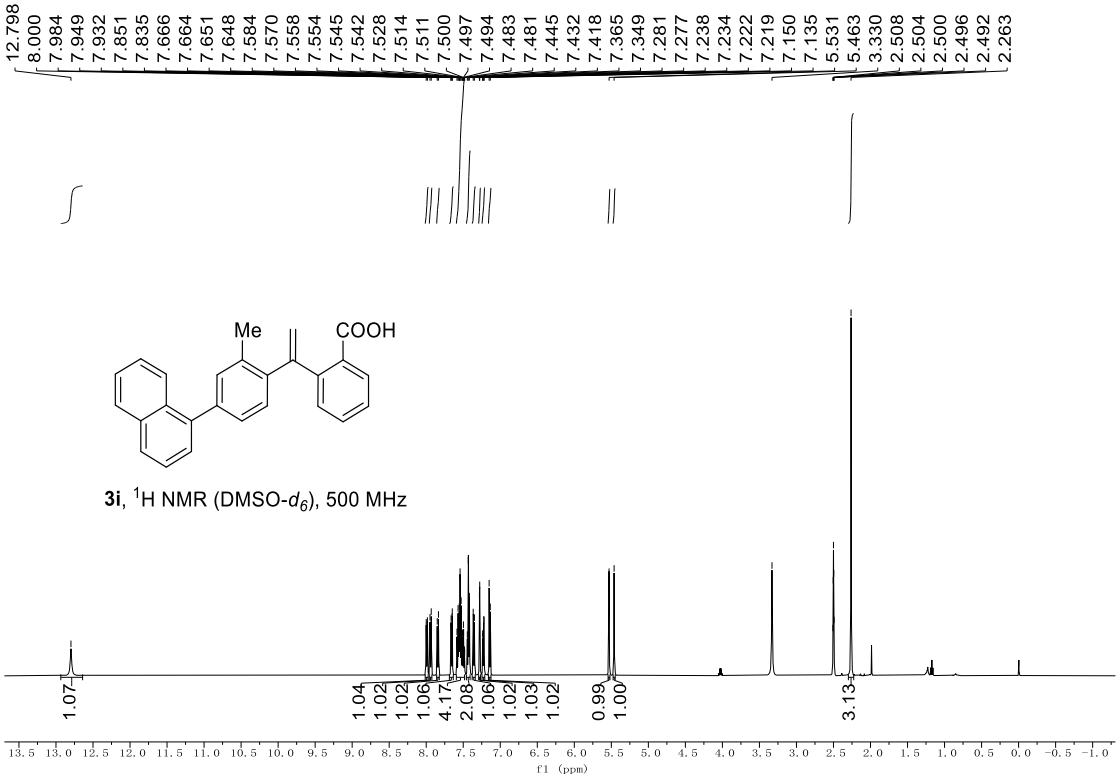
3g, ^{13}C {1H} NMR (DMSO-d_6), 126 MHz



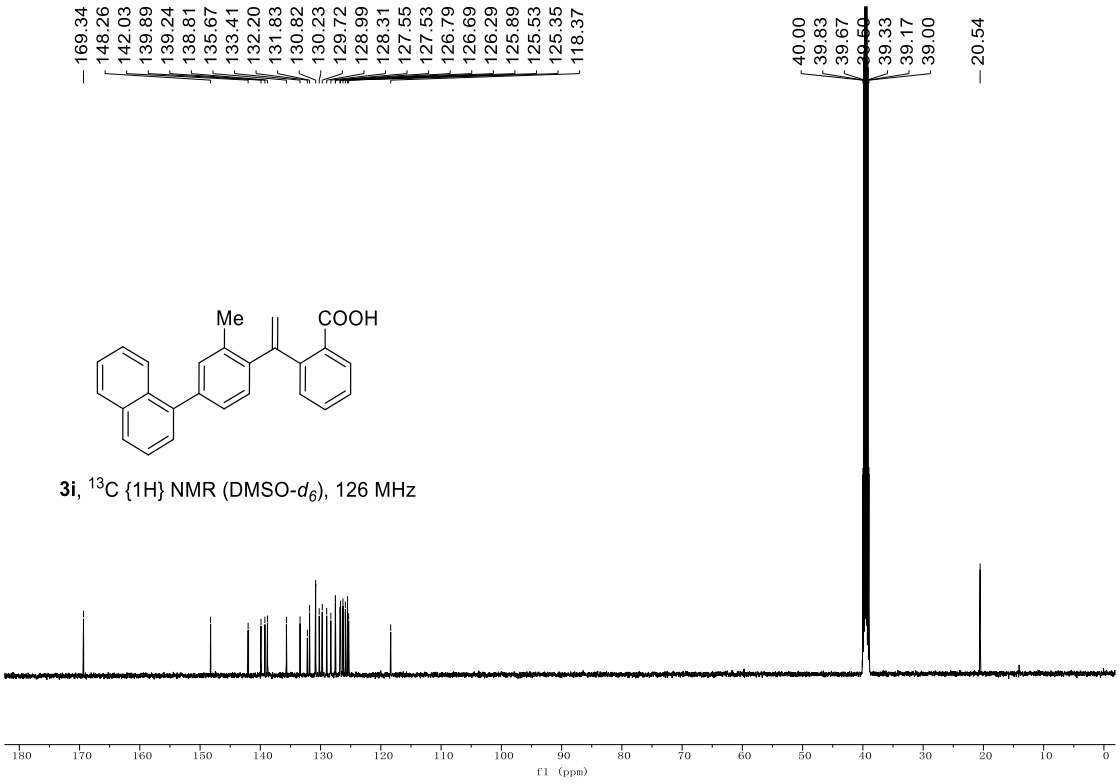
3h, ^{1}H NMR (DMSO-d_6), 500 MHz



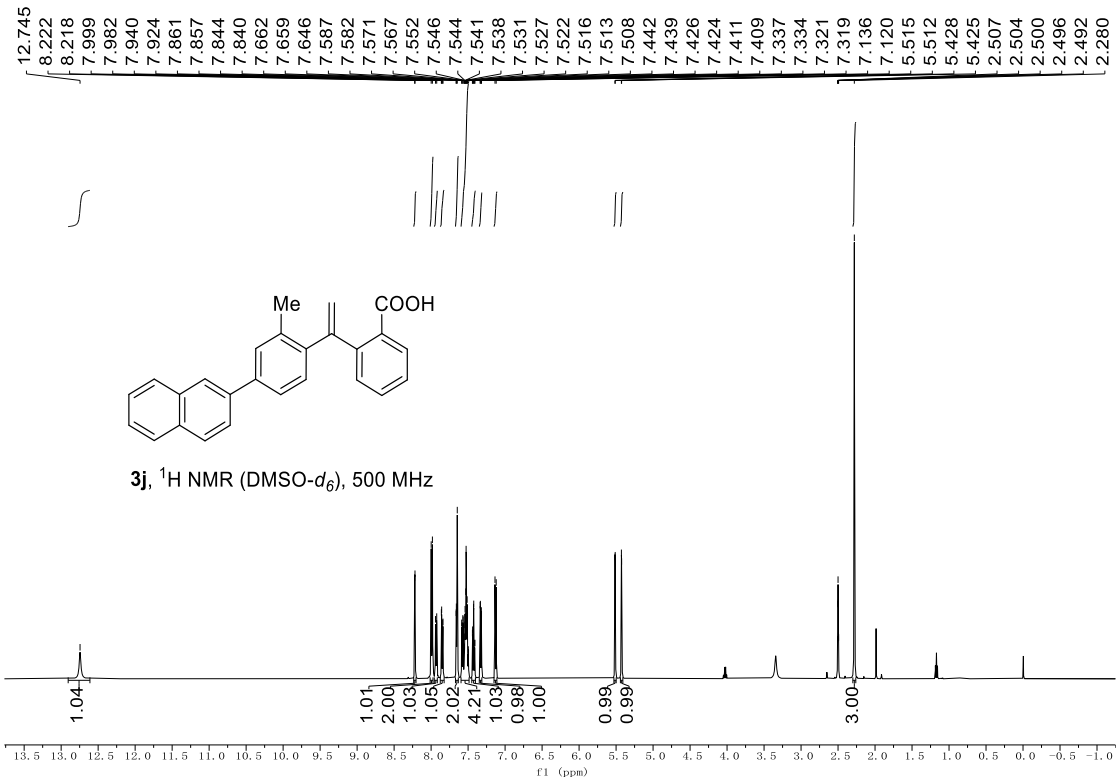
3g, ^{13}C {1H} NMR (DMSO-d_6), 126 MHz



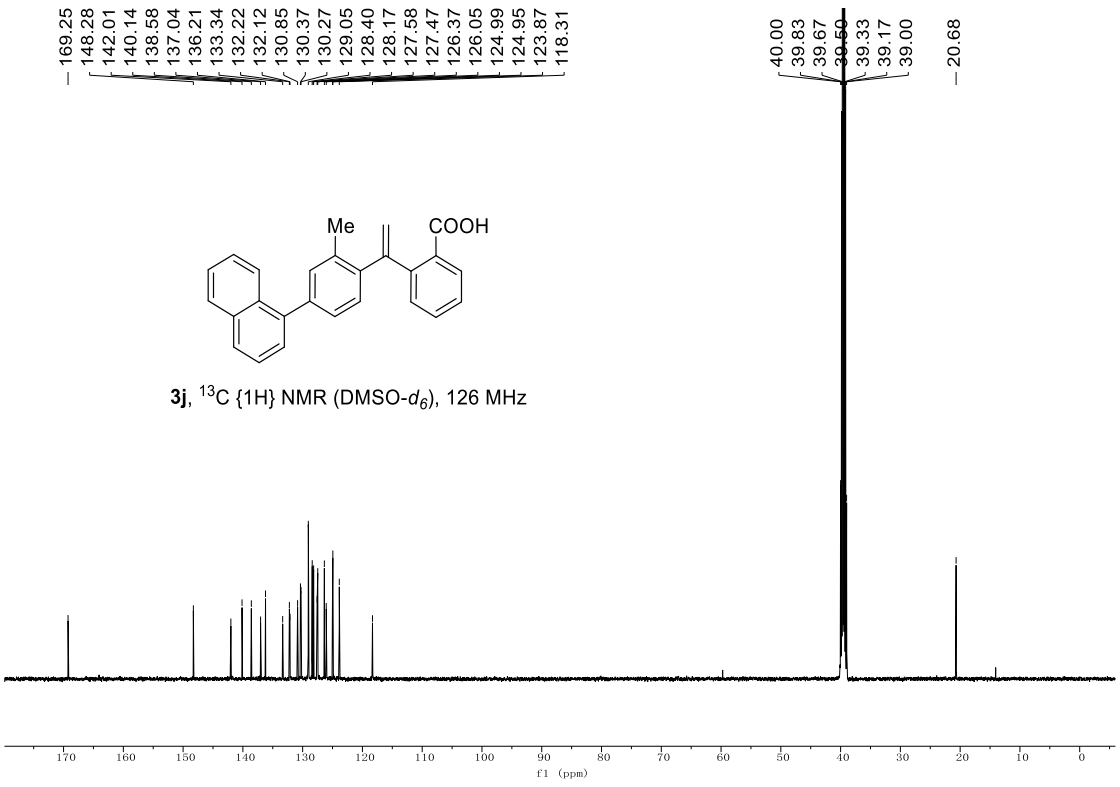
3i, ^{1}H NMR (DMSO-d_6), 500 MHz



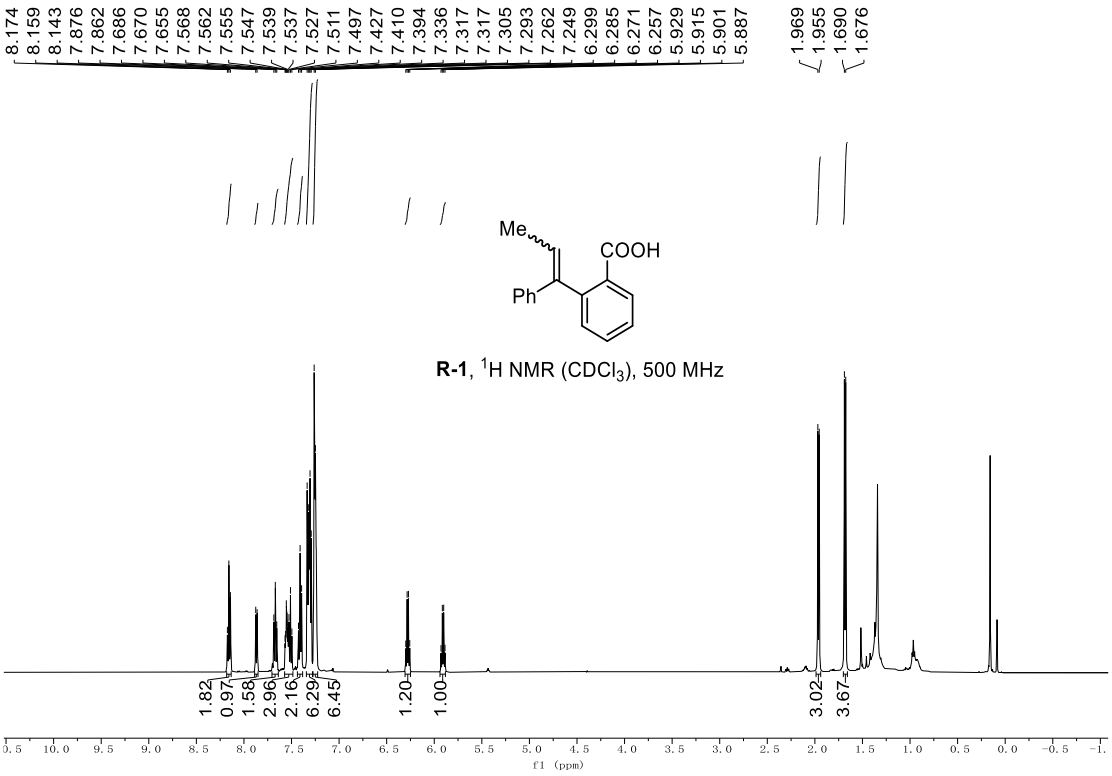
3i, ^{13}C {1H} NMR (DMSO-d_6), 126 MHz



3j, ^{1}H NMR (DMSO-d_6), 500 MHz

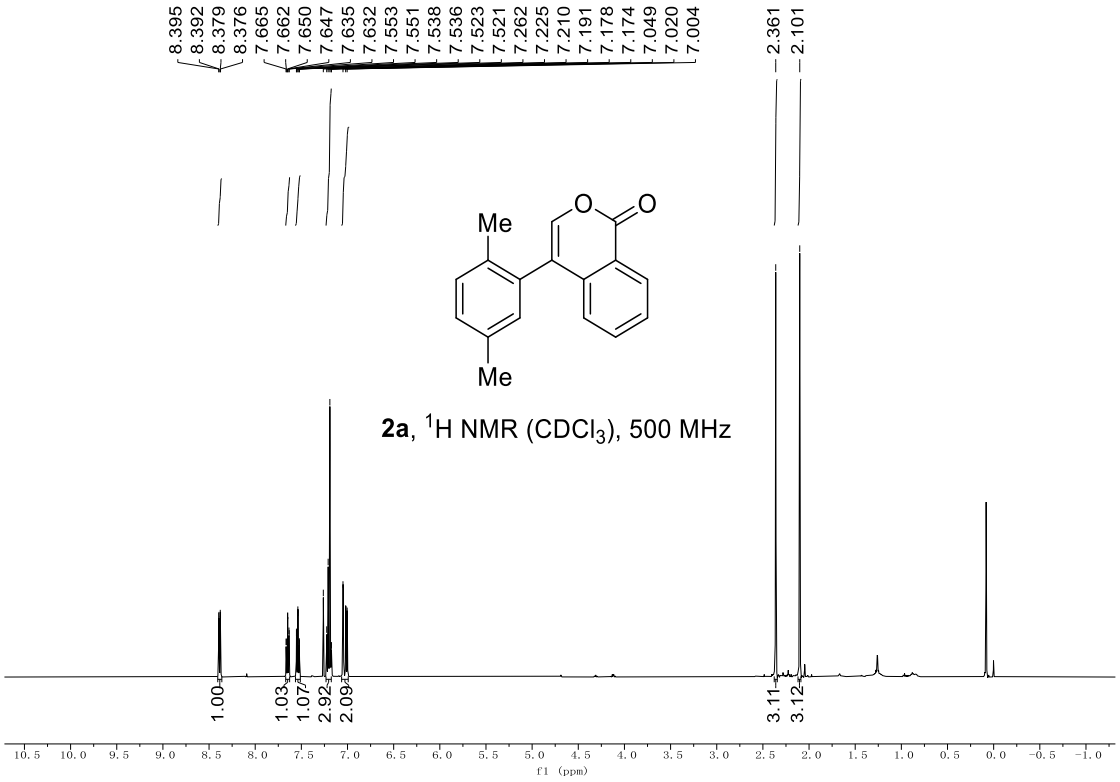


3j, ^{13}C {1H} NMR (DMSO-d_6), 126 MHz

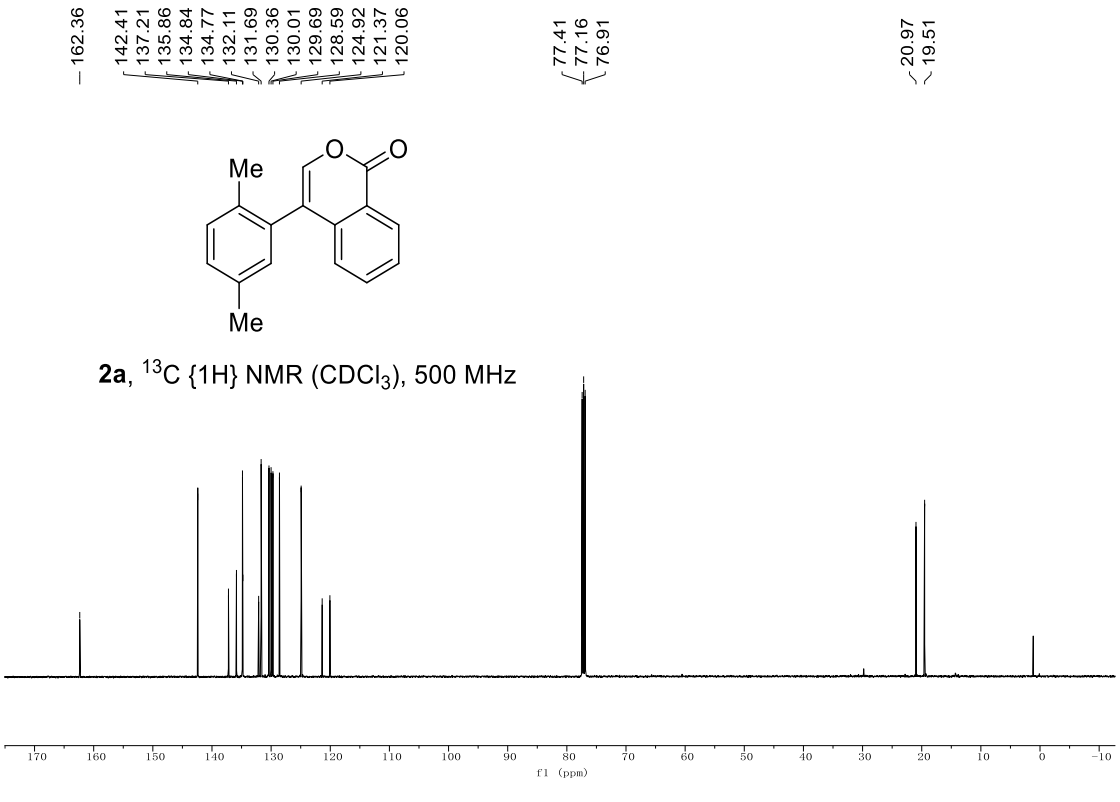


R-1, ^{1}H NMR ($CDCl_3$), 500 MHz

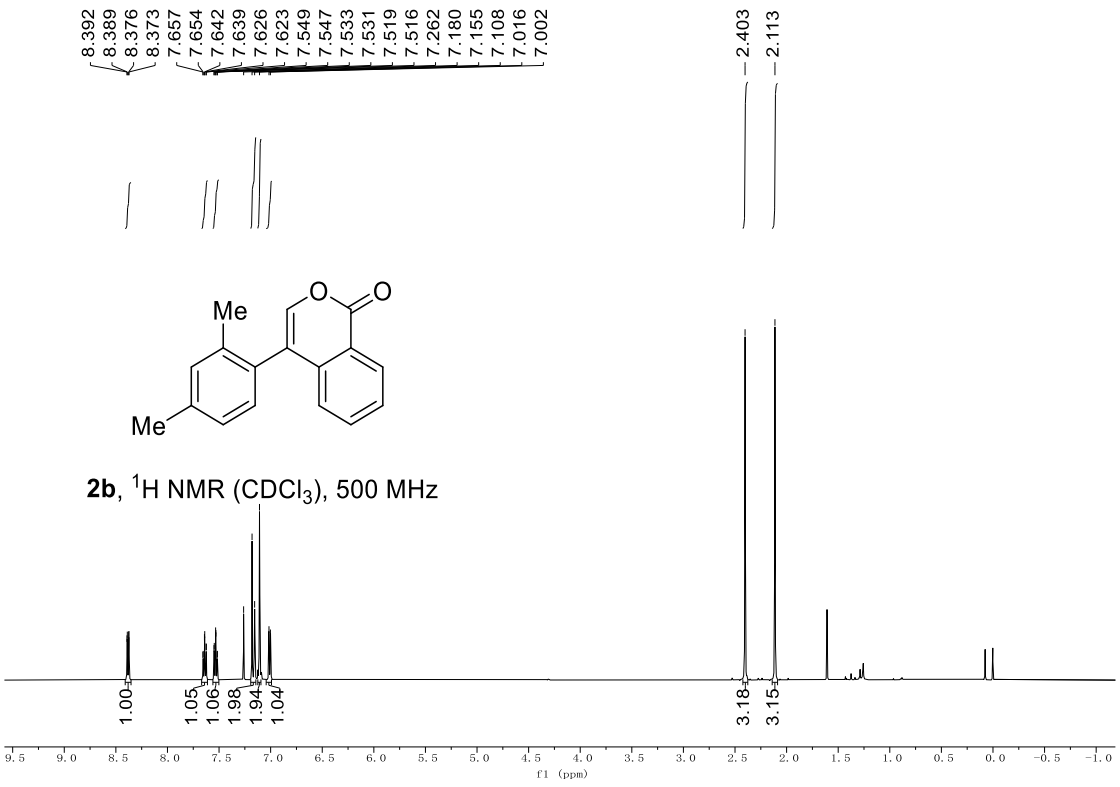
6.2 NMR Spectra of Products



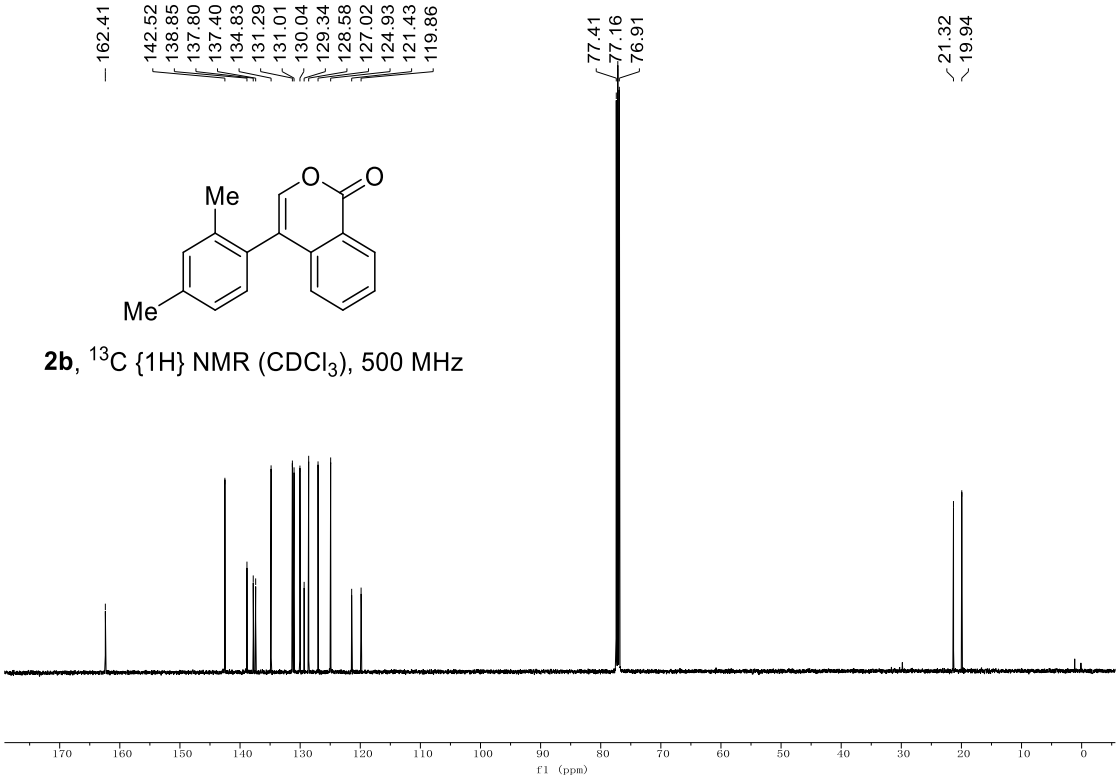
2a, ^{1}H NMR ($CDCl_3$), 500 MHz



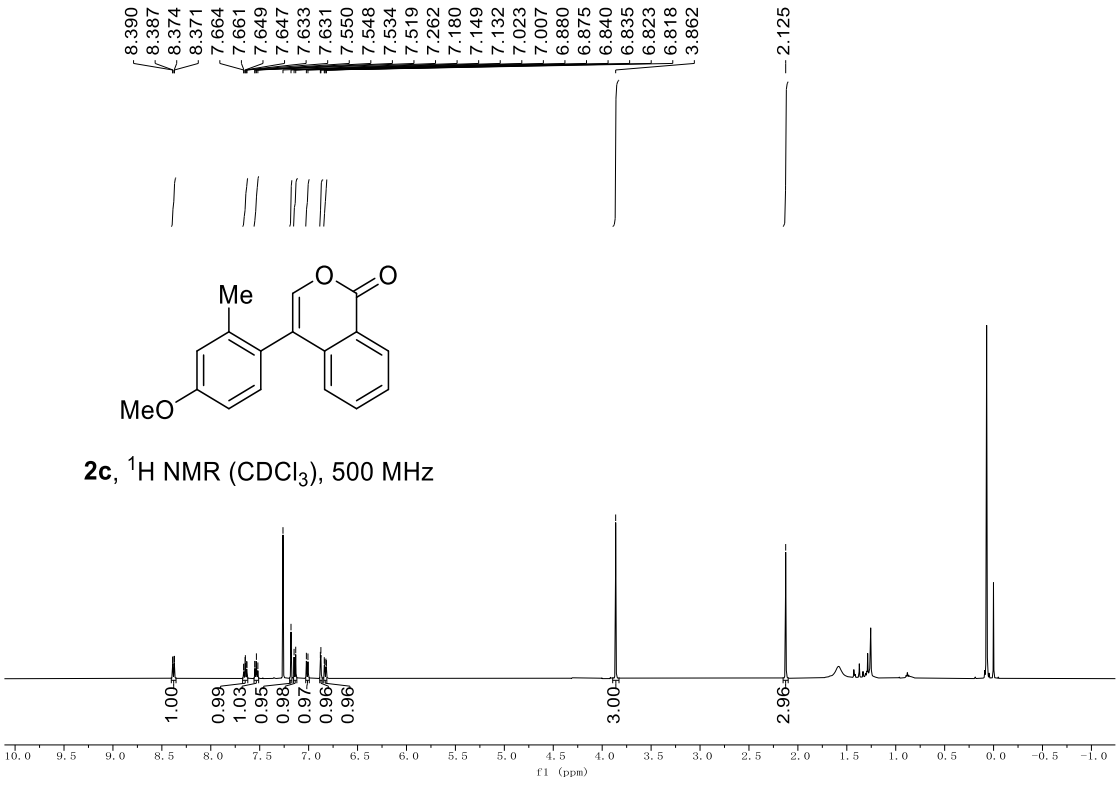
2a, ^{13}C {1H} NMR ($CDCl_3$), 500 MHz



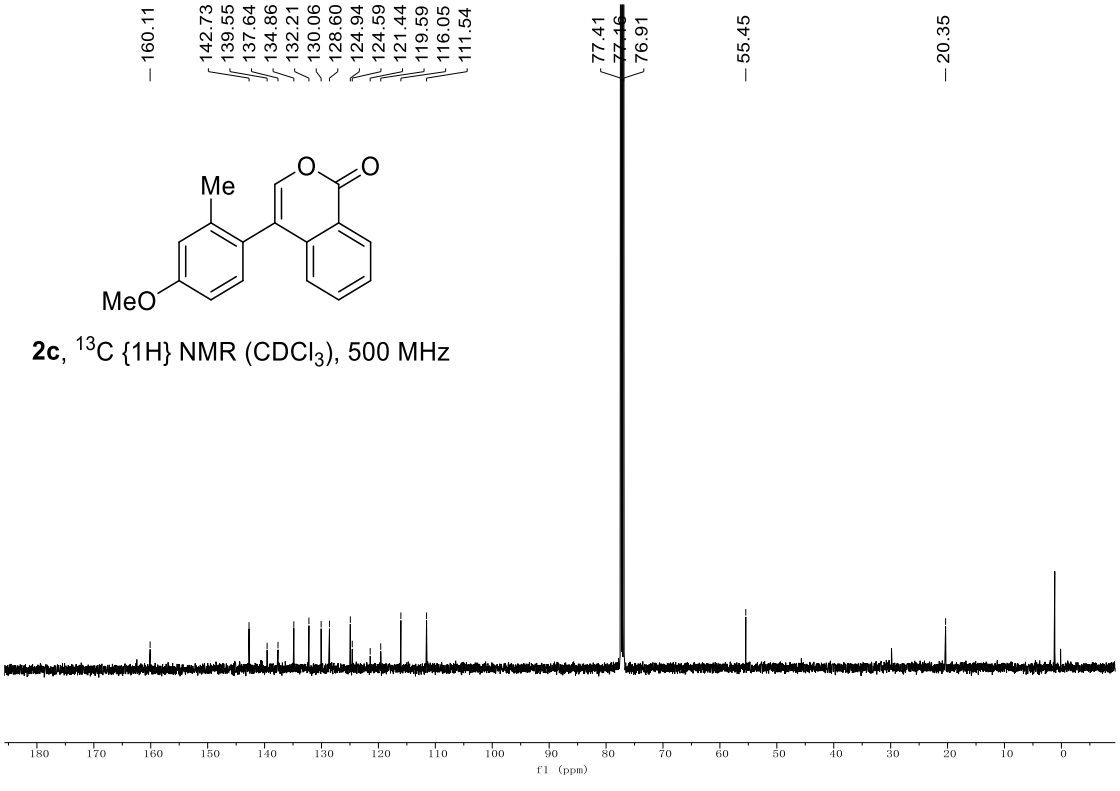
2b, ^{1}H NMR ($CDCl_3$), 500 MHz



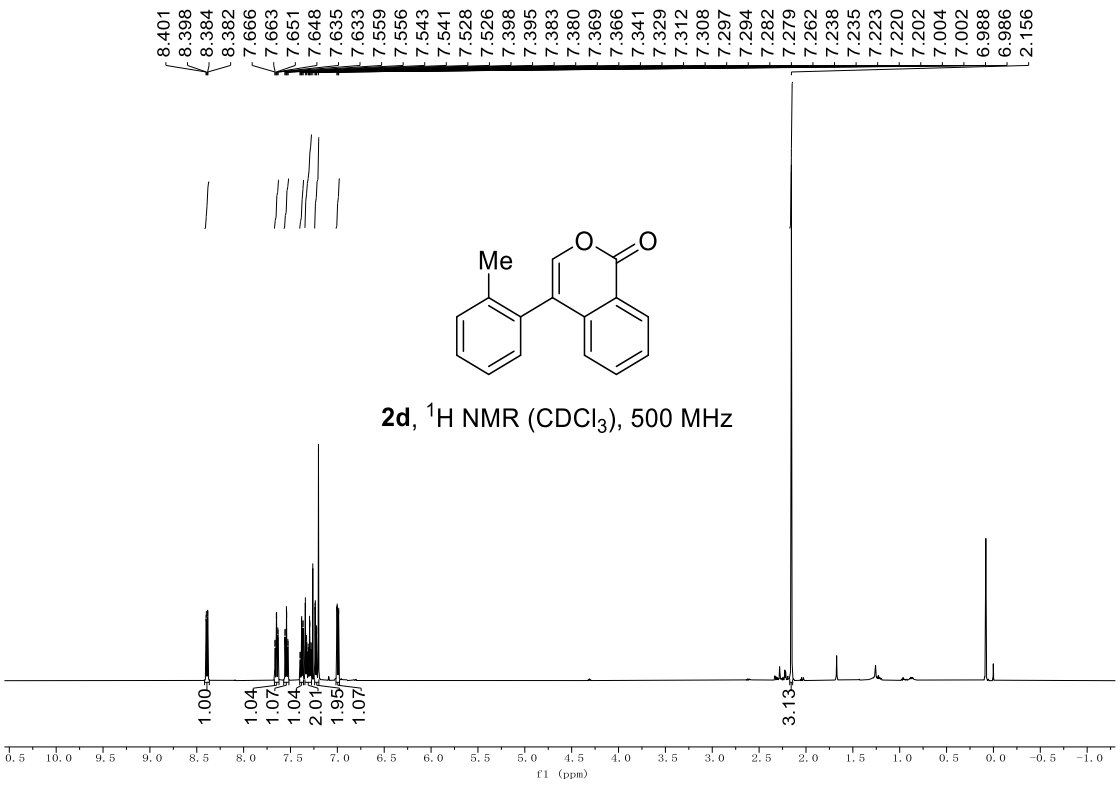
2b, ^{13}C {1H} NMR ($CDCl_3$), 500 MHz



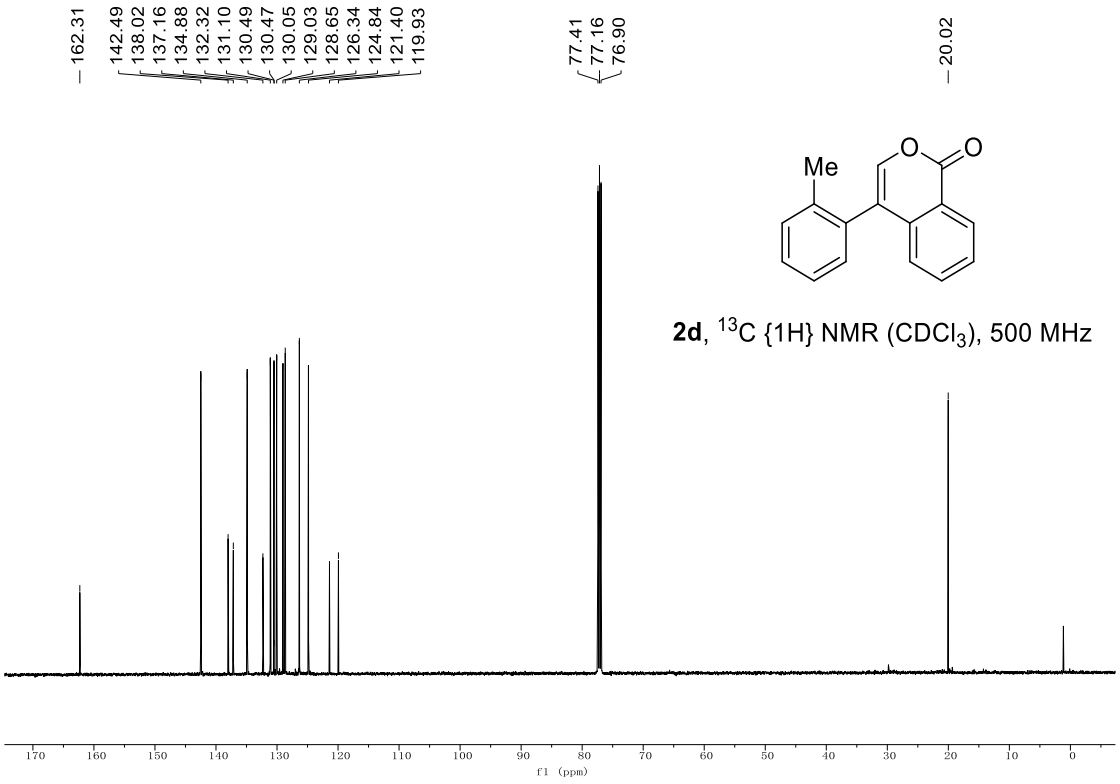
2c, ^{1}H NMR ($CDCl_3$), 500 MHz



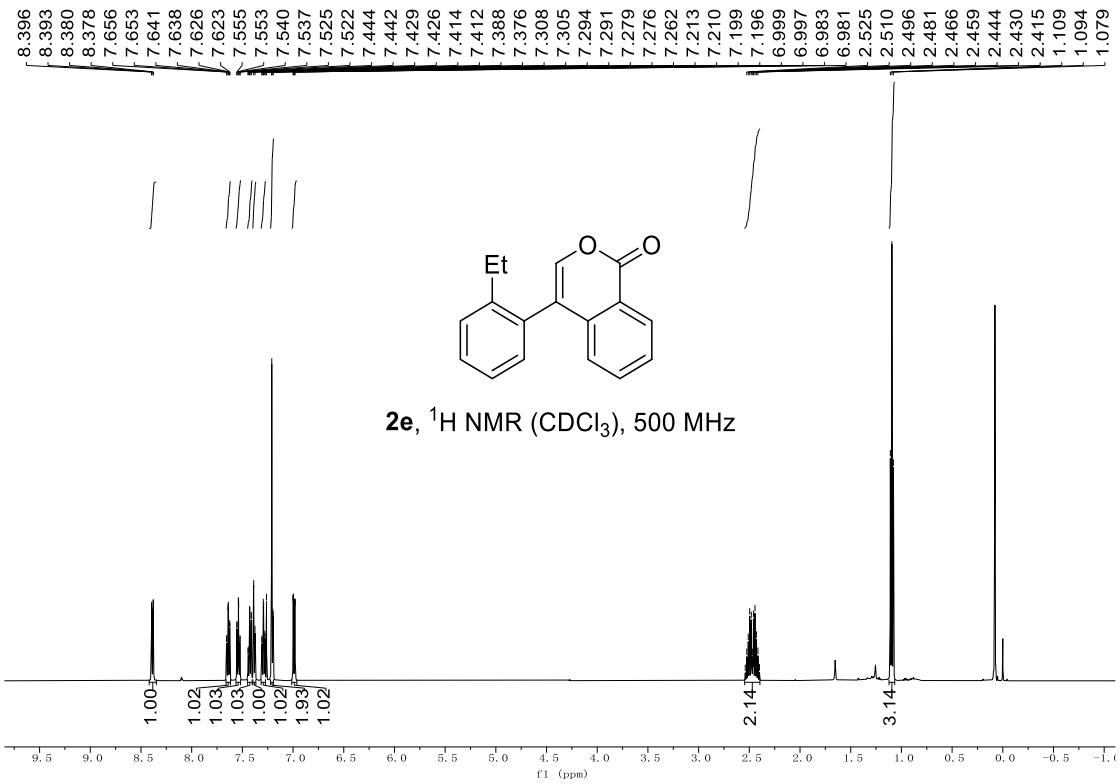
2c, ^{13}C {1H} NMR ($CDCl_3$), 500 MHz



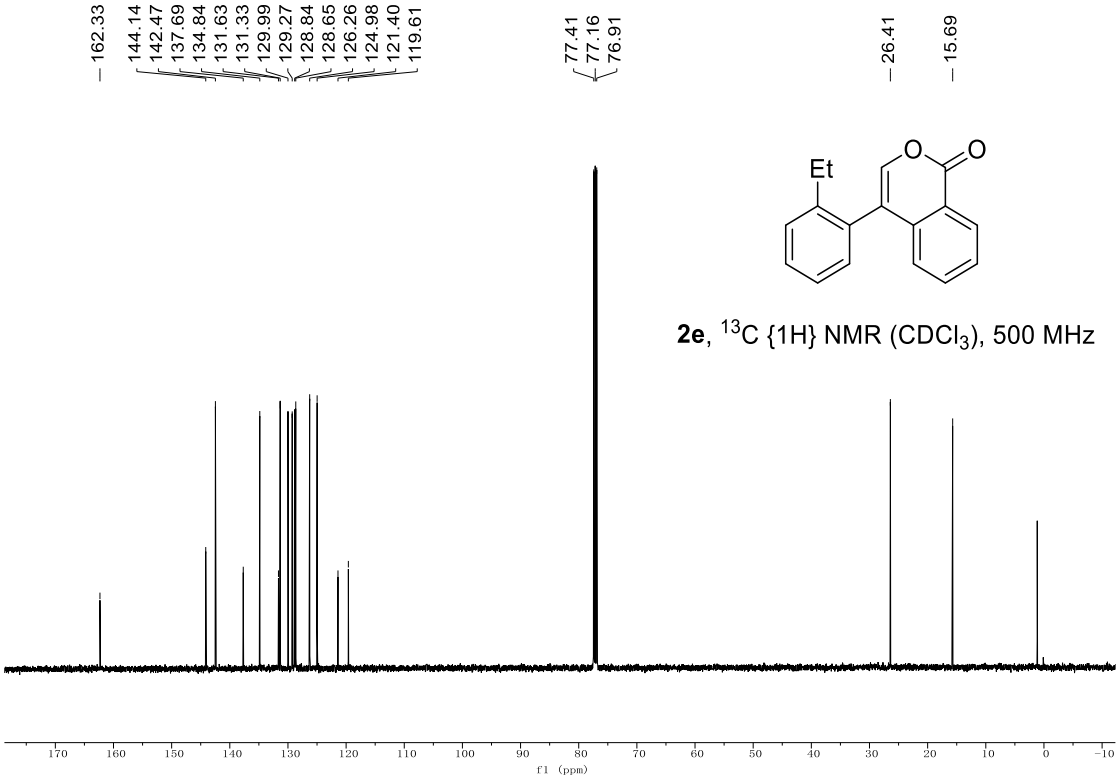
2d, ^{1}H NMR ($CDCl_3$), 500 MHz



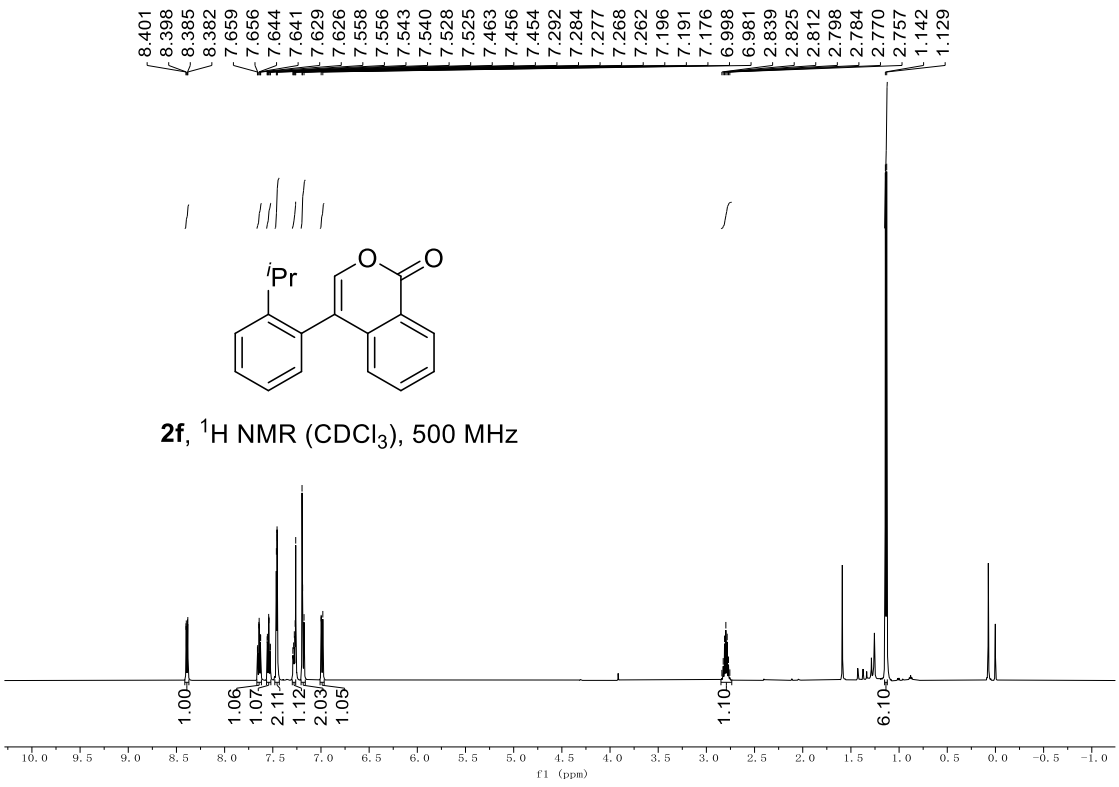
2d, ^{13}C {1H} NMR ($CDCl_3$), 500 MHz



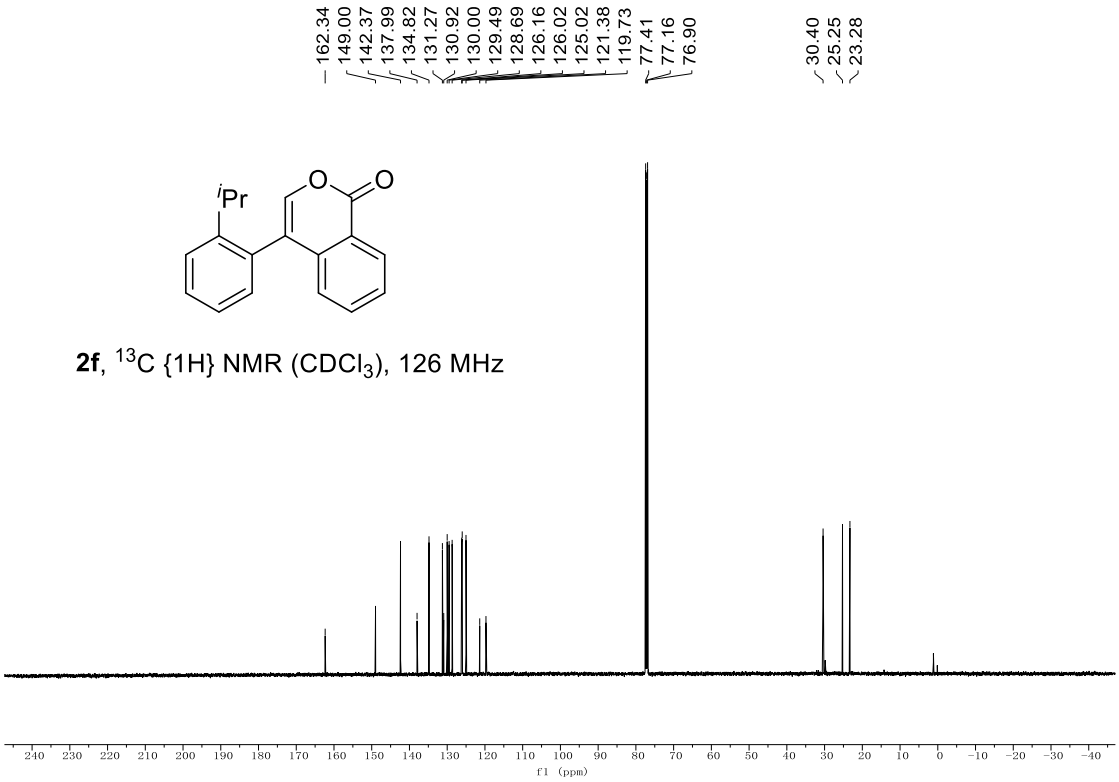
2e, ^{1}H NMR ($CDCl_3$), 500 MHz



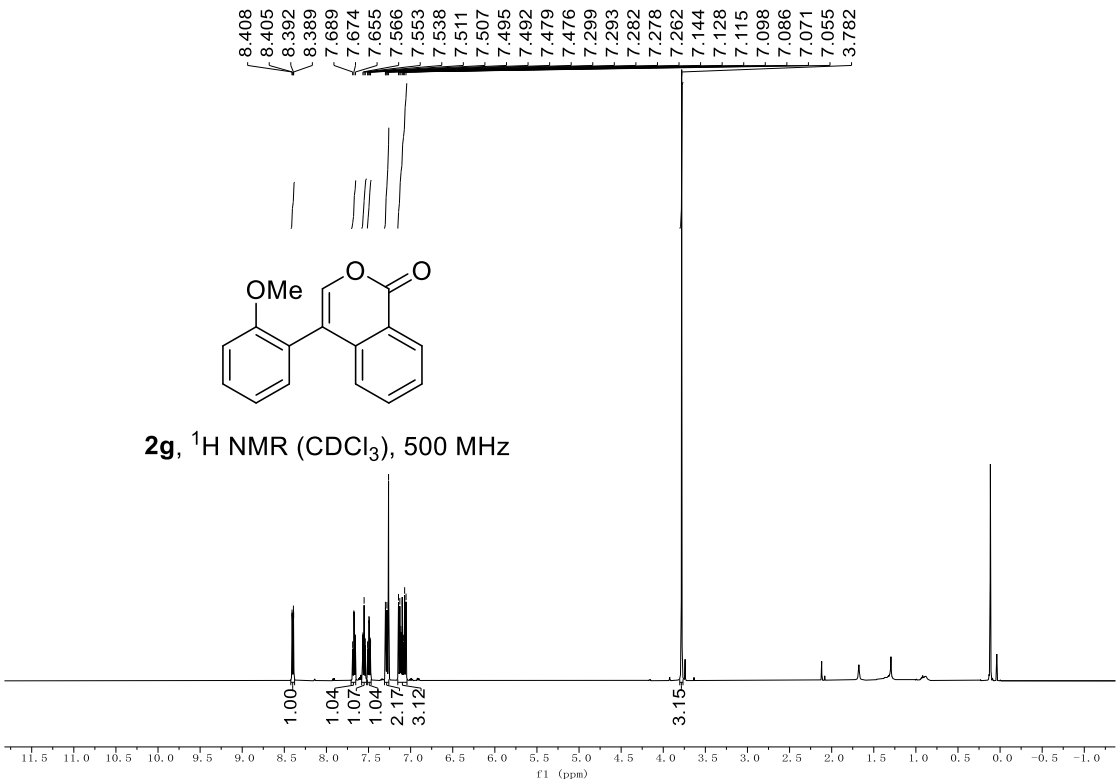
2e, ^{13}C {1H} NMR ($CDCl_3$), 500 MHz



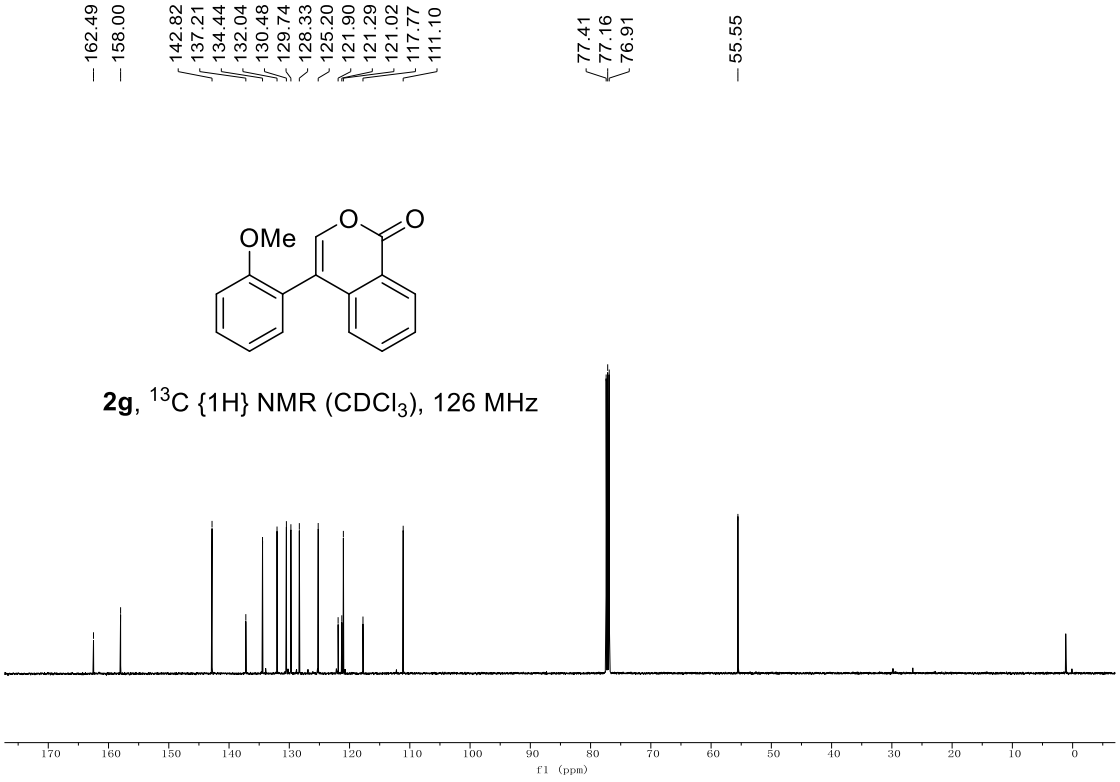
2f, ^{1}H NMR ($CDCl_3$), 500 MHz



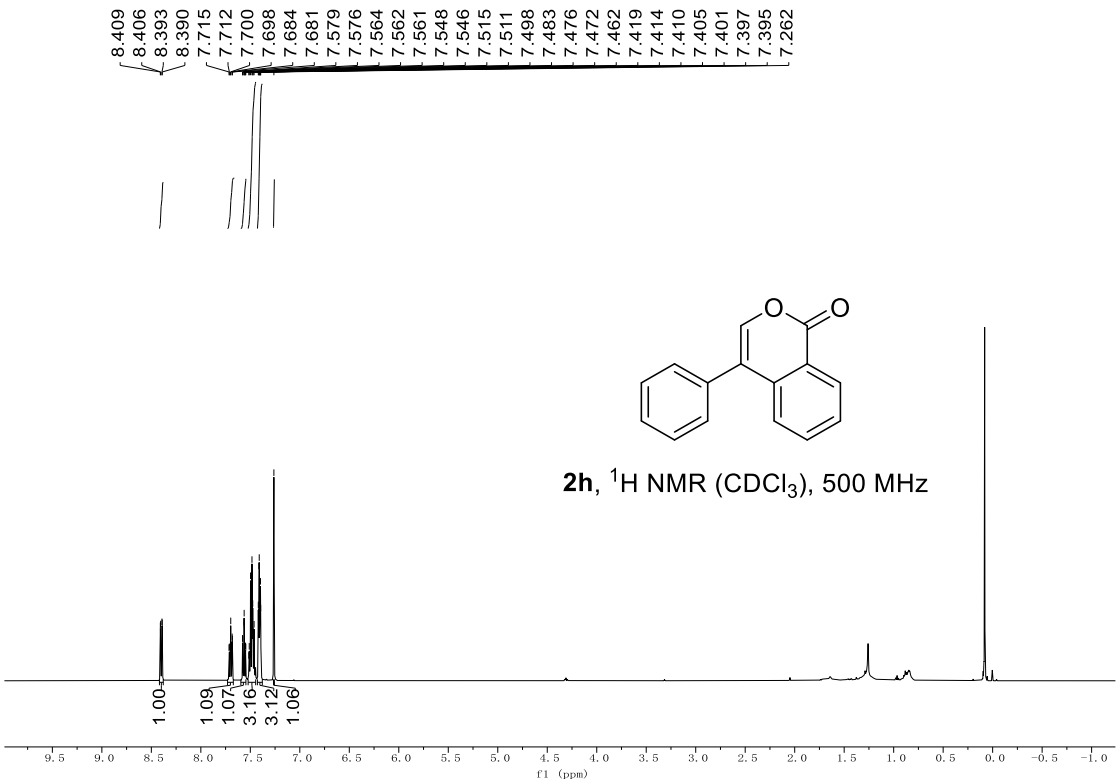
2f, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



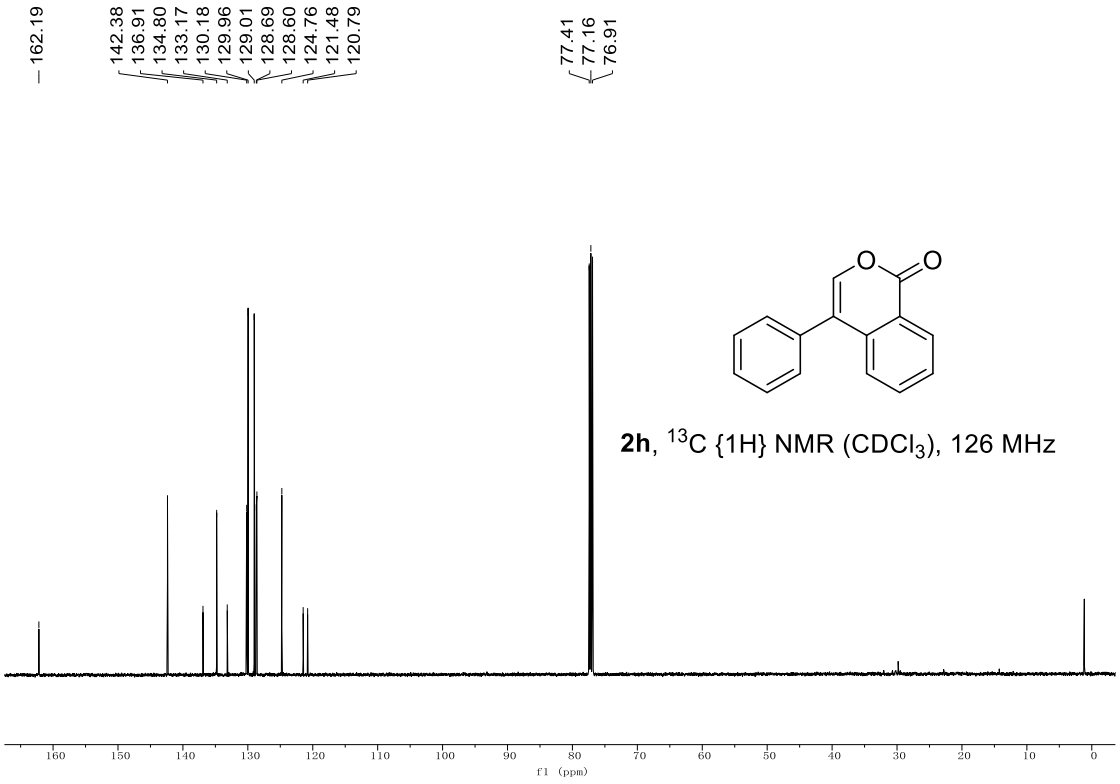
2g, ^{1}H NMR ($CDCl_3$), 500 MHz



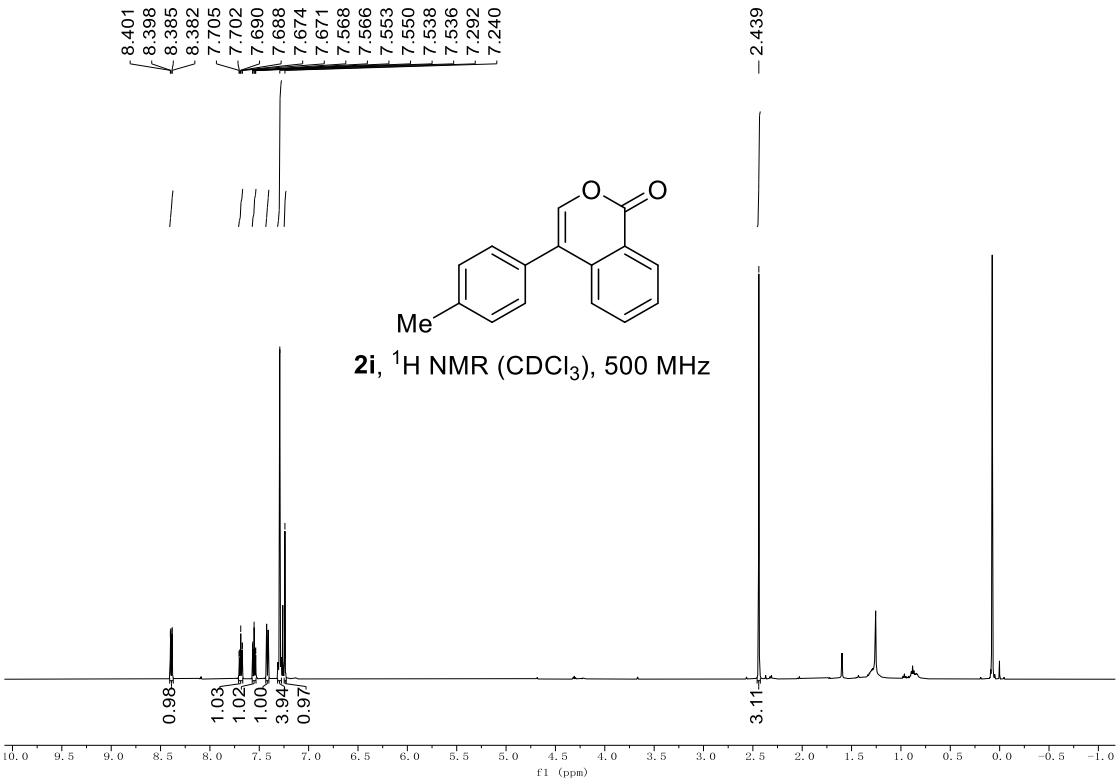
2g, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



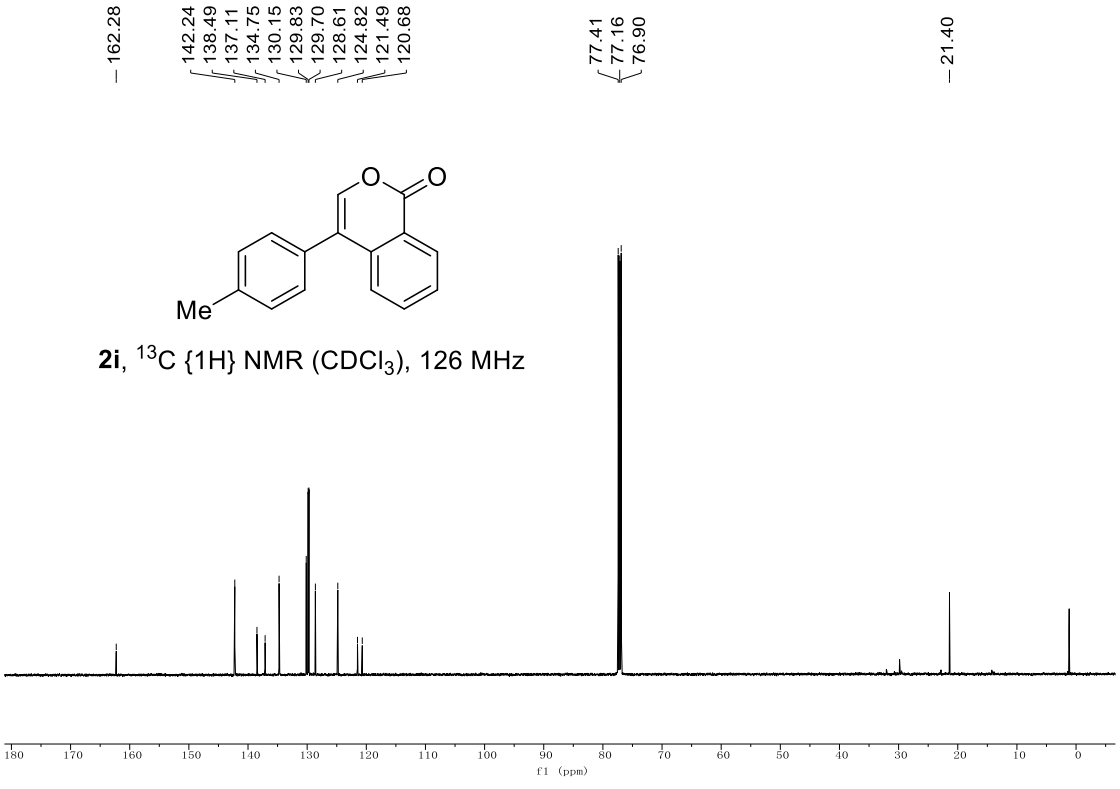
2h, ^{1}H NMR ($CDCl_3$), 500 MHz



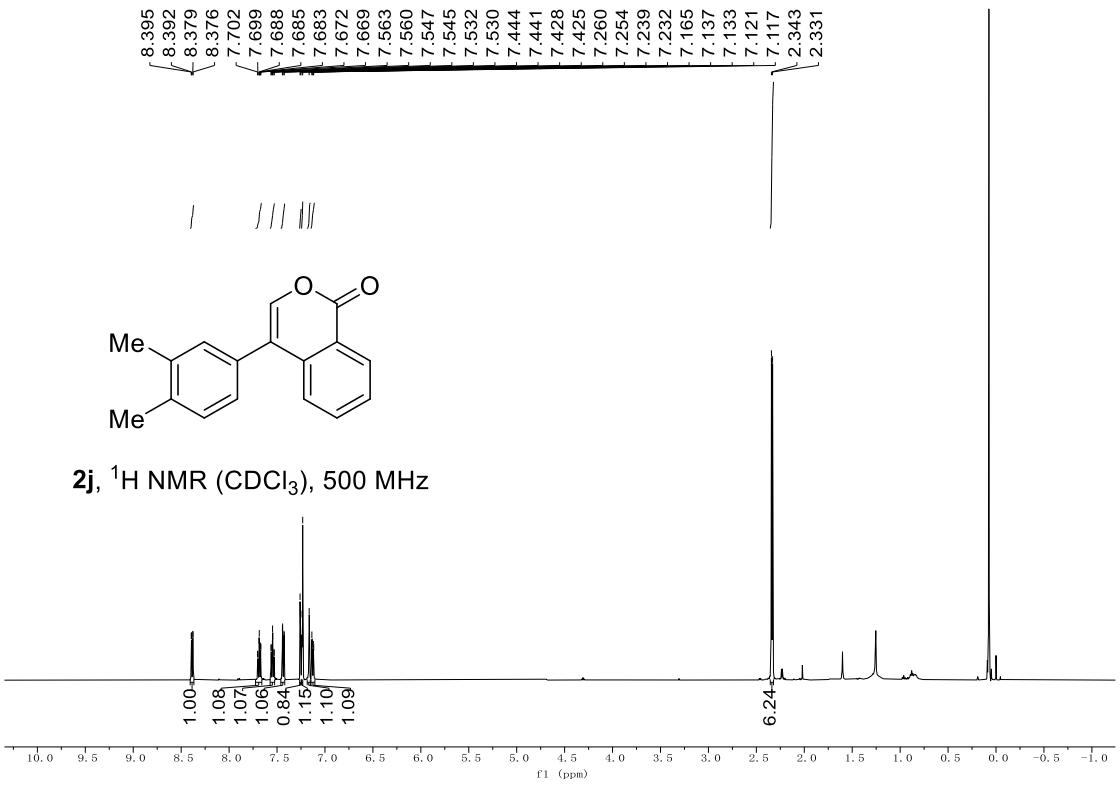
2h, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



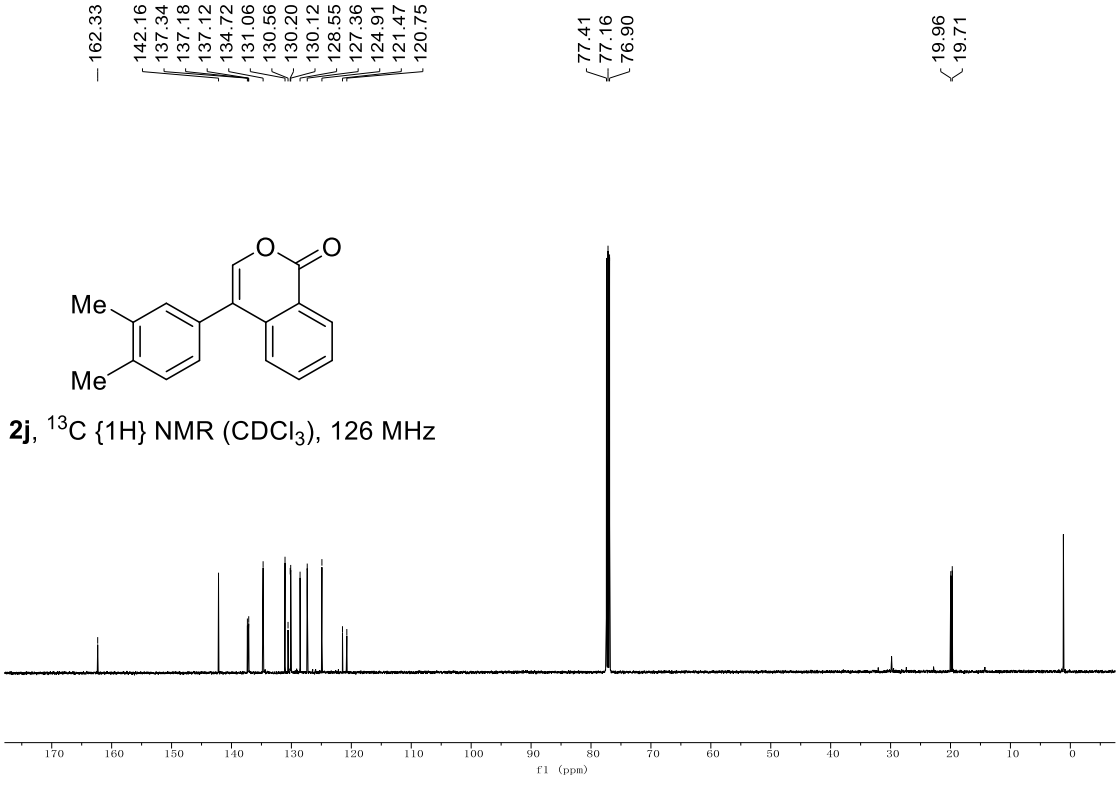
2i, ^{1}H NMR ($CDCl_3$), 500 MHz



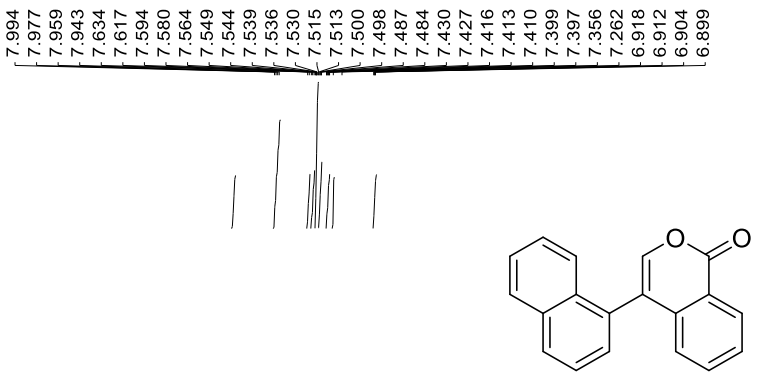
2i, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



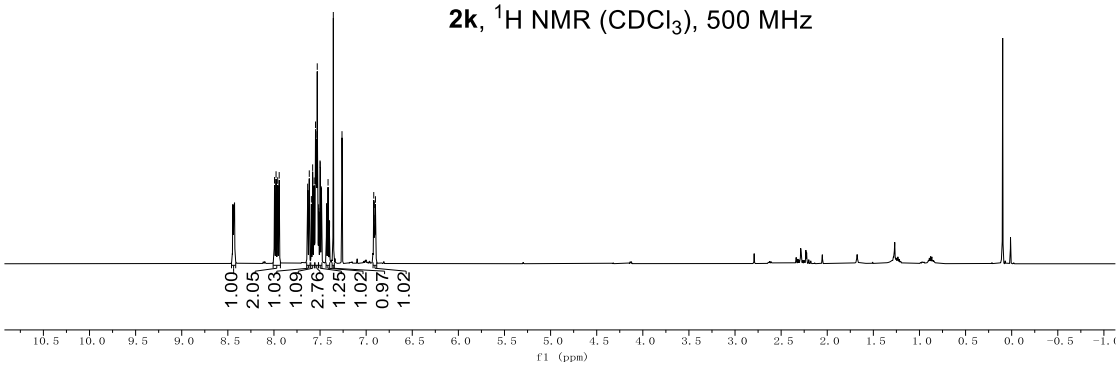
2j, ^{1}H NMR ($CDCl_3$), 500 MHz

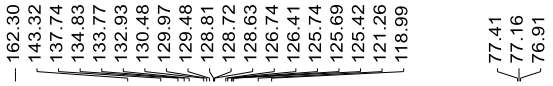


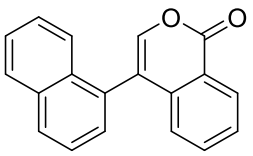
2j, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



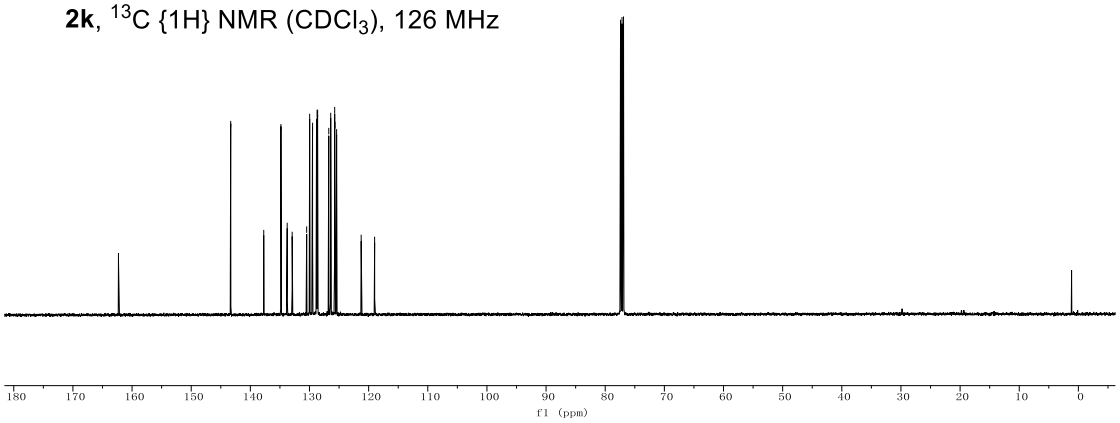
2k, ^{1}H NMR ($CDCl_3$), 500 MHz

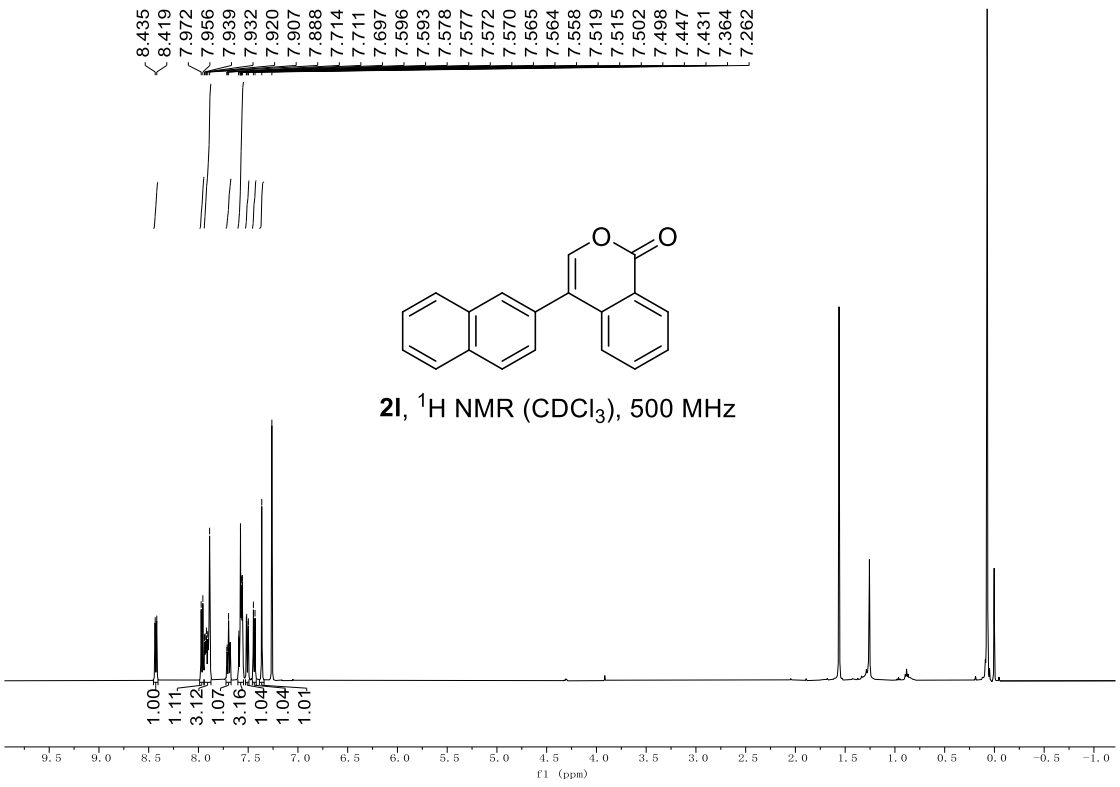




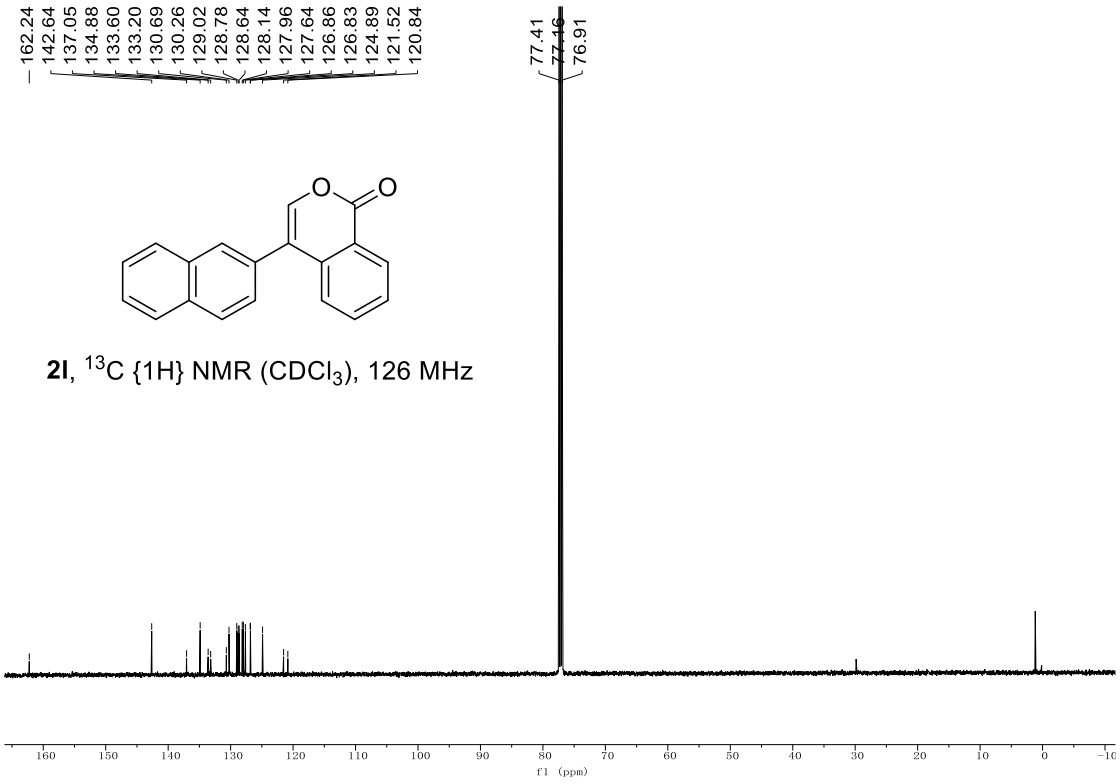


2k, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz

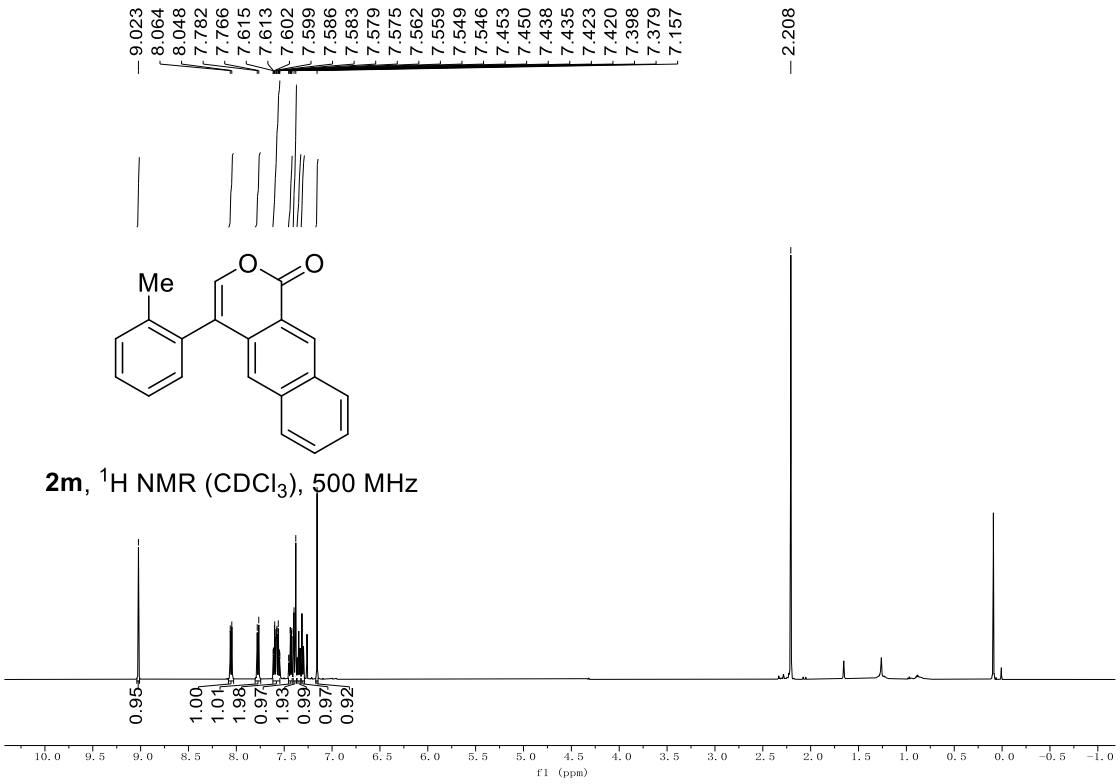




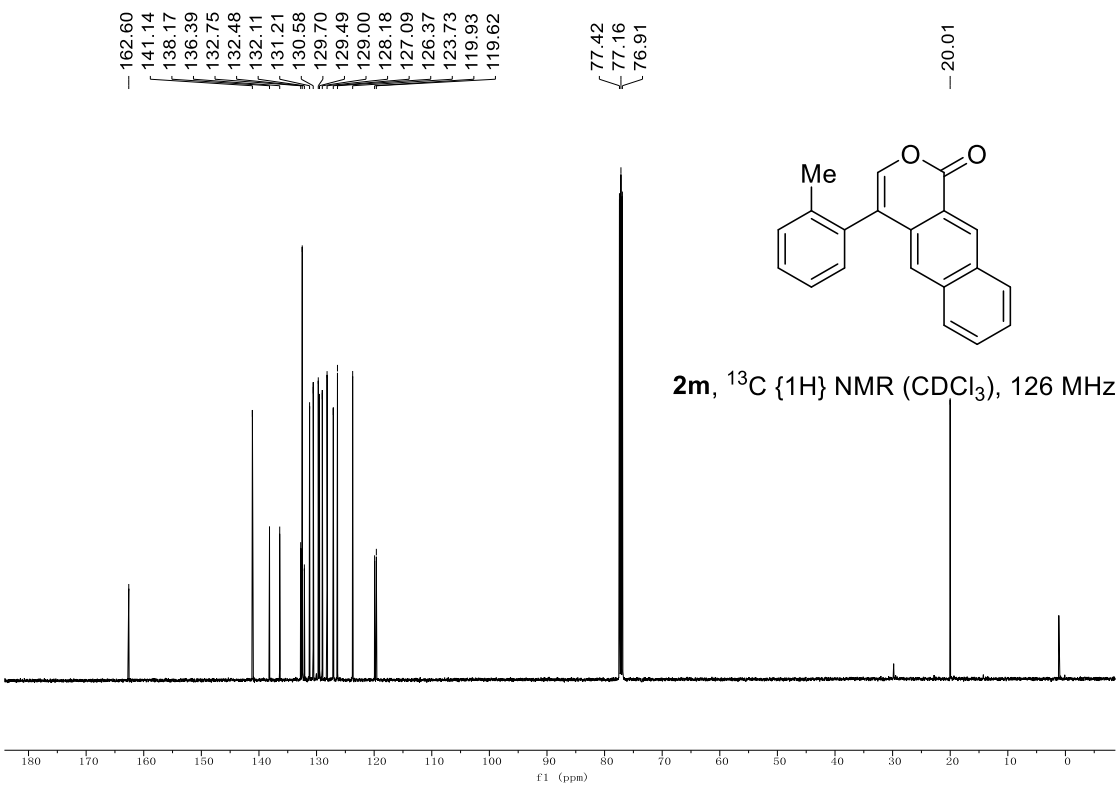
2l, ^{1}H NMR ($CDCl_3$), 500 MHz



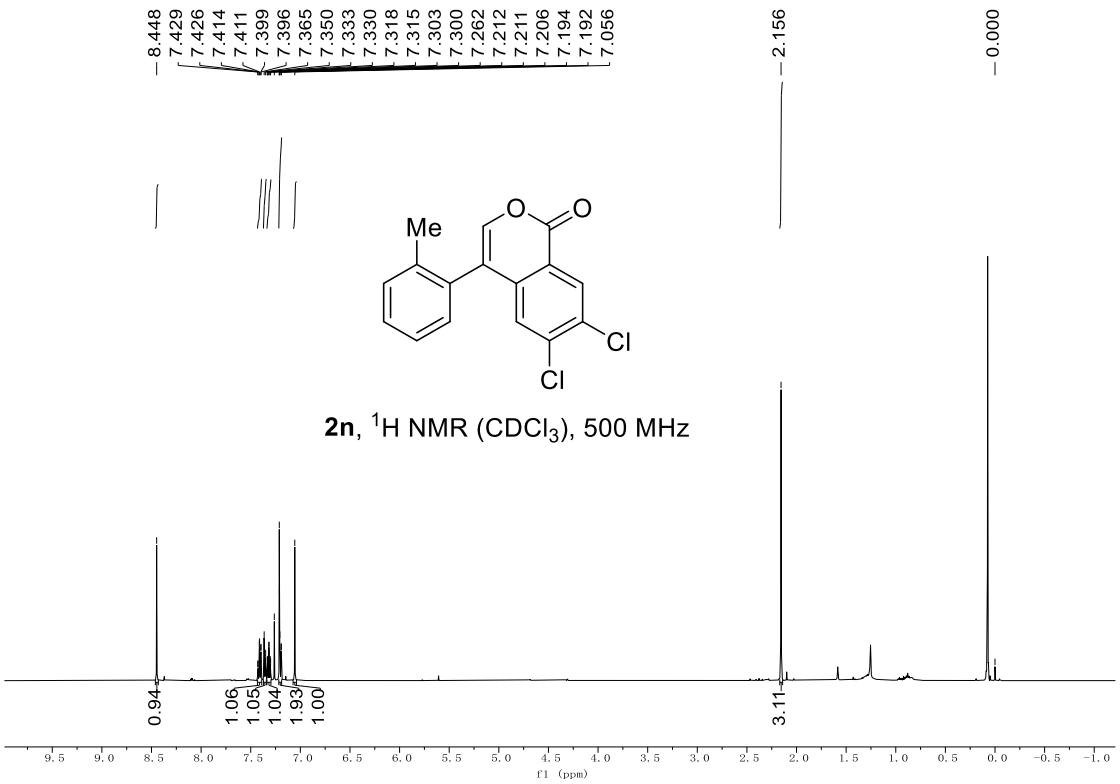
2l, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



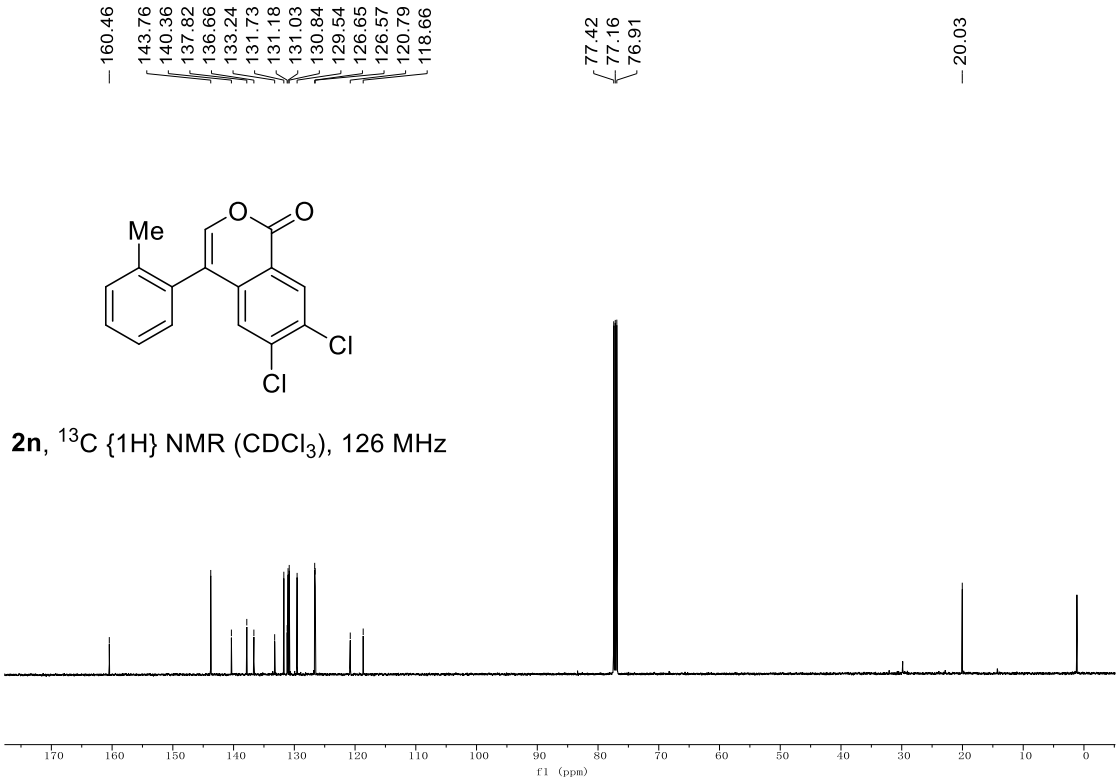
2m, ^{1}H NMR ($CDCl_3$), 500 MHz



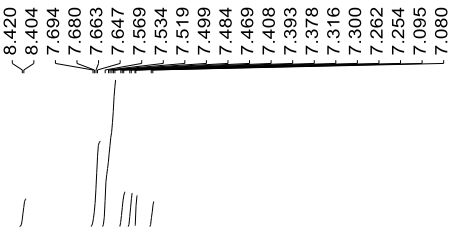
2m, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz

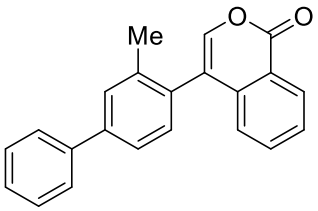


2n, ^{1}H NMR ($CDCl_3$), 500 MHz

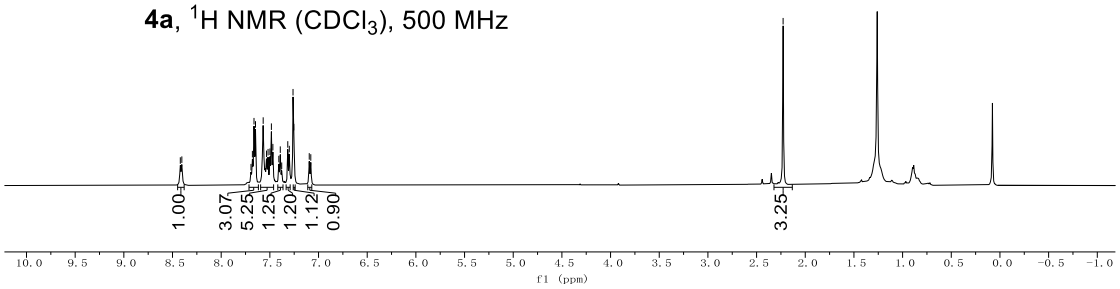


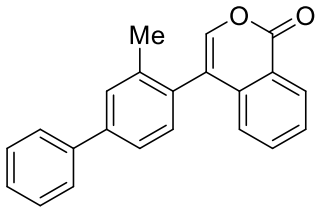
2n, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



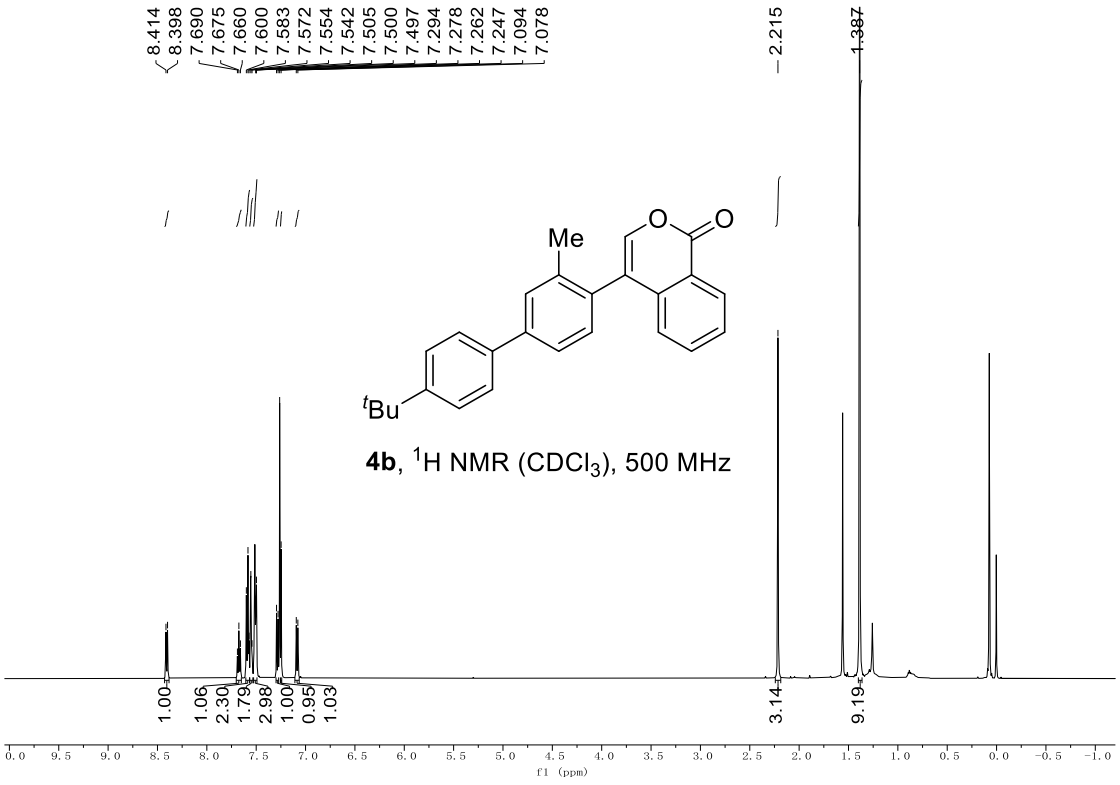


4a, ^{1}H NMR ($CDCl_3$), 500 MHz

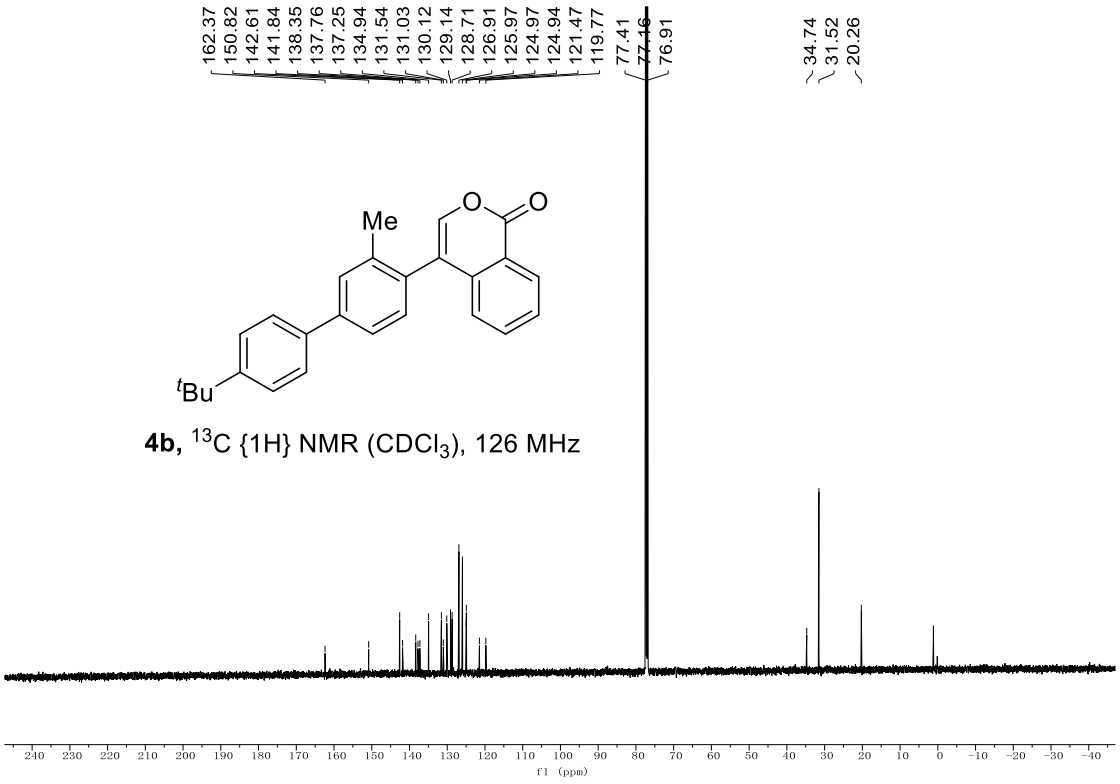




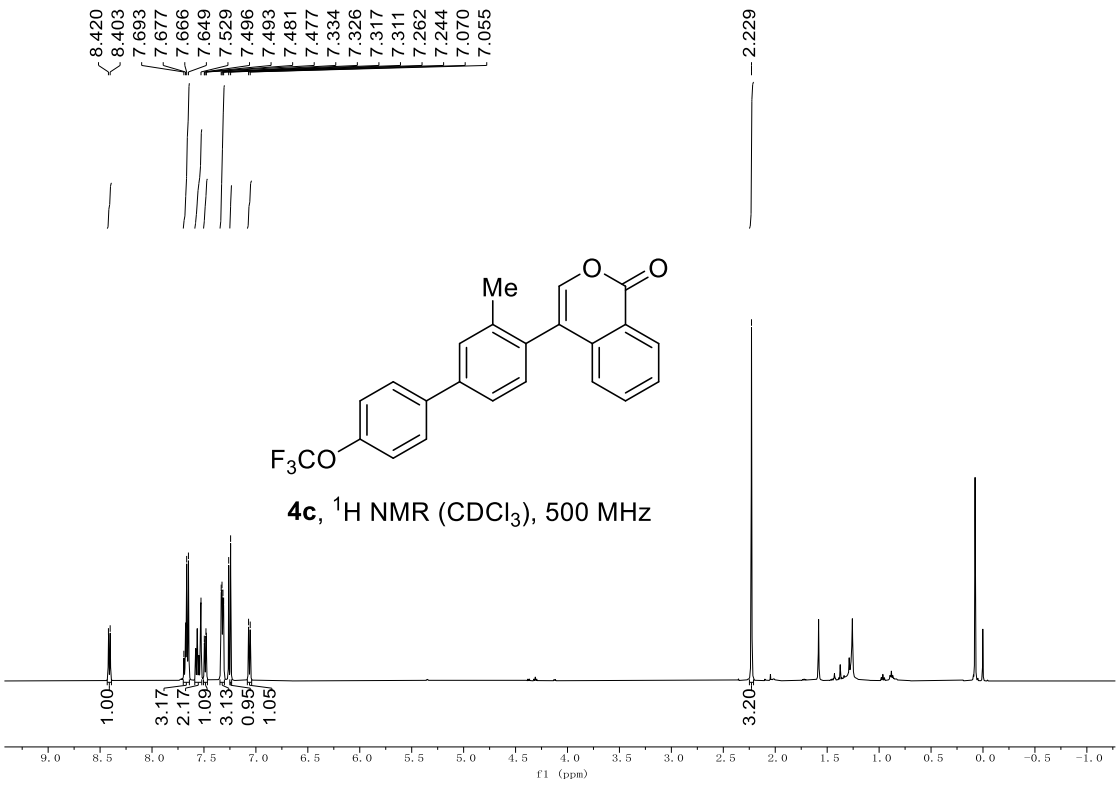
4a, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



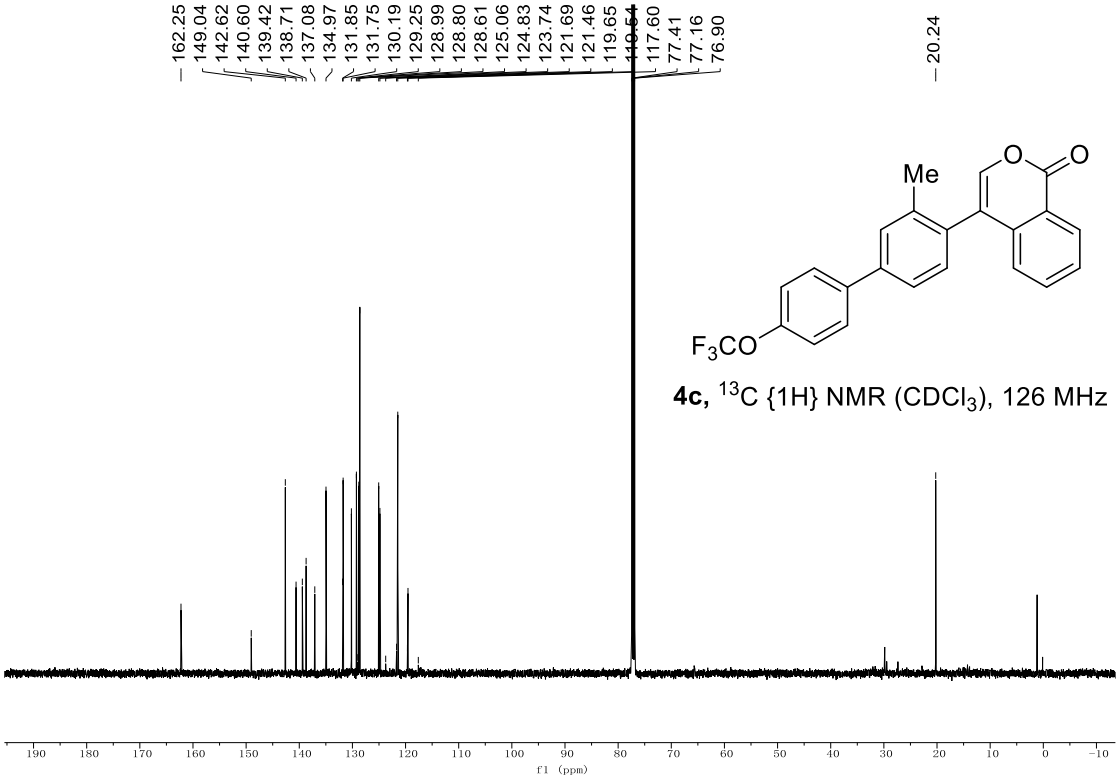
4b, ^{1}H NMR ($CDCl_3$), 500 MHz



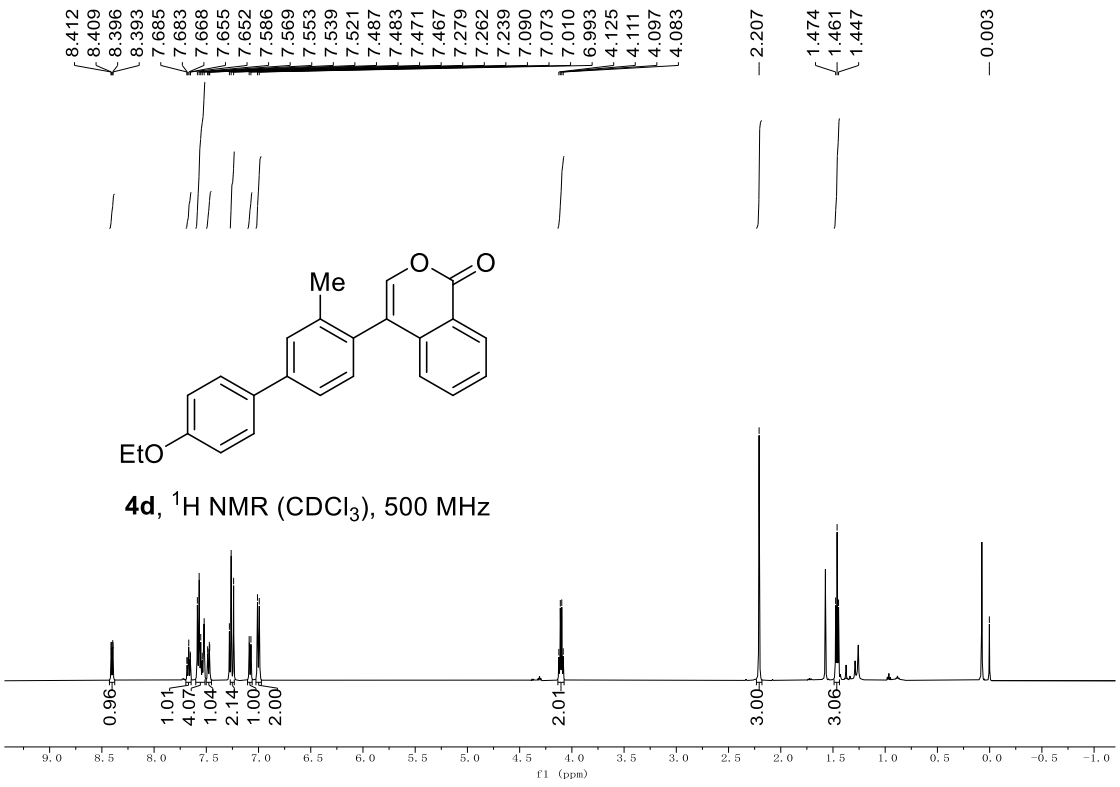
4b, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



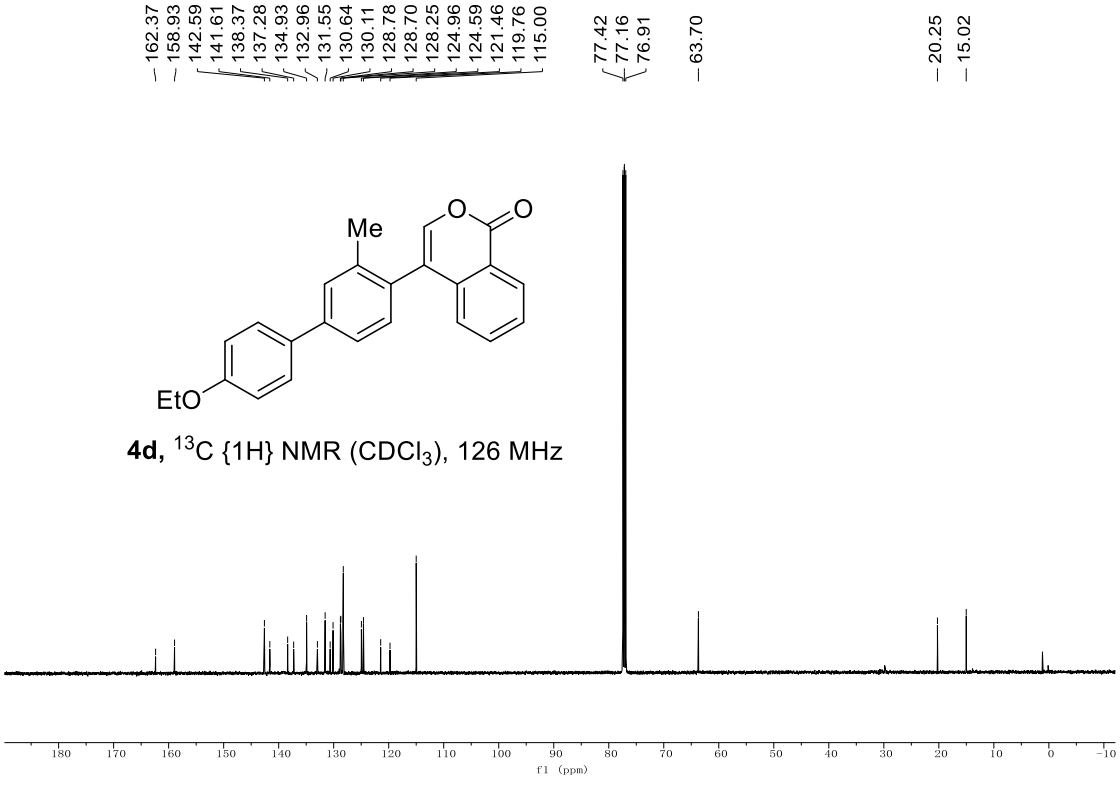
4c, ^{1}H NMR ($CDCl_3$), 500 MHz



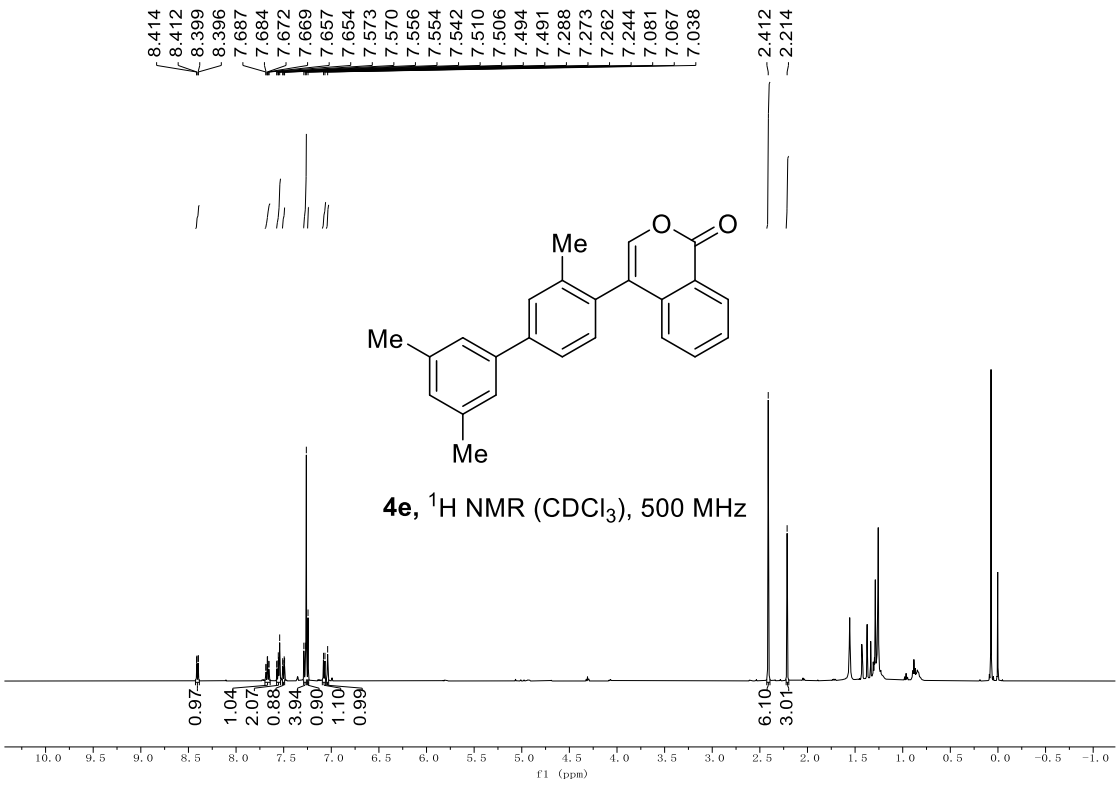
4c, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



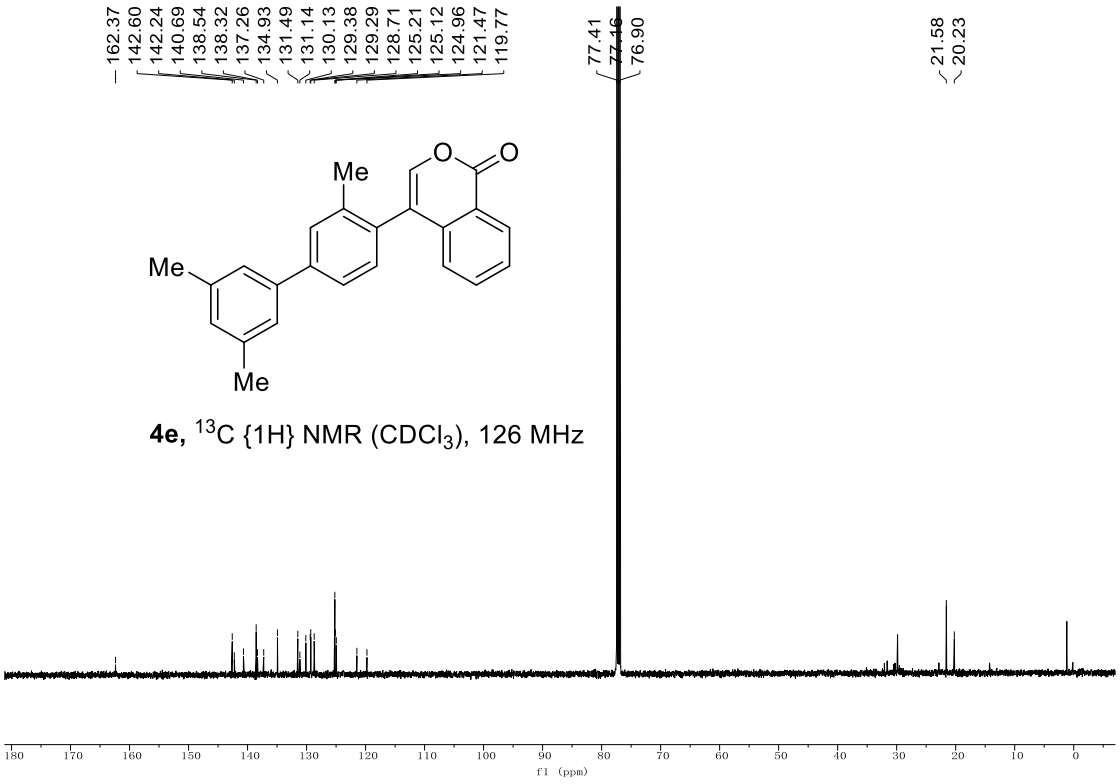
4d, ^{1}H NMR ($CDCl_3$), 500 MHz



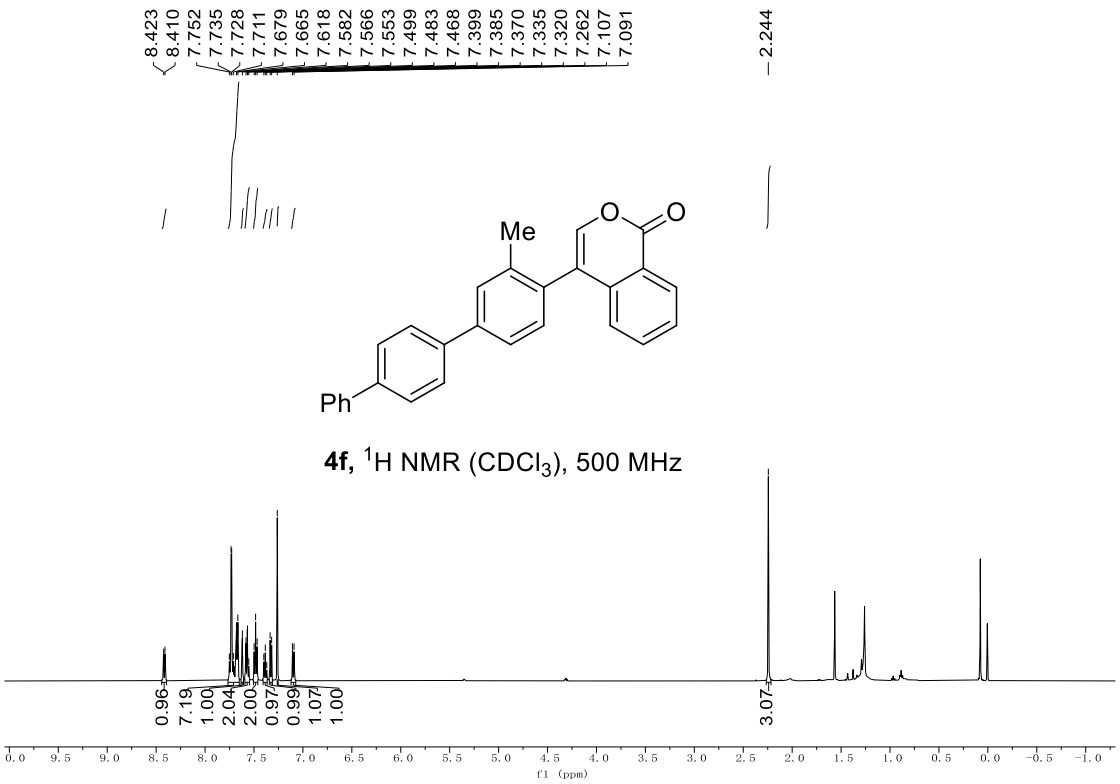
4d, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



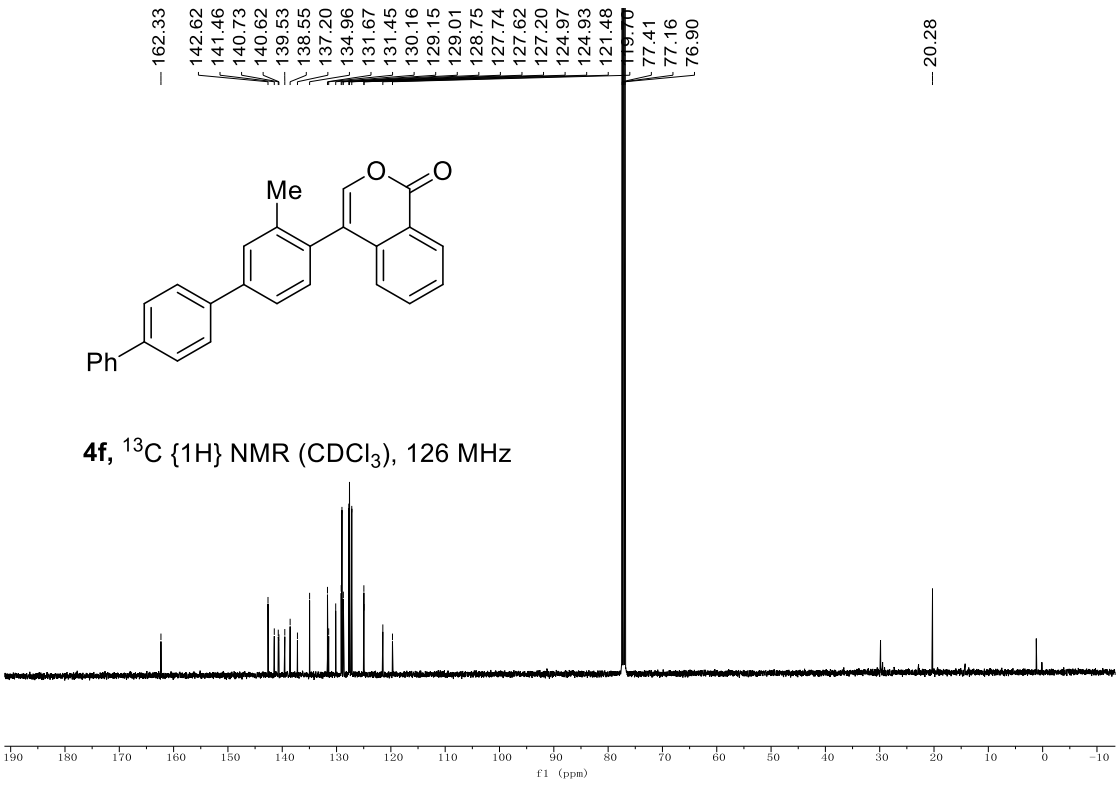
4e, ^{1}H NMR ($CDCl_3$), 500 MHz



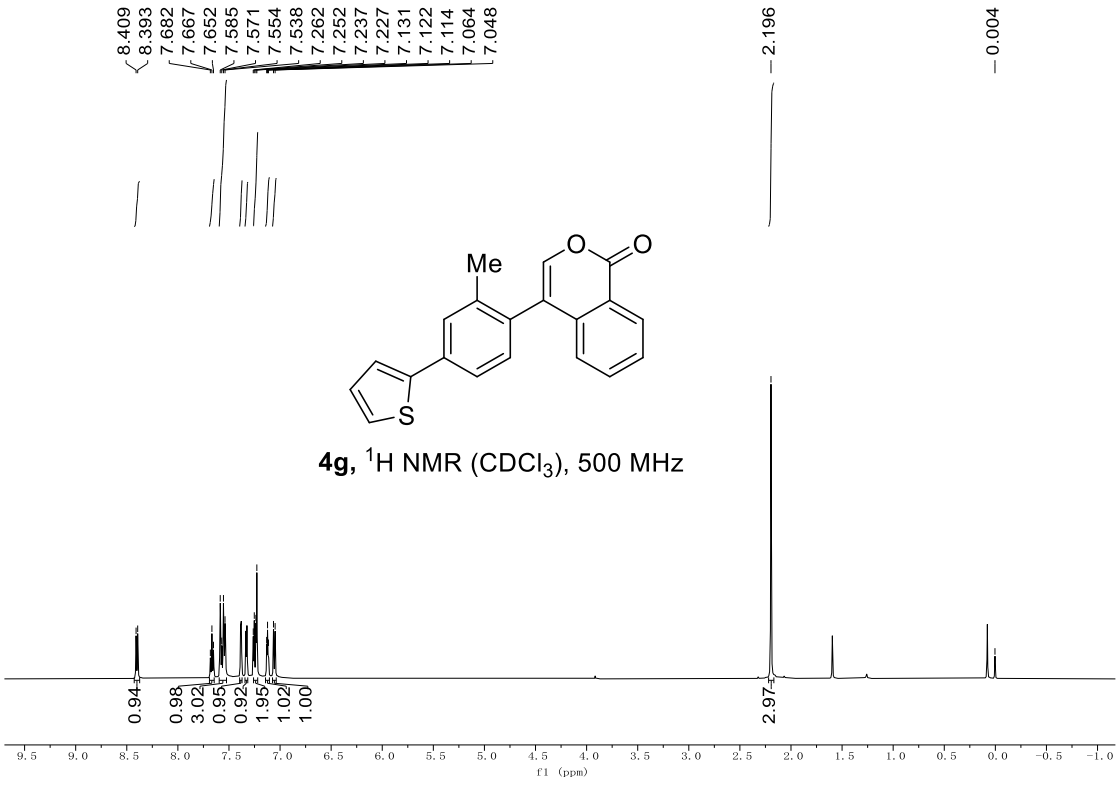
4e, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



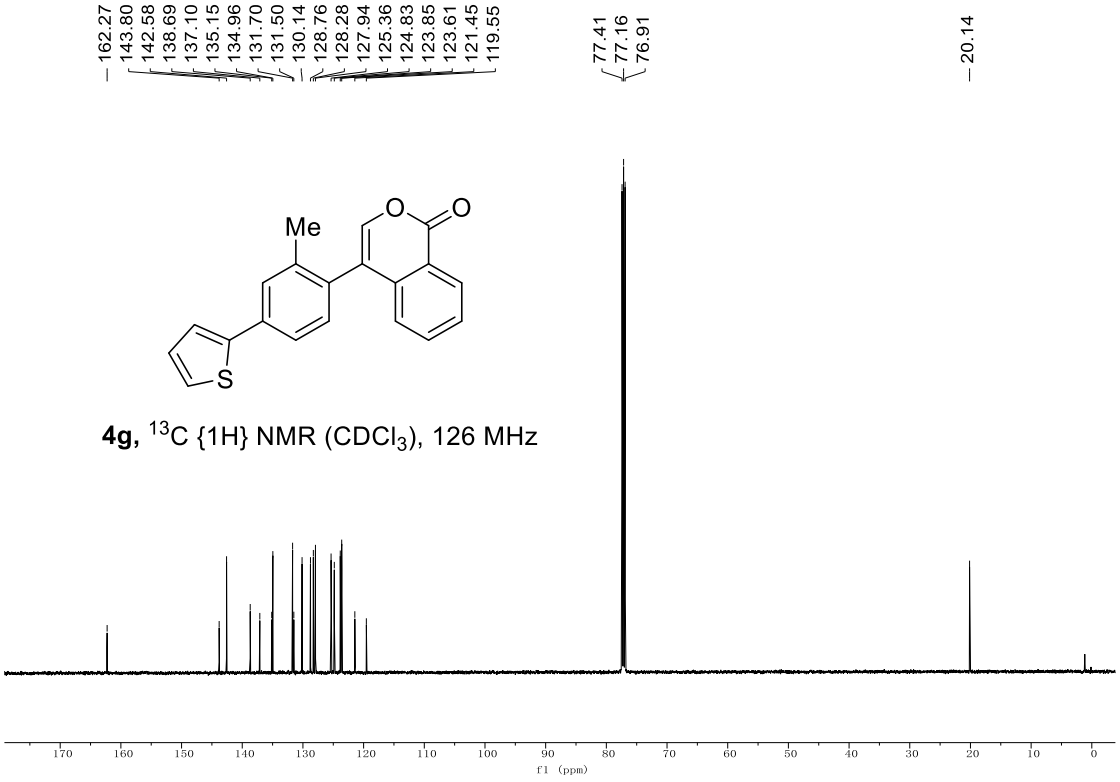
4f, ^{1}H NMR ($CDCl_3$), 500 MHz



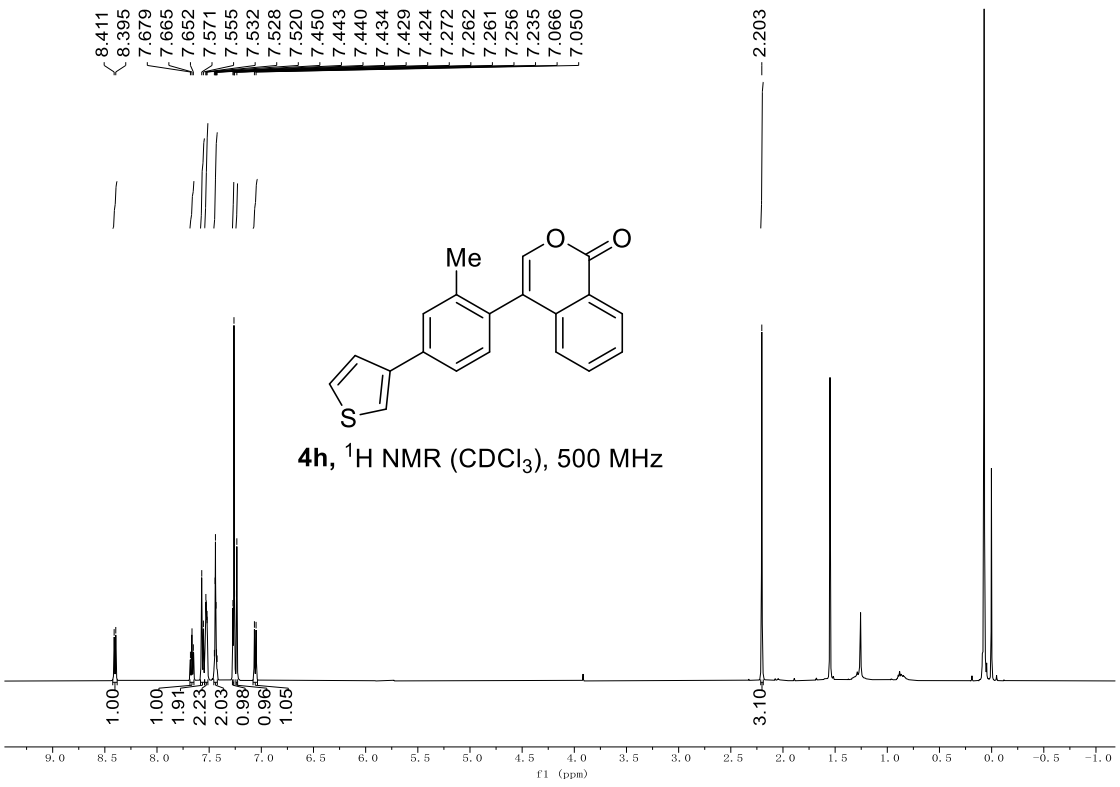
4f, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



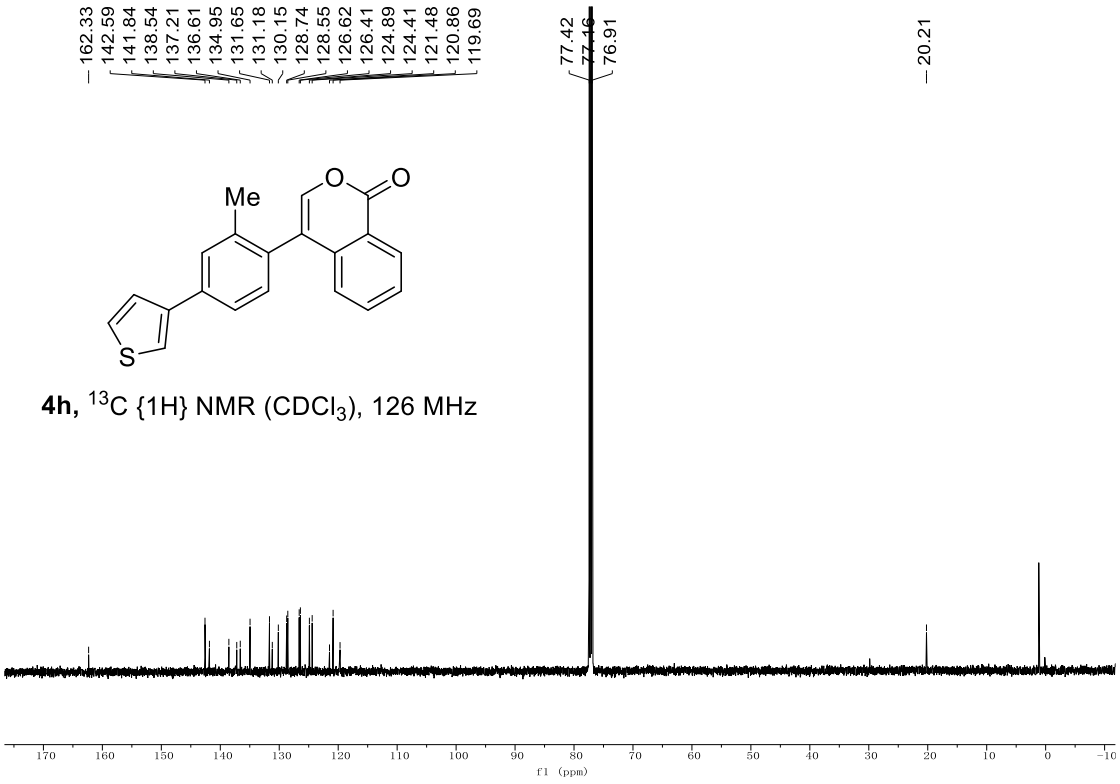
4g, ^{1}H NMR ($CDCl_3$), 500 MHz



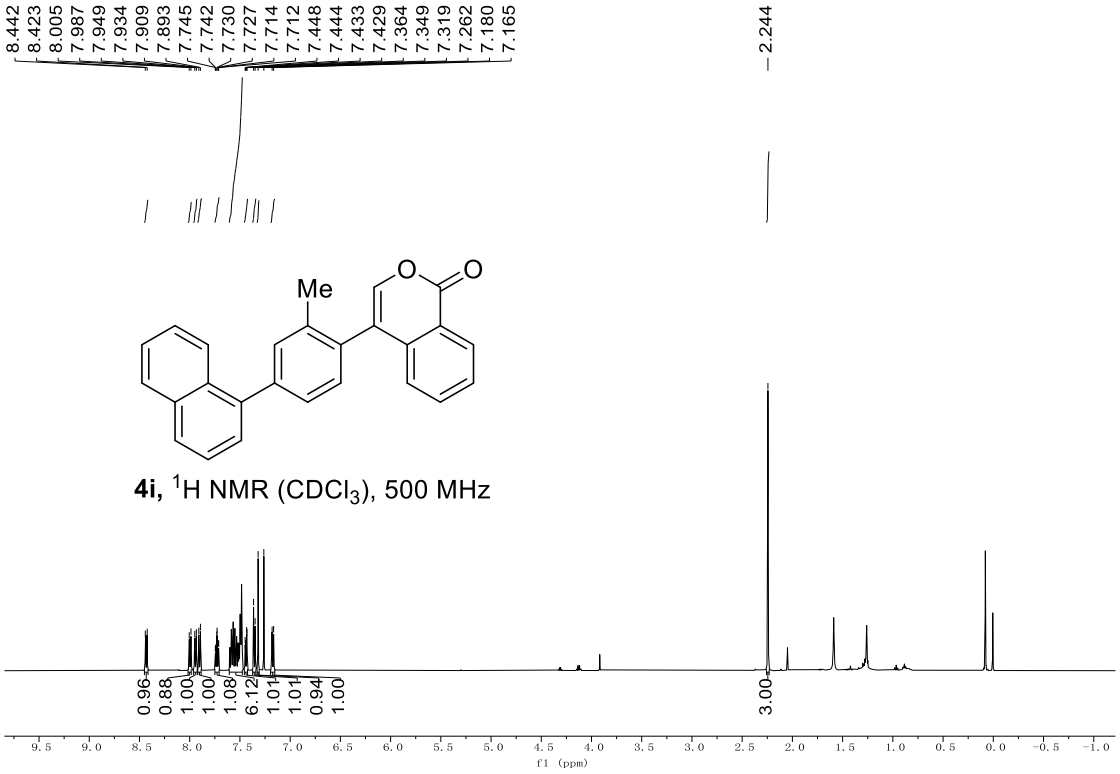
4g, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



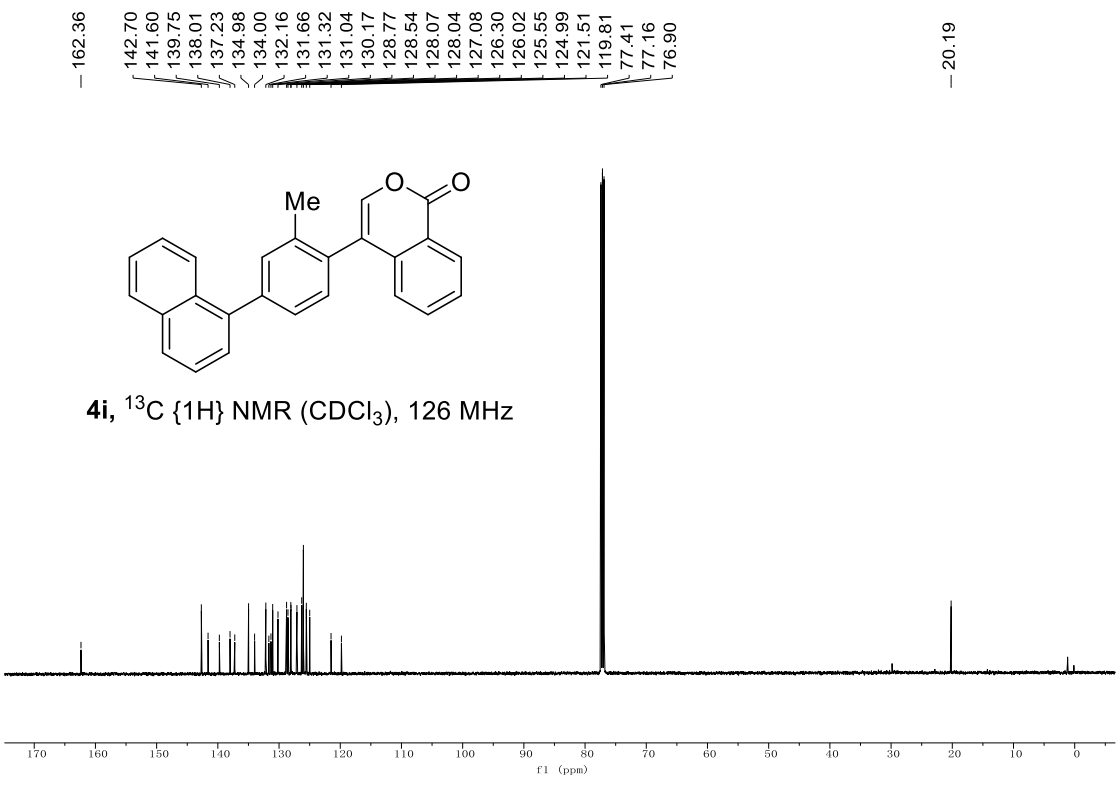
4h, ^{1}H NMR ($CDCl_3$), 500 MHz



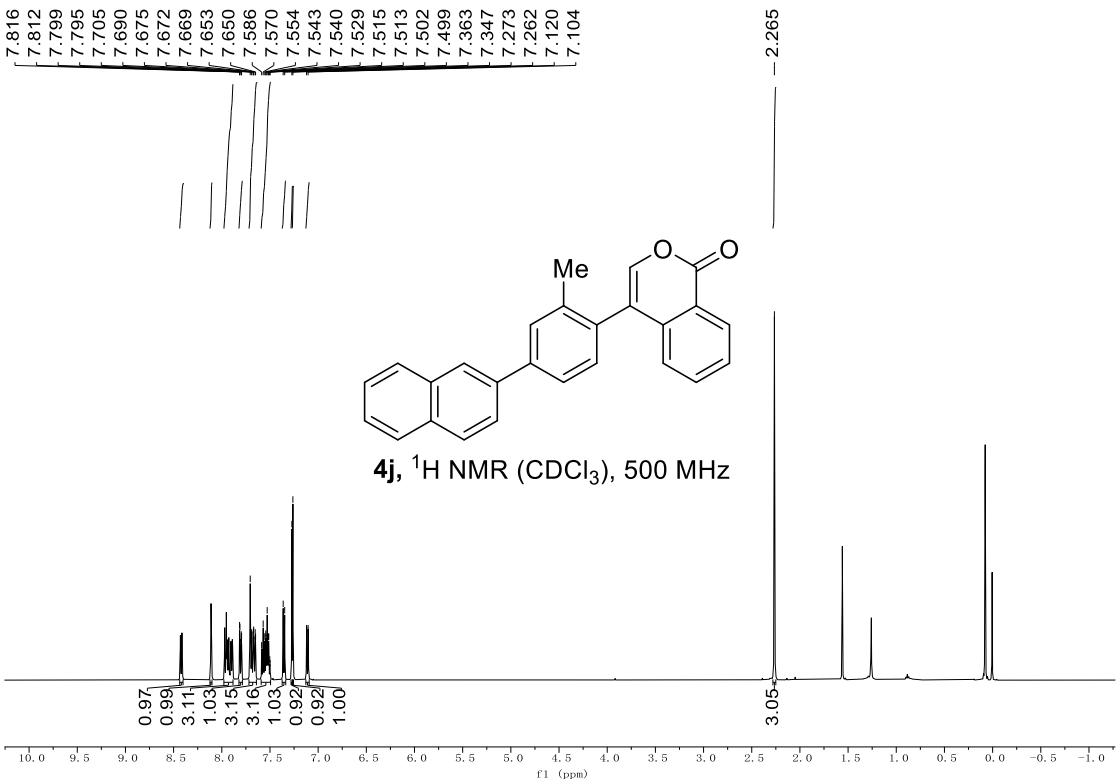
4h, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



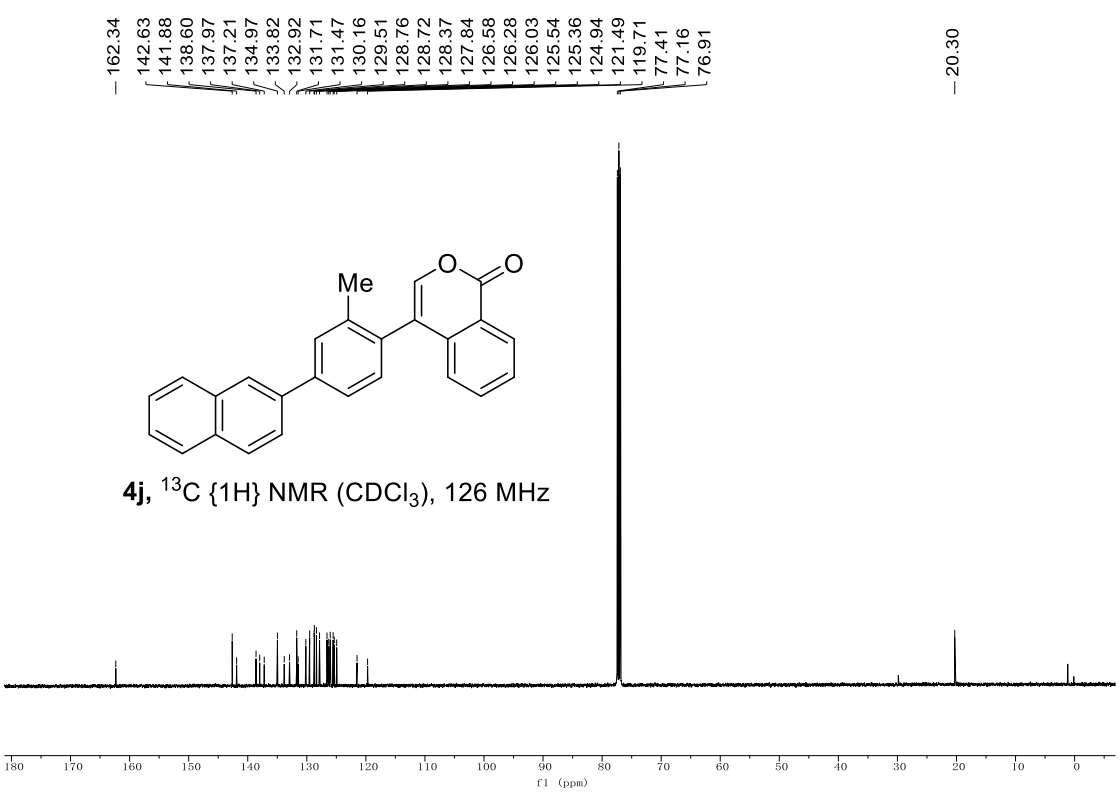
4i, ^{1}H NMR ($CDCl_3$), 500 MHz



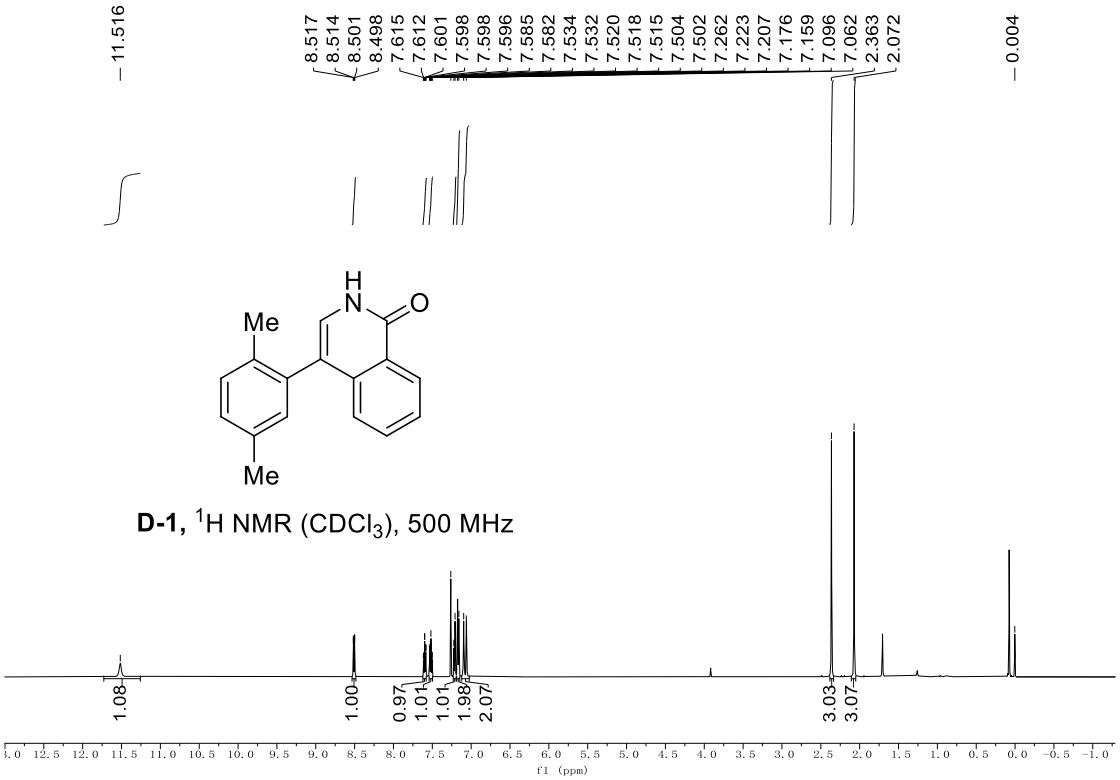
4i, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



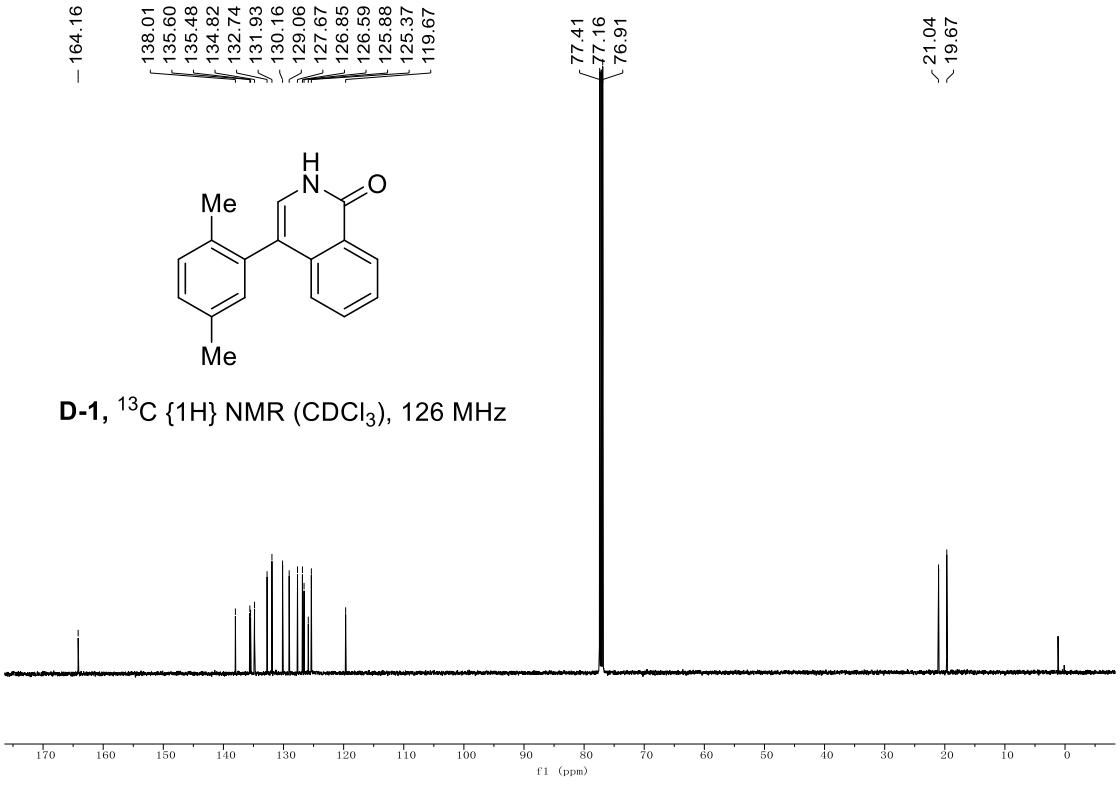
4j, ^{1}H NMR ($CDCl_3$), 500 MHz



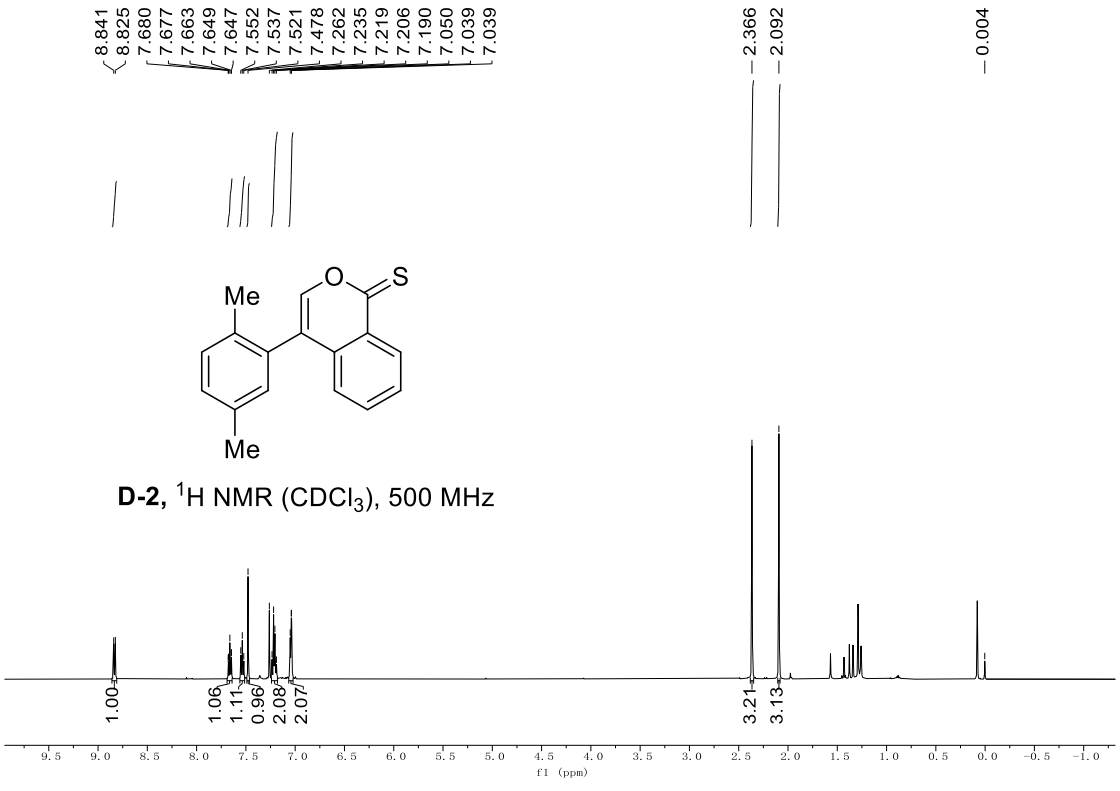
4j, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



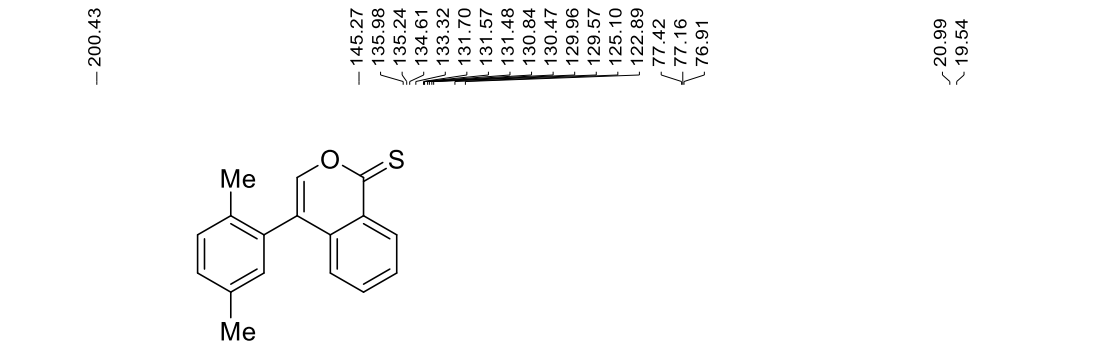
D-1, ^{1}H NMR ($CDCl_3$), 500 MHz



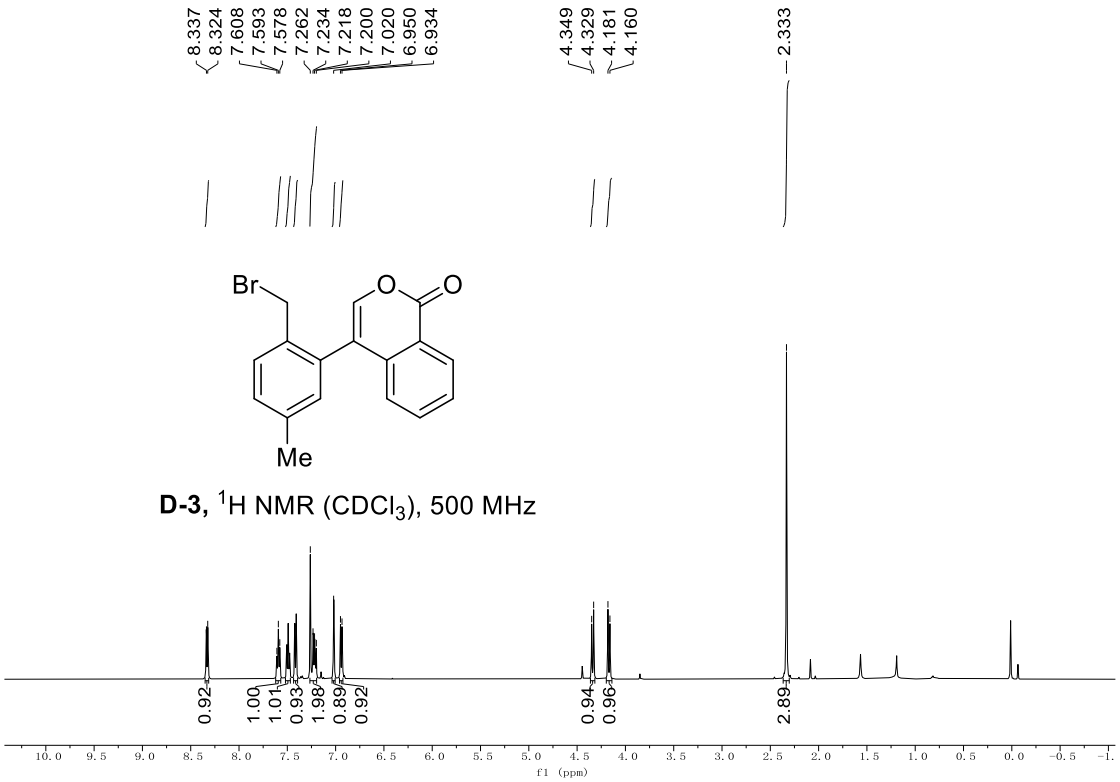
D-1, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



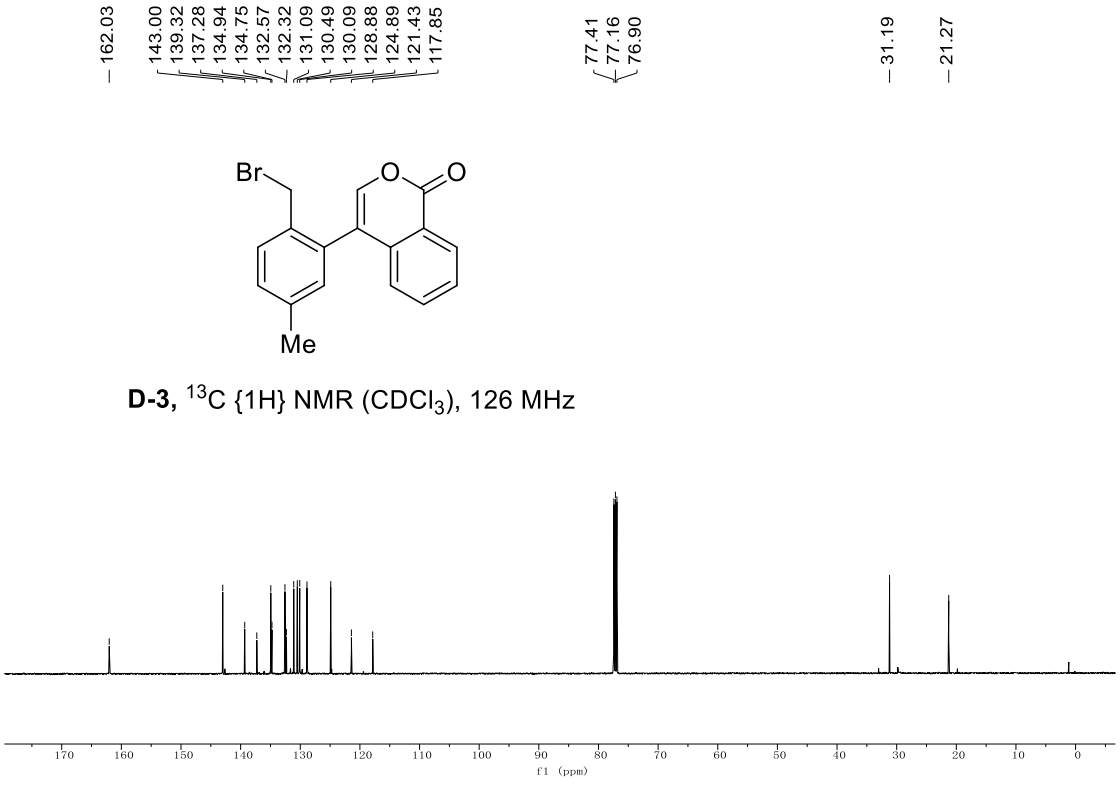
D-2, ^{1}H NMR ($CDCl_3$), 500 MHz



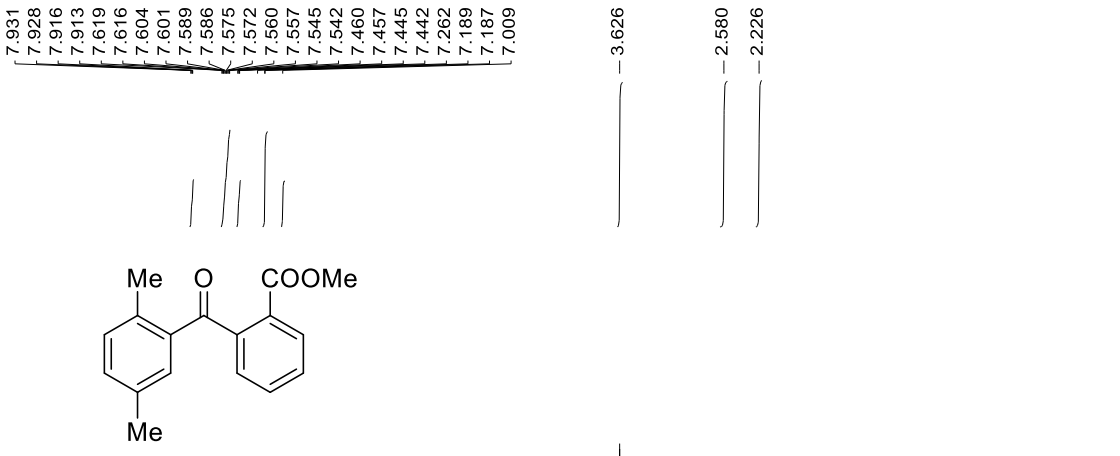
D-2, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



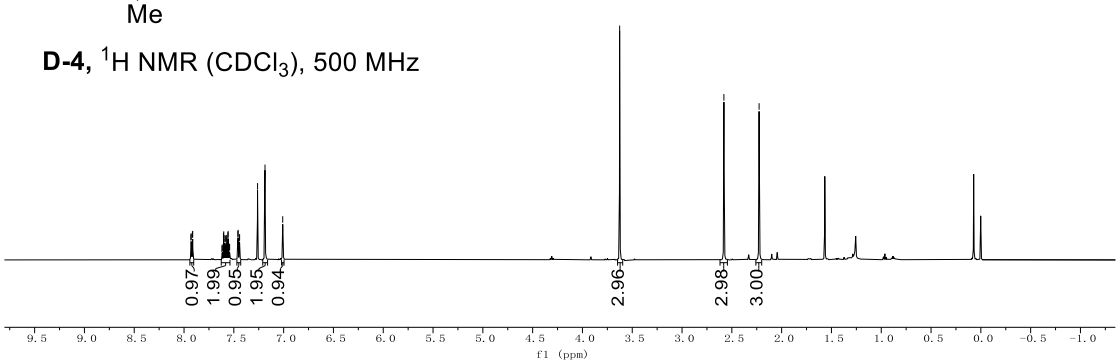
D-3, ^{1}H NMR ($CDCl_3$), 500 MHz

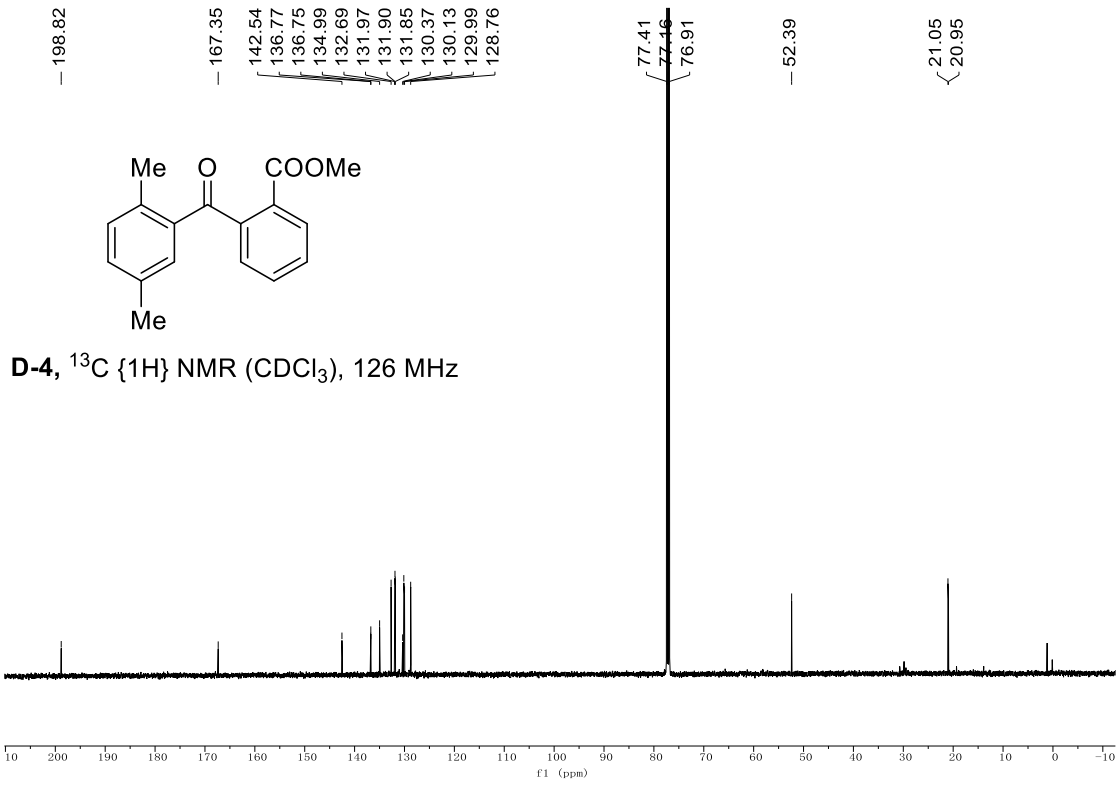


D-3, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz

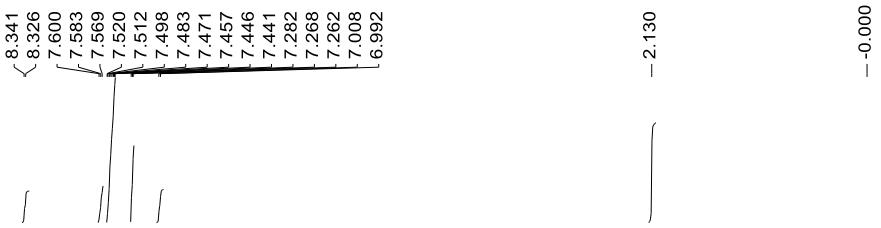


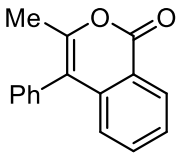
D-4, ^{1}H NMR ($CDCl_3$), 500 MHz



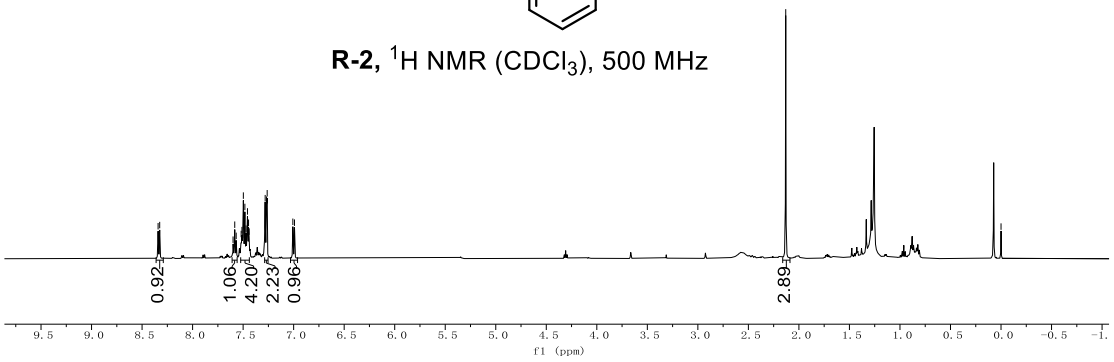


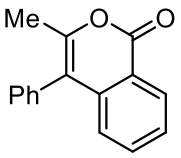
D-4, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



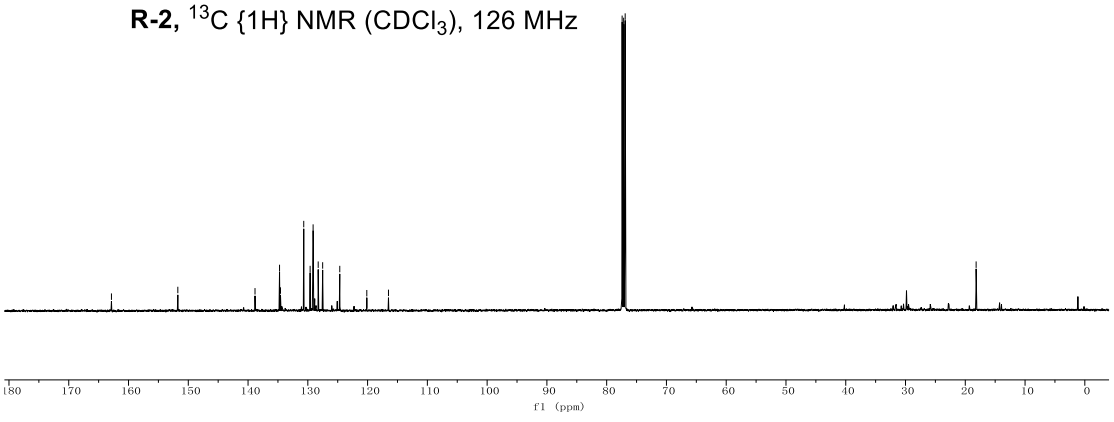


R-2, ^{1}H NMR ($CDCl_3$), 500 MHz





R-2, ^{13}C {1H} NMR ($CDCl_3$), 126 MHz



7. X-Ray Crystallography Data

Crystallographic data for **4g** has been deposited with the Cambridge Crystallographic Data Centre as deposition number **CCDC 2360419**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Single crystals of **4g** were obtained by slow evaporation of a solution containing **4g** in the mixture of hexane and DCM at room temperature. ORTEP view of **4g** was presented in **Figure S9**. A suitable crystal was selected and the crystal data and structure refinement results for compound **4g** are listed in the **Table S2**.

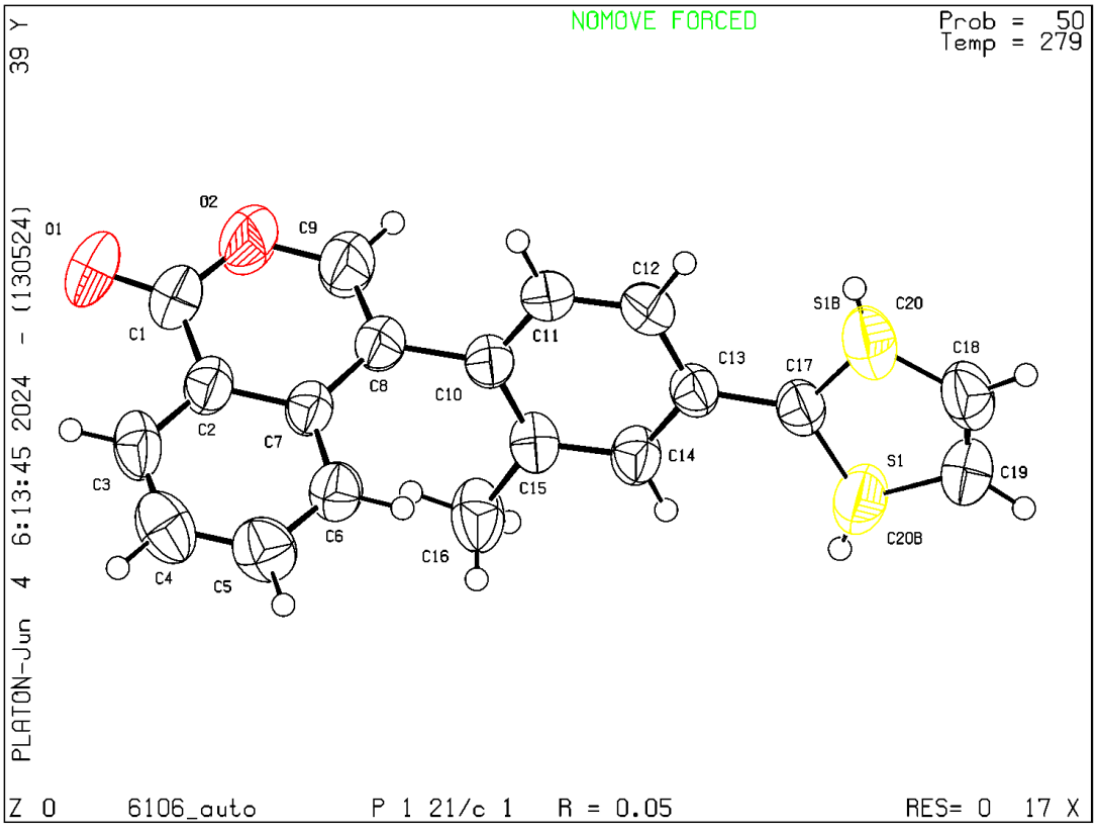


Figure S9. ORTEP View of **4g** with Thermal Ellipsoids Drawn at the 50% Probability Level

Table S2. Crystal Data and Structure Refinement for **4g**

Identification code	**4g**
Empirical formula	$C_{20}H_{14}O_2S$
Formula weight	318.399
Temperature/K	279.3(6)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.4267(14)
b/Å	19.636(2)
c/Å	9.2051(12)
α/°	90
β/°	110.751(16)
γ/°	90
Volume/Å^3	1593.3(4)
Z	4
ρ_{calc}g/cm^3	1.327
μ/mm^{-1}	0.210
F(000)	664.9
Crystal size/mm^3	0.21 × 0.18 × 0.05
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.14 to 52.74
Index ranges	$-13 \leq h \leq 11$, $-22 \leq k \leq 27$, $-12 \leq l \leq 10$
Reflections collected	13905
Independent reflections	3249 [R_{int} = 0.0470, R_{sigma} = 0.0546]
Data/restraints/parameters	3249/3/211
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0509, wR_2 = 0.1351
Final R indexes [all data]	R_1 = 0.0906, wR_2 = 0.1555
Largest diff. peak/hole / e Å^{-3}	0.23/-0.30

8. References

1. C. Xu and Q. Shen, Lewis Acid Mediated Trifluoromethylthio Lactonization/Lactamization, *Org. Lett.*, 2015, **17**, 4561-4563.
2. S. Zhang, L. Li, J. Zhang, J. Zhang, M. Xue and K. Xu, Electrochemical Fluoromethylation Triggered Lactonizations of Alkenes under Semi-Aqueous Conditions, *Chem. Sci.*, 2019, **10**, 3181-3185.
3. D. Parmar, M. S. Maji and M. Rueping, Catalytic and Asymmetric Fluorolactonisations of Carboxylic Acids through Anion Phase Transfer, *Chem. Eur. J.*, 2014, **20**, 83-86.
4. Y.-S. Xiong, B. Zhang, Y. Yu, J. Weng and G. Lu, Construction of Sulfonyl Phthalides *via* Copper-Catalyzed Oxysulfonylation of 2-Vinylbenzoic Acids with Sodium Sulfinates, *J. Org. Chem.*, 2019, **84**, 13465-13472.
5. S. Liu, L. Cheng and L. Liu, Synthesis of Biaryl Carboxylic Acids through a Cascade Suzuki-Miyaura Coupling/Friedel-Crafts Alkylation/Lewis-Acid-Catalyzed Rearrangement/Aromatization Process, *Org. Lett.*, 2024, **26**, 1902-1907.
6. M. Martineau, A. Somasundaram, J. B. Grimm, T. D. Gruber, D. Choquet, J. W. Taraska, L. D. Lavis and D. Perrais, Semisynthetic Fluorescent pH Sensors for Imaging Exocytosis and Endocytosis, *Nat. Commun.*, 2017, **8**, 1-10.
7. H. Zheng, X.-Q. Zhan, Q.-N. Bian and X.-J. Zhang, Advances in Modifying Fluorescein and Rhodamine Fluorophores as Fluorescent Chemosensors, *Chem. Commun.*, 2013, **49**, 429-447.
8. B. N. Hemric, K. Shen and Q. Wang, Copper-Catalyzed Amino Lactonization and Amino Oxygenation of Alkenes Using *o*-Benzoylhydroxylamines, *J. Am. Chem. Soc.*, 2016, **138**, 5813-5816.
9. X. Liu, M. Chen, C. Xiao, N. Xue and L. Zhang, Soluble Twisted Diarenoperylenes: Synthesis, Characterization, and Device Performance, *Org. Lett.*, 2018, **20**, 4512-4515.
10. S. Mondal, C. K. Giri and M. Baidya, Enaminone-Directed Ruthenium(II)-Catalyzed C-H Activation and Annulation of Arenes with Diazonaphthoquinones for Polycyclic Benzocoumarins, *Chem. Commun.*, 2023, **59**, 13187-13190.
11. Y. Kita, T. Yata, Y. Nishimoto, K. Chiba and M. Yasuda, Selective Oxymetalation of Terminal Alkynes *via* 6-endo Cyclization: Mechanistic Investigation and Application to the Efficient Synthesis of 4-Substituted Isocoumarins, *Chem. Sci.*, 2018, **9**, 6041-6052.
12. W.-H. Rao, Q. Li, L.-L. Jiang, Y.-G. Li, P. Xu, X.-W. Deng, M. Li, G.-D. Zou and X. Cao, Photoredox-catalyzed Acyl Lactonization of Alkenes with Aldehydes: Synthesis of Acyl Lactones, *J. Org. Chem.*, 2022, **87**, 14194-14207.
13. G. Golime, H. Y. Kim and K. Oh, Rhodium(I)-Catalyzed Decarbonylative Aerobic Oxidation of Cyclic α-Diketones: A Regioselective Single Carbon Extrusion Strategy, *Org. Lett.*, 2018, **20**, 942-945.