Supporting Information

Ru(II)-Catalyzed C-H Bond Activation/Annulation of N-iminopyridinium Ylides with Sulfoxonium Ylides

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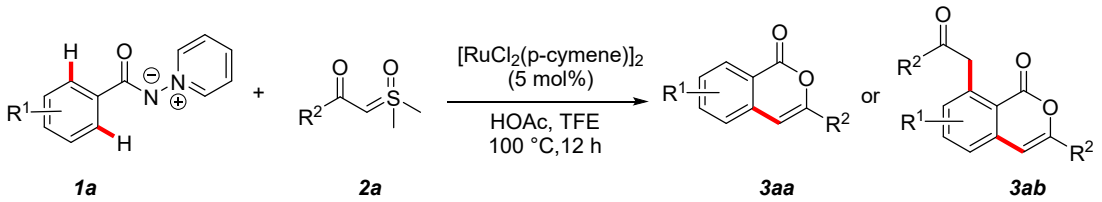
I. General Information.

All reagents and all solvents were used directly as obtained commercially unless otherwise noted. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 ºC on a JEOL 400 MHz and 100 MHz NMR spectrometers or Bruker 600 MHz and 150 MHz NMR spectrometers. For ^{1}H NMR, tetramethylsilane (TMS) served as internal standard (δ=0) and data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant(s) in Hz. For ^{13}C NMR, TMS (δ=0) was used as internal standard and spectra were obtained with complete proton decoupling. HPLC/MS analysis was carried out with gradient elution (5% CH_3CN to 100% CH_3CN) on a Q-Exactive Orbitrap MS (Thermo, MA, USA) mass spectrometer. (also used to produce high resolution mass spectra).

N-iminopyridinium ylides, [1]and sulfoxonium ylides[2], were prepared according to the reported literatures.

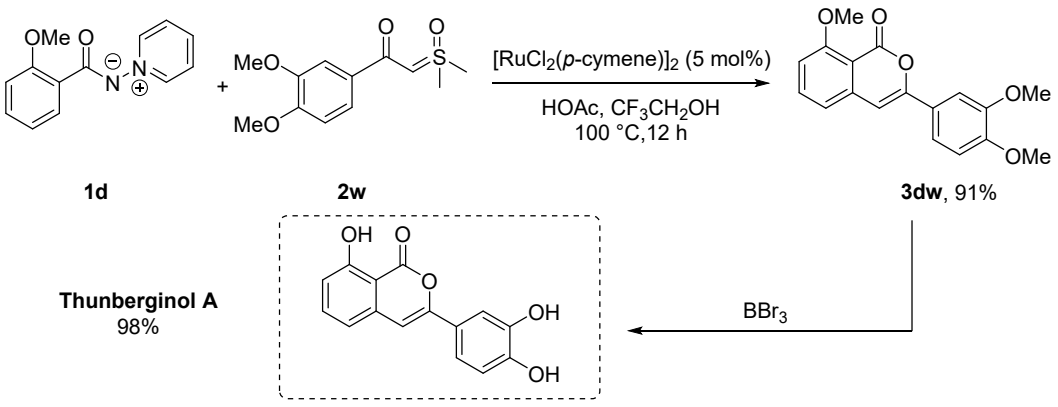
II. General procedure for preparation of 3



Representative Synthesis of Product 3: A glass bottle was charged with **1a** (39.6 mg, 0.2 mmol), **2a** (78.4 mg, 0.4 mmol), $[RuCl_2(p\text{-cymene})]_2$ (6.1 mg, 5 mol %), CH_3COOH (24 mg, 0.4 mmol), and TFE (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 20:1 (v/v) to give the corresponding product **3aa** (39.2 mg, 88%).

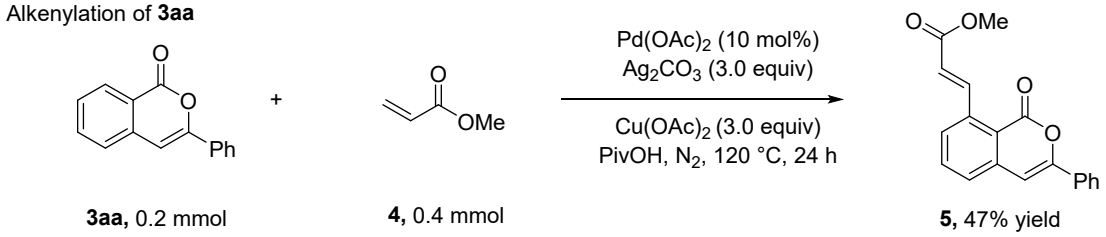
III. Synthesis of thunberginol A and derivatization of 3aa

Synthesis of thunberginol A



A glass bottle was charged with **1d** (45.6 mg, 0.2 mmol), **2w** (102 mg, 0.4 mmol), $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 5 mol %), CH_3COOH (24.0 mg, 0.4 mmol), and TFE (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h, then the solvent was removed and the residue was purified by silica gel chromatography using dichloromethane/methanol 20:1 (v/v) to give **3dw** (57 mg, 91%). Then, the mixture of **3dw** (35.0 mg, 1.12 mmol) and a 1M dichloromethane solution of BBr_3 (5.2 eq, 5.83

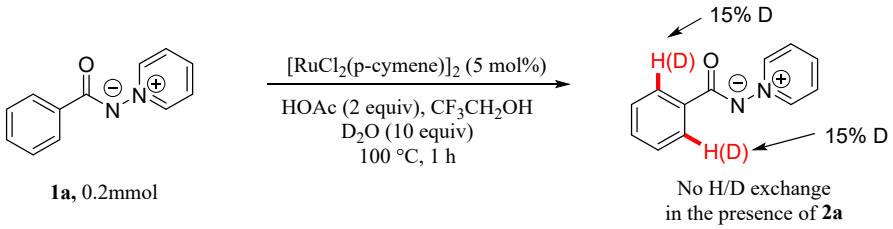
mmol) was stirred at room temperature under nitrogen for 2 hours. The solution was then poured into ice water (10 mL) and the mixture extracted with ethyl acetate (6 × 15 mL). The organic extract was washed with brine (10 mL), dried over magnesium sulphate and reduced in vacuo. The product was purified via flash column chromatography (30:1 Dichloromethane / methanol) to yield the natural product (30.1 mg, 98%) as a pale orange solid.



A Schlenk tube was charged with **3aa** (44.6 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 10 mol %), $Cu(OAc)_2$ (119.8 mg, 3 eq) and Ag_2CO_3 (165.4 mg, 3 eq) were combined in PivOH (2 ml) under N_2. The alkene **4** (34.4 mg, 0.4 mmol) was added slowly and the reaction mixture was heated to 120 ℃. The reaction mixture was diluted with CH_2Cl_2 and the excess $NaHCO_3$ was added to neutralize PivOH. After stirring the mixture for 10 min, the residue was washed with sequencially aqueous $NaHCO_3$ and NH_4Cl. The organic layer was dried over $MgSO_4$. Then the solvent was removed and the residue was purified by silica gel chromatography using dichloromethane/methanol 50:1 (v/v) to give **5** (60.4 mg, 47%).

V. Mechanistic Studies

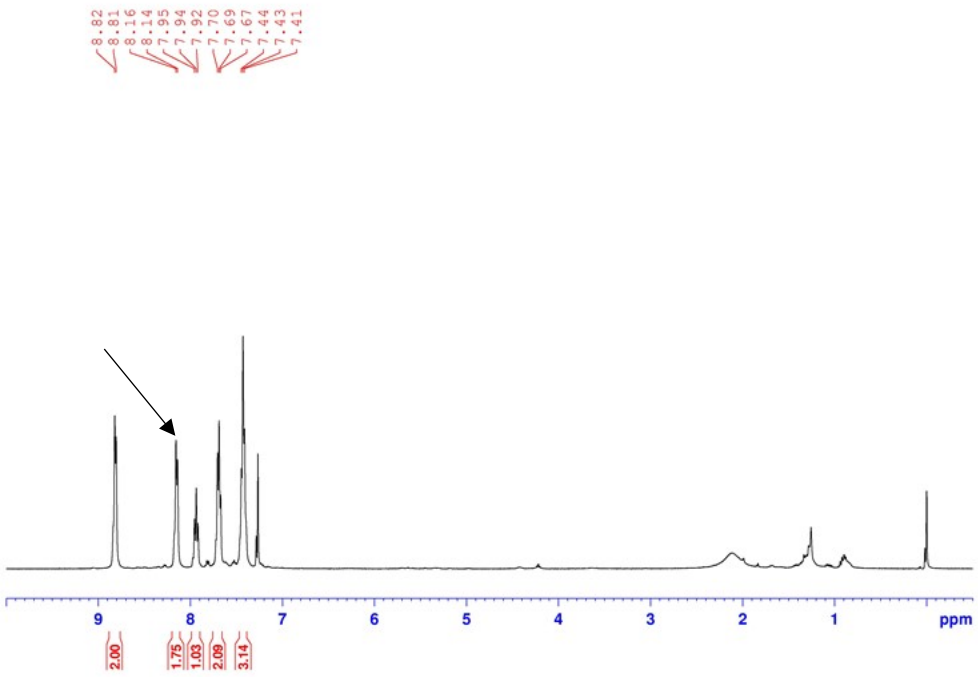
(a) Deuterium Experiments



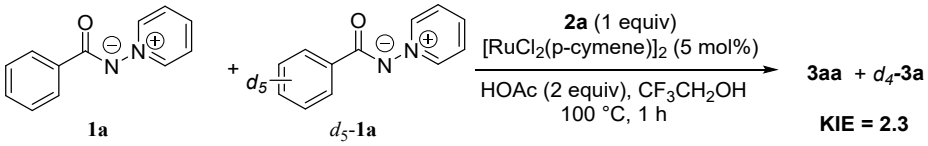
A glass bottle was charged with **1a** (39.6 mg, 0.2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (6.1 mg, 5 mol %), CH_3COOH (24.0 mg, 0.4 mmol), D_2O (32.0 mg, 2mmol) and TFE (2.0 mL). The reaction mixture

was stirred at 100 °C for 1 h, then the solvent was removed and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 20:1 (v/v) to give *d*-**1a** (13 mg). The extent of deuteration was determined on the basis of ^{1}H NMR analysis.

H/D Experiment in the absence of 2a

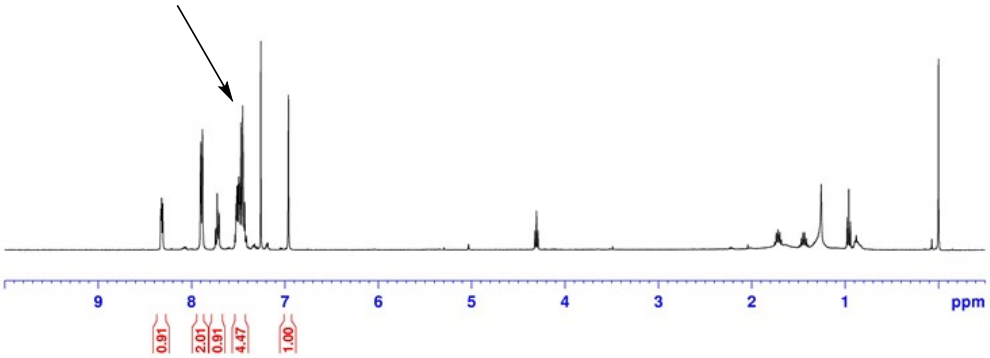


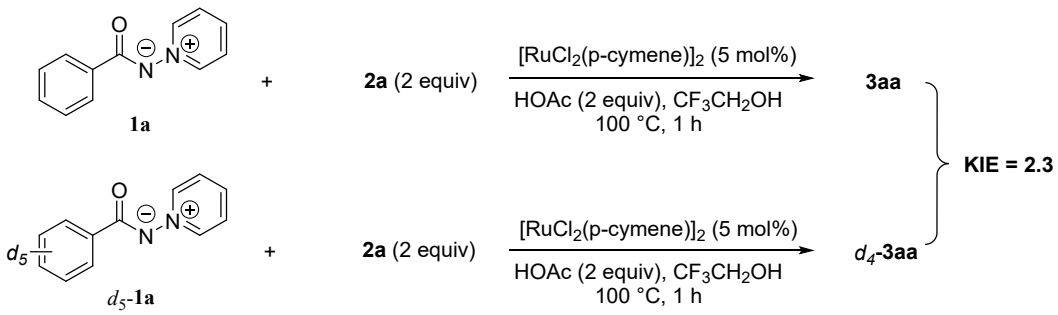
(b) Kinetic isotope effect KIE



A glass bottle was charged with **1a** (39.6 mg, 0.2 mmol), **2a** (78.4 mg, 0.4 mmol), $[RuCl_2(p\text{-cymene})]_2$ (6.1 mg, 5 mol %), CH_3COOH (24 mg, 0.4 mmol), and TFE (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 20:1 (v/v) to give the corresponding product **3aa** (39.2 mg, 88%).

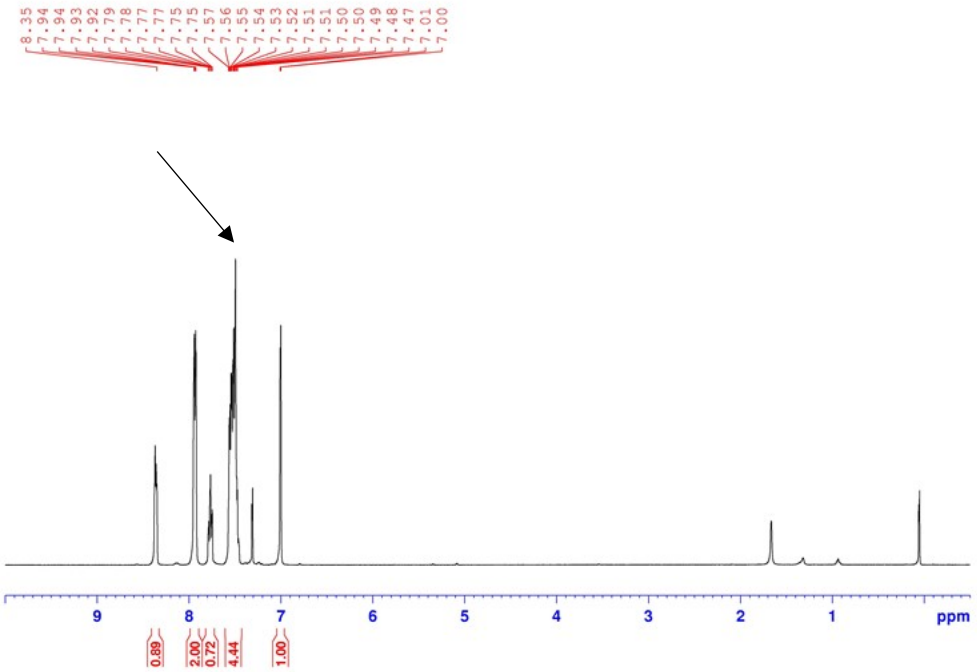
KIE = 2.3



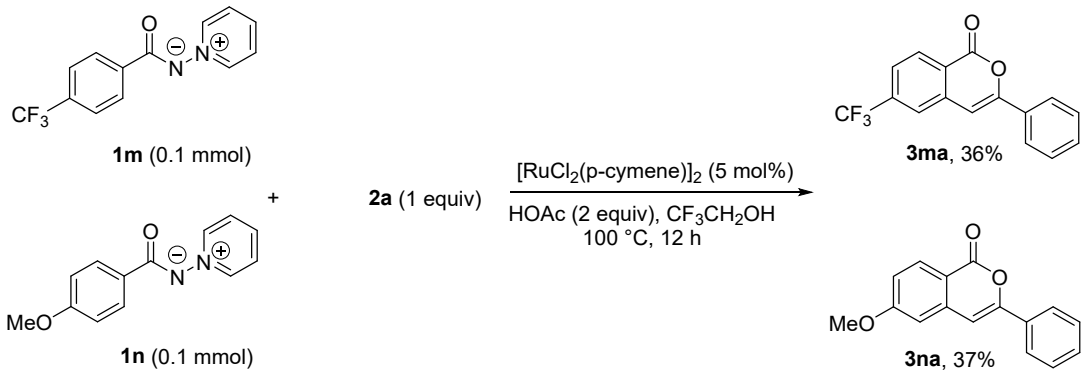


A glass bottle was charged with **1a** (19.8 mg, 0.1 mmol), **2a** (39.2 mg, 0.2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5 mol %), CH_3COOH (12.0 mg, 0.2 mmol), and TFE (1.0 mL). The reaction mixture was stirred at 100 °C for 1 h. And to another bottle was added d_5-**1a** (19.3 mg, 0.1 mmol), **2a** (39.2 mg, 0.2 mmol), $[Cp^*Rh(Cl)_2]_2$ (3.1 mg, 5 mol %), CH_3COOH (12.0 mg, 0.2 mmol), and TFE (1.0 mL). The reaction mixture was stirred at 100 °C for 1 h. After the completion of the reaction, the two reactions were combined, then the solvent was removed and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 20:1 (v/v) to obtain **3aa** and d_4-**3aa** (30mg). KIE value (kH/kD = 2.3) was determined on the basis of ^1H NMR analysis.

KIE = 2.3

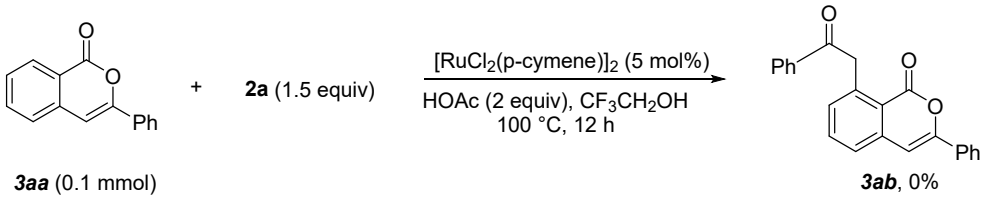


(c) Competitive experiment:



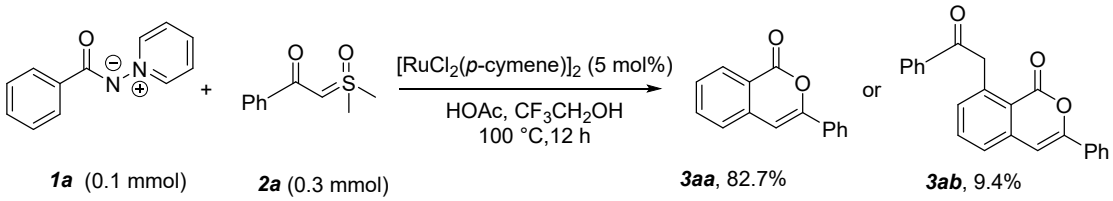
A glass bottle was charged with **1m** (26.6 mg, 0.1 mmol), **1n** (22.8 mg, 0.1 mmol), **2a** (19.6 mg, 0.1 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (3.1 mg, 5 mol %), CH_3COOH (12.0 mg, 0.2 mmol), and TFE (1.0 mL). The reaction mixture was stirred at 100 °C for 12 h, then the solvent was removed and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 20:1 (v/v) to give **3ma** (20.9 mg) and **3na** (18.8 mg) in 36% and 37% yield, respectively.

(d) Control experiment:



A glass bottle was charged with **3aa** (22.3 mg, 0.1 mmol), **2a** (29.4 mg, 0.15 mmol), [$RuCl_2$(*p*-

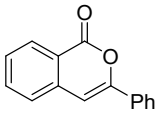
cymene)]$_2$ (3.1 mg, 5 mol %), CH_3COOH (12.0 mg, 0.2 mmol), and TFE (1.0 mL). The reaction mixture was stirred at 100 °C for 12 h. The formation of **3ab** was not observed by TLC, and **3aa** was fully recovered.



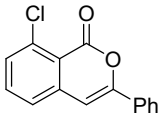
1a (0.1 mmol) ***2a*** (0.3 mmol) ***3aa***, 82.7% ***3ab***, 9.4%

A glass bottle was charged with **1a** (19.8 mg, 0.1 mmol), **2a** (29.4 mg, 0.3 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (3.1 mg, 5 mol %), CH_3COOH (12.0 mg, 0.2 mmol), and TFE (1.0 mL). The reaction mixture was stirred at 100 °C for 24 h, then the solvent was removed and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 20:1 (v/v) to give **3aa** (38.4 mg) and **3ab** (6.4 mg) in 83% and 9% yield, respectively. There was no significant increase in 3ab.

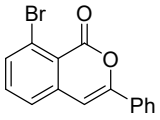
V. Characterization data for products



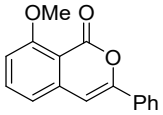
3-phenyl-1H-isochromen-1-one (3aa): white solid (39.2 mg, 88%). (This compound is known.[3]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 7.1 Hz, 2H), 7.71 – 7.67 (m, 1H), 7.48 – 7.42 (m, 5H), 6.92 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 153.6, 137.5, 134.9, 131.9, 130.0, 129.6, 128.8, 128.1, 126.0, 125.2, 120.5, 101.8.



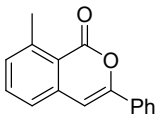
8-chloro-3-phenyl-1H-isochromen-1-one (3ba): white solid (41 mg, 80%). (This compound is known.[3]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.85 (m, 2H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.49 – 7.45 (m, 4H), 7.37 (d, *J* = 7.6 Hz, 1H), 6.87 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 154.3, 140.6, 137.2, 134.5, 131.4, 130.9, 130.3, 128.9, 125.3, 124.9, 117.6, 101.5.



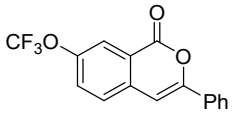
8-bromo-3-phenyl-1H-isochromen-1-one (3ca): white solid (26.8mg, 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 6.3 Hz, 2H), 7.73 (d, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 5H), 6.89 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 154.0, 140.6, 134.7, 134.6, 131.3, 130.3, 128.9, 125.7, 125.3, 125.0, 118.8, 101.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{15}H_9BrNaO_2^+$ ([M+Na]$^+$) 322.9678, found 322.9675.



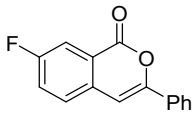
8-methoxy-3-phenyl-1H-isochromen-1-one (3da): white solid (34.4 mg, 68%). (This compound is known.[4]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 6.8 Hz, 2H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.07 (d, J = 7.7 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 4.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 159.0, 154.0, 140.5, 135.8, 131.9, 130.0, 128.8, 125.3, 118.1, 109.9, 109.3, 101.8, 56.3.



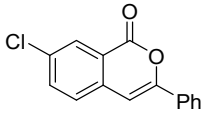
8-methyl-3-phenyl-1H-isochromen-1-one (3ea): white solid (26.2 mg, 55%). (This compound is known.[5]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.33 – 7.29 (m, 2H), 6.89 (s, 1H), 2.86 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.7, 153.2, 143.6, 139.1, 134.0, 132.0, 131.1, 129.8, 128.8, 125.2, 124.2, 119.0, 102.3, 23.2.



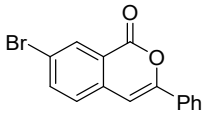
3-phenyl-7-(trifluoromethoxy)-1H-isochromen-1-one (3fa): white solid (53.4 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.89 – 7.86 (m, 2H), 7.56 (s, 2H), 7.48 – 7.45 (m, 3H), 6.96 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 154.2, 148.4, 136.1, 131.5, 130.3, 128.9, 128.1, 127.9, 125.3, 121.7, 121.1, 119.1, 100.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_9F_3NaO_3^+$ ([M+Na]$^+$) 329.0396, found 329.0391.



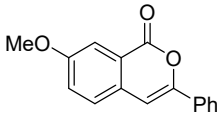
7-fluoro-3-phenyl-1H-isochromen-1-one (3ga): light yellow solid (28.2 mg, 59%). (This compound is known.[6]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.10 (m, 1H), 7.90 (d, *J* = 6.7 Hz, 1H), 7.47 – 7.42 (m, 5H), 7.16 (d, *J* = 1.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 157.3(d, *J* = 253.3 Hz), 154.3, 131.7, 130.3, 128.9, 128.4 (d, *J* = 7.7 Hz), 126.7 (d, *J* = 16.8 Hz), 125.4, 125.3(d, *J* = 4.2 Hz), 121.9 (d, *J* = 3.9 Hz), 120.2 (d, *J* = 19.8 Hz), 94.2 (d, *J* = 4.8 Hz).



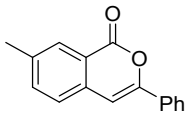
7-chloro-3-phenyl-1H-isochromen-1-one (3ha): light yellow solid (20.0 mg, 39%). (This compound is known.[9]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 6.6 Hz, 2H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 6.2 Hz, 3H), 7.43 – 7.39 (m, 1H), 7.31(s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 154.6, 135.6, 135.1, 131.7, 130.6, 130.5, 128.9, 128.5, 128.2, 125.6, 122.0, 98.0.



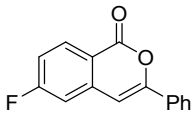
7-bromo-3-phenyl-1H-isochromen-1-one (3ia): white solid (16.2 mg, 27%). (This compound is known.[5]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.9 Hz, 1H), 7.93 (t, *J* = 7.6 Hz, 3H), 7.48 (d, *J* = 6.8 Hz, 3H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.30 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 154.7, 138.6, 137.0, 131.7, 130.4, 129.2, 128.9, 128.6, 125.6, 122.1, 120.7, 100.5.



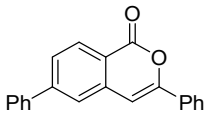
7-methoxy-3-phenyl-1H-isochromen-1-one (3ja): white solid (20.4 mg, 40%). (This compound is known.[6]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.73 (s, 1H), 7.47 – 7.38 (m, 4H), 7.31 (d, *J* = 8.4 Hz, 1H), 6.93 (s, 1H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 159.6, 151.7, 132.1, 131.2, 129.6, 128.8, 127.6, 124.9, 124.7, 121.7, 110.0, 101.6, 55.8.



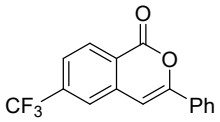
7-methyl-3-phenyl-1H-isochromen-1-one (3ka): white solid (44.8 mg, 95%). (This compound is known.[3]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.87 (d, *J* = 6.7 Hz, 2H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.45 – 7.39 (m, 4H), 6.93 (s, 1H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 152.8, 138.5, 136.2, 135.0, 132.1, 129.7, 129.4, 128.8, 125.9, 125.1, 120.4, 101.8, 21.4.



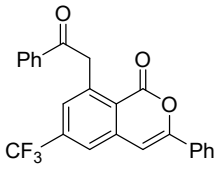
6-fluoro-3-phenyl-1H-isochromen-1-one (3la): white solid (39.4 mg, 82%). (This compound is known.[3]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 – 8.31 (m, 1H), 7.87 (d, *J* = 5.1 Hz, 2H), 7.46 (s, 3H), 7.20 – 7.13 (m, 2H), 6.91 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 165.5, 161.4, 154.9, 140.2 (d, *J* = 10.8 Hz), 133.0 (d, *J* = 10.5 Hz), 131.6, 130.4, 128.9, 125.4, 117.0, 116.5 (d, *J* = 23.4 Hz), 111.5 (d, *J* = 22.7 Hz) 101.2.



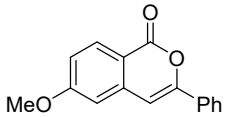
3,6-diphenyl-1H-isochromen-1-one (3ma): yellow solid (54.2 mg, 91%). (This compound is known.[3]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 6.9 Hz, 2H), 7.71 – 7.66 (m, 4H), 7.52 – 7.45 (m, 6H), 7.00 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.3, 154.0, 147.7, 139.5, 138.0, 130.3, 130.0, 129.1, 128.9, 128.7, 127.4, 127.2, 125.3, 124.2, 119.3, 102.0



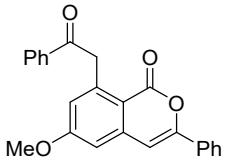
3-phenyl-6-(trifluoromethyl)-1H-isochromen-1-one (3na): white solid (41.8 mg, 72%). (This compound is known.[3]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 5.4 Hz, 2H), 7.77 (s, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.47 (s, 3H), 7.00 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 155.1, 137.9, 136.3 (q, *J* = 33.1 Hz), 131.3, 130.6, 130.6, 129.0, 125.4, 124.2 (q, *J* = 3.3 Hz), 123.1 (q, *J* = 4.0 Hz), 122.8, 121.9, 101.0.



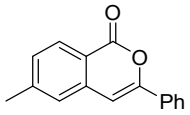
8-(2-oxo-2-phenylethyl)-3-phenyl-6-(trifluoromethyl)-1H-isochromen-1-one (3na'): white solid (21.1 mg, 26%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 5.8 Hz, 2H), 7.84 (s, 2H), 7.73 (s, 1H), 7.62 (s, 1H), 7.54 – 7.50 (m, 3H), 7.45 (s, 3H), 7.00 (s, 1H), 4.96 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 160.7, 154.8, 141.1, 139.8, 137.0, 135.7, 135.4, 133.2, 131.1, 130.5, 128.9, 128.7, 128.2, 128.0, 125.3, 122.7, 121.5, 101.7, 45.7. HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{15}F_3NaO_3^+$ ($[M+Na]^+$) 431.0866, found 431.0861.



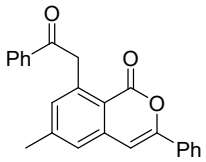
6-methoxy-3-phenyl-1H-isochromen-1-one (3oa): white solid (25.3 mg, 50%). (This compound is known.[3]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 1H), 7.88 (d, *J* = 6.8 Hz, 2H), 7.45 (d, *J* = 7.3 Hz, 3H), 7.02 (d, *J* = 8.7 Hz, 1H), 6.87 (d, *J* = 5.4 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 162.1, 154.1, 139.8, 132.0, 131.8, 130.0, 128.8, 125.3, 116.5, 113.7, 108.0, 101.8, 55.6.



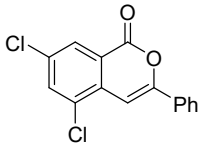
6-methoxy-8-(2-oxo-2-phenylethyl)-3-phenyl-1H-isochromen-1-one (3oa'): white solid (30.9 mg, 42%). (This compound is known.[5]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 1H), 7.88 (d, *J* = 6.8 Hz, 2H), 7.45 (d, *J* = 7.3 Hz, 3H), 7.02 (d, *J* = 8.7 Hz, 1H), 6.87 (d, *J* = 5.4 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 162.1, 154.1, 139.8, 132.0, 131.8, 130.0, 128.8, 125.3, 116.5, 113.7, 108.0, 101.8, 55.6.



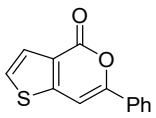
***6-methyl-3-phenyl-1H-isochromen-1-one (3pa)*: white solid (28.0 mg, 59%)**. (This compound is known.[3]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.0 Hz, 1H), 7.87 (d, *J* = 7.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 3H), 7.28 (s, 2H), 6.88 (s, 1H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 153.7, 146.0, 137.6, 132.1, 129.9, 129.6, 129.6, 128.8, 126.0, 125.2, 118.2, 101.8, 22.0.



6-methyl-8-(2-oxo-2-phenylethyl)-3-phenyl-1H-isochromen-1-one (3pa'): white solid (21.2 mg, 30%). (This compound is known.[5]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.3 Hz, 2H), 7.82 (d, *J* = 6.6 Hz, 2H), 7.58 (d, *J* = 6.8 Hz, 1H), 7.52 – 7.49 (m, 2H), 7.42 (d, *J* = 7.2 Hz, 3H), 7.13 (s, 1H), 6.89 (s, 1H), 4.86 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 161.7, 153.4, 145.3, 139.5, 139.4, 137.4, 133.6, 132.9, 131.9, 129.8, 128.8, 128.6, 128.3, 125.8, 125.1, 116.7, 102.3, 45.5, 21.7.

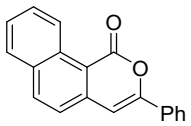


5,7-dichloro-3-phenyl-1H-isochromen-1-one (3qa): white solid (39.6 mg, 68%). (This compound is known.[6]) ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 (s, 1H), 8.12 (s, 1H), 7.99 (d, *J* = 3.5 Hz, 2H), 7.57 (s, 3H), 7.41 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.4, 154.9, 135.1, 134.2, 133.5, 131.5, 131.4, 130.7, 129.0, 128.1, 125.6, 122.6, 97.4.

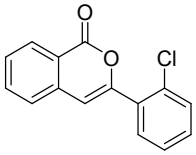


6-phenyl-4H-thieno[3,2-c]pyran-4-one (3ra): white solid (18.4 mg, 20%). (This compound is known.[3]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 3H), 7.46 (d, *J* = 6.5 Hz, 3H), 7.26 (d, *J* = 1.8 Hz, 1H), 7.13 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 156.4, 147.5, 136.8, 131.9, 130.1,

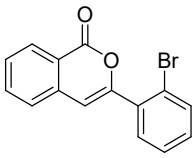
128.9, 125.4, 124.7, 123.0, 99.1.



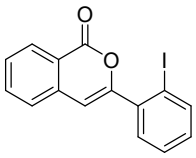
3-phenyl-1H-benzo[h]isochromen-1-one (3sa): yellow solid (50.8 mg, 93%). (This compound is known.[7]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.91 (s, br, 4H), 7.65 – 7.61 (m, 1H), 7.56 – 7.52 (m, 1H), 7.49 – 7.43 (m, 3H), 7.07 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 152.0, 136.6, 132.4, 132.2, 132.2, 132.0, 129.8, 129.4, 128.8, 127.7, 126.7, 125.2, 124.3, 119.0, 101.9.



3-(2-chlorophenyl)-1H-isochromen-1-one (3ab): white solid (38.4 mg, 75%). (This compound is known.[8]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.8 Hz, 1H), 7.77 – 7.73 (m, 2H), 7.57 – 7.49 (m, 3H), 7.37 (s, 2H), 6.99 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 151.4, 137.0, 134.9, 132.4, 131.6, 130.7, 129.6, 128.7, 127.0, 126.2, 120.7, 107.7.

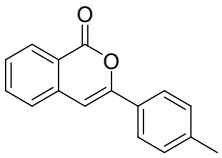


3-(2-bromophenyl)-1H-isochromen-1-one (3ac): white solid (51.4 mg, 85%). (This compound is known.[7]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.9 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.27 (m, 1H), 6.87 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.3, 153.0, 136.9, 134.9, 133.8, 131.0, 131.0, 129.7, 128.7, 127.5, 126.2, 121.9, 120.7, 107.4.

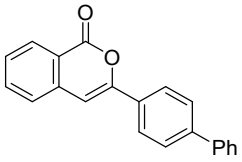


3-(2-iodophenyl)-1H-isochromen-1-one (3ad): white solid (50.8 mg, 93%). (This compound is

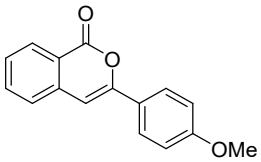
known.[9]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.9 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.58 – 7.51 (m, 3H), 7.46 – 7.42 (m, 1H), 7.15 – 7.11 (m, 1H), 6.74 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.3, 155.4, 140.2, 137.9, 136.9, 134.9, 131.1, 130.5, 129.7, 128.7, 128.2, 126.1, 120.7, 107.2, 96.4.



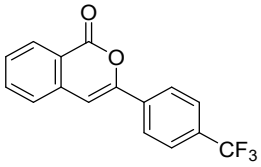
3-(p-tolyl)-1H-isochromen-1-one (3ae): white solid (33.6 mg, 71%). (This compound is known.[6]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 7.4 Hz, 2H), 7.72 – 7.68 (m, 1H), 7.48 (s, 2H), 7.27 (s, 1H), 6.90 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 153.8, 140.3, 137.7, 134.8, 129.6, 129.5, 129.2, 127.9, 125.8, 125.2, 120.4, 101.1, 21.4.



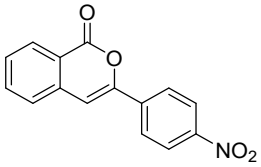
3-([1,1'-biphenyl]-4-yl)-1H-isochromen-1-one (3af): white solid (47.0 mg, 79%). (This compound is known.[6]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 7.7 Hz, 2H), 7.69 – 7.65 (m, 3H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.48 – 7.43 (m, 4H), 7.39 – 7.35 (m, 1H), 6.96 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 153.4, 142.7, 140.0, 137.6, 134.9, 130.8, 129.7, 128.9, 128.2, 127.9, 127.4, 127.1, 126.0, 125.7, 120.6, 101.8.



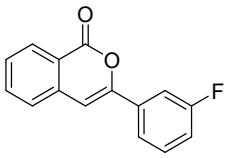
3-(4-methoxyphenyl)-1H-isochromen-1-one (3ag): white solid (33.9 mg, 67%). (This compound is known.[6]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.71 – 7.67 (m, 1H), 7.46 – 7.45 (m, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.82 (s, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 161.1, 153.7, 137.9, 134.8, 129.6, 127.7, 126.8, 125.7, 124.5, 120.1, *114*.2, 100.2, 55.4.



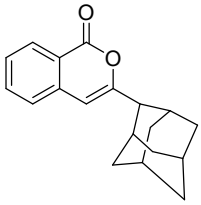
3-(4-(trifluoromethyl)phenyl)-1H-isochromen-1-one (3ah): white solid (42.0 mg, 72%) .(This compound is known.[3]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 7.9 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.76 – 7.71 (m, 3H), 7.57 – 7.53 (m, 2H), 7.05 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 152.0, 136.9, 135.3, 135.1, 131.8, 131.4, 129.8, 128.9, 126.3, 125.8 (q, *J* = 3.6 Hz), 125.5, 120.9, 103.4.



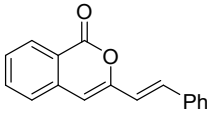
3-(4-nitrophenyl)-1H-isochromen-1-one (3ai): white solid (15.1 mg, 28%). (This compound is known.[8]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.32 (m, 3H), 8.07 (d, *J* = 8.5 Hz, 2H), 7.79 (t, *J* = 7.0 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.14 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 151.1, 148.3, 137.8, 136.5, 135.3, 129.9, 129.4, 126.6, 125.9, 124.2, 121.0, 104.9.



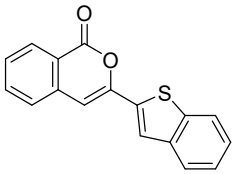
3-(3-fluorophenyl)-1H-isochromen-1-one (3aj): white solid (26.2 mg, 54%). (This compound is known.[6]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.9 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 9.8 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.46 – 7.41 (m, 1H), 7.13 (t, *J* = 8.2 Hz, 1H), 6.97 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 162.0 (d, *J* = 8.3 Hz), 152.3, 137.1, 135.0, 134.2 (d, *J* = 8.1 Hz), 130.5 (d, *J* = 8.3 Hz), 129.8, 128.6, 126.2, 120.9 (d, *J* = 2.8 Hz), 120.7, 116.9 (d, *J* = 21.4 Hz), 112.3 (d, *J* = 24.0 Hz), 102.6.



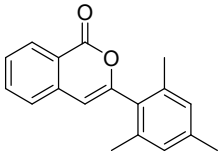
3-((1S,2S,5R,7S)-adamantan-2-yl)-1H-isochromen-1-one (3ak): white solid (25.6 mg, 46%). (This compound is known.[3]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.8 Hz, 1H), 7.68 – 7.65 (m, 1H), 7.46 – 7.42 (m, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 6.22 (s, 1H), 2.10 (s, 3H), 1.96 (s, 6H), 1.77 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 163.2, 137.8, 134.6, 129.4, 127.5, 125.5, 120.3, 99.7, 39.7, 37.2, 36.6, 28.0.



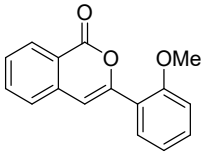
(E)-3-styryl-1H-isochromen-1-one (3al): white solid (42.6 mg, 86%). (This compound is known.[10]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.0 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.48 – 7.36 (m, 5H), 7.32 (d, *J* = 7.1 Hz, 1H), 6.71(d, *J* = 7.6 Hz, 1H), 6.46 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 152.6, 137.6, 135.8, 134.9, 133.0, 129.9, 128.9, 128.1, 127.1, 125.8, 120.9, 119.4, 105.8.



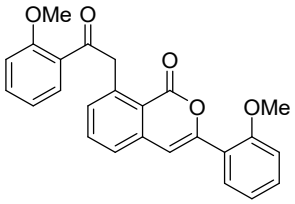
3-(benzo[b]thiophen-2-yl)-1H-isochromen-1-one (3am): white solid (36.7 mg, 66%). (This compound is known.[8]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.8 Hz, 1H), 7.81 (s, 1H), 7.76 (s, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.35 – 7.33 (m, 2H), 6.78 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 149.2, 139.7, 139.6, 137.0, 135.0, 134.9, 129.8, 128.4, 126.0, 125.8, 125.0, 124.5, 123.3, 122.3, 120.6, 102.9.



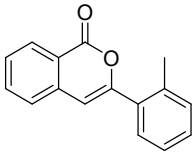
3-mesityl-1H-isochromen-1-one (3an): white solid (17.6 mg, 33%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.0 Hz, 1H), 7.80 – 7.77 (m, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 6.98 (s, 2H), 6.48 (s, 1H), 2.37 (s, 3H), 2.31 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 154.3, 139.4, 137.3, 134.8, 130.1, 129.6, 128.4, 128.2, 125.6, 120.4, 107.2, 60.4, 21.2, 20.0. HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{16}NaO_2^+$ ([M+Na]$^+$) 287.1043, found 287.1036.



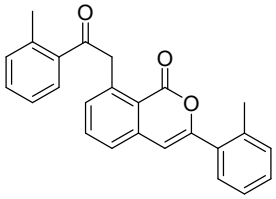
3-(2-methoxyphenyl)-1H-isochromen-1-one (3ao): white solid (33.7 mg, 67%). (This compound is known.[6]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.9 Hz, 1H), 8.03 – 8.01 (m, 1H), 7.77 – 7.73 (m, 1H), 7.55 – 7.51 (m, 2H), 7.45 – 7.41 (m, 2H), 7.14 – 7.05 (m, 2H), 4.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 157.2, 150.4, 138.1, 134.7, 130.8, 129.4, 128.8, 128.0, 126.3, 120.9, 120.7, 120.6, 111.4, 107.0, 55.6.



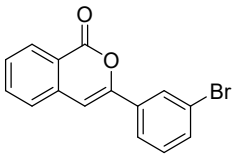
3-(2-methoxyphenyl)-8-(2-(2-methoxyphenyl)-2-oxoethyl)-1H-isochromen-1-one (3ao'): white solid (15.2 mg, 19%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 7.4 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.49 – 7.42 (m, 2H), 7.37 (s, 2H), 7.30 (d, *J* = 7.0 Hz, 1H), 7.06 – 6.99 (m, 4H), 4.88 (s, 2H), 3.96 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 161.8, 158.5, 157.2, 150.0, 140.0, 139.8, 134.0, 133.2, 132.0, 130.8, 130.6, 128.7, 128.7, 125.8, 120.8, 120.7, 119.2, 111.4, 111.3, 107.6, 55.6, 55.6, 50.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{20}NaO_5^+$ ([M+Na]$^+$) 423.1203, found 423.1193



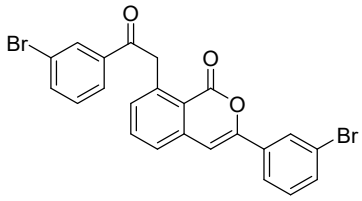
3-(o-tolyl)-1H-isochromen-1-one (3ap): white solid (29.7 mg, 63%). (This compound is known.[3]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 7.8 Hz, 1H), 7.75 – 7.72 (m, 1H), 7.54 – 7.47 (m, 3H), 7.37 – 7.33 (m, 1H), 7.29 (s, 1H), 6.61 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 155.6, 137.5, 136.8, 134.8, 132.8, 131.1, 129.8, 129.6, 129.2, 126.0, 125.8, 120.3, 105.9, 20.8.



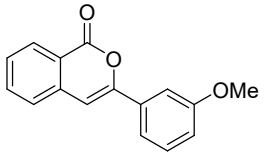
8-(2-oxo-2-(o-tolyl)ethyl)-3-(o-tolyl)-1H-isochromen-1-one (3ap'): white solid (19.9 mg, 27%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.4 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.51 (d, *J* = 7.1 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.1 Hz, 1H), 7.33 (d, *J* = 6.8 Hz, 3H), 7.28 (s, 1H), 6.61 (s, 1H), 4.84 (s, 2H), 2.50 (d, *J* = 6.8 Hz, 6H)). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.7, 162.0, 155.3, 139.5, 139.4, 138.5, 138.0, 136.8, 136.0, 134.3, 132.5, 132.3, 131.9, 131.2, 131.1, 129.7, 129.1, 128.7, 126.0, 125.7, 119.0, 106.5, 48.6, 21.2, 20.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{20}NaO_3^+$ ($[M+Na]^+$) 391.1305, found 391.1297.



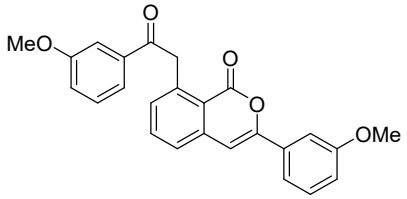
3-(3-bromophenyl)-1H-isochromen-1-one (3aq): white solid (51.4 mg, 85%). (This compound is known.[11]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.8 Hz, 1H), 8.01 (s, 1H), 7.80 – 7.71 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 3H), 7.34 – 7.30 (m, 1H), 6.94 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 152.0, 137.1, 135.0, 133.9, 132.8, 130.3, 129.7, 128.6, 128.2, 126.2, 123.7, 123.1, 120.7, 102.7.



3-(3-bromophenyl)-8-(2-(3-bromophenyl)-2-oxoethyl)-1H-isochromen-1-one (3aq'): white solid (11.7 mg, 12%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.98 (s, 1H), 7.76 – 7.69 (m, 3H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 5.4 Hz, 2H), 6.96 (s, 1H), 4.83 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 161.4, 151.8, 139.1, 139.1, 139.0, 135.9, 134.6, 133.6, 132.9, 132.6, 131.3, 130.3, 130.2, 128.1, 126.8, 126.1, 123.6, 123.1, 123.0, 119.1, 103.2, 45.7. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{14}Br_2NaO_3^+$ ($[M+Na]^+$) 518.9202, found 518.9183.

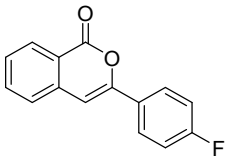


3-(3-methoxyphenyl)-1H-isochromen-1-one (3ar): white solid (37.8 mg, 75%). (This compound is known.[6]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.9 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.54 – 7.49 (m, 3H), 7.46 (s, 1H), 7.43 – 7.39 (m, 1H), 7.03 – 6.98 (m, 2H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 160.0, 153.4, 137.5, 134.9, 133.4, 129.9, 129.7, 128.2, 126.0, 120.6, 117.7, 116.0, 110.5, 102.1, 55.5.

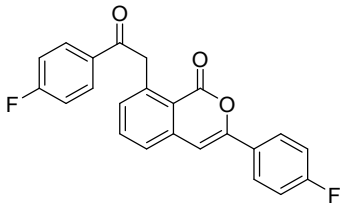


8-(2-oxo-2-(o-tolyl)ethyl)-3-(o-tolyl)-1H-isochromen-1-one (3ar'): white solid (18.4 mg, 23%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.50 – 7.44 (m, 3H), 7.40 – 7.30 (m, 3H), 7.18 (d, *J* = 7.9 Hz, 1H), 6.99 (d, *J* = 6.8 Hz, 2H), 4.93 (s, 2H), 3.90 (d, *J* = 9.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 161.7, 160.0, 159.8, 153.1, 139.5, 139.3, 138.6, 134.3, 133.1, 132.2, 129.8, 129.6, 125.8, 120.9, 119.5, 119.1, 117.6, 116.1, 112.5, 110.2, 102.6,

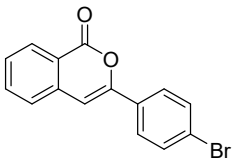
55.4, 45.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{20}NaO_5^+$ ([M+Na]$^+$) 423.1203, found 423.1193.



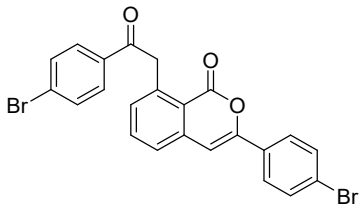
3-(4-fluorophenyl)-1H-isochromen-1-one (3as): white solid (29.7 mg, 62%). (This compound is known.[6]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.8 Hz, 1H), 7.89 – 7.86 (m, 2H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.15 (t, *J* = 8.7 Hz, 2H), 6.88 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 162.1, 152.8, 137.4, 134.9, 129.7, 128.3 (d, *J* = 3.1 Hz), 128.2, 127.3 (d, *J* = 8.5 Hz), 125.9, 120.4, 116.0 (d, *J* = 22.1 Hz), 101.5.



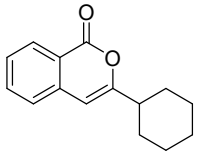
3-(4-fluorophenyl)-8-(2-(4-fluorophenyl)-2-oxoethyl)-1H-isochromen-1-one (3as'): white solid (23.3 mg, 31%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.17 (m, 2H), 7.88 – 7.85 (m, 2H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.25 – 7.16 (m, 4H), 6.94 (s, 1H), 4.91 (s, 2H). ^{13}C NMR (150 MHz, DMSO) δ 195.9, 165.4 (d, *J* = 249.9 Hz), 163.5 (d, *J* = 246.3 Hz), 161.0, 151.7, 140.0, 139.3, 135.2, 134.2, 133.0, 131.4 (d, *J* = 9.3 Hz), 128.5 (d, *J* = 2.5 Hz), 127.7 (d, *J* = 8.6 Hz), 126.4, 118.8, 116.6 (d, *J* = 21.9 Hz), 116.2 (d, *J* = 21.7 Hz), 103.0, 45.7. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{14}F_2NaO_3^+$ ([M+Na]$^+$) 399.0803, found 399.0798.



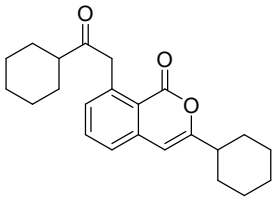
3-(4-bromophenyl)-1H-isochromen-1-one (3at): white solid (45.9 mg, 76%). (This compound is known.[3]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.7 Hz, 1H), 7.75 – 7.71 (m, 3H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.53 – 7.48 (m, 2H), 6.94 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 152.6, 137.2, 135.0, 132.1, 130.9, 128.5, 126.7, 126.1, 124.3, 120.6, 102.1.



3-(4-bromophenyl)-8-(2-(4-bromophenyl)-2-oxoethyl)-1H-isochromen-1-one (3at'): white solid (10.5 mg, 11%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.70 – 7.64 (m, 5H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 1H), 6.95 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 161.5, 152.4, 139.3, 139.2, 136.1, 134.5, 132.5, 132.1, 131.9, 130.6, 129.8, 128.1, 126.6, 126.0, 124.4, 119.0, 102.7, 45.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{14}Br_2NaO_3^+$ ($[M+Na]^+$) 518.9202, found 518.9197.

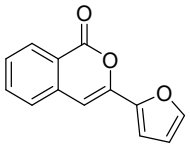


3-cyclohexyl-1H-isochromen-1-one (3au): white solid (32.6 mg, 71%). (This compound is known.[6]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.9 Hz, 1H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 6.23 (s, 1H), 2.48 – 2.41 (m, 1H), 2.04 (d, *J* = 12.2 Hz, 2H), 1.85 (d, *J* = 12.6 Hz, 2H), 1.48 – 1.23 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.2, 162.4, 137.8, 134.6, 129.5, 127.5, 125.2, 120.3, 100.9, 41.9, 30.6, 26.0.

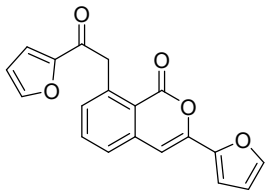


3-cyclohexyl-8-(2-cyclohexyl-2-oxoethyl)-1H-isochromen-1-one (3au'): white solid (12.0 mg, 17%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.9 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.27 – 7.26 (m, 1H), 7.12 (d, *J* = 7.3 Hz, 1H), 6.19 (s, 1H), 4.30 (s, 2H), 2.72 – 2.64 (m, 1H), 2.41 – 2.35 (m, 1H), 2.07 – 1.97 (m, 4H), 1.84 – 1.80 (m, 4H), 1.74 – 1.67 (m, 2H), 1.47 – 1.21 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.7, 162.5, 161.9, 139.5, 139.4, 134.0, 131.5, 124.8, 118.6, 101.5, 50.9, 47.8, 41.7, 30.5, 28.6, 26.0, 25.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{28}NaO_3^+$ ($[M+Na]^+$)

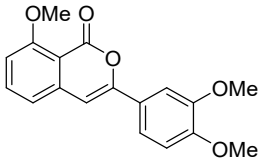
375.1931, found 375.1923.



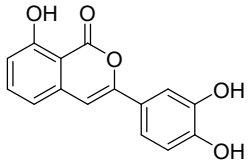
3-(furan-2-yl)-1H-isochromen-1-one (3av): white solid (20.8mg, 49%). (This compound is known.[7]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.1 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.51 (s, 1H), 7.48 – 7.45 (m, 2H), 6.94 (d, *J* = 2.8 Hz, 1H), 6.86 (s, 1H), 6.54 – 6.53 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 146.9, 146.1, 144.0, 137.3, 135.0, 129.8, 128.0, 126.0, 120.5, 112.1, 110.1, 100.0.



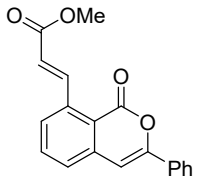
3-(furan-2-yl)-8-(2-(furan-2-yl)-2-oxoethyl)-1H-isochromen-1-one (3av'): white solid (10.2 mg, 16%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 2H), 7.49 (s, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 4.6 Hz, 2H), 6.57 (s, 1H), 6.50 (s, 1H), 4.75 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.9, 161.0, 154.6, 152.9, 146.8, 146.1, 146.0, 144.0, 139.2, 138.8, 134.4, 132.3, 125.9, 119.0, 117.0, 112.3, 112.1, 110.1, 100.6, 45.3. HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{12}NaO_5^+$ ($[M+Na]^+$) 343.0577, found 343.0572.



3-(3,4-dimethoxyphenyl)-8-methoxy-1H-isochromen-1-one (3dw): Yellow solid (57 mg, 91%). (This compound is known.[12]) ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.73 – 7.69 (m, 1H), 7.44 (d, *J* = 7.1 Hz, 1H), 7.38 (s, 1H), 7.27 (s, 1H), 7.13 (d, *J* = 6.9 Hz, 1H), 7.08 – 7.05 (m, 2H), 3.86 (t, *J* = 18.5 Hz, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.5, 158.0, 153.2, 150.9, 149.3, 140.8, 136.8, 124.4, 118.4, 118.4, 112.0, 110.6, 108.4, 100.9, 56.4, 56.1, 56.0.



3-(3,4-dihydroxyphenyl)-8-hydroxy-1H-isochromen-1-one (thunberginol A): Pale orange solid (30.1 mg, 98%). (This compound is known.[12]) ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.85 (s, 1H), 9.58 (s, 1H), 9.31 (s, 1H), 7.68 (t, J = 7.9 Hz, 1H), 7.28 (s, 1H), 7.23 (d, J = 9.0 Hz, 2H), 7.09 (d, J = 7.6 Hz, 1H), 6.92 (d, J = 8.2 Hz, 1H), 6.86 (d, J = 8.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.6, 160.9, 153.2, 148.3, 146.1, 139.0, 138.1, 122.8, 117.4, 117.0, 116.5, 114.5, 112.6, 105.7, 101.1.



methyl (E)-3-(1-oxo-3-phenyl-1H-isochromen-8-yl)acrylate (5): white solid (20.8mg, 49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 7.6 Hz, 1H), 8.21 (d, J = 15.8 Hz, 1H), 7.96 – 7.93 (m, 3H), 7.54 – 7.48 (m, 4H), 7.25 (d, J = 12.2 Hz, 1H), 6.51 (d, J = 15.7 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 161.9, 154.4, 139.4, 136.1, 132.8, 131.8, 131.6, 130.6, 130.4, 128.9, 127.9, 125.6, 121.9, 121.3, 97.5, 52.0. HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{14}NaO_4^+$ ([M+Na]$^+$) 329.0784, found 329.0779.

VI. References

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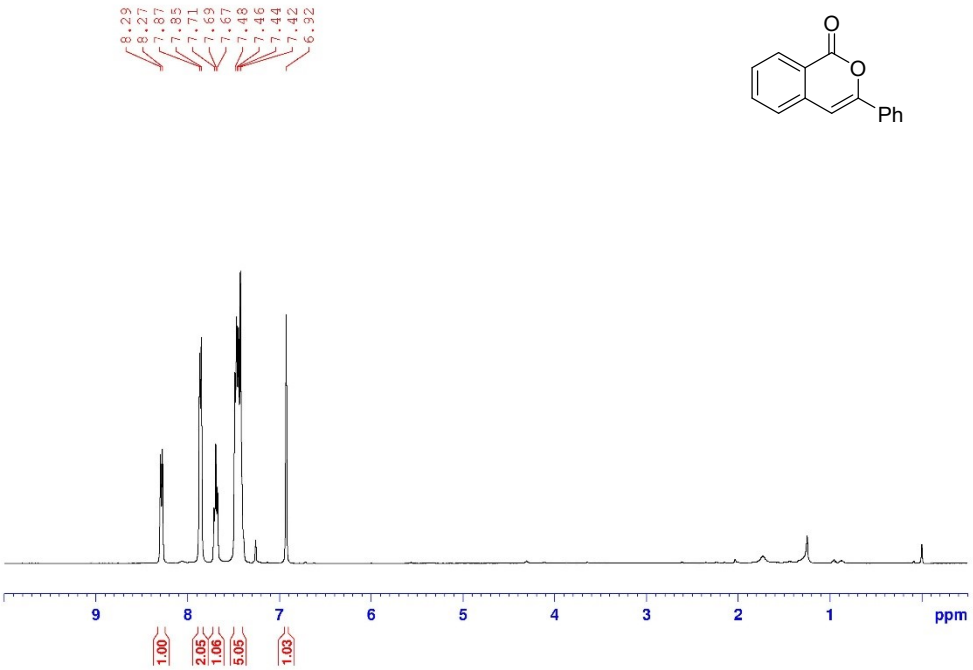
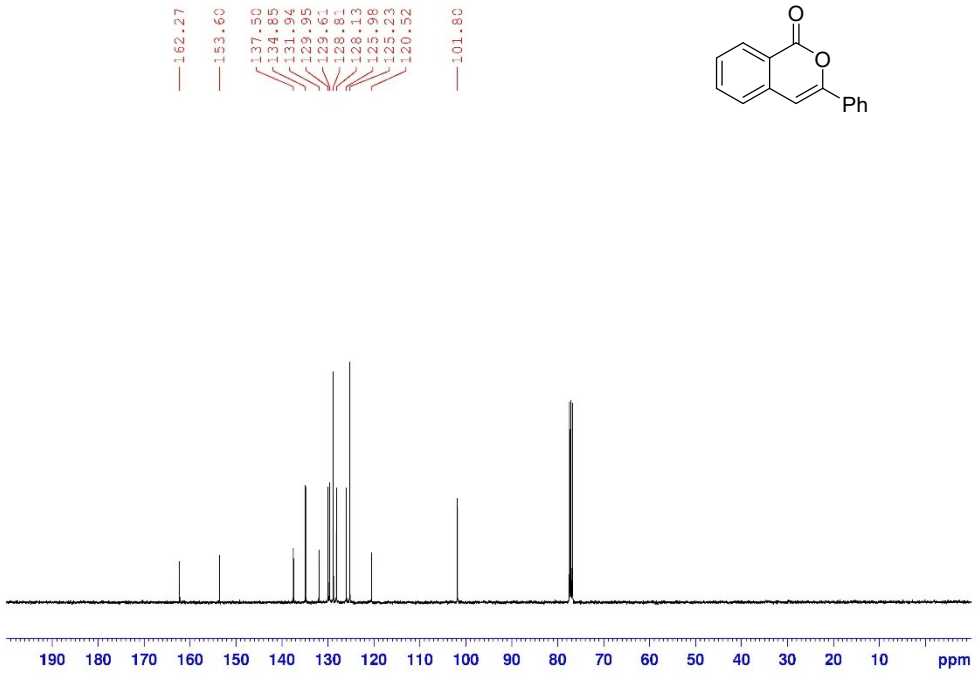
VII. 1H NMR and 13C NMR Spectra of New Compound

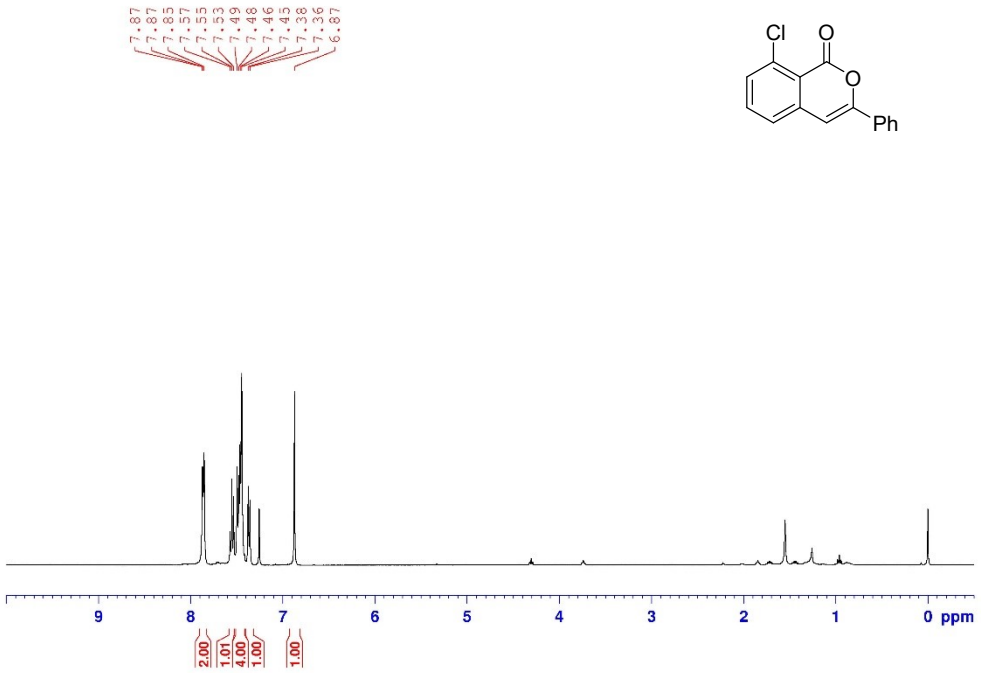
3aa, $CDCl_3$, 400 MHz



3aa, $CDCl_3$, 100 MHz



3ba, $CDCl_3$, 400 MHz



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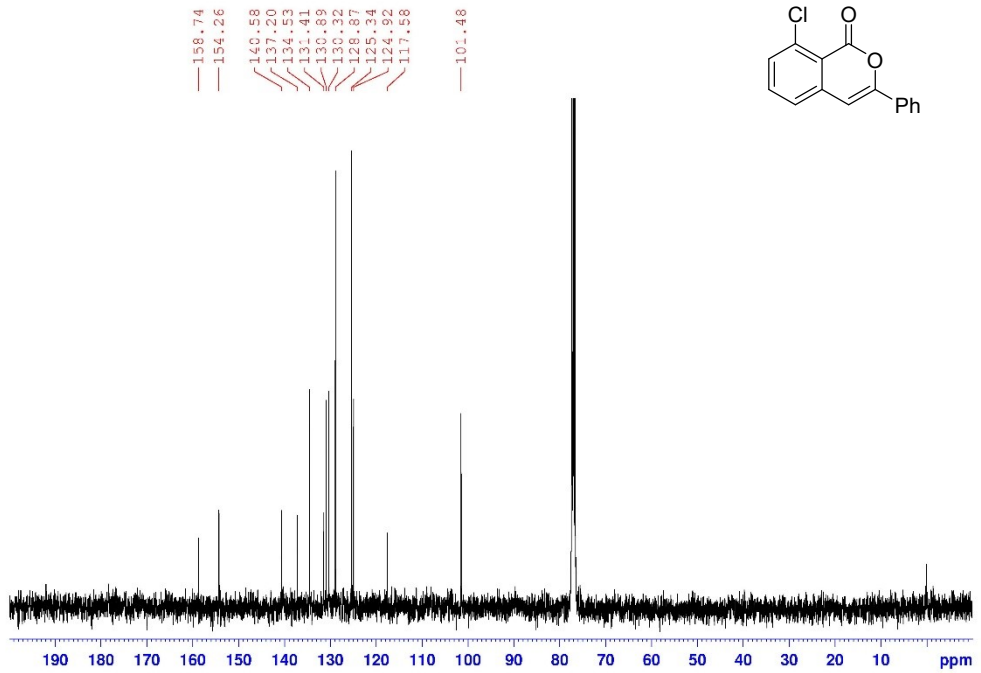
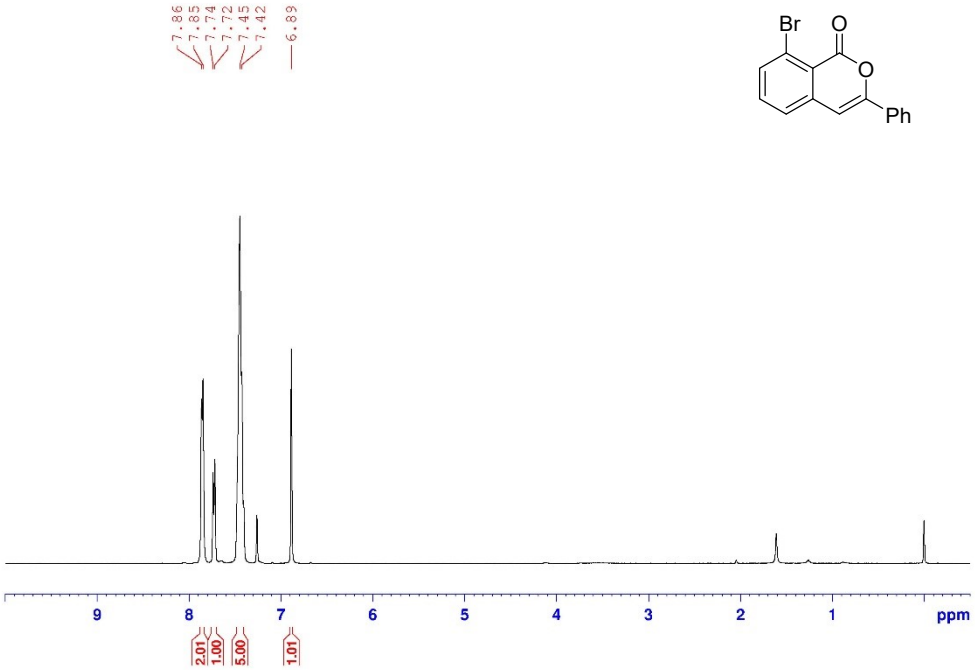


3ca, $CDCl_3$, 400 MHz



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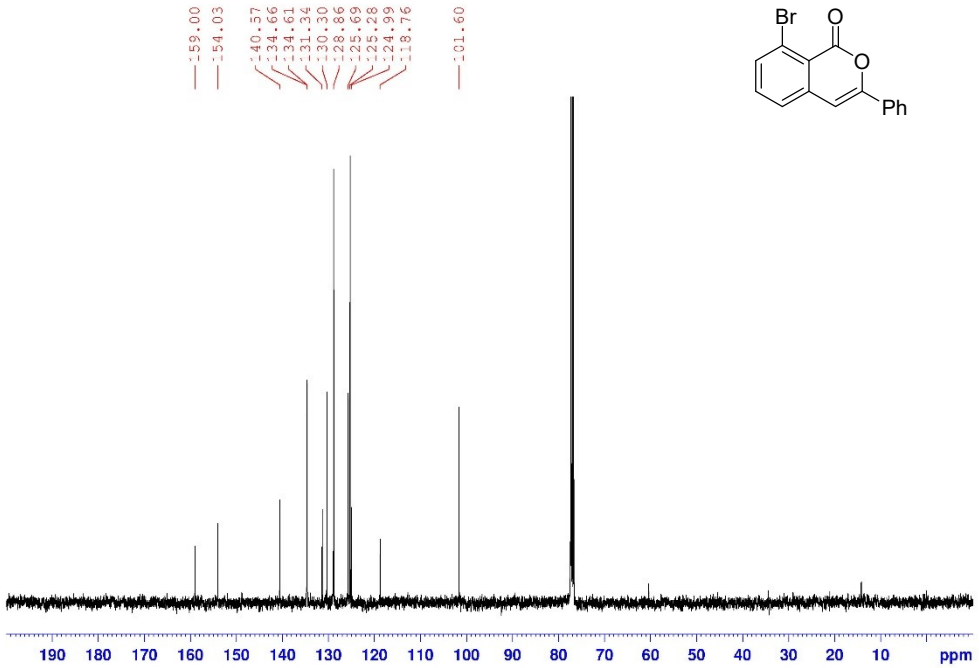

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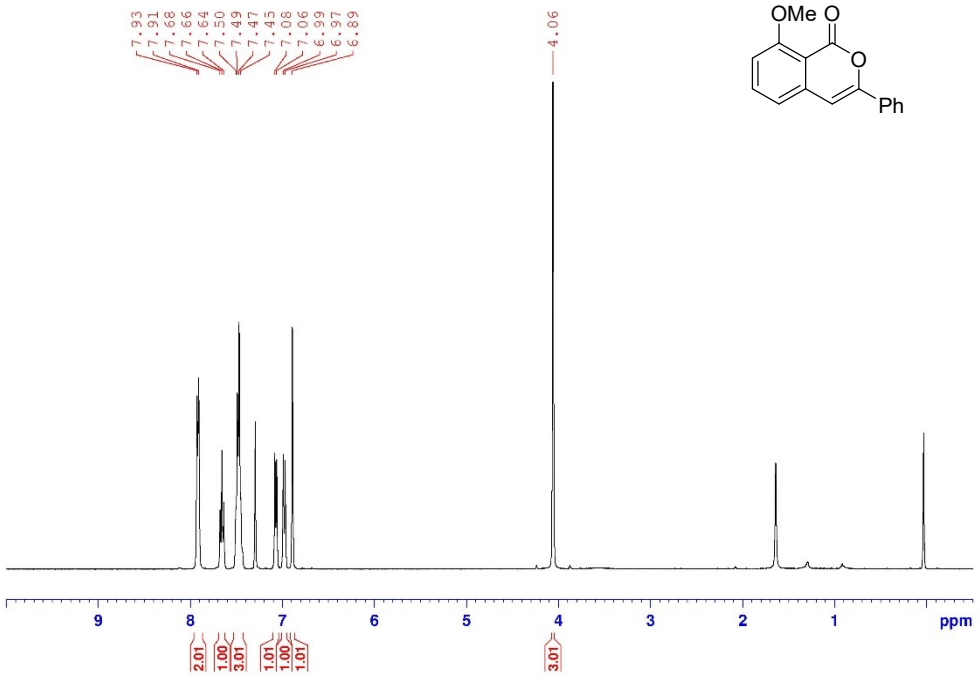
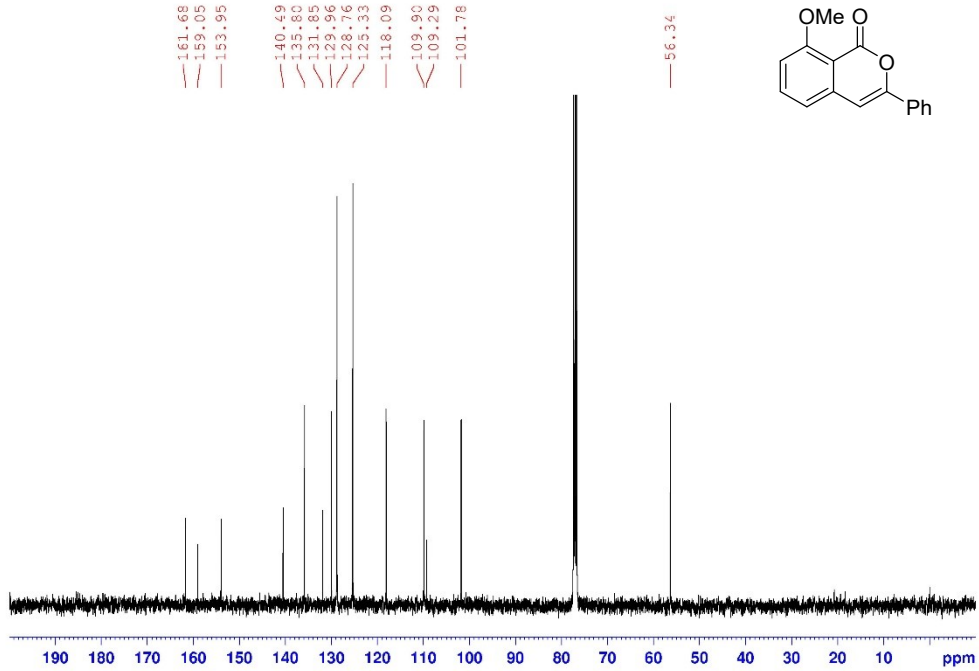


3da, $CDCl_3$, 100 MHz



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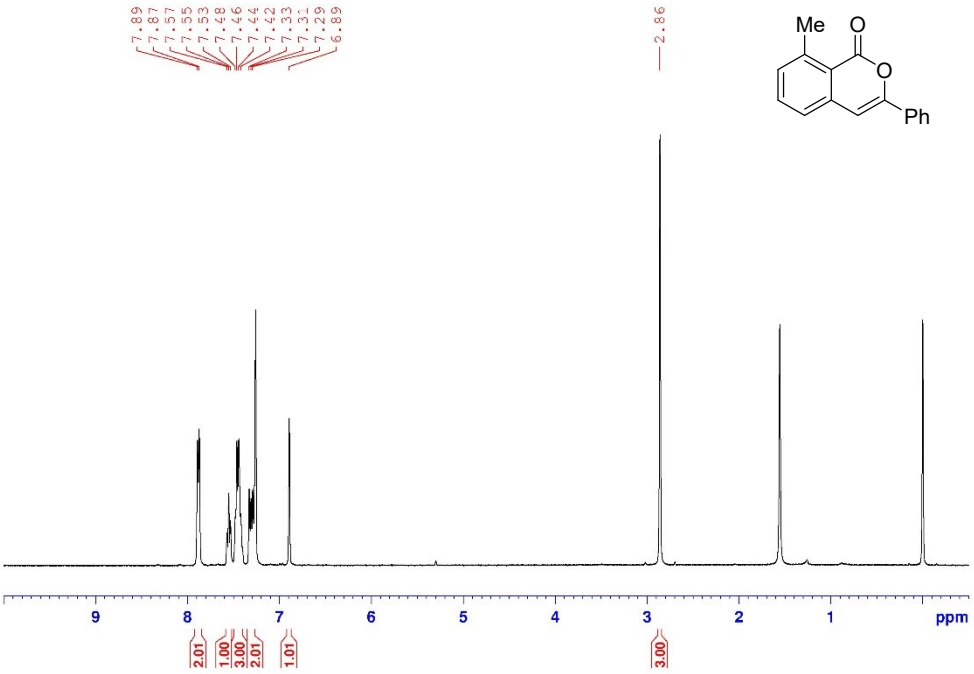
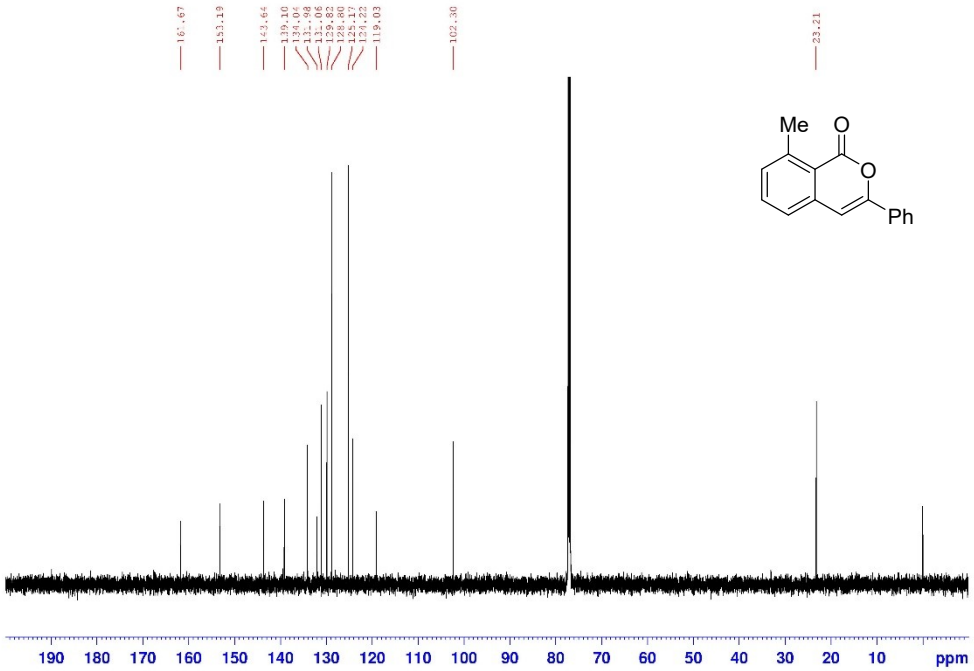


3ea, $CDCl_3$, 150 MHz



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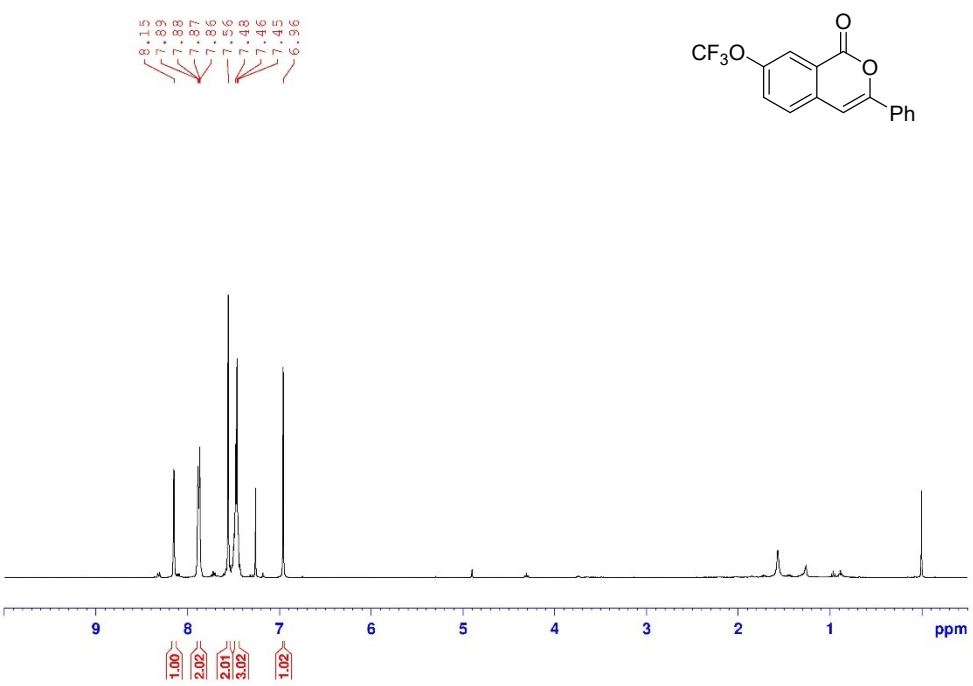

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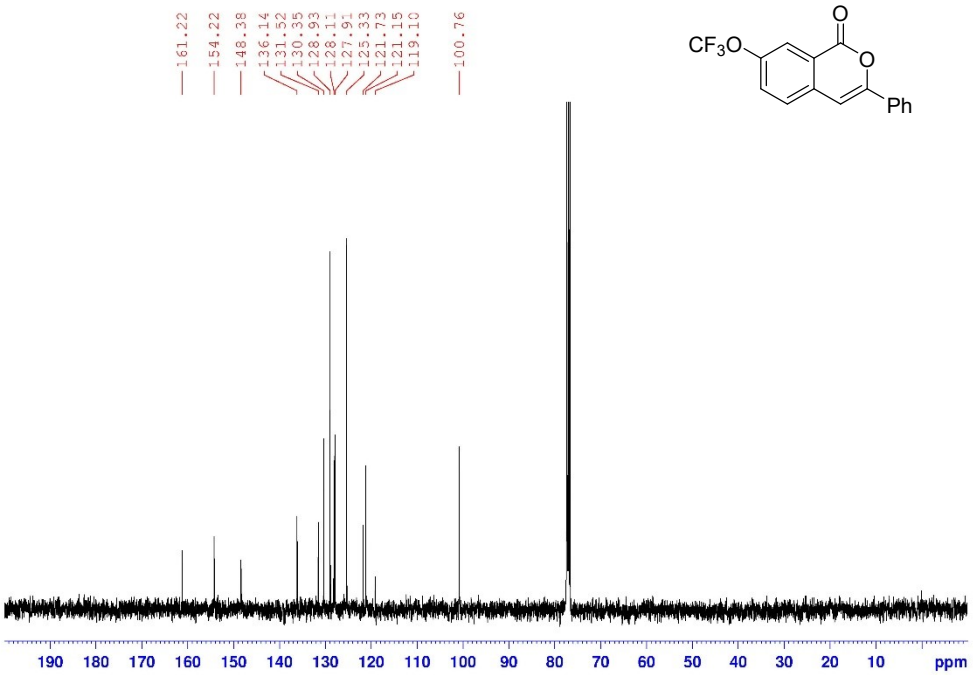

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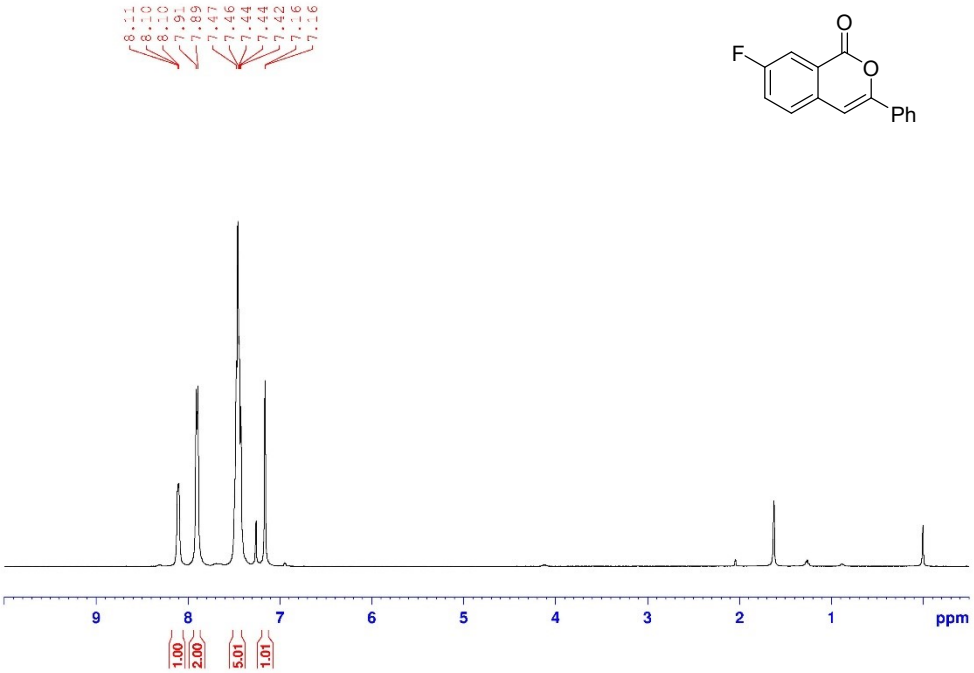
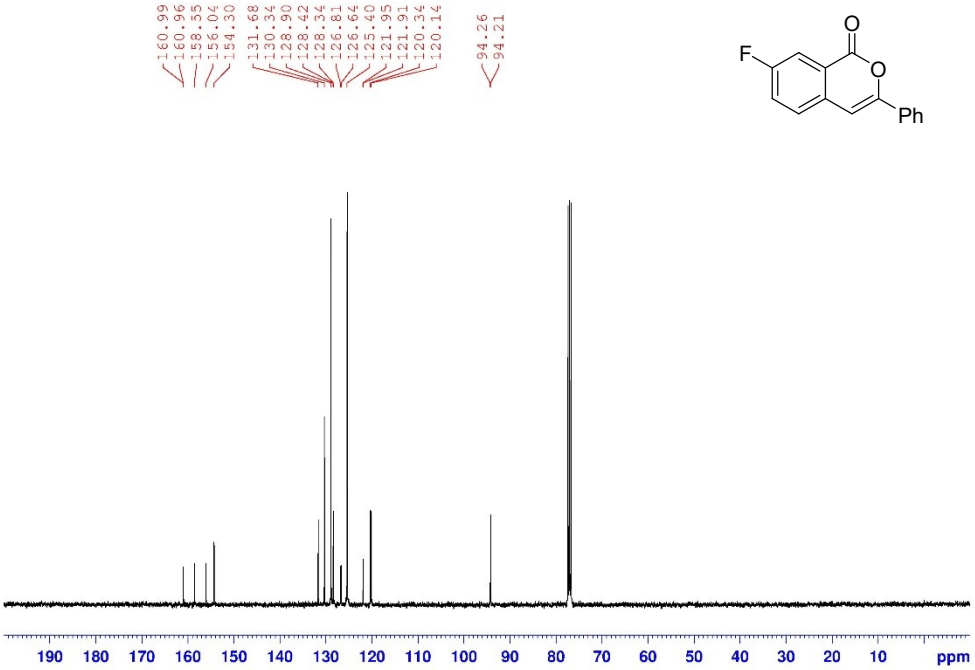
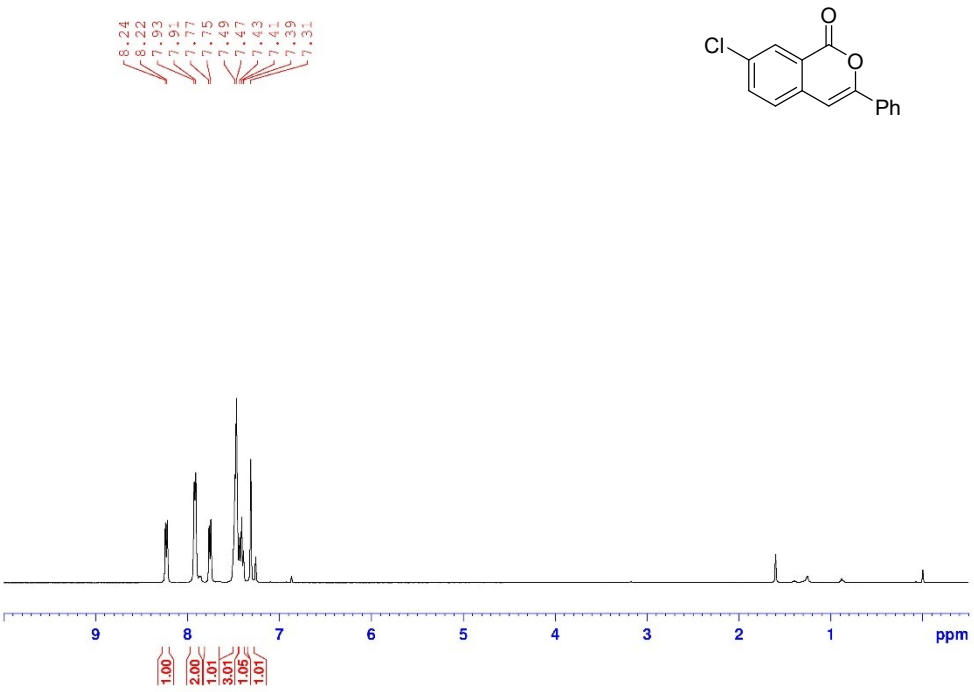


3ga, $CDCl_3$, 100 MHz



3ha, $CDCl_3$, 400 MHz



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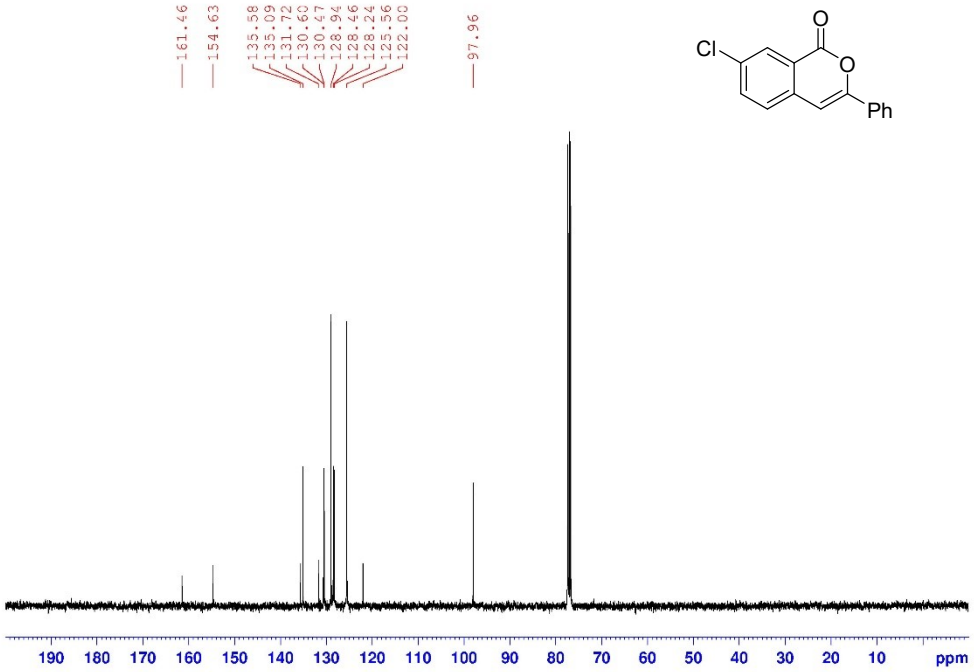
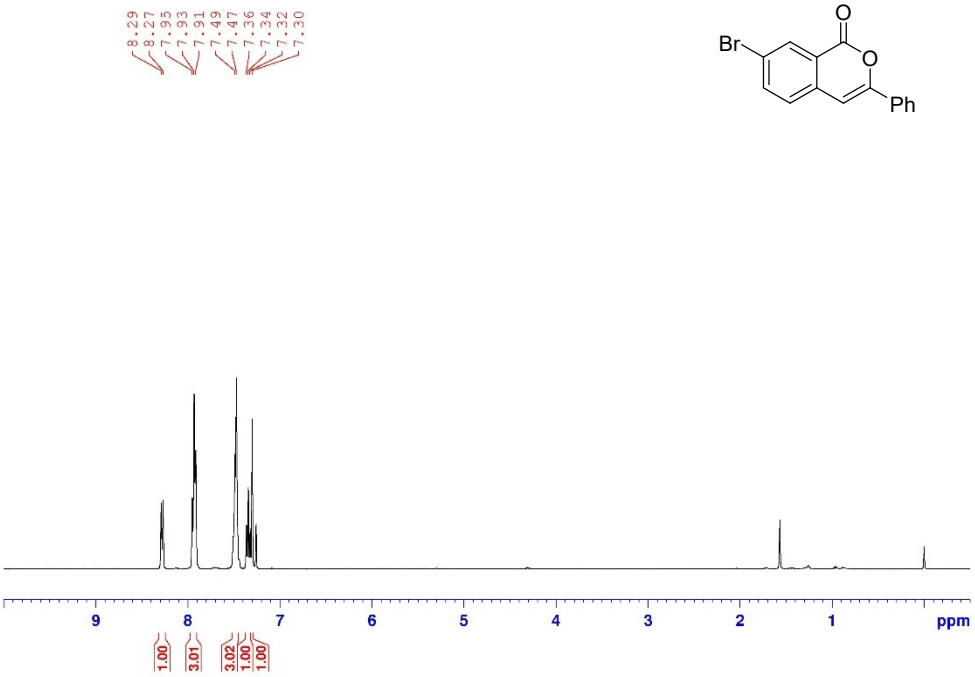


3ia, $CDCl_3$, 400 MHz



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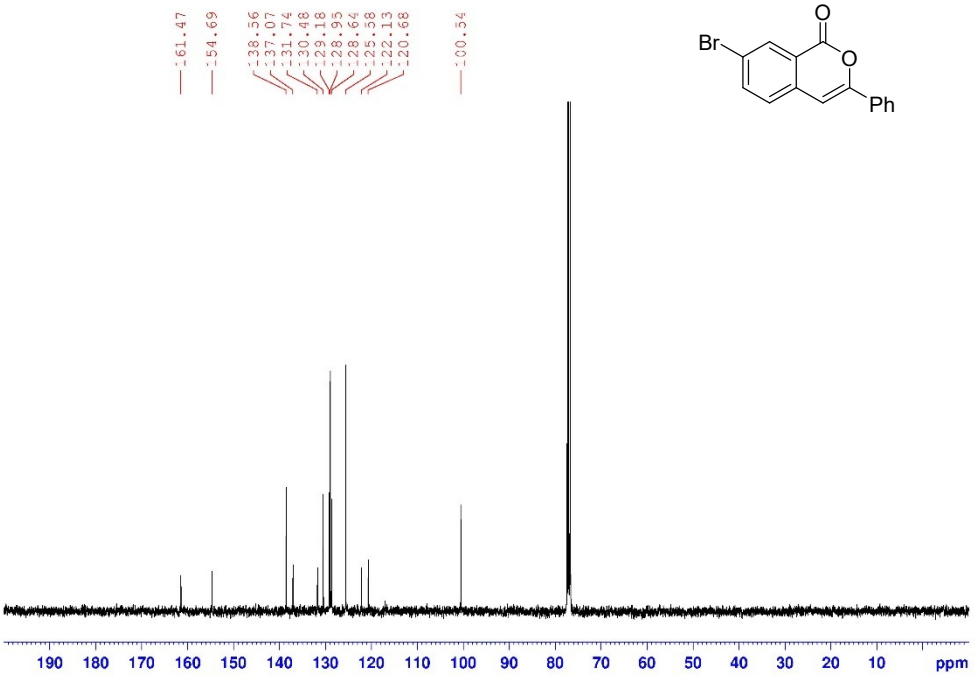

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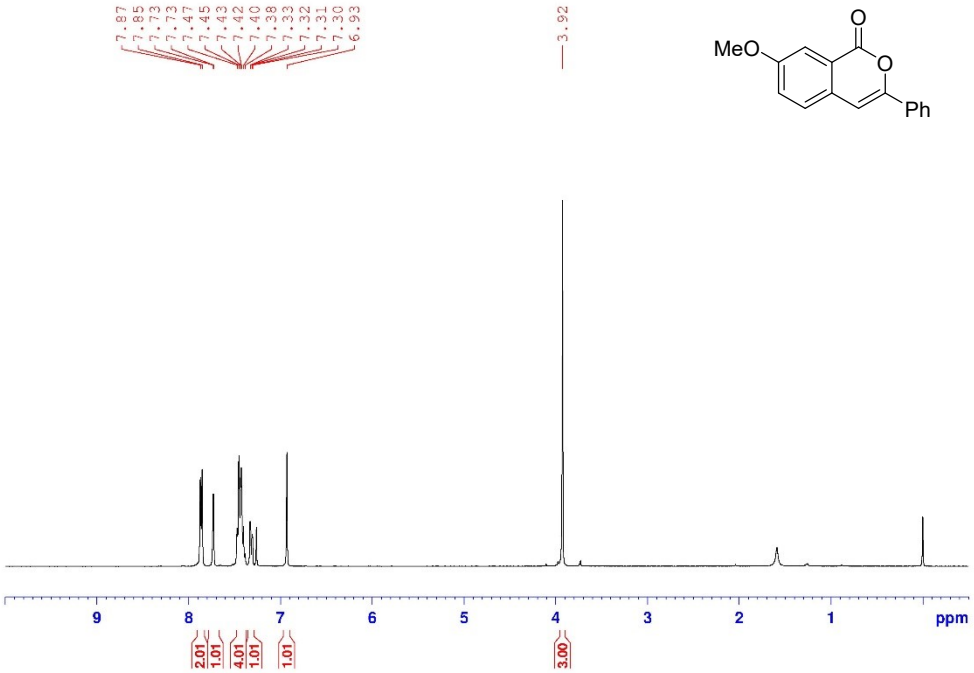

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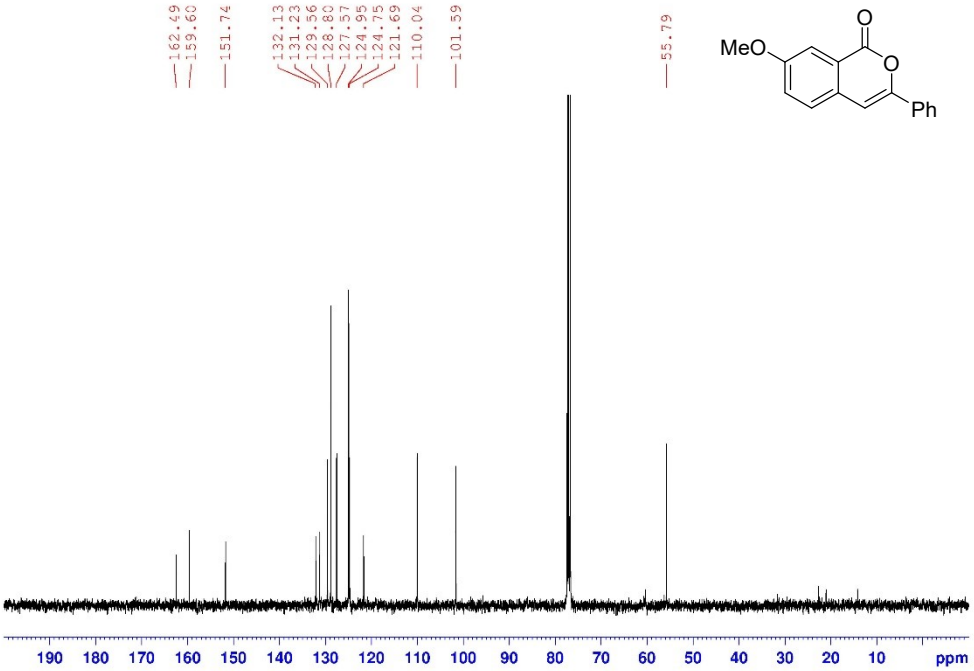

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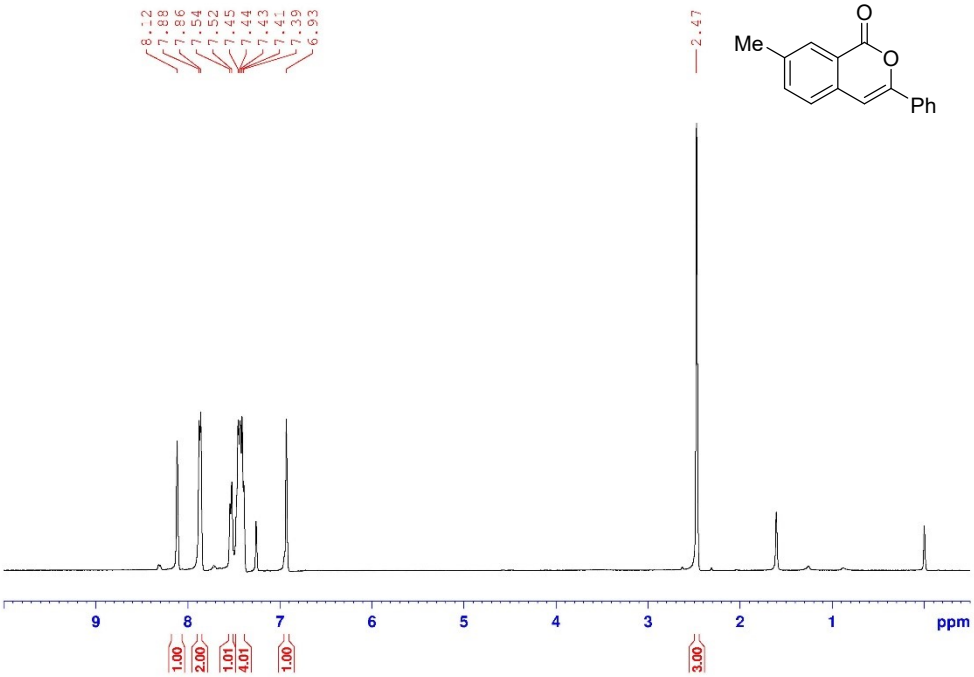

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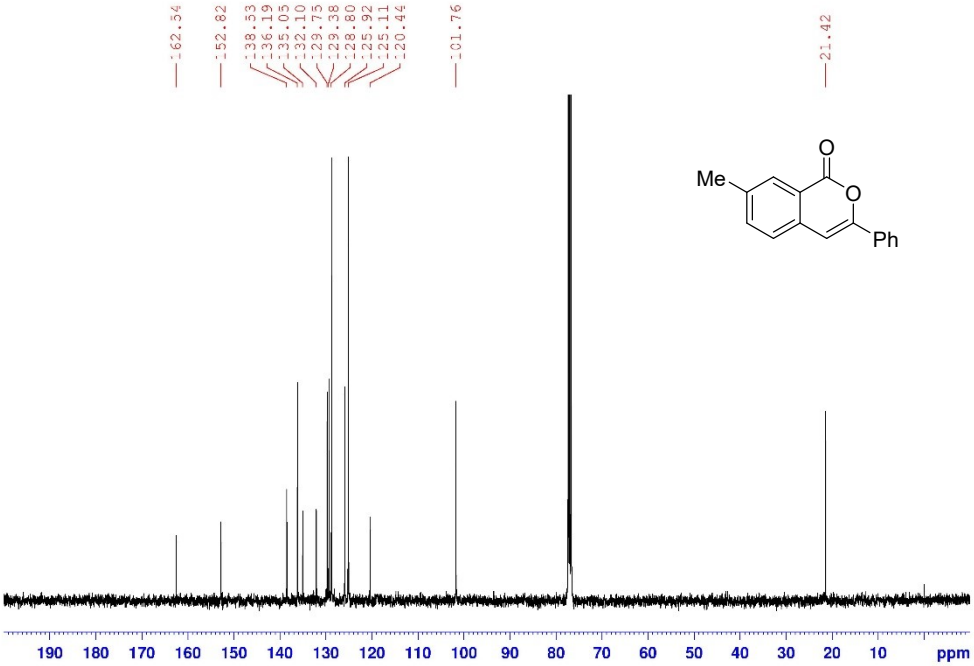

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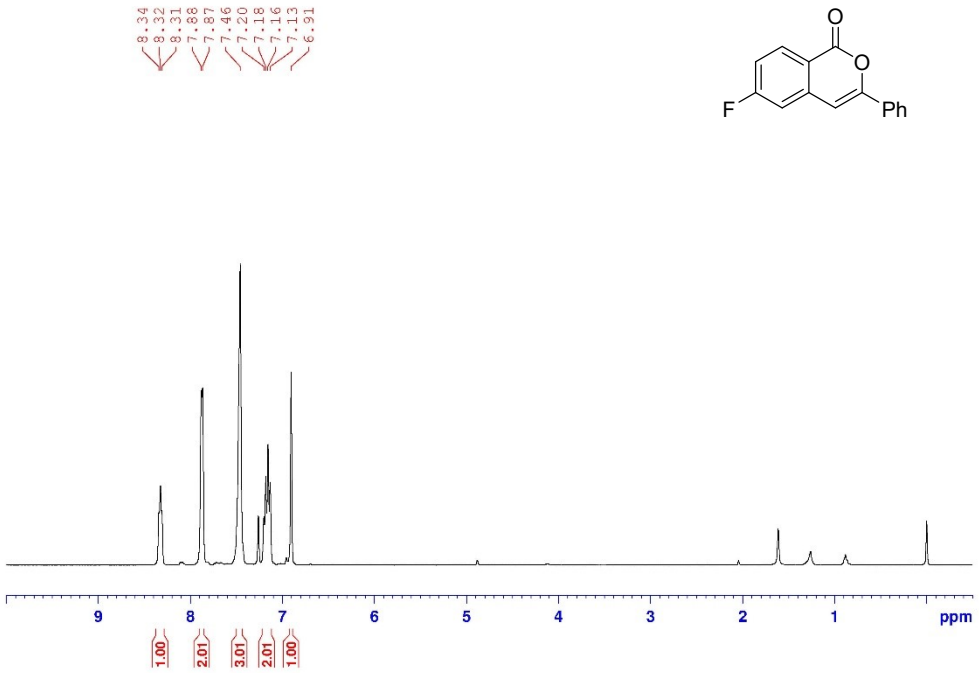

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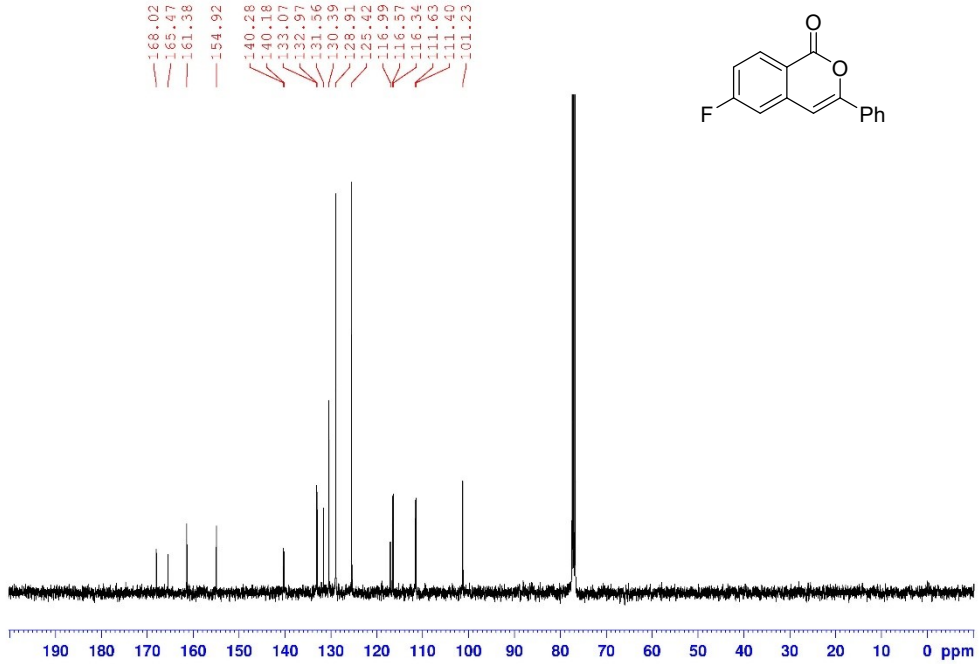

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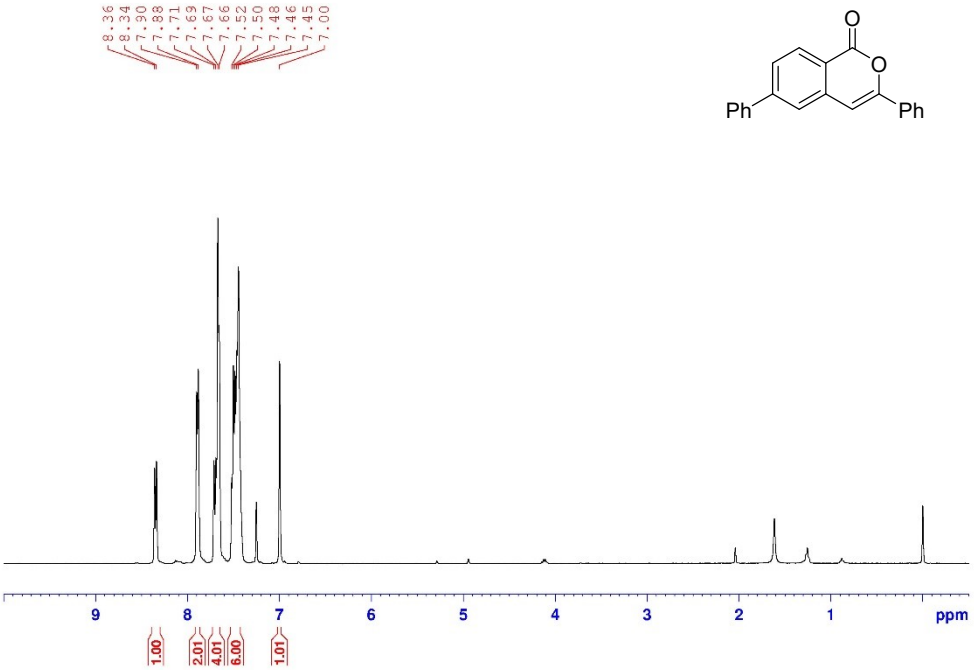

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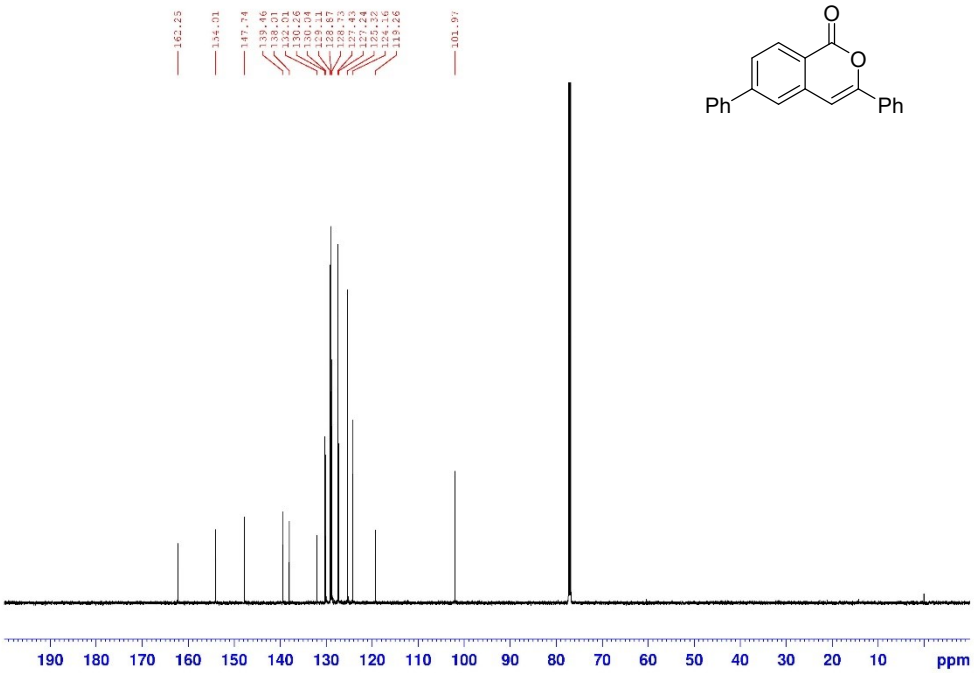

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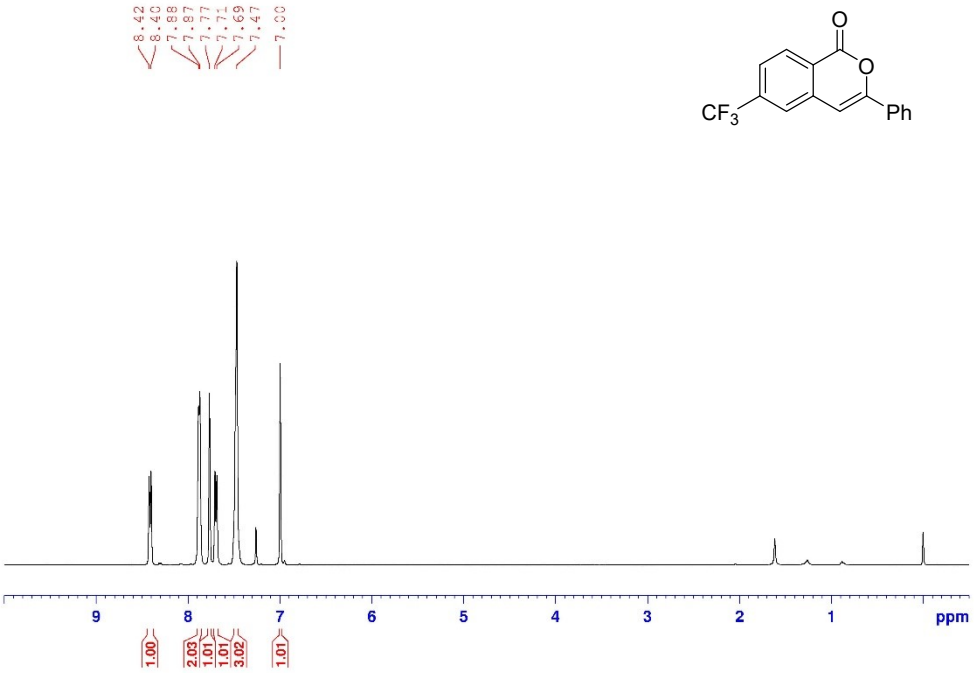

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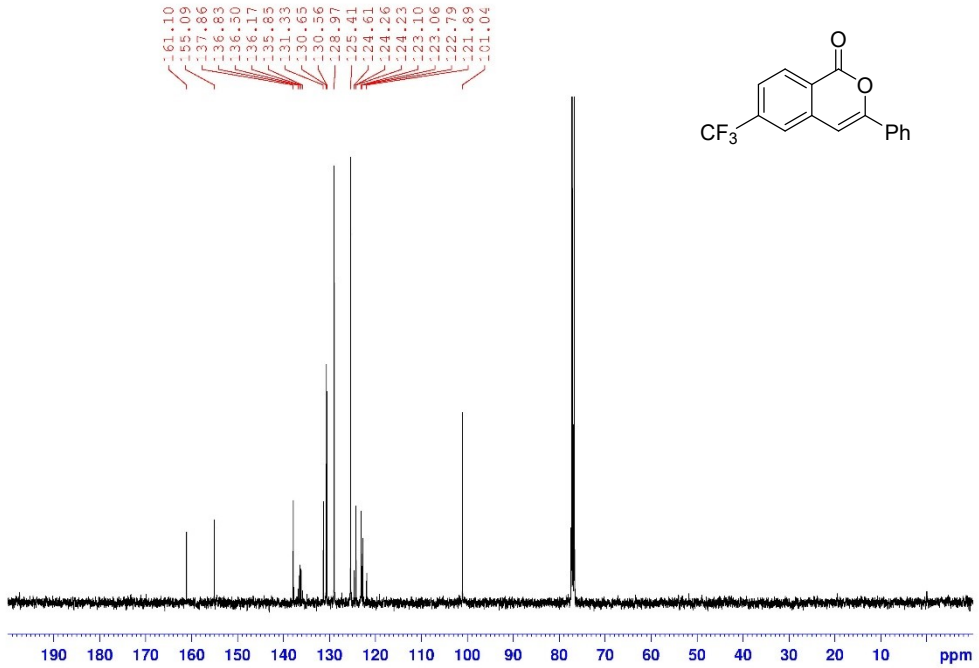

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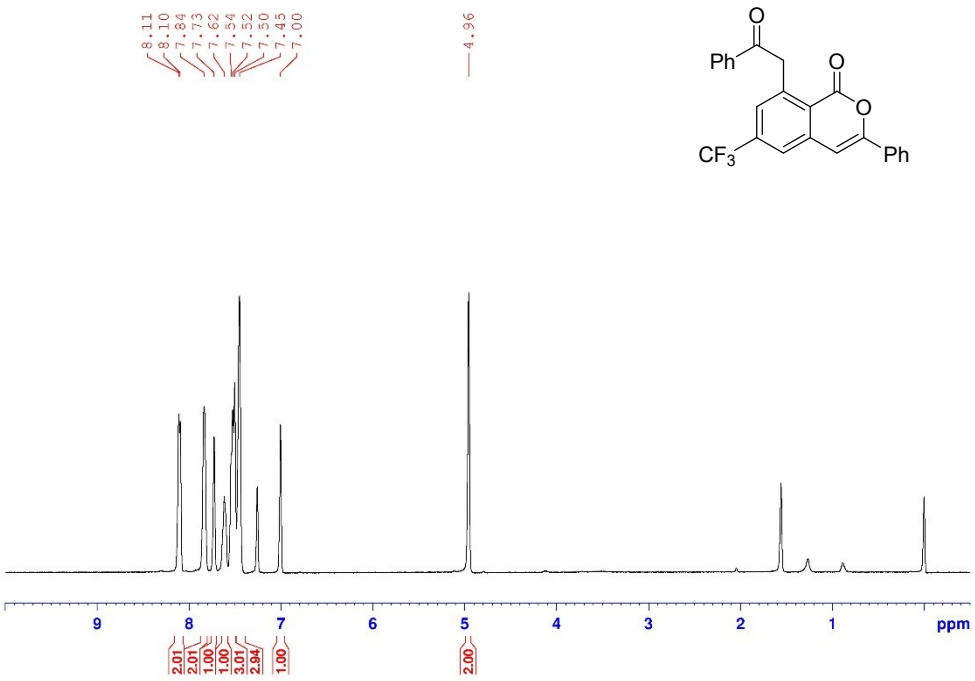

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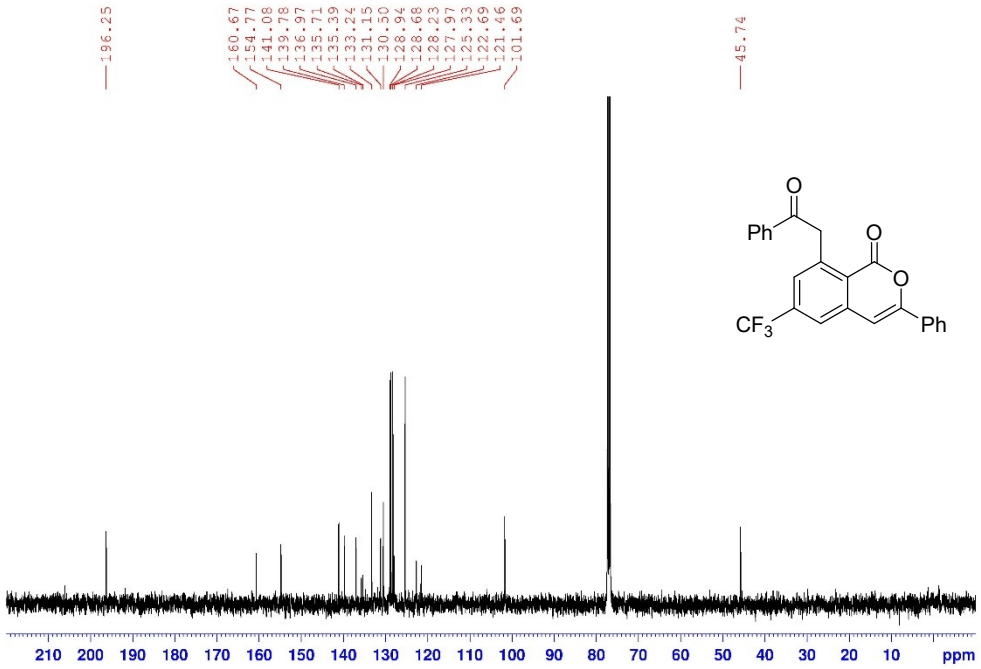
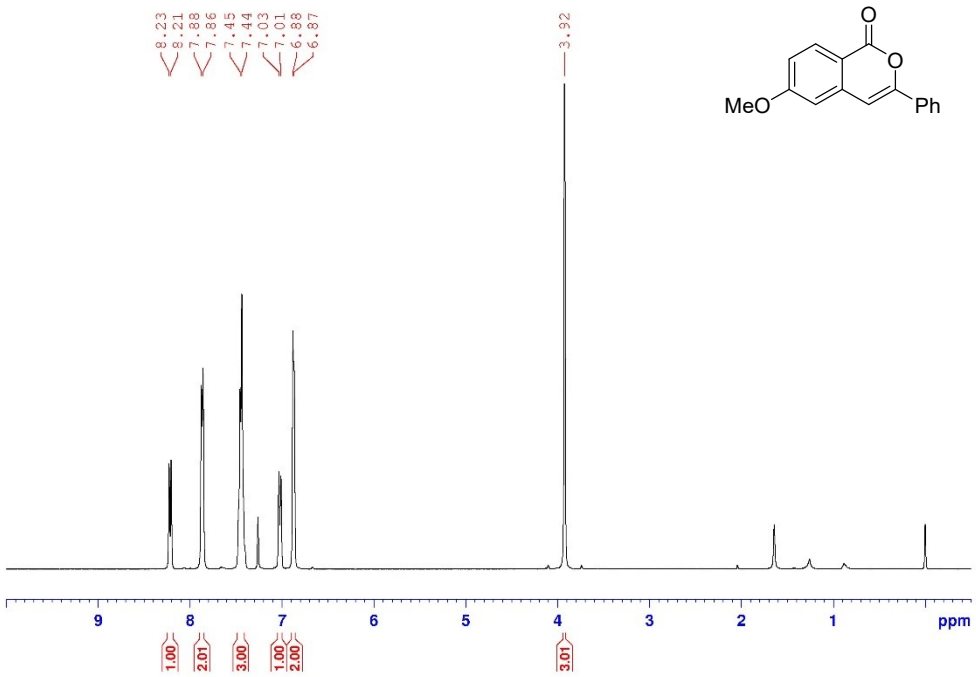


3oa, $CDCl_3$, 400 MHz



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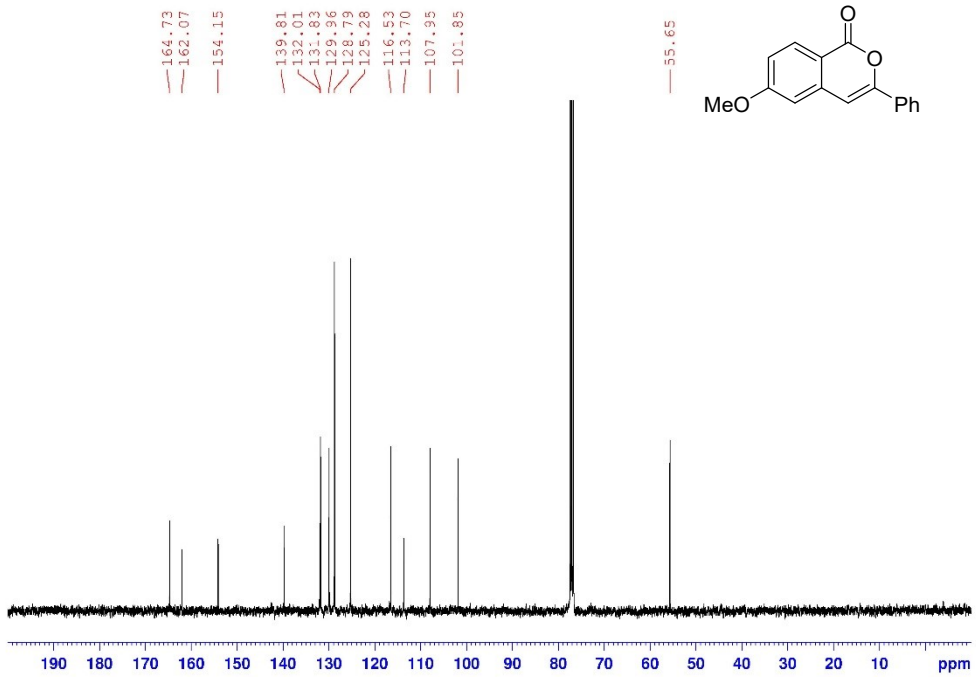
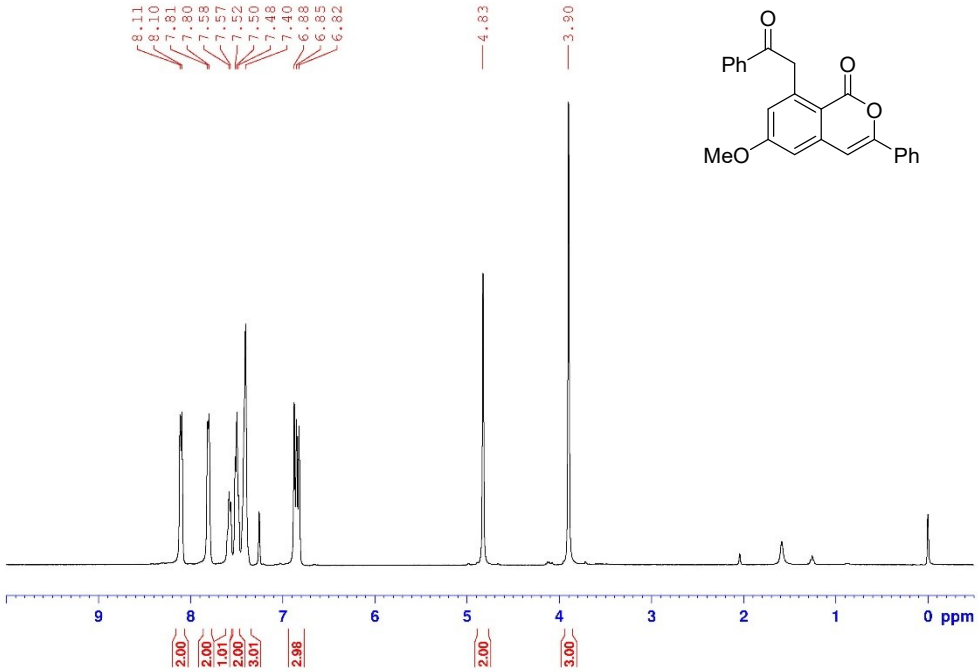


3oa', $CDCl_3$, 400 MHz



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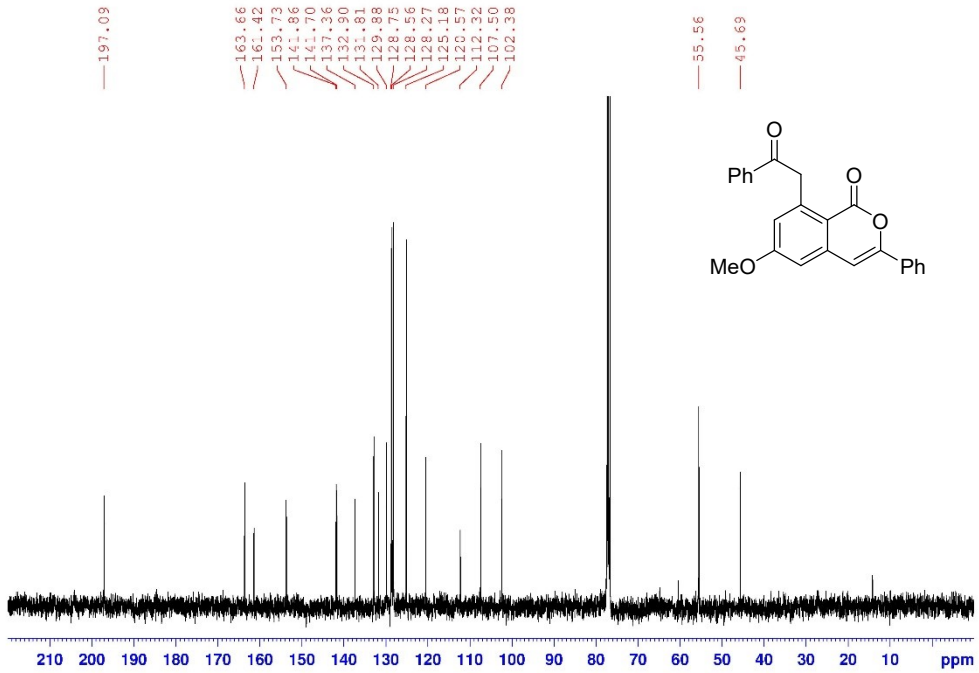

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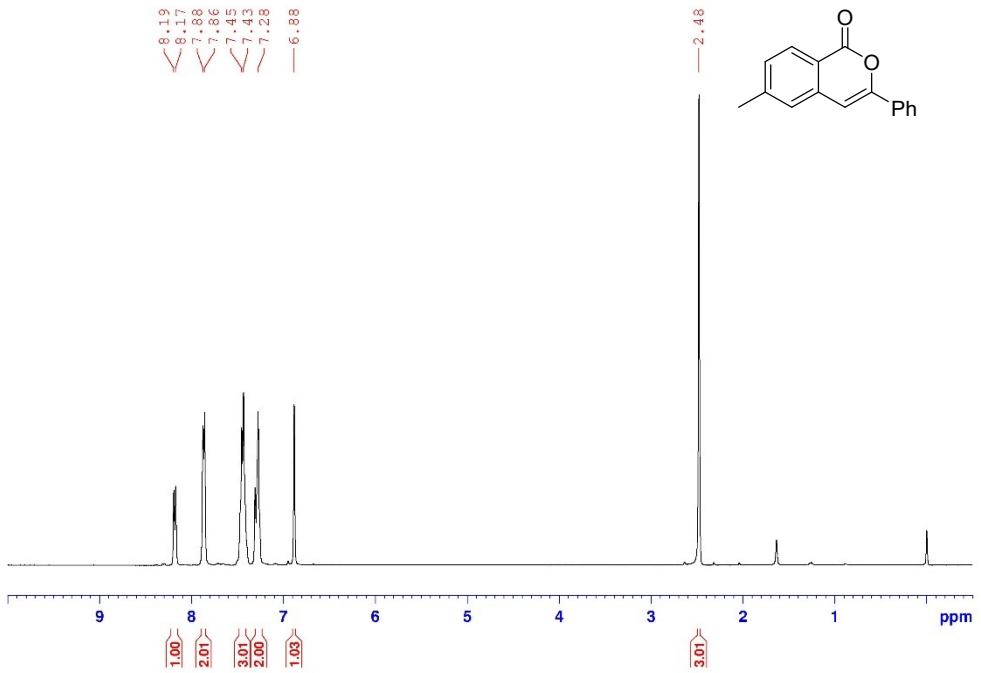

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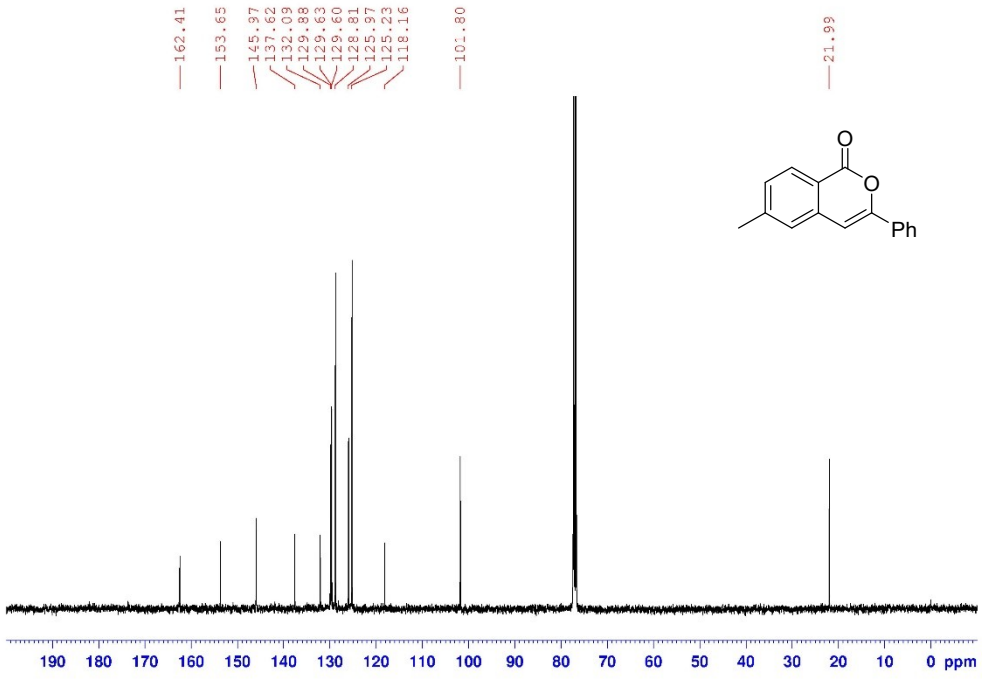

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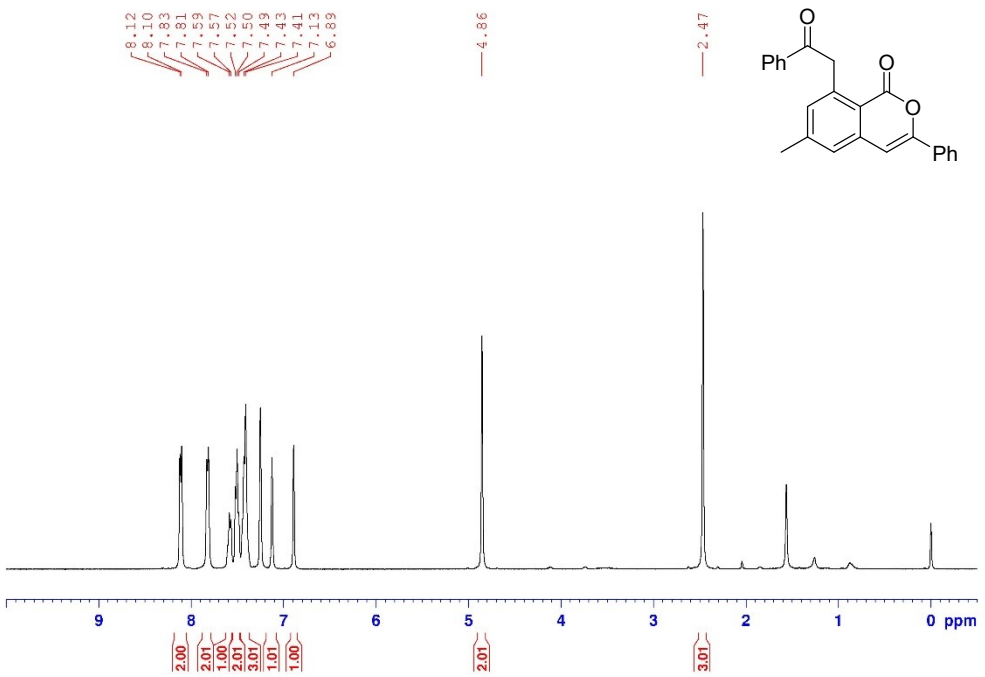

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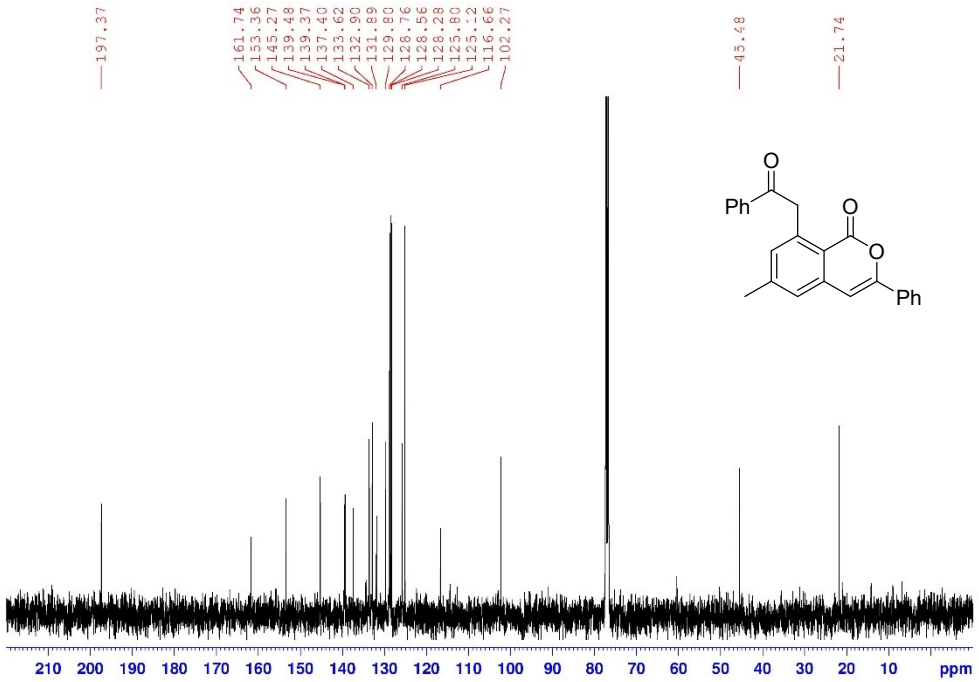
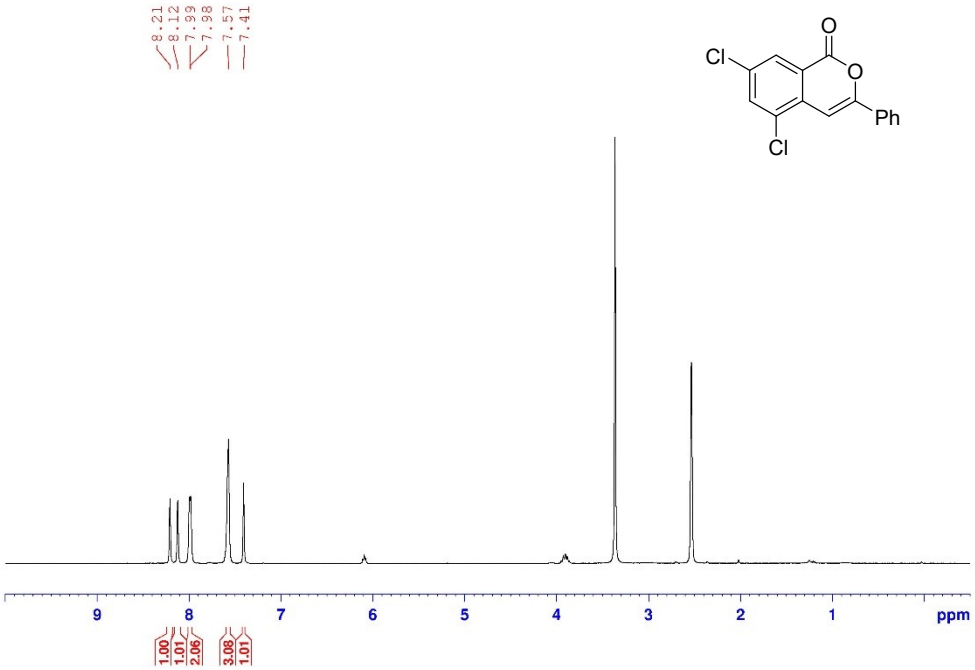
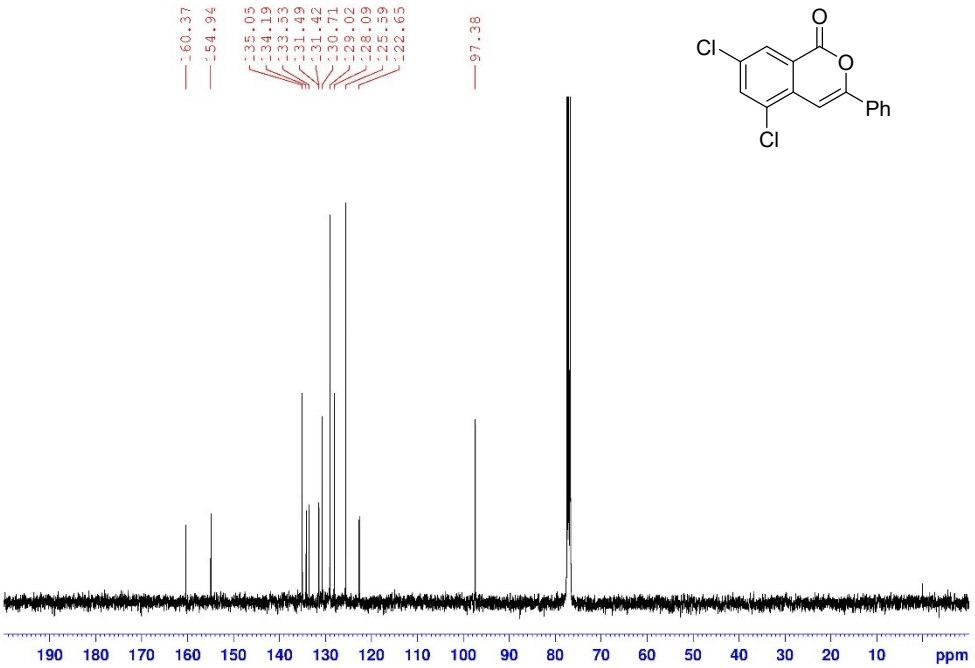


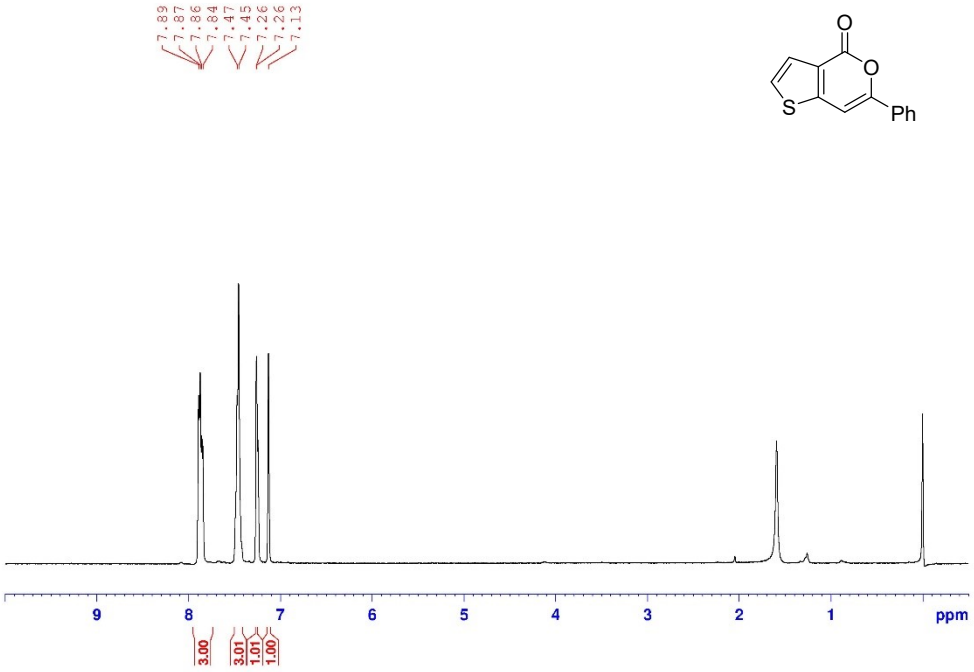
3qa, DMSO, 400 MHz



3qa, DMSO, 150 MHz



3ra, $CDCl_3$, 400 MHz



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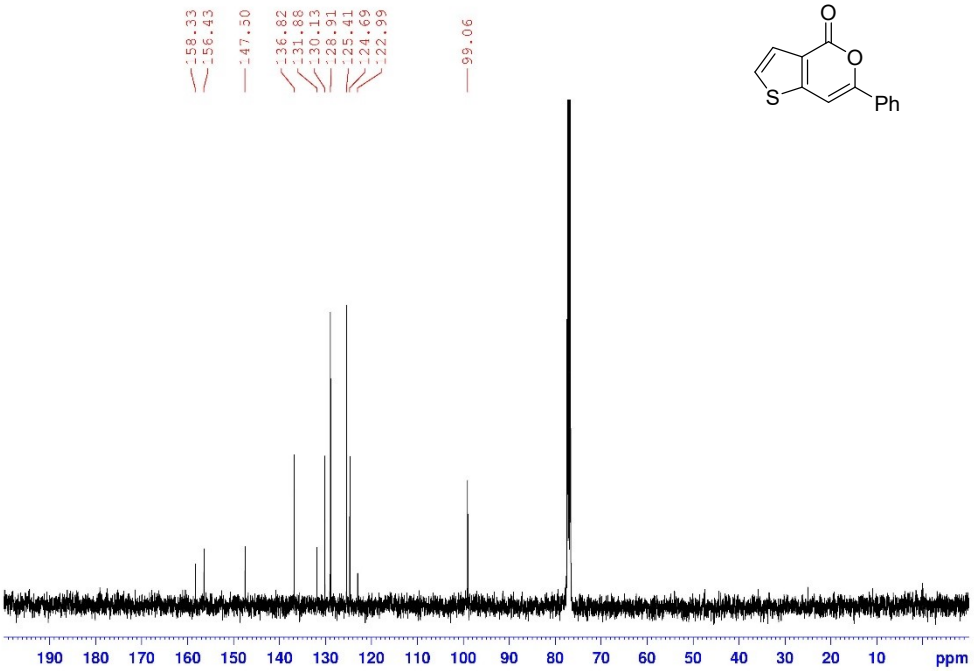
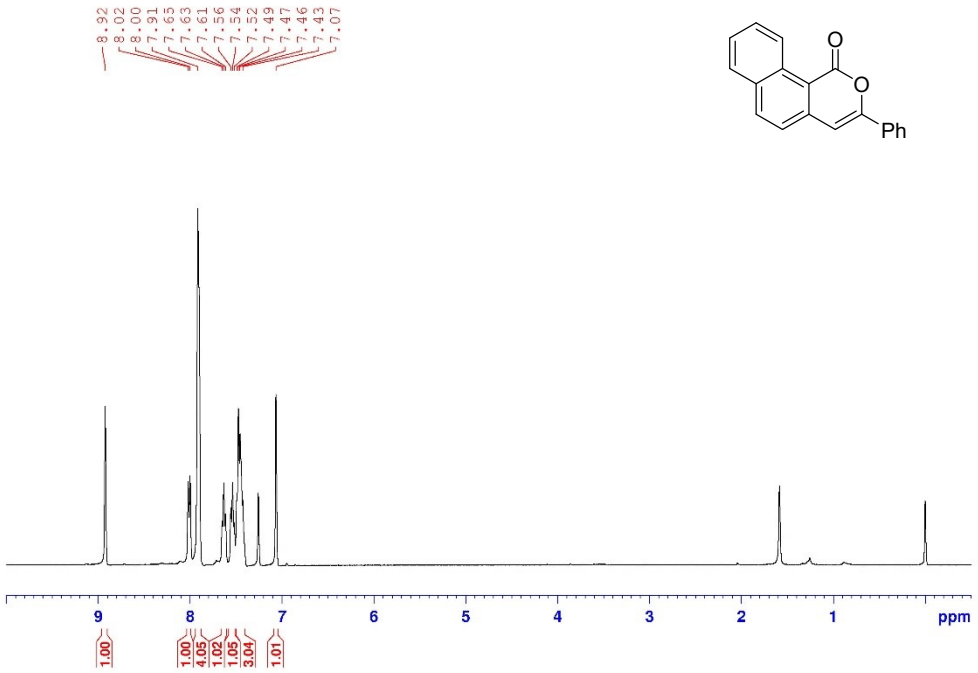


3sa, $CDCl_3$, 400 MHz



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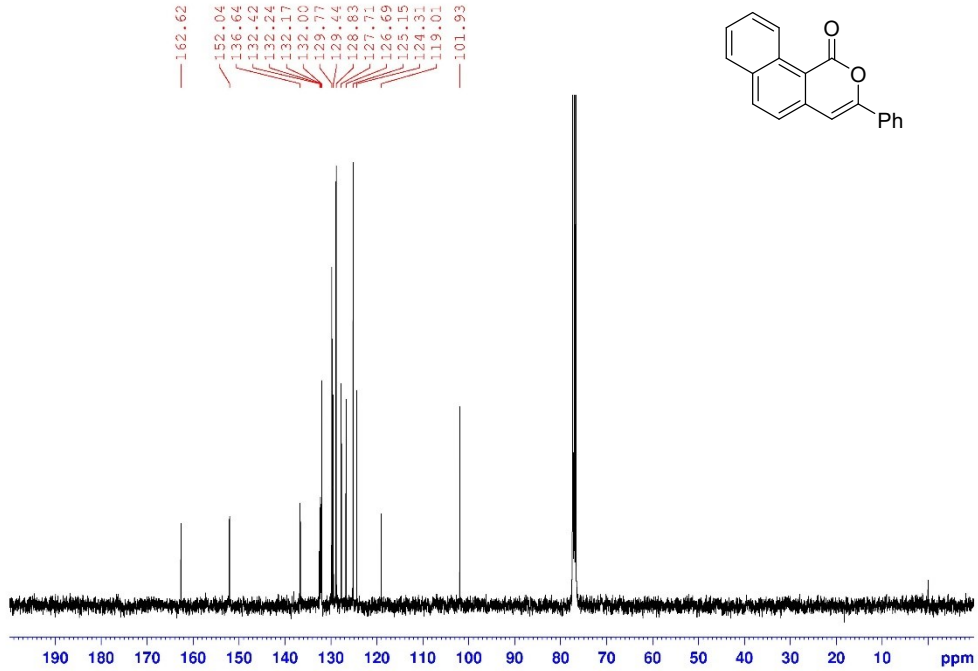

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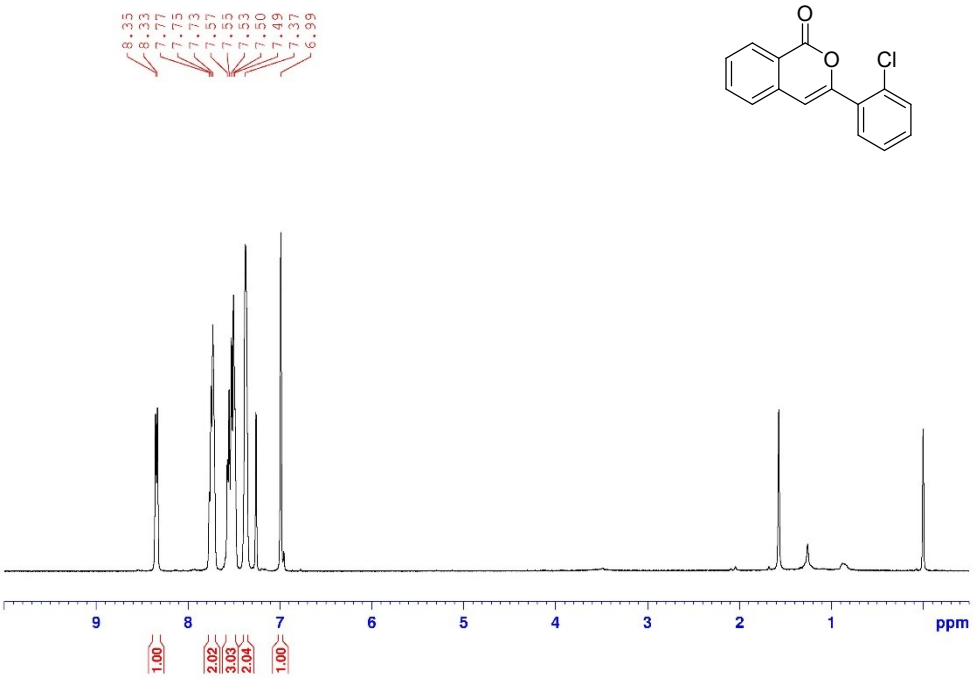
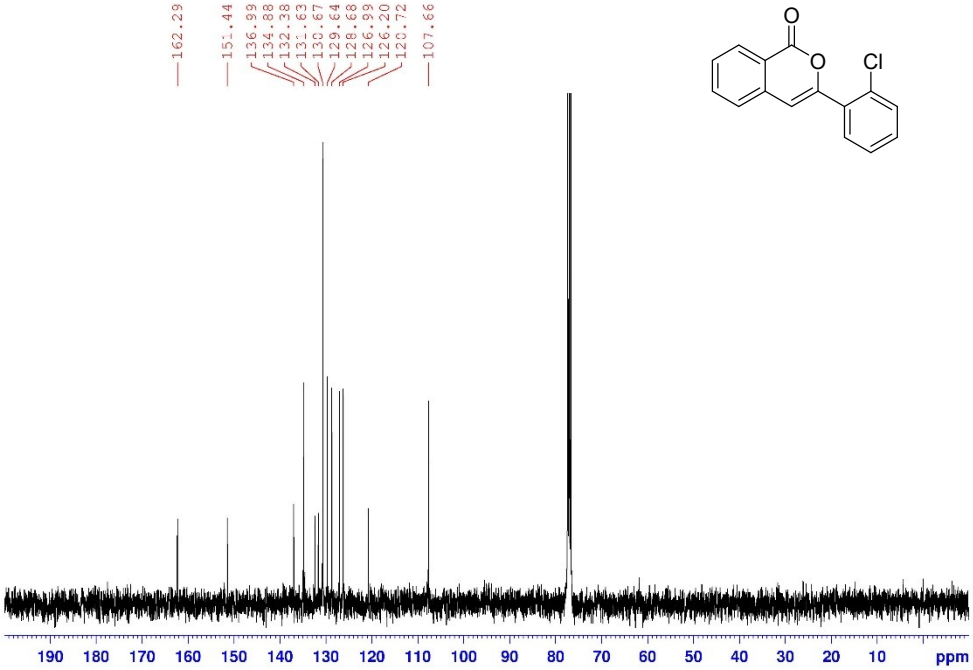
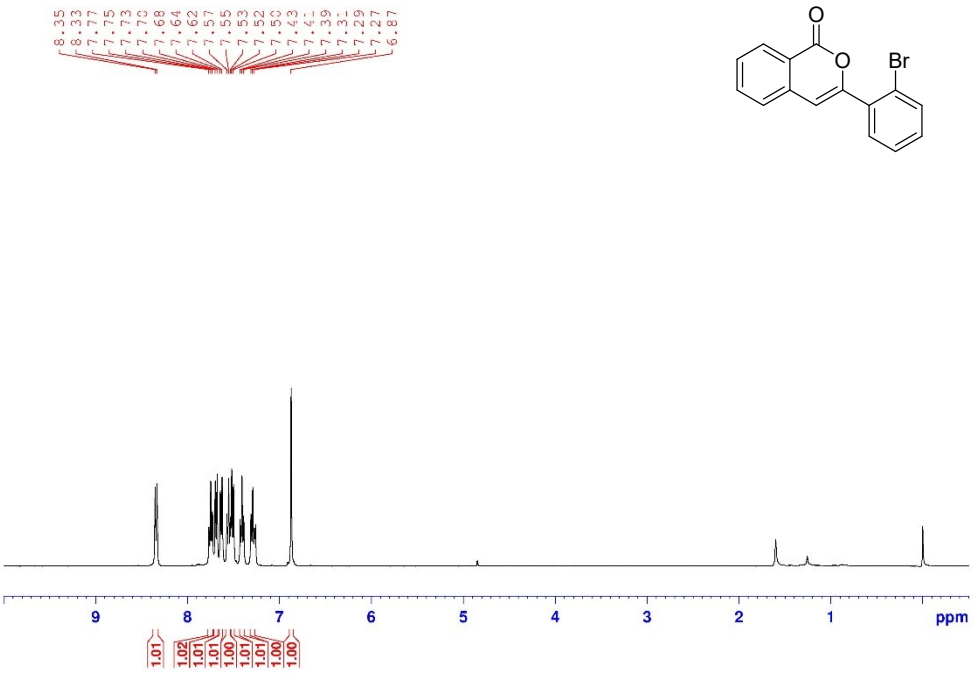


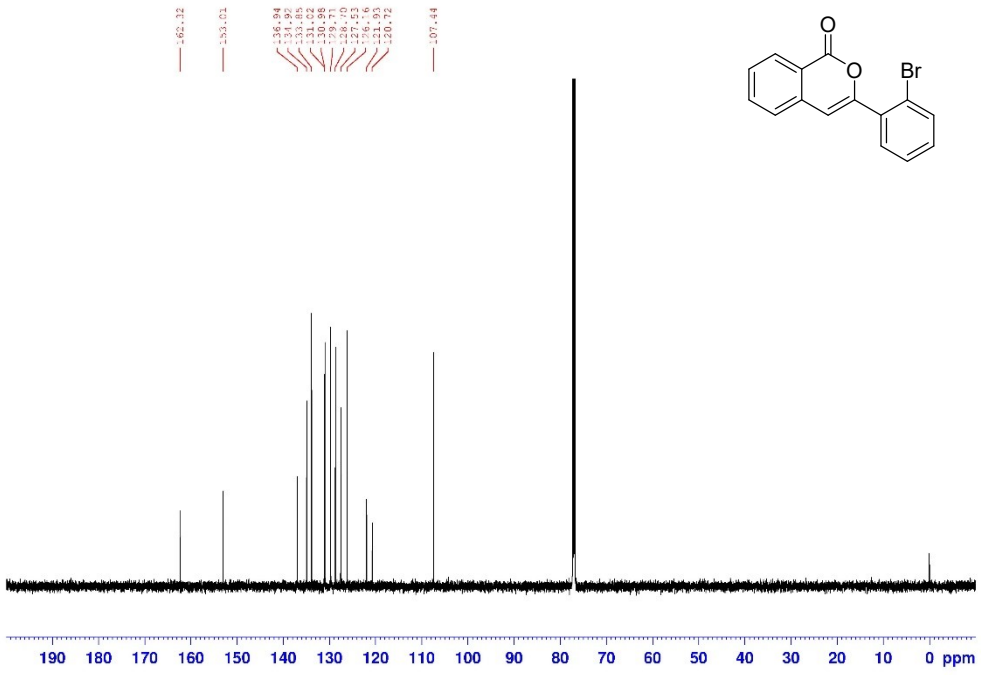
3ab, $CDCl_3$, 100 MHz



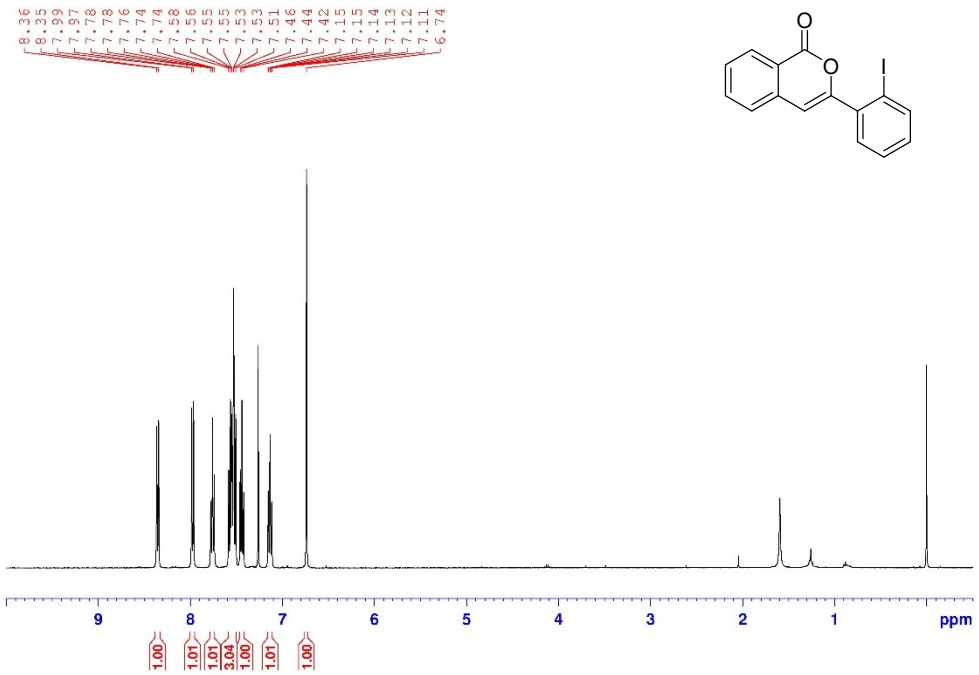
3ac, $CDCl_3$, 400 MHz



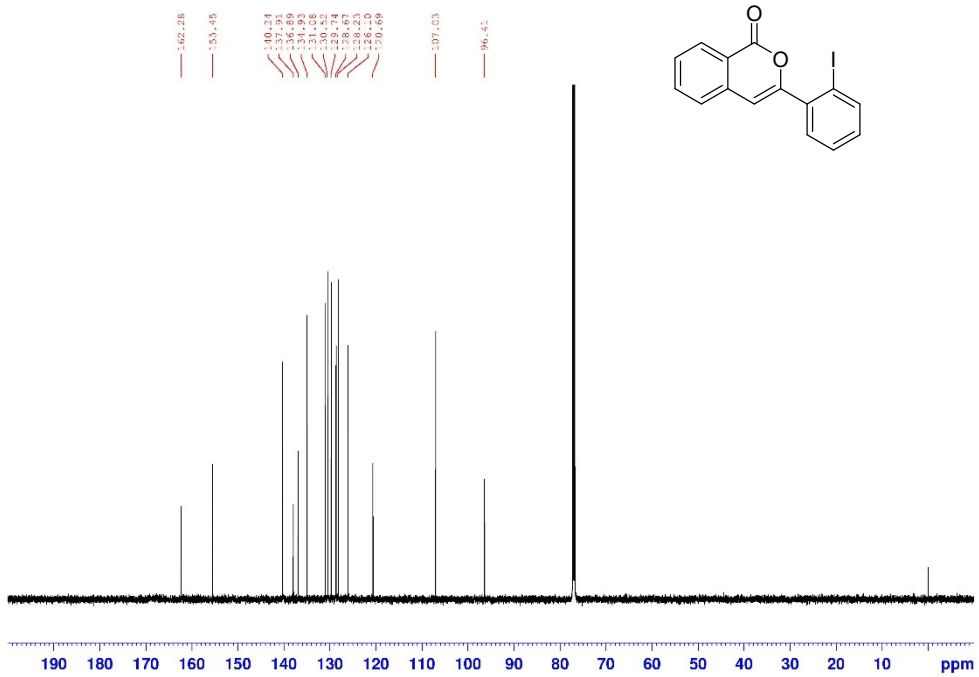
3ac, $CDCl_3$, 150 MHz



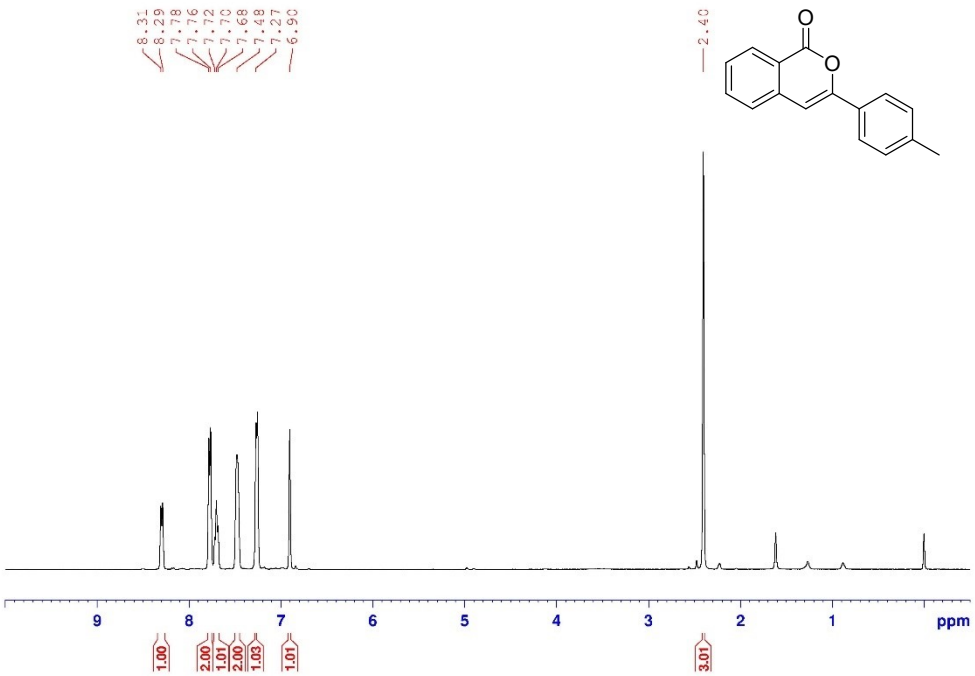
3ad, $CDCl_3$, 400 MHz



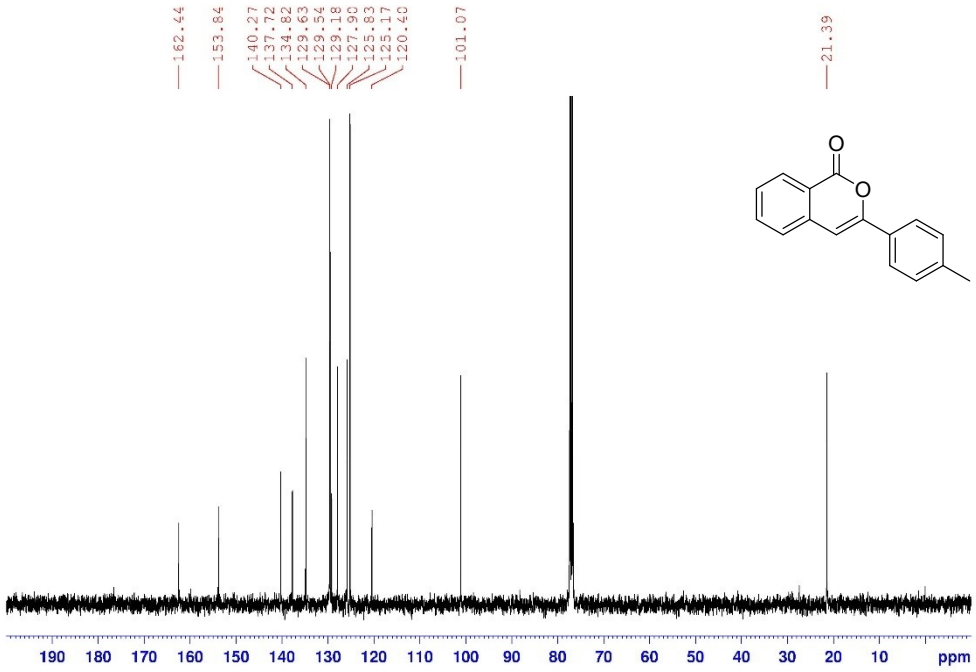
3ad, $CDCl_3$, 150 MHz



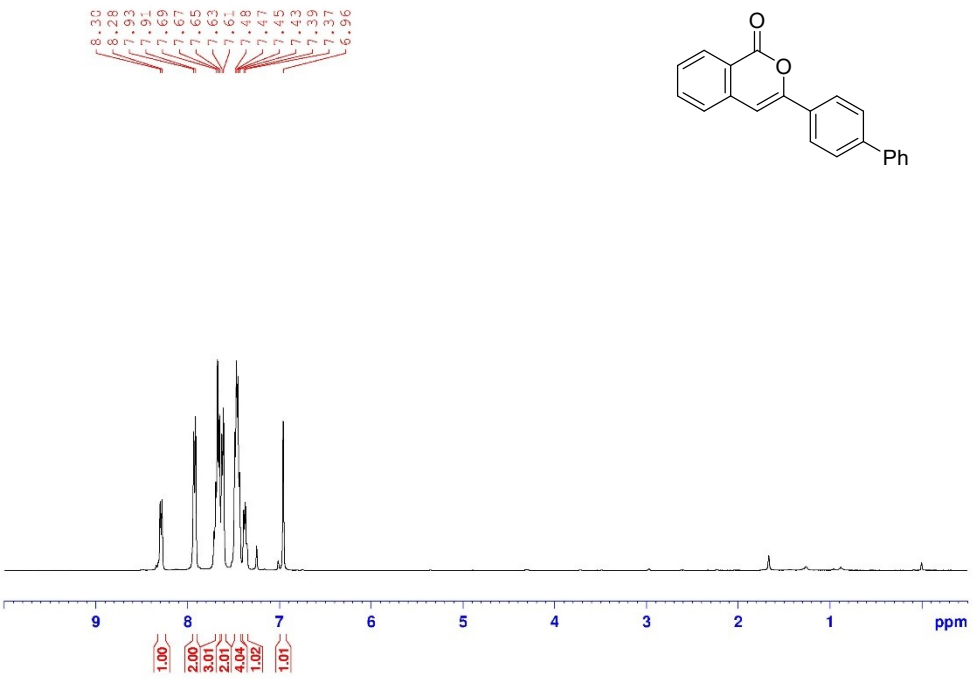
3ae, $CDCl_3$, 400 MHz



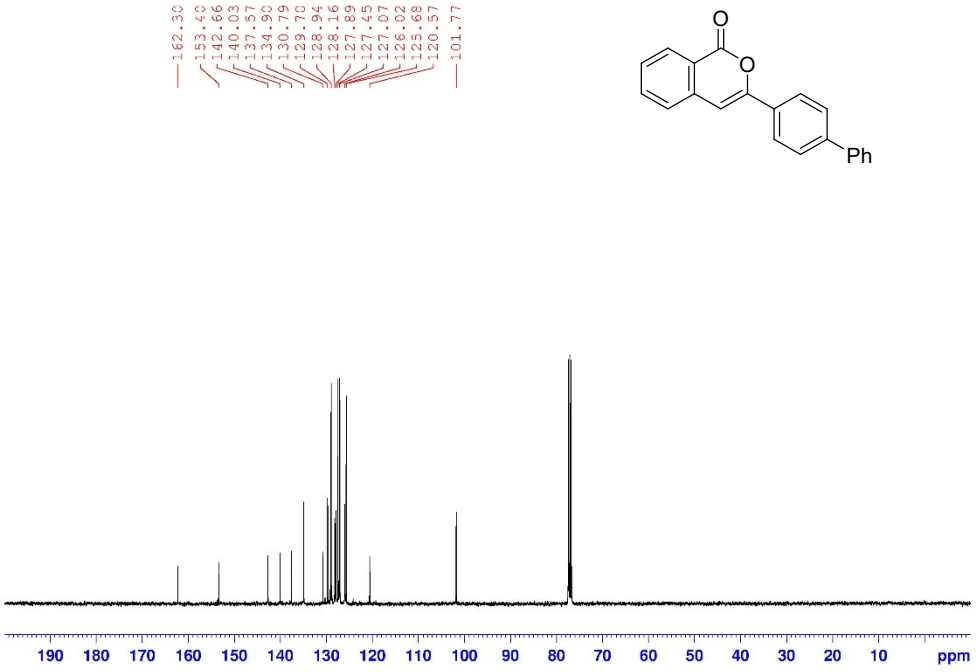
3ae, $CDCl_3$, 100 MHz



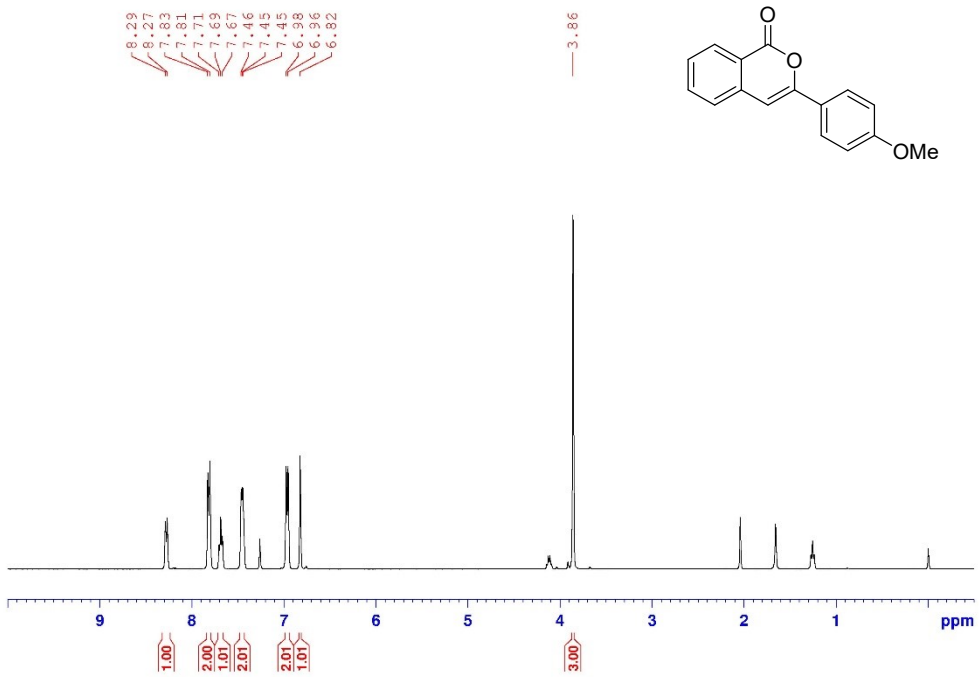
3af, $CDCl_3$, 400 MHz



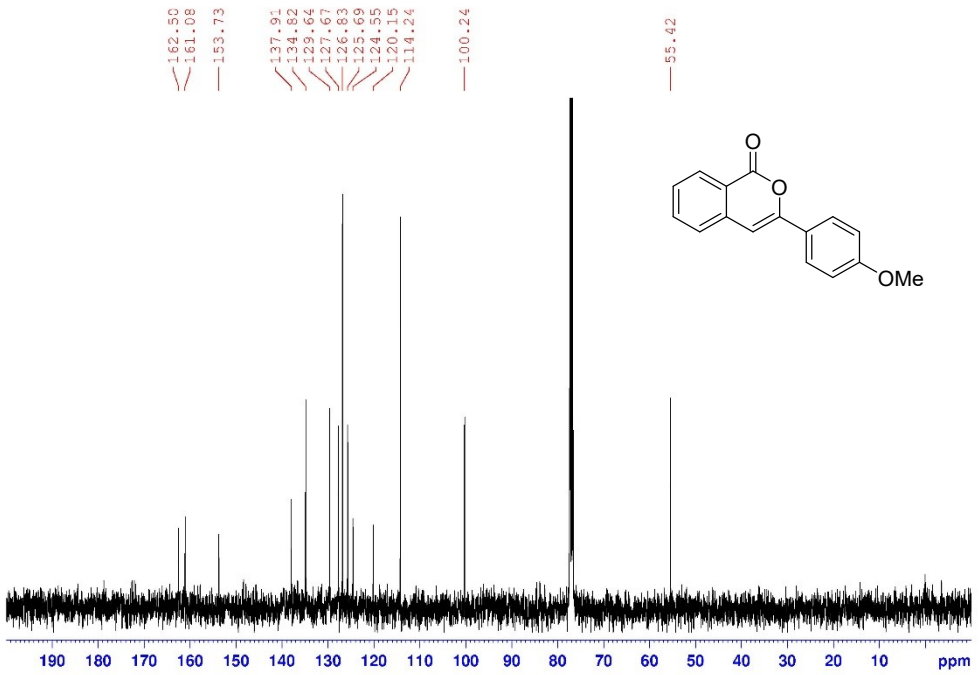
3af, $CDCl_3$, 100 MHz



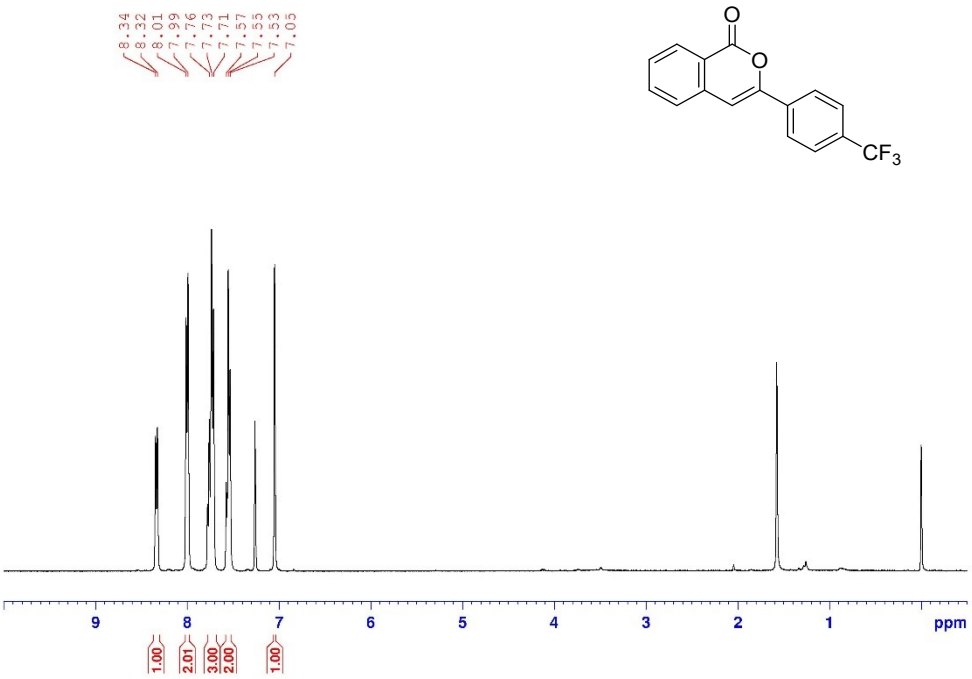
3ag, $CDCl_3$, 400 MHz



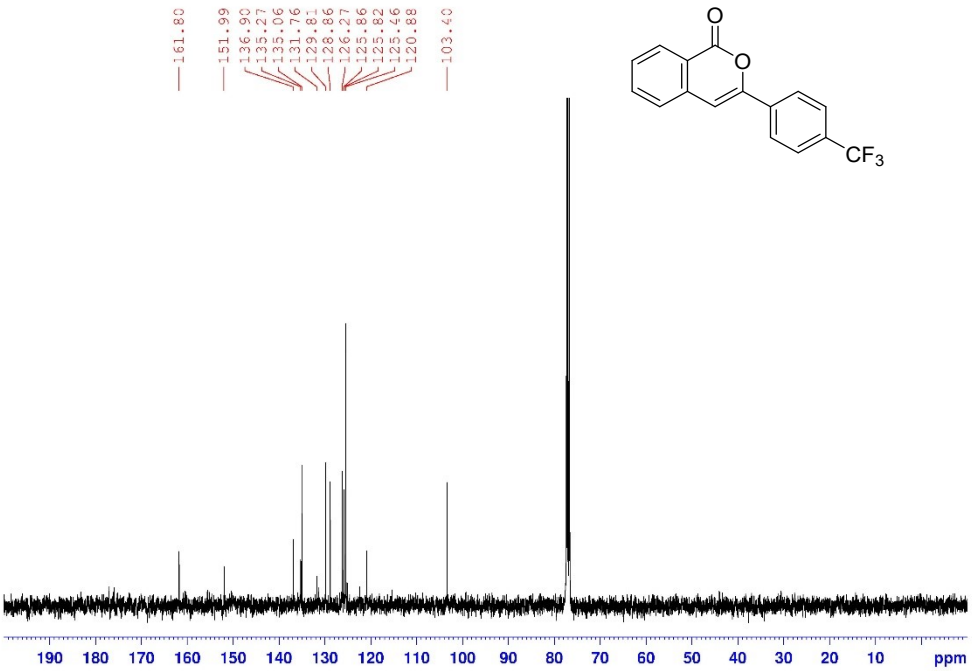
3ag, $CDCl_3$, 100 MHz



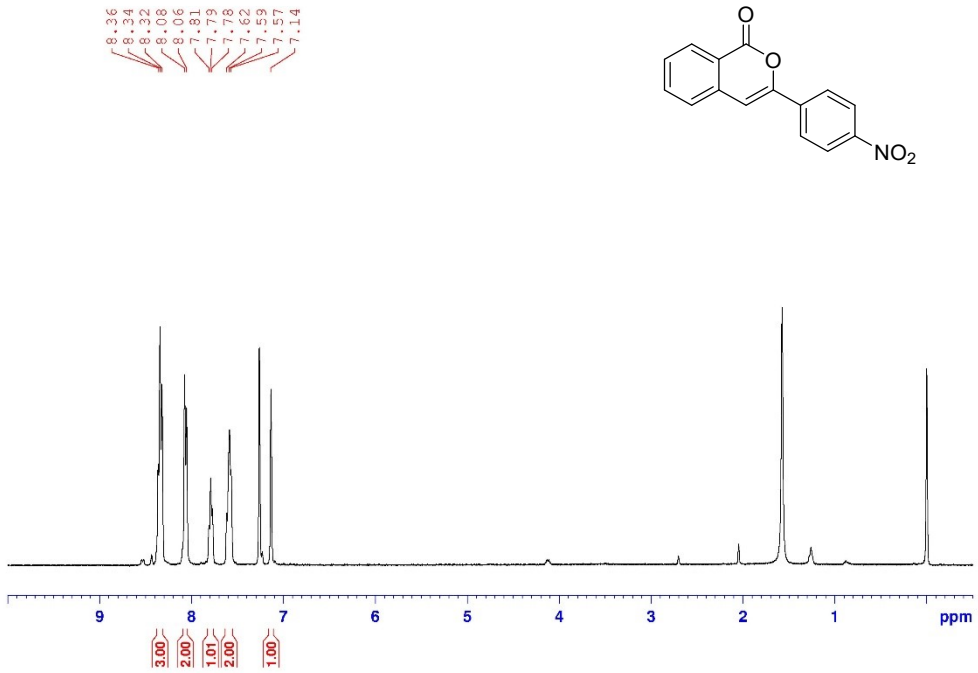
3ah, $CDCl_3$, 400 MHz



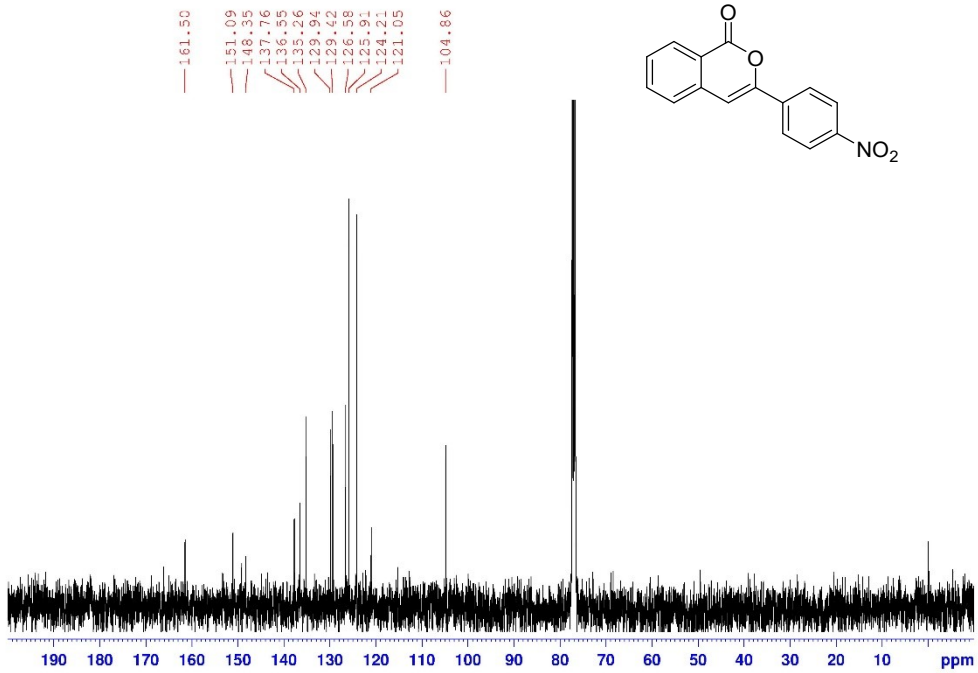
3ah, $CDCl_3$, 100 MHz



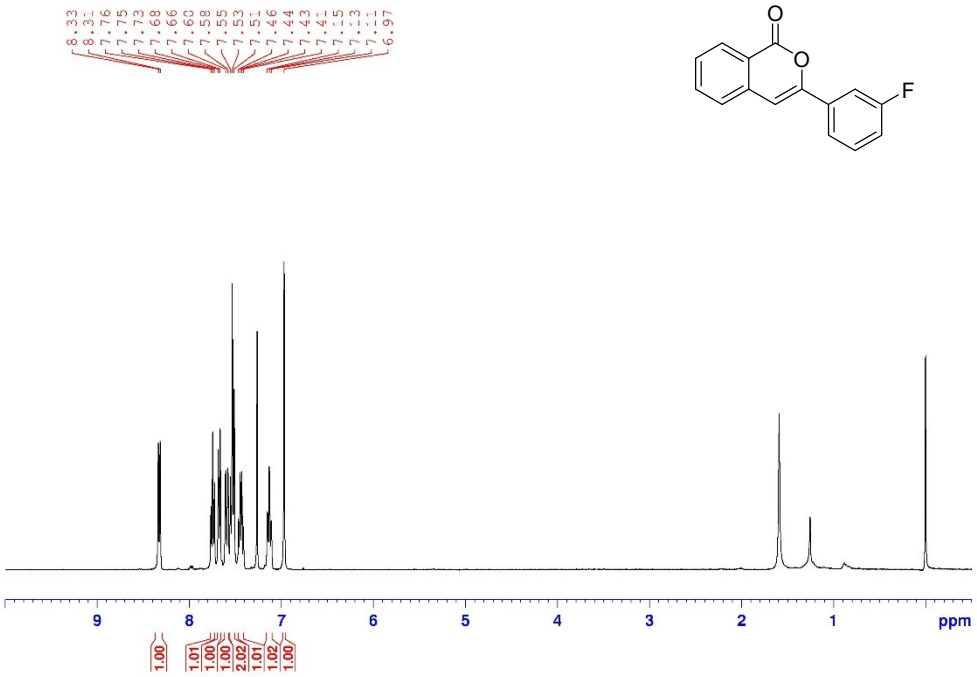
3ai, $CDCl_3$, 400 MHz



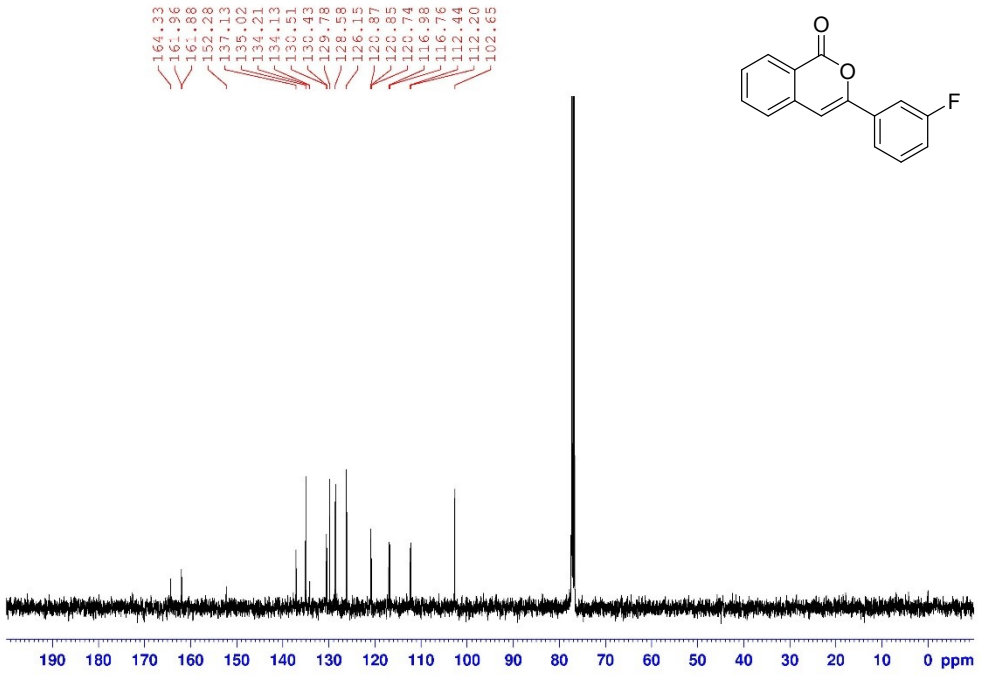
3ai, $CDCl_3$, 100 MHz



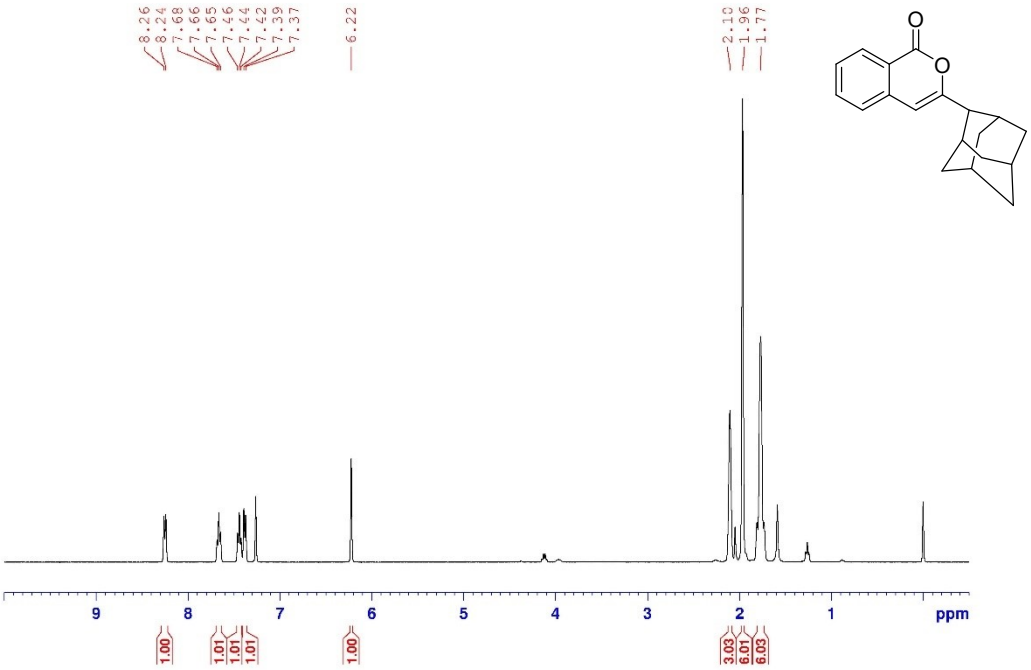
3aj, $CDCl_3$, 400 MHz



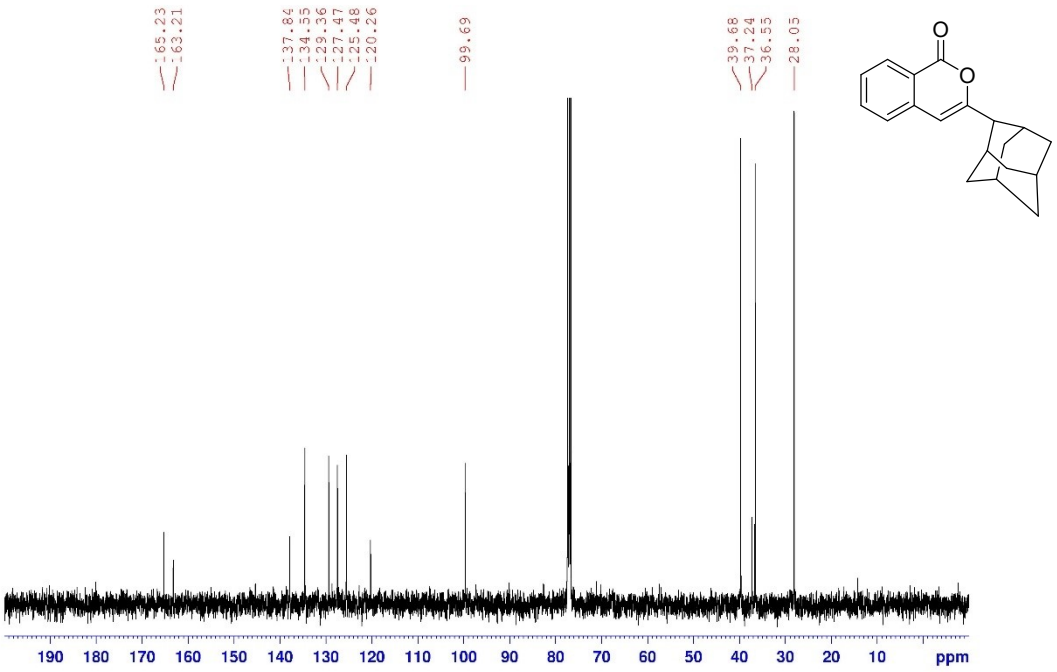
3aj, $CDCl_3$, 100 MHz



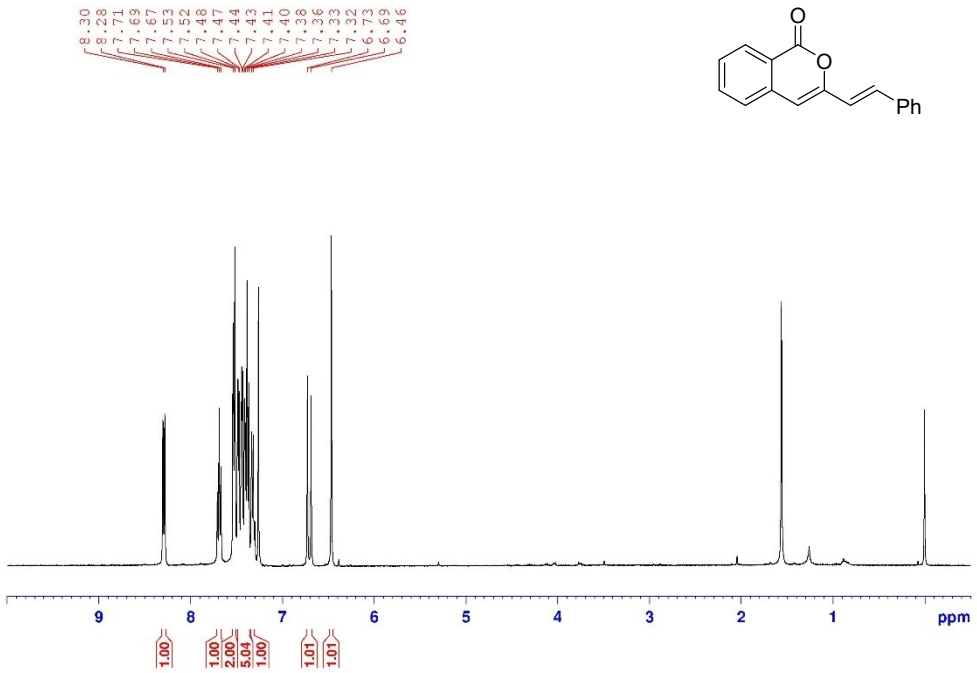
3ak, $CDCl_3$, 400 MHz



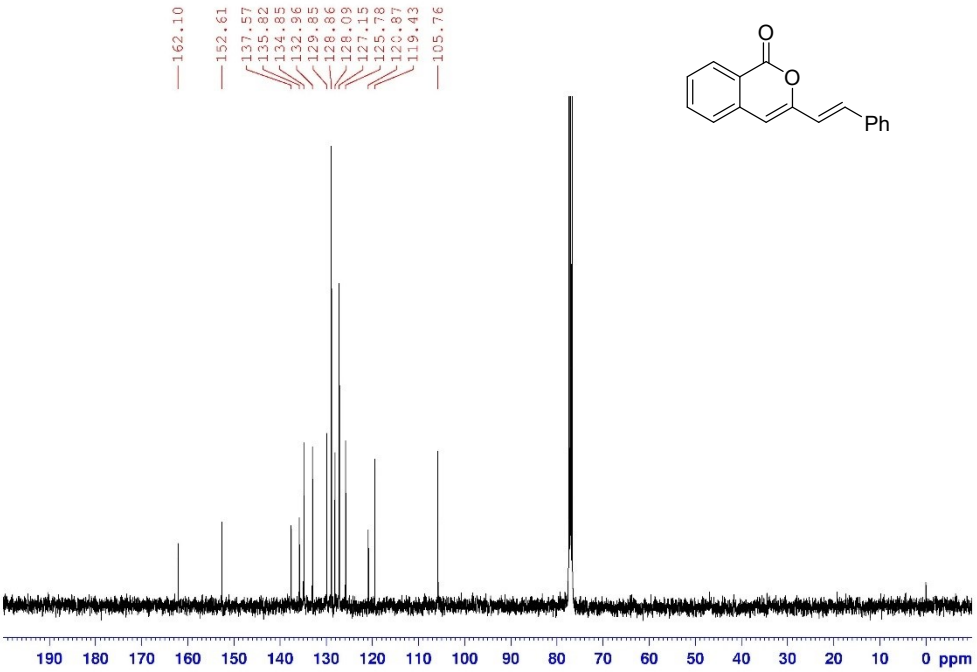
3ak, $CDCl_3$, 100 MHz



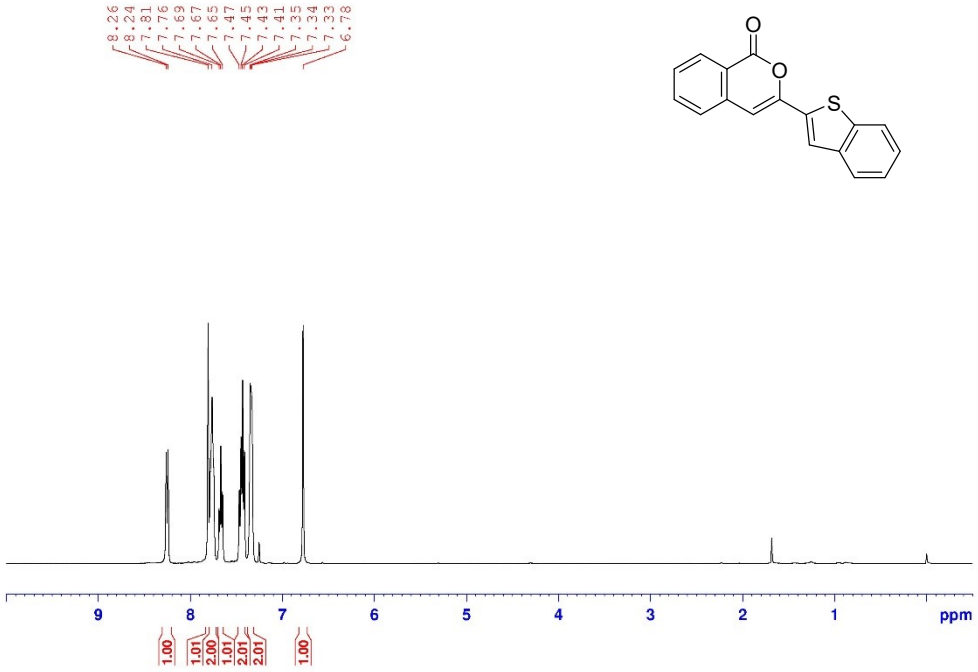
3al, $CDCl_3$, 400 MHz



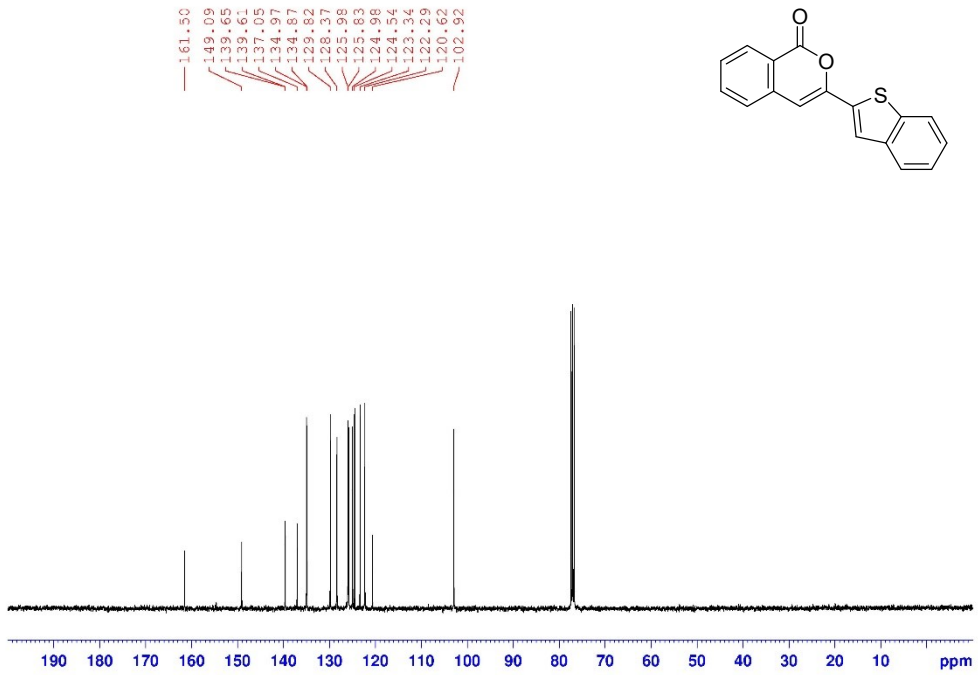
3al, $CDCl_3$, 100 MHz



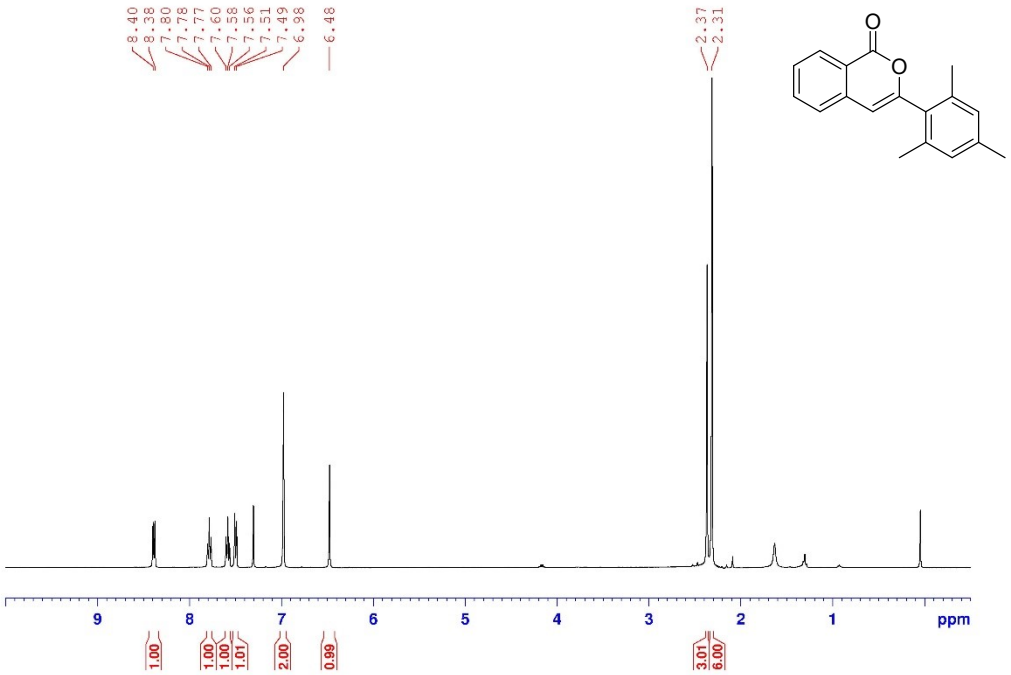
3am, $CDCl_3$, 400 MHz



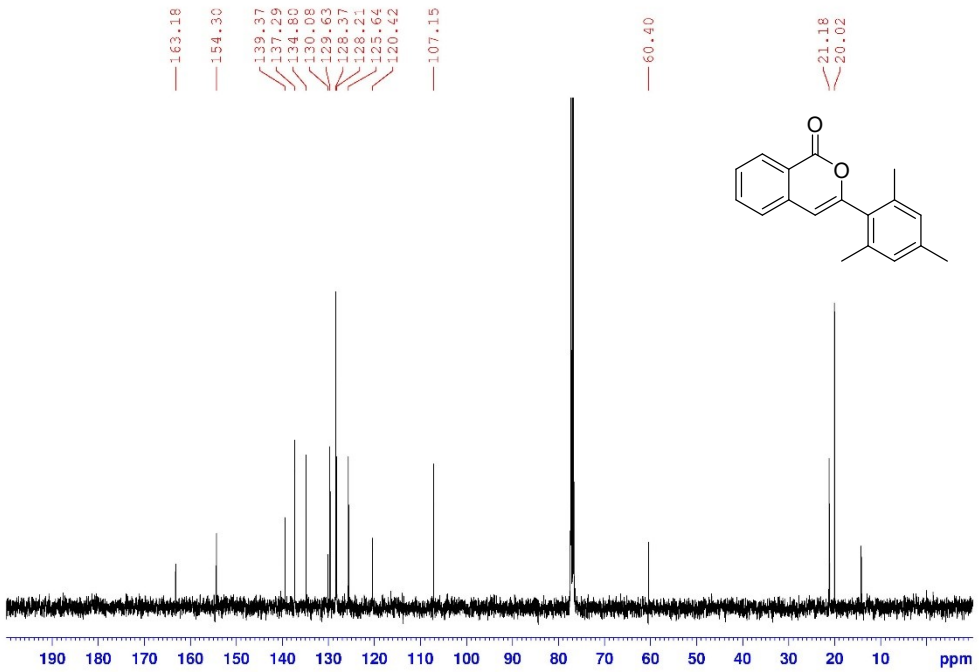
3am, $CDCl_3$, 100 MHz



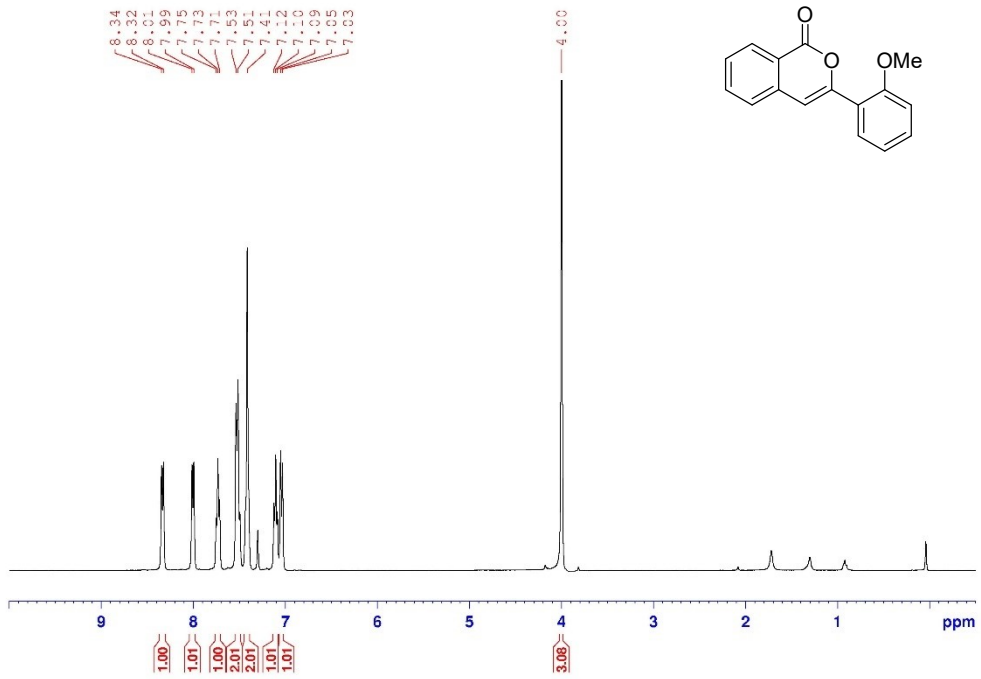
3an, $CDCl_3$, 400 MHz



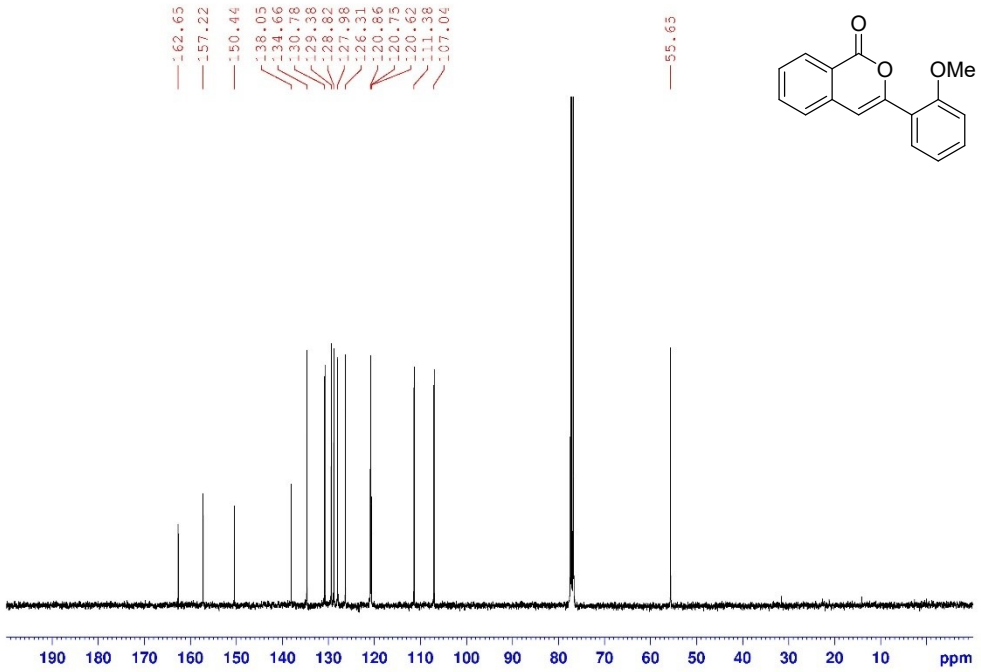
3an, $CDCl_3$, 100 MHz



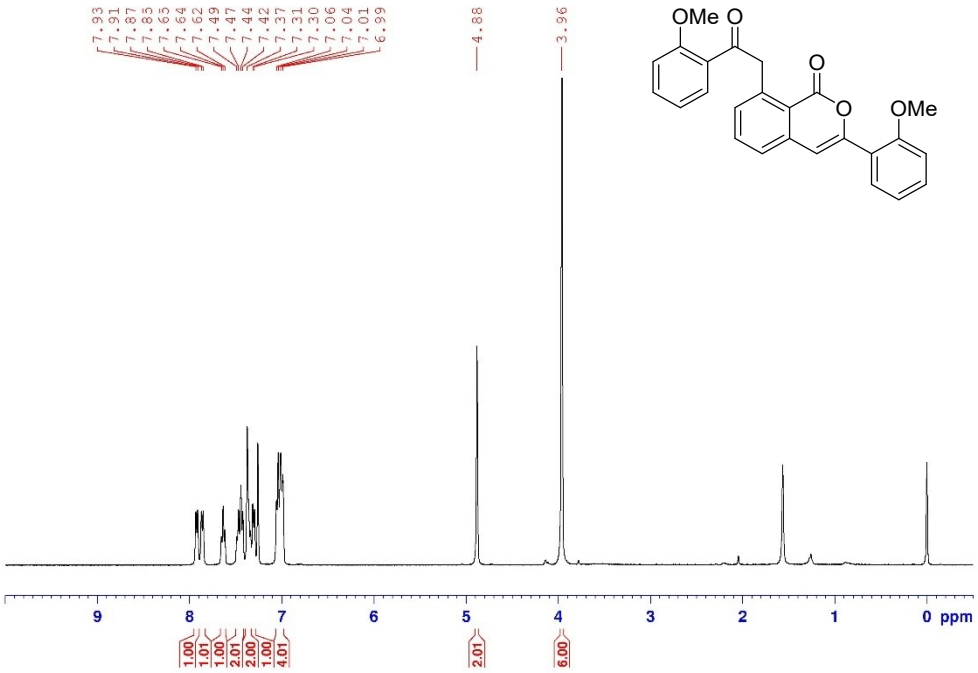
3ao, $CDCl_3$, 400 MHz



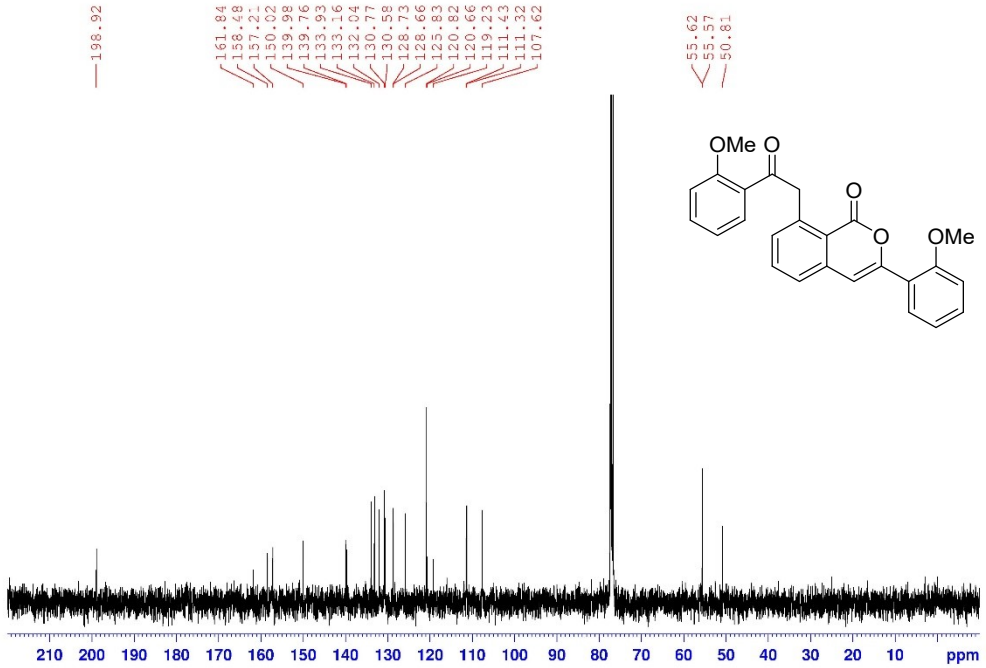
3ao, $CDCl_3$, 100 MHz



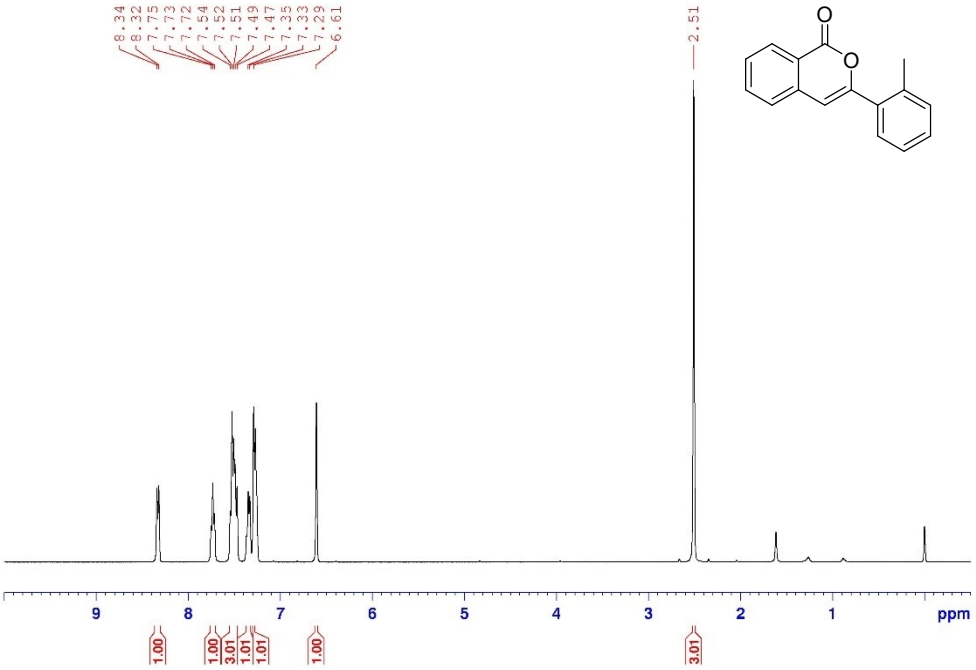
3ao', $CDCl_3$, 400 MHz



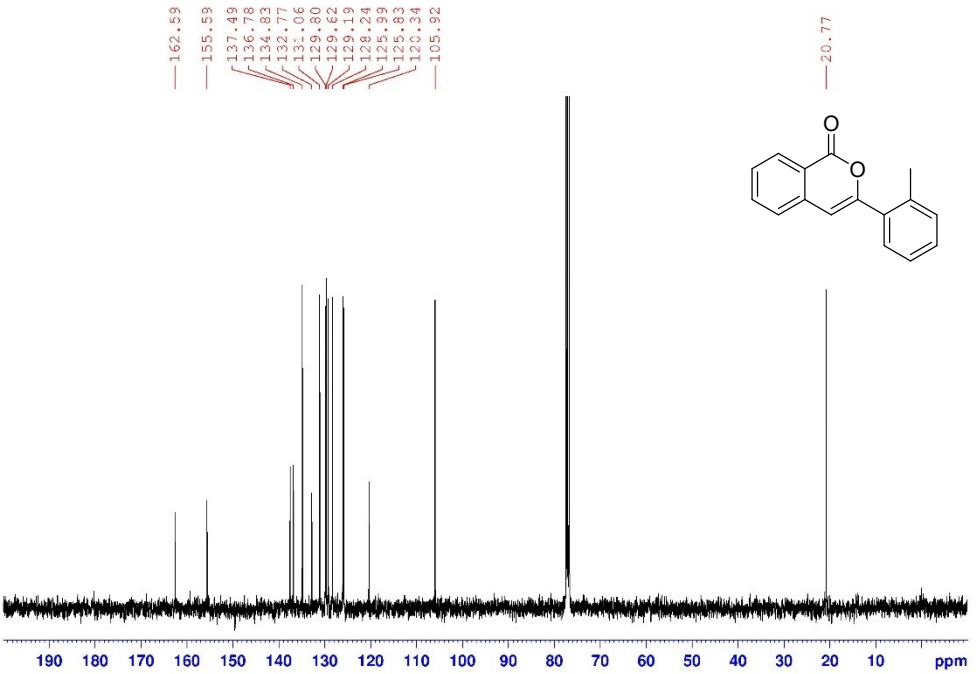
3ao', $CDCl_3$, 100 MHz



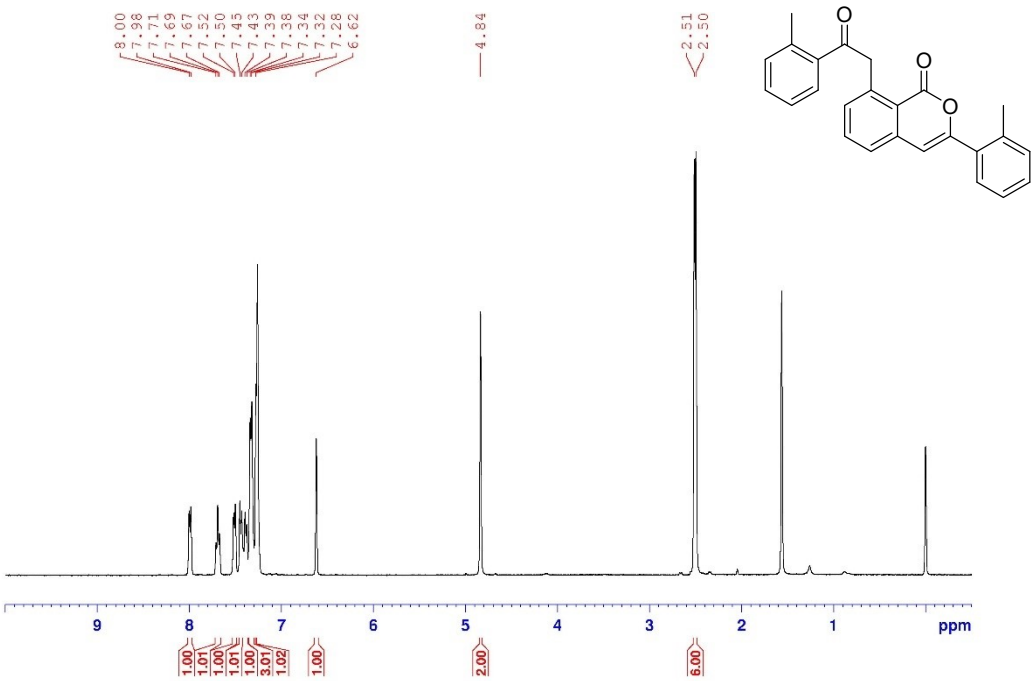
3ap, $CDCl_3$, 400 MHz



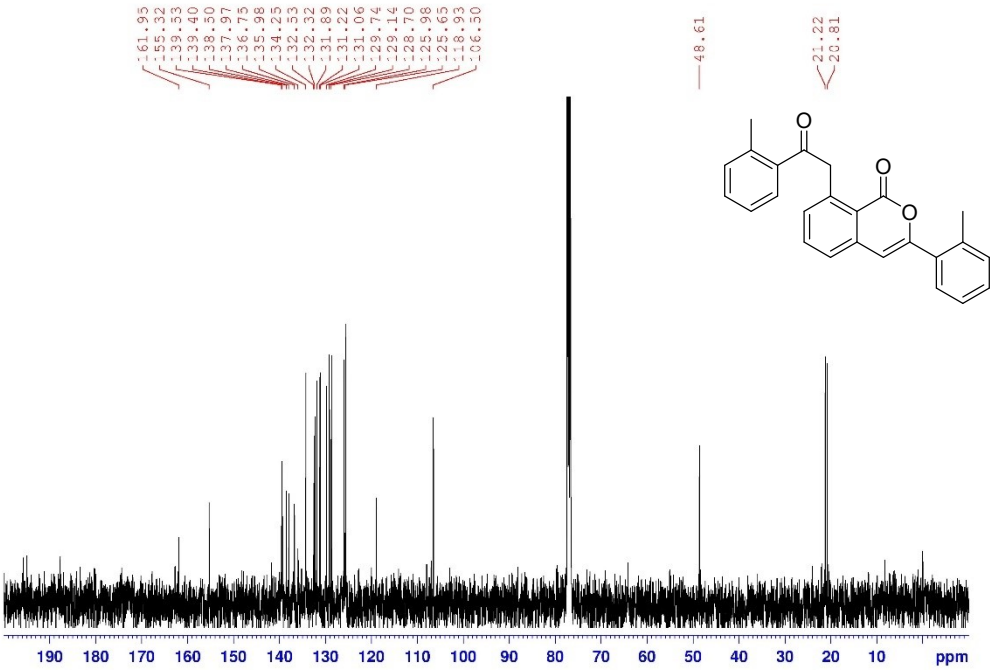
3ap, $CDCl_3$, 100 MHz



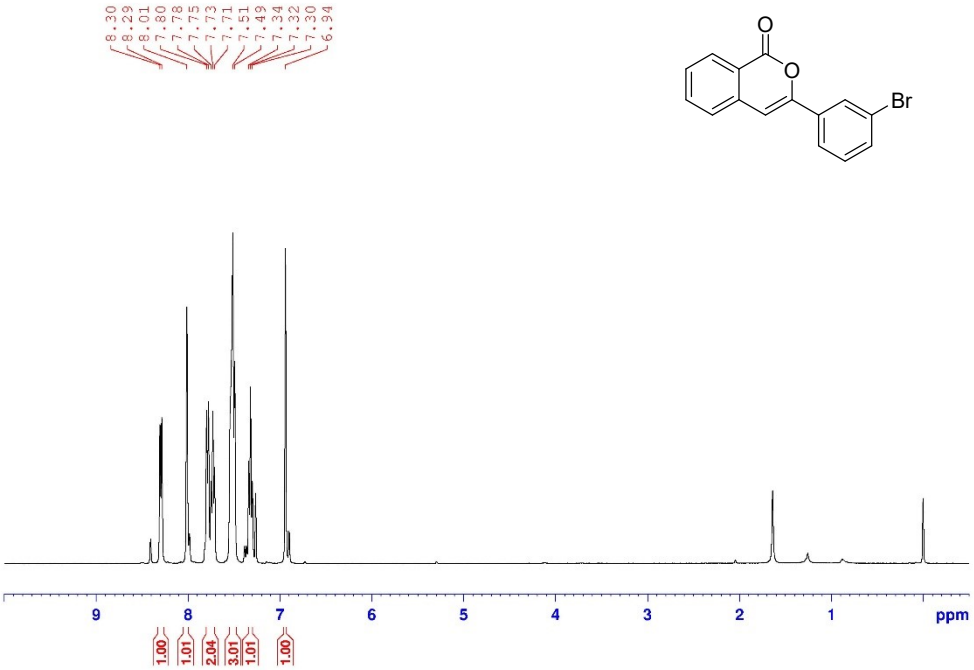
3ap', $CDCl_3$, 400 MHz



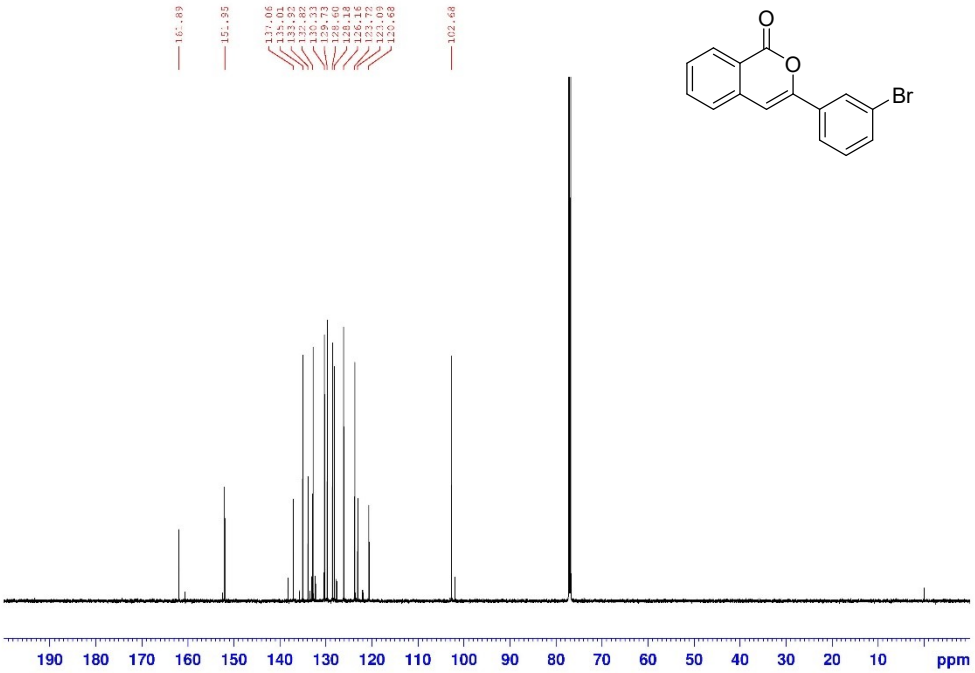
3ap', $CDCl_3$, 100 MHz



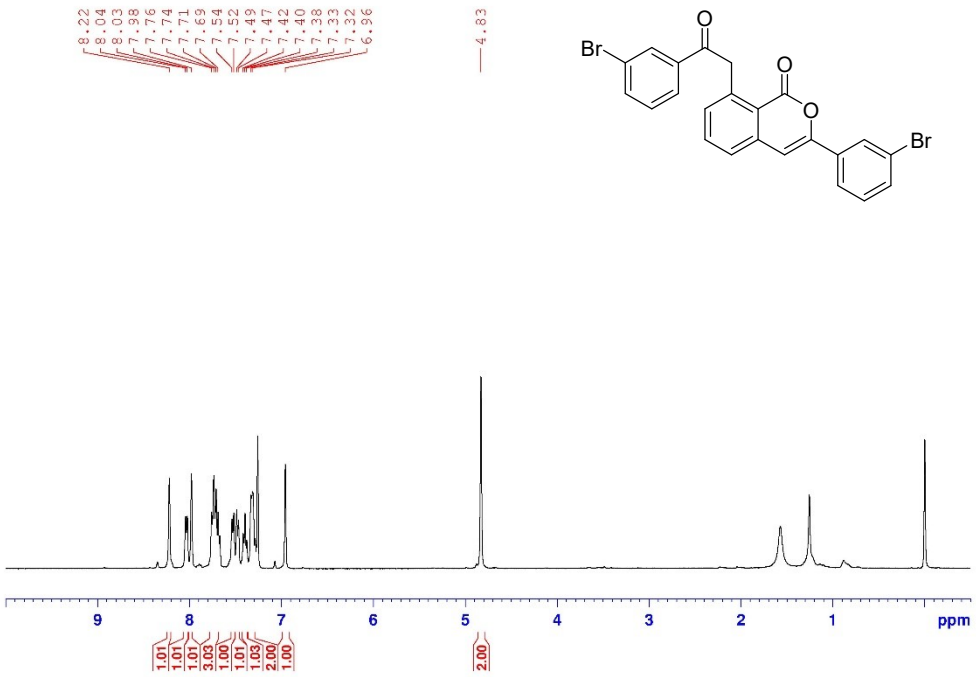
3aq, $CDCl_3$, 400 MHz



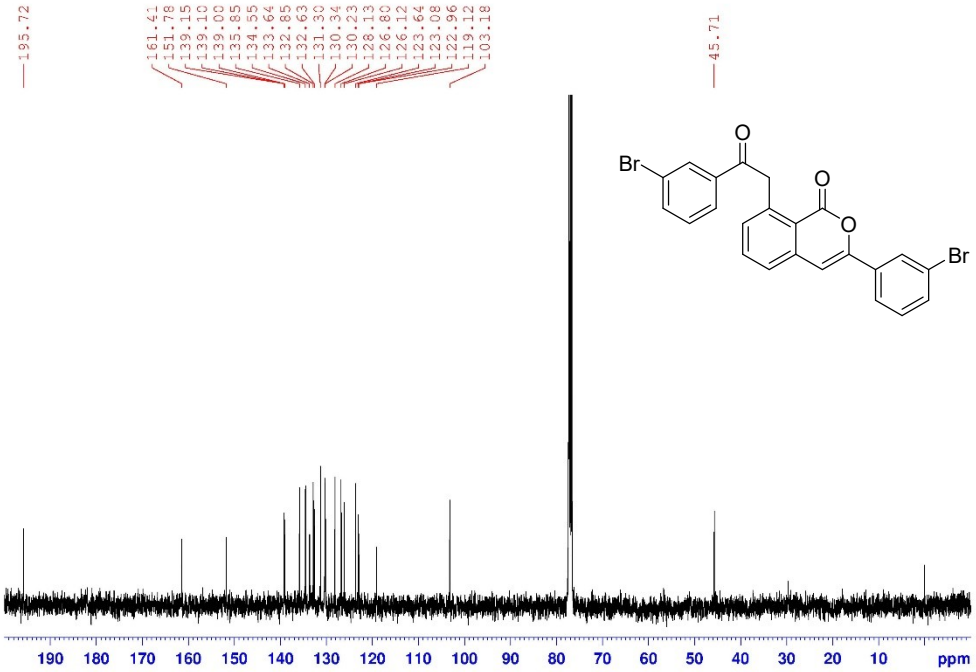
3aq, $CDCl_3$, 150 MHz



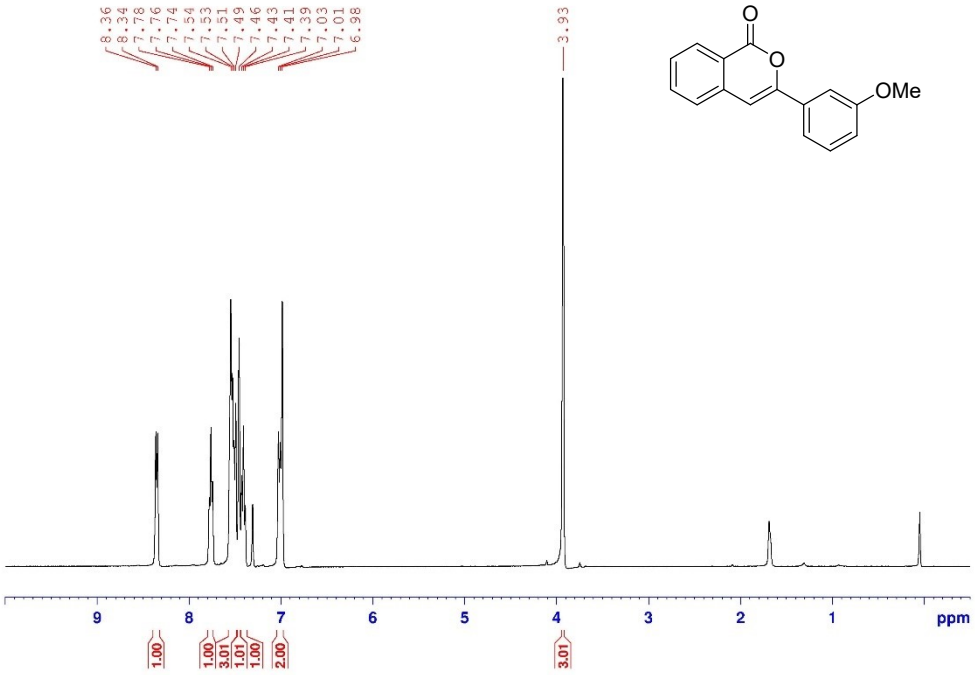
3aq', $CDCl_3$, 400 MHz



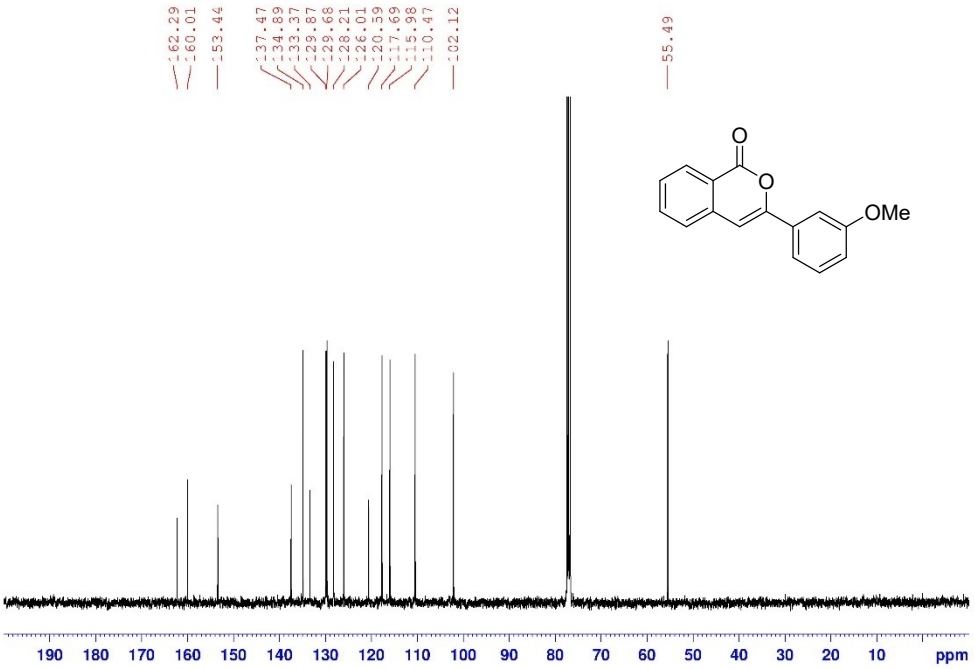
3aq', $CDCl_3$, 100 MHz



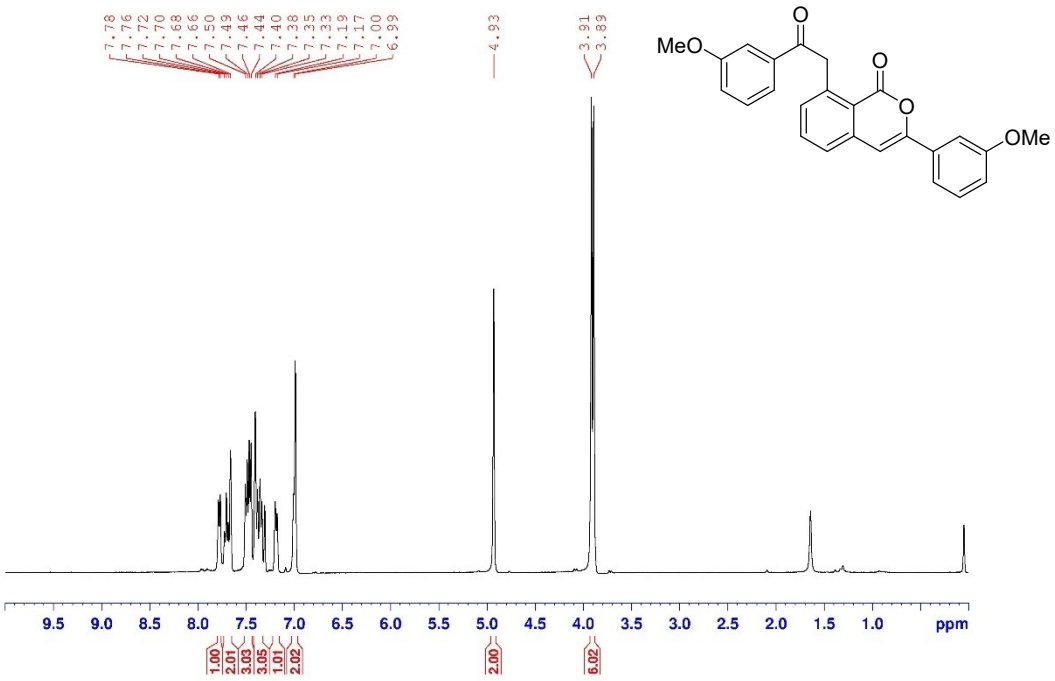
3ar, $CDCl_3$, 400 MHz



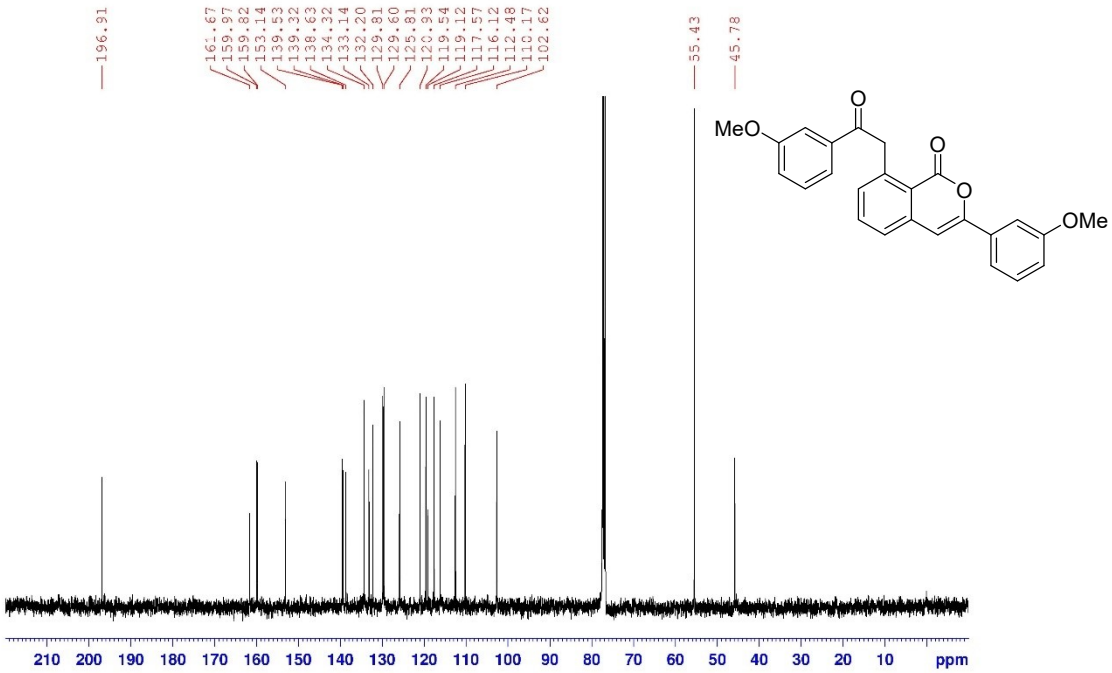
3ar, $CDCl_3$, 100 MHz



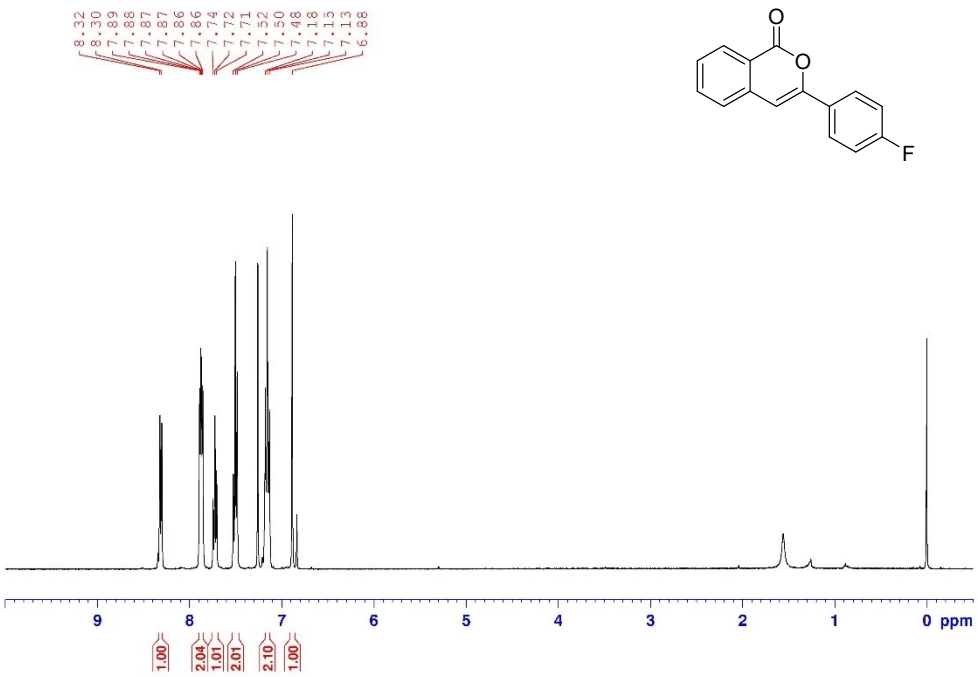
3ar', $CDCl_3$, 400 MHz



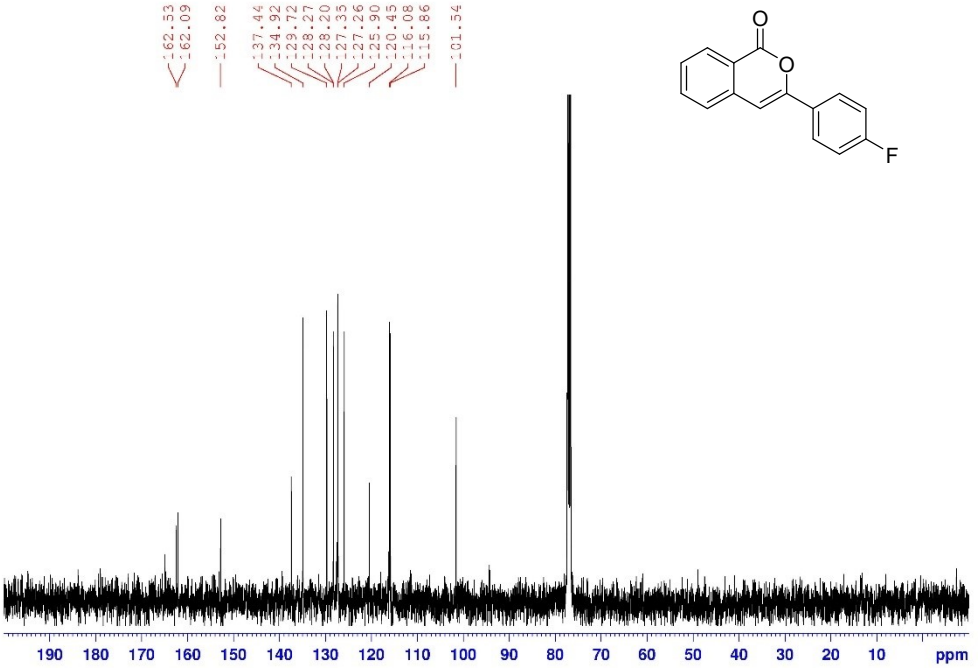
3ar', $CDCl_3$, 100 MHz



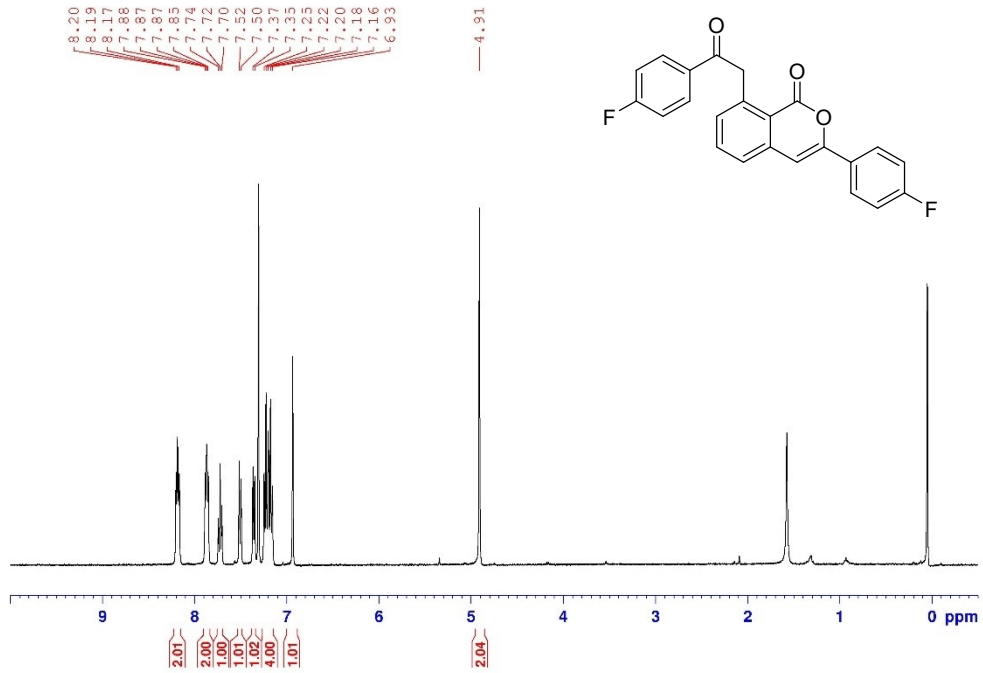
3as, $CDCl_3$, 400 MHz



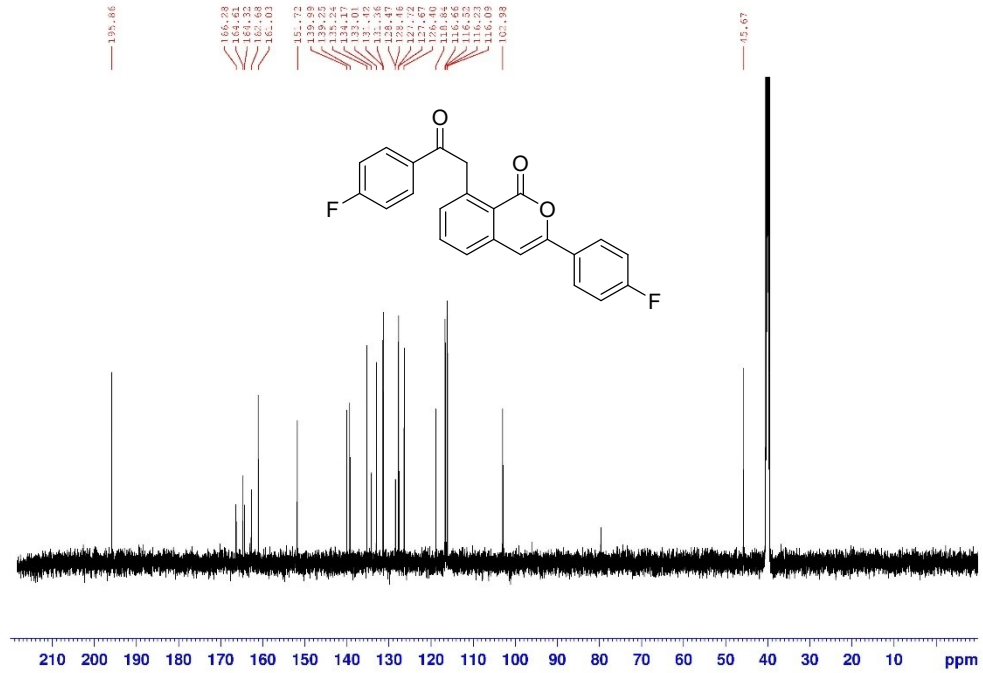
3as, $CDCl_3$, 100 MHz



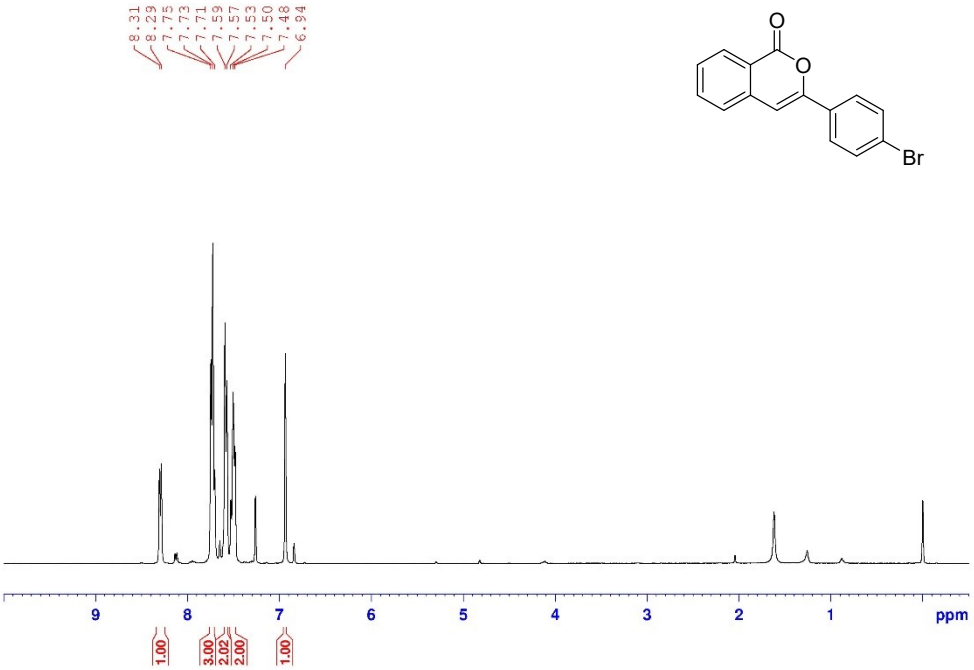
3as', $CDCl_3$, 400 MHz



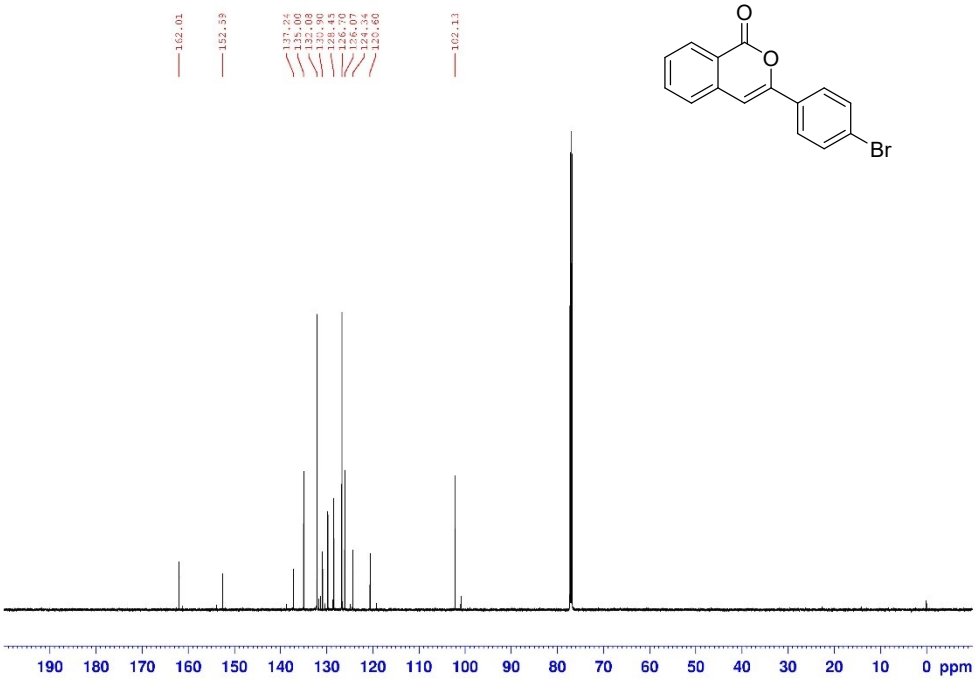
3as', $CDCl_3$, 150 MHz



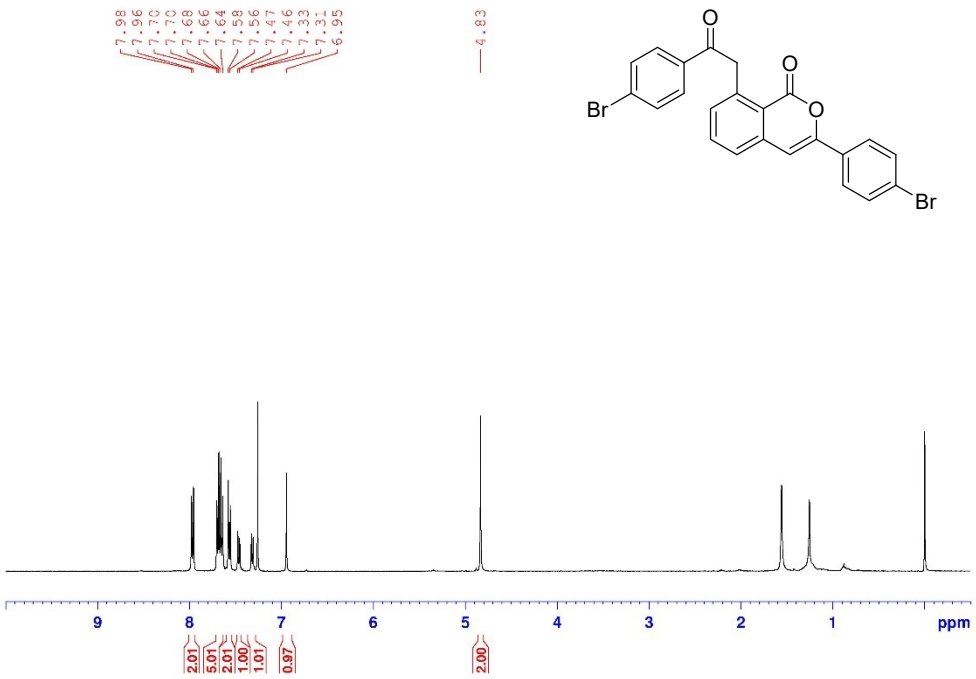
3at, $CDCl_3$, 400 MHz



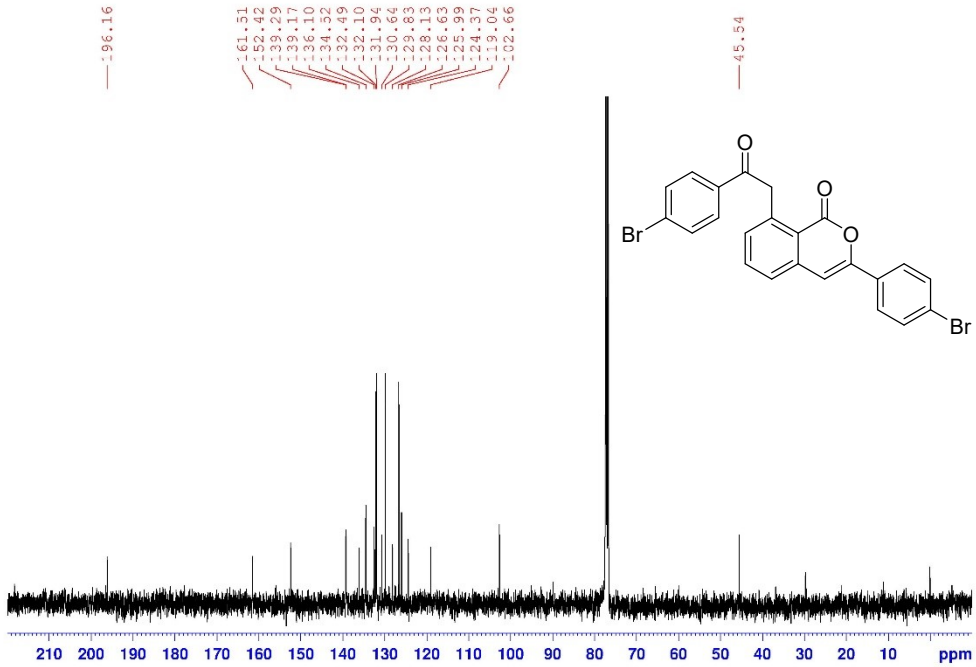
3at, $CDCl_3$, 150 MHz



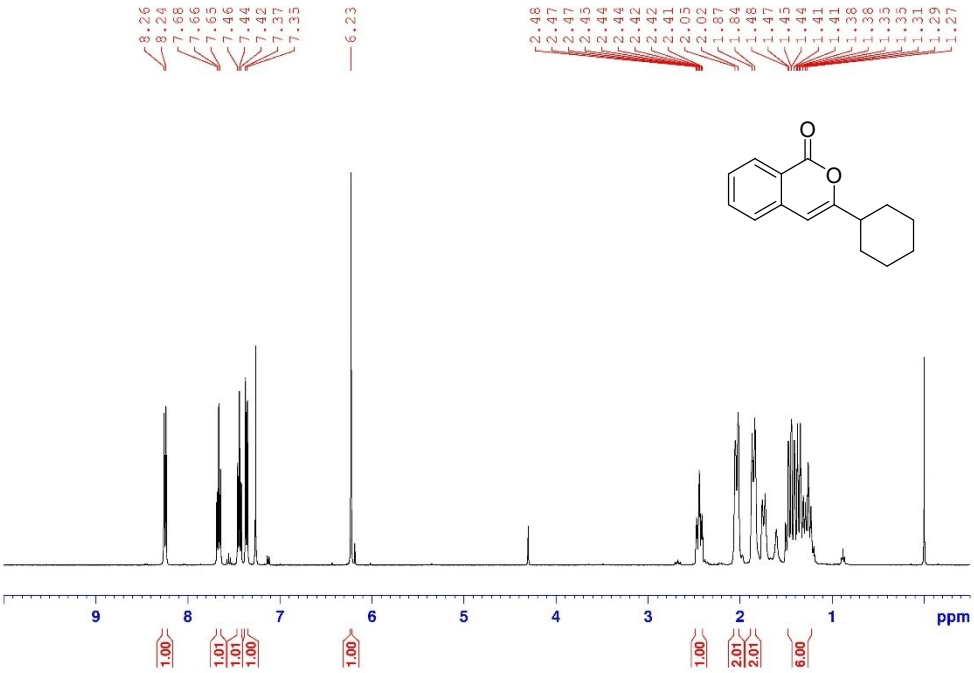
3at', $CDCl_3$, 400 MHz



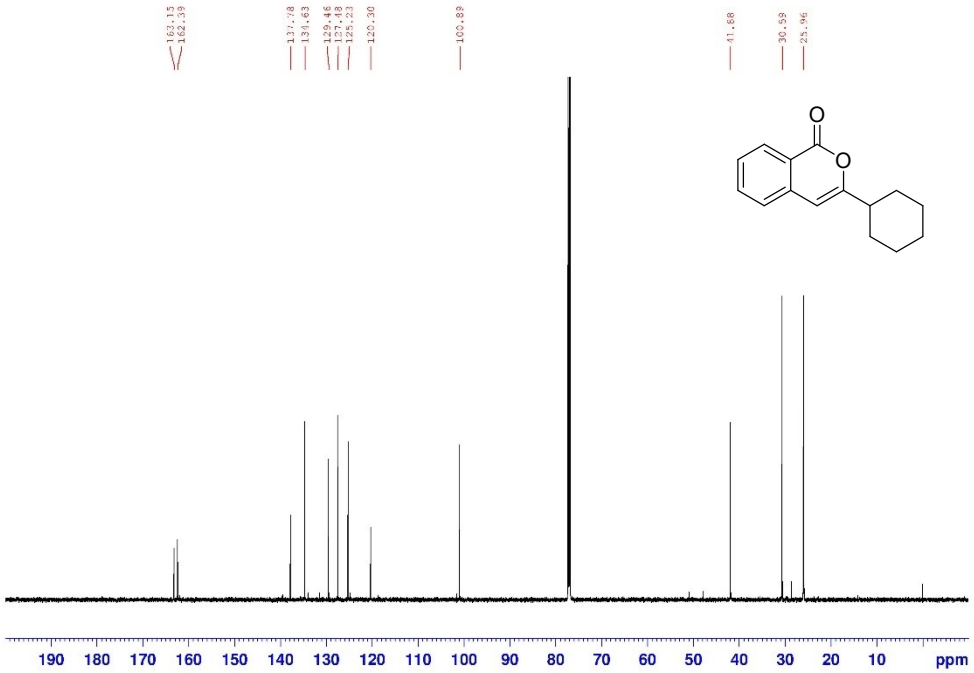
3at', $CDCl_3$, 100 MHz



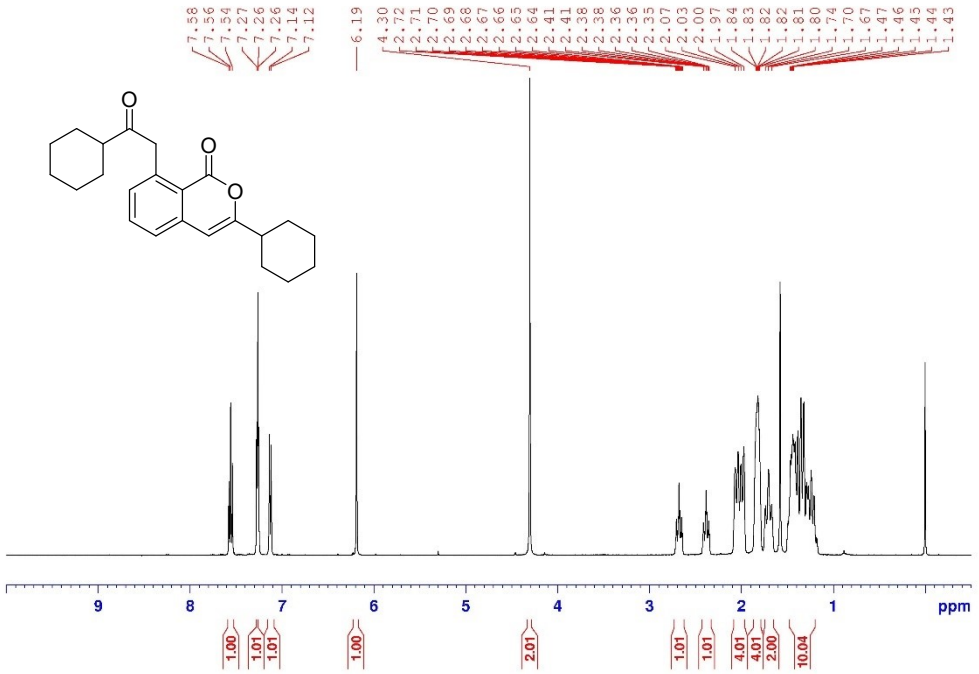
3au, $CDCl_3$, 400 MHz



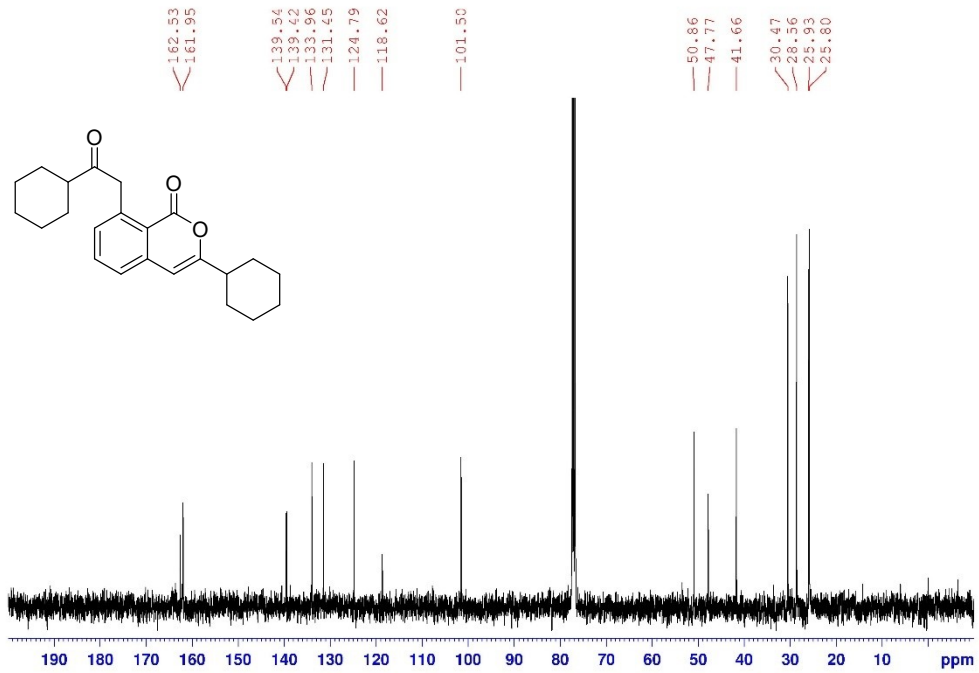
3au, $CDCl_3$, 100 MHz



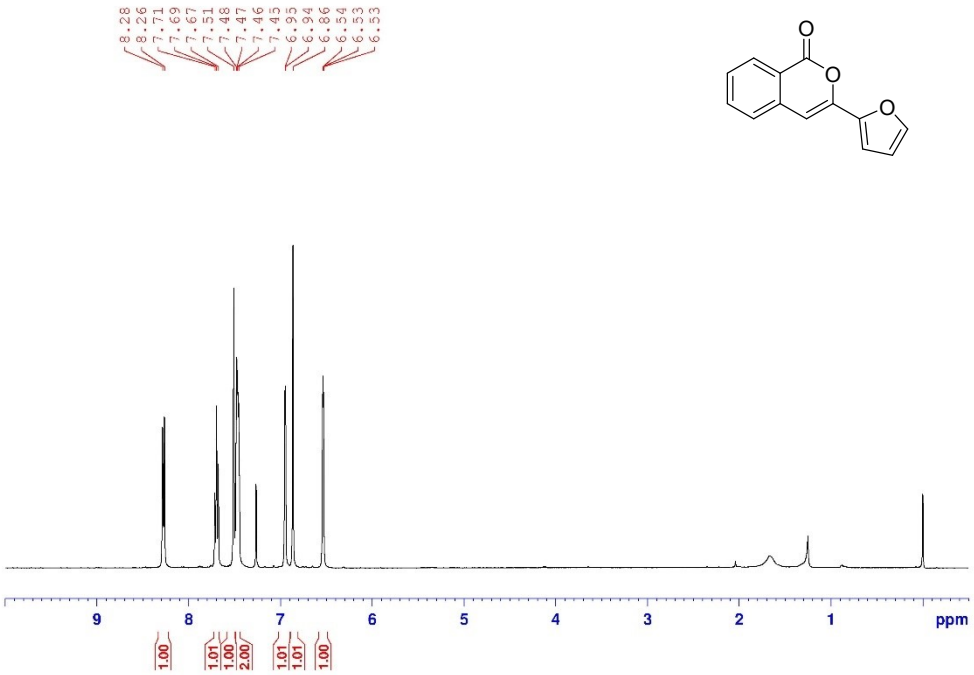
3au', $CDCl_3$, 400 MHz



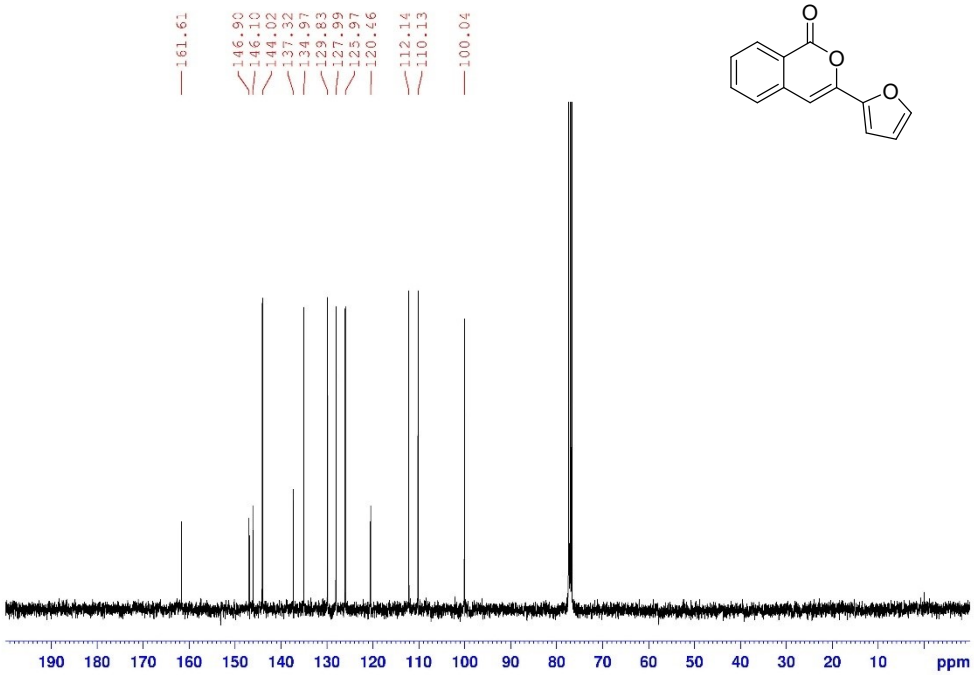
3au', $CDCl_3$, 100 MHz



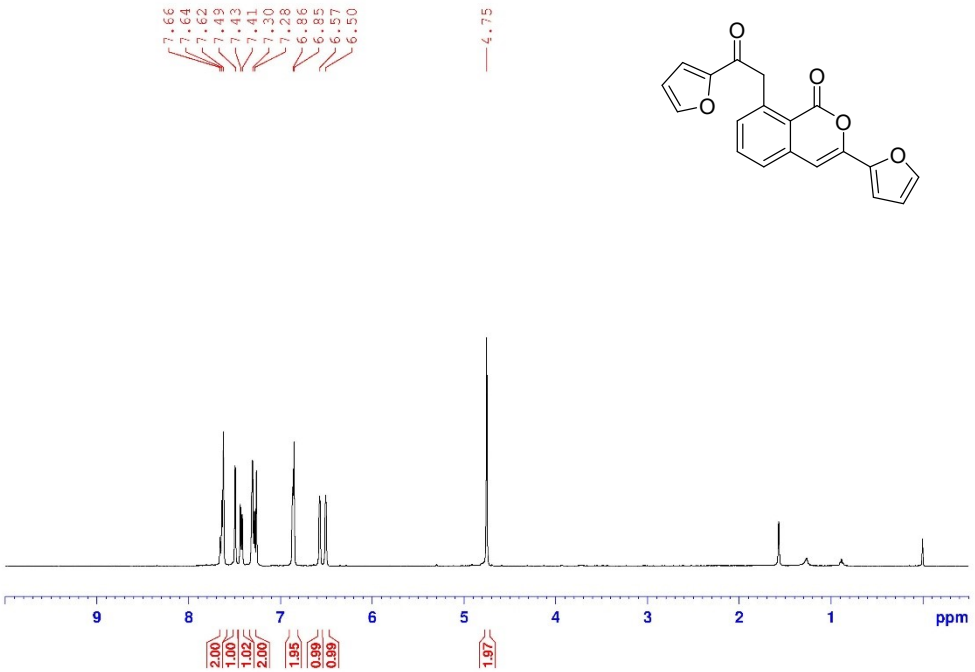
3av, $CDCl_3$, 400 MHz



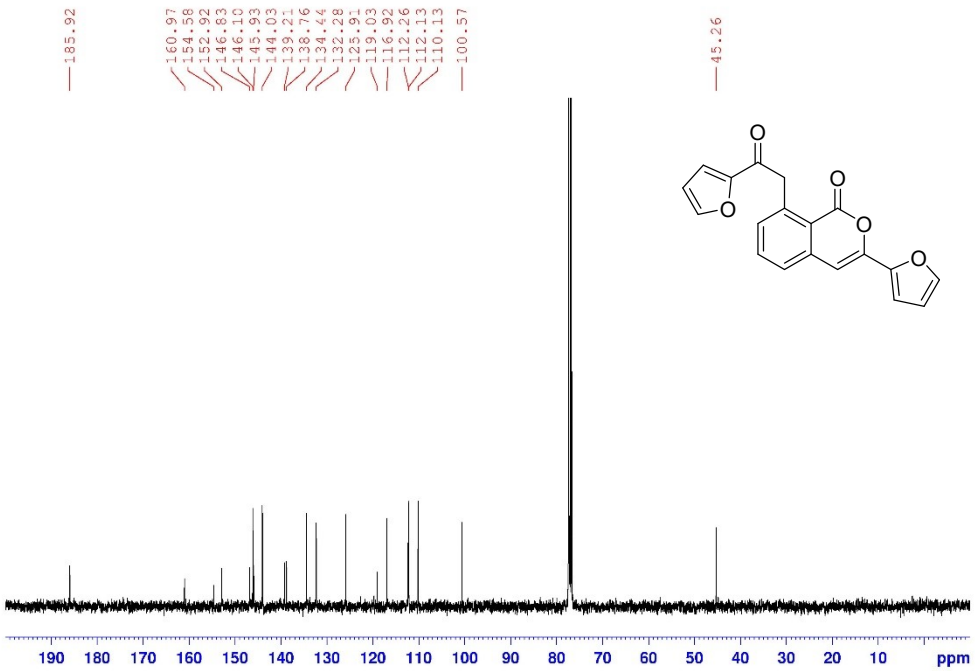
3av, $CDCl_3$, 100 MHz



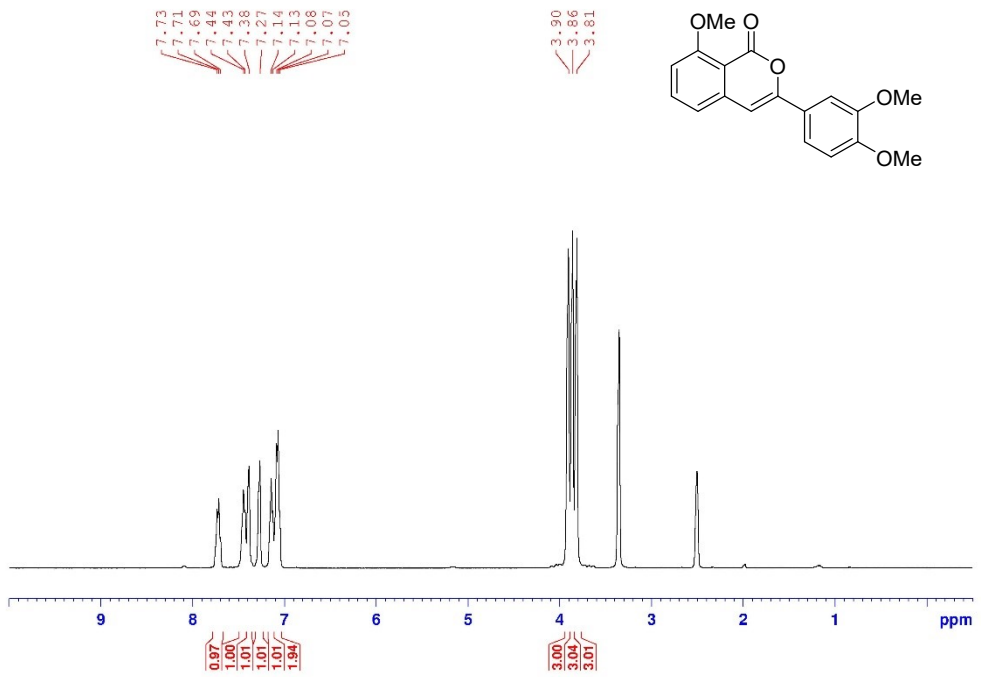
3av', $CDCl_3$, 400 MHz



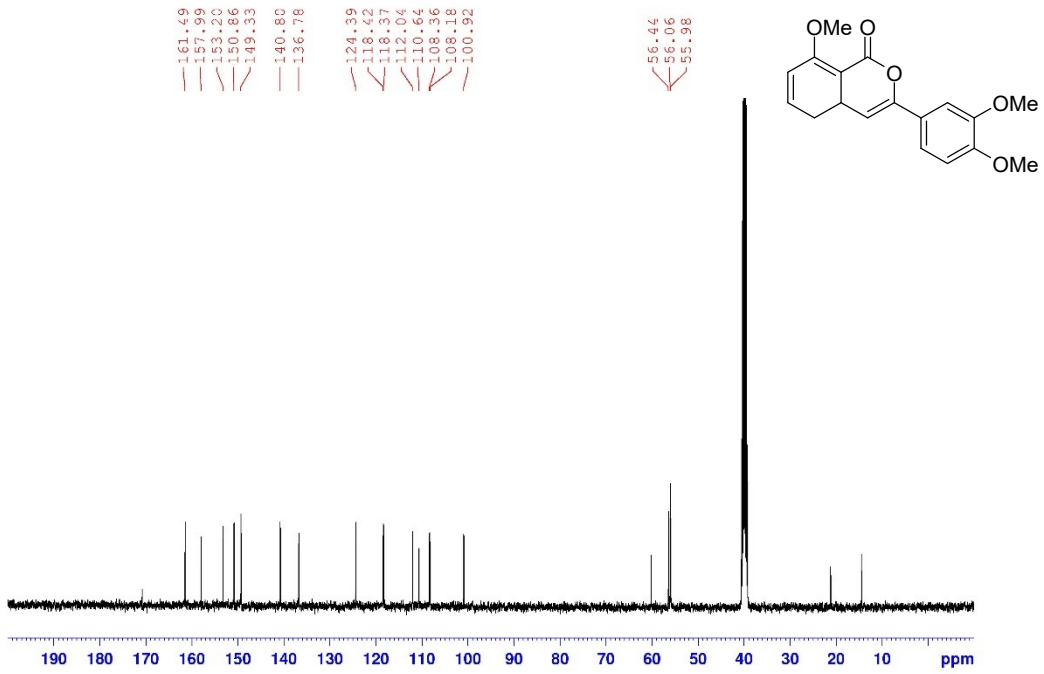
3av', $CDCl_3$, 100 MHz



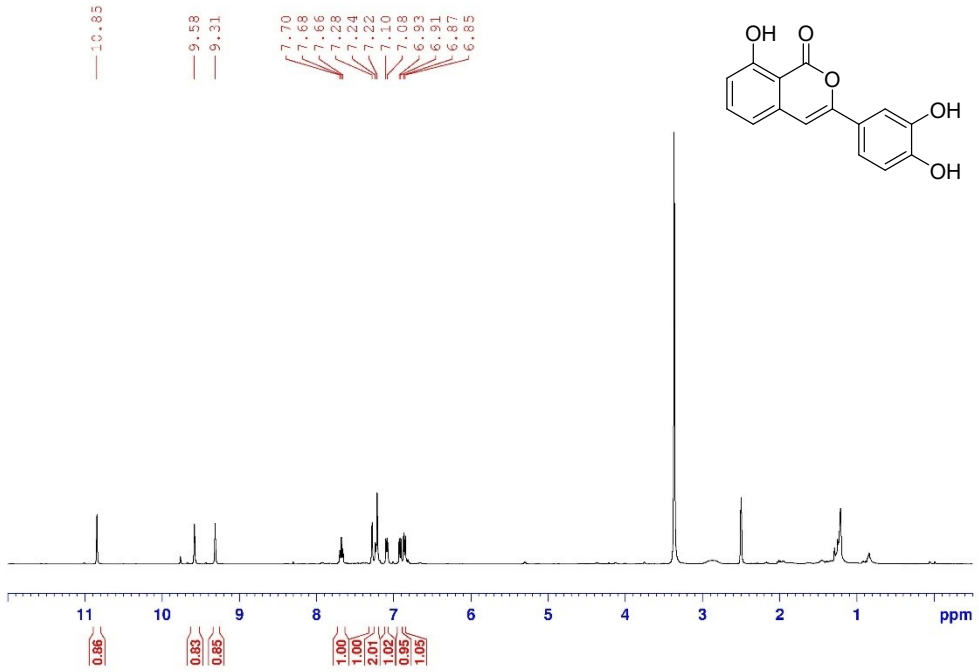
3dw, DMSO, 400MHz



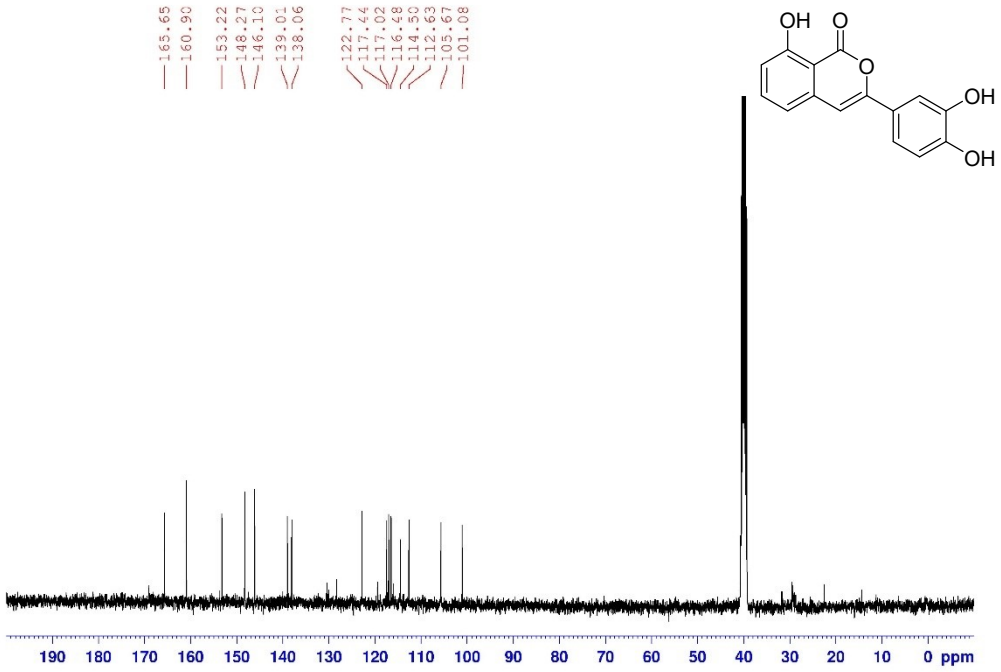
3dw, DMSO, 100MHz



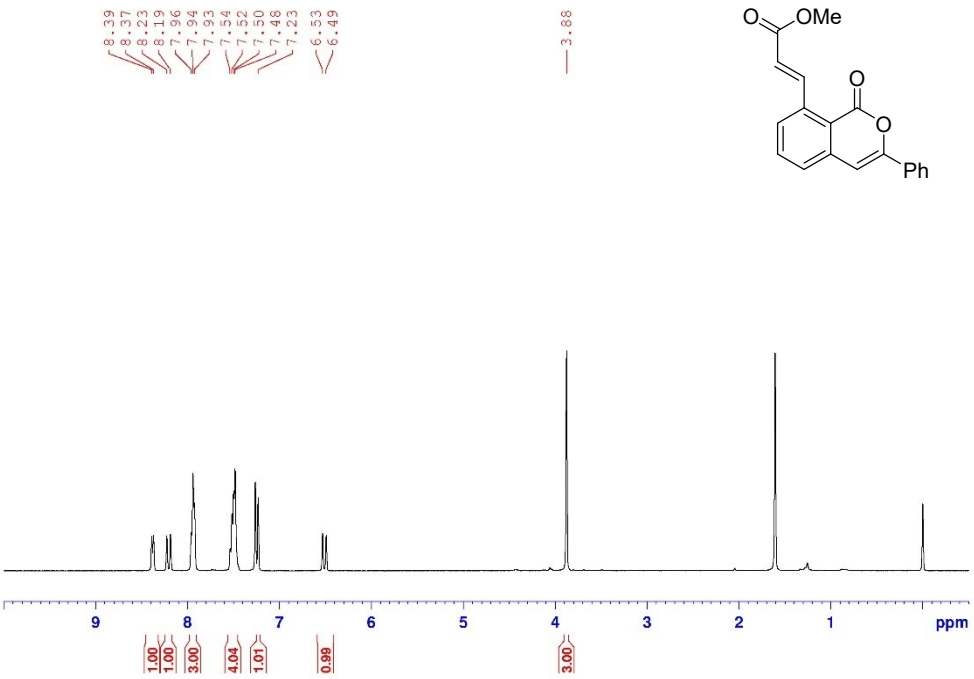
thunberginol A, DMSO-d_6, 400MHz



thunberginol A, DMSO-d_6,100MHz



5, $CDCl_3$, 400MHz



5, $CDCl_3$, 100MHz