NHC-Catalyzed Reactions of Aryloxyacetaldehydes: A Domino/Elimination/Conjugate Addition/Acylation Process for the Synthesis of Substituted Coumarins

Eric M. Phillips, Manabu Wadamoto, Howard S. Roth, Andrew W. Ott and Karl A. Scheidt*

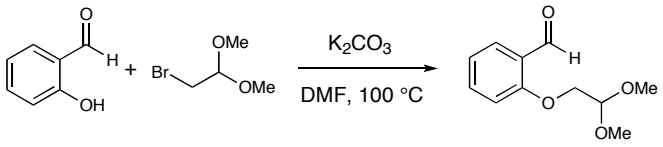
Department of Chemistry, Northwestern University,
2145 Sheridan Road, Evanston, Illinois 60208

Supporting Information

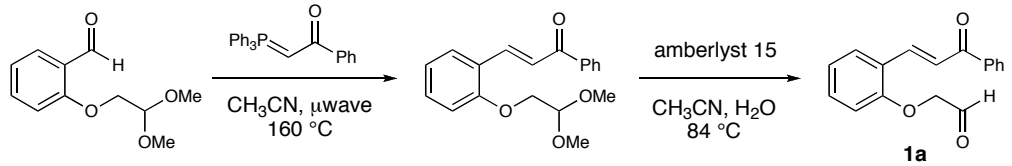
General Information

All reactions were carried out under a nitrogen atmosphere in flame-dried glassware with magnetic stirring. CH_3CN was purified by passage through a bed of activated alumina.[1] Reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego.[2] Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and ceric ammonium nitrate stain or potassium permangenate stain followed by heating. Infrared spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer. ^{1}H-NMR spectra were recorded on a Varian Inova 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data are reported as (ap = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration. Proton-decoupled ^{13}C-NMR spectra were recorded on a Varian Inova 500 (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.0 ppm). Mass spectra data were obtained on a Varian 1200 Quadrupole Mass Spectrometer and Micromass Quadro II Spectrometer.

General Procedure for the Synthesis of Aryloxy-acetaldehydes, illustrated with 1a



To a flame-dried 100 mL round bottom flask equipped with magnetic stirring bar, septum, and gas inlet was added salicyl aldehyde (2 mL, 20.0 mmol), DMF (20 mL, 1 M), and K_2CO_3 (2.80 g, 20.00 mmol). Bromoacetaldehyde dimethyl acetal (2.37 mL, 20.00 mmol) was added via syringe. The flask was then equipped with reflux condenser, placed in an oil bath, and heated to 100 °C. After 48 hrs the reaction was cooled to 23 °C. The mixture was diluted with Et_2O (50 mL) and washed with water (10 x 5 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting mixture was purified by flash column chromatography on silica gel with 20% EtOAc in hexanes as an eluent to afford 2.40 g (57% yield) of the aldehyde as a light yellow oil.



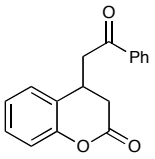
To an oven dried microwave vial was added the acetal (210 mg, 1.0 mmol), (benzoylmethylene)triphenylphosphorane (592 mg, 1.5 mmol), and CH_3CN (2 mL, 0.5 M). The

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometal.* **1996**, *15*, 1518-1520.
2. Perrin, D. D. and Armarego, W. L. *Purification of Laboratory Chemicals;* 3rd Ed., Pergamon Press, Oxford. 1988.

vial was purged with N_2, capped, and heated to 160 °C under microwave irradiation for 45 min with 20 s prestirring, normal absorption. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography on silica gel with 20% EtOAc in hexanes as an eluent to afford 319 mg (98% yield) of the enone as a yellow oil. Subsequently, to a 25 mL round bottom flask containing the enone (312 mg, 1 mmol) was added CH_3CN (10 mL, 0.1 M), H_2O[3] (2 mL), and amberlyst 15 resin (100 mg). The flask was then placed in an oil bath and heated to 84 °C for 24 hr. The reaction was cooled to 23 °C and diluted with 20 mL of CH_2Cl_2. The mixture was then washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The mixture was purified by flash column chromatography on silica gel with 30% EtOAc in hexanes to 50% EtOAc in hexanes as an eluent to afford 215 mg (81% yield) of aldehyde **1a** as a viscous yellow oil.[4]

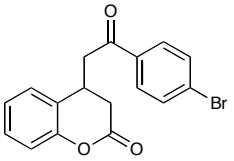
General Procedure for the Synthesis of 3,4-Dihydrocoumarins

To a flame-dried 25 mL round bottom flask equipped with a magnetic stirring bar, gas inlet tube, and septum was added the aldehyde (0.2 mmol) and CH_3CN (9 mL, 0.022 M). Then, a mixture containing azolium salt **C** (6 mg, 0.02 mmol), DBU (3 μL, 0.02 mmol), and 1 mL CH_3CN was added dropwise over 10 min via syringe. Upon consumption of the aldehyde (all reactions were completed within 12 hr), to the reaction was added 5 mL aqueous sat. NH_4Cl and 20 mL CH_2Cl_2. The layers were then separated. The aqueous layer was washed with CH_2Cl_2 (2 x 10 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude mixture was then purified by flash column chromatography on silica gel (5 g SiO_2) with 10% EtOAc in hexanes to 100% EtOAc as eluent to afford the corresponding 3,4-dihydrocoumarin.

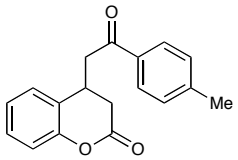


4-(2-oxo-2-phenylethyl)chroman-2-one (2a): Prepared according to general procedure using *(E)*-2-(2-(3-oxo-3-phenylprop-1-enyl)phenoxy)acetaldehyde (53 mg, 0.2 mmol) to afford 44 mg (83%) of **2a** as a yellow oil after 3 hr. Analytical data for **2a**: IR (film) 3063, 2918, 1769, 1683, 1593, 1453 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 3.91-3.89 (m, 1H), 3.33 (dd, *J* = 6.2, 17.7 Hz, 1H), 3.26 (dd, *J* = 6.7, 17.7 Hz, 1H), 2.96 (dd, *J* = 5.9, 16.3 Hz, 1H), 2.90 (dd, *J* = 3.9, 16.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.1, 168.3, 151.7, 136.6, 133.8, 129.0, 128.9, 128.3, 128.2, 126.1, 125.0, 117.5, 43.2, 35.0, 30.7; LRMS (ES): Mass calcd for $C_{17}H_{14}O_3$ $[M+Na]^+$, 289. Found $[M+Na]^+$, 289.

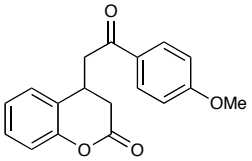
3. The synthesis of compound **8** required a 9:1 mixture of CH_3CN:H_2O^{18}.
4. All aldehydes were stored in benzene at –30 °C.



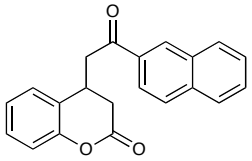
4-(2-(4-bromophenyl)-oxoethyl)chroman-2-one (2b): Prepared according to general procedure using (*E*)-2-(2-(3-(4-bromophenyl)-3-oxoprop-1-enyl)phenoxy)acetaldehyde (69 mg, 0.2 mmol) to afford 53 mg (77%) of **2b** as a light tan solid after 3 hr. Analytical data for **2b**: IR (film) 3063, 2918, 1751, 1674, 1566, 1484 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.31-7.27 (m, 2H), 7.14-7.09 (m, 2H), 3.88-3.86 (m, 1H), 3.27 (dd, J = 6.2, 17.7 Hz, 1H), 3.21 (dd, *J* = 7.5, 17.8, 1H), 2.95 (dd, *J* = 5.9, 16.3 Hz, 1H), 2.89 (dd, *J* = 3.3, 16.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.2, 168.2, 151.7, 135.3, 132.3, 129.8, 129.12, 129.10, 128.2, 125.9, 125.0, 117.5, 43.1, 34.9, 30.7; LRMS (ES): Mass calcd for $C_{17}H_{13}BrO_3$ $[M+H]^+$, 345. Found $[M+H]^+$, 345.



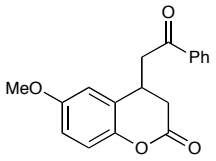
4-(2-oxo-2-*p*-tolylethyl)chroman-2-one (2c): Prepared according to general procedure using (*E*)-2-(2-(3-oxo-3-*p*-tolylprop-1-enyl)phenoxy)acetaldehyde (56 mg, 0.2 mmol) to afford 47 mg (84%) of **2c** as a light yellow oil after 12 hr. Analytical data for **2c**: IR (film) 3060, 2917, 1769, 1678, 1604, 1452 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.32-7.25 (m, 4H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 1H), 3.91-3.86 (m, 1H), 3.28 (dd, *J* = 5.8, 17.8, 1H), 3.23 (dd, *J* = 7.8, 17.6 Hz, 1H), 2.95 (dd, *J* = 5.9, 16.1 Hz, 1H), 2.88 (dd, *J* = 3.9, 16.1 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.7, 168.3, 151.7, 144.8, 134.2, 129.7, 128.9, 128.4, 128.2, 126.2, 125.0, 117.4, 43.0, 35.0, 30.8, 21.9; LRMS (ES): Mass calcd for $C_{18}H_{16}O_3$ $[M+Na]^+$, 303. Found $[M+Na]^+$, 303.



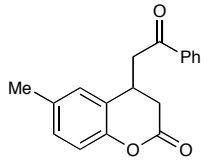
4-(2-(4-methoxyphenyl)-oxoethyl)chroman-2-one (2d): Prepared according to general procedure using *(E)*-2-(2-(3-(4-methoxyphenyl)-3-oxophenylprop-1-enyl)phenoxy)acetaldehyde (60 mg, 0.2 mmol) to afford 48 mg (80%) of **2d** as a yellow oil after 6 hr. Analytical data for **2d**: IR (film) 3067, 2918, 1767, 1675, 1511, 1458 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.31-7.26 (m, 2H), 7.13-7.08 (m, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.90-3.86 (m, 4H), 3.25 (dd, *J* = 6.3, 17.6 Hz, 1H), 3.19 (dd, *J* = 8.3, 18.1 Hz, 1H), 2.94 (dd, *J* = 5.9, 16.1 Hz, 1H), 2.88 (dd, *J* = 3.9, 16.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.6, 168.3, 164.1, 151.7, 130.6, 129.8, 128.9, 128.2, 126.3, 124.8, 117.4, 114.1, 55.8, 42.8, 35.0, 30.8; LRMS (ES): Mass calcd for $C_{18}H_{16}O_4$ $[M+Na]^+$, 319. Found $[M+Na]^+$, 319.



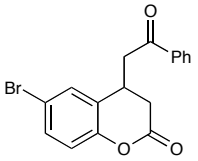
4-(2-(naphthalen-2-yl)-2-oxyethyl)chroman-2-one (2e): Prepared according to general procedure using (E)-2-(2-(3-(naphthalen-2-yl)-3-oxoprop-1-enyl)phenoxy)acetaldehyde (63 mg, 0.2 mmol) to afford 57 mg (90%) of **2e** as a yellow solid after 6 hr. Analytical data for **2e**: IR (film) 3062, 2918, 2852, 1767, 1679, 1459 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.89-7.86 (m, 2H), 7.61 (m, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.30-7.26 (m, 1H), 7.12 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 3.96-3.91 (m, 1H), 3.45 (dd, *J* = 6.4, 17.6 Hz, 1H), 3.38 (dd, *J* = 7.8, 17.6 Hz, 1H), 2.98 (dd, *J* = 5.9, 16.1 Hz, 1H), 2.93 (dd, *J* = 4.4, 16.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.0, 168.3, 151.8, 136.0, 133.9, 132.7, 130.2, 129.9, 129.1, 129.0, 128.9, 128.3, 128.0, 127.2, 126.2, 125.0, 123.8, 117.5, 43.2, 35.1, 30.9; LRMS (ES): Mass calcd for $C_{21}H_{16}O_3$ $[M+Na]^+$, 339. Found $[M+Na]^+$, 339.



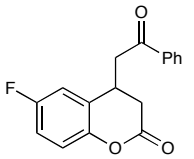
6-methoxy-4-(2-oxo-2-phenylethyl)chroman-2-one (2f): Prepared according to general procedure using (*E*)-2-(4-methoxy-2-(3-oxo-3-phenylprop-1-enyl)phenoxy)acetaldehyde (60 mg, 0.2 mmol) to afford 41 mg (68%) of **2f** as a yellow solid after 2.5 hr. Analytical data for **2f**: IR (film) 3050, 2916, 1765, 1686, 1493 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 1H), 6.82-6.80 (m, 1H), 6.80-7.78 (m, 1H), 3.84-3.80 (m, 1H), 3.78 (s, 3H), 3.29 (dd, *J* = 5.9, 18.1 Hz, 1H), 3.23 (dd, *J* = 7.8, 17.6 Hz, 1H), 2.91 (dd, *J* = 5.9, 16.1 Hz, 1H), 2.85 (dd, *J* = 3.9, 16.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.1, 168.5, 156.6, 145.6, 136.6, 133.9, 129.0, 128.8, 127.0, 118.2, 114.1, 113.1, 56.0, 43.1, 34.9, 31.0; LRMS (ES): Mass calcd for $C_{18}H_{16}O_4$ $[M+Na]^+$, 319. Found $[M+Na]^+$, 319.



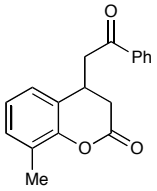
6-methyl-4-(2-oxo-2-phenylethyl)chroman-2-one (2g): Prepared according to general procedure using (*E*)-2-(4-methyl-2-(3-oxo-3-phenylprop-1-enyl)phenoxy)acetaldehyde (56 mg, 0.2 mmol) to afford 45 mg (80%) of **2g** as a yellow oil after 2 hr. Analytical data for **2g**: IR (film) 3061, 2918, 1766, 1682, 1594, 1491 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.09-7.06 (m, 2H), 6.96 (d, *J* = 8.3 Hz, 1H), 3.84-3.79 (m, 1H), 3.29 (dd, *J* = 5.8, 17.5 Hz, 1H), 3.22 (dd, *J* = 7.8, 18.1 Hz, 1H), 2.91 (dd, *J* = 5.9, 16.1 Hz, 1H), 2.86 (dd, *J* = 3.9, 16.1 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.2, 168.5, 149.6, 136.7, 134.7, 133.8, 129.5, 129.0, 128.5, 128.3, 125.8, 117.2, 43.2, 35.0, 30.7, 21.0; LRMS (ES): Mass calcd for $C_{18}H_{16}O_3$ $[M+Na]^+$, 303. Found $[M+Na]^+$, 303.



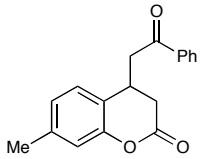
6-bromo-4-(2-oxo-2-phenylethyl)chroman-2-one (2h): Prepared according to general procedure using (*E*)-2-(4-bromo-2-(3-oxo-3-phenylprop-1-enyl)phenoxy)acetaldehyde (69 mg, 0.2 mmol) to afford 53 mg (77%) of **2h** as a pale yellow solid after 45 min. Analytical data for **2h**: IR (film) 3065, 2918, 2852, 1771, 1682, 1473 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.47-7.42 (m, 3H), 7.39 (d, *J* = 8.8 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 3.87-3.82 (m, 1H), 3.30 (dd, *J* = 6.3, 18.1 Hz, 1H), 3.24 (dd, *J* = 7.3, 18.1 Hz, 1H), 2.92 (dd, *J* = 5.9, 16.1 Hz, 1H), 2.87 (dd, *J* = 3.9, 16.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.6, 167.5, 150.8, 136.4, 134.0, 132.0, 131.1, 129.1, 128.3, 128.2, 119.2, 117.5, 43.0, 34.6, 30.5; LRMS (ES): Mass calcd for $C_{17}H_{13}BrO_3$ $[M+Na]^+$, 367. Found $[M+Na]^+$, 367.



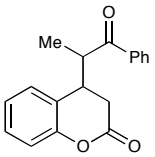
6-fluoro-4-(2-oxo-2-phenylethyl)chroman-2-one (2i): Prepared according to general procedure using (*E*)-2-(4-fluoro-2-(3-oxo-3-phenylprop-1-enyl)phenoxy)acetaldehyde (57 mg, 0.2 mmol) to afford 52 mg (91%) of **3i** as a yellow oil after 2 hr. Analytical data for **2i**: IR (film) 3063, 2904, 1770, 1688, 1557, 886 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.3 Hz, 2H), 7.60-7.57 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.06-7.03 (m, 2H), 6.96 (dt, *J* = 7.8, 7.8, 2.9 Hz, 1H), 3.88-3.84 (m, 1H), 3.30 (dd, *J* = 6.3, 17.6, Hz, 1H), 3.24 (dd, *J* = 7.4, 18.1 Hz, 1H), 2.92 (dd, *J* = 5.8, 16.1 Hz, 1H), 2.86 (dd, *J* = 3.9, 16.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.7, 167.8, 159.2 (d, *J* = 244.2 Hz), 147.7, 136.4, 134.0, 129.0, 128.3, 127.7 (d, *J* = 7.4 Hz), 118.7 (d, *J* = 8.6 Hz), 115.7 (d, *J* = 23.5 Hz), 114.9 (d, *J* = 23.5 Hz), 42.9, 34.6, 30.7; LRMS (ES): Mass calcd for $C_{17}H_{13}FO_3$ $[M+Na]^+$, 307. Found $[M+Na]^+$, 307.



8-methyl-4-(2-oxo-2-phenylmethyl)chroman-2-one (4): Prepared according to general procedure using (*E*)-2-(2-methyl-6-(3-oxo-3-phenylprop-1-enyl)phenoxy)acetaldehyde (56 mg, 0.2 mmol) to afford 37 mg (66%) of **4** as a yellow solid after 6 hr. Analytical data for **4**: IR (film) 3078, 2916, 2848, 1771, 1683, 1558 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.02-6.99 (m, 1H), 3.88-3.82 (m, 1H), 3.28 (dd, *J* = 5.8, 17.5 Hz, 1H), 3.23 (dd, *J* = 7.8, 17.6 Hz, 1H), 2.92 (dd, *J* = 5.4, 15.6 Hz, 1H), 2.87 (dd, *J* = 3.9, 16.1 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.2, 168.5, 150.0, 136.7, 133.8, 130.5, 129.0, 128.3, 126.8, 125.9, 125.6, 124.9, 43.1, 35.0, 30.9, 16.0; LRMS (ES): Mass calcd for $C_{18}H_{16}O_3$ $[M+Na]^+$, 303. Found $[M+Na]^+$, 303.

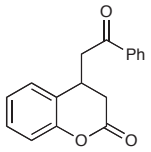


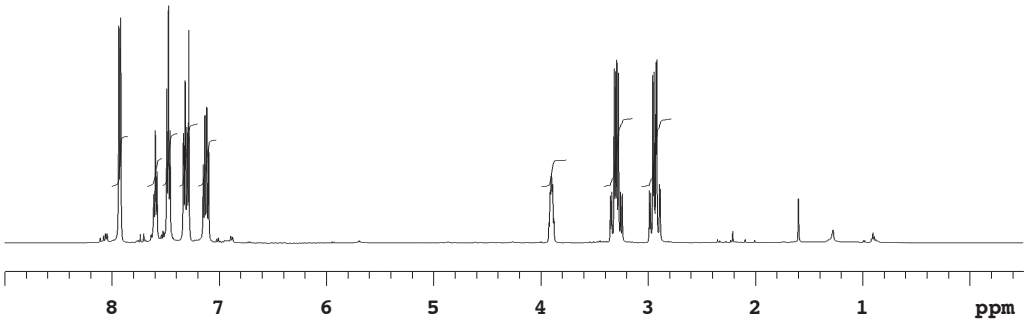
7-methyl-4-(2-oxo-2-phenylmethyl)chroman-2-one (6): Prepared according to general procedure using (*E*)-2-(5-methyl-2-(3-oxo-3-phenylprop-1-enyl)phenoxy)acetaldehyde (56 mg, 0.2 mmol) to afford 37 mg (66%) of **6** as a yellow solid after 6 hr. Analytical data for **6**: IR (film) 3061, 2926, 2861, 1778, 1680, 1610 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 2H), 7.58-7.55 (m, 1H), 7.46-7.43 (m, 2H), 7.17 (d, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.89 (s, 1H), 3.86-3.80 (m, 1H), 3.27 (dd, *J* = 6.4, 17.6 Hz, 1H), 3.21 (dd, *J* = 7.8, 18.1 Hz, 1H), 2.91 (dd, *J* = 5.9, 16.1 Hz, 1H), 2.85 (dd, *J* = 3.9, 16.1 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.2, 168.5, 151.6, 139.3, 136.6, 133.8, 129.0, 128.3, 127.9, 125.7, 122.9, 117.8, 43.3, 35.1, 30.4, 21.3; LRMS (ES): Mass calcd for $C_{18}H_{16}O_3$ $[M+Na]^+$, 303. Found $[M+Na]^+$, 303.

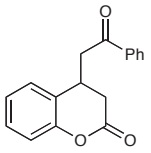


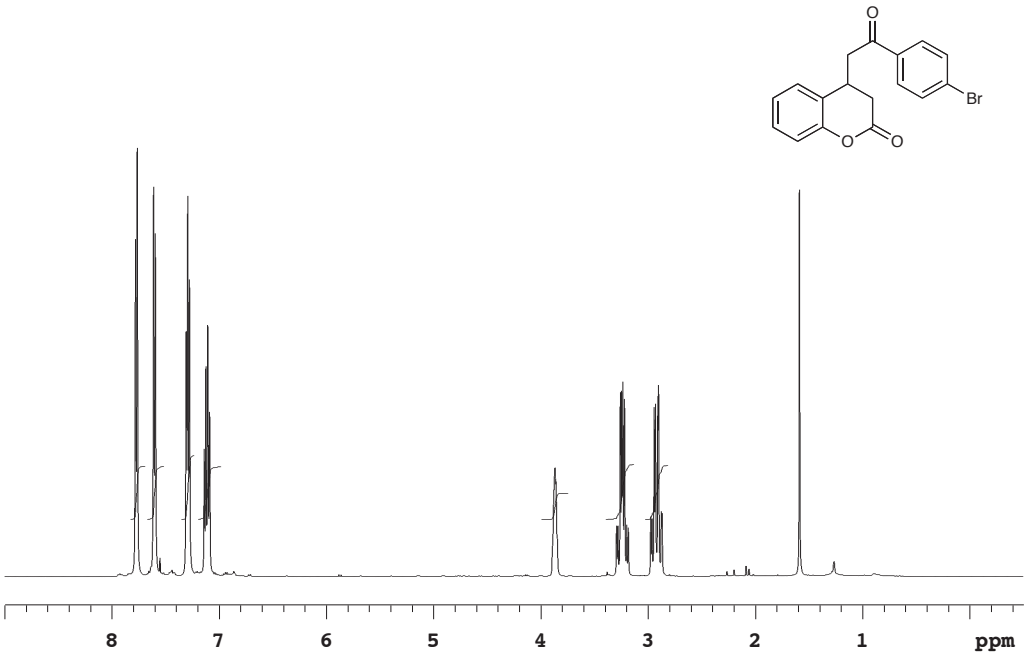
4-(1-oxo-1-phenylpropan-2-yl)chroman-2-one (8): Prepared according to general procedure using (E)-2-(2-(2-methyl-3-oxo-3-phenylprop-1-enyl)phenoxy)acetaldehyde (56 mg, 2 mmol) to afford 39 mg (70%) of **8** as a yellow oil and a mixture of diastereomers after 12 hr. Analytical data for **8**: IR (film) 3063, 2918, 2852, 1769, 1677, 1451 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.5 Hz, 2H, maj.), 7.75 (d, *J* = 7.5 Hz, 2H, min), 7.61 (t, *J* = 7.5 Hz, 1H, maj), 7.52-7.50 (m, 1H, min), 7.50 (d, *J* = 7.7 Hz, 2H, maj), 7.39 (t, *J* = 7.7 Hz, 2H, min), 7.34 (t, *J* = 7.3 Hz, 1H, maj), 7.25 (d, *J* = 6.8 Hz, 1H, maj), 7.19 (d, *J* = 7.7 Hz, 1H, min), 7.17 (d, *J* = 7.2 Hz, 1H, min), 7.16 (d, *J* = 7.1 Hz, 1H, maj), 7.12 (d, *J* = 8.1 Hz, 1H, maj), 7.04 (d, *J* = 8.0 Hz, 1H, min), 6.98 (t, *J* = 7.3 Hz, 1H, min), 3.72-3.68 (m, 1H, min), 3.64-3.59 (m, 1H, min), 3.63-3.53 (m, 2H, maj), 3.09 (dd, *J* = 2.7, 16.1 Hz, 1H, min), 2.85 (dd, *J* = 6.0, 16.1 Hz, 1H, min), 2.83 (dd, *J* = 3.1, 11.1 Hz, 1H, maj), 2.79 (dd, *J* = 2.3, 16.2 Hz, 1H, maj), 1.31 (d, *J* = 6.8 Hz, 3H, min), 1.14 (d, *J* = 6.8 Hz, 3H, maj); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.9, 202.5, 168.4, 168.3, 152.0, 151.8, 136.3, 134.0, 133.6, 129.9, 129.2 (2x), 129.1, 129.0, 128.9, 128.6 (2x), 128.4, 125.4, 124.8, 124.50, 124.56, 117.6, 117.4, 44.1, 43.6, 37.9, 37.4, 34.2, 32.2, 17.7, 15.1; LRMS (ES): Mass calcd for $C_{18}H_{16}O_3$ $[M+Na]^+$, 303. Found $[M+Na]^+$, 303.

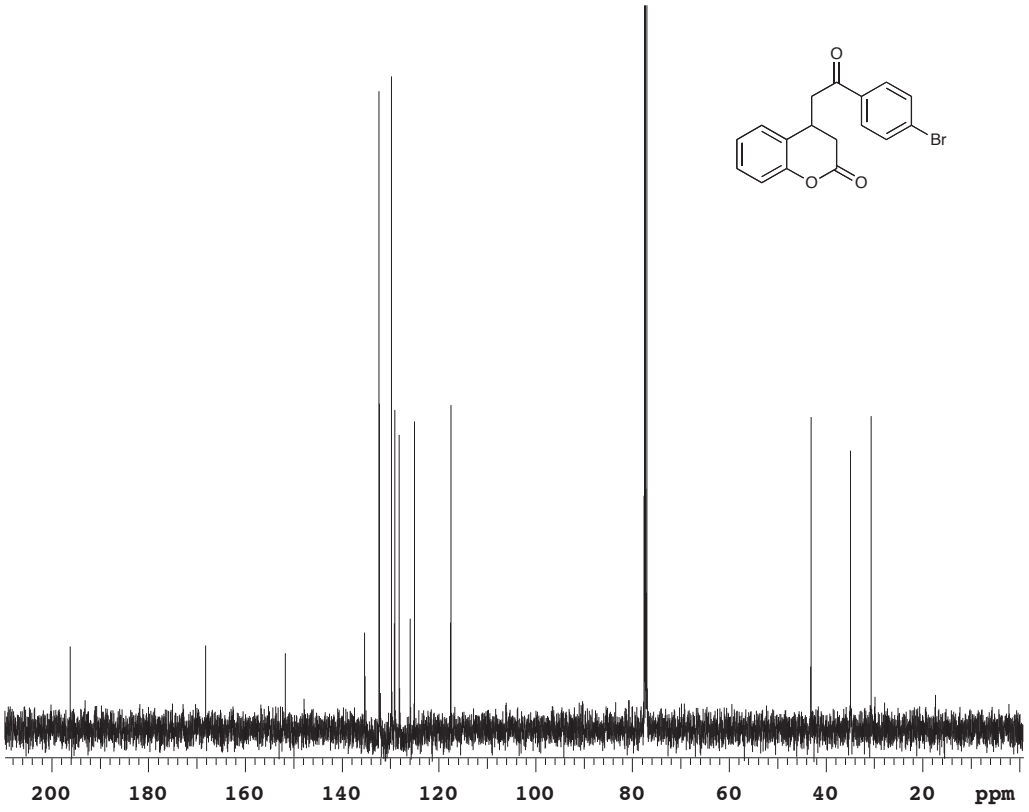
Selected NMR Spectra

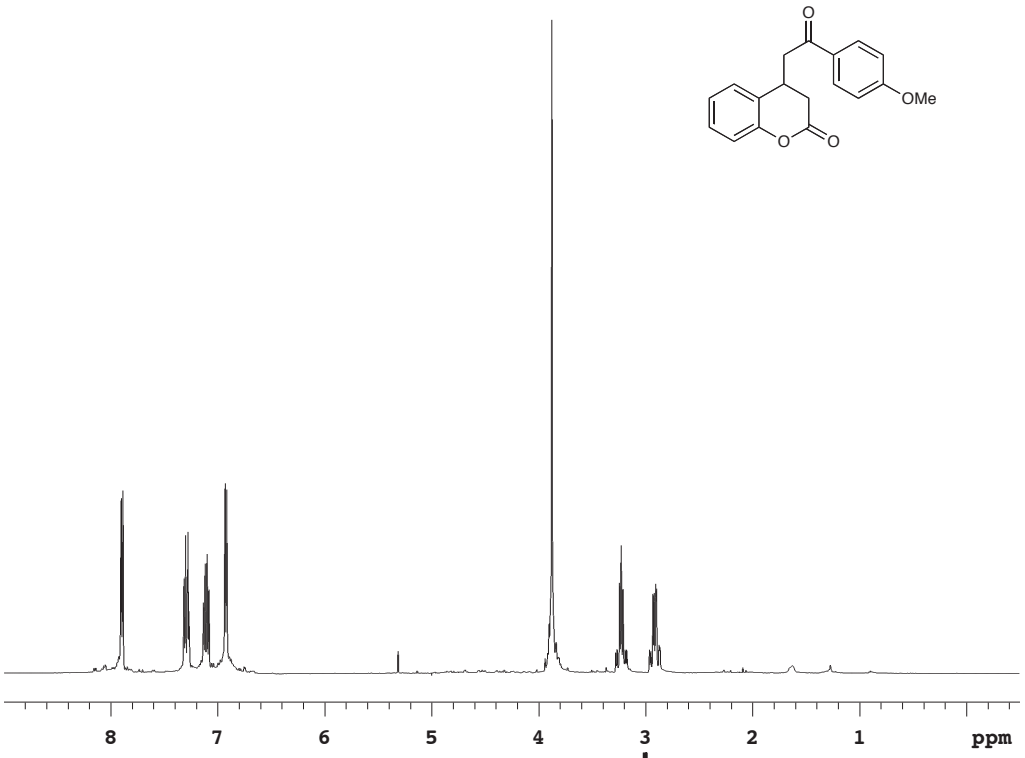


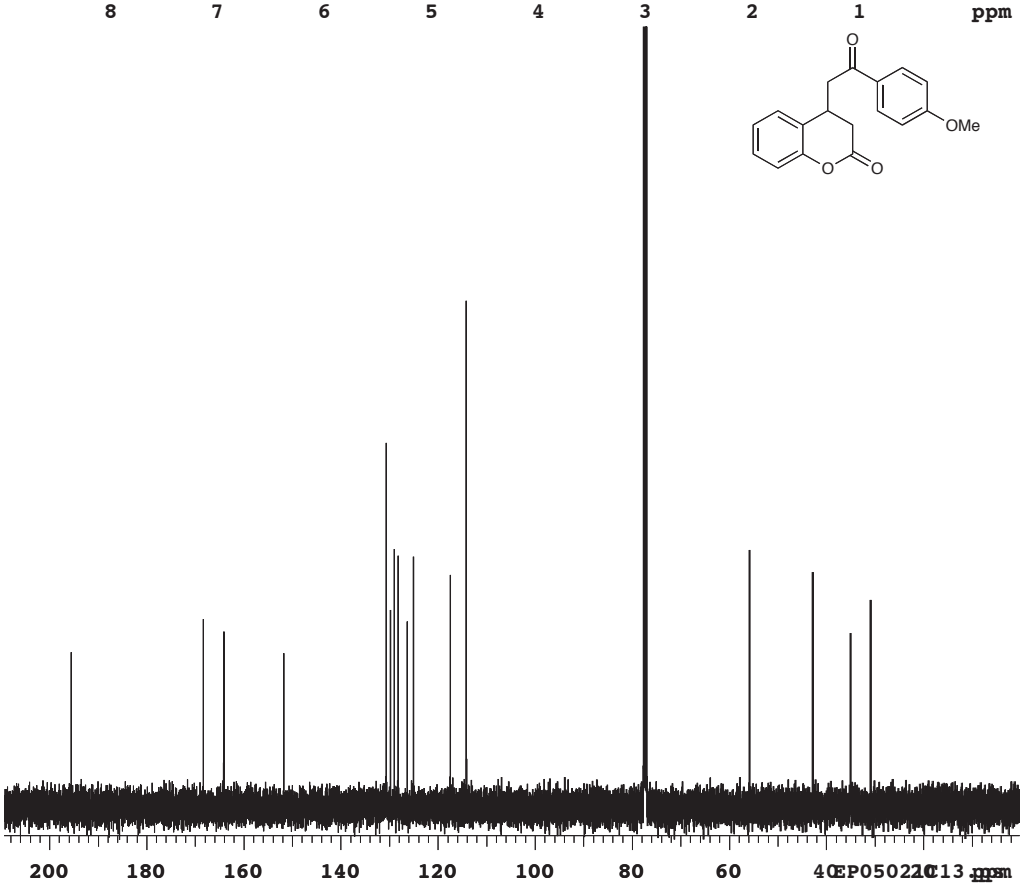


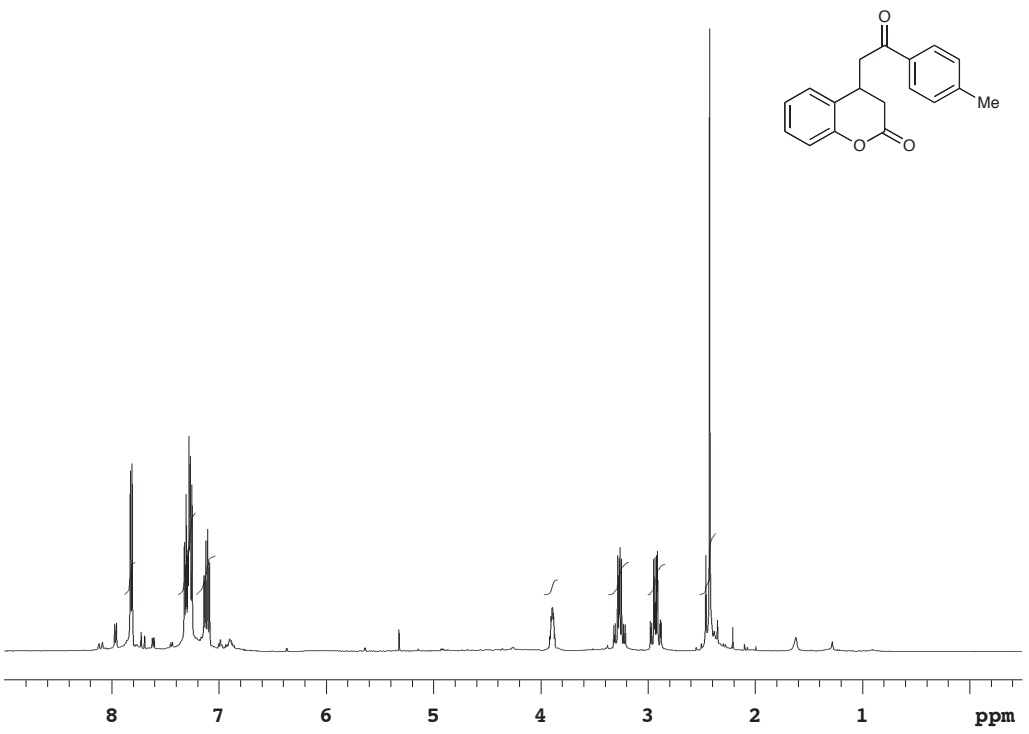


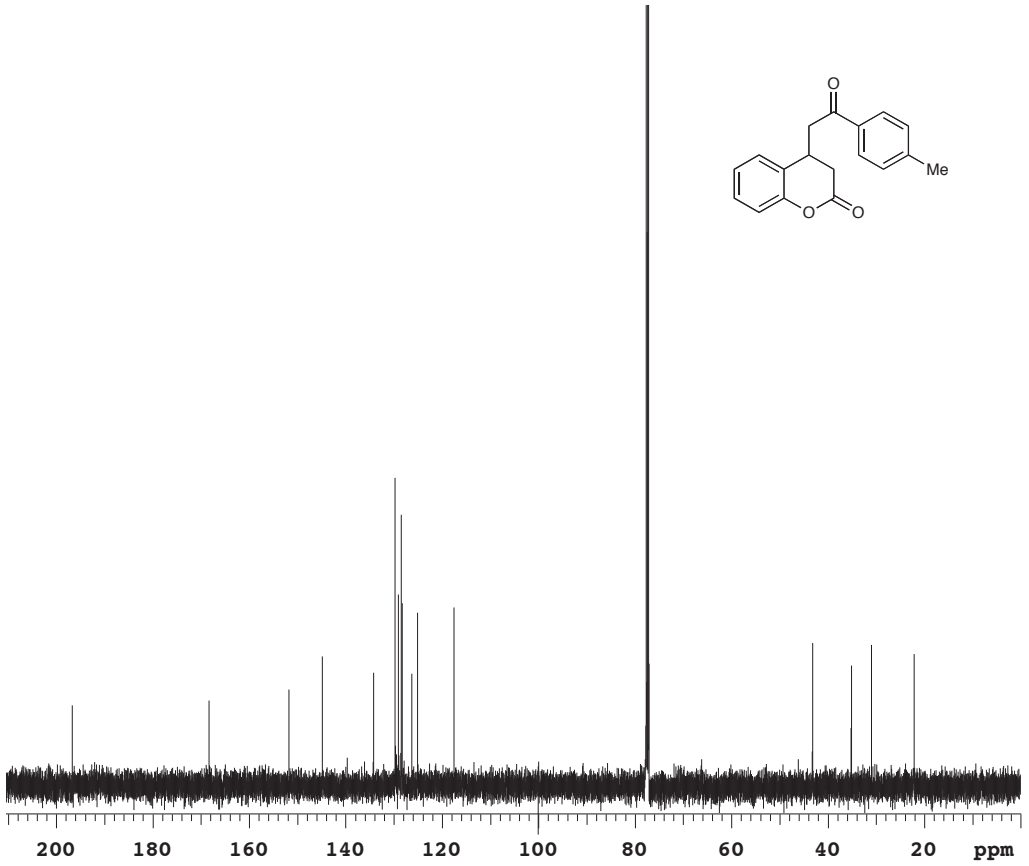

O
Br
O
O
8
7
6
5
4
3
2
1
ppm

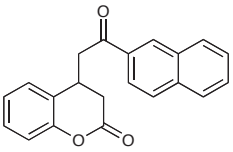

O
Br
O
O
200
180
160
140
120
100
80
60
40
20
ppm

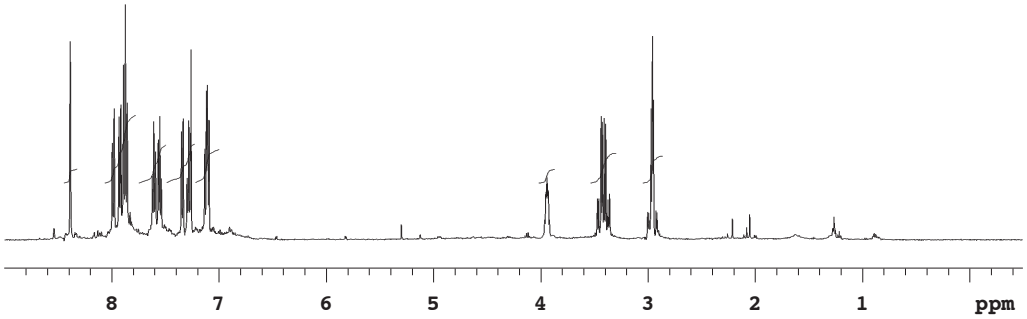

O
OMe
O
O
8
7
6
5
4
3
2
1
ppm

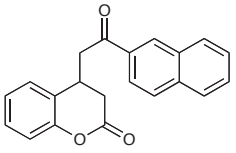

O
OMe
O
O
200
180
160
140
120
100
80
60
40
20
ppm


O
Me
O
O
8
7
6
5
4
3
2
1
ppm

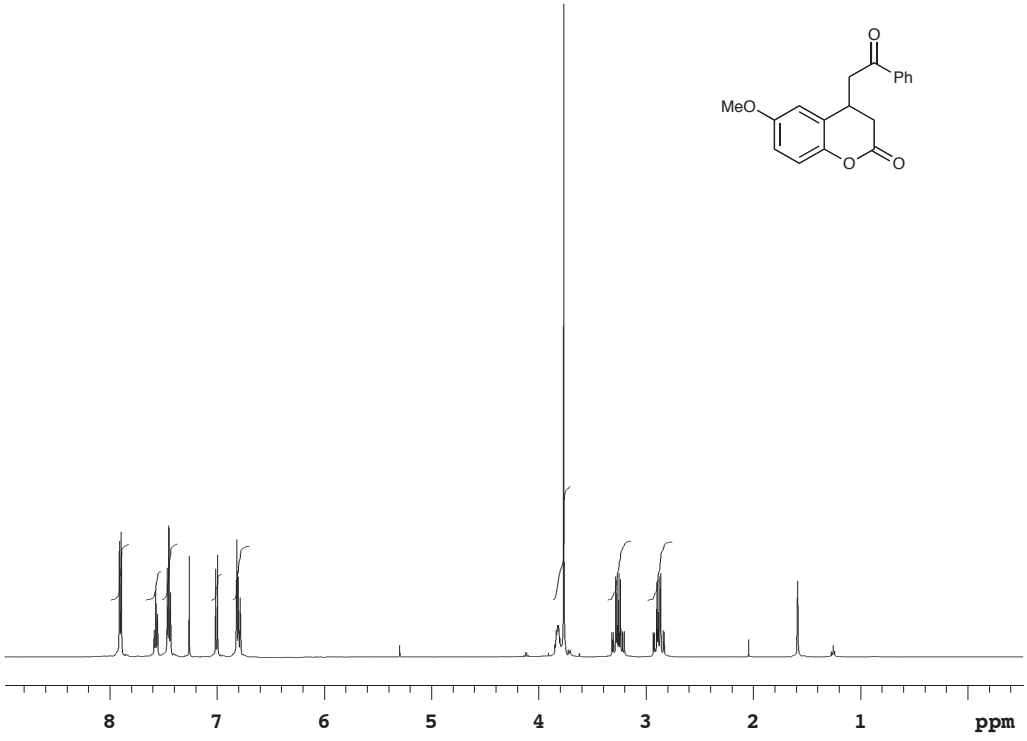

O
Me
O
O
200
180
160
140
120
100
80
60
40
20
ppm

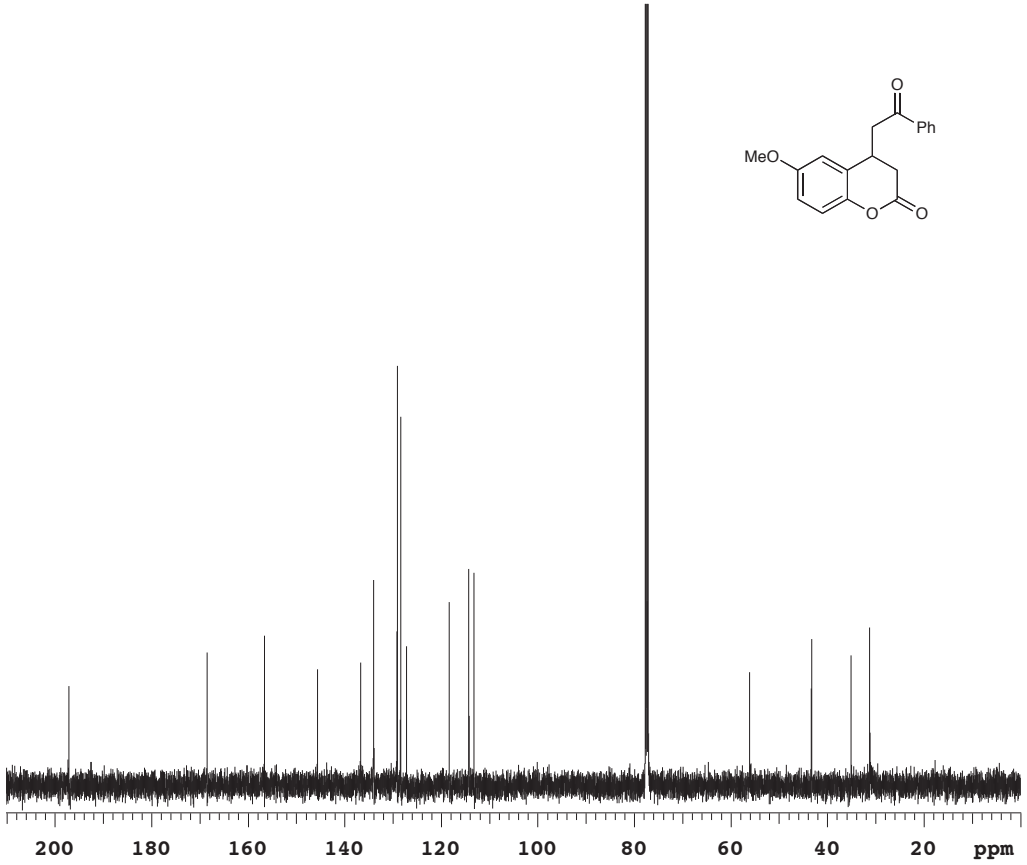

O
O
O

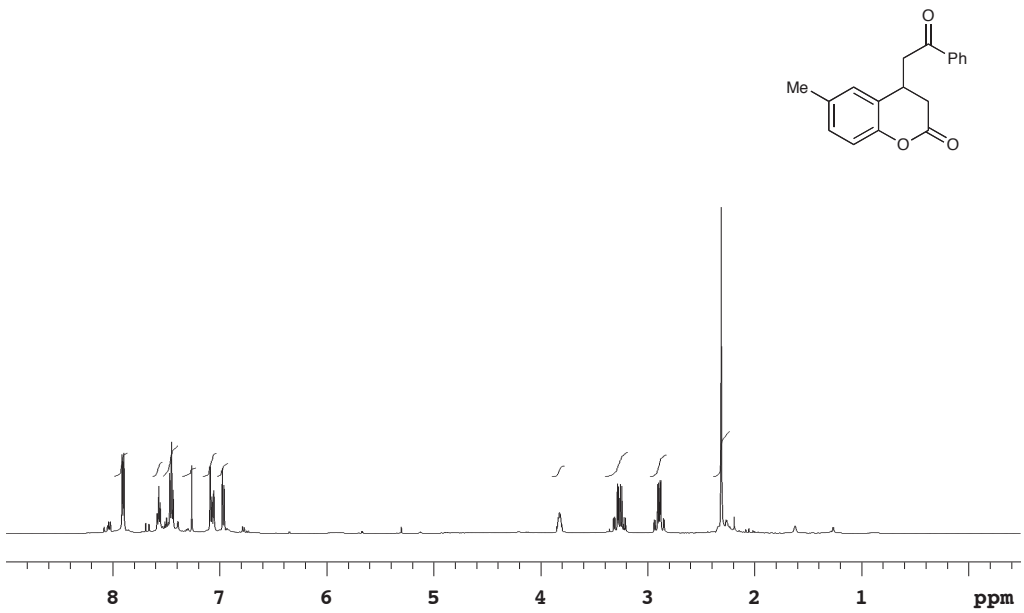

8
7
6
5
4
3
2
1
ppm

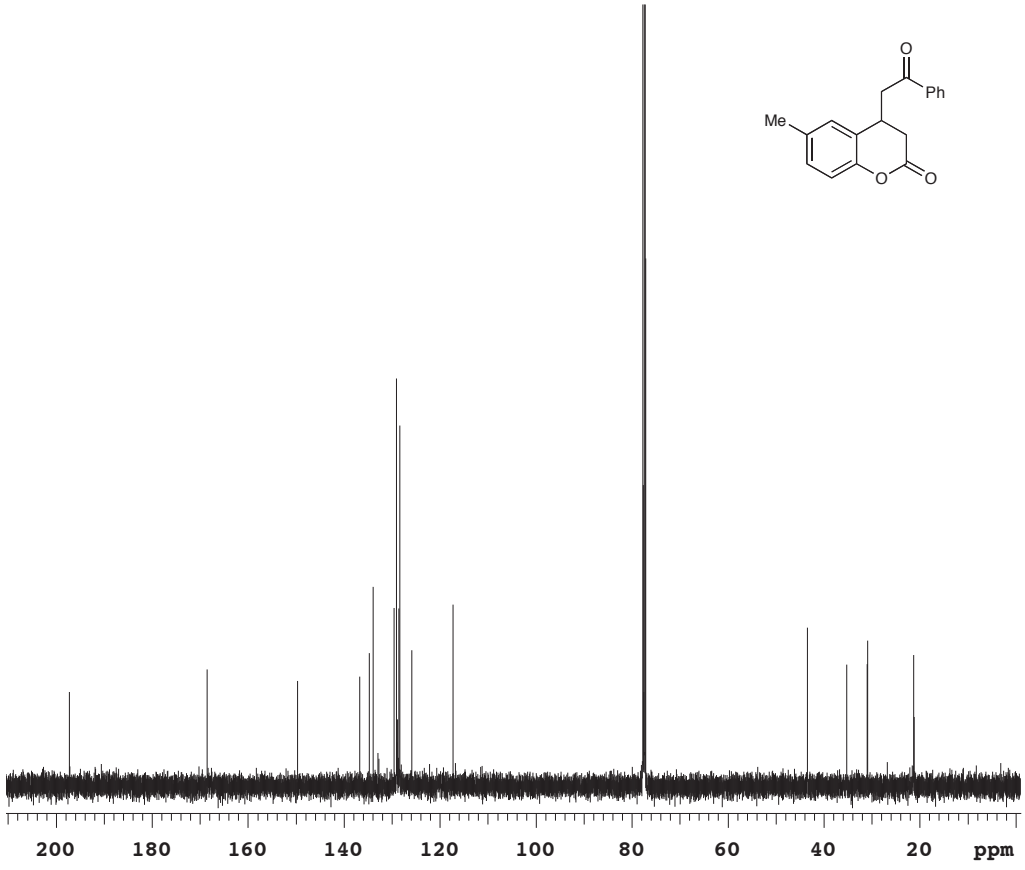

O
O
O

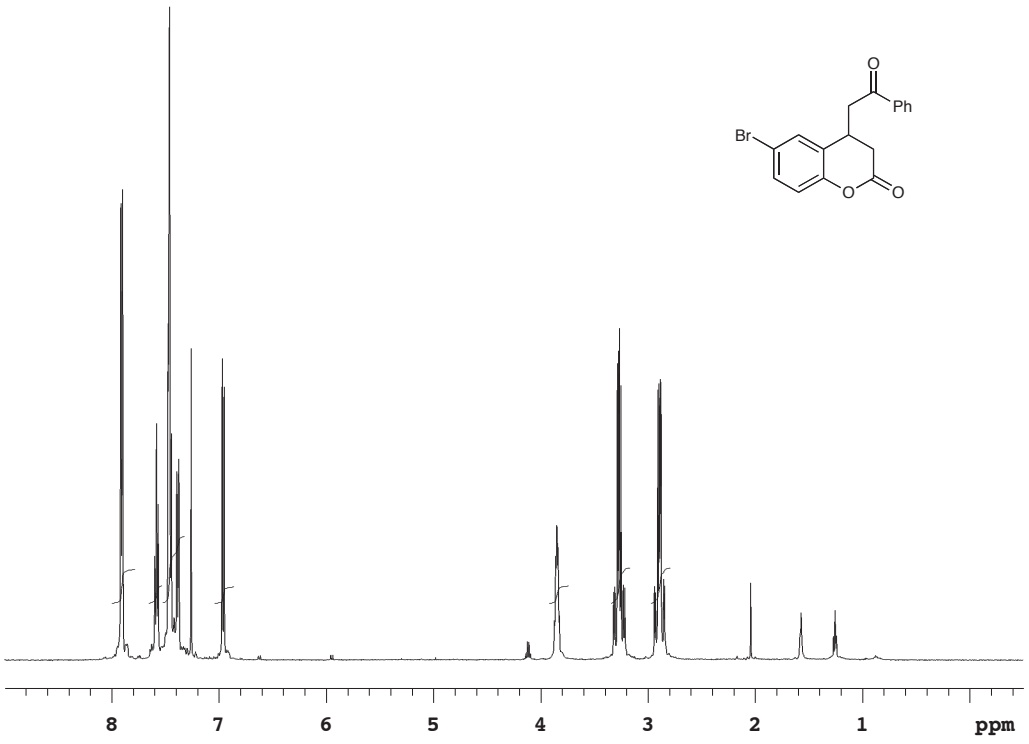
200
180
160
140
120
100
80
60
40
20
ppm

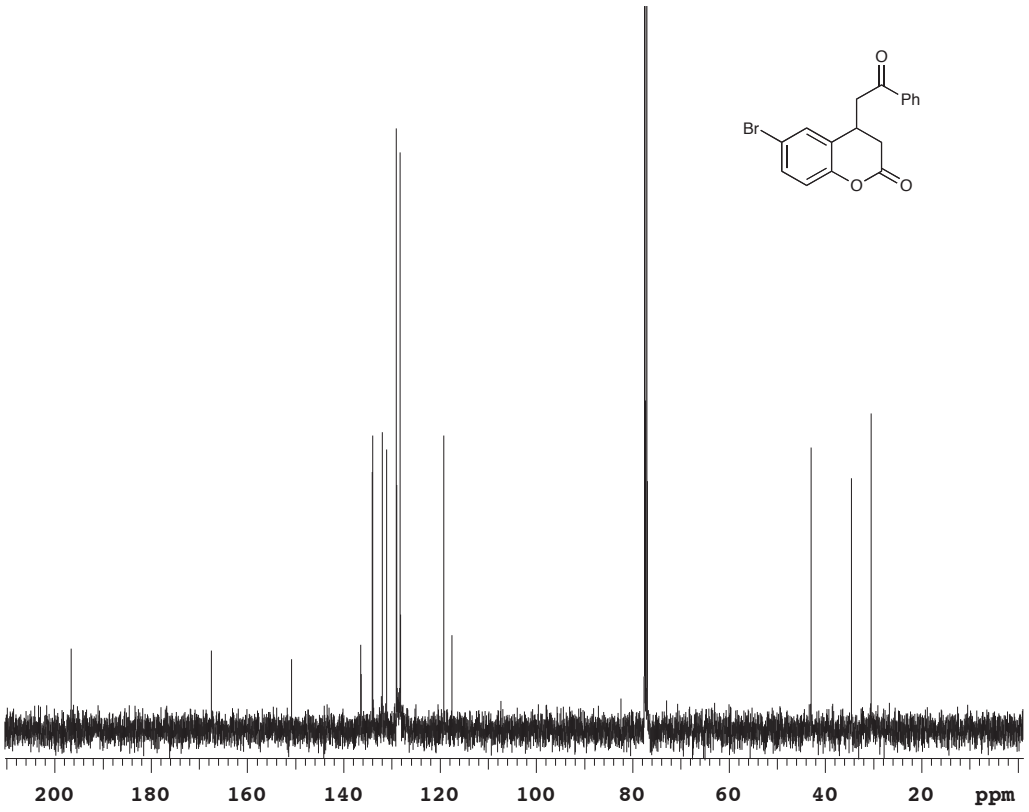

O
Ph
MeO
O
O
8
7
6
5
4
3
2
1
ppm

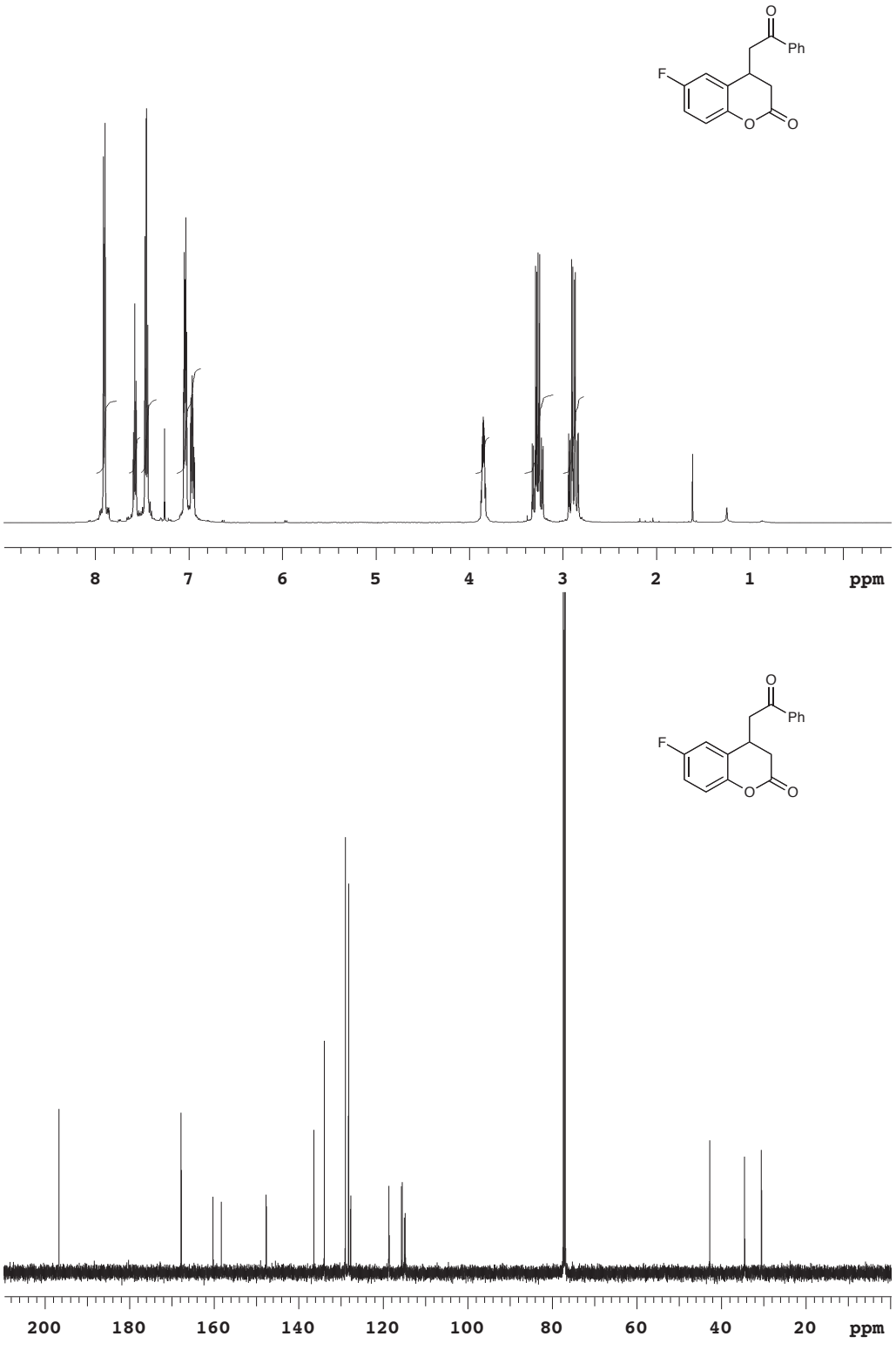

O
Ph
MeO
O
O
200
180
160
140
120
100
80
60
40
20
ppm

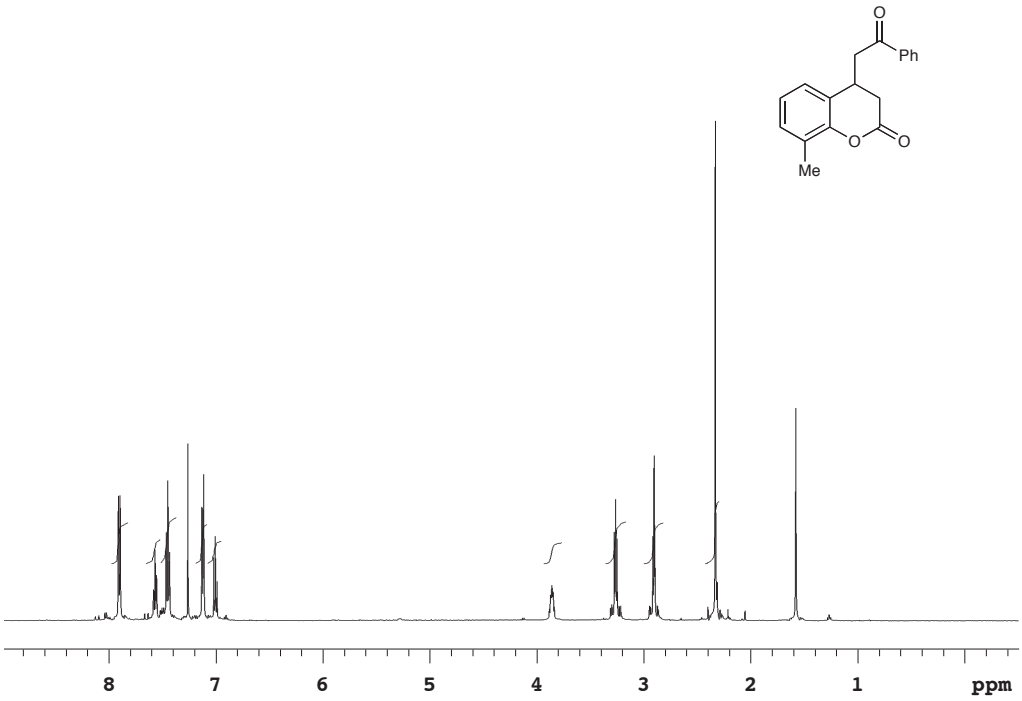

O
Ph
Me
O
O
8
7
6
5
4
3
2
1
ppm

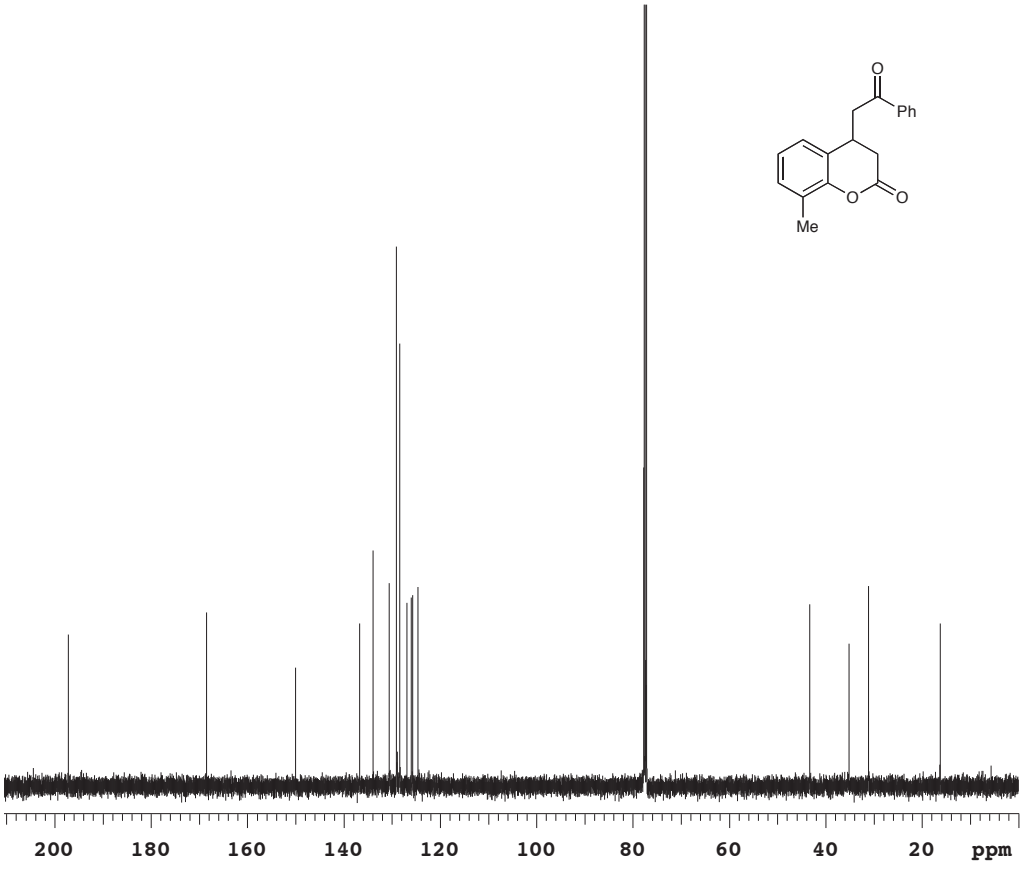

O
Ph
Me
O
O
200
180
160
140
120
100
80
60
40
20
ppm

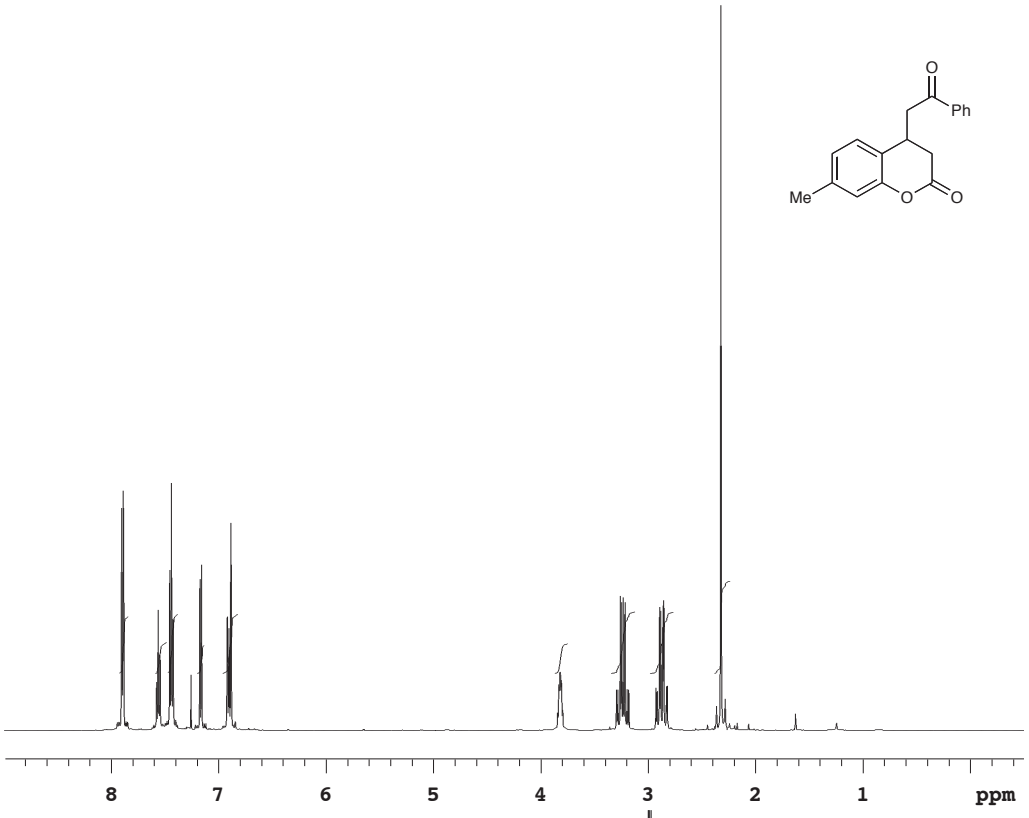

O
Ph
Br
O
O
8
7
6
5
4
3
2
1
ppm

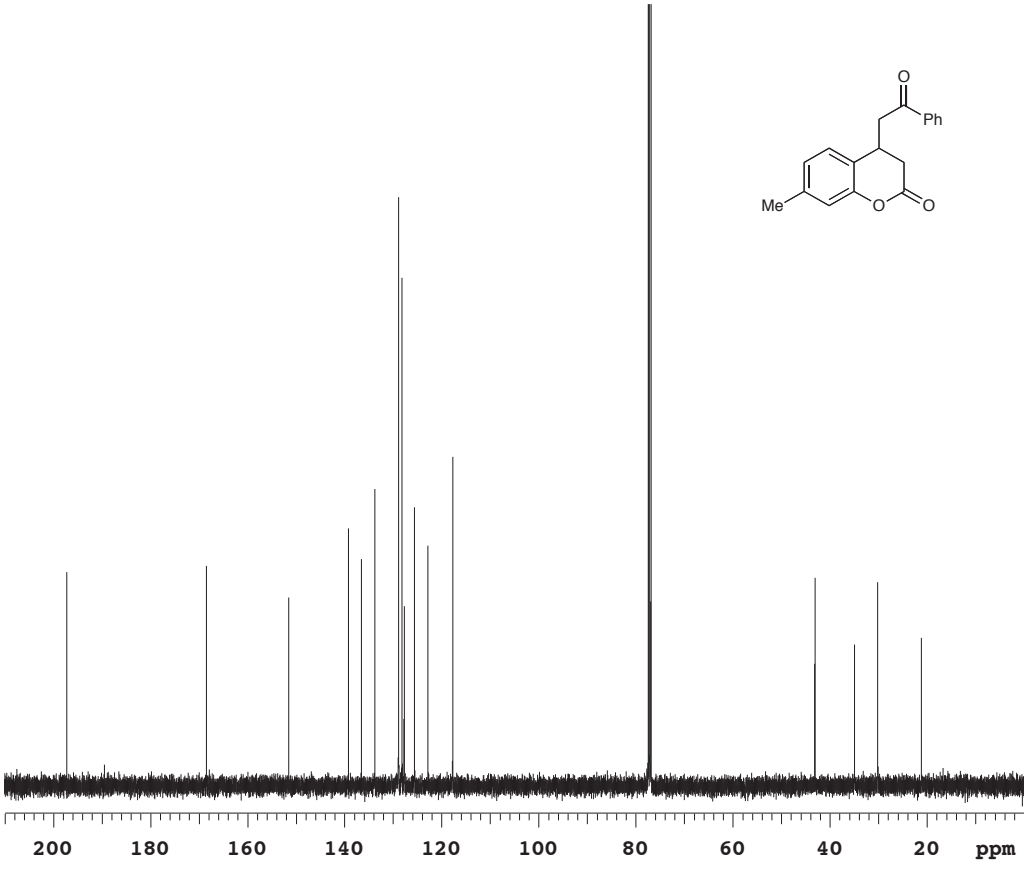

O
Ph
Br
O
O
200
180
160
140
120
100
80
60
40
20
ppm

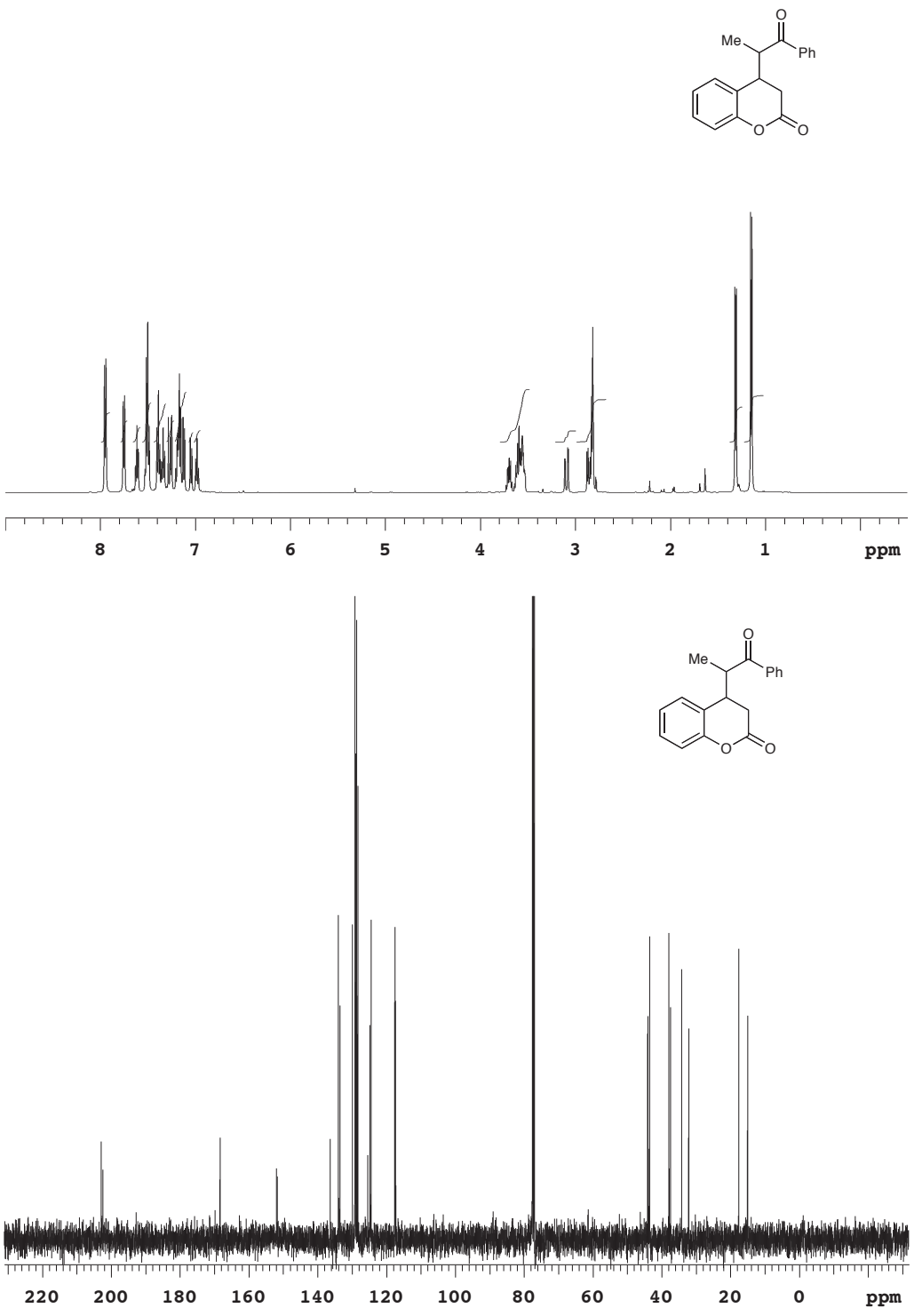

O
Ph
F
O
O
8
7
6
5
4
3
2
1
ppm
O
Ph
F
O
O
200
180
160
140
120
100
80
60
40
20
ppm


O
Ph
O
O
Me
8
7
6
5
4
3
2
1
ppm


O
Ph
O
O
Me
200
180
160
140
120
100
80
60
40
20
ppm


O
Ph
Me
O
O
8
7
6
5
4
3
2
1
ppm

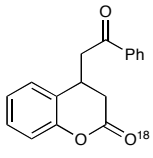

O
Ph
Me
O
O
200
180
160
140
120
100
80
60
40
20
ppm


O
Me
Ph
O
O
8
7
6
5
4
3
2
1
ppm
O
Me
Ph
O
O
220
200
180
160
140
120
100
80
60
40
20
0
ppm

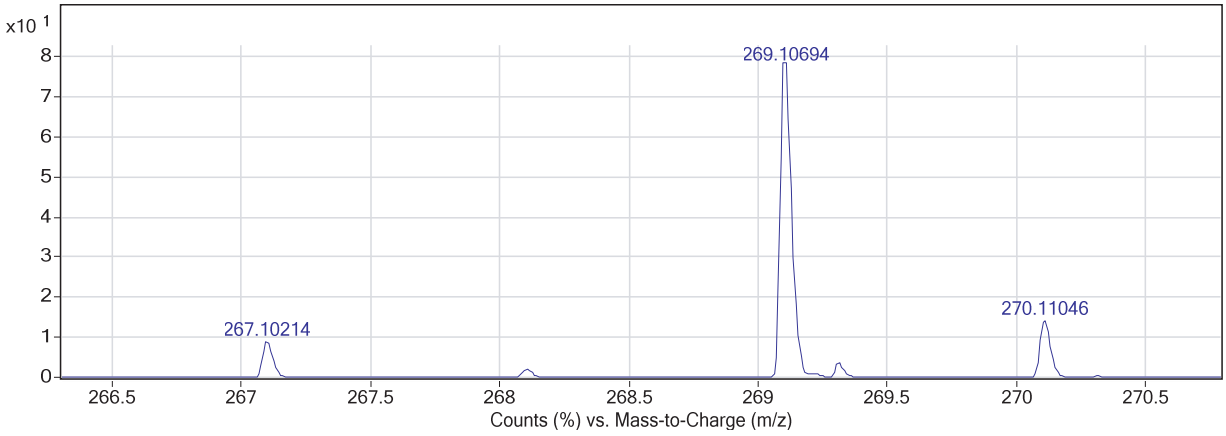
Procedure and Mass Spectrometry of Crossover Experiment

To a flame-dried 25 mL round bottom flask equipped with a magnetic stirring bar, gas inlet tube, and septum was added aldehydes **1j** (27 mg, 0.1 mmol) and **1g** (28 mg, 0.1 mmol) and CH_3CN (9 mL, 0.022 M). Then, a mixture containing azolium salt **C** (6 mg, 0.02 mmol), DBU (3 μL, 0.02 mmol), and 1 mL CH_3CN was added dropwise over 10 min via syringe. Upon consumption of the aldehydes, to the reaction was added 5 mL aqueous sat. NH_4Cl and 20 mL CH_2Cl_2. The layers were then separated. The aqueous layer was washed with CH_2Cl_2 (2 x 10 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude mixture was then purified by flash column chromatography on silica gel (5 g SiO_2) with 10% EtOAc in hexanes to 100% EtOAc as eluent to afford the corresponding 3,4-dihydrocoumarins as a mixture.

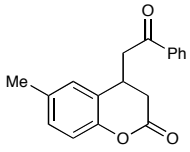
Mass Spectrometry Data for 2j



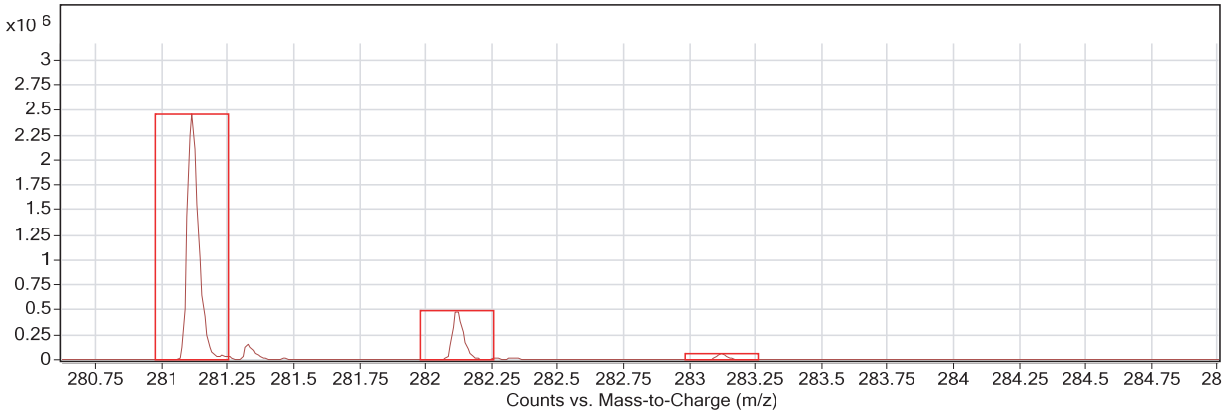
$C_{17}H_{14}O_3$
Mass: 268.09



Mass Spectrometry Data for 2g

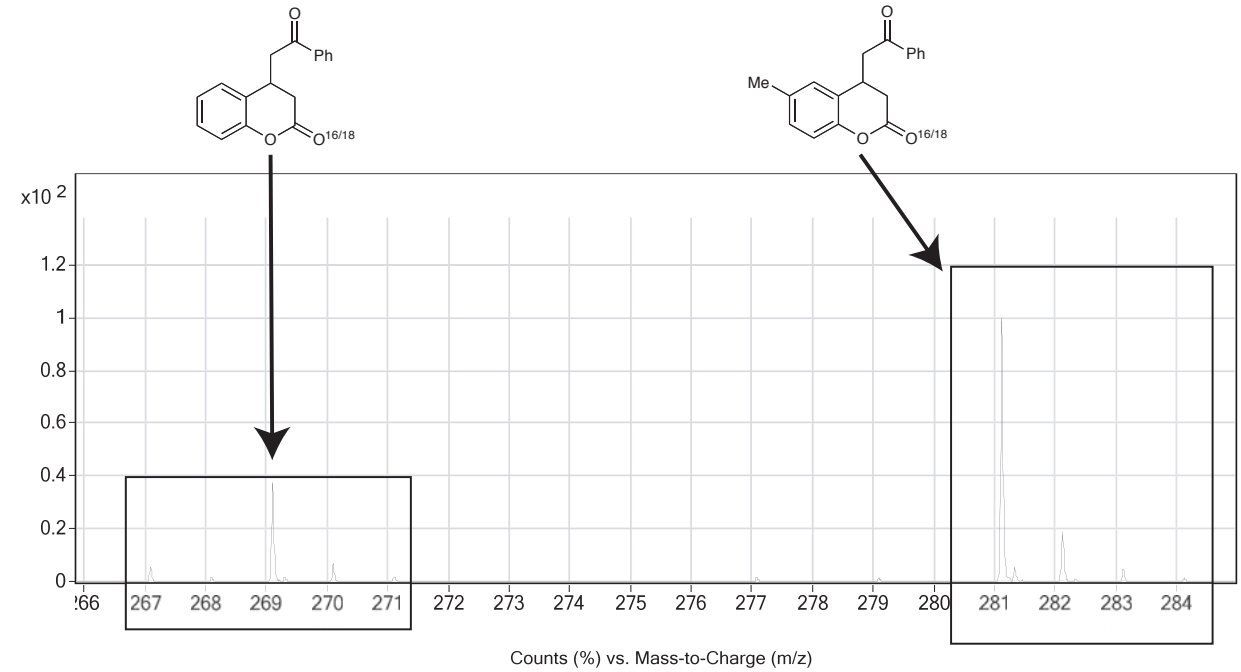


$C_{18}H_{16}O_3$
Mass: 280.11

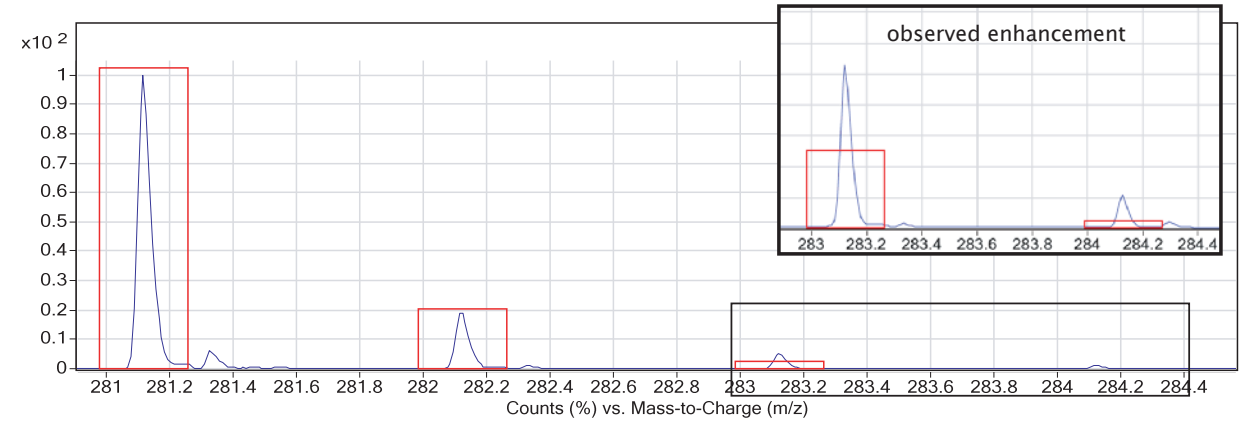


mass peak	theoretical abundance %	observed abundance %
281.12	100	100
282.12	19.78	18.88
283.12	2.47	2.08
284.13	0.23	–

Mass Spectrometry Data for crossover experiment with 1j and 1g



--- End of Report ---



mass peak	theoretical abundance %	Crossover abundance %
281.12	100	100
282.12	19.78	21.25
283.12	2.47	**7.22**
284.13	0.23	**1.08**

X-Ray Crystallography of 2b:

X-ray diffraction was performed at –120 °C and raw frame data were processed using SAINT. Molecular structure was solved using direct methods and refined by F2 by full-matrix least-squares techniques. The GOF = 1.057 for 193 variables refined to R1 = 0.0532 for 2639 reflections with I>2α(I). There was no absorption correction of Flack parameters. Further information is contained in the CIF file.