Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Organocatalytic condensation-ring opening-annulation cascade reactions between N-Bocindolin-2-ones/benzofuran-2(3H)-ones and salicylaldehydes for synthesis of 3-arylcoumarins

Yuyu Cheng, Pengfei Zhang, Yanwen Jia, Zhiqiang Fang and Pengfei Li*

Department of Chemistry, South University of Science and Technology of China, Shenzhen, 518055, P. R. China. E-mail: lipf@sustc.edu.cn; flyli1980@gmail.com

Supporting Information

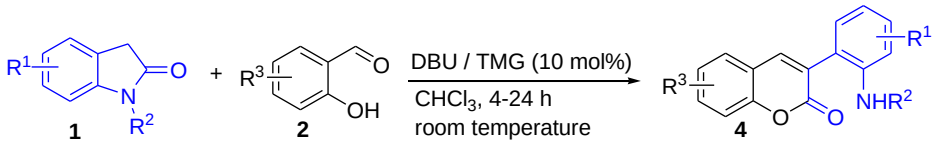
Contents

A: General Methods

All chemicals were used without further purification as commercially available unless otherwise noted. All reactions were performed under the standard conditions. Thin-layer chromatography (TLC) was performed on silica gel plates (60F-254) using UV-light (254 and 365 nm). Flash chromatography was conducted on silica gel (300–400 mesh). NMR (400/500 MHz for ^{1}H NMR, 100/126 MHz for ^{13}C NMR) spectra were recorded in $CDCl_3$ or Acetone-d_6 with TMS as the internal standard. Chemical shifts are reported in ppm and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; m, multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High resolution mass spectral (HRMS) analyses were measured using ESI techniques. Melting points were determined in a hanon auto melting point system (MP 450).

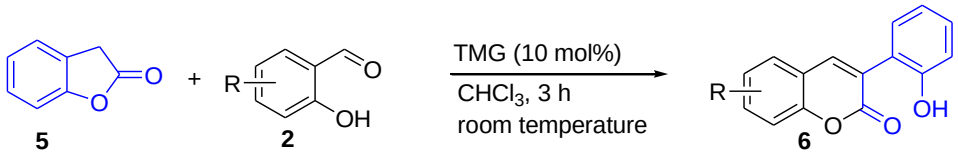
B: General Procedure

(1) General procedure for the synthesis of 3-arylcoumarins from indolin-2-ones derivatives 1 and salicylaldehydes 2



In a sealed tube, **1** (0.2 mmol), **2** (0.24 mmol), and DBU or TMG (10 mol%) were mixed in $CHCl_3$ (2.0 mL) and stirred at room temperature for the time given (4-24 h, monitored by TLC). After removal of the solvent, a crude residue was purified by SiO_2 flash column chromatography (petroleum ether / ethyl acetate) to give the corresponding 3-arylcoumarins **4**.

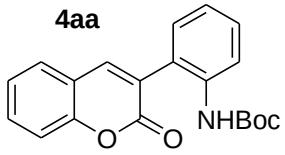
(2) General procedure for the synthesis of 3-arylcoumarins from benzofuran-2(3H)-one 5 and salicylaldehydes 2



In a sealed tube, **5** (0.2 mmol), **2** (0.24 mmol), and TMG (10 mol%) were mixed in $CHCl_3$ (2.0 mL) and stirred at room temperature for 3 h (monitored by TLC). After removal of the solvent, a crude residue was purified by SiO_2 flash column chromatography (petroleum ether / ethyl acetate) to give the corresponding 3-arylcoumarins **6**.

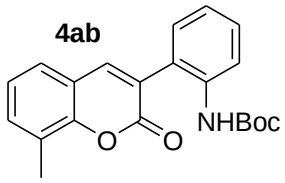
C: Characterization Data of 3-arylcoumarins

3-(2-Bocaminophenyl)coumarin (4aa)



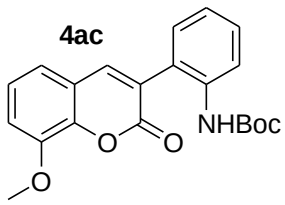
White solid, melting point 172-174 ^{o}C. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.83-7.81 (m, 2H), 7.63-7.59 (m, 2H), 7.46-7.43 (m, 2H), 7.39-7.36 (m, 1H), 7.29-7.27 (m, 1H), 7.22-7.19 (m, 1H), 7.05 (br s, 1H), 1.47 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 161.2, 153.7, 143.7, 136.5, 132.1, 130.8, 129.8, 128.3, 127.7, 124.9, 124.7, 124.5, 119.3, 116.7, 80.4, 28.3. HRMS: exact mass calculated for $[M+Na]^+$ ($C_{20}H_{19}NO_4Na$) requires m/z 360.1206, found m/z 360.1194.

3-(2-Bocaminophenyl)-8-methylcoumarin (4ab)



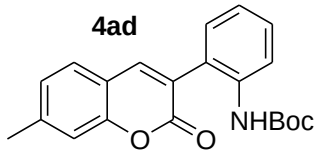
White solid, melting point 194-196 ^{o}C. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.82-7.79 (m, 2H), 7.44-7.39 (m, 3H), 7.26-7.23 (m, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.09 (br s, 1H), 2.53 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 161.4, 153.7, 152.2, 144.3, 136.6, 133.5, 130.8, 129.8, 128.2, 127.4, 126.3, 126.0, 124.7, 124.6, 124.4, 119.1, 80.4, 28.4, 15.6. HRMS: exact mass calculated for $[M-H]^-$ ($C_{21}H_{20}NO_4$) requires m/z 350.1398, found m/z 350.1404.

3-(2-Bocaminophenyl)-8-methoxylcoumarin (4ac)



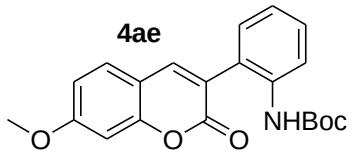
Yellow solid, melting point 152-154 ^{o}C. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.81-7.79 (m, 2H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.30-7.25 (m, 2H), 7.19-7.13 (m, 3H), 7.07 (br s, 1H), 4.01 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 160.8, 153.8, 147.2, 144.0, 143.5, 136.7, 130.8, 129.9, 128.2, 125.0, 124.8, 124.6, 120.1, 119.7, 113.8, 80.4, 56.4, 28.4. HRMS: exact mass calculated for $[M+Na]^+$ ($C_{21}H_{21}NO_5Na$) requires m/z 390.1312, found m/z 390.1303.

3-(2-Bocaminophenyl)-7-methylcoumarin (4ad)



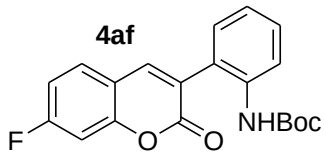
White solid, melting point 175-177 ^{o}C. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.80 (d, *J* = 8.0 Hz, 1H), 7.77 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.26-7.23 (m, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.06 (s, 1H), 2.50 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 161.5, 153.9, 153.8, 143.9, 143.6, 136.6, 130.8, 129.7, 128.0, 126.4, 126.3, 124.7, 124.4, 117.0, 116.9, 80.4, 28.4, 22.0. HRMS: exact mass calculated for $[M-H]^-$ ($C_{21}H_{20}NO_4$) requires m/z 350.1398, found m/z 350.1404.

3-(2-Bocaminophenyl)-7-methoxylcoumarin (**4ae**)



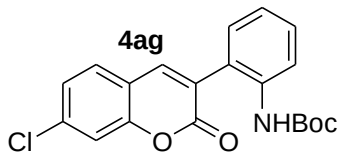
Yellow solid, melting point 188-190 ^{o}C. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.80 (d, *J* = 7.5 Hz, 1H), 7.74 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.07 (br s, 1H), 6.93-6.91 (m, 2H), 3.91 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 163.2, 161.6, 155.7, 153.8, 144.1, 136.6, 130.9, 129.6, 129.3, 128.4, 124.7, 124.4, 124.0, 113.4, 113.1, 100.6, 80.4, 56.0, 28.4. HRMS: exact mass calculated for $[M+H\text{-}Boc]^+$ ($C_{16}H_{14}NO_3$) requires m/z 268.0968, found m/z 268.0960.

3-(2-Bocaminophenyl)-7-fluorocoumarin (**4af**)



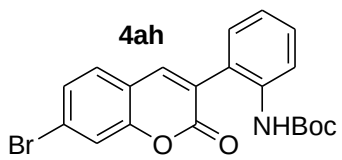
White solid, melting point 175-177 ^{o}C. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.77 (s, 2H), 7.58-7.55 (m, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.16-7.13 (m, 1H), 7.11-7.07 (m, 1H), 6.94 (br s, 1H), 1.44 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 164.7 (d, *J* = 255.5 Hz), 160.8, 154.9, 153.7, 143.2, 136.5, 130.8, 130.0, 129.9, 128.1, 126.5, 124.9, 124.7, 116.2, 113.3 (d, *J* = 23.2 Hz), 104.4 (d, *J* = 25.7 Hz), 80.5, 28.4. HRMS: exact mass calculated for $[M+Na]^+$ ($C_{20}H_{18}NO_4FNa$) requires m/z 378.1112, found m/z 378.1101.

3-(2-Bocaminophenyl)-7-chlorocoumarin (**4ag**)



Faint yellow solid, melting point 192-194 ^{o}C. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.78-7.76 (m, 2H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.44-7.41 (m, 2H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 6.93 (br s, 1H), 1.44 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 160.6, 154.0, 153.7, 142.9, 138.1, 136.5, 130.8, 130.1, 129.1, 128.1, 127.7, 125.6, 124.9, 124.8, 118.0, 117.1, 80.6, 28.4. HRMS: exact mass calculated for $[M\text{-}H]^-$ ($C_{20}H_{17}NO_4Cl$) requires m/z 370.0852, found m/z 370.0858.

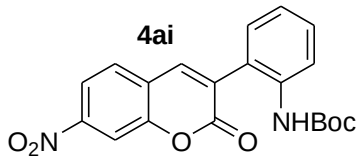
3-(2-Bocaminophenyl)-7-bromocoumarin (**4ah**)



Yellow solid, melting point 189-191 ^{o}C. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.77-7.75 (m, 2H), 7.60 (s, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.44-7.42 (m, 2H); 7.25 (d, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 6.92 (br s, 1H), 1.44 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 160.4, 153.9, 153.6, 142.9, 136.4, 130.7, 130.0, 129.1, 128.4, 128.1, 127.9, 126.0, 124.9, 124.7, 120.0, 118.3, 80.5. 28.3.

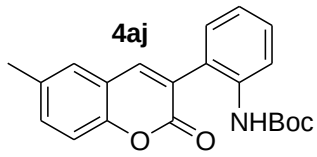
HRMS: exact mass calculated for $[M+H\text{-}Boc]^+$ ($C_{15}H_{11}NO_2Br$) requires m/z 315.9968, found m/z 315.9959.

3-(2-Bocaminophenyl)-7-nitrocoumarin (**4ai**)



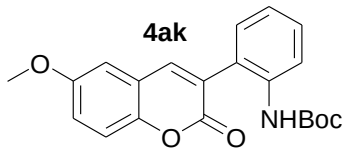
Yellow solid, melting point 142-144 ^oC. ^1H NMR (500 Hz, $CDCl_3$): δ (ppm) 8.24 (s, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.86 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 6.86 (br s, 1H), 1.42 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 159.8, 153.8, 153.2, 149.1, 141.3, 136.3, 131.4, 130.7, 130.6, 129.2, 128.0, 125.3, 124.2, 119.6, 112.5, 80.8, 28.3. HRMS: exact mass calculated for $[M+H\text{-}Boc]^+$ ($C_{15}H_{11}N_2O_4$) requires m/z 283.0713, found m/z 283.0709.

3-(2-Bocaminophenyl)-6-methylcoumarin (**4aj**)



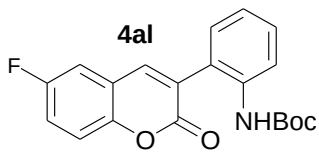
Faint yellow solid, melting point 153-155 ^oC. ^1H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.80 (d, *J* = 8.0 Hz, 1H), 7.76 (s, 1H), 7.44-7.40 (m, 2H), 7.36-7.32 (m, 2H), 7.26-7.24 (m, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.05 (br s, 1H), 2.45 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 161.5, 153.8, 152.0, 143.9, 136.7, 134.9, 133.3, 130.9, 129.9, 128.4, 128.1, 127.7, 124.8, 124.5, 119.2, 116.5, 80.5, 28.4, 21.0. HRMS: exact mass calculated for $[M+Na]^+$ ($C_{21}H_{21}NO_4Na$) requires m/z 374.1363, found m/z 374.1357.

3-(2-Bocaminophenyl)-6-methoxylcoumarin (**4ak**)



White solid, melting point 146-148 ^oC. ^1H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.80 (d, *J* = 8.0 Hz, 1H), 7.76 (s, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 9.0 Hz, 1H), 7.26-7.25 (m, 1H), 7.20-7.17 (m, 2H), 7.08 (br s, 1H), 6.99 (d, *J* = 3.0 Hz, 1H), 3.87 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 161.4, 156.6, 153.8, 148.3, 143.7, 136.7, 130.9, 129.9, 128.2, 124.8, 120.2, 119.8, 117.9, 110.0, 80.5, 56.0, 28.4. HRMS: exact mass calculated for $[M+Na]^+$ ($C_{21}H_{21}NO_5Na$) requires m/z 390.1312, found m/z 390.1302.

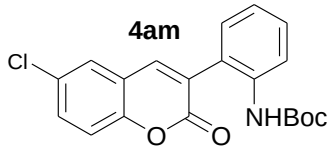
3-(2-Bocaminophenyl)-6-fluorocoumarin (**4al**)



White solid, melting point 172-174 ^oC. ^1H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.77 (d, *J* = 8.0 Hz, 1H), 7.75 (s, 1H), 7.45-7.40 (m, 2H), 7.33-7.29 (m, 1H); 7.27-7.25 (m, 2H), 7.19 (t, *J* = 7.5Hz, 1H), 6.97 (br s, 1H), 1.45 (s, 9H). ^{13}C

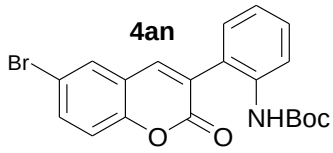
NMR (126 Hz, $CDCl_3$): δ (ppm) 160.8, 159.0 (d, *J* = 245.6 Hz), 153.6, 149.9, 142.6, 136.5, 130.7, 130.1, 129.0, 128.0, 124.9, 124.7, 120.0 (d, *J* = 9.1 Hz), 119.5 (d, *J* = 24.7 Hz), 118.3, 113.4 (d, *J* = 23.8 Hz), 80.5. 28.3. HRMS: exact mass calculated for $[M+Na]^+$ ($C_{20}H_{18}FNO_4Na$) requires m/z 378.1112, found m/z 378.1099.

3-(2-Bocaminophenyl)-6-chlorocoumarin (**4am**)



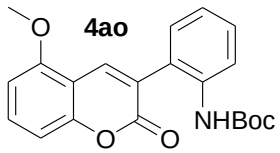
White solid, melting point 171-173 °C. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.80-7.74 (m, 2H), 7.57-7.38 (m, 4H), 7.29-7.20 (m, 2H), 6.95 (br s, 1H), 1.46 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 160.6, 153.7, 152.2, 142.3, 136.5, 132.0, 130.8, 130.3, 130.2, 129.0, 128.0, 127.5, 125.0, 124.8, 120.4, 118.2, 80.6. 28.4. HRMS: exact mass calculated for $[M+Na]^+$ ($C_{20}H_{18}ClNO_4Na$) requires m/z 394.0817, found m/z 394.0808.

3-(2-Bocaminophenyl)-6-bromocoumarin (**4an**)



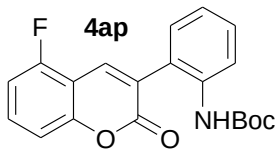
Faint yellow solid, melting point 195-197 °C. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.78 (d, *J* = 8.0 Hz, 1H), 7.72-7.67 (m, 3H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.25-7.18 (m, 2H), 7.08 (br s, 1H), 1.44 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 160.5, 153.6, 152.5, 142.1, 136.5, 134.8, 130.7, 130.4, 130.1, 129.0, 127.9, 124.9, 120.9, 118.4, 117.5, 80.5. 28.3. HRMS: exact mass calculated for $[M+Na]^+$ ($C_{20}H_{18}BrNO_4Na$) requires m/z 438.0311, found m/z 438.0307.

3-(2-Bocaminophenyl)-5-methoxylcoumarin (**4ao**)



White solid, melting point 169-171 °C. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 8.19 (s, 1H), 7.81 (d, *J* = 7.0 Hz, 1H), 7.50 (t, *J* = 8.3 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.08 (br s, 1H), 7.01 (d, *J* = 8.5 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 3.94 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 161.4, 156.6, 154.8, 153.7, 139.2, 136.6, 132.8, 131.0, 129.7, 128.4, 125.6, 124.6, 110.3, 108.9, 105.5, 80.4, 56.2, 28.4. HRMS: exact mass calculated for $[M-H]^-$ ($C_{21}H_{20}NO_5$) requires m/z 366.1347, found m/z 366.1352.

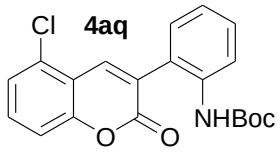
3-(2-Bocaminophenyl)-5-fluorocoumarin (**4ap**)



White solid, melting point 163-165 °C. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 8.03 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.57-7.52 (m, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.29-7.19 (m, 3H),

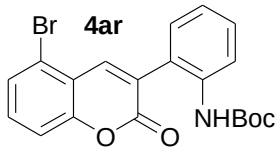
7.07 (t, *J* = 8.5 Hz, 1H), 6.92 (br s, 1H), 1.45 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 160.6, 158.8 (d, *J* = 256.7 Hz), 154.3, 153.7, 136.6, 136.5, 136.4, 132.5, 130.9, 130.2, 128.0, 124.9, 124.7, 112.6, 110.8 (d, *J* = 19.7 Hz), 109.8 (d, *J* = 19.0 Hz), 80.6, 28.4. HRMS: exact mass calculated for $[M+Na]^+$ ($C_{20}H_{18}NO_4FNa$) requires m/z 378.1112, found m/z 378.1106.

3-(2-Bocaminophenyl)-5-chlorocoumarin (**4aq**)



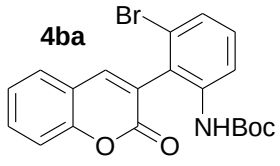
White solid, melting point 157-159 °C. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 8.18 (s, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 8.3 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H); 7.41 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 6.96 (br s, 1H), 1.47 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 160.5, 154.5, 153.7, 139.9, 136.6, 132.8, 132.1, 131.0, 130.2, 128.6, 125.6, 124.9, 118.0, 115.6, 80.6. 28.4. HRMS: exact mass calculated for $[M+H\text{-}Boc]^+$ ($C_{15}H_{11}NO_2Cl$) requires m/z 272.0473, found m/z 272.0466.

3-(2-Bocaminophenyl)-5-bromocoumarin (**4ar**)



White solid, melting point 166-168 °C. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 8.13 (s, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.47-7.41 (m, 2H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.95 (br s, 1H), 1.45 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 160.6, 154.3, 153.6, 142.4, 136.6, 132.4, 131.0, 130.2, 129.0, 128.9, 124.9, 122.7, 119.4, 116.3, 80.6, 28.4. HRMS: exact mass calculated for $[M+H]^+$ ($C_{20}H_{19}NO_4Br$) requires m/z 416.0492, found m/z 416.0480.

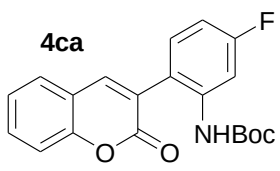
3-(2-Bocamino-6-bromophenyl)coumarin (**4ba**)



White solid, melting point 240-242 °C. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.90 (d, *J* = 8.0 Hz, 1H), 7.79 (s, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.46-7.44 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.29-7.26 (m, 1H), 6.41 (br s, 1H), 1.41 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 159.9, 154.3, 153.1, 145.8, 138.3, 132.6, 130.7, 128.7, 128.6, 127.4, 125.3, 125.0, 124.5, 122.0, 118.9, 117.1, 81.2, 28.3. HRMS: exact mass calculated for $[M+H\text{-}Boc]^+$ ($C_{15}H_{11}NO_2Br$) requires m/z 315.9968, found m/z 315.9960.

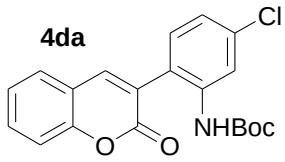
3-(2-Bocamino-4-fluorophenyl)coumarin (**4ca**)

White solid, melting point 171-173 °C. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.79 (s,



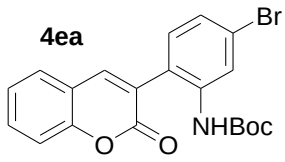
1H), 7.71 (d, *J* = 10.5 Hz, 1H), 7.63-7.58 (m, 2H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.09 (br s, 1H), 6.86 (t, *J* = 8.0 Hz, 1H), 1.46 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 163.6 (d, *J* = 248.1 Hz), 161.3, 153.8, 153.2, 144.2, 138.5 (d, *J* = 11.6 Hz), 132.4, 132.1 (d, *J* = 9.6 Hz), 128.4, 126.7, 125.1, 123.0, 119.3, 116.8, 111.2 (d, *J* = 22.1 Hz), 110.6 (d, *J* = 26.3 Hz), 81.0, 28.3. HRMS: exact mass calculated for $[M+H]^+$ ($C_{20}H_{19}NO_4F$) requires m/z 356.1293, found m/z 356.1290.

3-(2-Bocamino-4-chlorophenyl)coumarin (**4da**)



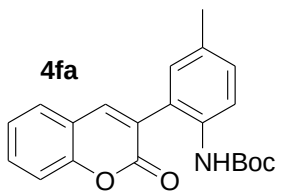
White solid, melting point 206-208 ^{o}C. ^{1}H NMR (400 Hz, $(CD_3)_2CO$): δ (ppm) 8.09 (d, *J* = 1.6 Hz, 2H), 7.99 (s, 1H), 7.73 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.68-7.64 (m, 1H), 7.41-7.35 (m, 3H), 7.18 (dd, *J* = 2.0, 8.2 Hz, 1H), 1.39 (s, 9H). ^{13}C NMR (100 Hz, $(CD_3)_2CO$): δ (ppm) 160.5, 154.9, 153.8, 144.2, 139.7, 135.1, 133.1, 132.8, 129.5, 127.0, 126.5, 125.4, 123.8, 122.3, 120.6, 117.0, 80.6, 28.4. HRMS: exact mass calculated for $[M-H]^-$ ($C_{20}H_{17}NClO_4$) requires m/z 370.0852, found m/z 370.0862.

3-(2-Bocamino-4-chlorophenyl)coumarin (**4ea**)



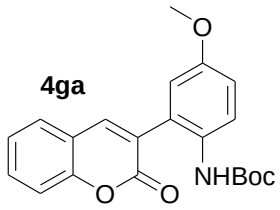
White solid, melting point 213-215 ^{o}C. ^{1}H NMR (400 Hz, $(CD_3)_2CO$): δ (ppm) 8.24 (d, *J* = 1.2 Hz, 1H), 8.08 (br s, 1H), 8.00 (s, 1H), 7.74 (dd, *J* = 1.4, 7.8 Hz, 1H), 7.68-7.64 (m, 1H), 7.41-7.37 (m, 2H), 7.35-7.29 (m, 2H), 1.39 (s, 9H). ^{13}C NMR (126 Hz, $(CD_3)_2CO$): δ (ppm) 160.4, 154.9, 153.8, 144.2, 139.9, 133.3, 132.8, 129.4, 127.1, 126.9, 126.7, 125.4, 125.1, 123.1, 120.6, 117.0, 80.5, 28.3. HRMS: exact mass calculated for $[M-H]^-$ ($C_{20}H_{17}NBrO_4$) requires m/z 414.0346, found m/z 414.0357.

3-(2-Bocamino-5-methylphenyl)coumarin (**4fa**)



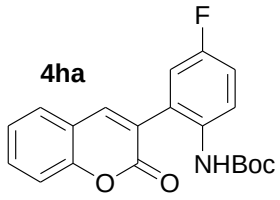
Yellow solid, melting point 194-196 ^{o}C. ^{1}H NMR (500 Hz, $(CD_3)_2CO$): δ (ppm) 7.94 (s, 1H), 7.74-7.63 (m, 4H), 7.40-7.37 (m, 2H), 7.22-7.19 (m, 2H), 2.33 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (126 Hz, $(CD_3)_2CO$): δ (ppm) 160.7, 154.7, 154.2, 143.6, 135.5, 134.0, 132.5, 132.0, 130.4, 129.3, 129.0, 128.3, 125.3, 124.1, 120.7, 116.9, 79.7, 28.4, 20.7. HRMS: exact mass calculated for $[M-H]^-$ ($C_{21}H_{20}NO_4$) requires m/z 350.1398, found m/z 350.1407.

3-(2-Bocamino-5-methoxylphenyl)coumarin (**4ga**)



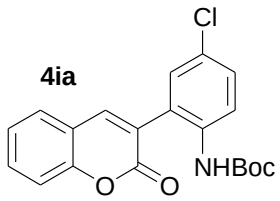
Faint yellow solid, melting point 164-166 ^{o}C. ^{1}H NMR (400 Hz, $(CD_3)_2CO$): δ (ppm) 7.95 (s, 1H), 7.72-7.70 (m, 1H), 7.66-7.58 (m, 3H), 7.40-7.36 (m, 2H), 7.00-6.96 (m, 2H), 3.81 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (100 Hz, $(CD_3)_2CO$): δ (ppm) 160.6, 157.4, 154.8, 154.5, 143.6, 132.6, 130.8, 129.3, 128.0, 125.4, 120.6, 116.9, 116.8, 115.3, 79.6, 55.9, 28.4. HRMS: exact mass calculated for $[M-H]^-$ ($C_{21}H_{20}NO_5$) requires m/z 366.1347, found m/z 366.1357.

3-(2-Bocamino-5-fluorophenyl)coumarin (**4ha**)



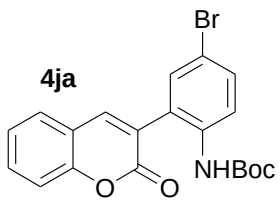
White solid, melting point 172-174 ^{o}C. ^{1}H NMR (400 Hz, $(CD_3)_2CO$): δ (ppm) 7.99 (s, 1H), 7.85-7.77 (m, 2H), 7.73 (dd, *J* = 1.8, 7.8 Hz, 1H), 7.68-7.63 (m, 1H), 7.04-7.37 (m, 2H), 7.22-7.16 (m, 2H), 1.36 (s, 9H). ^{13}C NMR (100 Hz, $(CD_3)_2CO$): δ (ppm) 160.9, 159.5 (d, *J* = 231.8 Hz), 154.8, 154.3, 144.0, 134.3 (d, *J* = 3.4 Hz), 132.8, 131.2, 129.5, 126.9, 126.3, 125.4, 120.5, 118.0 (d, *J* = 29.4 Hz), 117.0, 116.3 (d, *J* = 27.7 Hz), 80.0, 28.4. HRMS: exact mass calculated for $[M-H]^-$ ($C_{20}H_{17}NFO_4$) requires m/z 354.1147, found m/z 354.1157.

3-(2-Bocamino-5-chlorophenyl)coumarin (**4ia**)



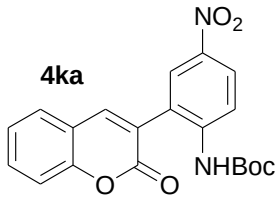
White solid, melting point 183-185 ^{o}C. ^{1}H NMR (400 Hz, $(CD_3)_2CO$): δ (ppm) 8.01 (s, 1H), 7.97 (br s, 1H), 7.91 (d, *J* = 13.6, 1H), 7.74 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.68-7.64 (m, 1H), 7.43-7.37 (m, 4H), 1.37 (s, 9H). ^{13}C NMR (100 Hz, $(CD_3)_2CO$): δ (ppm) 160.4, 154.9, 153.9, 144.3, 137.2, 132.8, 131.2, 130.2, 129.6, 129.5, 128.7, 126.7, 125.4, 124.9, 120.5, 117.0, 80.3, 28.4. HRMS: exact mass calculated for $[M-H]^-$ ($C_{20}H_{17}NClO_4$) requires m/z 370.0852, found m/z 370.0862.

3-(2-Bocamino-5-bromophenyl)coumarin (**4ja**)



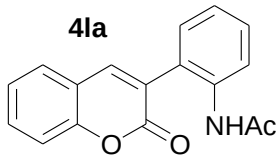
White solid, melting point 182-184 ^{o}C. ^{1}H NMR (400 Hz, $(CD_3)_2CO$): δ (ppm) 8.01 (s, 1H), 7.98 (br s, 1H), 7.87 (d, *J* = 9.6 Hz, 1H), 7.74 (dd, *J* = 1.4, 7.8 Hz, 1H), 7.68-7.64 (m, 1H), 7.57-7.54 (m, 2H), 7.41-7.37 (m, 2H), 1.37 (s, 9H). ^{13}C NMR (100 Hz, $(CD_3)_2CO$): δ (ppm) 160.4, 154.9, 153.9, 144.3, 137.7, 134.1, 132.8, 132.6, 130.4, 129.5, 126.6, 125.4, 125.1, 120.5, 117.0, 116.2, 80.3, 28.4. HRMS: exact mass calculated for $[M-H]^-$ ($C_{20}H_{17}NBrO_4$) requires m/z 414.0346, found m/z 414.0358.

3-(2-Bocamino-5-nitrophenyl)coumarin (**4ka**)



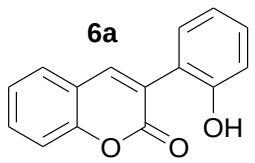
White solid, melting point 187-189 ^{o}C. ^{1}H NMR (400 Hz, $(CD_3)_2CO$): δ (ppm) 8.55 (br s, 1H), 8.39 (d, *J* = 8.8 Hz, 1H), 8.30-8.26 (m, 2H), 8.14 (s, 1H), 7.76 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.71-7.66 (m, 1H), 7.42-7.39 (m, 2H), 1.42 (s, 9H). ^{13}C NMR (100 Hz, $(CD_3)_2CO$): δ (ppm) 160.2, 155.1, 153.4, 145.2, 144.9, 143.2, 133.1, 129.7, 127.4, 127.2, 126.1, 125.4, 121.1, 120.5, 117.0, 81.3, 28.3. HRMS: exact mass calculated for $[M-H]^-$ ($C_{20}H_{17}N_2O_6$) requires m/z 381.1092, found m/z 381.1104.

3-(2-acetylaminophenyl)coumarin (**4la**)



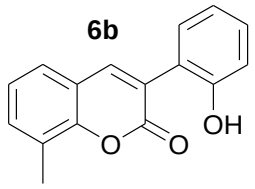
White solid, melting point 192-194 ^{o}C. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 8.17 (br s, 1H), 7.84 (s, 1H), 7.75 (d, *J* = 8.5, 1H), 7.63-7.59 (m, 2H), 7.47-7.42 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 7.0, 1H), 7.28-7.27 (m, 1H), 2.07 (s, 3H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 169.1, 161.7, 153.7, 144.4, 135.9, 132.3, 131.0, 130.0, 129.4, 128.5, 127.6, 126.5, 126.1, 125.2, 119.4, 116.7, 24.3. HRMS: exact mass calculated for $[M+H]^+$ ($C_{17}H_{14}NO_3$) requires m/z 280.0968, found m/z 280.0959.

3-(2-hydroxyphenyl)coumarin (6a)



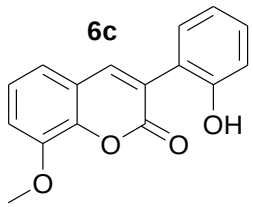
White solid, melting point 208-210 ^{o}C. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.95 (s, 1H), 7.63-7.60 (m, 3H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.41-7.36 (m, 2H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 163.4, 155.1, 153.3, 144.0, 132.3, 131.2, 130.8, 128.4, 127.6, 125.4, 123.3, 121.6, 119.7, 119.6, 116.8. HRMS: exact mass calculated for $[M+H]^+$ ($C_{15}H_{11}NO_3$) requires m/z 239.0703, found m/z 239.0698.

3-(2-hydroxyphenyl)-8-methylcoumarin (6b)



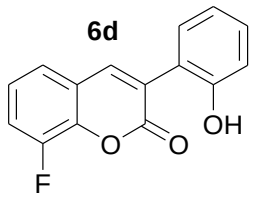
White solid, melting point 183-185 ^{o}C. ^{1}H NMR (400 Hz, $(CD_3)_2CO$): δ (ppm) 8.48 (s, 1H), 8.00 (s, 1H), 7.55 (d, *J* = 6.0 Hz, 1H), 7.48 (d, *J* = 6.4 Hz, 1H), 7.38 (dd, *J* = 1.4, 6.2 Hz, 1H), 7.28-7.25 (m, 2H), 6.98 (dd, *J* = 0.8, 7.2 Hz, 1H), 6.95-6.92 (m, 1H). ^{13}C NMR (100 Hz, $(CD_3)_2CO$): δ (ppm) 160.9, 156.0, 152.8, 143.4, 133.4, 131.9, 130.7, 126.9, 126.1, 124.9, 123.6, 120.4, 120.3, 117.1, 15.3. HRMS: exact mass calculated for $[M-H]^-$ ($C_{16}H_{11}O_3$) requires m/z 251.0714, found m/z 251.0715.

3-(2-hydroxyphenyl)-8-methoxylcoumarin (6c)



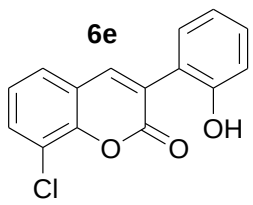
White solid, melting point 132-134 ^{o}C. ^{1}H NMR (500 Hz, $(CD_3)_2CO$): δ (ppm) 8.48 (s, 1H), 8.00 (s, 1H), 7.39 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.32-7.25 (m, 4H), 6.98 (dd, *J* = 1.0, 8.0 Hz, 1H), 6.95-6.92 (m, 1H), 3.98 (s, 3H). ^{13}C NMR (126 Hz, $(CD_3)_2CO$): δ (ppm) 160.6, 156.0, 147.9, 144.0, 143.3, 131.9, 130.7, 127.4, 125.2, 123.6, 121.2, 120.4, 117.1, 114.4, 56.6. HRMS: exact mass calculated for $[M-H]^-$ ($C_{16}H_{11}O_4$) requires m/z 267.0663, found m/z 267.0665.

8-fluoro-3-(2-hydroxyphenyl)coumarin (6d)



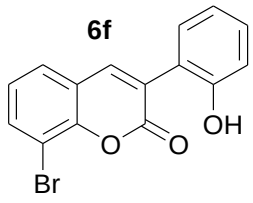
Faint yellow solid, melting point 201-203 ^{o}C. ^{1}H NMR (500 Hz, $(CD_3)_2CO$): δ (ppm) 8.55 (s, 1H), 8.05 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.50-7.46 (m, 1H), 7.40-7.34 (m, 2H), 7.29-7.26 (m, 1H), 6.99-6.98 (m, 1H), 6.95-6.92 (m, 1H). ^{13}C NMR (126 Hz, $(CD_3)_2CO$): δ (ppm) 159.3, 155.9, 150.8, 148.9, 142.5, 131.8, 130.9, 128.2, 125.3, 124.5 (d, *J* = 3.8 Hz), 123.2, 122.6, 120.3, 118.2 (d, *J* = 17.6 Hz), 116.9. HRMS: exact mass calculated for $[M+H]^+$ ($C_{15}H_{10}FO_3$) requires m/z 257.0608, found m/z 257.0604.

8-chloro-3-(2-hydroxyphenyl)coumarin (6e)



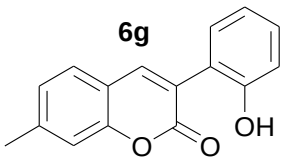
White solid, melting point 207-209 ^{o}C. ^{1}H NMR (400 Hz, $(CD_3)_2CO$): δ (ppm) 8.50 (s, 1H), 8.04 (s, 1H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.40-7.35 (m, 2H), 7.30-7.25 (m, 1H), 7.00-6.92 (m, 2H). ^{13}C NMR (100 Hz, $(CD_3)_2CO$): δ (ppm) 159.6, 156.0, 150.1, 142.6, 132.3, 131.9, 131.0, 128.1, 125.7, 123.1, 122.1, 121.1, 120.4, 117.0. HRMS: exact mass calculated for $[M+H]^+$ ($C_{15}H_{10}ClO_3$) requires m/z 273.0313, found m/z 273.0309.

8-bromo-3-(2-hydroxyphenyl)coumarin (6f)



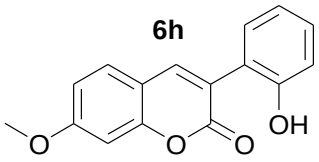
Faint yellow solid, melting point 217-219 ^{o}C. ^{1}H NMR (500 Hz, $(CD_3)_2CO$): δ (ppm) 8.53 (s, 1H), 8.03 (s, 1H), 7.87 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.75 (dd, *J* = 1.3, 7.8 Hz, 1H), 7.40 (dd, *J* = 1.8, 7.8 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.30-7.26 (m, 1H), 6.99 (dd, *J* = 0.8, 7.8 Hz, 1H), 6.96-6.93 (m, 1H). ^{13}C NMR (126 Hz, $(CD_3)_2CO$): δ (ppm) 159.7, 156.0, 151.1, 142.6, 135.4, 131.9, 131.0, 128.8, 128.0, 126.2, 123.0, 122.1, 120.3, 117.0, 109.7. HRMS: exact mass calculated for $[M-H]^-$ ($C_{15}H_8BrO_3$) requires m/z 316.9642, found m/z 316.9639.

3-(2-hydroxyphenyl)-7-methylcoumarin (6g)



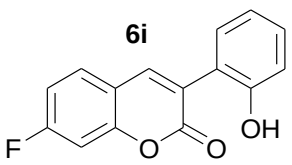
Faint yellow solid, melting point 144-146 ^{o}C. ^{1}H NMR (500 Hz, $(CD_3)_2CO$): δ (ppm) 8.45 (s, 1H), 7.97 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.36 (dd, *J* = 2.0, 7.5 Hz, 1H), 7.27-7.23 (m, 1H), 7.21-7.19 (m, 2H), 6.98-6.96 (m, 1H), 6.94-6.91 (m, 1H), 2.47 (s, 3H). ^{13}C NMR (126 Hz, $(CD_3)_2CO$): δ (ppm) 161.0, 155.9, 154.6, 143.5, 143.1, 131.9, 130.6, 128.9, 126.4, 126.0, 123.7, 120.4, 118.1, 117.1, 117.0, 21.7. HRMS: exact mass calculated for $[M+H]^+$ ($C_{16}H_{13}O_3$) requires m/z 253.0859, found m/z 253.0851.

3-(2-hydroxyphenyl)-7-methoxylcoumarin (6h)



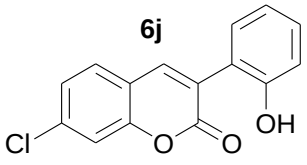
Faint yellow solid, melting point 160-162 ^{o}C. ^{1}H NMR (500 Hz, $(CD_3)_2CO$): δ (ppm) 8.42 (s, 1H), 7.96 (s, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.36 (dd, *J* = 1.8, 7.8 Hz, 1H), 7.26-7.23 (m, 1H), 6.97-6.90 (m, 4H), 3.94 (s, 3H). ^{13}C NMR (126 Hz, $(CD_3)_2CO$): δ (ppm) 163.7, 161.2, 156.3, 156.0, 143.5, 131.9, 130.5, 130.2, 123.8, 123.6, 120.4, 117.2, 114.1, 113.4, 101.1, 56.3. HRMS: exact mass calculated for $[M-H]^-$ ($C_{16}H_{11}O_4$) requires m/z 267.0663, found m/z 267.0665.

7-fluoro-3-(2-hydroxyphenyl)coumarin (6i)



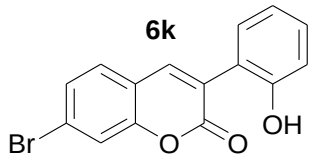
Yellow solid, melting point 202-204 ^{o}C. ^{1}H NMR (500 Hz, $(CD_3)_2CO$): δ (ppm) 8.50 (s, 1H), 8.02 (s, 1H), 7.81-7.78 (m, 1H), 7.36 (dd, *J* = 1.8, 7.8 Hz, 1H), 7.28-7.17 (m, 3H), 6.97 (dd, *J* = 1.0, 8.0 Hz, 1H), 6.94-6.91 (m, 1H). ^{13}C NMR (126 Hz, $(CD_3)_2CO$): δ (ppm) 165.0 (d, *J* = 250.7 Hz), 160.2, 155.9, 155.7, 155.6, 142.5, 131.9, 131.1 (d, *J* = 11.3 Hz), 130.8, 126.1, 123.3, 117.5, 117.0, 113.0 (d, *J* = 22.7 Hz), 104.3 (d, *J* = 26.5 Hz). HRMS: exact mass calculated for $[M-H]^-$ ($C_{15}H_8FO_3$) requires m/z 255.0463, found m/z 255.0464.

7-chloro-3-(2-hydroxyphenyl)coumarin (6j)



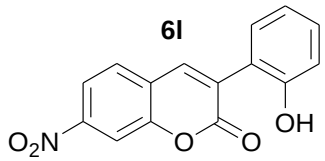
Faint yellow solid, melting point 181-183 ^{o}C. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.89 (s, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.46 (d, *J* = 2.0 Hz, 1H), 7.38-7.35 (m, 3H), 7.30 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.06-7.01 (m, 2H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 162.6, 154.9, 153.4, 143.0, 138.2, 131.3, 130.8, 129.1, 127.4, 126.0, 123.0, 121.6, 119.5, 118.2, 117.1. HRMS: exact mass calculated for $[M+H]^+$ ($C_{15}H_{10}ClO_3$) requires m/z 273.0313, found m/z 273.0305.

7-bromo-3-(2-hydroxyphenyl)coumarin (6k)



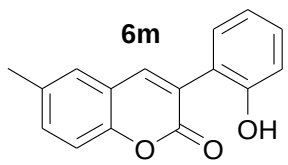
Faint yellow solid, melting point 186-188 ^{o}C. ^{1}H NMR (400 Hz, $(CD_3)_2CO$): δ (ppm) 8.47 (s, 1H), 8.01 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.54 (dd, *J* = 1.8, 8.2 Hz, 1H), 7.37 (dd, *J* = 2.0, 7.6 Hz, 1H), 7.29-7.24 (m, 1H), 6.99-6.91 (m, 2H). ^{13}C NMR (100 Hz, $(CD_3)_2CO$): δ (ppm) 159.9, 155.9, 154.9, 142.3, 131.8, 130.9, 130.5, 128.5, 127.6, 125.1, 123.3, 120.4, 120.1, 119.8, 117.1. HRMS: exact mass calculated for $[M+H]^+$ ($C_{15}H_{10}BrO_3$) requires m/z 316.9808, found m/z 316.9805.

3-(2-hydroxyphenyl)-7-nitrocoumarin (6l)



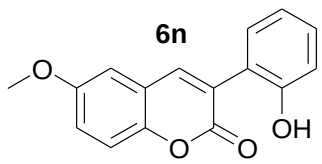
Yellow solid, melting point 228-230 ^{o}C. ^{1}H NMR (500 Hz, $(CD_3)_2CO$): δ (ppm) 8.68 (s, 1H), 8.22-8.17 (m, 3H), 8.01 (d, *J* = 7.5 Hz, 1H), 7.42 (dd, *J* = 1.8, 7.8 Hz, 1H), 7.31-7.28 (m, 1H), 7.00 (dd, *J* = 0.8, 8.3 Hz, 1H), 6.97-6.93 (m, 1H). ^{13}C NMR (126 Hz, $(CD_3)_2CO$): δ (ppm) 159.5, 156.0, 154.0, 149.7, 141.2, 131.8, 131.3, 130.5, 130.3, 125.8, 122.8, 120.4, 119.8, 116.9, 112.4. HRMS: exact mass calculated for $[M+H]^+$ ($C_{15}H_{10}NO_5$) requires m/z 284.0553, found m/z 284.0548.

3-(2-hydroxyphenyl)-6-methylcoumarin (6m)



White solid, melting point 187-189 ^{o}C. ^{1}H NMR (500 Hz, $(CD_3)_2CO$): δ (ppm) 8.46 (s, 1H), 7.96 (s, 1H), 7.51 (s, 1H), 7.44 (dd, *J* = 1.5, 8.5 Hz, 2H), 7.37 (dd, *J* = 1.8, 7.8 Hz, 1H), 7.28-7.24 (m, 2H), 6.97 (dd, *J* = 1.0, 8.0 Hz, 1H), 6.95-6.91 (m, 1H). ^{13}C NMR (126 Hz, $(CD_3)_2CO$): δ (ppm) 160.9, 156.0, 152.7, 143.0, 134.9, 132.2, 131.9, 130.7, 128.9, 127.2, 123.7, 120.4, 120.3, 117.1, 116.6, 20.7. HRMS: exact mass calculated for $[M-H]^-$ ($C_{16}H_{11}O_3$) requires m/z 251.0714, found m/z 251.0715.

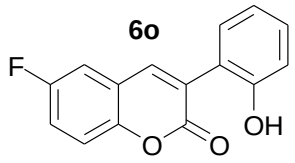
3-(2-hydroxyphenyl)-6-methoxylcoumarin (6n)



White solid, melting point 152-154 ^{o}C. ^{1}H NMR (500 Hz, $(CD_3)_2CO$): δ (ppm) 8.48 (s, 1H), 7.99 (s, 1H), 7.38 (dd, *J* = 2.0, 7.5 Hz, 1H), 7.32 (d, *J* = 9.0 Hz, 1H), 7.28-7.25 (m, 2H), 7.21 (dd, *J* = 3.0, 9.0 Hz, 1H), 6.98 (dd, *J* = 1.0, 8.0 Hz, 1H), 6.95-6.92 (m, 1H), 3.87 (s, 3H). ^{13}C NMR (126 Hz, $(CD_3)_2CO$): δ (ppm) 161.0, 157.1, 156.0, 148.9, 143.0, 131.9, 130.7, 127.6, 123.7, 121.0, 120.3, 119.9,

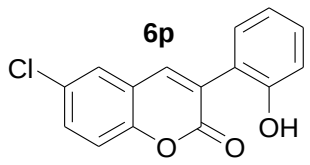
117.9, 117.2, 111.2, 56.2. HRMS: exact mass calculated for $[M+H]^+$ ($C_{16}H_{13}O_4$) requires m/z 269.0808, found m/z 269.0800.

6-fluoro-3-(2-hydroxyphenyl)coumarin (6o)



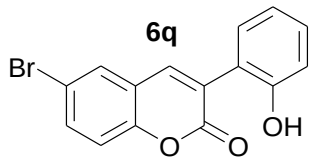
White solid, melting point 224-226 ^{o}C. ^{1}H NMR (500 Hz, $(CD_3)_2CO$): δ (ppm) 8.52 (s, 1H), 8.02 (s, 1H), 7.55-7.52 (m, 1H), 7.44-7.42 (m, 2H), 7.38 (dd, *J* = 1.8, 7.8 Hz, 1H), 7.29-7.26 (m, 1H), 6.98 (dd, *J* = 1.0, 8.0 Hz, 1H), 6.95-6.92 (m, 1H). ^{13}C NMR (126 Hz, $(CD_3)_2CO$): δ (ppm) 160.3, 159.6 (d, *J* = 241.9 Hz), 155.9, 150.9, 142.0, 131.9, 130.9, 128.4, 123.2, 121.5, 120.4, 119.3 (d, *J* = 25.2 Hz), 118.7 (d, *J* = 8.8 Hz), 117.0, 114.2 (d, *J* = 25.2 Hz). HRMS: exact mass calculated for $[M+H]^+$ ($C_{15}H_{10}FO_3$) requires m/z 257.0608, found m/z 257.0604.

6-chloro-3-(2-hydroxyphenyl)coumarin (6p)



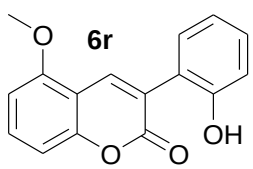
Faint yellow solid, melting point 218-220 ^{o}C. ^{1}H NMR (500 Hz, $(CD_3)_2CO$): δ (ppm) 8.55 (s, 1H), 8.01 (s, 1H), 7.80 (d, *J* = 2.5 Hz, 1H), 7.62 (dd, *J* = 2.5, 8.5 Hz, 1H), 7.42 (d, *J* = 9.0 Hz, 1H), 7.38 (dd, *J* = 1.8, 7.8 Hz, 1H), 7.29-7.26 (m, 1H), 6.98 (dd, *J* = 1.0, 8.0 Hz, 1H), 6.95-6.92 (m, 1H). ^{13}C NMR (126 Hz, $(CD_3)_2CO$): δ (ppm) 160.0, 155.9, 153.1, 141.7, 131.8, 131.0, 129.7, 128.5, 128.2, 123.2, 121.9, 120.3, 118.7, 117.0. HRMS: exact mass calculated for $[M+H]^+$ ($C_{15}H_{10}ClO_3$) requires m/z 273.0313, found m/z 273.0305.

6-bromo-3-(2-hydroxyphenyl)coumarin (6q)



Faint yellow solid, melting point 224-226 ^{o}C. ^{1}H NMR (500 Hz, $(CD_3)_2CO$): δ (ppm) 8.54 (s, 1H), 8.01 (s, 1H), 7.95 (d, *J* = 2.0 Hz, 1H), 7.76 (dd, *J* = 2.0, 9.0 Hz, 1H), 7.39-7.35 (m, 2H), 7.29-7.26 (m, 1H), 6.98 (dd, *J* = 1.0, 8.0 Hz, 1H), 6.95-6.92 (m, 1H). ^{13}C NMR (126 Hz, $(CD_3)_2CO$): δ (ppm) 160.0, 156.0, 153.6, 141.6, 134.7, 131.8, 131.3, 131.0, 128.5, 123.2, 122.4, 120.3, 119.0, 117.0. HRMS: exact mass calculated for $[M+H]^+$ ($C_{15}H_{10}BrO_3$) requires m/z 316.9808, found m/z 316.9801.

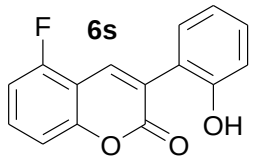
3-(2-hydroxyphenyl)-5-methoxylcoumarin (6r)



Faint yellow solid, melting point 160-162 ^{o}C. ^{1}H NMR (500 Hz, $(CD_3)_2CO$): δ (ppm) 8.47 (s, 1H), 8.17 (s, 1H), 7.54 (t, *J* = 8.3 Hz, 1H), 7.38 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.27-7.24 (m, 1H), 6.99-6.92 (m, 4H), 3.98 (s, 3H). ^{13}C NMR (126 Hz, $(CD_3)_2CO$):

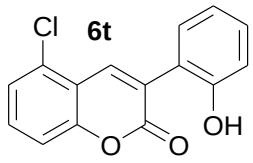
δ (ppm) 160.7, 157.2, 155.9, 155.5, 137.6, 133.1, 131.9, 130.6, 125.3, 123.7, 120.4, 117.1, 110.7, 109.2, 106.4, 56.6. HRMS: exact mass calculated for $[M+H]^+$ ($C_{16}H_{13}O_4$) requires m/z 269.0808, found m/z 269.0802.

5-fluoro-3-(2-hydroxyphenyl)coumarin (6s)



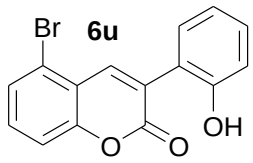
White solid, melting point 187-189 °C. ^{1}H NMR (500 Hz, $(CD_3)_2CO$): δ (ppm) 8.59 (s, 1H), 8.09 (s, 1H), 7.67-7.62 (m, 1H), 7.42 (dd, *J* = 1.8, 7.8 Hz, 1H), 7.30-7.26 (m, 1H), 7.24 (dd, *J* = 0.8, 8.3 Hz, 1H), 7.19-7.15 (m, 1H), 6.99 (dd, *J* = 1.0, 8.5 Hz, 1H), 6.96-6.93 (m, 1H). ^{13}C NMR (126 Hz, $(CD_3)_2CO$): δ (ppm) 159.8, 159.4 (d, *J* = 253.3 Hz), 155.9, 155.2, 134.9, 132.9 (d, *J* = 8.8 Hz), 131.9, 131.0, 127.6, 123.1, 120.3, 117.0, 113.1, 111.0 (d, *J* = 20.2 Hz), 110.3 (d, *J* = 18.9 Hz). HRMS: exact mass calculated for $[M+H]^+$ ($C_{15}H_{10}FO_3$) requires m/z 257.0608, found m/z 257.0601.

5-chloro-3-(2-hydroxyphenyl)coumarin (6t)



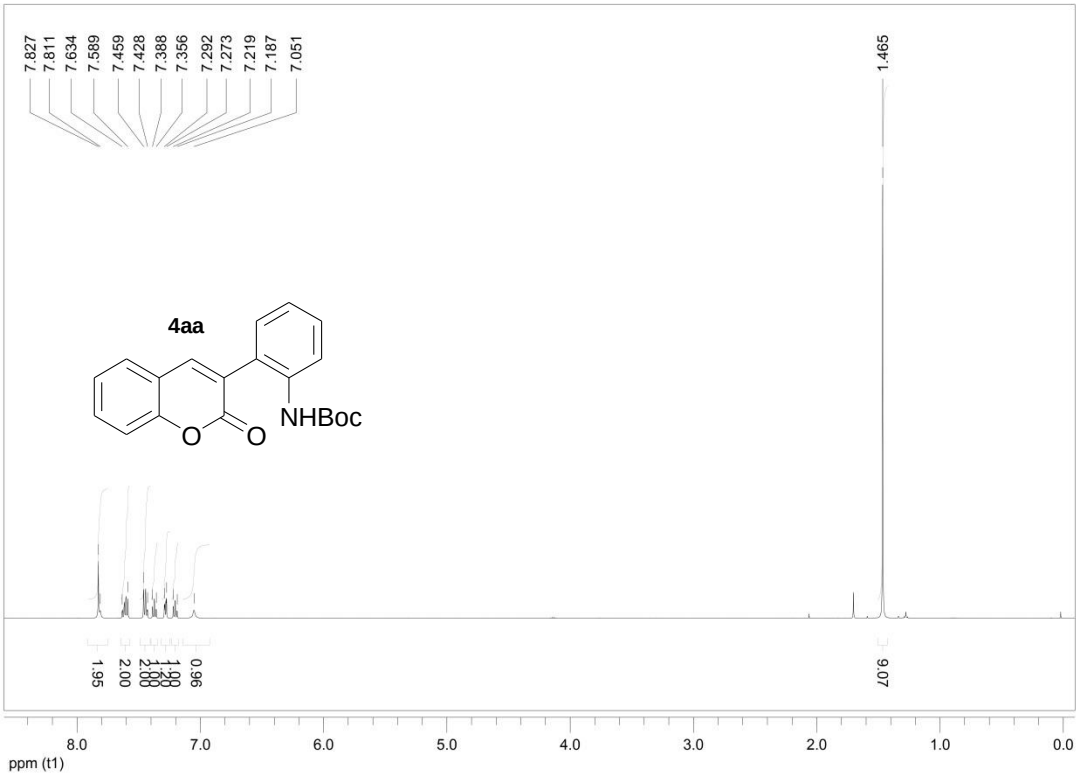
Faint yellow solid, melting point 203-205 °C. ^{1}H NMR (400 Hz, $(CD_3)_2CO$): δ (ppm) 8.56 (s, 1H), 8.22 (s, 1H), 7.62 (t, *J* = 8.1 Hz, 1H), 7.48-7.42 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.31-7.27 (m, 1H), 7.01-6.93 (m, 2H). ^{13}C NMR (100 Hz, $(CD_3)_2CO$): δ (ppm) 159.8, 155.9, 155.4, 138.3, 132.6, 132.0, 131.1, 128.4, 125.8, 123.1, 120.4, 118.8, 117.1, 116.3. HRMS: exact mass calculated for $[M+H]^+$ ($C_{15}H_{10}ClO_3$) requires m/z 273.0313, found m/z 273.0308.

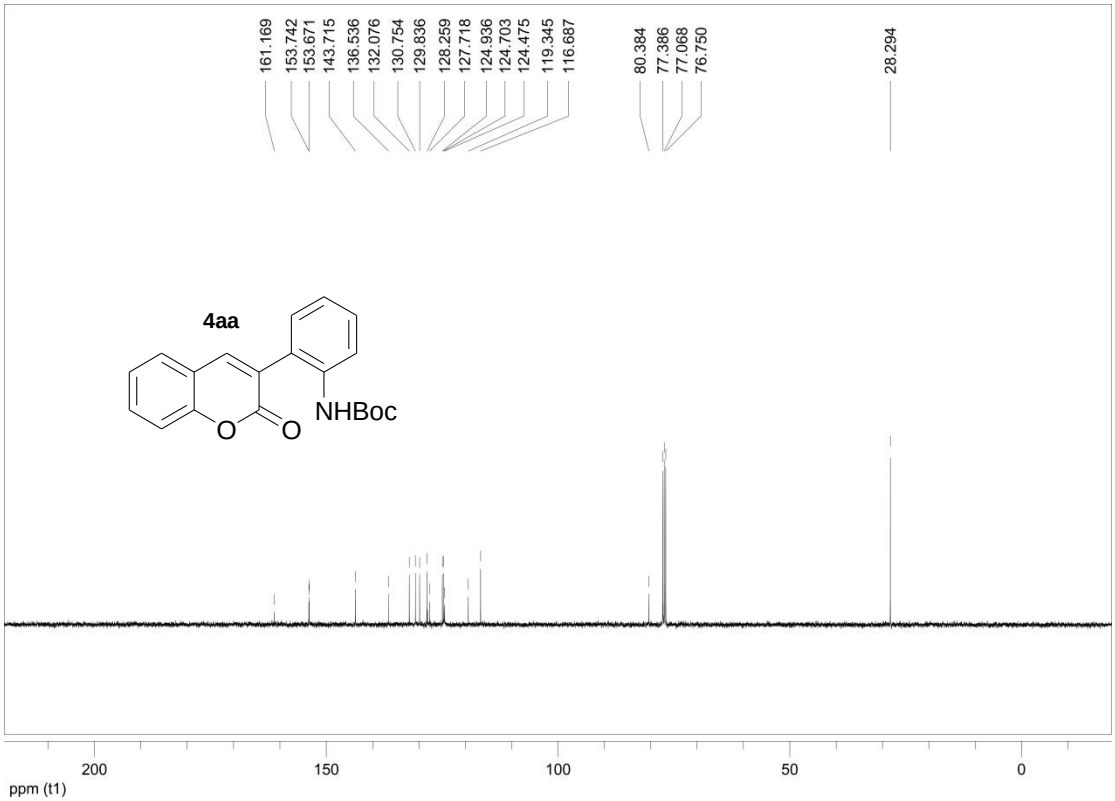
5-bromo-3-(2-hydroxyphenyl)coumarin (6u)

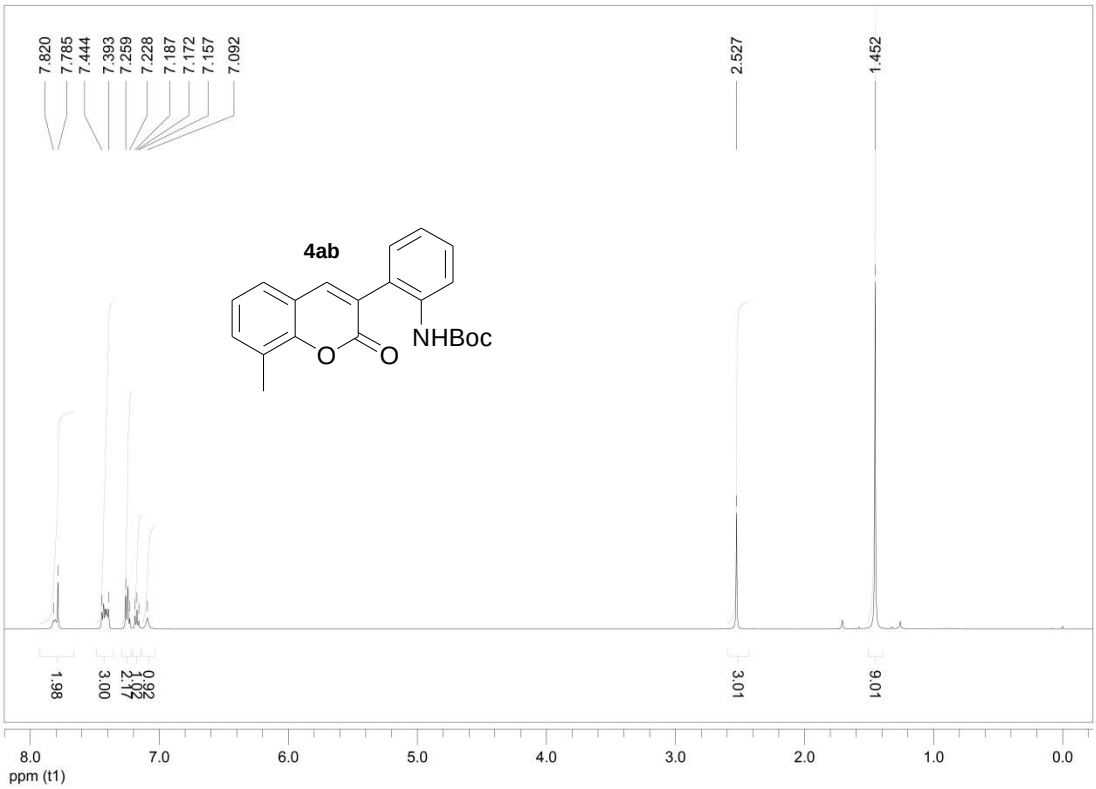


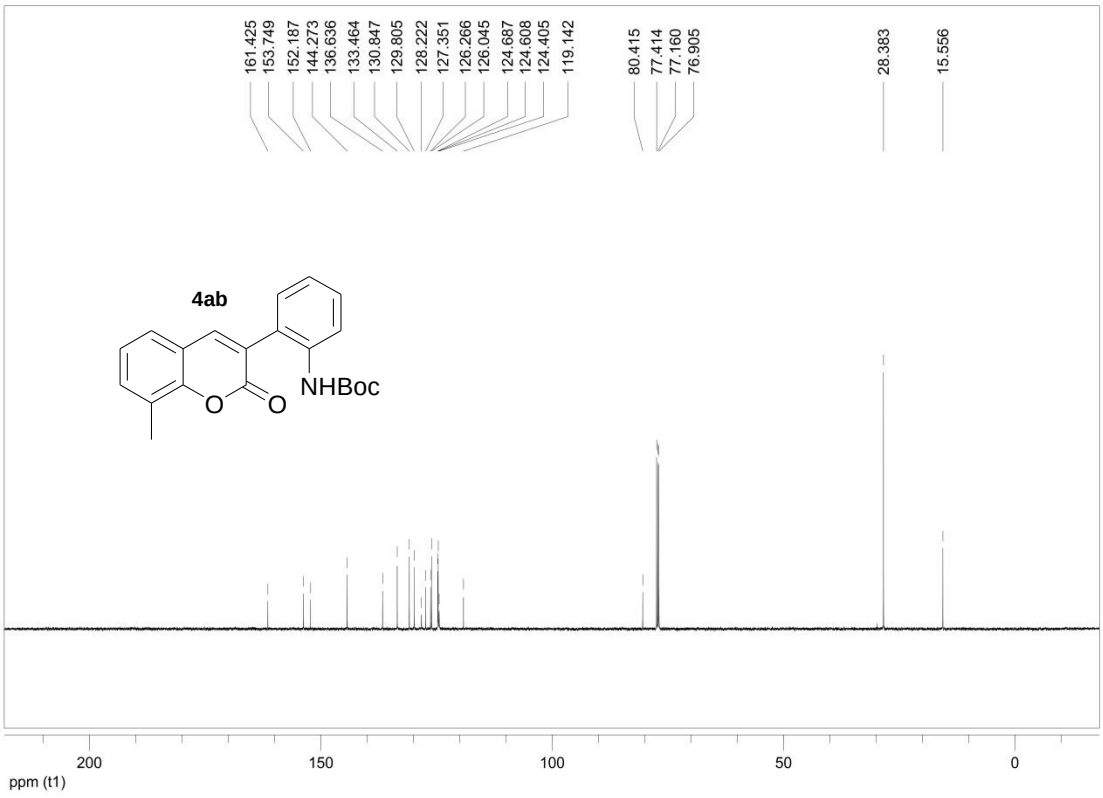
Faint yellow solid, melting point 206-208 °C. ^{1}H NMR (500 Hz, $(CD_3)_2CO$): δ (ppm) 8.61 (s, 1H), 8.19 (s, 1H), 7.65 (dd, *J* = 1.0, 8.0 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.45-7.41 (m, 2H), 7.31-7.27 (m, 1H), 7.02-7.00 (m, 1H), 6.97-6.94 (m, 1H). ^{13}C NMR (126 Hz, $(CD_3)_2CO$): δ (ppm) 159.7, 155.9, 155.2, 140.8, 133.0, 131.9, 131.1, 129.3, 128.6, 122.9, 122.5, 120.4, 120.2, 117.0, 116.9. HRMS: exact mass calculated for $[M+H]^+$ ($C_{15}H_{10}BrO_3$) requires m/z 316.9808, found m/z 316.9803.

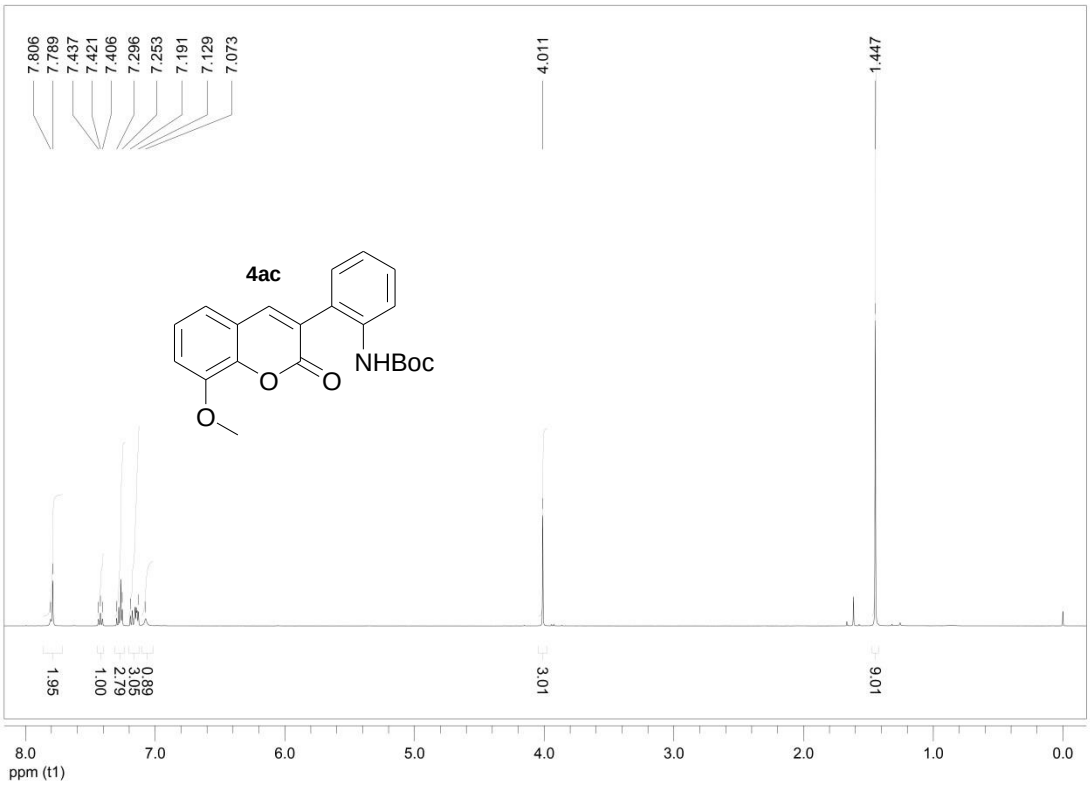
D: Copies of ^{1}H and ^{13}C NMR spectra of 3-arylcoumarins

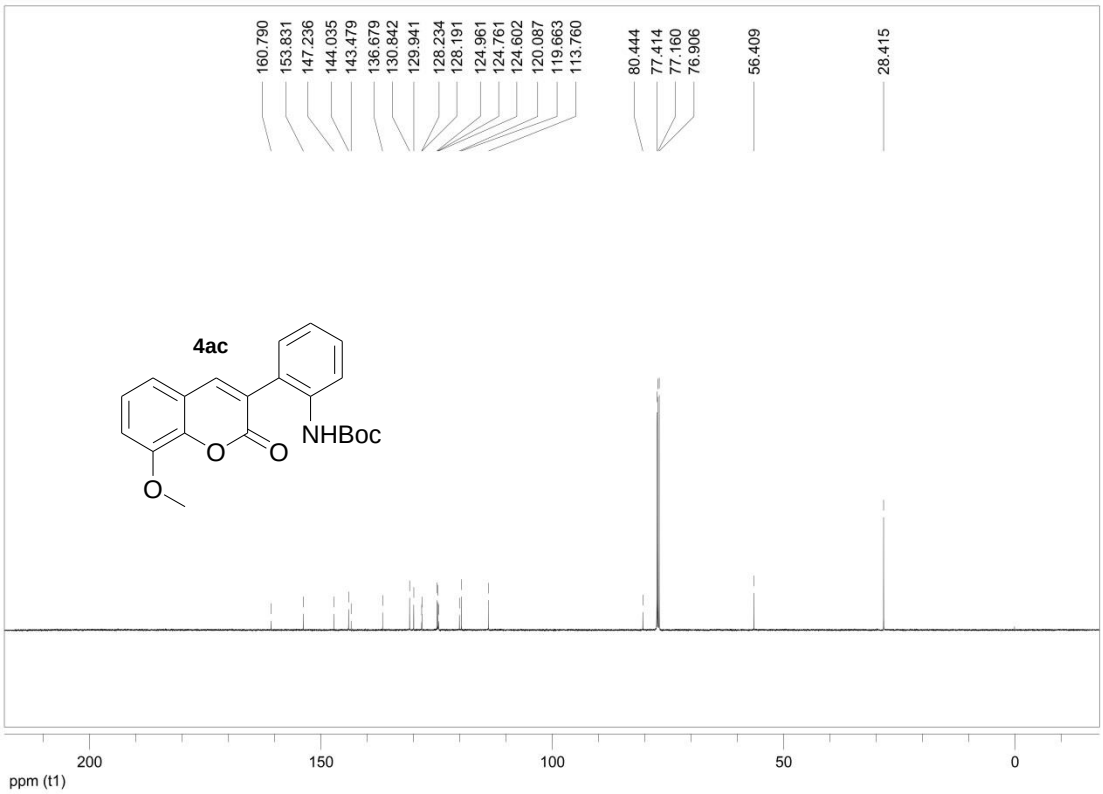


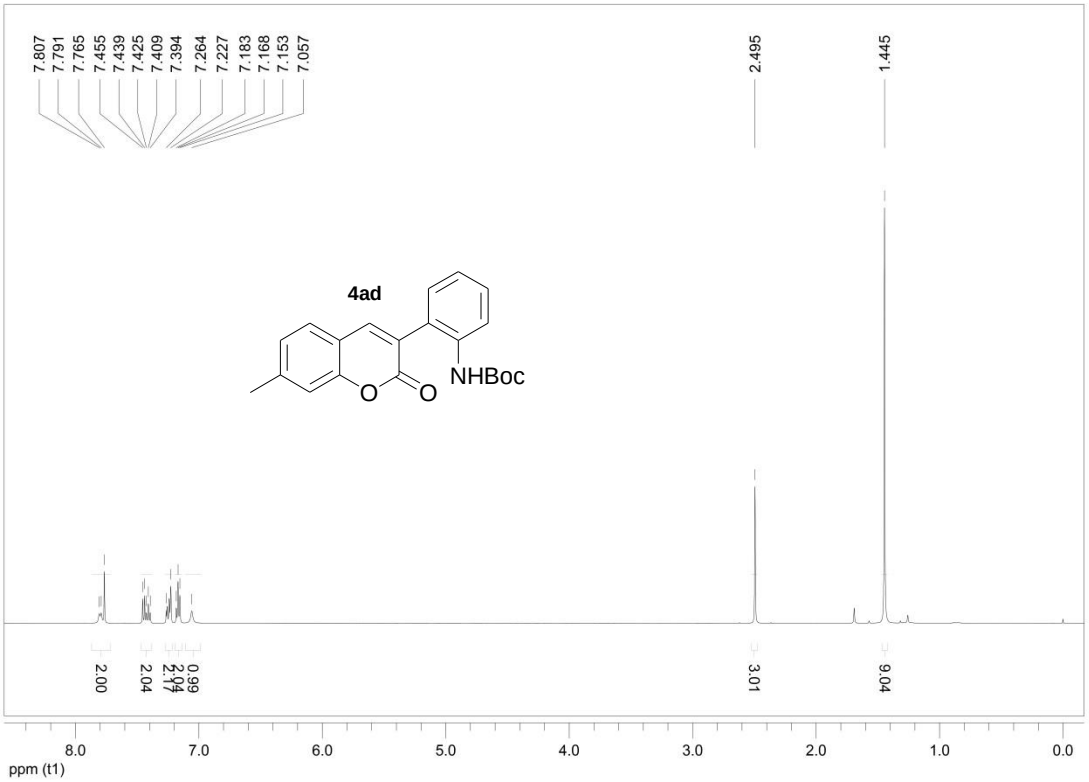


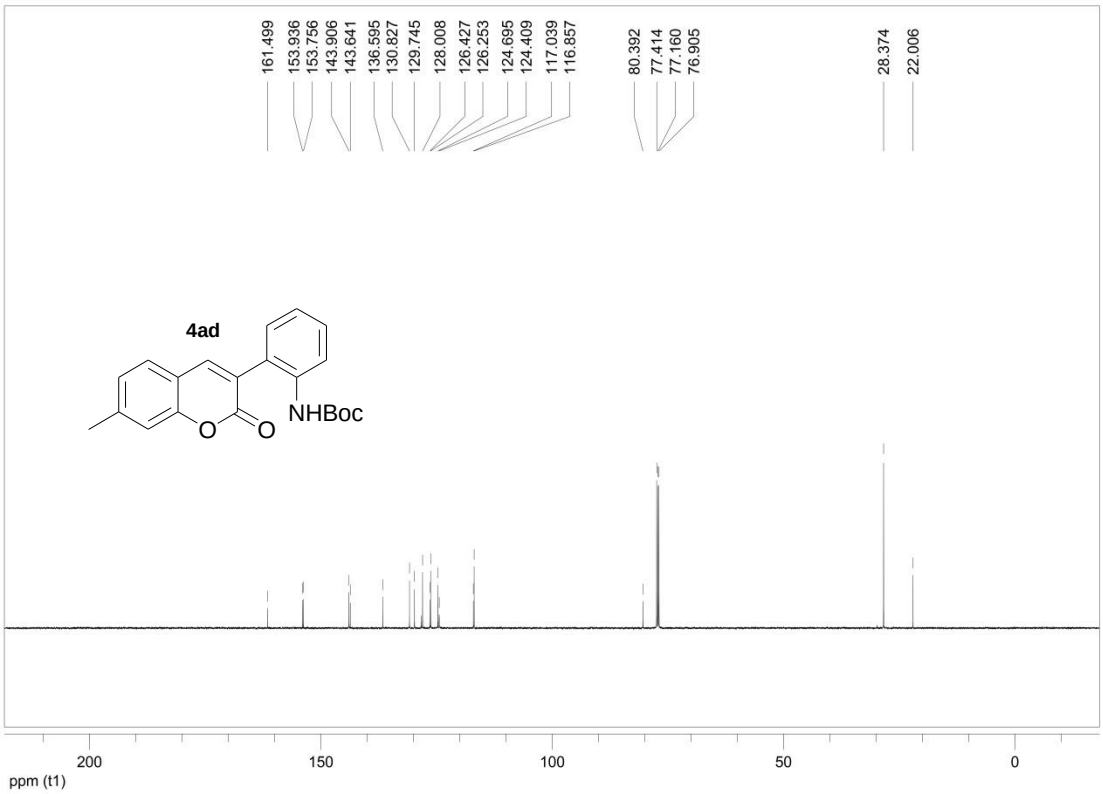

7.820
7.785
7.444
7.393
7.259
7.228
7.187
7.172
7.157
7.092
2.527
1.452
4ab
NHBoc
O
O
1.98
3.00
2.17
2.12
0.92
3.01
9.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

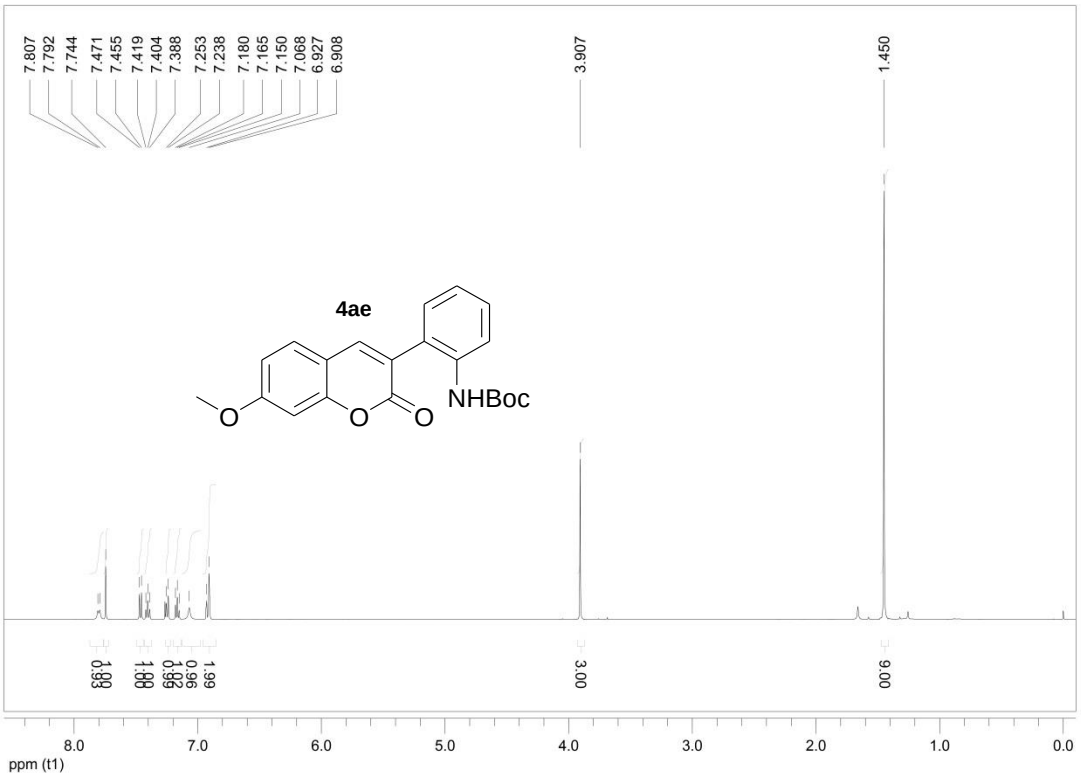

161.425
153.749
152.187
144.273
136.636
133.464
130.847
129.805
128.222
127.351
126.266
126.045
124.687
124.608
124.405
119.142
80.415
77.414
77.160
76.905
28.383
15.556
4ab
NHBoc
O
O
200
150
100
50
0
ppm (t1)

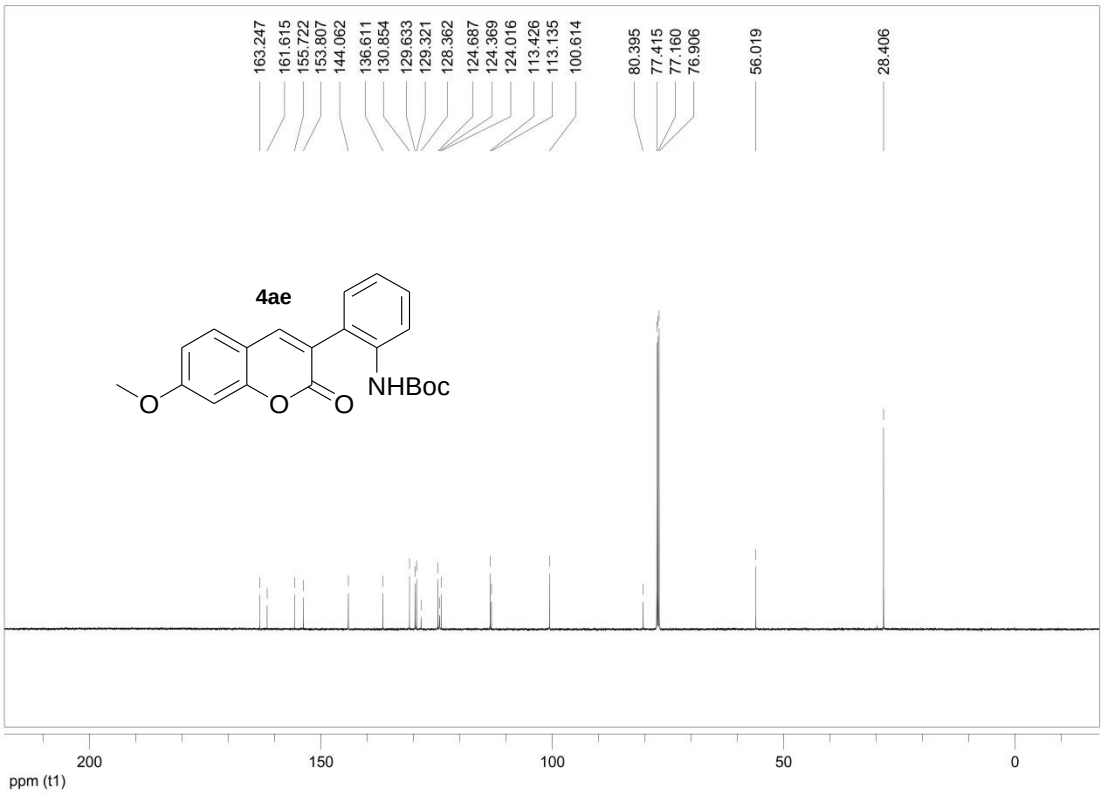

7.806
7.789
7.437
7.421
7.406
7.296
7.253
7.191
7.129
7.073
4.011
1.447
4ac
NHBoc
O
O
O
1.95
1.00
2.79
3.05
0.86
3.01
9.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

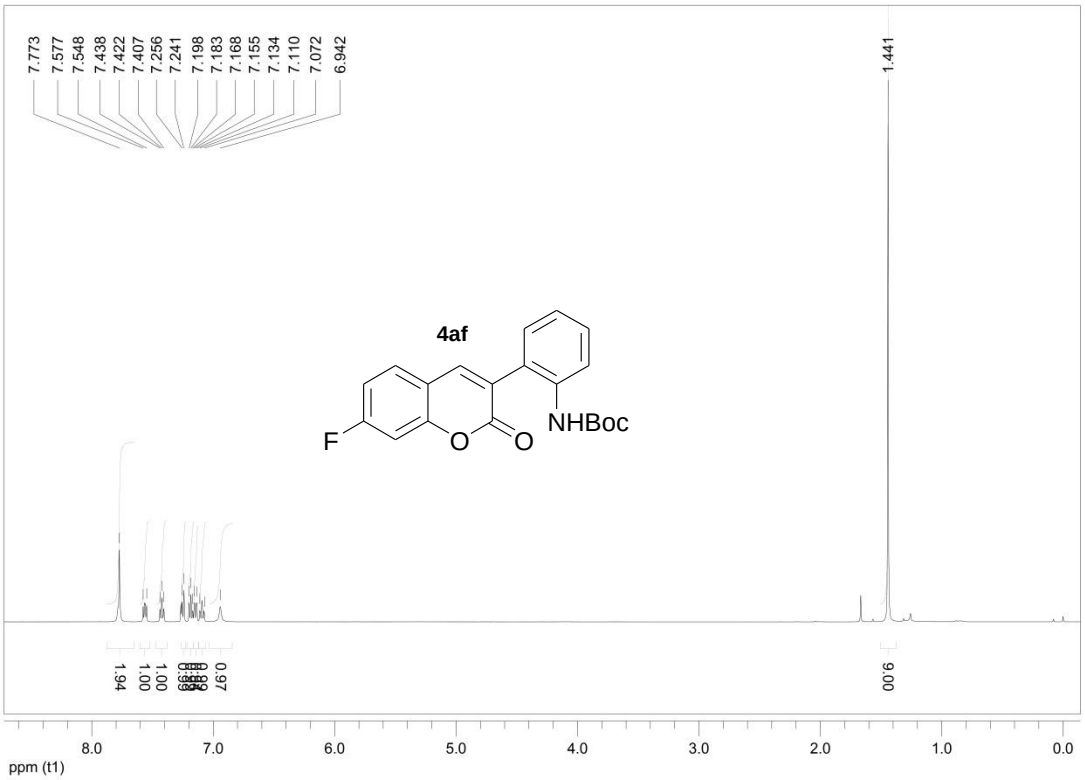

160.790
153.831
147.236
144.035
143.479
136.679
130.842
129.941
128.234
128.191
124.961
124.761
124.602
120.087
119.663
113.760
80.444
77.414
77.160
76.906
56.409
28.415
4ac
NHBoc
O
O
O
200
150
100
50
0
ppm (t1)

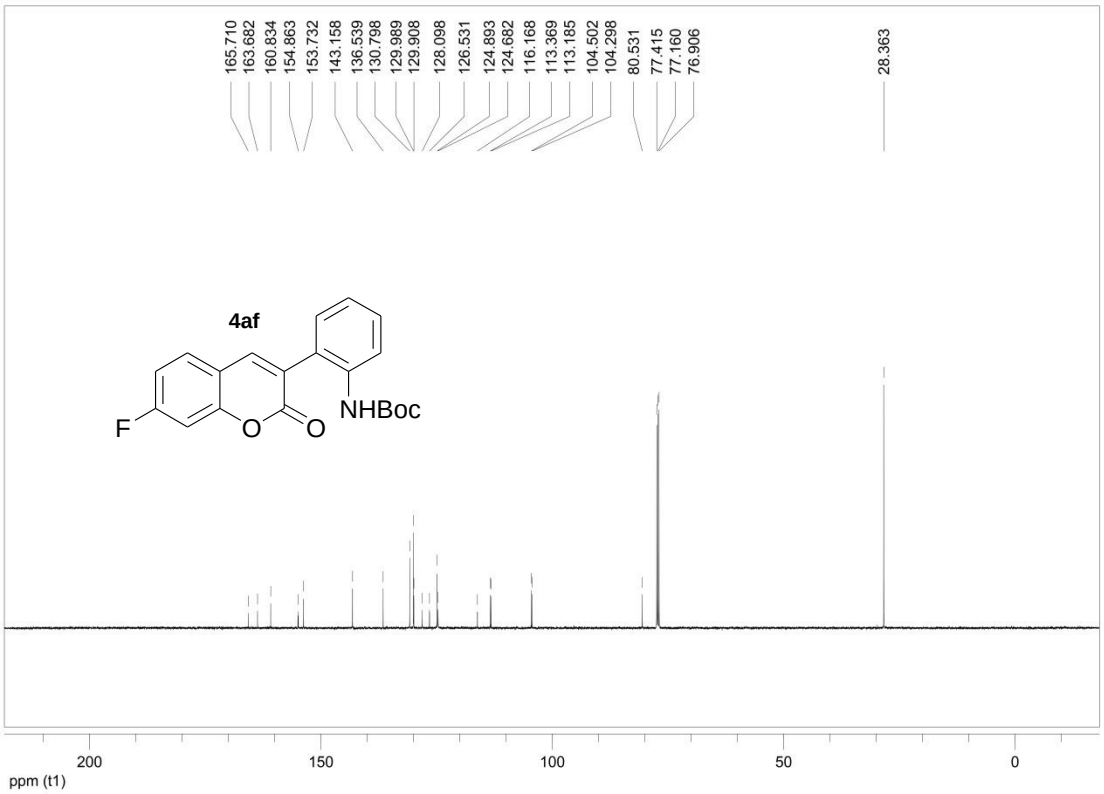

7.807
7.791
7.765
7.455
7.439
7.425
7.409
7.394
7.264
7.227
7.183
7.168
7.153
7.057
2.495
1.445
4ad
NHBoc
O
O
2.00
2.04
2.17
2.04
0.99
3.01
9.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


161.499
153.936
153.756
143.906
143.641
136.595
130.827
129.745
128.008
126.427
126.253
124.695
124.409
117.039
116.857
80.392
77.414
77.160
76.905
28.374
22.006
4ad
NHBoc
O
O
200
150
100
50
0
ppm (t1)

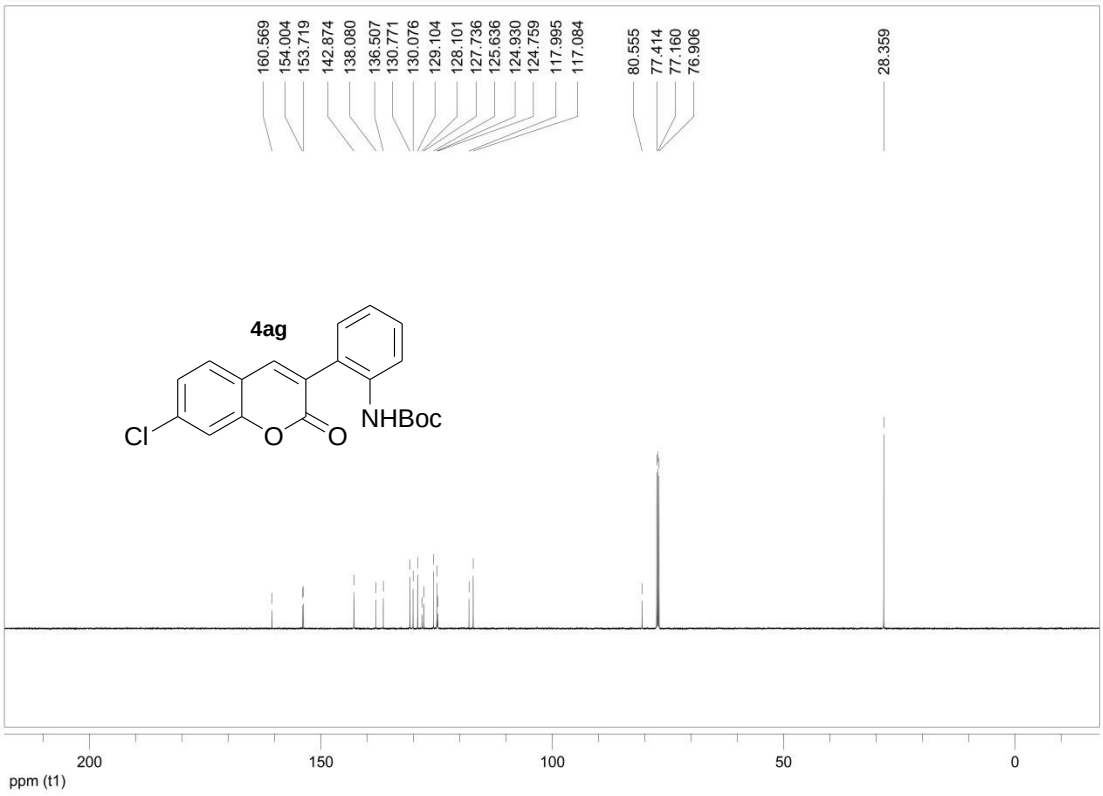

7.807
7.792
7.744
7.471
7.455
7.419
7.404
7.388
7.253
7.238
7.180
7.165
7.150
7.068
6.927
6.908
3.907
1.450
4ae
NHBoc
O
O
O
0.99
1.00
1.00
0.99
0.96
1.69
3.00
9.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

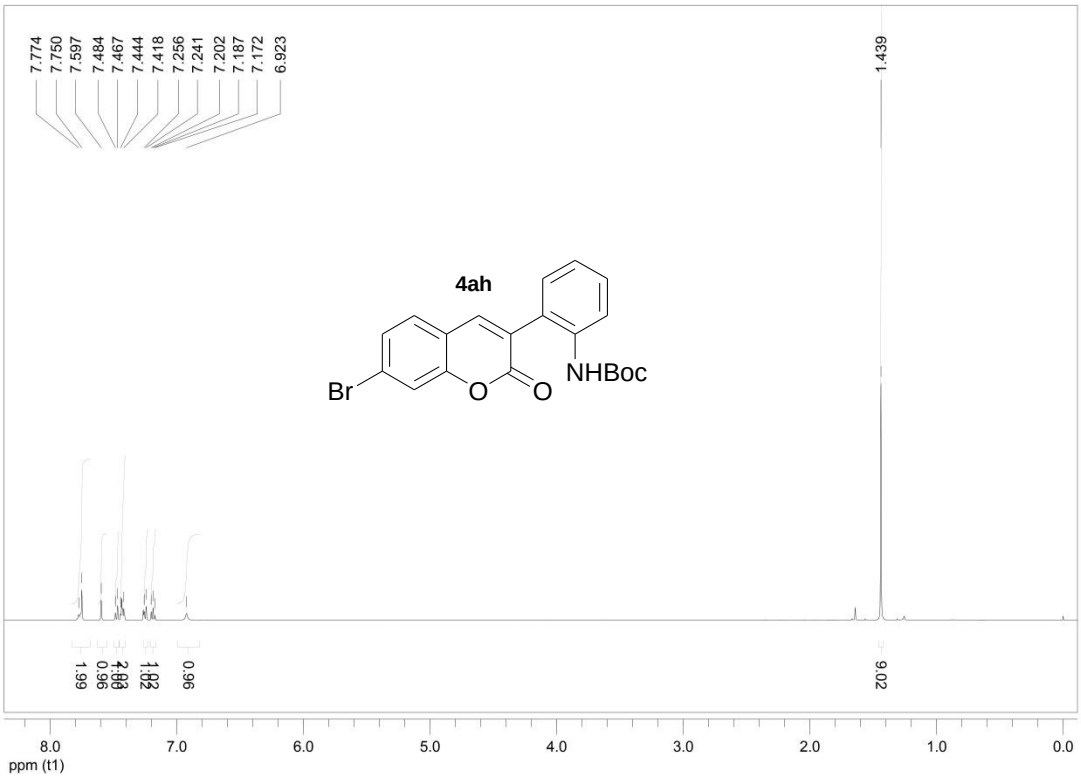

163.247
161.615
155.722
153.807
144.062
136.611
130.854
129.633
129.321
128.362
124.687
124.369
124.016
113.426
113.135
100.614
80.395
77.415
77.160
76.906
56.019
28.406
4ae
NHBoc
O
O
O
200
150
100
50
0
ppm (t1)

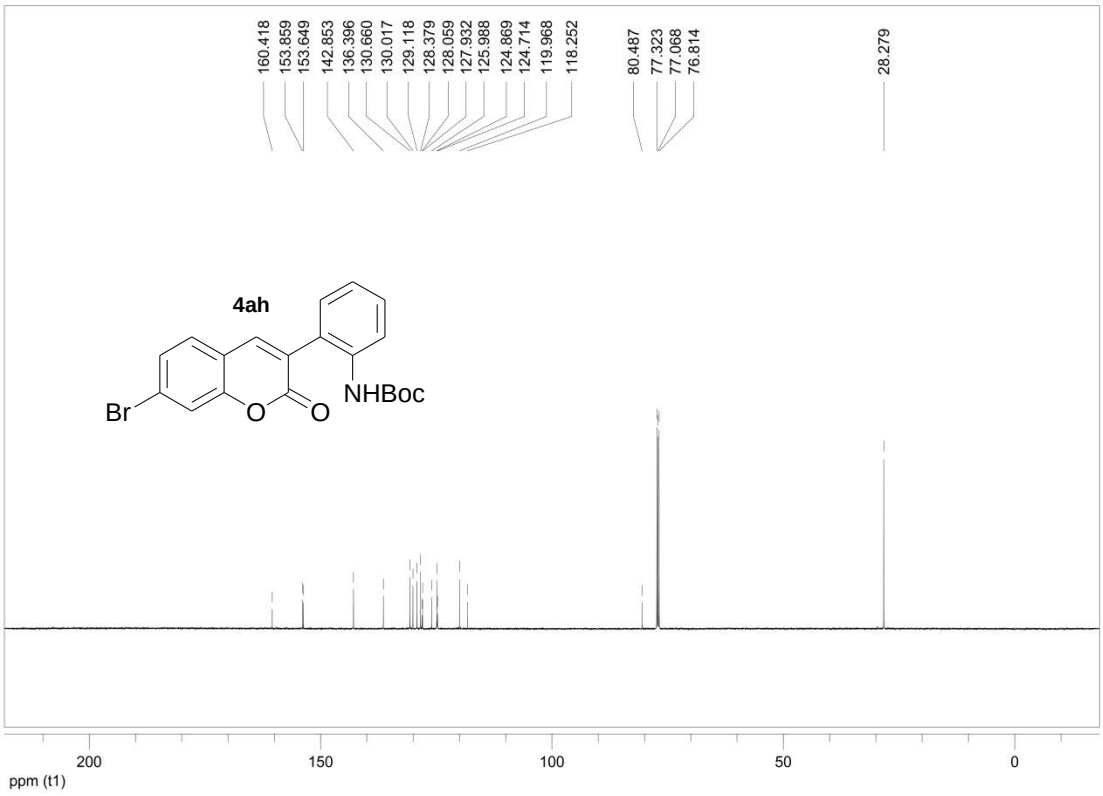

7.773
7.577
7.548
7.438
7.422
7.407
7.256
7.241
7.198
7.183
7.168
7.155
7.134
7.110
7.072
6.942
1.441
4af
F
O
O
NHBoc
1.94
1.00
1.00
0.97
9.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

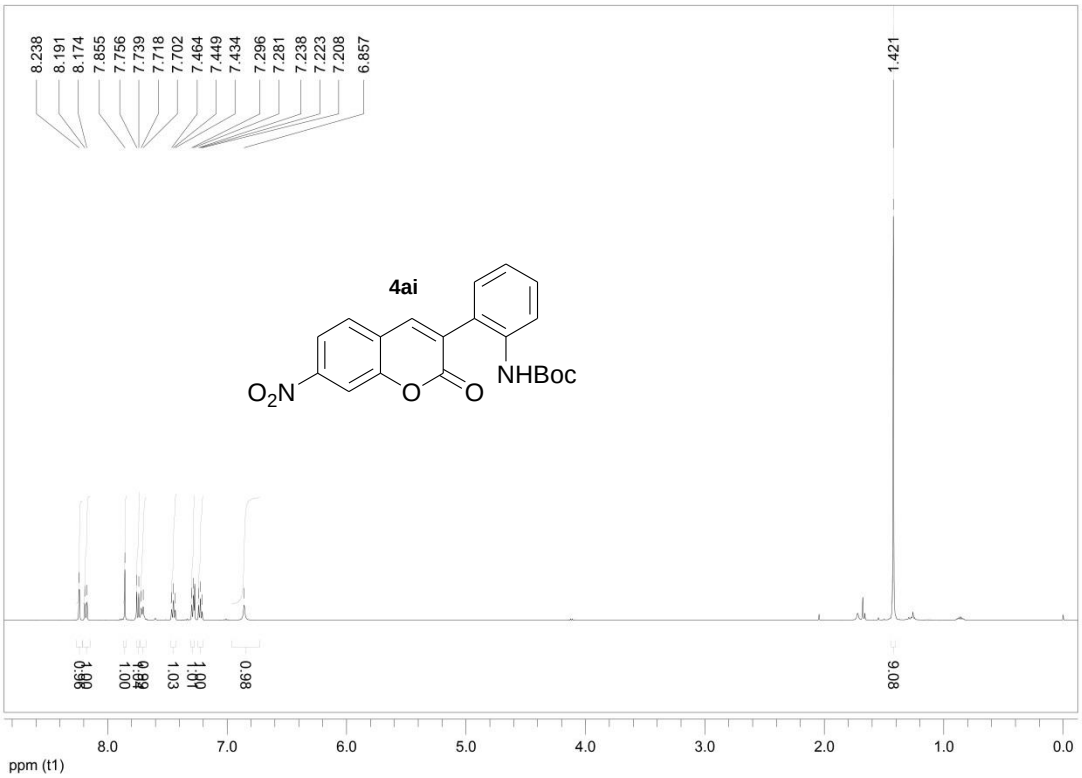

165.710
163.682
160.834
154.863
153.732
143.158
136.539
130.798
129.989
129.908
128.098
126.531
124.893
124.682
116.168
113.369
113.185
104.502
104.298
80.531
77.415
77.160
76.906
28.363
4af
F
O
O
NHBoc
200
150
100
50
0
ppm (t1)

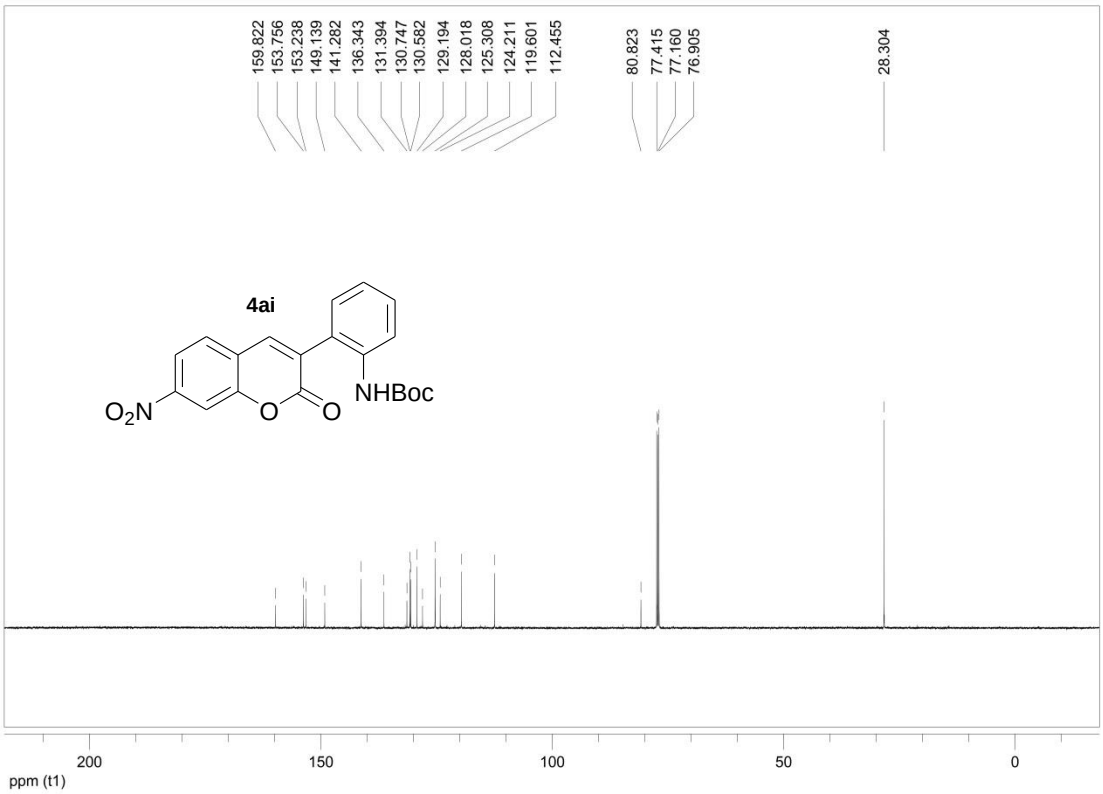

7.776
7.758
7.507
7.490
7.440
7.410
7.331
7.314
7.255
7.240
7.200
7.185
7.170
6.930
1.439
4ag
Cl
O
O
NHBoc
2.01
0.96
9.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

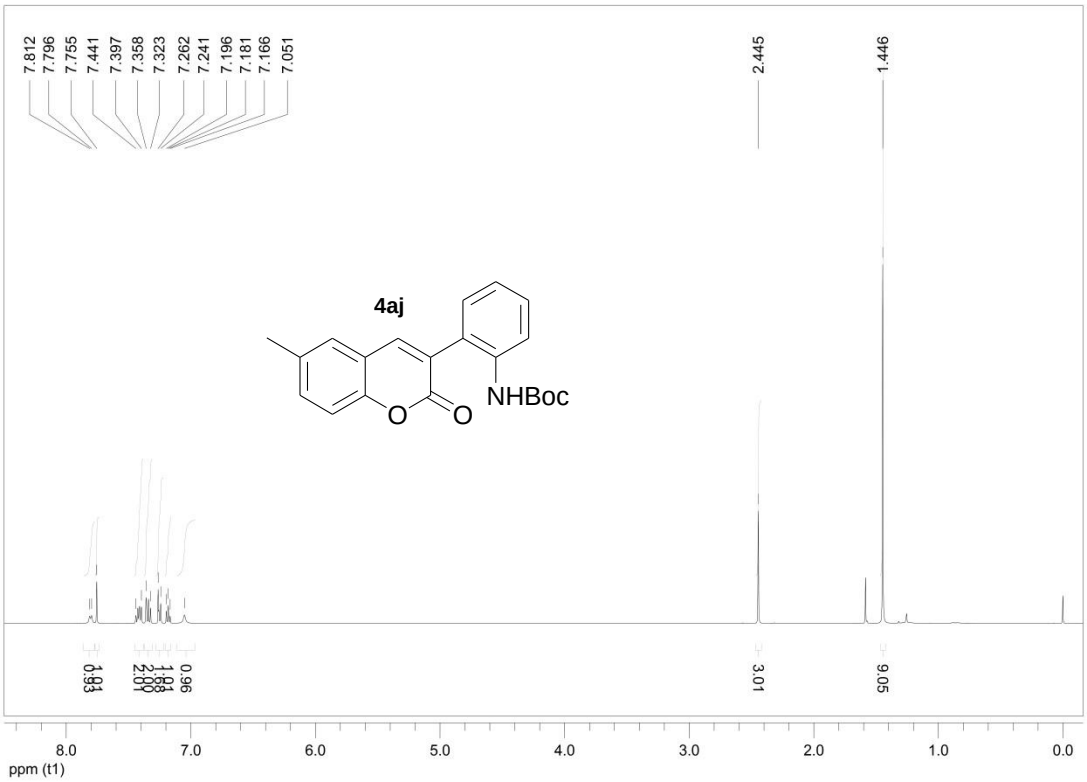

160.569
154.004
153.719
142.874
138.080
136.507
130.771
130.076
129.104
128.101
127.736
125.636
124.930
124.759
117.995
117.084
80.555
77.414
77.160
76.906
28.359
4ag
Cl
O
O
NHBoc
200
150
100
50
0
ppm (t1)

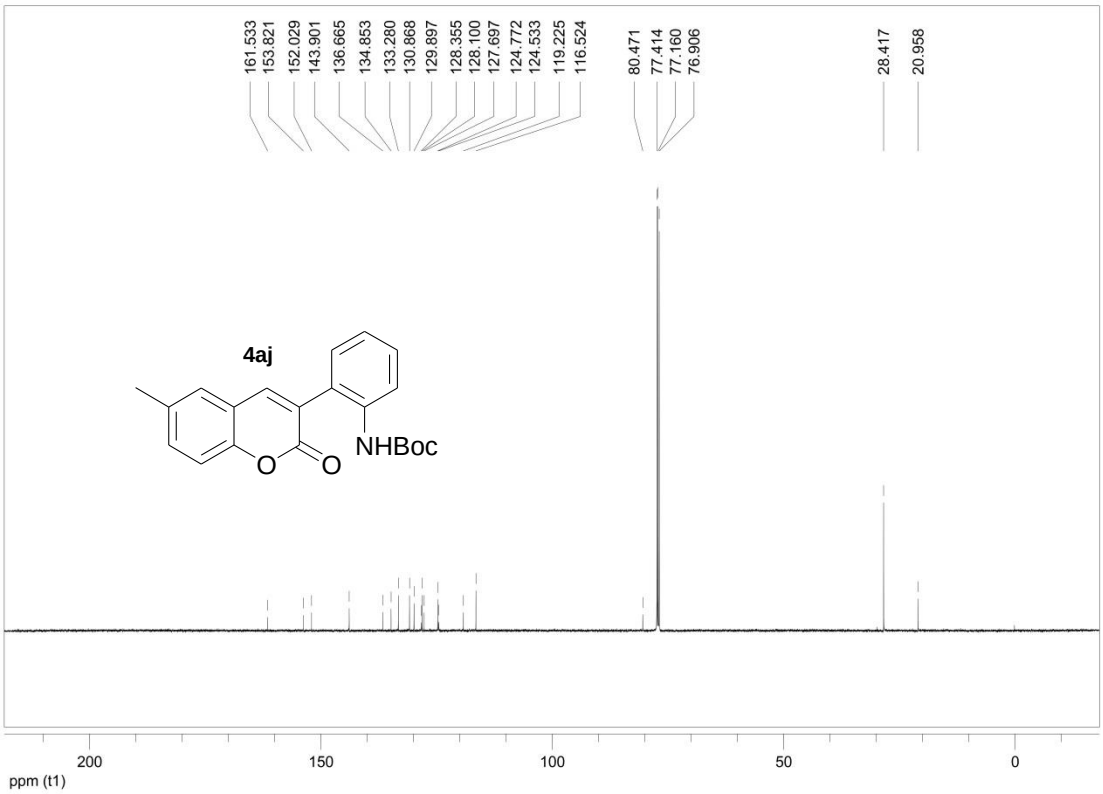

7.774
7.750
7.597
7.484
7.467
7.444
7.418
7.256
7.241
7.202
7.187
7.172
6.923
1.439
4ah
Br
O
O
NHBoc
1.99
0.96
2.12
1.02
0.96
9.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

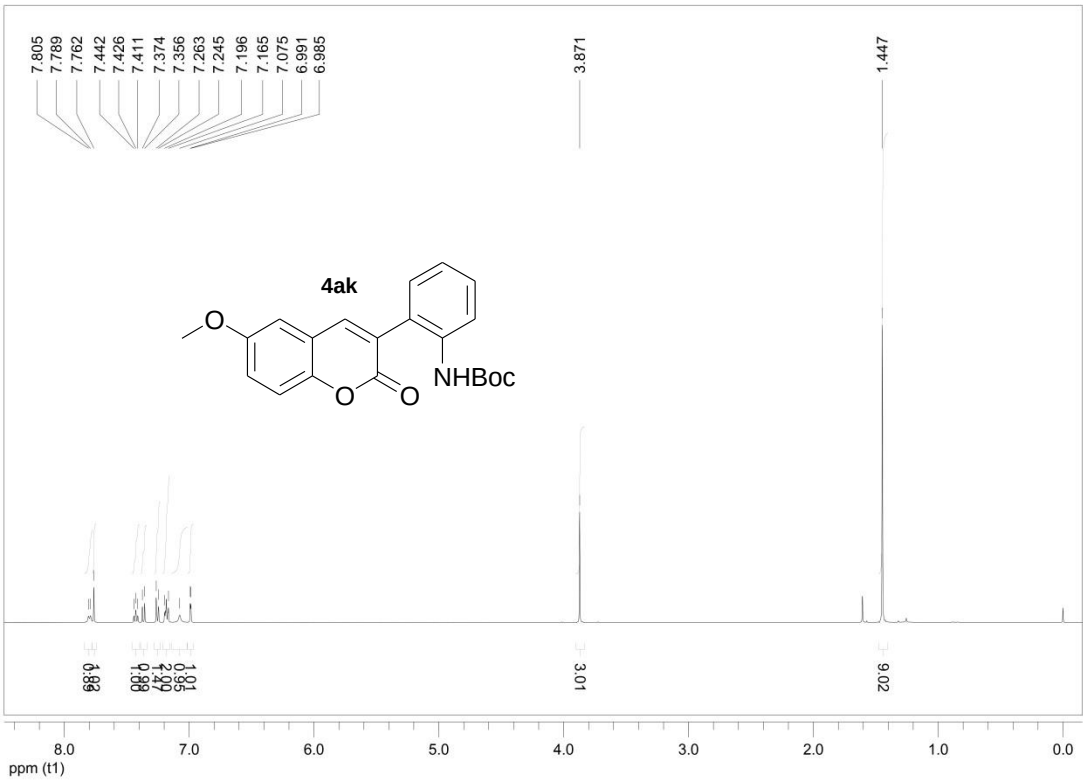

160.418
153.859
153.649
142.853
136.396
130.660
130.017
129.118
128.379
128.059
127.932
125.988
124.869
124.714
119.968
118.252
80.487
77.323
77.068
76.814
28.279
4ah
Br
O
O
NHBoc
200
150
100
50
0
ppm (t1)

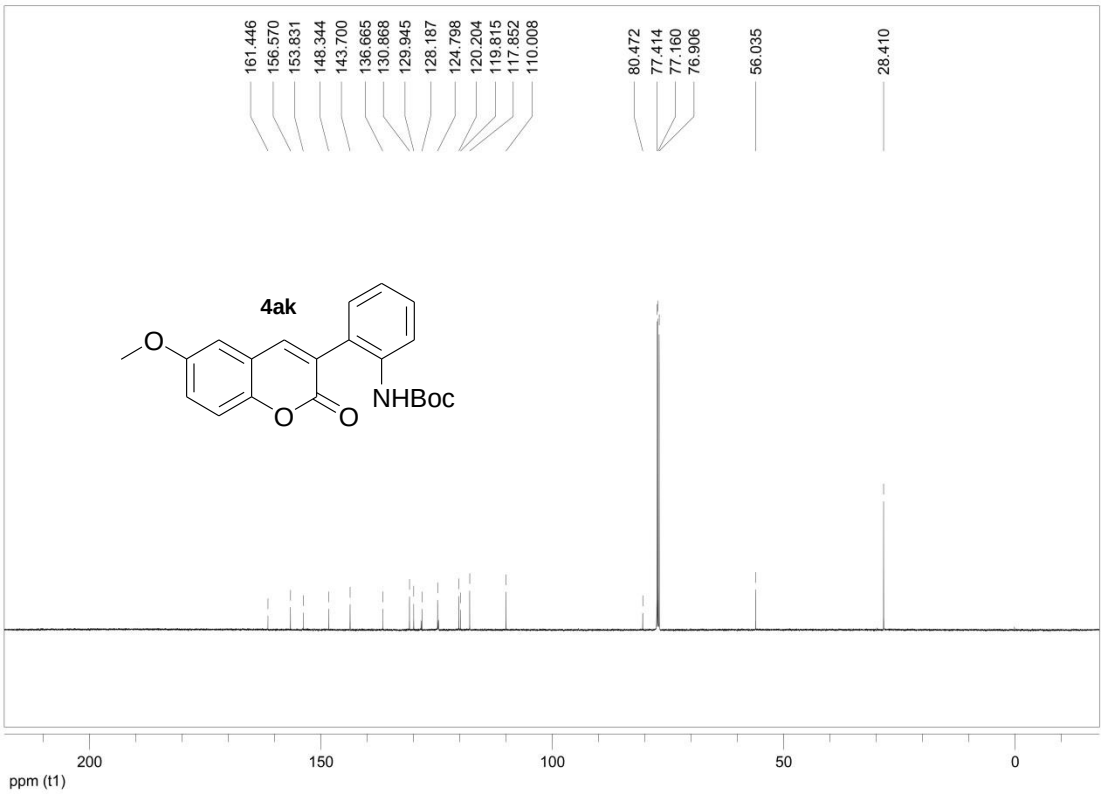

8.238
8.191
8.174
7.855
7.756
7.739
7.718
7.702
7.464
7.449
7.434
7.296
7.281
7.238
7.223
7.208
6.857
1.421
4ai
O2N
O
O
NHBoc
0.98
9.08
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

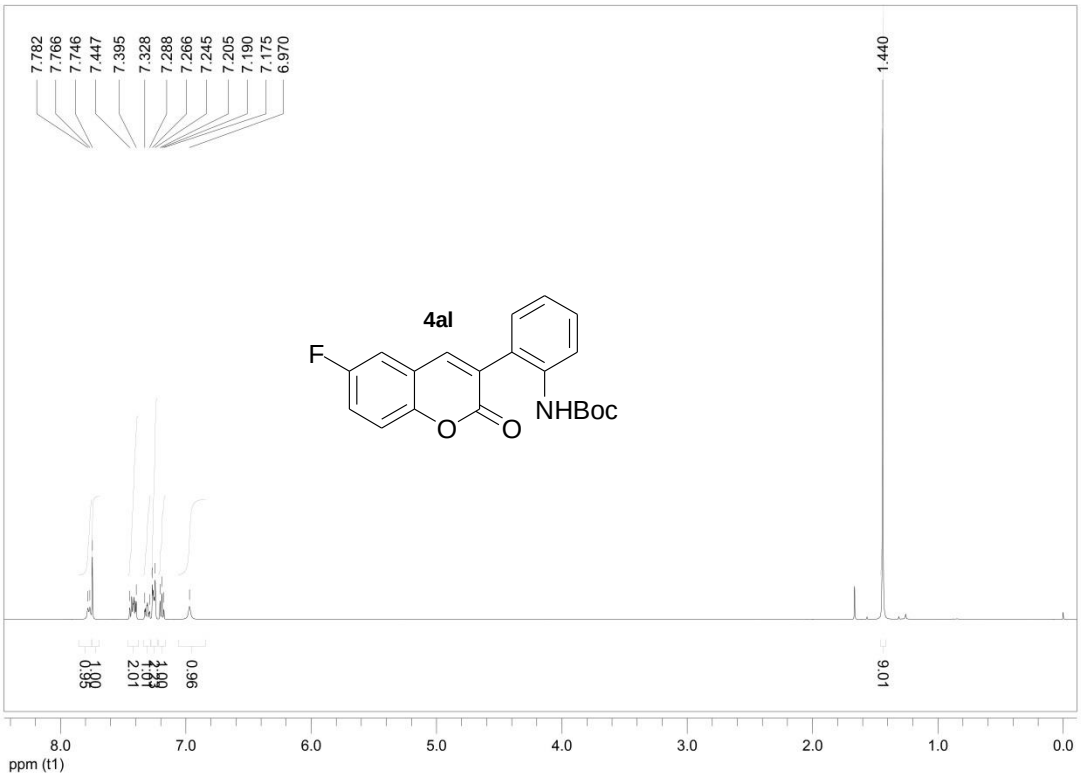

159.822
153.756
153.238
149.139
141.282
136.343
131.394
130.747
130.582
129.194
128.018
125.308
124.211
119.601
112.455
80.823
77.415
77.160
76.905
28.304
4ai
O2N
O
O
NHBoc
200
150
100
50
0
ppm (t1)

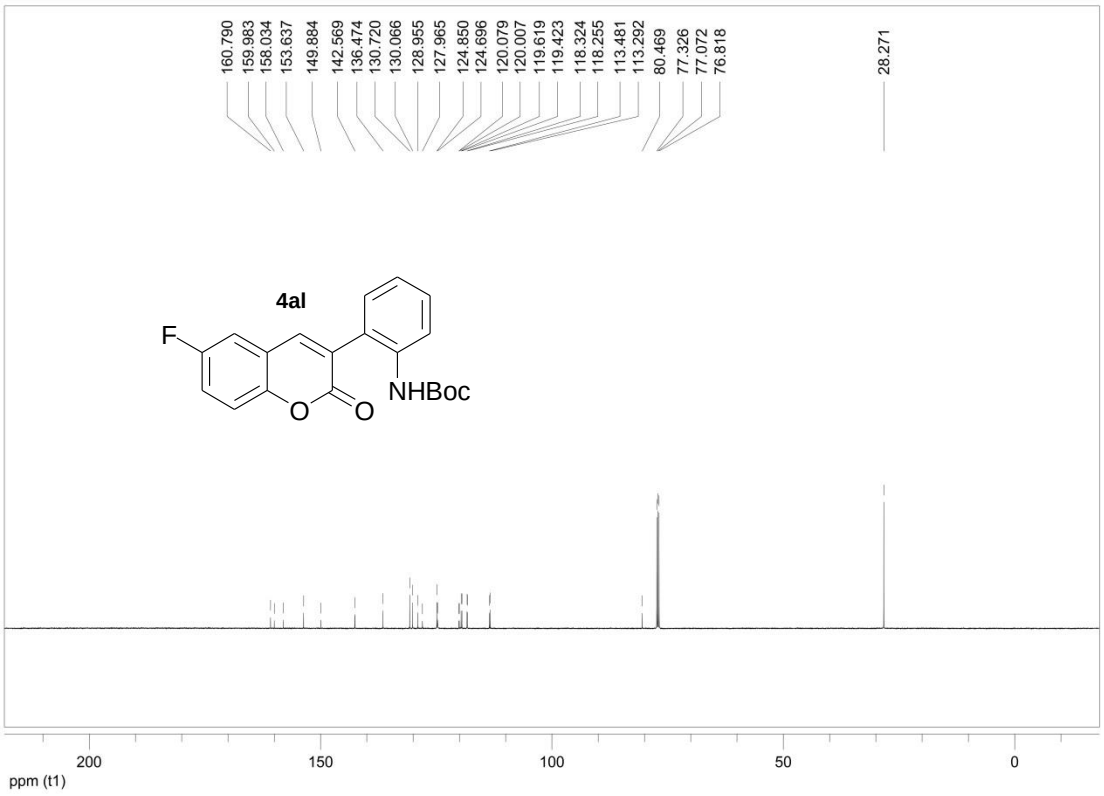

7.812
7.796
7.755
7.441
7.397
7.358
7.323
7.262
7.241
7.196
7.181
7.166
7.051
2.445
1.446
4aj
NHBoc
O
O
0.96
3.01
9.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

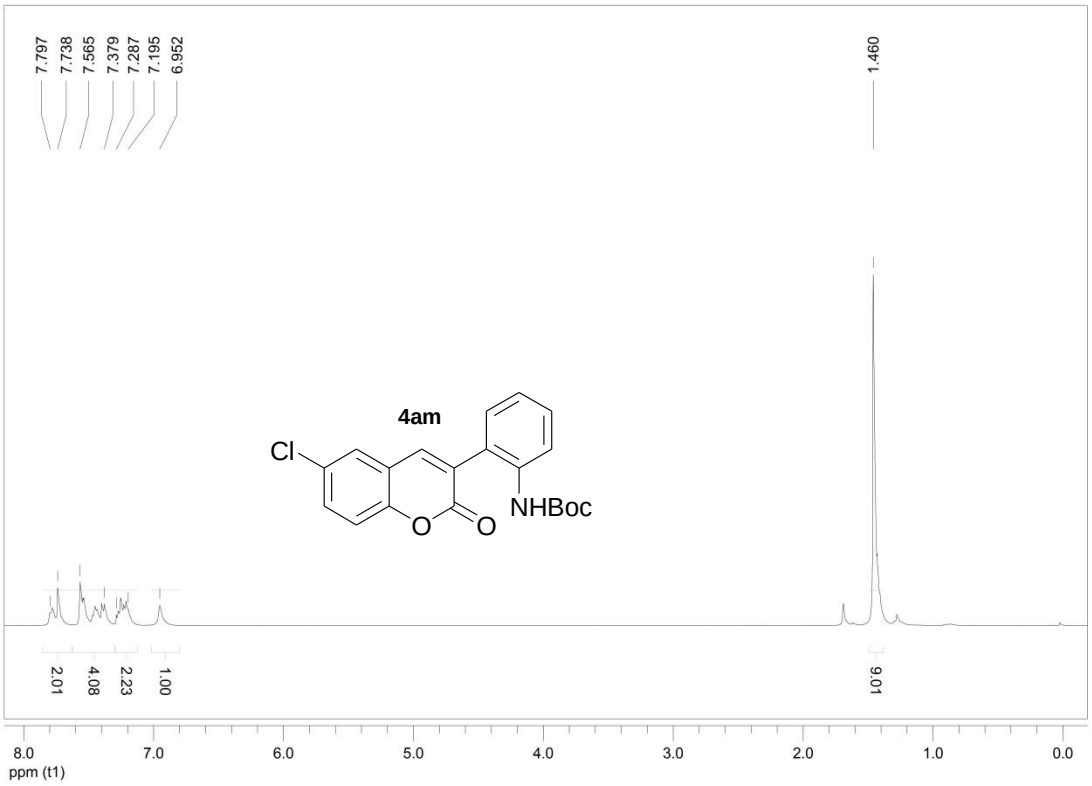

161.533
153.821
152.029
143.901
136.665
134.853
133.280
130.868
129.897
128.355
128.100
127.697
124.772
124.533
119.225
116.524
80.471
77.414
77.160
76.906
28.417
20.958
4aj
NHBoc
O
O
200
150
100
50
0
ppm (t1)

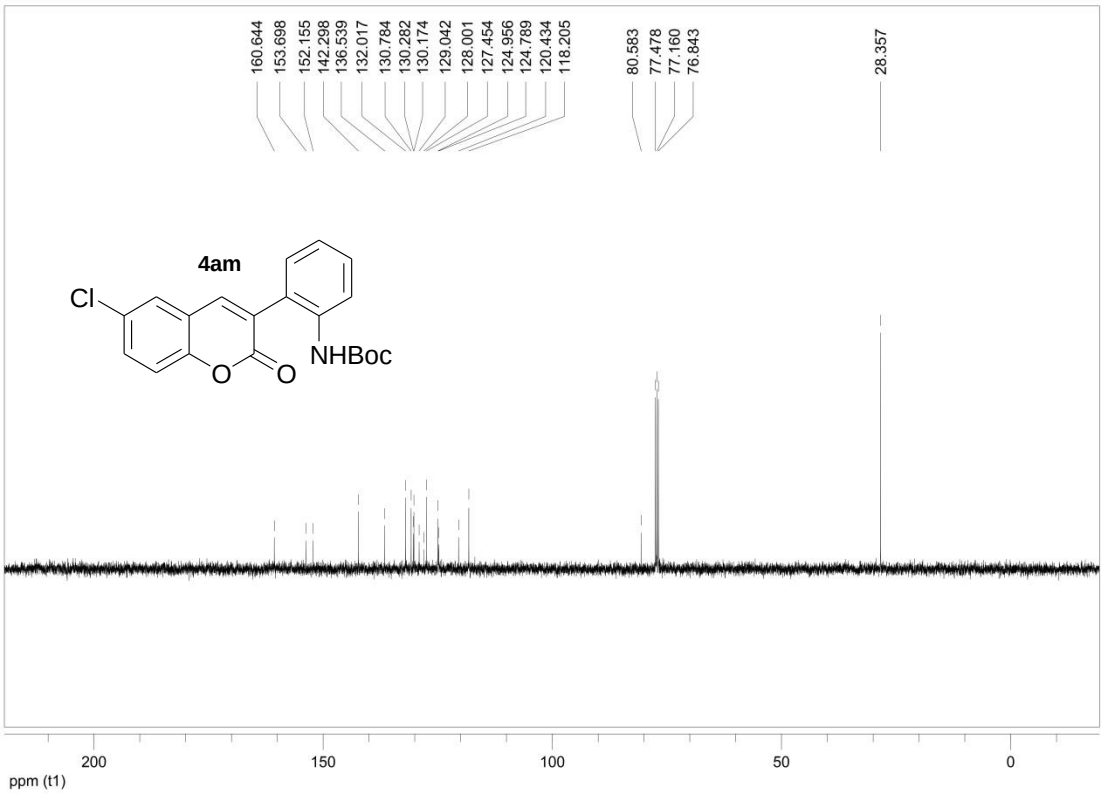

7.805
7.789
7.762
7.442
7.426
7.411
7.374
7.356
7.263
7.245
7.196
7.165
7.075
6.991
6.985
3.871
1.447
4ak
O
NHBoc
O
O
0.88
1.00
0.96
1.01
3.01
9.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

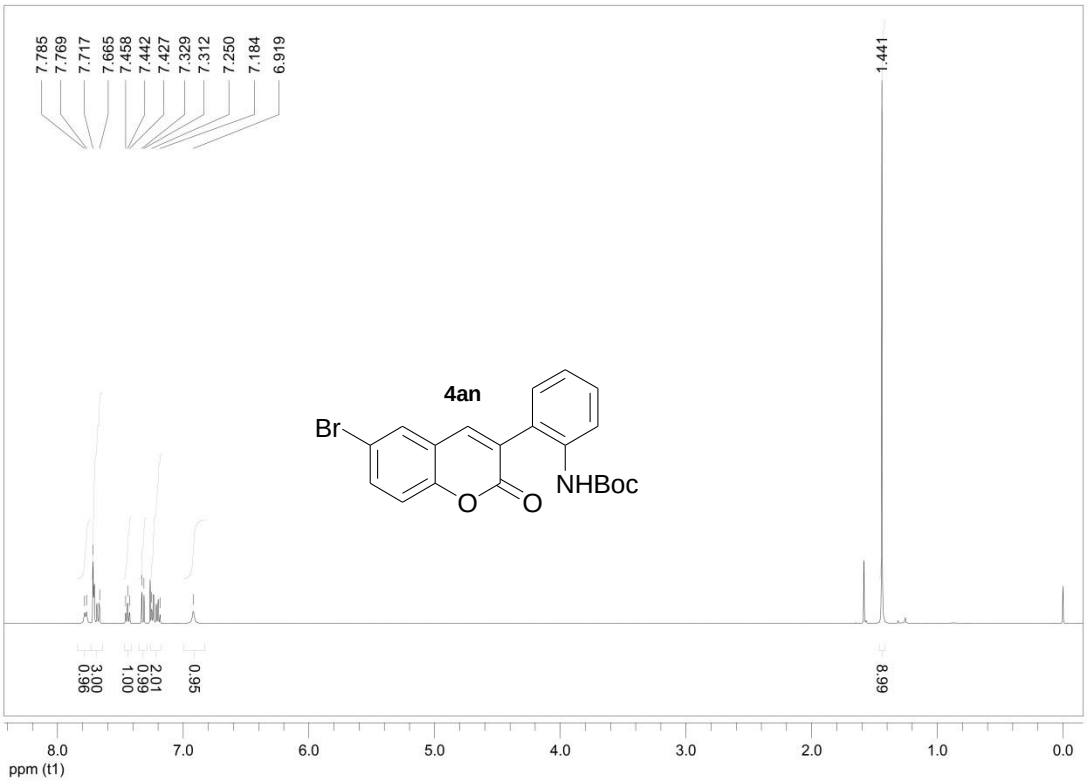

161.446
156.570
153.831
148.344
143.700
136.665
130.868
129.945
128.187
124.798
120.204
119.815
117.852
110.008
80.472
77.414
77.160
76.906
56.035
28.410
4ak
O
NHBoc
O
O
200
150
100
50
0
ppm (t1)

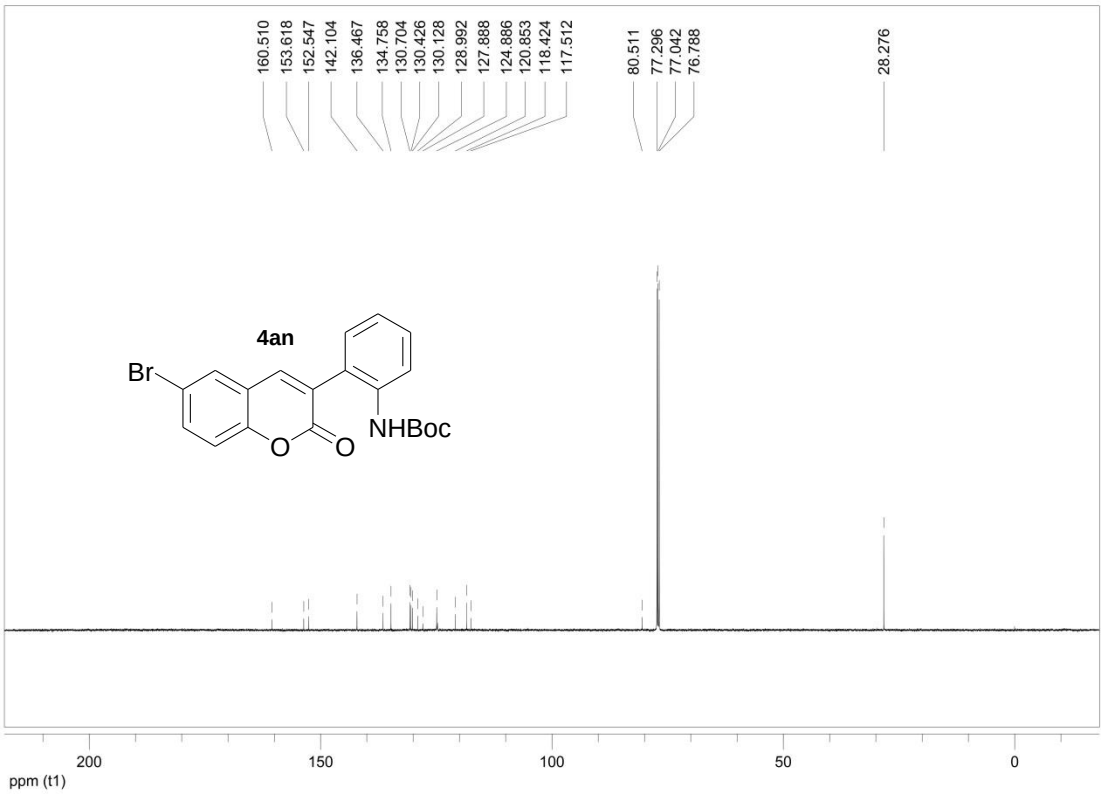

7.782
7.766
7.746
7.447
7.395
7.328
7.288
7.266
7.245
7.205
7.190
7.175
6.970
1.440
4al
F
NHBoc
O
O
1.00
1.00
2.01
1.01
1.00
0.96
9.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

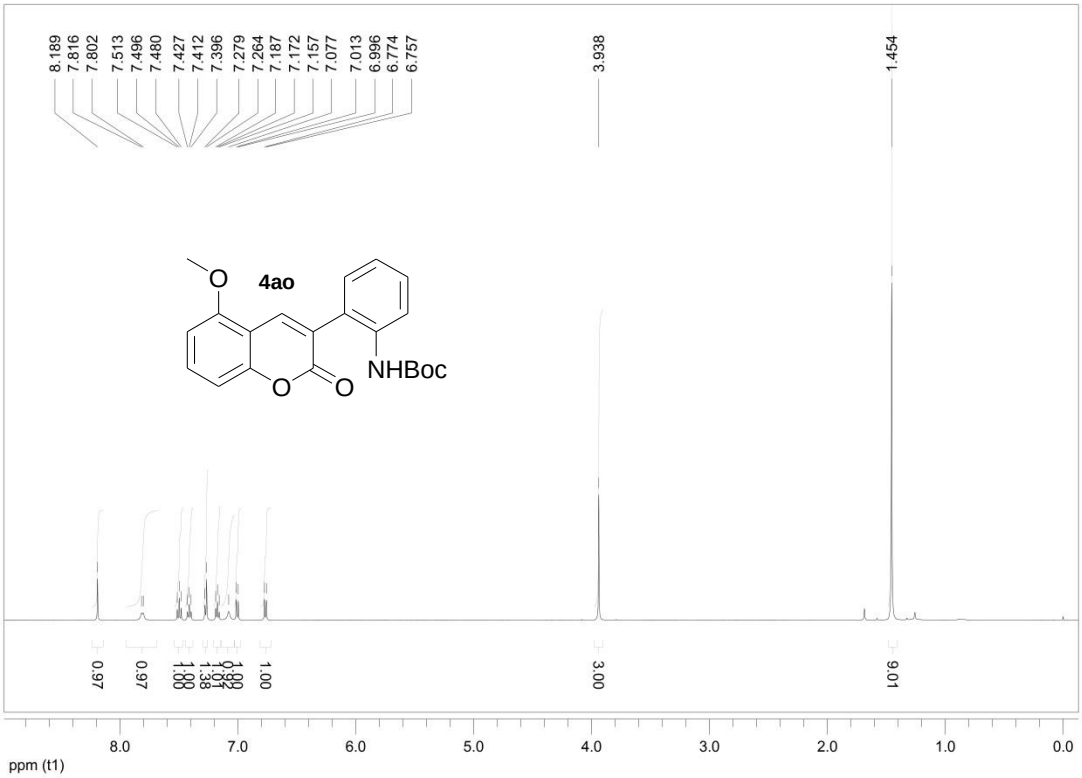

160.790
159.983
158.034
153.637
149.884
142.569
136.474
130.720
130.066
128.955
127.965
124.850
124.696
120.079
120.007
119.619
119.423
118.324
118.255
113.481
113.292
80.469
77.326
77.072
76.818
28.271
4al
F
NHBoc
O
O
200
150
100
50
0
ppm (t1)

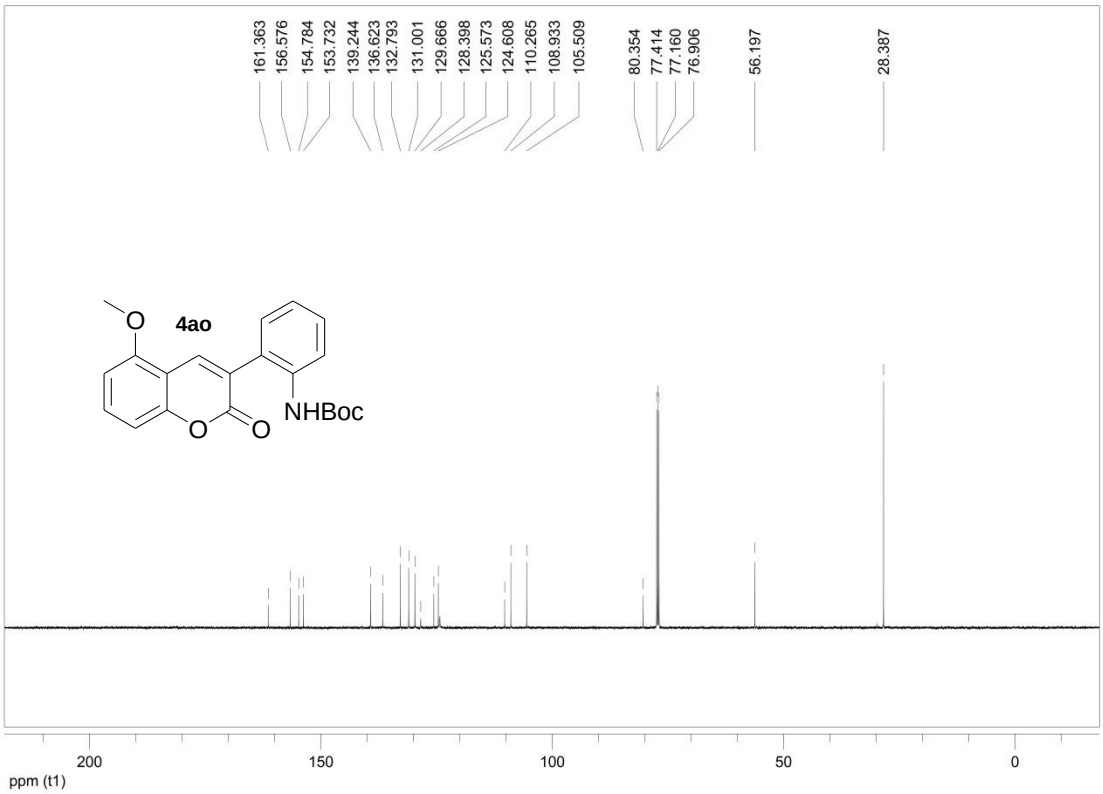

7.797
7.738
7.565
7.379
7.287
7.195
6.952
1.460
4am
Cl
NHBoc
O
O
2.01
4.08
2.23
1.00
9.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

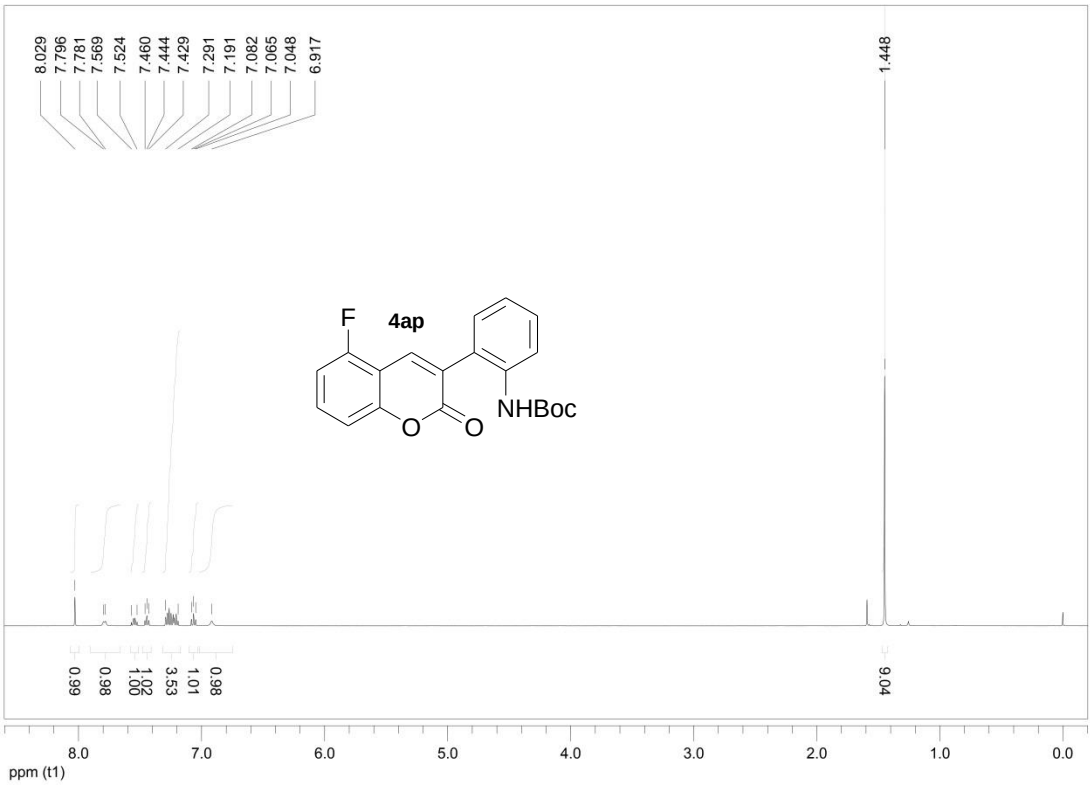

160.644
153.698
152.155
142.298
136.539
132.017
130.784
130.282
130.174
129.042
128.001
127.454
124.956
124.789
120.434
118.205
80.583
77.478
77.160
76.843
28.357
4am
Cl
NHBoc
O
O
200
150
100
50
0
ppm (t1)

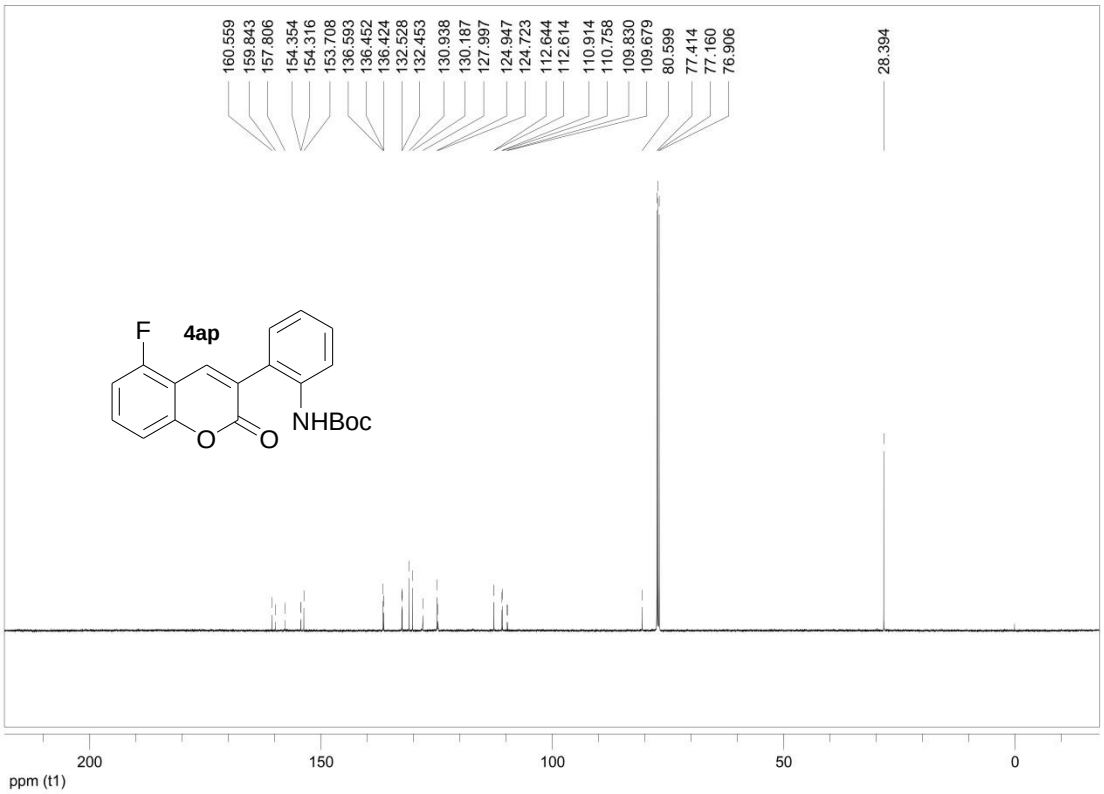

7.785
7.769
7.717
7.665
7.458
7.442
7.427
7.329
7.312
7.250
7.184
6.919
1.441
4an
Br
NHBoc
O
O
3.00
1.00
0.99
2.01
0.95
8.99
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

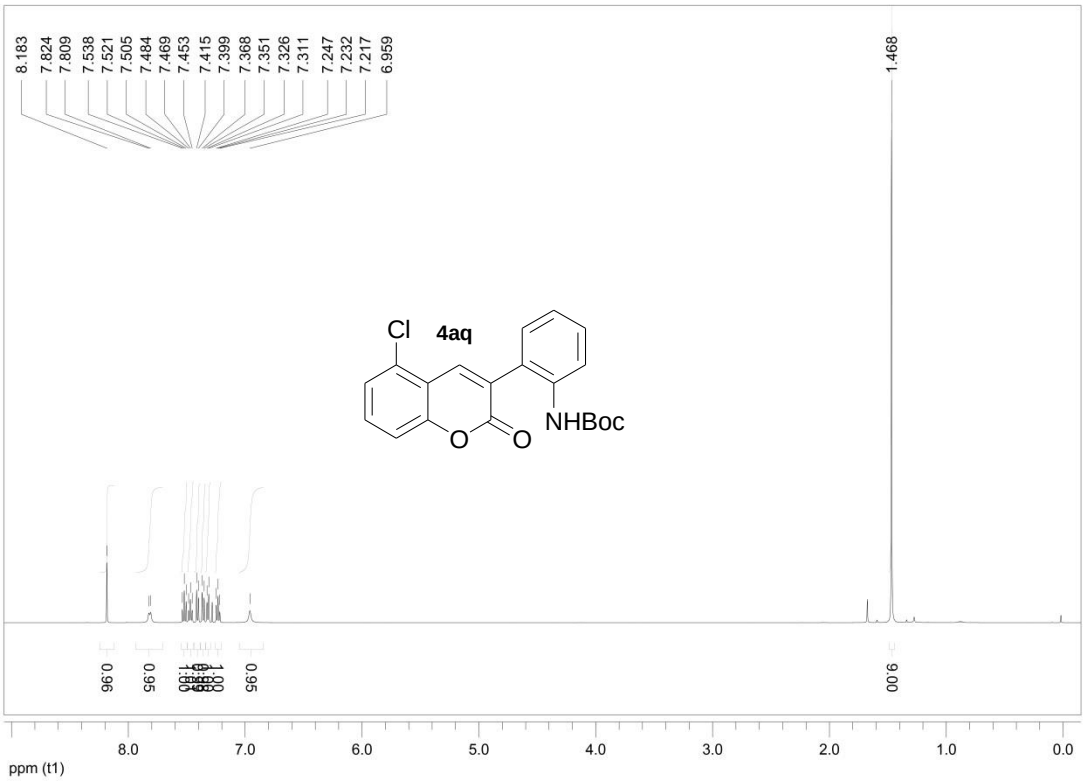

160.510
153.618
152.547
142.104
136.467
134.758
130.704
130.426
130.128
128.992
127.888
124.886
120.853
118.424
117.512
80.511
77.296
77.042
76.788
28.276
4an
Br
NHBoc
O
O
200
150
100
50
0
ppm (t1)

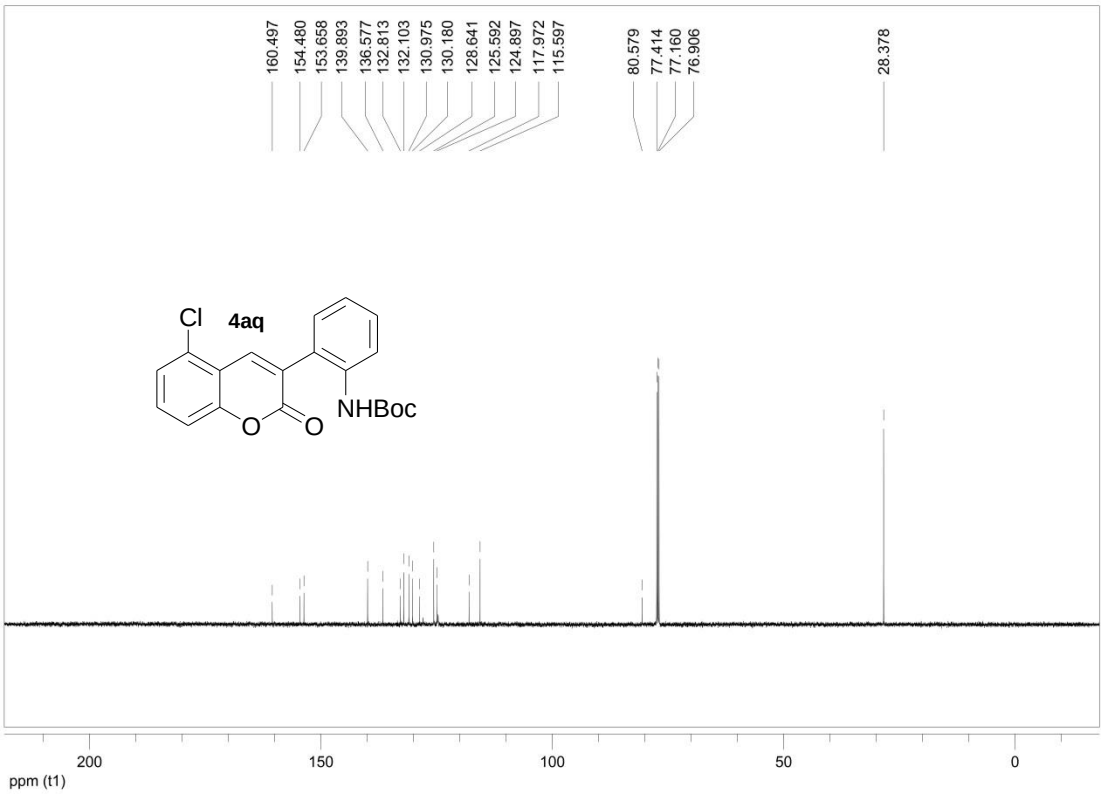

8.189
7.816
7.802
7.513
7.496
7.480
7.427
7.412
7.396
7.279
7.264
7.187
7.172
7.157
7.077
7.013
6.996
6.774
6.757
3.938
1.454
4ao
O
O
O
NHBoc
0.97
0.97
1.00
3.00
9.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

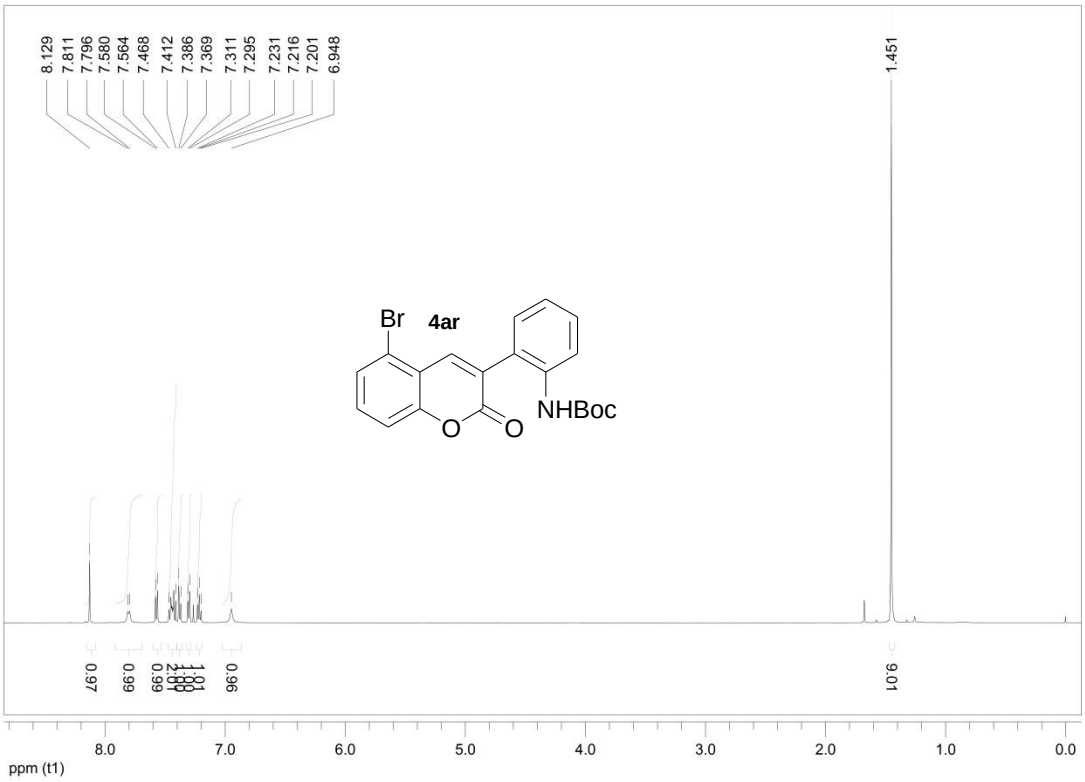

161.363
156.576
154.784
153.732
139.244
136.623
132.793
131.001
129.666
128.398
125.573
124.608
110.265
108.933
105.509
80.354
77.414
77.160
76.906
56.197
28.387
4ao
O
O
O
NHBoc
200
150
100
50
0
ppm (t1)

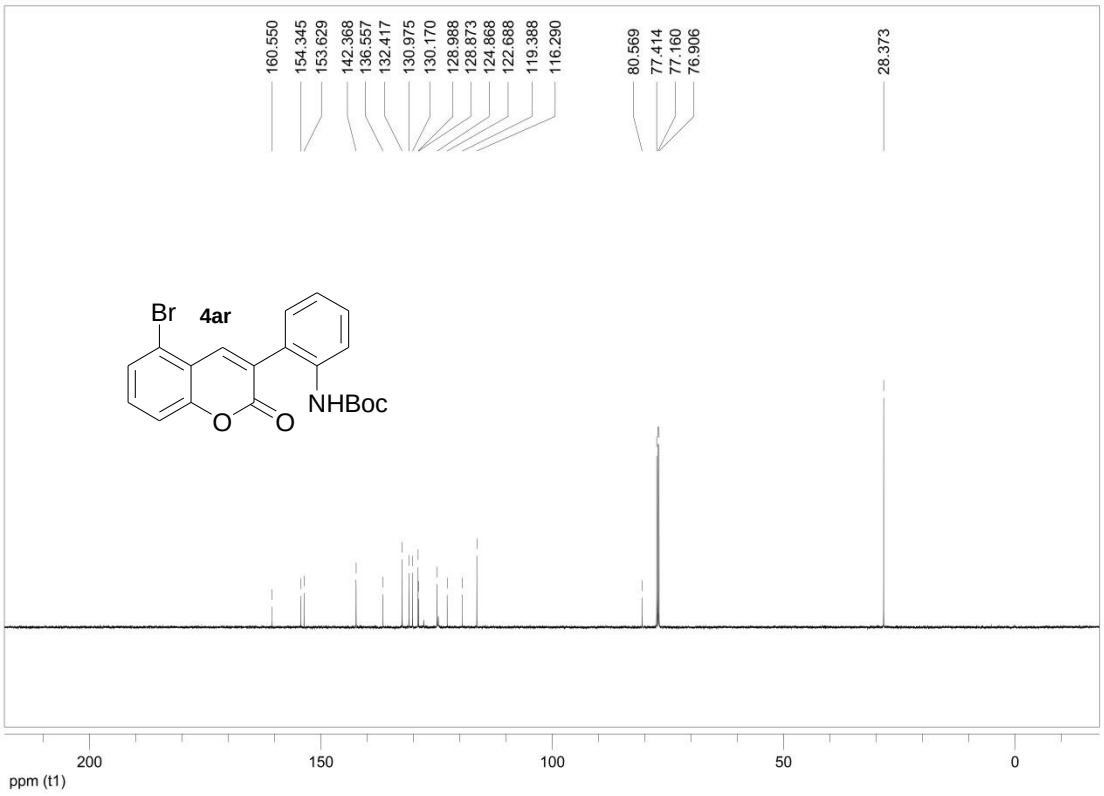

8.029
7.796
7.781
7.569
7.524
7.460
7.444
7.429
7.291
7.191
7.082
7.065
7.048
6.917
1.448
F
4ap
NHBoc
O
O
0.99
0.98
1.00
1.02
3.53
1.01
0.98
9.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

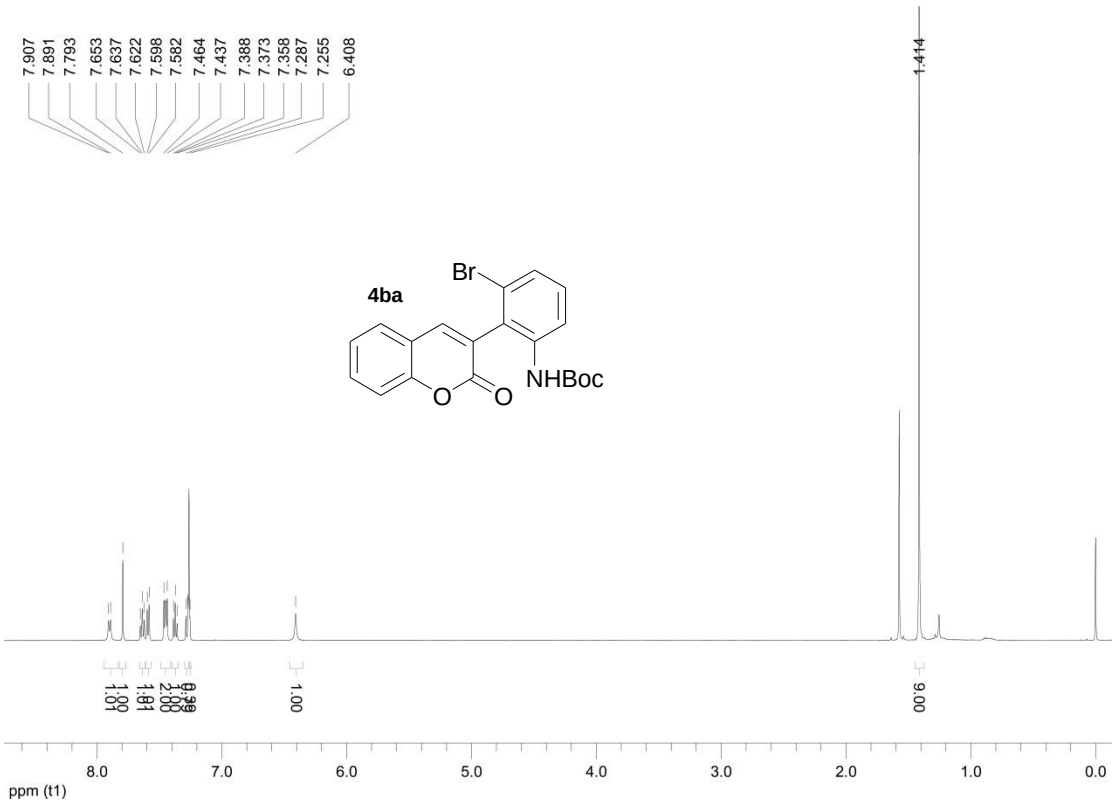

160.559
159.843
157.806
154.354
154.316
153.708
136.593
136.452
136.424
132.528
132.453
130.938
130.187
127.997
124.947
124.723
112.644
112.614
110.914
110.758
109.830
109.679
80.599
77.414
77.160
76.906
28.394
F
4ap
NHBoc
O
O
200
150
100
50
0
ppm (t1)

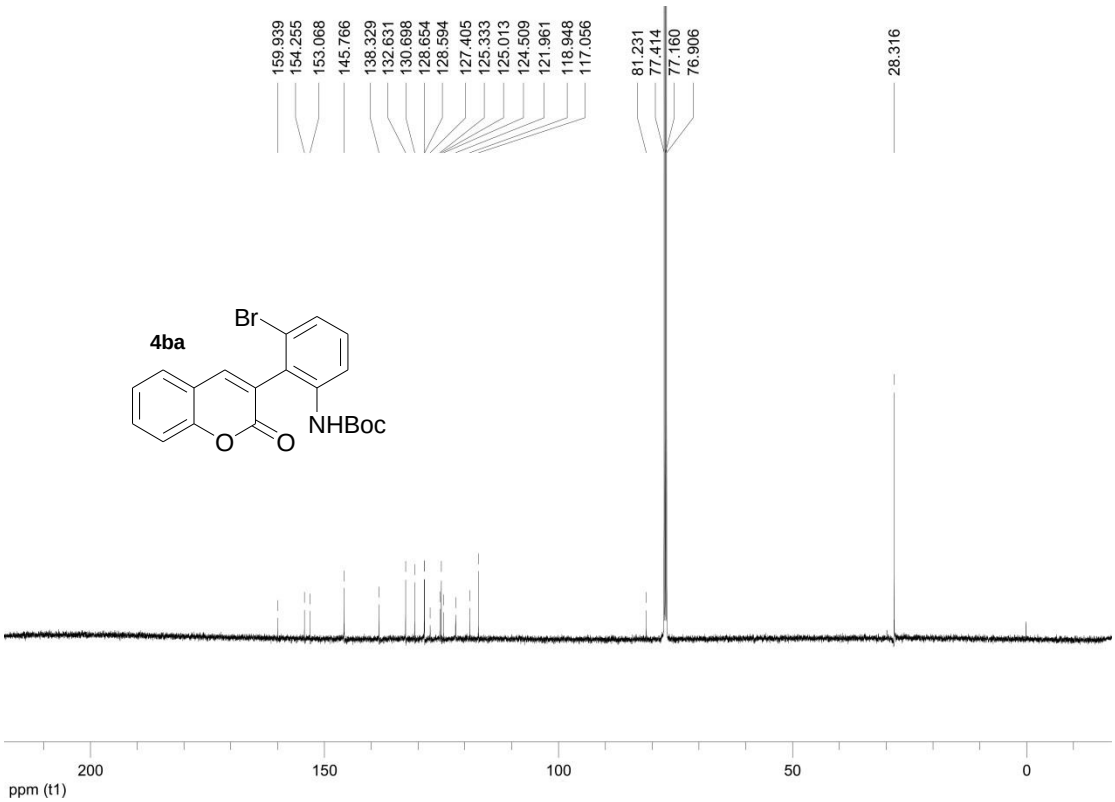

8.183
7.824
7.809
7.538
7.521
7.505
7.484
7.469
7.453
7.415
7.399
7.368
7.351
7.326
7.311
7.247
7.232
7.217
6.959
1.468
Cl
4aq
NHBoc
O
O
0.96
0.95
0.95
9.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

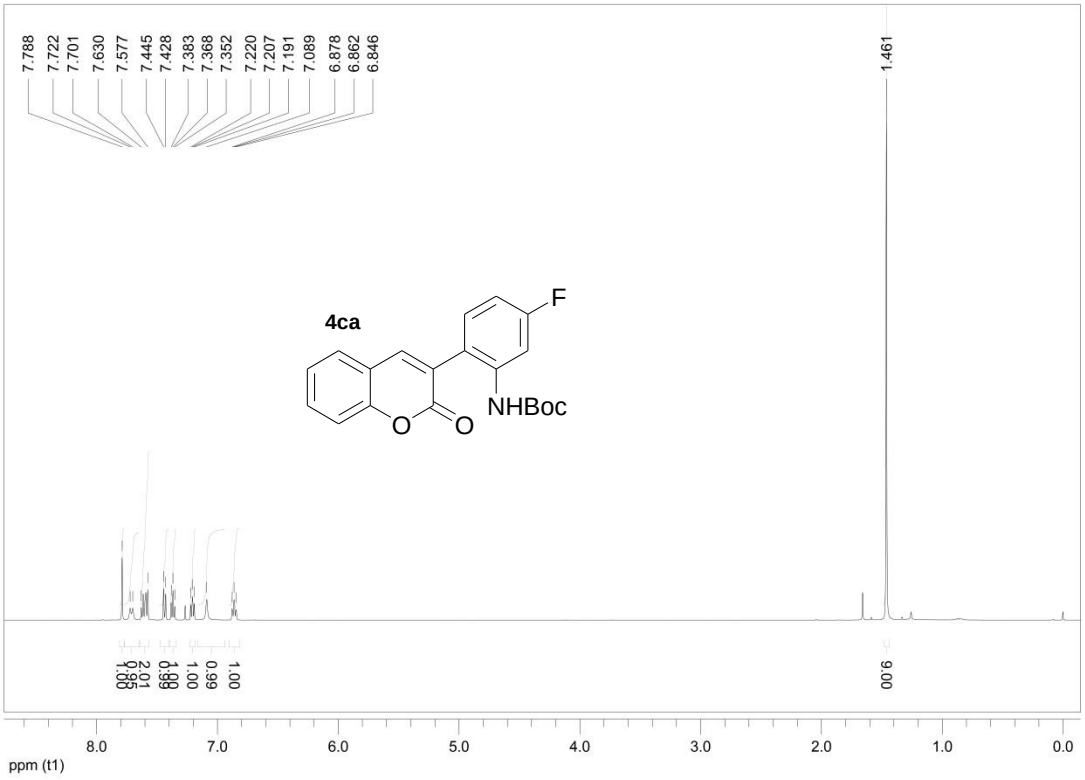

160.497
154.480
153.658
139.893
136.577
132.813
132.103
130.975
130.180
128.641
125.592
124.897
117.972
115.597
80.579
77.414
77.160
76.906
28.378
Cl
4aq
NHBoc
O
O
200
150
100
50
0
ppm (t1)

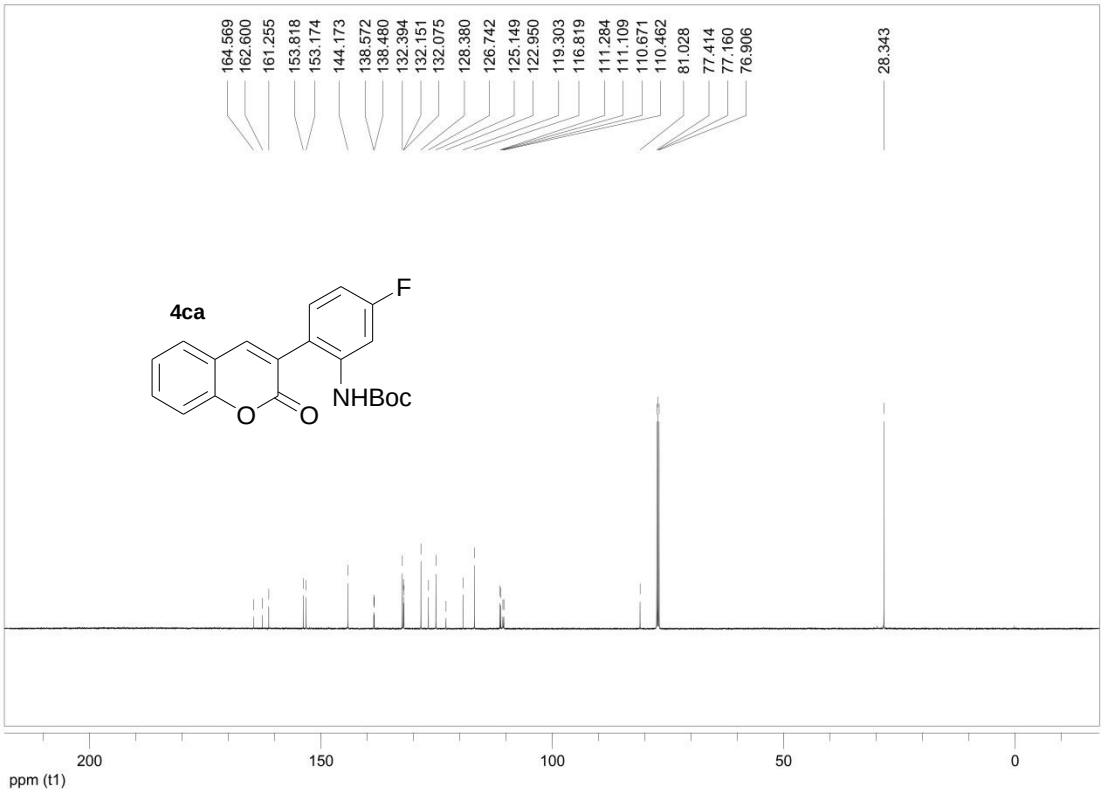

8.129
7.811
7.796
7.580
7.564
7.468
7.412
7.386
7.369
7.311
7.295
7.231
7.216
7.201
6.948
1.451
Br
4ar
NHBoc
O
O
0.97
0.99
0.99
0.96
9.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

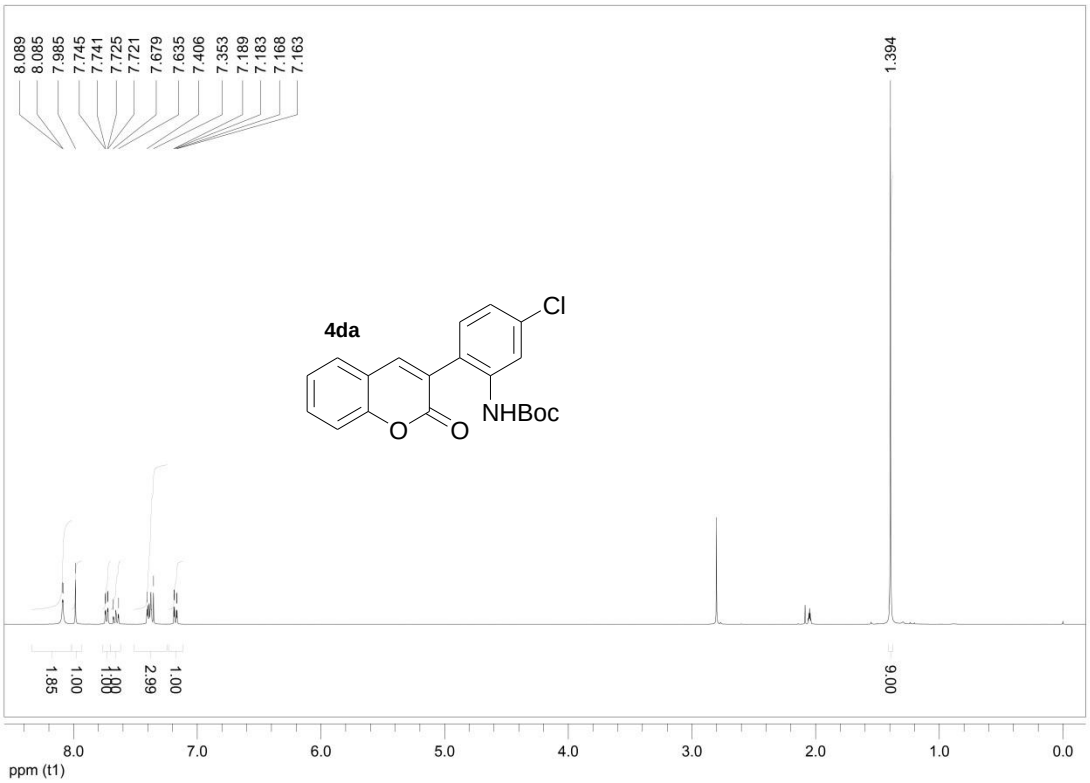

160.550
154.345
153.629
142.368
136.557
132.417
130.975
130.170
128.988
128.873
124.868
122.688
119.388
116.290
80.569
77.414
77.160
76.906
28.373
Br
4ar
NHBoc
O
O
200
150
100
50
0
ppm (t1)

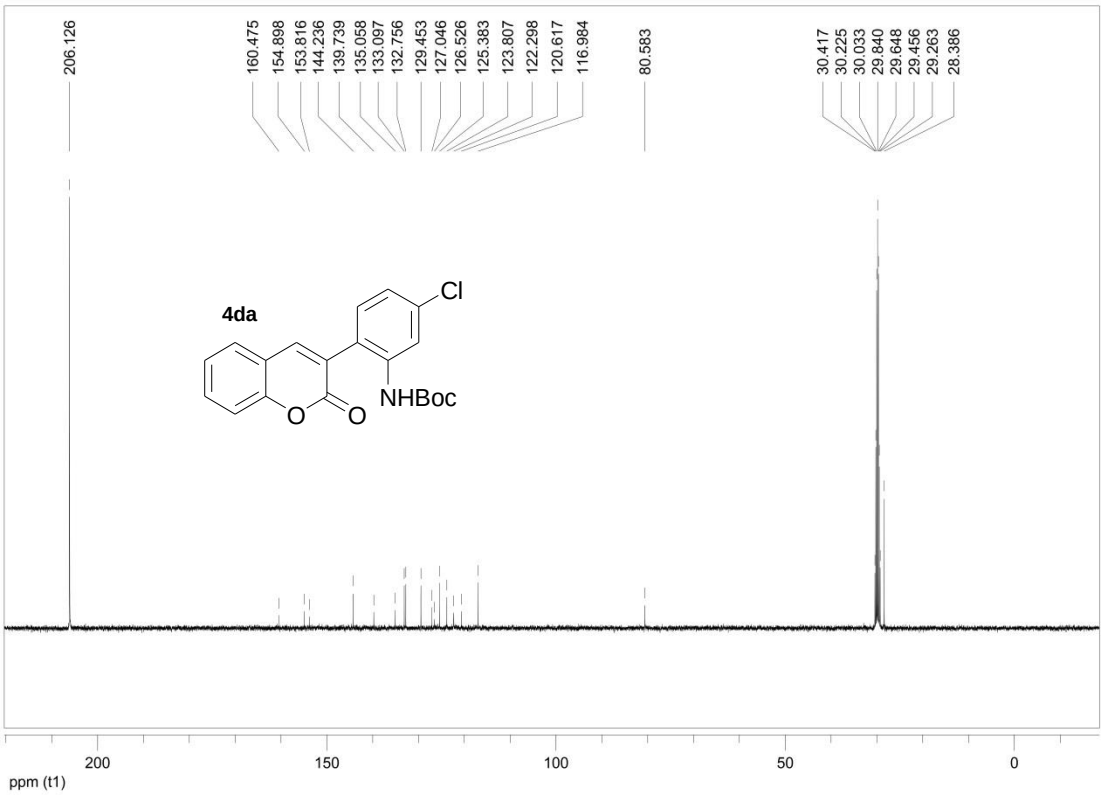

7.907
7.891
7.793
7.653
7.637
7.622
7.598
7.582
7.464
7.437
7.388
7.373
7.358
7.287
7.255
6.408
1.414
4ba
Br
NHBoc
O
O
1.00
9.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

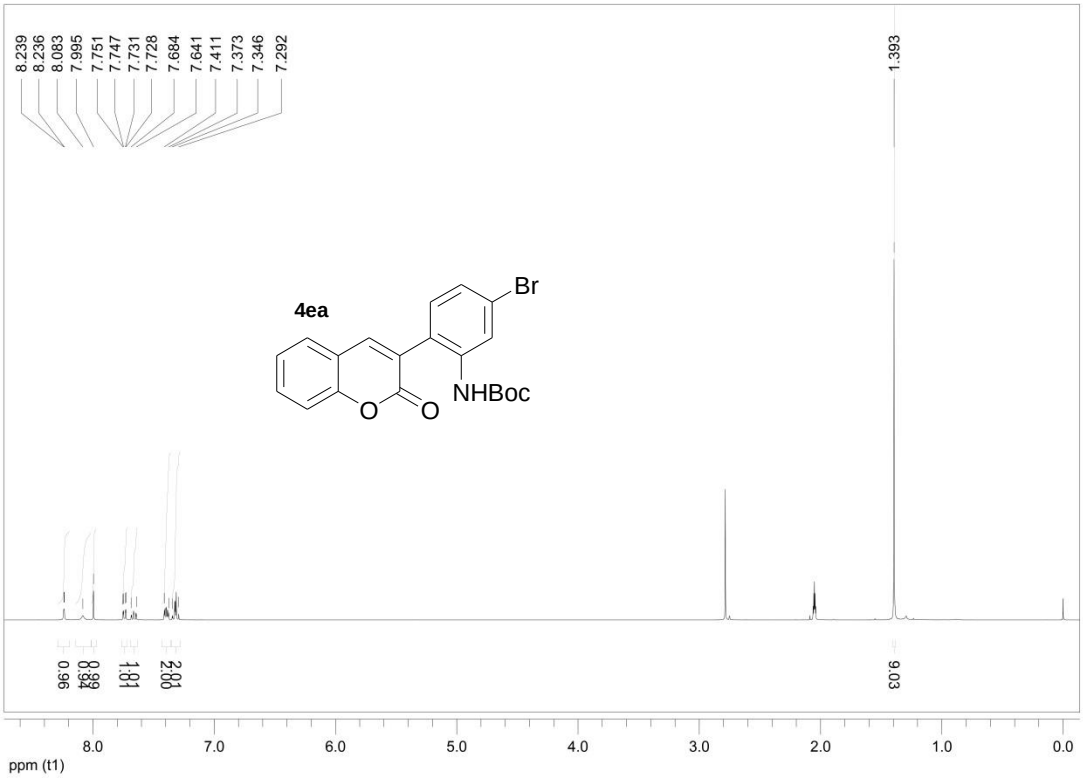

159.939
154.255
153.068
145.766
138.329
132.631
130.698
128.654
128.594
127.405
125.333
125.013
124.509
121.961
118.948
117.056
81.231
77.414
77.160
76.906
28.316
4ba
Br
NHBoc
O
O
200
150
100
50
0
ppm (t1)

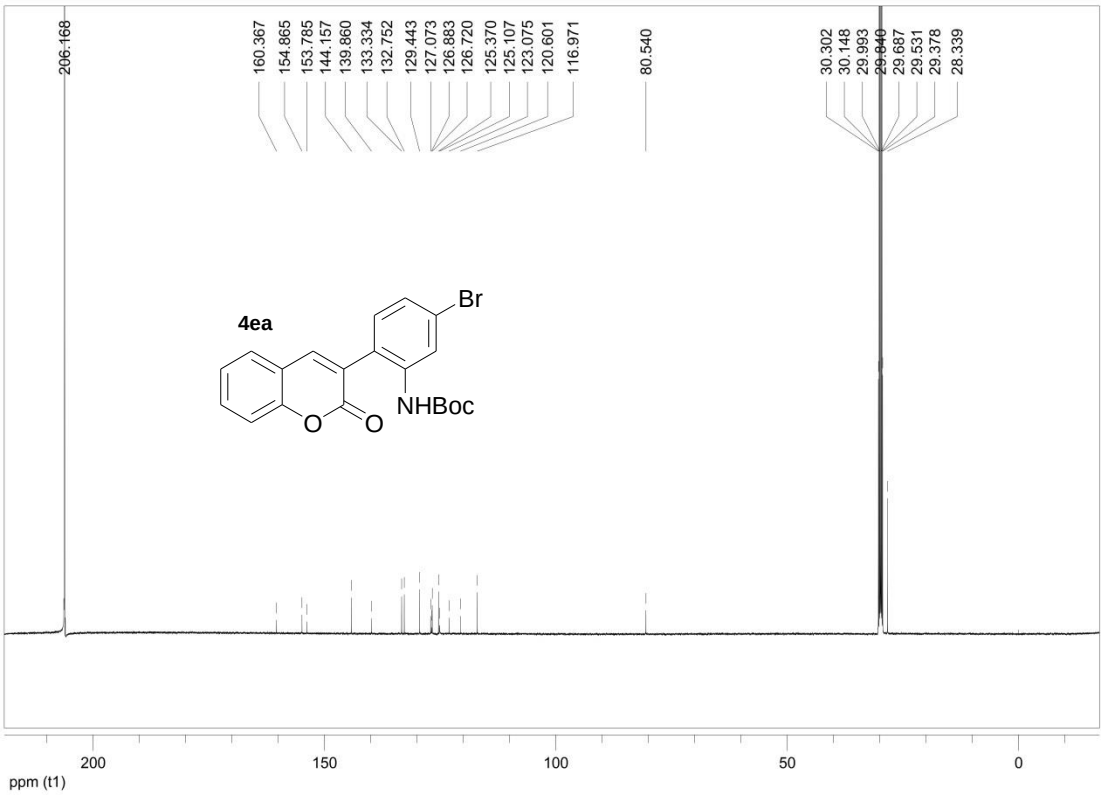

7.788
7.722
7.701
7.630
7.577
7.445
7.428
7.383
7.368
7.352
7.220
7.207
7.191
7.089
6.878
6.862
6.846
1.461
4ca
F
NHBoc
O
O
9.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

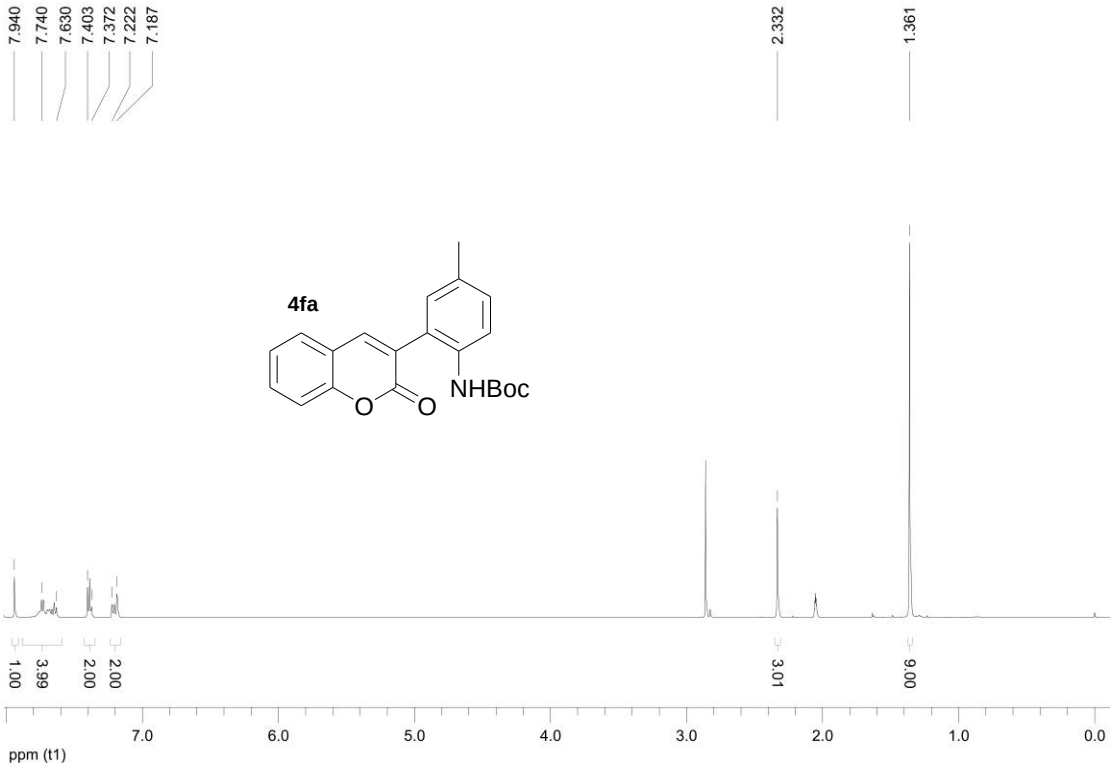

164.569
162.600
161.255
153.818
153.174
144.173
138.572
138.480
132.394
132.151
132.075
128.380
126.742
125.149
122.950
119.303
116.819
111.284
111.109
110.671
110.462
81.028
77.414
77.160
76.906
28.343
4ca
F
NHBoc
O
O
200
150
100
50
0
ppm (t1)

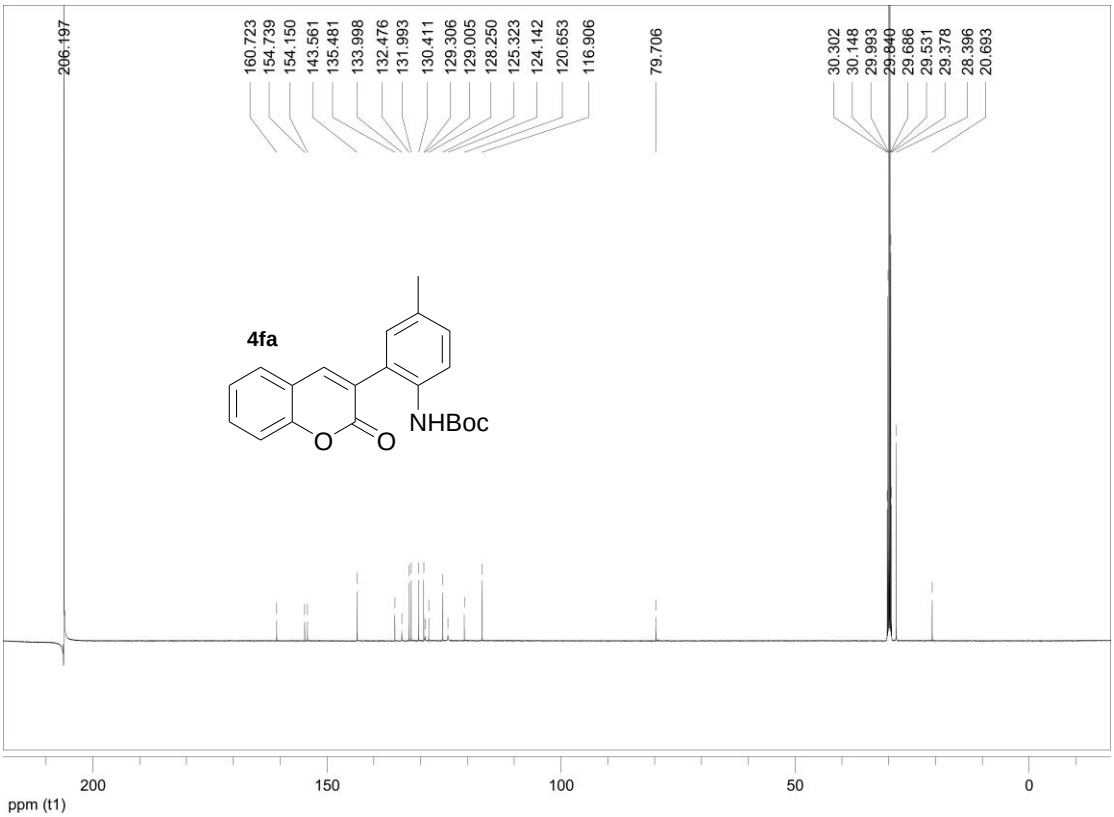

8.089
8.085
7.985
7.745
7.741
7.725
7.721
7.679
7.635
7.406
7.353
7.189
7.183
7.168
7.163
1.394
4da
Cl
NHBoc
O
O
1.85
1.00
1.88
1.88
2.66
1.00
9.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

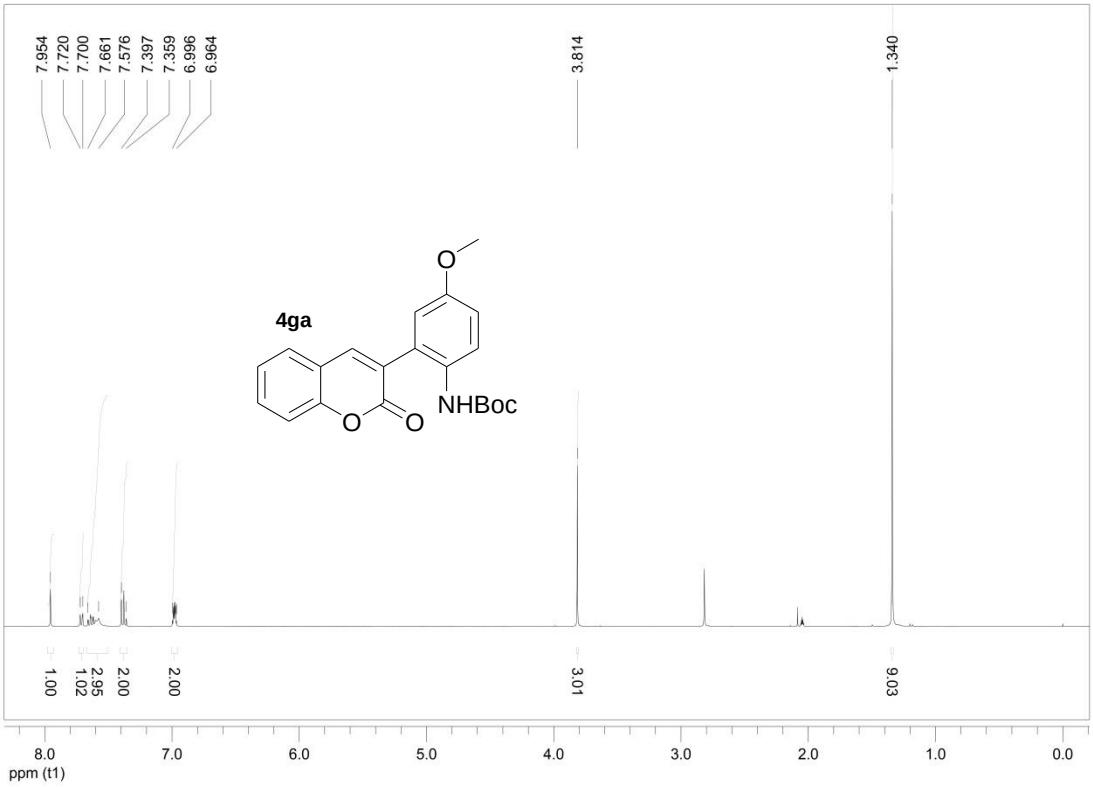

206.126
160.475
154.898
153.816
144.236
139.739
135.058
133.097
132.756
129.453
127.046
126.526
125.383
123.807
122.298
120.617
116.984
80.583
30.417
30.225
30.033
29.840
29.648
29.456
29.263
28.386
4da
Cl
NHBoc
O
O
200
150
100
50
0
ppm (t1)

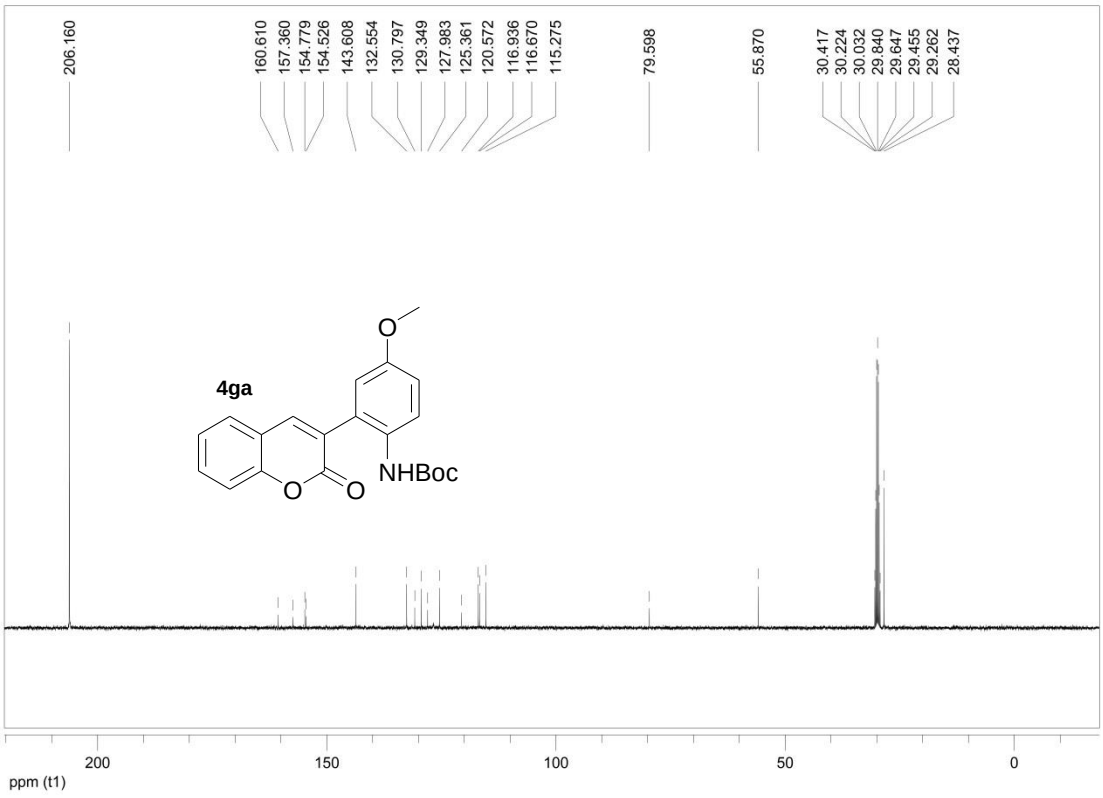

8.239
8.236
8.083
7.995
7.751
7.747
7.731
7.728
7.684
7.641
7.411
7.373
7.346
7.292
1.393
4ea
Br
NHBoc
O
O
0.96
0.99
0.99
1.01
2.00
2.01
9.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

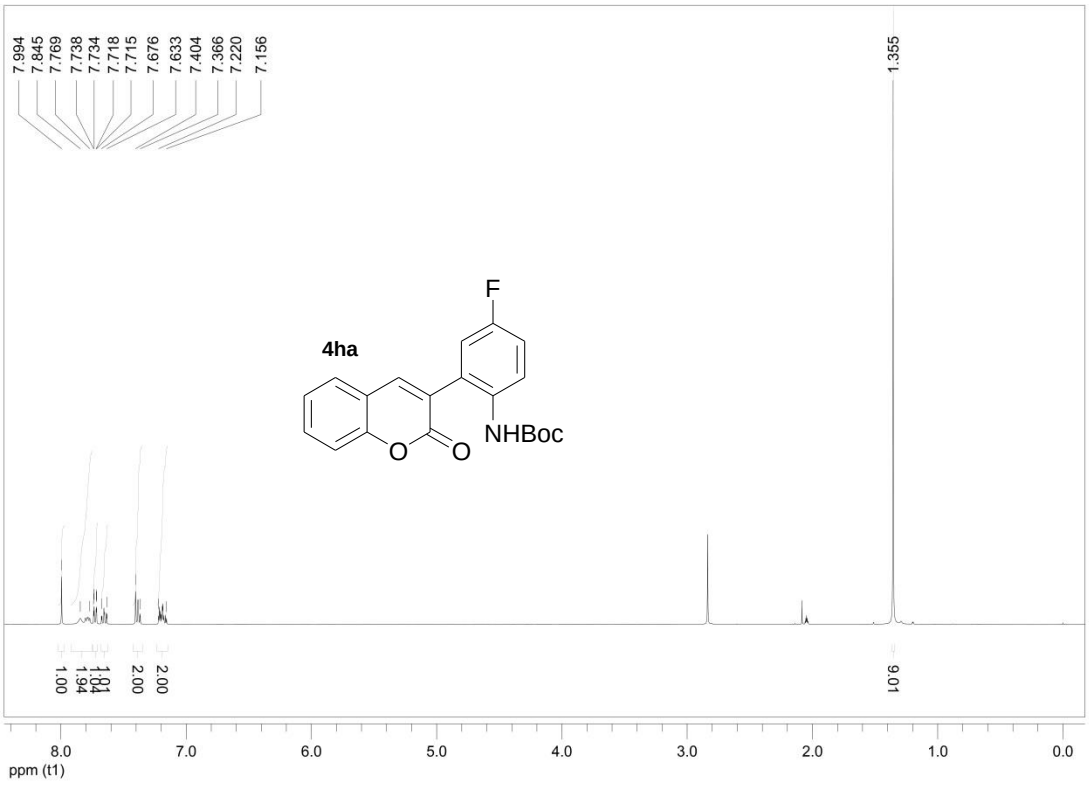

206.168
160.367
154.865
153.785
144.157
139.860
133.334
132.752
129.443
127.073
126.883
126.720
125.370
125.107
123.075
120.601
116.971
80.540
30.302
30.148
29.993
29.840
29.687
29.531
29.378
28.339
4ea
Br
NHBoc
O
O
200
150
100
50
0
ppm (t1)

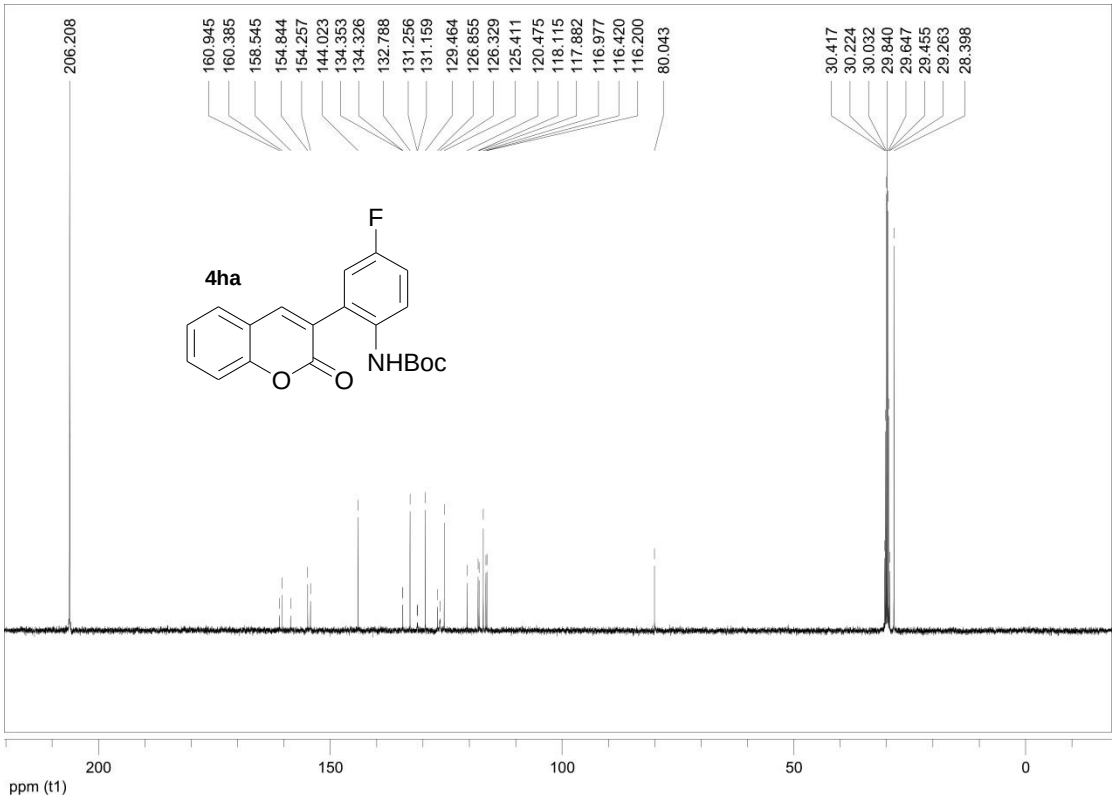

7.940
7.740
7.630
7.403
7.372
7.222
7.187
2.332
1.361
4fa
NHBoc
O
O
1.00
3.99
2.00
2.00
3.01
9.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

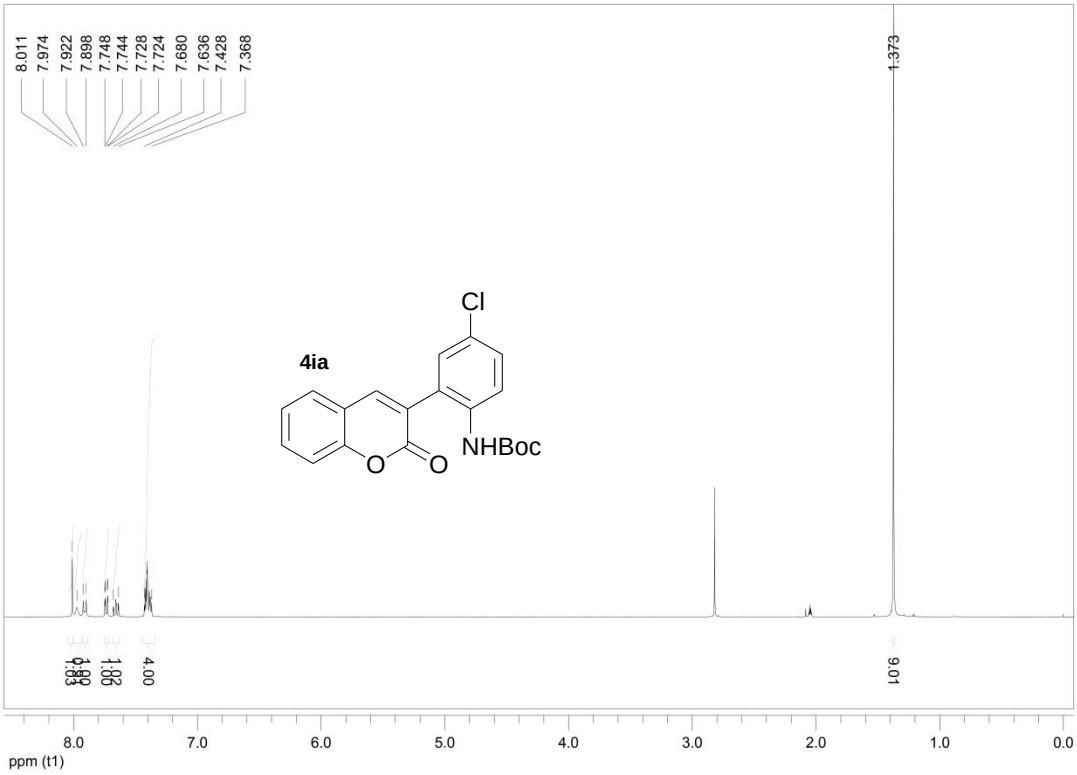

206.197
160.723
154.739
154.150
143.561
135.481
133.998
132.476
131.993
130.411
129.306
129.005
128.250
125.323
124.142
120.653
116.906
79.706
30.302
30.148
29.993
29.840
29.686
29.531
29.378
28.396
20.693
4fa
NHBoc
O
O
200
150
100
50
0
ppm (t1)

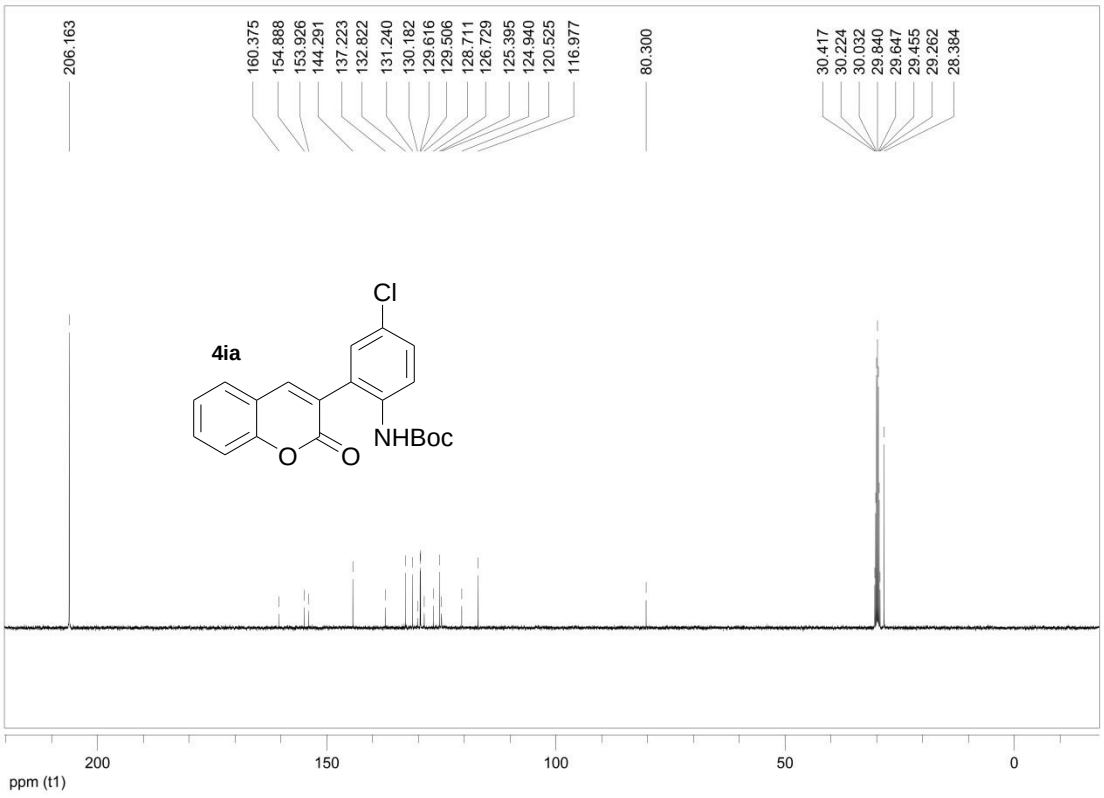

7.954
7.720
7.700
7.661
7.576
7.397
7.359
6.996
6.964
3.814
1.340
4ga
O
NHBoc
O
O
1.00
1.02
2.65
2.00
2.00
3.01
9.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

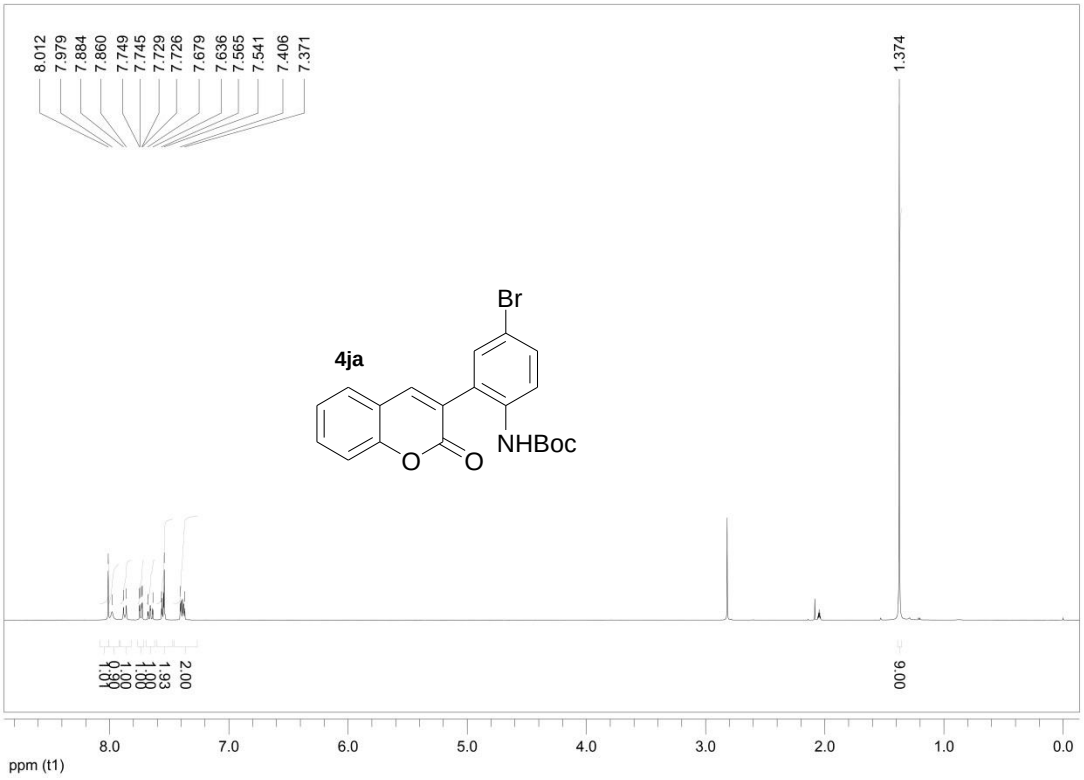

206.160
160.610
157.360
154.779
154.526
143.608
132.554
130.797
129.349
127.983
125.361
120.572
116.936
116.670
115.275
79.598
55.870
30.417
30.224
30.032
29.840
29.647
29.455
29.262
28.437
4ga
O
NHBoc
O
O
200
150
100
50
0
ppm (t1)

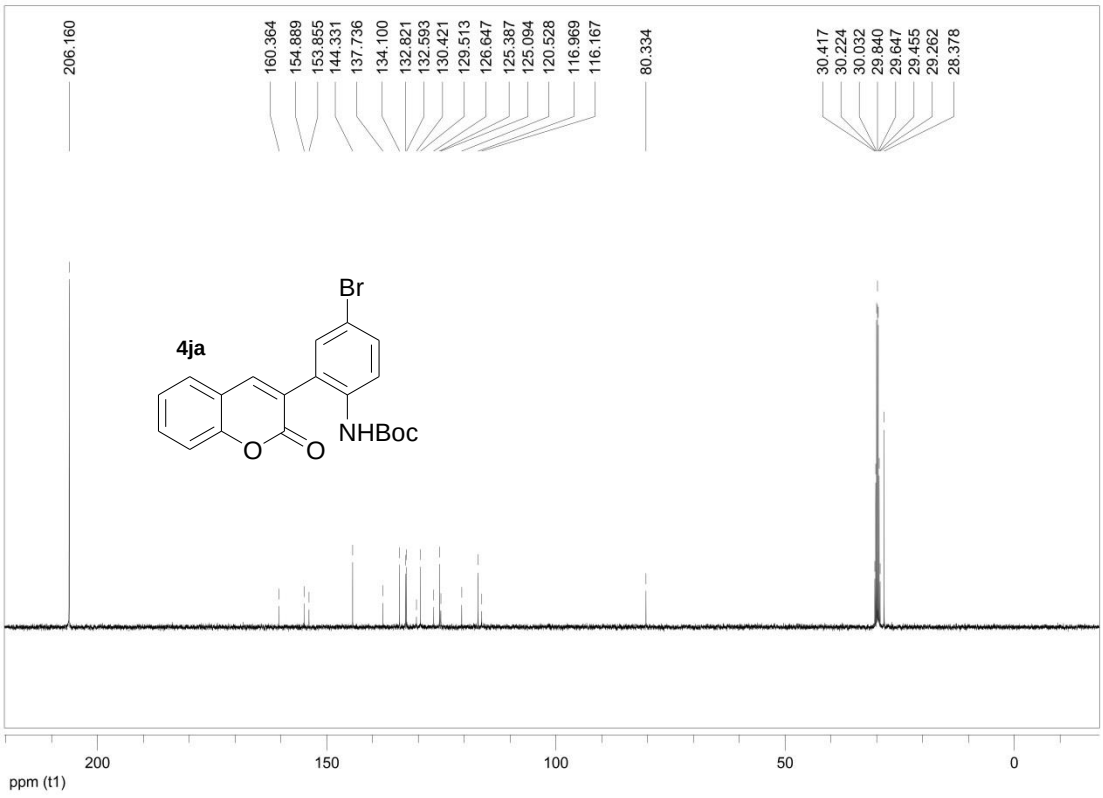

7.994
7.845
7.769
7.738
7.734
7.718
7.715
7.676
7.633
7.404
7.366
7.220
7.156
1.355
4ha
F
NHBoc
O
O
1.00
1.64
1.01
2.00
2.00
9.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

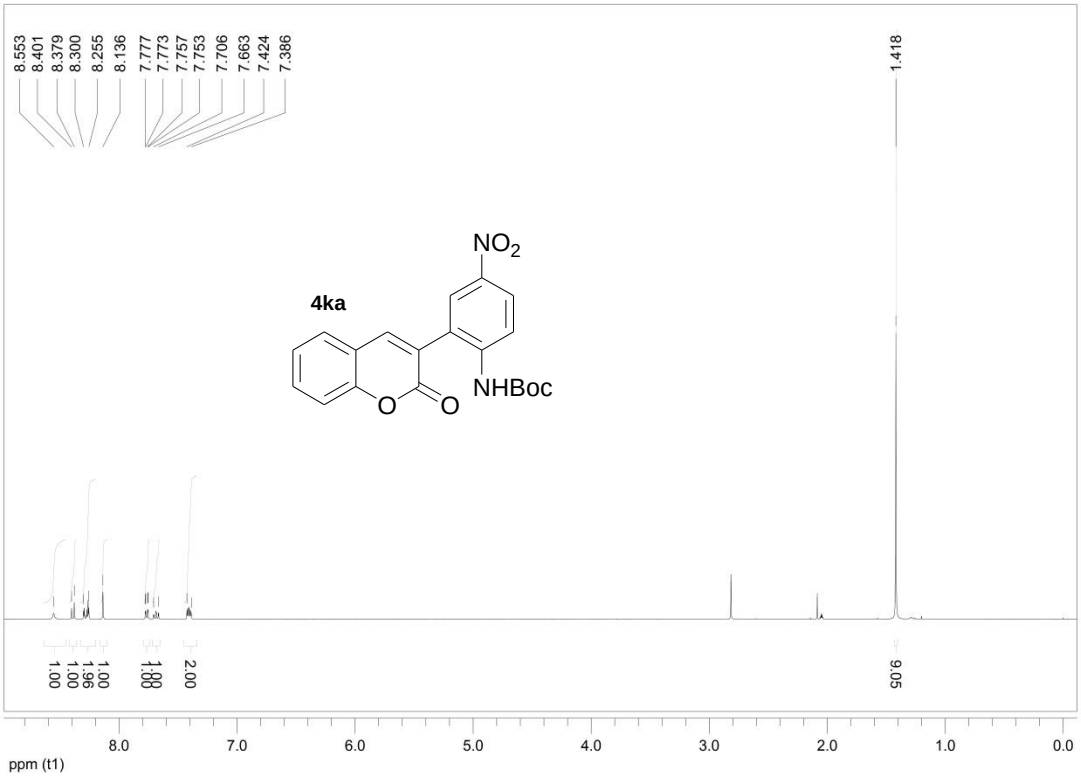

206.208
160.945
160.385
158.545
154.844
154.257
144.023
134.353
134.326
132.788
131.256
131.159
129.464
126.855
126.329
125.411
120.475
118.115
117.882
116.977
116.420
116.200
80.043
30.417
30.224
30.032
29.840
29.647
29.455
29.263
28.398
4ha
F
NHBoc
O
O
200
150
100
50
0
ppm (t1)

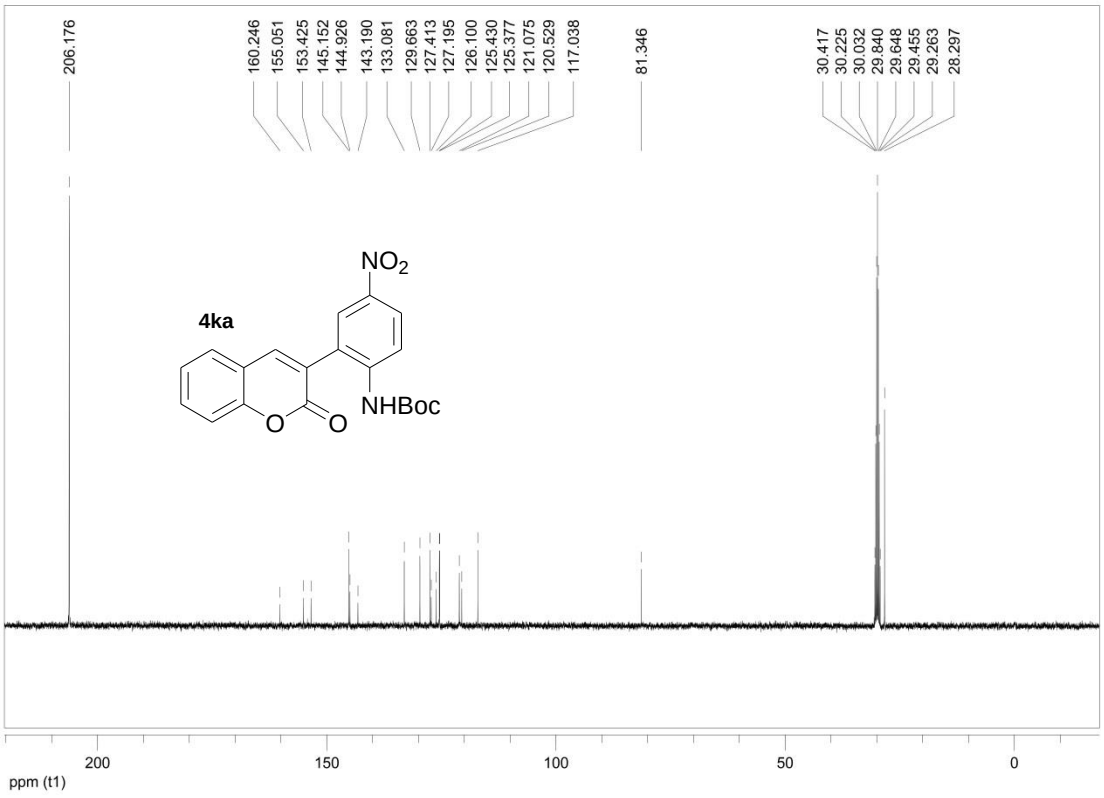

8.011
7.974
7.922
7.898
7.748
7.744
7.728
7.724
7.680
7.636
7.428
7.368
1.373
4.00
9.01
4ia
Cl
NHBoc
O
O
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


206.163
160.375
154.888
153.926
144.291
137.223
132.822
131.240
130.182
129.616
129.506
128.711
126.729
125.395
124.940
120.525
116.977
80.300
30.417
30.224
30.032
29.840
29.647
29.455
29.262
28.384
4ia
Cl
NHBoc
O
O
200
150
100
50
0
ppm (t1)

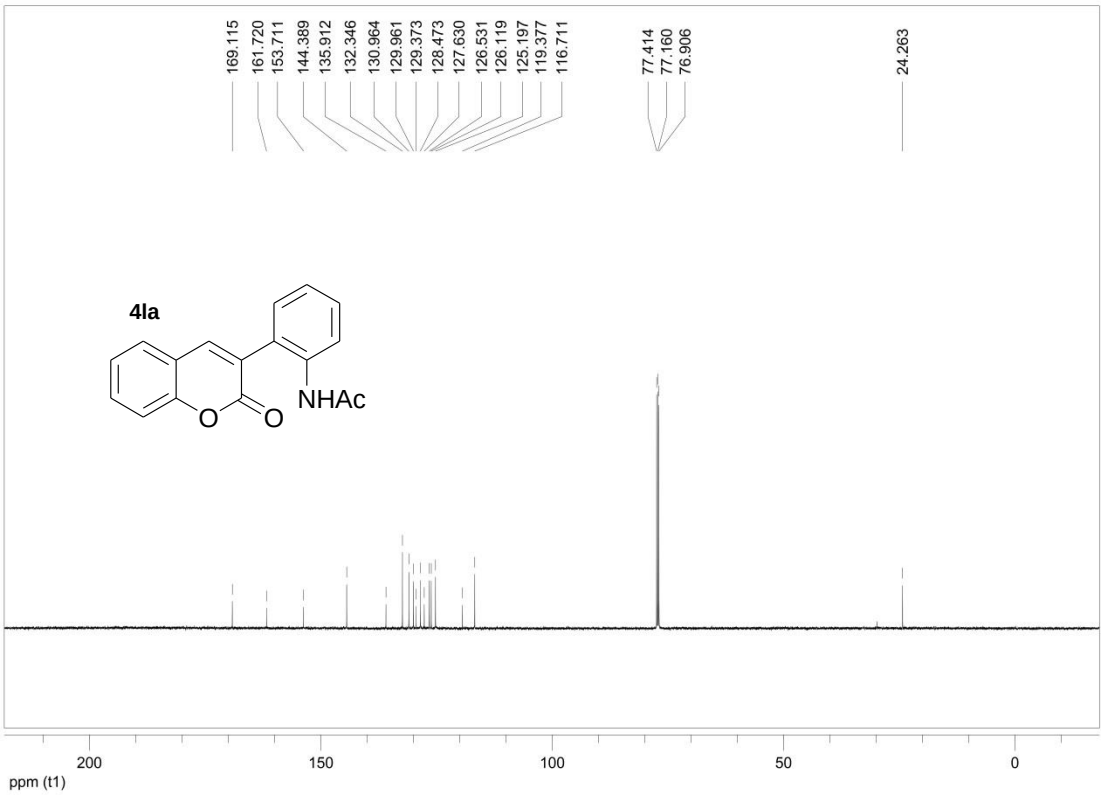

8.012
7.979
7.884
7.860
7.749
7.745
7.729
7.726
7.679
7.636
7.565
7.541
7.406
7.371
1.374
Br
4ja
NHBoc
O
O
1.00
0.98
1.00
1.00
1.93
2.00
9.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

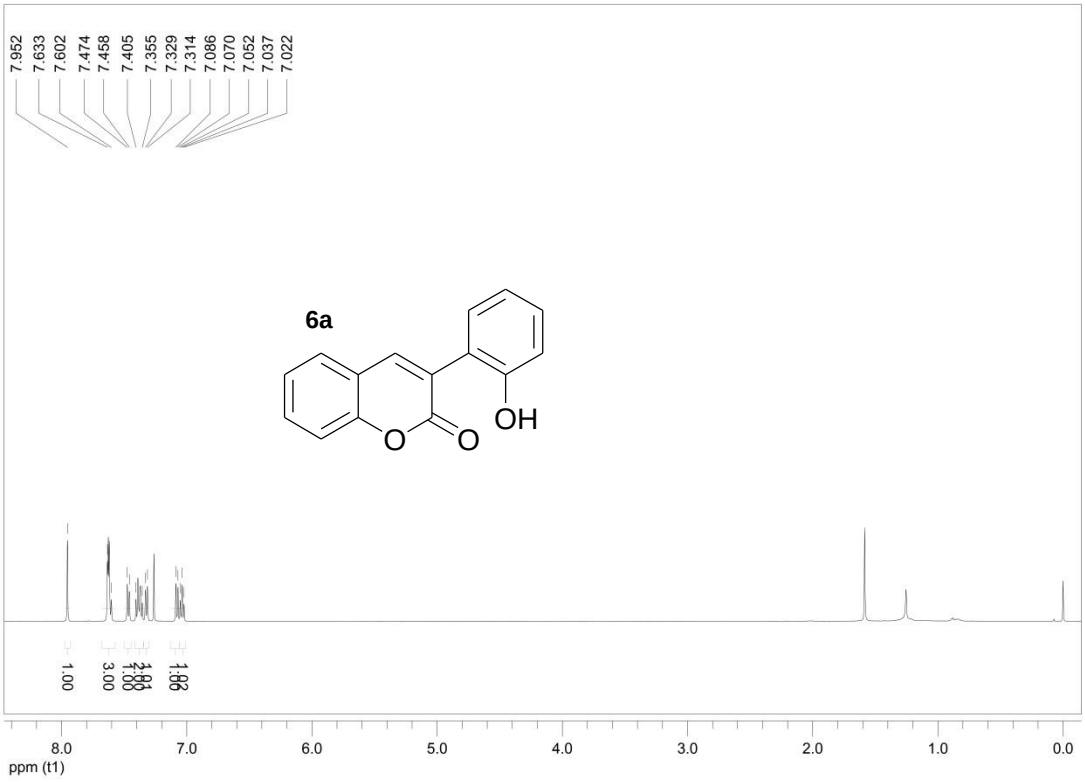

206.160
160.364
154.889
153.855
144.331
137.736
134.100
132.821
132.593
130.421
129.513
126.647
125.387
125.094
120.528
116.969
116.167
80.334
30.417
30.224
30.032
29.840
29.647
29.455
29.262
28.378
Br
4ja
NHBoc
O
O
200
150
100
50
0
ppm (t1)

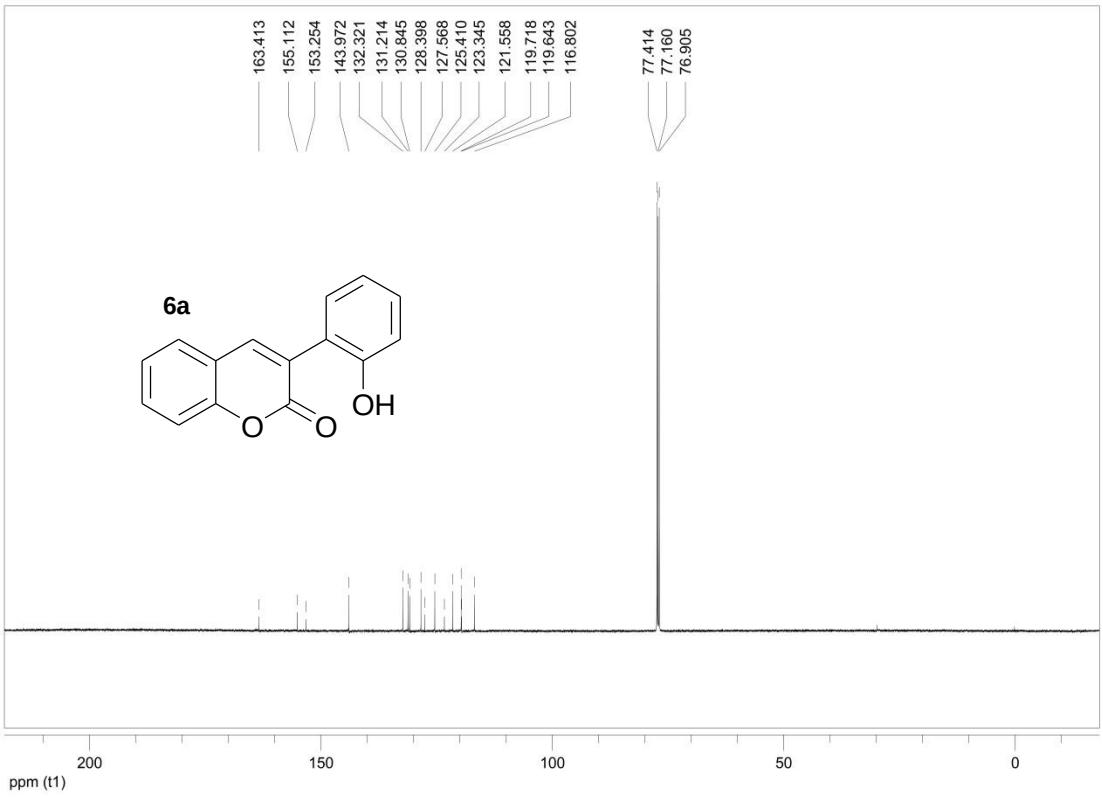

8.553
8.401
8.379
8.300
8.255
8.136
7.777
7.773
7.757
7.753
7.706
7.663
7.424
7.386
1.418
4ka
NO2
NHBoc
O
O
1.00
1.00
1.96
1.00
1.88
2.00
9.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

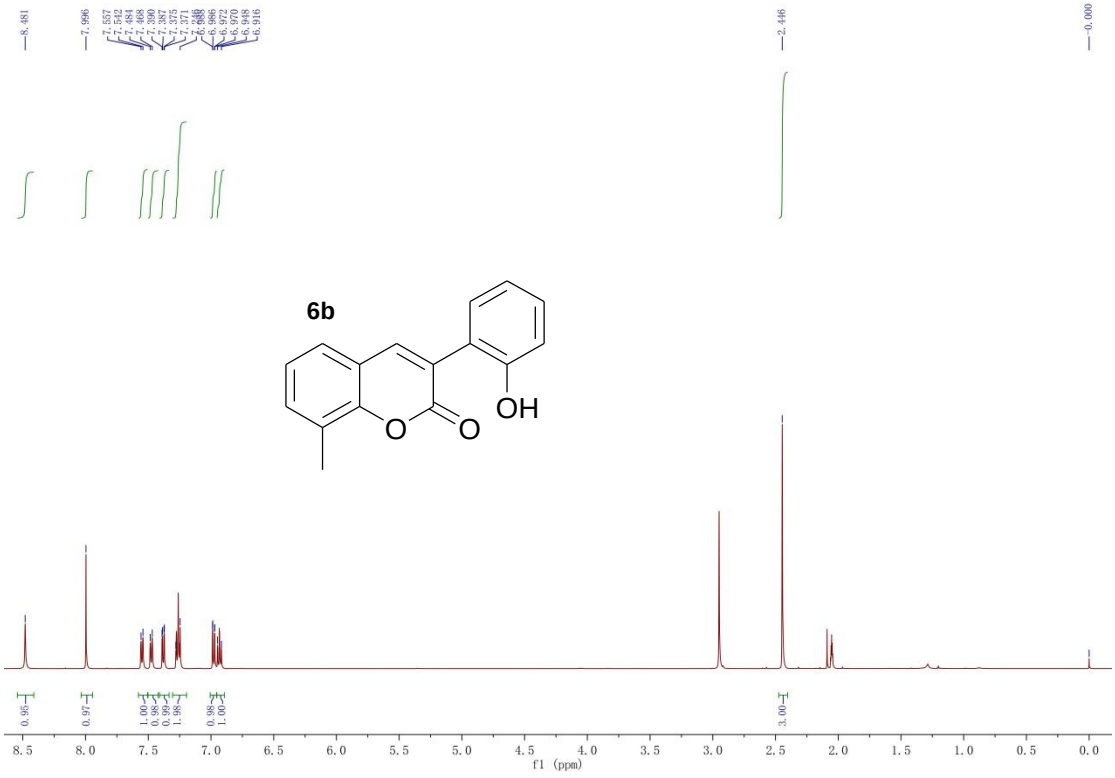

206.176
160.246
155.051
153.425
145.152
144.926
143.190
133.081
129.663
127.413
127.195
126.100
125.430
125.377
121.075
120.529
117.038
81.346
30.417
30.225
30.032
29.840
29.648
29.455
29.263
28.297
4ka
NO2
NHBoc
O
O
200
150
100
50
0
ppm (t1)

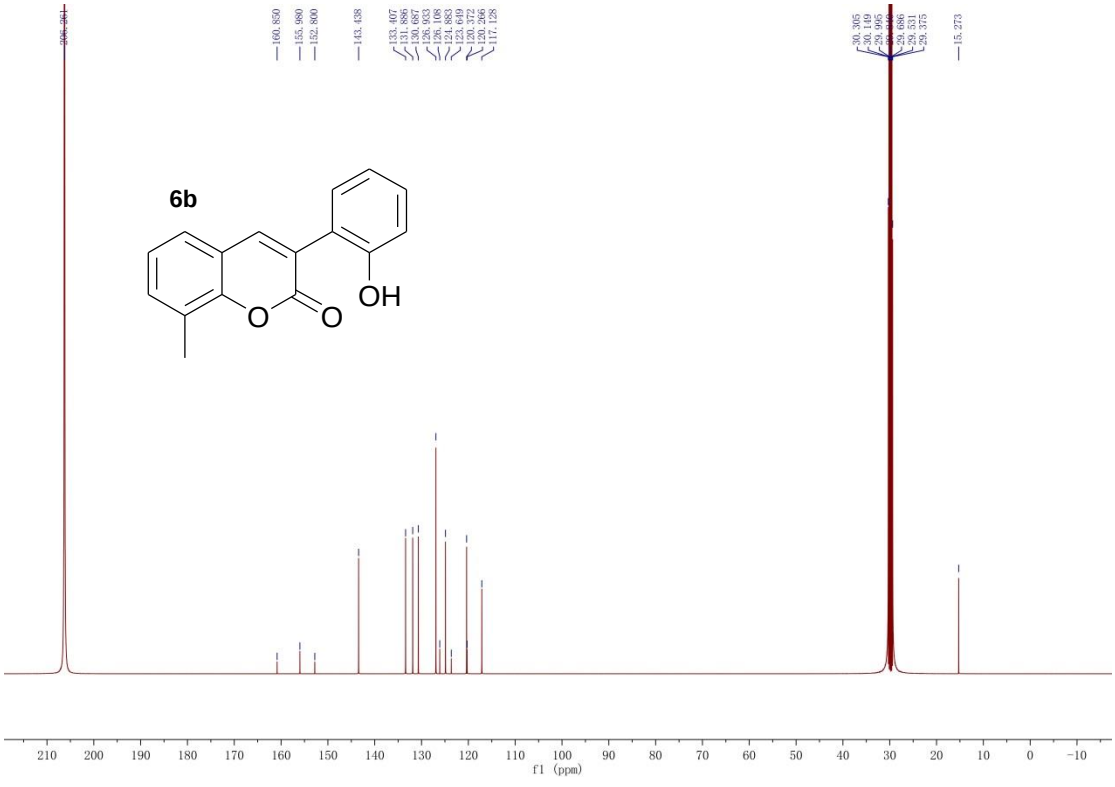

8.171
7.836
7.755
7.738
7.626
7.586
7.471
7.421
7.384
7.369
7.354
7.321
7.307
7.279
7.268
2.073
4la
NHAc
O
O
0.98
1.00
2.99
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

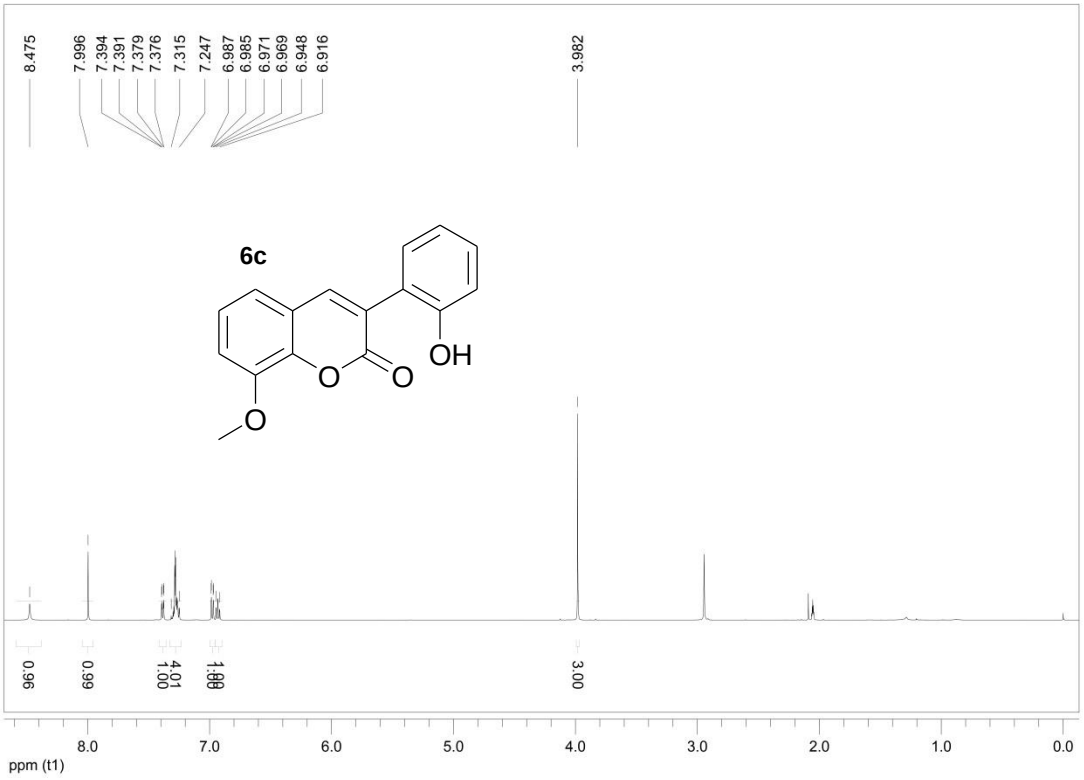

169.115
161.720
153.711
144.389
135.912
132.346
130.964
129.961
129.373
128.473
127.630
126.531
126.119
125.197
119.377
116.711
77.414
77.160
76.906
24.263
4la
NHAc
O
O
200
150
100
50
0
ppm (t1)

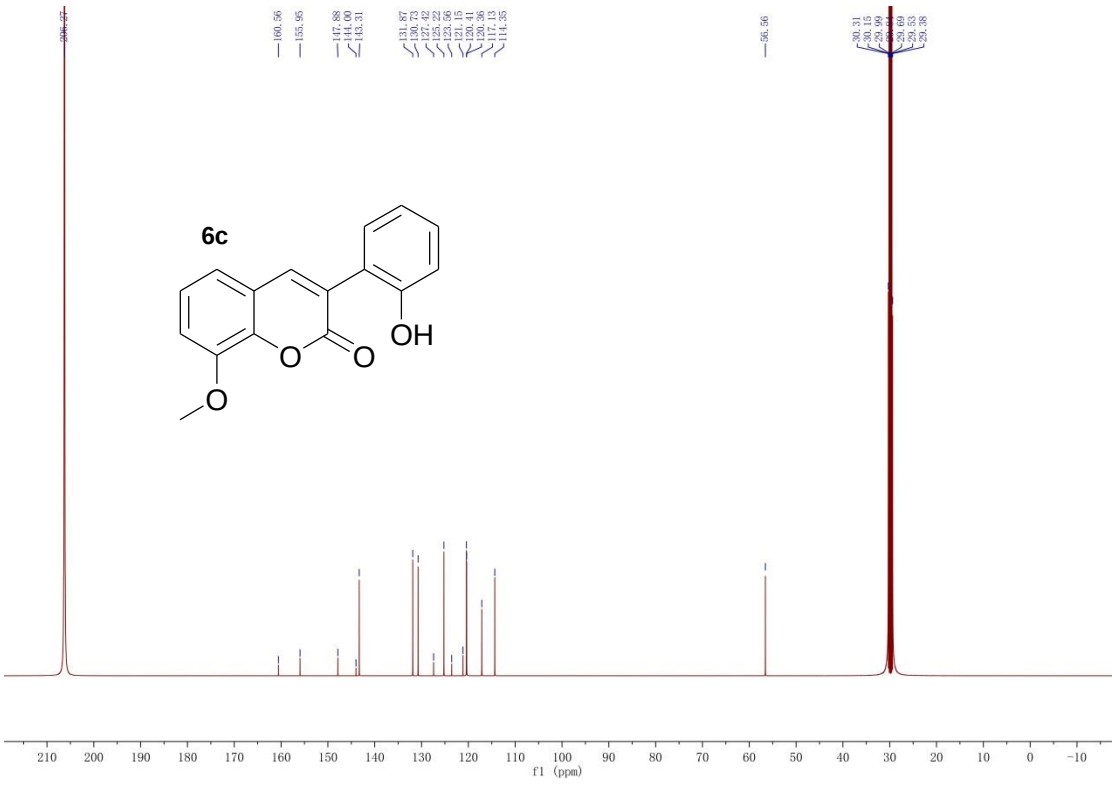

7.952
7.633
7.602
7.474
7.458
7.405
7.355
7.329
7.314
7.086
7.070
7.052
7.037
7.022
6a
OH
O
O
1.00
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

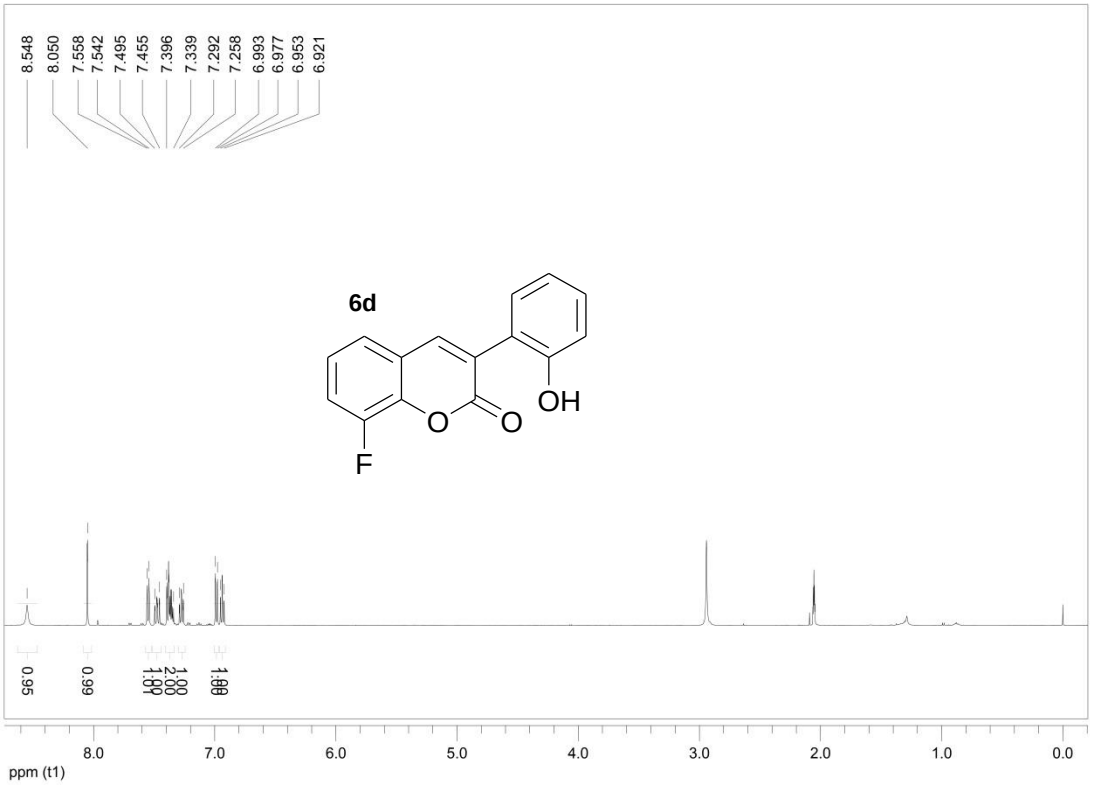

163.413
155.112
153.254
143.972
132.321
131.214
130.845
128.398
127.568
125.410
123.345
121.558
119.718
119.643
116.802
77.414
77.160
76.905
6a
OH
O
O
200
150
100
50
0
ppm (t1)

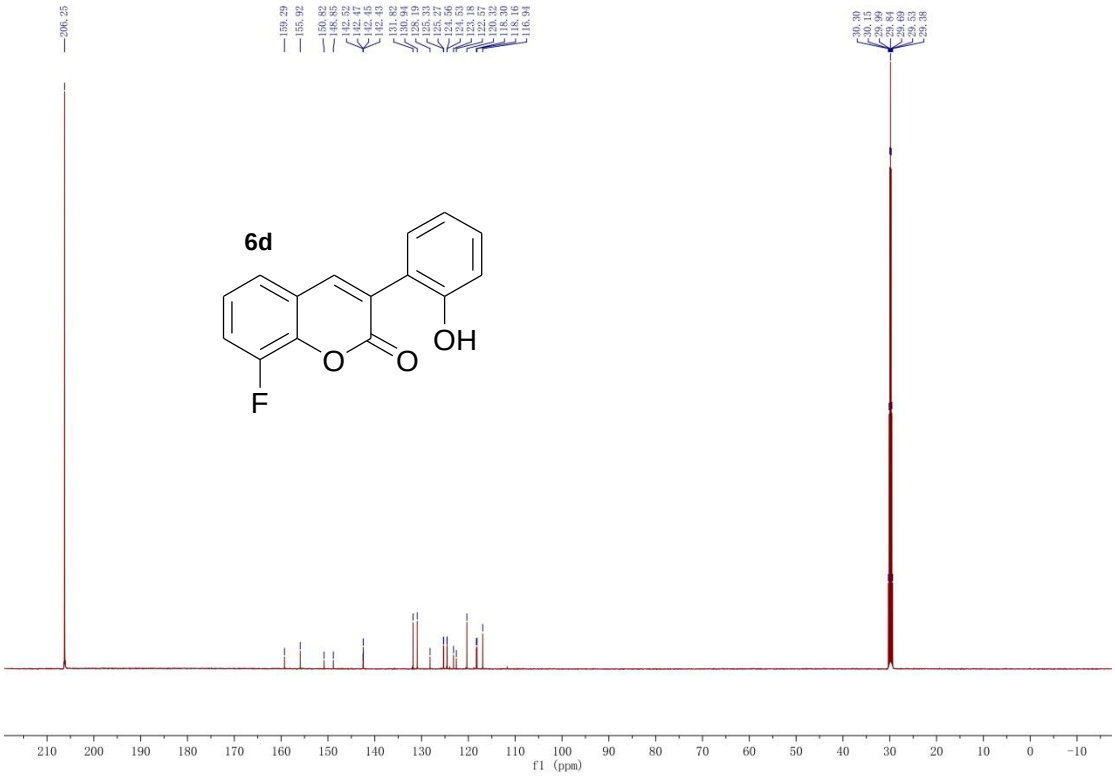

8.481
7.996
7.557
7.542
7.484
7.468
7.390
7.387
7.375
7.371
6.988
6.986
6.972
6.970
6.948
6.916
2.446
0.000
6b
OH
O
O
0.96
0.97
1.00
0.99
1.98
0.98
1.00
3.00
f1 (ppm)

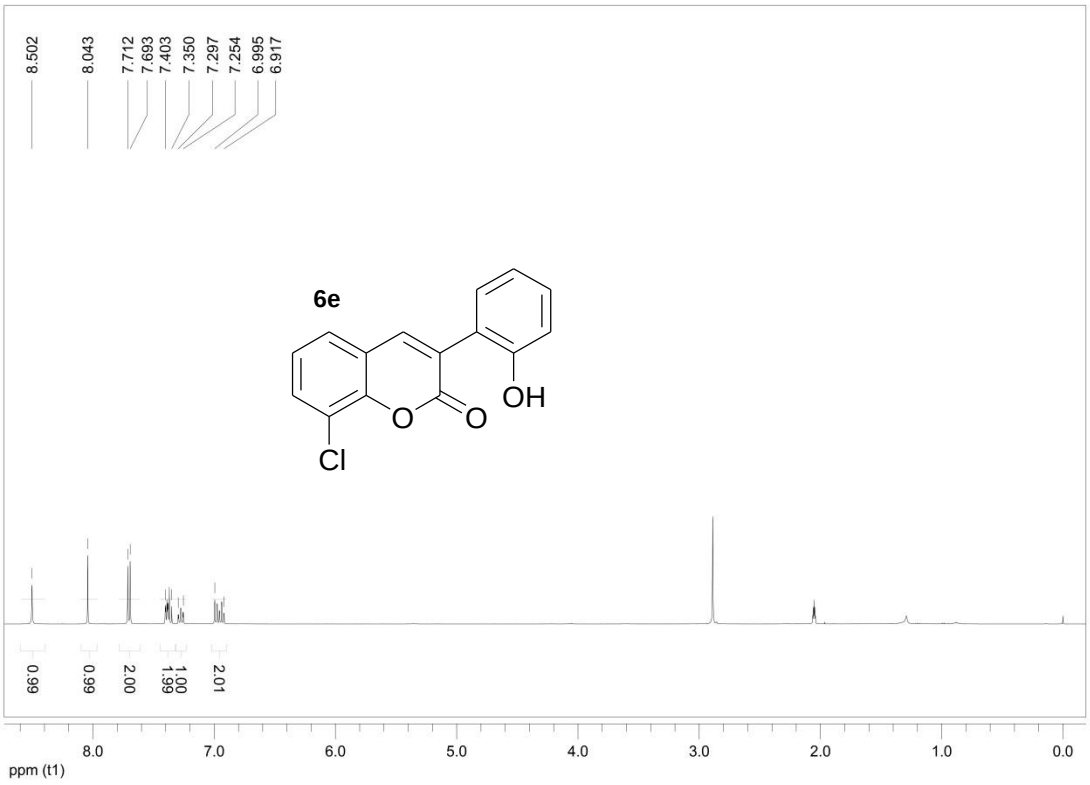

206.381
160.859
155.980
152.800
143.638
133.407
131.886
130.887
126.933
126.108
124.883
123.649
120.372
120.296
117.128
30.305
30.149
29.995
29.686
29.571
29.375
15.273
6b
OH
O
O
f1 (ppm)

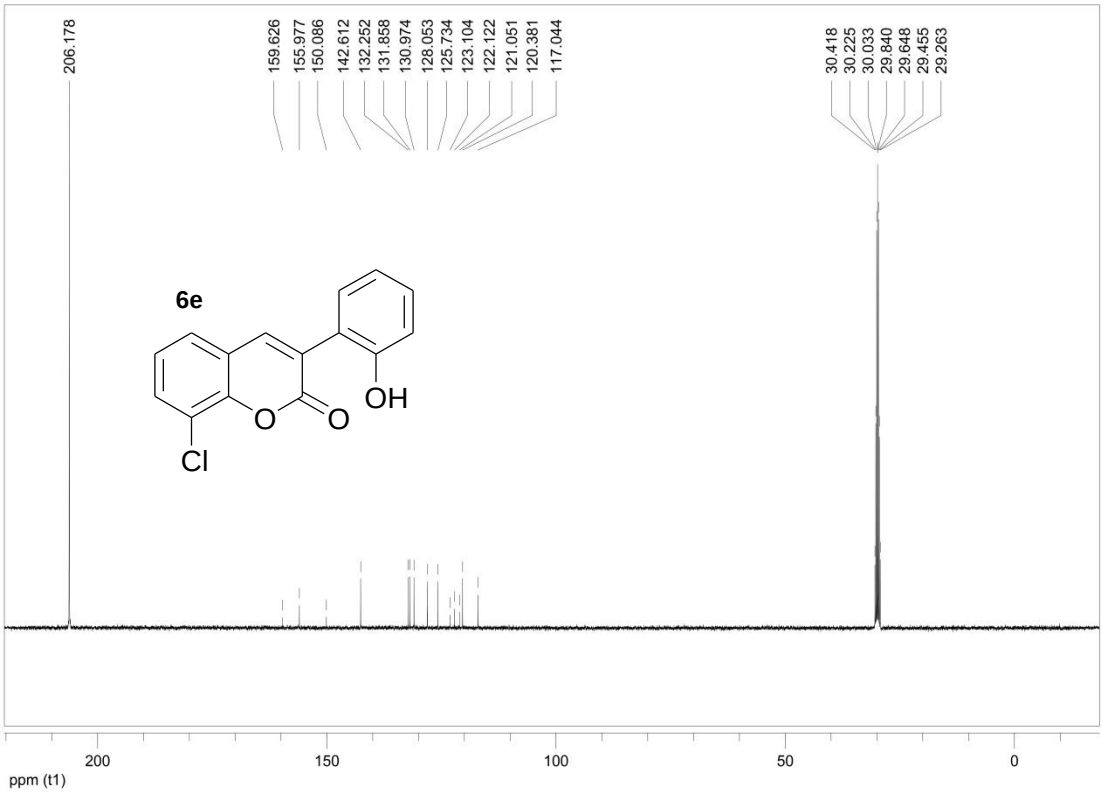

8.475
7.996
7.394
7.391
7.379
7.376
7.315
7.247
6.987
6.985
6.971
6.969
6.948
6.916
3.982
6c
OH
O
O
O
0.96
0.99
4.01
1.00
1.00
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

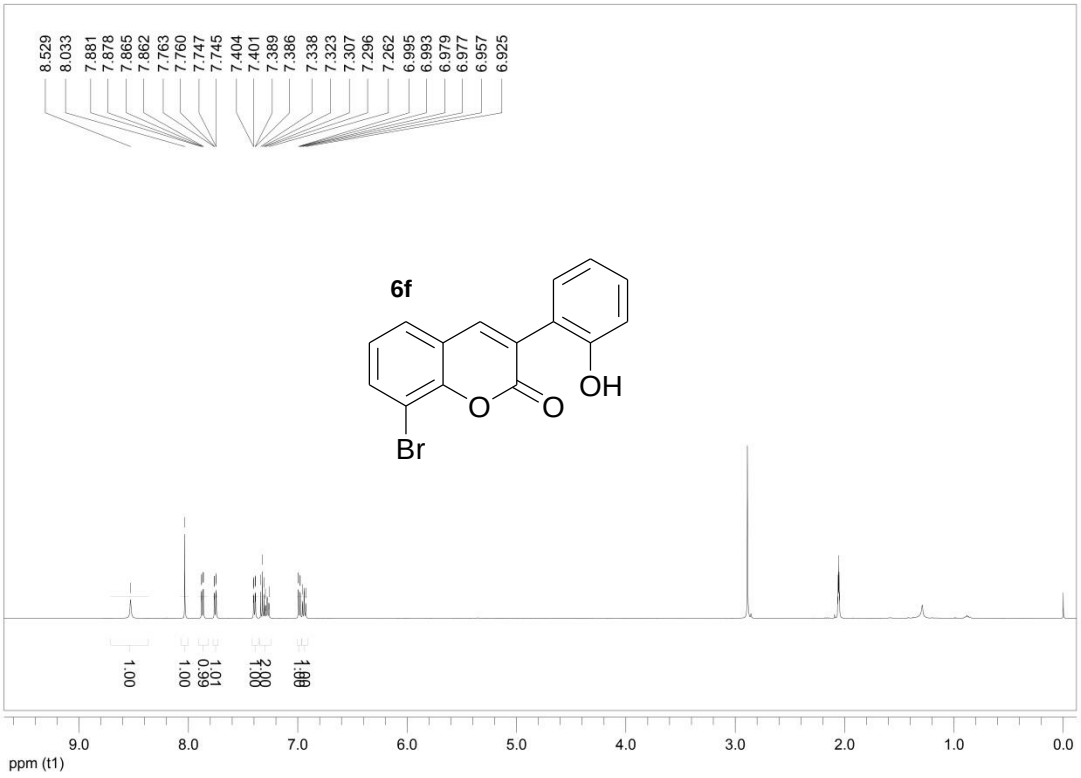

206.27
160.56
155.95
147.88
144.00
143.31
131.87
130.73
127.42
125.22
123.56
121.15
120.41
120.36
117.13
114.35
56.56
30.31
30.15
29.99
29.84
29.69
29.53
29.38
6c
OH
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

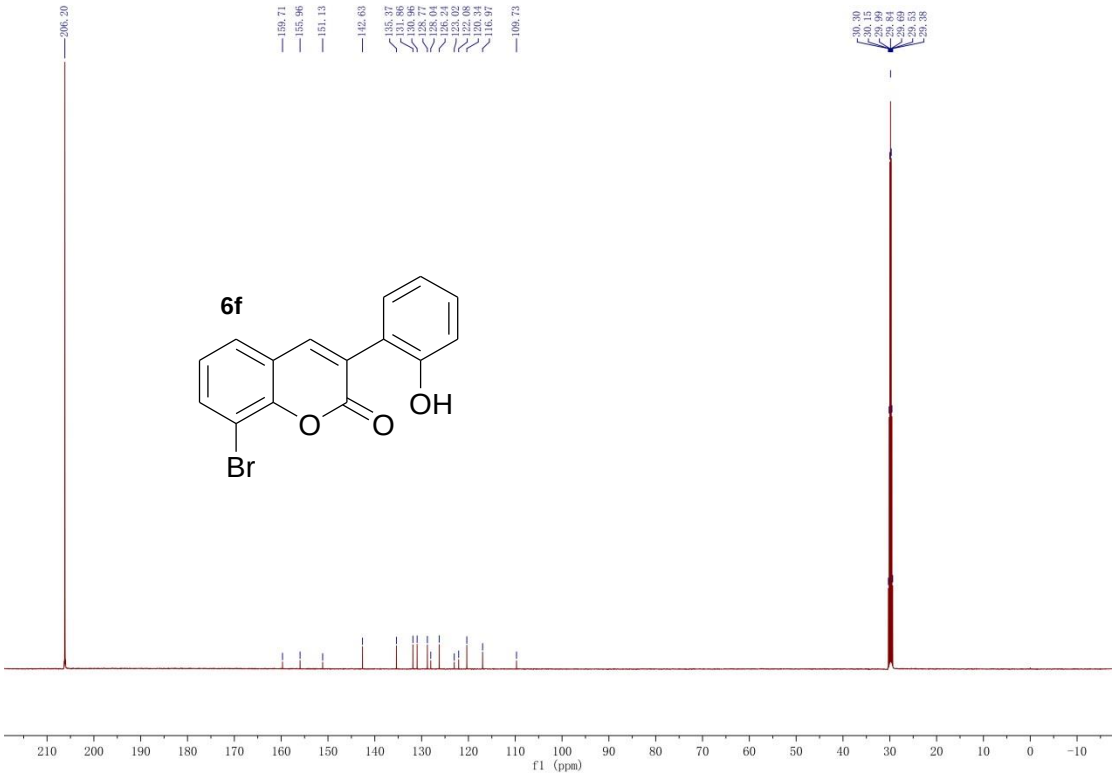

8.548
8.050
7.558
7.542
7.495
7.455
7.396
7.339
7.292
7.258
6.993
6.977
6.953
6.921
6d
OH
O
O
F
0.95
0.99
2.00
1.00
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

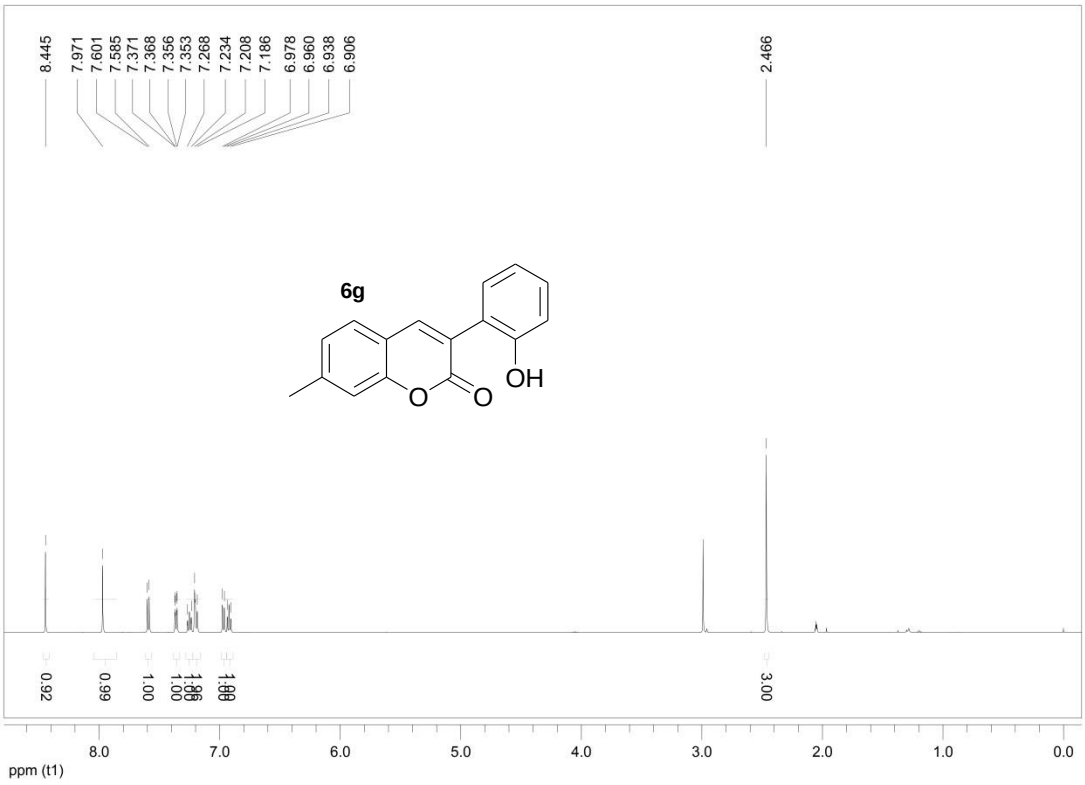

206.25
159.29
155.92
150.82
148.85
142.52
142.47
142.45
142.43
131.82
130.94
128.19
125.33
125.27
124.56
124.53
123.18
122.57
120.32
116.30
118.16
116.94
30.30
30.15
29.99
29.84
29.69
29.53
29.38
6d
OH
O
O
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

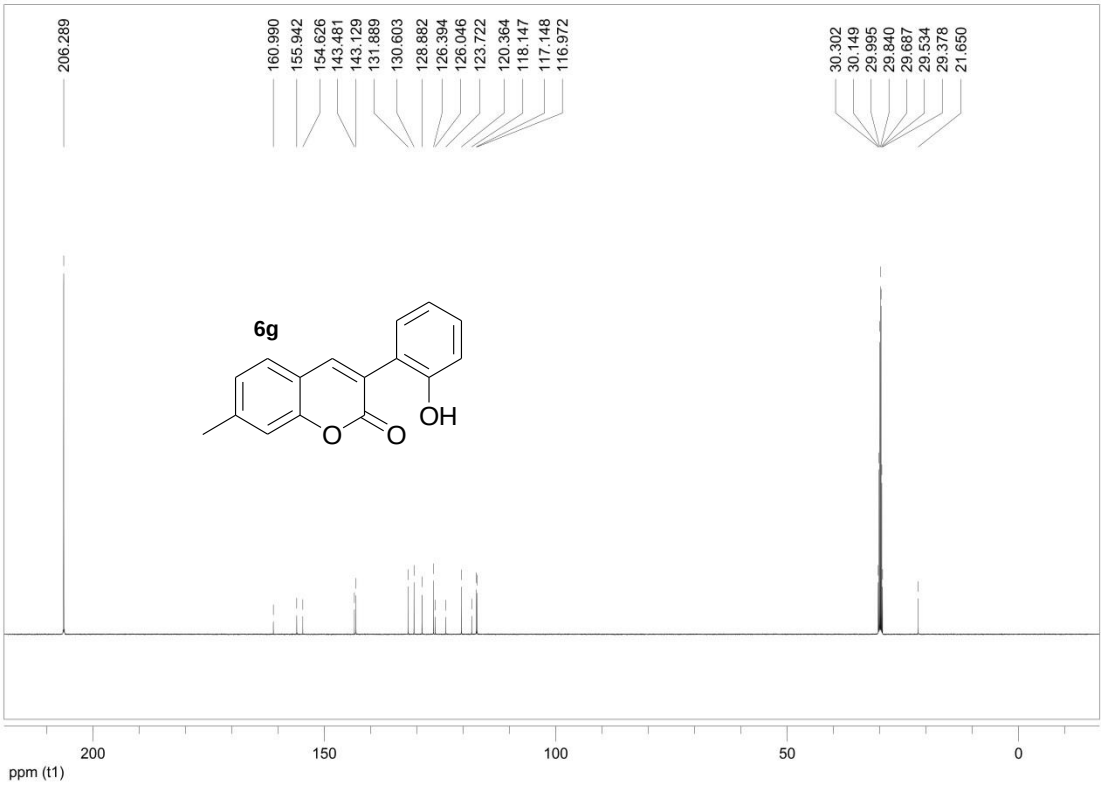

8.502
8.043
7.712
7.693
7.403
7.350
7.297
7.254
6.995
6.917
6e
OH
O
O
Cl
0.99
0.99
2.00
1.99
1.00
2.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

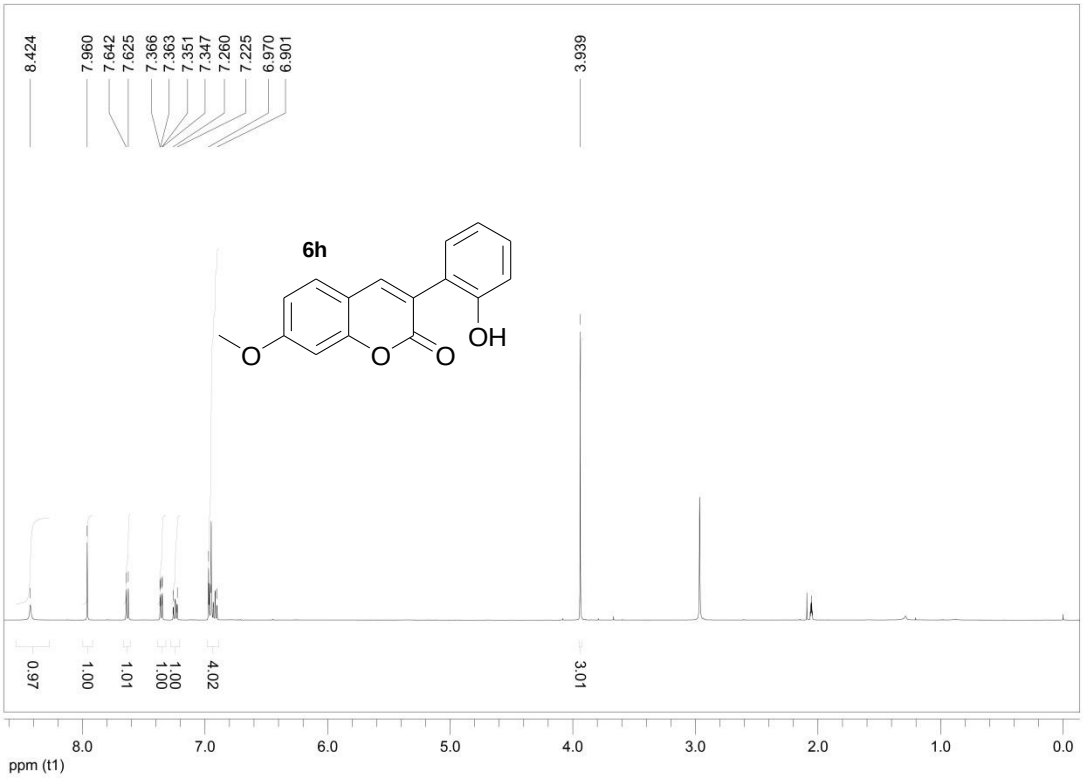

206.178
159.626
155.977
150.086
142.612
132.252
131.858
130.974
128.053
125.734
123.104
122.122
121.051
120.381
117.044
30.418
30.225
30.033
29.840
29.648
29.455
29.263
6e
OH
O
O
Cl
200
150
100
50
0
ppm (t1)

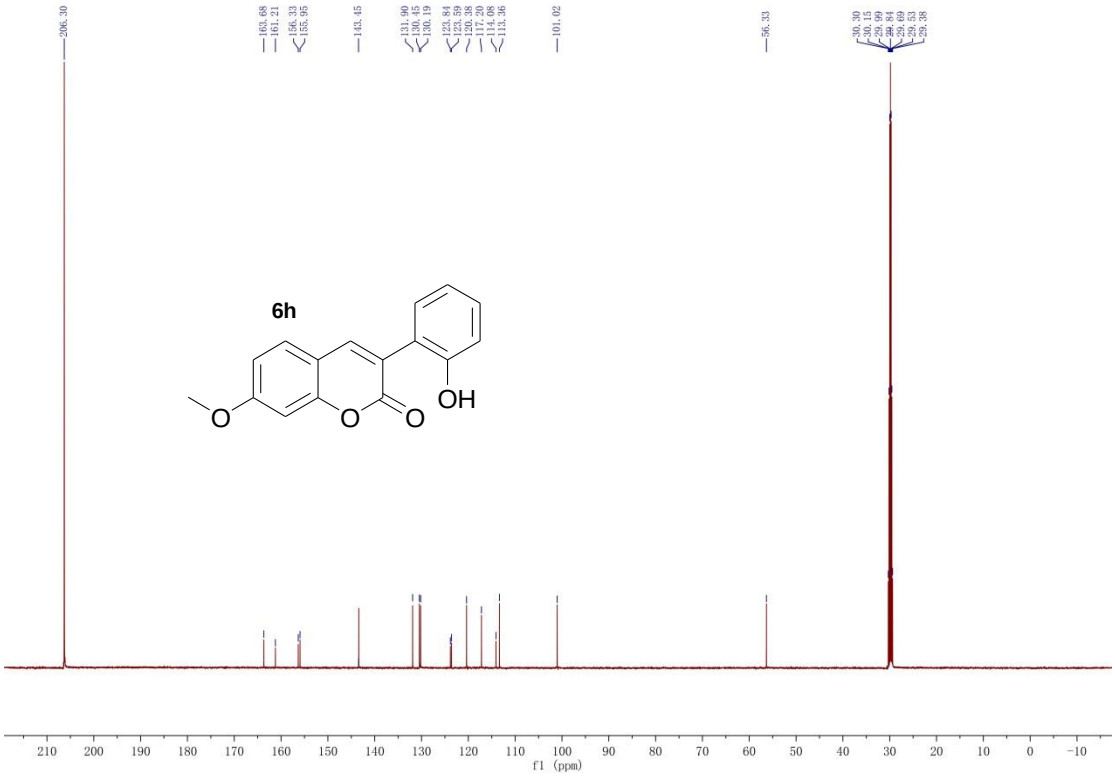

8.529
8.033
7.881
7.878
7.865
7.862
7.763
7.760
7.747
7.745
7.404
7.401
7.389
7.386
7.338
7.323
7.307
7.296
7.262
6.995
6.993
6.979
6.977
6.957
6.925
6f
OH
O
O
Br
1.00
1.00
0.99
1.01
2.00
2.00
1.00
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

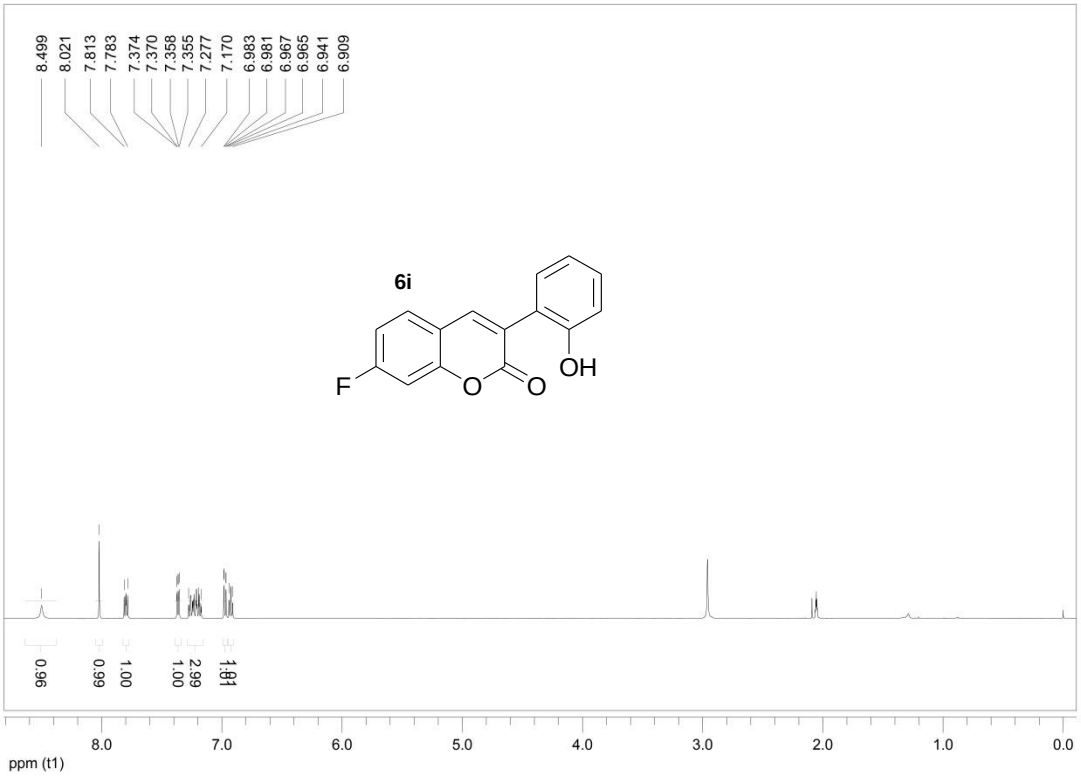

206.20
159.71
155.96
151.13
142.63
135.37
131.86
130.96
128.77
128.04
126.24
123.02
122.08
119.34
116.97
109.73
30.30
30.15
29.99
29.84
29.69
29.53
29.38
6f
OH
O
O
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

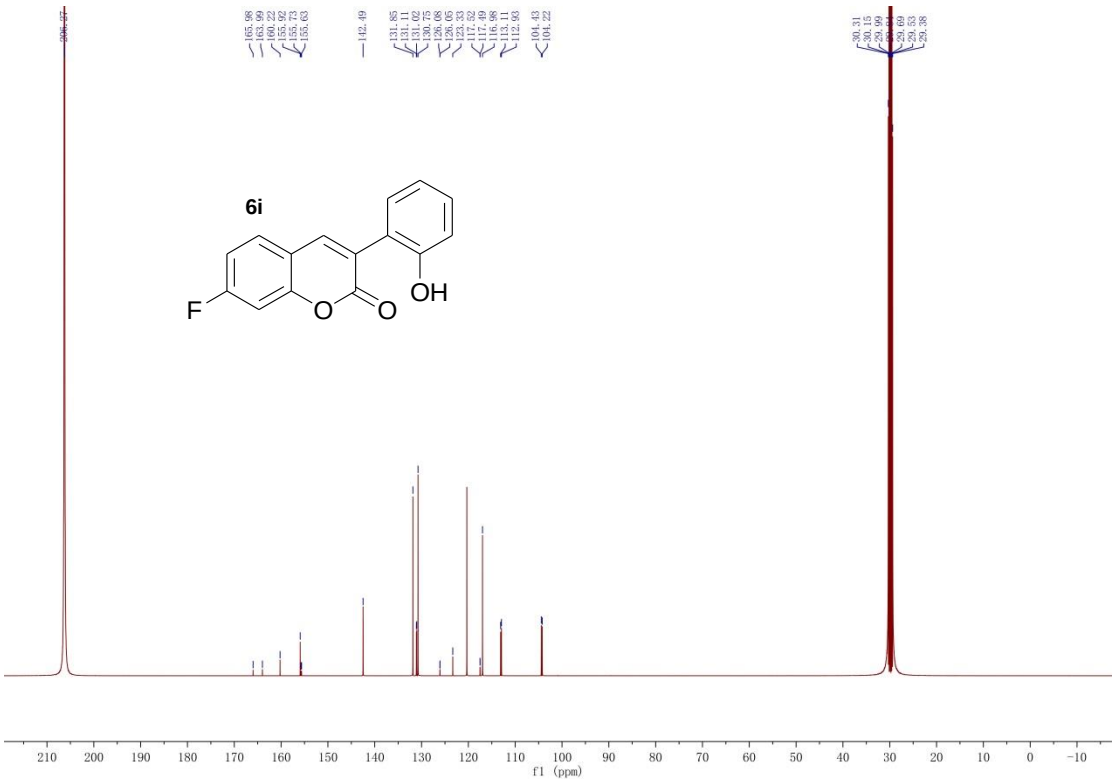

8.445
7.971
7.601
7.585
7.371
7.368
7.356
7.353
7.268
7.234
7.208
7.186
6.978
6.960
6.938
6.906
2.466
6g
OH
O
O
0.92
0.99
1.00
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

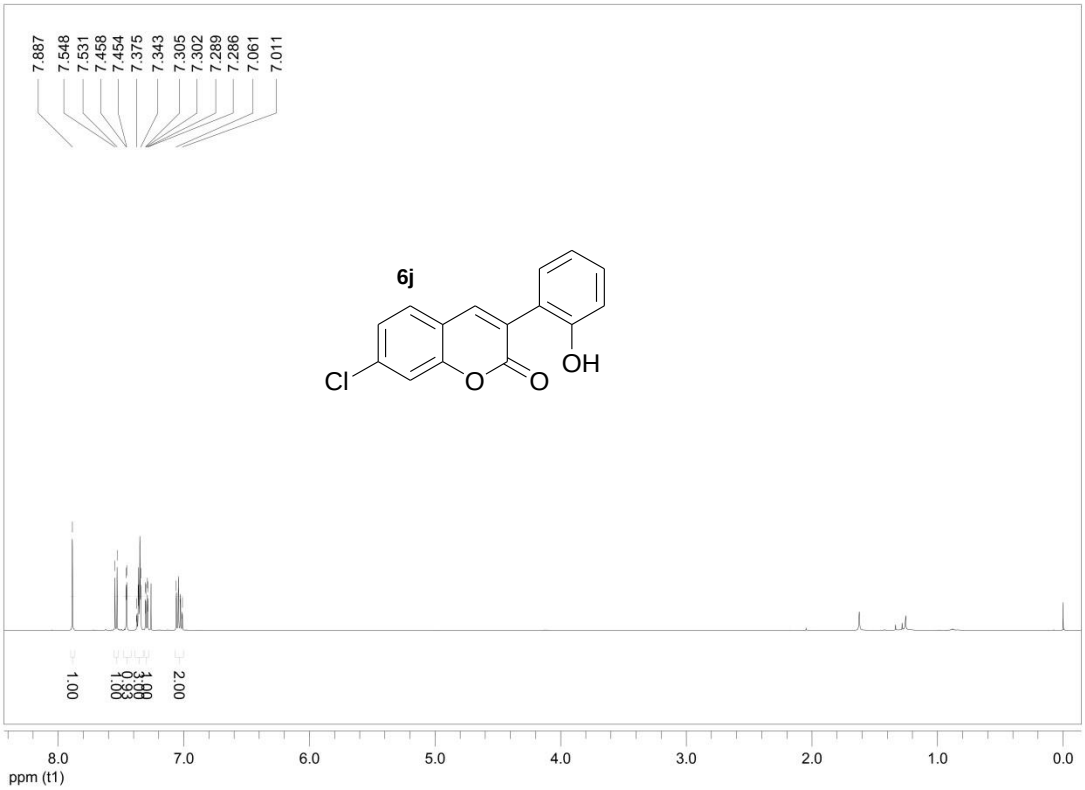

206.289
160.990
155.942
154.626
143.481
143.129
131.889
130.603
128.882
126.394
126.046
123.722
120.364
118.147
117.148
116.972
30.302
30.149
29.995
29.840
29.687
29.534
29.378
21.650
6g
OH
O
O
200
150
100
50
0
ppm (t1)

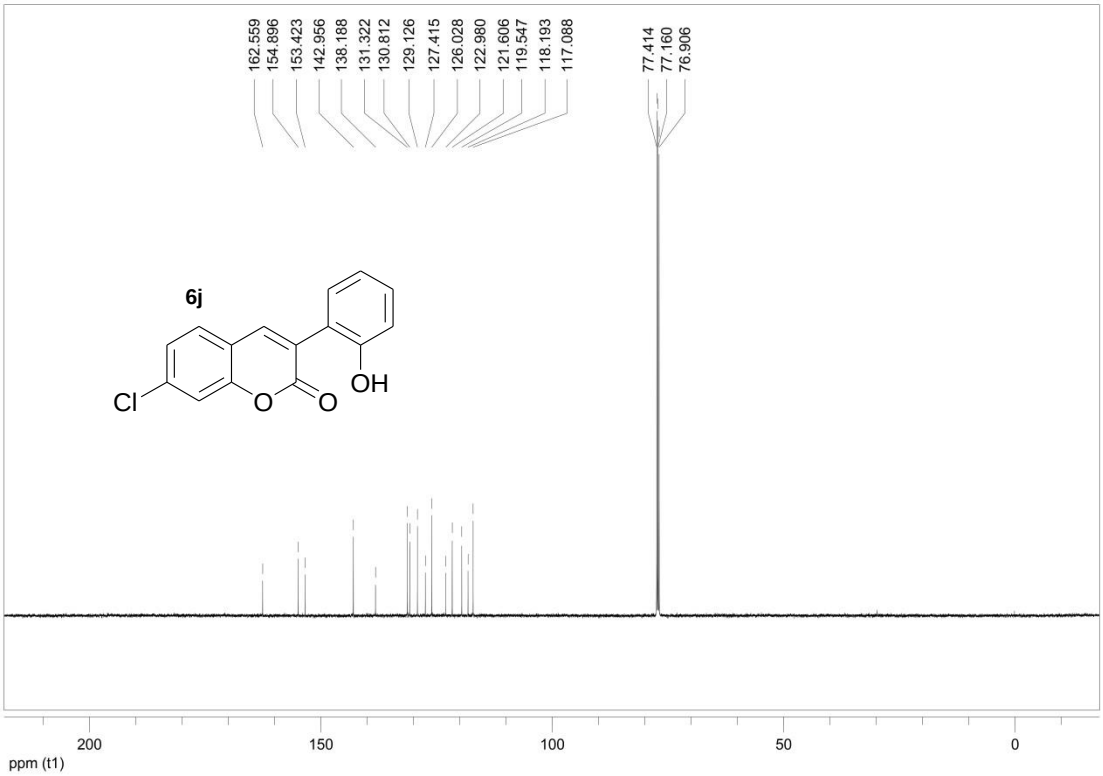

8.424
7.960
7.642
7.625
7.366
7.363
7.351
7.347
7.260
7.225
6.970
6.901
3.939
6h
OH
O
O
O
0.97
1.00
1.01
1.00
1.00
4.02
3.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

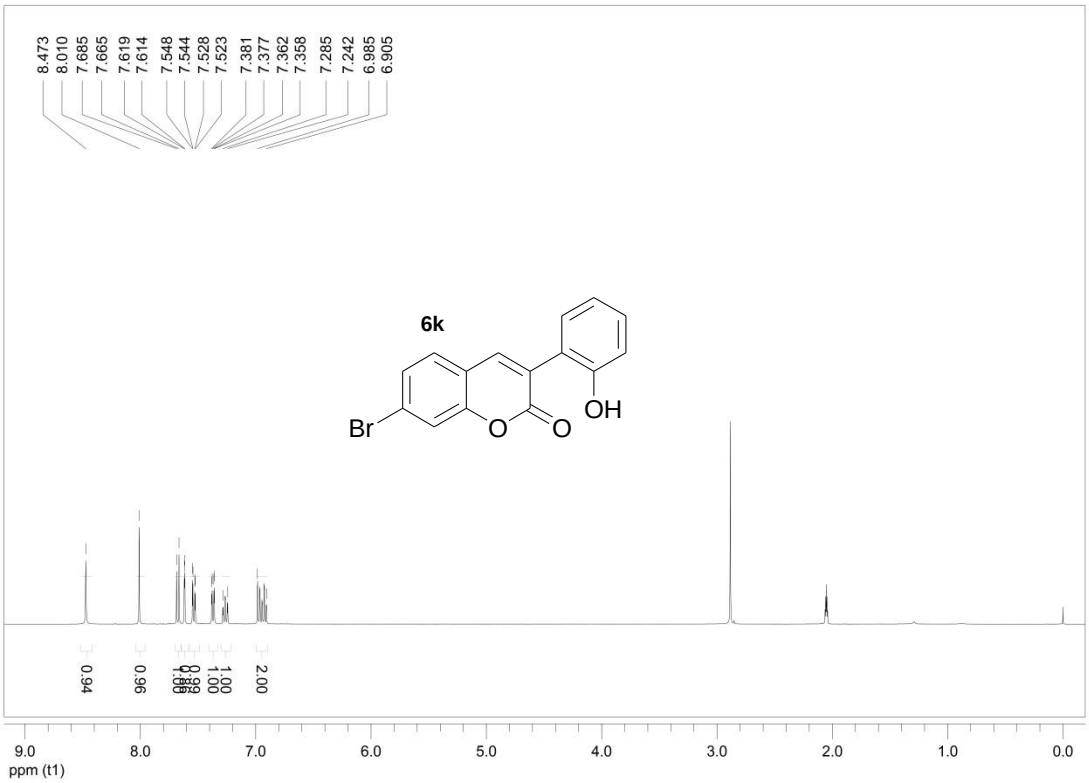

206.30
163.68
161.21
156.33
155.95
143.45
131.90
130.45
130.19
123.84
123.59
120.38
117.20
114.98
113.36
101.02
56.33
30.39
30.15
29.99
29.84
29.69
29.53
29.38
6h
OH
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

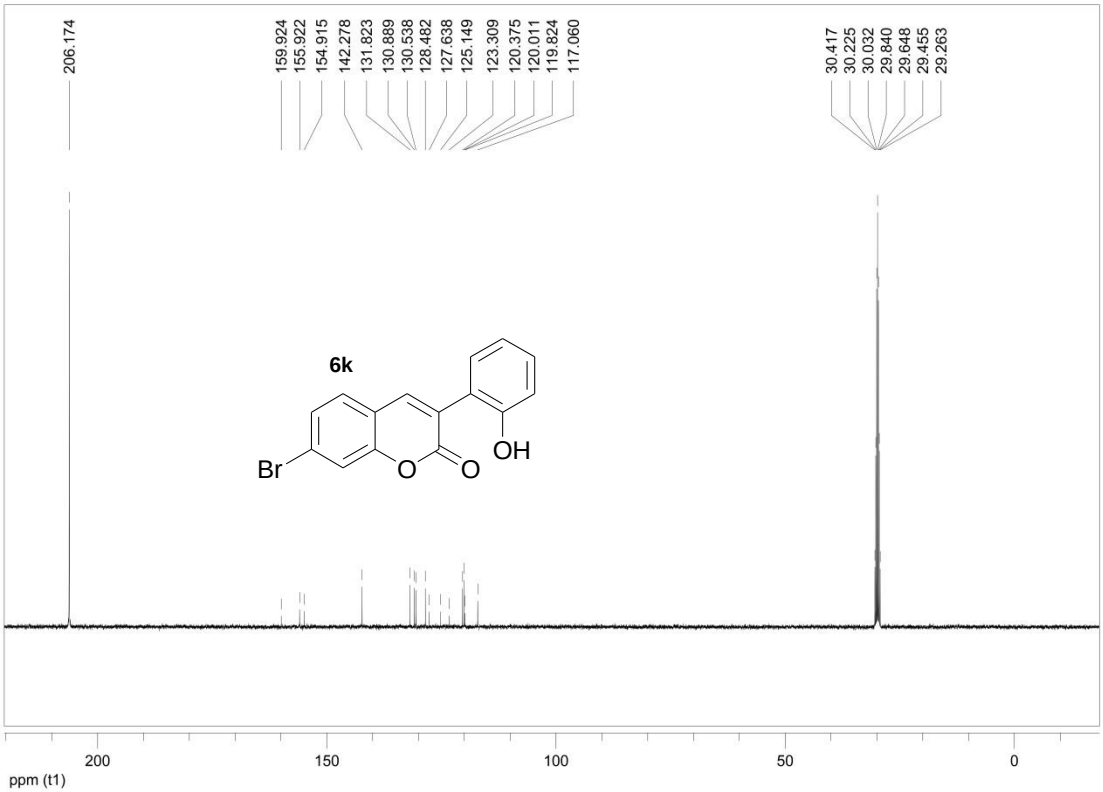

8.499
8.021
7.813
7.783
7.374
7.370
7.358
7.355
7.277
7.170
6.983
6.981
6.967
6.965
6.941
6.909
6i
F
O
O
OH
0.96
0.99
1.00
2.99
1.81
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

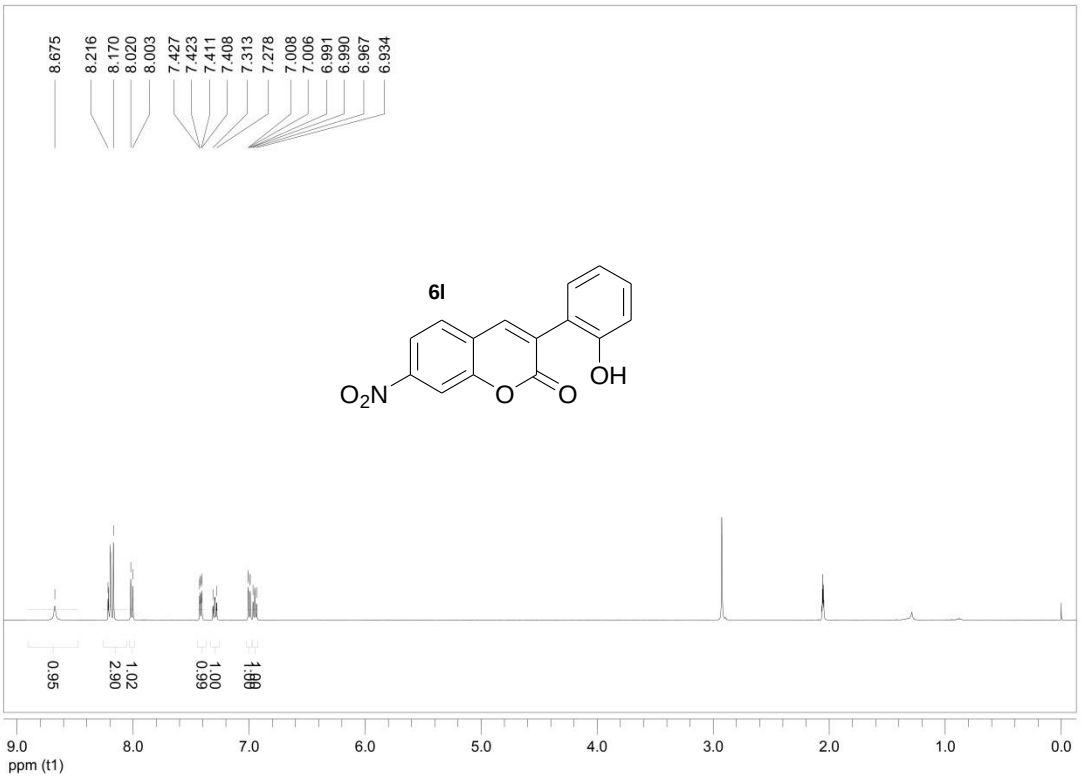

206.27
165.98
163.99
160.22
155.92
155.73
155.63
142.49
131.85
131.11
131.02
130.75
126.68
126.65
123.33
117.52
117.49
116.98
115.11
112.93
104.43
104.22
30.31
30.15
29.99
29.69
29.53
29.38
6i
F
O
O
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

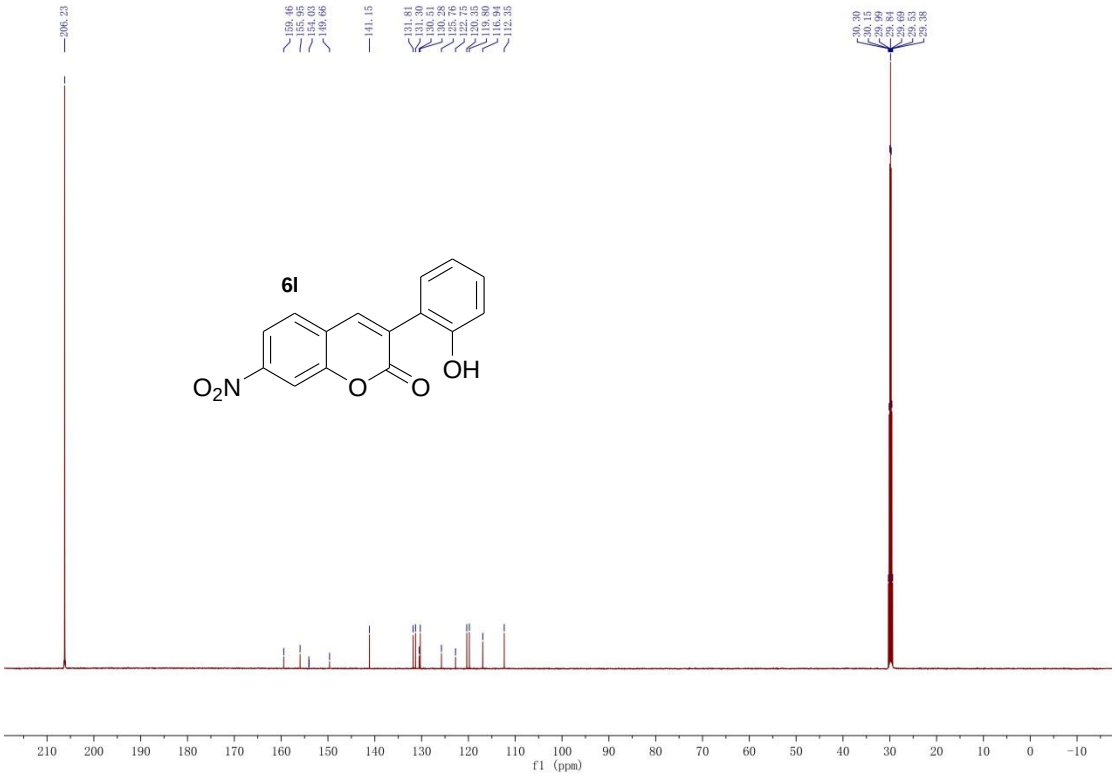

7.887
7.548
7.531
7.458
7.454
7.375
7.343
7.305
7.302
7.289
7.286
7.061
7.011
6j
Cl
O
O
OH
1.00
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

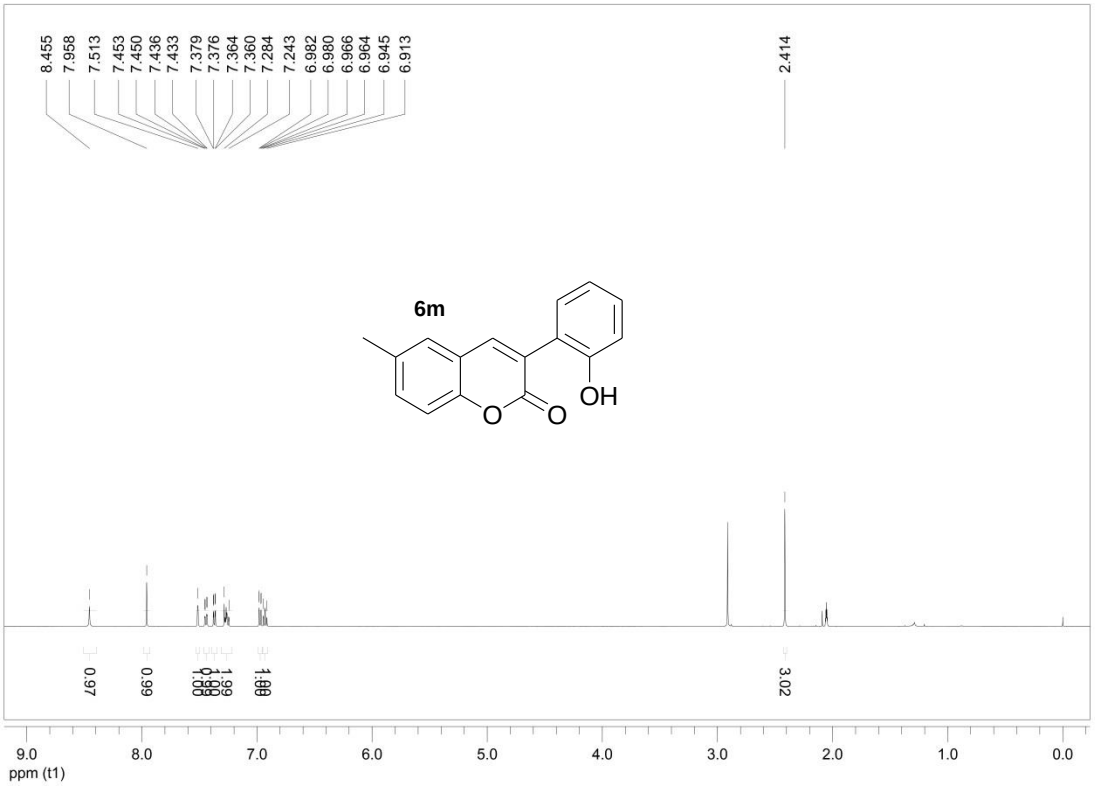

162.559
154.896
153.423
142.956
138.188
131.322
130.812
129.126
127.415
126.028
122.980
121.606
119.547
118.193
117.088
77.414
77.160
76.906
6j
Cl
O
O
OH
200
150
100
50
0
ppm (t1)

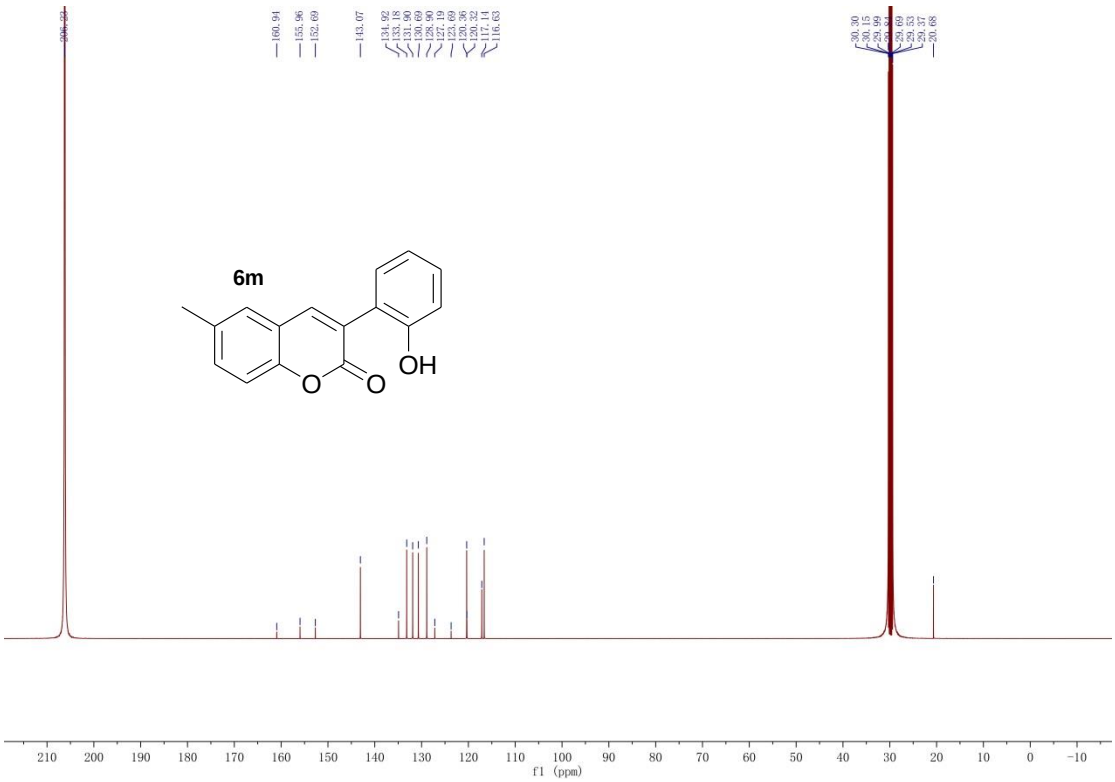

8.473
8.010
7.685
7.665
7.619
7.614
7.548
7.544
7.528
7.523
7.381
7.377
7.362
7.358
7.285
7.242
6.985
6.905
6k
Br
O
O
OH
0.94
0.96
1.00
1.00
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

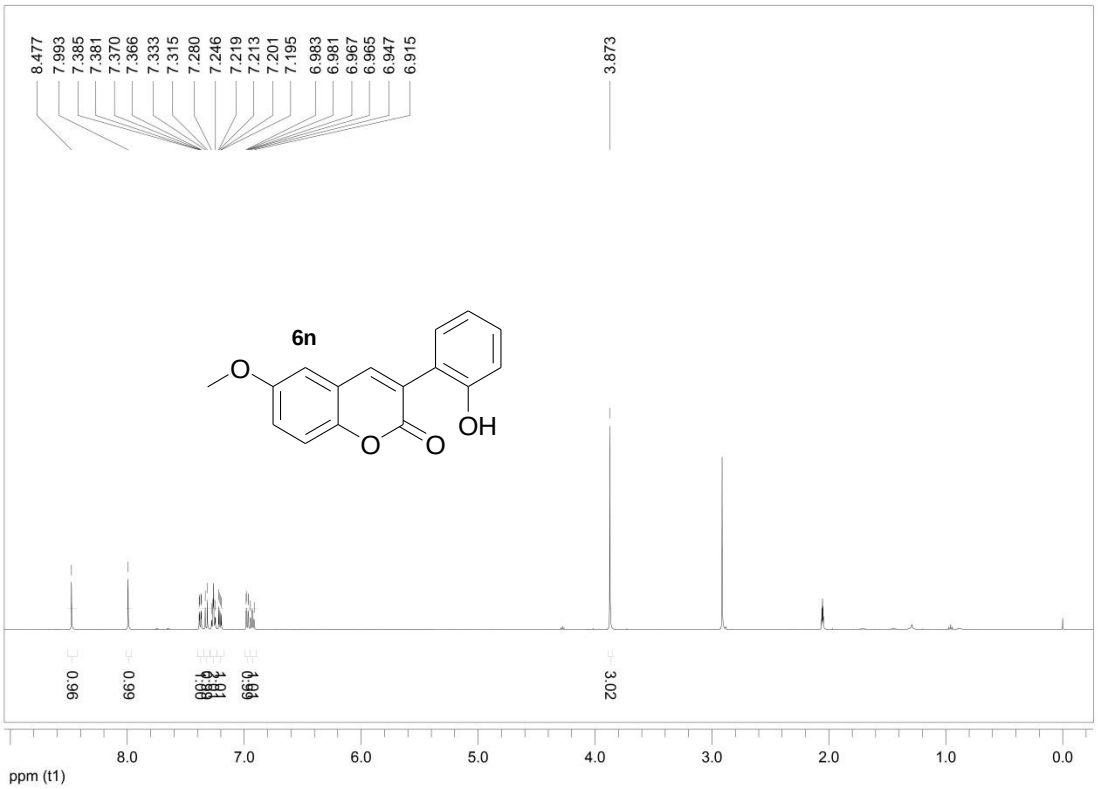

206.174
159.924
155.922
154.915
142.278
131.823
130.889
130.538
128.482
127.638
125.149
123.309
120.375
120.011
119.824
117.060
30.417
30.225
30.032
29.840
29.648
29.455
29.263
6k
Br
O
O
OH
200
150
100
50
0
ppm (t1)

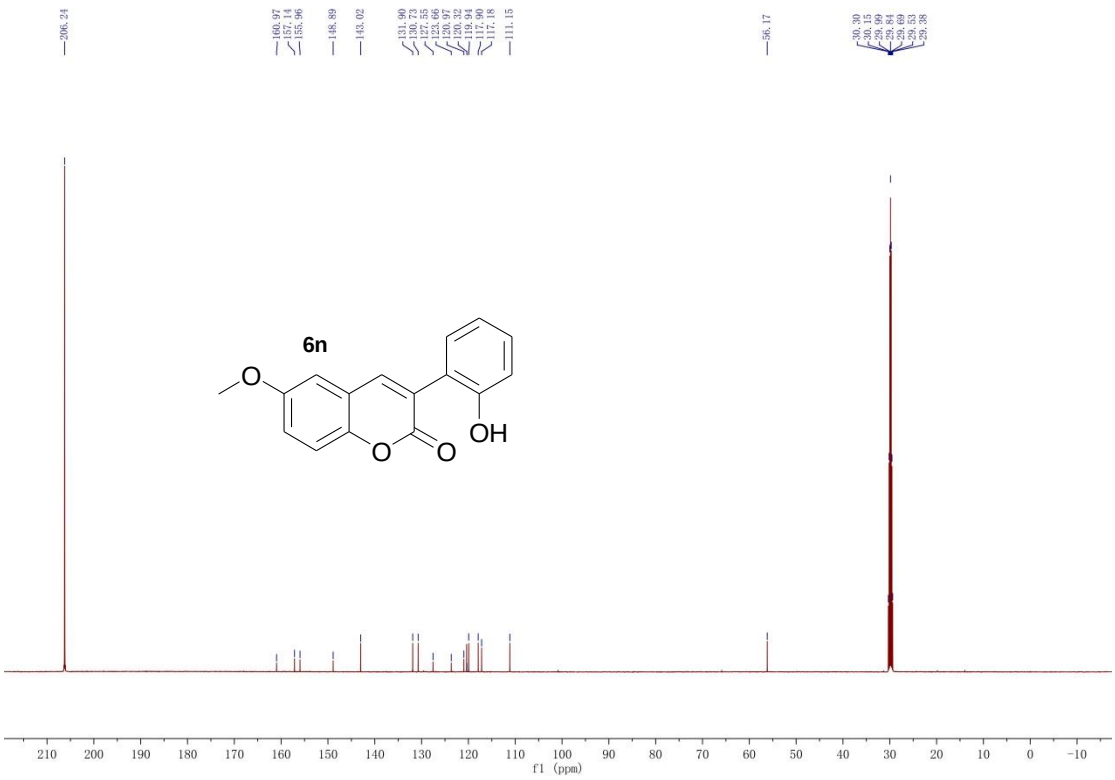

8.675
8.216
8.170
8.020
8.003
7.427
7.423
7.411
7.408
7.313
7.278
7.008
7.006
6.991
6.990
6.967
6.934
6l
O2N
O
O
OH
0.96
2.96
1.02
0.99
1.00
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

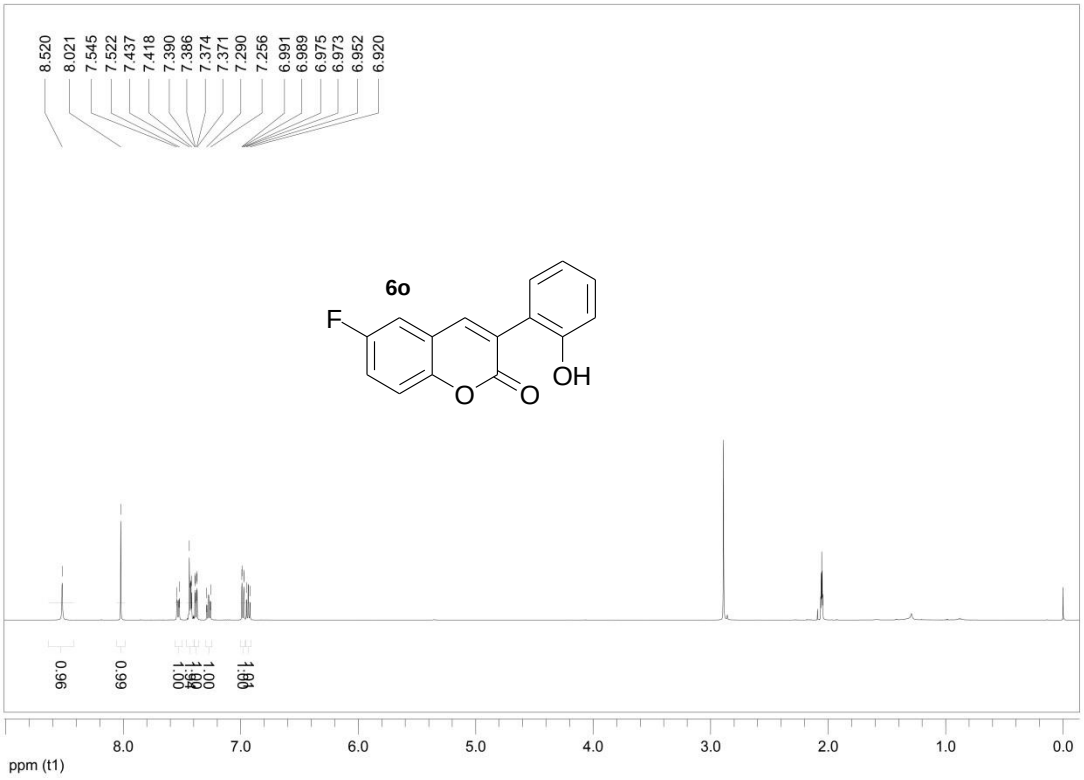

206.23
159.46
155.95
154.03
148.86
141.15
131.81
131.30
130.51
130.28
125.76
122.75
120.35
119.80
116.94
112.35
30.30
30.15
29.99
29.84
29.69
29.53
29.38
6l
O2N
O
O
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

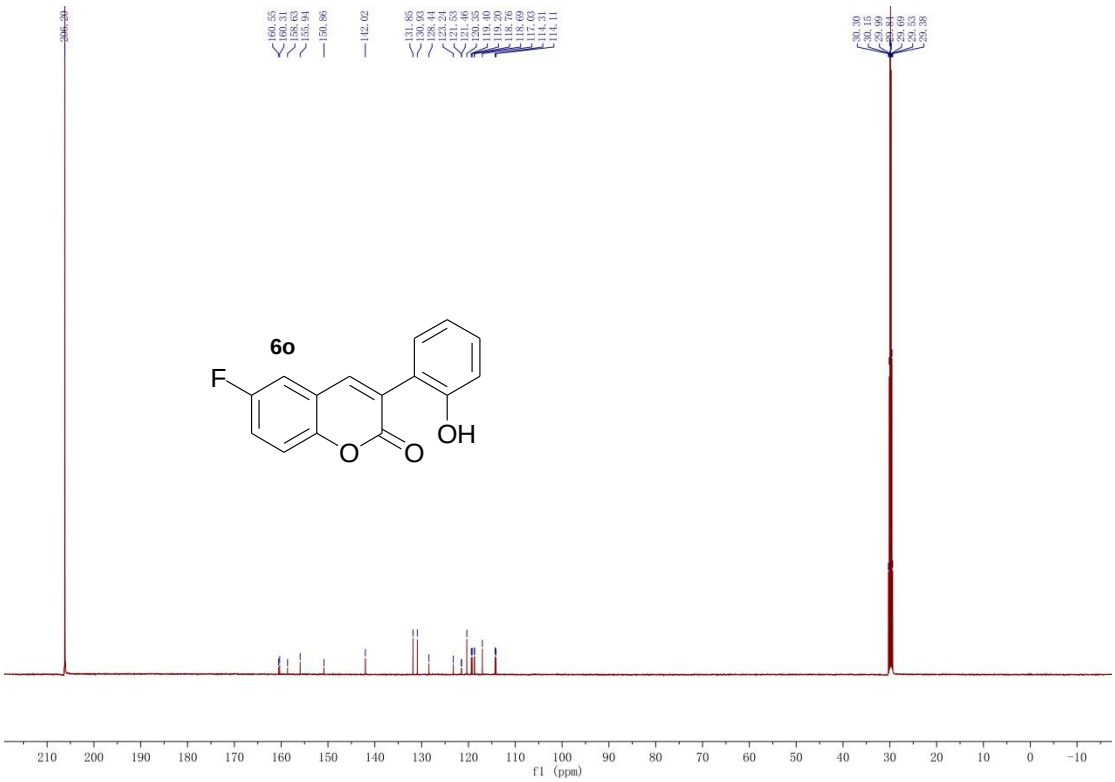

8.455
7.958
7.513
7.453
7.450
7.436
7.433
7.379
7.376
7.364
7.360
7.284
7.243
6.982
6.980
6.966
6.964
6.945
6.913
2.414
6m
OH
O
O
0.97
0.99
3.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

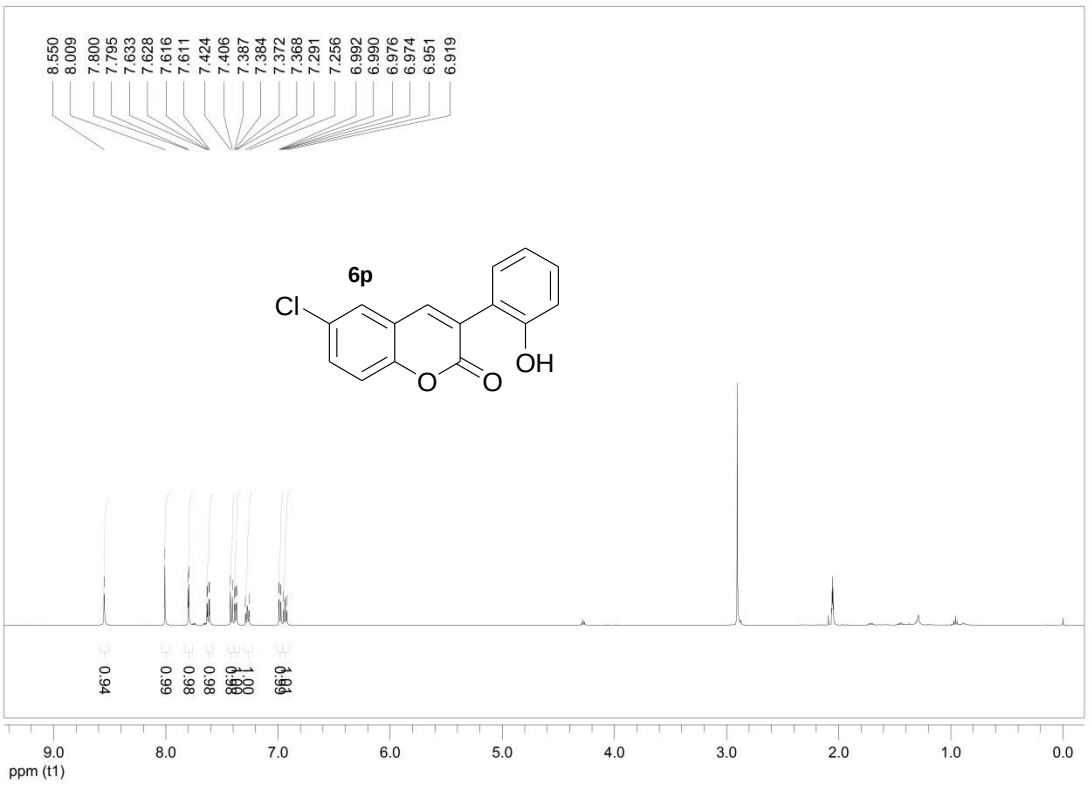

206.28
160.94
155.96
152.69
143.07
134.92
133.18
131.90
130.69
128.90
127.19
123.69
120.36
120.32
117.14
116.63
30.30
30.15
29.99
29.84
29.69
29.53
29.37
20.68
6m
OH
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

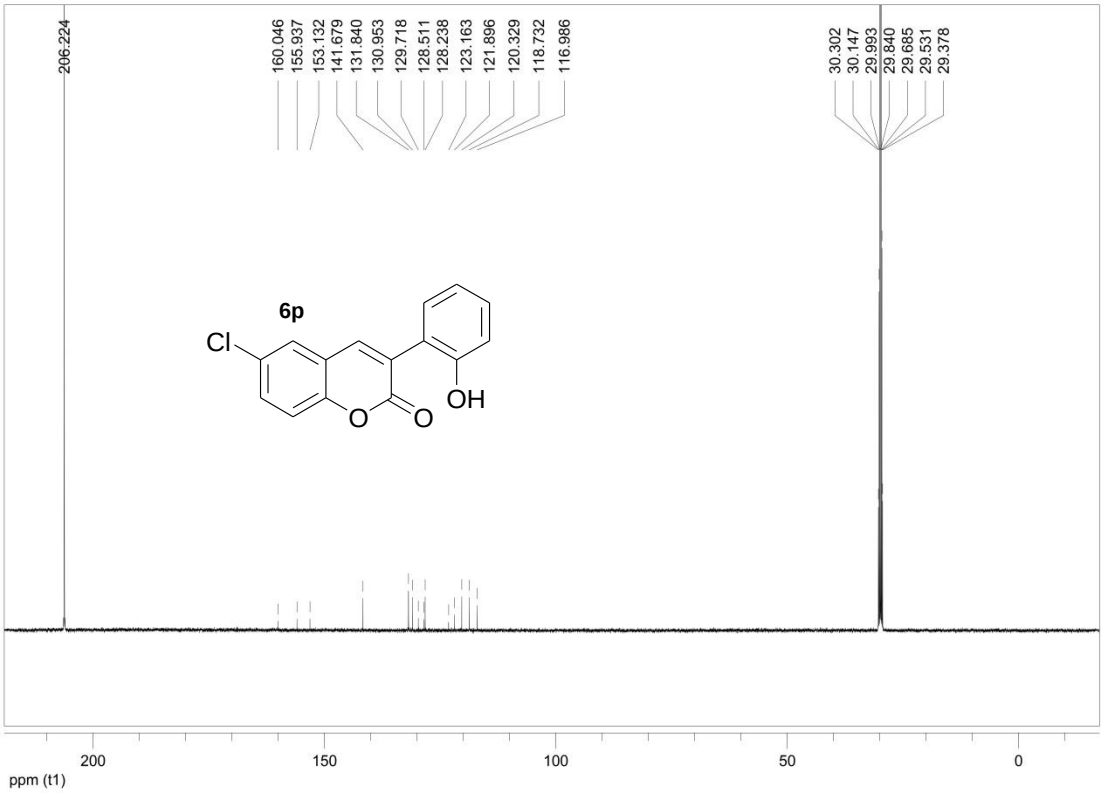

8.477
7.993
7.385
7.381
7.370
7.366
7.333
7.315
7.280
7.246
7.219
7.213
7.201
7.195
6.983
6.981
6.967
6.965
6.947
6.915
3.873
6n
O
O
O
OH
0.96
0.99
1.01
0.91
3.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

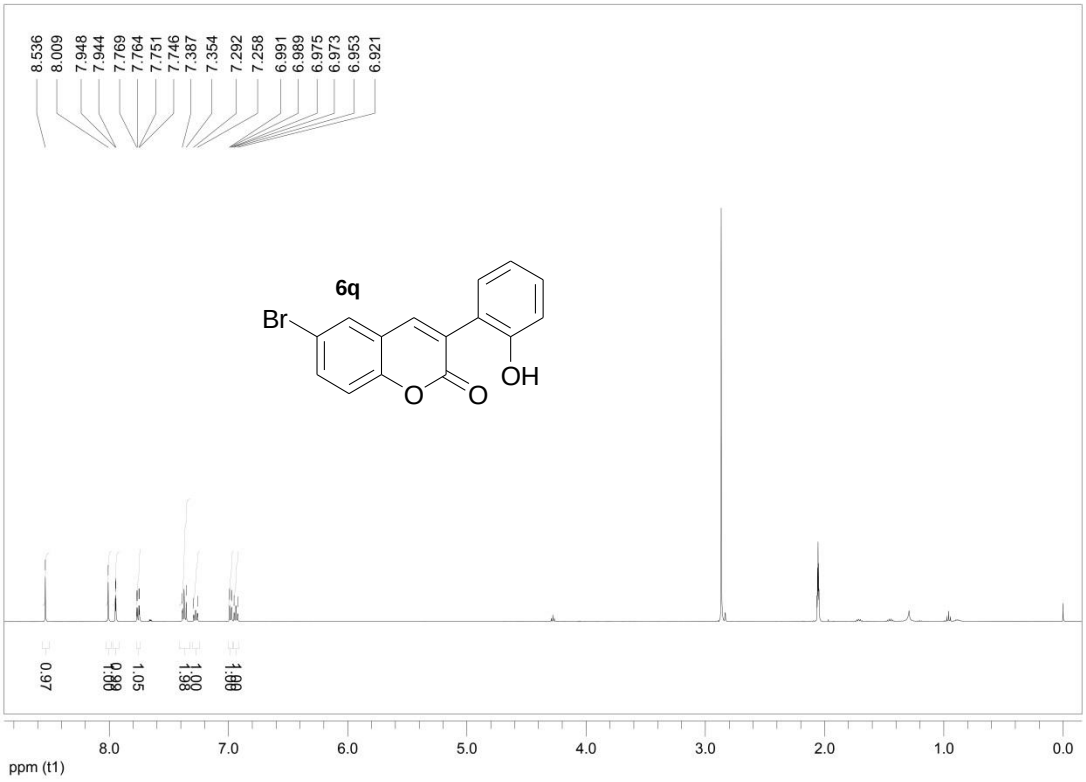

206.24
160.97
157.14
155.96
148.89
143.02
131.90
130.73
127.55
123.66
120.97
120.32
119.94
117.90
117.18
111.15
56.17
30.39
30.15
29.99
29.84
29.69
29.53
29.38
6n
O
O
O
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

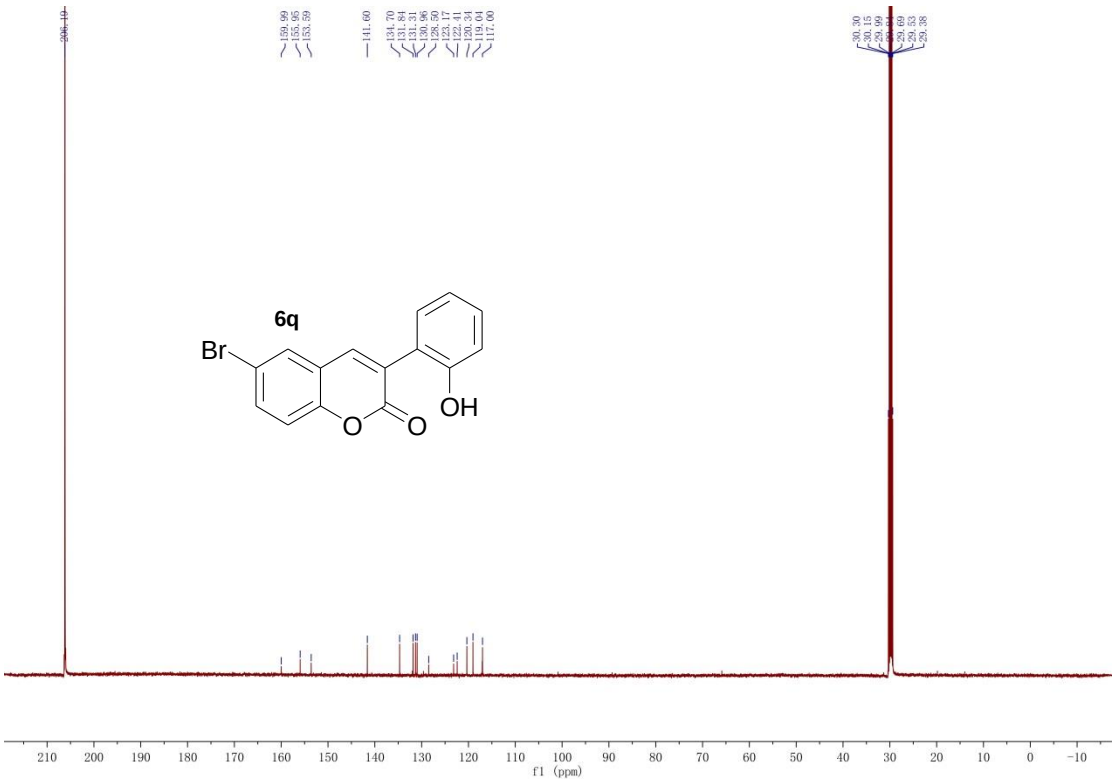

8.520
8.021
7.545
7.522
7.437
7.418
7.390
7.386
7.374
7.371
7.290
7.256
6.991
6.989
6.975
6.973
6.952
6.920
6o
F
O
O
OH
0.96
0.99
1.00
1.00
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

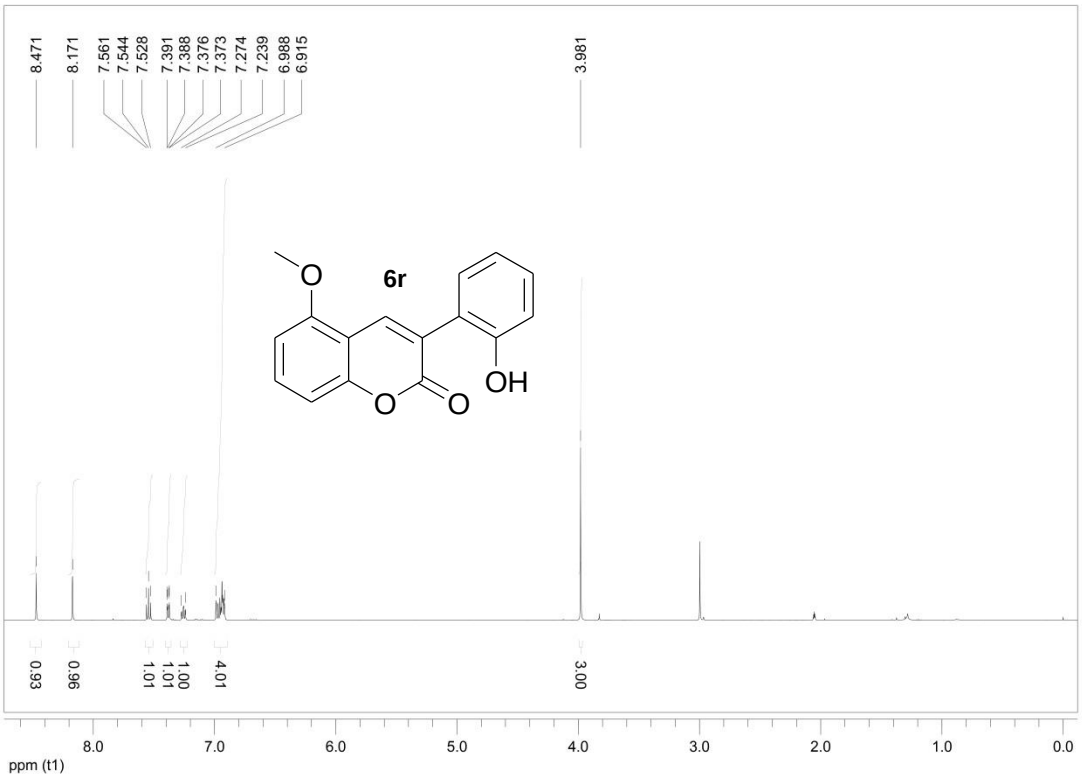

206.20
160.55
160.31
156.65
155.94
150.86
142.02
131.85
130.93
128.44
123.24
121.53
121.46
120.35
119.40
119.20
118.76
118.69
117.03
114.31
114.11
30.30
30.15
29.99
29.84
29.69
29.53
29.38
6o
F
O
O
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

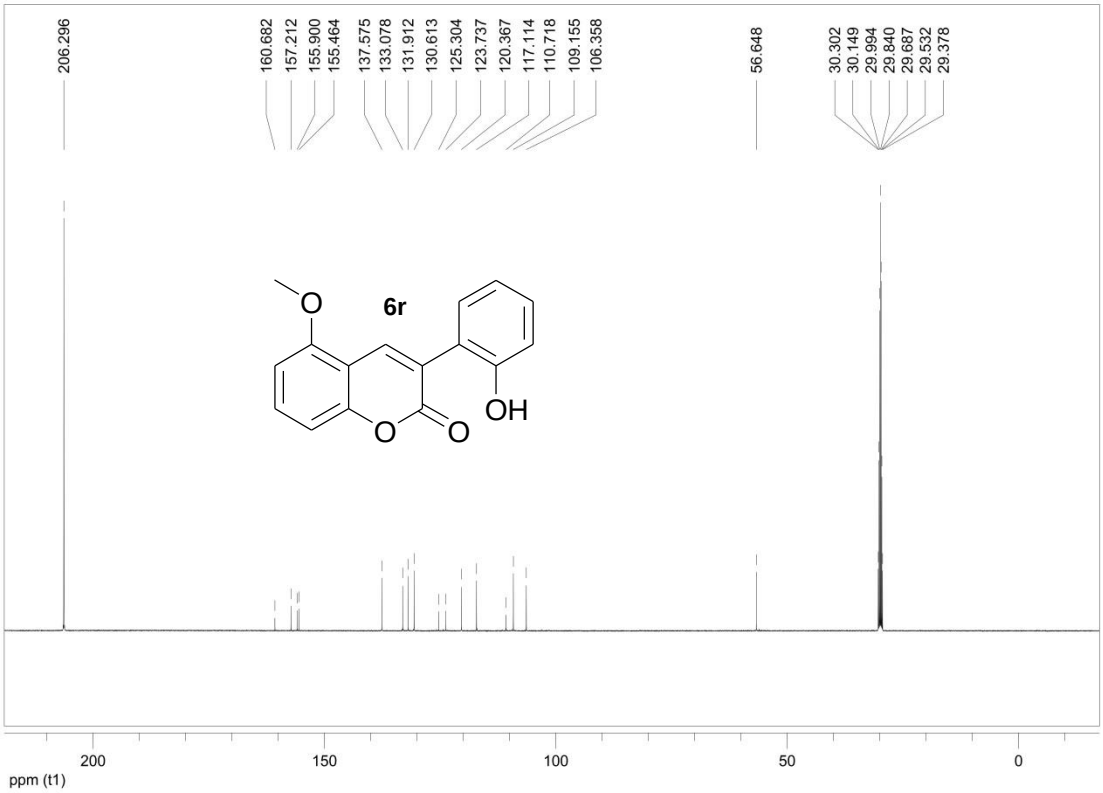

8.550
8.009
7.800
7.795
7.633
7.628
7.616
7.611
7.424
7.406
7.387
7.384
7.372
7.368
7.291
7.256
6.992
6.990
6.976
6.974
6.951
6.919
6p
Cl
OH
O
O
0.94
0.99
0.98
0.98
1.00
1.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

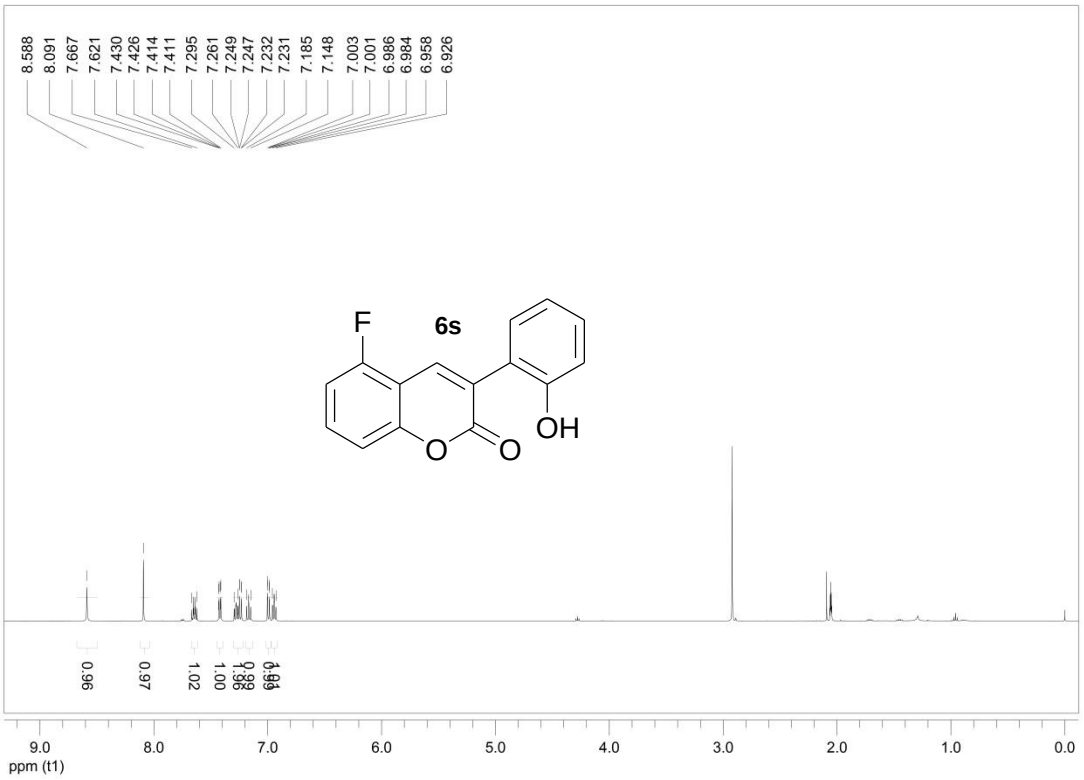

206.224
160.046
155.937
153.132
141.679
131.840
130.953
129.718
128.511
128.238
123.163
121.896
120.329
118.732
116.986
30.302
30.147
29.993
29.840
29.685
29.531
29.378
6p
Cl
OH
O
O
200
150
100
50
0
ppm (t1)

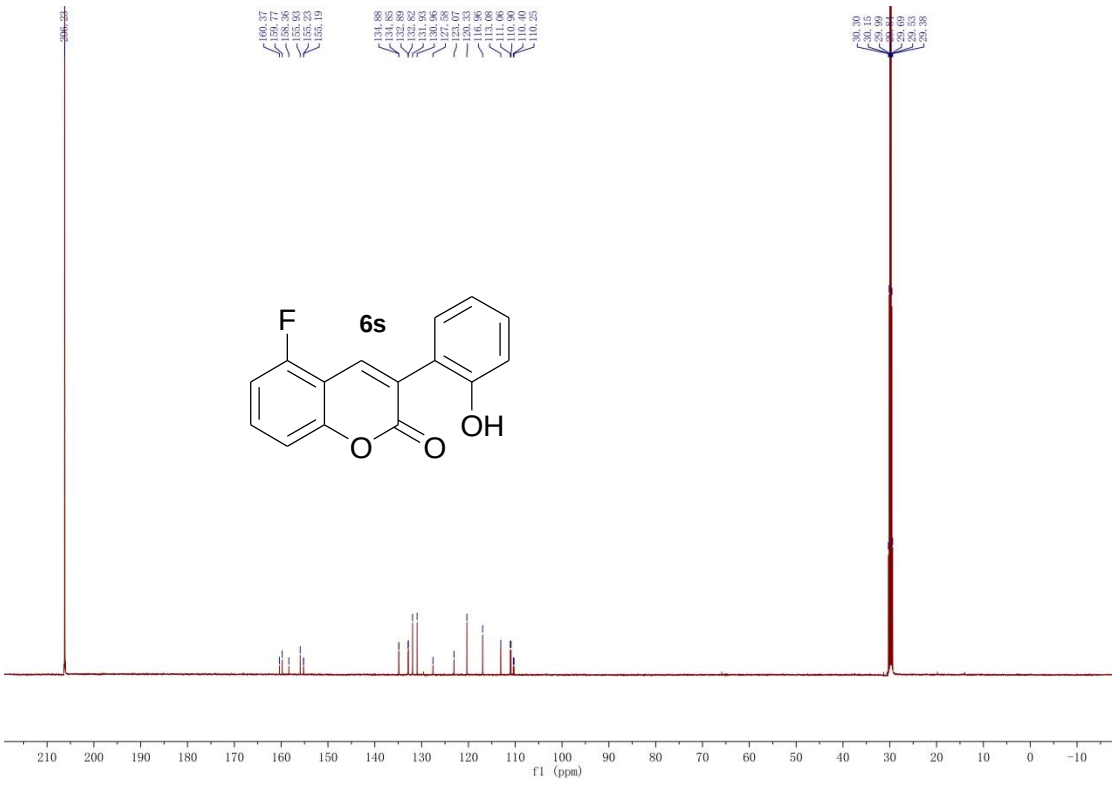

8.536
8.009
7.948
7.944
7.769
7.764
7.751
7.746
7.387
7.354
7.292
7.258
6.991
6.989
6.975
6.973
6.953
6.921
6q
Br
O
O
OH
0.97
1.05
ppm (t1)

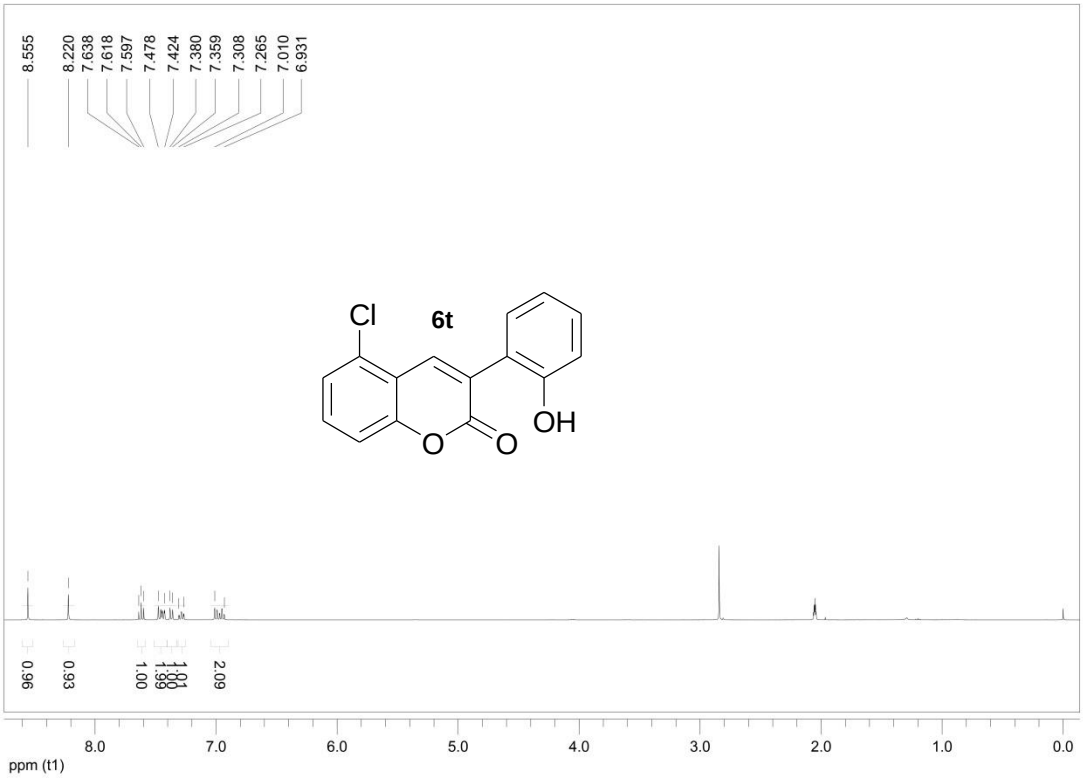

206.10
159.99
155.95
153.59
141.60
134.70
131.84
131.31
130.96
128.59
123.17
122.41
120.34
119.04
117.60
30.30
30.15
29.99
29.84
29.69
29.53
29.38
6q
Br
O
O
OH
f1 (ppm)

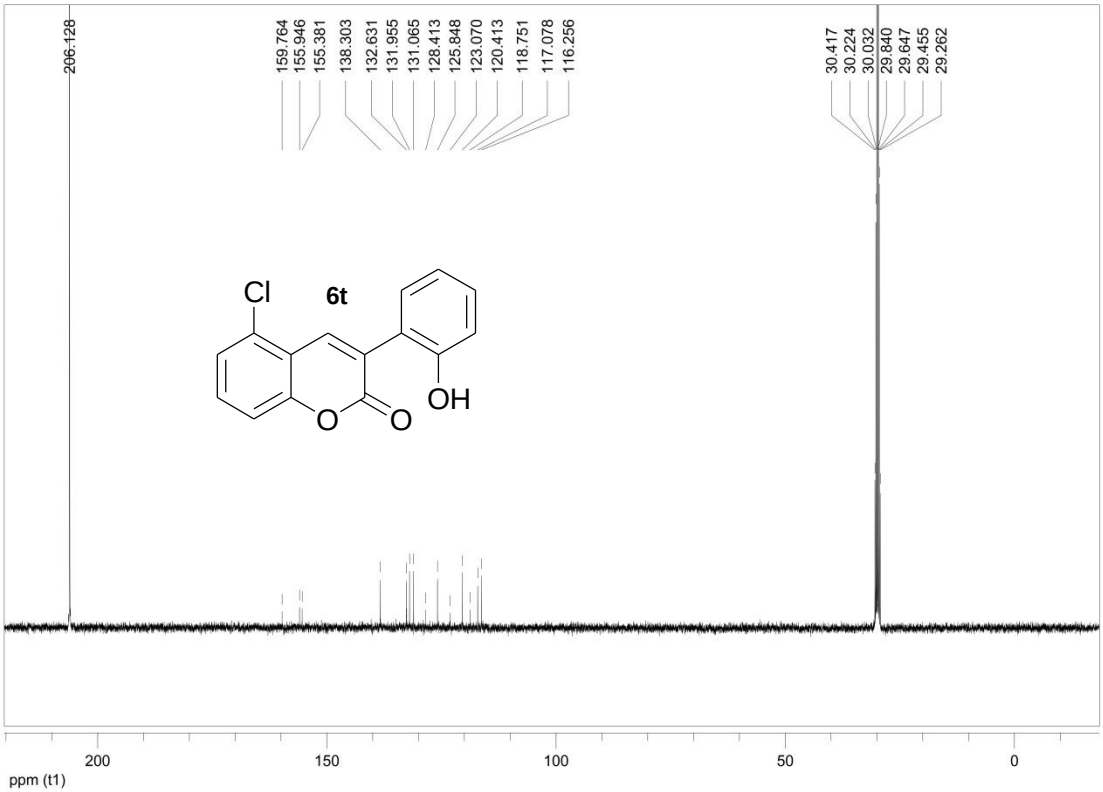

8.471
8.171
7.561
7.544
7.528
7.391
7.388
7.376
7.373
7.274
7.239
6.988
6.915
3.981
6r
O
OH
O
O
0.93
0.96
1.01
1.01
1.00
4.01
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

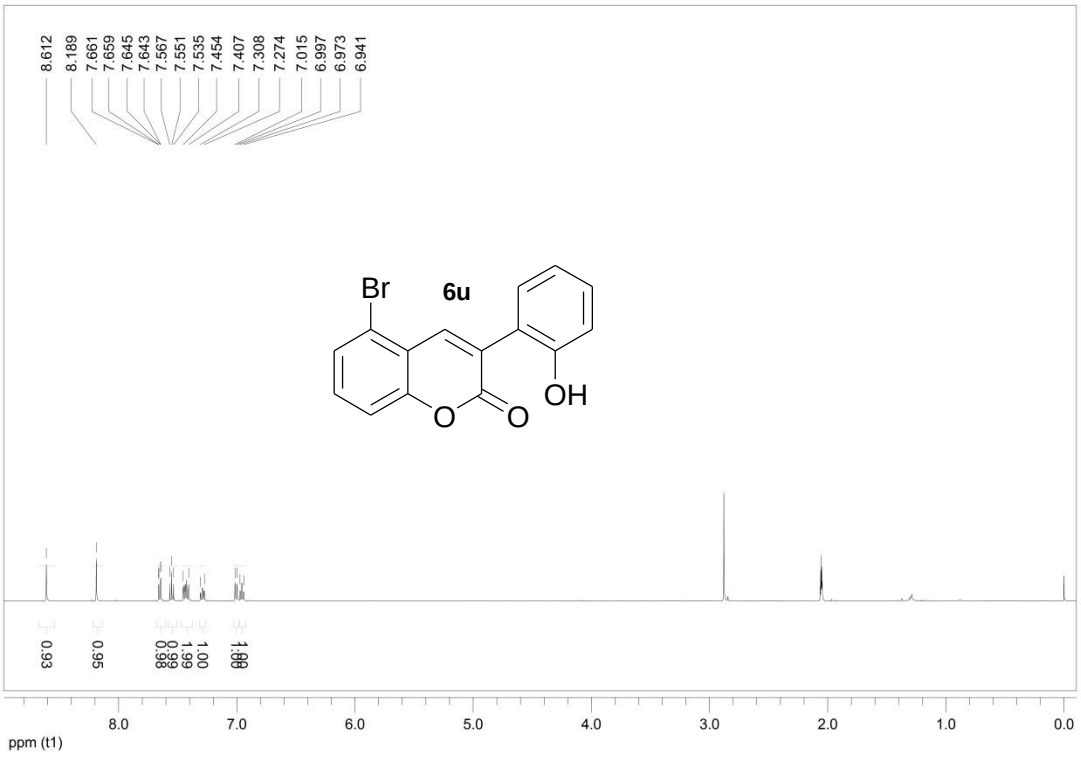

206.296
160.682
157.212
155.900
155.464
137.575
133.078
131.912
130.613
125.304
123.737
120.367
117.114
110.718
109.155
106.358
56.648
30.302
30.149
29.994
29.840
29.687
29.532
29.378
6r
O
OH
O
O
200
150
100
50
0
ppm (t1)

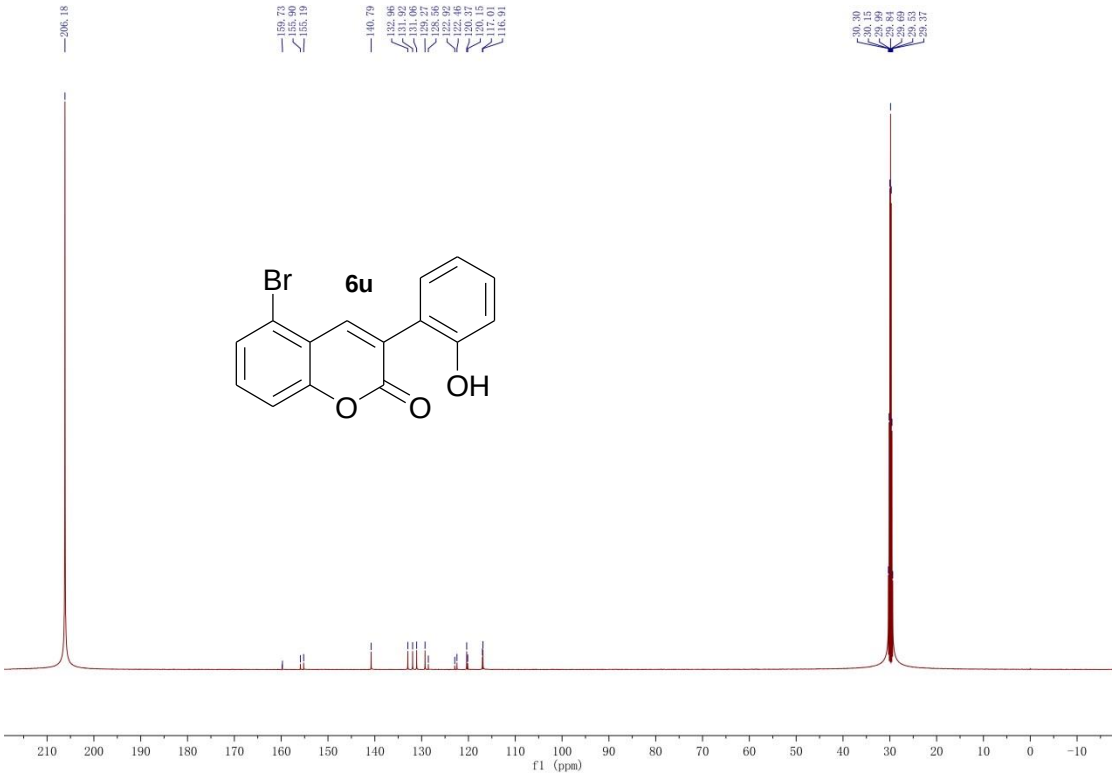

8.588
8.091
7.667
7.621
7.430
7.426
7.414
7.411
7.295
7.261
7.249
7.247
7.232
7.231
7.185
7.148
7.003
7.001
6.986
6.984
6.958
6.926
F
6s
O
O
OH
0.96
0.97
1.02
1.00
1.06
0.99
1.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


206.23
160.37
159.77
158.36
155.60
155.23
155.19
134.88
134.85
132.89
132.82
131.65
131.56
127.58
123.07
120.33
116.96
113.08
111.06
110.90
110.40
110.25
30.30
30.15
29.99
29.84
29.69
29.53
29.38
F
6s
O
O
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

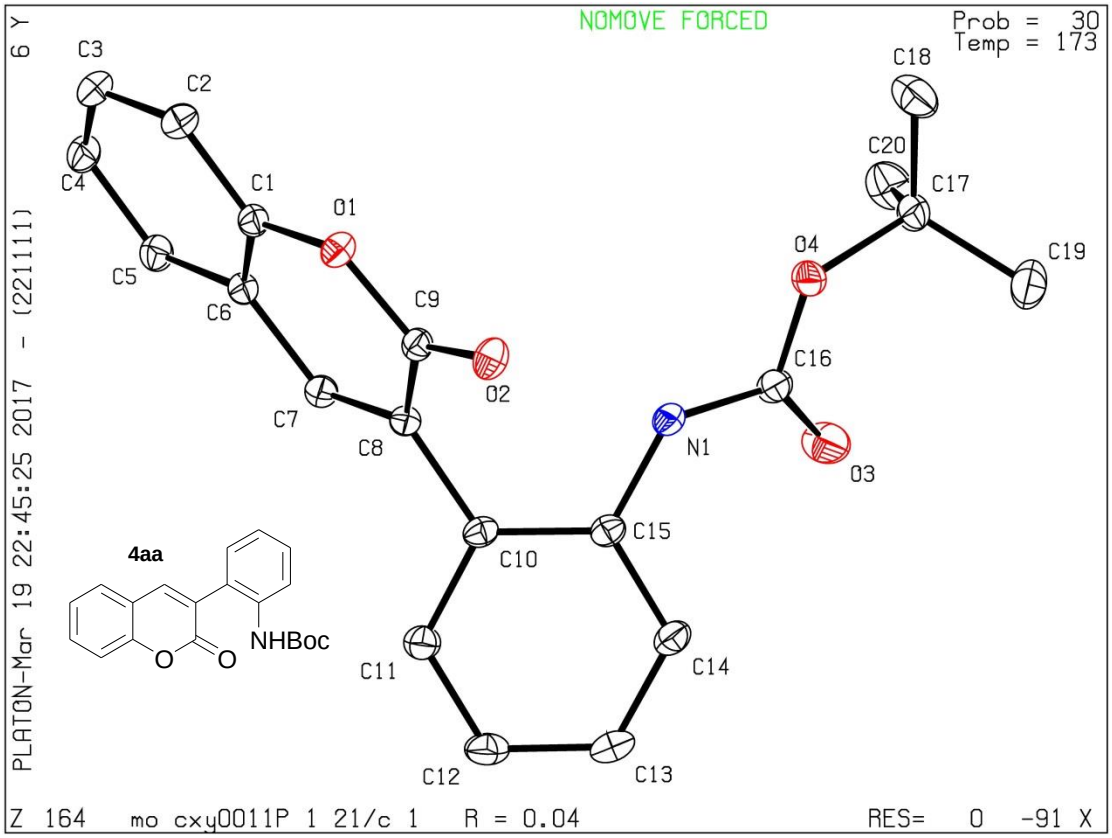

8.555
8.220
7.638
7.618
7.597
7.478
7.424
7.380
7.359
7.308
7.265
7.010
6.931
Cl
6t
OH
O
O
0.96
0.93
1.00
2.09
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


206.128
159.764
155.946
155.381
138.303
132.631
131.955
131.065
128.413
125.848
123.070
120.413
118.751
117.078
116.256
30.417
30.224
30.032
29.840
29.647
29.455
29.262
Cl
6t
OH
O
O
200
150
100
50
0
ppm (t1)

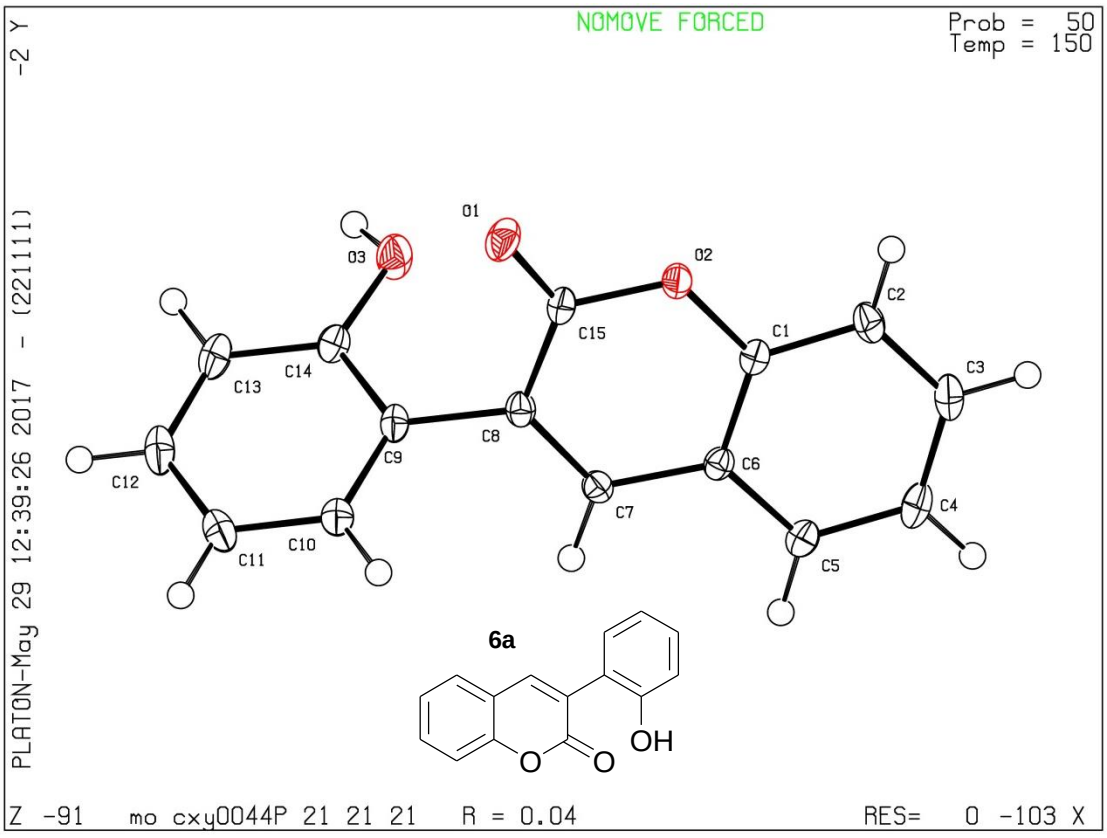

8.612
8.189
7.661
7.659
7.645
7.643
7.567
7.551
7.535
7.454
7.407
7.308
7.274
7.015
6.997
6.973
6.941
Br
6u
OH
O
O
0.93
0.95
0.98
1.99
1.00
1.00
ppm (t1)


206.18
159.73
155.90
155.19
140.79
132.96
131.92
131.06
128.27
126.86
122.92
122.46
120.37
120.15
117.01
116.91
30.30
30.15
29.99
29.84
29.69
29.53
29.37
Br
6u
OH
O
O
f1 (ppm)

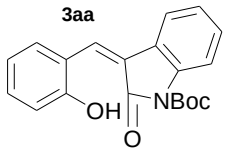
E: Single crystal X-ray crystallography of 4aa (CCDC 1555429)



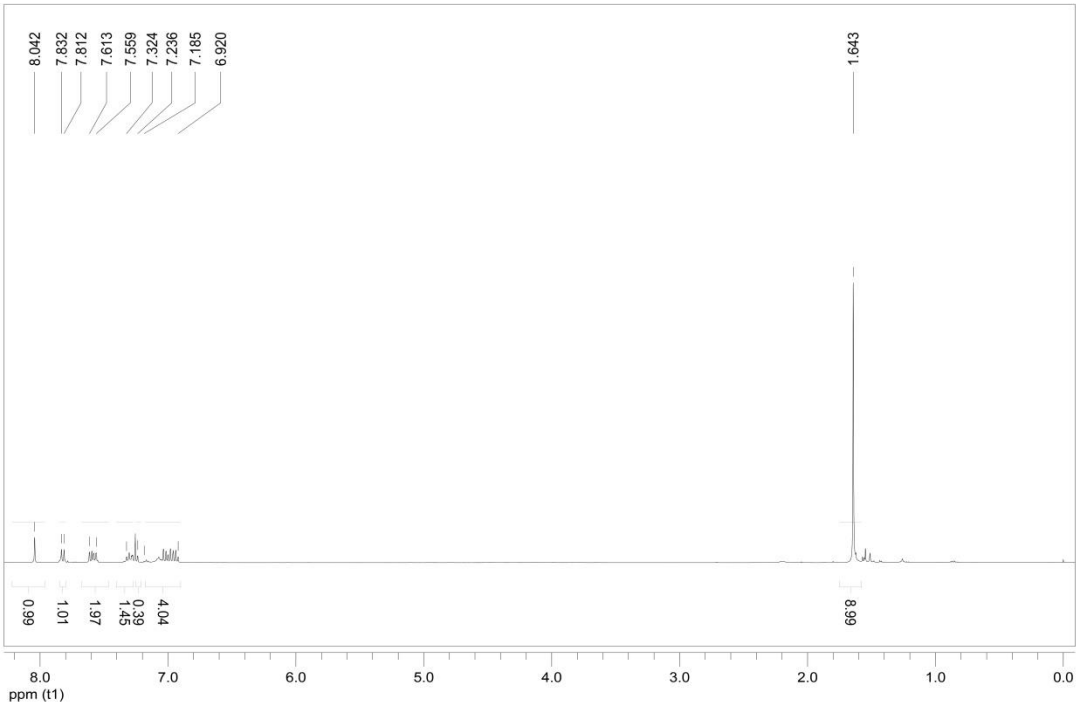
F: Single crystal X-ray crystallography of 6a (CCDC 1555430)

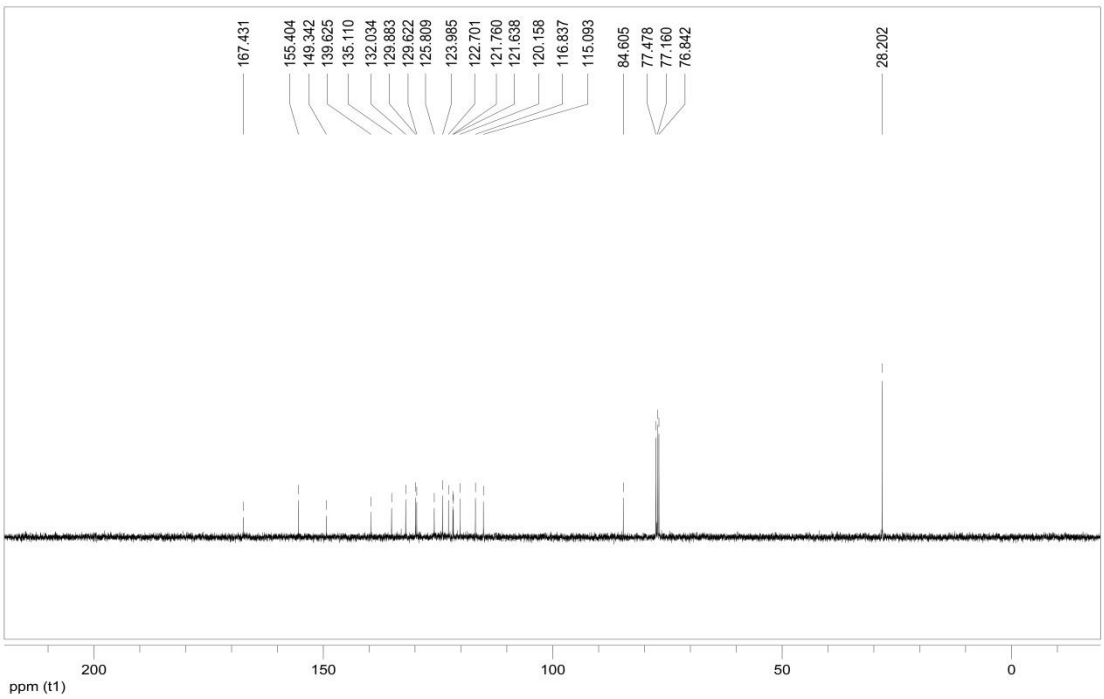


G: Characterization Data, Copies of ^{1}H and ^{13}C NMR spectra of 3aa

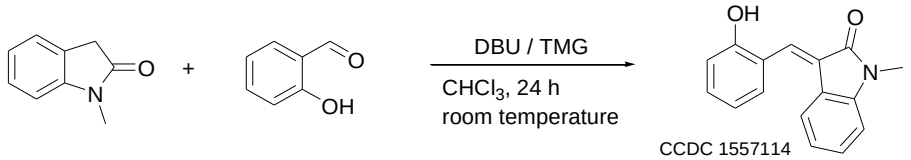


^{1}H NMR (400 Hz, $CDCl_3$): δ (ppm) 8.04 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.61-7.56 (m, 2H), 7.32-7.24 (m, 2H), 7.19-6.92 (m, 4H), 1.64 (s, 9H). ^{13}C NMR (100 Hz, $CDCl_3$): δ (ppm) 167.4, 155.4, 149.3, 139.6, 135.1, 132.0, 129.9, 129.6, 125.8, 124.0, 122.7, 121.8, 121.6, 120.2, 116.8, 115.1, 84.6, 28.2. HRMS: exact mass calculated for $[M+H\text{-}Boc]^{+}$ ($C_{15}H_{12}NO_2$) requires m/z 238.0863, found m/z 238.0858.





H: Single crystal X-ray crystallography of 3-(2-hydroxybenzylidene)-1-methylindolin-2-one (CCDC 1557114)



CCDC 1557114