

Supplementary information

A single precatalyst Tandem RCM-allylic oxidation sequence

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A General Remarks

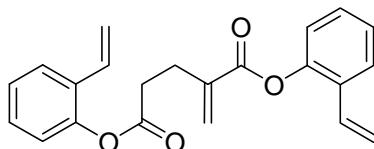
All experiments were conducted in dry reaction vessels under an atmosphere of dry nitrogen. Solvents were purified by standard procedures. ^1H NMR spectra were obtained at 300 MHz in CDCl_3 with Tetramethylsilane ($\delta = 0.00$ ppm) as an internal standard. Coupling constants (J) are given in Hz. ^{13}C NMR spectra were recorded at 75 MHz in CDCl_3 with CDCl_3 ($\delta = 77.0$ ppm) as an internal standard. The number of coupled protons was analyzed APT-experiments and is denoted by a number in parantheses following the chemical shift value. IR spectra were recorded in substance on NaCl or KBr plates. Wavenumbers (ν) are given in cm^{-1} . The peak intensities are defined as strong (s), medium (m) or weak (w). Mass spectra were obtained at 70 eV. The following starting materials were synthesized following literature procedures: **1a**,¹ **4a,c,e,f,g,m,n**,² **4j**,³ **5a**.²

¹ L. Polito, M. Cravini, L. Poletti and L. Lay, *Synth. Commun.*, 2006, **36**, 2203-2209.

² S. Chang and R. H. Grubbs, *J. Org. Chem.*, 1998, **63**, 864-866.

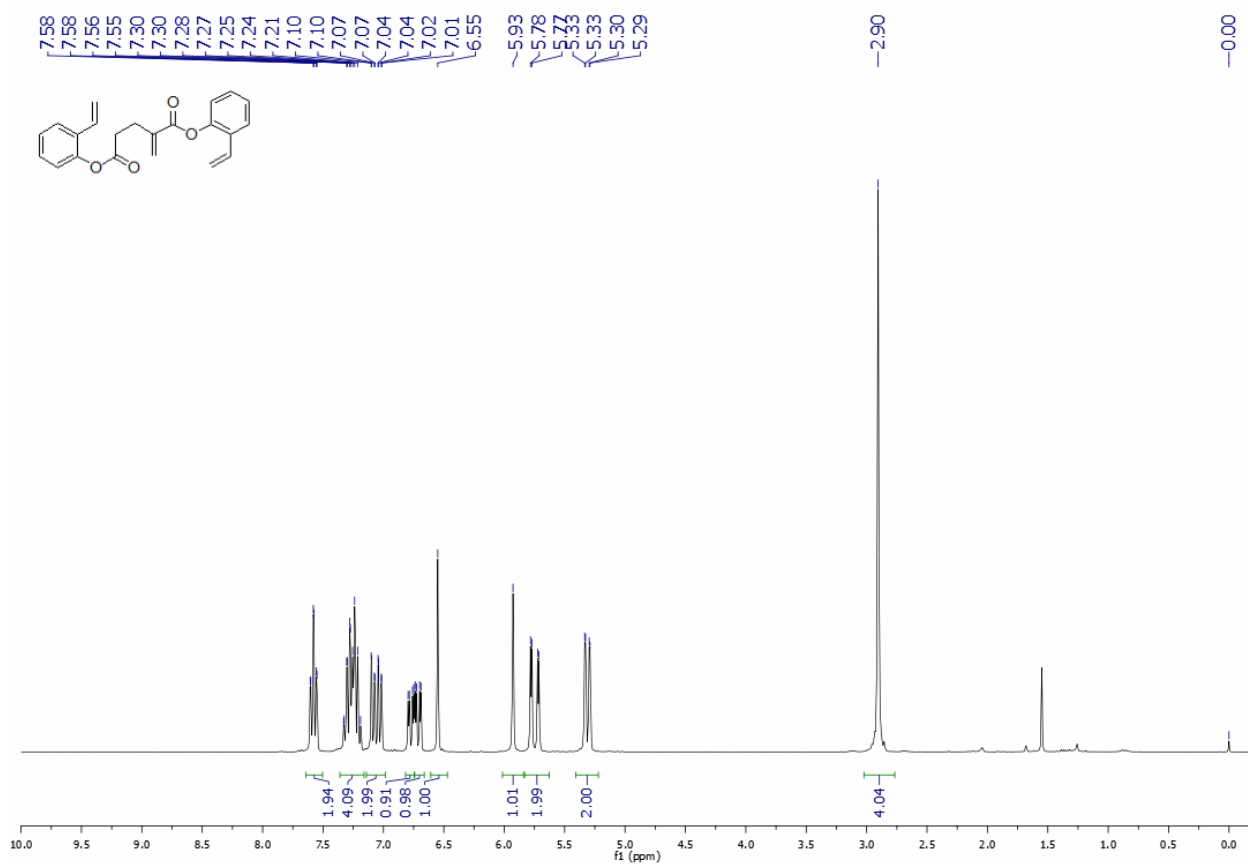
³ K.-S. Huang, S.-R. Li, Y.-F. Wang, Y.-L. Lin, Y.-H. Chen, T.-W. Tsai, C.-H. Yang and E.-C. Wang, *J. Chin. Chem. Soc.*, 2005, **52**, 159-167.

B Synthesis and characterization data of Rauhut Currier product bis-(2-vinylphenyl)-2-methylenepentandioate (**3**)

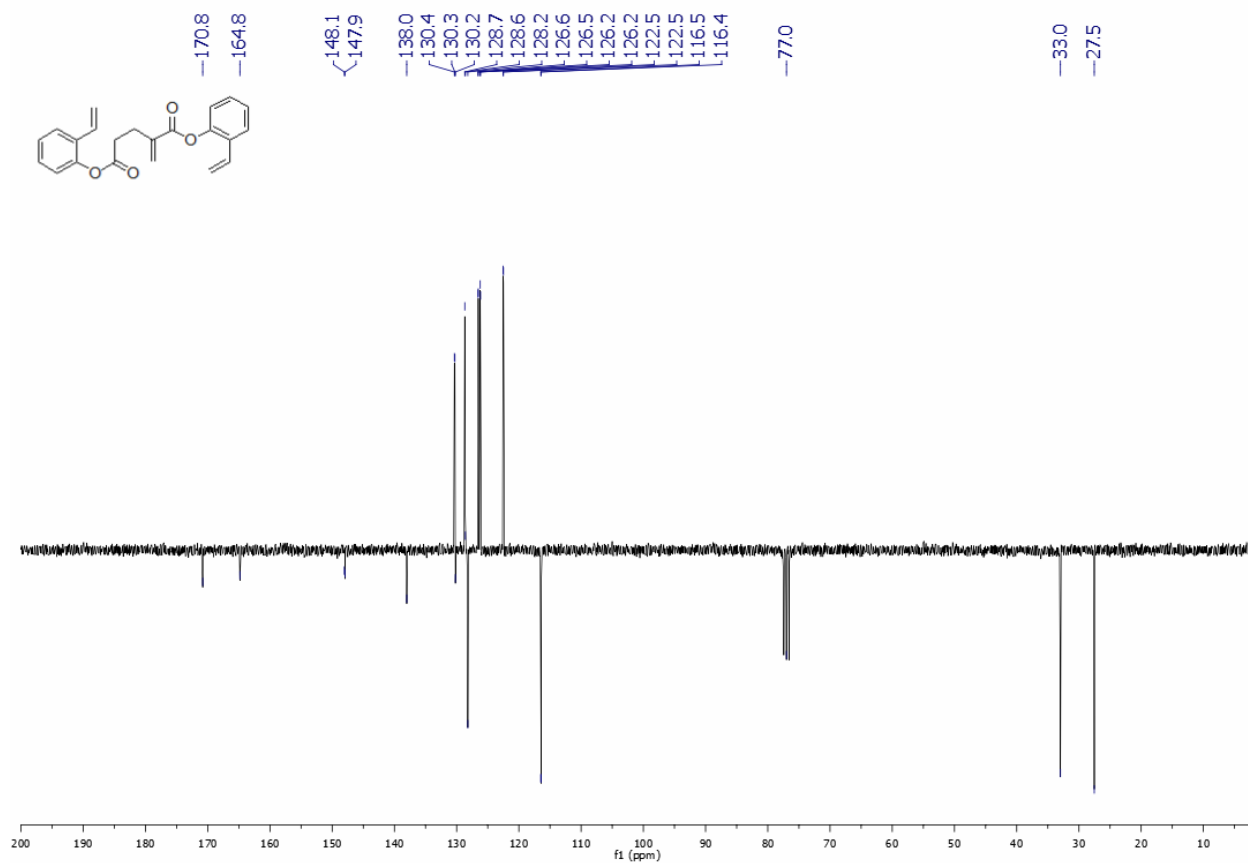


Acrylate **1a** (174 mg, 1.0 mmol) was dissolved in dry and degassed benzene (1.0 mL). Then the catalyst (**A**: 40 mg or PCy₃: 14 mg, 0.05 mmol) was added and the reaction mixture was stirred for 19 h at 40 °C. The solvent was removed in vacuo and the residue was purified by column chromatography on silica. After purification, **3** was obtained as a colourless liquid (with catalyst **A**: 21 mg, 12%, with PCy₃: 113 mg, 65%) ¹H-NMR: δ 7.58 (td, 2H, *J* = 7.6, 1.5), 7.34 – 7.17 (4H), 7.09 (dd, 1H, *J* = 7.8, 1.0), 7.03 (dd, 1H, *J* = 7.7, 0.9), 6.75 (dd, 1H, *J* = 17.6, 11.1), 6.75 (dd, 1H, *J* = 17.6, 11.1), 6.55 (s, 1H), 5.93 (s, 1H), 5.76 (d, 1H, *J* = 17.6), 5.75 (d, 1H, *J* = 17.6), 5.33 (d, 1H, *J* = 11.1), 5.31 (d, 1H, *J* = 11.1), 2.96 – 2.85 (4H); ¹³C-NMR: δ 170.8 (0), 164.8 (0), 148.1 (0), 147.9 (0), 138.0 (0), 130.4 (1), 130.3 (1), 130.2 (0), 128.7 (1), 128.6 (1), 128.2 (2), 126.6 (1), 126.5 (1), 126.2 (1), 126.2 (1), 122.5 (1), 122.5 (1), 116.5 (2), 116.4 (2), 33.0 (2), 27.5 (2); IR (neat, cm⁻¹): $\tilde{\nu}$ = 2954 (m), 2922 (w), 2853 (m), 1760 (m), 1733 (m), 1630 (w), 1483 (w), 1452 (m); HRMS (EI): calcd for C₂₂H₂₀O₄ [M]⁺: 348.1356, found: 348.1378; MS (EI): *m/z* 348 (M⁺, 2), 230 (15), 229 (100), 201 (24), 187 (14), 120 (21), 109 (23), 91 (38); Anal. calcd for C₂₂H₂₀O₄: C: 75.84, H: 5.79; found: C: 75.49, H: 5.22.

^1H NMR spectrum of 3



^{13}C NMR spectrum of 3



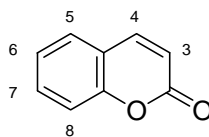
C General experimental procedures for Tandem RCM-allylic oxidation

General procedure A (without addition of NEt₃): Allyl ether **4** (1.0 mmol) was dissolved in dry and degassed benzene (1.0 mL). Catalyst **A** (40 mg, 5 mol%) or **B** (45.5 mg, 5 mol%) was then added. Immediately after addition of the catalyst, the reaction vessel was immersed in an oil bath preheated to 40 °C (electronic temperature control) and stirred for 2 h. After this time, ^tBuOOH (5.5 M in decane, 720 μL, 4.0 mmol) was added to the reaction mixture via syringe pump within 15 min. After complete addition of the oxidant, the mixture was stirred for another 3 h. The reaction mixture was diluted with MTBE (50 mL), and MgSO₄ was added to absorb any water and Ru-residues. It was filtered and all volatiles were removed in vacuo. The residue was purified by column chromatography on silica. Each experiment was repeated at least two times.

General procedure B (with addition of NEt₃): Allyl ether **4** (1.0 mmol) was dissolved in dry and degassed benzene (1.0 mL). Catalyst **A** (40 mg, 5 mol%) or **B** (45.5 mg, 5 mol%) was then added. Immediately after addition of the catalyst, the reaction vessel was immersed in an oil bath preheated to 40 °C (electronic temperature control) and stirred for 2 h. After this time, ^tBuOOH (5.5 M in decane, 720 μL, 4.0 mmol) was added to the reaction mixture via syringe pump within 15 min. After complete addition of the oxidant, the mixture was stirred for another 3 h. After this time, NEt₃ (2.5 mmol, 255 mg, 350 μL) was added, and the mixture was heated to 80 °C for 30 min. The reaction mixture was diluted with MTBE (50 mL), and MgSO₄ was added to absorb any water and Ru-residues. It was filtered and all volatiles were removed in vacuo. The residue was purified by column chromatography on silica. Each experiment was repeated at least two times.

D Specific details, analytical data and copies of spectra for coumarins 2

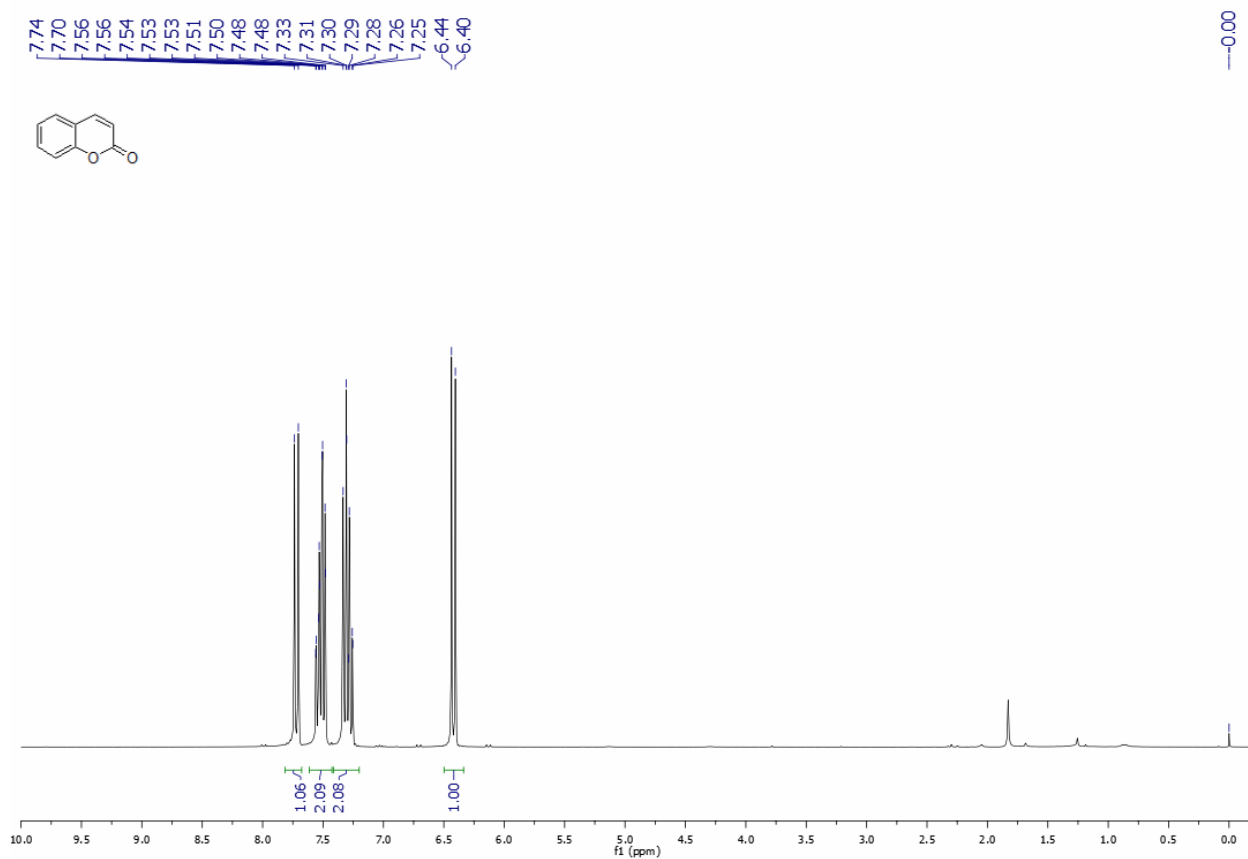
D1 2*H*-Chromen-2-one (**2a**)



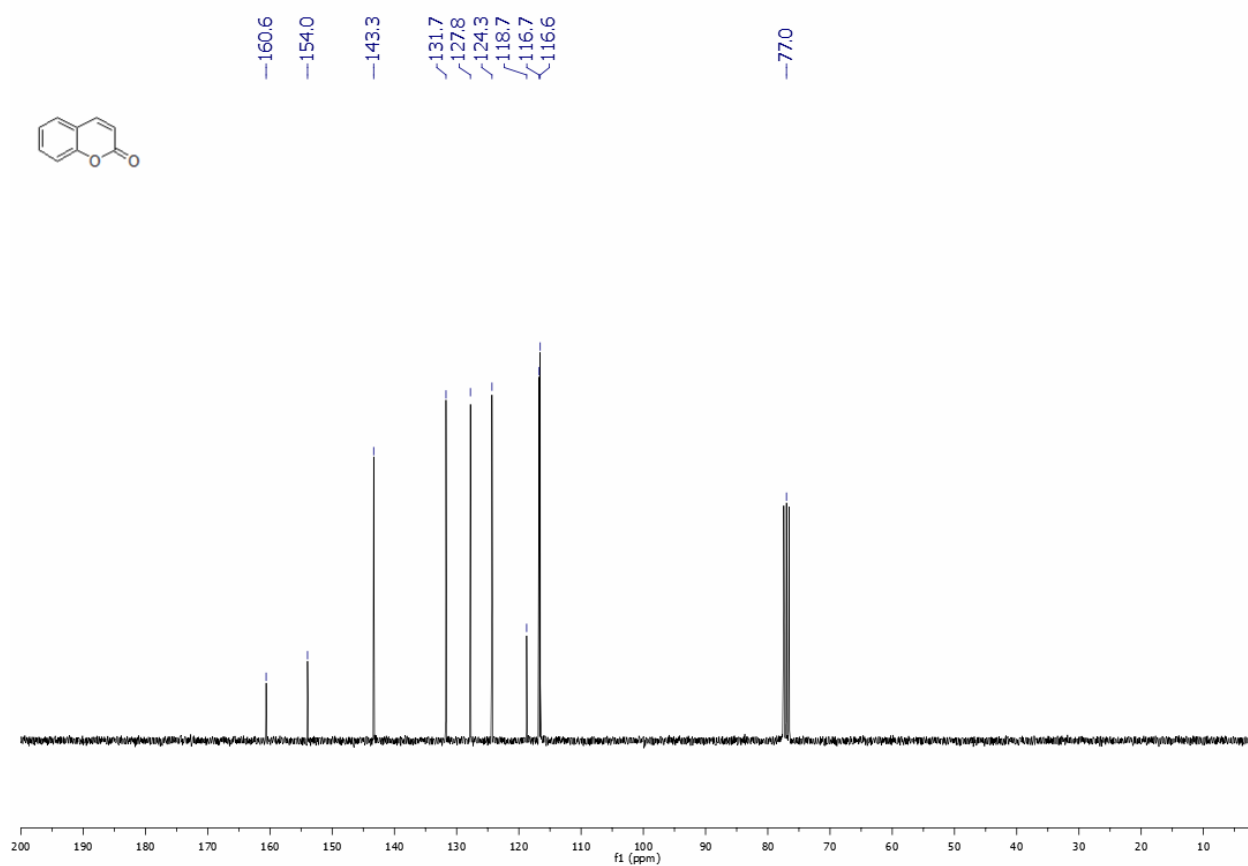
Following the general procedure A, 2*H*-chromen-2-one (**2a**) was obtained from **4a** (160 mg, 1.0 mmol) as a yellowish solid (with catalyst **A**: 85 mg, 58%, with catalyst **B**: 86 mg, 59%). Mp: 70 – 72°C;⁴ ¹H-NMR: δ 7.72 (d, 1H, $J = 9.6$, H-4), 7.58 – 7.45 (2H, H-5, H-7), 7.37 – 7.24 (2H, H-6, H-8), 6.42 (d, 1H, $J = 9.5$, H-3); ¹³C-NMR: δ 160.7 (0), 154.1 (0), 143.4 (1), 131.8 (1), 127.8 (1), 124.4 (1), 118.8 (0), 116.9 (1), 116.7 (1); IR (neat, cm⁻¹): $\tilde{\nu} = 3061$ (w), 2958 (w), 1711 (s), 1605 (s), 1453 (m), 1106 (m); HRMS (ESI): calcd for C₉H₇O₂ [M+H]⁺: 147.0446, found: 147.0451; MS (EI): m/z 146 (M⁺, 92), 118 (100), 90 (32), 89 (39), 63 (25); Anal. calcd for C₉H₇O₂: C: 73.97, H: 4.14; found: C: 73.80, H: 3.97.

⁴ Reported in the literature: mp = 67-68°C; J. Oyamada and T. Kitamura, *Tetrahedron*, 2006, **62**, 6918-6925.

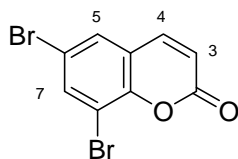
^1H NMR spectrum of 2a



^{13}C NMR spectrum of 2a



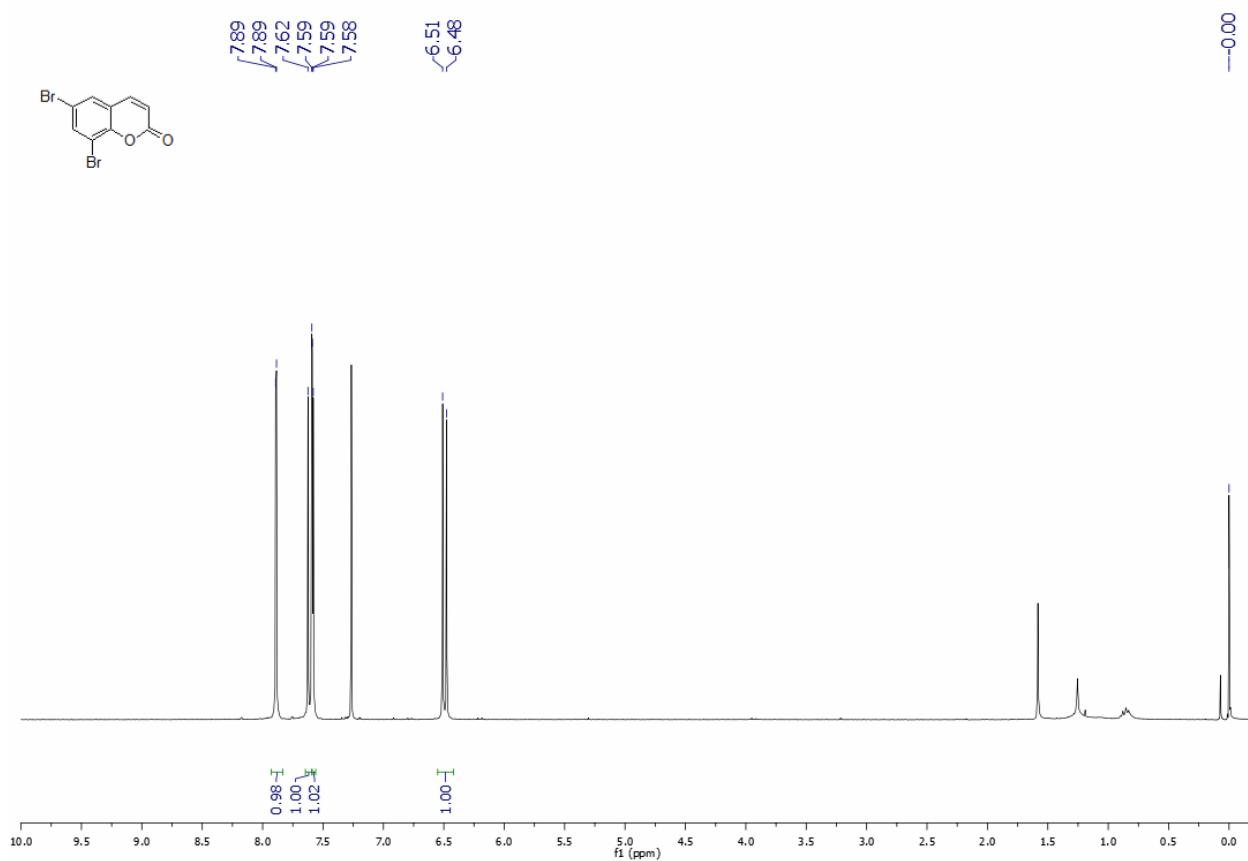
D2 6,8-Dibromo-2*H*-chromen-2-one (**2b**)



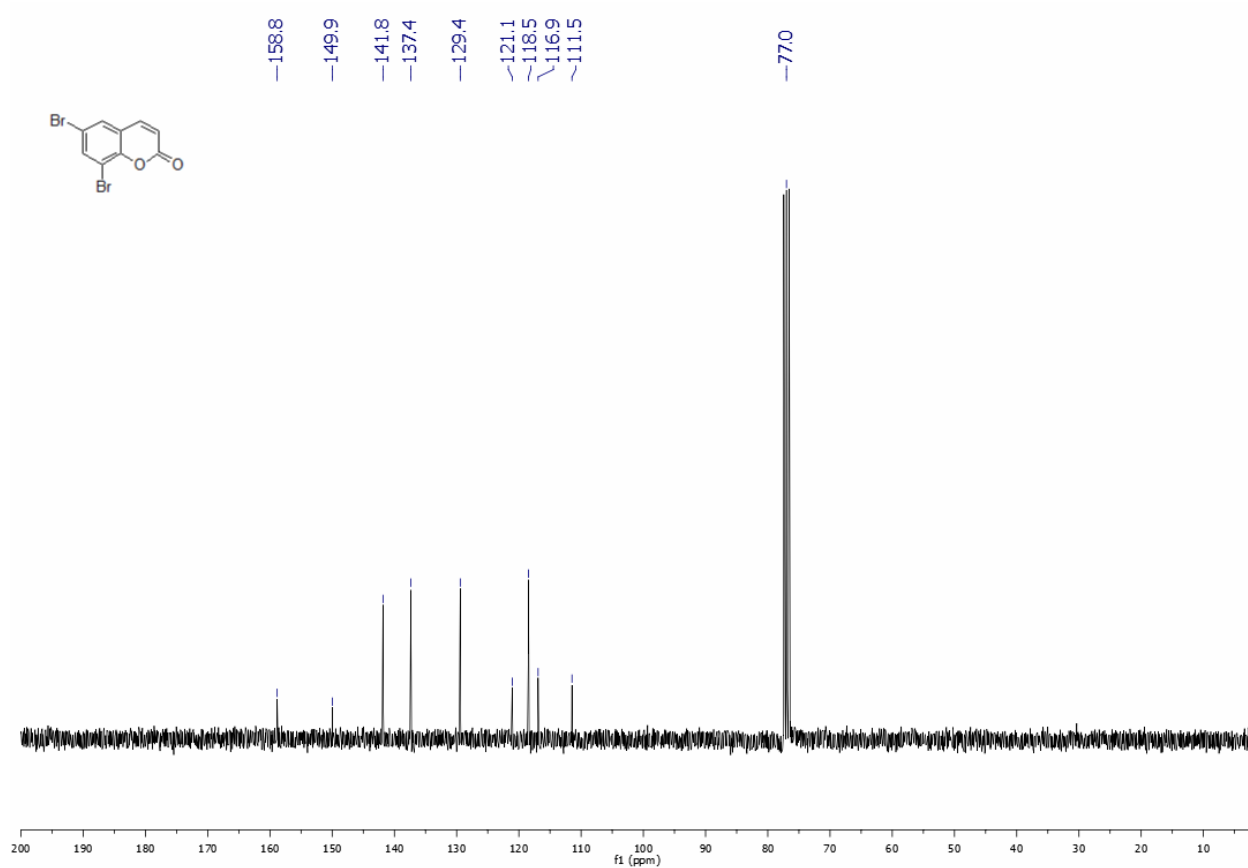
Following the general procedure A, 6,8-dibromo-2*H*-chromen-2-one (**2b**) was obtained from **4b** (159 mg, 0.5 mmol) together with the corresponding pyron **6b** (**2b** : **6b**, 10: 1) as a yellowish solid (with catalyst **A**: 85 mg, 56%, with catalyst **B**: 85 mg, 56%). Mp: 136 – 138°C;⁵ ¹H-NMR: δ 7.89 (d, 1H, $J = 2.2$, H-5), 7.61 (d, 1H, $J = 9.7$, H-4), 7.58 (d, 1H, $J = 2.2$, H-7), 6.50 (d, 1H, $J = 9.5$, H-3); ¹³C-NMR: δ 158.8 (0), 149.9 (0), 141.8 (1), 137.4 (1), 129.4 (1), 121.1 (0), 118.5 (1), 116.9 (0), 111.5 (0); IR (neat, cm⁻¹): $\tilde{\nu} = 3067$ (w), 1740 (s), 1655 (m), 1544 (m), 1442 (m), 1167 (m); HRMS (EI): calcd for C₉H₄O₂[79]Br₂ [M]⁺: 301.8578, found: 301.8584; MS (EI): m/z 306 (M⁺, 47), 304 (M⁺, 100), 302 (M⁺, 53), 278 (30), 276 (63), 274 (35), 197 (20), 195 (21), 169 (29), 167 (32); Anal. calcd for C₉H₄O₂Br₂: C: 35.57, H: 1.33; found: C: 35.79, H: 1.30.

⁵ Reported in the literature: 160°C; M. J. Bhukta and P. I. Ittyerah, *J. Indian Chem. Soc.*, 1965, **42**, 454-456.

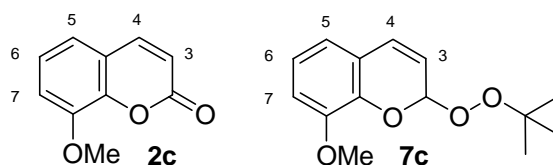
¹H NMR spectrum of 2b



¹³C NMR spectrum of 2b



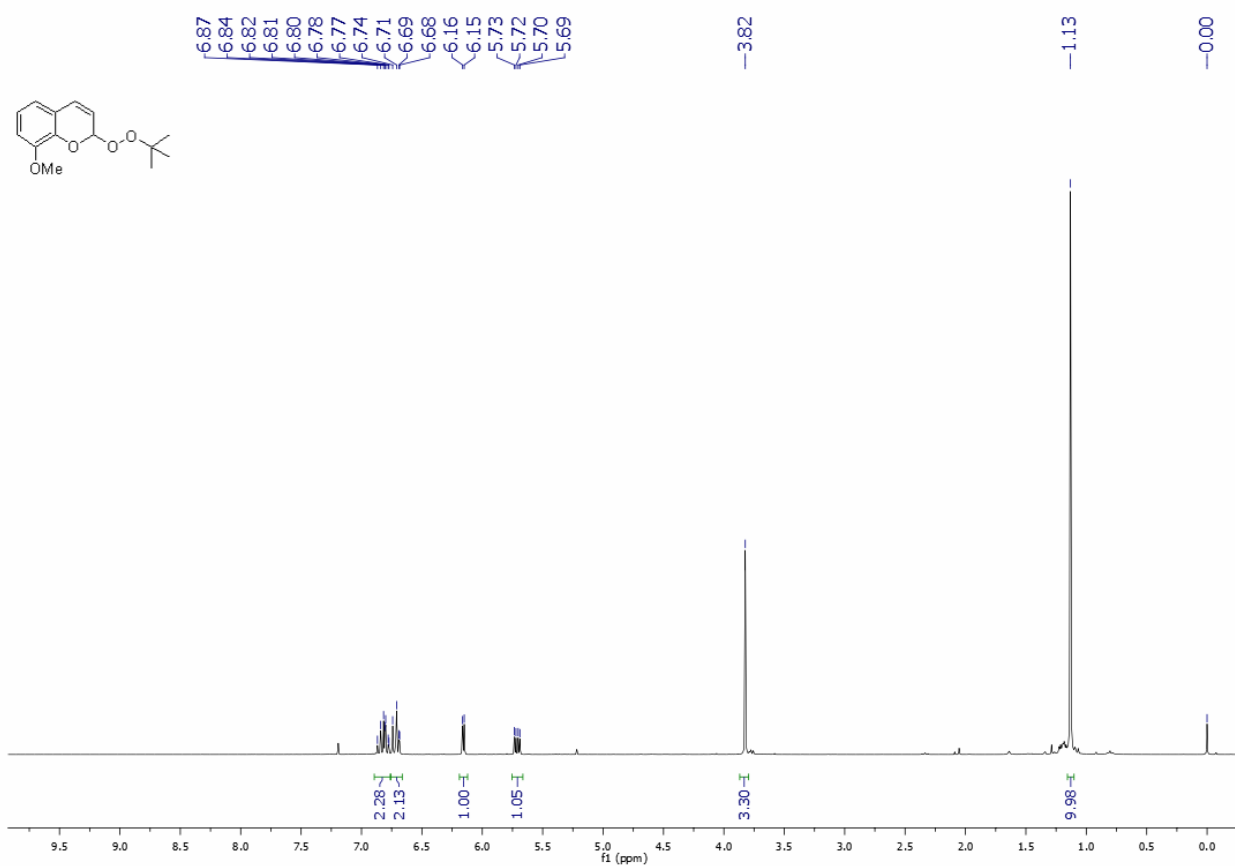
D3 8-Methoxy-2*H*-chromen-2-one (**2c**) and 2-(*tert*-butylperoxy)-8-methoxy-2*H*-chromene (**7c**)



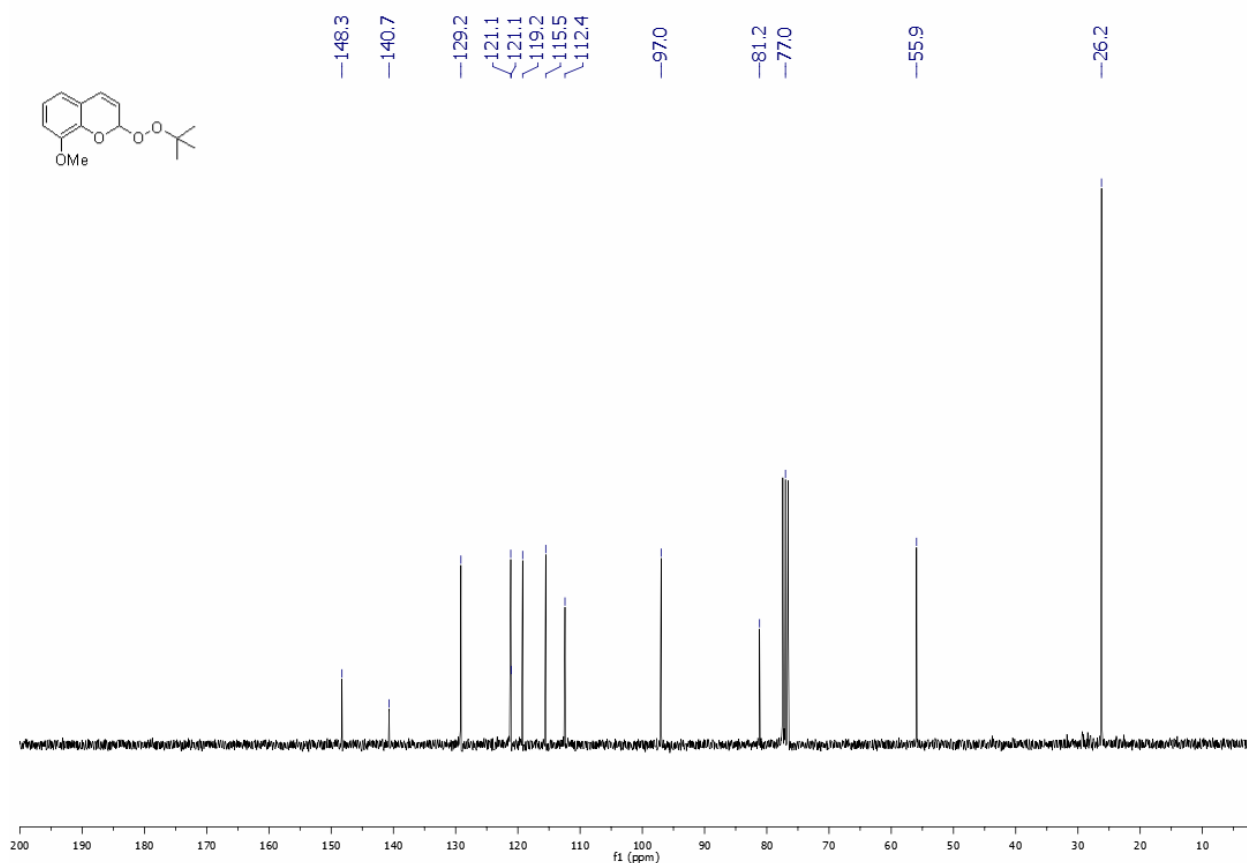
Following the general procedure A, 2-(*tert*-butylperoxy)-8-methoxy-2*H*-chromene (**7c**) and 8-methoxy-2*H*-chromen-2-one (**2c**) were synthesized from **4c** (190 mg, 1.0 mmol) using catalyst **A**. The products were separated by column chromatography on silica to give **7c** as a colourless liquid (43 mg, 17%) and **2c** as a yellowish solid (60 mg, 34%). *Analytical data for 2-(tert-butylperoxy)-8-methoxy-2H-chromene (7c)*: $^1\text{H-NMR}$: δ 6.92 (dd, 1H, $J = 8.1, 7.1$, H-6), 6.86 (dd, 1H, $J = 8.1, 1.9$, H-5), 6.80 (d, H, $J = 9.6$, H-4), 6.77 (dd, 1H, $J = 7.5, 1.9$, H-7), 6.23 (d, H, $J = 4.1$, H-2), 5.79 (dd, 1H, $J = 9.6, 4.1$, H-3), 3.90 (s, 3H, OCH_3), 1.20 (s, 9H, $\text{OC}(\text{CH}_3)_3$); $^{13}\text{C-NMR}$: δ 148.3 (0), 140.7 (0), 129.2 (1), 121.1 (1), 121.1 (0), 119.2 (1), 115.5 (1), 112.4 (1), 97.0 (1), 81.2 (0), 55.9 (3), 26.2 (3, 3C); IR (neat, cm^{-1}): $\tilde{\nu} = 2976$ (m), 1641 (m), 1576 (m), 1480 (m), 1363 (m), 1268 (s), 1210 (s), 1192 (s); HRMS (EI): calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4$ [M] $^+$: 250.1205, found: 250.1202; MS (EI): m/z 250 (M^+ , 1), 161 (100), 146 (12), 134 (13), 85 (14), 83 (18), 79 (12), 77 (12), 57 (12), 43 (21); Anal. calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4$: C: 67.18, H: 7.25; found: C: 66.83, H: 7.08. *Analytical data for 8-methoxy-2H-chromen-2-one (2c)*: Mp: 90 – 91°C; 6 $^1\text{H-NMR}$: δ 7.70 (d, 1H, $J = 9.6$, H-4), 7.21 (dd, 1H, $J = 8.0, 7.8$, H-6), 7.09 (dd, H, $J = 8.0, 1.4$, H-5/H-7), 7.06 (dd, H, $J = 7.5, 1.4$, H-5/H-7), 6.43 (d, 1H, $J = 9.6$, H-3), 3.96 (s, 3H, OCH_3); $^{13}\text{C-NMR}$: δ 160.1 (0), 147.2 (0), 143.7 (0), 143.5 (1), 124.21 (1), 119.4 (0), 119.2 (1), 116.8 (1), 113.8 (1), 56.2 (3); IR (neat, cm^{-1}): $\tilde{\nu} = 2933$ (w), 2847 (w), 1724 (s), 1608 (m), 1571 (m), 1467 (s), 1273 (s); HRMS (EI): calcd for $\text{C}_{10}\text{H}_8\text{O}_3$ [M] $^+$: 176.0473, found: 176.0482; MS (EI): m/z 176 (M^+ , 100), 161 (24), 148 (32), 147 (18), 133 (43), 105 (42), 77 (41), 51 (47), 50 (23); Anal. calcd for $\text{C}_{10}\text{H}_8\text{O}_3$: C: 68.18, H: 4.58; found: C: 67.86, H: 4.39.

⁶ Reported in the literature: 86-87°C°C; J. A. Panetta and H. Rapoport, *J. Org. Chem.*, 1982, **47**, 946-950.

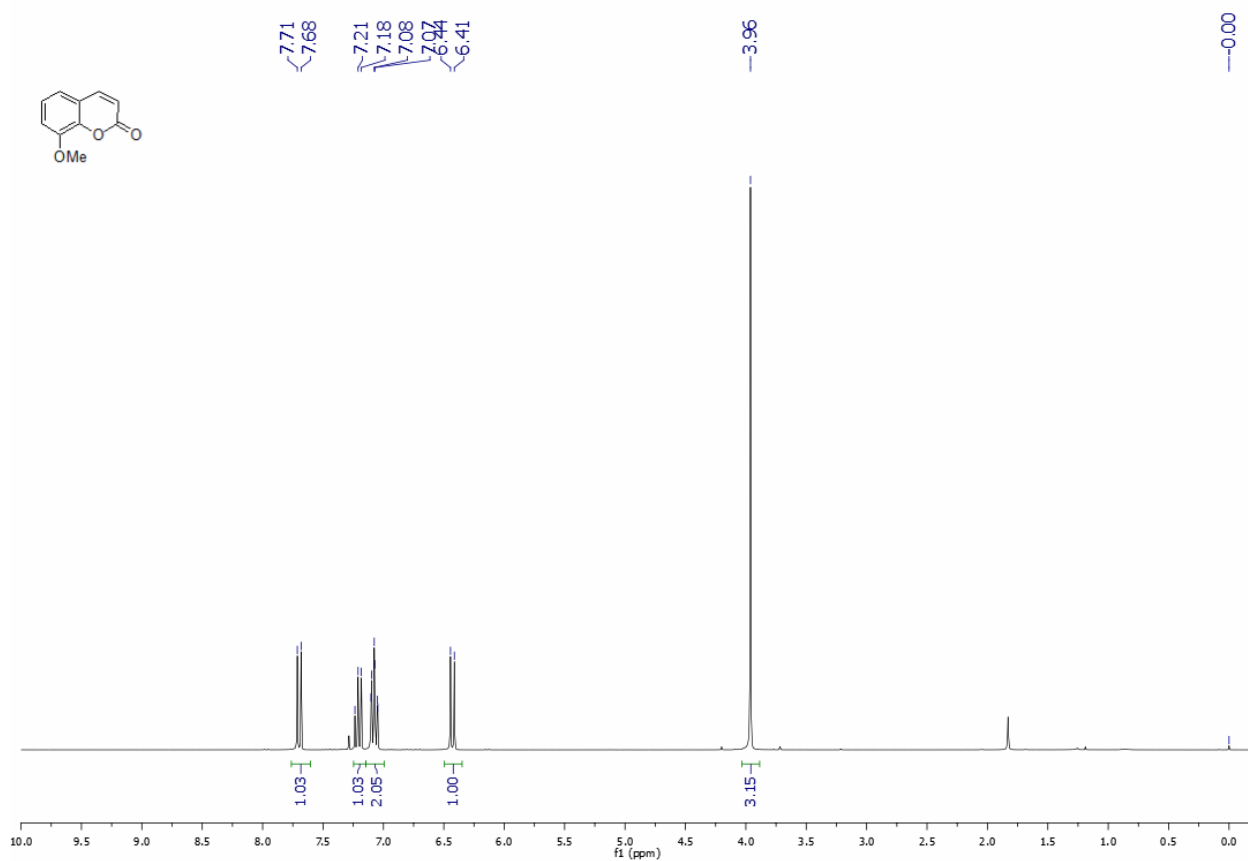
¹H NMR spectrum of 7c



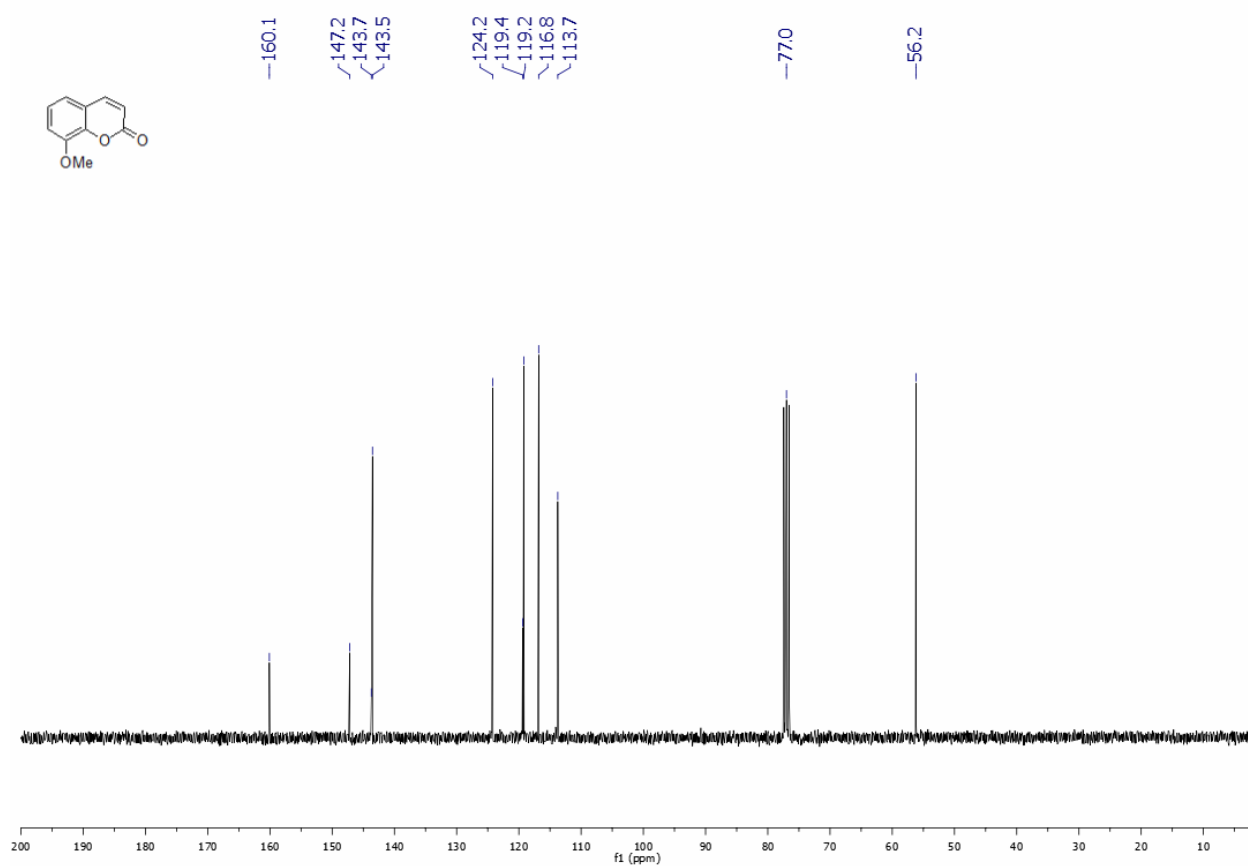
¹³C NMR spectrum of 7c



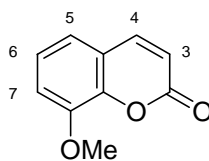
¹H NMR spectrum of 2c



¹³C NMR spectrum of 2c

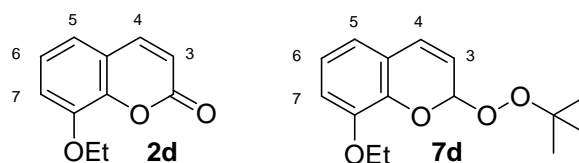


D4 Synthesis of 8-methoxy-2*H*-chromen-2-one (**2c**) with subsequent peroxide decomposition



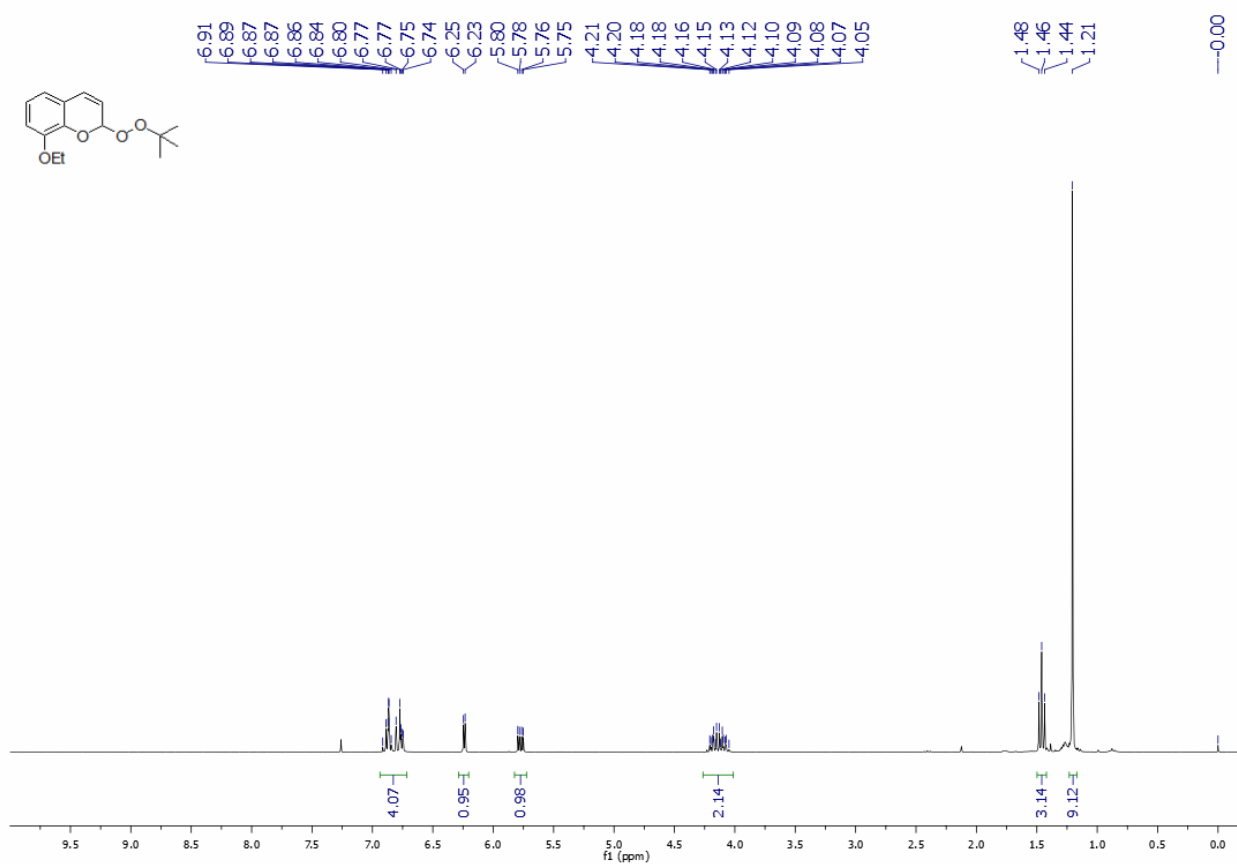
Following the general procedure B, 8-methoxy-2*H*-chromen-2-one (**2c**) was obtained from **4c** (190 mg, 1.0 mmol) as a yellowish solid (with catalyst **A**: 97 mg, 55%, with catalyst **B**: 100 mg, 57%). Analytical data for **2c** synthesized via this protocol are identical to those reported above.

D5 8-Ethoxy-2*H*-chromen-2-one (**2d**) and 2-(*tert*-butylperoxy)-8-ethoxy-2*H*-chromene (**7d**)

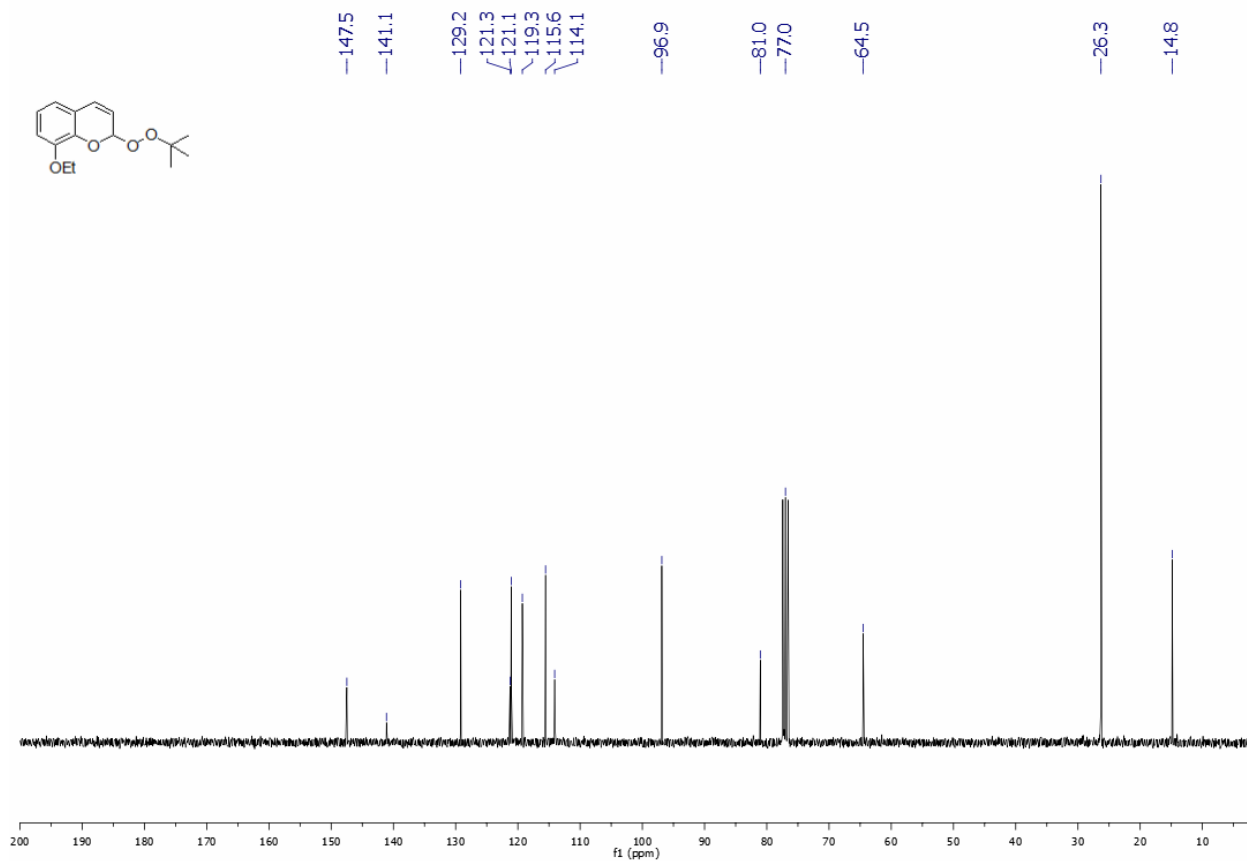


Following the general procedure A, 2-(*tert*-butylperoxy)-8-ethoxy-2*H*-chromene (**7d**) and 8-ethoxy-2*H*-chromen-2-one (**2d**) were synthesized from **4d** (204 mg, 1.0 mmol) using catalyst **A**. The products were separated by column chromatography on silica to give **7d** as a colourless liquid (40 mg, 15%) and **2d** as a yellowish solid (72 mg, 38%). *Analytical data of 2-(tert-butylperoxy)-8-ethoxy-2H-chromene (7d)*: ¹H-NMR: δ 6.92 – 6.83 (2H, H-6, H-7), 6.79 (d, 1H, *J* = 9.6, H-4), 6.76 (dd, 1H, *J* = 6.5, 1.7, H-5), 6.24 (d, 1H, *J* = 4.1, H-2), 5.78 (dd, 1H, *J* = 9.6, 4.1, H-3), 4.17 (dq, 1H, *J* = 9.6, 7.0, OCHHCH₃), 4.11 (dq, 1H, *J* = 9.6, 7.0, OCHHCH₃), 1.46 (t, 3H, *J* = 7.0, OCH₂CH₃), 1.21 (s, 9H, OC(CH₃)₃); ¹³C-NMR: δ 147.5 (0), 141.1 (0), 129.2 (1), 121.3 (0), 121.1 (1), 119.3 (1), 115.6 (1), 114.1 (1), 96.9 (1), 81.0 (0), 64.5 (2), 26.3 (3, 3C), 14.9 (3); IR (neat, cm⁻¹): $\tilde{\nu}$ = 2977 (m), 2932 (w), 1576 (m), 1471 (s), 1393 (m), 1363 (m), 1270 (s), 1210 (s); HRMS (EI): calcd for C₁₅H₂₀O₄ [M]⁺: 264.1362, found: 264.1347; MS (EI): *m/z* 264 (M⁺, 1), 175 (100), 147 (20), 134 (17), 107 (11), 77 (14), 57 (10), 43 (17); Anal. calcd for C₁₅H₂₀O₄: C: 68.16 H: 7.63; found: C: 68.11 H: 7.72. *Analytical data of 8-Ethoxy-2H-chromen-2-one (2d)*: Mp: 69 – 70°C; ¹H-NMR: δ 7.69 (d, 1H, *J* = 9.5, H-4), 7.17 (d, 1H, *J* = 7.7, H-5/7), 7.10 – 7.02 (2H, H-5/7, H-6), 6.42 (d, 1H, *J* = 9.6, H-3), 4.18 (q, 2H, *J* = 7.0, OCH₂CH₃), 1.50 (t, 3H, *J* = 7.0, OCH₂CH₃); ¹³C-NMR: δ 160.4 (0), 146.5 (0), 143.9 (0), 143.6 (1), 124.2 (1), 119.5 (0), 119.2 (1), 116.7 (1), 115.0 (1), 64.9 (2), 14.7 (3); IR (neat, cm⁻¹): $\tilde{\nu}$ = 3437 (w), 3083 (w), 2980 (w), 2933 (w), 1720 (s), 1605 (m), 1570 (m), 1462 (s), 1393 (m); HRMS (EI): calcd for C₁₁H₁₀O₃ [M]⁺: 190.0630, found: 190.0619; MS (EI): *m/z* 190 (M⁺, 45), 162 (90), 134 (100), 105 (19), 78 (28), 77 (31), 51 (24); Anal. calcd for C₁₁H₁₀O₃: C: 69.46, H: 5.30; found: C: 69.07, H: 5.15.

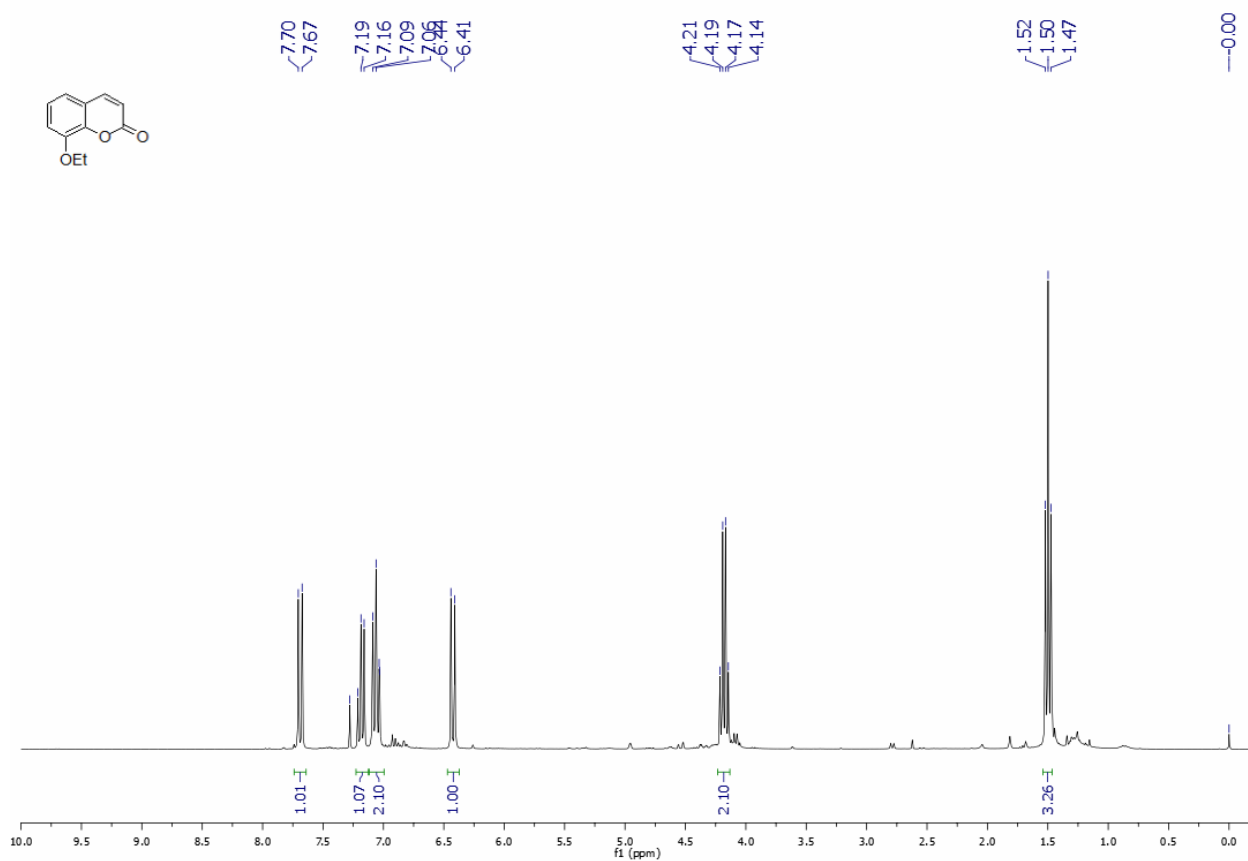
¹H NMR spectrum of 7d



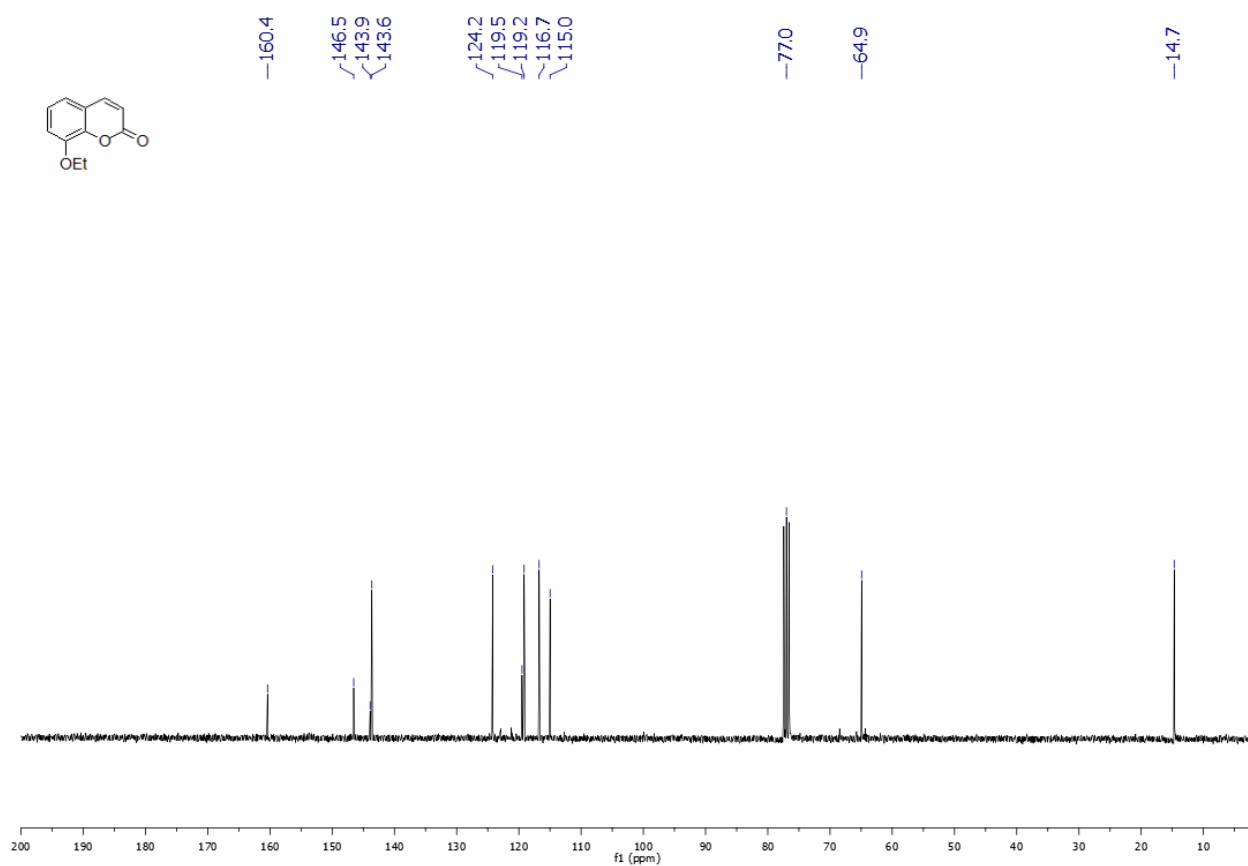
¹³C NMR spectrum of 7d



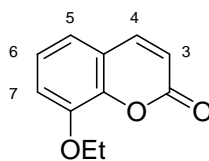
^1H NMR spectrum of 2d



^{13}C NMR spectrum of 2d

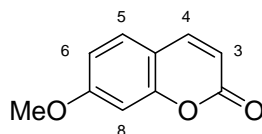


D6 Synthesis of 8-ethoxy-2*H*-chromen-2-one (**2d**) with subsequent peroxide decomposition



Following the general procedure B, 8-Ethoxy-2*H*-chromen-2-one (**2d**) was obtained from **4d** (204 mg, 1.0 mmol) as a yellowish solid (with catalyst **A**: 97 mg, 51%, with catalyst **B**: 97 mg, 51%). Analytical data for **2d** synthesized via this protocol are identical to those reported above.

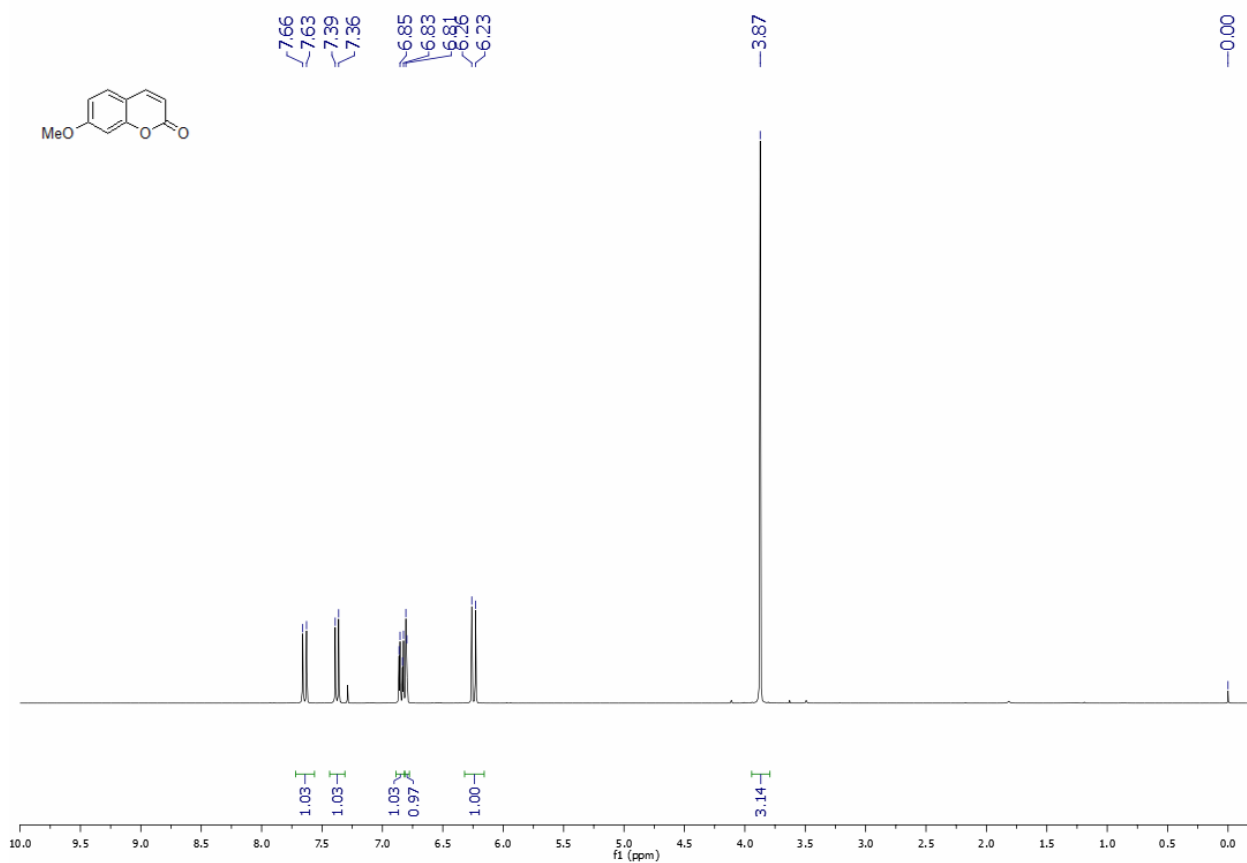
D7 7-Methoxy-2*H*-chromen-2-one (**2e**)



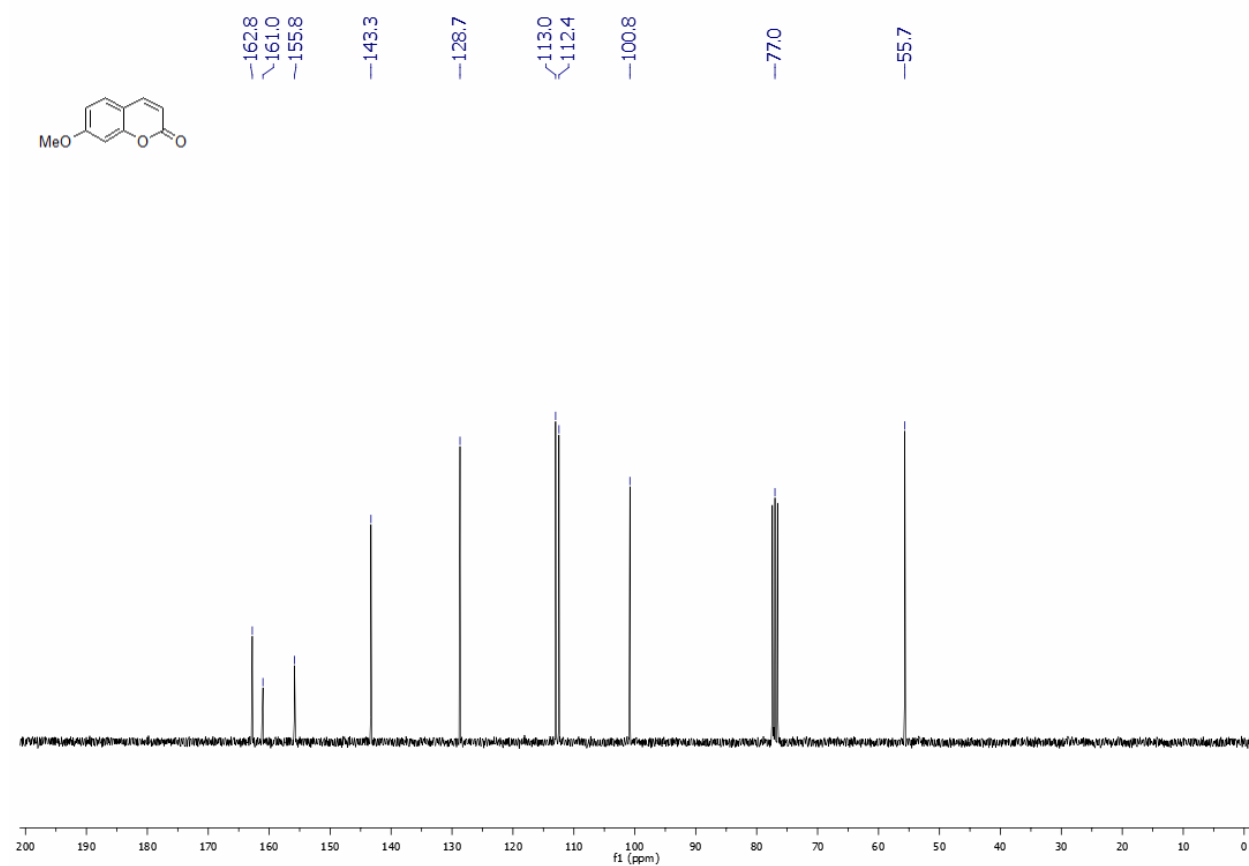
7-Methoxy-2*H*-chromen-2-one (**2e**) was synthesized following the general procedure A, using an initial concentration of **4e** (190 mg, 1.0 mmol) of 0.1 M. **2e** was obtained as a yellowish solid (with catalyst **A**: 71 mg, 40%, with catalyst **B**: 71 mg, 40%). Mp: 121 – 123°C;⁷ ¹H-NMR: δ 7.64 (d, 1H, $J = 9.6$, H-4), 7.38 (d, 1H, $J = 8.5$, H-5), 6.84 (dd, 1H, $J = 8.5, 2.4$, H-6), 6.80 (d, 1H, $J = 2.3$, H-8), 6.24 (d, 1H, $J = 9.5$, H-3), 3.87 (s, 3H, OCH₃); ¹³C-NMR: δ 162.8 (0), 161.1 (0), 155.8 (0), 143.3 C(1), 128.7 (1), 113.0 (0), 112.5 (1, 2C), 100.8 (1), 55.7 (3); IR (neat, cm⁻¹): $\tilde{\nu} = 2936$ (w), 1727 (s), 1609 (s), 1556 (m), 1507 (m), 1282 (m); HRMS (EI): calcd for C₁₀H₈O₃ [M]⁺: 176.0473, found: 176.0456; MS (EI): m/z 176 (M⁺, 93), 148 (100), 133 (76), 105 (15), 77 (19), 51 (13); Anal. calcd for C₁₀H₈O₃: C: 68.18, H: 4.58; found: C: 67.59, H: 4.33.

⁷ Reported in the literature: mp = 117-118°C; J. Oyamada and T. Kitamura, *Tetrahedron*, 2006, **62**, 6918-6925.

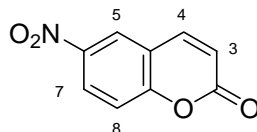
^1H NMR spectrum of 2e



^{13}C NMR spectrum of 2e



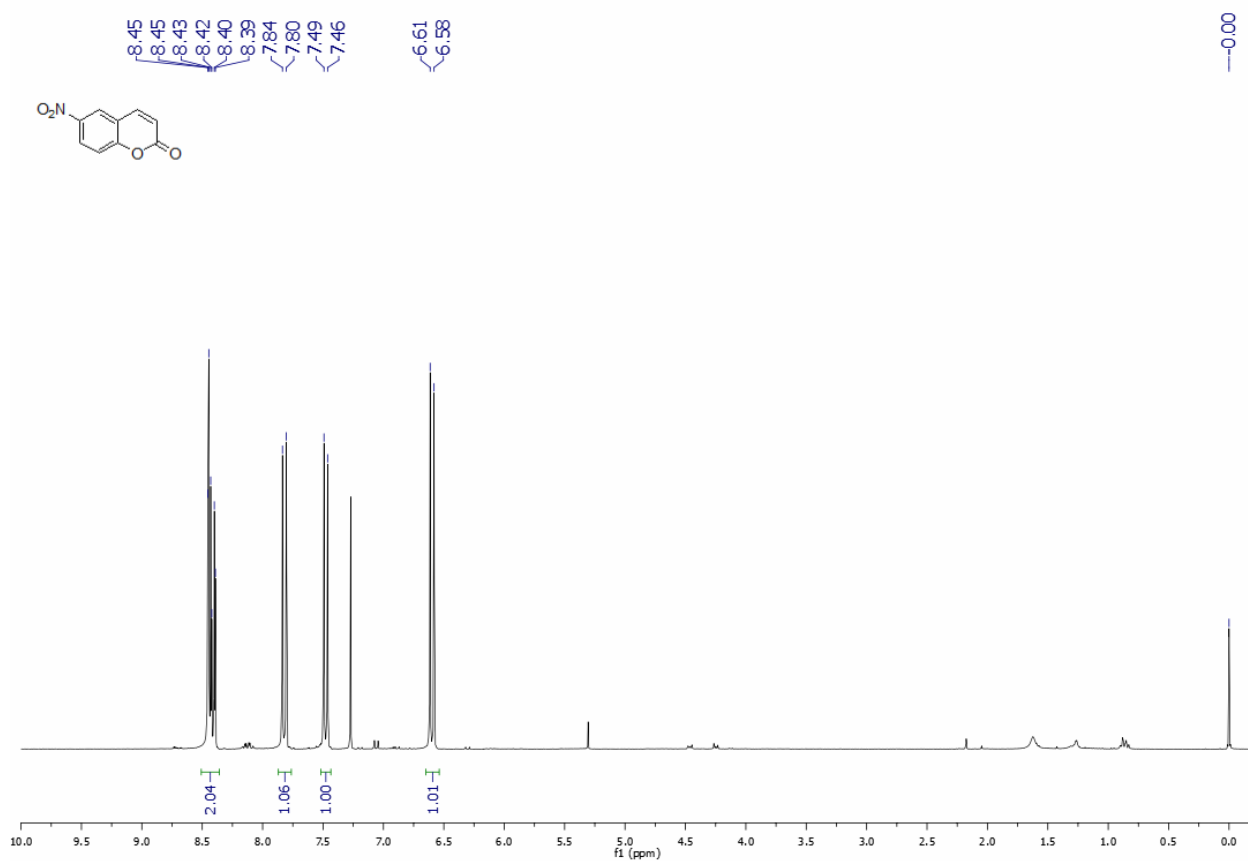
D8 6-Nitro-2*H*-chromen-2-one (**2f**)



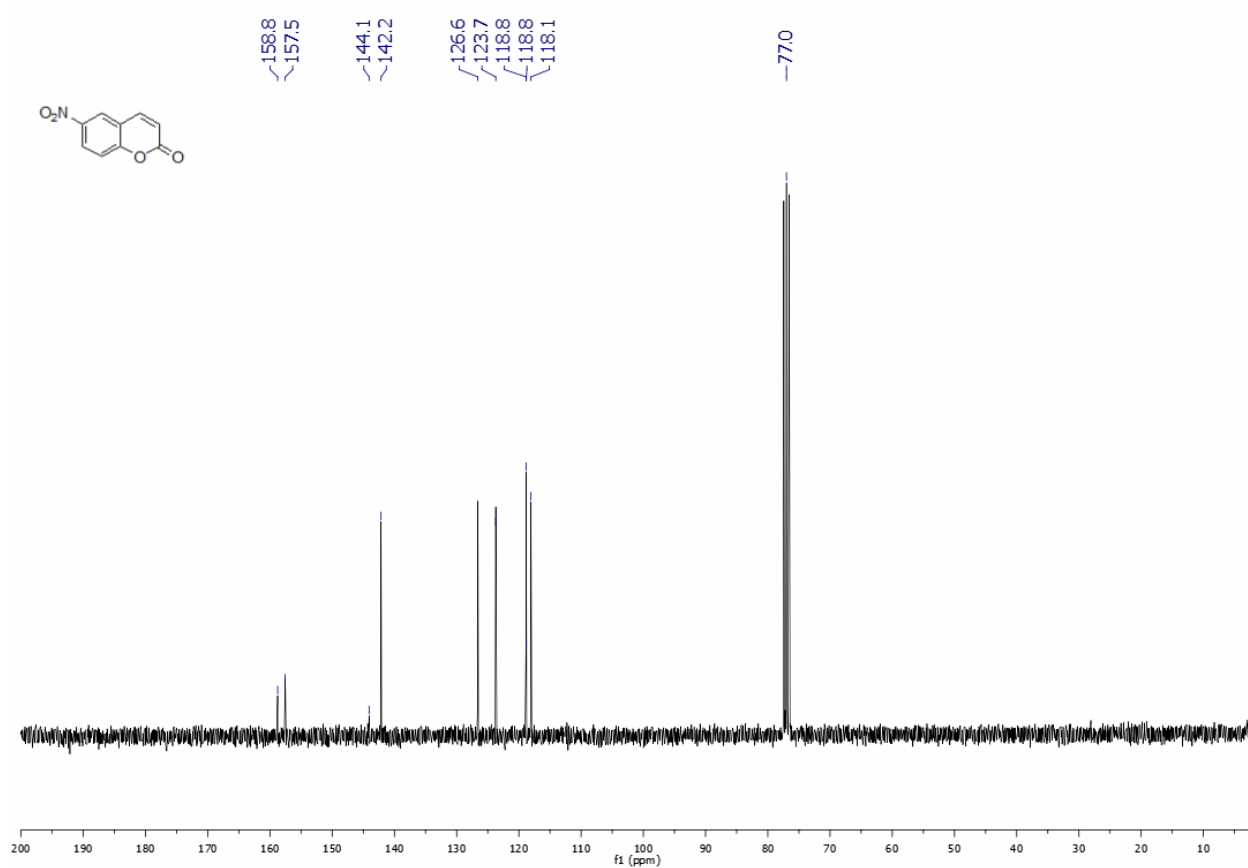
Following the general procedure A, 6-nitro-2*H*-chromen-2-one (**2f**) was obtained from **4f** (205 mg, 1.0 mmol) as a yellowish solid (with catalyst **A**: 120 mg, 63%, with catalyst **B**: 120 mg, 63%). Mp = 180-182°C;⁸ ¹H-NMR: δ 8.46 (d, 1H, $J = 2.6$, H-5), 8.41 (dd, 1H, $J = 9.0, 2.6$, H-7), 7.84 (d, 1H, $J = 9.7$, H-4), 7.48 (d, 1H, $J = 9.0$, H-8), 6.60 (d, 1H, $J = 9.7$, H-3); ¹³CNMR: δ 158.8 (0), 157.5 (0), 144.0 (0), 142.2 (1), 126.6 (1), 123.7 (1), 118.8 (1), 118.8 (0), 118.0 (1); IR (neat, cm⁻¹): $\tilde{\nu}$ = 3071 (w), 1736 (s), 1615 (s), 1517 (s), 1340 (s); HRMS (EI): calcd for C₉H₅O₄N [M]⁺: 191.0219, found: 191.0219; MS (EI): m/z 191 (M⁺, 67), 190 (19), 176 (28), 166 (27), 163 (27), 161 (22), 133 (40), 118 (22), 117 (49), 105 (23), 89 (75), 85 (41), 83 (39), 71 (55), 69 (38), 63 (64), 57 (44), 43 (51), 41 (73), 40 (100); Anal. calcd for C₉H₅O₄N: C: 56.55, H: 2.64, N: 7.33; found: C: 56.37, H: 2.67, N: 7.25.

⁸ Reported in the literature: 181-182°C; F. Jafarpour, N. Jalalimanesh, M. B. A. Olia and A. O. Kashani, *Tetrahedron*, 2010, **66**, 9508-9511.

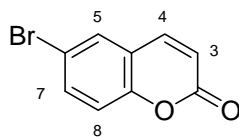
¹H NMR spectrum of 2f



¹³C NMR spectrum of 2f



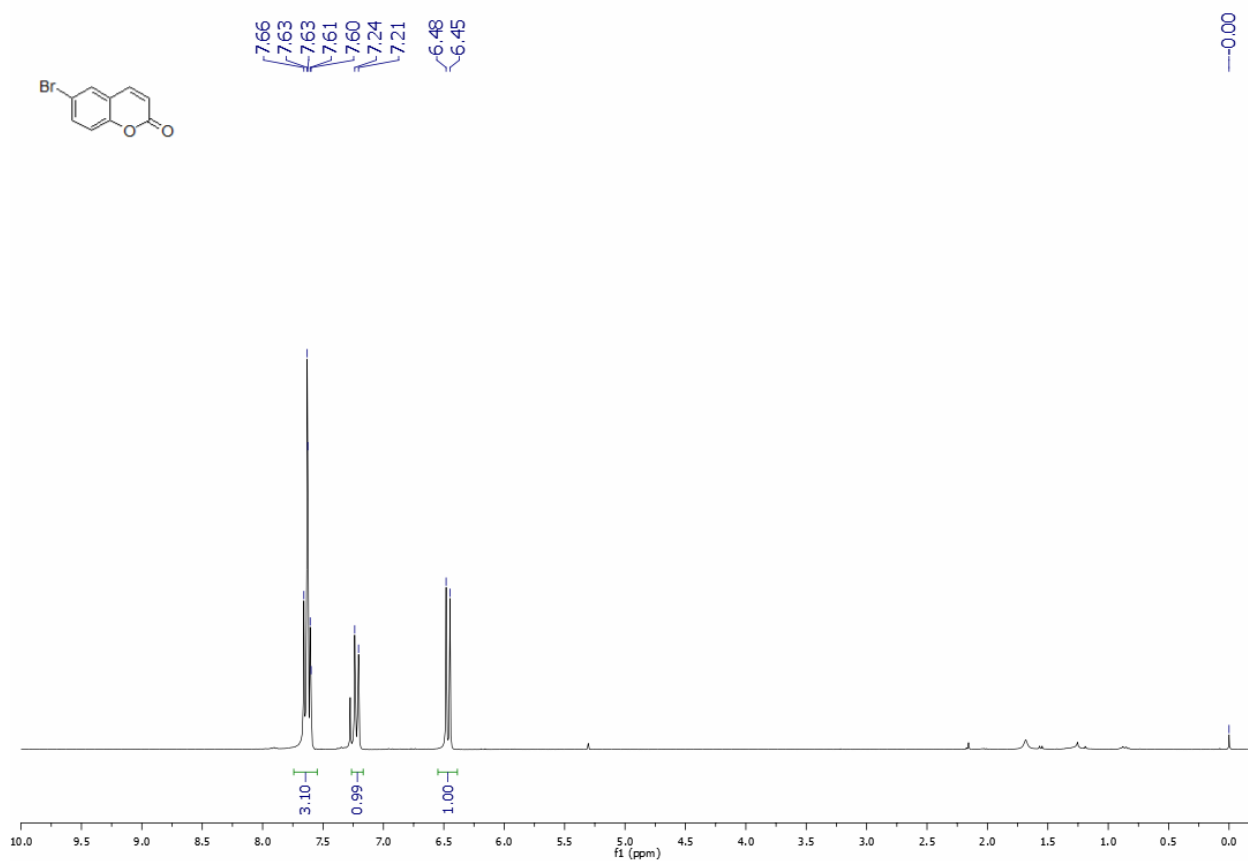
D9 6-Bromo-2*H*-chromen-2-one (**2g**)



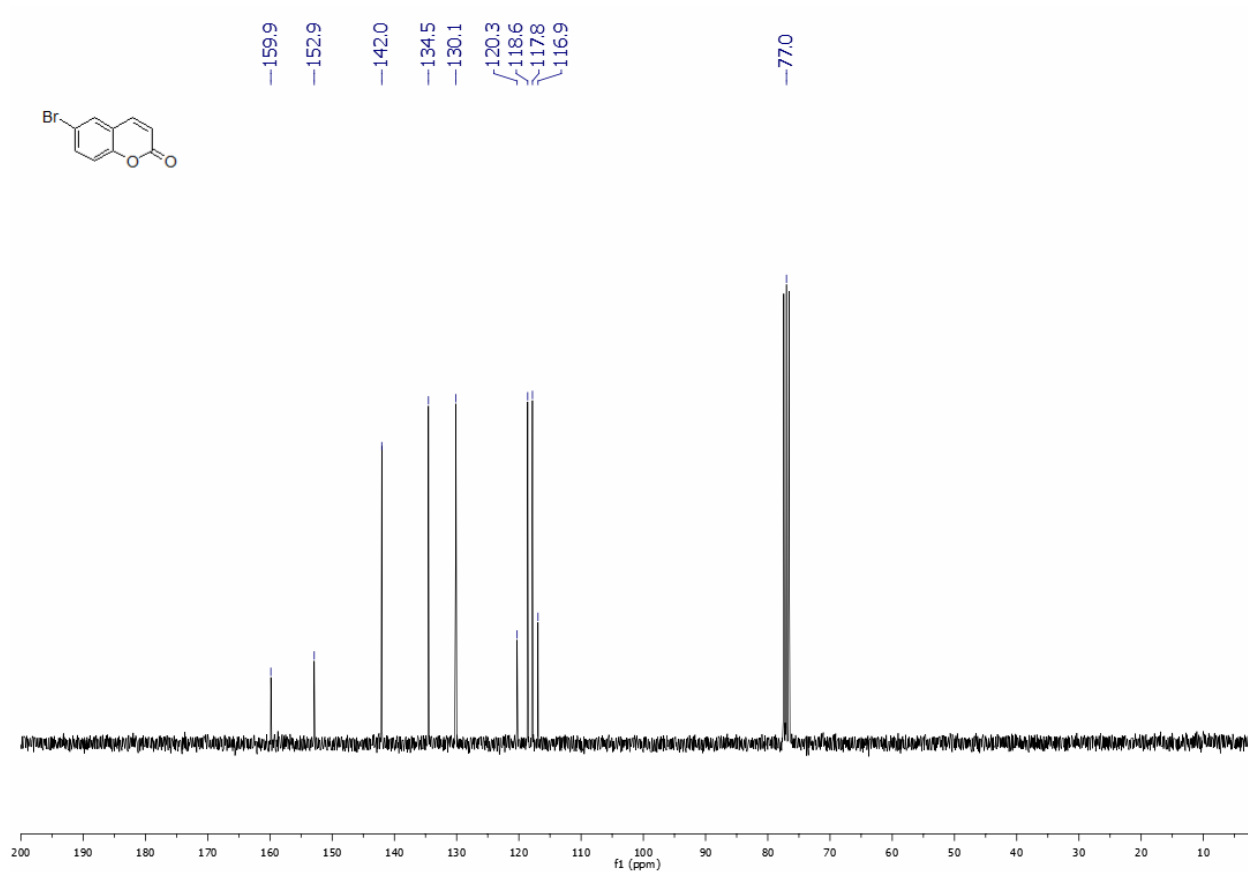
Following the general procedure A, 6-bromo-2*H*-chromen-2-one (**2g**) was obtained from **4g** (239 mg, 1.0 mmol) as a yellowish solid (with catalyst **A**: 137 mg, 61%, with catalyst **B**: 140 mg 62%). Mp: 157 – 159°C;⁹ ¹H-NMR: δ 7.67 – 7.58 (3H, H-5, H-7, H-8), 7.22 (d, 1H, J = 9.7, H-4), 6.47 (d, 1H, J = 9.6, H-3); ¹³C-NMR: δ 159.9 (0), 152.9 (0), 142.0 (1), 134.5 (1), 130.1 (1), 120.3 (0), 118.6 (1), 117.8 (1), 116.9 (0); IR (neat, cm⁻¹): $\tilde{\nu}$ = 3086 (w), 1721(s), 1600 (w), 1557 (w), 1476 (w); HRMS (EI): calcd for C₉H₅O₂[79]Br [M]⁺: 223.9473, found: 223.9493; MS (EI): m/z 226 (M⁺, 88), 224 (M⁺, 100), 198 (57), 196 (53), 117 (31), 89 (50), 62 (27); Anal. calcd for C₉H₅O₂Br: C: 48.03, H: 2.24; found: C: 47.98, H: 2.14.

⁹ Reported in the literature: mp = 160-163°C; J. Oyamada and T. Kitamura, *Tetrahedron*, 2006, **62**, 6918-6925.

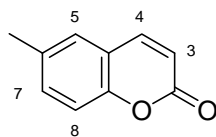
¹H NMR spectrum of 2g



¹³C NMR spectrum of 2g



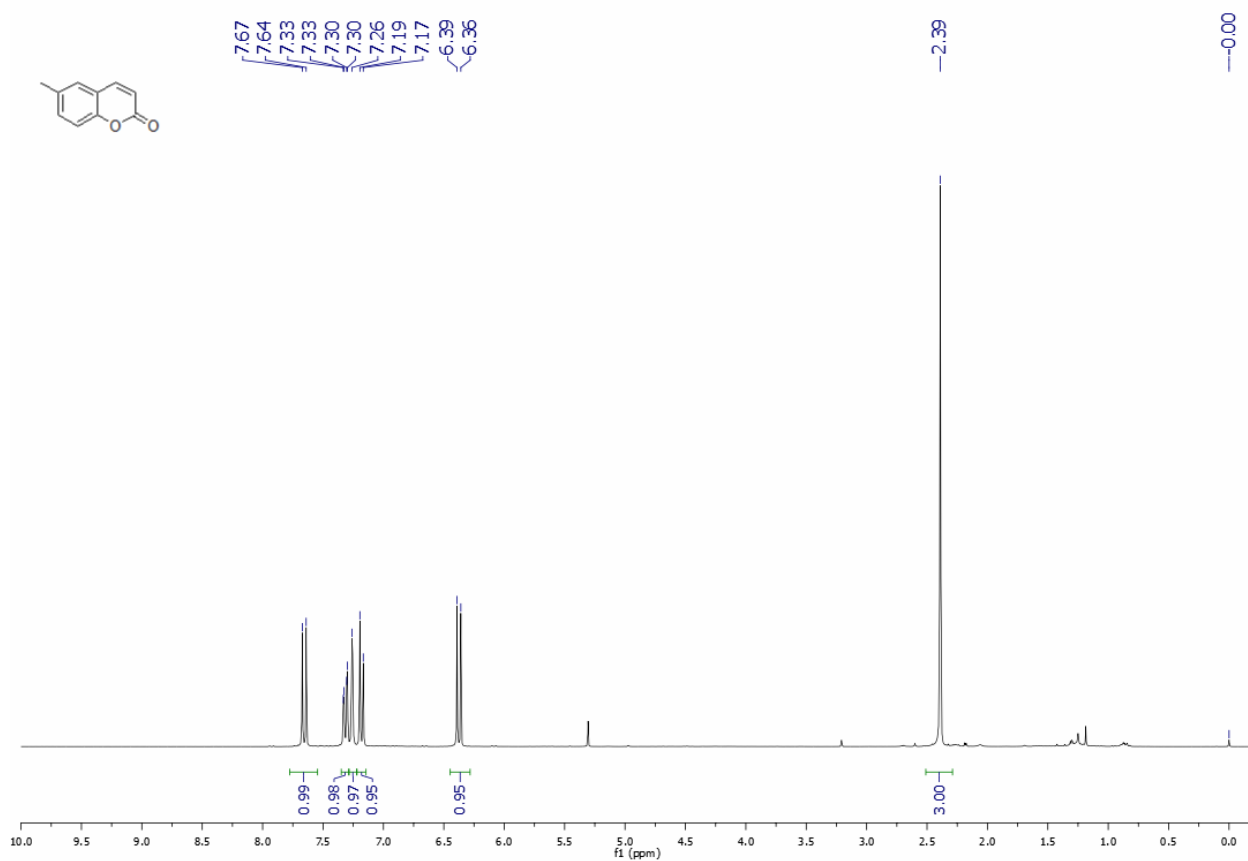
D10 6-Methyl-2*H*-chromen-2-one (**2h**)



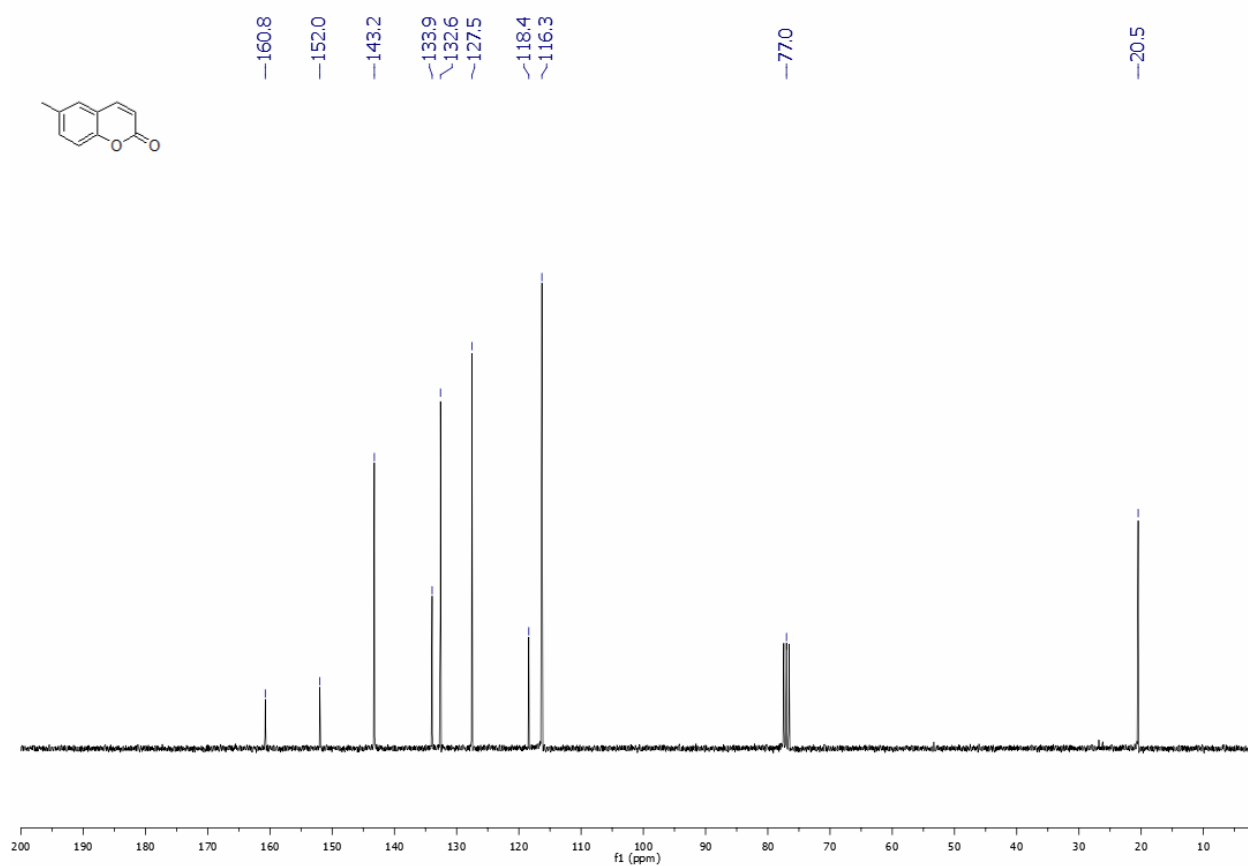
Following the general procedure A, 6-methyl-2*H*-chromen-2-one (**2h**) was obtained from **4h** (174 mg, 1.0 mmol) as a yellowish solid (with catalyst **A**: 83 mg, 52%, with catalyst **B**: 80 mg, 50%). Mp: 76 – 78 °C;¹⁰ ¹H-NMR: δ 7.66 (d, 1H, $J = 9.5$, H-4), 7.32 (dd, 1H, $J = 8.4$, 1.9, H-8), 7.26 (s (br), 1H, H-5), 7.18 (d, 1H, $J = 8.4$, H-7), 6.38 (d, 1H, $J = 9.6$, H-3), 2.39 (s, 3H, CH_3); ¹³C-NMR: δ 160.8 (0), 152.0 (0), 143.2 (1), 133.9 (0), 132.6 (1), 127.5 (1), 118.4 (0), 116.3 (1, 2C), 20.5 (3); IR (neat, cm^{-1}): $\tilde{\nu} = 3077$ (w), 2926 (w), 1716 (s), 1622 (m), 1573 (m); HRMS (EI): calcd for $C_{10}H_8O_2$ $[M]^+$: 160.0524, found: 160.0513; MS (EI): m/z 160 (M^+ , 75), 132 (100), 131 (100), 104 (33), 103 (24), 78 (23), 77 (32), 51 (24).

¹⁰ Reported in the literature: mp = 73.5-74°C; J. Oyamada and T. Kitamura, *Tetrahedron*, 2006, **62**, 6918-6925.

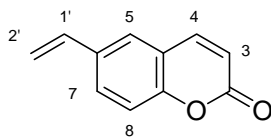
^1H NMR spectrum of 2h



^{13}C NMR spectrum of 2h

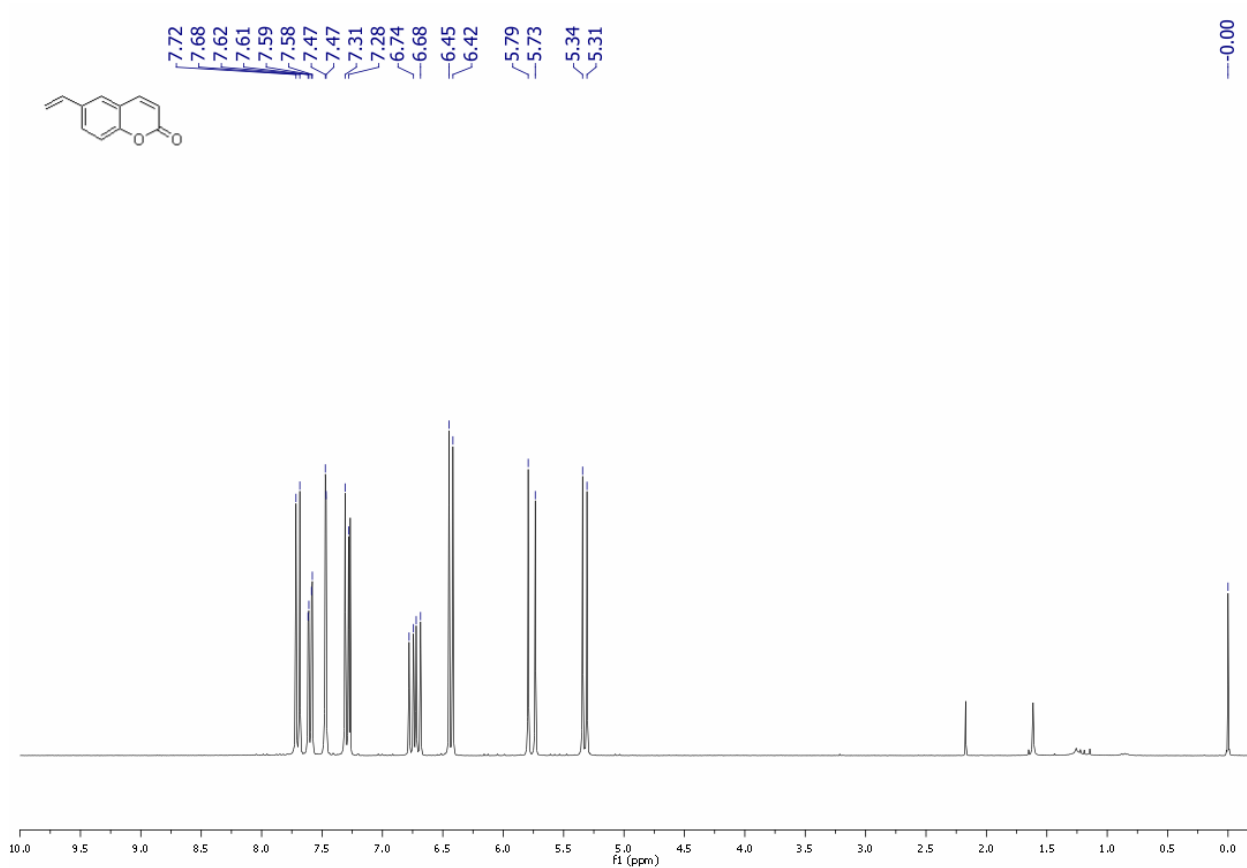


D11 6-Vinyl-2*H*-chromen-2-one (**2i**)

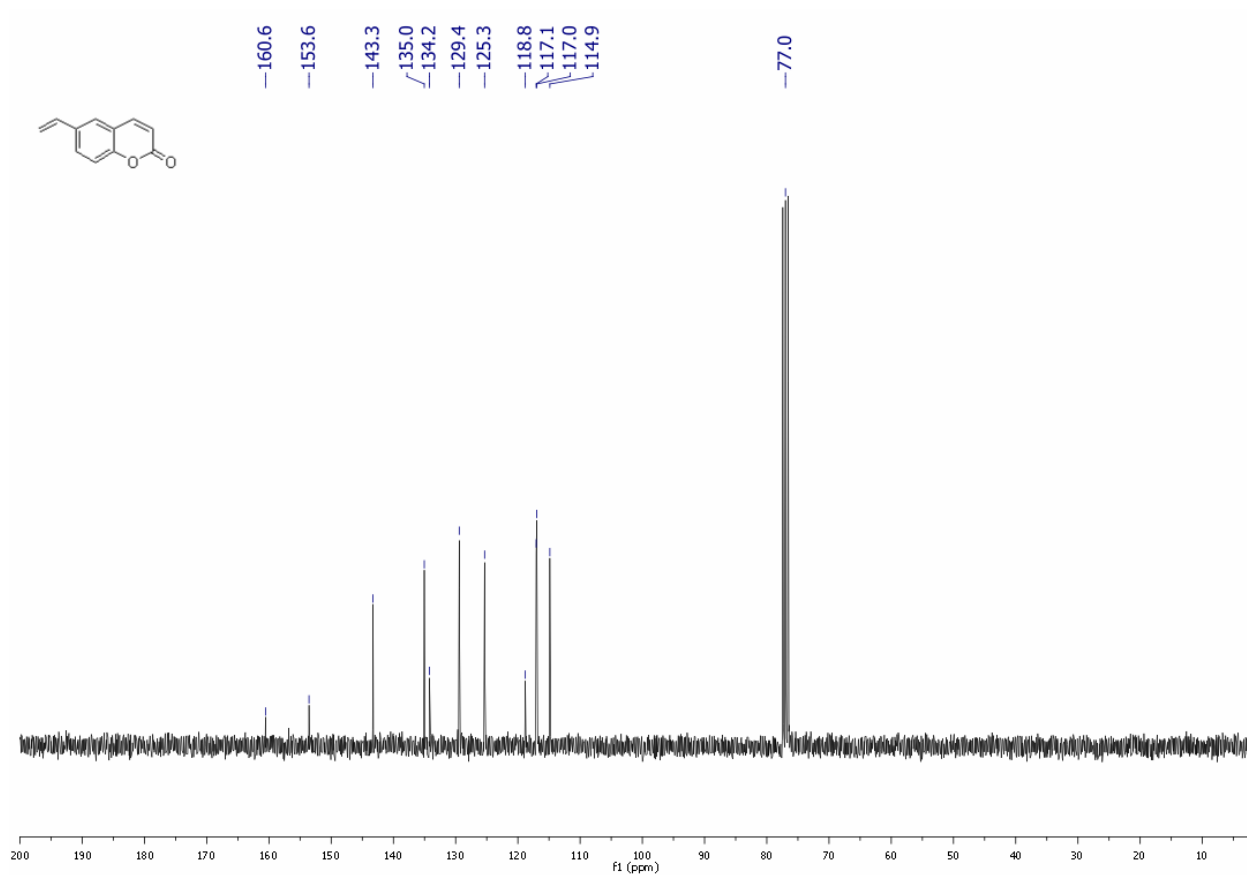


Following the general procedure A, 6-vinyl-2*H*-chromen-2-one (**2i**) was obtained from **4i** (186 mg, 1.0 mmol) as a yellowish solid (with catalyst **A**: 52 mg, 30%, with catalyst **B**: 57 mg, 33%). Mp: 69 – 71°C; ¹H-NMR: δ 7.70 (d, 1H, *J* = 9.5, H-4), 7.60 (dd, 1H, *J* = 8.6, 1.8, H-7), 7.47 (d, 1H, *J* = 1.8, H-5), 7.30 (d, 1H, *J* = 8.6, H-8), 6.63 (dd, 1H, *J* = 17.6, 10.9, H-1'), 6.43 (d, 1H, *J* = 9.7, H-3), 5.76 (d, 1H, *J* = 17.6, H-2'(trans)), 5.32 (d, 1H, *J* = 10.9, H-2' (cis)); ¹³C-NMR: δ 160.5 (0), 153.6 (0), 143.3 (1), 135.0 (1), 134.2 (0), 129.4 (1), 125.3 (1), 118.8 (0), 117.0 (1), 117.0 (1), 114.9 (2); IR (neat, cm⁻¹): $\tilde{\nu}$ = 2975 (w), 1723 (s), 1622 (m), 1570 (m), 1489 (w), 1159 (m); HRMS (EI): calcd for C₁₁H₈O₂ [M]⁺: 172.0524, found: 172.0518; MS (EI): *m/z* 172 (M⁺, 100), 144 (77), 129 (23), 115 (73), 83 (25), 57 (63); Anal. calcd for C₁₁H₈O₂: C: 76.73, H: 4.68; found: C: 75.91, H: 4.49.

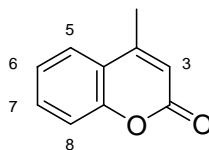
¹H NMR spectrum of 2i



¹³C NMR spectrum of 2i



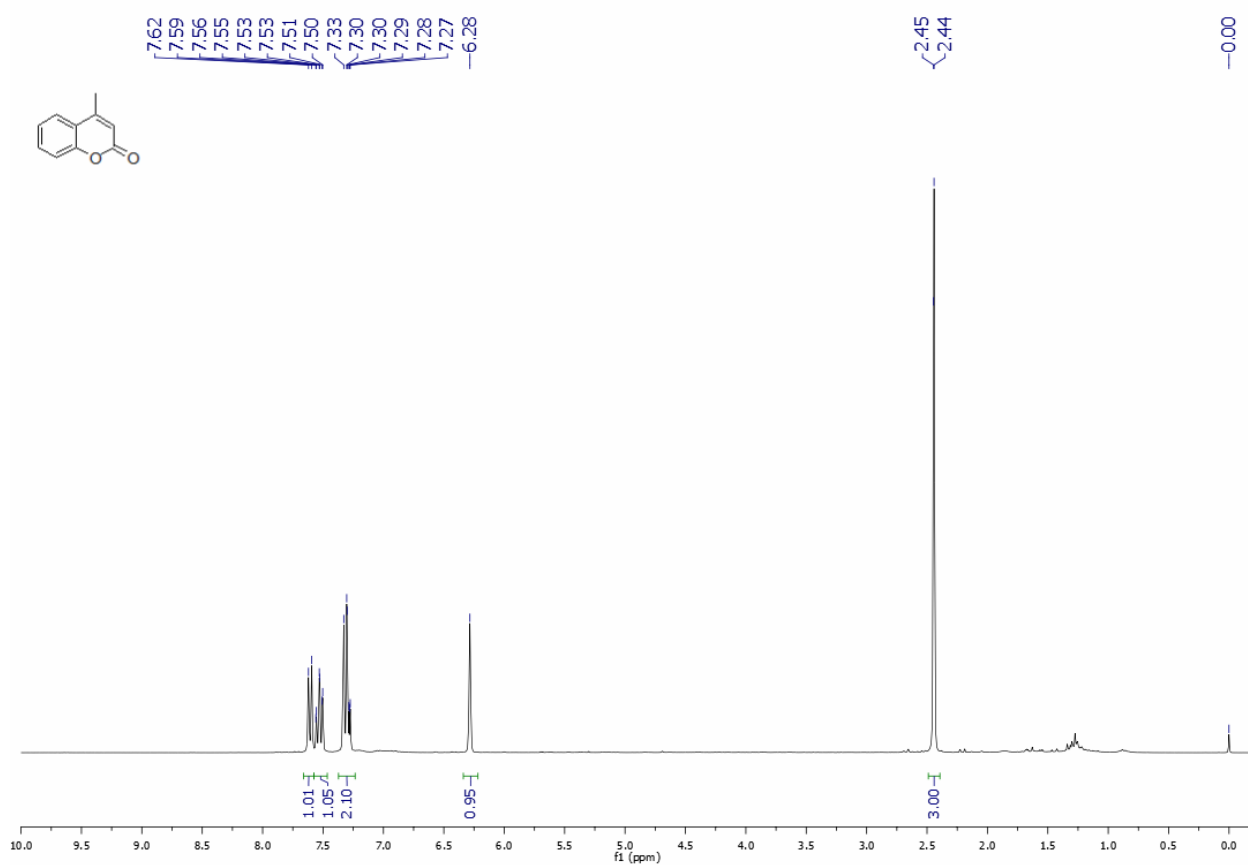
D12 4-Methyl-2*H*-chromen-2-one (**2j**)



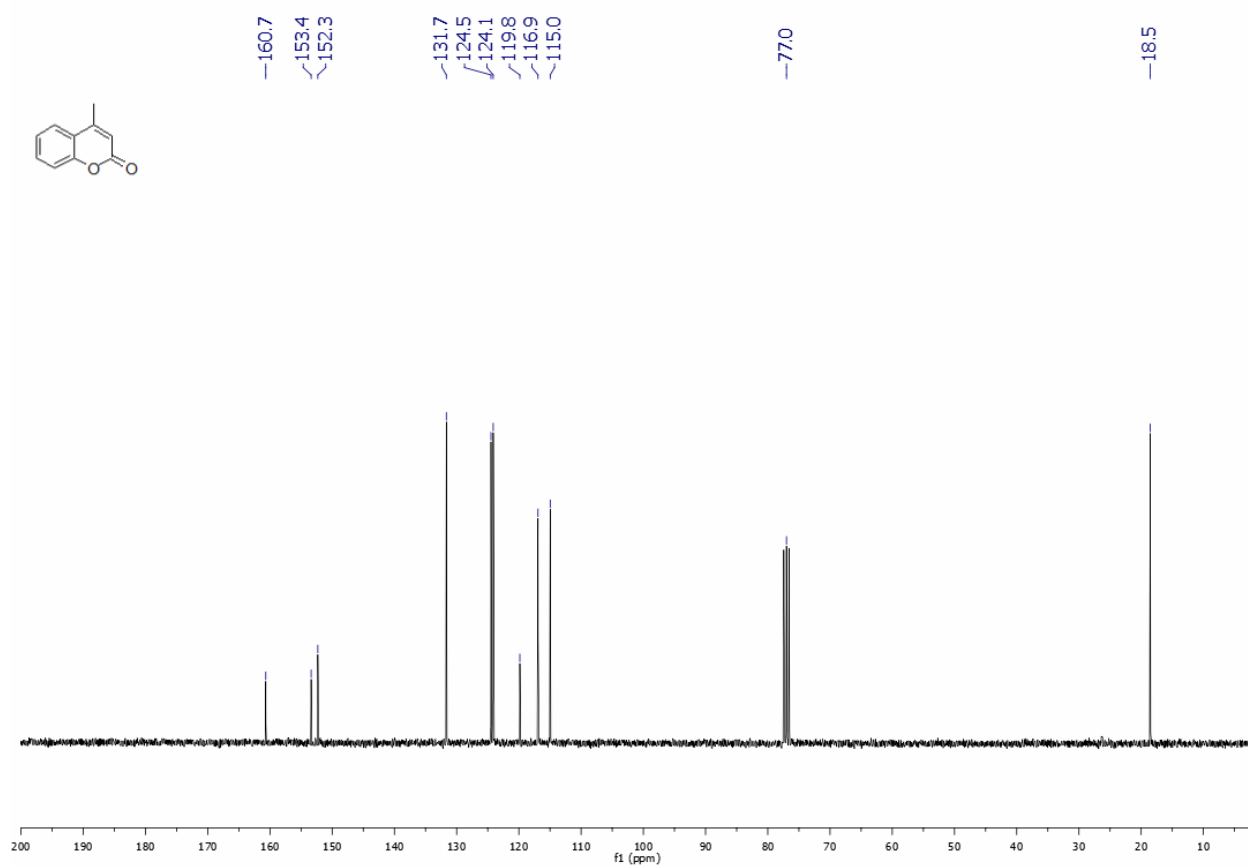
Following the general procedure A, 4-methyl-2*H*-chromen-2-one (**2j**) was obtained from **4j** (174 mg, 1.0 mmol) as a yellowish solid (with catalyst **A**: 48 mg, 30%, with catalyst **B**: 53 mg, 33%). Mp: 69 – 71 °C; ¹¹ ¹H-NMR: δ 7.61 (d, 1H, $J = 7.9$, H-5), 7.53 (m, 1H, H7), 7.35 – 7.26 (2H, H-6, H8), 6.28 (s (br), 1H, H-3), 2.44 (m, 3H, CH_3); ¹³C-NMR: δ 160.7 (0), 153.4 (0), 152.3 (0), 131.7 (1), 124.5 (1), 124.1 (1), 119.8 (0), 116.9 (1), 115.0 (1), 18.5 (3); IR (neat, cm^{-1}): $\tilde{\nu} = 3056$ (w), 2981 (w), 1723 (s), 1626 (m), 1609 (m), 1265 (m); HRMS (EI): calcd for $C_{10}H_8O_2$ $[M]^+$: 160.0524, found: 160.0510; MS (EI): m/z 160 (M^+ , 73), 132 (69), 131 (100), 121 (23), 103 (20), 77 (27), 43 (27), 39 (29).

¹¹ Reported in the literature: 75-76 °C; J. Koeber, *Z. Naturforsch. B*, 2005, **60**, 792-796.

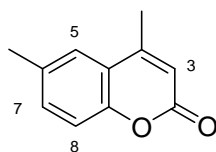
¹H NMR spectrum of 2j



¹³C NMR spectrum of 2j



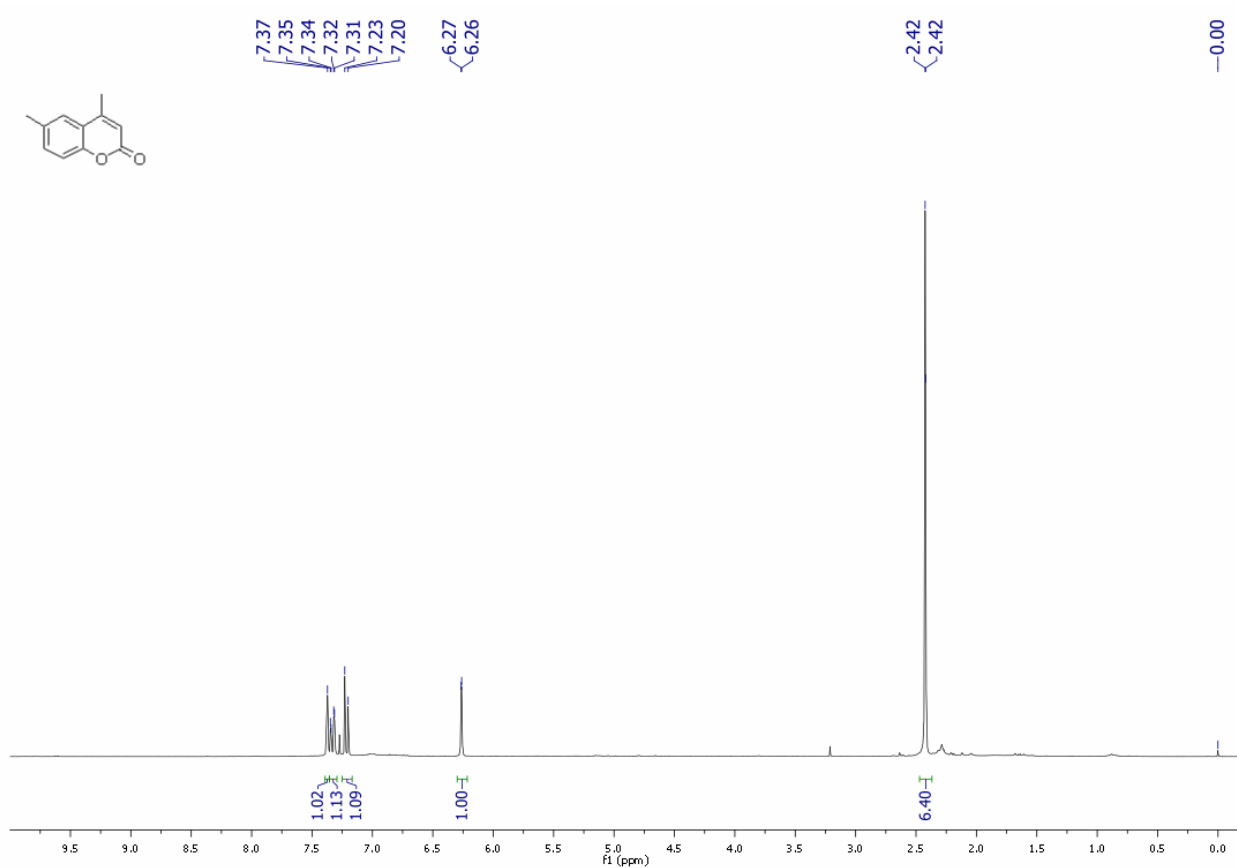
D13 4,6-Dimethyl-2*H*-chromen-2-one (**2k**)



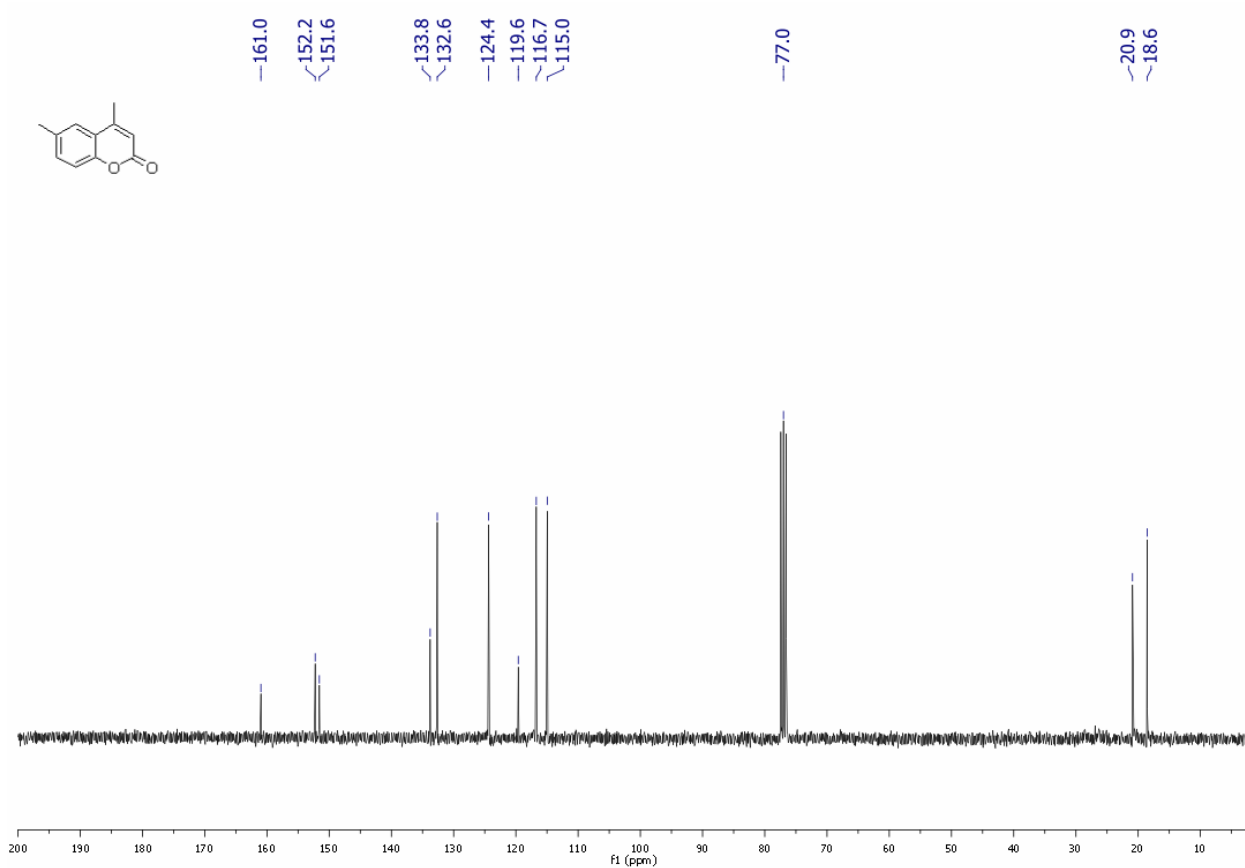
Following the general procedure A, 4,6-dimethyl-2*H*-chromen-2-one (**2k**) was obtained from **4k** (188 mg, 1.0 mmol) as a yellowish solid (with catalyst **A**: 61 mg, 35%, with catalyst **B**: 52 mg, 30%). Mp: 152 – 154°C;¹² ¹H-NMR: δ 7.38 (s (br), 1H, H-5), 7.33 (dd, 1H, $J = 8.5$, 1.8, H-7), 7.22 (d, 1H, $J = 8.5$, H-8), 6.27 (m, 1H, H-3), 2.42 (s, 3H, CH₃), 2.42 (s, 3H, CH₃); ¹³C-NMR: δ 161.0 (0), 152.3 (0), 151.6 (0), 133.8 (0), 132.6 (1), 124.4 (1), 119.6 (0), 116.7 (1), 115.0 (1), 20.9 (3), 18.6 (3); IR (neat, cm⁻¹): $\tilde{\nu} = 2924$ (w), 1709 (s), 1624 (m), 1610 (m), 1571 (m); HRMS (EI): calcd for C₁₁H₁₀O₂ [M]⁺: 174.0681, found: 174.0664; MS (EI): m/z 174 (M⁺, 78), 146 (65), 145 (100), 131 (26), 117 (18), 115 (30), 91 (18), 77 (15).

¹² Reported in the literature: 151-153°C; H. Sharghi and M. Jokar, *Heterocycles*, 2007, **71**, 2721-2733.

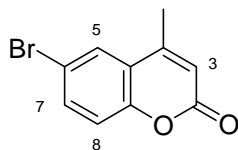
^1H NMR spectrum of 2k



^{13}C NMR spectrum of 2k



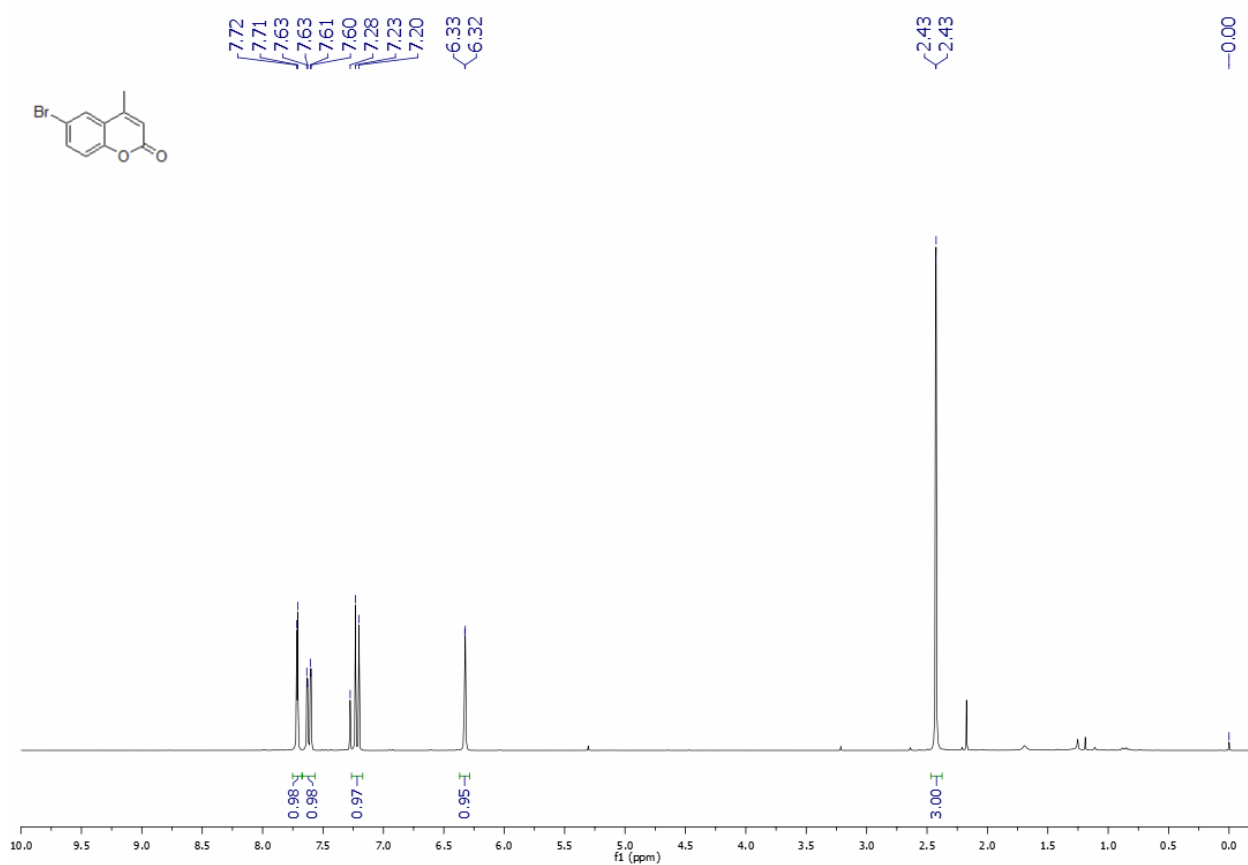
D14 6-Bromo-4-methyl-2*H*-chromen-2-one (**2I**)



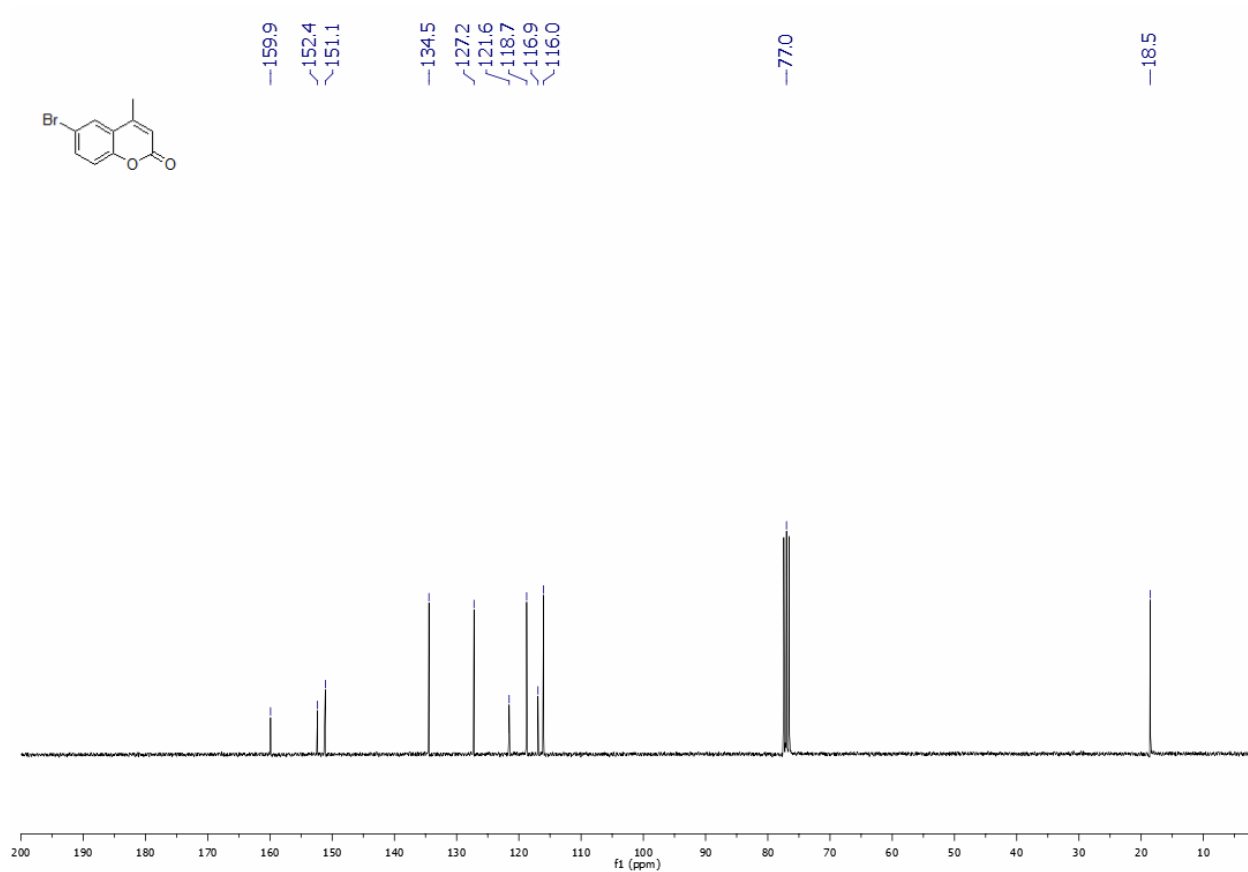
Following the general procedure A, 6-bromo-4-methyl-2*H*-chromen-2-one (**2I**) was obtained from **4I** (253 mg, 1.0 mmol) as a yellowish solid (with catalyst **A**: 120 mg, 50%, with catalyst **B**: 107 mg, 45%). Mp: 187 – 189°C; ¹³H-NMR: δ 7.72 (d, 1H, *J* = 2.2, H-5), 7.62 (dd, 1H, *J* = 8.7, 2.3, H-7), 7.22 (d, 1H, *J* = 8.7, H-8), 6.33 (m, 1H, H-3), 2.43 (d, 3H, *J* = 1.3, CH₃); ¹³C-NMR: δ 159.9 (0) 152.4 (0), 151.1 (0), 134.5 (1), 127.2 (1), 121.6 (0), 118.8 (1), 116.9 (0), 116.0 (1), 18.5 (3); IR (neat, cm⁻¹): $\tilde{\nu}$ = 3092 (w), 2928 (w), 1749 (s), 1598 (w), 1556 (w), 1479 (m), 1413 (m), 1380 (m), 1357 (m); HRMS (EI): calcd for C₁₀H₇O₂[79]Br [M]⁺: 237.9629, found: 237.9626; MS (EI): *m/z* 240 (M⁺, 95), 238 (M⁺, 100), 212 (68), 211 (88), 210 (75), 209 (91), 131 (74), 103 (77), 102 (58), 77 (98), 63 (56), 51 (87), 39 (54); Anal. calcd for C₁₀H₇O₂Br: C: 50.24, H: 2.95; found: C: 50.21, H: 2.85.

¹³ Reported in the literature: mp = 184-186°C; L.-Q. Wu, C.-G. Yang, Y.-F. Wu and L.-M. Yang, *J. Chin. Chem. Soc.*, 2009, **56**, 606-608.

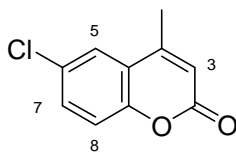
¹H NMR spectrum of 2l



¹³C NMR spectrum of 2l



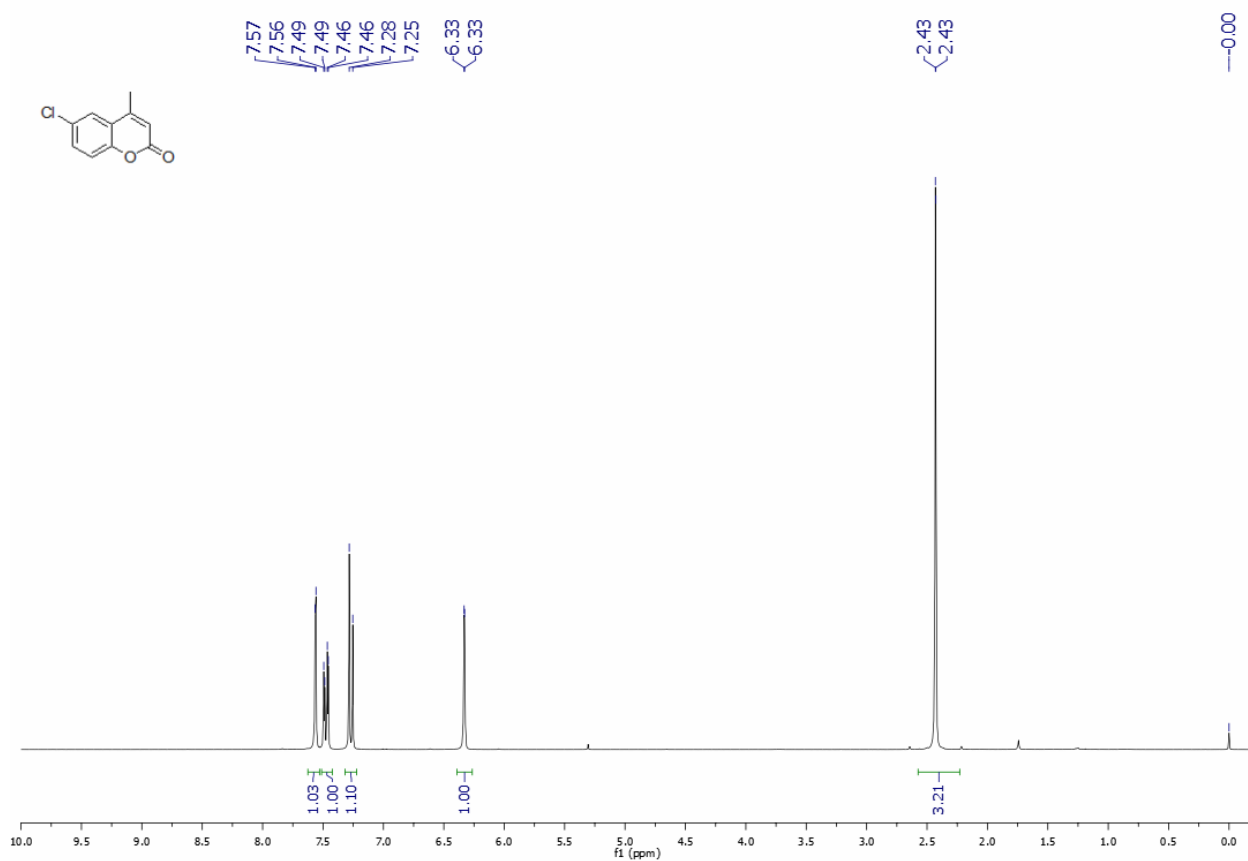
D15 6-Chloro-4-methyl-2H-chromen-2-one (**2m**)



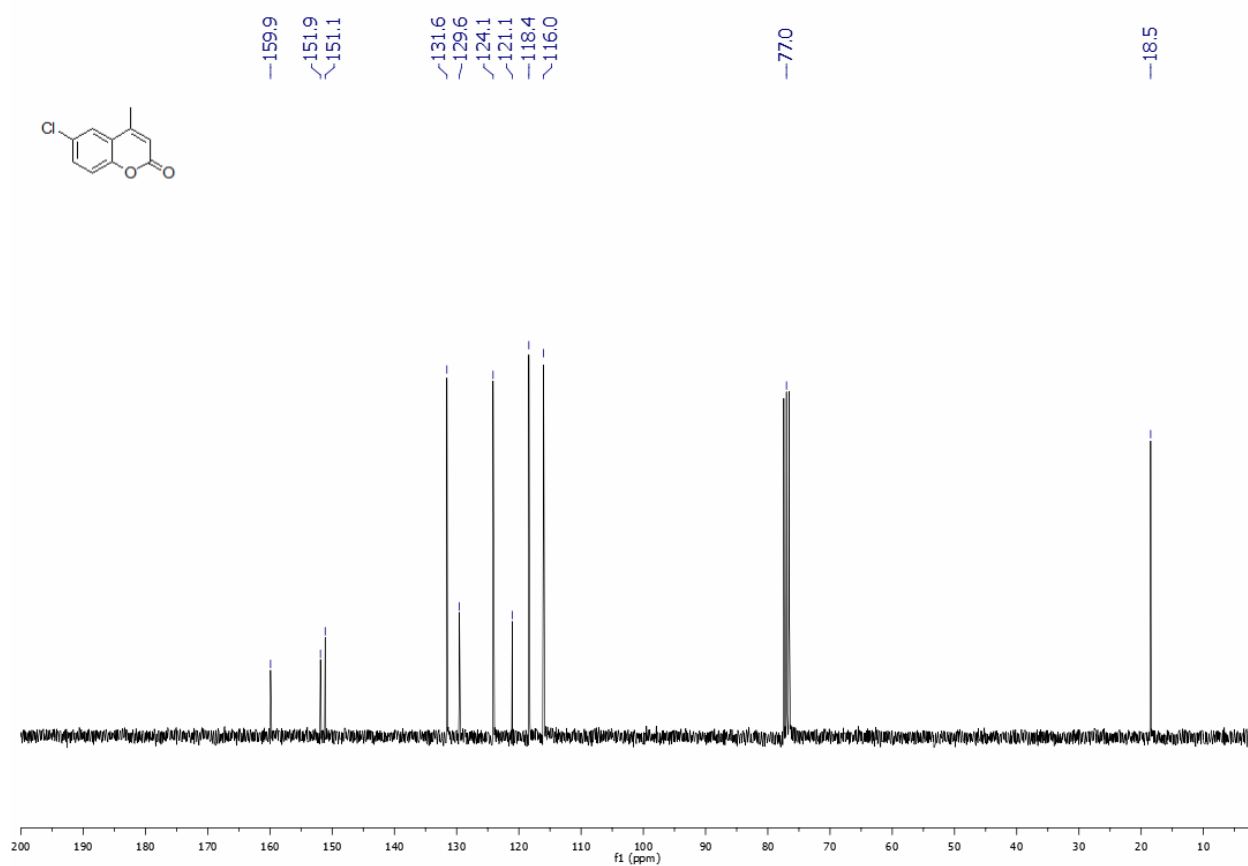
Following the general procedure A, 6-Chloro-4-methyl-2H-chromen-2-one (**2m**) was obtained from **4m** (209 mg, 1.0 mmol) as a yellowish solid (with catalyst **A**: 92 mg, 47%, with catalyst **B**: 86 mg, 44%). Mp: 191 – 193°C;¹⁴ ¹H-NMR: δ 7.56 (d, 1H, $J = 2.4$, H-5), 7.48 (dd, 1H, $J = 8.7, 2.4$, H-7), 7.27 (d, 1H, $J = 8.8$, H-8), 6.33 (m, 1H, H-3), 2.43 (d, 3H, $J = 1.3$, CH_3); ¹³C-NMR: δ 159.9 (0), 151.9 (0), 151.1 (0), 131.6 (1), 129.6 (0), 124.2 (1), 121.1 (0), 118.4 (1), 116.0 (1), 18.5 (3); IR (neat, cm^{-1}): $\bar{\nu} = 2924$ (w), 1720 (s), 1625 (w), 1600 (w), 1484 (w), 1417 (m); HRMS (EI): calcd for $C_{10}H_7O_2[^{35}Cl] [M]^+$: 194.0135, found: 194.0122; MS (EI): m/z 196 (M^+ , 21), 194 (M^+ , 65), 168 (25), 167 (40), 166 (73), 165 (100), 155 (15), 131 (26), 103 (25), 77 (28), 57 (27), 51 (27), 43 (27); Anal. calcd for $C_{10}H_7O_2Cl$: C: 61.72, H: 3.63; found: C: 61.37, H: 3.40.

¹⁴ Reported in the literature: mp = 184-186°C; P. Goswami, *Synth. Commun.*, 2009, **39**, 2271 - 2278.

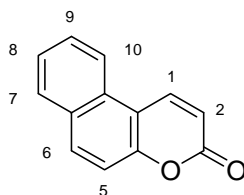
^1H NMR spectrum of 2m



^{13}C NMR spectrum of 2m



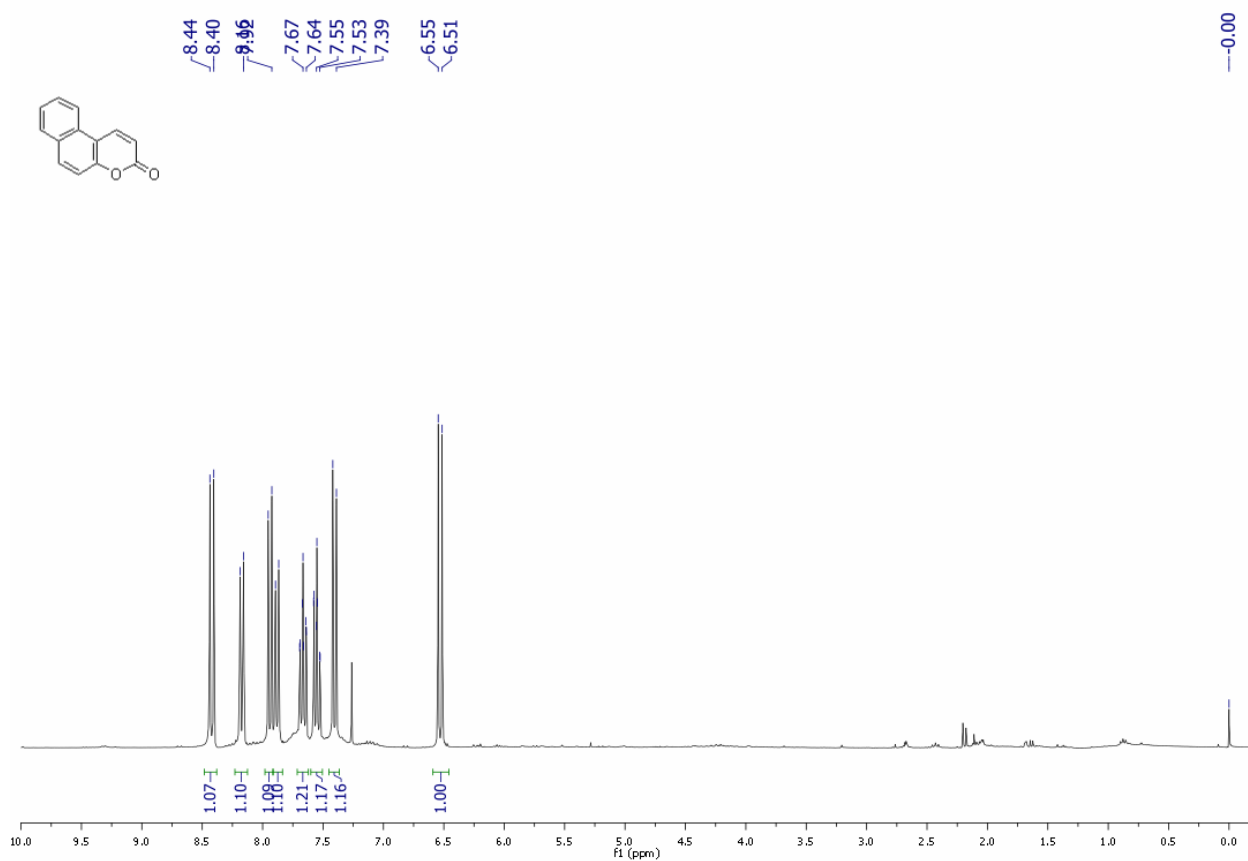
D16 3*H*-Benzo[*f*]chromen-3-one (**2n**)



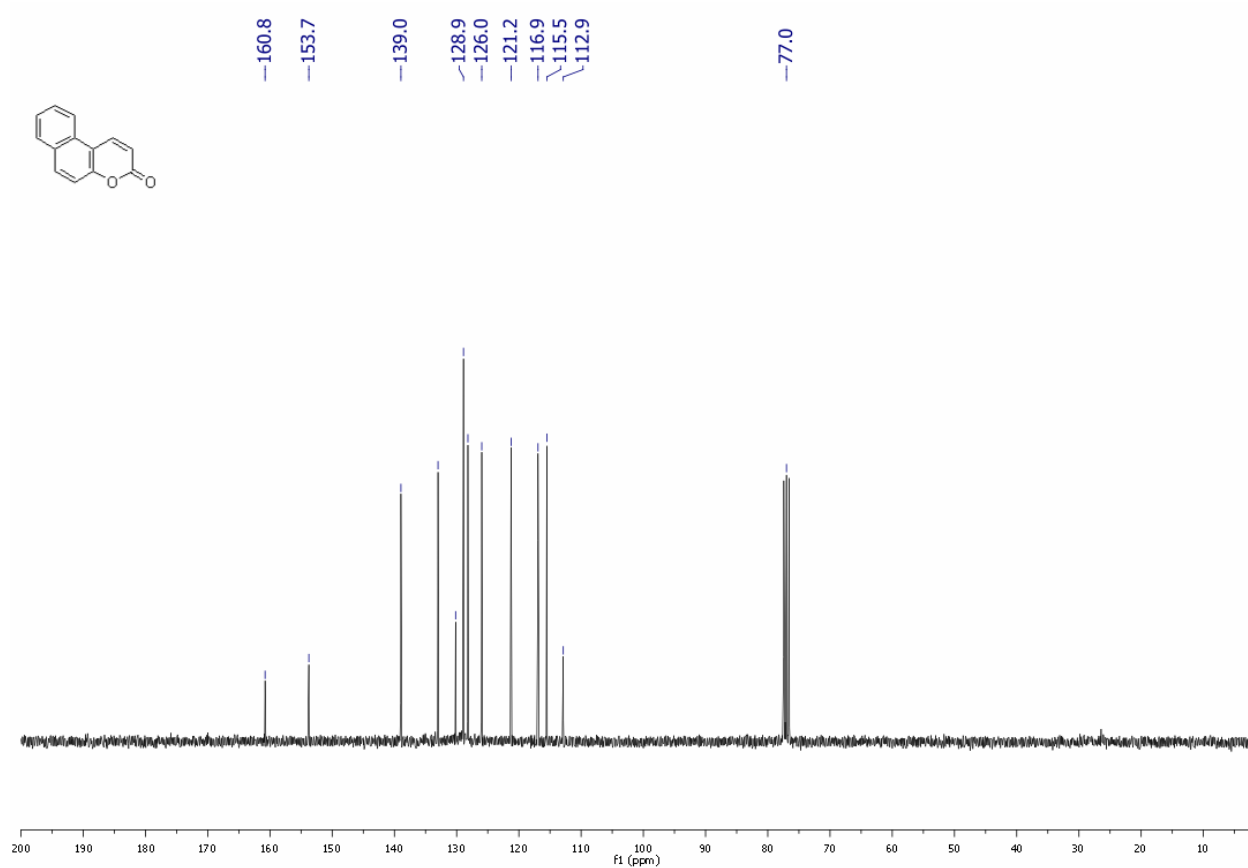
Following the general procedure A, 3*H*-benzo[*f*]chromen-3-one (**2n**) was obtained from **4n** (210 mg, 1.0 mmol) as a yellowish solid (with catalyst **A**: 77 mg, 39%, with catalyst **B**: 77 mg, 39%). Mp: 119 – 121°C;¹⁵ ¹H-NMR: δ 8.42 (d, 1H, J = 9.8, H-1), 8.18 (d, 1H, J = 8.4, H-10), 7.94 (d, 1H, J = 9.0, H-6), 7.88 (d, 1H, J = 8.0, H-7), 7.67 (ddd, 1H, J = 8.4, 7.0, 1.4, H-9), 7.55 (ddd, 1H, J = 8.1, 7.1, 1.1, H-8), 7.41 (d, 1H, J = 9.0, H-5), 6.53 (d, 1H, J = 9.7, H-2); ¹³C-NMR: δ 160.8 (0), 153.8 (0), 139.0 (1), 133.0 (1), 130.2 (0), 128.9 (1), 128.9 (0), 128.2 (1), 126.0 (1), 121.3 (1), 116.9 (1), 115.5 (1), 112.9 (0); IR (neat, cm⁻¹): $\tilde{\nu}$ = 3067 (w), 2928 (w), 1717 (s), 1631 (m), 1563 (s), 1514 (m), 1175 (m); HRMS (EI): calcd for C₁₃H₈O₂ [M]⁺: 196.0524, found: 196.0528; MS (EI): m/z 196 (M⁺, 63), 168 (90), 140 (34), 139 (100), 85 (42), 83 (33).

¹⁵ Reported in the literature: mp = 117-118°C; J. Oyamada and T. Kitamura, *Tetrahedron*, 2006, **62**, 6918-6925.

¹H NMR spectrum of 2n



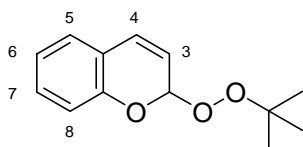
¹³C NMR spectrum of 2n



D17 Control experiment: allylic oxidation in the absence of Ru-catalyst

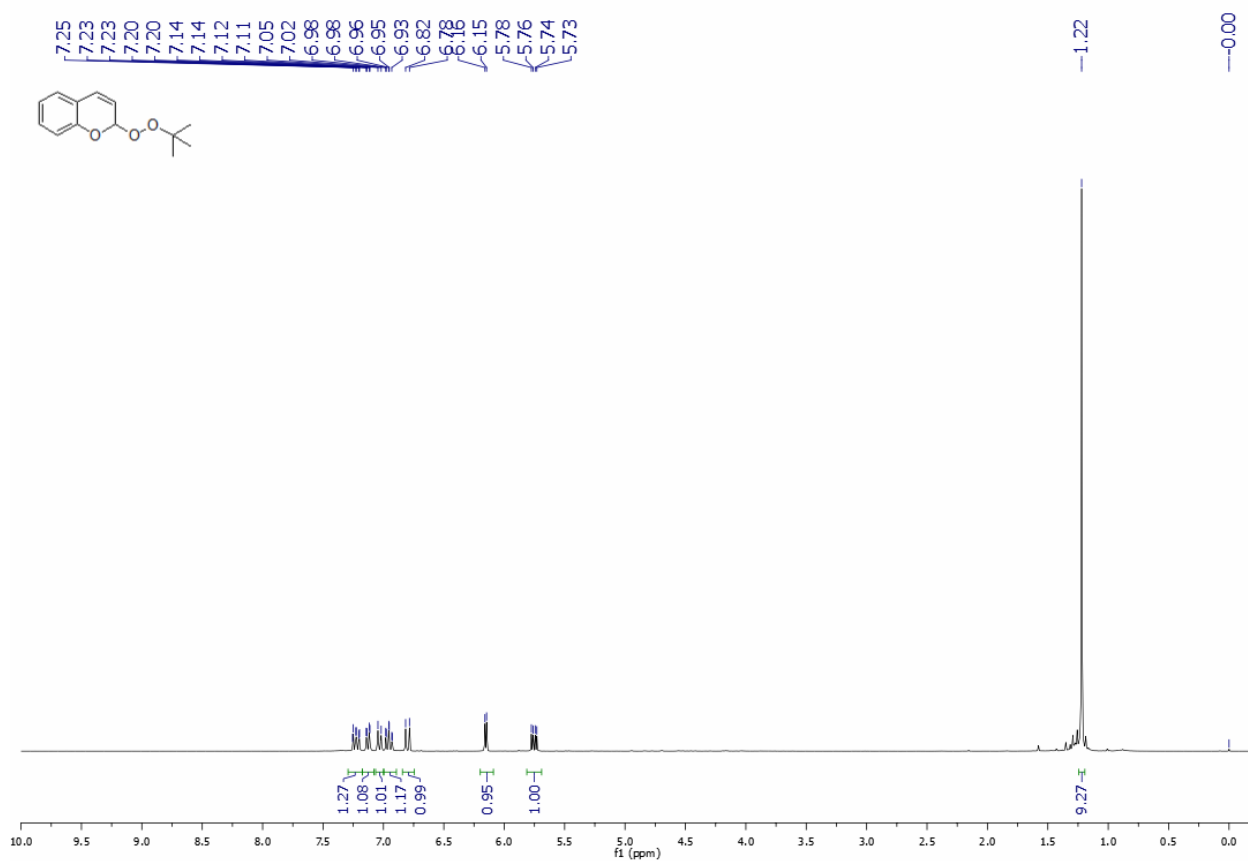
Purified (via kugelrohr distillation) chromene **5a** (132 mg, 1.0 mmol) was dissolved in ethyl acetate (10 mL) and immersed in an oil bath preheated to 40 °C. To this solution was added ^tBuOOH (5.5 M in decane, 720 μL, 4.0 mmol) via syringe pump within 15 min. The reaction mixture was stirred for 72 h at 40 °C. Then all volatiles were removed in vacuo. After column chromatography on silica unreacted chromene **5a** (41 mg, 31%), coumarin **2a** (20 mg, 14%) and 2-(*tert*-butylperoxy)-2*H*-chromene (**7a**, 79 mg, 36%) were isolated.

Analytical data for 2-(*tert*-butylperoxy)-2*H*-chromene (**7a**):

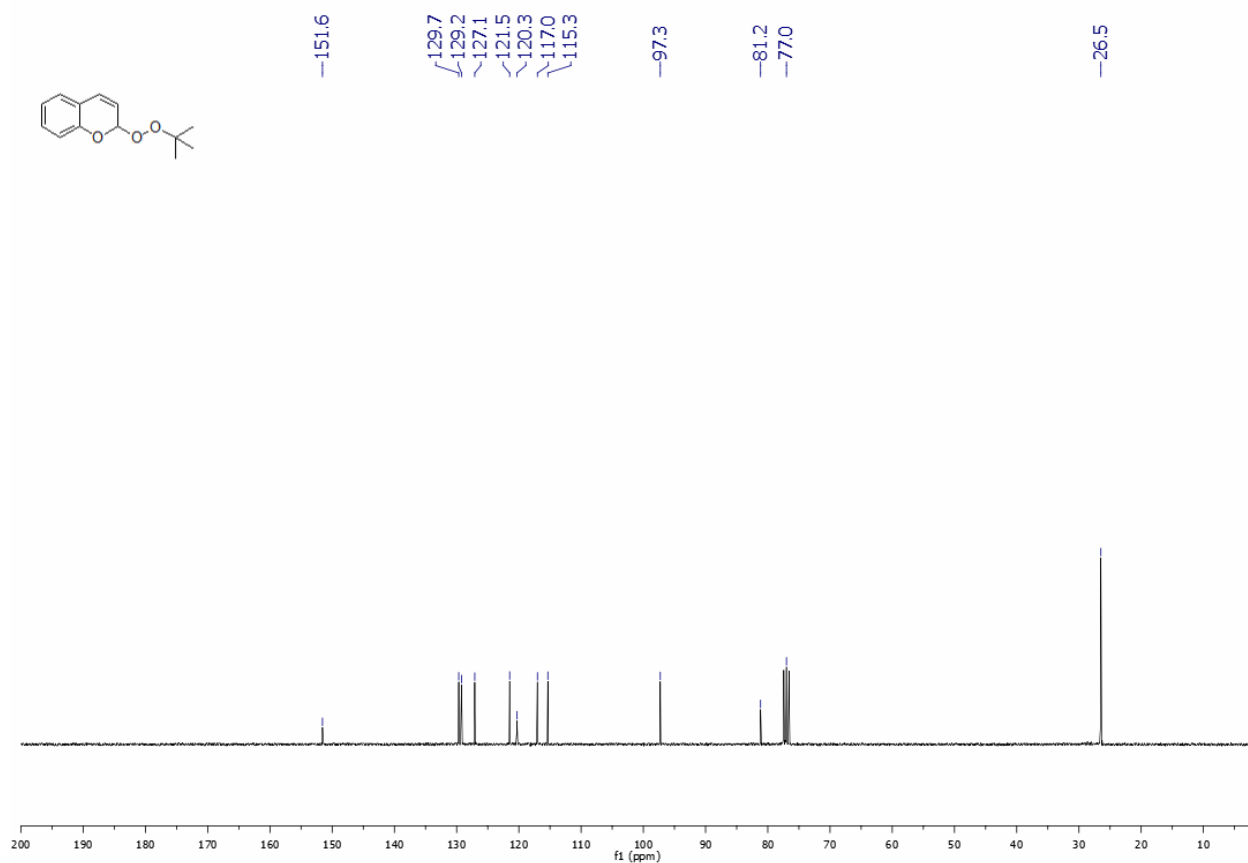


Colourless oil. ¹H-NMR: δ 7.23 (m, 1H, H-7), 7.13 (dd, 1H, *J* = 7.5, 1.6, H-5), 7.03 (d, 1H, *J* = 8.1, H-8), 6.95 (td, 1H, *J* = 7.5, 1.1, H-6), 6.80 (d, 1H, *J* = 9.6, H-4), 6.15 (d, 1H, *J* = 4.0, H-2), 5.75 (dd, 1H, *J* = 9.6, 4.0, H-3), 1.22 (s, 9H, C(CH₃)₃); ¹³C-NMR: δ 151.6 (0), 129.7 (1), 129.2 (1), 127.1 (1), 121.5 (1), 120.3 (0), 117.0 (1), 115.3 (1), 97.3 (1), 81.2 (0), 26.5 (3, 3C); IR (neat, cm⁻¹): $\tilde{\nu}$ = 2977 (w), 1640 (m), 1608 (m), 1488 (m), 1458 (m), 1363 (m), 1313 (m); HRMS (ESI): calcd for C₁₃H₁₆O₃Na [M+Na]⁺: 243.0997, found: 243.0992; MS (EI): *m/z* 220 (M⁺, 8), 147 (13), 131 (100), 121 (13), 77 (17), 73 (94), 57 (82), 55 (16), 43 (39), 41 (22); Anal. calcd for C₁₃H₁₆O₃: C: 70.89, H: 7.32; found: C: 70.26, H: 7.30.

¹H NMR spectrum of 7a



¹³C NMR spectrum of 7a



D18 Control experiment 2: allylic oxidation of **5a** catalyzed by Ru-catalyst **A**

Purified (via Kugelrohr distillation) chromene **5a** (132 mg, 1.0 mmol) was dissolved in dry and degassed benzene (1.0 mL). Catalyst **A** (40 mg, 0.05 mmol) was then added. Immediately after addition of the catalyst, the reaction vessel was immersed in an oil bath preheated to 40 °C (electronic temperature control) and the solution was stirred for 5 min. Then ^tBuOOH (5.5 M in decane, 720 μL, 4.0 mmol) was added to the reaction mixture via syringe pump within 15 min. After complete addition of the oxidant, the mixture was stirred for another 3 h. It was diluted with MTBE (50 mL), and MgSO₄ was added to absorb water and Ru residues. The mixture was filtered and all volatiles were removed in vacuo. The residue was purified by column chromatography on silica. Coumarin **2a** was obtained as a yellowish solid (70 mg, 48%). Analytical data were identical with those reported in section D1.