Supporting Information

for

Ring-closing-metathesis-based synthesis of annellated coumarins from 8-allylcoumarins

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Full experimental procedures, characterization data and copies of $^1$H and $^{13}$C NMR spectra of all compounds
**Contents:**

- General methods  
  S3
- General procedures and analytical data  
  S3
- References  
  S25
- Copies of spectra  
  S27
General methods. All experiments were conducted in dry reaction vessels under an atmosphere of dry nitrogen. Solvents were purified by standard procedures. $^1$H NMR spectra were obtained at 300 MHz in CDCl$_3$ with CHCl$_3$ ($\delta = 7.26$ ppm) as an internal standard. Coupling constants are given in Hz. $^{13}$C NMR spectra were recorded at 75 MHz in CDCl$_3$ with CDCl$_3$ ($\delta = 77.1$ ppm) as an internal standard. Whenever the solubility or stability of the sample or signal separation were insufficient in CDCl$_3$, it was replaced by one of the following solvents: acetone-$d_6$ (acetone-$d_5$ as internal standard for $^1$H NMR spectroscopy, $\delta = 2.05$ ppm, CD$_3$COCD$_3$ as internal standard for $^{13}$C NMR spectroscopy, $\delta = 29.8$ ppm); DMSO-$d_6$ (DMSO-$d_5$ as internal standard for $^1$H NMR spectroscopy, $\delta = 2.50$ ppm, DMSO-$d_6$ as internal standard for $^{13}$C NMR spectroscopy, $\delta = 39.5$ ppm). IR spectra were recorded as ATR-FTIR spectra. Wavenumbers ($\nu$) are given in cm$^{-1}$. The peak intensities are defined as strong (s), medium (m) or weak (w). Low- and high-resolution mass spectra were obtained by EI–TOF or ESI–TOF. The general procedures for the synthesis of compounds 8, 9 and 10 stated below follow closely procedures previously reported by us [1].

General procedure for the synthesis of coumarins 8 from MOM-protected coumarins 7. To a solution of the appropriate MOM-ether 7 (1.00 mmol) in methanol (20 mL) was added aq. HCl (3 M, 100 µL) and the solution was heated to 65 °C for 1 h. Upon cooling to ambient temperature, water (30 mL) and ethyl acetate (30 mL) were added. The organic layer was separated, and the aqueous layer extracted twice with ethyl acetate (30 mL each). The combined organic extracts were dried with MgSO$_4$, filtered, and evaporated. The residue was purified by column chromatography on silica, using hexanes-MTBE mixtures of increasing polarity.

General procedure for the synthesis of 8-allylcoumarins 8 from allyl ethers 5. Ylide 6 (522 mg, 1.50 mmol) and the corresponding allyl ether 5 (1.00 mmol) were dissolved in N,N-
diethylaniline (10 mL) in a vessel suitable for microwave irradiation. The vessel was sealed and irradiated in a dedicated microwave reactor for 10 min. at 250 °C. Upon cooling to ambient temperature the mixture was diluted with ethyl acetate (50 mL) and washed three times with aq. HCl (2 M, 30 mL each). After evaporation of all volatiles the residue was redissolved in methanol (20 mL) and aq. HCl (100 µL) was added. The mixture was heated to 65 °C for 1 h and then cooled to ambient temperature. From this point work-up was carried out as described above for the synthesis starting from compounds 7.

**8-Allyl-7-hydroxy-2H-chromen-2-one (8a)**[1]. Starting from 7a (246 mg, 1.00 mmol) compound 8a (166 mg, 0.82 mmol, 82%) was obtained. Starting from 5a (222 mg, 1.00 mmol) compound 8a (119 mg, 0.59 mmol, 59%) was obtained. Colourless solid, mp 162 – 163 °C (literature: 162 – 163 °C[1]). Other analytical data have been published previously[1].

![8a](image)

**8-Allyl-7-hydroxy-4-phenyl-2H-chromen-2-one (8b)**[2]. Starting from 7b (322 mg, 1.00 mmol) compound 8b (253 mg, 0.91 mmol, 91%) was obtained. Starting from 5b (298 mg, 1.00 mmol) compound 8b (195 mg, 0.70 mmol, 70%) was obtained. Yellowish solid, mp 190 - 193 °C (literature: 190 – 192 °C[3]); ¹H NMR (300 MHz, acetone-¿6) δ 7.59 – 7.48 (5H), 7.19 (d, J = 8.8 Hz, 1H), 6.89 (d, J = 8.8 Hz, 1H), 6.09 (s, 1H), 6.02 (ddt, J = 16.4, 10.0, 6.3 Hz, 1H), 5.09 (dm, J = 17.1 Hz, 1H), 4.98 (dm, J = 10.0 Hz, 1H), 3.61 (dm, J = 6.3 Hz, 2H); ¹³C NMR (75 MHz, acetone-¿6) δ 161.0, 159.6, 157.0, 154.7, 136.9, 136.2, 130.2, 129.6, 129.3, 126.6, 115.6, 114.9, 112.8, 112.6, 111.5, 27.7; IR (ATR) ν 3210 (bm), 1683 (s), 1600 (s), 1561 (s), 1444 (w), 1372 (s), 1312 (s), 1111 (m), 1058 (m); HRMS (EI) calcd for C₁₈H₁₄O₃ [M⁺] 278.0943, found 278.0946.
8-Allyl-7-hydroxy-6-methoxy-2H-chromen-2-one (8c)[4]. Starting from 7c (276 mg, 1.00 mmol) compound 8c (195 mg, 0.84 mmol, 84%) was obtained. Starting from 5c (252 mg, 1.00 mmol) compound 8c (93 mg, 0.40 mmol, 40%) was obtained. Yellowish solid, mp 146 - 148 °C (no mp or other data reported in the literature); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.57 (d, \(J = 9.4\) Hz, 1H), 6.74 (s, 1H), 6.37 (s, 1H), 6.23 (d, \(J = 9.4\) Hz, 1H), 5.98 (ddt, \(J = 16.6, 10.0, 6.3\) Hz, 1H), 5.09 (dm, \(J = 17.1\) Hz, 1H), 4.99 (dm, \(J = 10.0\) Hz, 1H), 3.92 (s, 3H), 3.60 (d, \(J = 6.3\) Hz, 2H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 161.7, 148.4, 147.8, 143.9, 143.8, 134.8, 115.7, 114.4, 113.1, 111.2, 105.6, 56.5, 27.1; IR (ATR) \(\nu\) 3335 (bm), 3016 (w), 1703 (s), 1570 (s), 1489 (m), 1419 (m), 1282 (s), 1152 (m), 1094 (m); HRMS (EI) calcd for C\(_{13}\)H\(_{12}\)O\(_4\) [M\(^+\)] 232.0736, found 232.0732.

8-Allyl-7-hydroxy-4-methyl-2H-chromen-2-one (8d)[5]. Starting from 7d (260 mg, 1.00 mmol) compound 8d (192 mg, 0.89 mmol, 89%) was obtained. Starting from 5d (236 mg, 1.00 mmol) compound 8d (143 mg, 0.66 mmol, 66%) was obtained. Yellowish solid, mp 193 - 195 °C (literature: 198 – 199 °C[5]); \(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 10.44 (s, 1H), 7.46 (d, \(J = 8.7\) Hz, 1H), 6.87 (d, \(J = 8.7\) Hz, 1H), 6.10 (s, 1H), 5.90 (ddt, \(J = 17.9, 9.3, 6.1\) Hz, 1H), 4.97 – 4.89 (m, 2H), 3.43 (d, \(J = 6.1\) Hz, 2H), 2.34 (d, \(J = 1.0\) Hz, 3H); \(^13\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 160.3, 158.7, 153.7, 152.6, 135.4, 123.9, 115.0, 112.7, 112.0, 111.9, 110.0, 26.5, 18.2; IR (ATR) \(\nu\) 3217 (bw), 3006 (w), 1683 (m), 1603 (m), 1572 (m), 1385 (m), 1311 (w), 1275 (m); HRMS (EI) calcd for C\(_{13}\)H\(_{12}\)O\(_3\) [M\(^+\)] 216.0786, found 216.0794.

**General procedure for the synthesis of allyl ethers 9.** The corresponding 7-hydroxycoumarin 8 (1.00 mmol) and allyl bromide (128 \(\mu\)L, 1.50 mmol) were dissolved in acetone (5 mL) and K\(_2\)CO\(_3\) (280 mg, 2.00 mmol) was added. The mixture was heated to 50 °C and stirred for 16 h, cooled to ambient temperature, and brine (20 mL) and ethyl acetate (30
mL) were added. The organic layer was separated and the aqueous layer was extracted twice with ethyl acetate (30 mL each). The combined organic extracts were dried with MgSO₄, filtered and evaporated. The residue was purified by column chromatography on silica using hexanes-MTBE mixtures of increasing polarity.

8-Allyl-7-(allyloxy)-2H-chromen-2-one (9a). Starting from 8a (202 mg, 1.00 mmol) compound 9a (235 mg, 0.97 mmol, 97%) was obtained. Yellowish solid, mp 96 - 98 °C (literature: 82 – 84 °C[6]); ¹H NMR (300 MHz, CDCl₃) δ 7.61 (d, J = 9.5 Hz, 1H), 7.29 (d, J = 8.6 Hz, 1H), 6.82 (d, J = 8.6 Hz, 1H), 6.23 (d, J = 9.4 Hz, 1H), 6.12 – 5.89 (m, 2H), 5.43 (dm, J = 17.3 Hz, 1H), 5.30 (dm, J = 10.6 Hz, 1H), 5.08 (dm, J = 17.1 Hz, 1H), 4.98 (dm, J = 10.0 Hz, 1H), 4.63 (dm, J = 5.0 Hz, 2H), 3.62 (dm, J = 6.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 161.4, 159.4, 153.1, 143.8, 135.2, 132.6, 126.7, 117.8, 116.6, 115.6, 113.2, 113.1, 108.7, 69.4, 27.1; IR (ATR) ν 3069 (w), 2980 (w), 1715 (s), 1602 (s), 1493 (m), 1408 (m), 1275 (s), 1066 (s), 1027 (s); HRMS (EI) calcd for C₁₅H₁₄O₃ [M⁺] 242.0943, found 242.0954.

8-Allyl-7-(allyloxy)-4-phenyl-2H-chromen-2-one (9b). Starting from 8b (278 mg, 1.00 mmol) compound 9b (293 mg, 0.92 mmol, 92%) was obtained. Orange-coloured solid, mp 94 – 96 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.58 – 7.50 (m, 3H), 7.49 – 7.42 (m, 2H), 7.33 (d, J = 8.9 Hz, 1H), 6.80 (d, J = 8.9 Hz, 1H), 6.24 (s, 1H), 6.14 – 5.97 (m, 2H), 5.46 (dm, J = 17.3 Hz, 1H), 5.33 (dm, J = 10.6 Hz, 1H), 5.17 (dm, J = 17.1 Hz, 1H), 5.05 (dm, J = 10.0 Hz, 1H), 4.67 (dm, J = 4.9 Hz, 2H), 3.72 (dm, J = 6.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 161.3, 159.3, 156.1, 153.2, 135.9, 135.3, 132.7, 129.6, 128.9, 128.5, 125.9, 117.8, 116.8, 115.6, 113.2, 112.1, 108.4, 69.4, 27.3; IR (ATR) ν 3078 (w), 2980 (w), 1715 (s), 1596 (s), 1490 (m), 1445 (m), 1371 (s), 1275 (s), 1116 (s), 1066 (m), 991 (m); HRMS (EI) calcd for C₂₁H₁₈O₃ [M⁺] 318.1256, found 318.1248.
8-Allyl-7-(allyloxy)-6-methoxy-2H-chromen-2-one (9c). Starting from 8c (232 mg, 1.00 mmol) compound 9c (258 mg, 0.95 mmol, 95%) was obtained. Yellowish solid, mp 73 - 75 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\) \(\delta\) 7.61 (d, \(J = 9.5\) Hz, 1H), 6.81 (s, 1H), 6.31 (d, \(J = 9.5\) Hz, 1H), 6.15 – 5.91 (m, 2H), 5.38 (dm, \(J = 17.2\) Hz, 1H), 5.24 (dm, \(J = 10.4\) Hz, 1H), 5.06 (dm, \(J = 17.1\) Hz, 1H), 5.00 (dm, \(J = 10.0\) Hz, 1H), 4.58 (dm, \(J = 5.8\) Hz, 2H), 3.88 (s, 3H), 3.63 (dm, \(J = 6.3\) Hz, 2H); \(^1\)C NMR (75 MHz, CDCl\(_3\) \(\delta\) 161.3, 150.0, 149.7, 147.6, 143.5, 135.5, 133.8, 122.9, 118.0, 115.9, 115.0, 114.7, 107.5, 74.4, 56.2, 28.0; IR (ATR) \(\nu\) 3079 (w), 2938 (w), 1716 (s), 1605 (m), 1565 (s), 1480 (m), 1402 (s), 1285 (s), 1100 (s), 1057 (m); HRMS (EI) calcd for C\(_{16}\)H\(_{16}\)O\(_4\) [M\(^+\)] 272.1049, found 242.1054.

8-Allyl-7-(allyloxy)-4-methyl-2H-chromen-2-one (9d).[7] Starting from 8d (216 mg, 1.00 mmol) compound 9d (233 mg, 0.91 mmol, 91%) was obtained. Yellowish solid, mp 92 – 94 °C (literature: 94 °C[7]); \(^1\)H NMR (300 MHz, CDCl\(_3\) \(\delta\) 7.42 (d, \(J = 8.8\) Hz, 1H), 6.83 (d, \(J = 8.8\) Hz, 1H), 6.11 (s, 1H), 6.09 – 5.88 (m, 2H), 5.43 (dm, \(J = 17.3\) Hz, 1H), 5.30 (dm, \(J = 10.6\) Hz, 1H), 5.07 (dm, \(J = 17.1\) Hz, 1H), 4.97 (dm, \(J = 10.0\) Hz, 1H), 4.64 (dm, \(J = 4.9\) Hz, 2H), 3.63 (dm, \(J = 6.4\) Hz, 2H), 2.37 (d, \(J = 1.0\) Hz, 3H); \(^1\)C NMR (75 MHz, CDCl\(_3\) \(\delta\) 161.4, 159.2, 152.7, 152.6, 135.3, 132.7, 123.3, 117.7, 116.6, 115.5, 114.1, 112.2, 108.4, 69.4, 27.2, 18.8; IR (ATR) \(\nu\) 3092 (w), 2973 (w), 1709 (s), 1602 (s), 1567 (s), 1503 (m), 1432 (m), 1382 (s), 1277 (s), 1223 (s), 1120 (s), 1054 (s); HRMS (EI) calcd for C\(_{16}\)H\(_{16}\)O\(_3\) [M\(^+\)] 256.1099, found 256.1095.

General procedure for the synthesis of enol ethers 10. To a solution of the corresponding allyl ether 9 (1.00 mmol) in toluene (10 mL) was added [RuClH(CO)(PPh\(_3\))\(_3\)] (48 mg, 0.05 mmol, 5 mol %). The solution was heated to 65 °C and stirred for 12 h, cooled to ambient
temperature and all volatiles were evaporated in vacuo. The residue was purified by column chromatography on silica using hexanes-MTBE mixtures of increasing polarity as eluent.

**8-(Prop-1-en-1-yl)-7-(prop-1-en-1-yloxy)-2H-chromen-2-one (10a).** Starting from 9a (242 mg, 1.00 mmol) compound 10a (225 mg, 0.93 mmol, 93%) was obtained as a mixture of diastereoisomers. Brownish oil; NMR-data of the major isomer (Z,E)-10a obtained from the mixture: \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.64 (d, \(J = 9.5\) Hz, 1H), 7.26 (d, \(J = 8.6\) Hz, 1H), 6.97 – 6.82 (m, 2H), 6.80 – 6.68 (m, 1H), 6.44 – 6.36 (m, 1H), 6.30 (d, \(J = 9.4\) Hz, 1H), 5.06 (dq, \(J = 6.8, 6.5\) Hz, 1H), 2.00 (dd, \(J = 6.3, 1.2\) Hz, 3H), 1.77 (dd, \(J = 6.9, 1.8\) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 160.9, 157.5, 152.4, 143.8, 140.1, 134.1, 126.1, 118.8, 114.1, 113.7, 111.4, 109.7, 20.2, 9.6, one quaternary carbon was not unambiguously assignable. Characteristic signals of (E,E)-10a obtained from the mixture: \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 5.50 (dq, \(J = 12.1, 7.0\) Hz, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 12.2.

**4-Phenyl-8-(prop-1-en-1-yl)-7-(prop-1-en-1-yloxy)-2H-chromen-2-one (10b).** Starting from 9b (318 mg, 1.00 mmol) compound 10b (299 mg, 0.94 mmol, 94%) was obtained as a mixture of diastereoisomers. Brownish solid; NMR-data of the major isomer (Z,E)-10b obtained from the mixture: \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.54 – 7.48 (m, 3H), 7.45 – 7.39 (m, 2H), 7.23 (d, \(J = 9.0\) Hz, 1H), 6.96 – 6.74 (m, 3H), 6.42 – 6.43 (m, 1H), 6.26 (s, 1H), 5.04 (dq, \(J = 6.9, 6.5\) Hz, 1H), 2.05 – 1.97 (m, 3H), 1.75 (dd, \(J = 6.9, 1.6\) Hz, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 161.1, 157.6, 156.2, 152.6, 140.2, 135.9, 134.3, 129.6, 128.9, 128.6, 125.5, 119.1, 115.9, 114.3, 112.7, 111.1, 109.9, 20.4, 9.8. Characteristic signals of (E,E)-10b obtained from the mixture: \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 5.48 (dq, \(J = 12.1, 7.0\) Hz, 1H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 12.4.
6-Methoxy-8-(prop-1-en-1-yl)-7-(prop-1-en-1-yloxy)-2H-chromen-2-one (10c). Starting from 9c (272 mg, 1.00 mmol) compound 10c (272 mg, 1.00 mmol, quant.) was obtained as a mixture of diastereoisomers. Brownish solid; NMR-data of the major isomer (Z,E)-10c obtained from the mixture: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.62 (d, $J = 9.5$ Hz, 1H), 6.90 – 6.74 (m, 2H), 6.62 (dm, $J = 16.1$ Hz, 1H), 6.36 (d, $J = 9.4$ Hz, 1H), 6.09 (dq, $J = 6.1$, 1.6 Hz, 1H), 4.68 (dq, $J = 6.7$, 6.5 Hz, 1H), 3.87 (s, 3H), 1.97 (dd, $J = 6.6$, 1.8 Hz, 3H), 1.79 (dd, $J = 6.9$, 1.6 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 161.0, 160.9, 149.3, 144.6, 143.7, 135.3, 120.9, 119.1, 115.4, 115.3, 107.8, 103.5, 56.7, 20.3, 9.3, one quaternary carbon not observed due to signal overlap. Characteristic signals of (E,E)-10c obtained from the mixture: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.96 (dq, $J = 12.4$, 7.0 Hz, 1H).

4-Methyl-8-(prop-1-en-1-yl)-7-(prop-1-en-1-yloxy)-2H-chromen-2-one (10d). Starting from 9d (256 mg, 1.00 mmol) compound 10d (256 mg, 1.00 mmol, quant.) was obtained as a mixture of diastereoisomers. Brownish oil; NMR-data of the major isomer (Z,E)-10d obtained from the mixture: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.36 (d, $J = 8.9$ Hz, 1H), 6.90 (d, $J = 8.9$ Hz, 1H), 6.87 – 6.65 (m, 2H), 6.43 – 6.33 (m, 1H), 6.16 (s, 1H), 5.03 (dq, $J = 6.8$, 6.2 Hz, 1H), 2.38 (d, $J = 1.0$ Hz, 3H), 1.98 (dd, $J = 5.7$, 0.8 Hz, 3H), 1.74 (dd, $J = 6.9$, 1.8 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 161.1, 157.4, 152.8, 151.9, 140.3, 134.1, 122.8, 119.1, 115.2, 112.7, 111.1, 110.7, 109.7, 20.3, 19.1, 9.7. Characteristic signals of (E,E)-10d obtained from the mixture: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.47 (dq, $J = 12.2$, 7.0 Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 12.4.

General procedure for the synthesis of furanocoumarins 3 and oxepinocoumarins 11. The appropriate precursors 9 or 10 (1.00 mmol) were dissolved in toluene (10 mL) and precatalyst A (42 mg, 0.05 mmol, 5 mol %) was added. The mixture was heated to 90 °C until
TLC indicated complete conversion (ca. 1 h), cooled to ambient temperature and evaporated in vacuo. The residue was purified by column chromatography on silica using hexanes-MTBE mixtures of increasing polarity as eluents to furnish the products 3 or 11, respectively.

8,11-Dihydro-2H-oxepino[2,3-h]chromen-2-one (11a)[6]. Starting from 9a (242 mg, 1.00 mmol) compound 11a (197 mg, 0.92 mmol, 92%) was obtained. Colourless solid, mp 103 - 105 °C (literature: 119 – 121 °C[6]); 1H NMR (300 MHz, CDCl₃) δ 7.62 (d, J = 9.5 Hz, 1H), 7.20 (d, J = 8.5 Hz, 1H), 7.07 (dm, J = 12.2 Hz, 1H), 6.88 (d, J = 8.5 Hz, 1H), 6.27 (d, J = 9.5 Hz, 1H), 6.17 (dt, J = 12.1, 4.5 Hz, 1H), 4.30 (t, J = 4.9 Hz, 2H), 2.75 (qd, J = 4.6, 1.9 Hz, 2H); 13C NMR (75 MHz, CDCl₃) δ 162.6, 160.9, 153.0, 144.0, 132.7, 126.7, 119.0, 117.1, 115.5, 113.9, 113.5, 70.6, 34.3; IR (ATR) ν 2965 (w), 2890 (w), 1712 (s), 1590 (s), 1490 (m), 1404 (m), 1338 (m), 1286 (m), 1229 (s), 1109 (s), 1067 (m); HRMS (EI) calcd for C₁₃H₁₀O₃ [M⁺] 214.0630, found 214.0625.

4-Phenyl-8,11-dihydro-2H-oxepino[2,3-h]chromen-2-one (11b). Starting from 9b (318 mg, 1.00 mmol) compound 11b (229 mg, 0.79 mmol, 79%) was obtained. Deviating from the general procedure, the reaction was run in CH₂Cl₂ (20 mL) at ambient temperature. Colourless solid, mp 117 - 120 °C; 1H NMR (300 MHz, CDCl₃) δ 7.53 – 7.48 (m, 3H), 7.44 – 7.39 (m, 2H), 7.29 (d, J = 8.6 Hz, 1H), 6.93 (d, J = 8.6 Hz, 1H), 6.27 (s, 1H), 5.94 (dm, J = 11.1 Hz, 1H), 5.58 (dm, J = 11.3 Hz, 1H), 4.66 (tm, J = 4.1 Hz, 2H), 3.84 (dm, J = 5.3 Hz, 2H); 13C NMR (75 MHz, CDCl₃) δ 162.2, 161.0, 156.3, 151.7, 135.8, 129.7, 128.9, 128.5, 127.5, 126.3, 126.1, 123.8, 118.0, 115.6, 113.2, 71.0, 22.6; IR (ATR) ν 3057 (w), 2845 (w), 1718 (s), 1592 (s), 1488 (m), 1444 (m), 1368 (s), 1270 (s), 1164 (m), 1069 (s); HRMS (EI) calcd for C₁₉H₁₄O₃ [M⁺] 290.0943, found 290.0952.
6-Methoxy-8,11-dihydro-2H-oxepino[2,3-h]chromen-2-one (11c).

Starting from 9c (272 mg, 1.00 mmol) compound 11c (193 mg, 0.79 mmol, 79%) was obtained. Colourless solid, mp 118 - 120 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.62 (d, \(J = 9.5\) Hz, 1H), 6.81 (s, 1H), 6.32 (d, \(J = 9.5\) Hz, 1H), 5.88 (dm, \(J = 11.0\) Hz, 1H), 5.52 (dm, \(J = 11.4\) Hz, 1H), 4.65 (dq, \(J = 4.4, 2.2\) Hz, 2H), 3.88 (s, 3H), 3.75 (dq, \(J = 5.4, 1.8\) Hz, 2H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 161.2, 151.1, 149.4, 145.6, 143.8, 127.7, 126.0, 125.5, 115.1, 115.0, 107.4, 70.5, 56.4, 22.3; IR (ATR) \(\nu\) 2938 (w), 2841 (w), 1712 (s), 1604 (m), 1568 (m), 1486 (m), 1406 (s), 1284 (s), 1144 (s), 1108 (s), 1056 (s); HRMS (EI) calcd for C\(_{14}\)H\(_{12}\)O\(_4\) [M\(^+\)] 244.0736, found 244.0725.

4-Methyl-8,11-dihydro-2H-oxepino[2,3-h]chromen-2-one (11d)[6,7]. Starting from 9d (256 mg, 1.00 mmol) compound 11d (176 mg, 0.77 mmol, 77%) was obtained. Colourless solid, mp 79 - 81 °C (literature: 109 – 111 °C[6]); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.42 (d, \(J = 8.6\) Hz, 1H), 7.00 (d, \(J = 8.6\) Hz, 1H), 6.19 (s, 1H), 5.90 (dm, \(J = 11.0\) Hz, 1H), 5.55 (dm, \(J = 11.2\) Hz, 1H), 4.64 (dq, \(J = 4.2, 2.1\) Hz, 2H), 3.78 (dq, \(J = 5.3, 1.8\) Hz, 2H), 2.40 (d, \(J = 1.1\) Hz, 3H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 162.1, 161.1, 152.8, 151.0, 127.5, 126.2, 123.7, 123.4, 118.0, 116.5, 113.2, 71.1, 22.5, 19.0; IR (ATR) \(\nu\) 2978 (w), 2929 (w), 1723 (s), 1594 (m), 1568 (m), 1486 (m), 1406 (s), 1284 (s), 1144 (s), 1108 (s), 1056 (s); HRMS (EI) calcd for C\(_{14}\)H\(_{12}\)O\(_3\) [M\(^+\)] 228.0786, found 228.0782.

2H-Furo[2,3-h]chromen-2-one (angelicin, 3a)[8,9]. Starting from 10a (242 mg, 1.00 mmol) compound 3a (177 mg, 0.95 mmol, 95%) was obtained. Colourless solid, mp 137 – 139 °C (literature: 139 °C[8]); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.78 (d, \(J = 9.6\) Hz, 1H), 7.67 (d, \(J = 2.2\) Hz, 1H), 7.40 (dd, \(J = 8.5, 0.8\) Hz, 1H), 7.34 (d, \(J = 8.5\) Hz, 1H), 7.09 (dd, \(J = 2.2, 0.8\) Hz, 1H), 6.36 (d, \(J = 9.6\) Hz, 1H); \(^13\)C
NMR (75 MHz, CDCl$_3$) $\delta$ 160.8, 157.4, 148.5, 145.9, 144.6, 123.9, 116.9, 114.1, 113.6, 108.8, 104.1; IR (ATR) $\nu$ 3164 (w), 3082 (w), 1711 (s), 1615 (s), 1535 (m), 1442 (m), 1402 (m), 1336 (m), 1270 (s), 1114 (s), 1055 (s); HRMS (EI) calcd for C$_{11}$H$_6$O$_3$ [M$^+$] 186.0317, found 186.0312.

4-Phenyl-2H-furo[2,3-h]chromen-2-one (3b).[10] Starting from 10b (318 mg, 1.00 mmol) compound 3b (233 mg, 0.89 mmol, 89%) was obtained. Colourless solid, mp 182 - 183 °C (literature: 165 – 166 °C[10]); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.70 (d, $J = 2.2$ Hz, 1H), 7.56 – 7.51 (m, 3H), 7.50 – 7.45 (m, 2H), 7.40 (d, $J = 8.9$ Hz, 1H), 7.36 (dd, $J = 8.9$, 0.8 Hz, 1H), 7.19 (dd, $J = 2.2$, 0.8 Hz, 1H), 6.34 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 160.9, 157.5, 157.0, 148.8, 146.0, 136.0, 129.8, 129.0, 128.6, 123.2, 117.3, 113.8, 113.0, 108.5, 104.5; IR (ATR) $\nu$ 3122 (w), 3062 (w), 1713 (s), 1606 (m), 1599 (m), 1443 (m), 1370 (s), 1265 (m), 1243 (m), 1159 (m), 1064 (s); HRMS (EI) calcd for C$_{17}$H$_{10}$O$_3$ [M$^+$] 262.0630, found 262.0634.

6-Methoxy-2H-furo[2,3-h]chromen-2-one (sphondin, 3c).[9] Starting from 10c (272 mg, 1.00 mmol) compound 3c (212 mg, 0.98 mmol, 98%) was obtained. Colourless solid, mp 190 – 192 °C (literature: 190 – 192 °C[11]); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J = 9.6$ Hz, 1H), 7.70 (d, $J = 2.1$ Hz, 1H), 7.12 (d, $J = 2.1$ Hz, 1H), 6.77 (s, 1H), 6.39 (d, $J = 9.6$ Hz, 1H), 4.04 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 161.1, 147.1, 146.1, 144.5, 143.3, 143.2, 118.7, 114.6, 113.7, 104.7, 103.9, 56.7; IR (ATR) $\nu$ 3115 (w), 3066 (w), 1732 (s), 1582 (m), 1395 (m), 1345 (m), 1308 (m), 1336 (m), 1192 (m), 1172 (m), 1040 (m); HRMS (EI) calcd for C$_{12}$H$_6$O$_4$ [M$^+$] 216.0423, found 216.0420.
4-Methyl-2H-furo[2,3-h]chromen-2-one (3d).\[10\] Starting from 10d (256 mg, 1.00 mmol) compound 3d (200 mg, 1.00 mmol, quant.) was obtained. Colourless solid, mp 190 - 192 °C (literature: 190 – 192 °C\[12\]); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.66 (d, $J = 2.2$ Hz, 1H), 7.49 (d, $J = 8.8$ Hz, 1H), 7.42 (d, $J = 8.8$ Hz, 1H), 7.11 (d, $J = 2.1$ Hz, 1H), 6.24 (s, 1H), 2.48 (d, $J = 0.9$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 160.9, 157.3, 153.7, 148.0, 145.9, 120.6, 117.0, 114.6, 112.9, 108.5, 104.4, 19.5; IR (ATR) $\nu$ 3135 (w), 3108 (w), 1704 (s), 1614 (s), 1529 (m), 1437 (m), 1373 (s), 1262 (s), 1143 (m), 1063 (s), 1035 (m); HRMS (EI) calcd for C$_{12}$H$_8$O$_3$ [M$^+$] 200.0473, found 200.0476.

**General procedure for the synthesis of acrylates 12.** The appropriate 8-allylcoumarin 8 (1.00 mmol) was dissolved in DMF (5.0 mL) and NEt$_3$ (180 $\mu$L, 1.30 mmol) was added. The solution was cooled to 0 °C and a solution of acryloyl chloride (117 $\mu$L, 1.30 mmol) in DMF (1.0 mL) was added dropwise. The mixture was stirred for 12 h at ambient temperature and the reaction was then quenched by addition of aq. NH$_4$Cl (5 mL). Ethyl acetate (10 mL) was added, the organic layer was separated and the aqueous layer was extracted twice with ethyl acetate (10 mL each). The combined organic layers were dried with MgSO$_4$, filtered and evaporated. The residue was purified by column chromatography on silica using hexanes-ethyl acetate mixtures as eluents to furnish the acrylates 12.

8-allyl-2-oxo-2H-chromen-7-ylacrylate (12a). Starting from 8a (202 mg, 1.00 mmol) compound 12a (236 mg, 0.92 mmol, 92%) was obtained. Colourless solid, mp 74 - 76 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.69 (d, $J = 9.6$ Hz, 1H), 7.39 (d, $J = 8.5$ Hz, 1H), 7.08 (d, $J = 8.5$ Hz, 1H), 6.64 (dd, $J = 17.3$, 1.2 Hz, 1H), 6.39 (d, $J = 9.6$ Hz, 1H), 6.34 (dd, $J = 17.3$, 10.5 Hz, 1H), 6.08 (dd, $J = 10.4$, 1.2 Hz, 1H), 5.88 (ddt, $J = 16.4$, 10.0, 6.3 Hz, 1H), 5.04 (dm, $J = 17.0$ Hz, 1H), 5.01 (dm, $J = 10.0$ Hz, 1H), 3.55 (d, $J = 6.3$ Hz, 2H); $^{13}$C NMR (75 MHz,
CDCl$_3$) $\delta$ 164.0, 160.4, 153.0, 151.7, 143.4, 134.1, 133.6, 127.4, 126.3, 121.2, 119.2, 117.0, 116.5, 116.0, 27.9; IR (ATR) $\nu$ 3080 (w), 1728 (s), 1602 (s), 1400 (s), 1292 (m), 1230 (s), 1138 (s), 1104 (s), 1052 (m), 1019 (m); HRMS (EI) calcd for C$_{13}$H$_{12}$O$_4$ [M$^+$] 256.0736, found 256.0725.

8-Allyl-2-oxo-4-phenyl-2H-chromen-7-ylacrylate (12b). Starting from 8b (278 mg, 1.00 mmol) compound 12b (309 mg, 0.93 mmol, 93%) was obtained.

Colourless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.54 – 7.48 (m, 3H), 7.46 – 7.41 (m, 2H), 7.39 (d, $J$ = 8.8 Hz, 1H), 7.02 (d, $J$ = 8.8 Hz, 1H), 6.65 (d, $J$ = 17.3 Hz, 1H), 6.35 (dd, $J$ = 17.3, 10.5 Hz, 1H), 6.34 (s, 1H), 6.08 (d, $J$ = 10.5 Hz, 1H), 5.92 (ddt, $J$ = 16.8, 10.2, 6.6 Hz, 1H), 5.13 – 4.95 (m, 2H), 3.61 (d, $J$ = 6.3 Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 163.9, 160.4, 155.8, 153.0, 151.6, 135.4, 134.2, 133.6, 129.8, 129.0, 128.5, 127.3, 125.6, 121.3, 118.7, 117.2, 116.4, 114.5, 28.2; IR (ATR) $\nu$ 2925 (w), 1719 (s), 1636 (m), 1575 (m), 1464 (s), 1400 (s), 1351 (m), 1233 (m), 1134 (s), 982 (m), 907(m); HRMS (EI) calcd for C$_{21}$H$_{16}$O$_4$ [M$^+$] 332.1049, found 332.1040.

8-Allyl-6-methoxy-2-oxo-2H-chromen-7-ylacrylate (12c). Starting from 8c (232 mg, 1.00 mmol) compound 12c (255 mg, 0.89 mmol, 89%) was obtained.

Yellowish oil; $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J$ = 9.5 Hz, 1H), 6.87 (s, 1H), 6.64 (dd, $J$ = 17.3, 1.2 Hz, 1H), 6.39 (d, $J$ = 9.9 Hz, 1H), 6.36 (dd, $J$ = 17.3, 10.3 Hz, 1H), 6.07 (dd, $J$ = 10.4, 1.3 Hz, 1H), 5.86 (ddt, $J$ = 16.5, 10.0, 6.4 Hz, 1H), 5.06 (dm, $J$ = 17.1 Hz, 1H), 5.01 (dm, $J$ = 10.0 Hz, 1H), 3.84 (s, 3H), 3.54 (d, $J$ = 6.4 Hz, 2H); $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$ 163.3, 160.7, 148.6, 146.9, 143.4, 141.7, 134.0, 133.4, 127.1, 122.9, 116.8, 116.7, 116.4, 107.5, 56.5, 28.2; IR (ATR) $\nu$ 3091 (w), 2941 (w), 1719 (s), 1636 (m), 1575 (m), 1464 (m), 1400 (s), 1351 (m), 1233 (m), 1134 (s), 982 (m), 907(m); HRMS (EI) calcd for C$_{22}$H$_{16}$O$_4$ [M$^+$] 334.1065, found 334.1065.
1290 (s), 1240 (m), 1131 (s), 1102 (s); HRMS (EI) calcd for C_{16}H_{14}O_5 [M^+] 286.0841, found 286.0848.

8-allyl-4-methyl-2-oxo-2H-chromen-7-ylacrylate (12d). Starting from 8d (216 mg, 1.00 mmol) compound 12d (232 mg, 0.86 mmol, 86%) was obtained. Colourless solid, mp 67 - 69 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.52 (d, J = 8.7 Hz, 1H), 7.10 (d, J = 8.7 Hz, 1H), 6.65 (dd, J = 17.3, 1.1 Hz, 1H), 6.35 (dd, J = 17.3, 10.5 Hz, 1H), 6.27 (q, J = 1.0 Hz, 1H), 6.09 (dd, J = 10.4, 1.1 Hz, 1H), 5.88 (ddt, J = 16.4, 10.0, 6.3 Hz, 1H), 5.03 (dm, J = 17.0 Hz, 1H), 5.00 (dm, J = 10.0 Hz, 1H), 3.56 (d, J = 6.3 Hz, 2H), 2.43 (d, J = 1.1 Hz, 3H); ^13C NMR (75 MHz, CDCl_3) δ 164.0, 160.5, 152.5, 152.4, 151.5, 134.3, 133.6, 127.4, 123.0, 121.2, 118.8, 118.1, 116.4, 114.5, 28.1, 19.0; IR (ATR) ν 3082 (w), 2982 (w), 1723 (s), 1631 (m), 1599 (s), 1402 (m), 1383 (m), 1233 (m), 1137 (s), 1046 (s); HRMS (EI) calcd for C_{16}H_{14}O_4 [M^+] 270.0892, found 270.0883.

General procedure for the synthesis of oxepin-2-one coumarins 13. The appropriate acrylate 12 (1.00 mmol) was dissolved in toluene (100 mL) and heated to 110 °C. At this temperature precatalyst A (42 mg, 0.05 mmol, 5 mol %) was added and the solution was stirred at 110 °C for 16 h. After cooling to ambient temperature, the solution was evaporated and the residue was purified by column chromatography on silica, using hexanes-ethyl acetate mixtures of increasing polarity as eluents, to furnish compounds 13.

2H-Oxepino[2,3-h]chromen-2,8(11H)-dione (13a). Starting from 12a (256 mg, 1.00 mmol) compound 13a (185 mg, 0.81 mmol, 81%) was obtained. Colourless solid, mp 211 - 213 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.75 (d, J = 9.6 Hz, 1H), 7.51 (d, J = 8.6 Hz, 1H), 7.30 (d, J = 9.6 Hz, 1H), 7.19 (d, J = 8.6 Hz, 1H), 6.45 (d, J = 9.6 Hz, 1H), 6.24 (dt, J = 9.8, 6.7 Hz, 1H), 3.15 (d, J = 6.7 Hz, 2H); ^13C NMR (75 MHz, CDCl_3) δ 167.0, 159.9, 152.1, 151.9, 143.1,
4-Phenyl-2H-oxepino[2,3-h]chromen-2,8(11H)-dione (13b).

Starting from 12b (332 mg, 1.00 mmol) compound 13b (240 mg, 0.79 mmol, 79%) was obtained. Colourless solid, mp 194 – 196 °C; 1H NMR (300 MHz, CDCl3) δ 7.57 – 7.52 (m, 3H), 7.50 (d, J = 8.9 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.35 (d, J = 9.8 Hz, 1H), 7.12 (d, J = 8.9 Hz, 1H), 6.38 (s, 1H), 6.24 (dt, J = 9.8, 6.7 Hz, 1H), 3.15 (d, J = 6.7 Hz, 2H); 13C NMR (75 MHz, CDCl3) δ 167.1, 160.0, 155.6, 152.1, 152.0, 135.1, 130.1, 129.2, 128.5, 127.3, 124.6, 124.5, 117.2, 116.8, 115.8, 114.5, 34.7; IR (ATR) ν 3059 (w), 2923 (w), 1773 (s), 1718 (s), 1586 (s), 1445 (m), 1419 (m), 1370 (s), 1233 (m), 1208 (m), 1117 (m), 1068 (s), 1031 (m); HRMS (EI) calcd for C19H12O5 [M⁺] 304.0736, found 304.0732.

6-Methoxy-2H-oxepino[2,3-h]chromen-2,8(11H)-dione (13c). Starting from 12c (286 mg, 1.00 mmol) compound 13c (235 mg, 0.91 mmol, 91%) was obtained. Colourless solid, mp 245 – 247 °C; 1H NMR (300 MHz, CDCl3) δ 7.68 (d, J = 9.5 Hz, 1H), 7.28 (d, J = 9.5 Hz, 1H), 6.96 (s, 1H), 6.44 (d, J = 9.5 Hz, 1H), 6.26 (dt, J = 9.7, 6.7 Hz, 1H), 3.95 (s, 3H), 3.13 (d, J = 6.7 Hz, 2H); 13C NMR (75 MHz, CDCl3) δ 167.0, 160.2, 147.7, 145.5, 143.1, 142.1, 125.3, 124.3, 117.9, 116.6, 114.9, 108.3, 56.7, 34.9; IR (ATR) ν 2918 (w), 2854 (w), 1726 (s), 1568 (m), 1456 (m), 1408 (m), 1281 (s), 1123 (s), 1074 (s); HRMS (EI) calcd for C14H10O5 [M⁺] 258.0528, found 258.0533.

4-Methyl-2H-oxepino[2,3-h]chromen-2,8(11H)-dione (13d). Starting from 12d (270 mg, 1.00 mmol) compound 13d (208 mg, 0.86 mmol, 86%) was obtained.
Colourless solid, mp 213 - 215 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.61 (d, \(J = 8.8\) Hz, 1H), 7.29 (d, \(J = 9.8\) Hz, 1H), 7.19 (d, \(J = 8.8\) Hz, 1H), 6.30 (s, 1H), 6.21 (dt, \(J = 9.6, 6.8\) Hz, 1H), 3.12 (d, \(J = 6.7\) Hz, 2H), 2.46 (s, 3H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 167.2, 160.0, 152.2, 152.0, 151.3, 124.8, 124.6, 124.4, 117.3, 116.7, 116.6, 114.5, 34.6, 19.0; IR (ATR) \(\nu\) 3082 (w), 2926 (w), 1764 (s), 1732 (s), 1593 (s), 1383 (m), 1235 (m), 1206 (m), 1174 (m), 1065 (s); HRMS (EI) calcd for C\(_{14}\)H\(_{10}\)O\(_4\) [M\(^+\)] 242.0579, found 242.0575.

\((E)-4\)-Methyl-2-oxo-8-(prop-1-en-1-yl)-2H-chromen-7-ylacrylate (14d). Compound 12d (270 mg, 1.00 mmol) was dissolved in toluene (10 mL) and [RuClH(CO)(PPh\(_3\))\(_3\)] (77 mg, 0.08 mmol, 8 mol %) was added. The mixture was heated at 110 °C for 12 h, cooled to ambient temperature and evaporated. The residue was purified by column chromatography on silica using hexanes-MTBE mixtures as eluent to furnish the title compound 14d (270 mg, 1.00 mmol, quant.) as a mixture of E/Z-isomers. Brownish oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.46 (d, \(J = 8.7\) Hz, 1H), 7.05 (d, \(J = 8.7\) Hz, 1H), 6.65 (d, \(J = 17.2\) Hz, 1H), 6.59 - 6.49 (m, 1H), 6.35 (dd, \(J = 17.3, 10.4\) Hz, 1H), 6.27 (s, 1H), 6.08 (d, \(J = 10.5\) Hz, 1H), 2.43 (s, 3H), 1.91 (d, \(J = 5.5\) Hz, 3H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 164.0, 160.5, 152.4, 151.9, 150.4, 134.8, 134.3, 133.5, 127.5, 127.4, 122.7, 119.0, 118.2, 114.4, 20.0, 19.1.

General procedure for the synthesis of 8-(prop-1-enyl)coumarins 16. To a solution of the corresponding MOM-protected 8-allylcoumarin 7 (1.00 mmol) in toluene (10 mL) was added [RuClH(CO)(PPh\(_3\))\(_3\)] (48 mg, 0.05 mmol, 5 mol %). It was heated at 65 °C for 12 h, cooled to ambient temperature and evaporated. The residue was redissolved in methanol (20 mL) and aq. HCl (3 M, 100 μL) was added. The solution was heated at 65 °C for 1 h, cooled to ambient temperature and diluted with water (30 mL) and ethyl acetate (30 mL). The organic layer was separated and the aqueous layer was extracted twice with ethyl acetate (30 mL).
each). The combined organic layers were dried with MgSO₄, filtered and evaporated. The residue was purified by column chromatography on silica using hexanes-ethyl acetate mixtures as eluent to furnish the compounds 16.

**(E)-7-Hydroxy-8-(prop-1-en-1-yl)-2H-chromen-2-one** (16a). Starting from 7a (246 mg, 1.00 mmol) compound 16a (192 mg, 0.95 mmol, 95%) was obtained. Yellowish solid, mp 180 – 182 °C; ¹H NMR (300 MHz, acetone-d₆) δ 9.42 (s(br), 1H), 7.84 (d, J = 9.5 Hz, 1H), 7.34 (d, J = 8.5 Hz, 1H), 6.91 (d, J = 8.5 Hz, 1H), 6.84 (dq, J = 16.1, 6.4 Hz, 1H), 6.73 (dq, J = 16.1, 1.4 Hz, 1H), 6.18 (d, J = 9.5 Hz, 1H), 1.94 (dd, J = 6.3, 1.4 Hz, 3H); ¹³C NMR (75 MHz, acetone-d₆) δ 161.0, 159.2, 153.9, 145.3, 132.7, 127.8, 120.6, 113.5, 113.2, 113.1, 112.6, 20.1; IR (ATR) ν 3314 (br), 2957 (w), 1690 (s), 1590 (s), 1558 (s), 1405 (m), 1298 (s), 1247 (s), 1107 (s), 1026 (m); HRMS (EI) calcd for C₁₂H₁₀O₃ [M⁺] 202.0630, found 202.0633.

**(E)-7-Hydroxy-4-phenyl-8-(prop-1-en-1-yl)-2H-chromen-2-one** (16b). Starting from 7b (322 mg, 1.00 mmol) compound 16b (225 mg, 0.81 mmol, 81%) was obtained. Colourless solid, mp 204 – 206 °C; ¹H NMR (300 MHz, DMSO-d₆) δ 10.80 (s, 1H), 7.56 – 7.45 (m, 5H), 7.10 (d, J = 8.8 Hz, 1H), 6.86 (d, J = 8.8 Hz, 1H), 6.79 (dq, J = 16.1, 6.3 Hz, 1H), 6.66 (dq, J = 16.1, 1.3 Hz, 1H), 6.14 (s, 1H), 1.93 (dd, J = 6.3, 1.1 Hz, 3H); ¹³C NMR (75 MHz, DMSO-d₆) δ 159.9, 158.8, 155.9, 152.4, 135.4, 131.3, 129.4, 128.7, 128.3, 125.4, 119.8, 112.6, 111.8, 110.8, 110.0, 19.8; IR (ATR) ν 3104 (br), 2955 (w), 1666 (s), 1593 (m), 1547 (s), 1371 (s), 1304 (m), 1282 (m), 1107 (m), 1071 (m); HRMS (EI) calcd for C₁₈H₁₄O₃ [M⁺] 278.0943, found 278.0941.
(E)-7-Hydroxy-6-methoxy-8-(prop-1-en-1-yl)-2H-chromen-2-one (16c). Starting from 7c (276 mg, 1.00 mmol) compound 16c (232 mg, 1.00 mmol, quant.) was obtained. Yellowish solid, mp 152 – 154 °C; \(^1\)H NMR (300 MHz, DMSO-\(d_6\) \(\delta\) 9.92 (s, 1H), 7.90 (d, \(J = 9.4\) Hz, 1H), 7.13 (s, 1H), 6.77 (dq, \(J = 16.1, 6.5\) Hz, 1H), 6.61 (dq, \(J = 16.1, 1.4\) Hz, 1H), 6.24 (d, \(J = 9.4\) Hz, 1H), 3.86 (s, 3H), 1.92 (dd, \(J = 6.2, 1.2\) Hz, 3H); \(^13\)C NMR (75 MHz, DMSO-\(d_6\) \(\delta\) 160.4, 148.2, 147.0, 144.9, 144.5, 131.5, 119.8, 111.9, 111.5, 110.3, 107.2, 56.2, 19.7; IR (ATR) \(\nu\) 3347 (br), 2933 (w), 1702 (s), 1566 (s), 1484 (m), 1418 (m), 1285 (s), 1152 (m), 1102 (m); HRMS (EI) calcd for C\(_{13}\)H\(_{12}\)O\(_4\) [M\(^+\)] 232.0736, found 232.0746.

(E)-7-Hydroxy-4-methyl-8-(prop-1-en-1-yl)-2H-chromen-2-one (16d)[5]. Starting from 7d (260 mg, 1.00 mmol) compound 16d (199 mg, 0.92 mmol, 92%) was obtained. Colourless solid, mp 216 – 218 °C (no mp or other characterization data published in the literature); \(^1\)H NMR (300 MHz, DMSO-\(d_6\) \(\delta\) 10.68 (s, 1H), 7.43 (d, \(J = 8.7\) Hz, 1H), 6.88 (d, \(J = 8.7\) Hz, 1H), 6.75 (dq, \(J = 16.3, 6.3\) Hz, 1H), 6.61 (d, \(J = 16.2\) Hz, 1H), 6.13 (s, 1H), 2.35 (s, 3H), 1.91 (d, \(J = 6.3\) Hz, 3H); \(^13\)C NMR (75 MHz, DMSO-\(d_6\) \(\delta\) 160.1, 158.6, 153.9, 151.8, 131.2, 123.8, 120.0, 112.4, 112.1, 111.3, 110.0, 19.9, 18.4; IR (ATR) \(\nu\) 3269 (br), 2955 (w), 1676 (s), 1600 (m), 1566 (s), 1443 (m), 1389 (m), 1367 (m), 1282 (m), 1058 (m); HRMS (EI) calcd for C\(_{13}\)H\(_{12}\)O\(_3\) [M\(^+\)] 216.0786, found 216.0797.

**General procedure for the synthesis of allyl ethers 17.** The corresponding coumarin 16 (1.00 mmol) was dissolved in acetone (5 mL) and K\(_2\)CO\(_3\) (280 mg, 2.00 mmol) and allyl bromide (128 µL, 1.50 mmol) were added. The mixture was heated at 50 °C for 16 h, cooled to ambient temperature and brine (20 mL) and ethyl acetate (30 mL) were added. The organic layer was separated and the aqueous layer was extracted twice with ethyl acetate (30 mL each). The combined organic extracts were dried with MgSO\(_4\), filtered and evaporated. The
residue was purified by column chromatography on silica, using hexanes-MTBE mixtures as eluent, to furnish compounds 17.

\[(E)-7-(\text{ Allyloxy})-8-(\text{ prop-1-en-1-yl})-2H-\text{ chromen-2-one} \quad (17a).\]

Starting from 16a (202 mg, 1.00 mmol) compound 17a (225 mg, 0.93 mmol, 93%) was obtained. Yellowish oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.60 (d, \( J = 9.5 \) Hz, 1H), 7.22 (d, \( J = 8.6 \) Hz, 1H), 6.87 (dq, \( J = 16.2, 6.3 \) Hz, 1H), 6.82 (d, \( J = 8.6 \) Hz, 1H), 6.73 (dq, \( J = 16.2, 1.3 \) Hz, 1H), 6.23 (d, \( J = 9.4 \) Hz, 1H), 6.07 (ddt, \( J = 17.2, 10.5, 5.1 \) Hz, 1H), 5.43 (dm, \( J = 17.3 \) Hz, 1H), 5.32 (dm, \( J = 10.5 \) Hz, 1H), 4.65 (dm, \( J = 5.0 \) Hz, 2H), 1.97 (dd, \( J = 6.2, 1.3 \) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 161.2, 159.0, 152.5, 144.0, 133.7, 132.6, 126.3, 119.2, 118.2, 115.1, 113.2, 113.1, 109.0, 69.8, 20.3; IR (ATR) \( \nu \) 2912 (w), 1716 (s), 1594 (s), 1557 (m), 1490 (m), 1404 (m), 1272 (s), 1244 (s), 1114 (s); HRMS (EI) calcd for C\(_{15}\)H\(_{14}\)O\(_3\) [M\(^+\)] 242.0943, found 242.0937.

\[(E)-7-(\text{ Allyloxy})-4-\text{ phenyl}-8-(\text{ prop-1-en-1-yl})-2H-\text{ chromen-2-one} \quad (17b).\]

Starting from 16b (278 mg, 1.00 mmol) compound 17b (283 mg, 0.89 mmol, 89%) was obtained. Yellowish oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.52 – 7.48 (m, 3H), 7.44 – 7.39 (m, 2H), 7.23 (d, \( J = 8.9 \) Hz, 1H), 6.95 – 6.74 (m, 3H), 6.21 (s, 1H), 6.07 (ddt, \( J = 17.2, 10.4, 5.1 \) Hz, 1H), 5.43 (dm, \( J = 17.3 \) Hz, 1H), 5.32 (dm, \( J = 10.6 \) Hz, 1H), 4.65 (dm, \( J = 5.1 \) Hz, 2H), 1.99 (d, \( J = 5.9 \) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 161.2, 159.0, 156.3, 152.6, 136.0, 133.7, 132.7, 129.6, 128.8, 128.5, 125.6, 119.5, 118.1, 117.1, 113.3, 112.1, 108.7, 69.8, 20.3; IR (ATR) \( \nu \) 3070 (w), 2911 (w), 1714 (s), 1588 (s), 1552 (m), 1445 (m), 1370 (s), 1273 (s), 1112 (s), 1074 (s); HRMS (EI) calcd for C\(_{21}\)H\(_{18}\)O\(_3\) [M\(^+\)] 318.1256, found 318.1246.
(E)-7-(Allyloxy)-6-methoxy-8-(prop-1-en-1-yl)-2H-chromen-2-one (17c). Starting from 16c (232 mg, 1.00 mmol) compound 17c (245 mg, 0.90 mmol, 90%) was obtained. Yellowish oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J = 9.5$ Hz, 1H), 6.89 (dq, $J = 16.2$, 6.6 Hz, 1H), 6.75 (s, 1H), 6.65 (dq, $J = 16.2$, 1.6 Hz, 1H), 6.31 (d, $J = 9.5$ Hz, 1H), 6.06 (ddt, $J = 17.1$, 10.4, 5.9 Hz, 1H), 5.35 (dm, $J = 17.1$ Hz, 1H), 5.23 (dm, $J = 10.5$ Hz, 1H), 4.52 (d, $J = 5.9$ Hz, 2H), 3.87 (s, 3H), 1.95 (d, $J = 6.6$, 1.6 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 161.1, 150.1, 149.1, 147.0, 143.8, 134.6, 133.8, 121.2, 119.7, 118.1, 114.9, 114.8, 107.4, 74.2, 56.3, 20.1; IR (ATR) $\nu$ 2936 (w), 1715 (s), 1597 (m), 1558 (s), 1460 (m), 1400 (m), 1288 (s), 1142 (s), 1102 (s). HRMS (EI) calcd for C$_{16}$H$_{16}$O$_4$ [M$^+$] 272.1049, found 272.1046.

(E)-7-(Allyloxy)-4-methyl-8-(prop-1-en-1-yl)-2H-chromen-2-one (17d)[13]. Starting from 16d (216 mg, 1.00 mmol) compound 17d (256 mg, 1.00 mmol, quant.) was obtained. Yellowish oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.35 (d, $J = 8.9$ Hz, 1H), 6.82 (dq, $J = 16.2$, 6.0 Hz, 1H), 6.82 (d, $J = 8.8$ Hz, 1H), 6.73 (dm, $J = 16.3$ Hz, 1H), 6.12 (s, 1H), 6.07 (ddt, $J = 17.2$, 10.6, 5.2 Hz, 1H), 5.43 (dm, $J = 17.3$ Hz, 1H), 5.32 (dm, $J = 10.5$ Hz, 1H), 4.65 (dm, $J = 5.0$ Hz, 2H), 2.37 (d, $J = 1.1$ Hz, 3H), 1.96 (d, $J = 5.0$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 161.2, 158.8, 152.8, 151.9, 133.5, 132.7, 122.9, 119.5, 118.1, 114.9, 114.1, 112.1, 108.6, 69.7, 20.3, 18.9; IR (ATR) $\nu$ 2917 (w), 1715 (s), 1597 (m), 1558 (s), 1460 (m), 1400 (m), 1288 (s), 1142 (s), 1102 (s). HRMS (EI) calcd for C$_{16}$H$_{16}$O$_3$ [M$^+$] 256.1099, found 256.1093.

General procedure for the synthesis of pyran-2-one coumarins 15. A solution of the corresponding diene 17 (1.00 mmol) in benzene (10 mL) was heated to 40 °C and precatalyst B (42 mg, 0.05 mmol, 5 mol %) was added. The solution was heated at 40 °C until the starting material was fully consumed (TLC, ca 1 h). A solution of tert-BuOOH in decane (5.5
M, 364 μL, 4.00 mmol) was then slowly added via syringe and stirring at 40 °C was continued for 1 h. After cooling to ambient temperature the reaction mixture was diluted with ethyl acetate (30 mL), dried with MgSO₄, filtered and evaporated. The residue was purified by column chromatography on silica, using hexanes-ethyl acetate mixtures of increasing polarity as eluent, to furnish compounds 15.

**2H,8H-Pyran[2,3-f]chromen-2,8-dione (15a)**[14]. Starting from 17a (242 mg, 1.00 mmol) compound 15a (120 mg, 0.56 mmol, 56%) was obtained. Colourless solid, mp 200 – 203 °C (267 – 269 °C[14]); ¹H NMR (300 MHz, DMSO-d₆) δ 8.29 (d, J = 9.7 Hz, 1H), 8.13 (d, J = 9.6 Hz, 1H), 7.94 (d, J = 8.6 Hz, 1H), 7.39 (d, J = 8.8 Hz, 1H), 6.61 (d, J = 9.8 Hz, 1H), 6.54 (d, J = 9.6 Hz, 1H); ¹³C NMR (75 MHz, DMSO-d₆) δ 159.0, 159.0, 155.4, 150.0, 144.1, 136.8, 131.3, 116.7, 115.0, 114.7, 112.9, 107.7; IR (ATR) ν 3078 (w), 1731 (s), 1623 (m), 1570 (m), 1405 (w), 1250 (w), 1167 (m), 1116 (m); HRMS (EI) calcd for C₁₂H₆O₄ [M⁺] 214.0266, found 214.0261.

**4-Phenyl-2H,8H-pyran[2,3-f]chromen-2,8-dione (15b)**[15]. Starting from 17b (318 mg, 1.00 mmol) compound 15b (119 mg, 0.41 mmol, 41%) was obtained. Colourless solid, mp 216 – 218 °C (no mp or other data reported in the literature); ¹H NMR (300 MHz, CDCl₃) δ 8.38 (d, J = 9.8 Hz, 1H), 7.64 (d, J = 9.0 Hz, 1H), 7.58 – 7.53 (m, 3H), 7.47 – 7.42 (m, 2H), 7.19 (d, J = 9.0 Hz, 1H), 6.55 (d, J = 9.8 Hz, 1H), 6.39 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 159.5, 159.4, 156.3, 155.8, 150.8, 137.0, 134.8, 130.3, 129.8, 129.3, 128.5, 117.2, 115.0, 114.1, 113.1, 108.8; IR (ATR) ν 3068 (w), 2934 (w), 1721 (s), 1623 (m), 1565 (m), 1384 (m), 1279 (m), 1161 (m), 1104 (s); HRMS (EI) calcd for C₁₈H₁₀O₄ [M⁺] 290.0579, found 290.0576.
6-Methoxy-2H,8H-pyrano[2,3-f]chromen-2,8-dione (15c) [4].

Starting from 17c (272 mg, 1.00 mmol) compound 15c (110 mg, 0.45 mmol, 45%) was obtained. Colourless solid, mp 269 – 271 °C (no mp reported in the literature [4]); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.28 (d, $J = 9.8$ Hz, 1H), 7.70 (d, $J = 9.6$ Hz, 1H), 7.07 (s, 1H), 6.55 (d, $J = 9.8$ Hz, 1H), 6.45 (d, $J = 9.6$ Hz, 1H), 4.00 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 159.5, 158.7, 146.9, 144.9, 144.7, 143.0, 136.8, 117.6, 116.3, 114.0, 111.2, 109.5, 57.1; IR (ATR) $\nu$ 3120 (w), 1732 (s), 1622 (m), 1469 (m), 1416 (m), 1285 (m), 1135 (m), 1075 (m); HRMS (EI) calcd for C$_{13}$H$_8$O$_5$ [M$^+$] 244.0372, found 244.0367.

4-Methyl-2H,8H-pyrano[2,3-f]chromen-2,8-dione (15d) [16].

Starting from 17d (256 mg, 1.00 mmol) compound 15d (107 mg, 0.47 mmol, 47%) was obtained. Colourless solid, mp 222 – 224 °C (269 – 272 °C[16]); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.32 (d, $J = 9.8$ Hz, 1H), 7.74 (d, $J = 8.9$ Hz, 1H), 7.26 (d, $J = 8.9$ Hz, 1H), 6.53 (d, $J = 9.8$ Hz, 1H), 6.45 (d, $J = 9.6$ Hz, 1H), 4.00 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 159.5, 156.2, 153.0, 152.5, 150.2, 137.1, 127.4, 121.5, 117.1, 115.9, 114.2, 113.2, 19.1; IR (ATR) $\nu$ 2972 (w), 2926 (w), 1720 (s), 1601 (s), 1387 (m), 1264 (m), 1184 (m), 1074 (s); HRMS (EI) calcd for C$_{13}$H$_8$O$_4$ [M$^+$] 228.0423, found 228.0425.

$N$-Allyl-$N$-(8-allyl-4-methyl-2-oxo-2H-chromen-7-yl)acetamide (19).

To a solution of 18 (257 mg, 1.00 mmol) in acetone (5 mL) was added K$_2$CO$_3$ and allyl bromide (256 $\mu$L, 3.00 mmol). The mixture was heated to 50 °C for 16 h, cooled to ambient temperature and brine (20 mL) and ethyl acetate (30 mL) were added. The organic layer was separated and the aqueous layer was extracted twice with ethyl acetate (30 mL each). The combined organic extracts were dried with MgSO$_4$, filtered and evaporated. The residue was purified by column chromatography on
silica with hexanes-ethyl acetate (1 : 1 (v/v)) mixture as eluent to furnish compound 19 (322 mg, 1.00 mmol, quant.). Yellow solid, mp 102 - 104 °C; $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 7.74 (d, $J = 8.4$ Hz, 1H), 7.25 (d, $J = 8.4$ Hz, 1H), 6.45 (s, 1H), 5.94 (ddt, $J = 16.9, 10.2, 6.3$ Hz, 1H), 5.82 (dddd, $J = 17.3, 10.3, 7.4, 5.4$ Hz, 1H), 5.10 – 4.94 (m, 4H), 4.72 (dd, $J = 14.8, 5.3$ Hz, 1H), 3.61 (dd, $J = 14.8, 7.5$ Hz, 1H), 3.46 (d, $J = 6.1$ Hz, 2H), 2.45 (s, 3H), 1.67 (s, 3H); $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 169.3, 159.8, 153.6, 152.4, 144.1, 135.0, 133.6, 126.2, 125.8, 124.6, 119.9, 118.7, 117.0, 115.0, 51.3, 29.9, 22.9, 18.7; IR (ATR) $\nu$ 3079 (w), 2980 (w), 1730 (s), 1663 (s), 1599 (s), 1419 (m), 1386 (s), 1299 (m), 1254 (m); HRMS (EI) calcd for C$_{18}$H$_{19}$O$_3$N [M$^+$] 297.1365, found 297.1354.

$(E,E)$-N-(4-Methyl-2-oxo-8-(prop-1-en-1-yl)-2H-chromen-7-yl)-N-(prop-1-en-1-yl)acetamide (20). To a solution of 19 (297 mg, 1.00 mmol) in toluene (10 mL) was added [RuClH(CO)(PPh$_3$)$_3$] (48 mg, 0.05 mmol, 5 mol %). The solution was heated to 65 °C for 12 h, cooled to ambient temperature and evaporated. The residue was purified by column chromatography on silica, using hexanes-ethyl acetate mixture (1 : 1 (v/v)) as eluent to furnish compound 20 (280 mg, 0.94 mmol, 94%) as a mixture of diastereoisomers. NMR data for the major isomer $(E,E)$-20: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.53 (d, $J = 8.3$ Hz, 1H), 7.40 (dm, $J = 14.6$ Hz, 1H), 7.06 (d, $J = 8.3$ Hz, 1H), 6.72 (dq, $J = 16.1, 6.6$ Hz, 1H), 6.35 (s, 1H), 6.29 (dm, $J = 16.3$ Hz, 1H), 4.38 (dq, $J = 14.5, 6.9$ Hz, 1H), 2.46 (s, 3H), 1.91 (d, $J = 6.7$ Hz, 3H), 1.76 (s, 3H), 1.62 (d, $J = 6.9$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 167.9, 160.1, 152.2, 152.1, 140.2, 136.3, 128.0, 125.5, 125.4, 123.4, 120.4, 119.5, 115.6, 109.6, 23.0, 20.3, 19.2, 15.2.

7-Acetyl-4-methyl-8,11-dihydrochromeno[7,8-b]azepin-2(7H)-one (21). To a solution of 19 (297 mg, 1.00 mmol) in toluene (10 mL) was added precatalyst A (42 mg, 0.05 mmol, 5 mol %) and the solution was heated to 90 °C until the starting material was fully consumed.
(TLC, ca 1 h). The mixture was evaporated and the residue was purified by column chromatography on silica, using hexanes-ethyl acetate mixture (1 : 1 (v/v)) as eluent, to furnish compound 21 (266 mg, 0.99 mmol, 99%). Colourless solid, mp 147 - 150 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.53 (d, $J = 8.3$ Hz, 1H), 7.15 (d, $J = 8.3$ Hz, 1H), 6.28 (s, 1H), 5.81 – 5.70 (m, 1H), 5.54 – 5.44 (m, 1H), 5.41 – 5.30 (m, 1H), 3.91 (dd, $J = 16.3$, 8.6 Hz, 1H), 3.44 – 3.30 (2H), 2.43 (s, 3H), 1.84 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 169.4, 160.2, 152.2, 150.4, 145.5, 128.4, 127.3, 123.6, 123.5, 123.4, 119.8, 115.2, 44.7, 22.2, 22.1, 19.0; IR (ATR) $\nu$ 3026 (w), 2982 (w), 1726 (s), 1666 (s), 1599 (s), 1426 (m), 1381 (s), 1306 (m), 1234 (m); HRMS (El) calcd for C$_{16}$H$_{15}$O$_3$N [M$^+$] 269.1052, found 269.1056.

References


$^1$H NMR (300 MHz, acetone-$d_6$) of 8b
$^{13}$C NMR (75 MHz, acetone-$d_6$) of 8b
$^1$H NMR (300 MHz, CDCl$_3$) of 8c
$\text{C NMR (75 MHz, CDCl}_3\text{) of 8c}$
$^1$H NMR (300 MHz, DMSO-$d_6$) of 8d
$^{13}$C NMR (75 MHz, DMSO-$d_6$) of 8d
$^1$H NMR (300 MHz, CDCl$_3$) of 9a
$^{13}$C NMR (75 MHz, CDCl$_3$) of 9a
$^1$H NMR (300 MHz, CDCl$_3$) of 9b
$^{13}$C NMR (75 MHz, CDCl$_3$) of 9b
$^1$H NMR (300 MHz, CDCl$_3$) of 9c
$^{13}$C NMR (75 MHz, CDCl$_3$) of 9c

![NMR Spectrum](image)
$^1$H NMR (300 MHz, CDCl$_3$) of 9d
$^{13}$C NMR (75 MHz, CDCl$_3$) of 9d
$^1$H NMR (300 MHz, CDCl$_3$) of 10a
$^{13}$C NMR (75 MHz, CDCl$_3$) of 10a
$^1$H NMR (300 MHz, CDCl$_3$) of 10b
$^{13}$C NMR (150 MHz, CDCl$_3$) of 10b
$^1$H NMR (300 MHz, CDCl$_3$) of 10c
$^{13}$C NMR (150 MHz, CDCl$_3$) of 10c
$^1$H NMR (300 MHz, CDCl$_3$) of 10d
$^{13}$C NMR (150 MHz, CDCl$_3$) of 10d
$^1$H NMR (300 MHz, CDCl$_3$) of 11a
$^{13}$C NMR (75 MHz, CDCl$_3$) of 11a
$^1$H NMR (300 MHz, CDCl$_3$) of 11b
$^{13}$C NMR (75 MHz, CDCl$_3$) of 11b
$^1$H NMR (300 MHz, CDCl$_3$) of 11c
$^{13}$C NMR (75 MHz, CDCl$_3$) of 11c
$^1$H NMR (300 MHz, CDCl$_3$) of 11d
$^{13}$C NMR (75 MHz, CDCl$_3$) of 11d
$^1$H NMR (300 MHz, CDCl$_3$) of 3a
$^{13}$C NMR (75 MHz, CDCl$_3$) of 3a
$^1$H NMR (300 MHz, CDCl$_3$) of 3b
$^{13}$C NMR (75 MHz, CDCl$_3$) of 3b
$^1$H NMR (300 MHz, CDCl$_3$) of 3c
$^{13}$C NMR (75 MHz, CDCl$_3$) of 3c

3c
$^1$H NMR (300 MHz, CDCl$_3$) of 3d
$^{13}$C NMR (75 MHz, CDCl$_3$) of 3d
\(^1\text{H NMR (300 MHz, CDCl}_3\) of 12a

12a
$^{13}$C NMR (75 MHz, CDCl$_3$) of 12a
\(^1\)H NMR (300 MHz, CDCl\(_3\)) of 12b
$^{13}$C NMR (75 MHz, CDCl$_3$) of 12b
$^1$H NMR (300 MHz, CDCl$_3$) of 12c
$^{13}\text{C NMR (75 MHz, CDCl}_3\text{)}$ of 12c
$^1$H NMR (300 MHz, CDCl$_3$) of 12d
$^{13}$C NMR (75 MHz, CDCl$_3$) of 12d
$^1$H NMR (300 MHz, CDCl$_3$) of 13a
$^{13}$C NMR (75 MHz, CDCl$_3$) of 13a

13a
$^1$H NMR (300 MHz, CDCl$_3$) of 13b
$^{13}$C NMR (75 MHz, CDCl$_3$) of 13b
$^1$H NMR (300 MHz, CDCl$_3$) of 13c
$^{13}$C NMR (75 MHz, CDCl$_3$) of 13c

13c
$^1$H NMR (300 MHz, CDCl$_3$) of 13d
$^{13}$C NMR (75 MHz, CDCl$_3$) of 13d
$^1$H NMR (300 MHz, CDCl$_3$) of 14d
$^{13}$C NMR (75 MHz, CDCl$_3$) of 14d
$^1$H NMR (300 MHz, acetone-$d_6$) of 16a
$^{13}$C NMR (75 MHz, acetone-$d_6$) of 16a
$^1$H NMR (300 MHz, DMSO-$d_6$) of 16b
$^{13}$C NMR-APT (75 MHz, DMSO-$d_6$) of 16b
$^1$H NMR (300 MHz, DMSO-$d_6$) of 16c
$^{13}$C NMR-APT (75 MHz, DMSO-$d_6$) of 16c
$^1$H NMR (300 MHz, DMSO-$_{d6}$) of 16d
$^{13}$C NMR (75 MHz, DMSO-$d_6$) of 16d
$^1$H NMR (300 MHz, CDCl$_3$) of 17a
$^{13}$C NMR (75 MHz, CDCl$_3$) of 17a
$^1$H NMR (300 MHz, CDCl$_3$) of 17b
$^{13}$C NMR-APT (75 MHz, CDCl$_3$) of 17b
$^1$H NMR (300 MHz, CDCl$_3$) of 17c
$^{13}$C NMR-APT (75 MHz, CDCl$_3$) of 17c
$^1$H NMR (300 MHz, CDCl$_3$) of 17d
$^{13}$C NMR (75 MHz, CDCl$_3$) of 17d
\(^1\)H NMR (300 MHz, DMSO-\(\text{d}_6\)) of 15a
$^{13}$C NMR (75 MHz, DMSO-$d_6$) of 15a
$^1$H NMR (300 MHz, CDCl$_3$) of 15b
$^{13}$C NMR (75 MHz, CDCl$_3$) of 15b
$^{1}$H NMR (300 MHz, CDCl$_3$) of 15c

15c
$^{13}$C NMR (75 MHz, CDCl$_3$) of 15c
$^1$H NMR (300 MHz, CDCl$_3$) of 15d
$^{13}$C NMR (75 MHz, CDCl$_3$) of 15d
$^1$H NMR (300 MHz, DMSO-$d_6$) of 19
$^{13}$C NMR (75 MHz, DMSO-$d_6$) of 19
$^1$H NMR (300 MHz, CDCl$_3$) of 20
$^{13}$C NMR (75 MHz, CDCl$_3$) of 20
$^1$H NMR (300 MHz, CDCl$_3$) of 21
$^{13}$C NMR (75 MHz, CDCl$_3$) of 21