

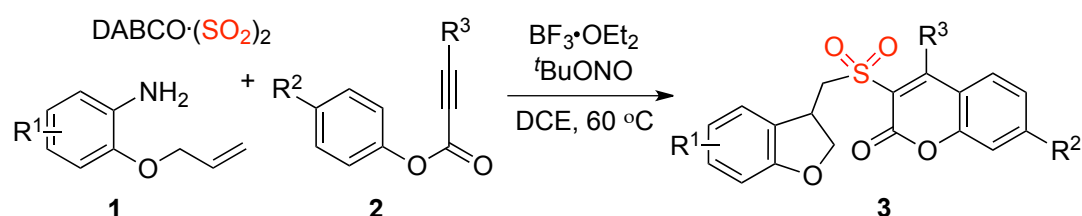
Supporting Information

1. General experimental method (S2).
2. General experimental procedure and characterization data (S3-S8).
3. ^1H and ^{13}C NMR spectra of compounds **3** (S9-S34).

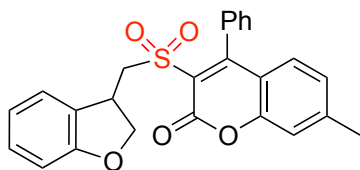
General experimental methods:

Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63µm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25–35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument.

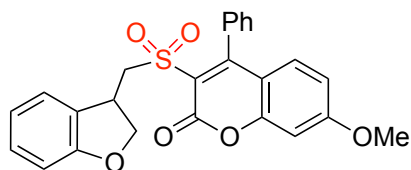
General experimental procedure for the three-component reaction of 2-(allyloxy)anilines 1, DABCO-bis(sulfur dioxide), and aryl propiolates 2:



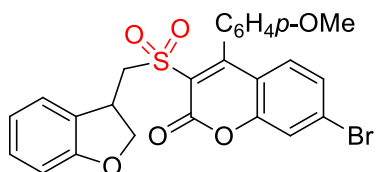
$^t\text{BuONO}$ (0.40 mmol, 2.0 equiv.) was added dropwisely to a solution of 2-(allyloxy)aniline **1** (0.30 mmol, 1.5 equiv.) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.24 mmol, 1.2 equiv.) in DCE (1.5 mL) at 0°C . After 15 minutes, the mixture was warmed up to room temperature and transferred to a pre-heated mixture of aryl propiolate **2** (0.20 mmol, 1.0 equiv.) and $\text{DABCO} \cdot (\text{SO}_2)_2$ (0.30 mmol, 1.5 equiv.) in DCE (0.5 mL) under N_2 atmosphere via a syringe. The reaction was stirred at 60°C overnight. After completion of reaction as indicated by TLC, the solvent was evaporated and the residue was purified directly by flash column chromatography ($\text{EtOAc}/n\text{-hexane}$, 1:4) to give rise to the corresponding product **3**.



3-(((2,3-dihydrobenzofuran-3-yl)methyl)sulfonyl)-7-methyl-4-phenyl-2H-chromen-2-one (**3a**): ^1H NMR (400 MHz, CDCl_3): δ 7.56 – 7.51 (m, 3H), 7.31 – 7.24 (m, 3H), 7.18 – 7.12 (m, 2H), 7.05 (d, $J = 8.3$ Hz, 1H), 6.95 (d, $J = 8.3$ Hz, 1H), 6.86 (t, $J = 7.4$ Hz, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 4.64 (t, $J = 9.2$ Hz, 1H), 4.50 – 4.46 (m, 1H), 4.10 – 4.00 (m, 2H), 3.69-3.63 (m, 1H), 2.49(s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.88, 159.70, 157.04, 153.83, 147.43, 131.93, 129.64, 129.44, 129.21, 128.16, 128.04, 127.81, 127.18, 126.76, 126.54, 124.38, 122.95, 120.83, 117.58, 117.03, 109.91, 75.97, 59.31, 36.56, 21.95; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{20}\text{NaO}_5\text{S}^+$: 455.0929 ($\text{M} + \text{Na}^+$), found: 455.0910.

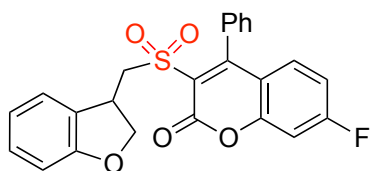


3-(((2,3-dihydrobenzofuran-3-yl)methyl)sulfonyl)-7-methoxy-4-phenyl-2H-chromen-2-one (**3b**): ^1H NMR (400 MHz, CDCl_3): δ 7.59– 7.47 (m, 3H), 7.29 – 7.26 (m, 2H), 7.17 – 7.10 (m, 2H), 6.97 (d, $J = 9.0$ Hz, 1H), 6.87 – 6.82 (m, 2H), 6.77 (t, $J = 7.8$ Hz, 2H), 4.62 (t, $J = 9.3$ Hz, 1H), 4.48 – 4.44 (m, 1H), 4.07– 3.98 (m, 2H), 3.91 (s, 3H), 3.66– 3.60 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.54, 160.95, 159.64, 157.19, 155.97, 132.14, 131.19, 129.31, 129.12, 128.08, 127.97, 127.73, 127.09, 126.79, 124.33, 120.75, 113.86, 113.35, 109.83, 100.37, 75.94, 59.15, 56.15, 36.52; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{20}\text{NaO}_6\text{S}^+$: 471.0878 ($\text{M} + \text{Na}^+$), found: 471.0883.

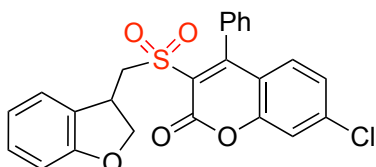


7-bromo-3-(((2,3-dihydrobenzofuran-3-yl)methyl)sulfonyl)-4-(4-methoxyphenyl)-2H-chromen-2-one (**3c**): ^1H NMR (400 MHz, CDCl_3): δ 7.58 (s, 1H), 7.37 (d, $J = 8.6$ Hz, 1H), 7.26 – 7.03 (m, 7H), 6.84 (t, $J = 7.4$ Hz, 1H), 6.76 (d, $J = 8.0$ Hz, 1H), 4.63 (t, $J = 9.3$ Hz,

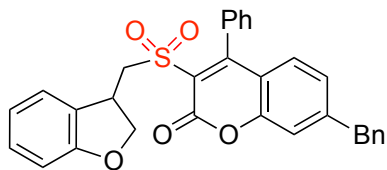
1H), 4.50 – 4.46 (m, 1H), 4.05 – 4.99 (m, 2H), 3.90 (s, 3H), 3.70 – 3.64 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.78, 160.24, 159.64, 156.25, 153.54, 130.80, 129.63, 129.22, 128.95, 128.65, 126.60, 124.36, 122.98, 120.80, 120.14, 119.19, 113.80, 113.76, 109.88, 75.83, 59.32, 55.29, 36.49; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{19}\text{BrNaO}_6\text{S}^+$: 548.9983 ($\text{M} + \text{Na}^+$), found: 548.9998.



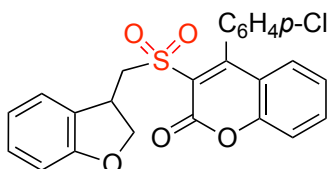
3-(((2,3-dihydrobenzofuran-3-yl)methyl)sulfonyl)-7-fluoro-4-phenyl-2H-chromen-2-one (**3d**): ^1H NMR (400 MHz, CDCl_3): δ 7.63 – 7.49 (m, 3H), 7.30 – 7.26 (m, 2H), 7.17 – 7.08 (m, 4H), 6.97 (t, $J = 8.4$ Hz, 1H), 6.85 (t, $J = 7.4$ Hz, 1H), 6.76 (d, $J = 8.0$ Hz, 1H), 4.62 (t, $J = 9.3$ Hz, 1H), 4.48 – 4.44 (m, 1H), 4.06 – 3.98 (m, 2H), 3.68 – 3.62 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.33 (d, $^1J_{\text{C-F}} = 260.5$ Hz), 160.24, 159.65, 156.44, 155.09, 132.18 (d, $^3J_{\text{C-F}} = 10.8$ Hz), 131.51, 129.68, 129.23, 128.31, 128.19, 127.71, 127.09, 126.58, 124.35, 120.82, 116.72, 113.64 (d, $^2J_{\text{C-F}} = 22.6$ Hz), 109.90, 104.61, 104.35, 75.82, 59.26, 36.47; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{17}\text{FNaO}_5\text{S}^+$: 459.0678 ($\text{M} + \text{Na}^+$), found: 459.0663.



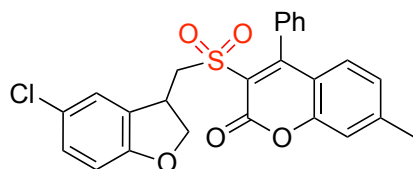
7-chloro-3-(((2,3-dihydrobenzofuran-3-yl)methyl)sulfonyl)-4-phenyl-2H-chromen-2-one (**3e**): ^1H NMR (400 MHz, CDCl_3): δ 7.63 – 7.52 (m, 3H), 7.45 (s, 1H), 7.31 – 7.12 (m, 5H), 7.02 (d, $J = 8.7$ Hz, 1H), 6.86 (t, $J = 7.4$ Hz, 1H), 6.78 (d, $J = 8.0$ Hz, 1H), 4.64 (t, $J = 9.3$ Hz, 1H), 4.50 – 4.46 (m, 1H), 4.07 – 4.00 (m, 2H), 3.71 – 3.64 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.06, 159.68, 156.24, 153.79, 141.59, 131.32, 130.82, 129.76, 129.29, 128.37, 128.25, 127.75, 127.14, 126.57, 125.92, 124.38, 120.86, 118.58, 117.20, 109.95, 75.84, 59.34, 36.50; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{17}\text{ClNaO}_5\text{S}^+$: 475.0383 ($\text{M} + \text{Na}^+$), found: 475.0386.



7-benzyl-3-(((2,3-dihydrobenzofuran-3-yl)methyl)sulfonyl)-4-phenyl-2H-chromen-2-one (**3f**): ^1H NMR (400 MHz, CDCl_3): δ 7.56 – 7.50 (m, 3H), 7.32– 7.22 (m, 6H), 7.17 – 7.05 (m, 5H), 6.98 (d, $J = 8.3$ Hz, 1H), 6.85 (t, $J = 7.4$ Hz, 1H), 6.77 (d, $J = 8.0$ Hz, 1H), 4.62 (t, $J = 9.2$ Hz, 1H), 4.48– 4.44 (m, 1H), 4.08 – 3.98 (m, 4H), 3.67 – 3.61 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.71, 159.62, 156.85, 153.84, 150.31, 138.56, 131.81, 129.87, 129.40, 129.14, 128.90, 128.80, 128.10, 127.98, 127.75, 127.10, 126.83, 126.68, 126.01, 124.32, 120.77, 118.01, 116.81, 109.83, 75.88, 59.21, 41.83, 36.49; HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{25}\text{O}_5\text{S}^+$: 509.1423 ($\text{M} + \text{H}^+$), found: 509.1417.

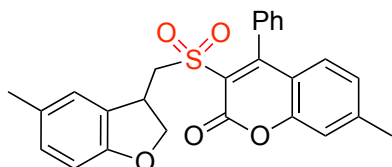


4-(4-chlorophenyl)-3-(((2,3-dihydrobenzofuran-3-yl)methyl)sulfonyl)-2H-chromen-2-one (**3g**): ^1H NMR (400 MHz, CDCl_3): δ 7.74 – 7.70 (m, 1H), 7.56 – 7.54 (m, 2H), 7.46 (d, $J = 8.3$ Hz, 1H), 7.31 – 7.08 (m, 6H), 6.88 (t, $J = 7.4$ Hz, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 4.66 (t, $J = 9.2$ Hz, 1H), 4.53 – 4.49 (m, 1H), 4.11 – 4.02 (m, 2H), 3.75 – 3.69 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.62, 159.44, 156.49, 153.63, 135.78, 135.32, 130.02, 129.54, 129.22, 128.64, 128.61, 128.50, 126.51, 125.29, 124.35, 120.81, 119.58, 117.05, 109.87, 75.76, 59.26, 36.47; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{17}\text{ClNaO}_5\text{S}^+$: 475.0383 ($\text{M} + \text{Na}^+$), found: 475.0366.

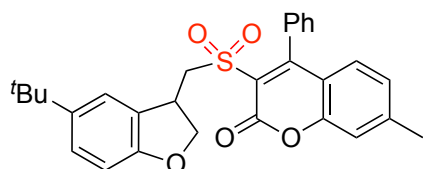


3-(((5-chloro-2,3-dihydrobenzofuran-3-yl)methyl)sulfonyl)-7-methyl-4-phenyl-2H-chromen-2-one (**3h**): ^1H NMR (400 MHz, CDCl_3) δ 7.60 – 7.48 (m, 3H), 7.30 – 7.25 (m, 3H), 7.14 (s, 1H), 7.09 – 7.05 (m, 2H), 6.96 (d, $J = 8.3$ Hz, 1H), 6.70 (d, $J = 8.5$ Hz, 1H), 4.67 (t, $J = 9.4$ Hz, 1H), 4.53 – 4.49 (m, 1H), 4.05 – 3.99 (m, 2H), 3.72 – 3.66 (m, 1H),

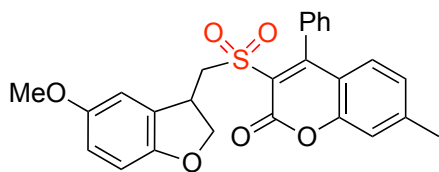
2.49 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.97, 158.47, 157.05, 153.85, 147.56, 131.86, 129.66, 129.51, 129.16, 128.79, 128.20, 128.10, 127.83, 127.20, 126.61, 124.62, 117.54, 117.08, 110.88, 76.58, 59.17, 36.57, 21.98; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{19}\text{ClNaO}_5\text{S}^+$: 489.0539 (M + Na^+), found:.



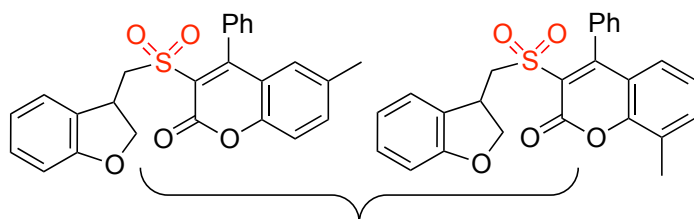
7-methyl-3-(((5-methyl-2,3-dihydrobenzofuran-3-yl)methyl)sulfonyl)-4-phenyl-2H-chromen-2-one (**3i**): ^1H NMR (400 MHz, CDCl_3) δ 7.60 – 7.49 (m, 3H), 7.31 – 7.24 (m, J = 9.2 Hz, 3H), 7.06 (d, J = 8.3 Hz, 1H), 7.01 – 6.88 (m, 3H), 6.67 (d, J = 8.1 Hz, 1H), 4.61 (t, J = 9.2 Hz, 1H), 4.52 – 4.33 (m, 1H), 4.10 (d, J = 14.6 Hz, 1H), 4.01 - 3.95 (m, 1H), 3.66 - 3.60 (m, 1H), 2.49 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.83, 157.58, 157.04, 153.80, 147.39, 131.92, 130.20, 129.62, 129.58, 129.40, 128.14, 128.01, 127.80, 127.17, 126.69, 126.53, 124.83, 117.58, 117.00, 109.40, 76.04, 59.24, 36.68, 21.93, 20.66; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{22}\text{NaO}_5\text{S}^+$: 469.1086 (M + Na^+), found: 469.1080.



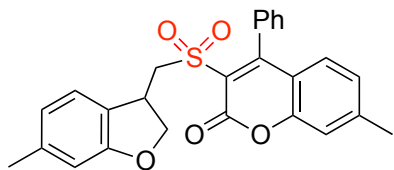
3-(((5-(tert-butyl)-2,3-dihydrobenzofuran-3-yl)methyl)sulfonyl)-7-methyl-4-phenyl-2H-chromen-2-one (**3j**): ^1H NMR (400 MHz, CDCl_3): δ 7.51 – 7.51 (m, 3H), 7.31 – 7.25 (m, 3H), 7.18 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 8.4 Hz, 1H), 6.96 (d, J = 8.3 Hz, 1H), 6.72 (d, J = 8.2 Hz, 1H), 4.63 (t, J = 9.2 Hz, 1H), 4.49 – 4.45 (m, 1H), 4.10 – 3.99 (m, 2H), 3.73 – 3.67 (m, 1H), 2.49 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 160.87, 157.48, 153.84, 147.43, 144.09, 131.96, 129.66, 129.43, 128.18, 128.04, 127.80, 127.19, 126.55, 126.37, 126.13, 121.13, 117.04, 109.13, 76.17, 59.36, 36.71, 31.66, 21.96; HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{28}\text{NaO}_5\text{S}^+$: 511.1555 (M + Na^+), found: 511.1548.



3-(((5-methoxy-2,3-dihydrobenzofuran-3-yl)methyl)sulfonyl)-7-methyl-4-phenyl-2H-chromen-2-one (**3k**): ^1H NMR (400 MHz, CDCl_3): ^1H NMR (400 MHz, CDCl_3): δ 7.61 – 7.48 (m, 3H), 7.30 – 7.23 (m, 3H), 7.05 (d, $J = 8.3$ Hz, 1H), 6.95 (d, $J = 8.4$ Hz, 2H), 6.75 (s, 1H), 6.72 – 6.63 (m, 2H), 4.61 (t, $J = 9.2$ Hz, 1H), 4.46 – 4.42 (m, 1H), 4.06 – 3.96 (m, 2H), 3.72 (s, 3H), 3.69 – 3.63 (m, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.85, 157.02, 154.33, 153.80, 153.69, 147.42, 131.91, 129.61, 129.40, 128.13, 128.02, 127.76, 127.60, 127.20, 126.52, 122.90, 117.56, 117.00, 114.64, 110.10, 109.92, 76.19, 59.08, 56.00, 37.02, 21.92; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{22}\text{NaO}_5\text{S}^+$: 485.1035 ($\text{M} + \text{Na}^+$), found: 485.1030.



3-(((2,3-dihydrobenzofuran-3-yl)methyl)sulfonyl)-6-methyl-4-phenyl-2H-chromen-2-one(**3l**) and
 3-(((2,3-dihydrobenzofuran-3-yl)methyl)sulfonyl)-8-methyl-4-phenyl-2H-chromen-2-one(**3l'**): ^1H NMR (400 MHz, CDCl_3): δ 7.56 – 7.47 (m, 4H), 7.32 – 7.25 (m, 3H), 7.17 – 7.09 (m, 2H), 6.92 – 6.82 (m, 2H), 6.75 (d, $J = 8.0$ Hz, 1H), 4.62 (t, $J = 9.3$ Hz, 1H), 4.47– 4.43 (m, 1H), 4.11 – 3.98 (m, 2H), 3.66 – 3.60 (m, 1H), 2.51 (s, 0.85H), 2.27 (s, 2.11H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.73, 159.60, 156.86, 151.84, 136.35, 136.29, 135.11, 131.98, 131.73, 129.41, 129.34, 129.28, 129.12, 128.12, 128.05, 128.00, 127.93, 127.80, 127.76, 127.61, 127.16, 127.13, 126.67, 126.49, 124.59, 124.32, 123.95, 120.74, 119.54, 116.65, 109.80, 75.86, 59.24, 36.51, 36.45, 20.85, 15.40; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{20}\text{NaO}_5\text{S}^+$: 455.0929 ($\text{M} + \text{Na}^+$), found: 455.0914.



7-methyl-3-(((6-methyl-2,3-dihydrobenzofuran-3-yl)methyl)sulfonyl)-4-phenyl-2H-chromen-2-one (**3m**): ^1H NMR (400 MHz, CDCl_3): δ 7.60 – 7.50 (m, 3H), 7.31 – 7.24 (m, 3H), 7.05 (d, $J = 7.7$ Hz, 2H), 6.95 (d, $J = 8.3$ Hz, 1H), 6.67 (d, $J = 7.0$ Hz, 1H), 6.60 (s, 1H), 4.62 (t, $J = 9.2$ Hz, 1H), 4.48 – 4.44 (m, 1H), 4.07 – 3.97 (m, 2H), 3.68 – 3.62 (m, 1H), 2.49 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.80, 159.94, 153.82, 147.37, 139.59, 131.94, 129.62, 129.41, 128.15, 128.03, 127.81, 127.20, 126.52, 123.95, 123.74, 121.58, 117.60, 117.02, 110.57, 76.15, 59.33, 36.35, 21.94, 21.45; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{22}\text{NaO}_5\text{S}^+$: 469.1086 (M + Na^+), found: 469.1080.

