Supplementary Information

Visible |ight-induced cascade sulfonylation/annulation of *ortho*-allyloxyl chalcones with sodium sulfinates for the synthesis of sulfonated chromane derivatives

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1. General Information

All chemicals were obtained from commercial sources and used without further purification unless otherwise stated. The substrates **1** were prepared according to literature procedures.[1] Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 ºC). ^{1}H and ^{13}C NMR data were recorded with Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. Melting point was determined using X-4 made by Peking Taike Apparatus Co. Ltd. High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument.

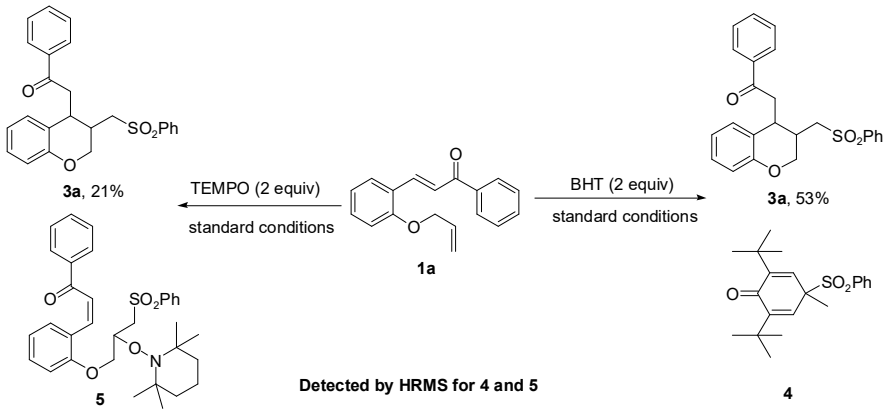
2. General procedure for synthesis of the substrates 1

A suspension of 2-hydroxychalcone (1.12 g, 5 mmol), allyl bromide (0.91 g, 7.5 mmol) and K_2CO_3 (1.04 g, 7.5 mmol) in DMF (2.5 mL) was stirred overnight at room temperature. Reaction mixture was diluted with water (10 mL) and EtOAc (10 mL), sequentially washed with aqueous sodium bicarbonate, brine, and water and dried over anhydrous Na_2SO_4. The solvent was filtered and evaporated under reduced pressure to afford a crude solid, which was purified by column chromatography on silica gel (EtOAc: petroleum ether) to afford the desired products **1**.

3. General procedure for the decarboxylative cyclization reactions

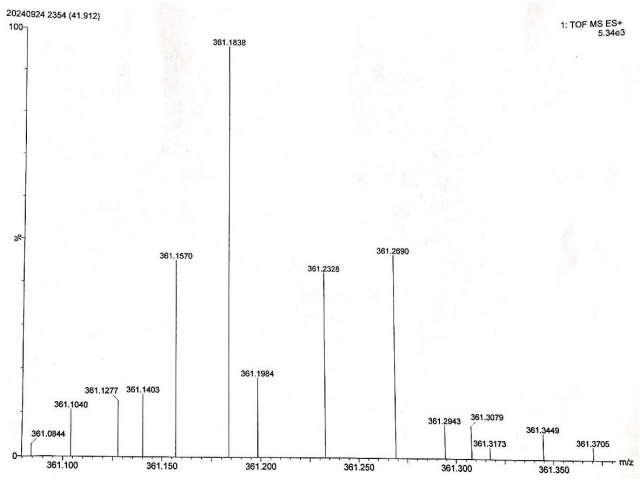
ortho-allyloxyl chalcone **1**(0.3 mmol), **2** (0.45 mmol, 1.5 equiv.), eosin Y (0.5 mol %), AcOH (1.35 mmol, 4.5 equiv.), and DMSO (2 mL) at room temperature. The reaction mixture was degassed by sparging with nitrogen for 10 min with an outlet needle and then irradiated with Kessil 18 W 456 nm LEDs at room temperature for 4 h. The reaction mixture was diluted with 1 M NaOH aqueous solution (10 mL), extracted with DCE (3×10 mL), dried with Na_2SO_4, and concentrated in vacuo. The crude residue was purified by flash column chromatography to afford the pure desired product **3**.

4. Mechanistic study

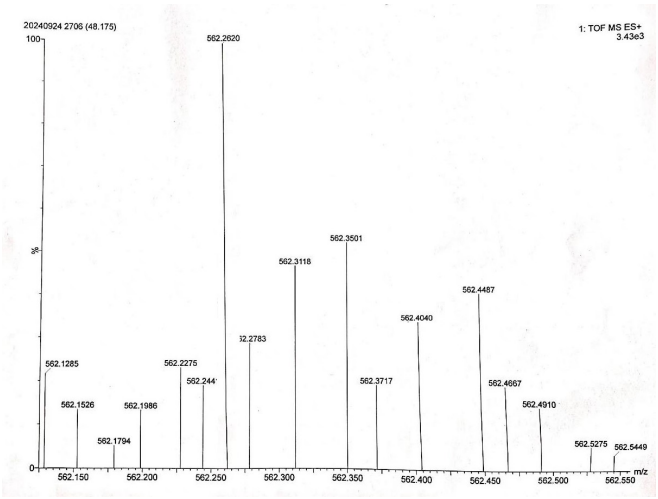


HRMS of product 4 and 5

The trapping adducts	Formula (M)	Ion Formula	Measured m/z	Calc m/z
4	$C_{21}H_{28}O_3S$	$M+H]^+$	361.1838	361.1837
5	$C_{33}H_{39}NO_5S$	$M+H]^+$	562.2620	562.2627

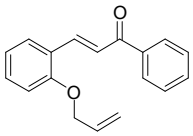


HRMS of product 4

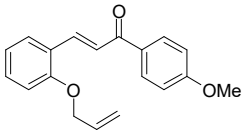


HRMS of product 5

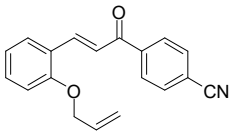
5. Characterization Data for 1 and 3



3-(2-Allyloxy-phenyl)-1-phenyl-propenone (1a)[1] colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 15.9 Hz, 1H), 8.07–7.98 (m, 2H), 7.71–7.62 (m, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.38–7.33 (m, 1H), 7.05–6.91 (m, 2H), 6.11 (ddt, *J* = 15.8, 10.5, 5.2 Hz, 1H), 5.50 – 5.42 (m, 1H), 5.37 – 5.30 (m, 1H), 4.64 (d, *J* = 5.1 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.2, 157.9, 140.5, 138.5, 132.9, 132.6, 131.6, 129.5, 128.6, 124.2, 123.1, 121.0, 118.0, 112.6, 69.2. HRMS (ESI) Calcd for $C_{18}H_{17}O_2$ $[M+H]^+$ 265.1229, found 265.1227.

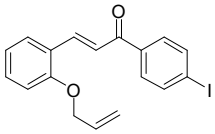


3-(2-Allyloxy-phenyl)-1-(4-methoxy-phenyl)-propenone (1b), colorless liquid.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 15.8 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.71–7.61 (m, 2H), 7.37–7.29 (m, 1H), 6.96 (dq, *J* = 16.9, 8.2 Hz, 4H), 6.11 (ddt, *J* = 15.7, 10.4, 5.2 Hz, 1H), 5.50–5.42 (m, 1H), 5.36 – 5.29 (m, 1H), 4.63 (d, *J* = 5.0 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.3, 163.3, 157.8, 139.6, 132.9, 131.5, 131.4, 130.8, 129.5, 124.5, 123.0, 121.0, 118.0, 113.8, 112.6, 69.2, 55.5. HRMS (ESI) Calcd for $C_{19}H_{19}O_3$ $[M+H]^+$ 295.1334, found 295.1337.

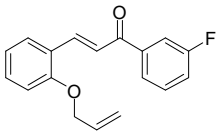


4-[3-(2-Allyloxy-phenyl)-acryloyl]-benzonitrile (1c) colorless liquid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 15.8 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.66–7.58 (m, 2H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.11 (ddt, *J* = 16.1, 10.5, 5.2 Hz, 1H), 5.45 (d, *J* = 17.3 Hz, 1H), 5.35 (d, *J* = 10.5 Hz, 1H), 4.65 (d, *J* = 5.0 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 189.9, 158.1, 142.3, 141.9, 132.7, 132.4, 132.3, 129.9, 128.9, 123.7, 122.2, 121.1, 118.2, 118.1, 115.7, 112.6, 69.3. HRMS (ESI) Calcd for $C_{19}H_{16}NO_2$

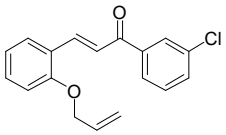
$[M+H]^+$ 290.1181, found 290.1182.



3-(2-Allyloxy-phenyl)-1-(4-iodo-phenyl)-propenone (1d) colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 15.8 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.64–7.58 (m, 2H), 7.39–7.32 (m, 1H), 6.99 (t, *J* = 7.3 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.10 (ddt, *J* = 15.8, 10.5, 5.2 Hz, 1H), 5.49–5.41 (m, 1H), 5.37–5.31 (m, 1H), 4.67–4.61 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.3, 157.9, 141.1, 137.8, 132.8, 131.9, 130.0, 129.7, 129.6, 124.0, 122.5, 121.0, 118.1, 112.6, 100.3, 69.2. HRMS (ESI) Calcd for $C_{18}H_{16}IO_2$ $[M+H]^+$ 391.0195, found 391.0194.

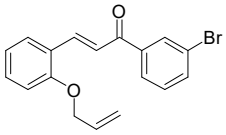


3-(2-Allyloxy-phenyl)-1-(3-fluoro-phenyl)-propenone (1e) colorless liquid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 15.8 Hz, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 9.4 Hz, 1H), 7.66–7.61 (m, 2H), 7.50–7.45 (m, 1H), 7.40–7.35 (m, 1H), 7.28 (dt, *J* = 8.1, 3.7 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.12 (ddt, *J* = 15.9, 10.5, 5.2 Hz, 1H), 5.50–5.44 (m, 1H), 5.38–5.33 (m, 1H), 4.65 (d, *J* = 5.2 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.7, 158.0, 141.3, 132.8, 131.9, 130.2, 130.1, 129.7, 124.2, 124.2, 124.0, 122.6, 121.0, 119.6, 119.4, 118.1, 115.4, 115.3, 112.6, 69.2. HRMS (ESI) Calcd for $C_{18}H_{16}FO_2$ $[M+H]^+$ 283.1134, found 283.1137.

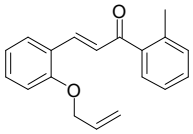


3-(2-Allyloxy-phenyl)-1-(3-chloro-phenyl)-propenone (1g) colorless liquid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 15.8 Hz, 1H), 7.98 (s, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.64–7.60 (m, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 8.3 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.11 (dtt, *J*

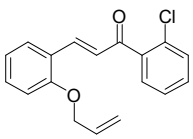
= 16.0, 10.8, 5.9 Hz, 1H), 5.49–5.44 (m, 1H), 5.37–5.33 (m, 1H), 4.64 (d, *J* = 5.2 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 189.7, 158.0, 141.4, 140.2, 134.8, 132.8, 132.4, 131.9, 129.9, 129.8, 128.7, 126.6, 124.0, 122.6, 121.0, 118.2, 112.6, 69.3. HRMS (ESI) Calcd for $C_{18}H_{16}ClO_2$ $[M+H]^+$ 299.0839, found 299.0843.



3-(2-Allyloxy-phenyl)-1-(3-bromo-phenyl)-propenone (1g) colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 16.3 Hz, 1H), 7.67–7.61 (m, 1H), 7.60–7.56 (m, 1H), 7.44–7.29 (m, 4H), 7.17 (d, *J* = 16.3 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.00 (ddt, *J* = 17.1, 10.0, 4.9 Hz, 1H), 5.35–5.21 (m, 2H), 4.60–4.53 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.4, 157.7, 142.5, 141.4, 133.4, 132.6, 132.2, 131.1, 129.2, 129.0, 127.2, 126.6, 123.7, 121.1, 119.5, 117.4, 112.7, 69.1. HRMS (ESI) Calcd for $C_{18}H_{16}BrO_2$ $[M+H]^+$ 343.0334, found 343.0337.

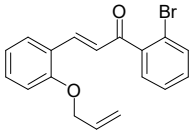


3-(2-Allyloxy-phenyl)-1-o-tolyl-propenone (1h) colorless liquid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 16.2 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.34 (dt, *J* = 15.7, 7.9 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 16.2 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.01 (ddt, *J* = 15.8, 10.2, 5.0 Hz, 1H), 5.36–5.30 (m, 1H), 5.27–5.23 (m, 1H), 4.57 (d, *J* = 4.9 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 197.3, 157.6, 141.6, 139.4, 136.8, 132.7, 131.8, 131.2, 130.2, 128.9, 128.1, 127.4, 125.4, 124.0, 121.0, 117.5, 112.6, 69.1, 20.2. HRMS (ESI) Calcd for $C_{19}H_{19}O_2$ $[M+H]^+$ 279.1385, found 279.1384.

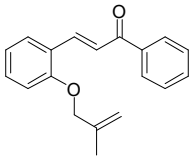


3-(2-Allyloxy-phenyl)-1-(2-chloro-phenyl)-propenone (1i) colorless liquid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 16.2 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H),

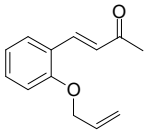
7.45 (dd, *J* = 12.0, 7.9 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 16.2 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.01 (ddt, *J* = 15.5, 9.6, 4.5 Hz, 1H), 5.31 (d, *J* = 17.3 Hz, 1H), 5.24 (d, *J* = 10.6 Hz, 1H), 4.57 (d, *J* = 3.4 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 194.5, 157.7, 142.2, 139.4, 132.6, 132.2, 131.3, 131.1, 130.2, 129.3, 129.0, 126.8, 126.7, 123.7, 121.1, 117.5, 112.6, 69.1. HRMS (ESI) Calcd for $C_{18}H_{16}ClO_2$ $[M+H]^+$ 299.0839, found 299.0845.



3-(2-Allyloxy-phenyl)-1-(2-bromo-phenyl)-propenone (1j) colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 16.3 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.44–7.28 (m, 4H), 7.17 (d, *J* = 16.3 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.00 (ddt, *J* = 15.5, 10.2, 4.9 Hz, 1H), 5.35–5.27 (m, 1H), 5.27–5.20 (m, 1H), 4.56 (d, *J* = 4.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.3, 157.7, 142.5, 141.4, 133.4, 132.6, 132.2, 131.1, 129.2, 129.0, 127.2, 126.6, 123.7, 121.1, 119.5, 117.4, 112.7, 69.1. HRMS (ESI) Calcd for $C_{18}H_{16}BrO_2$ $[M+H]^+$ 343.0334, found 343.0338.

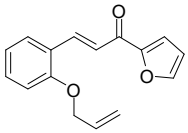


3-[2-(2-Methyl-allyloxy)-phenyl]-1-phenyl-propenone (1k) colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 15.9 Hz, 1H), 8.05–7.99 (m, 2H), 7.69–7.63 (m, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.1 Hz, 1H), 7.00 (t, *J* = 7.3 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 5.14 (s, 1H), 5.04 (s, 1H), 4.54 (s, 2H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.3, 158.0, 140.6, 132.5, 131.6, 129.4, 128.6, 123.1, 120.9, 113.3, 112.6, 72.2, 19.6. HRMS (ESI) Calcd for $C_{19}H_{19}O_2$ $[M+H]^+$ 279.1385, found 279.1389.

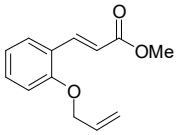


4-(2-Allyloxy-phenyl)-but-3-en-2-one (1l)[2] yellow liquid.^{1}H NMR (400 MHz,

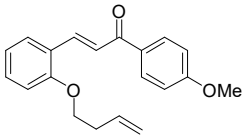
Chloroform-*d*) δ 7.93 (d, *J* = 16.5 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.37 – 7.31 (m, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.76 (d, *J* = 16.5 Hz, 1H), 6.09 (ddt, *J* = 21.0, 10.4, 5.1 Hz, 1H), 5.48 – 5.40 (m, 1H), 5.35 – 5.29 (m, 1H), 4.65 – 4.60 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.0, 157.3, 138.7, 132.9, 131.7, 128.3, 127.8, 123.7, 121.1, 117.8, 112.6, 69.2, 27.1.



3-(2-Allyloxy-phenyl)-1-furan-2-yl-propenone (1m) yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 15.9 Hz, 1H), 7.67 – 7.55 (m, 3H), 7.38 – 7.32 (m, 1H), 7.29 (d, *J* = 3.1 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.64 – 6.52 (m, 1H), 6.12 (ddt, *J* = 15.8, 10.4, 5.2 Hz, 1H), 5.53 – 5.43 (m, 1H), 5.37 – 5.29 (m, 1H), 4.65 (d, *J* = 5.0 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.6, 158.0, 154.0, 146.3, 139.6, 132.9, 131.7, 129.6, 124.1, 122.2, 121.0, 118.0, 117.2, 112.6, 112.4, 69.3. HRMS (ESI) Calcd for $C_{16}H_{15}O_3$ $[M+H]^+$ 255.1021, found 255.1022.

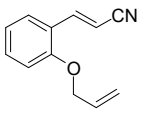


3-(2-Allyloxy-phenyl)-acrylic acid methyl ester (1n)[3] colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 16.2 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.35 – 7.28 (m, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.54 (d, *J* = 16.2 Hz, 1H), 6.14 – 6.02 (m, 1H), 5.47 – 5.39 (m, 1H), 5.34 – 5.28 (m, 1H), 4.64 – 4.59 (m, 2H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 157.3, 140.2, 132.9, 131.4, 128.9, 123.7, 120.9, 118.4, 117.8, 112.5, 69.2, 51.6.

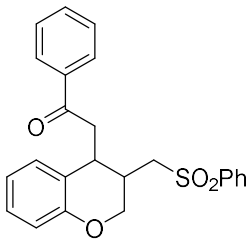


3-(2-But-3-enyloxy-phenyl)-1-(4-methoxy-phenyl)-propenone (1o) colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 8.00 (m, 3H), 7.69 (d, *J* = 15.8 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.37 – 7.30 (m, 1H), 6.96 (dt, *J* = 16.3, 8.2 Hz, 4H), 5.95 (ddt, *J* = 13.4, 10.2, 6.7 Hz, 1H), 5.26 – 5.17 (m, 1H), 5.13 (d, *J* = 10.2 Hz, 1H), 4.11 (t, *J* =

6.5 Hz, 2H), 3.87 (s, 3H), 2.64 (q, *J* = 6.4, 5.9 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.5, 163.3, 158.2, 139.9, 134.3, 131.5, 131.4, 130.8, 130.0, 124.3, 123.1, 120.8, 117.4, 113.7, 112.2, 67.7, 55.5, 33.6. HRMS (ESI) Calcd for $C_{20}H_{21}O_3$ $[M+H]^+$ 309.1491, found 309.1492.



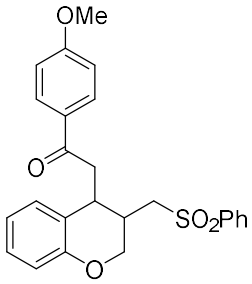
3-(2-Allyloxy-phenyl)-acrylonitrile (1p) [4] colorless liquid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 16.8 Hz, 1H), 7.40 – 7.34 (m, 2H), 6.99 – 6.90 (m, 2H), 6.11 – 6.02 (m, 2H), 5.42 (d, *J* = 17.3 Hz, 1H), 5.34 (d, *J* = 11.8 Hz, 1H), 4.60 (d, *J* = 5.4 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.2, 146.4, 132.5, 132.3, 128.9, 122.8, 122.7, 121.0, 119.0, 118.5, 112.6, 97.0, 69.3.



1-phenyl-2-(3-((phenylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3a)

According to the general procedure, (E)-3-(2-(allyloxy)phenyl)-1-phenylprop-2-en-1-one（2a）(79 mg, 0.3 mmol) afforded 3a (112 mg, 0.276 mmol, 92 % yield) in white solid, anti/syn=1.5:1(60%:40%);

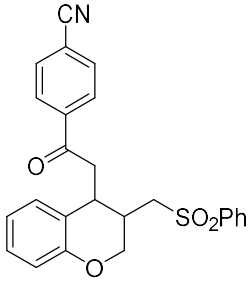
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94−7.87 (m, 4H), 7.65−7.57 (m, 2H), 7.55−7.51 (m, 2H), 7.47 (dd, *J* = 15.6, 7.8 Hz, 2H), 7.13−7.08 (m, 1H), 7.04 (d, *J* = 7.8 Hz, 0.4 × 1H, syn), 6.94 (d, *J* = 7.8 Hz, 0.6 × 1H, anti), 6.87−6.78 (m, 2H), 4.43−4.38 (m, 1H), 4.26 (dd, *J* = 11.4, 6.0 Hz, 0.6 × 1H, anti), 4.17 (d, *J* = 11.4 Hz, 0.4 × 1H, syn), 3.90 (q, *J* = 5.7 Hz, 0.6 × 1H, anti), 3.44−3.42 (m, 0.4 × 1H, syn), 3.41−3.27 (m, 2H), 3.19−3.06 (m, 2H), 2.80−2.78 (m, 0.6 × 1H, anti), 2.60−2.58 (m, 0.4 × 1H, syn); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 197.8, 139.2, 136.6, 133.9, 133.8, 133.6, 133.5, 130.2, 129.5, 129.4, 128.8, 128.8, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 123.6, 121.3, 120.9, 117.2, 116.8, 67.5, 64.0, 57.1, 53.7, 47.1, 40.7, 35.2, 33.6, 31.7, 30.9. HRMS (ESI) Calcd for $C_{24}H_{23}O_4S$ $[M+H]^+$ 407.1317, found 407.1321.



1-(4-methoxyphenyl)-2-(3-((phenylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3b)

According to the general procedure, 2b (88 mg, 0.3 mmol) afforded 3b (118 mg, 0.270 mmol, 90 % yield) in white solid, anti/syn=1.5:1(60%:40%);

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92−7.87 (m, 4H), 7.64−7.60 (m, 1H), 7.55−7.51 (m, 2H), 7.12−7.07 (m, 1H), 7.03 (d, *J* = 7.2 Hz, 0.4 × 1H, syn), 6.95−6.94 (m, 0.6 × 1H, anti), 6.93−6.92 (m, 2H), 6.86−6.83 (m, 0.4 × 1H, syn), 6.80−6.77 (m, 0.6 × 2H, anti), 4.40 (t, *J* = 12.0 Hz, 1H), 4.26 (dd, *J* = 10.2 Hz, 6.0 Hz, 0.6 × 1H, anti), 4.17 (d, *J* = 12 Hz, 0.4 × 1H, syn), 3.88 (s, 0.6 × 3H, anti), 3.87 (s, 0.4 × 3H, syn), 3.86−3.85 (m, 0.6 × 1H, anti), 3.42−3.41 (m, 0.4 × 1H, syn), 3.35−3.18 (m, 2H), 3.15−3.06 (m, 2H), 2.77−2.76 (m, 0.6 × 1H, anti), 2.59−2.57 (m, 0.4 × 1H, syn); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.3, 133.9, 133.7, 130.5, 130.4, 130.2, 129.7, 129.5, 129.3, 128.2, 128.2, 128.0, 123.8, 121.2, 120.8, 117.1, 116.8, 113.9, 67.4, 64.0, 57.1, 55.6, 53.7, 46.7, 40.4, 35.4, 33.8, 31.7, 31.0. HRMS (ESI) Calcd for $C_{25}H_{25}O_5S$ $[M+H]^+$ 437.1423, found 437.1422.

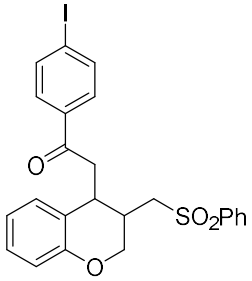


4-(2-(3-((phenylsulfonyl)methyl)chroman-4-yl)acetyl)benzonitrile(3c)

According to the general procedure, 2c (87 mg, 0.3 mmol) afforded 3c (114 mg, 0.264 mmol, 88 % yield) in white solid, anti/syn=1.5:1(60%:40%);

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.07−8.01 (m, 2H), 7.94−7.87 (m, 2H), 7.80−7.77 (m, 2H), 7.65 (q, *J* = 7.2 Hz, 1H), 7.57−7.54 (m, 2H), 7.15−7.10 (m, 1H),

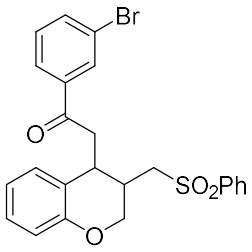
7.02 (d, J = 7.2 Hz, 0.4 × 1H, syn), 6.92 (d, J = 7.8 Hz, 0.6 × 1H, anti), 6.87−6.80 (m, 2H), 4.42−4.36 (m, 1H), 4.17−4.14 (m, 1H), 3.92 (q, J = 5.4 Hz, 0.6 × 1H, anti), 3.49−3.47 (m, 0.4 × 1H, syn), 3.44−3.31 (m, 2H), 3.30−3.28 (m, 0.4 × 1H, syn), 3.21−3.17 (m, 0.6 × 1H, anti), 3.08−3.05 (m, 1H), 2.88−2.85 (m, 0.6 × 1H, anti), 2.65−2.64 (m, 0.4 × 1H, syn); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 196.8, 139.6, 134.1, 133.9, 132.6, 132.6, 130.1, 129.5, 129.4, 128.6, 128.6, 128.5, 128.5, 127.9, 127.9, 127.6, 122.9, 121.4, 121.0, 117.3, 117.0, 116.8, 116.7, 68.1, 64.1, 57.1, 53.9, 47.4, 40.7, 35.0, 33.6, 31.5, 30.6. HRMS (ESI) Calcd for $C_{25}H_{22}O_4S$ $[M+H]^+$ 432.1270, found 432.1274.



1-(4-iodophenyl)-2-(3-((phenylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3d)

According to the general procedure ,3d (117mg, 0.3 mmol) afforded 3d (139 mg, 0.261 mmol, 87 % yield) in white solid, anti/syn=1.5:1(60%:40%);

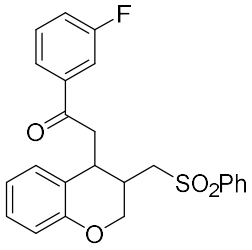
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92−7.81 (m, 4H), 7.66−7.61 (m, 3H), 7.56−7.52 (m, 2H), 7.13−7.08 (m, 1H), 7.02 (d, J = 7.2 Hz, 0.4 × 1H, syn), 6.91 (d, J = 7.8 Hz, 0.6 × 1H, anti), 6.86−6.78 (m, 2H), 4.42−4.36 (m, 1H), 4.22 (q, J = 5.4 Hz, 0.6 × 1H, anti), 4.15 (dd, J = 11.4, 1.2 Hz, 0.4 × 1H, syn), 3.88 (q, J = 6.0 Hz, 0.6 × 1H, anti), 3.44−3.41 (m, 0.4 × 1H, syn), 3.36−3.22 (m, 2H), 3.19−3.05 (m, 2H), 2.82−2.78 (m, 0.6 × 1H, anti), 2.60−2.59 (m, 0.4 × 1H, syn); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 197.3, 153.6, 139.2, 138.1, 135.9, 134.0, 133.8, 130.2, 129.6, 129.5, 129.4, 128.4, 128.3, 127.9, 127.9, 127.8, 123.3, 121.3, 120.9, 117.2, 116.9, 101.6, 67.7, 64.0, 57.1, 53.7, 47.0, 40.4, 35.2, 33.7, 31.6, 30.8. HRMS (ESI) Calcd for $C_{24}H_{22}O_4IS$ $[M+H]^+$ 533.0284, found 533.0286.



1-(3-bromophenyl)-2-(3-((phenylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3e)

According to the general procedure, 2e (103 mg, 0.3 mmol) afforded 3a (121 mg, 0.249 mmol, 83 % yield) in white solid, anti/syn=1.38:1(58%:42%);

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.93−7.83 (m, 3H), 7.73−7.62 (m, 2H), 7.57−7.53 (m, 2H), 7.38−7.34 (m, 1H), 7.03 (d, *J* = 7.8 Hz, 0.4 × 1H, syn), 6.92 (d, *J* = 7.8 Hz, 0.6 × 1H, anti), 6.87−6.80 (m, 2H), 4.43−4.37 (m, 1H), 4.25 (q, *J* = 5.4 Hz, 0.6 × 1H, anti), 4.16 (d, *J* = 11.4 Hz, 0.4 × 1H, syn), 3.89 (q, *J* = 6.0 Hz, 0.6 × 1H, anti), 3.44−3.42 (m, 0.4 × 1H, syn), 3.38−3.24 (m, 2H), 3.20−3.06 (m, 2H), 2.81−2.79 (m, 0.6 × 1H, anti), 2.58−2.57 (m, 0.4 × 1H, syn); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 196.5, 153.6, 139.1, 138.3, 136.4, 136.3, 134.0, 133.8, 131.2, 130.4, 130.1, 129.5, 129.4, 128.4, 128.4, 128.0, 128.0, 127.7, 126.7, 126.6, 123.2, 123.1, 121.4, 120.9, 117.2, 116.9, 67.7, 64.0, 57.1, 53.7, 47.2, 40.5, 35.1, 33.6, 31.6, 30.8. HRMS (ESI) Calcd for $C_{24}H_{22}O_4BrS$ $[M+H]^+$ 485.0422, found 485.0424.

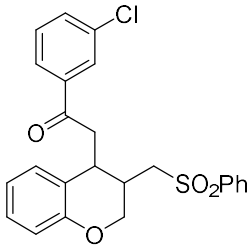


1-(3-fluorophenyl)-2-(3-((phenylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3f)

According to the general procedure, 2f (85 mg, 0.3 mmol) afforded 3f (106 mg, 0.249 mmol, 83 % yield) in white solid, anti/syn=1.5:1(60%:40%);

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 24, 7.8 Hz, 2H), 7.71 (dd, *J* = 20.4, 7.8 Hz, 1H), 7.66−7.60 (m, 2H), 7.55 (q, *J* = 8.4 Hz, 2H), 7.48−7.43 (m, 1H), 7.31−7.28 (m, 1H), 7.14−7.09 (m, 1H), 7.03 (d, *J* = 7.8 Hz, 0.4 × 1H, syn), 6.93 (d, *J* = 7.8 Hz, 0.6 × 1H, anti), 6.82−6.79 (m, 2H), 4.24 (q, *J* = 6 Hz, 0.6 × 1H, anti), 4.16

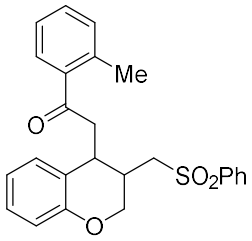
(d, J = 12 Hz, 0.4 × 1H, syn), 3.90 (q, J = 6.0 Hz, 0.6 × 1H, anti), 3.45−3.42 (m, 0.4 × 1H, syn), 3.39−3.25 (m, 2H), 3.20−3.06 (m, 2H), 2.83−2.79 (m, 0.6 × 1H, anti), 2.60−2.58 (m, 0.4 × 1H, syn); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 196.6, 163.7, 162.1, 153.7, 153.6, 139.7, 139.1, 138.7, 134.0, 133.8, 130.5, 130.4, 130.1, 129.5, 129.4, 128.4, 128.4, 128.0, 128.0, 127.7, 123.9, 123.9, 123.9, 123.3, 122.5, 121.3, 120.9, 120.6, 120.5, 120.5, 117.2, 116.9, 115.0, 114.9, 114.9, 114.8, 67.7, 64.0, 57.1, 53.7, 47.2, 40.7, 35.2, 33.6, 31.6, 30.8. HRMS (ESI) Calcd for $C_{24}H_{22}O_4FS$ $[M+H]^+$ 425.1223, found 425.1220.



1-(3-chlorophenyl)-2-(3-((phenylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3g)

According to the general procedure, 2g (89 mg, 0.3 mmol) afforded 3g (112 mg, 0.255 mmol, 85 % yield) in white solid, anti/syn=1:3(25%:75%);

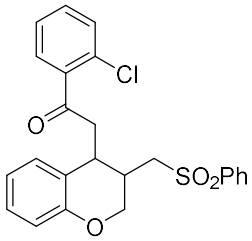
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93−7.87 (m, 3H), 7.81 (dd, J = 18, 7.8 Hz, 1H), 7.67−7.61 (m, 1H), 7.57−7.53 (m, 3H), 7.44−7.40 (m, 1H), 7.14−7.09 (m, 1H), 7.03 (d, J = 7.2 Hz, 0.75 × 1H, syn), 6.92 (d, J = 7.8 Hz, 0.25 × 1H, anti), 6.87−6.80 (m, 2H), 4.42−4.37 (m, 1H), 4.25 (q, J = 5.4 Hz, 0.25 × 1H, anti), 4.16 (d, J = 11.4 Hz, 0.75 × 1H, syn), 3.89 (dd, J = 12, 6.6 Hz, 0.25 × 1H, anti), 3.44−3.42 (m, 0.75 × 1H, syn), 3.38−3.28 (m, 2H), 3.27−3.24 (m, 0.25 × 2H, anti), 3.20−3.06 (m, 0.75 × 2H, syn), 2.82−2.79 (m, 0.25 × 1H, anti), 2.60−2.57 (m, 0.75 × 1H, syn); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 195.9, 153.7, 139.7, 138.1, 135.1, 134.0, 133.8, 133.4, 133.4, 130.1, 130.1, 129.5, 129.4, 128.4, 128.4, 128.2, 128.0, 128.0, 127.7, 126.3, 126.2, 122.4, 121.3, 120.9, 117.2, 116.9, 67.7, 64.0, 57.1, 53.7, 47.2, 40.6, 35.1, 33.6, 31.6, 30.8. HRMS (ESI) Calcd for $C_{24}H_{22}O_4ClS$ $[M+H]^+$ 441.0927, found 441.0927.



2-(3-((phenylsulfonyl)methyl)chroman-4-yl)-1-(o-tolyl)ethan-1-one (3h)

According to the general procedure, 2h (83 mg, 0.3 mmol) afforded 3a (110 mg, 0.261 mmol, 87 % yield) in white solid, anti/syn=1:1(50%:50%);

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93−7.88 (m, 2H), 7.65−7.52 (m, 4H), 7.41−7.36 (m, 1H), 7.27−7.26 (m, 0.5 × 1H, anti), 7.25−7.25 (m, 1H), 7.25−7.22 (m, 0.5 × 1H, syn), 7.12−7.08 (m, 1H), 7.04 (d, *J* = 7.8 Hz, 0.5 × 1H, syn), 6.95 (d, *J* = 7.8 Hz, 0.5 × 1H, anti), 6.86−6.79 (m, 2H), 4.45−4.37 (m, 1H), 4.24 (q, *J* = 6 Hz, 0.5 × 1H, anti), 4.14 (dd, *J* = 11.4, 1.8 Hz, 0.5 × 1H, syn), 3.87 (q, *J* = 6 Hz, 0.5 × 1H, anti), 3.41−3.39 (m, 0.5 × 1H, syn), 3.37−3.34 (m, 0.5 × 1H, anti), 3.33−3.27 (m, 1H), 3.22−3.13 (m, 1H), 3.10−3.07 (m, 1H), 3.06−3.05 (m, 0.5 × 1H, syn), 2.84−2.80 (m, 0.5 × 1H, anti), 2.56−2.50 (m, 0.5 × 1H, syn), 2.5 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 201.4, 138.7, 137.3, 133.9, 133.8, 132.3, 132.2, 131.8, 131.8, 130.2, 129.5, 129.4, 128.6, 128.6, 128.3, 128.2, 128.0, 127.9, 127.8, 125.9, 125.8, 123.6, 121.3, 120.9, 117.2, 116.8, 67.5, 63.9, 57.0, 53.8, 49.9, 43.4, 35.5, 34.0, 31.7, 30.8, 21.6, 21.5. HRMS (ESI) Calcd for $C_{25}H_{25}O_4S$ $[M+H]^+$ 421.1474, found 421.1478.

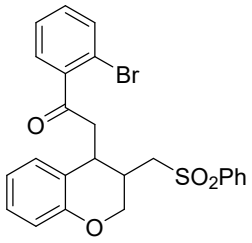


1-(2-chlorophenyl)-2-(3-((phenylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3i)

According to the general procedure, 2i (89 mg, 0.3 mmol) afforded 3i (117 mg, 0.267 mmol, 89 % yield) in white solid, anti/syn=0.8:1(45%:55%);

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.95−7.90 (m, 2H), 7.66−7.63 (m, 1H), 7.58−7.54 (m, 2H), 7.50 (d, *J* = 7.8 Hz, 0.45 × 1H, anti), 7.43 (s, 0.55 × 1H, syn), 7.42−7.38 (m, 2H), 7.35−7.31 (m, 1H), 7.12−7.09 (m, 1H), 7.05 (d, *J* = 7.8 Hz, 0.55 × 1H, syn), 7.01 (d, *J* = 7.8 Hz, 0.45 × 1H, anti), 6.87−6.79 (m, 2H), 4.43−4.38 (m, 1H),

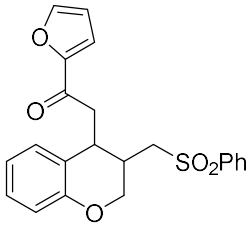
4.23 (dd, J = 11.4, 6 Hz, 0.45 × 1H, anti), 4.16−4.13 (m, 0.55 × 1H, syn), 3.85 (q, J = 6 Hz, 0.45 × 1H, anti), 3.44−3.39 (m, 1H), 3.37−3.32 (m, 0.55 × 2H, syn), 3.28 (dd, J = 18, 9 Hz, 0.55 × 1H, syn), 3.18−3.13 (m, 0.45 × 2H, anti), 3.09−3.02 (m, 1H), 2.88−2.84 (m, 0.45 × 1H, anti), 2.62−2.59 (m, 0.55 × 1H, syn); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 200.8, 200.6, 139.6, 139.3, 134.0, 133.8, 132.2, 132.1, 130.7, 130.6, 130.2, 129.5, 129.4, 129.4, 129.1, 128.4, 128.3, 128.0, 127.9, 127.2, 122.3, 121.3, 120.9, 117.2, 116.9, 67.4, 63.9, 57.0, 53.8, 51.4, 45.1, 35.4, 33.9, 31.5, 30.7. HRMS (ESI) Calcd for $C_{24}H_{22}O_4ClS$ $[M+H]^+$ 441.0927, found 441.0928.



1-(2-bromophenyl)-2-(3-((phenylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3j)

According to the general procedure, 2j (103 mg, 0.3 mmol) afforded 3j (121 mg, 0.249 mmol, 83 % yield) in white solid, anti/syn=1:1(50%:50%);

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (dd, J = 21.0, 8.1 Hz, 2H), 7.67 – 7.54 (m, 4H), 7.44 – 7.29 (m, 3H), 7.13 – 7.02 (m, 2H), 6.87 – 6.78 (m, 2H), 4.45 – 4.37 (m, 1H), 4.22 – 4.13 (m, 1H), 3.84 (q, J = 5.7 Hz, 0.5 × 1H, anti), 3.42 – 3.29 (m, 2H), 3.25 (dd, J = 17.9, 8.9 Hz, 0.5 × 1H, syn), 3.19 – 3.03 (m, 2H), 2.91–2.85 (m, 0.5 × 1H, anti), 2.64–2.62 (m, 0.5 × 1H, syn), ^{13}C NMR (151 MHz, Chloroform-*d*) δ 201.6, 201.4, 139.6, 139.3, 134.0, 133.9, 133.8, 133.7, 132.0, 131.9, 130.2, 129.5, 129.4, 128.9, 128.5, 128.4, 128.3, 128.0, 127.7, 123.3, 122.3, 121.3, 120.9, 118.7, 117.2, 116.9, 67.3, 63.9, 57.0, 54.0, 51.1, 44.8, 35.3, 33.8, 31.5, 30.8. HRMS (ESI) Calcd for $C_{24}H_{22}O_4BrS$ $[M+H]^+$ 485.0422, found 485.0426.

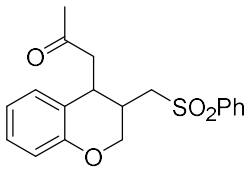


1-(furan-2-yl)-2-(3-((phenylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3k)

According to the general procedure, 2k (76 mg, 0.3 mmol) afforded 3k (102 mg,

0.258 mmol, 86 % yield) in yellow solid, anti/syn=1:1(50%:50%);

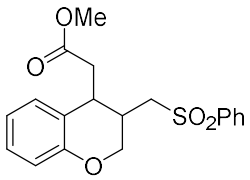
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94–7.89 (m, 2H), 7.65–7.53 (m, 4H), 7.21 (dt, *J* = 6.0, 2.9 Hz, 1H), 7.10 (q, *J* = 8.6 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 0.5 × 1H, anti), 6.95 (d, *J* = 7.8 Hz, 0.5 × 1H, syn), 6.86 – 6.78 (m, 2H), 6.55 (m, 1H), 4.38 (t, *J* = 9.9 Hz, 1H), 4.27–4.24 (m, 0.5 × 1H, anti), 4.20 (d, *J* = 11.4 Hz, 0.5 × 1H, syn), 3.83 (q, *J* = 6.3 Hz, 0.5 × 1H, anti), 3.42–3.39 (m, 0.5 × 1H, syn), 3.31 (dd, *J* = 14.7, 7.8 Hz, 0.5 × 1H, anti), 3.26–3.23 (m, 0.5 × 1H, syn), 3.22–3.09 (m, 2H), 3.05–3.00 (m, 1H), 2.7 –2.76 (m, 0.5 × 1H, anti), 2.58–2.56 (m, 0.5 × 1H, syn). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.9, 186.6, 152.6, 146.7, 134.0, 133.8, 130.3, 129.5, 129.4, 128.3, 128.3, 128.0, 128.0, 127.9, 123.4, 121.3, 120.8, 117.7, 117.6, 117.1, 116.8, 112.6, 112.6, 67.1, 64.0, 57.0, 53.7, 46.9, 40.5, 35.2, 33.5, 31.5, 30.9. HRMS (ESI) Calcd for $C_{22}H_{21}O_5S$ $[M+H]^+$ 397.1110, found 397.1114.



1-(3-((phenylsulfonyl)methyl)chroman-4-yl)propan-2-one (3l)

According to the general procedure, 2l (61 mg, 0.3 mmol) afforded 3a (80 mg, 0.234 mmol, 78 % yield) in colorless oil, anti/syn=1.5:1(60%:40%);

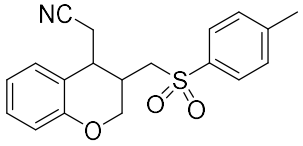
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93−7.91 (m, 2H), 7.66 (q, *J* = 6.8 Hz, 1H), 7.60−7.54 (m, 2H), 7.11−7.08 (m, 1H), 7.00 (d, *J* = 7.2 Hz, 0.4 × 1H, syn), 6.91 (d, *J* = 7.2 Hz, 0.6 × 1H, anti), 6.87−6.76 (m, 2H), 4.36−4.30 (m, 1H), 4.14−4.07 (m, 0.6 × 2H, anti), 3.31−3.26 (m, 0.4 × 2H, syn), 3.15−2.96 (m, 2H), 2.89−2.82 (m, 1H), 2.75−2.72 (m, 1H), 2.71−2.66 (m, 0.6 × 1H, anti), 2.51−2.50 (m, 0.4 × 1H, syn), 2.21 (s, 0.6 × 3H, anti), 2.17 (s, 0.4 × 3H, syn);^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.4, 153.6, 134.0, 133.8, 130.1, 129.5, 129.4, 128.3, 128.2, 128.0, 127.9, 127.5, 123.3, 121.3, 120.9, 117.1, 116.8, 67.9, 57.1, 53.8, 52.2, 45.1, 34.9, 33.4, 31.6, 30.3. HRMS (ESI) Calcd for $C_{20}H_{21}O_5S$ $[M+H]^+$ 373.1110, found 373.1112.



methyl 2-(3-((phenylsulfonyl)methyl)chroman-4-yl)acetate (3m)

According to the general procedure, 2m (65 mg, 0.3 mmol) afforded 3m (73 mg, 0.204 mmol, 68 % yield) in colorless oil, anti/syn=0.54:1(35%:65%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93−7.91 (m, 2H), 7.68−7.63 (m, 1H), 7.59−7.54 (m, 2H), 7.13−7.09 (m, 1H), 7.04 (d, *J* = 6.8 Hz, 0.35 × 1H, anti), 6.99 (d, *J* = 7.6 Hz, 0.65 × 1H, syn), 6.88−6.79 (m, 2H), 4.33−4.30 (m, 0.65 × 1H, syn), 4.29−4.25 (m, 1H), 4.13−4.10 (m, 0.35 × 1H, anti), 3.71 (s, 3H), 3.61 (q, *J* = 6.8 Hz, 0.35 × 2H, anti), 3.32−3.11 (m, 0.65 × 2H, syn), 3.08−2.96 (m, 1H), 2.82−2.62 (m, 2H), 2.60−2.56 (m, 0.35 × 1H, anti), 2.47 (dd, *J* = 16, 7.6 Hz, 0.65 × 1H, syn); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.2, 153.4, 139.5, 134.0, 133.8, 130.2, 129.5, 129.4, 128.5, 128.4, 127.9, 127.9, 127.6, 122.8, 121.3, 120.9, 117.2, 116.9, 67.0, 63.9, 57.1, 53.0, 52.1, 51.9, 42.7, 36.4, 36.3, 35.0, 31.1, 30.5. HRMS (ESI) Calcd for $C_{19}H_{21}O_6S$ $[M+H]^+$ 361.1110, found 361.1112.

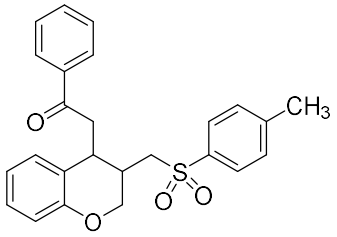


2-(3-(tosylmethyl)chroman-4-yl)acetonitrile (3n)

According to the general procedure, 2n (74 mg, 0.4 mmol) afforded 3n (85 mg, 0.248 mmol, 62 % yield) in colorless oil, anti/syn=1:1(50%:50%);

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.8 Hz, 2H), 7.39−7.37 (m, 2H), 7.20−7.14 (m, 2H), 6.93 (q, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 4.28−4.24 (m, 1H), 4.21−4.19 (m, 0.5 × 1H, anti), 4.14−4.11 (m, 0.5 × 1H, syn), 3.48 (q, *J* = 6 Hz, 0.5 × 1H, anti), 3.29−3.24 (m, 1H), 3.15 (d, *J* = 6 Hz, 1H), 3.03−2.99 (m, 0.5 × 1H, syn), 2.91−2.88 (m, 0.5 × 1H, anti), 2.82−2.78 (m, 0.5 × 1H, syn), 2.76−2.63 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 153.5, 136.1, 136.1, 130.4, 130.3, 130.2, 129.8, 129.3, 128.5, 128.1, 128.0, 121.7, 119.4, 117.5, 117.2, 65.9, 64.2, 57.1, 53.6, 34.5, 31.4, 31.2, 25.7, 20.3. HRMS (ESI) Calcd for $C_{19}H_{20}NO_3S$ $[M+H]^+$

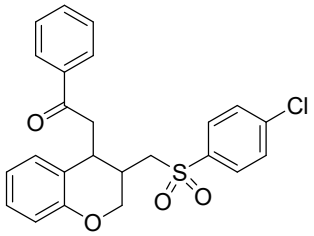
342.1164, found 342.1166.



1-phenyl-2-(3-(tosylmethyl)chroman-4-yl)ethan-1-one (3o)

According to the general procedure, 2o (79 mg, 0.3 mmol) afforded 3o (112 mg, 0.267 mmol, 89 % yield) in colorless oil, anti/syn=1.5:1(60%:40%);

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93−7.91 (m, 2H), 7.79−7.74 (m, 2H), 7.60−7.56 (m, 1H), 7.49−7.45 (m, 2H), 7.33−7.29 (m, 2H), 7.12−7.08 (m, 1H), 7.04 (d, *J* = 7.8 Hz, 0.4 × 1H, syn), 6.93 (d, *J* = 7.8 Hz, 0.6 × 1H, anti), 6.86−6.77 (m, 2H), 4.41−4.38 (m, 1H), 4.26−4.23 (m, 0.6 × 1H, anti), 4.16 (d, *J* = 11.4 Hz, 0.4 × 1H, syn), 3.88 (q, *J* = 6.0 Hz, 0.6 × 1H, anti), 3.44−3.42 (m, 0.4 × 1H, syn), 3.38−3.26 (m, 2H), 3.17−3.03 (m, 2H), 2.77−2.73 (m, 0.6 × 1H, anti), 2.58−2.55 (m, 0.4 × 1H, syn), 2.43 (s, 0.4 × 3H, syn), 2.40 (s, 0.6 × 3H, anti); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.8, 145.0, 136.6, 136.2, 133.5, 133.5, 130.2, 130.1, 130.0, 128.8, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 123.7, 121.3, 120.8, 117.2, 116.8, 67.5, 64.0, 57.2, 53.8, 47.1, 40.7, 35.2, 33.6, 31.7, 31.0, 21.7. HRMS (ESI) Calcd for $C_{25}H_{25}O_4S$ $[M+H]^+$ 421.1474, found 421.1476.

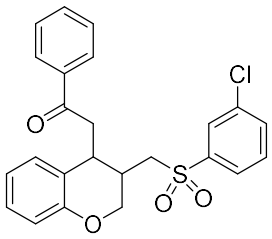


2-(3-(((4-chlorophenyl)sulfonyl)methyl)chroman-4-yl)-1-phenylethan-1-one (3p)

According to the general procedure, 2p (79 mg, 0.3 mmol) afforded 3p (111 mg, 0.252 mmol, 84 % yield) in colorless oil, anti/syn=1.5:1(60%:40%);

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93−7.92 (m, 2H), 7.88−7.86 (m, 0.4 × 2H, syn), 7.81−7.79 (m, 0.6 × 2H, anti), 7.62−7.57 (m, 1H), 7.53−7.46 (m, 4H), 7.15−7.10 (m, 1H), 7.06−7.04 (m, 0.4 × 1H, syn), 6. 97−6.95 (m, 0.6 × 1H, anti), 6.89−6.80 (m, 2H), 4.42−4.38 (m, 1H), 4.32−4.29 (m, 0.6 × 1H, anti), 4.17−4.14 (m, 0.4 × 1H, syn),

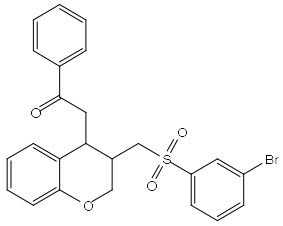
3.90 (dt, *J* = 5.6 Hz, 0.6 × 1H, anti), 3.43−3.41 (m, 0.4 × 1H, syn), 3.40−3.06 (m, 4H), 2.82−2.74 (m, 0.6 × 1H, anti), 2.55−2.53 (m, 0.4 × 1H, syn); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.8, 153.6, 138.1, 136.5, 133.6, 133.6, 130.2, 129.8, 129.7, 129.5, 129.5, 128.8, 128.8, 128.4, 128.3, 128.1, 128.1, 127.7, 123.4, 122.6, 121.4, 121.0, 117.2, 116.9, 67.4, 63.8, 57.2, 53.6, 47.1, 40.5, 35.2, 33.7, 31.7, 30.7. HRMS (ESI) Calcd for $C_{24}H_{22}O_4ClS$ $[M+H]^+$ 441.0927, found 441.0929.



2-(3-(((3-chlorophenyl)sulfonyl)methyl)chroman-4-yl)-1-phenylethan-1-one (3q)

According to the general procedure, 2q (79 mg, 0.3 mmol) afforded 3q (112 mg, 0.255 mmol, 85 % yield) in colorless oil, anti/syn=1.5:1(60%:40%);

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.95−7.86 (m, 3H), 7.82 (d, *J* = 7.8 Hz, 0.4 × 1H, syn), 7.76 (d, *J* = 7.8 Hz, 0.6 × 1H, anti), 7.62−7.55 (m, 2H), 7.51−7.44 (m, 3H), 7.14−7.10 (m, 1H), 7.04 (d, *J* = 7.8 Hz, 0.4 × 1H, syn), 6.93 (d, *J* = 7.8 Hz, 0.6 × 1H, anti), 6.88−6.80 (m, 2H), 4.43−4.39 (m, 1H), 4.33−4.31 (m, 0.6 × 1H, anti), 4.16 (d, *J* = 12 Hz, 0.4 × 1H, syn), 3.92 (q, *J* = 6.0 Hz, 0.6 × 1H, anti), 3.44−3.34 (m, 2H), 3.33−3.29 (m, 0.4 × 1H, syn), 3.20−3.07 (m, 2H), 2.84−2.81 (m, 0.6 × 1H, anti), 2.60−2.57 (m, 0.4 × 1H, syn); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.8, 153.6, 138.1, 136.5, 133.6, 133.6, 130.2, 129.8, 129.7, 129.5, 129.5, 128.8, 128.8, 128.4, 128.3, 128.1, 128.1, 127.7, 123.4, 122.6, 121.4, 121.0, 117.2, 116.9, 67.4, 63.8, 57.2, 53.6, 47.1, 40.5, 35.2, 33.7, 31.7, 30.7. HRMS (ESI) Calcd for $C_{24}H_{22}O_4ClS$ $[M+H]^+$ 441.0927, found 441.0931.

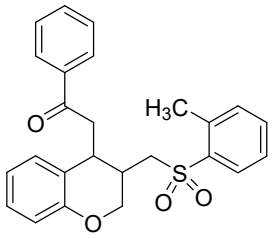


2-(3-(((3-bromophenyl)sulfonyl)methyl)chroman-4-yl)-1-phenylethan-1-one (3r)

According to the general procedure, 2r (79 mg, 0.3 mmol) afforded 3r (129 mg, 0.267

mmol, 89 % yield) in colorless oil, anti/syn=1:1(50%:50%);

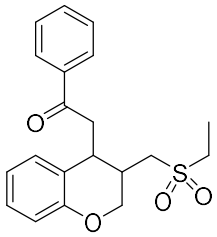
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.11–8.09 (m, 0.5 × 1H, anti), 8.03–8.01 (m, 0.5 × 1H, syn), 7.95−7.93 (m, 2H), 7.88−7.71 (m, 2H), 7.62−7.57(m, 1H), 7.51−7.37 (m, 3H), 7.15−7.10 (m, 1H), 7.06−7.04 (m, 0.5 × 1H, syn), 6.97−6.95 (m, 0.5 × 1H, anti), 6.89−6.81 (m, 2H), 4.44−4.40 (m, 1H), 4.35−4.31 (m, 0.5 × 1H, anti), 4.16 (d, *J* = 12 Hz, 0.5 × 1H, syn), 3.92 (q, *J* = 6.0 Hz, 0.5 × 1H, anti), 3.44−3.34 (m, 2H), 3.33−3.29 (m, 0.5 × 1H, syn), 3.20−3.07 (m, 2H), 2.86−2.81 (m, 0.5 × 1H, anti), 2.60−2.58 (m, 0.5 × 1H, syn); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.1, 141.5, 137.0, 136.9, 136.5, 133.6, 133.5, 131.0, 130.9, 130.9, 130.2, 128.8, 128.8, 128.4, 128.3, 128.2, 128.1, 127.7, 126.5, 121.4, 121.0, 117.2, 116.9, 67.6, 63.8, 57.1, 53.6, 47.1, 40.5, 35.2, 33.7, 31.6, 30.7. HRMS (ESI) Calcd for $C_{24}H_{22}O_4BrS$ $[M+H]^+$ 485.0422, found 485.0424.



1-phenyl-2-(3-((o-tolylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3s)

According to the general procedure, 2s (79 mg, 0.3 mmol) afforded 3s (108 mg, 0.258 mmol, 86 % yield) in colorless oil, anti/syn=1:1(50%:50%);

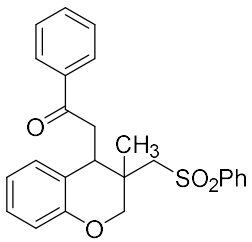
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01–7.90 (m, 3H), 7.62−7.56 (m, 1H), 7.52−7.44(m, 3H), 7.37−7.27 (m, 2H), 7.14−7.08 (m, 1H), 7.05−7.02 (m, 0.5 × 1H, syn), 6.94 (d, *J* = 7.6 Hz, 0.5 × 1H, anti), 6.87−6.78 (m, 2H), 4.43−4.37 (m, 1H), 4.26 (dd, *J* = 11.2, 5.6 Hz, 0.5 × 1H, anti), 4.15 (d, *J* = 11.6 Hz, 0.5 × 1H, syn), 3.94−3.90 (m, 0.5 × 1H, anti), 3.43−3.32 (m, 2H), 3.29−3.24 (m, 0.5 × 1H, syn), 3.22−3.09 (m, 2H), 2.82−2.77 (m, 0.5 × 1H, anti), 2.67 (s, 0.5 × 1H, anti), 2.64 (s, 0.5 × 1H, syn), 2.60−2.55 (m, 0.5 × 1H, syn); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.8, 153.7, 137.9, 137.3, 136.6, 133.9, 133.8, 133.5, 133.5, 132.9, 132.8, 130.2, 130.2, 130.0, 128.8, 128.7, 128.3, 128.2, 128.1, 127.9, 126.8, 126.6, 123.7, 121.3, 120.9, 117.1, 116.8, 67.6, 64.0, 56.1, 52.6, 47.2, 40.8, 35.4, 33.7, 31.8, 30.9, 20.3. HRMS (ESI) Calcd for $C_{25}H_{25}O_4S$ $[M+H]^+$ 421.1474, found 421.1477.



1-phenyl-2-(3-((o-tolylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3t)

According to the general procedure, 2t (79 mg, 0.3 mmol) afforded 3t (77 mg, 0.216 mmol, 72 % yield) in white solid, anti/syn=7:1(87.5%:12.5%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09−8.07 (m, 0.125 × 2H, syn), 8.03–7.97 (m, 0.875 × 2H, anti), 7.60 (dd, *J* = 8.3, 6.3 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.16–7.10 (m, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.84 (dt, *J* = 7.6, 3.1 Hz, 2H), 4.49–4.33 (m, 2H), 4.00 (q, *J* = 5.7 Hz, 1H), 3.47 (dd, *J* = 17.6, 6.2 Hz, 1H), 3.25 (dd, *J* = 17.6, 6.4 Hz, 1H), 3.08–2.91 (m, 5H), 1.38 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.1, 153.6, 136.5, 133.6, 128.9, 128.3, 128.2, 128.0, 123.6, 121.0, 116.9, 67.5, 49.2, 48.4, 41.1, 33.8, 30.3, 6.7. HRMS (ESI) Calcd for $C_{20}H_{23}O_4S$ $[M+H]^+$ 359.1317, found 359.1322.

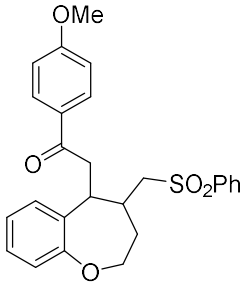


2-(3-methyl-3-((phenylsulfonyl)methyl)chroman-4-yl)-1-phenylethan-1-one (3u)

According to the general procedure, 2u (83 mg, 0.3 mmol) afforded 3u (101 mg, 0.240 mmol, 80 % yield) in white solid, anti/syn=1.5:1(60%:40%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02−8.00 (m, 0.6 × 1H, anti),7.93–7.84 (m, 3H), 7.65−7.63 (m, 0.4 × 1H, syn), 7.61−7.44(m, 6H), 7.10−7.05 (m, 1H), 6.87−6.85 (m, 0.6 × 1H, anti), 6.80−6.73 (m, 2H), 6.70 (d, *J* = 8 Hz, 0.4 × 1H, syn), 4.57 (d, *J* = 11.2 Hz, 0.4 × 1H, syn), 4.36−4.32 (m, 0.6 × 1H, anti), 4.05−3.96 (m, 1H), 3.76−3.71 (m, 1H), 3.41−3.33 (m, 0.6 × 1H, anti), 3.29−3.28 (m, 0.4 × 1H, syn), 3.26−3.15 (m, 2H), 3.08−3.03 (m, 1H), 1.45 (s, 0.4 × 3H, syn), 1.31 (s, 0.6 × 3H, anti), ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.8, 141.5, 133.7, 133.5, 133.4, 130.1, 129.3, 129.3, 128.9, 128.8, 128.4, 128.3, 128.1, 128.1, 128.0, 127.6, 127.6, 121.3, 121.2, 116.7,

116.5, 71.3, 68.8, 61.6, 58.0, 43.8, 42.0, 40.2, 38.9, 36.0, 35.7, 20.8, 18.5. HRMS (ESI) Calcd for $C_{25}H_{25}O_4S$ $[M+H]^+$ 421.1474, found 421.1475.



1-(4-methoxyphenyl)-2-(4-((phenylsulfonyl)methyl)-2,3,4,5-tetrahydrobenzo[b]oxepin-5-yl)ethan-1-one (3v)

According to the general procedure, 2v (154 mg, 0.5 mmol) afforded 3v (97 mg, 0.275 mmol, 57 % yield) in white solid, anti/syn=1.5:1(60%:40%);

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.9 (s, 2H), 7.9 – 7.8 (m, 1H), 7.8 (d, *J* = 6.7 Hz, 1H), 7.7 – 7.6 (m, 1H), 7.6 – 7.5 (m, 2H), 7.1 – 7.0 (m, 2H), 6.9 (dd, *J* = 17.9, 6.4 Hz, 2H), 6.8 (dd, *J* = 18.7, 6.9 Hz, 2H), 4.3 (dd, *J* = 36.3, 10.6 Hz, 1H), 3.8 (s, 3H), 3.7 (t, *J* = 17.5 Hz, 1H), 3.6 – 3.5 (m, 1H), 3.2 (d, *J* = 14.0 Hz, 1H), 3.1 – 2.9 (m, 1H), 2.8 (d, *J* = 16.8 Hz, 1H), 2.6 (s, 1H), 2.3 (d, *J* = 13.9 Hz, 1H), 2.2 (q, *J* = 12.5, 11.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.0, 159.5, 139.6, 133.8, 132.4, 130.4, 130.0, 129.4, 129.4, 128.8, 128.4, 128.0, 127.9, 124.2, 124.0, 122.2, 122.0, 113.7, 113.6, 71.8, 68.1, 58.5, 55.5, 45.5, 40.7, 37.3, 35.0, 34.2, 32.3, 30.7. HRMS (ESI) Calcd for $C_{25}H_{25}O_4S$ $[M+H]^+$ 421.1474, found 421.1477.

6. References

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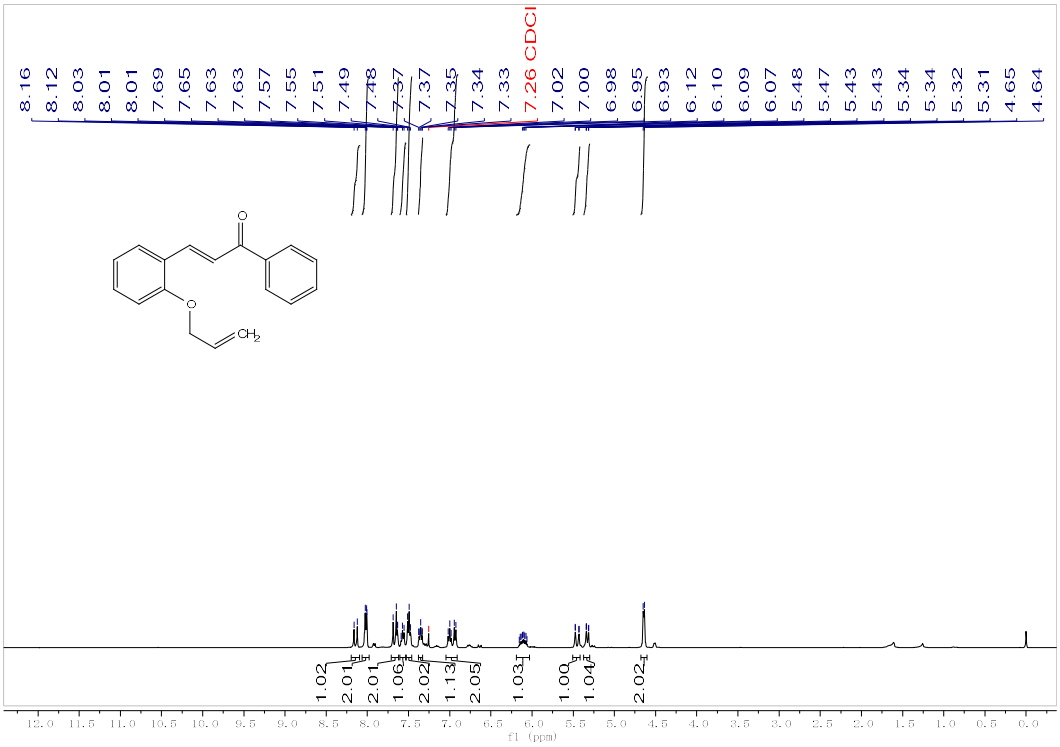
2 M. Chwastek, M. Pieczykolan, S. Stecko, *J. Org. Chem*. **2016**, *81*, 19, 9046-9074.

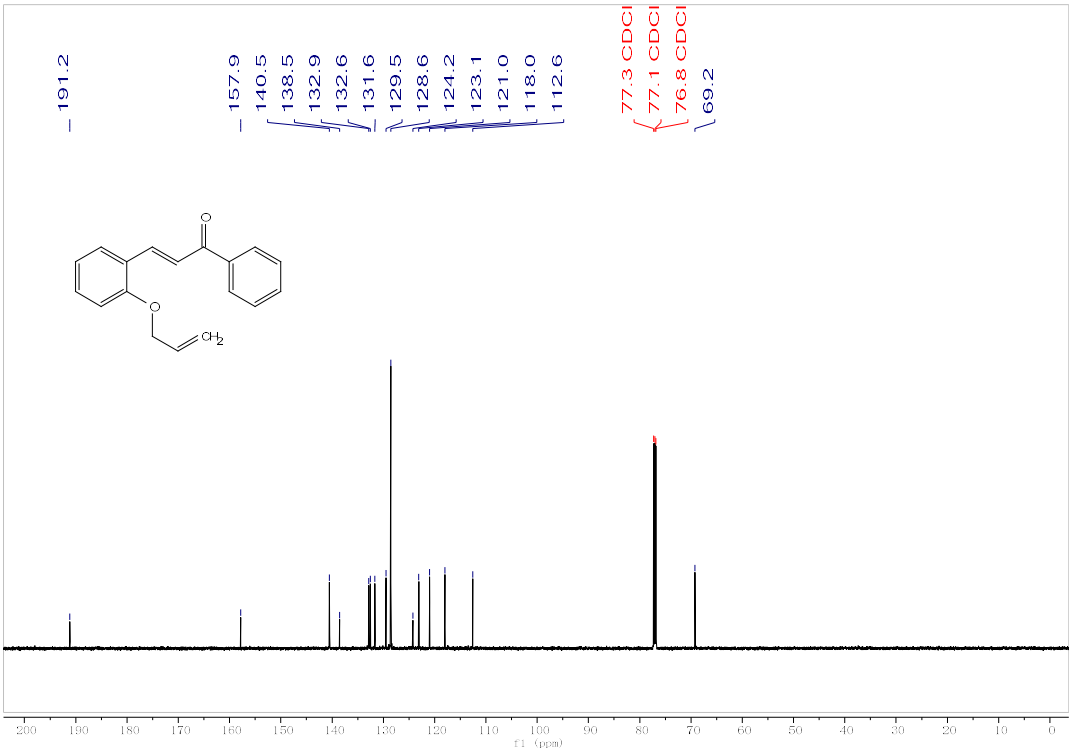
3 D. Konrádová, H. Kozubíková, K. Doležal, J. Pospíšil, *Eur. J. Org. Chem*. **2017**, 5204-5213.

4 A. S. Pankova, V. V. Voronin, M. A. Kuznetsov, *Tetrahedron Lett*. **2009**, *50*, 5990-5993.

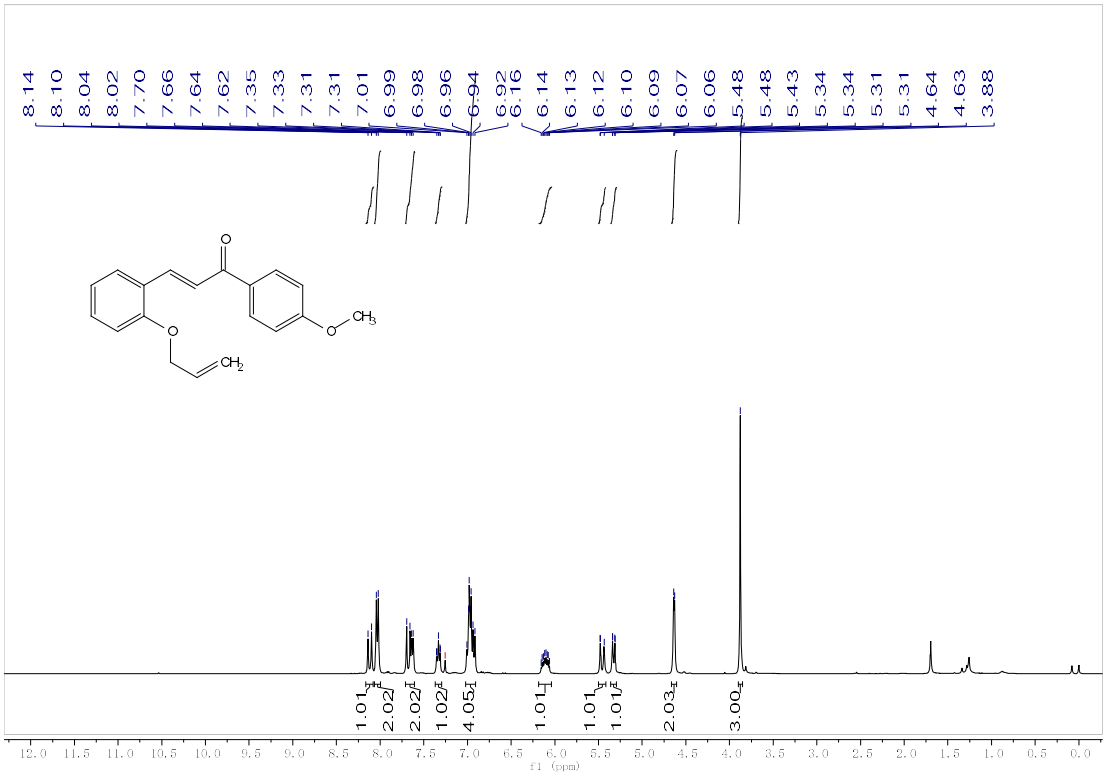
7. NMR Spectra

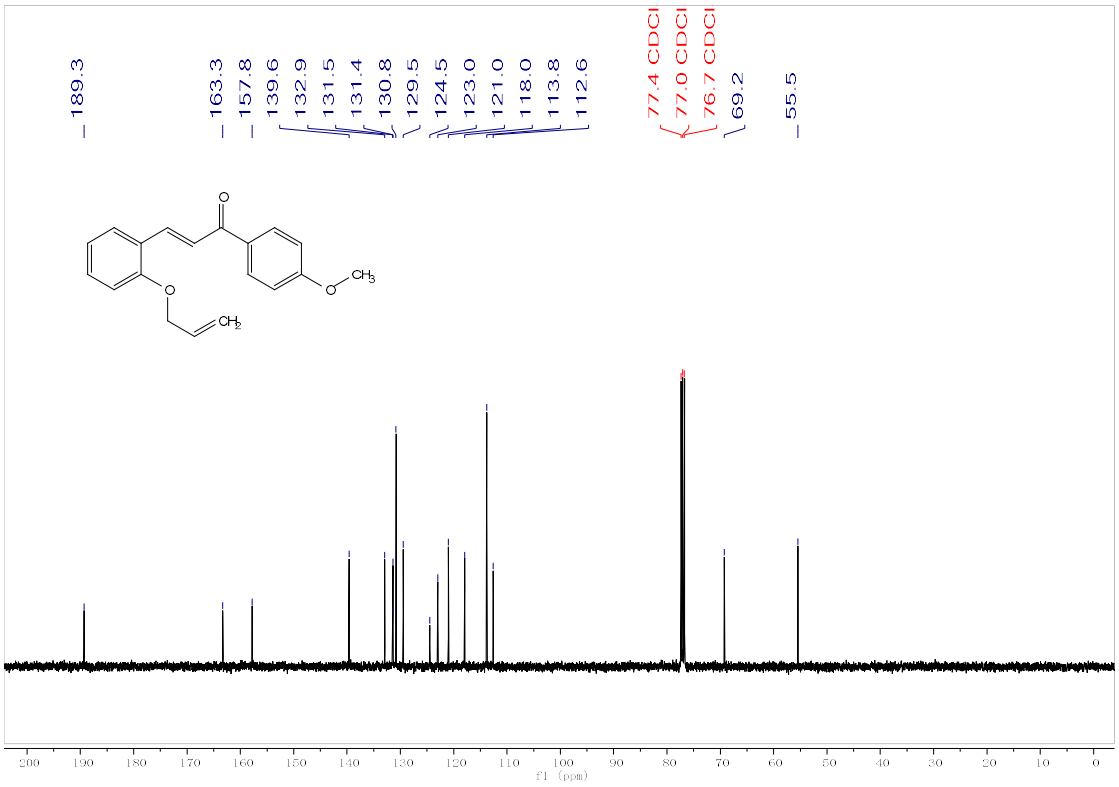
3-(2-Allyloxy-phenyl)-1-phenyl-propenone (1a)



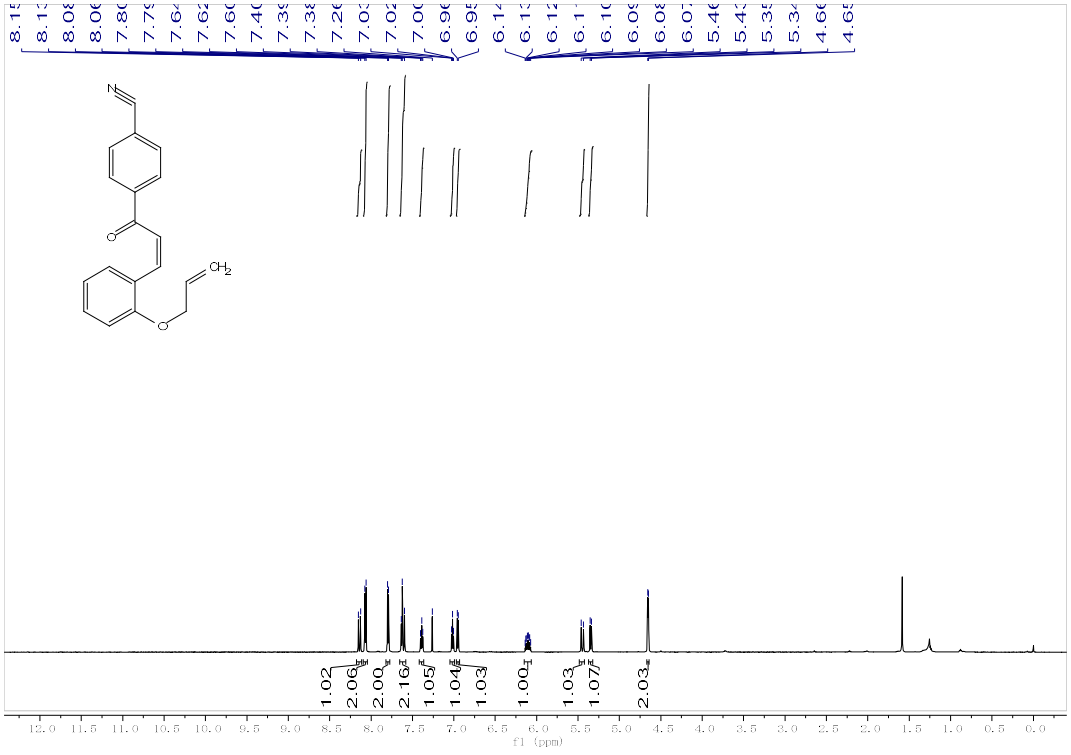


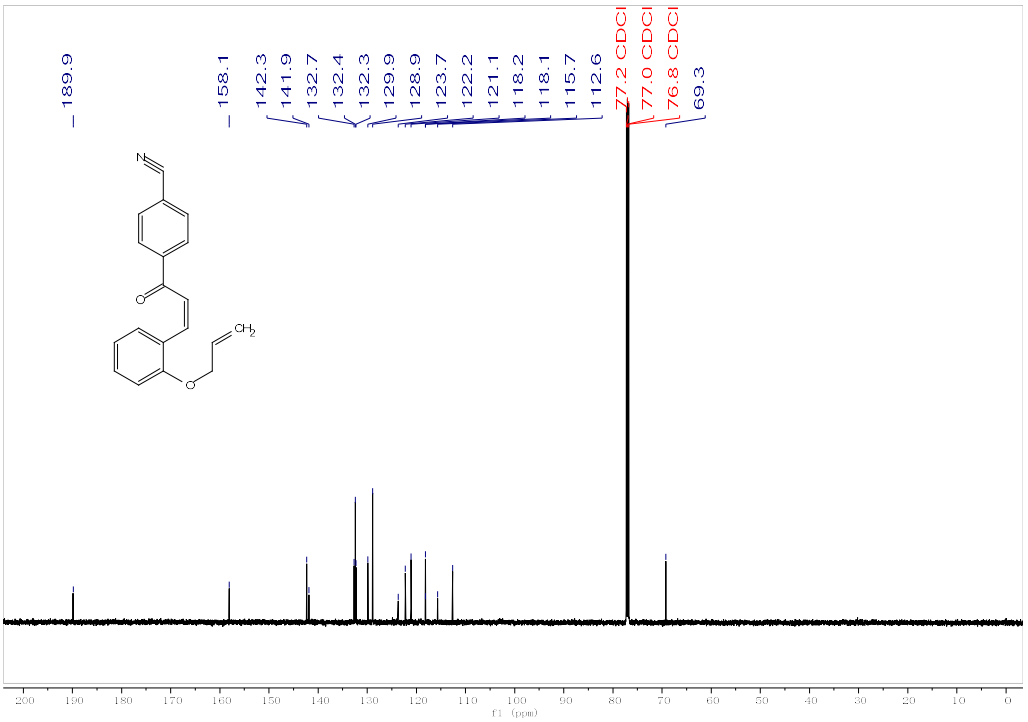
3-(2-Allyloxy-phenyl)-1-(4-methoxy-phenyl)-propenone (1b)



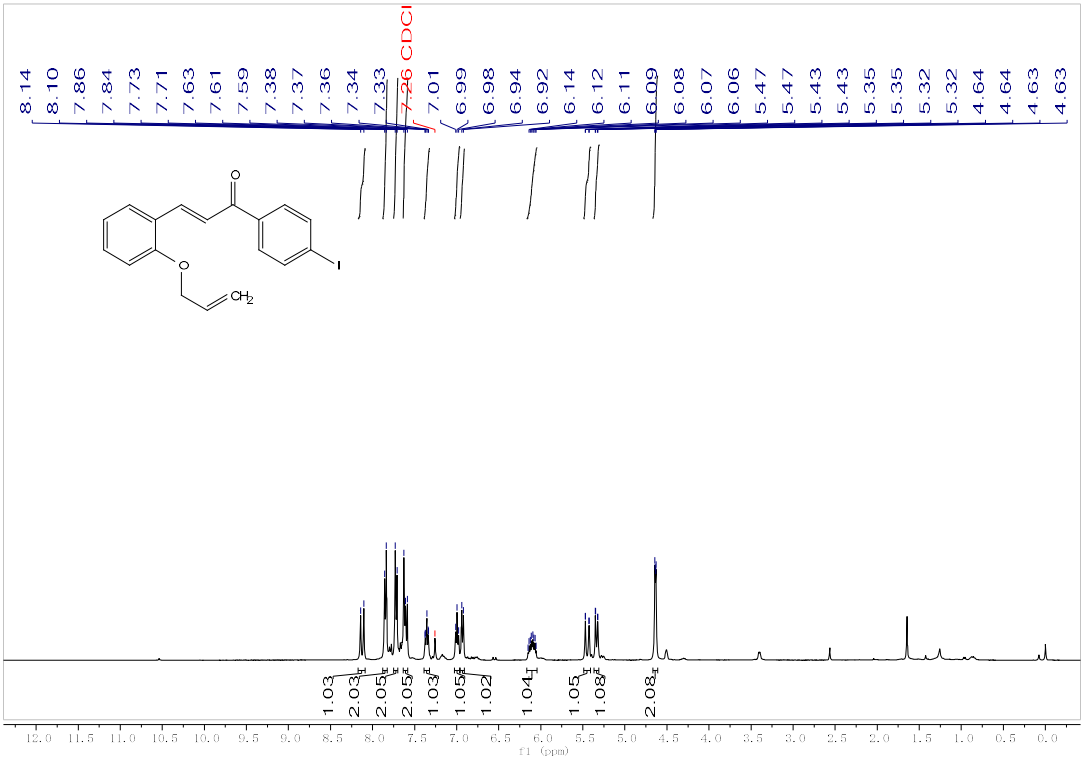


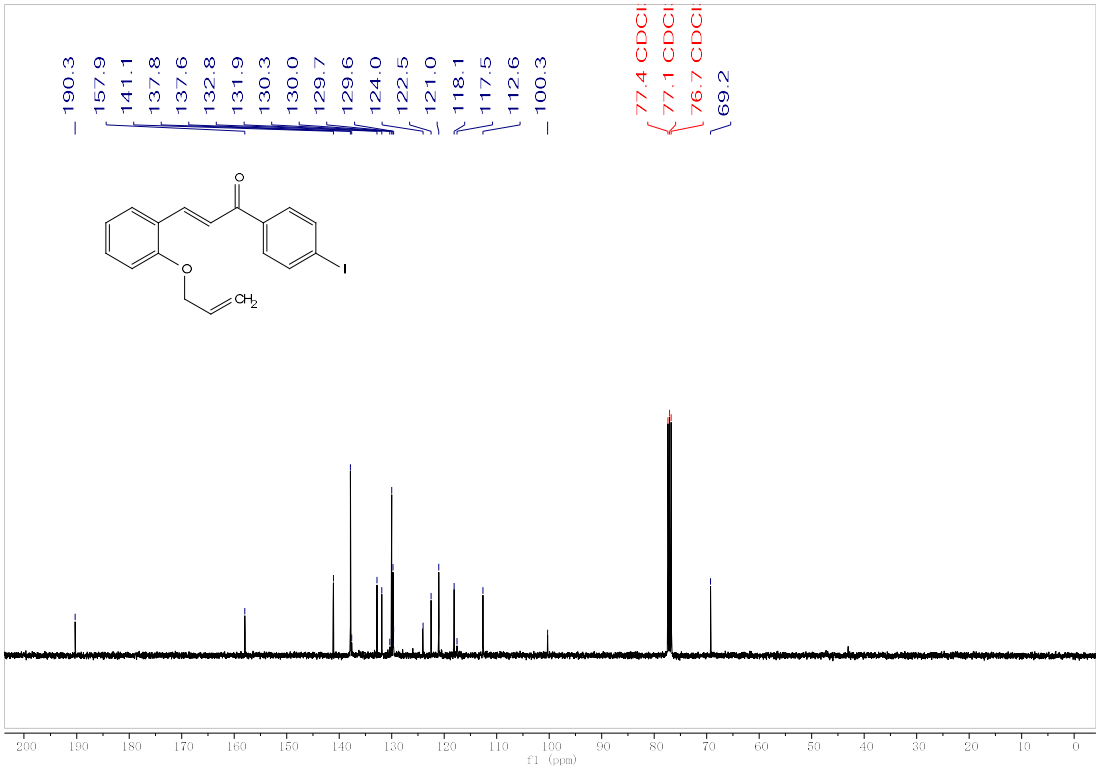
4-[3-(2-Allyloxy-phenyl)-acryloyl]-benzonitrile (c)



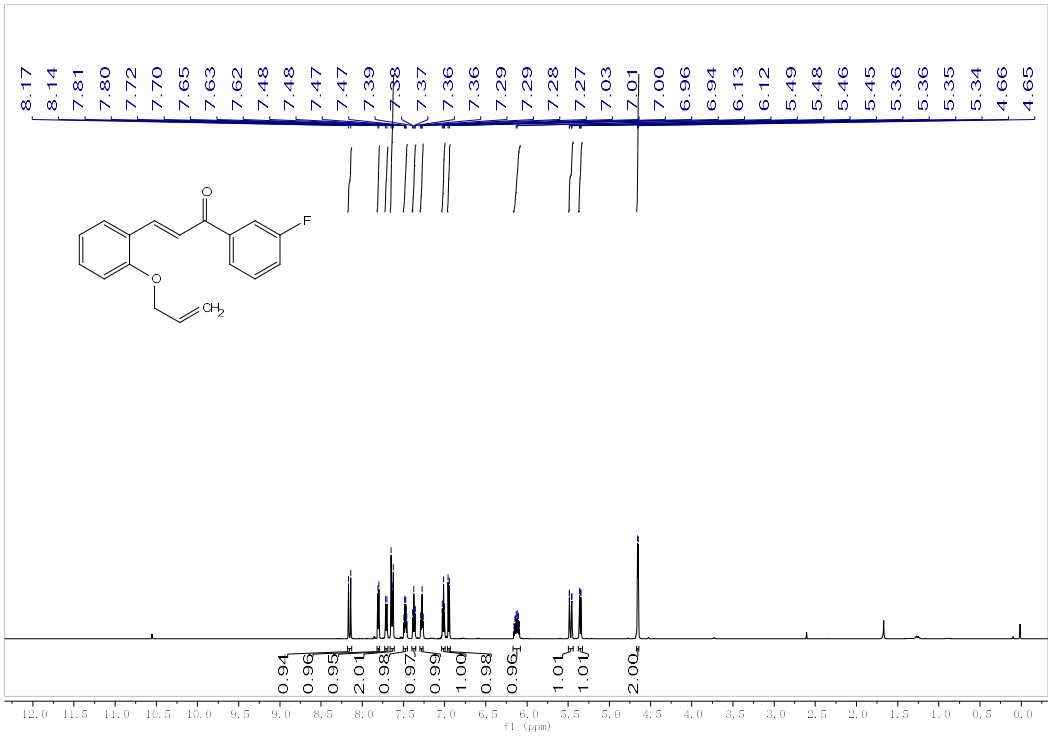


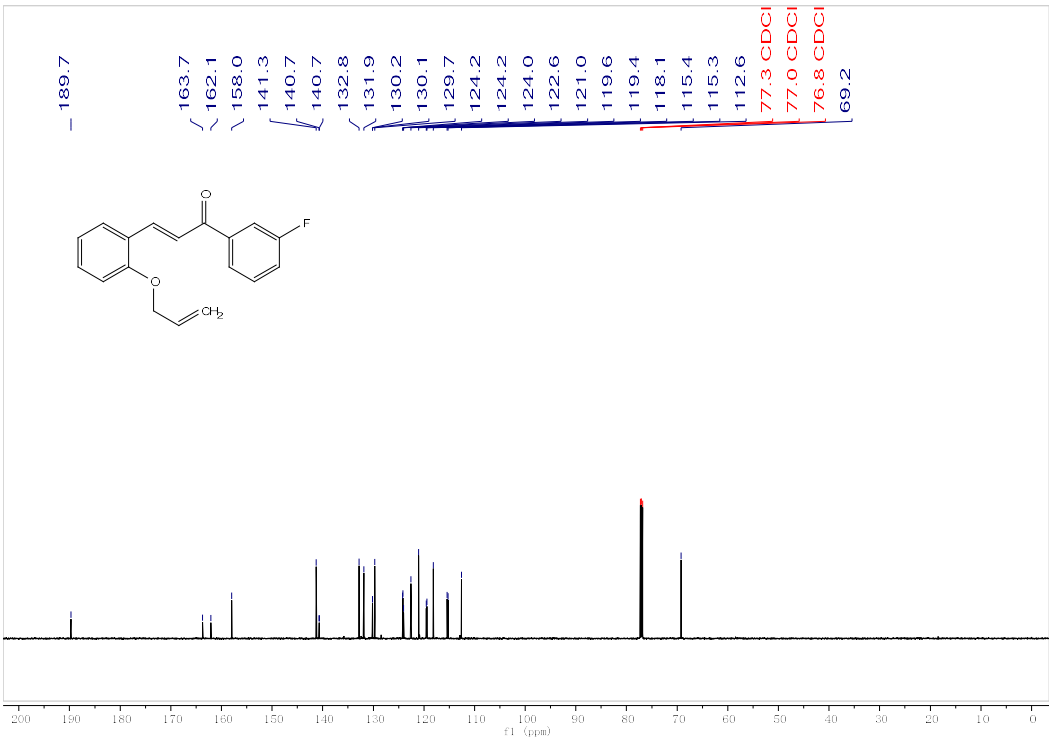
3-(2-Allyloxy-phenyl)-1-(4-iodo-phenyl)-propenone (1d)



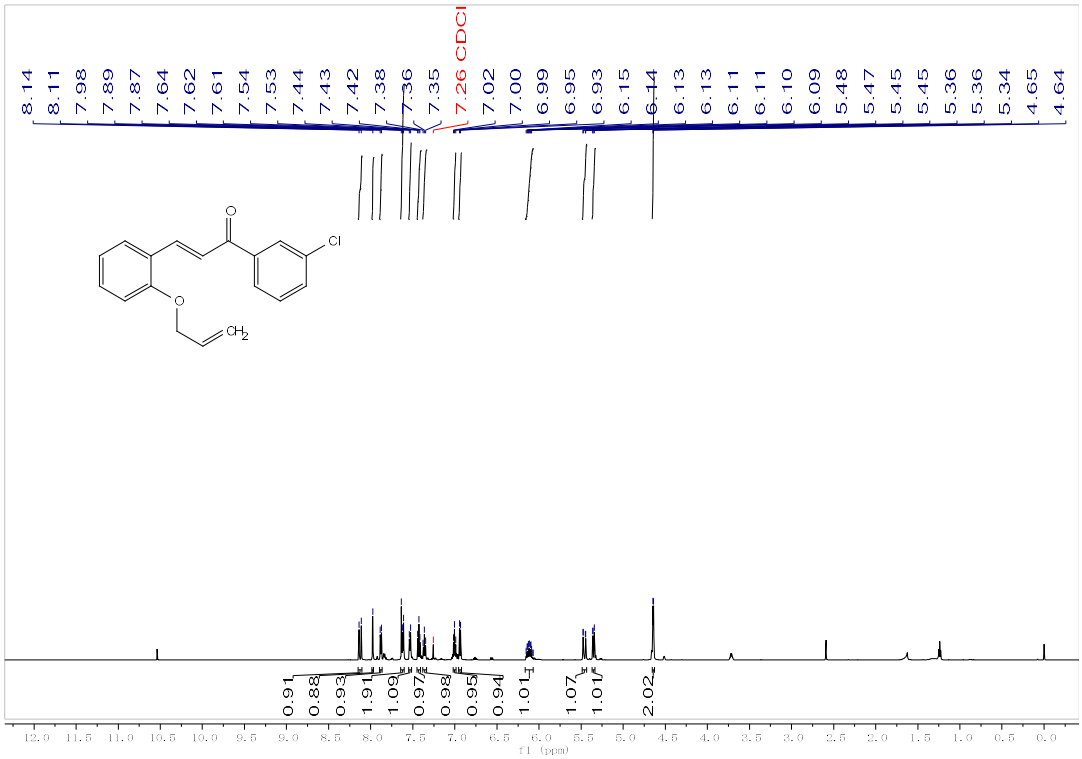


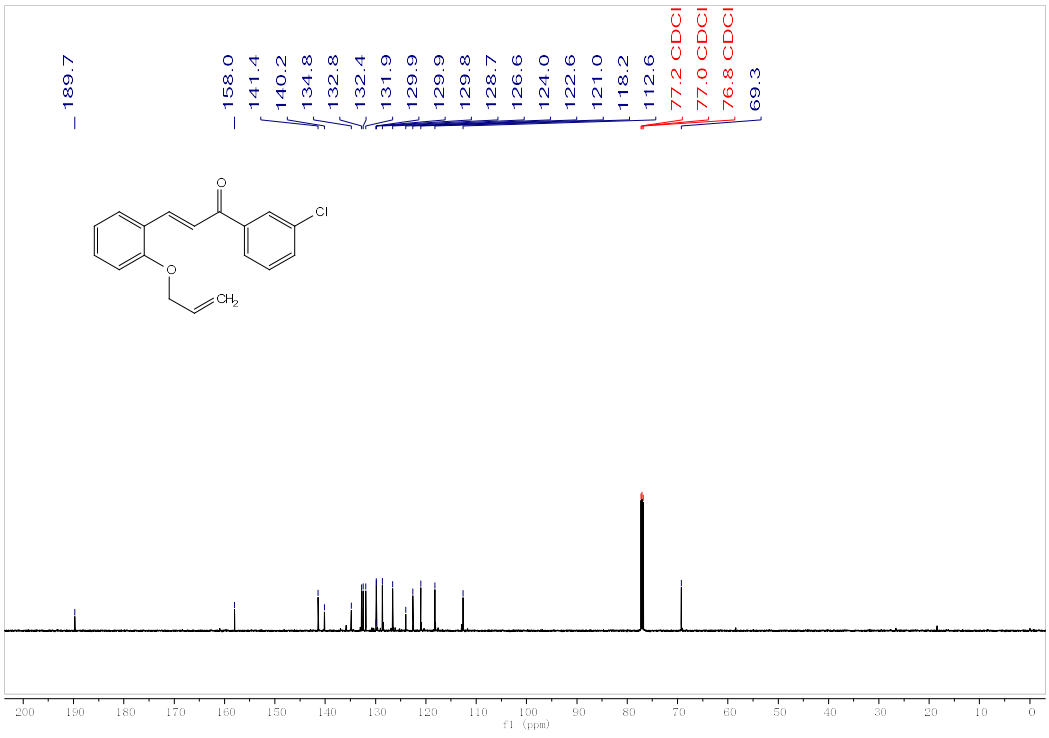
3-(2-Allyloxy-phenyl)-1-(3-fluoro-phenyl)-propenone (1e)



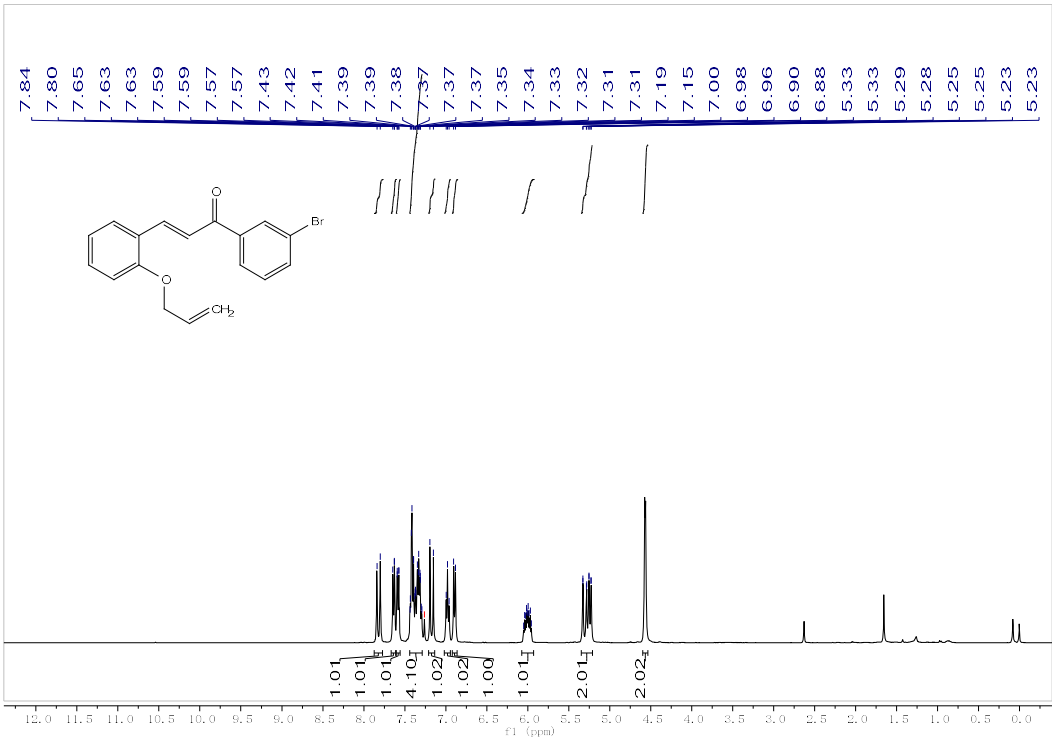


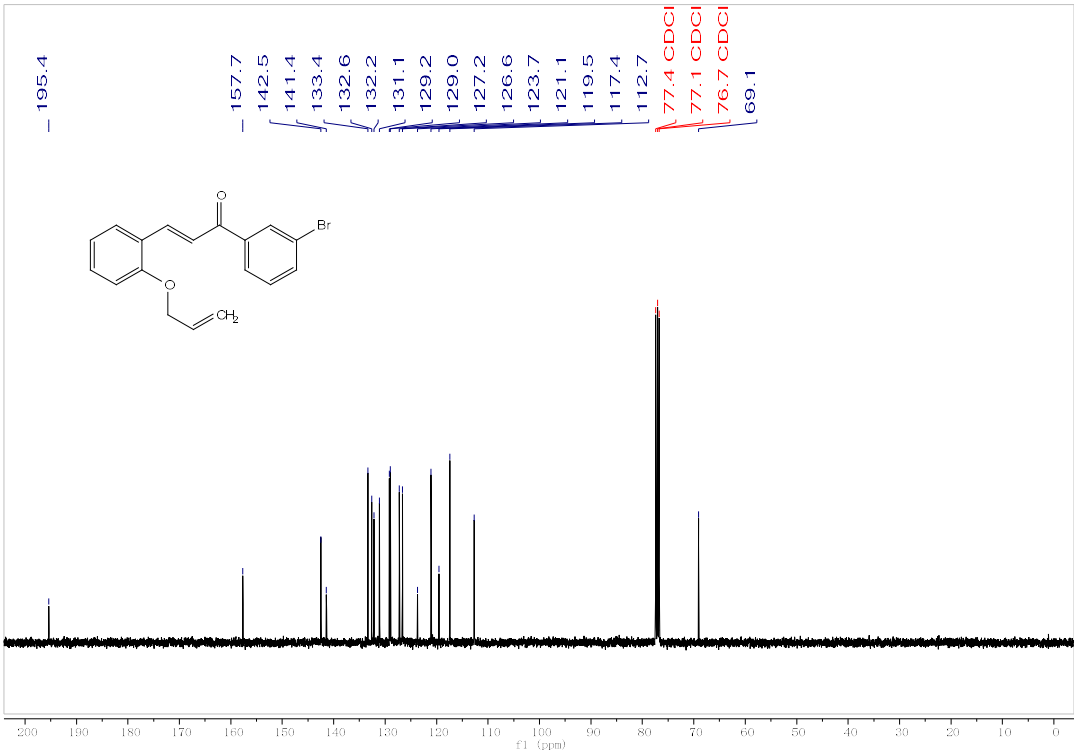
3-(2-Allyloxy-phenyl)-1-(3-chloro-phenyl)-propenone (1g)



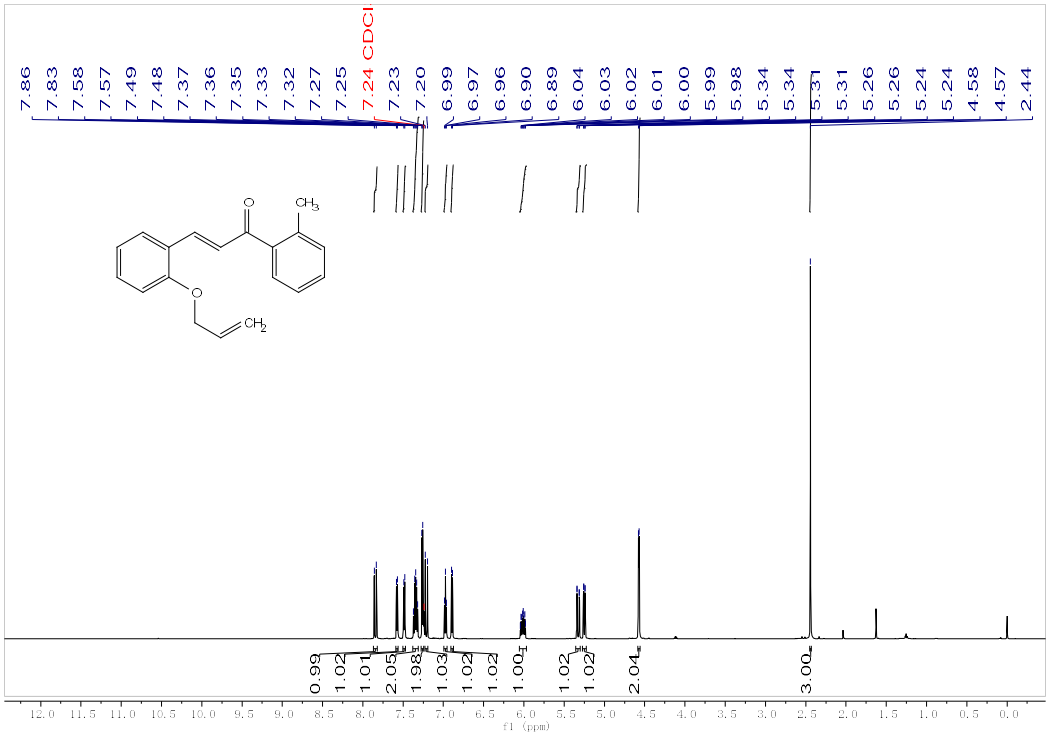


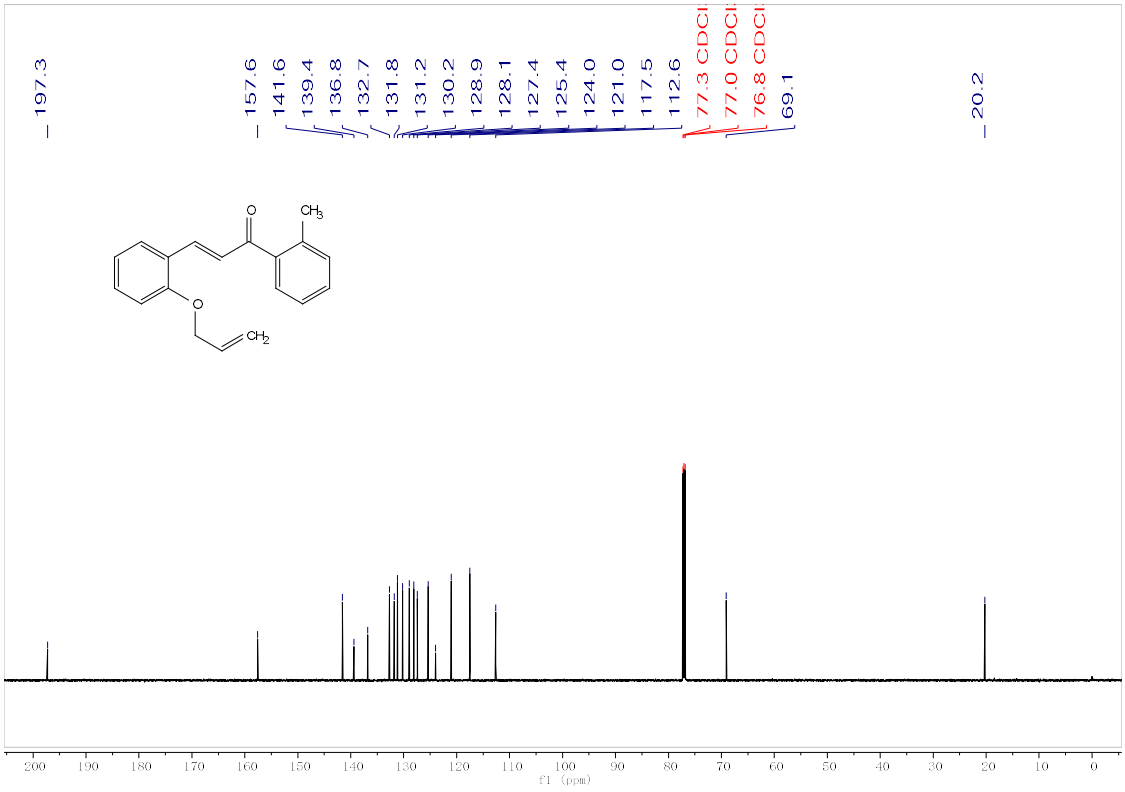
3-(2-Allyloxy-phenyl)-1-(3-bromo-phenyl)-propenone (1g)



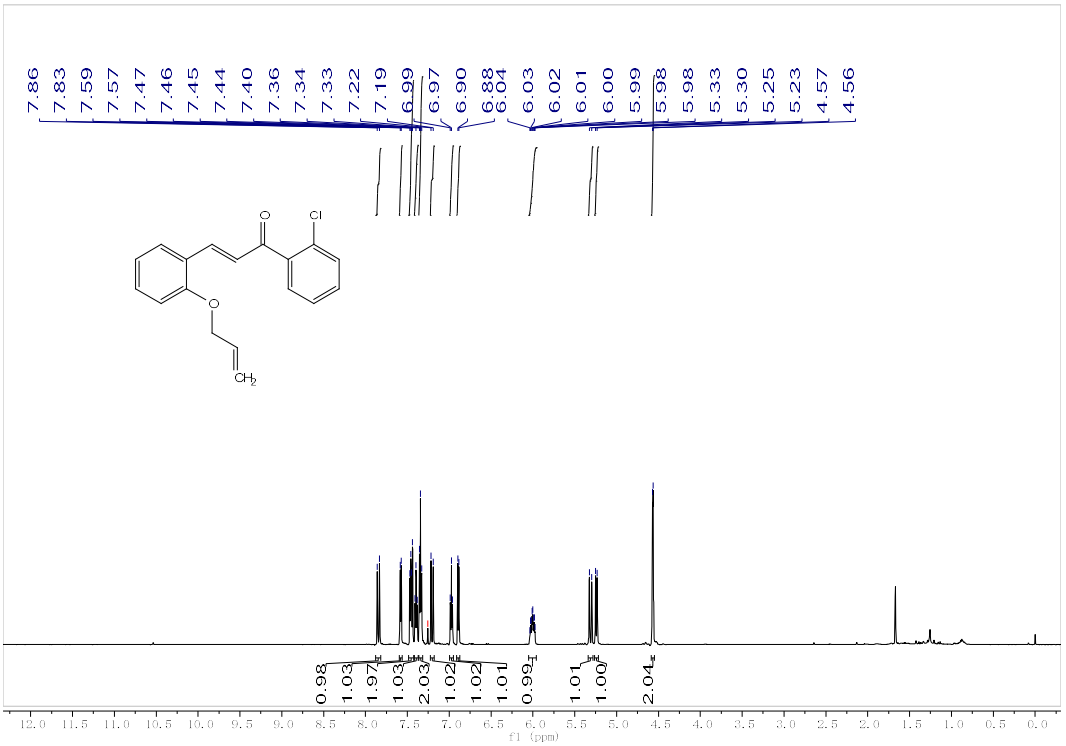


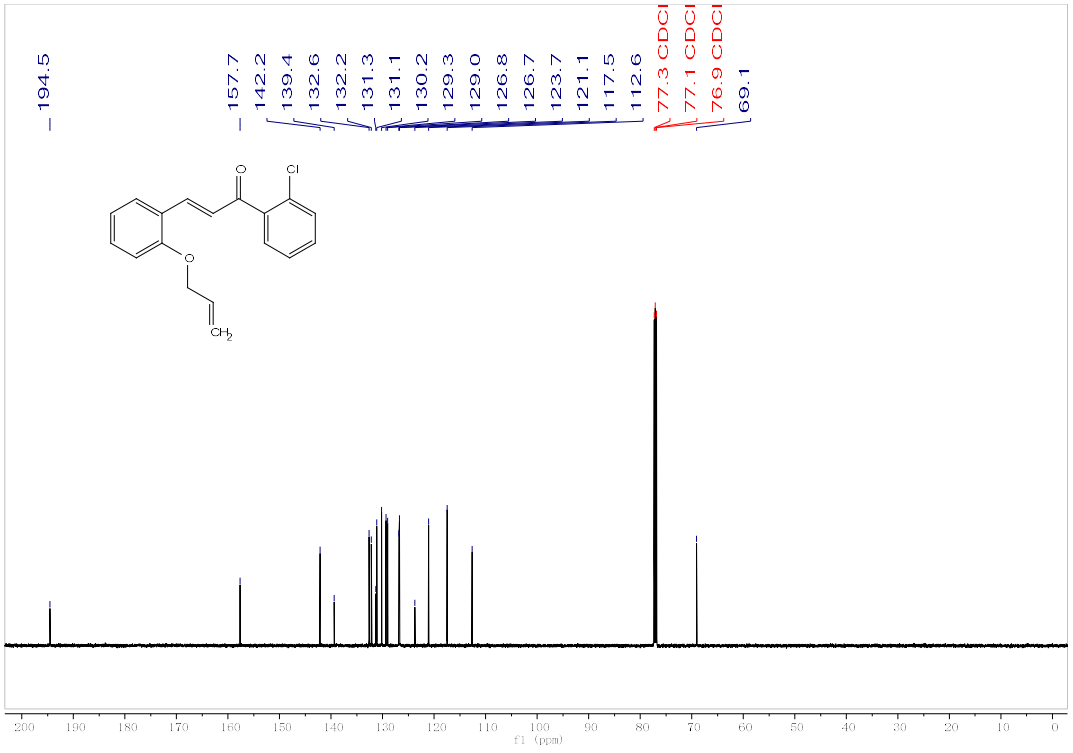
3-(2-Allyloxy-phenyl)-1-o-tolyl-propenone (1h)



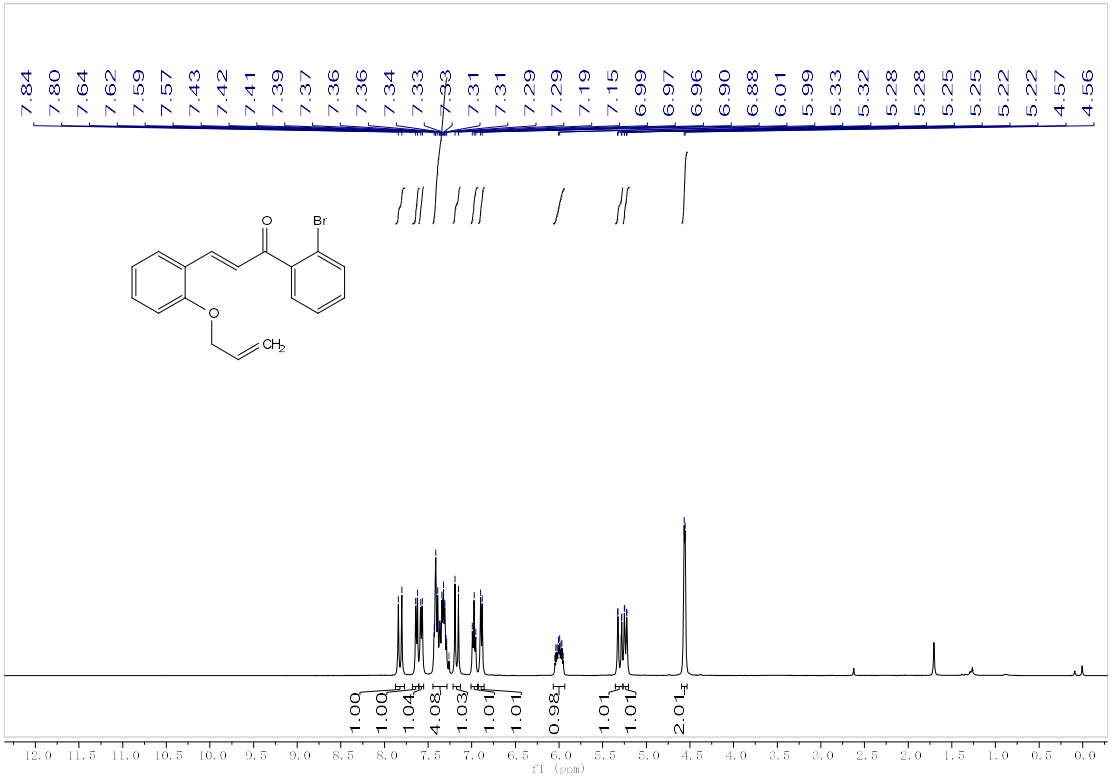


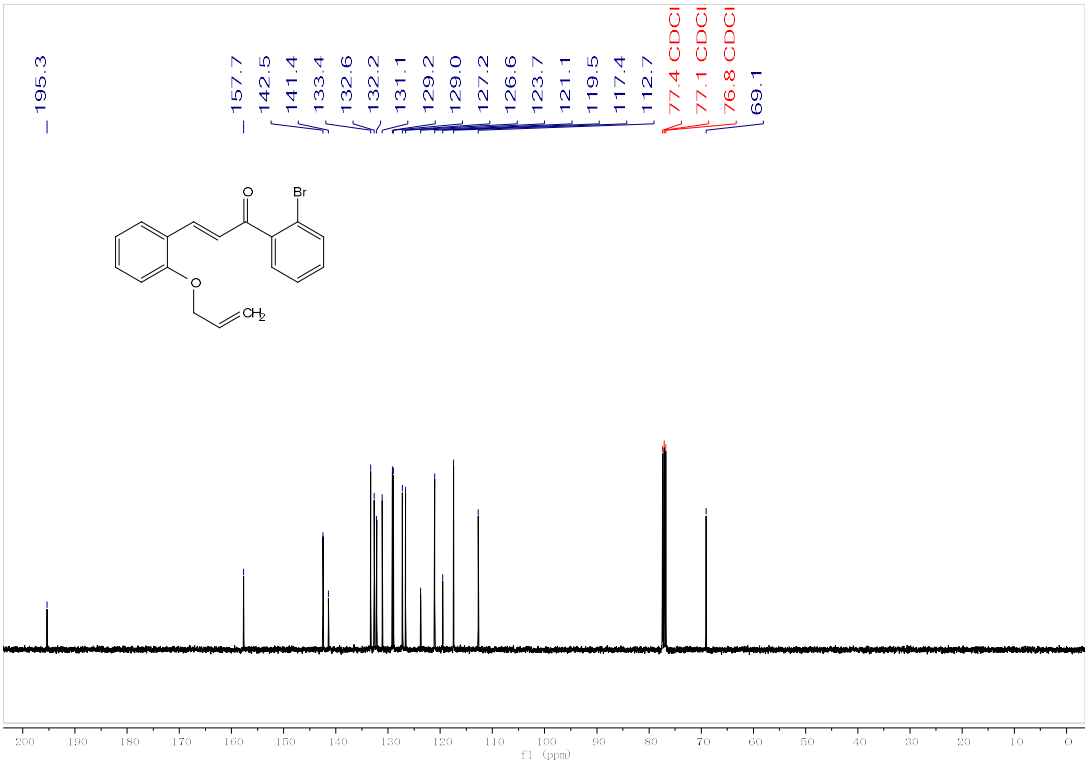
3-(2-Allyloxy-phenyl)-1-(2-chloro-phenyl)-propenone (1i)



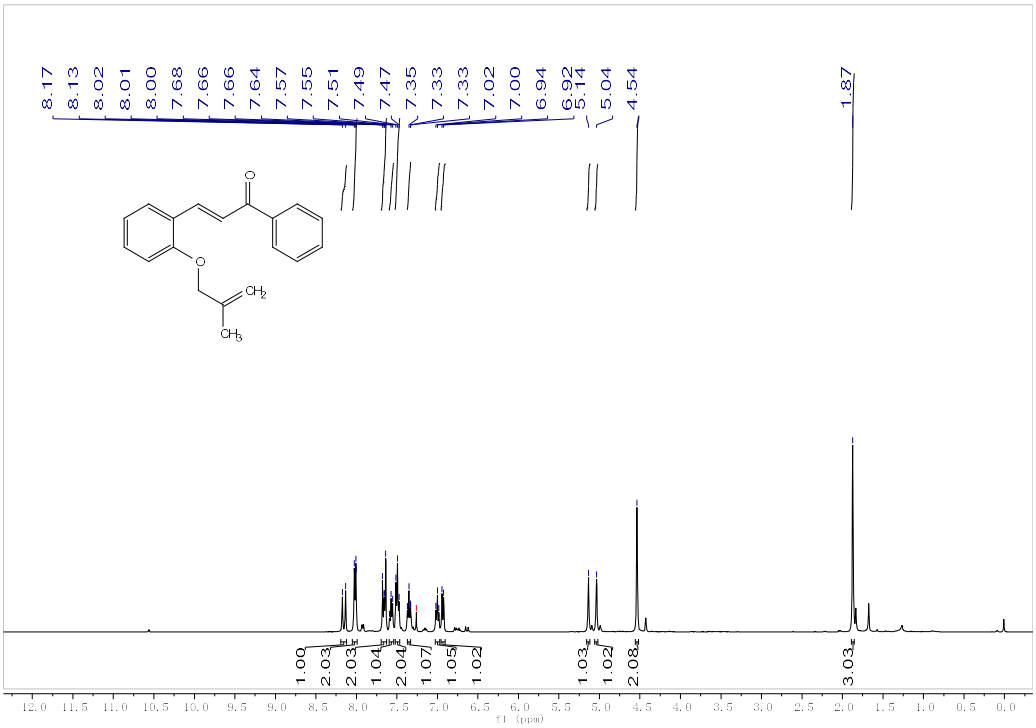


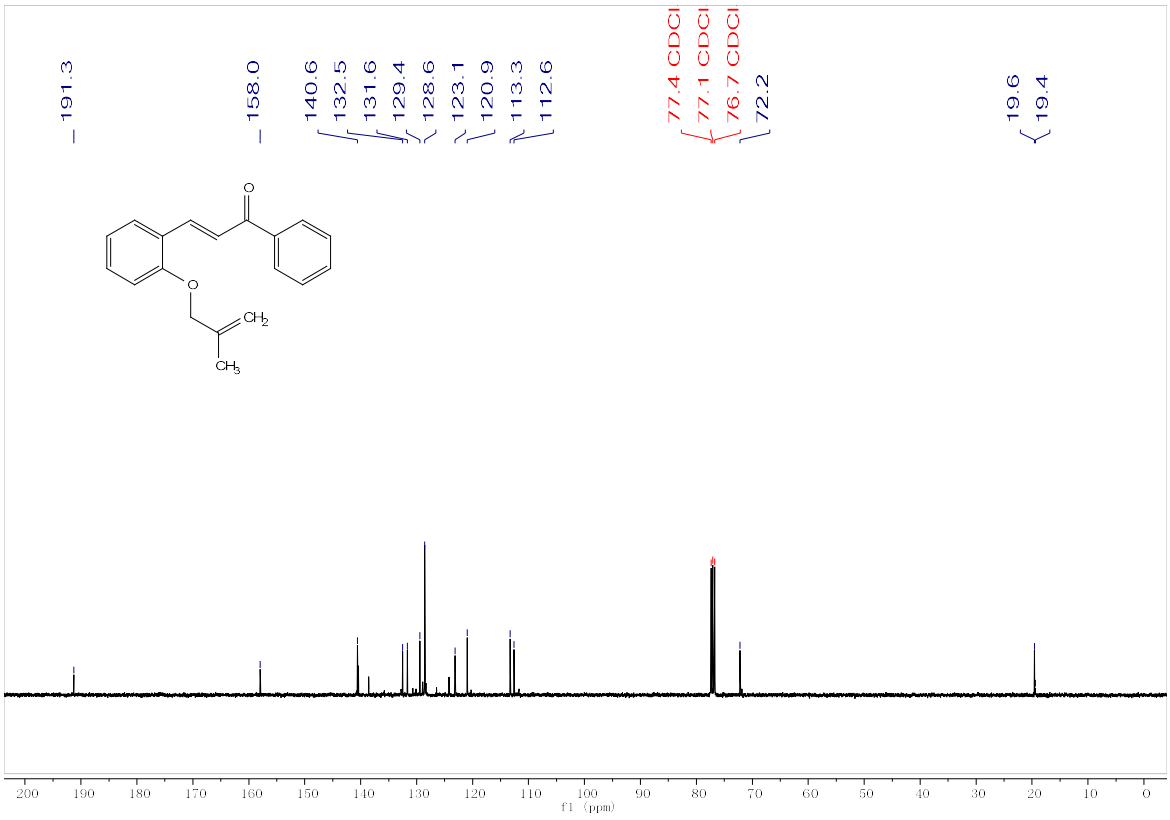
3-(2-Allyloxy-phenyl)-1-(2-bromo-phenyl)-propenone (1j)



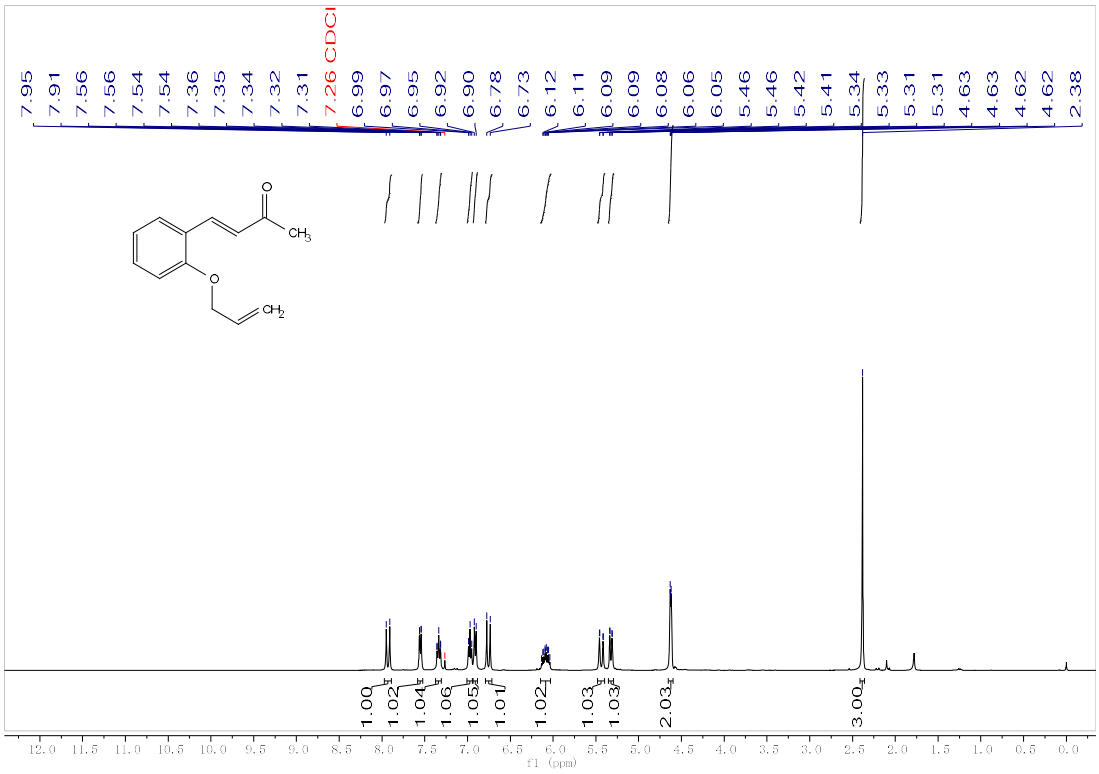


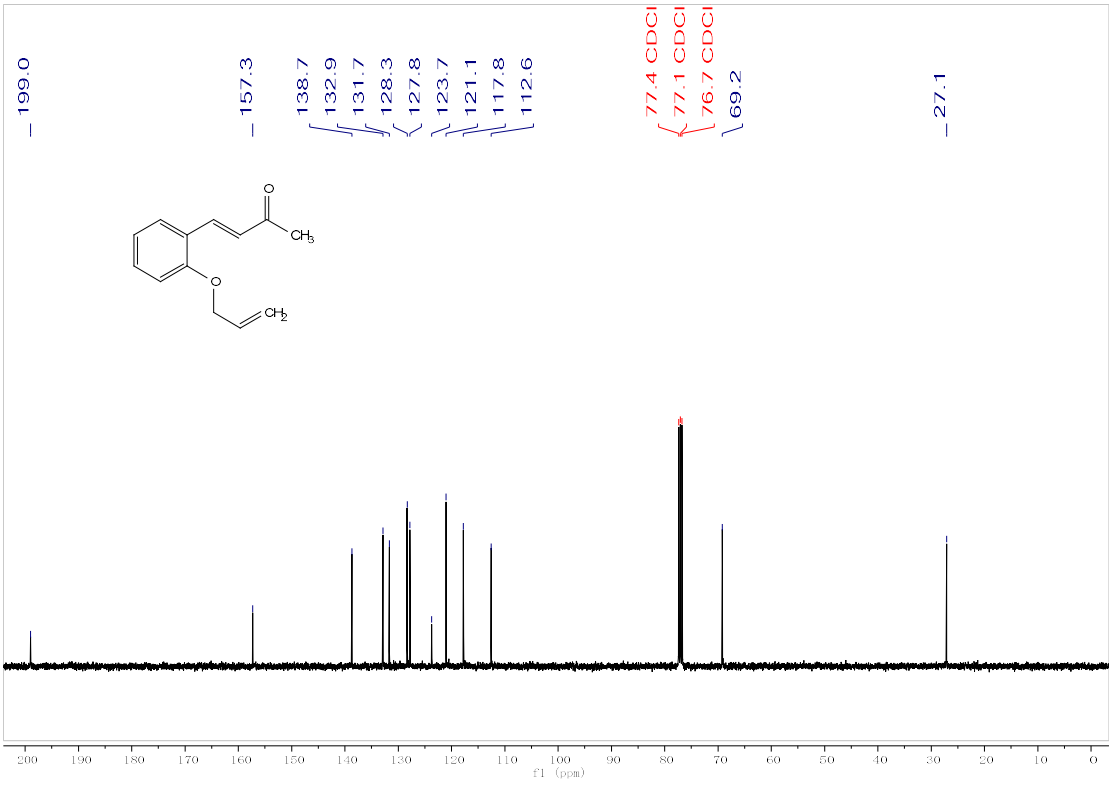
3-[2-(2-Methyl-allyloxy)-phenyl]-1-phenyl-propenone (1k)



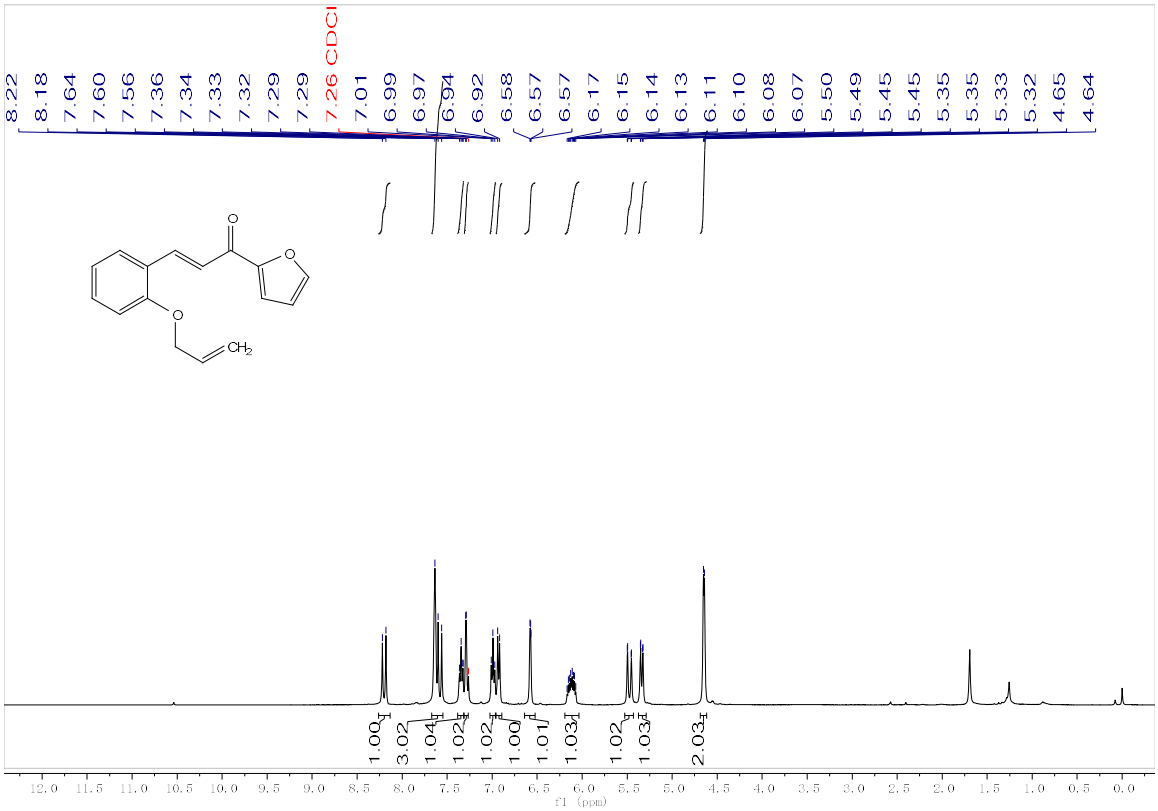


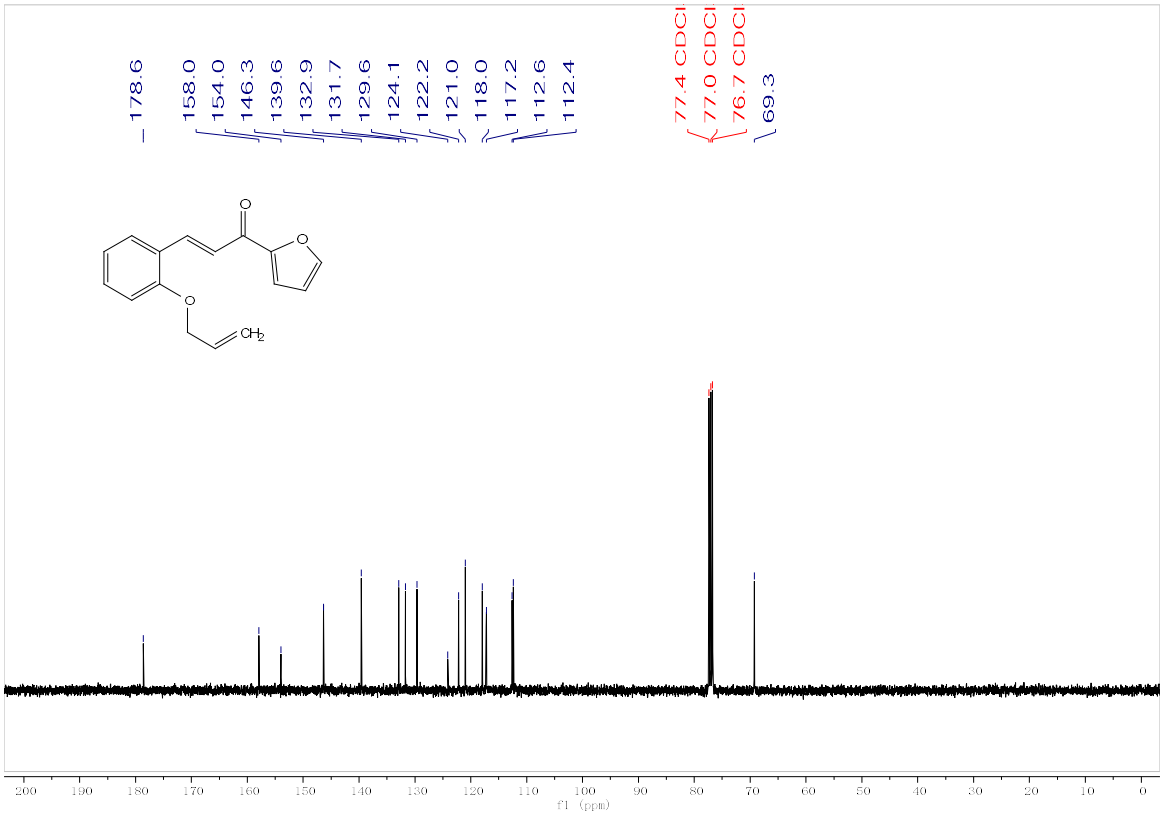
4-(2-Allyloxy-phenyl)-but-3-en-2-one (1l)



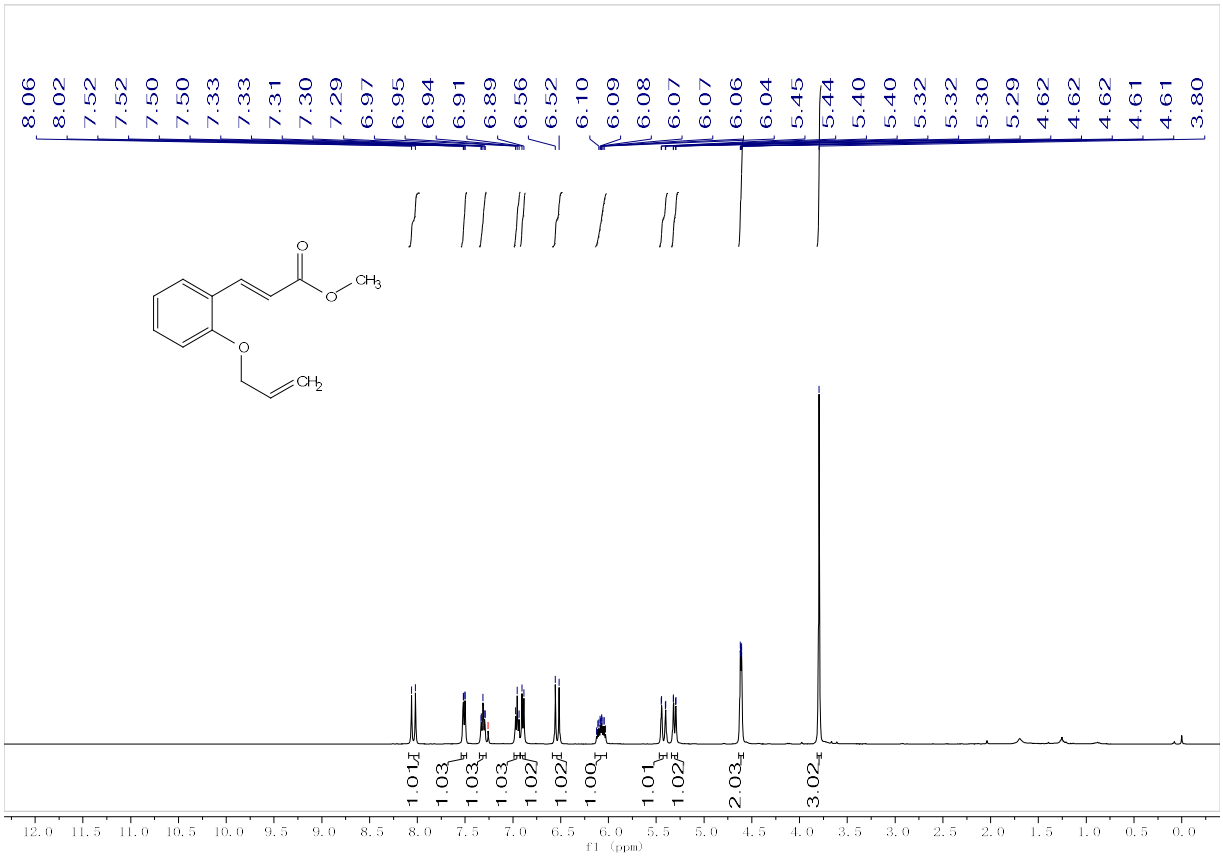


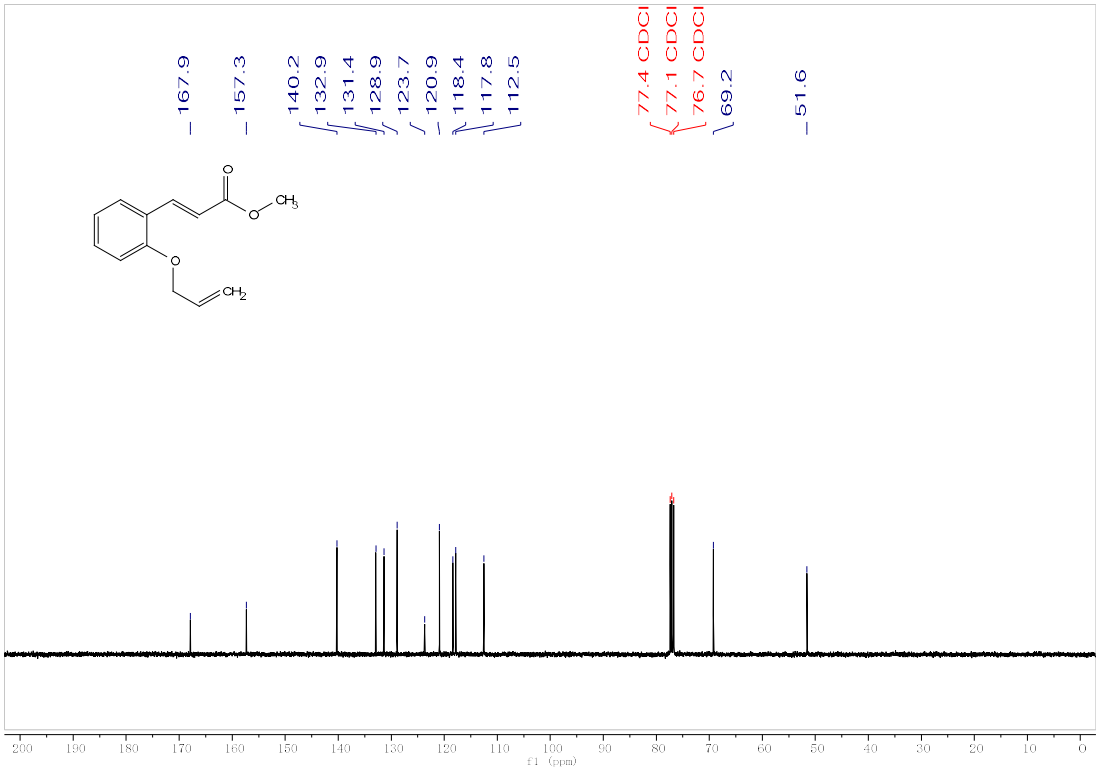
3-(2-Allyloxy-phenyl)-1-furan-2-yl-propenone (1m)



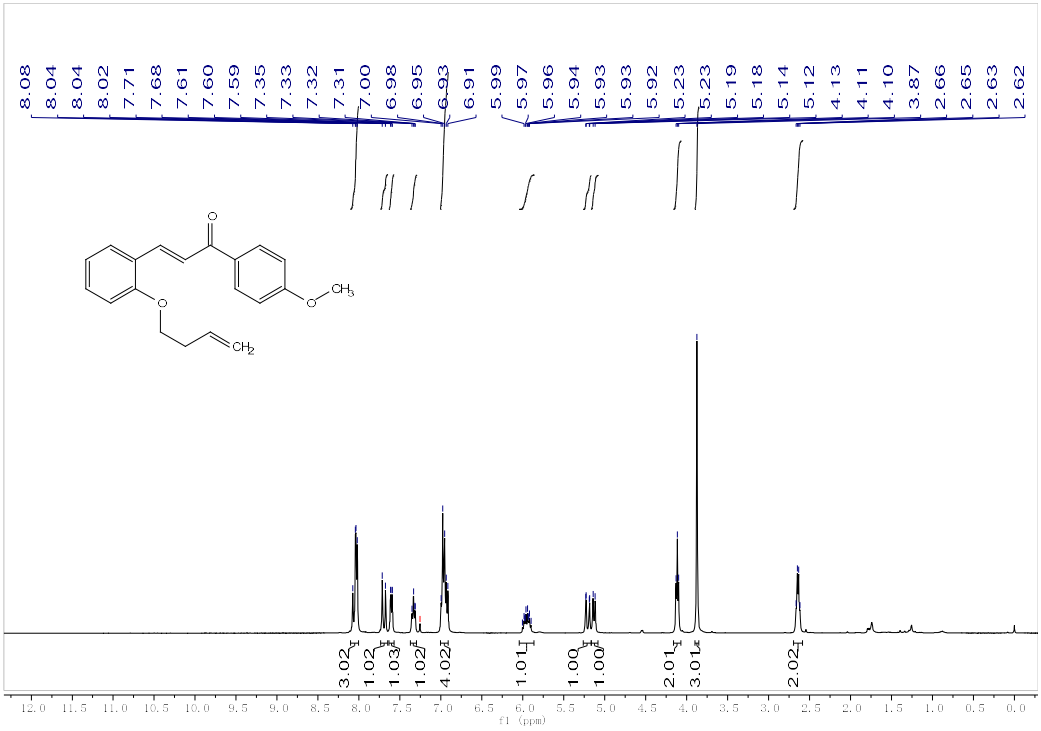


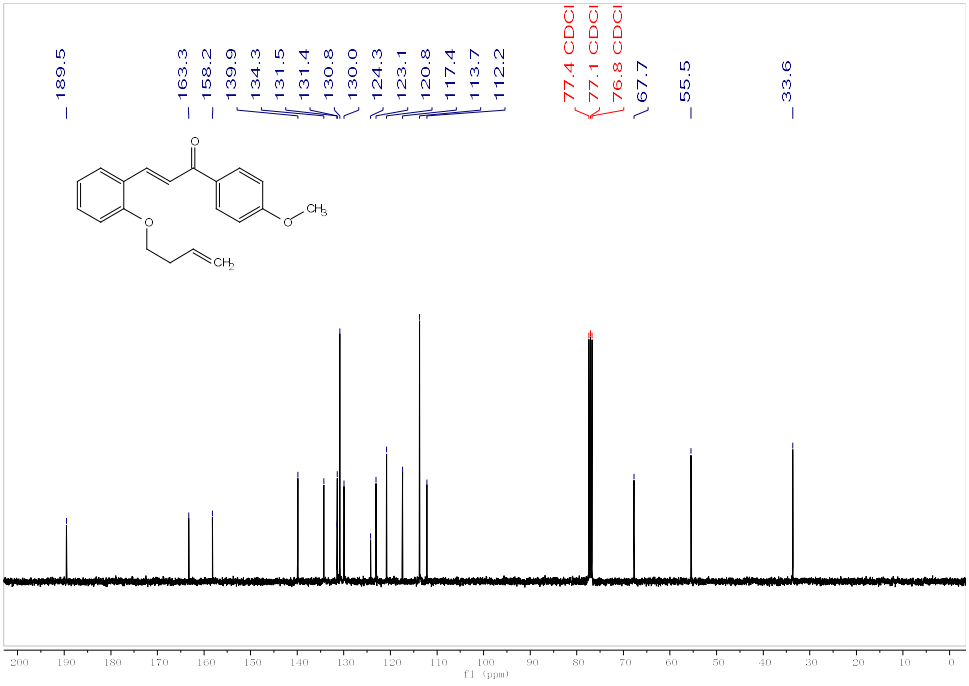
3-(2-Allyloxy-phenyl)-acrylic acid methyl ester (1n)



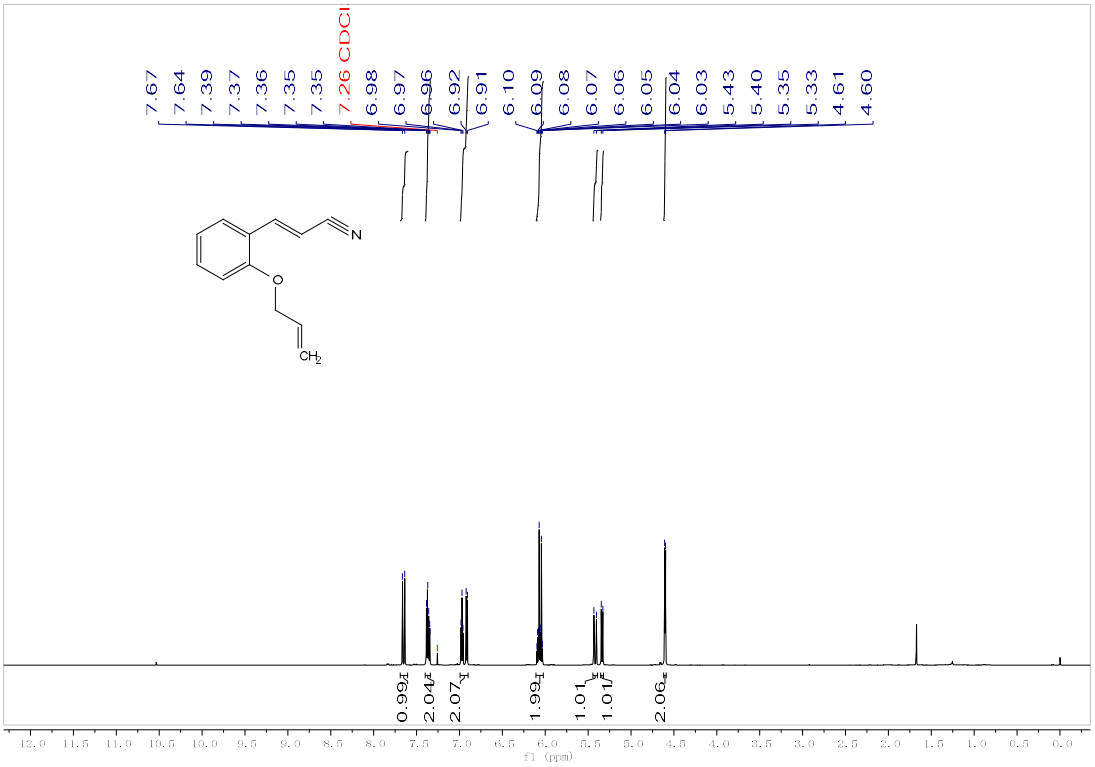


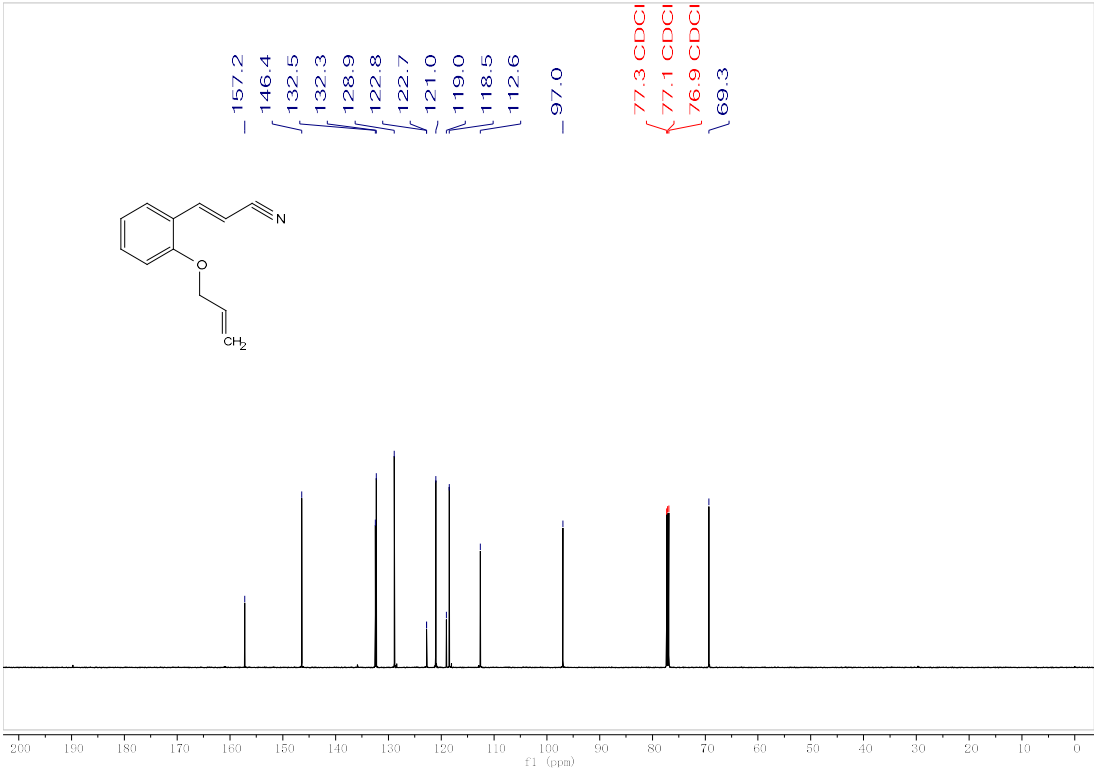
3-(2-But-3-enyloxy-phenyl)-1-(4-methoxy-phenyl)-propenone (1o)



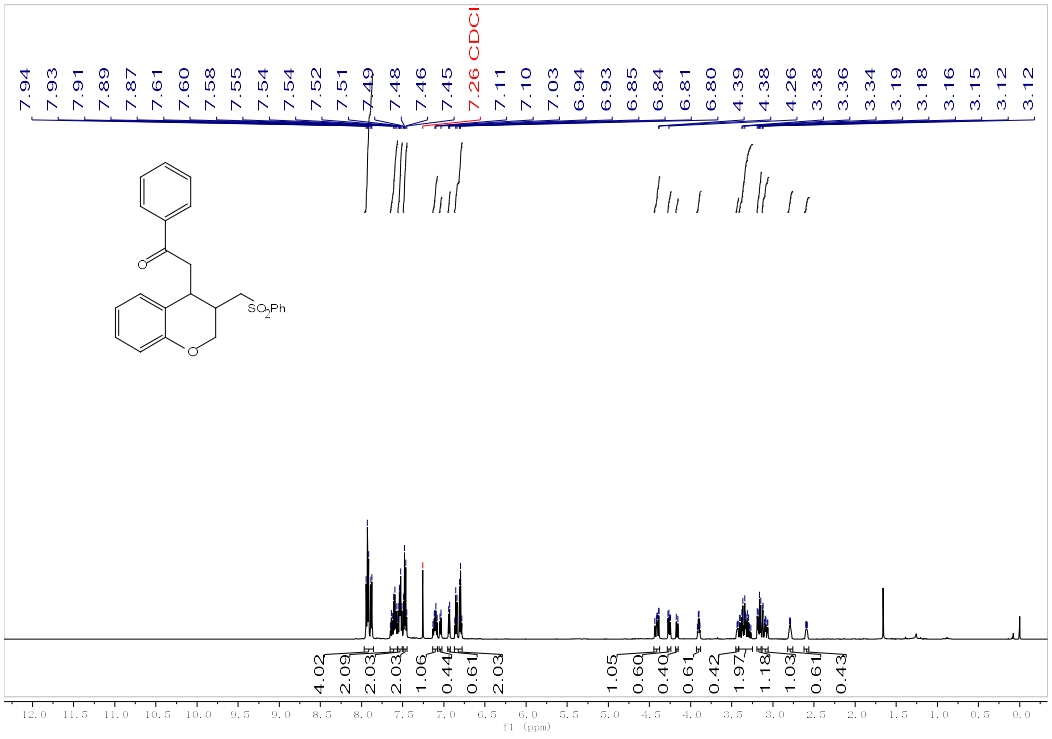


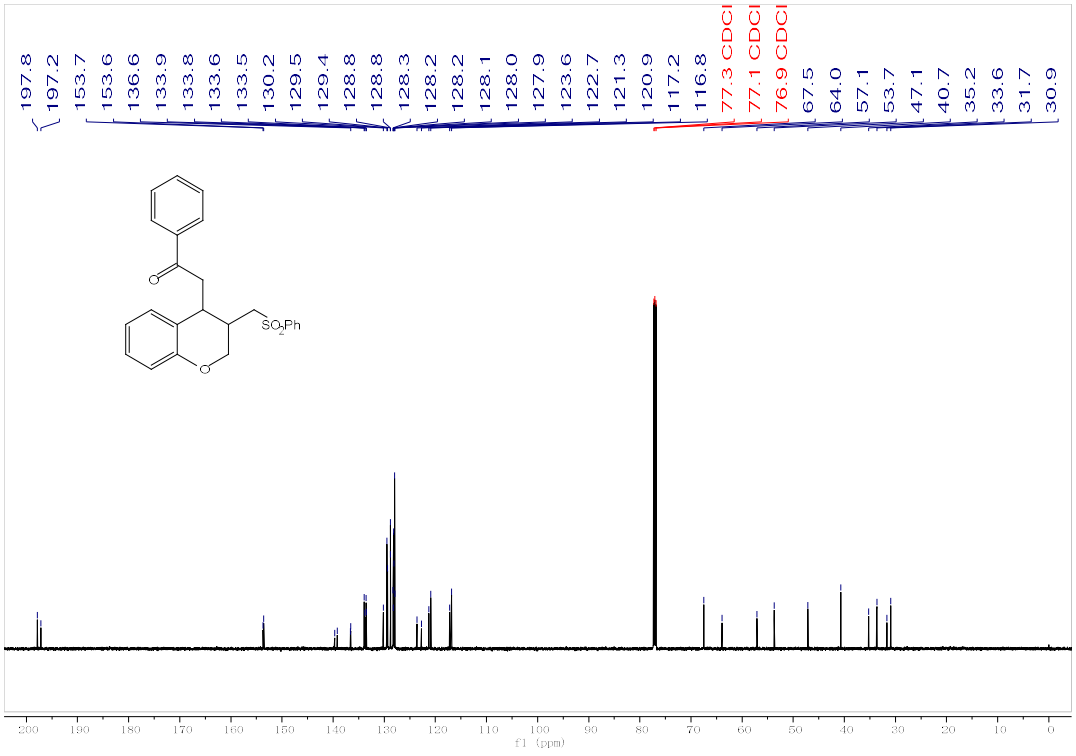
3-(2-Allyloxy-phenyl)-acrylonitrile (1p)



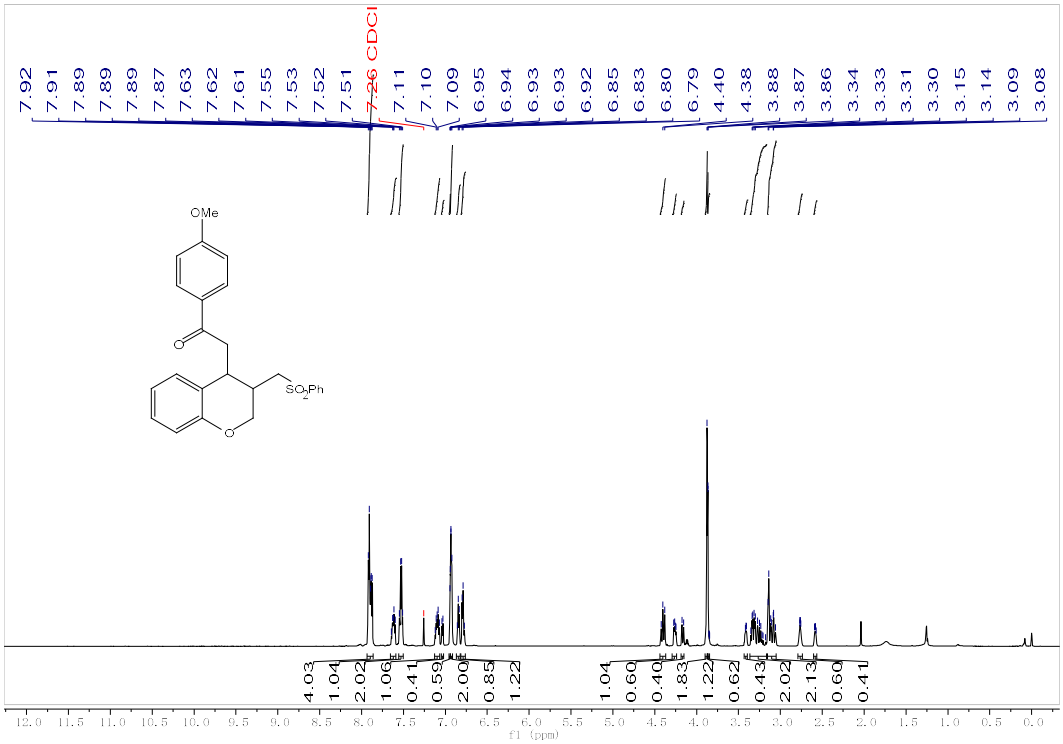


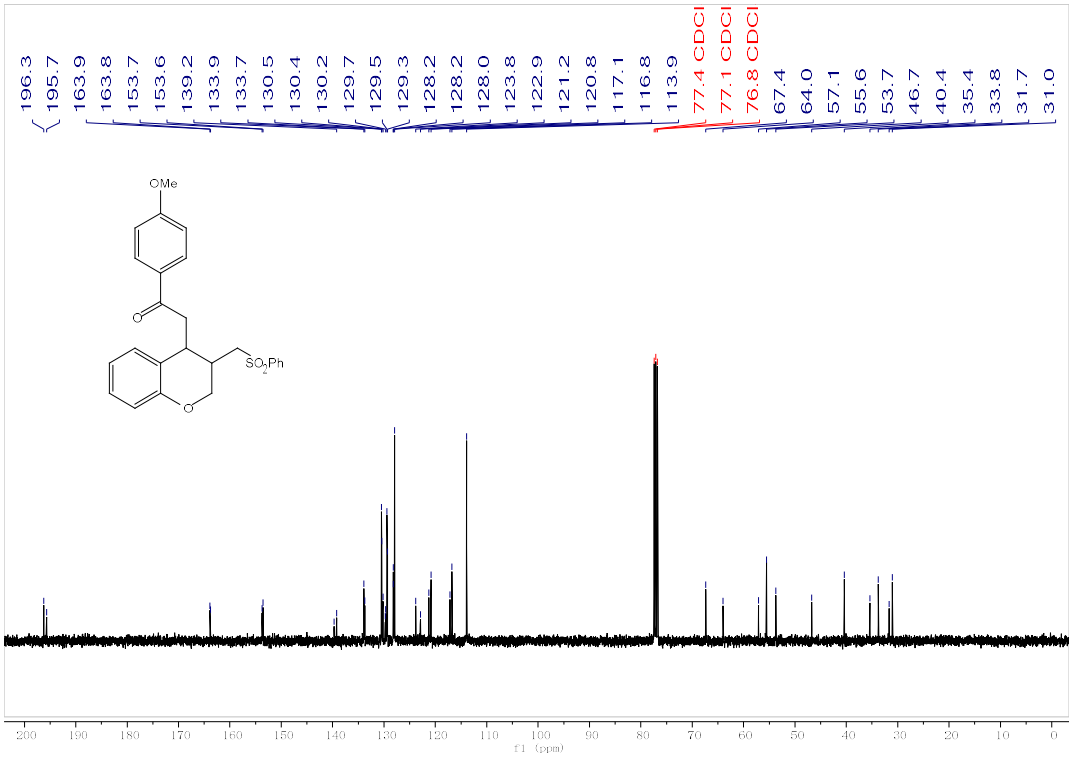
1-phenyl-2-(3-((phenylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3a)



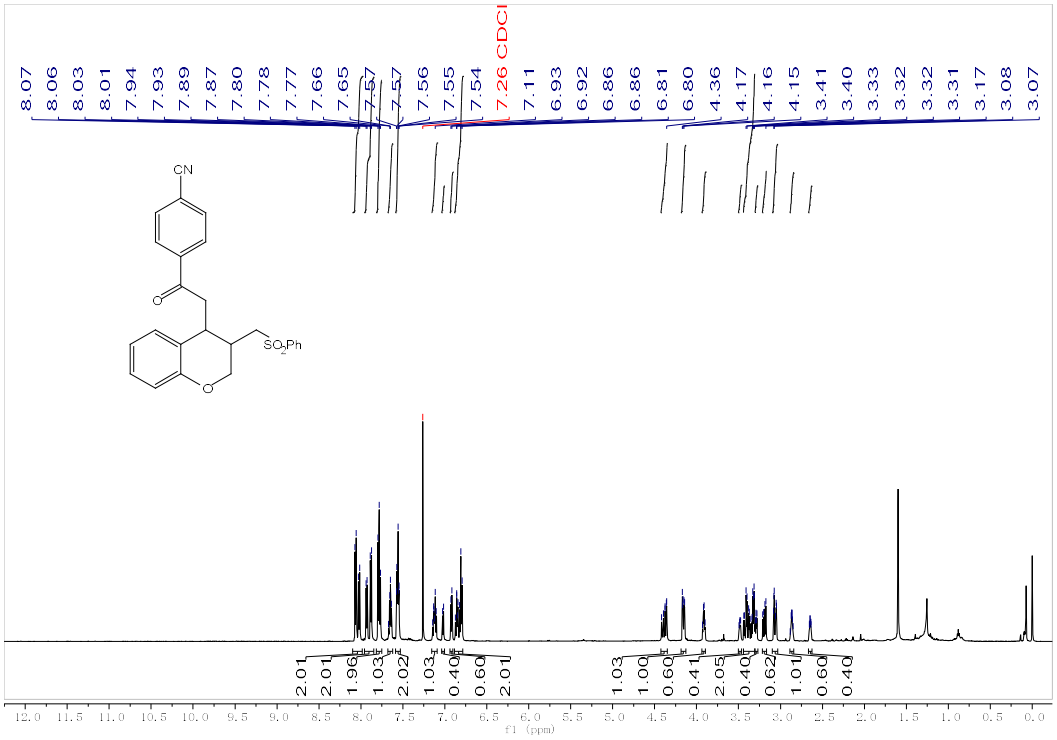


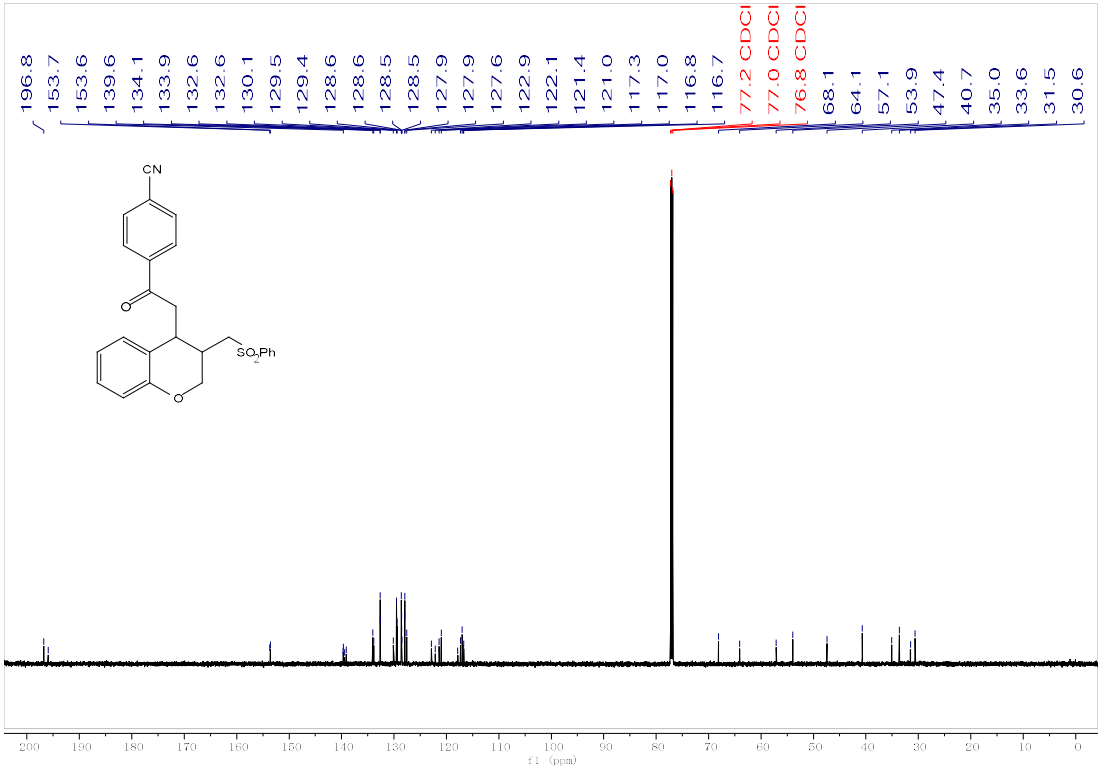
1-(4-methoxyphenyl)-2-(3-((phenylsulfonyl)methyl)chroman-4-yl)ethan-1-one(3b)



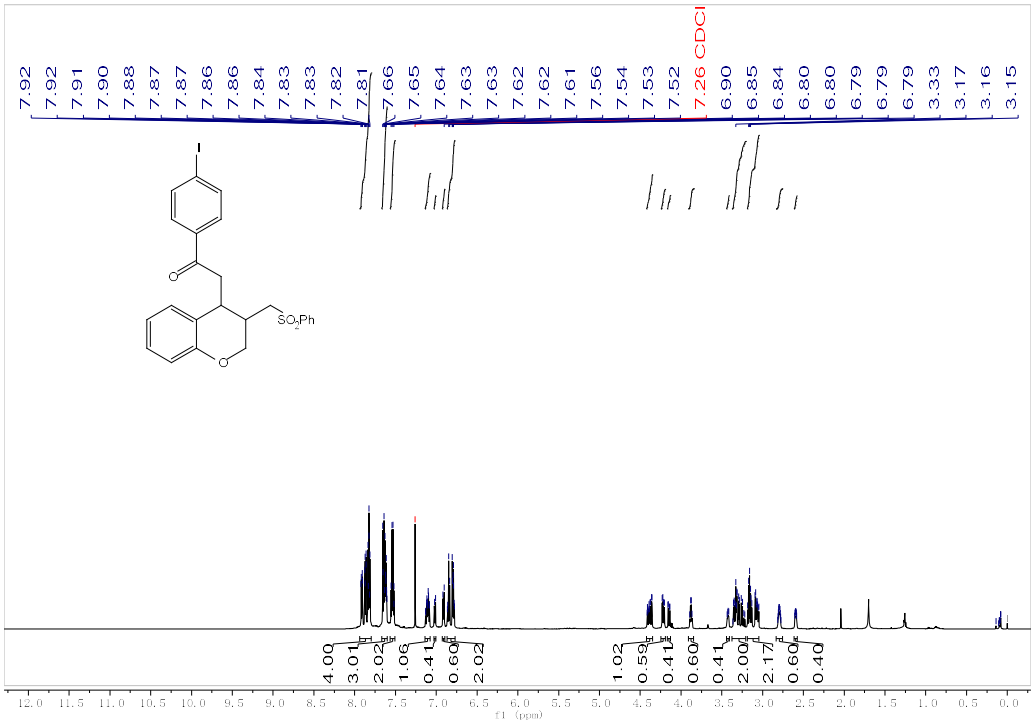


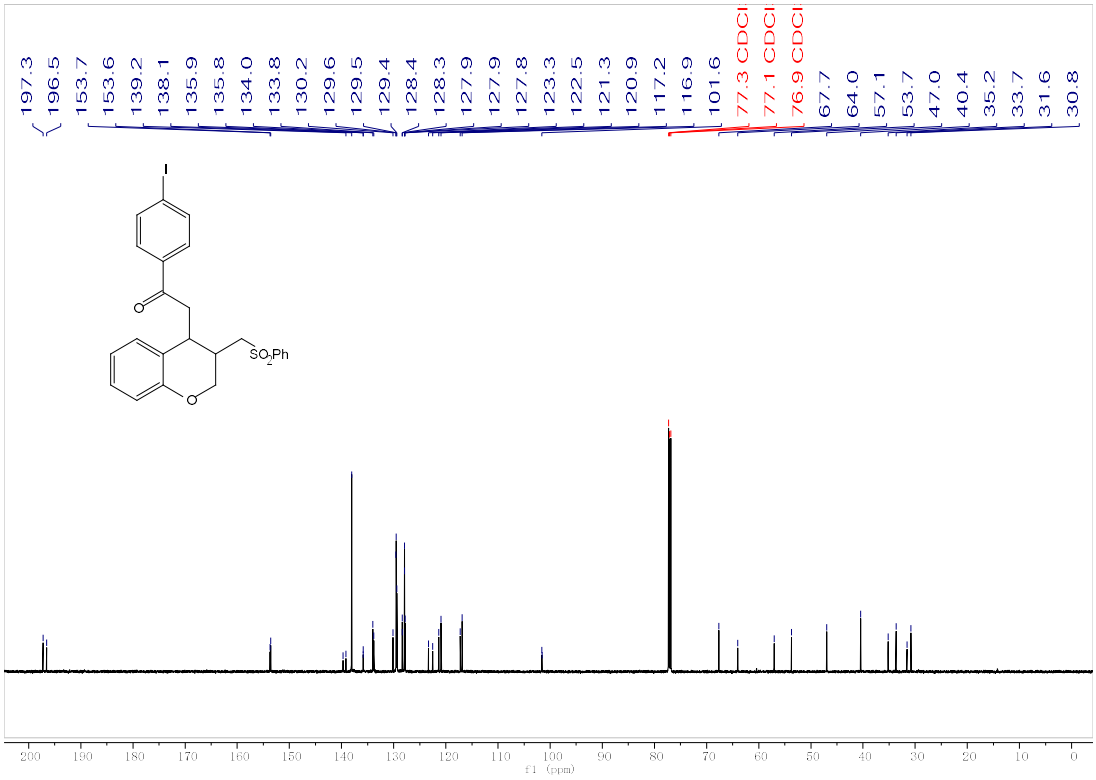
4-(2-(3-((phenylsulfonyl)methyl)chroman-4-yl)acetyl)benzonitrile(3c)



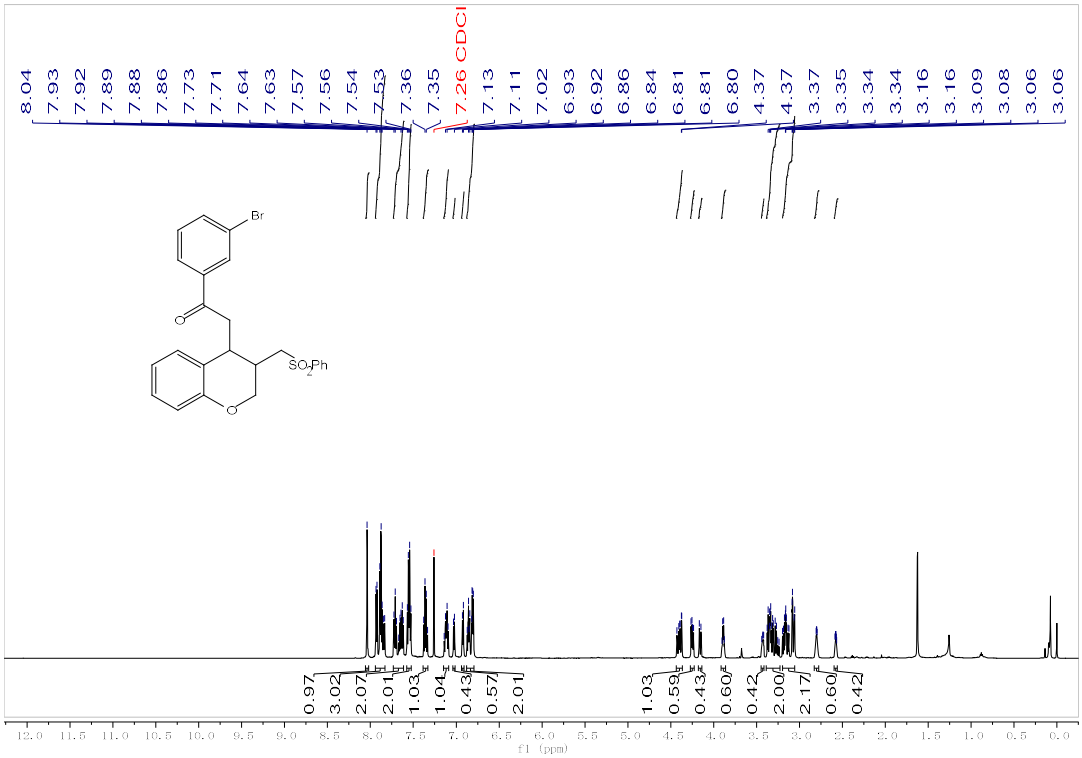


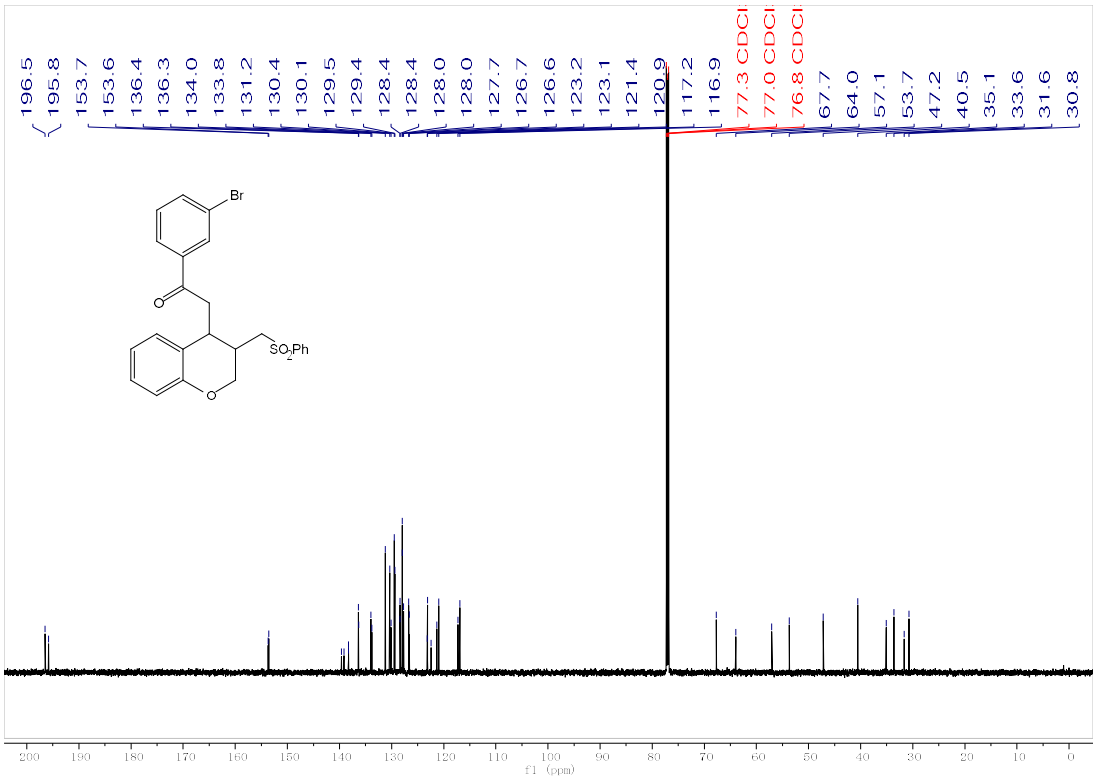
1-(4-iodophenyl)-2-(3-((phenylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3d)



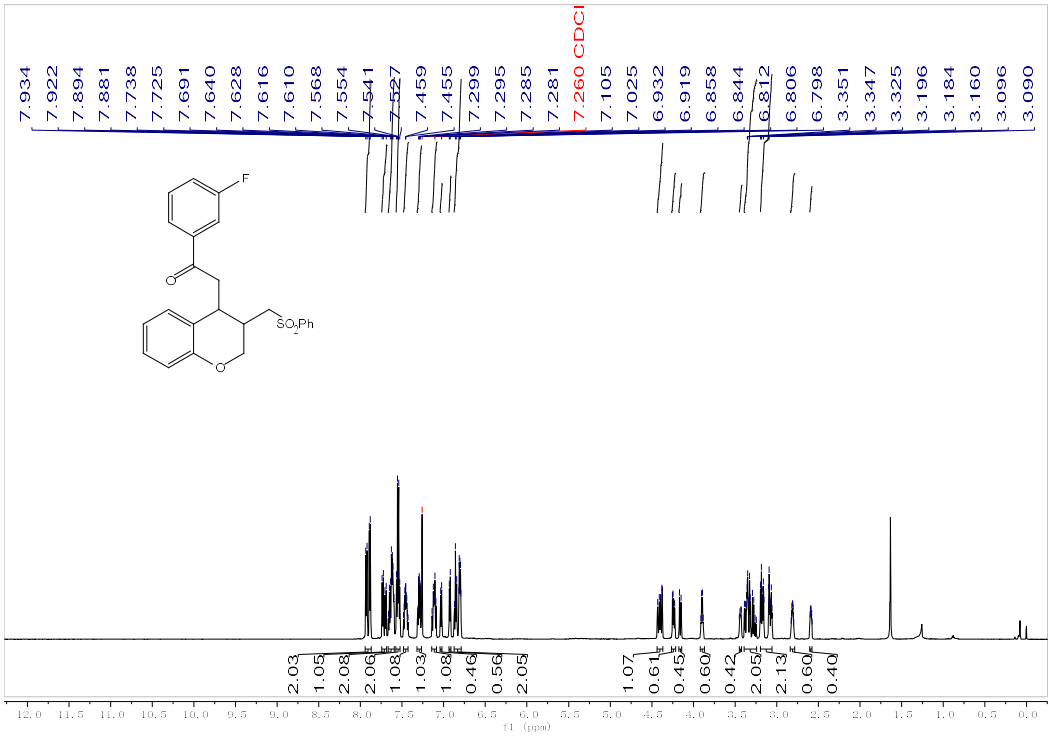


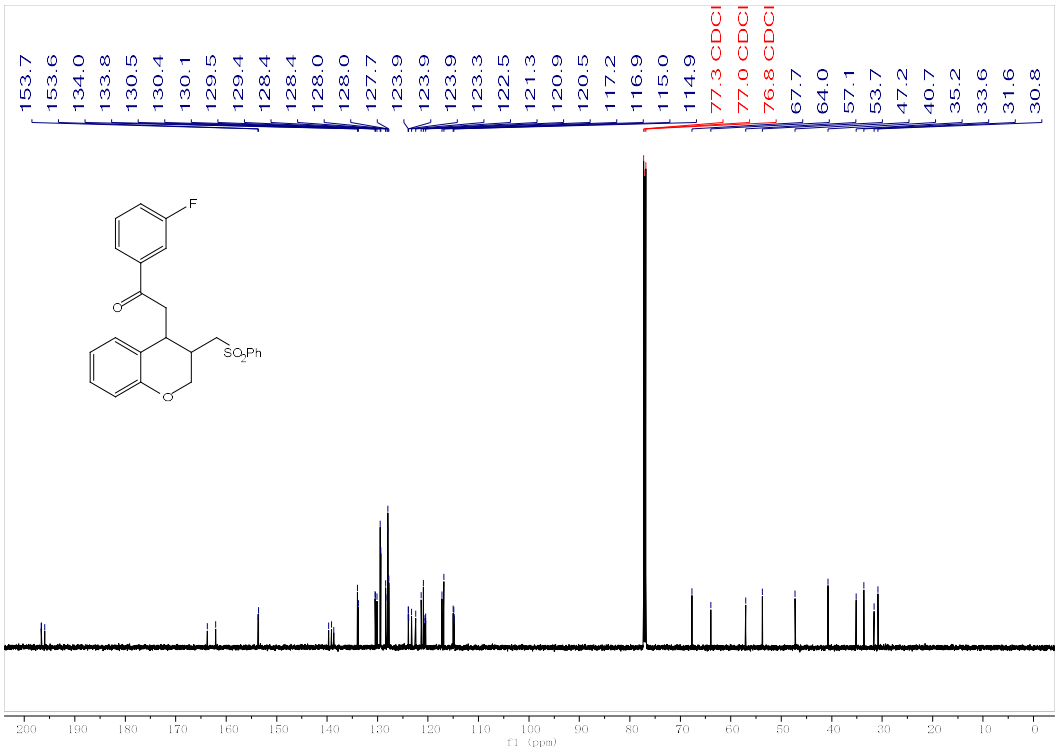
1-(3-bromophenyl)-2-(3-((phenylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3e)



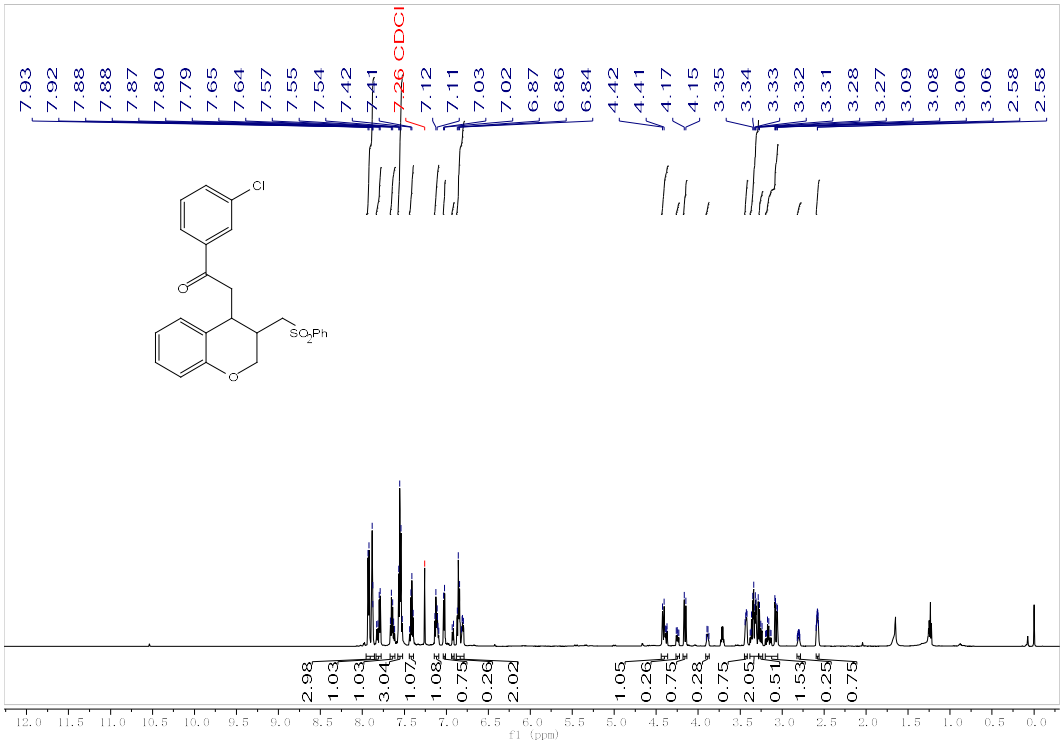


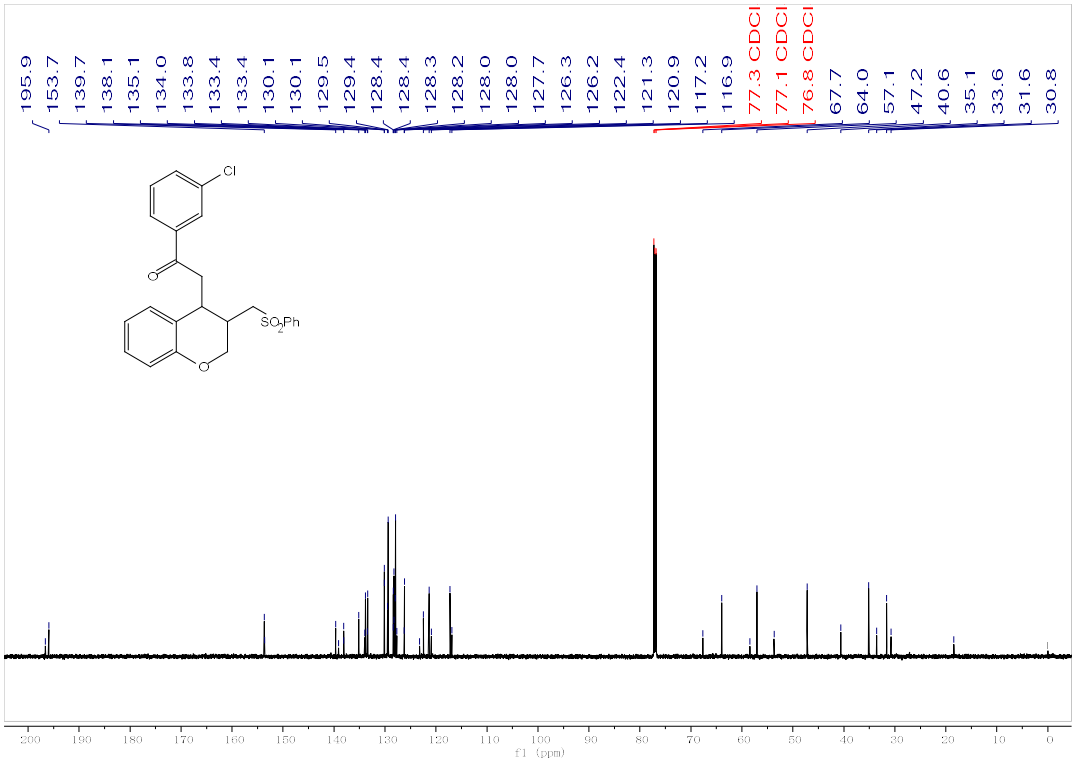
1-(3-fluorophenyl)-2-(3-((phenylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3f)



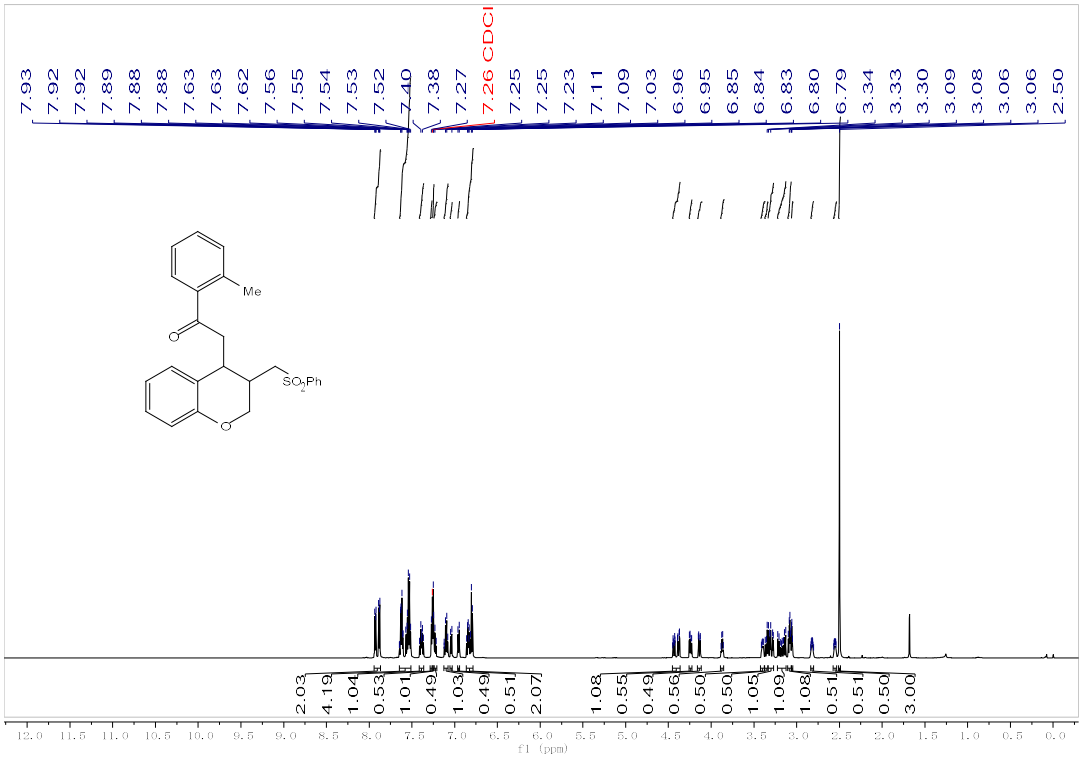


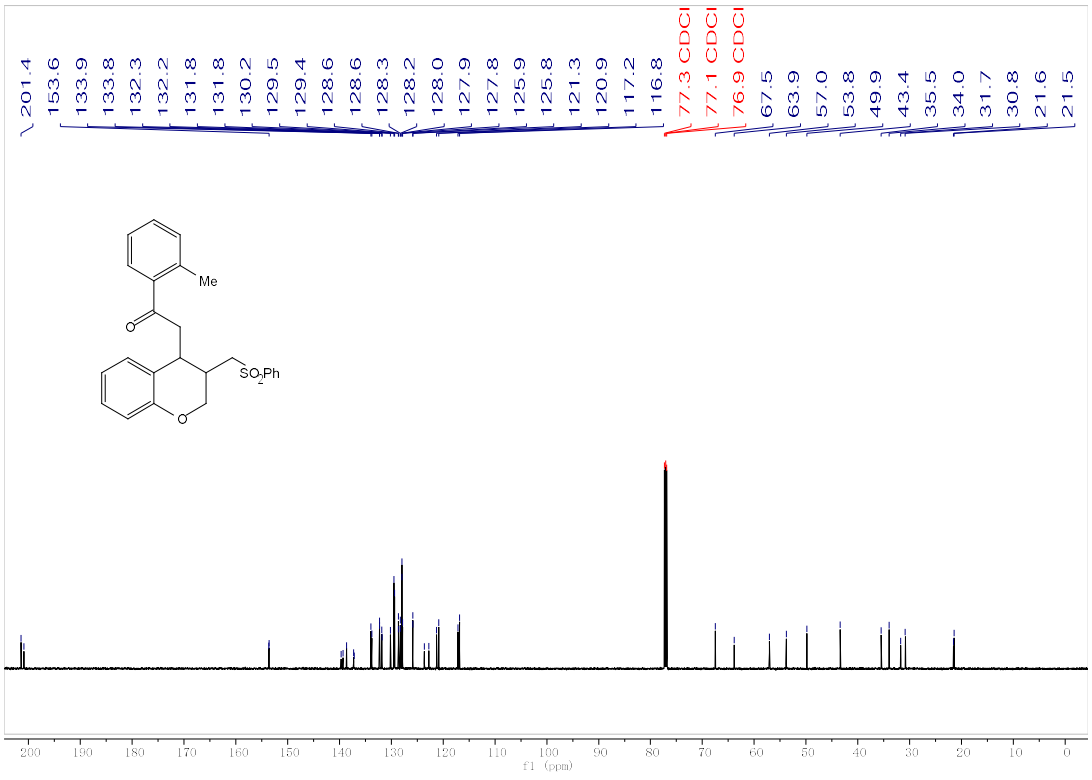
1-(3-chlorophenyl)-2-(3-((phenylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3g)



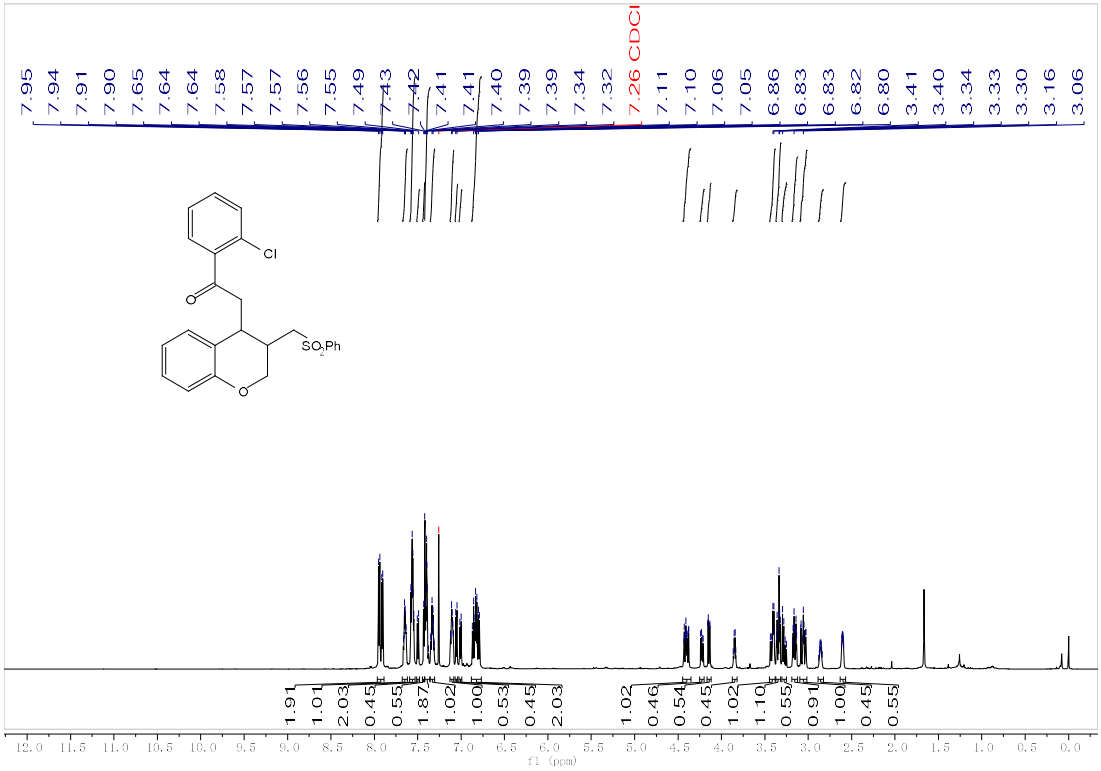


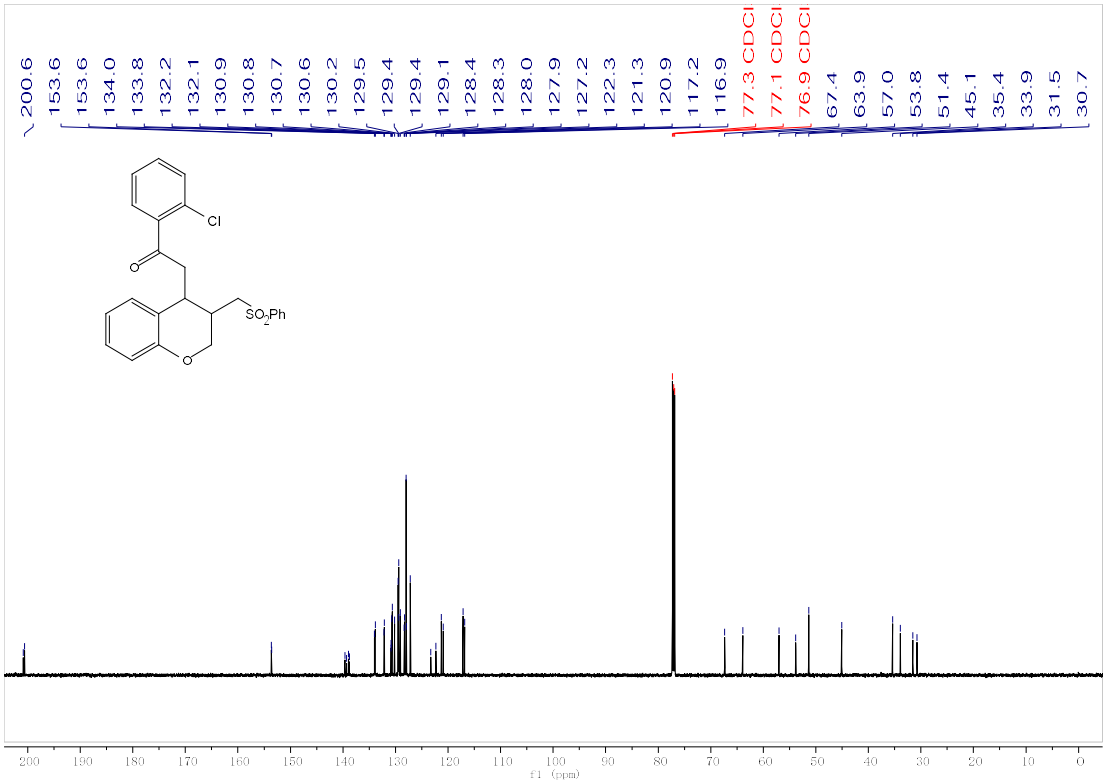
2-(3-((phenylsulfonyl)methyl)chroman-4-yl)-1-(o-tolyl)ethan-1-one (3h)



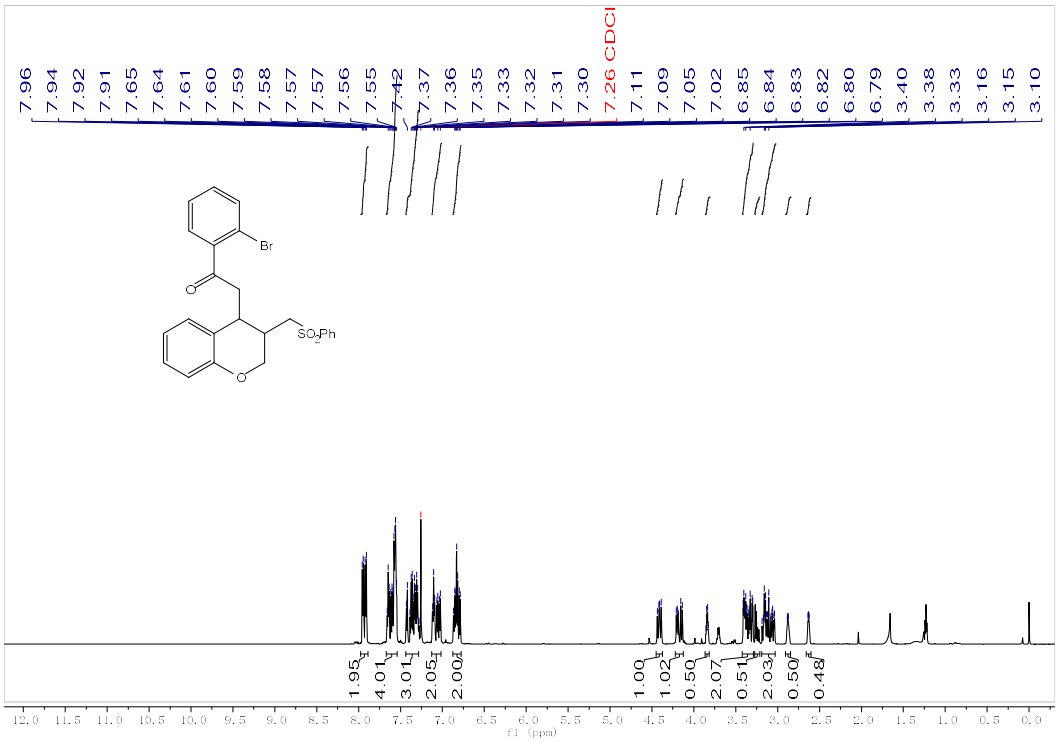


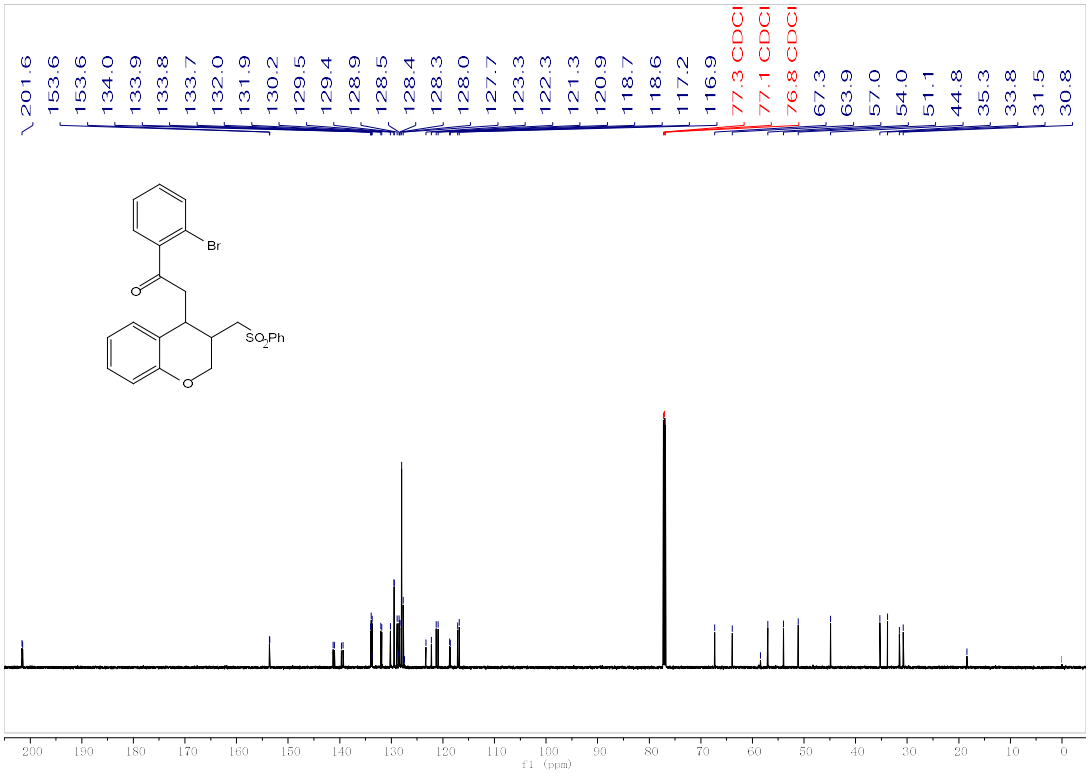
1-(2-chlorophenyl)-2-(3-((phenylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3i)



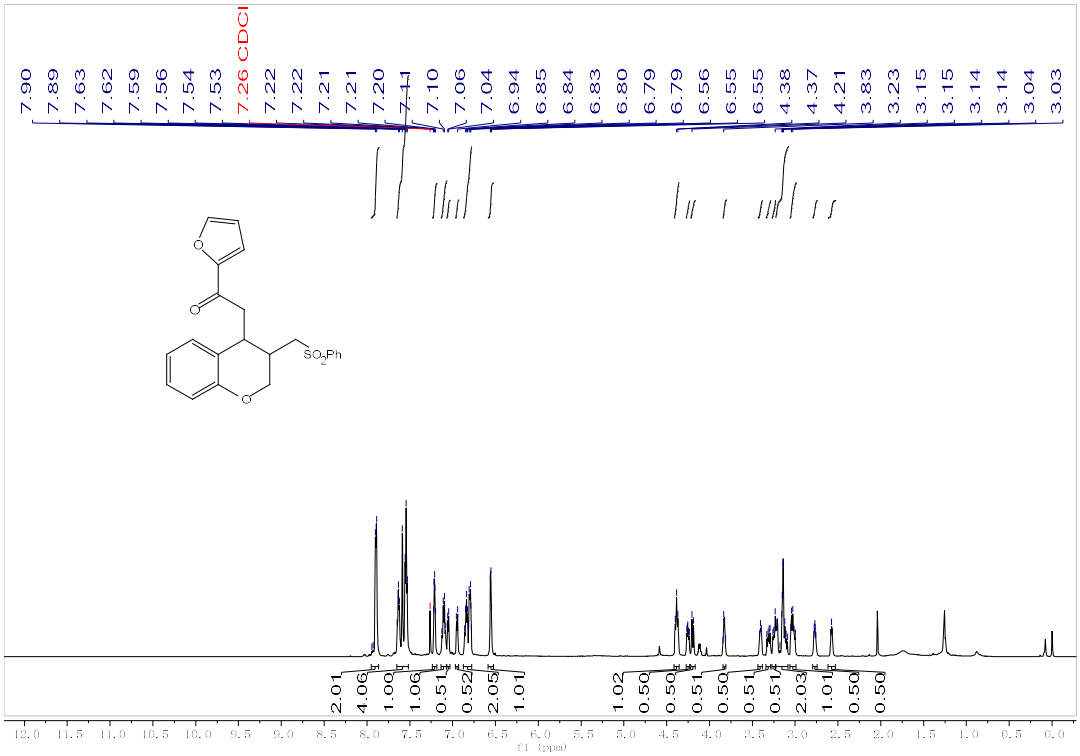


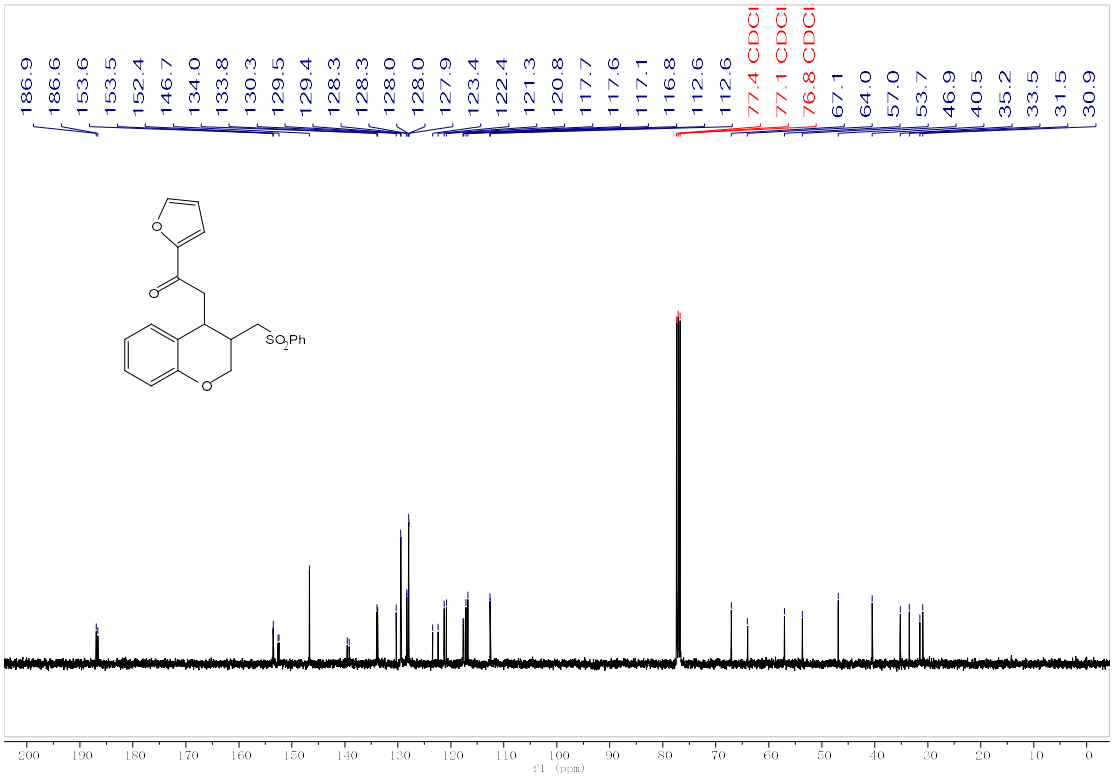
1-(2-bromophenyl)-2-(3-((phenylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3j)



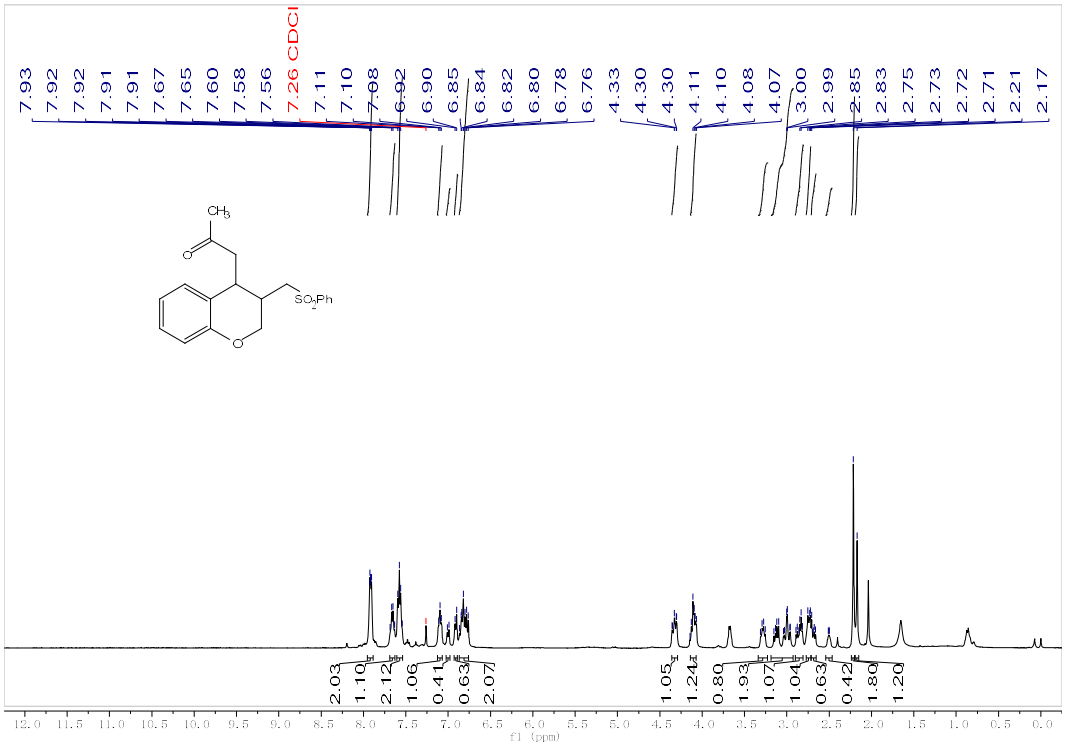


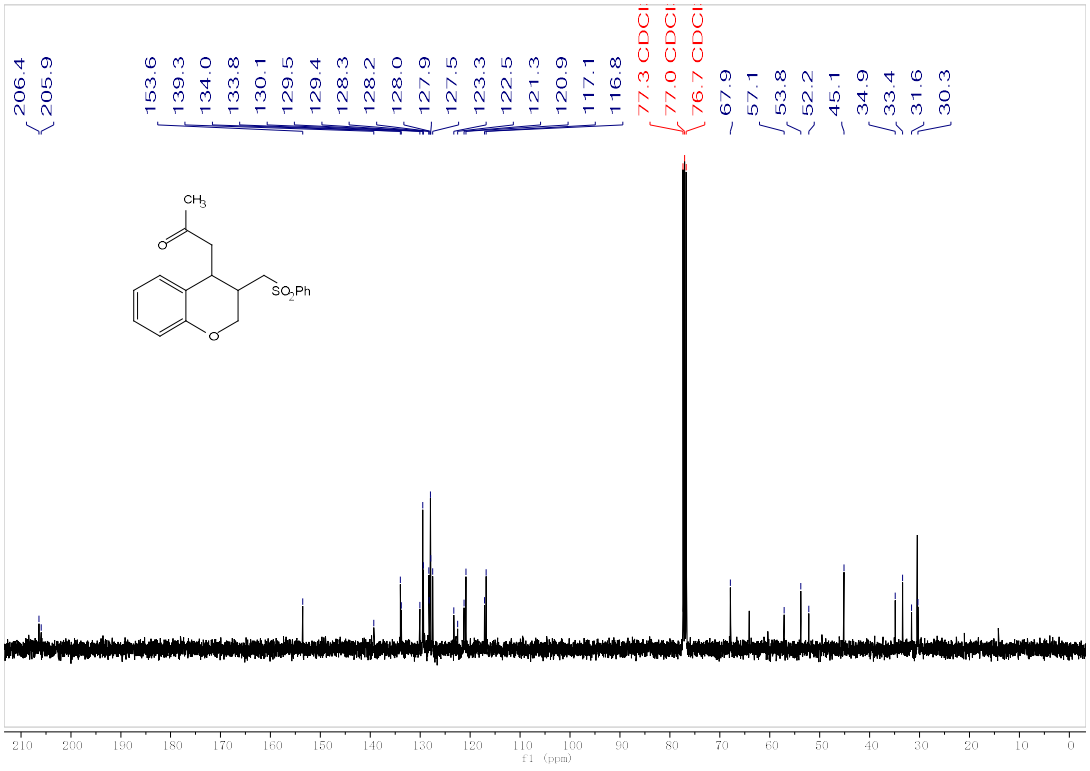
1-(furan-2-yl)-2-(3-((phenylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3k)



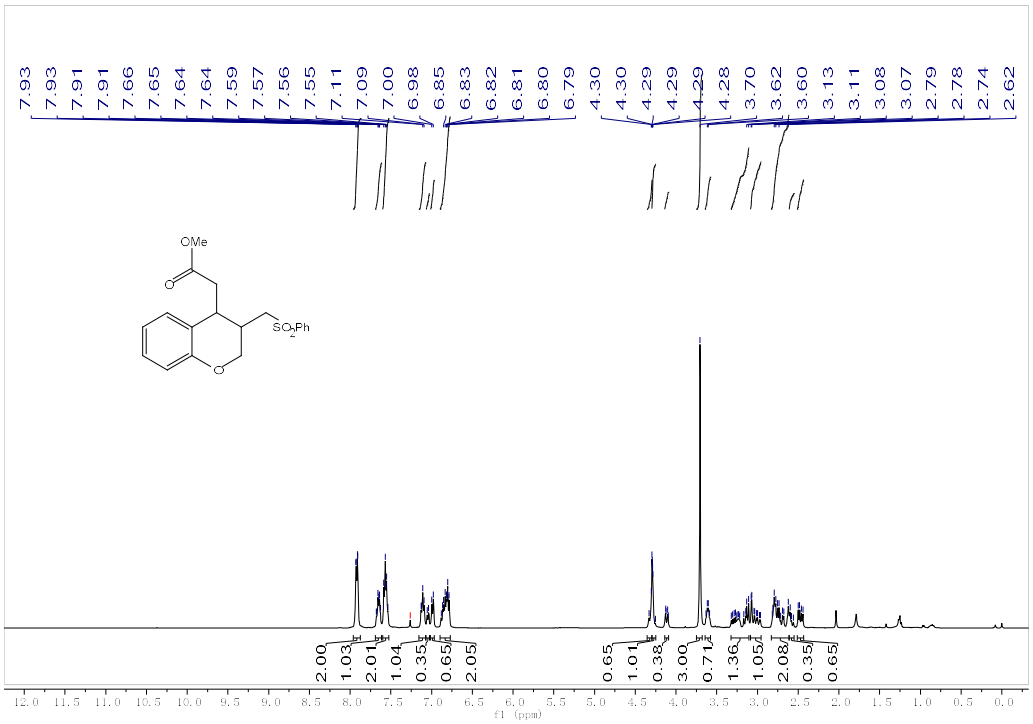


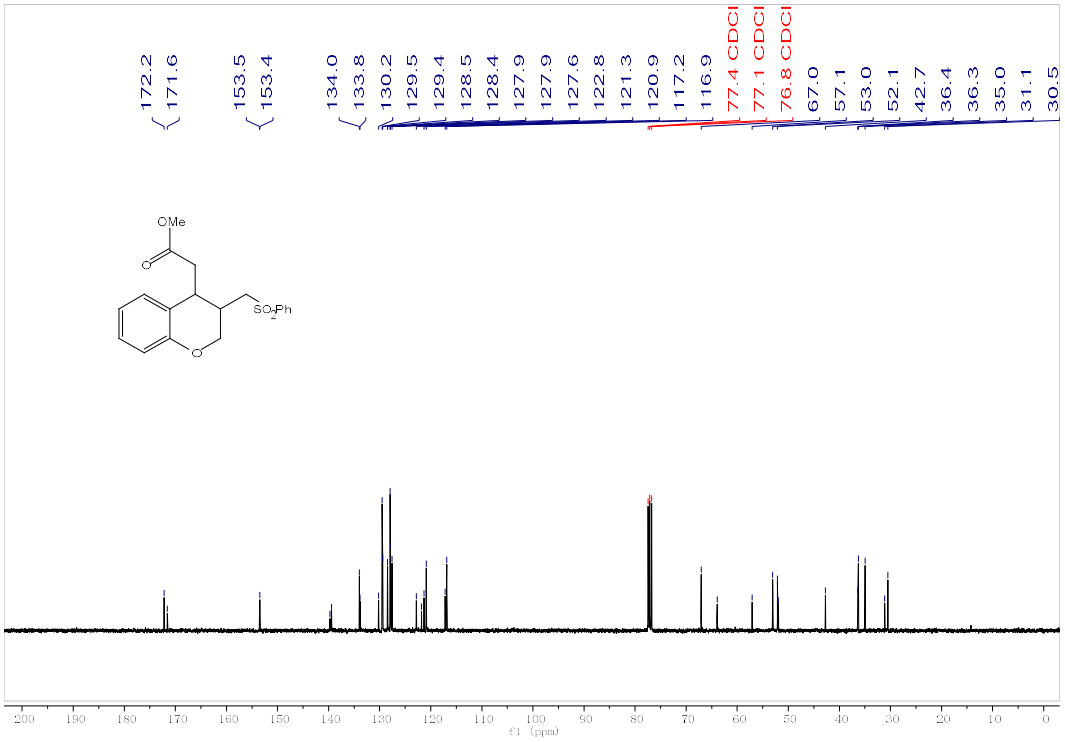
1-(3-((phenylsulfonyl)methyl)chroman-4-yl)propan-2-one (3l)



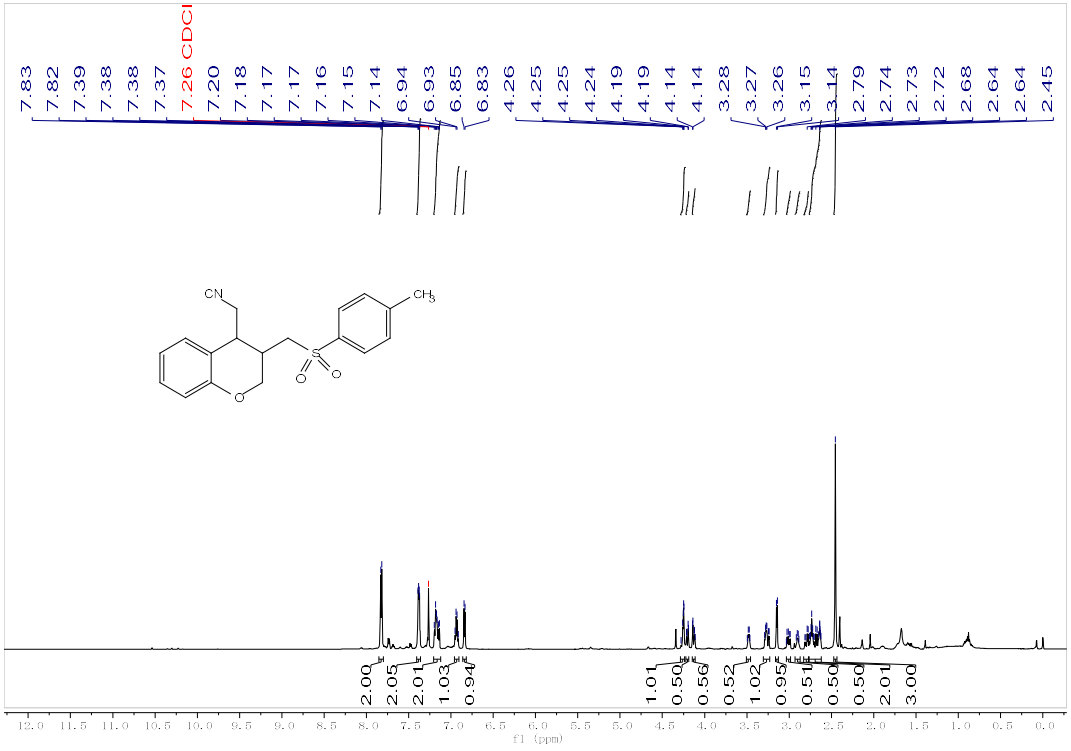


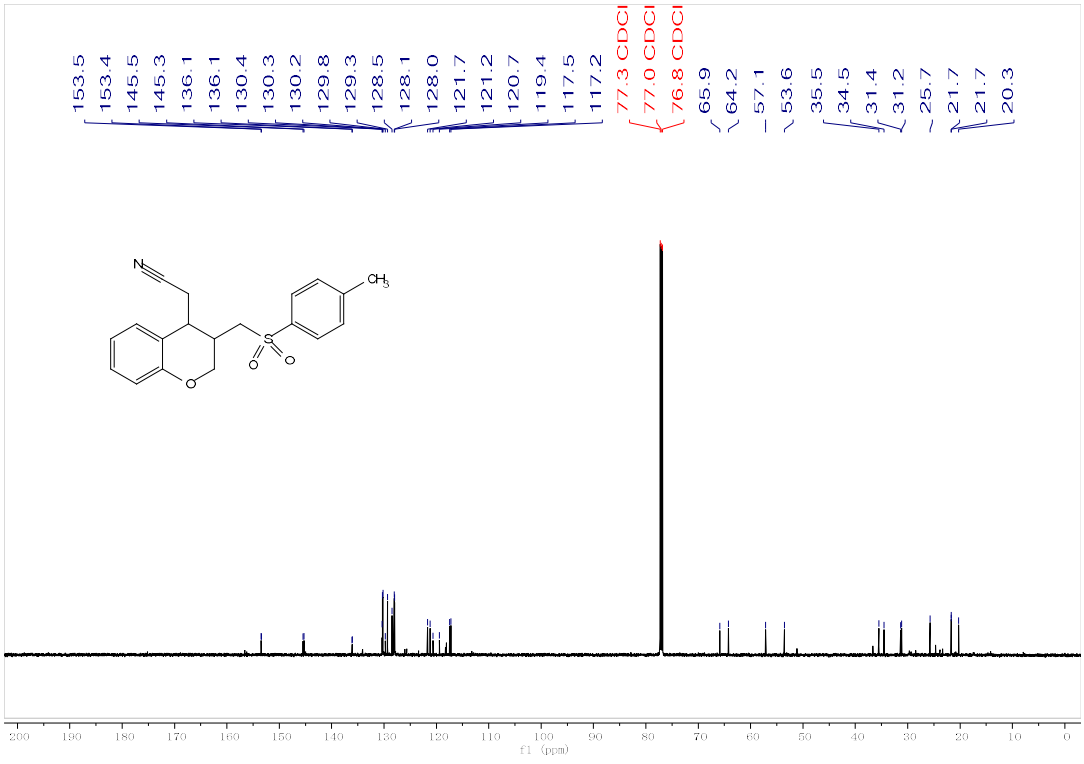
methyl 2-(3-((phenylsulfonyl)methyl)chroman-4-yl)acetate (3m)



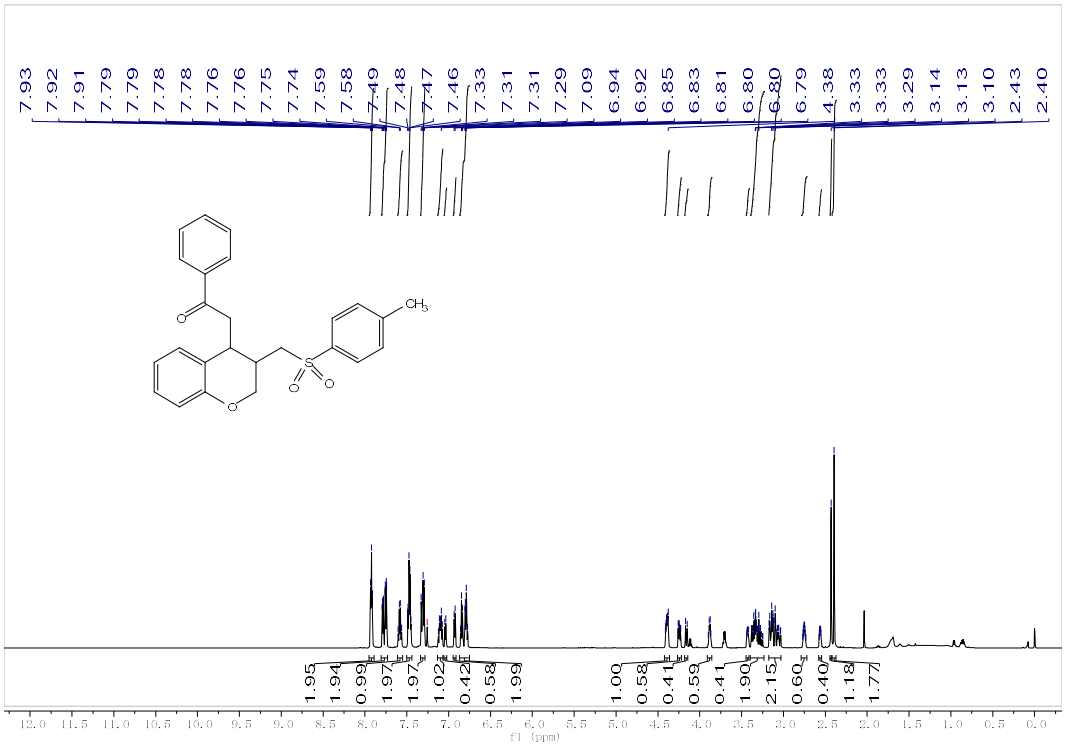


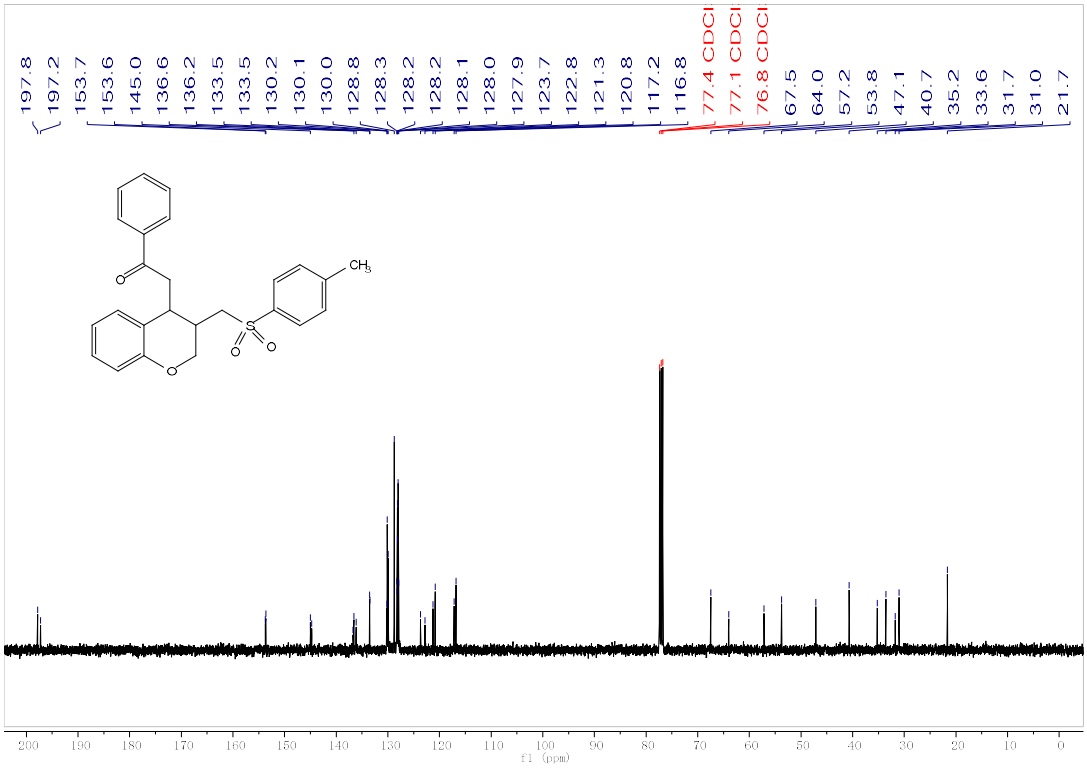
2-(3-(tosylmethyl)chroman-4-yl)acetonitrile (3n)



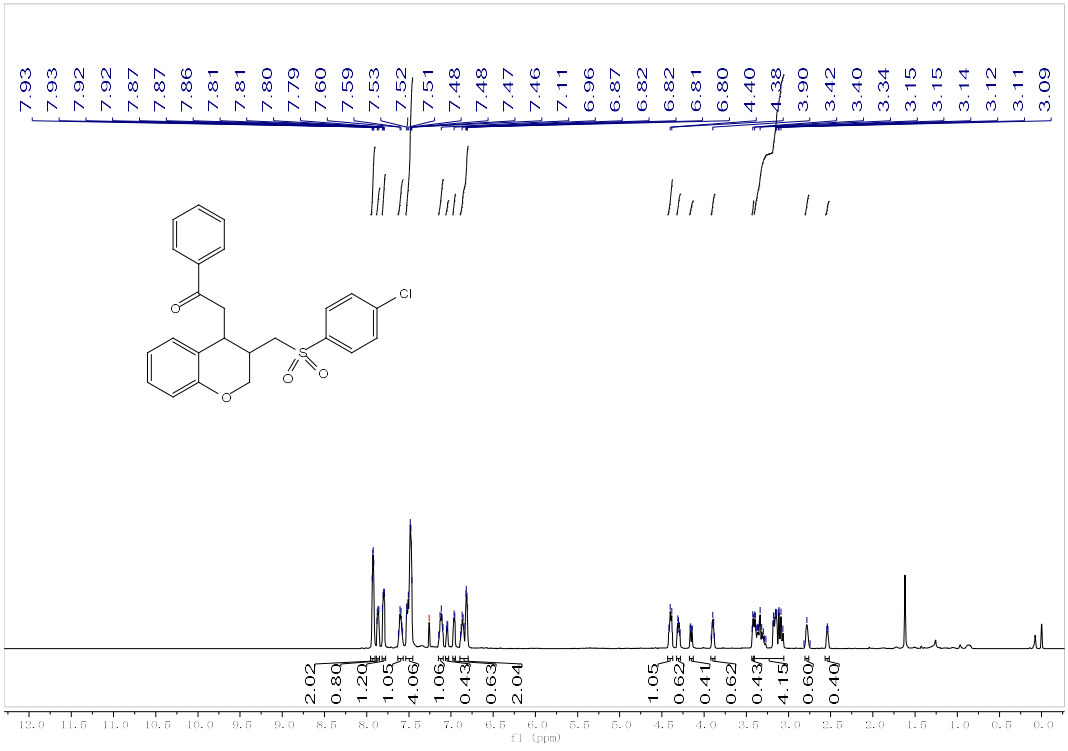


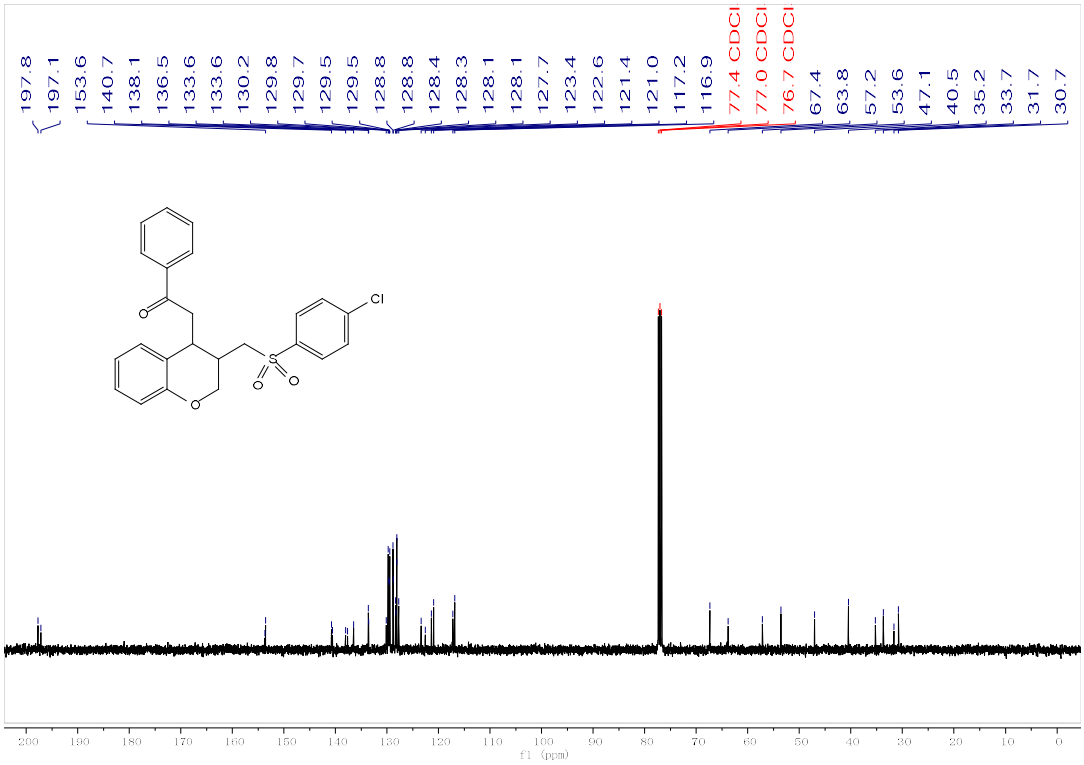
1-phenyl-2-(3-(tosylmethyl)chroman-4-yl)ethan-1-one (3o)



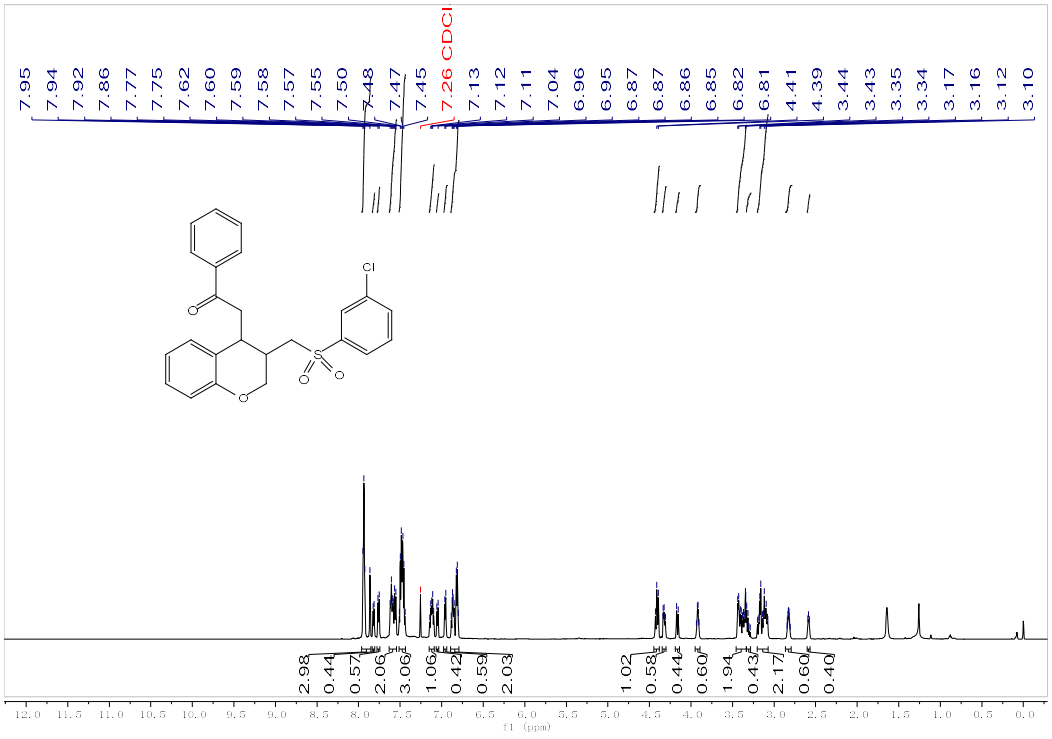


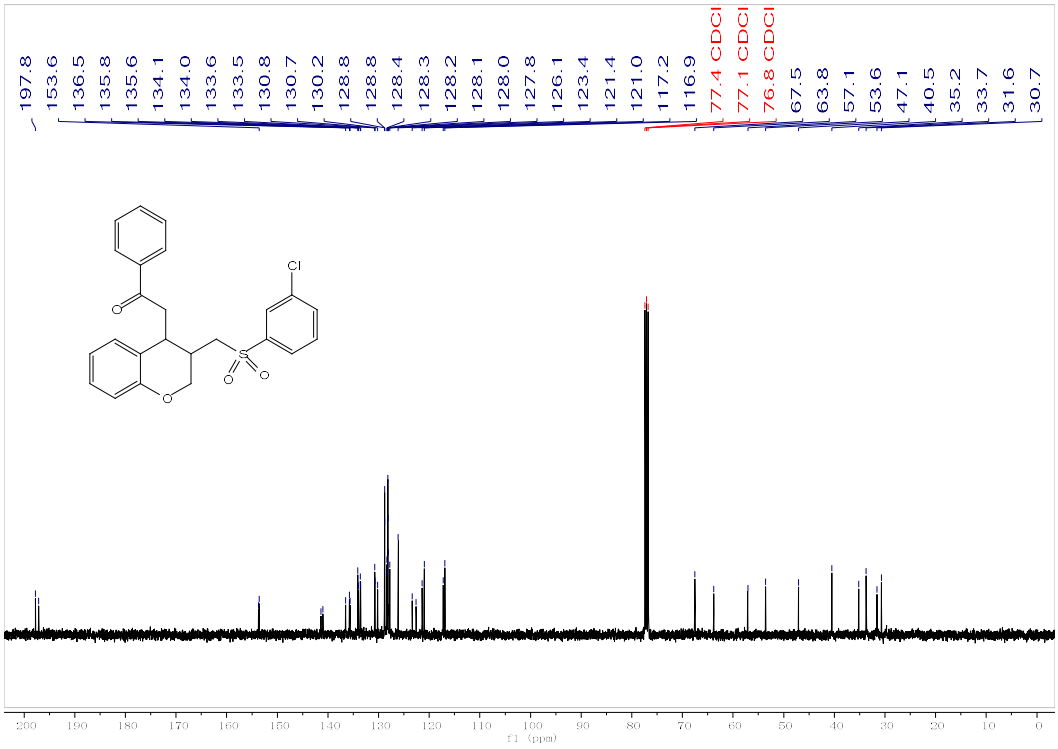
2-(3-(((4-chlorophenyl)sulfonyl)methyl)chroman-4-yl)-1-phenylethan-1-one (3p)



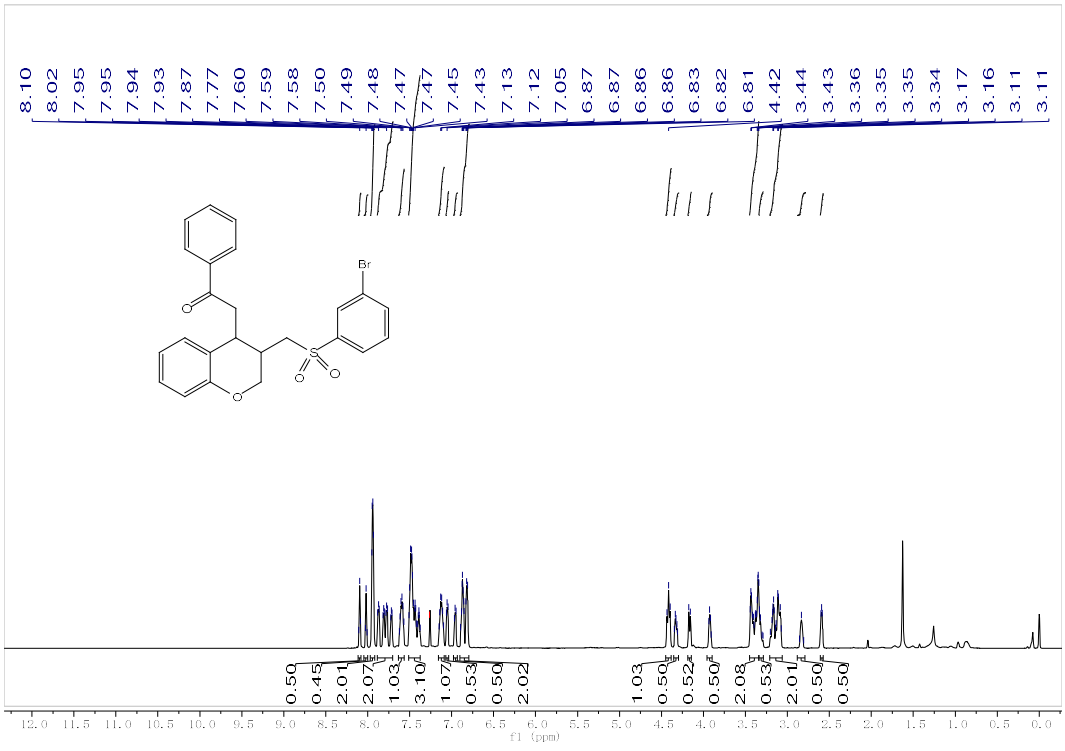


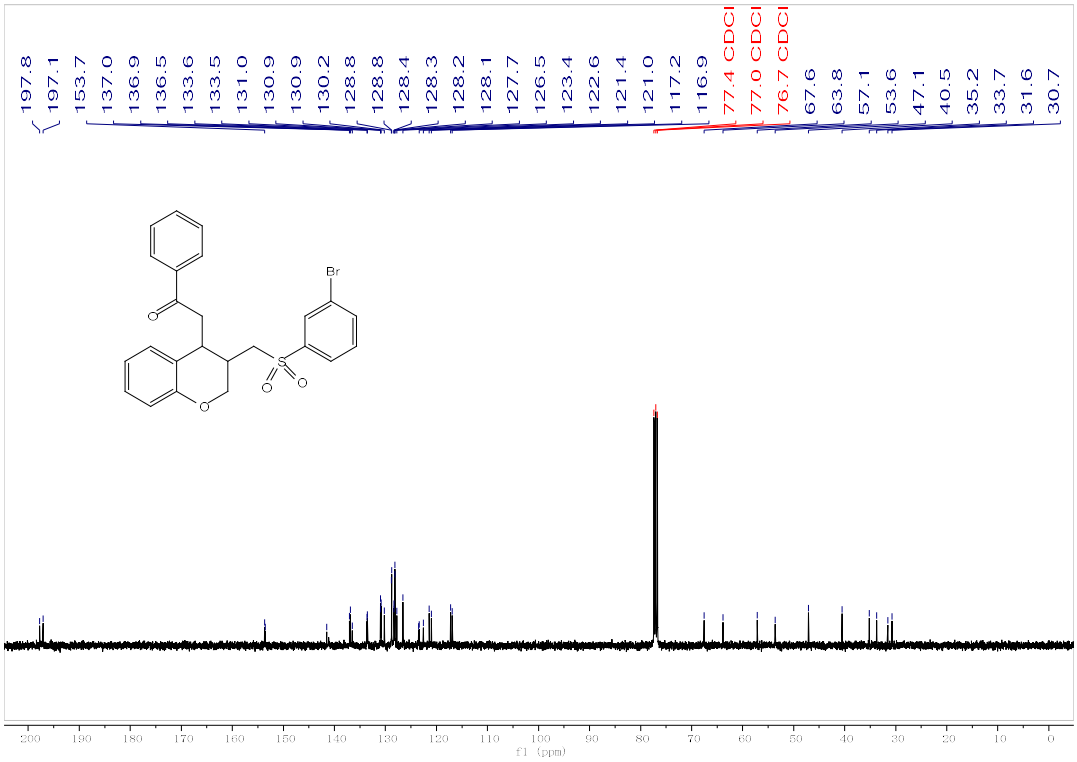
2-(3-(((3-chlorophenyl)sulfonyl)methyl)chroman-4-yl)-1-phenylethan-1-one (3q)



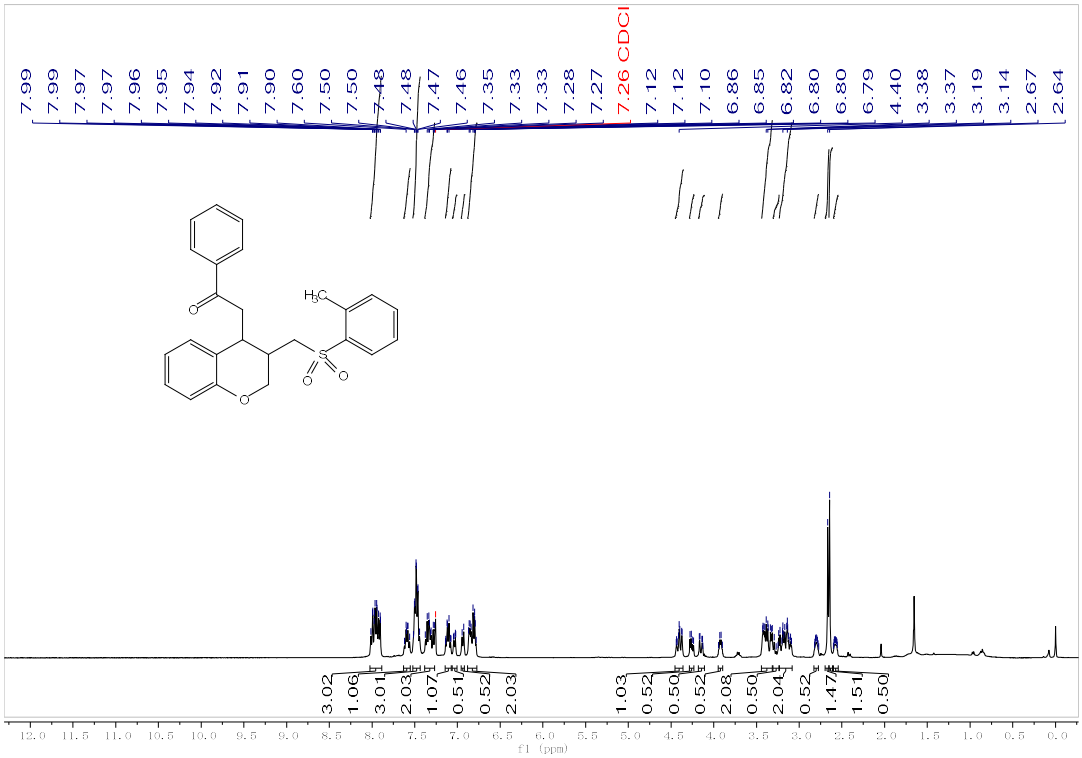


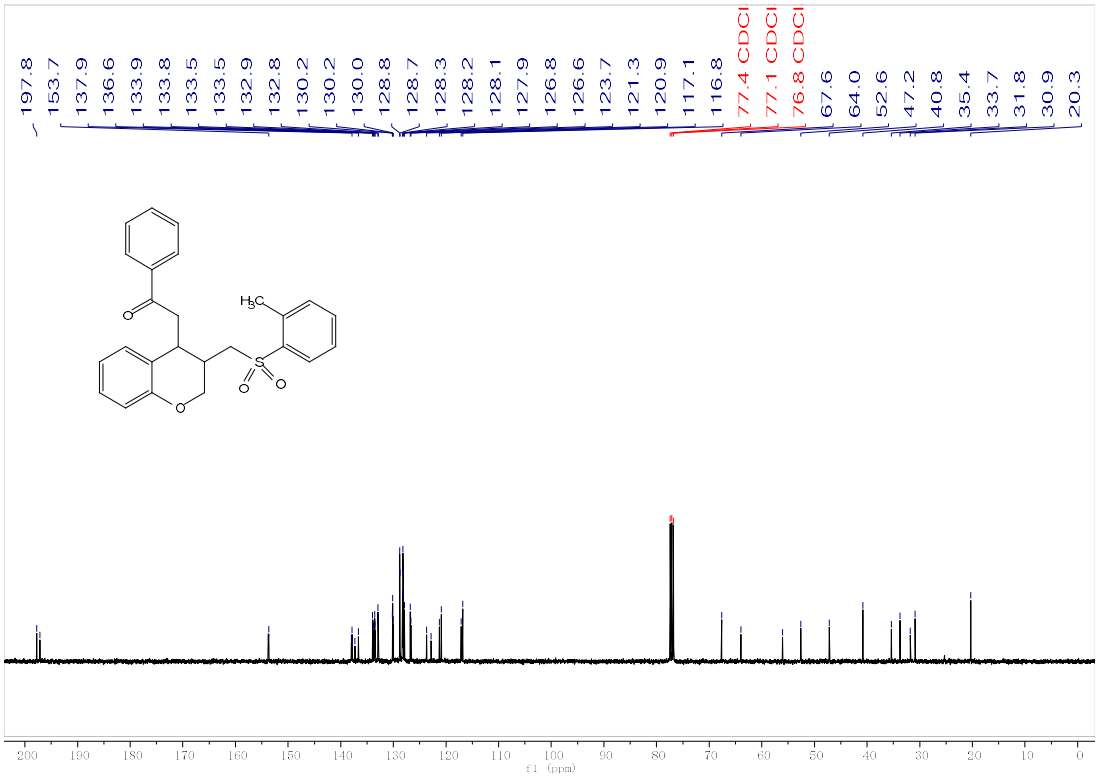
2-(3-(((3-bromophenyl)sulfonyl)methyl)chroman-4-yl)-1-phenylethan-1-one (3r)



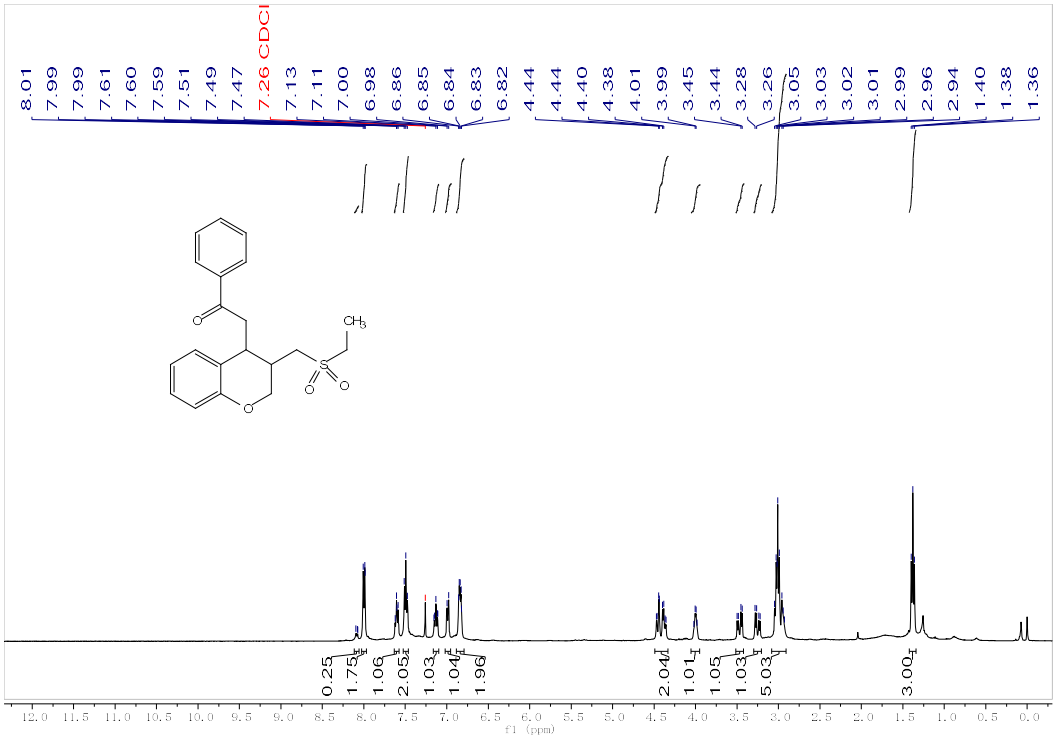


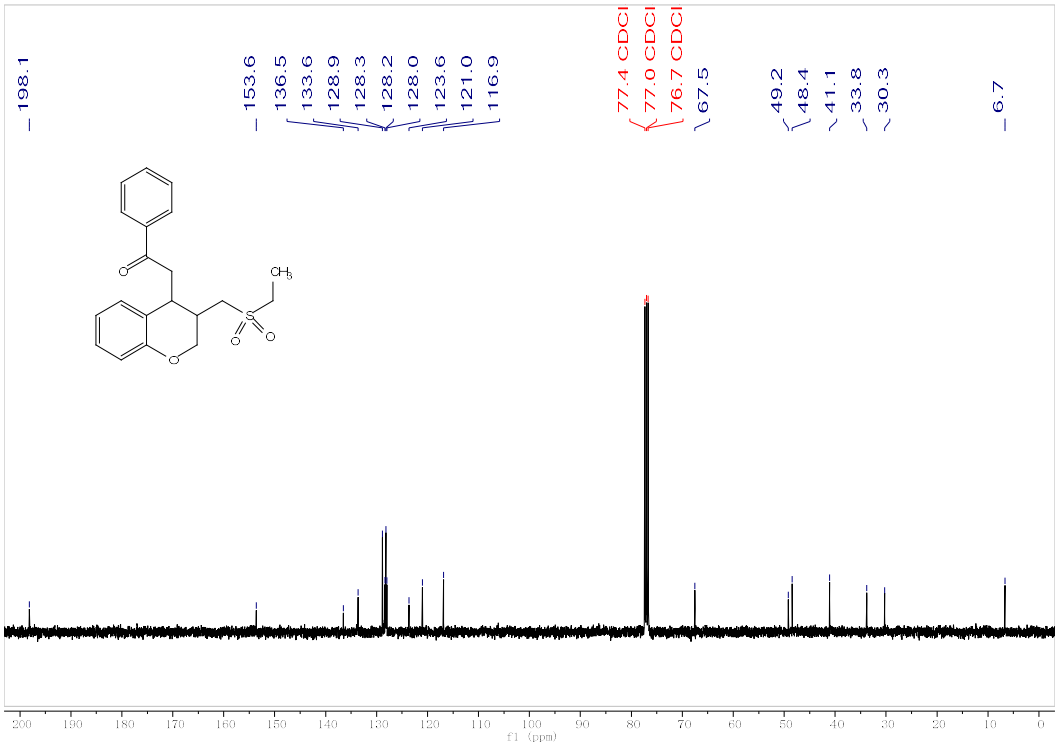
1-phenyl-2-(3-((o-tolylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3s)



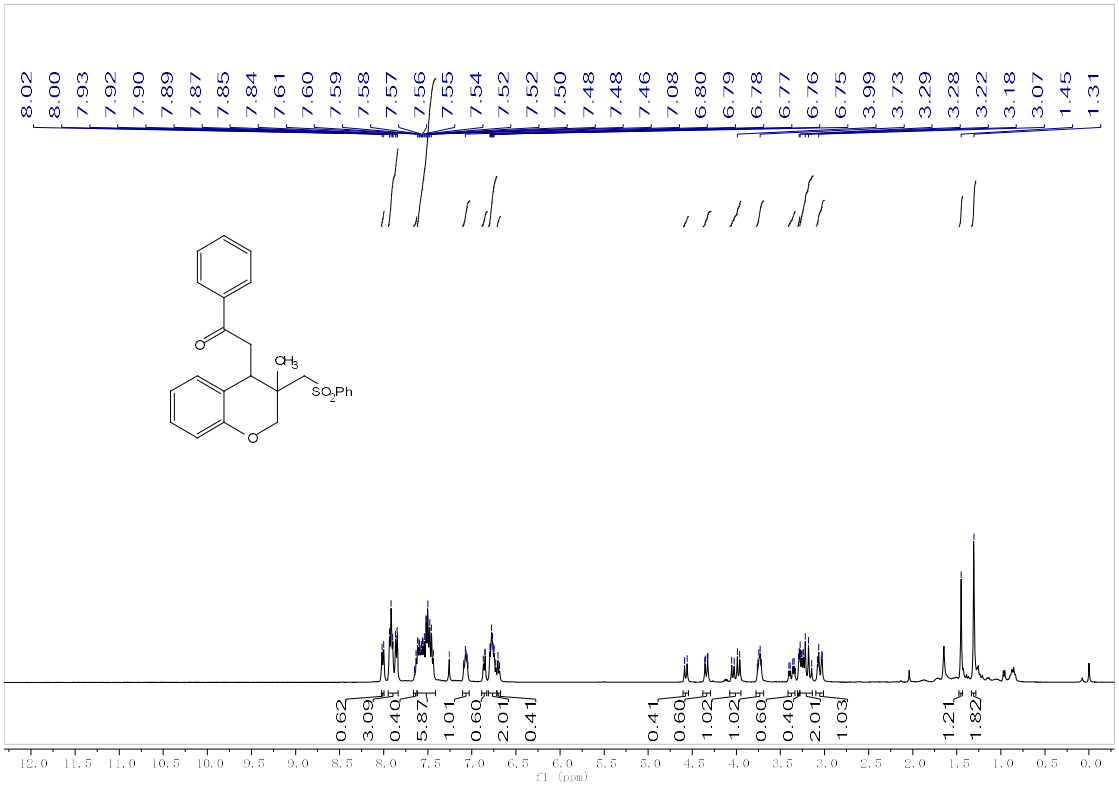


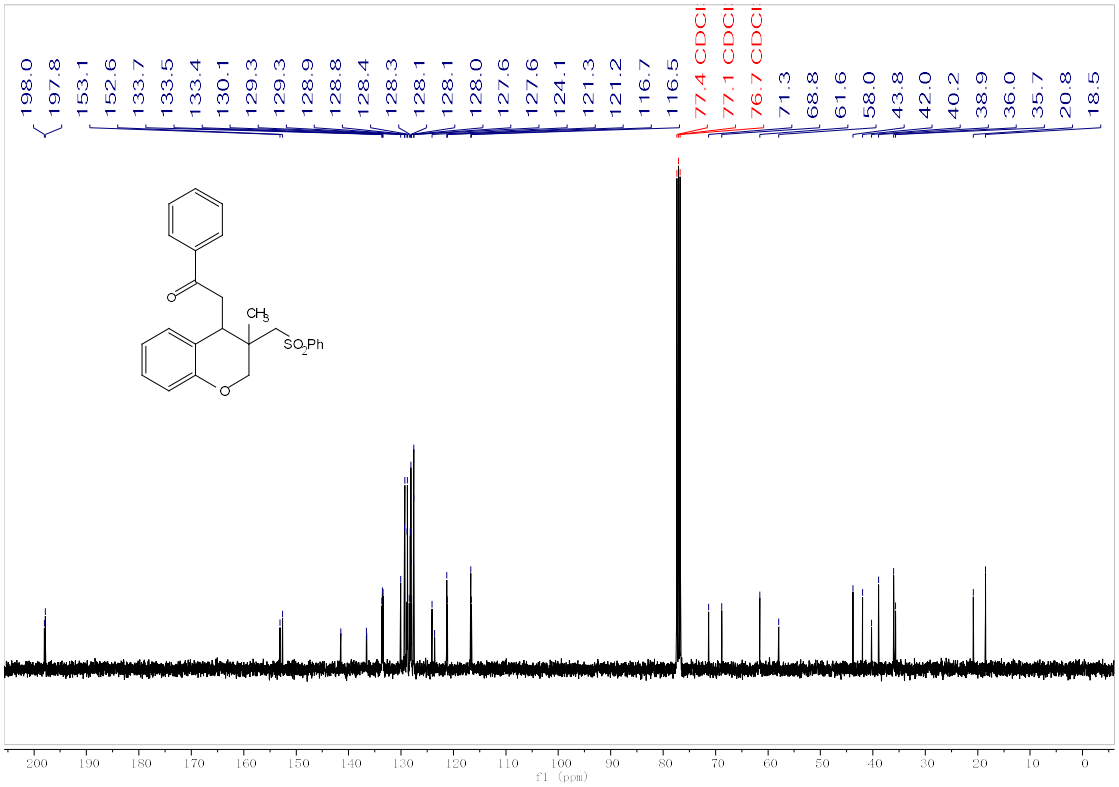
1-phenyl-2-(3-((o-tolylsulfonyl)methyl)chroman-4-yl)ethan-1-one (3t)





2-(3-methyl-3-((phenylsulfonyl)methyl)chroman-4-yl)-1-phenylethan-1-one (3u)





1-(4-methoxyphenyl)-2-(4-((phenylsulfonyl)methyl)-2,3,4,5-tetrahydrobenzo[b]oxepin-5-yl)ethan-1-one (3v)