Supporting information

Direct access to functionalized 4-nitromethyl-chromenes via a domino reaction under catalyst-free conditions

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I. General information

^{1}H and ^{13}C NMR spectra were determined in $CDCl_3$ on 400, 500 or 600 MHz NMR spectrometer and chemical shifts were reported in ppm from internal TMS (δ). High-resolution mass spectral analysis (HRMS) were measured using ESI ionization. Column chromatography was performed with 200-300 mesh silica gel. All of the reagents were used directly as obtained commercially unless otherwise noted. a, β-unsaturated ketones were prepared according to reported procedures.

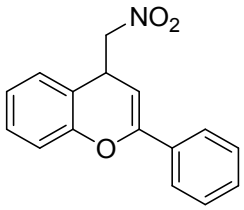
II. Experimental procedures

Typical procedure for preparation of 4-(nitromethyl)-2-phenyl-4H-chromene

0.25mmol (E)-3-(2-hydroxyphenyl)-1-phenylprop-2-en-1-one (**1a**) and 18mmol (1mL) CH_3NO_2 was added to solvent of 4mL EtOH and the reaction mixture was stirred overnight at 110℃ under air atmosphere. After the completion of the reaction as monitored by TLC, the reaction mixture was cooled to room temperature. And the reaction solution was concentrated under vacuum to obtain crude mixture. Then the crude mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate).

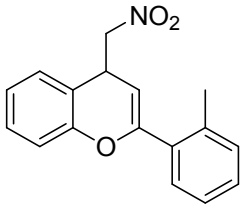
III. NMR data and HRMS data

2a 4-(nitromethyl)-2-phenyl-4*H*-chromene



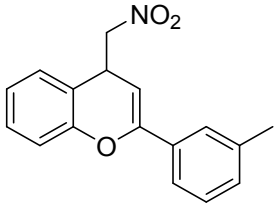
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.48 – 7.40 (m, 3H), 7.34 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.22 – 7.12 (m, 3H), 5.57 (d, *J* = 4.6 Hz, 1H), 4.65 – 4.47 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 151.4, 133.4, 129.3, 129.1, 128.5 (2C), 128.2, 125.0 (2C), 124.3, 118.5, 117.3, 94.9, 81.7, 34.2. HRMS (ESI, m/z): calcd for $C_{16}H_{14}NO_3$ $[M+H]^+$ 268.0968, found 268.0970.

2b 4-(nitromethyl)-2-(o-tolyl)-4*H*-chromene



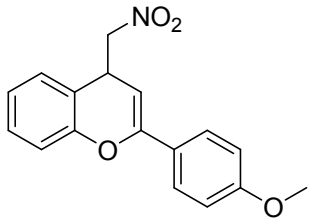
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.26 (m, 4H), 7.23 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.17 (td, *J* = 7.6, 1.0 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 5.17 (d, *J* = 4.7 Hz, 1H), 4.62 (ddd, *J* = 19.3, 11.7, 6.9 Hz, 2H), 4.54 – 4.45 (m, 1H), 2.45 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 151.9, 136.8, 134.3, 130.6, 129.4, 129.3, 129.1, 128.2, 125.8, 124.3, 118.5, 117.2, 98.5, 81.9, 34.5, 20.3. HRMS (ESI, m/z): calcd for $C_{17}H_{16}NO_3$ $[M+H]^+$ 282.1125, found 282.1129.

2c 4-(nitromethyl)-2-(m-tolyl)-4*H*-chromene



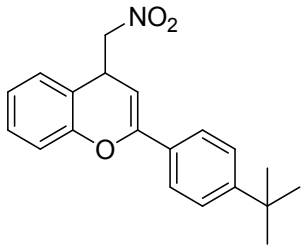
^{1}H NMR (500 MHz, CDCl3) δ 7.52 (d, J = 7.8 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.23 (d, J = 7.3 Hz, 1H), 7.21 – 7.17 (m, 2H), 7.16 – 7.12 (m, 1H), 5.54 (d, J = 4.6 Hz, 1H), 4.61 (dd, J = 11.4, 5.5 Hz, 1H), 4.56 – 4.47 (m, 2H), 2.43 (s, 3H).^{13}C NMR (126 MHz, CDCl3) δ 151.8, 151.6, 138.1, 133.4, 130.0, 129.1, 128.4, 128.1, 125.7, 124.2, 122.2, 118.5, 117.3, 94.7, 81.8, 34.3, 21.5. HRMS (ESI, m/z): calcd for $C_{17}H_{16}NO_3$ $[M+H]^+$ 282.1125, found 282.1127.

2d 2-(4-methoxyphenyl)-4-(nitromethyl)-4*H*-chromene



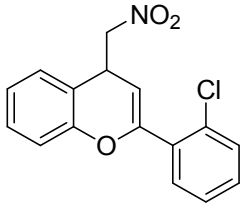
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.61 (m, 2H), 7.36 – 7.30 (m, 1H), 7.16 (tdd, *J* = 14.8, 10.7, 4.3 Hz, 3H), 6.95 (dd, *J* = 9.3, 2.5 Hz, 2H), 5.43 (d, *J* = 4.8 Hz, 1H), 4.60 (dd, *J* = 11.7, 5.9 Hz, 1H), 4.56 – 4.44 (m, 2H), 3.87 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 160.4, 151.8, 151.2, 129.0, 128.1, 126.4 (2C), 126.0, 124.1, 118.6, 117.3, 113.8 (2C), 93.0, 81.8, 55.4, 34.3. HRMS (ESI, m/z): calcd for $C_{17}H_{16}NO_4$ $[M+H]^+$ 298.1074, found 298.1077.

2e 2-(4-(tert-butyl)phenyl)-4-(nitromethyl)-4*H*-chromene



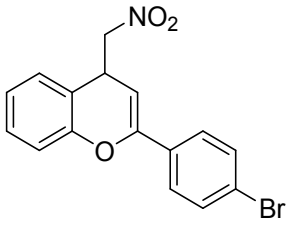
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.53 (dd, *J* = 16.7, 8.3 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.35 – 7.31 (m, 1H), 7.21 – 7.11 (m, 3H), 5.52 (d, *J* = 4.6 Hz, 1H), 4.61 (dd, *J* = 11.3, 5.5 Hz, 1H), 4.55 – 4.45 (m, 2H), 1.38 (s, 9H).^{13}C NMR (151 MHz, $CDCl_3$) δ 152.5, 151.9, 151.5, 130.6, 129.0, 128.1, 125.4 (2C), 124.8 (2C), 124.1, 118.6, 117.3, 94.1, 81.8, 34.7, 34.3, 31.3 (3C). HRMS (ESI, m/z): calcd for $C_{20}H_{22}NO_3$ $[M+H]^+$ 324.1594, found 324.1591.

2f 2-(2-chlorophenyl)-4-(nitromethyl)-4*H*-chromene



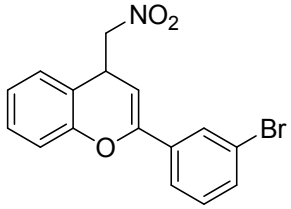
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 1H), 7.50 – 7.45 (m, 1H), 7.39 – 7.30 (m, 3H), 7.23 – 7.10 (m, 3H), 5.37 (d, *J* = 4.8 Hz, 1H), 4.70 – 4.56 (m, 2H), 4.51 (dt, *J* = 11.9, 6.0 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 150.6, 133.4, 133.1, 130.7, 130.4, 130.3, 129.2, 128.2, 126.8, 124.4, 118.4, 117.3, 100.3, 81.6, 34.4. HRMS (ESI, m/z): calcd for $C_{16}H_{13}ClNO_3$ $[M+H]^+$ 302.0578, found 302.0575.

2g 2-(2-bromophenyl)-4-(nitromethyl)-4*H*-chromene



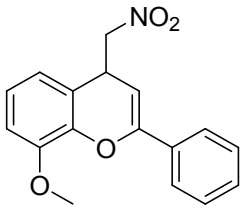
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 4H), 7.36 – 7.31 (m, 1H), 7.22 – 7.12 (m, 3H), 5.55 (d, *J* = 4.7 Hz, 1H), 4.66 – 4.44 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 150.5, 132.3, 131.6 (2C), 129.2, 128.1, 126.6 (2C), 124.4, 123.4, 118.3, 117.3, 95.3, 81.6, 34.2. HRMS (ESI, m/z): calcd for $C_{16}H_{13}BrNO_3$ $[M+H]^+$ 346.0073, found 346.0070.

2h 2-(3-bromophenyl)-4-(nitromethyl)-4*H*-chromene



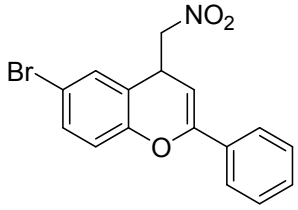
^{1}H NMR (500 MHz, CDCl3) δ 7.87 (t, J = 1.8 Hz, 1H), 7.63 (dd, J = 7.9, 1.1 Hz, 1H), 7.53 (ddd, J = 7.9, 1.7, 0.8 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.21 – 7.13 (m, 3H), 5.57 (d, J = 4.7 Hz, 1H), 4.61 (dd, J = 11.6, 5.6 Hz, 1H), 4.51 (ddd, J = 12.4, 8.0, 5.3 Hz, 2H).^{13}C NMR (126 MHz, CDCl3) δ 151.5, 150.0, 135.4, 132.2, 130.0, 129.2, 128.1, 128.1, 124.5, 123.6, 122.7, 118.2, 117.3, 96.0, 81.6, 34.1. HRMS (ESI, m/z): calcd for $C_{16}H_{13}BrNO_3$ $[M+H]^+$ 346.0073, found 346.0076.

2j 8-methoxy-4-(nitromethyl)-2-phenyl-4*H*-chromene



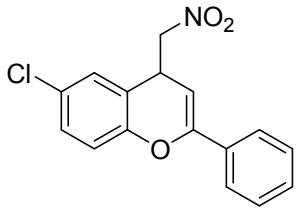
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.39 (tdd, *J* = 6.9, 4.6, 2.3 Hz, 3H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.88 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.74 (dd, *J* = 7.8, 0.9 Hz, 1H), 5.53 (d, *J* = 4.7 Hz, 1H), 4.59 – 4.41 (m, 3H), 3.92 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 147.6, 140.6, 132.3, 128.2, 127.4 (2C), 124.1 (2C), 122.9, 118.4, 118.4, 110.4, 93.6, 80.6, 55.2, 33.3. HRMS (ESI, m/z): calcd for $C_{17}H_{16}NO_4$ $[M+H]^+$ 298.1074, found 298.1076.

2k 6-bromo-4-(nitromethyl)-2-phenyl-4*H*-chromene



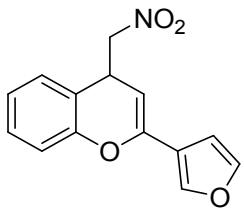
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.46 – 7.41 (m, 4H), 7.33 (d, *J* = 2.2 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 1H), 5.55 (d, *J* = 4.9 Hz, 1H), 4.60 (dd, *J* = 12.2, 5.8 Hz, 1H), 4.53 (dd, *J* = 12.2, 8.1 Hz, 1H), 4.45 (dt, *J* = 8.0, 5.4 Hz, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.3, 150.9, 132.9, 132.2, 130.8, 130.8, 129.5, 128.5, 125.1, 125.0, 120.5, 119.1, 116.3, 94.6, 81.4, 34.0. HRMS (ESI, m/z): calcd for $C_{16}H_{13}BrNO_3$ $[M+H]^+$ 346.0073, found 346.0071.

2l 6-chloro-4-(nitromethyl)-2-phenyl-4*H*-chromene



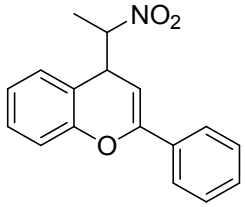
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.47 – 7.41 (m, 3H), 7.29 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.12 (d, *J* = 8.7 Hz, 1H), 5.54 (d, *J* = 4.9 Hz, 1H), 4.60 (dd, *J* = 12.2, 5.9 Hz, 1H), 4.53 (dd, *J* = 12.2, 8.0 Hz, 1H), 4.44 (dt, *J* = 7.8, 5.4 Hz, 1H).^{13}C NMR (151 MHz, CDCl3) δ 151.4, 150.4, 133.0, 129.5, 129.2, 128.9, 128.5 (2C), 127.8, 125.0 (2C), 120.1, 118.7, 94.4, 81.4, 34.1. HRMS (ESI, m/z): calcd for $C_{16}H_{13}ClNO_3$ $[M+H]^+$ 302.0578, found 302.0576.

2n 2-(furan-3-yl)-4-(nitromethyl)-4*H*-chromene



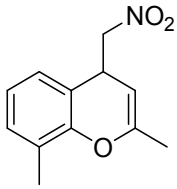
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 0.9 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.19 – 7.10 (m, 3H), 6.70 (d, *J* = 3.3 Hz, 1H), 6.49 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.58 (d, *J* = 4.8 Hz, 1H), 4.60 (dd, *J* = 12.0, 6.1 Hz, 1H), 4.54 (dd, *J* = 12.0, 7.8 Hz, 1H), 4.50 – 4.46 (m, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 151.2, 147.7, 144.1, 143.0, 129.1, 128.2, 124.3, 118.5, 117.3, 111.3, 107.8, 93.6, 81.6, 33.6. HRMS (ESI, m/z): calcd for $C_{14}H_{12}NO_4$ $[M+H]^+$ 258.0761, found 258.0758.

5a 4-(1-nitroethyl)-2-phenyl-4H-chromene



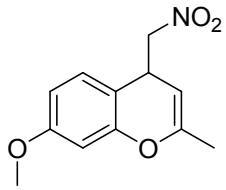
Dr. (5:3) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (ddd, *J* = 8.9, 7.6, 1.6 Hz, 3H), 7.49 – 7.41 (m, 5H), 7.38 – 7.32 (m, 2H), 7.16 (dddd, *J* = 30.2, 21.9, 7.7, 1.5 Hz, 5H), 5.57 (d, *J* = 5.5 Hz, 1H), 5.41 (d, *J* = 5.1 Hz, 1H), 4.83 – 4.74 (m, 1H), 4.67 – 4.58 (m, 1H), 4.51 (t, *J* = 5.0 Hz, 1H), 4.36 (t, *J* = 5.5 Hz, 1H), 1.47 (d, *J* = 6.7 Hz, 2H), 1.44 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 152.3, 152.2, 152.1, 133.4, 129.3 (2C), 129.0, 128.9, 128.8, 128.5 (2C), 128.1, 125.1 (2C), 125.1 (2C), 124.3, 124.1, 119.0, 118.1, 117.2, 117.0, 95.6, 92.8, 87.7, 87.5, 40.3, 39.6, 14.6, 13.5. HRMS (ESI, m/z): calcd for $C_{17}H_{16}NO_3$ $[M+H]^+$ 282.1125, found 282.1123.

5b 2,8-dimethyl-4-(nitromethyl)-4H-chromene



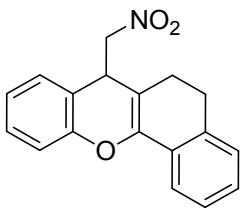
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.08 (m, 1H), 7.00 – 6.93 (m, 2H), 4.78 (dd, *J* = 4.5, 0.9 Hz, 1H), 4.46 (ddd, *J* = 19.9, 11.7, 7.1 Hz, 2H), 4.26 (dt, *J* = 6.7, 5.4 Hz, 1H), 2.28 (s, 3H), 1.99 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 150.8, 150.0, 130.1, 126.2, 125.6, 123.2, 117.8, 94.7, 82.2, 34.3, 19.4, 15.8. .

5c 7-methoxy-2-methyl-4-(nitromethyl)-4H-chromene



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.6 Hz, 1H), 6.65 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.52 (d, *J* = 2.6 Hz, 1H), 4.76 (dd, *J* = 4.4, 0.9 Hz, 1H), 4.43 (ddd, *J* = 19.6, 11.7, 7.0 Hz, 2H), 4.20 (dt, *J* = 6.7, 5.7 Hz, 1H), 3.80 (s, 3H), 1.95 (t, *J* = 1.0 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 152.5, 150.5, 128.7, 110.7, 110.3, 101.7, 95.0, 82.1, 55.4, 33.5, 19.4.

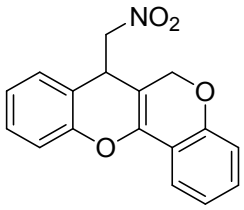
5d 7-(nitromethyl)-6,7-dihydro-5H-benzo[c]xanthene



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.36 – 7.25 (m, 3H), 7.23 – 7.16 (m, 3H), 7.15

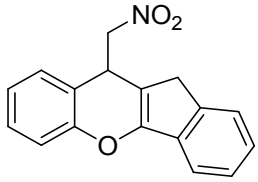
– 7.09 (m, 1H), 4.60 (dd, *J* = 11.5, 5.4 Hz, 1H), 4.52 (dd, *J* = 11.5, 7.2 Hz, 1H), 4.36 – 4.27 (m, 1H), 2.93 (t, *J* = 7.9 Hz, 2H), 2.60 – 2.37 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 145.4, 135.9, 129.5, 129.0, 128.3, 128.0, 127.4, 126.6, 124.0, 121.6, 119.6, 117.0, 105.4, 80.1, 39.6, 28.0, 25.4. HRMS (ESI, m/z): calcd for $C_{18}H_{17}NO_3$ $[M+H]^+$ 295.1203, found 295.12006.

5e 7-(nitromethyl)-6,7-dihydrochromeno[4,3-b]chromene



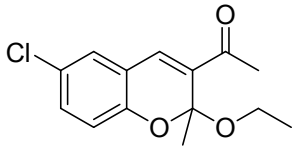
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.26 (td, *J* = 8.0, 1.6 Hz, 1H), 7.21 – 7.12 (m, 3H), 7.03 (td, *J* = 7.5, 1.0 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 4.93 (dd, *J* = 39.7, 13.3 Hz, 2H), 4.61 (dd, *J* = 12.1, 5.5 Hz, 1H), 4.52 (dd, *J* = 12.1, 6.9 Hz, 1H), 4.29 (t, *J* = 6.2 Hz, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 154.6, 151.3, 143.0, 130.4, 129.3, 128.2, 124.5, 122.0, 121.5, 118.9, 117.9, 117.3, 115.9, 99.1, 79.9, 66.5, 36.1. HRMS (ESI, m/z): calcd for $C_{17}H_{14}NO_4$ $[M+H]^+$ 296.0917, found 296.0919.

5f 10-(nitromethyl)-10,11-dihydroindeno[1,2-b]chromene



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.28 – 7.25 (m, 1H), 7.23 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.20 – 7.15 (m, 1H), 4.82 (t, *J* = 6.3 Hz, 1H), 4.73 – 4.66 (m, 2H), 3.41 (dd, *J* = 84.8, 21.7 Hz, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 151.9, 150.5, 141.2, 137.0, 129.1, 128.8, 126.7, 126.2, 124.3, 124.2, 118.6, 118.0, 117.9, 110.1, 81.4, 36.5, 35.0. HRMS (ESI, m/z): calcd for $C_{17}H_{14}NO_3$ $[M+H]^+$ 289.0968, found 289.0971.

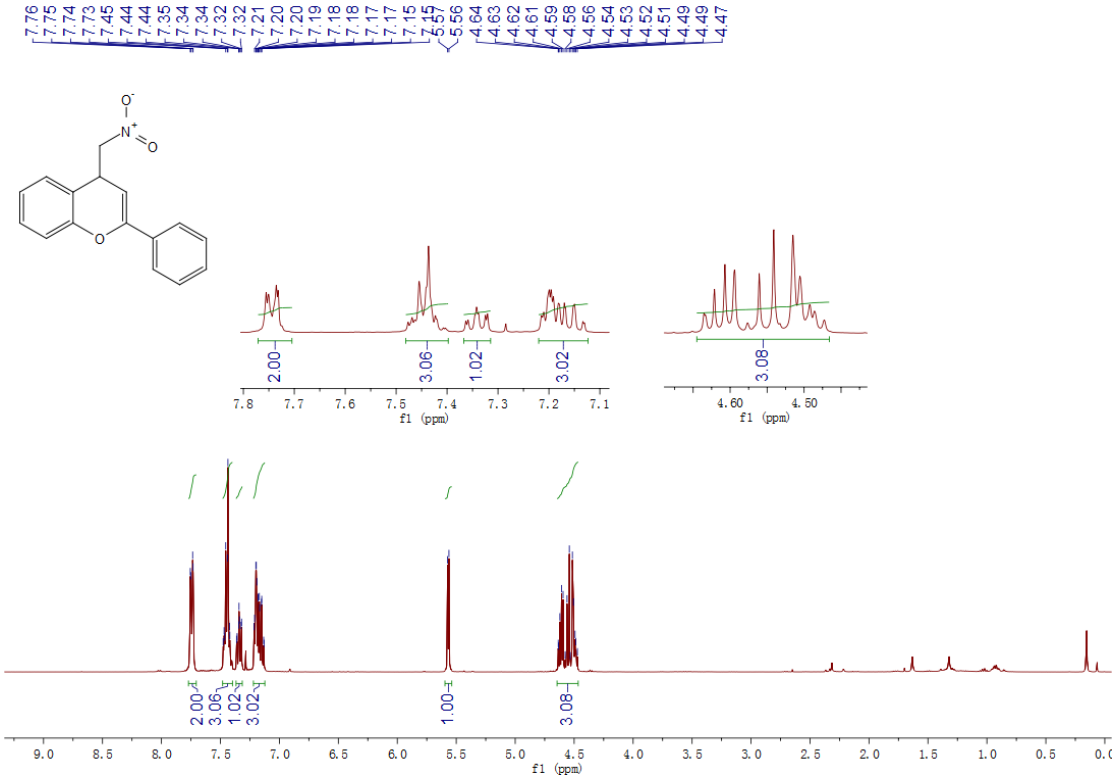
e 1-(6-chloro-2-ethoxy-2-methyl-2H-chromen-3-yl)ethanone

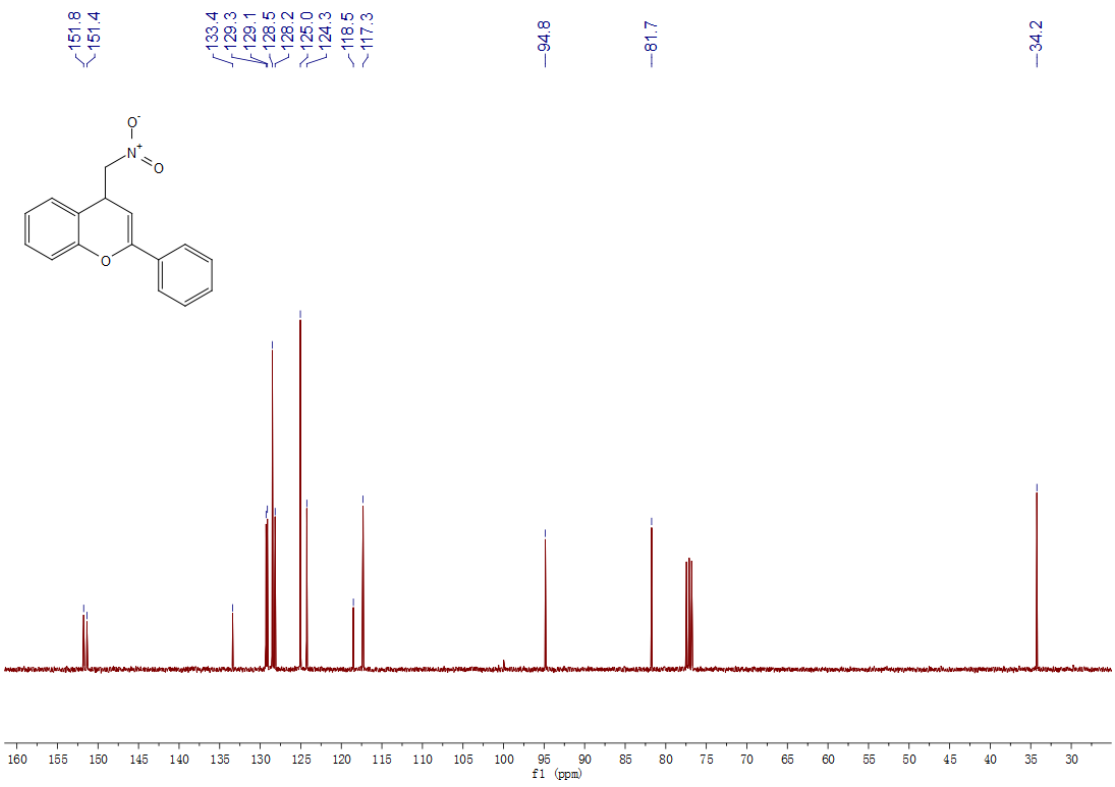


^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.30 – 7.21 (m, 2H), 6.89 (d, *J* = 8.6 Hz, 1H), 3.60 – 3.44 (m, 2H), 2.47 (s, 3H), 1.91 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 195.7, 152.3, 134.2, 133.7, 132.1, 128.0, 126.1, 120.0, 117.5, 101.7, 58.5, 27.3, 25.5, 15.2.

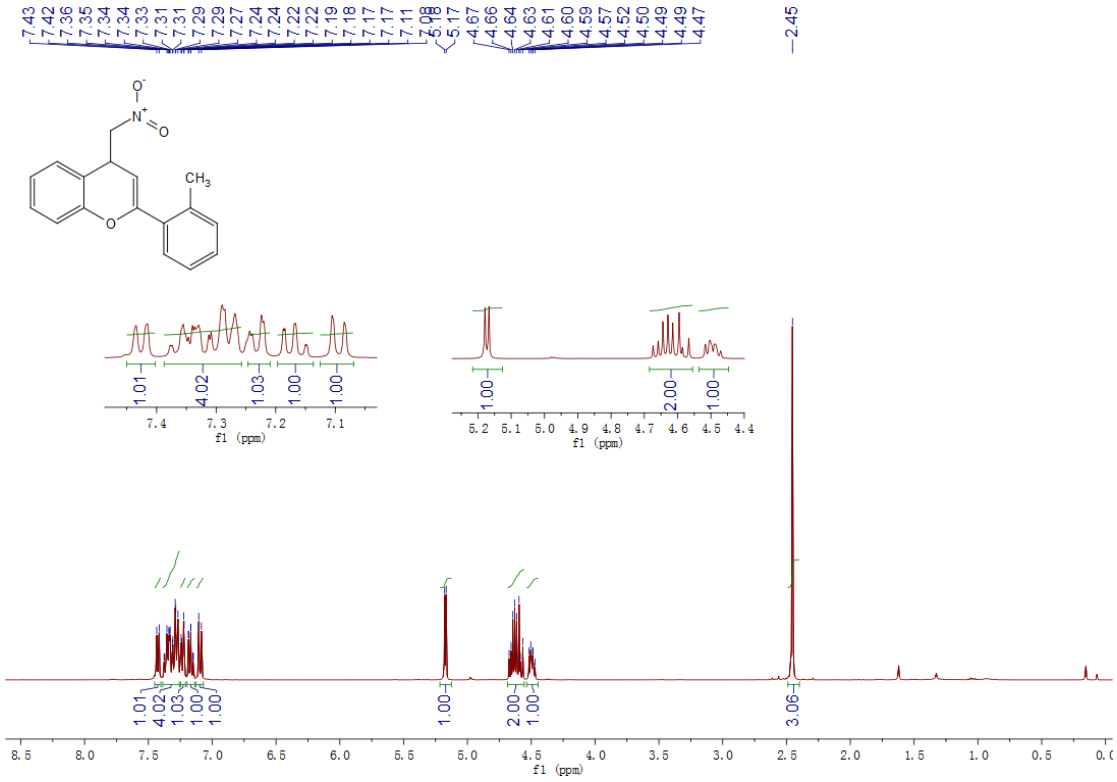
Ⅳ. ^{1}H and ^{13}C NMR spectra

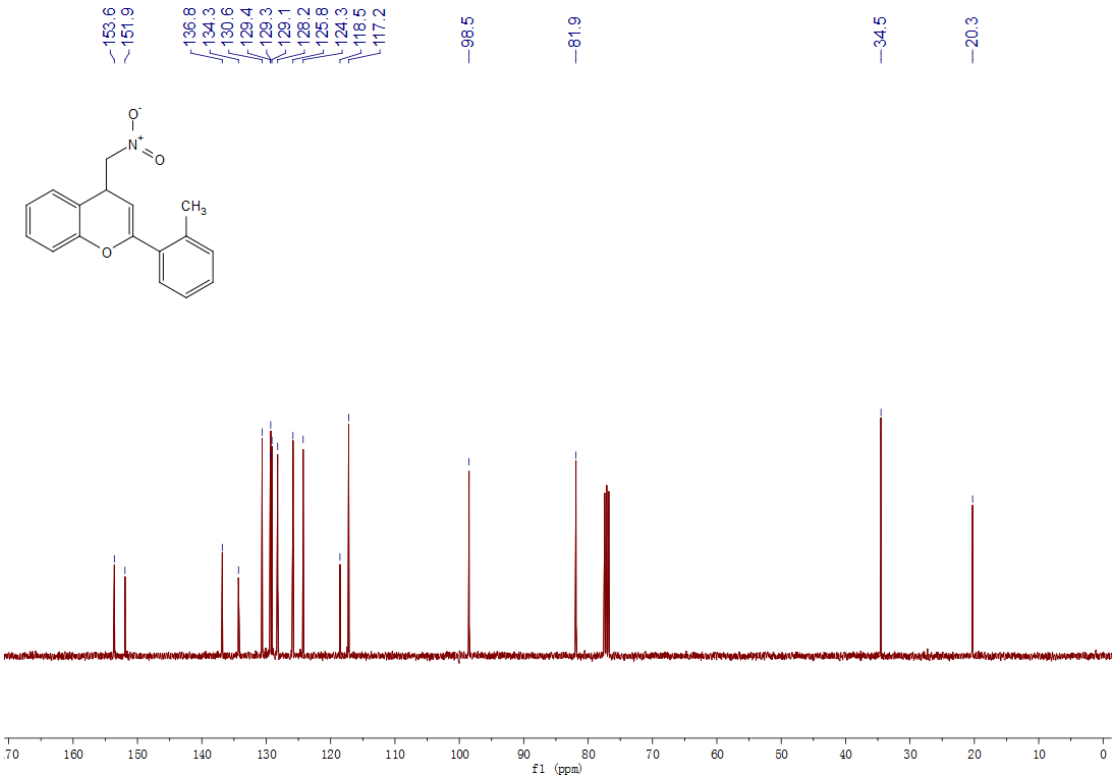
2a 4-(nitromethyl)-2-phenyl-4H-chromene



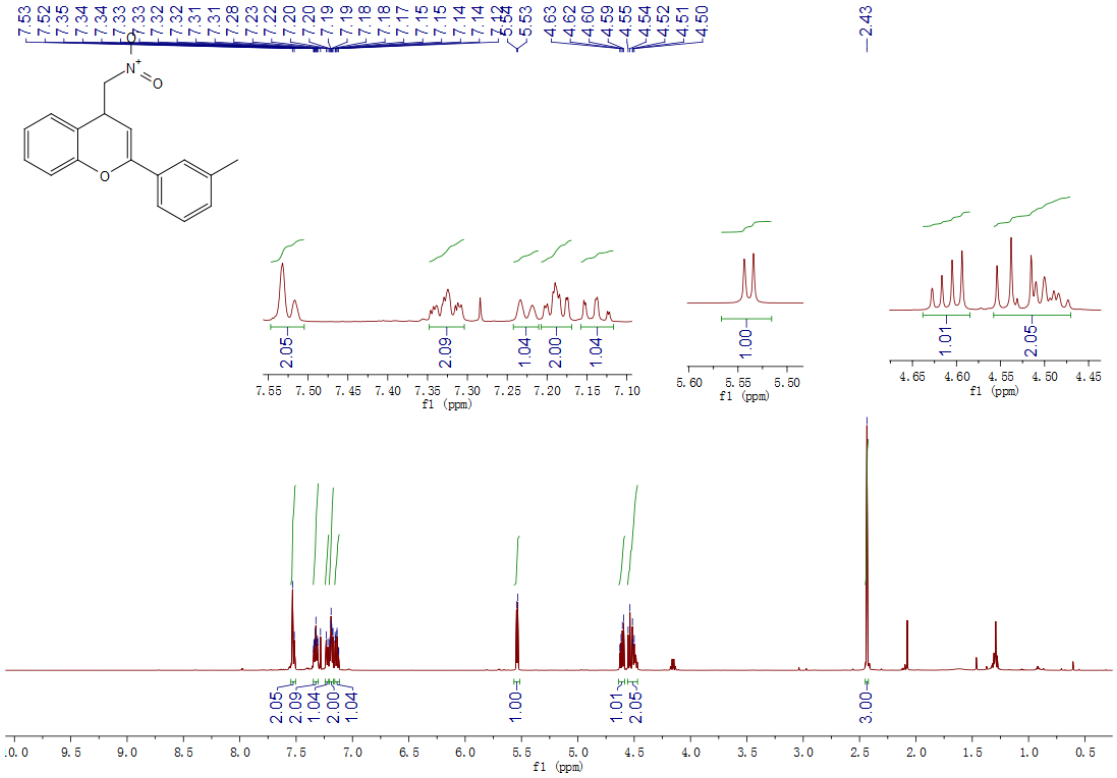


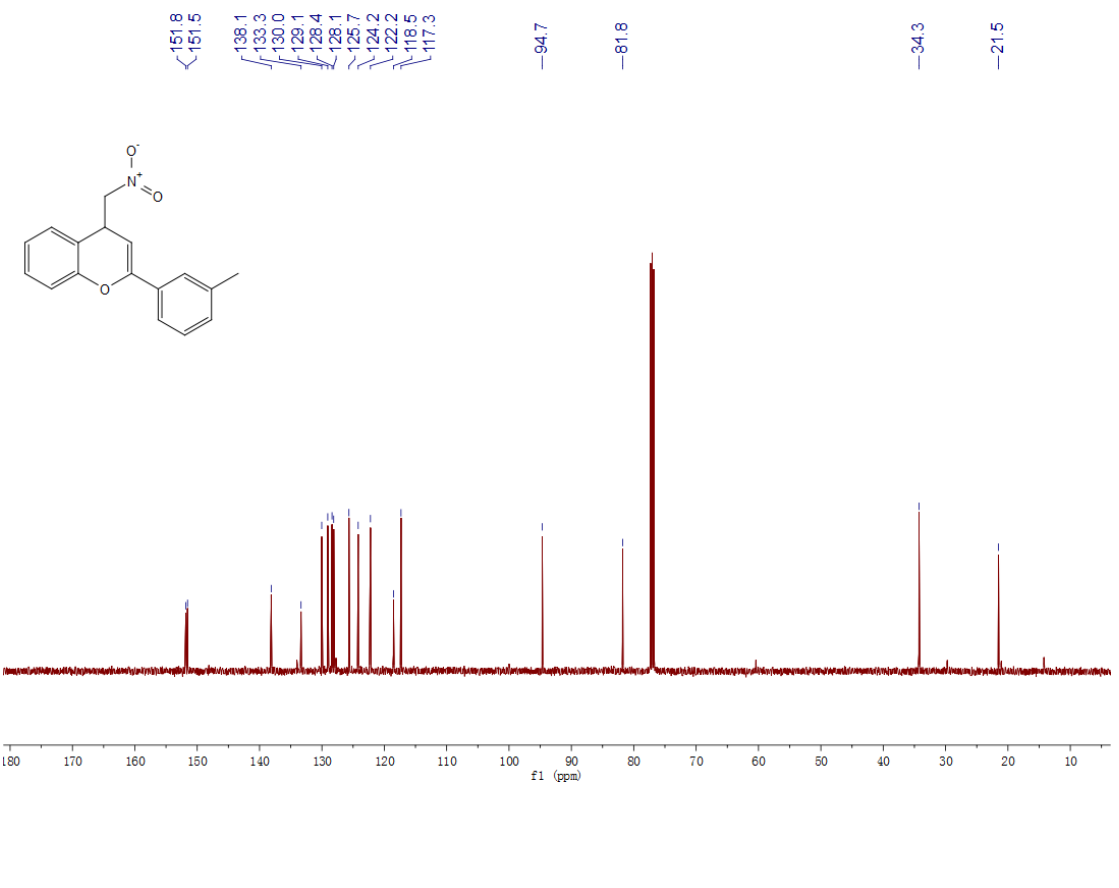
2b 4-(nitromethyl)-2-(o-tolyl)-4H-chromene



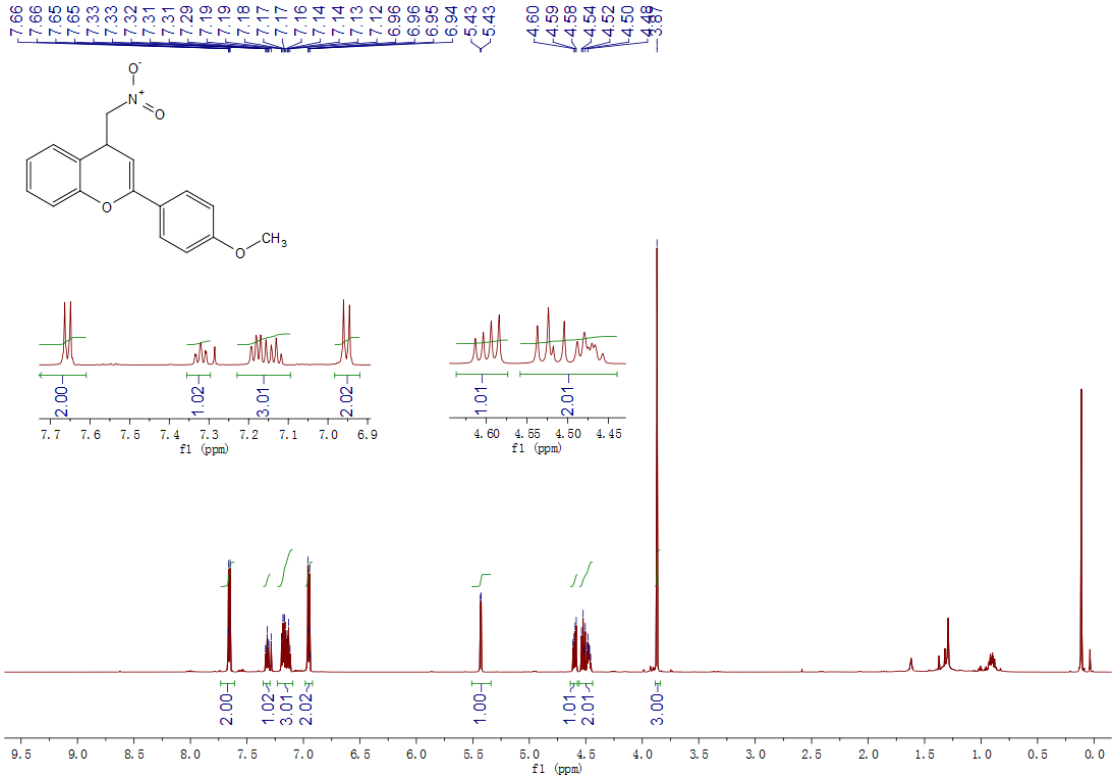


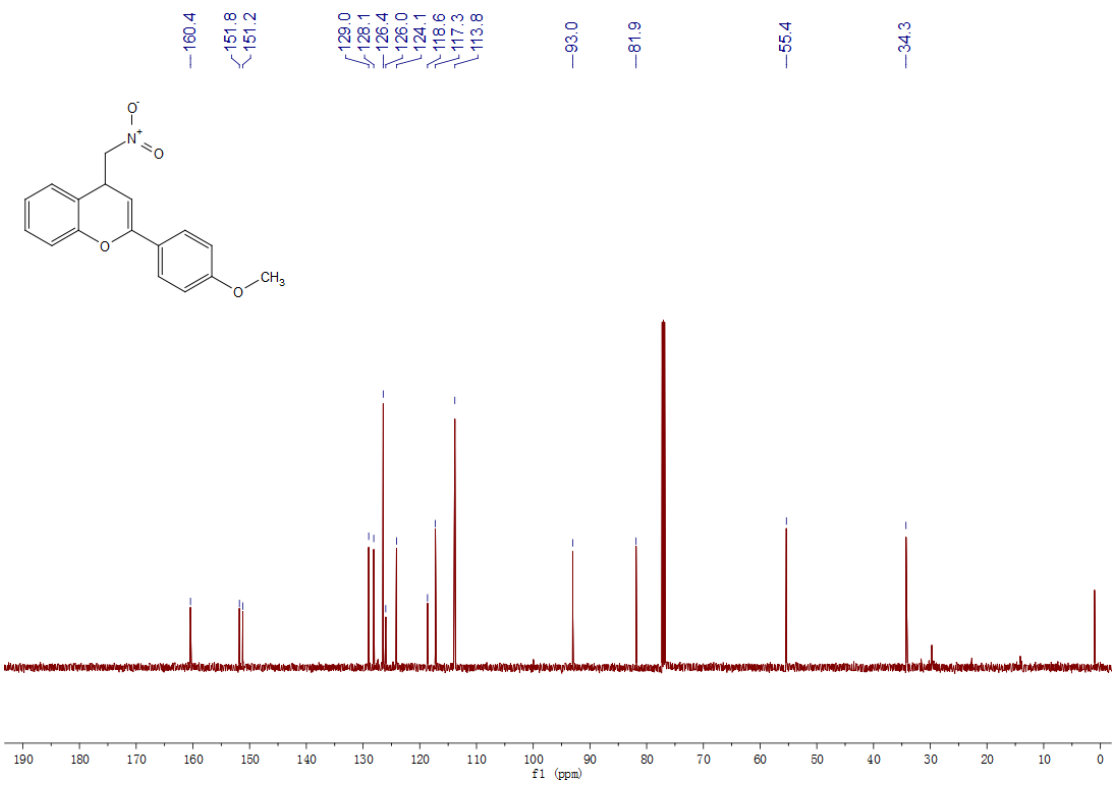
2c 4-(nitromethyl)-2-(m-tolyl)-4H-chromene



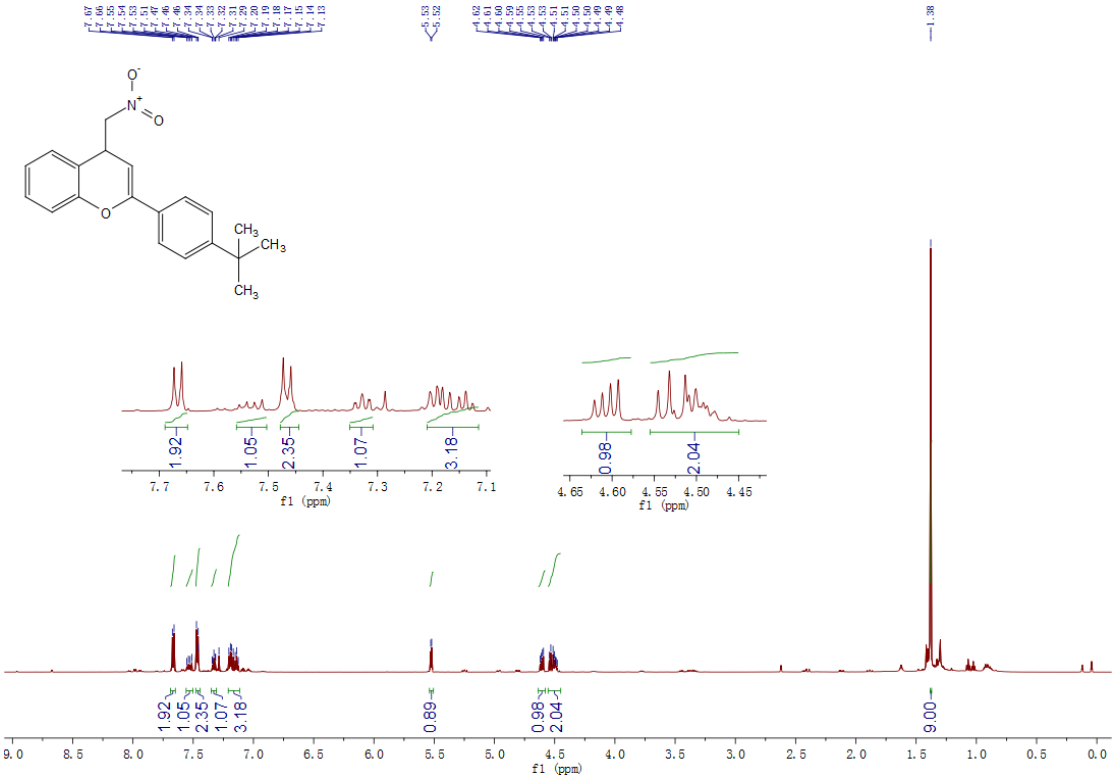


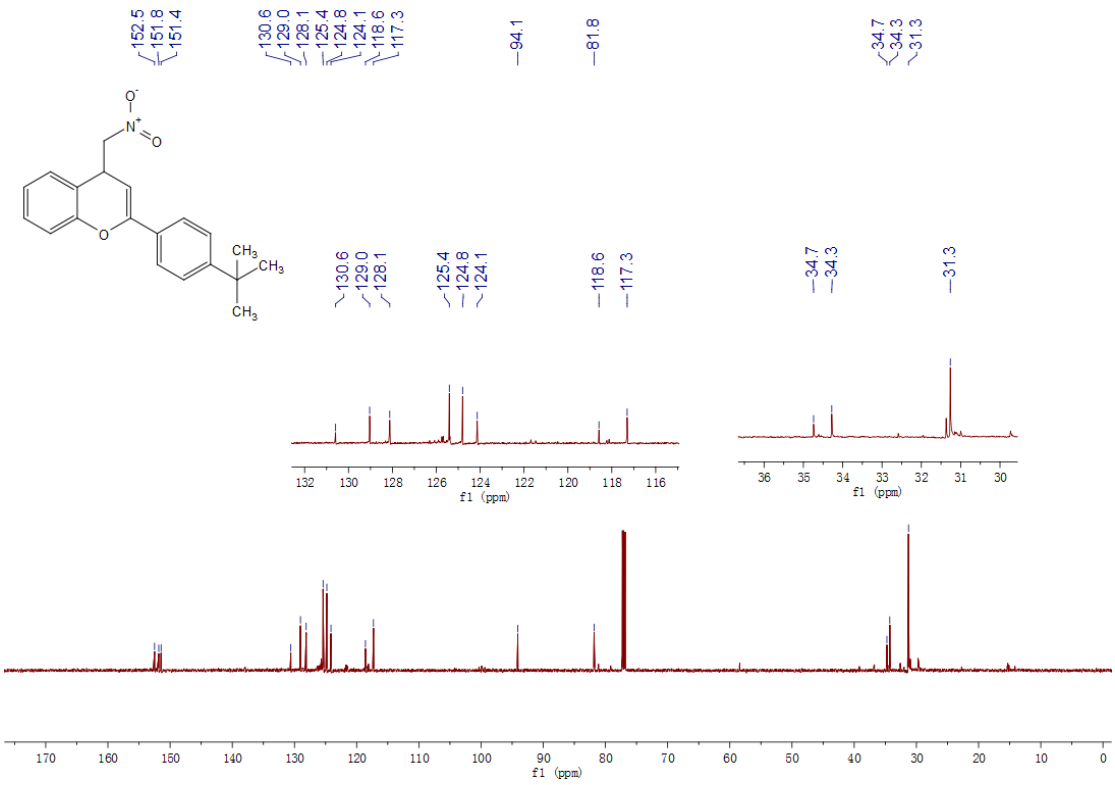
2d 2-(4-methoxyphenyl)-4-(nitromethyl)-4H-chromene





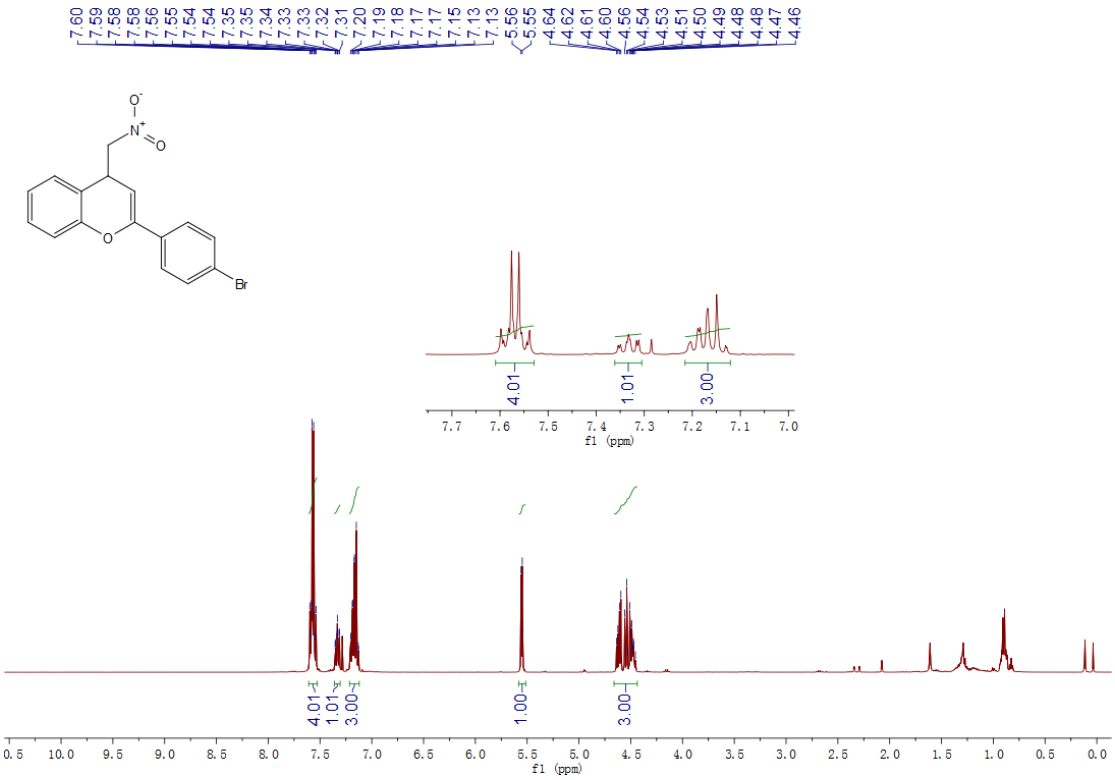
2e 2-(4-(tert-butyl)phenyl)-4-(nitromethyl)-4H-chromene

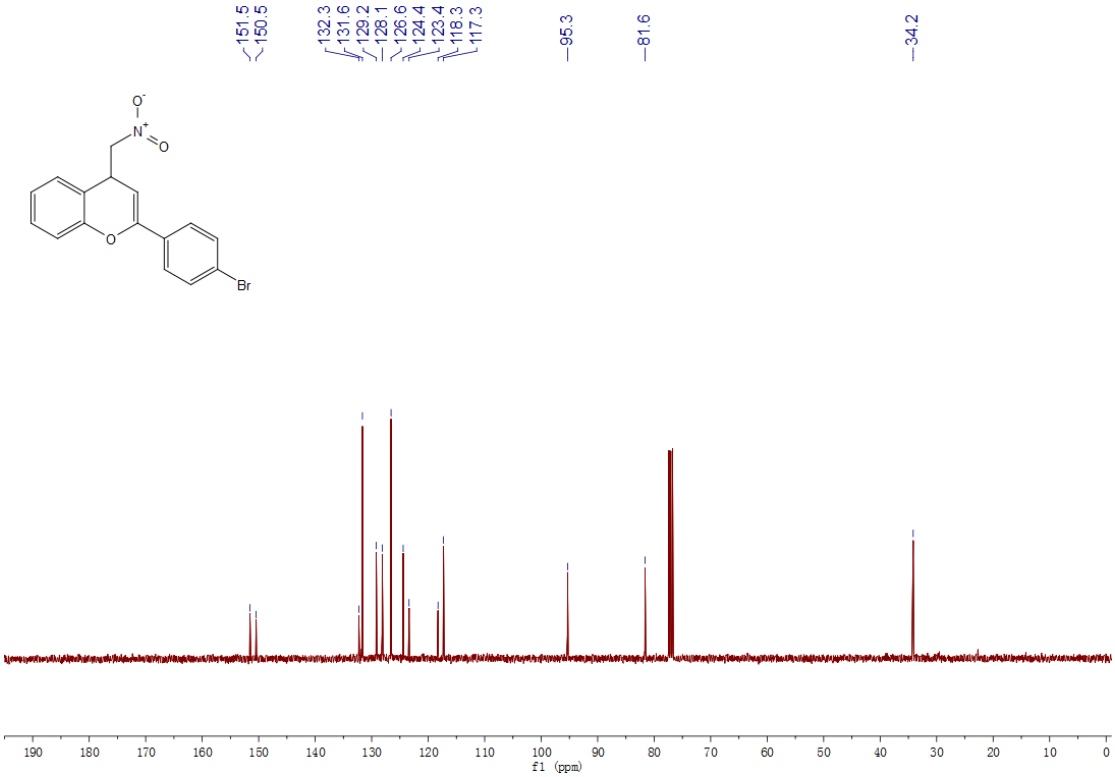




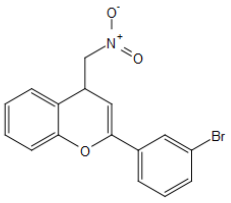
2f 2-(2-chlorophenyl)-4-(nitromethyl)-4H-chromene

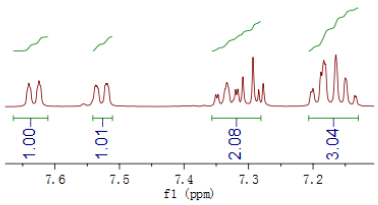
2g 2-(4-bromophenyl)-4-(nitromethyl)-4H-chromene

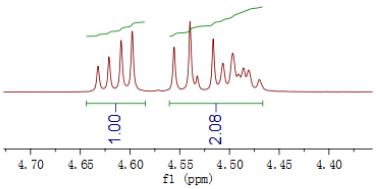


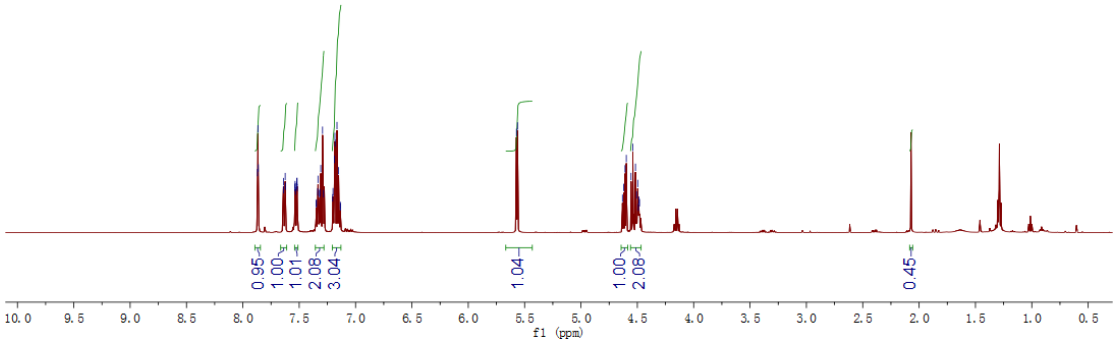


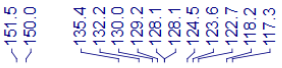
2h 2-(3-bromophenyl)-4-(nitromethyl)-4H-chromene

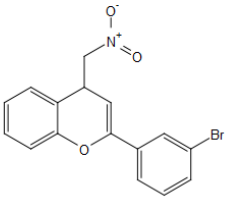


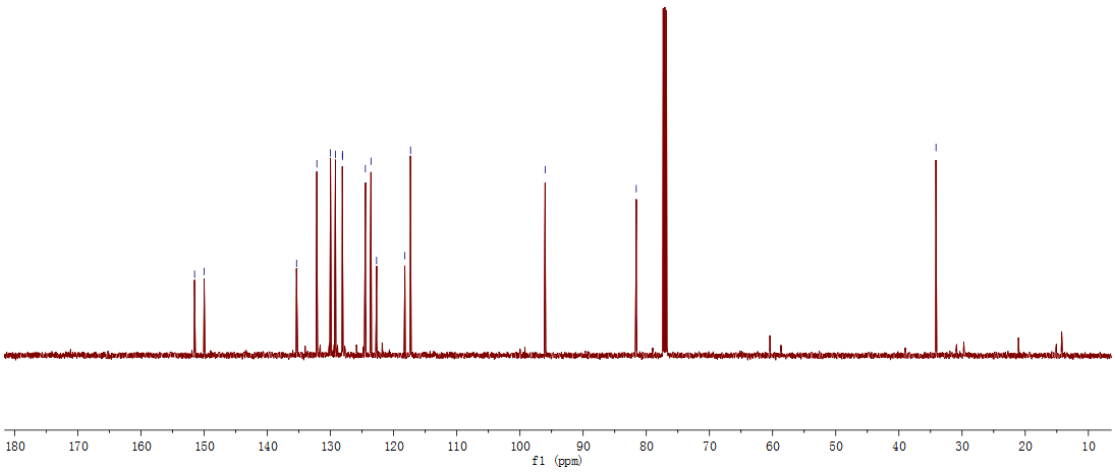




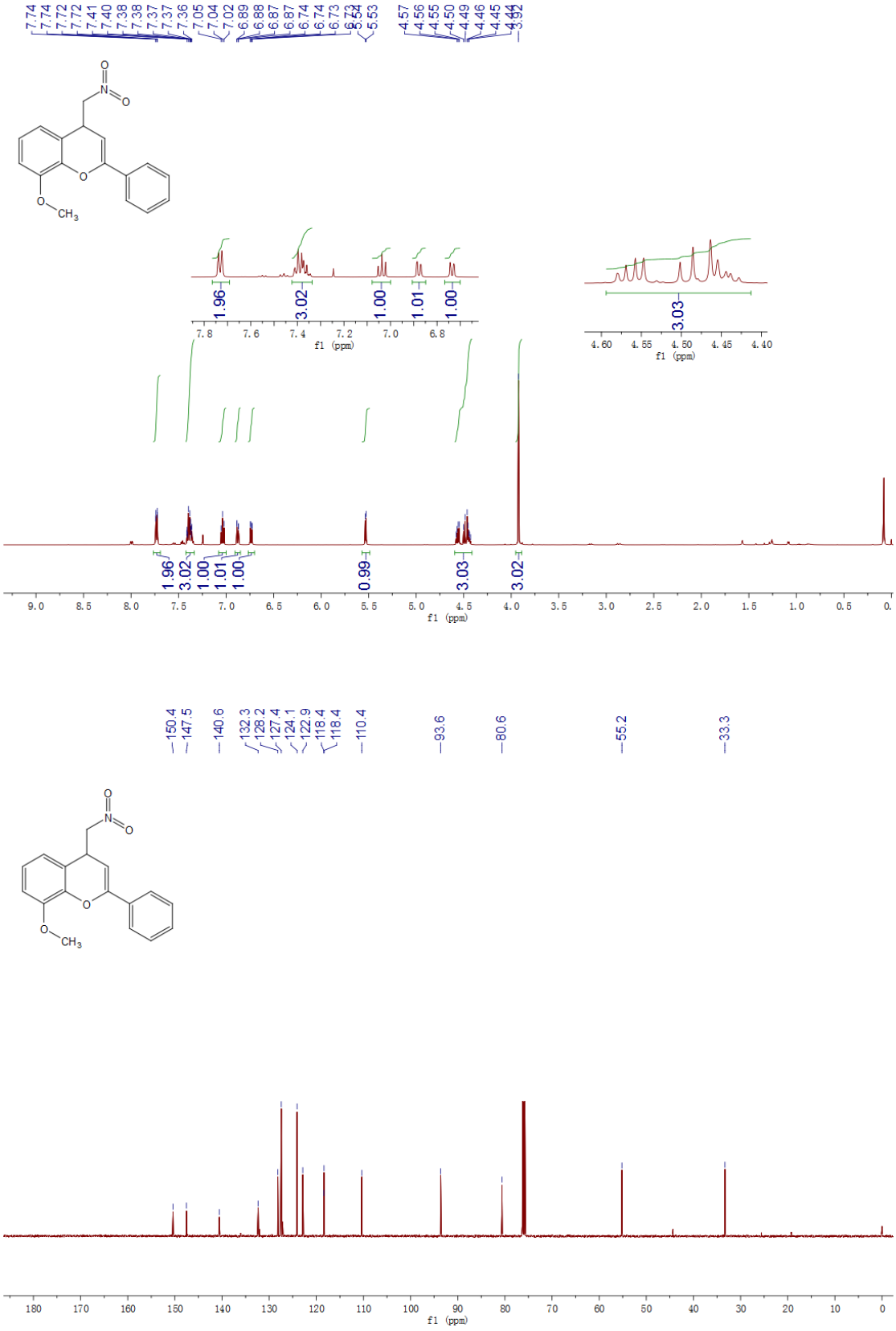




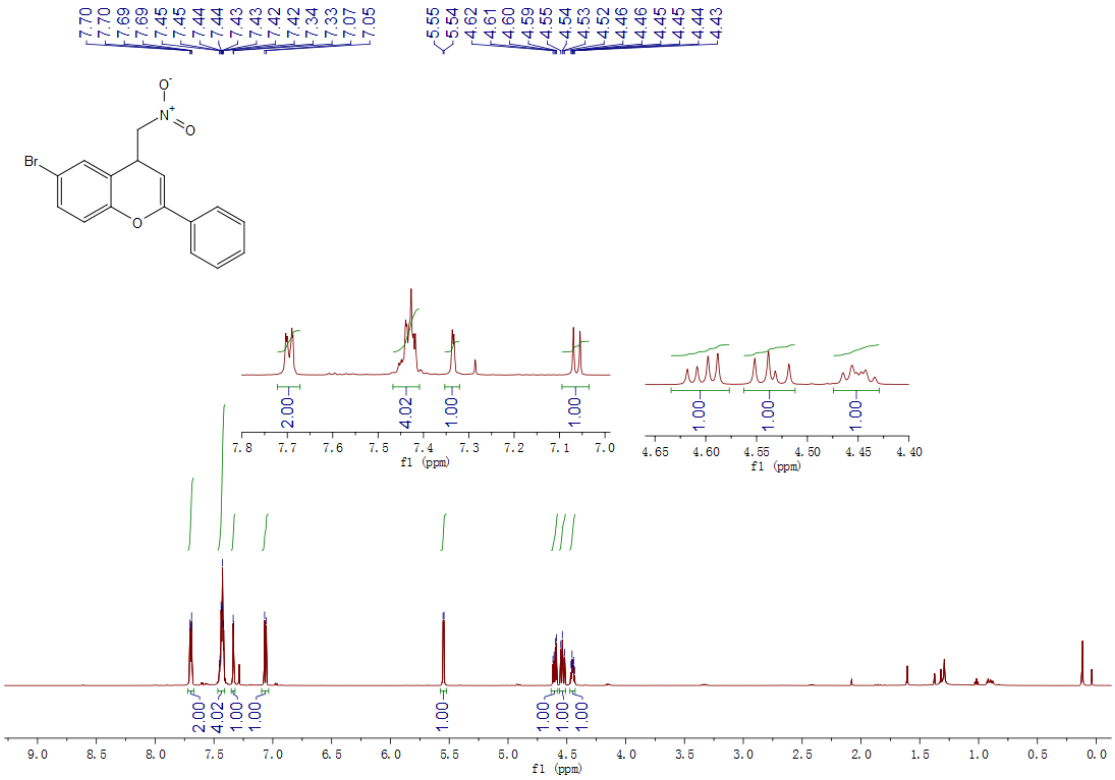


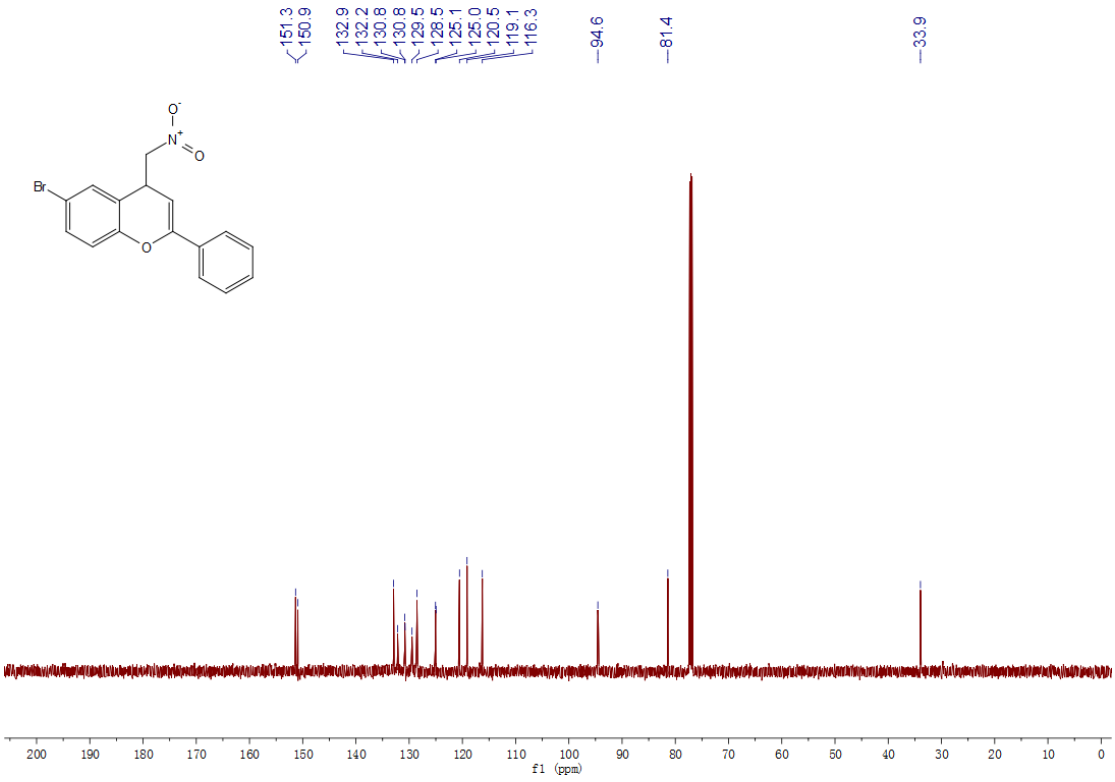


2j 8-methoxy-4-(nitromethyl)-2-phenyl-4H-chromene

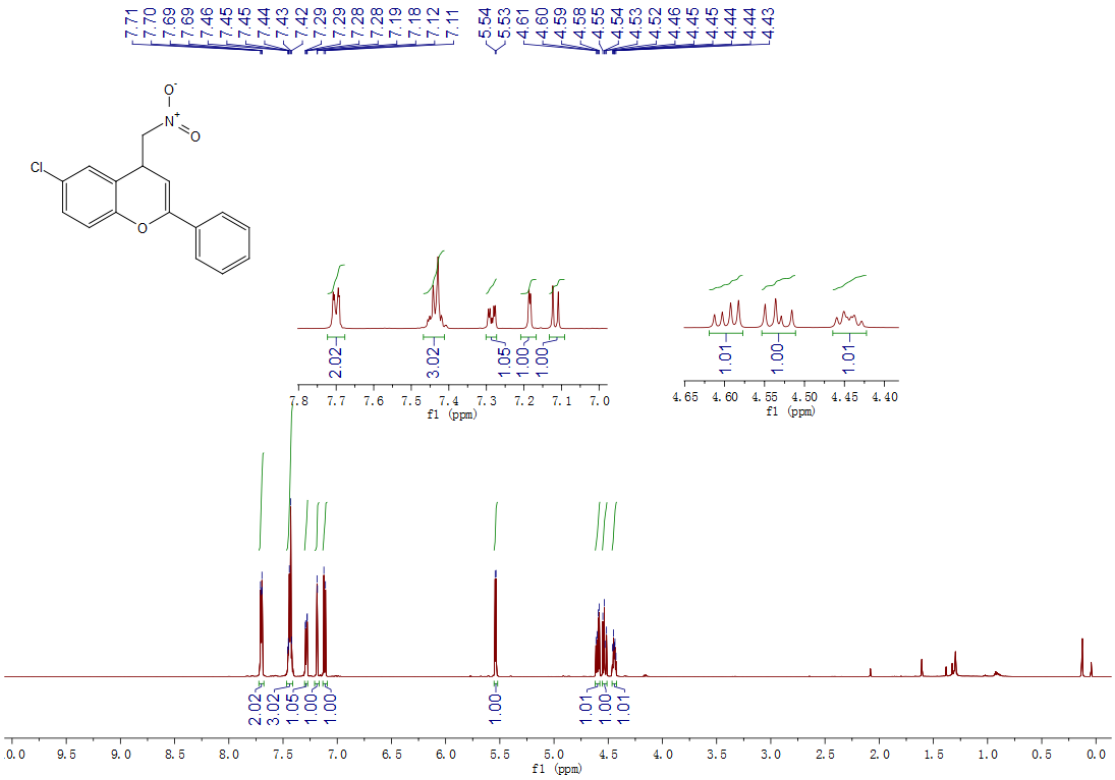


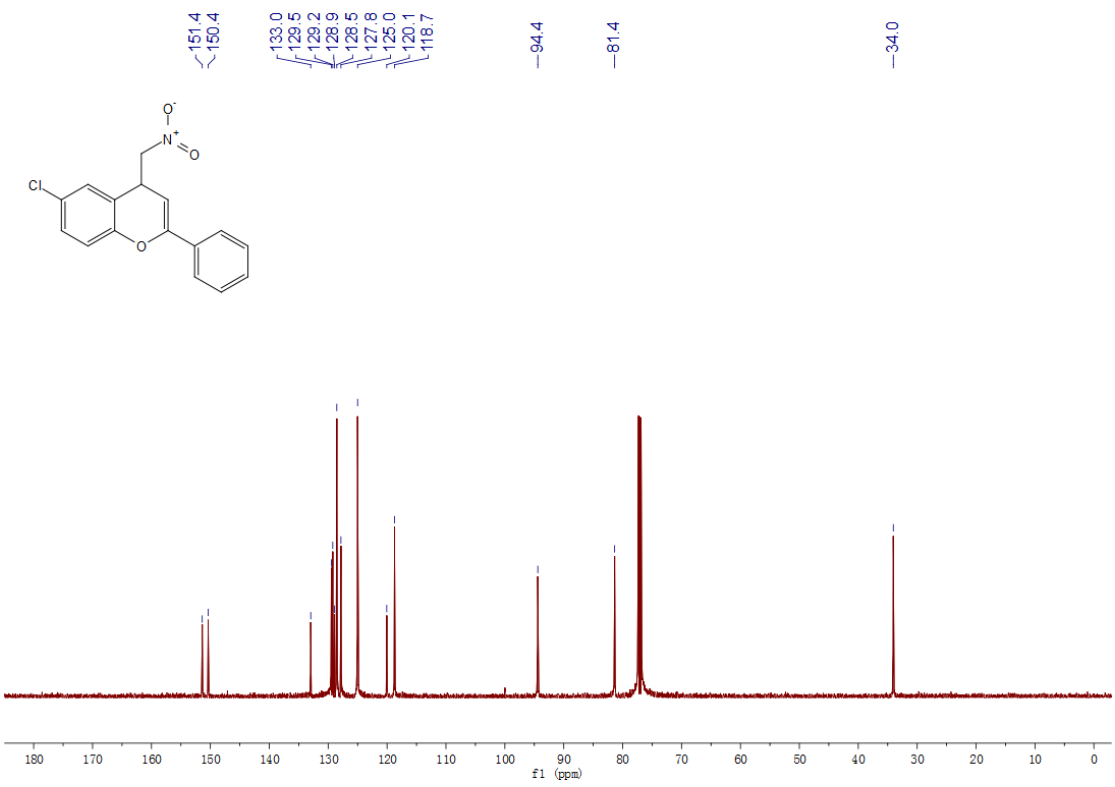
2k 6-bromo-4-(nitromethyl)-2-phenyl-4H-chromene



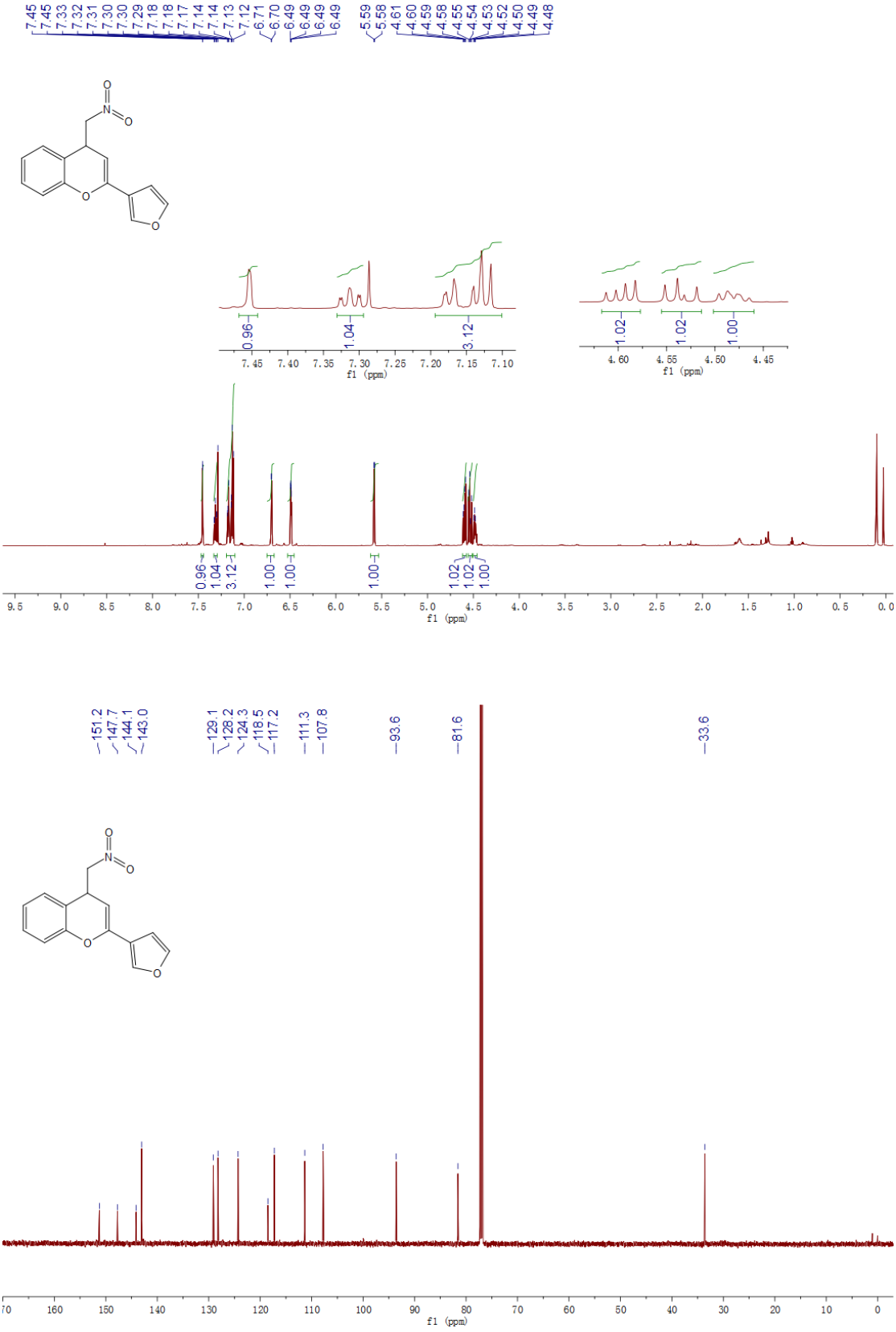


2l 6-chloro-4-(nitromethyl)-2-phenyl-4H-chromene

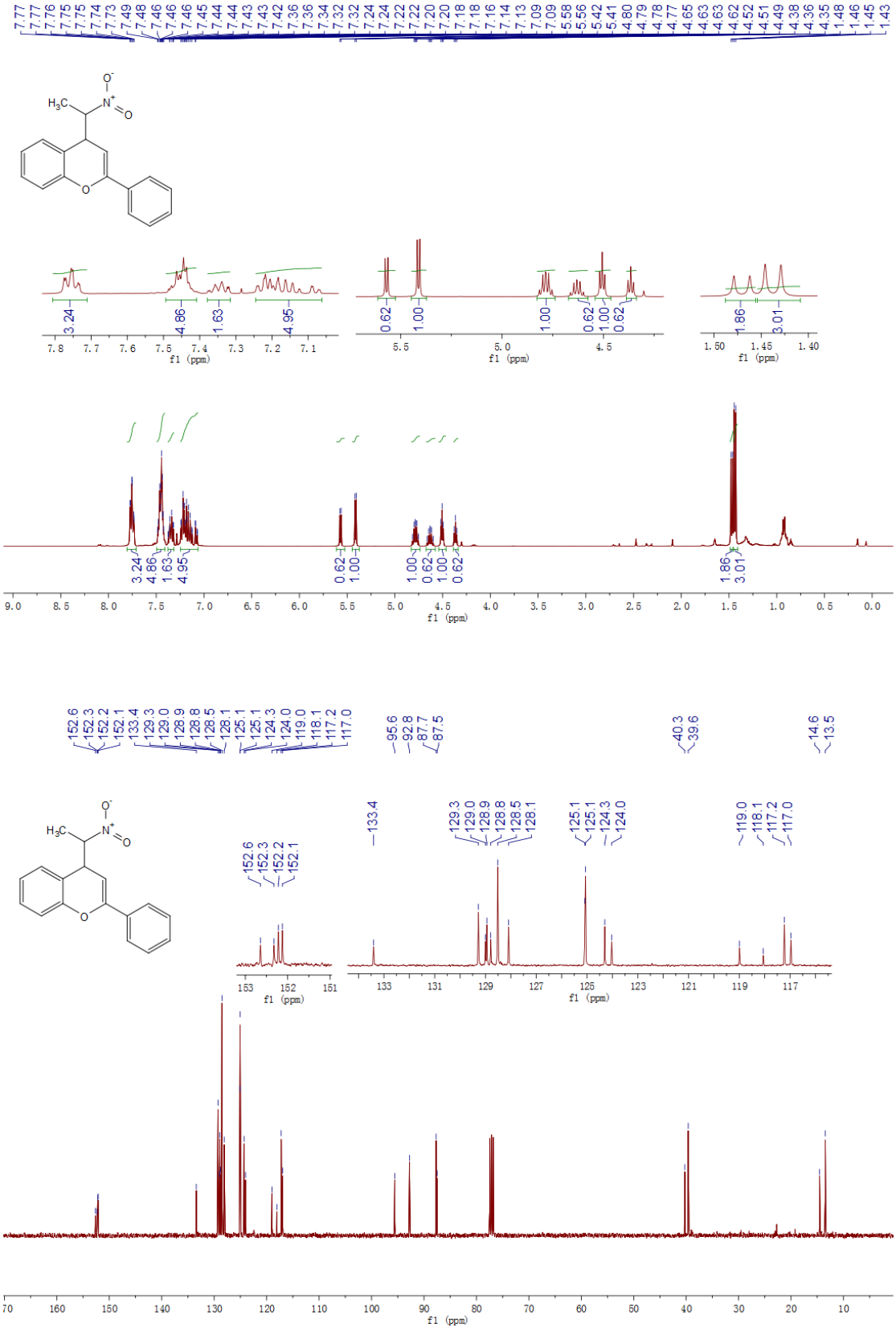




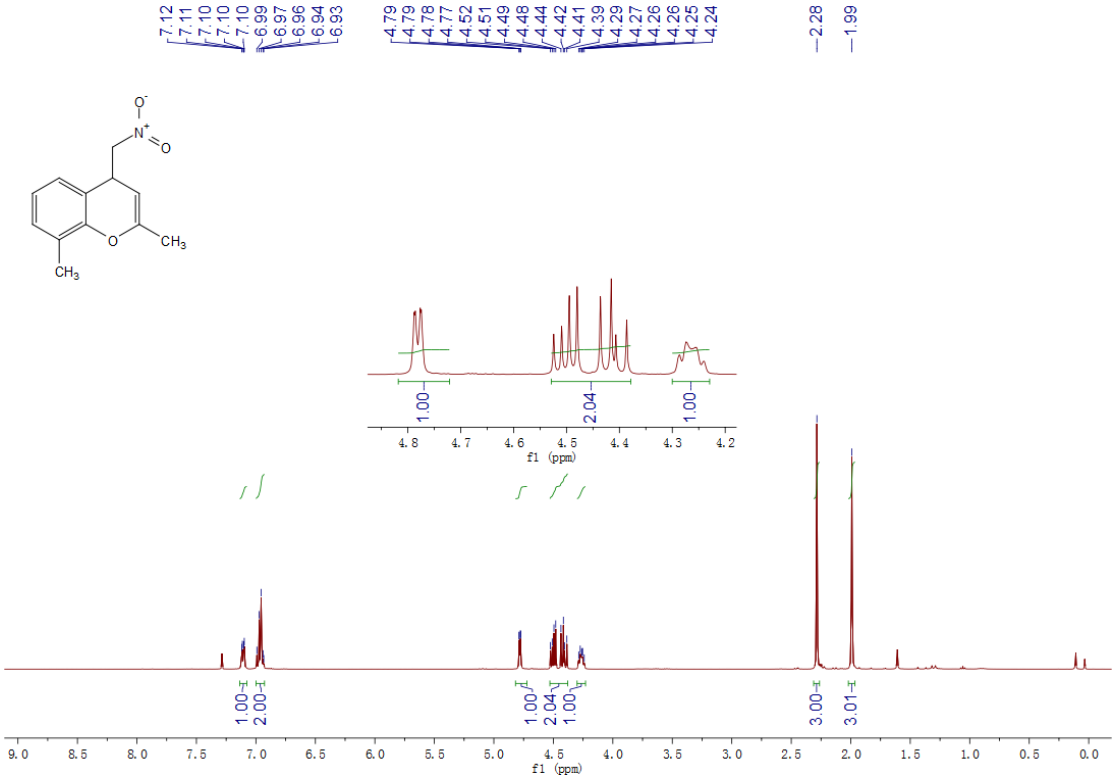
2n 2-(furan-3-yl)-4-(nitromethyl)-4H-chromene

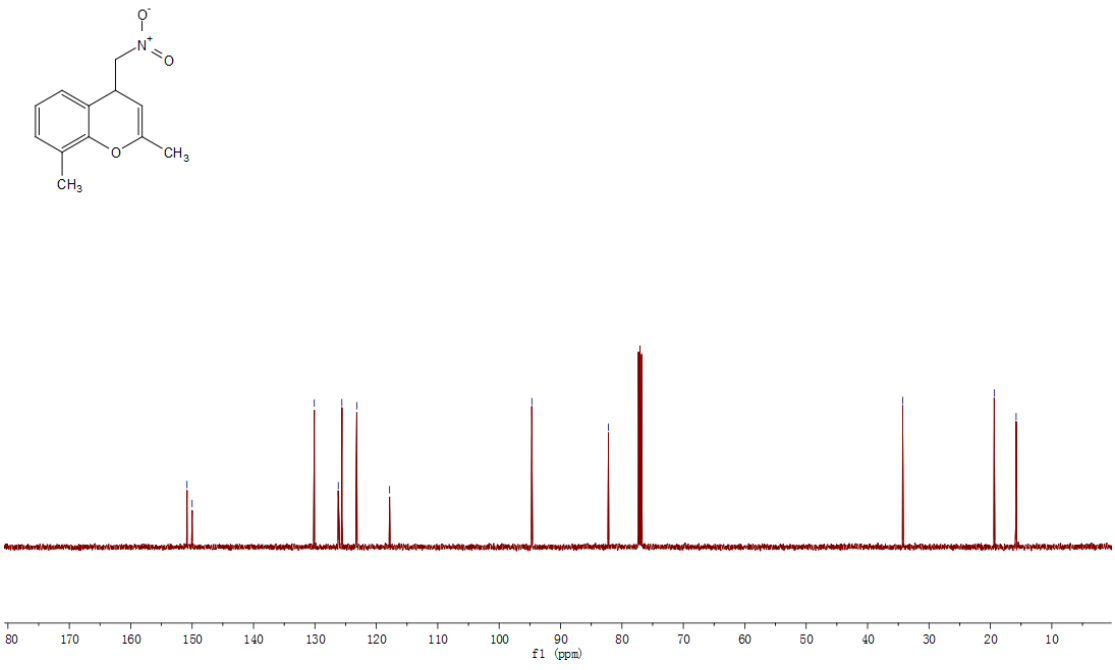


5a 4-(1-nitroethyl)-2-phenyl-4H-chromene

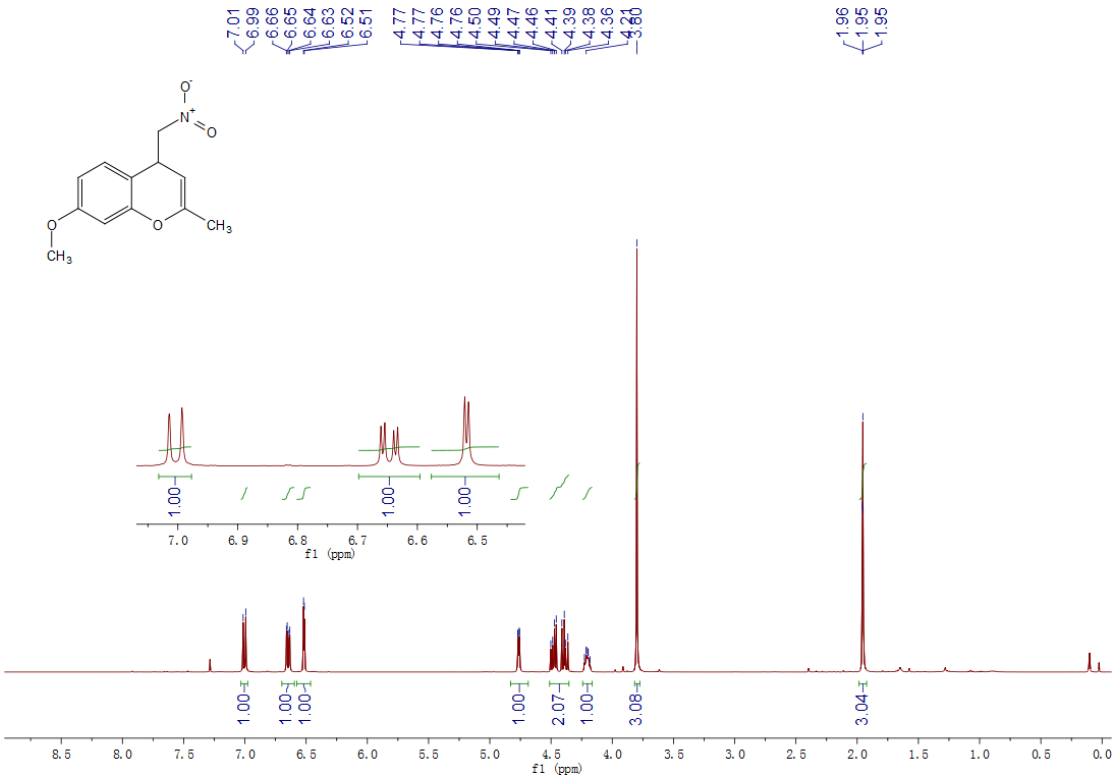


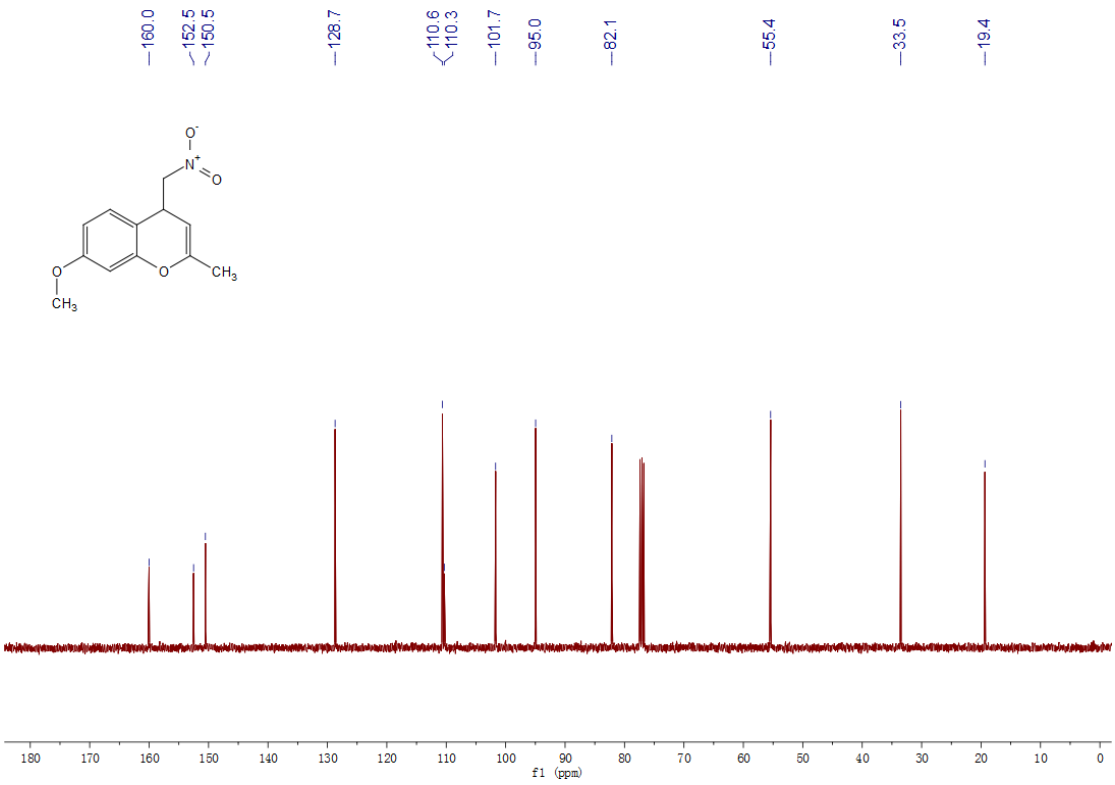
5b 2,8-dimethyl-4-(nitromethyl)-4H-chromene



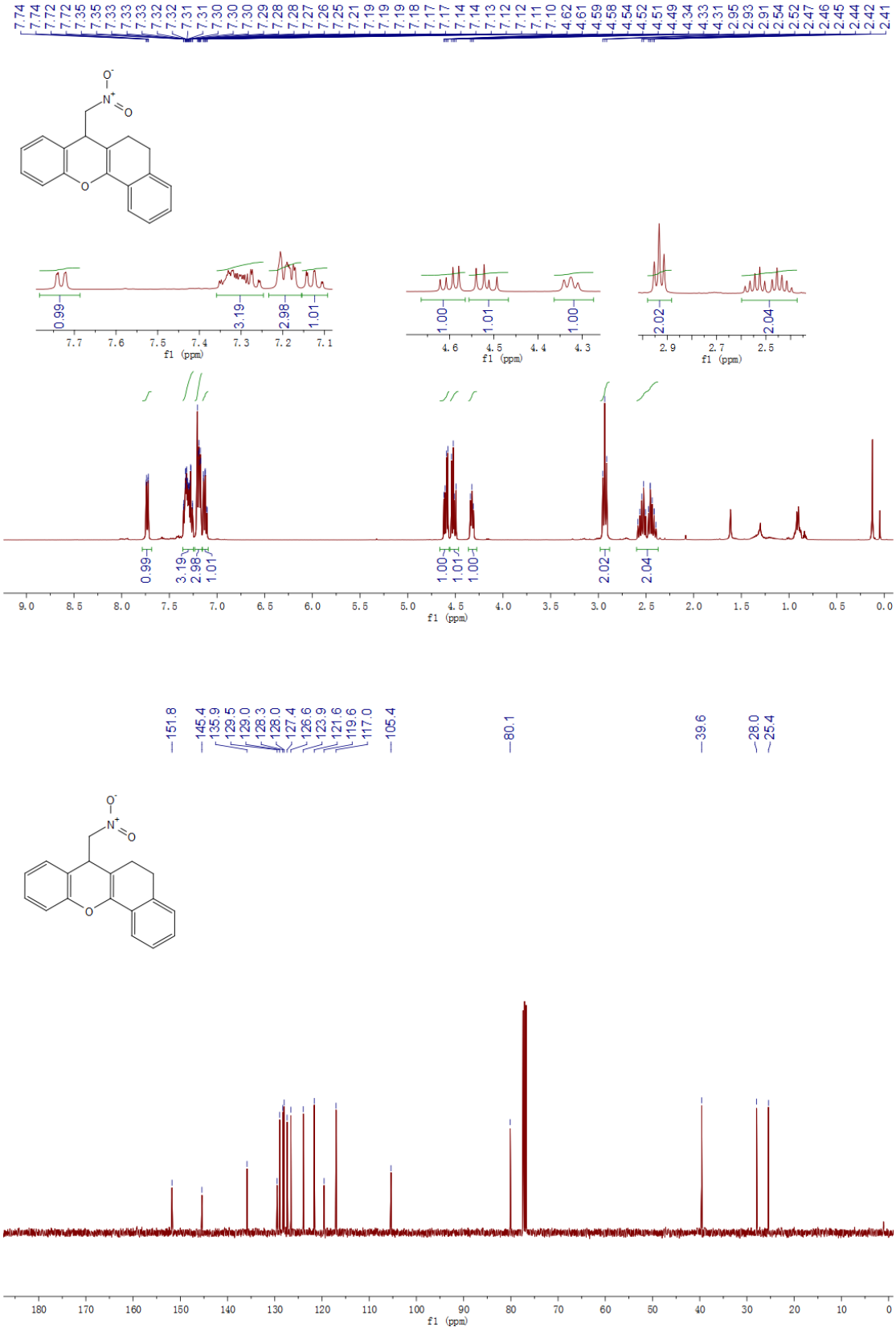


5c 7-methoxy-2-methyl-4-(nitromethyl)-4H-chromene

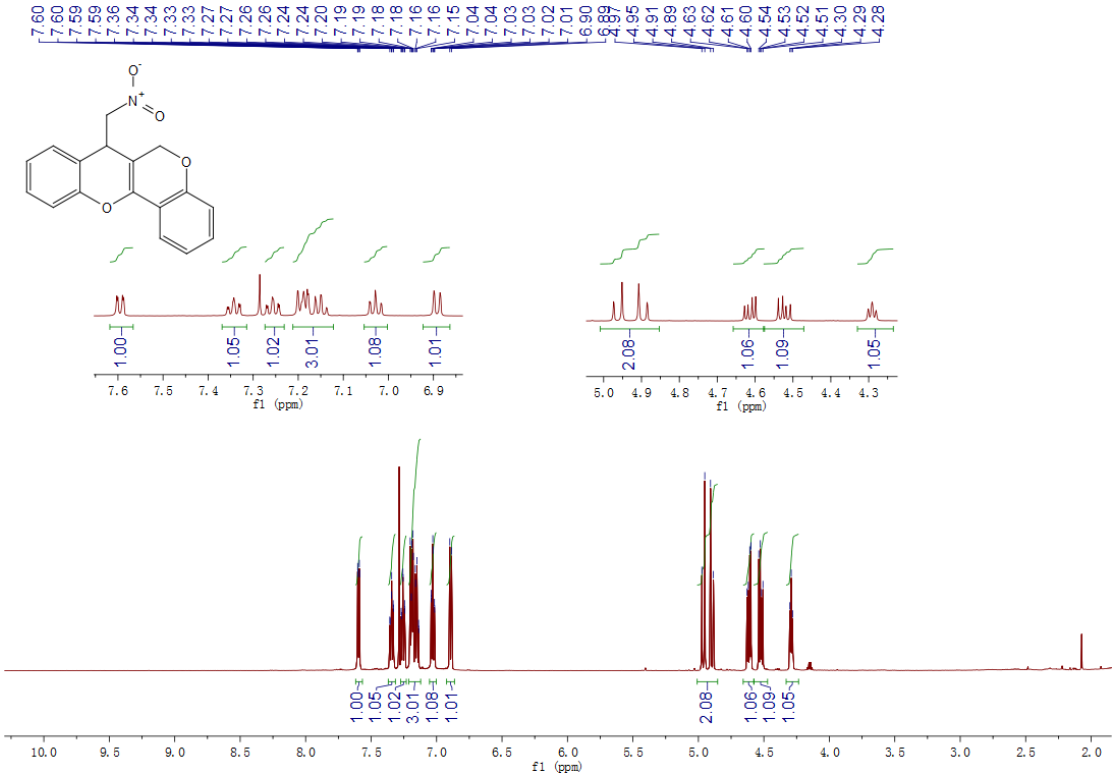


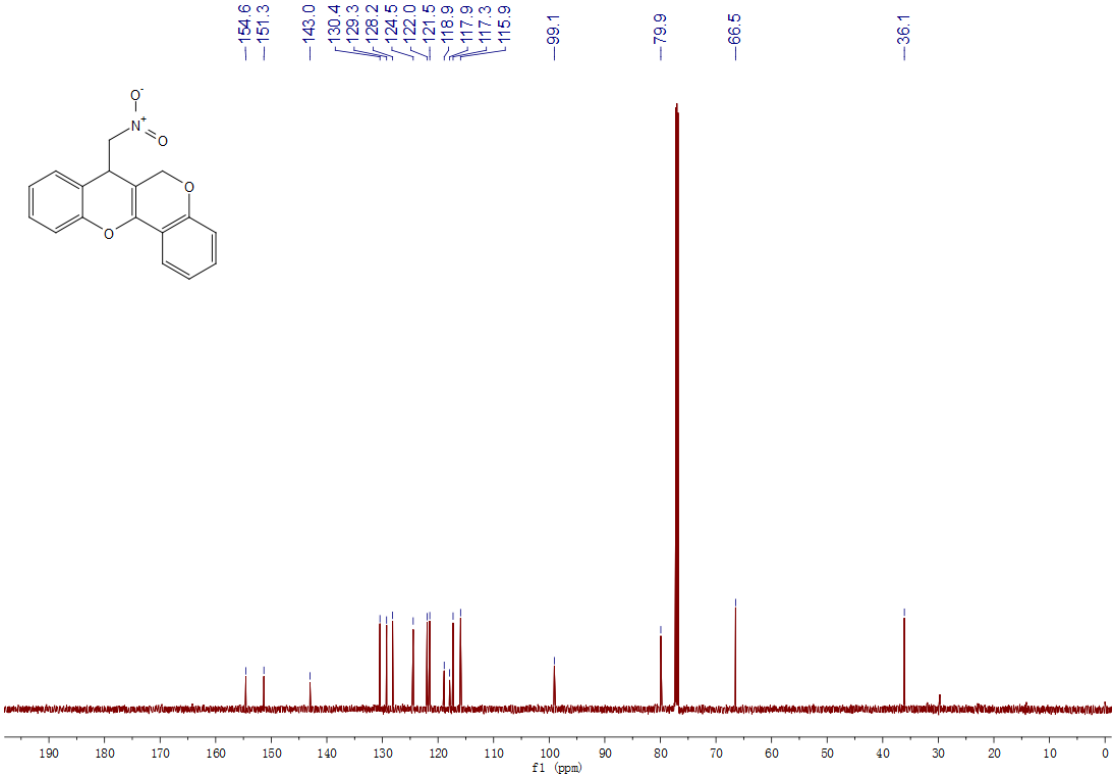


5d 7-(nitromethyl)-6,7-dihydro-5H-benzo[c]xanthene

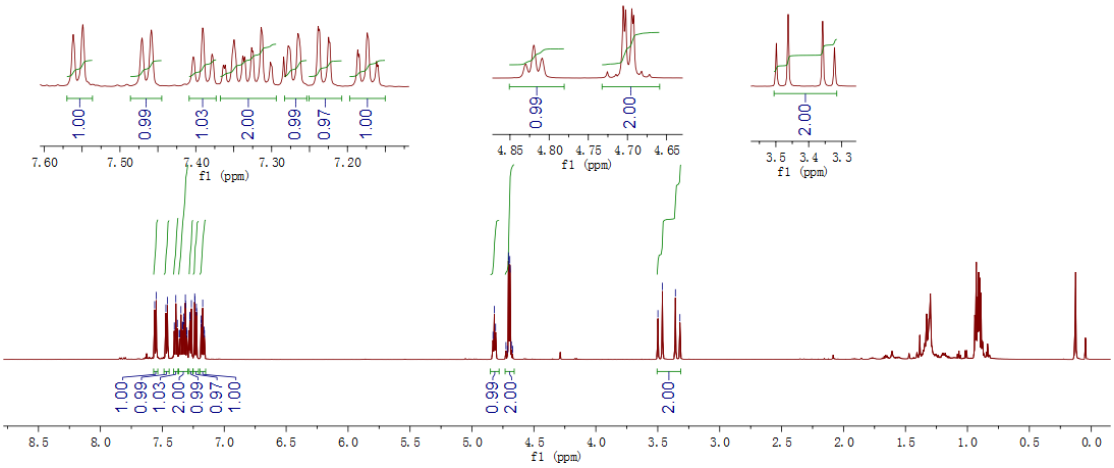


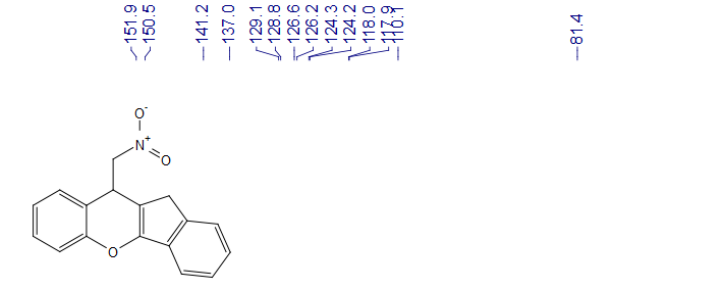
5e 7-(nitromethyl)-6,7-dihydrochromeno[4,3-b]chromene





5f 10-(nitromethyl)-10,11-dihydroindeno[1,2-b]chromene





e 1-(6-chloro-2-ethoxy-2-methyl-2H-chromen-3-yl)ethanone