Supporting Information

Tin(II)-catalyzed dehydrative cross-coupling of 2*H*-chromene hemiacetals with ketones

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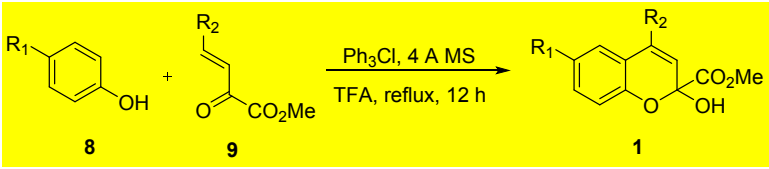
2. General Information

All reactions were carried out under an argon atmosphere except noted. Dichloromethane and toluene were distilled prior to use under a nitrogen atmosphere. Silica gel (200–300 mesh) was used for flash chromatography. The *N*-acyl pyrroles were prepared according to the literature procedures.[1–8] Formyl chloride, alkenes, and other reagents were purchased from commercial sources and used directly. High-resolution mass spectra (HRMS) were recorded by using an Electrothemal LTQ-Orbitrap mass spectrometer. Melting points were measured by using a Gongyi X-5 microscopy digital melting point apparatus and are uncorrected. ^{1}H and ^{13}C-NMR spectra were recorded with a Bruker Avance III 400 MHz NMR spectrometer with $CDCl_3$ as solvent. The chemical shifts are reported in ppm relative to $CDCl_3$ (δ = 7.26) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.0) for ^{13}C NMR. Coupling constants (*J*) are quoted in Hz. NMR data of known compounds is in agreement with literature values. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m).

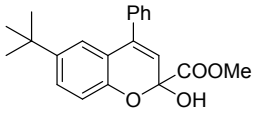
3. Experimental Procedures

3.1 General procedure for the synthesis of 2H-chromene hemiacetals 1



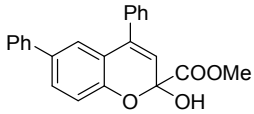
To a solution of phenols **8** (0.10 mmol) and β,γ-unsaturated α-ketoesters **9** (0.11 mmol) in TFA (1 mL) were added trityl chloride (0.11 mmol) and 4 Å molecular sieves (0.10 g). The resulting mixture was stirred under reflux for 12 h, and concentrated. To the residue were added ethyl acetate (20 mL) and saturated aqueous sodium hydrogen carbonate (10 mL). The two layers were separated, and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by column chromatography (20% ethyl acetate in petroleum ether) over silica gel to afford 2*H*-chromene hemiacetals **1**

2*H*-Chromene hemiacetal 1a



90% yield; 30.5 mg; white solid; m p = 115-116 C; ^{1}H NMR (400MHz, $CDCl_3$): δ/ppm = 7.49-7.45 (m, 5H), 7.34 (dd, 1H, *J* = 8.4, 2.4 Hz), 7.24 (d, 1H, *J* = 2.4 Hz), 7.03 (d, 1H, *J* = 8.4 Hz), 5.87 (s, 1H), 4.48 (s, 1H), 3.93 (s, 3H), 1.24 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ/ppm = 169.8, 148.2, 144.6, 139.4, 137.1, 128.8, 128.4, 128.3, 127.0, 123.1, 119.3, 117.0, 116.4, 93.3, 53.8, 34.3, 31.4; IR (film): ν_{max} = 3467, 2960, 1743, 1489, 1287, 1236, 1149, 1026, 768, 698 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{21}H_{23}O_4[M+H]^+$: 339.1591, found: 339.1595.

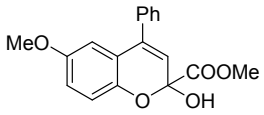
2*H*-Chromene hemiacetal 1b



87% yield; 28.9 mg; pale yellow solid; m p = 63 64 C; ^{1}H NMR (400MHz, $CDCl_3$) δ/ppm = 7.52-7.28 (m, 12H), 7.15 (d, 1H, *J* = 8.4 Hz), 5.90 (s, 1H), 4.60 (s, 1H), 3.92 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ/ppm = 169.7, 150.0, 140.6, 139.2, 136.9, 135.3, 128.9, 128.8, 128.7, 128.6, 128.5, 127.0, 126.9, 124.9, 120.4, 117.5, 117.4, 93.4, 53.9; IR (film): ν_{max} = 3436, 1749, 1480, 1253, 1237, 1157,

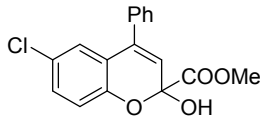
1140, 1123, 1050, 1022, 826, 761, 700 cm^{-1}. HRMS (ESI) m/z : calcd for $C_{23}H_{19}O_4[M+H]^+$: 359.1278, found: 359.1279.

2*H*-Chromene hemiacetal 1c



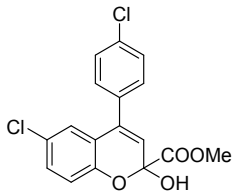
85% yield; 25.2 mg; foam; ^1H NMR (400MHz, $CDCl_3$) δ/ppm = 7.45-7.44 (m, 5H), 7.11-7.08 (m, 1H), 7.00 6.97 (m, 2H), 5.84 (s, 1H), 4.41 (s, 1H), 3.91 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100MHz, CDCl 3) δ/ppm = 170.0, 148.5, 139.4, 137.4, 131.5, 130.8, 129.1, 128.7, 128.5, 126.7, 120.1, 117.4, 117.0, 93.5, 54.0, 21.0; IR (film): ν_{max} = 3443, 2954, 2928, 2855, 1753, 1489, 1242, 1124, 1046, 822, 761, 703 cm^{-1} . H RMS (ESI) m/z : calcd for $C_{18}H_{17}O_4$ $[M+H]^+$: 297.1121, found: 297.1124.

2*H*-Chromene hemiacetal 1d



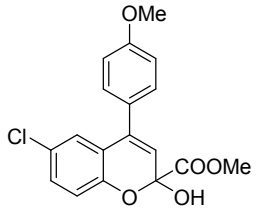
86% yield; 27.2 mg; foam; ^1H NMR (400MHz, $CDCl_3$) δ/ppm = 7.46 7.39 (m, 5H), 7.23 (dd, 1H, *J* = 8.7, 2.4 Hz), 7.14 (d, 1H, *J* = 2.4 Hz), 7.00 (d, 1H, J = 8.7 Hz), 5.87 (s, 1H), 4.54 (s, 1H), 3.91 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ/ppm = 169.5, 149.0, 138.4, 136.3, 129.7, 128.7, 128.7, 127.0, 125.9, 121.6, 118.4, 118.1, 93.3, 54.0; IR (film): ν_{max} = 3446, 3029, 2954, 1755, 1475, 1 253, 1046, 936, 821, 764, 702 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{17}H_{14}ClO_4$ $[M+H]^+$: 317.0575, found: 317.0576.

2*H*-Chromene hemiacetal 1e



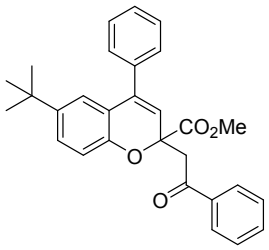
78% yield; 24.4 mg; foam; ^1H NMR (400MHz, $CDCl_3$) δ/ppm = 7.46 7.41 (m, 5H), 7.01 (d, 1 H, *J* = 8.7 Hz), 6.85 (dd, 1H, *J* = 8.7, 3.0 Hz), 6.72 (d, 1H, *J* = 3.0 Hz), 5.88 (s, 1H), 4.33 (s, 1H), 3.91 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ/ppm = 169.8, 154.4, 139.1, 137.0, 128.8, 128.7, 128.5, 128.5, 120.8, 117.8, 117.7, 115.5, 111.4, 93. 2, 55.8, 53.9; IR (film): ν_{max} = 3440, 2952, 1755, 1488, 1260, 1219, 1048, 829, 762, 703 cm^{-1} . HRMS (ESI) m/z: calcd for $C_{18}H_{16}O_5Na$ $[M+Na]^+$: 335.0890, found: 335.0892.

2*H*-Chromene hemiacetal 1f

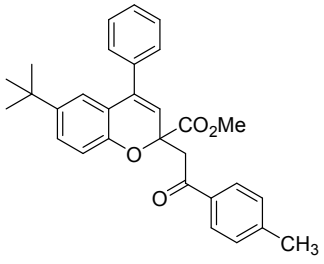


86% yield; 32.1 mg; foam ; ^{1}H NMR (400MHz, $CDCl_3$) δ/ppm = 7.43 7.37 (m, 4H), 7.33 (dd, 1H, *J* = 8.4, 2.4 Hz), 7.15 (d, 1H, *J* = 2.4 Hz), 7.00 (d, 1H, *J* = 8.4 Hz), 5.85 (s, 1H), 4.68 (s, 1H), 3.88 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ/ppm = 169.7, 148.2, 144.8, 138.5, 135. 6, 134.4, 130.2, 128.7, 127.2, 122.9, 119.0, 117.4, 116.6, 93.2, 53.8, 34.3, 31.4; IR (film): ν_{max} = 3439, 2961, 1751, 1489, 1243, 1130, 826, 754 cm^{-1}. HRMS (ESI) m/z : calcd for $C_{21}H_{22}ClO_4[M+H]^+$: 373.1201, found: 373.1203.

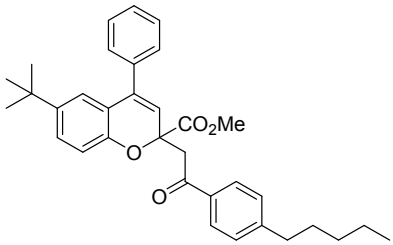
3.2 Characterization Data of the products



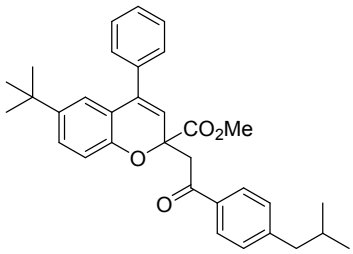
Methyl 6-(tert-butyl)-2-(2-oxo-2-phenylethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3aa): yellow oil, 72.2 mg, 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, 2H, *J* = 7.6 Hz), 7.56 (t, 1H, *J* =7.2 Hz), 7.43–7.40 (m, 7H), 7.19 (dd, 1H, *J* =2.0 Hz, 8.4Hz), 7.07 (s, 1H), 6.87 (d, 1H, *J* =8.4 Hz), 5.83 (s, 1H), 3.94 (d, 1H, *J* = 16.4 Hz), 3.83 (s, 5H), 3.76 (d, 1H, *J* = 16.4 Hz), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.5, 171.5, 150.1, 144.2, 137.9, 137.4, 136.7, 133.4, 128.7, 128.6, 128.4, 128.3, 128.2, 126.9, 122.9, 121.1, 120.0, 116.2, 79.1, 77.3, 76.7, 52.9, 46.3, 34.2, 31.3; Calcd for $C_{29}H_{28}O_4Na$ $[M+Na]^+$: 463.4866. Found: 463.4723.



Methyl 6-(tert-butyl)-2-(2-oxo-2-(p-tolyl)ethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3ab): colorless oil, 76.4 mg, 84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (t, 2H, *J* = 7.2 Hz), 7.42–7.34 (m, 6H), 7.21 (d, 2H, *J* = 7.2 Hz), 7.08 (s, 1H), 6.86 (d, 1H, *J* = 8.4 Hz), 6.08 (s, 1H), 3.70 (d, 1H, *J* = 8.0 Hz), 3.61 (s, 3H), 3.52 (d, 1H, *J* = 8.0 Hz), 2.43 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.3, 171.2, 150.4, 144.0, 141.3, 137.9, 137.7, 134.3, 129.3, 128.6, 128.3, 128.0, 126.9, 126.6, 122.8, 120.2, 115.9, 82.4, 77.3, 76.7, 52.5, 47.4, 34.2, 31.3, 21.6; Calcd for $C_{30}H_{30}O_4Na$ [M+Na]+: 477.5660. Found: 477.3721.

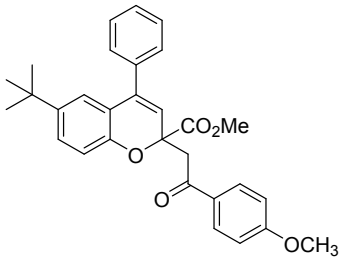


Methyl 6-(tert-butyl)-2-(2-oxo-2-(4-pentylphenyl)ethyl)-4-phenyl-2*H*-chromene-2- carboxylate (3ac): yellow oil, 89.9 mg, 88%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, 2H, *J* = 7.2 Hz), 7.42–7.40 (m, 5H), 7.20 (d, 1H, *J* = 8.4 Hz), 7.07 (s, 1H), 6.88 (d, 3H, *J* = 8.4 Hz), 5.85 (s, 1H), 3.93 (d, 1H, *J* = 16.4 Hz), 3.84 (s, 3H), 3.67 (d, 1H, *J* = 16.4 Hz), 2.66 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.2, 171.6, 150.1, 149.2, 144.1, 137.8, 137.5, 134.4, 128.7, 128.3, 128.1, 126.9, 122.9, 121.3, 120.1, 116.2, 79.1, 77.3, 76.7, 52.9, 46.2, 35.9, 31.3, 22.4; Calcd for $C_{34}H_{38}O_4Na$ $[M+Na]^+$: 533.6740. Found: 533.1798.

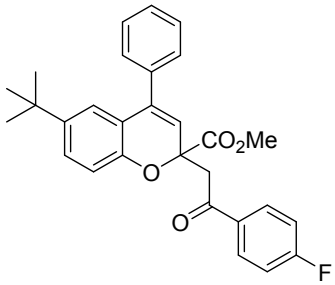


Methyl 6-(tert-butyl)-2-(2-(4-isobutylphenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3ad): yellow oil, 86.4 mg, 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44–7.38 (m, 6H), 7.19 (d, 1H, *J* = 4.0 Hz), 6.99 (d, 2H, *J* = 8.4 Hz), 6.83 (d, 2H, *J* = 23.2 Hz), 6.75 (d, 1H, *J* = 9.6 Hz), 6.32 (s, 1H), 3.92 (d, 1H, *J* = 18.0 Hz), 3.80 (s, 3H), 3.67 (d, 1H, *J* = 18.0 Hz), 2.42 (d, 2H, *J* = 16.0 Hz), 1.80 (m, 2H, *J* = 19.2 Hz), 1.22 (s, 9H), 0.88 (d, 6H, *J* = 28 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.2, 168.5, 151.3, 145.9, 140.2, 135.6, 133.7, 129.5, 128.6, 128.4, 127.9, 124.8, 123.2, 116.7,

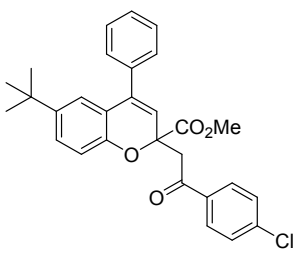
114.2, 112.6, 89.4, 77.3, 76.7, 51.7, 44.6, 41.6, 34.7, 31.3, 29.0, 22.9; Calcd for $C_{33}H_{36}O_4Na$ $[M+Na]^+$: 519.6470. Found: 519.7829.



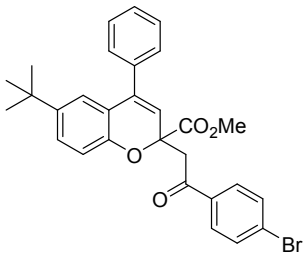
Methyl 6-(tert-butyl)-2-(2-(4-methoxyphenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3ae): yellow oil, 83.8 mg, 89%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, 2H, *J* = 8.4 Hz), 7.43–7.36 (m, 5H), 7.25 (dd, 1H, *J* = 6.8 Hz, 17.6 Hz), 7.06 (s, 1H), 6.95 (d, 2H, *J* = 8.8 Hz), 6.75 (d, 1H, *J* = 8.2 Hz), 5.94 (s, 1H), 3.92 (s, 2H), 3.84 (d, 1H, *J* = 20.4 Hz), 3.69 (s, 3H), 3.60 (d, 1H, *J* = 20.4 Hz), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.9, 169.6, 165.2, 151.3, 145.4, 140.7, 135.8, 130.3, 129.4, 128.7, 128.3, 127.9, 124.9, 123.2, 116.8, 115.4, 114.8, 112.6, 79.8, 77.3, 76.7, 55.8, 52.6, 45.5, 34.2, 31.3; Calcd for $C_{30}H_{30}O_5Na$ $[M+Na]^+$: 493.5650. Found: 493.4677.



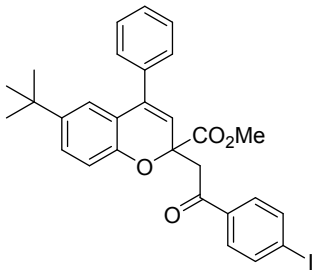
Methyl 6-(tert-butyl)-2-(2-(4-fluorophenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2- carboxylate (3af): yellow oil, 74.3 mg, 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (t, 2H, *J* = 6.4 Hz), 7.42–7.37 (m, 6H), 7.15 (dd, 3H, *J* = 8.4 Hz, 29.6 Hz), 7.09 (s, 1H), 6.85 (d, 1H, *J* = 4.4 Hz), 5.82 (s, 1H), 3.89 (d, 1H, *J* = 16.4 Hz), 3.83 (s, 3H), 3.63 (d, 1H, *J* = 16.4 Hz), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.0, 171.5, 167.2, 140.0, 144.2, 138.0, 137.4, 131.1, 128.6, 128.4, 128.2, 125.0, 122.9, 116.2, 115.8, 115.6, 79.1, 77.3, 76.7, 53.0, 46.2, 34.2, 31.3; Calcd for $C_{29}H_{27}FO_4Na$ $[M+Na]^+$: 481.5294. Found: 481.8143.



Methyl 6-(tert-butyl)-2-(2-(4-chlorophenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2- carboxylate (3ag): yellow oil, 78.8 mg, 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, 2H, *J* = 11.2 Hz), 7.58 (d, 2H, *J* = 8.0 Hz), 7.41–7.36 (m, 6H), 7.06 (s, 1H), 6.65 (d, 1H, *J* = 8.4 Hz), 5.81 (s, 1H), 3.89 (d, 1H, *J* = 16.0 Hz), 3.81 (s, 3H), 3.64 (d, 1H, *J* = 16.0 Hz), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 208.0, 194.6, 171.5, 149.8, 144.2, 139.9, 138.0, 137.1, 134.8, 129.6, 128.8, 128.4, 128.2, 128.1, 126.9, 122.8, 120.6, 119.8, 116.0, 78.9, 77.3, 76.7, 50.0, 46.0, 34.0, 31.1; Calcd for $C_{29}H_{27}ClO_4Na$ $[M+Na]^+$: 497.9810. Found: 497.3258.

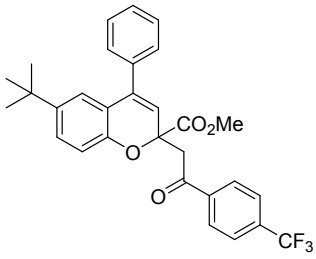


Methyl 2-(2-(4-bromophenyl)-2-oxoethyl)-6-(tert-butyl)-4-phenyl-2*H*-chromene-2-carboxylate (3ah): yellow oil, 75.8 mg, 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, 2H, *J* = 8.0 Hz), 7.58 (d, 2H, *J* = 8.0 Hz), 7.42–7.37 (m, 5H), 7.19 (d, 1H, *J* = 8.4 Hz), 7.05 (s, 1H), 6.85 (d, 2H, *J* = 8.4 Hz), 5.81 (s, 1H), 3.87 (d, 1H, *J* = 16.4 Hz), 3.69 (s, 3H), 3.62 (d, 1H, *J* =16.4 Hz), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.7, 171.4, 149.9, 144.3, 137.3, 135.4, 131.9, 129.8, 128.6, 128.4, 128.2, 127.0, 122.9, 120.9, 120.0, 116.2, 79.1, 77.3, 76.7, 53.0, 46.1, 34.2, 31.3; Calcd for $C_{29}H_{27}BrO_4Na$ $[M+Na]^+$: 542.4350. Found: 542.4388.

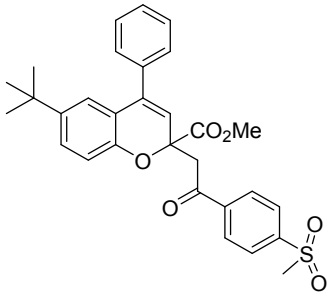


Methyl 6-(tert-butyl)-2-(2-(4-iodophenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3ai): yellow oil, 83.8 mg, 74%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, 2H, *J* = 7.6 Hz), 7.63 (d, 2H, *J* = 7.6 Hz), 7.41–7.38 (m, 5H), 7.19 (d, 1H, *J* = 8.4 Hz), 7.06 (s, 1H), 6.85 (d, 1H, *J* = 8.4 Hz), 5.81 (s, 1H), 3.88 (s, 3H), 3.85 (d, 1H, *J* = 16.6 Hz), 3.61 (d, 1H, *J* = 16.6 Hz), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.0, 171.4, 145.0, 144.3, 138.1, 137.9, 135.9, 129.7, 128.6, 128.4, 127.0,

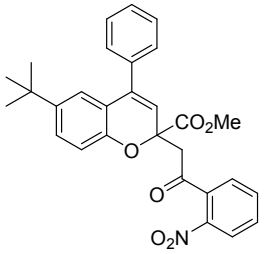
123.0, 120.9, 120.0, 116.2, 101.5, 79.1, 77.3, 76.7, 53.0, 46.1, 34.2, 31.3; Calcd for $C_{29}H_{27}IO_4Na$ $[M+Na]^+$: 589.4355. Found: 589.8212.



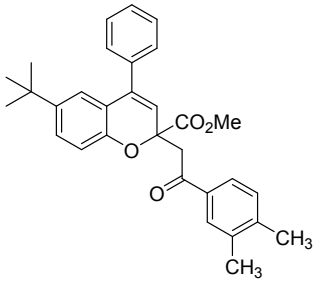
Methyl 6-(tert-butyl)-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3aj): foam, 62.0 mg, 61%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, 2H, *J* = 7.6 Hz), 7.71 (d, 2H, *J* = 7.6 Hz), 7.42–7.38 (m, 5H), 7.19 (d, 1H, *J* = 8.0 Hz), 7.06 (s, 1H), 6.84 (d, 1H, *J* = 8.4 Hz), 5.82 (s, 1H), 3.92 (d, 1H, *J* = 16.8 Hz), 3.84 (s, 3H), 3.67 (d, 1H, *J* = 16.8 Hz), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.8, 171.3, 149.9, 144.3, 139.3, 134.8, 128.6, 128.6, 128.4, 128.3, 127.0, 125.6, 125.6, 123.0, 122.1, 120.7, 119.9, 116.1, 79.1, 77.3, 76.7, 53.0, 46.4, 34.2, 31.3; Calcd for $C_{29}H_{27}F_3O_4Na$ $[M+Na]^+$: 531.5372. Found: 531.8330.



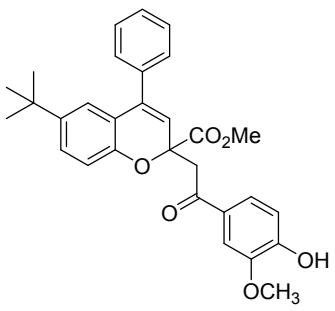
Methyl 6-(tert-butyl)-2-(2-(4-(methylsulfonyl)phenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3ak): yellow oil, 69.5 mg, 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (d, 2H, *J* = 16.8 Hz), 7.88 (d, 2H, *J* = 20.0 Hz), 7.46–7.39 (m, 6H), 7.17 (d, 1H, *J* =6.0 Hz), 6.71 (d, 2H, *J* =18.0 Hz), 6.34 (s, 1H), 3.95 (d, 1H, *J* = 18.4 Hz), 3.83 (s, 3H), 3.71 (d, 1H, *J* = 18.4 Hz), 3.39 (s, 3H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.8, 170.9, 151.1, 145.4, 141.7, 140.1, 135.8, 129.9, 128.7, 128.3, 128.2, 127.9, 124.8, 123.2, 116.1, 115.6, 112.6, 79.5, 82.4, 77.3, 76.7, 52.7, 47.5, 42.6, 34.7, 31.4; Calcd for $C_{30}H_{30}O_6SNa$ $[M+Na]^+$: 541.6240. Found: 541.6839.



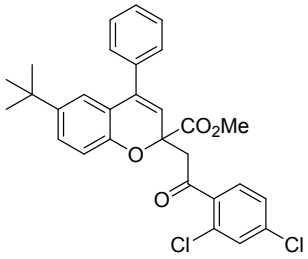
Methyl 6-(tert-butyl)-2-(2-(2-nitrophenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3al): foam, 63.1 mg, 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (dd, 4H, *J* = 9.6 Hz, 25.6 Hz), 7.42–7.36 (m, 5H), 7.25 (dd, 1H, *J* = 2.4 Hz, 18.0 Hz), 7.17 (s, 1H), 6.75 (d, 1H, *J* = 12.0 Hz), 6.14 (s, 1H), 3.84 (d, 1H, *J* = 18.0 Hz), 3.79 (s, 3H), 3.60 (d, 1H, *J* = 18.0 Hz), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.9, 169.2, 152.3, 151.3, 145.5, 142.8, 140.1, 135.8, 130.9, 128.6, 128.3, 128.0, 125.4, 123.8, 123.2, 116.2, 115.6, 112.6, 79.9, 76.7, 52.6, 45.2. 34.6, 31.3; Calcd for $C_{29}H_{27}NO_6Na$ $[M+Na]^+$: 508.5360. Found: 508.4972.



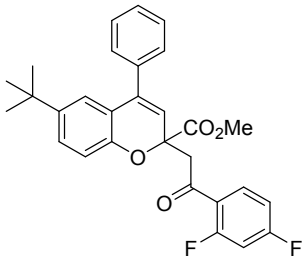
Methyl 6-(tert-butyl)-2-(2-(3,4-dimethylphenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene- 2-carboxylate (3am): yellow oil, 80.0 mg, 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (s, 1H), 7.40–7.39 (m, 5H), 7.19 (d, 2H, *J* = 8.0 Hz), 7.07 (s, 1H), 6.66 (d, 1H, *J* = 7.6 Hz), 6.87 (d, 1H, *J* = 8.0 Hz), 5.84 (s, 1H), 3.92 (d, 1H, *J* = 16.4 Hz), 3.83 (s, 3H), 3.63 (d, 1H, *J* = 16.4 Hz), 2.29 (d, 6H, *J* = 6.8 Hz), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.4, 171.6, 150.1, 144.1, 143.0, 137.8, 137.5, 136.9, 134.6, 129.8, 129.4, 128.7, 128.3, 128.1, 126.8, 126.0, 122.9, 121.4, 120.1, 116.3, 79.2, 77.3, 76.7, 52.9, 46.1, 34.2, 31.3, 20.0, 19.7; Calcd for $C_{31}H_{32}O_4Na$ $[M+Na]^+$: 491.5930. Found: 491.5178.



Methyl 6-(tert-butyl)-2-(2-(4-hydroxy-3-methoxyphenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3an): yellow oil, 89.5 mg, 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.50 (s, 1H), 7.54 (dd, 1H, *J* = 6.0 Hz, 21.6 Hz), 7.43–7.35 (m, 6H), 7.26 (s, 1H), 7.17 (d, 1H, *J* = 4.0 Hz), 7.10 (d, 1H, *J* = 16.0 Hz), 6.73 (d, 1H, *J* = 9.2 Hz), 6.27 (s, 1H), 4.00 (s, 3H), 3.84 (d, 1H, *J* = 12.0 Hz), 3.72 (s, 3H), 3.59 (d, 1H, *J* = 12.0 Hz), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.9, 169.4, 153.2, 151.3, 149.1, 145.4, 140.2, 135.3, 131.6, 128.6, 128.3, 127.9, 123.9,123.215, 122.2, 116.8, 115.5, 113.6, 112.6, 110.8, 79.9, 77.3, 76.7, 57.1, 52.6, 45.3, 34.5, 31.4; Calcd for $C_{30}H_{30}O_6Na$ $[M+Na]^+$: 509.5640. Found: 509.5028.

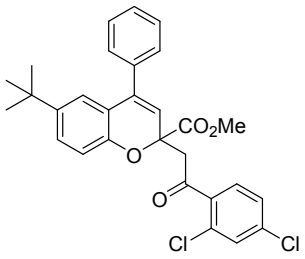


Methyl 6-(tert-butyl)-2-(2-(3,5-dihydroxyphenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3ao): yellow oil, 85.1 mg, 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.01 (s, 2H), 7.91–7.58 (m, 6H), 7.15 (d, 1H, *J* = 10.0 Hz), 6.88 (d, 2H, *J* = 14.8 Hz), 6.74 (d, 1H, *J* = 12.0 Hz), 6.44 (t, 1H, *J* = 2.0 Hz), 6.04 (s, 1H), 4.27 (d, 1H, *J* = 11.6 Hz), 4.03 (s, 3H), 3.95 (d, 1H, *J* = 11.6 Hz), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.0, 169.5, 159.2, 151.0, 145.1, 140.1, 139.4, 134.3, 128.6, 128.4, 127.9, 124.0, 123.3, 116.2, 115.8, 112.8, 108.9, 107.2, 79.8, 77.3, 76.7, 52.6, 45.2, 34.6, 31.3; Calcd for $C_{29}H_{28}O_6Na$ $[M+Na]^+$: 495.5370. Found: 495.5044.

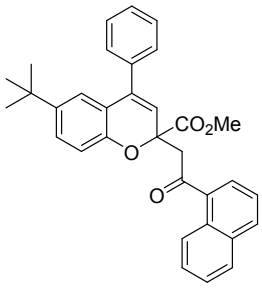


Methyl 6-(tert-butyl)-2-(2-(2,4-difluorophenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3ap): yellow oil, 63.9 mg, 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (q, 1H, *J* = 8.0 Hz), 7.42–7.38 (m, 5H), 7.19 (d, 1H, *J* = 8.4 Hz), 7.05 (s, 1H), 6.95 (t, 1H, *J* = 8.0 Hz), 6.87–6.82 (m, 2H), 5.74 (s, 1H), 3.91 (d, 1H, *J* = 18.0 Hz), 3.83 (s, 3H), 3.71 (d, 1H, *J* = 18.0 Hz), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.1, 171.6, 164.8, 161.6, 150.1, 144.1, 138.1, 137.4, 132.8, 128.6,

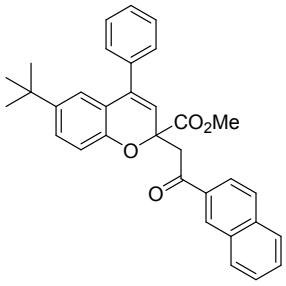
128.4, 126.9, 122.9, 121.8, 120.8, 119.8, 116.0, 112.4, 112.2, 78.9, 77.3, 76.7, 52.9, 50.9, 34.2, 31.3; Calcd for $C_{29}H_{26}F_2O_4Na$ $[M+Na]^+$: 499.5198. Found: 499.5521.



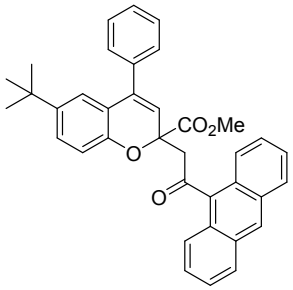
Methyl 6-(tert-butyl)-2-(2-(2,4-dichlorophenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3aq): yellow oil, 64.2 mg, 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, 1H, *J* = 16.0 Hz), 7.75 (d, 1H, *J* = 5.6 Hz), 7.19 (dd, 1H, *J* = 5.3 Hz, 20.8 Hz), 7.50–7.40 (m, 6H), 7.23 (d, 1H, *J* = 4.8 Hz), 6.75 (d, 1H, *J* = 28.0 Hz), 5.98 (s, 1H), 3.91 (d, 1H, *J* = 22.0 Hz), 3.83 (s, 3H), 3.71 (d, 1H, *J* = 22.0 Hz), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.1, 169.6, 152.0, 144.1, 140.9, 136.6, 136.0, 135.4, 131.3, 130.6, 129.9, 128.6, 128.2, 127.8, 127.0, 124.8, 124.0, 117.2, 115.1, 112.3, 83.9, 77.3, 76.7, 53.0, 42.9, 34.2, 31.4; Calcd for $C_{29}H_{26}Cl_2O_4Na$ $[M+Na]^+$: 532.4230. Found: 532.4198.



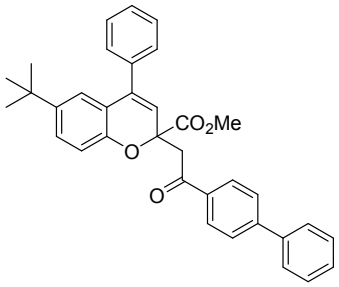
Methyl 6-(tert-butyl)-2-(2-(naphthalen-1-yl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3ar): colorless oil, 79.5 mg, 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.83 (d, 1H, *J* = 8.4 Hz), 8.28 (t, 2H, *J* = 5.6 Hz), 8.03 (d, 1H, *J* = 8.1 Hz), 7.77 (dt, 2H, *J* = 7.2 Hz, 23.2 Hz), 7.69–7.56 (m, 6H), 7.47 (s, 1H), 7.40 (d, 1H, *J* = 8.4 Hz), 7.08 (d, 1H, *J* = 8.4 Hz), 6.05 (s, 1H), 4.19 (d, 1H, *J* = 16.0 Hz), 4.06 (s, 3H), 3.88 (d, 1H, *J* =16.0 Hz), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.5, 171.6, 150.1, 144.2, 138.0, 137.4, 135.5, 135.2, 135.1, 133.9, 133.0, 130.1, 128.4, 127.0, 126.5, 125.9, 125.5, 124.2, 121.1, 116.2, 115.3, 112.2, 79.5, 77.3, 76.7, 53.0, 49.5, 34.2, 31.3; Calcd for $C_{33}H_{30}O_4Na$ $[M+Na]^+$: 513.5990. Found: 513.5577.



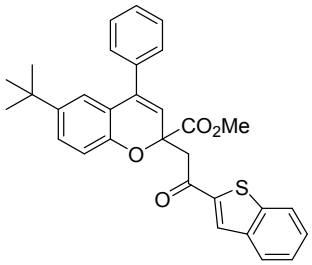
Methyl 6-(tert-butyl)-2-(2-(naphthalen-2-yl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3as): colorless oil, 78.5 mg, 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.59 (s, 1H), 8.19 (d, 1H, *J* = 8.4 Hz), 8.08 (t, 2H, *J* = 6.0 Hz), 8.04 (d, 1H, *J* = 7.6 Hz), 7.74 (dt, 2H, *J* = 7.2 Hz, 24.8 Hz), 7.59–7.43 (m, 6H), 7.34 (d, 1H, *J* = 8.4 Hz), 7.03 (d, 1H, *J* = 8.4 Hz), 6.06 (s, 1H), 4.27 (d, 1H, *J* = 16.4 Hz), 4.03 (s, 3H), 3.95 (d, 1H, *J* = 16.4 Hz), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.6, 171.64, 150.1, 144.2, 138.0, 135.7, 134.0, 132.4, 130.3, 129.6, 128.7, 128.4, 128.2, 127.8, 127.0, 126.8, 123.8, 122.9, 121.2, 120.1, 116.3, 79.3, 77.3, 76.7, 53.0, 46.2, 34.2, 31.3; Calcd for $C_{33}H_{30}O_4Na$ $[M+Na]^+$: 513.5990. Found: 513.7393.



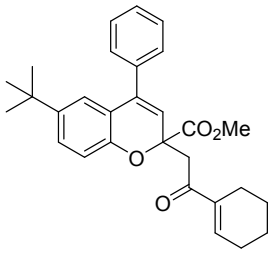
Methyl 2-(2-(anthracen-9-yl)-2-oxoethyl)-6-(tert-butyl)-4-phenyl-2*H*-chromene-2- carboxylate (3at): yellow oil, 84.3 mg, 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (t, 1H, *J* = 9.2 Hz), 8.02 (d, 1H, *J* = 8.8 Hz), 8.28 (q, 1H, *J* = 8.8 Hz), 7.63–7.58 (m, 4H), 7.41–7.23 (m, 5H), 7.17 (s, 1H), 6.75 (d, 1H, *J* = 12.0 Hz), 6.14 (s, 1H), 3.84 (d, 1H, *J* = 18.0 Hz), 3.79 (s, 3H), 3.60 (d, 1H, *J* = 18.0 Hz), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.0, 168.6, 158.1, 144.1, 139.0, 137.4, 135.3, 132.3, 130.3, 128.7, 128.4, 128.1, 127.3, 126.7, 125.7, 125.9, 124.8, 124.3, 123.2, 116.4, 115.6, 112.3, 79.2, 77.3, 76.7, 52.9, 46.2, 34.2, 31.4; Calcd for $C_{37}H_{32}O_4Na$ $[M+Na]^+$: 563.6590. Found: 563.6567.



Methyl 2-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)-6-(tert-butyl)-4-phenyl-2*H*-chromene- 2-carboxylate (3au): yellow oil, 73.4 mg, 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, 2H, *J* = 24.4 Hz), 7.63 (d, 4H, *J* = 18.0 Hz), 7.41 (t, 3H, *J* = 11.2 Hz), 7.33–7.12 (m, 5H), 7.02 (s, 1H), 6.75 (d, 1H, *J* = 13.6 Hz), 6.13 (s, 1H,), 3.84 (d, 1H, *J* = 22.0 Hz), 3.78 (s, 3H), 3.60 (d, 1H, *J* = 22.0 Hz), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.5, 168.6, 151.9, 145.5, 145.2, 140.9, 140.0, 135.9, 135.6, 129.4, 129.3, 128.7, 128.3, 127.9, 127.8, 127.4, 124.9, 123.2, 116.2, 115.3, 112.6, 81.9, 77.3, 76.7, 52.8, 42.2, 34.5, 31.3; Calcd for $C_{35}H_{32}O_4Na$ $[M+Na]^+$: 539.6370. Found: 539.6218.

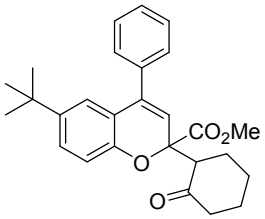


Methyl 2-(2-(benzo[b]thiophen-2-yl)-2-oxoethyl)-6-(tert-butyl)-4-phenyl-2*H*-chromene-2-carboxylate (3av): yellow oil, 73.5 mg, 74%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (d, 1H, *J* = 8.0 Hz), 8.28 (dd, 1H, *J* = 8.8 Hz, 54.0 Hz), 7.46–7.27 (m, 1H), 7.17 (s, 2H), 6.75 (d, 5H, *J* = 12.0 Hz), 6.13 (s, 1H), 3.84 (d, 1H, *J* = 18.0 Hz), 3.69 (s, 3H), 3.57 (d, 1H, *J* = 18.0 Hz), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.5, 168.6, 158.1, 146.2, 145.5, 144.6, 140.0, 139.3, 128.7, 128.4, 128.0, 124.7, 124.4, 124.3, 123.3, 122.9, 116.6, 116.1, 115.3, 112.3, 81.9, 77.3, 76.7, 52.7, 42.2, 34.4, 31.3; Calcd for $C_{31}H_{28}O_4SNa$ $[M+Na]^+$: 519.6210. Found: 519.5991.

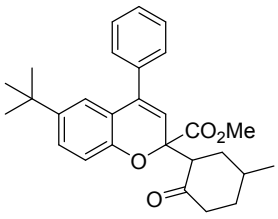


Methyl 6-(tert-butyl)-2-(2-(cyclohex-1-en-1-yl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3aw): Milky white solid, 45.2 mg, 54%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53–7.34 (m, 6H), 7.18 (d, 1H, *J* = 4.8 Hz), 6.75 (d, 1H, *J* = 7.6 Hz), 6.29 (s, 1H), 3.76 (s, 3H), 3.28 (t, 1H, *J* = 19.6 Hz), 2.56–2.13 (m, 2H), 1.87–1.61 (m, 6H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.5, 167.9, 151.7, 150.3, 145.5, 140.1, 137.6, 135.9, 128.6, 128.3, 127.9, 124.9, 123.2, 116.5, 115.6,

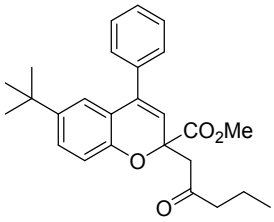
112.6, 84.1, 77.3, 76.7, 51.7, 41.6, 35.7, 35.7, 31.3, 26.9, 23.8, 22.4, 21.9; Calcd for $C_{29}H_{32}O_4Na$ $[M+Na]^+$: 467.5710. Found: 467.4917.



Methyl 6-(tert-butyl)-2-(2-oxocyclohexyl)-4-phenyl-2*H*-chromene-2-carboxylate (3ax): yellow oil, 47.6 mg, 55%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53–7.33 (m, 5H), 7.18 (d, 1H, *J* =12.8 Hz), 6.75 (d, 1H, *J* =8.4 Hz), 6.28 (s, 1H), 3.76 (s, 3H), 3.28 (t, 1H, *J* = 16.0 Hz), 2.44 (t, 2H, *J* = 16.4 Hz), 2.10–1.82 (m, 5H), 1.68–1.50 (m, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 211.0, 168.8, 151.7, 146.3, 140.6, 135.8, 128.2, 127.8, 124.3, 123.3, 128.6, 116.7, 112.6, 89.0, 77.3, 76.7, 52.6, 44.6, 41.9, 34.5, 31.3, 26.9, 24.3, 20.9; Calcd for $C_{27}H_{30}O_4Na$ $[M+Na]^+$: 441.5370. Found: 441.9835.

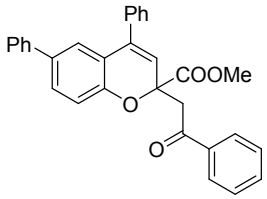


Methyl 6-(tert-butyl)-2-(5-methyl-2-oxocyclohexyl)-4-phenyl-2*H*-chromene-2-carboxylate (3ay): milky oil, 59.6 mg, 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42–7.23 (m, 5H), 7.17 (s, 1H), 6.75 (d, 1H, *J* = 12.0 Hz), 6.62 (t, 1H, *J* = 10.0 Hz), 6.14 (s, 1H), 3.84 (d, 1H, *J* = 22.0 Hz), 3.79 (s, 3H), 3.60 (d, 1H, *J* =22.0 Hz), 2.24 (t, 2H, *J* = 17.2 Hz), 1.93 (dd, 2H, *J* = 16.8 Hz, 31.2 Hz), 1.78–1.62 (m, 2H), 1.58–1.42 (m, 2H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 211.5, 167.8, 150.7, 148.3, 143.6, 135.7, 128.7, 128.2, 127.8, 126.3, 125.2, 123.6, 122.7, 115.6, 89.1, 77.3,76.7, 51.6, 41.6, 40.3, 35.7, 34.0, 32.0, 31.3, 30.0, 26.9, 22.0; Calcd for $C_{28}H_{32}O_4Na$ $[M+Na]^+$: 455.5600. Found: 455.8372.

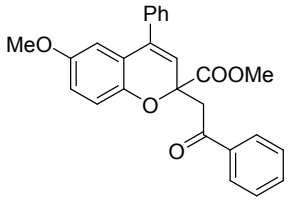


Methyl 6-(tert-butyl)-2-(2-oxopentyl)-4-phenyl-2*H*-chromene-2-carboxylate (3az): yellow oil, 44.7 mg, 55%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41–7.34 (m, 5H), 7.22 (d, 1H, *J* = 8.4 Hz), 7.04 (s,

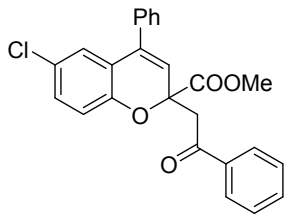
1H), 6.91 (d, 1H, *J* = 8.4 Hz), 5.70 (s, 1H), 3.81 (s, 3H), 3.28 (d, 1H, *J* = 16.0 Hz), 3.13 (d, 1H, *J* = 16.0 Hz), 2.42 (t, 2H, *J* = 7.2 Hz), 1.60 (qd, 2H, *J* = 7.2 Hz), 1.19 (s, 9H), 0.90 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 206.5, 171.4, 150.1, 144.2, 137.8, 137.4, 128.6, 128.4, 128.2, 126.9, 123.0, 121.1, 120.0, 116.1, 79.0, 77.3, 76.7, 52.9, 49.9, 45.8, 34.2, 31.3, 16.9, 13.6; Calcd for $C_{26}H_{30}O_4Na$ $[M+Na]^+$: 429.5220. Found: 429.5959.



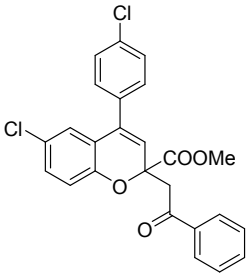
Methyl 2-(2-oxo-2-phenylethyl)-4,6-diphenyl-2*H*-chromene-2-carboxylate (3ba): yellow oil, 76.4 mg, 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (s, 1H), 7.77 (d, 1H, *J* = 10.0 Hz), 7.29–7.47 (m, 4H), 7.14–7.20 (m, 5H), 6.96 (d, 1H, *J* = 12.0 Hz), 6.28 (s, 1H), 3.74 (s, 3H), 2.55 (t, 2H, *J* = 10.8,Hz), 2.41 (t, 2H, *J* = 10.8 Hz); ^{13}C NMR (100 MHz, CDCl3) δ: 168.5, 155.4, 142.1, 140.9, 140.0, 135.1, 133.2, 129.3, 128.8, 128.7, 128.3, 128.2, 127.9, 127.6, 126.8, 116.4, 116.0, 113.6, 90.1, 77.3, 76.7, 52.6, 36.2, 27.2; Calcd for $C_{31}H_{24}O_4Na$ $[M+Na]^+$: 483.1675. Found: 483.4783.



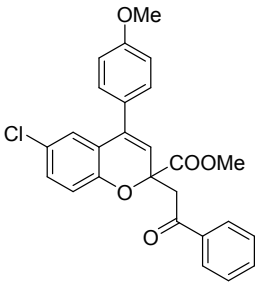
Methyl 6-methoxy-2-(2-oxo-2-phenylethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3ca): yellow oil, 68.8 mg, 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38–7.29 (m, 5H), 7.19–7.07 (m, 5H), 6.81 (d, 1H, *J* = 20.0 Hz), 6.73 (d, 1H, *J* = 2.4 Hz), 6.61 (dd, 1H, *J* = 2.4 Hz, 6.4 Hz), 6.28 (s, 1H), 3.79 (s, 3H), 3.67 (s, 3H), 2.54 (t, 2H, *J* = 10.4 Hz), 2.41 (t, 2H, *J* = 10.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.5, 152.1, 146.8, 142.1, 140.1, 135.2, 128.8, 128.6, 128.3, 128.1, 127.9, 126.0, 116.6, 116.1, 114.5, 111.2, 90.2, 77.3, 76.7, 55.9, 52.7, 36.2, 27.1; Calcd for $C_{26}H_{22}O_4Na$ $[M+Na]^+$: 437.4567. Found: 437.6989.



methyl 6-chloro-2-(2-oxo-2-phenylethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3da): milky oil, 71.2 mg, 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38–7.30 (m, 5H), 7.19–7.11 (m, 5H), 7.07 (d, 1H, *J* = 4.0 Hz), 6.98 (dd, 1H, *J* = 3.2 Hz, 12.0 Hz), 6.89 (d, 1H, *J*= 10.0 Hz), 6.37 (s, 1H), 3.68 (s, 3H), 2.55 (t, 2H, *J* = 10.4 Hz), 2.41 (t, 2H, *J* = 10.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.4, 152.2, 142.1, 140.1, 135.3, 129.7, 128.9, 128.6, 128.3, 128.2, 127.9, 127.0, 126.0, 125.8, 116.5, 115.7, 114.2, 90.2, 77.3, 76.7, 52.7, 36.3, 27.1; Calcd for $C_{25}H_{19}ClO_4Na$ $[M+Na]^+$: 441.8730. Found: 441.7361.



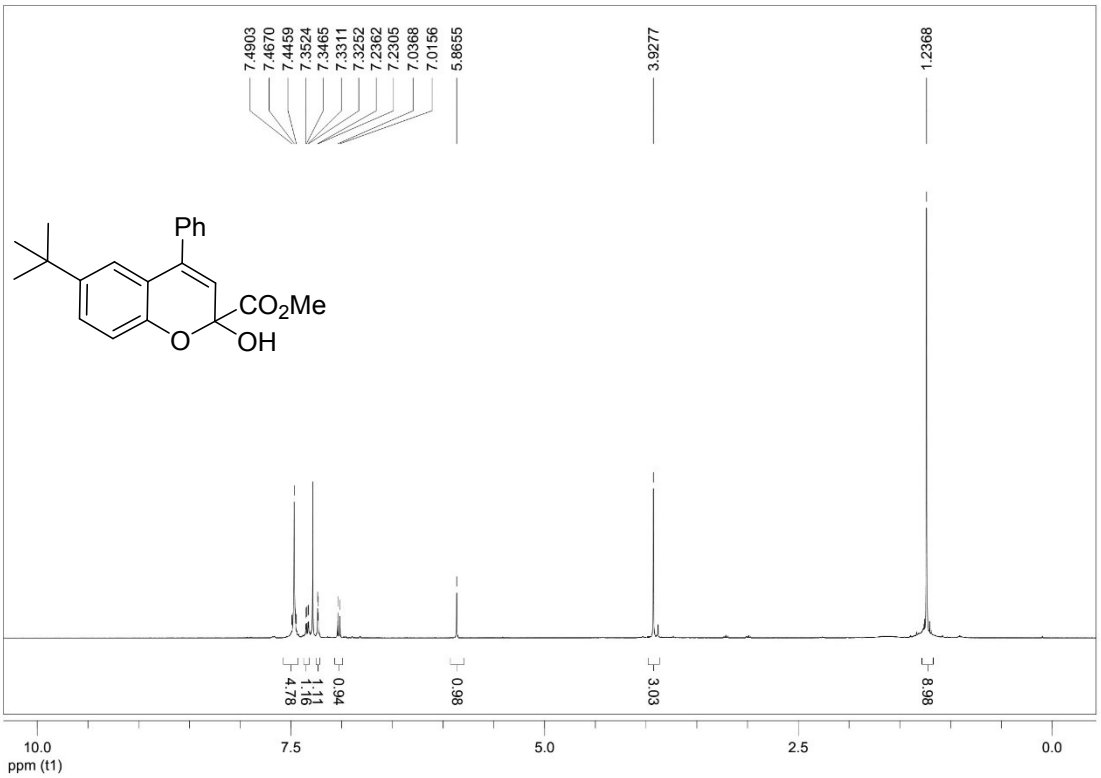
Methyl 6-chloro-4-(4-chlorophenyl)-2-(2-oxo-2-phenylethyl)-2*H*-chromene-2- carboxylate (3ea): milky oil, 73.3 mg, 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, 2H, *J* = 4.0 Hz), 7.60–7.45 (m, 8H), 7.38 (d, 1H, *J* = 4.0 Hz), 6.78 (d, 1H, *J* = 16.0 Hz), 6.29 (s, 1H), 3.83 (s, 3H), 2.57–2.25 (m, 1H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.5, 155.1, 145.5, 142.0, 138.1, 135.2, 133.6, 128.8, 128.7, 128.1, 127.8, 126.0, 124.8, 123.2, 116.2, 116.0, 112.1, 90.1, 77.3, 76.7, 52.7, 36.3, 34.7, 31.3, 27.1; Calcd for $C_{25}H_{18}Cl_2O_4Na$ $[M+Na]^+$: 476.3150. Found: 476.3777.

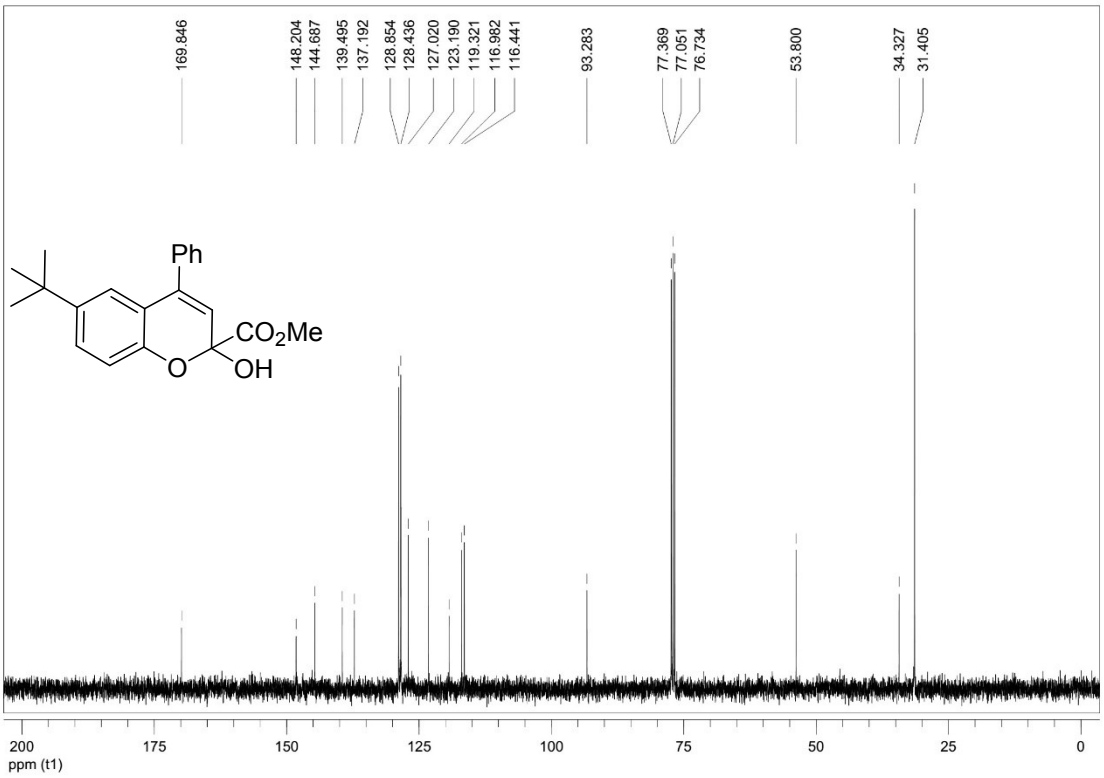


Methyl 6-chloro-4-(4-methoxyphenyl)-2-(2-oxo-2-phenylethyl)-2*H*-chromene-2- carboxylate (3ea): milky oil, 72.7 mg, 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (d, 2H, *J* = 18.0 Hz), 7.20 (dd, 1H, *J* = 4.8 Hz, 8.8 Hz), 7.09–7.15 (m, 6H), 7.04 (d, 2H, *J* = 4.0 Hz), 6.90 (d, 1H, *J* = 16.0 Hz), 6.79 (d, 1H, *J* = 11.2 Hz), 6.29 (s, 1H), 3.79 (s, 3H), 3.63 (s, 3H), 2.25–2.57 (m, 2H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.4, 159.9, 152.1, 145.4, 142.1, 135.2, 132.3, 129.8, 128.8, 128.1, 126.9, 124.4, 123.2, 116.2, 116.0, 112.6, 90.1, 77.3, 76.7, 56.0, 52.6, 36.2, 34.3, 31.2, 27.3; Calcd for $C_{26}H_{21}ClO_5Na$ $[M+Na]^+$: 471.8990. Found: 471.7392.

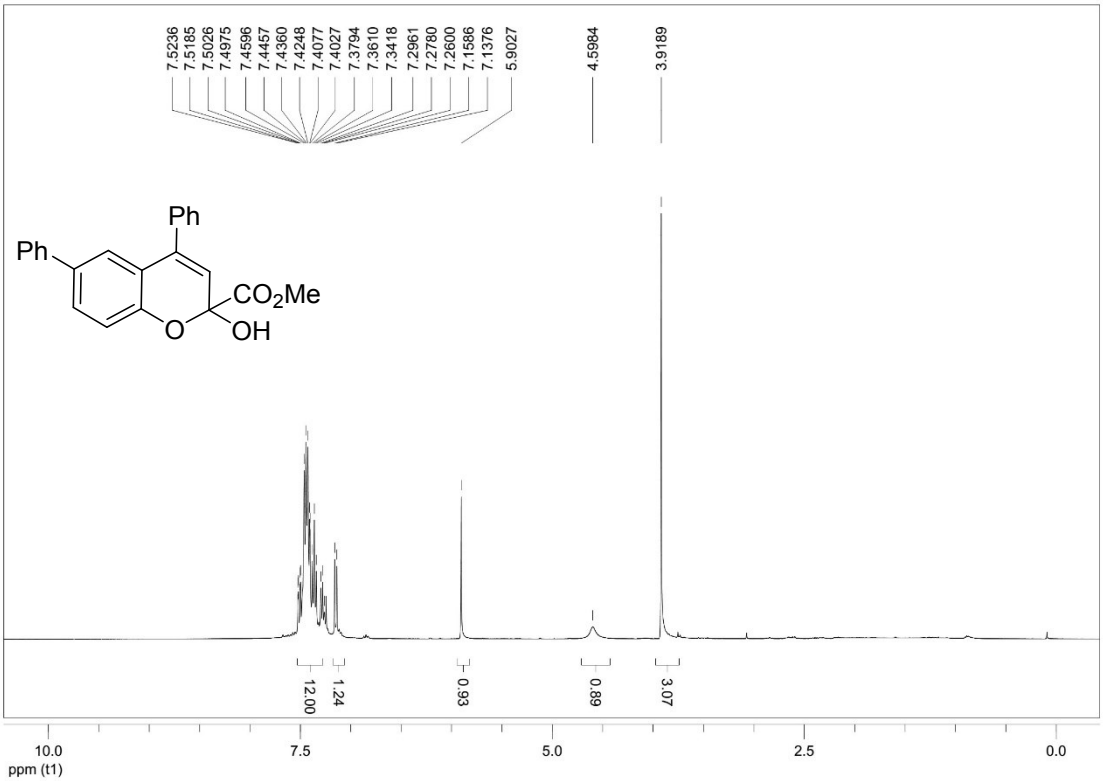
4. NMR Spectra for Products

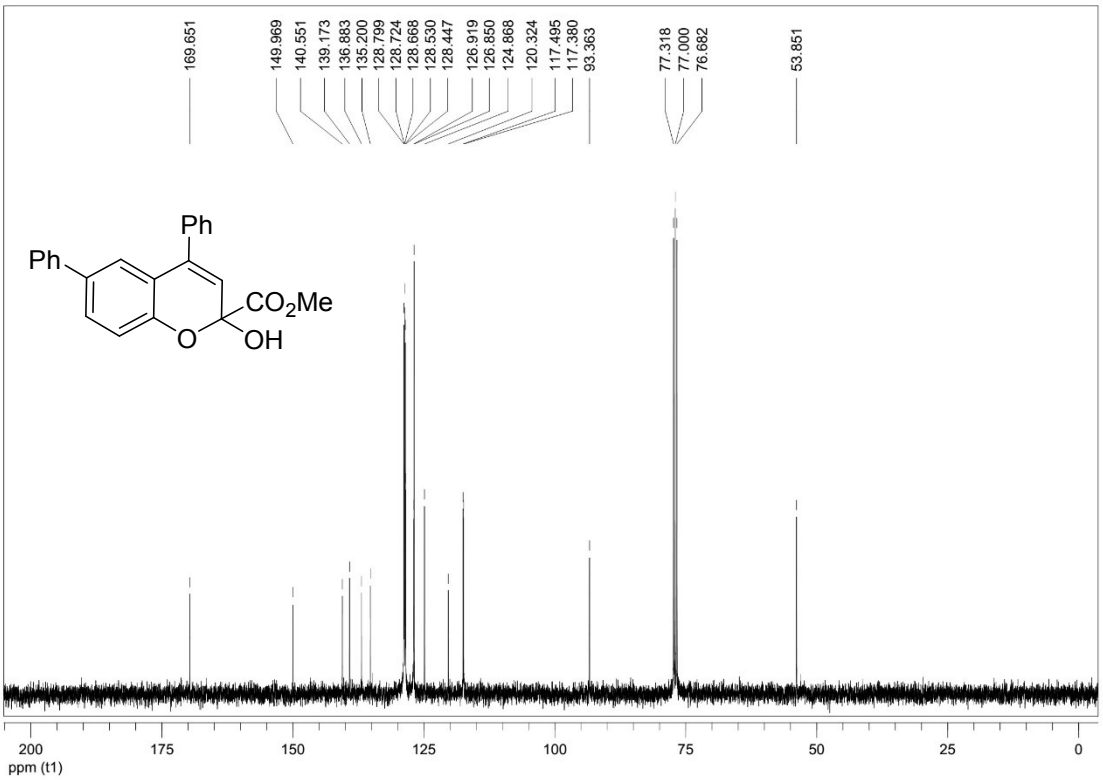
2*H*-Chromene hemiacetal **1a**



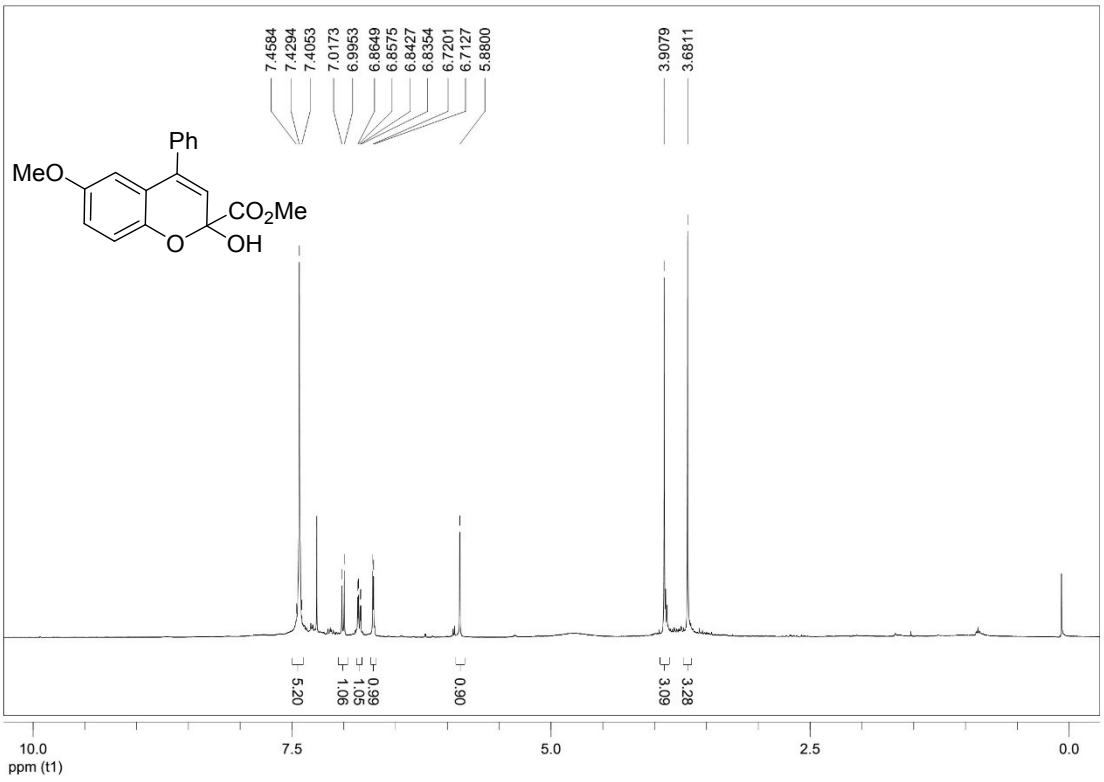


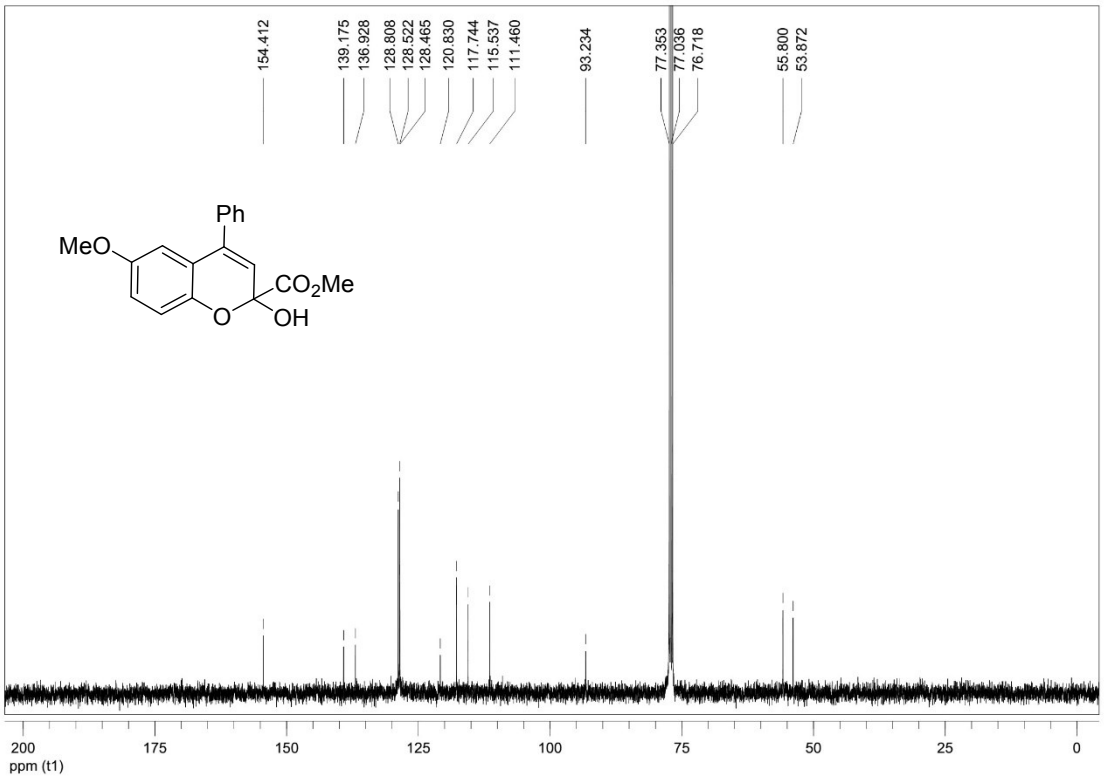
2*H*-Chromene hemiacetal **1b**



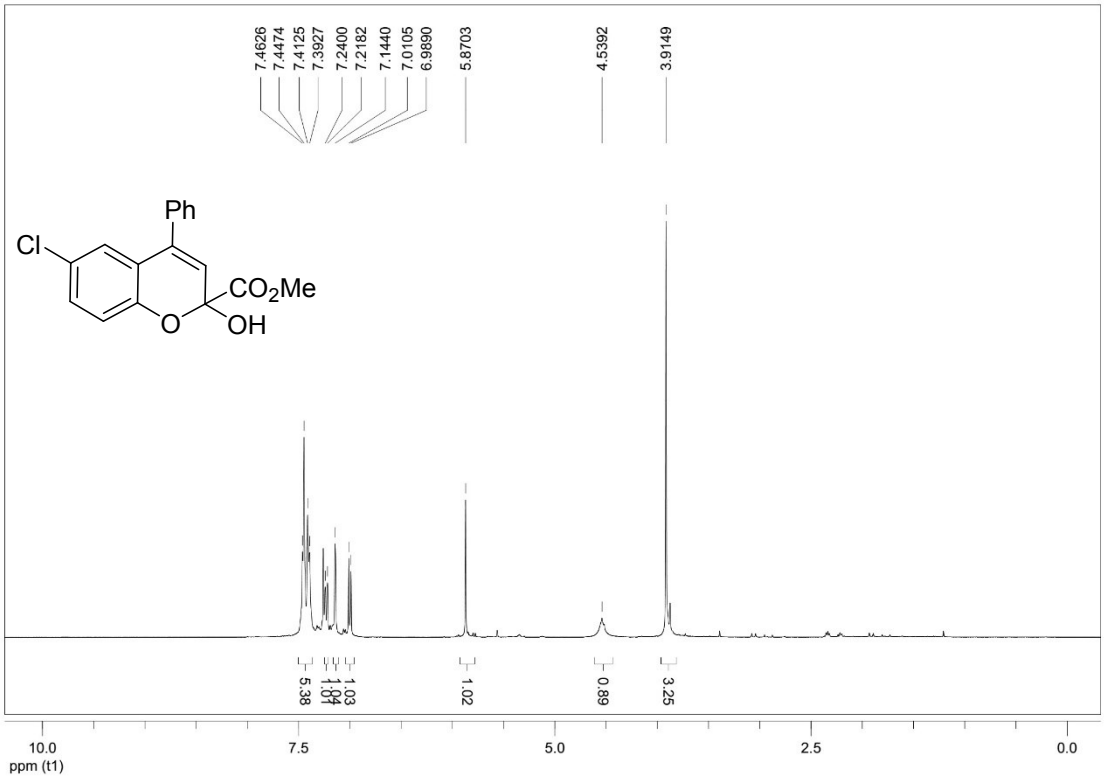


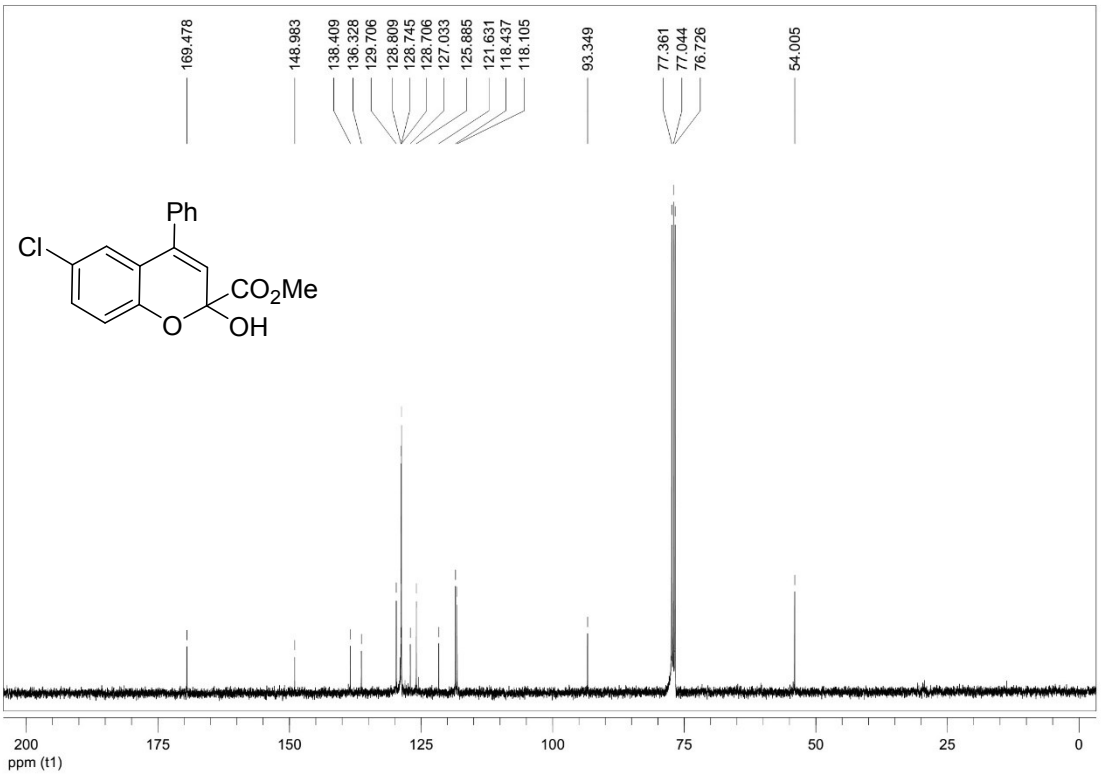
2*H*-Chromene hemiacetal **1c**



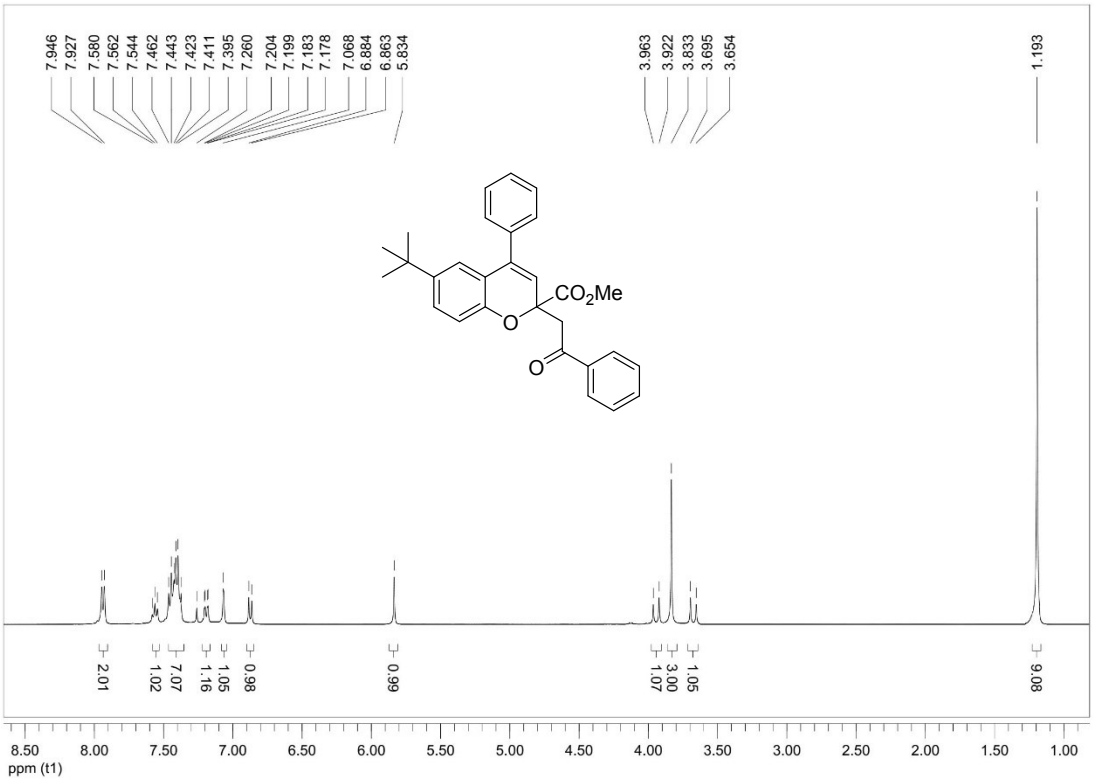


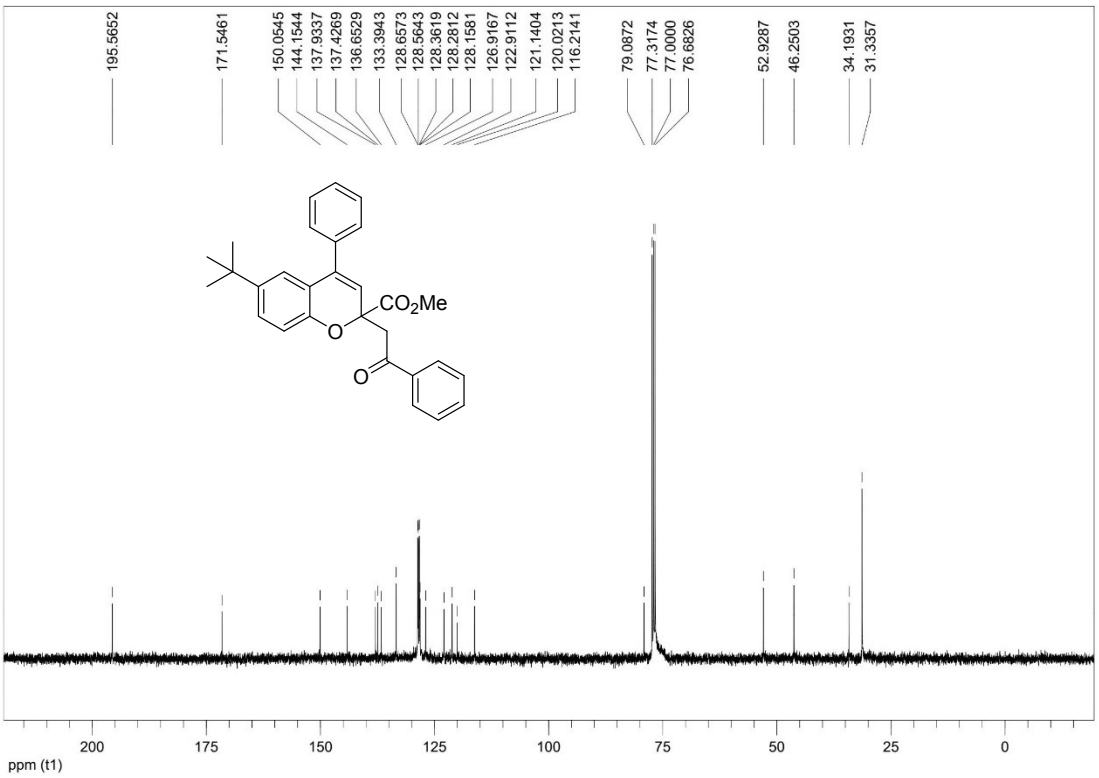
2*H*-Chromene hemiacetal **1d**



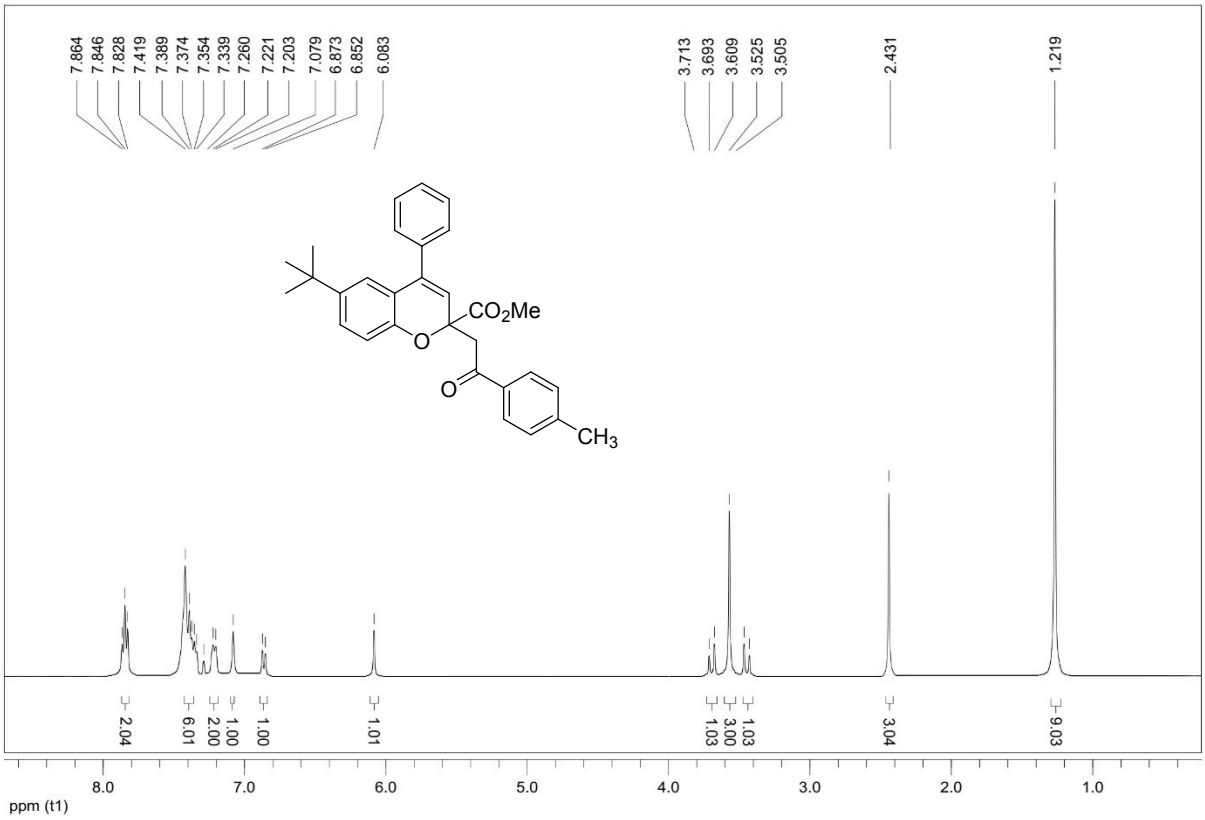


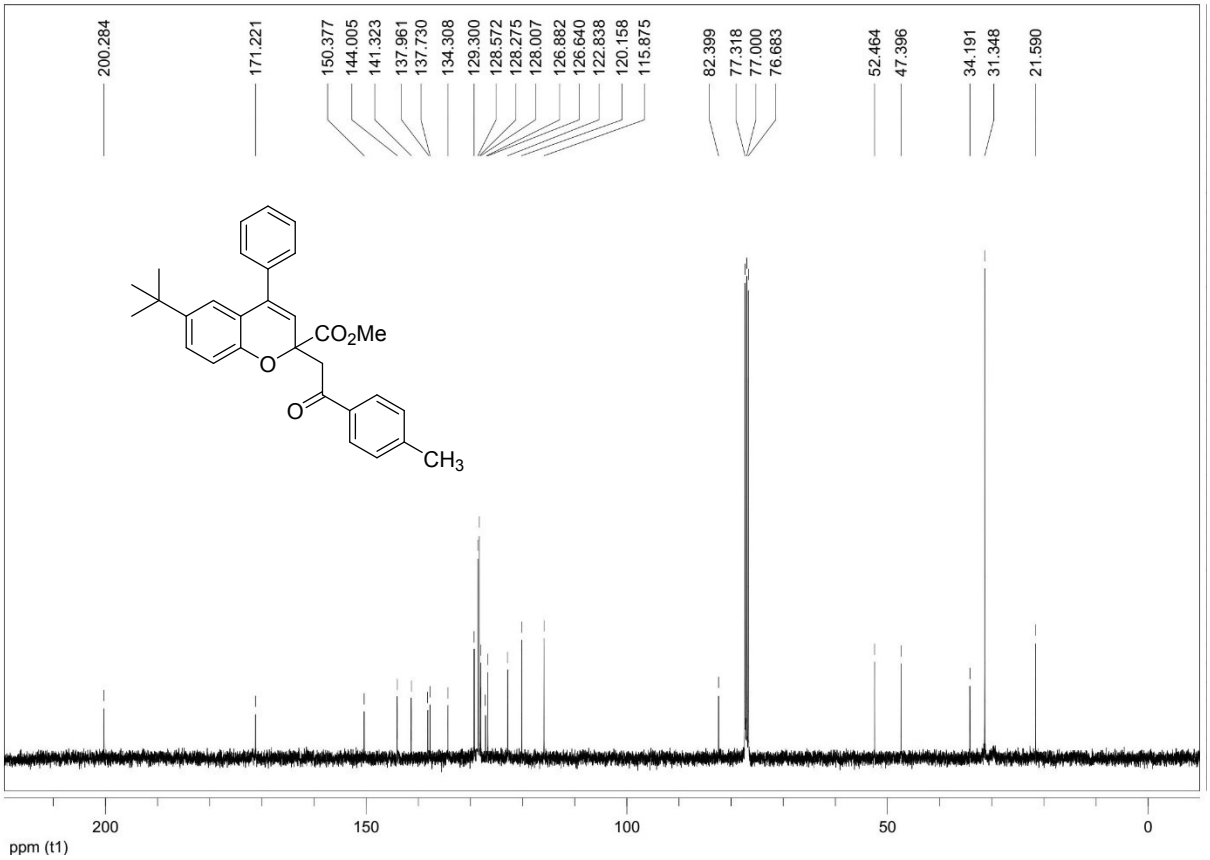
Methyl 6-(tert-butyl)-2-(2-oxo-2-phenylethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3aa)



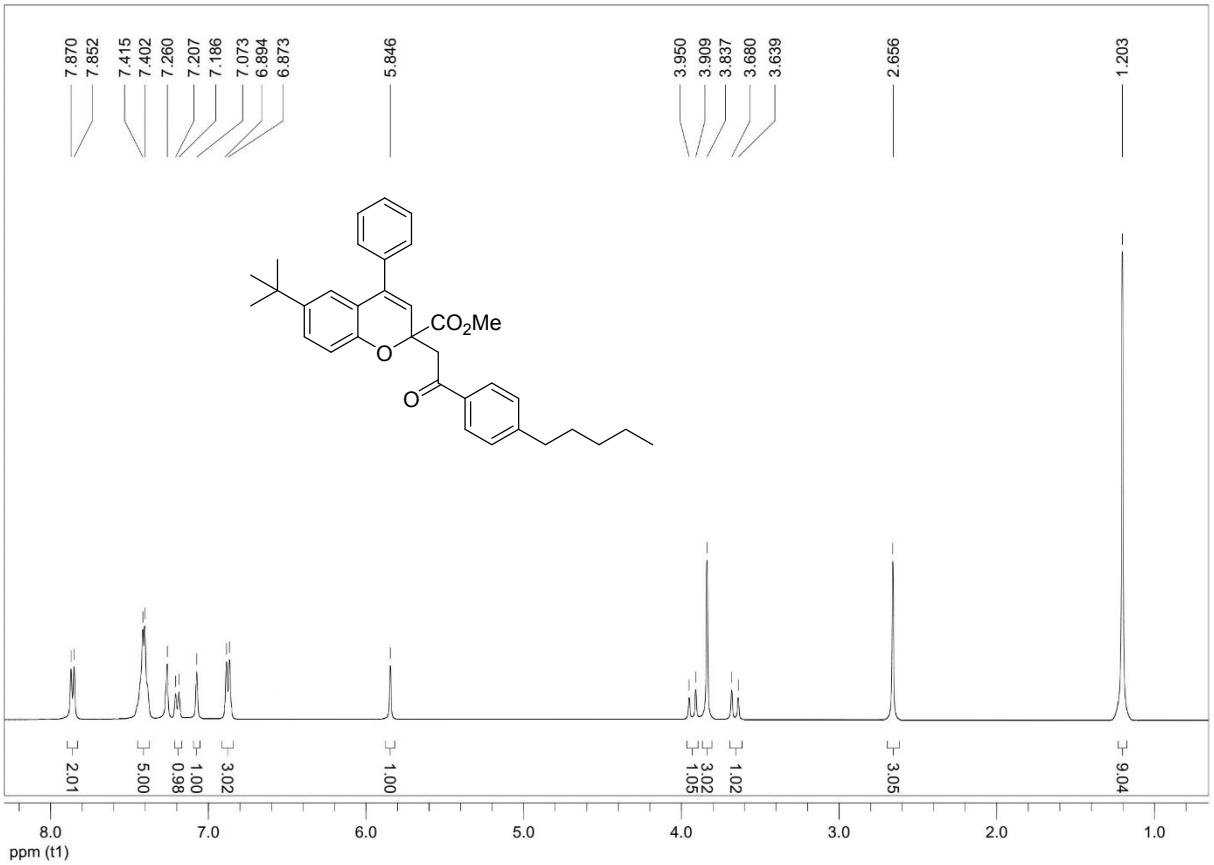


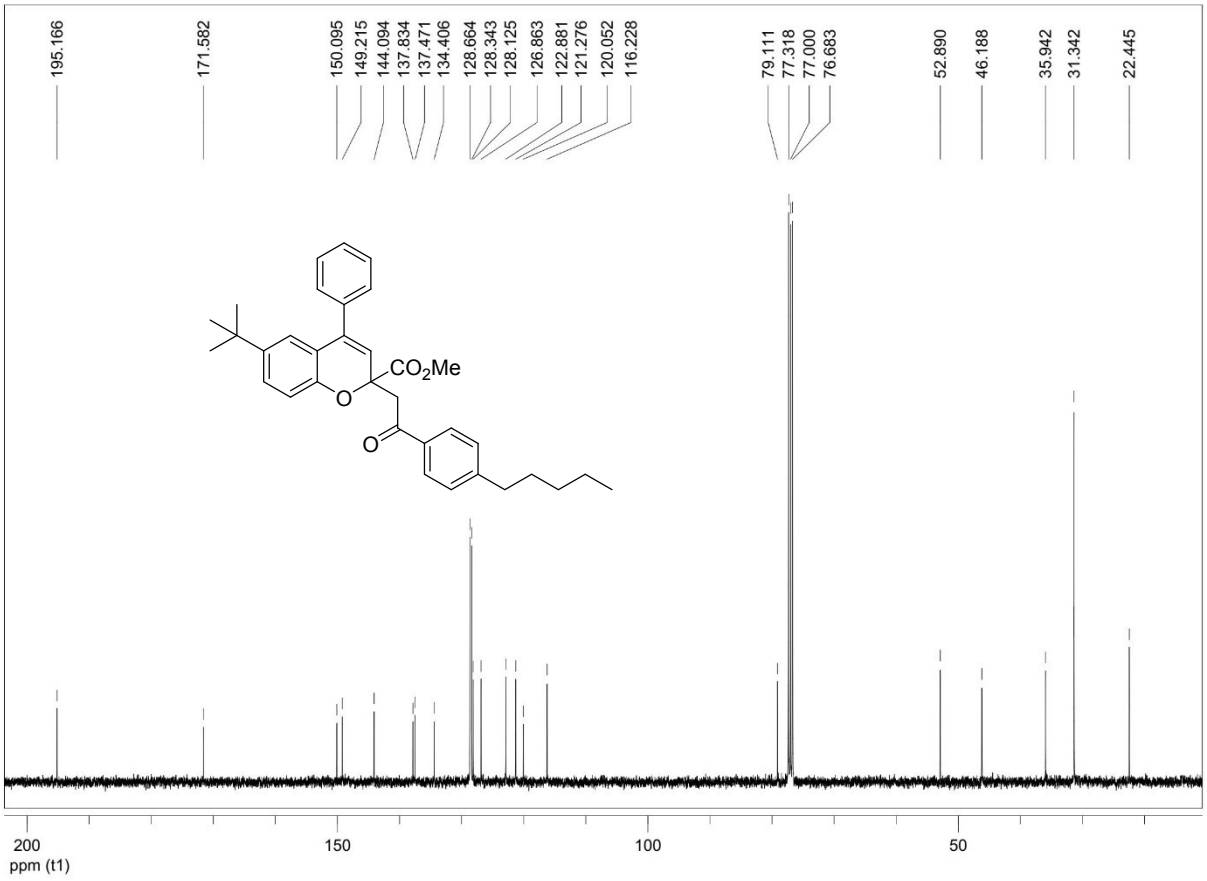
Methyl 6-(tert-butyl)-2-(2-oxo-2-(p-tolyl)ethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3ab)



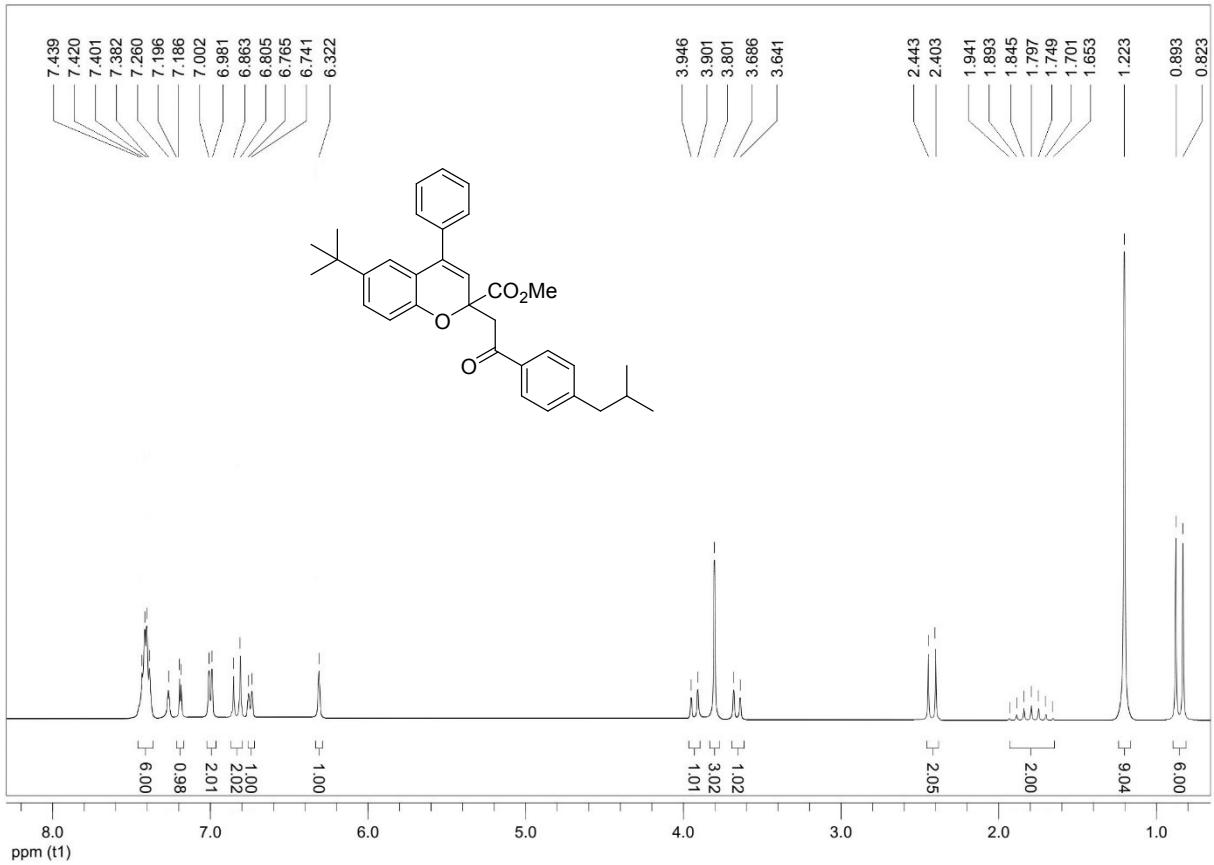


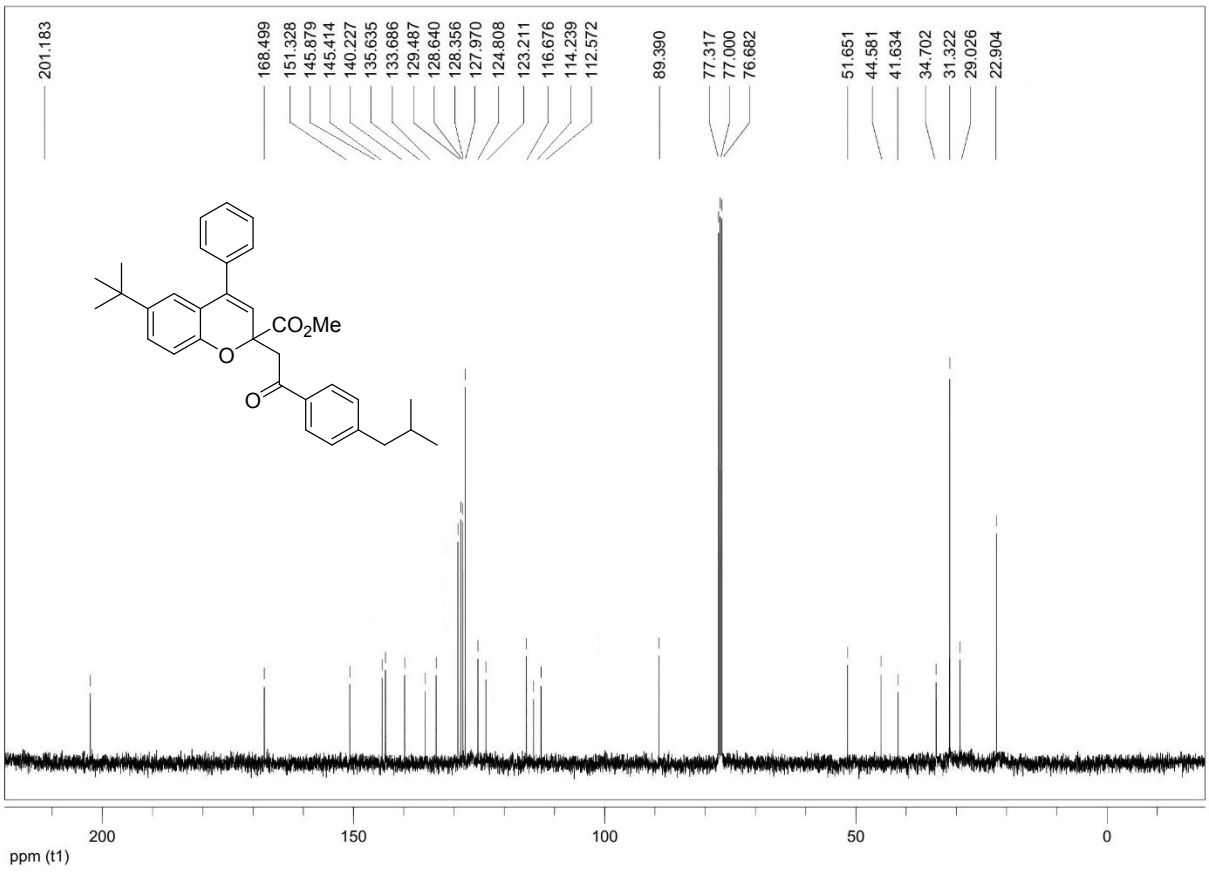
Methyl 6-(tert-butyl)-2-(2-oxo-2-(4-pentylphenyl)ethyl)-4-phenyl-2*H*-chromene-2- carboxylate (3ac)



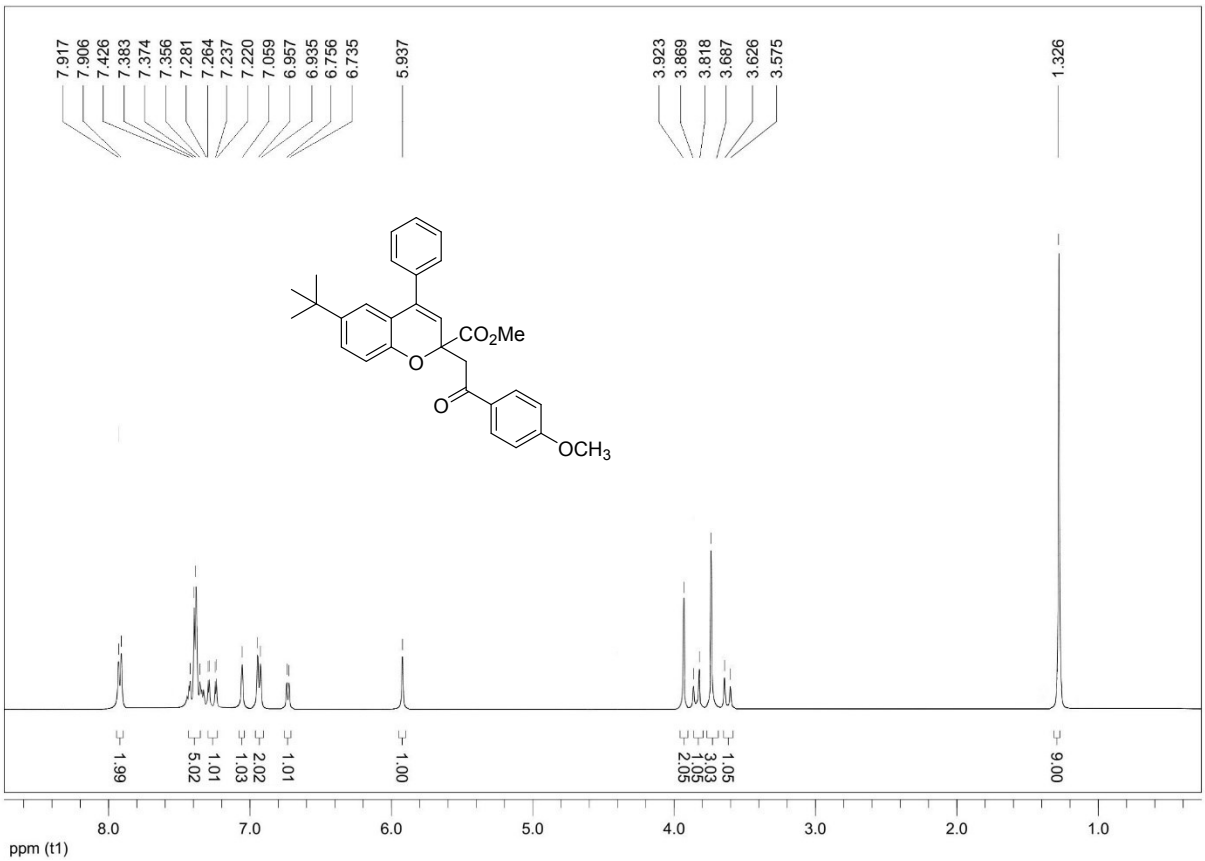


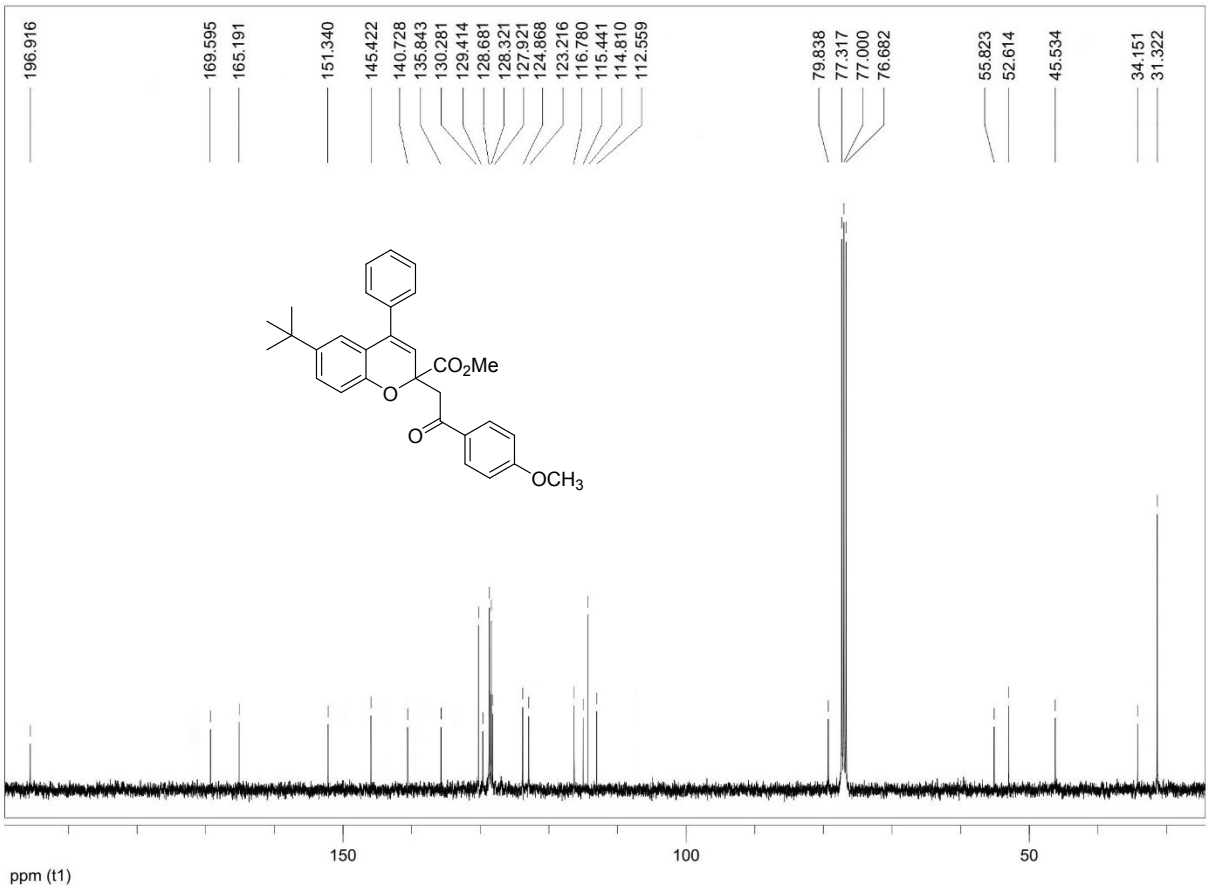
Methyl 6-(tert-butyl)-2-(2-(4-isobutylphenyl)-2-oxoethyl)-4-phenyl-2H-chromene-2- carboxylate (3ad)



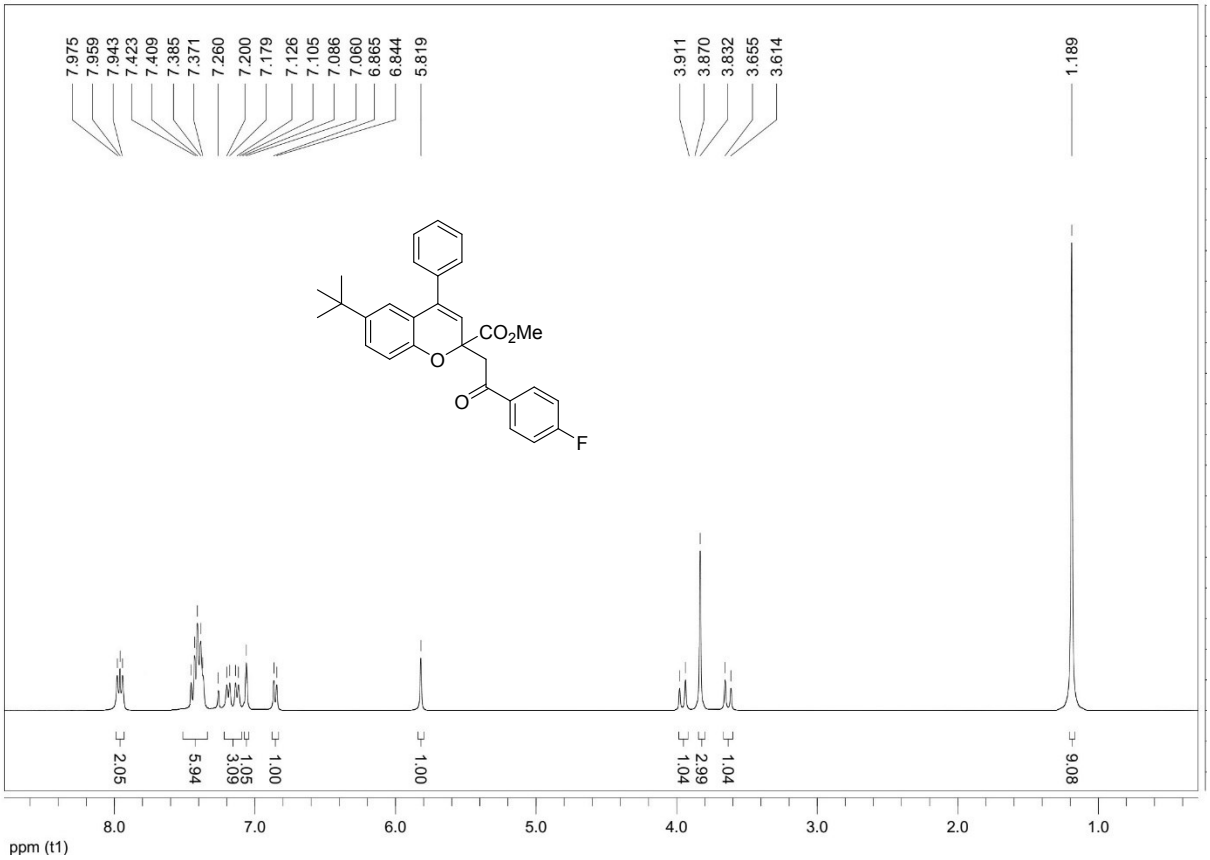


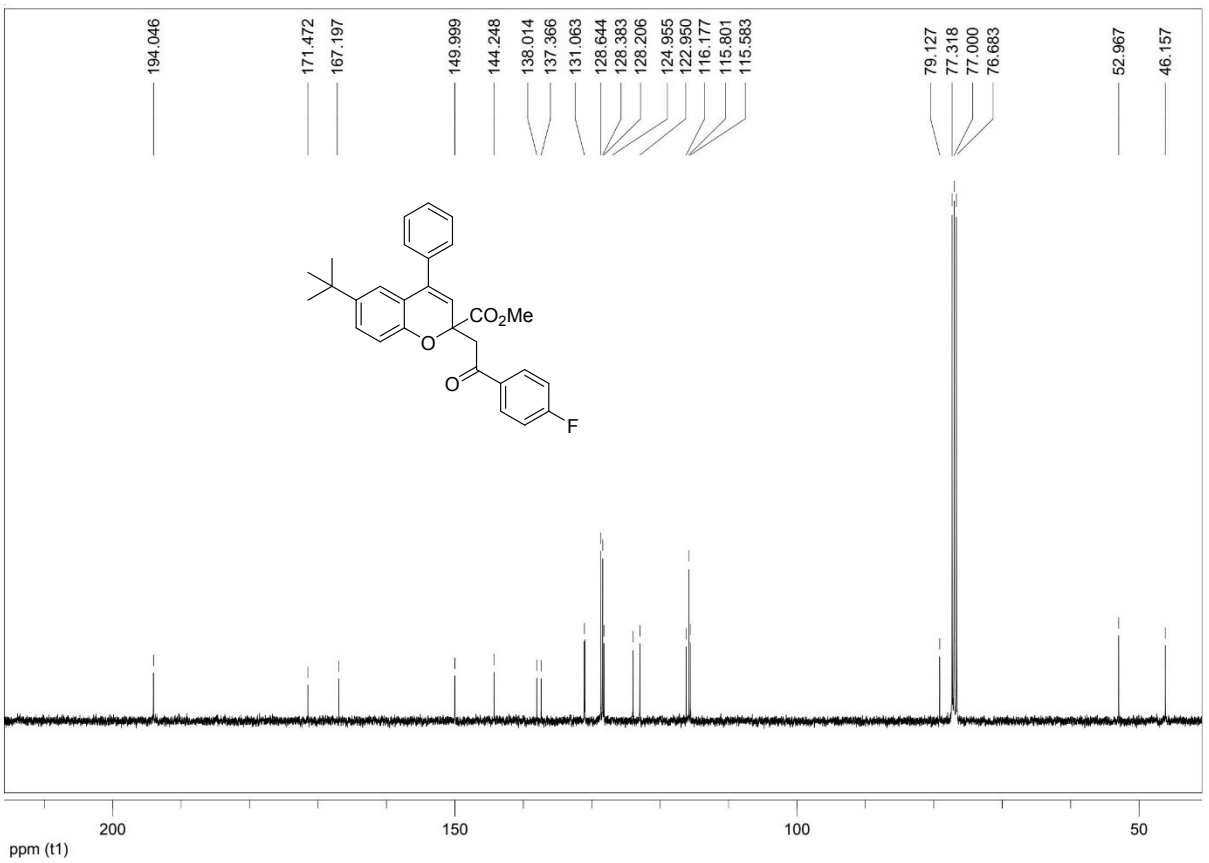
Methyl 6-(tert-butyl)-2-(2-(4-methoxyphenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2- carboxylate (3ae)



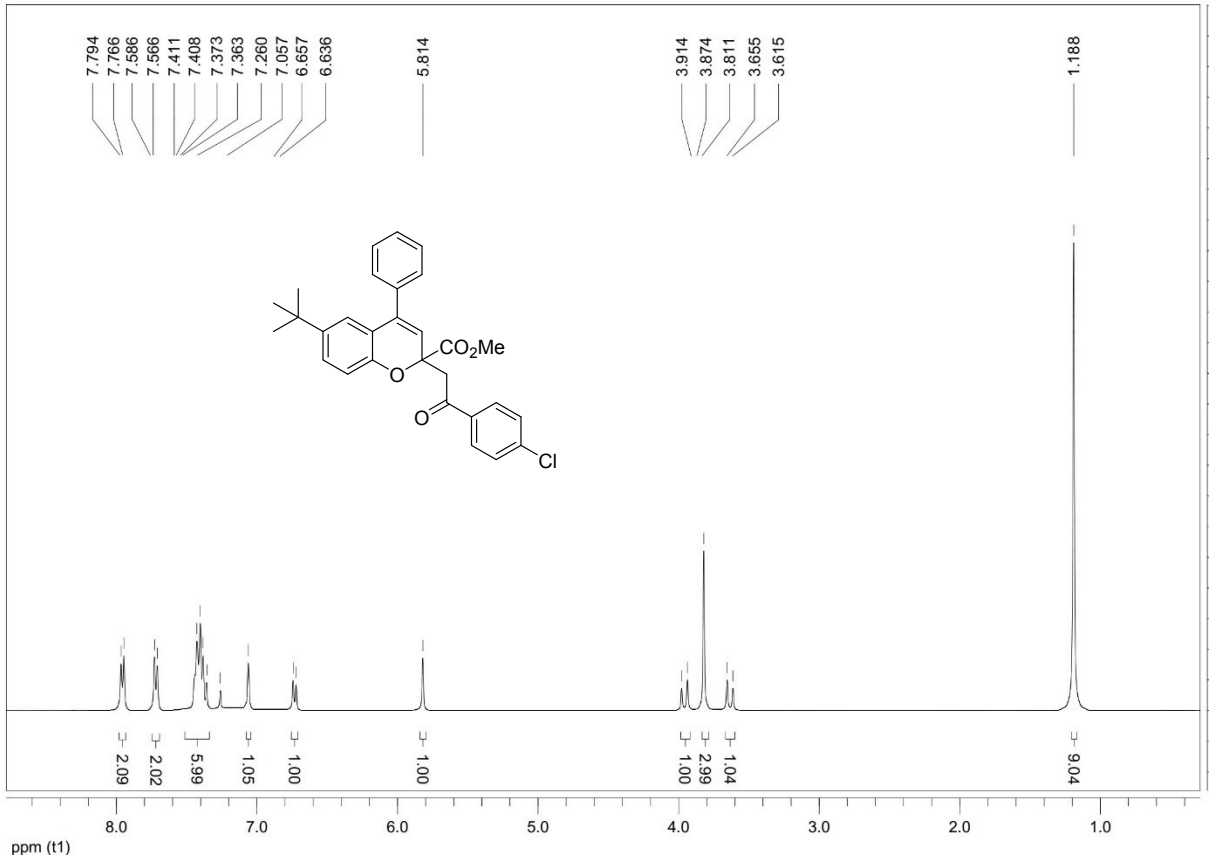


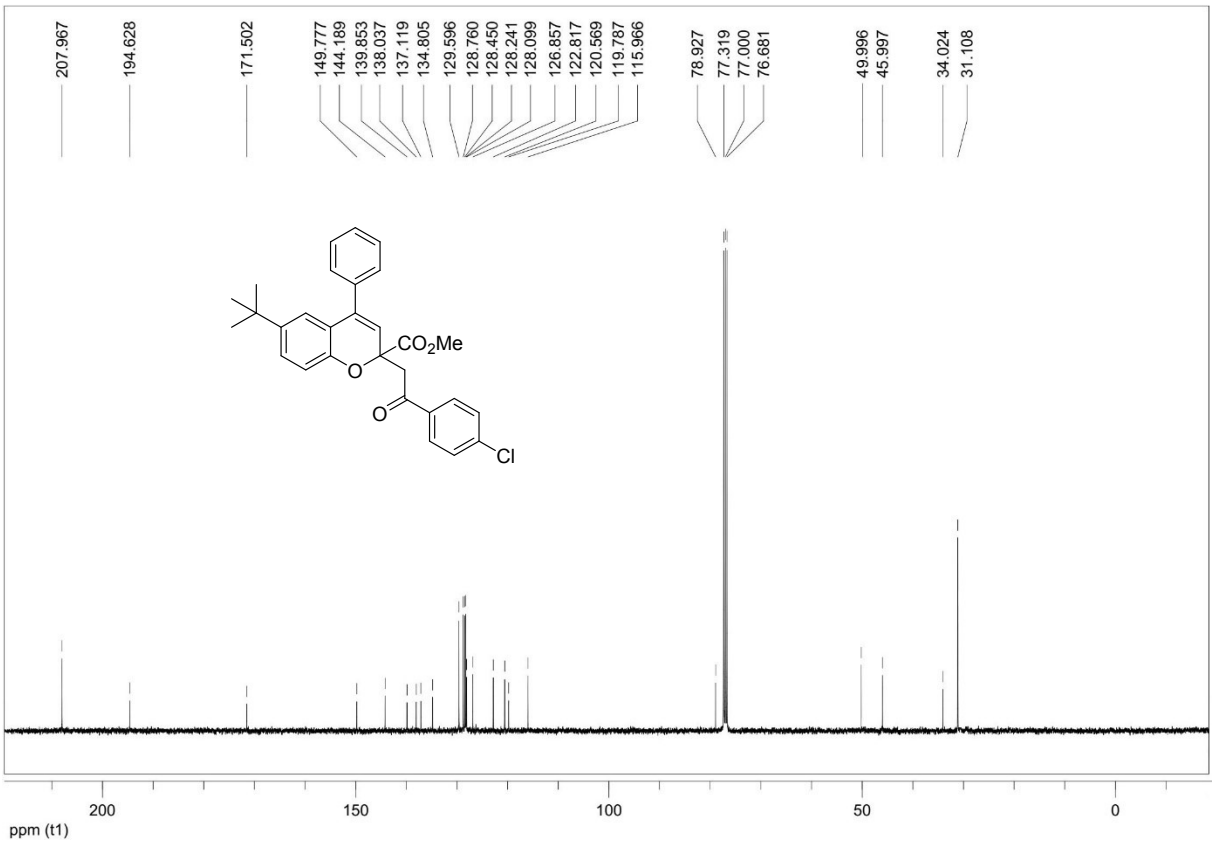
Methyl 6-(tert-butyl)-2-(2-(4-fluorophenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2- carboxylate (3af)



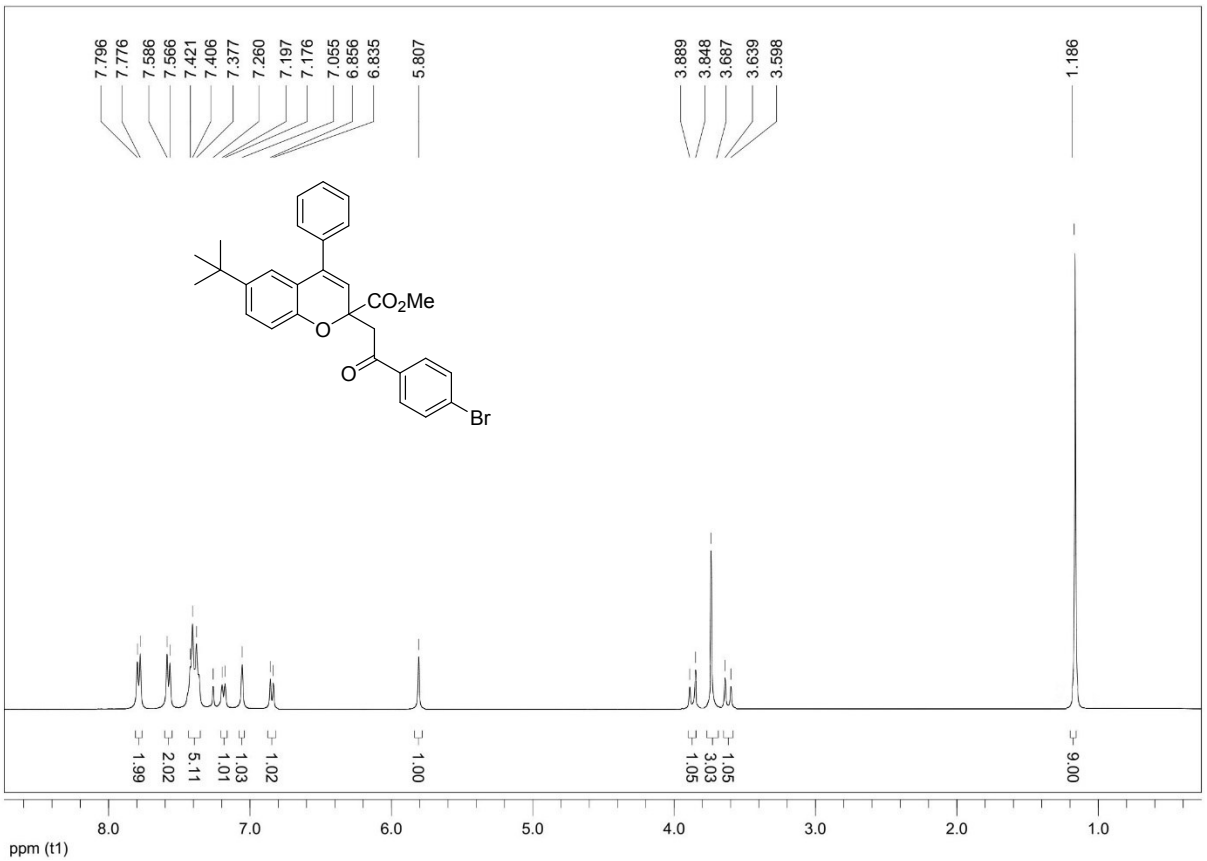


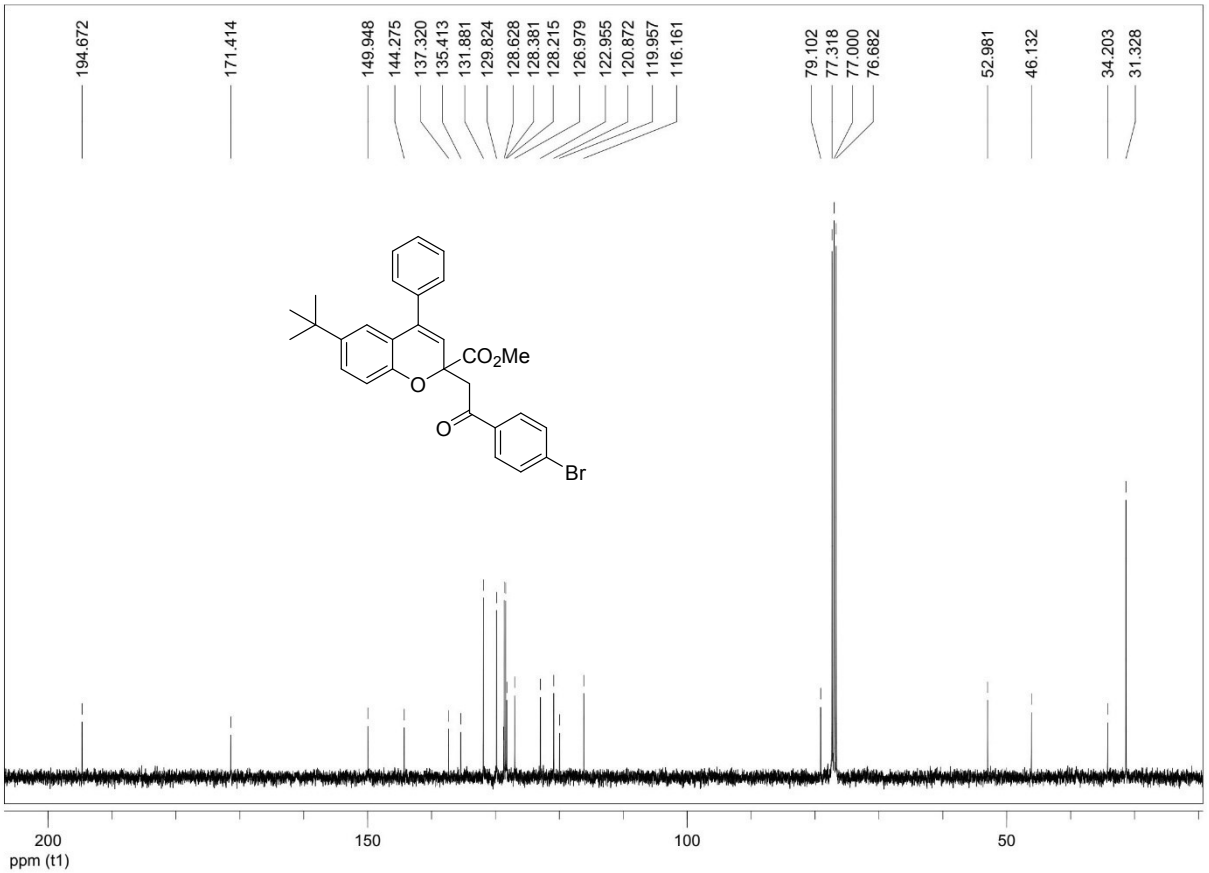
Methyl 6-(tert-butyl)-2-(2-(4-chlorophenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2- carboxylate (3ag)



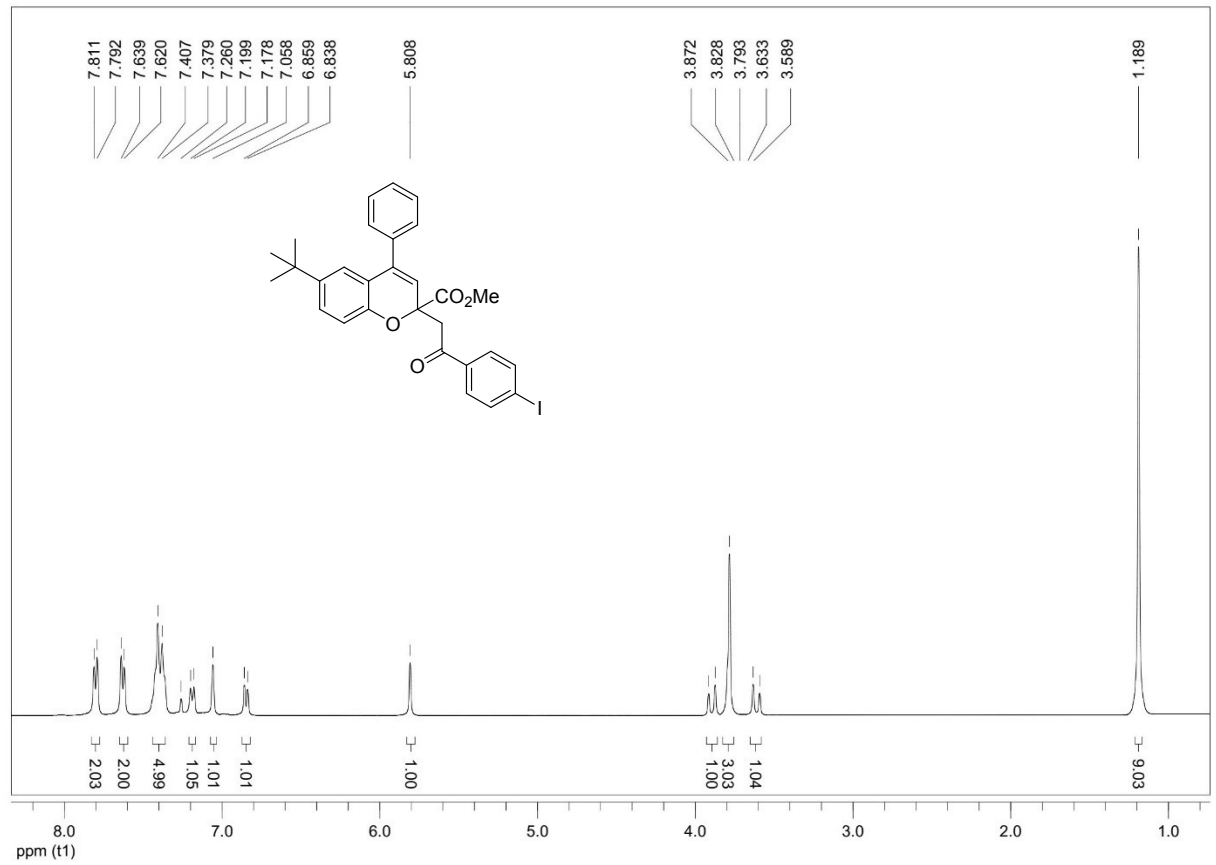


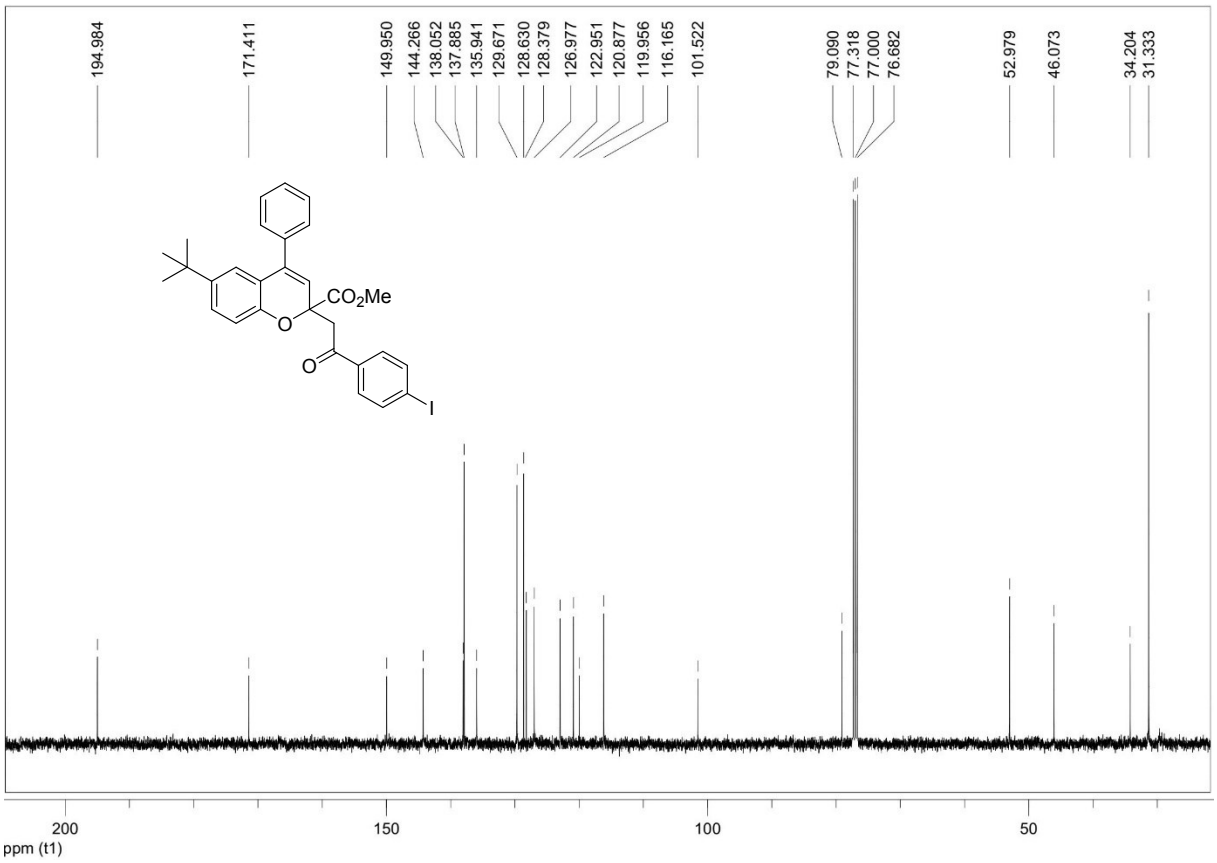
Methyl 2-(2-(4-bromophenyl)-2-oxoethyl)-6-(tert-butyl)-4-phenyl-2H-chromene-2- carboxylate (3ah)



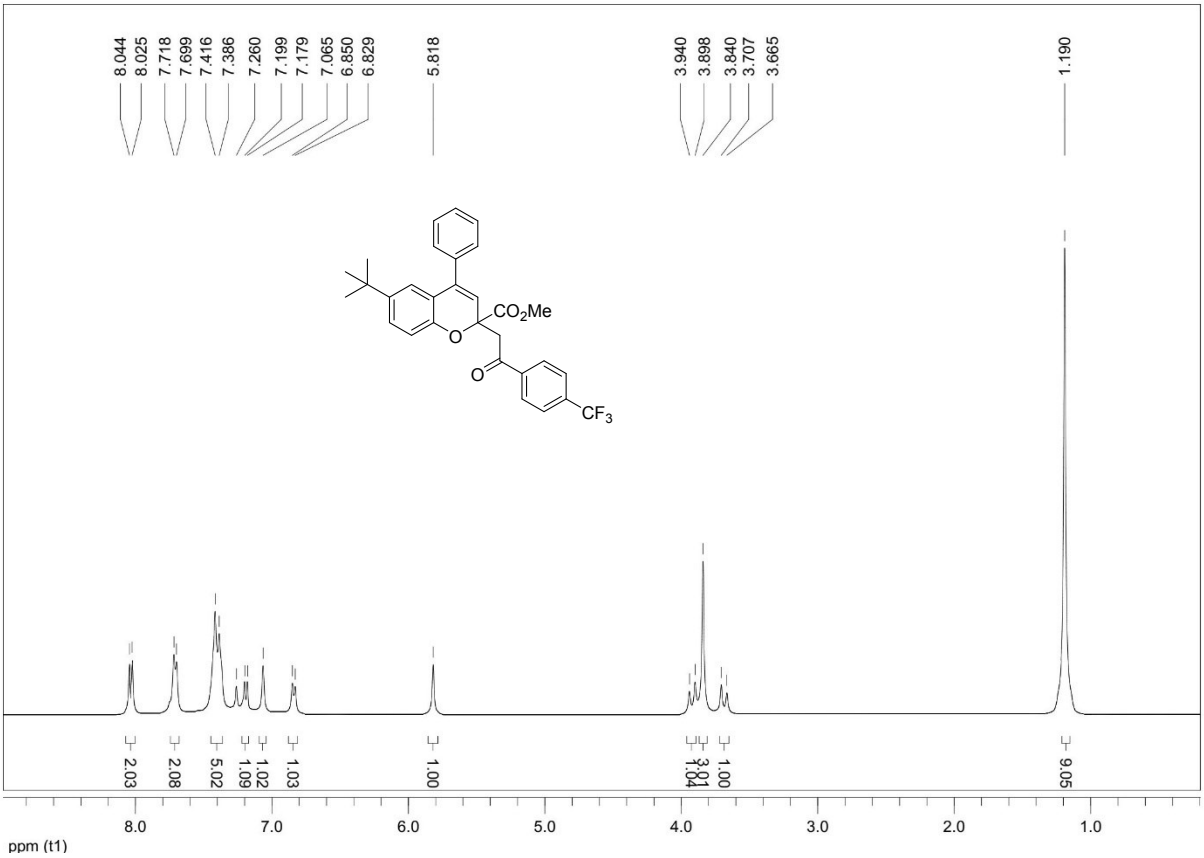


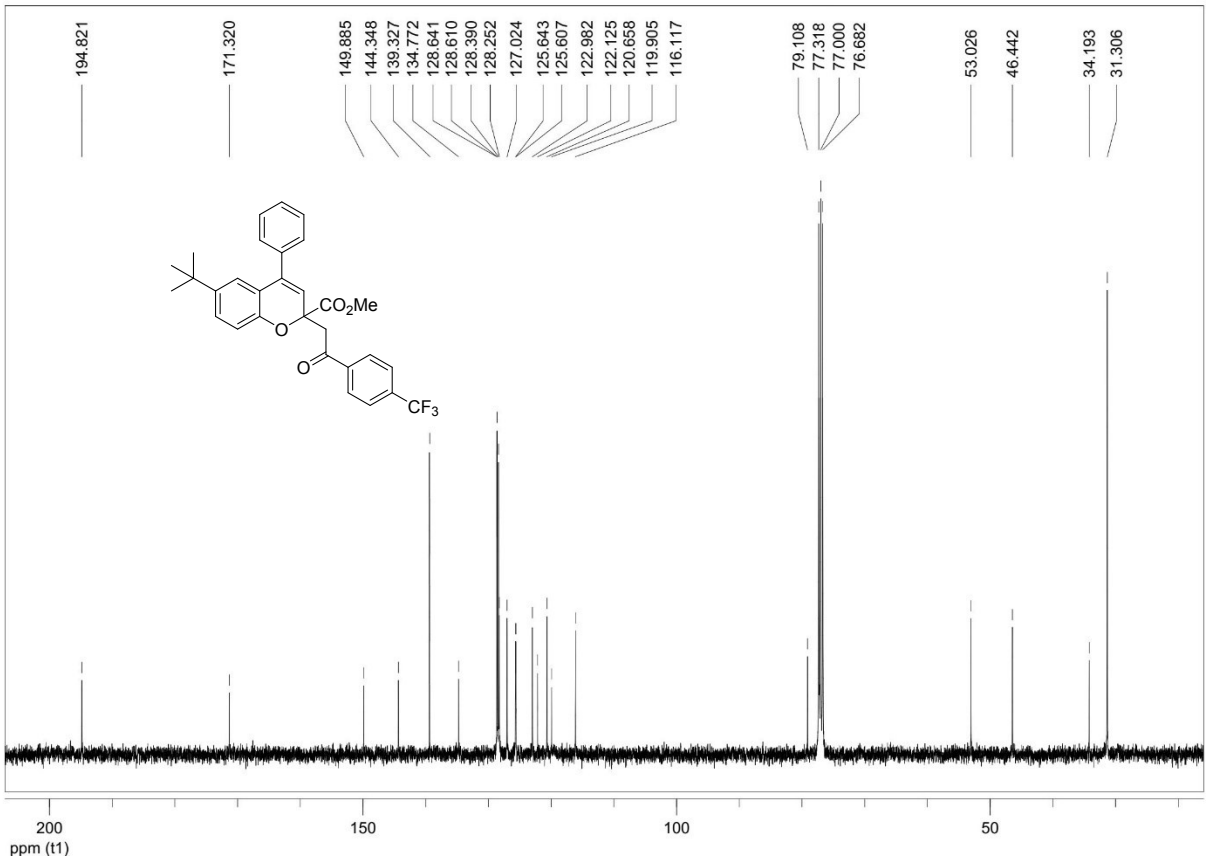
Methyl 6-(tert-butyl)-2-(2-(4-iodophenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2- carboxylate (3ai)



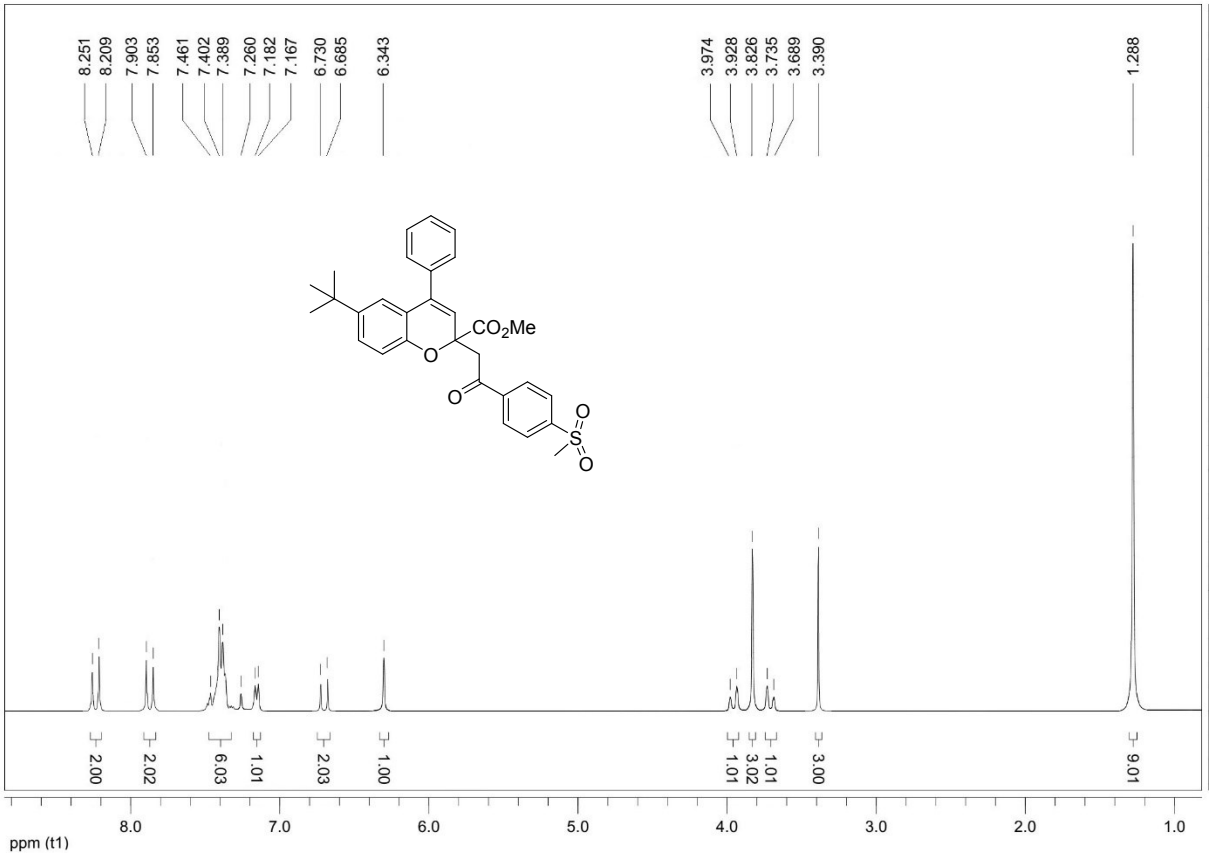


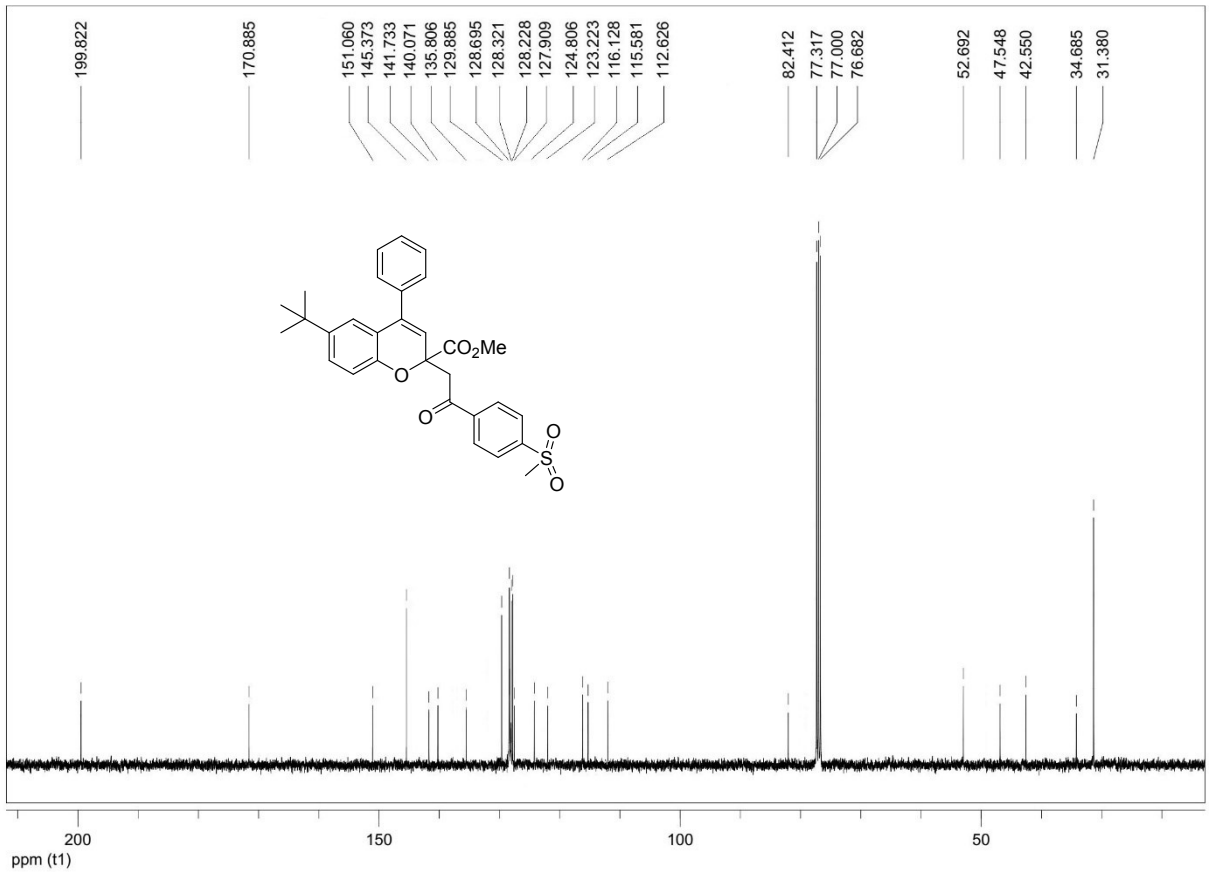
Methyl 6-(tert-butyl)-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3aj)



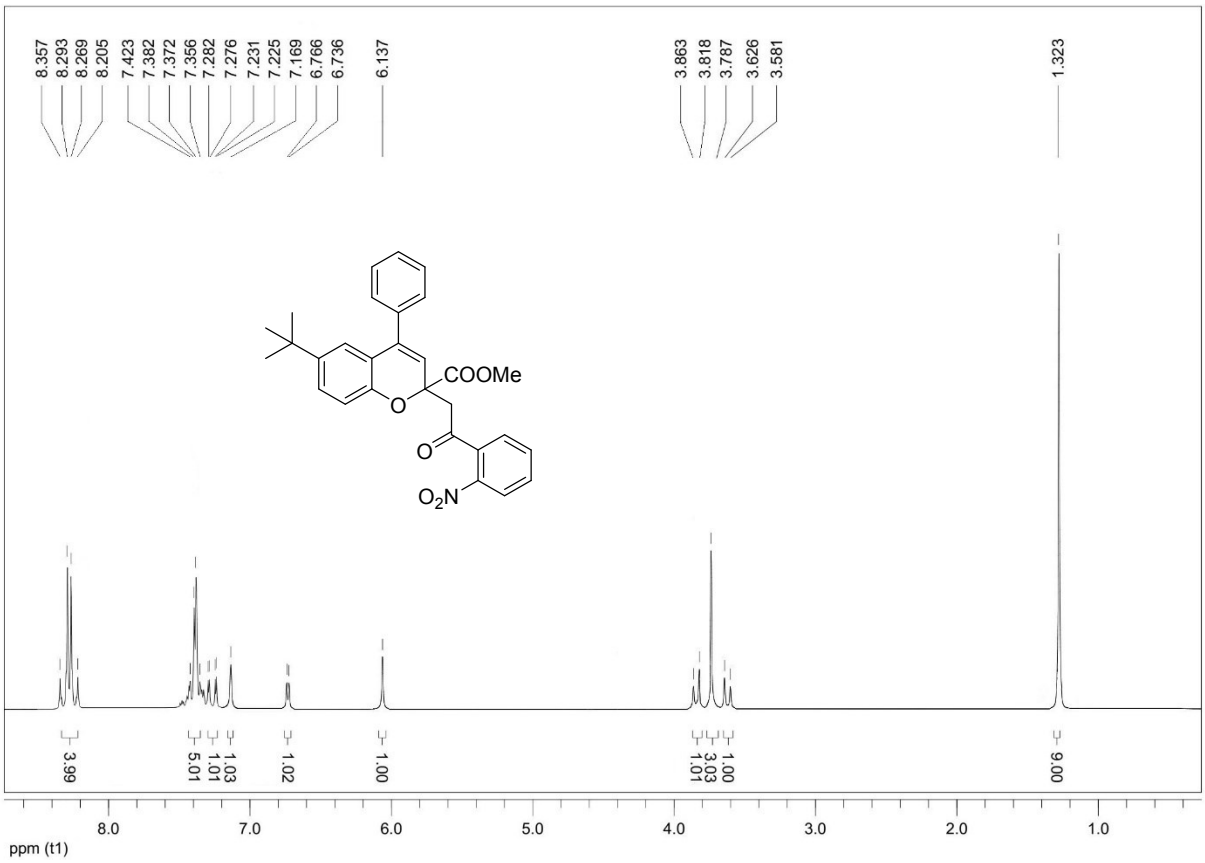


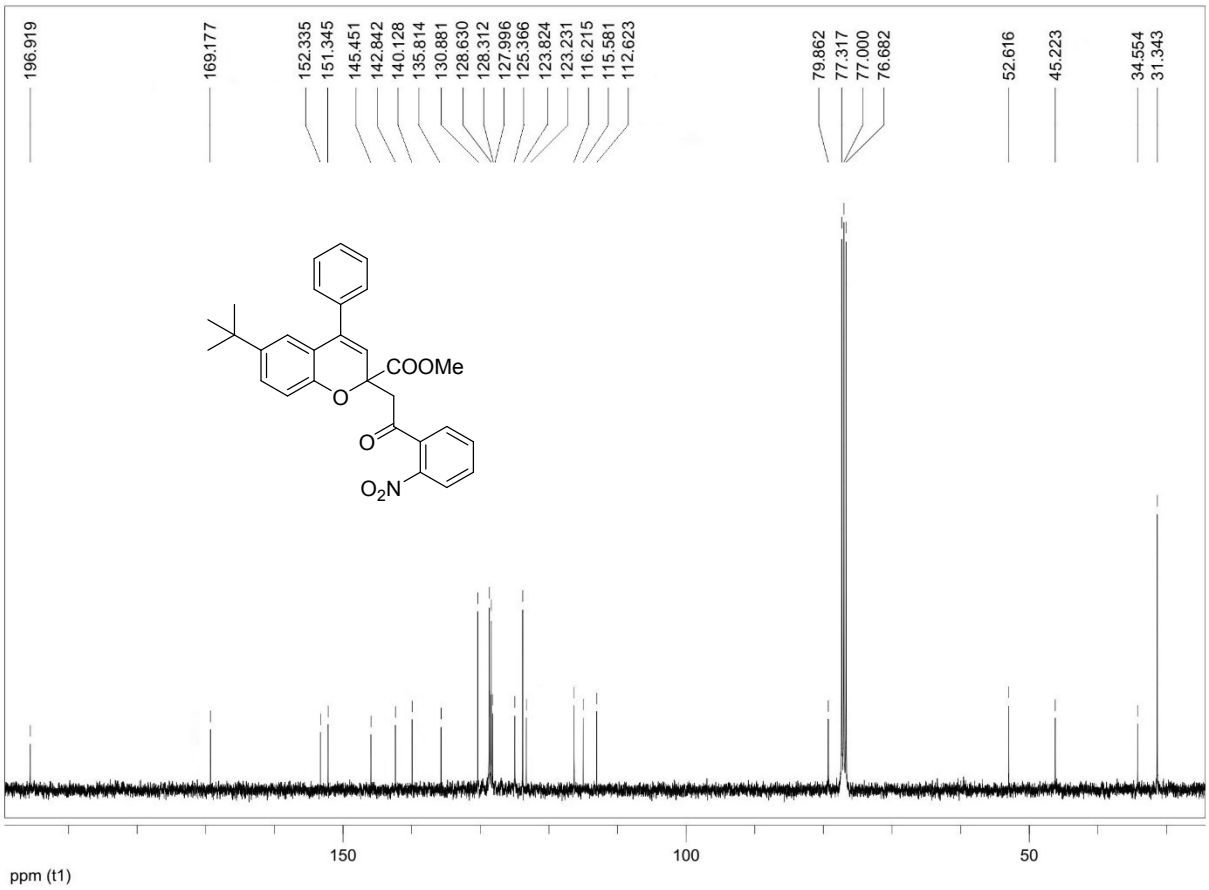
Methyl 6-(tert-butyl)-2-(2-(4-(methylsulfonyl)phenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3ak)



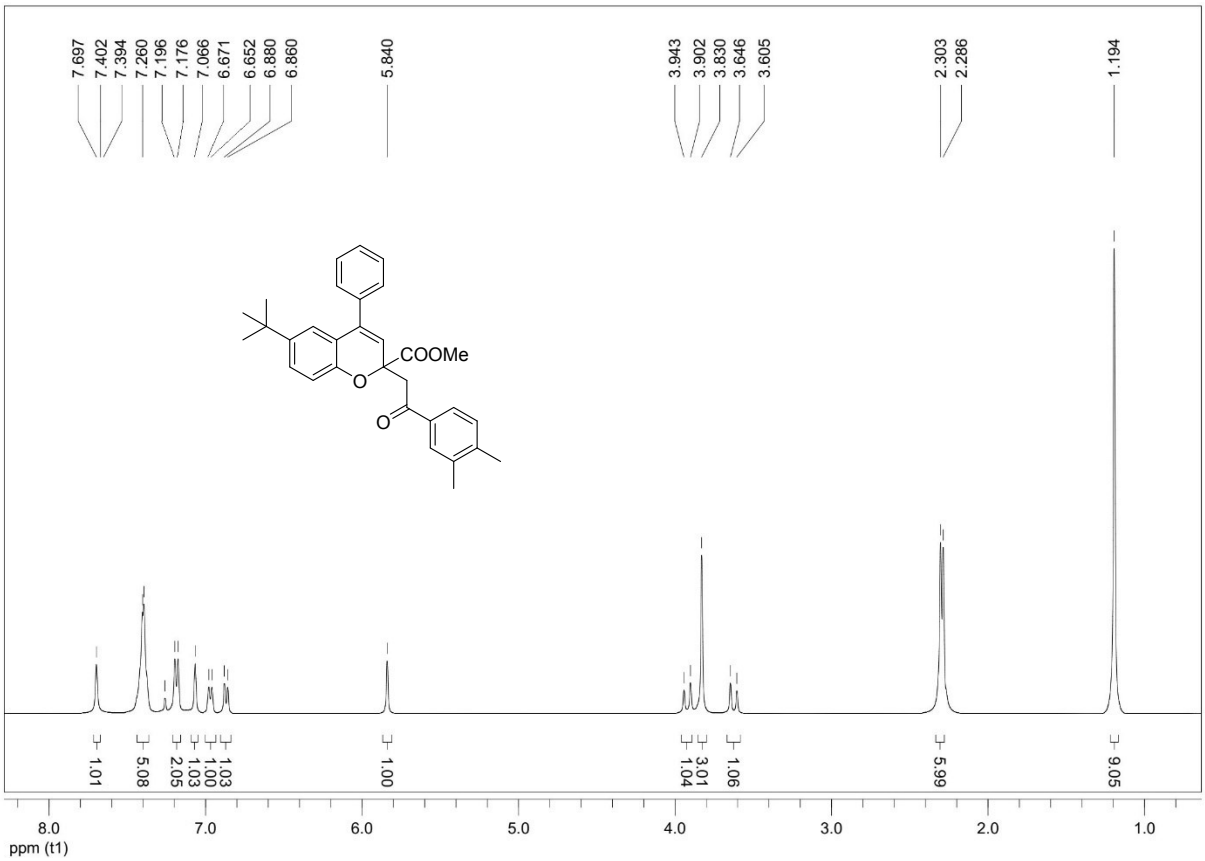


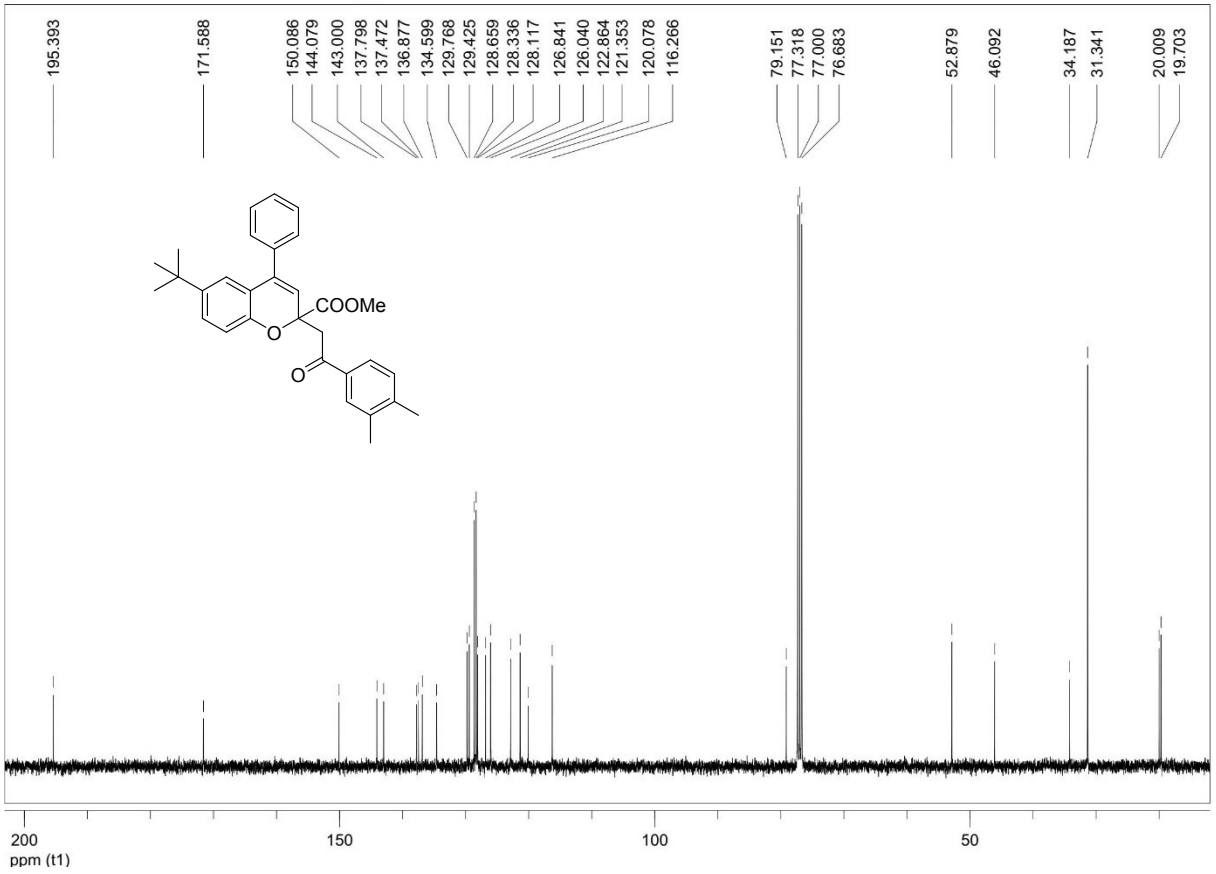
Methyl 6-(tert-butyl)-2-(2-(2-nitrophenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2- carboxylate (3al)



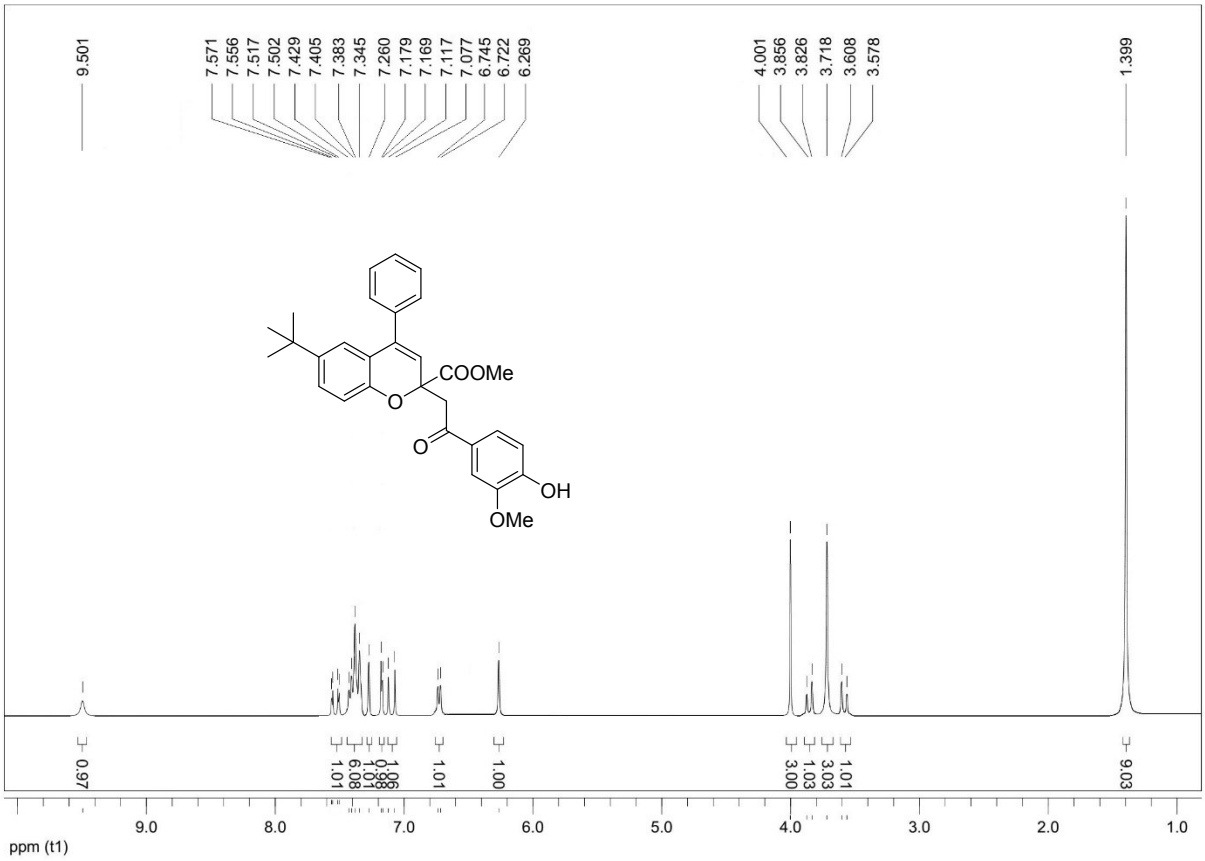


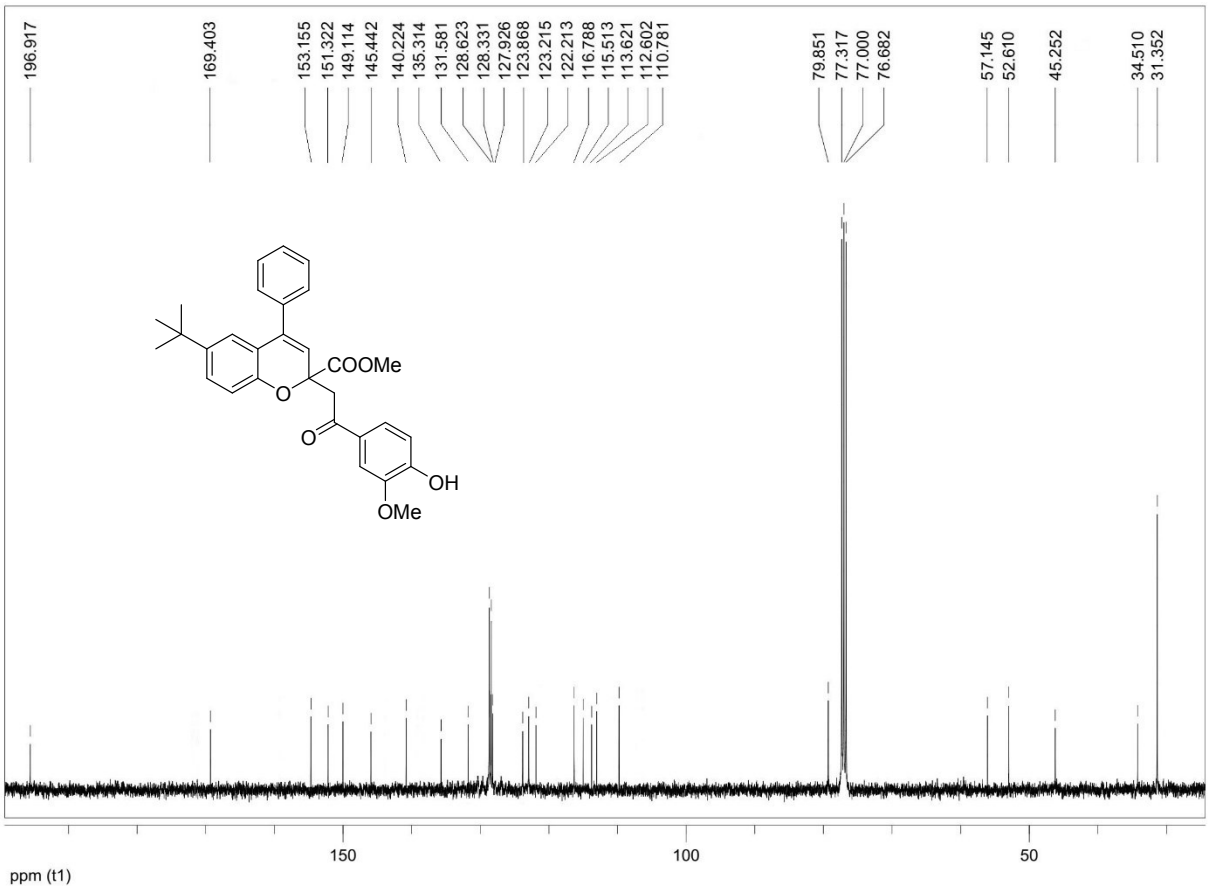
Methyl 6-(tert-butyl)-2-(2-(3,4-dimethylphenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene- 2-carboxylate (3am)



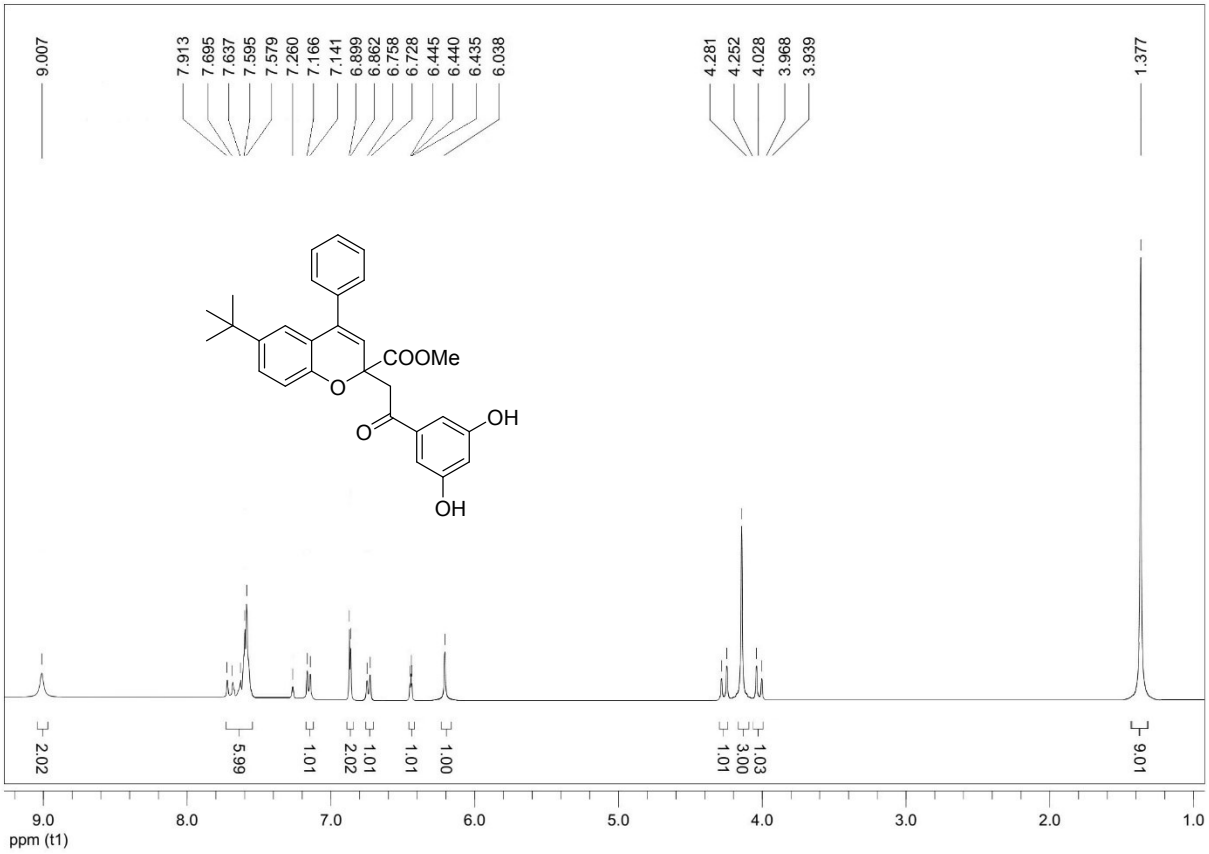


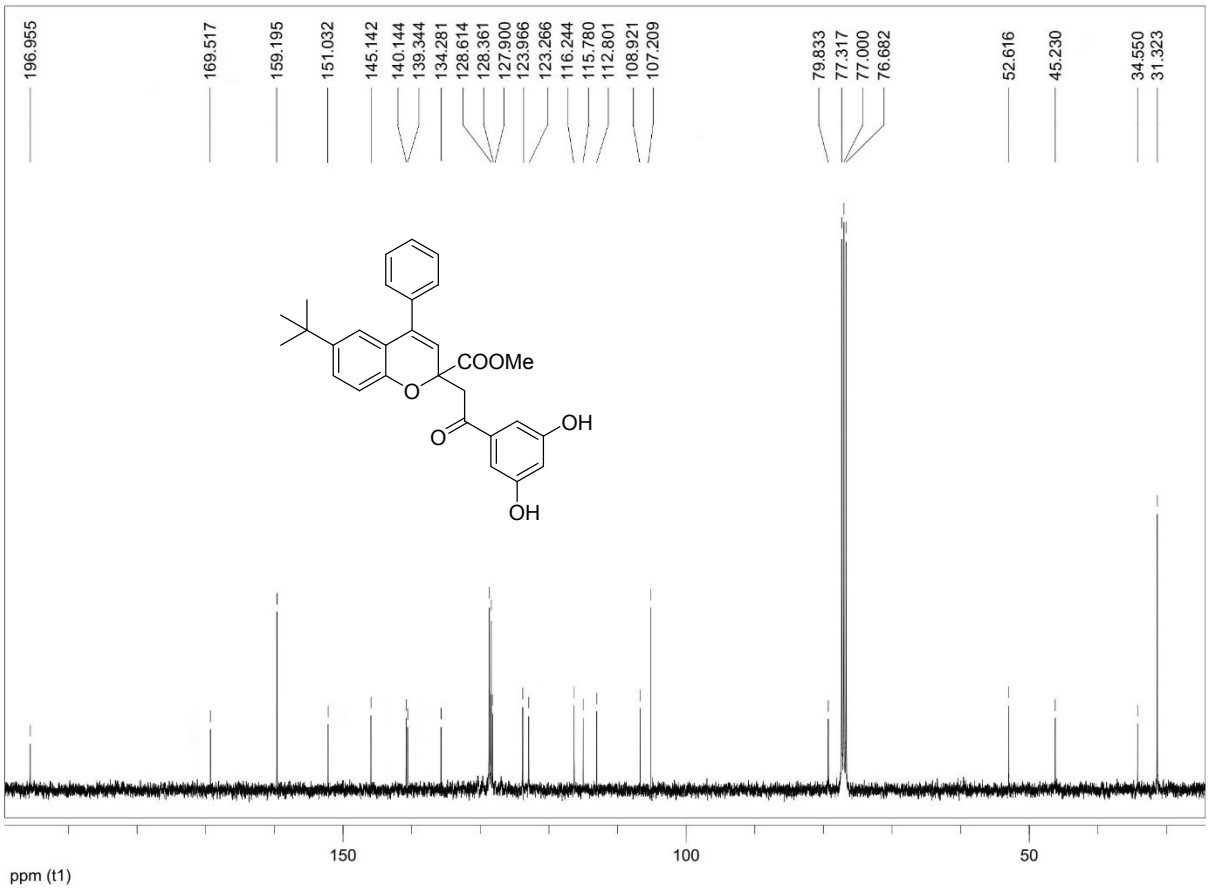
Methyl6-(tert-butyl)-2-(2-(4-hydroxy-3-methoxyphenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2-carboxylate(3an)



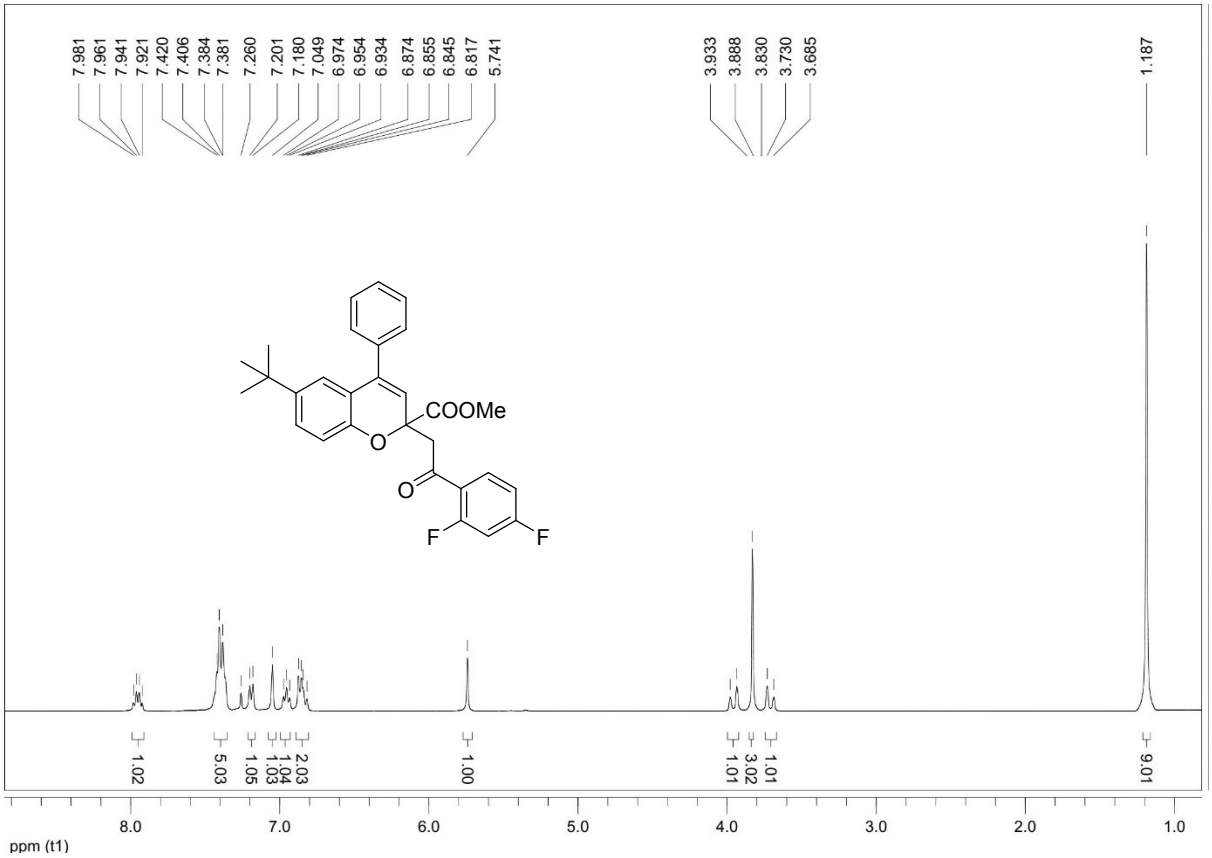


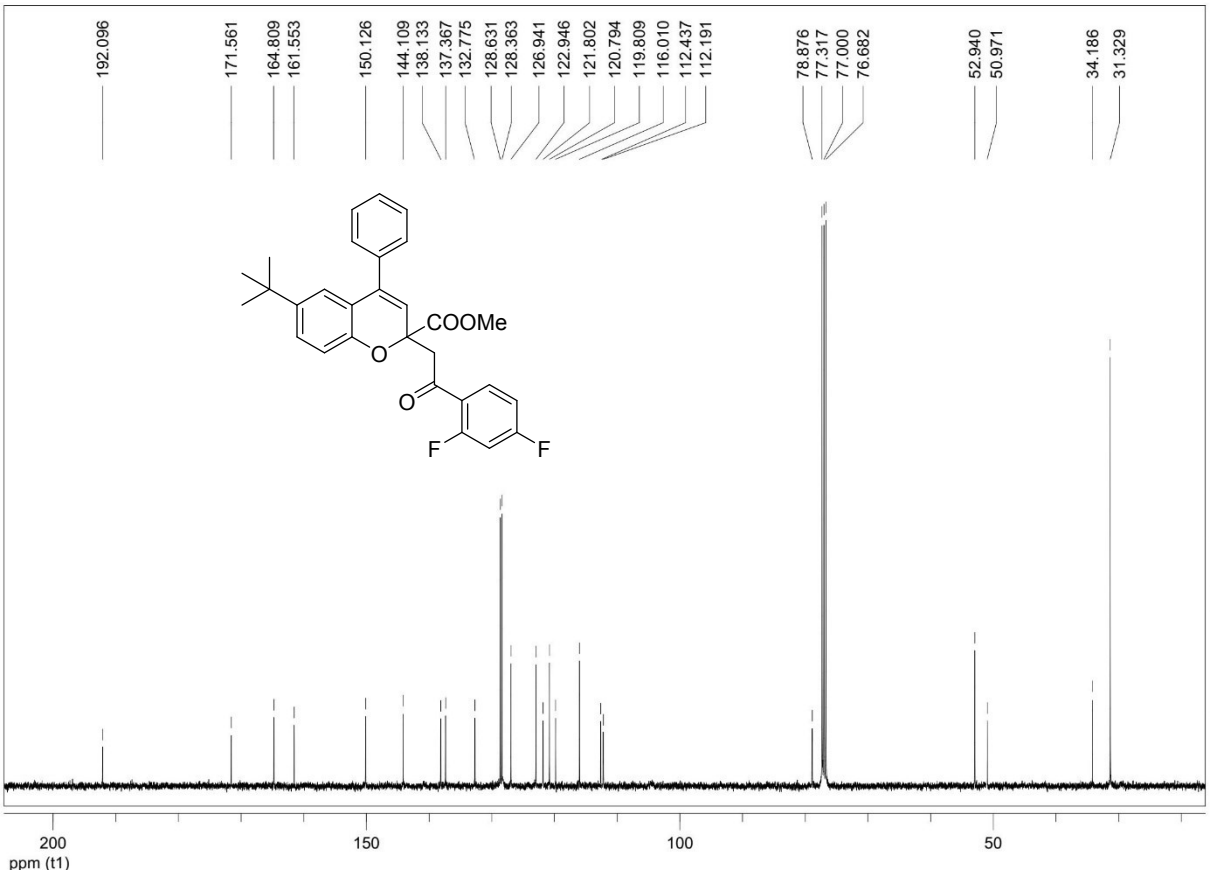
Methyl 6-(tert-butyl)-2-(2-(3,5-dihydroxyphenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene- 2-carboxylate (3ao)



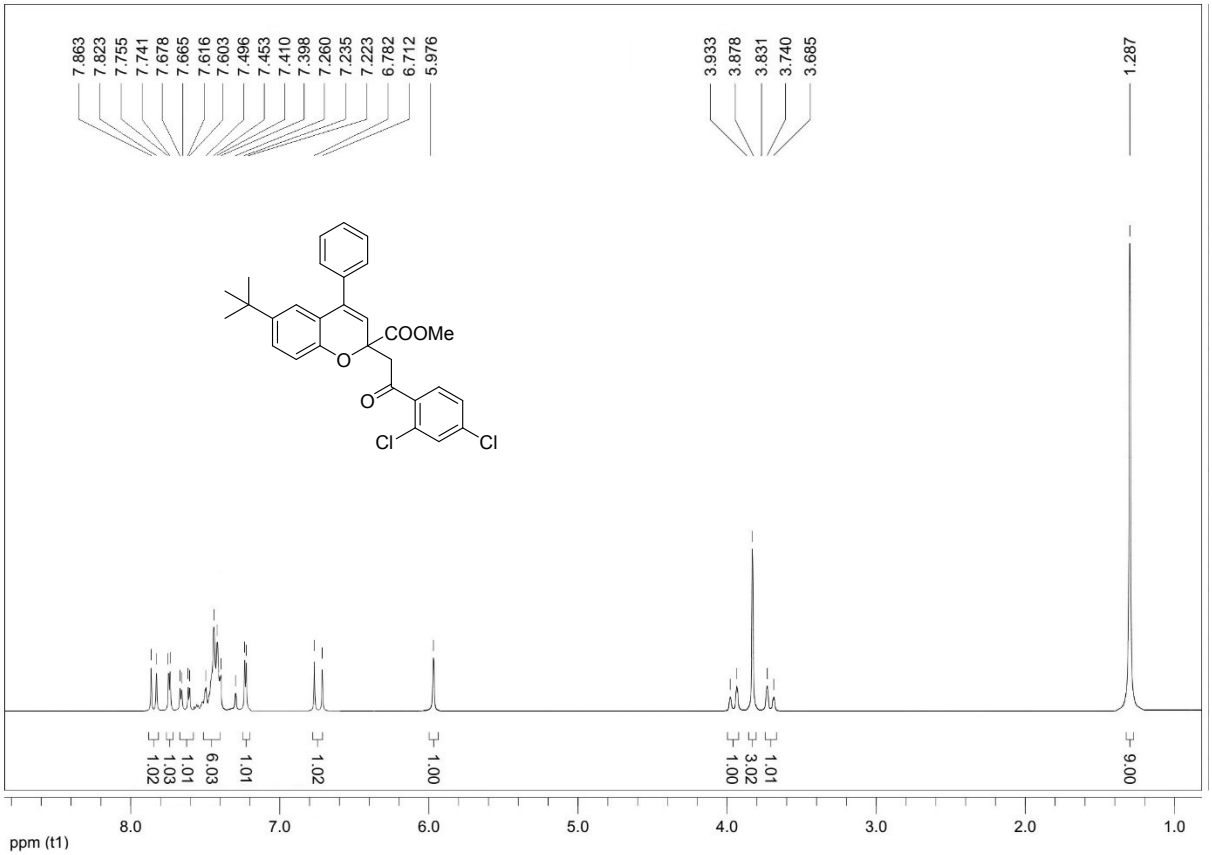


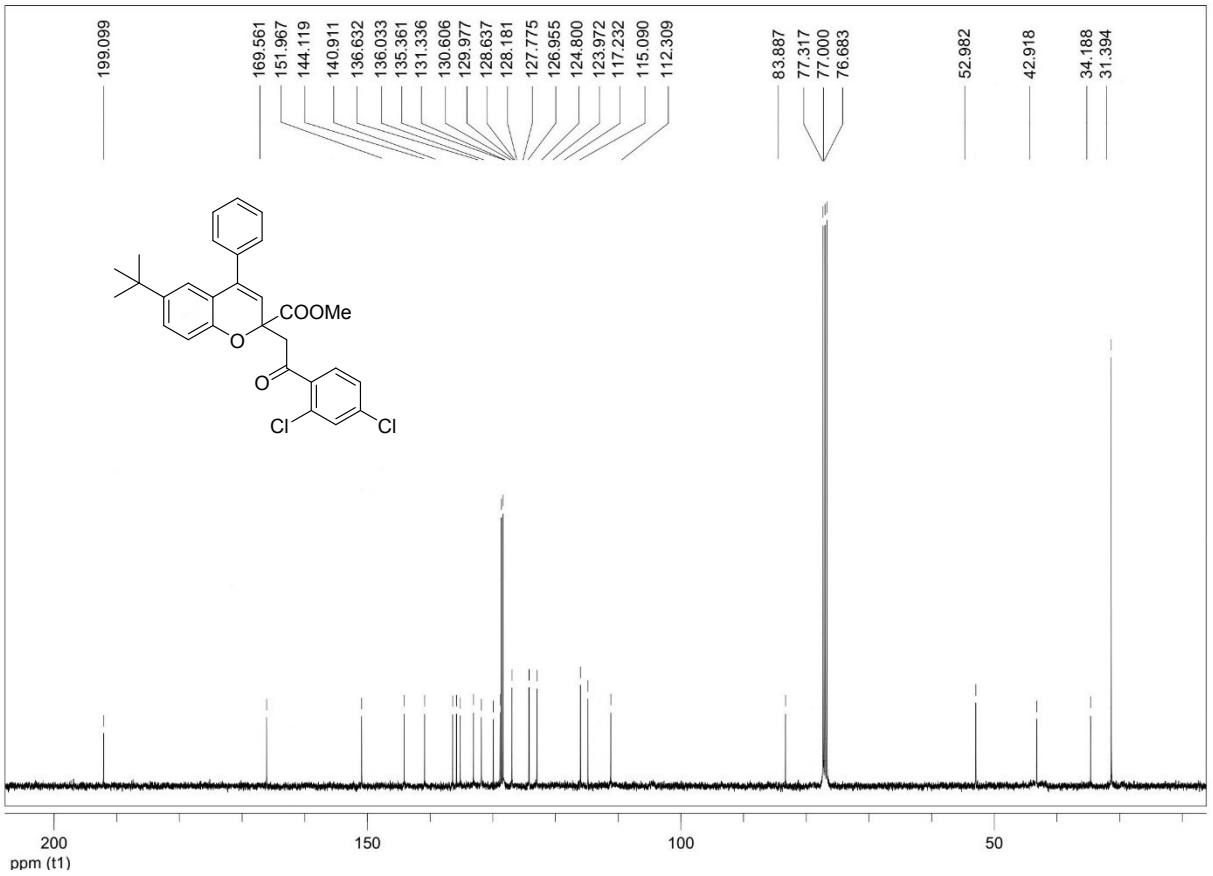
Methyl 6-(tert-butyl)-2-(2-(2,4-difluorophenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2- carboxylate (3ap)



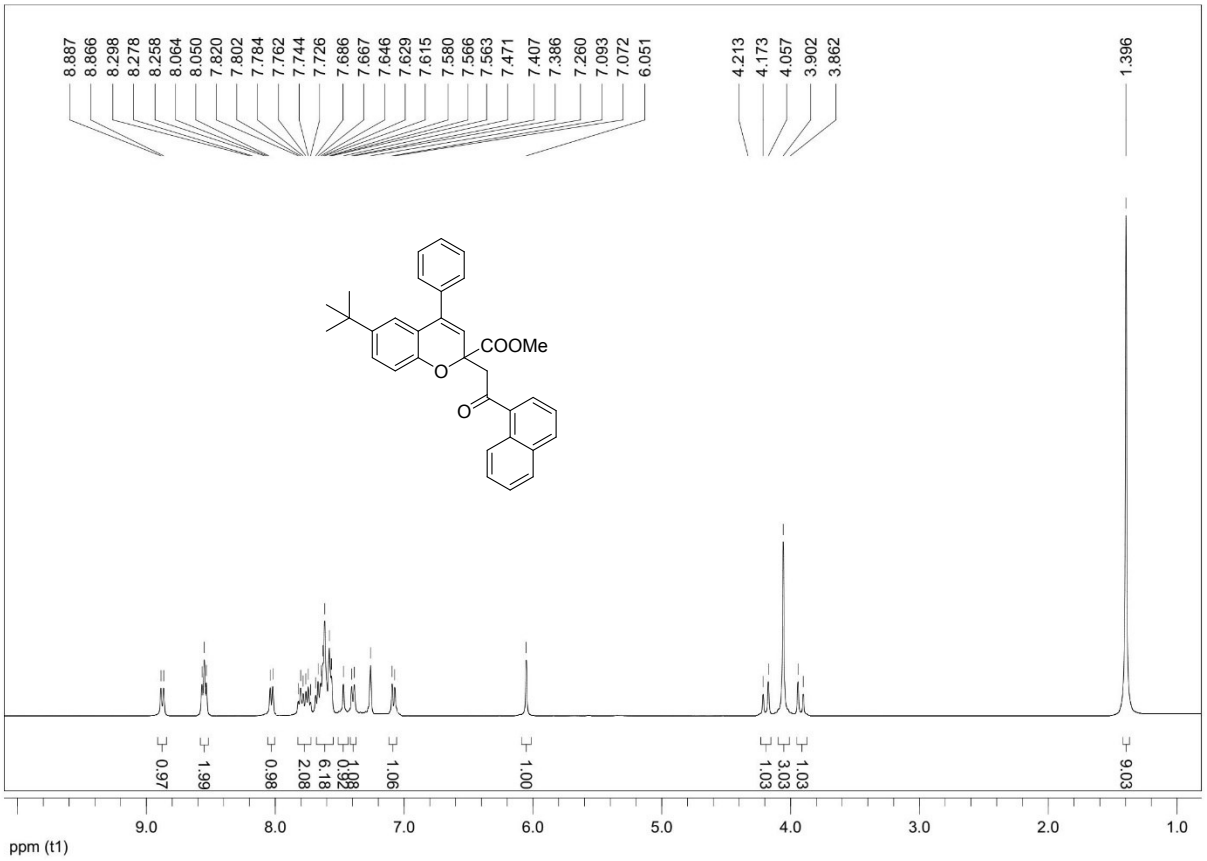


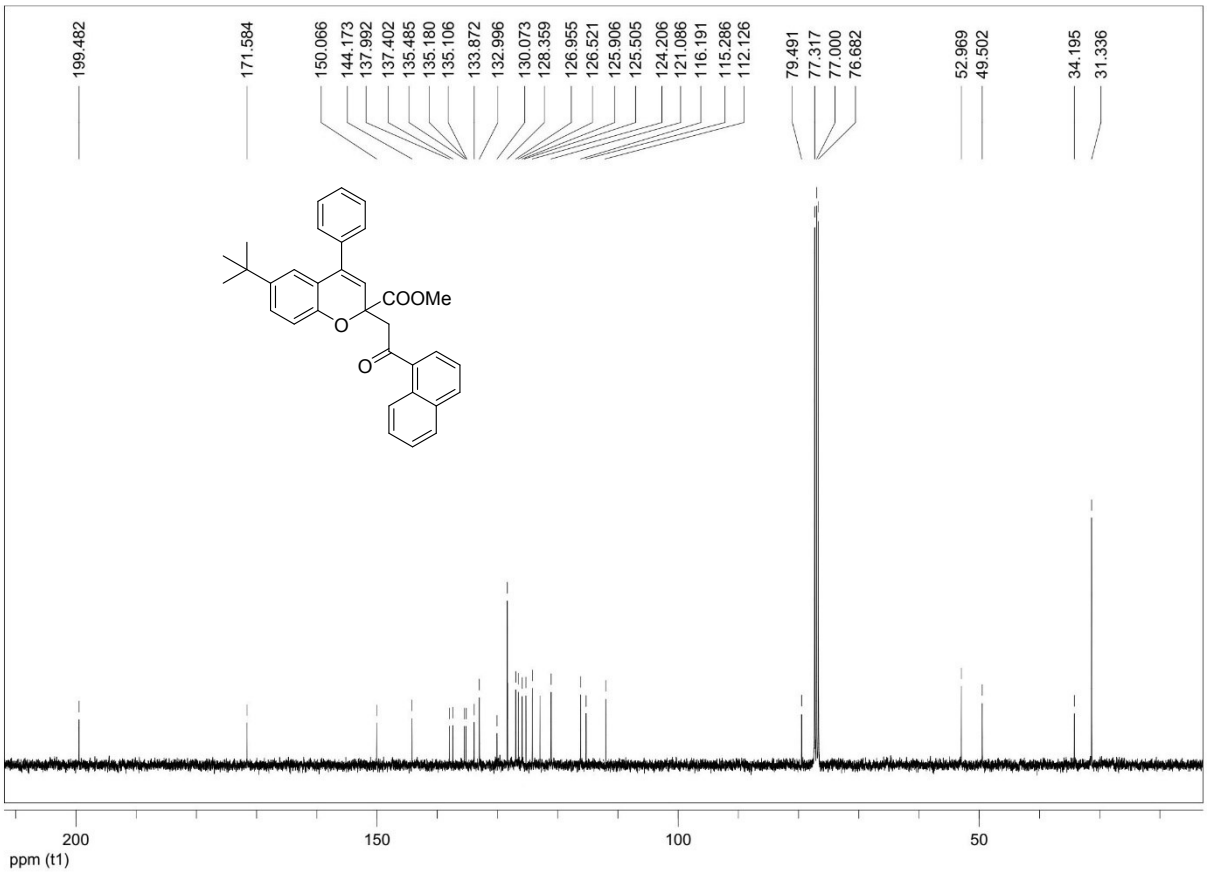
Methyl 6-(tert-butyl)-2-(2-(2,4-dichlorophenyl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2- carboxylate (3aq)



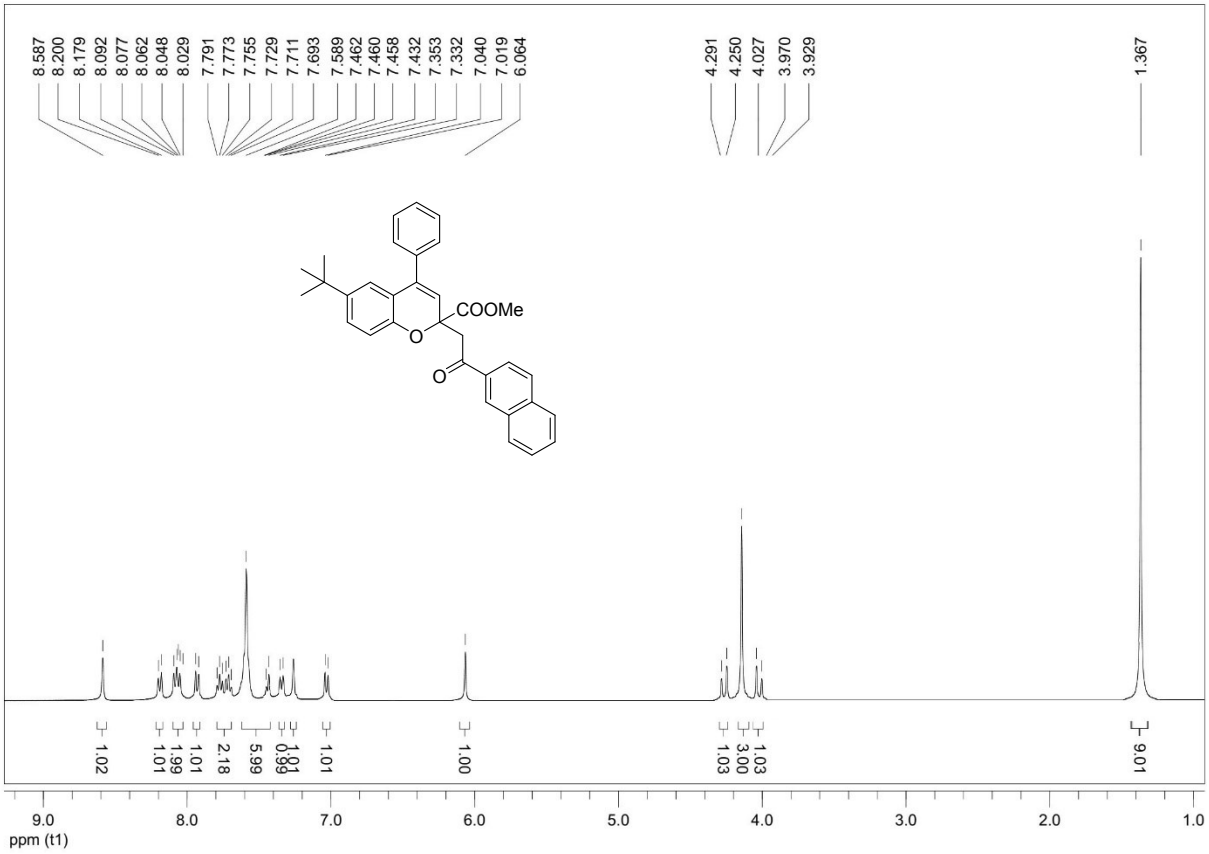


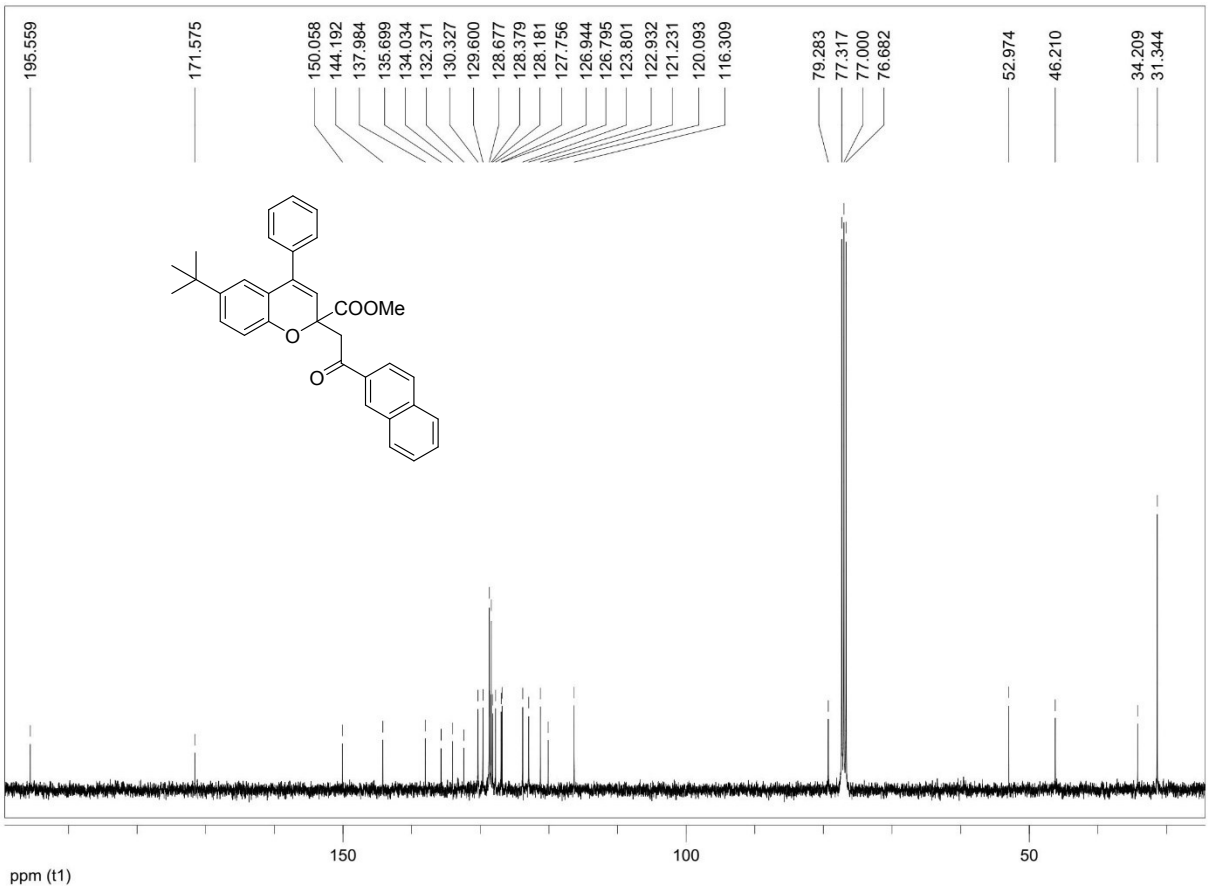
Methyl 6-(tert-butyl)-2-(2-(naphthalen-1-yl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2- carboxylate (3ar)



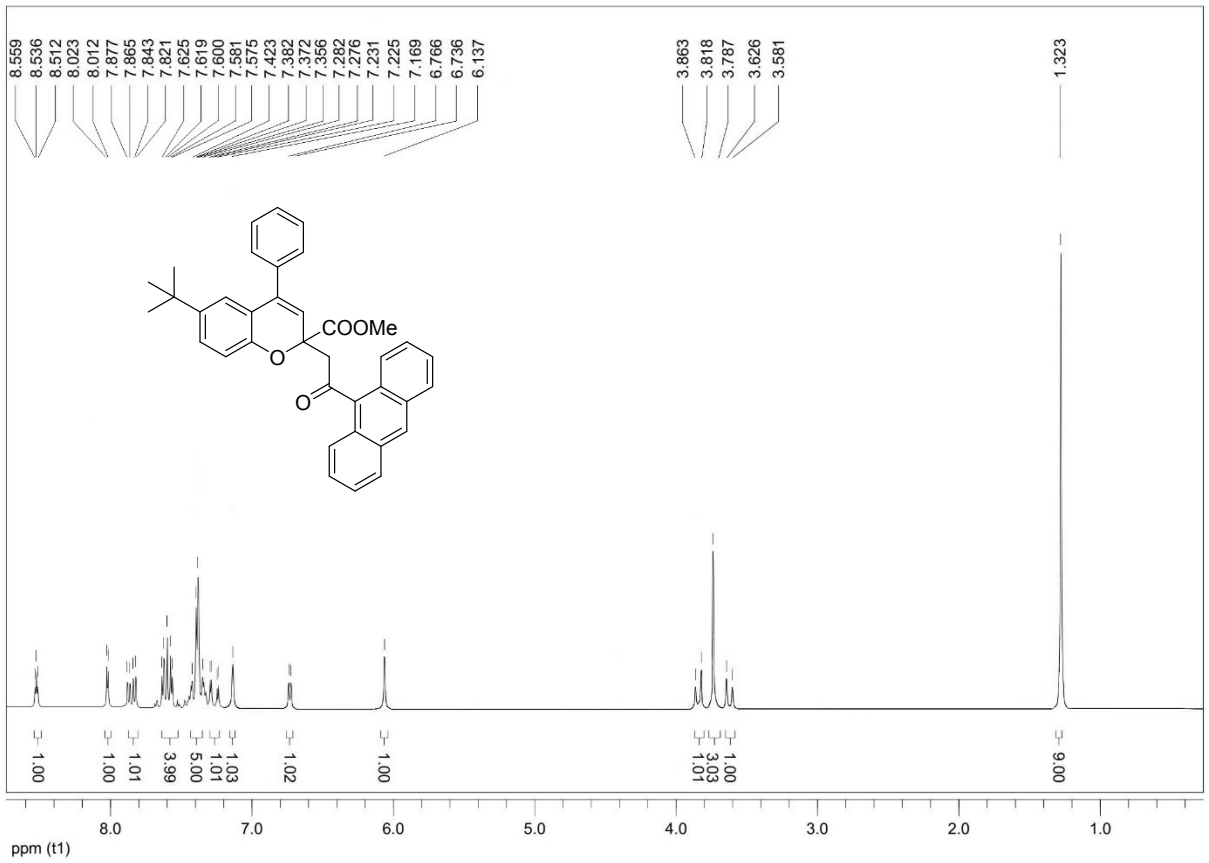


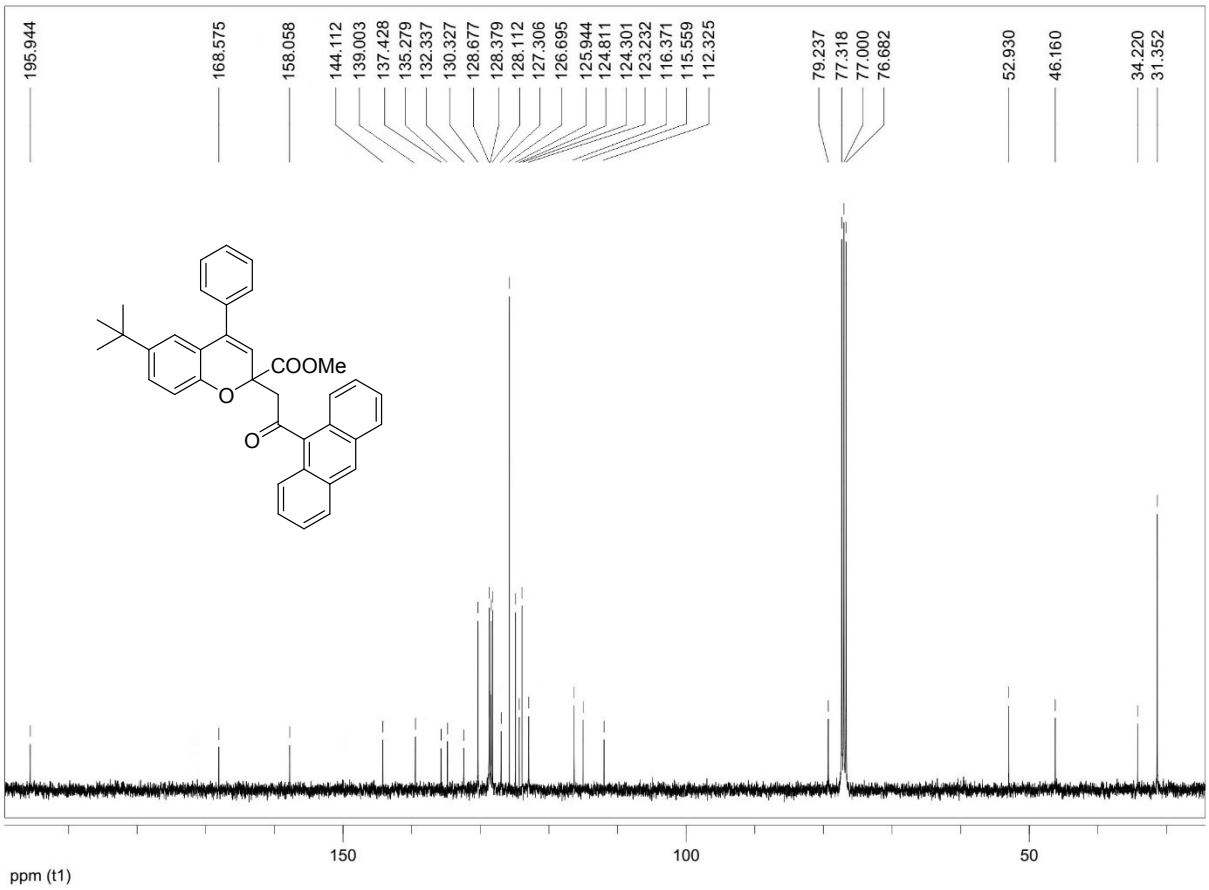
Methyl 6-(tert-butyl)-2-(2-(naphthalen-2-yl)-2-oxoethyl)-4-phenyl-2*H*-chromene-2- carboxylate (3as)



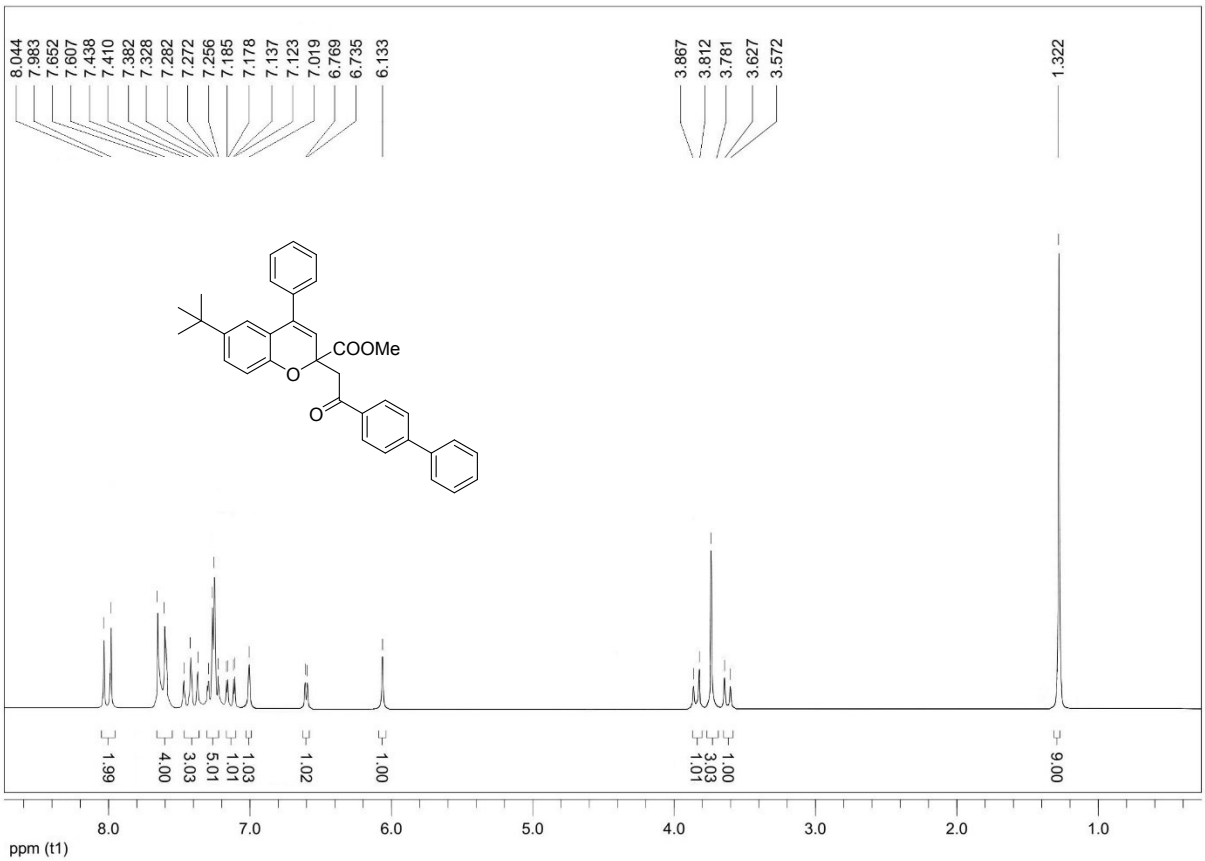


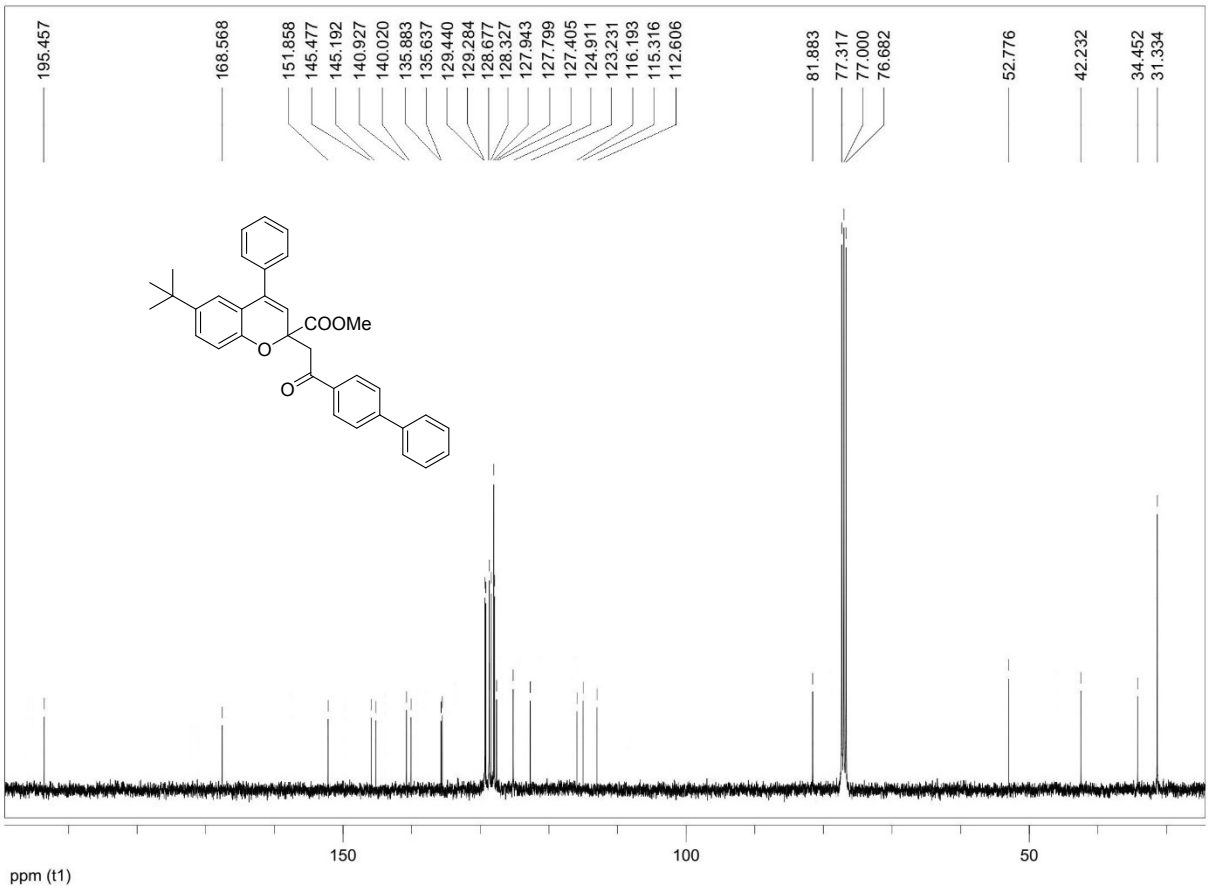
Methyl 2-(2-(anthracen-9-yl)-2-oxoethyl)-6-(tert-butyl)-4-phenyl-2*H*-chromene-2- carboxylate (3at)



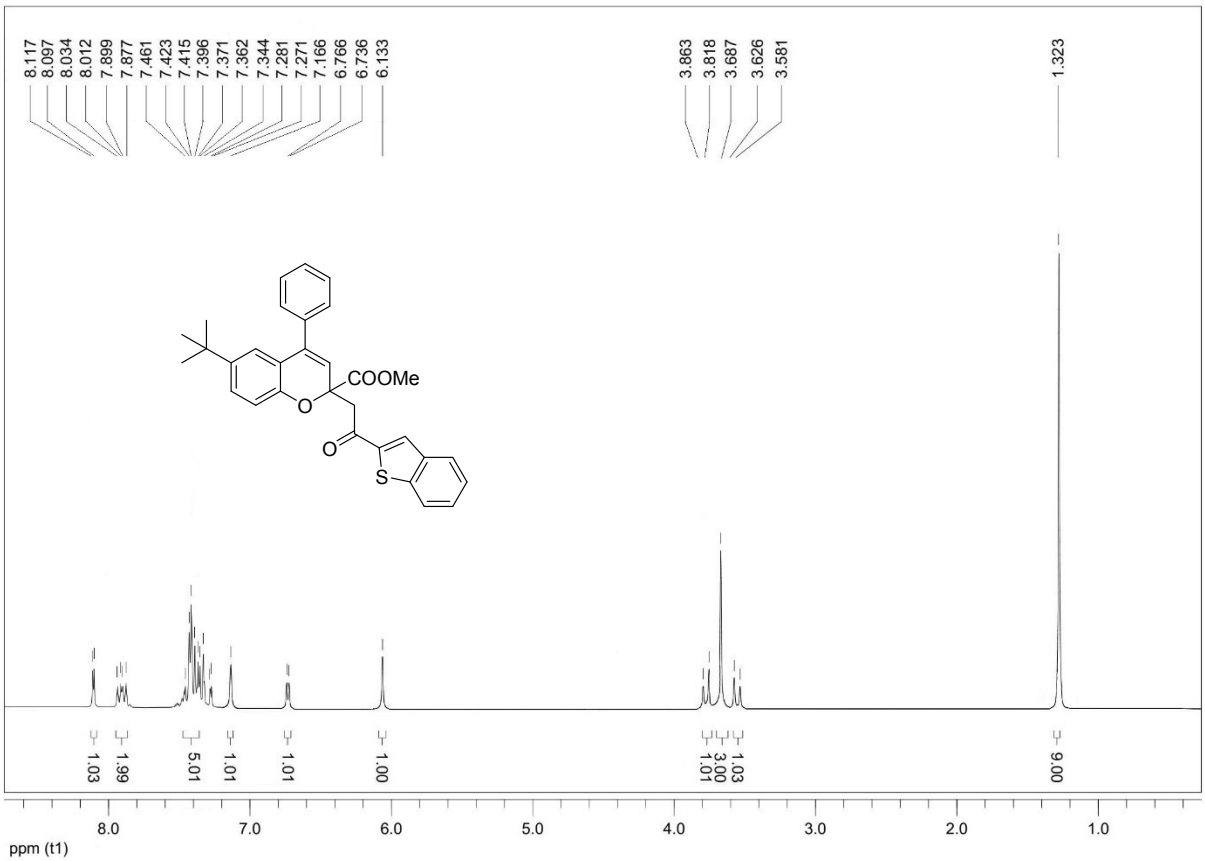


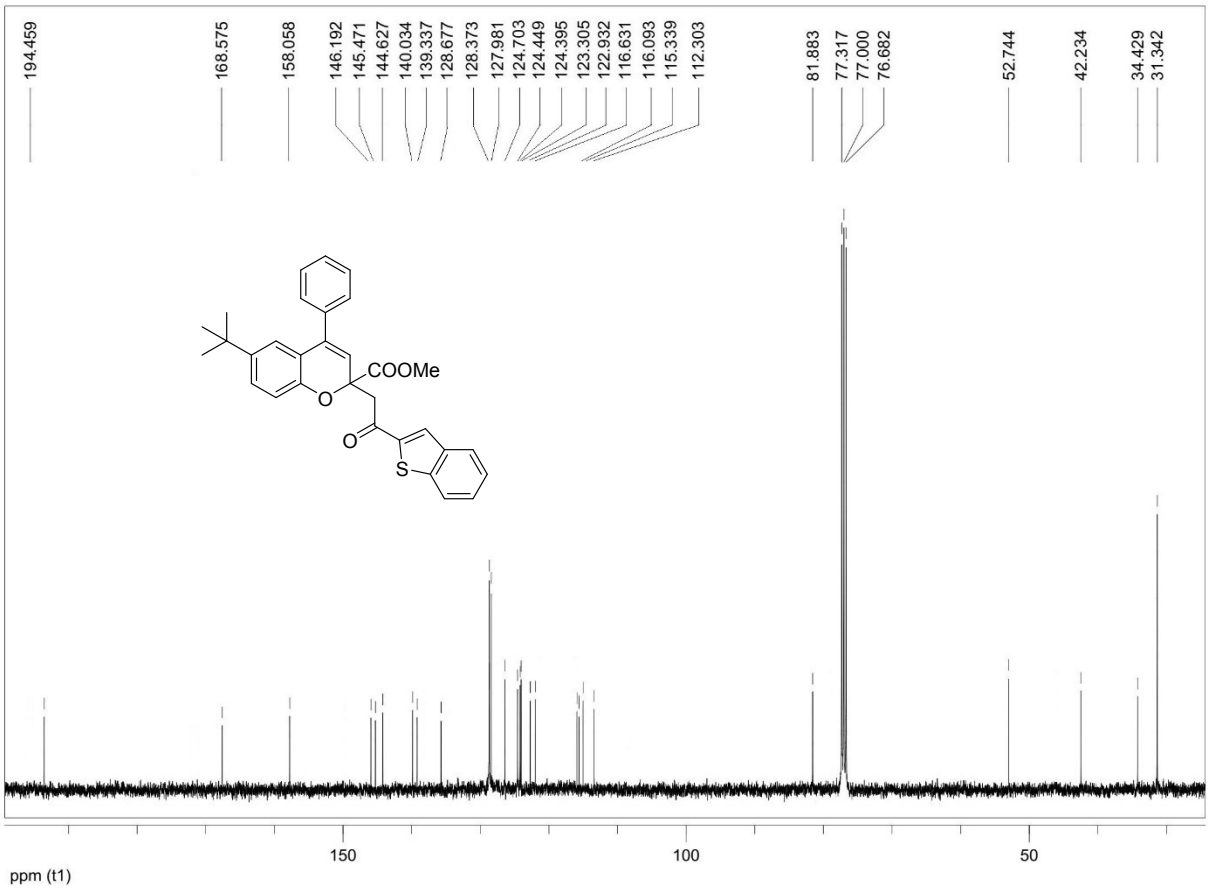
Methyl 2-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)-6-(tert-butyl)-4-phenyl-2*H*-chromene- 2-carboxylate (3au)



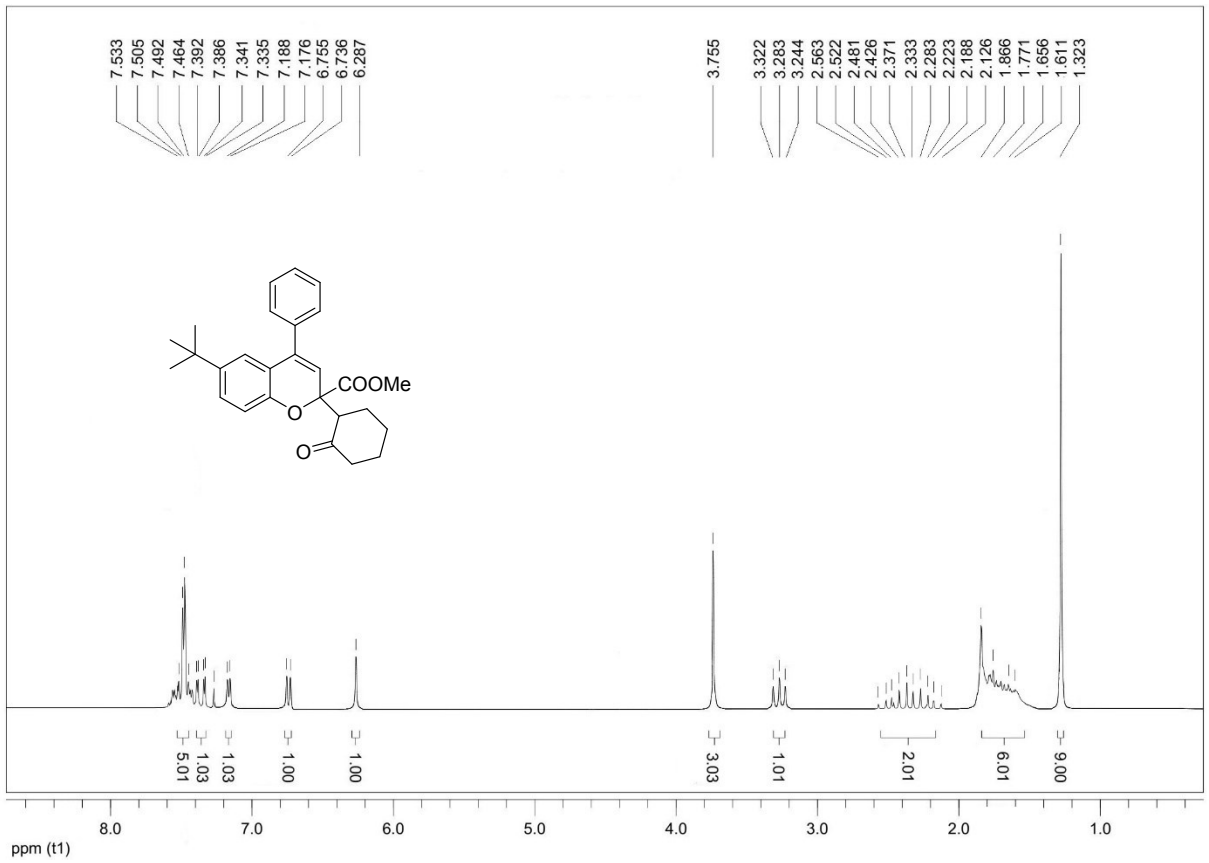


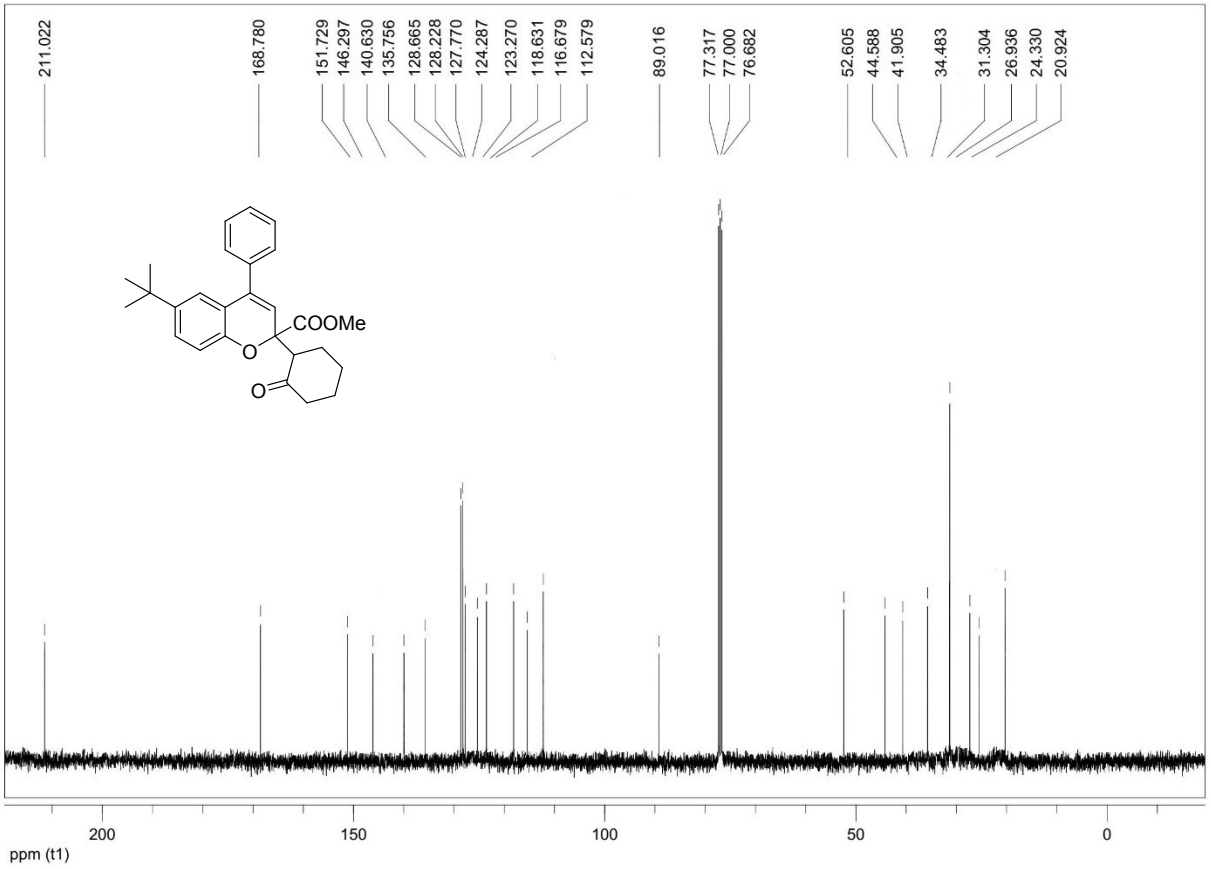
Methyl 2-(2-(benzo[b]thiophen-2-yl)-2-oxoethyl)-6-(tert-butyl)-4-phenyl-2*H*- chromene-2-carboxylate (3av)



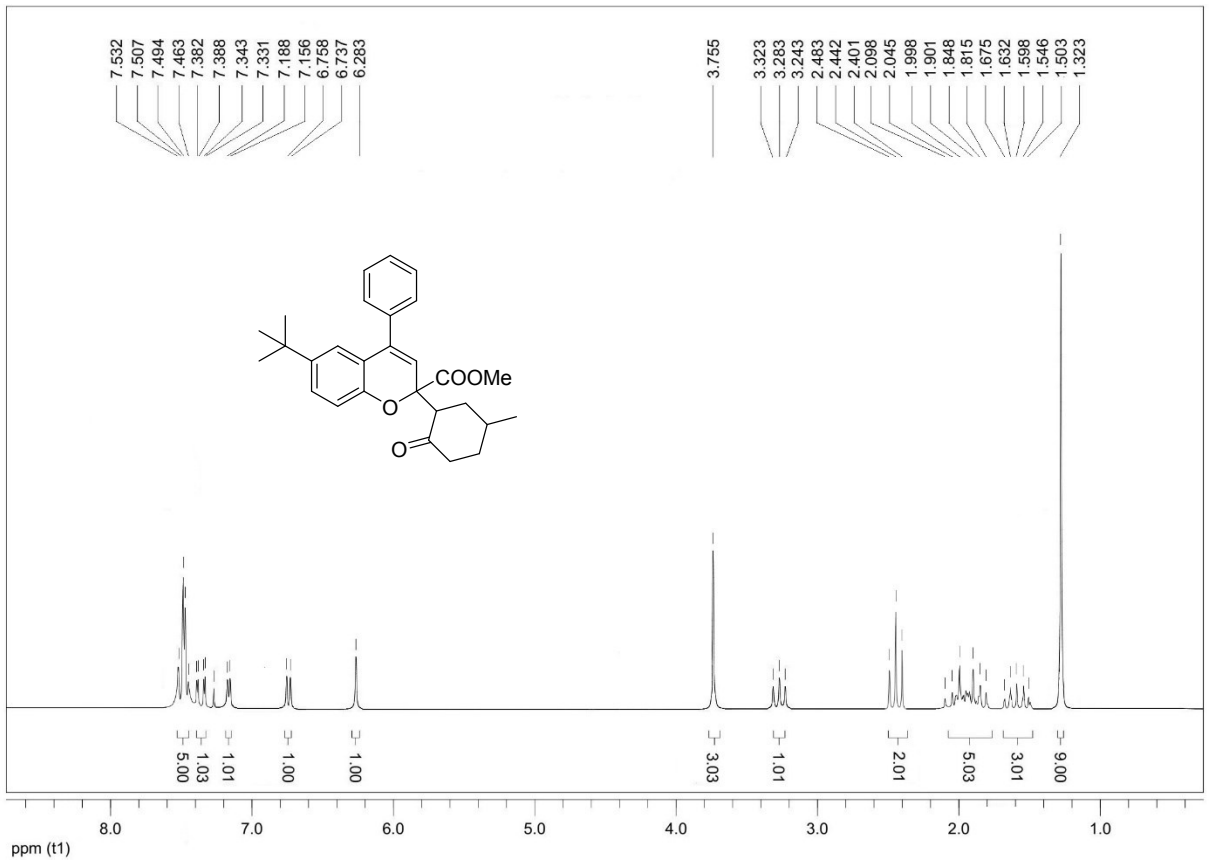


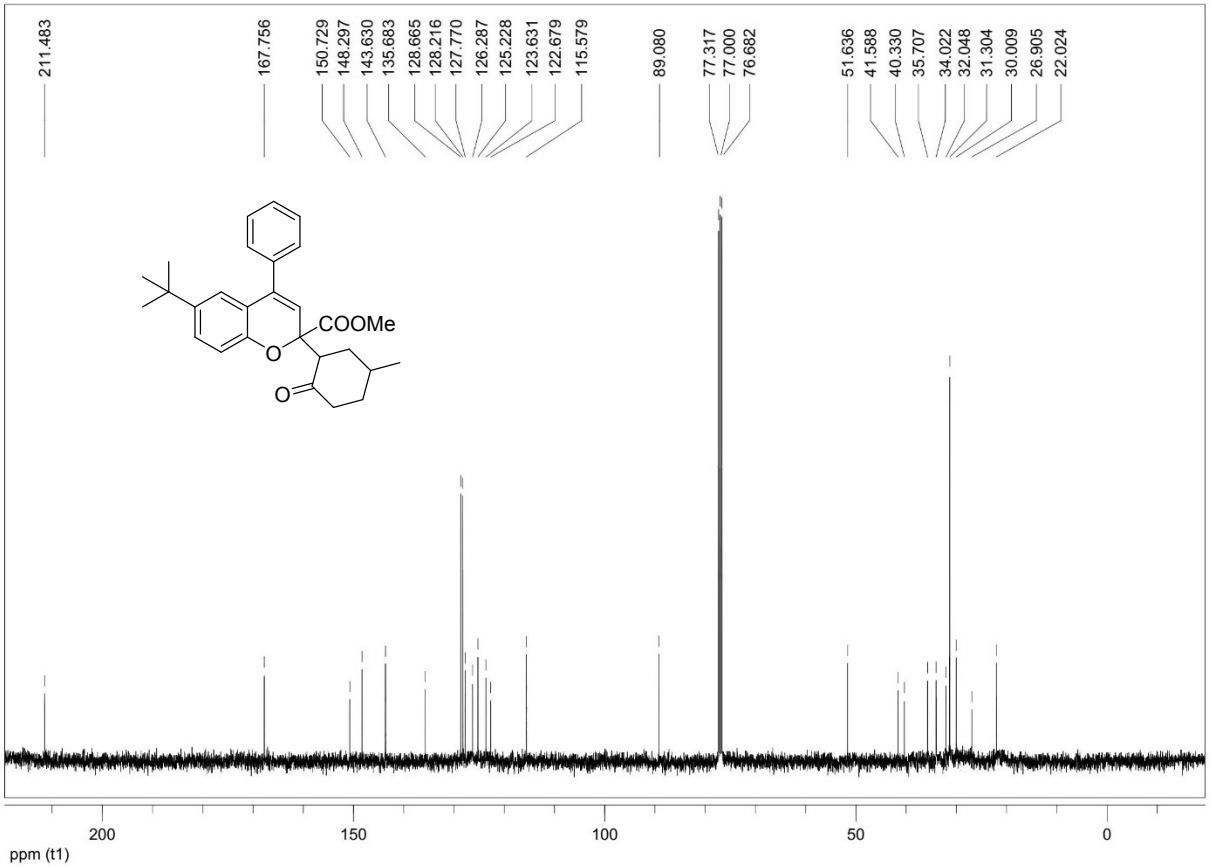
Methyl 6-(tert-butyl)-2-(2-oxocyclohexyl)-4-phenyl-2*H*-chromene-2-carboxylate (3aw)



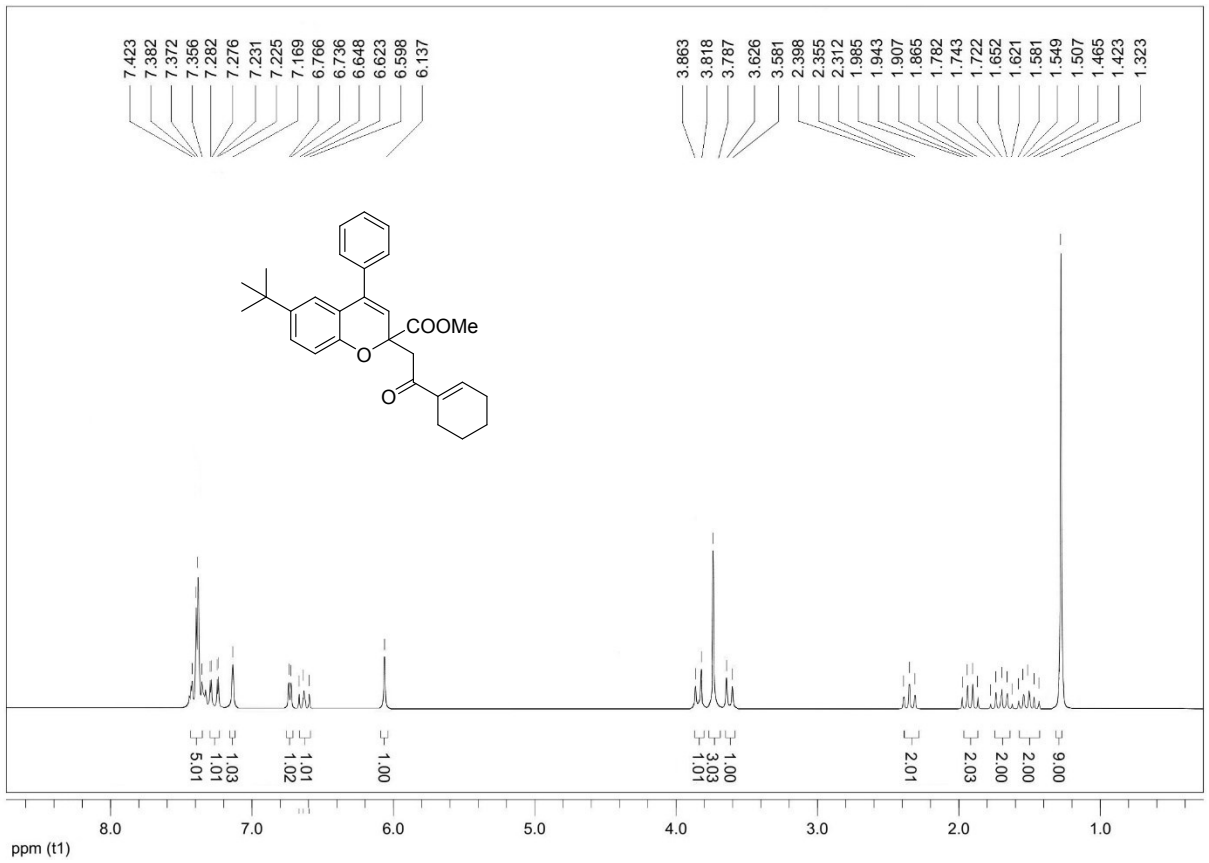


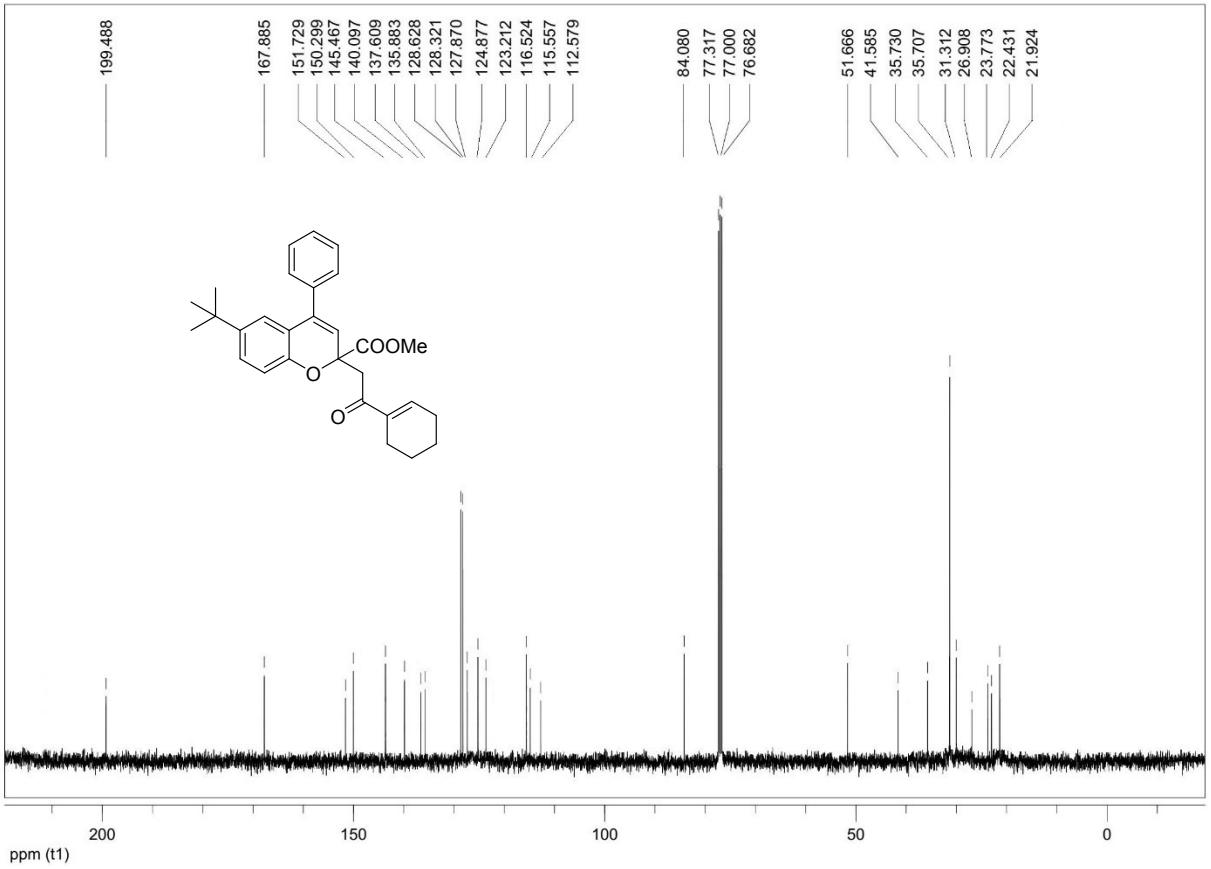
Methyl 6-(tert-butyl)-2-(5-methyl-2-oxocyclohexyl)-4-phenyl-2*H*-chromene-2- carboxylate (3ax)



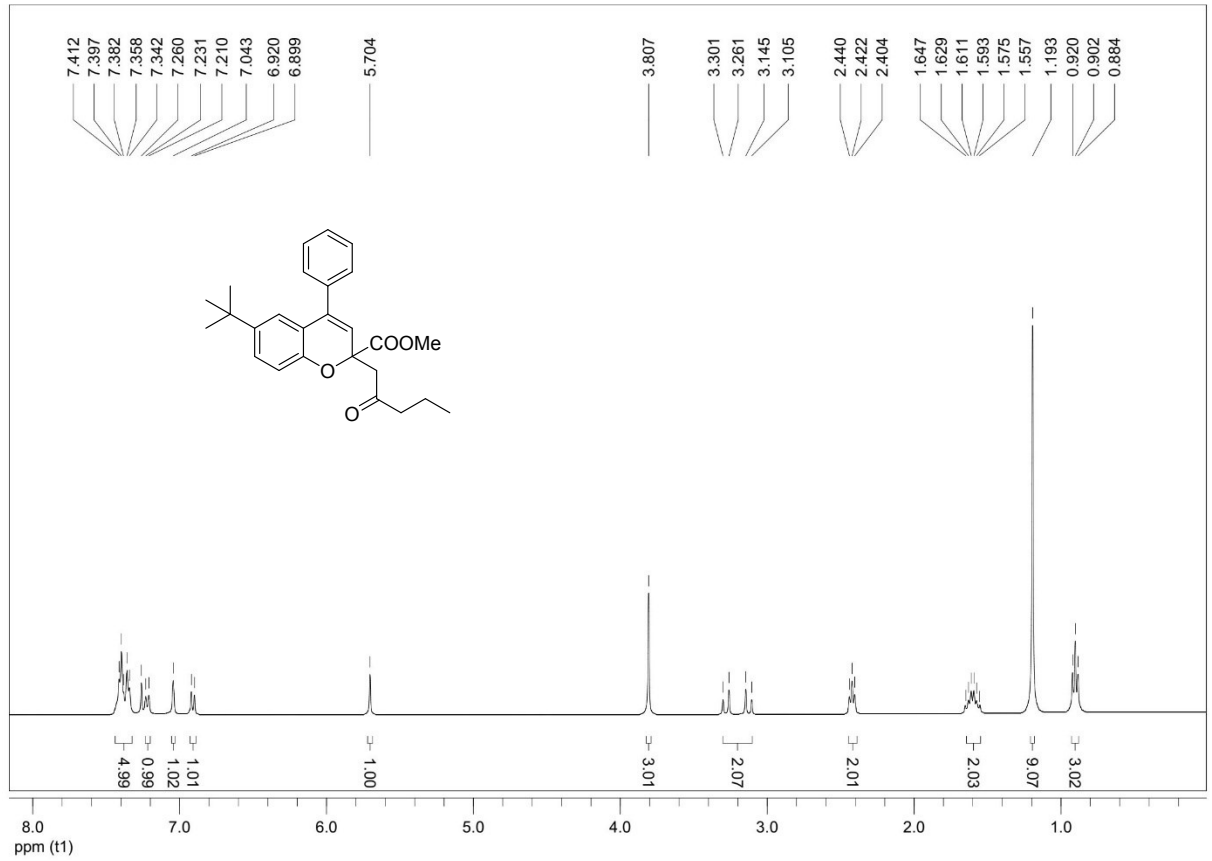


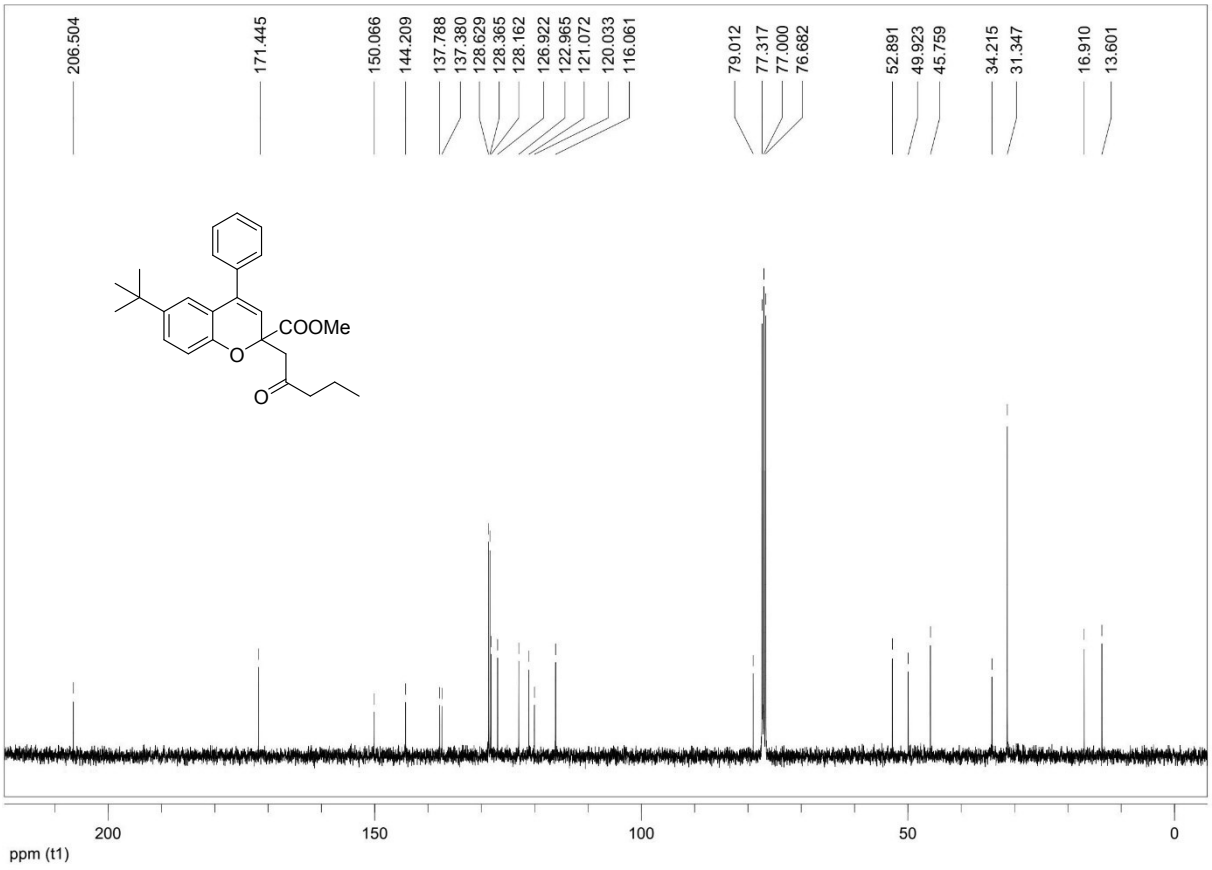
Methyl 6-(tert-butyl)-2-(2-(cyclohex-1-en-1-yl)-2-oxoethyl)-4-phenyl-2*H*-chromene- 2-carboxylate (3ay)



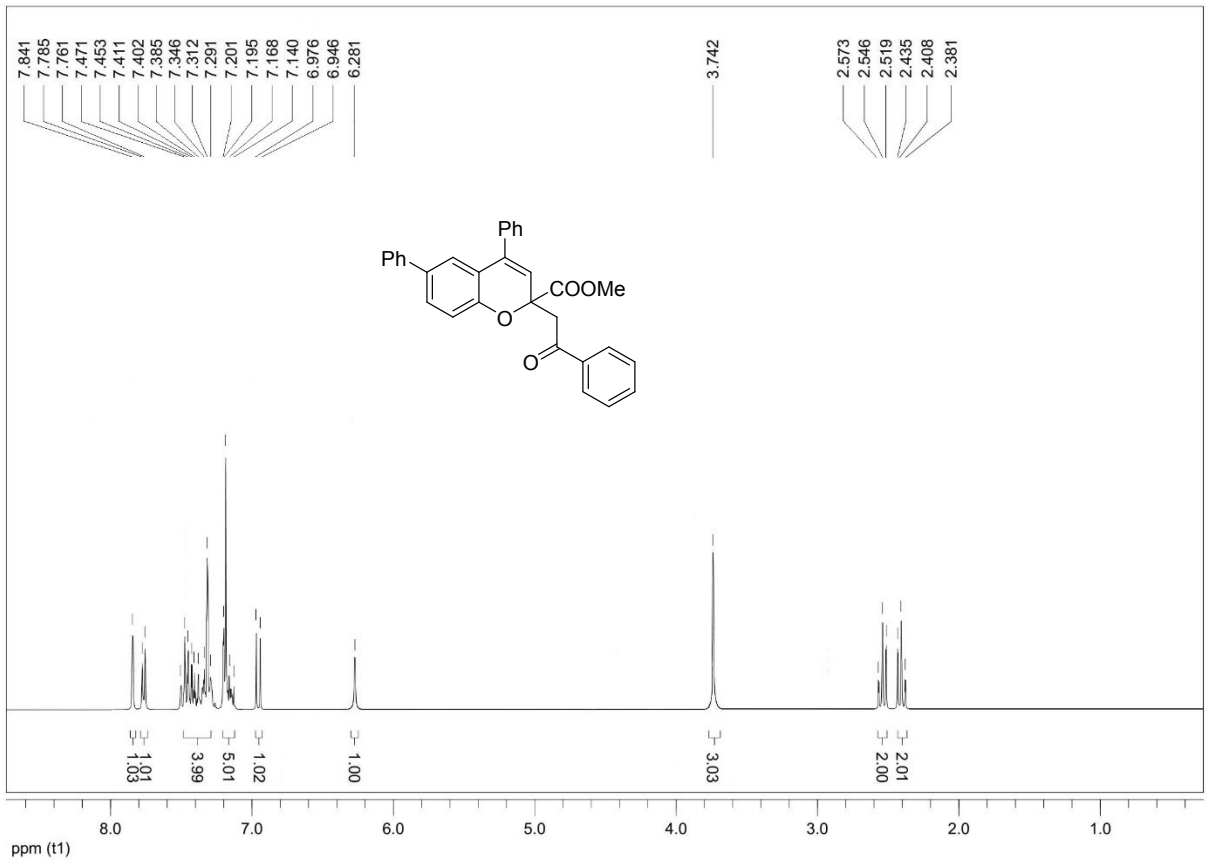


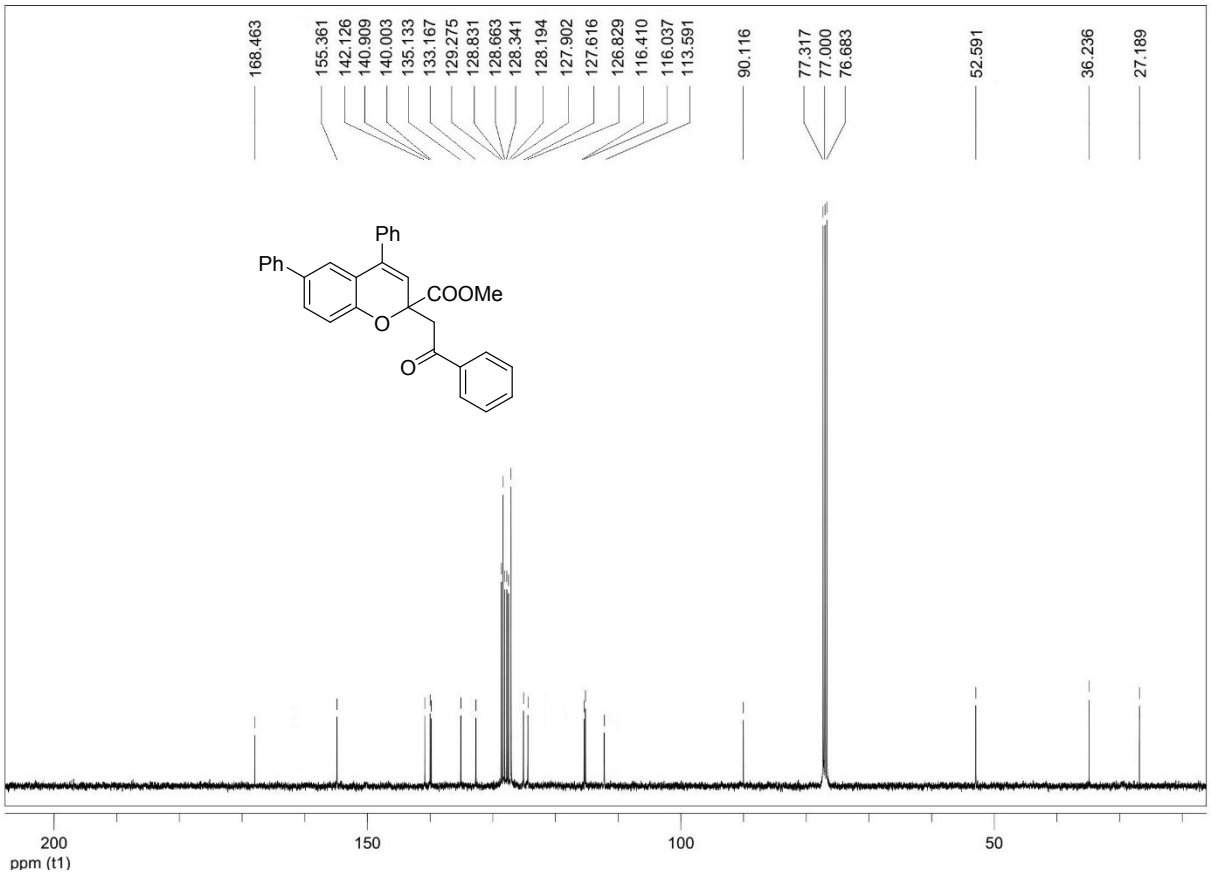
Methyl 6-(tert-butyl)-2-(2-oxopentyl)-4-phenyl-2*H*-chromene-2-carboxylate (3az)



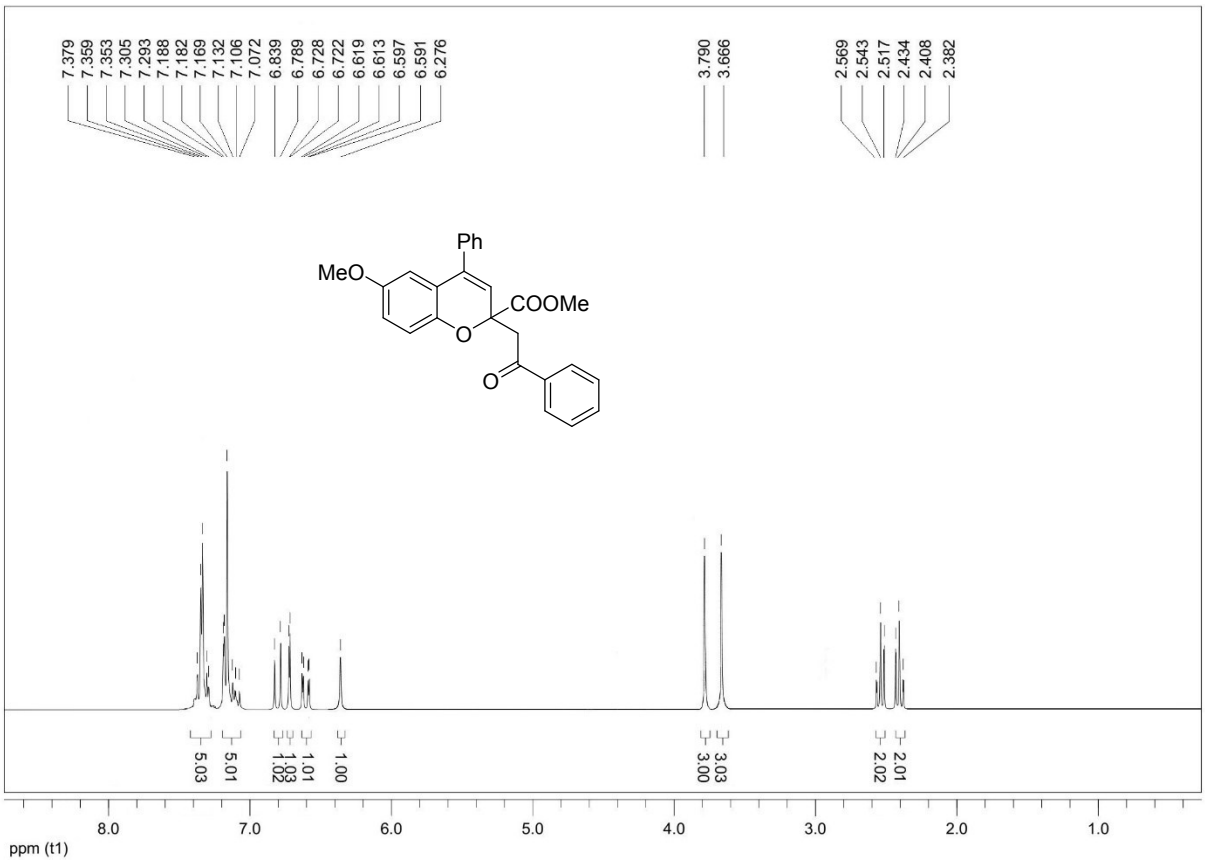


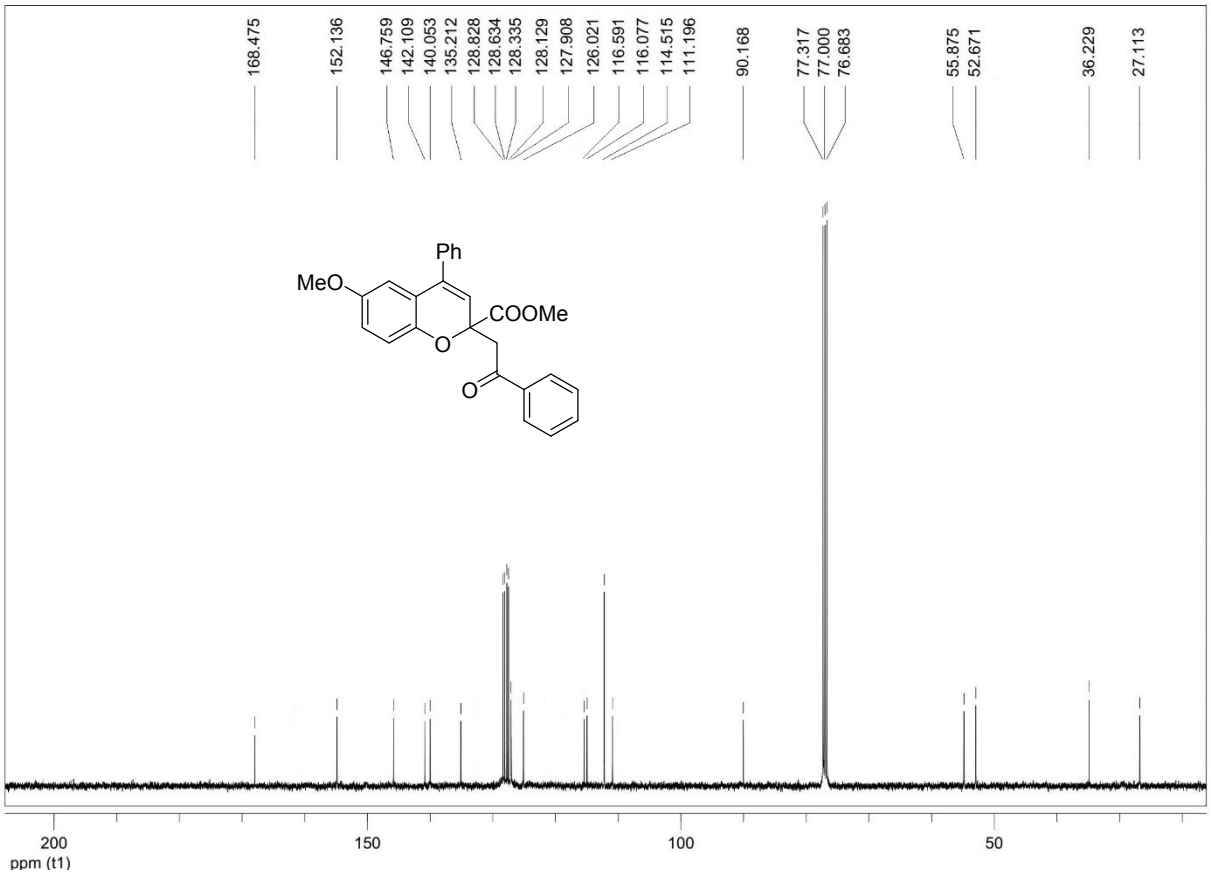
Methyl 2-(2-oxo-2-phenylethyl)-4,6-diphenyl-2*H*-chromene-2-carboxylate (3ba)



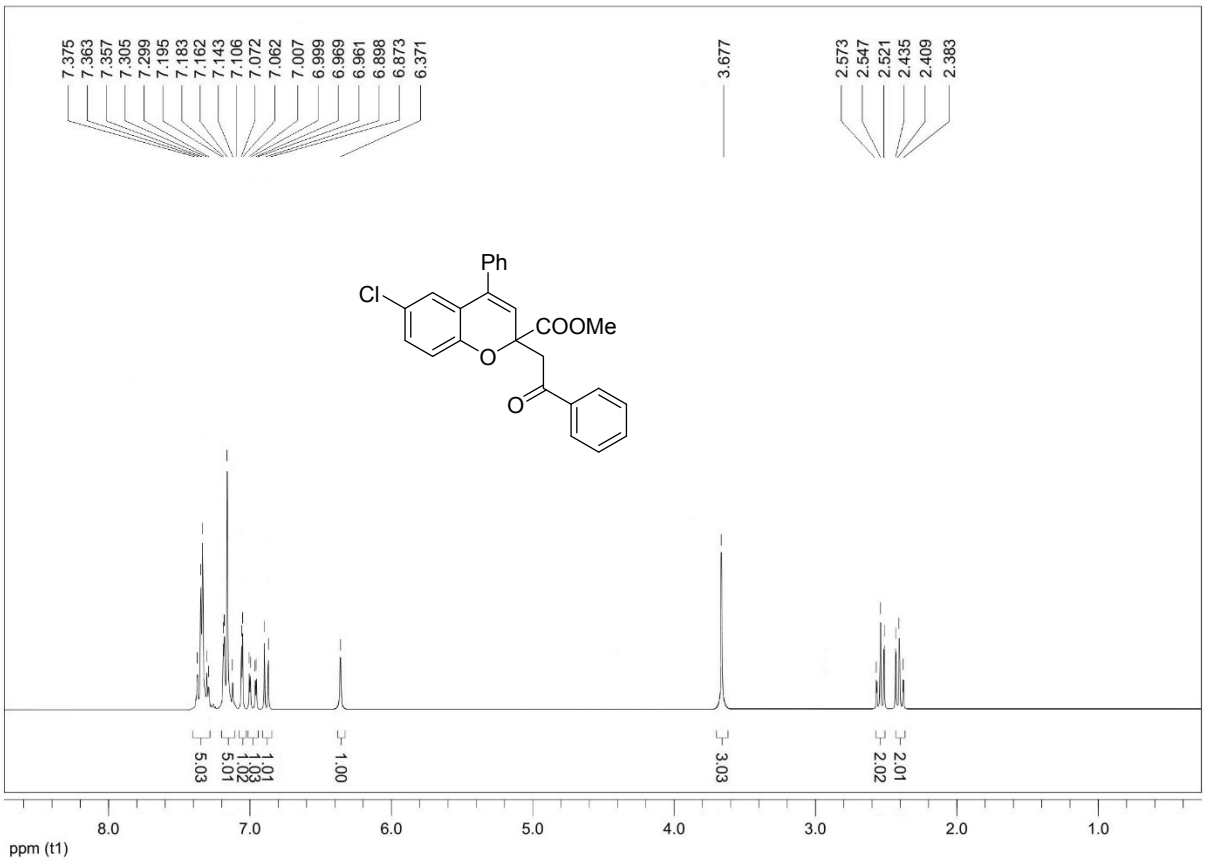


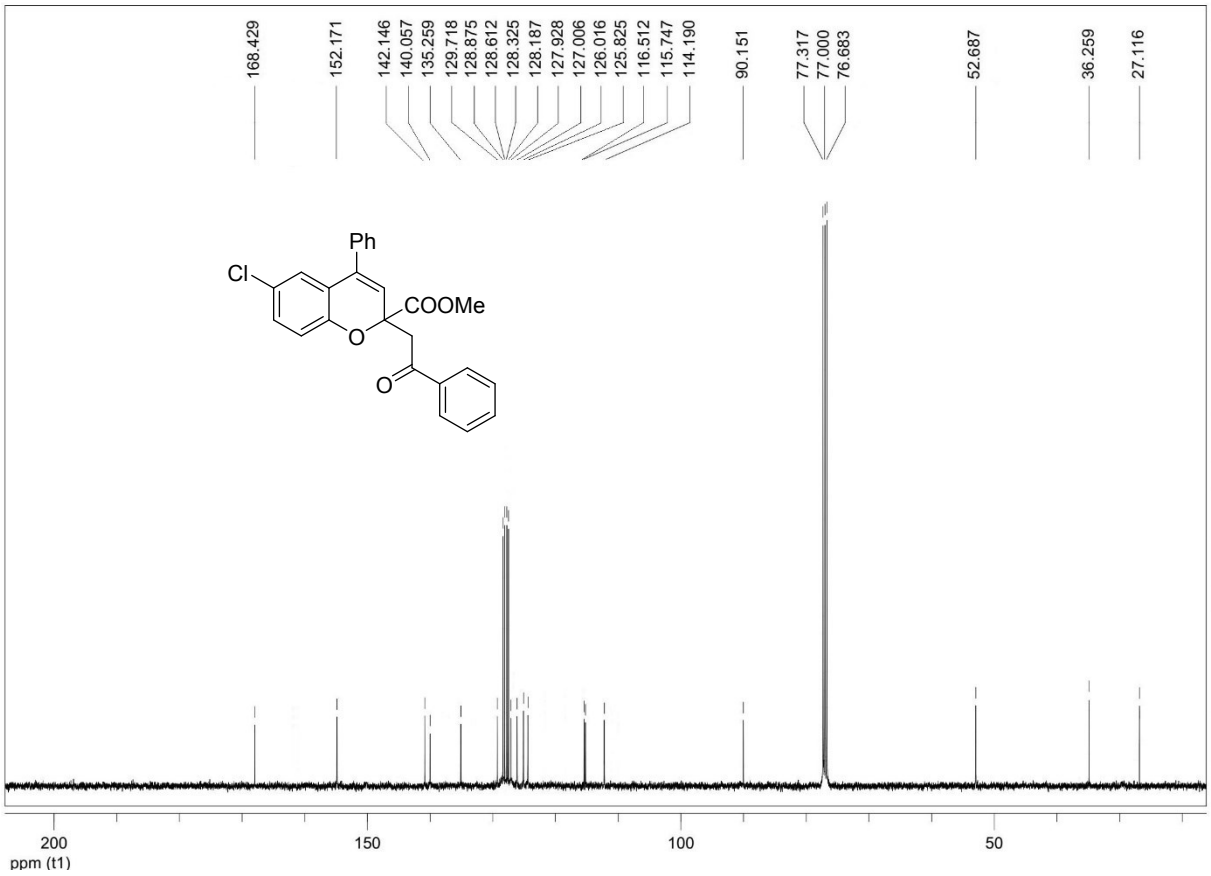
Methyl 6-methoxy-2-(2-oxo-2-phenylethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3ca)



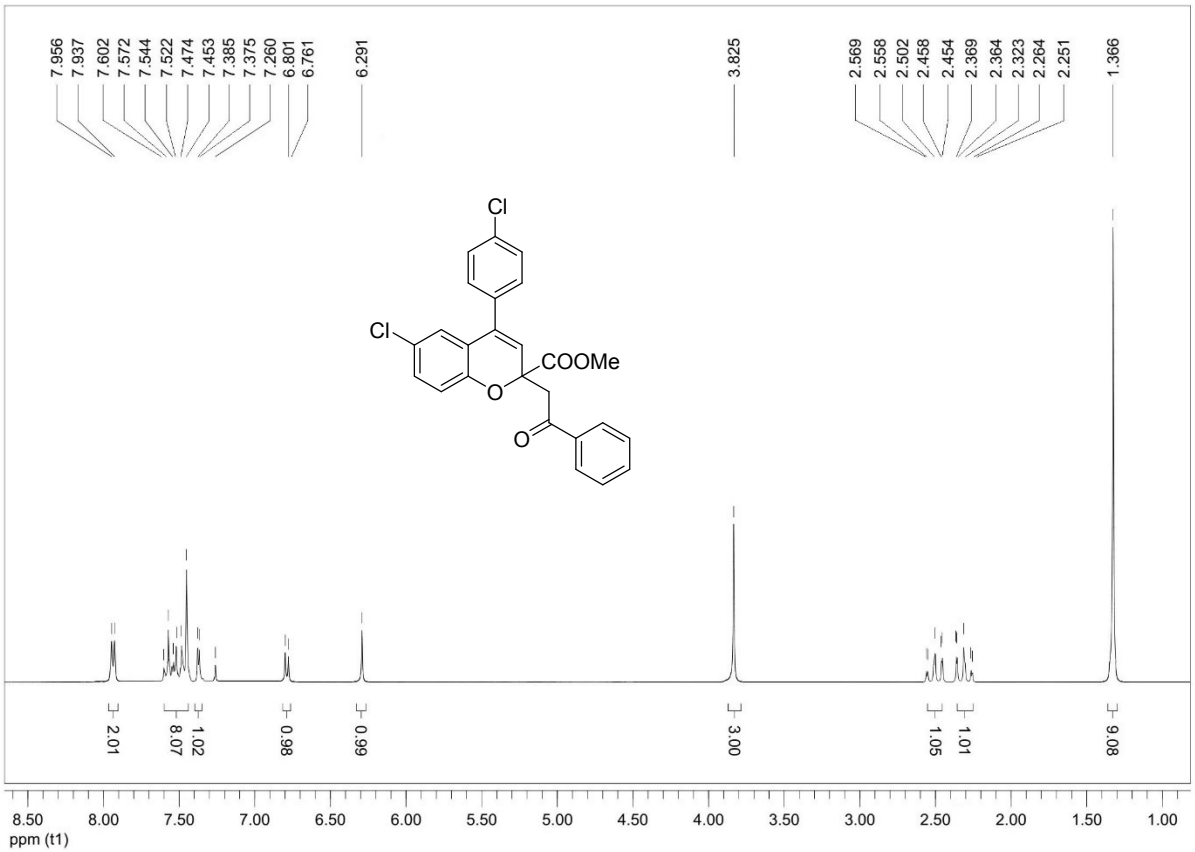


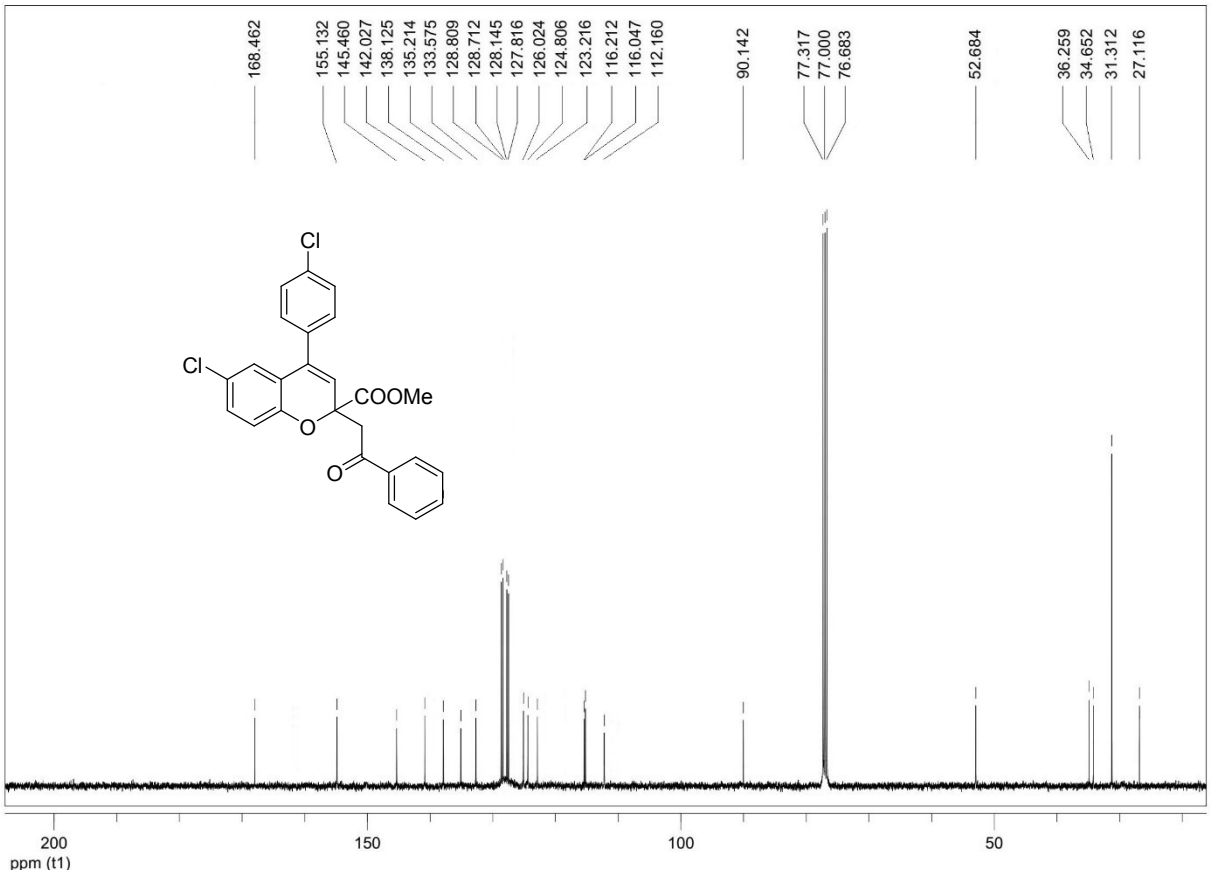
methyl 6-chloro-2-(2-oxo-2-phenylethyl)-4-phenyl-2*H*-chromene-2-carboxylate (3da)



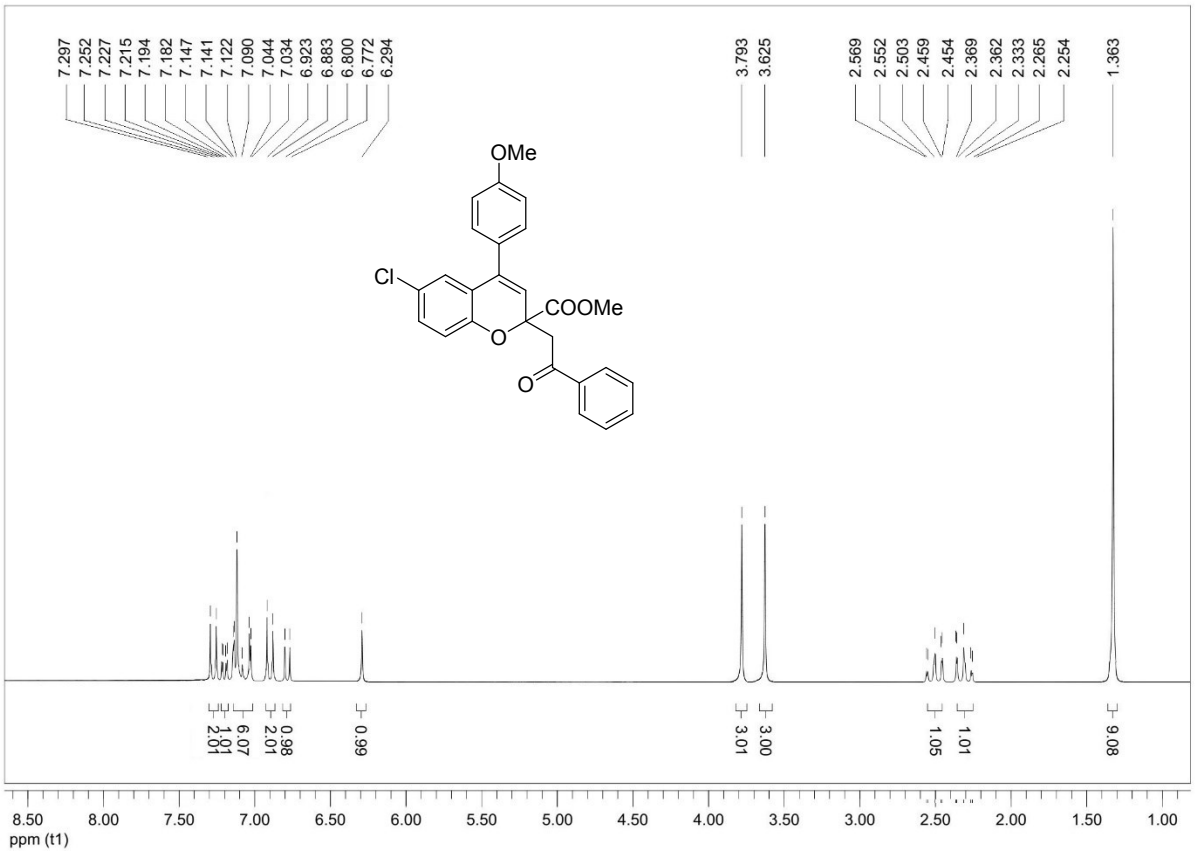


Methyl 6-chloro-4-(4-chlorophenyl)-2-(2-oxo-2-phenylethyl)-2*H*-chromene-2- carboxylate (3ea)





Methyl 6-chloro-4-(4-methoxyphenyl)-2-(2-oxo-2-phenylethyl)-2*H*-chromene-2- carboxylate (3fa)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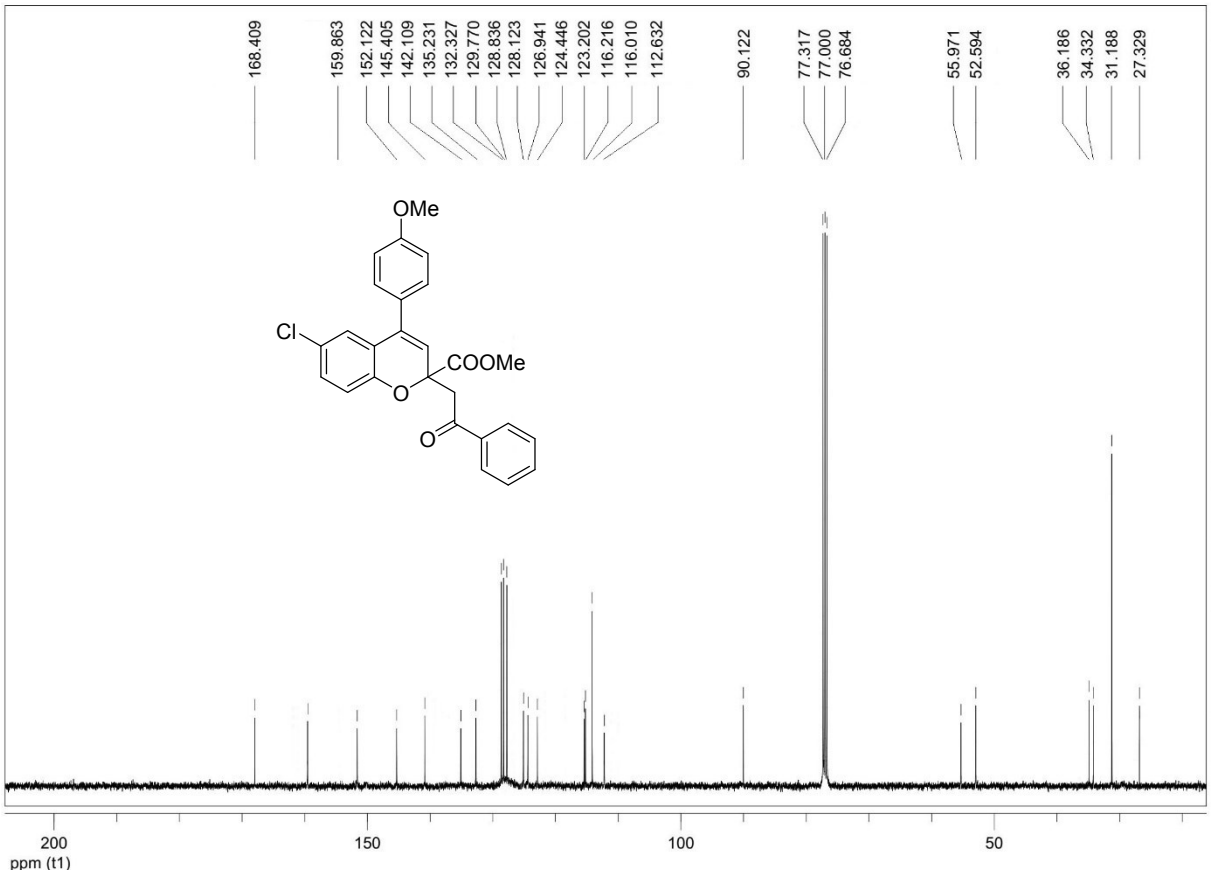
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ppm (t1)