Supporting Information

Oxidant Free Synthesis of 2-Pyrones via NHC-Catalyzed [3+3] Annulation of Bromoenals with 2-Chloro-1,3-diketones

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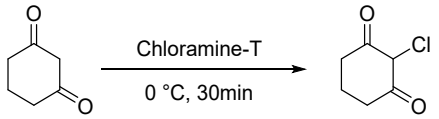
I. General information:

Commercially available materials purchased from Alfa Aesar or Sigma-Aldrich were used as received, except aldehydes that were purified *via* distillation or column chromatography prior to use. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker (300 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to chloroform (δ = 7.26, singlet). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets), m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker (300 MHz) (75 MHz) spectrometer. High resolution mass spectrometry (HRMS) analysis was performed using electrospray ionization (ESI) with a quadrupole-time of flight (QTOF) mass analyzer.

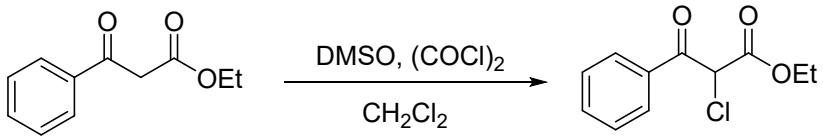
HRMS (ESI) analysis was performed by The Analytical Instrumentation Center at College of Chemistry and Materials Science, Jinan University, and (HRMS) data were reported with ion mass/charge (m/z) ratios as values in atomic mass units. Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp.

II. Synthesis of substrates



S2a **2a**

Substrates **2a**, **2u** and **2v** were synthesized according to the reported method.[1] **S2a** (5.0 g, 44.6 mmol) was dissolved in THF (15 mL) and water (50 mL), which was subsequently cooled to 0 °C. After dropwise addition of chloramine-T (10.2 g, 44.6 mmol) in water (20 mL), this mixture was stirred for 30 min and then filtered. The residue was washed with water (5 mL). The filtrate was acidified to pH = 2 with concentrated HCl and the acidic mixture was saturated with NaCl. This mixture was extracted four times with THF and the collected organic phases were dried thoroughly with MgSO4. After concentration under vacuum, **2a** was obtained in 75% yield （4.9g）.

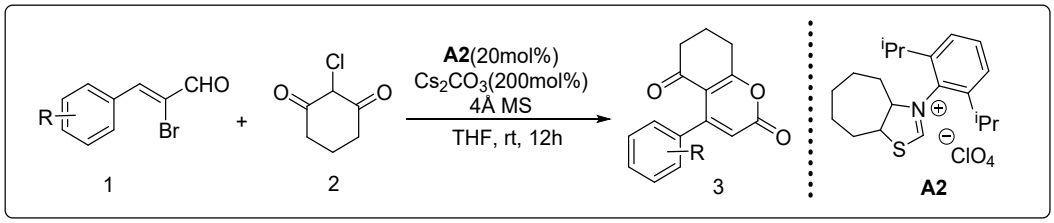


S2w **2w**

Substrate **2w** was synthesized according to the reported method.[2] The solution of DMSO (15 mmol, 3 equivalents) and the substrate **S2w** (5 mmol, 1 equivalent) in CH_2Cl_2 (10 mL) was cooled at 0 °C, then a solution of oxalyl chloride (15 mmol, 3 equivalents) in CH_2Cl_2 (10 mL) was added dropwise to the mixture. The reaction was stirred for 20 min at 0 °C. Solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (petroleum ether/EtOAc = 60:1) to give pale yellow oil product **2w**, 1.08 g, 95% yield.

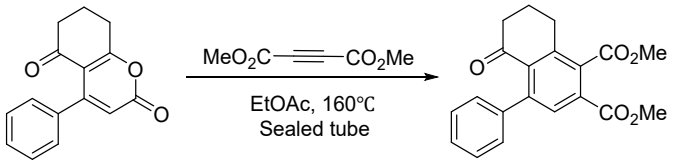
III. General procedure for the catalytic synthesis of products 3.

General procedure for the reaction of Unsaturated aldehydes **1** with 2-chlorocyclohexane-1,3-dione **2**.



To a dry schlenk reaction tube equipped with a magnetic stir bar, was added α-Bromocinnamaldehyde **1** (21.1 mg, 0.1 mmol), 2-chlorocyclohexane-1,3-dione **2** (21.9 mg, 0.15 mmol)**,** NHC **A2** (8.3 mg, 0.02 mmol), Cs_2CO_3 (65.2 mg, 0.2 mmol) and 4A MS powder (50 mg). The schlenk tube was then evacuated and refilled with dry N_2. Anhydrous THF (1 mL) was added. The mixture was stirred at rt for 12 h. Solvent was removed under reduced pressure, and the residue was purified via column chromatography on silica gel with hexane/EtOAc (typically 3:1) as eluent to afford the products **3**.

IV. Synthetic transformations of 3.

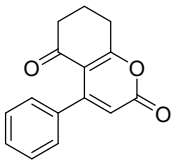


A mixture of **3** (48.1 mg, 0.2 mmol) and dimethyl acetylenedicarboxylate (85.2 mg, 0.6 mmol) in ethyl acetate (1.5 mL) was heated at 160 °C for 6 h in a sealed tube. Solvent was removed under reduced pressure, and the residue was purified via column chromatography on silica gel with hexane/EtOAc (5:1) as eluent to afford the product **4** (54.1mg, 80%yield).

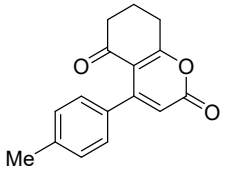
V. References

[1] R. Boers, P. Gast, A. Hoff, H. de Groot and J. Lugtenburg, *Eur. J. Org. Chem.*, 2002, 189-202.
[2] Z. Xi, Y. Liu, H. Wang, D. Guan, Y. Liu, B. Sun, H. Tian and S. Liang, *ChemistrySelect*, 2021, **6**, 10883.

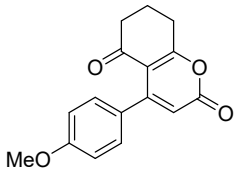
VI. Characterization of Products.



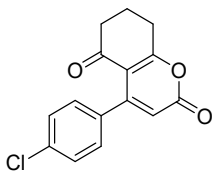
4-phenyl-7,8-dihydro-2H-chromene-2,5(6H)-dione (3a): Yield: 23.1 mg (96%), yellowish solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 3H), 7.20 – 7.17 (m, 2H), 6.07 (s, 1H), 2.93 (t, J = 6.3 Hz, 2H), 2.52 (t, J = 6.5 Hz, 2H), 2.19 – 2.10 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.2, 175.0, 159.5, 156.7, 137.4, 128.9, 128.0, 127.1, 114.4, 114.2, 38.2, 29.2, 19.8; HRMS (ESI, m/z): calcd. for $C_{15}H_{12}O_3[M]^+$240.0786, found 240.0782.



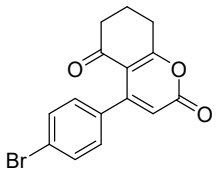
4-(p-tolyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3b): Yield: 18.8 mg (74%), yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.07 (s, 1H), 2.93 (t, *J* = 6.3 Hz, 2H), 2.54 (t, *J* = 6.3 Hz, 2H), 2.39 (s, 3H), 2.20 – 2.11 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.3, 174.9, 159.7, 156.8, 139.2, 134.5, 128.8, 127.2, 114.4, 114.2, 38.3, 29.3, 21.5, 19.9; HRMS (ESI, m/z): calcd. for $C_{16}H_{14}O_3[M+H]^+$ 255.1016, found 255.1023.



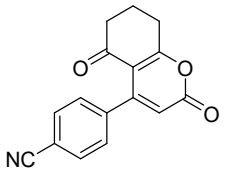
4-(4-methoxyphenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3c): Yield: 16.2 mg (60%), yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.06 (s, 1H), 3.84 (s, 3H), 2.93 (t, *J* = 6.3 Hz, 2H), 2.54 (t, *J* = 6.3 Hz, 2H), 2.20 – 2.11 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.5, 175.0, 160.5, 159.7, 156.4, 129.5, 128.9, 114.3, 113.8, 113.5, 55.4, 38.4, 29.4, 19.8; HRMS (ESI, m/z): calcd. for $C_{16}H_{14}O_4[M+H]^+$ 271.0965, found 271.0973.



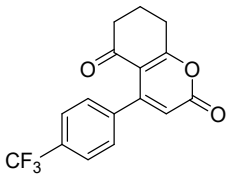
4-(4-chlorophenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3d): Yield: 23.9 mg (87%), white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.04 (s, 1H), 2.93 (t, *J* = 6.3 Hz, 2H), 2.53 (t, *J* = 6.4 Hz, 2H), 2.20 – 2.11 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.3, 175.3, 159.2, 155.5, 135.8, 135.2, 128.6, 128.3, 114.6, 114.0, 38.2, 29.3, 19.8; HRMS (ESI, m/z): calcd. for $C_{15}H_{11}ClO_3[M+H]^+$ 275.0469, found 275.0471.



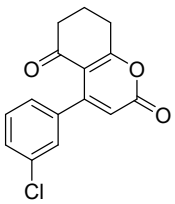
4-(4-bromophenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3e): Yield: 30 mg (94%), white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.04 (s, 1H), 2.93 (t, *J* = 6.3 Hz, 2H), 2.52 (t, *J* = 6.3 Hz, 2H), 2.19 – 2.10 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.2, 175.3, 159.2, 155.5, 136.3, 131.2, 128.8, 123.3, 114.6, 113.9, 38.2, 29.3, 19.8; HRMS (ESI, m/z): calcd. for $C_{15}H_{11}BrO_3[M+H]^+$ 318.9964, found 318.9962.



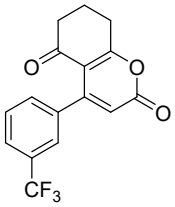
4-(2,5-dioxo-5,6,7,8-tetrahydro-2H-chromen-4-yl)benzonitrile (3f): Yield: 21.8 mg (82%), yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 6.05 (s, 1H), 2.96 (t, *J* = 6.3 Hz, 2H), 2.53 (t, *J* = 6.3 Hz, 2H), 2.22 – 2.12 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.2, 175.7, 158.8, 154.6, 142.1, 131.8, 127.9, 118.5, 115.0, 113.6, 112.7, 38.0, 29.3, 19.8; HRMS (ESI, m/z): calcd. for $C_{16}H_{10}NO_3[M-H]^-$ 264.0666, found 264.0655.



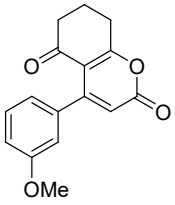
4-(4-(trifluoromethyl)phenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3g): Yield: 29.3 mg (95%), white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.06 (s, 1H), 2.95 (t, *J* = 6.3 Hz, 2H), 2.53 (t, *J* = 6.7 Hz, 2H), 2.21 – 2.12 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.2, 175.5, 159.0, 155.2, 141.1, 131.1, 130.6, 127.5, 125.8, 125.1, 125.1, 125.0, 125.0, 122.2, 115.0, 113.9, 38.1, 29.2, 19.8; HRMS (ESI, m/z): calcd. for $C_{16}H_{11}F_3O_3[M+H]^+$ 309.0733, found 309.0740.



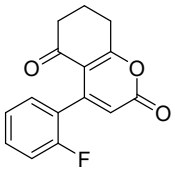
4-(3-chlorophenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3h): Yield: 24.7 mg (90%), yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 2H), 7.17 (s, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.05 (s, 1H), 2.93 (t, *J* = 6.3 Hz, 2H), 2.53 (t, *J* = 6.3 Hz, 2H), 2.20 – 2.11 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.1, 175.3, 159.2, 155.1, 139.1, 134.0, 129.3, 129.0, 127.2, 125.4, 114.8, 113.9, 38.1, 29.3, 19.8; HRMS (ESI, m/z): calcd. for $C_{15}H_{11}ClO_3[M+H]^+$ 275.0469, found 275.0476.



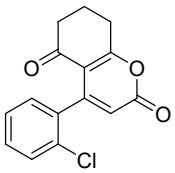
4-(3-(trifluoromethyl)phenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3i): Yield: 29.6 mg (96%), yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.43 (m, 1H), 7.43 (s, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 6.05 (s, 1H), 2.93 (t, *J* = 6.3 Hz, 2H), 2.51 (t, *J* = 6.3 Hz, 2H), 2.20 – 2.11 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.2, 175.5, 159.0, 155.1, 138.2, 130.6, 130.5, 130.1, 129.7, 128.4, 126.3, 125.7, 125.6, 125.6, 125.5, 125.5, 124.1, 124.1, 124.0, 123.9, 122.1, 115.0, 113.7, 38.0, 29.2, 19.7; HRMS (ESI, m/z): calcd. for $C_{16}H_{11}F_3O_3[M+H]^+$ 309.0733, found 309.0740.



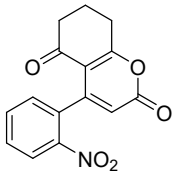
4-(3-methoxyphenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3j): Yield: 21.4 mg (79%), yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.9 Hz, 1H), 6.97 – 6.90 (m, 1H), 6.78 – 6.71 (m, 2H), 6.09 (s, 1H), 3.81 (s, 3H), 2.93 (t, *J* = 6.3 Hz, 2H), 2.53 (t, *J* = 6.3 Hz, 2H), 2.20 – 2.11 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.1, 174.9, 159.6, 159.2, 156.5, 138.8, 129.1, 119.6, 114.5, 114.4, 114.1, 113.2, 55.4, 38.3, 29.3, 19.9; HRMS (ESI, m/z): calcd. for $C_{16}H_{14}O_4[M+H]^+$ 271.0965, found 271.0971.



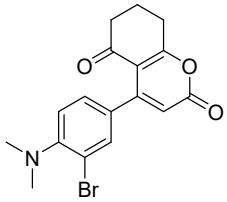
4-(2-fluorophenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3k): Yield: 21.4 mg (83%), yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 1H), 7.24 – 7.16 (m, 2H), 7.10 – 7.00 (m, 1H), 6.11 (s, 1H), 2.93 (t, *J* = 6.3 Hz, 2H), 2.53 (t, *J* = 6.7 Hz, 2H), 2.20 – 2.10 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.4, 174.0, 160.7, 159.5, 157.4, 151.0, 131.1, 131.0, 128.6, 128.6, 125.8, 125.6, 124.4, 124.4, 115.4, 115.2, 114.9, 114.5, 37.8, 29.1, 19.8; HRMS (ESI, m/z): calcd. for $C_{15}H_{11}FO_3[M+H]^+$ 259.0765, found 259.0773.



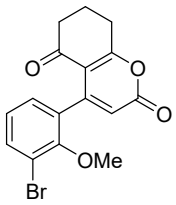
4-(2-chlorophenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3l): Yield: 21.2 mg (77%), yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 3H), 7.18 – 7.13 (m, 1H), 6.05 (s, 1H), 3.01 – 2.86 (m, 2H), 2.65 – 2.52 (m, 1H), 2.48 – 2.37 (m, 1H), 2.21 – 2.08 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.2, 174.0, 159.6, 153.9, 136.8, 131.5, 129.9, 129.1, 128.2, 127.0, 115.0, 114.6, 37.6, 29.1, 19.9; HRMS (ESI, m/z): calcd. for $C_{15}H_{11}ClO_3[M+H]^+$ 275.0469, found 275.0479.



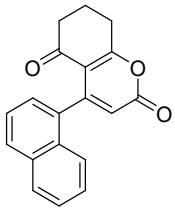
4-(2-nitrophenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3m): Yield: 27.0 mg (94%), yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.42 – 7.33 (m, 1H), 7.31 – 7.22 (m, 1H), 7.14 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.03 (s, 1H), 3.03 – 2.85 (m, 2H), 2.65 – 2.54 (m, 1H), 2.49 – 2.38 (m, 1H), 2.21 – 2.09 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.2, 174.1, 159.7, 155.3, 138.8, 132.3, 130.0, 128.2, 127.5, 121.1, 114.9, 114.5, 37.6, 29.1, 19.9; HRMS (ESI, m/z): calcd. for $C_{15}H_{11}NO_5[M-H]^-$ 284.0564, found 284.0566.



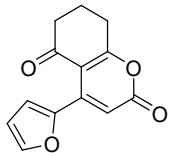
4-(3-bromo-4-(dimethylamino)phenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3n): Yield: 30.9 mg (85%), yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 2.1 Hz, 1H), 7.10 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.04 (s, 1H), 2.92 (t, *J* = 6.3 Hz, 2H), 2.85 (s, 6H), 2.54 (t, *J* = 6.3 Hz, 2H), 2.20 – 2.11 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.3, 175.2, 159.4, 154.9, 152.6, 132.9, 132.2, 127.4, 119.5, 117.7, 114.2, 114.0, 44.1, 38.2, 29.3, 19.8; HRMS (ESI, m/z): calcd. for $C_{17}H_{17}BrNO_3[M+H]^+$ 362.0386, found 362.0388.



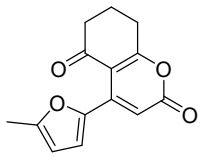
4-(3-bromo-2-methoxyphenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3o): Yield: 24.4 mg (70%), white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.21 (d, *J* = 2.5 Hz, 1H), 6.73 (d, *J* = 8.8 Hz, 1H), 6.04 (s, 1H), 3.69 (s, 3H), 2.91 (s, 2H), 2.46 (t, *J* = 6.3 Hz, 2H), 2.16 – 2.10 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.3, 173.0, 159.8, 155.3, 152.4, 133.0, 130.5, 129.1, 115.0, 114.8, 112.8, 112.0, 55.8, 37.8, 28.9, 20.0; HRMS (ESI, m/z): calcd. for $C_{16}H_{13}BrO_4[M+H]^+$ 349.0070, found 349.0066.



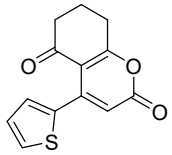
4-(naphthalen-1-yl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3p): Yield: 21.8 mg (75%), yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.52 – 7.45 (m, 3H), 7.44 – 7.38 (m, 1H), 7.22 (dd, *J* = 7.0, 1.2 Hz, 1H), 6.20 (s, 1H), 3.07 – 2.95 (m, 2H), 2.46 – 2.36 (m, 2H), 2.19 – 2.10 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.6, 174.5, 159.6, 155.9, 135.9, 133.1, 130.8, 129.0, 128.7, 126.6, 126.1, 125.2, 124.5, 124.1, 115.5, 115.3, 37.9, 29.2, 19.9; HRMS (ESI, m/z): calcd. for $C_{19}H_{14}O_3[M+H]^+$ 291.1016, found 291.1024.



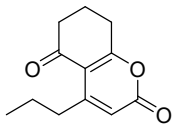
4-(furan-2-yl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3q): Yield: 22.6 mg (98%), yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 1.1 Hz, 1H), 6.98 (d, *J* = 2.9 Hz, 1H), 6.53 – 6.49 (m, 1H), 6.49 (s, 1H), 2.87 (t, *J* = 6.3 Hz, 2H), 2.60 (t, *J* = 6.3 Hz, 2H), 2.18 – 2.09 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.4, 174.8, 159.8, 148.0, 145.0, 142.5, 116.5, 113.0, 112.4, 110.0, 38.4, 29.4, 19.7; HRMS (ESI, m/z): calcd. for $C_{13}H_{10}O_4[M+H]^+$ 231.0652, found 231.0657.



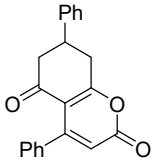
4-(5-methylfuran-2-yl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3r): Yield: 23.7 mg (97%), yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.95 (d, *J* = 3.5 Hz, 1H), 6.47 (s, 1H), 6.11 (d, *J* = 2.4 Hz, 1H), 2.84 (t, *J* = 6.3 Hz, 2H), 2.58 (t, *J* = 6.3 Hz, 2H), 2.33 (s, 3H), 2.15 – 2.06 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 174.6, 160.1, 156.0, 146.0, 142.1, 119.3, 112.8, 109.3, 107.7, 38.4, 29.5, 19.6, 13.9; HRMS (ESI, m/z): calcd. for $C_{14}H_{12}O_4[M+H]^+$ 245.0808, found 245.0819.



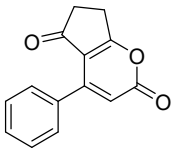
4-(thiophen-2-yl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3s): Yield: 20.7 mg (84%), yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 5.1 Hz, 1H), 7.15 (d, *J* = 3.7 Hz, 1H), 7.07 – 7.04 (m, 1H), 6.23 (s, 1H), 2.91 (t, *J* = 6.3 Hz, 2H), 2.58 (t, *J* = 6.5 Hz, 2H), 2.20 – 2.10 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.2, 174.8, 159.2, 149.0, 137.5, 129.3, 128.3, 127.3, 114.3, 114.1, 38.3, 29.3, 19.7; HRMS (ESI, m/z): calcd. for $C_{13}H_{10}O_3S[M+H]^+$ 247.0423, found 247.0427.



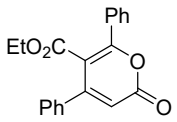
4-propyl-7,8-dihydro-2H-chromene-2,5(6H)-dione (3t): Yield: 10.7 mg (52%), yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.99 (s, 1H), 2.93 – 2.78 (m, 4H), 2.58 – 2.51 (m, 2H), 2.09 (p, J = 6.4 Hz, 2H), 1.59 – 1.46 (m, 2H), 0.99 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.4, 175.1, 160.3, 159.9, 114.5, 112.3, 39.0, 36.6, 29.4, 22.3, 19.8, 14.0; HRMS (ESI, m/z): calcd. for $C_{12}H_{14}O_3[M+H]^+$ 207.1016, found 207.1016.



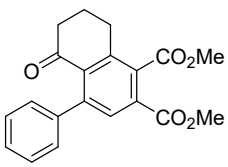
4,7-diphenyl-7,8-dihydro-2H-chromene-2,5(6H)-dione (3u): Yield: 29.1 mg (92%), white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 5H), 7.36 – 7.27 (m, 3H), 7.25 – 7.19 (m, 2H), 6.10 (s, 1H), 3.63 – 3.48 (m, 1H), 3.16 (d, J = 8.0 Hz, 2H), 2.80 (d, J = 6.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.4, 174.0, 159.4, 156.5, 141.2, 137.1, 129.1, 129.0, 128.0, 127.6, 127.2, 126.6, 114.5, 113.9, 45.2, 37.8, 36.6; HRMS (ESI, m/z): calcd. for $C_{21}H_{16}O_3[M+H]^+$ 317.1172, found 317.1178.



4-phenyl-6,7-dihydrocyclopenta[b]pyran-2,5-dione (3v): Yield: 20.1 mg (89%), yellowish solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.41 (m, 5H), 6.17 (s, 1H), 3.10 – 2.92 (m, 2H), 2.78 – 2.64 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 186.9, 160.7, 154.0, 133.0, 130.7, 128.6, 128.3, 115.5, 111.7, 34.8, 25.9; HRMS (ESI, m/z): calcd. for $C_{14}H_{10}O_3[M+H]^+$ 227.0707, found 227.0703.



methyl 2-oxo-4,6-diphenyl-2H-pyran-5-carboxylate (3w): Yield: 23.0 mg (75%), yellowish solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.60 (m, 2H), 7.50 – 7.41 (m, 6H), 7.39 – 7.33 (m, 2H), 6.28 (s, 1H), 3.93 (q, J = 7.1 Hz, 2H), 0.86 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 161.1, 160.6, 156.2, 136.4, 131.8, 131.2, 129.8, 128.8, 128.6, 128.3, 127.0, 113.7, 112.8, 62.0, 13.4; HRMS (ESI, m/z): calcd. for $C_{20}H_{16}O_4[M]^+$ 320.1049, found 320.1053.

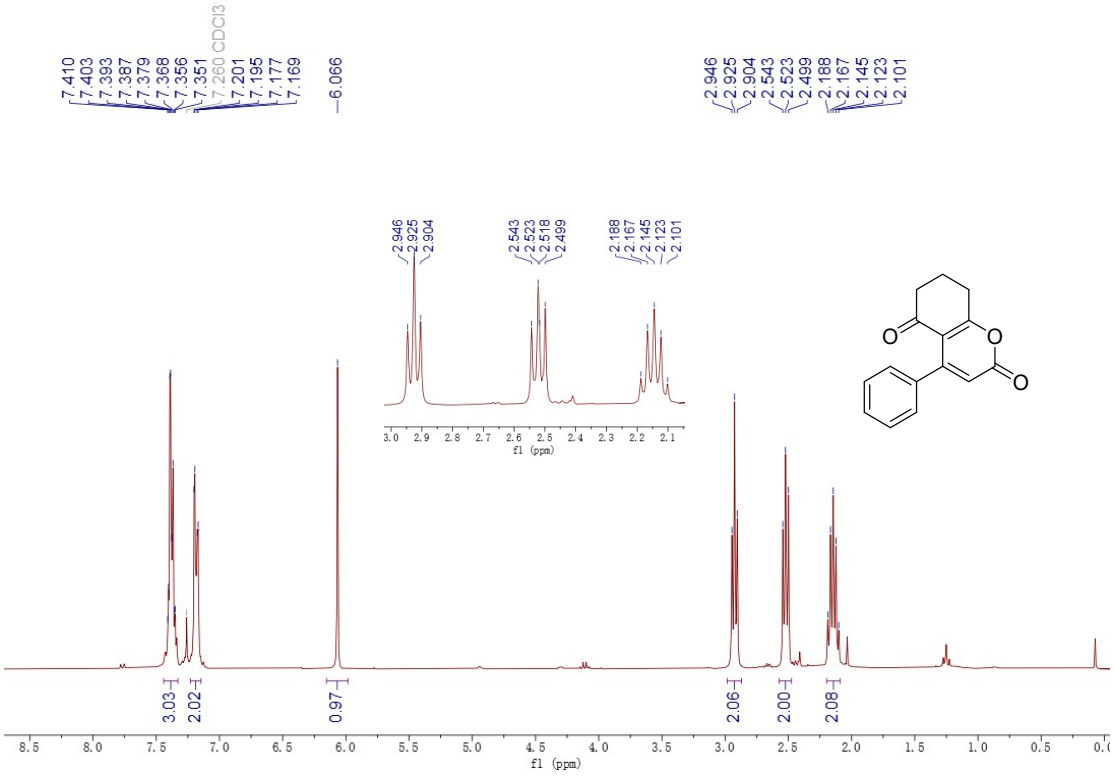


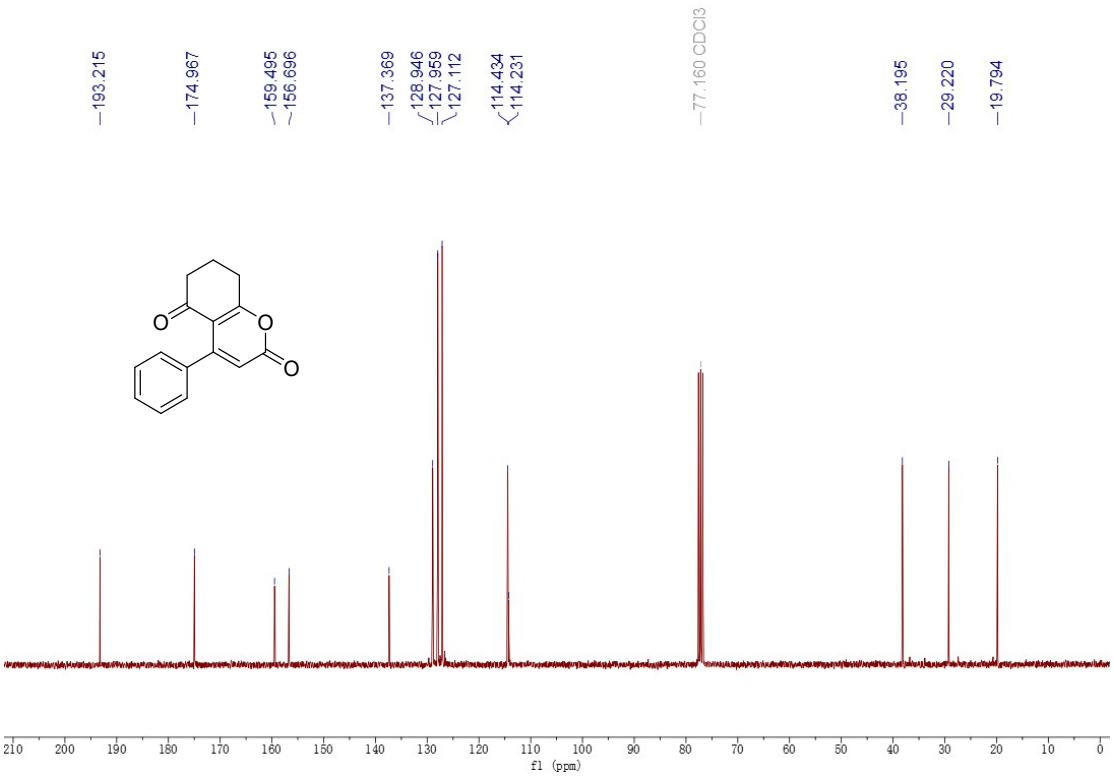
dimethyl 5-oxo-4-phenyl-5,6,7,8-tetrahydronaphthalene-1,2-dicarboxylate (4): Yield: 54.1 mg (80%), yellowish solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.46 – 7.34 (m, 3H), 7.24 – 7.15

(m, 2H), 3.99 (s, 3H), 3.90 (s, 3H), 2.98 (t, *J* = 6.2 Hz, 2H), 2.66 (t, *J* = 6.3 Hz, 2H), 2.21 – 2.12 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.6, 168.9, 165.4, 145.0, 142.5, 141.4, 134.8, 134.4, 131.4, 129.8, 128.1, 128.1, 127.4, 52.9, 52.9, 40.0, 27.4, 22.4; HRMS (ESI, m/z): calcd. for $C_{21}H_{16}O_3[M+H]^+$ 339.1227, found 339.1237.

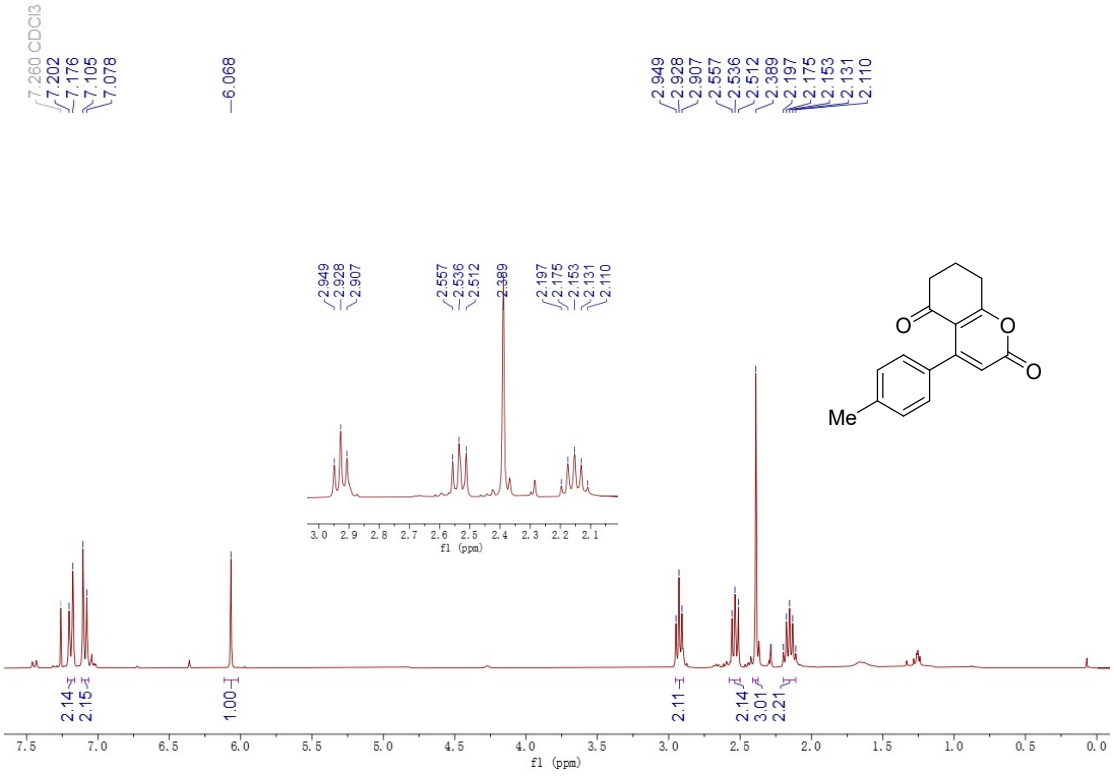
VII. ^{1}H and ^{13}C NMR spectra of new compounds.

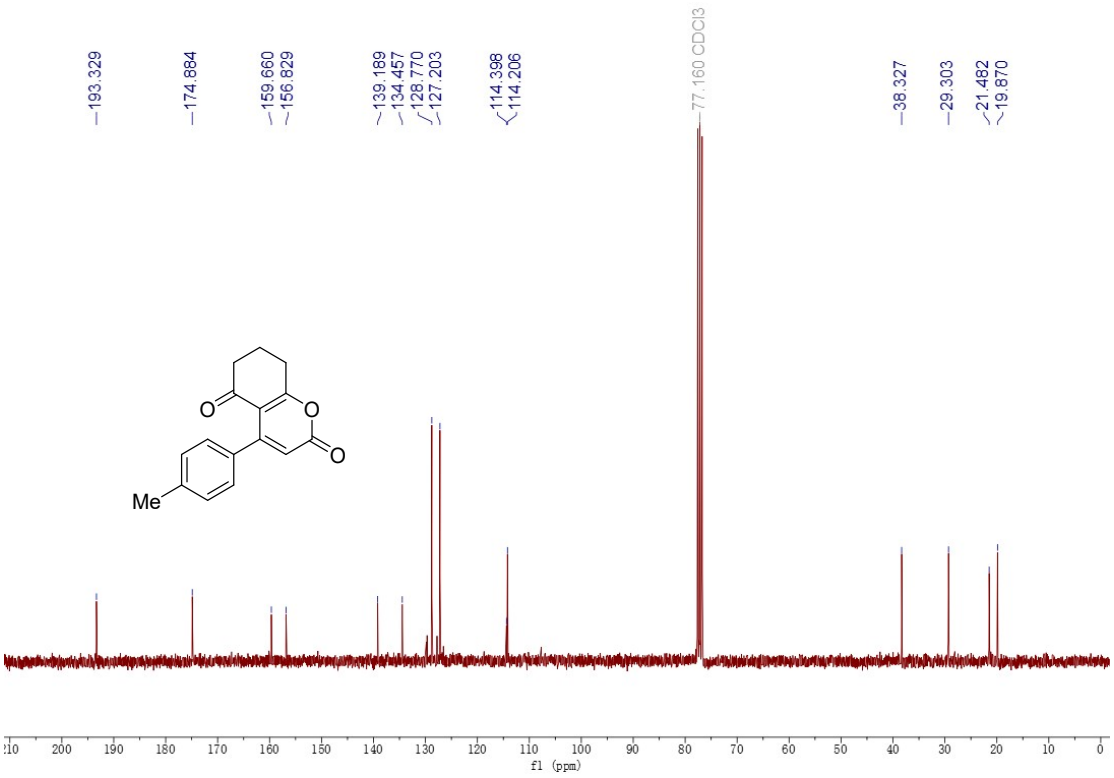
phenyl-7,8-dihydro-2H-chromene-2,5(6H)-dione (3a)



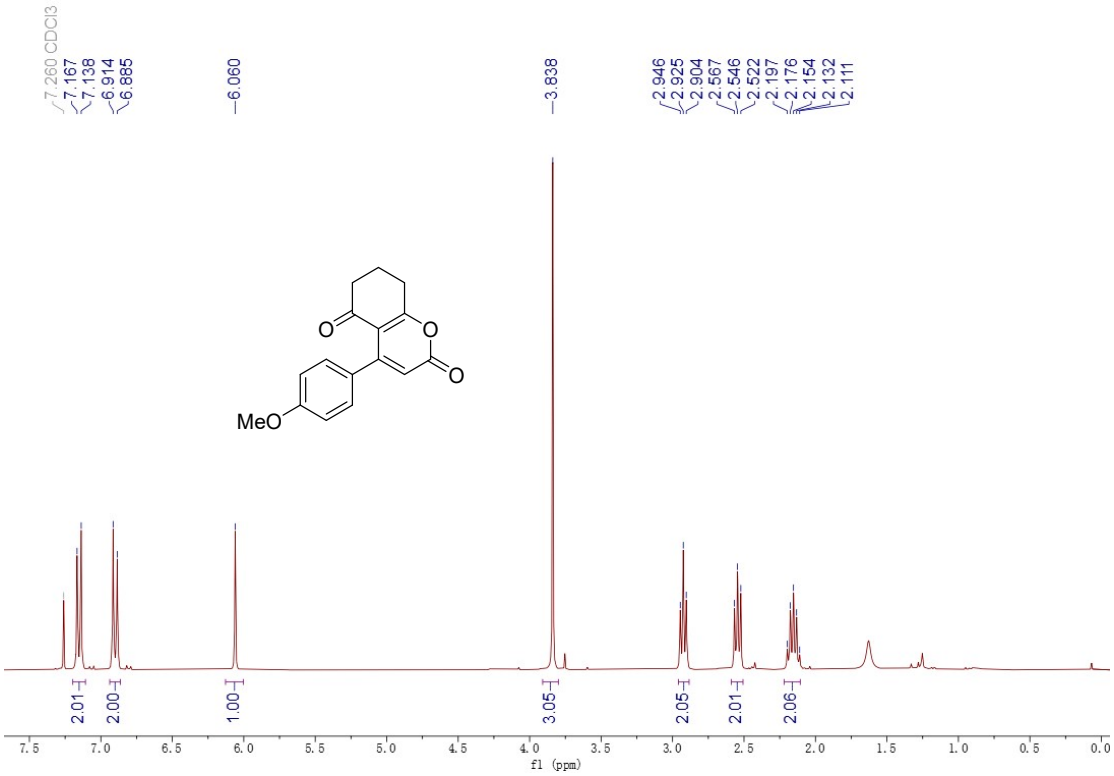


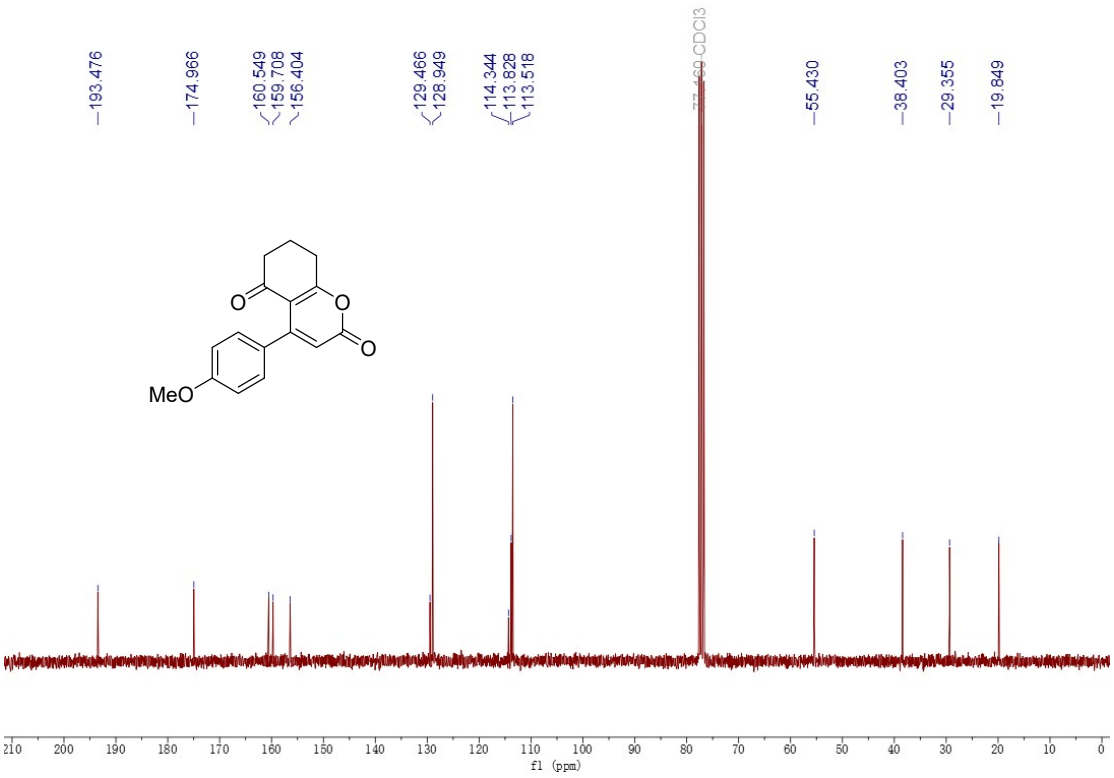
4-(p-tolyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3b)



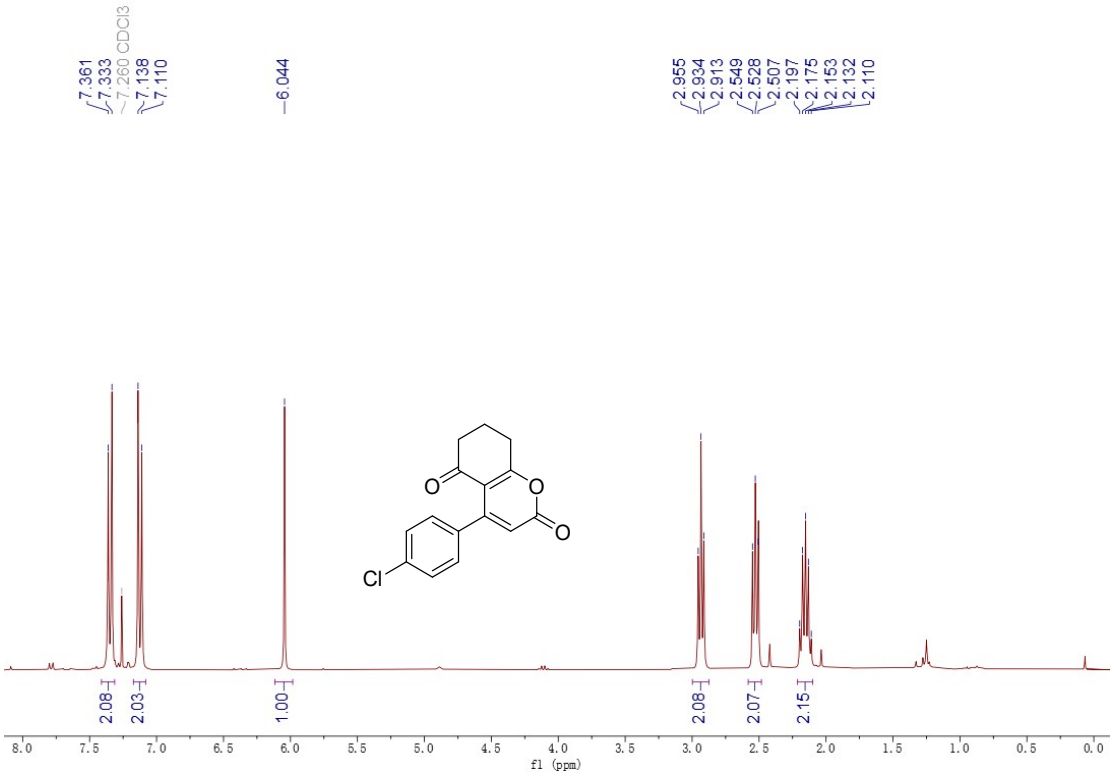


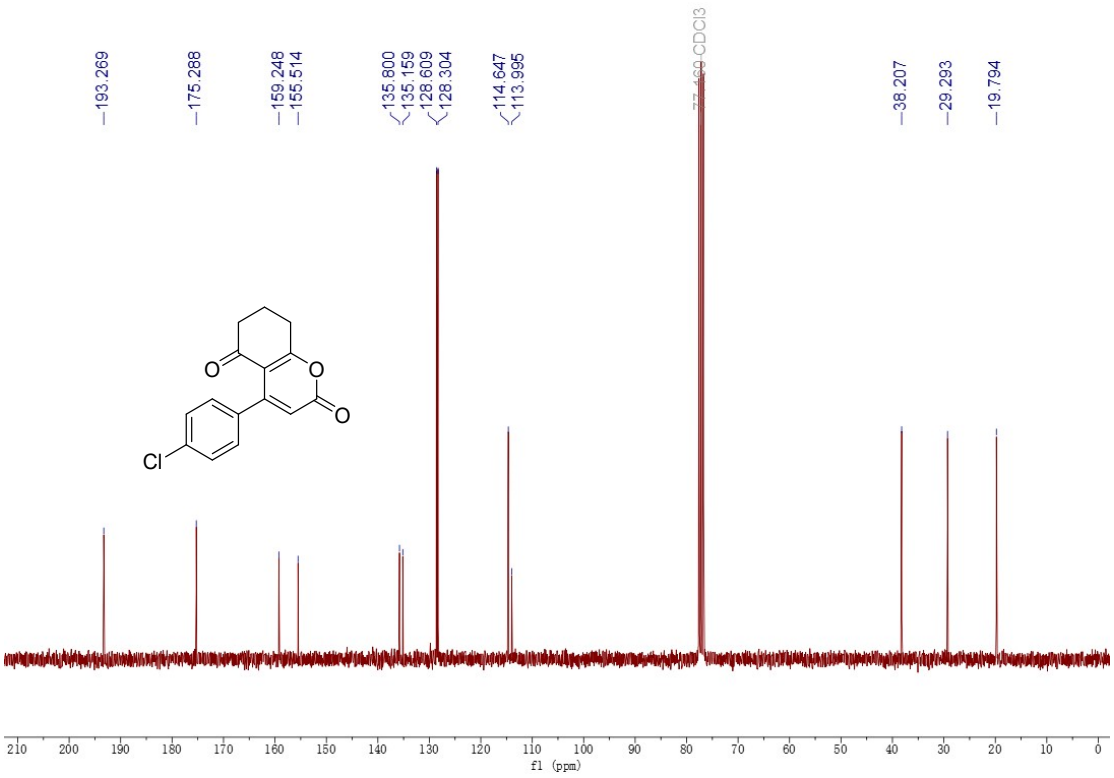
4-(4-methoxyphenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3c)



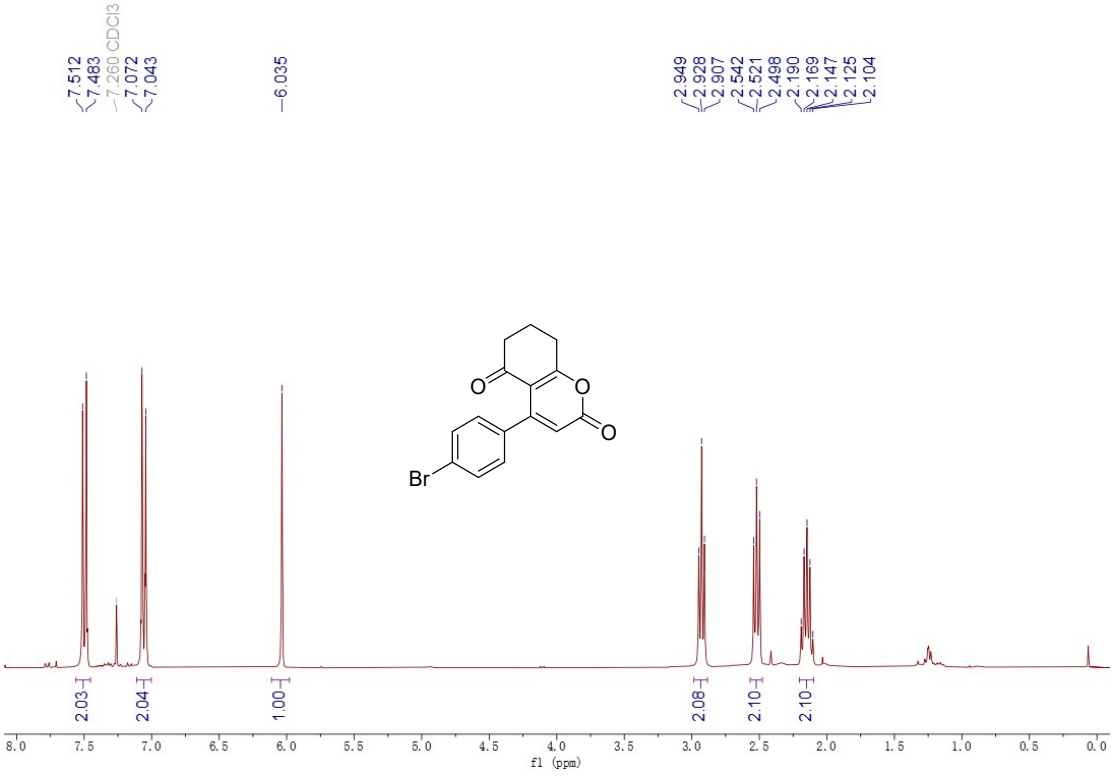


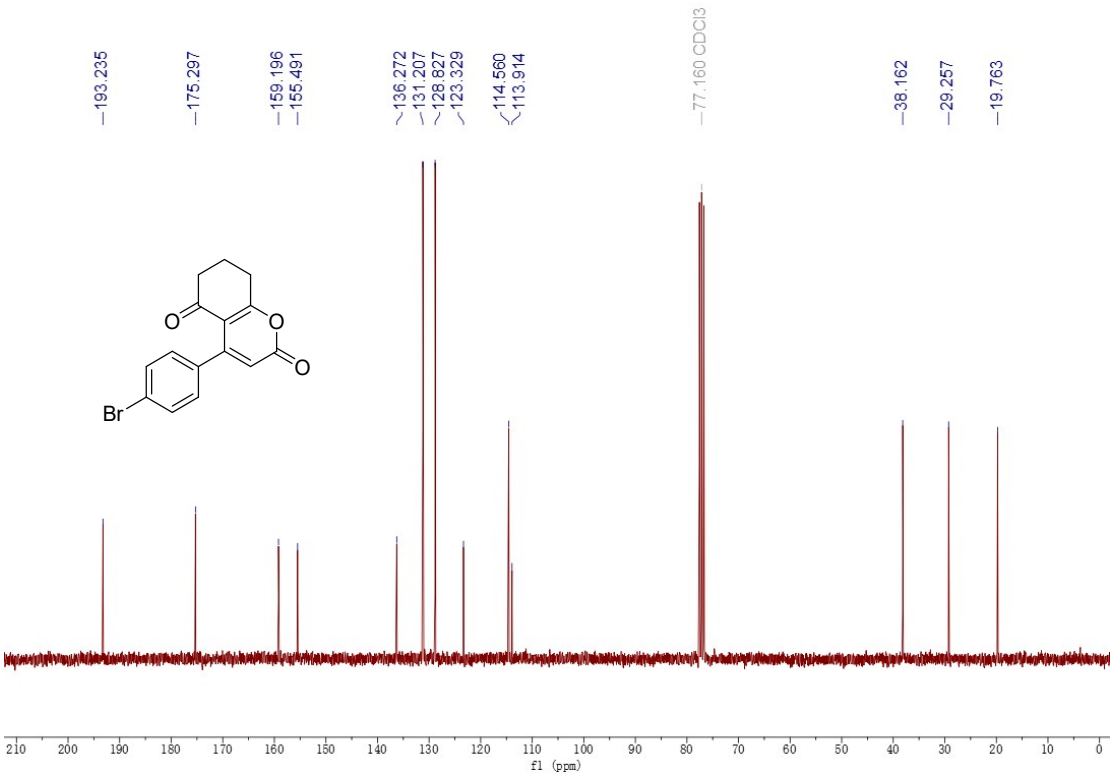
4-(4-chlorophenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3d)



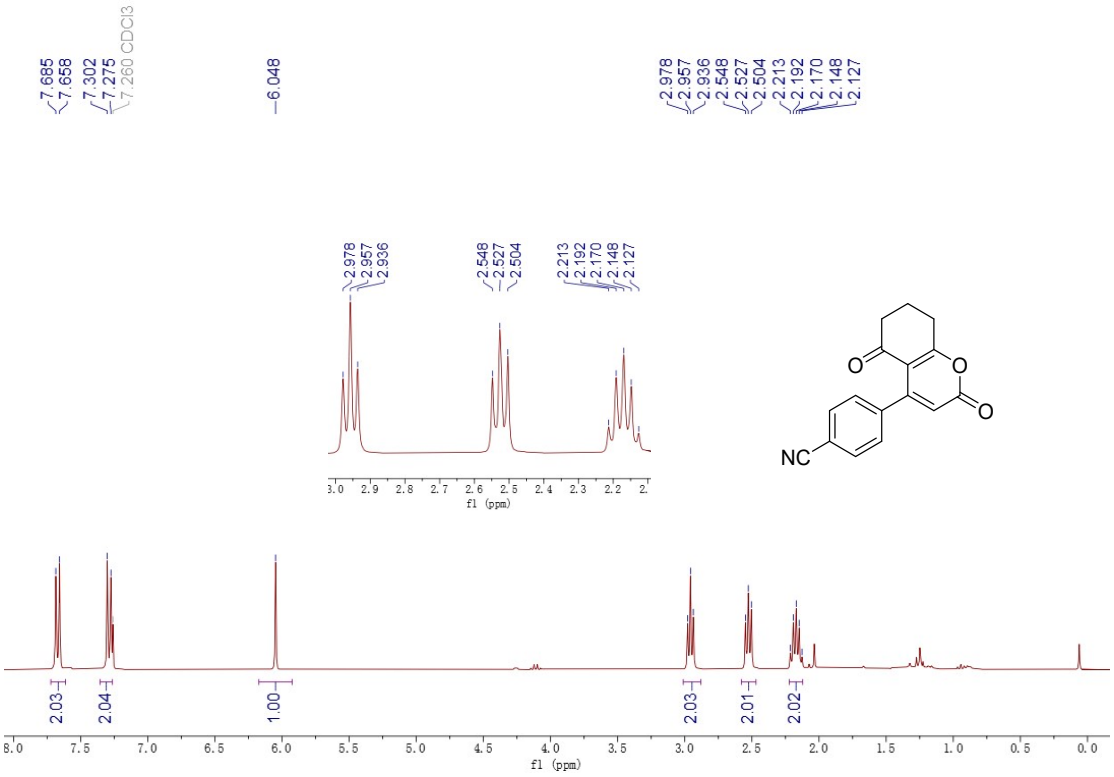


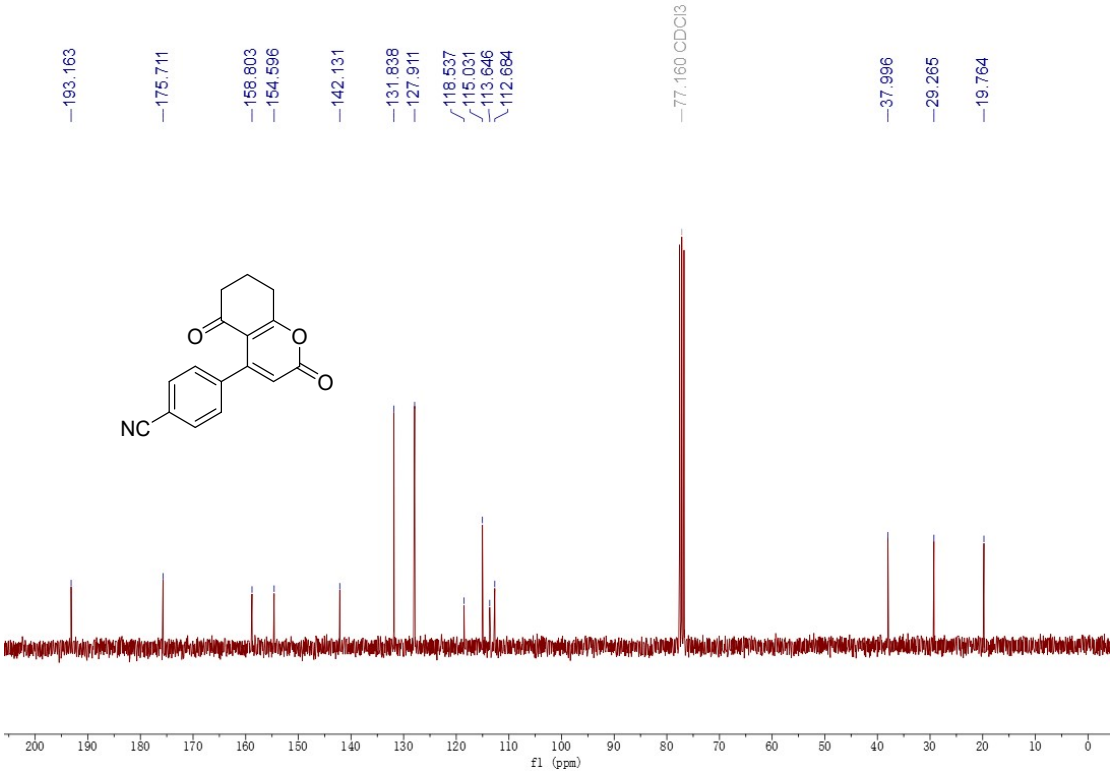
4-(4-bromophenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3e)



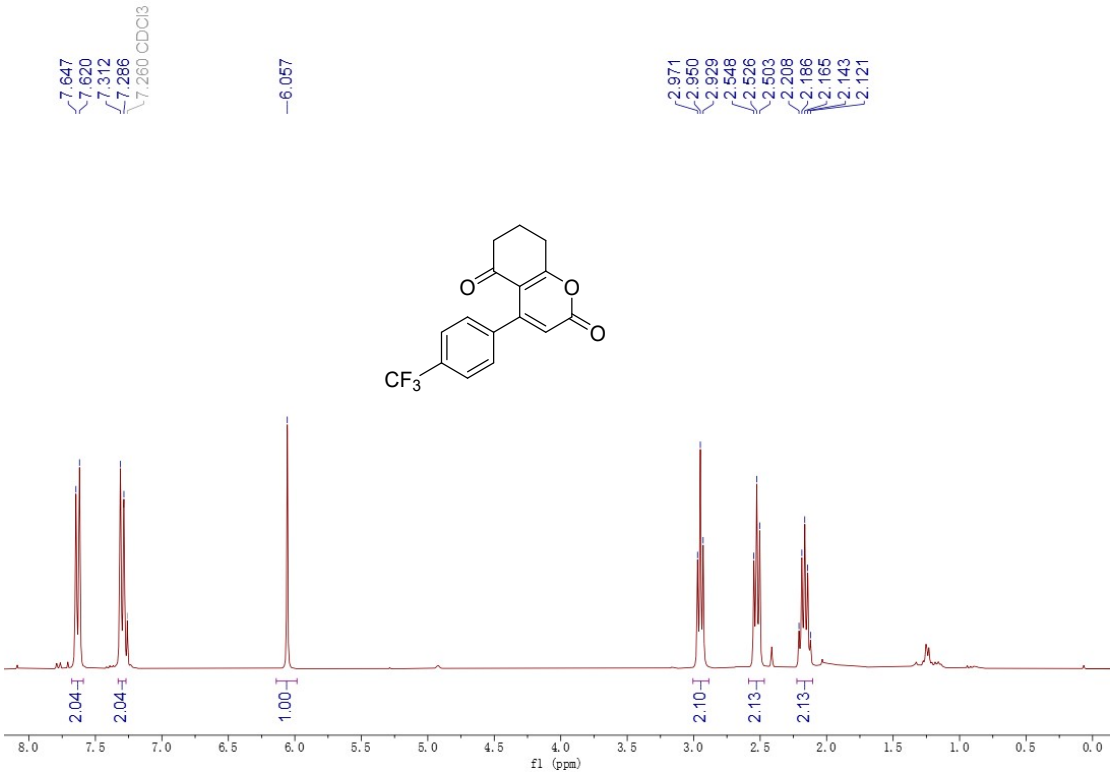


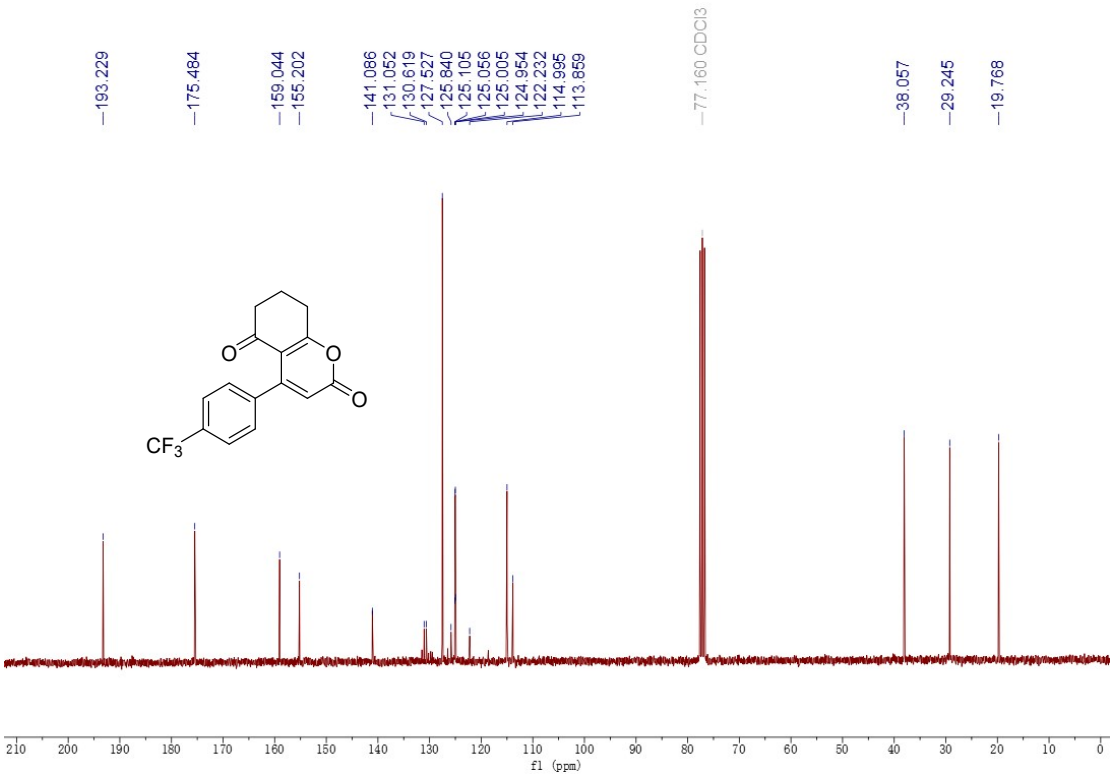
4-(2,5-dioxo-5,6,7,8-tetrahydro-2H-chromen-4-yl)benzonitrile (3f)



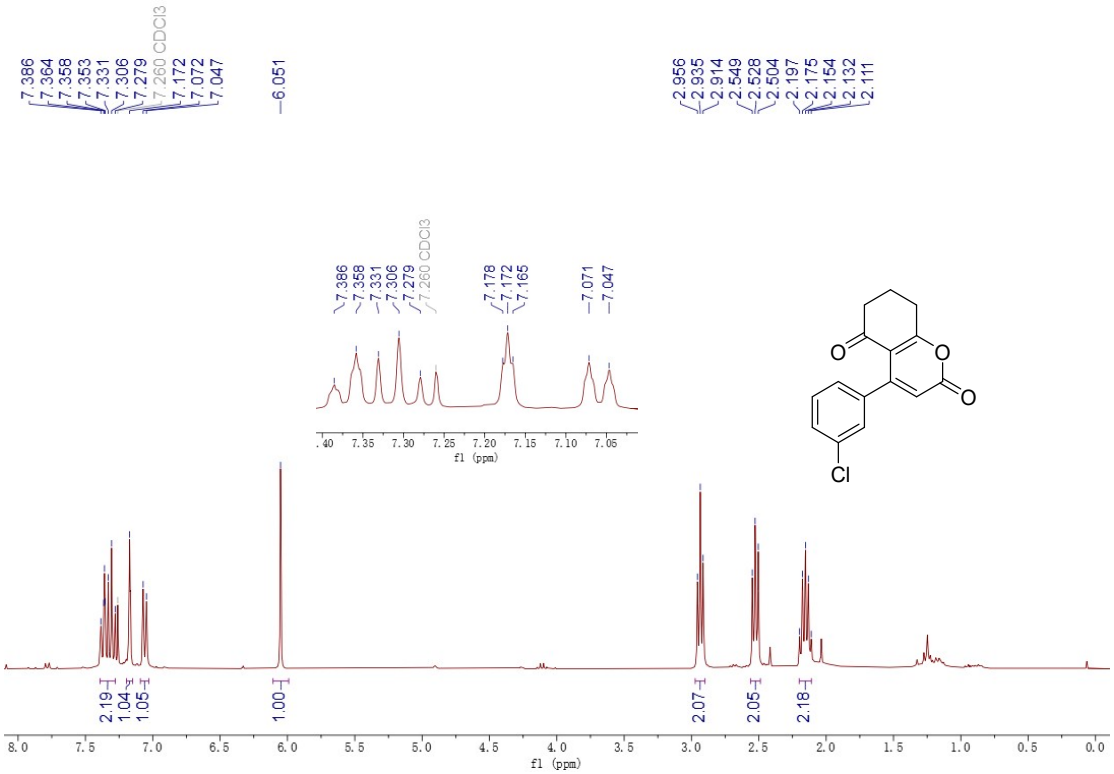


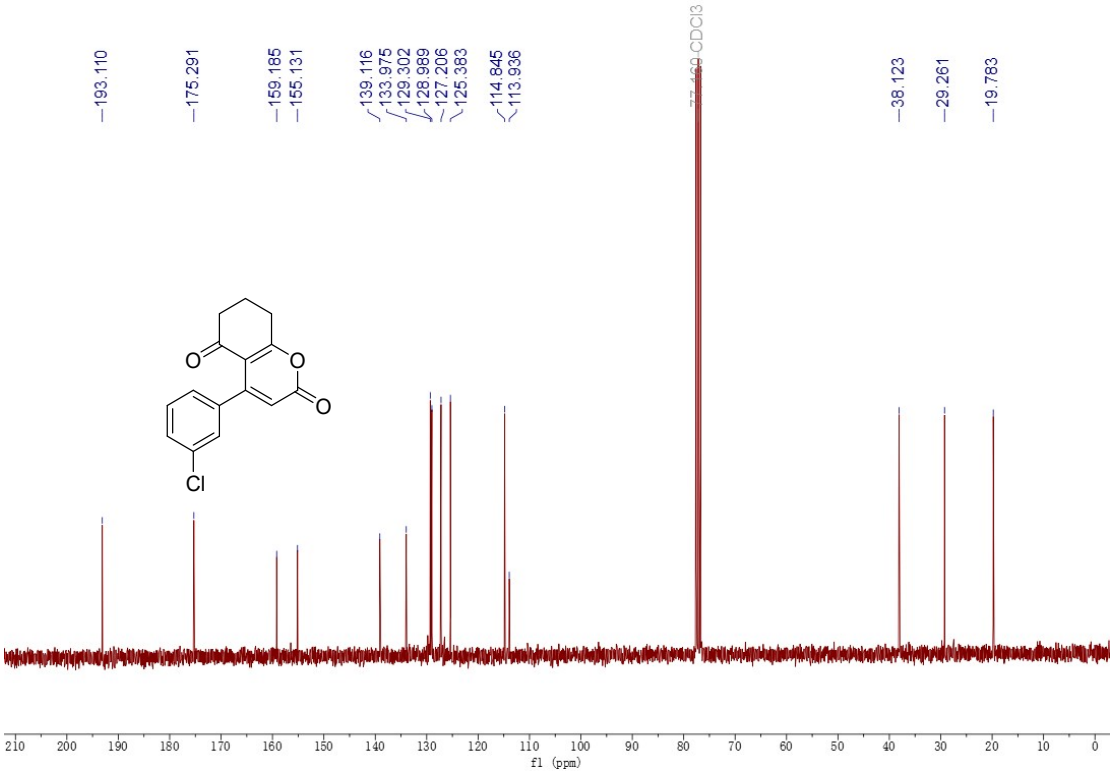
4-(4-(trifluoromethyl)phenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3g)



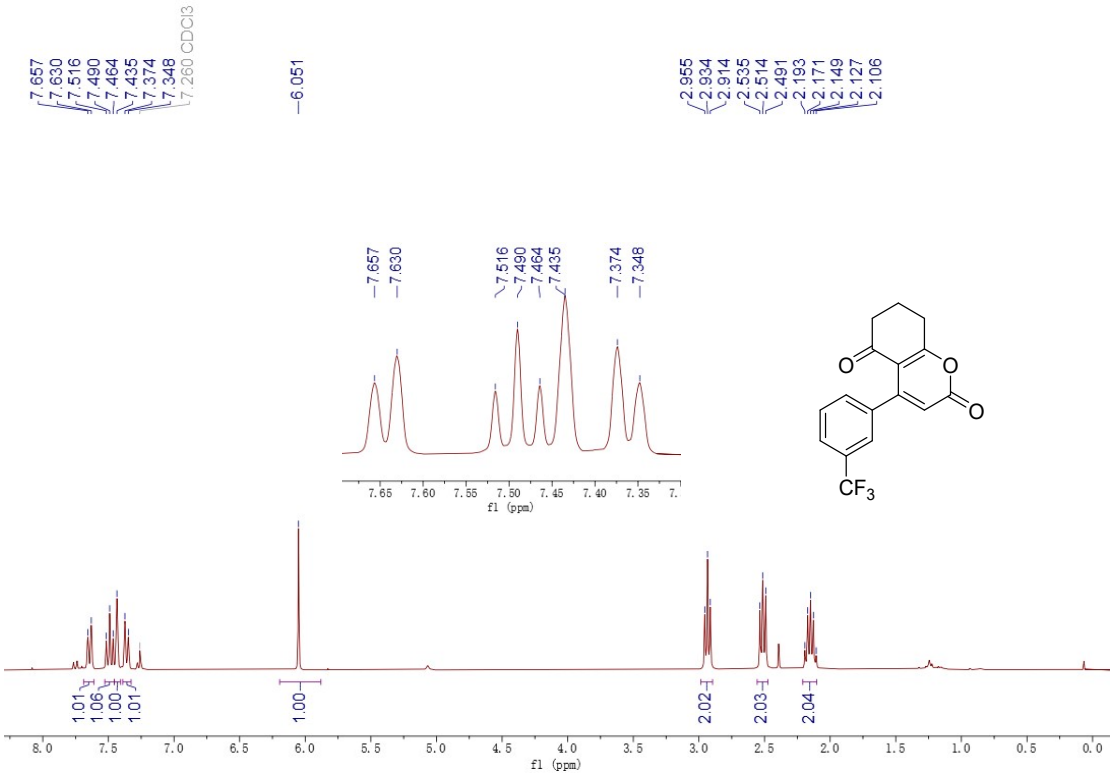


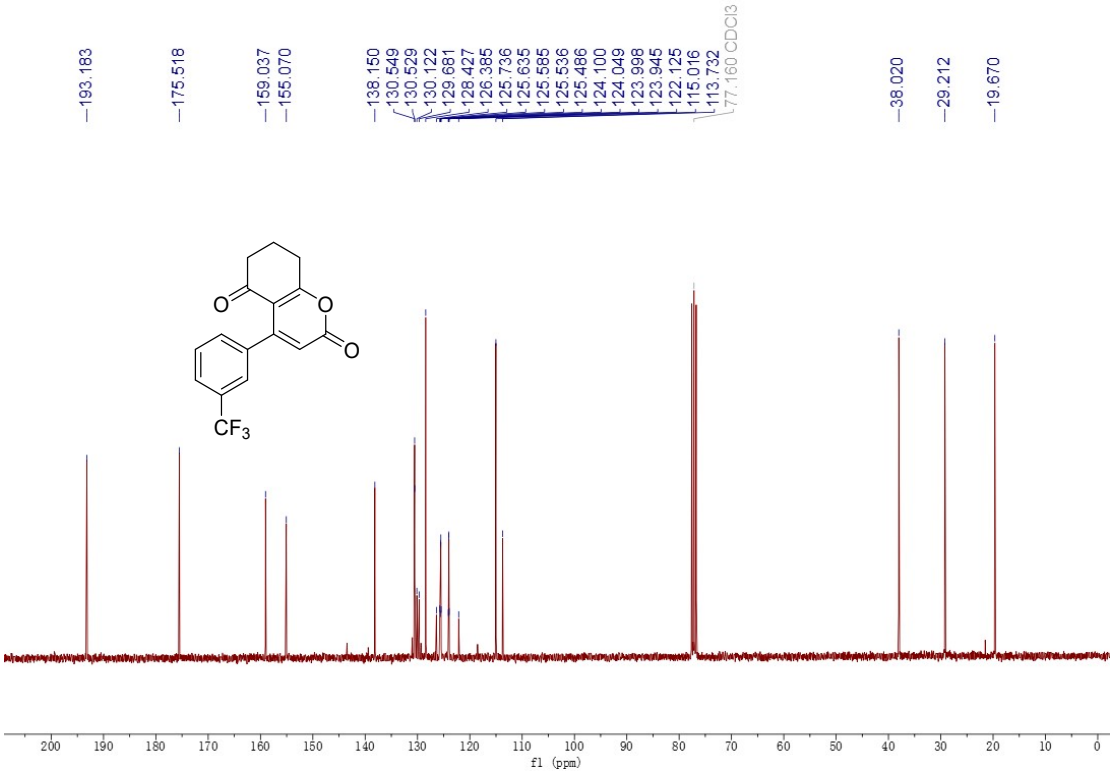
4-(3-chlorophenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3h)



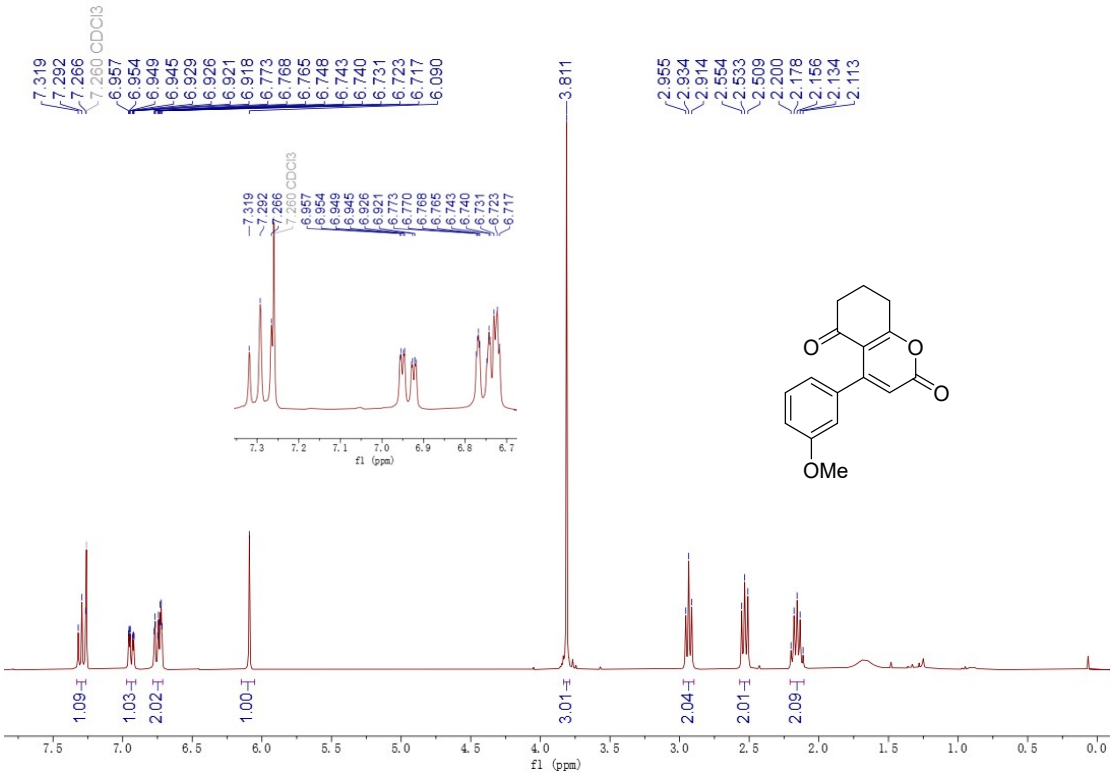


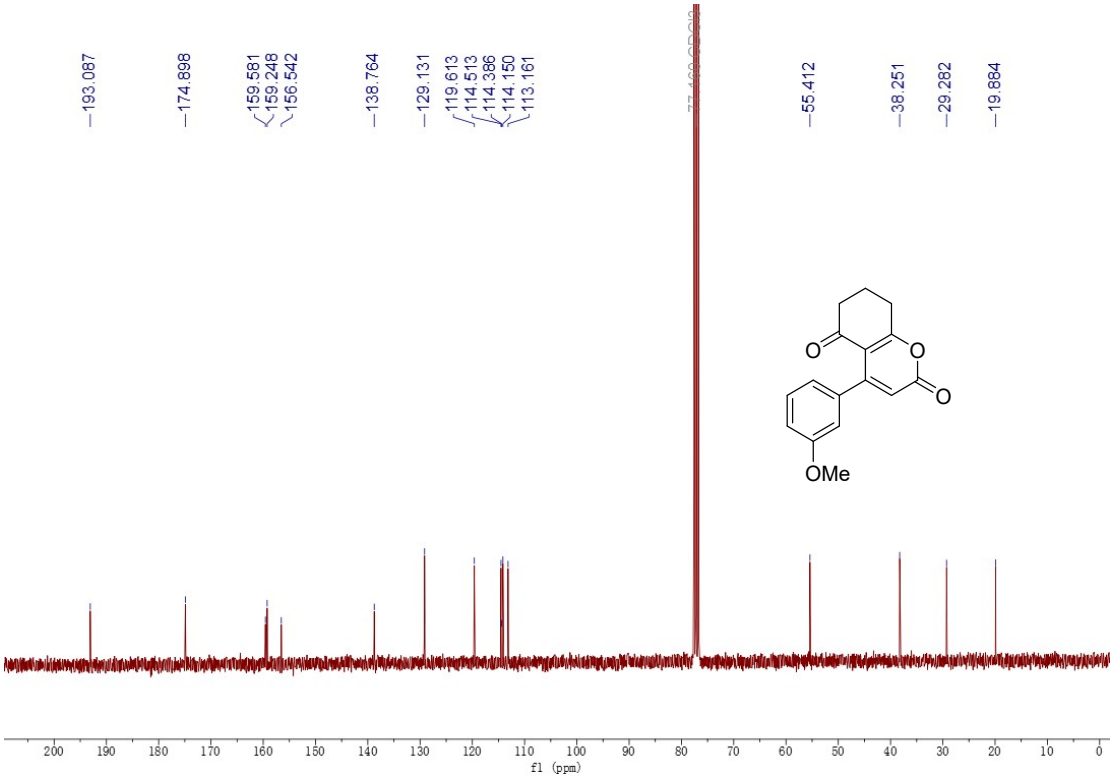
4-(3-(trifluoromethyl)phenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3i)



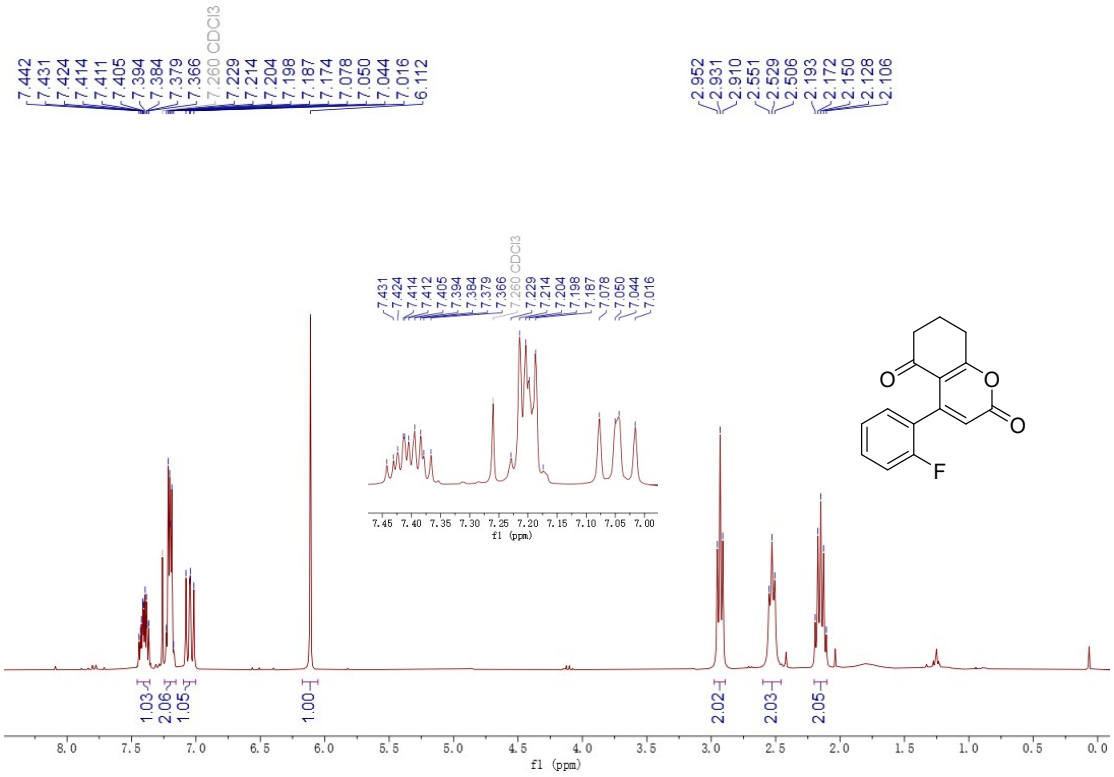


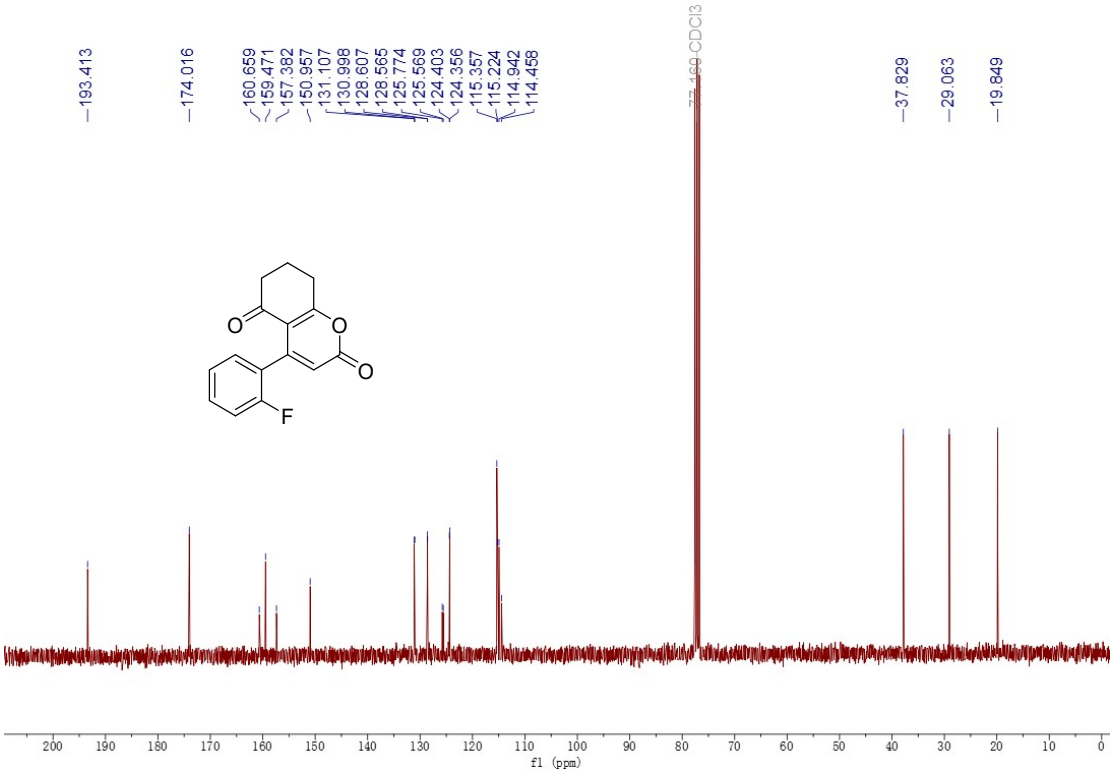
4-(3-methoxyphenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3j)



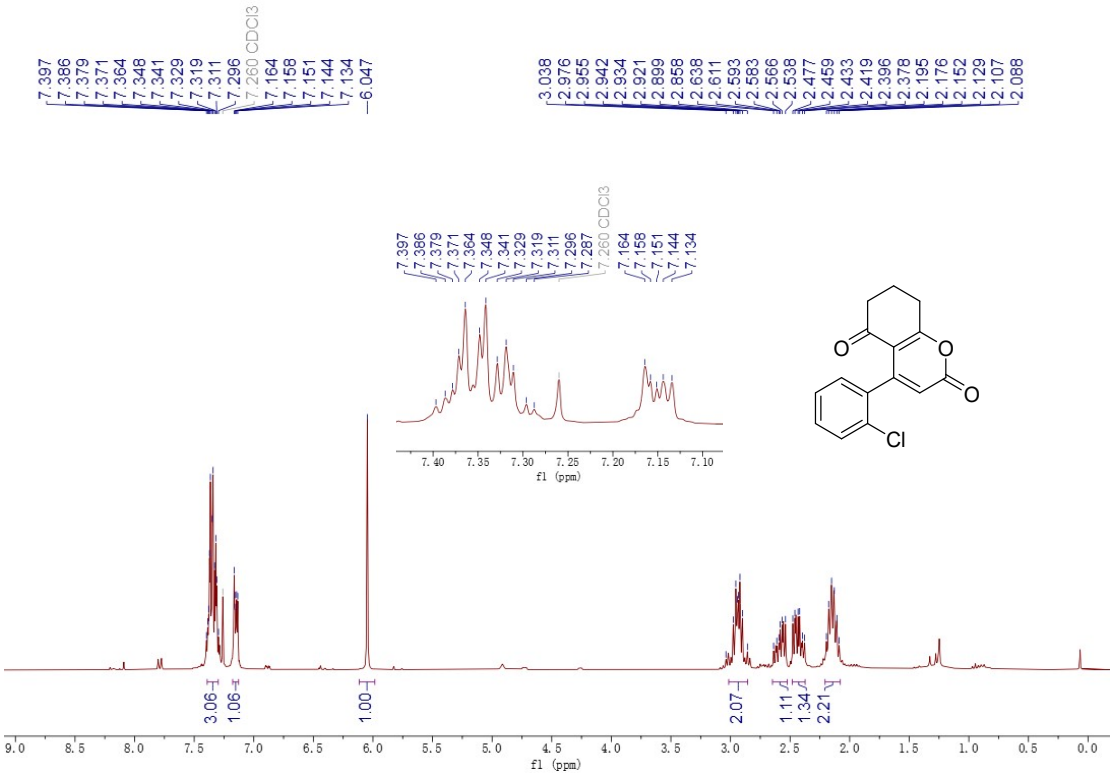


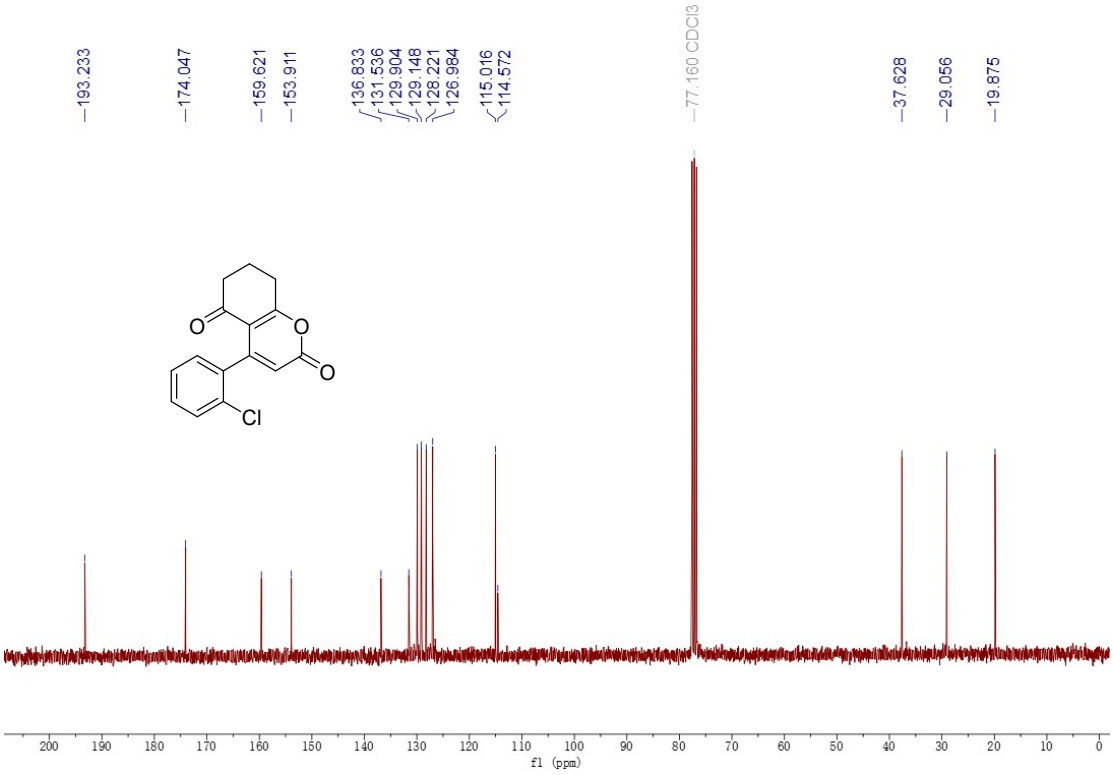
4-(2-fluorophenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3k)



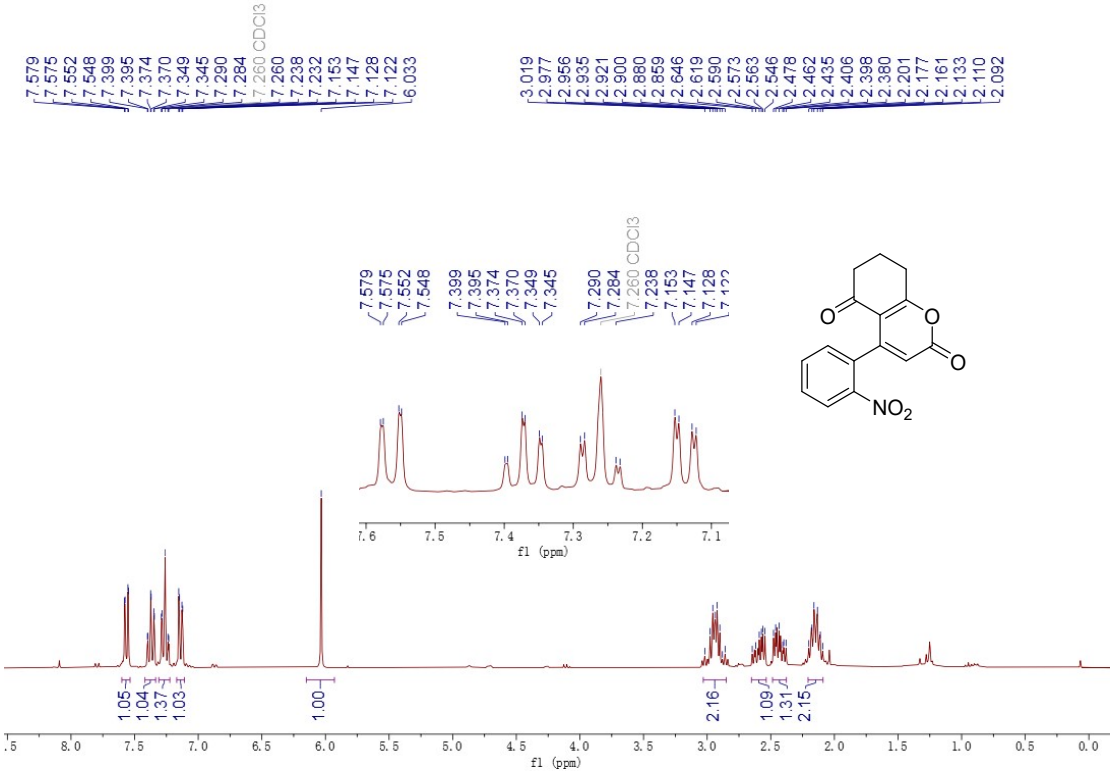


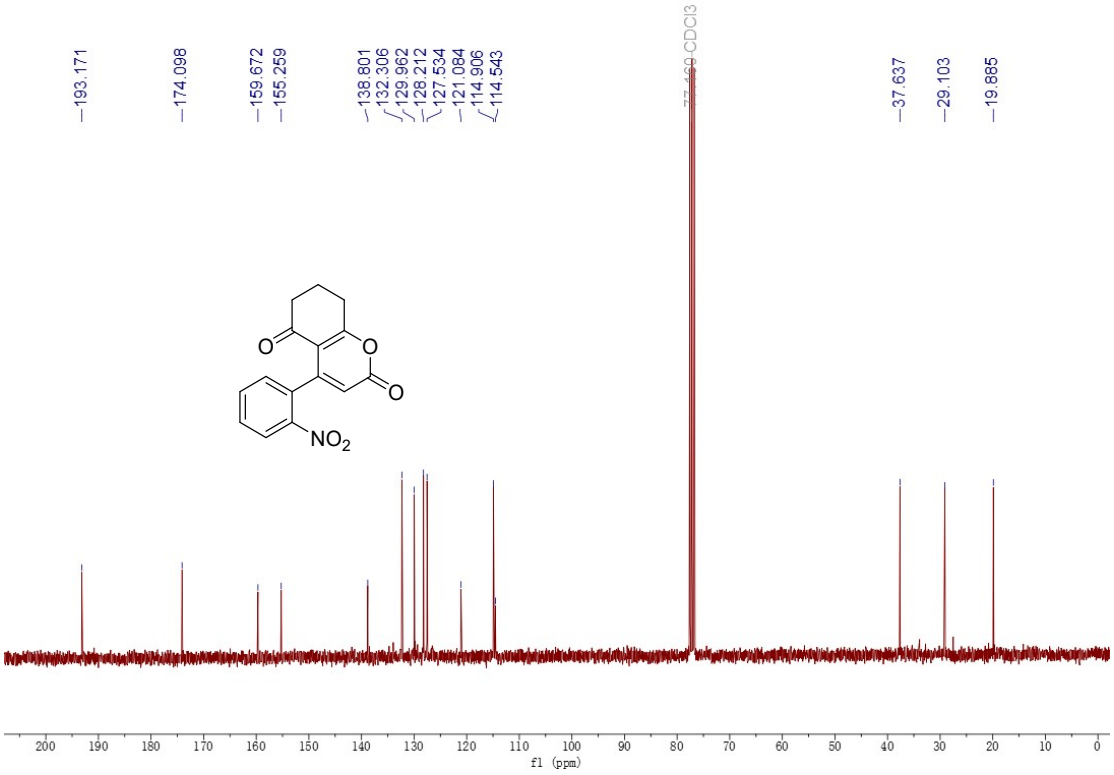
4-(2-chlorophenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3l)



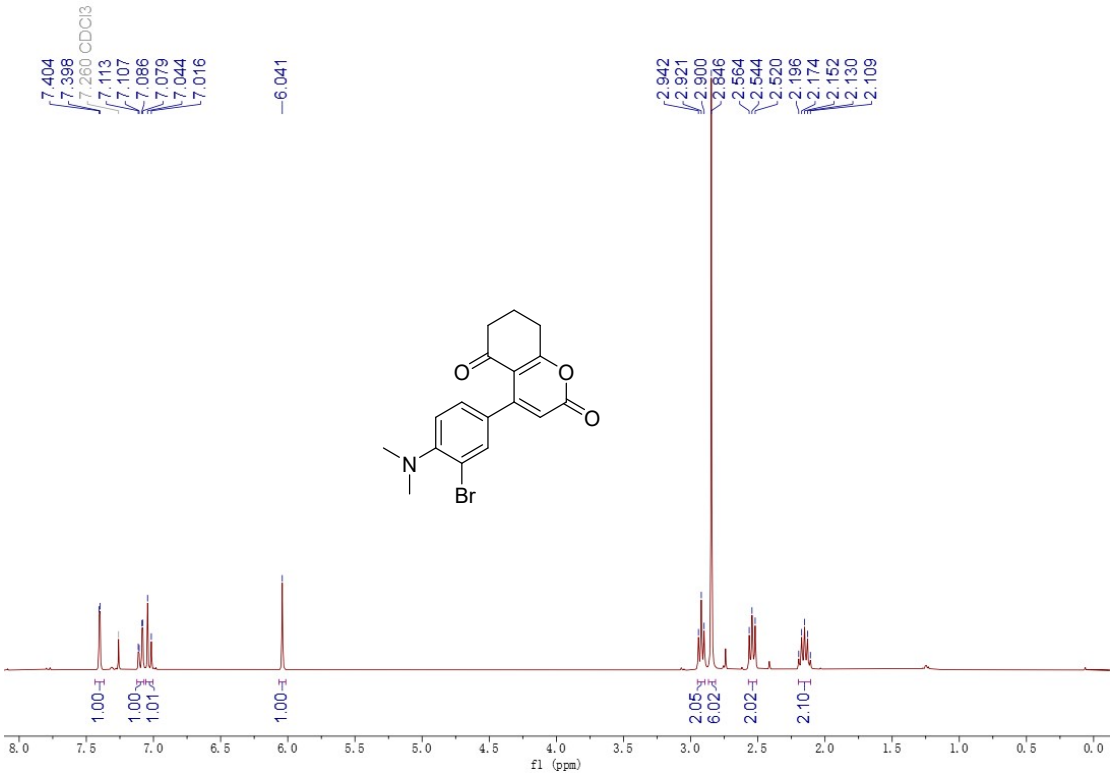


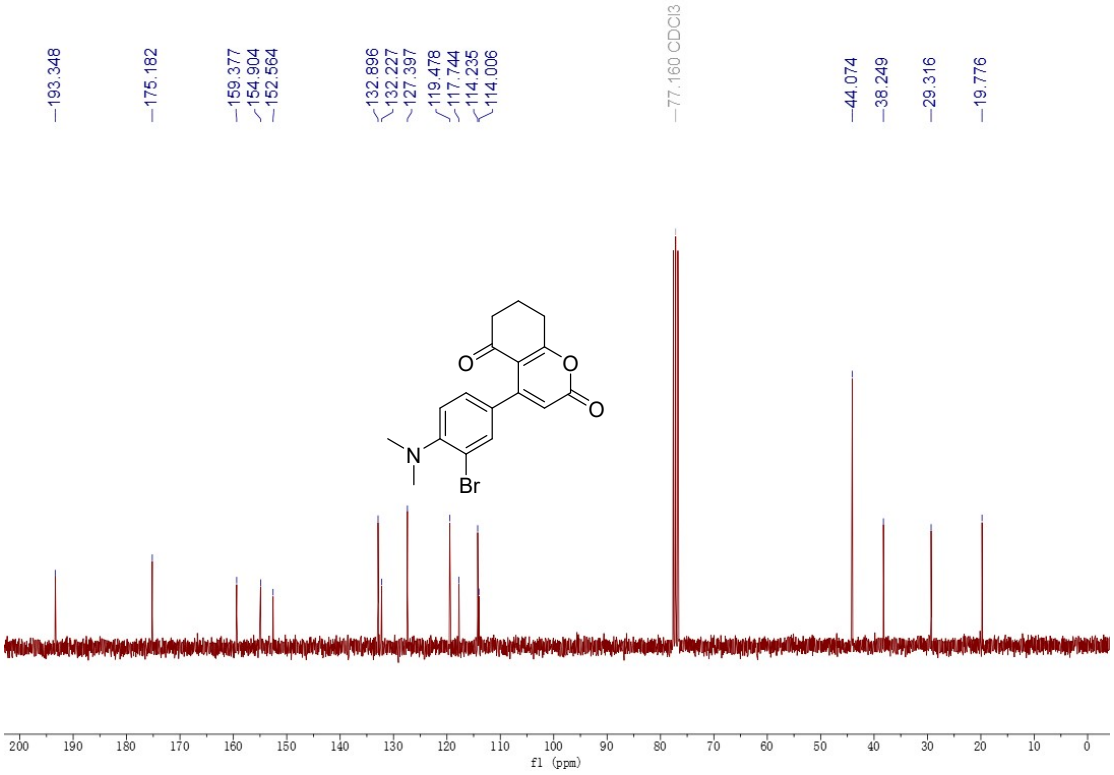
4-(2-nitrophenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3m)





4-(3-bromo-4-(dimethylamino)phenyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3n)





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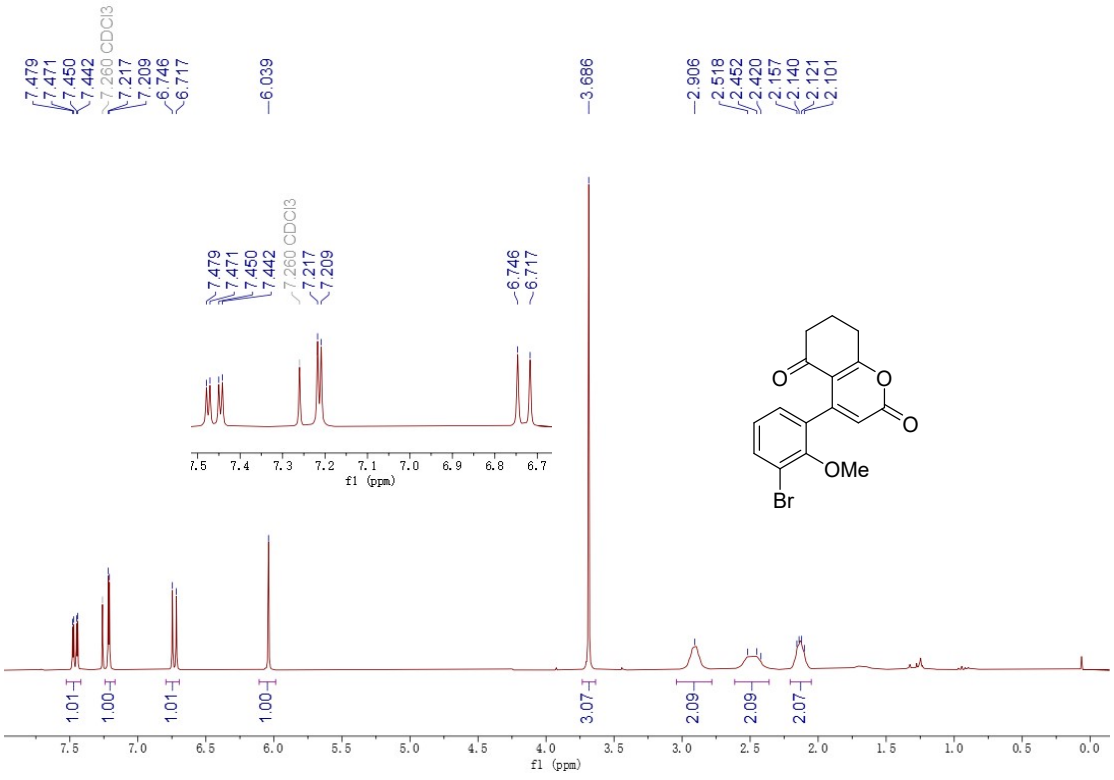
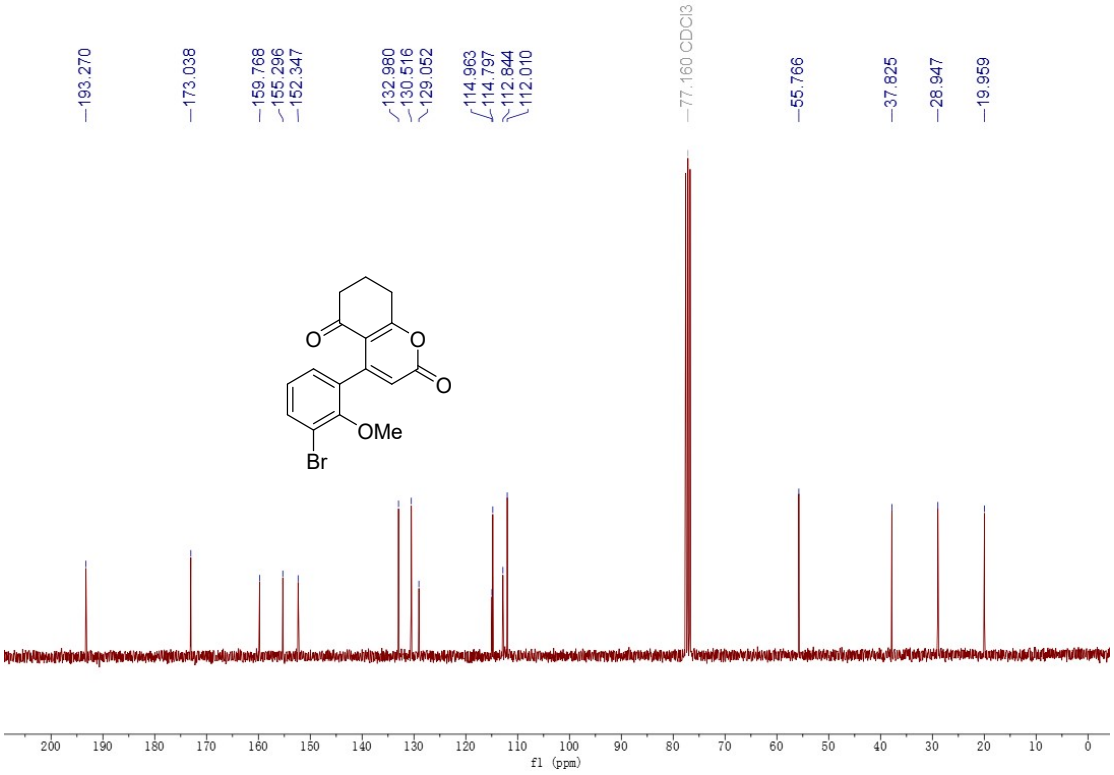
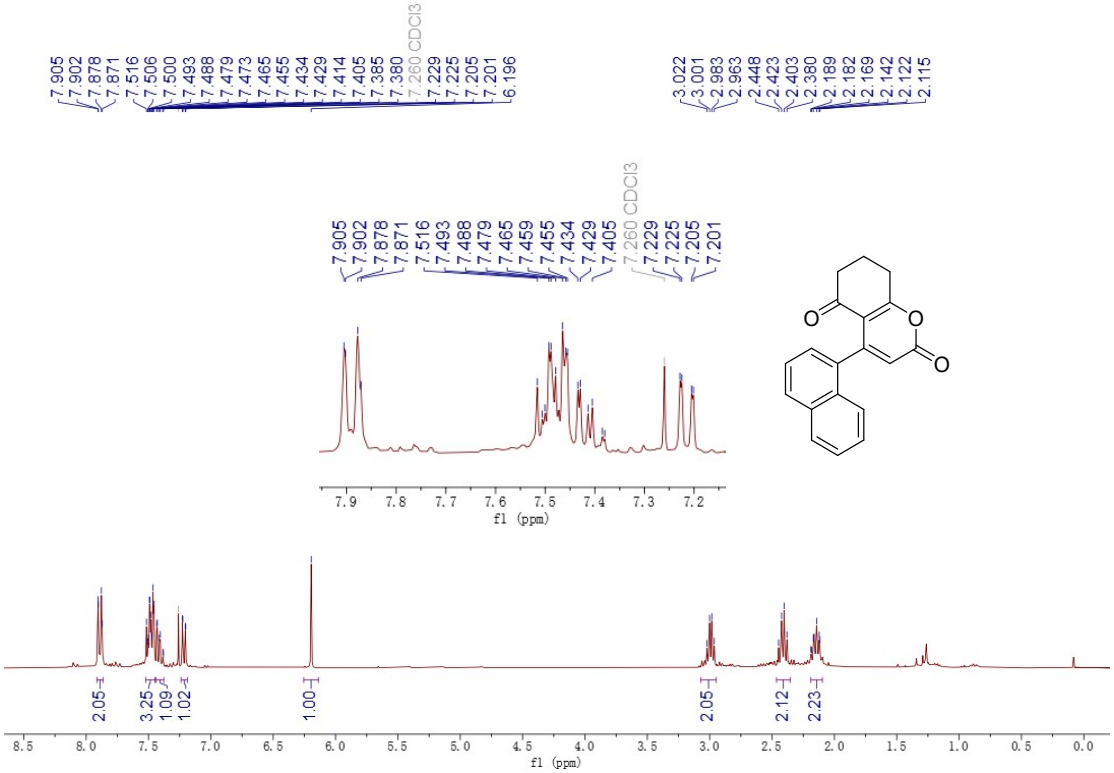
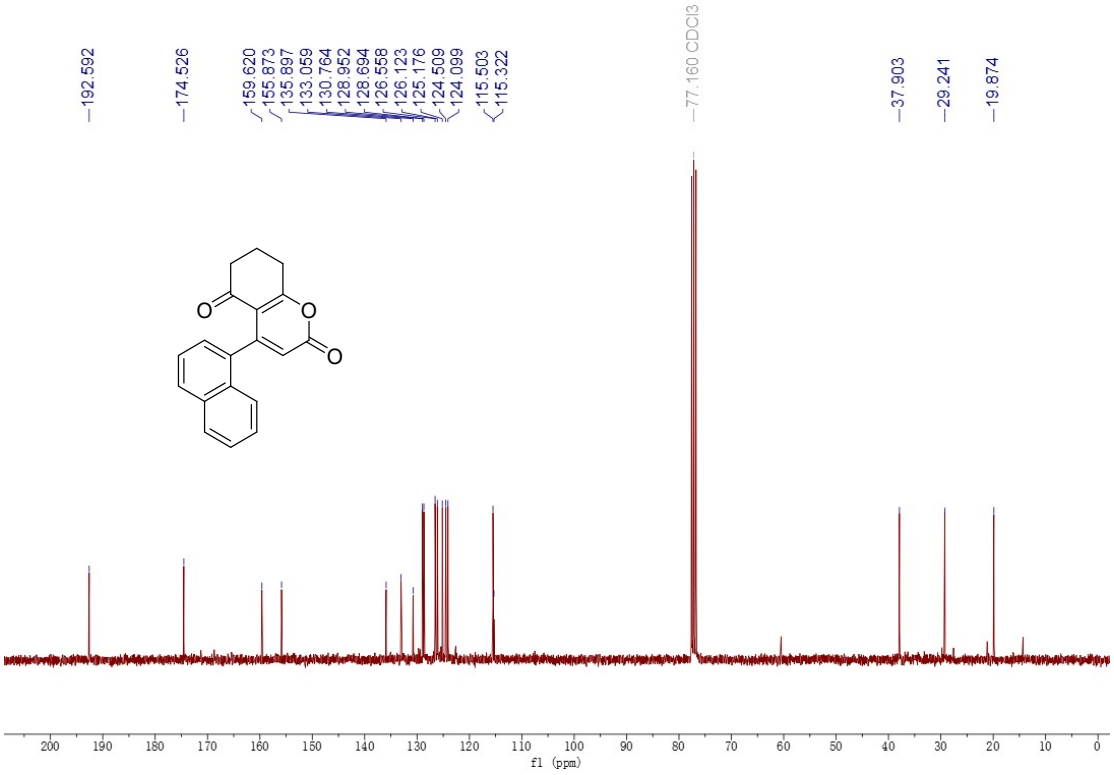


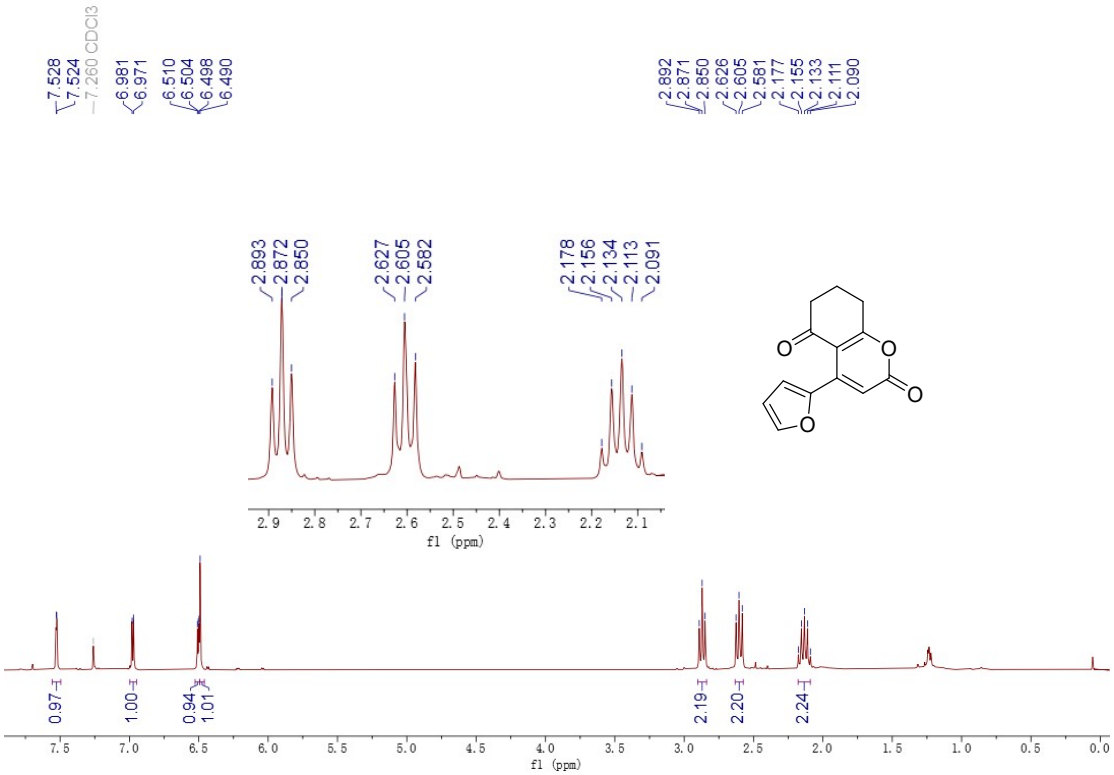


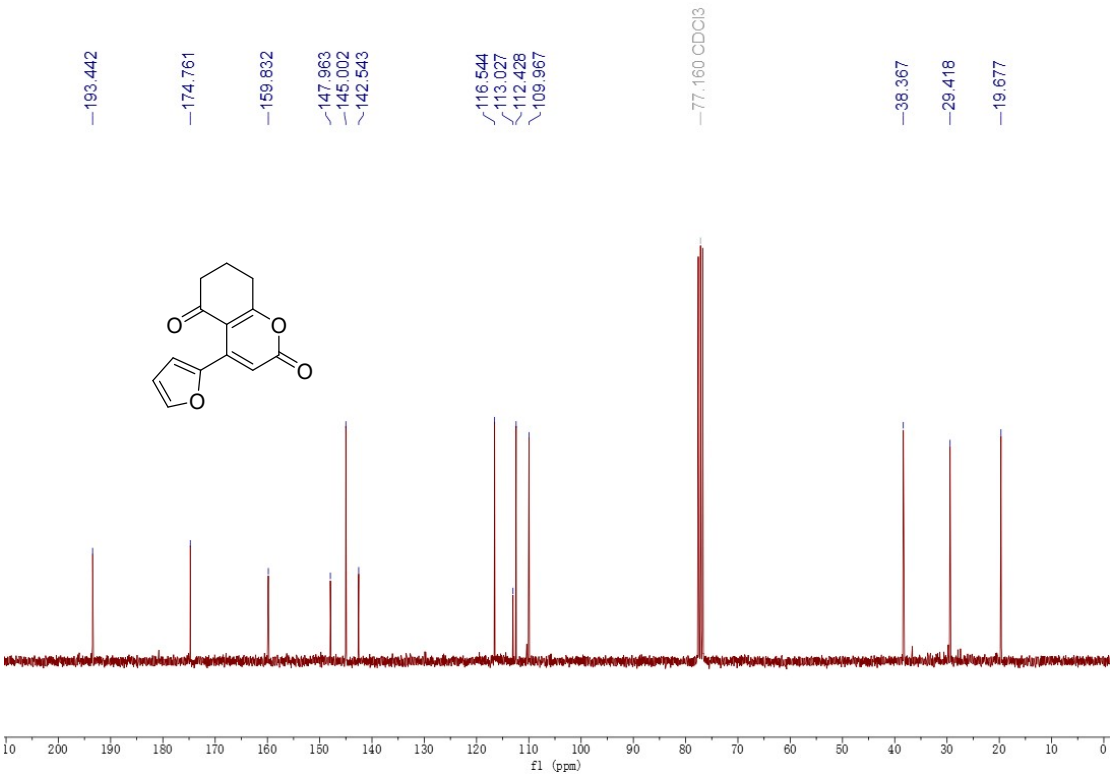
4-(naphthalen-1-yl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3p)



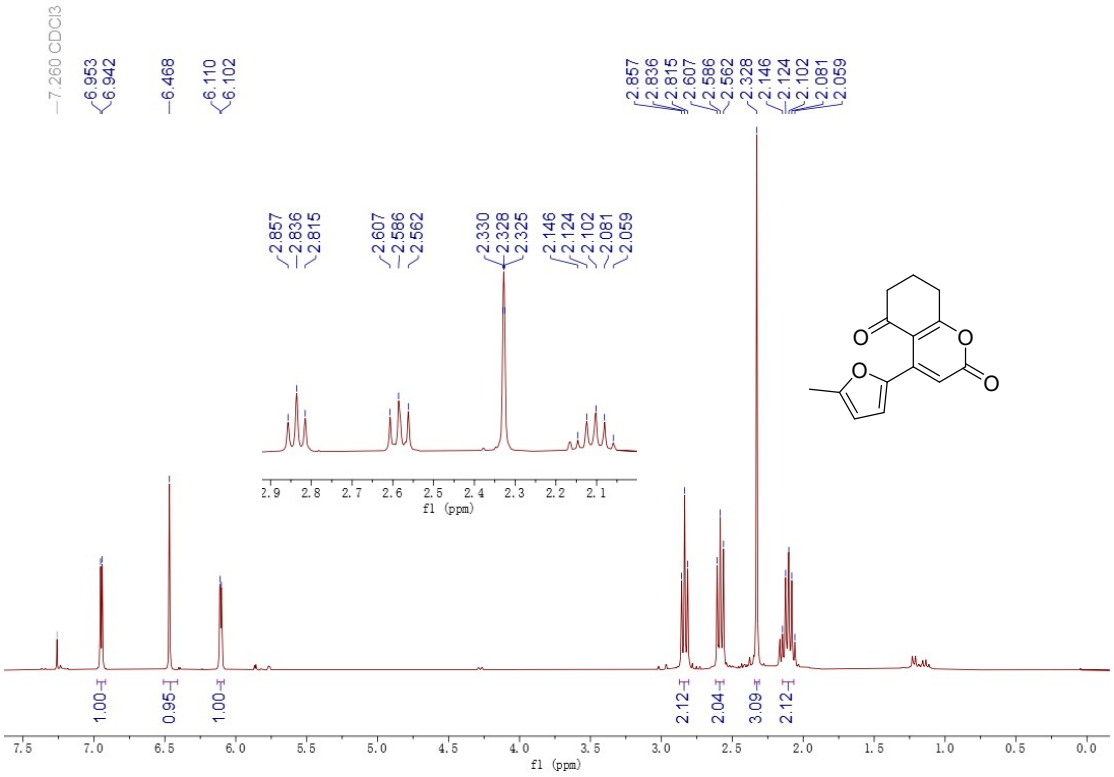


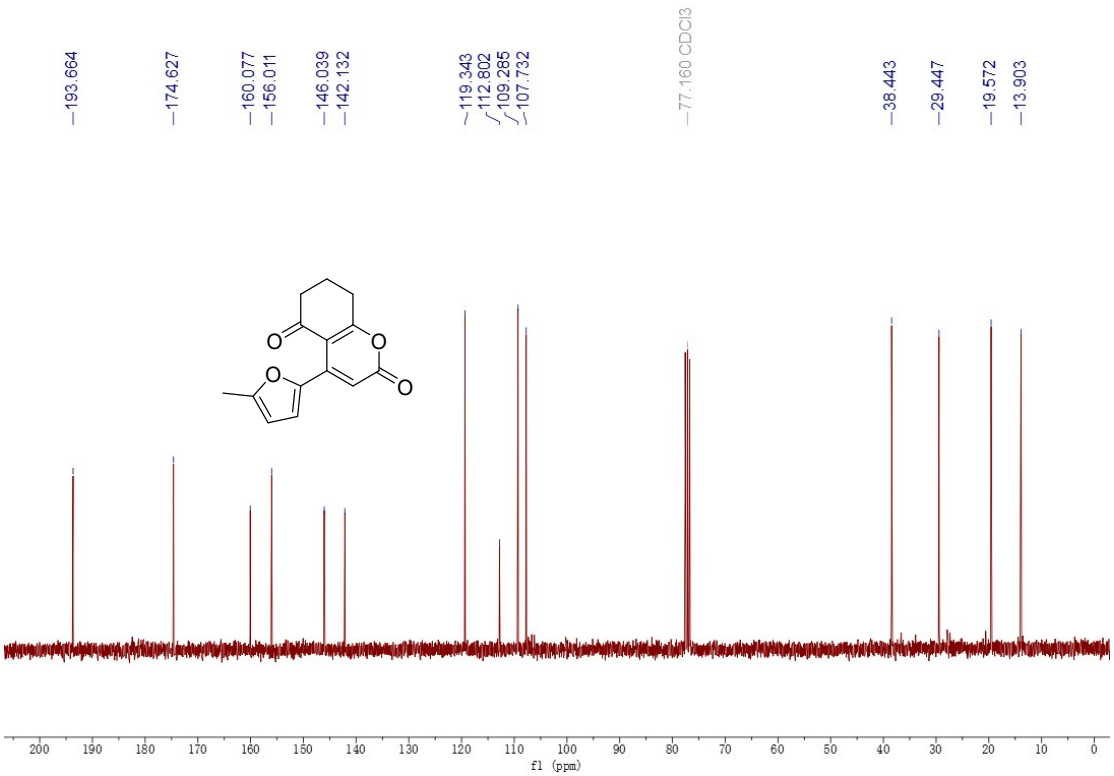
4-(furan-2-yl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3q)



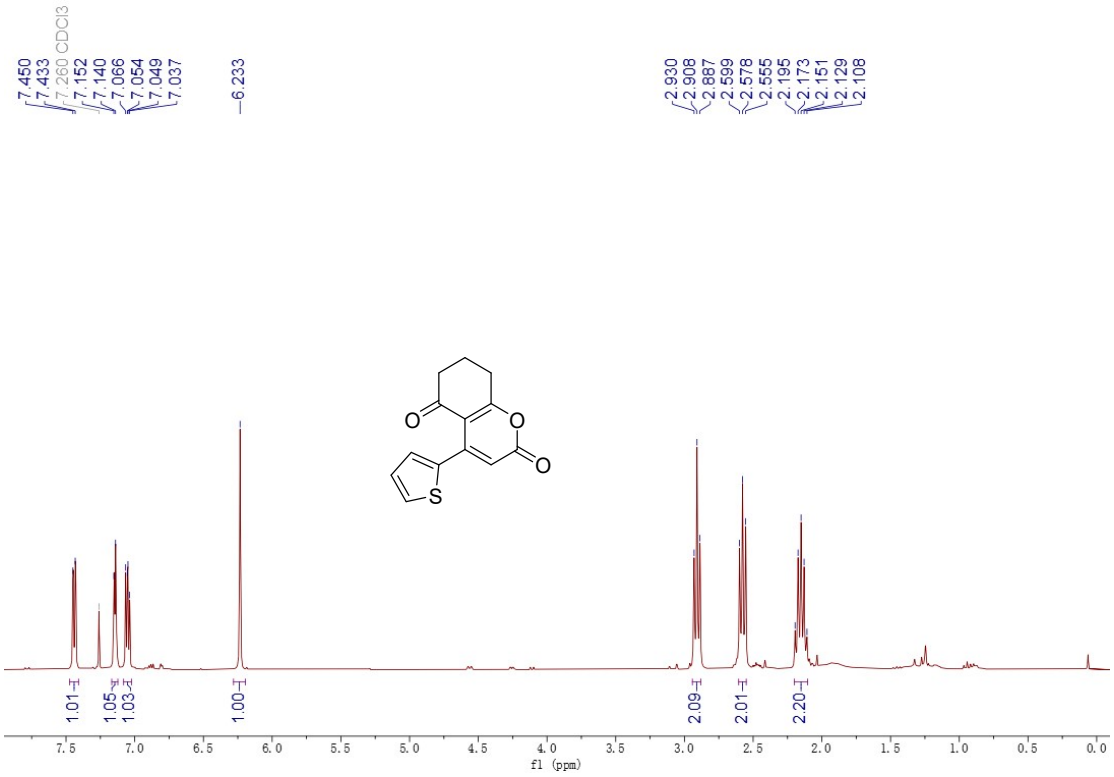


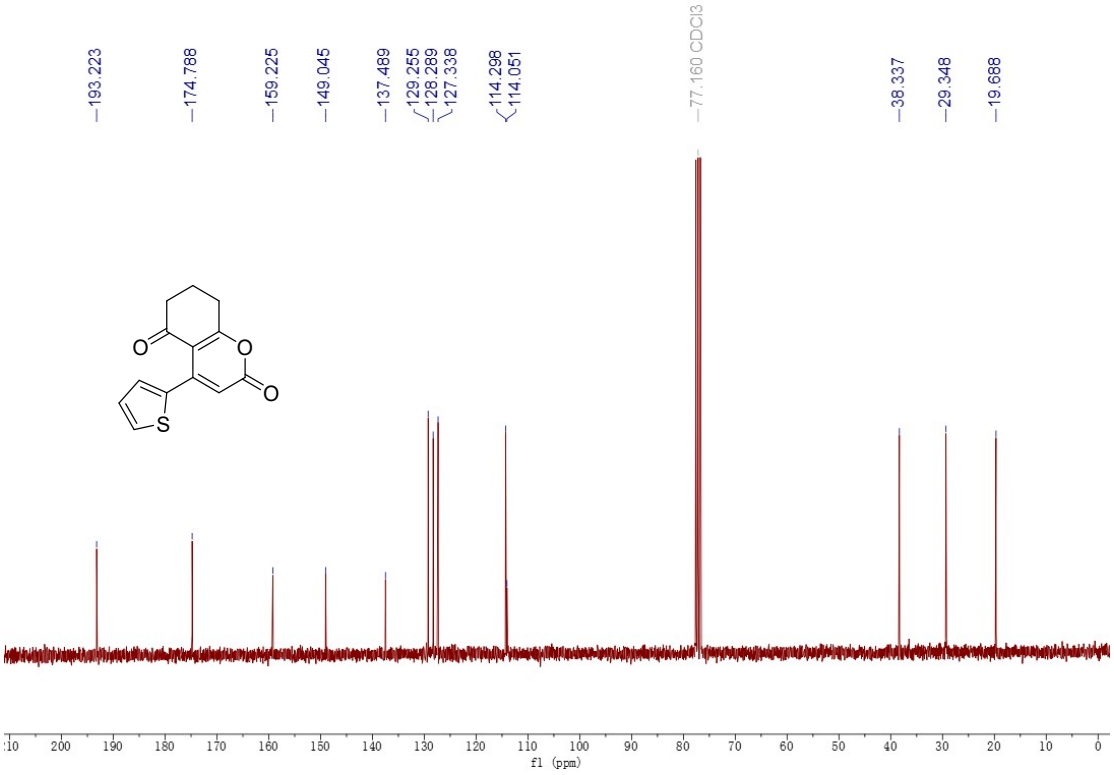
4-(5-methylfuran-2-yl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3r)



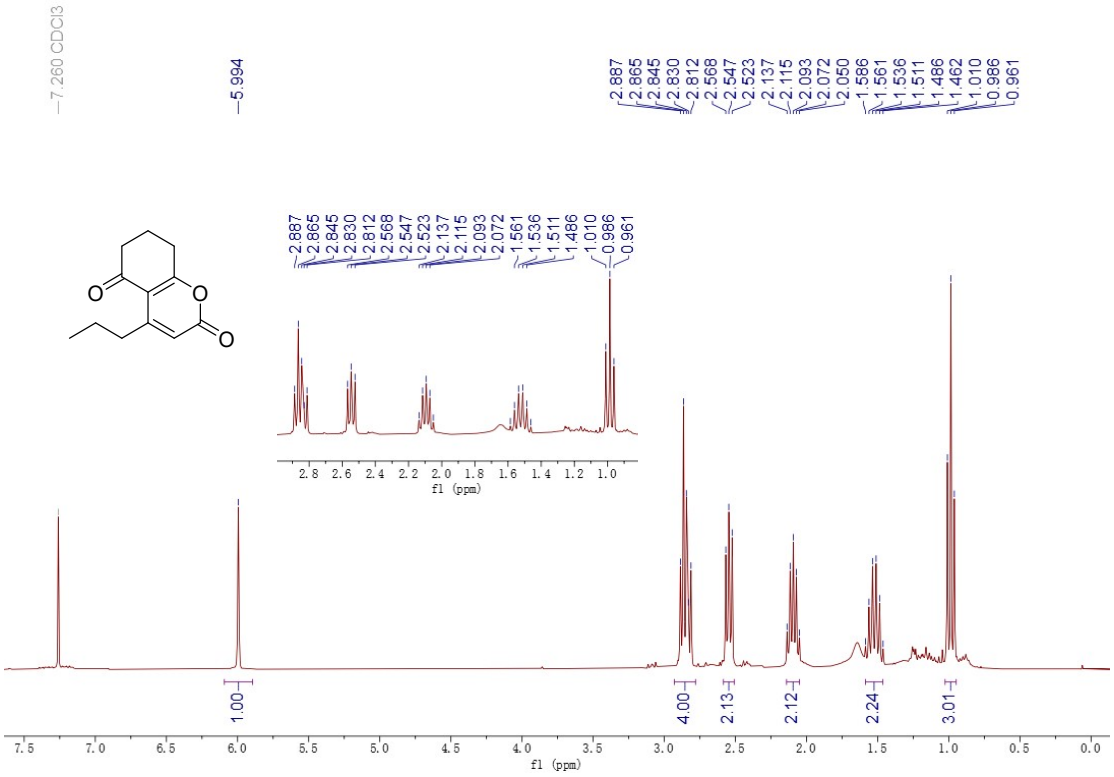


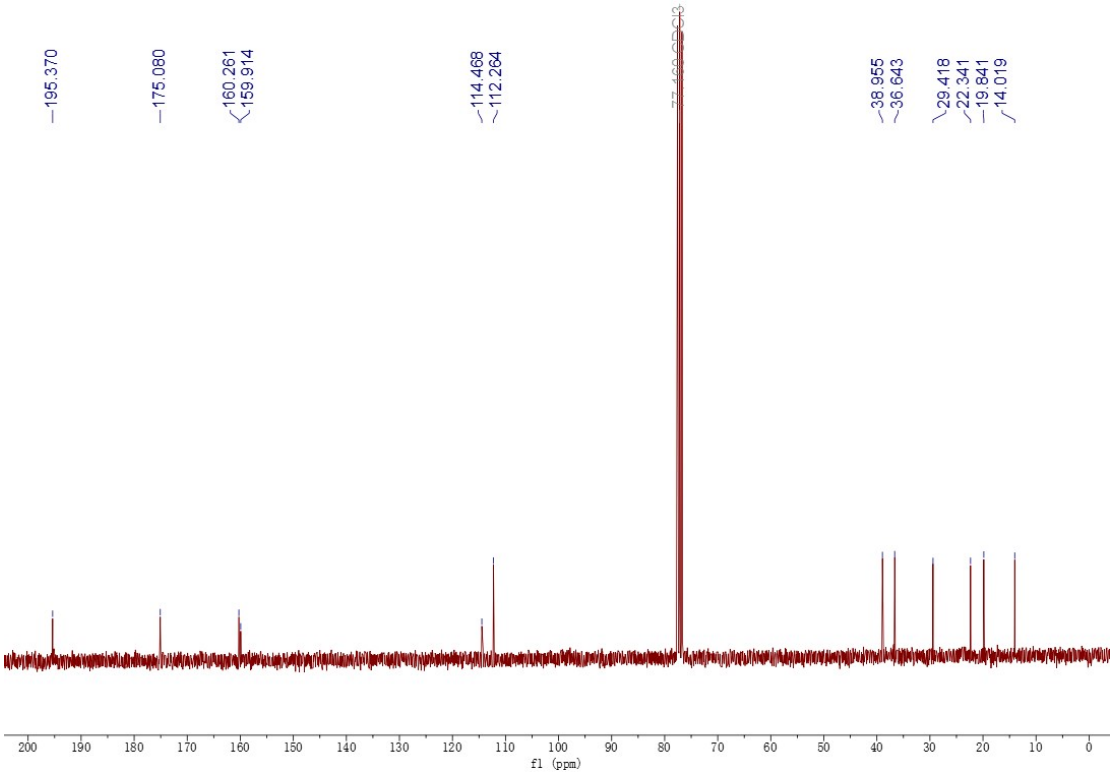
4-(thiophen-2-yl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3s)



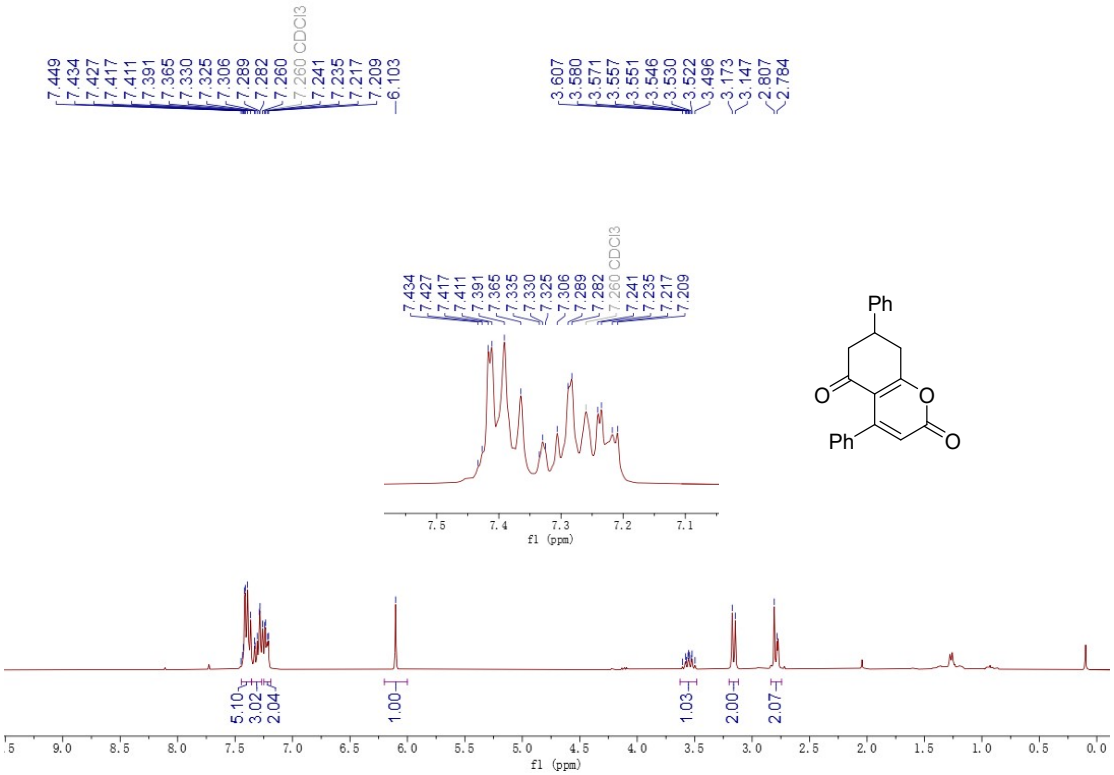


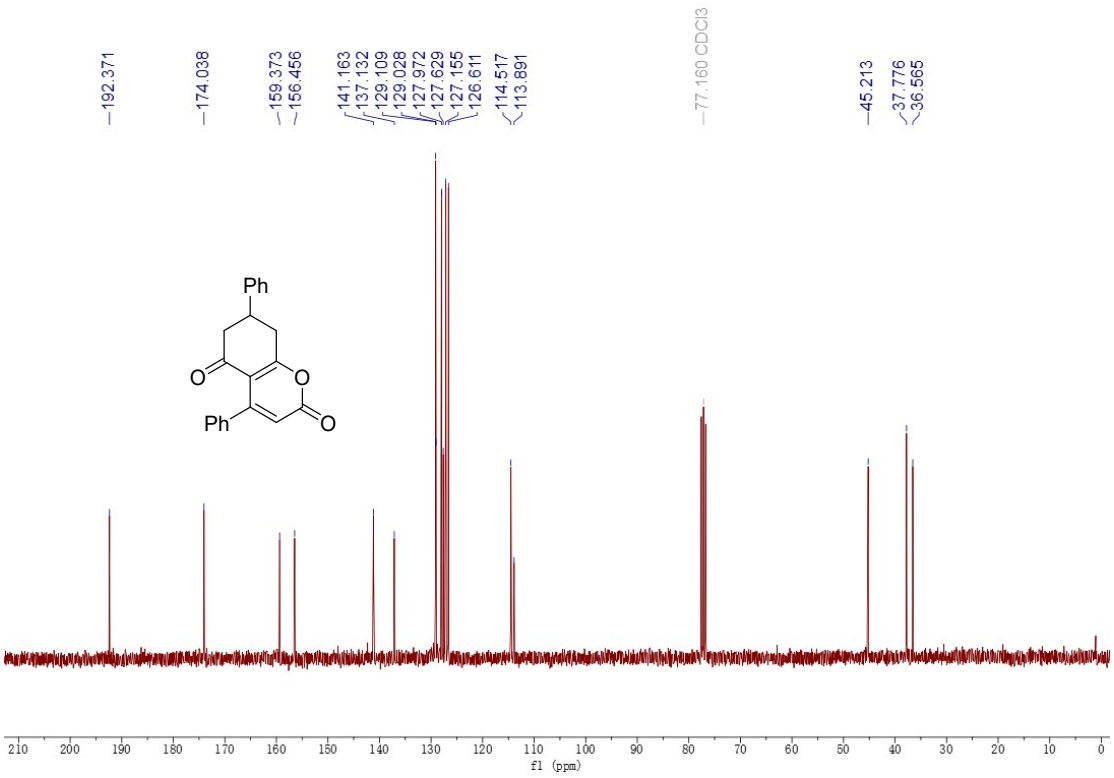
4-propyl-7,8-dihydro-2H-chromene-2,5(6H)-dione (3t)



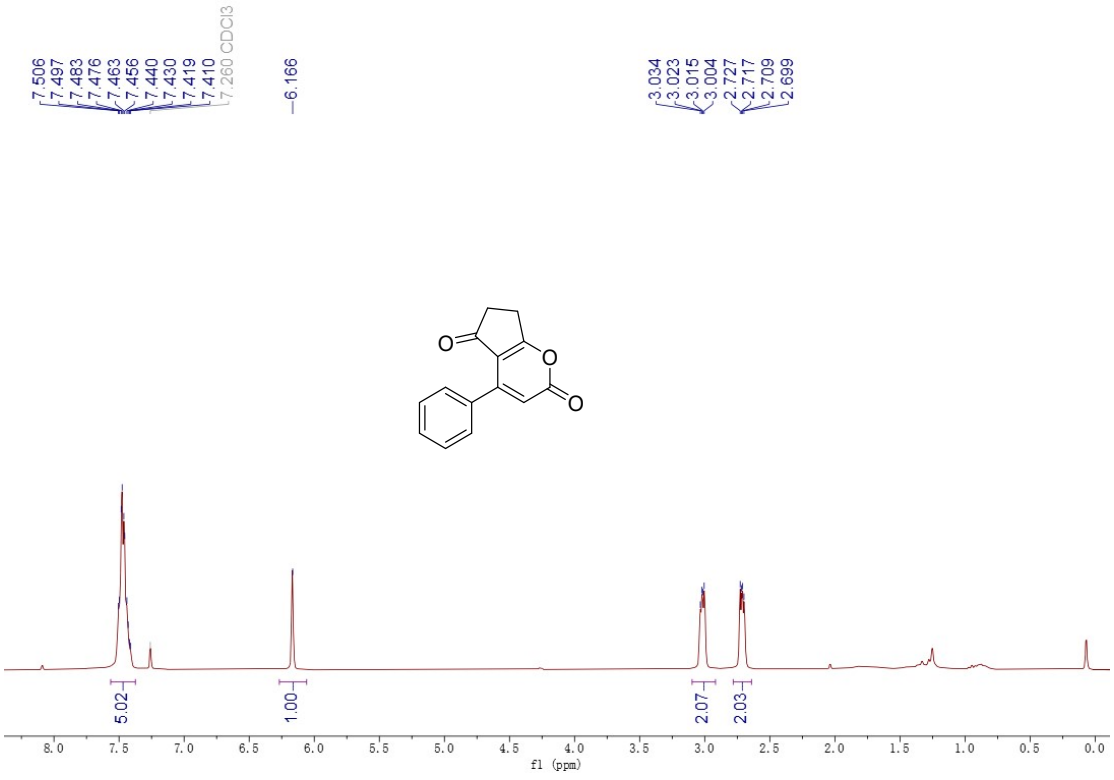


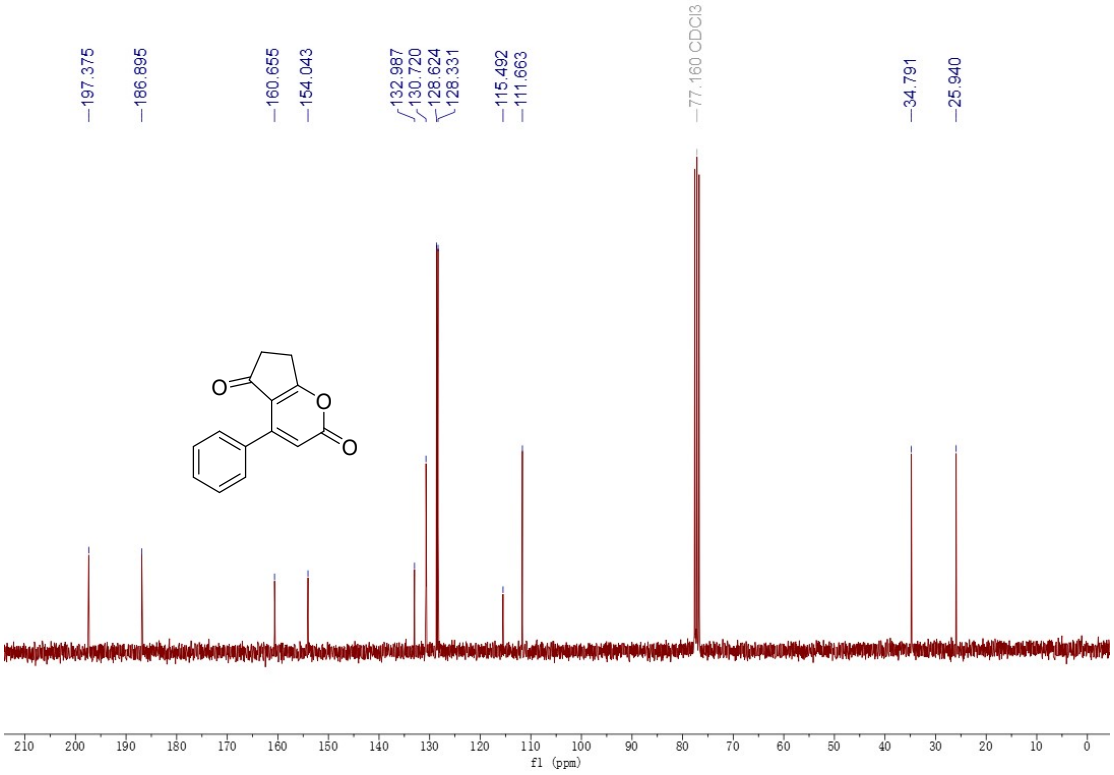
4,7-diphenyl-7,8-dihydro-2H-chromene-2,5(6H)-dione (3u)



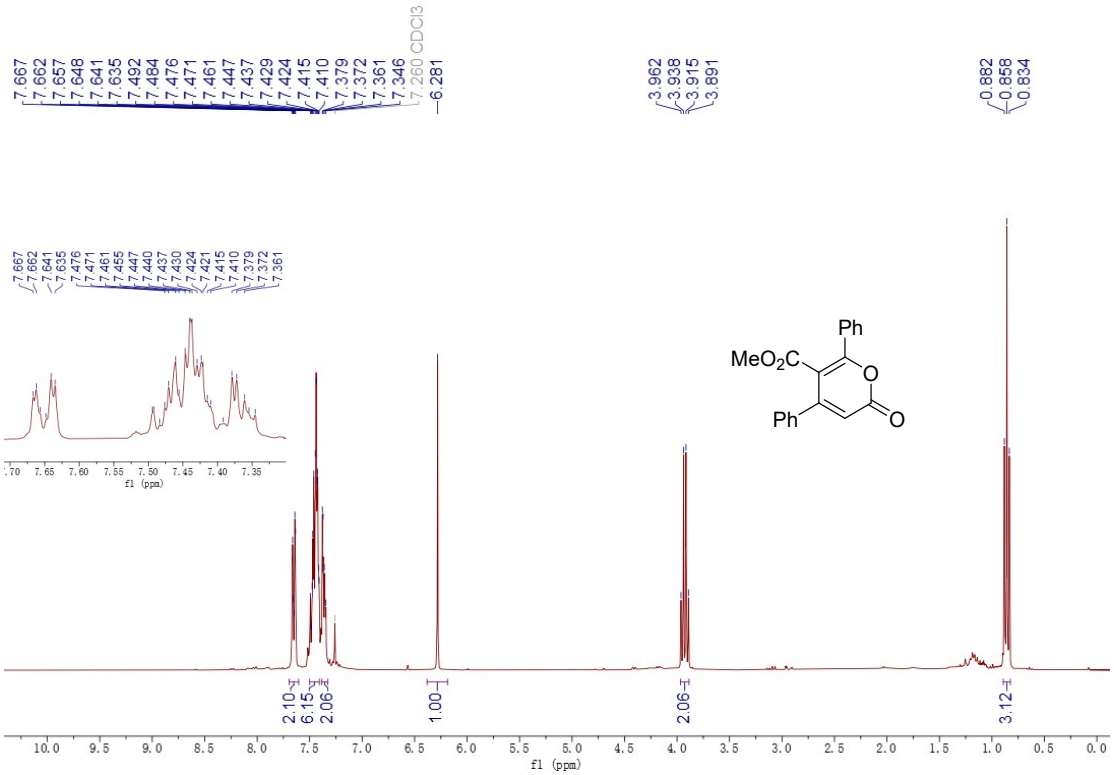


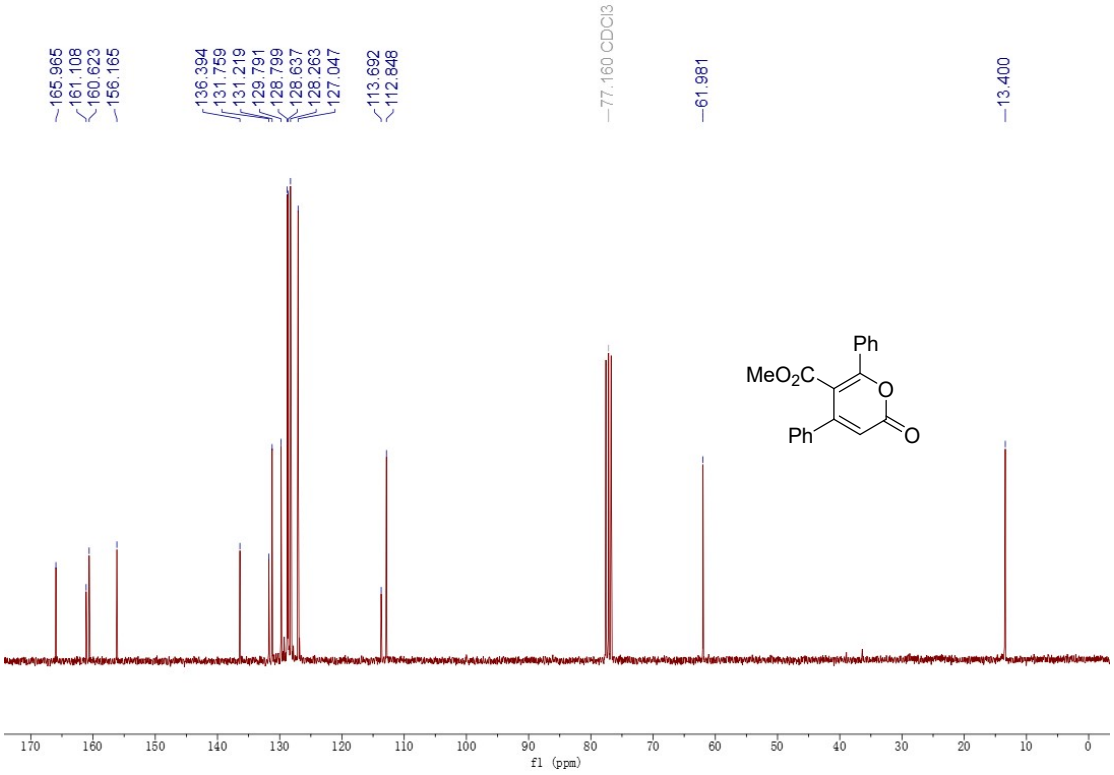
4-phenyl-6,7-dihydrocyclopenta[b]pyran-2,5-dione (3v)



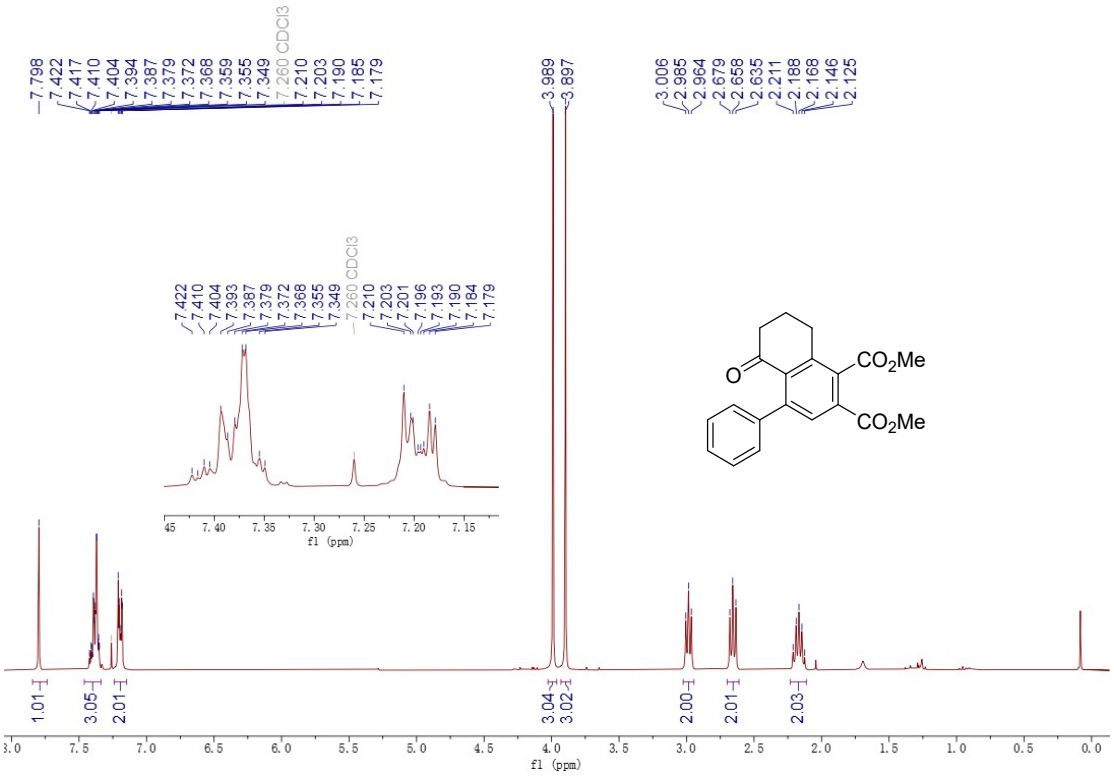


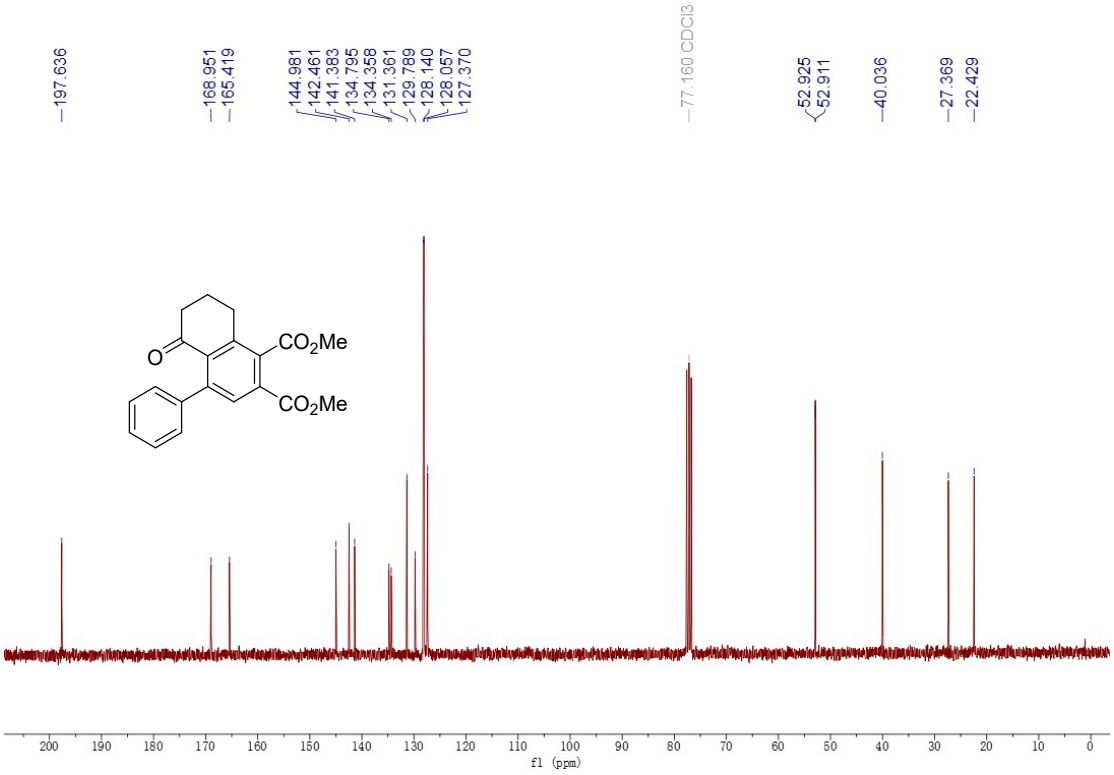
methyl 2-oxo-4,6-diphenyl-2H-pyran-5-carboxylate (3w)





dimethyl 5-oxo-4-phenyl-5,6,7,8-tetrahydronaphthalene-1,2-dicarboxylate (4)

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