Synthesis of Flavones via the Stork-Danheiser reaction

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Table of contents

1. General Information

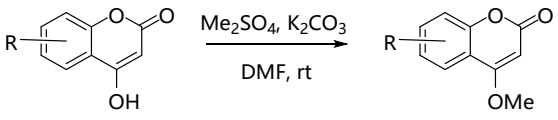
Unless otherwise noted, all reactions were performed in oven-dried round-bottom flasks under argon atmosphere. DME, Et_2O, THF and toluene were freshly distilled with sodium/benzophenone ketyl under argon atmosphere. All other reagents were used from commercial sources without further purification, unless otherwise noted. The silica gel (200-300 meshes, Anhui LiangChen Silicon Material Co. Ltd., Huoshan, China) was used for column chromatography. Thin layer chromatography (TLC) was carried out on GF plates (0.25 mm layer thickness, Anhui LiangChen Silicon Material Co. Ltd., Huoshan, China). Visualization was accomplished with UV light (254 nm) and/or by phosphomolybdic acid (50 g/L) in ethanol following heating as developing agents. Yields reported were based on isolated and spectroscopically pure compounds.

^1H and ^{13}C NMR spectra were recorded on AVANCE III HD 400, 500 or 600 MHz spectrometers (Bruker, German) using chloroform-d ($CDCl_3$) as the internal standard (^1H NMR, $CHCl_3$ at 7.26 ppm; ^{13}C NMR, $CDCl_3$ at 77.16 ppm) at ambient temperature. ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, br = broad, m = multiplet), coupling constants (Hz), and integration. HRMS (ESI) was taken on Thermo LTQ Orbitrup Discovery. IR spectroscopy was scanned with KBr pellets on Perkin Elemr Spectrum Two™ spectrophotometer. Melting points are obtained with a calibrated digital thermometer probe (using pure naphthalene and ice-water mixture as the references).

2. Synthesis and Characterizations of Substrates

The 4-hydroxycoumarin precursors were commercially available, and the methylated 4-hydroxycoumarin precursors **2a-2k** were prepared according to the literature procedures.[1-3]

Table S1. Alkylation of 4-hydroxycoumarin

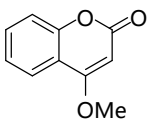


(R = H, Me, MeO, CF_3, CF_3O, F, Cl) **2a-2k**

2.1. General procedure for Alkylation of 4-hydroxycoumarin

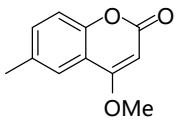
To a solution of 4-hydroxycoumarin (10 mmol, 1.0 eq.) in 5 mL DMF in the presence of K_2CO_3 (3.45 g, 25 mmol, 2.5 eq.) was added dimethyl sulfate (1.94 mL, 20 mmol, 2.0 eq.) dropwise, the solution was stirred at rt. for 2 h. The resulting solution was poured to 50 mL H_2O and let stand for 1 h at 4 °C. Then the suspension was filtered and the solid was washed by H_2O. The solid was dried and recrystallized from ethyl acetate to afford the 4-alkoxycoumarin **2**.

2.2. Characterizations of 4-alkoxycoumarin



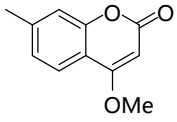
2a

4-methoxy-2H-chromen-2-one (2a): A white needle-like crystal, yield 89%, m.p. 120.9-123.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (dd, J = 7.9, 1.4 Hz, 1H), 7.54 (dt, J = 7.8, 1.6 Hz, 1H), 7.30 (d, J = 8.3 Hz, 1H), 7.6 (dt, J = 7.6, 0.9 Hz, 1H), 5.69 (s, 1H), 3.99 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5 (s), 163.0 (s), 153.4 (s), 132.5 (s), 124.0 (s), 123.1 (s), 116.8 (s), 115.7 (s), 90.2 (s), 56.5 (s). FT-IR(KBr) ν_{max} cm^{-1}: 3074, 2949, 1734, 1624, 1450, 1392, 1246, 1186, 935, 850, 773. HRMS (ESI) calcd. for: $C_{10}H_9O_3^+$, $[M+H]^+$: 177.0546; found: 177.0547.



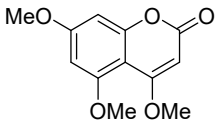
2b

4-methoxy-6-methyl-2H-chromen-2-one (2b): An off-white needle-like crystal, yield 89%, m.p. 116.4-118.2 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 1.0 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.19 (d, *J* = 8.5 Hz, 1H), 5.66 (s, 1H), 3.98 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.6, 163.3, 151.6, 133.8, 133.5, 122.8, 116.6, 115.4, 90.2, 56.4, 21.0. FT-IR(Neat) ν_{max} cm^{-1}:3074, 2943, 1677, 1624, 1604, 1455, 1212, 1105, 986, 825, 734, 531. HRMS (ESI) calcd. for: $C_{11}H_{11}O_3^+$, $[M+H]^+$: 191.0703; found: 191.0702.



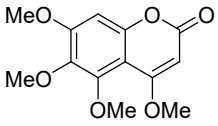
2c

4-methoxy-7-methyl-2H-chromen-2-one (2c): A white needle-like crystal, yield 86%, m.p. 179.5-180.0 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (dt, *J* = 8.1, 2.0 Hz, 1H), 7.05 (dd, *J* = 10.0, 5.3 Hz, 2H), 5.60 (s, 1H), 3.95 (s, 4H), 2.40 (s, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 163.3, 153.4, 143.6, 125.2, 122.7, 116.9, 113.2, 89.2, 56.3, 21.7. FT-IR(Neat) ν_{max} cm^{-1}: 3074, 1705, 1617, 1558, 1391, 1244, 1163, 960, 840. HRMS (ESI) calcd. for: $C_{11}H_{11}O_3^+$, $[M+H]^+$: 191.0703; found: 191.0702.



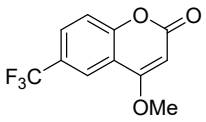
2d

4,5,7-trimethoxy-2H-chromen-2-one (2d). A yellow powder, yield 66%, m.p. 193.7-194.4°C. ^{1}H NMR (500 MHz, DMSO-*d6*) δ 6.55 (s, 1H), 6.46 (s, 1H), 5.57 (s, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (126 MHz, DMSO-*d6*) δ 171.2, 168.6, 163.0, 161.5, 158.5, 99.6, 95.7, 93.4, 86.4, 56.6, 56.3, 55.8. FT-IR(KBr) ν_{max} cm^{-1}: 3078, 2968, 1722, 1608, 1462, 1386, 1260, 1157, 1112, 1059, 974, 828. HRMS (ESI) calcd. for: $C_{12}H_{13}O_5^+$, $[M+H]^+$: 237.0757; found: 254.0757.



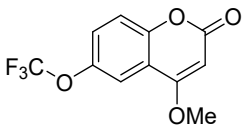
2e

4,5,6,7-tetramethoxy-2H-chromen-2-one (2e). A white powder, yield 85%, m.p. 145.6-146.6 °C.^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.65 (s, 1H), 5.57 (s, 1H), 3.97 (s, 3H), 3.91 (s, 3H), 3.88 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.3, 163.0, 157.0, 151.5, 151.0, 140.2, 103.8, 96.7, 88.3, 62.3, 61.4, 56.7, 56.4. FT-IR(KBr) ν_{max} cm^{-1}: 3083, 2944, 1717, 1602, 1459, 1376, 1267, 1098, 1024, 973, 822. HRMS (ESI) calcd. for: $C_{13}H_{15}O_6^+$, $[M+H]^+$: 267.0863; found: 267.0867.



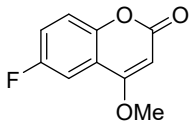
2f

4-methoxy-6- trifluoromethyl-2H-chromen-2-one (2f): A white plate crystal, yield 63%, m.p. 141.2-143.8 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 7.78 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.41 (d, *J* = 8.7 Hz, 1H), 5.76 (s, 1H), 4.03 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.6, 161.9, 155.2, 129.2 (q, *J* = 3.0 Hz), 126.6 *J* = 33.9 Hz), 123.7 (q, *J* = 272.6 Hz), 121.2 (d, *J* = 3.9 Hz), 117.7, 116.0, 91.2, 56.8. FT-IR(Neat) ν_{max} cm^{-1}: 2955, 1716, 1634, 1610, 1465, 1241, 1113, 919, 835. HRMS (ESI) calcd. for: $C_{10}H_8F_3O_3^+$, 245.0420; found: 245.0439.



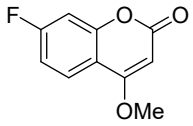
2g

4-methoxy-6-trifluoromethoxy-2H-chromen-2-one (2g): A white needle-like crystal, yield 88%, m.p. 146.0-146.8 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 2.8 Hz, 1H), 7.39 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.33 (d, *J* = 9.0 Hz, 1H), 5.74 (s, 1H), 4.01 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.5, 162.2, 151.5, 145.1 (d, *J* = 2.1 Hz), 125.6, 120.5 (q, *J* = 257.8 Hz), 118.5, 116.7, 115.6, 91.1, 56.7. FT-IR(Neat) ν_{max} cm^{-1}: 3079, 2924, 1713, 1629, 1573, 1453, 1208, 1148, 985, 933, 855. HRMS (ESI) calcd. for: $C_{10}H_8F_3O_4^+$: 261.0369; found: 261.0369.



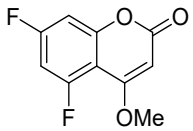
2h

6-fluoro-4-methoxy-2H-chromen-2-one (2h). A white powder, yield 86%, m.p. 162.3-163.0 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.31-7.20 (m, 2H), 5.73 (s, 1H), 4.00 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.7, 162.6, 158.7 (d, *J* = 243.8 Hz), 149.5, 112.0 (d, *J* = 24.5 Hz), 118.5 (d, *J* = 8.3 Hz), 116.6 (d, *J* = 9.0 Hz), 108.94 (d, *J* = 25.5 Hz), 90.9, 56.6. FT-IR(KBr) ν_{max} cm^{-1}: 3075, 1728, 1631, 1579, 1460, 1381, 1263, 1092, 945, 846. HRMS (ESI) calcd. for: $C_{10}H_8FO_3^+$, $[M+H]^+$: 195.0452; found: 195.0455.



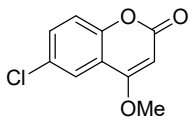
2i

7-fluoro-4-methoxy-2H-chromen-2-one (2i). A white powder, yield 82%, m.p. 221.2-221.8 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.80 (dd, *J* = 8.8, 6.0 Hz, 1H), 7.09-6.95 (m, 2H), 5.65 (s, 1H), 4.00 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.2, 164.2, 162.8, 154.7, 125.06, 112.3, 112.2, 104.3, 89.29, 56.58. FT-IR(KBr) ν_{max} cm^{-1}: 3079, 1707, 1627, 1445, 1392, 1245, 1142, 966, 856. HRMS (ESI) calcd. for: $C_{10}H_8FO_3^+$, $[M+H]^+$: 195.0452; found: 195.0455.



2j

5,7-difluoro-4-methoxy-2H-chromen-2-one (2j). A white powder, yield 64%; m.p. 180.6-181.3 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.31 (dd, *J* = 9.5, 3.0 Hz, 2H), 5.91 (s, 1H), 3.97 (s, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.6, 163.6 (dd, *J* = 251.0, 15.6 Hz), 160.6, 158.9 (dd, *J* = 260.2, 15.4 Hz), 154.8 (dd, *J* = 16.2, 7.0 Hz), 101.3 (t, *J* = 26.7 Hz), 100.9 (dd, *J* = 25.9, 4.2 Hz), 89.9, 57.4. FT-IR(KBr) ν_{max} cm^{-1}: 3083, 2958, 1731, 1634, 1441, 1390, 1269, 1139, 1084, 966, 840. HRMS (ESI) calcd. for: $C_{10}H_7F_2O_3^+$, $[M+H]^+$: 213.0358; found: 213.0362.

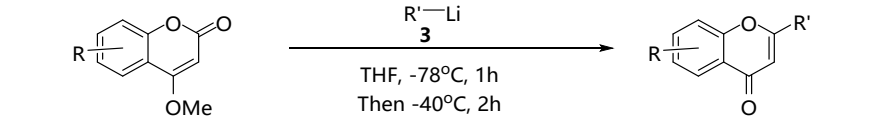


2k

4-methoxy-6-chloro-2H-chromen-2-one (2k): A white needle-like crystal, yield 53%, m.p. 162.8-165.3 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (t, *J* = 2.0 Hz, 1H), 7.47 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.24 (dd, *J* = 8.9, 1.2 Hz, 1H), 5.70 (s, 1H), 3.99 (s, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.4, 162.3, 151.8, 132.5, 129.6, 122.8, 118.3, 116.9, 90.9, 56.7. FT-IR(Neat) ν_{max} cm^{-1}: 3074, 2922, 1704, 1622, 1604, 1561, 1451, 1368, 1236, 1112, 941, 825. HRMS (ESI) calcd. for: $C_{10}H_8ClO_3^+$: 211.0156; found: 211.0158.

3. Synthesis and Characterizations of Flavones

3.1. General procedure for preparation of flavones:

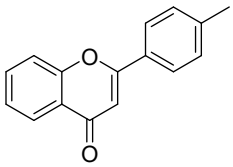


(R = H, Me, MeO, CF_3, CF_3O, F, Cl) **2**

(R = H, Me, MeO, CF_3, CF_3O, F, Cl) **1**

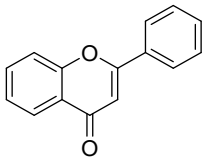
The aryl lithium solution **3** was prepared by lithium-iodine exchange reaction. To aryl iodide **3** (2 mmol, 2.0 eq.) in 10 mL anhydrous THF was added a solution of *t*-BuLi (3.1 mL, 4 mmol, 1.3 M in pentane, 4.0 eq.) at -78 °C, the mixture was stirred for 1 h at -78 °C and for another hour under rt and cooled back to -78 °C. Then the solution of the corresponding aryl lithium was added to a solution of coumarin analogs (1.0 mmol, 1.0 eq.) in 5 mL anhydrous THF at -78 °C. The mixture was stirred at -78 °C 1 h and -40 °C for 1-2 h, the reaction was quenched by slowly adding 10 mL 1 M HCl and the resulting solution was vigorously stirred at rt. for 1 h. The mixture was separated, and aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate) to afford the desired flavone **1aa-1ak**. Compounds **1aq, 1ar** were prepared by using *n*-BuLi (2.0 M in hexane) and *t*-BuLi (1.3 M in pentane) as the nucleophilic reagents. Compound **1am-1aq, 1b-1k** were prepared by using 3.0 eq aryl lithium as nucleophilic reagents.

3.2. Characterizations of Flavones



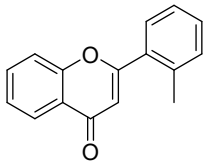
1aa

2-(*p*-tolyl)-4H-chromen-4-one (1aa): A white needle-like crystal, yield 49%, m.p. 111.2-113.5 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.22 (dt, *J* = 7.9, 1.7 Hz, 1H), 7.80 (dd, *J* = 8.3, 2.3 Hz, 2H), 7.67 (tt, *J* = 7.1, 1.9 Hz, 1H), 7.54 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.43 – 7.36 (m, 1H), 7.31 (dd, *J* = 8.4, 2.2 Hz, 2H), 6.78 (d, *J* = 2.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.5, 163.7, 156.4, 142.4, 133.7, 129.9, 129.1, 126.3, 125.8, 125.2, 124.1, 118.2, 107.1, 21.6. FT-IR(KBr) ν_{max} cm^{-1}: 3061, 3034, 1639, 1606, 1466, 1372, 1124, 753. HRMS (ESI) calcd. for: $C_{16}H_{13}O_2^+$, $[M+H]^+$: 237.0910, found: 237.0893



1ab

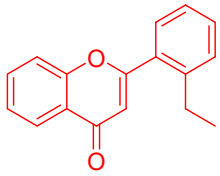
2-phenyl-4H-chromen-4-one (1ab): A slightly yellow solid, yield 51%, m.p. 111.0-113.0 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 5.8 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.55-7.50 (m, 3H), 7.42 (t, *J* = 7.5 Hz, 1H), 6.83 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.6, 163.6, 156.4, 133.9, 132.0, 131.7, 129.2, 126.44, 125.9, 125.4, 124.1, 118.2, 107.8. FT-IR(KBr) ν_{max} cm^{-1}: 3071, 1647, 1606, 1466, 1376, 1129, 769. HRMS (ESI) calcd. for: $C_{15}H_{11}O^{2+}$, $[M+H]^+$: 223.0754, found: 223.0759.



1ac

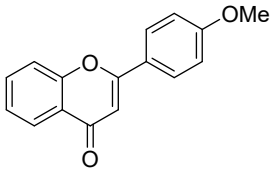
2-(o-tolyl)-4H-chromen-4-one (1ac): A white needle-like crystal, yield 78%, m.p. 45.6-47.6 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.0 Hz, 2H), 7.34 (d, *J* = 7.5 Hz,

2H), 6.49 (s, 1H), 2.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.4, 166.3, 156.7, 137.0, 133.9, 132.8, 131.4, 130.9, 129.4, 126.4, 125.9, 125.4, 124.0, 118.2, 112.1, 20.7. FT-IR(KBr) ν_{max} cm^{-1}: 3059, 1639, 1603, 1466, 1375, 1129, 770. HRMS (ESI) calcd. for: $C_{16}H_{13}O_2^+$, $[M+H]^+$: 237.0910, found: 237.0913.



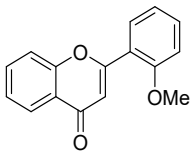
1ad

2-(2-ethylphenyl)-4H-chromen-4-one (1ad): A yellow crystal, yield 86%, m.p. 51.2-52.0 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.69 (td, *J* = 8.6, 1.7 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.48 – 7.41 (m, 3H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.32 (td, *J* = 7.4, 1.3 Hz, 1H), 2.79 (q, *J* = 7.5 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.4, 166.7, 156.6, 143.2, 133.9, 132.4, 131.0, 129.8, 129.6, 126.3, 125.9, 125.4, 124.0, 118.2, 112.1, 26.9, 15.8. FT-IR(Neat) ν_{max} cm^{-1}: 3067, 2965, 1641, 1608, 1466, 1363, 1210, 1120, 908, 752. HRMS (ESI) calcd. for: $C_{17}H_{15}O_2^+$, $[M+H]^+$: 251.1067, found: 251.1066.



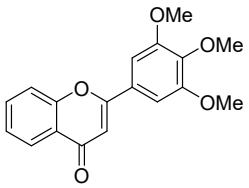
1ae

2-(4-methoxyphenyl)-4H-chromen-4-one (1ae): A slightly yellow solid, yield 58%, m.p. 156.1-157.0 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.05 (d, *J* = 8.7 Hz, 2H), 8.03 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.81 (t, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.94 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 177.0, 162.7, 162.2, 155.6, 134.1, 128.2, 125.4, 124.8, 123.3, 118.4, 114.6, 105.5, 55.6. FT-IR(KBr) ν_{max} cm^{-1}: 3050, 1649, 1608, 1466, 1382, 1268, 1124, 827, 768. HRMS (ESI) calcd. for $C_{16}H_{13}O_3^+$, $[M+H]^+$: 253.0859 , found 253.0858.



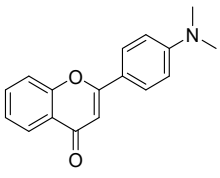
1af

2-(2-methoxyphenyl)-4H-chromen-4-one (1af): A slightly orange solid, yield 56%, m.p. 90.2-93.4 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 7.9 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.14 (s, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.9, 160.9, 158.0, 156.5, 133.5, 132.4, 129.3, 125.6, 124.9, 123.9, 120.9, 120.8, 118.0, 112.7, 111.8, 55.7. FT-IR(KBr) ν_{max} cm^{-1}: 3076, 1644, 1608, 1469, 1375, 1256, 1127, 1020, 757. HRMS (ESI) calcd. for: $C_{16}H_{13}O3^{+}$, $[M+H]^{+}$: 253.0859, found: 253.0864.



1ag

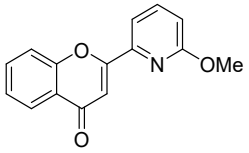
2-(3,4,5-trimethoxyphenyl)-4H-chromen-4-one (1ag): A slightly orange solid, yield 45%, m.p. 127.5-128.8 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 7.9 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.14 (s, 2H), 6.78 (s, 1H), 3.96 (s, 6H), 3.93 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.4, 163.3, 156.2, 153.6, 141.3, 133.8, 127.0, 125.7, 125.3, 123.9, 118.1, 107.4, 103.8, 61.1, 56.4. FT-IR(KBr) ν_{max} cm^{-1}: 3062, 2942, 1652, 1604, 1466, 1367, 1128, 749. HRMS (ESI) calcd. for: $C_{18}H_{15}O_2^{+}$, $[M+H]^{+}$: 299.1067, found:299.1072.



1ah

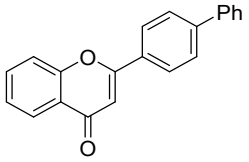
2-(4-(dimethylamino)phenyl)-4H-chromen-4-one (1ah): An orange solid, yield 68%, m.p. 156.0-157.1 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 8.9 Hz, 2H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 8.9 Hz, 2H), 6.70 (s, 1H), 3.06 (s, 6H). ^{13}C NMR (126

MHz, $CDCl_3$) δ 164.4, 156.3, 152.6, 133.3, 127.8, 125.7, 124.9, 118.3, 118.0, 111.7, 104.5, 40.2. FT-IR(KBr) ν_{max} cm^{-1}: 3060, 2901, 1632, 1597, 1521, 1464, 1368, 1201, 822, 754. HRMS (ESI) calcd. for $C_{17}H_{16}NO_2^+$, $[M+H]^+$: 266.1176, Found 266.1174。



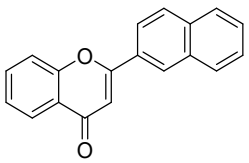
1ai

2-(6-methoxypyridin-2-yl)-4H-chromen-4-one (1ai): A white solid, yield 46%, m.p. 163.2-163.8 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 7.9 Hz, 1H), 7.76 – 7.69 (m, 3H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.46 (s, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 4.01 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.0, 163.9, 161.8, 156.2, 146.7, 139.4, 134.0, 126.0, 125.4, 124.6, 118.2, 114.4, 114.2, 108.6, 53.7. FT-IR(KBr) ν_{max} cm^{-1}: 3070, 3010, 2955, 1652, 1607, 1568, 1466, 1374, 1276, 1028, 878, 805. HRMS (ESI) calcd. for: $C_{15}H_{12}NO_3^+$, $[M+H]^+$: 254.0812; found: 254.0814



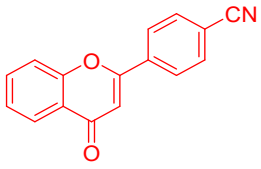
1aj

2-([1,1'-biphenyl]-4-yl)-4H-chromen-4-one (1aj): White flakes, yield 57%, m.p. 155.8-157.4 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 7.9 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 2H), 7.76 (d, *J* = 7.9 Hz, 2H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.40-7.45 (m, 2H), 6.88 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.6, 163.3, 156.4, 144.6, 139.9, 133.9, 130.7, 129.2, 128.4, 127.8, 127.3, 126.9, 125.9, 125.4, 124.2, 118.2, 107.6. FT-IR(KBr) ν_{max} cm^{-1}: 3066, 3019, 1642, 1603, 1471, 1376, 1127, 766, 687. HRMS (ESI) calcd.. for: $C_{21}H_{15}O_2^+$, $[M+H]^+$: 299.1067, found: 299.1072.



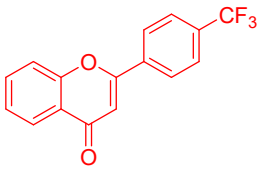
1ak

2-(naphthalen-2-yl)-4H-chromen-4-one (1ak): Slightly orange flakes, yield 40%, m.p. 162.8-163.6 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 8.26 (d, *J* = 7.8 Hz, 1H), 8.01 – 7.94 (m, 2H), 7.91 (dd, *J* = 13.1, 8.7 Hz, 2H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 6.96 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.6, 163.5, 156.5, 134.8, 133.9, 133.1, 129.2, 129.1, 128.2, 128.0, 127.2, 127.1, 125.9, 125.4, 124.2, 122.7, 118.3, 108.1. FT-IR(KBr) ν_{max} cm^{-1}: 3070, 1636, 1597, 1462, 1376, 1131, 750. HRMS (ESI) calcd. for $C_{19}H_{13}O_2^+$ $[M+H]^+$: 273.0910, Found 273.0911



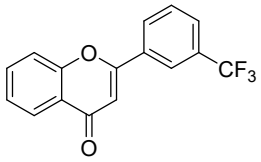
1al

4-(4-oxo-4H-chromen-2-yl)benzonitrile (1al): A white needle-like crystal, 20% yield, m.p. 198.2-200.7 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 (dd, *J* = 8.0, 1.8 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.74 (td, *J* = 8.7, 1.7 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 6.87 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.2, 161.0, 156.3, 136.1, 134.4, 132.9, 126.9, 126.0, 125.8, 124.0, 118.2, 118.1, 115.1, 109.3. FT-IR(Neat) ν_{max} cm^{-1}: 3079, 2924, 164, 1601, 1465, 1377, 1224, 1118, 838, 758, 541. HRMS (ESI) calcd. for $C_{16}H_{10}NO_2^+$ $[M+H]^+$: 248.0706, found: 248.0714.



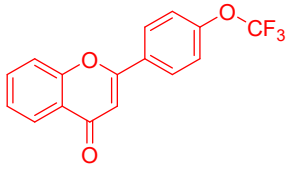
1am

2-(4-(trifluoromethyl)phenyl)-4H-chromen-4-one (1am): A white needle-like crystal, 27% yield, m.p. 130.6-131.4 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.73 (td, *J* = 8.6, 1.7 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 6.87 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.4, 161.8, 156.4, 135.4, 134.3, 133.5, 133.2, 126.8, 126.2 (q, *J* = 3.8 Hz), 126.0, 125.7, 124.1, 123.8 (q, *J* = 273.6 Hz), 118.3, 108.9. FT-IR(Neat) ν_{max} cm^{-1}: 3072, 2921, 1634, 1607, 1467, 1377, 1320, 1168, 1110, 840, 756. HRMS (ESI) calcd. for: $C_{17}H_{12}F_3O_2^+$. $[M+H]^+$: 291.0627, found: 291.0632.



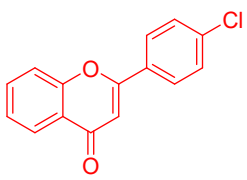
1an

2-(3-(trifluoromethyl)phenyl)-4H-chromen-4-one (1an): A white needle-like crystal, m.p. 142.6-144.4 °C, yield 37%. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 8.0 Hz, 1H), 8.19 (s, 1H), 8.09 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.77 – 7.70 (m, 1H), 7.67 (t, *J* = 7.9 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 6.86 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.3, 161.7, 156.3, 134.2, 132.9, 131.9 (q, $^{2}J_{C\text{-}F}$ = 33.0 Hz), 129.8, 129.5, 128.8, 128.2(q, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 125.9, 125.7, 124.1, 123.8(q, $^{1}J_{C\text{-}F}$ = 273.0 Hz), 123.2(q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 118.3, 108.5. FT-IR(KBr) ν_{max} cm^{-1}: 3083, 2922, 1662, 1608, 1466, 1383, 1339, 1259, 1118, 779, 696. HRMS (ESI) calcd. for: $C_{16}H_{10}F_3O_2^+$, $[M+H]^+$: 291.0627, found: 291.0633.



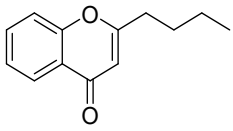
1ao

2-(4-(trifluoromethoxy)phenyl)-4H-chromen-4-one (1ao): A white needle-like crystal, yield 42%, m.p. 135.6-136.3 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.95 (d, *J* = 8.9 Hz, 2H), 7.69 (td, *J* = 7.9, 7.1, 1.8 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 6.78 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.3, 162.0, 156.3, 151.6 (d, *J* = 1.8 Hz), 134.1, 130.4, 128.2, 125.9, 125.5, 124.0, 121.2, 120.4, (q, *J* = 260.6 Hz), 118.2, 108.0. FT-IR(Neat) ν_{max} cm^{-1}: 3074, 1641, 1607, 1508, 1469, 1249, 1169, 906, 758. HRMS (ESI) calcd. for: $C_{16}H_{10}F_3O_3^+$. $[M+H]^+$: 307.0577, found: 307.0576.



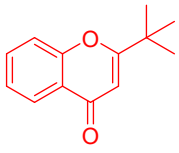
1ap

2-(4-chlorophenyl)-4H-chromen-4-one (1ap): A white needle-like crystal, yield 18%, m.p. 176.4-177.3 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.86 (d, *J* = 8.7 Hz, 2H), 7.71 (td, *J* = 7.9, 7.1, 1.7 Hz, 1H), 7.56 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.47 – 7.38 (m, 1H), 6.79 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.4, 162.4, 156.3, 138.0, 134.1, 130.4, 129.5, 127.7, 125.9, 125.5, 124.0, 118.2, 107.8. FT-IR(Neat) ν_{max} cm^{-1}: 3091, 2926, 1641, 1606, 1466, 1373, 1090, 827, 771. HRMS (ESI) calcd. for: $C_{15}H_{10}ClO_2^+$, $[M+H]^+$: 257.0364, found: 257.0396



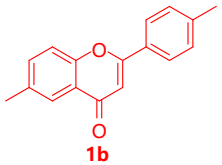
1aq

2-butyl-4H-chromen-4-one (1aq): A slightly yellow solid, yield 68%, m.p. 28.8-29.4 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 6.17 (s, 1H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.72 (p, *J* = 7.6 Hz, 2H), 1.43 (p, *J* = 7.3, 6.8 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 178.5, 169.9, 156.6, 133.5, 125.8, 125.0, 123.9, 118.0, 109.9, 34.2, 29.0, 22.2, 13.8. FT-IR(KBr) ν_{max} cm^{-1}: 3065, 2958, 1655, 1607, 1466, 1384, 1221, 1121, 760. HRMS (ESI) calcd. for $C_{13}H_{15}O_2^+$ $[M+H]^+$: 203.1067, found: 203.1067.



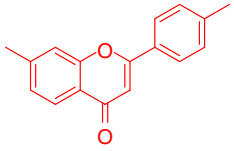
1ar

2-(tert-butyl)-4H-chromen-4-one (1ar): A slightly yellow solid, yield 64%, m.p. 63.9-65.8 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.17 (td, *J* = 8.2, 2.0 Hz, 1H), 7.64 (qd, *J* = 8.7, 1.9 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.36 (qd, *J* = 7.6, 2.3 Hz, 1H), 6.31 – 6.21 (m, 1H), 1.35 (s, 3H), 1.34 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 179.8, 176.2, 156.6, 133.6, 125.7, 124.9, 123.6, 118.0, 106.8, 36.6, 28.0. FT-IR(Neat) ν_{max} cm^{-1}: 3072, 2961, 1647, 1607, 1466, 1360, 1230, 1134, 938, 757. HRMS (ESI) calcd. for $C_{13}H_{15}O_2^+$ $[M+H]^+$: 203.1067, found: 203.1090.



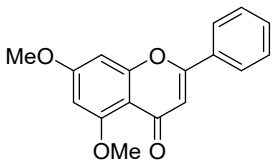
1b

6-methyl-2-(*p*-tolyl)-4H-chromen-4-one(1b). A white powder, yield 42%, m.p. 134.2-136.0 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.49 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.78 (s, 1H), 2.46 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.7, 163.6, 154.6, 142.3, 135.2, 135.0, 129.8, 129.2, 126.3, 125.2, 123.7, 117.9, 106.9, 21.7, 21.1. FT-IR(Neat) ν_{max} cm^{-1}: 2921, 1640, 1613, 1435, 1362, 1223, 1038, 814. HRMS (ESI) calcd. for: $C_{17}H_{15}O_2^+$, $[M+H]^+$: 251.1067, found: 251.1068.



1c

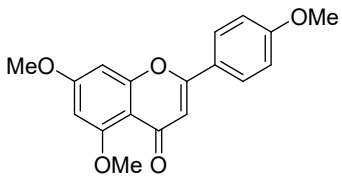
7-methyl-2-(*p*-tolyl)-4H-chromen-4-one(1c): A white powder, yield 48%, m.p. 130.1-131.9 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.35 (s, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.21 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.75 (s, 1H), 2.49 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.5, 163.4, 156.5, 145.1, 142.2, 129.8, 129.2, 126.7, 126.3, 125.5, 121.8, 117.9, 107.0, 21.9, 21.6. FT-IR(Neat) ν_{max} cm^{-1}: 3052, 1635, 1613, 1421, 1368, 1158, 1043, 812. HRMS (ESI) calcd. for: $C_{17}H_{15}O_2^+$, $[M+H]^+$: 251.1067, found: 251.1066.



1da

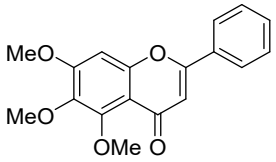
5,7-dimethoxy-2-phenyl-4H-chromen-4-one (1da): A yellow needle-like crystal, yield 47%, m.p. 136.4-138.8 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 7.4, 2.3 Hz, 2H), 7.50 (dd, *J* = 5.5, 1.7 Hz, 3H), 6.69 (s, 1H), 6.57 (d, *J* = 2.3 Hz, 1H), 6.38 (d, *J* = 2.3 Hz, 1H), 3.96 (s, 3H), 3.91 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.7, 164.2, 161.1, 160.8, 160.1, 131.7, 131.3, 129.1, 126.1, 109.2, 96.3, 93.0, 56.6,

55.9. FT-IR(KBr) ν_{max} cm^{-1}: 3072, 2939, 1650, 1608, 1460, 1347, 1255, 1200, 1118, 821, 764. HRMS (ESI) calcd. for $C_{17}H_{15}O_4^+$ [M+H]$^+$: 283.0965, found: 283.0965.



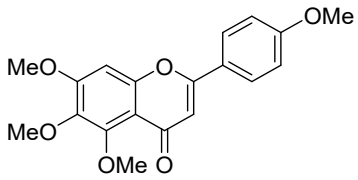
1db

5,7-dimethoxy-2-(4-methoxyphenyl)-4H-chromen-4-one (1db): A slightly yellow solid, yield 49%, m.p. 157.2-159.2 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.57 (s, 1H), 6.52 (d, *J* = 2.3 Hz, 1H), 6.33 (d, *J* = 2.3 Hz, 1H), 3.93 (s, 3H), 3.88 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.7, 164.0, 162.1, 160.9, 160.7, 159.9, 127.7, 123.8, 114.4, 109.2, 107.7, 96.1, 92.8, 56.5, 55.8, 55.6. FT-IR(KBr) ν_{max} cm^{-1}: 3528, 2929, 1643, 1598, 1464, 1351, 1254, 1181, 1031, 829. HRMS (ESI) calcd. for $C_{18}H_{17}O_5^+$ [M+H]$^+$: 313.1071, found: 313.1071.



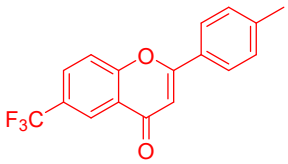
1ea

5,6,7-trimethoxy-2-phenyl-4H-chromen-4-one (1ea): A white needle-like crystal, yield 44%, m.p. 157.3-159.7 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 7.7, 2.1 Hz, 2H), 7.59 – 7.39 (m, 3H), 6.81 (s, 1H), 6.67 (s, 1H), 3.99 (s, 3H), 3.98 (s, 3H), 3.92 (s, 3H) ^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.2, 161.1, 157.8, 154.6, 152.6, 140.4, 131.6, 131.3, 129.0, 126.0, 113.0, 108.4, 96.3, 62.2, 61.6, 56.3. FT-IR(KBr) ν_{max} cm^{-1}: 3068, 2928, 1636, 1602, 1456, 1353, 1200, 1121, 1043, 815, 767. HRMS (ESI) calcd. for $C_{18}H_{17}O_5^+$ [M+H]$^+$: 313.1071, found: 313.1071.



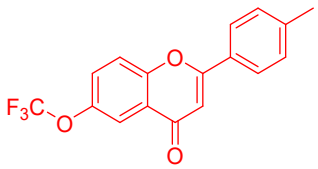
1eb

5,6,7-trimethoxy-2-(4-methoxyphenyl)-4H-chromen-4-one (1eb): A slightly yellow needle-like crystal, yield 58%, m.p. 157.6-159.0 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.9 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 6.78 (s, 1H), 6.58 (s, 1H), 3.98 (s, 3H), 3.97 (s, 3H), 3.91 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 177.3, 162.3, 161.3, 157.8, 154.6, 152.7, 140.5, 127.8, 124.0, 114.6, 113.0, 107.2, 96.4, 62.3, 61.6, 56.4, 55.6. FT-IR(KBr) ν_{max} cm^{-1}: 3064, 2936, 1636, 1603, 1457, 1353, 1258, 1207, 1118, 1022, 841. HRMS (ESI) calcd. for $C_{19}H_{19}O_6^+$ [M+H]$^+$: 343.1176, found: 343.1175.



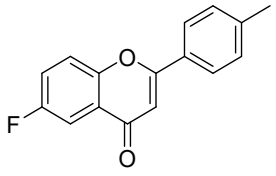
1f

2-(p-tolyl)-6-(trifluoromethyl)-4H-chromen-4-one (1f): A slightly yellow needle-like crystal, yield 54%, m.p. 198.4-201.3 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.53 (d, *J* = 1.6 Hz, 1H), 7.91 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.83 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.5, 164.3, 157.8, 143.0, 130.2 (q, *J* = 3.1 Hz), 130.0, 128.4, 128.0 (q, *J* = 77.8 Hz), 127.6, 126.4, 124.0 (q, *J* = 3.93 Hz), 123.7, (q, *J* = 272.5 Hz) 119.3, 115.3, 107.3, 21.7. FT-IR(Neat) ν_{max} cm^{-1}: 3069, 2924, 1645, 1615, 1510, 1452, 1323, 1261, 1113, 817, 607. HRMS (ESI) calcd. for: $C_{17}H_{12}F_3O_2^+$. [M+H]$^+$: 305.0784, found: 305.0812



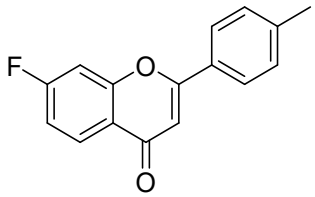
1g

2-(*p*-tolyl)-6-(trifluoromethoxy)-4H-chromen-4-one (1g): A slightly yellow needle-like crystal, yield 50%, m.p. 164.2-164.5 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 1.6 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 9.0 Hz, 1H), 7.52 (dd, *J* = 9.1, 3.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.78 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.4, 164.1, 154.2, 146.1 (d, *J* = 2.1 Hz), 142.8, 130.0, 128.6, 127.0, 126.4, 125.0, 120.6 (q, *J* = 258.8 Hz), 120.2, 117.4, 106.7, 21.6. FT-IR(Neat) ν_{max} cm^{-1}: 3079, 2962, 1634, 1616, 1480, 1252, 1159, 820, 737. HRMS (ESI) calcd. for: $C_{17}H_{12}F_3O_3^+$. $[M+H]^+$: 321.0733, found: 321.0760.



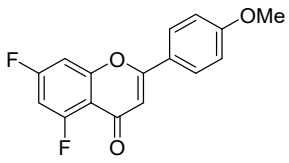
1h

6-fluoro-2-(p-tolyl)-4H-chromen-4-one (1h): A yellow solid, yield 48%, m.p. 149.8-151.2 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 8.2, 3.1 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.58 (dd, *J* = 9.1, 4.1 Hz, 1H), 7.42 (ddd, *J* = 9.1, 7.6, 3.1 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 2H), 6.79 (d, *J* = 0.5 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.7, 164.0, 159.7 (d, $^{1}J_{CF}$ = 247.0 Hz), 152.6, 142.6, 130.0, 128.8, 126.4, 125.3 (d, $^{3}J_{CF}$ = 7.2 Hz), 121.9 (d, $^{2}J_{CF}$ = 25.2 Hz), 120.2 (d, $^{3}J_{CF}$ = 7.6 Hz), 110.8 (d, $^{2}J_{CF}$ = 23.7 Hz), 106.4, 21.7. FT-IR(KBr) ν_{max} cm^{-1}: 3070, 2920, 1640, 1583, 1480, 1384, 1179, 816. HRMS (ESI) calcd. for $C_{16}H_{12}FO_2^+$ $[M+H]^+$: 255.0816, found: 255.0816.



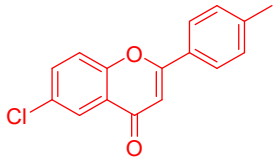
1i

7-fluoro-2-(p-tolyl)-4H-chromen-4-one (1i): A white crystal, yield 51%, m.p. 153.8-156.6 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.22 (ddd, *J* = 8.8, 6.3, 1.5 Hz, 1H), 7.78 (dd, *J* = 8.3, 2.0 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.23 (dt, *J* = 9.0, 2.2 Hz, 1H), 7.13 (tt, *J* = 8.5, 1.9 Hz, 1H), 6.76 (d, *J* = 1.8 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.6, 165.7 (d, $^{1}J_{CF}$ = 254.6 Hz), 164.0, 157.3 (d, $^{3}J_{CF}$ = 13.3 Hz), 142.6, 129.9, 128.6, 128.27 (d, $^{3}J_{CF}$ = 10.7 Hz), 126.3, 120.9, 114.0 (d, $^{2}J_{CF}$ = 22.4 Hz), 107.1, 104.9 (d, $^{2}J_{CF}$ = 25.1 Hz), 21.7. FT-IR(KBr) ν_{max} cm^{-1}: 3071, 1643, 1624, 1442, 1366, 1252, 1149, 814. HRMS (ESI) calcd. for $C_{16}H_{12}FO_2^+$ $[M+H]^+$: 255.0816, found: 255.0814.



1j

5,7-difluoro-2-(4-methoxyphenyl)-4H-chromen-4-one (1j): A white needle-like crystal, yield 45%, m.p. 257.3-259.9 °C. ^{1}H NMR [500 MHz, Chloroform-*d*/CF_3COOH (one drop)] δ 7.93 (d, *J* = 9.0 Hz, 2H), 7.24 (dt, *J* = 8.5, 2.0 Hz, 1H), 7.20 (s, 1H), 7.07 (d, *J* = 8.9 Hz, 2H), 6.98 (ddd, *J* = 10.9, 8.8, 2.4 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$/CF_3COOH(one drop)) δ 178.8, 167.0, 166.2 (dd, *J* = 259.7, 14.9 Hz), 164.3, 162.7 (dd, *J* = 265.1 Hz, 14.1 Hz), 158.2 (dd, *J* = 15.8, 5.5 Hz), 129.3, 121.6, 115.2, 109.6 (dd, *J* = 10.2, 5.4 Hz), 104.8, 103.5 (t, *J* = 24.9 Hz), 101.8 (dd, *J* = 24.8, 5.1 Hz), 55.9. FT-IR(KBr) ν_{max} cm^{-1}: 3081, 1640, 1616, 1515, 1426, 1381, 1300, 1143, 1028, 827. HRMS (ESI) calcd. for $C_{16}H_{11}F_2O_3^+$ $[M+H]^+$: 289.0671, found: 289.0670.



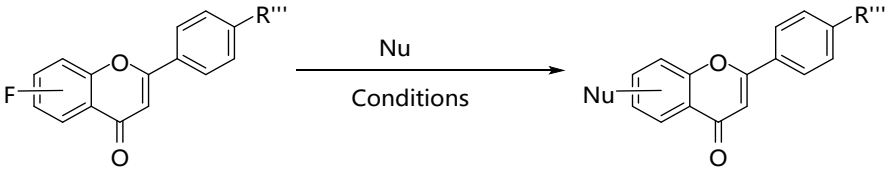
1k

6-methyl-2-(*p*-tolyl)-4H-chromen-4-one (1k). A white powder, yield 56%, m.p. 185.0-186.4 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 2.6 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.61 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.50 (d, *J* = 8.9 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.77 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.3, 164.0, 154.6, 142.7, 133.9, 131.2, 130.0, 128.6, 126.4, 125.2, 125.0, 119.9, 106.9, 21.7.

FT-IR(Neat) ν_{max} cm^{-1}: 2921, 1635, 1612, 1567, 1436, 1358, 1115, 1035, 814. HRMS (ESI) calcd. for: $C_{16}H_{12}ClO_2^+$. $[M+H]^+$: 271.0520, found: 271.0519.

4. Derivatization of fluoroflavone

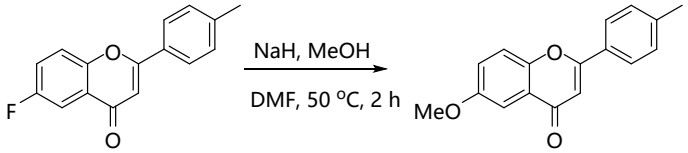
Table S2. Derivatization of fluoroflavone



(R''' = Me, OMe)

4.1. Alcoholysis of 1h, 1i, 1j

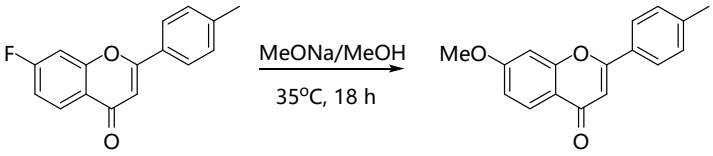
Alcoholysis of **1h:**



1h **1ha**

MeOH (0.18 mL, 4.5 mmol, 10.0 eq.) and NaH [72 mg (60 wt%, mineral oil dispersion), 1.8 mmol, 4.0 eq.] were added to a solution of fluoroflavone **1h** (115 mg, 0.45 mmol, 1.0 eq.) in 3 mL DMF. The solution was stirred for 2 h at 50 °C. The reaction mixture was acidified by adding 10 mL 1 M HCl. The mixture was separated, and aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (silica gel, petroleum ether: ethyl acetate 3:1 v/v) to afford 60 mg **1ha** as a yellow solid, yield 50%, m.p. 144.6-146.9 °C,. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 3.1 Hz, 1H), 7.50 (d, J = 9.1 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.28 (dd, J = 9.1, 3.1 Hz, 1H), 6.79 (s, 1H), 3.91 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.5, 163.5, 157.1, 151.2, 142.3, 129., 129.2, 126.3, 124.7, 123.8, 119.6, 106.4, 105.0, 56.1, 21.7. FT-IR(KBr) ν_{max} cm^{-1}: 2925, 1635, 1616, 1487, 1357, 1024, 826. HRMS (ESI) calcd. for $C_{17}H_{15}O_3^+$ $[M+H]^+$: 267.1016, found: 267.1014.

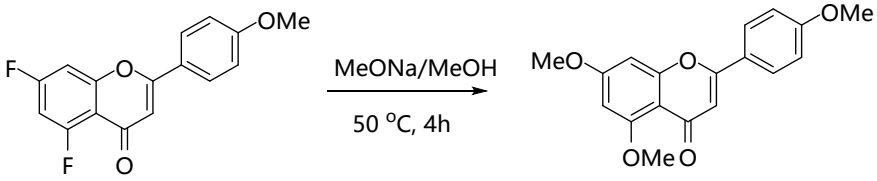
Alcoholysis of **1i:**



1i **1ia**

A solution of fluoroflavone **1i** (150 mg, 0.59 mmol, 1.0 eq.) was stirred in the presence of NaOMe (320 mg, 5.9 mmol, 10.0 eq.) at 35 ℃ for 12 h. The reaction mixture was concentrated in vacuo and purified by column chromatography (silica gel, petroleum ether: ethyl acetate 3:1 v/v) to afford 108 mg **1ia** as a slightly yellow needle-like crystal, yield 69%, m.p. 128.8-130.6 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 2H), 6.95 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.93 (d, *J* = 2.3 Hz, 1H), 6.71 (s, 1H), 3.91 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 178.0, 164.2, 163.3, 158.0, 142.1, 129.8, 129.1, 127.1, 126.2, 117.9, 114.4, 107.0, 100.5, 55.9, 21.6. FT-IR(KBr) ν_{max} cm^{-1}: 3029, 2955, 1652, 1605, 1439, 1376, 1273, 1160, 1022, 812. HRMS (ESI) calcd. for $C_{17}H_{15}O_3^+$ $[M+H]^+$: 267.1016, found: 267.1016.

Alcoholysis of **1j:**

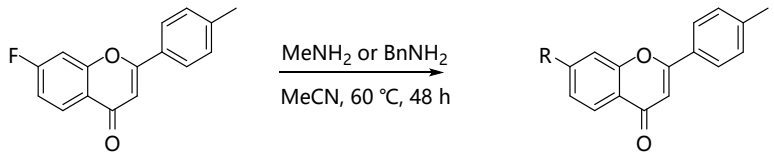


1j **1db**

A solution of fluoroflavone **1j** (80 mg, 0.28 mmol, 1.0 eq.) was stirred in the presence of NaOMe (159 mg, 2.8 mmol, 10 eq.) at 50 °C for 4 h. The reaction mixture was concentrated in vacuo and purified by column chromatography (silica gel, petroleum ether: ethyl acetate 2:1 v/v) to afford 72 mg of **1db** as a slightly yellow solid, yield 83% m.p. 146.0-148.4 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.59 (s, 1H), 6.52 (d, *J* = 2.3 Hz, 1H), 6.33 (d, *J* = 2.3 Hz, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 3.85 (s, 3H). 13C NMR (126 MHz, Chloroform-d) δ 177.9, 164.0, 162.1, 160.9, 160.8, 159.9, 127.7, 123.8, 114.4, 109.2, 107.6, 96.1, 92.8, 56.5, 55.8, 55.6. HRMS (ESI) calcd. for $C_{18}H_{17}O_5^+$ $[M+H]^+$: 313.1071, found: 313.1070.

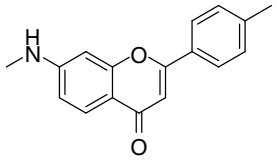
4.2. Aminolysis, Mercaptolysis and azidation of 1i

Aminolysis of 1i:



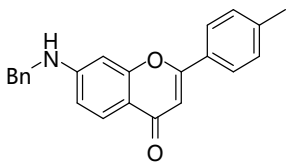
1i **1ib,** R=NHMe
1ic, R=NHBn

General procedure: A solution of fluoroflavone **1i** (40 mg, 0.16 mmol, 1.0 eq.) was stirred in the presence of amine (1.6 mmol, 10 eq.) at 60 ℃ for 48 h. The reaction mixture was concentrated in vacuo and purified by column chromatography (silica gel, petroleum ether: ethyl acetate 1:1 v/v) to afford **1ib** or **1ic**.



1ib

7-(methylamino)-2-(p-tolyl)-4H-chromen-4-one (1ib). A yellow solid, yield 73%, m.p. 152.0-153.4 °C,. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, J = 8.7 Hz, 1H), 7.79 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.68 (s, 1H), 6.63 (dd, J = 8.7, 2.2 Hz, 1H), 6.53 (d, J = 2.1 Hz, 1H), 4.42 (s, 1H), 2.95 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 178.0, 162.6, 159.0, 154.0, 141.7, 129.8, 129.6, 126.8, 126.1, 114.9, 112.8, 106.9, 96.4, 30.4, 21.6. FT-IR(Neat) ν_{max} cm^{-1}: 3306, 2920, 2852, 1622, 1581, 1412, 1370, 1250, 1186, 1098, 908, 816, 480. HRMS (ESI) calcd. for $C_{17}H_{16}NO_2^+$, 266.1174, found: 266.1176.

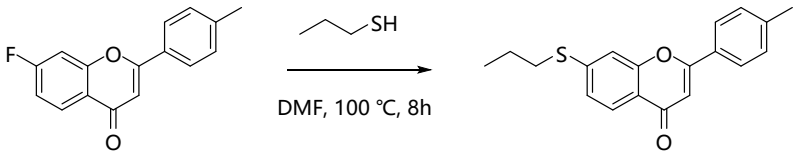


1ic

7-(benzylamino)-2-(p-tolyl)-4H-chromen-4-one (1ic). A yellow powder, yield 86%, m.p. 172.0-174.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$/DMSO-d_6 3:1) δ 7.78 (d, J = 8.8 Hz, 1H), 7.68 (d, J = 8.1 Hz, 2H), 7.33-7.25 (m, 4H), 7.23-7.18 (m, 3H), 6.70 (dd, J = 8.8, 1.9 Hz, 1H), 6.51 (s, 1H), 6.46 (d, J = 1.8 Hz, 2H), 4.35 (d, J = 5.5 Hz, 2H), 2.34 (s,

3H). 13C NMR (151 MHz, DMSO-d6) δ 176.7, 161.5, 158.0, 153.0, 140.9, 137.7, 129.0, 128.5, 128.0, 126.7, 126.7, 125.4, 125.2, 113.4, 112.5, 105.7, 95.7, 46.5, 20.8. FT-IR(Neat) ν_{max} cm^{-1}: 3265, 2920, 2853, 1609, 1558, 1434, 1380, 1251, 1151, 809, 714, 584, 474. HRMS (ESI) calcd. for $C_{23}H_{20}NO_2^+$, 342.1489, found: 342.1487.

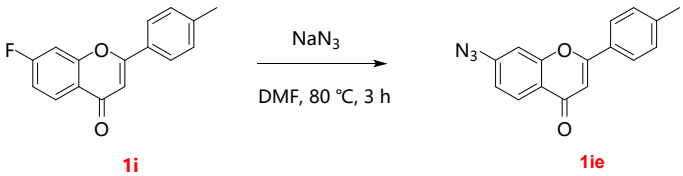
Mercaptolysis of 1i:



1i **1id**

A solution of fluoroflavone **1i** (50 mg, 0.2 mmol, 1.0 eq.) in 1.0 ml DMF was stirred in the presence of propanethiol (22 mg, 0.3 mmol, 1.5 eq.) at 100 ℃ for 1 h. The reaction mixture was concentrated in vacuo and purified by column chromatography (silica gel, petroleum ether: ethyl acetate 5:1 v/v) to afford 38 mg **1id** as a white powder, yield 62%, m.p. 117.6-119.0 °C**.** ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.30 (s, 1H), 7.28 (d, J = 7.8 Hz, 2H), 7.21 (d, J = 8.4 Hz, 1H), 6.71 (s, 1H), 3.00 (t, J = 7.3 Hz, 2H), 2.40 (s, 3H), 1.84-1.54 (m, 2H), 1.08 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.9, 163.2, 156.6, 146.2, 142.2, 129.8, 128.9, 126.2, 125.7, 123.8, 121.0, 114.3, 107.1, 34.1, 22.1, 21.1, 13.6. FT-IR(Neat) ν_{max} cm^{-1}: 3067, 2962, 2922, 1628, 1591, 1417, 1370, 1040, 912, 816. HRMS (ESI) calcd. for $C_{19}H_{19}SO_2^+$, 311.1100, found: 311.1109.

Azidation of 1i:



1i **1ie**

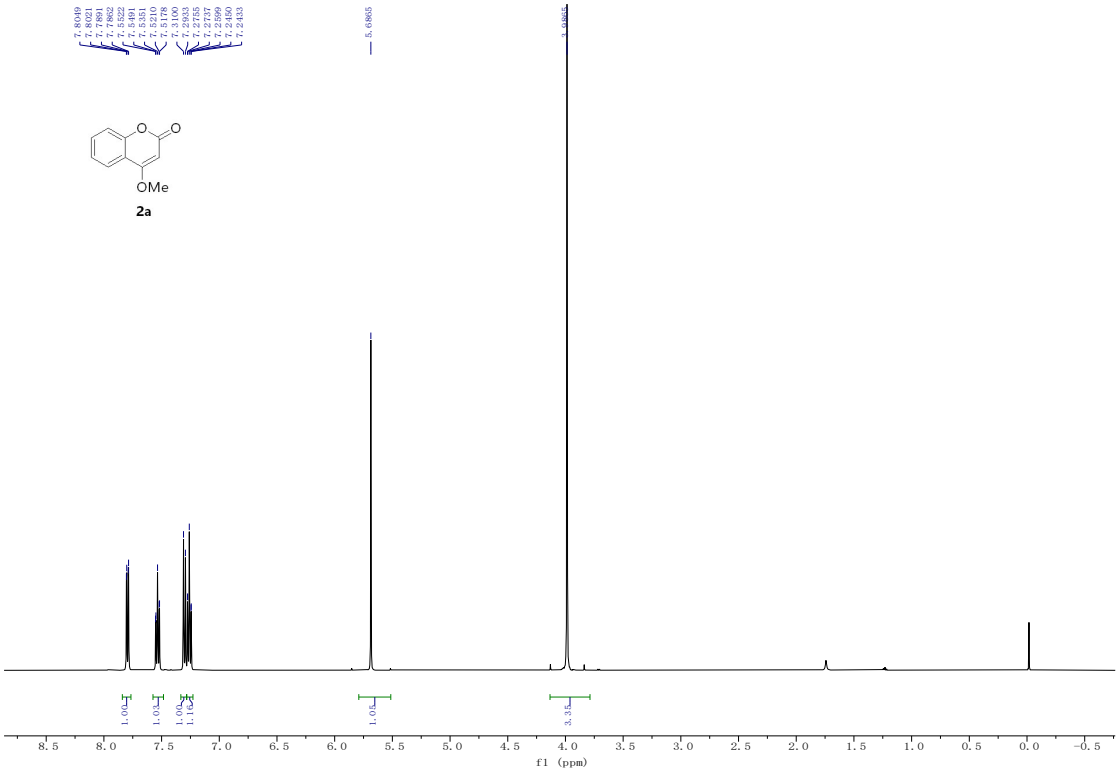
A solution of fluoroflavone **1i** (40 mg, 0.16 mmol, 1.0 eq.) in 1.0 ml DMF was stirred in the presence of NaN_3 (1.6 mmol, 10 eq.) at 80 ℃ for 3 h. The reaction mixture was concentrated in vacuo and purified by column chromatography (silica gel, petroleum ether: ethyl acetate 5:1 v/v) to afford **1ie** as an off-white powder, yield 90%, m.p. 138.0-139.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 2.0 Hz, 1H), 7.06 (dd, J = 8.5, 2.0 Hz, 1H),

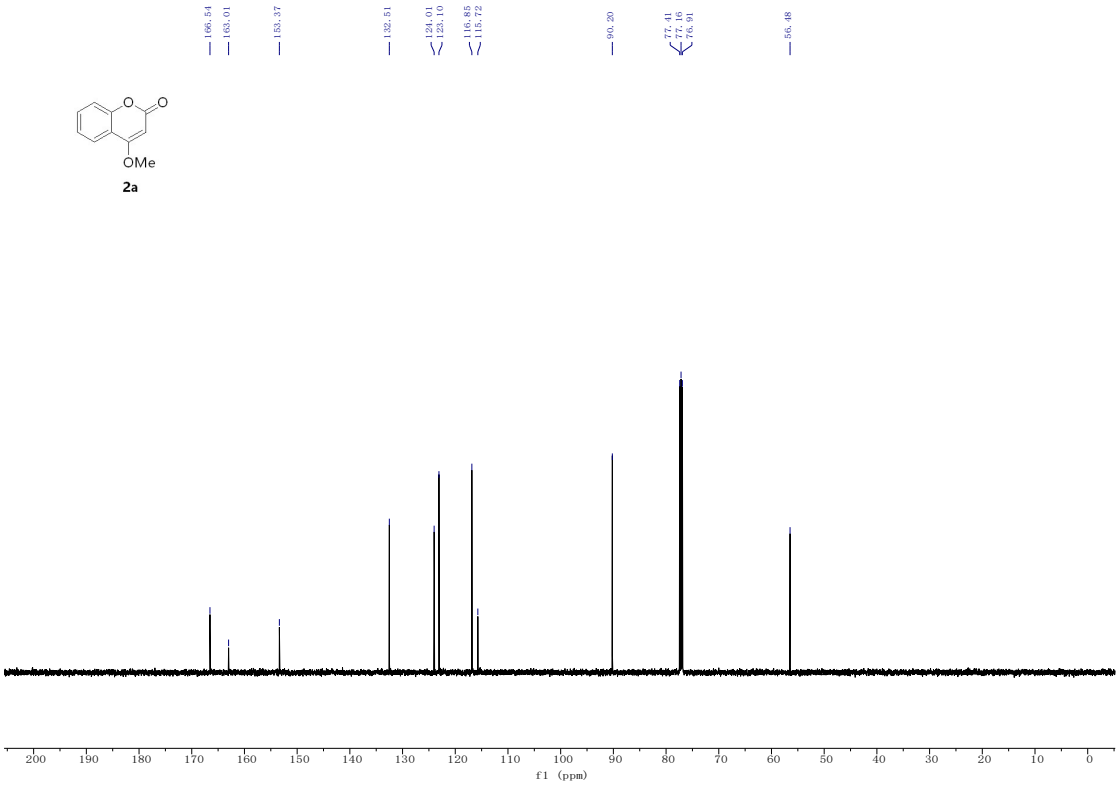
6.75 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.6, 163.7, 157.3, 145.9, 142.6, 130.0, 128.8, 127.8, 126.3, 121.2, 116.8, 107.7, 107.2, 21.7. FT-IR(Neat) ν_{max} cm^{-1}: 3064, 2918, 2115, 1645, 1601, 1442, 1373, 1287, 1037, 812. HRMS (ESI) calcd. for $C_{16}H_{12}N_3O_2^+$, 278.0924, found: 278.0927.

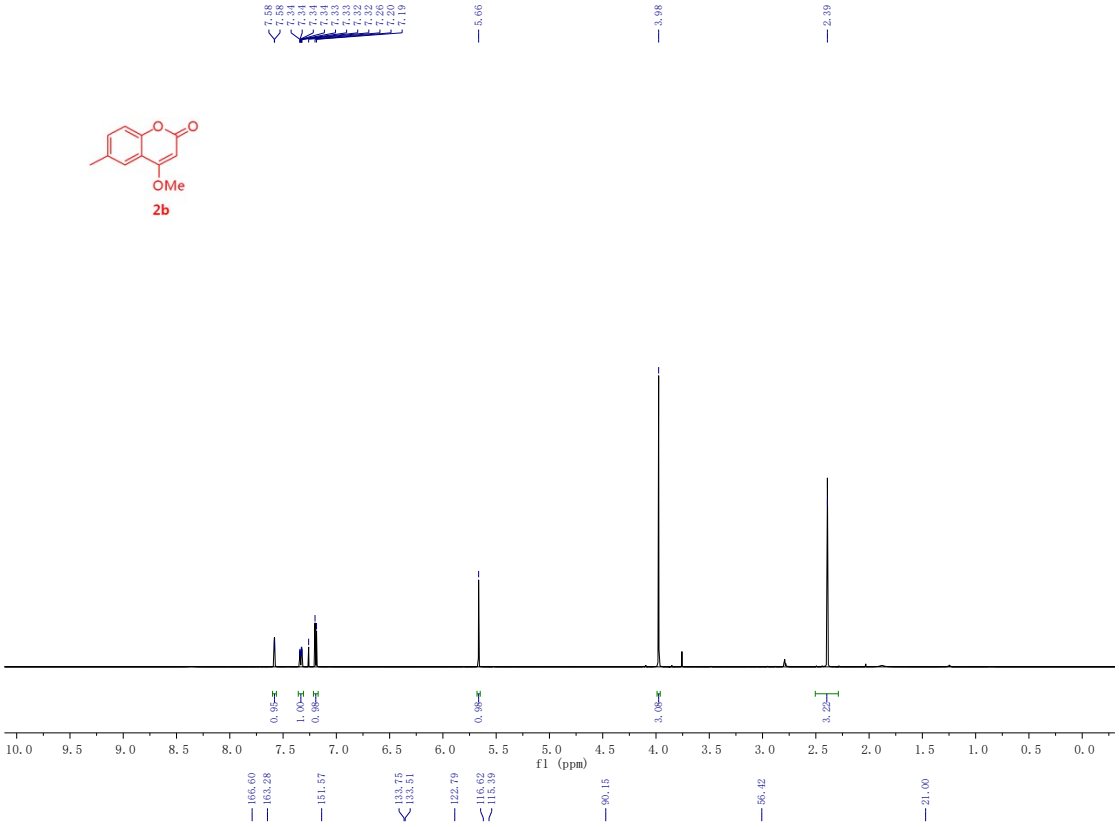
5. Reference:

1. P. Kumari, S. Gupta, C. Narayana, S. Ahmad, N. Vishnoi, S. Singh and R. Sagar, Stereoselective synthesis of carbohydrate fused pyrano[3,2-c]pyranones as anticancer agents, *New Journal of Chemistry*, 2018, **42**, 13985-13997.
2. S. Combes, J.-P. Finet and D. Siri, On the optical activity of the 3-aryl-4-hydroxycoumarin isolated from Millettia griffoniana: molecular modelling and total synthesis, *Journal of the Chemical Society, Perkin Transactions 1*, 2002, DOI: 10.1039/B108707J, 38-44.
3. G. Pandey, C. Muralikrishna and U. T. Bhalerao, Mushroom tyrosinase catalysed synthesis of coumestans, bebzofuranderivatives and related heterocyclic compounds, *Tetrahedron*, 1989, **45**, 6867-6874.

6. NMR spectra copies for synthetic compounds



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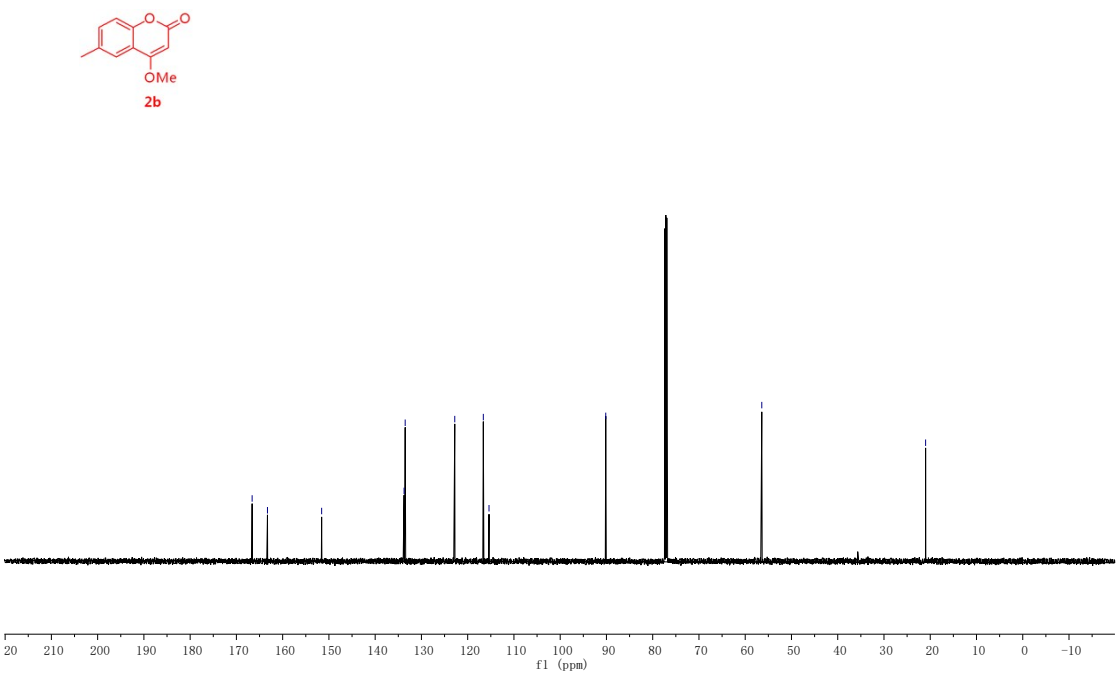
7.34
7.34
7.34
7.34
7.34
7.33
7.33
7.32
7.32
7.20
7.19
5.66
3.98
2.39
OMe
2b
0.95
1.00
0.98
0.98
3.08
3.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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163.28
151.57
133.75
133.51
122.79
116.62
115.39
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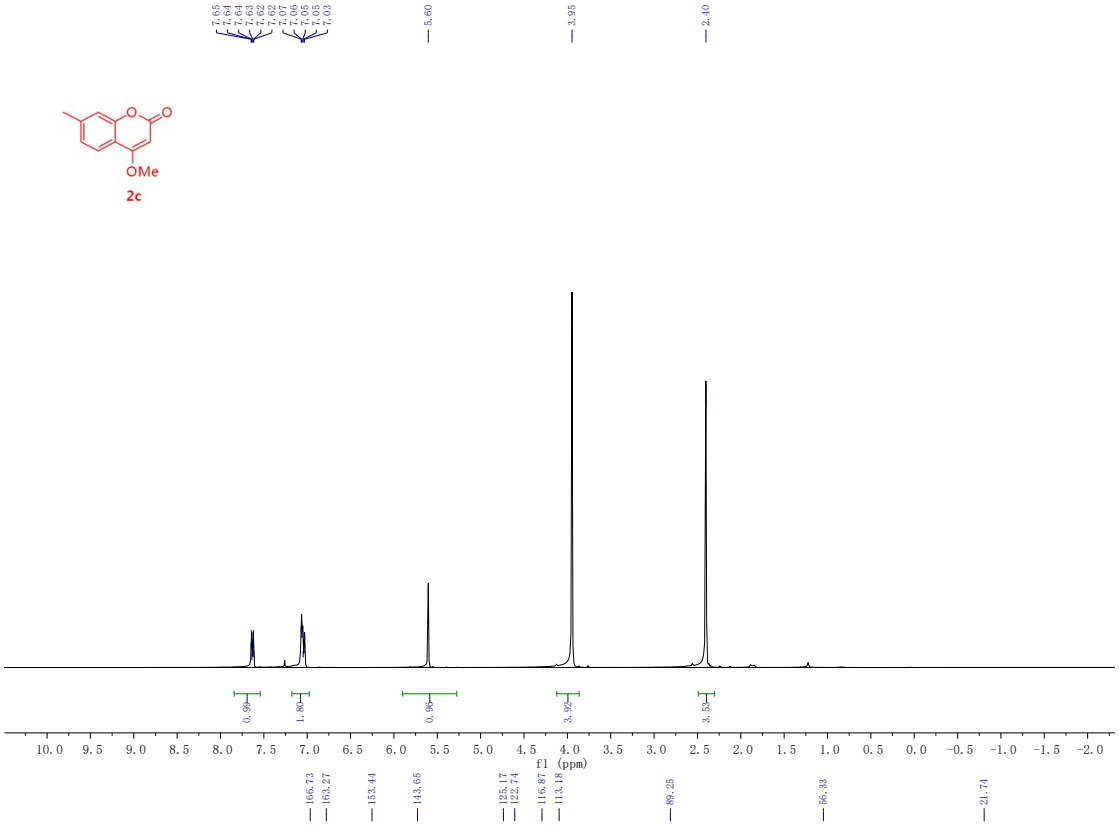
56.42
21.00
OMe
2b
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.64
7.63
7.62
7.62
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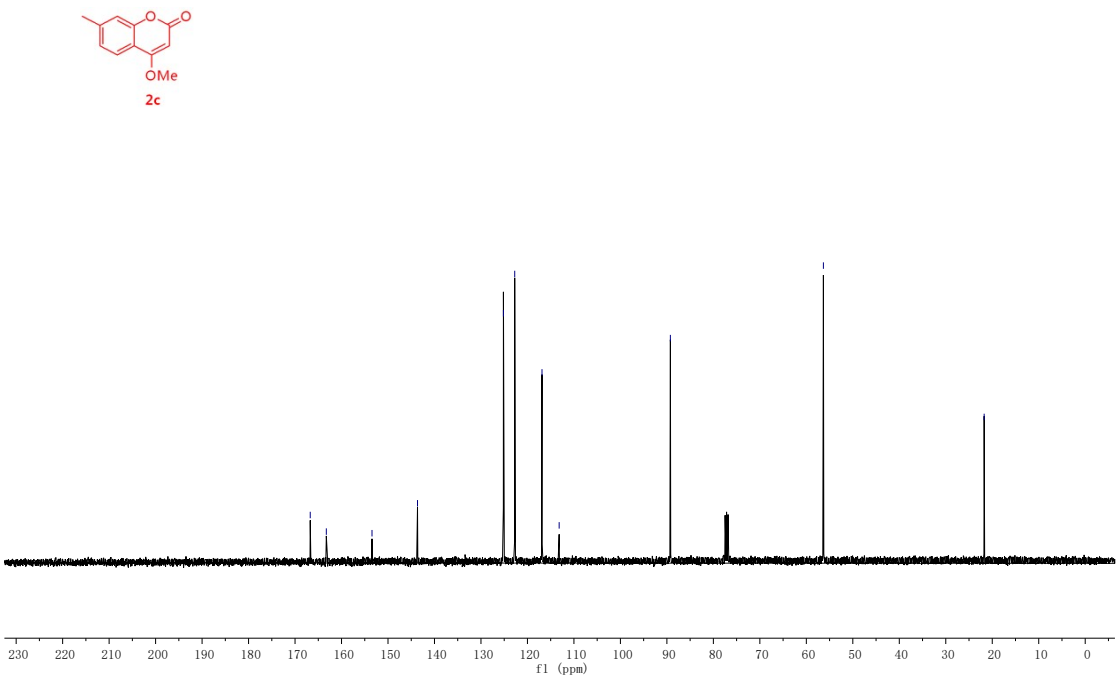
7.06
7.05
7.03
5.60
3.95
2.40
OMe
2c
0.99
1.80
0.96
3.92
3.53
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)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143.65
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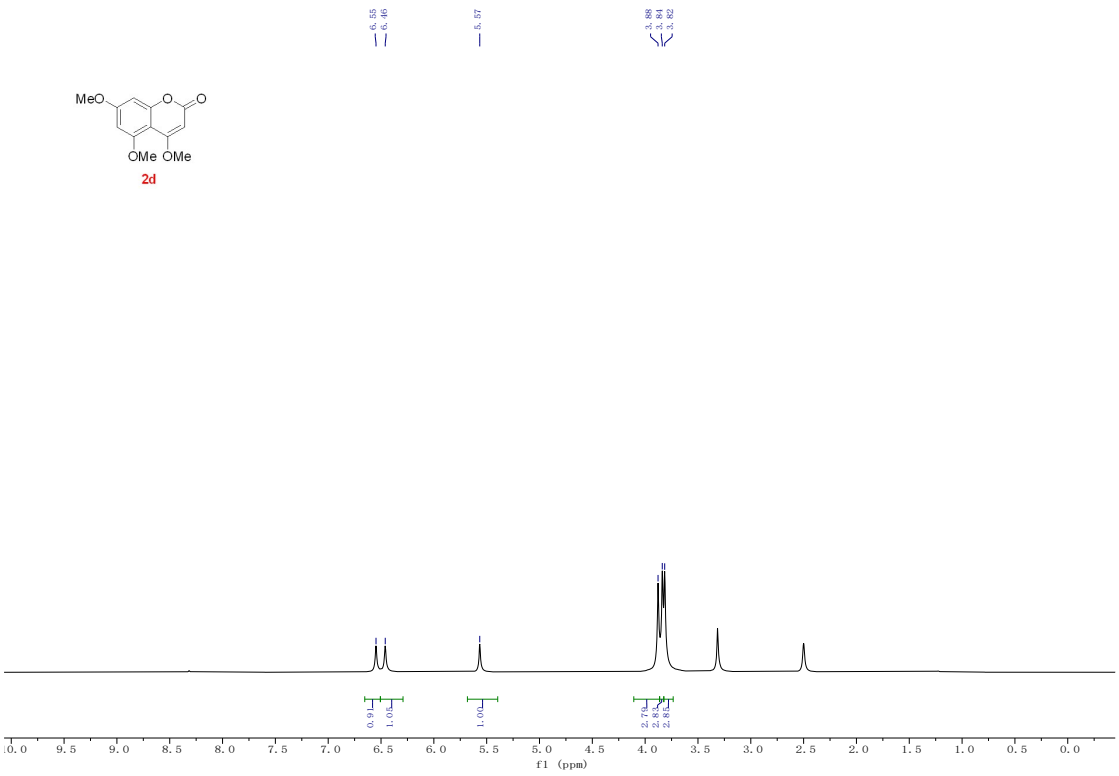
122.74
116.87
113.18
89.25
56.33
21.74
OMe
2c
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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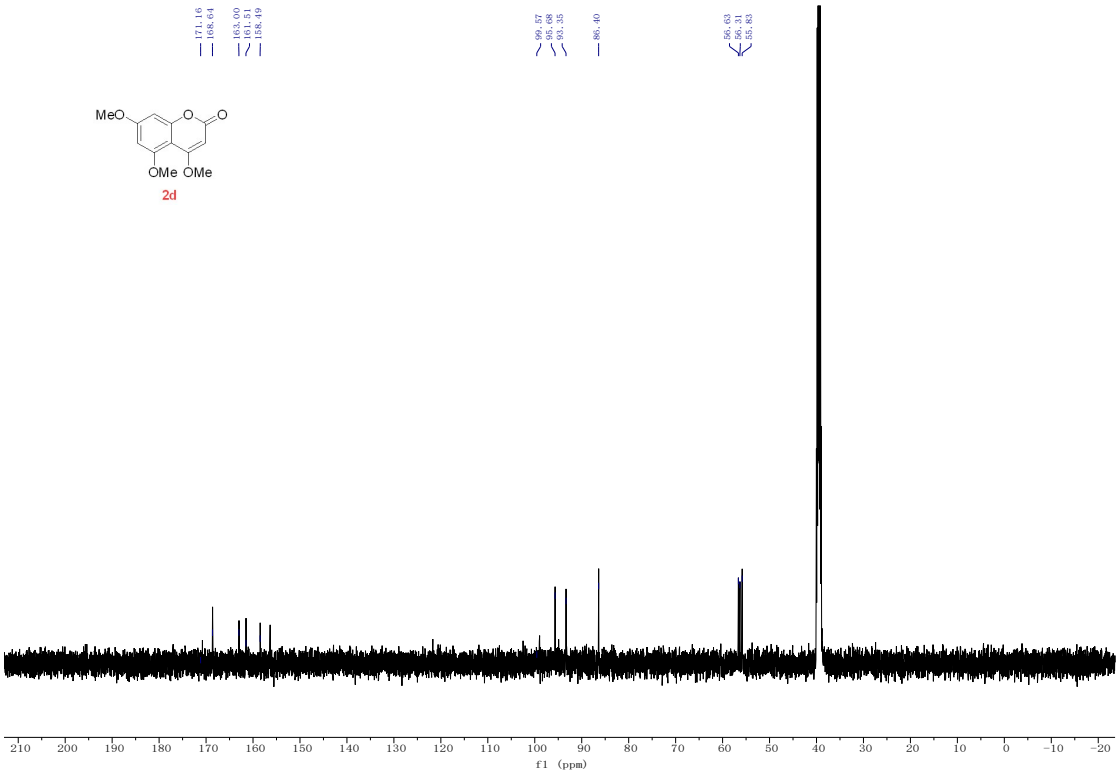
2.83
2.85
f1 (ppm)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56.63
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55.83
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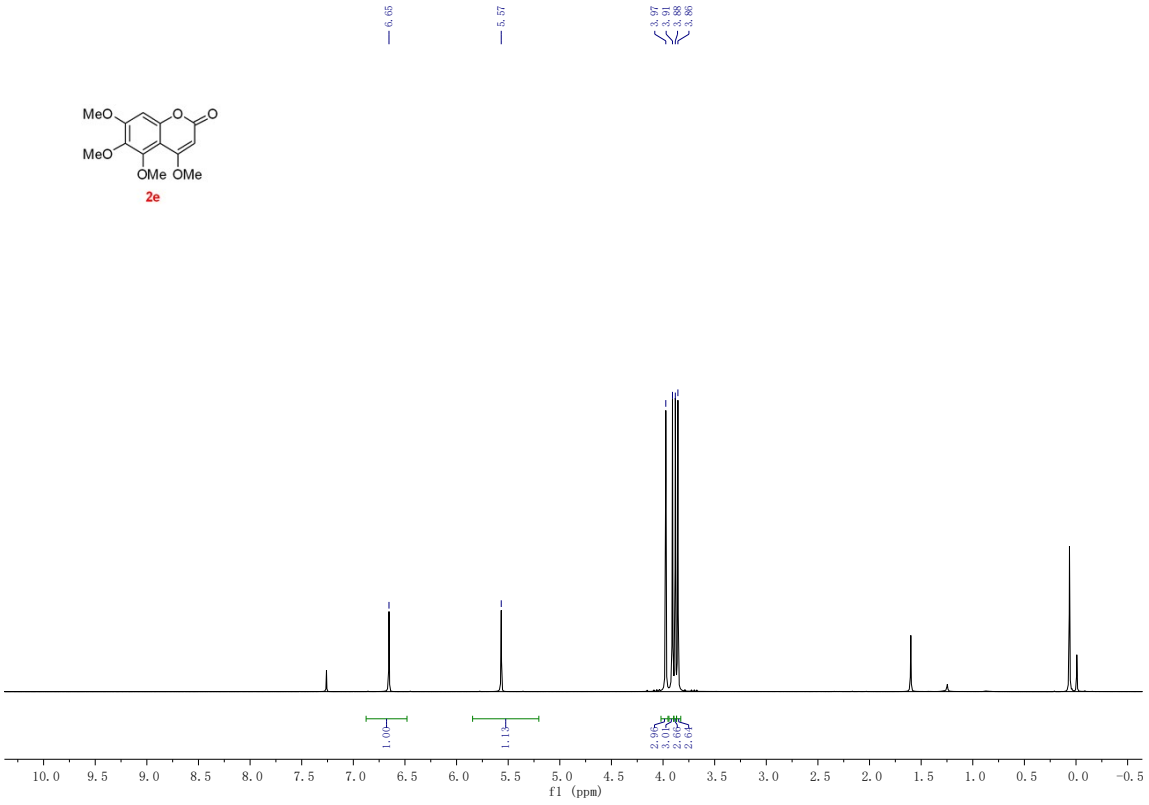
OMe OMe
2d
f1 (ppm)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3.88
3.86
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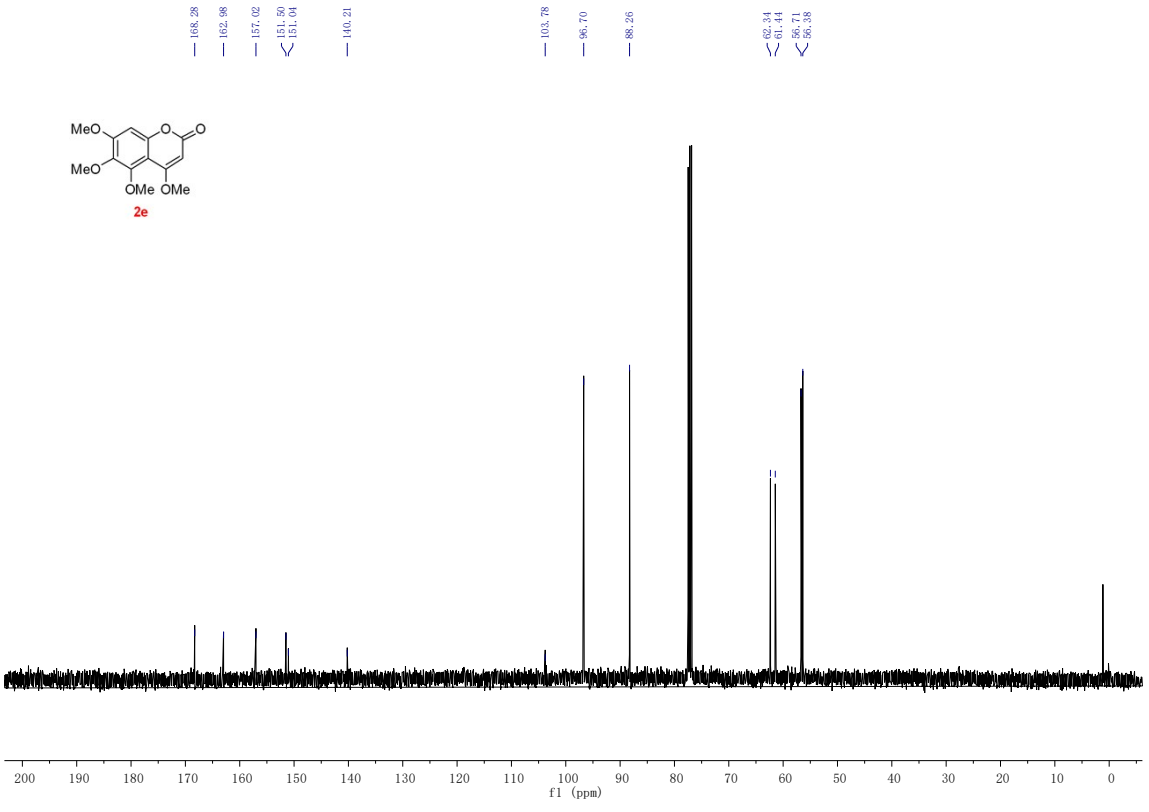
MeO
OMe OMe
O
O
2e
1.00
1.13
2.96
3.01
2.69
2.64
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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151.04
140.21
103.78
96.70
88.26
62.34
61.44
56.71
56.38
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MeO
OMe OMe
O
O
2e
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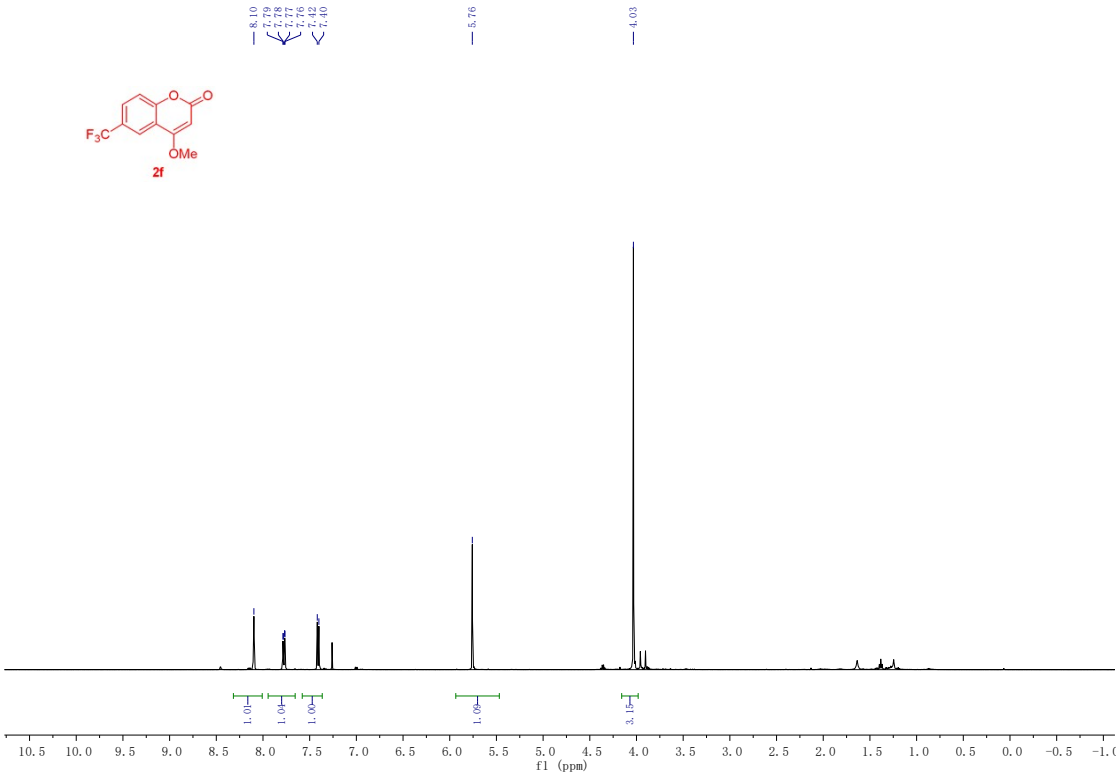
f1 (ppm)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7.78
7.77
7.76
7.42
7.40
5.76
4.03
F3C
OMe
2f
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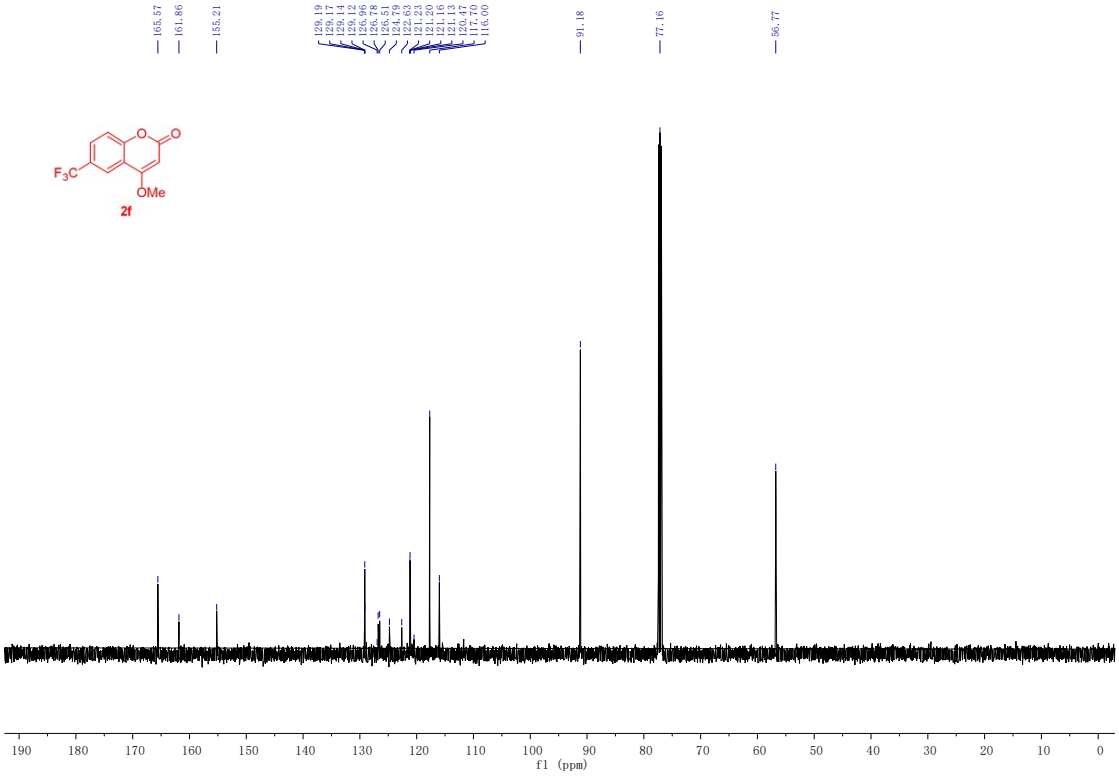
1.01
1.00
1.00
3.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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121.16
121.13
120.47
117.70
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56.77
F3C
OMe
2f
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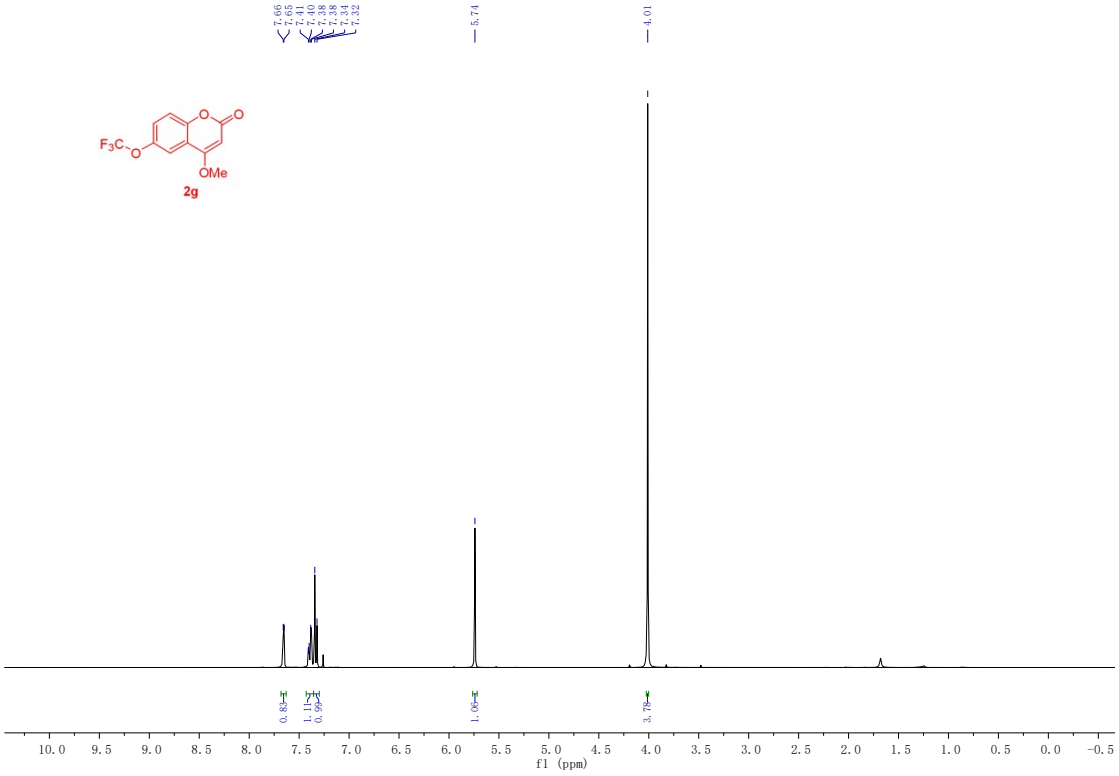
f1 (ppm)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7.32
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4.01
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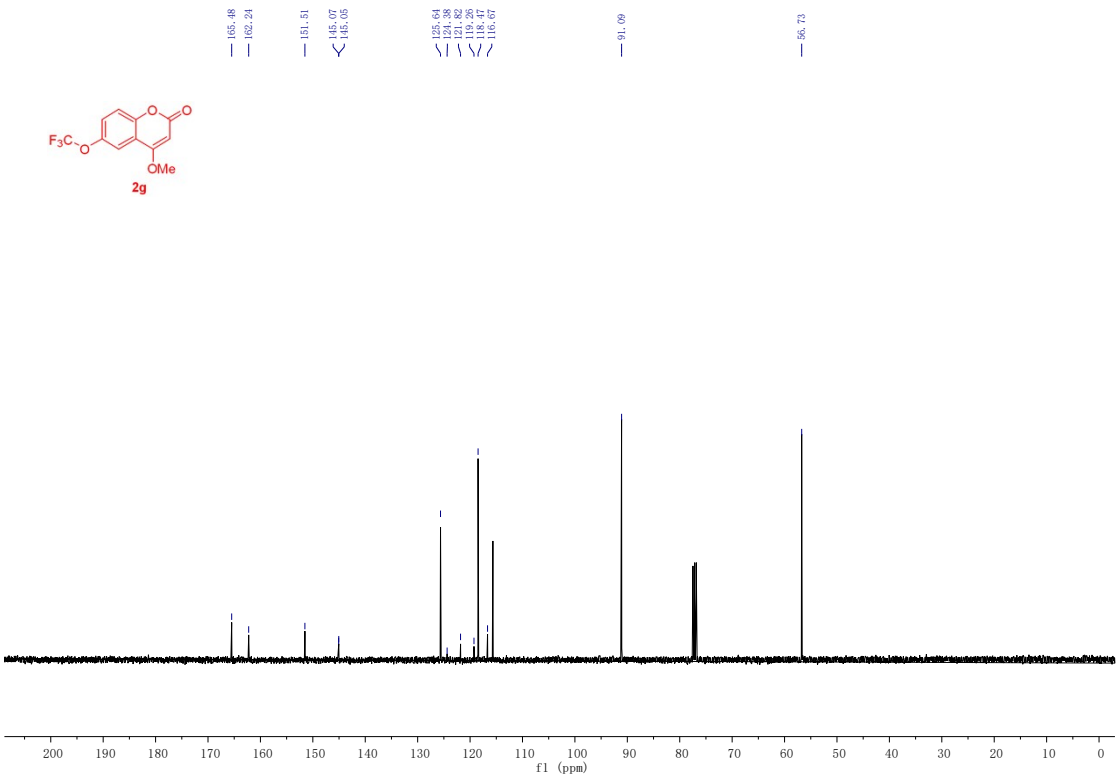
O
OMe
2g
0.82
1.11
0.99
1.04
3.78
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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O
OMe
2g
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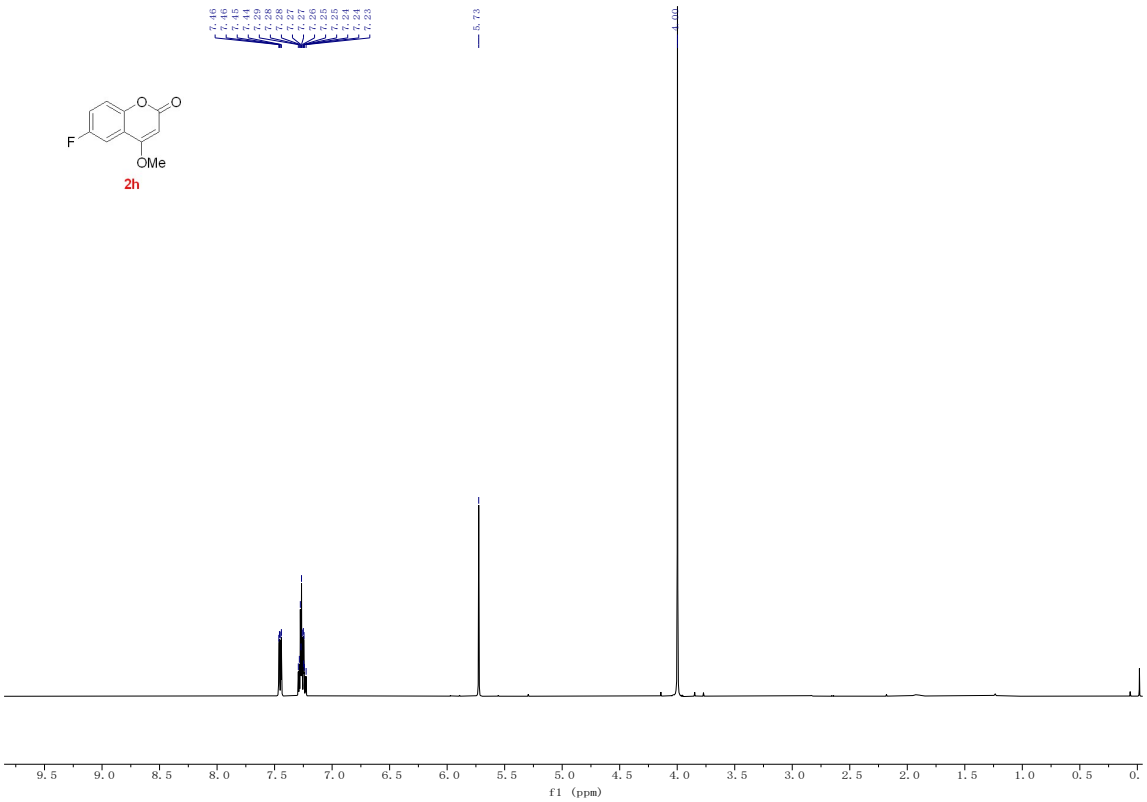
f1 (ppm)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O
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OMe
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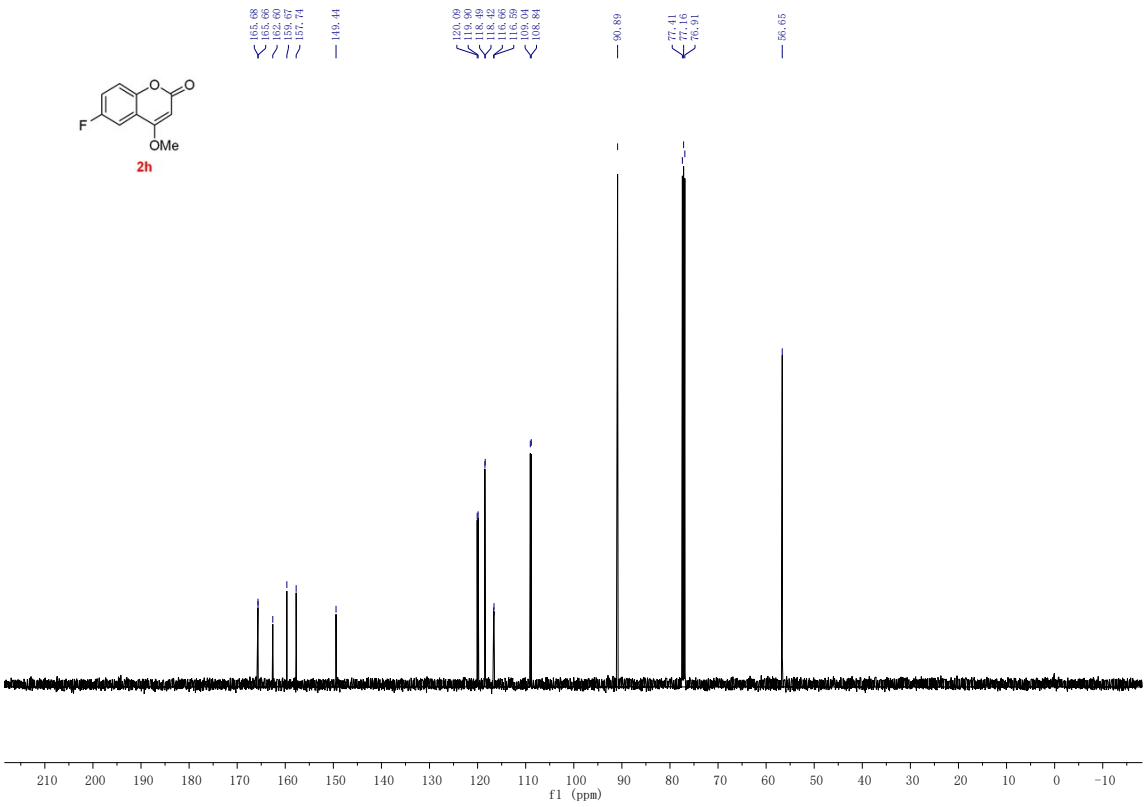
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200
190
180
170
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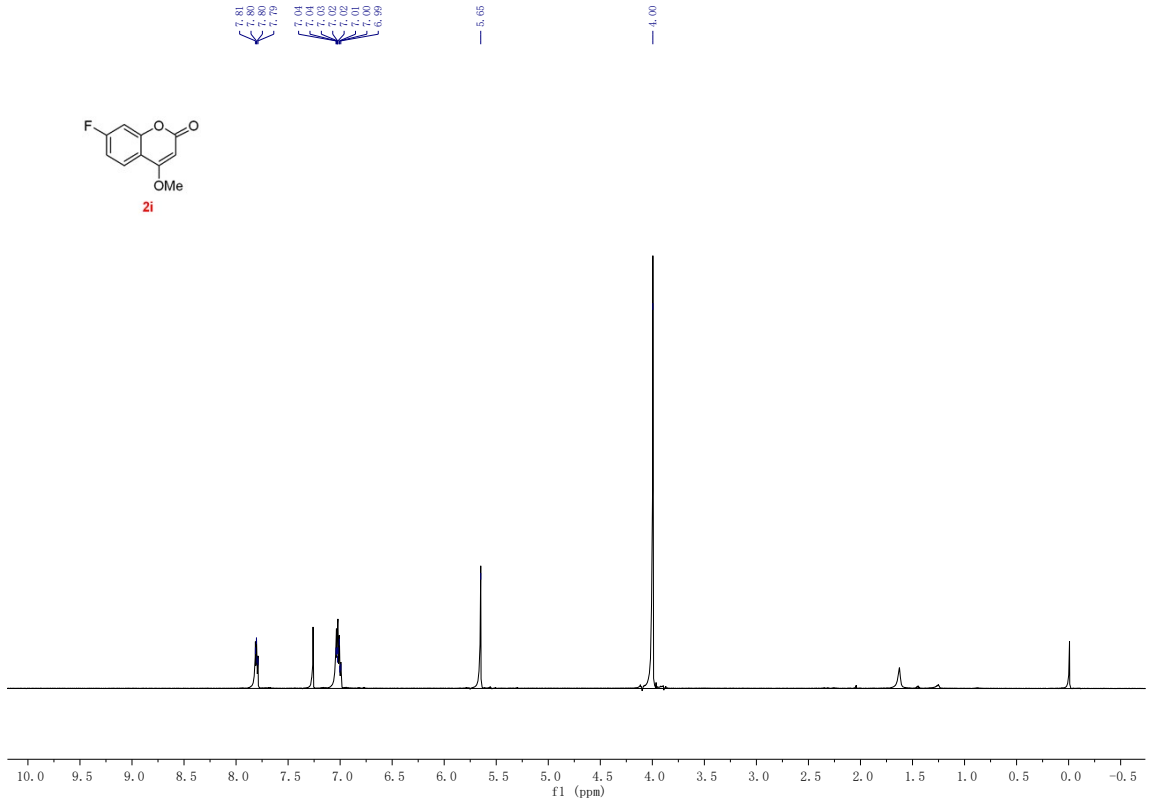
f1 (ppm)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4.00
F
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O
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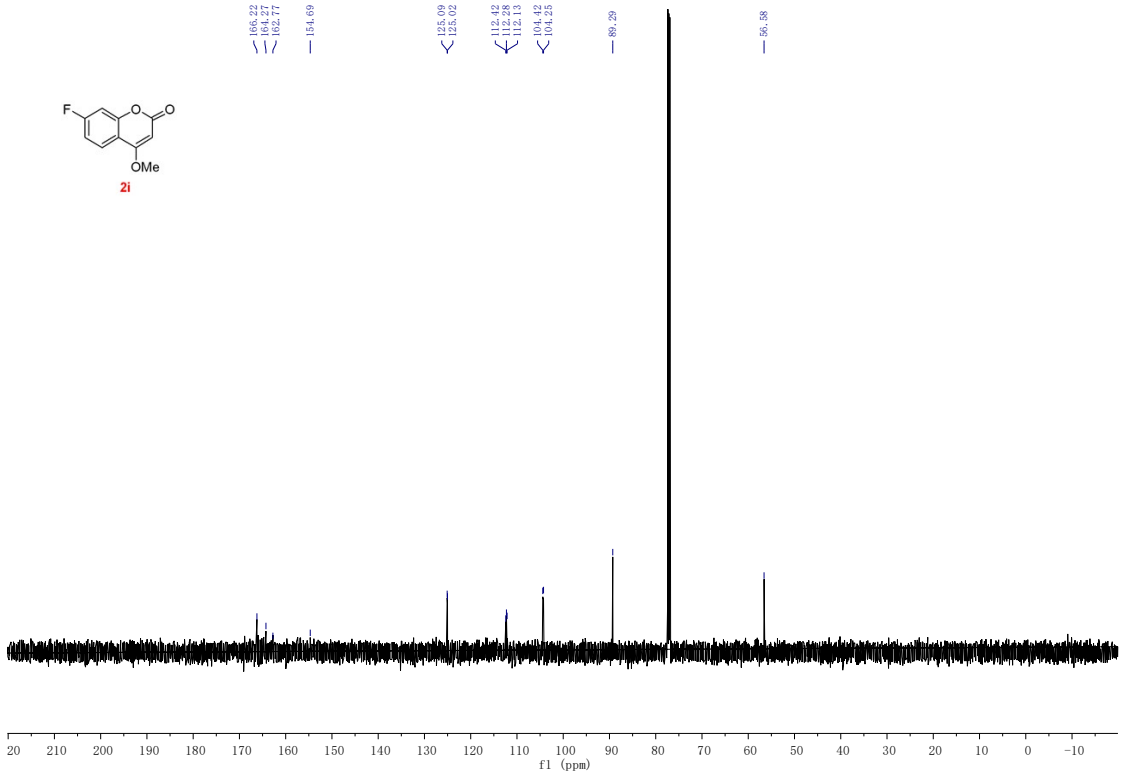
2i
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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O
O
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2i
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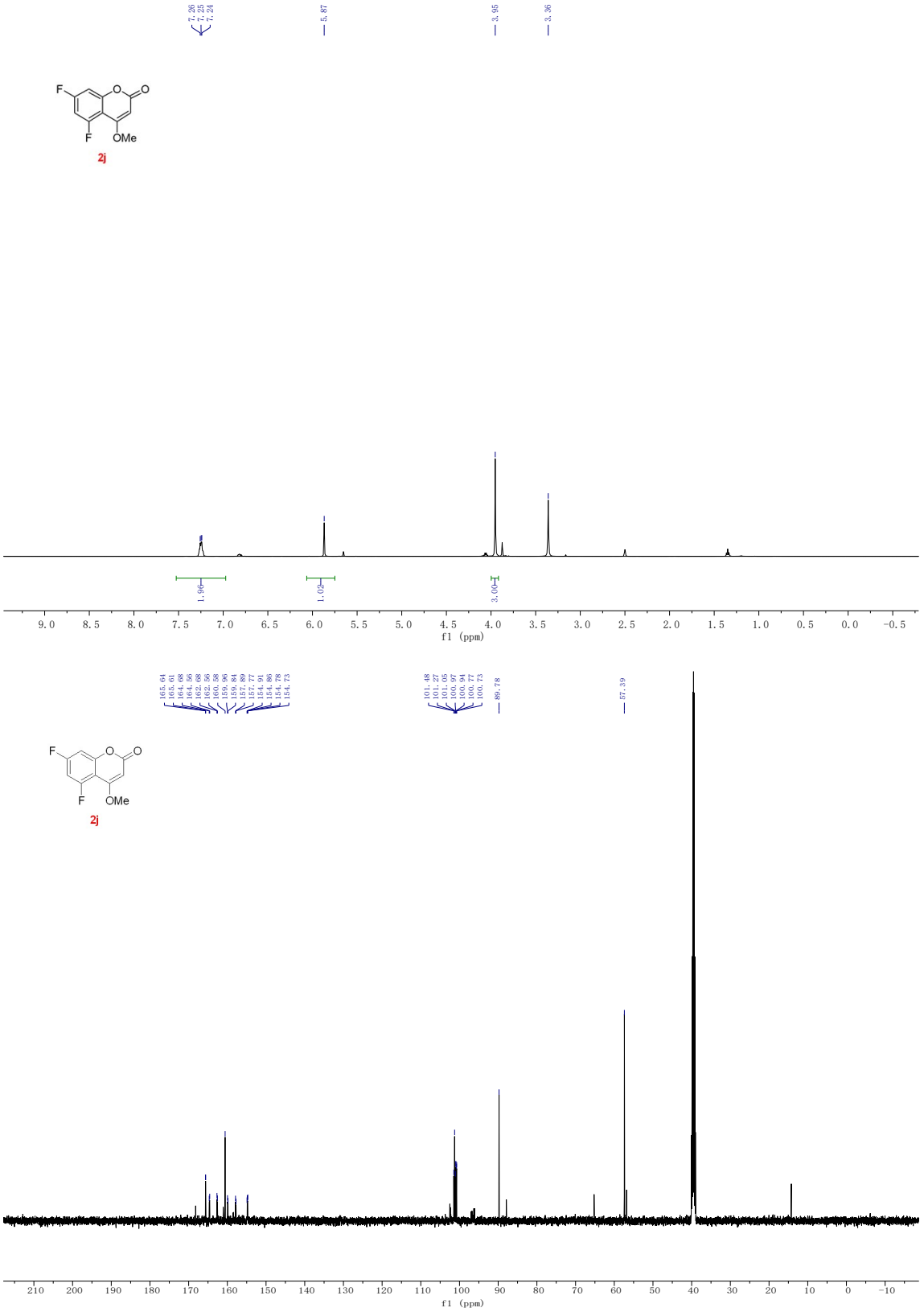
f1 (ppm)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2j
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3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
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154.73
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100.94
100.77
100.73
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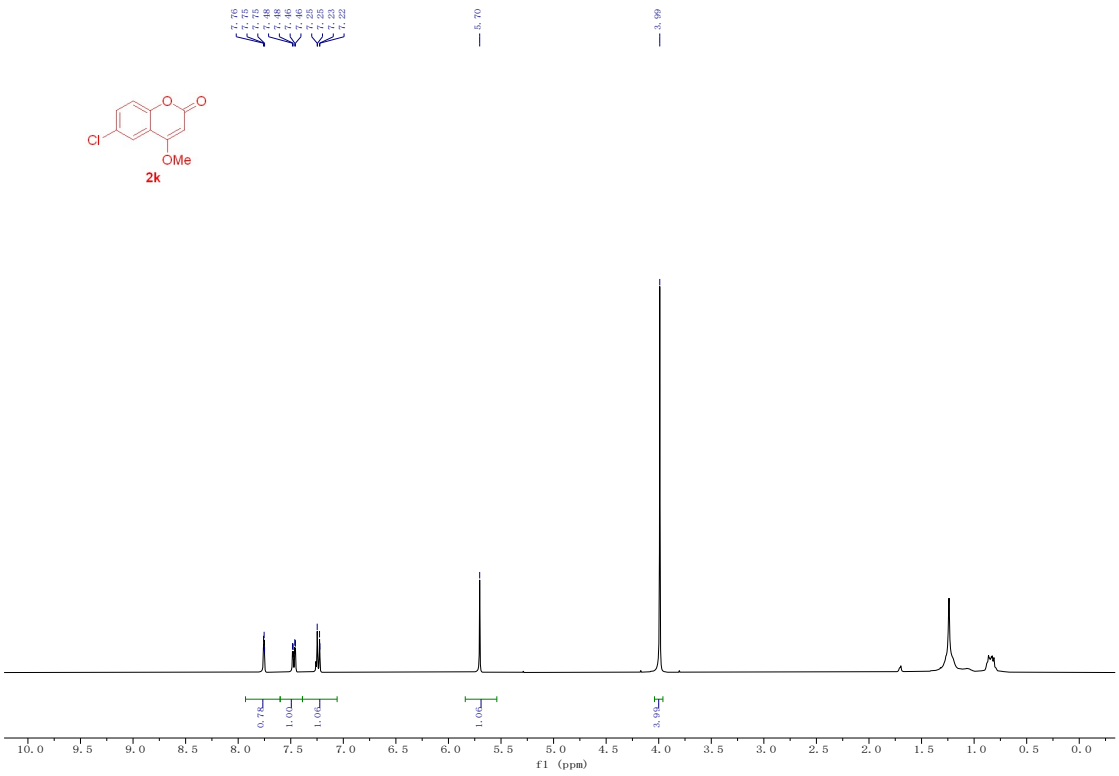
O
O
F
OMe
2j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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O
OMe
2k
0.78
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1.06
1.06
3.96
10.0
9.5
9.0
8.5
8.0
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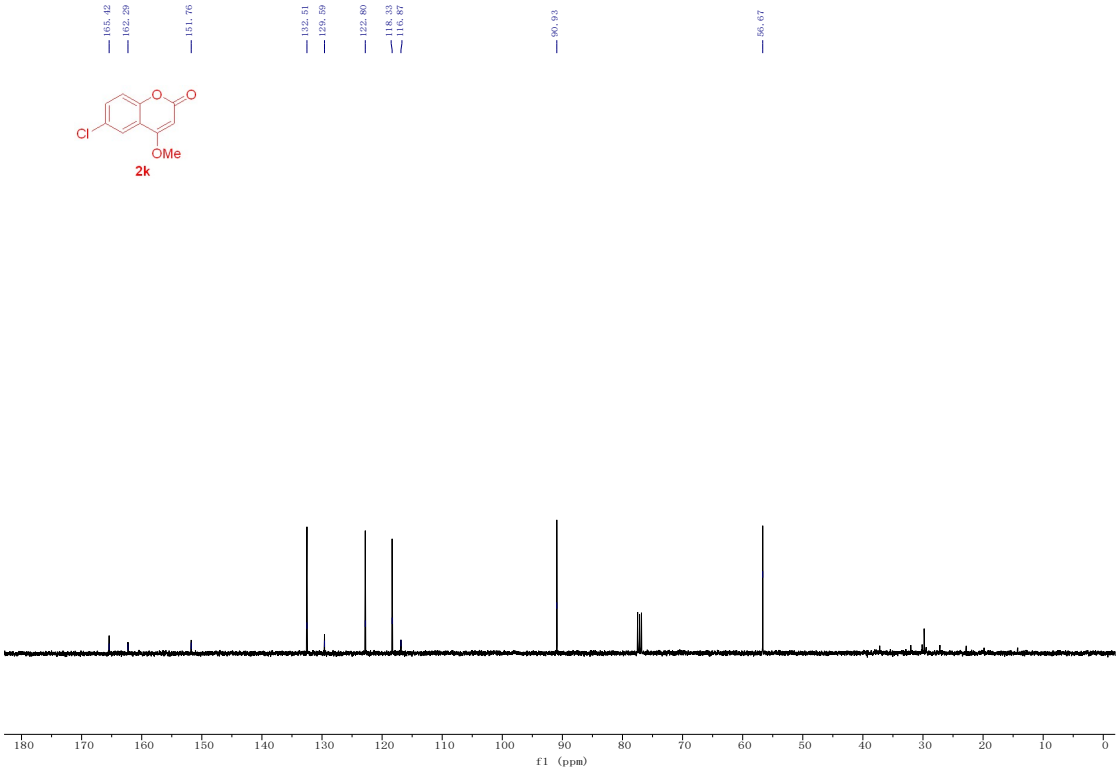
f1 (ppm)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Cl
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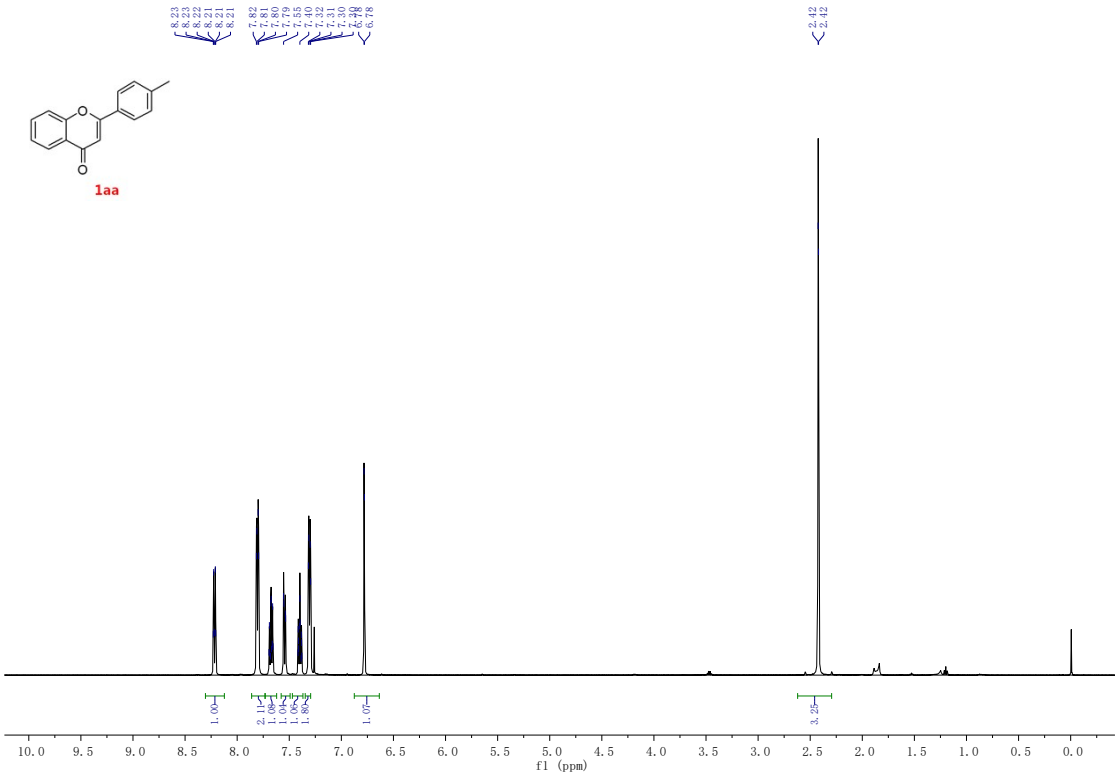
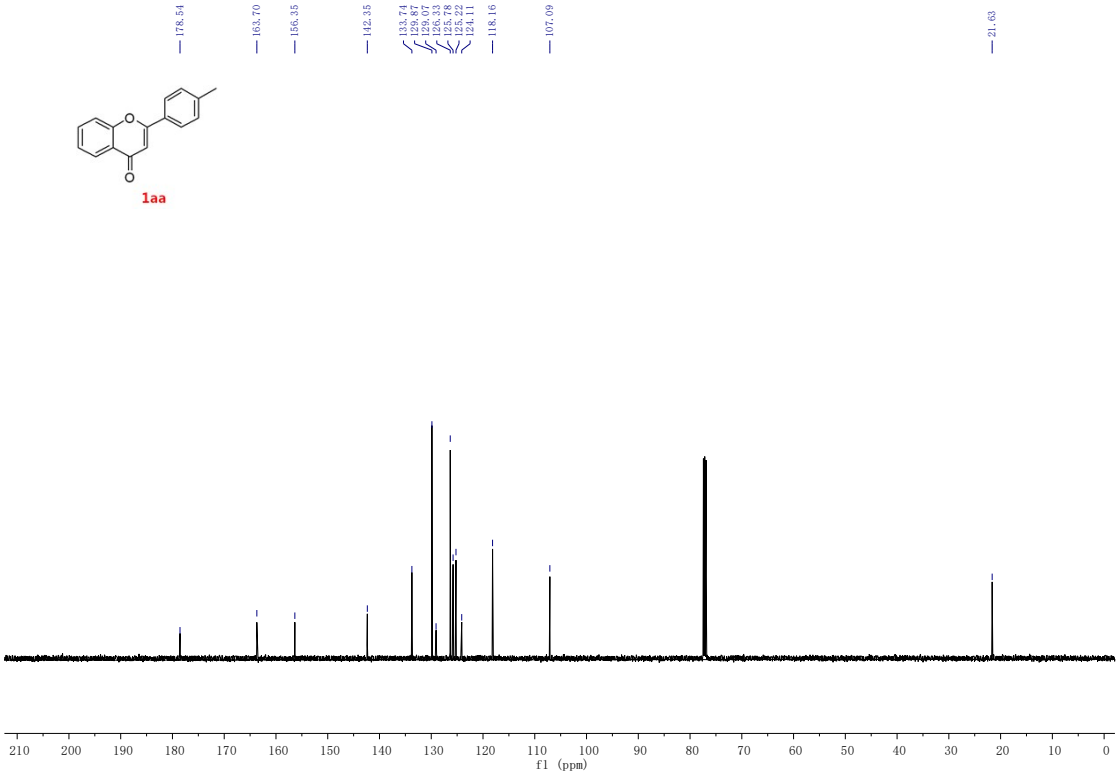
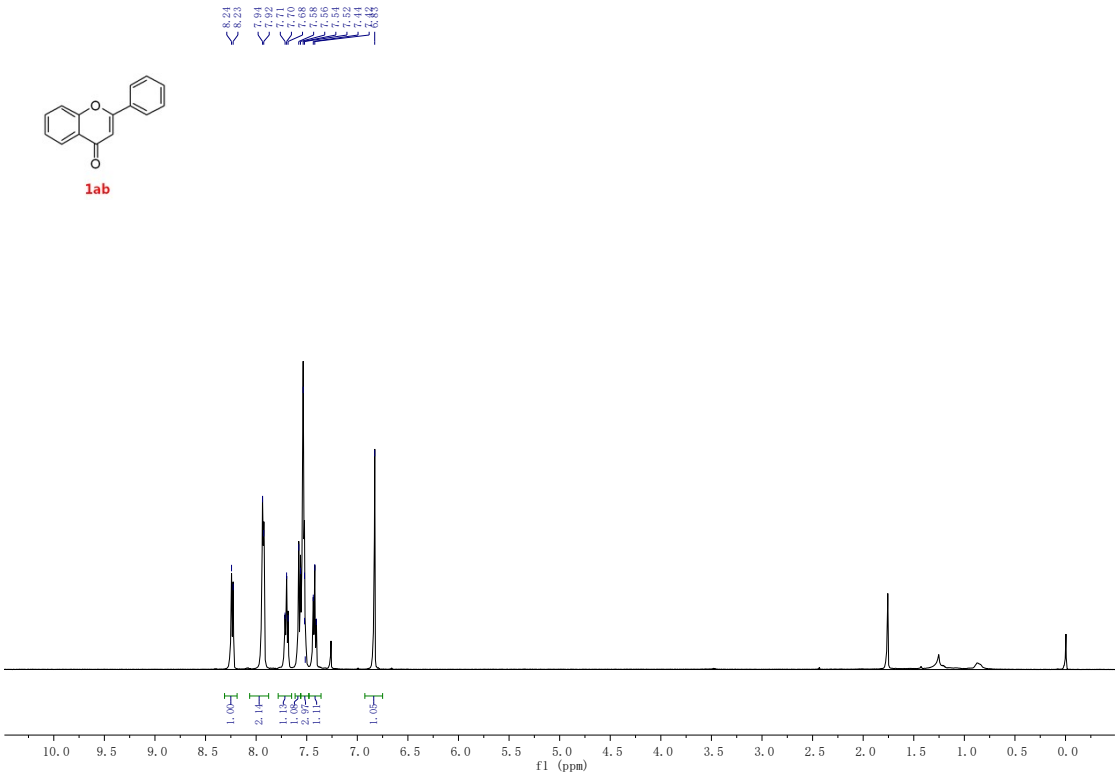
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.23
8.23
8.22
8.21
8.21
7.82
7.81
7.80
7.79
7.55
7.40
7.32
7.31
7.30
6.78
6.78
2.42
2.42
1aa
1.00
2.11
1.08
1.04
1.06
1.80
1.07
3.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


178.54
163.70
156.35
142.35
133.74
129.87
129.07
126.33
125.78
125.22
124.11
118.16
107.09
21.63
1aa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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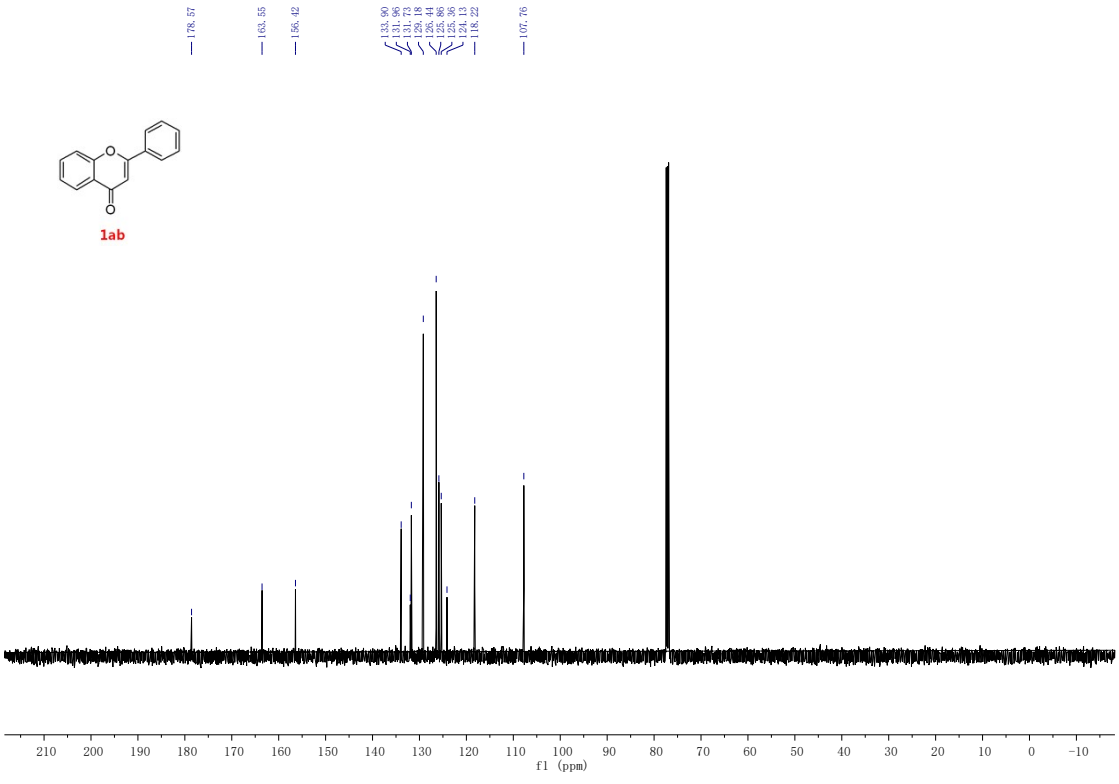
8.23
7.94
7.92
7.71
7.70
7.68
7.58
7.56
7.54
7.52
7.44
7.42
6.82
1ab
1.00
2.14
1.08
1.08
2.05
1.11
1.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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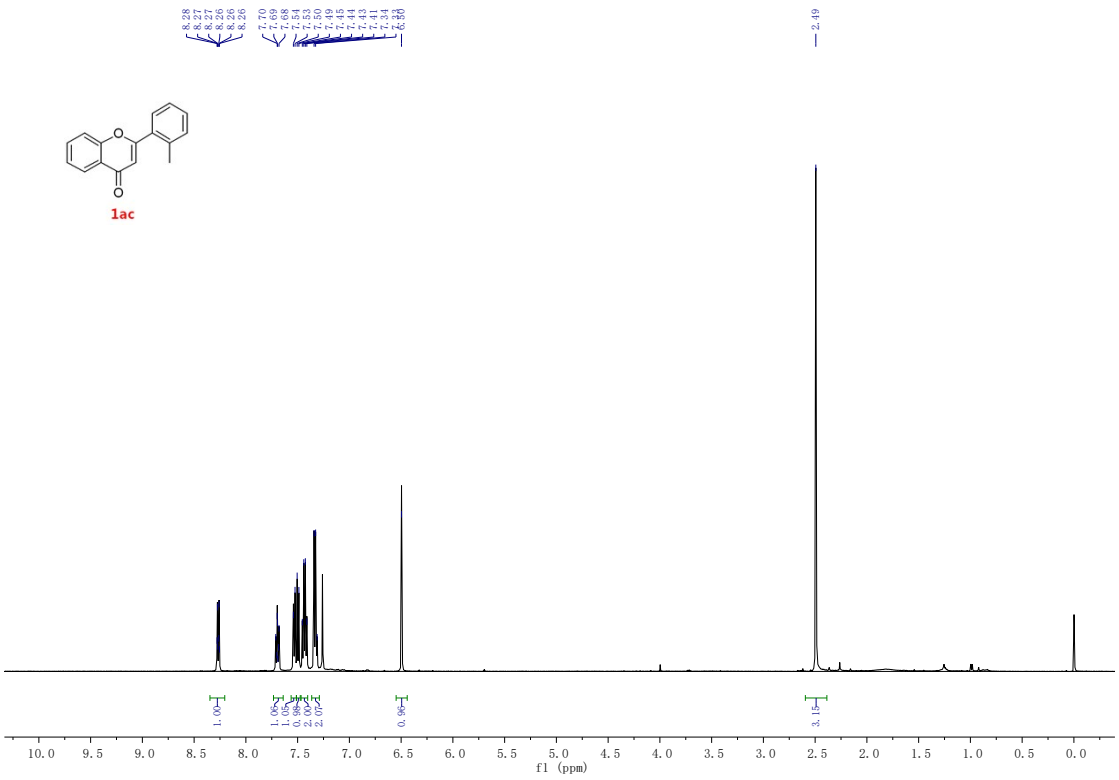
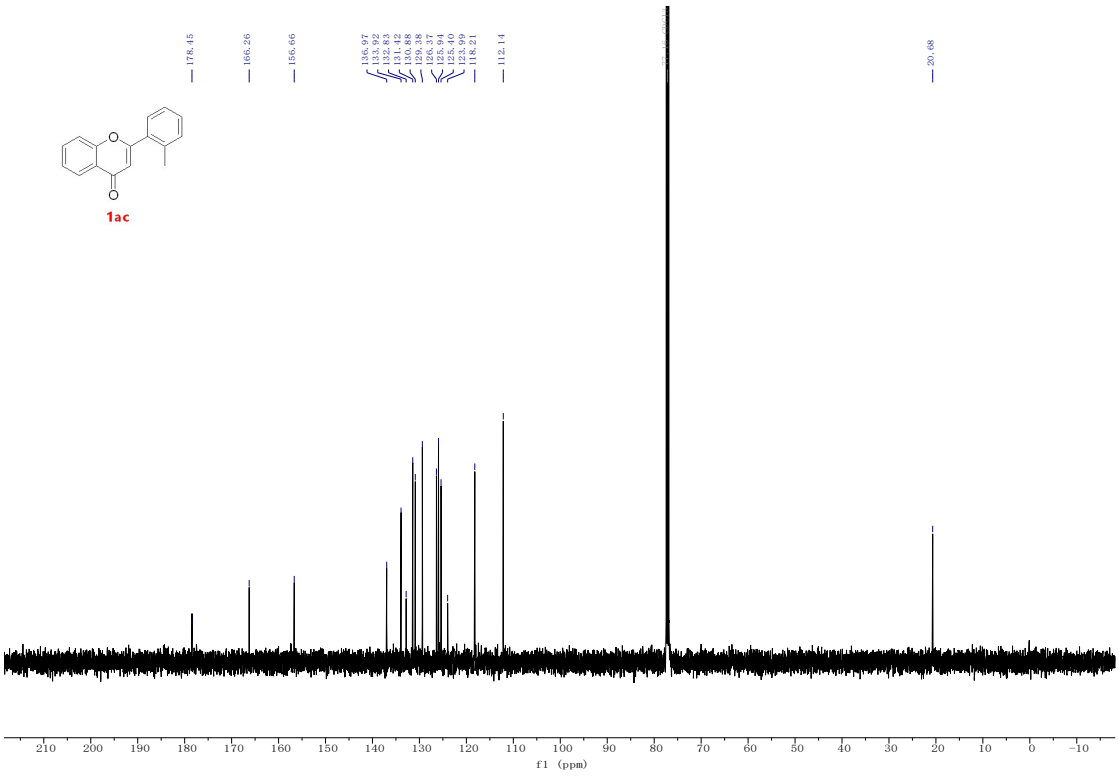
163.55
156.42
133.90
131.95
131.73
129.18
126.44
125.86
125.36
124.13
118.22
107.76
1ab
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.28
8.27
8.27
8.26
8.26
8.26
7.70
7.69
7.68
7.54
7.53
7.50
7.49
7.45
7.44
7.43
7.41
7.34
7.33
6.30
2.49
1ac
1.00
1.06
1.05
0.88
2.07
0.98
3.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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166.26
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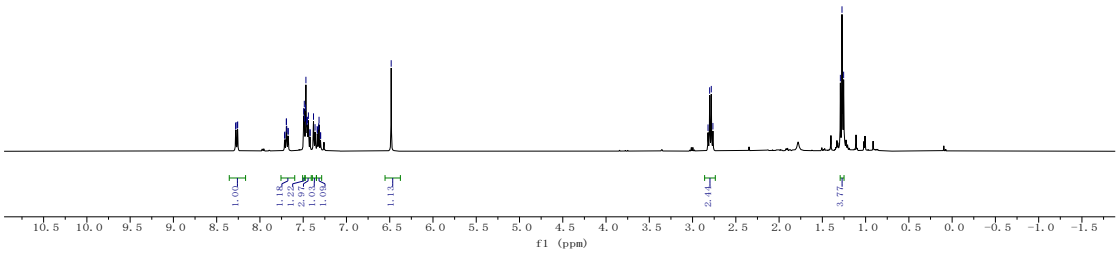
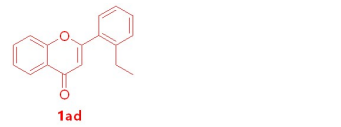
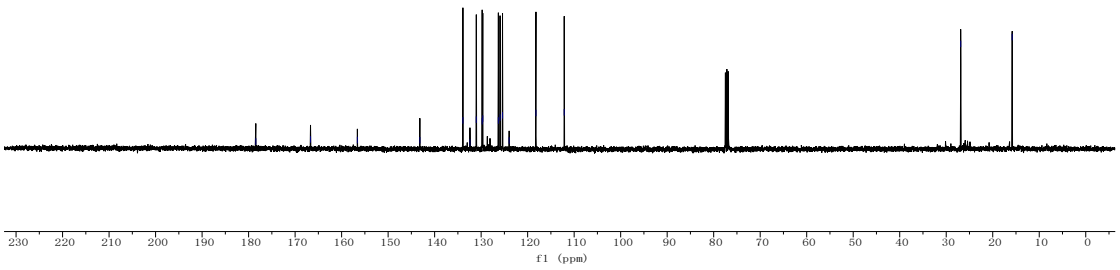
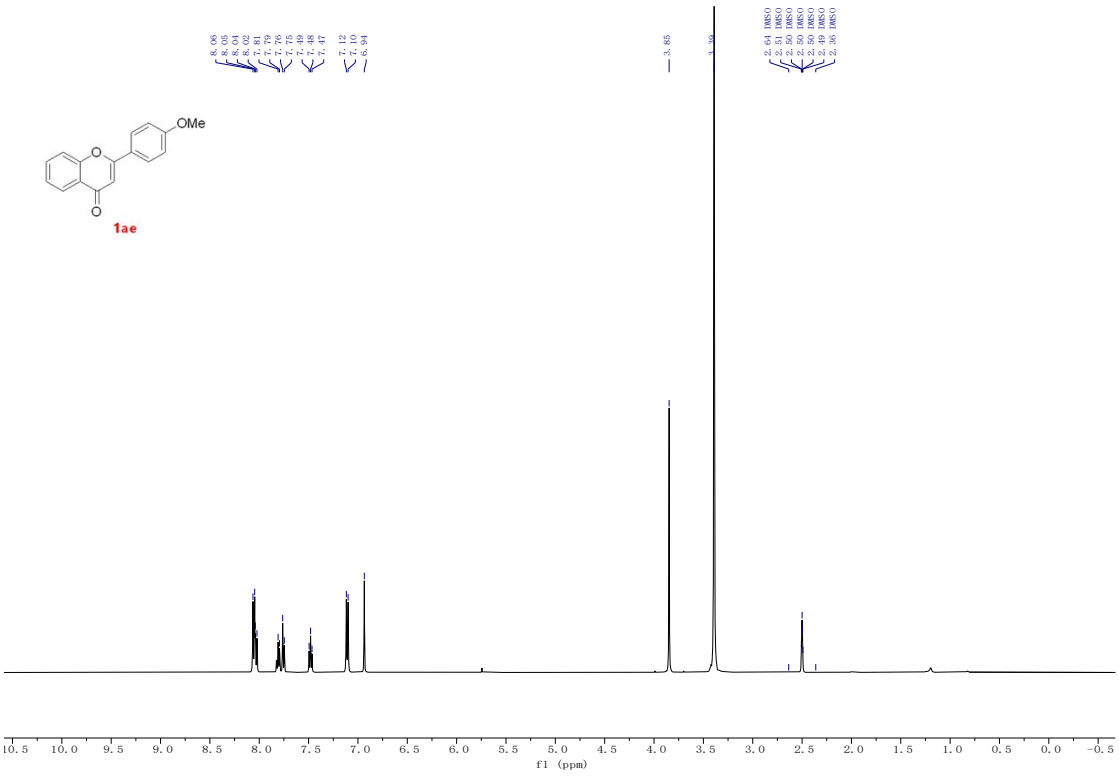
136.97
133.92
132.83
131.42
130.88
129.38
126.37
125.94
125.40
123.99
118.21
112.14
77.48
77.16
76.84
20.68
1ac
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

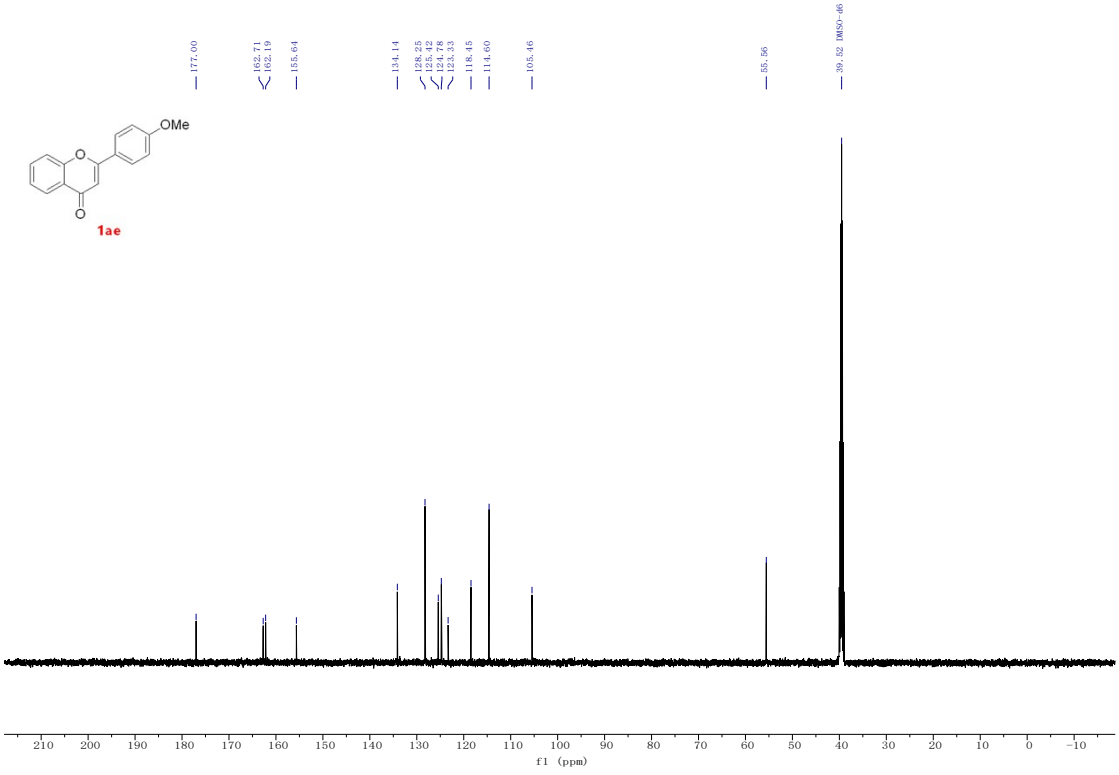

1ad

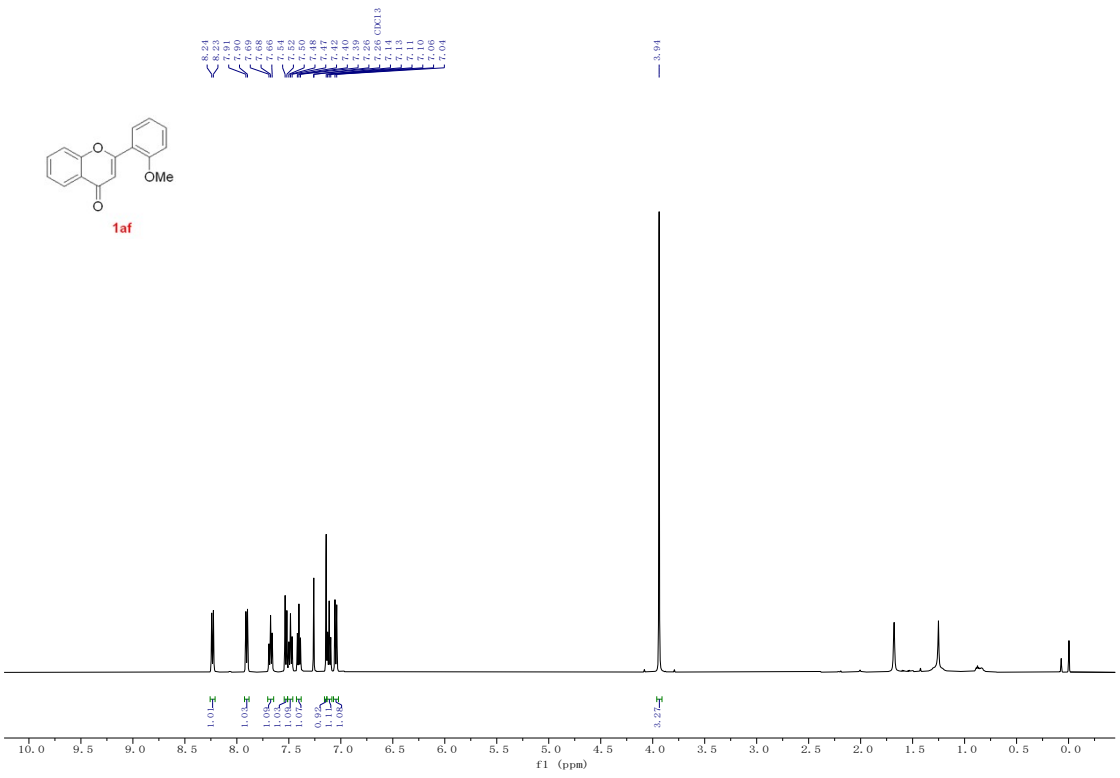

f1 (ppm)

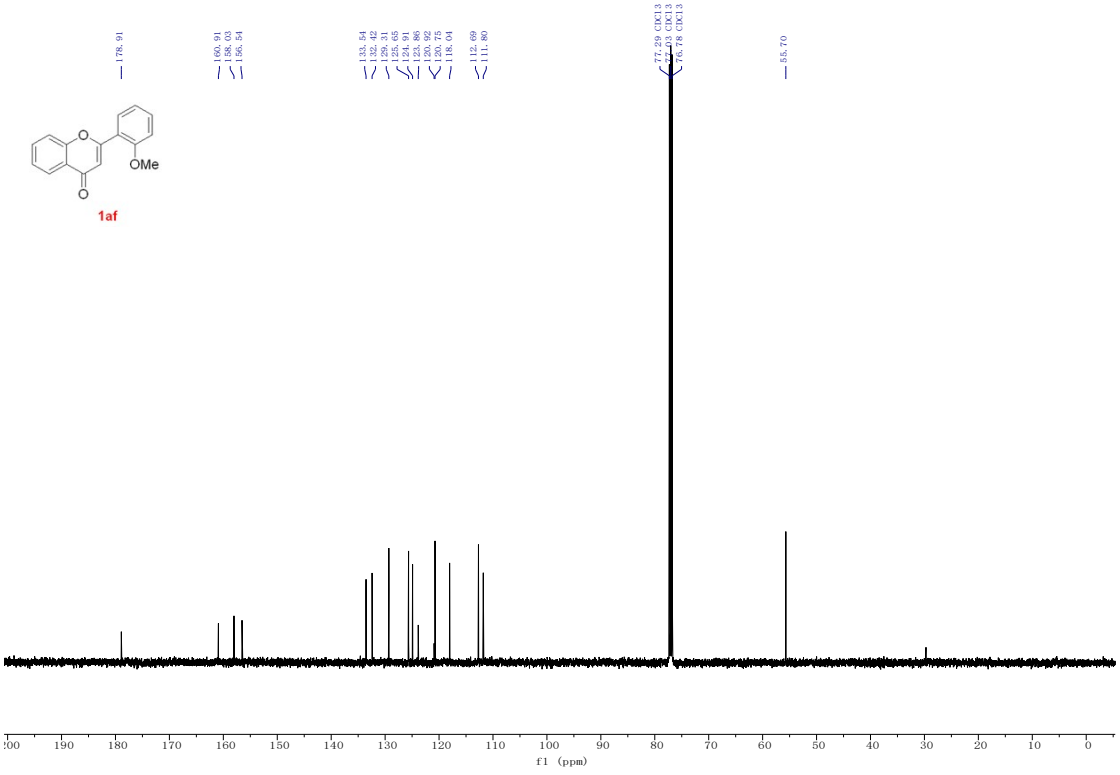

1ad

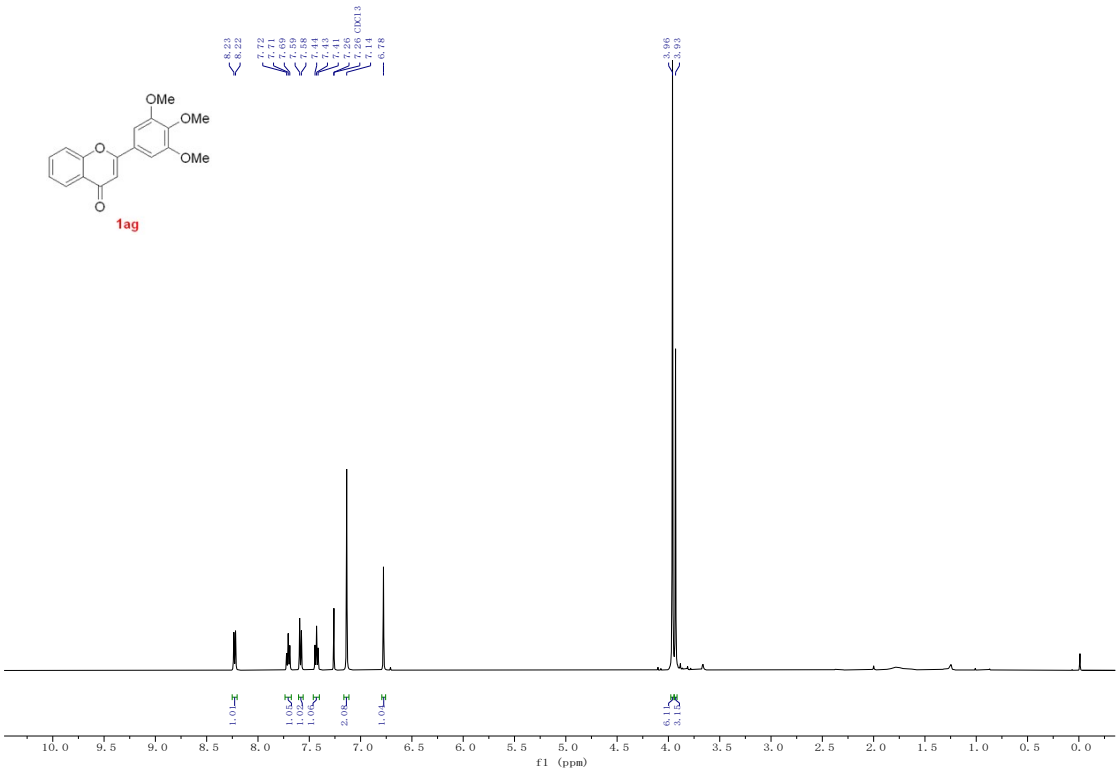

f1 (ppm)

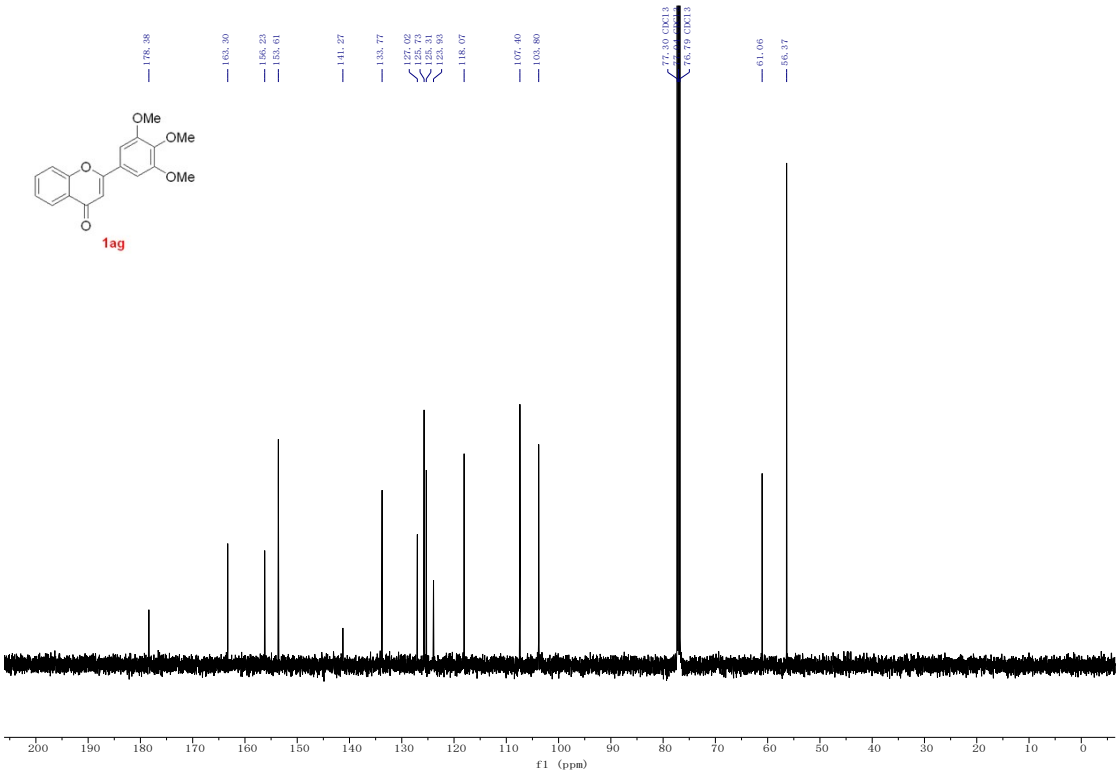

8.06
8.05
8.04
8.02
7.81
7.79
7.75
7.49
7.48
7.47
7.12
7.10
6.94
3.85
3.39
2.64 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.36 DMSO
OMe
O
O
1ae
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

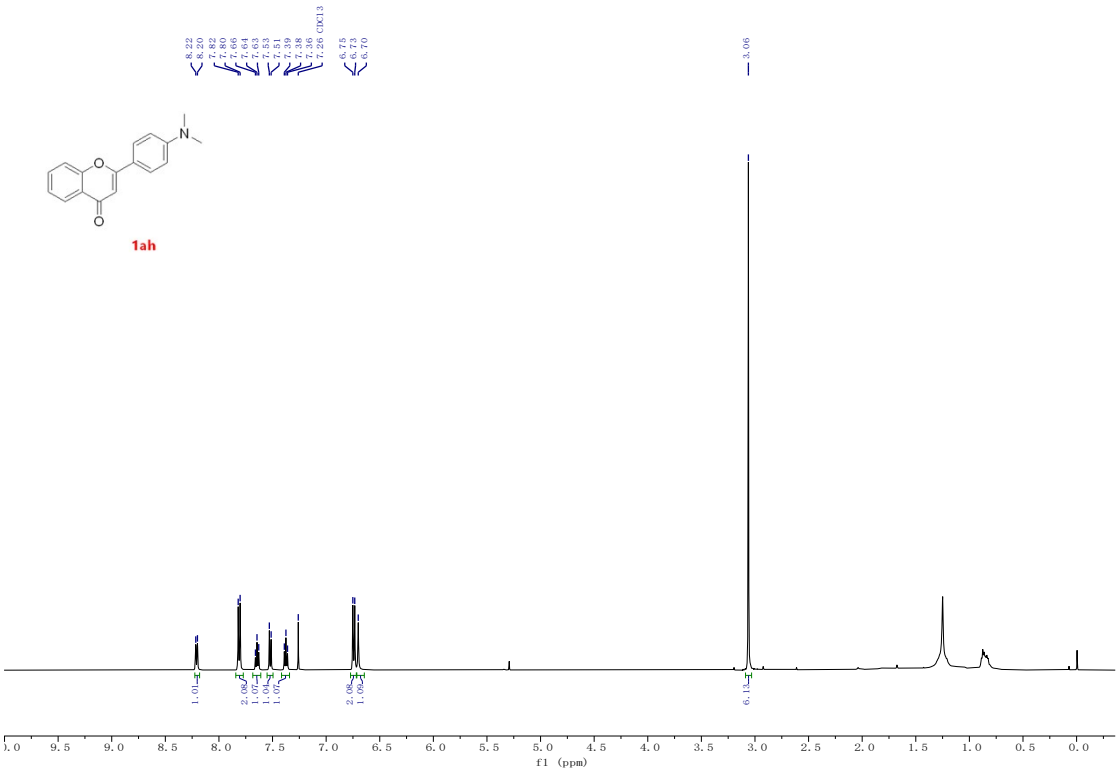

177.00
162.71
162.19
155.64
134.14
128.25
128.42
124.78
123.33
118.45
114.60
105.46
55.56
39.52 DMSO-d6
OMe
O
O
1ae
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

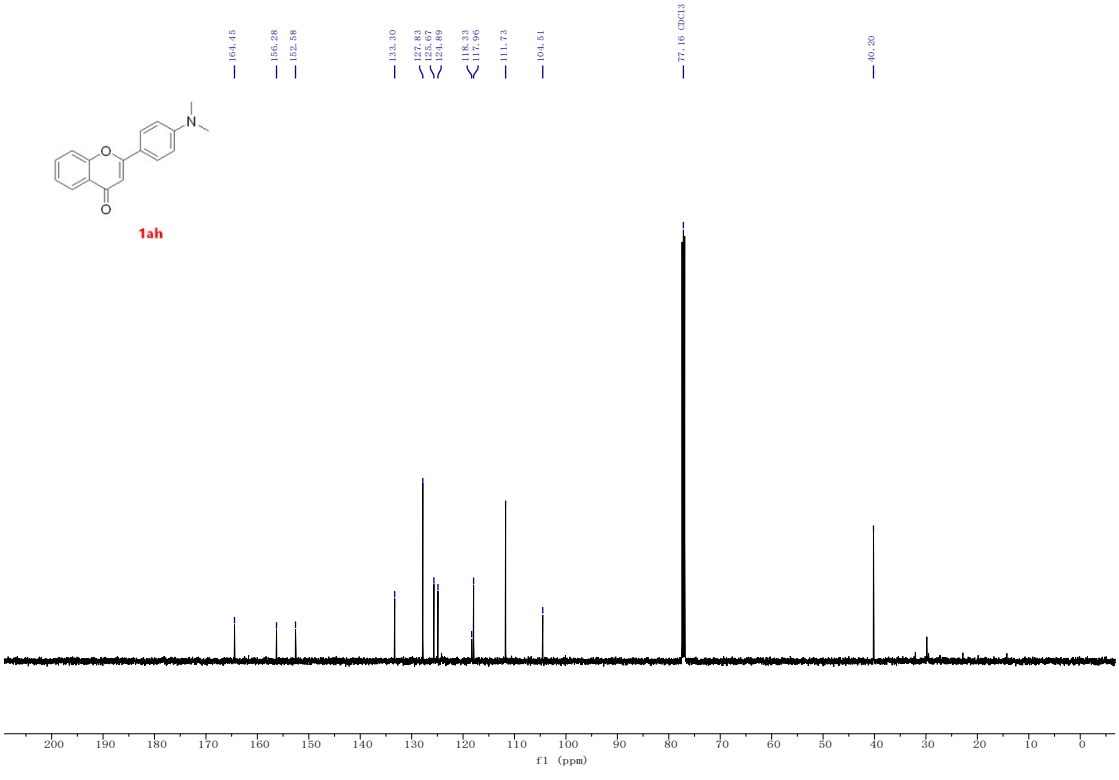

8.24
8.23
7.91
7.90
7.69
7.68
7.66
7.64
7.52
7.50
7.48
7.47
7.42
7.40
7.39
7.26 CDCl3
7.14
7.13
7.11
7.10
7.06
7.04
3.94
OMe
O
O
1af
1.01
1.03
1.08
1.03
1.04
1.07
0.95
1.11
1.08
3.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


178.91
160.91
158.03
156.54
133.54
132.42
129.31
125.65
124.91
123.86
120.92
120.75
118.04
112.69
111.80
77.29 CDCl3
77.03 CDCl3
76.78 CDCl3
55.70
OMe
O
O
1af
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OMe
OMe
OMe
O
O
1ag
8.23
8.22
7.72
7.71
7.69
7.59
7.58
7.44
7.43
7.41
7.26
7.26 CDCl3
7.14
6.78
3.96
3.93
1.01
1.01
1.02
1.06
2.08
1.04
6.11
3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


178.38
163.30
156.23
153.61
141.27
133.77
127.02
125.73
125.31
123.93
118.07
107.40
103.80
77.30 CDCl3
77.04
76.79 CDCl3
61.06
56.37
OMe
OMe
OMe
O
O
1ag
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.22
8.20
7.82
7.80
7.66
7.64
7.63
7.53
7.51
7.39
7.38
7.36
7.26 CDCl3
6.75
6.73
6.70
3.06
1ah
1.01
2.08
1.07
1.04
1.07
2.08
1.09
6.13
f1 (ppm)


164.45
156.28
152.58
133.30
127.83
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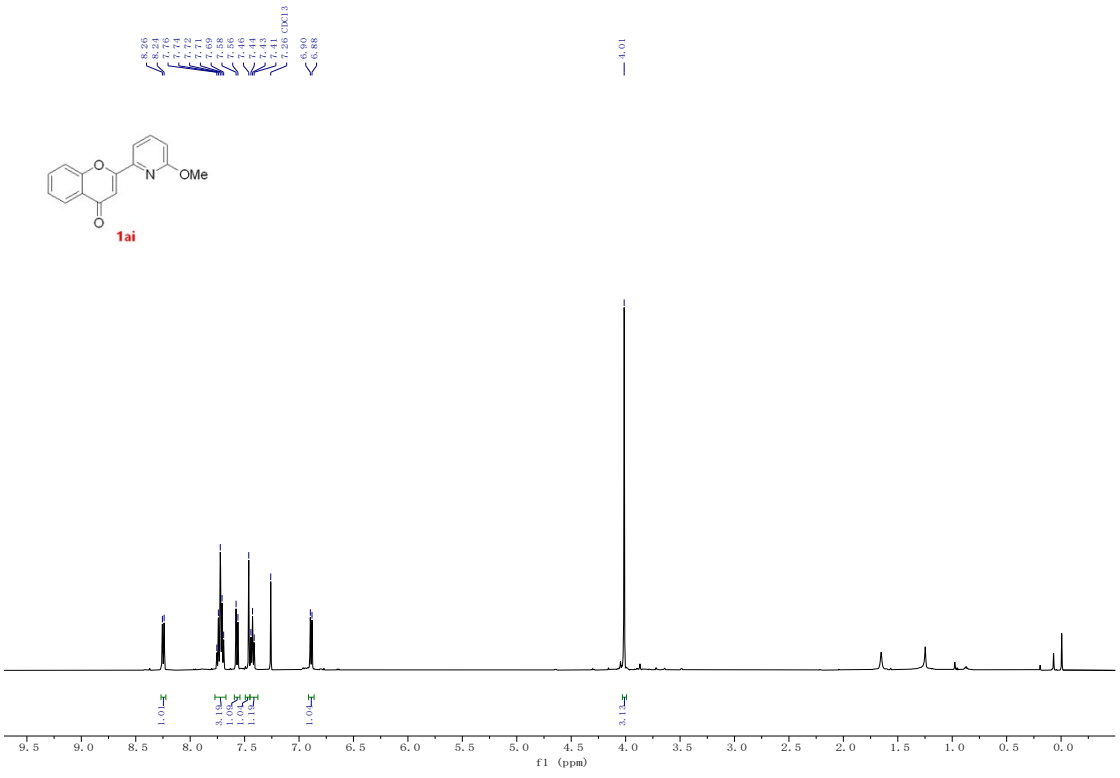
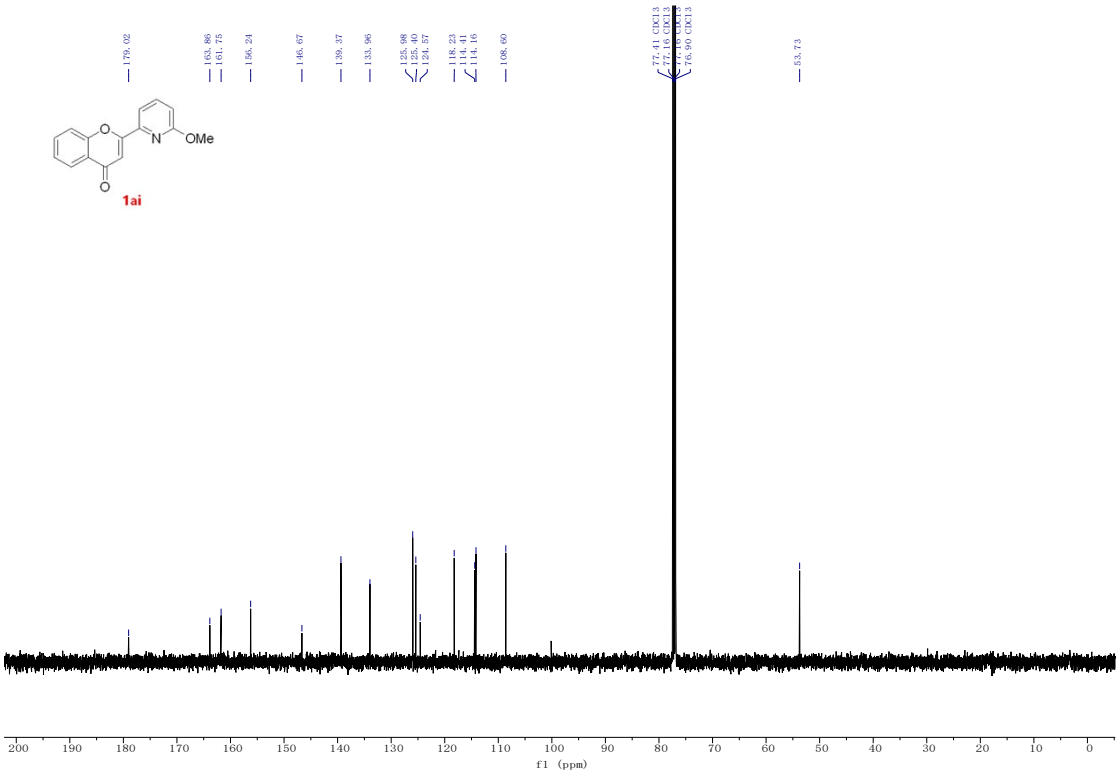
124.89
118.33
117.96
111.73
104.51
77.16 CDCl3
40.20
1ah
f1 (ppm)


8.26
8.24
7.76
7.74
7.72
7.71
7.69
7.58
7.56
7.46
7.44
7.43
7.41
7.26 CDCl3
6.90
6.88
4.01
OMe
1ai
1.01
3.14
1.05
1.03
1.14
1.04
3.13
f1 (ppm)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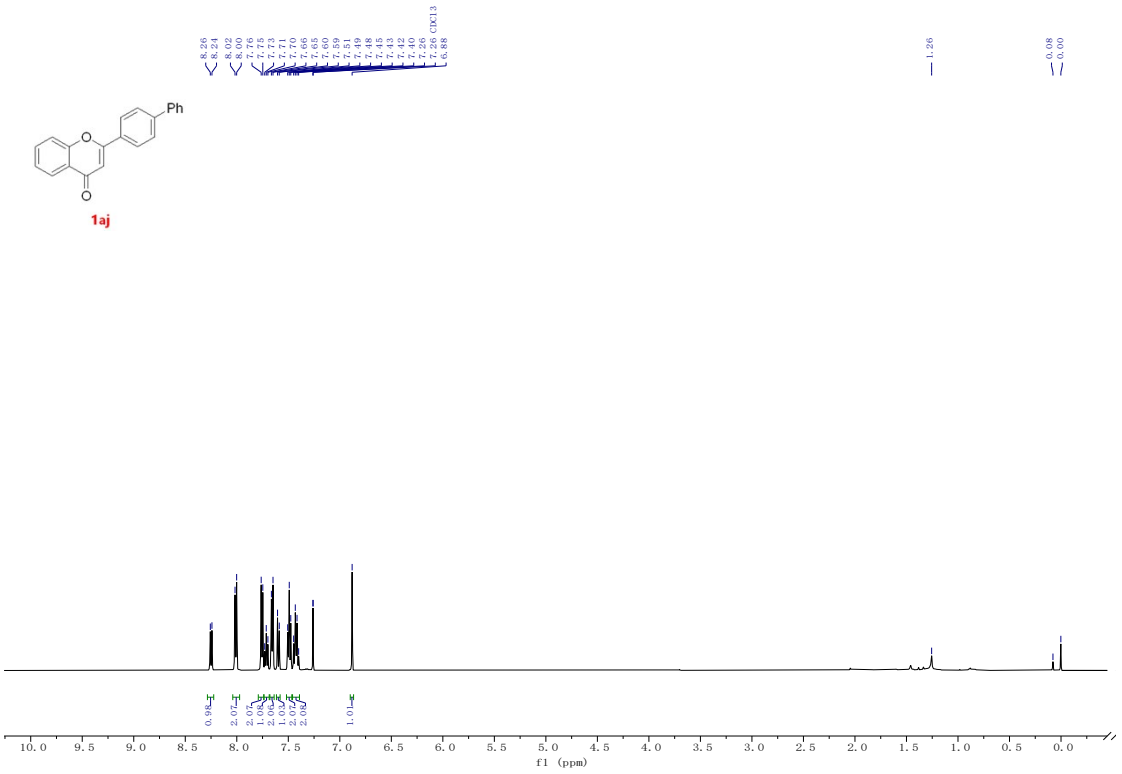
163.86
161.75
156.24
146.67
139.37
133.96
125.98
125.40
124.67
118.23
114.41
114.16
108.60
77.41 CDCl3
77.16 CDCl3
76.90 CDCl3
53.73
OMe
1ai
f1 (ppm)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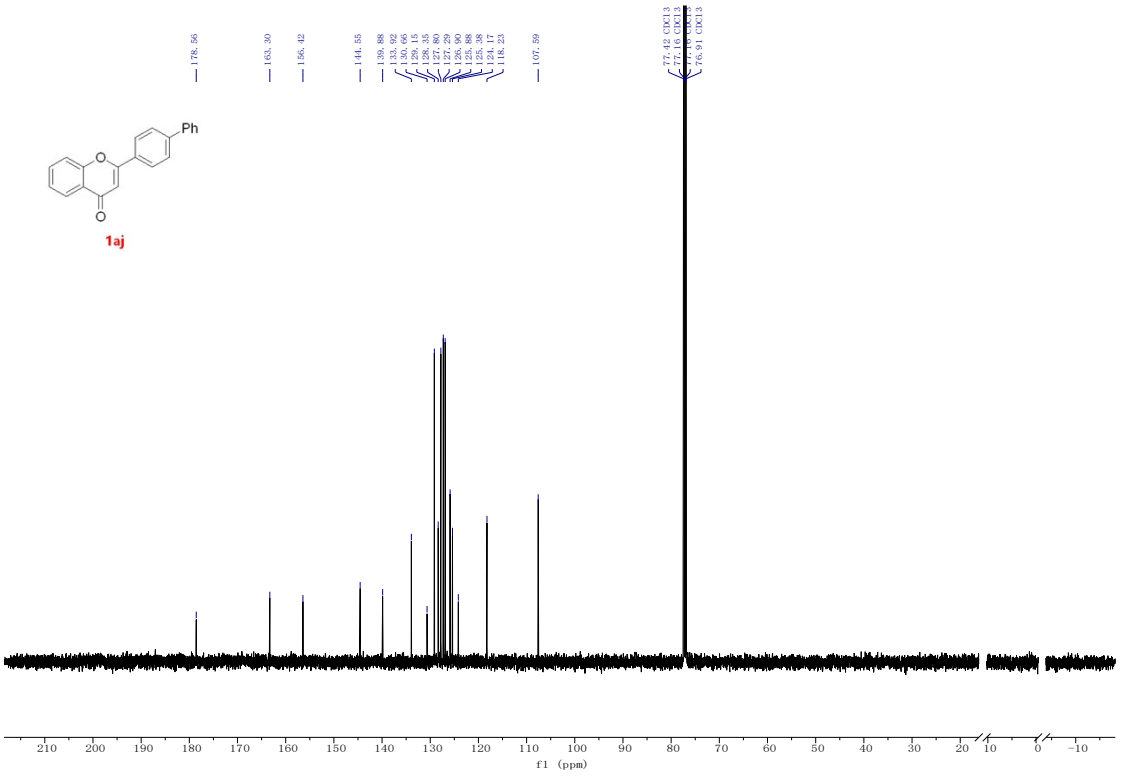
8.24
8.02
8.00
7.76
7.75
7.73
7.71
7.70
7.66
7.65
7.60
7.59
7.51
7.49
7.48
7.45
7.43
7.42
7.40
7.38
7.26 CDCl3
6.88
1.26
0.08
0.00
Ph
O
O
1aj
0.98
2.07
2.07
1.04
2.04
2.02
2.02
2.00
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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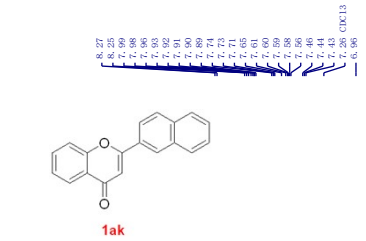
144.55
139.88
133.82
130.66
129.15
128.35
127.80
127.29
126.90
125.38
124.17
118.23
107.59
77.42 CDCl3
77.16 CDCl3
76.91 CDCl3
Ph
O
O
1aj
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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8.25
7.99
7.98
7.95
7.93
7.92
7.91
7.90
7.89
7.74
7.73
7.71
7.65
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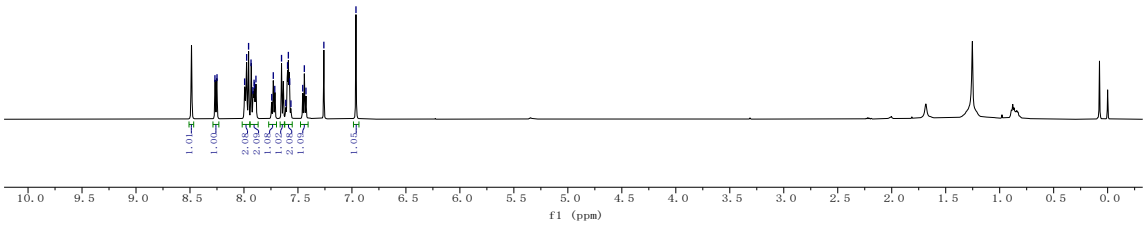
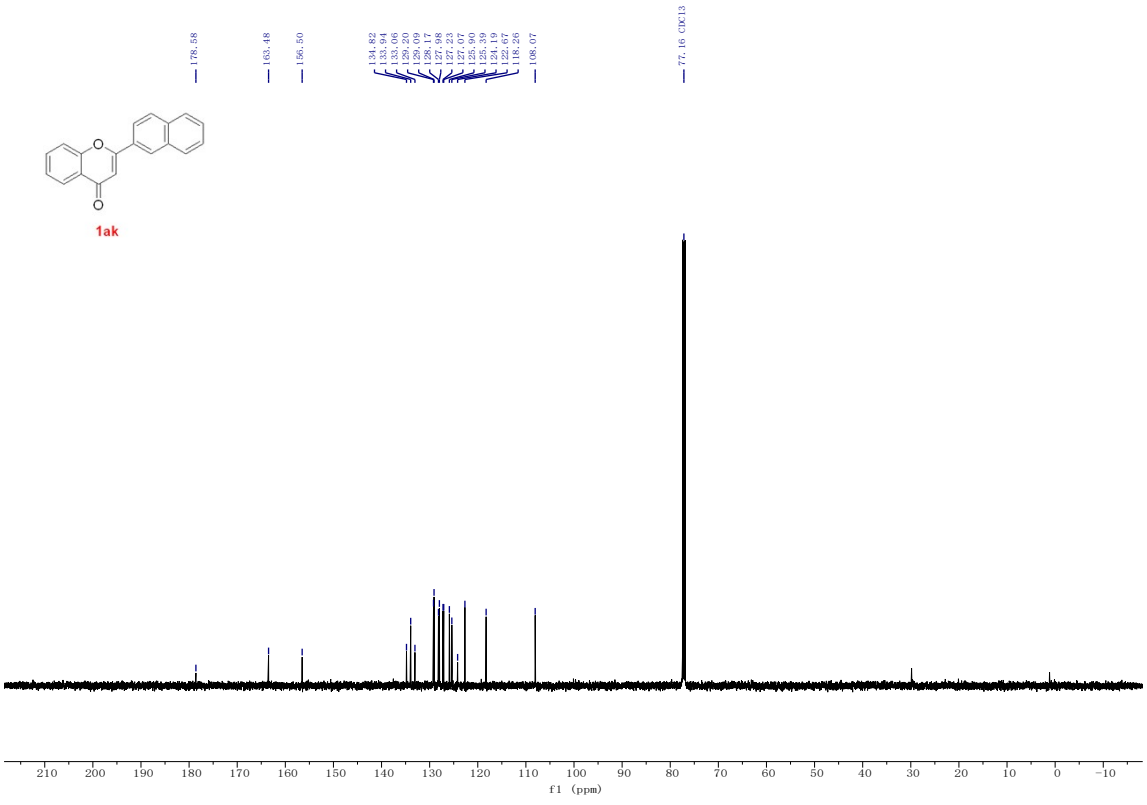
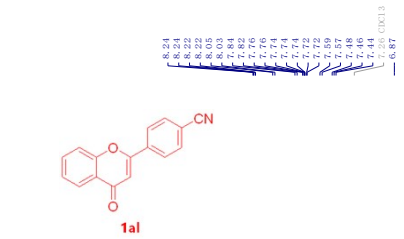
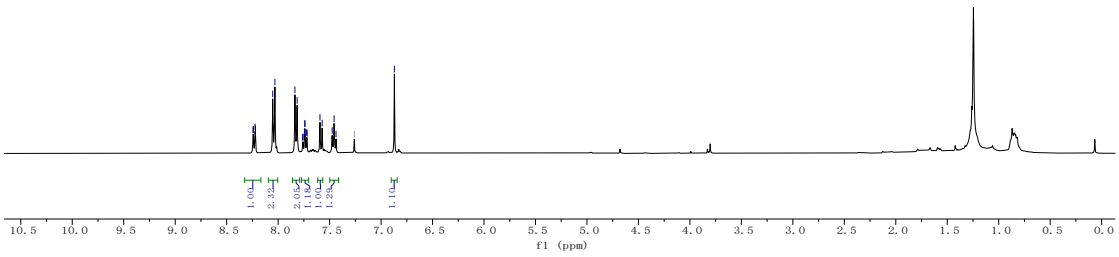
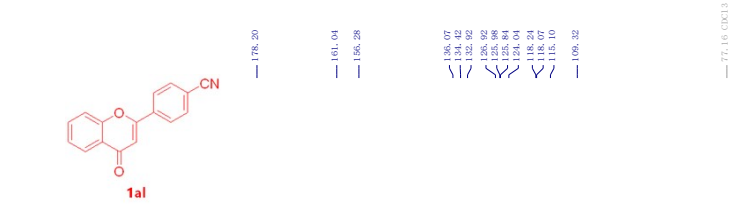
7.59
7.58
7.56
7.45
7.44
7.43
7.26 CDCl3
6.96
1ak

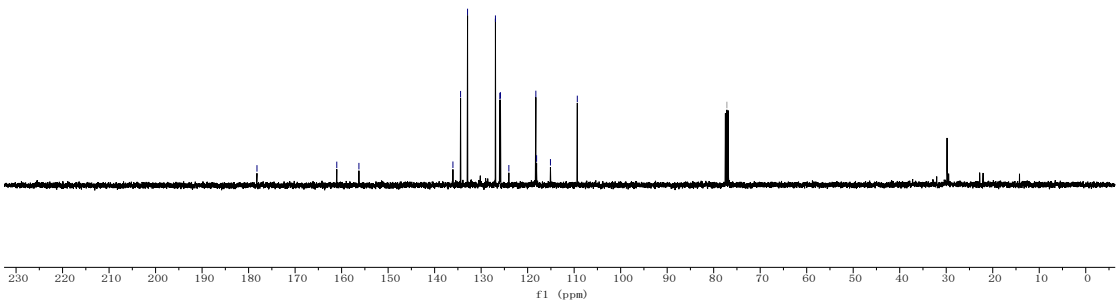

1.01
1.00
2.09
2.09
1.06
1.02
2.08
1.09
1.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

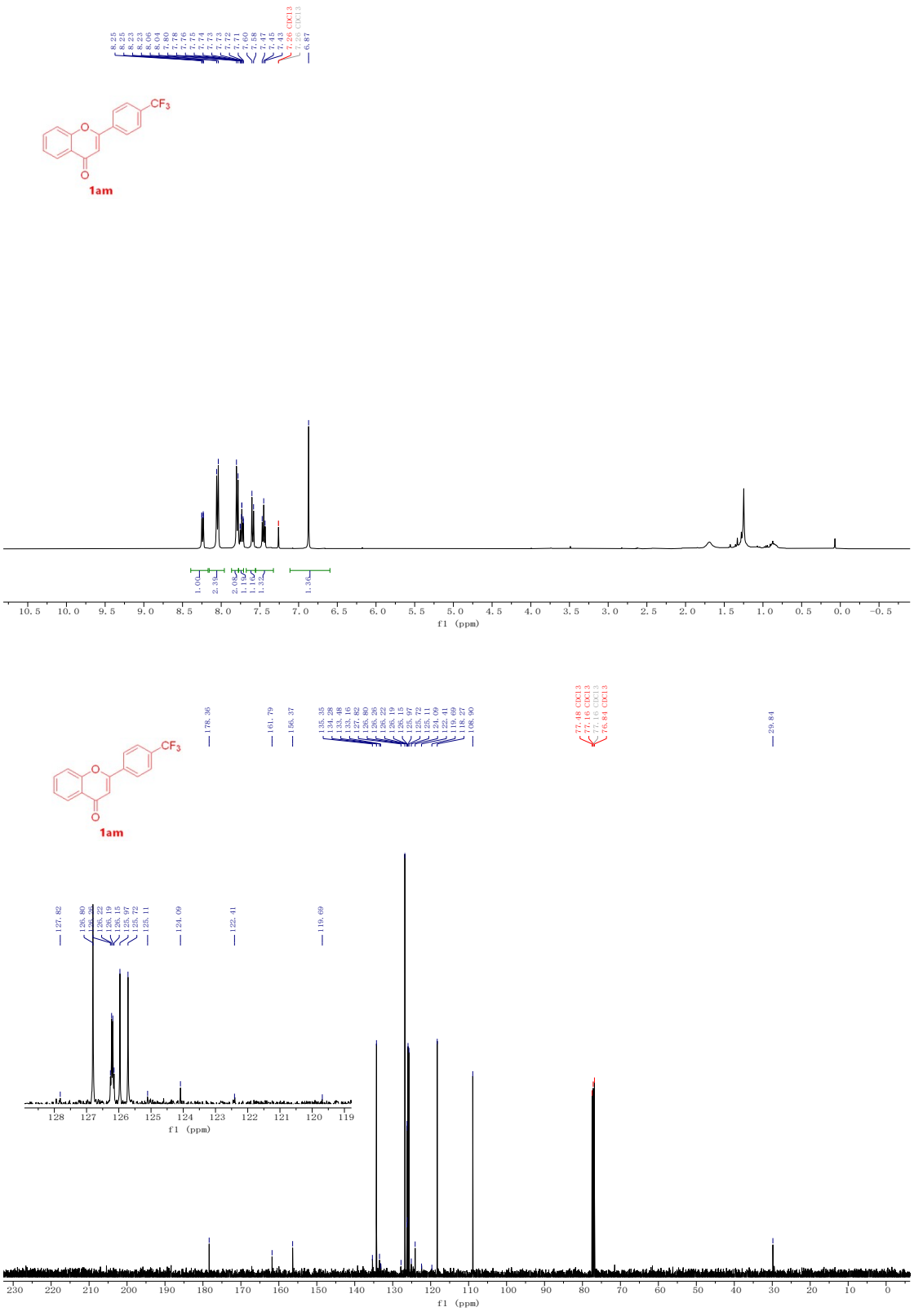

178.58
163.48
156.50
134.82
133.94
133.66
129.50
129.09
128.17
127.98
127.23
127.07
125.90
125.39
124.19
122.67
118.26
108.07
77.16 CDCl3
1ak
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

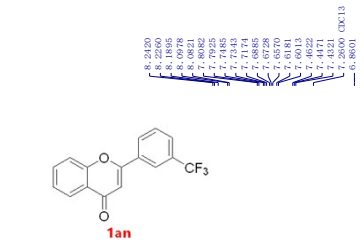

8.24
8.24
8.22
8.22
8.05
8.03
7.84
7.82
7.76
7.76
7.74
7.74
7.71
7.71
7.72
7.59
7.57
7.48
7.46
7.44
6.87
CDCl3
CN
O
O
1al


1.00
2.33
2.03
2.12
1.04
1.28
1.10
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


178.20
161.04
156.28
136.07
134.42
132.92
126.92
125.98
125.84
124.04
118.24
118.07
115.10
109.32
77.16
CDCl3
CN
O
O
1al


230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1am
f1 (ppm)
1am
f1 (ppm)
f1 (ppm)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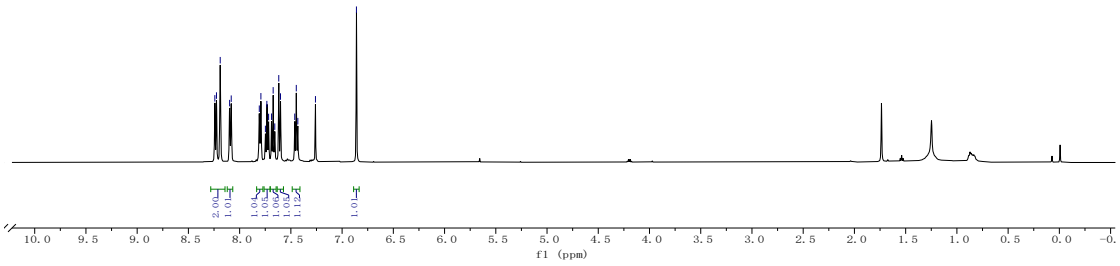
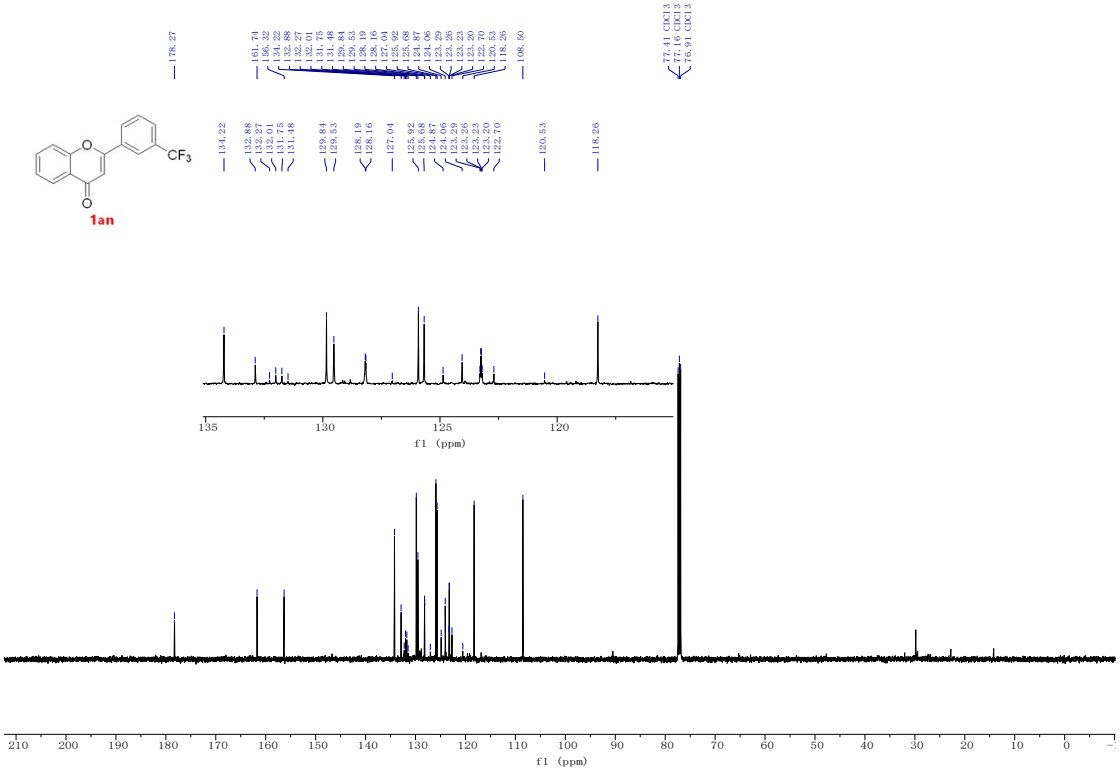
8.2260
8.1695
8.1536
8.0821
7.8082
7.7925
7.7586
7.7343
7.7174
7.6888
7.6728
7.6570
7.6181
7.6013
7.4622
7.4471
7.4321
7.2600 CDCl3
6.8601
CF3
O
O
1an


2.00
1.01
1.01
1.04
1.04
1.05
1.03
1.12
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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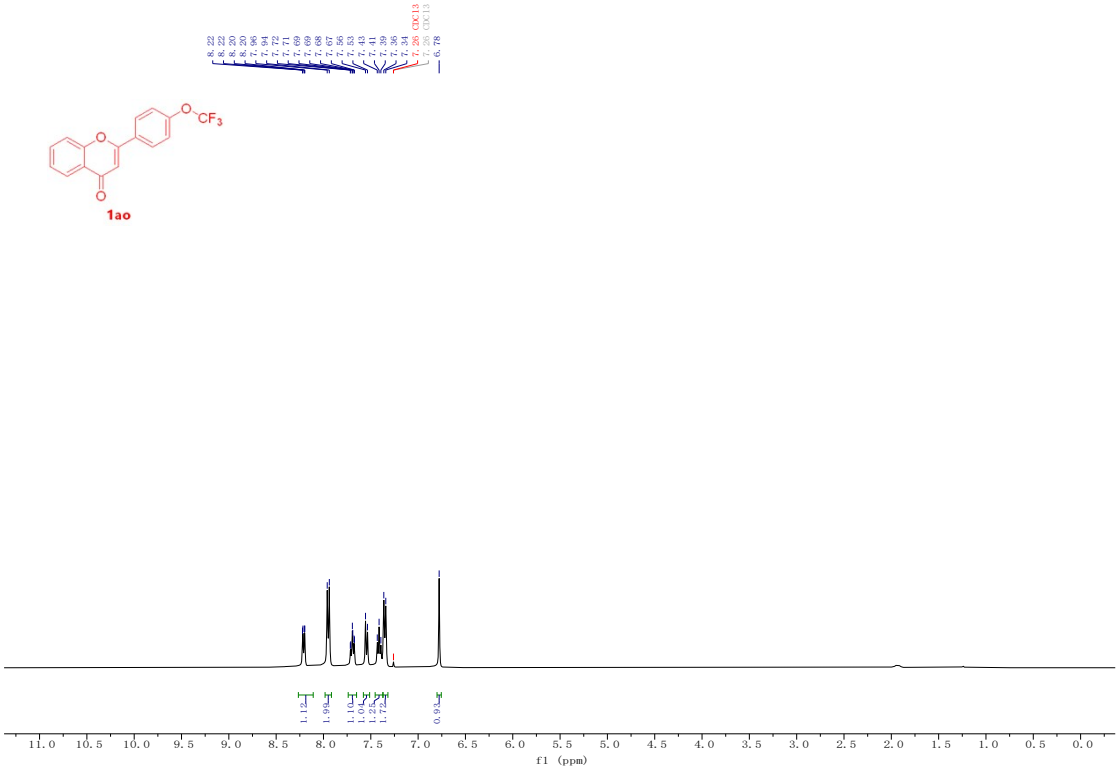
161.74
160.32
134.22
132.88
132.27
132.01
131.75
131.48
129.84
129.53
128.19
128.16
127.04
125.92
125.68
124.87
124.06
123.29
123.26
123.23
123.20
122.70
120.53
118.26
108.50
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
CF3
O
O
1an
135 130 125 120
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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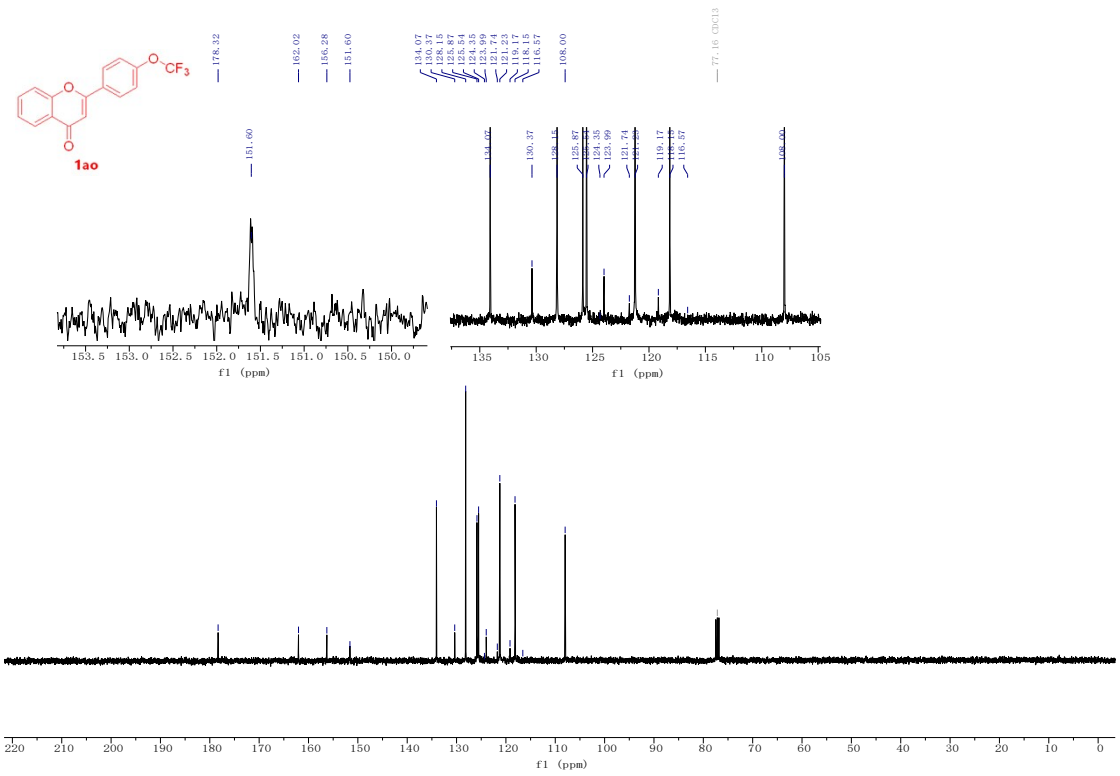
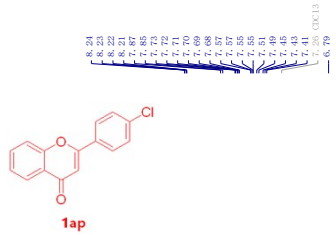
f1 (ppm)


1ao
f1 (ppm)
f1 (ppm)
f1 (ppm)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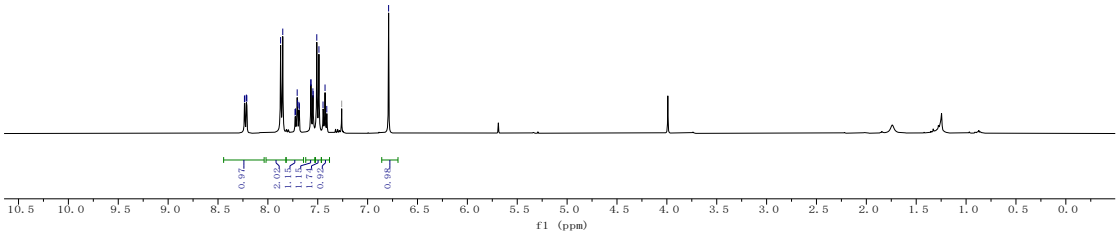
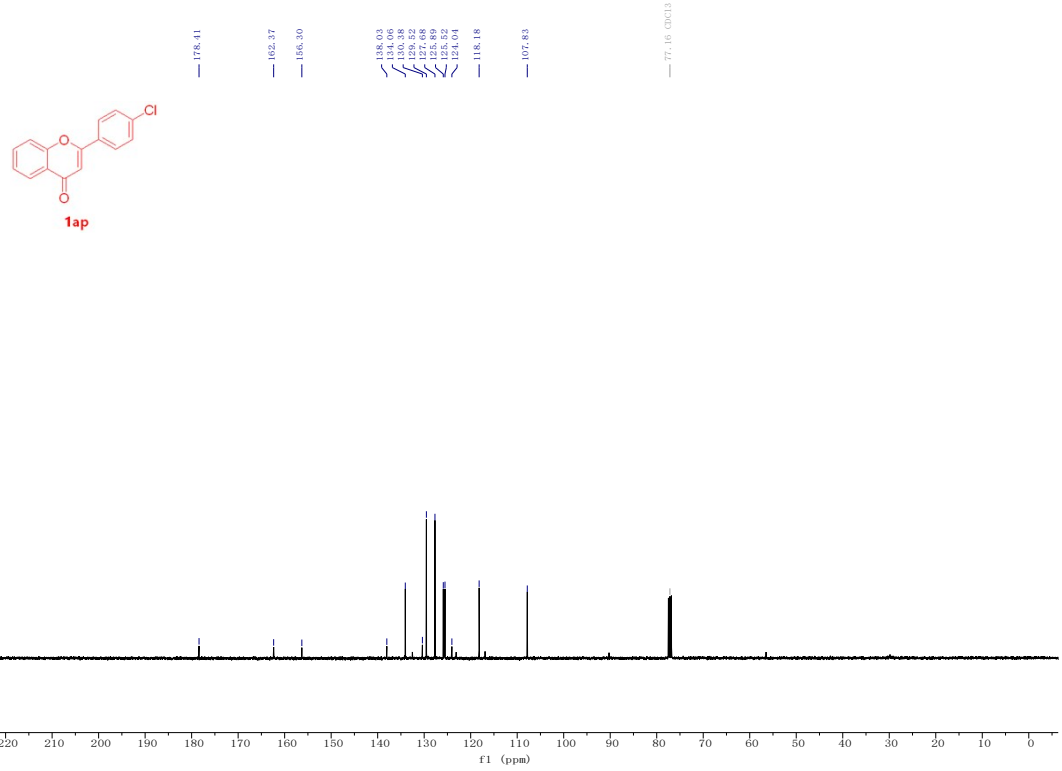
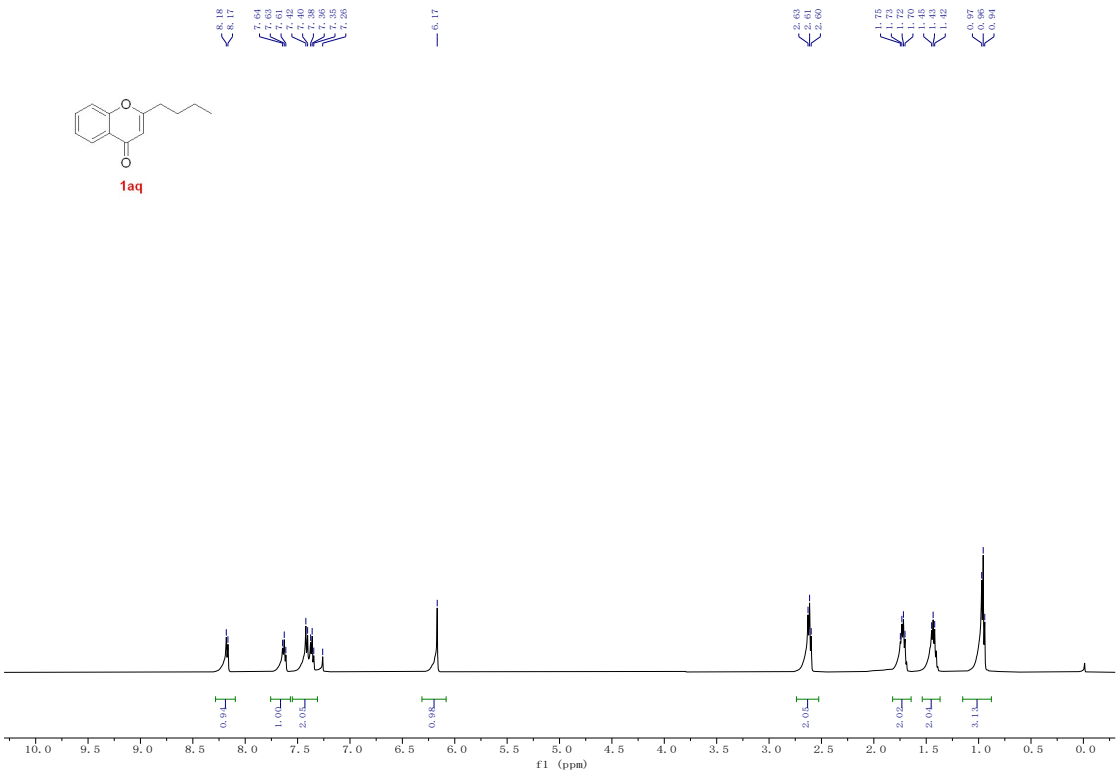
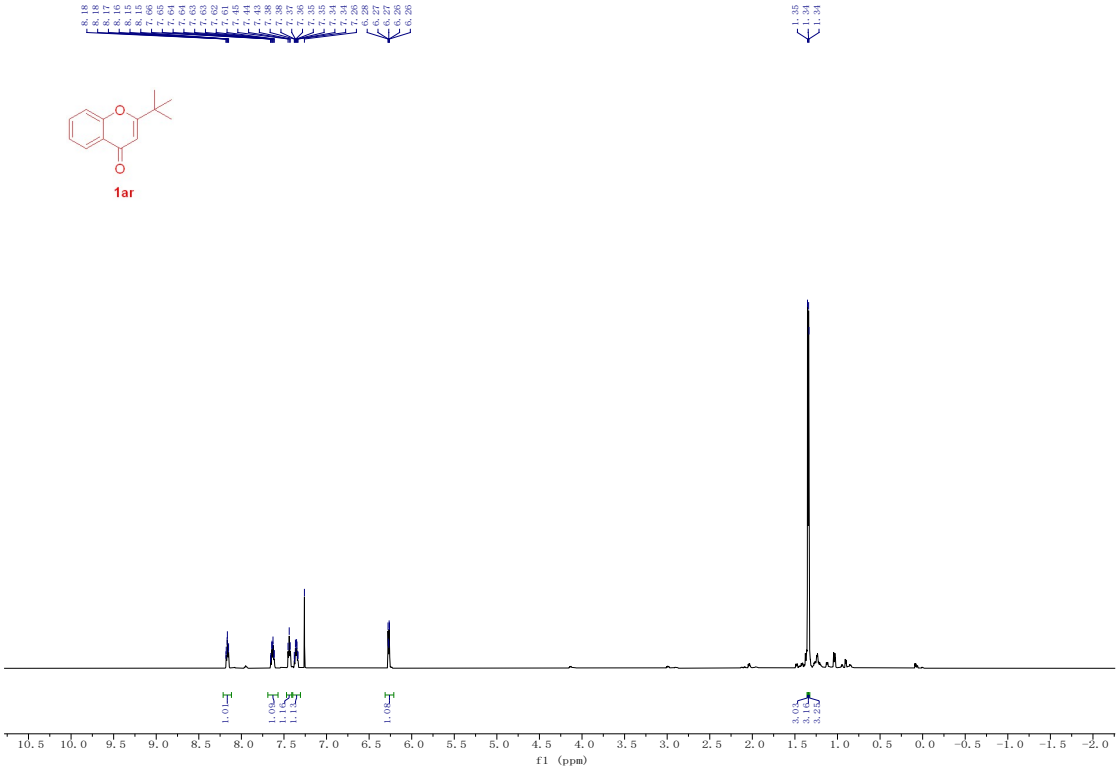
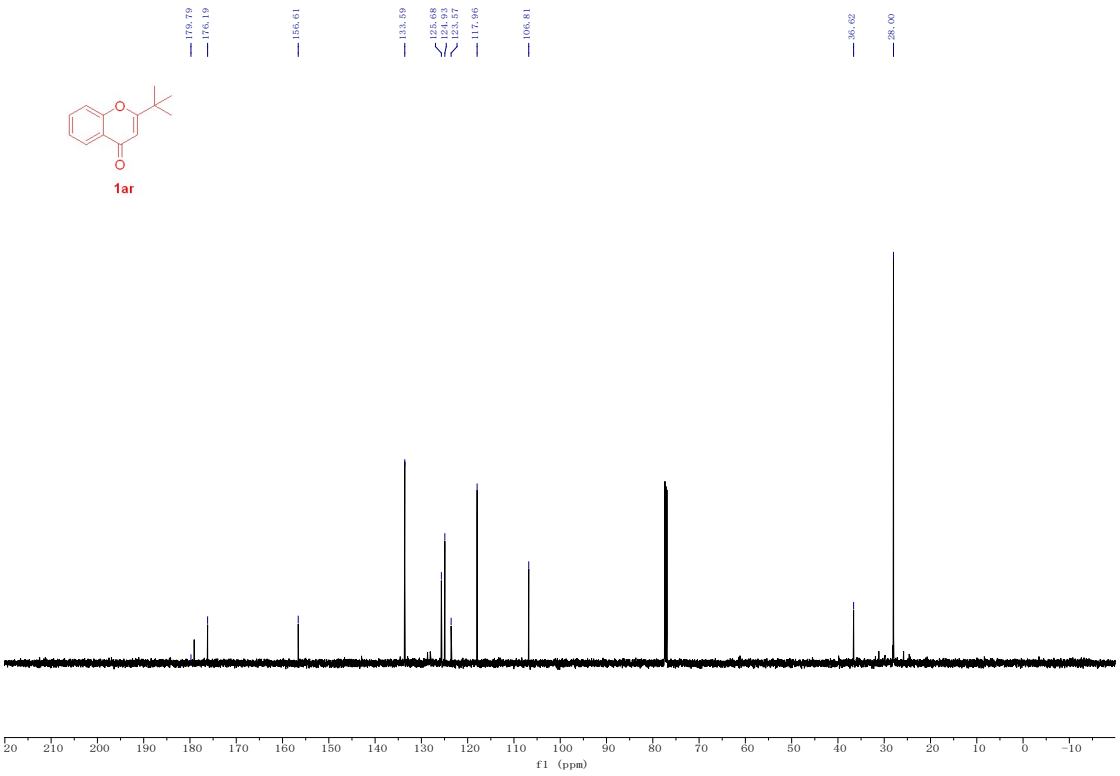
8.23
8.22
8.21
7.87
7.85
7.73
7.72
7.71
7.70
7.69
7.68
7.67
7.57
7.55
7.51
7.49
7.45
7.43
7.41
7.26 CDCl3
6.79
Cl
O
O
1ap

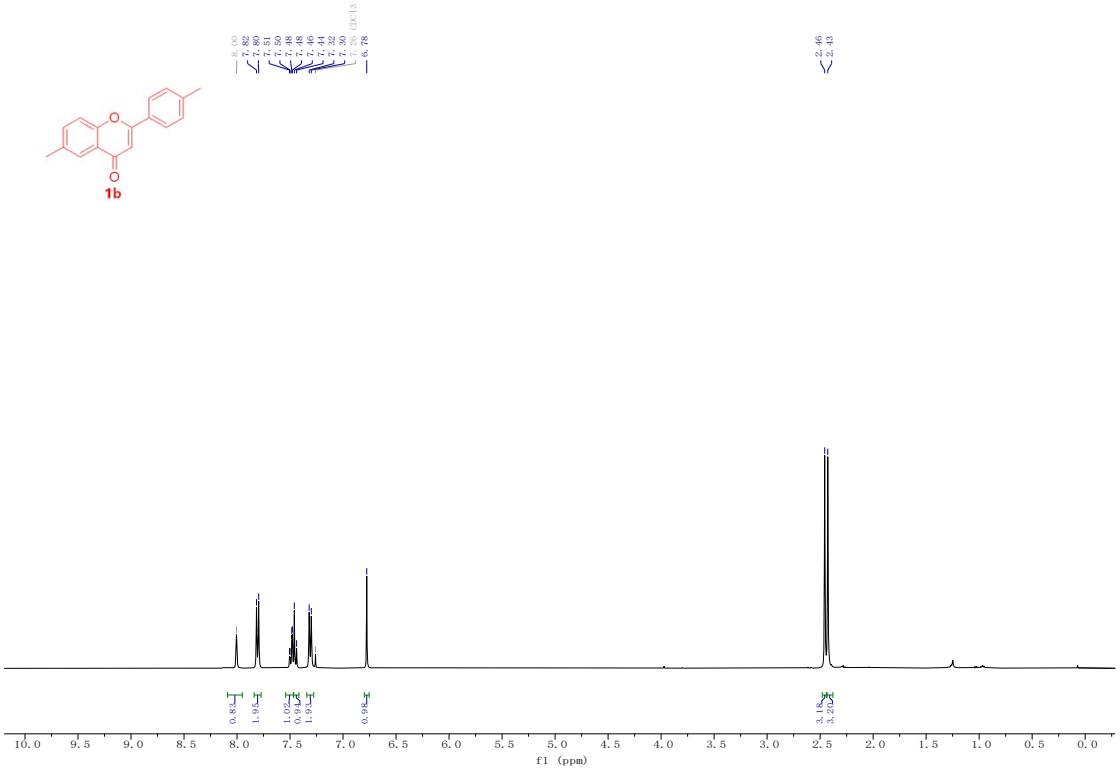

0.97
2.02
1.15
1.14
1.77
0.93
0.98
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

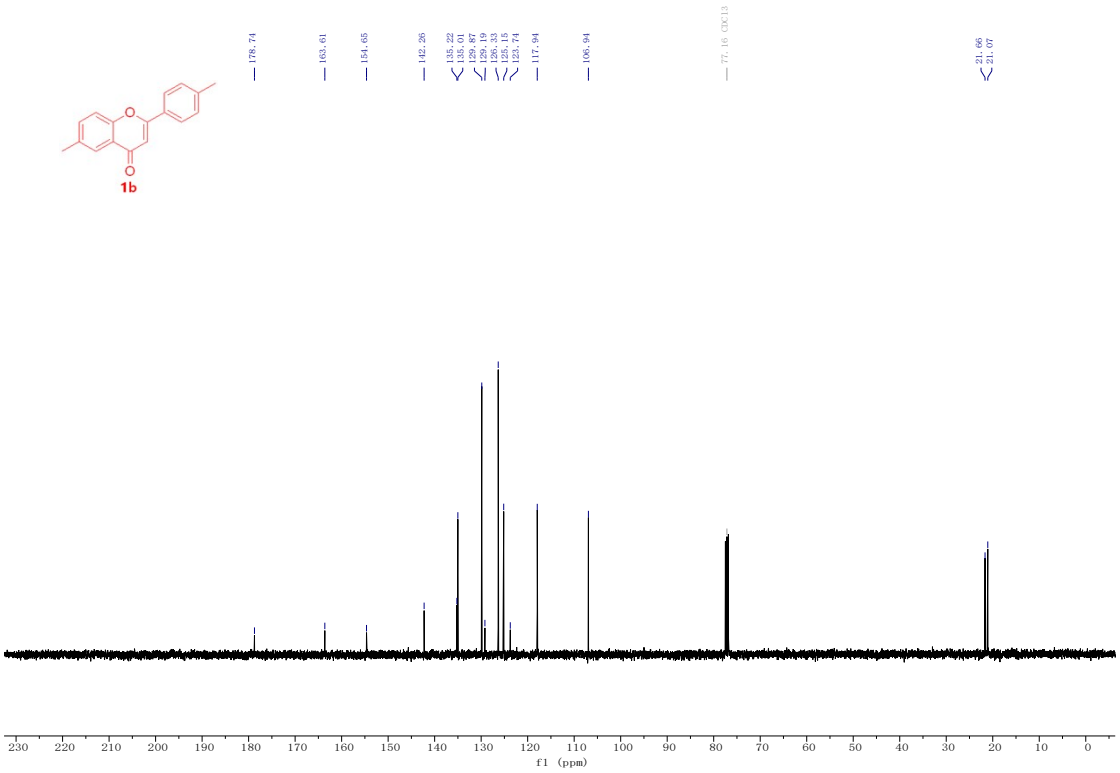

178.41
162.37
156.30
138.03
134.06
130.38
129.52
127.68
125.89
125.52
124.04
118.18
107.83
77.16 CDCl3
Cl
O
O
1ap
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

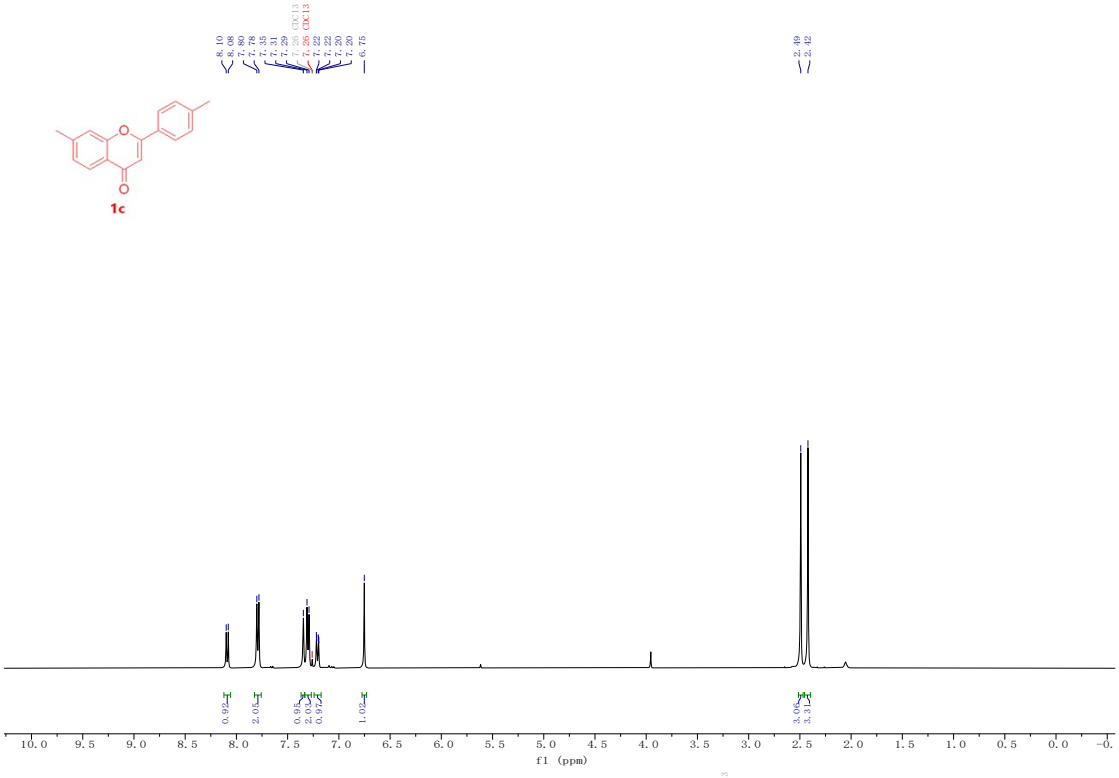

8.18
8.17
7.64
7.63
7.61
7.42
7.40
7.38
7.36
7.35
7.26
6.17
2.63
2.61
2.60
1.75
1.73
1.72
1.70
1.45
1.43
1.42
0.97
0.96
0.94
1aq
0.94
1.00
2.05
0.98
2.01
2.02
2.04
3.13
f1 (ppm)
178.49
169.93
156.65
133.50
125.79
124.98
123.89
117.96
109.92
77.42
77.16
77.16
CDCl3
76.91
34.15
28.98
22.23
13.83
1aq
f1 (ppm)

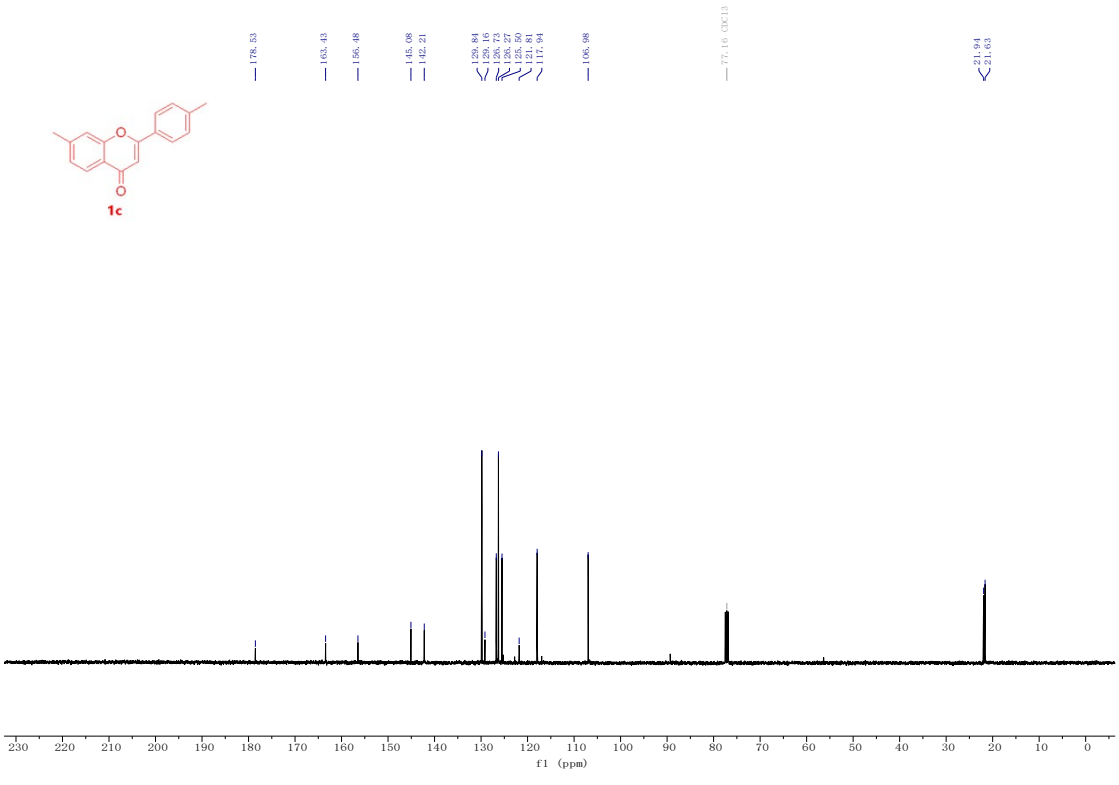

8.18
8.18
8.17
8.16
8.15
8.15
7.66
7.65
7.64
7.64
7.63
7.63
7.62
7.61
7.61
7.45
7.44
7.43
7.38
7.38
7.37
7.36
7.35
7.35
7.34
7.34
7.28
6.28
6.27
6.26
6.26
1.35
1.34
1.34
1ar
1.01
1.09
1.14
1.17
1.08
3.03
3.16
3.23
f1 (ppm)


179.79
176.19
156.61
133.59
125.68
124.93
123.57
117.96
106.81
36.62
28.00
1ar
f1 (ppm)


8.00
7.82
7.80
7.51
7.50
7.48
7.46
7.44
7.32
7.30
7.26 CDCl3
6.78
2.46
2.43
1b
0.83
1.94
1.02
0.92
1.94
0.94
3.18
3.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


178.74
163.61
154.65
142.26
135.22
135.01
129.87
129.19
126.33
123.15
123.74
117.94
106.94
77.16 CDCl3
21.66
21.07
1b
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.10
8.08
7.89
7.78
7.35
7.31
7.29
7.26
CDCl3
7.25
CDCl3
7.22
7.22
7.20
7.20
6.75
2.49
2.42
1c
0.92
2.01
0.95
2.03
0.97
1.02
3.06
3.31
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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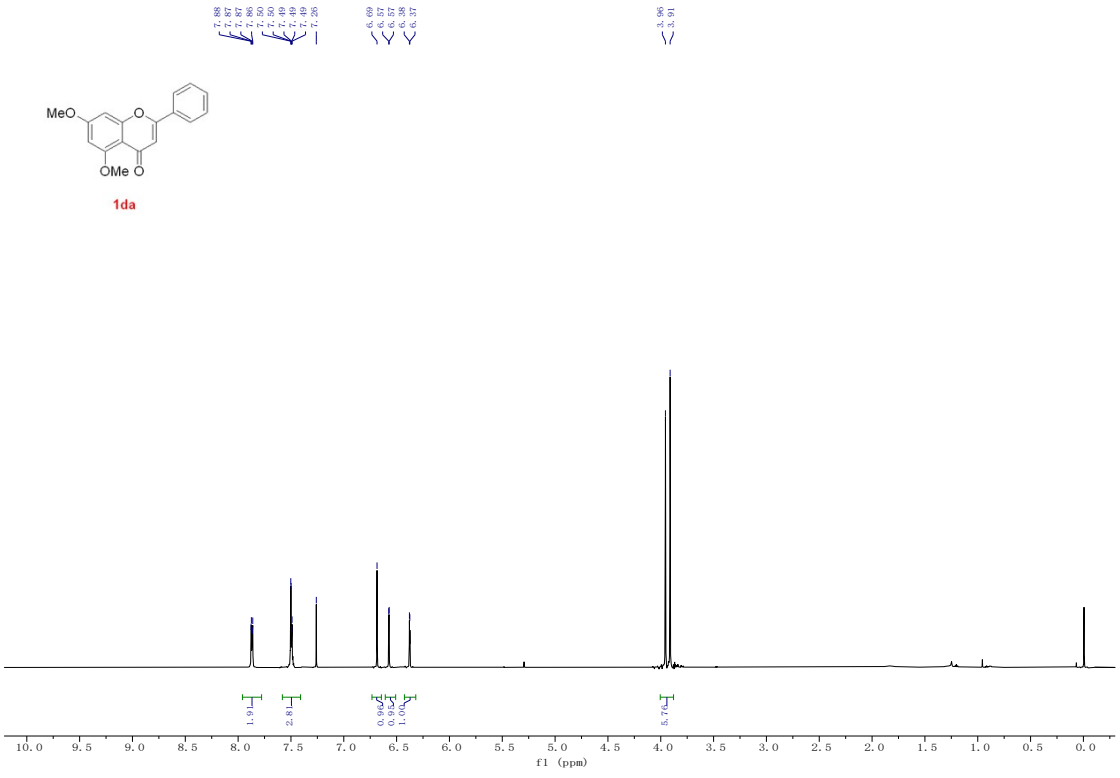
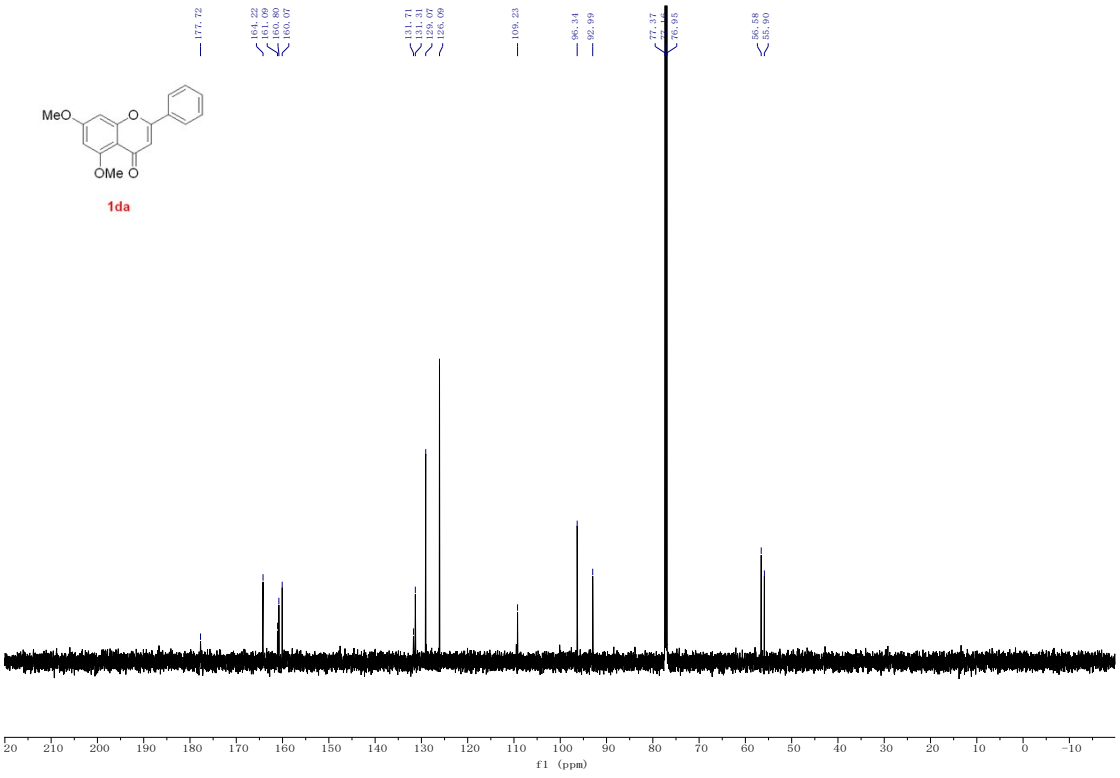
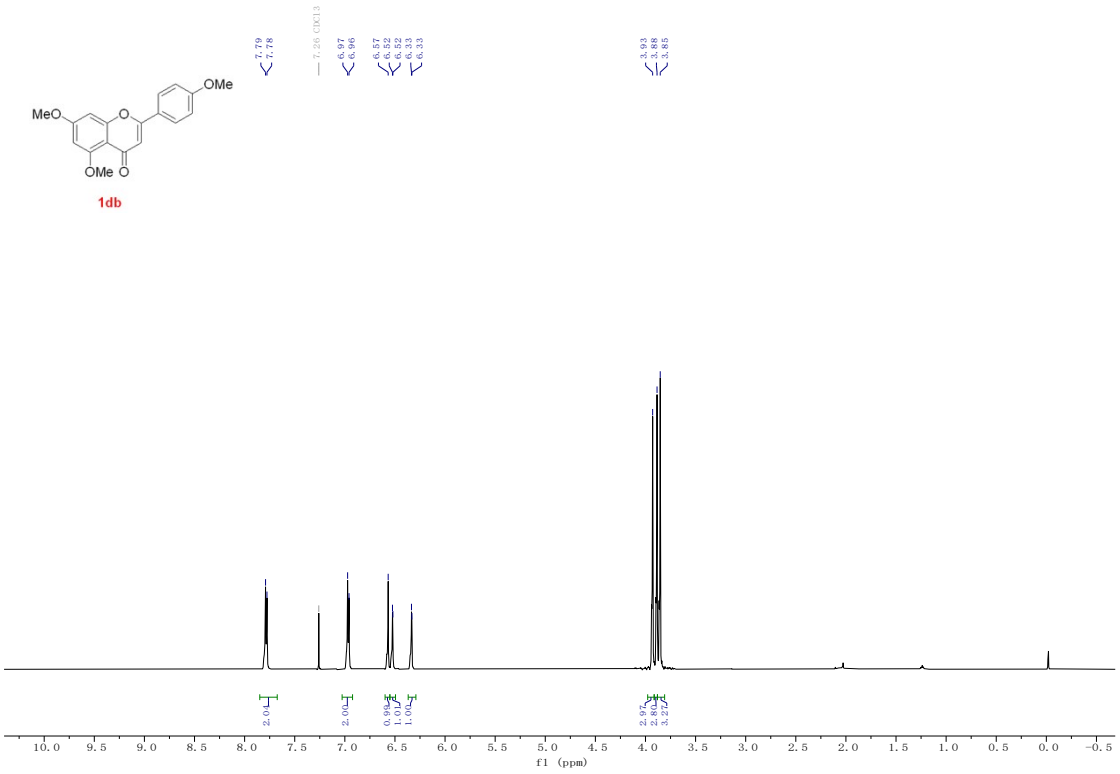
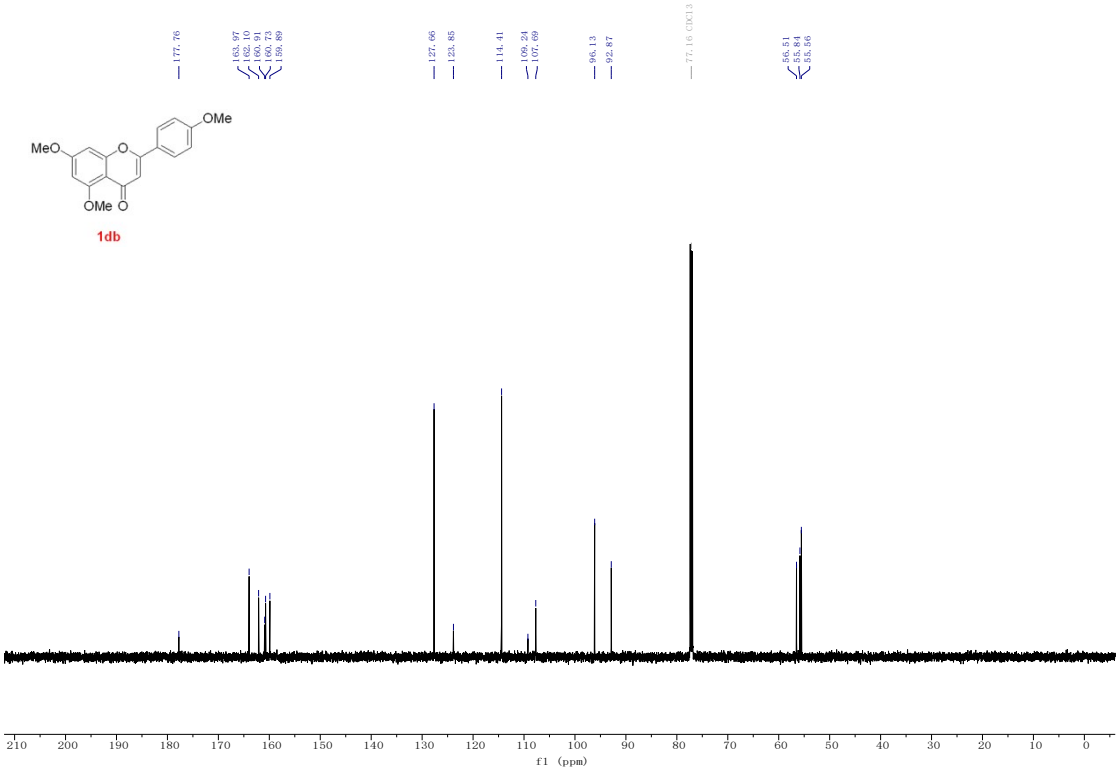
163.43
156.48
145.08
142.21
129.84
129.16
126.73
126.27
121.80
121.81
117.94
106.98
77.16
CDCl3
21.94
21.63
1c
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


MeO
OMe O
1da
f1 (ppm)


MeO
OMe O
1da
f1 (ppm)


7.79
7.78
7.26 CDCl3
6.97
6.96
6.57
6.52
6.52
6.33
6.33
3.93
3.88
3.85
MeO
OMe
OMe
O
1db
2.04
2.00
0.99
1.01
1.00
2.97
2.81
3.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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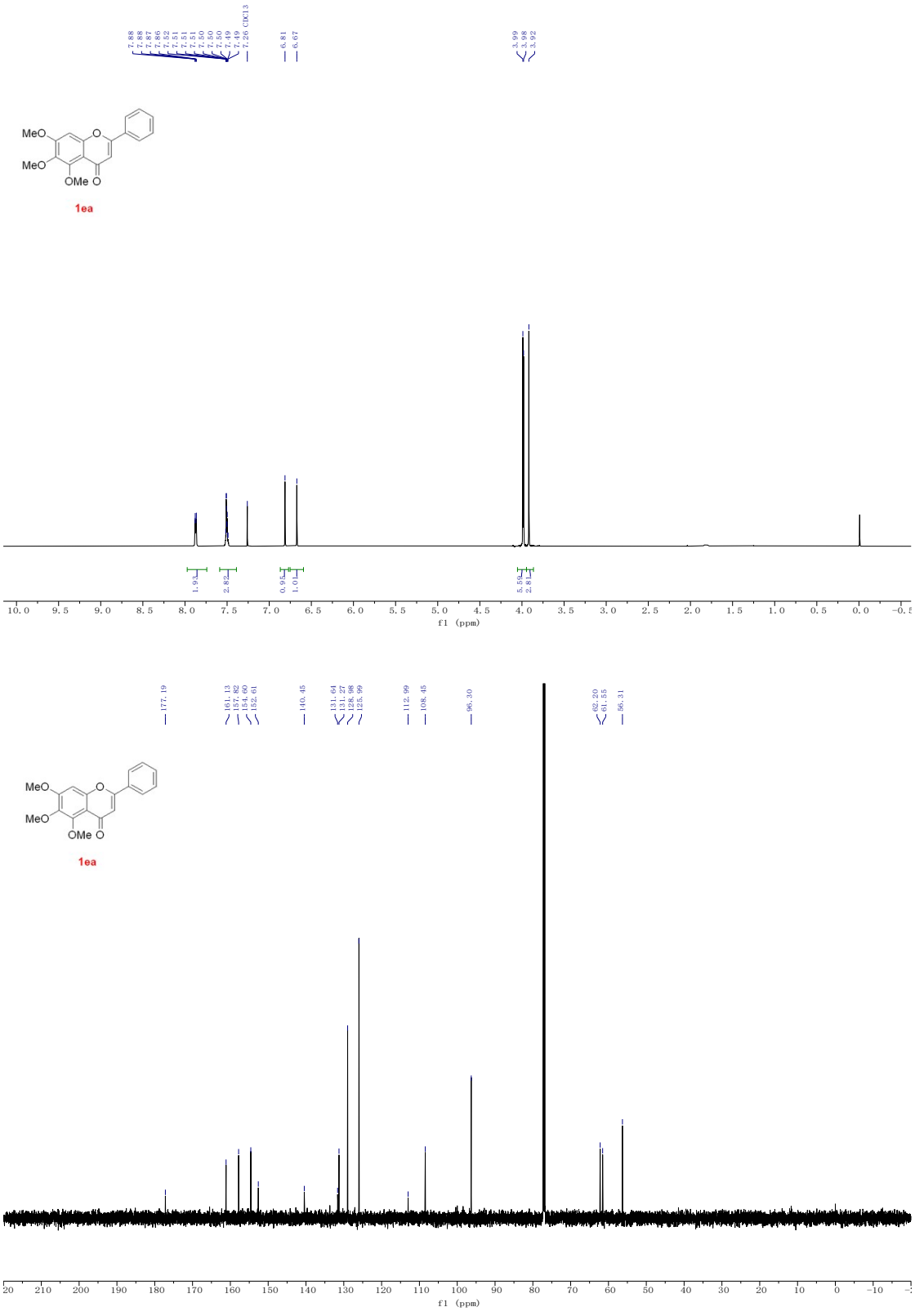
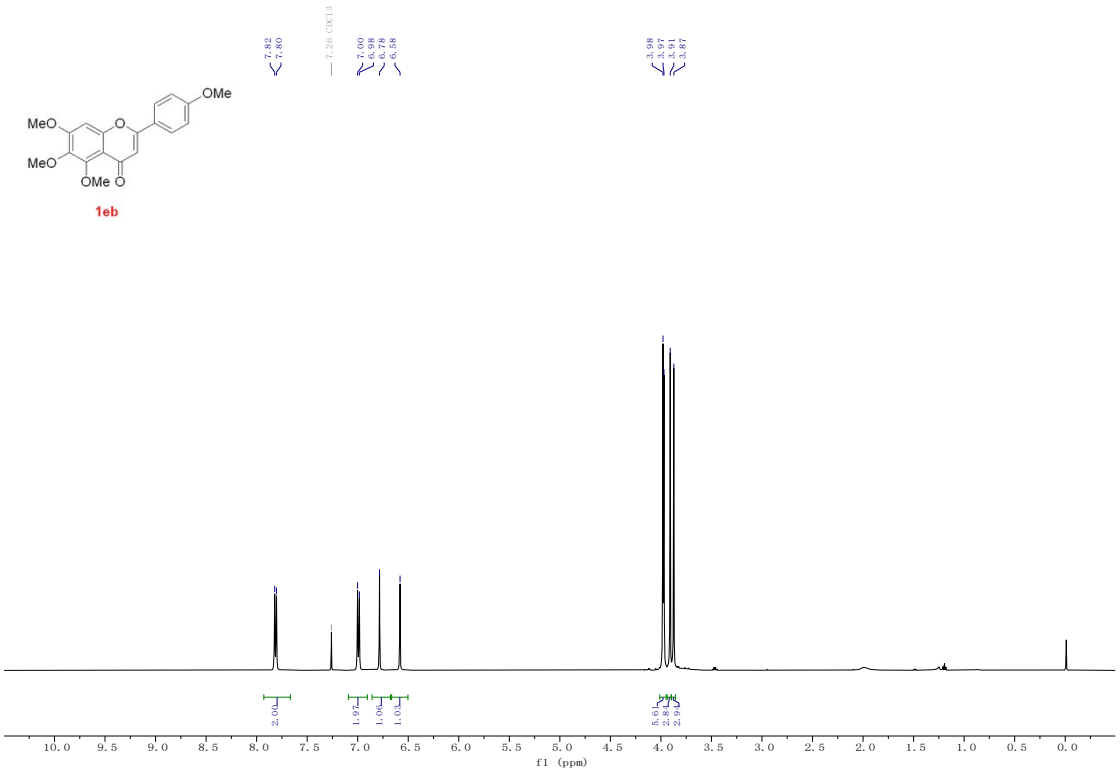
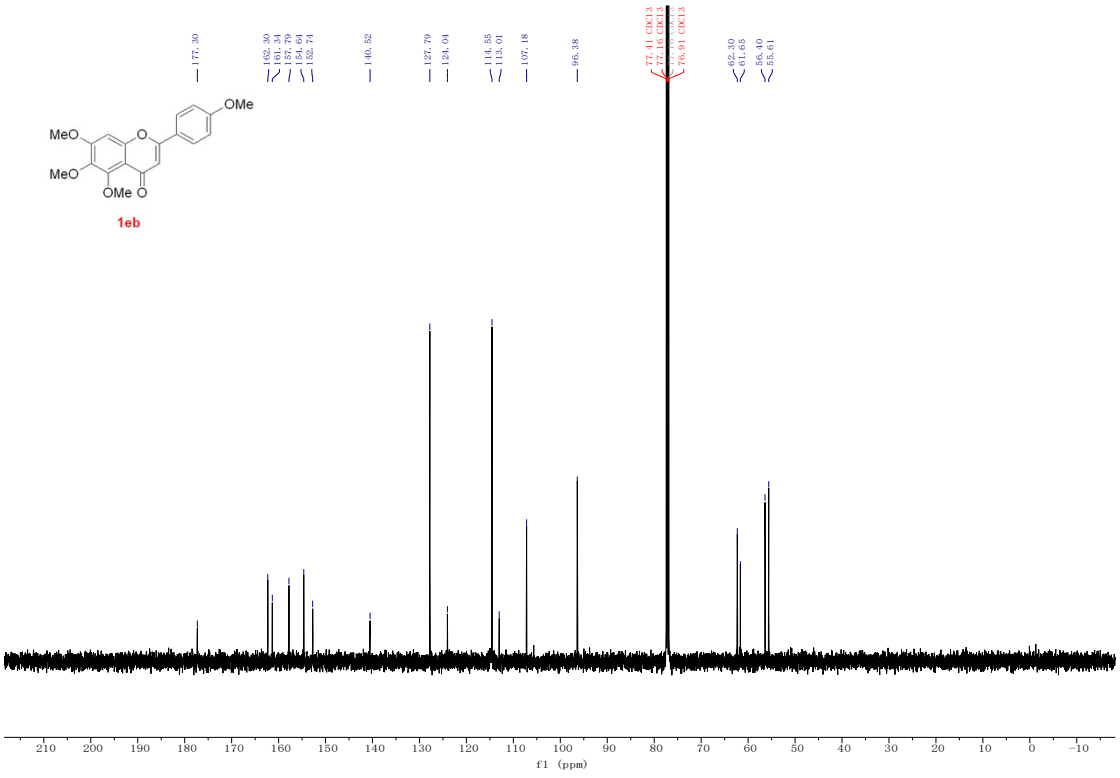
163.97
162.10
160.91
160.73
159.89
127.66
123.85
114.41
109.24
107.69
96.13
92.87
77.16 CDCl3
56.51
55.84
55.56
MeO
OMe
OMe
O
1db
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.88
7.88
7.87
7.86
7.52
7.51
7.51
7.51
7.50
7.50
7.49
7.49
7.26 CDCl3
6.81
6.67
3.99
3.98
3.92
MeO
MeO
OMe O
1ea
1.93
2.82
0.95
1.01
5.58
2.81
f1 (ppm)
177.19
161.13
157.82
154.60
152.61
140.45
131.64
131.27
128.98
125.99
112.99
108.45
96.30
62.20
61.55
56.31
MeO
MeO
OMe O
1ea
f1 (ppm)


7.82
7.80
7.26 CDCl3
7.00
6.98
6.78
6.58
3.98
3.97
3.91
3.87
MeO
MeO
OMe
OMe O
1eb
2.00
1.97
1.06
1.03
5.61
2.84
2.94
f1 (ppm)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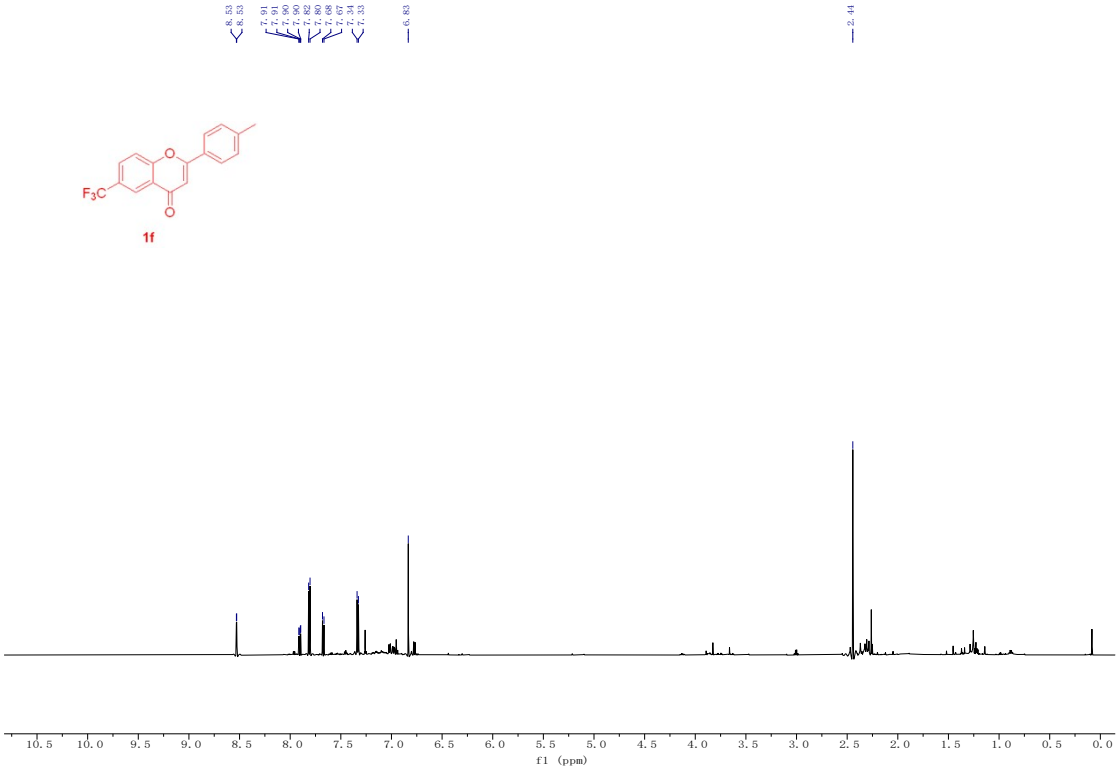
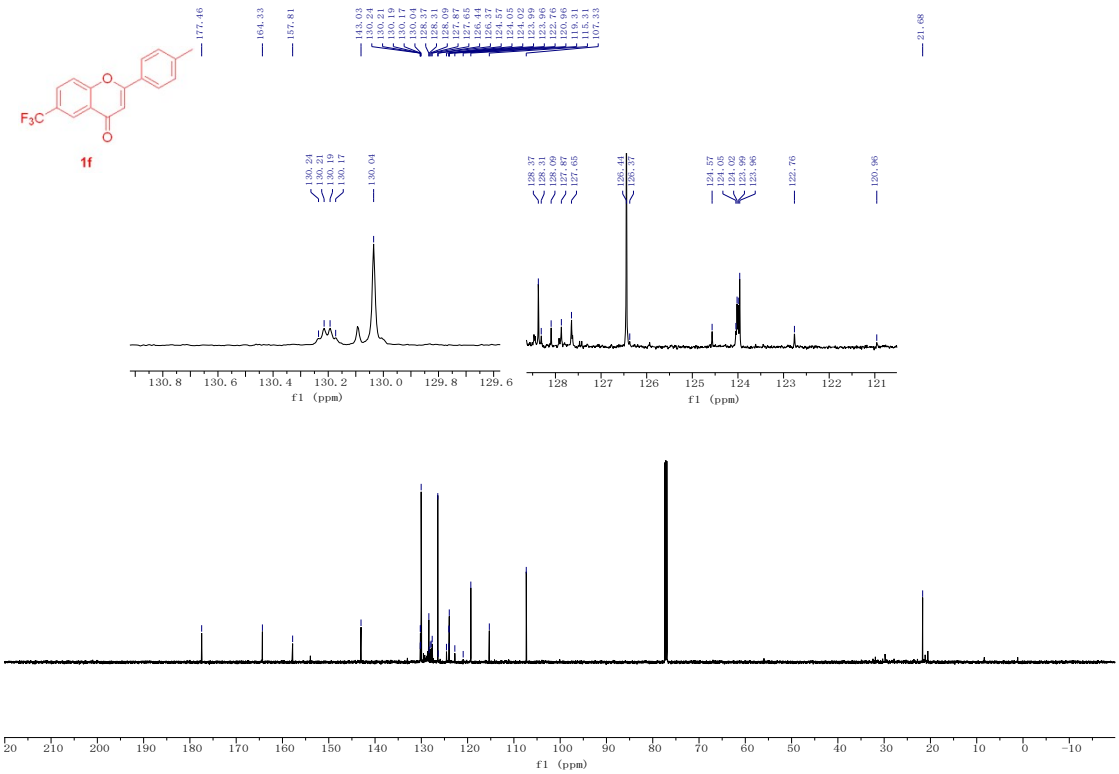
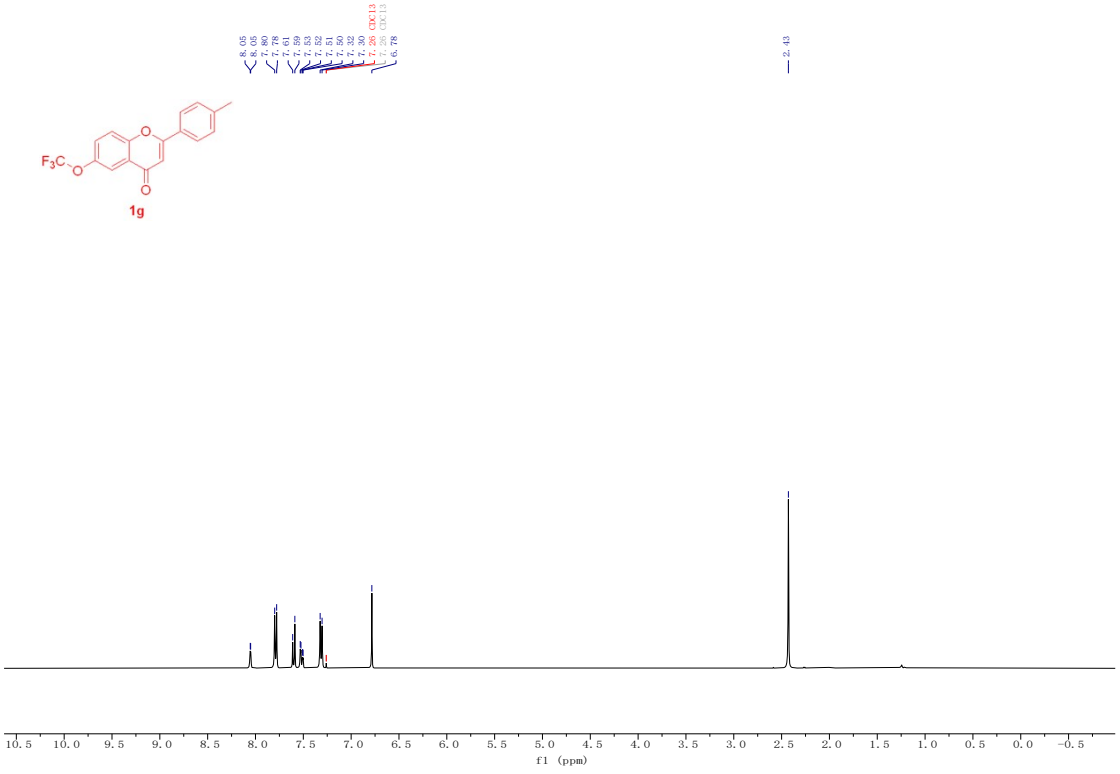
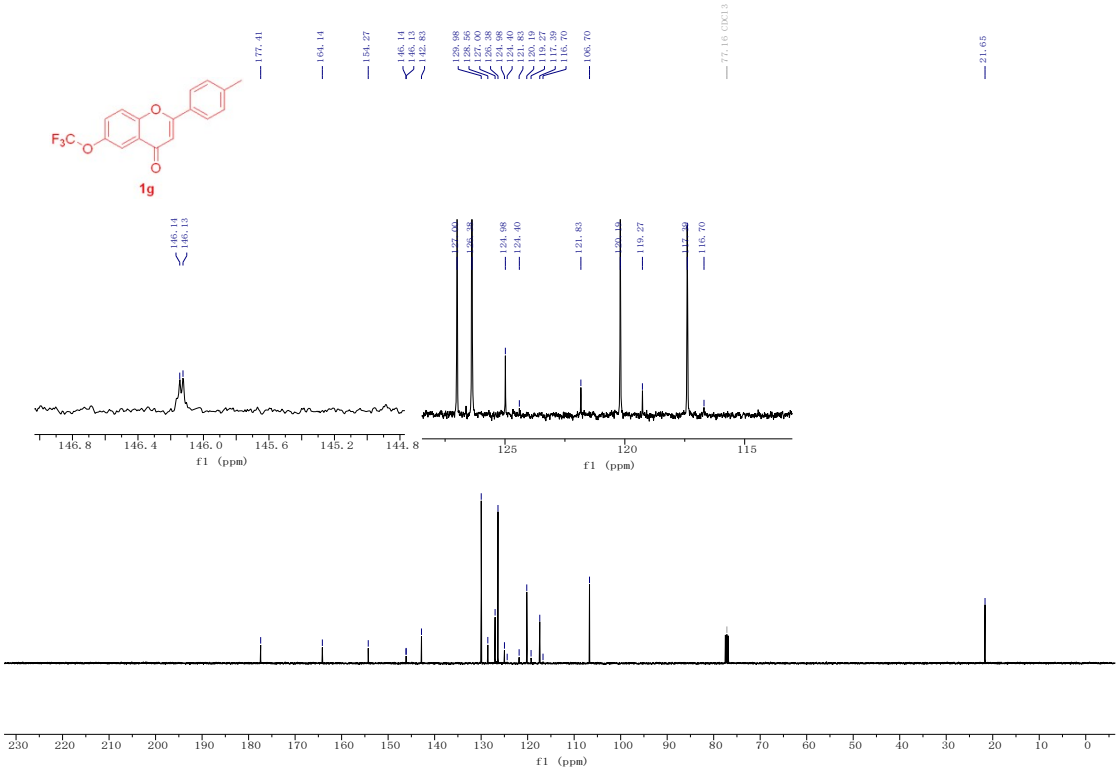
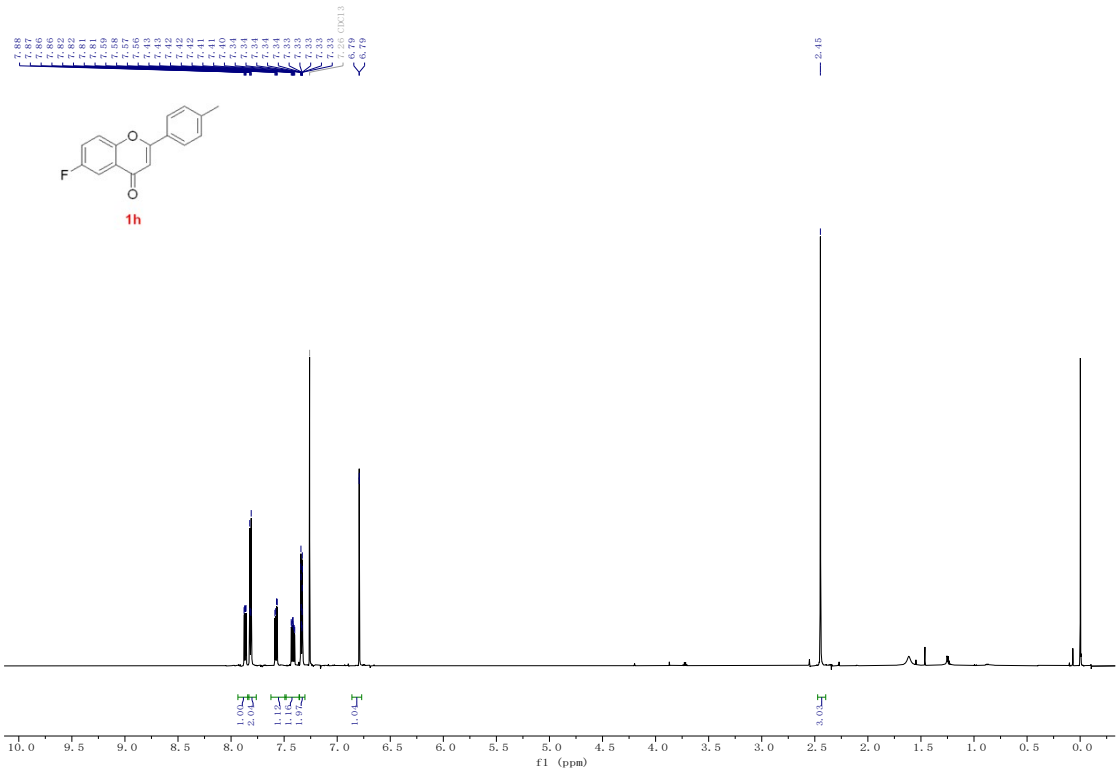
162.30
161.34
157.79
154.64
152.74
140.82
127.79
124.04
114.55
113.01
107.18
96.38
77.41 CDCl3
77.15 CDCl3
76.91 CDCl3
62.30
61.45
56.40
55.61
MeO
MeO
OMe
OMe O
1eb
f1 (ppm)

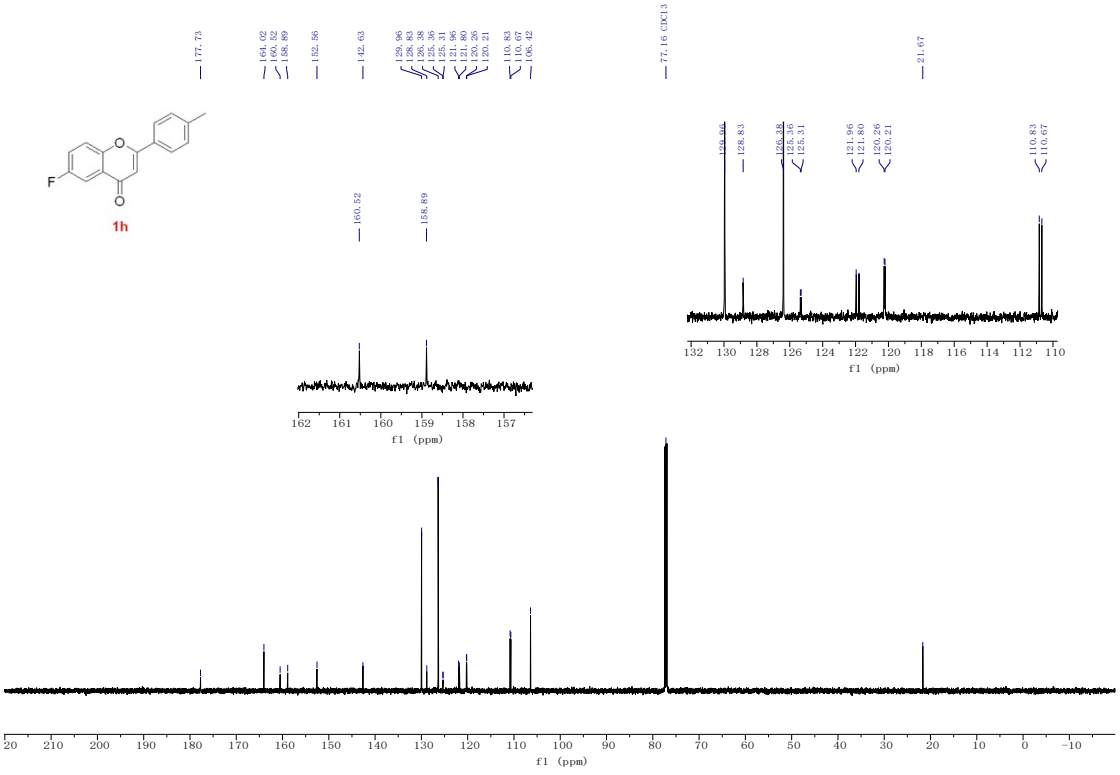

8.53
8.53
7.91
7.91
7.90
7.90
7.82
7.80
7.68
7.67
7.34
7.33
6.83
2.44
F3C
O
O
1f
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

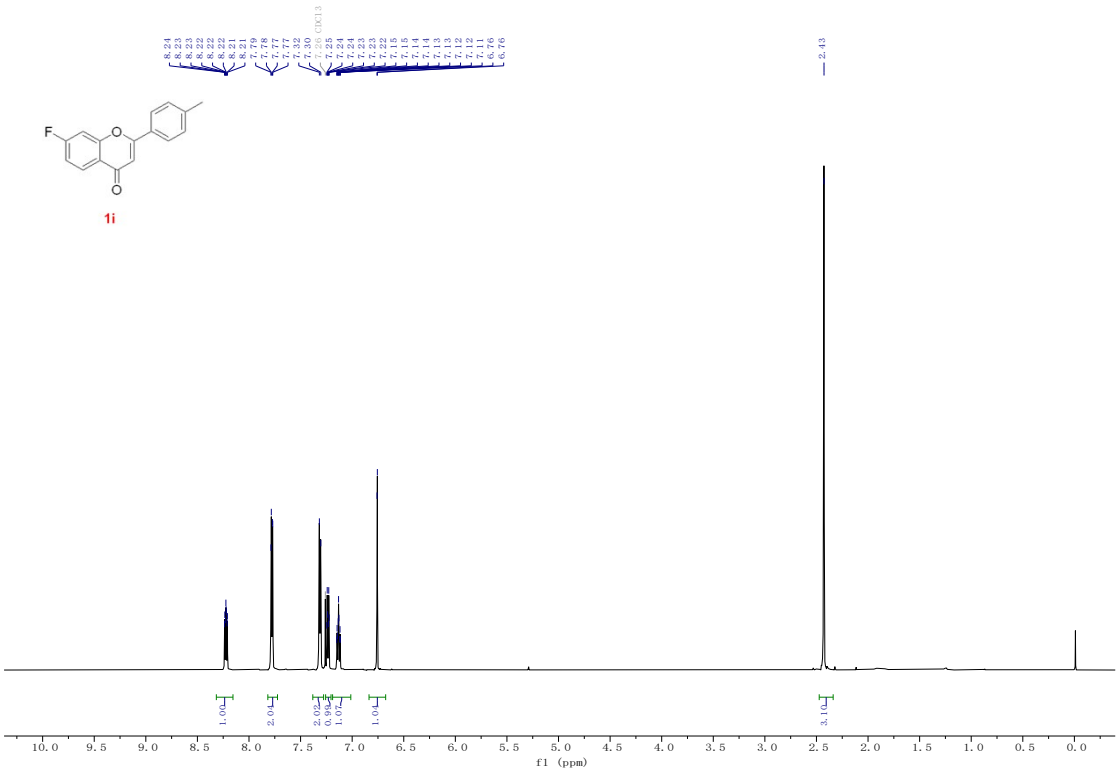

177.46
164.33
157.81
143.03
130.24
130.21
130.19
130.17
130.04
128.37
128.31
128.09
127.87
127.65
126.44
126.37
124.57
124.05
124.02
123.98
123.96
122.76
120.96
114.11
115.31
107.33
21.68
F3C
O
O
1f
130.24
130.21
130.19
130.17
130.04
128.37
128.31
128.09
127.87
127.65
126.44
126.37
124.57
124.05
124.02
123.98
123.96
122.76
120.96
130.8 130.6 130.4 130.2 130.0 129.8 129.6
f1 (ppm)
128 127 126 125 124 123 122 121
f1 (ppm)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

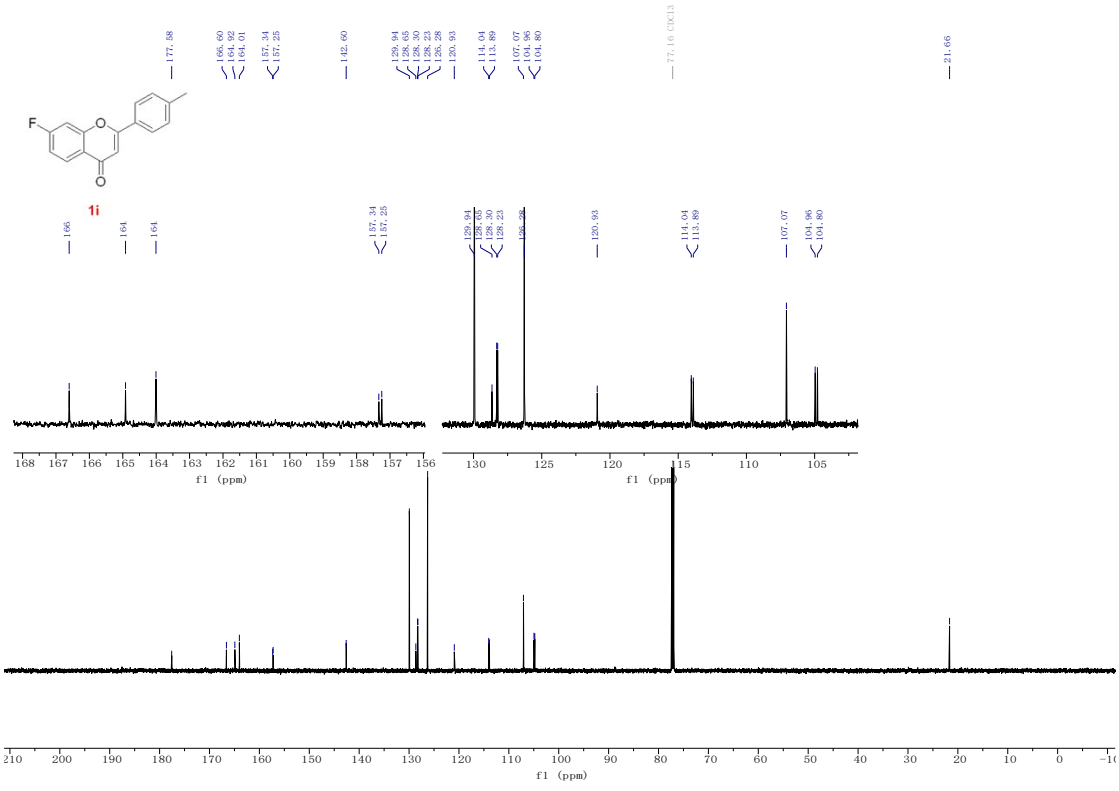

8.05
8.05
7.80
7.78
7.61
7.59
7.55
7.52
7.51
7.50
7.32
7.30
CDCl3
7.25
CDCl3
6.78
2.43
F3C
O
O
O
1g
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

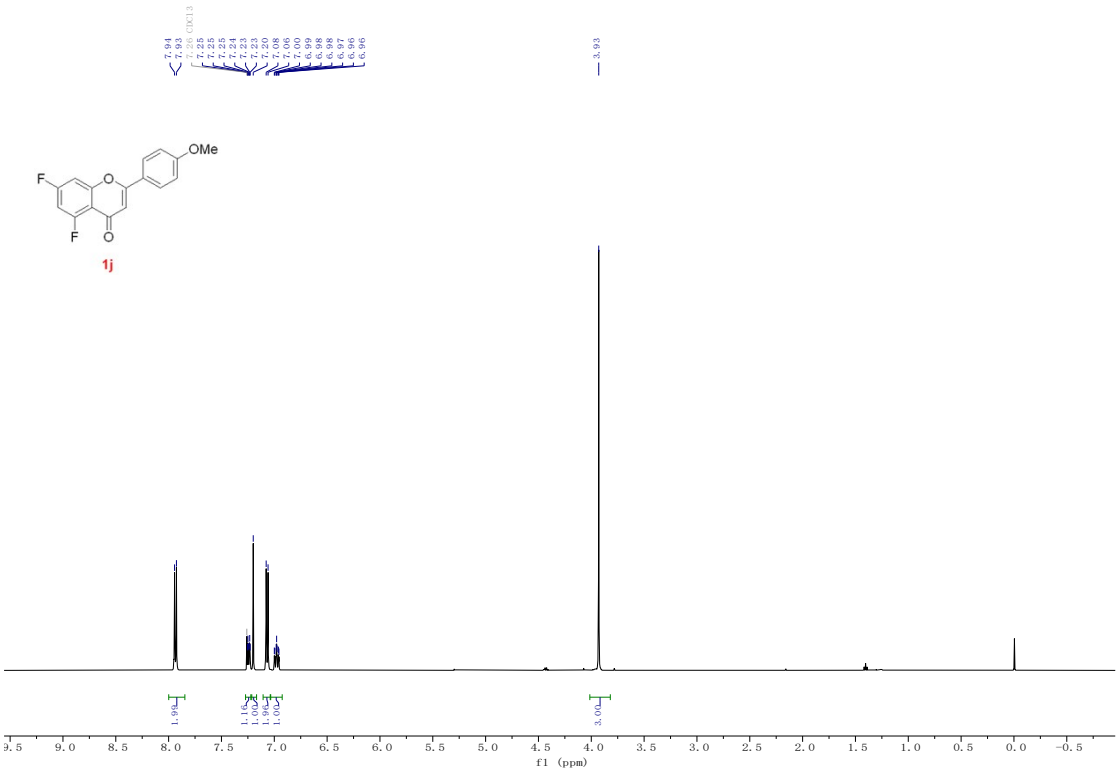

177.41
164.14
154.27
146.14
146.13
142.83
129.98
128.56
127.60
126.38
124.98
124.40
121.83
120.19
119.27
117.39
116.70
106.70
77.16 CDCl3
21.65
F3C
O
O
O
1g
146.14
146.13
124.98
124.40
121.83
119.27
116.70
146.8 146.4 146.0 145.6 145.2 144.8
f1 (ppm)
125 120 115
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

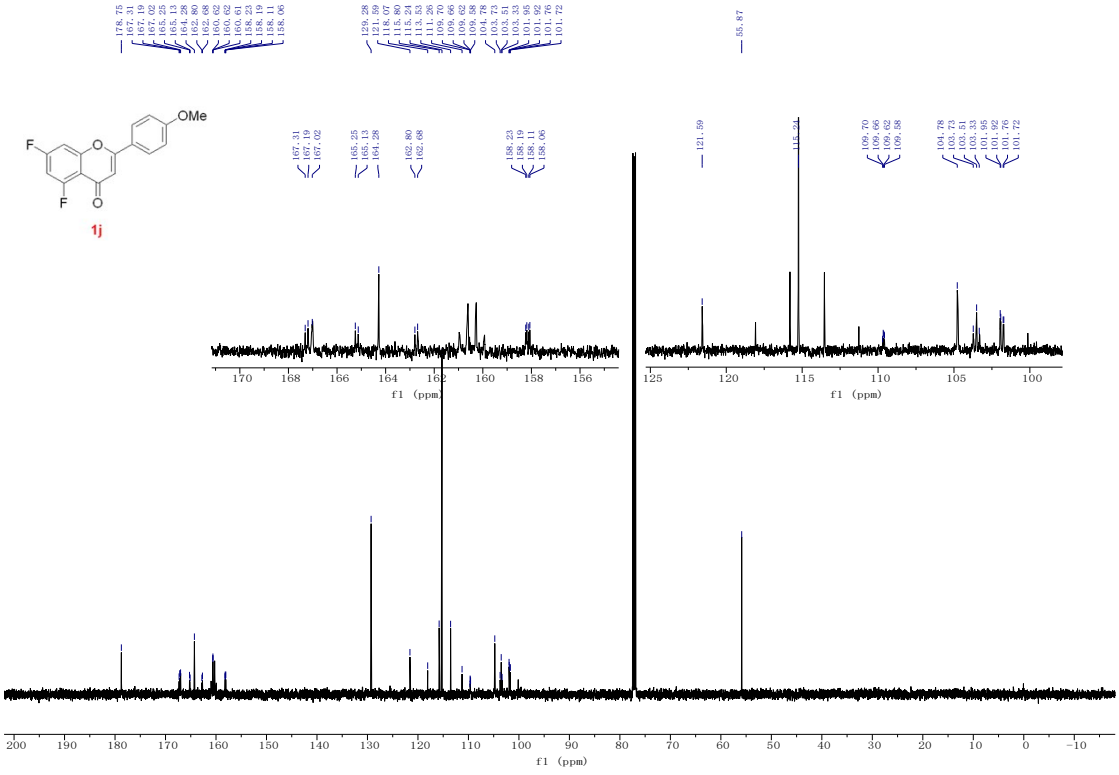

1h
f1 (ppm)

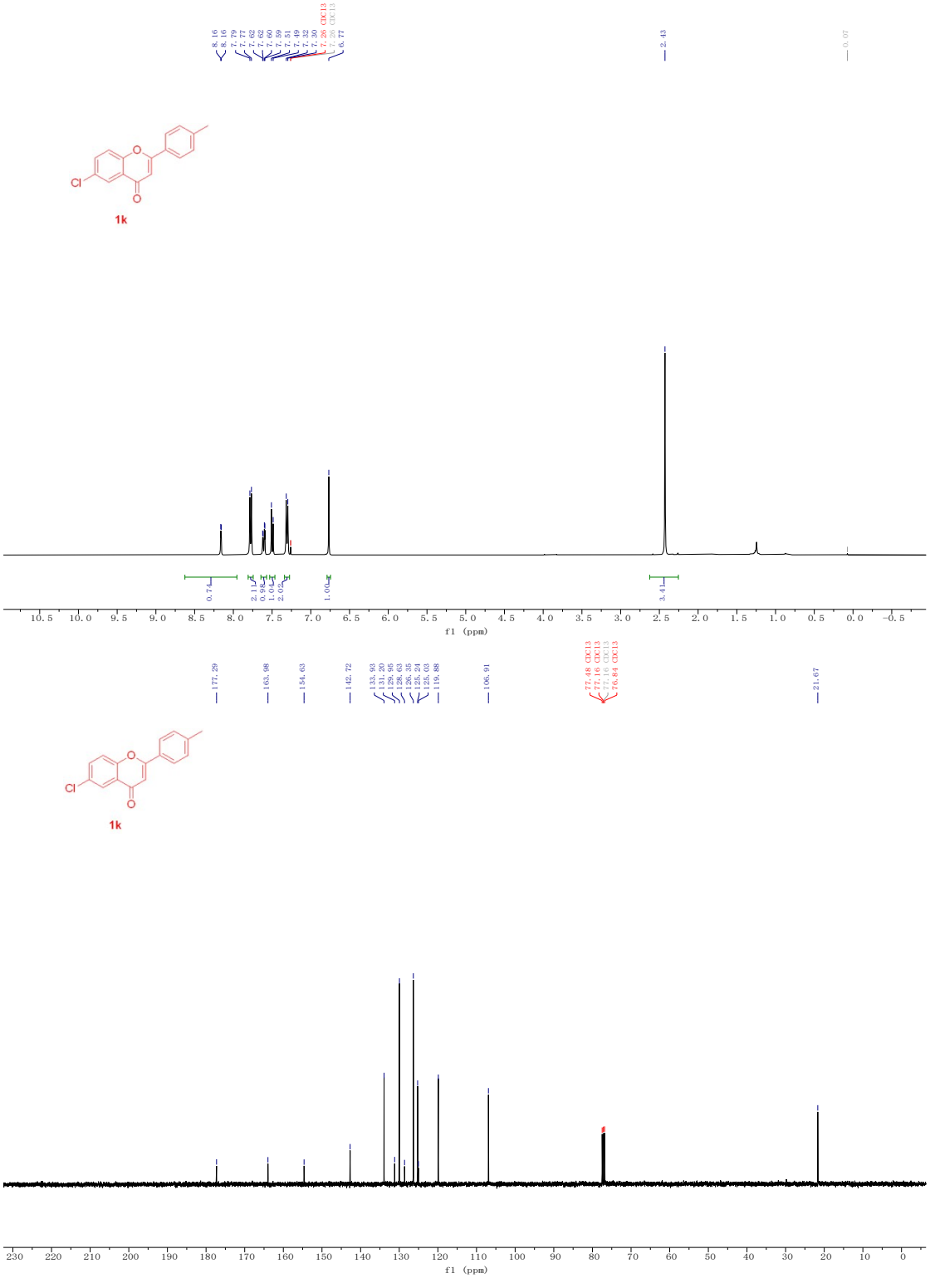

1h
f1 (ppm)

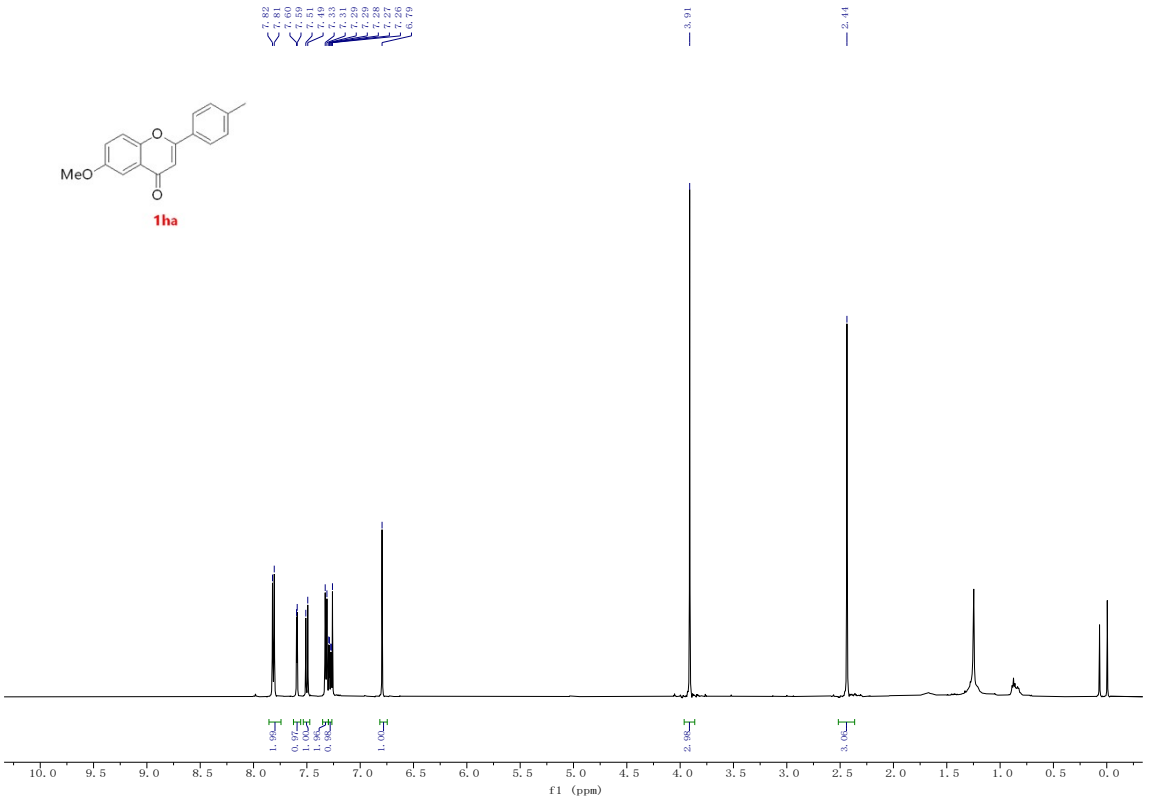

1i
f1 (ppm)

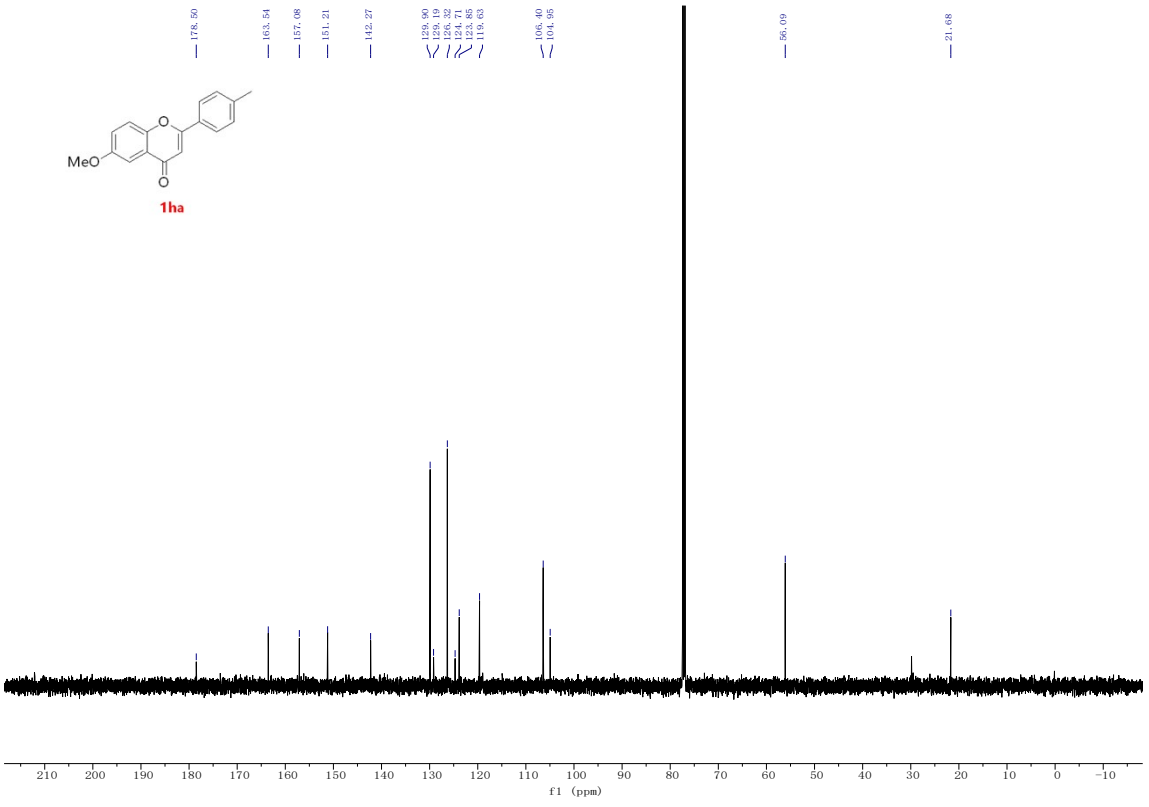

1i
f1 (ppm)

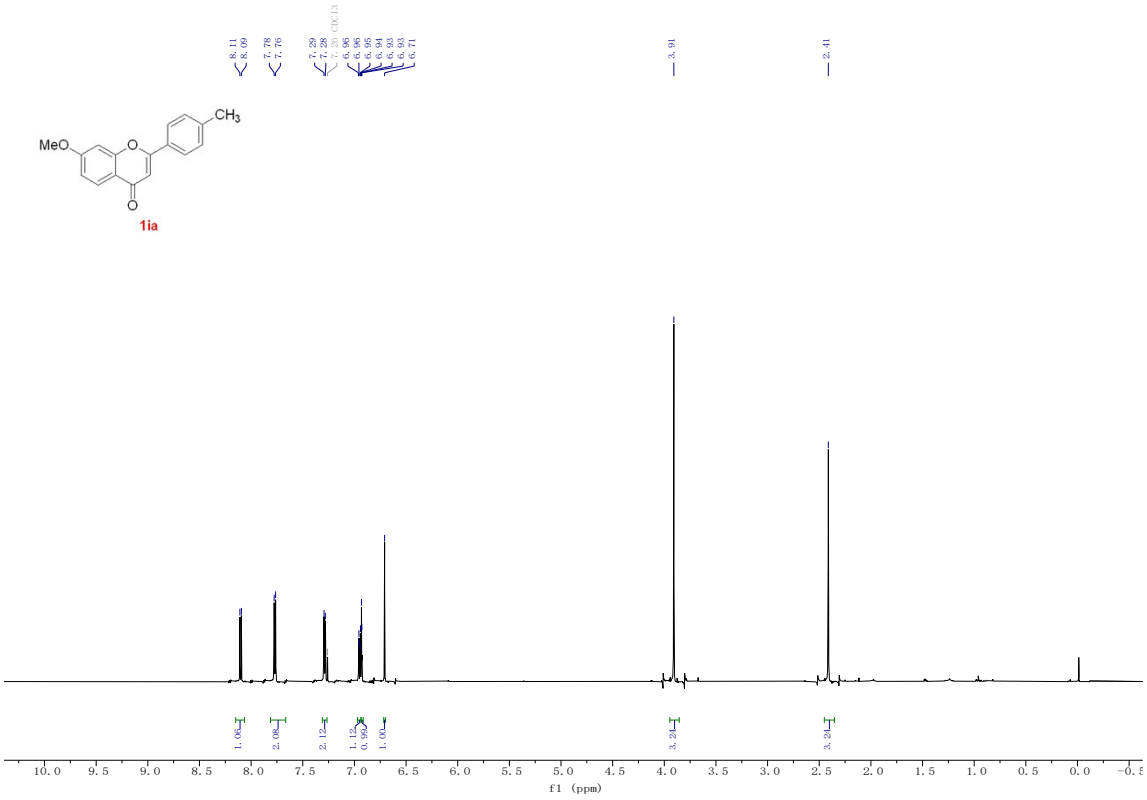

7.94
7.93
7.26 CDCl3
7.25
7.25
7.25
7.24
7.23
7.23
7.20
7.08
7.06
7.00
6.99
6.98
6.98
6.97
6.96
6.96
6.95
3.93
OMe
F
O
F
O
1j
1.98
1.02
1.00
1.94
1.00
3.00
f1 (ppm)

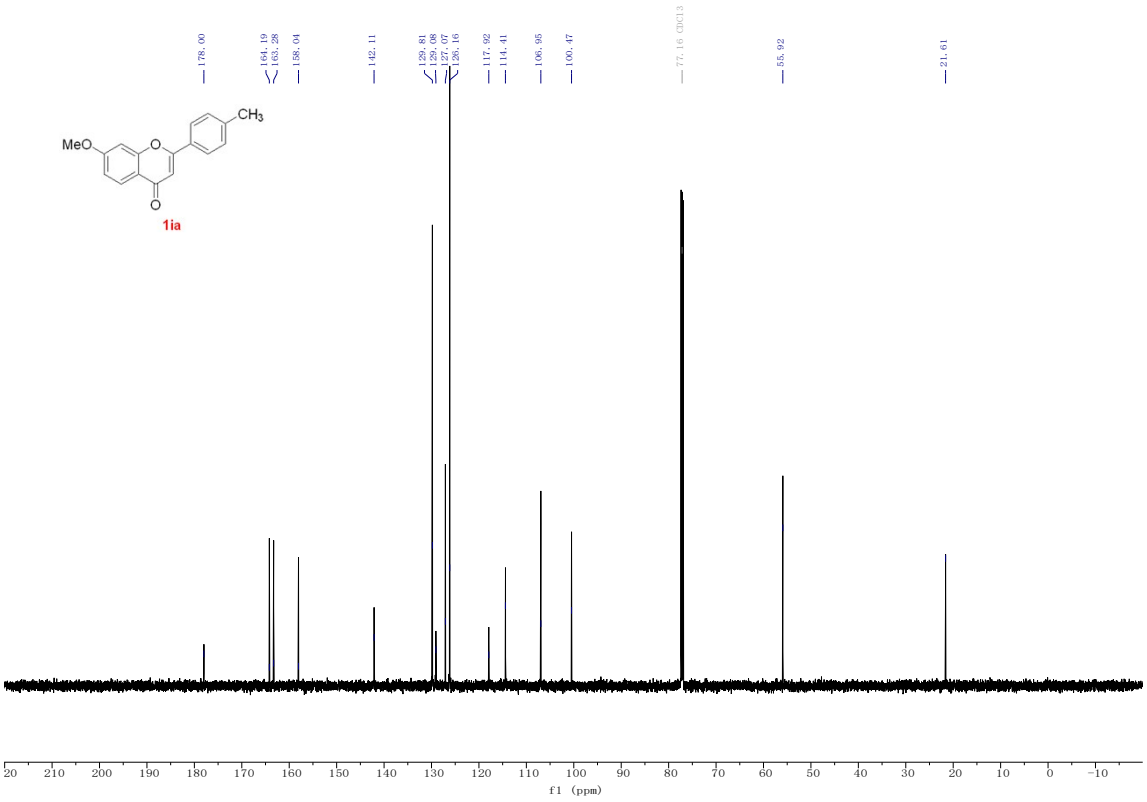

178.75
167.31
167.19
167.02
165.25
165.13
164.98
162.80
162.68
160.62
160.61
158.23
158.19
158.11
158.06
129.28
121.59
118.07
115.80
115.54
113.53
111.25
109.70
109.66
109.62
109.58
104.78
103.73
103.51
103.33
101.95
101.92
101.76
101.72
55.87
OMe
F
O
F
O
1j
f1 (ppm)
f1 (ppm)
f1 (ppm)

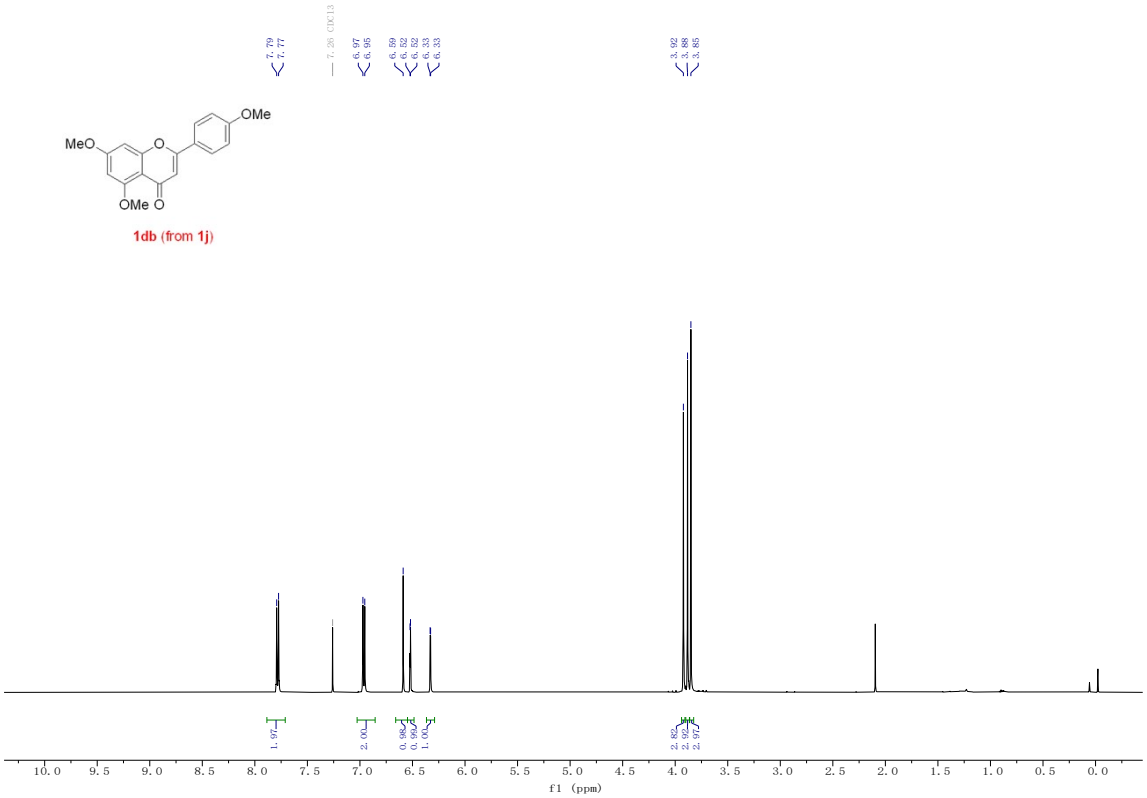

8.16
8.16
7.79
7.77
7.62
7.62
7.60
7.59
7.51
7.49
7.32
7.30
7.26 CDCl3
7.26 CDCl3
6.77
2.43
0.07
Cl
O
O
1k
0.74
2.11
0.96
1.04
2.02
1.00
3.41
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
177.29
163.98
154.63
142.72
133.93
131.20
128.95
128.63
126.15
125.24
125.03
119.88
106.91
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
21.67
Cl
O
O
1k
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

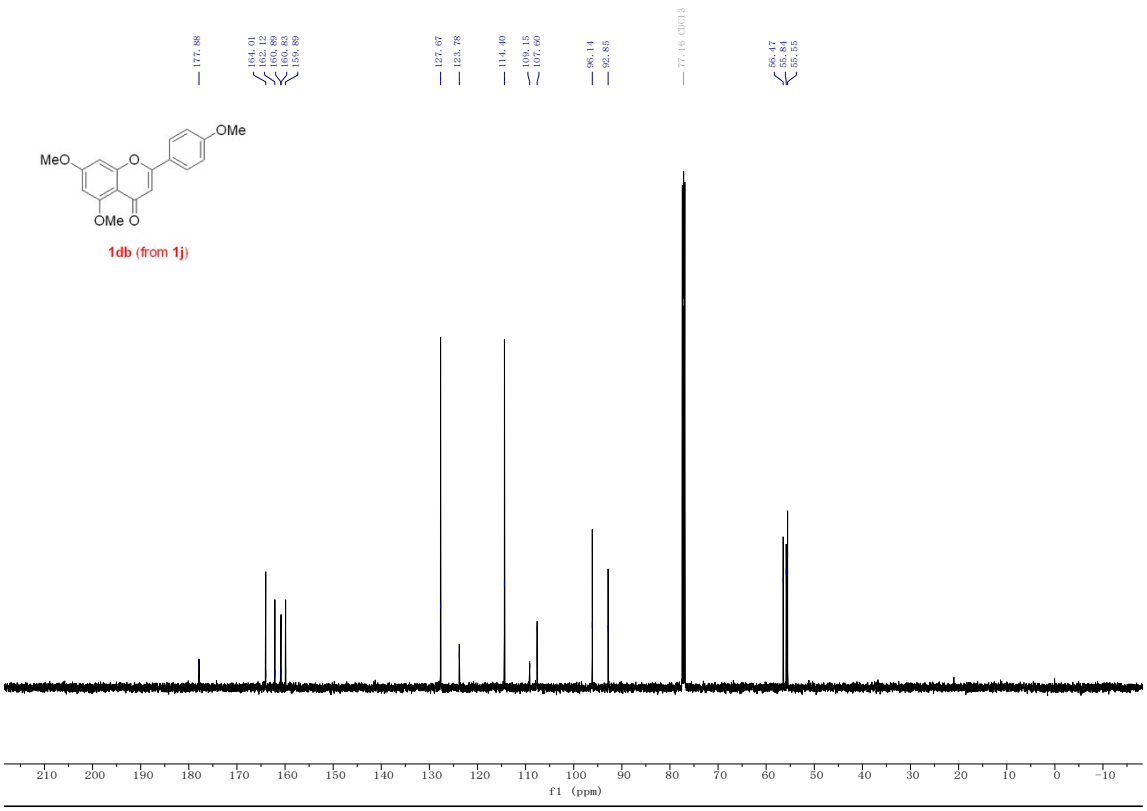

7.82
7.81
7.60
7.59
7.51
7.49
7.33
7.31
7.29
7.29
7.28
7.27
7.26
6.79
3.91
2.44
MeO
O
O
1ha
1.99
0.97
1.00
1.96
0.98
1.00
2.98
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

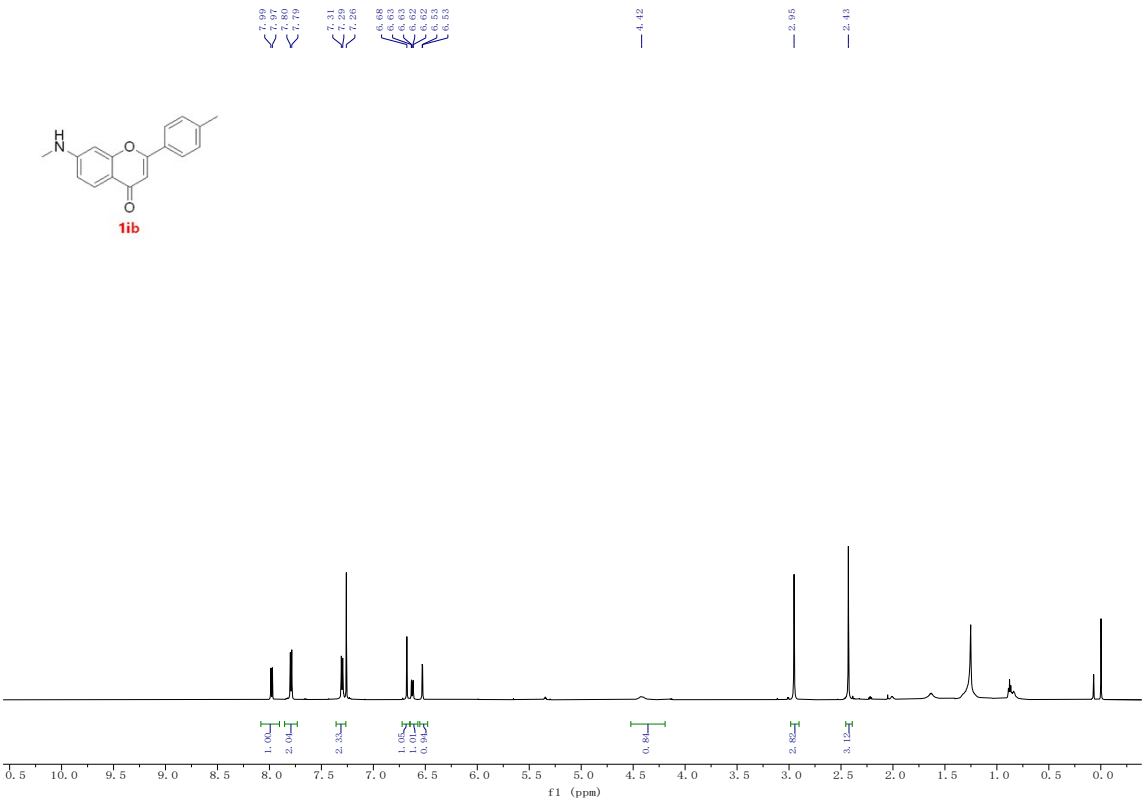

178.50
163.54
157.08
151.21
142.27
129.90
129.19
126.32
124.71
123.85
119.63
106.40
104.95
56.09
21.68
MeO
O
O
1ha
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

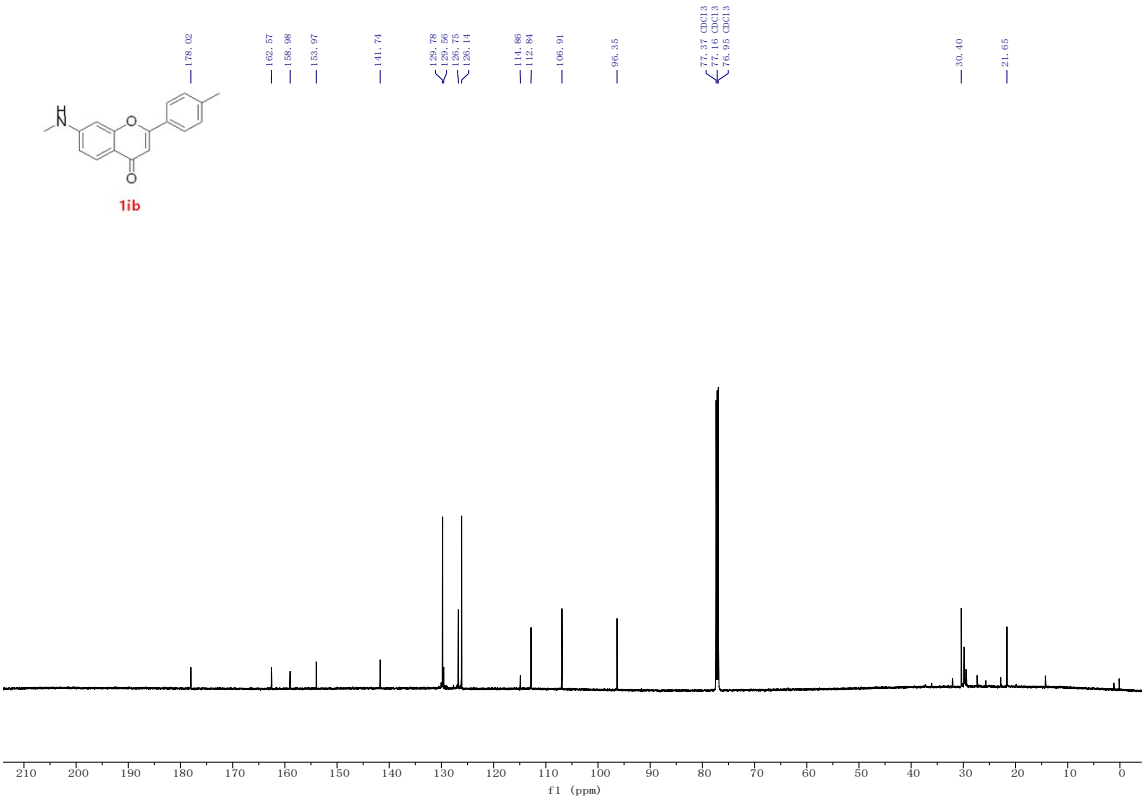

8.11
8.09
7.78
7.76
7.29
7.28
6.96
6.95
6.94
6.93
6.71
3.91
2.41
MeO
CH3
O
O
1ia
1.06
2.08
2.12
1.12
0.99
1.00
3.24
3.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

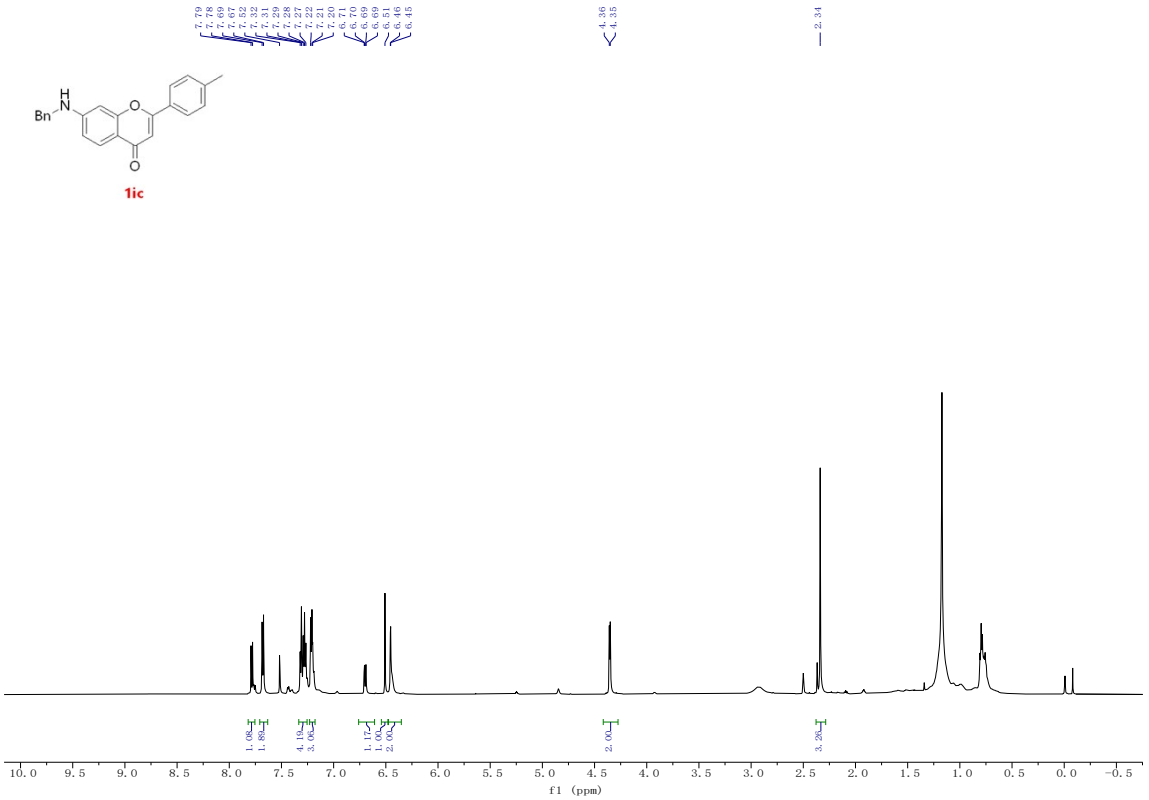

178.00
164.19
163.28
158.04
142.11
129.81
129.08
127.07
126.16
117.92
114.41
106.95
100.47
77.16 CDCl3
55.92
21.61
MeO
CH3
O
O
1ia
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

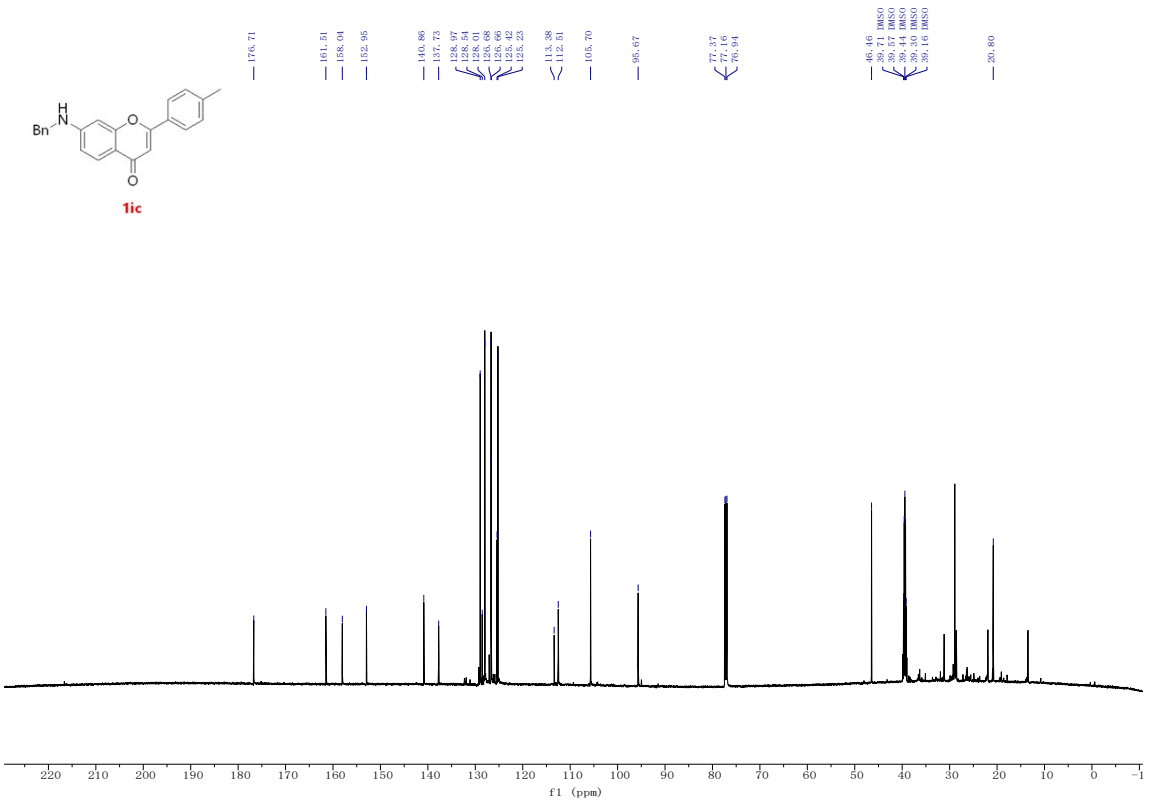

7.79
7.77
7.26 CDCl3
6.97
6.95
6.59
6.52
6.52
6.33
6.33
3.92
3.88
3.85
OMe
MeO
OMe O
1db (from 1j)
1.97
2.00
0.98
0.99
1.00
2.82
2.92
2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

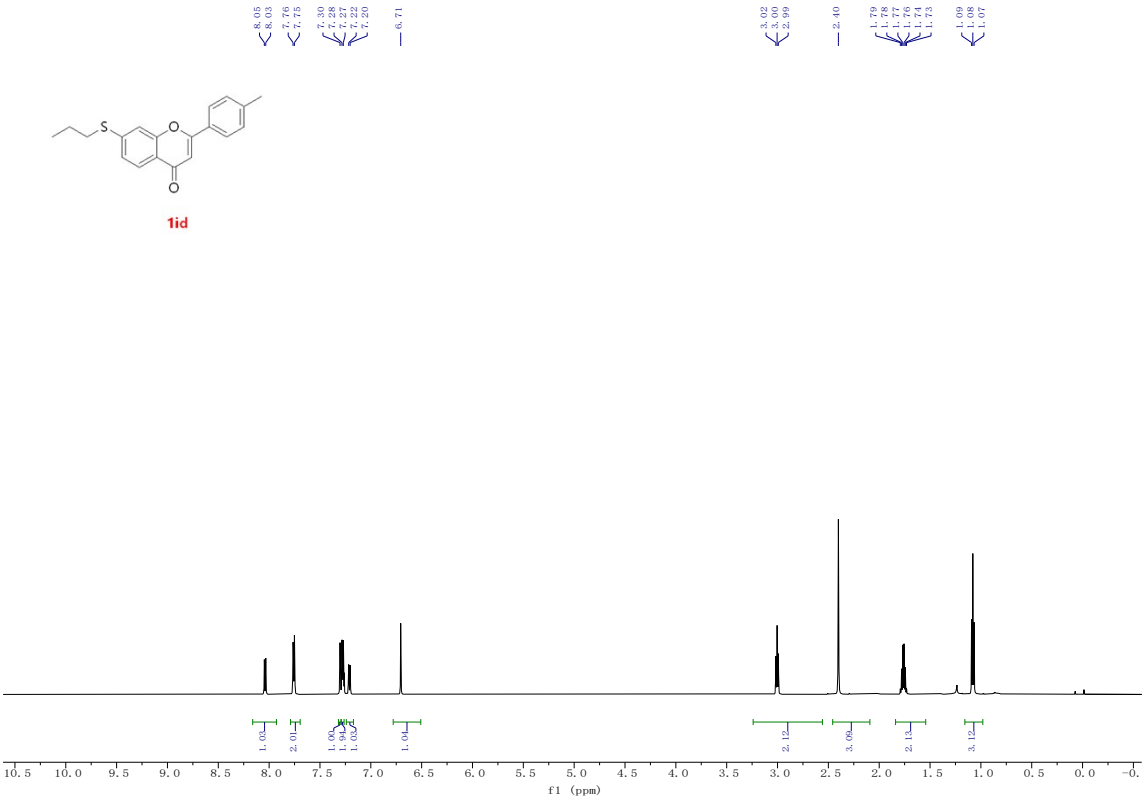

177.88
164.01
162.12
160.89
160.83
159.89
127.67
123.78
114.40
109.15
107.60
96.14
92.85
77.16 CDCl3
56.47
55.84
55.55
OMe
MeO
OMe O
1db (from 1j)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

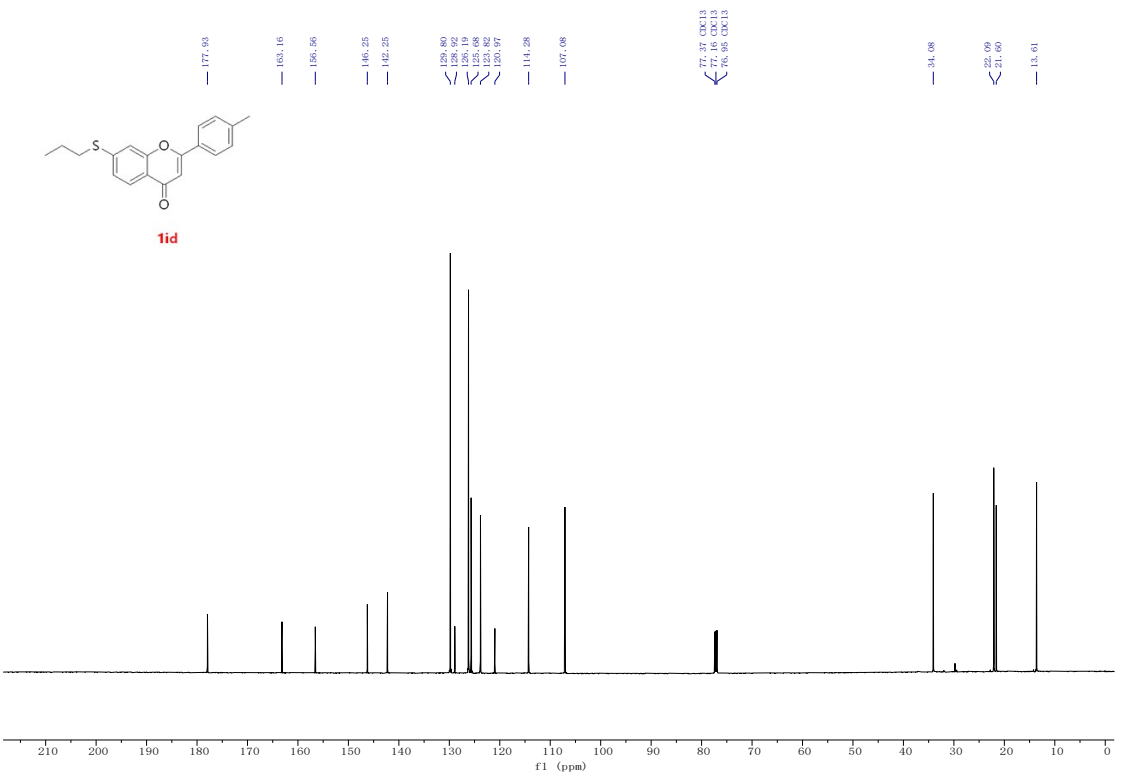

7.99
7.97
7.80
7.79
7.31
7.29
7.26
6.68
6.65
6.63
6.62
6.62
6.53
6.53
4.42
2.95
2.43
1ib
1.00
2.04
2.33
1.05
1.01
0.94
0.84
2.82
3.12
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

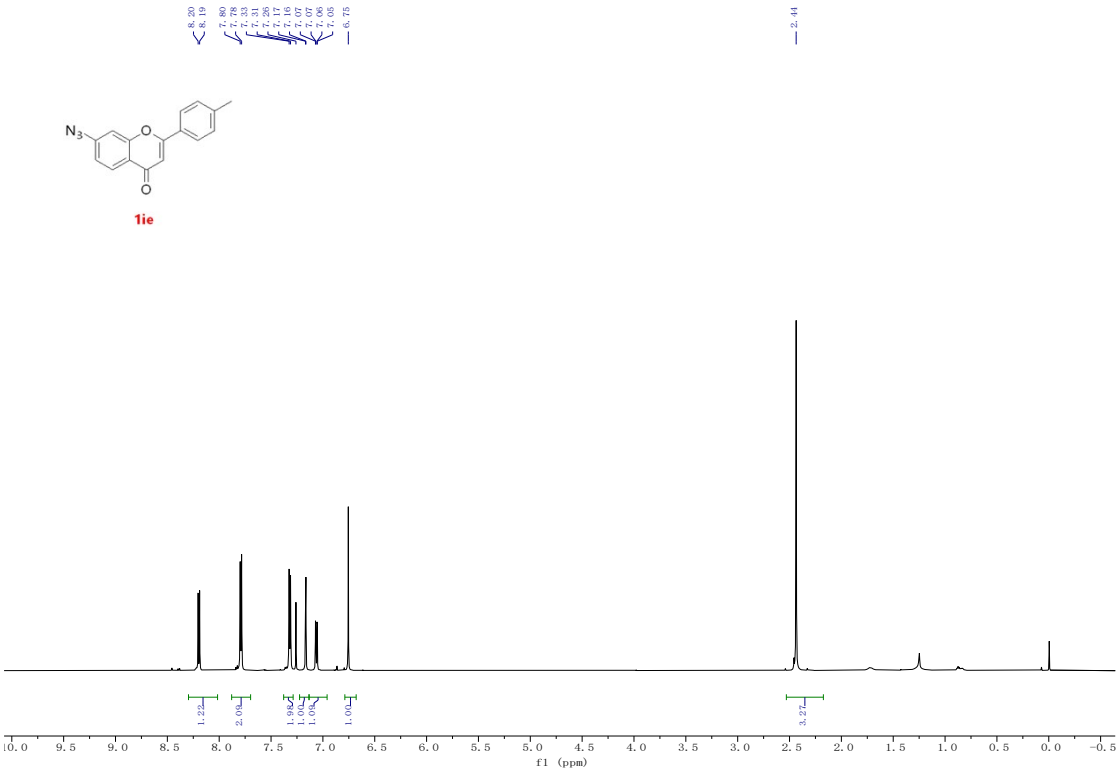

178.02
162.57
158.98
153.97
141.74
129.78
129.56
126.75
126.14
114.86
112.84
106.91
96.35
77.37 CDCl3
77.05 CDCl3
76.95 CDCl3
30.40
21.65
1ib
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.79
7.78
7.69
7.67
7.32
7.31
7.29
7.28
7.27
7.22
7.21
7.20
6.71
6.70
6.69
6.69
6.51
6.46
6.45
4.36
4.35
2.34
Bn
N
H
O
O
1ic
1.08
1.85
4.19
3.06
1.17
1.00
2.00
2.00
3.26
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

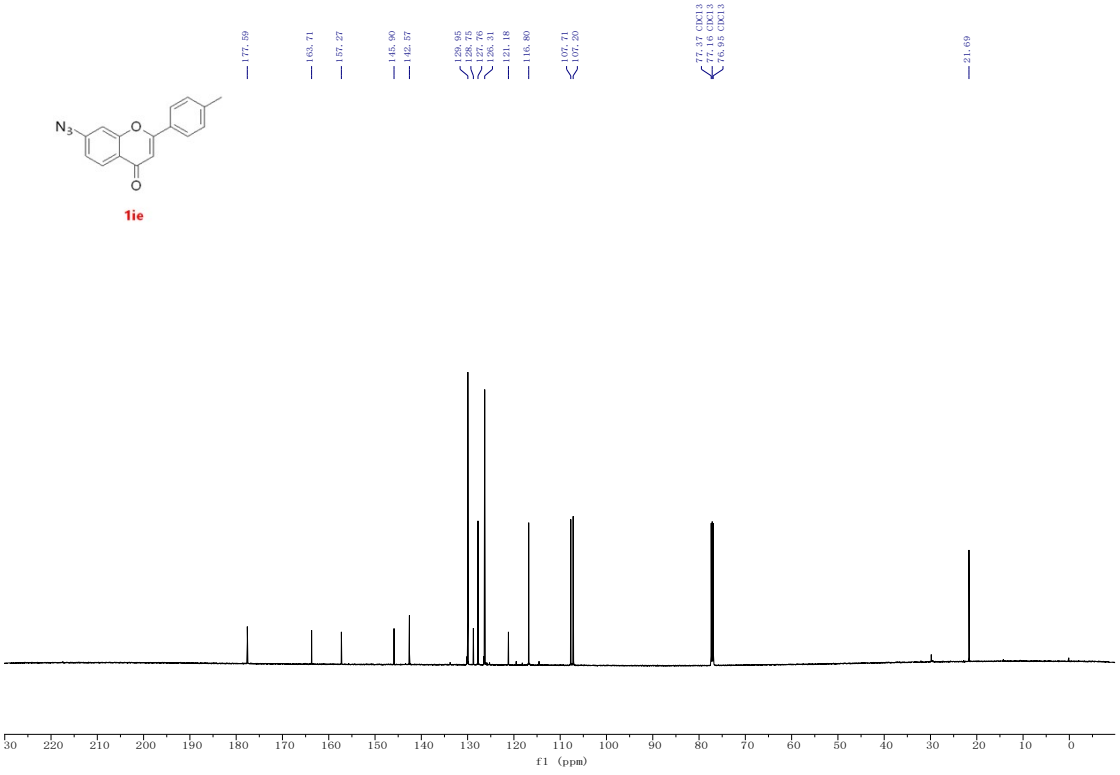

176.71
161.51
158.04
152.95
140.86
137.73
128.97
128.84
128.01
126.68
126.66
125.42
125.23
113.38
112.51
105.70
95.67
77.37
77.16
76.94
46.46
39.71 DMSO
39.57 DMSO
39.44 DMSO
39.30 DMSO
39.16 DMSO
20.80
Bn
N
H
O
O
1ic
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


8.05
8.03
7.76
7.75
7.30
7.28
7.27
7.22
7.20
6.71
3.02
3.00
2.99
2.40
1.79
1.78
1.77
1.77
1.76
1.74
1.73
1.09
1.08
1.07
1id
1.03
2.01
1.00
1.94
1.03
1.04
2.12
3.09
2.13
3.12
f1 (ppm)


177.93
163.16
156.56
146.25
142.25
129.80
128.92
126.19
125.68
123.82
120.97
114.28
107.08
77.37 CDCl3
77.05 CDCl3
76.95 CDCl3
34.08
22.09
21.60
13.61
1id
f1 (ppm)


8.20
8.19
7.80
7.78
7.33
7.31
7.28
7.17
7.16
7.07
7.07
7.06
7.05
6.75
2.44
1.22
2.00
1.98
1.00
1.08
1.00
3.27
f1 (ppm)

1ie


177.59
163.71
157.27
145.90
142.57
129.95
128.75
127.76
126.31
121.18
116.80
107.71
107.20
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
21.69
f1 (ppm)

1ie