Supporting Information

Annulation of 2,3-diphenyl-4*H*-chromen-4-ones *via* photo-induced hydrogen evolution

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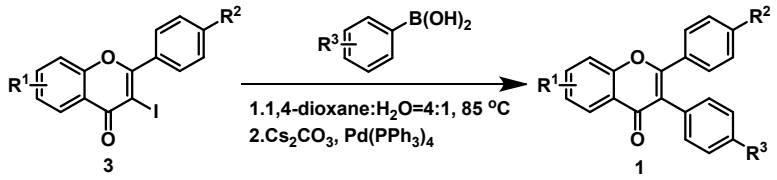
1. Experimental Procedures

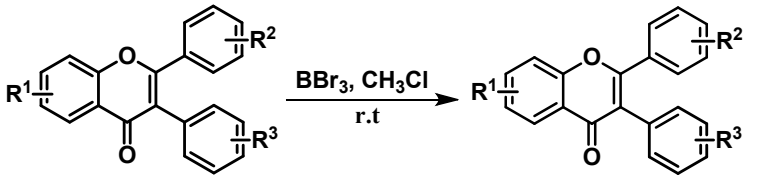
1.1 Synthesis of 2,3-diphenyl-4*H*-chromen-4-one (1)[1]



R^1=H, OMe, F, Me; R^2=H, Me, F, OMe ; R^3=H, Cl, Me, F, t-Bu

The mixture of 3-iodo-2-phenyl-4*H*-chromen-4-one **3a** (139 mg, 0.4 mmol), phenylboronic acid (122 mg, 1 mmol), Cs_2CO_3 (652 mg, 2 mmol) and $Pd(PPh_3)_4$ (1 % mmol, 11.5 mmg) was dissolved in a mixed solvent composed of dioxane and water (10 ml, 4:1, v/v). The reaction mixture was allowed to stir at 85 °C for 6 h under Ar. Then, the mixture was poured into the water (10 ml) and then extracted with ethyl acetate (20 ml×3). The combined organic layer dried over (Mg_2SO_4) and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/petroleum ether, 1:12) to give the desired product **1a** (yield, 83 %).

Similarly, compounds **1a-1z** and were prepared with the same method described above.

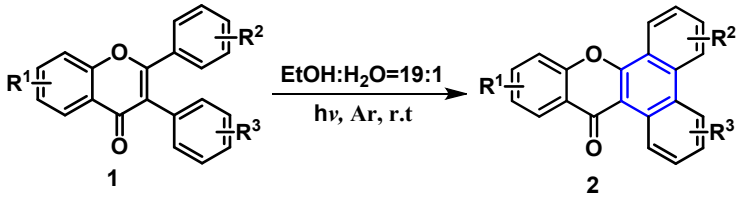


1b:R_1=Me, R_2=OMe, R_3=H
1P:R_1=OMe, R_2=Me, R_3=t-Bu

1ab:R_1=Me, R_2=OH, R_3=H
1aa:R_1=OH, R_2=Me, R_3=t-Bu

The cold diluted solution of BBr_3 (625 mg, 2.5 mmol) was added to a stirring solution of compound **1b** (171 mg, 0.5 mmol) or **1p** (199 mg, 0.5 mmol) in dry chloroform (10 mL) under the ice bath. The mixture was stirred at the ice bath for 30 min and refluxed for overnight. After cooling to room temperature, the excess BBr_3 was quenched by adding MeOH (5 mL). The volatiles were removed under the reduced pressure and purified by column chromatography to give **1b** (91.8 mg, 56 %) or **1p** (yield, 60 %).[2]

1.2 Synthesis of 14*H*-dibenzo[*a*,*c*]xanthen-14-one derivatives (2)

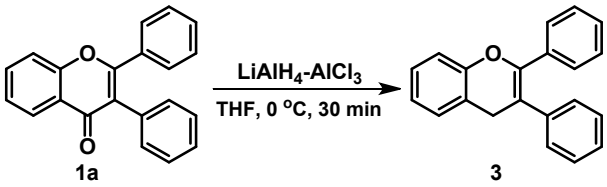


R^1=H, OMe, Me, F, OH; R^3=H, Cl, Me, F, t-Bu; R^2=H, Me, OMe, F, OH

Substrate 2,3-diphenyl-4*H*-chromen-4-one **1a** (149 mg, 0.5 mmol) was dissolved in a mixture of EtOH-H_2O (100 mL, 19:1, v/v) at ambient temperature in a quartz tube. The mixture was deaerated for 3 min by bubbling argon and irradiated with a high pressure mercury lamp (500 W) at room temperature for 3 h. Then the reaction mixture were removed under reduced pressure and purified by column chromatographied (ethyl acetate/petroleum ether, 1:50) to give **2a** (yield, 63 %).

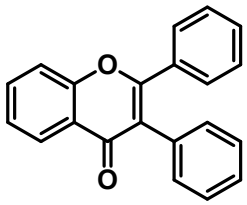
Similarly, compounds **2a-2z** were prepared with the same method as described above.

1.3 Synthesis of 2,3-diphenyl-4*H*-chromene (3)

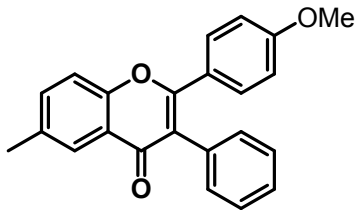


The mixture of 2,3-diphenyl-4*H*-chromen-4-one **1a** (149 mg, 0.5 mmol) and aluminium chloride (333 mg, 2.5 mmol) were dissolved in absolute THF (10 ml) at ice bath. Then the $LiAlH_4$ (6 ml) was added drop by drop. The solution was stirred at the room temperature for 30 min under Ar, poured into the saturated ammonium chloride to quench the reaction. The mixture was extracted with ethyl acetate (20 ml×3) and combined organic layer dried over (Mg_2SO_4), concentrated under reduced pressure. Then the oily residue were purified by column chromatographied (petroleum ether) to give **3** (yield, 44 %).

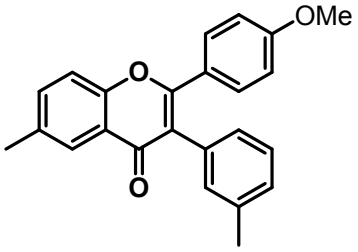
2. Characterization Data for Compounds



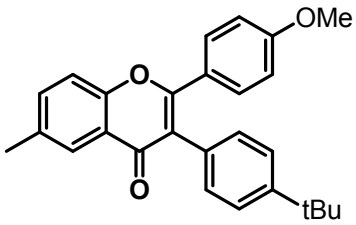
2,3-diphenyl-4*H*-chromen-4-one (1a):[3] Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.30 (d, *J* = 7.9 Hz, 1H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.42 (dd, *J* = 15.1, 7.7 Hz, 3H), 7.35-7.26 (m, 6H), 7.22 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 177.48, 161.62, 156.22, 133.81, 133.46, 133.00, 131.37, 130.20, 129.72, 128.40, 128.22, 127.74, 126.55, 125.22, 123.69, 123.12, 118.11.



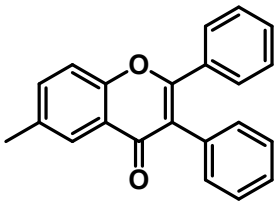
2-(4-methoxyphenyl)-6-methyl-3-phenyl-4*H*-chromen-4-one (1b):[4] Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.05 (s, 1H), 7.49 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.36-7.27 (m, 5H), 7.25-7.22 (m, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 177.48, 161.29, 160.94, 154.37, 134.94, 134.89, 133.59, 131.36, 131.33, 128.45, 127.55, 125.71, 125.69, 123.26, 122.03, 117.75, 113.58, 55.40, 21.12.



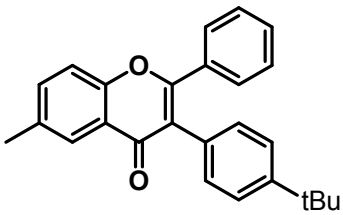
2-(4-methoxyphenyl)-6-methyl-3-(*m*-tolyl)-4*H*-chromen-4-one (1c): Yield: 89%. White soild. m.p. 135.7-137.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.05 (s, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.20-7.18 (m, 1H), 7.10 (s, 2H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 2.48 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 177.61, 161.08, 160.92, 154.36, 137.94, 134.89, 134.85, 133.45, 131.95, 131.30, 128.41, 128.37, 128.32, 125.77, 125.72, 123.26, 122.16, 117.73, 113.55, 55.41, 21.62, 21.14; IR (KBr), *v* (cm^{-1}) 2914, 2565, 2038, 1778, 1608, 1485, 1363, 1257, 1024, 825, 696, 522; HRMS (ESI): calc. for $C_{24}H_{20}O_3$ $[M+Na]^+$ 379.1310, found 379.1308.



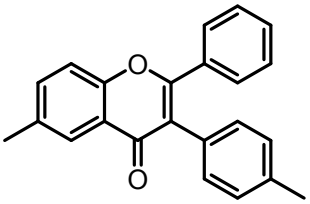
3-(4-(*tert*-butyl)phenyl)-2-(4-methoxyphenyl)-6-methyl-4*H*-chromen-4-one (1d): Yield: 92% (146.5 mg). White soild. m.p. 169.8-171.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.04 (s, 1H), 7.48 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.36-7.31 (m, 4H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.47 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 177.62, 161.11, 160.87, 154.38, 150.35, 134.84, 134.79, 131.35, 130.89, 130.38, 125.95, 125.75, 125.40, 123.31, 121.95, 117.72, 113.51, 55.41, 34.68, 31.49, 21.13; IR (KBr), *v* (cm^{-1}) 2962, 1606, 1500, 1363, 1255, 1022, 925, 829, 594, 532; HRMS (ESI): calc. for $C_{27}H_{26}O_3$ $[M+Na]^+$ 421.1780, found 421.1773.



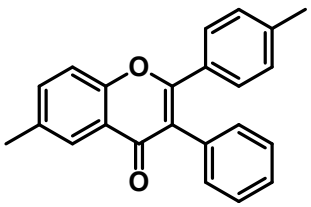
6-methyl-2,3-diphenyl-4*H*-chromen-4-one (1e):[4] Yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12 (s, 1H), 7.56 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 1H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.41-7.27 (m, 8H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 177.49, 161.47, 154.48, 135.12, 135.06, 133.56, 133.17, 131.39, 130.09, 129.69, 128.36, 128.17, 127.66, 125.76, 123.32, 122.93, 117.86, 21.14.



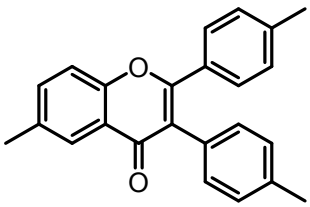
3-(4-(*tert*-butyl)phenyl)-6-methyl-2-phenyl-4*H*-chromen-4-one (1f): Yield: 91%. White soild. m.p. 185.6-188.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06 (s, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.43-7.37 (m, 3H), 7.30 (d, *J* = 8.2 Hz, 3H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 2.47 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) δ 177.61, 161.25, 154.44, 150.44, 134.97, 134.94, 133.71, 130.90, 129.95, 129.68, 128.05, 125.74, 125.28, 123.31, 122.77, 117.80, 34.64, 31.44, 21.11. IR (KBr), *v* (cm^{-1}) 2960, 1639, 1485, 1367, 1230, 1049, 929, 837, 696, 553. HRMS (ESI): calc. for $C_{26}H_{24}O_2$ $[M+Na]^+$ 391.1674, found 391.1670.



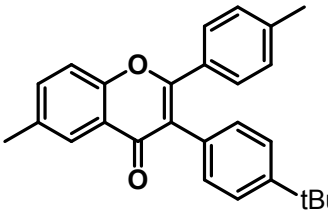
6-methyl-2-phenyl-3-(*p*-tolyl)-4*H*-chromen-4-one (1g): Yield: 87%. White soild. m.p. 197.8-201.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06 (s, 1H), 7.49 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.44-7.38 (m, 3H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.29-7.25 (m, 2H), 7.10 (s, 4H), 2.47 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 177.64, 161.24, 154.48, 137.32, 135.02, 134.97, 133.73, 131.19, 130.05, 129.98, 129.68, 129.15, 128.15, 125.78, 123.31, 122.86, 117.83, 21.44, 21.12; IR (KBr), *v* (cm^{-1}) 2920, 1637, 1485, 1363, 1228, 1045, 925, 819, 698, 511; HRMS (ESI): calc. for $C_{23}H_{18}O_2$ $[M+H]^+$ 327.1385, found 327.1378.



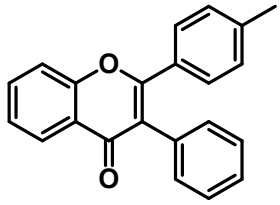
6-methyl-3-phenyl-2-(*p*-tolyl)-4*H*-chromen-4-one (1h):[4] Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06 (s, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.31–7.25 (m, 5H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 2H), 2.48 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 177.52, 161.61, 154.49, 140.45, 135.02, 134.96, 133.45, 131.40, 130.70, 129.63, 128.91, 128.38, 127.58, 125.77, 123.35, 122.59, 117.84, 21.54, 21.14.



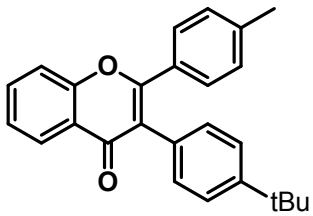
6-methyl-2,3-di-p-tolyl-4*H*-chromen-4-one (1i): Yield: 86%. White soild. m.p. 203.1-205.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.05 (s, 1H), 7.48 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.11 (s, 4H), 7.07 (d, *J* = 8.2 Hz, 2H), 2.47 (s, 3H), 2.33 (d, *J* = 5.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 177.65, 161.35, 154.45, 140.31, 137.22, 134.90, 134.86, 131.15, 130.82, 130.29, 129.59, 129.16, 128.88, 125.75, 123.30, 122.48, 117.79, 21.53, 21.45, 21.11; IR (KBr), *v* (cm^{-1}) 2920, 1795, 1639, 1481, 1361, 1224, 1045, 925, 817, 634, 509; HRMS (ESI): calc. for $C_{24}H_{20}O_2$ $[M+H]^+$ 341.1542, found 341.1531.



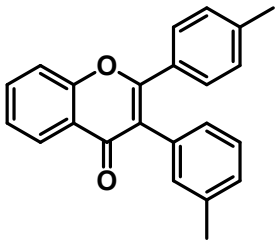
3-(4-(*tert*-butyl)phenyl)-6-methyl-2-(*p*-tolyl)-4*H*-chromen-4-one (1j): Yield: 94%. White soild. m.p. 188.6-191.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.05 (s, 1H), 7.48 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.30 (dd, *J* = 15.7, 8.2 Hz, 4H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 2.47 (s, 3H), 2.32 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 177.67, 161.36, 154.44, 150.38, 140.29, 134.88, 134.86, 130.87, 130.82, 130.19, 129.62, 128.82, 125.73, 125.33, 123.31, 122.42, 117.78, 34.67, 31.48, 21.55, 21.12; IR (KBr), *v* (cm^{-1}) 3055, 2952, 1892, 1645, 1483, 1363, 1228, 1105, 1020, 929, 817, 659, 551; HRMS (ESI): calc. for $C_{27}H_{26}O_2$ $[M+Na]^+$ 405.1830, found 405.1824.



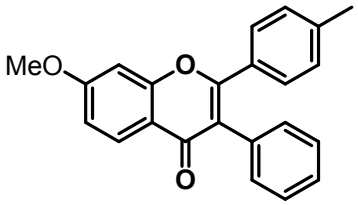
3-phenyl-2-(*p*-tolyl)-4*H*-chromen-4-one (1k):[5] Yield: 84%. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.30 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.71-7.68 (m, Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.44-7.41 (m, 1H), 7.33-7.28 (m, 5H), 7.25-7.22 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 177.47, 161.77, 156.26, 140.57, 133.68, 133.32, 131.39, 130.63, 129.66, 128.96, 128.40, 127.65, 126.55, 125.11, 123.77, 122.82, 118.07, 21.52.



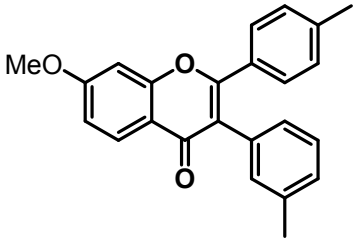
3-(4-(*tert*-butyl)phenyl)-2-(*p*-tolyl)-4*H*-chromen-4-one (1l): Yield: 92%. White soild. m.p. 148.2-150.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.33-8.24 (m, 1H), 7.69 (dd, *J* = 11.3, 4.2 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.32 (dd, *J* = 10.8, 8.4 Hz, 4H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 2.34 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 177.65, 161.48, 156.13, 150.45, 140.42, 133.60, 130.81, 130.64, 129.99, 129.63, 128.85, 126.47, 125.35, 125.01, 123.62, 122.54, 118.01, 34.67, 31.47, 21.56; IR (KBr), *v* (cm^{-1}) 3037, 2956, 1639, 1465, 1377, 1228, 1107, 1016, 879, 765, 621, 563; HRMS (ESI): calc. for $C_{26}H_{24}O_2$ $[M+Na]^+$ 391.1674, found 391.1672.



3-(*m*-tolyl)-2-(*p*-tolyl)-4*H*-chromen-4-one (1m): Yield: 90%. Yellow soild. m.p. 159.6-161.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.27 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.68-7.64 (m, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.12-7.05 (m, 4H), 6.96 (d, *J* = 7.5 Hz, 1H), 2.31 (d, *J* = 3.9 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 177.53, 161.50, 156.08, 140.44, 137.81, 133.60, 133.04, 131.87, 130.48, 129.52, 128.83, 128.43, 128.26, 128.23, 126.38, 125.00, 123.56, 122.76, 117.98, 21.54, 21.47; IR (KBr), *v* (cm^{-1}) 3028, 2916, 1818, 1635, 1461, 1377, 1220, 1137, 1051, 827, 759, 702, 501; HRMS (ESI): calc. for $C_{23}H_{18}O_2$ $[M+Na]^+$ 349.1204, found 349.1207.

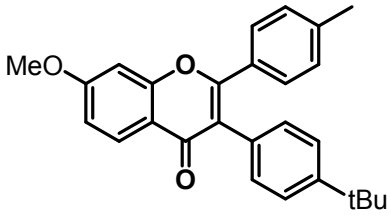


7-methoxy-3-phenyl-2-(*p*-tolyl)-4*H*-chromen-4-one (1n):[5] Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.18 (d, *J* = 8.9 Hz, 1H), 7.31-7.24 (m, 5H), 7.24-7.17 (m, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.98 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.91 (d, *J* = 2.3 Hz, 1H), 3.91 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.84, 164.19, 161.27, 157.86, 140.37, 133.31, 131.35, 130.57, 129.53, 128.89, 128.33, 127.86, 127.54, 122.52, 117.53, 114.53, 100.14, 55.94, 21.52.

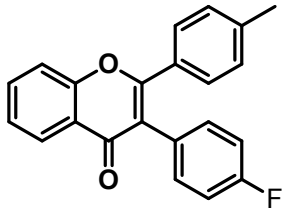


7-methoxy-3-(*m*-tolyl)-2-(*p*-tolyl)-4*H*-chromen-4-one (1o): Yield: 93%. White soild. m.p. 153.7-154.9 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.17 (d, *J* = 8.8 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.07 (dd, *J* = 20.6, 8.5 Hz, 4H), 6.98-6.93 (m, 2H), 6.90 (d, *J* = 2.0 Hz, 1H), 3.90 (s, 3H), 2.31 (d, *J* = 8.0 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 176.94, 164.14, 161.07, 157.81, 140.28, 137.75, 133.13, 131.92, 130.57, 129.45, 128.82, 128.36, 128.27, 128.22, 127.80, 122.60, 117.48, 114.47, 100.09, 55.89, 21.54, 21.48; IR (KBr), *v* (cm^{-1}) 3024, 2918, 1919, 1629, 1438, 1355,

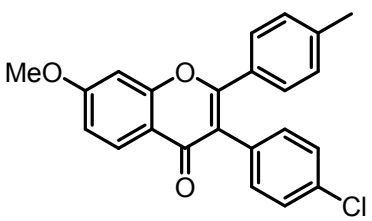
1261, 1170, 1016, 829, 702, 528; HRMS (ESI): calc. for $C_{24}H_{20}O_3$ $[M+Na]^+$ 379.1310, found 379.1308.



3-(4-(*tert*-butyl)phenyl)-7-methoxy-2-(*p*-tolyl)-4*H*-chromen-4-one (1p): Yield: 96%. White soild. m.p. 137.5-140.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.18 (d, *J* = 8.9 Hz, 1H), 7.30 (dd, *J* = 13.3, 8.2 Hz, 4H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.98 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.91 (d, *J* = 2.2 Hz, 1H), 3.92 (s, 3H), 2.33 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 177.05, 164.14, 161.05, 157.85, 150.37, 140.25, 130.85, 130.74, 130.07, 129.56, 128.84, 127.90, 125.31, 122.38, 117.56, 114.47, 100.10, 55.94, 34.67, 31.48, 21.56; IR (KBr), *v* (cm^{-1}) 2958, 1915, 1620, 1438, 1367, 1253, 1022, 929, 827, 621, 563, 476; HRMS (ESI): calc. for $C_{26}H_{23}O_3$ $[M+H]^+$ 399.1960, found 399.1957.

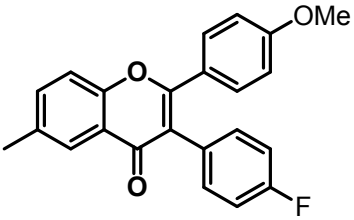


3-(4-fluorophenyl)-2-(*p*-tolyl)-4*H*-chromen-4-one (1q): Yield: 85%. White soild. m.p. 170.1-172.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.27 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 7.3 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.20 (dd, *J* = 8.0, 5.7 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 177.40, 162.36 (d, ^1J = 245.33 Hz), 161.96, 156.16, 140.76, 133.80, 133.06 (d, ^3J = 8.03 Hz), 130.35, 129.59, 129.10 (d, ^4J = 3.74 Hz), 129.05, 126.44, 125.21, 123.55, 121.70, 118.08, 115.45 (d, ^2J = 21.33 Hz), 21.53; IR (KBr), *v* (cm^{-1}) 3041, 1917, 1762, 1631, 1463, 1377, 1226, 1043, 1012, 875, 765, 715, 621, 514; HRMS (ESI): calc. for $C_{22}H_{15}FO_2$ $[M+Na]^+$ 353.0954, found 353.0952.

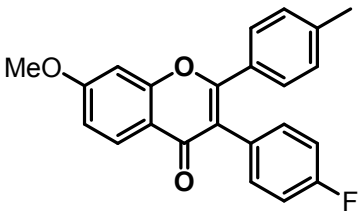


3-(4-chlorophenyl)-7-methoxy-2-(*p*-tolyl)-4*H*-chromen-4-one (1r): Yield: 75%. Yellow soild. m.p. 188.1-189.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.17 (d, *J* = 8.9 Hz, 1H), 7.27 (dd, *J* = 8.3, 1.8 Hz, 4H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.00

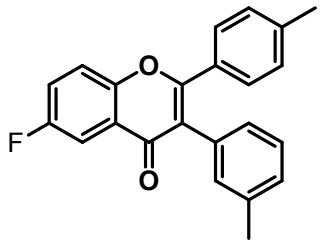
(dd, J = 8.9, 2.4 Hz, 1H), 6.92 (d, J = 2.3 Hz, 1H), 3.92 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.69, 164.40, 161.69, 157.90, 140.76, 133.59, 132.78, 131.81, 130.27, 129.54, 129.12, 128.63, 127.88, 121.40, 117.37, 114.76, 100.22, 55.99, 21.56; IR (KBr), v (cm^{-1}) 3041, 1627, 1444, 1377, 1255, 1091, 1012, 929, 823, 511; HRMS (ESI): calc. for $C_{23}H_{17}ClO_3$ $[M+H]^+$ 377.0944, found 377.0939.



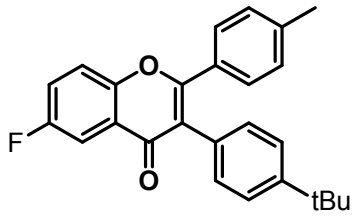
3-(4-fluorophenyl)-2-(4-methoxyphenyl)-6-methyl-4*H*-chromen-4-one (1s): Yield: 75%. Gray soild. m.p. 179.2-182.4 °C.^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.04 (s, 1H), 7.50 (dd, J = 8.5, 1.4 Hz, 1H), 7.42 (d, J = 8.5 Hz, 1H), 7.32 (d, J = 8.7 Hz, 2H), 7.20 (dd, J = 8.2, 5.6 Hz, 2H), 7.03-7.00 (m, 2H), 6.79 (d, J = 8.7 Hz, 2H), 3.80 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 177.40, 162.30 (d, ^1J = 244.92 Hz), 161.48, 161.06, 154.36, 135.08, 135.01, 133.08 (d, ^3J = 8.12 Hz), 131.31, 129.46 (d, ^4J = 3.44 Hz), 125.68, 125.50, 123.16, 121.02, 117.77, 115.50 (d, ^2J = 21.51 Hz), 113.71, 55.43, 21.12; IR (KBr), v (cm^{-1}) 2960, 1899, 1610, 1508, 1367, 1251, 1043, 927, 833, 522; HRMS (ESI): calc. for $C_{23}H_{17}FO_2$ $[M+Na]^+$ 383.1059, found 383.1059.



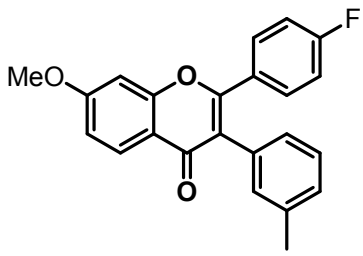
3-(4-fluorophenyl)-7-methoxy-2-(*p*-tolyl)-4*H*-chromen-4-one (1t): Yield: 82%. White soild. m.p. 208.1-210.5 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.17 (d, J = 8.9 Hz, 1H), 7.28-7.25 (m, 2H), 7.19 (dd, J = 8.5, 5.6 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 7.02-6.97 (m, 3H), 6.92 (d, J = 2.3 Hz, 1H), 3.92 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.81, 164.31, 162.32 (d, ^1J = 245.07 Hz), 161.52, 157.88, 140.59, 133.07 (d, ^3J = 8.03 Hz), 130.40, 129.52, 129.16 (d, ^4J = 3.43 Hz), 129.03, 127.84, 121.51, 117.41, 115.41 (d, ^2J = 21.36 Hz), 114.68, 100.17, 55.97, 21.54; IR (KBr), v (cm^{-1}) 2977, 1629, 1506, 1380, 1255, 1012, 929, 829, 603, 518; HRMS (ESI): calc. for $C_{23}H_{17}FO_3$ $[M+Na]^+$ 383.1059, found 383.1063.



6-fluoro-3-(*m*-tolyl)-2-(*p*-tolyl)-4*H*-chromen-4-one (1u): Yield: 91%. White soild. m.p. 126.3-128.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.91 (dd, *J* = 8.1, 2.8 Hz, 1H), 7.53 (dd, *J* = 9.0, 3.9 Hz, 1H), 7.44-7.39 (m, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.11-7.07 (m, 4H), 6.95 (d, *J* = 7.4 Hz, 1H), 2.32 (d, *J* = 8.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) 176.92, 161.87, 159.65 (d, ^{1}J = 244.47 Hz), 152.38, 140.74, 137.99, 132.78, 131.87, 130.32, 129.58, 128.95, 128.64, 128.39, 128.25, 124.78 (d, ^{3}J = 7.39 Hz), 122.23, 121.91 (d, ^{2}J = 25.35 Hz), 120.15 (d, ^{3}J = 7.98 Hz), 111.22 (d, ^{2}J = 23.38 Hz), 21.59, 21.56; IR (KBr), *v* (cm^{-1}) 3035, 2921, 1627, 1481, 1359, 1272, 1188, 1095, 962, 757, 711, 495; HRMS (ESI): calc. for $C_{23}H_{17}FO_2$ $[M+Na]^+$ 367.1110, found 367.1111.

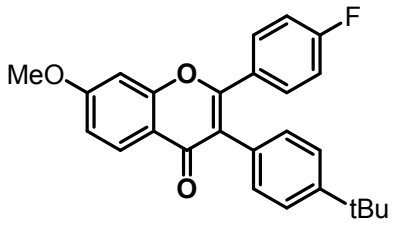


3-(4-(*tert*-butyl)phenyl)-6-fluoro-2-(*p*-tolyl)-4*H*-chromen-4-one (1v): Yield: 77%. White soild. m.p. 170.8-173.5 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.91 (dd, *J* = 8.3, 3.1 Hz, 1H), 7.53 (dd, *J* = 9.1, 4.2 Hz, 1H), 7.43-7.38 (m, 1H), 7.35-7.28 (m, 4H), 7.16-7.13 (m, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 2.34 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.94, 161.81, 159.63 (d, ^{1}J = 244.56 Hz), 152.39, 150.66, 140.67, 130.79, 130.42, 129.69, 129.63, 128.92, 125.43, 124.78 (d, ^{3}J = 7.31 Hz), 121.97 (d, ^{4}J = 2.25 Hz), 121.84 (d, ^{2}J = 23.12 Hz), 120.12 (d, ^{3}J = 7.94 Hz), 111.22 (d, ^{2}J = 23.41 Hz), 34.71, 31.47, 21.58; IR (KBr), *v* (cm^{-1}) 3047, 2958, 1919, 1635, 1481, 1369, 1272, 1103, 1043, 941, 831, 559; HRMS (ESI): calc. for $C_{26}H_{23}FO_2$ $[M+Na]^+$ 409.1580, found 409.1578.

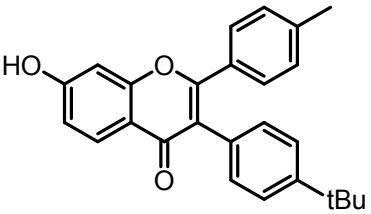


2-(4-fluorophenyl)-7-methoxy-3-(*m*-tolyl)-4*H*-chromen-4-one (1w): Yield: 84%. Yellow soild. m.p. 210.1-213.5 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.18 (d, *J* = 8.9 Hz, 1H), 7.39 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.12-7.06 (m, 2H), 7.01-6.91 (m, 5H), 3.92 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.80,

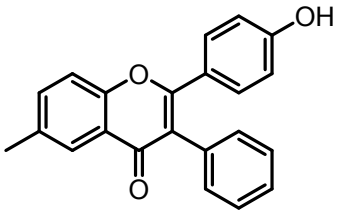
164.31, 163.46 (d, ^{1}J = 250.15 Hz), 159.87, 157.79, 138.00, 132.79, 131.88, 131.73 (d, ^{3}J = 8.59 Hz), 129.63 (d, ^{4}J = 3.48 Hz), 128.62, 128.38, 128.27, 127.93, 122.98, 117.49, 115.33 (d, ^{2}J = 21.76 Hz), 114.64, 100.14, 55.96, 21.54; IR (KBr), v (cm^{-1}) 3022, 2916, 1629, 1444, 1375, 1261, 1012, 948, 835, 700, 534; HRMS (ESI): calc. for $C_{23}H_{17}FO_3$ $[M+Na]^+$383.1059, found 383.1066.



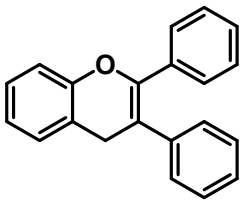
3-(4-(*tert*-butyl)phenyl)-2-(4-fluorophenyl)-7-methoxy-4*H*-chromen-4-one (1x): Yield: 60%. White soild. m.p. 179.9-182.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.18 (d, J = 8.8 Hz, 1H), 7.38 (dd, J = 8.2, 5.6 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 6.99 (dd, J = 8.8, 1.6 Hz, 1H), 6.93 (dd, J = 17.4, 8.9 Hz, 3H), 3.92 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 176.86, 163.44 (d, ^{1}J = 251.22 Hz), 159.89, 157.79, 150.67, 131.78 (d, ^{3}J = 8.31 Hz), 130.85, 129.75 (d, ^{4}J = 3.15 Hz), 129.70, 127.95, 125.42, 122.73, 117.51, 115.30 (d, ^{2}J = 21.75 Hz), 114.61, 100.12, 55.96, 34.69, 31.45; IR (KBr), v (cm^{-1}) 3060, 2962, 1625, 1444, 1384, 1261, 1109, 1024, 931, 833, 619, 518; HRMS (ESI): calc. for $C_{26}H_{23}FO_3$ $[M+Na]^+$ 425.1529, found 425.1525.



3-(4-(*tert*-butyl)phenyl)-7-hydroxy-2-(*p*-tolyl)-4*H*-chromen-4-one (1y): Yield: 62%. White soild. m.p. 296.6-298.5 °C. ^{1}H NMR (600 MHz, DMSO) δ (ppm) 10.81 (s, 1H), 7.92 (d, J = 8.7 Hz, 1H), 7.31 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.94 (dd, J = 8.7, 2.0 Hz, 1H), 6.90 (d, J = 2.0 Hz, 1H), 2.27 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, DMSO) δ (ppm) 175.54, 162.71, 160.42, 157.26, 149.54, 139.84, 130.76, 130.27, 130.26, 129.22, 128.64, 127.16, 124.67, 121.38, 115.53, 115.10, 102.15, 34.25, 31.12, 20.88; IR (KBr), v (cm^{-1}) 3201, 2960, 1618, 1452, 1271, 1172, 931, 833, 702, 513; HRMS (ESI): calc. for $C_{26}H_{24}O_3$ $[M+Na]^+$ 407.1623, found 407.1619.



2-(4-hydroxyphenyl)-6-methyl-3-phenyl-4*H*-chromen-4-one (1z): Yield: 66%. White soild. m.p. 277.6-279.5 °C. ^{1}H NMR (600 MHz, DMSO) δ (ppm) 10.01 (s, 1H), 7.87 (s, 1H), 7.65 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.33-7.28 (m, 3H), 7.23-7.20 (m, 2H), 7.17 (dd, *J* = 7.9, 1.3 Hz, 2H), 6.67-6.65 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (150 MHz, DMSO) δ (ppm) 175.96, 161.32, 159.15, 153.69, 135.14, 134.72, 133.64, 131.14, 131.11, 127.98, 127.16, 124.50, 123.25, 122.42, 120.99, 118.06, 114.91, 20.47; IR (KBr), *v* (cm^{-1}) 3168, 1606, 1434, 1367, 1280, 1176, 1060, 933, 844, 740, 595, 516; HRMS (ESI): calc. for $C_{22}H_{16}O_3$ $[M+Na]^+$ 351.0977, found 351.0933.



2,3-diphenyl-4*H*-chromene (3): Yield: 44%. White soild. m.p. 77.6-79.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.32 -7.28 (m, 2H), 7.21-7.10 (m, 5H), 7.04 (d, *J* = 7.6 Hz, 1H), 3.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 151.93, 146.86, 140.38, 135.26, 129.52, 129.02, 128.67, 128.37, 128.21, 127.92, 127.64, 126.70, 123.43, 120.70, 116.27, 110.59, 31.23; IR (KBr), *v* (cm^{-1}) 3053, 2920, 1946, 1585, 1488, 1357, 1242, 1114, 995, 756, 655, 545.

3 . References

1. G. Priyadarshani, S. Amrutkar, A. Nayak, U. C. Banerjee, C. N. Kundu and S. K. Guchhait, *Eur. J. Med. Chem.* **2016**, *122*, 43-54.
2. Che, H.; Lim, H.; Kim, H. P.; Park, H**.** *Eur. J. Med. Chem.* **2011,***46*, 4657-4660.
3. S. Baruah, P. P. Kaishap and S. Gogoi, *Chem. Commun.* **2016**, *52*, 13004-13007.
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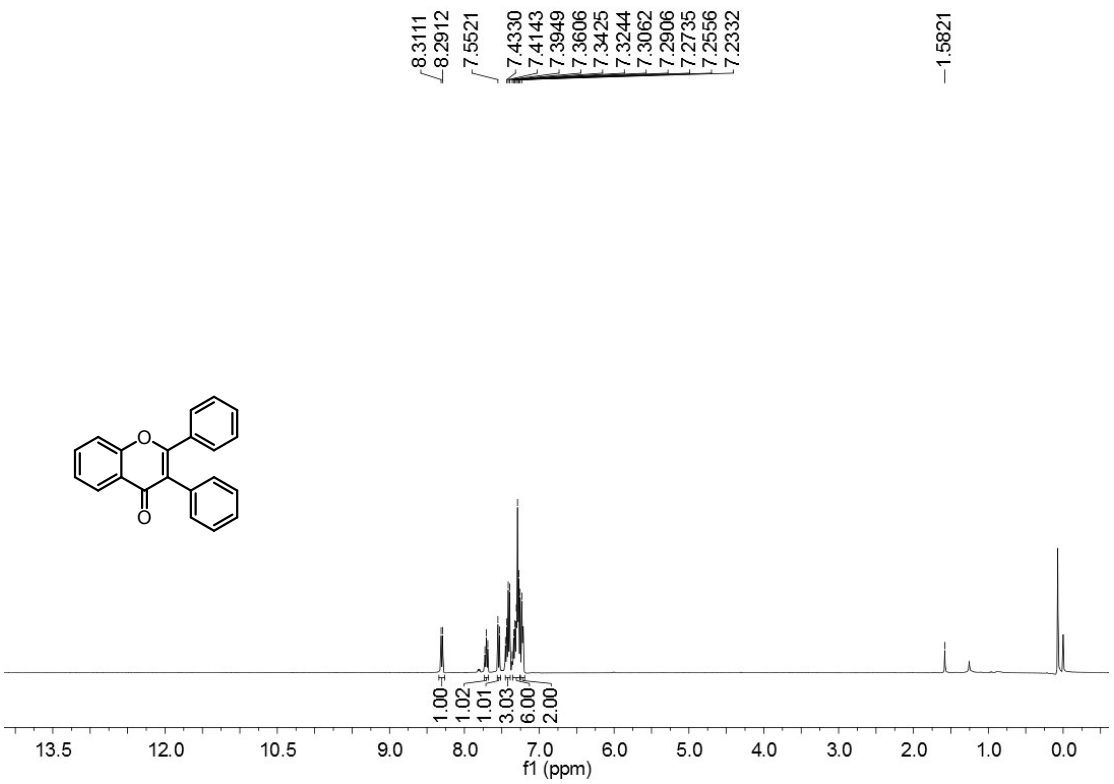
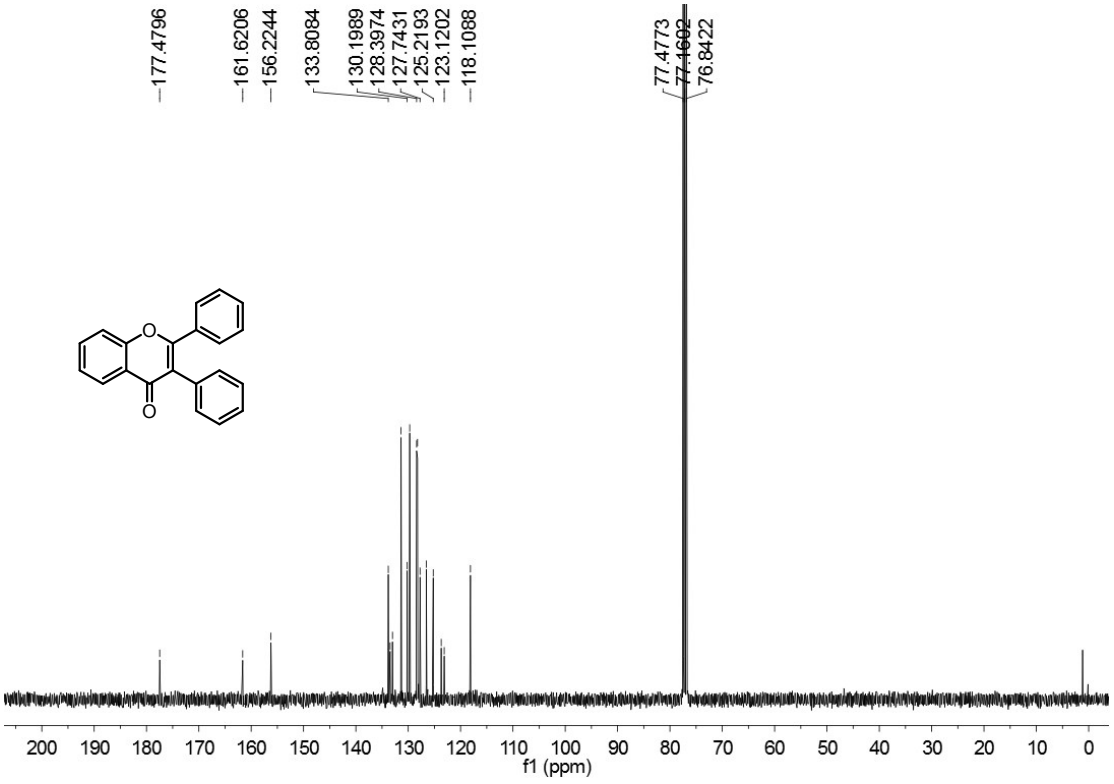
5. C. Shen, W. Li, H. Yin, A. Spannenberg, T. Skrydstrup and X.-F. Wu, *Adv. Synth. Catal*. **2016**, *358*, 466-479.

4. ^{1}H, ^{13}C NMR for cpmpounds 1, 2 and 3

1a





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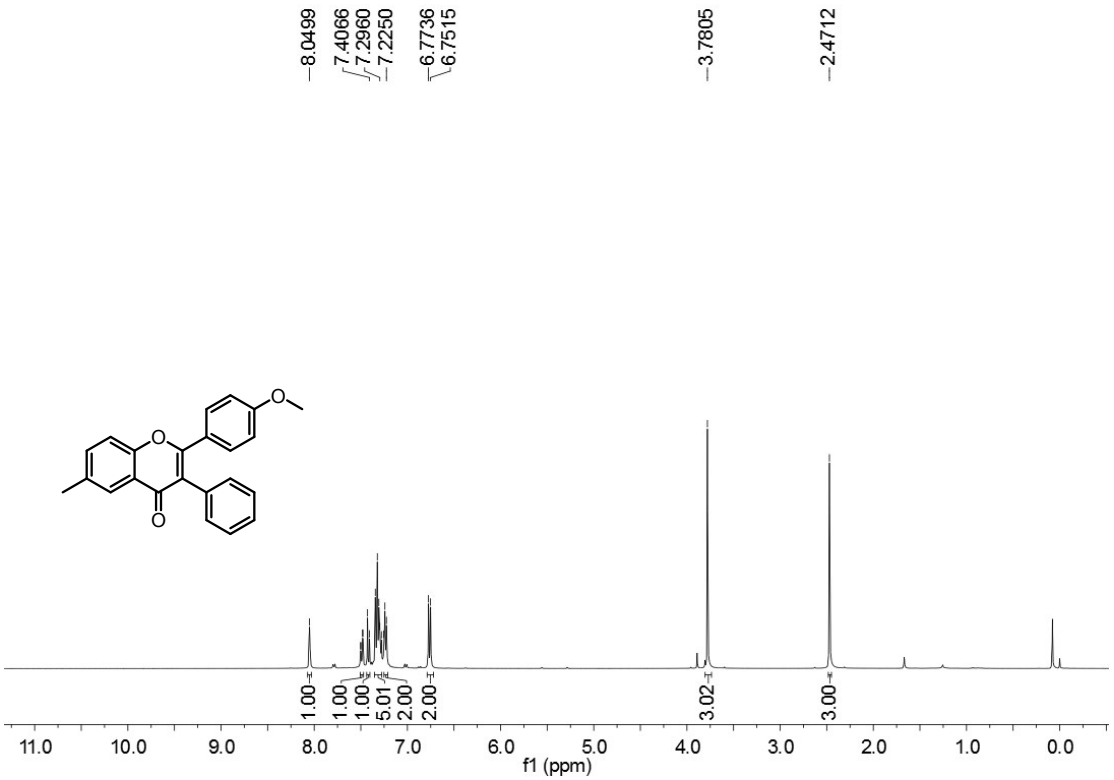
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2.00
2.00
3.02
3.00
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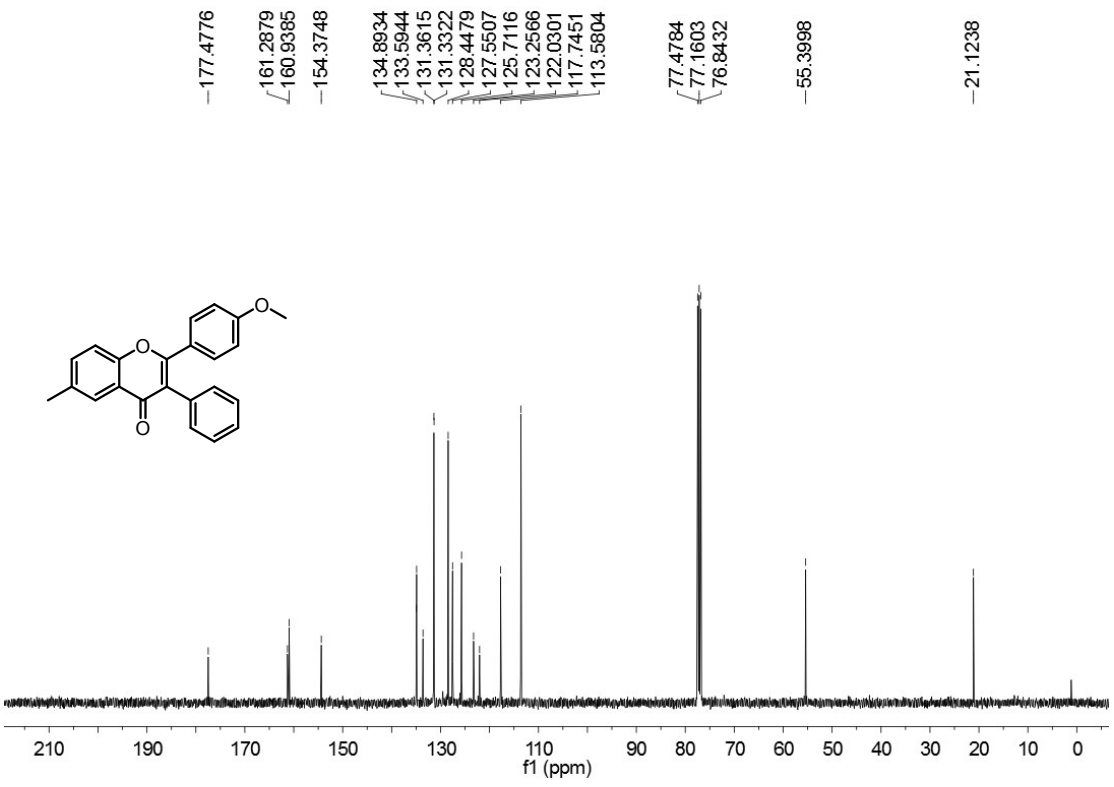
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127.5507
125.7116
123.2566
122.0301
117.7451
113.5804
77.4784
77.1603
76.8432
55.3998
21.1238
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130
110
90
80
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30
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10
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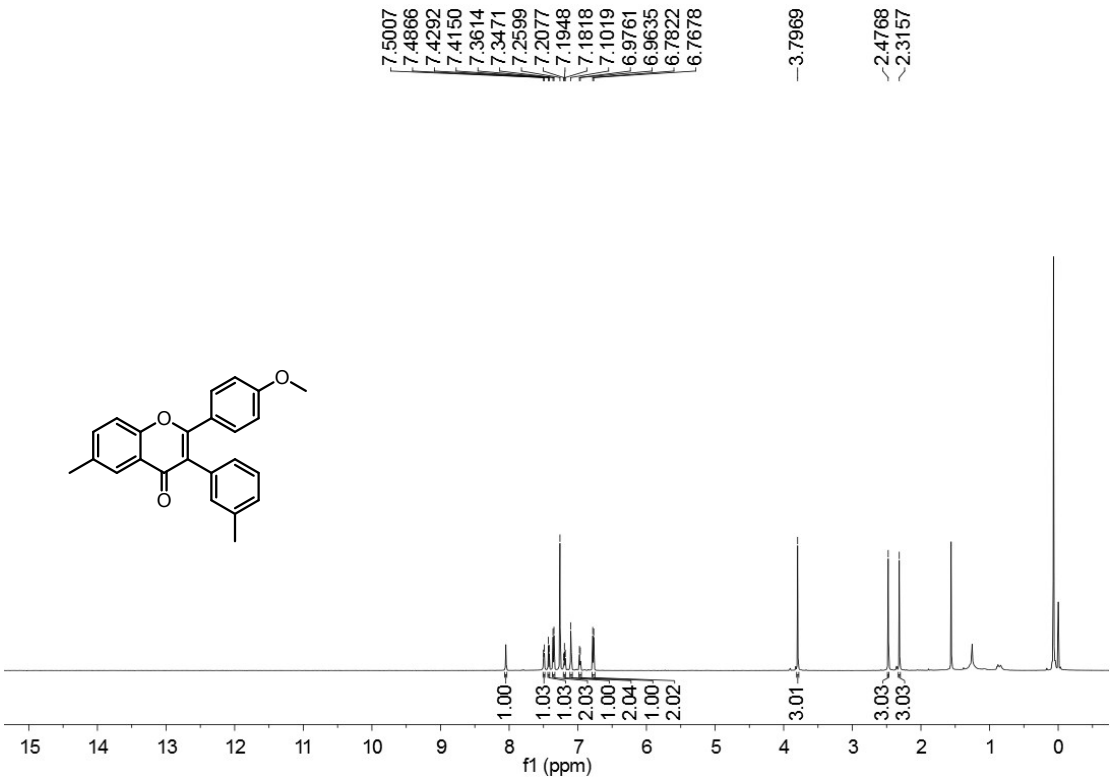
f1 (ppm)

1c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6.9635
6.7822
6.7678
3.7969
2.4768
2.3157
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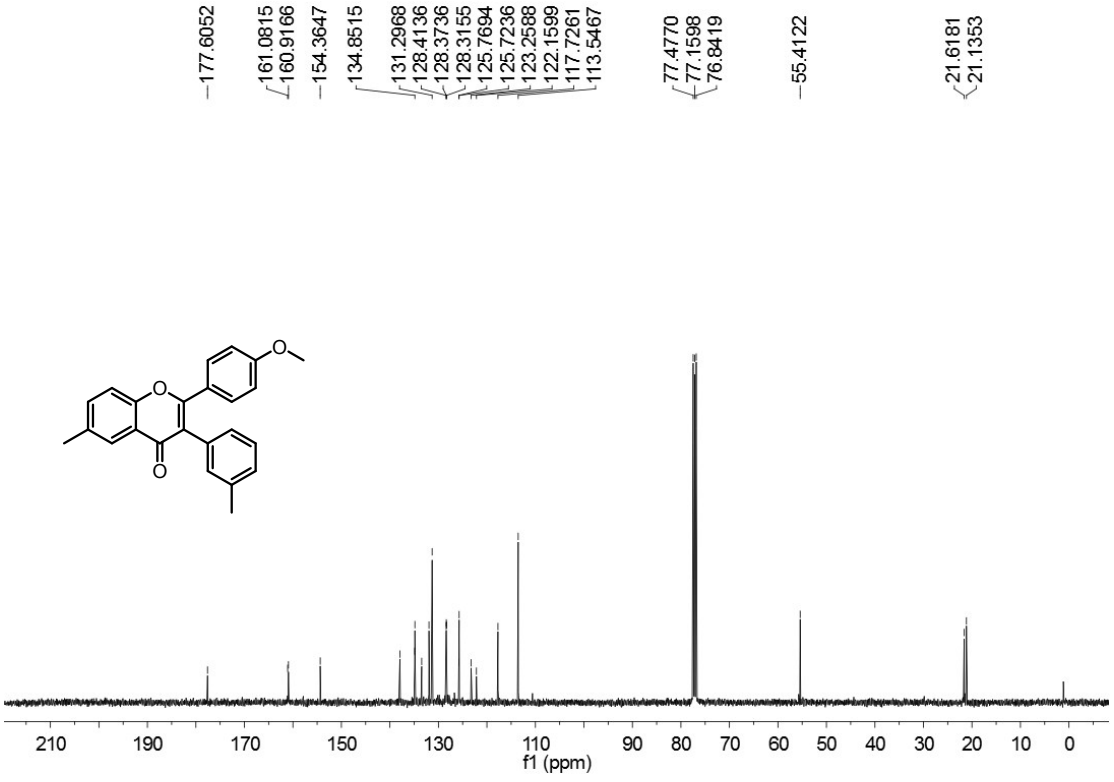
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123.2588
122.1599
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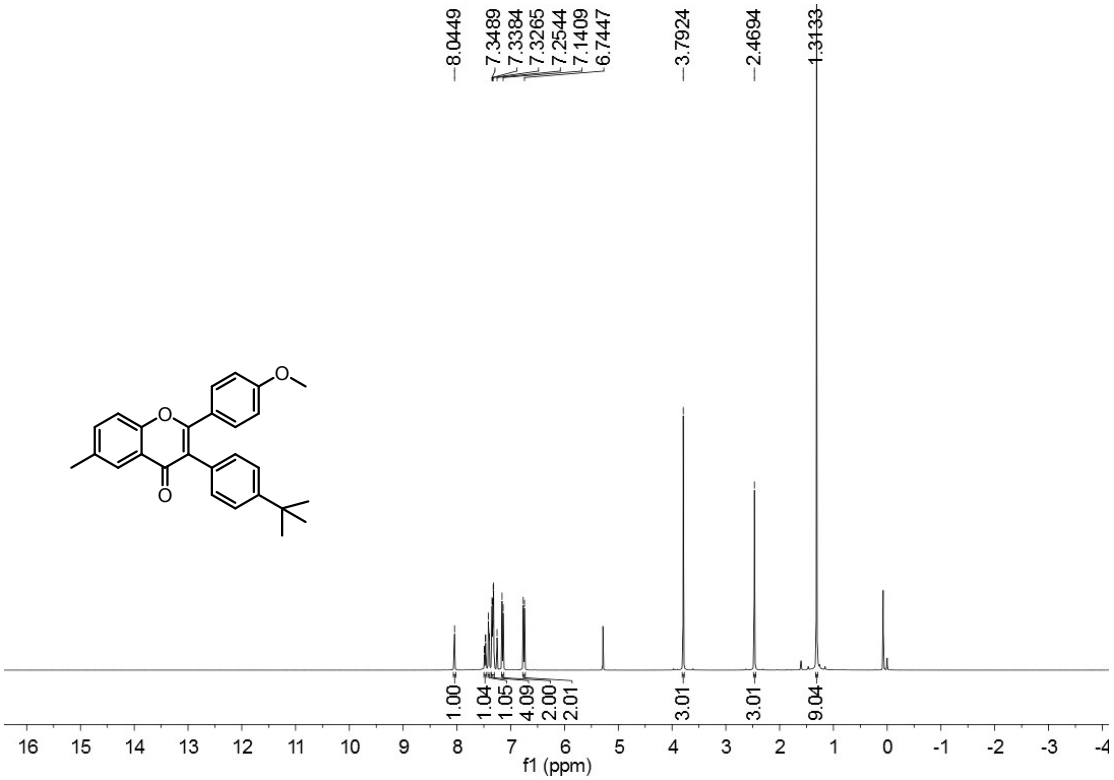
21.1353
f1 (ppm)

1d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2.00
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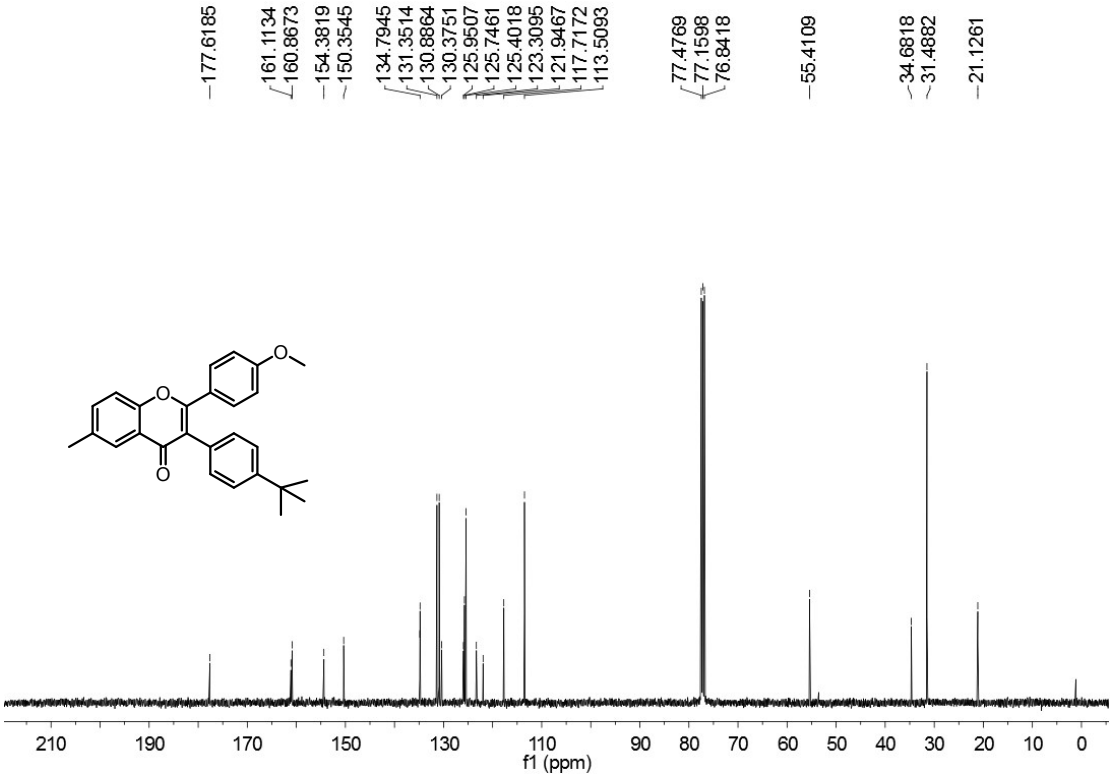
f1 (ppm)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76.8418
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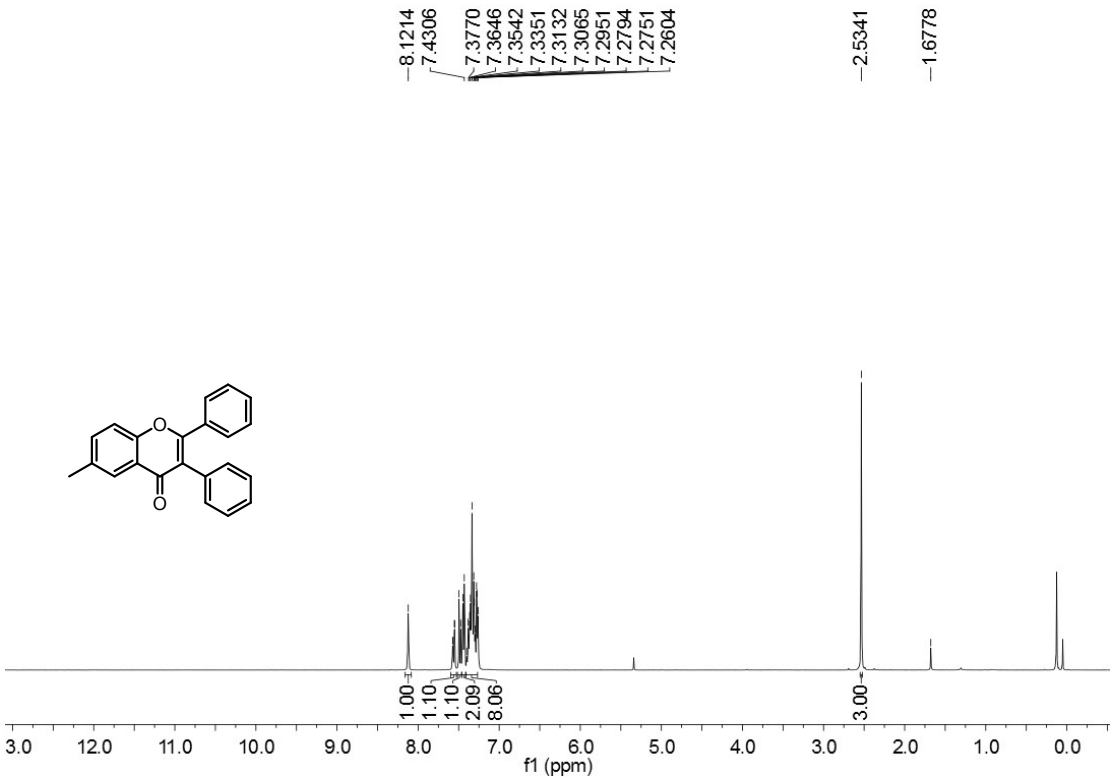
1e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1.10
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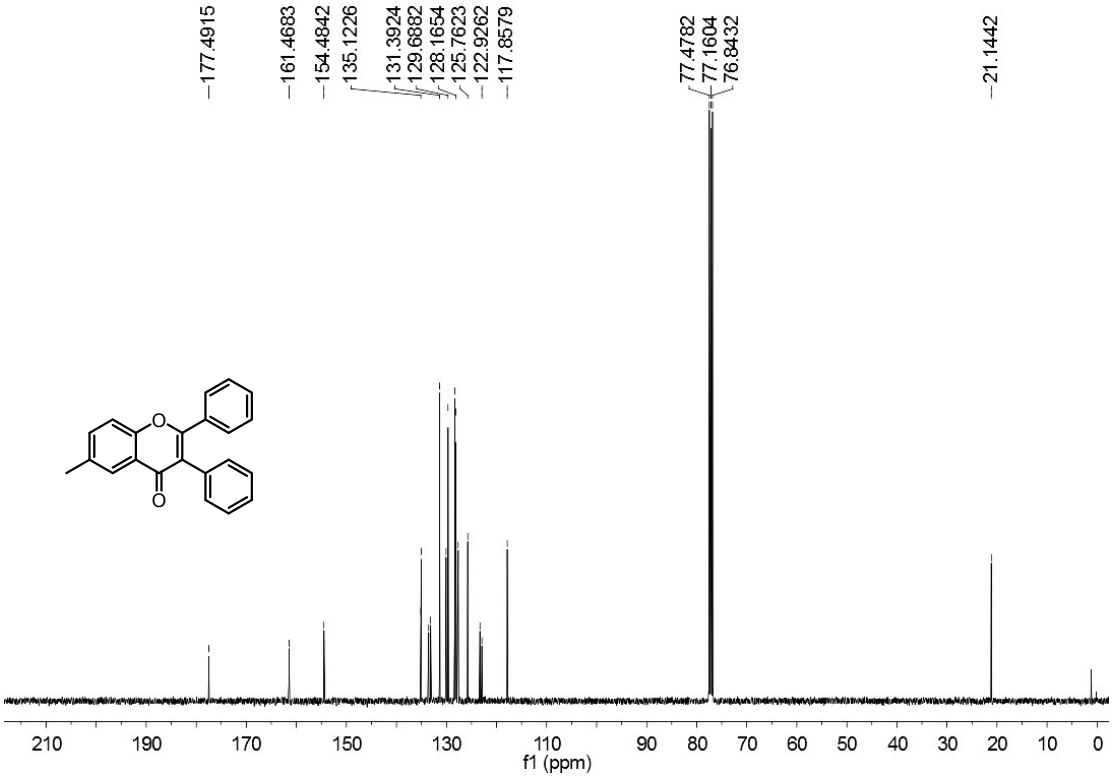
3.00
f1 (ppm)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76.8432
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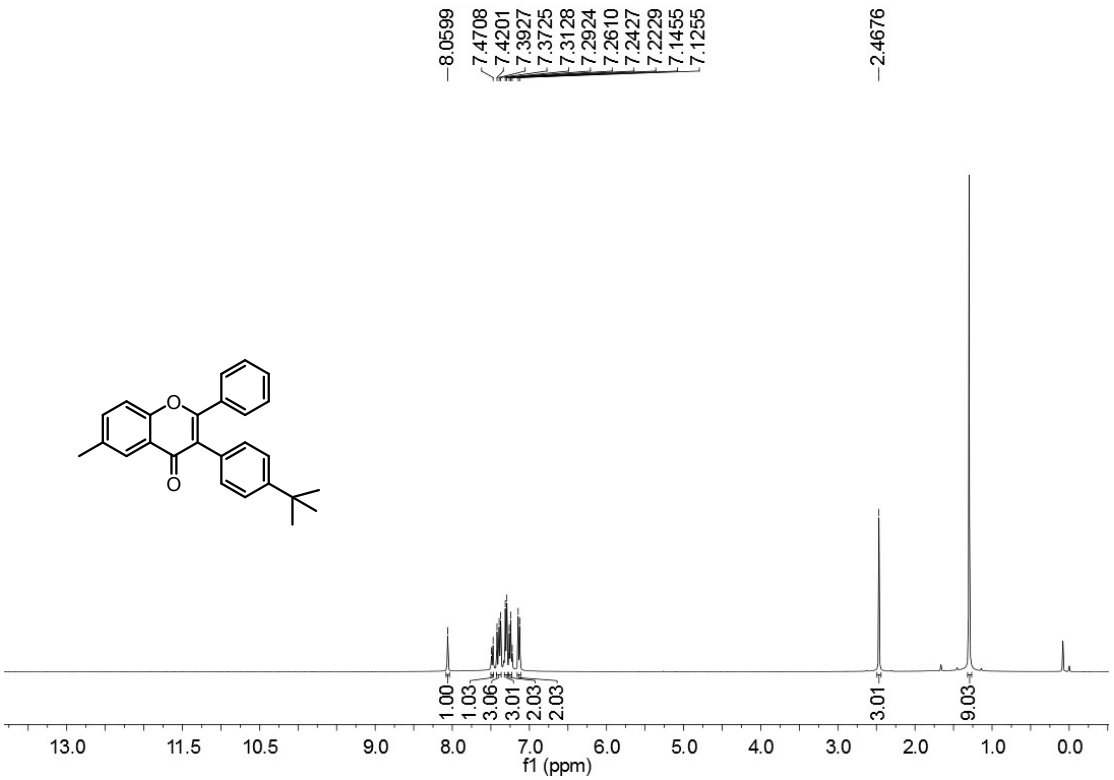
f1 (ppm)

1f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3.01
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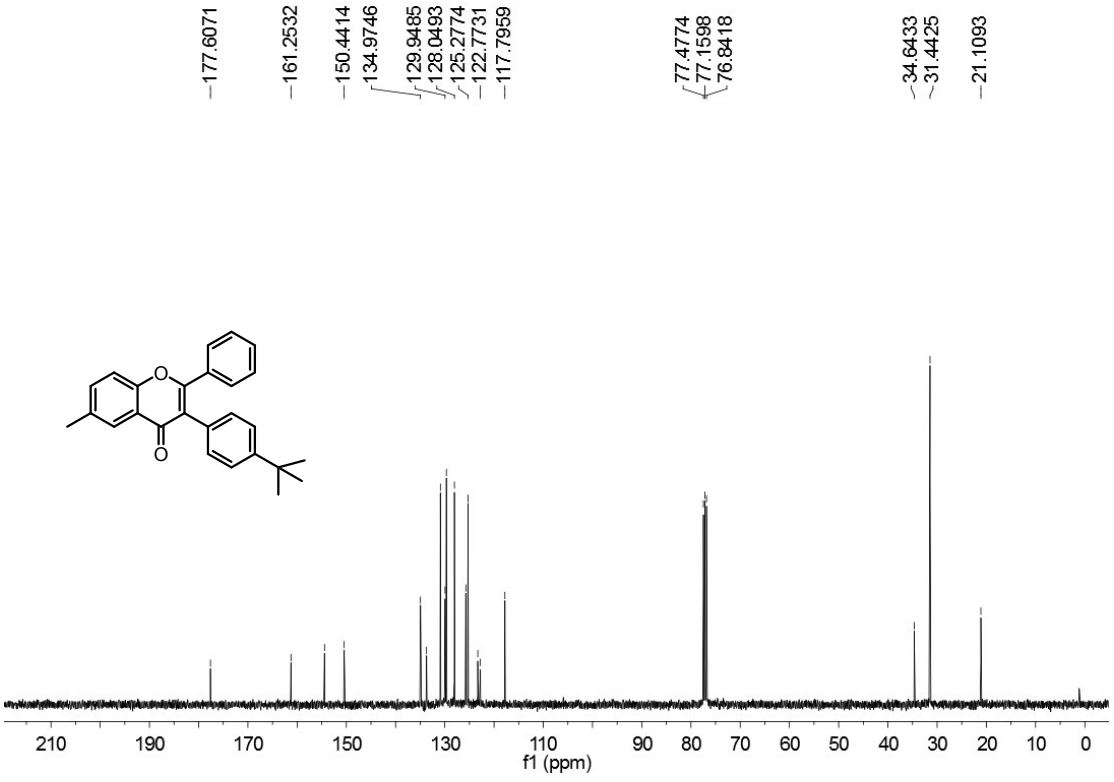
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76.8418
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31.4425
21.1093
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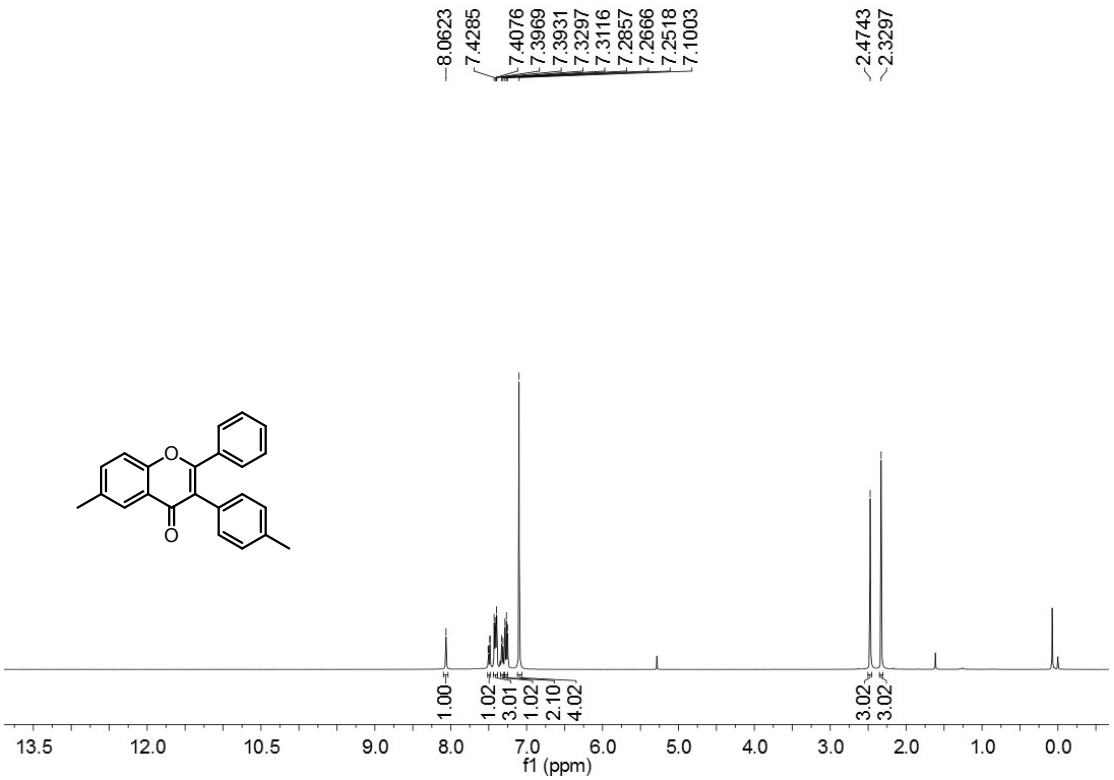
50
40
30
20
10
0
f1 (ppm)

1g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2.3297
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3.01
1.02
2.10
4.02
3.02
3.02
13.5
12.0
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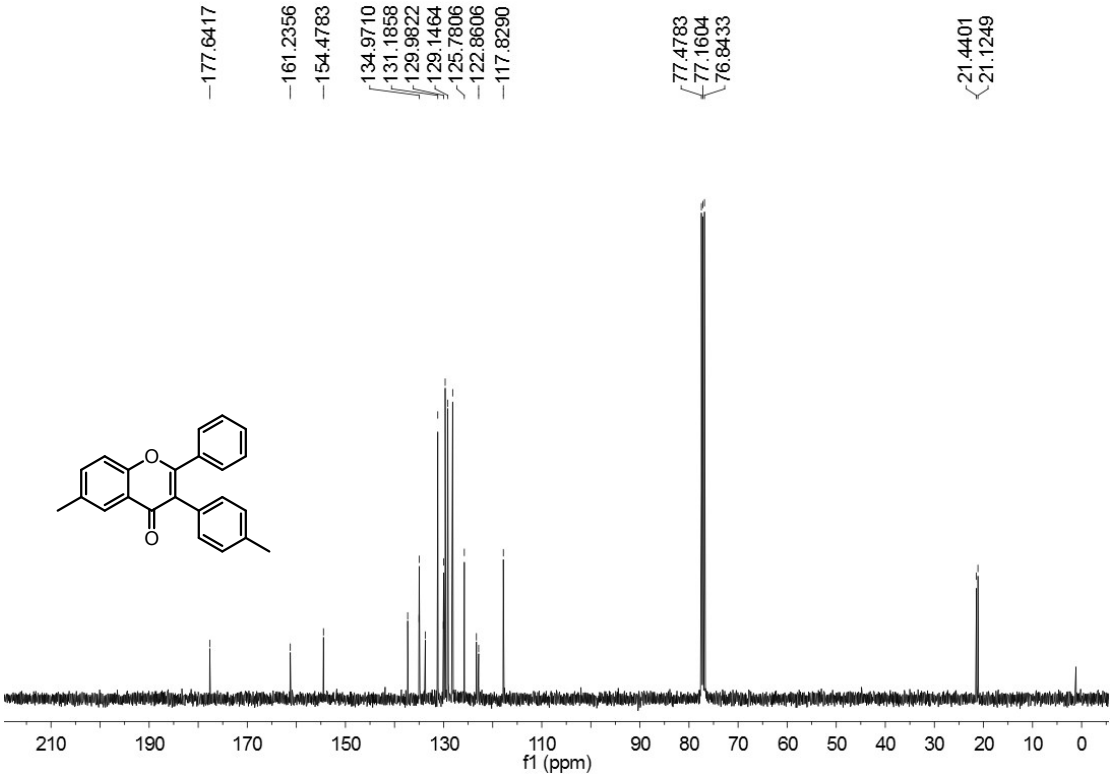
0.0
f1 (ppm)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80
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30
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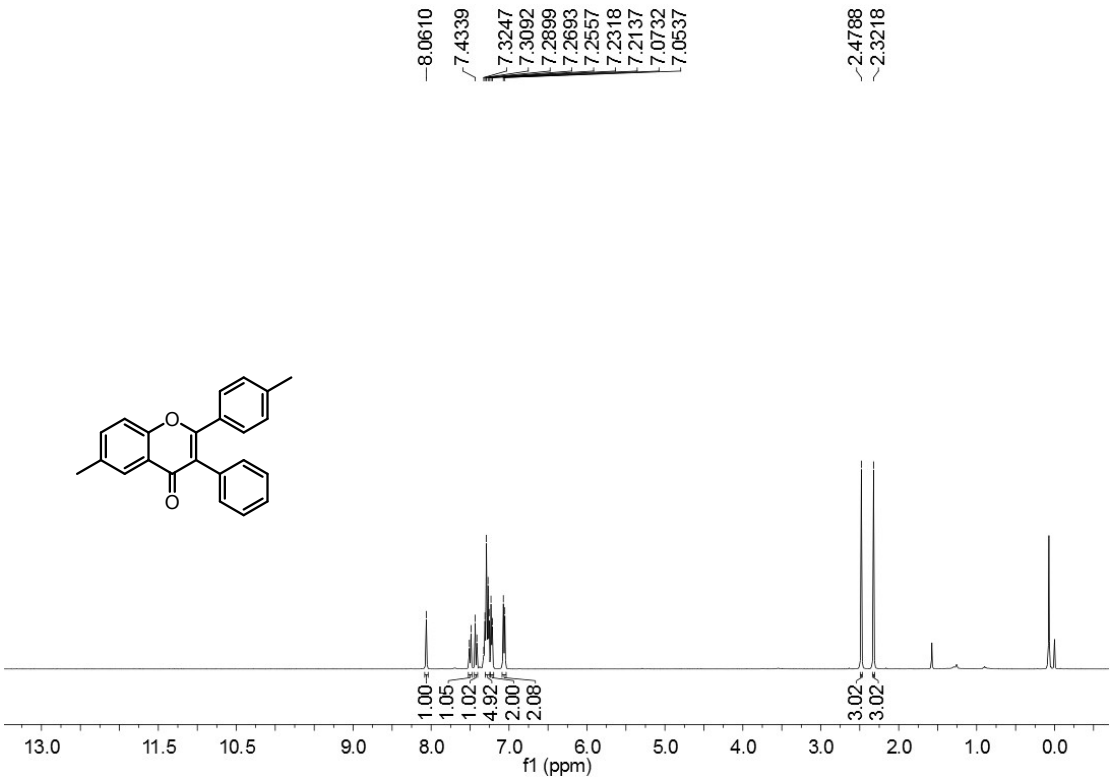
1h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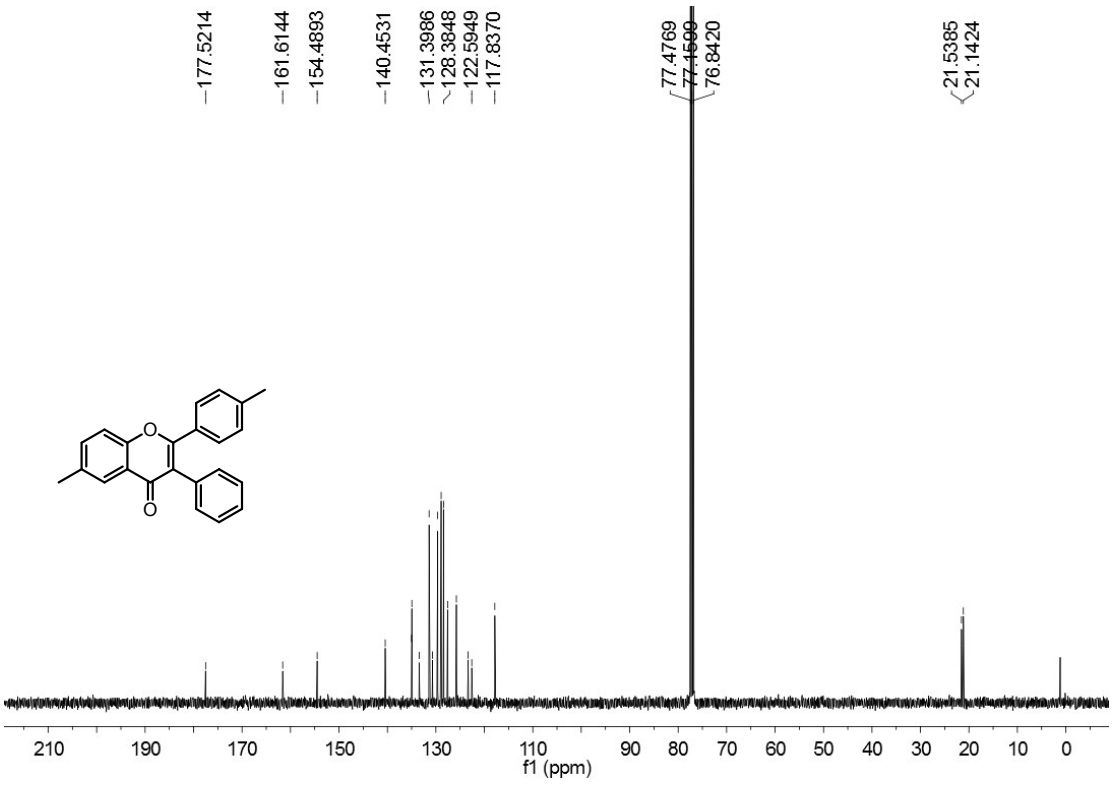
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80
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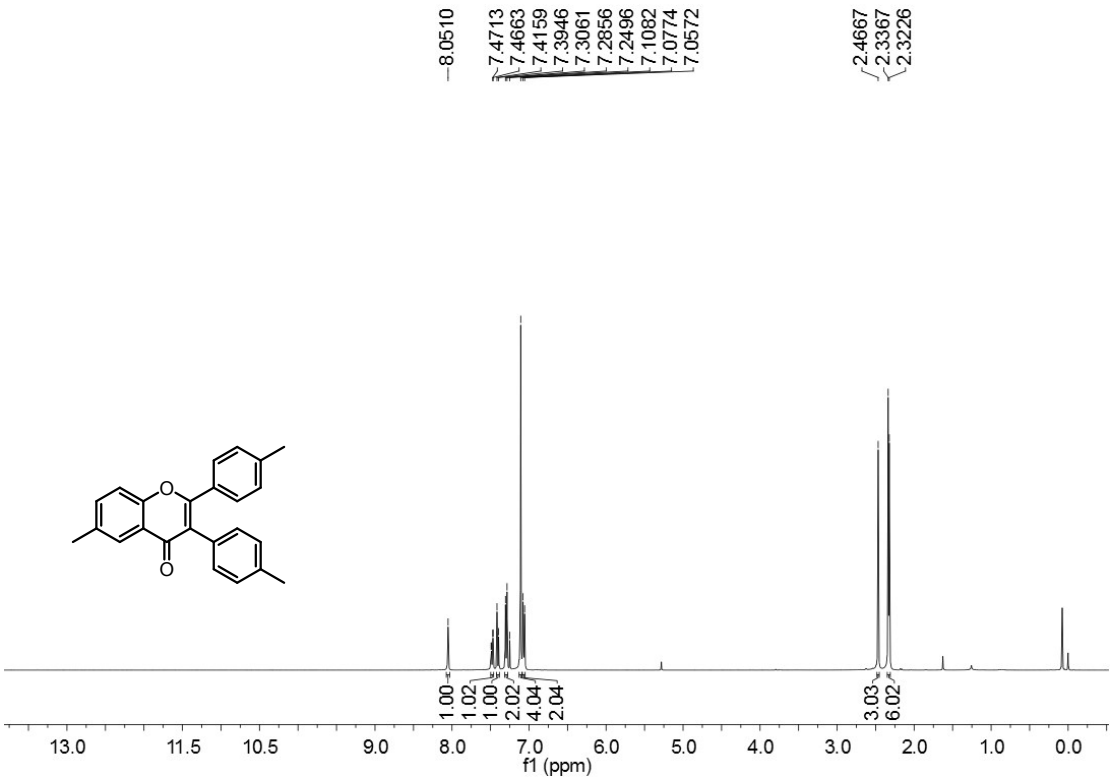
40
30
20
10
0
f1 (ppm)

1i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2.02
4.04
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3.03
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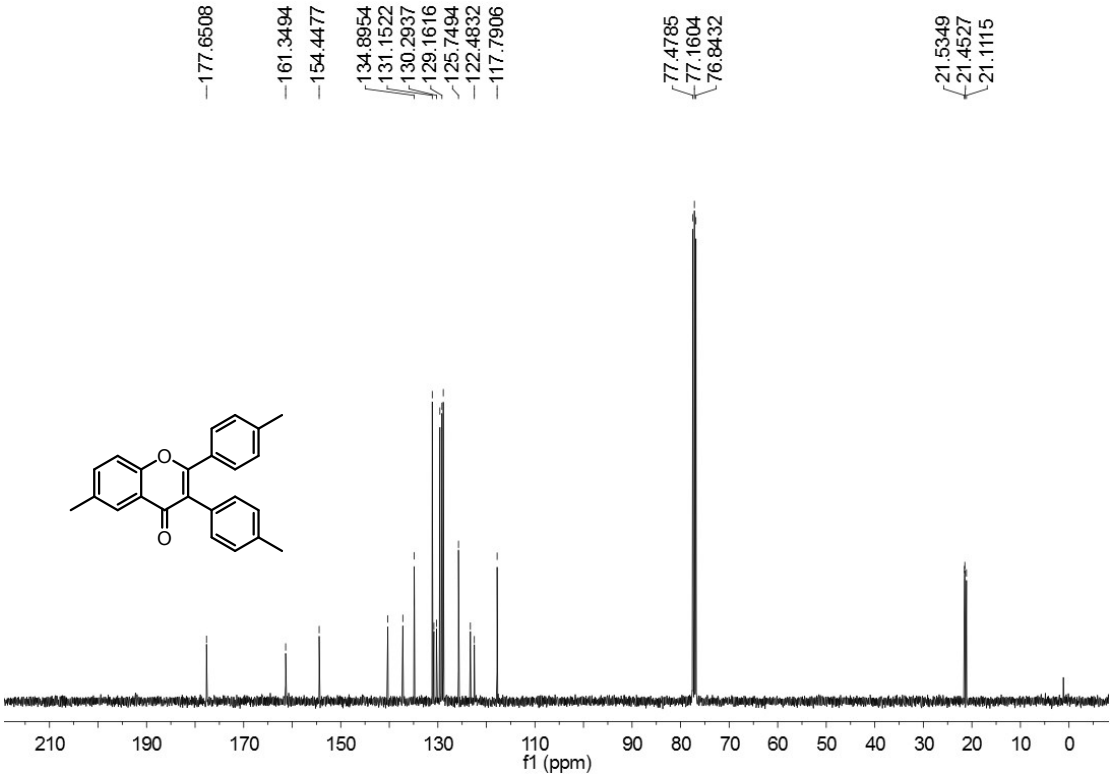
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21.1115
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30
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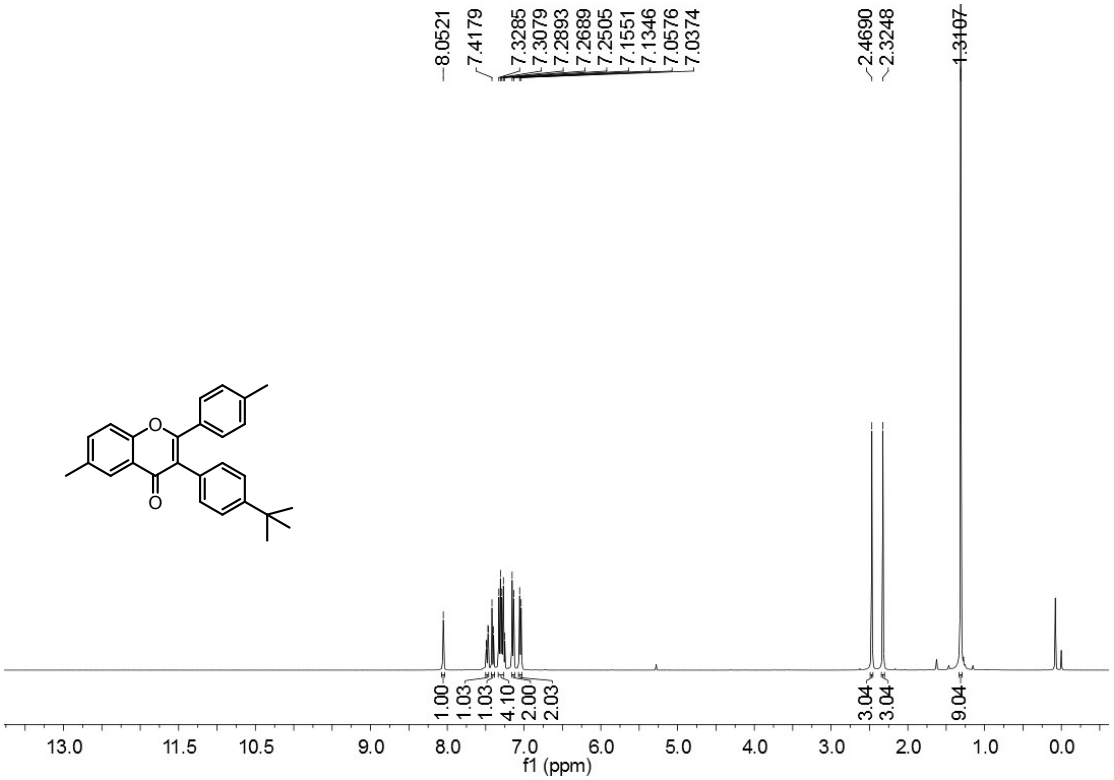
1j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5.0
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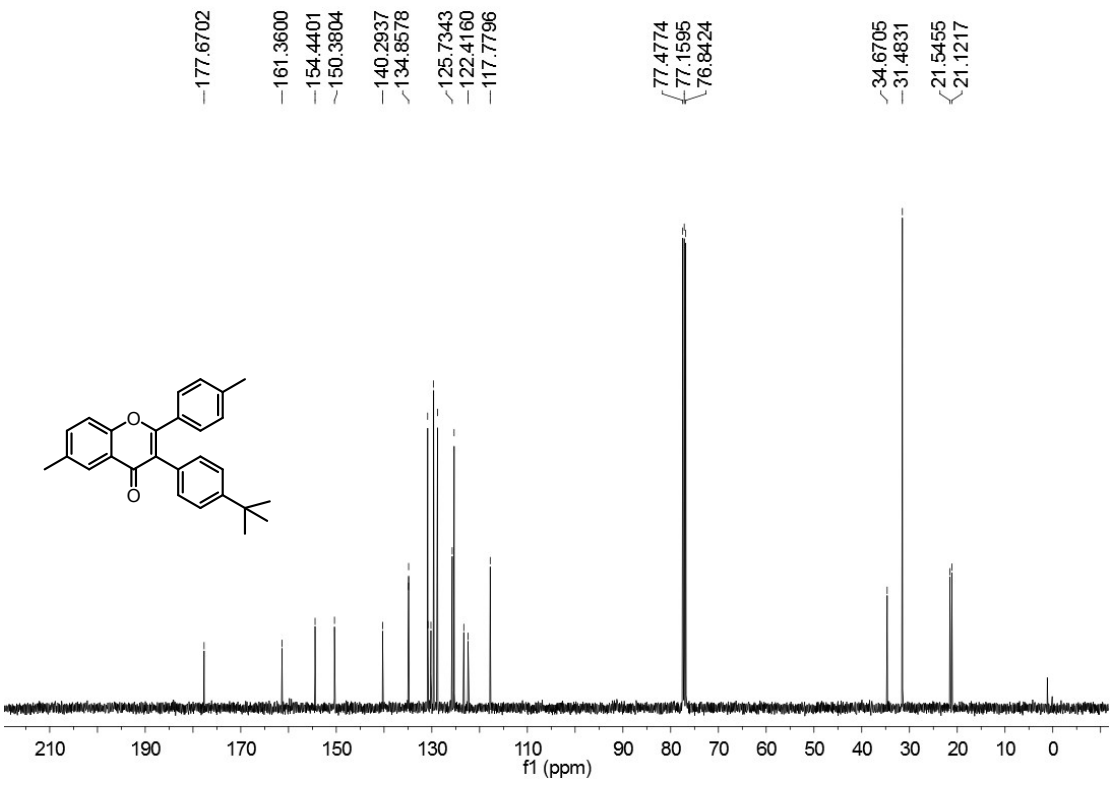
f1 (ppm)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21.5455
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30
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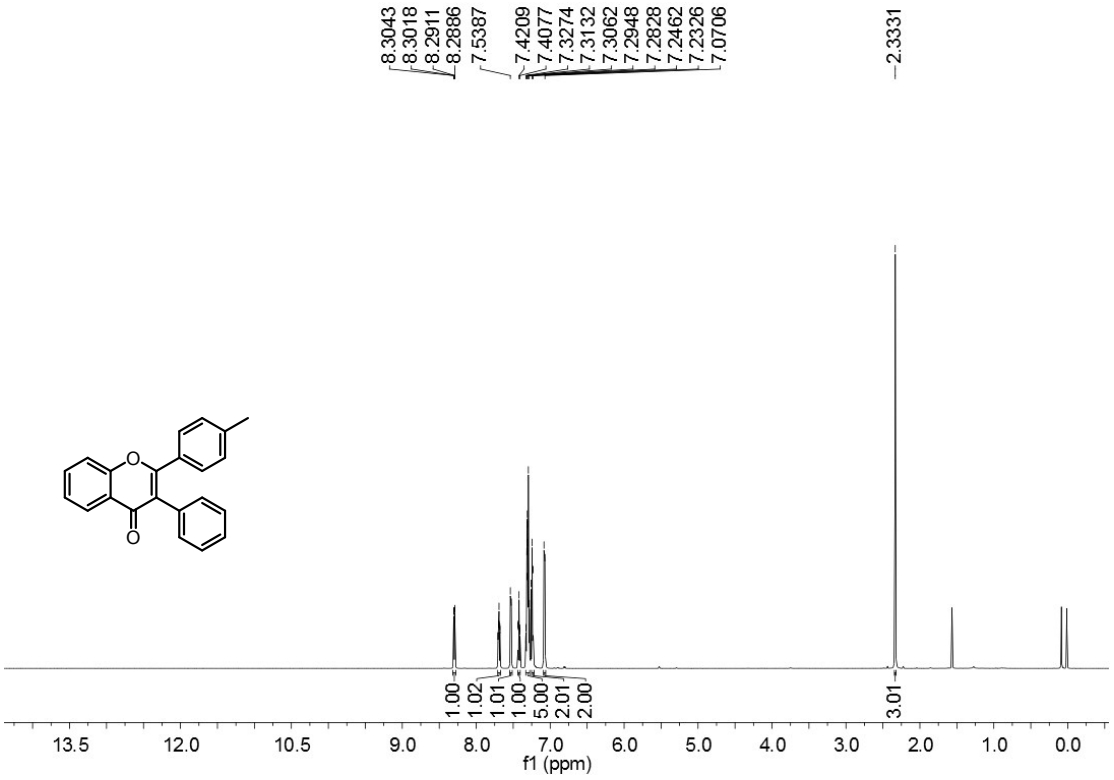
1k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1.00
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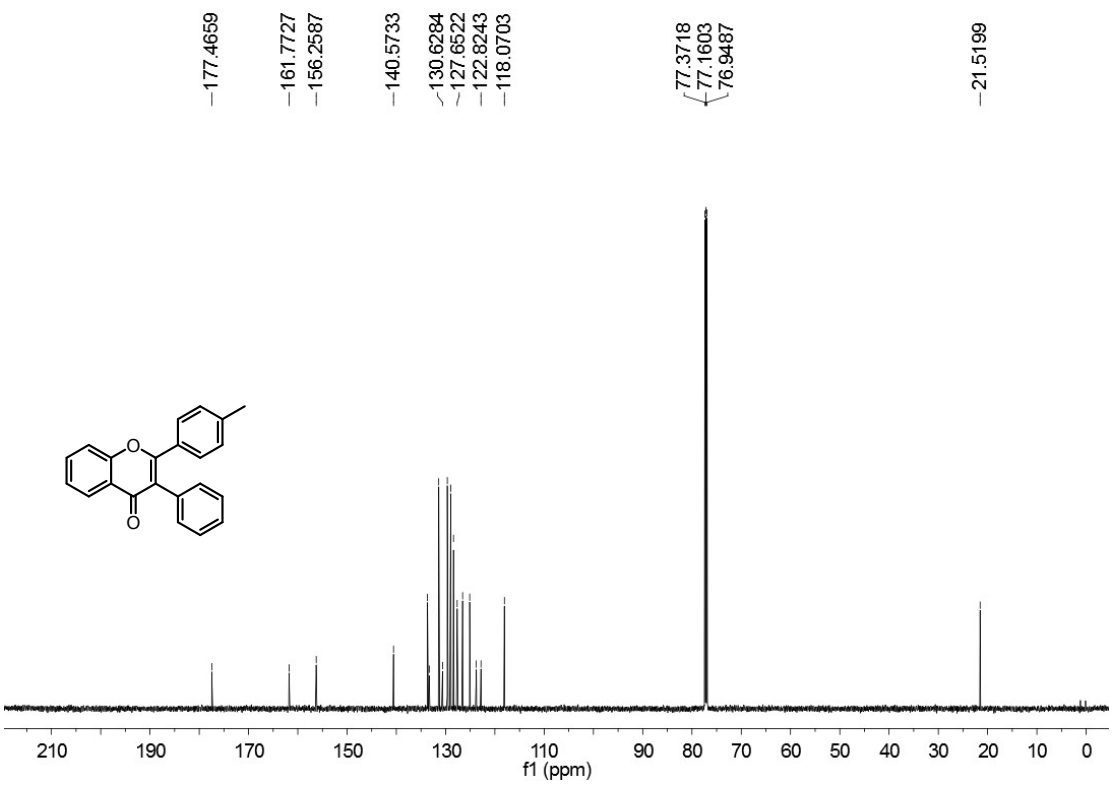
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110
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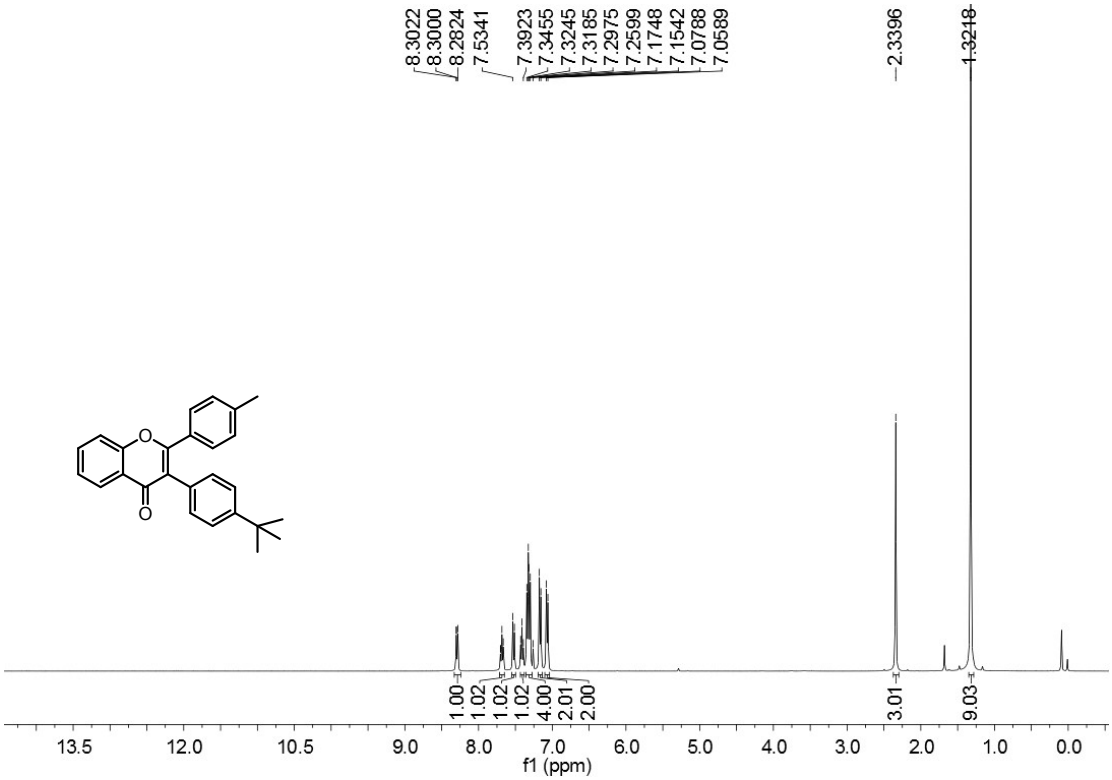
1l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7.0788
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1.02
1.02
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2.01
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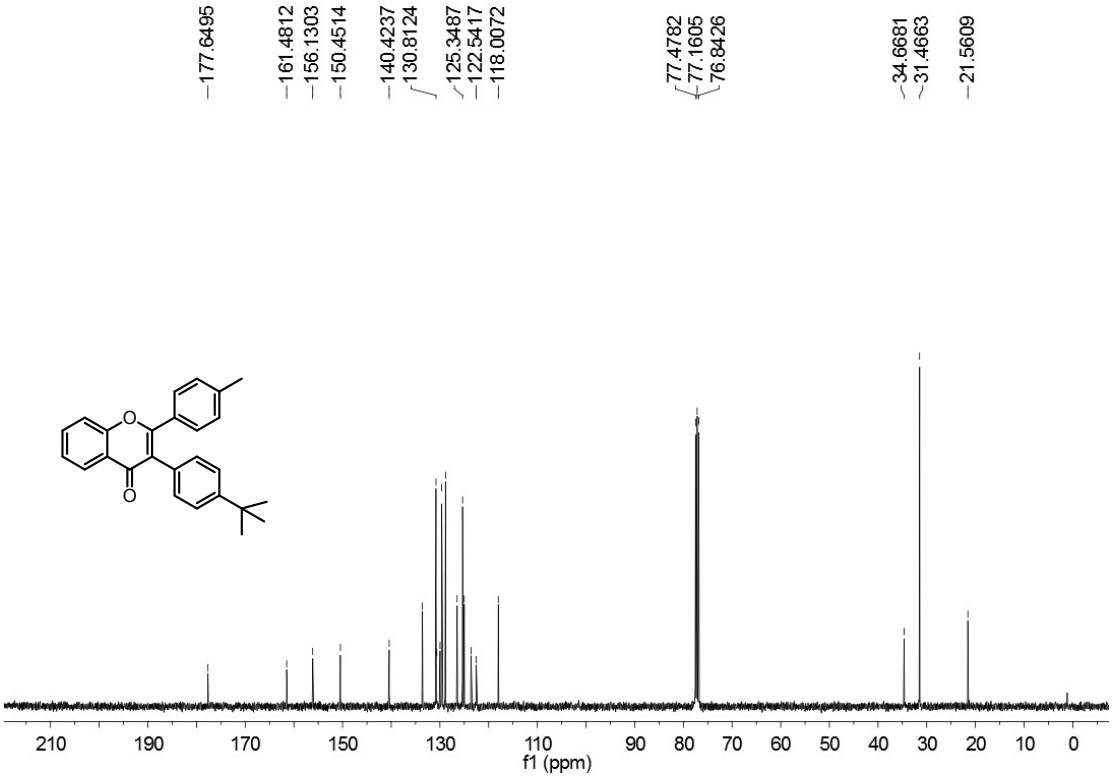
f1 (ppm)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21.5609
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10
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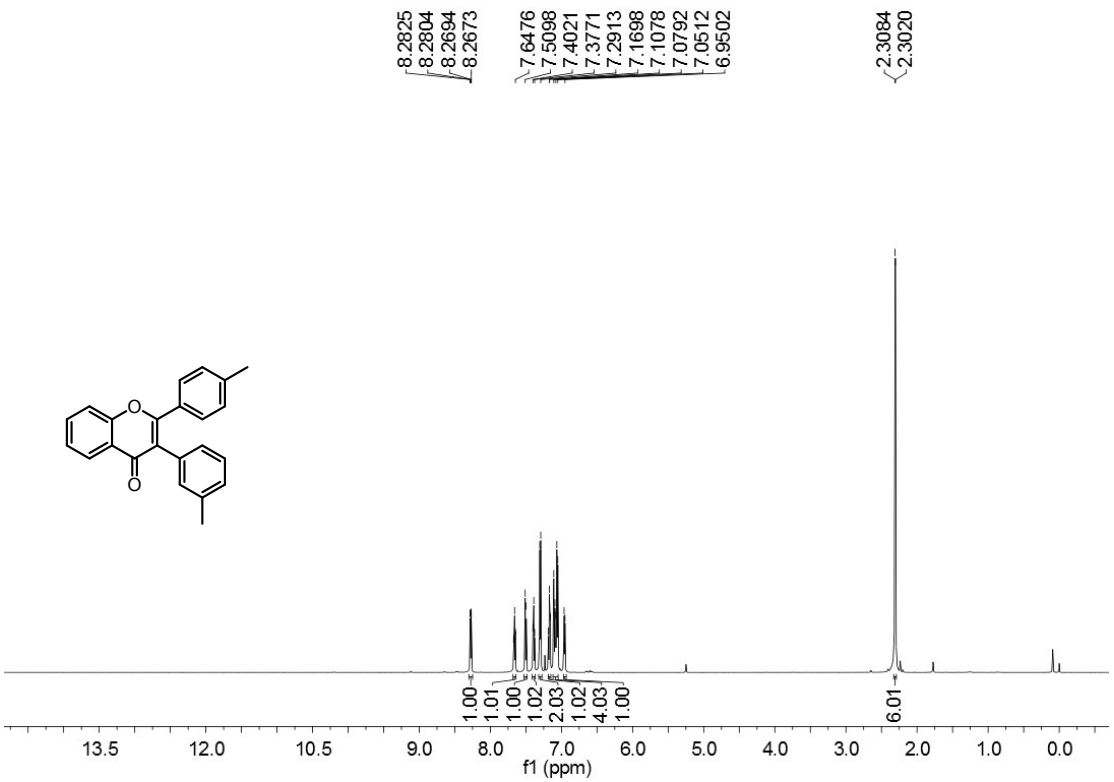
f1 (ppm)

1m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1.02
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13.5
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5.0
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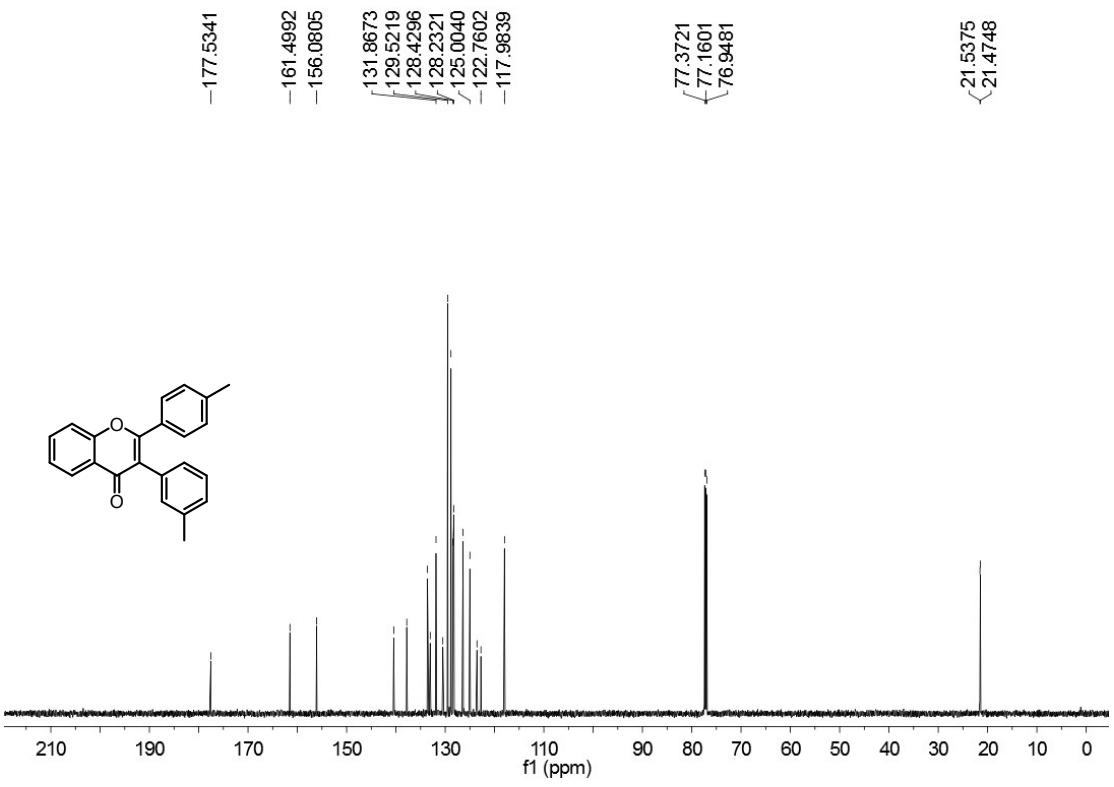
f1 (ppm)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80
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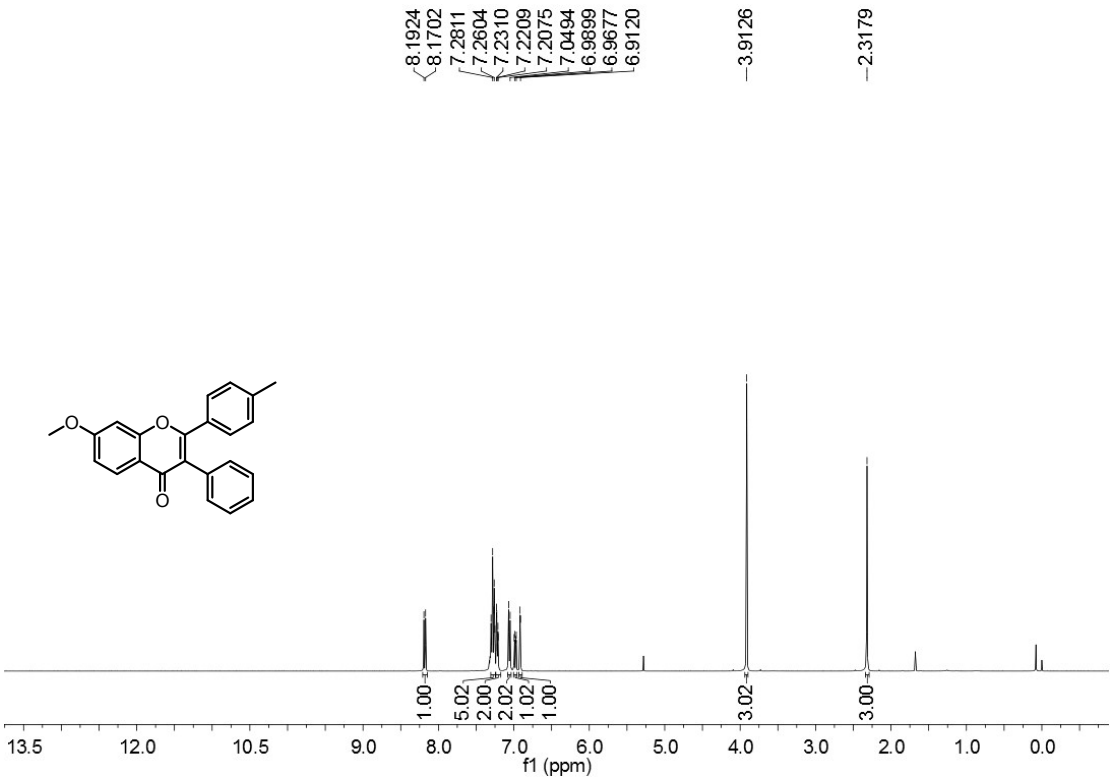
30
20
10
0
f1 (ppm)

1n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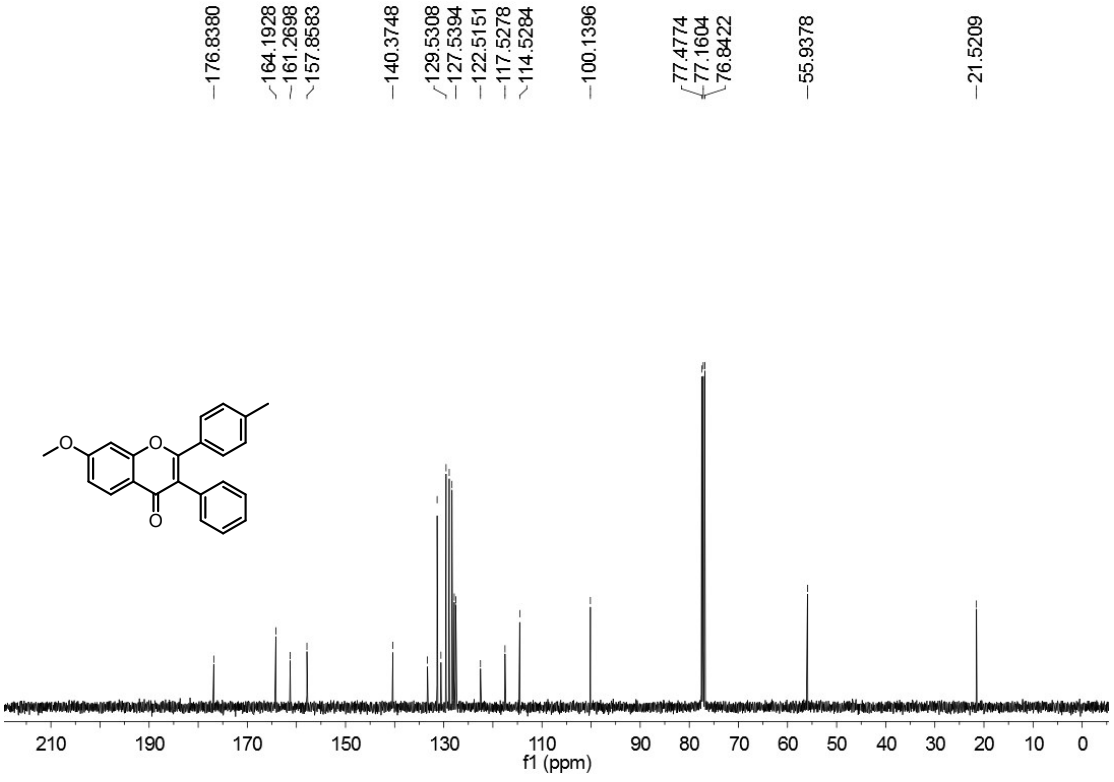
5.02
2.00
2.02
1.02
1.00
3.02
3.00
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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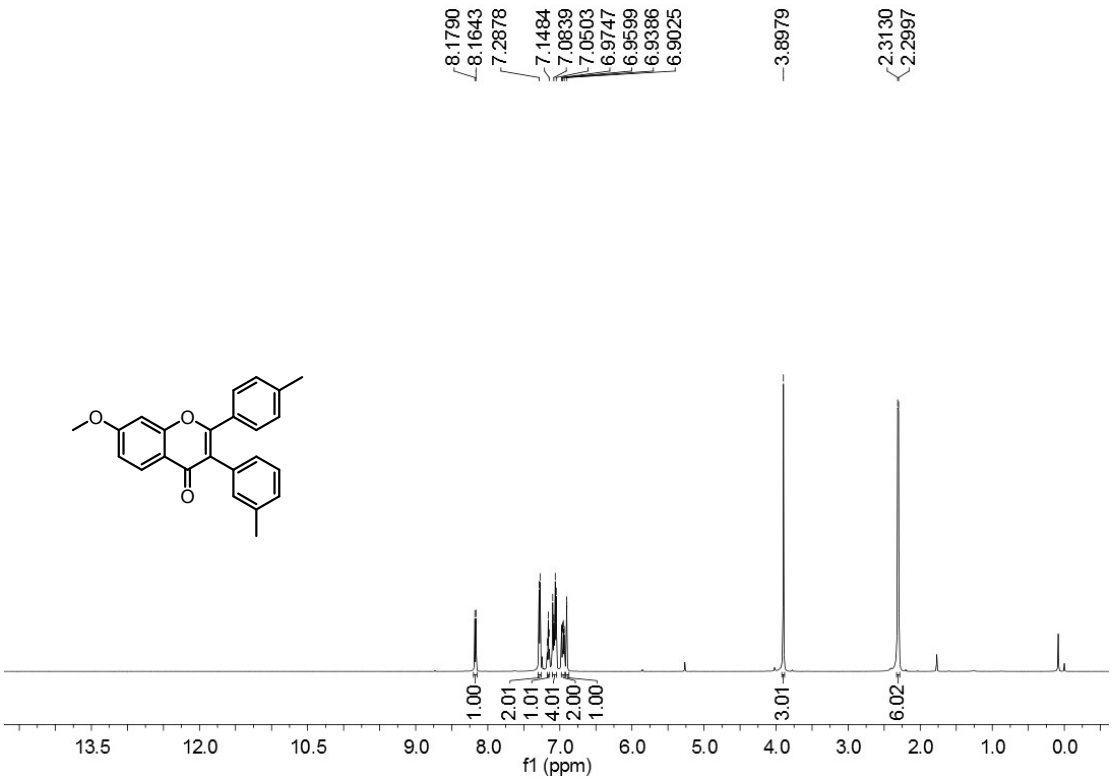
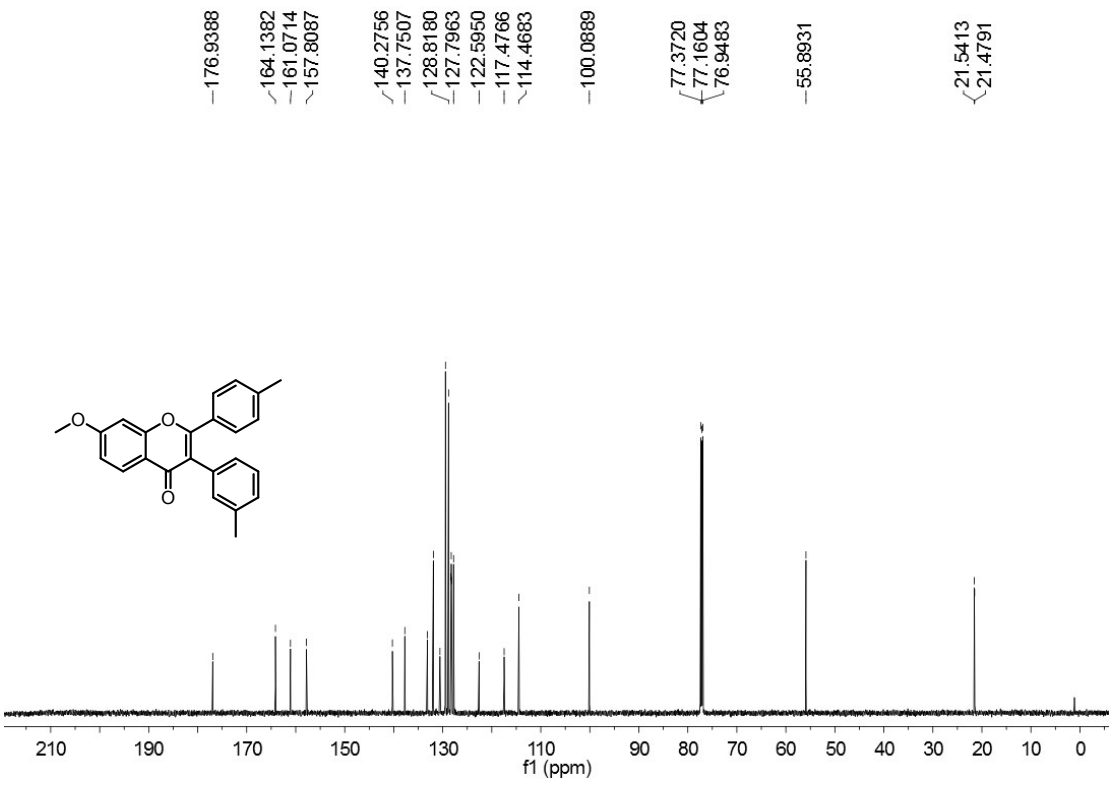
161.2698
157.8583
140.3748
129.5308
127.5394
122.5151
117.5278
114.5284
100.1396
77.4774
77.1604
76.8422
55.9378
21.5209
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1o


8.1790
8.1643
7.2878
7.1484
7.0839
7.0503
6.9747
6.9599
6.9386
6.9025
3.8979
2.3130
2.2997
1.00
2.01
1.01
4.01
2.00
1.00
3.01
6.02
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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161.0714
157.8087
140.2756
137.7507
128.8180
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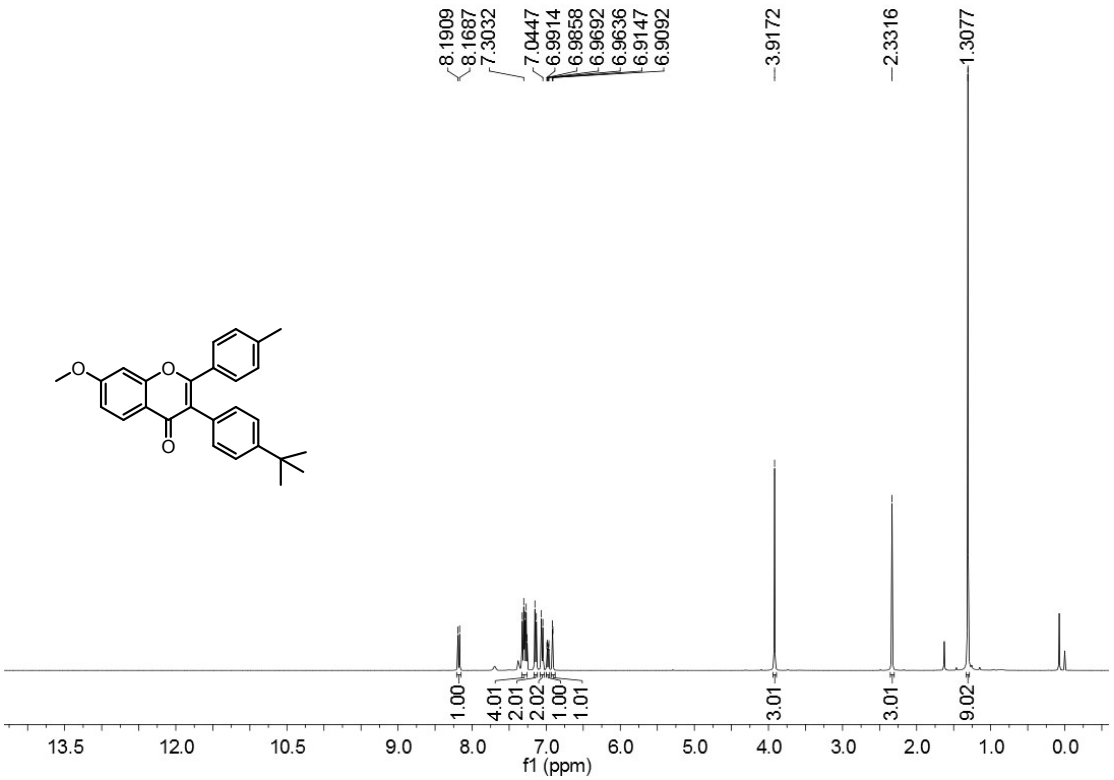
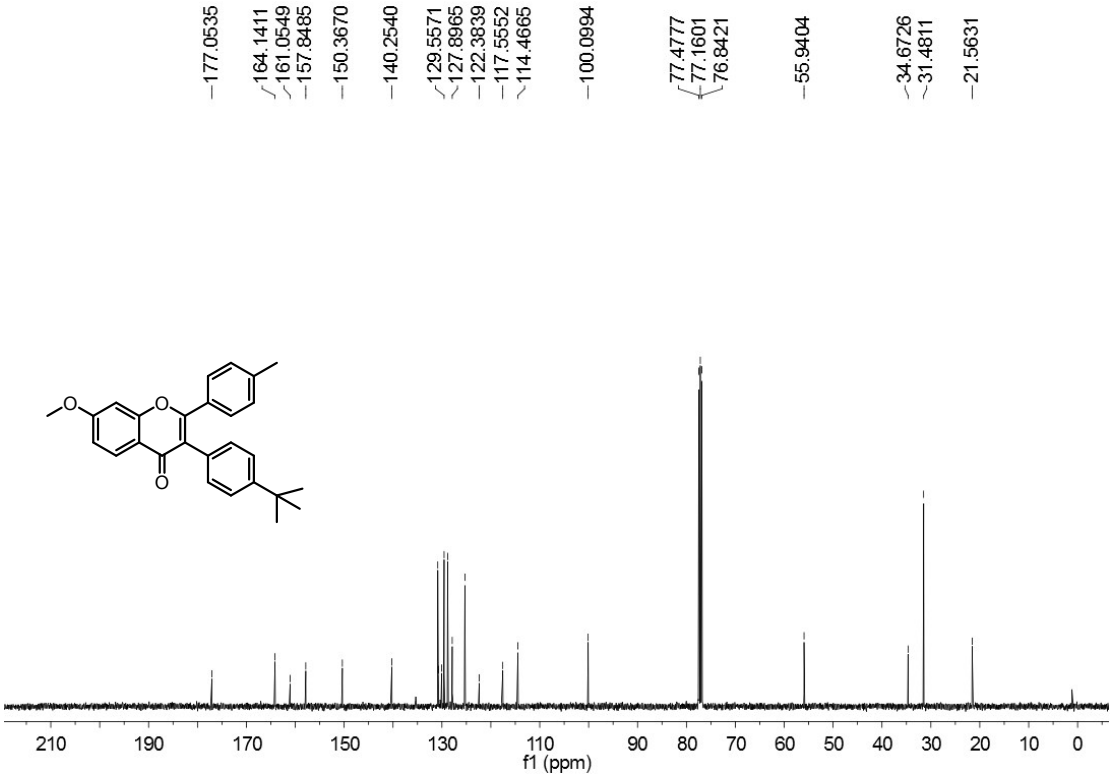
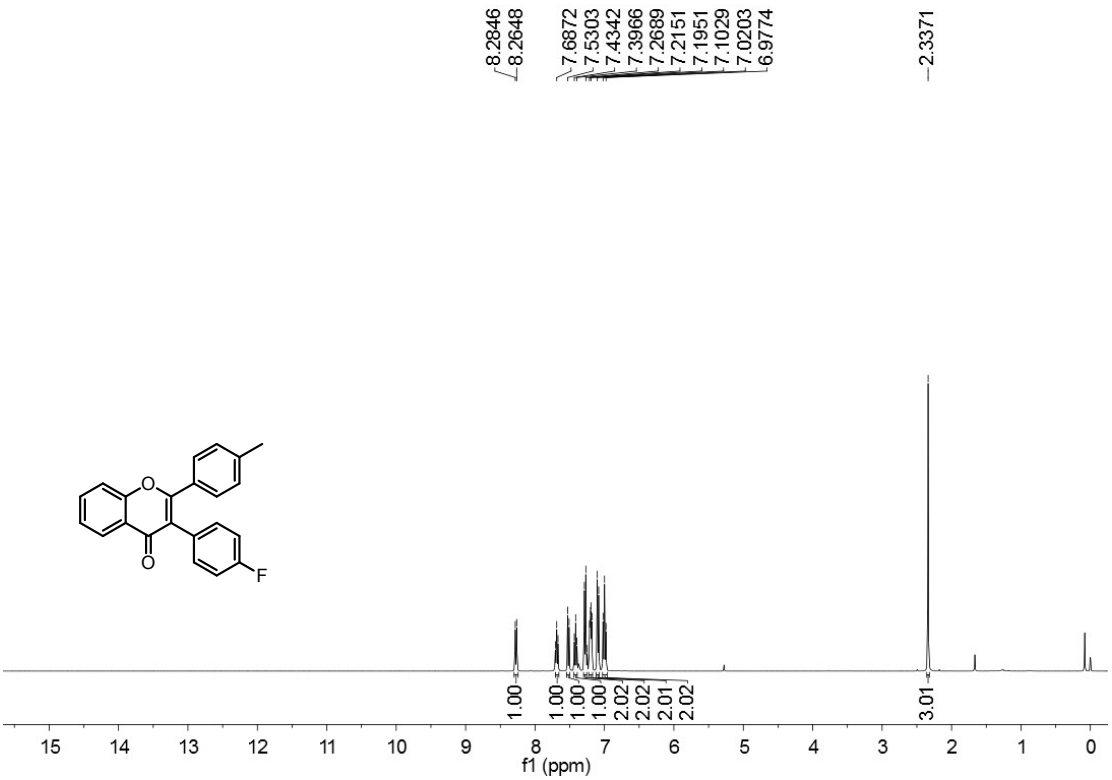
122.5950
117.4766
114.4683
100.0889
77.3720
77.1604
76.9483
55.8931
21.5413
21.4791
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

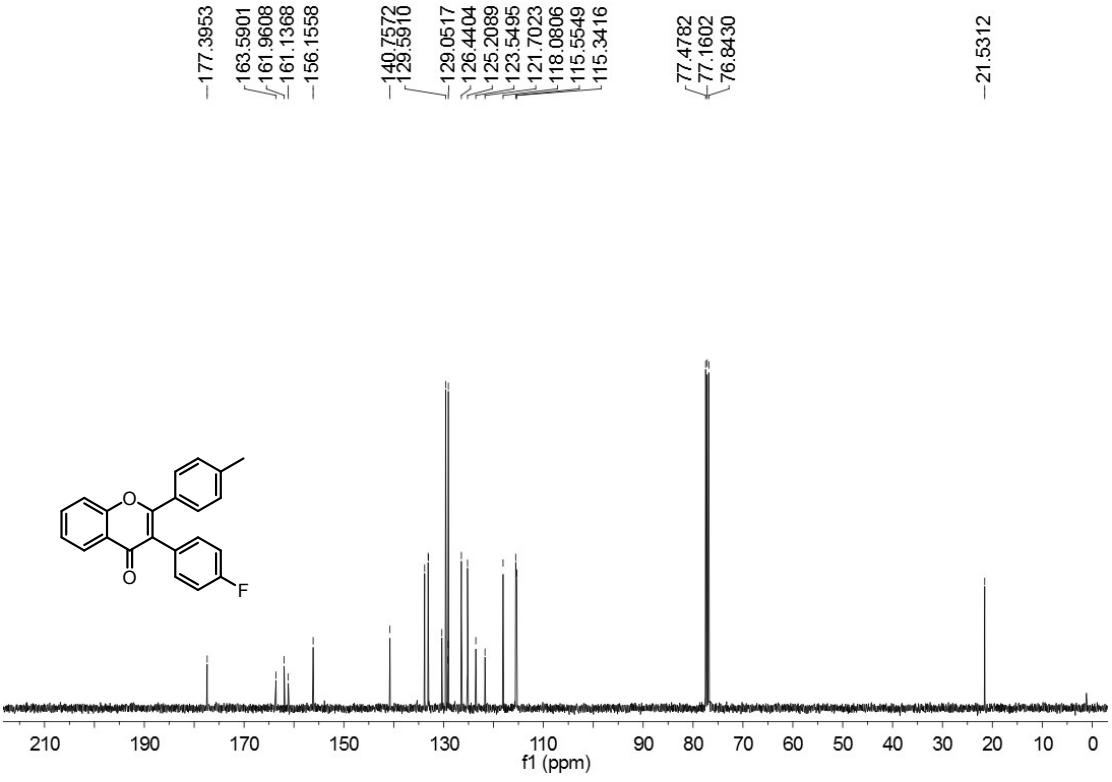
1p


8.1909
8.1687
7.3032
7.0447
6.9914
6.9858
6.9692
6.9636
6.9147
6.9092
3.9172
2.3316
1.3077
1.00
4.01
2.01
2.02
1.00
1.01
3.01
3.01
9.02
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


177.0535
164.1411
161.0549
157.8485
150.3670
140.2540
129.5571
127.8965
122.3839
117.5552
114.4665
100.0994
77.4777
77.1601
76.8421
55.9404
34.6726
31.4811
21.5631
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1q


8.2846
8.2648
7.6872
7.5303
7.4342
7.3966
7.2689
7.2151
7.1951
7.1029
7.0203
6.9774
2.3371
O
O
F
1.00
1.00
1.00
1.00
2.02
2.02
2.01
2.02
3.01
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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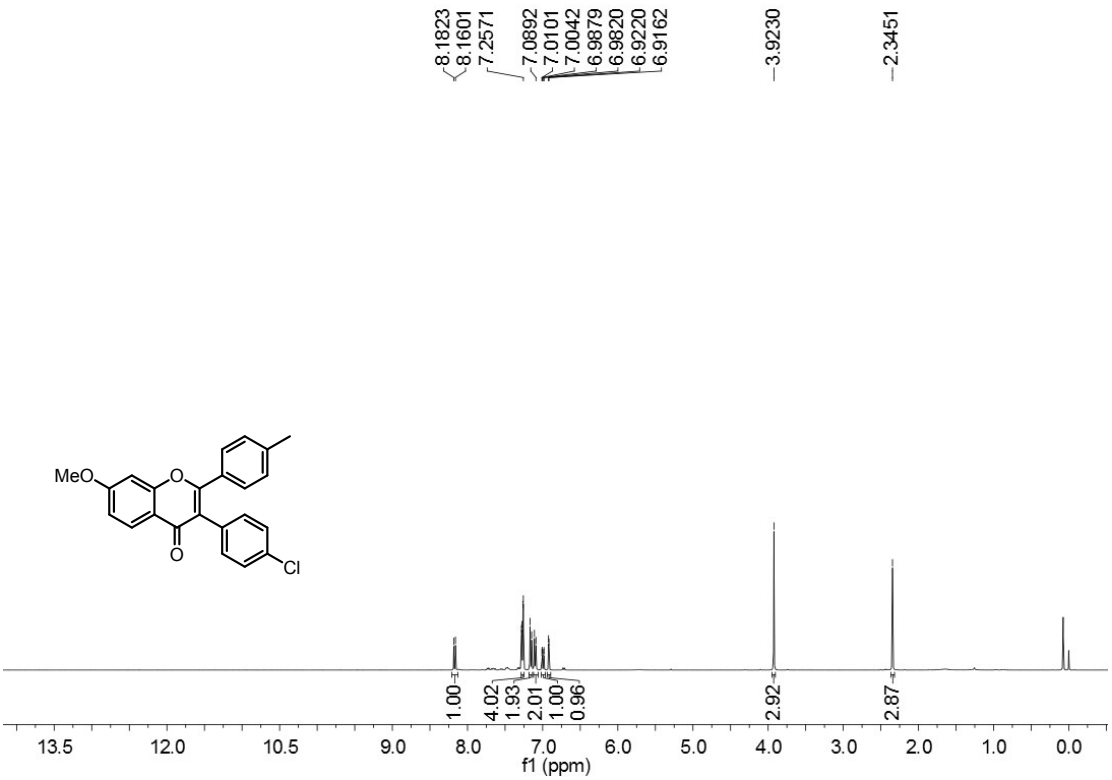
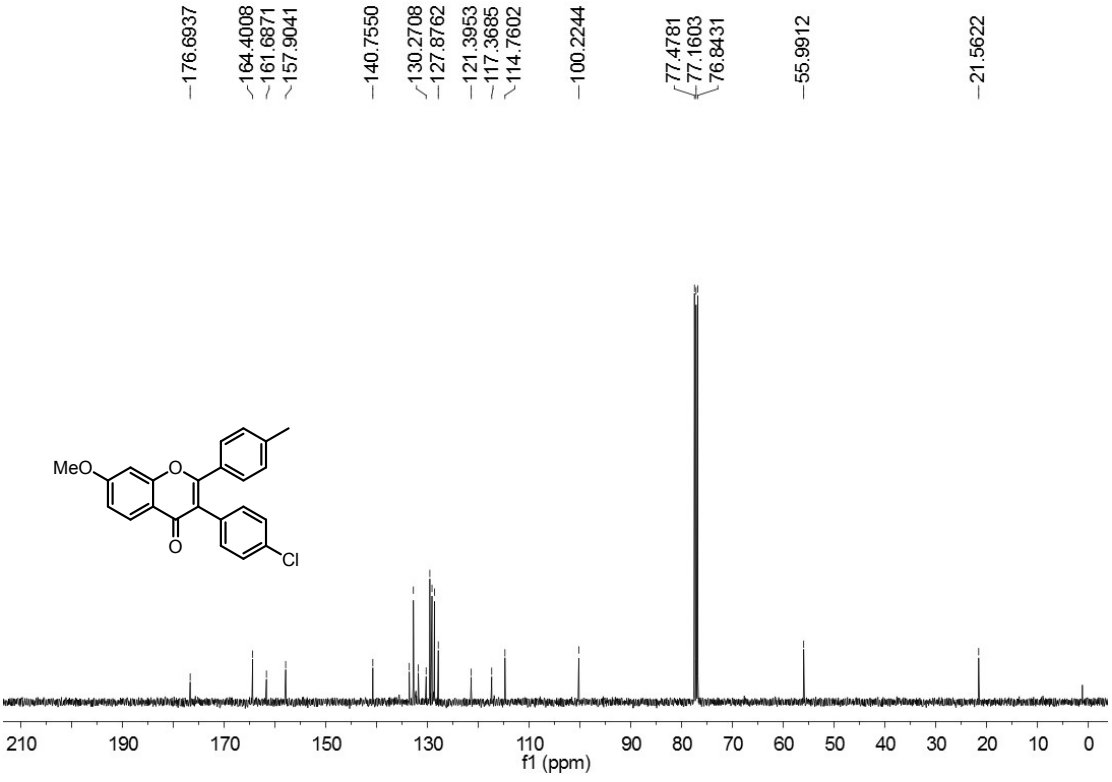
163.5901
161.9608
161.1368
156.1558
140.7572
129.5910
129.0517
126.4404
125.2089
123.5495
121.7023
118.0806
115.5549
115.3416
77.4782
77.1602
76.8430
21.5312
O
O
F
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1r


8.1823
8.1601
7.2571
7.0892
7.0101
7.0042
6.9879
6.9820
6.9220
6.9162
3.9230
2.3451
MeO
O
O
Cl
1.00
4.02
1.93
2.01
1.00
0.96
2.92
2.87
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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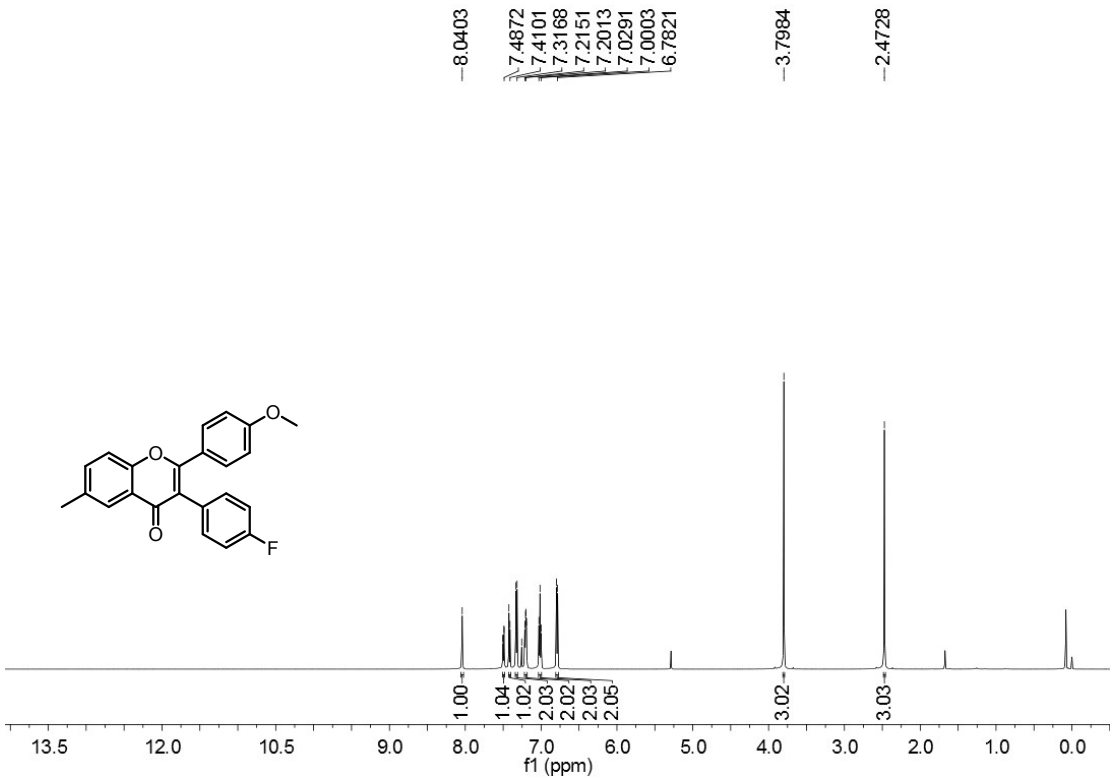
161.6871
157.9041
140.7550
130.2708
127.8762
121.3953
117.3685
114.7602
100.2244
77.4781
77.1603
76.8431
55.9912
21.5622
MeO
O
O
Cl
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1s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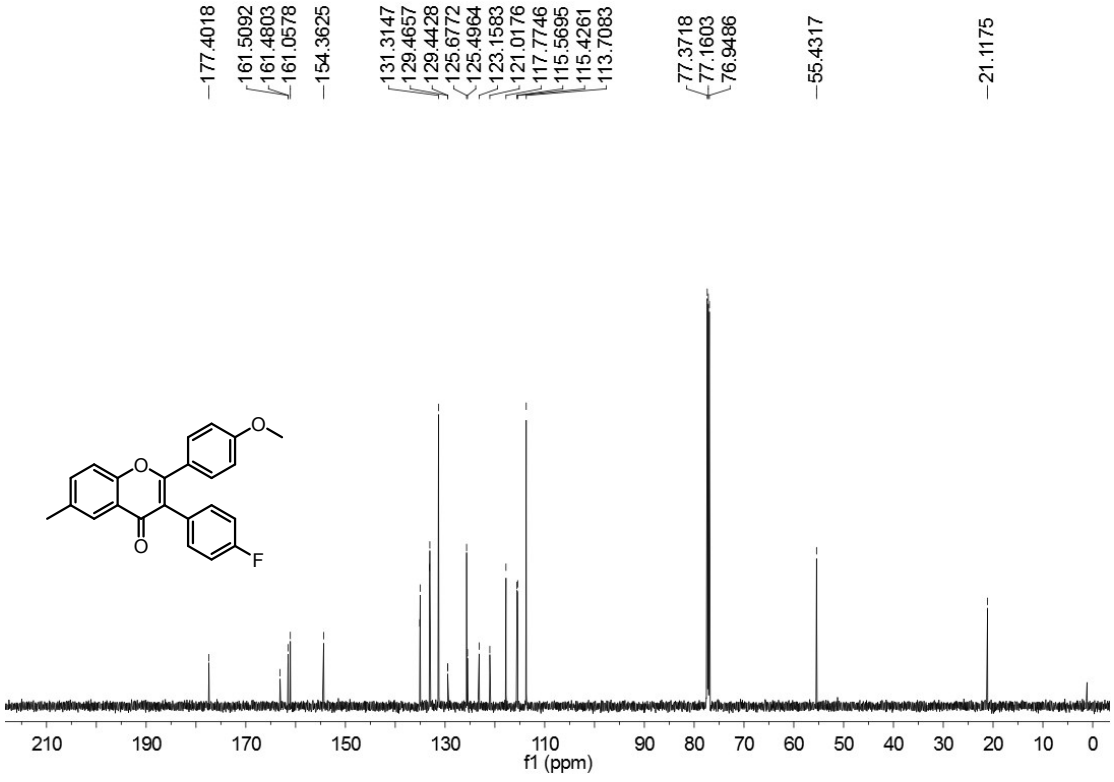
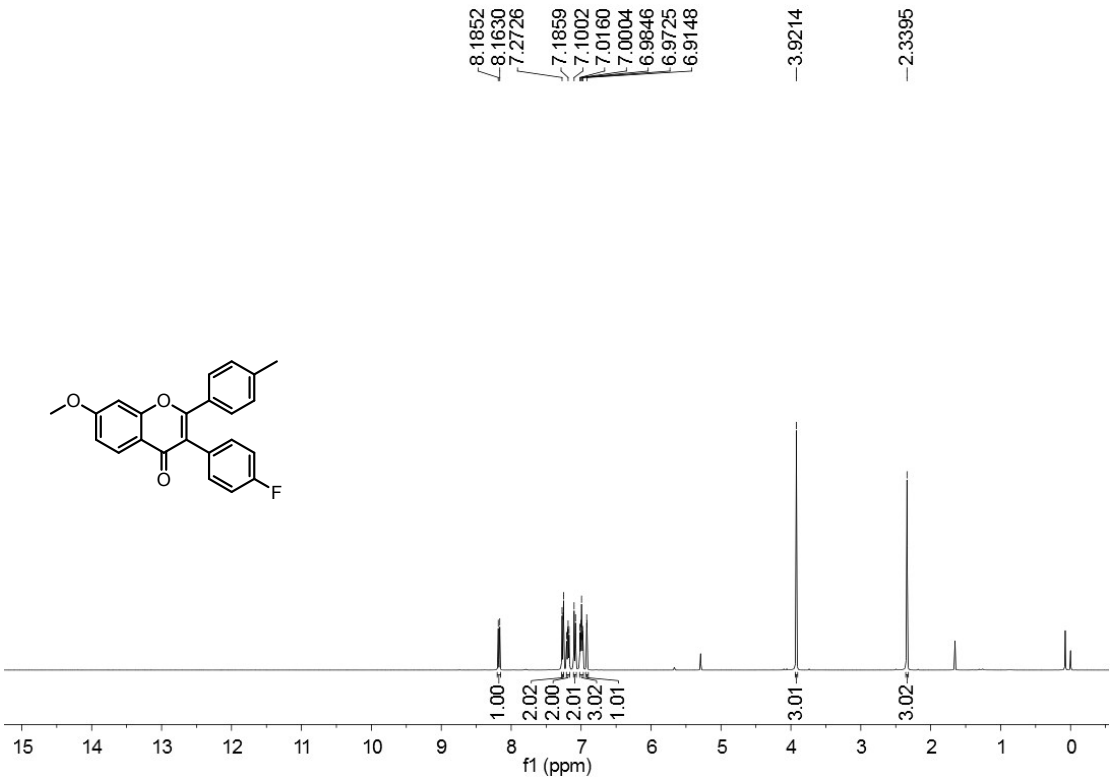
7.4872
7.4101
7.3168
7.2151
7.2013
7.0291
7.0003
6.7821
3.7984
2.4728
O
O
F
1.00
1.04
1.02
2.03
2.02
2.03
2.05
3.02
3.03
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


177.4018
161.5092
161.4803
161.0578
154.3625
131.3147
129.4657
129.4428
125.6772
125.4964
123.1583
121.0176
117.7746
115.5695
115.4261
113.7083
77.3718
77.1603
76.9486
55.4317
21.1175
O
O
F
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1t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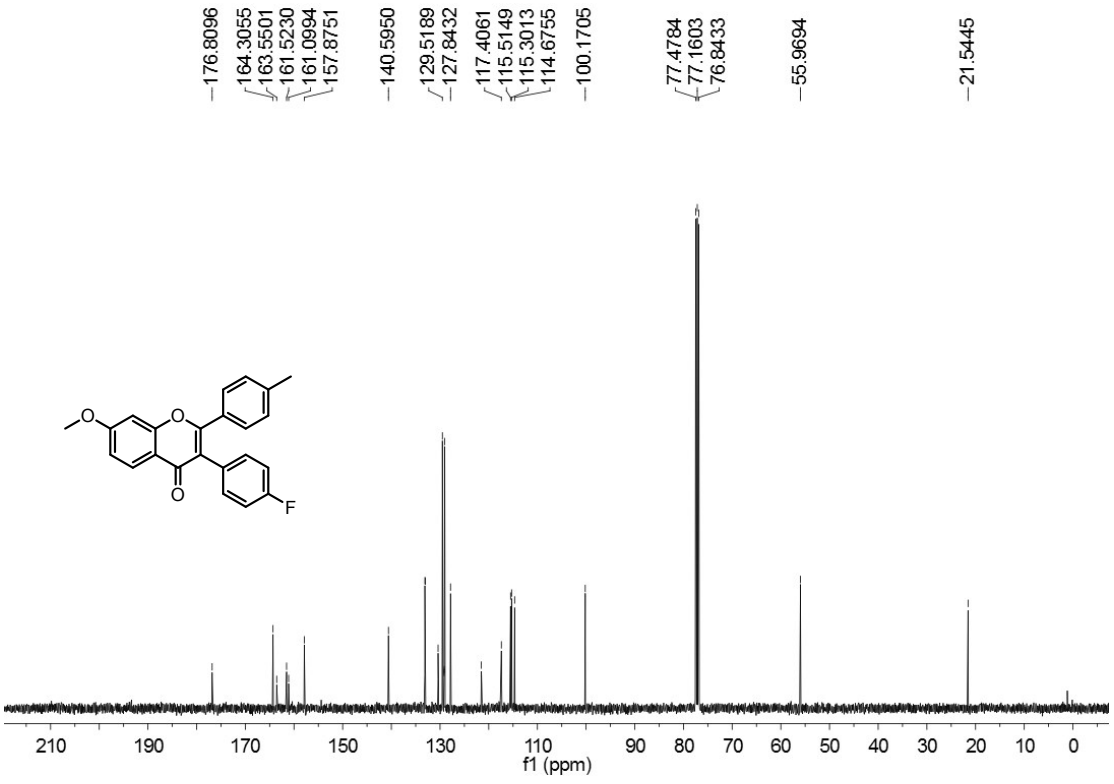
8.1630
7.2726
7.1859
7.1002
7.0160
7.0004
6.9846
6.9725
6.9148
3.9214
2.3395
O
O
O
F
1.00
2.02
2.00
2.01
3.02
1.01
3.01
3.02
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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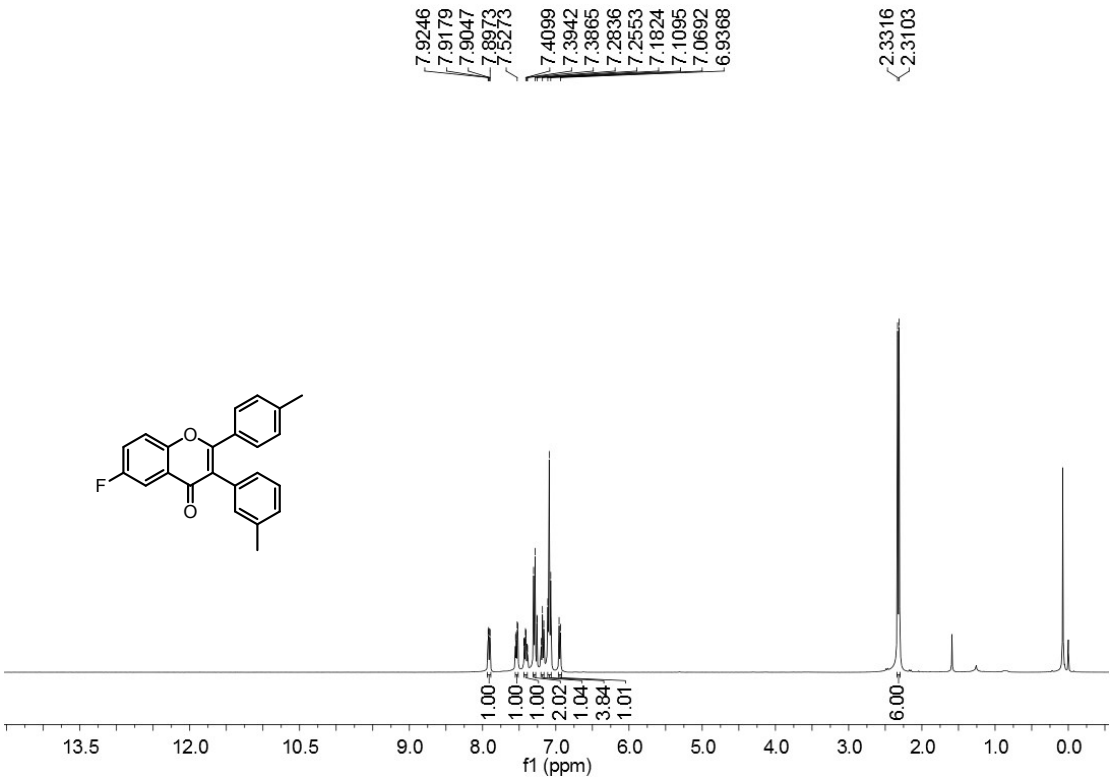
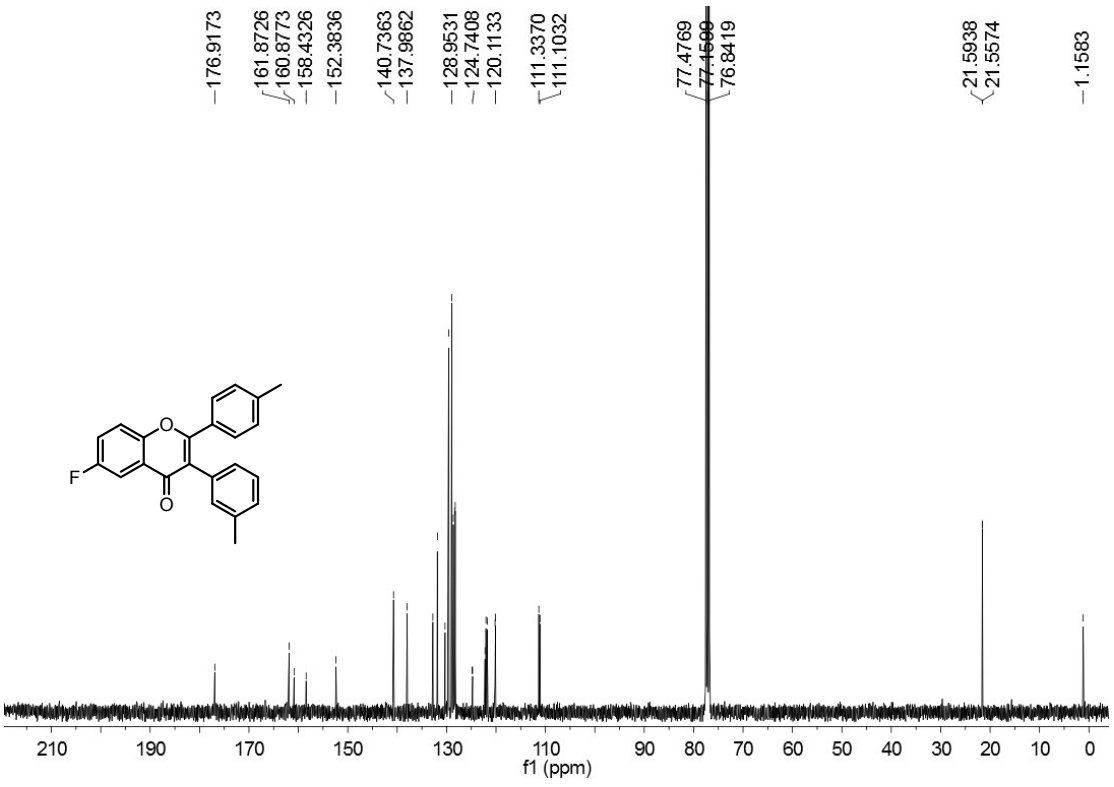
163.5501
161.5230
161.0994
157.8751
140.5950
129.5189
127.8432
117.4061
115.5149
115.3013
114.6755
100.1705
77.4784
77.1603
76.8433
55.9694
21.5445
O
O
O
F
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

1u


7.9246
7.9179
7.9047
7.8973
7.5273
7.4099
7.3942
7.3865
7.2836
7.2553
7.1824
7.1095
7.0692
6.9368
2.3316
2.3103
F
O
O
1.00
1.00
1.00
2.02
1.04
3.84
1.01
6.00
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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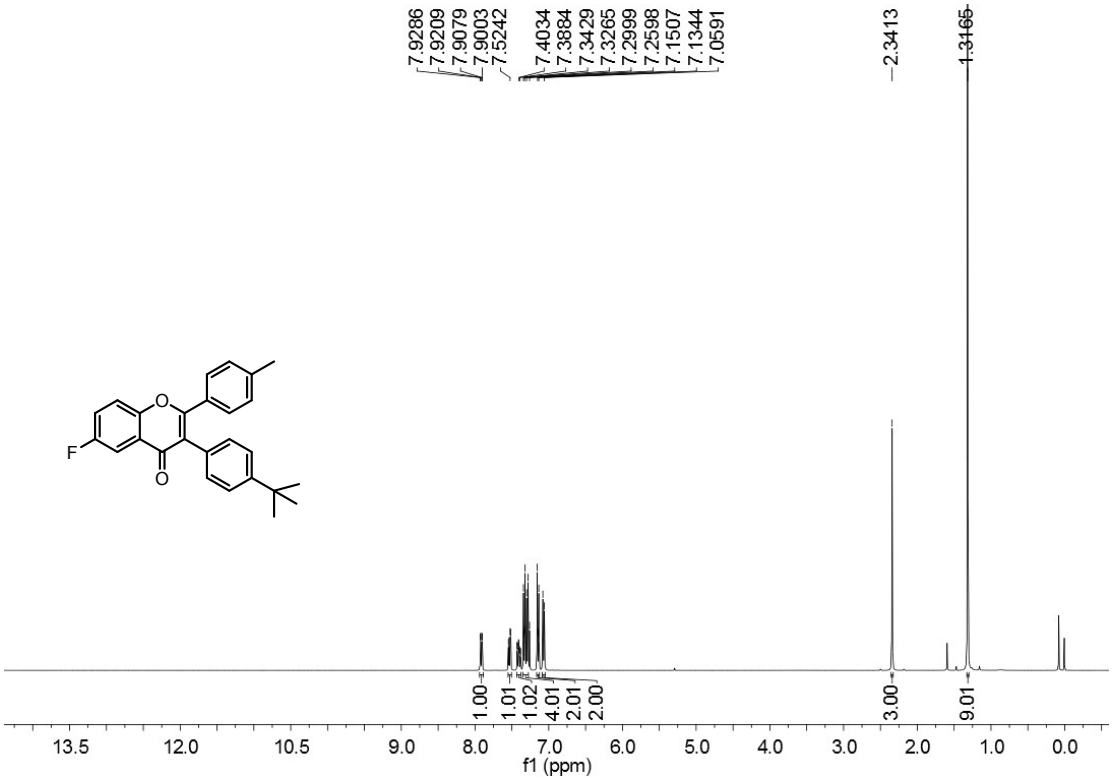
160.8773
158.4326
152.3836
140.7363
137.9862
128.9531
124.7408
120.1133
111.3370
111.1032
77.4769
77.1590
76.8419
21.5938
21.5574
1.1583
F
O
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1v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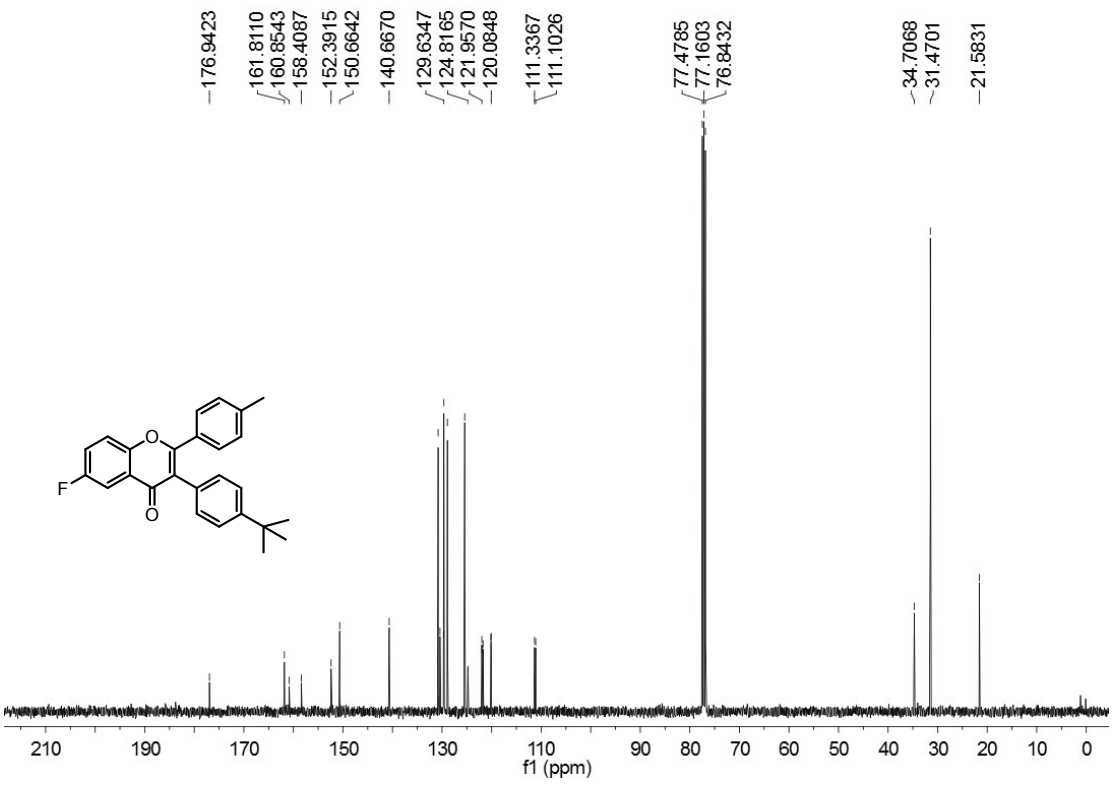
7.9079
7.9003
7.5242
7.4034
7.3884
7.3429
7.3265
7.2999
7.2598
7.1507
7.1344
7.0591
2.3413
1.3165
F
O
O
1.00
1.01
1.02
4.01
2.01
2.00
3.00
9.01
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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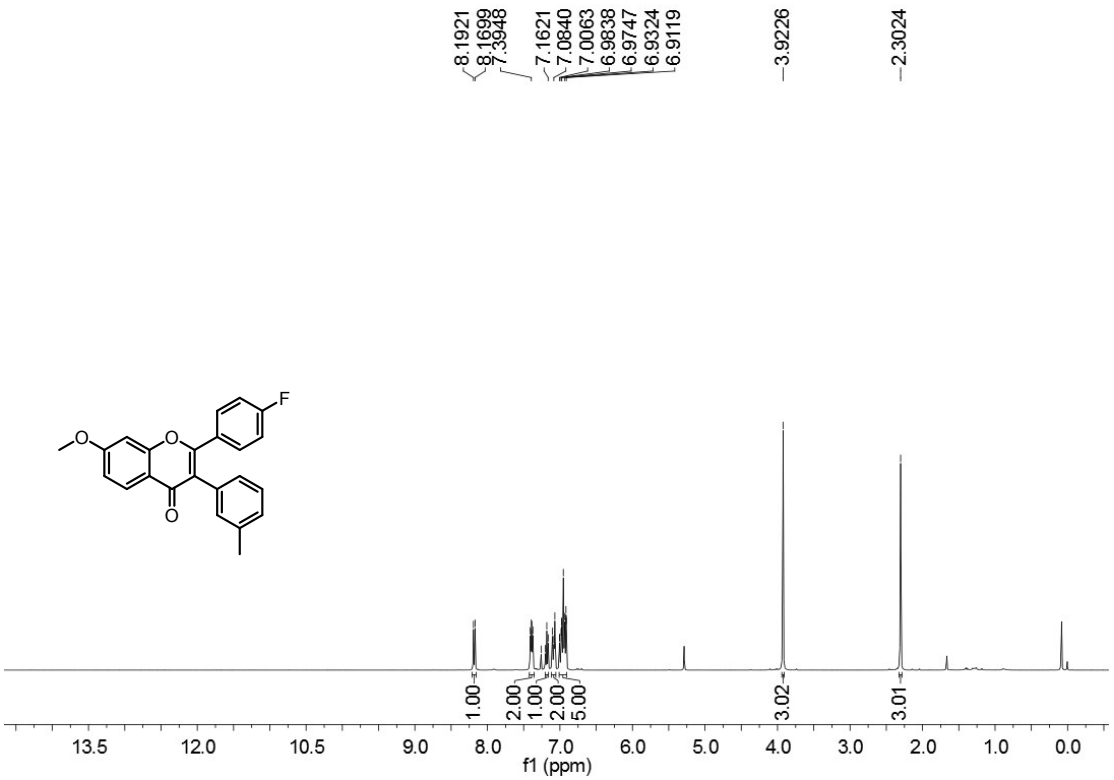
158.4087
152.3915
150.6642
140.6670
129.6347
124.8165
121.9570
120.0848
111.3367
111.1026
77.4785
77.1603
76.8432
34.7068
31.4701
21.5831
F
O
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1w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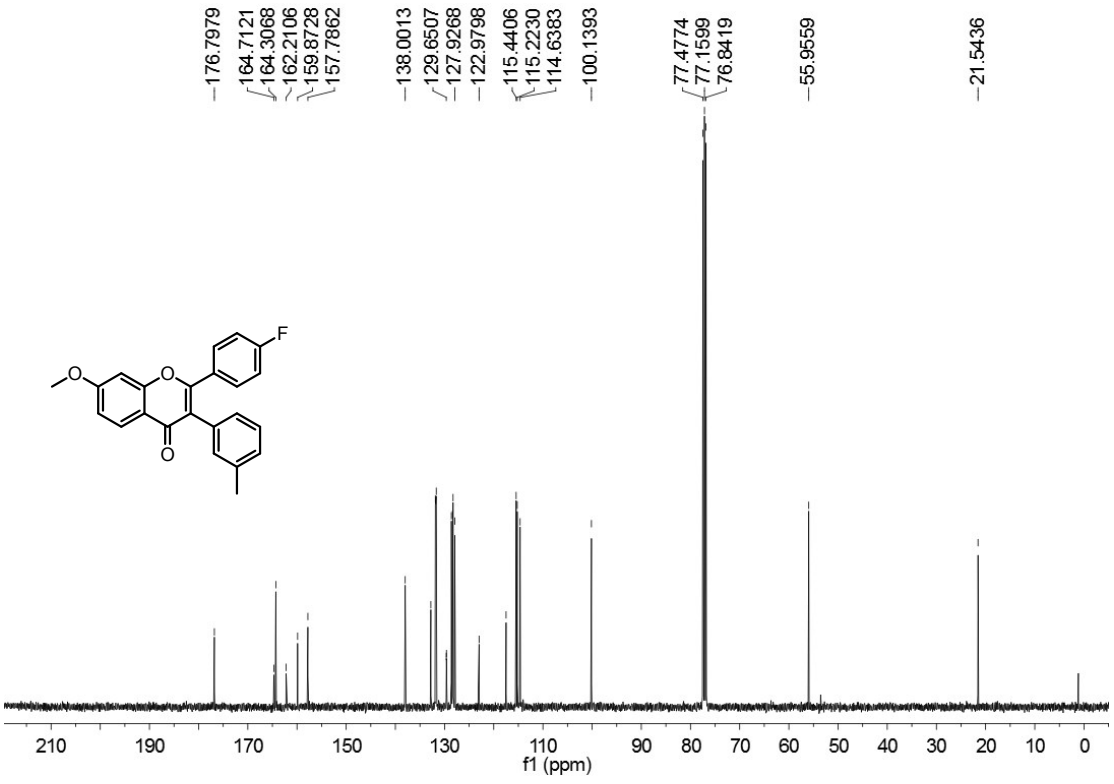
7.3948
7.1621
7.0840
7.0063
6.9838
6.9747
6.9324
6.9119
3.9226
2.3024
F
O
O
O
1.00
2.00
1.00
2.00
5.00
3.02
3.01
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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164.3068
162.2106
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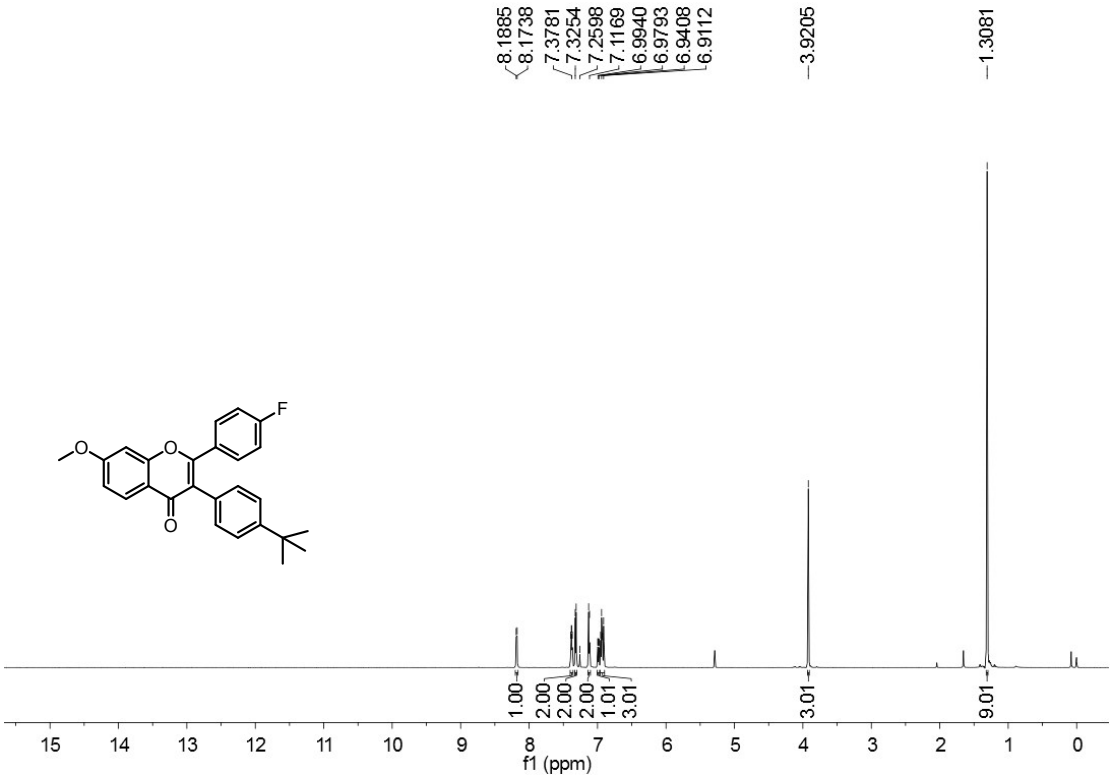
157.7862
138.0013
129.6507
127.9268
122.9798
115.4406
115.2230
114.6383
100.1393
77.4774
77.1599
76.8419
55.9559
21.5436
F
O
O
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1x


8.1885
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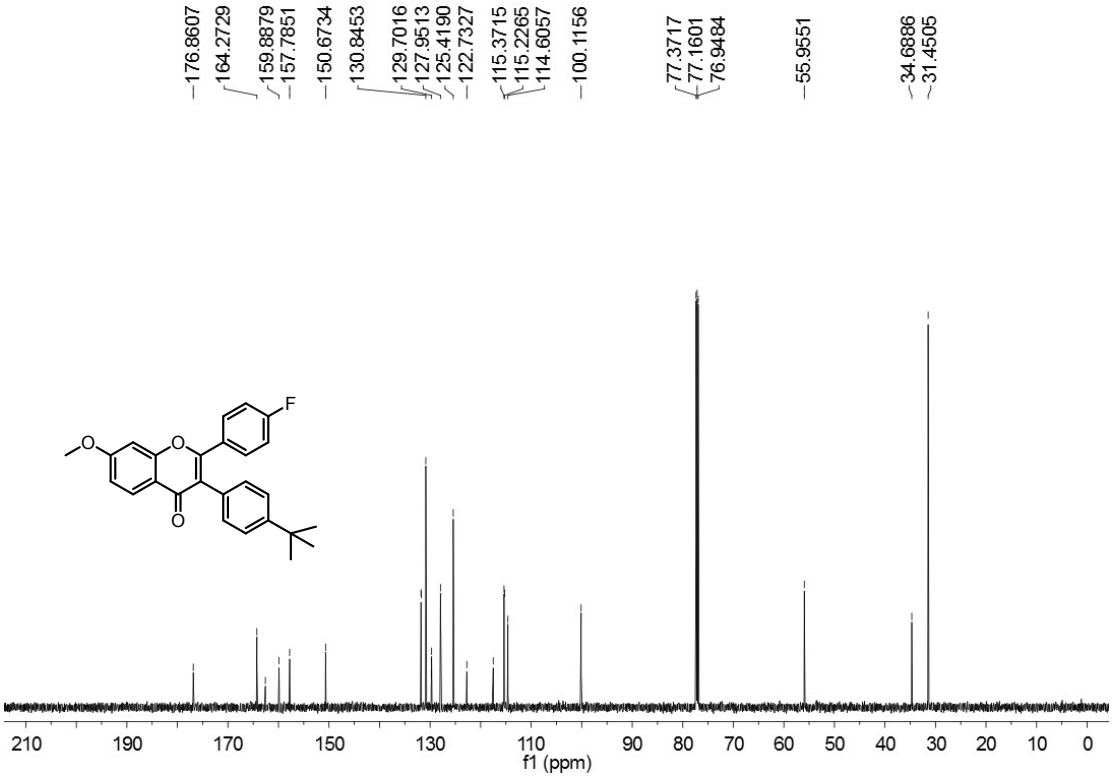
7.3781
7.3254
7.2598
7.1169
6.9940
6.9793
6.9408
6.9112
3.9205
1.3081
F
O
O
O
1.00
2.00
2.00
2.00
1.01
3.01
3.01
9.01
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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157.7851
150.6734
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129.7016
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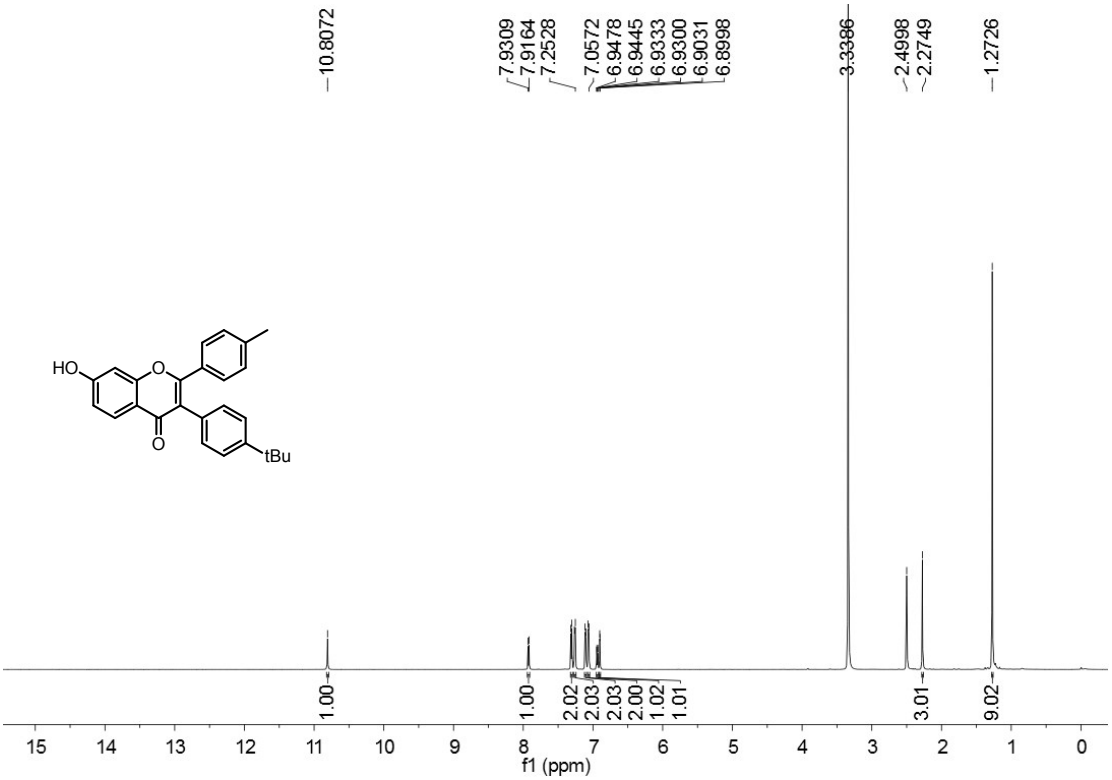
125.4190
122.7327
115.3715
115.2265
114.6057
100.1156
77.3717
77.1601
76.9484
55.9551
34.6886
31.4505
F
O
O
O
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

1y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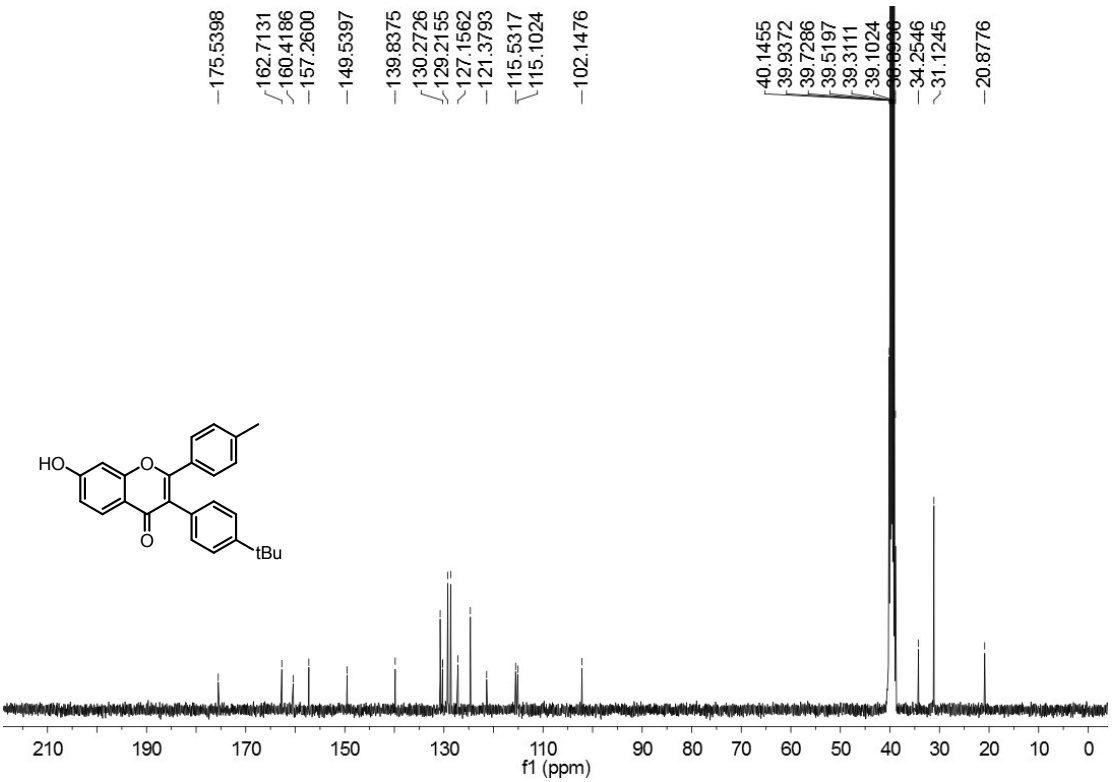
7.9164
7.2528
7.0572
6.9478
6.9445
6.9333
6.9300
6.9031
6.8998
3.3386
2.4998
2.2749
1.2726
HO
O
O
tBu
1.00
1.00
2.02
2.03
2.03
2.00
1.02
1.01
3.01
9.02
f1 (ppm)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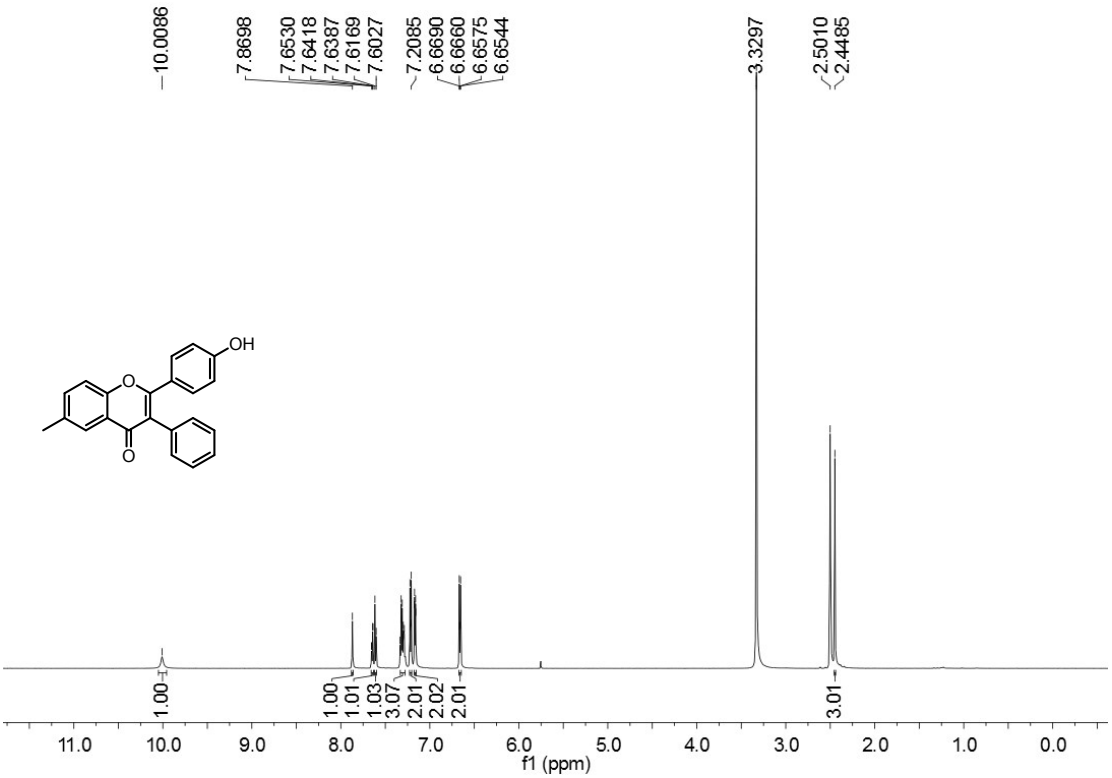
157.2600
149.5397
139.8375
130.2726
129.2155
127.1562
121.3793
115.5317
115.1024
102.1476
40.1455
39.9372
39.7286
39.5197
39.3111
39.1024
34.2546
31.1245
20.8776
HO
O
O
tBu
f1 (ppm)

1z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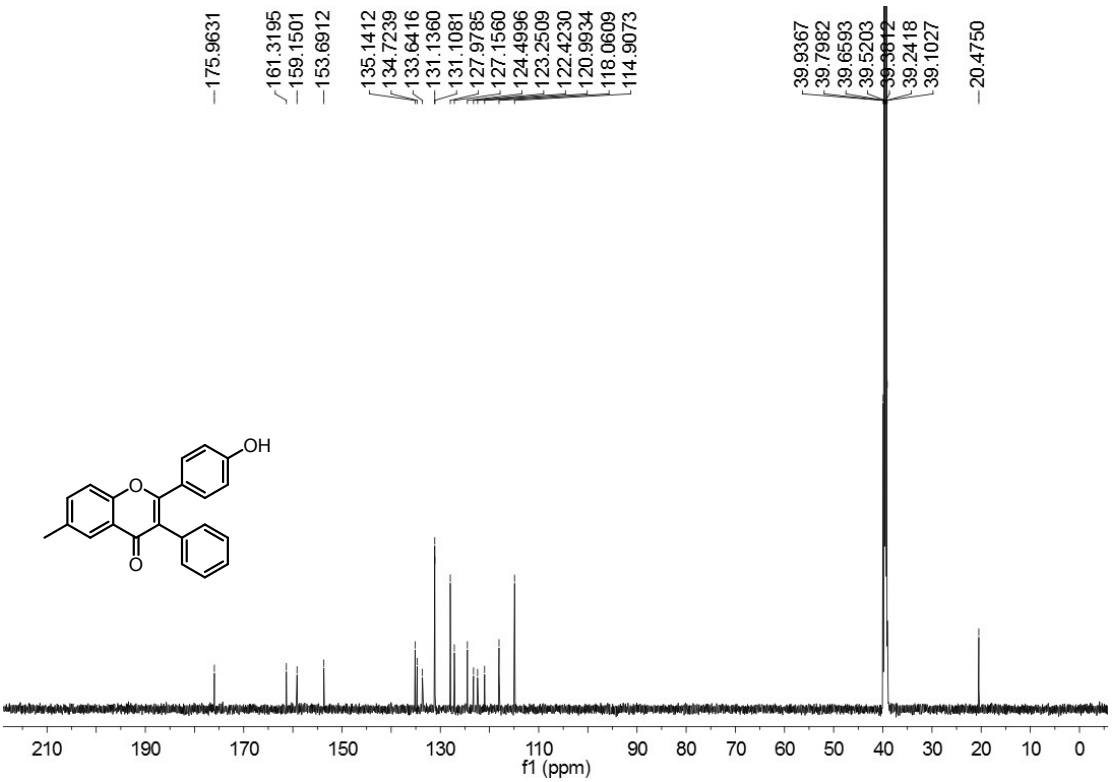
7.6530
7.6418
7.6387
7.6169
7.6027
7.2085
6.6690
6.6660
6.6575
6.6544
3.3297
2.5010
2.4485
OH
O
O
1.00
1.00
1.01
1.03
3.07
2.01
2.02
2.01
3.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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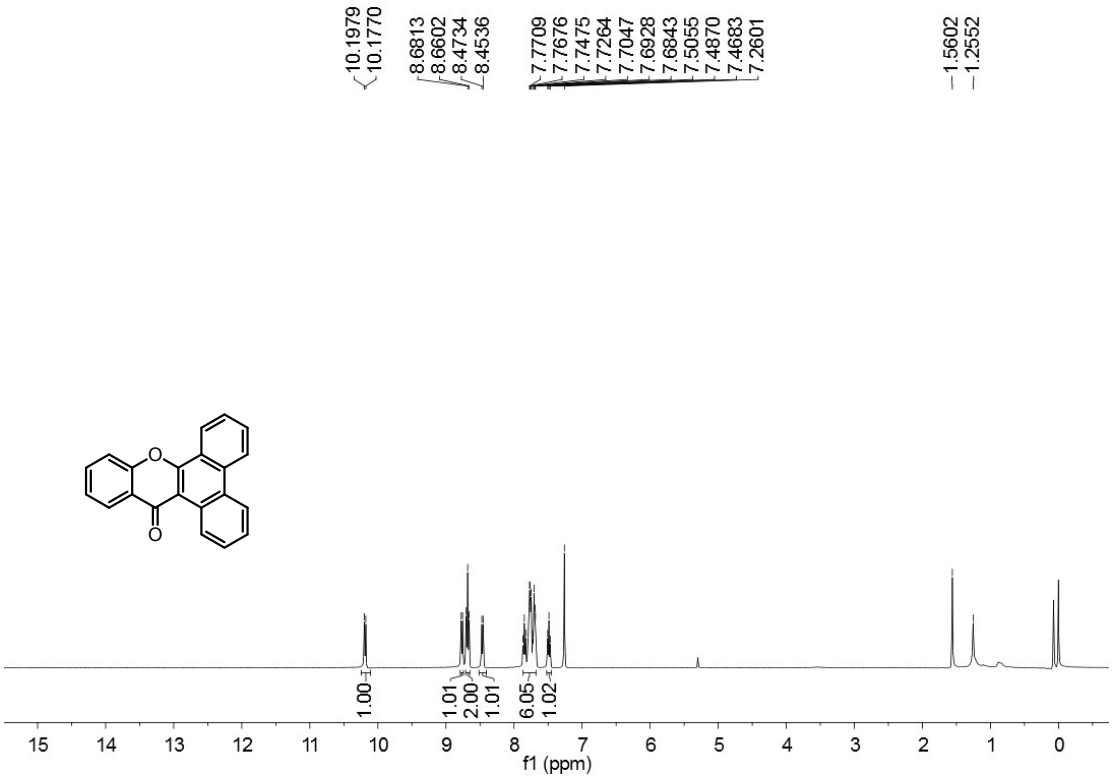
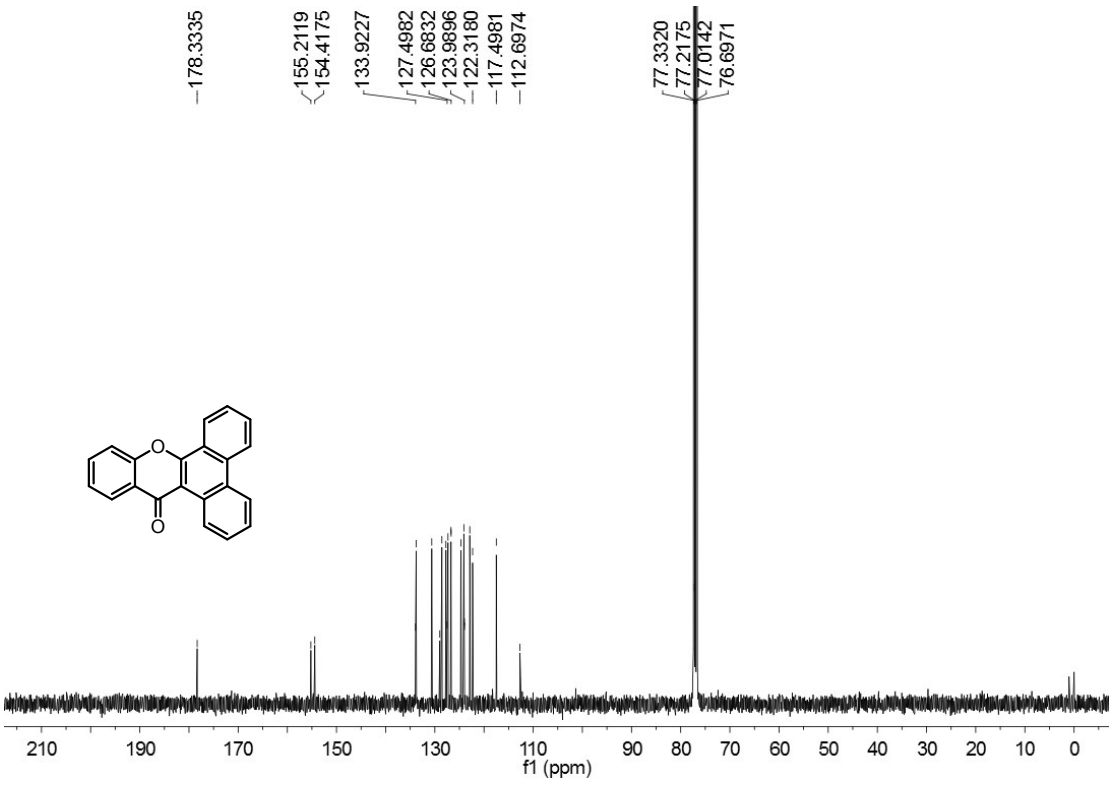
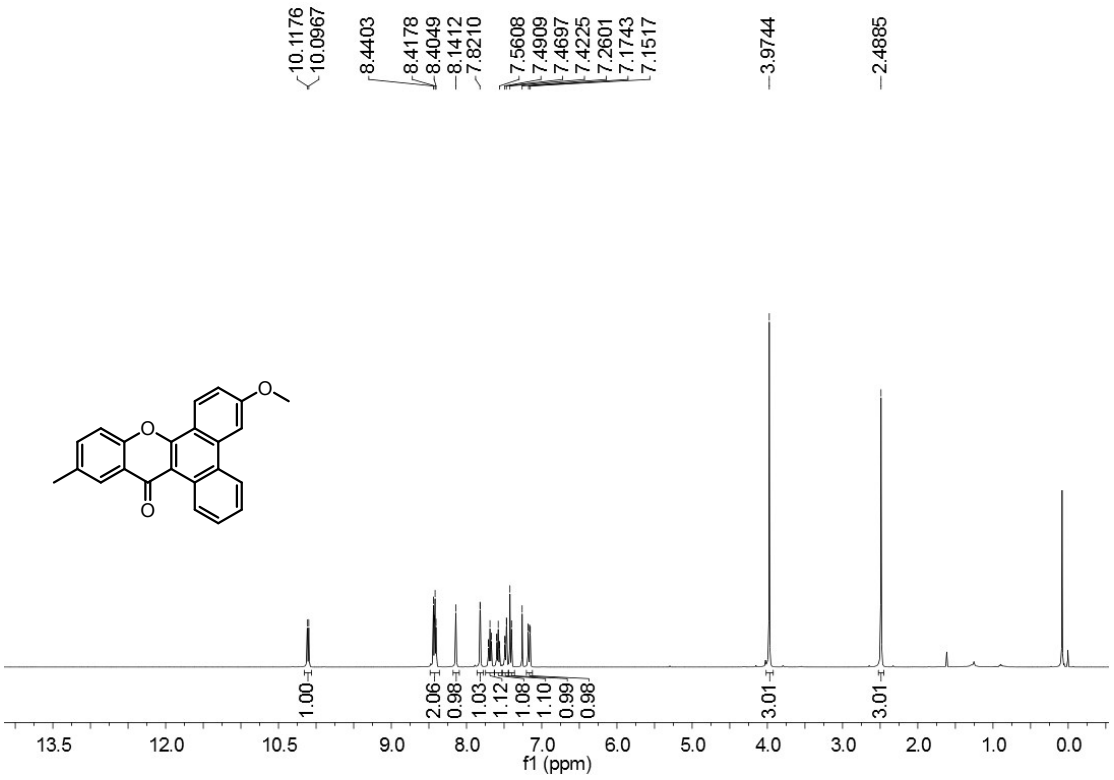
159.1501
153.6912
135.1412
134.7239
133.6416
131.1360
131.1081
127.9785
127.1560
124.4996
123.2509
122.4230
120.9934
118.0609
114.9073
39.9367
39.7982
39.6593
39.5203
39.3812
39.2418
39.1027
20.4750
OH
O
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

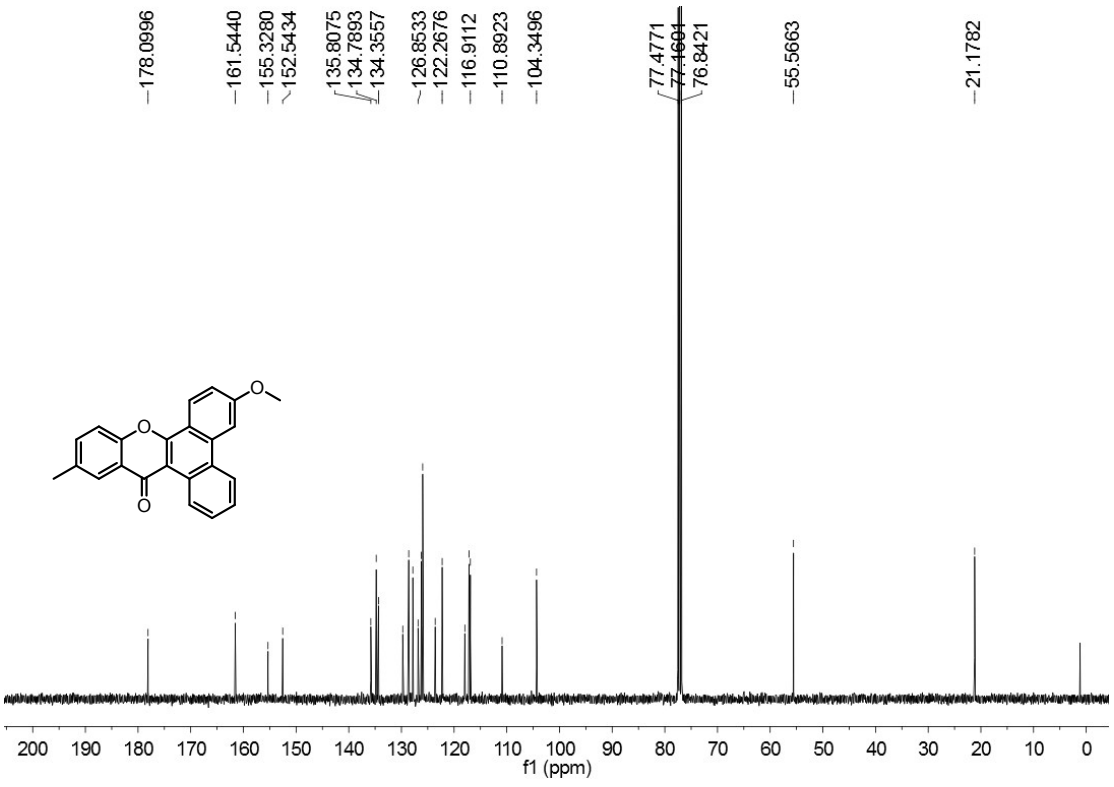
2a


10.1979
10.1770
8.6813
8.6602
8.4734
8.4536
7.7709
7.7676
7.7475
7.7264
7.7047
7.6928
7.6843
7.5055
7.4870
7.4683
7.2601
1.5602
1.2552
1.00
1.01
2.00
1.01
6.05
1.02
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

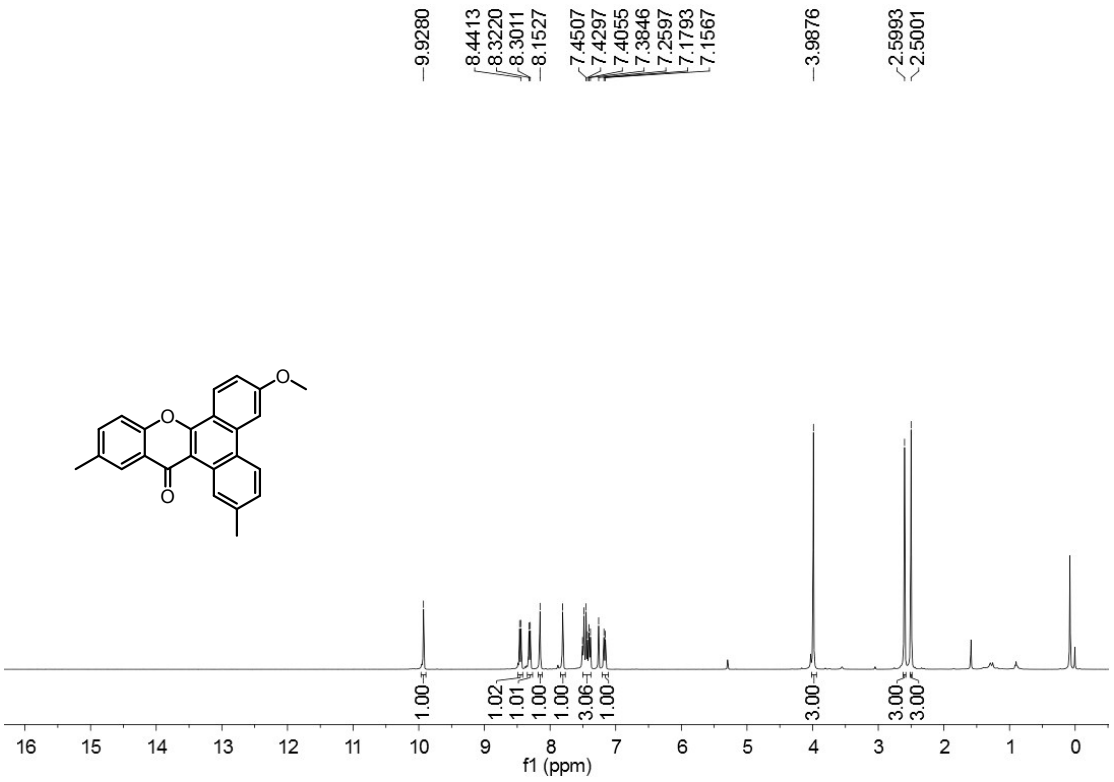

178.3335
155.2119
154.4175
133.9227
127.4982
126.6832
123.9896
122.3180
117.4981
112.6974
77.3320
77.2175
77.0142
76.6971
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

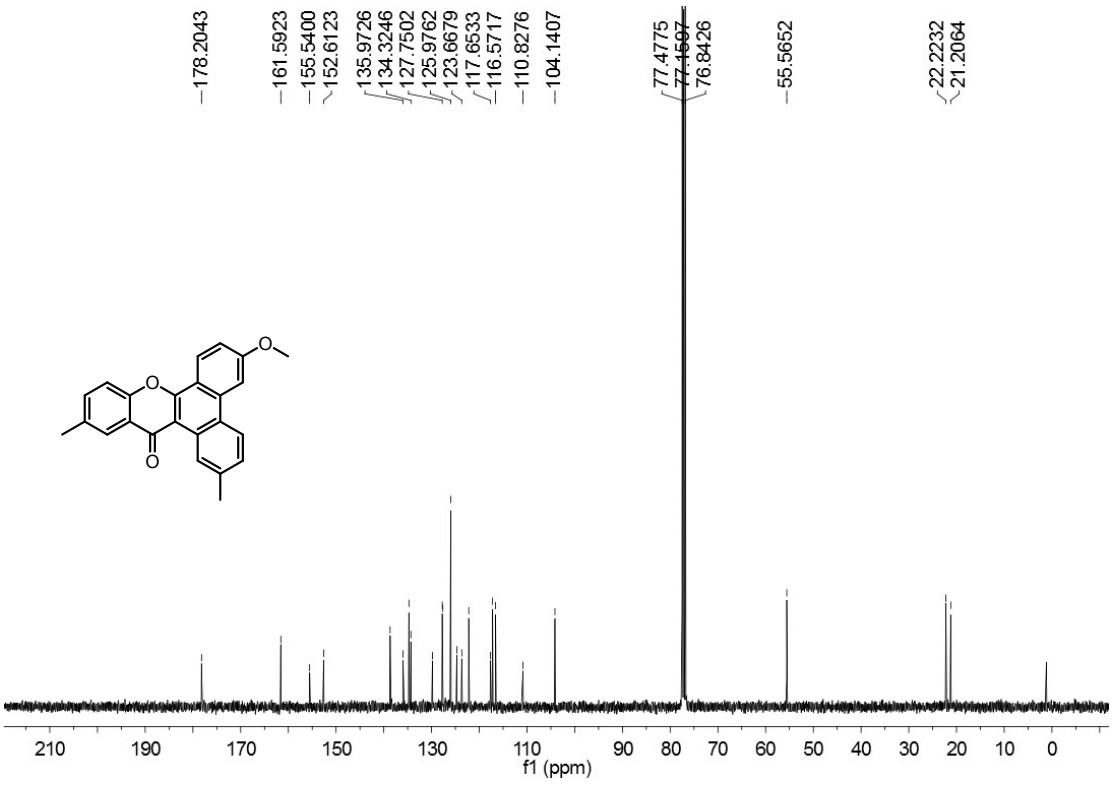
2b


10.1176
10.0967
8.4403
8.4178
8.4049
8.1412
7.8210
7.5608
7.4909
7.4697
7.4225
7.2601
7.1743
7.1517
3.9744
2.4885
1.00
2.06
0.98
1.03
1.12
1.08
1.10
0.99
0.98
3.01
3.01
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

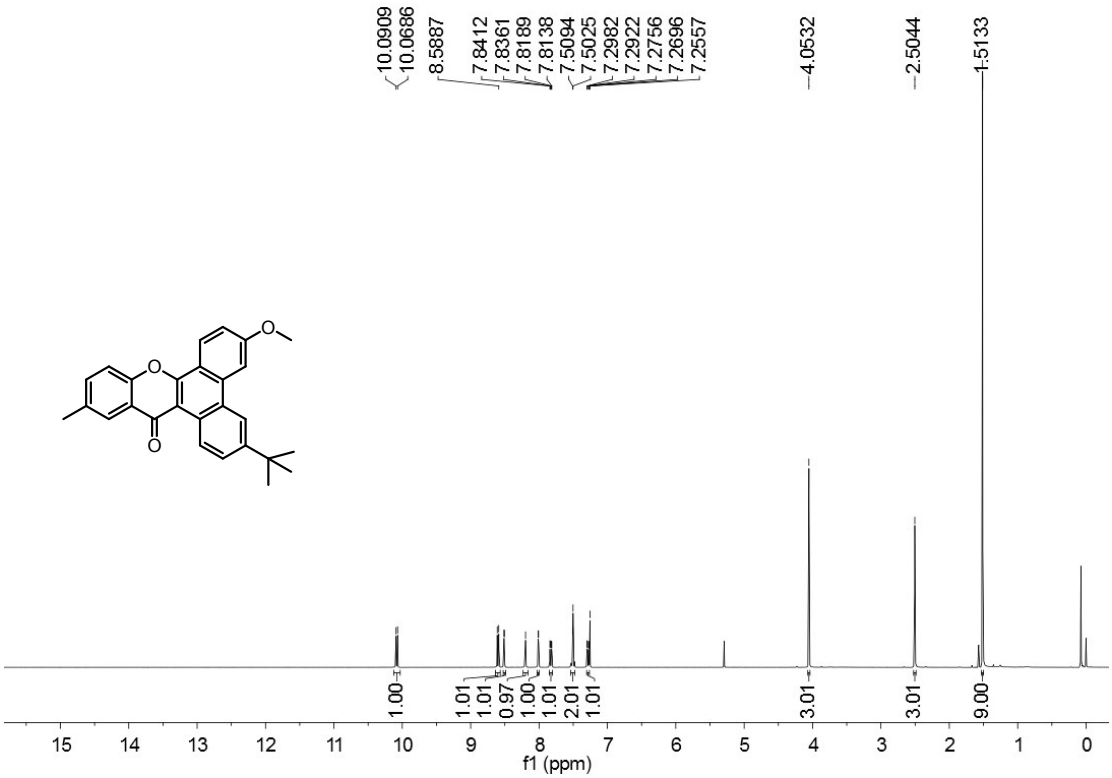

178.0996
161.5440
155.3280
152.5434
135.8075
134.7893
134.3557
126.8533
122.2676
116.9112
110.8923
104.3496
77.4771
77.1601
76.8421
55.5663
21.1782
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

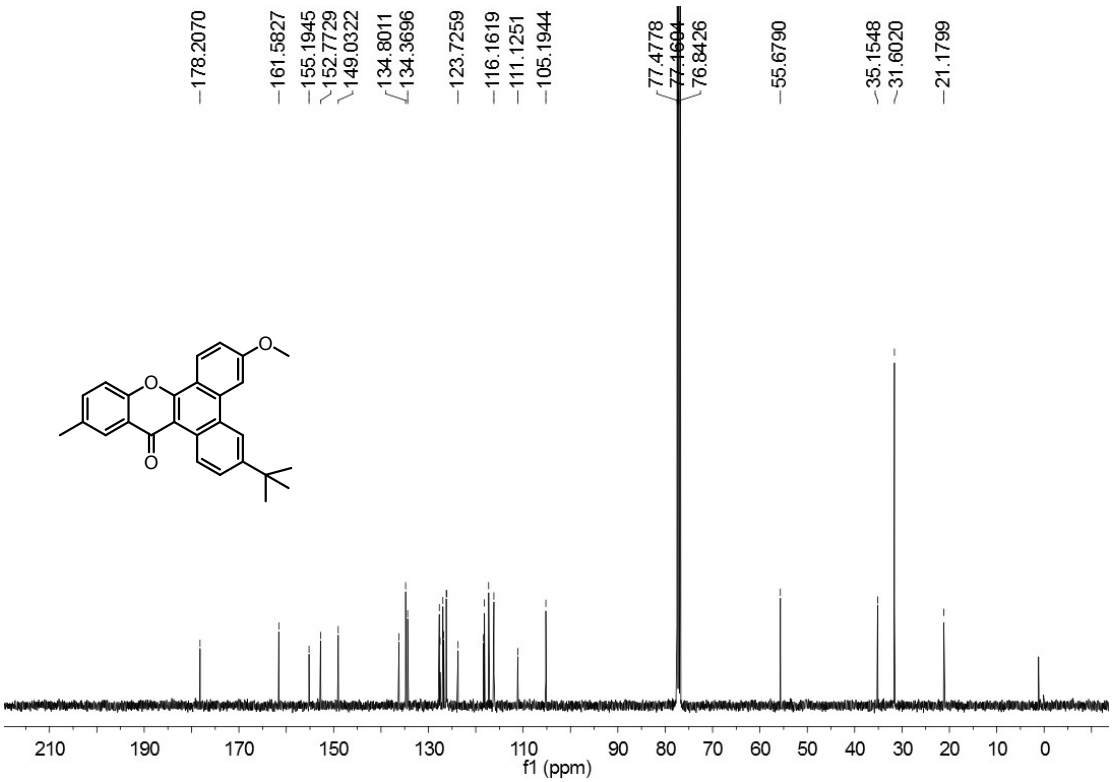
2c


9.9280
8.4413
8.3220
8.3011
8.1527
7.4507
7.4297
7.4055
7.3846
7.2597
7.1793
7.1567
3.9876
2.5993
2.5001
1.00
1.02
1.01
1.00
1.00
3.06
1.00
3.00
3.00
3.00
f1 (ppm)

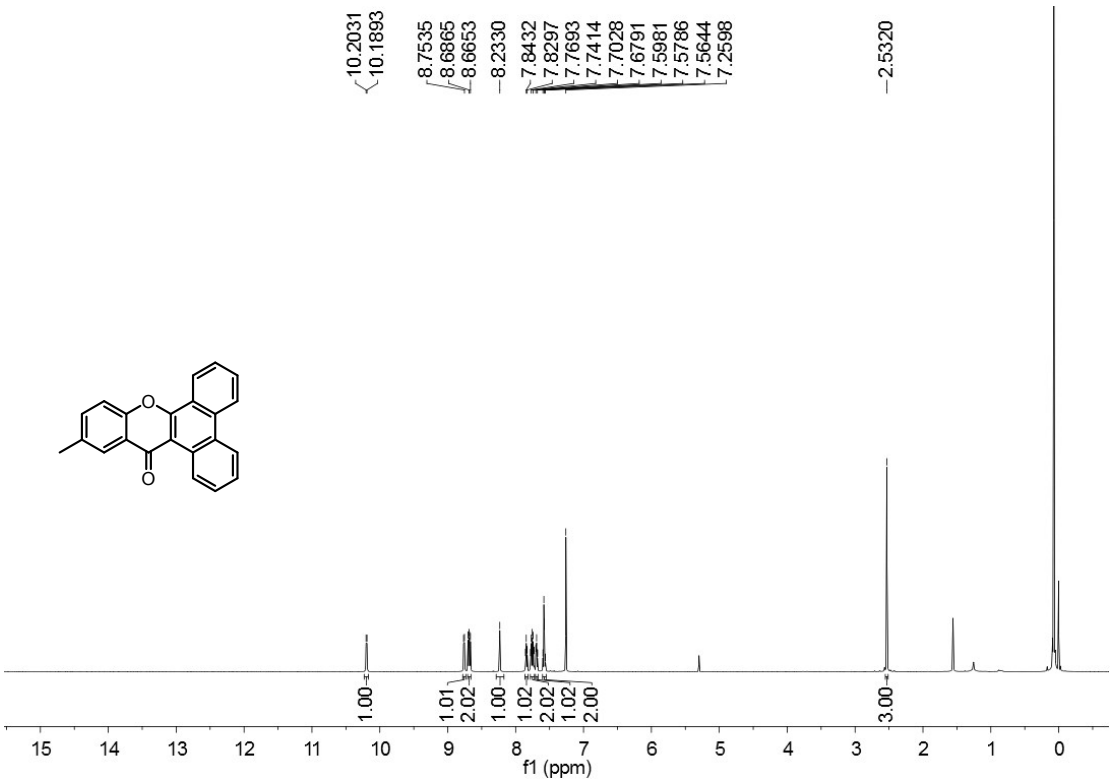

178.2043
161.5923
155.5400
152.6123
135.9726
134.3246
127.7502
125.9762
123.6679
117.6533
116.5717
110.8276
104.1407
77.4775
77.1597
76.8426
55.5652
22.2232
21.2064
f1 (ppm)

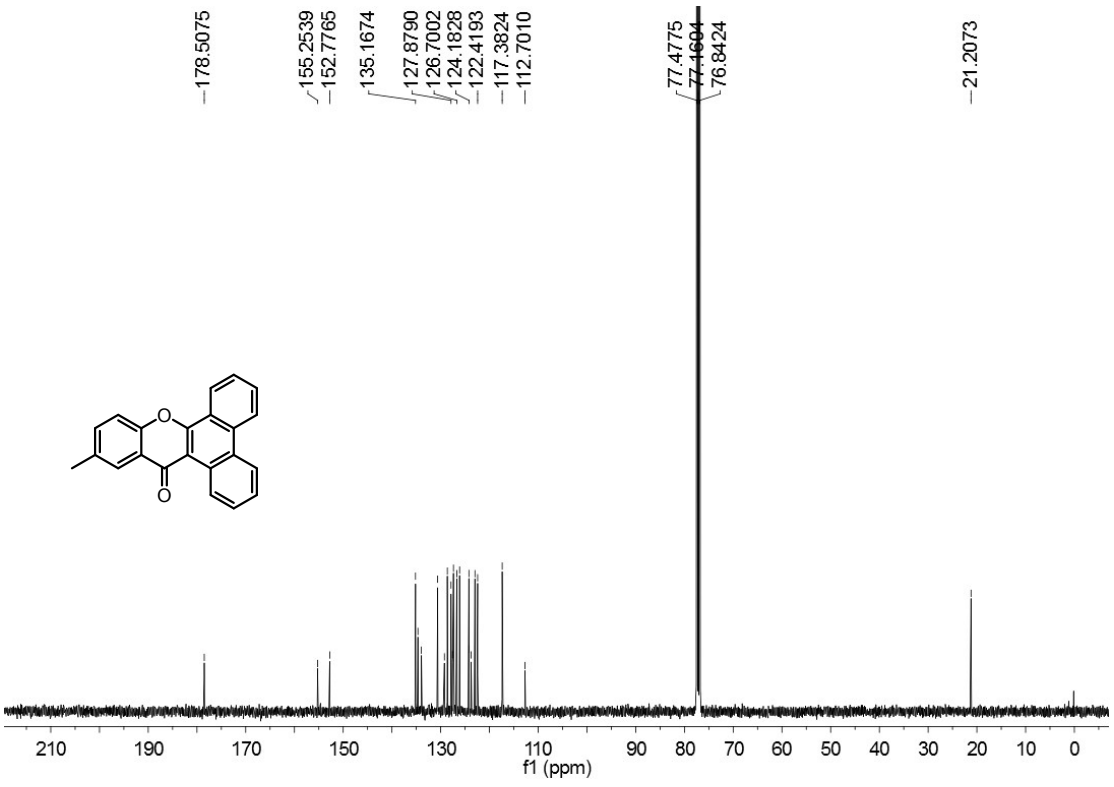
2d


10.0909
10.0686
8.5887
7.8412
7.8361
7.8189
7.8138
7.5094
7.5025
7.2982
7.2922
7.2756
7.2696
7.2557
4.0532
2.5044
1.5133
1.00
1.01
1.01
0.97
1.00
1.01
2.01
1.01
3.01
3.01
9.00
f1 (ppm)

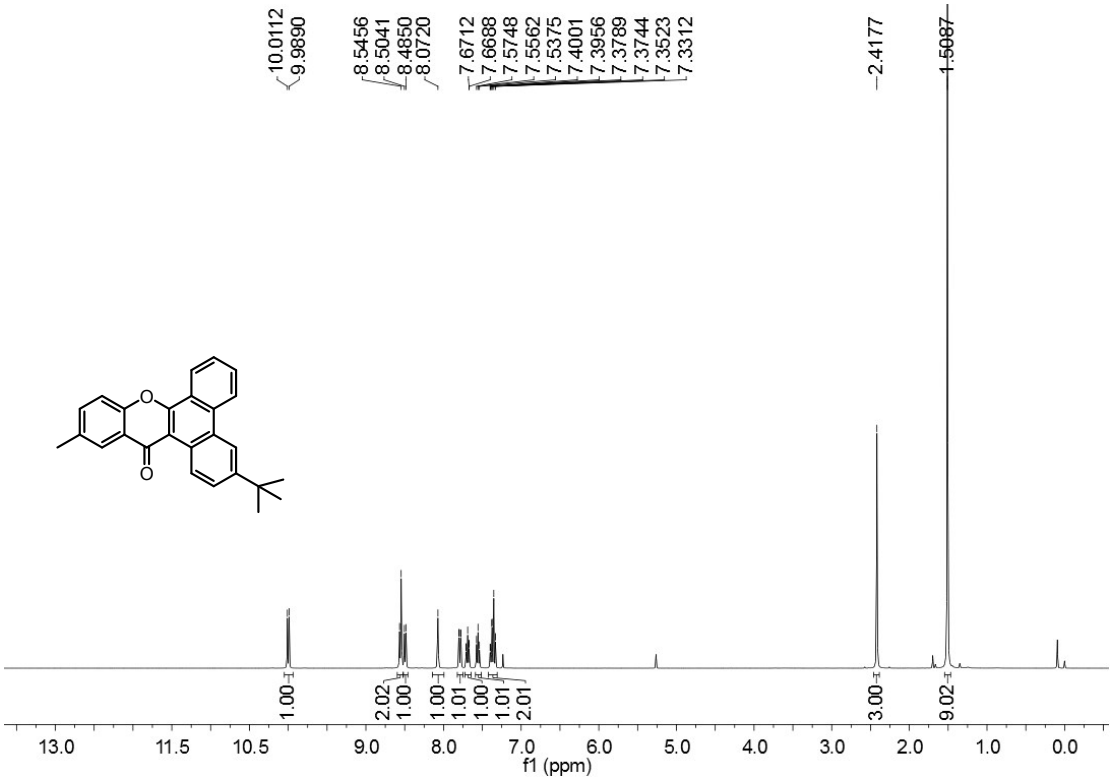

178.2070
161.5827
155.1945
152.7729
149.0322
134.8011
134.3696
123.7259
116.1619
111.1251
105.1944
77.4778
77.1604
76.8426
55.6790
35.1548
31.6020
21.1799
f1 (ppm)

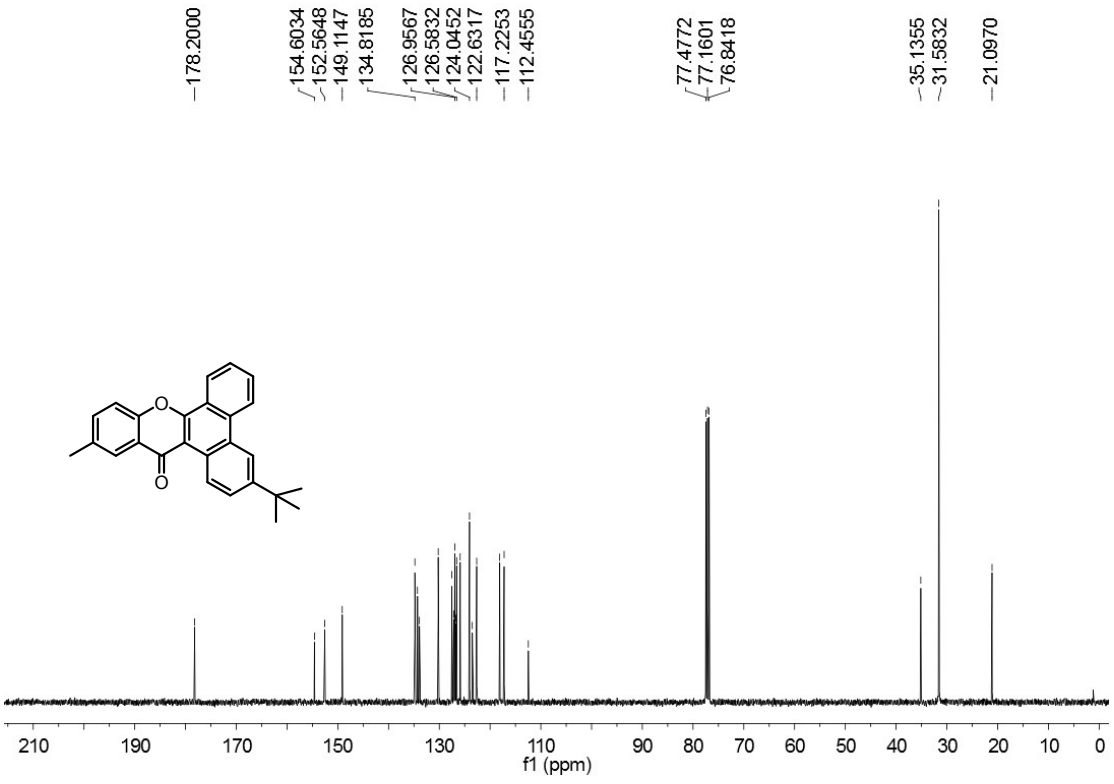
2e


10.2031
10.1893
8.7535
8.6865
8.6653
8.2330
7.8432
7.8297
7.7693
7.7414
7.7028
7.6791
7.5981
7.5786
7.5644
7.2598
2.5320
1.00
1.01
2.02
1.00
1.02
2.02
1.02
2.00
3.00
f1 (ppm)

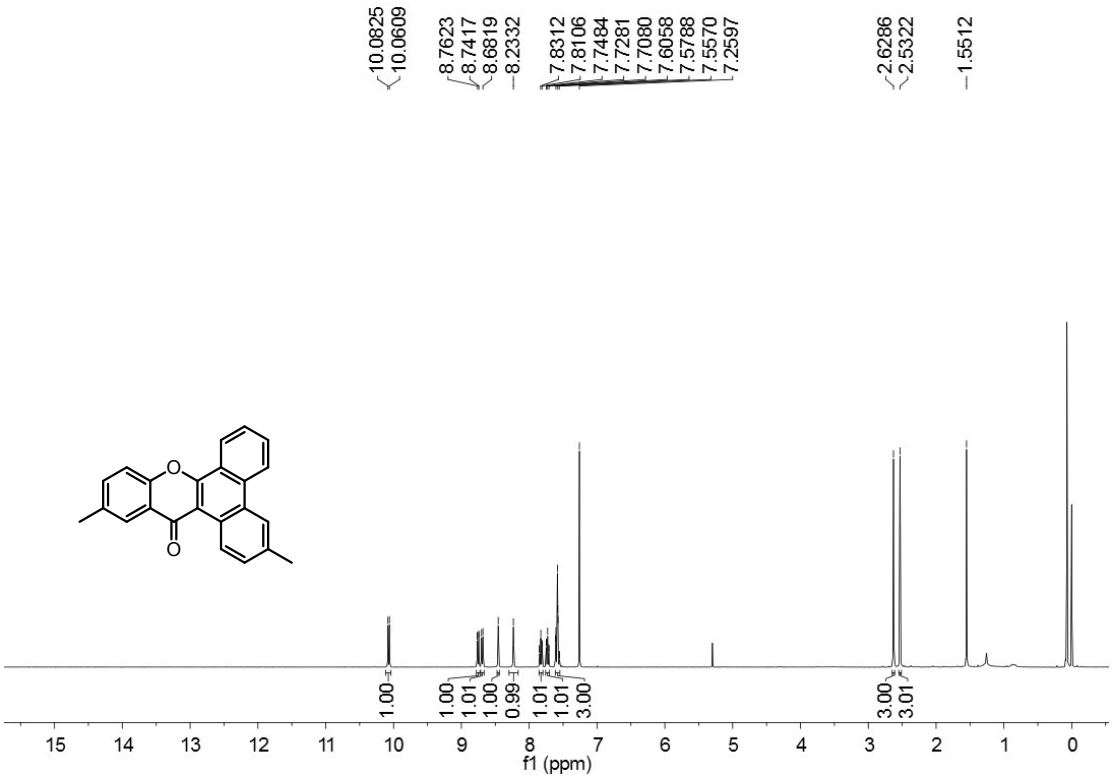

178.5075
155.2539
152.7765
135.1674
127.8790
126.7002
124.1828
122.4193
117.3824
112.7010
77.4775
77.1604
76.8424
21.2073
f1 (ppm)

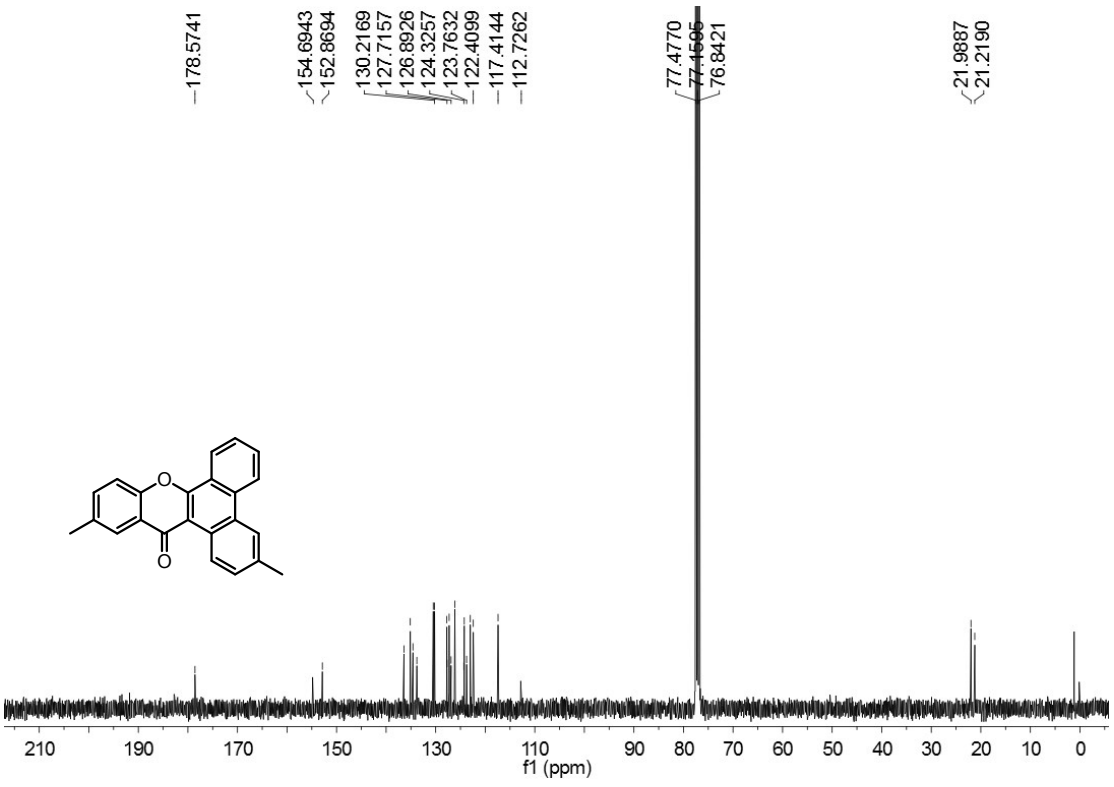
2f


10.0112
9.9890
8.5456
8.5041
8.4850
8.0720
7.6712
7.6688
7.5748
7.5562
7.5375
7.4001
7.3956
7.3789
7.3744
7.3523
7.3312
2.4177
1.5087
1.00
2.02
1.00
1.00
1.01
1.00
1.01
2.01
3.00
9.02
13.0
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

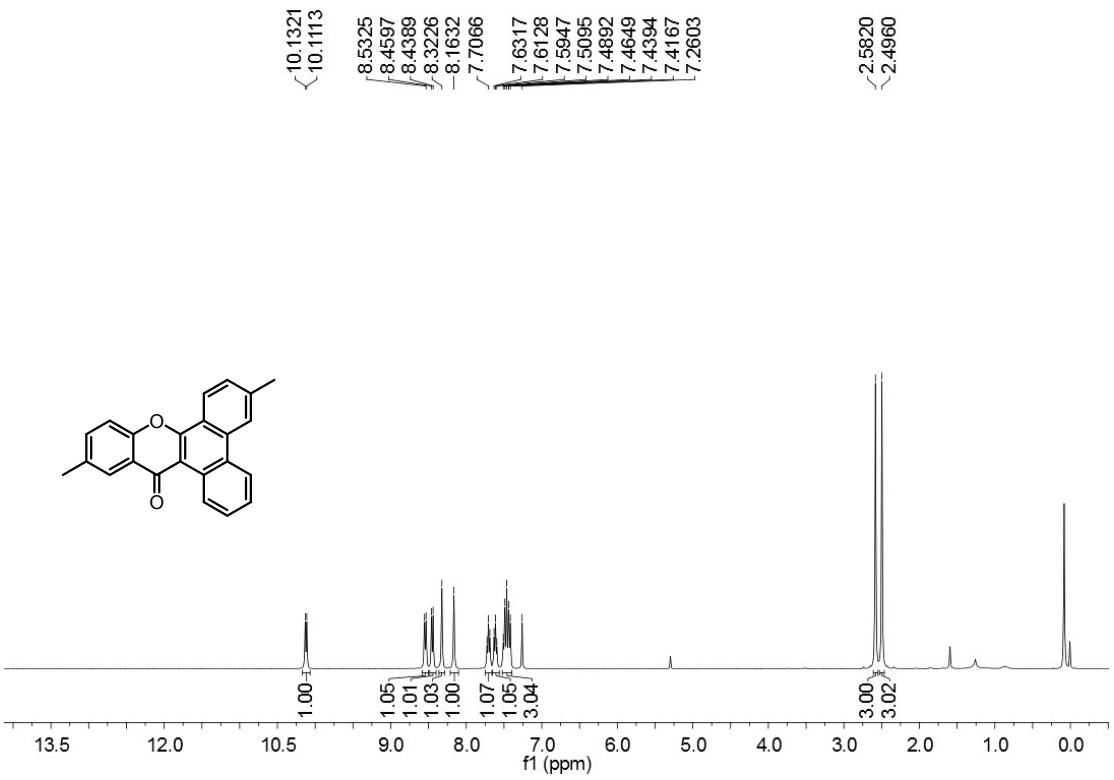

178.2000
154.6034
152.5648
149.1147
134.8185
126.9567
126.5832
124.0452
122.6317
117.2253
112.4555
77.4772
77.1601
76.8418
35.1355
31.5832
21.0970
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

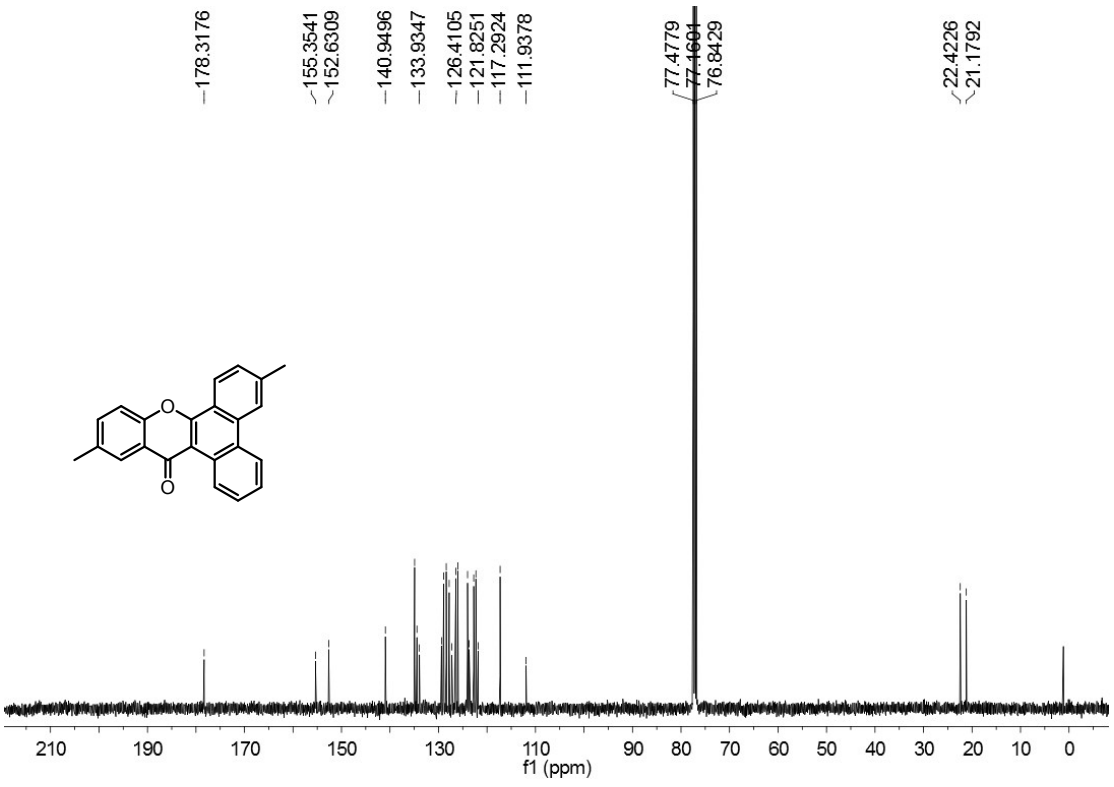
2g


10.0825
10.0609
8.7623
8.7417
8.6819
8.2332
7.8312
7.8106
7.7484
7.7281
7.7080
7.6058
7.5788
7.5570
7.2597
2.6286
2.5322
1.5512
1.00
1.00
1.01
1.00
0.99
1.01
1.01
3.00
3.00
3.01
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

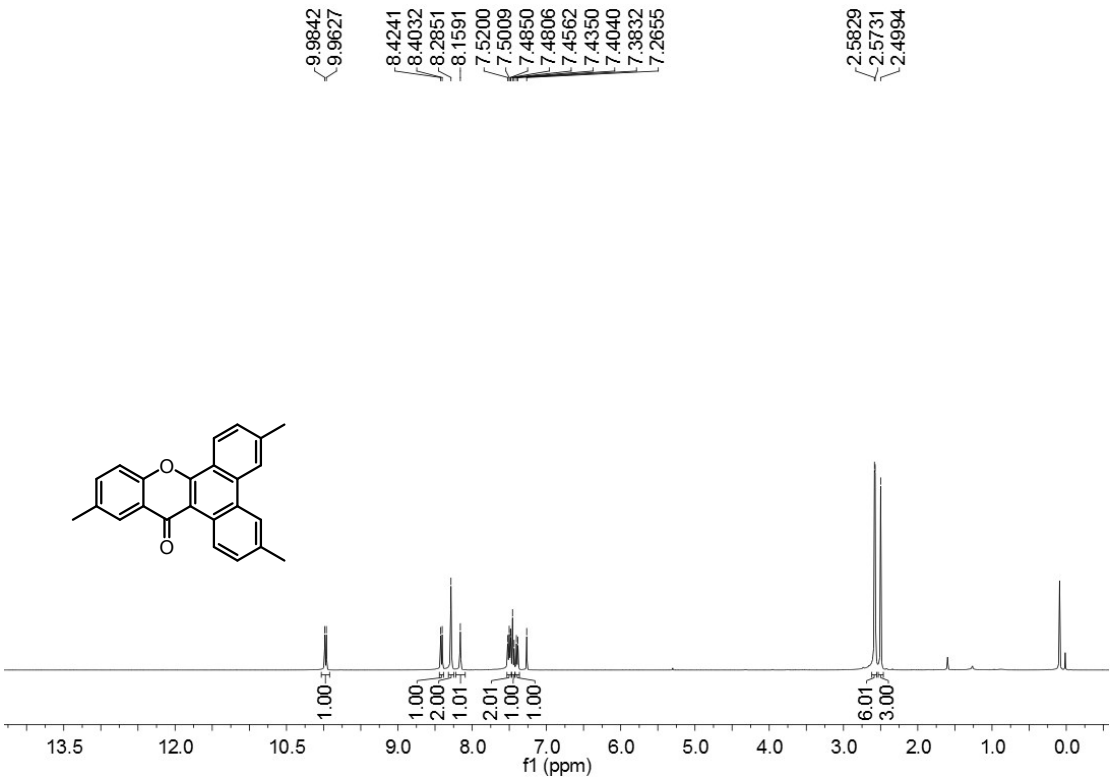

178.5741
154.6943
152.8694
130.2169
127.7157
126.8926
124.3257
123.7632
122.4099
117.4144
112.7262
77.4770
77.1566
76.8421
21.9887
21.2190
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

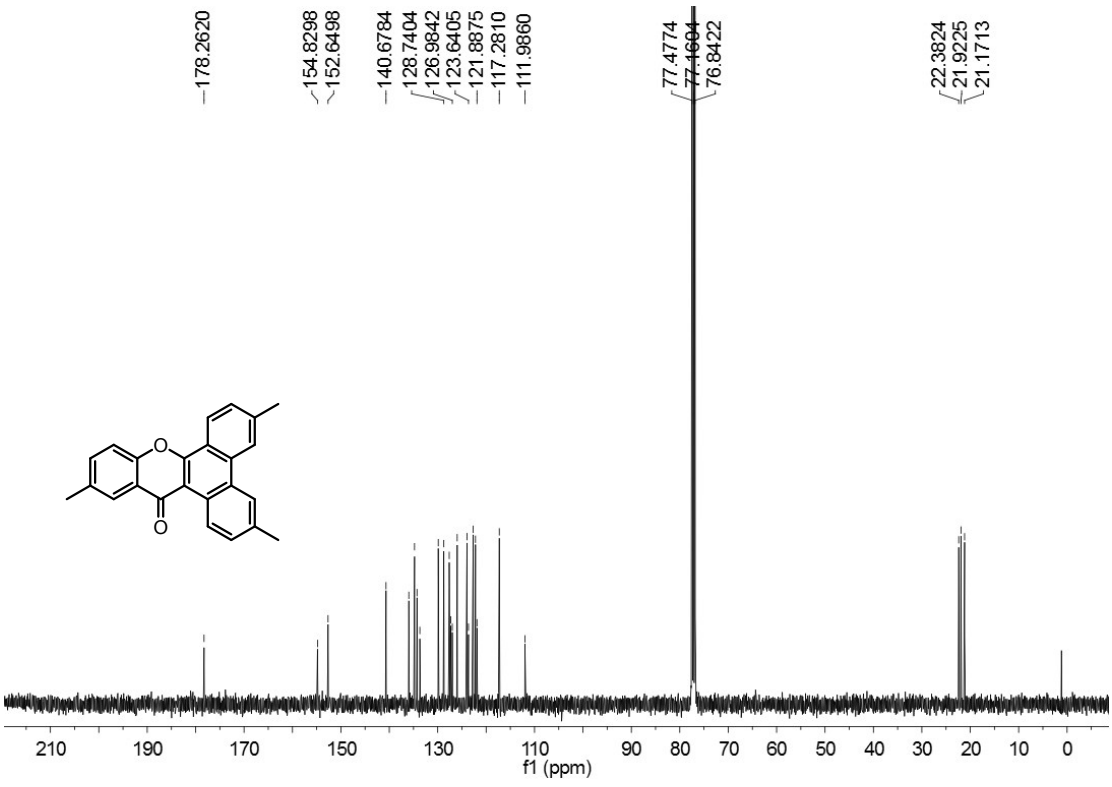
2h


10.1321
10.1113
8.5325
8.4597
8.4389
8.3226
8.1632
7.7066
7.6317
7.6128
7.5947
7.5095
7.4892
7.4649
7.4394
7.4167
7.2603
2.5820
2.4960
1.00
1.05
1.01
1.03
1.00
1.07
1.05
3.04
3.00
3.02
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


178.3176
155.3541
152.6309
140.9496
133.9347
126.4105
121.8251
117.2924
111.9378
77.4779
77.4601
76.8429
22.4226
21.1792
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2i


9.9842
9.9627
8.4241
8.4032
8.2851
8.1591
7.5200
7.5009
7.4850
7.4806
7.4562
7.4350
7.4040
7.3832
7.2655
2.5829
2.5731
2.4994
1.00
1.00
2.00
1.01
2.01
1.00
1.00
6.01
3.00
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


178.2620
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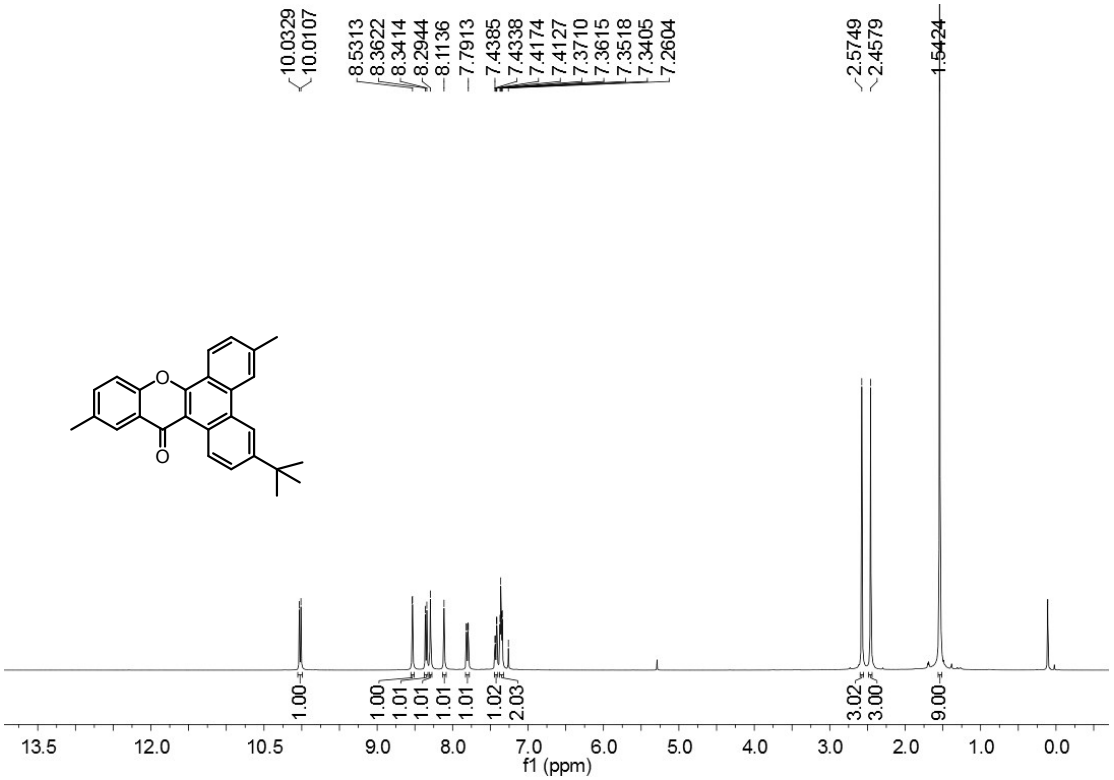
152.6498
140.6784
128.7404
126.9842
123.6405
121.8875
117.2810
111.9860
77.4774
77.1604
76.8422
22.3824
21.9225
21.1713
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2j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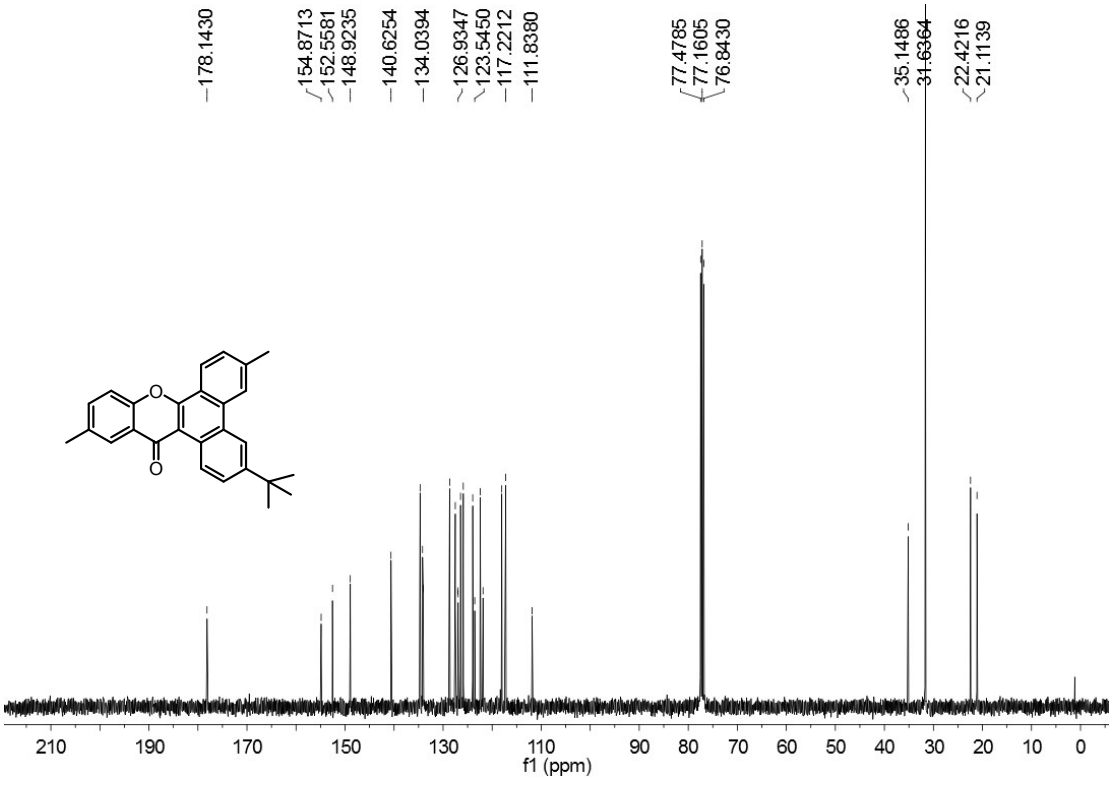
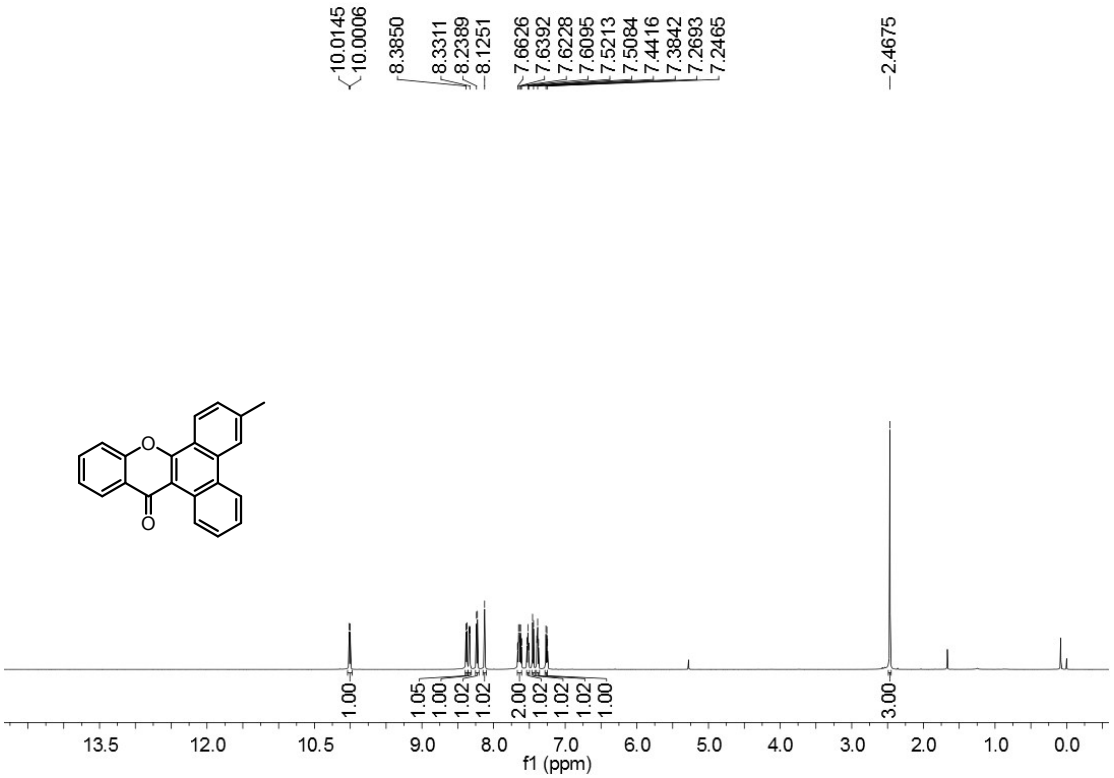
8.5313
8.3622
8.3414
8.2944
8.1136
7.7913
7.4385
7.4338
7.4174
7.4127
7.3710
7.3615
7.3518
7.3405
7.2604
2.5749
2.4579
1.5424
1.00
1.00
1.01
1.01
1.01
1.01
1.02
2.03
3.02
3.00
9.00
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


178.1430
154.8713
152.5581
148.9235
140.6254
134.0394
126.9347
123.5450
117.2212
111.8380
77.4785
77.1605
76.8430
35.1486
31.6364
22.4216
21.1139
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2k


10.0145
10.0006
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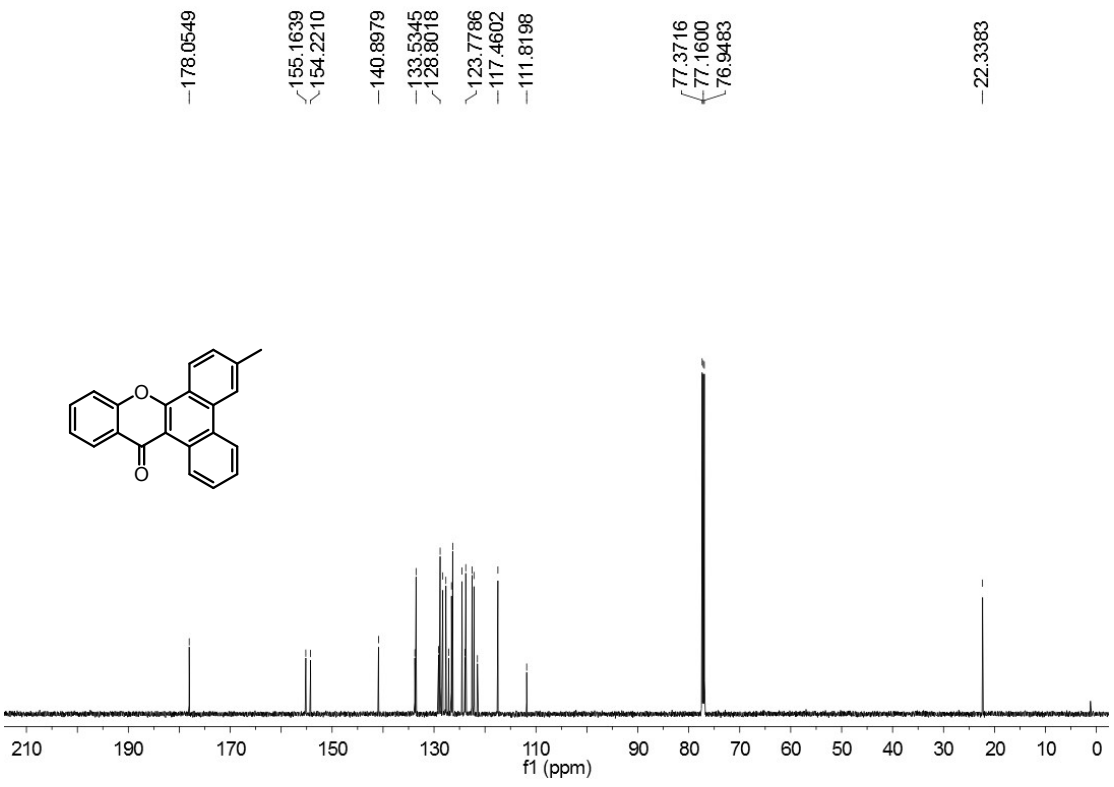
8.2389
8.1251
7.6626
7.6392
7.6228
7.6095
7.5213
7.5084
7.4416
7.3842
7.2693
7.2465
2.4675
1.00
1.05
1.00
1.02
1.02
2.00
1.02
1.02
1.02
1.00
3.00
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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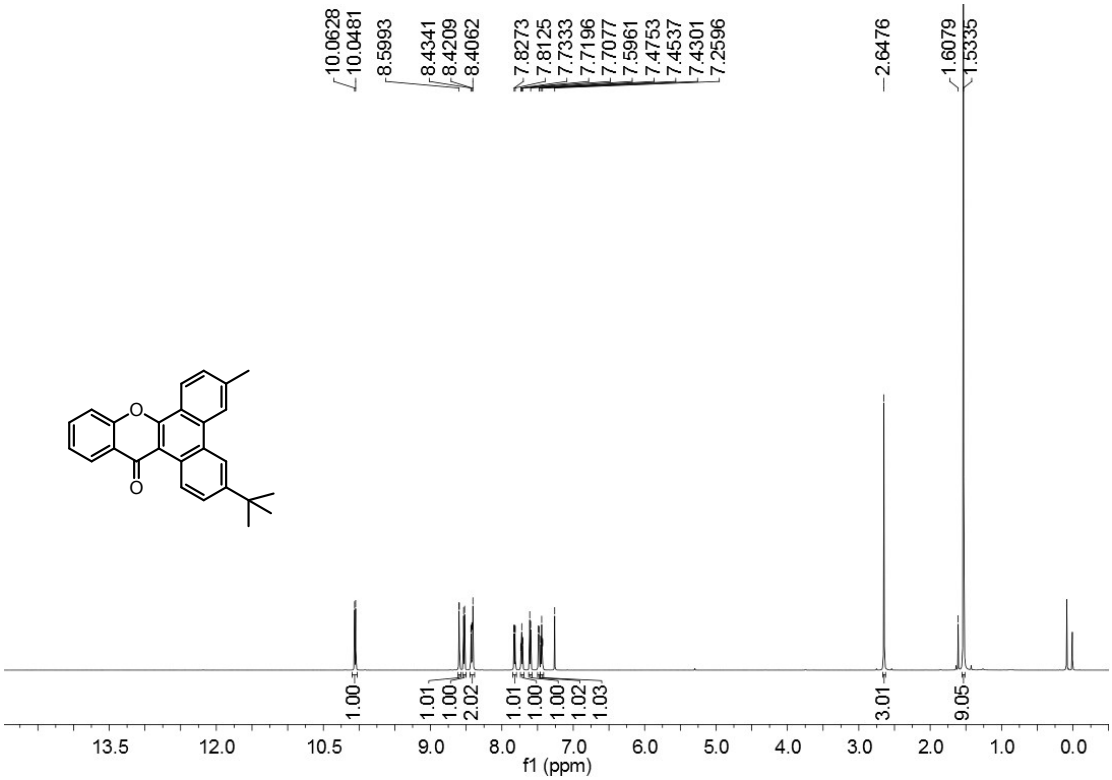
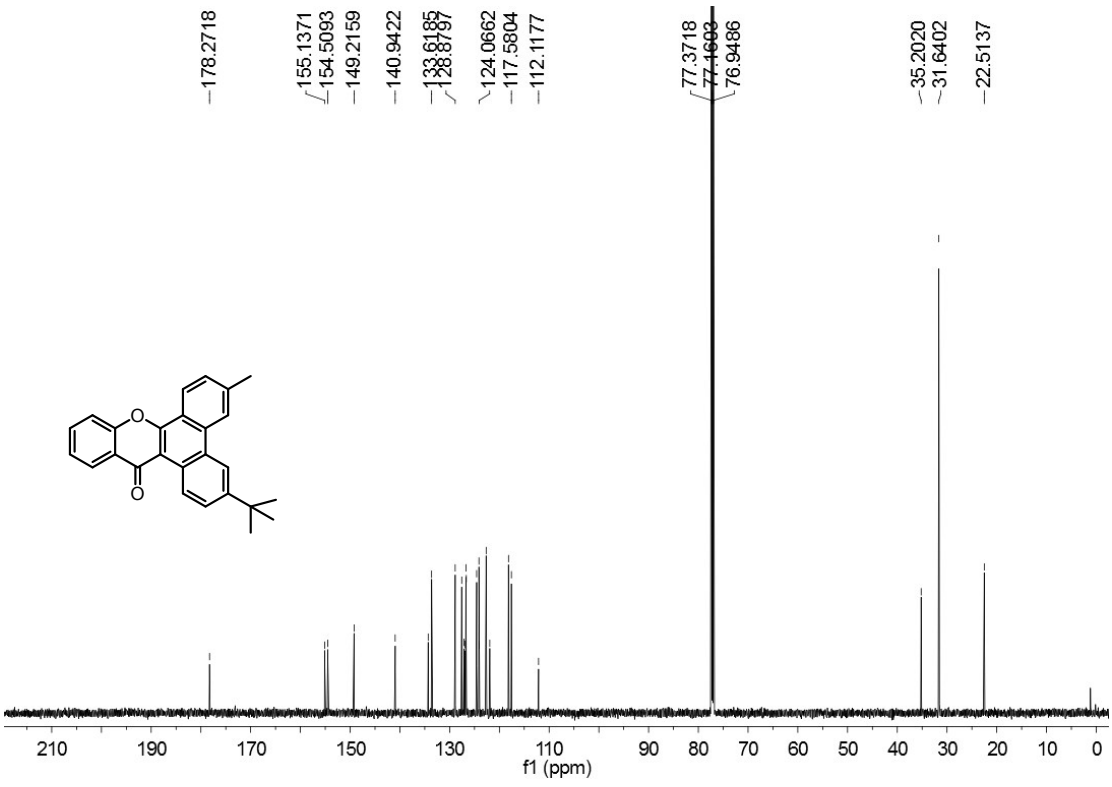
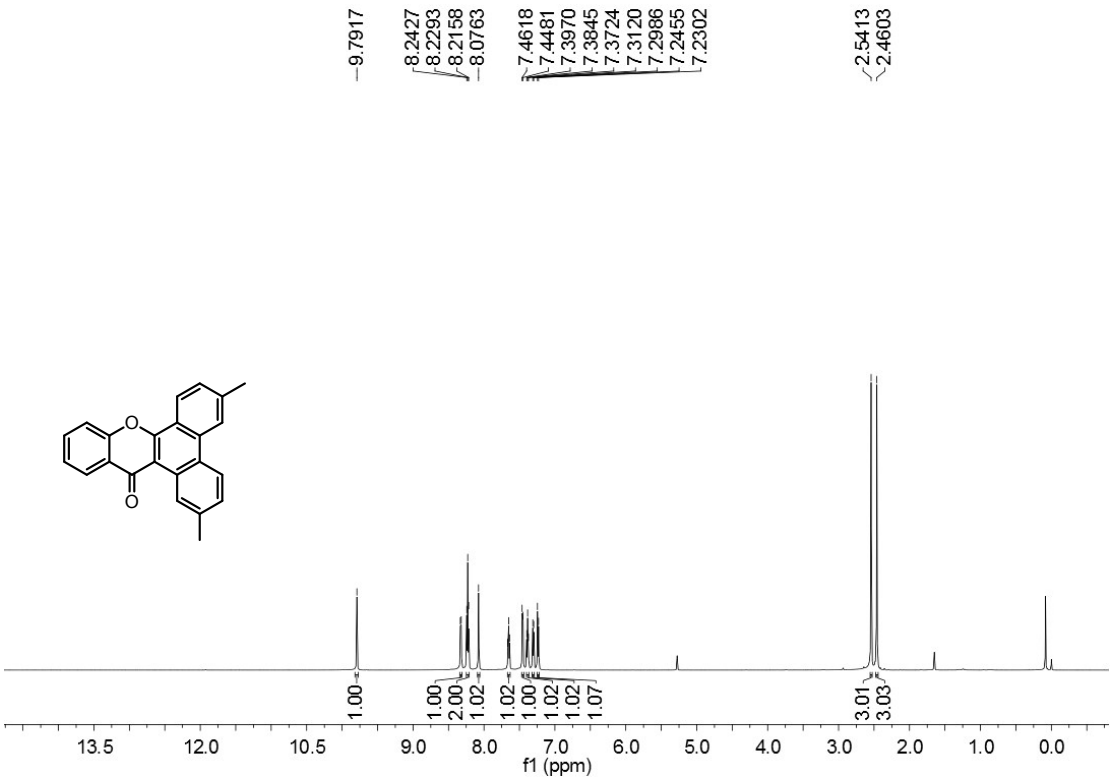
154.2210
140.8979
133.5345
128.8018
123.7786
117.4602
111.8198
77.3716
77.1600
76.9483
22.3383
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2l


10.0628
10.0481
8.5993
8.4341
8.4209
8.4062
7.8273
7.8125
7.7333
7.7196
7.7077
7.5961
7.4753
7.4537
7.4301
7.2596
2.6476
1.6079
1.5335
1.00
1.01
1.00
2.02
1.01
1.00
1.00
1.02
1.03
3.01
9.05
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


178.2718
155.1371
154.5093
149.2159
140.9422
133.6185
128.8797
124.0662
117.5804
112.1177
77.3718
77.1603
76.9486
35.2020
31.6402
22.5137
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2m


9.7917
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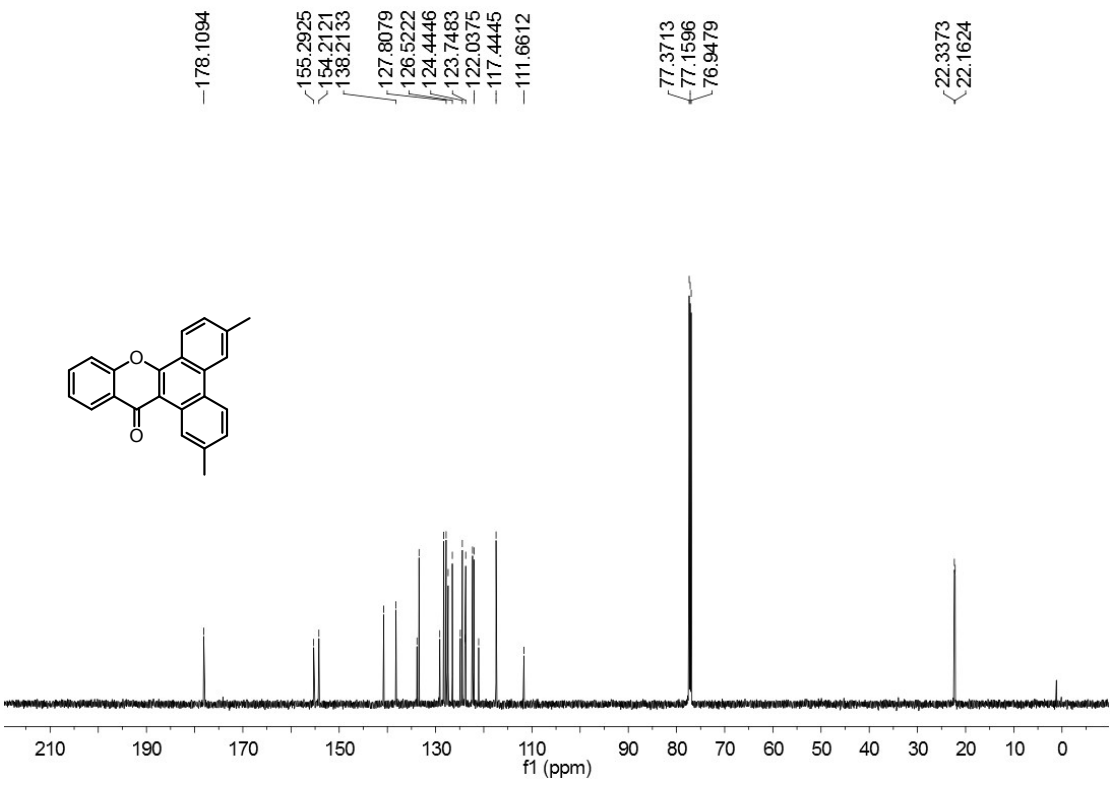
8.2293
8.2158
8.0763
7.4618
7.4481
7.3970
7.3845
7.3724
7.3120
7.2986
7.2455
7.2302
2.5413
2.4603
1.00
1.00
2.00
1.02
1.02
1.00
1.02
1.02
1.07
3.01
3.03
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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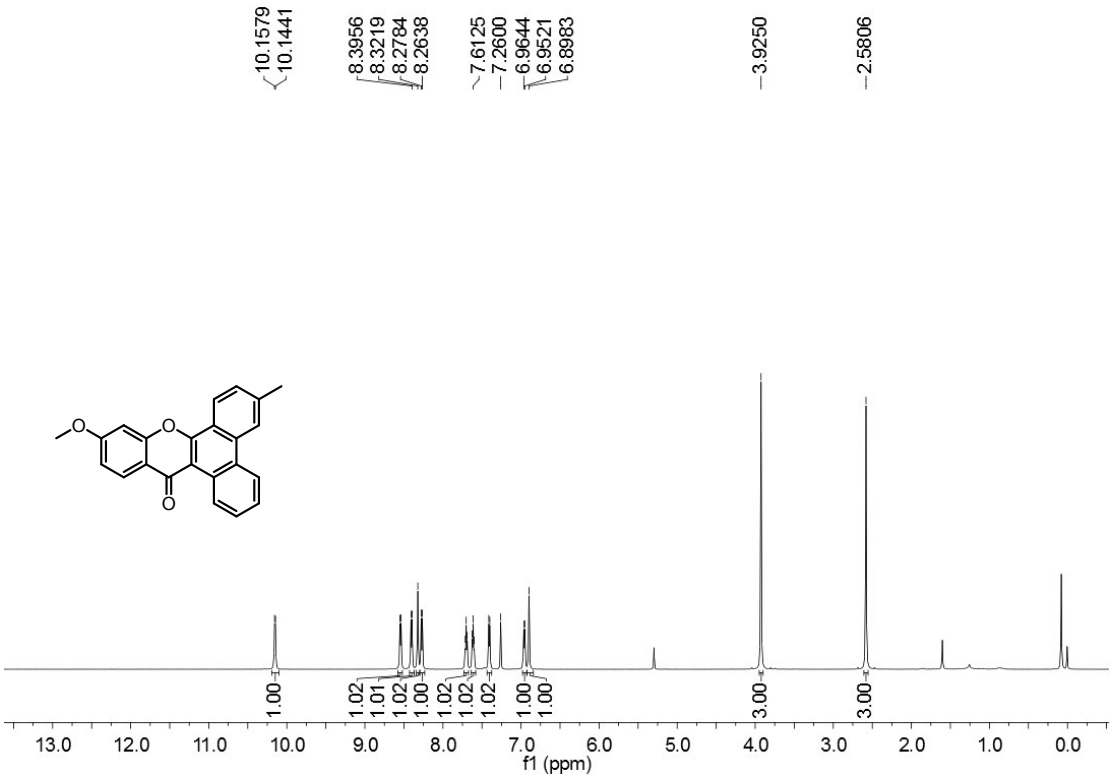
155.2925
154.2121
138.2133
127.8079
126.5222
124.4446
123.7483
122.0375
117.4445
111.6612
77.3713
77.1596
76.9479
22.3373
22.1624
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2n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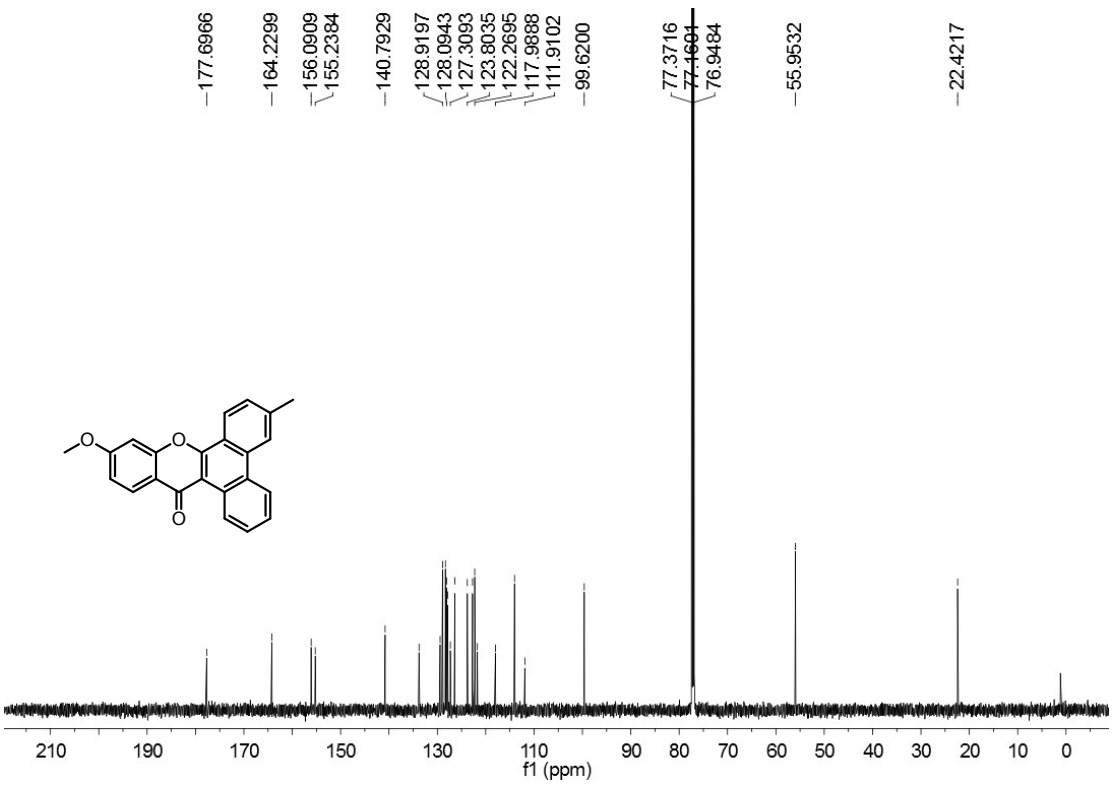
10.1441
8.3956
8.3219
8.2784
8.2638
7.6125
7.2600
6.9644
6.9521
6.8983
3.9250
2.5806
1.00
1.02
1.01
1.02
1.00
1.02
1.02
1.02
1.00
1.00
3.00
3.00
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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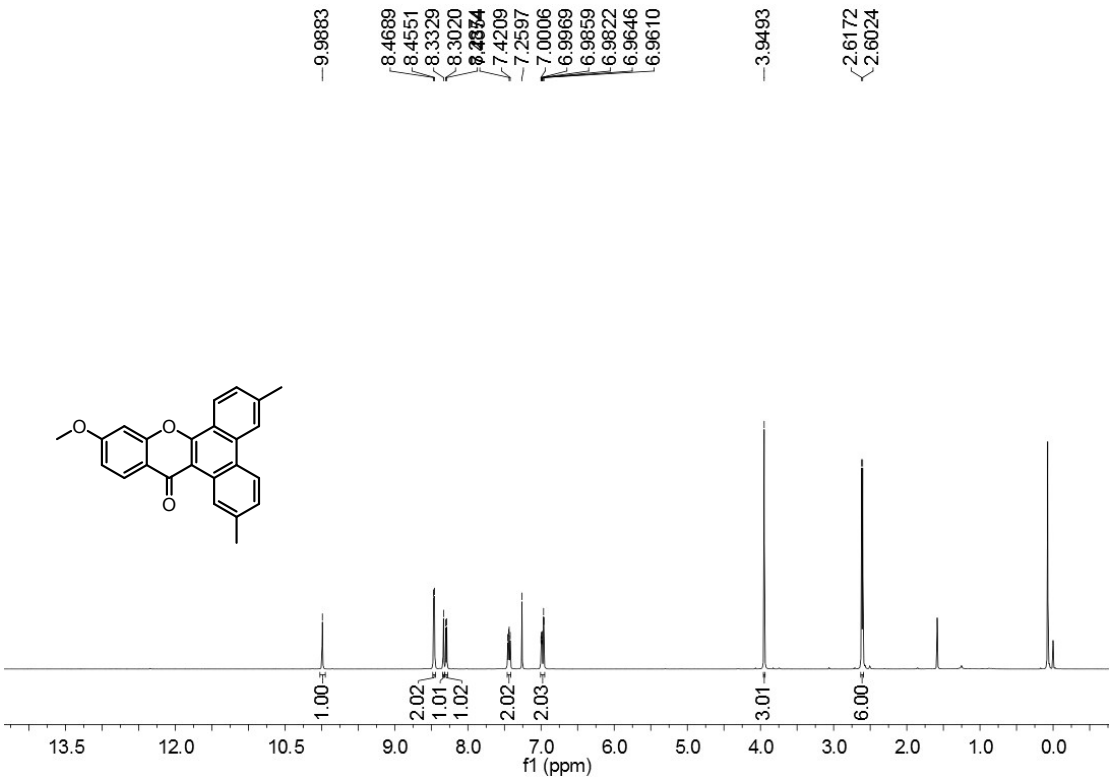
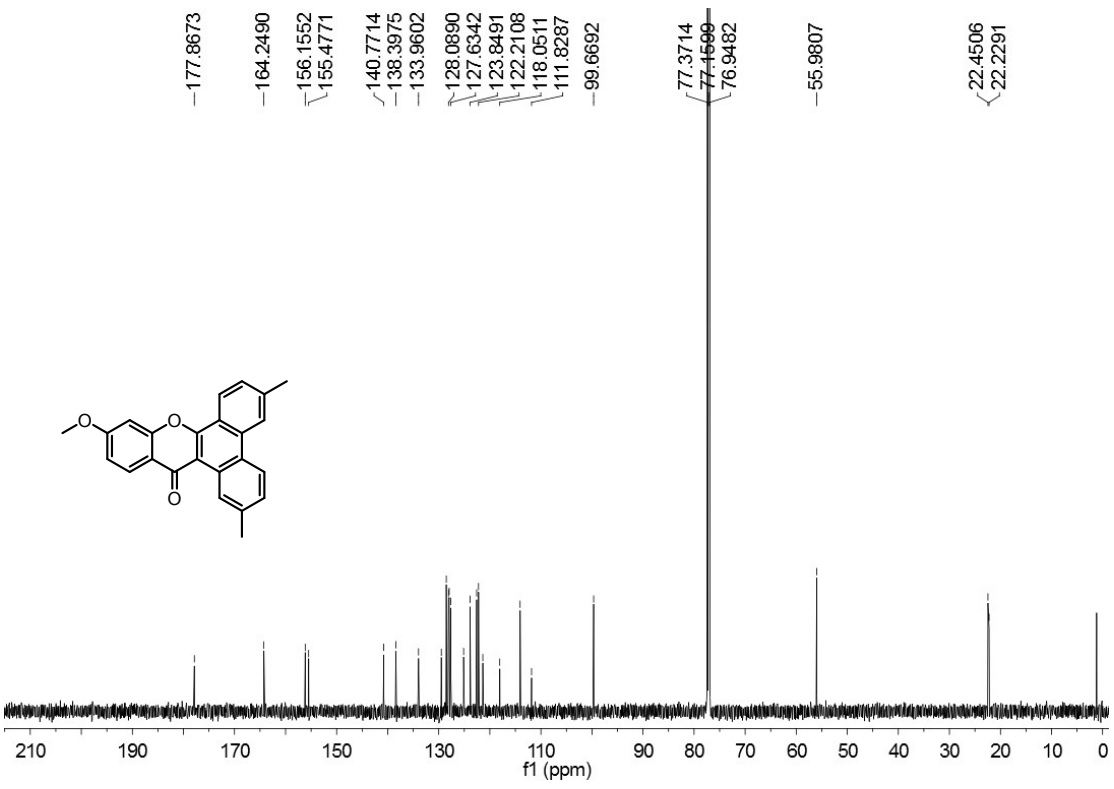
156.0909
155.2384
140.7929
128.9197
128.0943
127.3093
123.8035
122.2695
117.9888
111.9102
99.6200
77.3716
77.1601
76.9484
55.9532
22.4217
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2o


9.9883
8.4689
8.4551
8.3329
8.3020
7.4209
7.2597
7.0006
6.9969
6.9859
6.9822
6.9646
6.9610
3.9493
2.6172
2.6024
1.00
2.02
1.01
1.02
2.02
2.03
3.01
6.00
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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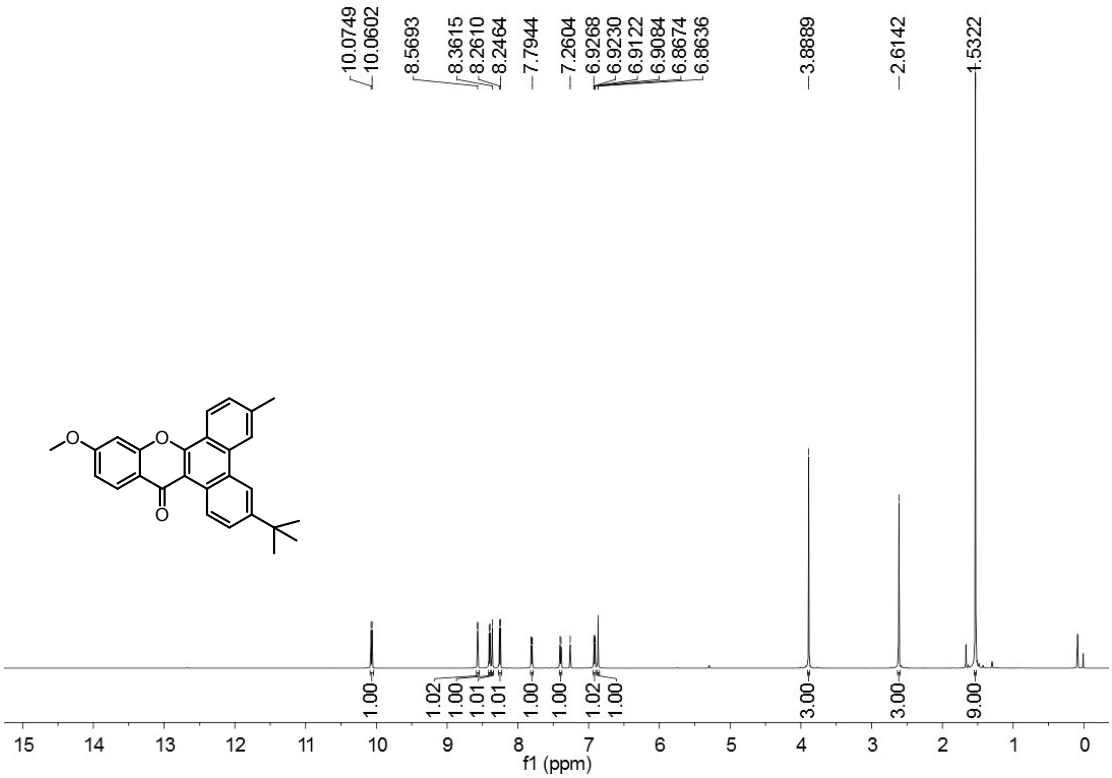
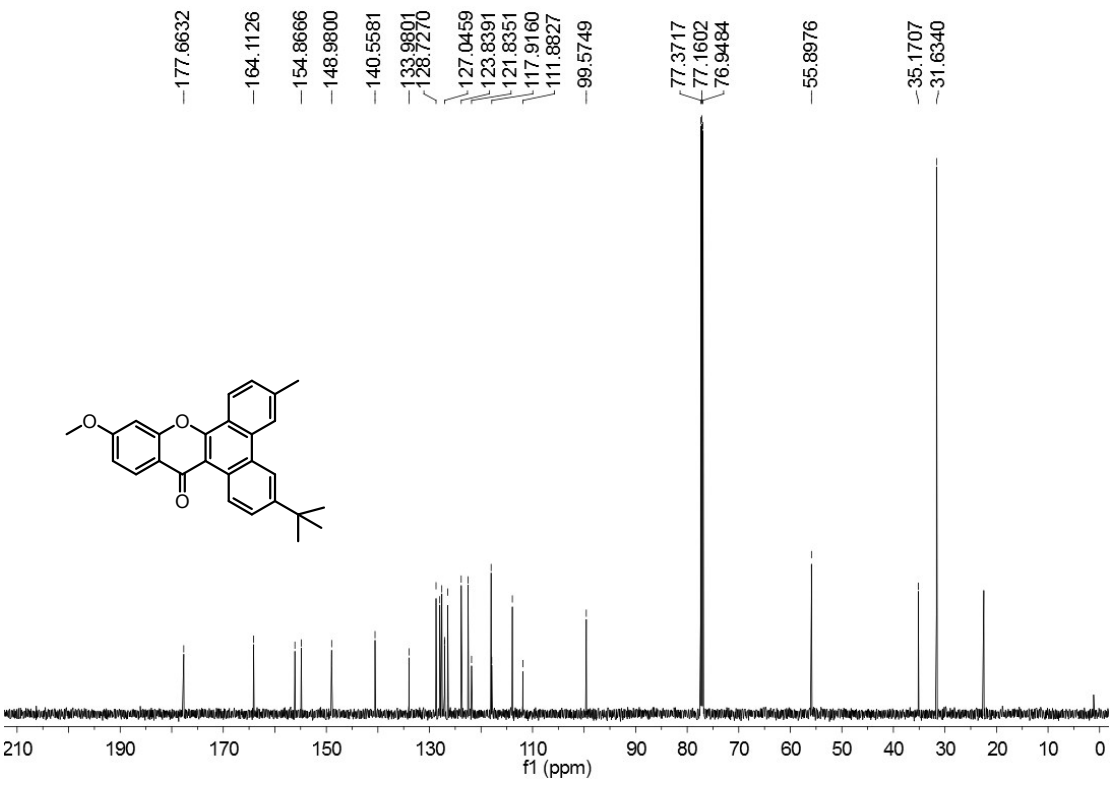
156.1552
155.4771
140.7714
138.3975
133.9602
128.0890
127.6342
123.8491
122.2108
118.0511
111.8287
99.6692
77.3714
77.1590
76.9482
55.9807
22.4506
22.2291
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2p


10.0749
10.0602
8.5693
8.3615
8.2610
8.2464
7.7944
7.2604
6.9268
6.9230
6.9122
6.9084
6.8674
6.8636
3.8889
2.6142
1.5322
1.00
1.02
1.00
1.01
1.01
1.00
1.00
1.02
1.00
3.00
3.00
9.00
f1 (ppm)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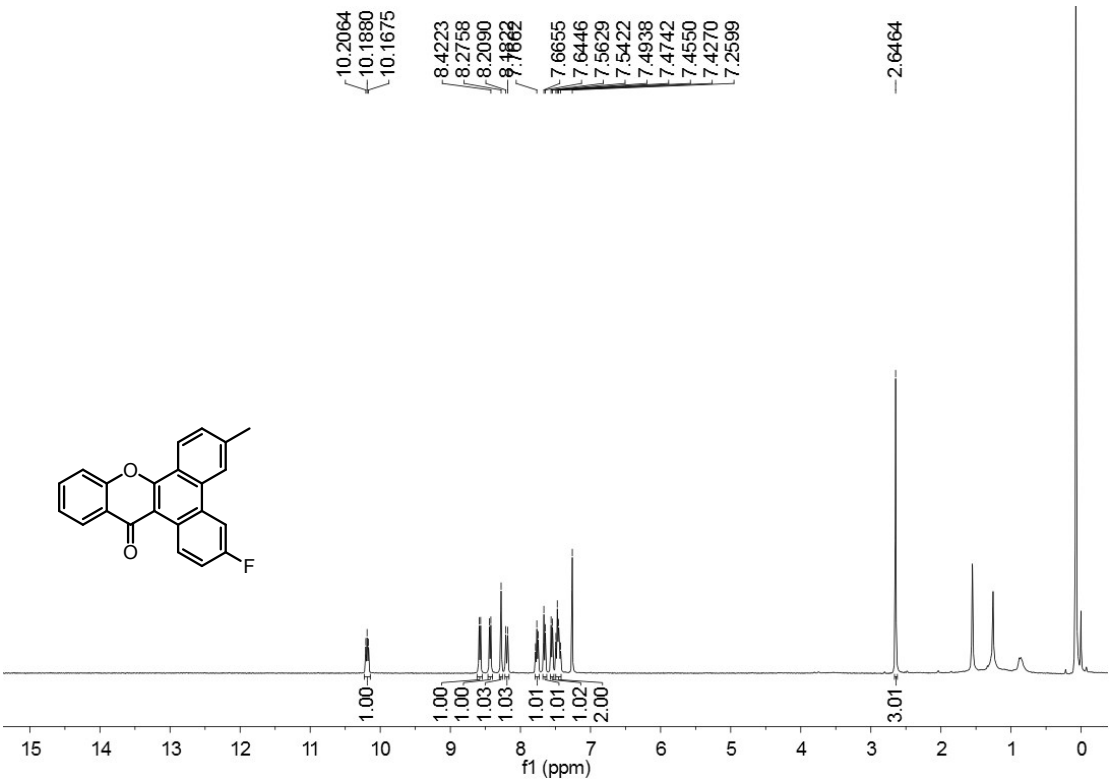
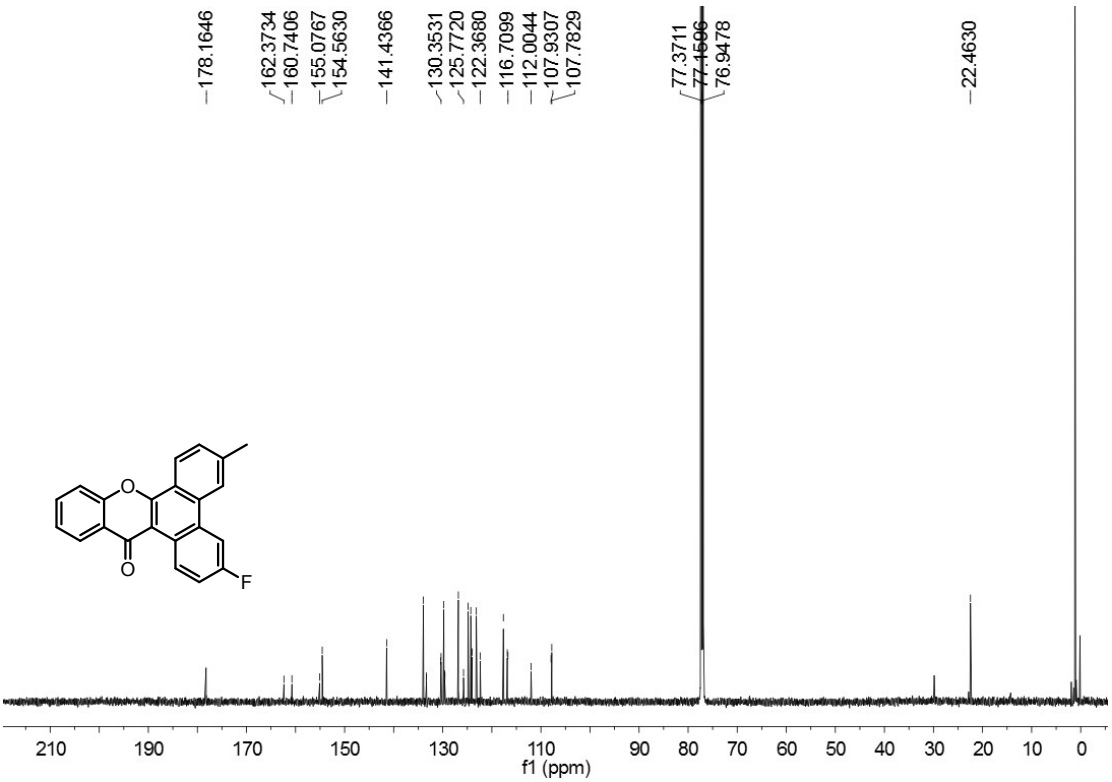
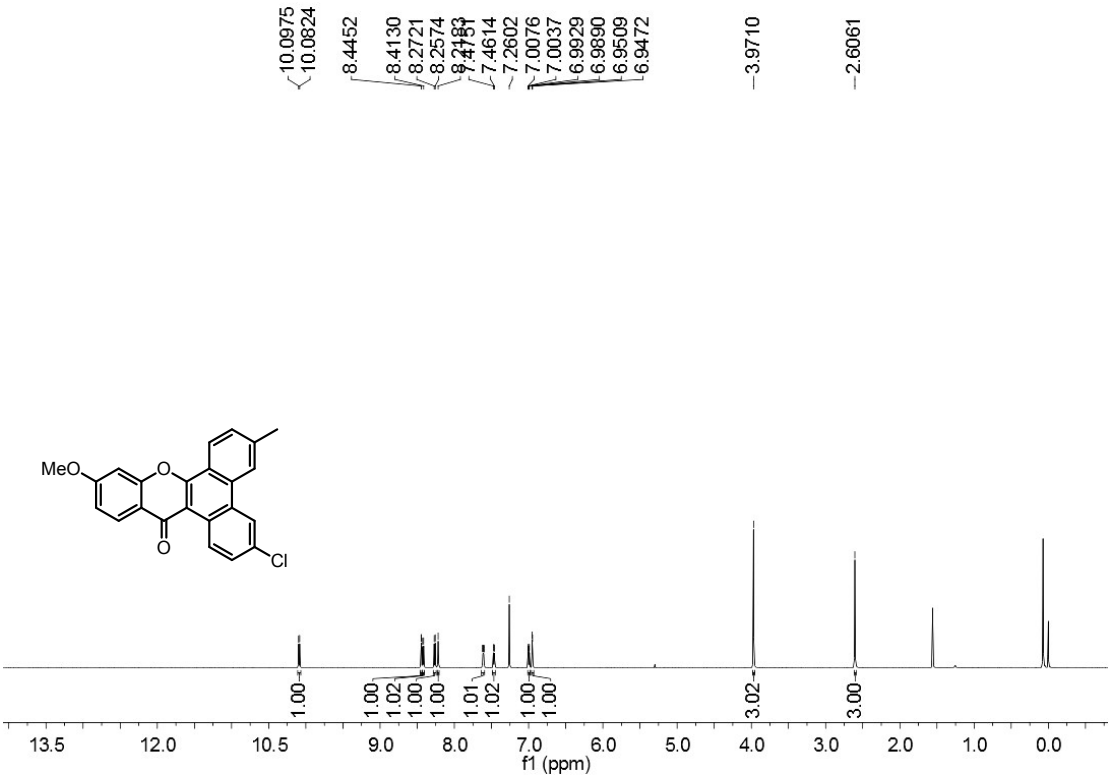
164.1126
154.8666
148.9800
140.5581
133.9801
128.7270
127.0459
123.8391
121.8351
117.9160
111.8827
99.5749
77.3717
77.1602
76.9484
55.8976
35.1707
31.6340
f1 (ppm)

2q


10.2064
10.1880
10.1675
8.4223
8.2758
8.2090
7.6655
7.6446
7.5629
7.5422
7.4938
7.4742
7.4550
7.4270
7.2599
2.6464
1.00
1.00
1.00
1.03
1.03
1.01
1.01
1.02
2.00
3.01
f1 (ppm)


178.1646
162.3734
160.7406
155.0767
154.5630
141.4366
130.3531
125.7720
122.3680
116.7099
112.0044
107.9307
107.7829
77.3711
77.1596
76.9478
22.4630
f1 (ppm)

2r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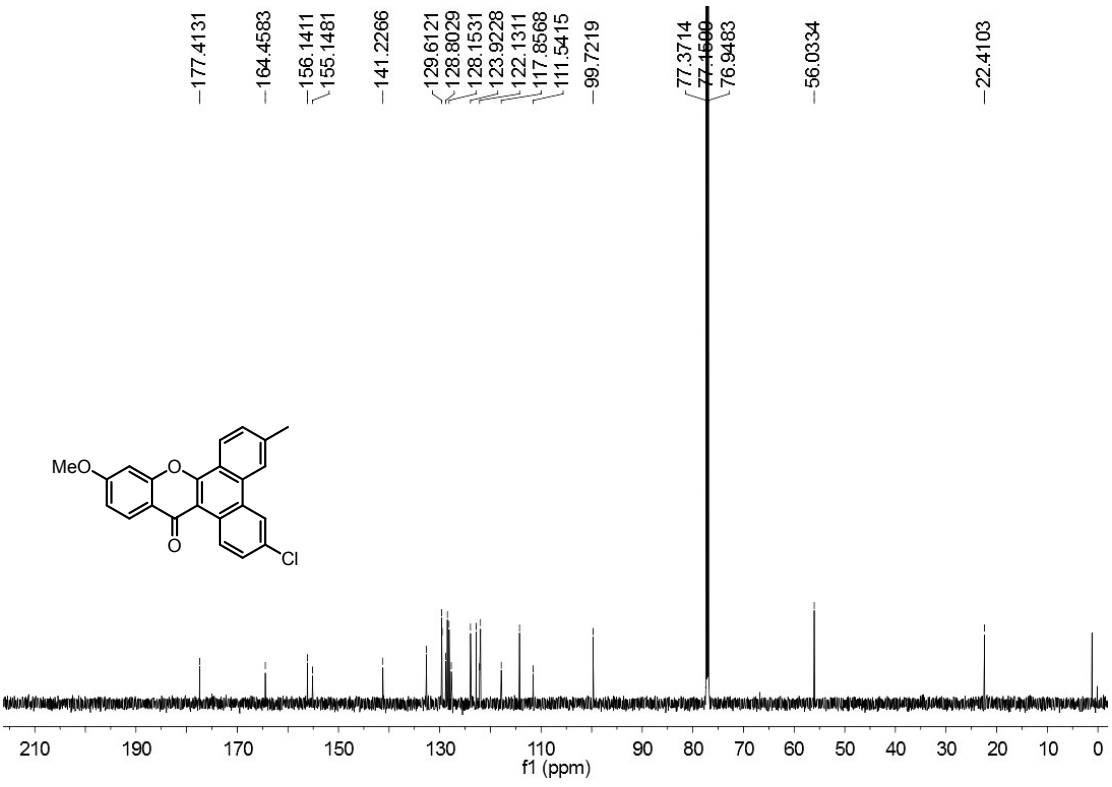
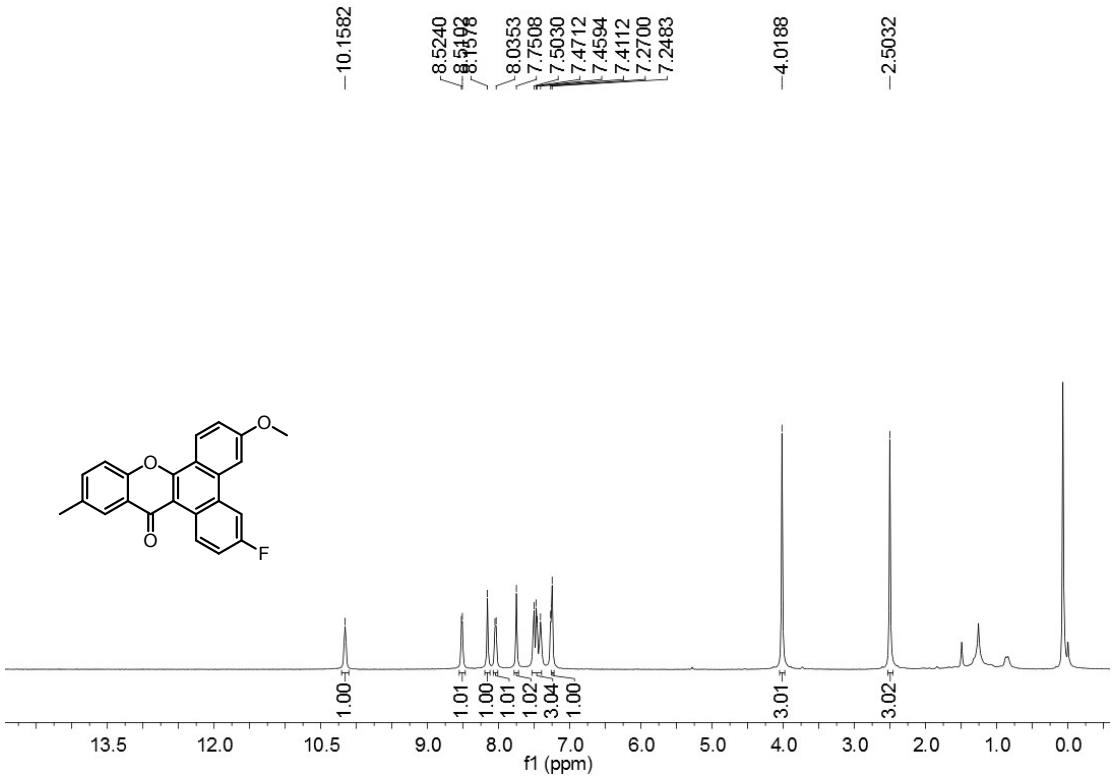
10.0824
8.4452
8.4130
8.2721
8.2574
7.4614
7.2602
7.0076
7.0037
6.9929
6.9890
6.9509
6.9472
3.9710
2.6061
MeO
O
O
Cl
1.00
1.00
1.02
1.00
1.00
1.01
1.02
1.00
1.00
3.02
3.00
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


177.4131
164.4583
156.1411
155.1481
141.2266
129.6121
128.8029
128.1531
123.9228
122.1311
117.8568
111.5415
99.7219
77.3714
77.1600
76.9483
56.0334
22.4103
MeO
O
O
Cl
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2s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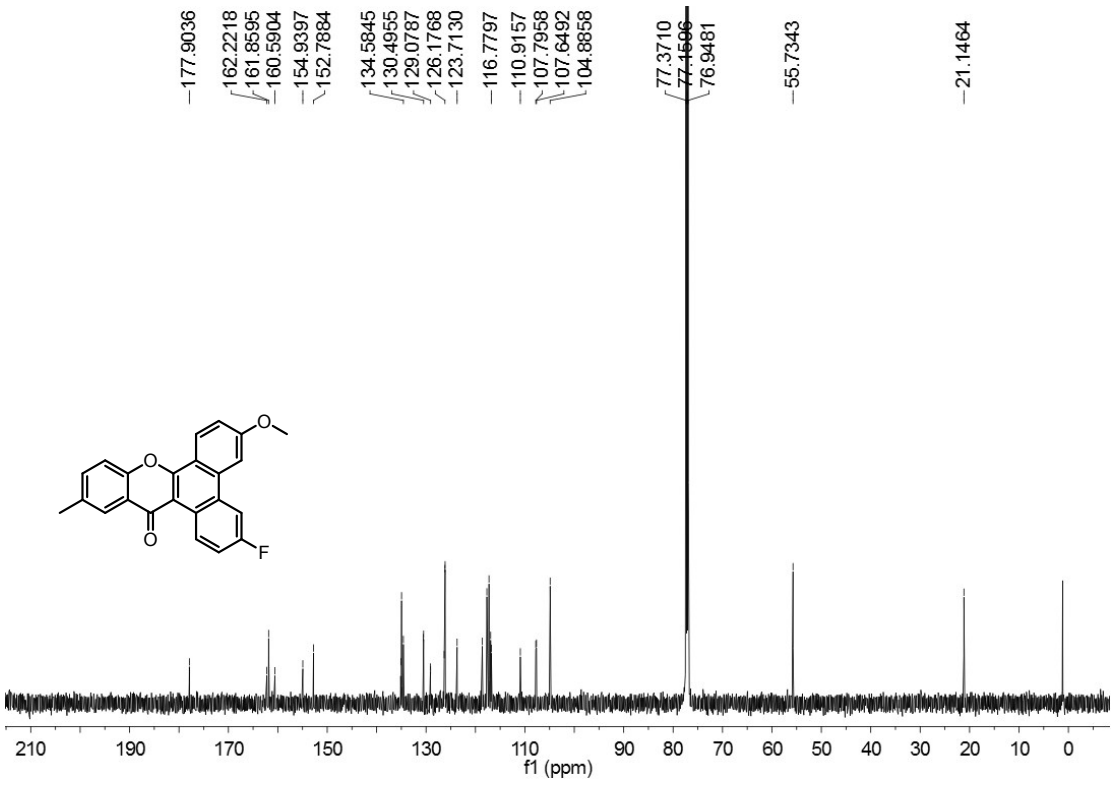
8.5240
8.5192
8.1578
8.0353
7.7508
7.5030
7.4712
7.4594
7.4112
7.2700
7.2483
4.0188
2.5032
1.00
1.01
1.00
1.01
1.02
3.04
1.00
3.01
3.02
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
O
O
O
F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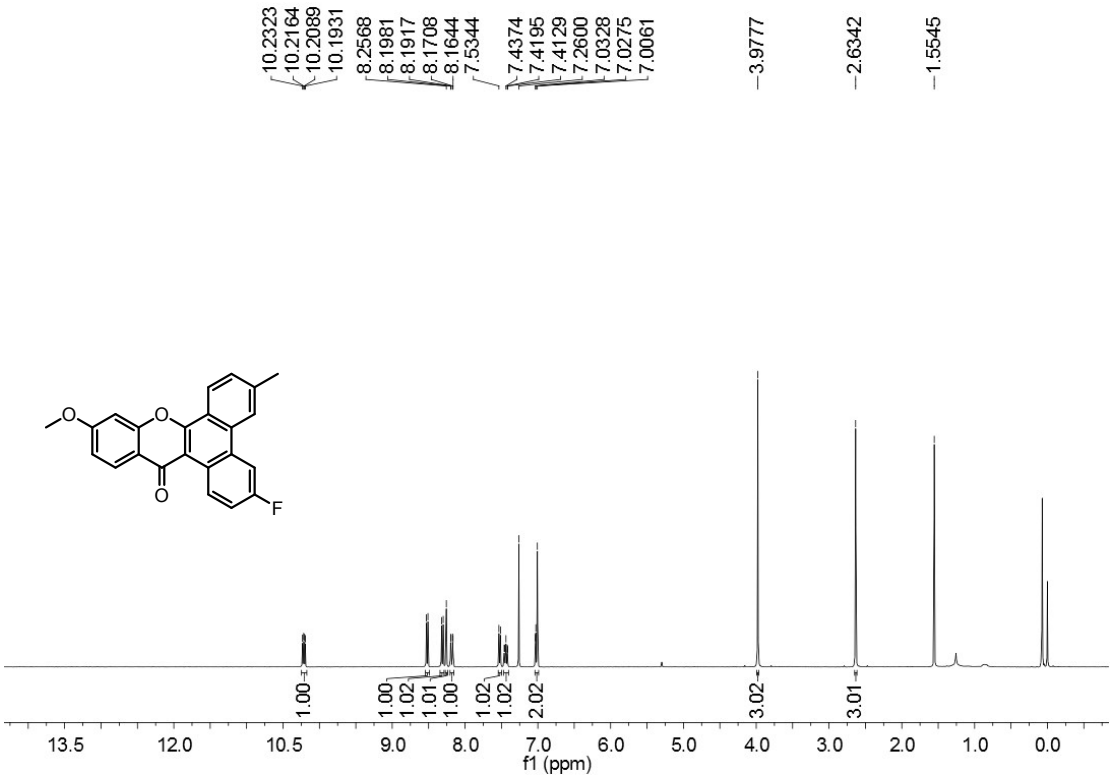
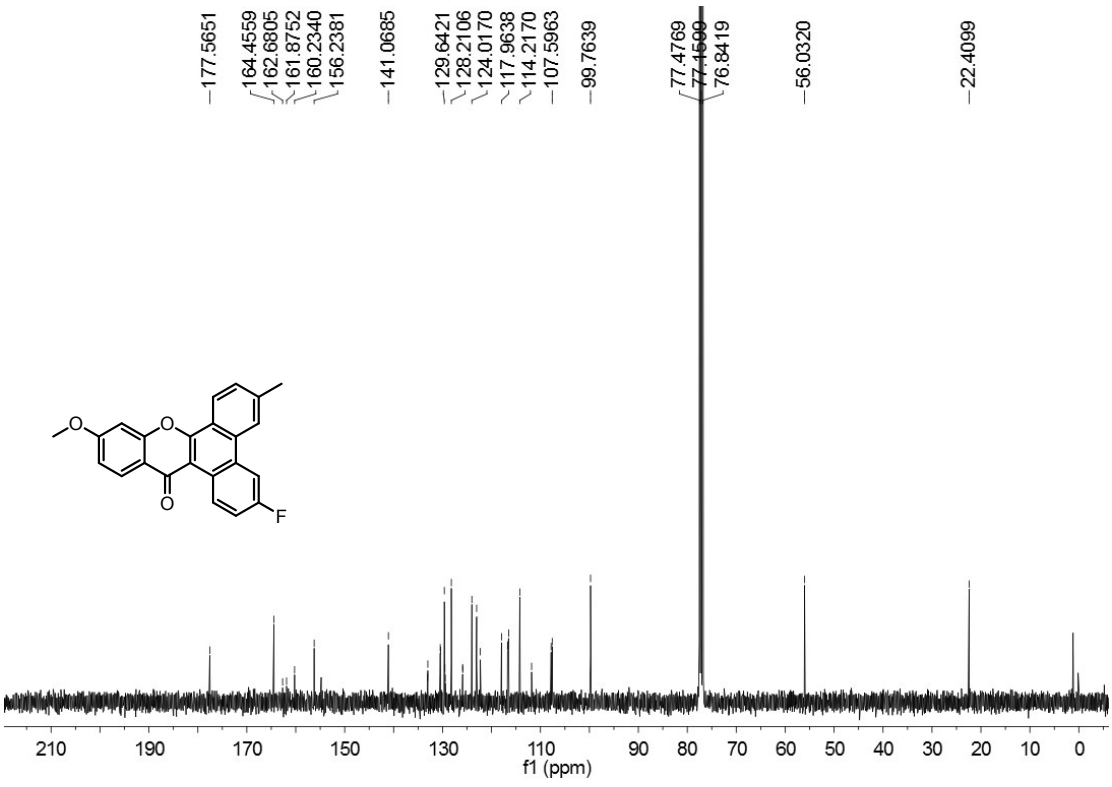
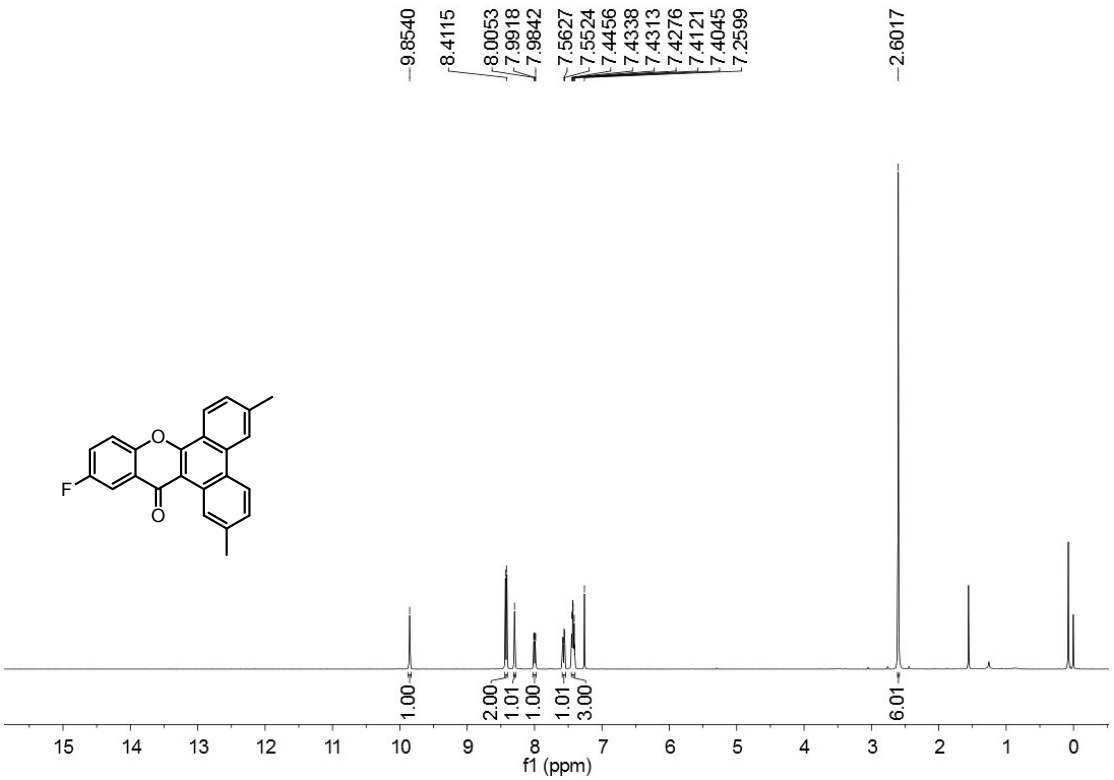
162.2218
161.8595
160.5904
154.9397
152.7884
134.5845
130.4955
129.0787
126.1768
123.7130
116.7797
110.9157
107.7958
107.6492
104.8858
77.3710
77.1596
76.9481
55.7343
21.1464
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
O
O
F

2t


10.2323
10.2164
10.2089
10.1931
8.2568
8.1981
8.1917
8.1708
8.1644
7.5344
7.4374
7.4195
7.4129
7.2600
7.0328
7.0275
7.0061
3.9777
2.6342
1.5545
O
O
O
F
1.00
1.00
1.02
1.01
1.00
1.02
1.02
2.02
3.02
3.01
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


177.5651
164.4559
162.6805
161.8752
160.2340
156.2381
141.0685
129.6421
128.2106
124.0170
117.9638
114.2170
107.5963
99.7639
77.4769
77.1599
76.8419
56.0320
22.4099
O
O
O
F
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2u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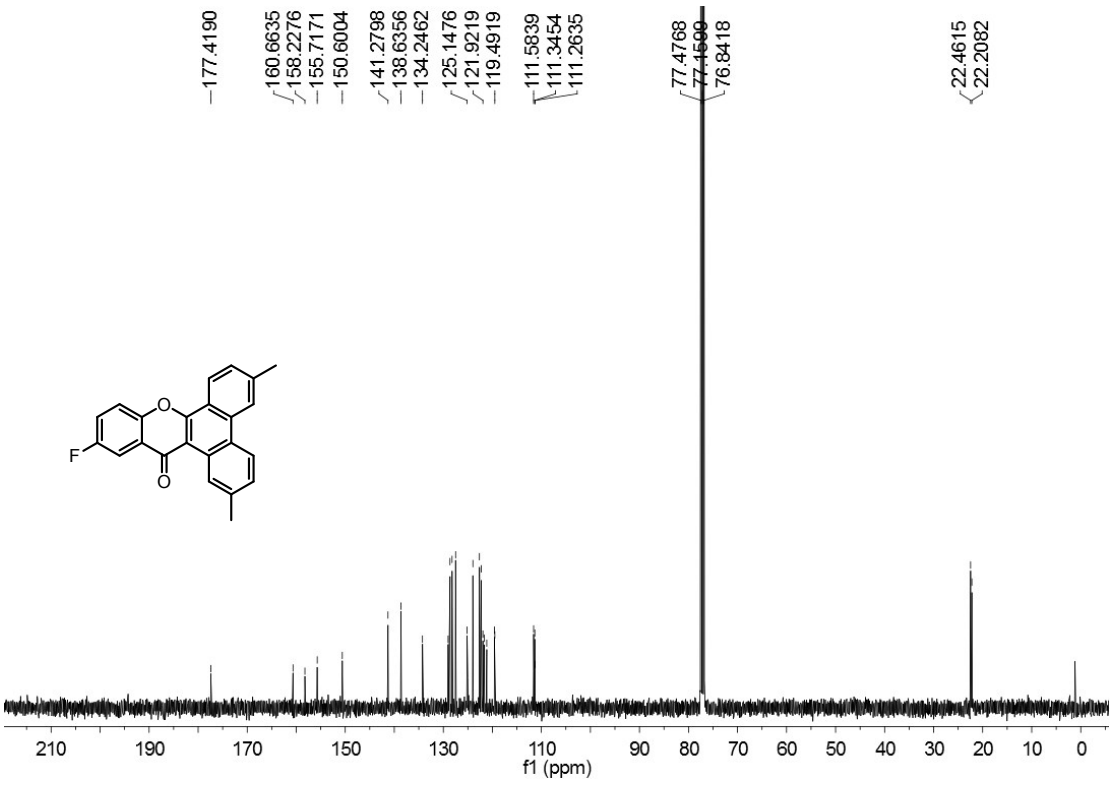
8.0053
7.9918
7.9842
7.5627
7.5524
7.4456
7.4338
7.4313
7.4276
7.4121
7.4045
7.2599
2.6017
1.00
2.00
1.01
1.00
1.01
3.00
6.01
f1 (ppm)


177.4190
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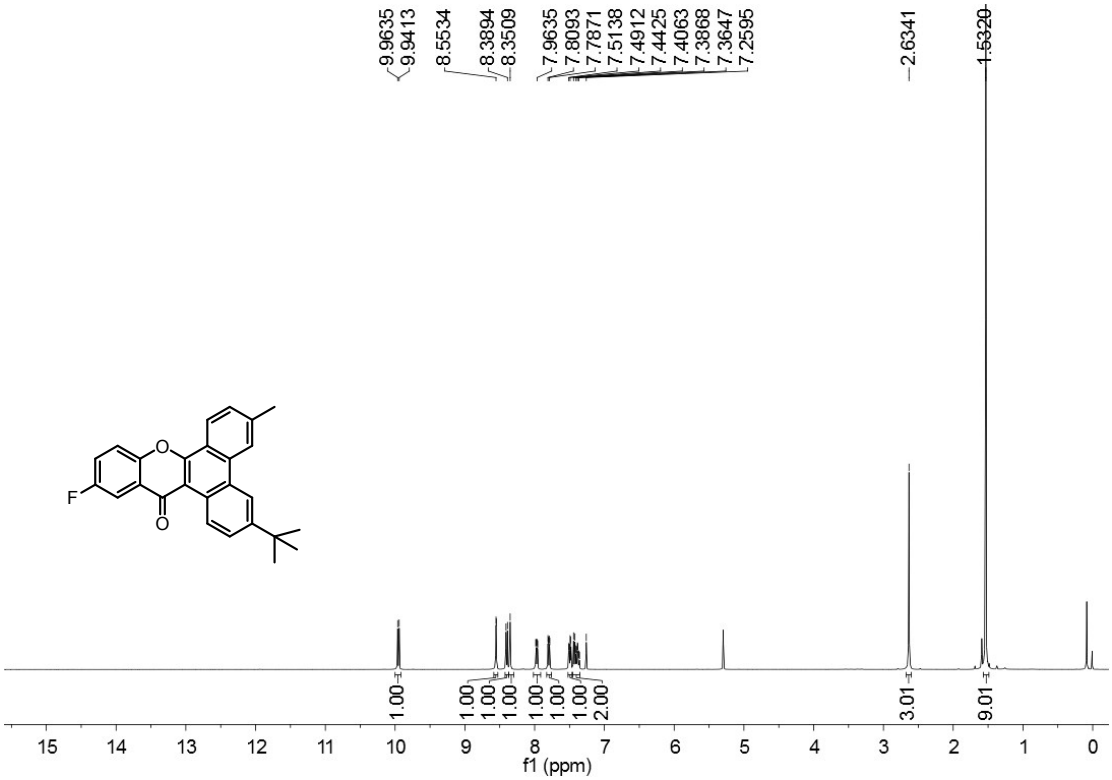
158.2276
155.7171
150.6004
141.2798
138.6356
134.2462
125.1476
121.9219
119.4919
111.5839
111.3454
111.2635
77.4768
77.1590
76.8418
22.4615
22.2082
f1 (ppm)

2v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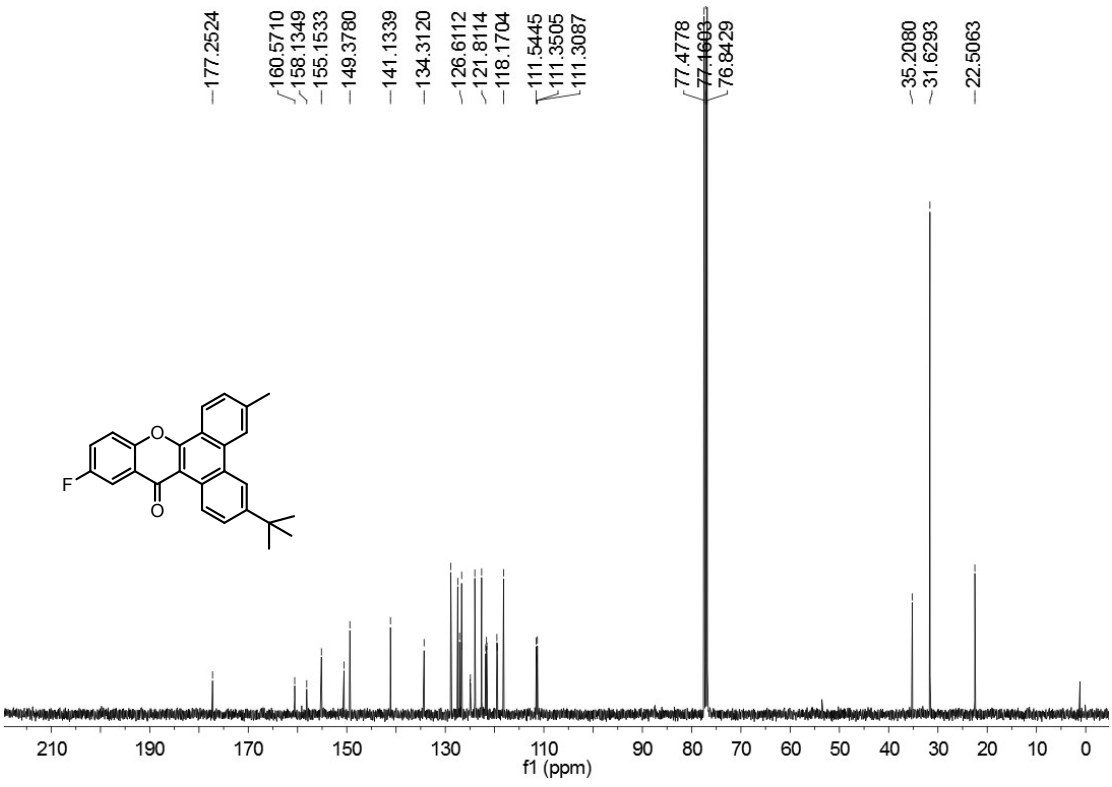
9.9413
8.5534
8.3894
8.3509
7.9635
7.8093
7.7871
7.5138
7.4912
7.4425
7.4063
7.3868
7.3647
7.2595
2.6341
1.5320
1.00
1.00
1.00
1.00
1.00
1.00
2.00
3.01
9.01
F
O
O
f1 (ppm)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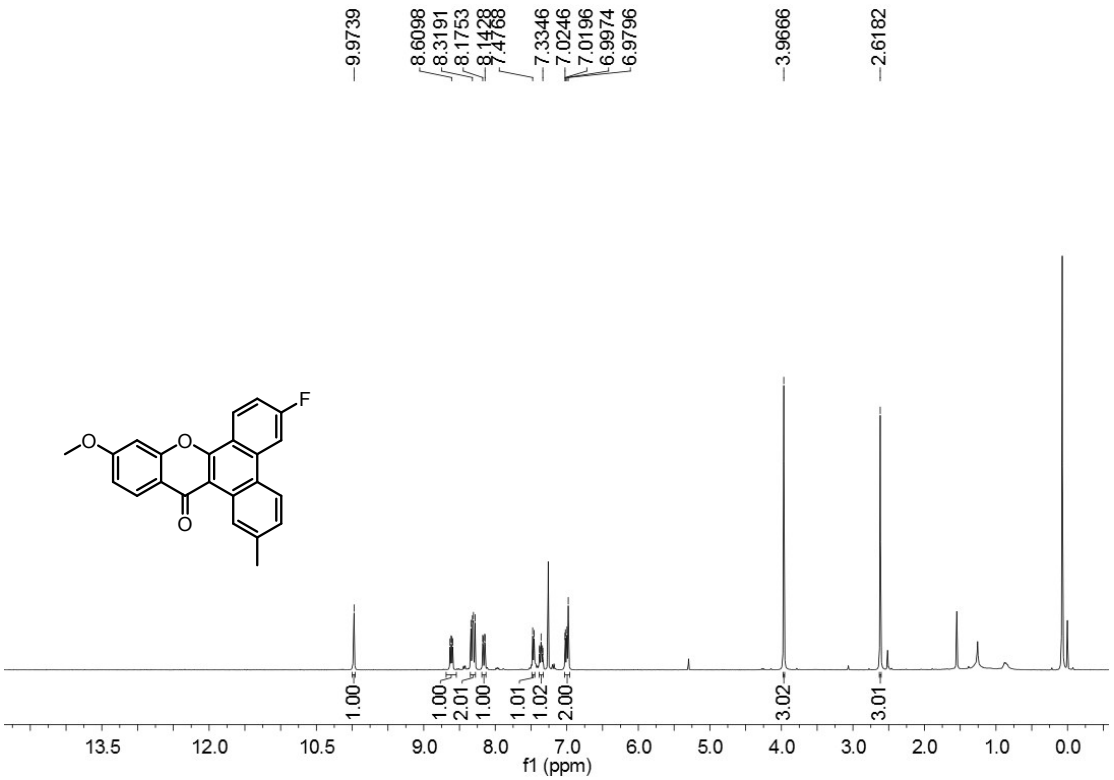
158.1349
155.1533
149.3780
141.1339
134.3120
126.6112
121.8114
118.1704
111.5445
111.3505
111.3087
77.4778
77.1603
76.8429
35.2080
31.6293
22.5063
F
O
O
f1 (ppm)

2w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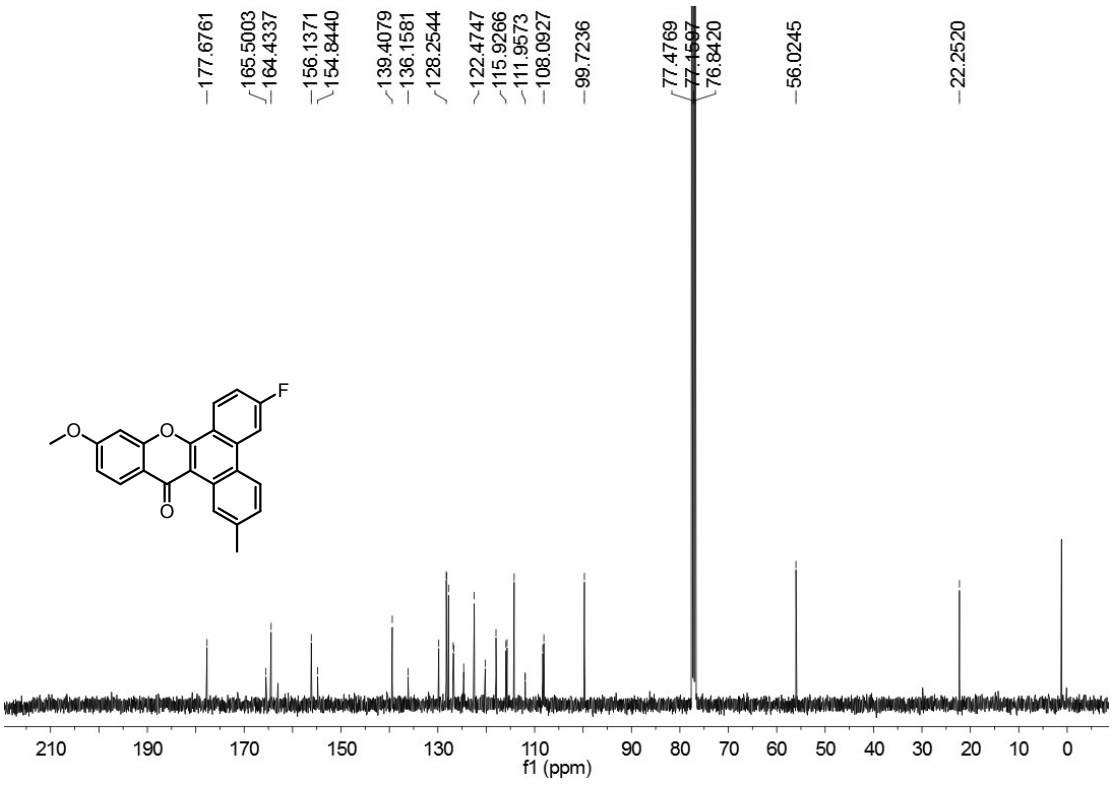
8.3191
8.1753
8.1428
7.4768
7.3346
7.0246
7.0196
6.9974
6.9796
3.9666
2.6182
F
O
O
O
1.00
1.00
2.01
1.00
1.01
1.02
2.00
3.02
3.01
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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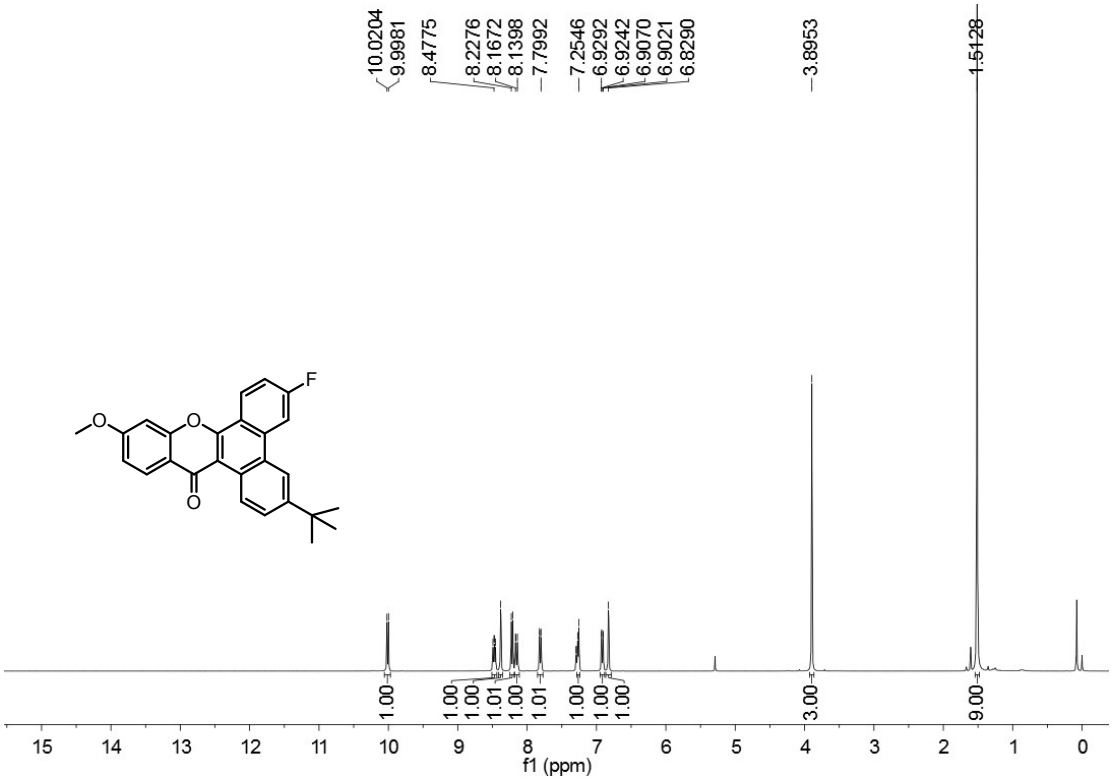
164.4337
156.1371
154.8440
139.4079
136.1581
128.2544
122.4747
115.9266
111.9573
108.0927
99.7236
77.4769
77.1567
76.8420
56.0245
22.2520
F
O
O
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2x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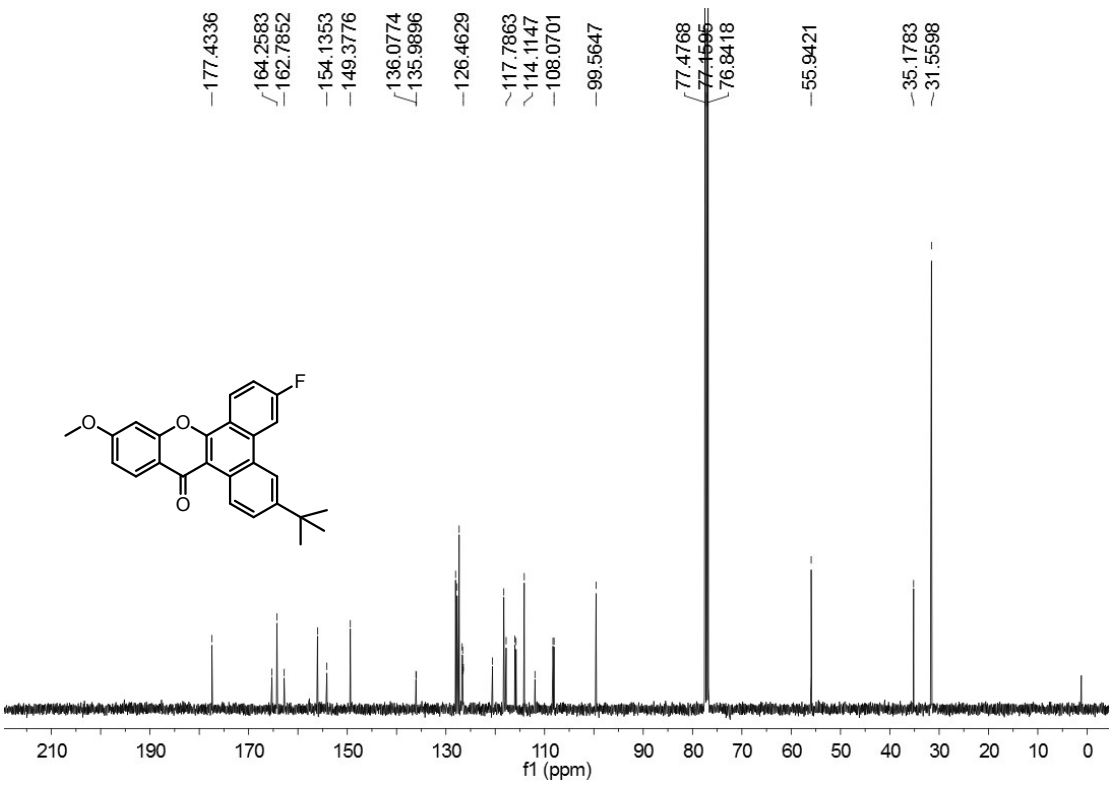
8.4775
8.2276
8.1672
8.1398
7.7992
7.2546
6.9292
6.9242
6.9070
6.9021
6.8290
3.8953
1.5128
1.00
1.00
1.00
1.01
1.00
1.01
1.00
1.00
1.00
3.00
9.00
F
O
O
O
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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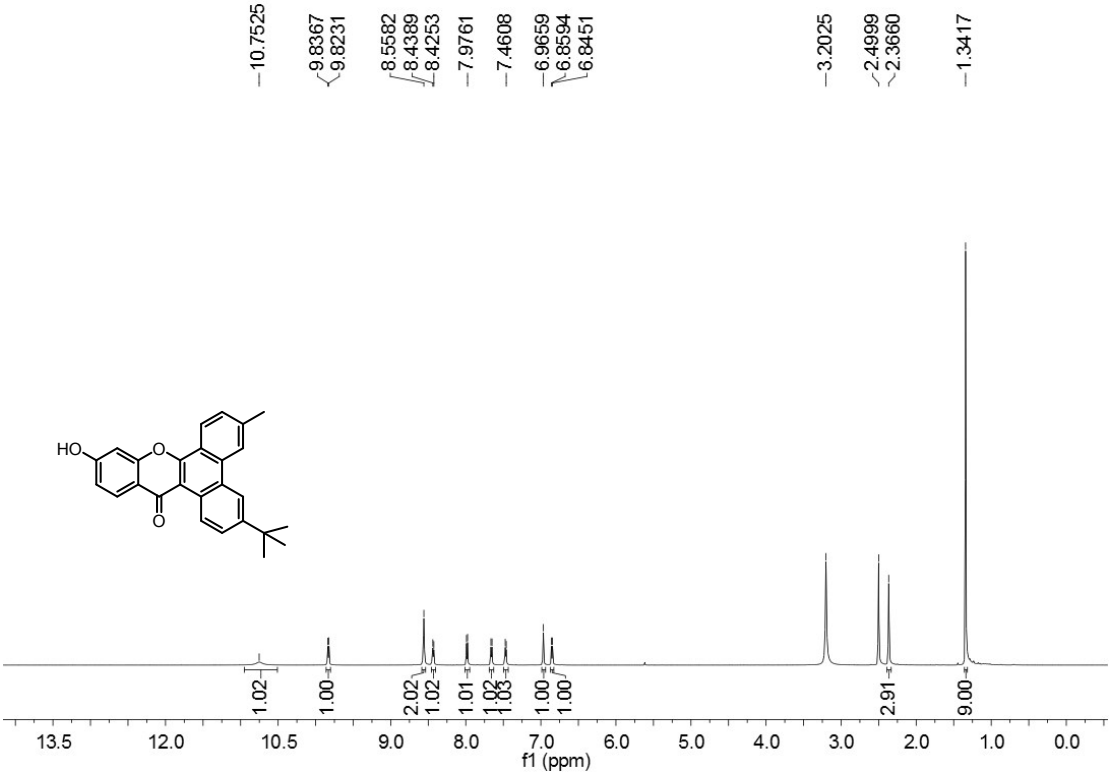
162.7852
154.1353
149.3776
136.0774
135.9896
126.4629
117.7863
114.1147
108.0701
99.5647
77.4768
77.1596
76.8418
55.9421
35.1783
31.5598
F
O
O
O
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2y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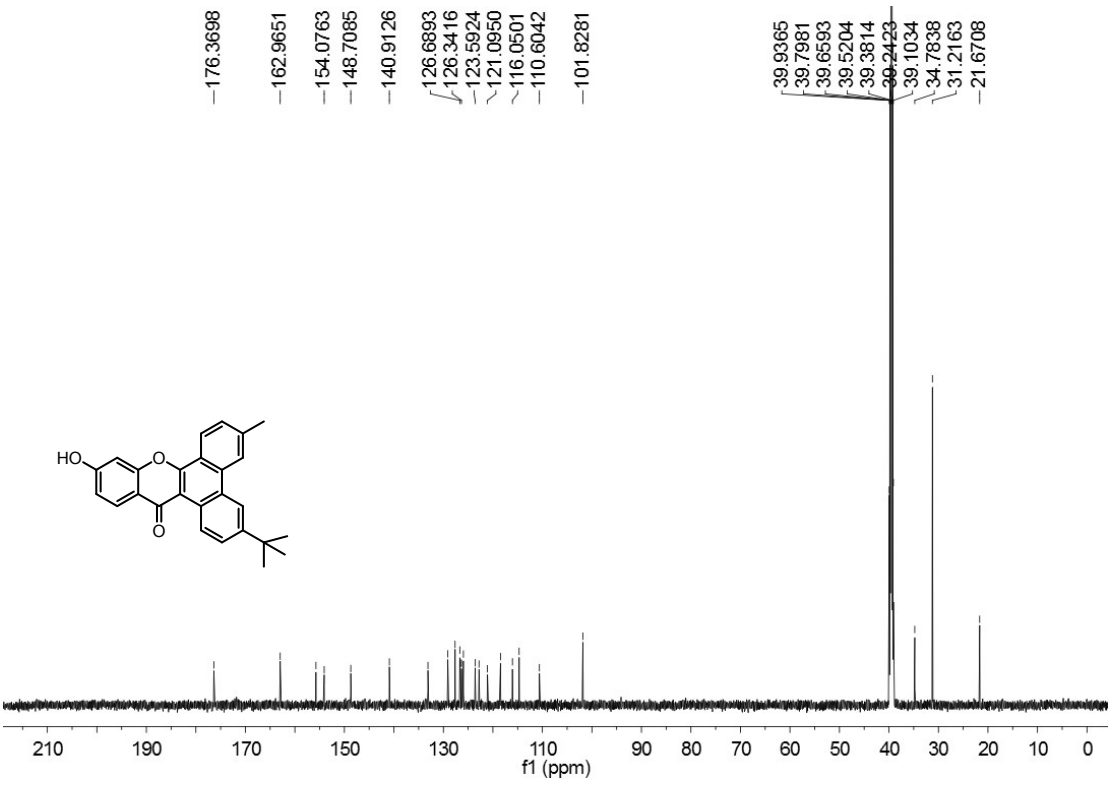
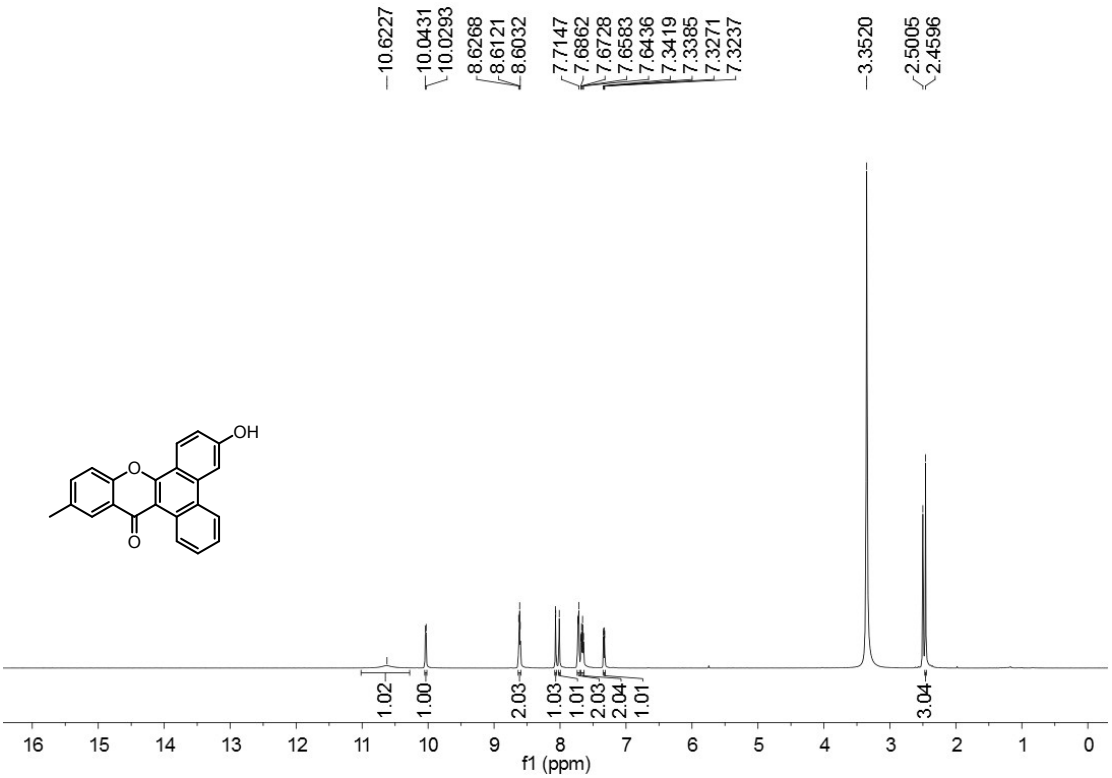
9.8367
9.8231
8.5582
8.4389
8.4253
7.9761
7.4608
6.9659
6.8594
6.8451
3.2025
2.4999
2.3660
1.3417
HO
O
O
1.02
1.00
2.02
1.02
1.01
1.02
1.03
1.00
1.00
2.91
9.00
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


176.3698
162.9651
154.0763
148.7085
140.9126
126.6893
126.3416
123.5924
121.0950
116.0501
110.6042
101.8281
39.9365
39.7981
39.6593
39.5204
39.3814
39.2423
39.1034
34.7838
31.2163
21.6708
HO
O
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2z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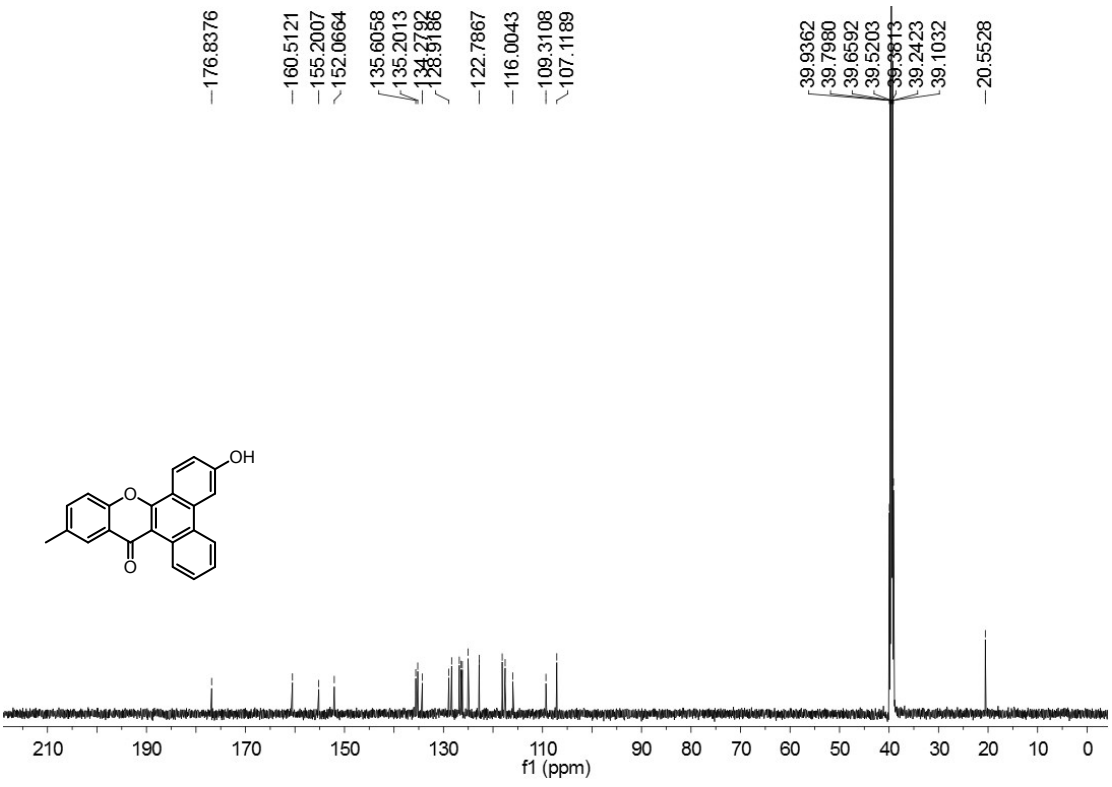
10.0431
10.0293
8.6268
8.6121
8.6032
7.7147
7.6862
7.6728
7.6583
7.6436
7.3419
7.3385
7.3271
7.3237
3.3520
2.5005
2.4596
OH
O
O
1.02
1.00
2.03
1.03
1.01
2.03
2.04
1.01
3.04
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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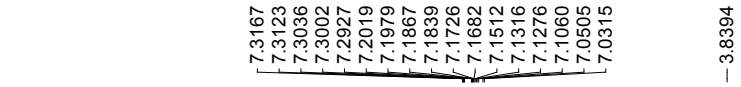
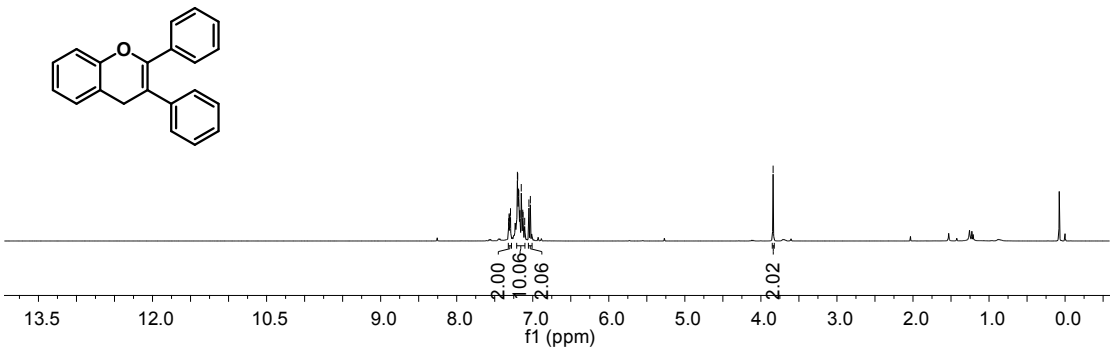
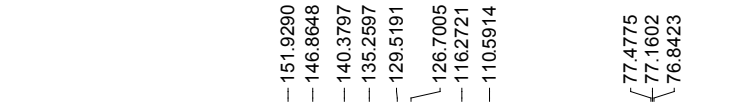
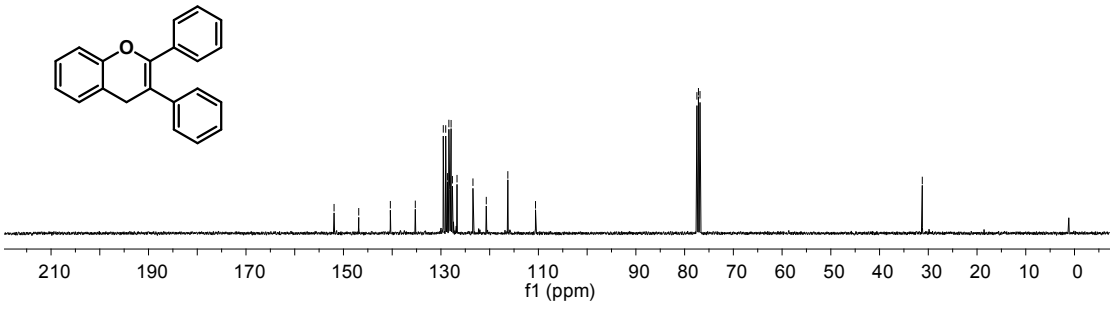
160.5121
155.2007
152.0664
135.6058
135.2013
122.7867
116.0043
109.3108
107.1189
39.9362
39.7980
39.6592
39.5203
39.3813
39.2423
39.1032
20.5528
OH
O
O
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3


7.3167
7.3123
7.3036
7.3002
7.2927
7.2019
7.1979
7.1867
7.1839
7.1726
7.1682
7.1512
7.1316
7.1276
7.1060
7.0505
7.0315
3.8394


2.00
10.06
2.06
2.02
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


151.9290
146.8648
140.3797
135.2597
129.5191
126.7005
116.2721
110.5914
77.4775
77.1602
76.8423
31.2317


210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5. Detection the generation of H_2 by GC

5.1 The conditions of GC

Using Ar as carrier gas, thermal conductivity detector (TCD temperature was 120 ^oC) and stainless steel column (column length 2 m, column temperature at 40 ^oC, Tam TDS-01 60~80 mesh) were used for gas chromatography analysis. Under the conditions of gas velocity of 0.06 Mpa and the flow rate of 60 mL/min, gas was analysized at room temperature with injection of 20 uL.

5.2 The experimental photo-induced hydrogen evolution of 1n

The chromatographic ethanol (250 mL) was degassed for an hour by ultrasonic. Then, sodium sulfite (28 g) and hydroquinone (2.2 g) was added and the mixture was refluxed for 3 h to remove the solvent deoxidization. The compound of **1n** (171 mg, 0.5 mmol) was dissolved in 100 mL deoxidization chromatographic ethanol at room temperature in a quartz tube I. In the same conditions, quartz tube II without compound **1n** was prepared. All operations above were conducted in argon atmosphere. After strict sealing, quartz tube I and II were irradiated with a high-pressure mercury lamp (500 W) at room temperature for 3 hours and the yield of **2n** was 54%.

5.3 The results and discussion of detection H_2

According to the experiment data, the reference substance H_2 retention time tR_1 was 1.4713 min (Figure 1); the retention time tR_2 in the quartz tube I was 1.4533 min (Figure 2). That is to say that there was generated H_2 in the tube I. The quartz tube II was not found H_2. It is indicated that the annulation of **1n** was hydrogen evolution.

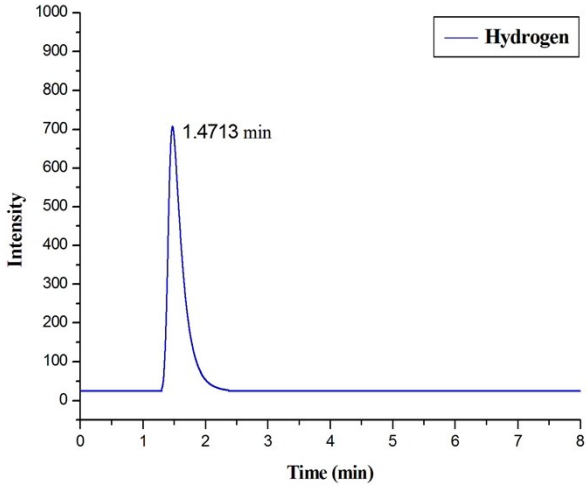


Figure 1 Chromatogram of reference substance H_2

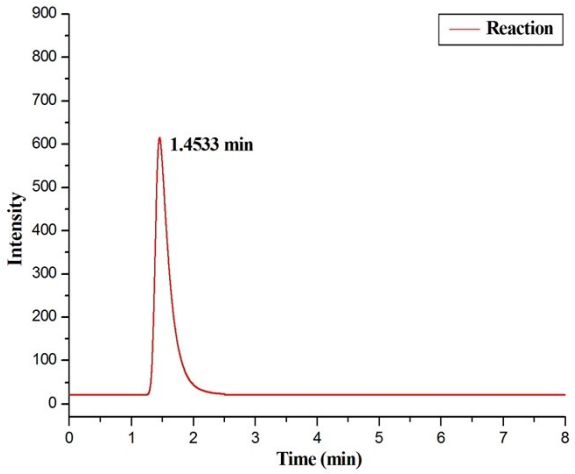


Figure 2 Chromatogram of gas in the tube I