Supporting information

Reagent-Free Intramolecular Hydrofunctionalization: A Regioselective 6-*endo*-dig Cyclization of *o*-Alkynoylphenols

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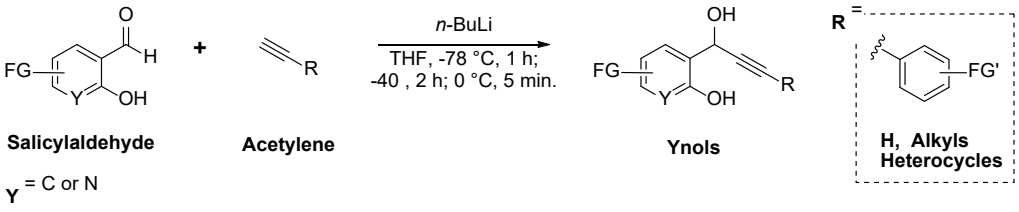
Contents

I. General Information

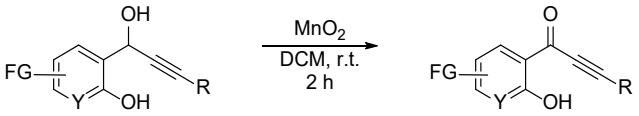
Unless noted otherwise, all reagents were purchased from commercial sources and used as received. Air or moisture labile reactions were conducted in oven-dried glassware under argon atmosphere. Reaction progress was monitored by thin layer-chromatography (TLC) using silica gel F_{254} plates. Products were purified by flash column chromatography using silica gel 60 (70–230 mesh) or by using the Biotage 'Isolera One' system with indicated solvents. High-resolution mass spectrometry was performed with LCQ Fleet-Thermo Scientifics recorded in positive ion mode with electrospray ionization (ESI) source. DMSO recycle or DMSO direct evaporation was performed in Biotage® V-10 Touch, Walk-up, Walk-away Evaporation System at 56 °C. NMR spectra were recorded on a Jeol RESONANCE ECZ 400S (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Chemical shifts were reported in ppm from tetramethylsilane (TMS) with the solvent resonance resulting from incomplete deuteration as the internal reference ($CDCl_3$: 7.26 ppm, CD_3OD: 3.31 ppm, DMSO: 2.5 ppm, 3.33 ppm of water peak) or relative to TMS (δ 0.0). Data are reported as follows: chemical shift δ, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, td = triplet of doublet, ddd = doublet of doublets of doublets, ddt = doublet of doublet of triplets), coupling constants (Hz), number of protons. ^{13}C NMR spectra were recorded on a Jeol RESONANCE ECZ 400S (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from tetramethyl silane with the solvent as the internal reference ($CDCl_3$: 77.16 ppm).

II. Experimental sections

1. General procedure for *o*-alkynoylphenols 1.[1, 2]



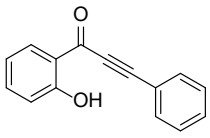
To a solution of aryl acetylene or alkyl acetylene derivative (2.5 mmol, 2.5 eq) in anhydrous THF (2 mL) was dropwise added *n*-BuLi (2 mmol, 2 eq, 2.5 M in THF) at -78 °C under nitrogen atmosphere. After 1 h stirring, a solution of corresponding salicylaldehyde (1 mmol in 2 mL anhydrous THF) was dropwise added at -40 °C. The reaction mixture was stirred at -40 °C for 2 h and heated up to 0 °C then quenched with ice water. The THF was removed by rotary evaporator and extracted with EtOAc twice. The collected EtOAc layer was washed with brine, dried over magnesium sulfate, filtered, and concentrated. The afforded crude was used for the next step without further purification (purified by flash column chromatography, if needed).



Ynols **Ynone, 1(a–dd)**

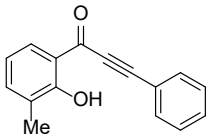
To a solution of ynol in DCM was added MnO_2 (400.0 mg, 4.6 mmol, 4.6 eq) at room temperature. The reaction mixture was stirred till all ynol consumed (monitored by silica gel TLC plate). The reaction mixture was filtered through a pad of celite, and the filtrate was concentrated. Then, residue was purified by flash column chromatography (petroleum ether/EtOAc (5~10%, gradient elution)) on silica gel to afford ynone derivatives (*o*-alkynoylphenols **1**).

1-(2-Hydroxyphenyl)-3-phenylprop-2-yn-1-one (1a)[3]



1a

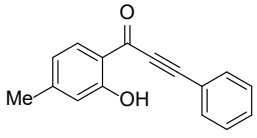
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.74 (s, 1H), 8.13 (ddd, J = 7.7, 1.7, 0.6 Hz, 1H), 7.76 – 7.67 (m, 2H), 7.53 (ddt, J = 14.5, 7.0, 1.6 Hz, 2H), 7.45 (ddd, J = 8.4, 4.3, 1.0 Hz, 2H), 7.04 – 6.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.40, 162.95, 137.28, 133.26 (2C), 133.15, 131.31, 128.91 (2C), 120.93, 119.84, 119.54, 118.28, 96.15, 85.83; HRMS-ESI m/z calculated for $C_{15}H_{10}O_2$ $[M+H]^+$ 223.0754, found 223.0747.



1b

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.03 (s, 1H), 7.99 (ddd, J = 8.0, 1.7, 0.5 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.50 (dd, J = 5.2, 3.7 Hz, 1H), 7.44 (ddd, J = 8.4, 4.4, 1.1 Hz, 2H), 7.42 – 7.37 (m, 1H), 6.93 – 6.87 (m, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.48, 161.39, 137.99, 133.17 (2C), 131.15, 130.71, 128.81 (2C), 127.29, 120.22, 119.90, 118.87, 95.77, 86.02, 15.37; HRMS-ESI *m*/*z* calculated for $C_{16}H_{12}O_2$ $[M+H]^+$ 237.0910, found 237.0908.

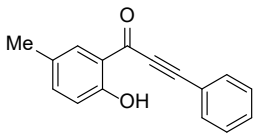
1-(2-Hydroxy-4-methylphenyl)-3-phenylprop-2-yn-1-one (1c)[5]



1c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.9 Hz, 1H), 7.69 (ddd, J = 7.2, 2.9, 1.7 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.48 – 7.40 (m, 2H), 6.84 – 6.77 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.77, 163.04, 149.29, 133.22 (2C), 133.03, 131.18, 128.88 (2C), 120.95, 119.97, 118.91, 118.30, 95.54, 85.85, 22.32; HRMS-ESI *m*/*z* calculated for $C_{16}H_{12}O_2$ $[M+H]^+$ 237.0910, found 237.0906.

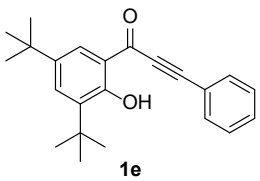
1-(2-Hydroxy-5-methylphenyl)-3-phenylprop-2-yn-1-one (1d)[6]



1d

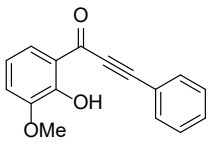
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.59 (s, 1H), 7.88 (dd, J = 1.6, 0.6 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.55 – 7.49 (m, 1H), 7.48 – 7.42 (m, 2H), 7.35 (ddd, J = 8.5, 2.3, 0.4 Hz, 1H), 6.91 (d, J = 8.5 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.33, 160.96, 138.48, 133.21 (2C), 132.66, 131.23, 128.90 (2C), 128.73, 120.55, 119.94, 118.06, 95.91, 85.90, 20.68; HRMS-ESI *m*/*z* calculated for $C_{16}H_{12}O_2$ $[M+H]^+$ 237.0910, found 237.0902.

1-(3,5-Di-*tert*-butyl-2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (1e)[7]



1e

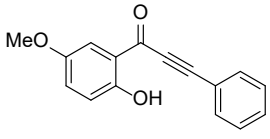
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.46 (s, 1H), 8.04 (d, J = 2.5 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.61 (d, J = 2.4 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.46 (dt, J = 8.5, 3.9 Hz, 2H), 1.44 (s, 9H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$)δ 183.12, 160.79, 140.90, 138.03, 133.27 (2C), 132.44, 131.19, 128.96 (2C), 127.03, 120.17, 120.10, 95.77, 86.30, 35.28, 34.43, 31.43 (3C), 29.48 (3C); HRMS-ESI *m*/*z* calculated for $C_{23}H_{26}O_2$ $[M+H]^+$ 335.2006, found 335.1996.



1f

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.02 (s, 1H), 7.74 (dd, J = 8.1, 1.4 Hz, 1H), 7.72 – 7.68 (m, 2H), 7.55 – 7.49 (m, 1H), 7.47 – 7.42 (m, 2H), 7.12 (dd, J = 7.9, 1.0 Hz, 1H), 6.94 (t, J = 8.0 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)δ 182.58, 153.38, 148.81, 133.27 (2C), 131.32, 128.89 (2C), 124.18, 120.98, 119.81, 118.89, 117.93, 96.24, 86.09, 56.42; HRMS-ESI *m*/*z* calculated for $C_{16}H_{12}O_3$ $[M+H]^+$ 253.0859, found 253.0853.

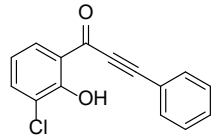
1-(2-Hydroxy-5-methoxyphenyl)-3-phenylprop-2-yn-1-one (1g)[6]



1g

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.39 (s, 1H), 7.73 – 7.66 (m, 2H), 7.59 (d, J = 3.1 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.45 (ddd, J = 8.3, 4.4, 1.0 Hz, 2H), 7.17 (dd, J = 9.1, 3.1 Hz, 1H), 6.96 (d, J = 9.0 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.93, 157.59, 152.25, 133.25 (2C), 131.36, 128.97 (2C), 125.63, 120.45, 119.86, 119.31, 114.87, 96.19, 85.88, 56.04; HRMS-ESI *m*/*z* calculated for $C_{16}H_{12}O_3$ $[M+H]^+$ 253.0859, found 253.0855

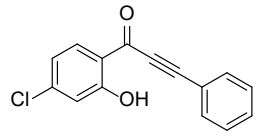
1-(3-Chloro-2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (1h)[9]



1h

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.30 (s, 1H), 8.08 (dd, J = 8.0, 1.6 Hz, 1H), 7.73 – 7.69 (m, 2H), 7.63 (ddd, J = 7.8, 1.6, 0.5 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.48 – 7.43 (m, 2H), 6.97 (t, J = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.99, 158.53, 137.13, 133.38 (2C), 131.62 (2C), 128.98 (2C), 122.82, 121.78, 119.62, 119.51, 97.23, 85.69; HRMS-ESI *m*/*z* calculated for $C_{15}H_9ClO_2$ $[M+H]^+$ 257.0364, found 257.0356.

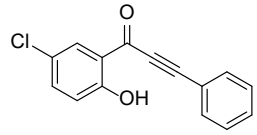
1-(4-Chloro-2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (1i)[10]



1i

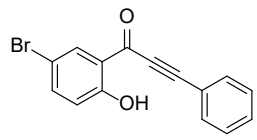
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.88 (s, 1H), 8.03 (d, J = 8.5 Hz, 1H), 7.74 – 7.66 (m, 2H), 7.51 (dd, J = 5.2, 3.8 Hz, 1H), 7.44 (ddd, J = 8.3, 4.3, 0.9 Hz, 2H), 7.02 (d, J = 1.9 Hz, 1H), 6.96 (dd, J = 8.5, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.45, 163.39, 143.31, 134.06, 133.30 (2C), 131.50, 128.94 (3C), 120.31, 119.56, 118.39, 96.69, 85.59; HRMS-ESI *m*/*z* calculated for $C_{15}H_9ClO_2$ $[M+H]^+$ 257.0364, found 257.0353.

1-(5-Chloro-2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (1j)[9]



1j

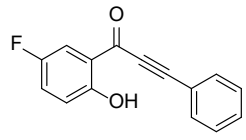
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.67 (s, 1H), 8.07 (d, J = 2.6 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.57 – 7.52 (m, 1H), 7.50 – 7.44 (m, 3H), 6.98 (d, J = 8.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.38, 161.43, 137.16, 133.44 (2C), 131.97, 131.66, 129.01 (2C), 124.22, 121.45, 120.05, 119.45, 97.22, 85.47; HRMS-ESI *m*/*z* calculated for $C_{15}H_9ClO_2$ $[M+H]^+$ 257.0364, found 257.0352.



1k

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.69 (s, 1H), 8.21 (d, J = 2.5 Hz, 1H), 7.76 – 7.66 (m, 2H), 7.60 (dd, J = 8.9, 2.5 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.50 – 7.43 (m, 2H), 6.92 (d, J = 8.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.26, 161.86, 139.87, 135.05, 133.43 (2C), 131.64, 129.00 (2C), 122.07, 120.40, 119.44, 111.04, 97.28, 85.46; HRMS-ESI *m*/*z* calculated for $C_{15}H_9BrO_2$ $[M+H]^+$ 300.9859, found 300.9845.

1-(5-Fluoro-2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (1l)[7]

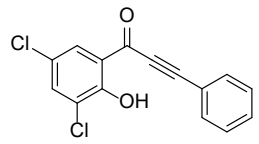


1l

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.52 (s, 1H), 7.79 (dd, J = 8.5, 3.1 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.54 (ddd, J = 6.6, 3.9, 1.4 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.31 – 7.25 (m, 1H), 6.98 (dd, J = 9.1, 4.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.45, 159.17 (d, J = 1.5 Hz), 156.41, 154.03, 133.41

(2C), 131.62, 129.00 (2C), 125.01 (d, J = 23.9 Hz), 119.77 (d, J = 7.3 Hz), 119.47, 117.55 (d, J = 23.7 Hz), 96.91, 85.51; HRMS-ESI m/z calculated for $C_{15}H_9FO_2$ $[M+H]^+$ 241.0660, found 241.0647.

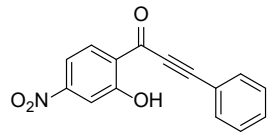
1-(3,5-Dichloro-2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (1m)



1m

Obtained as yellow solid, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.22 (s, 1H), 8.01 (d, J = 2.5 Hz, 1H), 7.73 (dt, J = 2.6, 0.9 Hz, 1H), 7.71 (d, J = 1.5 Hz, 1H), 7.62 (d, J = 2.5 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.50 – 7.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.96, 157.28, 136.64, 133.53 (2C), 131.93, 130.61, 129.07 (2C), 124.01, 124.00, 121.86, 119.16, 98.28, 85.37; HRMS-ESI m/z calculated for $C_{15}H_8Cl_2O_2$ $[M+H]^+$ 290.9974, found 290.9964.

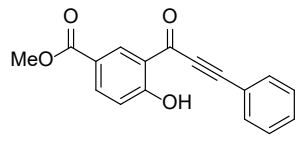
1-(2-Hydroxy-4-nitrophenyl)-3-phenylprop-2-yn-1-one (1n)



1n

Obtained as yellow solid, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.87 (s, 1H), 8.41 – 8.24 (m, 1H), 7.84 (d, J = 2.0 Hz, 1H), 7.80 (dd, J = 8.7, 2.2 Hz, 1H), 7.73 (dd, J = 8.2, 1.2 Hz, 2H), 7.60 – 7.54 (m, 1H), 7.48 (dd, J = 11.7, 4.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.51, 163.06, 152.53, 134.26, 133.55 (2C), 132.06, 129.11 (2C), 124.27, 119.08, 113.95, 113.79, 98.76, 85.69; HRMS-ESI m/z calculated for $C_{15}H_9NO_4$ $[M+Na]^+$ 290.0424, found 290.0410.

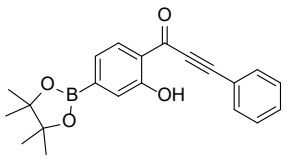
Methyl 4-hydroxy-3-(3-phenylpropioloyl)benzoate (1o)



1o

Obtained as yellow solid, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.14 (s, 1H), 8.89 (d, J = 2.1 Hz, 1H), 8.18 (dd, J = 8.8, 2.1 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.54 (ddd, J = 6.7, 3.9, 1.4 Hz, 1H), 7.46 (ddd, J = 6.9, 4.4, 1.3 Hz, 2H), 7.05 (d, J = 8.8 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.12, 166.25, 165.92, 137.77, 135.73, 133.55 (2C), 131.66, 128.98 (2C), 121.77, 120.37, 119.51, 118.54, 97.68, 85.54, 52.39; HRMS-ESI m/z calculated for $C_{17}H_{12}NO_4$ $[M+H]^+$ 281.0809, found 281.0808.

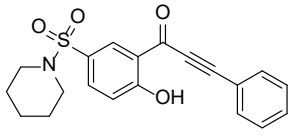
1-(2-Hydroxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-3-phenylprop-2-yn-1-one (1p)



1p

Obtained as yellow solid, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.57 (s, 1H), 8.09 (d, J = 7.8 Hz, 1H), 7.70 (dd, J = 5.2, 3.3 Hz, 2H), 7.55 – 7.49 (m, 1H), 7.44 (dd, J = 11.3, 4.7 Hz, 3H), 7.37 (d, J = 8.1 Hz, 1H), 1.36 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.56, 161.95, 133.31 (2C), 131.97, 131.33, 128.93 (3C), 124.98, 124.67, 122.39, 119.90, 96.25, 86.04, 84.55 (2C), 25.02 (4C); HRMS-ESI *m/z* calculated for $C_{21}H_{21}BO_4$ $[M+H]^+$ 349.1606, found 349.1606.

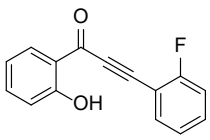
1-(2-Hydroxy-5-(piperidin-1-ylsulfonyl)phenyl)-3-phenylprop-2-yn-1-one (1q)



1q

Obtained as yellow solid, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.12 (s, 1H), 8.58 (d, J = 2.3 Hz, 1H), 7.86 (dd, J = 8.8, 2.3 Hz, 1H), 7.72 (dt, J = 8.6, 1.7 Hz, 2H), 7.59 – 7.52 (m, 1H), 7.46 (ddd, J = 6.8, 4.5, 1.1 Hz, 2H), 7.13 (d, J = 8.8 Hz, 1H), 3.08 – 3.01 (m, 4H), 1.66 (dt, J = 11.3, 5.8 Hz, 4H), 1.48 – 1.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.65, 165.64, 135.40, 133.69 (2C), 133.51, 132.01, 129.13 (2C), 127.72, 120.31, 119.37, 119.15, 98.68, 85.32, 47.09 (2C), 25.30 (2C), 23.60; HRMS-ESI *m/z* calculated for $C_{20}H_{19}NO_4S$ $[M+H]^+$ 370.1108, found 370.1108.

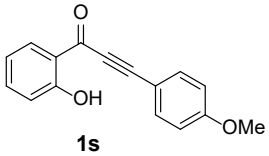
3-(2-Fluorophenyl)-1-(2-hydroxyphenyl)prop-2-yn-1-one (1r)



1r

Obtained as yellow solid, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.68 (s, 1H), 8.18 (dd, J = 8.2, 1.8 Hz, 1H), 7.67 (ddd, J = 7.9, 7.3, 1.8 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.25 – 7.16 (m, 2H), 7.03 – 6.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.99, 163.92 (d, J = 255.9 Hz), 162.89, 137.37, 134.80, 133.36 (d, J = 8.4 Hz), 133.27, 124.59 (d, J = 3.8 Hz), 120.78, 119.67, 118.14, 116.06 (d, J = 20.4 Hz), 108.72 (d, J = 15.2 Hz), 90.19 (d, J = 3.2 Hz), 89.20; HRMS-ESI *m/z* calculated for $C_{15}H_9FO_2$ $[M+H]^+$ 241.0660, found 241.0650.

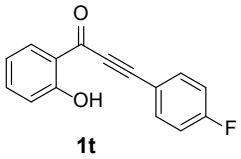
1-(2-Hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-yn-1-one (1s)[11]



1s

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.83 (s, 1H), 8.12 (ddd, J = 7.8, 1.7, 0.8 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.55 – 7.48 (m, 1H), 7.02 – 6.92 (m, 4H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.44, 162.88, 162.20, 137.02, 135.41 (2C), 133.07, 120.97, 119.44, 118.24, 114.67 (2C), 111.59, 97.54, 85.92, 55.63; HRMS-ESI *m/z* calculated for $C_{16}H_{12}O_3$ $[M+H]^+$ 253.0859, found 253.0857.

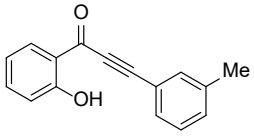
3-(4-Fluorophenyl)-1-(2-hydroxyphenyl)prop-2-yn-1-one (1t)[7]



1t

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.71 (s, 1H), 8.17 – 8.04 (m, 1H), 7.76 – 7.67 (m, 2H), 7.60 – 7.47 (m, 1H), 7.21 – 7.11 (m, 2H), 7.06 – 6.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.22, 165.65, 163.04 (d, J = 14.8 Hz), 137.32, 135.63, 135.54, 133.03, 120.85, 119.54, 118.32, 116.61, 116.38, 115.98 (d, J = 3.3 Hz), 94.97, 85.76; HRMS-ESI m/z calculated for $C_{15}H_9FO_2$ $[M+H]^+$ 241.0660, found 241.0650.

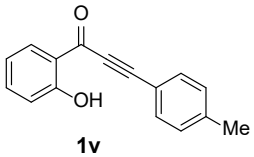
1-(2-Hydroxyphenyl)-3-(*m*-tolyl)prop-2-yn-1-one (1u)[5]



1u

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.77 (s, 1H), 8.17 – 8.11 (m, 1H), 7.56 – 7.48 (m, 3H), 7.35 – 7.32 (m, 2H), 7.03 – 6.97 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.46, 162.95, 138.79, 137.23, 133.74, 133.17, 132.28, 130.45, 128.81, 120.98, 119.65, 119.52, 118.27, 96.58, 85.63, 21.34; HRMS-ESI m/z calculated for $C_{16}H_{12}O_2$ $[M+H]^+$ 237.0910, found 237.0904.

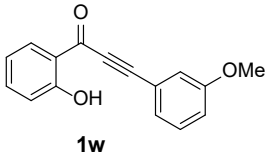
1-(2-Hydroxyphenyl)-3-(*p*-tolyl)prop-2-yn-1-one (1v)[5]



1v

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.79 (s, 1H), 8.17 – 8.10 (m, 1H), 7.60 (d, J = 8.1 Hz, 2H), 7.55 – 7.50 (m, 1H), 7.28 – 7.26 (m, 1H), 7.25 – 7.23 (m, 1H), 6.99 (t, J = 7.5 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.47, 162.92, 142.19, 137.15, 133.34 (2C), 133.15, 129.72 (2C), 120.96, 119.49, 118.25, 116.72, 96.95, 85.77, 21.96; HRMS-ESI m/z calculated for $C_{16}H_{12}O_2$ $[M+H]^+$ 237.0910, found 237.0902.

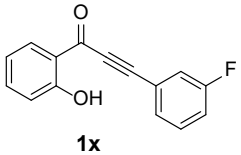
1-(2-Hydroxyphenyl)-3-(3-methoxyphenyl)prop-2-yn-1-one (1w)[9]



1w

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.73 (s, 1H), 8.12 (ddd, J = 7.5, 1.7, 0.7 Hz, 1H), 7.58 – 7.49 (m, 1H), 7.38 – 7.32 (m, 1H), 7.29 (dt, J = 7.6, 1.3 Hz, 1H), 7.19 (dd, J = 2.6, 1.4 Hz, 1H), 7.06 (ddd, J = 8.2, 2.7, 1.2 Hz, 1H), 6.99 (td, J = 7.8, 0.8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.38, 162.99, 159.68, 137.31, 133.17, 130.03, 125.79, 120.96, 120.79, 119.56, 118.31, 118.06, 117.79, 96.05, 85.53, 55.62; HRMS-ESI m/z calculated for $C_{16}H_{12}O_3$ $[M+H]^+$ 253.0859, found 253.0854.

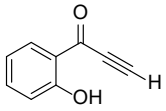
3-(3-Fluorophenyl)-1-(2-hydroxyphenyl)prop-2-yn-1-one (1x)[12]



1x

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.70 – 11.60 (m, 1H), 8.15 – 8.04 (m, 1H), 7.55 (ddd, J = 7.7, 7.2, 1.7 Hz, 1H), 7.49 (ddd, J = 7.3, 1.9, 0.8 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.41 – 7.36 (m, 1H), 7.25 – 7.19 (m, 1H), 7.06 – 6.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.04, 163.00, 162.44 (d, J = 248.6 Hz), 137.47, 133.05, 130.66 (d, J = 8.5 Hz), 129.10 (d, J = 3.3 Hz), 121.63 (d, J = 9.3 Hz), 120.82, 119.83 (d, J = 23.2 Hz), 119.61, 118.72 (d, J = 21.2 Hz), 118.34, 93.96 (d, J = 3.4 Hz), 86.01; HRMS-ESI m/z calculated for $C_{15}H_9FO_2$ $[M+H]^+$ 241.0660, found 241.0650.

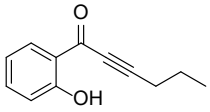
1-(2-Hydroxyphenyl)prop-2-yn-1-one (1y)[13]



1y

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.44 (s, 1H), 8.05 (dd, J = 7.8, 1.6 Hz, 1H), 7.61 – 7.48 (m, 1H), 6.98 (dd, J = 12.0, 4.7 Hz, 2H), 3.59 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.71, 163.01, 137.78, 133.38, 120.50, 119.75, 118.29, 83.52, 79.13.

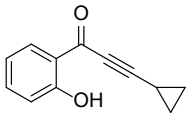
1-(2-Hydroxyphenyl)hex-2-yn-1-one (1z)



1z

Obtained as yellow semi-solid, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.73 (s, 1H), 8.02 (dd, J = 7.9, 1.7 Hz, 1H), 7.55 – 7.43 (m, 1H), 7.02 – 6.91 (m, 2H), 2.52 (t, J = 7.0 Hz, 2H), 1.73 (h, J = 7.2 Hz, 2H), 1.09 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.76, 162.86, 137.01, 133.30, 120.85, 119.38, 118.12, 99.92, 78.79, 21.42, 21.39, 13.74; HRMS-ESI m/z calculated for $C_{12}H_{12}FO_2$ $[M+H]^+$ 189.0911, found 189.0910.

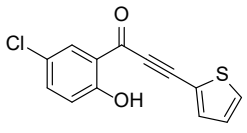
3-Cyclopropyl-1-(2-hydroxyphenyl)prop-2-yn-1-one (1aa)[5]



1aa

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.74 (s, 1H), 7.98 – 7.92 (m, 1H), 7.52 – 7.45 (m, 1H), 6.98 – 6.89 (m, 2H), 1.61 – 1.52 (m, 1H), 1.12 – 1.02 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.37, 162.77, 136.85, 133.18, 120.81, 119.33, 118.09, 104.37, 74.44, 10.27 (2C), 0.27; HRMS-ESI m/z calculated for $C_{12}H_{10}O_2$ $[M+H]^+$ 187.0754, found 187.0745.

1-(5-Chloro-2-hydroxyphenyl)-3-(thiophen-2-yl)prop-2-yn-1-one (1cc)

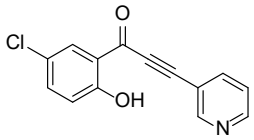


1cc

Obtained as yellow solid, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.66 (s, 1H), 7.99 (d, J = 2.6 Hz, 1H), 7.66 (dd, J = 3.7, 1.1 Hz, 1H), 7.61 (dd, J = 5.1, 1.1 Hz, 1H), 7.47 (dd, J = 8.9, 2.6 Hz, 1H), 7.15 (dd, J = 5.1, 3.7 Hz, 1H), 6.97 (d, J = 8.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.76, 161.36, 137.75, 137.06, 132.95, 131.70, 128.18, 124.21, 121.23, 120.04,

119.18, 91.29, 90.26; HRMS-ESI *m*/*z* calculated for $C_{13}H_7ClO_2S$ $[M+H]^+$ 262.9929, found 262.9928.

1-(2-Hdroxyphenyl)-3-(pyridin-3-yl)prop-2-yn-1-one (1dd)



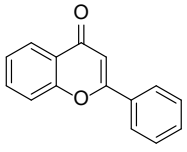
1dd

Obtained as yellow solid, 30% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.53 (s, 1H), 8.94 (s, 1H), 8.74 (d, J = 4.1 Hz, 1H), 8.09 – 7.95 (m, 2H), 7.50 (dd, J = 8.9, 2.6 Hz, 1H), 7.43 (dd, J = 7.9, 4.9 Hz, 1H), 6.99 (d, J = 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.80, 161.55, 153.37, 151.29, 140.33, 137.56, 131.80, 124.43 , 123.64, 121.21, 120.20, 117.03, 92.71, 87.89; HRMS-ESI *m*/*z* calculated for $C_{14}H_8ClNO_2$ $[M+H]^+$ 258.0317, found 258.0315.

2. General procedure for synthesis of *γ*-benzopyranone 2 (cyclization).

To the precursors (**1a**–**1dd**) was added pure DMSO (1.0 mL) at room temperature and stirred until complete cyclization. The reaction mixture was quenched with water and extracted with EtOAc. Combined organic layer was washed with saturated aqueous NH_4Cl, dried over sodium sulfate, filtered, and evaporated. The residue was purified by column chromatography (in case of poor regioselective cyclization) on silica gel column chromatography (eluent, indicated ratio of petroleum ether/EtOAc mixture) or direct concentrated (in case of reaction with >99:1/*endo:exo* ratio) to afford the final *γ*-benzopyranone 2 (i.e., flavone) derivatives.

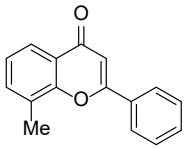
2-Phenyl-4*H*-chromen-4-one (2a)[14]



2a

To 1-(2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (**1a**, 11.1 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 2 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated to afford compound **2a** (9.9 mg, yield 89%) as a white solid. ^{1}H NMR (400MHz, $CDCl_3$) δ 8.27 – 8.21 (m, 1H), 7.97 – 7.91 (m, 2H), 7.75 – 7.68 (m, 1H), 7.61 – 7.56 (m, 1H), 7.56 – 7.50 (m, 3H), 7.43 (ddd, J = 8.1, 7.1, 1.1 Hz, 1H), 6.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.62, 163.56, 156.38, 133.95, 131.87, 131.77, 129.19 (2C), 126.43 (2C), 125.83, 125.38, 124.04, 118.23, 107.69; HRMS-ESI *m*/*z* calculated for $C_{15}H_{10}O_2$ $[M+H]^+$ 223.0754, found 223.0747.

8-Methyl-2-phenyl-4*H*-chromen-4-one (2b)[15]

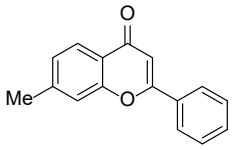


2b

To 1-(2-hydroxy-3-methylphenyl)-3-phenylprop-2-yn-1-one (**1b**, 11.8 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 2.5 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated then purified using silica gel column chromatography (petroleum ether/EtOAc = 5/1) to afford compound **2b** (10.3 mg, yield 87%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (ddd, J = 7.9, 1.3, 0.5 Hz, 1H), 7.99 – 7.91 (m, 2H), 7.60 – 7.51 (m, 4H), 7.37 – 7.29 (m, 1H), 6.87 (s, 1H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.96, 163.06, 154.82, 134.84, 132.15, 131.67, 129.20 (3C), 127.62, 126.31 (2C), 124.88, 123.42, 107.40, 15.93; HRMS-ESI m/z calculated for $C_{16}H_{12}O_2$ $[M+H]^+$ 237.0910, found 237.0906.

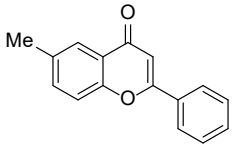
7-Methyl-2-phenyl-4*H*-chromen-4-one (2c)[15]



2c

To 1-(2-hydroxy-4-methylphenyl)-3-phenylprop-2-yn-1-one (**1c**, 11.8 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 2.5 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over MgSO4, filtered, and concentrated then purified using silica gel column chromatography (petroleum ether/EtOAc = 5/1) to afford compound **2c** (10.2 mg, yield 86%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.1 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.56 – 7.51 (m, 3H), 7.39 (s, 1H), 7.26 – 7.23 (m, 1H), 6.82 (s, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.54, 163.28, 156.56, 145.26, 132.07, 131.62, 129.16 (2C), 126.87, 126.38 (2C), 125.59, 121.85, 118.00, 107.67, 21.99; HRMS-ESI m/z calculated for $C_{16}H_{12}O_2$ $[M+H]^+$ 237.0910, found 237.0903.

6-Methyl-2-phenyl-4*H*-chromen-4-one (2d)[14]

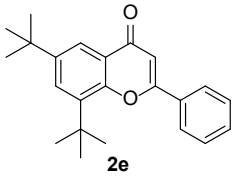


2d

To 1-(2-hydroxy-5-methylphenyl)-3-phenylprop-2-yn-1-one (**1d**, 11.8 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 3 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated then purified using silica gel column chromatography (petroleum ether/EtOAc = 5/1) to afford compound **2d** (9.1 mg, yield 77%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.01 (m, 1H), 7.98 – 7.91 (m, 2H), 7.57 – 7.46 (m, 5H), 6.86 (s, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 178.75, 163.48, 154.74,

135.39, 135.16, 132.11, 131.67, 129.18 (2C), 126.45 (2C), 125.24, 123.78, 118.00, 107.62, 21.10; HRMS-ESI *m*/*z* calculated for $C_{16}H_{12}O_2$ $[M+H]^+$ 237.0910, found 237.0901.

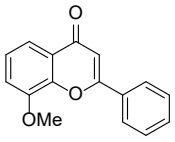
6,8-Di-*tert*-butyl-2-phenyl-4*H*-chromen-4-one (2e)



2e

To 1-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (**1e**, 16.7 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 2.5 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated then purified using silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford compound **2e** (14 mg, yield 79%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 2.4 Hz, 1H), 8.01 – 7.94 (m, 2H), 7.75 (d, J = 2.4 Hz, 1H), 7.64 – 7.50 (m, 3H), 6.86 (s, 1H), 1.60 (s, 9H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.33, 163.50, 153.53, 147.93, 138.60, 132.40, 131.65, 129.37 (2C), 129.32, 126.62 (2C), 119.91, 107.37, 35.44, 35.19, 31.51 (3C), 30.44 (3C); HRMS-ESI *m*/*z* calculated for $C_{23}H_{26}O_2$ $[M+H]^+$ 335.2006, found 335.2000.

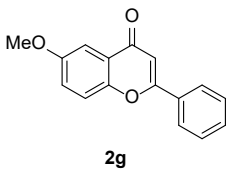
8-Methoxy-2-phenyl-4*H*-chromen-4-one (2f)[15]



2f

To 1-(2-hydroxy-3-methoxyphenyl)-3-phenylprop-2-yn-1-one (**1f**, 12.6 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 8 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated then purified using silica gel column chromatography (petroleum ether/EtOAc = 5/1) to afford compound **2f** (11.6 mg, yield 92%) as a light-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.77 (dd, J = 8.1, 1.5 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.33 (t, J = 8.0 Hz, 1H), 7.19 (dd, J = 8.0, 1.4 Hz, 1H), 6.84 (s, 1H), 4.03 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 178.68, 149.29, 146.84, 132.00, 131.73, 129.20 (3C), 126.54 (2C), 125.13, 125.00, 116.61, 114.60, 107.52, 56.54; HRMS-ESI *m*/*z* calculated for $C_{16}H_{12}O_3$ $[M+H]^+$ 253.0859, found 253.0853.

6-Methoxy-2-phenyl-4*H*-chromen-4-one (2g)[15]

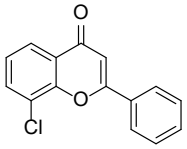


2g

To 1-(2-hydroxy-5-methoxyphenyl)-3-phenylprop-2-yn-1-one (**1g**, 12.6 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 5 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated then purified using silica gel column

chromatography (petroleum ether/EtOAc = 5/1) to afford compound **2g** (11.7 mg, yield 93%) as a light-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.89 (m, 2H), 7.61 (d, J = 3.1 Hz, 1H), 7.58 – 7.50 (m, 4H), 7.31 (dd, J = 9.1, 3.1 Hz, 1H), 6.86 (s, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.44, 163.37, 157.14, 151.22, 131.97, 131.62, 129.13 (2C), 126.36 (2C), 124.62, 123.98, 119.61, 106.91, 104.94, 56.05; HRMS-ESI *m*/*z* calculated for $C_{16}H_{12}O_3$ $[M+H]^+$ 253.0859, found 253.0849.

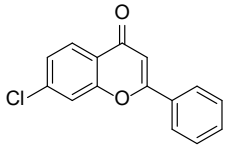
8-Chloro-2-phenyl-4*H*-chromen-4-one (2h)[15]



2h

To 1-(3-chloro-2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (**1h**, 12.8 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 2 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated to afford compound **2h** (12.3 mg, yield 96%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, J = 8.0, 1.6 Hz, 1H), 8.02 (dd, J = 7.6, 2.2 Hz, 2H), 7.77 (dd, J = 7.8, 1.6 Hz, 1H), 7.62 – 7.51 (m, 3H), 7.36 (t, J = 7.9 Hz, 1H), 6.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.95, 163.42, 152.05, 134.13, 132.12, 131.41, 129.32 (2C), 126.58 (2C), 125.49, 125.39, 124.46, 123.53, 107.47; HRMS-ESI *m*/*z* calculated for $C_{15}H_9ClO_2$ $[M+H]^+$ 257.0364, found 257.0356.

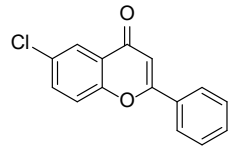
7-Chloro-2-phenyl-4*H*-chromen-4-one (2i)[16]



2i

To 1-(4-chloro-2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (**1i**, 12.8 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 2 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated to afford compound **2i** (12.2 mg, yield 95%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.5 Hz, 1H), 7.91 (dd, J = 7.9, 1.8 Hz, 2H), 7.62 (d, J = 1.9 Hz, 1H), 7.59 – 7.51 (m, 3H), 7.40 (dd, J = 8.5, 1.9 Hz, 1H), 6.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.68, 163.73, 156.50, 139.92, 131.99, 131.51, 129.27 (2C), 127.24, 126.43 (2C), 126.24, 122.65, 118.33, 107.92; HRMS-ESI *m*/*z* calculated for $C_{15}H_9ClO_2$ $[M+H]^+$ 257.0364, found 257.0354.

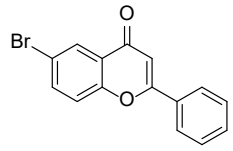
6-Chloro-2-phenyl-4*H*-chromen-4-one (2j)[15]



2j

To 1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (**1j**, 12.8 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 2 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated to afford compound **2j** (10.6 mg, yield 94%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 2.6 Hz, 1H), 7.98 – 7.86 (m, 2H), 7.65 (dd, J = 8.8, 2.7 Hz, 1H), 7.60 – 7.50 (m, 4H), 6.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.30, 163.83, 154.71, 134.09, 132.00, 131.54, 131.34, 129.25 (2C), 126.46 (2C), 125.31, 125.04, 119.94, 107.60; HRMS-ESI m/z calculated for $C_{15}H_9ClO_2$ $[M+H]^+$ 257.0364, found 257.0353.

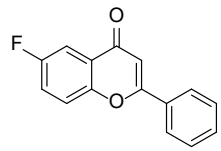
6-Bromo-2-phenyl-4*H*-chromen-4-one (2k)[15]



2k

To 1-(5-bromo-2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (**1k**, 15.1 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 2 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated to afford compound **2k** (13.8 mg, yield 92%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 2.5 Hz, 1H), 7.96 – 7.88 (m, 2H), 7.79 (dd, J = 8.9, 2.5 Hz, 1H), 7.61 – 7.51 (m, 3H), 7.48 (d, J = 8.9 Hz, 1H), 6.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.20, 163.86, 155.18, 136.89, 132.04, 131.56, 129.28 (2C), 128.56, 126.49 (2C), 125.45, 120.20, 118.84, 107.74; HRMS-ESI m/z calculated for $C_{15}H_9BrO_2$ $[M+H]^+$ 300.9859, found 300.9847.

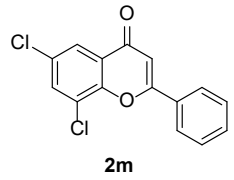
6-Fluoro-2-phenyl-4*H*-chromen-4-one (2l)[15]



2l

To 1-(5-fluoro-2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (**1l**, 12 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 2 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated to afford compound **2l** (10.3 mg, yield 86%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.88 (dd, J = 8.1, 3.0 Hz, 1H), 7.63 – 7.51 (m, 4H), 7.47 – 7.40 (m, 1H), 6.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.76, 163.84, 160.97, 158.52, 152.60 (d, J = 1.8 Hz), 131.80 (d, J = 27.3 Hz), 129.24 (2C), 126.46 (2C), 125.31 (d, J = 7.3 Hz), 122.05 (d, J = 25.5 Hz), 120.31 (d, J = 8.0 Hz), 110.79 (d, J = 23.6 Hz), 107.03; HRMS-ESI m/z calculated for $C_{15}H_9FO_2$ $[M+H]^+$ 241.0660, found 241.0646.

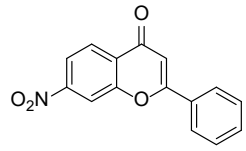
6,8-Dichloro-2-phenyl-4*H*-chromen-4-one (2m)[17]



2m

To 1-(3,5-dichloro-2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (**1m**, 14.6 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 5 minutes at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated to afford compound **2m** (13.8 mg, yield 95%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 2.5 Hz, 1H), 8.02 – 7.96 (m, 2H), 7.75 (d, J = 2.5 Hz, 1H), 7.61 – 7.53 (m, 3H), 6.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.69, 163.69, 150.68, 133.97, 132.37, 131.09, 131.06, 129.40 (2C), 126.61 (2C), 125.92, 124.68, 124.08, 107.40; HRMS-ESI *m*/*z* calculated for $C_{15}H_8Cl_2O_2$ $[M+H]^+$ 290.9974, found 290.9960.

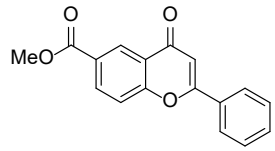
7-Nitro-2-phenyl-4*H*-chromen-4-one (2n)[18]



2n

To 1-(2-hydroxy-4-nitrophenyl)-3-phenylprop-2-yn-1-one (**1n**, 13.4 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 5 minutes at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated to afford compound **2n** (12.9 mg, yield 97%) as a white solid. ^{1}H NMR (400MHz, $CDCl_3$) δ 8.49 (d, J = 2.1 Hz, 1H), 8.41 (d, J = 8.7 Hz, 1H), 8.24 (dd, J = 8.7, 2.1 Hz, 1H), 8.00 – 7.92 (m, 2H), 7.65 – 7.54 (m, 3H), 6.92 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.97, 164.94, 155.76, 150.81, 132.54, 130.94, 129.45 (2C), 127.95, 127.85, 126.59 (2C), 119.63, 114.66, 108.41; HRMS-ESI *m*/*z* calculated for $C_{15}H_9NO_4$ $[M+Na]^+$ 290.0424, found 290.0415.

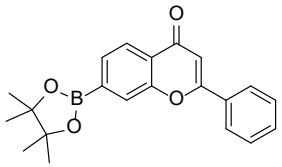
Methyl 4-oxo-2-phenyl-4H-chromene-6-carboxylate (2o)[19]



2o

To methyl 4-hydroxy-3-(3-phenylpropioloyl)benzoate (**1o**, 14.0 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 5 minutes at room temperature. The DMSO was evaporated to afford compound **2o** (quantitative yield) as a white solid. ^{1}H NMR (400MHz, $CDCl_3$) δ 8.93 (d, J = 2.1 Hz, 1H), 8.37 (dd, J = 8.8, 2.2 Hz, 1H), 7.94 (dd, J = 7.7, 1.8 Hz, 2H), 7.64 (d, J = 8.8 Hz, 1H), 7.60 – 7.52 (m, 3H), 6.87 (s, 1H), 3.97 (s, 3H).

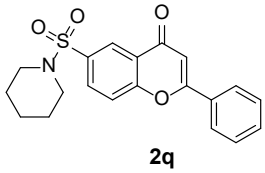
2-Phenyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-chromen-4-one (2p)[20]



2p

To 1-(2-Hydroxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-3-phenylprop-2-yn-1-one (**1p**, 17.4 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 24 h at 120 °C. The DMSO was evaporated to afford compound **2n** (quantitative yield) as a white solid. ^{1}H NMR (400MHz, $CDCl_3$) δ 8.21 (d, J = 7.8 Hz, 1H), 8.05 (s, 1H), 7.97 – 7.93 (m, 2H), 7.82 (d, J = 7.8 Hz, 1H), 7.52 (dd, J = 9.1, 3.6 Hz, 3H), 6.94 (s, 1H), 1.38 (s, 12H).

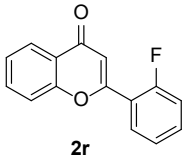
2-Phenyl-6-(piperidin-1-ylsulfonyl)-4*H*-chromen-4-one (2q)



2q

To 1-(2-hydroxy-5-(piperidin-1-ylsulfonyl)phenyl)-3-phenylprop-2-yn-1-one (**1q**, 18.5 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 6 h at room temperature. The DMSO was evaporated to afford compound **2q** (quantitative yield) as a white solid. ^{1}H NMR (400MHz, $CDCl_3$) δ 8.61 (d, J = 2.2 Hz, 1H), 8.07 (dd, J = 8.7, 2.3 Hz, 1H), 7.97 – 7.90 (m, 2H), 7.72 (d, J = 8.8 Hz, 1H), 7.61 – 7.53 (m, 3H), 6.89 (s, 1H), 3.09 – 3.02 (m, 4H), 1.69 – 1.63 (m, 4H), 1.46 – 1.40 (m, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ δ 177.26, 164.16, 158.20, 134.05, 132.53, 132.34, 131.18, 129.39 (2C), 126.56 (2C), 126.36, 124.10, 119.49, 108.11, 47.18 (2C), 25.26 (2C), 23.60; HRMS-ESI *m*/*z* calculated for $C_{20}H_{19}NO_4S$ $[M+H]^+$ 370.1108, found 370.1108.

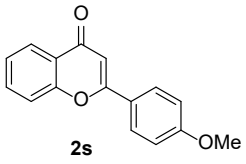
2-(2-Fluorophenyl)-4*H*-chromen-4-one (2r)[21]



2r

To 3-(2-fluorophenyl)-1-(2-hydroxyphenyl)prop-2-yn-1-one (**1r**, 12.0 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 2 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated to afford compound **2r** (10.7 mg, yield 89%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 – 8.18 (m, 1H), 8.03 – 7.90 (m, 1H), 7.83 – 7.68 (m, 1H), 7.62 – 7.50 (m, 2H), 7.50 – 7.41 (m, 1H), 7.39 – 7.31 (m, 1H), 7.26 – 7.20 (m, 1H), 6.94 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.51, 161.93, 159.38, 158.94, 156.47, 134.00, 133.01 (d, J = 8.8 Hz), 129.16, 125.84, 125.40, 124.75 (d, J = 3.8 Hz), 123.93, 118.19, 117.08 (d, J = 23.1 Hz), 112.52 (d, J = 12.0 Hz); HRMS-ESI *m*/*z* calculated for $C_{15}H_9FO_2$ $[M+H]^+$ 241.0660, found 241.0651.

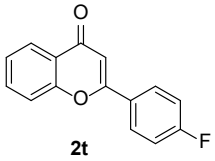
2-(4-Methoxyphenyl)-4*H*-chromen-4-one (2s)[14, 22]



2s

To 1-(2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-yn-1-one (**1s**, 12.6 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 2 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated to afford compound **2s** (11.1 mg, yield 88%) as a light-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.20 (m, 1H), 7.95 – 7.87 (m, 2H), 7.74 – 7.66 (m, 1H), 7.61 – 7.53 (m, 1H), 7.42 (ddd, J = 8.1, 7.1, 1.1 Hz, 1H), 7.08 – 7.00 (m, 2H), 6.79 (s, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.52, 163.63, 162.60, 156.35, 133.73, 128.18 (2C), 125.82, 125.24, 124.16, 124.05, 118.10, 114.63 (2C), 106.30, 55.65; HRMS-ESI m/z calculated for $C_{16}H_{12}O_3$ $[M+H]^+$ 253.0859, found 253.0854.

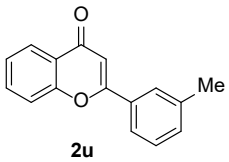
2-(4-Fluorophenyl)-4*H*-chromen-4-one (2t)[22]



2t

To 3-(4-fluorophenyl)-1-(2-hydroxyphenyl)prop-2-yn-1-one (**1t**, 12.0 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 2 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated to afford compound **2t** (11.2 mg, yield 93%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, J = 7.9, 1.7 Hz, 1H), 7.99 – 7.90 (m, 2H), 7.71 (ddd, J = 8.6, 7.2, 1.7 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.44 (td, J = 7.6, 0.9 Hz, 1H), 7.22 (t, J = 8.6 Hz, 2H), 6.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.43, 166.18, 163.66, 162.58, 156.34, 134.00, 128.66 (d, J = 8.9 Hz), 128.14 (d, J = 3.3 Hz), 125.90, 125.48, 124.01, 118.15, 116.56, 116.34, 107.52 (d, J = 1.4 Hz); HRMS-ESI m/z calculated for $C_{15}H_9FO_2$ $[M+H]^+$ 241.0660, found 241.0648.

2-(*m*-Tolyl)-4*H*-chromen-4-one (2u)[22]

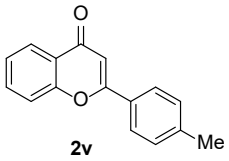


2u

To 1-(2-hydroxyphenyl)-3-(*m*-tolyl)prop-2-yn-1-one (**1u**, 11.8 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 2 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated to afford compound **2u** (10.6 mg, yield 90%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.22 (m, 1H), 7.76 – 7.67 (m, 3H), 7.58 (ddd, J = 8.5, 1.1, 0.4 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.39 – 7.33 (m, 1H), 6.82 (s, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.62, 163.83, 156.46, 139.01, 133.88, 132.58, 131.91, 129.10, 127.03, 125.86, 125.35, 124.12, 123.69, 118.24,

107.70, 21.66; HRMS-ESI *m*/*z* calculated for $C_{16}H_{12}O_2$ $[M+H]^+$ 237.0910, found 237.0906.

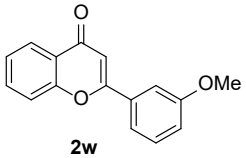
2-(*p*-Tolyl)-4*H*-chromen-4-one (2v)[22]



2v

To 1-(2-hydroxyphenyl)-3-(*p*-tolyl)prop-2-yn-1-one (**1v**, 11.8 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 2 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated to afford compound **2v** (10.8 mg, yield 91%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, J = 8.0, 1.6 Hz, 1H), 7.86 – 7.80 (m, 2H), 7.72 – 7.66 (m, 1H), 7.57 (dd, J = 8.4, 0.7 Hz, 1H), 7.42 (ddd, J = 8.1, 7.1, 1.1 Hz, 1H), 7.37 – 7.31 (m, 2H), 6.82 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 178.62, 163.84, 156.40, 142.44, 133.83, 129.92 (2C), 129.09, 126.40 (2C), 125.83, 125.30, 124.09, 118.20, 107.09, 21.68; HRMS-ESI *m*/*z* calculated for $C_{16}H_{12}O_2$ $[M+H]^+$ 237.0910, found 237.0901.

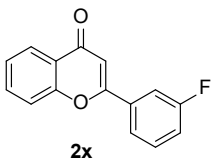
2-(3-Methoxyphenyl)-4*H*-chromen-4-one (2w)[16]



2w

To 1-(2-hydroxyphenyl)-3-(3-methoxyphenyl)prop-2-yn-1-one (**1w**, 12.6 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 2 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated then purified using silica gel column chromatography (petroleum ether/EtOAc = 4/1) to afford compound **2w** (10.7 mg, yield 85%) as a light-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, J = 8.0, 1.7 Hz, 1H), 7.71 (ddd, J = 8.5, 7.1, 1.7 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.53 (ddd, J = 7.7, 1.6, 0.7 Hz, 1H), 7.48 – 7.40 (m, 3H), 7.09 (ddd, J = 8.2, 2.6, 0.9 Hz, 1H), 6.84 (s, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.63, 163.46, 160.19, 156.42, 133.97, 133.30, 130.30, 125.87, 125.42, 124.10, 118.92, 118.26, 117.37, 111.94, 107.95, 55.64; HRMS-ESI *m*/*z* calculated for $C_{16}H_{12}O_3$ $[M+H]^+$ 253.0859, found253.0854.

2-(3-Fluorophenyl)-4*H*-chromen-4-one (2x)[15]

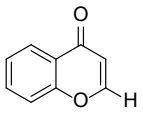


2x

To 3-(3-fluorophenyl)-1-(2-hydroxyphenyl)prop-2-yn-1-one (**1x**, 12.0 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 2 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated then purified using silica gel column

chromatography (petroleum ether/EtOAc = 5/1) to afford compound **2x** (10.9 mg, yield 91%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.21 (m, 1H), 7.75 – 7.69 (m, 2H), 7.65 (ddd, J = 9.7, 2.5, 1.7 Hz, 1H), 7.58 (ddd, J = 8.5, 1.0, 0.5 Hz, 1H), 7.51 (td, J = 8.1, 5.7 Hz, 1H), 7.44 (ddd, J = 8.1, 7.1, 1.1 Hz, 1H), 7.28 – 7.22 (m, 1H), 6.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.43, 164.42, 162.04 (d, J = 2.9 Hz), 161.96, 156.32, 134.14, 130.89 (d, J = 8.2 Hz), 125.92, 125.58, 124.09, 122.13 (d, J = 3.3 Hz), 118.66 (d, J = 21.3 Hz), 118.24, 113.51 (d, J = 23.9 Hz), 108.30; HRMS-ESI m/z calculated for $C_{15}H_9FO_2$ $[M+H]^+$ 241.0660, found 241.0649.

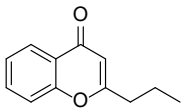
4*H*-Chromen-4-one (2y)[3]



2y

To 1-(2-hydroxyphenyl)prop-2-yn-1-one (**1y**, 7.3 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 30 minutes at room temperature. The reaction mixture (DMSO) was concentrated to afford compound **2y** (quantitative yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, J = 8.0, 1.7 Hz, 1H), 7.86 (d, J = 6.0 Hz, 1H), 7.68 (ddd, J = 8.7, 7.1, 1.7 Hz, 1H), 7.43 (ddd, J = 15.2, 8.3, 0.8 Hz, 2H), 6.35 (d, J = 6.1 Hz, 1H).

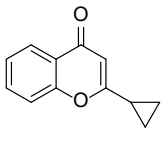
2-Propyl-4*H*-chromen-4-one (2z)[3]



2z

To 1-(2-hydroxyphenyl)hex-2-yn-1-one (**1z**, 9.4 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 5 minutes at room temperature. The reaction mixture (DMSO) was concentrated to afford compound **2z** (quantitative yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, J = 8.0, 1.6 Hz, 1H), 7.64 (ddd, J = 8.7, 7.1, 1.7 Hz, 1H), 7.46 – 7.35 (m, 2H), 6.20 (s, 1H), 2.63 – 2.58 (m, 2H), 1.78 (dt, J = 14.7, 7.4 Hz, 2H), 1.03 (t, J = 7.4 Hz, 3H).

2-Cyclopropyl-4*H*-chromen-4-one (2aa)[23]

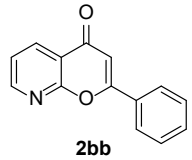


2aa

To 3-cyclopropyl-1-(2-hydroxyphenyl)prop-2-yn-1-one (**1aa**, 9.3 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 2 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated to afford compound **2aa** (8.4 mg, yield 90%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, J = 8.3, 1.7 Hz, 1H), 7.65 – 7.58 (m, 1H), 7.39 – 7.33 (m, 2H), 6.21 (s, 1H), 1.90 (tt, J = 8.3, 5.0 Hz, 1H), 1.20 – 1.07 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.82, 170.37, 156.20, 133.33, 125.81,

125.01, 124.06, 117.68, 107.97, 14.67, 8.67 (2C); HRMS-ESI *m*/*z* calculated for $C_{12}H_{10}O_2$ $[M+H]^+$ 187.0754, found 187.746.

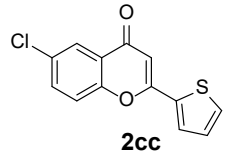
2-Phenyl-4*H*-pyrano[2,3-*b*]pyridin-4-one (2bb)[24]



2bb

To 1-(2-hydroxypyridin-3-yl)-3-phenylprop-2-yn-1-one (**1bb**, 11.2 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 2 h at room temperature. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated to afford compound **2bb** (9.8 mg, yield 88%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, J = 4.6, 2.0 Hz, 1H), 8.59 (dd, J = 7.7, 2.0 Hz, 1H), 8.05 – 7.94 (m, 2H), 7.60 – 7.42 (m, 4H), 6.86 (s, 1H).

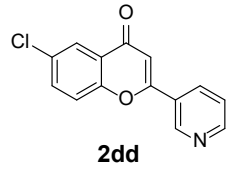
6-Chloro-2-(thiophen-2-yl)-4*H*-chromen-4-one (2cc)



2cc

To 1-(5-chloro-2-hydroxyphenyl)-3-(thiophen-2-yl)prop-2-yn-1-one (**1cc**, 13.1 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 5 minutes at room temperature. The reaction solvent was evaporated to afford compound **2cc** (13 mg, yield 99%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 2.6 Hz, 1H), 7.72 (dd, J = 3.8, 1.1 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.48 (d, J = 8.9 Hz, 1H), 7.19 (dd, J = 5.0, 3.8 Hz, 1H), 6.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.73, 159.46, 154.33, 134.84, 134.05, 131.40, 130.85, 128.95, 128.75, 125.31, 125.02, 119.77, 106.11; HRMS-ESI *m*/*z* calculated for $C_{13}H_7ClO_2S$ $[M+H]^+$ 262.9929, found 262.9928.

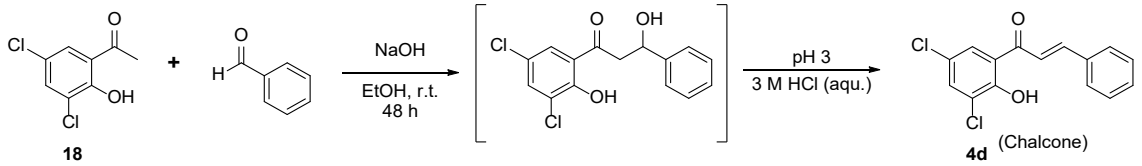
6-Chloro-2-(pyridin-3-yl)-4H-chromen-4-one (2dd)



2dd

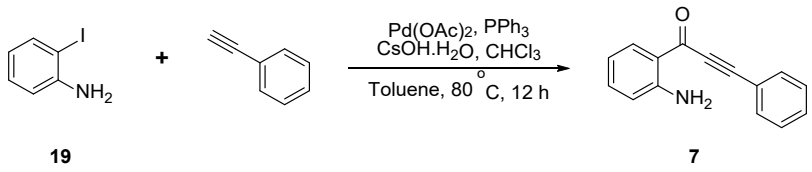
To 1-(2-hdroxyphenyl)-3-(pyridin-3-yl)prop-2-yn-1-one (**1dd**, 19.9 mg, 0.05 mmol) was added DMSO (1 mL) and stirred for 7 h at 80 °C. The reaction mixture was quenched with water and extracted with EtOAc. Combined EtOAc layer was dried over $MgSO_4$, filtered, and concentrated then purified using silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford compound **2dd** (9.8 mg, yield 76%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.33 (dd, J = 2.3, 0.6 Hz, 1H), 8.80 (dd, J = 4.8, 1.6 Hz, 1H), 8.53 (ddd, J = 8.1, 2.3, 1.6 Hz, 1H), 7.98 (dd, J = 2.0, 1.1 Hz, 1H), 7.93 – 7.88 (m, 2H), 7.65 (ddd, J = 8.1, 4.9, 0.8 Hz, 1H), 7.25 (d, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 175.95, 160.99, 154.36, 152.21, 147.38, 134.39, 134.28, 130.14, 127.14, 124.51, 124.08, 123.84, 121.26, 107.86; HRMS-ESI *m*/*z* calculated for $C_{14}H_8ClNO_2$ $[M+H]^+$ 258.0317, found 258.0316.

3. Preparation of chalcone substrate 4d.[25]



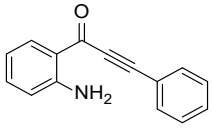
To a stirring solution of 3,5-dichloro-2-hydroxyacetophenone (**18**) (4.9 mmol) in EtOH (16.0 mL) was added benzaldehyde (4.9 mmol) at room temperature. After 5 min of stirring, the pallets of NaOH (14.6 mmol) were added then stirring continued for 48 h. The pH of the reaction mixture was adjusted to 5 using 3M HCl aqueous solution. The yellow precipitate obtained was collected by simple filtration, washed with EtOH and vacuum dried. Thus, obtained crude product was further dissolved in Et_2O then insoluble matters were filtered off. Filtrate was concentrated to afford the 3,5-dichloro-2-hydroxychalcone (**4d**) as yellow solid (73% yield).

4. Preparation of amine substrate 7.[26]



To a stirring solution of 2-iodoaniline (**19**) (0.5 mmol) in toluene (5.0 mL) was added phenylacetylene (0.6 mmol), $Pd(OAc)_2$ (0.013 mmol), PPh_3 (0.05 mmol), $CsOH{\cdot}H_2O$ and $CHCl_3$ (1.5 mmol) at room temperature. The resulting mixture was stirred at 80 °C for 12 h. The reaction mixture was cooled to room temperature, filtered through a pad of celite and then the filtrate was concentrated. The crude residue was purified by silica gel column chromatography (eluent, Hex/EtOAc: 10/1) to afford the aniline substrate **7** as a yellow solid (61% yield).

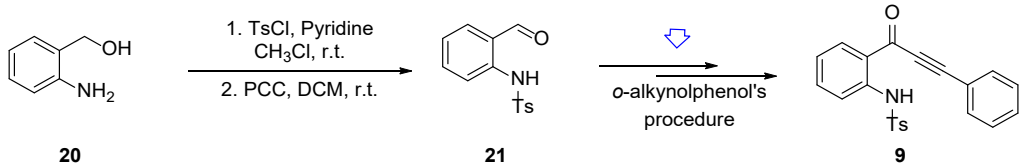
1-(2-aminophenyl)-3-phenylprop-2-yn-1-one (**7**)[27]



7

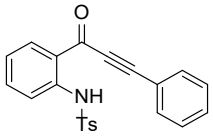
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, J = 8.1, 1.4 Hz, 1H), 7.67 (dd, J = 8.1, 1.3 Hz, 2H), 7.56 – 7.38 (m, 3H), 7.38 – 7.29 (m, 1H), 6.80 – 6.70 (m, 1H), 6.67 (d, J = 8.3 Hz, 1H), 6.33 (Br s, 1H).

5. Preparation of Ts-amine substrate 9



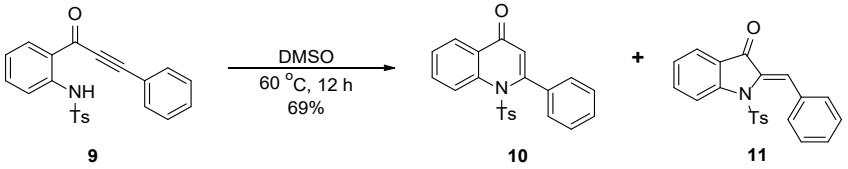
N-(2-Formylphenyl)-4-methylbenzenesulfonamide (**21**) was first prepared by reported method [28] then Ts-amide substrate **9** was obtained similar to *o*-alkynoylphenols.

4-Methyl-*N*-(2-(3-phenylpropioloyl)phenyl)benzenesulfonamide (9)[29]



9

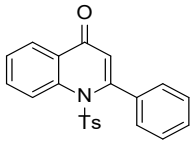
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.99 (s, 1H), 8.32 (d, J = 7.9 Hz, 1H), 7.86 – 7.79 (m, 2H), 7.78 – 7.72 (m, 2H), 7.69 – 7.60 (m, 2H), 7.54 (ddd, J = 6.7, 4.5, 1.2 Hz, 2H), 7.48 (d, J = 7.9 Hz, 1H), 7.38 (d, J = 8.1 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 2.33 (s, 3H).



9 **10** **11**

The substrate **9** (0.05 mmol) obtained from the previous step was dissolved in DMSO (1.0 mL) then stirred at 60 °C for 12 h to obtain 69% of 6-*endo*-dig product **10** along with 5-*exo*-dig product **11**.

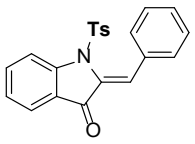
2-Phenyl-1-tosylquinolin-4(1*H*)-one (10)[30]



10

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 8.1 Hz, 1H), 7.94 (dd, J = 7.8, 1.6 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.71 – 7.66 (m, 1H), 7.55 – 7.48 (m, 3H), 7.47 – 7.42 (m, 1H), 7.10 – 7.02 (m, 4H), 6.45 (s, 1H), 2.31 (s, 3H).

(*E*)-2-Benzylidene-1-tosylindolin-3-one (11)[30]

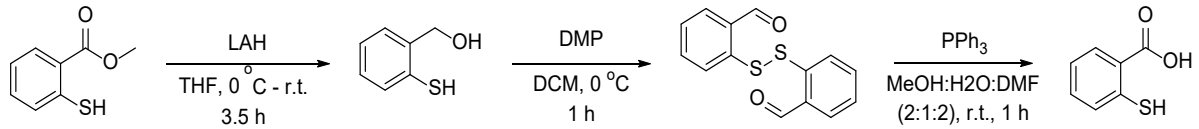


11

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dt, J = 8.4, 0.7 Hz, 1H), 8.00 (s, 1H), 7.90 – 7.85 (m, 2H), 7.73 – 7.60 (m, 2H), 7.47 – 7.41 (m, 5H), 7.14 (dd, J = 7.5, 6.9 Hz, 2H), 2.33 (s, 3H).

6. Preparation of thiol substrate 8

1. Preparation of 2-mercaptobenzaldehyde **25**.[31-34]

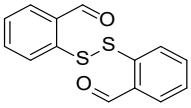


22 **23** **24** **25**

To methylthiosalicylate (**22**) (3.0 mmol) in THF (5.0 mL) was added LAH (9.0 mmol) portion wise over 30 min. at 0 °C and stirred at room temperature for 3 h. The mixture was quenched with NH_4Cl solution at 0 °C and allowed to stir for 30 min. The solid precipitate formed was filtered off using a pad of celite. Filtrate was extracted with DCM. Combined organic layer was dried over $MgSO_4$, filtered and concentrated to afford (2-mercaptophenyl)methanol (**23**) as a white solid (crude product).

The crude **23** obtained from the first step was further dissolved in DCM (5.0 mL) then added DMP (2.1 mmol) portion wise at 0 °C. The resulting mixture was stirred at room temperature for 1 h followed by dilution with DCM and $NaHCO_3$ solution. The mixture was extracted with DCM, dried over $MgSO_4$, filtered and concentrated. The concentrated crude product was purified gel silica gel column chromatography (eluent, Hex/EtOAc: 5/1) to afford 2-mercaptobenzaldehyde dimmer **24** as a pale-yellow solid (56% yield for two steps).

2,2'-Disulfanediyldibenzaldehyde (24)[35]

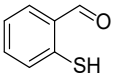


24

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 – 10.21 (m, 2H), 7.87 (dd, J = 7.5, 1.6 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.49 (ddd, J = 8.1, 7.4, 1.6 Hz, 2H), 7.39 (td, J = 7.4, 1.1 Hz, 2H).

The dimmer **24** (0.4 mmol) was further treated with PPh_3 (1.0 mmol) in a solvent mixture of MeOH:H_2O:DMF (2:1:2, 5.0 mL) at room temperature for 1 h. The reaction mixture was extracted with DCM then the combined organic layer was dried over $MgSO_4$, filtered and concentrated. Concentrated crude was purified by silica gel column chromatography (eluent, Hex/EtOAc : 4/1) to afford 2-mercaptobenzaldehyde (**25**) as a pale-yellow semi solid (82% yield).

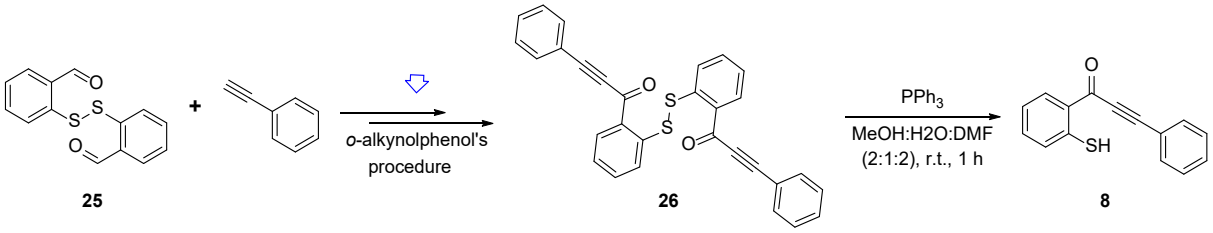
2-Mercaptobenzaldehyde (25)[34]



25

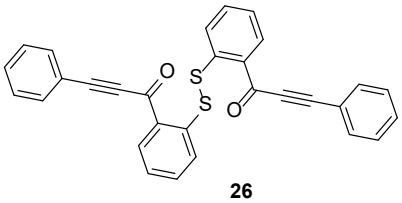
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.73 (dd, J = 7.6, 1.6 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.34 – 7.27 (m, 2H), 5.52 (s, 1H).

2. Thiol substrate **8**.[5, 31]



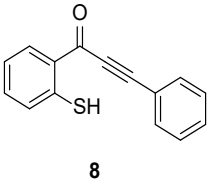
2-Mercaptobenzaldehyde dimmer **25** (0.7 mmol) as an aldehyde substrate was treated with phenylacetylene (2.2 mmol) in THF (5.0 mL) solution. The reaction mixture after workup was further oxidized with MnO_2 like the procedure used in *o*-alkynoylphenols preparation to afford A. Then compound A treating with PPh_3 gave thiol substrate 8.

1,1'-(Disulfanediylbis(2,1-phenylene))bis(3-phenylprop-2-yn-1-one) (26)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 – 8.43 (m, 2H), 7.85 (dd, J = 8.2, 0.8 Hz, 2H), 7.74 – 7.69 (m, 4H), 7.55 – 7.42 (m, 8H), 7.36 (dd, J = 4.1, 3.6 Hz, 2H).

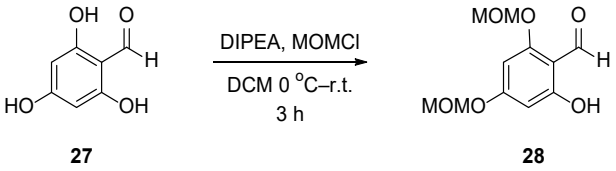
1-(2-Mercaptophenyl)-3-phenylprop-2-yn-1-one (8)[5]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.95 (ddd, J = 7.7, 1.3, 0.6 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.58 (dd, J = 7.1, 1.3 Hz, 1H), 7.51 (ddd, J = 12.4, 4.7, 3.5 Hz, 3H), 7.44 (d, J = 7.3 Hz, 1H), 7.35 – 7.29 (m, 1H).

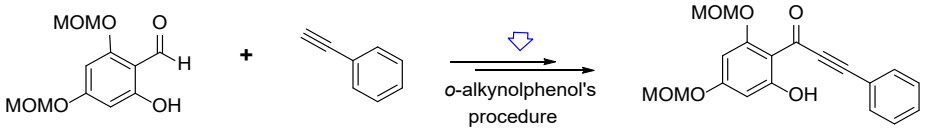
7. Preparation of natural products

A) Preparation of 5,7-dihydroxyflavone (**14**)



Following the literature procedure,[36] to a solution of compound **27** (6.5 mmol) in DCM (20 mL) was added DIPEA (16.2 mmol). After stirring the mixture at 0 °C for 10 min. under nitrogen atmosphere was added MOMCl (14.3 mmol) dropwise then stirred at r.t. for 3 h. The reaction mixture was concentrated, diluted with EtOAc, and washed with H_2O for three times. The organic

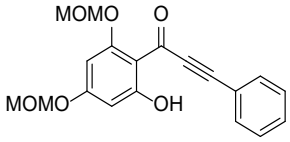
layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (Hex/EtOAc : 10/1) to afford 2-hydroxy-2,6-bis(methoxymethoxy)benzaldehyde (**28**)[37] as a pale-yellow solid (73% yield).



28 **12**

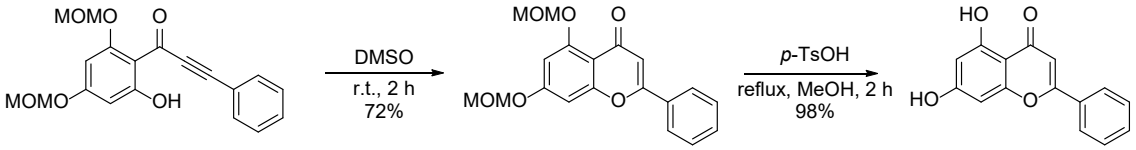
Compound **12** was prepared using the general procedure used for *o*-alkynoylphenol preparation from compound **28**.

1-(2-Hydroxy-4,6-bis(methoxymethoxy)phenyl)-3-phenylprop-2-yn-1-one (**12**)



12

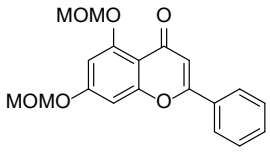
^{1}H NMR (400 MHz, $CDCl_3$) δ 13.29 (s, 1H), 7.66 – 7.60 (m, 2H), 7.42 (ddd, J = 13.0, 11.7, 7.2 Hz, 3H), 6.27 (dd, J = 9.4, 2.3 Hz, 2H), 5.30 (s, 2H), 5.20 (s, 2H), 3.52 (s, 3H), 3.49 (s, 3H).



12 **13** **14**

Compound **12** (0.1 mmol) obtained from the previous step was simply dissolved in DMSO (2.0 mL) which led to full cyclization to compound **13** in 2 h with 72% isolated yield. The compound **13** (0.05 mmol) further refluxed with *p*-TsOH (0.1 mmol) in MeOH (2.0 mL) afforded 5,7-dihydroxyflavone (**14**) as a pale-yellow solid (98% yield).

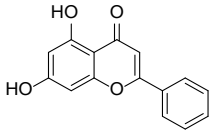
5,7-bis(Methoxymethoxy)-2-phenyl-4*H*-chromen-4-one (**13**)[38]



13

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 5.2, 3.4 Hz, 2H), 7.48 – 7.40 (m, 2H), 7.38 (dd, J = 4.9, 3.6 Hz, 1H), 6.77 (s, 1H), 6.64 (d, J = 1.8 Hz, 1H), 6.52 (d, J = 1.8 Hz, 1H), 5.37 (s, 2H), 5.25 (s, 2H), 3.54 (s, 3H), 3.52 (s, 3H).

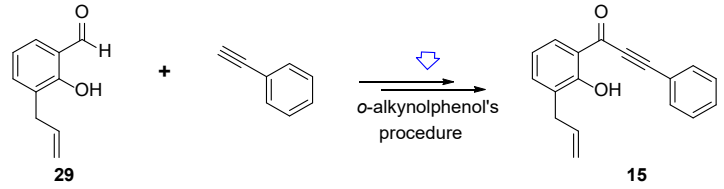
5,7-Dihydroxy-2-phenyl-4*H*-chromen-4-one (14)[39]



14

^{1}H NMR (400 MHz, MeOH-d_4) δ 7.87 (d, J = 7.3 Hz, 2H), 7.44 (t, J = 7.4 Hz, 2H), 7.38 (d, J = 7.2 Hz, 1H), 6.66 (s, 1H), 6.22 (s, 1H), 6.04 (s, 1H).

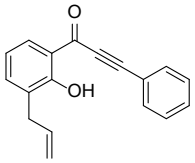
B) Preparation of flavone acetic acid (FAA, **17**)



29 **15**

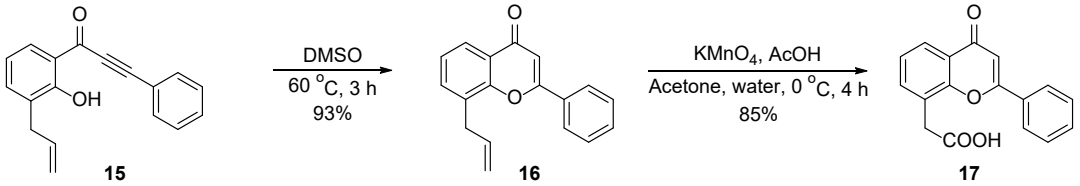
Compound **15** was prepared by using general procedure of o-alkynoylphenols. 3-Allyl-2-hydroxybenzaldehyde (**29**) (0.6 mmol) was treated with phenylacetylene (1.9 mmol) which was further oxidized with MnO_2 to afford compound **15** as white solid (65% yield).

1-(3-Allyl-2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (15)



15

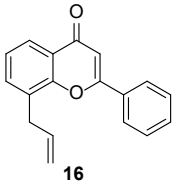
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.08 (d, J = 0.5 Hz, 1H), 8.02 (dd, J = 8.0, 1.7 Hz, 1H), 7.74 – 7.64 (m, 2H), 7.57 – 7.49 (m, 1H), 7.48 – 7.36 (m, 3H), 7.03 – 6.87 (m, 1H), 6.11 – 5.95 (m, 1H), 5.11 (dt, J = 12.6, 1.6 Hz, 2H), 3.45 (d, J = 6.6 Hz, 2H).



15 **16** **17**

Compound **15** (0.1 mmol) obtained from the previous step was simply dissolved in DMSO (2.0 mL) which led to full cyclization to compound **16** in 2 h with 93% isolated yield. Compound 16 (0.04 mmol) was further treated with $KMnO_4$ (2.8 mmol) as described in literature[40] to afford FAA (**17**) as a white solid (85% yield).

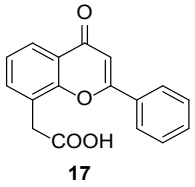
8-Allyl-2-phenyl-4*H*-chromen-4-one (16)[41]



16

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, J = 7.9, 1.7 Hz, 1H), 8.04 – 7.87 (m, 2H), 7.66 – 7.49 (m, 4H), 7.37 (t, J = 7.6 Hz, 1H), 6.90 (s, 1H), 6.19 – 6.01 (m, 1H), 5.25 – 5.11 (m, 2H), 3.78 (d, J = 6.5 Hz, 2H).

2-(4-Oxo-2-phenyl-4*H*-chromen-8-yl)acetic acid (17)[41]



17

^{1}H NMR (400 MHz, DMSO-d_6) δ 88.16 – 8.04 (m, 2H), 7.98 (dd, J = 7.9, 1.7 Hz, 1H), 7.76 (dd, J = 7.3, 1.7 Hz, 1H), 7.67 – 7.54 (m, 3H), 7.52 – 7.40 (m, 1H), 7.06 (s, 1H), 4.01 (s, 2H).

Real-time, reaction progress monitoring

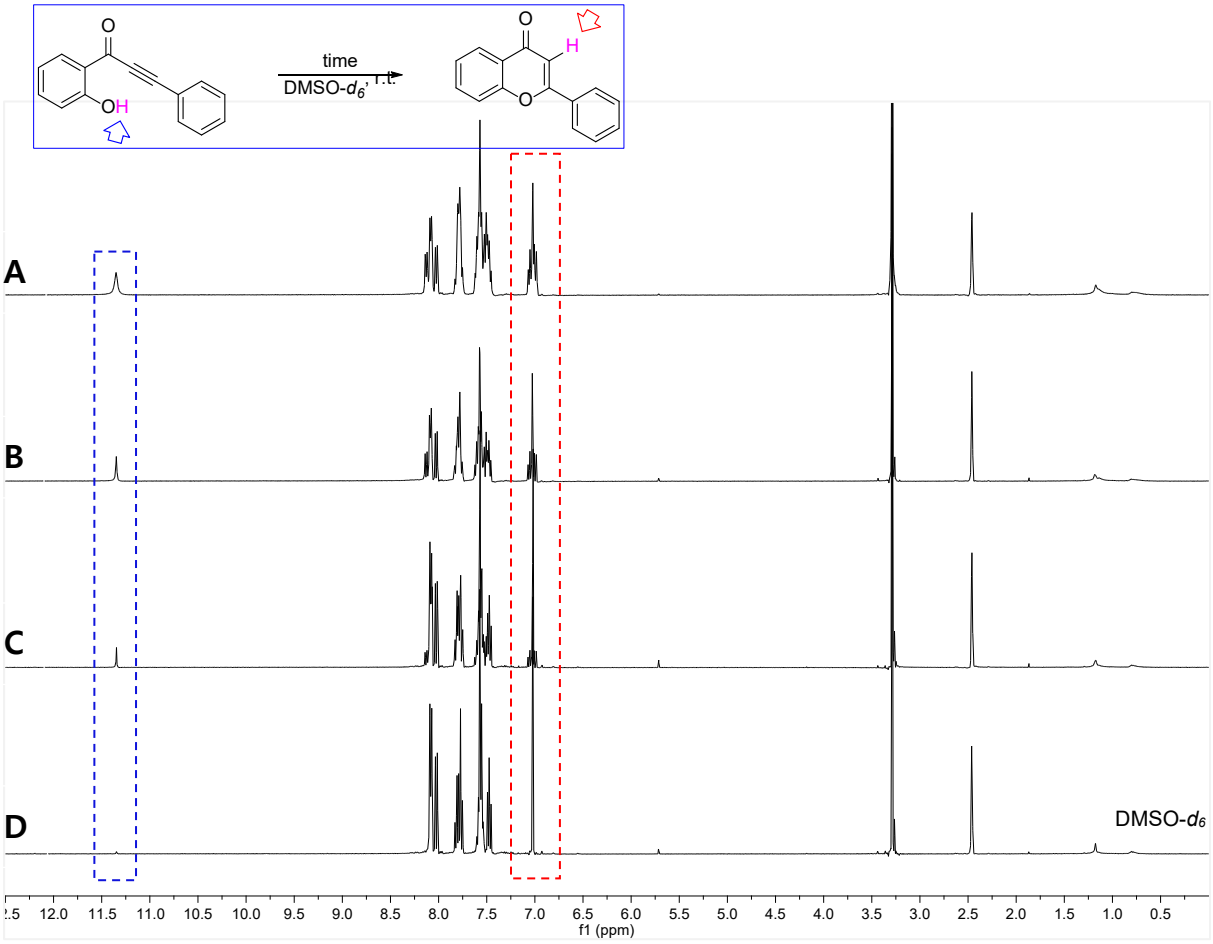
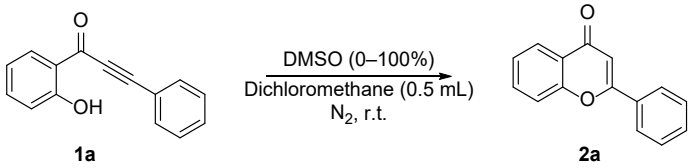


Fig. S1. Real-time reaction progress, monitored by ^{1}H NMR spectrometer (0.05M in DMSO-*d6*) (**A**) 0 min.; (**B**) 10 min.; (**C**) 30 min.; (**D**) 60 min.

Table S1. Determination of role of DMSO in *o*-hydroalkoxylation.[a]

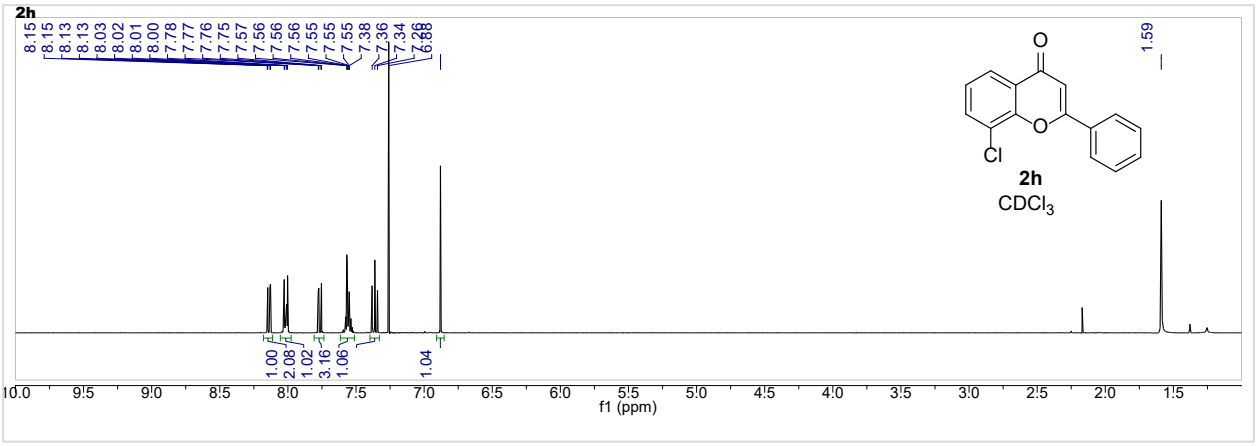


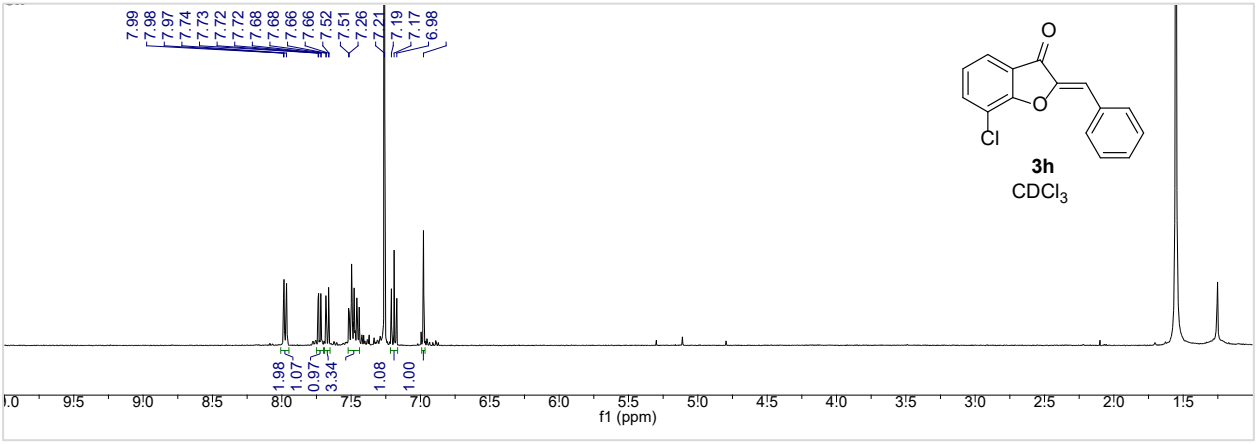
1a **2a**

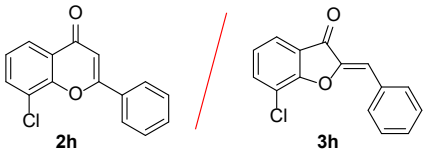
Entry	DMSO (v/v %)	Conv. (%)[b] / time
1	0	0 / 72 h
2	5	0 / 72 h
3	10	trace / 72 h
4	20	trace / 5 h
5	50	50 / 72 h
6	67	90 / 72 h
7	83	90 / 72 h
8	90	90 / 72 h
9	100	100 / 2 h

[a] DMSO (%) was calculated based on dichloromethane solvent volume (0.5 mL, 0.05 M).
[b] Conversion (%) was estimated by silica gel TLC and crude (reaction mixture) ^{1}H NMR observation based on **1a** consumption.

Evaluation of the water effect in DMSO reaction system

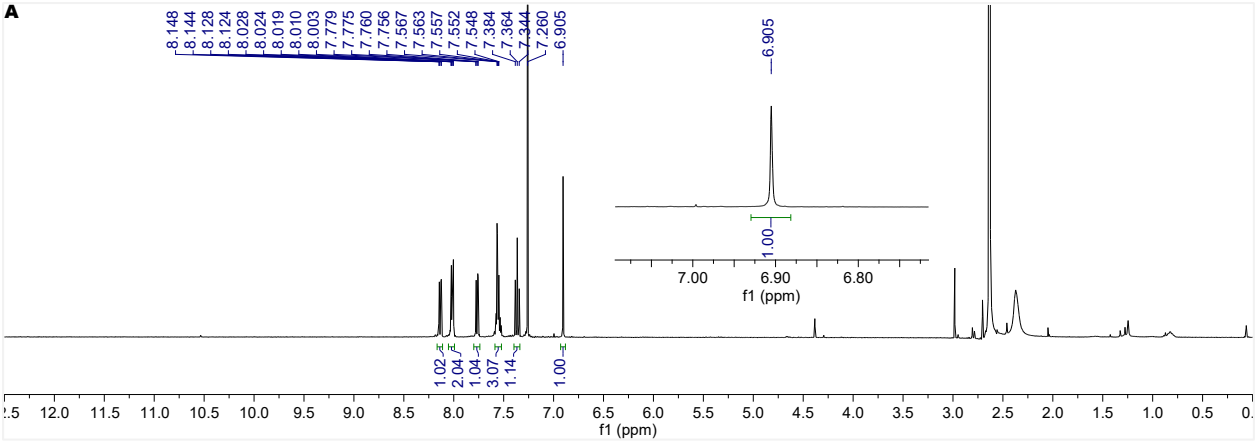


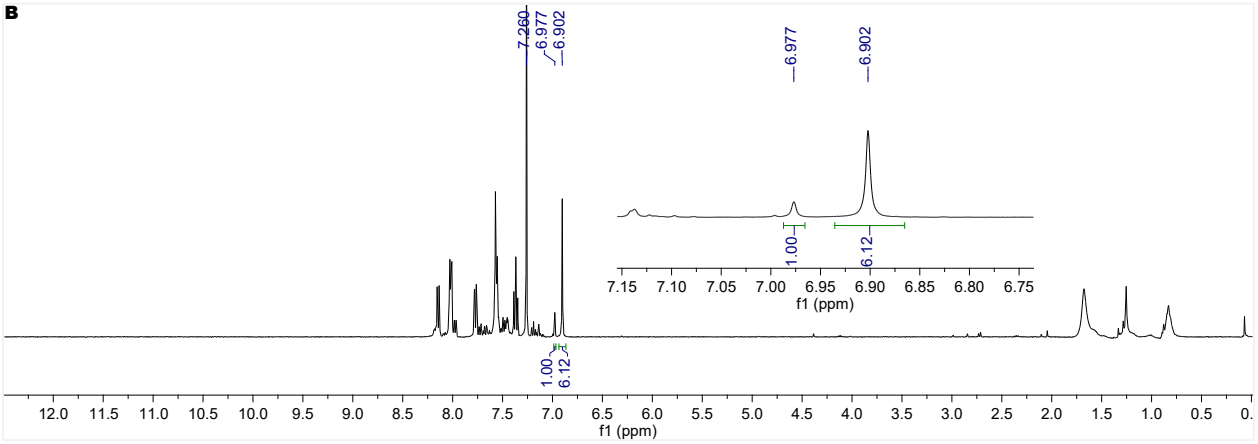


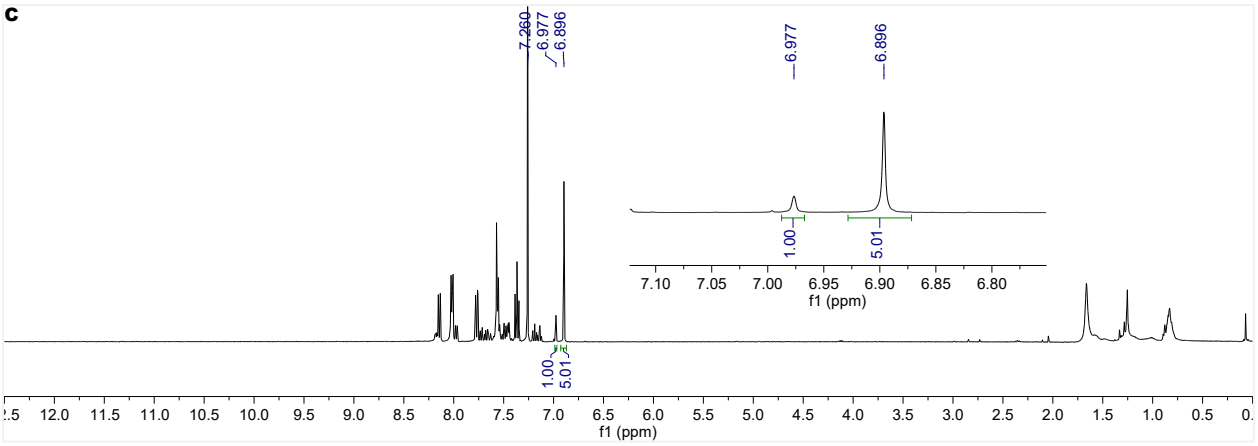


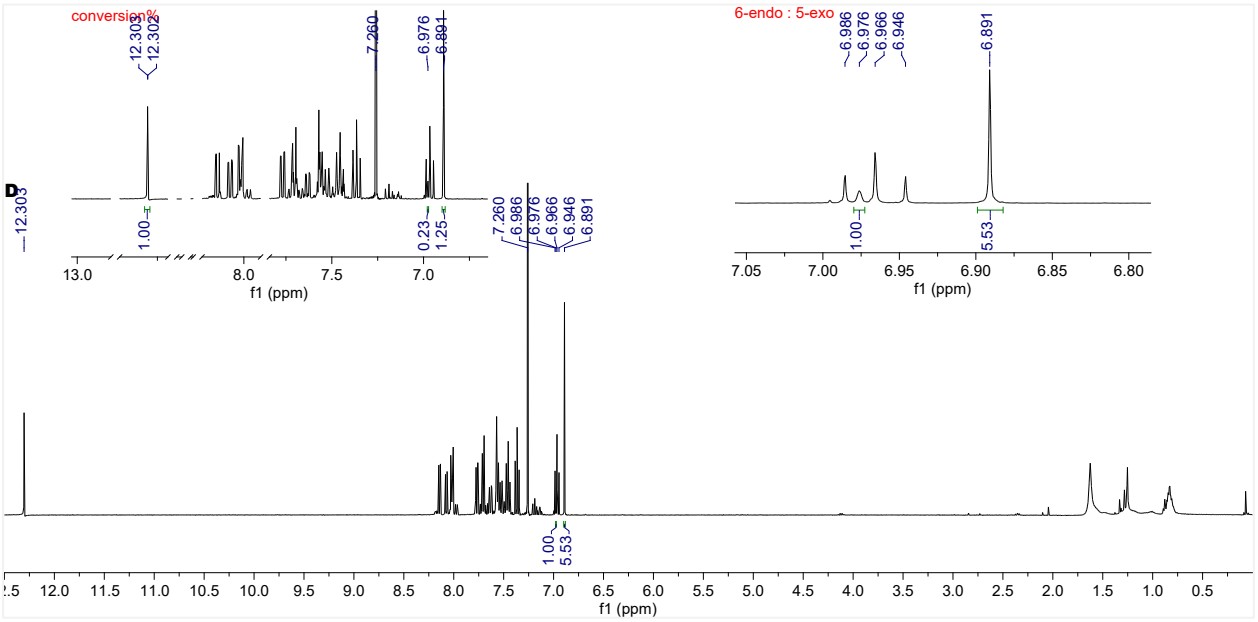
2h
6-*endo*-dig

3h
5-*exo*-dig






c
7.260
6.977
6.896
6.977
6.896
1.00
5.01
7.10 7.05 7.00 6.95 6.90 6.85 6.80
f1 (ppm)
1.00
5.01
f1 (ppm)


D
conversion%
12.303
12.302
7.260
6.976
6.891
12.303
1.00
0.23
1.25
13.0 8.0 7.5 7.0
f1 (ppm)
7.260
6.986
6.976
6.966
6.946
6.891
1.00
5.53
f1 (ppm)
6-endo : 5-exo
6.986
6.976
6.966
6.946
6.891
1.00
5.53
7.05 7.00 6.95 6.90 6.85 6.80
f1 (ppm)
1.00
5.53
f1 (ppm)

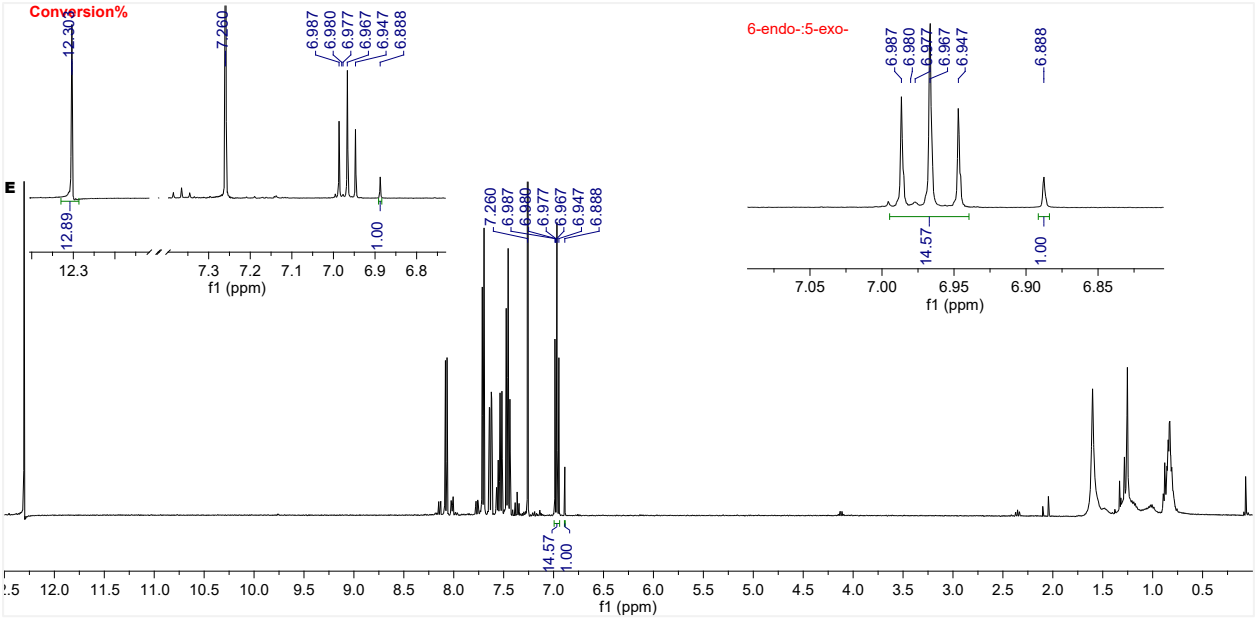
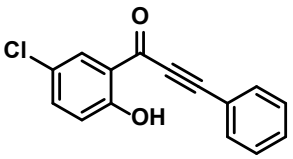


Fig. S2 All reactions were carried out using 0.15 mL of solvent in concentration of < 0.05 M where water was used as an additive in DMSO reaction mixture. (A) DMSO(100%), 2 h, r.t., 100% conversion, 6-*endo*- : 5-*exo*- (>99:1). (B) DMSO(75%+water), 2 h, r.t., 100% conversion, 6-*endo*- : 5-*exo*- (6:1). (C) DMSO(50%+water), 24 h, r.t., 100% conversion, 6-*endo*- : 5-*exo*- (5:1). (D) DMSO(25%+water), 24 h, r.t., 60% conversion, 6-*endo*- : 5-*exo*- (5:1). (E) DMSO(0%)+water(100%), 24 h, r.t., trace conversion, 6-*endo*- : 5-*exo*- (not determined).

III. Evaluation of green chemistry metrics for the synthesis



1j

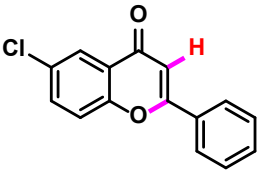
1.10 g

$C_{15}H_9ClO_2$

256.69

DMSO

r.t.. 2 h

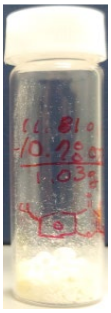


2j

1.03 g

$C_{15}H_9ClO_2$

256.69



Yield of desired product (2j) = **94%**

Atom Economy (%) = $\frac{\text{mass of desired product}}{\text{total mass of all reactants}} \times 100 = \frac{256.69}{256.69} \times 100 = 100\%$

Atom Efficiency (%) = (% yield of product x % atom economy) x 100 = (94% x 100%) x 100 = **94%**

Carbon Efficiency (%) = $\frac{\text{amount of carbon in desired product}}{\text{total amount of carbon presented in all reactants}} \times 100 = \frac{15}{15} \times 100 = 100\%$

Reaction Mass Efficiency (%) = $\frac{\text{mass of isolated product}}{\text{mass of all reactants}} \times 100 = \frac{1.03}{1.10} \times 100 = 93.6\%$

Reactant	**1-(5-chloro-2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (1j)**	**1.10 g**	**4.29 mmol**	**FW 256.69**
Solvent	**dimethyl sulfoxide**	**282 mL**	**49.9 mmol**	**FW 78.13**
Product	**6-chloro-2-phenyl-4*H*-chromen-4-one (2j)**	**1.03 g**	**4.01 mmol**	**FW 256.69**

DMSO recovered, 276.4 mL (based on solvent reclamation efficacy of Biotage® V-10 Touch system)
Actual amount of solvent used = (282 - 276.4) mL = 5.6 mL [6.1 g (*d* = 1.1 g/ml)]

E-factor = $\frac{\text{total waste (Kg)}}{\text{total product (kg)}} = \frac{(1.10 + 6.1) - 1.03}{1.03} = \frac{6.17}{1.03}$ = **6.0 Kg/Kg product** (based on DMSO recovered)

IV. Computational Details

Details of DFT calculations

To understand the factors controlling the selectivity of 6-*endo*-dig and 5-*exo*-dig cyclizations, we performed density functional theory (DFT) calculations for three cyclization reactions of **1a**, **1m** (with di-chloro substitutions in the phenolic ring), and **8** (with the thiol substitution in the phenolic ring) in DMSO.

GaussView[42] was used to build all initial structures. All DFT calculations were carried out at the M06-2X/def2-TZVP//PCM M06-2X/6-31+G(d) level of theory using the M06-2X functional[43] and the polarizable continuum model (PCM)[44] for solvation free energies in DMSO implemented in the Gaussian 09 program.[45] The M06-2X is a hybrid-meta-GGA functional with an improved medium-range correlation energy. For all structures of the reactant complex (RC), the transition state (ts), and the product complex (PC) optimized at the PCM M06-2X/6-31+G(d) level of theory in DMSO, the relative energies (ΔE_s) of each structure in DMSO were calculated as the sum of the relative single-point energy ($\Delta E_{0,dTZ}$) at the M06-2X/def2-TZVP level of theory and the relative solvation free energies ($\Delta\Delta G_s$) obtained at the PCM M06-2X/6-31+G(d) level of theory in DMSO. The intrinsic reaction coordinate (IRC) method[46] was often used to verify a transition state whether it connects the reactants and products. However, as in most cases, the IRC calculation did not step all the way to the minimum on either side of the path, especially for large molecules studied in the present work and further optimizations were followed.

Vibrational frequencies were calculated for all RC, ts, and PC at the PCM M06-2X/6-31+G(d) level of theory in DMSO at 25 °C and 1 atm. The scale factor used is 0.9440 that was chosen to reproduce experimental frequency of 1707 cm^{-1} for the amide I band of *N*-methylacetamide in Ar and N_2 matrixes.[47] This is because its unscaled frequency was calculated to be 1808 cm^{-1} at the M06-2X/6-31+G(d) level of theory. The zero-point energy correction and the thermal energy corrections were employed in calculating the Gibbs free energy of each structure at 25 °C in DMSO. Each transition state was also confirmed by checking whether it has one imaginary frequency after frequency calculations in DMSO. Here, the ideal gas, rigid rotor, and harmonic oscillator approximations were used for the translational, rotational, and vibrational contributions to the Gibbs free energy, respectively.[48]

The relative acidity of the phenolic H atom and the strength of O–H···O_{DMSO} H-bond of the optimized RC for **1a**, **1m**, and **8** was analyzed using the natural bond orbital (NBO) method[49] at

the M06-2X/def2-TZVP level of theory. The relative acidity of the phenolic H atom can be described in terms of the Wiberg index.[50] The strength of the O–H···O_{DMSO} H-bond can be described by the second-order perturbation energy (ΔE_2) of the lone pair orbitals of the DMSO oxygen with the phenolic O–H antibonding orbital, which is called the hyperconjugation due to the charge transfer.[49]

The RC of **1a** can have a few possible conformations depending on the orientation of the phenolic OH group. First, we built an intramolecular H-bonded structure and the non-H-bonded structure. For the latter structure, initial structures with three orientations of *trans*, *gauche*–, and *gauche*+ for the C1–C2–O2–H sequence were built and followed by optimization at the PCM M06-2X/6-31+G(d) level of theory in DMSO. The three structures finally optimized in DMSO are shown in Fig. S3. The atomic numberings of **1a** are shown in Fig. S3a. At the M06-2X/def2-TZVP//PCM M06-2X/6-31+G(d) level of theory in DMSO, the most preferred conformation (Fig. S3a) was 0.44 kcal $mmol^{-1}$ more stable in free energy than the conformation with an intramolecular H-bond in *o*-alkynophenol (Fig. S3b). The most preferred structure of RC for **1a** (Fig. S3a) had an intermolecular H-bond between the phenolic OH group and the oxygen of DMSO with a short distance d(OH···O_{DMSO}) = 1.62 Å. The third conformation (Fig. S3c) was 1.18 kcal $mmol^{-1}$ less stable in free energy than the most preferred conformation. The thermodynamic properties of these three structures are listed in Table S2, whose Cartesian coordinates are listed at the bottom of the Supporting Information. The corresponding absolute values of thermodynamic properties are listed in Table S3.

Using the most preferred conformation of RC for **1a** (Fig. S3a) in DMSO, the initial structures of transition states for 6-*endo*-dig and 5-*exo*-dig cyclizations were generated and optimized at the PCM M06-2X/6-31+G(d) level of theory in DMSO. In each initial structure of ts, the phenolic oxygen O2 atom was positioned at equal distances from the alkyno C9 (α) and C10 (β) atoms for both the 6-*endo*-dig and 5-*exo*-dig cyclizations. Then, the IRC calculations for ts of **1a** were performed and followed by further optimizations to obtain RC and PC for **1a** in DMSO. The optimized structures of RC, ts, and PC for **1a** are shown in Fig. S4, in which the essential H-bonds are represented by broken lines. The initial structures of ts for **1m** and **8** were generated from the optimized ts structures of **1a** at the PCM M06-2X/6-31+G(d) level of theory in DMSO and optimized at the same level of theory in DMSO. In addition, the IRC-optimization procedure was applied to each optimized ts structure of **1m** and **8** to obtain the corresponding RC and PC at the

same level of theory in DMSO. The optimized structures of RC, ts, and PC for **1m** and **8** are shown in Fig. S5 and S6, respectively, in which the essential H-bonds are represented by broken lines. The thermodynamic properties of optimized structures of RC, ts, and PC for **1a**, **1m**, and **8** are listed in Table S4, whose Cartesian coordinates are listed at the bottom of the Supporting Information. The corresponding absolute values of thermodynamic properties are listed in Table S5. Each barrier ($\Delta G^{\ddagger}$) to ts was calculated using corresponding relative free energies (ΔG) of RC and ts.

The most preferred structure of RC for **1a** had an intermolecular H-bond between the phenolic O–H group and the oxygen of DMSO, as described above (Fig. S3a). In the structures of ts for competing cyclization pathways (Fig. S4), there were a nucleophilic attack of the phenolic oxygen to the alkyno C10 (β) atom with a distance of 1.81 Å for the 6-*endo*-dig approach (or the alkyno C9 (α) atom with a distance of 1.73 Å for the 5-*exo*-dig approach) and a partially dissociated phenolic proton located between the phenolic oxygen and the oxygen of DMSO (Fig. S4). Then, the protonated DMSO migrated to the alkyno (α) atom (or the alkyno (β) atom) and the cyclization was completed to yield the 6-*endo*-dig (or 5-*exo*-dig) product complex (PC). Finally, DMSO was located to form H-bonds with the lactone oxygen and the hydrogen atoms of alkeno and phenyl groups in both PCs.

The optimized structures of RC, ts, and PC for **1m** with *di*-chloro substitutions in the phenolic ring were quite similar to those of **1a**, although there are some differences in molecular geometries (see Fig. S4 and S5). In particular, the lengths of the phenolic O–H were 1.52 and 1.59 Å for ts of 6-*endo*-dig and 5-*exo*-dig pathways of **1m**, which are about 0.1 Å longer than those of **1a**, which indicates the increase of the acidity of the phenolic proton due to the EWG substitutions by Cl atoms.

The relative acidity of the phenolic H atom and the strength of O–H···O_{DMSO} H-bond of the optimized RC for **1a**, **1m**, and **8** was analyzed using the natural bond orbital (NBO) method[49] at the M06-2X/def2-TZVP level of theory. The relative acidity of the phenolic H atom can be described in terms of the Wiberg index.[50] We can say that the acidity of the phenolic H atom increased when the Wiberg index became smaller, *i.e.*, the O–H bond become weaker. The strength of O(S)–H···O_{DMSO} H-bond can be described by the second-order perturbation energy (ΔE_2) of the lone pair orbitals of the DMSO oxygen with the phenolic O(S)–H antibonding orbital, which is called the hyperconjugation due to the charge transfer.[49] The values of the Wiberg index were

calculated as 0.615, 0.580, and 0.906 e for RC for **1a**, **1m**, and **8**, respectively. This indicates that the acidity of the phenolic H atom increased due to the EWG substitutions by Cl atoms for **1m** parallel to the increase of the O–H bond length (1.005 to 1.016 Å). Although the S–H bond length of RC for **8** was 1.36 Å and longer than those of RC for **1m** and **8**, its Wiberg index was calculated to be greater than those of RC for **1a** and **1m**, which might be ascribed to the donation of 3*d* orbital of the S atom to the S–H bond. The ΔE_2 values of the O(S)–H···O_{DMSO} H-bond were calculated as 38.2, 45.2, and 11.97 kcal $mmol^{-1}$ for RC for **1a**, **1m**, and **8**, respectively. The stronger O–H···O_{DMSO} H-bond was formed for RS of **1m** than that of **1a** and the weakest H-bond was found for RS of **8**, which is parallel to the H-bond lengths of 1.59, 1.63, and 1.95 Å for RC of **1m**, **1a**, and **8**, respectively.

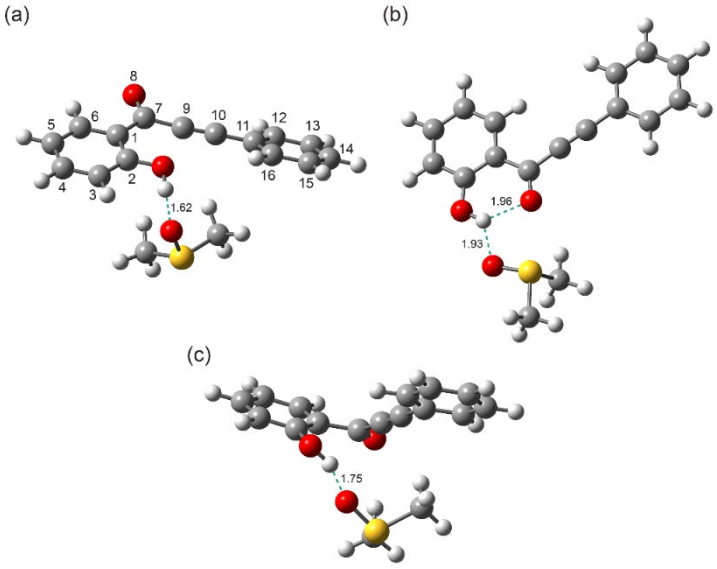


Fig. S3 Three feasible structures of RC for **1a** optimized at the PCM M06-2X/6-31+G(d) level of theory in DMSO. The essential H-bonds (Å) are represented by broken lines.

Table S2. Relative thermodynamic properties (kcal mmol^{-1}) of three feasible structures of RC for **1a** at the M06-2X/def2-TZVP//PCM M06-2X/6-31+G(d) level of theory in DMSO

Conformer[a]	ΔE^b	ΔH^b	ΔG^b
a	0.30	0.00	0.00
b	0.00	0.12	0.44
c	1.57	1.59	1.18

[a] Conformers as shown in Fig. S3. [b] *E*, *H*, and *G* stand for electronic energies, enthalpies, and Gibbs free energies calculated at the PCM M06-2X/6-31+G(d) level of theory in DMSO. The *H* and *G* values were obtained by scaling the vibrational frequencies with a factor of 0.9440. Each ΔE value was calculated by the sum of the single-point energy ($\Delta E_{e,sp2}$) at the M06-2X/def2-TZVP level of theory and the solvation free energy (ΔG_s) at the M06-2X/def2-TZVP level of theory in DMSO.

Table S3. Absolute electronic energies, enthalpies, and Gibbs free energies (hartree) of RC for **1a** at the M06-2X/def2-TZVP//PCM M06-2X/6-31+G(d) level of theory in DMSO

Conformer[a]	$E_0{}^b$	H^b	G^b	$E_{0,sp1}{}^c$	$E_{0,dTZ}{}^d$
a	-1280.840430	-1280.544523	-1280.622278	-1280.820612	-1281.189461
b	-1280.841327	-1280.544746	-1280.621986	-1280.820248	-1281.188685
c	-1280.838030	-1280.541606	-1280.620010	-1280.820321	-1281.189551

[a] Conformers as shown in Fig. S3. [b] E_e, *H*, and *G* stand for electronic energies, enthalpies, and Gibbs free energies calculated at the PCM M06-2X/6-31+G(d) level of theory in DMSO. The *H* and *G* values were obtained by scaling the vibrational frequencies with a factor of 0.9440. [c] Single-point energies calculated at the M06-2X/6-31+G(d) level of theory. The solvation free energy (ΔG_s) was calculated from the difference between E_0 and $E_{0,sp1}$. [d] Single-point energies calculated at the M06-2X/def2-TZVP level of theory.

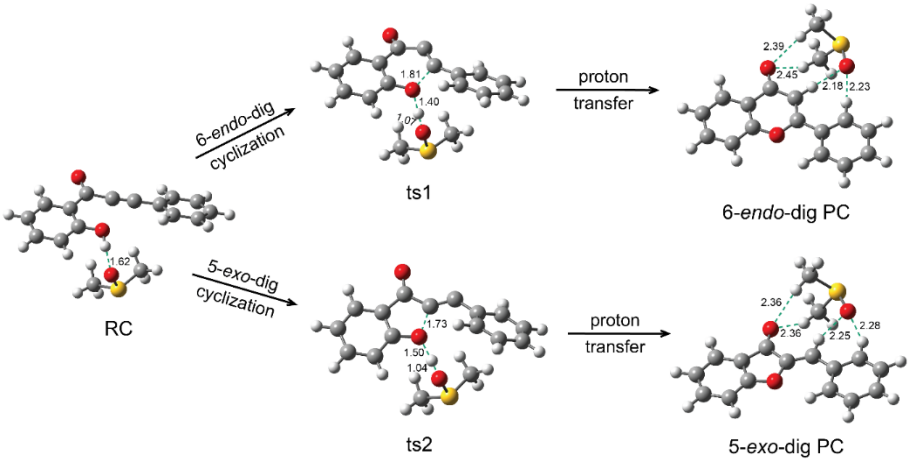


Fig. S4 The structures of RC, ts, and PC for **1a** optimized at the PCM M06-2X/6-31+G(d) level of theory in DMSO. The essential H-bonds (Å) are represented by broken lines.

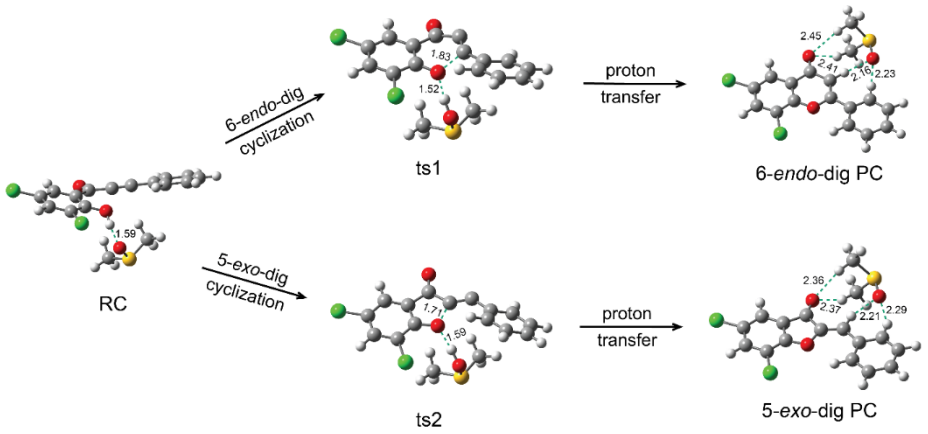


Fig. S5 The structures of RC, ts, and PC for **1m** optimized at the PCM M06-2X/6-31+G(d) level of theory in DMSO. The essential H-bonds (Å) are represented by broken lines.

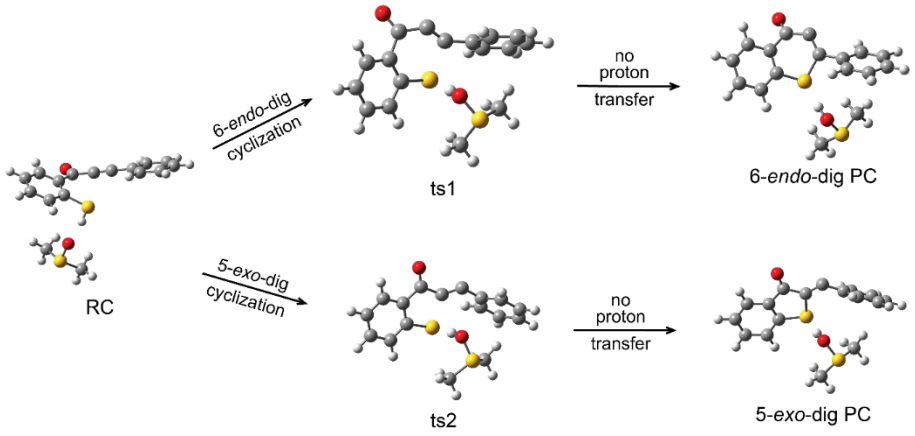


Fig. S6 The structures of RC, ts, and PC for **8** optimized at the PCM M06-2X/6-31+G(d) level of theory in DMSO. The essential H-bonds (Å) are represented by broken lines.

Table S4. Relative thermodynamic properties (kcal mmol^{-1}) of of RC, ts, and PC for **1a**, **1m**, and **8** at the M06-2X/def2-TZVP//PCM M06-2X/6-31+G(d) level of theory in DMSO

	Conformer[a]		ΔE^b	ΔH^b	ΔG^b
1a	6-*endo*-dig	RC	0.00	0.00	0.00
		ts1	34.61	32.83	35.63
		PC	-35.52	-34.15	-32.32
	5-*exo*-dig	RC	0.00	0.00	0.00
		ts2	34.51	32.75	36.42
		PC	-23.00	-22.07	-20.07
1m	6-*endo*-dig	RC	0.00	0.00	0.00
		ts1	32.15	30.86	33.39
		PC	-35.28	-33.89	-33.56
	5-*exo*-dig	RC	0.00	0.00	0.00
		ts2	33.85	32.75	35.89
		PC	-22.46	-21.43	-20.21
8	6-*endo*-dig	RC	0.00	0.00	0.00
		ts1	23.75	23.42	28.98
		PC	20.36	21.00	25.11
	5-*exo*-dig	RC	0.00	0.00	0.00
		ts2	20.41	19.95	24.89
		PC	17.22	17.44	22.44

[a] Conformers as shown in Fig. S3. [b] *E*, *H*, and *G* stand for electronic energies, enthalpies, and Gibbs free energies calculated at the PCM M06-2X/6-31+G(d) level of theory in DMSO. The *H* and *G* values were obtained by scaling the vibrational frequencies with a factor of 0.9440. Each ΔE value was calculated by the sum of the single-point energy ($\Delta E_{e,sp2}$) at the M06-2X/def2-TZVP level of theory and the solvation free energy (ΔG_s) at the M06-2X/def2-TZVP level of theory in DMSO.

Table S5. Absolute electronic energies, enthalpies, and Gibbs free energies (hartree) of RC, ts, and PC for **1a**, **1m**, and **8** at the M06-2X/def2-TZVP//PCM M06-2X/6-31+G(d) level of theory in DMSO

	Conformers[a]		E_0[b]	H[b]	G[b]	$E_{0,sp1}$[c]	$E_{0,dTZ}$[d]
1a	6-*endo*-dig	RC	-1280.840430	-1280.544523	-1280.622278	-1280.820612	-1281.189461
		ts1	-1280.790510	-1280.497443	-1280.570724	-1280.753031	-1281.116650
		PC	-1280.901935	-1280.603839	-1280.678688	-1280.887189	-1281.251137
	5-*exo*-dig	RC	-1280.840430	-1280.544523	-1280.622278	-1280.820612	-1281.189461
		ts2	-1280.790482	-1280.497395	-1280.569299	-1280.752838	-1281.116631
		PC	-1280.882202	-1280.584808	-1280.659384	-1280.867690	-1281.231423
1m	6-*endo*-dig	RC	-2199.972843	-2199.692966	-2199.776641	-2199.953872	-2200.391078
		ts1	-2199.927555	-2199.649741	-2199.729380	-2199.893143	-2200.324396
		PC	-2200.033809	-2199.751715	-2199.834873	-2200.020490	-2200.452949
	5-*exo*-dig	RC	-2199.972843	-2199.692966	-2199.776641	-2199.953872	-2200.391078
		ts2	-2199.924846	-2199.646726	-2199.725404	-2199.889228	-2200.320482
		PC	-2200.013842	-2199.732323	-2199.814050	-2200.000620	-2200.432620
8	6-*endo*-dig	RC	-1603.782180	-1603.489769	-1603.572015	-1603.763024	-1604.134015
		ts1	-1603.749261	-1603.457383	-1603.530772	-1603.708645	-1604.074701
		PC	-1603.754011	-1603.460580	-1603.536262	-1603.697649	-1604.064370
	5-*exo*-dig	RC	-1603.782180	-1603.489769	-1603.572015	-1603.763024	-1604.134015
		ts2	-1603.754641	-1603.462959	-1603.537336	-1603.716857	-1604.082857
		PC	-1603.758431	-1603.465669	-1603.539948	-1603.709368	-1604.076671

[a] Conformers as shown in Fig. S4–S6. [b] E_e, H, and G stand for electronic energies, enthalpies, and Gibbs free energies calculated at the PCM M06-2X/6-31+G(d) level of theory in DMSO. The H and G values were obtained by scaling the vibrational frequencies with a factor of 0.9440. [c] Single-point energies calculated at the M06-2X/6-31+G(d) level of theory. The solvation free energy (ΔG_s) was calculated from the difference between E_0 and $E_{0,sp1}$. [d] Single-point energies calculated at the M06-2X/def2-TZVP level of theory.

Cartesian coordinates of (1) three feasible structures of RC for **1a** and (2) RC, ts, and PC for **1a**, **1m**, and **8** optimized at the PCM M06-2X/6-31+G(d) level of theory in DMSO

(1) RC for **1a**

Conformer a

C	-2.171064	-0.282222	-0.638364
C	-2.210861	-1.582096	-0.092375
C	-3.459002	-2.145301	0.229331
C	-4.639646	-1.447278	0.042706
C	-4.586039	-0.147828	-0.478606
C	-3.371081	0.427974	-0.8165
H	-3.468921	-3.148789	0.643051
H	-5.59174	-1.898081	0.302507
H	-5.502222	0.417139	-0.6263
H	-3.322835	1.433366	-1.22607
O	-0.995659	0.262667	-0.990881
H	-1.085864	1.256609	-1.107885
C	-1.010862	-2.402539	0.210302
O	-1.115811	-3.557244	0.614807
C	0.3265	-1.847335	0.075158
C	1.488304	-1.50383	0.013273
C	2.837817	-1.035846	-0.090744
C	3.848989	-1.597549	0.704272
C	3.149982	-0.006403	-0.993532
C	5.153805	-1.125282	0.601587
H	3.602755	-2.396917	1.396669
C	4.458323	0.455713	-1.093477
H	2.363673	0.416616	-1.612644
C	5.459824	-0.100007	-0.294955
H	5.933333	-1.559177	1.220302
H	4.696721	1.25071	-1.793551
H	6.479477	0.265129	-0.373401
S	-0.471398	3.267941	0.472115
O	-1.077606	2.867055	-0.892871
C	1.07255	2.339907	0.597071
H	1.495513	2.492249	1.592842
H	0.862929	1.281146	0.415768
H	1.752426	2.735404	-0.159574
C	-1.409846	2.343885	1.706856
H	-1.362399	1.275927	1.477018
H	-0.983672	2.54724	2.692245
H	-2.440348	2.700781	1.664725

Conformer b

C	1.972653	2.335621	-0.01926
C	0.623909	1.905433	-0.013635
C	-0.401647	2.87128	0.039261
C	-0.120762	4.223853	0.085501
C	1.219235	4.639062	0.080044
C	2.246402	3.713072	0.028731
H	-1.43346	2.531583	0.043198
H	-0.924582	4.951048	0.126424
H	1.458912	5.697977	0.115828
H	3.286522	4.023965	0.023483
O	3.043247	1.533638	-0.067551
H	2.849283	0.567019	-0.114512
C	0.292077	0.474006	-0.058187
O	1.151719	-0.40738	-0.098461
C	-1.110688	0.095877	-0.053453
C	-2.26939	-0.263561	-0.050024
C	-3.643092	-0.666277	-0.04435
C	-4.654525	0.306821	-0.006048
C	-3.981052	-2.028604	-0.075843
C	-5.989567	-0.082958	0.000838
H	-4.384383	1.358367	0.017833
C	-5.319308	-2.408338	-0.068474
H	-3.19325	-2.775197	-0.106339
C	-6.322772	-1.438503	-0.030168
H	-6.770914	0.670196	0.03131
H	-5.580088	-3.461875	-0.092424
H	-7.366073	-1.73963	-0.024544
S	3.348607	-2.361205	-0.33687
O	4.002986	-0.978392	-0.218867
C	2.73704	-2.747297	1.316727
H	2.383673	-3.780946	1.338878
H	3.547084	-2.594416	2.034437
H	1.911803	-2.061614	1.512781
C	4.731051	-3.523302	-0.354449
H	5.267913	-3.376323	-1.293019
H	5.383713	-3.306688	0.49485
H	4.345142	-4.54423	-0.302516

Conformer c

C	-1.99853	-1.456814	-0.746894
C	-2.126976	-0.906152	0.543432
C	-3.225519	-1.268844	1.338254
C	-4.151969	-2.203177	0.898254
C	-3.986488	-2.783427	-0.364448
C	-2.927305	-2.408828	-1.181259

H	-3.314696	-0.820572	2.323807
H	-4.986856	-2.487389	1.530238
H	-4.698165	-3.52262	-0.720763
H	-2.808945	-2.825213	-2.176952
O	-1.016435	-1.111983	-1.612343
H	-0.753563	-0.174093	-1.467682
C	-1.114635	-0.00739	1.158148
O	-1.411379	0.83935	1.992093
C	0.282716	-0.251659	0.838681
C	1.458048	-0.461059	0.624636
C	2.843142	-0.69159	0.348413
C	3.224883	-1.735289	-0.509715
C	3.821404	0.129577	0.93165
C	4.5726	-1.951798	-0.777979
H	2.461852	-2.365876	-0.956335
C	5.166643	-0.094283	0.656357
H	3.517478	0.935357	1.593382
C	5.543038	-1.133597	-0.196328
H	4.866968	-2.760361	-1.439887
H	5.922009	0.541968	1.10715
H	6.593988	-1.306901	-0.407686
S	-0.704552	2.987154	-1.047889
O	-1.123224	1.520151	-1.231993
C	0.676918	2.99189	0.115804
H	0.948869	4.031718	0.313879
H	0.38188	2.478921	1.034301
H	1.509421	2.474409	-0.364602
C	-1.952974	3.670747	0.060697
H	-2.895803	3.689354	-0.488242
H	-2.028193	3.020298	0.93584
H	-1.665085	4.686552	0.341498

(2) **1a**

(a) RC

C	-2.171064	-0.282222	-0.638364
C	-2.210861	-1.582096	-0.092375
C	-3.459002	-2.145301	0.229331
C	-4.639646	-1.447278	0.042706
C	-4.586039	-0.147828	-0.478606
C	-3.371081	0.427974	-0.8165
H	-3.468921	-3.148789	0.643051
H	-5.59174	-1.898081	0.302507
H	-5.502222	0.417139	-0.6263
H	-3.322835	1.433366	-1.22607
O	-0.995659	0.262667	-0.990881
H	-1.085864	1.256609	-1.107885
C	-1.010862	-2.402539	0.210302
O	-1.115811	-3.557244	0.614807
C	0.3265	-1.847335	0.075158
C	1.488304	-1.50383	0.013273
C	2.837817	-1.035846	-0.090744
C	3.848989	-1.597549	0.704272
C	3.149982	-0.006403	-0.993532
C	5.153805	-1.125282	0.601587
H	3.602755	-2.396917	1.396669
C	4.458323	0.455713	-1.093477
H	2.363673	0.416616	-1.612644
C	5.459824	-0.100007	-0.294955
H	5.933333	-1.559177	1.220302
H	4.696721	1.25071	-1.793551
H	6.479477	0.265129	-0.373401
S	-0.471398	3.267941	0.472115
O	-1.077606	2.867055	-0.892871
C	1.07255	2.339907	0.597071
H	1.495513	2.492249	1.592842
H	0.862929	1.281146	0.415768
H	1.752426	2.735404	-0.159574
C	-1.409846	2.343885	1.706856
H	-1.362399	1.275927	1.477018
H	-0.983672	2.54724	2.692245
H	-2.440348	2.700781	1.664725

(b) 6-*endo*-dig ts1

C	-1.740771	0.044813	-0.500198
C	-2.538486	-0.989966	0.041789
C	-3.935062	-0.906192	-0.076539
C	-4.548966	0.16273	-0.709322
C	-3.752272	1.188988	-1.235288
C	-2.370745	1.134852	-1.133002
H	-4.525057	-1.713492	0.348898
H	-5.630005	0.206768	-0.795916
H	-4.215751	2.035961	-1.733688
H	-1.754093	1.928307	-1.547549
O	-0.40414	0.035098	-0.409381
H	0.285232	1.227903	-0.680825
C	-1.93916	-2.143672	0.763516
O	-2.622444	-2.815199	1.540029
C	-0.531825	-2.427	0.503671
C	0.291469	-1.583162	0.013922
C	1.701439	-1.371917	-0.296048
C	2.120725	-0.67159	-1.435006
C	2.66373	-1.886076	0.586356
C	3.478374	-0.475472	-1.676857

H	1.381918	-0.284394	-2.129119
C	4.019793	-1.688568	0.340718
H	2.334442	-2.425668	1.469515
C	4.430594	-0.976819	-0.788084
H	3.792312	0.070677	-2.561443
H	4.755437	-2.082822	1.035377
H	5.488091	-0.815941	-0.975588
S	1.149424	2.785623	0.640323
O	0.804019	2.157969	-0.78124
C	1.965222	1.451434	1.525621
H	2.281515	1.847753	2.493624
H	1.275453	0.613794	1.647911
H	2.836568	1.16012	0.933847
C	-0.434178	2.822635	1.490673
H	-1.071934	3.525136	0.952004
H	-0.868613	1.820086	1.500811
H	-0.25507	3.182784	2.506192

(c) 6-*endo*-dig PC

C	-2.726455	-0.074773	0.025523
C	-2.170526	-1.353796	-0.045852
C	-3.029779	-2.463725	-0.050645
C	-4.400651	-2.288404	0.016092
C	-4.937058	-0.991213	0.089371
C	-4.108769	0.119408	0.094274
H	-2.587336	-3.453585	-0.109271
H	-5.062378	-3.148314	0.012071
H	-6.012583	-0.85309	0.142333
H	-4.502619	1.129069	0.149876
O	-1.951262	1.046645	0.032444
H	1.115049	-0.295565	-0.163422
C	-0.705457	-1.497667	-0.115038
O	-0.153191	-2.602178	-0.17517
C	0.030496	-0.250404	-0.108071
C	-0.604494	0.947605	-0.036146
C	0.05431	2.270262	-0.024257
C	-0.715139	3.441614	-0.017893
C	1.454198	2.365163	-0.020428
C	-0.094957	4.688674	-0.010254
H	-1.797644	3.377443	-0.020656
C	2.065863	3.614653	-0.012206
H	2.071461	1.470548	-0.021727
C	1.296004	4.779641	-0.007403
H	-0.701503	5.589165	-0.006861
H	3.149912	3.678683	-0.008166
H	1.779256	5.752278	-0.00073
S	3.842884	-1.806448	0.081017
O	3.296728	-0.38572	-0.110843
C	3.092698	-2.795208	-1.232119
H	3.372186	-3.842467	-1.091313
H	2.006703	-2.671091	-1.18544
H	3.492769	-2.429187	-2.179317
C	2.907064	-2.505738	1.460375
H	3.162248	-1.92553	2.348828
H	1.839077	-2.434021	1.235108
H	3.206956	-3.547698	1.599022

(d) 5-*exo*-dig ts2

C	2.056639	0.089894	0.34084
C	2.764417	-1.04337	-0.077171
C	4.159611	-1.063317	-0.085936
C	4.846701	0.069369	0.332487
C	4.131896	1.201415	0.759682
C	2.740325	1.232598	0.773289
H	4.684432	-1.957602	-0.411877
H	5.931629	0.08368	0.337598
H	4.679009	2.079303	1.092176
H	2.201227	2.109595	1.119998
O	0.724075	-0.043183	0.280519
H	-0.130125	1.088686	0.756117
C	1.829179	-2.10987	-0.442101
O	2.136165	-3.223192	-0.860211
C	0.437265	-1.669998	-0.221385
C	-0.746561	-2.175337	-0.268381
C	-2.027924	-1.60254	0.091402
C	-3.137049	-1.739855	-0.764511
C	-2.209277	-0.903536	1.301927
C	-4.362408	-1.157193	-0.448852
H	-3.020568	-2.297415	-1.690185
C	-3.44531	-0.353504	1.631578
H	-1.366806	-0.795517	1.980473
C	-4.525828	-0.463627	0.752754
H	-5.197242	-1.256306	-1.137366
H	-3.561639	0.17881	2.571976
H	-5.485153	-0.021294	1.004861
S	-1.124678	2.695034	-0.371625
O	-0.654045	1.958475	0.96613
C	-1.925211	1.401867	-1.322753
H	-2.230056	1.842181	-2.275667
H	-1.229933	0.571812	-1.471285
H	-2.803201	1.086383	-0.754842
C	0.390234	2.909669	-1.315335
H	1.026143	3.599879	-0.759422
H	0.874944	1.941639	-1.458523

H	0.112442	3.352834	-2.274757

(e) 5-*exo*-dig PC

C	2.968332	0.565195	-0.00172
C	2.780128	-0.815581	0.0059
C	3.875809	-1.681294	0.006086
C	5.147921	-1.122036	-0.00139
C	5.312868	0.274573	-0.008998
C	4.227264	1.148623	-0.00929
H	3.72759	-2.757192	0.012035
H	6.023895	-1.762021	-0.00143
H	6.31732	0.687316	-0.014905
H	4.353558	2.225733	-0.015171
O	1.790203	1.266168	-0.000708
H	-1.217402	-0.216932	0.020091
C	1.32927	-1.034305	0.012302
O	0.697692	-2.082186	0.01888
C	0.758699	0.342616	0.008061
C	-0.548058	0.646331	0.011797
C	-1.196593	1.955965	0.006961
C	-0.500009	3.178417	-0.000055
C	-2.603004	1.974885	0.009374
C	-1.199334	4.381645	-0.004522
H	0.583675	3.186845	-0.001879
C	-3.29592	3.181789	0.004727
H	-3.136811	1.026976	0.014956
C	-2.595934	4.38897	-0.002241
H	-0.651498	5.319447	-0.009884
H	-4.38202	3.181573	0.006567
H	-3.135065	5.331888	-0.005881
S	-3.238435	-2.781131	-0.011351
O	-3.217727	-1.248631	0.044998
C	-2.155295	-3.326577	1.327104
H	-2.038206	-4.411958	1.272846
H	-1.191521	-2.821325	1.220763
H	-2.640579	-3.05305	2.265713
C	-2.154726	-3.225565	-1.385926
H	-2.637952	-2.880145	-2.3016
H	-1.190104	-2.731787	-1.240215
H	-2.03977	-4.311983	-1.414782

(3) **1m**

(a) RC

C	-1.466708	0.069255	-0.392708
C	-1.627193	-1.181321	0.238466
C	-2.898859	-1.754212	0.367202
C	-4.00842	-1.099895	-0.132794
C	-3.882059	0.133091	-0.770098
C	-2.623297	0.698507	-0.895474
H	-2.992177	-2.714801	0.86259
Cl	-5.589958	-1.818619	0.021644
H	-4.750719	0.64417	-1.172181
Cl	-2.46199	2.221516	-1.719635
O	-0.250506	0.607189	-0.512275
H	-0.233193	1.621557	-0.459943
C	-0.497553	-1.963884	0.82554
O	-0.716846	-2.861606	1.629226
C	0.866841	-1.703693	0.413615
C	2.034228	-1.594062	0.101624
C	3.391995	-1.392151	-0.301088
C	4.436321	-2.074827	0.342736
C	3.678349	-0.49397	-1.342769
C	5.751966	-1.855928	-0.052623
H	4.207241	-2.767406	1.146906
C	4.996592	-0.28399	-1.732716
H	2.863361	0.027669	-1.836638
C	6.03302	-0.962777	-1.088212
H	6.559299	-2.382244	0.44691
H	5.216416	0.409149	-2.538841
H	7.061427	-0.795425	-1.394349
S	1.046142	3.111751	1.272744
O	0.155227	3.091951	0.007958
C	2.4065	1.983502	0.908691
H	3.010964	1.852964	1.809877
H	1.984297	1.031078	0.576536
H	3.006002	2.439074	0.118567
C	0.185221	2.079934	2.478561
H	0.02785	1.084169	2.05598
H	0.788589	2.026899	3.387653
H	-0.769163	2.564128	2.691876

(b) 6-*endo*-dig ts1

C	-1.029979	-0.148932	-0.362373
C	-1.673367	-1.265463	0.224591
C	-3.069528	-1.361548	0.227988
C	-3.837389	-0.366262	-0.345266
C	-3.239197	0.752231	-0.927199
C	-1.858467	0.847102	-0.928872
H	-3.52983	-2.227876	0.693149
Cl	-5.580983	-0.490644	-0.343959
H	-3.840016	1.535829	-1.377307
Cl	-1.103841	2.238367	-1.657507

O	0.286049	-0.004063	-0.378901
H	1.064595	1.285023	-0.146277
C	-0.883862	-2.34541	0.887986
O	-1.409984	-3.049732	1.74899
C	0.496424	-2.497676	0.45549
C	1.17932	-1.572476	-0.097331
C	2.513773	-1.218429	-0.56352
C	2.730797	-0.372753	-1.660727
C	3.616071	-1.774659	0.104473
C	4.02845	-0.090448	-2.078781
H	1.880749	0.056801	-2.180897
C	4.910986	-1.48903	-0.318185
H	3.441571	-2.425287	0.95667
C	5.120395	-0.644592	-1.40965
H	4.187411	0.564144	-2.930655
H	5.756617	-1.922179	0.207745
H	6.131124	-0.419152	-1.736944
S	1.551903	2.293792	1.74034
O	1.643558	2.081779	0.160021
C	2.017247	0.702291	2.430524
H	1.952344	0.792101	3.517789
H	1.347741	-0.076719	2.05766
H	3.049796	0.513247	2.130378
C	-0.213225	2.302499	2.077242
H	-0.637278	3.16082	1.553341
H	-0.66342	1.366286	1.739773
H	-0.337535	2.422459	3.155852

(c) 6-*endo*-dig PC

C	-1.784714	0.508553	-0.009986
C	-1.539426	-0.863772	-0.043085
C	-2.608859	-1.766905	-0.040048
C	-3.899712	-1.279407	-0.00418
C	-4.161903	0.096505	0.028475
C	-3.103694	0.986292	0.025212
H	-2.399737	-2.831237	-0.065881
Cl	-5.245627	-2.385677	0.000875
H	-5.181742	0.465307	0.056067
Cl	-3.39415	2.693657	0.063102
O	-0.790304	1.424703	-0.009264
H	1.905939	-0.5702	-0.097139
C	-0.137029	-1.333313	-0.081412
O	0.144619	-2.533312	-0.114793
C	0.857688	-0.282134	-0.074525
C	0.506395	1.027945	-0.038386
C	1.434683	2.174411	-0.027271
C	0.935535	3.484074	-0.01949
C	2.821591	1.961362	-0.024304
C	1.812066	4.566087	-0.010352
H	-0.135813	3.654998	-0.021016
C	3.689604	3.048334	-0.015197
H	3.228769	0.953511	-0.026974
C	3.18982	4.352048	-0.008507
H	1.416374	5.577107	-0.004707
H	4.761659	2.875922	-0.0126
H	3.872032	5.196896	-0.001372
S	4.226494	-2.653066	0.077773
O	3.986992	-1.140465	-0.018044
C	3.299868	-3.376278	-1.294447
H	3.357696	-4.465624	-1.227546
H	2.262397	-3.035047	-1.233551
H	3.772456	-3.036153	-2.217597
C	3.153411	-3.230644	1.411642
H	3.517883	-2.778804	2.335837
H	2.126427	-2.92037	1.198295
H	3.225587	-4.319282	1.47818

(d) 5-*exo*-dig ts2

C	1.309175	0.155591	-0.41858
C	1.894075	1.310772	0.111403
C	3.27037	1.449327	0.264168
C	4.068496	0.386923	-0.130747
C	3.517307	-0.783098	-0.666764
C	2.1415	-0.900516	-0.812171
H	3.693433	2.359851	0.677336
Cl	5.803452	0.494754	0.03441
H	4.161883	-1.600758	-0.973182
Cl	1.445154	-2.340614	-1.489164
O	-0.019541	0.180868	-0.492735
H	-0.971432	-1.082642	-0.310047
C	0.836431	2.277328	0.446834
O	1.016303	3.385168	0.939774
C	-0.480416	1.71939	0.095686
C	-1.710859	2.115704	0.106657
C	-2.912411	1.446169	-0.361858
C	-4.112058	1.569132	0.363422
C	-2.929937	0.681802	-1.546276
C	-5.269039	0.910153	-0.045442
H	-4.118547	2.178643	1.263596
C	-4.098986	0.060898	-1.97758
H	-2.013727	0.583152	-2.122698
C	-5.26966	0.158235	-1.221971
H	-6.177696	0.99864	0.543823
H	-4.093055	-0.517905	-2.897193

H	-6.176548	-0.340382	-1.551696
S	-1.570217	-2.227831	1.468879
O	-1.519427	-1.913476	-0.099383
C	-2.367911	-0.785772	2.174574
H	-2.406945	-0.933364	3.256664
H	-1.803338	0.11418	1.915794
H	-3.377678	-0.747404	1.760957
C	0.121068	-1.992007	2.027786
H	0.744443	-2.70262	1.481778
H	0.435007	-0.960783	1.852394
H	0.139807	-2.224367	3.095132

(e) 5-*exo*-dig PC

C	-2.008562	0.573582	-0.000661
C	-1.87949	-0.811138	-0.00511
C	-2.992616	-1.648264	-0.005716
C	-4.237184	-1.035199	-0.001822
C	-4.380734	0.359902	0.002598
C	-3.258814	1.180005	0.003194
H	-2.888122	-2.728317	-0.009274
Cl	-5.678243	-2.014492	-0.002489
H	-5.370625	0.804494	0.005575
Cl	-3.39482	2.904481	0.008226
O	-0.821319	1.236058	-0.00085
H	2.141485	-0.339294	-0.015929
C	-0.429547	-1.078629	-0.00852
O	0.155565	-2.149918	-0.01181
C	0.183204	0.275799	-0.006304
C	1.497675	0.543756	-0.009535
C	2.183299	1.832753	-0.006789
C	1.524658	3.076405	0.003128
C	3.589682	1.805938	-0.013948
C	2.26246	4.256157	0.00591
H	0.441556	3.121308	0.008839
C	4.320705	2.989992	-0.01118
H	4.09353	0.841749	-0.021859
C	3.658745	4.218161	-0.001186
H	1.745507	5.211251	0.013922
H	5.406128	2.95542	-0.016789
H	4.227501	5.143422	0.001114
S	4.056947	-2.977263	0.008939
O	4.049795	-1.44458	-0.048049
C	2.962942	-3.51425	-1.324069
H	2.837091	-4.598535	-1.268224
H	2.004187	-3.000432	-1.214749
H	3.44622	-3.245664	-2.265119
C	2.976637	-3.411162	1.389413
H	3.469946	-3.074219	2.302856
H	2.017855	-2.904075	1.251907
H	2.847957	-4.496045	1.416416

(3) **8**

(a) RC

C	1.145163	0.986248	-0.529552
C	0.679181	2.173159	0.072616
C	1.403759	3.364436	-0.093609
C	2.564805	3.405569	-0.850118
C	3.024914	2.22948	-1.445799
C	2.327679	1.038263	-1.284641
H	1.022799	4.262527	0.382618
H	3.103299	4.339117	-0.976725
H	3.93373	2.235595	-2.040616
H	2.711257	0.123539	-1.72827
S	0.340089	-0.590544	-0.322879
H	1.41115	-1.311643	-0.747444
C	-0.554066	2.295308	0.90712
O	-0.643816	3.145797	1.782932
C	-1.686702	1.439217	0.618558
C	-2.666981	0.764227	0.38154
C	-3.783877	-0.074602	0.076227
C	-4.932896	-0.049693	0.882924
C	-3.721622	-0.93428	-1.032713
C	-6.006544	-0.880446	0.580282
H	-4.971713	0.61717	1.738696
C	-4.801454	-1.760161	-1.327236
H	-2.828054	-0.944762	-1.649559
C	-5.94219	-1.734637	-0.522437
H	-6.894583	-0.86259	1.204241
H	-4.754589	-2.42374	-2.185041
H	-6.78326	-2.380583	-0.755863
S	4.009368	-2.395769	0.225217
O	3.151115	-2.13785	-1.022732
C	2.962581	-3.355241	1.340767
H	3.473972	-3.474864	2.298694
H	2.008486	-2.83713	1.469567
H	2.807032	-4.33128	0.878521
C	4.002227	-0.848459	1.158493
H	2.96972	-0.526413	1.322025
H	4.5148	-1.009768	2.109938
H	4.54239	-0.108063	0.565664

(b) 6-*endo*-dig ts1

C	-2.106743	0.187423	0.594542
C	-2.752974	-0.861269	-0.096813
C	-4.036752	-0.657199	-0.625694
C	-4.689041	0.561017	-0.499344
C	-4.056692	1.598215	0.191699
C	-2.791272	1.407687	0.733249
H	-4.513502	-1.486245	-1.141544
H	-5.677934	0.701284	-0.924805
H	-4.549519	2.55906	0.310329
H	-2.311902	2.215594	1.279796
S	-0.494145	0.063097	1.333185
H	0.209617	0.945674	-0.278756
C	-2.172682	-2.23255	-0.271033
O	-2.905576	-3.218054	-0.205604
C	-0.749905	-2.325255	-0.517933
C	0.208217	-1.670422	-0.011167
C	1.6624	-1.543168	0.031493
C	2.378849	-1.57475	-1.174129
C	2.358108	-1.42098	1.240715
C	3.7698	-1.490671	-1.164601
H	1.836731	-1.66277	-2.111174
C	3.749071	-1.338748	1.244998
H	1.805124	-1.396138	2.175863
C	4.459105	-1.373527	0.04393
H	4.315057	-1.512076	-2.103626
H	4.278059	-1.247955	2.189104
H	5.542889	-1.30617	0.049025
S	1.516605	2.615238	-0.865868
O	0.515078	1.399543	-1.153876
C	2.7539	1.898358	0.220789
H	3.48882	2.677579	0.435442
H	2.284163	1.535725	1.136991
H	3.223421	1.08106	-0.332123
C	0.605	3.664265	0.273136
H	0.320263	3.089927	1.157268
H	1.255308	4.501456	0.538023
H	-0.272303	4.028173	-0.264072

(c) 6-*endo*-dig PC

C	2.195484	0.576085	0.012378
C	3.07299	-0.516708	-0.036369
C	4.398923	-0.340714	0.375076
C	4.846124	0.894738	0.828546
C	3.967618	1.98298	0.849427
C	2.648082	1.830278	0.437138
H	5.073026	-1.191643	0.322666
H	5.874412	1.017947	1.154679
H	4.310255	2.953236	1.196577
H	1.965105	2.675576	0.457984
S	0.517243	0.391076	-0.528308
H	-0.906153	1.503903	0.653057
C	2.613215	-1.823511	-0.623388
O	3.392115	-2.436576	-1.36866
C	1.294881	-2.287689	-0.263174
C	0.292544	-1.413579	-0.19215
C	-1.121801	-1.696272	0.17848
C	-1.66052	-1.197492	1.372895
C	-1.935261	-2.469875	-0.657087
C	-2.978098	-1.476449	1.731016
H	-1.033977	-0.601968	2.033521
C	-3.260153	-2.737635	-0.308521
H	-1.52173	-2.856174	-1.584936
C	-3.784737	-2.242569	0.886043
H	-3.375512	-1.094142	2.666944
H	-3.88219	-3.333968	-0.9699
H	-4.814986	-2.453122	1.157848
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O	-1.690618	2.000611	1.031657
C	-3.059188	0.954923	-1.054656
H	-3.814004	1.223263	-1.798291
H	-2.146553	0.606284	-1.541895
H	-3.458889	0.204702	-0.367792
C	-1.767001	3.410573	-1.248131
H	-0.918649	2.823653	-1.606114
H	-2.425306	3.688233	-2.074577
H	-1.438913	4.303416	-0.714565

(d) 5-*exo*-dig ts2

C	-2.360226	0.128186	0.679538
C	-2.819841	-0.926568	-0.122191
C	-4.162762	-1.002775	-0.504292
C	-5.054388	-0.021975	-0.09003
C	-4.597249	1.03311	0.710914
C	-3.262793	1.113102	1.098697
H	-4.484344	-1.833917	-1.126142
H	-6.098328	-0.069782	-0.383467
H	-5.292456	1.801563	1.037477
H	-2.91915	1.931314	1.725466
S	-0.658907	0.097971	1.133798
C	-1.828819	-1.933118	-0.560911
O	-2.134018	-2.920609	-1.221101
C	-0.426761	-1.651673	-0.190099
C	0.739219	-2.083067	-0.498424
C	2.058031	-1.658536	-0.091388

C	2.364998	-1.475235	1.272081
C	3.069429	-1.418699	-1.04168
C	3.63996	-1.071831	1.665779
H	1.597824	-1.665845	2.017983
C	4.33373	-0.992246	-0.644216
H	2.848787	-1.570356	-2.094888
C	4.628419	-0.822768	0.711948
H	3.860009	-0.945421	2.722446
H	5.096985	-0.803499	-1.394106
H	5.619662	-0.504852	1.021234
H	0.125825	0.802026	-0.578185
S	1.361766	2.547627	-1.042545
O	0.553447	1.212005	-1.411419
C	2.42319	2.04945	0.318467
H	3.028428	2.919021	0.585944
H	1.820147	1.713357	1.164151
H	3.062008	1.245888	-0.057183
C	0.149047	3.568849	-0.196895
H	-0.249868	3.028996	0.664369
H	0.658296	4.484691	0.111436
H	-0.634128	3.800864	-0.920214

(e) 5-*exo*-dig PC

C	-2.358731	0.174923	0.616908
C	-2.917772	-0.840849	-0.162749
C	-4.283551	-0.840958	-0.451826
C	-5.083096	0.182622	0.042933
C	-4.51553	1.197575	0.826469
C	-3.154469	1.20382	1.12329
H	-4.69767	-1.64093	-1.059981
H	-6.146516	0.199097	-0.173973
H	-5.146108	1.994099	1.210837
H	-2.72339	1.990233	1.736211
S	-0.628052	-0.020882	0.90169
C	-1.949108	-1.860668	-0.631044
O	-2.273825	-2.832445	-1.306303
C	-0.561303	-1.547189	-0.206929
C	0.552917	-2.17247	-0.588938
C	1.863382	-1.745971	-0.116779
C	2.186782	-1.698051	1.256989
C	2.890464	-1.441236	-1.036002
C	3.474117	-1.375041	1.684847
H	1.421284	-1.94374	1.98983
C	4.167801	-1.094106	-0.605315
H	2.671333	-1.492619	-2.099886
C	4.473095	-1.067	0.759552
H	3.696671	-1.360539	2.748803
H	4.935305	-0.858108	-1.338153
H	5.474924	-0.814471	1.09411
H	0.254393	0.944589	-0.747783
S	1.676916	2.596363	-0.927003
O	0.780296	1.384094	-1.484216
C	2.50088	1.919113	0.517834
H	3.141271	2.711941	0.912129
H	1.76882	1.600132	1.261716
H	3.110094	1.079807	0.174272
C	0.482836	3.703903	-0.173263
H	-0.083405	3.177677	0.597829
H	1.045358	4.535902	0.257432
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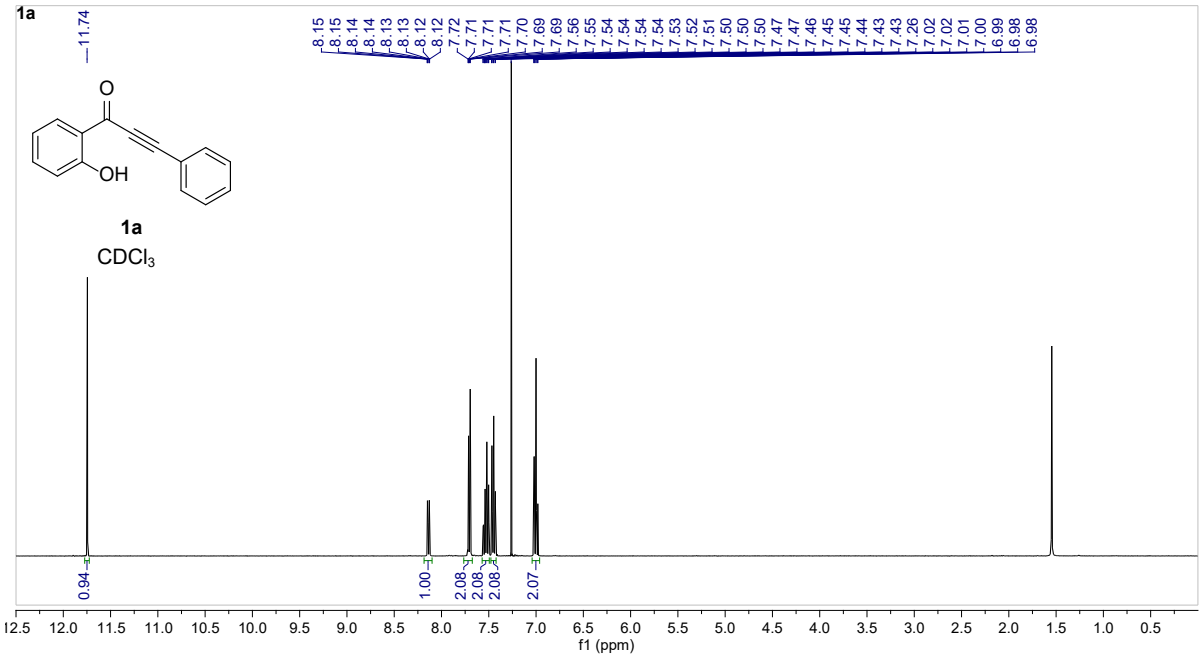
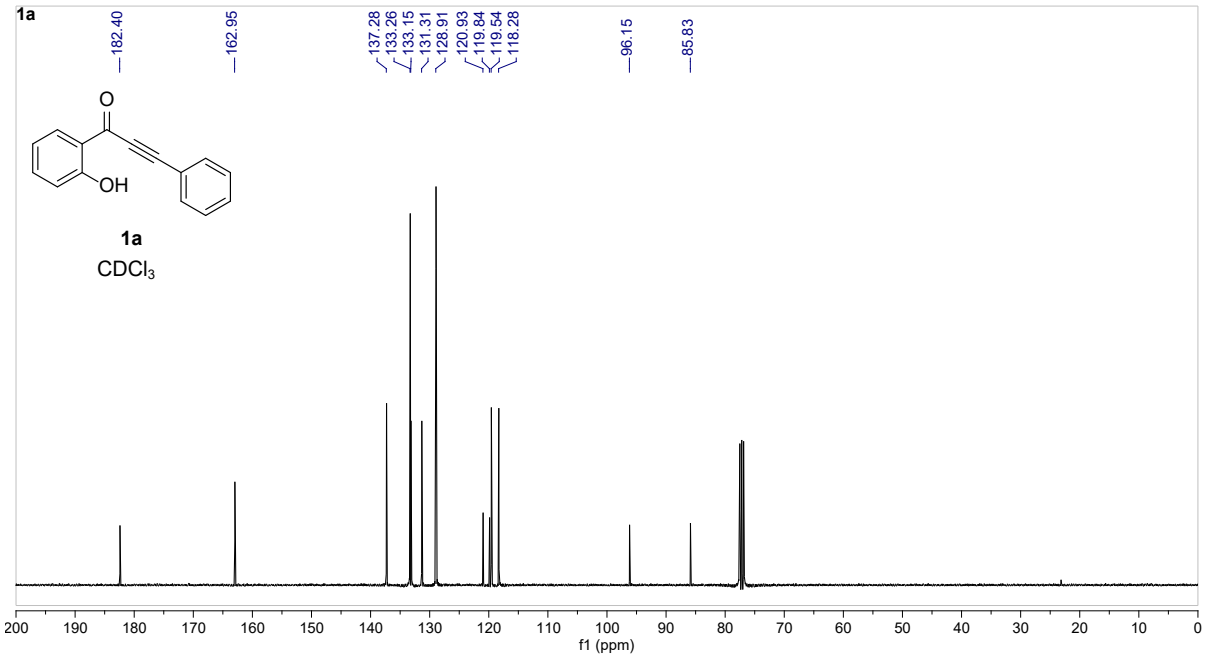
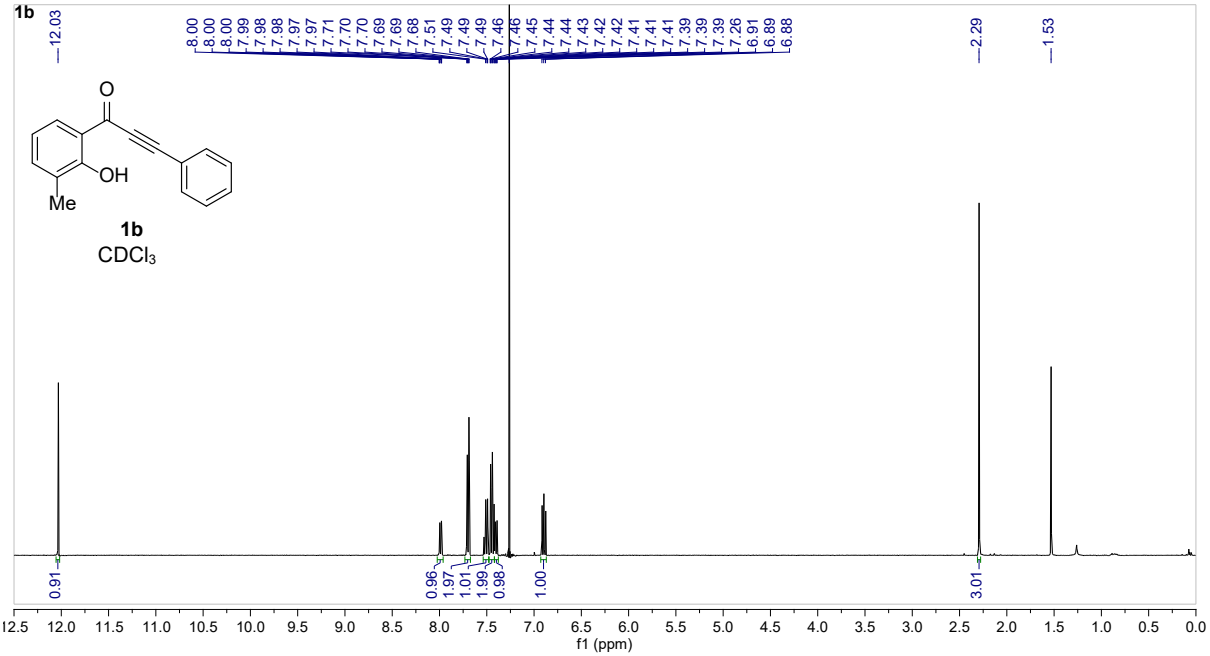
VI. NMR Spectra of o-alkynoylphenols 1.



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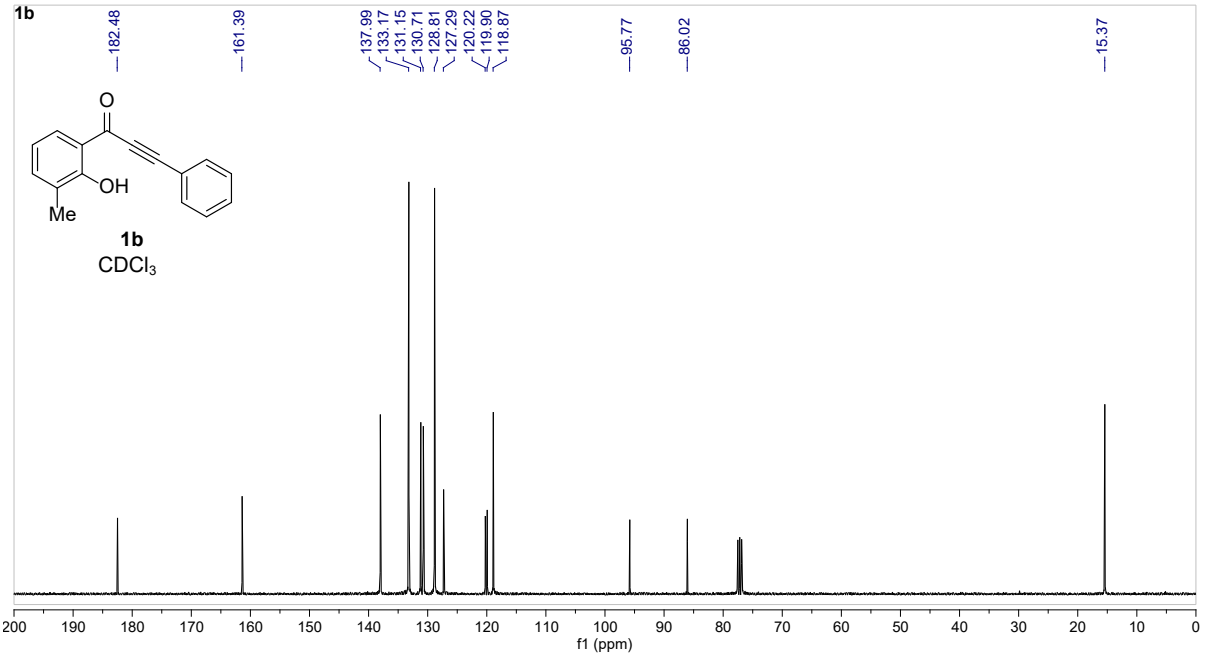
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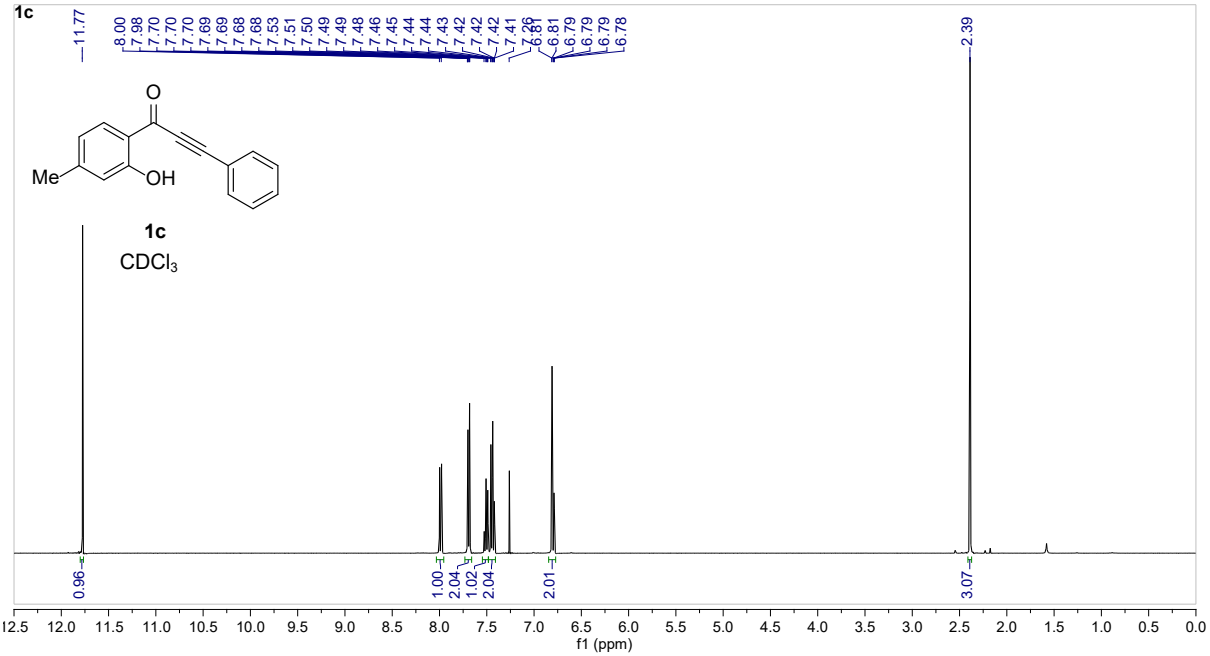
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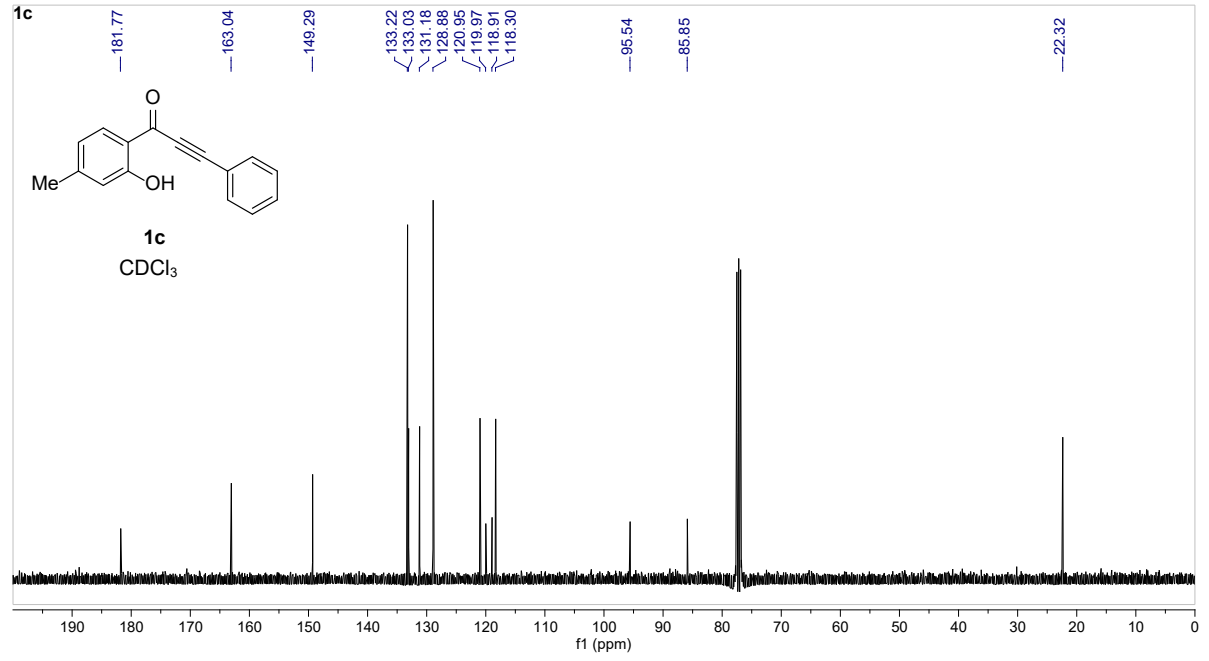
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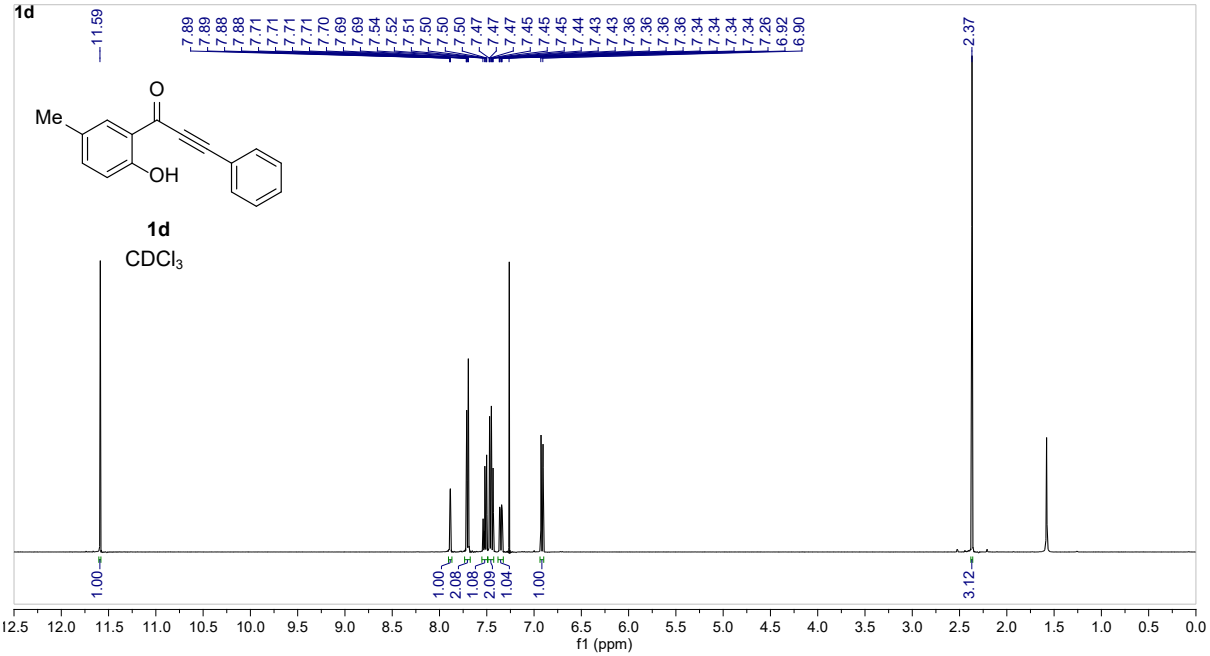
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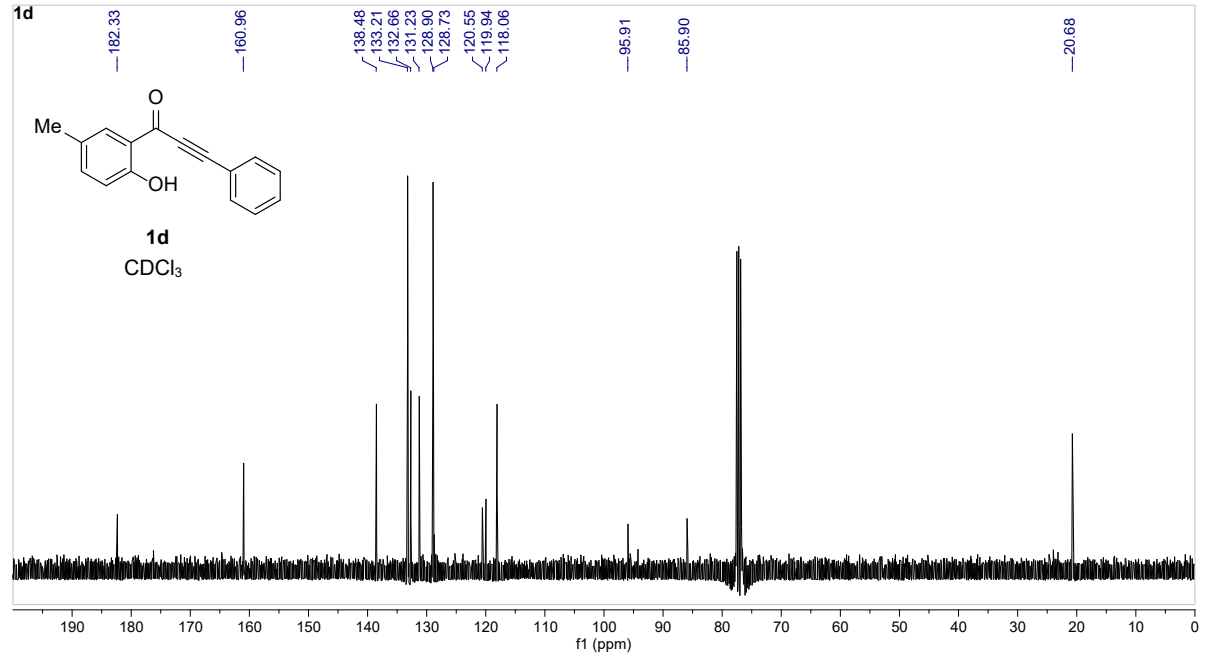
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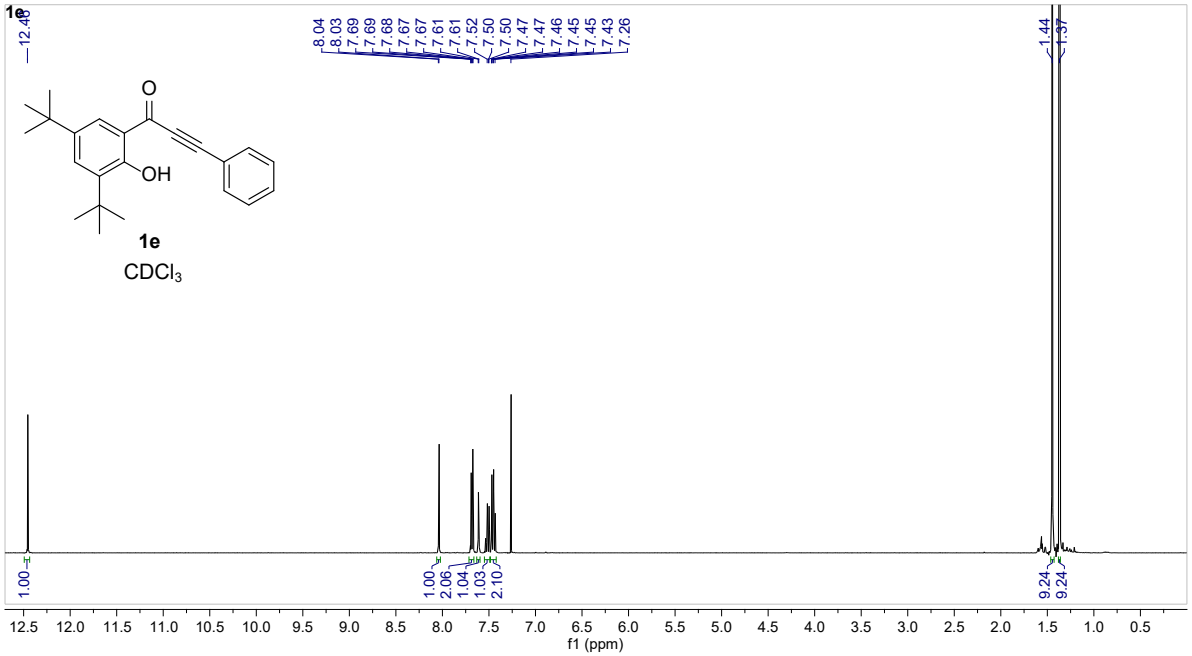
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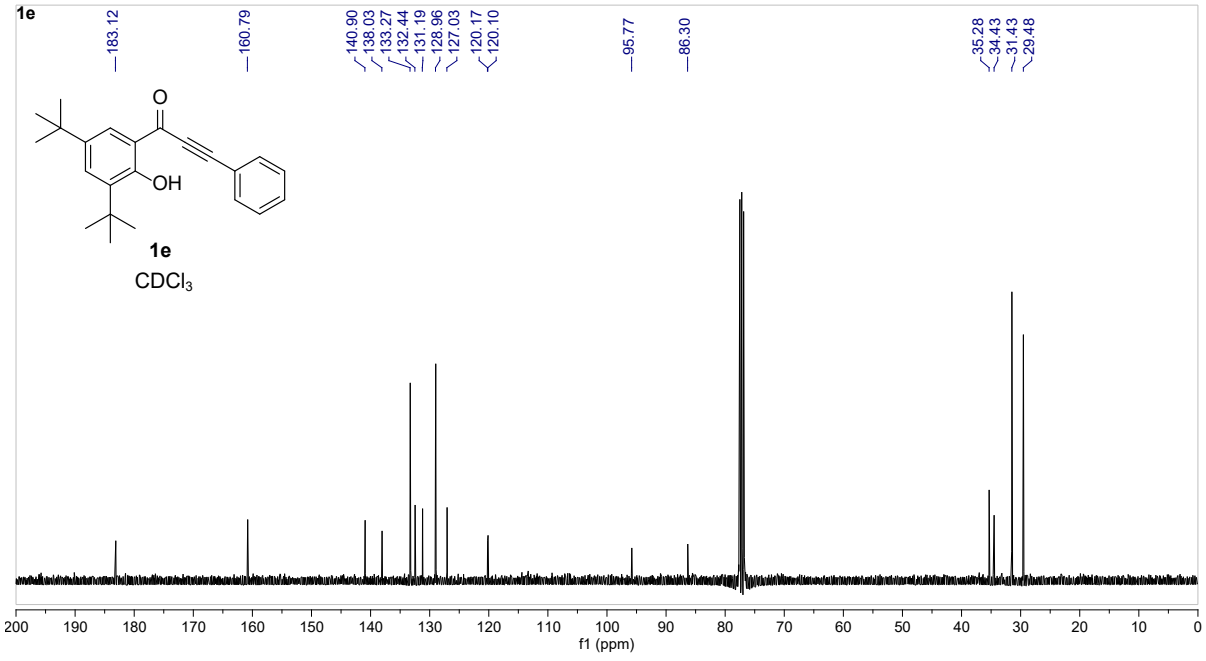
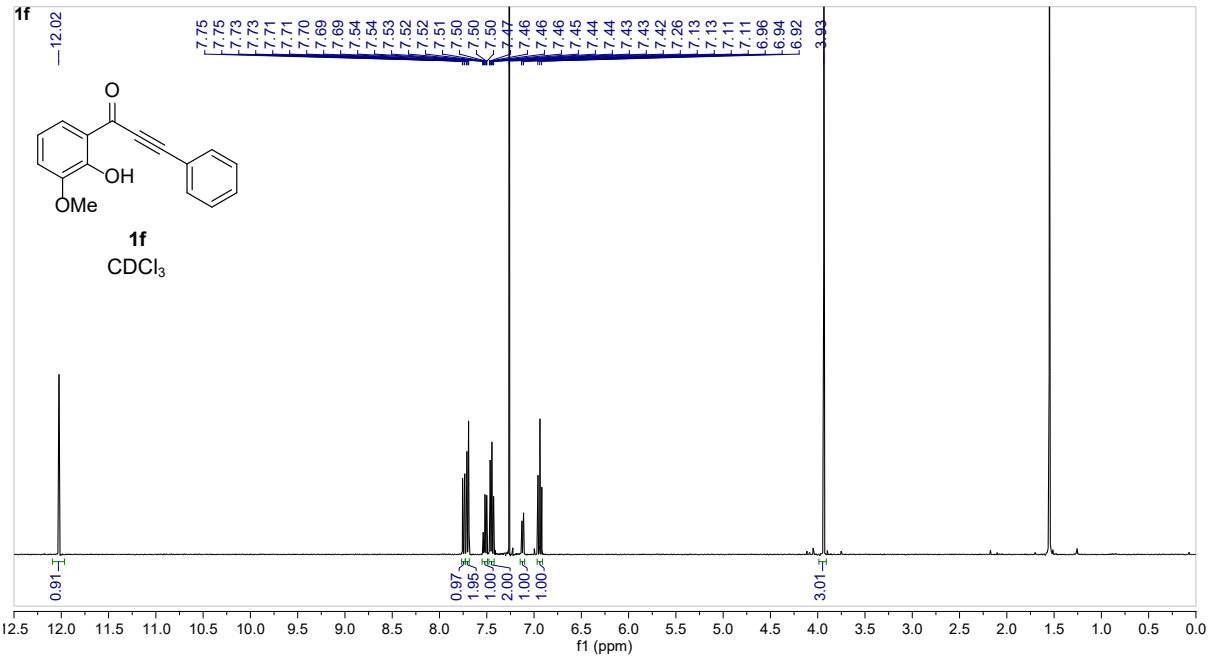
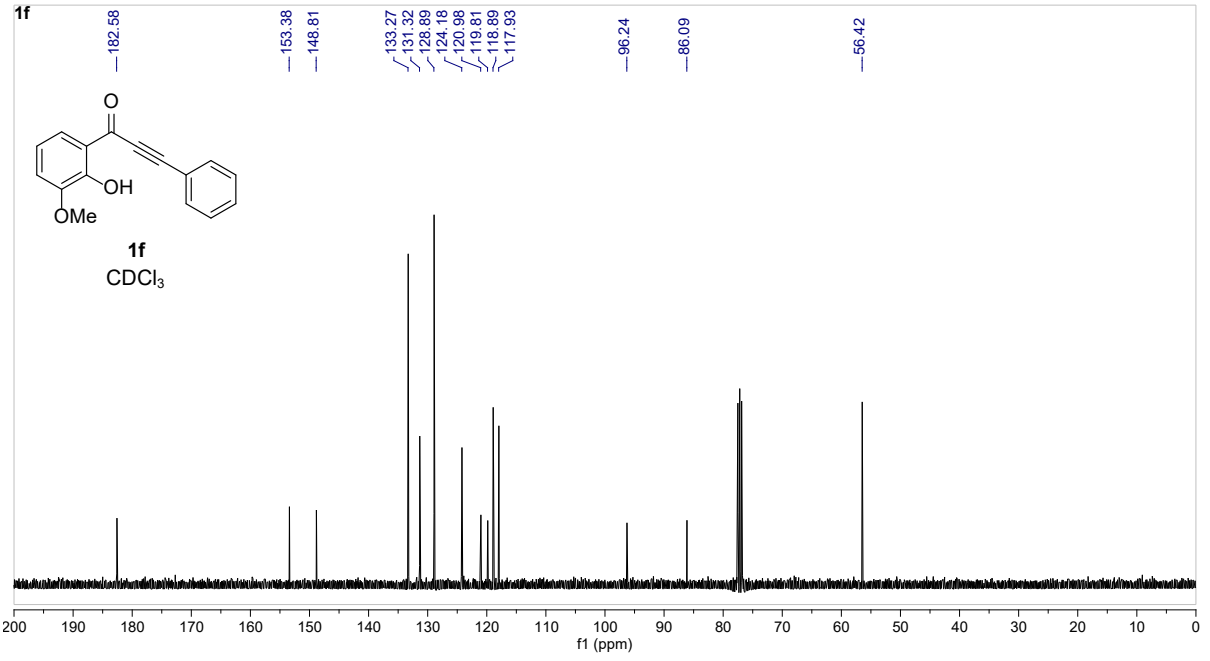
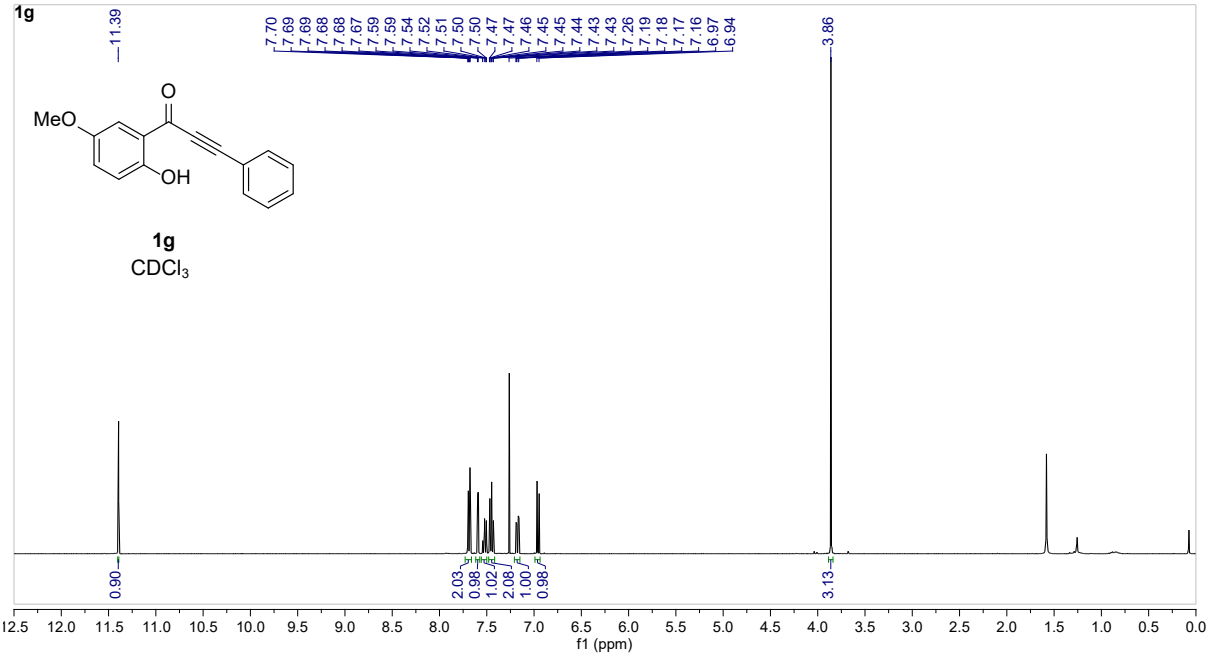
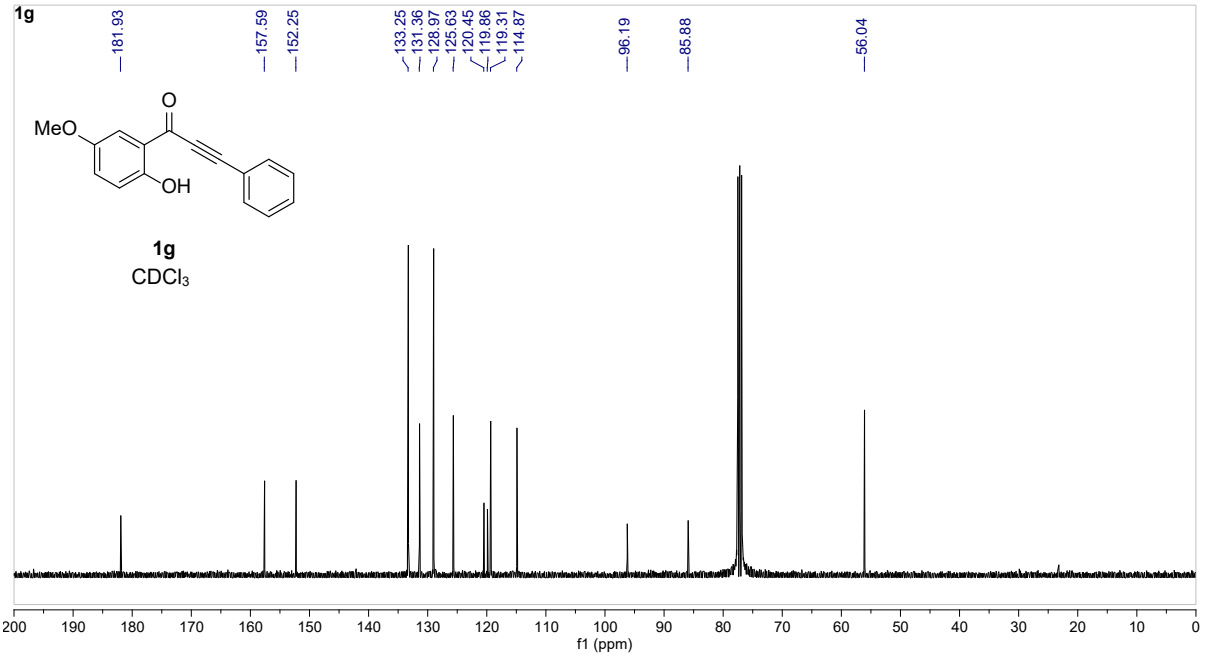
9.24
9.24
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

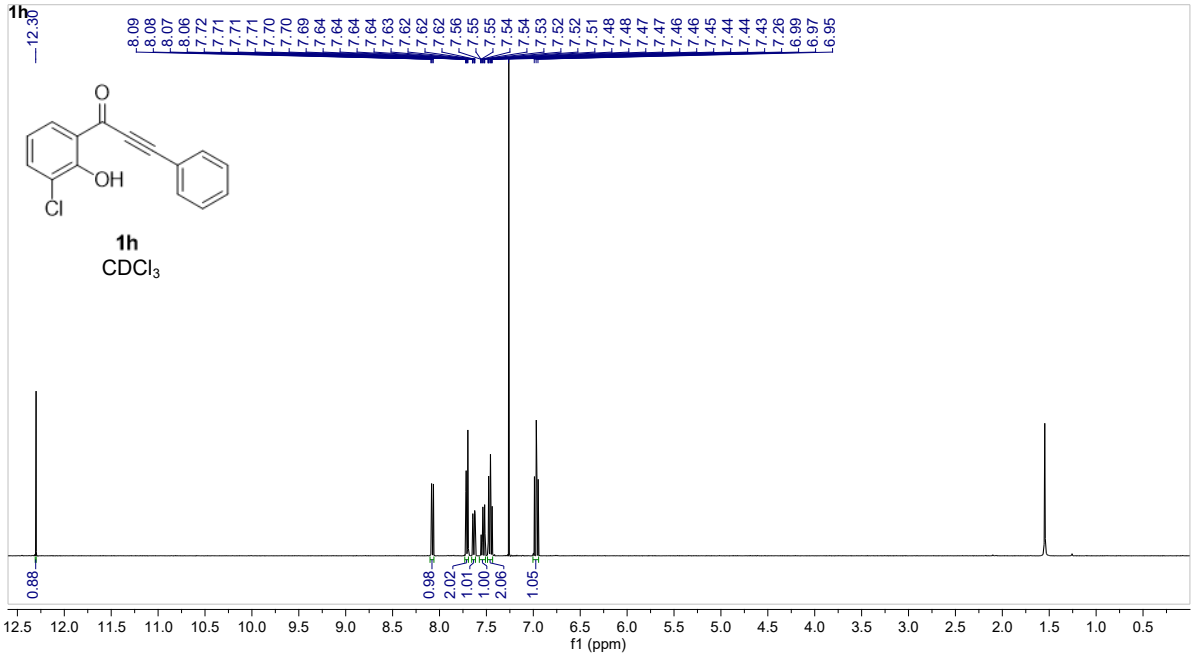

1e
183.12
160.79
140.90
138.03
133.27
132.44
131.19
128.96
127.03
120.17
120.10
95.77
86.30
35.28
34.43
31.43
29.48
O
OH
1e
CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

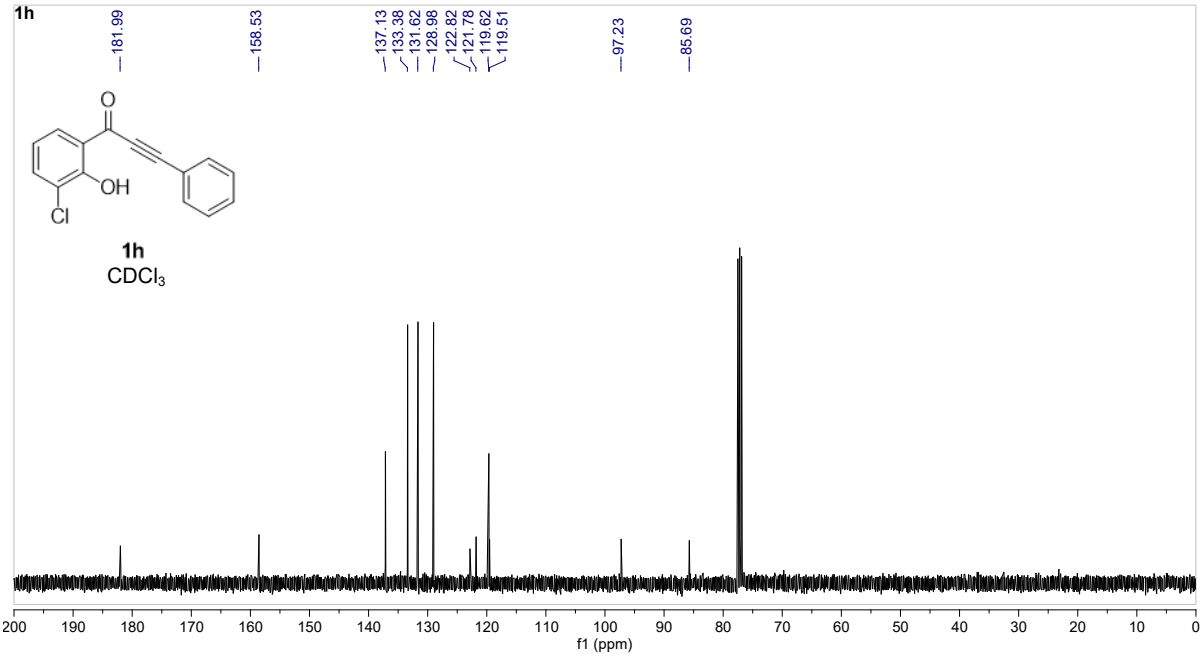

1f
12.02
7.75
7.75
7.73
7.73
7.71
7.71
7.70
7.69
7.69
7.54
7.54
7.53
7.52
7.52
7.51
7.50
7.50
7.50
7.47
7.46
7.46
7.46
7.45
7.44
7.44
7.43
7.43
7.42
7.26
7.13
7.13
7.11
7.11
6.96
6.94
6.92
3.93
O
OH
OMe
1f
CDCl3
0.91
0.97
1.95
1.00
2.00
1.00
1.00
3.01
f1 (ppm)

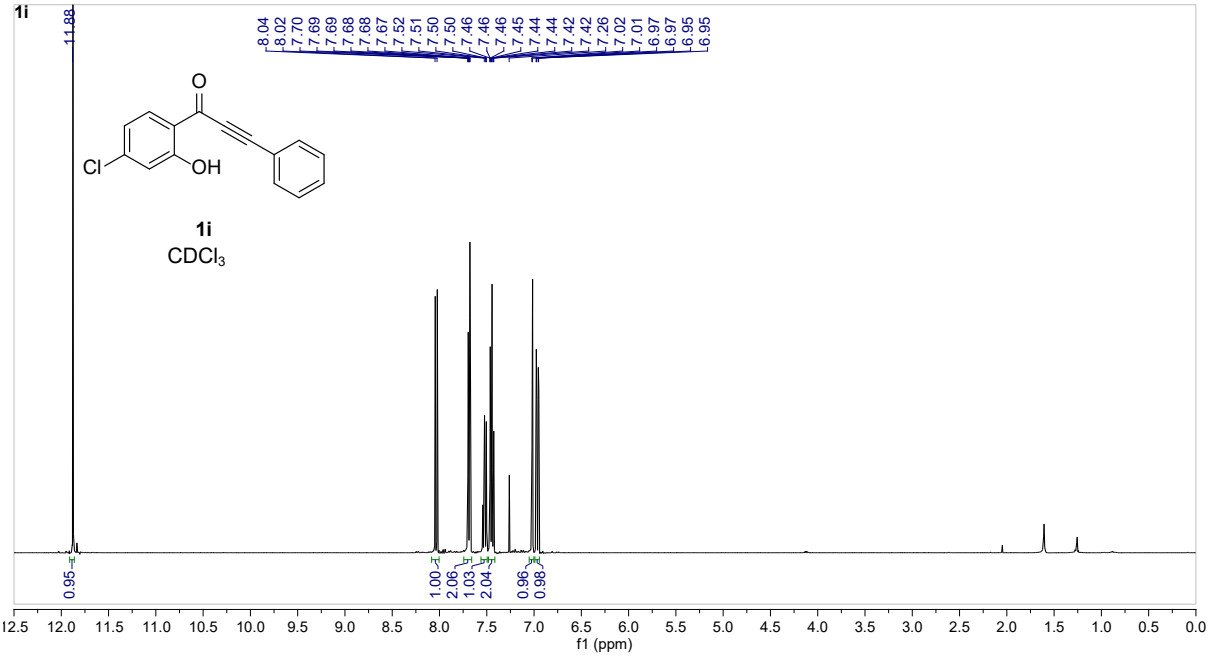

1f
182.58
153.38
148.81
133.27
131.32
128.89
124.18
120.98
119.81
118.89
117.93
96.24
86.09
56.42
O
OH
OMe
1f
CDCl3
f1 (ppm)

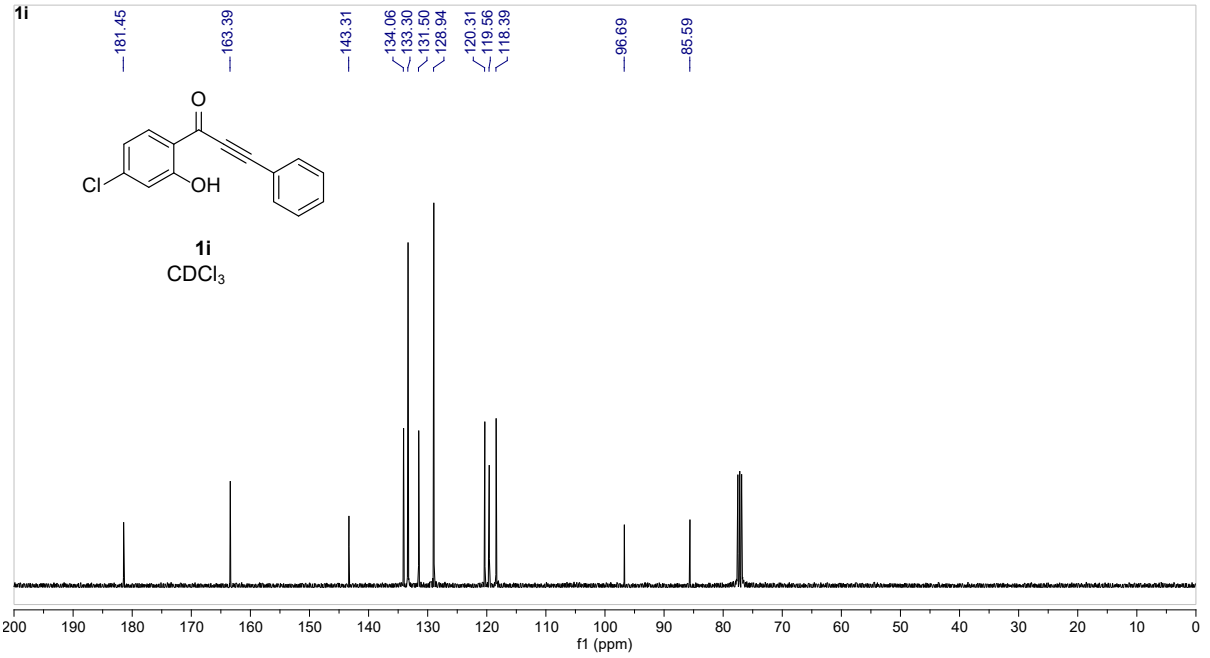

1g
11.39
7.70
7.69
7.69
7.68
7.68
7.67
7.59
7.59
7.54
7.52
7.51
7.50
7.50
7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.26
7.19
7.18
7.17
7.16
6.97
6.94
3.86
MeO
O
OH
1g
CDCl3
0.90
2.03
0.98
1.02
2.08
1.00
0.98
3.13
f1 (ppm)

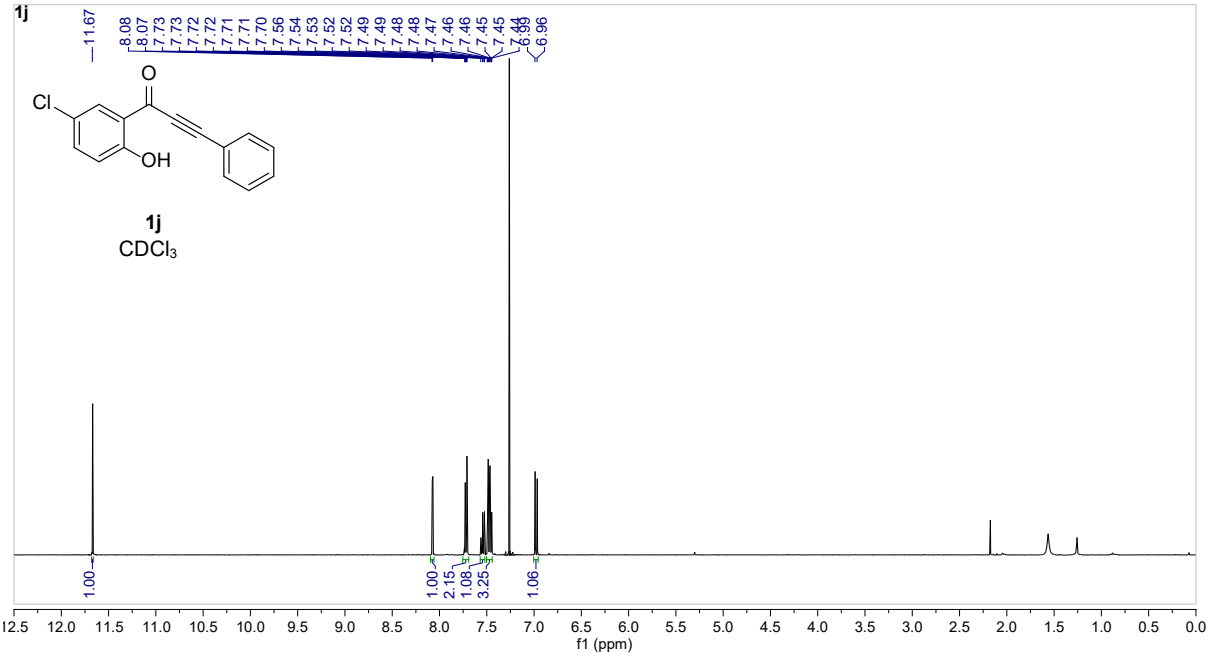

1g
181.93
157.59
152.25
133.25
131.36
128.97
125.63
120.45
119.86
119.31
114.87
96.19
85.88
56.04
MeO
O
OH
1g
CDCl3
f1 (ppm)

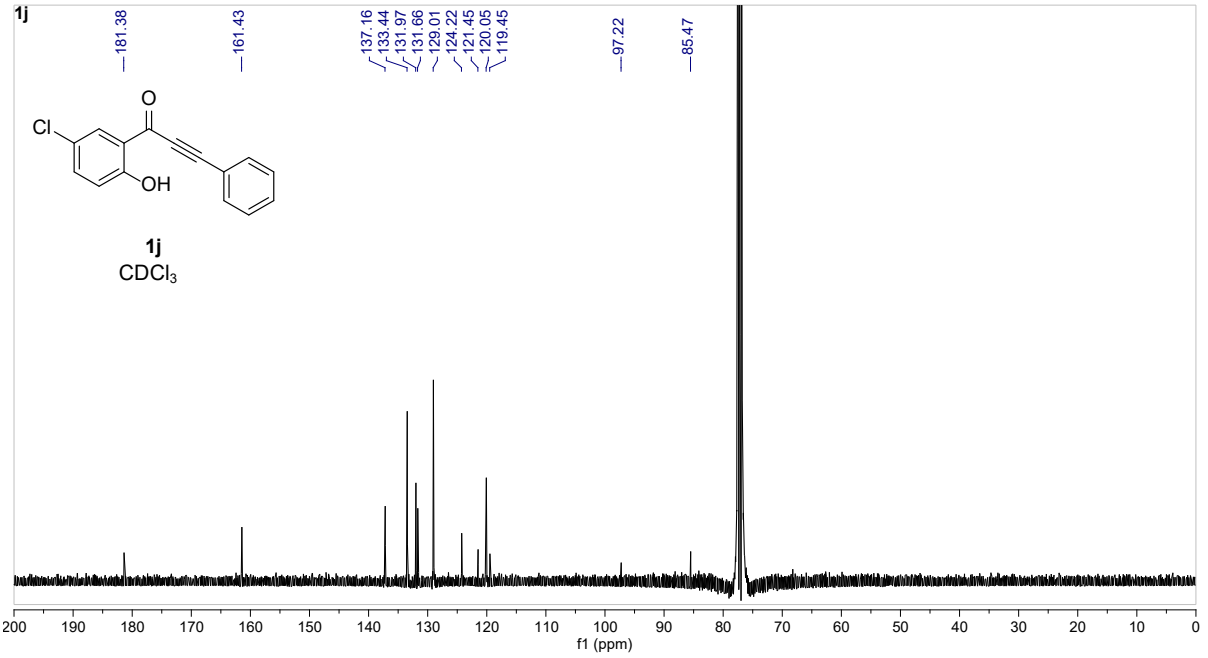

1h
12.30
8.09
8.08
8.07
8.06
7.72
7.71
7.71
7.70
7.70
7.69
7.64
7.64
7.64
7.64
7.63
7.62
7.62
7.62
7.56
7.55
7.55
7.54
7.54
7.53
7.52
7.52
7.51
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.26
6.99
6.97
6.95
O
OH
Cl
1h
CDCl3
0.88
0.98
2.02
1.01
1.00
2.06
1.05
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 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
f1 (ppm)

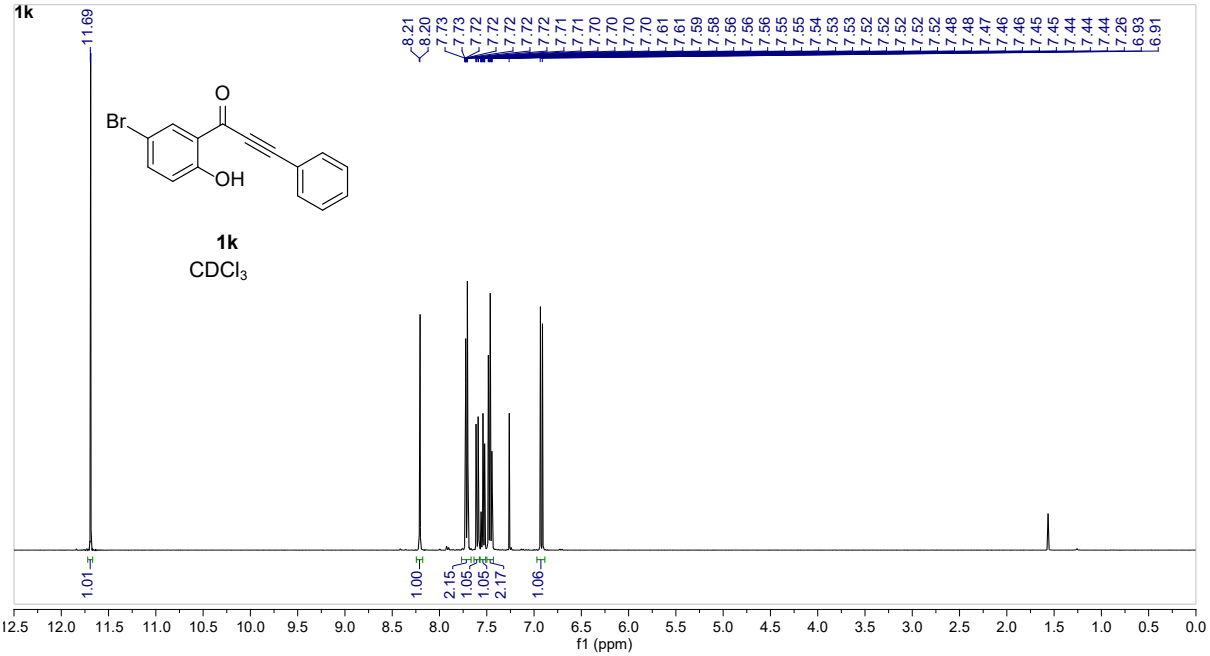

1h
181.99
158.53
137.13
133.38
131.62
128.98
122.82
121.78
119.62
119.51
97.23
85.69
O
OH
Cl
1h
CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

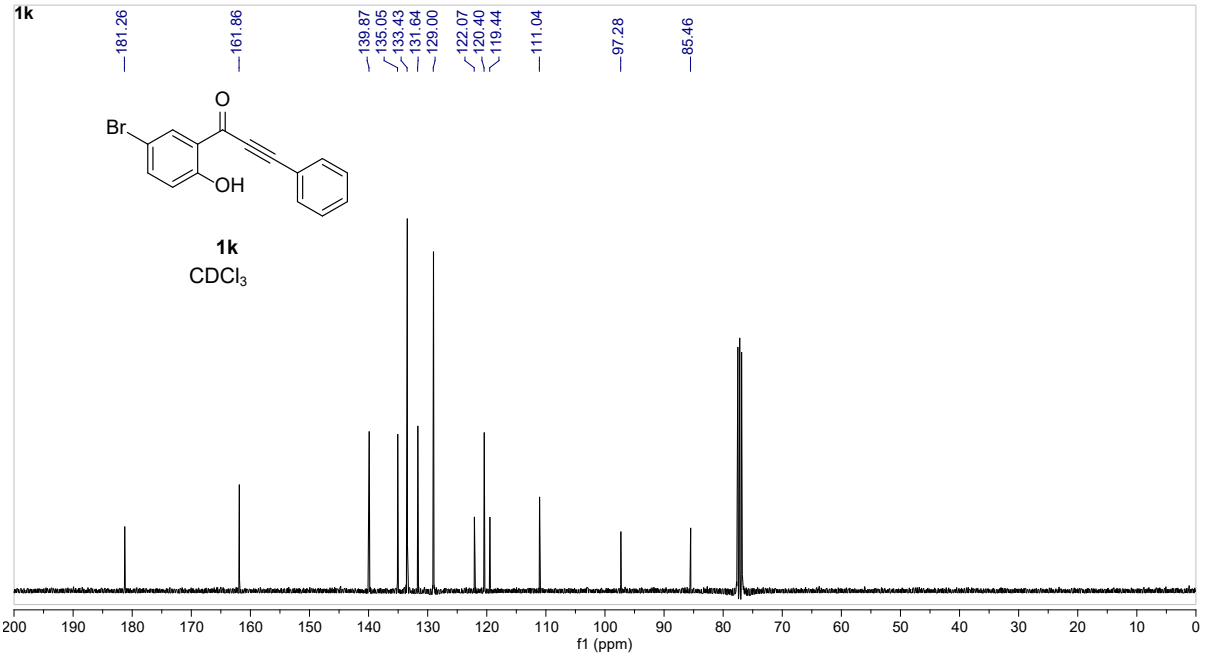

1i
11.88
8.04
8.02
7.70
7.69
7.69
7.68
7.68
7.67
7.52
7.51
7.50
7.50
7.46
7.46
7.46
7.45
7.44
7.44
7.42
7.42
7.26
7.02
7.01
6.97
6.97
6.95
6.95
O
Cl
OH
1i
CDCl3
0.95
1.00
2.06
1.03
2.04
0.96
0.98
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

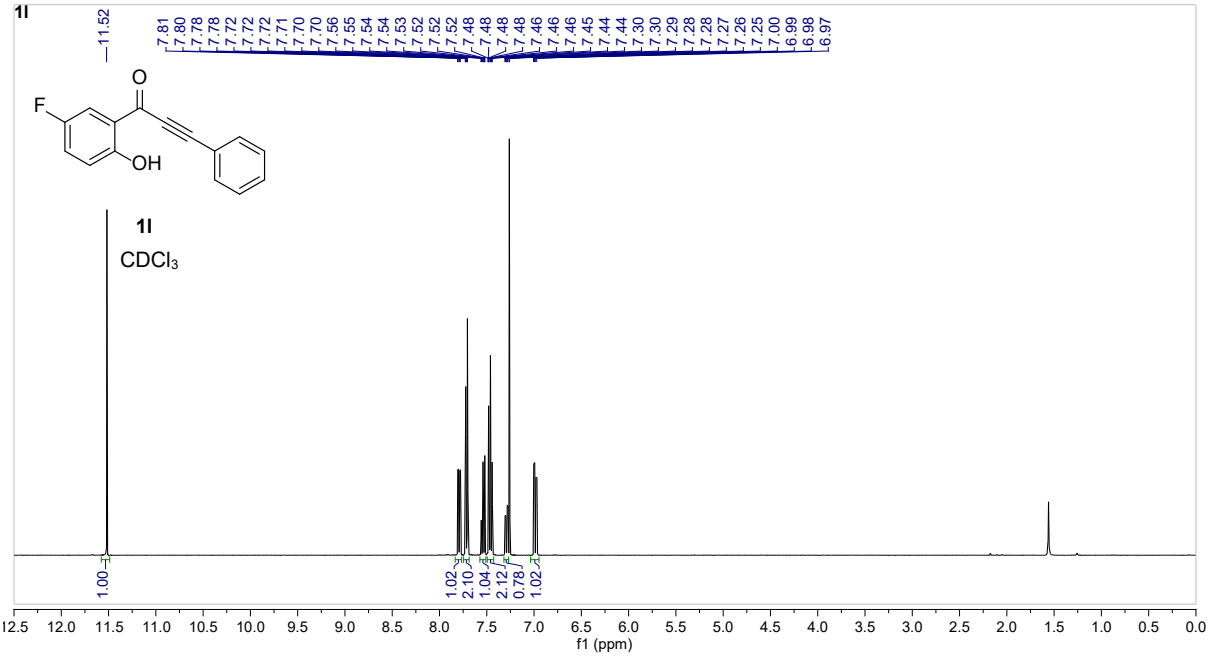

1i
181.45
163.39
143.31
134.06
133.30
131.50
128.94
120.31
119.56
118.39
96.69
85.59
O
Cl
OH
1i
CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

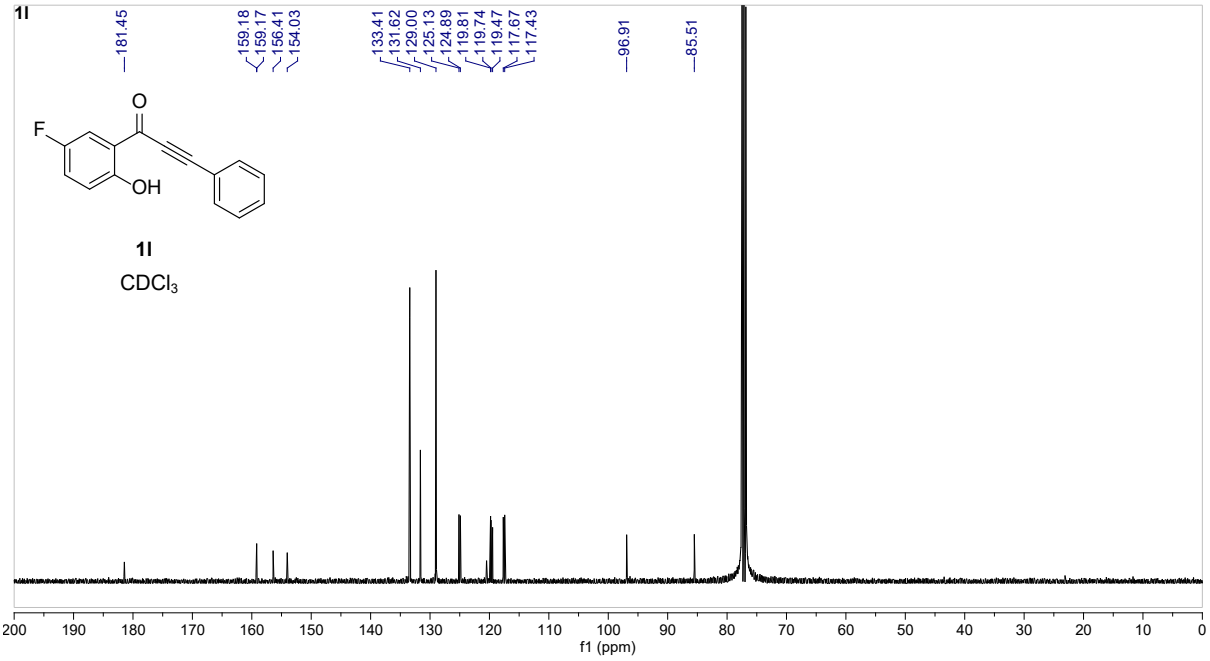

1j
11.67
8.08
8.07
7.73
7.73
7.72
7.72
7.71
7.71
7.70
7.56
7.54
7.53
7.52
7.52
7.49
7.49
7.48
7.48
7.47
7.46
7.46
7.45
7.45
7.44
6.99
6.96
Cl
O
OH
1j
CDCl3
1.00
1.00
2.15
1.08
3.25
1.06
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

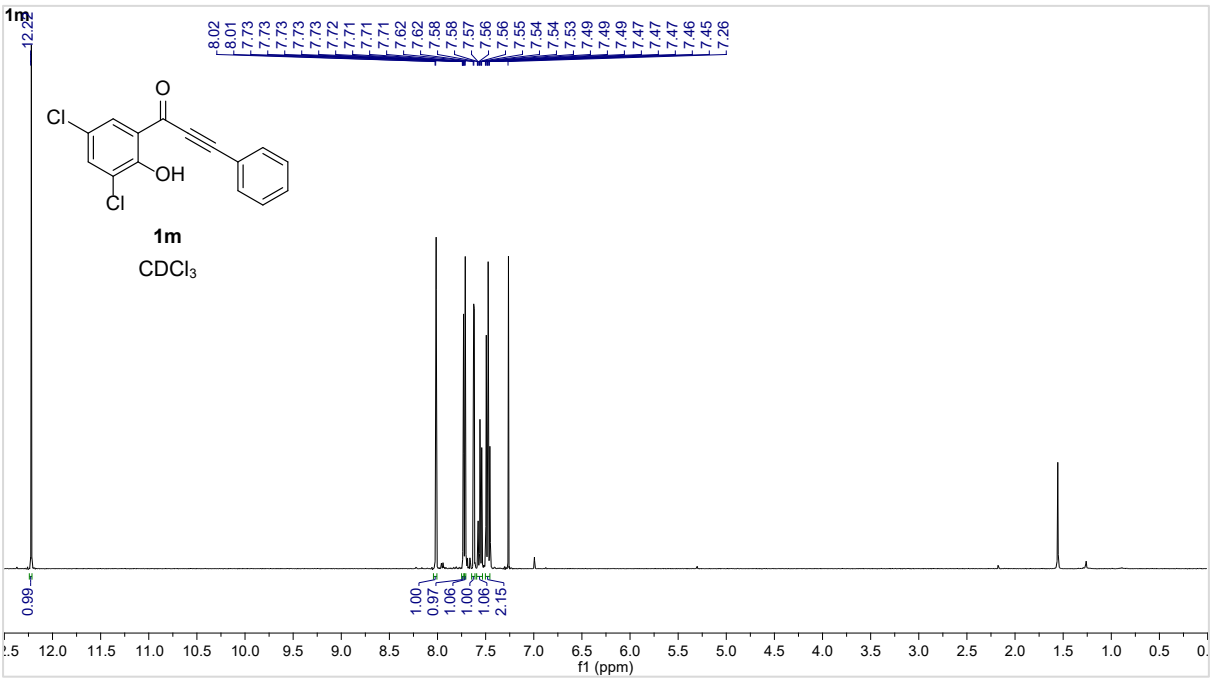

1j
181.38
161.43
137.16
133.44
131.97
131.66
129.01
124.22
121.45
120.05
119.45
97.22
85.47
Cl
O
OH
1j
CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

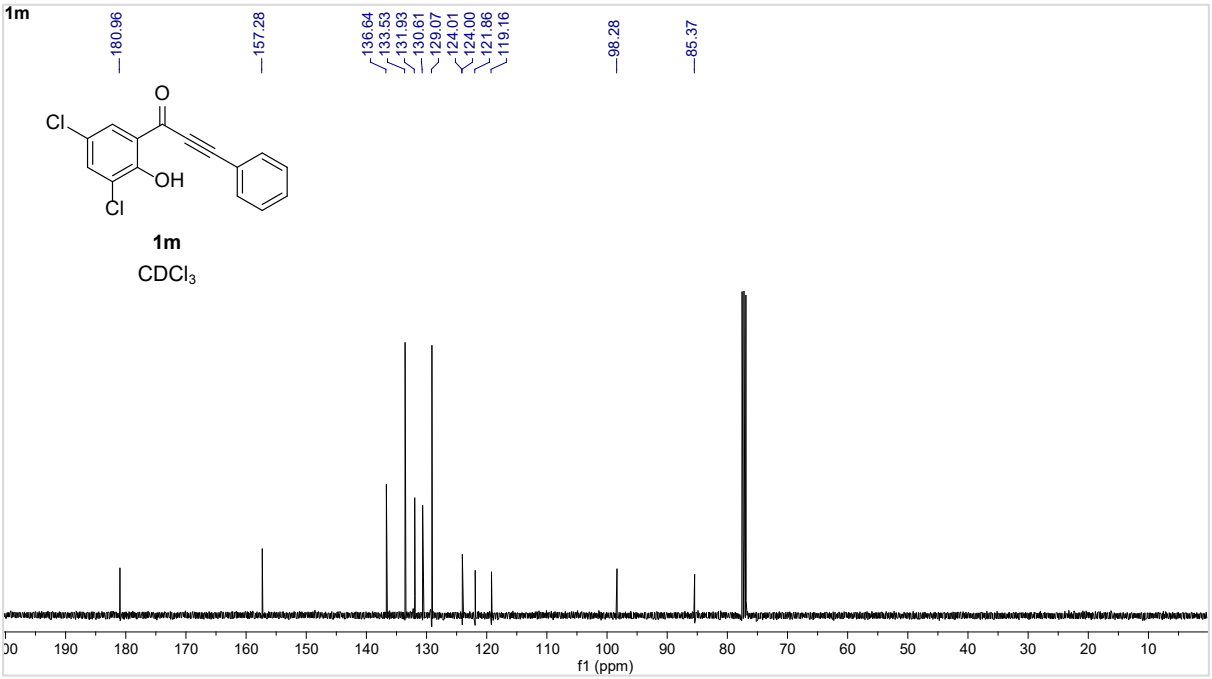

1k
11.69
8.21
8.20
7.73
7.72
7.72
7.72
7.72
7.72
7.71
7.71
7.70
7.70
7.70
7.70
7.61
7.61
7.59
7.58
7.56
7.56
7.56
7.55
7.55
7.54
7.53
7.53
7.52
7.52
7.52
7.52
7.52
7.48
7.48
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.44
7.26
6.93
6.91
Br
O
OH
1k
CDCl3
1.01
1.00
2.15
1.05
1.05
2.17
1.06
f1 (ppm)

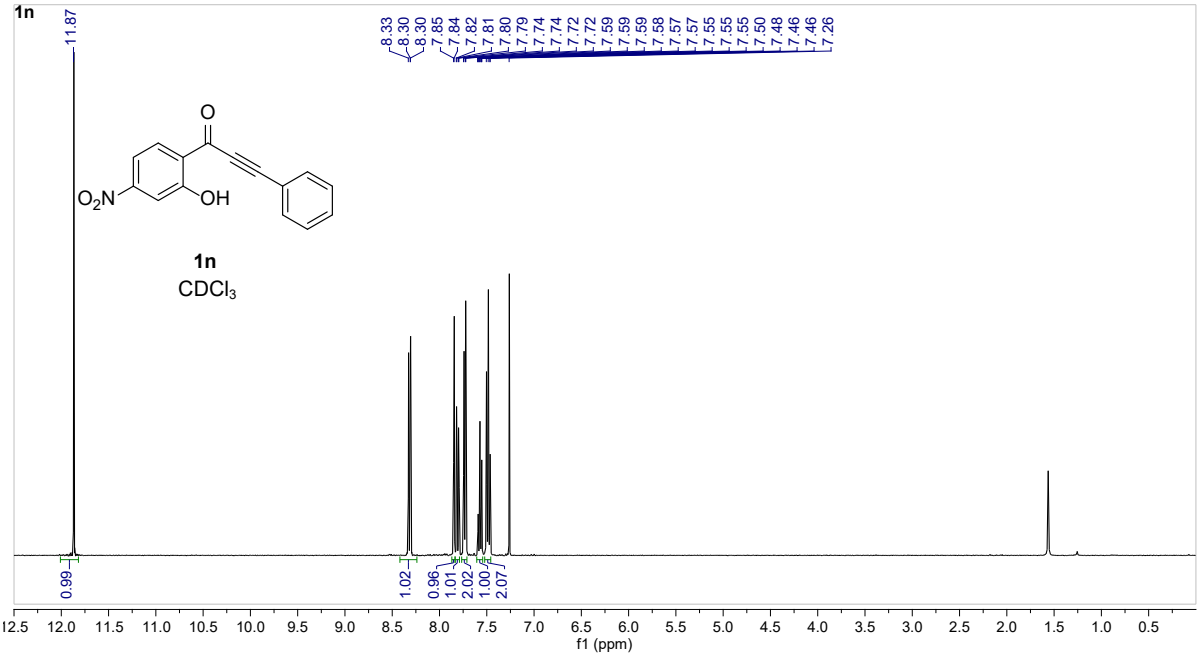

1k
181.26
161.86
139.87
135.05
133.43
131.64
129.00
122.07
120.40
119.44
111.04
97.28
85.46
Br
O
OH
1k
CDCl3
f1 (ppm)

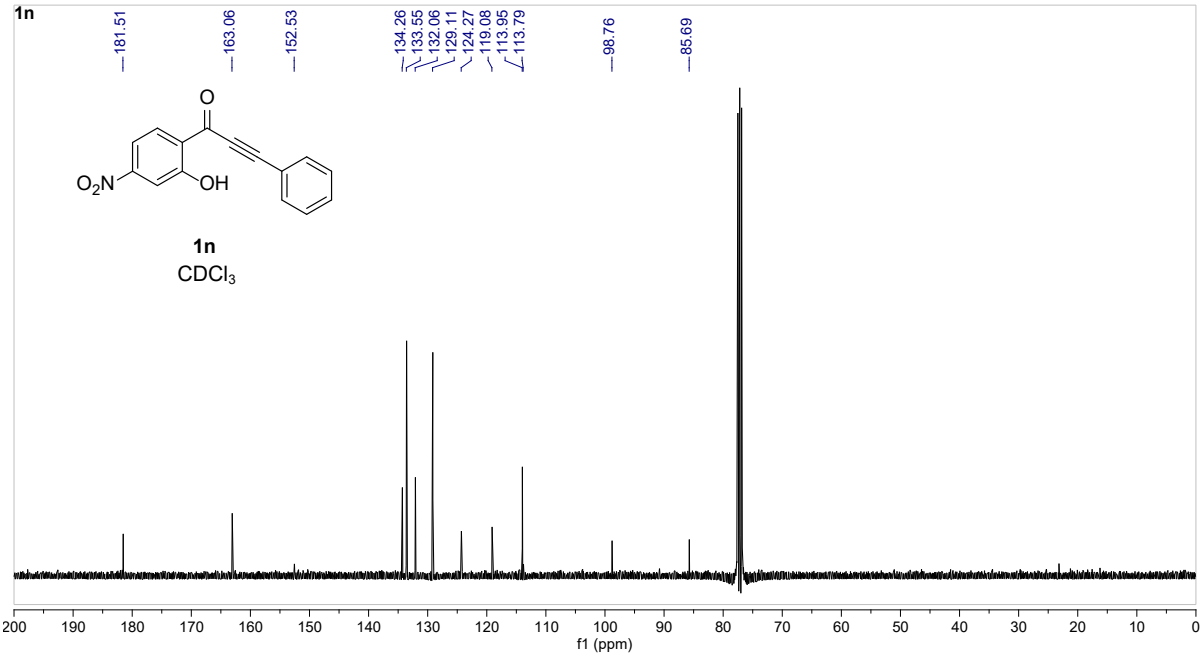

1l
11.52
7.81
7.80
7.78
7.78
7.72
7.72
7.72
7.71
7.70
7.70
7.56
7.55
7.54
7.54
7.53
7.52
7.52
7.52
7.48
7.48
7.48
7.48
7.46
7.46
7.46
7.45
7.44
7.44
7.30
7.30
7.29
7.28
7.28
7.27
7.26
7.25
7.00
6.99
6.98
6.97
O
F
OH
1l
CDCl3
1.00
1.02
2.10
1.04
2.12
0.78
1.02
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 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)

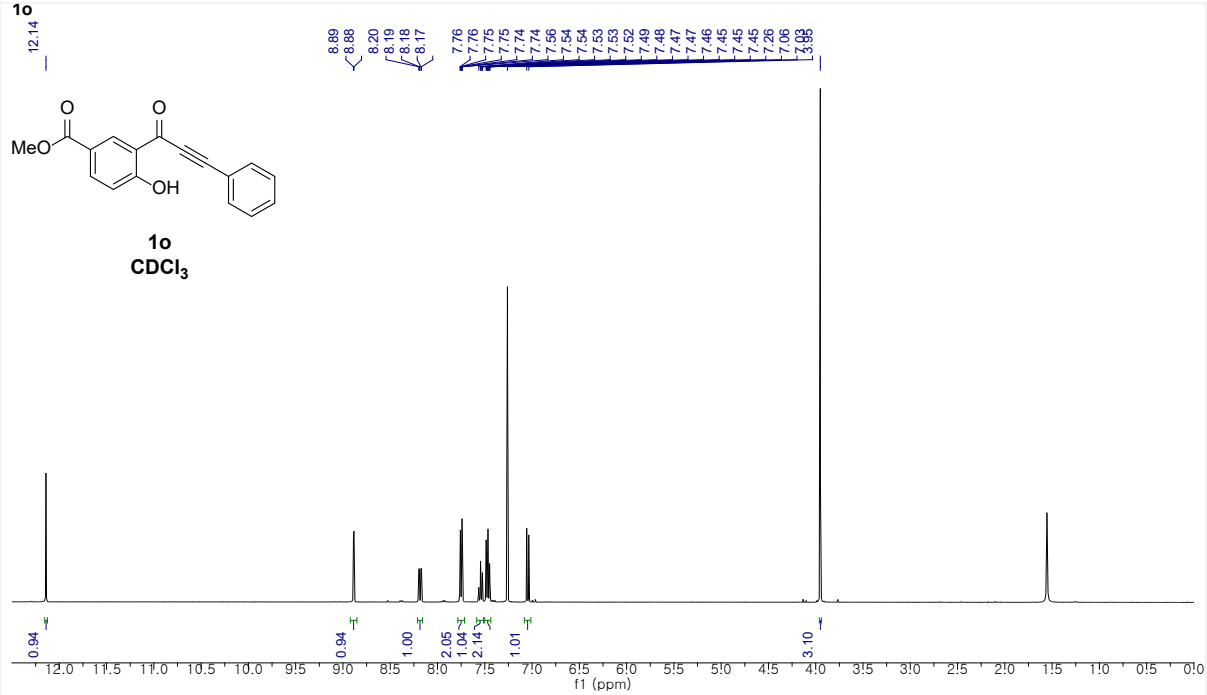

1l
181.45
159.18
159.17
156.41
154.03
133.41
131.62
129.00
125.13
124.89
119.81
119.74
119.47
117.67
117.43
96.91
85.51
O
F
OH
1l
CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

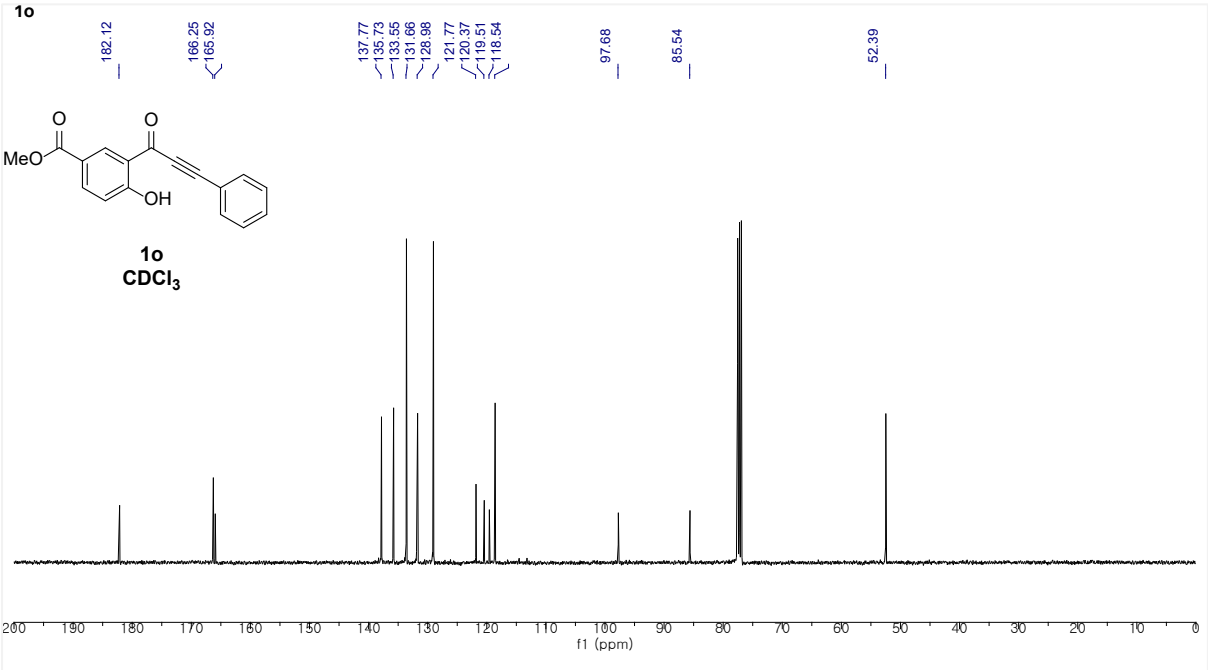

1m
12.22
8.02
8.01
7.73
7.73
7.73
7.73
7.72
7.71
7.71
7.71
7.62
7.58
7.58
7.57
7.56
7.56
7.55
7.54
7.54
7.53
7.49
7.49
7.49
7.47
7.47
7.47
7.46
7.45
7.26
Cl
O
OH
Cl
1m
CDCl3
0.99
1.00
0.97
1.06
1.00
1.06
2.15
f1 (ppm)

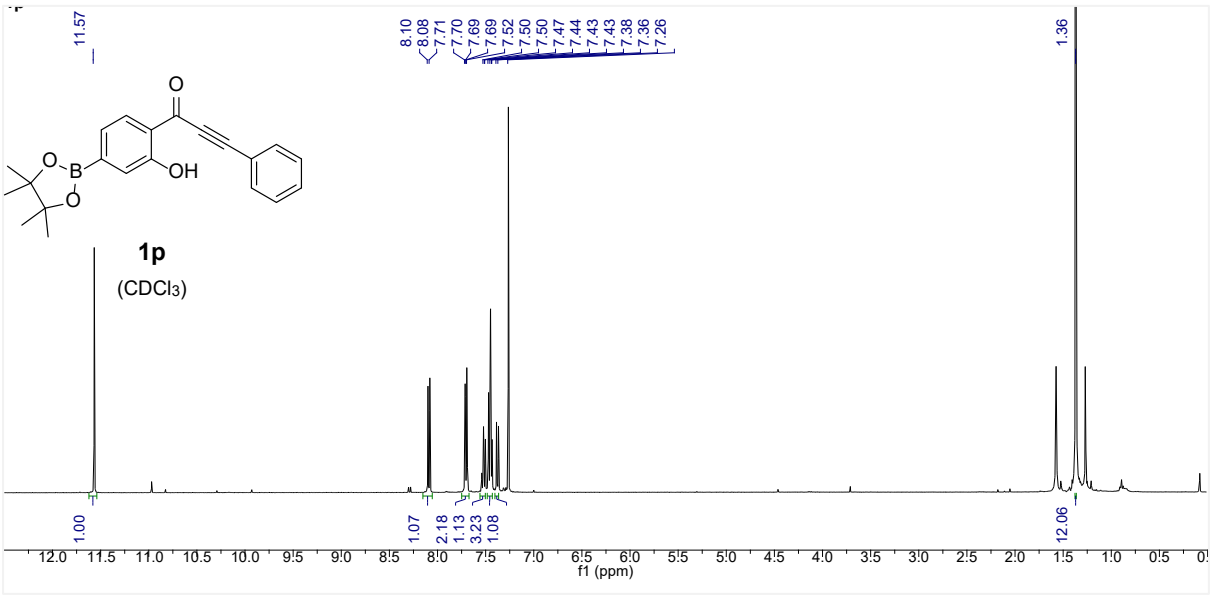

1m
180.96
157.28
136.64
133.53
131.93
130.61
129.07
124.01
124.00
121.86
119.16
98.28
85.37
Cl
O
OH
Cl
1m
CDCl3
f1 (ppm)

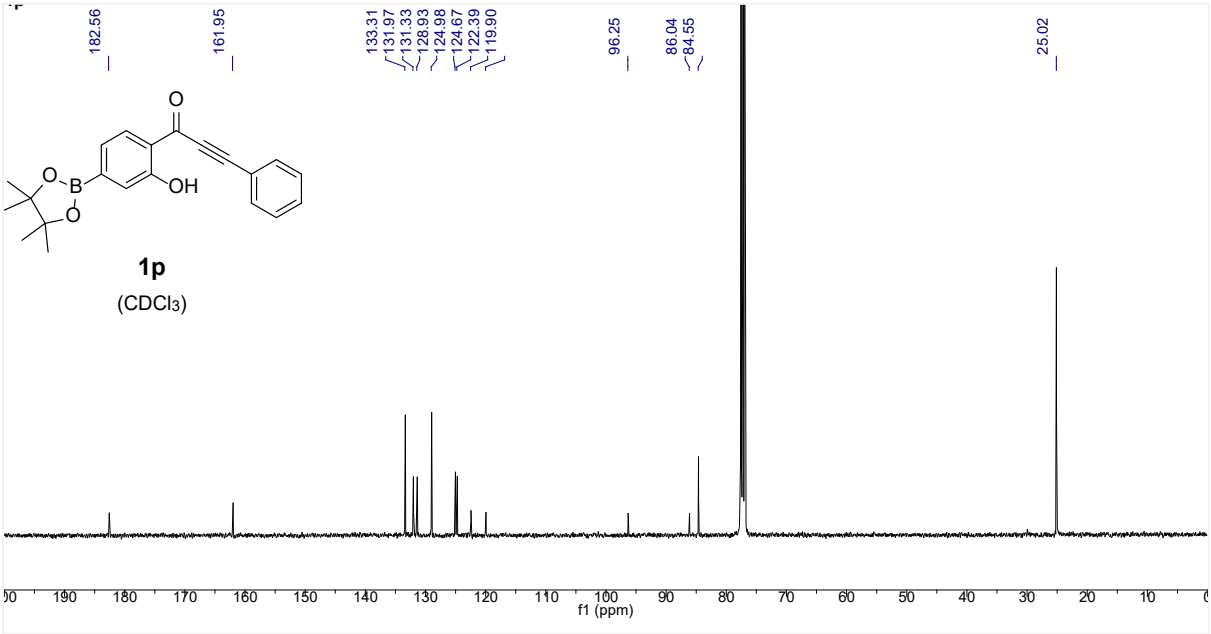

1n
11.87
8.33
8.30
8.30
7.85
7.84
7.82
7.81
7.80
7.79
7.74
7.74
7.72
7.72
7.59
7.59
7.59
7.58
7.57
7.57
7.55
7.55
7.55
7.50
7.48
7.46
7.46
7.26
O
O2N
OH
1n
CDCl3
0.99
1.02
0.96
1.01
2.02
1.00
2.07
f1 (ppm)

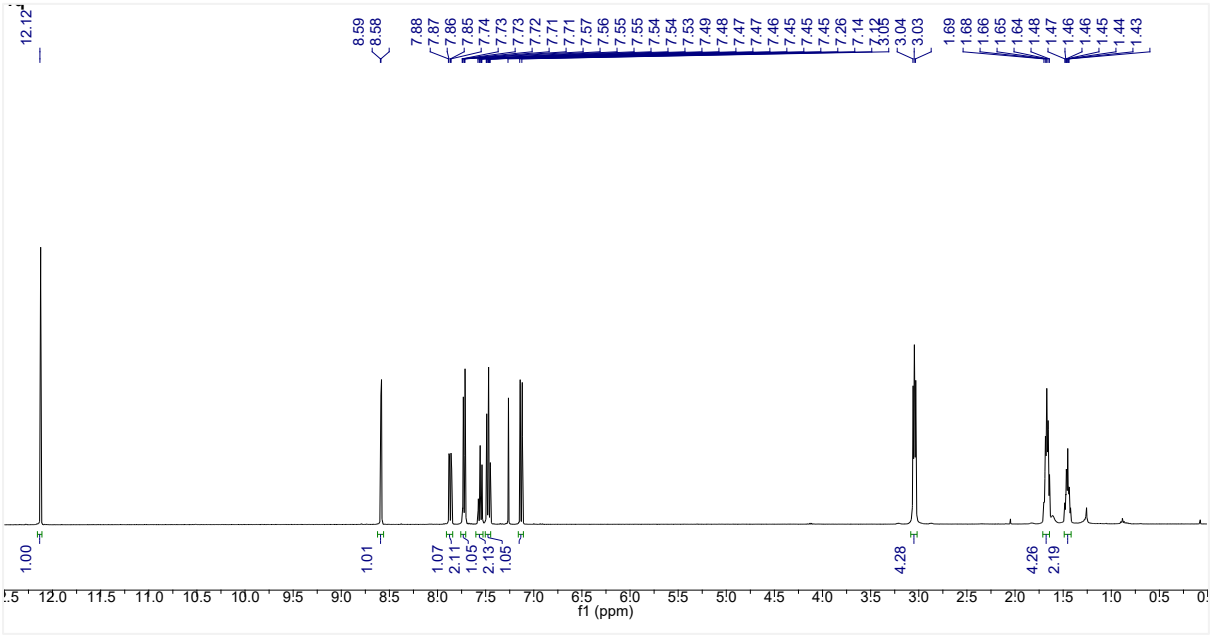

1n
181.51
163.06
152.53
134.26
133.55
132.06
129.11
124.27
119.08
113.95
113.79
98.76
85.69
O
O2N
OH
1n
CDCl3
f1 (ppm)

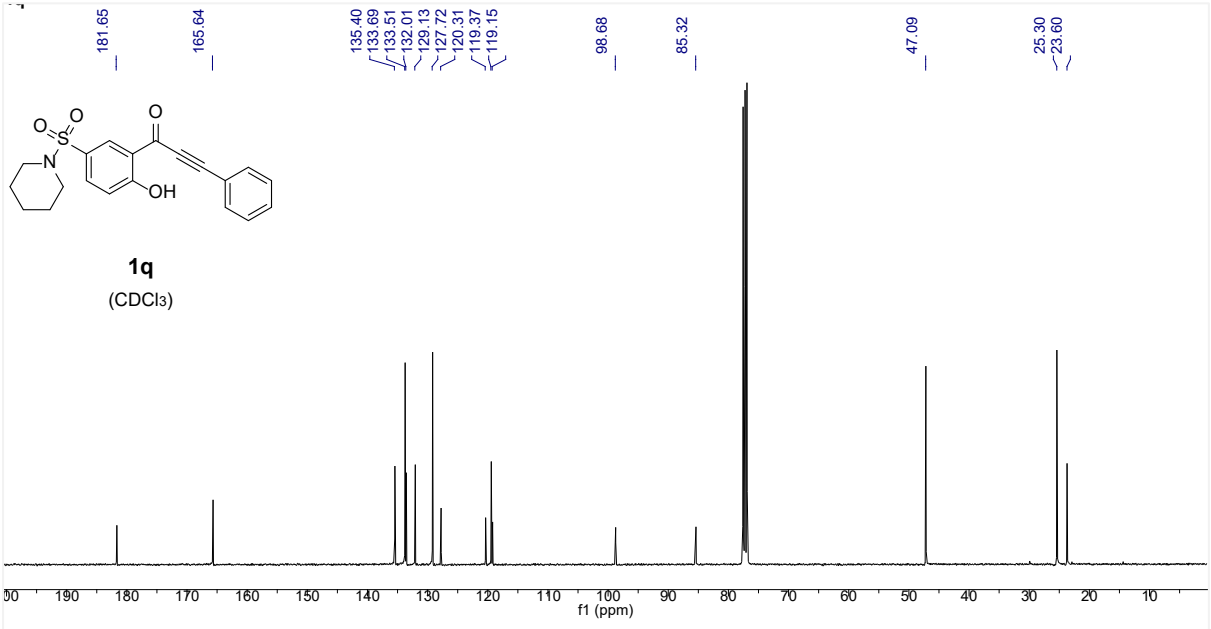

1o
12.14
8.89
8.88
8.20
8.19
8.18
8.17
7.76
7.76
7.75
7.75
7.74
7.74
7.56
7.54
7.54
7.53
7.53
7.52
7.49
7.48
7.47
7.47
7.46
7.45
7.45
7.45
7.26
7.06
3.93
MeO
O
O
OH
1o
CDCl3
0.94
0.94
1.00
2.05
1.04
2.14
1.01
3.10
f1 (ppm)

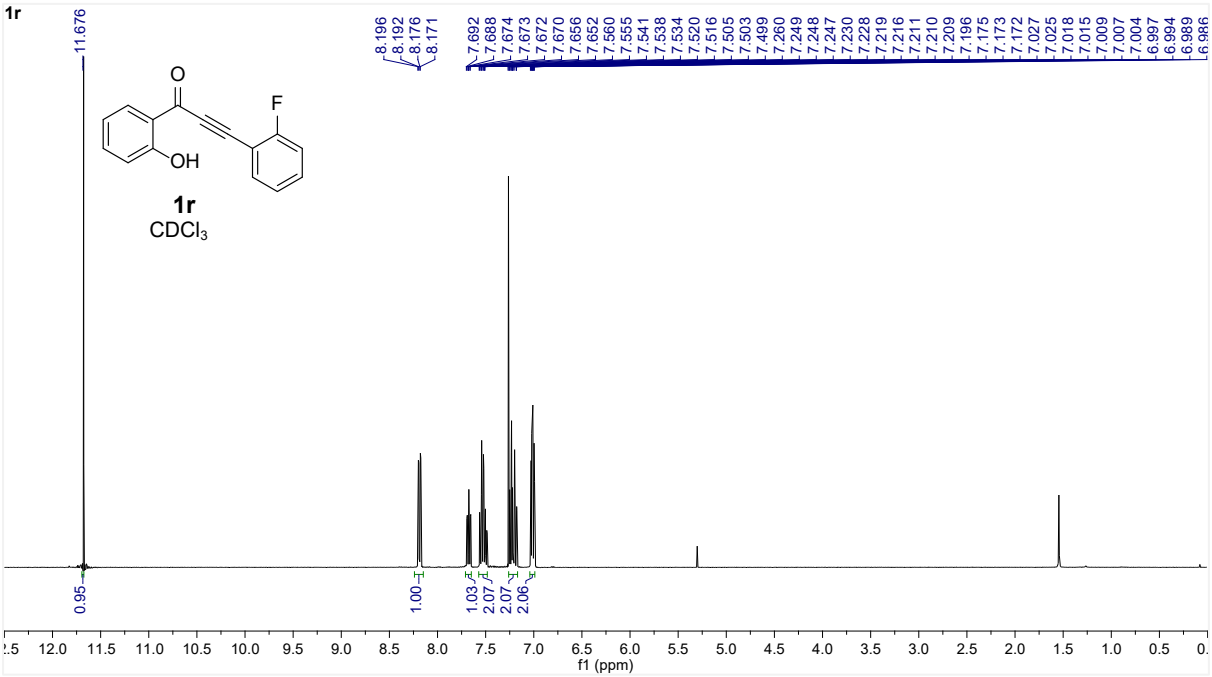

1o
182.12
166.25
165.92
137.77
135.73
133.55
131.66
128.98
121.77
120.37
119.51
118.54
97.68
85.54
52.39
MeO
O
O
OH
1o
CDCl3
f1 (ppm)

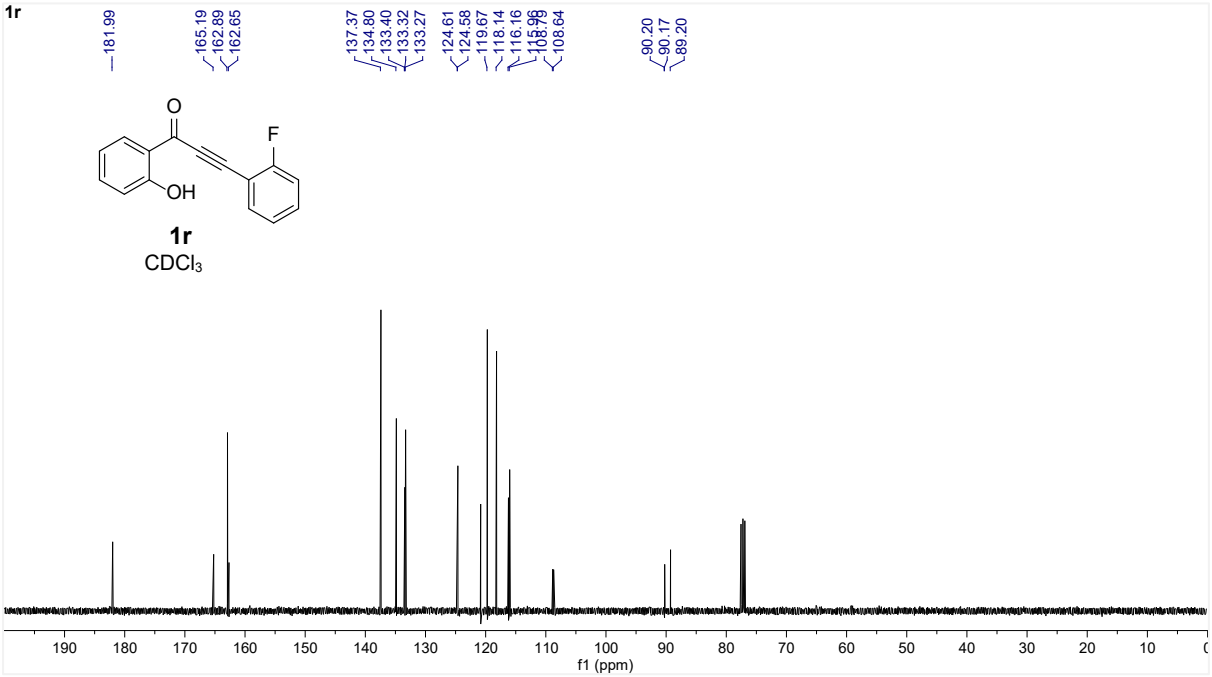

11.57
8.10
8.08
7.71
7.70
7.69
7.52
7.50
7.47
7.44
7.43
7.43
7.38
7.36
7.26
1.36
O
O
B
O
OH
1p
(CDCl3)
1.00
1.07
2.18
1.13
3.23
1.08
12.06
f1 (ppm)

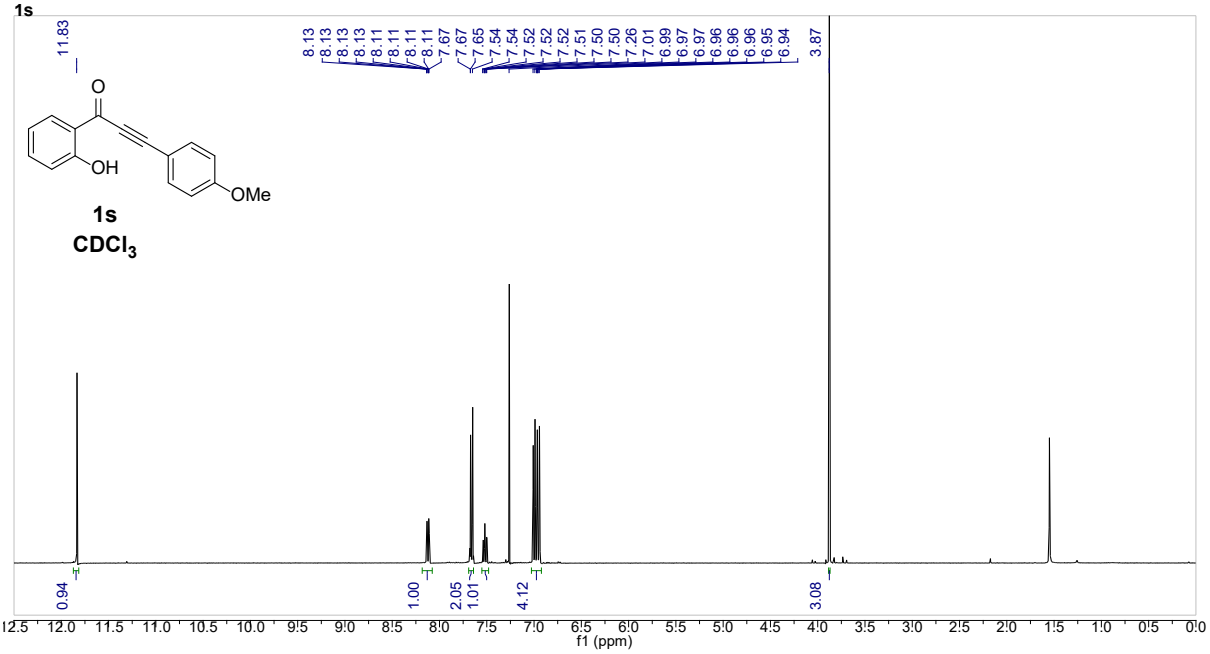

182.56
161.95
133.31
131.97
131.33
128.93
124.98
124.67
122.39
119.90
96.25
86.04
84.55
25.02
O
O
B
O
OH
1p
(CDCl3)
f1 (ppm)

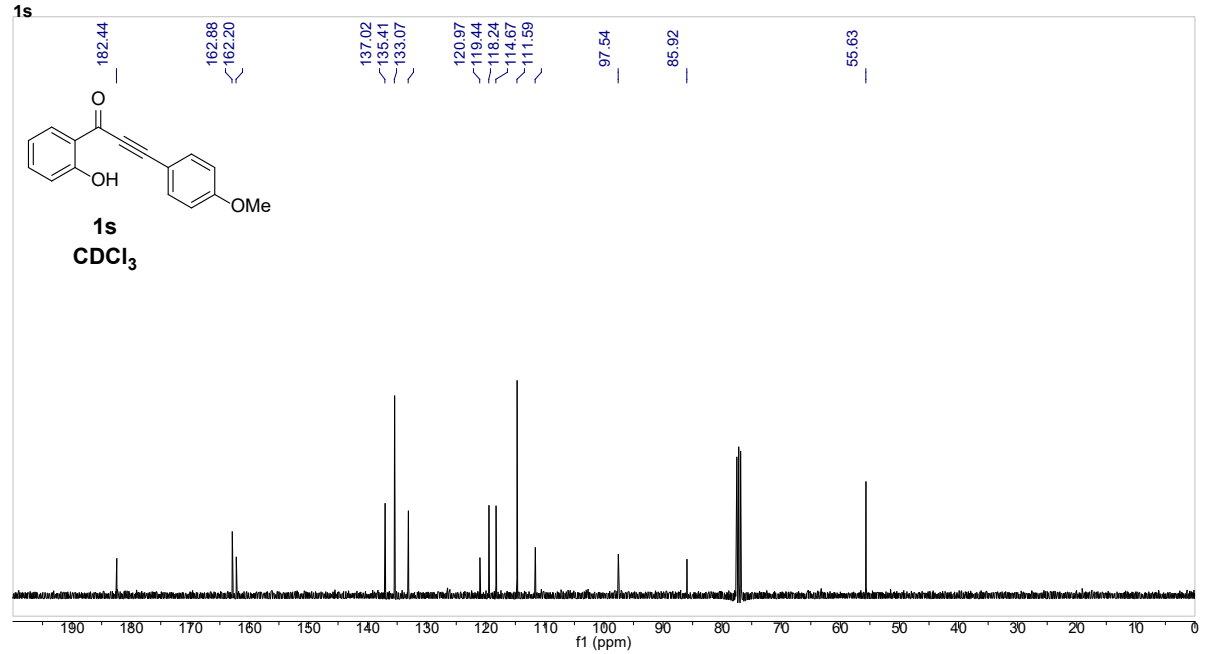

12.12
8.59
8.58
7.88
7.87
7.86
7.85
7.74
7.73
7.72
7.71
7.57
7.56
7.55
7.55
7.54
7.54
7.53
7.49
7.48
7.47
7.47
7.46
7.45
7.45
7.45
7.26
7.14
3.05
3.04
3.03
1.69
1.68
1.66
1.65
1.64
1.48
1.47
1.46
1.46
1.45
1.44
1.43
1.00
1.01
1.07
2.11
1.05
2.13
1.05
4.28
4.26
2.19
f1 (ppm)

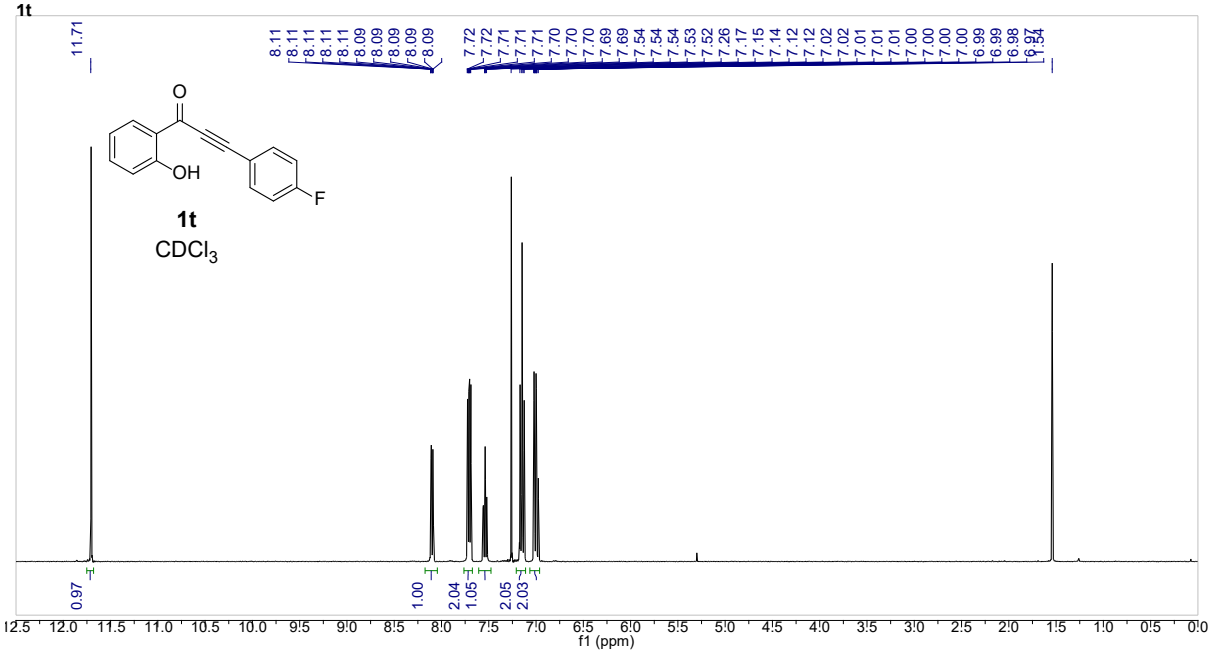

181.65
165.64
135.40
133.69
133.51
132.01
129.13
127.72
120.31
119.37
119.15
98.68
85.32
47.09
25.30
23.60
O
O
S
O
N
OH
1q
(CDCl3)
f1 (ppm)

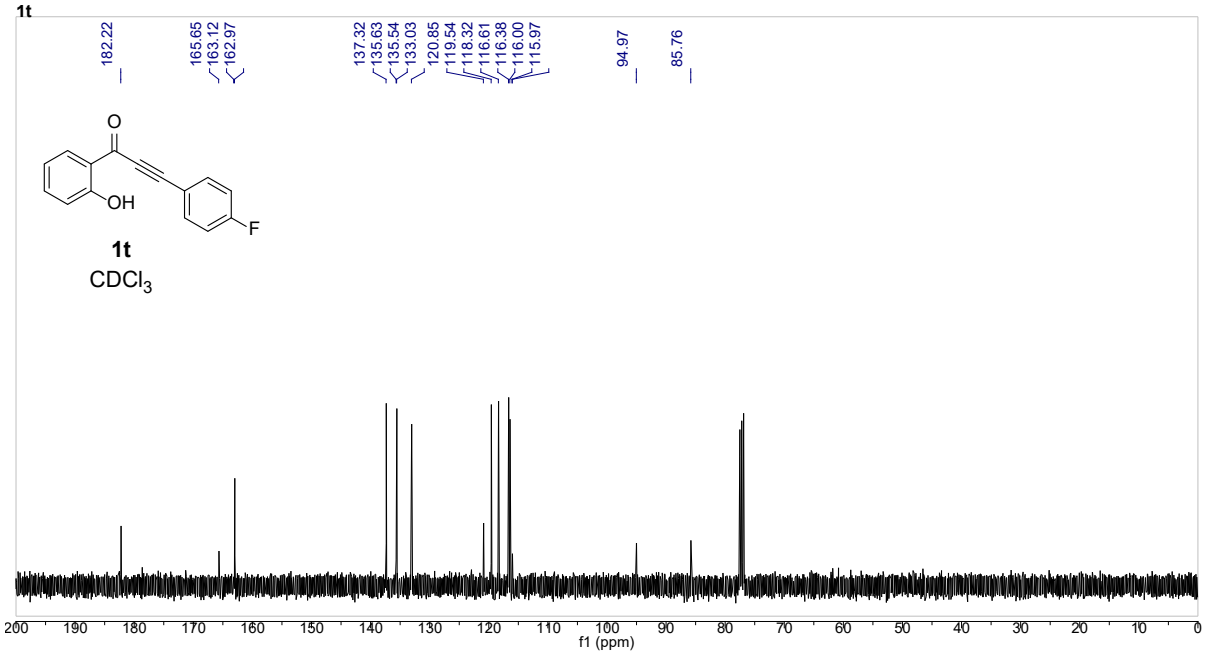

1r
11.676
8.196
8.192
8.176
8.171
7.692
7.688
7.674
7.673
7.672
7.670
7.656
7.652
7.560
7.555
7.541
7.538
7.534
7.520
7.516
7.505
7.503
7.499
7.260
7.249
7.248
7.247
7.230
7.228
7.219
7.216
7.211
7.210
7.209
7.196
7.175
7.173
7.172
7.027
7.025
7.018
7.015
7.009
7.007
7.004
6.997
6.994
6.989
6.986
O
F
OH
1r
CDCl3
0.95
1.00
1.03
2.07
2.07
2.06
f1 (ppm)

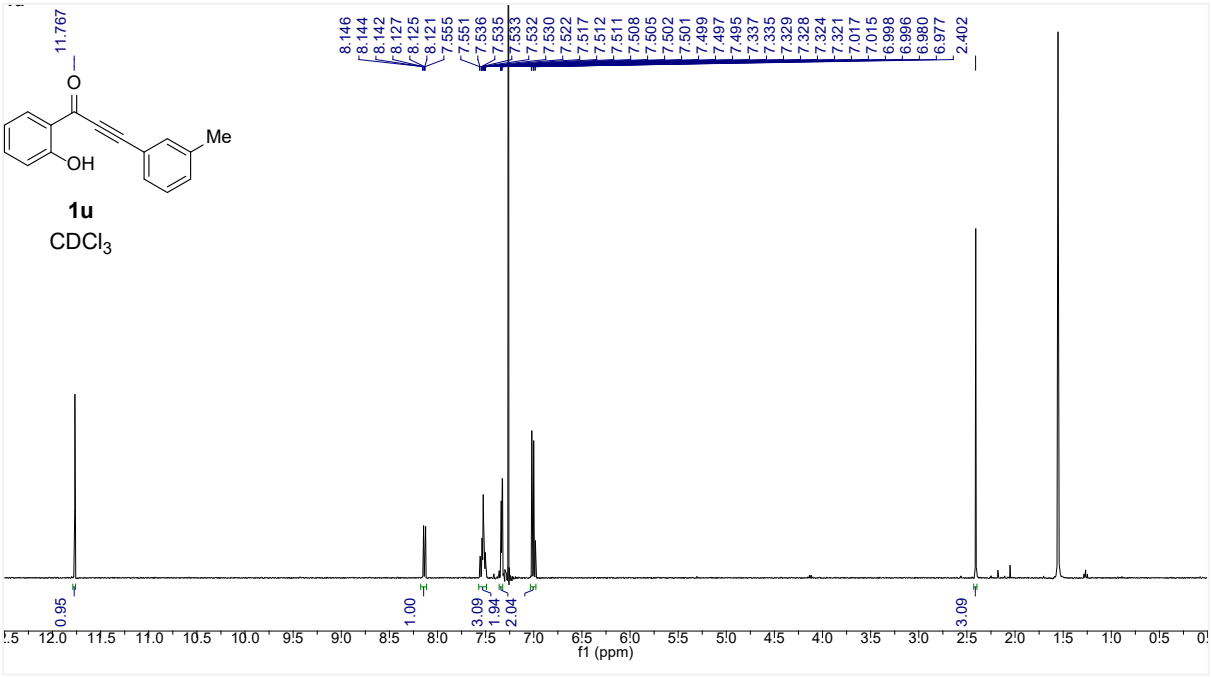

1r
181.99
165.19
162.89
162.65
137.37
134.80
133.40
133.32
133.27
124.61
124.58
119.67
118.14
116.16
115.96
115.79
108.79
108.64
90.20
90.17
89.20
O
F
OH
1r
CDCl3
f1 (ppm)

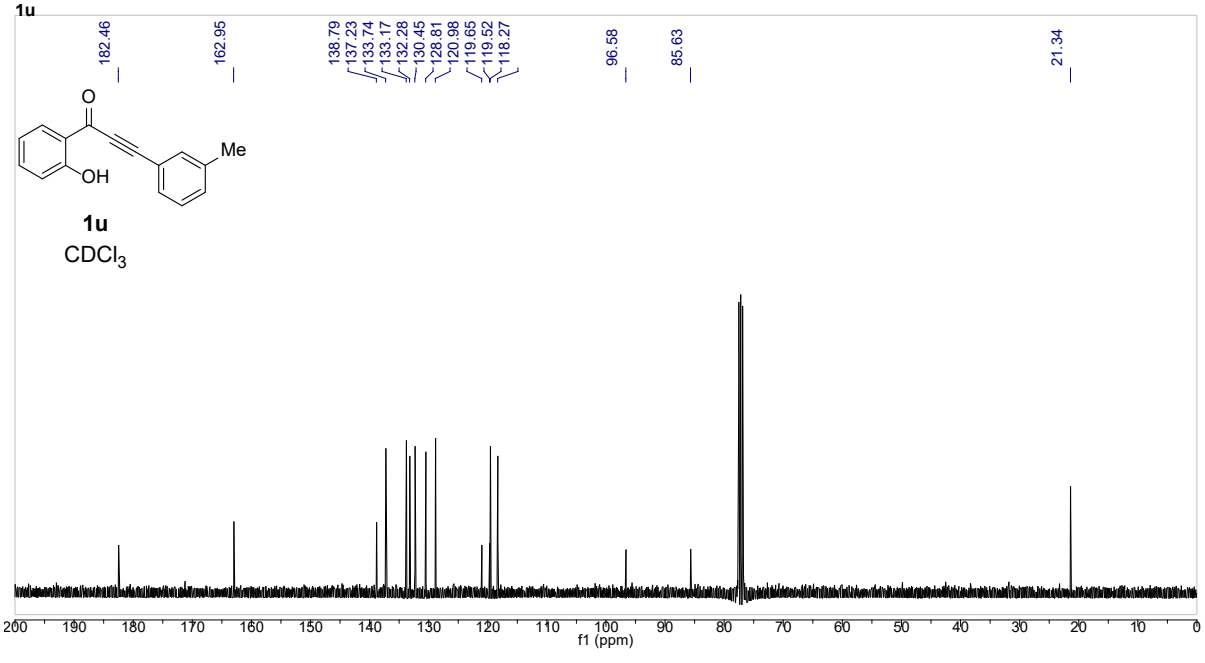

1s
11.83
8.13
8.13
8.13
8.13
8.11
8.11
8.11
8.11
7.67
7.67
7.65
7.54
7.54
7.52
7.52
7.52
7.51
7.50
7.50
7.26
7.01
6.99
6.97
6.97
6.96
6.96
6.96
6.95
6.94
3.87
O
OH
OMe
1s
CDCl3
0.94
1.00
2.05
1.01
4.12
3.08
f1 (ppm)

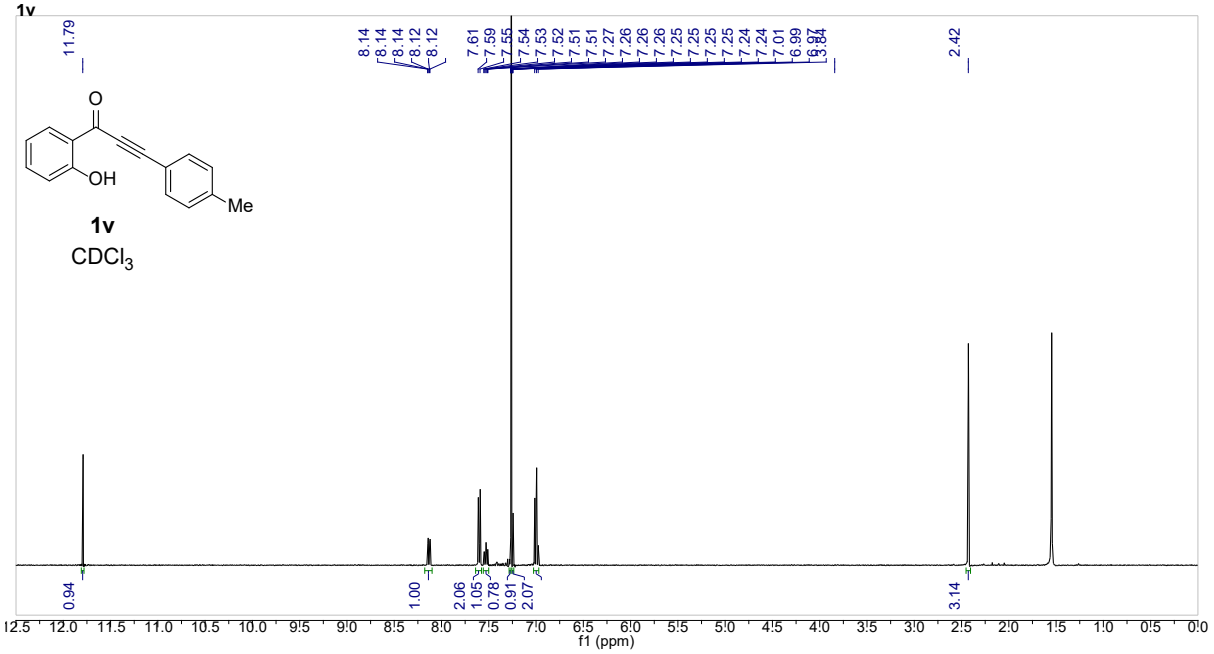

1s
182.44
162.88
162.20
137.02
135.41
133.07
120.97
119.44
118.24
114.67
111.59
97.54
85.92
55.63
O
OH
OMe
1s
CDCl3
f1 (ppm)

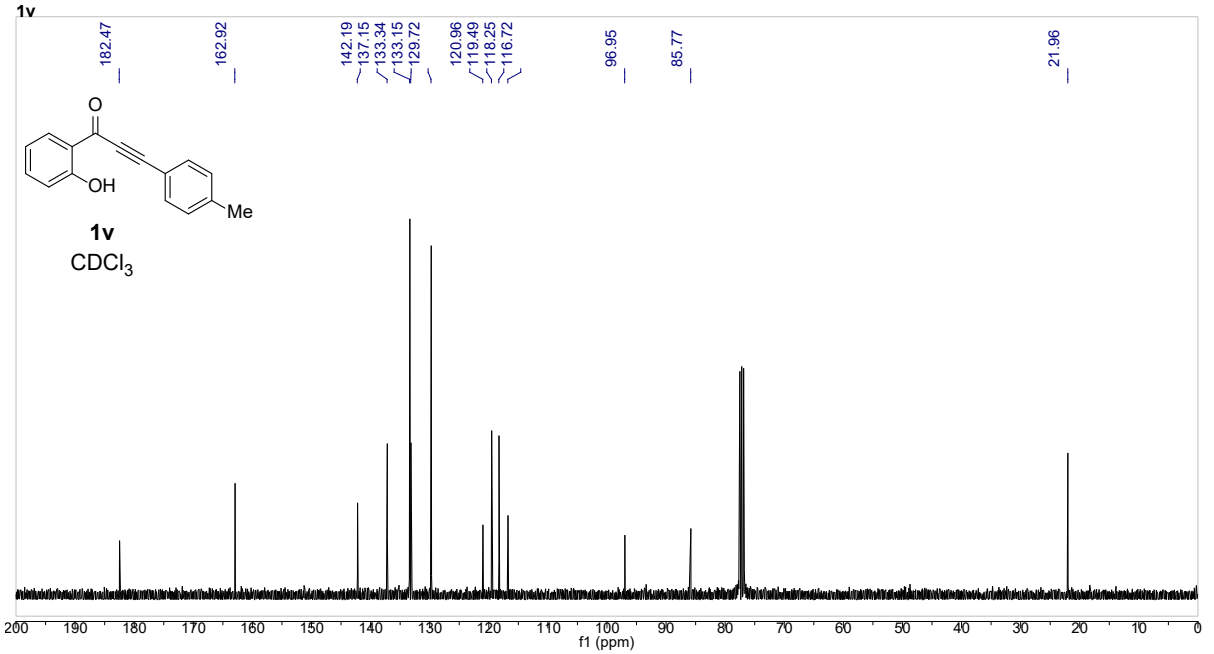

1t
11.71
8.11
8.11
8.11
8.11
8.09
8.09
8.09
8.09
8.09
7.72
7.72
7.71
7.71
7.71
7.70
7.70
7.70
7.69
7.69
7.54
7.54
7.54
7.53
7.52
7.26
7.17
7.15
7.14
7.12
7.12
7.02
7.02
7.01
7.01
7.01
7.00
7.00
7.00
7.00
6.99
6.99
6.98
6.97
6.94
O
OH
F
1t
CDCl3
0.97
1.00
2.04
1.05
2.05
2.03
f1 (ppm)

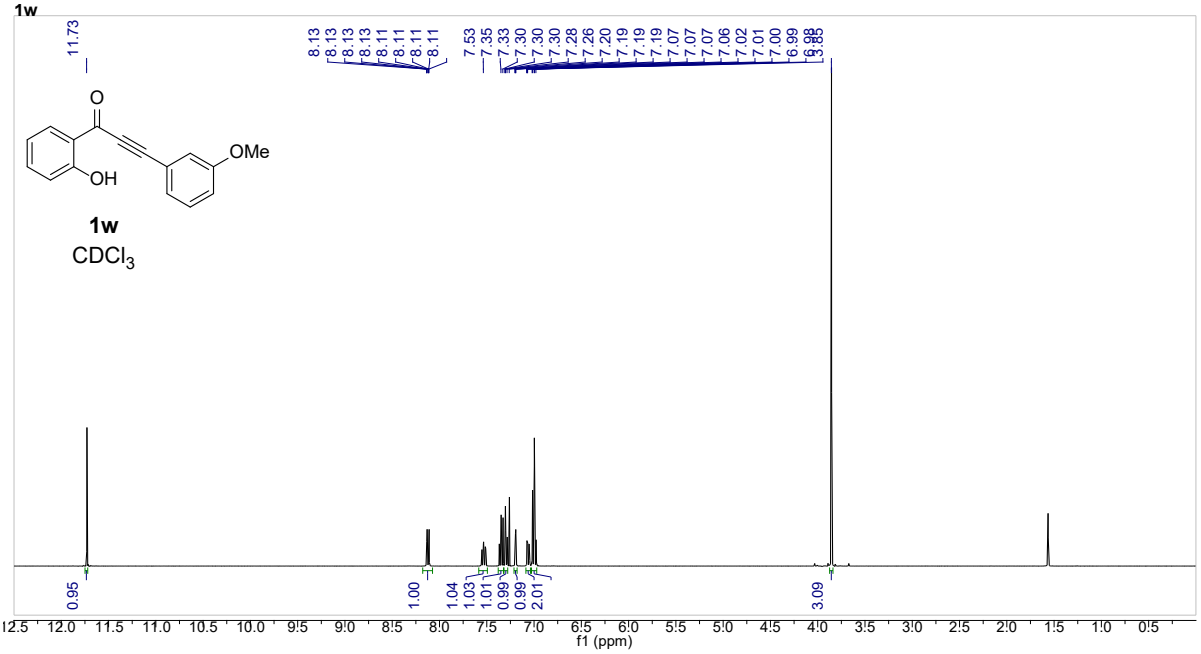

1t
182.22
165.65
163.12
162.97
137.32
135.63
135.54
133.03
120.85
119.54
118.32
116.61
116.38
116.00
115.97
94.97
85.76
O
OH
F
1t
CDCl3
f1 (ppm)

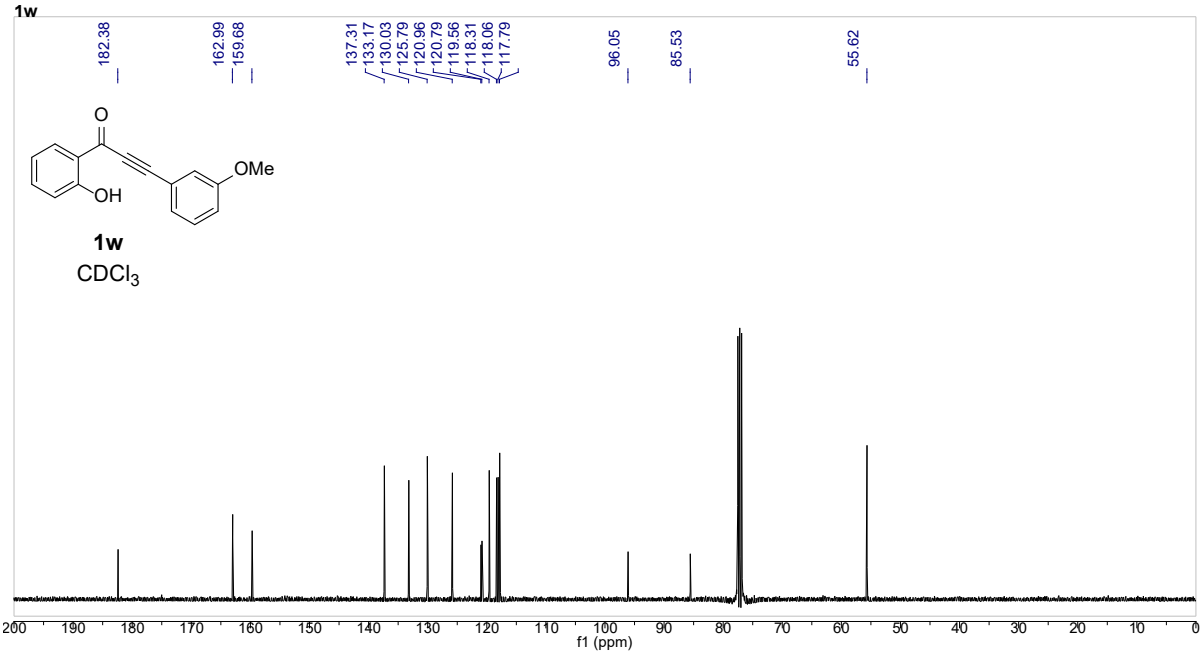

11.767
8.146
8.144
8.142
8.127
8.125
8.121
7.555
7.551
7.536
7.535
7.533
7.532
7.530
7.522
7.517
7.512
7.511
7.508
7.505
7.502
7.501
7.499
7.497
7.495
7.337
7.335
7.329
7.328
7.324
7.321
7.017
7.015
6.998
6.996
6.980
6.977
2.402
O
OH
Me
1u
CDCl3
0.95
1.00
3.09
1.94
2.04
3.09
f1 (ppm)

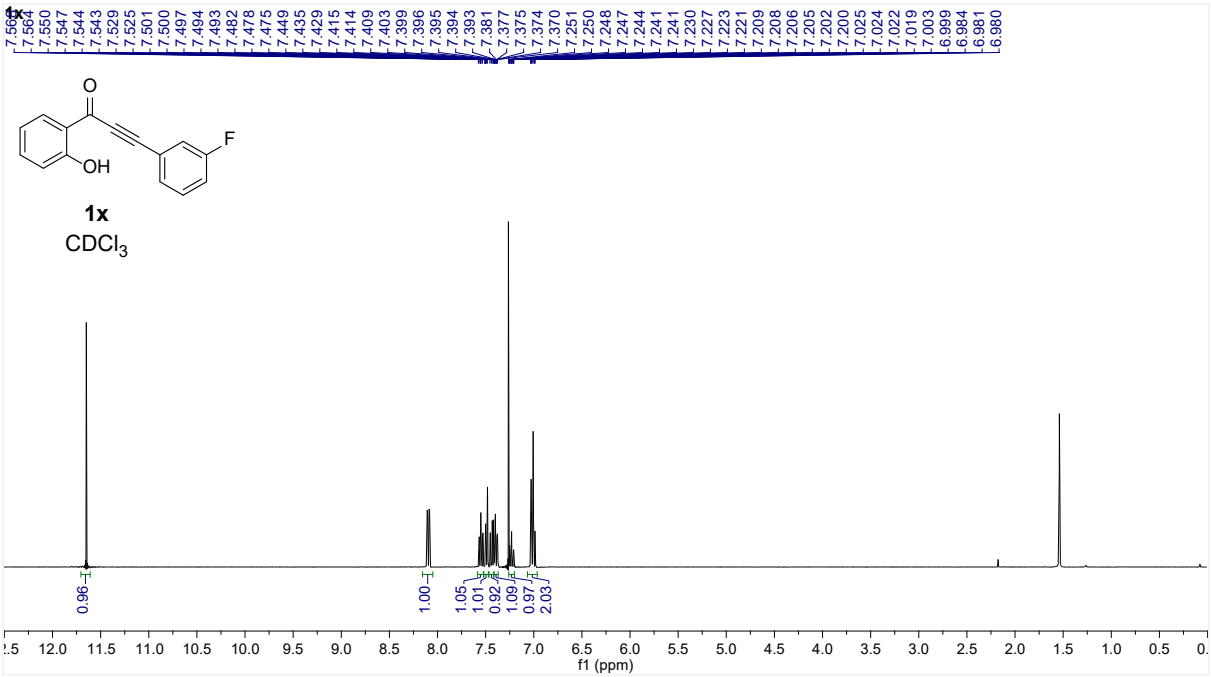

1u
182.46
162.95
138.79
137.23
133.74
133.17
132.28
130.45
128.81
120.98
119.65
119.52
118.27
96.58
85.63
21.34
O
OH
Me
1u
CDCl3
f1 (ppm)

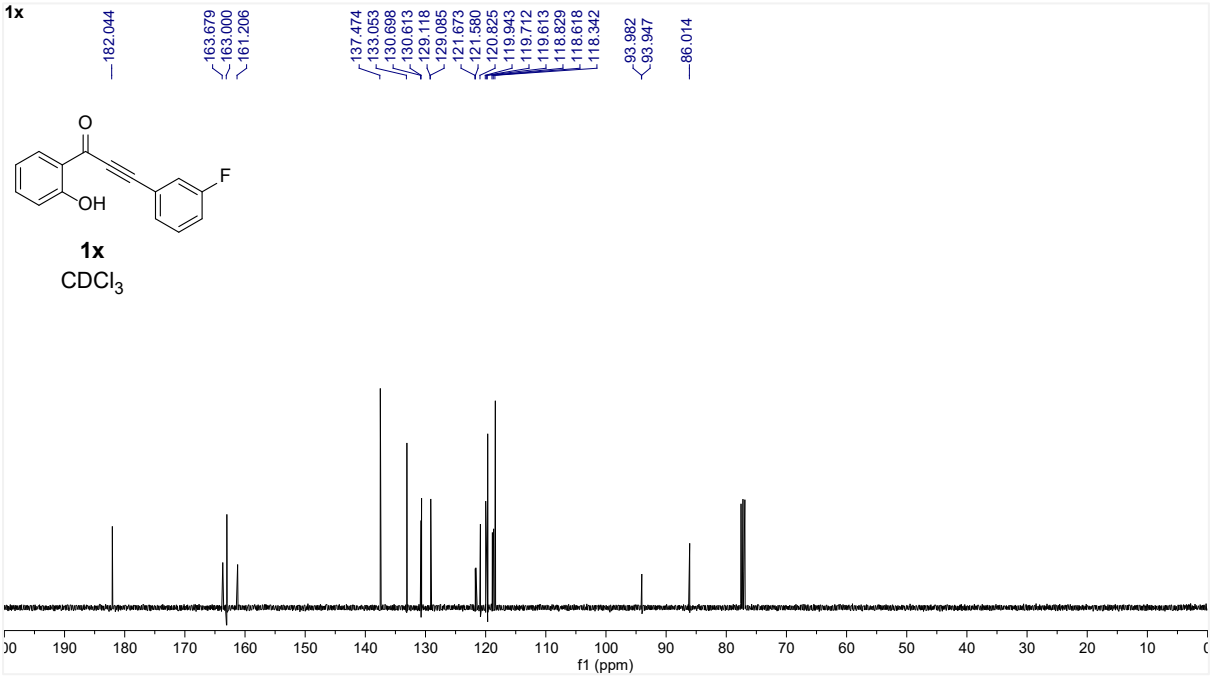

1v
11.79
8.14
8.14
8.14
8.12
8.12
7.61
7.59
7.55
7.54
7.53
7.52
7.51
7.51
7.27
7.26
7.26
7.25
7.25
7.25
7.24
7.24
7.01
6.99
3.84
2.42
O
OH
Me
1v
CDCl3
0.94
1.00
2.06
1.05
0.78
0.91
2.07
3.14
f1 (ppm)

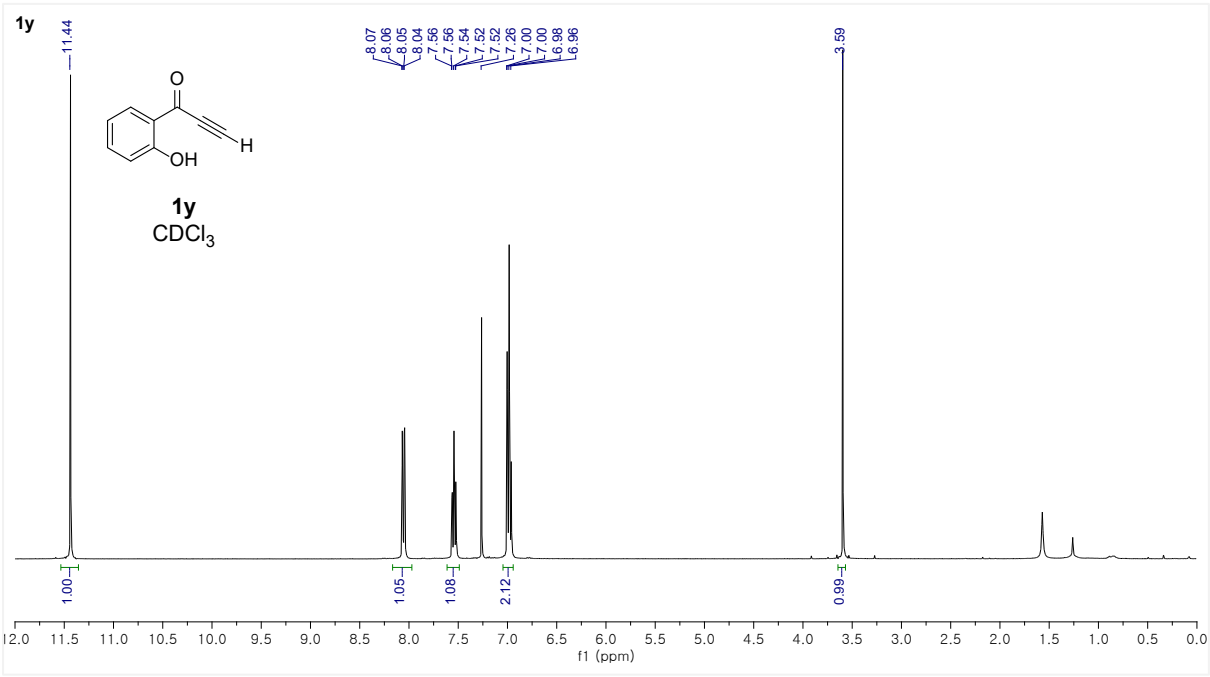

1v
182.47
162.92
142.19
137.15
133.34
133.15
129.72
120.96
119.49
118.25
116.72
96.95
85.77
21.96
O
OH
Me
1v
CDCl3
f1 (ppm)

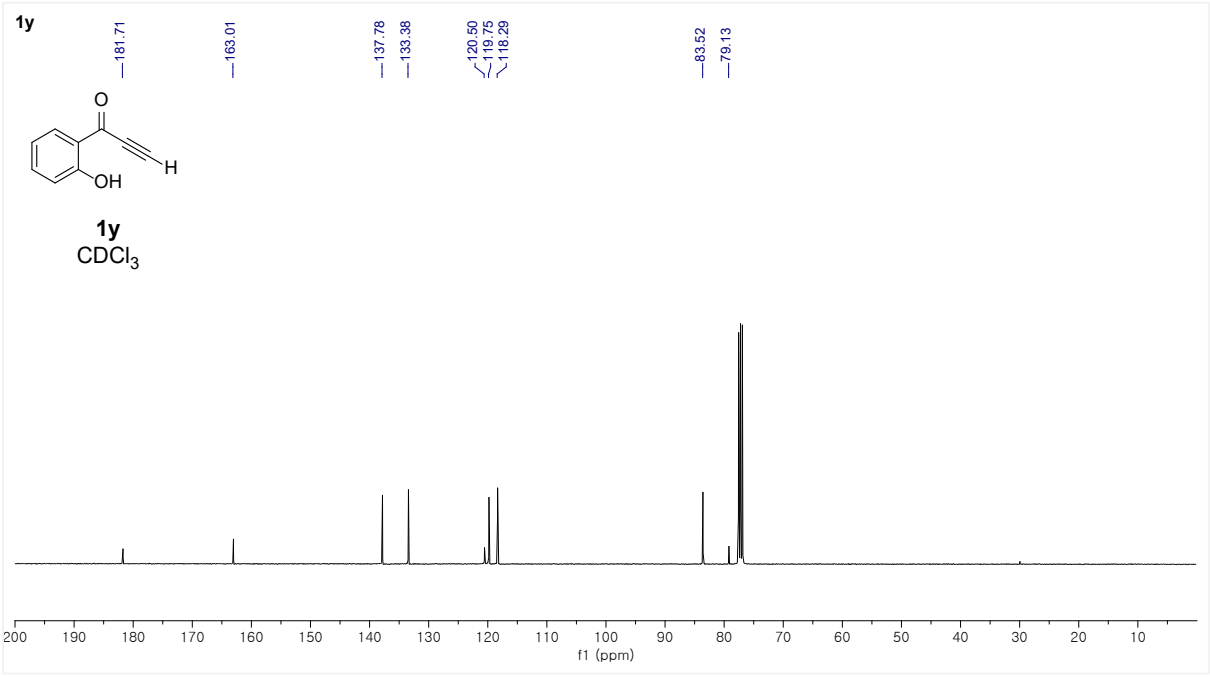

1w
11.73
8.13
8.13
8.13
8.13
8.11
8.11
8.11
8.11
7.53
7.35
7.33
7.30
7.30
7.30
7.28
7.26
7.20
7.19
7.19
7.19
7.07
7.07
7.07
7.06
7.02
7.01
7.00
6.99
O
OMe
OH
1w
CDCl3
0.95
1.00
1.04
1.03
1.01
0.99
0.99
2.01
3.09
f1 (ppm)

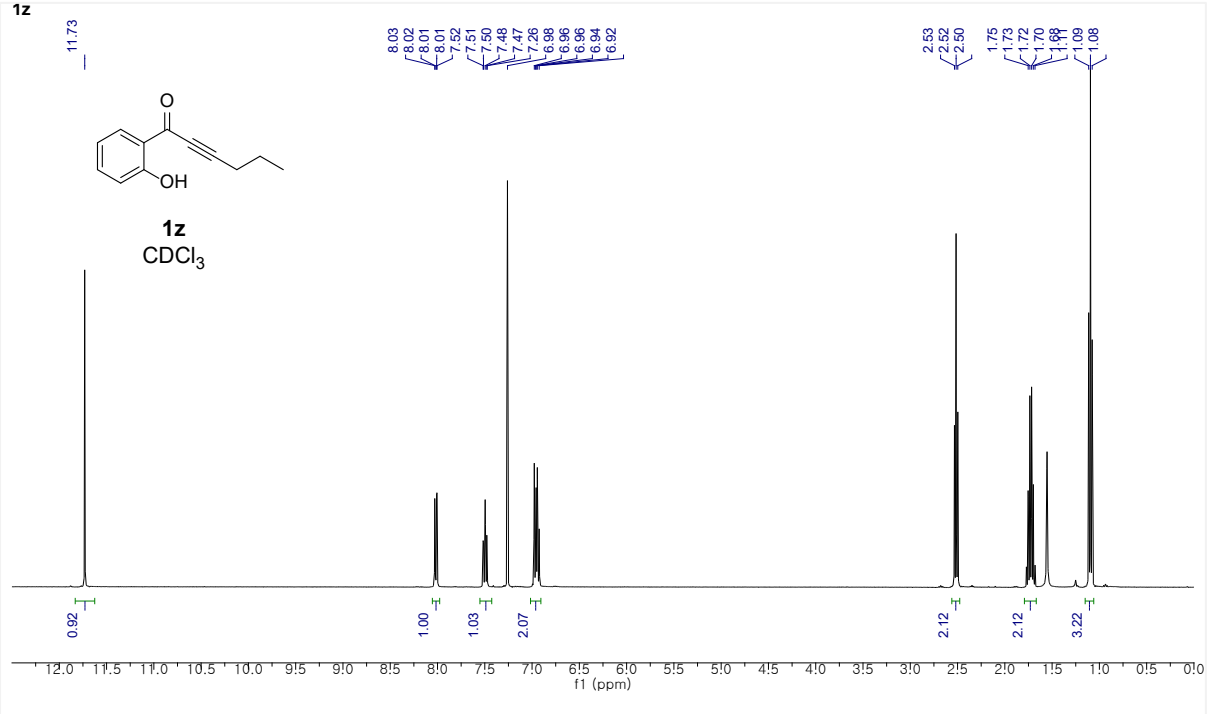

1w
182.38
162.99
159.68
137.31
133.17
130.03
125.79
120.96
120.79
119.56
118.31
118.06
117.79
96.05
85.53
55.62
O
OMe
OH
1w
CDCl3
f1 (ppm)

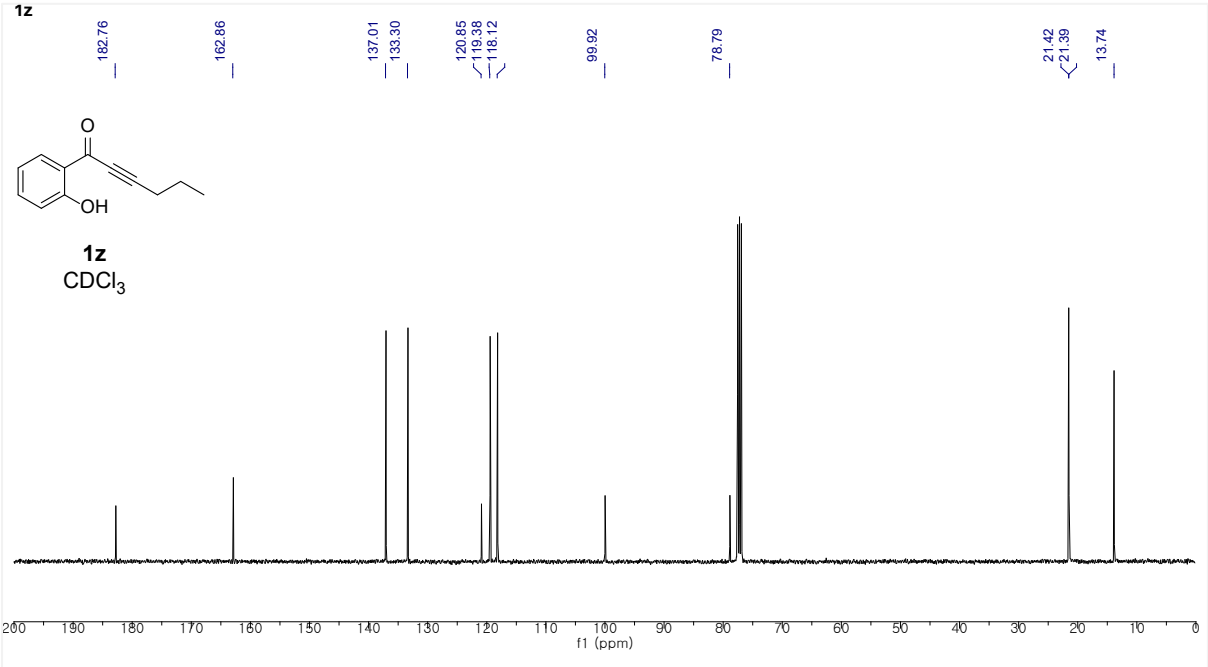

1x
7.564
7.550
7.547
7.544
7.543
7.529
7.525
7.501
7.500
7.497
7.494
7.493
7.482
7.478
7.475
7.449
7.435
7.429
7.415
7.414
7.409
7.403
7.399
7.396
7.395
7.394
7.393
7.381
7.377
7.375
7.374
7.370
7.251
7.250
7.248
7.247
7.244
7.241
7.241
7.230
7.227
7.223
7.221
7.209
7.208
7.206
7.205
7.202
7.200
7.025
7.024
7.022
7.019
7.003
6.999
6.984
6.981
6.980
O
OH
F
1x
CDCl3
0.96
1.00
1.05
1.01
0.92
1.09
0.97
2.03
f1 (ppm)

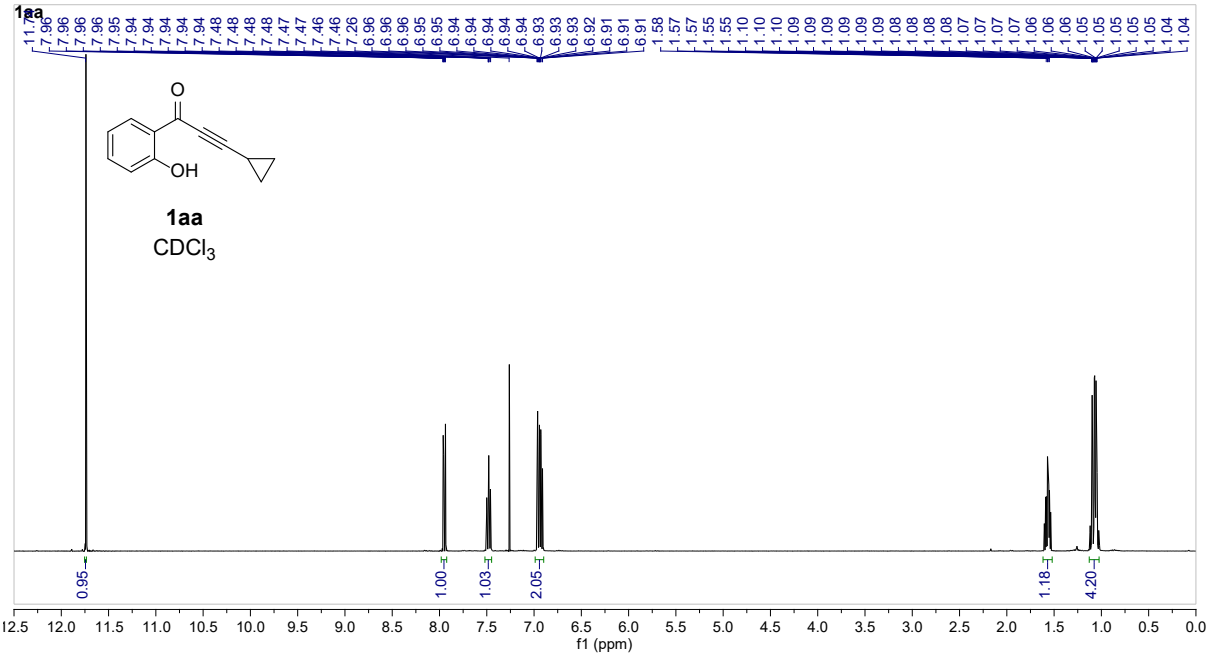

1x
182.044
163.679
163.000
161.206
137.474
133.053
130.698
130.613
129.118
129.085
121.673
121.580
120.825
119.943
119.712
119.613
118.829
118.618
118.342
93.982
93.947
86.014
O
OH
F
1x
CDCl3
f1 (ppm)

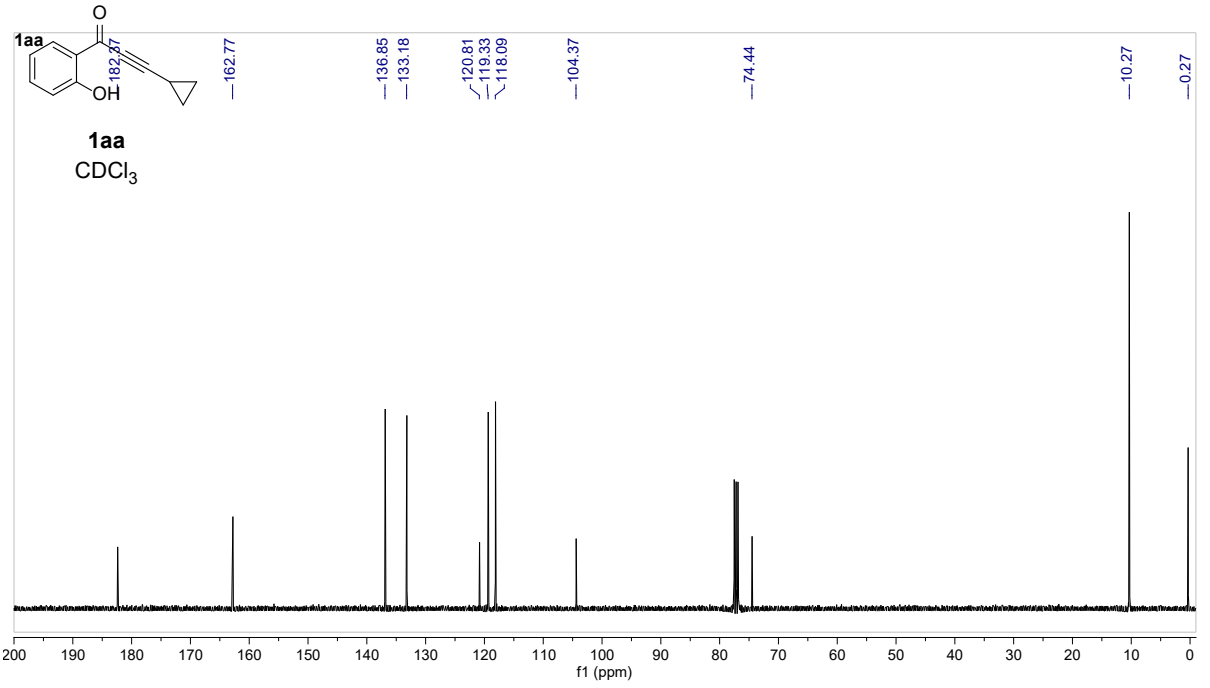

1y
11.44
8.07
8.06
8.05
8.04
7.56
7.56
7.54
7.52
7.52
7.26
7.00
7.00
6.98
6.96
3.59
O
OH
H
1y
CDCl3
1.00
1.05
1.08
2.12
0.99
f1 (ppm)

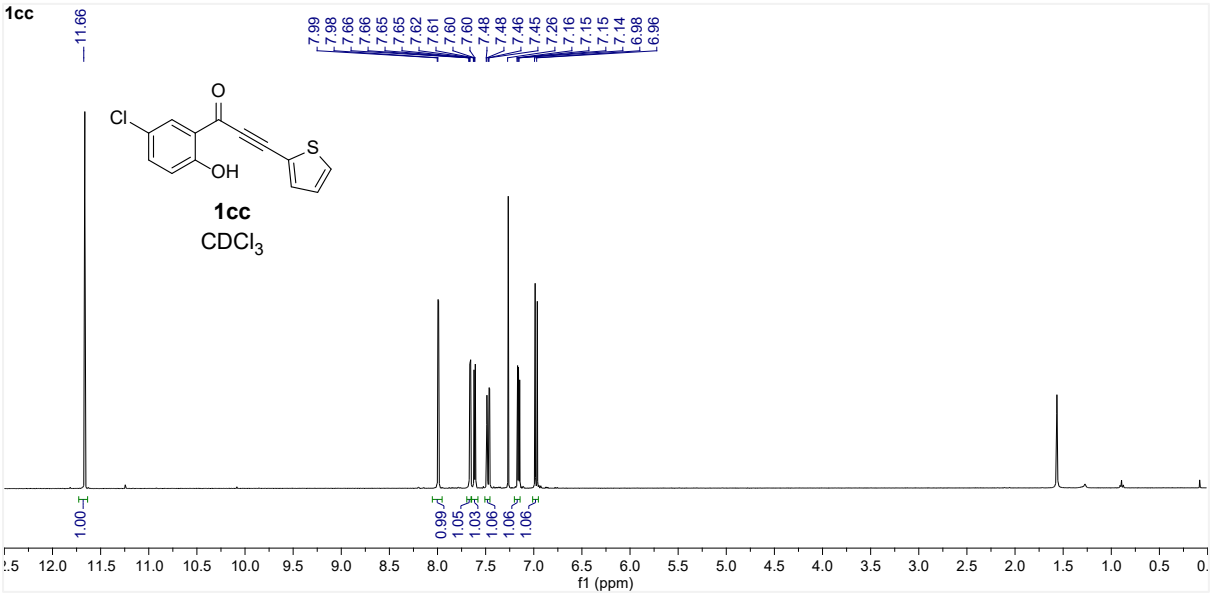

1y
181.71
163.01
137.78
133.38
120.50
119.75
118.29
83.52
79.13
O
OH
H
1y
CDCl3
f1 (ppm)

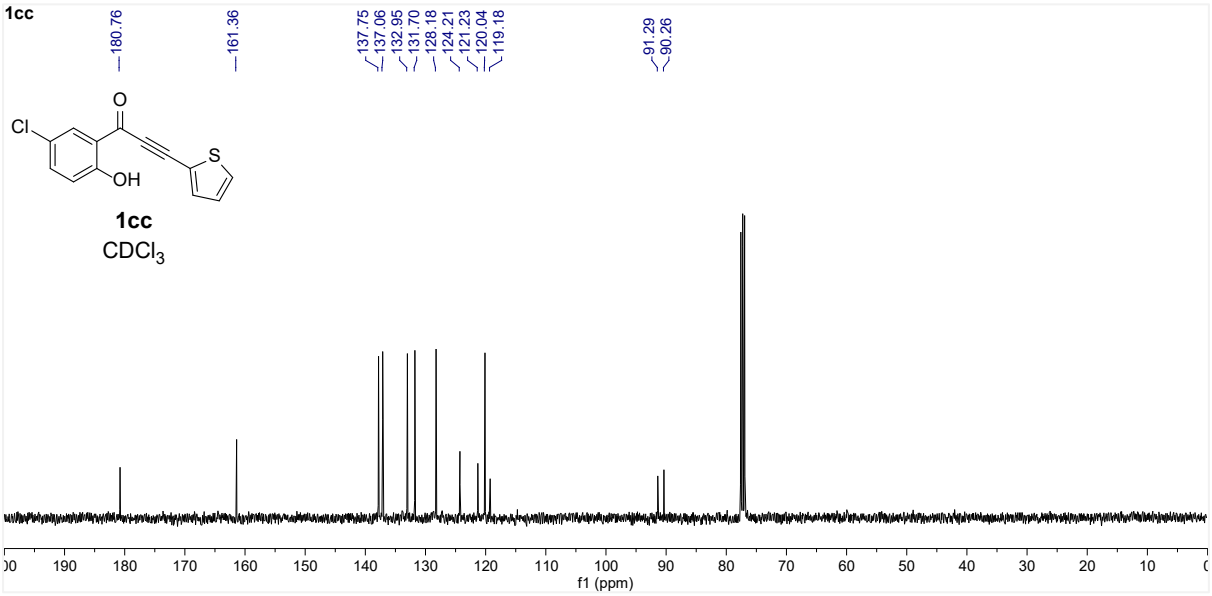

1z
11.73
8.03
8.02
8.01
8.01
7.52
7.51
7.50
7.48
7.47
7.26
6.98
6.96
6.96
6.94
6.92
2.53
2.52
2.50
1.75
1.73
1.72
1.70
1.68
1.11
1.09
1.08
O
OH
1z
CDCl3
0.92
1.00
1.03
2.07
2.12
2.12
3.22
f1 (ppm)

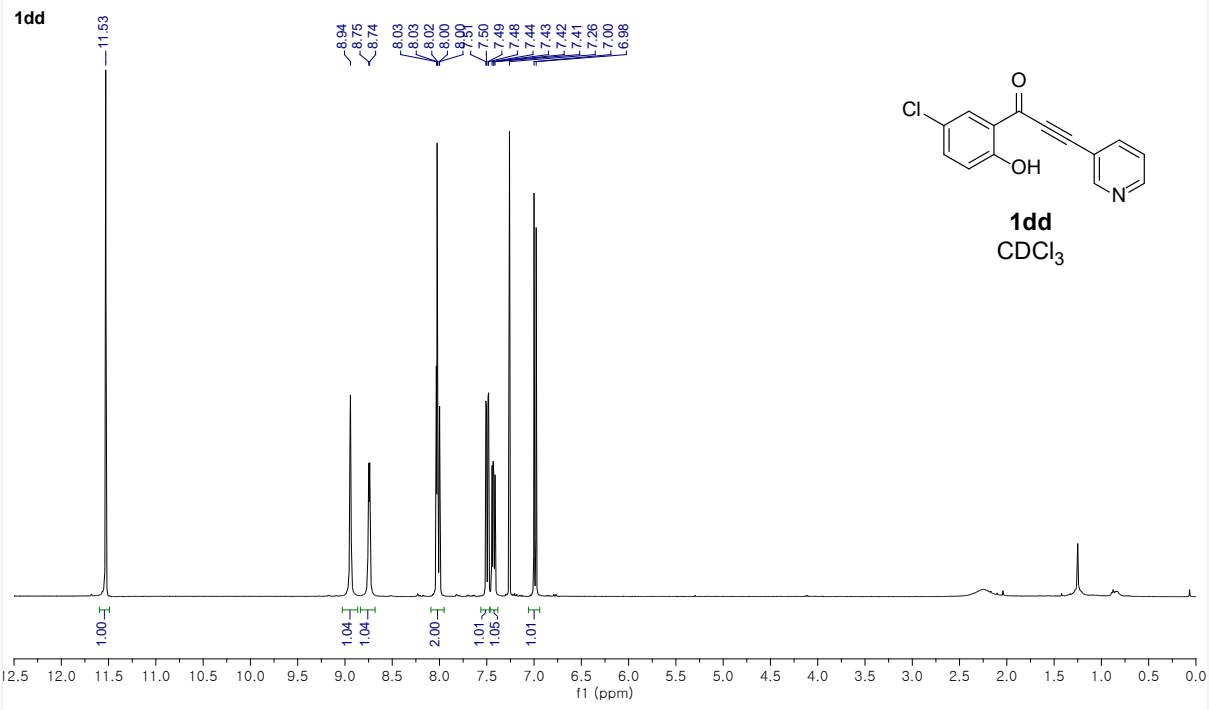

1z
182.76
162.86
137.01
133.30
120.85
119.38
118.12
99.92
78.79
21.42
21.39
13.74
O
OH
1z
CDCl3
f1 (ppm)

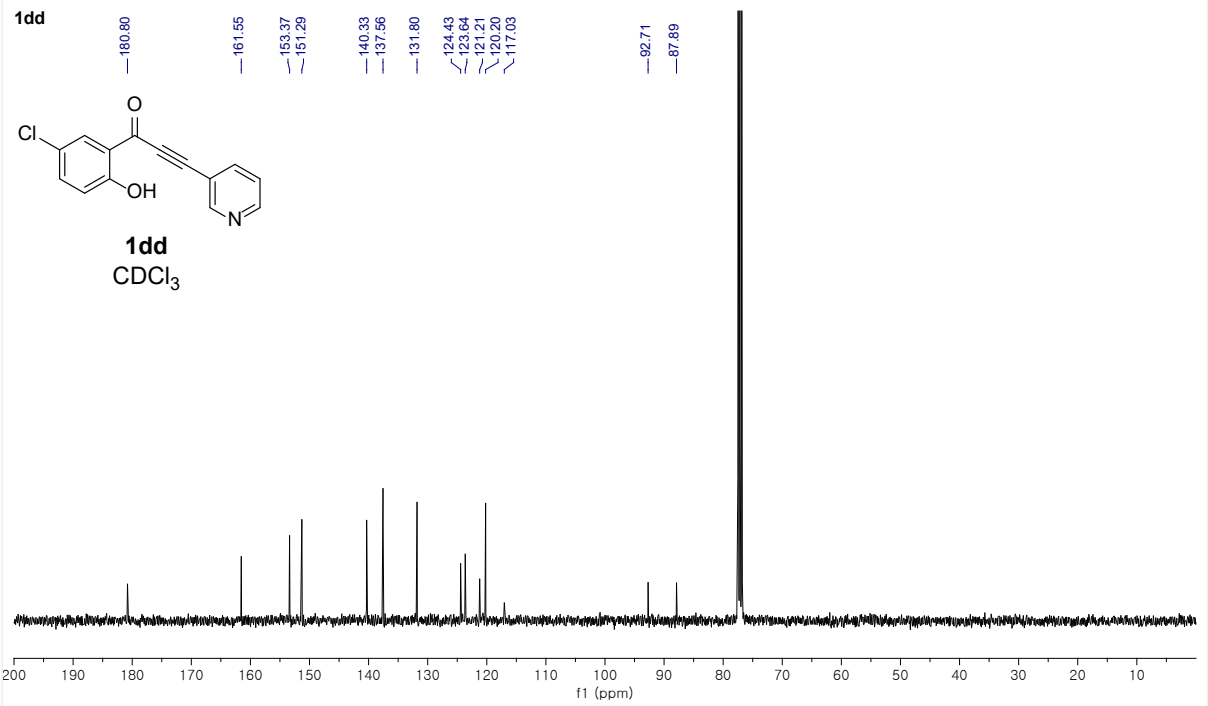

1aa
O
OH
1aa
CDCl3
0.95
1.00
1.03
2.05
1.18
4.20
f1 (ppm)

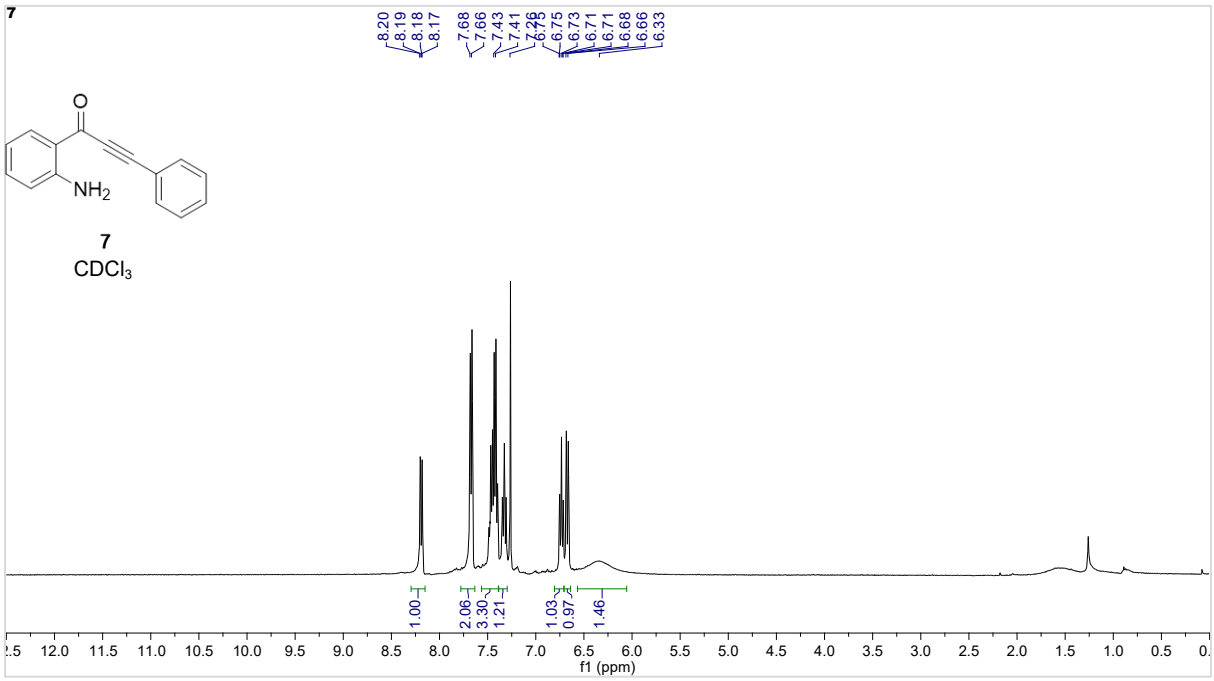

O
1aa
OH
1aa
CDCl3
182.47
162.77
136.85
133.18
120.81
119.33
118.09
104.37
74.44
10.27
0.27
f1 (ppm)

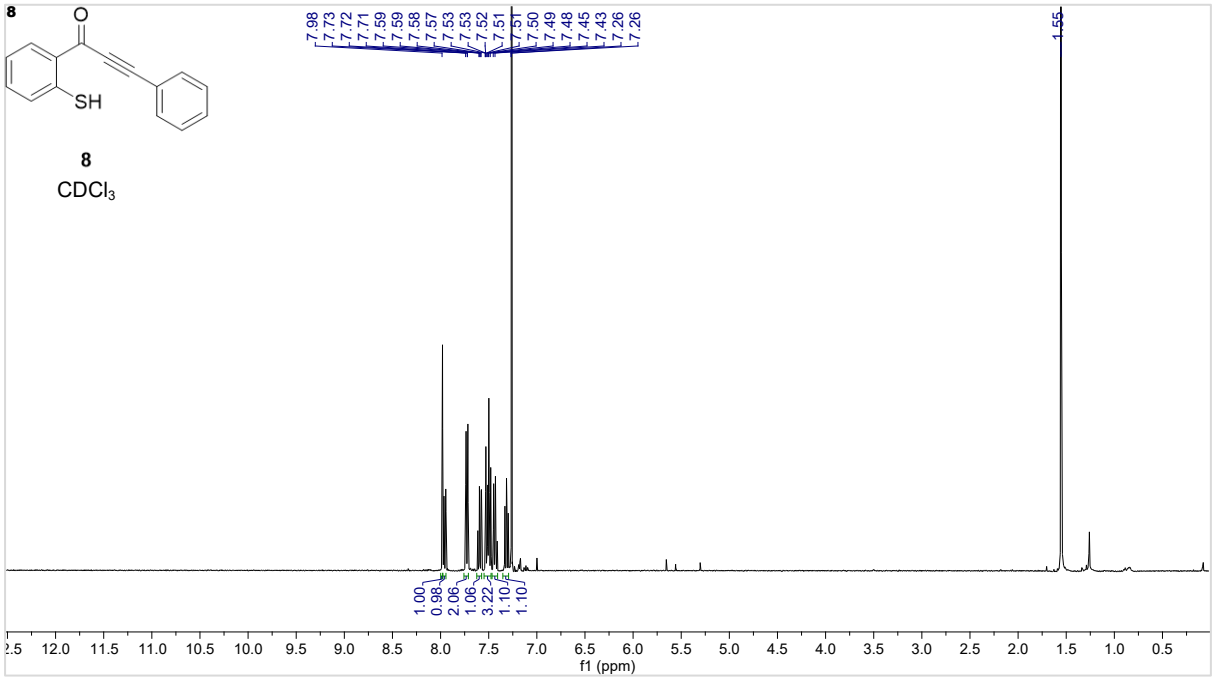

1cc
11.66
7.99
7.98
7.66
7.66
7.65
7.65
7.62
7.61
7.60
7.60
7.48
7.48
7.46
7.45
7.26
7.16
7.15
7.15
7.14
6.98
6.96
Cl
O
S
OH
1cc
CDCl3
1.00
0.99
1.05
1.03
1.06
1.06
1.06
f1 (ppm)

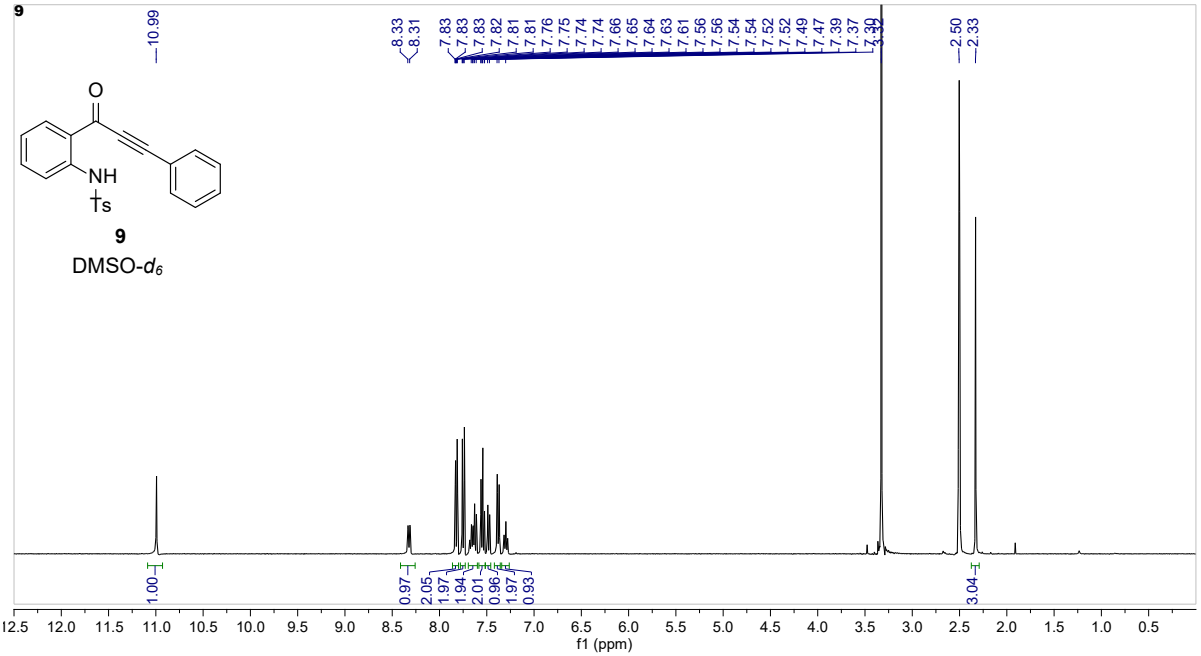

1cc
180.76
161.36
137.75
137.06
132.95
131.70
128.18
124.21
121.23
120.04
119.18
91.29
90.26
Cl
O
S
OH
1cc
CDCl3
f1 (ppm)

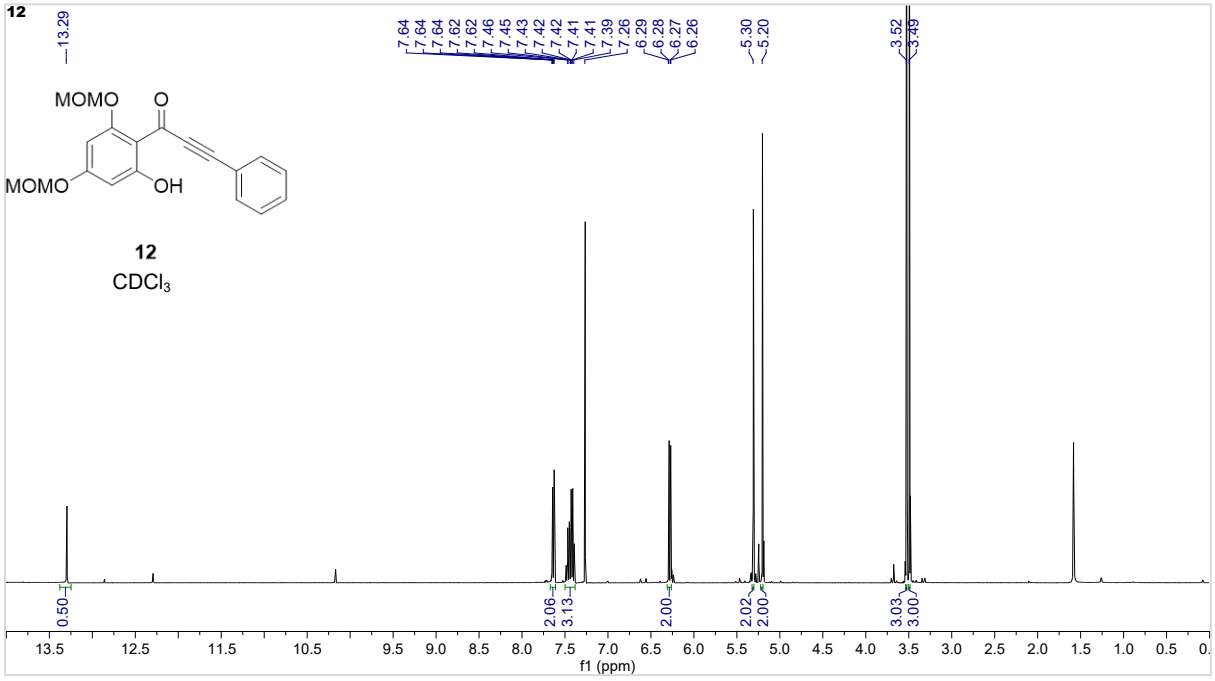

1dd
11.53
8.94
8.75
8.74
8.03
8.03
8.02
8.00
8.00
7.91
7.50
7.49
7.48
7.44
7.43
7.42
7.41
7.26
7.00
6.98
Cl
O
OH
N
1dd
CDCl3
1.00
1.04
1.04
2.00
1.01
1.05
1.01
f1 (ppm)

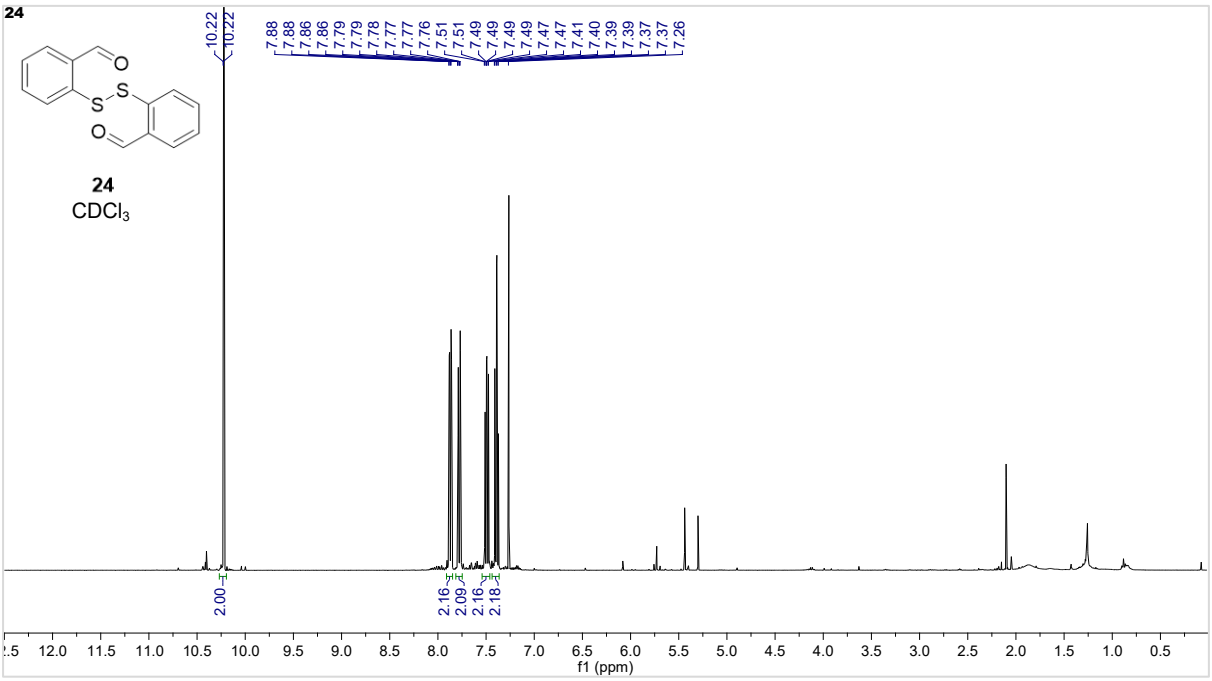

1dd
180.80
161.55
153.37
151.29
140.33
137.56
131.80
124.43
123.64
121.21
120.20
117.03
92.71
87.89
Cl
O
OH
N
1dd
CDCl3
f1 (ppm)

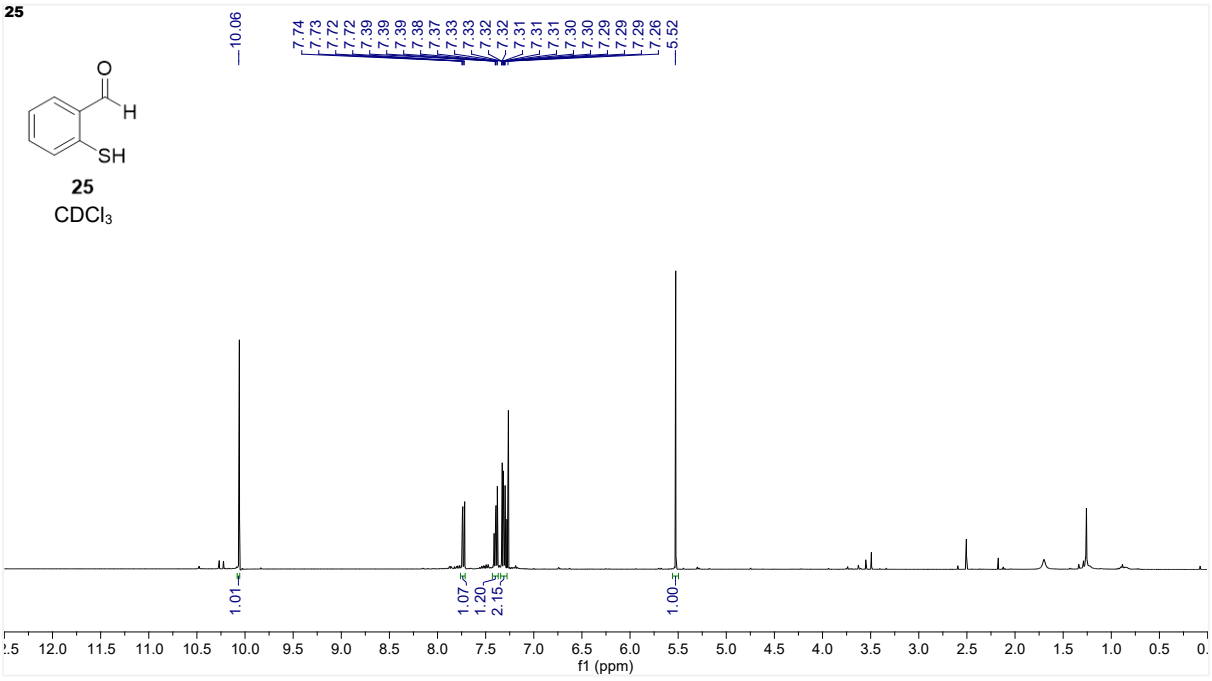

7
8.20
8.19
8.18
8.17
7.68
7.66
7.43
7.41
6.75
6.73
6.71
6.71
6.68
6.66
6.33
O
NH2
7
CDCl3
1.00
2.06
3.30
1.21
1.03
0.97
1.46
f1 (ppm)

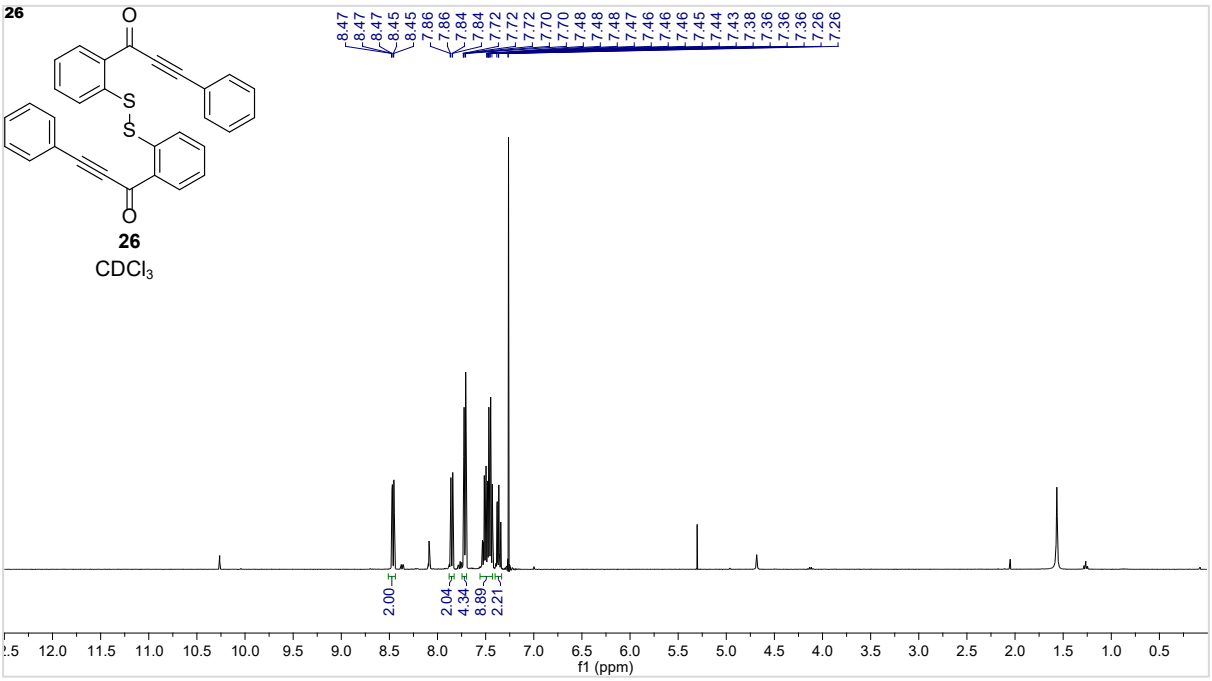

8
7.98
7.73
7.72
7.71
7.59
7.59
7.58
7.57
7.53
7.53
7.52
7.51
7.51
7.50
7.49
7.48
7.45
7.43
7.26
7.26
1.55
O
SH
8
CDCl3
1.00
0.98
2.06
1.06
3.22
1.10
1.10
f1 (ppm)

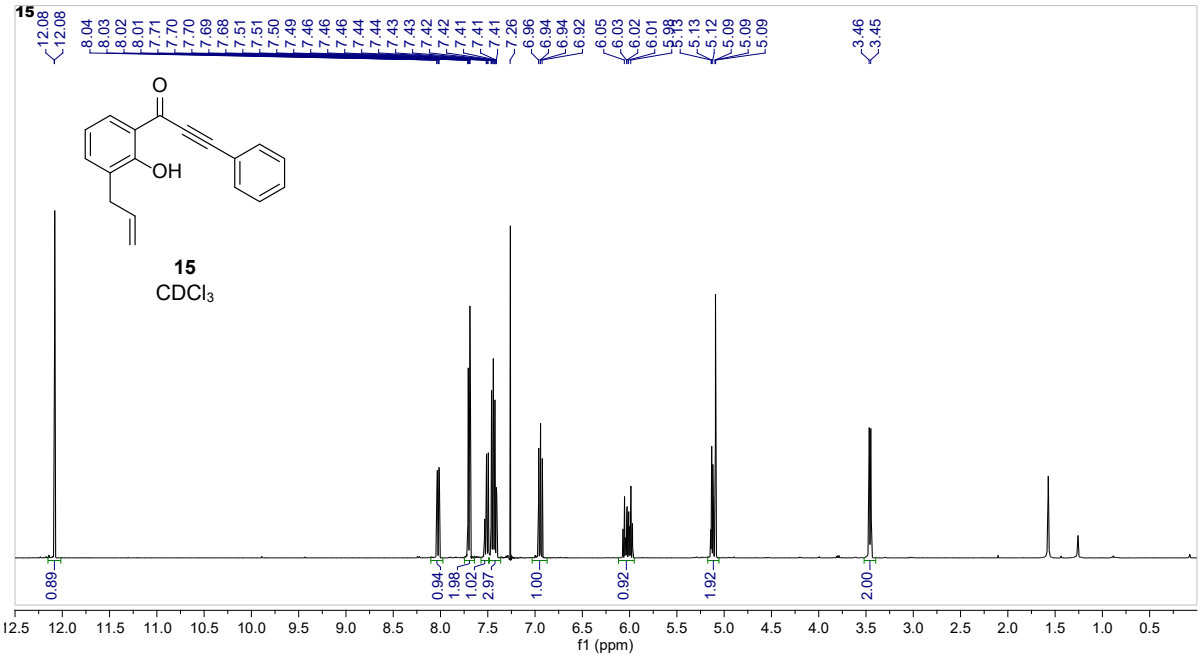

9
10.99
8.33
8.31
7.83
7.83
7.83
7.82
7.81
7.81
7.76
7.75
7.74
7.74
7.66
7.65
7.64
7.63
7.61
7.56
7.56
7.54
7.54
7.52
7.52
7.49
7.47
7.39
7.37
7.30
3.32
2.50
2.33
O
NH
Ts
9
DMSO-d6
1.00
0.97
2.05
1.97
1.94
2.01
0.96
1.97
0.93
3.04
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


12
13.29
7.64
7.64
7.64
7.62
7.62
7.46
7.45
7.43
7.42
7.42
7.41
7.41
7.39
7.26
6.29
6.28
6.27
6.26
5.30
5.20
3.52
3.49
MOMO
O
MOMO
OH
12
CDCl3
0.50
2.06
3.13
2.00
2.02
2.00
3.03
3.00
13.5 12.5 11.5 10.5 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.
f1 (ppm)

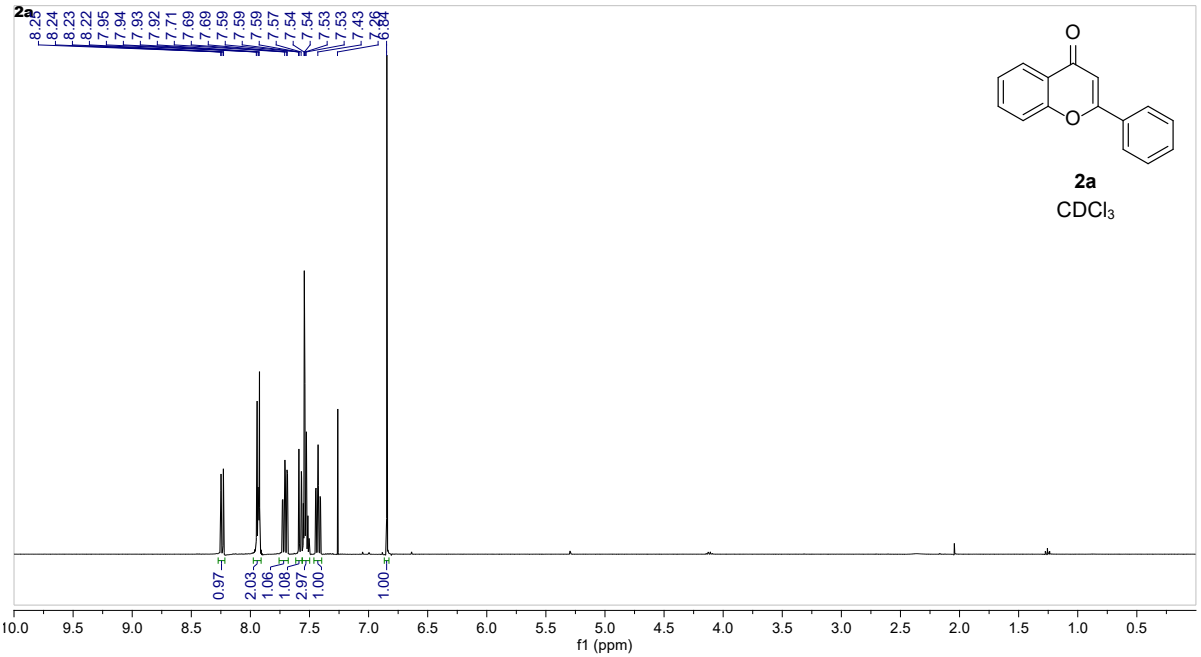

24
10.22
10.22
7.88
7.88
7.86
7.86
7.86
7.79
7.79
7.78
7.77
7.77
7.76
7.51
7.51
7.49
7.49
7.49
7.49
7.47
7.47
7.41
7.40
7.39
7.39
7.37
7.37
7.26
O
S
S
O
24
CDCl3
2.00
2.16
2.09
2.16
2.18
f1 (ppm)

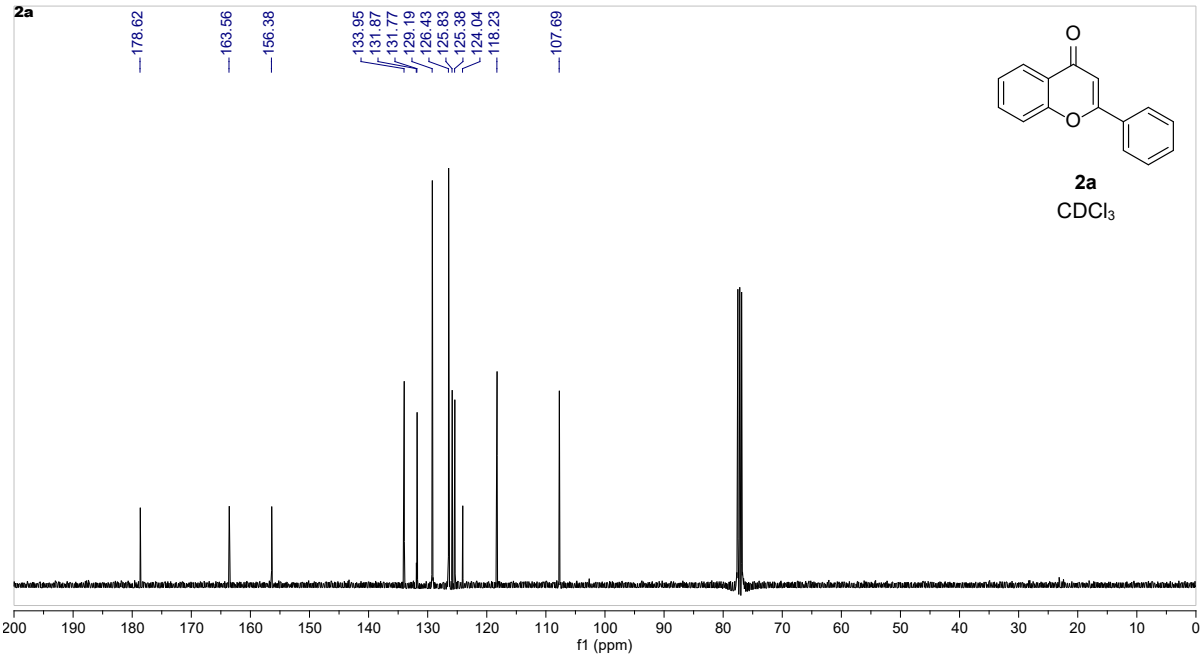

25
10.06
7.74
7.73
7.72
7.72
7.39
7.39
7.39
7.38
7.37
7.33
7.33
7.32
7.32
7.31
7.31
7.31
7.30
7.30
7.29
7.29
7.29
7.26
5.52
O
H
SH
25
CDCl3
1.01
1.07
1.20
2.15
1.00
f1 (ppm)

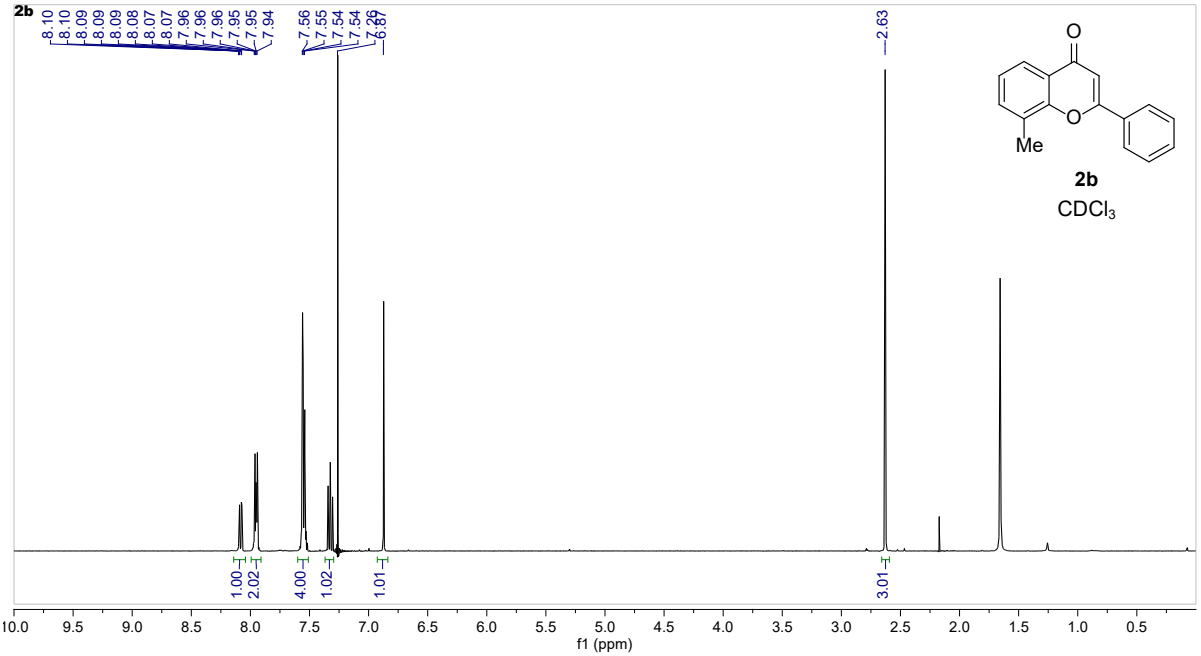

26
O
S
S
O
26
CDCl3
8.47
8.47
8.47
8.45
8.45
7.86
7.84
7.84
7.72
7.72
7.72
7.70
7.70
7.48
7.48
7.48
7.47
7.46
7.46
7.46
7.45
7.44
7.43
7.38
7.36
7.36
7.26
7.26
2.00
2.04
4.34
8.89
2.21
f1 (ppm)

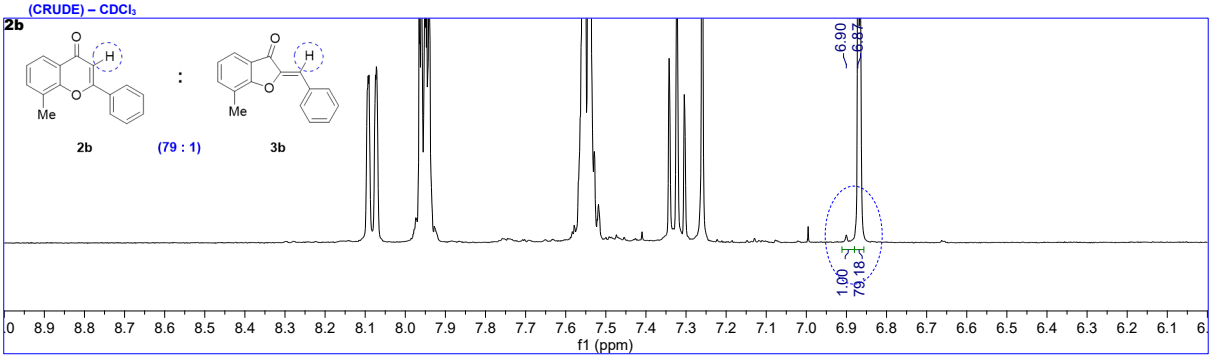

15
12.08
12.08
8.04
8.03
8.02
8.01
7.71
7.70
7.70
7.69
7.68
7.51
7.51
7.50
7.49
7.46
7.46
7.46
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.41
7.26
6.96
6.94
6.94
6.92
6.05
6.03
6.02
6.01
5.98
5.13
5.12
5.09
5.09
5.09
3.46
3.45
O
OH
15
CDCl3
0.89
0.94
1.98
1.02
2.97
1.00
0.92
1.92
2.00
f1 (ppm)

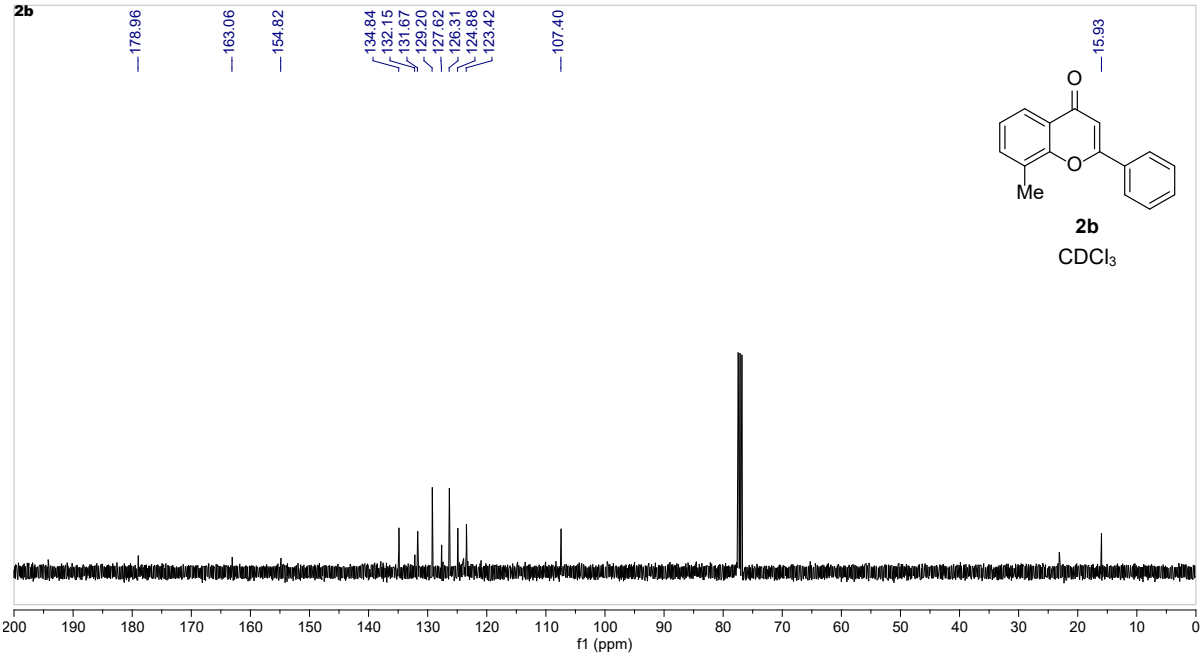
VII.NMR Spectra of *γ*-benzopyranone 2 (flavone).

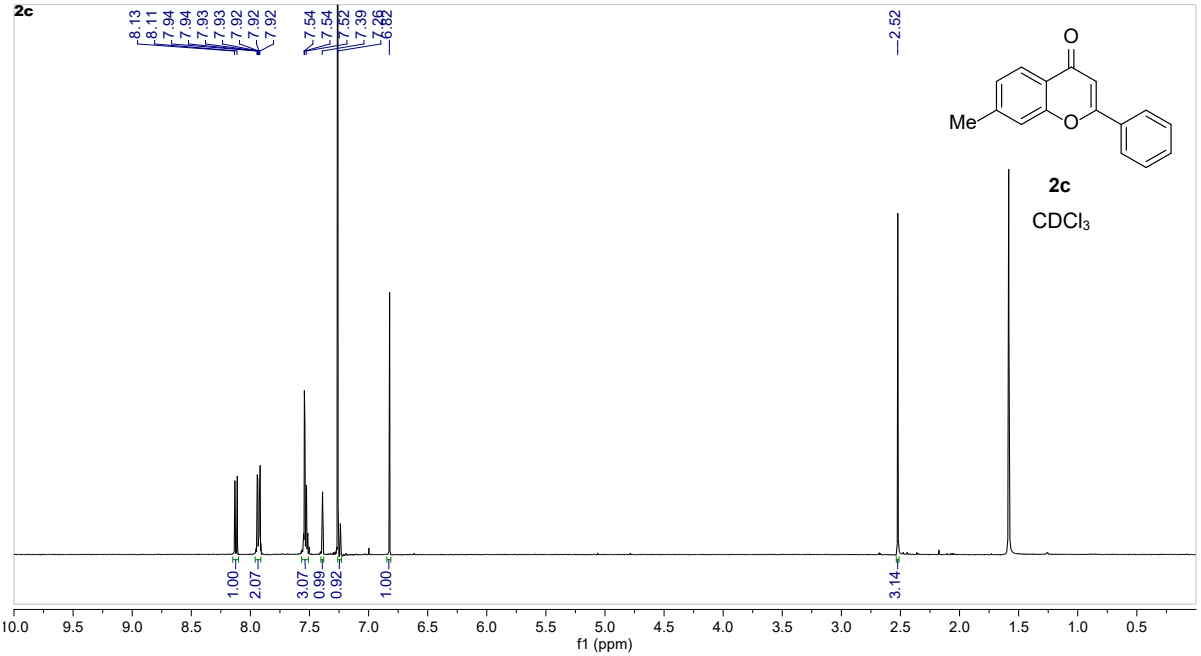


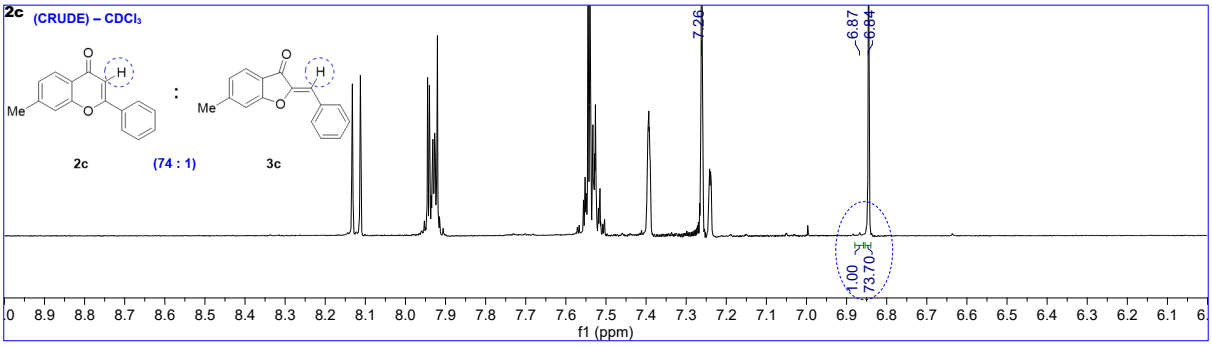


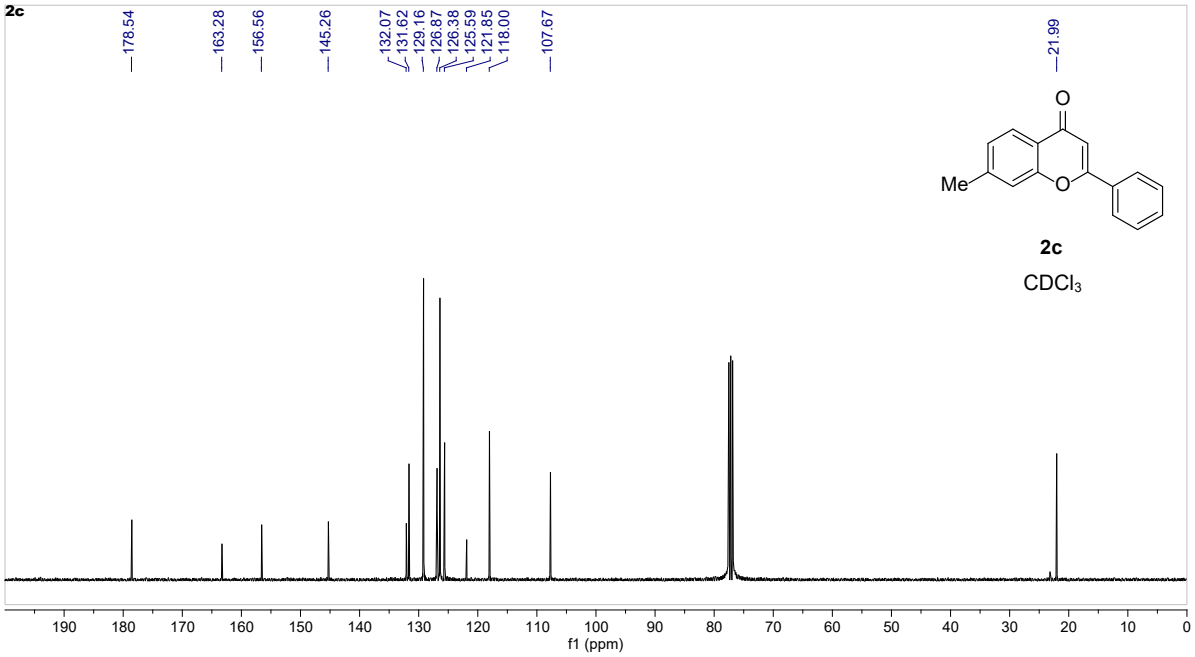

2b
8.10
8.09
8.08
8.07
7.96
7.95
7.94
7.56
7.55
7.54
7.26
6.87
2.63
1.00
2.02
4.00
1.02
1.01
3.01
O
O
Me
2b
CDCl3
f1 (ppm)

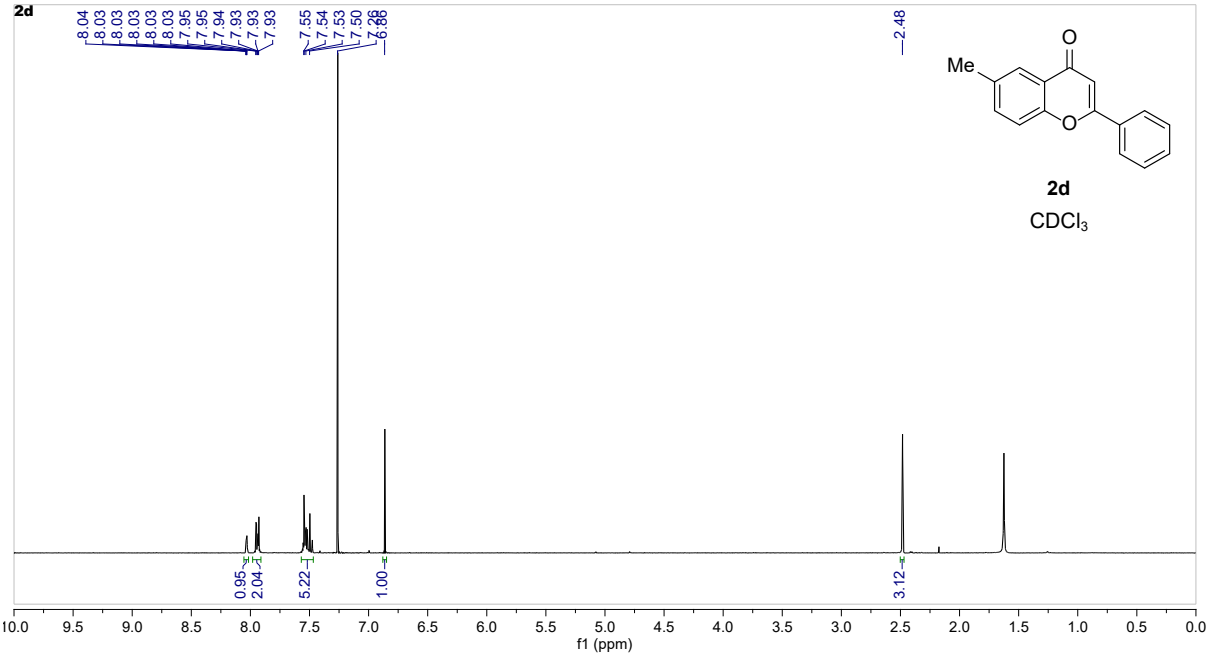

(CRUDE) – CDCl3
2b
H
O
O
Me
2b
(79 : 1)
3b
6.90
6.87
1.00
79.18
f1 (ppm)

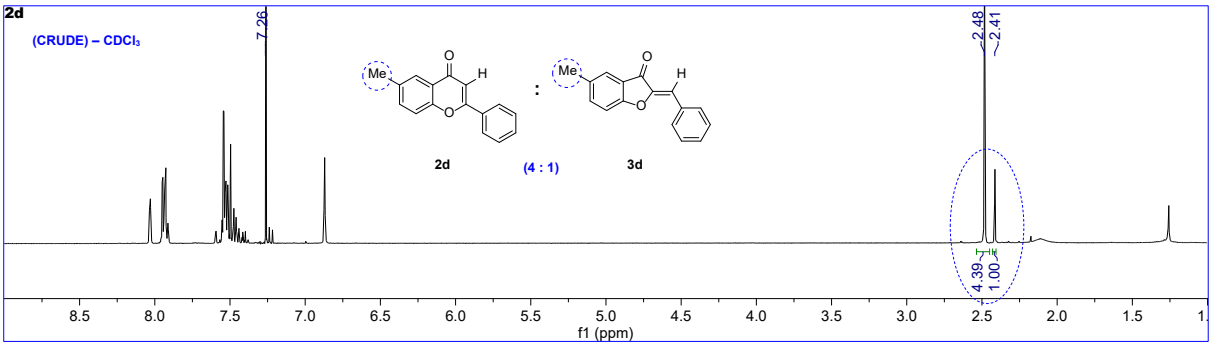

2b
178.96
163.06
154.82
134.84
132.15
131.67
129.20
127.62
126.31
124.88
123.42
107.40
15.93
O
O
Me
2b
CDCl3
f1 (ppm)

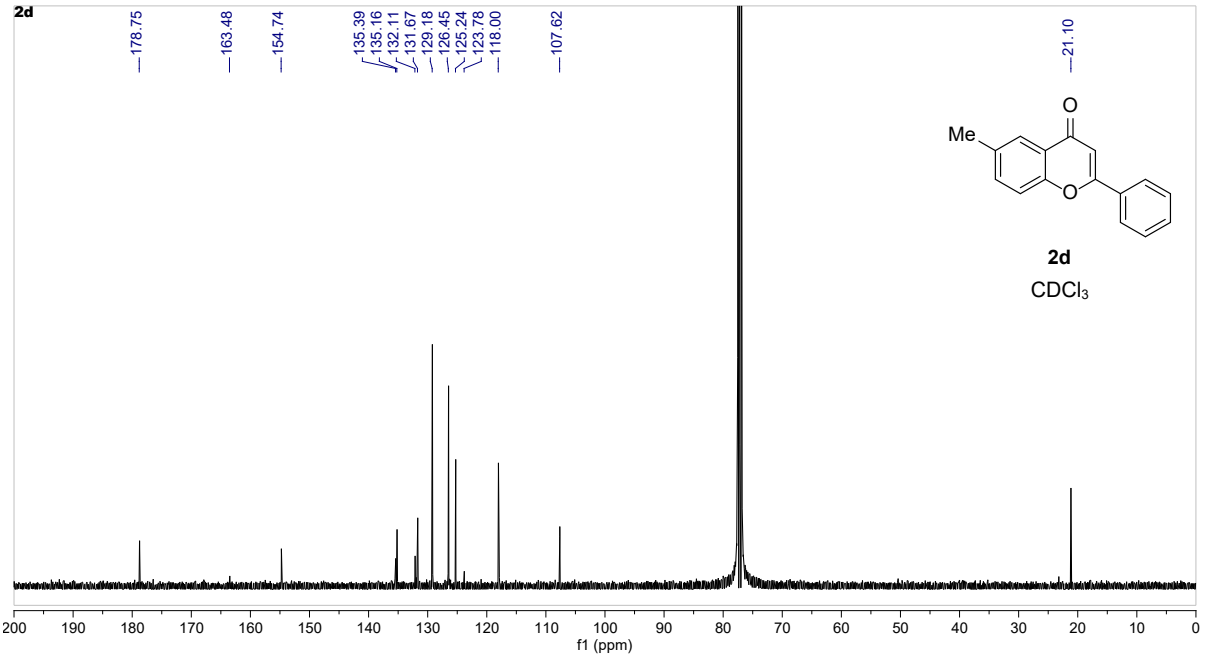

2c
8.13
8.11
7.94
7.94
7.93
7.93
7.92
7.92
7.92
7.92
7.54
7.54
7.52
7.39
6.82
2.52
Me
O
2c
CDCl3
1.00
2.07
3.07
0.99
0.92
1.00
3.14
f1 (ppm)

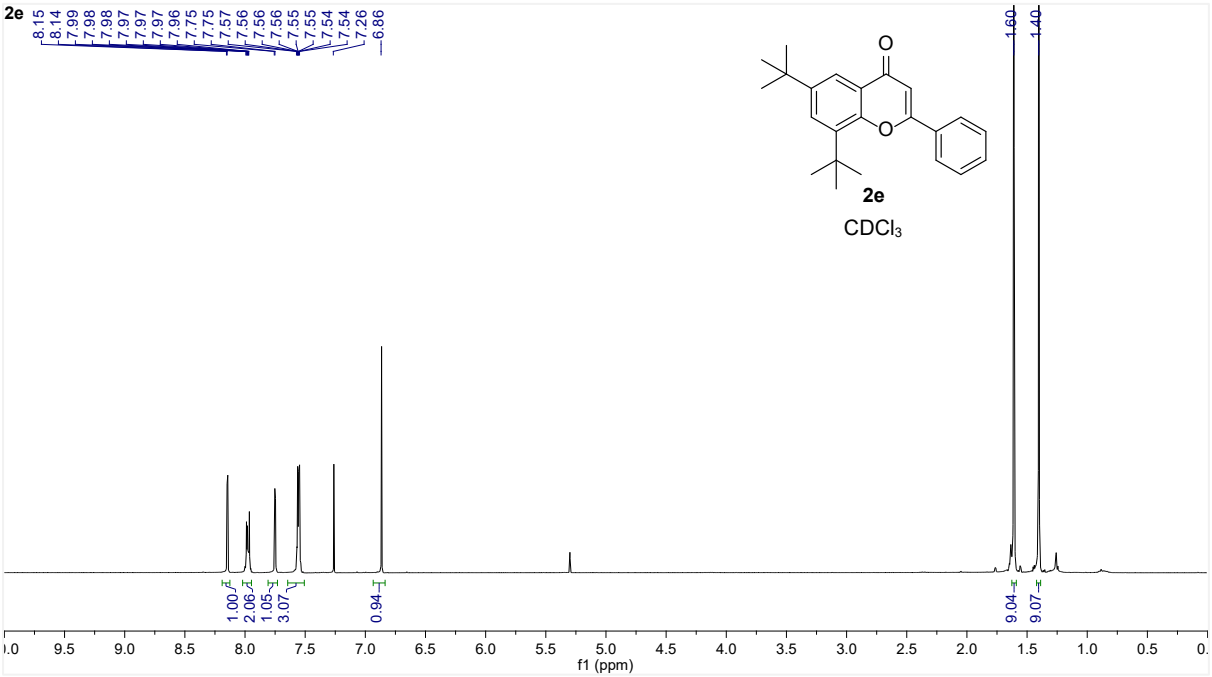

2c (CRUDE) – CDCl3
Me
H
2c
(74 : 1)
3c
7.26
6.87
6.84
1.00
73.70
f1 (ppm)

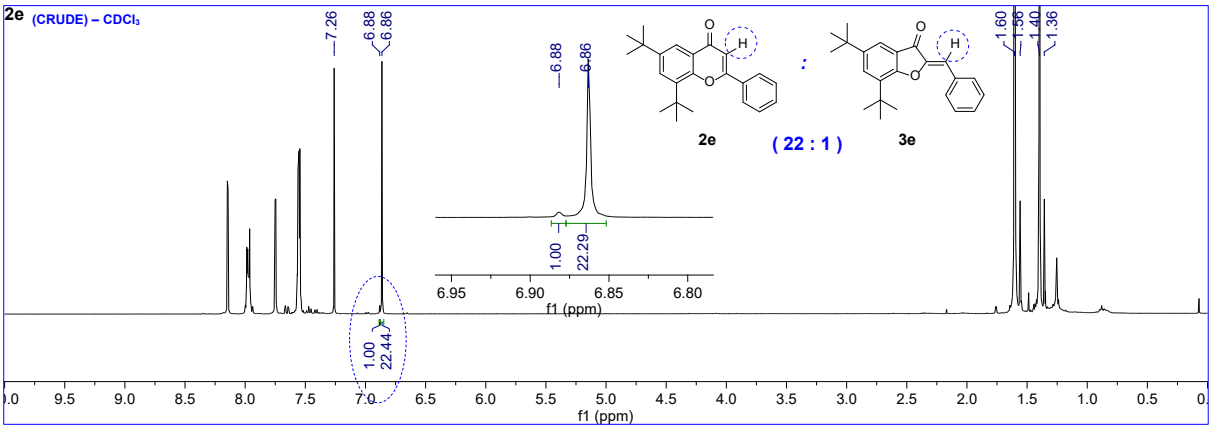

2c
178.54
163.28
156.56
145.26
132.07
131.62
129.16
126.87
126.38
125.59
121.85
118.00
107.67
21.99
Me
O
2c
CDCl3
f1 (ppm)

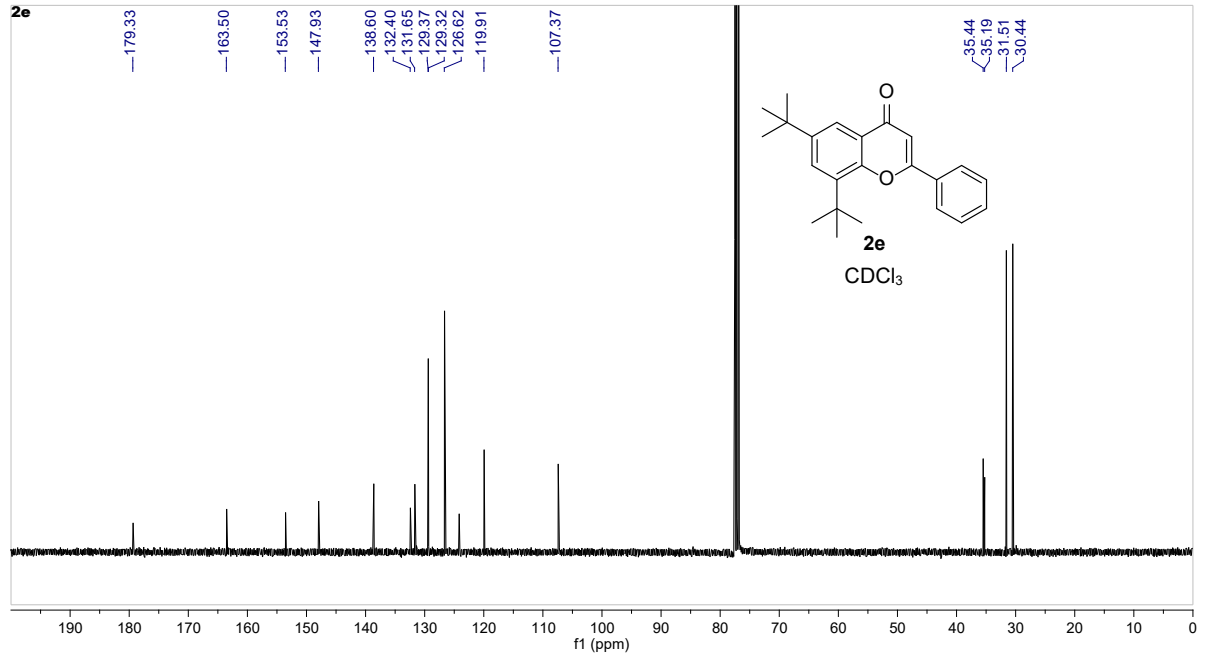

2d
8.04
8.03
8.03
8.03
8.03
8.03
7.95
7.95
7.94
7.93
7.93
7.93
7.55
7.54
7.53
7.50
7.48
7.48
2.48
Me
O
O
2d
CDCl3
0.95
2.04
5.22
1.00
3.12
f1 (ppm)

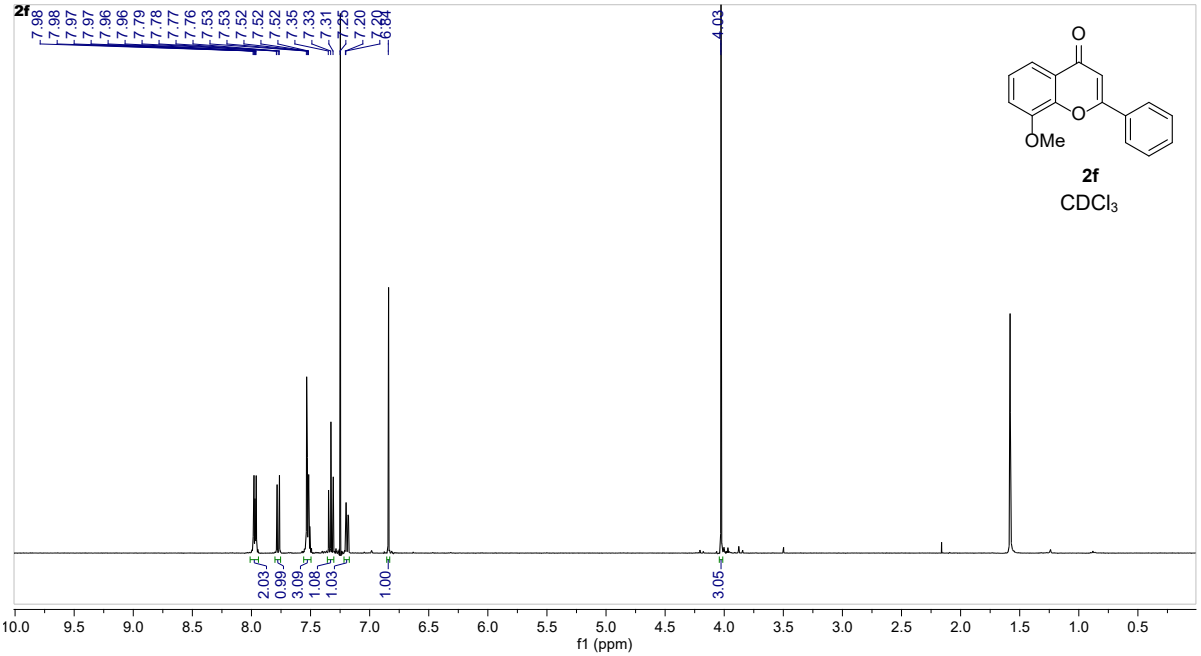

2d
(CRUDE) – CDCl3
7.26
Me
O
H
O
2d
(4 : 1)
Me
O
H
O
3d
2.48
2.41
4.39
1.00
f1 (ppm)

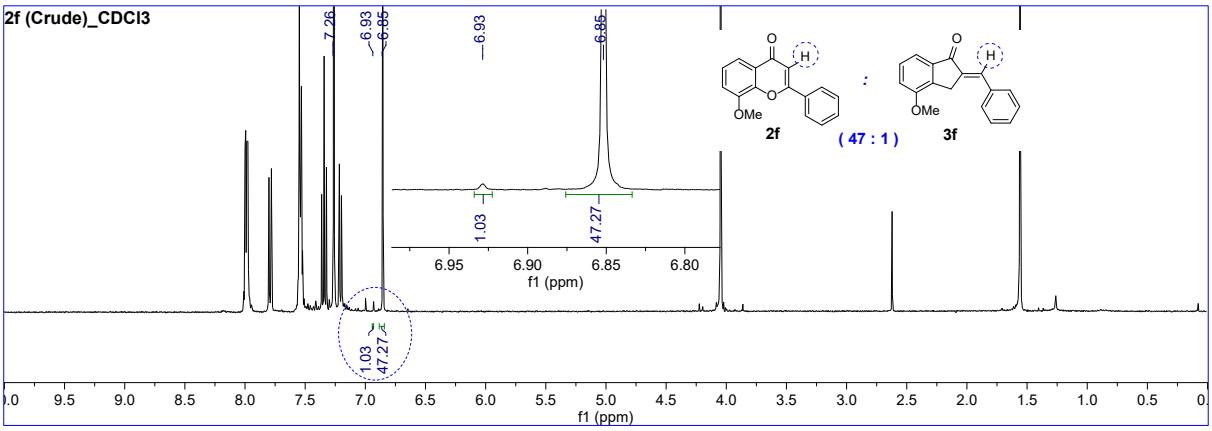

2d
178.75
163.48
154.74
135.39
135.16
132.11
131.67
129.18
126.45
125.24
123.78
118.00
107.62
21.10
Me
O
O
2d
CDCl3
f1 (ppm)

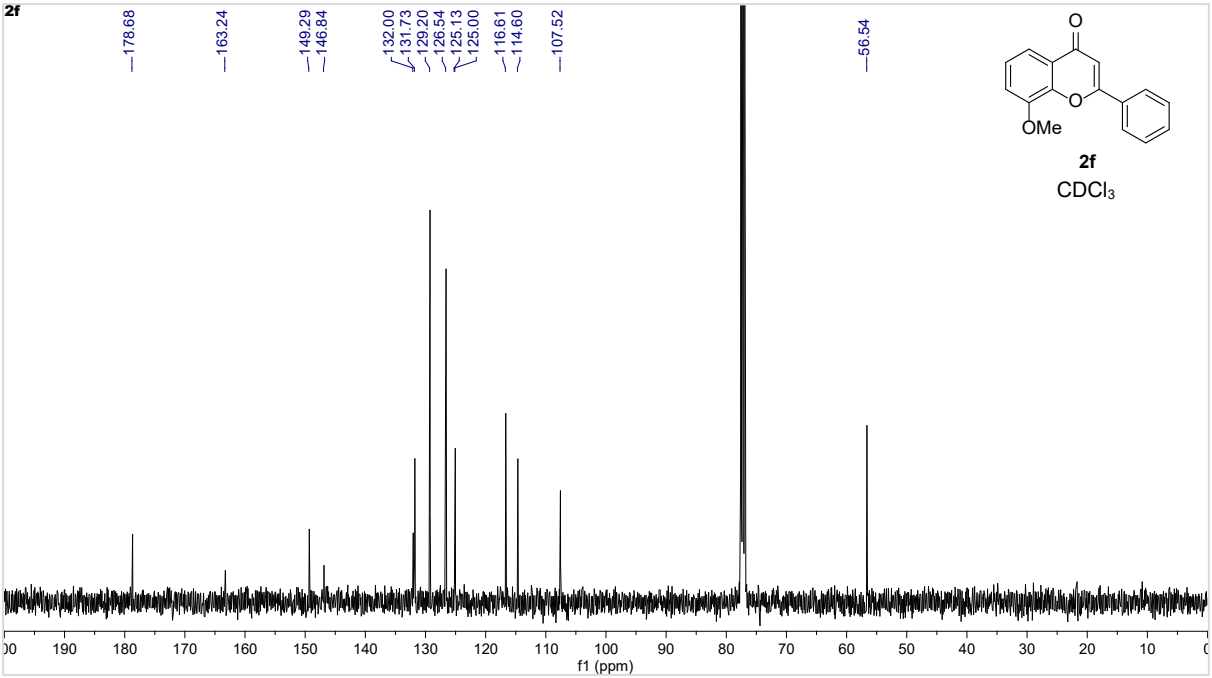

2e
8.15
8.14
7.99
7.98
7.98
7.97
7.97
7.97
7.96
7.75
7.75
7.57
7.56
7.56
7.56
7.55
7.55
7.54
7.54
7.26
6.86
1.60
1.40
O
O
2e
CDCl3
1.00
2.06
1.05
3.07
0.94
9.04
9.07
f1 (ppm)

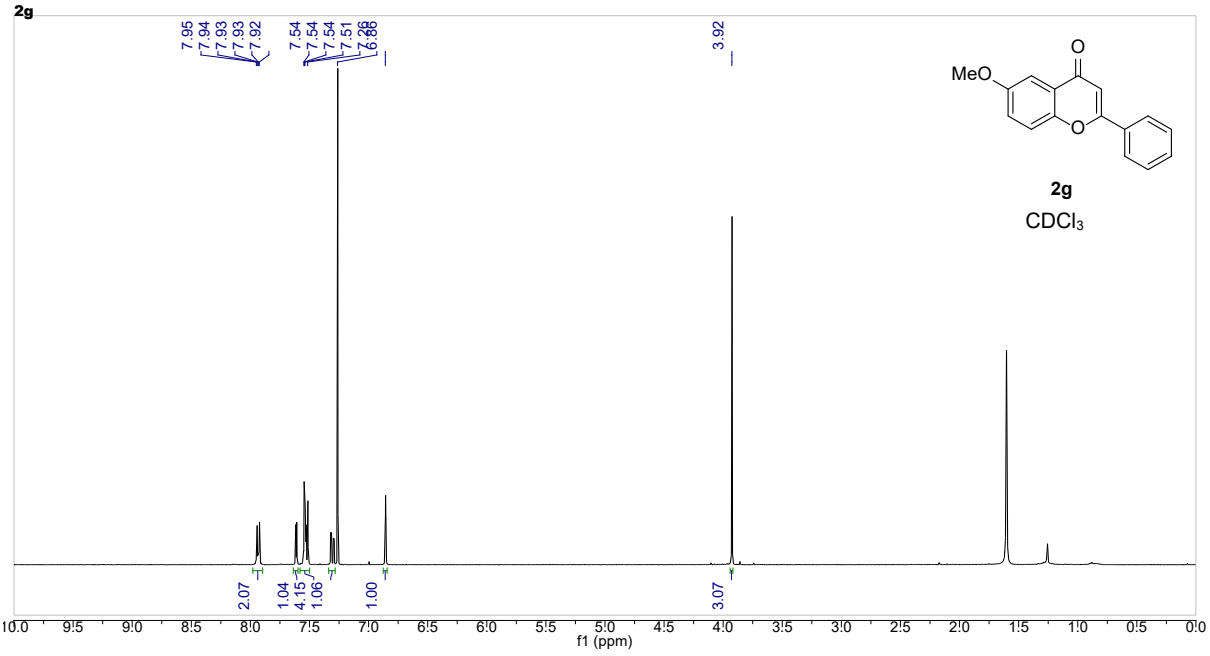

2e (CRUDE) – CDCl3
7.26
6.88
6.86
6.88
6.86
1.60
1.56
1.40
1.36
2e
(22 : 1)
3e
1.00
22.29
6.95
6.90
6.85
6.80
f1 (ppm)
1.00
22.44
f1 (ppm)

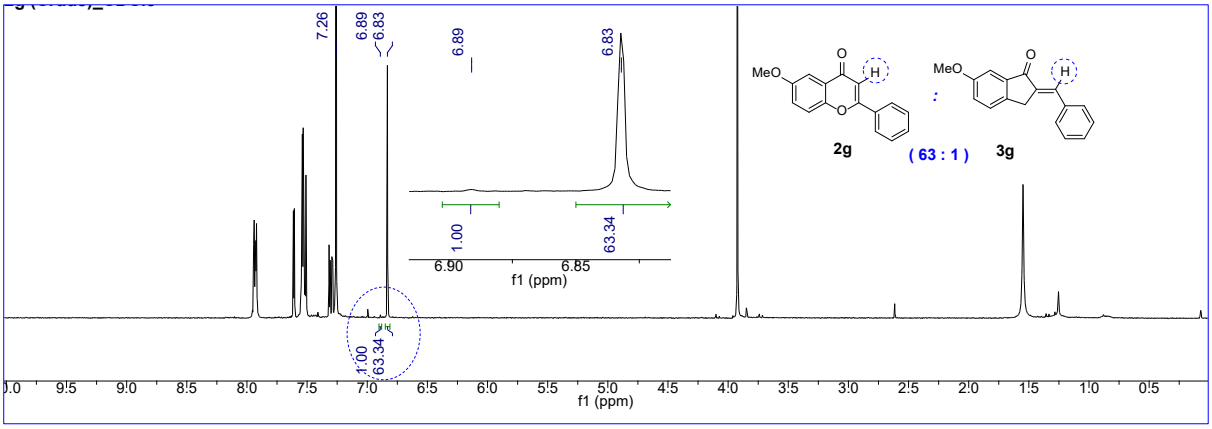

2e
179.33
163.50
153.53
147.93
138.60
132.40
131.65
129.37
129.32
126.62
119.91
107.37
35.44
35.19
31.51
30.44
O
O
2e
CDCl3
f1 (ppm)

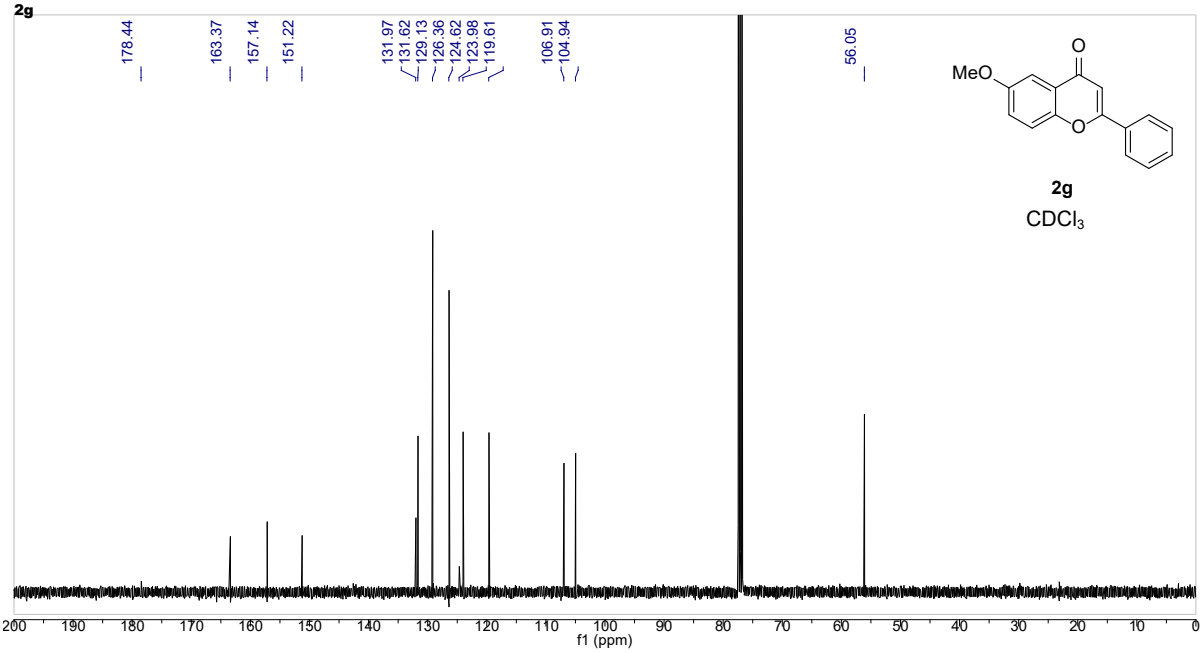

2f
7.98
7.98
7.97
7.97
7.96
7.96
7.79
7.78
7.77
7.76
7.53
7.53
7.52
7.52
7.52
7.35
7.33
7.31
7.25
7.20
6.84
4.03
2.03
0.99
3.09
1.08
1.03
1.00
3.05
OMe
2f
CDCl3
f1 (ppm)

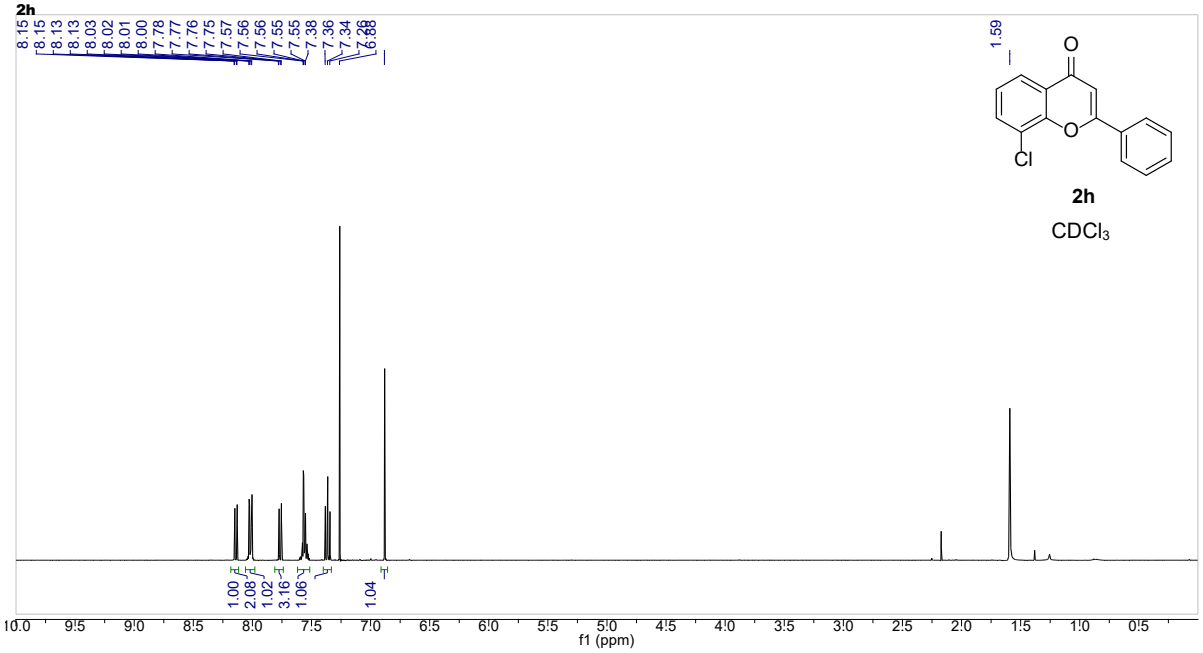

2f (Crude)_CDCl3
7.26
6.93
6.85
6.93
6.85
1.03
47.27
6.95
6.90
6.85
6.80
f1 (ppm)
OMe
2f
(47 : 1)
3f
f1 (ppm)

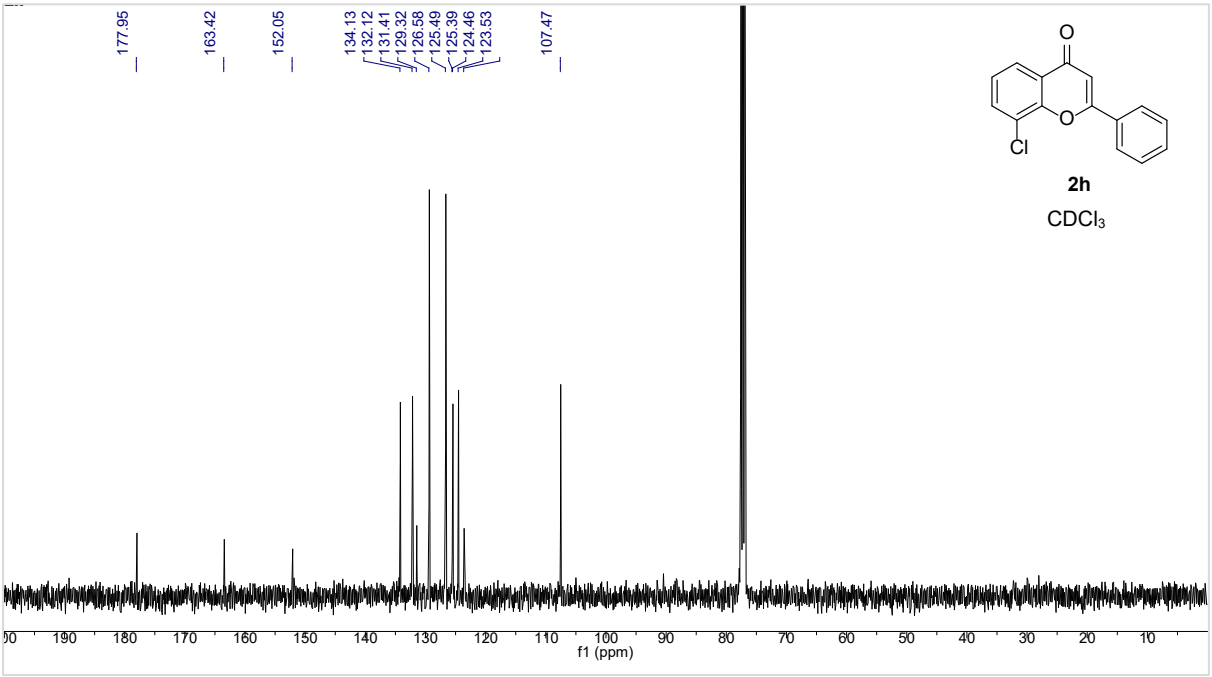

2f
178.68
163.24
149.29
146.84
132.00
131.73
129.20
128.54
125.13
125.00
116.61
114.60
107.52
56.54
OMe
2f
CDCl3
f1 (ppm)

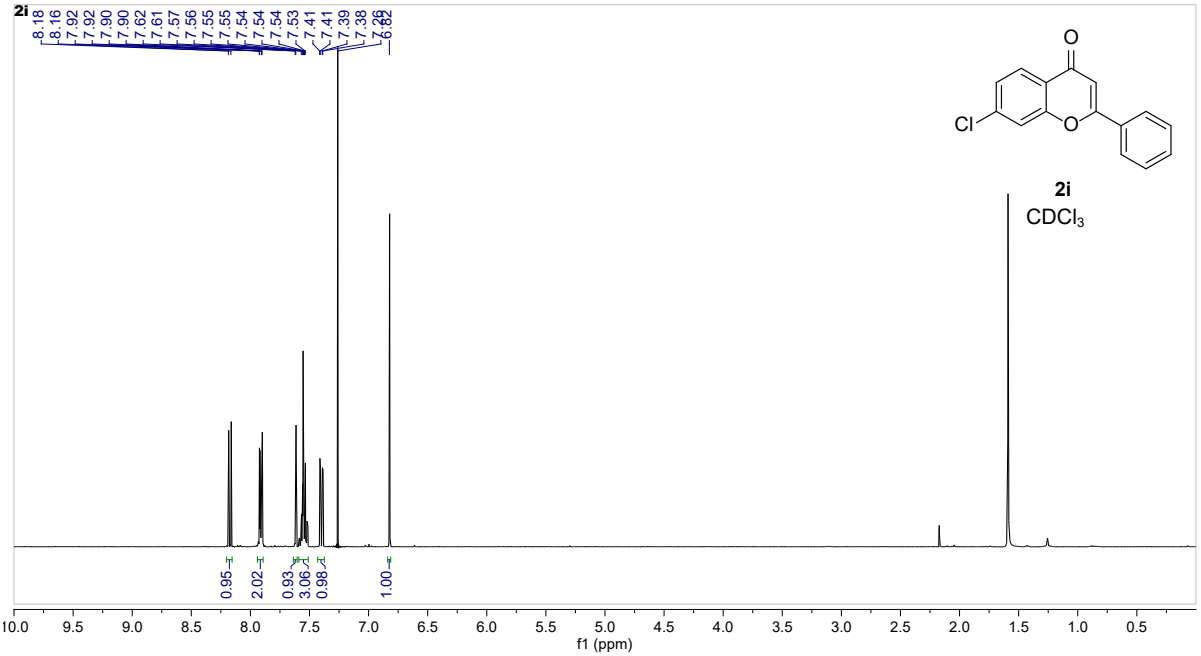

2g
7.95
7.94
7.93
7.93
7.92
7.54
7.54
7.54
7.51
7.26
6.88
3.92
MeO
O
O
2g
CDCl3
2.07
1.04
4.15
1.06
1.00
3.07
f1 (ppm)

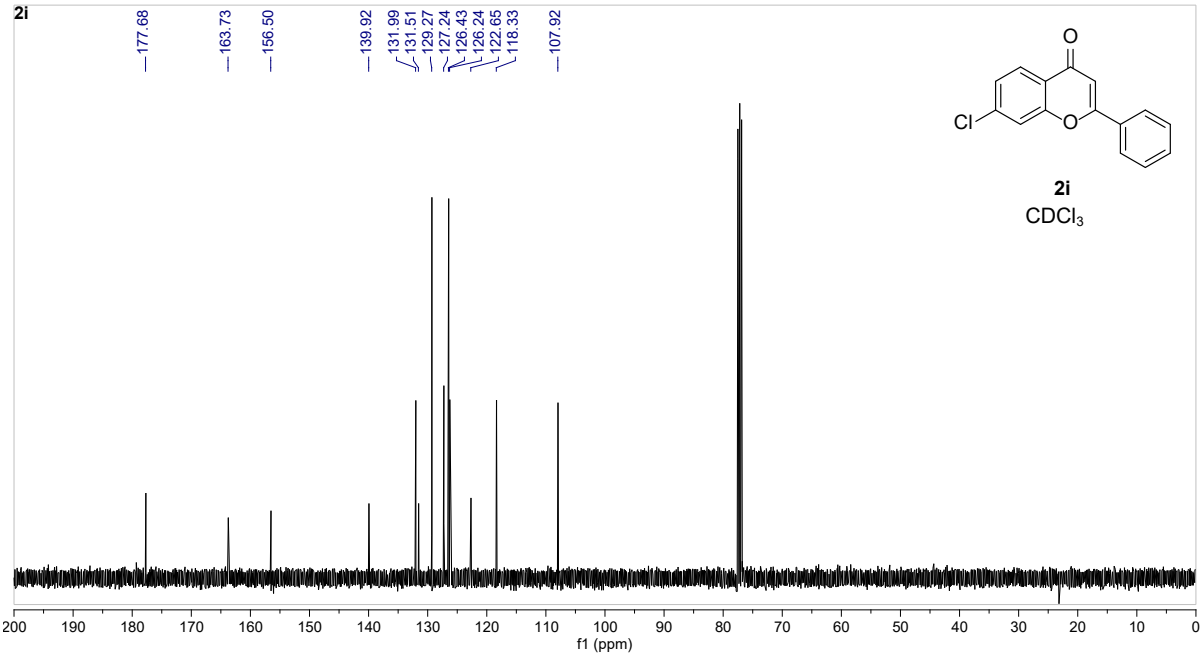

7.26
6.89
6.83
6.89
6.83
1.00
63.34
6.90
6.85
f1 (ppm)
MeO
O
H
2g
(63 : 1)
3g
1.00
63.34
f1 (ppm)

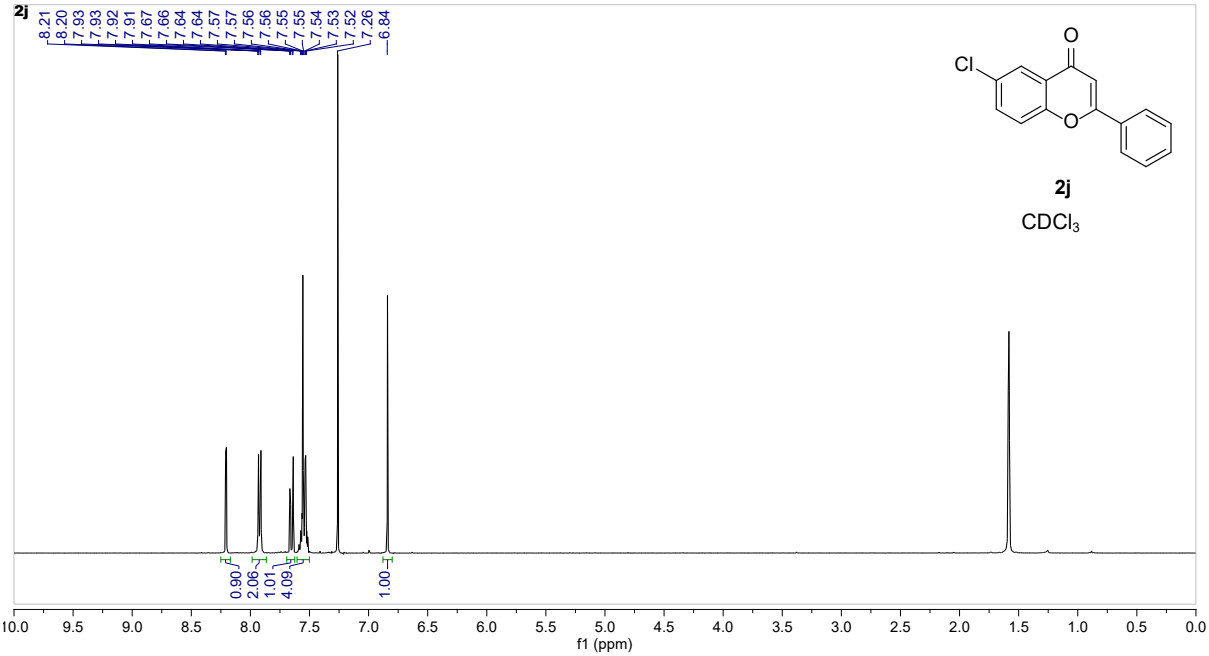

2g
178.44
163.37
157.14
151.22
131.97
131.62
129.13
126.36
124.62
123.98
119.61
106.91
104.94
56.05
MeO
O
O
2g
CDCl3
f1 (ppm)

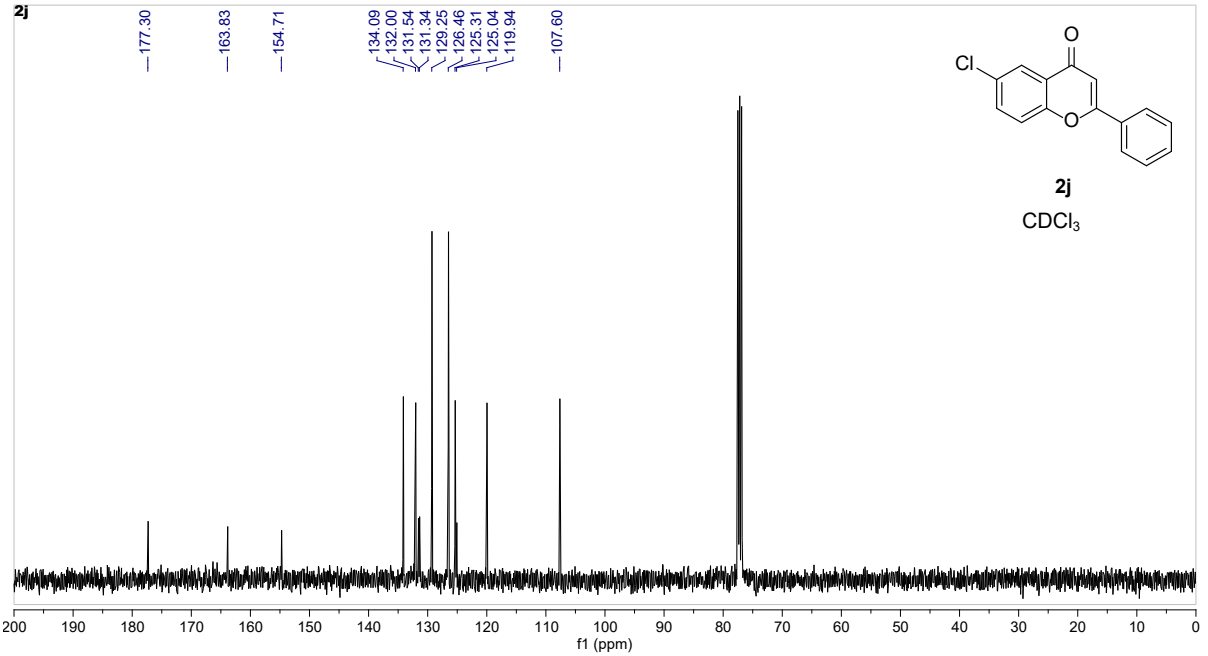

2h
8.15
8.15
8.13
8.13
8.03
8.02
8.01
8.00
7.78
7.77
7.76
7.75
7.57
7.56
7.56
7.55
7.55
7.38
7.36
7.34
1.59
1.00
2.08
1.02
3.16
1.06
1.04
f1 (ppm)
O
O
Cl
2h
CDCl3

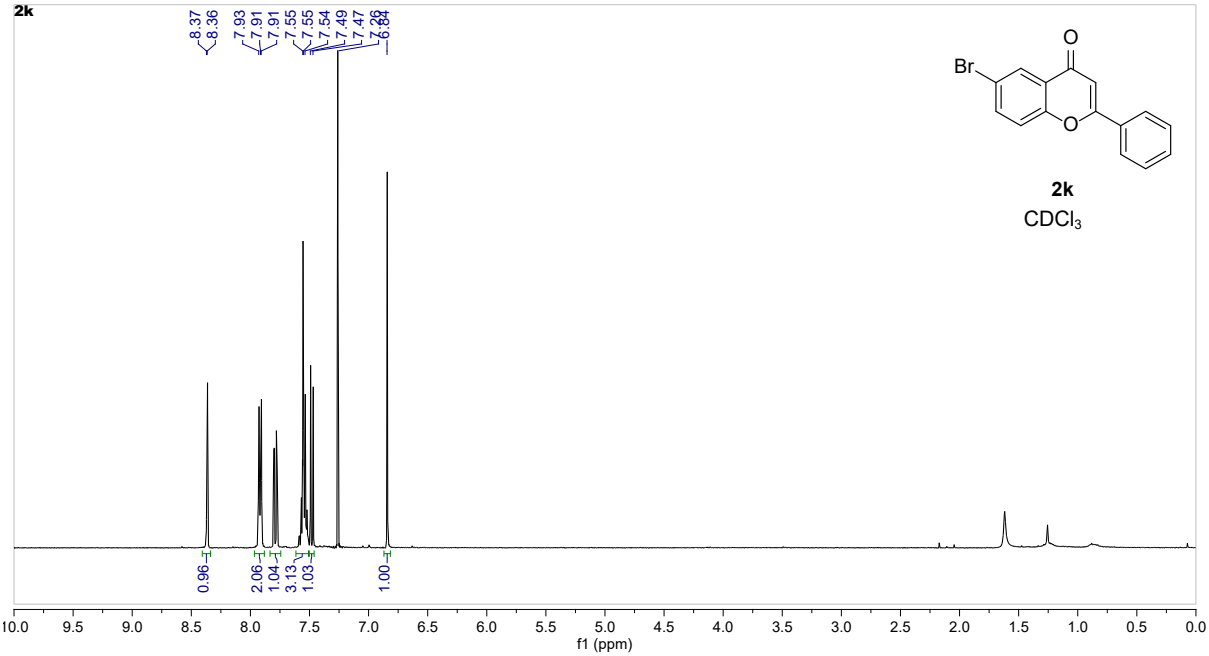

177.95
163.42
152.05
134.13
132.12
131.41
129.32
126.58
125.49
125.39
124.46
123.53
107.47
f1 (ppm)
O
O
Cl
2h
CDCl3

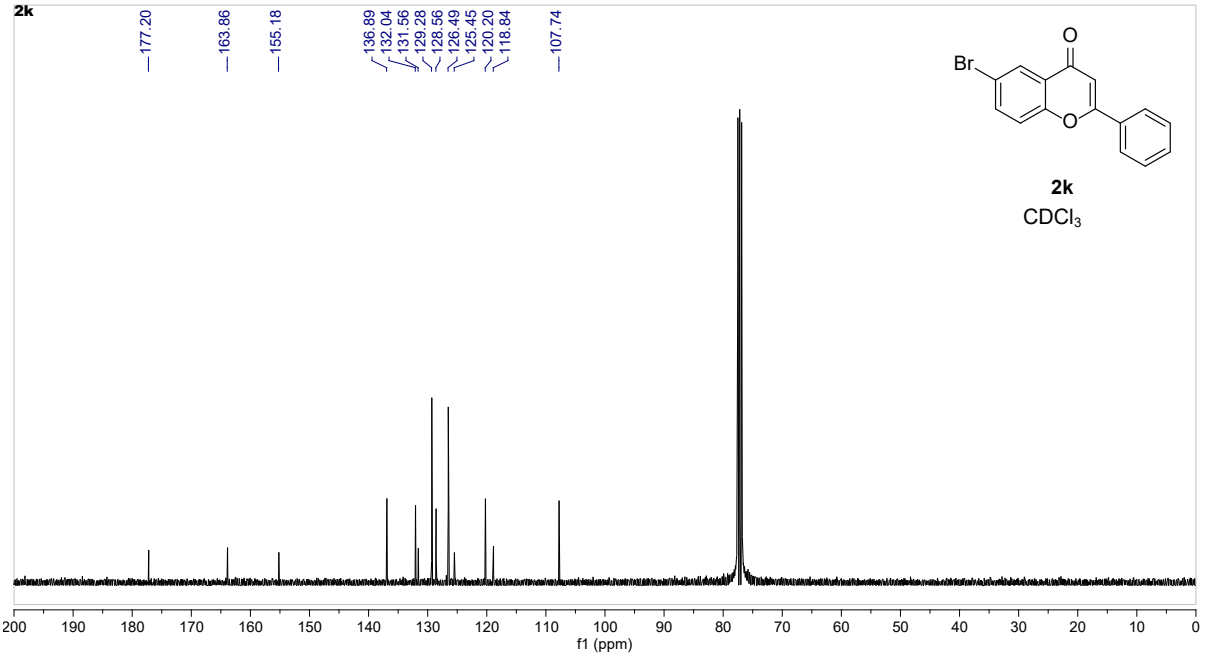

2i
8.18
8.16
7.92
7.92
7.90
7.90
7.62
7.61
7.57
7.56
7.55
7.55
7.54
7.54
7.54
7.53
7.41
7.41
7.39
7.38
6.82
0.95
2.02
0.93
3.06
0.98
1.00
f1 (ppm)
O
Cl
O
2i
CDCl3

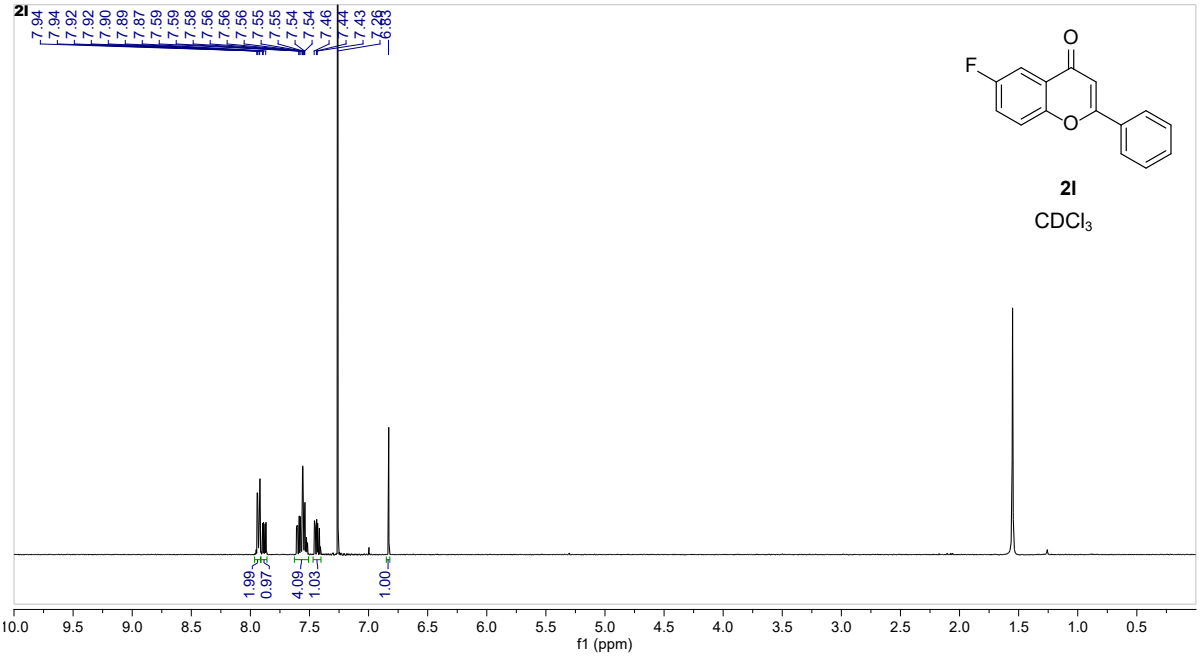

2i
177.68
163.73
156.50
139.92
131.99
131.51
129.27
127.24
126.43
126.24
122.65
118.33
107.92
f1 (ppm)
O
Cl
O
2i
CDCl3

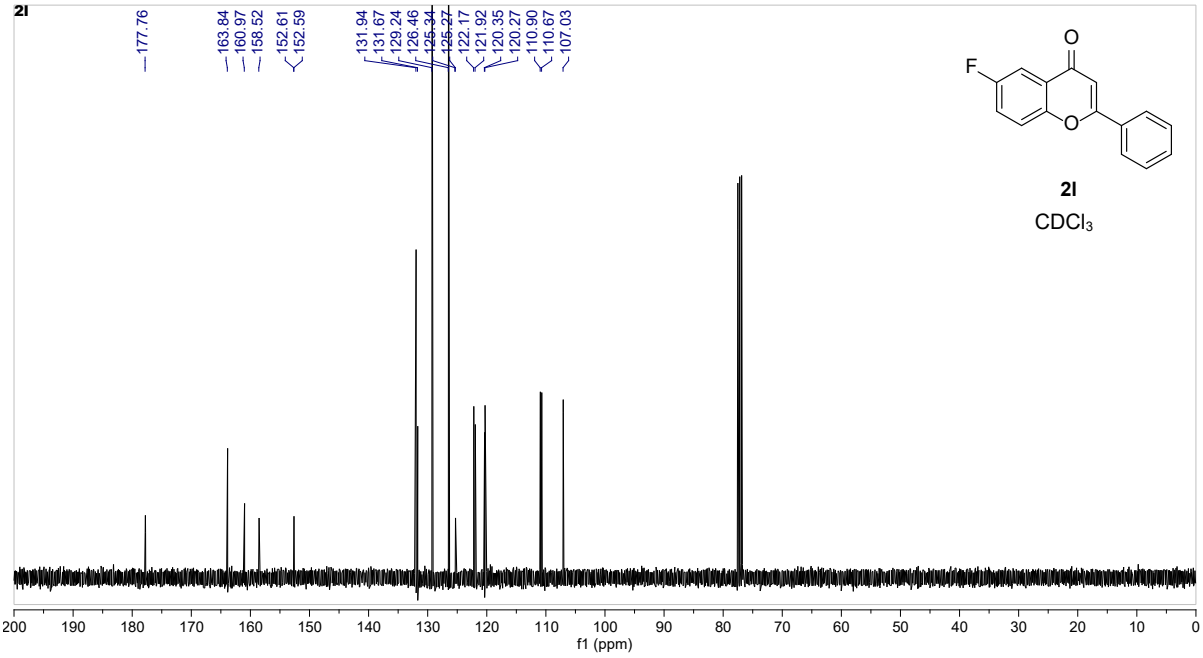

2j
8.21
8.20
7.93
7.93
7.92
7.91
7.67
7.66
7.64
7.64
7.57
7.57
7.56
7.56
7.55
7.55
7.54
7.53
7.52
7.26
6.84
0.90
2.06
1.01
4.09
1.00
Cl
O
O
2j
CDCl3
f1 (ppm)

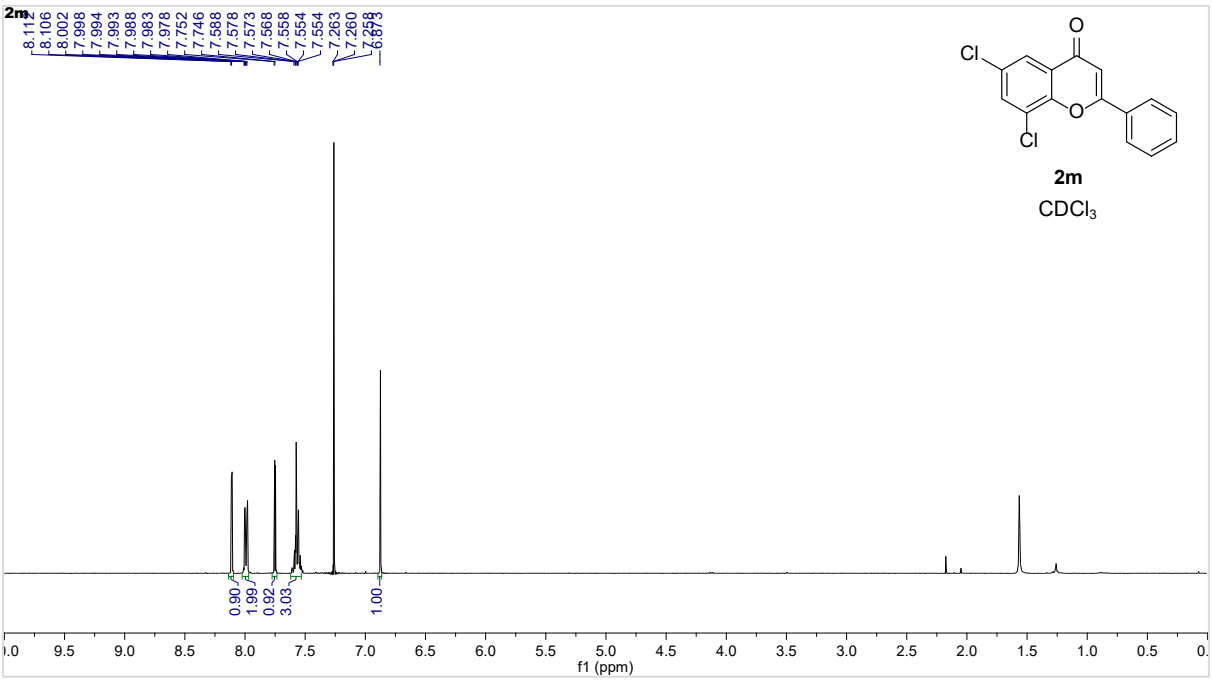

2j
177.30
163.83
154.71
134.09
132.00
131.54
131.34
129.25
126.46
125.31
125.04
119.94
107.60
Cl
O
O
2j
CDCl3
f1 (ppm)

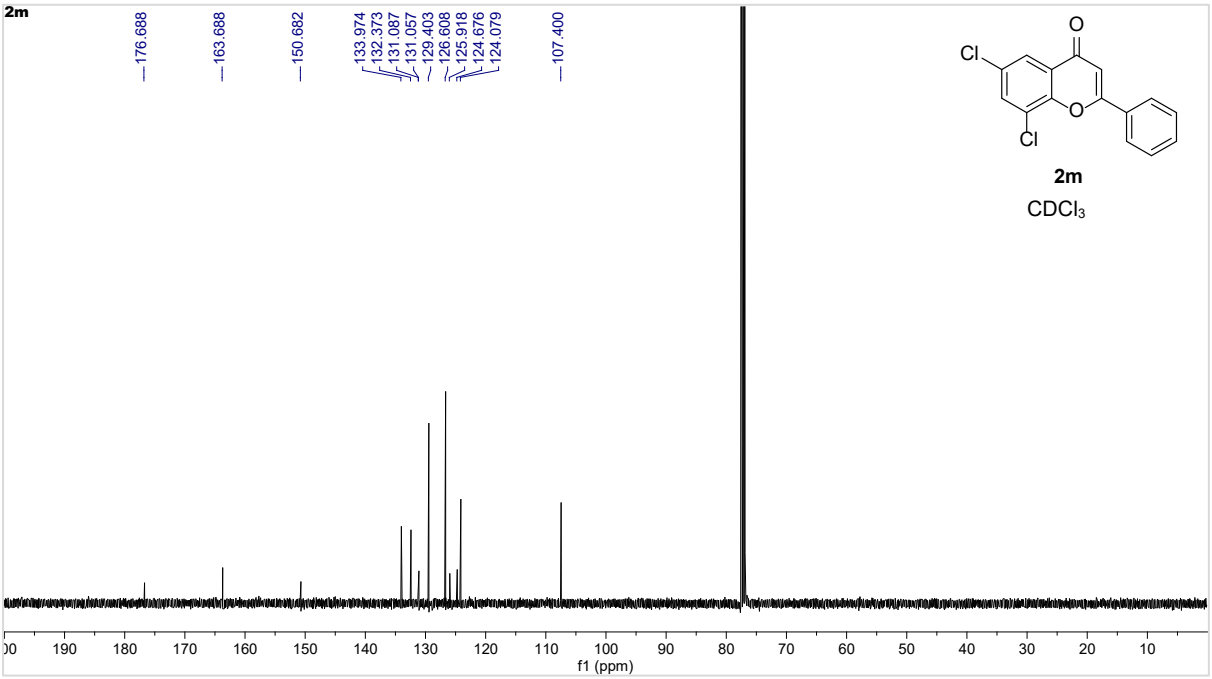

2k
8.37
8.36
7.93
7.91
7.91
7.55
7.55
7.54
7.49
7.47
6.84
0.96
2.06
1.04
3.13
1.03
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
Br
O
O
2k
CDCl3

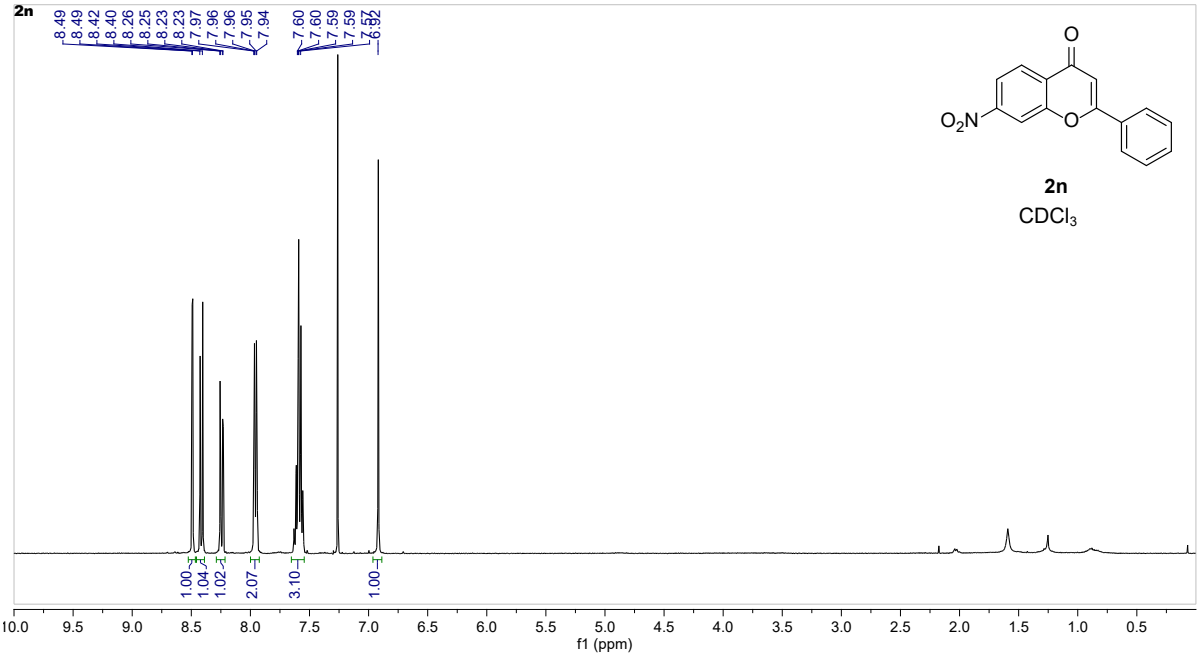

2k
177.20
163.86
155.18
136.89
132.04
131.56
129.28
128.56
126.49
125.45
120.20
118.84
107.74
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Br
O
O
2k
CDCl3

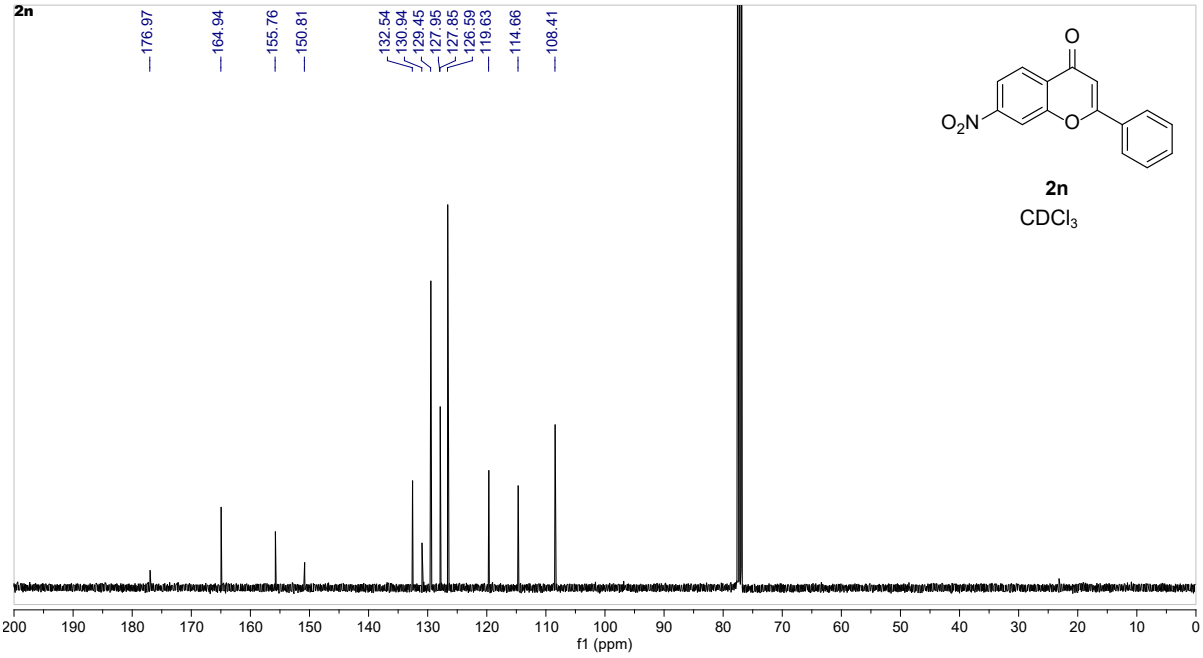

2l
7.94
7.94
7.92
7.92
7.90
7.89
7.87
7.59
7.59
7.58
7.56
7.56
7.56
7.55
7.55
7.54
7.54
7.46
7.44
7.43
6.83
O
F
O
2l
CDCl3
1.99
0.97
4.09
1.03
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

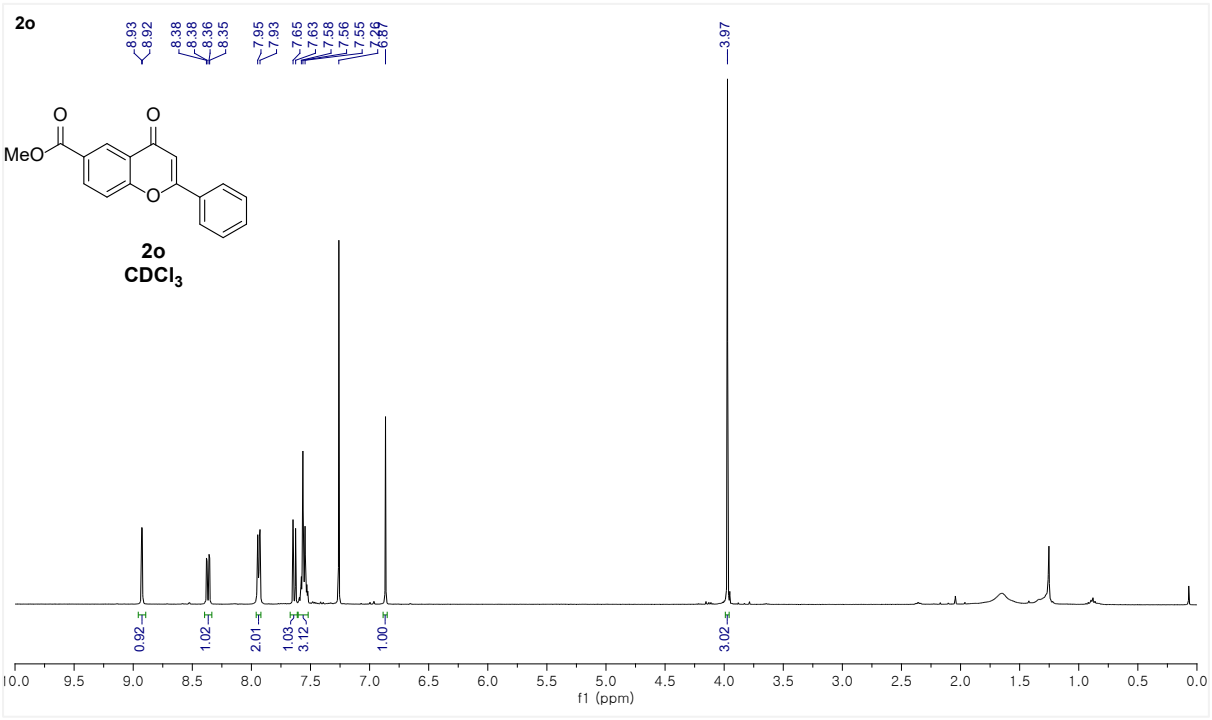

2l
177.76
163.84
160.97
158.52
152.61
152.59
131.94
131.67
129.24
126.46
125.34
125.27
122.17
121.92
120.35
120.27
110.90
110.67
107.03
O
F
O
2l
CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

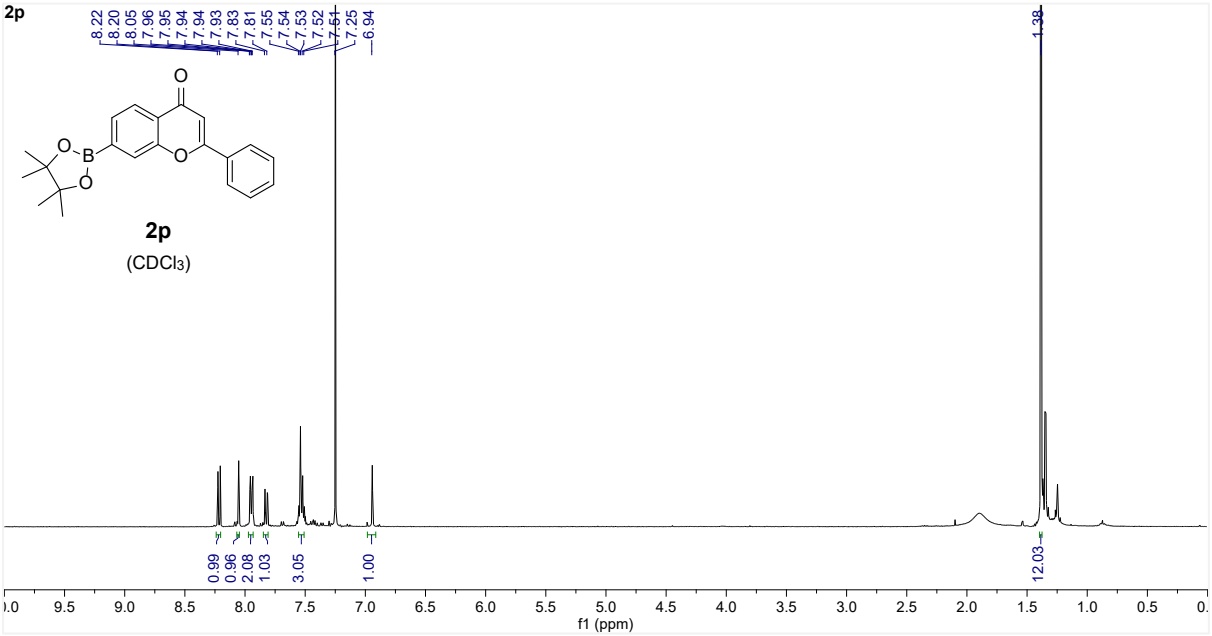

2m
8.117
8.106
8.002
7.998
7.994
7.993
7.988
7.983
7.978
7.752
7.746
7.588
7.578
7.573
7.568
7.558
7.554
7.263
7.260
7.258
6.893
0.90
1.99
0.92
3.03
1.00
f1 (ppm)
Cl
O
Cl
O
2m
CDCl3

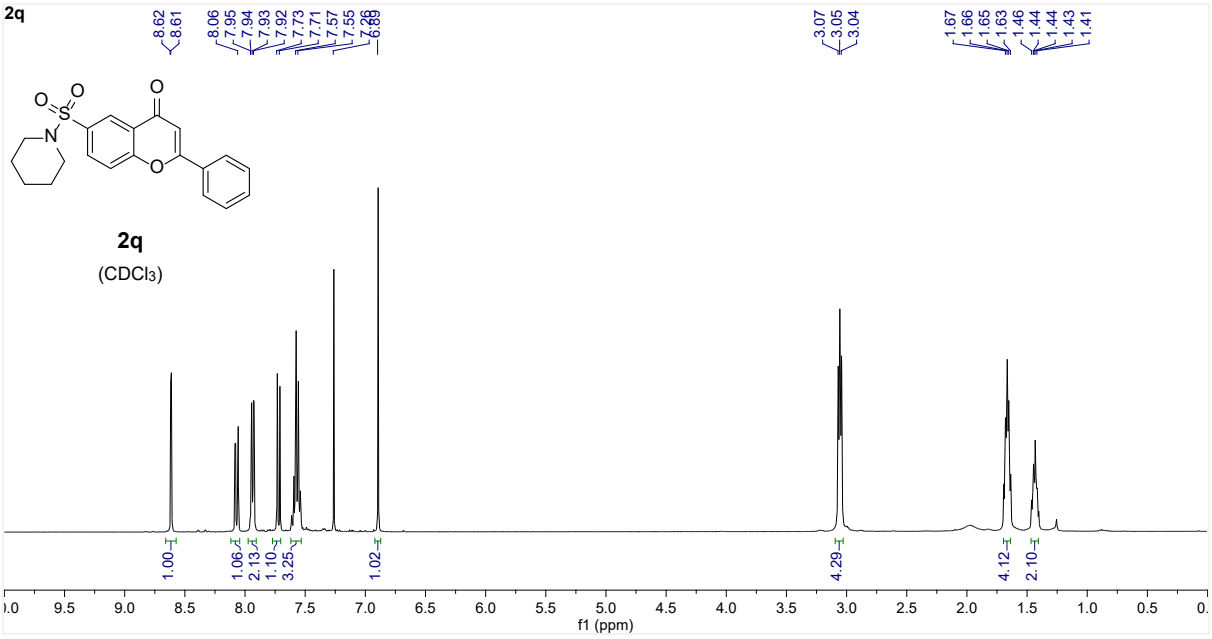

2m
176.688
163.688
150.682
133.974
132.373
131.087
131.057
129.403
126.608
125.918
124.676
124.079
107.400
f1 (ppm)
Cl
O
Cl
O
2m
CDCl3

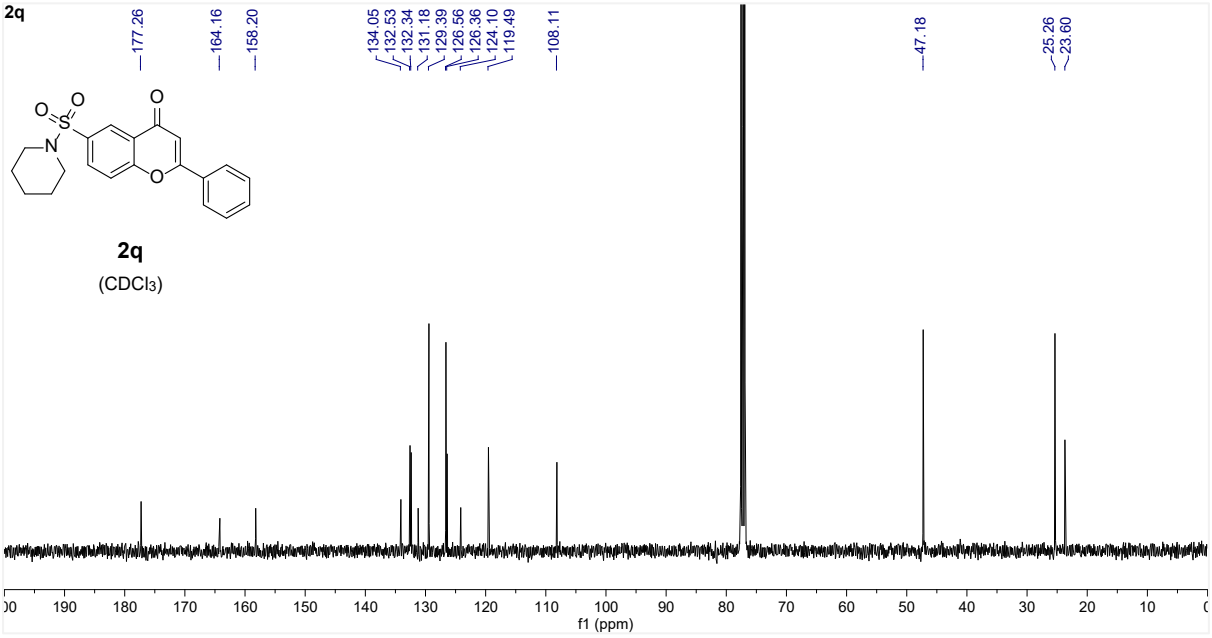

2n
8.49
8.49
8.42
8.40
8.26
8.25
8.23
8.23
7.97
7.96
7.96
7.95
7.94
7.60
7.60
7.59
7.59
7.57
6.92
1.00
1.04
1.02
2.07
3.10
1.00
O
O2N
O
2n
CDCl3
f1 (ppm)

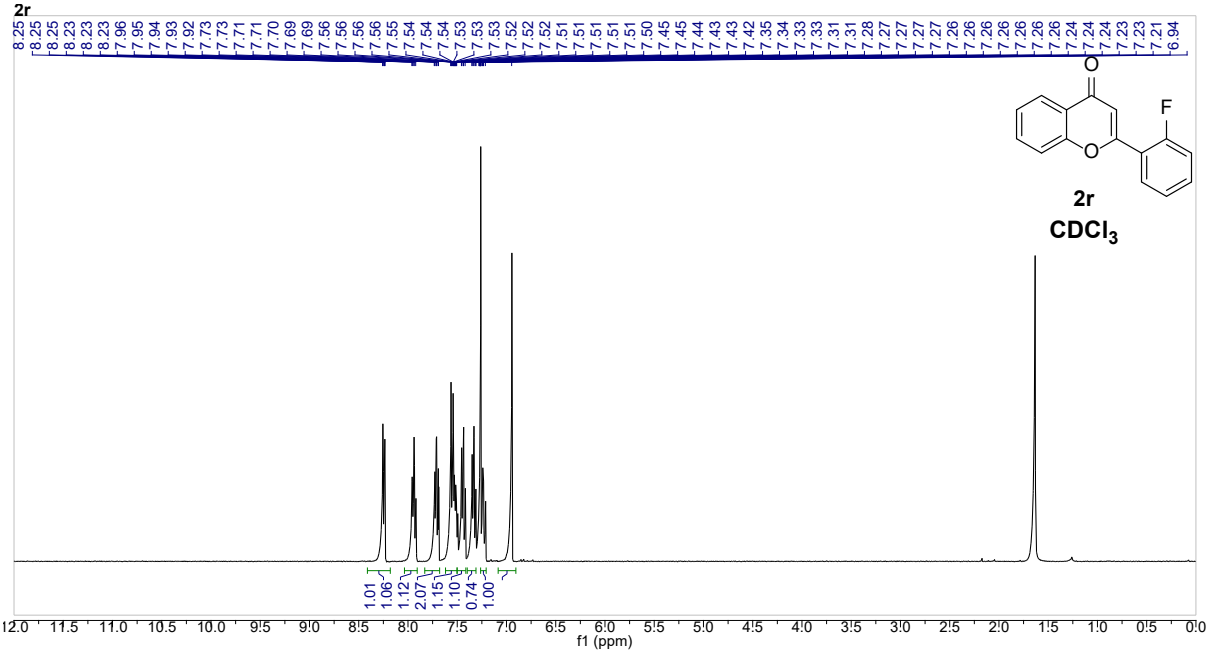

2n
176.97
164.94
155.76
150.81
132.54
130.94
129.45
127.95
127.85
126.59
119.63
114.66
108.41
O
O2N
O
2n
CDCl3
f1 (ppm)

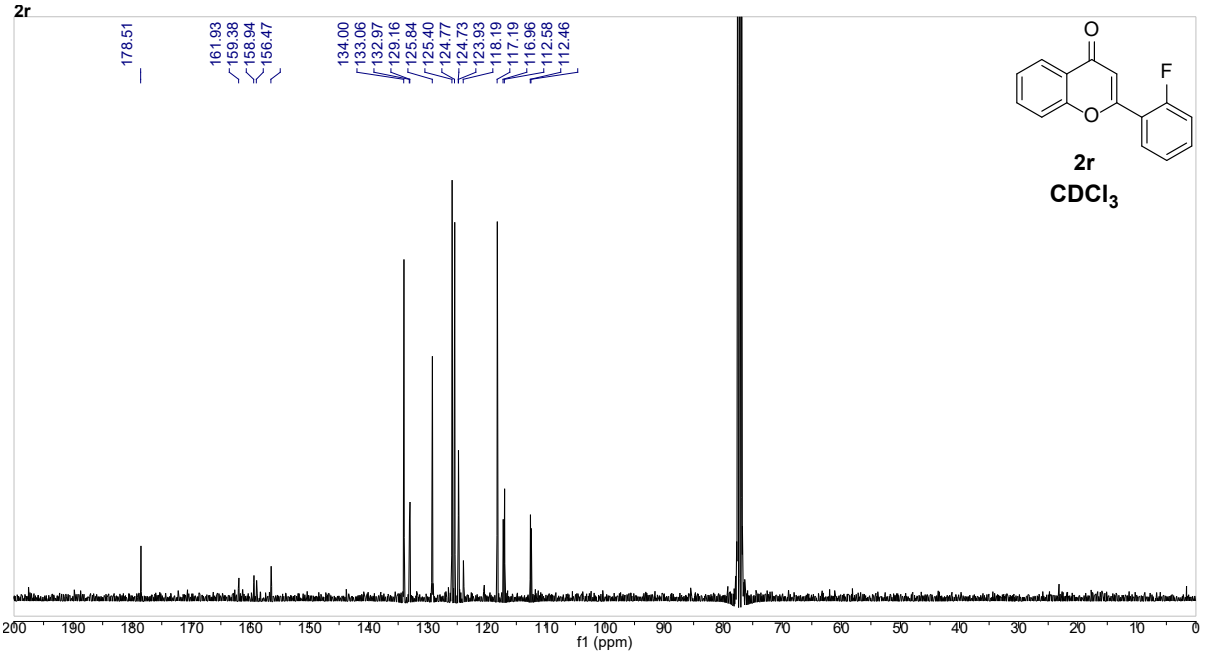

2o
8.93
8.92
8.38
8.38
8.36
8.35
7.95
7.93
7.65
7.63
7.58
7.56
7.55
7.26
6.87
3.97
MeO
O
O
O
2o
CDCl3
0.92
1.02
2.01
1.03
3.12
1.00
3.02
f1 (ppm)

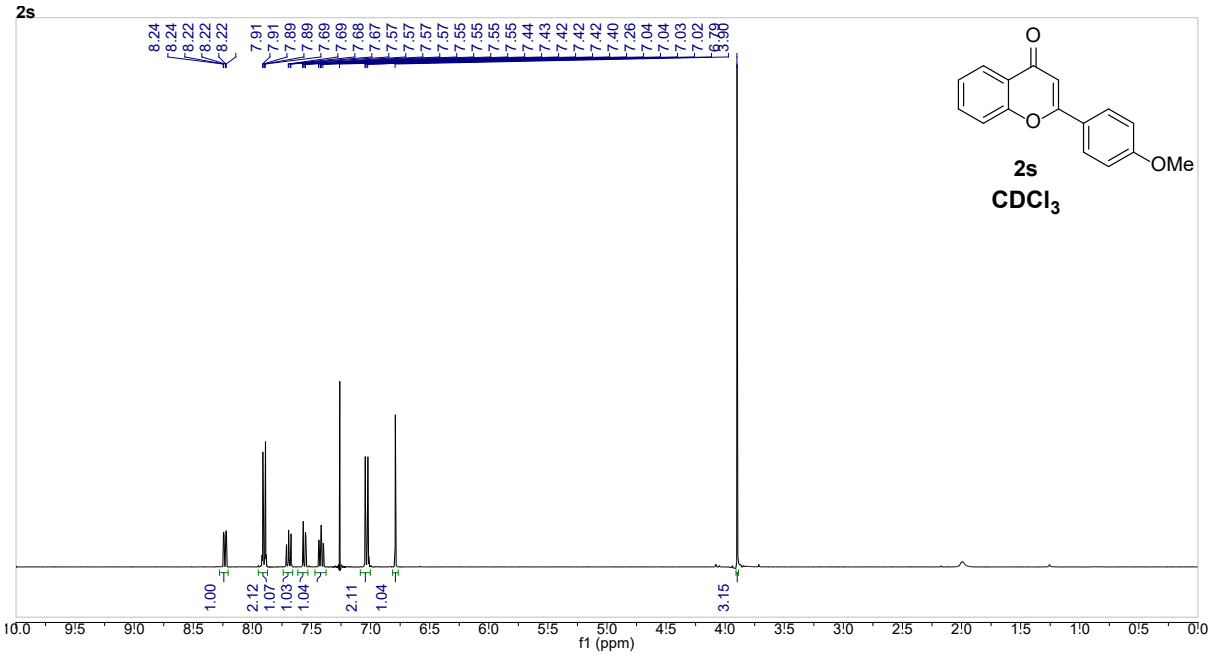

2p
8.22
8.20
8.05
7.96
7.95
7.94
7.94
7.93
7.83
7.81
7.55
7.54
7.53
7.52
7.51
7.25
6.94
1.38
O
O
B
O
O
2p
(CDCl3)
0.99
0.96
2.08
1.03
3.05
1.00
12.03
f1 (ppm)

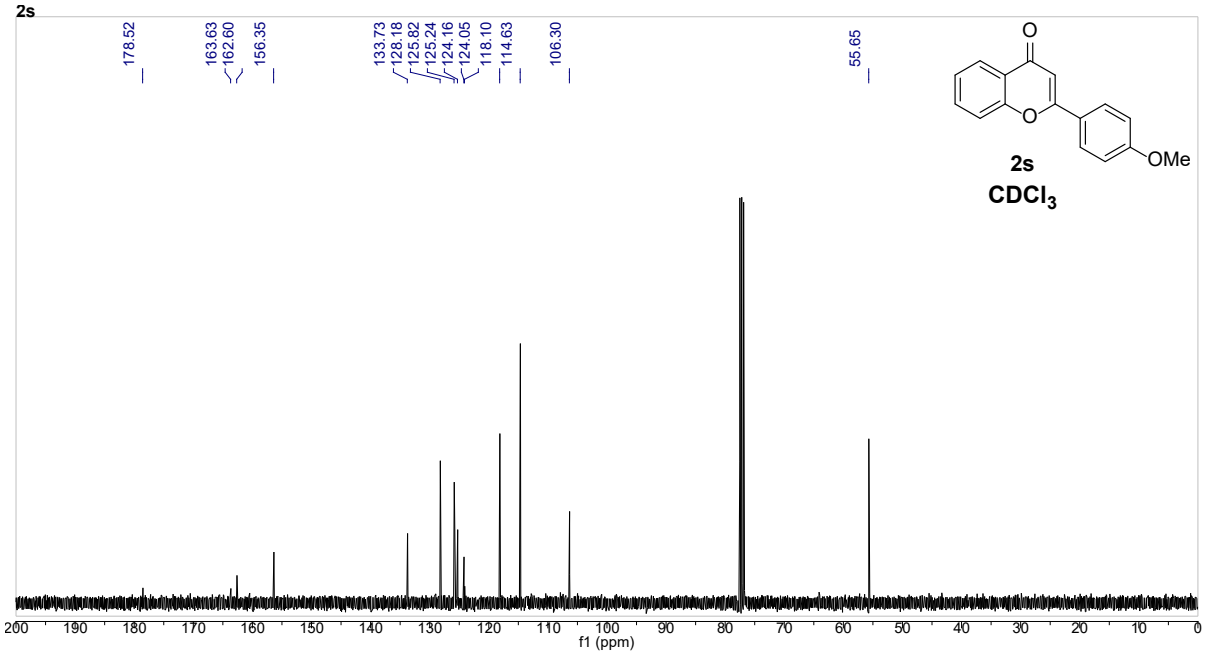

2q
8.62
8.61
8.06
7.95
7.94
7.93
7.92
7.73
7.71
7.57
7.55
7.26
6.88
3.07
3.05
3.04
1.67
1.66
1.65
1.63
1.46
1.44
1.44
1.43
1.41
2q
(CDCl3)
1.00
1.06
2.13
1.10
3.25
1.02
4.29
4.12
2.10
f1 (ppm)

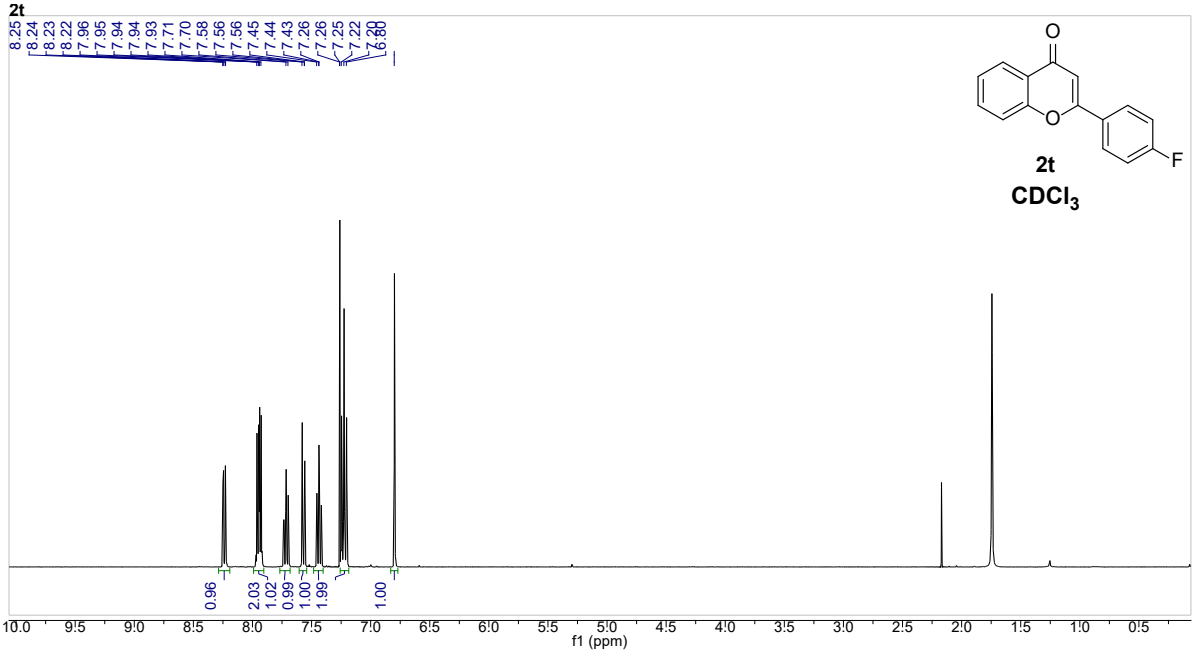

2q
177.26
164.16
158.20
134.05
132.53
132.34
131.18
129.39
126.56
126.36
124.10
119.49
108.11
47.18
25.26
23.60
2q
(CDCl3)
f1 (ppm)

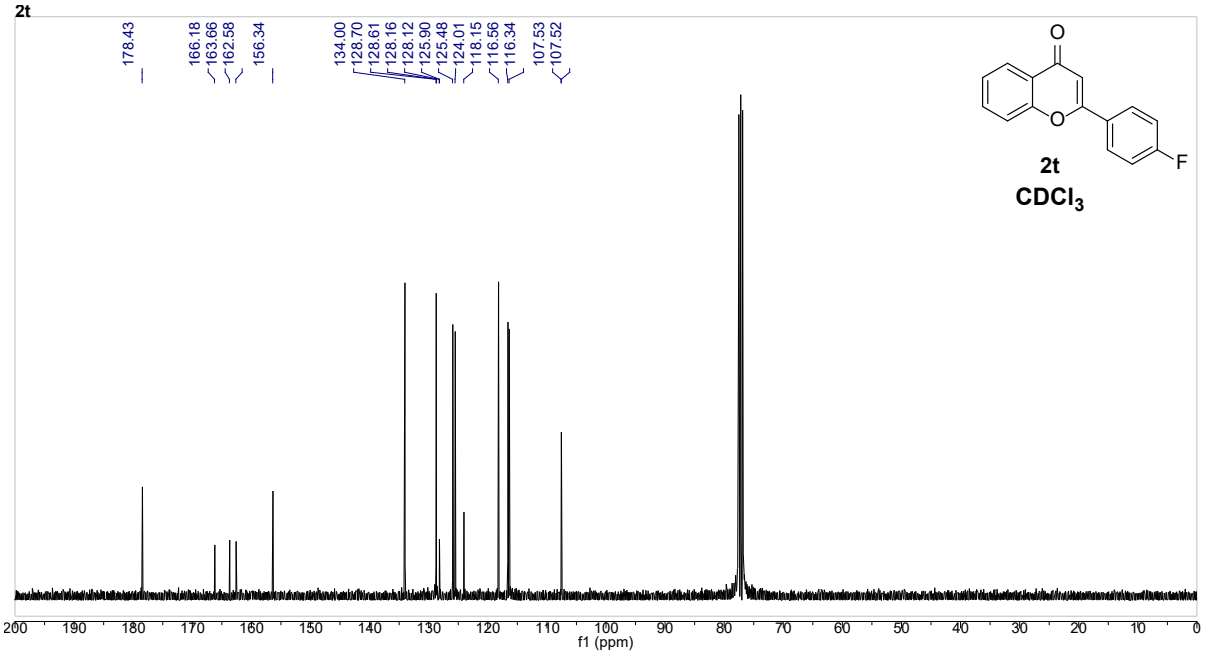

2r
O
F
O
2r
CDCl3
f1 (ppm)

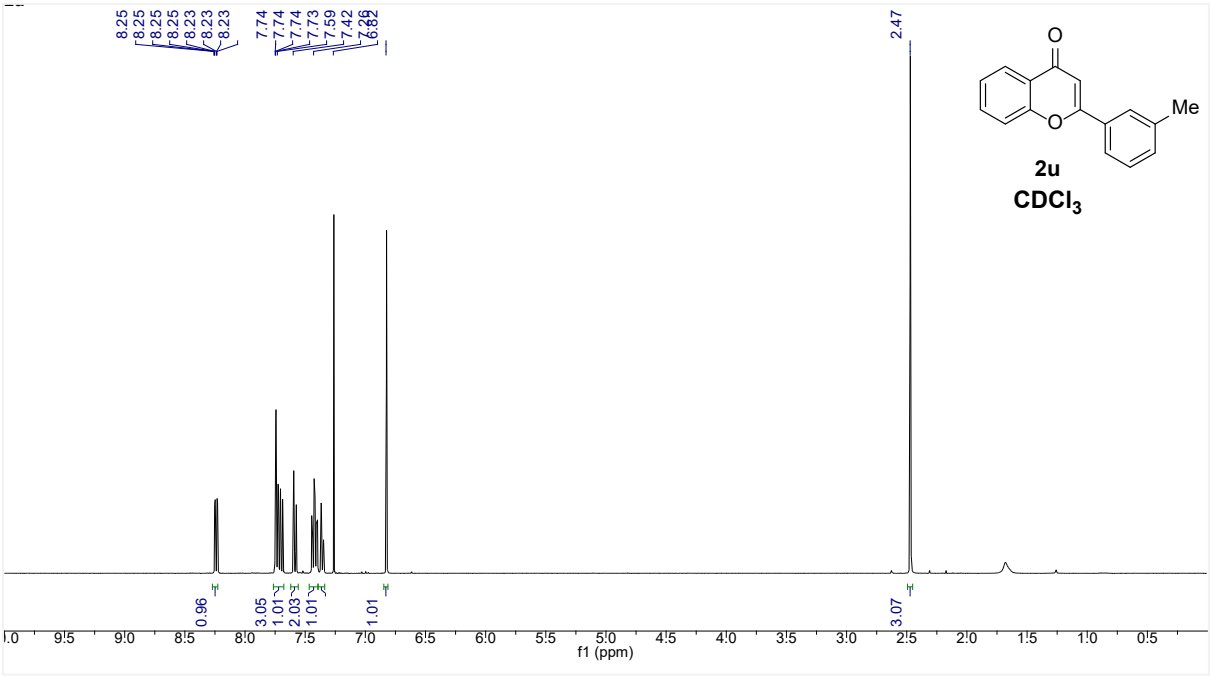

2r
O
F
O
2r
CDCl3
f1 (ppm)

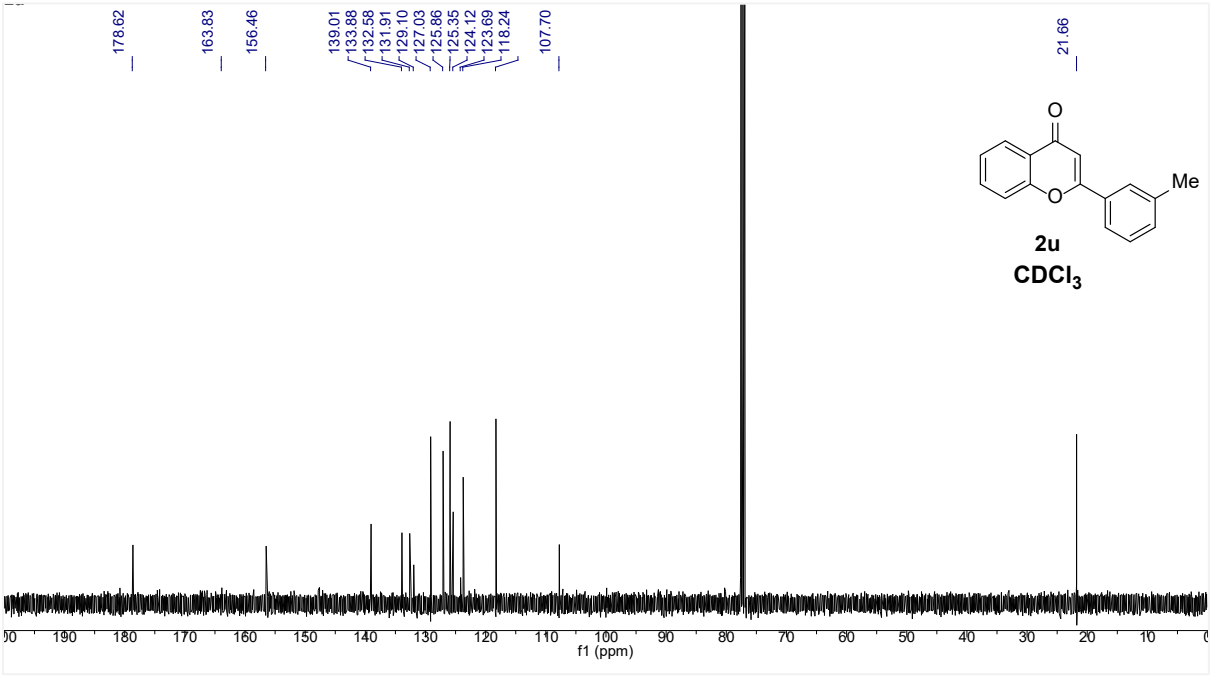

2s
8.24
8.24
8.22
8.22
7.91
7.91
7.89
7.89
7.69
7.69
7.68
7.67
7.57
7.57
7.57
7.55
7.55
7.55
7.44
7.43
7.42
7.42
7.42
7.40
7.26
7.04
7.04
7.03
7.02
3.90
1.00
2.12
1.07
1.03
1.04
2.11
1.04
3.15
f1 (ppm)
O
O
OMe
2s
CDCl3

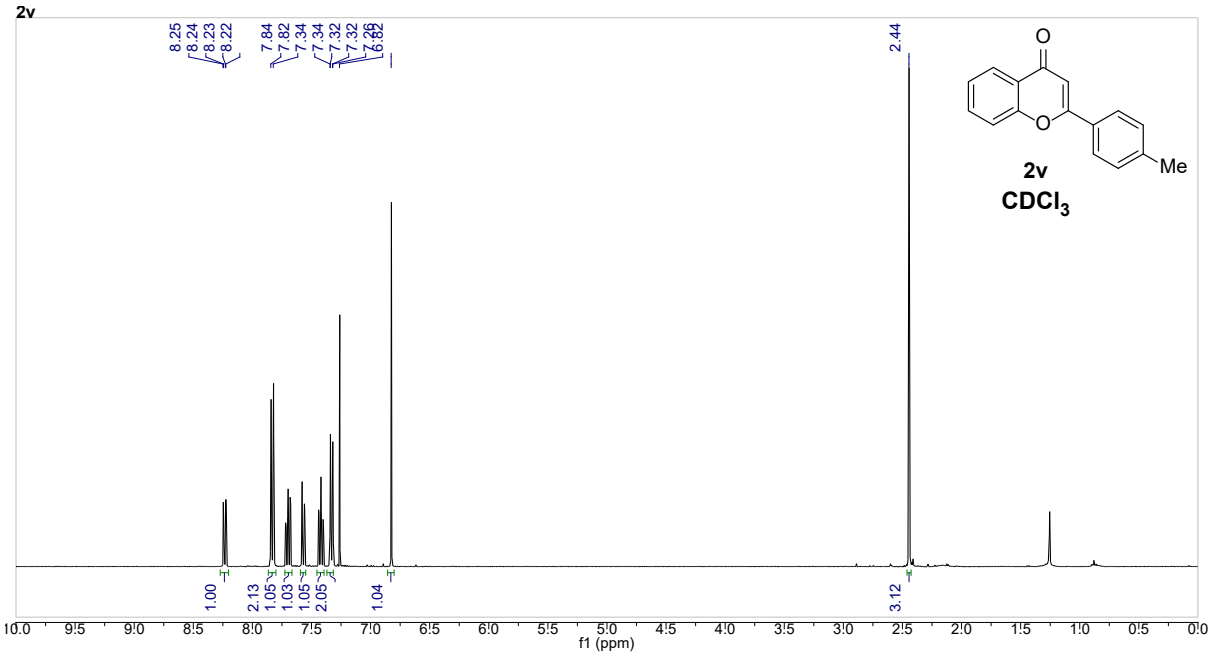

2s
178.52
163.63
162.60
156.35
133.73
128.18
125.82
125.24
124.16
124.05
118.10
114.63
106.30
55.65
f1 (ppm)
O
O
OMe
2s
CDCl3

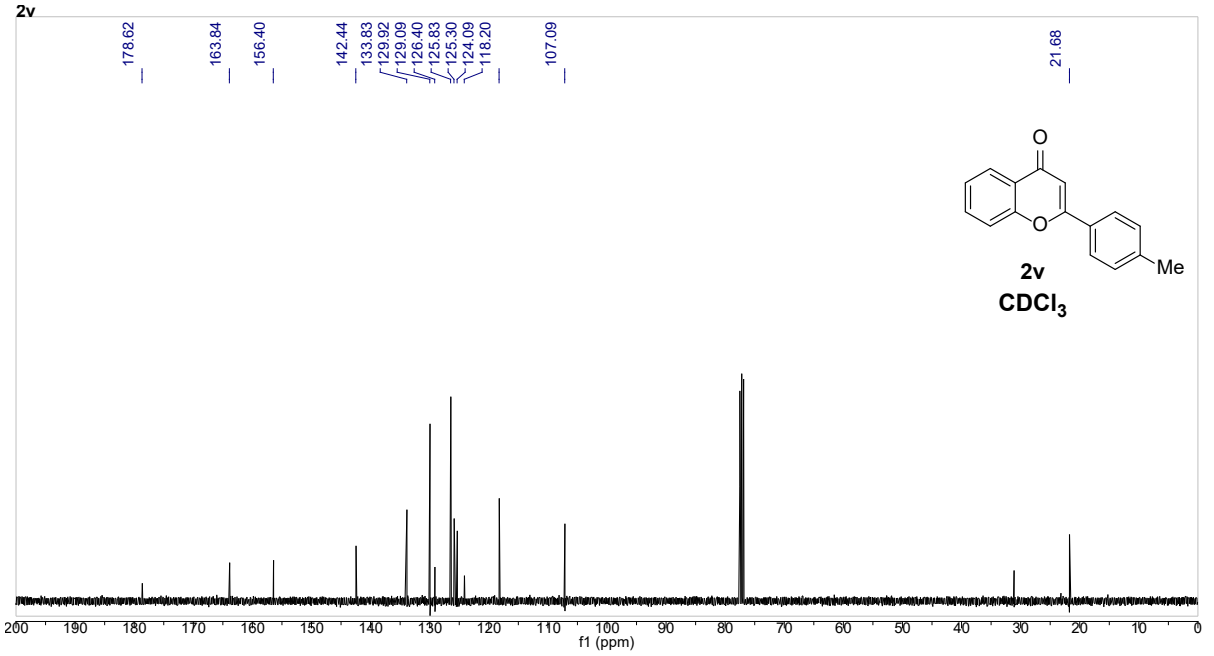

2t
8.25
8.24
8.23
8.22
7.96
7.95
7.94
7.94
7.93
7.71
7.70
7.58
7.56
7.56
7.45
7.44
7.43
7.26
7.26
7.25
7.22
6.80
0.96
2.03
1.02
0.99
1.00
1.99
1.00
f1 (ppm)
O
O
F
2t
CDCl3

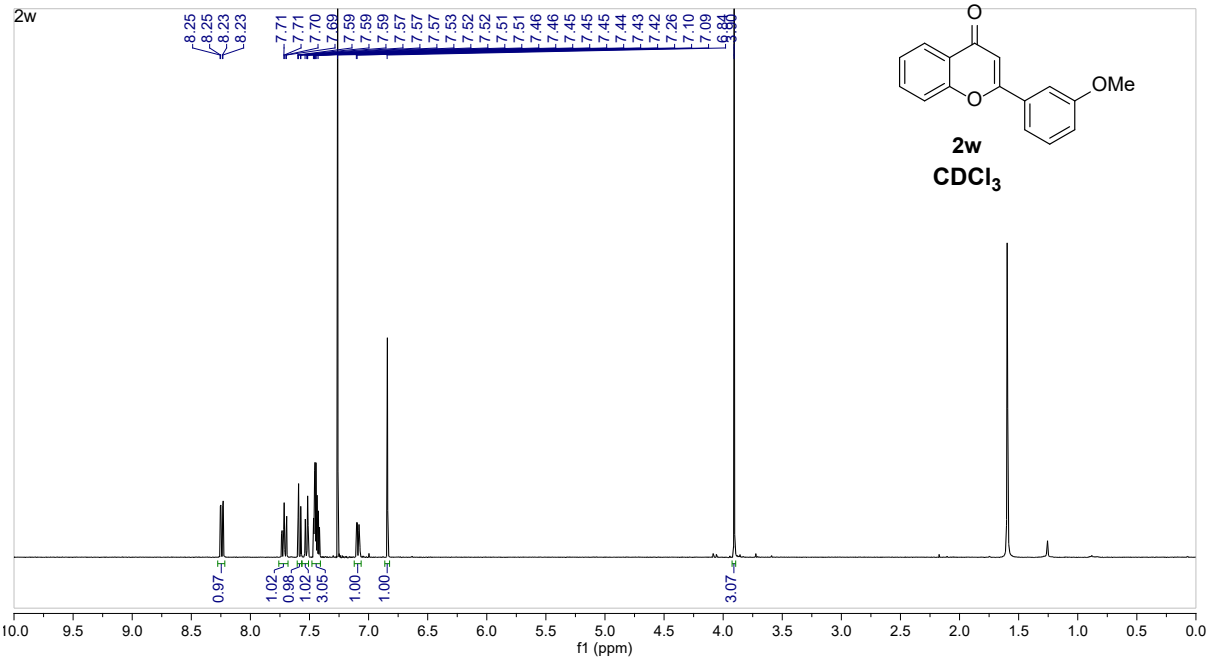

2t
178.43
166.18
163.66
162.58
156.34
134.00
128.70
128.61
128.16
128.12
125.90
125.48
124.01
118.15
116.56
116.34
107.53
107.52
f1 (ppm)
O
O
F
2t
CDCl3

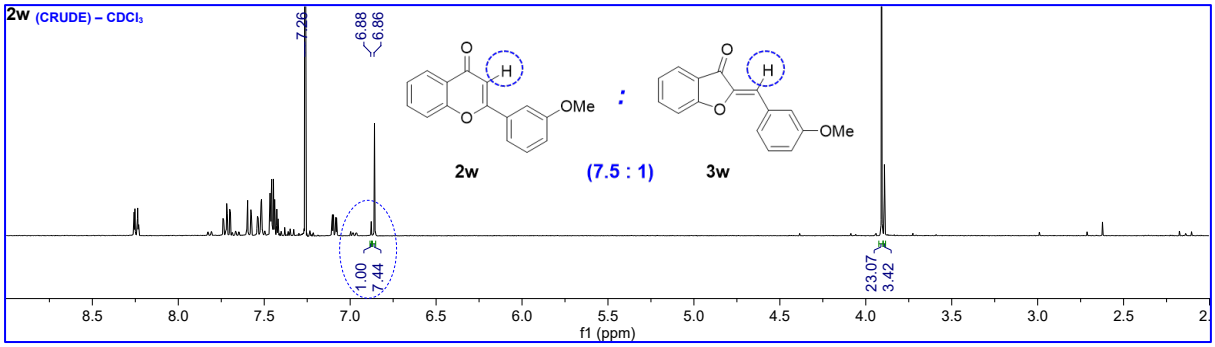

8.25
8.25
8.25
8.25
8.23
8.23
8.23
7.74
7.74
7.74
7.73
7.59
7.42
7.26
6.82
2.47
O
O
Me
2u
CDCl3
0.96
3.05
1.01
2.03
1.01
1.01
3.07
f1 (ppm)

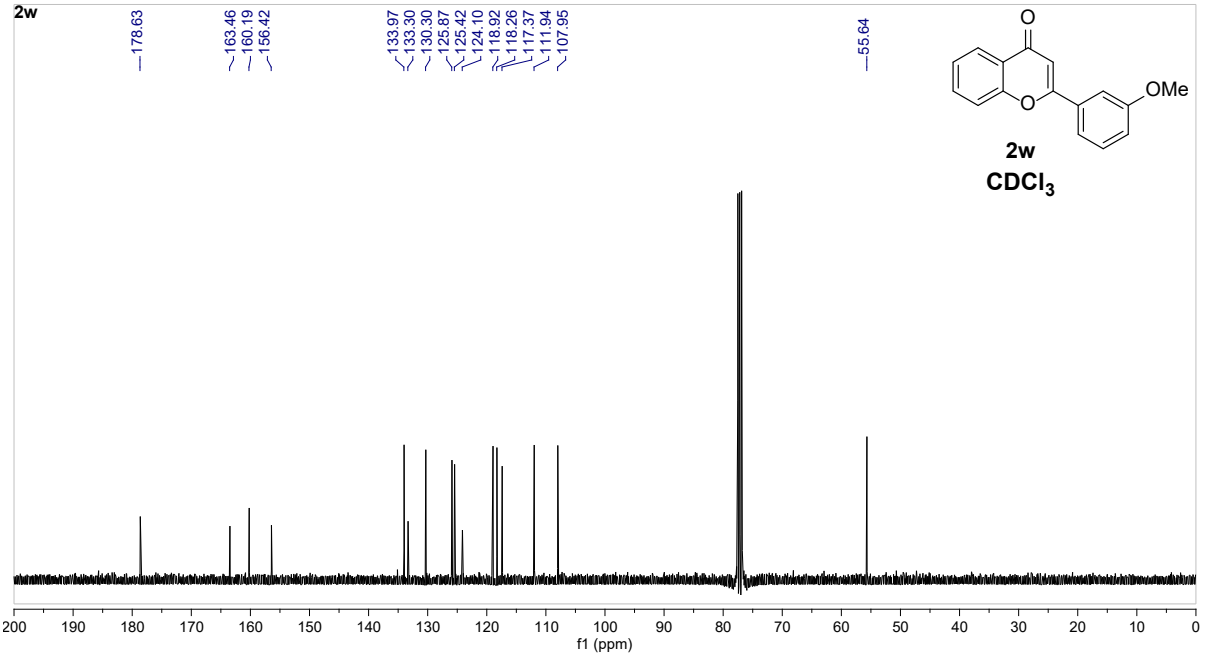

178.62
163.83
156.46
139.01
133.88
132.58
131.91
129.10
127.03
125.86
125.35
124.12
123.69
118.24
107.70
21.66
O
O
Me
2u
CDCl3
f1 (ppm)

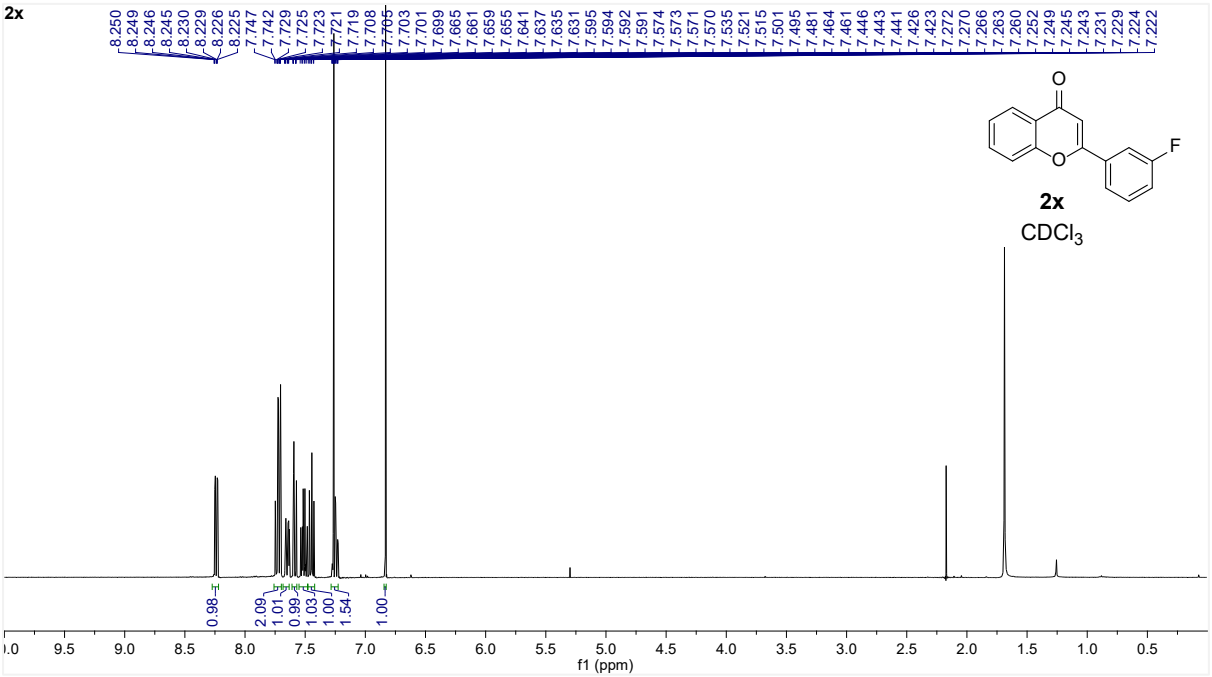

2v
8.25
8.24
8.23
8.22
7.84
7.82
7.34
7.34
7.32
7.32
7.26
6.82
2.44
1.00
2.13
1.05
1.03
1.05
2.05
1.04
3.12
f1 (ppm)
O
O
Me
2v
CDCl3

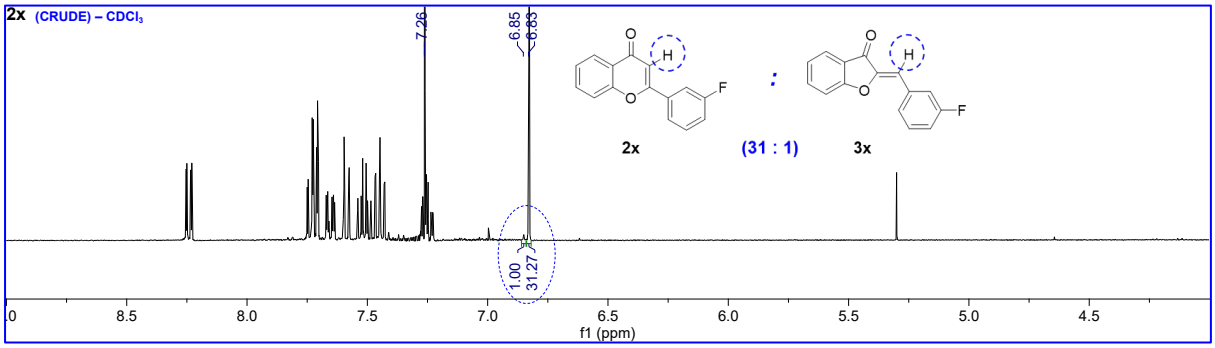

2v
178.62
163.84
156.40
142.44
133.83
129.92
129.09
126.40
125.83
125.30
124.09
118.20
107.09
21.68
f1 (ppm)
O
O
Me
2v
CDCl3

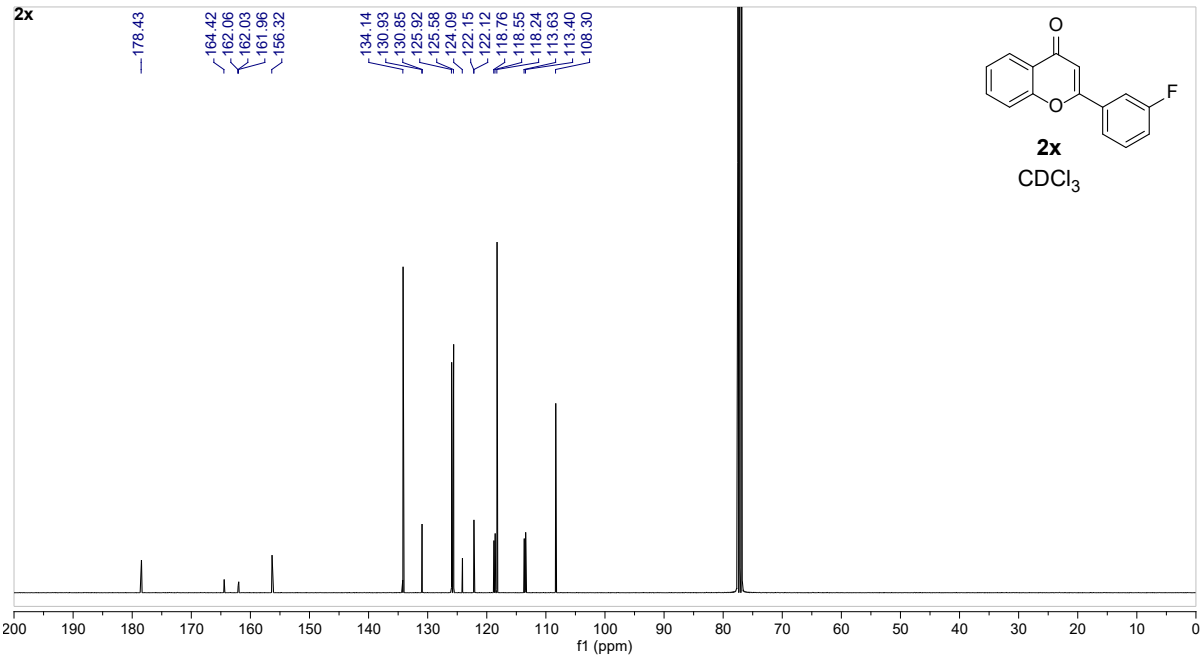

2w
8.25
8.25
8.23
8.23
7.71
7.71
7.70
7.69
7.59
7.59
7.59
7.57
7.57
7.57
7.53
7.52
7.52
7.51
7.51
7.46
7.46
7.45
7.45
7.45
7.44
7.43
7.42
7.26
7.10
7.09
6.84
6.84
3.84
OMe
2w
CDCl3
0.97
1.02
0.98
1.02
3.05
1.00
1.00
3.07
f1 (ppm)

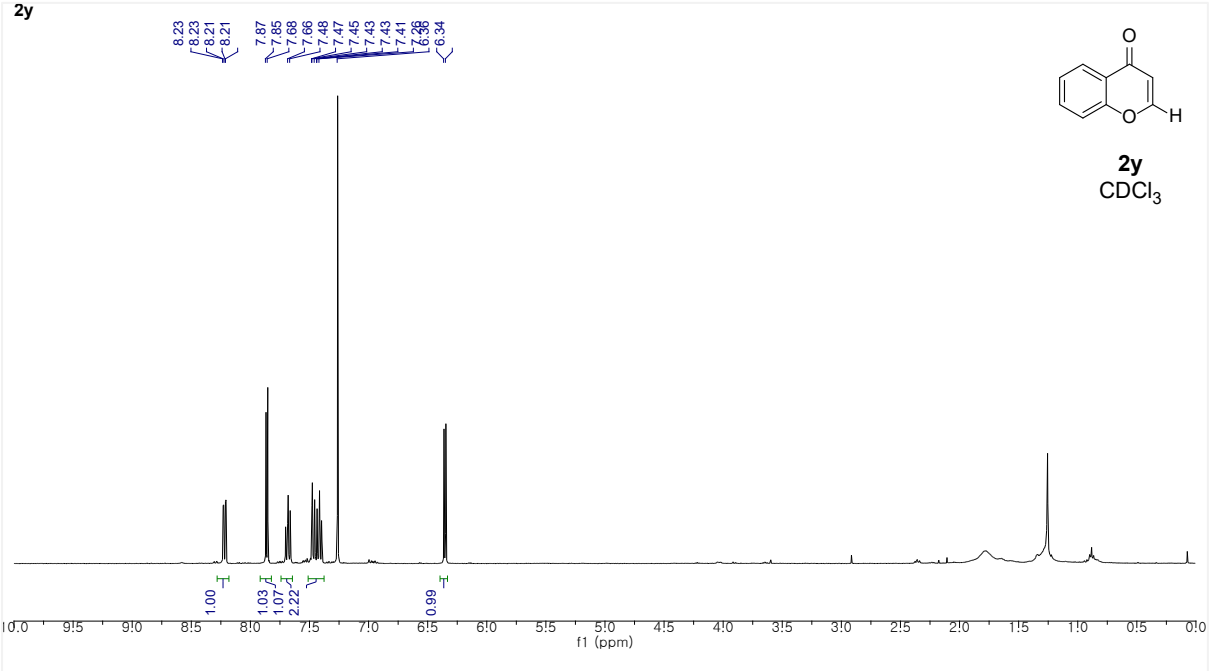

2w (CRUDE) – CDCl3
7.26
6.88
6.86
H
OMe
2w
(7.5 : 1)
3w
1.00
7.44
23.07
3.42
f1 (ppm)

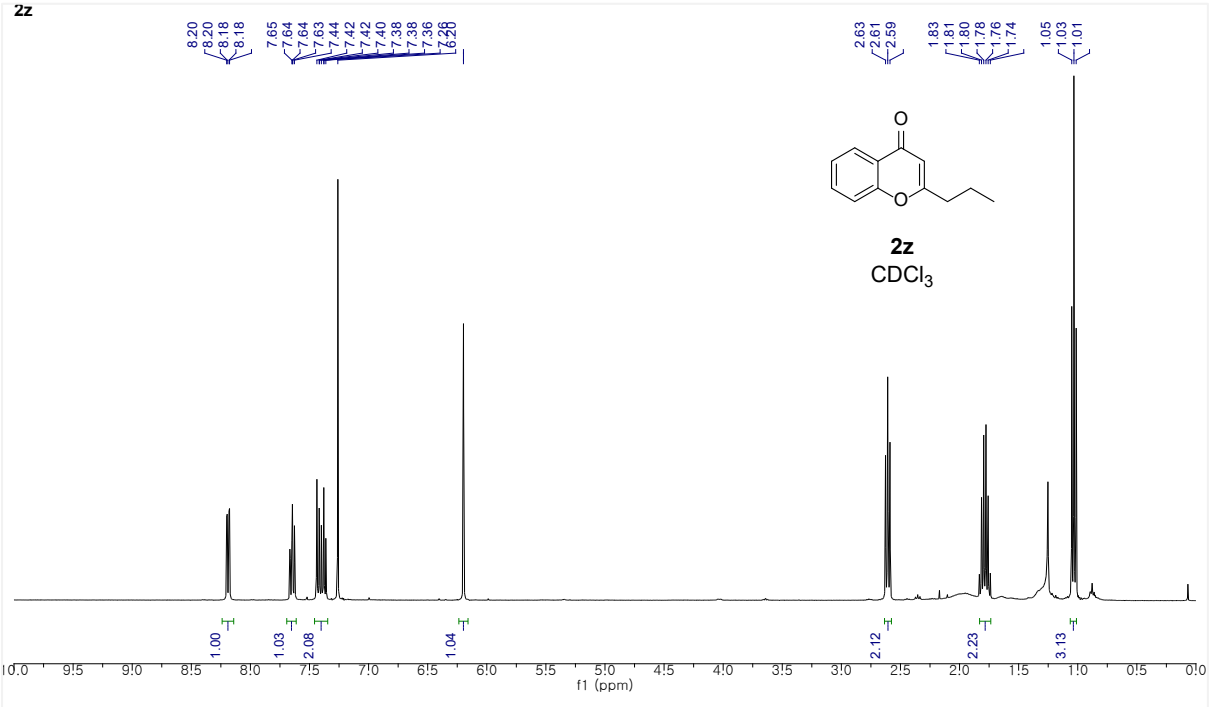

2w
178.63
163.46
160.19
156.42
133.97
133.30
130.30
125.87
125.42
124.10
118.92
118.26
117.37
111.94
107.95
55.64
OMe
2w
CDCl3
f1 (ppm)

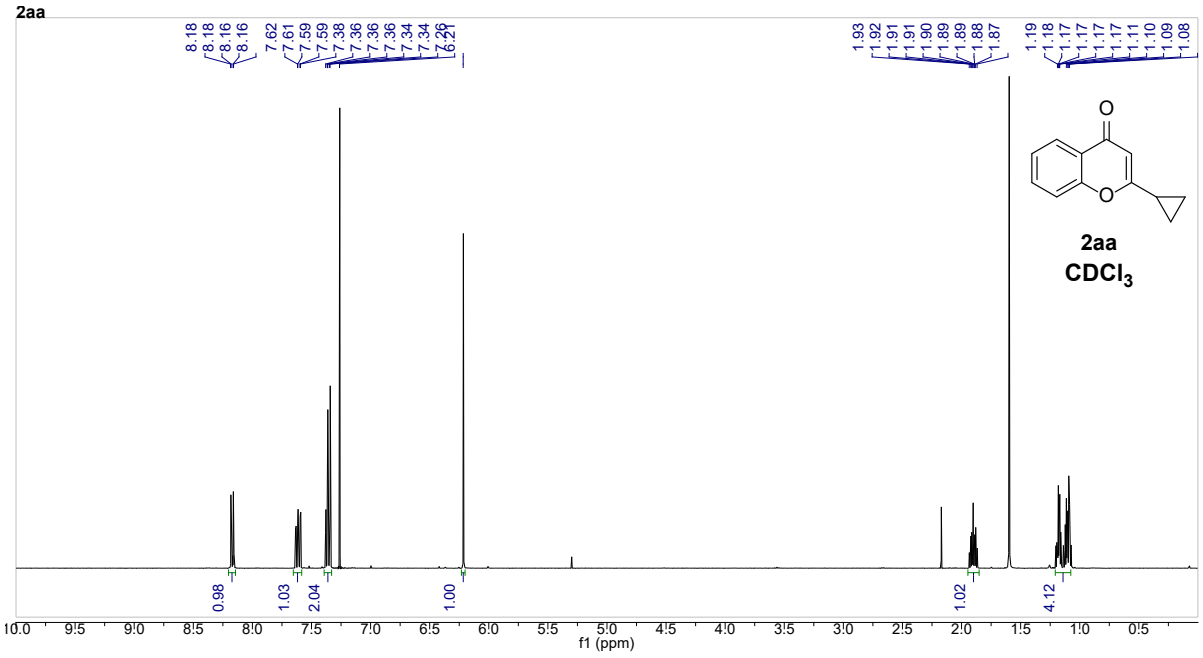

2x
8.250 8.249 8.246 8.245 8.230 8.229 8.226 8.225 7.747 7.742 7.729 7.725 7.723 7.721 7.719 7.708 7.705 7.703 7.701 7.699 7.665 7.661 7.659 7.655 7.641 7.637 7.635 7.631 7.595 7.594 7.592 7.591 7.574 7.573 7.571 7.570 7.535 7.521 7.515 7.501 7.495 7.481 7.464 7.461 7.446 7.443 7.441 7.426 7.423 7.272 7.270 7.266 7.263 7.260 7.252 7.249 7.245 7.243 7.231 7.229 7.224 7.222
O
O
F
2x
CDCl3
0.98 2.09 1.01 0.99 1.03 1.00 1.54 1.00
f1 (ppm)

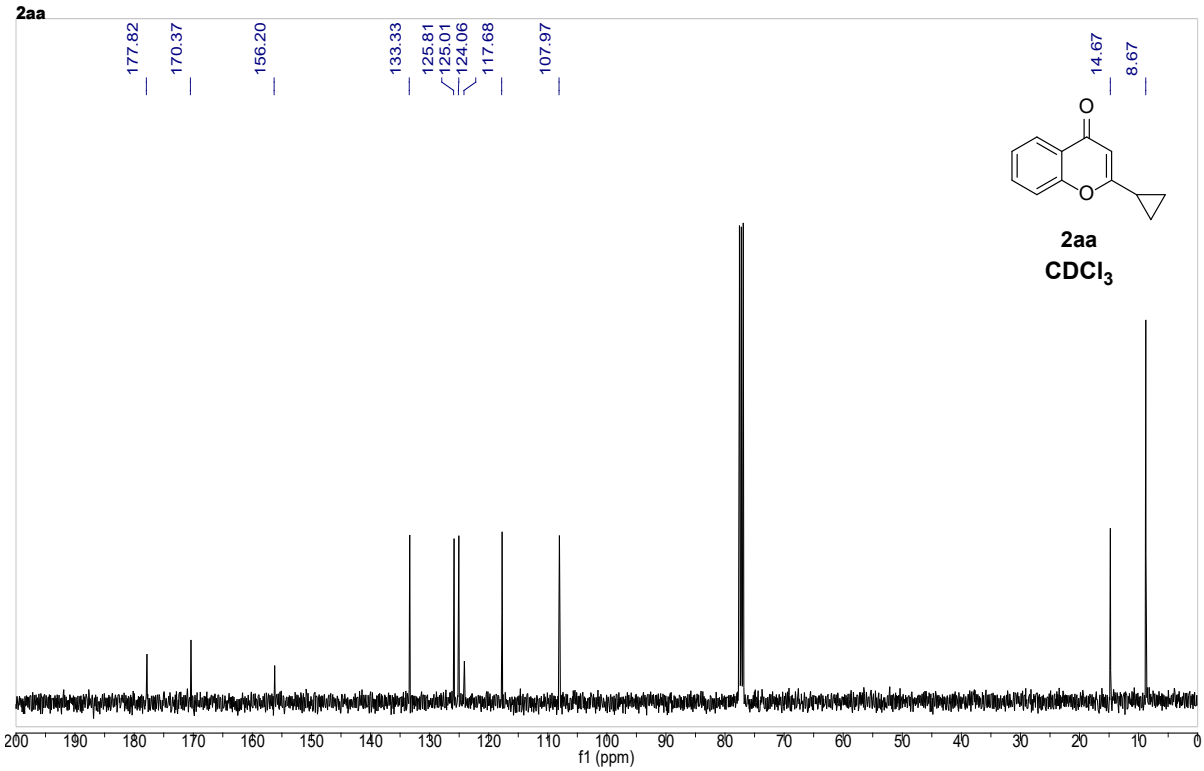

2x (CRUDE) – CDCl3
7.26
6.85
6.83
H
O
O
F
2x
(31 : 1)
3x
1.00 31.27
f1 (ppm)

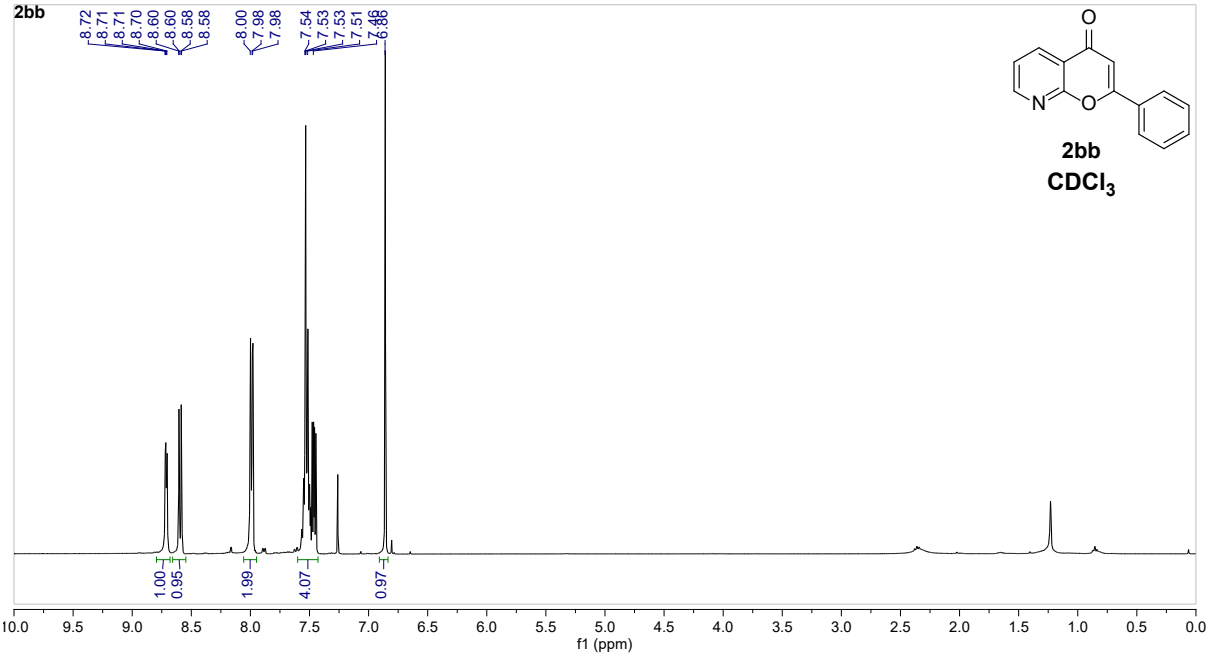

2x
178.43
164.42 162.06 162.03 161.96 156.32
134.14 130.93 130.85 125.92 125.58 124.09 122.15 122.12 118.76 118.55 118.24 113.63 113.40 108.30
O
O
F
2x
CDCl3
f1 (ppm)

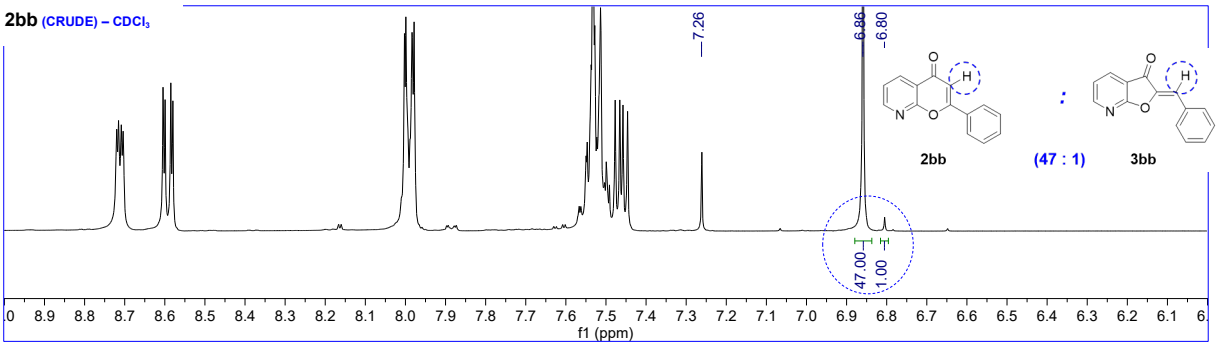

2y
8.23
8.23
8.21
8.21
7.87
7.85
7.68
7.66
7.48
7.47
7.45
7.43
7.43
7.41
6.34
O
O
H
2y
CDCl3
1.00
1.03
1.07
2.22
0.99
f1 (ppm)

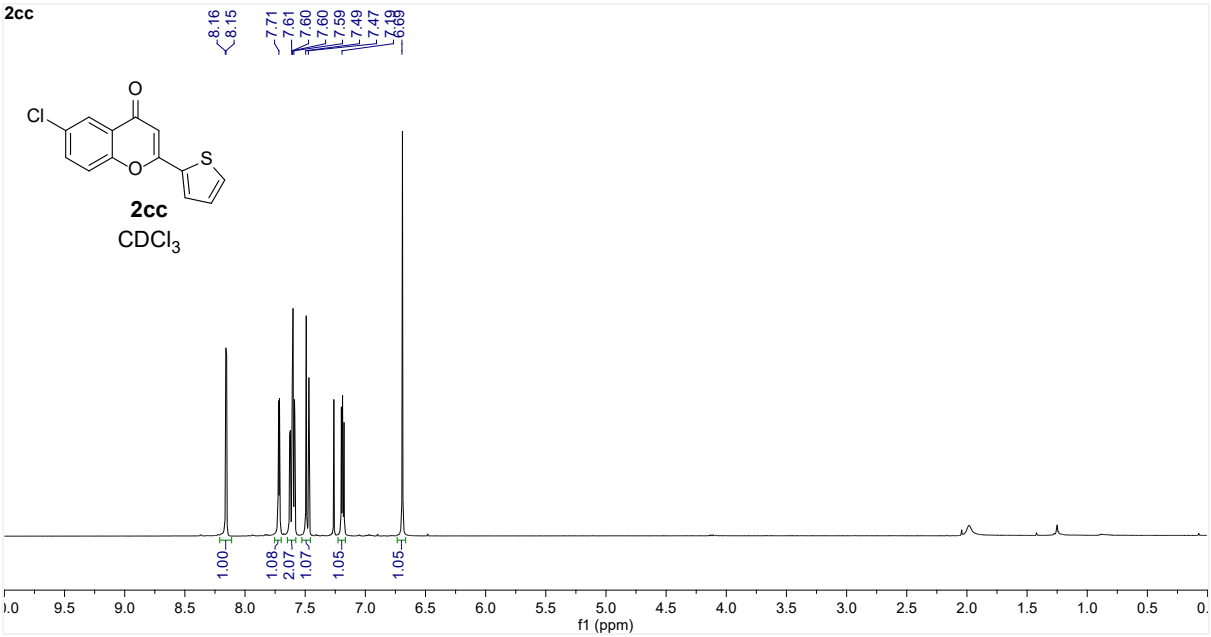

2z
8.20
8.20
8.18
8.18
7.65
7.64
7.64
7.63
7.44
7.42
7.42
7.40
7.38
7.38
7.36
2.63
2.61
2.59
1.83
1.81
1.80
1.78
1.76
1.74
1.05
1.03
1.01
O
O
2z
CDCl3
1.00
1.03
2.08
1.04
2.12
2.23
3.13
f1 (ppm)

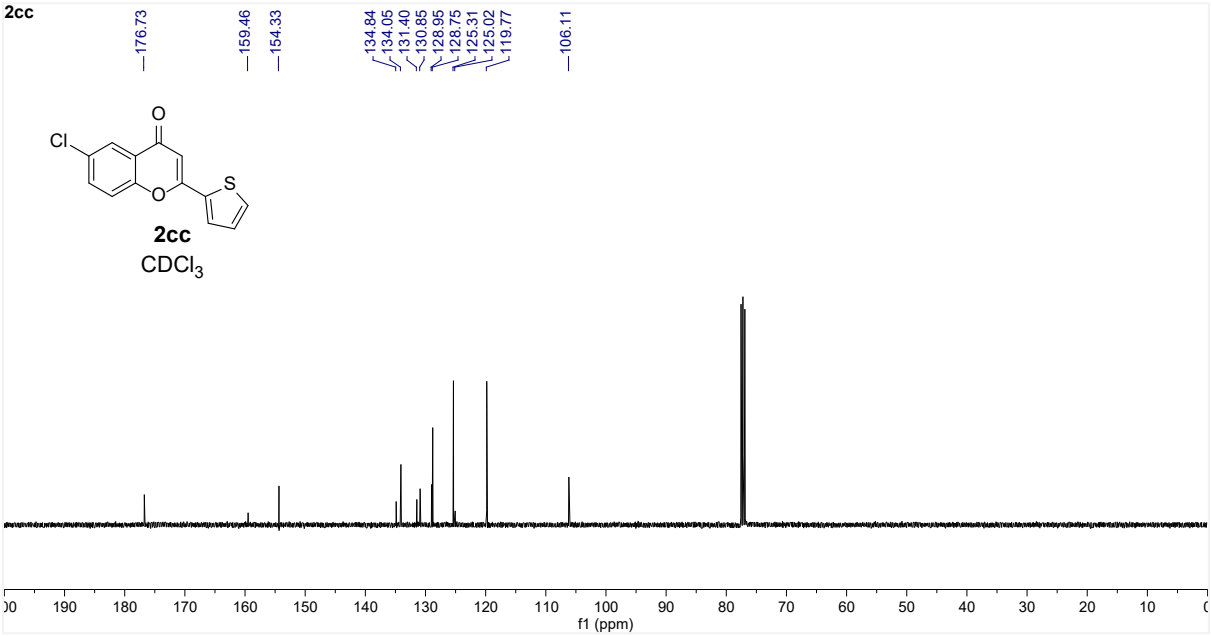

2aa
8.18
8.18
8.16
8.16
7.62
7.61
7.59
7.59
7.38
7.36
7.36
7.34
7.34
7.26
1.93
1.92
1.91
1.91
1.90
1.89
1.89
1.88
1.87
1.19
1.18
1.17
1.17
1.17
1.17
1.11
1.10
1.09
1.08
0.98
1.03
2.04
1.00
1.02
4.12
f1 (ppm)
2aa
CDCl3

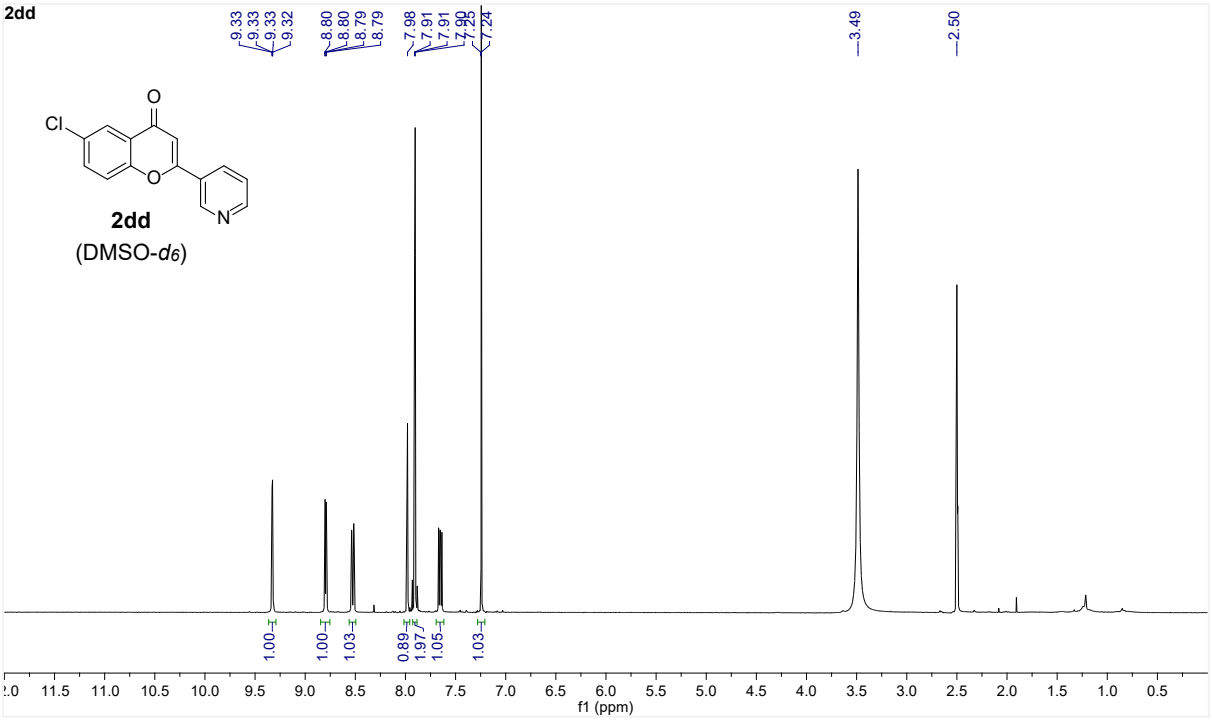

2aa
177.82
170.37
156.20
133.33
125.81
125.01
124.06
117.68
107.97
14.67
8.67
f1 (ppm)
2aa
CDCl3

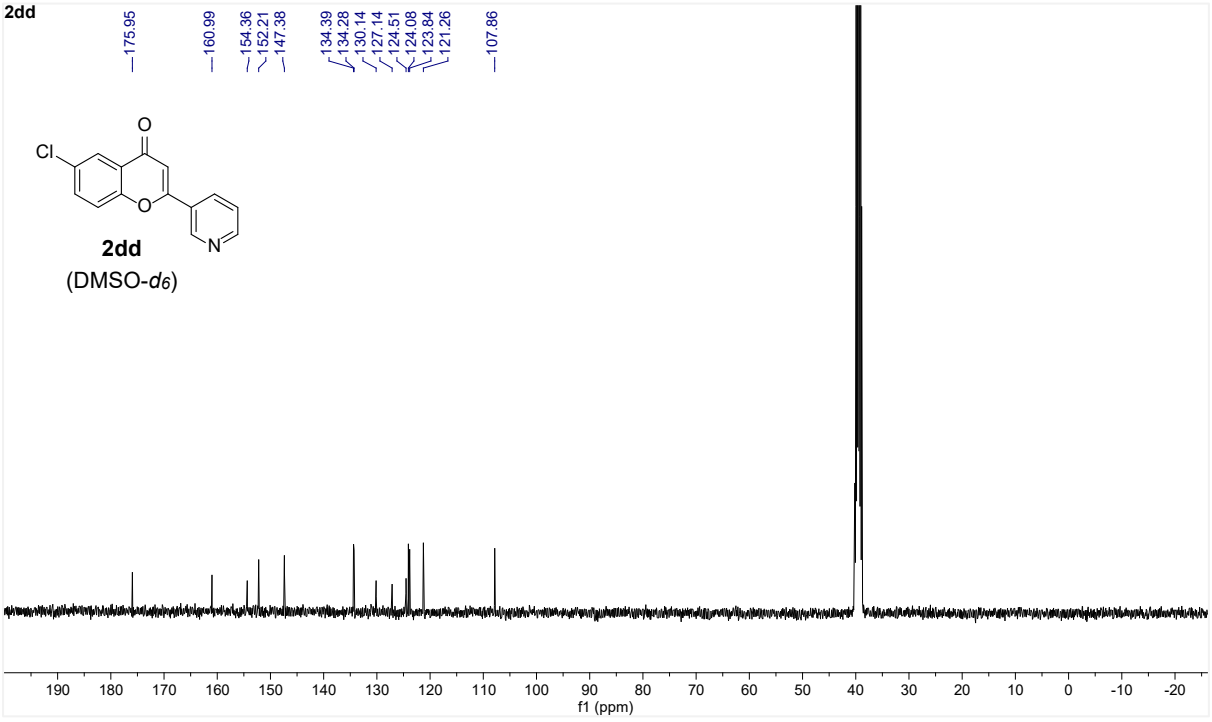

2bb
8.72
8.71
8.71
8.70
8.60
8.60
8.58
8.58
8.00
7.98
7.98
7.54
7.53
7.53
7.51
7.46
6.86
1.00
0.95
1.99
4.07
0.97
f1 (ppm)
2bb
CDCl3

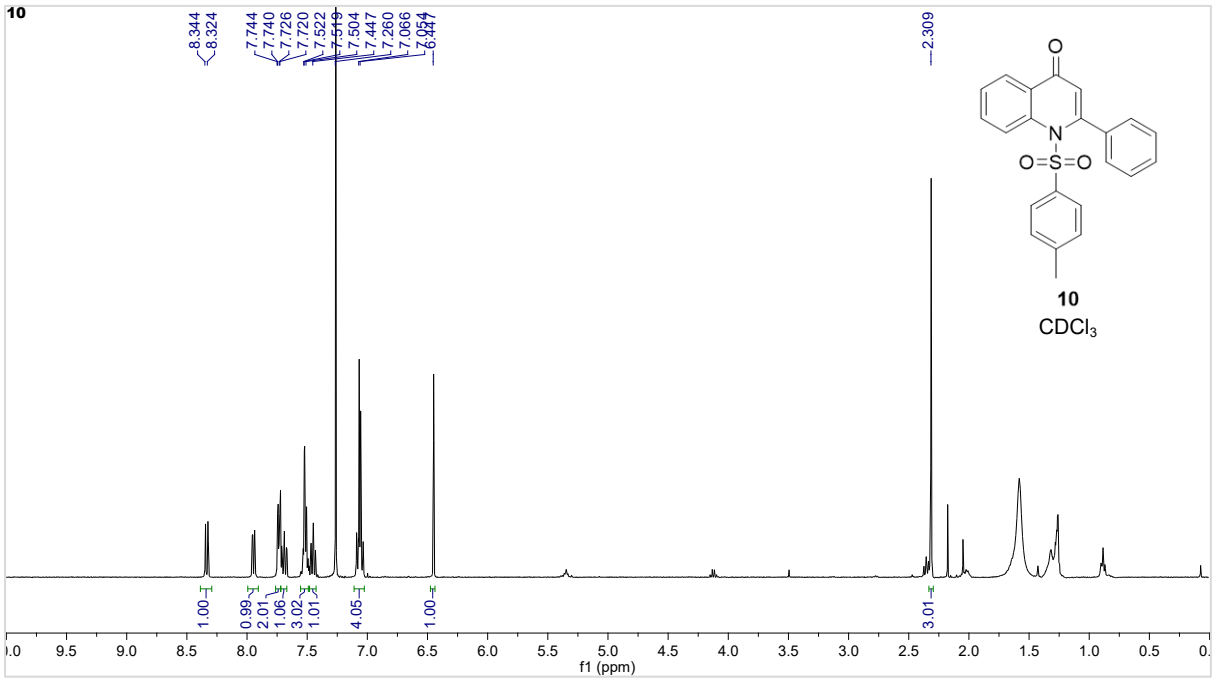

2bb (CRUDE) – CDCl3
7.26
6.86
6.80
2bb
(47 : 1)
3bb
47.00
1.00
f1 (ppm)

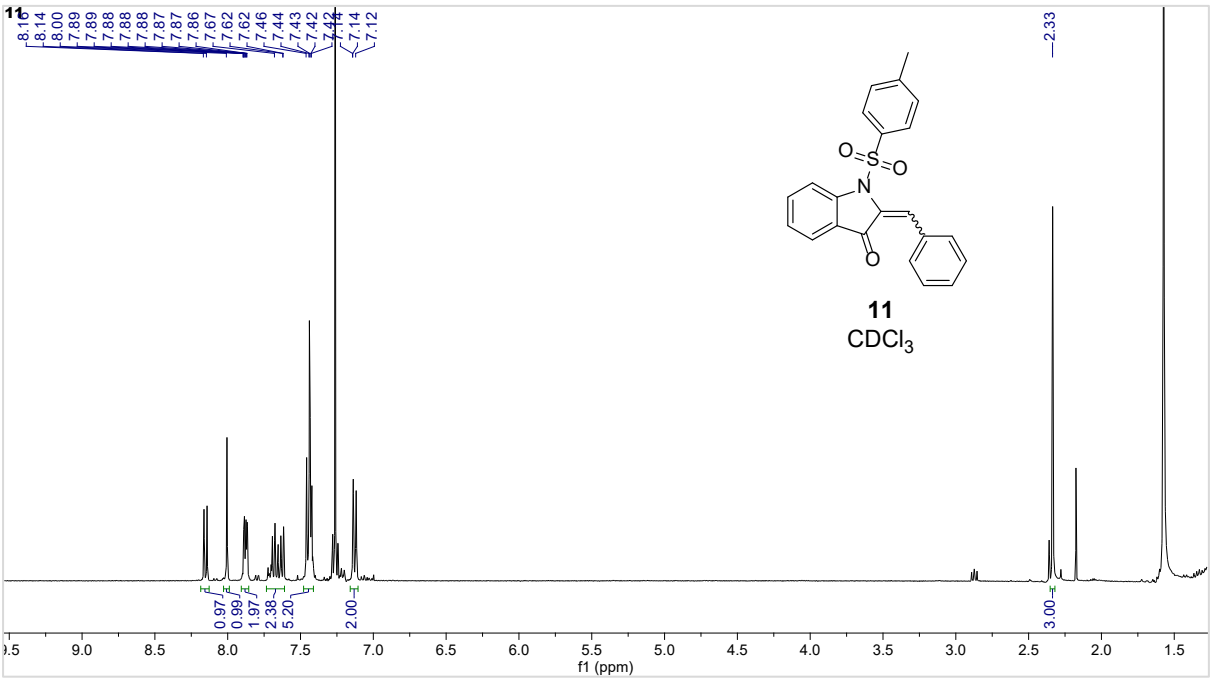

2cc
8.16
8.15
7.71
7.61
7.60
7.60
7.59
7.49
7.47
7.19
6.89
O
Cl
S
O
2cc
CDCl3
1.00
1.08
2.07
1.07
1.05
1.05
f1 (ppm)

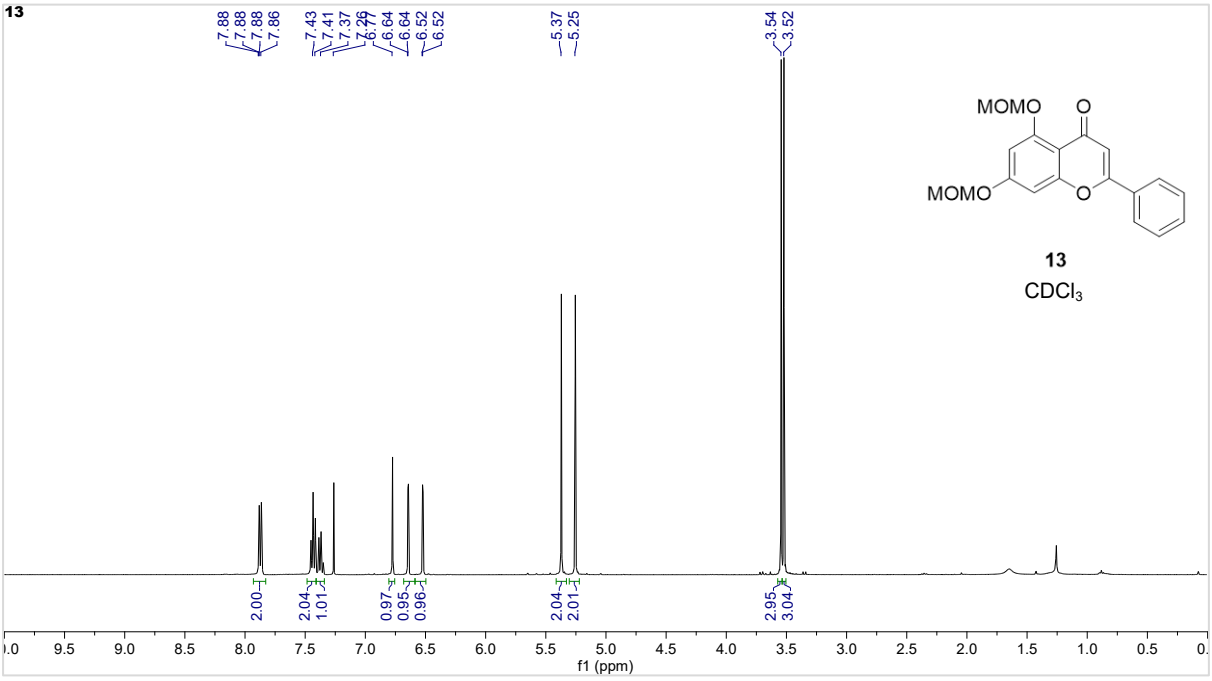

2cc
176.73
159.46
154.33
134.84
134.05
131.40
130.85
128.95
128.75
125.31
125.02
119.77
106.11
O
Cl
S
O
2cc
CDCl3
f1 (ppm)

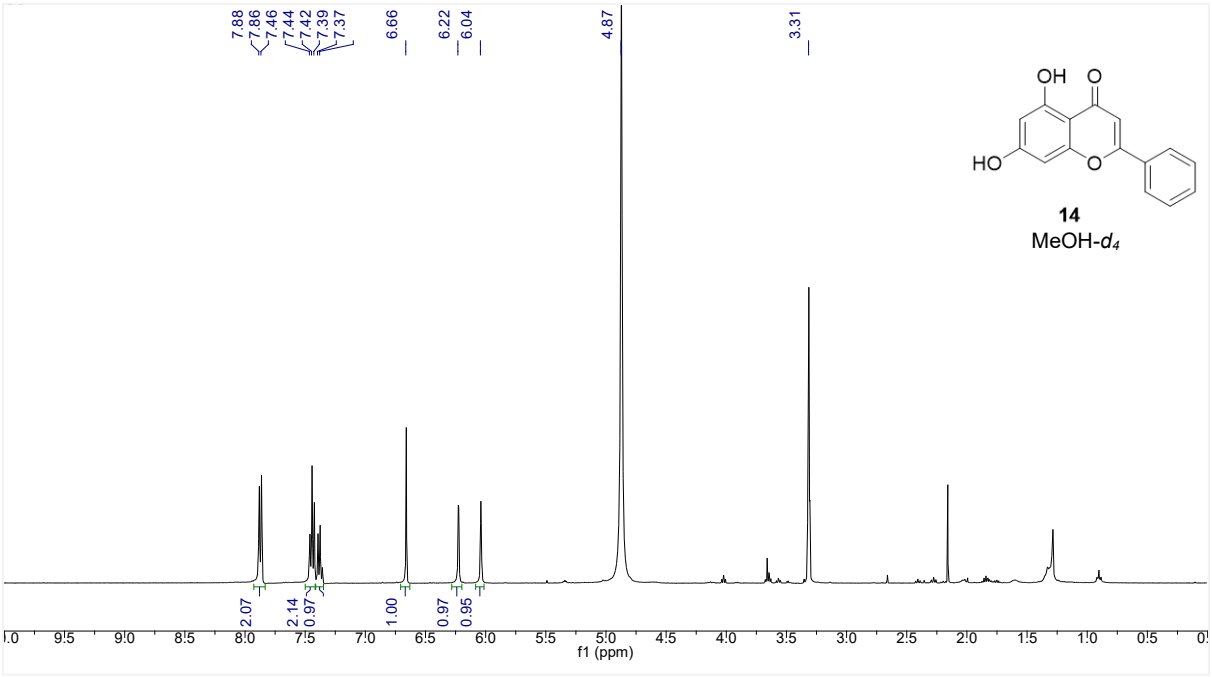

2dd
9.33
9.33
9.33
9.32
8.80
8.80
8.79
8.79
7.98
7.91
7.91
7.90
7.25
7.24
3.49
2.50
Cl
O
O
N
2dd
(DMSO-d6)
1.00
1.00
1.03
0.89
1.97
1.05
1.03
f1 (ppm)

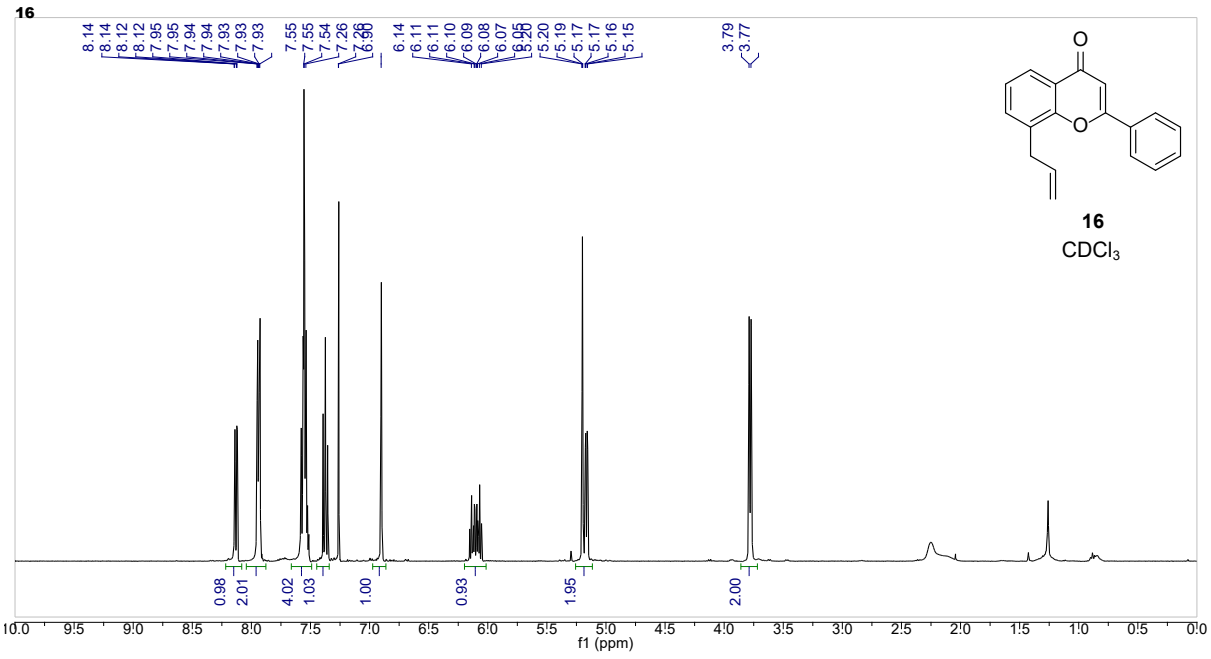

2dd
175.95
160.99
154.36
152.21
147.38
134.39
134.28
130.14
127.14
124.51
124.08
123.84
121.26
107.86
Cl
O
O
N
2dd
(DMSO-d6)
f1 (ppm)

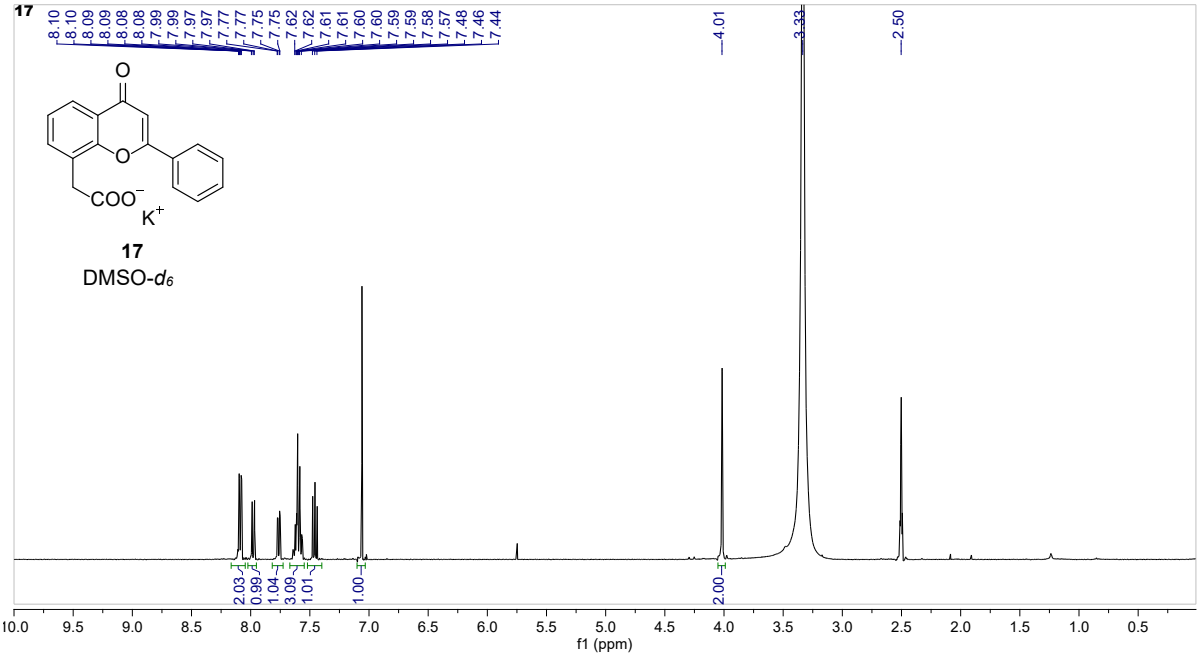

10
8.344
8.324
7.744
7.740
7.726
7.720
7.522
7.519
7.504
7.447
7.260
7.066
7.054
6.547
2.309
1.00
0.99
2.01
1.06
3.02
1.01
4.05
1.00
3.01
f1 (ppm)
10
CDCl3


11
8.16
8.14
8.00
7.89
7.89
7.88
7.88
7.88
7.87
7.87
7.86
7.67
7.62
7.62
7.46
7.44
7.43
7.42
7.14
7.12
2.33
0.97
0.99
1.97
2.38
5.20
2.00
3.00
f1 (ppm)
11
CDCl3


13
7.88
7.88
7.88
7.86
7.43
7.41
7.37
6.64
6.64
6.52
6.52
5.37
5.25
3.54
3.52
2.00
2.04
1.01
0.97
0.95
0.96
2.04
2.01
2.95
3.04
f1 (ppm)
MOMO
O
MOMO
O
13
CDCl3


7.88
7.86
7.46
7.44
7.42
7.39
7.37
6.66
6.22
6.04
4.87
3.31
OH
O
HO
O
14
MeOH-d_4
2.07
2.14
0.97
1.00
0.97
0.95
f1 (ppm)

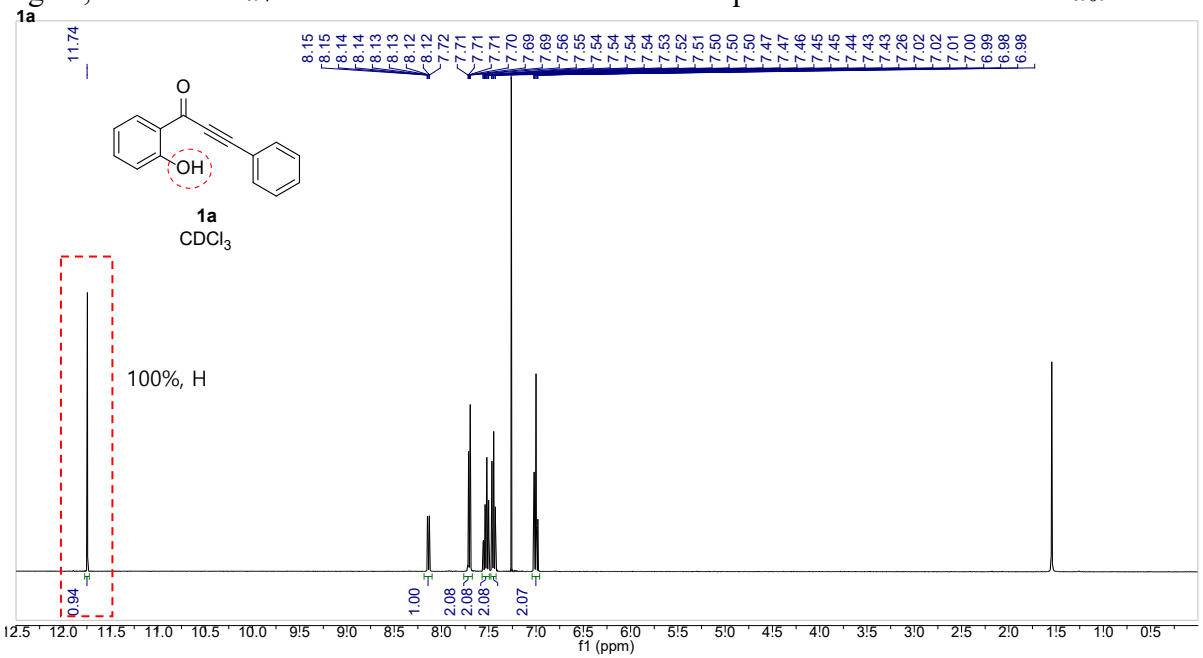

16
8.14
8.14
8.12
8.12
7.95
7.95
7.94
7.94
7.93
7.93
7.93
7.55
7.55
7.54
7.54
7.26
6.14
6.11
6.11
6.10
6.09
6.08
6.07
5.20
5.19
5.17
5.17
5.16
5.15
3.79
3.77
O
O
16
$CDCl_3$
0.98
2.01
4.02
1.03
1.00
0.93
1.95
2.00
f1 (ppm)

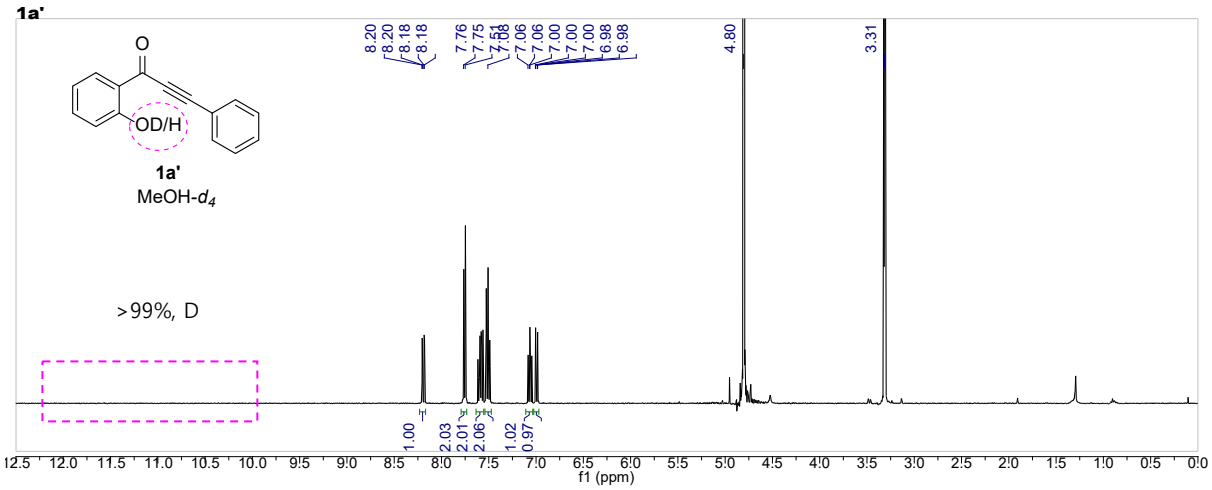

17
8.10
8.10
8.09
8.09
8.08
8.08
8.08
7.99
7.99
7.97
7.97
7.77
7.77
7.75
7.75
7.62
7.62
7.61
7.61
7.60
7.60
7.59
7.59
7.58
7.57
7.48
7.46
7.44
4.01
3.33
2.50
O
O
COO⁻
K⁺
17
DMSO-d6
2.03
0.99
1.04
3.09
1.01
1.00
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

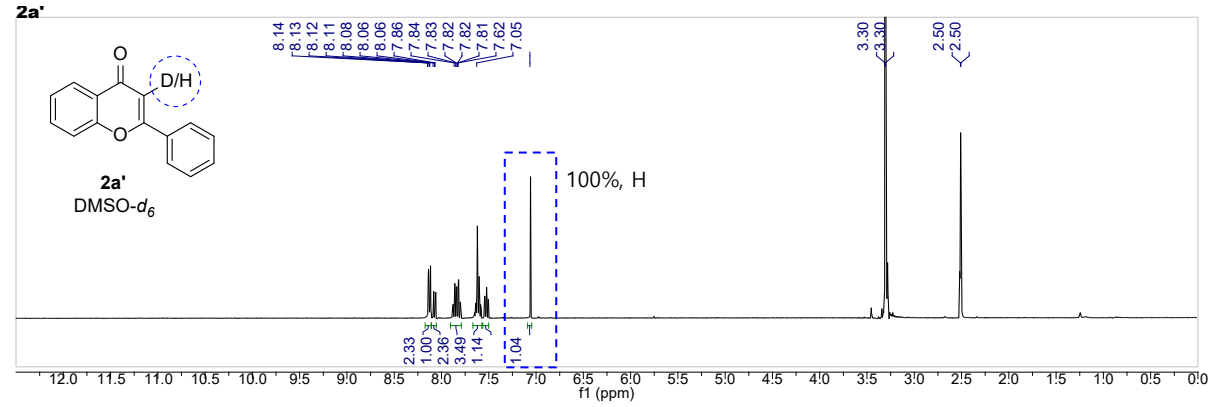
VIII. Comparison between proton *vs* deuterium labeled ^{1}H NMR spectra

The ^{1}H NMR of compound **1a** was initially acquired in $CDCl_3$The same sample was concentrated and acquired ^{1}H NMR in MeOD-d_4.

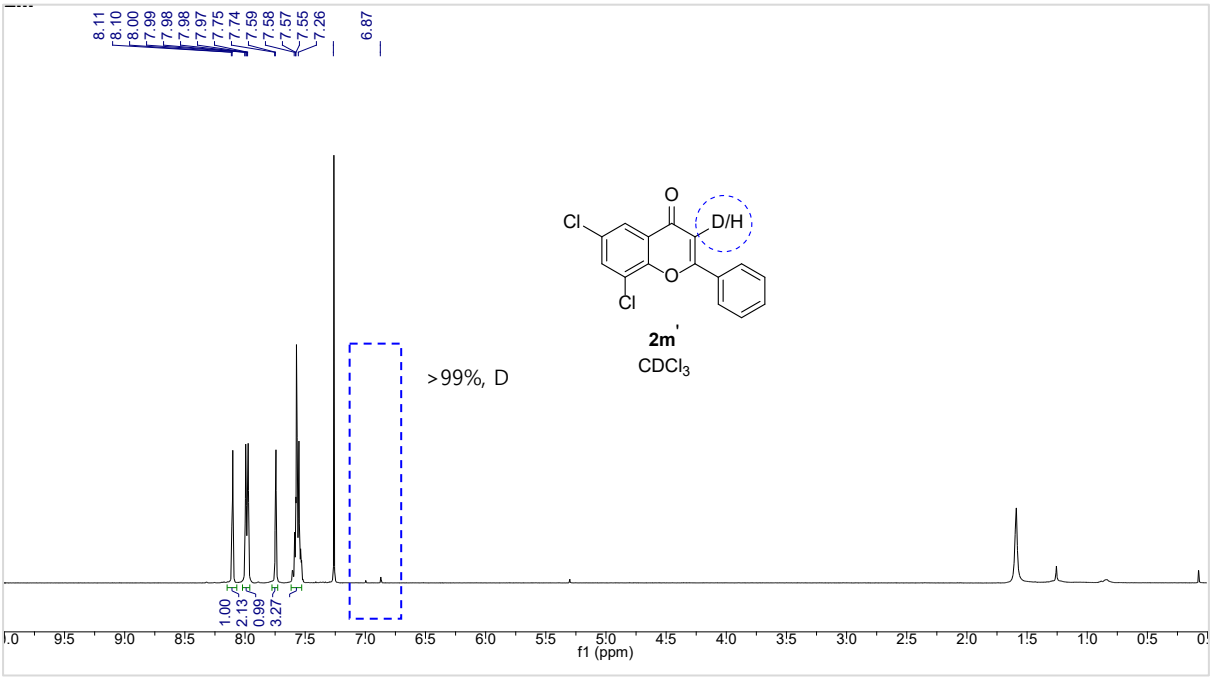
Again, the MeOD-d_4 solution after concentration was acquired ^{1}H NMR in DMSO-d_6.





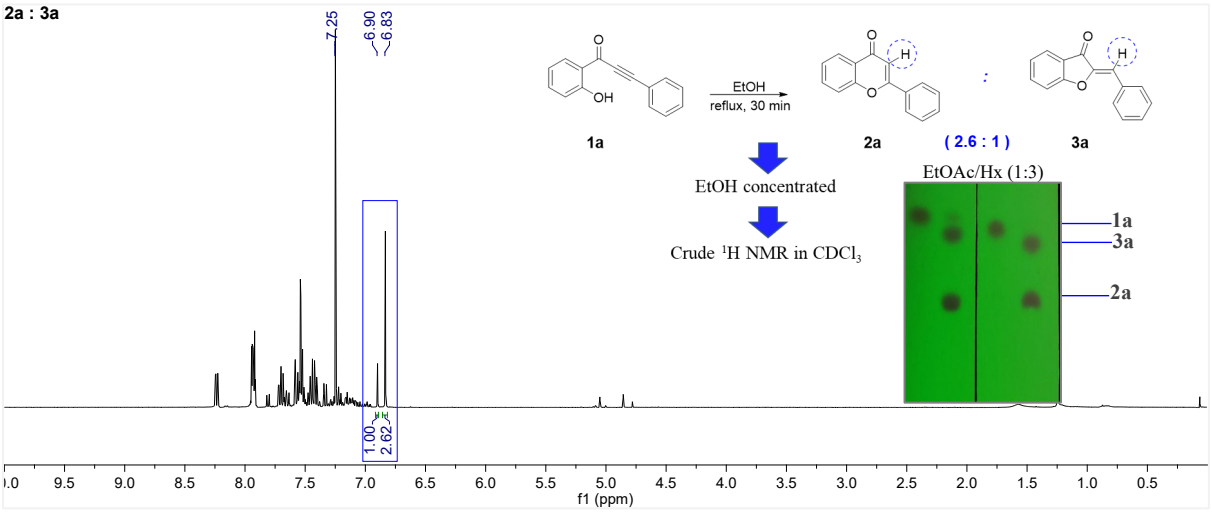


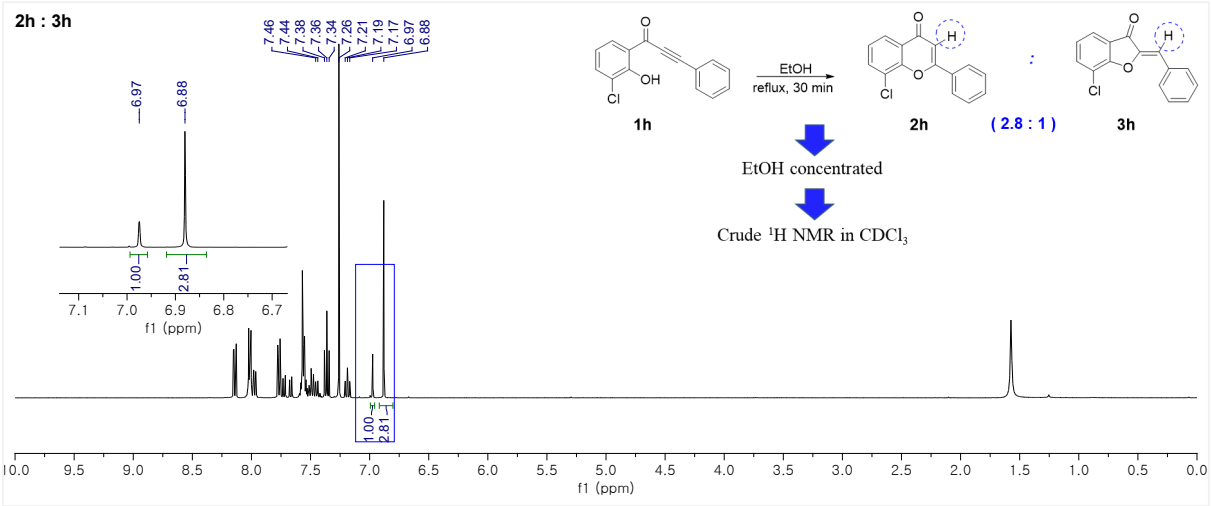
Compound **1m** was initially treated with MeOD-d_4.
The same sample was concentrated and acquired ^{1}H NMR in DMSO-d_6.

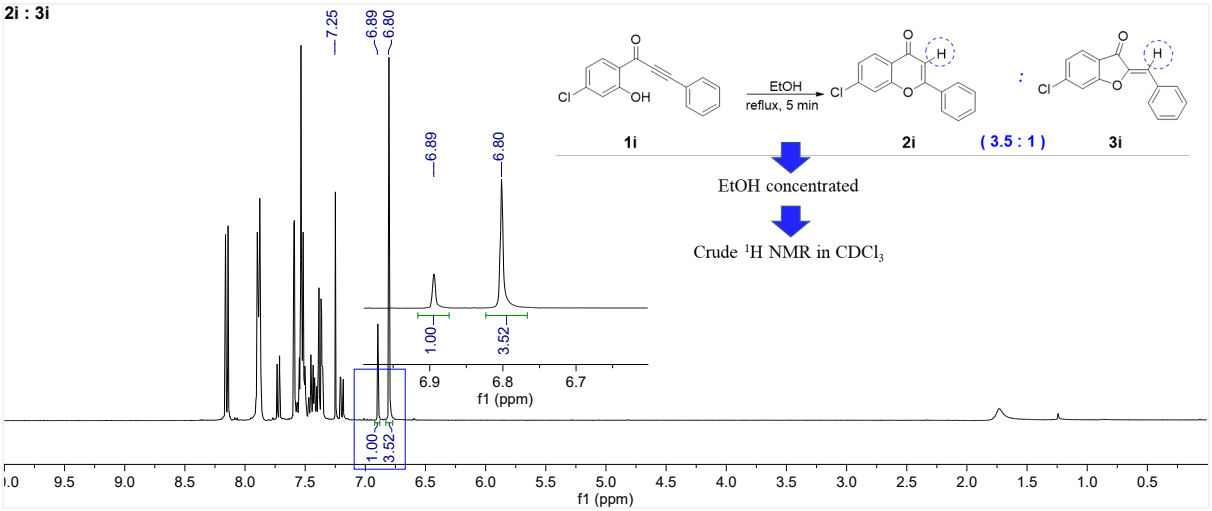


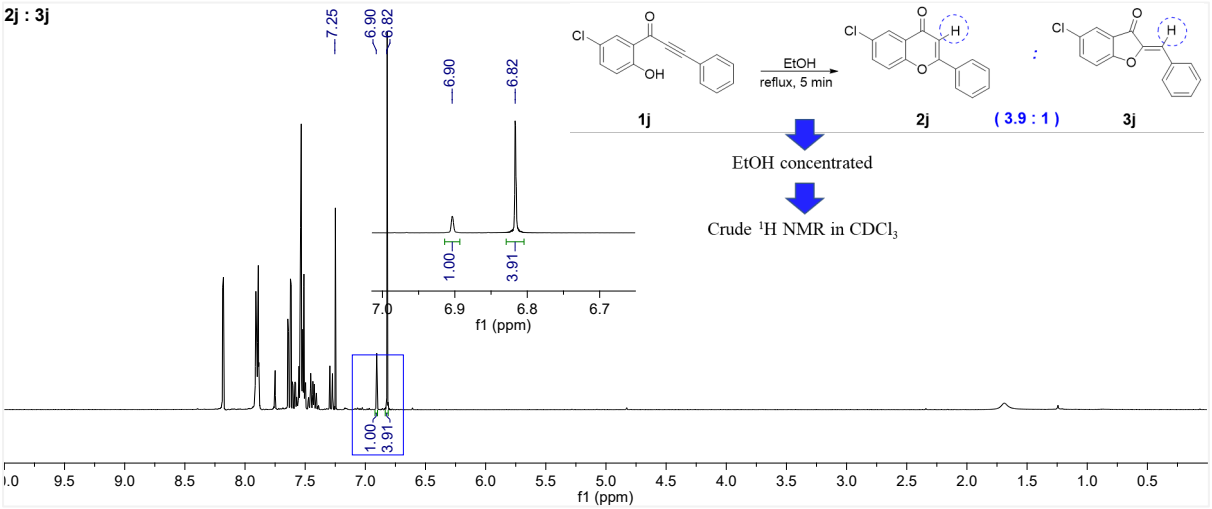
IX. Ratio of 6-*endo-* : 5-*exo-* cyclized product in EtOH reaction (analysis of crude ^{1}H NMR spectra)

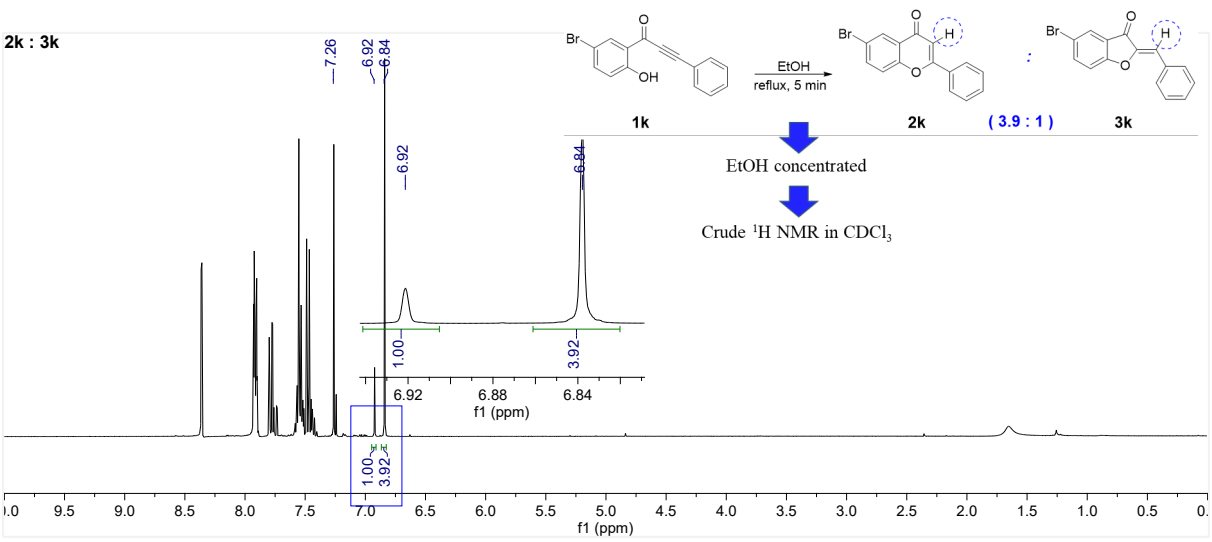
All the reactions were conducted using 1 mL of EtOH in concentration of < 0.05 M in indicated temperature. The reaction mixtures were concentrated and dried after completion then ^{1}H NMRs were monitored with crude sample.

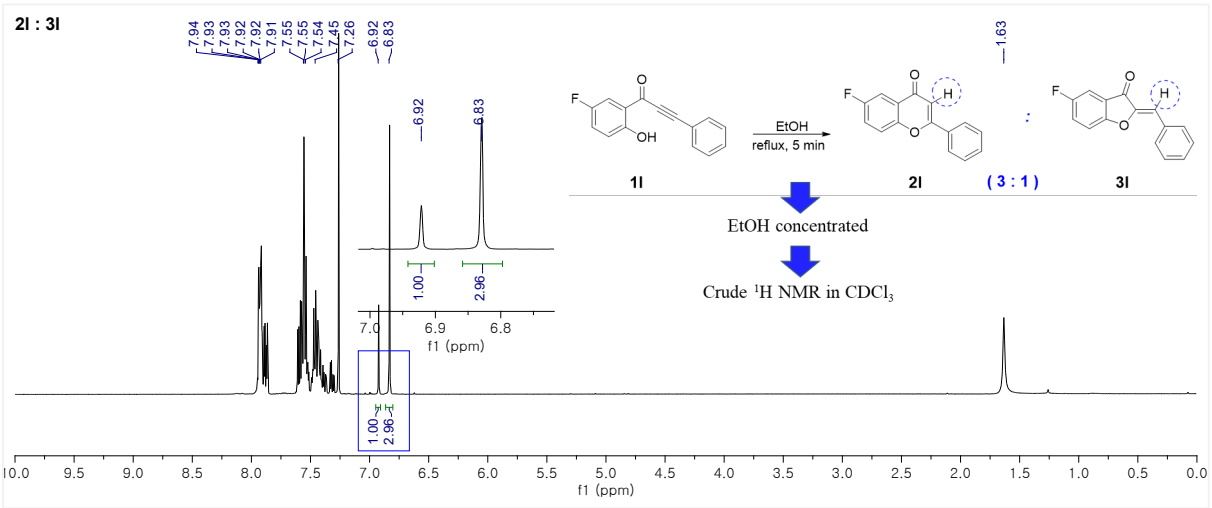


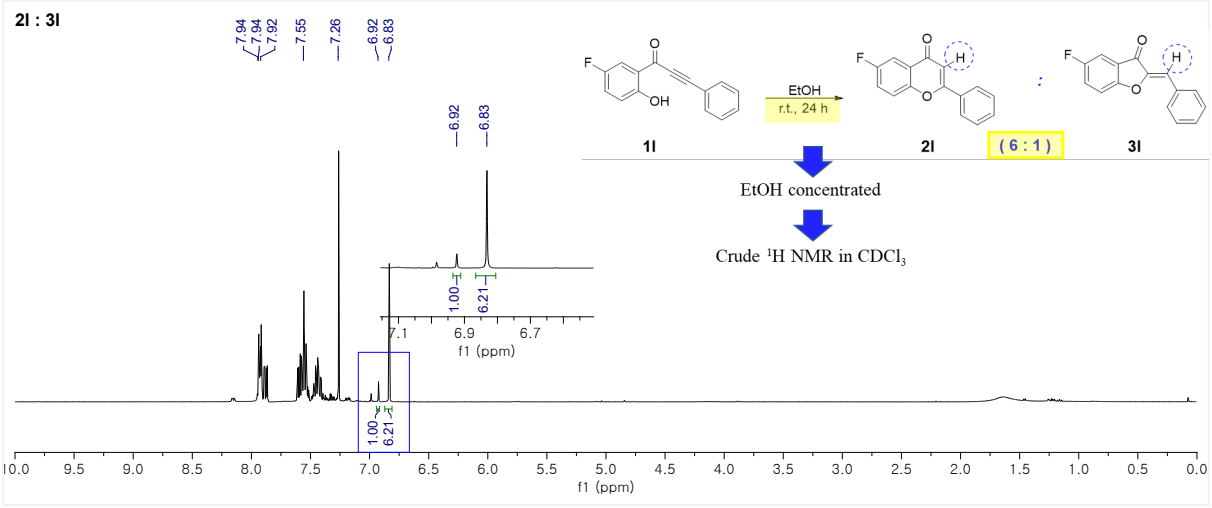


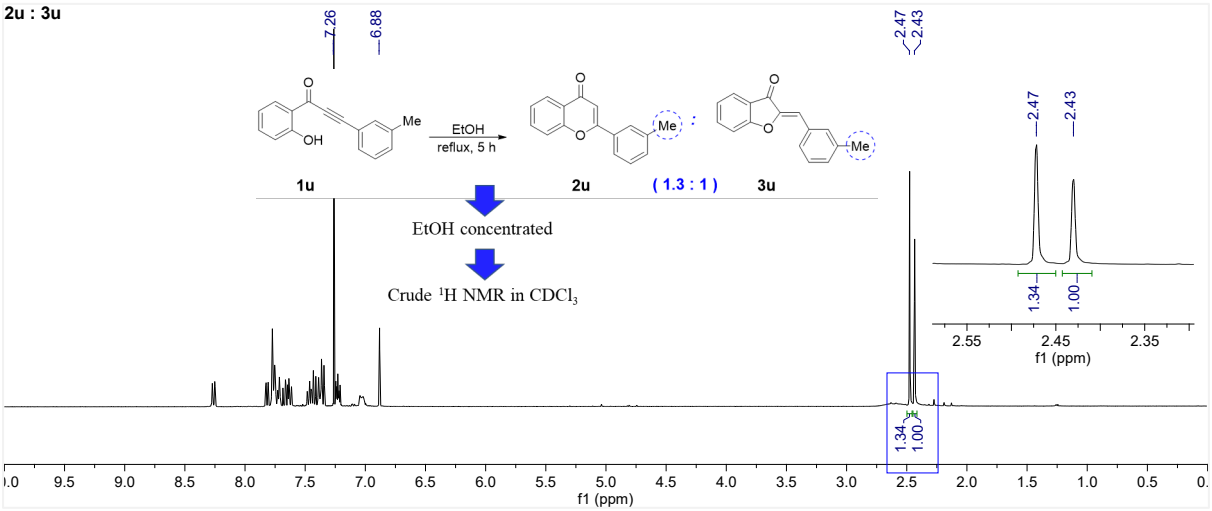

2i : 3i
7.25
6.89
6.80
6.89
6.80
1.00
3.52
6.9
6.8
6.7
f1 (ppm)
1.00
3.52
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
Cl
OH
O
EtOH
reflux, 5 min
H
1i
2i
(3.5 : 1)
3i
EtOH concentrated
Crude ^{1}H NMR in $CDCl_3$


2j : 3j
7.25
6.90
6.82
6.90
6.82
1.00
3.91
7.0
6.9
6.8
6.7
f1 (ppm)
1.00
3.91
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
f1 (ppm)
Cl
OH
O
EtOH
reflux, 5 min
H
1j
2j
(3.9 : 1)
3j
EtOH concentrated
Crude ^{1}H NMR in $CDCl_3$


2k : 3k
7.26
6.92
6.84
1.00
3.92
6.92
6.88
6.84
f1 (ppm)
Br
OH
1k
EtOH
reflux, 5 min
2k
(3.9 : 1)
3k
EtOH concentrated
Crude ^{1}H NMR in $CDCl_3$


2l : 3l
7.94
7.93
7.93
7.92
7.92
7.91
7.55
7.55
7.54
7.45
7.26
6.92
6.83
1.63
1.00
2.96
7.0
6.9
6.8
f1 (ppm)
F
OH
1l
EtOH
reflux, 5 min
2l
(3 : 1)
3l
EtOH concentrated
Crude ^{1}H NMR in $CDCl_3$


2l : 3l
7.94
7.94
7.92
7.55
7.26
6.92
6.83
1.00
6.21
7.1
6.9
6.7
f1 (ppm)
F
OH
1l
EtOH
r.t., 24 h
2l
(6 : 1)
3l
EtOH concentrated
Crude ^{1}H NMR in $CDCl_3$

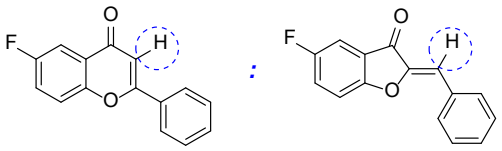


X. DMSO recycle using Biotage® V-10 Touch system

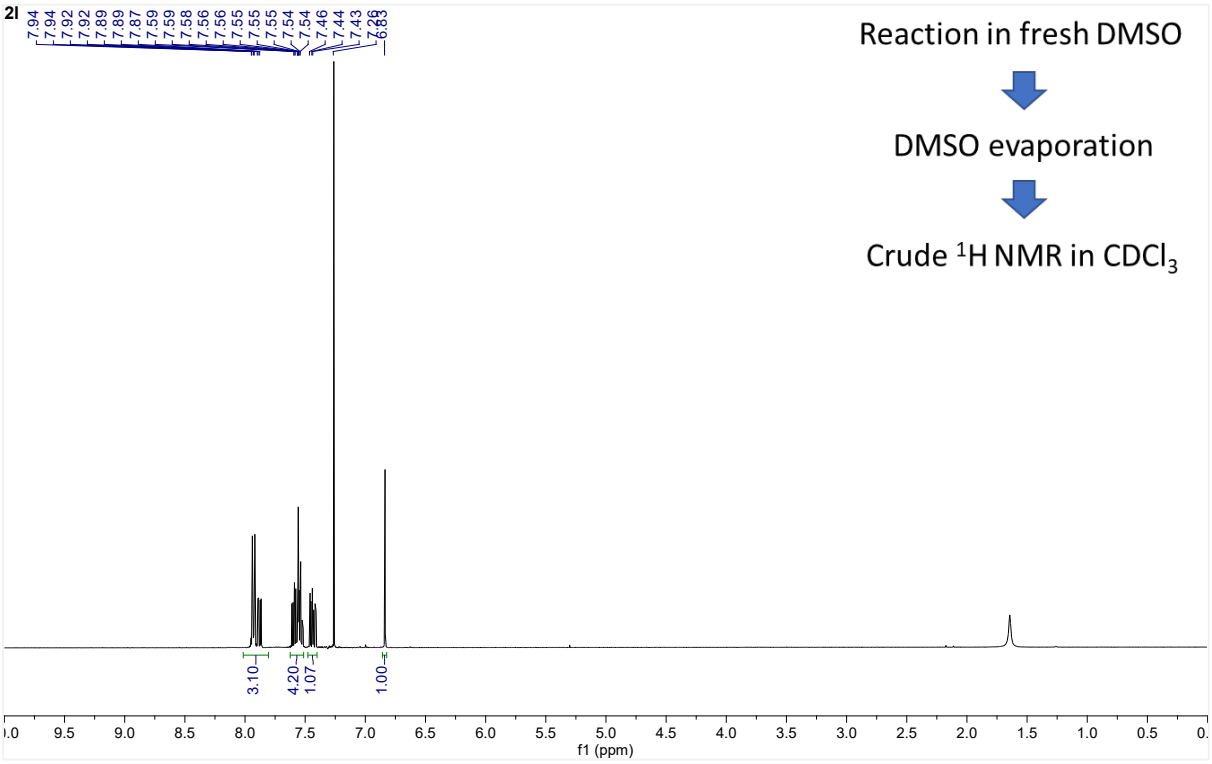
1-(5-Fluoro-2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (**1l**, 120 mg, 0.05 mmol) was added in DMSO (10 mL) and stirred for 3 h at room temperature. The reaction mixture (DMSO) was evaporated at 56 °C in and collected (recycled, 7.3 mL) in Biotage® V-10 Touch system. Dried crude was obtained as a product **2l** (quantitative yield).

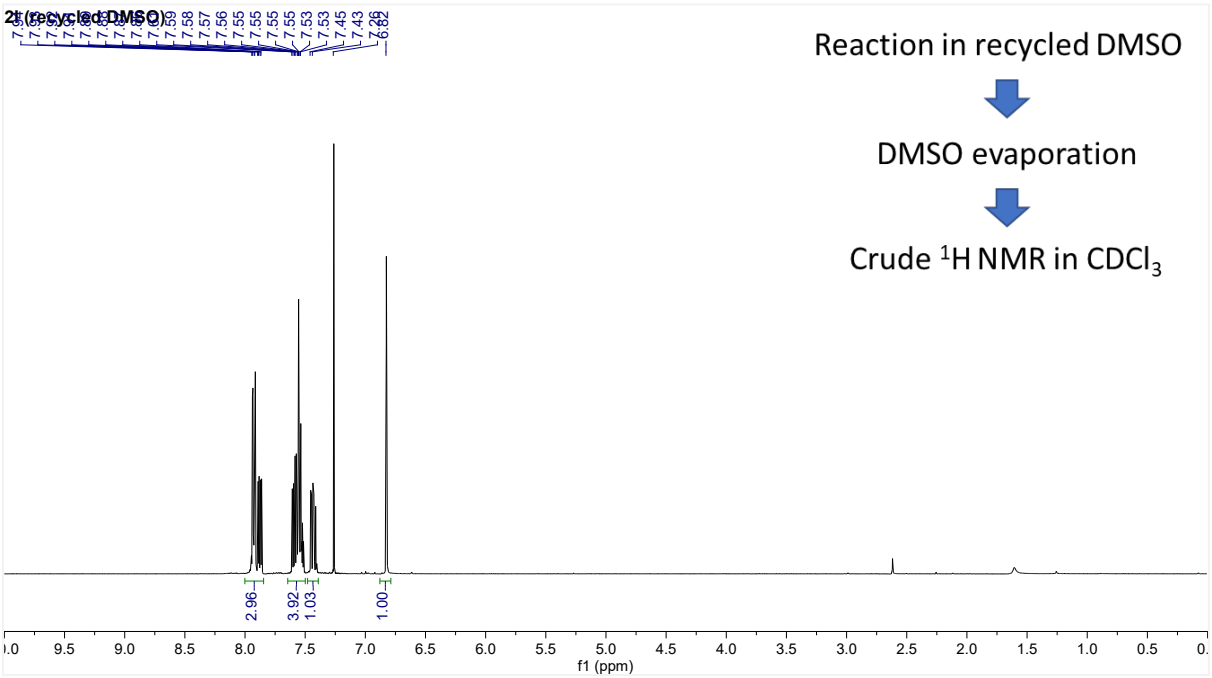
The recycled DMSO was used as a reaction solvent in another batch where compound **1l** (12.0 mg, 0.05 mmol) was dissolved in 1 mL of DMSO. After completion of reaction, the DMSO was evaporated to afford **2l** (quantitative yield) and ^{1}H NMR was monitored in $CDCl_3$ with crude sample.

1l **2l**


O
F
H
O
:
O
F
H
O

2l **(>99 : 1)** **3l**


2l
Reaction in fresh DMSO
DMSO evaporation
Crude ^{1}H NMR in $CDCl_3$
3.10
4.20
1.07
1.00
f1 (ppm)


2l (recycled DMSO)
Reaction in recycled DMSO
DMSO evaporation
Crude ^{1}H NMR in $CDCl_3$
2.96
3.92
1.03
1.00
f1 (ppm)