Supporting Information

Imidazole-Catalysed Construction of Bridged Bicyclo [3.3.1] Ketals via formal [3+3] Cycloaddition of Naphthols and 2-Hydroxyl Chromene Derivatives.

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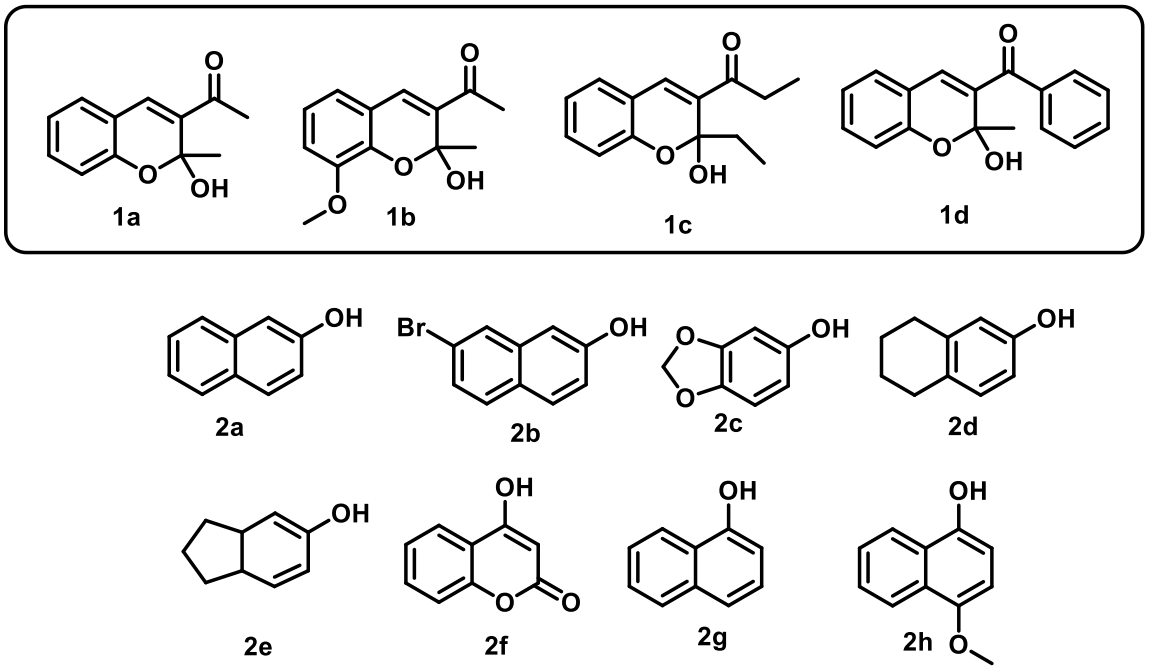
[1] General Information

All the reagents and solvents used in experimentation were of analytical or laboratory grade and used without further purification unless otherwise stated. The reactions were monitored on Merck aluminium silica gel thin layer chromatography (TLC, UV 254nm) plates. Column chromatography was carried out on silica gel (100-200 and 230-400 mesh). ^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker Avance III HD 500 and Bruker AVANCE 400 MHZ spectrometer. Using deuterated chloroform as solvent, TMS was considered as an internal standard for calibration. Chemical shifts are reported in parts per million (ppm) shift (δ-value) based on the peak of the solvent. Signal patterns are indicated as s, singlet; bs, broad singlet; d, doublet; dd, double doublet; t, triplet; m, multiplet. Coupling constants (J) are given in Hertz. Column chromatography was done in 100-200 Å mesh silica gel of Merck Company. All solvents were distilled for purification in column chromatography. Reagents and starting materials were used as received from company. High Resolution Mass Spectra (HRMS) were recorded on Q-TOF mass spectrometer at CSIR-CIMAP, Lucknow, India. The X-ray intensity data were collected from a Bruker APEX-II CCD diffractometer at CSIR-CIMAP, using CuKα (λ = 1.54178 Å) radiation. Data were acquired using a combination of ϕ and ω scans at room temperature (300 K).

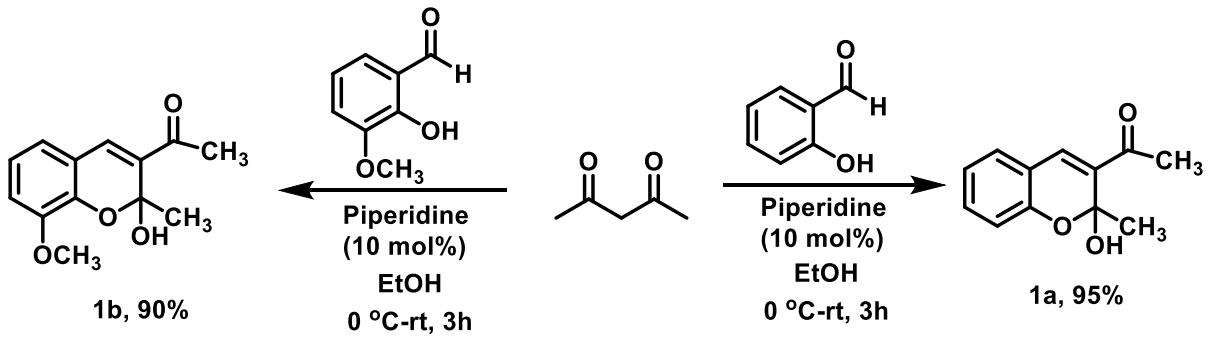
Data collection was performed through the APEX5 software, while SAINT package was used for cell determination and data reduction. The structures were solved by direct methods using SHELXS-97 (Sheldrick, 2008) and were refined against F^2 with full-matrix least squares method using SHELXL-2014 (Sheldrick, 2015). All the heavy atoms very refined anisotropically, while the hydrogen atoms were placed at ideal geometries and were refined using a riding atom model.[1,2]

2. Preparation of Substrates

2.1. The substrates examined in this report

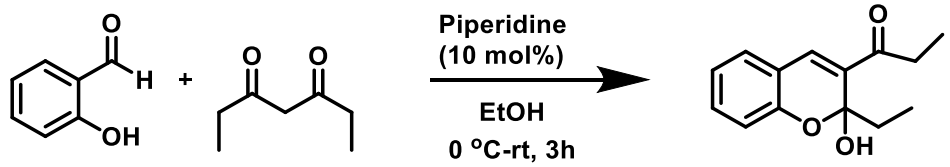


2.2. General Procedure for (1a and 1b):



A general literature procedure was followed for the synthesis of starting materials.[3,4] A 100 mL single-port flask was charged with substituted salicylaldehyde (1g,1.0 equiv.), acetyl acetone (1.1 equiv), and absolute EtOH (25 mL). Then piperidine (0.1 equiv) was added. The mixture was stirred at room temperature for 6-20 h until the complete consumption of the starting materials monitored by TLC. Then the reaction mixture was concentrated under reduced pressure and recrystallized (CH_2Cl_2: n-pentane = 1:10) afforded the corresponding analytically pure products **1a** and **1b** in 95% (1.6g) and 90% (1.4g) yields, respectively.

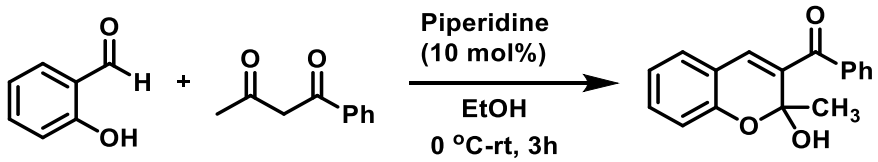
For 1c:



1c

A 100 mL single-port flask was charged with salicylaldehyde (1g,1 equiv.), heptane-3,5-dione (1.1 equiv) and absolute Ethanol (10 mL). Then piperidine (0.1 equiv.) was added at 0°c. The mixture was stirred at room temperature for 3 h until the complete consumption of the starting materials monitored by TLC. Then the reaction mixture was concentrated under reduced pressure and the residue was purified by a silica gel column chromatography (petroleum ether: ethyl acetate = 10:1) to afford the product **1c** as yellow solid (1.7 g, 89% yield).

For 1d:

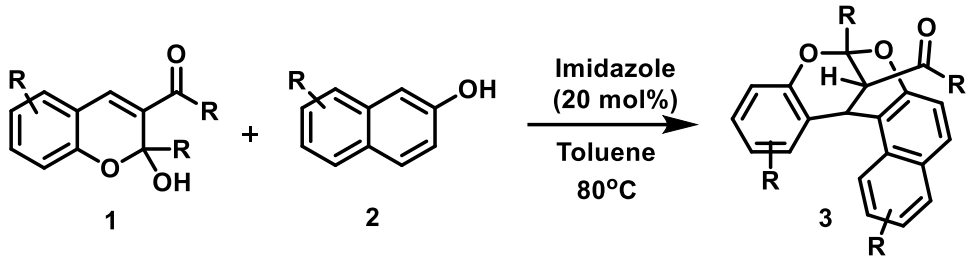


1d

A 100 mL single-port flask was charged with salicylaldehyde (1g,1 equiv.), 1-phenyl 1,3-butanedione (1.1 equiv.) and absolute EtOH (25 mL). Then piperidine (0.1 equiv.) was added at 0°C. The mixture was stirred at room temperature for 3h until the complete consumption of the starting materials monitored by TLC. Then the reaction mixture was concentrated under reduced

pressure and the residue was purified by a silica gel column chromatography (petroleum ether: ethyl acetate = 10:1) to afford the product **1d** as yellow oil (937 mg, 70% yield).

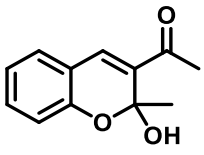
3. General Procedure for the Synthesis of bridged bicyclo [3.3.1] ketals.



To a 10 mL glass vial was added 2-hydroxy-2-methylchromene derivatives **1a-1d** (1.1 equiv.), 1- or 2- naphthols **2a−2h** (1.0 equiv), imidazole (20 mol%) in toluene. The resulting suspension was stirred at 100ºC for 2−24 h until the complete consumption of the starting materials monitored by TLC. The reaction mixture was concentrated and residue was purified by silica gel (100-200 mesh) in ethyl acetate/ hexane to afford desired compound **3** in good to excellent yield.

4. Spectral data:

1-(2-Hydroxy-2-methyl-2H-chromen-3-yl)-ethanone (1a)



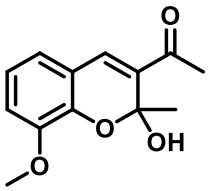
Yellow solid, Yield; 95%

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (s, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 6.99 (d, J = 9.4 Hz,2 H), 4.70 (s, 1H), 2.46 (s, 3H), 1.80 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 198.4, 153.1, 135.04, 133.1, 128.9, 121.8, 118.7, 116.9, 98.9, 27.9, 26.3, 21.02.

HRMS (ESI-): m/z: [M-H]+ calculated for $C_{12}H_{11}O_3$: 203.0708 found: 203.0738.

(2-Hydroxy-8-methoxy-2-methyl-2H-chromen-3-yl)-ethanone (1b)



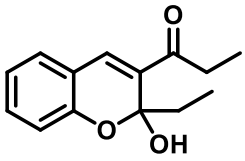
Pale yellow solid, Yield; 90%;

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (s, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 9.4 Hz, 1H), 3.89 (s, 3H), 2.47 (s, 3H), 1.93 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 197.8, 148.2, 142.4, 135.0, 133.3, 121.5, 120.8, 119.5, 115.2, 98.9, 56.2, 27.8, 26.6.

HRMS (ESI-): m/z: [M-H]+ calculated for $C_{13}H_{13}O_4$: 233.0814 found: 233. 0829.

1-(2-ethyl-2-hydroxy-2H-chromen-3-yl)-propan-1-one (1c)



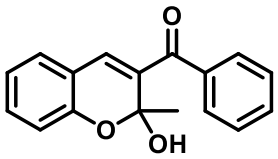
Pale yellow solid, Yield; 89%

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (m, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 9.4 Hz, 1H), 3.89 (s, 3H), 2.47 (s, 3H), 1.93 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.3, 148.6, 134.9, 121.49, 119.5, 115.3, 98.8, 56.26, 29.70, 27.80, 26.59.

HRMS (ESI-): m/z: [M-H]+ calculated for $C_{14}H_{15}O_3$: 231.1021 found: 231.1033.

(2-hydroxy-2-methyl-2H-chromen-3-yl)(phenyl)methanone (1d)



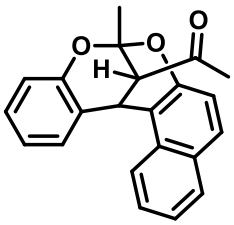
Yellow solid, Yield; 70%

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.3 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.35 – 7.32 (m, 1H), 7.17 – 7.13 (m, 1H), 7.03 – 6.95 (m, 3H), 4.34 (s, 1H), 1.93 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 195.6, 152.6, 137.4, 135.5, 133.0, 132.7, 129.8, 128.8, 128.6, 121.9, 118.9, 117.1, 98.3, 27.3.

HRMS (ESI-): m/z: [M-H]+ calculated for $C_{17}H_{13}O_3$: 265.0865 found: 265.0887.

1-(6-methyl-14H-6,14-methanobenzo[d]naphtho[1,2-g][1,3]dioxocin-15-yl)ethan-1-one (3a):



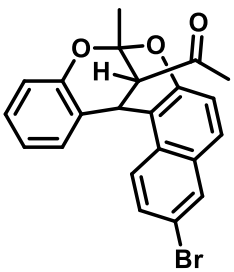
General procedure was followed with 2-hydroxy-2-methylchromene derivatives **1a** (155 mg, 0.762 mmol), 2- naphthol **2a** (100 mg, 0.694 mmol) and imidazole (9.4 mg, 20 mol%) and heated at 100 ^{o}C in 4 mL toluene for 5 h, until the complete consumption of the starting materials monitored by TLC. The reaction mixture was concentrated and residue was purified by silica gel (100-200 mesh) in 15% ethyl acetate: hexane, provide **3a** as a white solid (190 mg, 83%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, *J* = 9.2 Hz, 0.5H), 8.10 (d, *J* = 9.2 Hz, 0.5H), 7.91 (d, *J* = 2.0 Hz, 0.5H), 7.89 (d, *J* = 2.0 Hz, 0.5H), 7.67 (dd, *J* = 6.6, 2.0 Hz, 0.5H), 7.64 (dd, *J* = 6.6, 2.0 Hz, 0.5H), 7.52 (s, 0.5H), 7.50 (s, 0.5H), 7.39 (dd, *J* =7.5, 1.3 Hz, 0.5H), 7.33 (dd, *J* = 7.5, 1.3 Hz, 0.5H), 7.15-7.06 (m, 3H), 6.90 (t, *J* = 8.6, 8.6Hz, 1H), 6.85 (dd, *J*=1.2, 7.5Hz, 0.5H), 6.81 (dd, *J*=1.2, 7.5 Hz, 0.5H) 5.32 (dd, *J* = 8.4,7.4 Hz, 1H), 4.95 (d, *J* = 2.4 Hz, 0.5H), 4.89 (d, *J* = 2.4 Hz, 0.5 H), 3.34 (d, *J* = 2.3 Hz, 0.5H), 3.29 (d, *J* = 2.4 Hz, 0.5H), 2.25 (s, 1.5H), 2.16 (s, 1.5H), 1.98 (s, 1.5H), 1.90 (s, 1.56.H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 203.9, 203.4, 152.3, 151.6, 149.1, 130.8, 130.2, 129.8, 129.5, 129.1, 129.0, 128.9, 128.7, 128.3, 128.2, 127.1, 127.0, 126.6, 126.0, 123.8, 123.7, 122.0, 121.4, 121.1, 121.0, 1182, 116.5, 116.4, 97.4, 51.1, 50.9, 32.2, 32.0, 29.7, 29.4, 25.3.

HRMS (ESI-): m/z: [M-H]+ calculated for $C_{22}H_{17}O_3$: 329.1197 found: 329.1190.

1-(10-bromo-6-methyl-14H-6,14-methanobenzo[d]naphtho[1,2-g][1,3]dioxocin-15-yl)ethan-1-one (3b): General procedure was followed with 2-hydroxy-2-methylchromene derivatives **1a** (155 mg, 0.762 mmol), 6-bromo-2- naphthol **2b** (100 mg, 0.450 mmol) and imidazole (9.4 mg, 20 mol%) and heated at 100 ^{o}C in 4 mL toluene for 8h, until the complete consumption of the starting materials monitored by TLC. The reaction mixture was concentrated and residue was purified by silica gel (100-200 mesh) in 12% ethyl acetate: hexane, provide **3b** as a white solid (170 mg, 93%).



White solid, yield; 93%

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.8 Hz, 0.5H), 8.11 (d, *J*=8.8Hz,0.5H), 7.91(d, *J* = 8.8Hz, 0.5H), 7.90 (d, *J* = 1.9Hz, 0.5H), 7.68-7.64 (m, 1H), 7.52 (s, 0.5H), 7.50 (s, 0.5H),

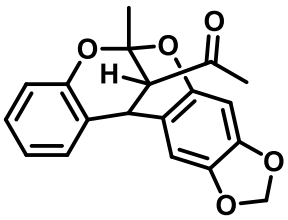
7.40 (dd, *J* = 7.6, 1.6 Hz, 0.5H), 7.35 (dd, *J* = 7.6, 1.6 Hz, 0.5H), 7.16-7.06 (m, 2H), 6.92-6.88 (m, 1H), 6.85-6.80 (m, 1H),

4.90 (d, *J* = 2.3 Hz, 0.45H), 3.35 (d, *J* = 2.5 Hz, 0.55H), 3.30 (d, *J* = 2.5Hz, 0.45H), 2.26 (s, 1.3H), 2.17 (s, 1.7H), 1.20 (s, 1.6H), 1.99 (s, 1.4H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 203.6, 203.2, 152.2, 151.5, 150.1, 149.4, 131.0, 130.9, 130.6, 130.1, 130.2, 129.3, 128.8, 128.5, 128.3, 128.0, 127.8, 127.0, 126.5, 125.6, 123.1, 122.9, 128.0, 127.8, 127.0, 126.5, 125.6, 123.1, 122.9, 121.7, 121.5, 121.1, 119.43, 119.40, 118.5, 117.6, 117.4, 116.5, 114.7, 97.5, 97.4, 51.0, 50.6, 32.2, 32.0, 30.0, 29.7, 29.5, 25.3, 25.2.

HRMS (ESI-): m/z: [M-H]+ calculated for $C_{22}H_{16}BrO_3$: 407.0283 found: 407.0268.

1-(6-methyl-13H-6,13-methano[1,3]dioxolo[4',5':4,5]benzo[1,2-d]benzo[g][1,3]dioxocin-14-yl)ethan-1-one (3c):



General procedure was followed with 2-hydroxy-2-methylchromene derivatives **1a** (162 mg, 0.796 mmol), 3,4 methylenedioxyphenol **2c** (100 mg, 0.723 mmol) and imidazole (10 mg, 20 mol%) and heated at 100 ^{o}C in 4 mL toluene for 10 h, until the complete consumption of the starting materials monitored by TLC. The reaction mixture was concentrated and residue was purified by silica gel (100-200 mesh) in in 15% ethyl acetae: hexane, provide **3c** as a white solid (175 mg, 75%).

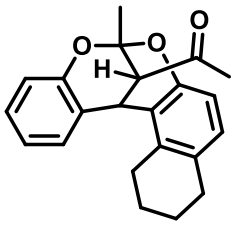
White solid, Yield; 75%.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15-7.014 (m, 2H), 6.89-6.84 (m, 2H), 6.62 (s, 0.5H), 6.58 (s, 0.6 H), 6.44 (s, 0.6H), 6.41 (s,0.4H), 5.87 (d, *J*=12.3 Hz, 1H), 5.79 (s, 1H), 4.07 (s, 1H), 3.22 (d, *J* = 2.2 Hz, 0.4H), 3.18 (d, *J* = 2.2 Hz, 0.6H), 2.20 (s, 1.8H), 2.16 (s, 1.3H), 1.90 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 203.7, 203.6, 151.8, 151.2, 147.5 147.3, 146.5, 145.8, 142.2,141.9, 128.4, 128.3,126.8, 126.7, 126.3, 122.8, 121.6, 121.1, 118.2, 116.4, 116.3, 114.2, 106.1, 105.7, 101.1, 98.7, 98.6, 97.7, 97.6 51.2, 51.0, 37.5, 29.5, 29.5, 25.4, 25.

HRMS (ESI-): m/z: $[M-H]^+$calculated for $C_{19}H_{15}O_5$: 323.0919 found: 323.0958

1-(6-methyl-11,12,13,14-tetrahydro-10*H*-6,14-methanobenzo[d]naphtho[1,2-*g*][1,3]dioxocin-15-yl)ethan-1-one (3d)



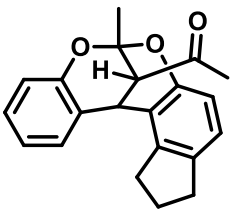
General procedure was followed with 2-hydroxy-2-methylchromene derivatives **1a** (206 mg, 1.01mmol), tetrahydro -2- naphthol **2d** (100 mg, 0.675 mmol) and imidazole (9 mg, 20 mol%) and heated at 100 ^{o}C in 4 mL toluene for 12 h, until the complete consumption of the starting materials monitored by TLC. The reaction mixture was concentrated and residue was purified by silica gel (100-200 mesh) in in 18% ethyl acetate: hexane, provide **3d** as a white solid (198 mg, 88 %).

White solid, Yield: 88%.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19 (d, *J*=7.6, 0.6H), 7.14 (d, *J* = 7.6 Hz, 0.4H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.88-6.82 (m, 3H), 6.61 (s, 0.6H), 6.59 (s, 0.4H) 4.14 (s, 1H), 3.23 (d, *J* = 2.1 Hz, 0.4H), 3.21 (d, *J* = 2.1 Hz, 0.6H), 2.69-2.59 (m, 4H), 2.20 (s, 2H), 2.17 (s, 2H), 2.17 (s, 1H), 1.9 (s, 3H), 1.72-1.67 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 203.9, 203.8, 151.8, 151.3, 149.1, 148.6, 137.6, 137.4, 130.4, 130.1, 128.4, 128.4, 127.3, 127.1, 127.0, 126.7, 126.5, 124.1, 122.9, 122.6, 121.2, 119.9, 116.4, 116.4,116.2, 116.1, 97.6, 97.5, 51.5, 51.4, 37.8, 29.7, 29.6, 29.5, 29.3 29.2, 28.6, 25.5, 23.3, 23.2, 23.0, 22.9.

HRMS (ESI-): m/z: $[M-H]^+$ calculated for $C_{22}H_{21}O_3$: 333.1491 found: 333.1485.



1-(6-methyl-10,11,12,13-tetrahydro-6,13-methanobenzo[d]indeno[4,5-*g*][1,3]dioxocin-14-yl)ethan-1-one (3e): General procedure was followed with 2-hydroxy-2-methylchromene derivatives **1a** (167 mg, 0.819 mmol), 2-indanol **2e** (100 mg, 0.745 mmol) and imidazole (10 mg, 20 mol%) and heated at 100 ^{o}C in 4 mL toluene for 5h,until the complete consumption of the starting materials monitored by TLC. The reaction mixture was concentrated and residue was purified by silica gel (100-200 mesh) in in 18% ethyl acetate: Hexane, provide **3e** as a white solid (183 mg, 77%).

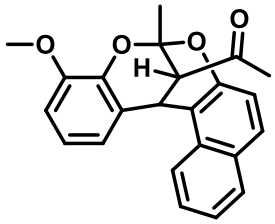
White solid, Yield: 77%.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (d, *J* = 7.4 Hz, 0.4H), 7.13 (d, J=7.4 Hz, 0.6H), 7.09 (d, *J* =7.8 Hz, 0.4H), 7.07 (d, *J* =7.8 Hz, 0.6H), 7.03 (s, 0.6 H), 6.97 (s, 4H), 6.89-6.84 (m, 2H), 6.76 (m, 0.4H), 6.74 (s, 0.6 H), 6.70 (s, 0.2H) 4.16 (bs, 1H), 3.22-3.23 (m, 1H), 2.74-2.82 (m, 4H), 2.19 (s, 1.2H), 2.18 (s, 1.8H), 1.98-2.03 (m, 2H), 1.91 (s, 1.2H), 1.907 (s, 1,8H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 204.0, 151.8, 151.2, 150.2, 149.7, 145.0, 144.8, 137.4, 137.0, 128.2, 127.1, 127.0, 126.5, 124.3, 122.9, 122.5, 122.0, 121.6, 121.2, 120.1, 116.4, 116.4, 112.3, 112.3, 97.7, 97.6, 51.4, 51.3, 37.8, 32.8, 32.0, 29.6, 25.8, 25.6, 25.5.

HRMS (ESI+): m/z: $[M+H]^+$ calculated for $C_{21}H_{19}O_3$: 319.1334 found: 319.1331

1-(4-methoxy-6-methyl-14*H*-6,14-methanobenzo[d]naphtho[1,2-*g*][1,3]dioxocin-15-yl)ethan-1-one (3f): General procedure was followed with 2-hydroxy-2-methylchromene



derivatives **1b** (179 mg, 0.763 mmol), 2- naphthol **2a** (100 mg, 0.694 mmol) and imidazole (9.4 mg, 20 mol%) and heated at 100 ^{o}C in 4 mL toluene for 6h, until the complete consumption of the starting materials monitored by TLC. The reaction mixture was concentrated and residue was purified by silica gel (100-200 mesh), 12% ethyl acetate in Hexane, provide **3f** as a white solid (183 mg, 73%).

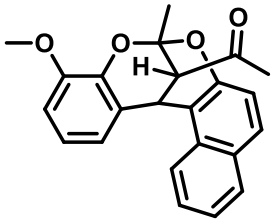
White solid, yield: 73%

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (d, *J* = 7.93 Hz, 0.5H) 8.20 (d, *J* = 7.9 Hz 0.5H), 7.71(t, *J* = 7.4 Hz, 1H), 7.61-7.57 (m, 2H),7.39 (d, *J* = 7.6 Hz, 0.5H), 7.35 (d, *J* = 7.6 Hz, 0.5H), 7.14 (d, *J*=8.9, 0.5H), 7.11 (d, *J*=8.9Hz, 0.5H), 7.08 (dd, *J*= 7.8,1.2Hz, 0.5H), 7.03 (dd, *J*=7.8, 1.2 Hz, 0.5H) 6.80-6.75 (m, 1H), 6.69-6.67 (m,1H), 5.04 (d, *J* = 3.3,Hz,0.5H), 4.98 (d, J=3.3Hz, 0.5H), 3.8 (s, 3H), 3.36 (d, *J* = 2.5 Hz, 0.5H), 3.3 (d, *J* = 2.5 Hz, 0.5H), 2.25 (s, 1.5H), 2.14 (s, 1.5H), 2.08 (s, 1.5H), 2.07 (s, 1.5H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 203.6, 147.7, 146.4, 141.2, 133.7, 133.5, 127.4, 127.4, 126.3, 125.6, 124.8, 124.5, 124.20, 123.7, 122.1, 122.0, 121.5, 121.3, 121.0, 120.2, 118.9, 118.3, 116.3, 111.0, 110.6, 98.05, 98.01, 56.07, 56.0, 51.2, 37.64, 37.60, 98.0, 56.07, 56.0, 51.24, 37.64, 37.60, 29.7, 29.6, 26.4, 25.5, 25.4.

HRMS (ESI+): m/z calcd for $C_{23}H_{21}O_4$ $[M+H]^+$cal:361.1440, found:361.1435.

11-(4-methoxy-6-methyl-14*H*-6,14-methanobenzo[d]naphtho[1,2-*g*][1,3]dioxocin-15-yl)ethan-1-one (3g): General procedure was followed as with 2-hydroxy-2-methylchromene



derivatives **1b** (115 mg, 0.493 mmol), 7-bromo-2- naphthol **2b** (100 mg, 0.448 mmol) and imidazole (6.1 mg, 20 mol%) and heated at 100 ^{o}C in 4 mL toluene for 12 h, until the complete consumption of the starting materials monitored by TLC. The reaction mixture was concentrated and residue was purified by silica gel (100-200 mesh), 12% ethyl acetate in Hexane, provide **3g** as a white solid (180 mg, 91.4%).

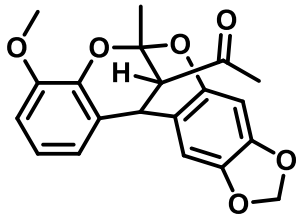
White solid, yield: 91.4%.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.7 Hz, 0.5H), 8.08 (d, *J* = 8.7 Hz, 0.5H), 7.91 (d, *J* = 2.1Hz, 0.5H), 7.89 (d, *J* = 2.1 Hz, 0.5H), 7.66-7.63 (m, 1H), 7.51 (s, 0.5H), 7.49 (s, 0.5H), 7.15 (d, *J* = 8.9 Hz, 0.5H), 7.11 (d, *J*=8.9Hz, 0.5H), 7.01 (dd, *J*=1.4, 7.7 Hz, 0.5H), 6.99 (dd, J= 1.4, 7.7 Hz, 0.5H), 6.80-6.75 (m, 1H), 6.70-6.68 (m, 1H),4.96 (d, *J* = 2.3 Hz, 0.5H), 4.90 (d, *J* = 2.3Hz, 0.5H), 3.81 (s, 3H), 3.37 (d, *J* = 2.5 Hz, 0.5H), 3.28 (d, *J* = 2.5 Hz, 0.5H), 2.26 (s, 1.5H), 2.16 (s, 1.5H), 2.07 (s, 1.5H), 2.06 (s, 1.5H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.4, 153.1, 144.5, 135.4, 132.0, 128.8, 122.9, 117.3, 116.3, 99.1, 27.8, 26.3, 21.9.

HRMS (ESI+): m/z: $[M+H]^+$ calculated for $C_{23}H_{20}BrO_4$: 439.0545 found: 439.0558

1-(4-methoxy-6-methyl-13*H*-6,13-methano[1,3]dioxolo[4',5':4,5]benzo[1,2-d]benzo[*g*][1,3]dioxocin-14-yl)ethan-1-one (3h): General procedure was followed with 2-hydroxy-2-methylchromene derivatives **1b** (186 mg, 0.796 mmol), 3,4 methylenedioxyphenol **2c** (100 mg, 0.724 mmol) and imidazole (9.8 mg, 20 mol%) and heated at 100 ^{o}C in 4 mL toluene for 5 h until the complete consumption of the starting materials monitored by TLC. The reaction mixture was concentrated and residue was purified by silica gel (100-200 mesh) 16% ethyl acetate in Hexane, provide **3h** as a white solid (200 mg, 78%).



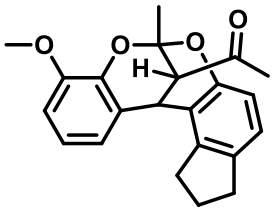
White solid, Yield; 78%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84-6.79 (m, 1H), 6.77 (d, *J* = 1.5 Hz, 1H), 6.76 (d, *J* = 1.5 Hz, 1H), 6.72 (d, *J* = 7.80 Hz, 1H), 6.5 (s, 1H), 5.84 (d, *J* = 1.41 Hz, 1H), 5.80 (d, *J* = 1.41 Hz,1H), 4.07 (d, *J* = 2.87 Hz, 1H), 3.8 (s, 3H), 3.21 (d, *J* = 2.45 Hz, 1H), 2.2 (s, 3H), 1.9 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 203.7, 147.9, 147.4, 146.6, 142.1, 140.6, 127.5, 121.2, 118.2, 114.1, 110.7, 106.0, 101.2, 98.7, 97.7, 56.0, 51.0, 37.4, 29.5, 25.3.

HRMS (ESI+): m/z: $[M+H]^+$ calculated for $C_{20}H_{19}O_6$: 355.1182 found: 355.1174

1-(4-methoxy-6-methyl-10,11,12,13-tetrahydro-6,13-methanobenzo[*d*]indeno[4,5-*g*][1,3]dioxocin-14-yl)ethan-1-one (3i): General procedure was followed with 2-hydroxy-2-methylchromene derivatives **1b** (.192 mg, 0.819 mmol), 2- Indanol **2e** (100 mg, 0.745 mmol) and imidazole (10 mg, 20 mol%) and heated at 100 ^oC in 4 mL toluene for 5h until the complete consumption of the starting materials monitored by TLC. The reaction mixture was concentrated and residue was purified by silica gel (100-200 mesh), 15 % ethyl acetate in Hexane, provide **3i** as a white solid (180 mg, 69%).



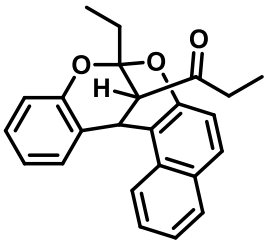
White solid, yield: 69%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01 (s, 0.5H), 6.95 (s, 0.5H), 6.81-6.67 (m, 4H), 4.15-4.13 (m, 1H), 3.79 (s, 3H), 3.20 (d, *J* = 2.27 Hz, 0.5H), 3.19 (d, *J* = 2.27 Hz, 0.5H), 2.80-2.71 (m, 4H), 2.17 (s, 1.5H), 2.15 (s, 1.5H), 2.02-1.08 (m, 2H), 1.97 (s, 1.6H), 1.96 (s, 1.6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 204.1, 204.0, 150.3, 150.0, 148.0, 145.0, 144.7, 141.2, 140.6, 137.2, 136.9, 127.8, 124.3,123.9, 121.8, 121.5, 121.2, 111.0, 110.6, 37.8, 37.7, 32.8, 32.0, 31.6, 25.8, 25.6, 25.6, 25.4.

HRMS (ESI+): m/z: $[M+H]^+$ calculated for $C_{22}H_{23}O_4$: 351.1596 found: 351.1589.

1-(6-ethyl-14*H*-6,14-methanobenzo[*d*]naphtho[1,2-*g*][1,3]dioxocin-15-yl)propan-1-one (3j): General procedure was followed with 2-hydroxy-2-methylchromene derivatives **1c** (177 mg, 0.762 mmol), **2a** (100 mg, 0.694 mmol) and imidazole (9.4 mg, 20 mol%) and heated at 100 ^oC in 4 mL toluene for 8h until the complete consumption of the starting materials monitored by TLC.



The reaction mixture was concentrated and residue was purified by silica gel (100-200 mesh) 20% ethyl acetate, provide **3j** as a white solid (200 mg, 80%).

White solid, Yield: 80%.

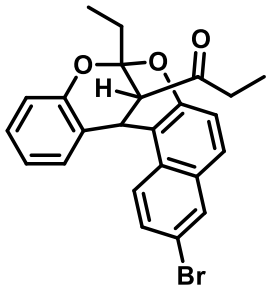
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.8 Hz, 0.5H), 8.22 (d, *J* = 8.8 Hz, 0.5H), 7.62 (t, *J* = 7.5, 1H), 7.60-7.54 (m, 2H), 7.45-7.31 (m, 2H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.08-7.03 (m, 1H), 6.92-6.89 (m,1H), 6.83-6.76 (m,1H), 4.95 (d, *J*=2.2 Hz, 0.5H), 4.90 (d, *J*=2.2 Hz, 0.5H)

4.87 (s, 0.4H), 4.81 (s, 0.5H), 3.39 (s, 0.6H), 3.34 (s, 0.4H), 2.61-2.53 (m, 1H), 2.50-2.44 (m, 1H), 2.35 -2.29 (m, 1H), 2.25 -2.19 (m, 1H), 1.17 (dt, *J* = 7.11, 7.49 Hz, 3H), 1,01 (dd, *J* = 6.6,7.4 Hz, 1.4H), 0.982 (dd, *J* = 7.1,7.4 Hz, 1.9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 206.4, 206.1, 152.3, 152.0, 150.2, 149.8, 131.02, 131.0 ,127.0, 126.0, 123.2, 123.0, 122.2, 121.4, 121.1,119.5, 119.4, 119.0, 117.4, 117.2, 116.3, 115.0, 99.4, 99.3, 48.0, 47.6, 35.70, 35.5, 32.14, 32.01, 30.74, 30.67.

HRMS (ESI-): m/z: $[M-H]^+$ calculated for $C_{24}H_{21}O_3$: 357.1491found: 357.1491.

1-(11-bromo-6-ethyl-14*H*-6,14-methanobenzo[*d*]naphtho[1,2-*g*][1,3]dioxocin-15-yl)propan-1-one (3k): General procedure was followed with 2-hydroxy-2-methylchromene derivatives **1c** (114 mg, 0.493 mmol), 7-bromo-2-naphthol **2b** (100 mg, 0.448 mmol) and imidazole (6.1 mg, 20 mol%) and heated at 100 ^oC in 4 mL toluene for 5 h until the complete consumption of the starting materials monitored by TLC. The reaction mixture was concentrated and residue was purified by silica gel (100-200 mesh) 16% ethyl acetate, provide **3k** as a white solid (170 mg, 87%).

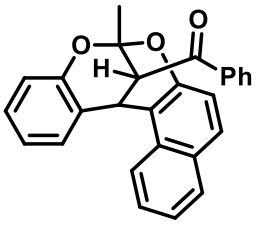


White solid, yield**:** 87%**.**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 9.3 Hz, 0.4H), 8.08 (d, *J* = 9.3 Hz, 0.6H), 7.87 (d, *J* = 1.7 Hz, 0.4H), 7.85 (d, *J* = 1.7Hz, 0.6H), 7.64-7.59 (m,1H), 7.47 (s, 0.5H), 7.45 (s,0.5H)7.39 (dd, *J* = 7.6, Hz, 0.5H), 7.30 (d, *J* = 7.6 Hz,0.5H), 7.14-7.03 (m, 2H), 6.91 (s, 0.5H), 6.89 (s,0.5H), 6.83-6.76 (m, 1H), 4.87 (d, *J* = 1.9 Hz, 0.6H), 4.83 (d, *J* = 1.9 Hz, 0.4H), 2.67-2.17 (m, 4H), 1.15 (t, *J* = 7.3 Hz, 3H), 1.00 (t, *J* = 7.3 Hz, 1.4H), 0.90 (t, J= 7.3 Hz, 1.8H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.4, 153.1, 144.5, 135.4, 132.0, 128.8, 122.9, 117.3, 116.3, 99.1, 27.8, 26.3, 21.9.

HRMS (ESI+): m/z: $[M+H]^+$ calculated for $C_{24}H_{22}BrO_3$: 437.0752 Found: 437.0776

(6-methyl-14*H*-6,14-methanobenzo[*d*]naphtho[1,2-*g*][1,3]dioxocin-15-yl)(phenyl)methanone (3l): 

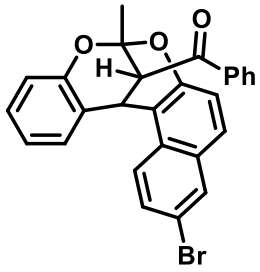
General procedure was followed with 2-hydroxy-2-methylchromene derivatives **1d** (203 mg, 0.762 mmol), 2-naphthol **2a** (100 mg, 0.694 mmol) and imidazole (9.4 mg, 20 mol%) and heated at 100 ^oC in 4 mL toluene for 5 h until the complete consumption of the starting materials monitored by TLC. The reaction mixture was concentrated and residue was purified by silica gel (100-200 mesh) 15% ethyl acetate, provide **3l** as a white solid (200 mg, 73 %).

White solid, Yield:73%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.5 Hz, 0.5H), 8.79 (d, *J* = 8.5 Hz, 0.5H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.88 (d, *J* = 8.6 Hz, 1H) 7.79 (d, *J* = 8.1 Hz, 0.5H), 7.72 (d, *J* = 8.1 Hz, 0.5H), 7.66-7.53 (m, 3H) 7.48-7.35 (m, 3H), 7.30-7.05 (m, 3H) , 6.98 (t, *J* = 9.7 Hz, 1H), 6.85 (t, *J*= 6.9 Hz, 0.5H) 6.75 (t, *J* = 7.3 Hz, 0.5H), 5.0 (d, *J* = 2.2 Hz, 0.5H), 4.96 (d, *J* = 2.2Hz, 0.5H), 4.31 (d, *J* = 2.2 Hz, 0.43H), 4.26 (d, *J* = 2.2 Hz, 0.47H), 1.9 (d, *J*=2.2 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 195.6, 195.2, 152.7, 151.8, 150.1, 149.3, 136.1, 133.7, 133.6, 130.8, 130.5, 129.8, 129.6, 129.1, 129.0, 128.9, 128.8, 128.4, 128.3, 127.2, 127.0, 126.8, 126.7, 126.3, 123.8, 123.4, 121.8, 121.5, 121.2, 121.1, 121.1, 118.5, 118.2, 116.7, 116.1, 114.1, 98.1, 97.9, 45.0, 44.7, 33.6, 33.2, 29.8, 25.2.

HRMS (ESI+): m/z: $[M+H]^+$ calculated for $C_{27}H_{21}O_3$: 393.1491, found:393.1483.

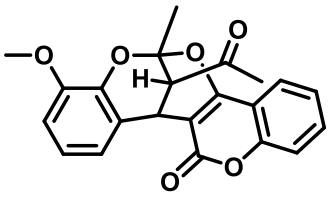
(11-bromo-6-methyl-14*H*-6,14-methanobenzo[*d*]naphtho[1,2-*g*][1,3]dioxocin-15-yl)(phenyl)methanone (3m):  General procedure was followed with 2-hydroxy-2-methylchromene derivatives **1d** (131 mg, 0.493 mmol), 7-bromo-2- naphthol **2b** (100 mg, 0.448 mmol) and imidazole (6.1 mg, 20 mol%) and heated at 100 ^{o}C in 4 mL toluene for 5 h until the complete consumption of the starting materials monitored by TLC. The reaction mixture was concentrated and residue was purified by silica gel (100-200 mesh) 12% ethyl acetate, provide **3b** as a white solid (196 mg, 93%).

White solid, Yield; 93%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.8Hz, 0.5H), 7.92-7.84 (m, 3H), 7.65-7.44 (m, 5H), 7.37 (d, *J* = 6.97 Hz, 0.5H), 7.23-7.07 (m, 3H), 6.98 (t, *J* = 8.6Hz, 1H), 6.96 (d, *J* = 7.38 Hz, 1H), 6.86 (t, *J* = 8.0 Hz, 0.5H), 6.78 (t, *J* = 7.3 Hz, 0.5H), 4.92 (d, *J*=2.12, 0.5H), 4.89 (d, *J*=2.12, 0.5H), 4.31 (d, *J*=2.37, 0.47H), 4.25 (d, *J*=2.37 Hz, 0.43H), 1.9 (d, *J*=2.2 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 195.4, 195.13, 151.6, 150.3,149.5, 136.1, 136.0, 133.7, 130.9, 130.7, 130.2, 129.8, 129.3, 128.2, 127.7, 127.0, 126.8, 126.5, 126.0, 123.2, 123.9, 121.5, 121.2, 121.1, 119.6, 119.2, 118.7, 117.5, 116.7, 116.1, 98.0, 97.8, 44.8, 44.5, 33.5, 33.1, 25.1.

HRMS (ESI-): m/z: $[M-H]^+$ calculated for $C_{27}H_{18}BrO_3$: 469.0439, found:471.0433

15-acetyl-10-methoxy-8-methyl-1*H*,14H-8,14-methanobenzo[7,8][1,3]dioxocino[5,4-c]chromen-1-one (3n):  General procedure was followed with 2-hydroxy-2-methylchromene derivatives **1b** (155 mg, 0.762 mmol), 4-hydroxy coumarin **2f** (100 mg, 0.694 mmol) and imidazole (9.4 mg, 20 mol%) and heated at 100 ^{o}C in 4 mL toluene for 5 h, until the complete consumption of the starting materials monitored by TLC. The reaction mixture was concentrated and residue was purified by silica gel (100-200 mesh) 25% ethyl acetate in hexane, provide **3n** as a white solid (194 mg, 83%).

White solid, yield: 83%.

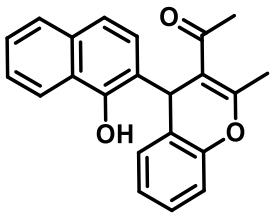
^{1}H NMR (400 MHz, $CDCl_3$): 7.84 (d, *J* = 6.6 Hz, 0.6H), 7.76 (d, *J* = 6.6 Hz, 0.4H), 7.46 (s,1H), 7.22 (s, 2H), 7.11 (d, *J* = 7.83 Hz, 0.6H), 7.04 (d, *J* = 7.83 Hz, 0.4H), 6.91-6.84 (m, 1H), 6.79-6.74

(m, 1H), 4.6 (d, *J* = 10.3 Hz, 1H), 3.83(s, 3H), 3.38 (s, 0.5H), 3.23 (s, 0.5H), 2.31 (s, 1.8H), 2.23 (s, 1.2H), 2.16 (s, 1.4H), 2.10 (s, 1.7H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 202.6, 201.8, 161.6, 161.1, 159.0, 157.9, 152.4, 147.8, 147.5, 140.7, 139.7, 132.2, 132.1, 126.1, 124.1, 124.0, 123.2, 123.0, 120.0, 119.5, 116.6, 116.5, 114.5, 111.6, 111.0, 105.8, 102.0, 100.2, 100.1, 99.0, 30.6, 30.3, 30.0, 24.7, 24.4.

HRMS (ESI+): m/z: $[M+H]^+$calculated for $C_{22}H_{19}O_6$: 379.1182, found:379.1196

1-(4-(1-hydroxynaphthalen-2-yl)-2-methyl-4H-chromen-3-yl)-ethan-1-one) (4a): General procedure was followed with 2-hydroxy-2-methylchromene derivatives **1a** (779 mg, 3.81 mmol), 1- naphthol **2b** (500 mg, 3.47 mmol) and imidazole (47 mg, 20 mol%) and heated at 100 ºC in 40 mL toluene for 2 h, minor amount of unreacted **2b** was monitored by TLC. The reaction mixture was concentrated and residue was purified by silica gel (100-200 mesh) 10% ethyl acetate in hexane, provide 4**a** as a white solid (861mg, 75%).



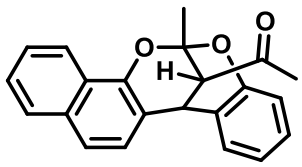
White solid, Yield: 75%.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (d, *J* = 7.56 Hz, 1H), 7.5 (d, *J* = 7.56 Hz, 1H), 7.49-7.43 (m, 2H), 7.42 7.38 (m, 1H), 7.28-7.27 (m, 1H), 7.22-7.20 (m,1H), 7.12 -7.08 (m, 1H), 6.09-6.86 (m, 2H), 4.34 (d, *J* = 2.46, 1H), 3.38 (d, *J* = 2.49 Hz, 1H,), 2.24 (s, 3H), 2.11 (s,3H).

^{13}CNMR: (125 MHz, $CDCl_3$): 203.7, 151.9, 146.3, 133.6, 128.45, 127.5, 126.9, 126.2, 125.7, 121.7, 121.6, 121.1,116.4, 98.1, 51.2, 37.8, 29.5,25.3.

HRMS (ESI-): m/z: $[M-H]^+$calculated for $C_{22}H_{17}O_3$: 329.1178 found:329.1188

1-(8-methyl-14H-8,14-methanobenzo[d]naphtho[2,1-g]-[1,3]-dioxocin-15-yl)-ethan-1-one



(5a): In a round bootom flask **4a** (0.5mg, .151mmol), $Cu(OTf)_2$ (.054mg, .0151mmol) and 1ml toluene was added. The reaction mixture was stirred at rt for 12 h resulted **5a** as a white solid (45 mg, 90%).

White solid, Yield: 90%.

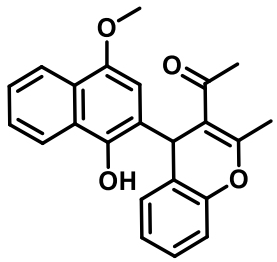
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 7.64 Hz, 0.5H), 8.25 (d, *J* = 7.64 Hz, 0.4H), 8.02 (d, *J* = 8.0 Hz, 0.6H), 7.40 (td, *J* = 7.5, 1.3 Hz, 1H), 7.35 (td, *J* = 7.5, 1.3 Hz, 1H), 7.00 (td, *J* = 7.4,

Hz, 0.9 H), 6.51 (s, 0.9H), 6.46 (s, 0.6H), 4.15 (d, *J* = 2.3 Hz, 0.9H), 4.13 (d, *J* = 2.3 Hz, 0.6H), 3.89 (s, 2.8H), 3.87 (s, 0.2H), 3.30 (d, *J* = 2.3H, 0.9H), 3.16 (d, *J* = 2.3Hz, 0.6H), 2.14 (s, 2.8H, 2.07 (s, 0.3H), 1.98 (s, 3H).

^{13}CNMR (101MHz, $CDCl_3$): 203.9, 203.4, 152.4, 152.3,151.6,149.8, 149.05, 130.8, 130.2, 129.8, 129.5, 129.1, 129.03, 128.9, 128.7, 128.3, 128.1, 127.7, 127.1, 127.0, 126.9, 126.6, 126.5, 126.35, 126.0, 123.8, 123.7, 123.5, 122.0, 121.3, 121.4, 121.0, 121.0, 118.3, 118.2, 116.4, 116.7, 114.3, 109.5, 97.4, 51.2, 50.9, 32.1, 32.0, 29.7, 29.3, 25.3.

HRMS (ESI-): m/z: $[M-H]^+$ calculated for $C_{22}H_{17}O_3$: 329.1178 found: 329.1188.

1-(4-(1-hydroxy-4-methoxynaphthalen-2-yl)-2-methyl-4H-chromen-3-yl)-ethan-1-one:(4b)



General procedure was followed with 2-hydroxy-2-methylchromene derivatives **1a** (257 mg, 1.26 mmol), 4-methoxy-1- naphthol **2h** (200 mg, 1.15 mmol) and imidazole (15 mg, 20 mol%) and heated at 100 ^oC in 4 mL toluene for 4h, reaction was montitored by TLC. The reaction mixture was concentrated and residue was purified by silica gel (100-200 mesh) 12% ethyl acetate, provide **4b** as a white solid (280mg, 68%).

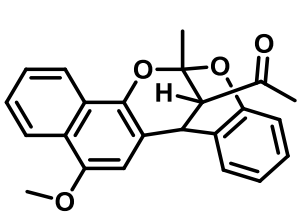
White solid, Yield: 68%.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.5 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.49-7.41 (m, 2H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.68, 7.66 Hz, 1H), 6.90 (m, 2H), 6.5 (s,1H), 4.29 (d, *J* = 2.29 Hz, 1H), 3.9 (s, 3H), 3.38 (d, *J* = 2.29 Hz,1H), 2.22 (s, 3H), 2.06 (s,3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 203.8, 152.2, 139.9, 128.4, 126.7, 126.3, 125.6, 125.4, 125.1, 122.8, 121.8, 121.5, 121.4, 119.2, 116.3, 102.3, 97.8, 55.3, 51.5, 38.2, 29.7, 29.6, 25.3.

HRMS (ESI+): m/z: $[M+H]^+$calculated for $C_{23}H_{21}O_4$: 361.1440 found:361.1435

1-(2-methoxy-8-methyl-14H-8,14-methanobenzo[d]naphtho[2,1-g]-[1,3]-dioxocin-15-yl)-



ethan-1-one (5b): In a round bootom flask **4b** (200 mg, .56 mmol), $Cu(OTf)_2$ (20 mg, .055mmol) and 4 ml toluene was added. The reaction mixture was stirred at rt for 10 h. resulted **5b** as a white solid (175 mg, 85%).

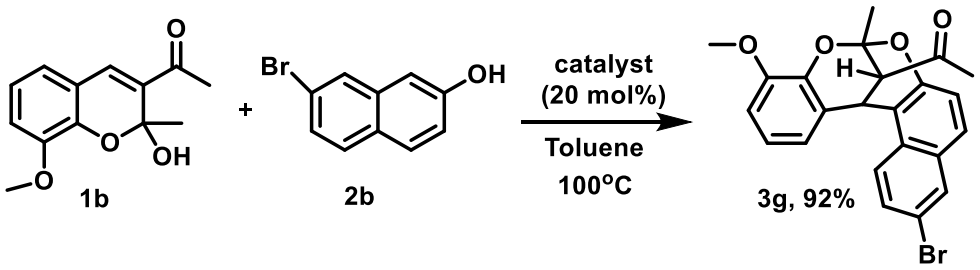
White solid, Yield: 85%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (dd, *J* = 8.6, 8.8 Hz, 1H), 7.90 (dd, *J* = 2.0, 8.2 Hz, 1H), 7.66-7.62 (m, 1H), 7.51 (d, *J* = 8.9 Hz, 1H), 7.18-7.09 (m, 2H), 7.01 (dd, *J* = 1.9, 7.6, Hz, 0.5H), 6.96 (dd, *J* = 1.5, 7.7 Hz, 0.5H), 6.80-6.75 (m, 1H), 6.70-6. 67(m, 1H), 5.0 (d, *J* = 2.3Hz, 0.5H), 4.90 (d, *J* = 2.3Hz, 0.5H), 3.81 (s, 2.8H), 3.37 (d, J=2.5Hz, 0.5H), 3.28 (d, *J* = 2.5Hz, 0.5H), 2.26 (s,1.5 H), 2.16 (s, 1.5 H), 2.06 (d, J=2.0Hz, 3H).

^{13}CNMR (101MHz, $CDCl_3$): 203.8, 152.3, 150.03, 139.9, 128.4, 126.4, 125.6, 125.5, 125.1, 122.8, 121.8, 121.5, 121.4, 119.2, 116.3, 102.3, 97.8, 55.8, 51.5, 38.2, 29.61, 25.3.

HRMS (ESI+): m/z: $[M+H]^+$calculated for $C_{23}H_{21}O_4$: 361.1440 found:361.1435

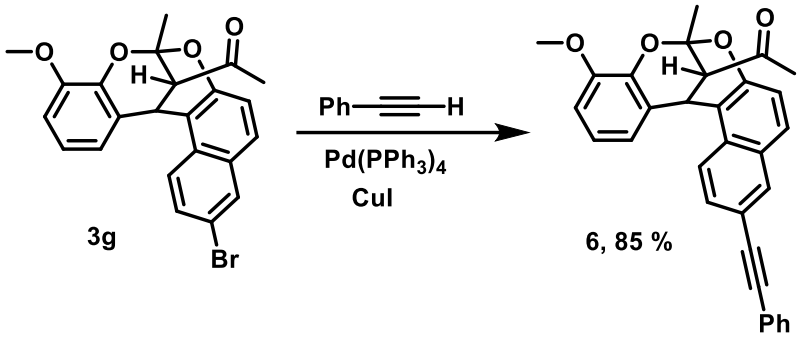
5. Gram Scale Synthesis and Synthetic Transformations:



A 100 mL flask equipped with a stirring bar was charged with 2-hydroxy-2-methylchromene derivative **1b** (2.32 g, 4.93 mmol), 7-bromo-2-naphthol (**2b**, 2.0 g, 4.48 mmol), imidazole (20 mol%) and toluene (30.0 mL). The resulting suspension was stirred at 100 ºC for 12 h until the complete consumption of the starting materials monitored by TLC. The reaction mixture was concentrated and residue was purified by silica gel (100-200 mesh) in hexane: ethyl acetate to afford desired compound **3g** in 3.62 g, 92% yield, as white solid.

5.1 Sonogashira Coupling: Compound **3g** (50 mg, 0.11 mmol) was taken in an oven dried Schlenck tube degassed under nitrogen atmosphere then 5 mL dry triethylamine, $Pd(PPh_3)_4$ (0.05 mmol) and CuI (0.025 mmol) was added after 15 min. Phenyl acetylene (0.22 mmol) was added

to the reaction mixture and stirred at 80°C for 18h, resulted **6** as a single product (43 mg, 85%).

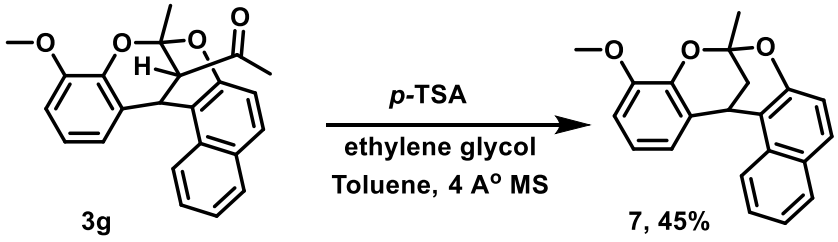


White solid, Yield: 85%, **^{1}HNMR (400MHz, $CDCl_3$):** δ 8.19 (dd, J=8.8, 8.8 Hz, 1H), 8.09 (d, J=8.3 Hz, 0.5H), 7.96 (d, J=5.1Hz, 1H), 7.8 (d, J=8.3 Hz, 0.5H), 7.7-7.4 (m,5H), 7.35-7.34 (m,3H), 7.15-7.09 (m, 2H), 7.05-6.98 (m, 2H), 5.01 (d, J=2.39Hz, 0.5H), 4.9 (td, J=2.9, 2.9 Hz, 0.5H), 3.81 (s, 2H), 3.33 (s, 1H), 2.26(s, 1H), 2.16 (s, 1H), 2.14 (s,1H), 2.07 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 203.2, 203.2, 150.8, 150.3, 148.0, 147.8, 141.0, 132.5, 132.4, 131.6, 131.0, 131.0, 130.2, 130.1, 129.6, 129.5, 129.4, 129.3, 128.8, 128.5, 128.4, 128.4, 128.3, 128.3, 127.9, 126.6, 126.5, 123.4, 123.3, 122.9, 122.8, 121.6, 121.4, 121.3, 121.1, 119.5, 119.0, 118.6, 118.4, 117.3, 114.6, 114.6, 110.9, 110.6, 110.6, 97.5, 97.5, 97.5, 89.6, 56.1, 56.0, 51.1, 50.6, 50.5, 32.0, 31.9, 31.9, 29.5, 29.5, 25.4, 25.2..

HRMS (ESI+): m/z: $[M+H]^+$calculated for $C_{31}H_{25}O_4$: 461.1753 found:461.1755

5.2. Deacetylation: Starting material **3g** (50 mg, 0.11mmol) was refluxed in the presence of ethylene glycol (9.2 µl, 1.5 equiv) and p-TSA (20 mol %) in dry toluene using Dean stark apparatus at 80°C for 24 h. afforded deacetyled product **7** in 18 mg, 45% yield. (starting not consumed even after 24 h).



White solid, Yield: 45%.

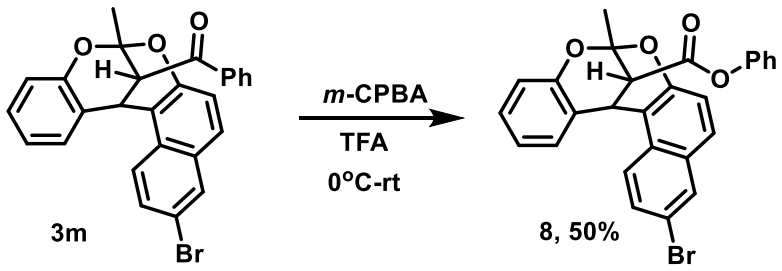
^{1}HNMR (400MHz, $CDCl_3$): δ 8.15 (d, *J* = 2.09 Hz, 1H), 7.88 (d, *J*=2.19Hz, 1H) 7.64 (dd, *J*=2.18, 2.18 Hz, 1H), 7.49 (d, *J* = 8.85 Hz, 1H), 7.11 (d, *J* = 8.16Hz 1H), 7.01 (dd, *J* = 1.36, 1.36 Hz, 1H), 6.77 (t, *J*=8.31, 7.81 Hz, 1H), 6.69 (dd, *J* =1.49, 1.33 Hz, 1H), 4.71 (t, *J* = 3.05, 2.69 Hz, 1H), 3.81 (s,3H), 2.39 (dd, *J* = 3.17, 3.13 Hz, 1H), 2.28 (dd, *J* = 3.16, 3.03 Hz, 1H), 1.99 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): 150.04, 148.01, 141.68, 130.71, 130.64, 129.78, 129.37, 127.15, 126.49, 123.56, 120.72, 119.02, 118.41, 117.11, 110.23, 97.58, 55.97, 30.97, 28.29, 21.17.

HRMS (ESI+): m/z: $[M+H]^+$calculated for $C_{21}H_{18}BrO_3$: 397.0439 found:397.0440

5.3. Bayer Villiger Oxidation:

A 100 mL Single-pot flask was charged with **3m** (50 mg, 0.106 mmol, 1.0 eq.), mCPBA, (48 mg, 0.276 mmol, 2.6 eq.) dry DCM under N_2 atmosphere was reaction mixture was cooled at 0°C. After cooling of the reaction mixture TFA (12 mg, 1.0 eq, 0.106 mmol) was added to the reaction mixture. After addition reaction was allow to stirred at rt for 24h to get desired compound **8** (27 mg, 50)

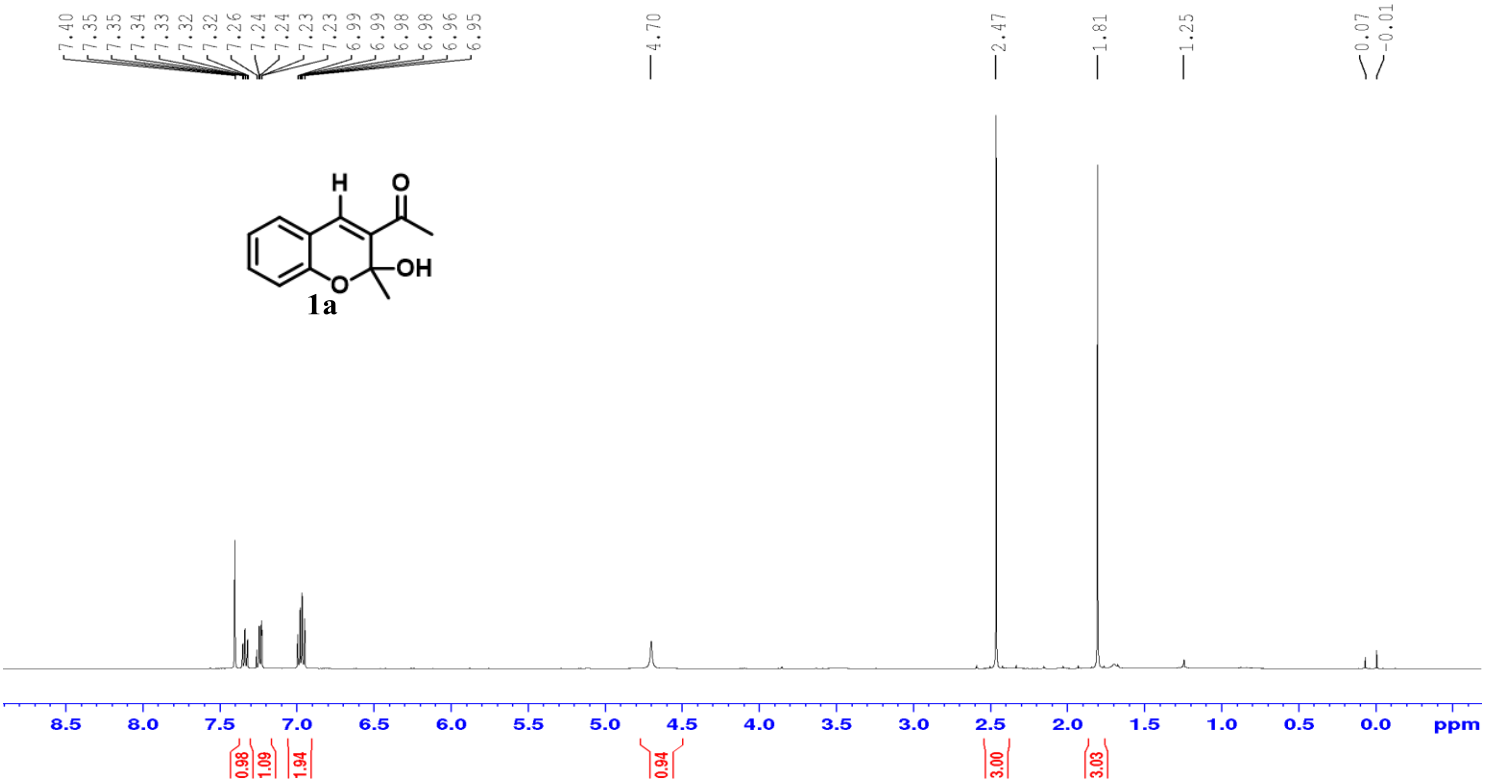


White solid, Yield; 50%.

^{1}HNMR (400MHz, $CDCl_3$): δ 7.62 (dd, *J* =2.0, 8.2Hz, 1H), 7.54 (d, J=1.9 Hz, 1H) 7.50-7.44 (m, 2H), 7.40 (d, J=8.1Hz, 2H), 7.31 (t, 2H)), 7.24 (d, J=9.17, 1H), 7.16-7.11 (m, 1H), 6.91 (d, J= 8.15, 1H), 6.67 (t, 1H), 6.50 (dd, *J* =1.6, 8.1 Hz, 1H), 5.88 (d, *J* = 9.7 Hz, 1H), 4.21 (d, *J* = 4.0 Hz, 1H) 3.69 (d, *J* = 3.7 Hz, 1H), 2.11 (s, 3H).

^{13}C NMR (101MHZ, $CDCl_3$): 198.37, 141.01, 140.90, 136.75, 133.20, 132.59, 132.41, 131.92, 130.57, 128.71, 127.41, 126.86, 126.80, 126.20, 122.98, 121.24, 119.75, 115.97, 107.78, 96.03, 55.88, 47.86, 22.34. **HRMS (ESI+):** m/z: $[M+H]^+$calculated for $C_{27}H_{20}BrO_4$: 487.0545 found:487.0545

6. Spectra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7.34
7.33
7.32
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7.26
7.24
7.24
7.23
7.23
6.99
6.99
6.98
6.98
6.96
6.95
4.70
2.47
1.81
1.25
0.07
-0.01
H
O
OH
O
1a
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
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1.0
0.5
0.0
ppm
0.98
1.09
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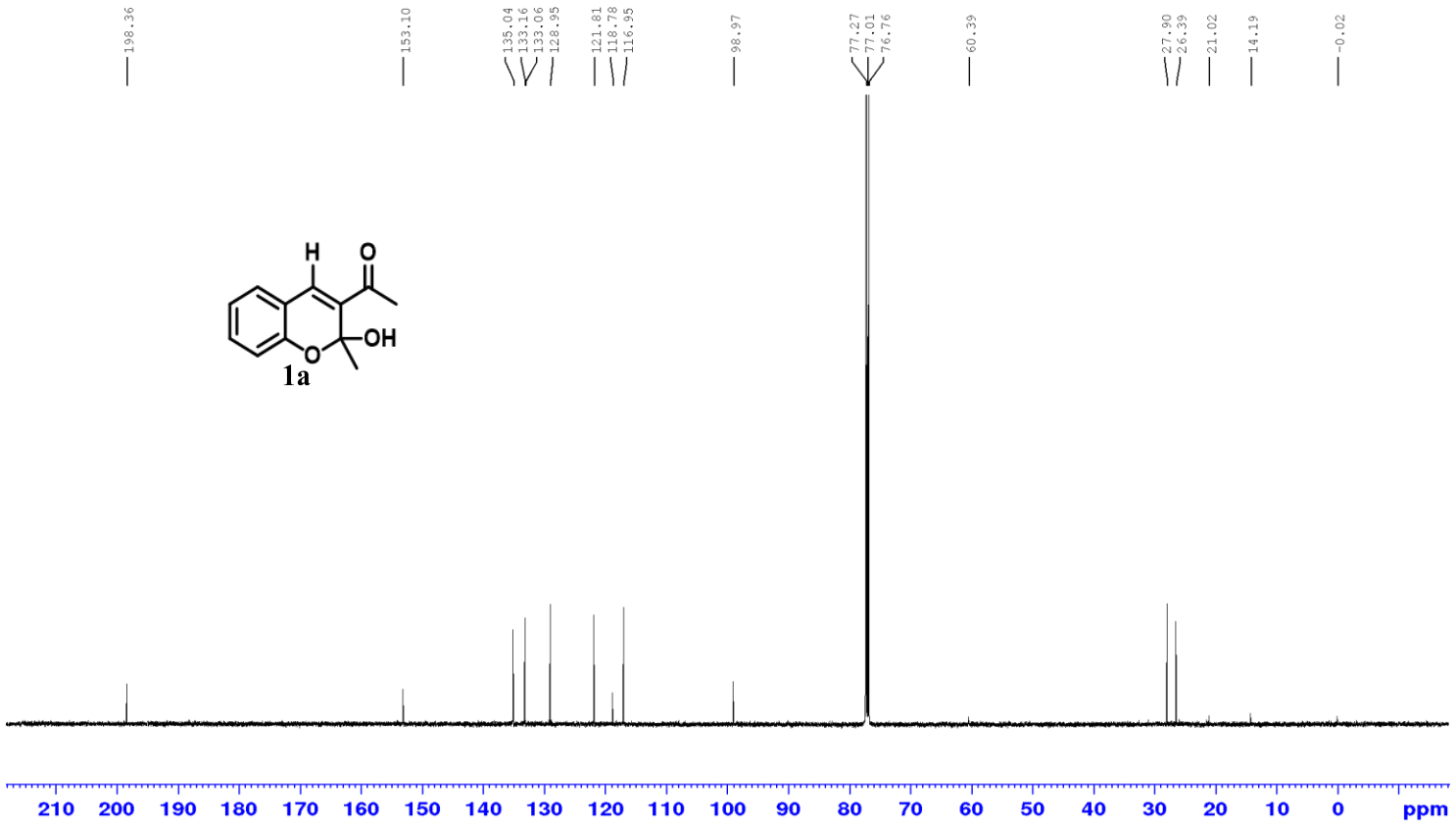
0.94
3.00
3.03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133.06
128.95
121.81
118.78
116.95
98.97
77.27
77.01
76.76
60.39
27.90
26.39
21.02
14.19
-0.02
H
O
OH
O
1a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
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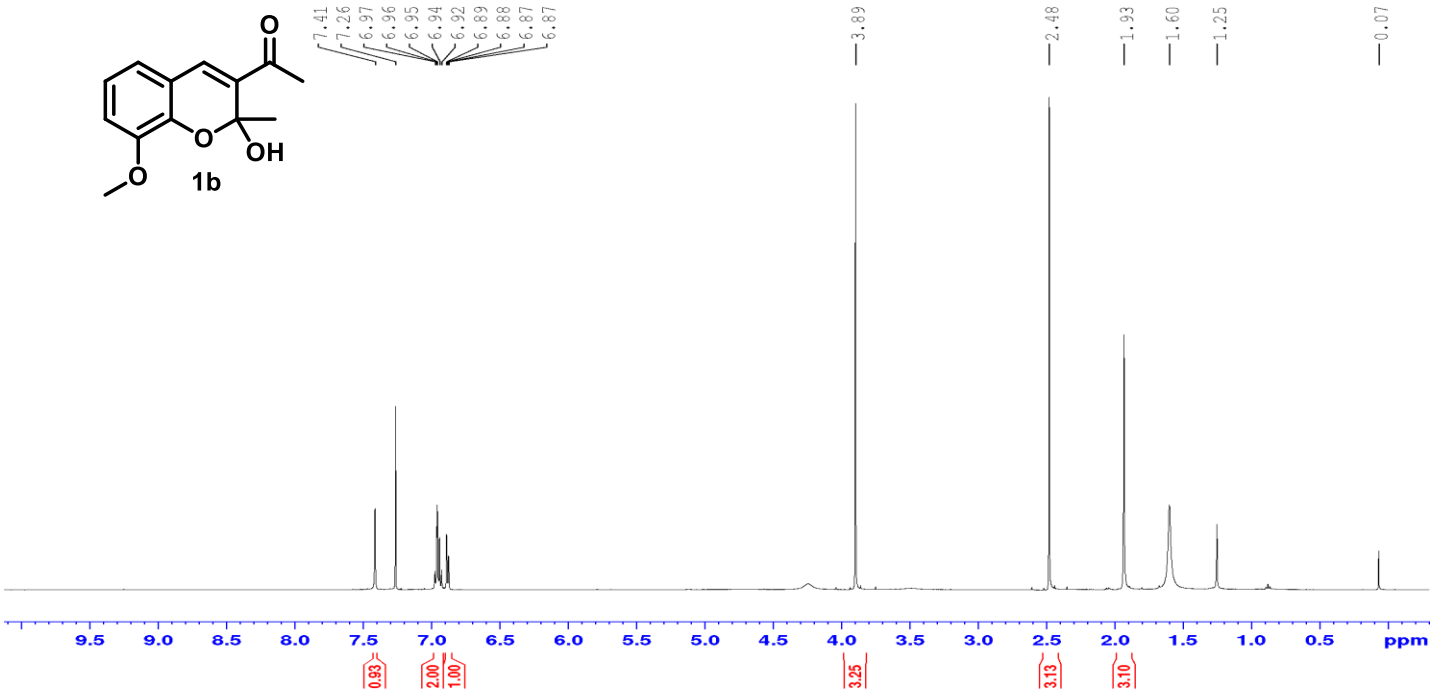
30
20
10
0
ppm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6.89
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1.93
1.60
1.25
0.07
O
O
OH
O
1b
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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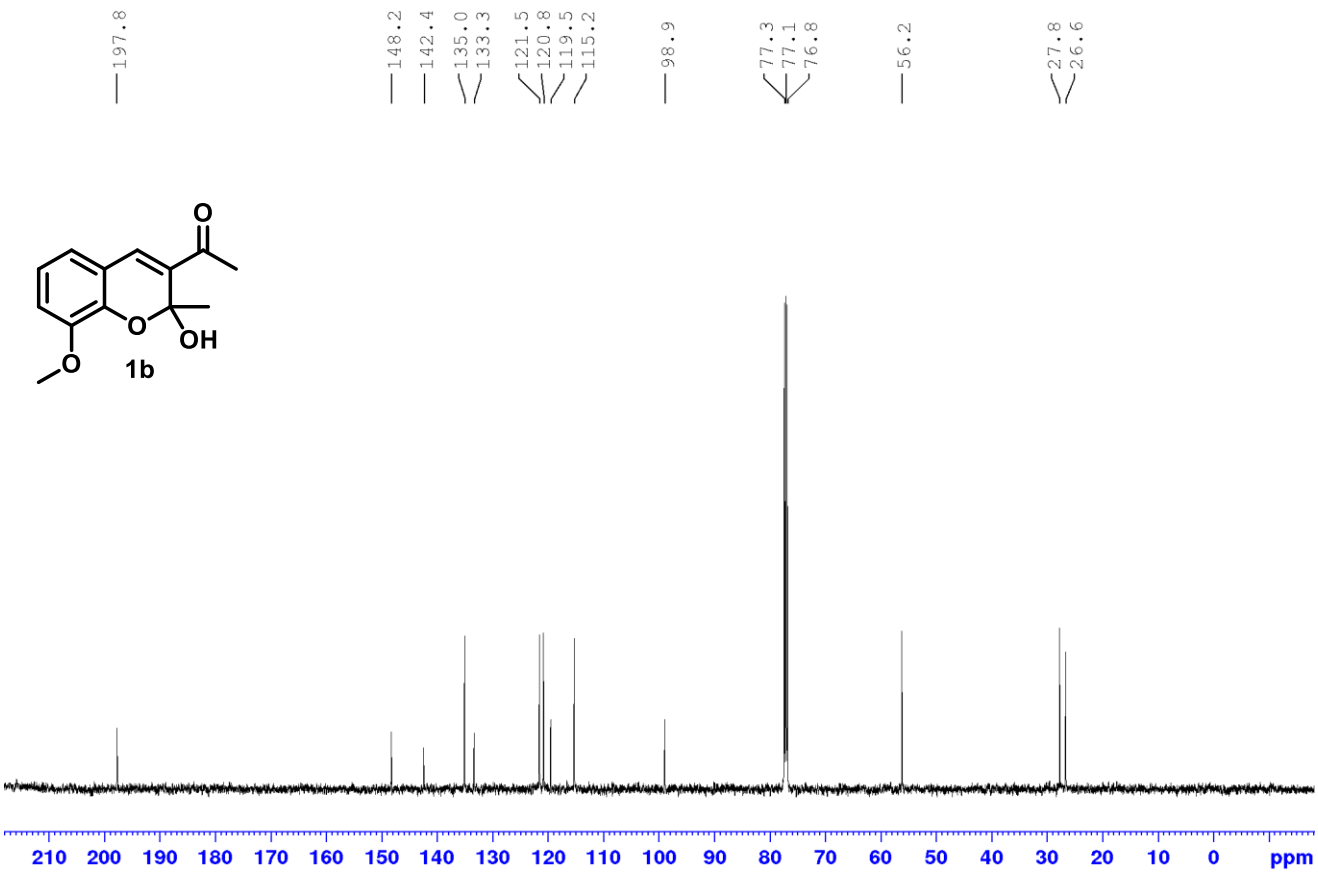
2.00
1.00
3.25
3.13
3.10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120.8
119.5
115.2
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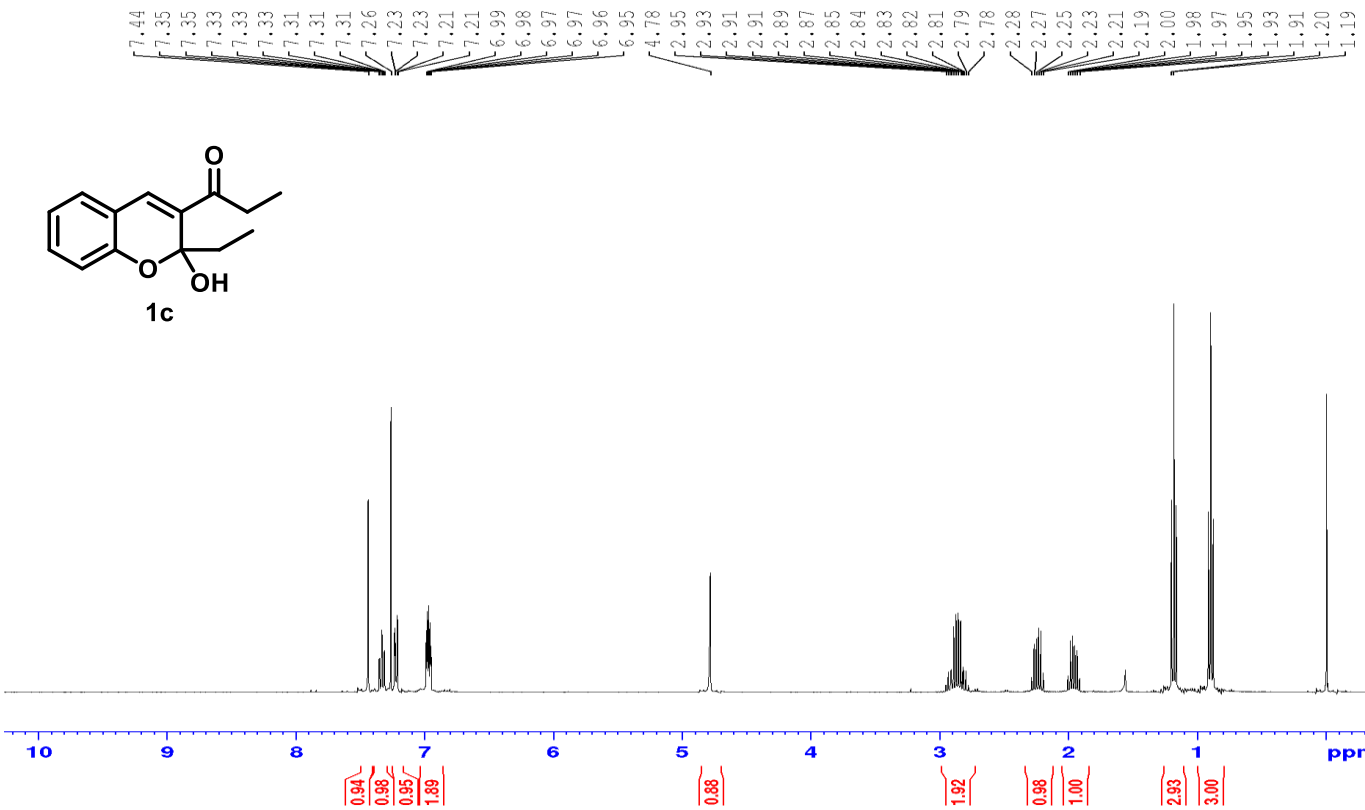
77.3
77.1
76.8
56.2
27.8
26.6
O
O
OH
O
1b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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6.97
6.97
6.96
6.95
4.78
2.95
2.93
2.91
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2.89
2.87
2.85
2.84
2.83
2.82
2.81
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1c
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7
6
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4
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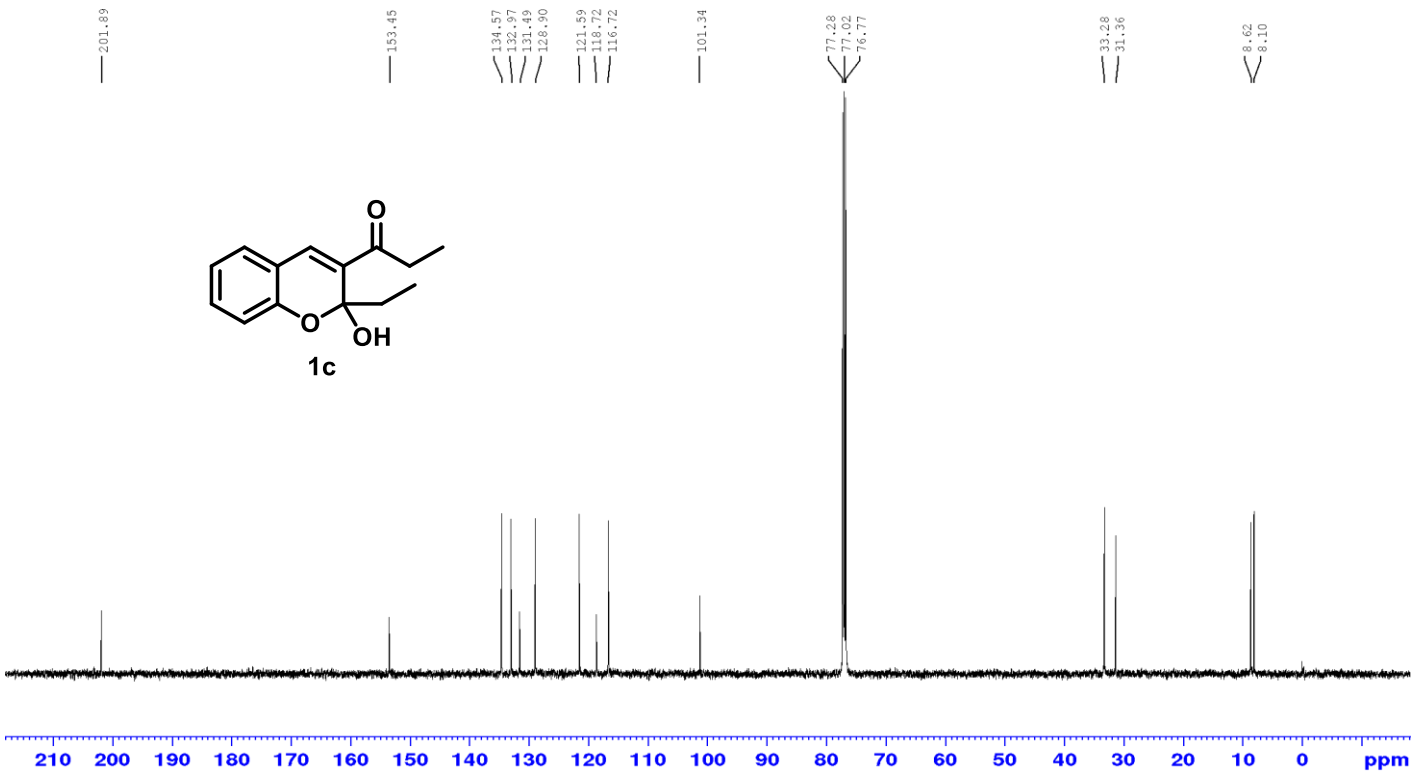
3.00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132.97
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76.77
33.28
31.36
8.62
8.10
O
O
OH
1c
210
200
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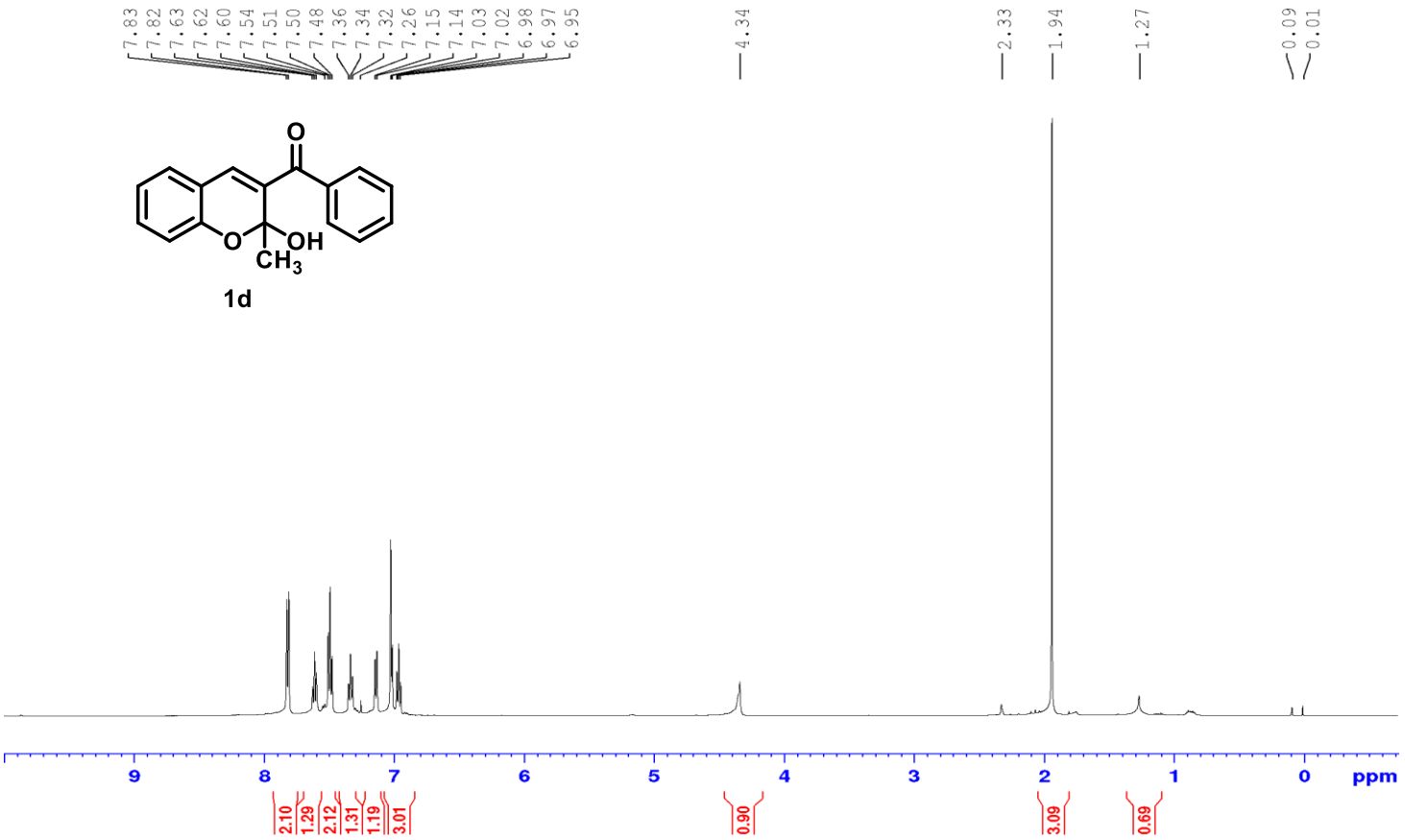
ppm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7.34
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7.26
7.15
7.14
7.03
7.02
6.98
6.97
6.95
4.34
2.33
1.94
1.27
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0.01
O
O
OH
CH3
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8
7
6
5
4
3
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1
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3.01
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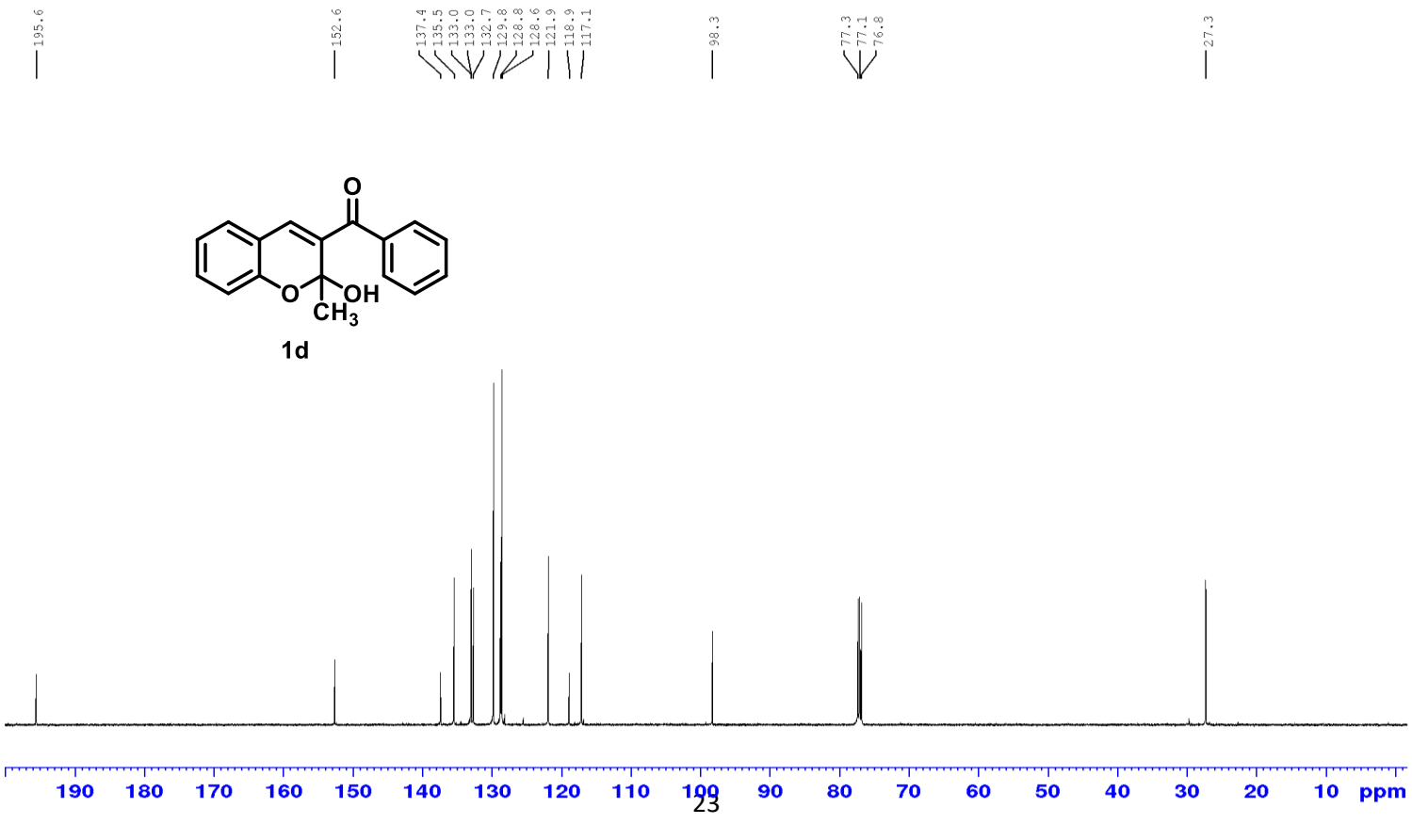
3.09
0.69

1d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OH
CH3
190
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140
130
120
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100
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80
70
60
50
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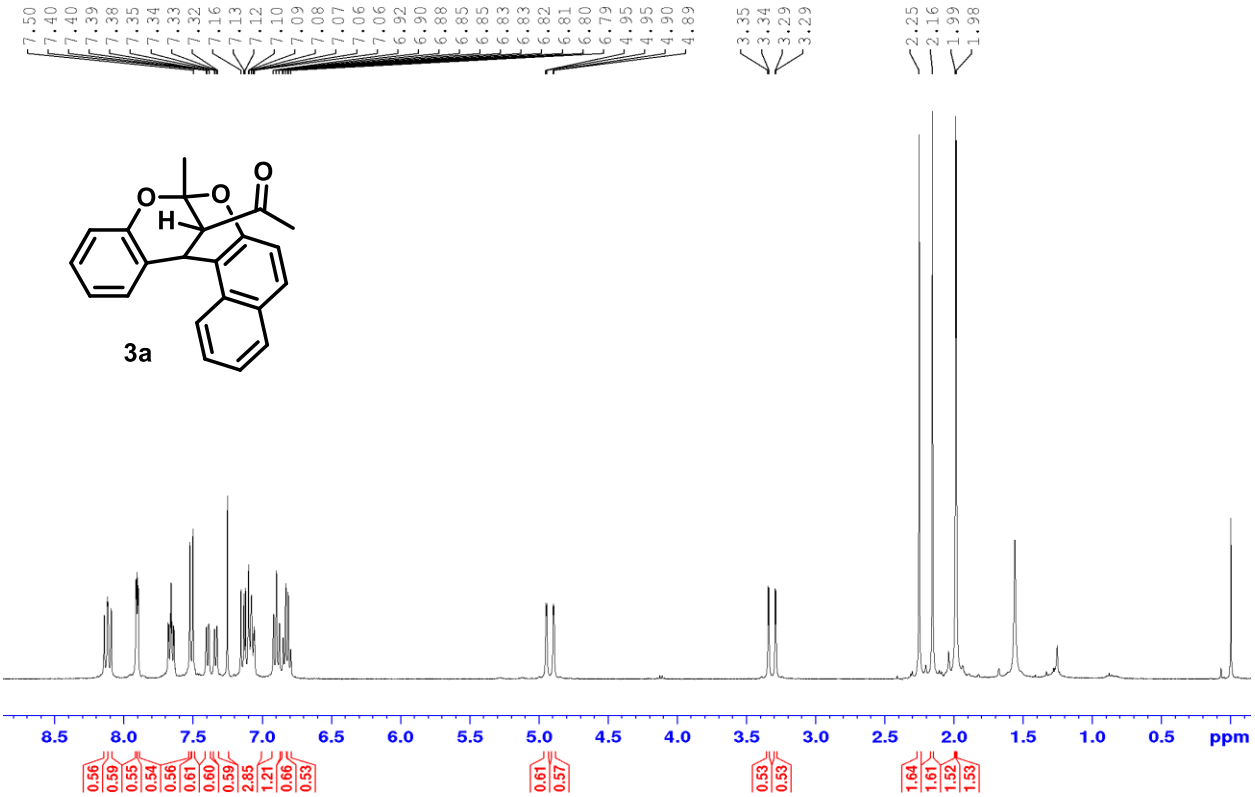
10
ppm

1d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7.33
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7.12
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7.06
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4.90
4.89
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3.34
3.29
3.29
2.25
2.16
1.99
1.98
O
O
H
O
3a
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7.5
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6.5
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3.0
2.5
2.0
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0.54
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0.60
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0.53
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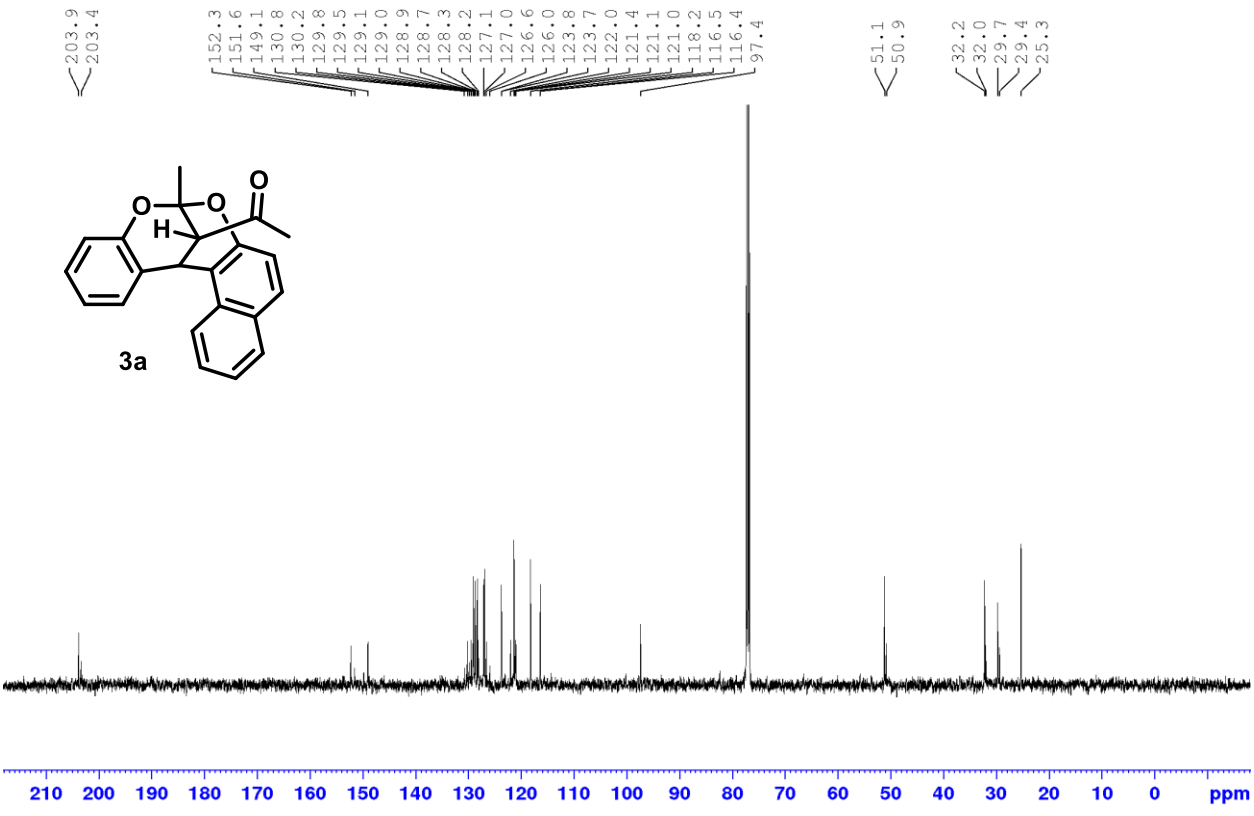
1.61
1.52
1.53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128.3
128.2
127.1
127.0
126.6
126.0
123.8
123.7
122.0
121.4
121.1
121.0
118.2
116.5
116.4
97.4
51.1
50.9
32.2
32.0
29.7
29.4
25.3
O
O
H
O
3a
210
200
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60
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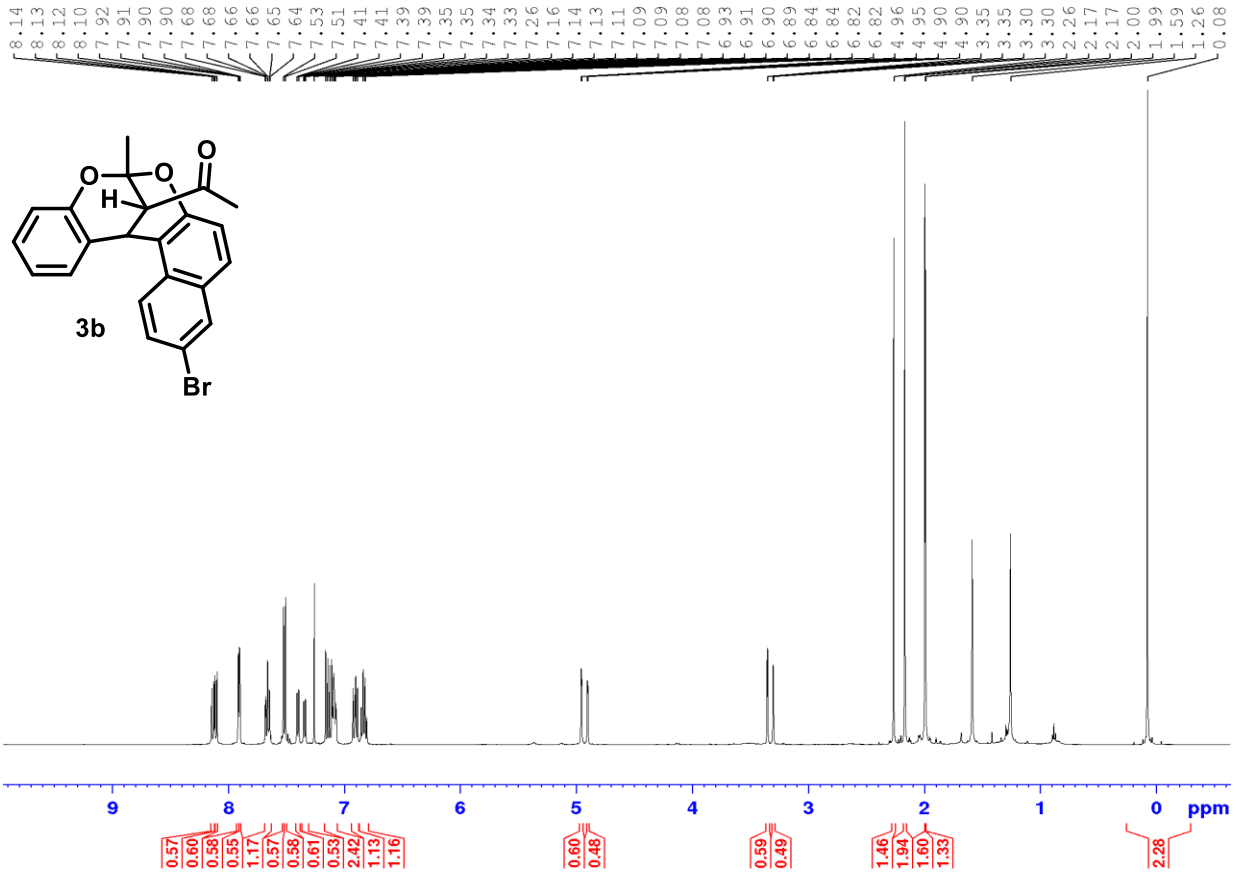
ppm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7.90
7.90
7.68
7.68
7.66
7.66
7.65
7.64
7.53
7.51
7.41
7.41
7.39
7.39
7.35
7.35
7.34
7.33
7.26
7.16
7.14
7.13
7.11
7.09
7.09
7.08
7.08
6.93
6.91
6.90
6.89
6.84
6.84
6.82
6.82
4.96
4.95
4.90
4.90
3.35
3.35
3.30
3.30
2.26
2.17
2.17
2.00
1.99
1.59
1.26
0.08
O
O
O
H
3b
Br
9
8
7
6
5
4
3
2
1
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ppm
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0.58
0.55
1.17
0.57
0.58
0.61
0.53
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0.49
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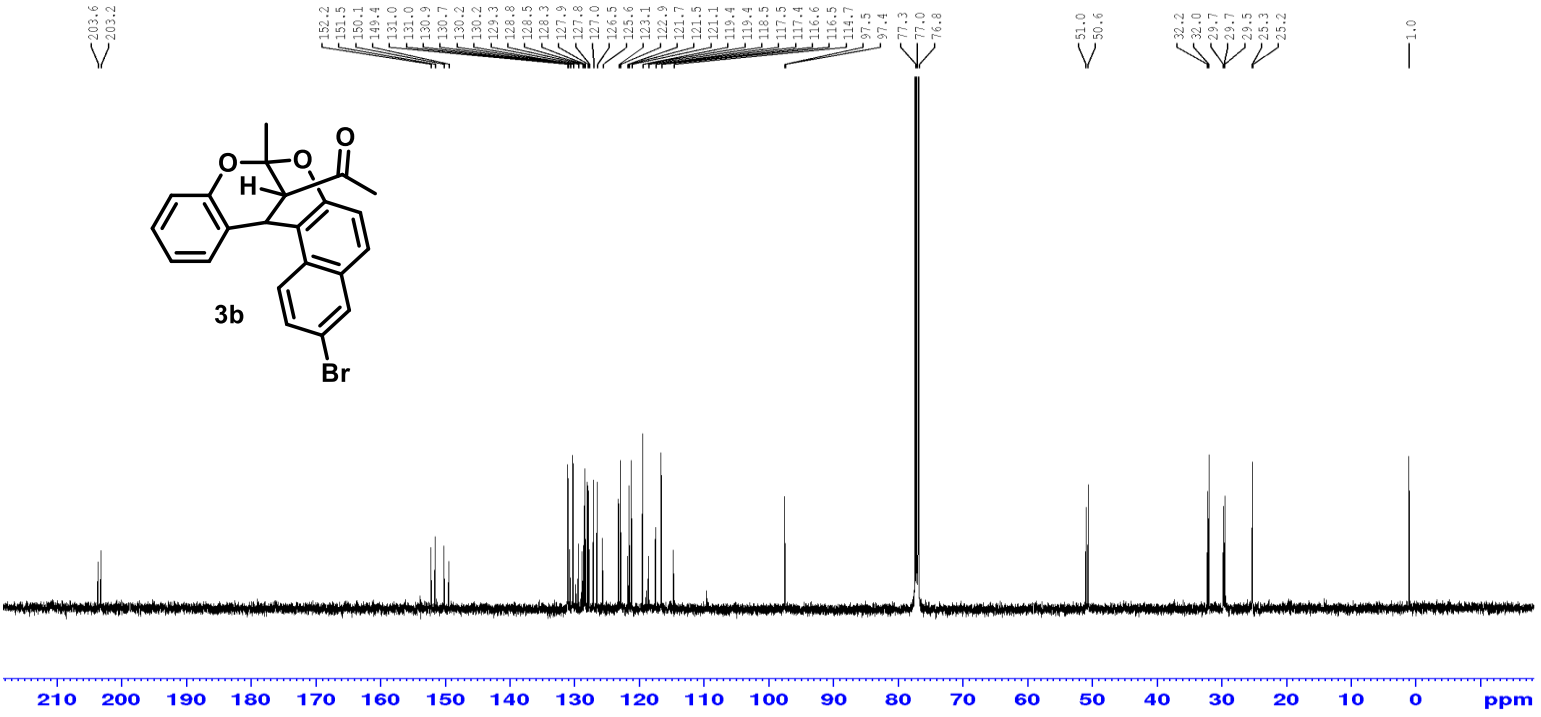
1.60
1.33
2.28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128.3
127.9
127.8
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123.1
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121.7
121.5
121.1
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118.5
117.5
117.4
116.6
116.5
114.7
97.5
97.4
77.3
77.0
76.8
51.0
50.6
32.2
32.0
29.7
29.7
29.5
25.3
25.2
1.0
O
O
O
H
3b
Br
210
200
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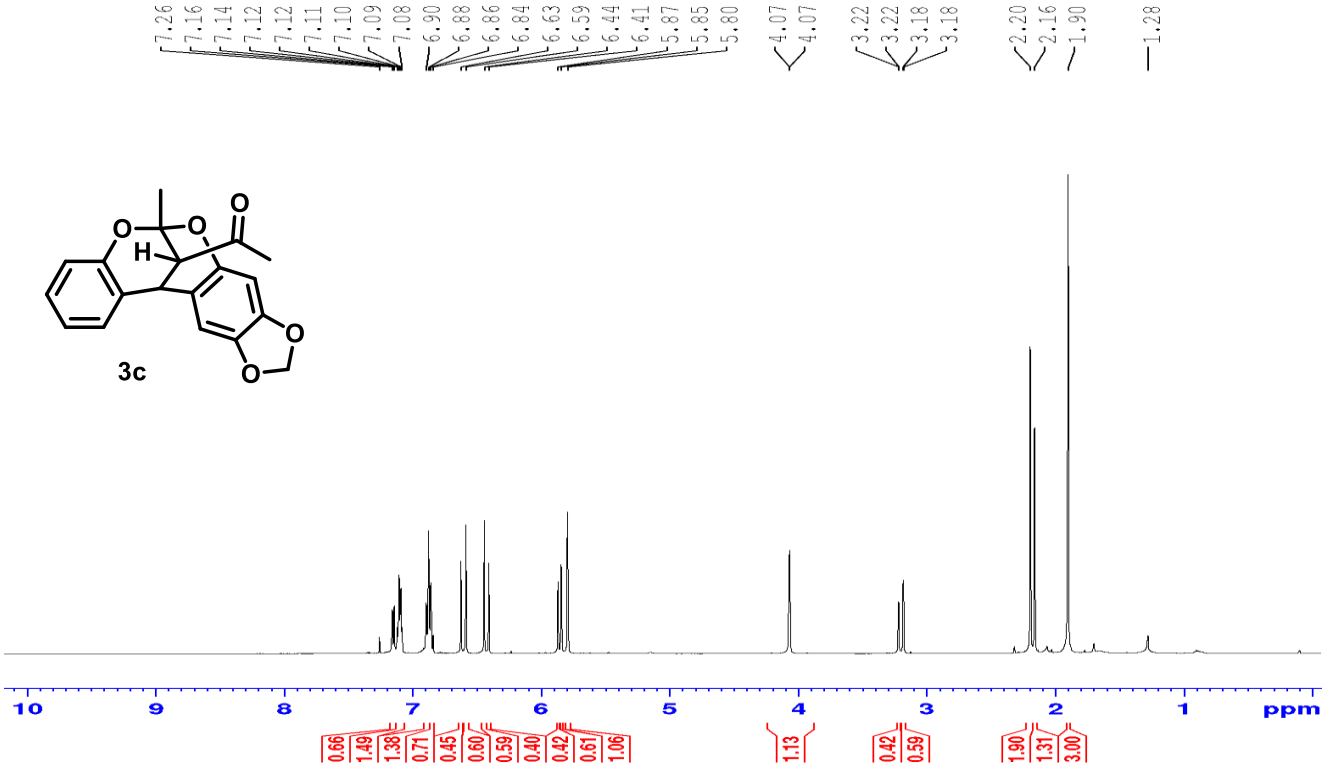
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6.84
6.63
6.59
6.44
6.41
5.87
5.85
5.80
4.07
4.07
3.22
3.22
3.18
3.18
2.20
2.16
1.90
1.28
3c
10
9
8
7
6
5
4
3
2
1
ppm
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0.71
0.45
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0.42
0.59
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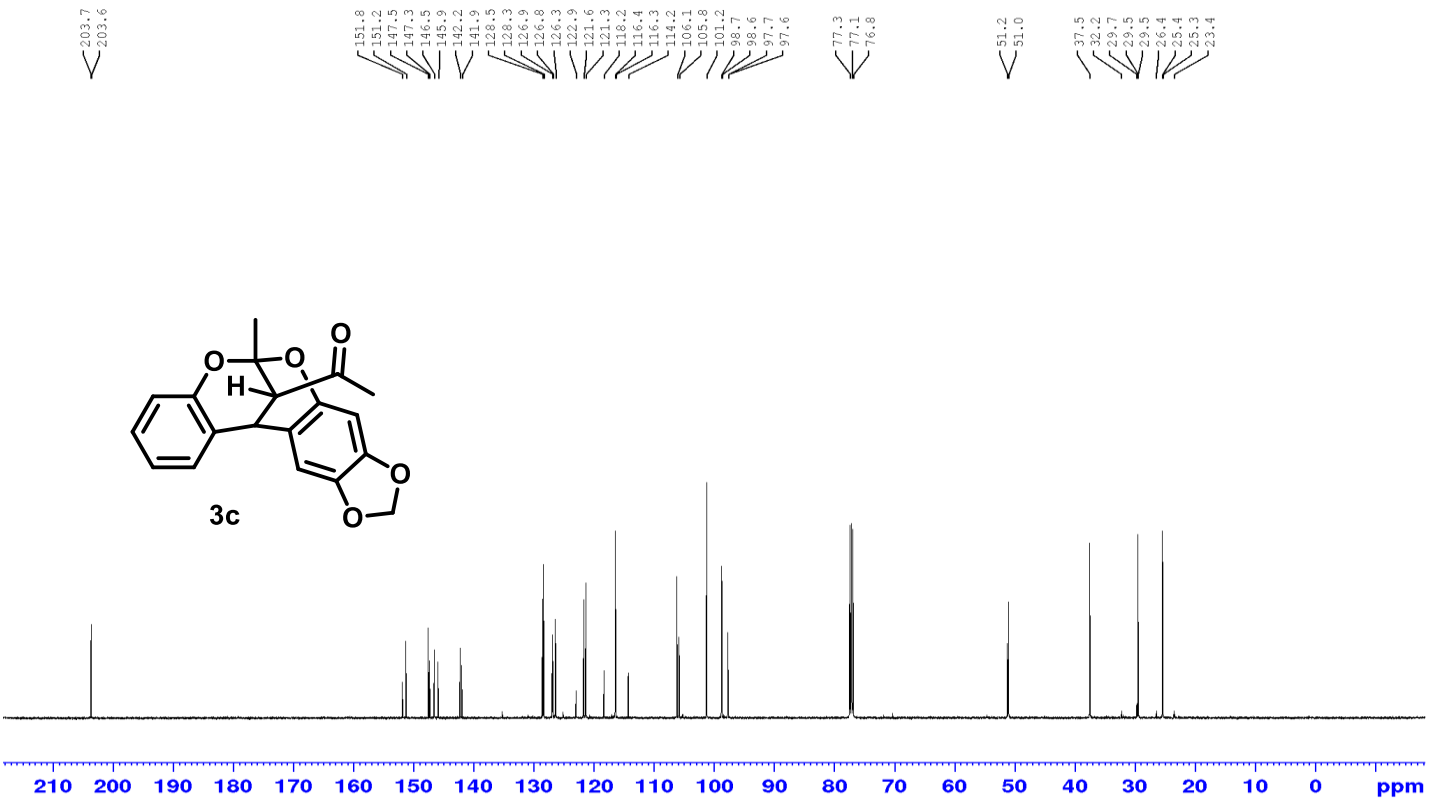
3.00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126.8
126.3
122.9
121.6
121.3
118.2
116.4
116.3
114.2
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105.8
101.2
98.7
98.6
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76.8
51.2
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32.2
29.7
29.5
29.5
26.4
25.4
25.3
23.4
3c
210
200
190
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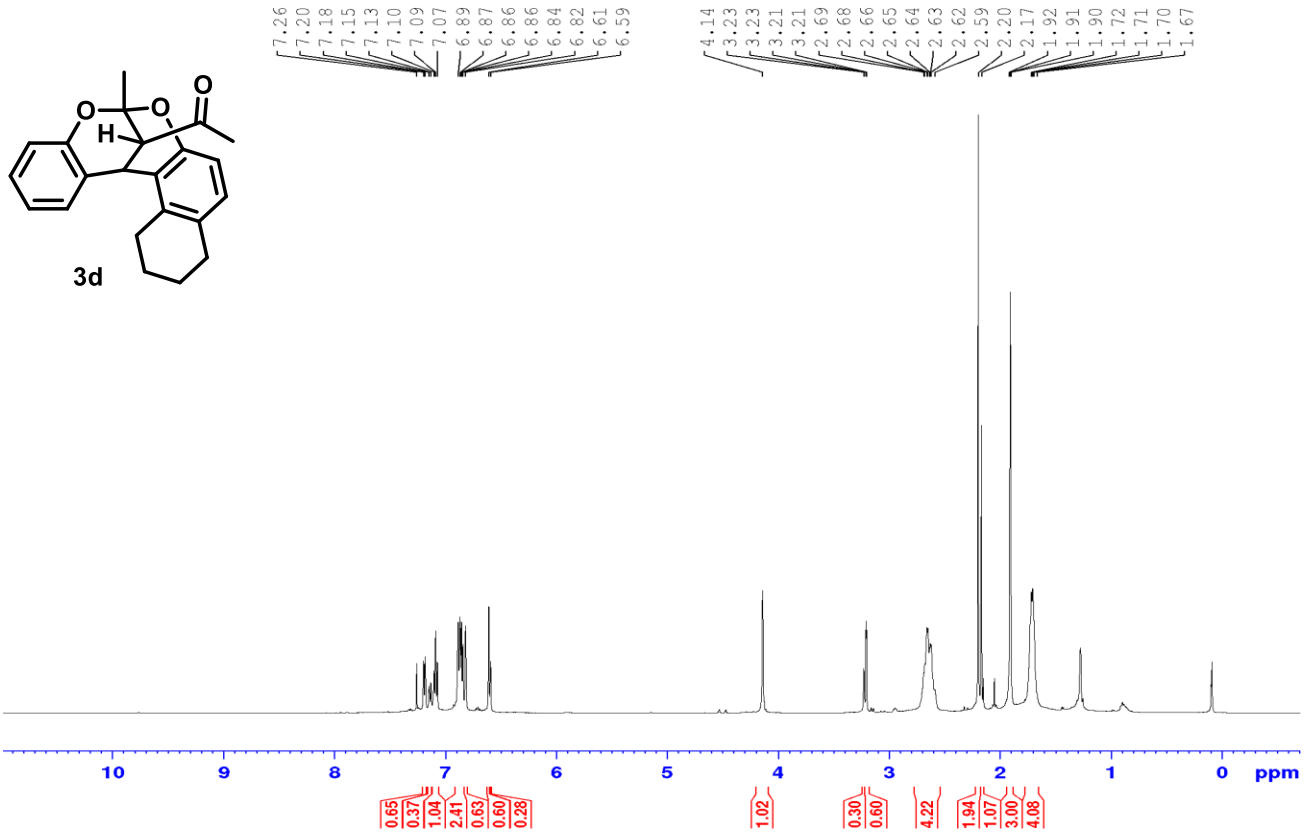
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6.82
6.61
6.59
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3.23
3.21
3.21
2.69
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2.66
2.65
2.64
2.63
2.62
2.59
2.20
2.17
1.92
1.91
1.90
1.72
1.71
1.70
1.67
O
O
H
O
3d
10
9
8
7
6
5
4
3
2
1
0
ppm
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0.37
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4.22
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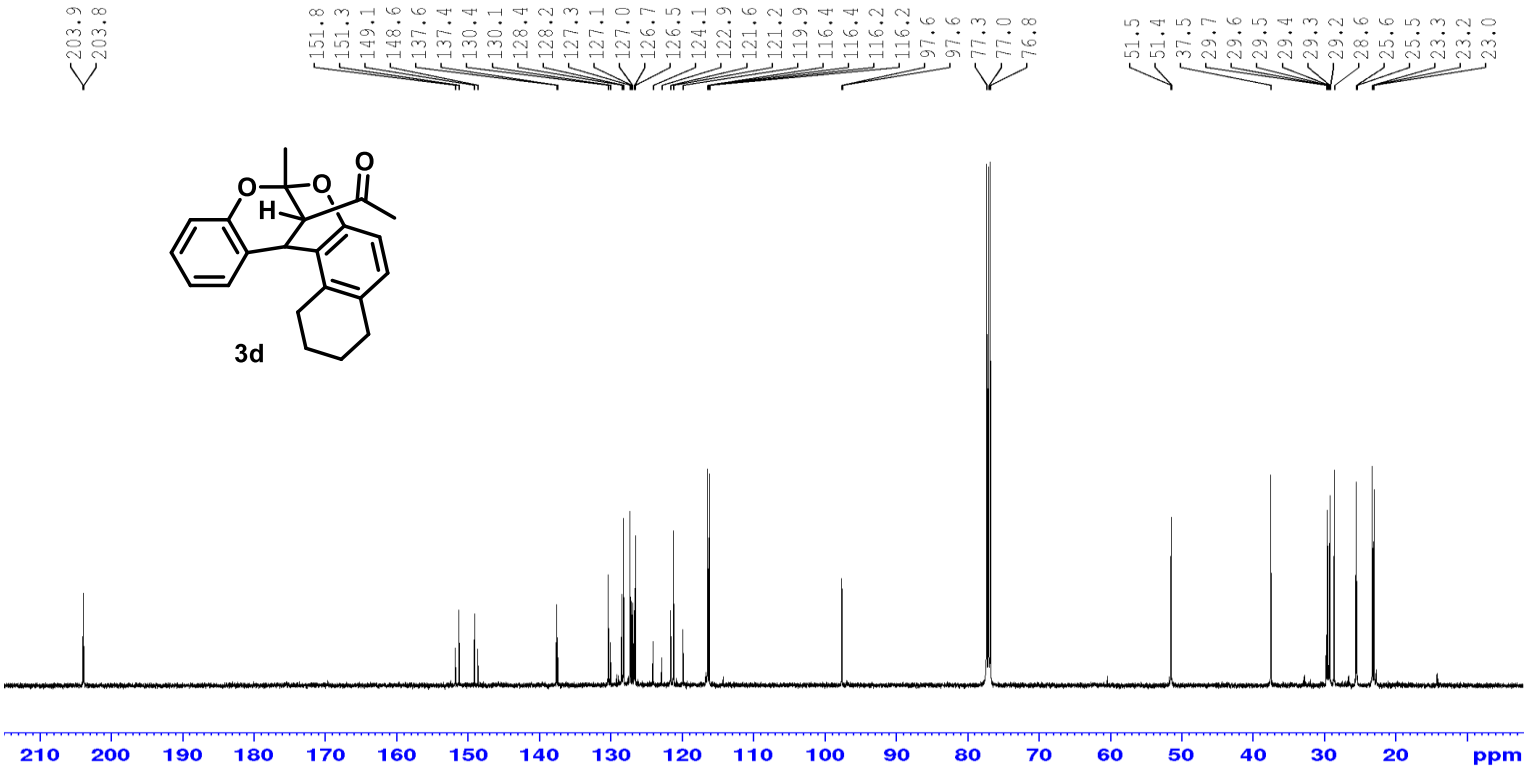
1.07
3.00
4.08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137.4
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127.1
127.0
126.7
126.5
124.1
122.9
121.6
121.2
119.9
116.4
116.4
116.2
116.2
97.6
97.6
77.3
77.0
76.8
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51.4
37.5
29.7
29.6
29.5
29.4
29.3
29.2
28.6
25.6
25.5
23.3
23.2
23.0
O
O
H
O
3d
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200
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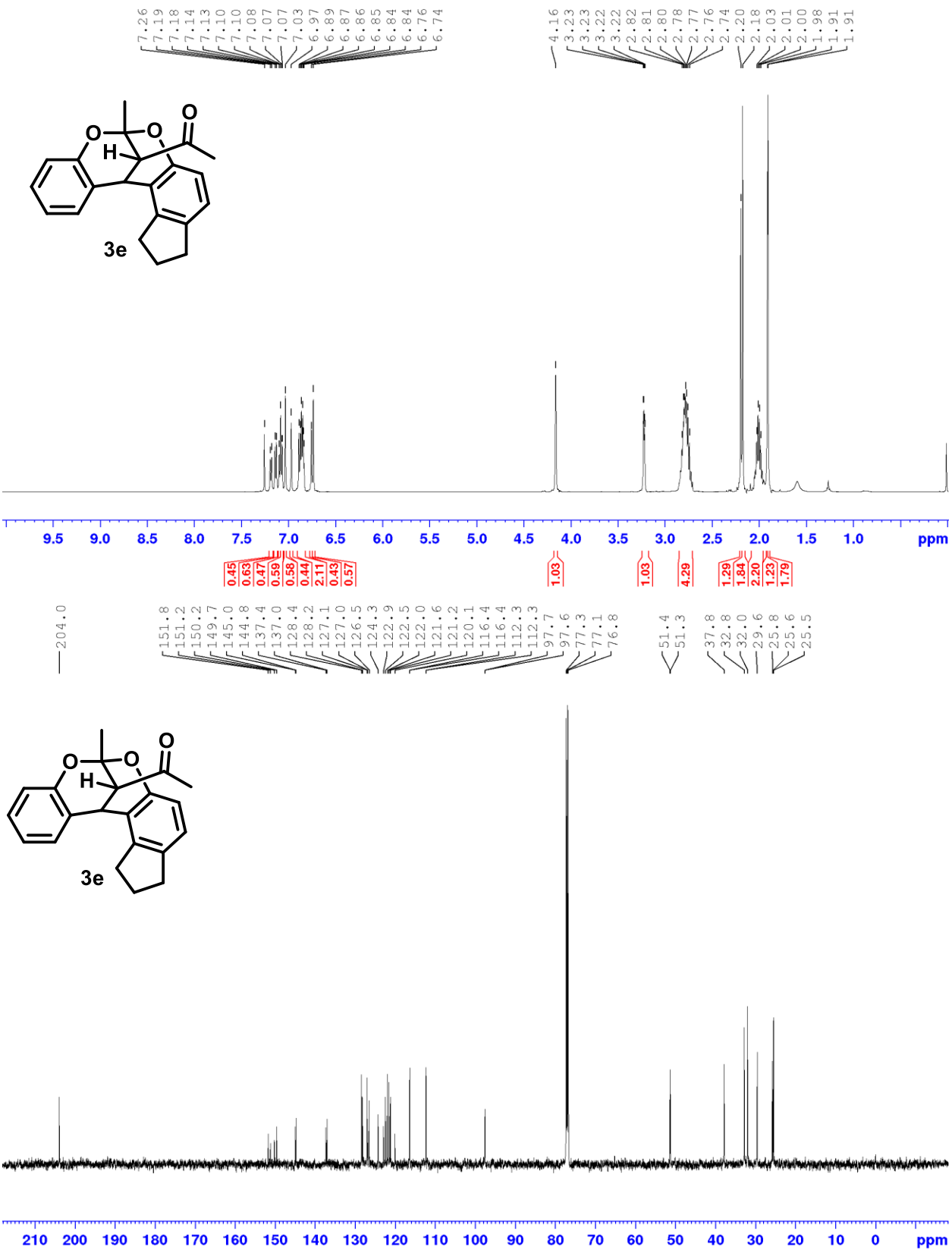
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.19
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7.14
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7.10
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7.07
7.03
6.97
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6.87
6.86
6.85
6.84
6.84
6.76
6.74
4.16
3.23
3.23
3.22
3.22
2.82
2.81
2.80
2.78
2.77
2.76
2.74
2.20
2.18
2.03
2.01
2.00
1.98
1.91
1.91
O
O
O
H
3e
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 ppm
0.45
0.63
0.47
0.59
0.58
0.44
2.11
0.43
0.57
1.03
1.03
4.29
1.29
1.84
2.20
1.23
1.79
204.0
151.8
151.2
150.2
149.7
145.0
144.8
137.4
137.0
128.4
128.2
127.1
127.0
126.5
124.3
122.9
122.5
122.0
121.6
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116.4
116.4
112.3
112.3
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77.1
76.8
51.4
51.3
37.8
32.8
32.0
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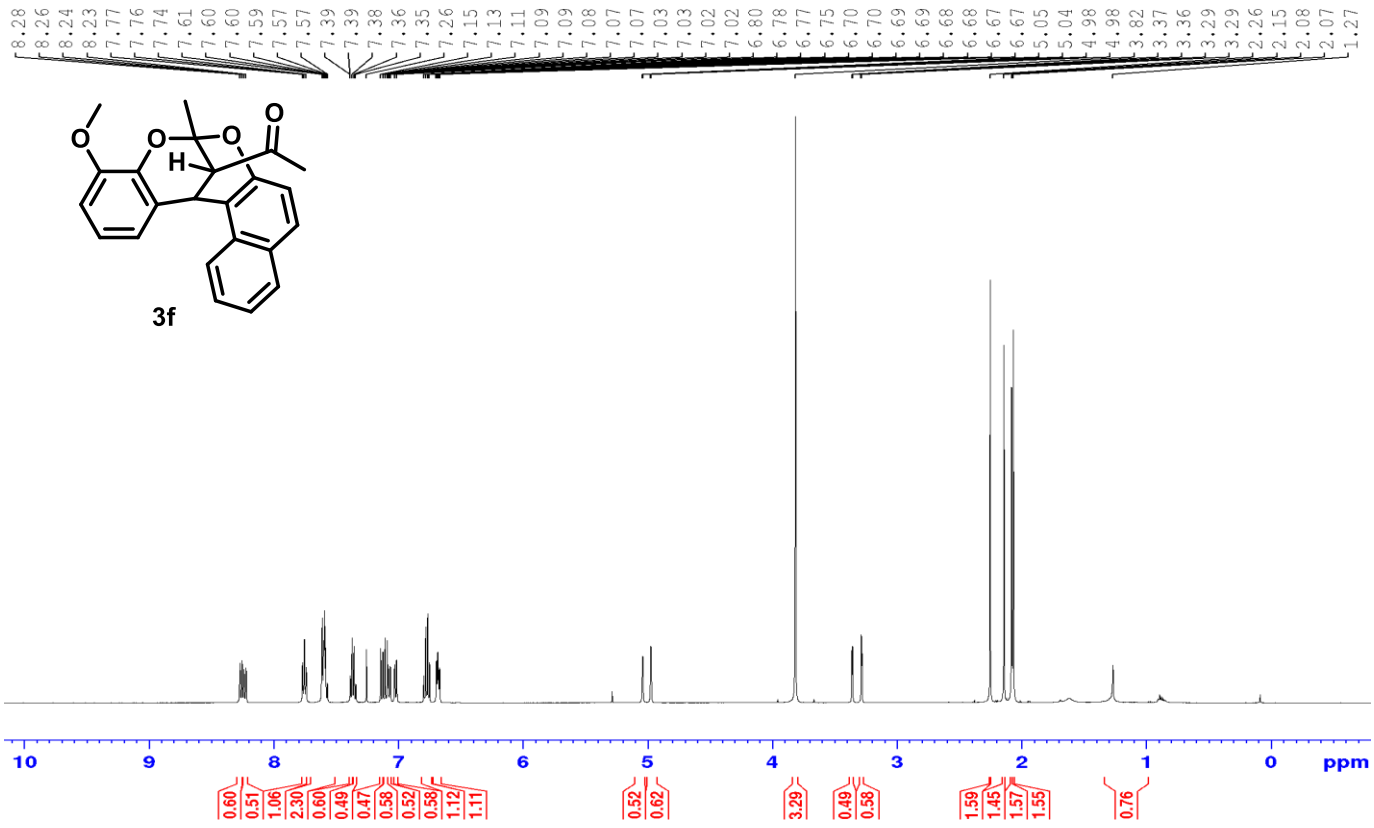
25.5
O
O
O
H
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.57
7.39
7.39
7.38
7.36
7.35
7.26
7.15
7.13
7.11
7.09
7.09
7.08
7.07
7.07
7.03
7.03
7.02
7.02
6.80
6.78
6.77
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6.69
6.69
6.68
6.67
6.67
5.05
5.04
4.98
4.98
3.82
3.37
3.36
3.29
3.29
2.26
2.15
2.08
2.07
1.27
O
O
O
H
O
3f
10
9
8
7
6
5
4
3
2
1
0
ppm
0.60
0.51
1.06
2.30
0.60
0.49
0.47
0.58
0.52
0.58
1.12
1.11
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0.62
3.29
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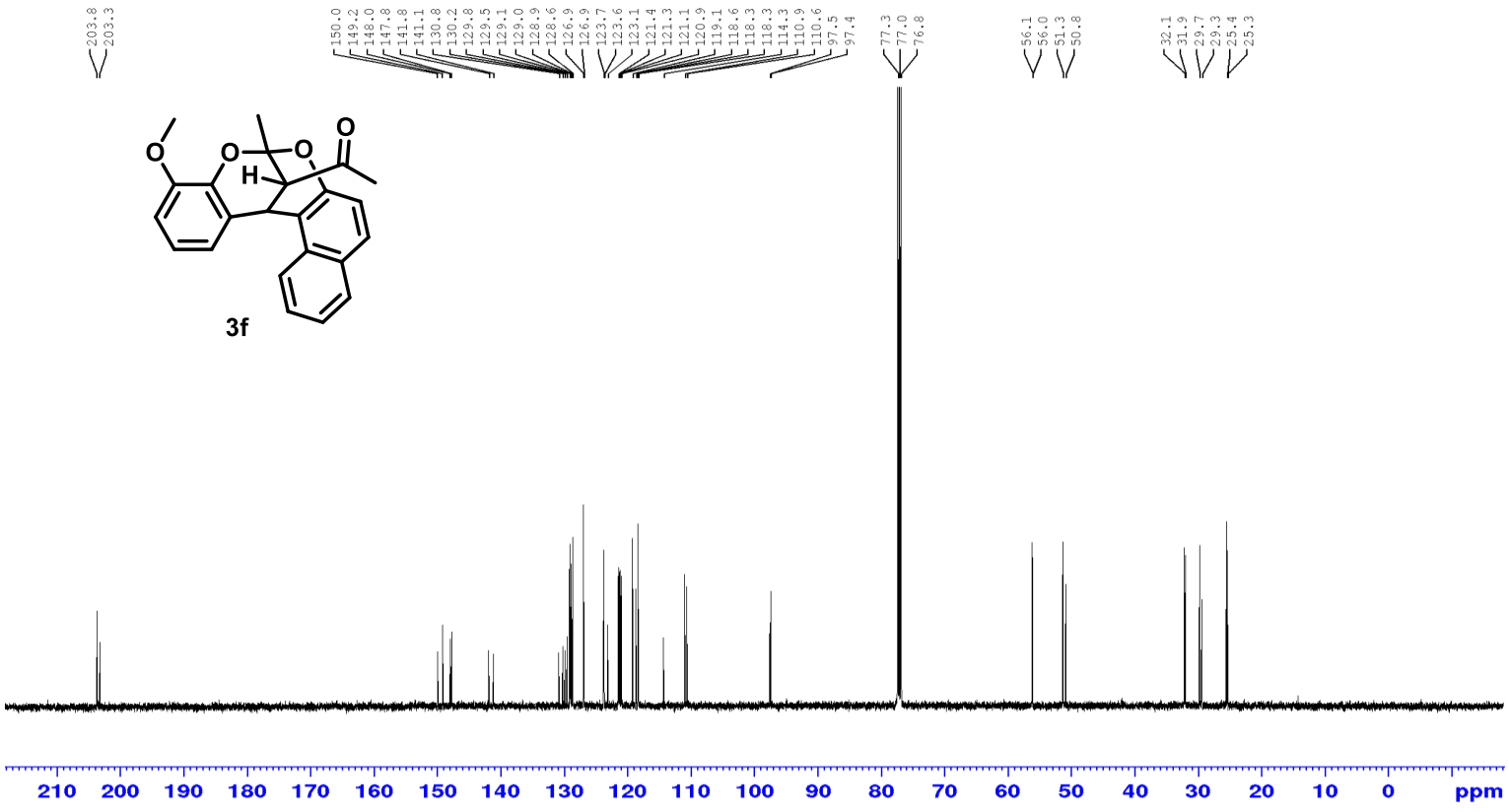
1.59
1.45
1.57
1.55
0.76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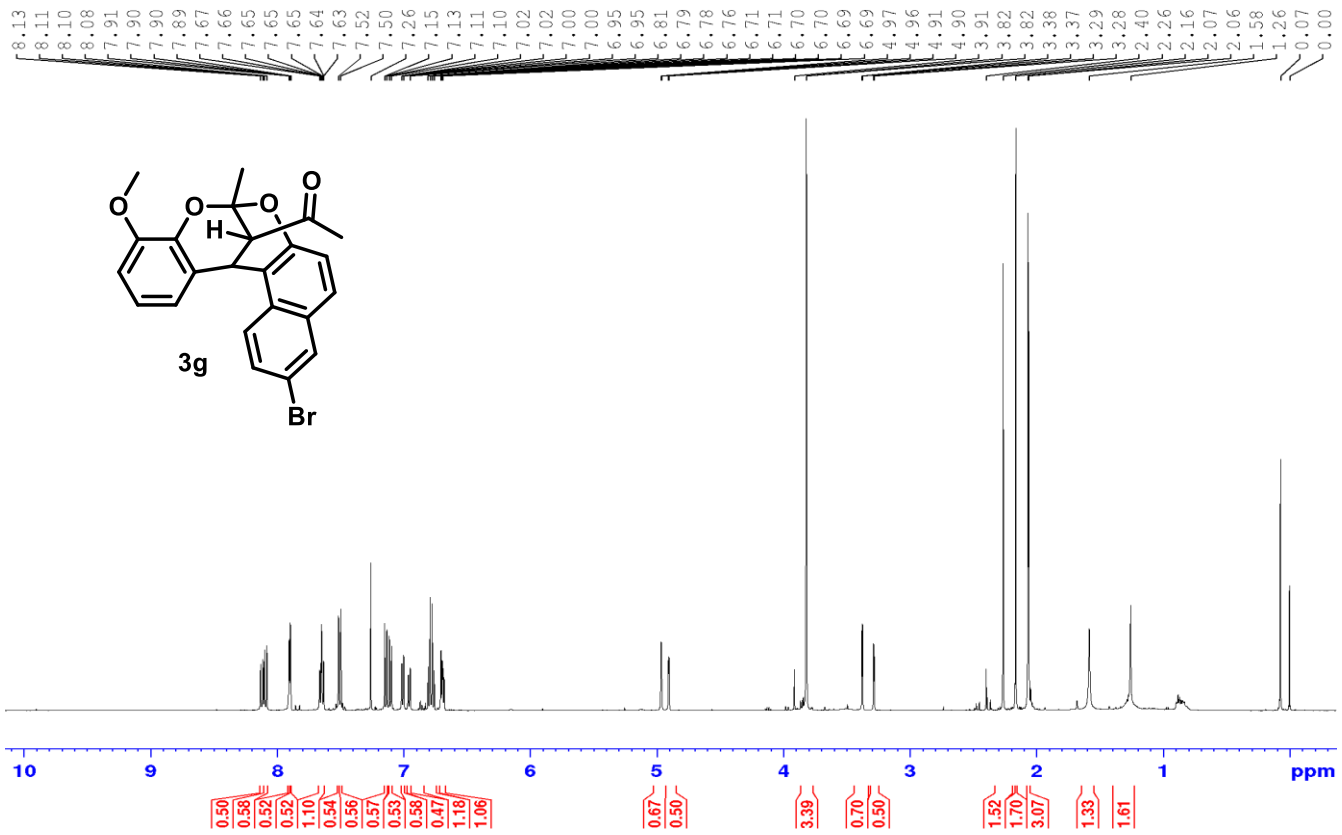
130.8
130.2
129.8
129.5
129.1
129.0
128.9
128.6
126.9
126.9
123.7
123.6
123.1
121.4
121.3
121.1
120.9
119.1
118.6
118.3
118.3
114.3
110.9
110.6
97.5
97.4
77.3
77.0
76.8
56.1
56.0
51.3
50.8
32.1
31.9
29.7
29.3
25.4
25.3
O
O
O
H
O
3f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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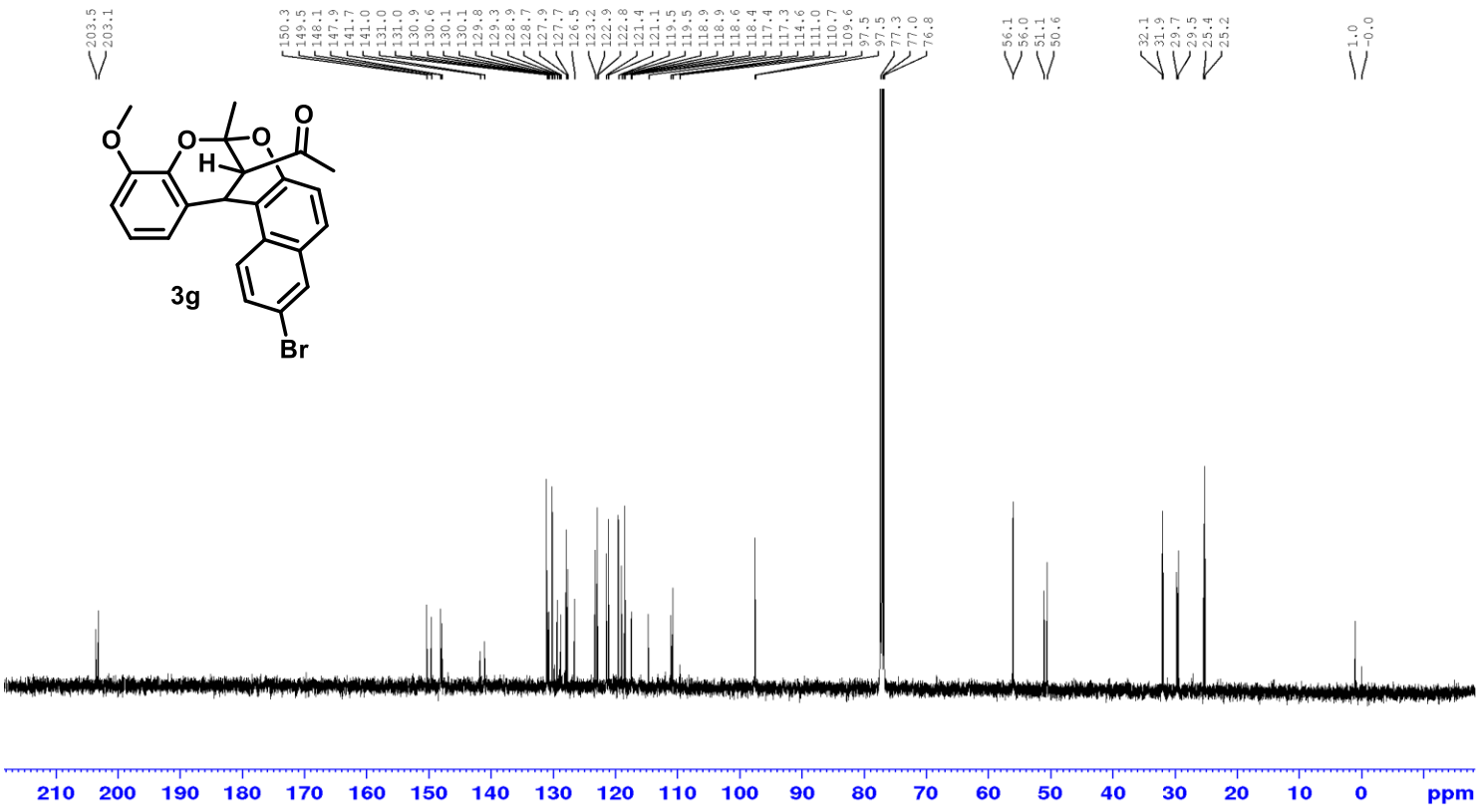
O
O
O
H
O
3g
Br
10 9 8 7 6 5 4 3 2 1 ppm
0.50 0.58 0.52 0.52 1.10 0.54 0.56 0.57 0.53 0.58 0.47 1.18 1.06
0.67 0.50
3.39
0.70 0.50
1.52 1.70 3.07
1.33
1.61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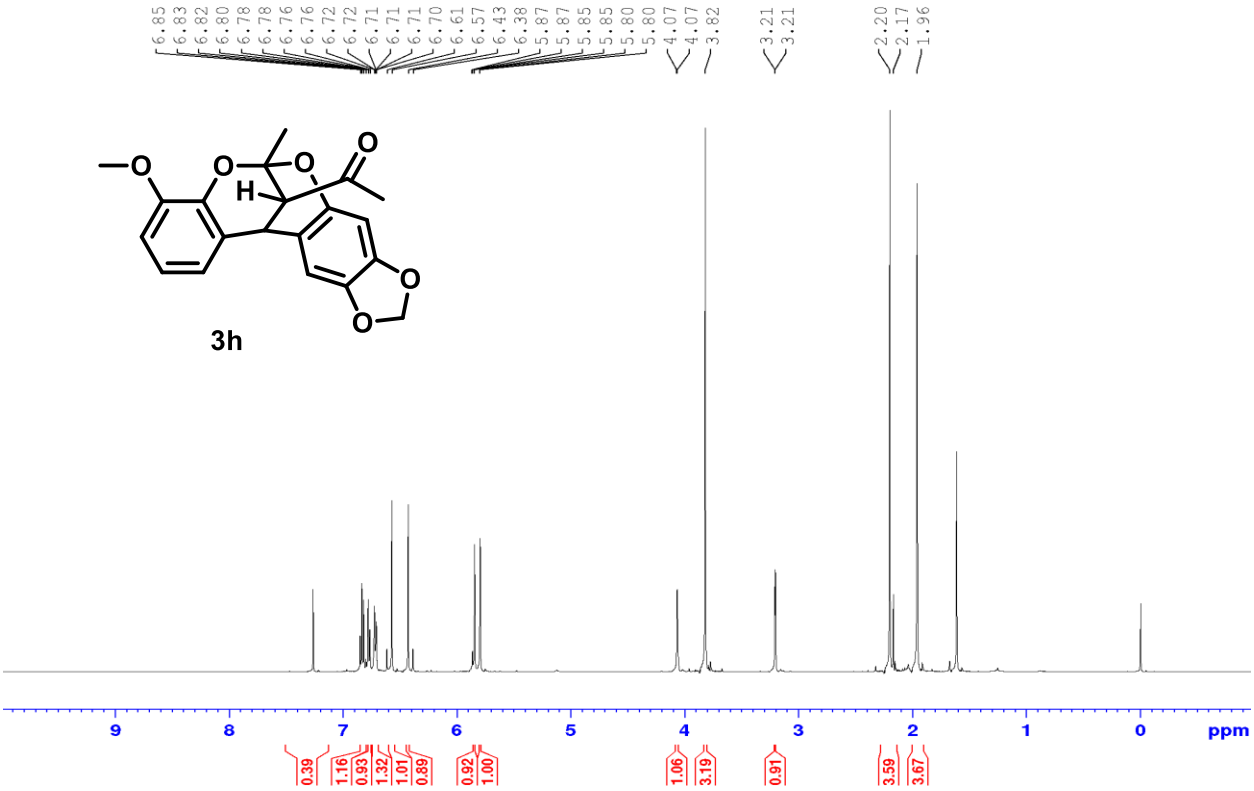
56.1 56.0 51.1 50.6
32.1 31.9 29.7 29.5 25.4 25.2
1.0 -0.0
O
O
O
H
O
3g
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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6.78
6.76
6.76
6.72
6.72
6.71
6.71
6.71
6.70
6.61
6.57
6.43
6.38
5.87
5.87
5.85
5.85
5.80
5.80
4.07
4.07
3.82
3.21
3.21
2.20
2.17
1.96
O
O
O
O
H
O
O
3h
9
8
7
6
5
4
3
2
1
0
ppm
0.39
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0.93
1.32
1.01
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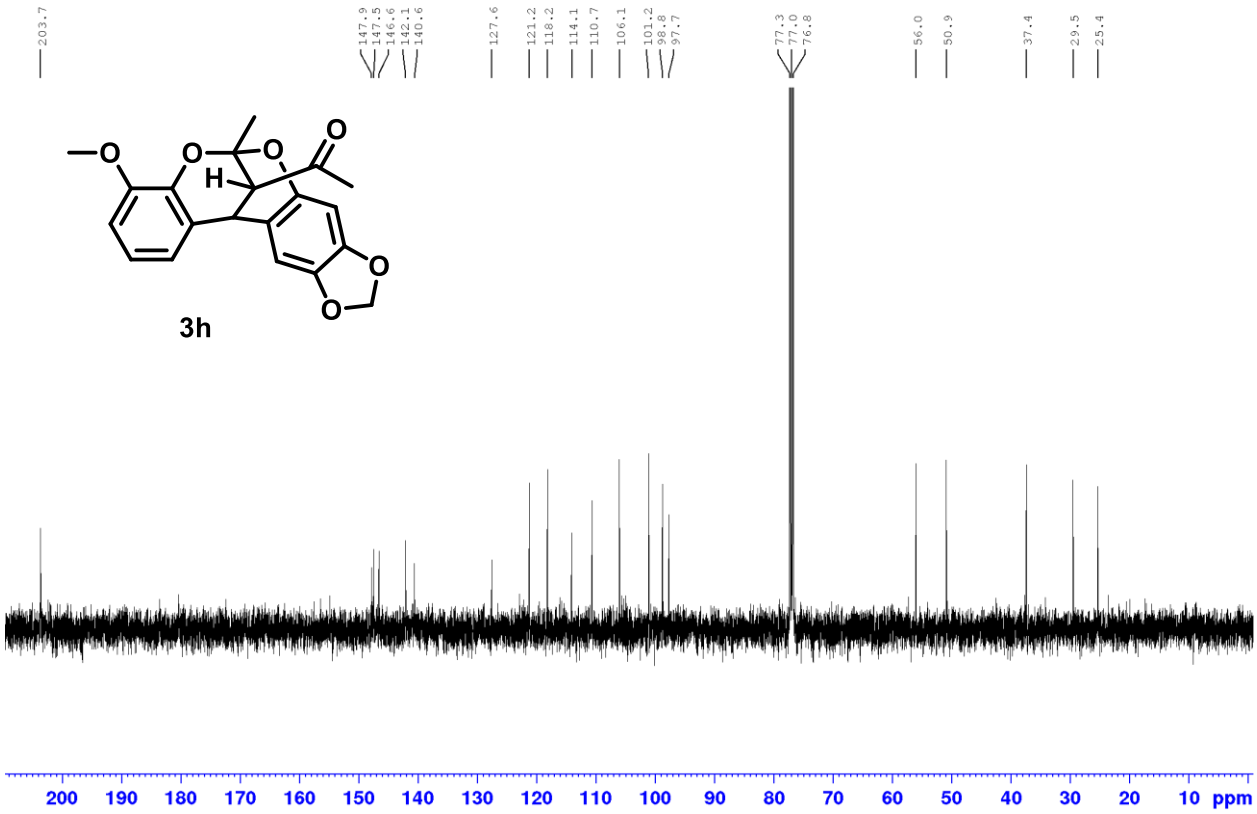
0.92
1.00
1.06
3.19
0.91
3.59
3.67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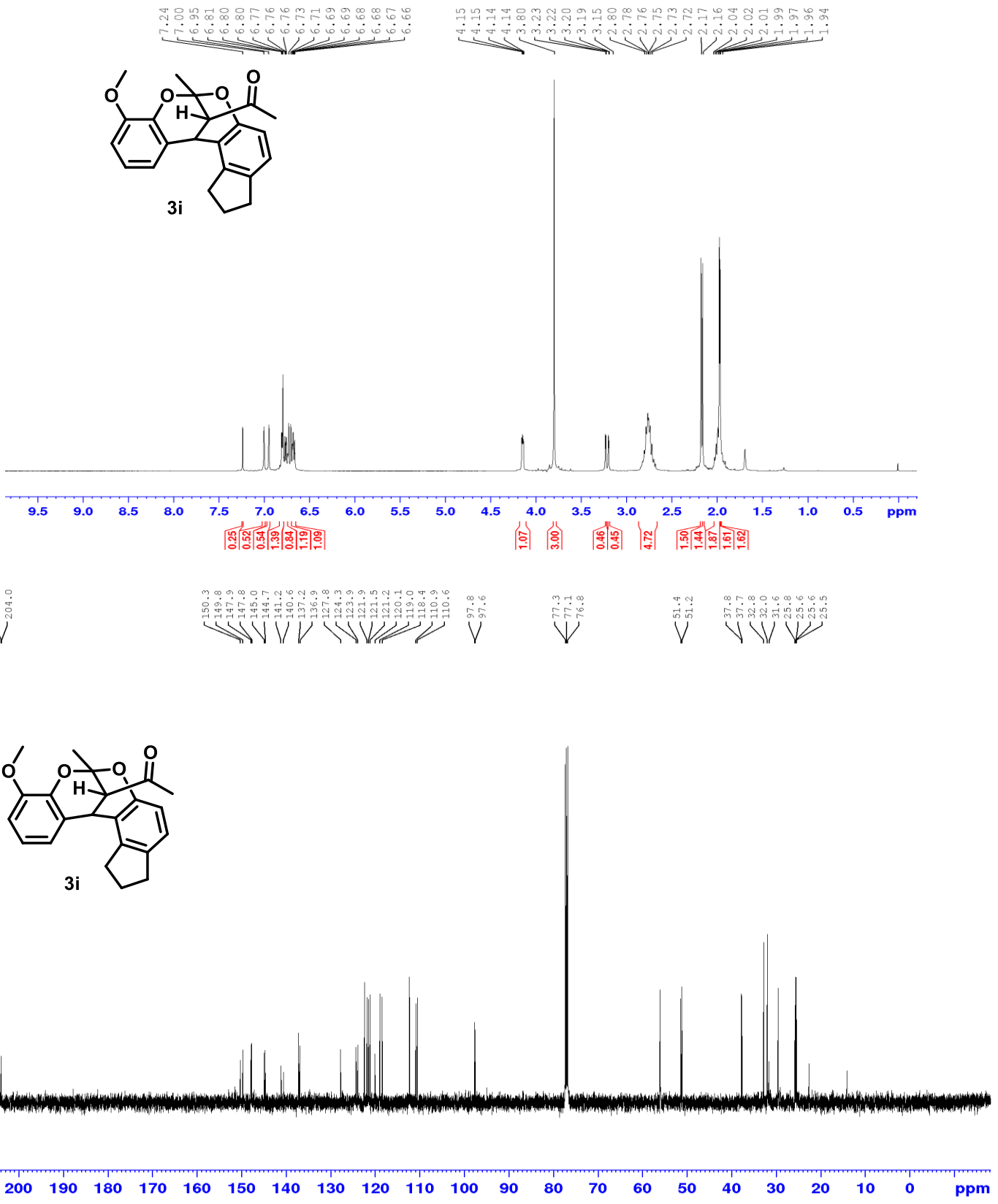
127.6
121.2
118.2
114.1
110.7
106.1
101.2
98.8
97.7
77.3
77.0
76.8
56.0
50.9
37.4
29.5
25.4
O
O
O
O
H
O
O
3h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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6.76
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6.73
6.71
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6.69
6.68
6.68
6.67
6.66
4.15
4.15
4.14
4.14
3.80
3.23
3.22
3.20
3.19
3.15
2.80
2.78
2.76
2.75
2.73
2.72
2.17
2.16
2.04
2.02
2.01
1.99
1.97
1.96
1.94
3i
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 ppm
0.25
0.52
0.54
1.38
0.84
1.19
1.09
1.07
3.00
0.46
0.45
4.72
1.50
1.44
1.87
1.61
1.62
204.0
204.0
150.3
149.8
147.9
147.8
145.0
144.7
141.2
140.6
137.2
136.9
127.8
124.3
123.9
121.9
121.5
121.2
120.1
119.0
118.4
110.9
110.6
97.8
97.6
77.3
77.1
76.8
51.4
51.2
37.8
37.7
32.8
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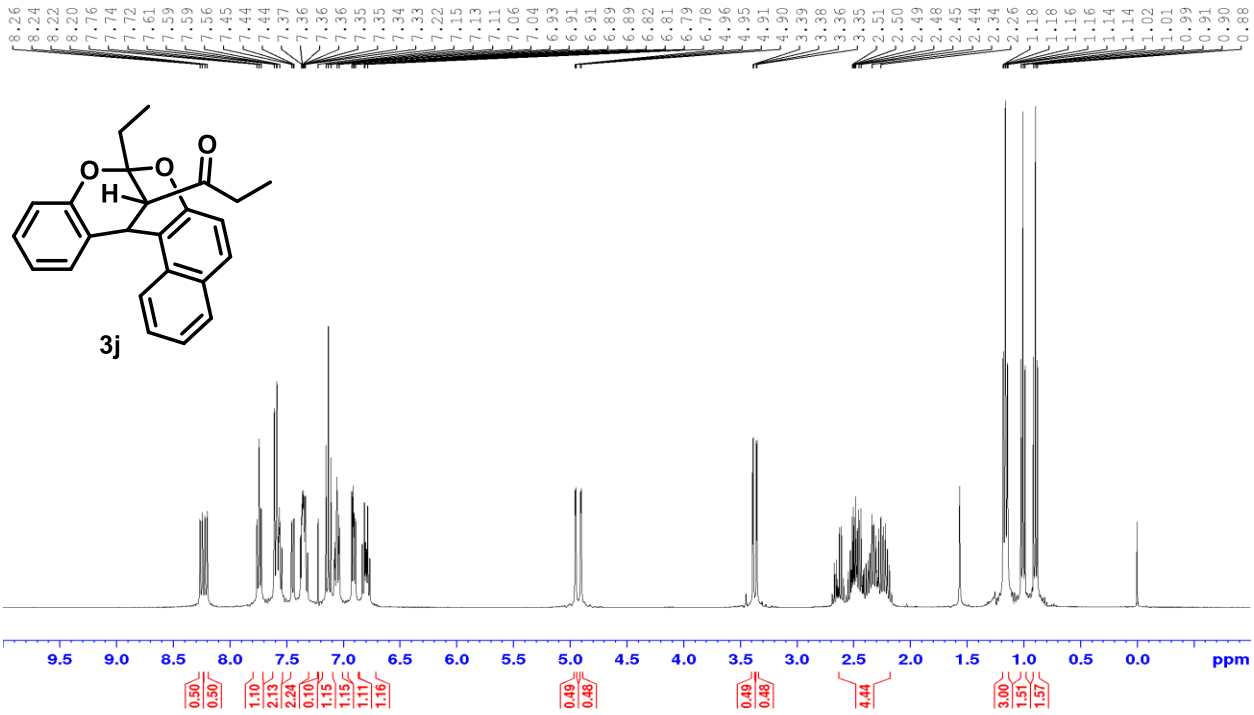
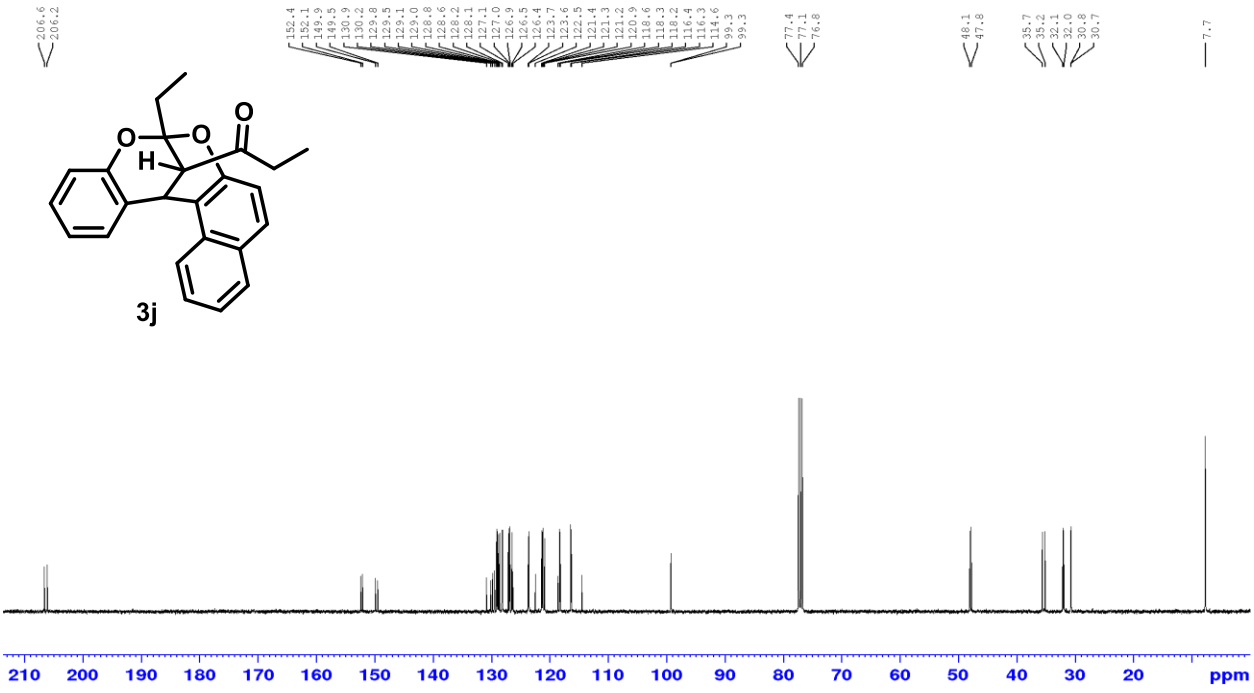
25.8
25.6
25.6
25.5
3i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


3j
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 ppm


3j
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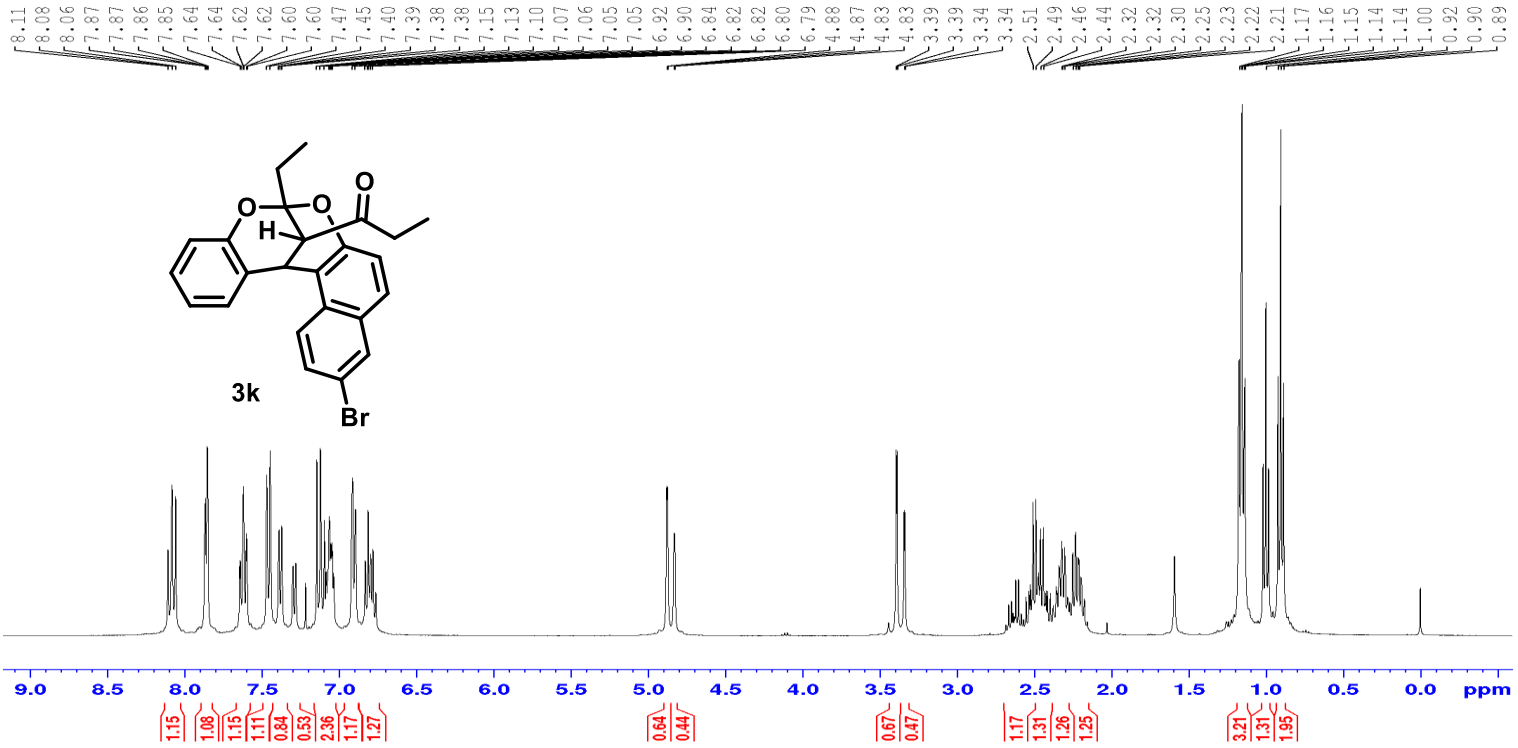
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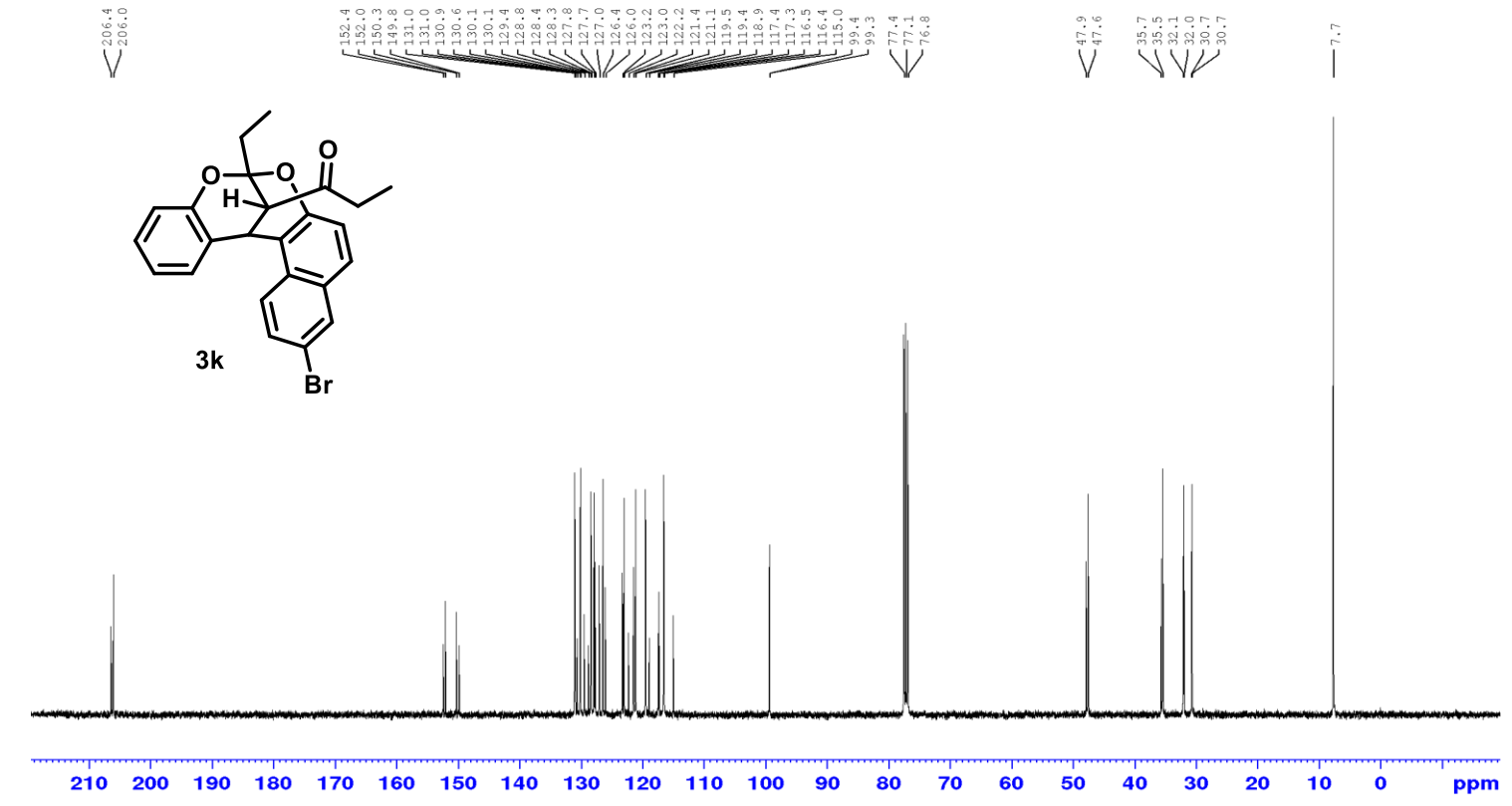
O
O
O
H
3k
Br
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.15 1.08 1.15 1.11 0.84 0.53 2.36 1.17 1.27 0.64 0.44 0.67 0.47 1.17 1.31 1.26 1.25 3.21 1.31 1.95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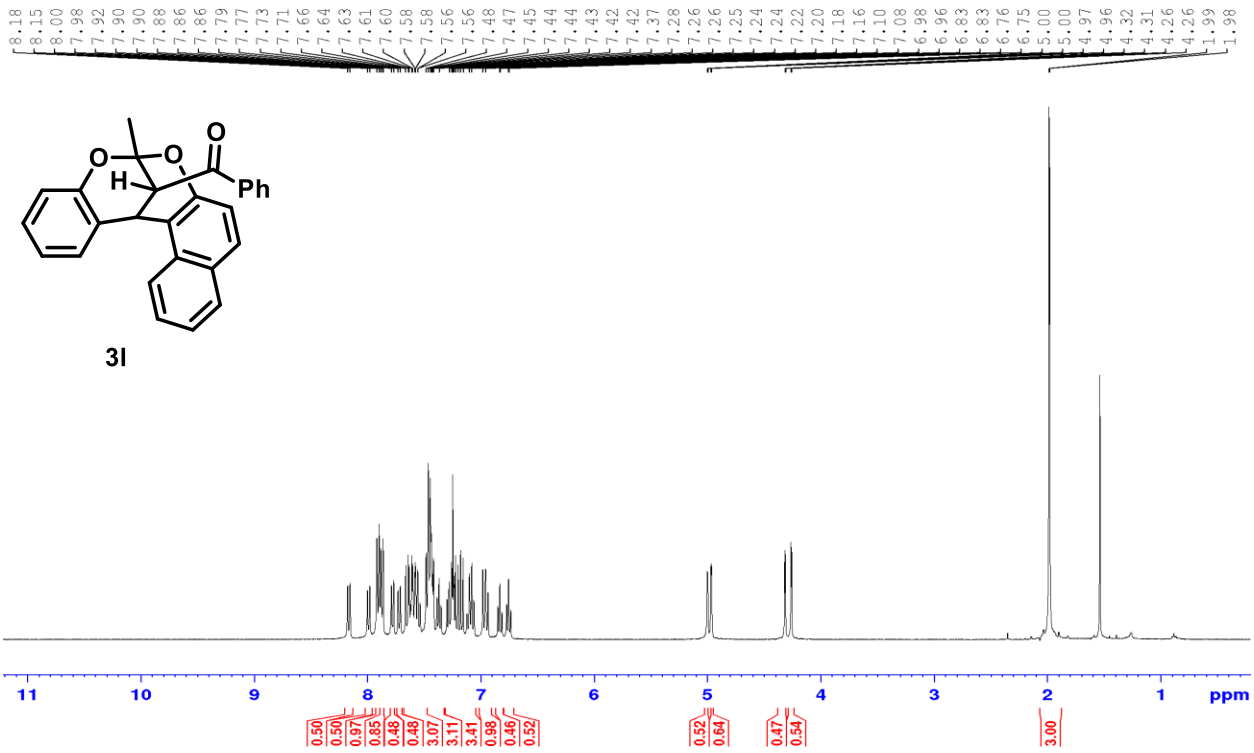
O
O
O
H
3k
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.86
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7.77
7.73
7.71
7.66
7.64
7.63
7.61
7.60
7.58
7.58
7.56
7.56
7.48
7.47
7.45
7.44
7.44
7.43
7.42
7.42
7.37
7.28
7.26
7.26
7.25
7.24
7.24
7.22
7.20
7.18
7.16
7.10
7.08
6.98
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6.83
6.76
6.75
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5.00
4.97
4.96
4.32
4.31
4.26
4.26
1.99
1.98
O
O
O
H
Ph
3l
11
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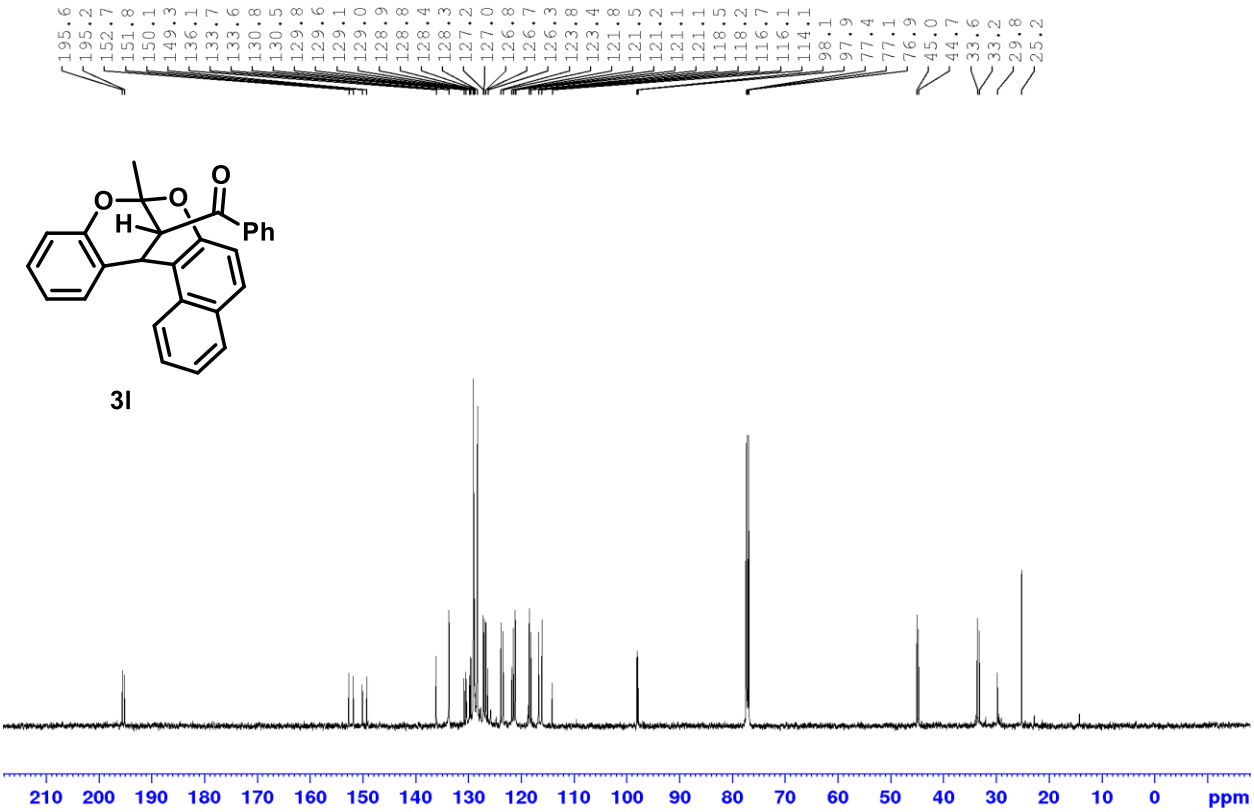
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O
O
H
Ph
3l
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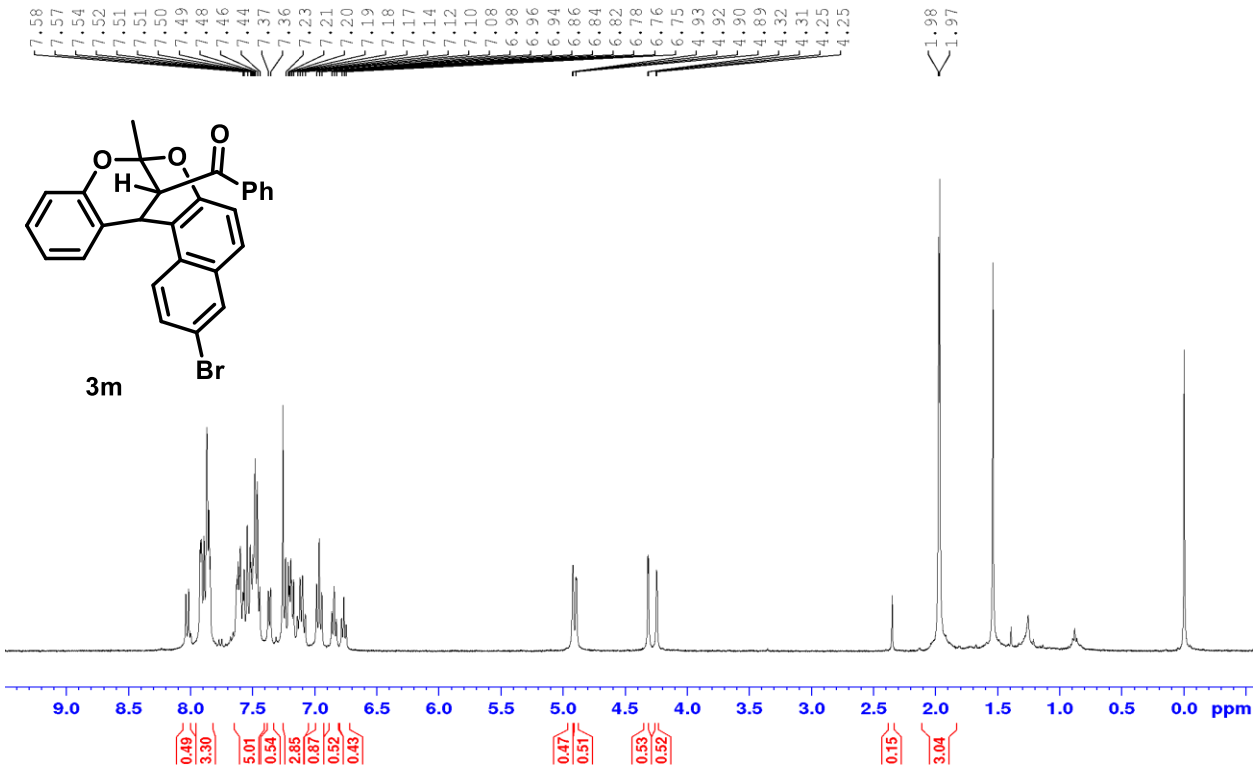
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1.97
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O
O
H
Ph
Br
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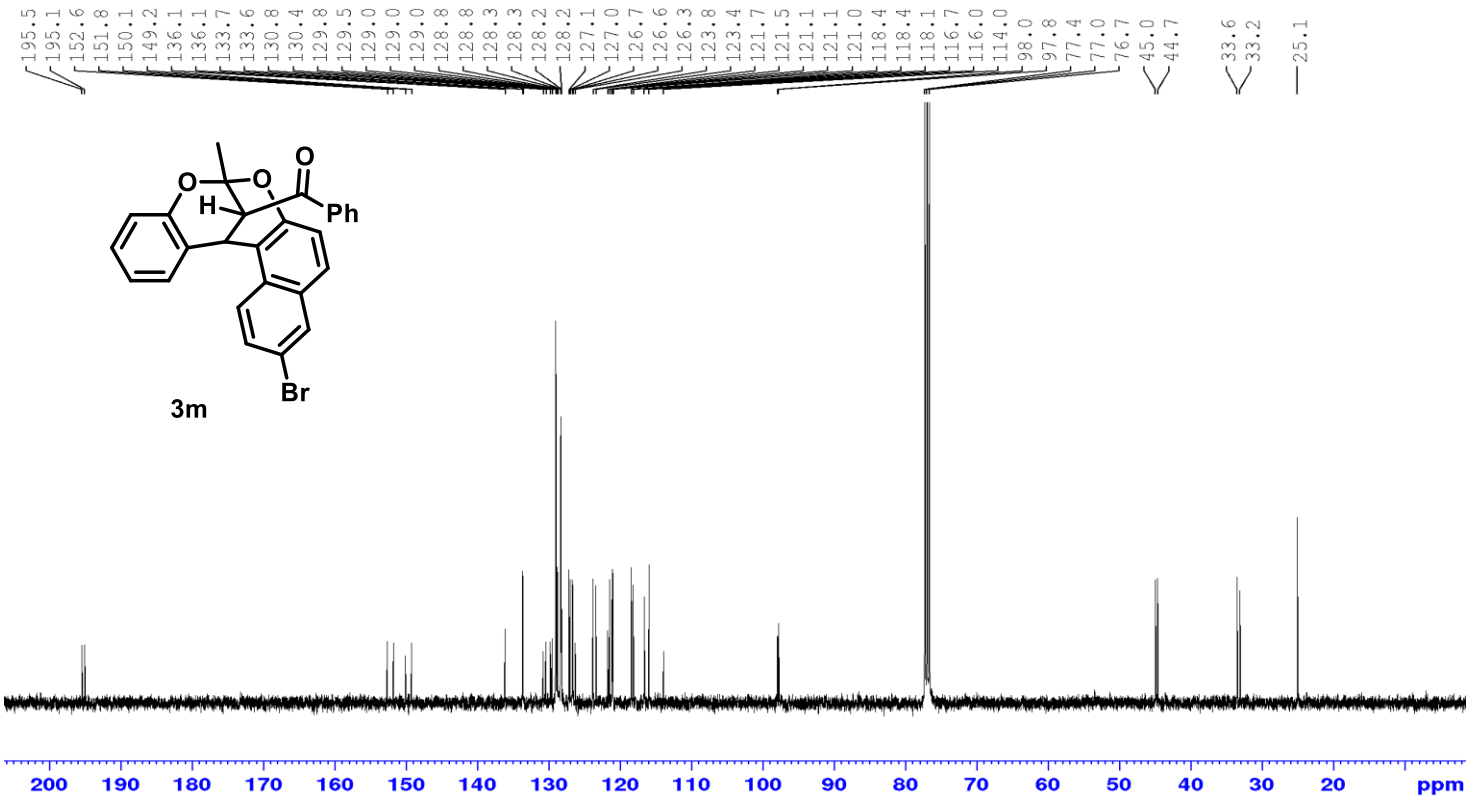
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33.6
33.2
25.1
O
O
O
H
Ph
Br
3m
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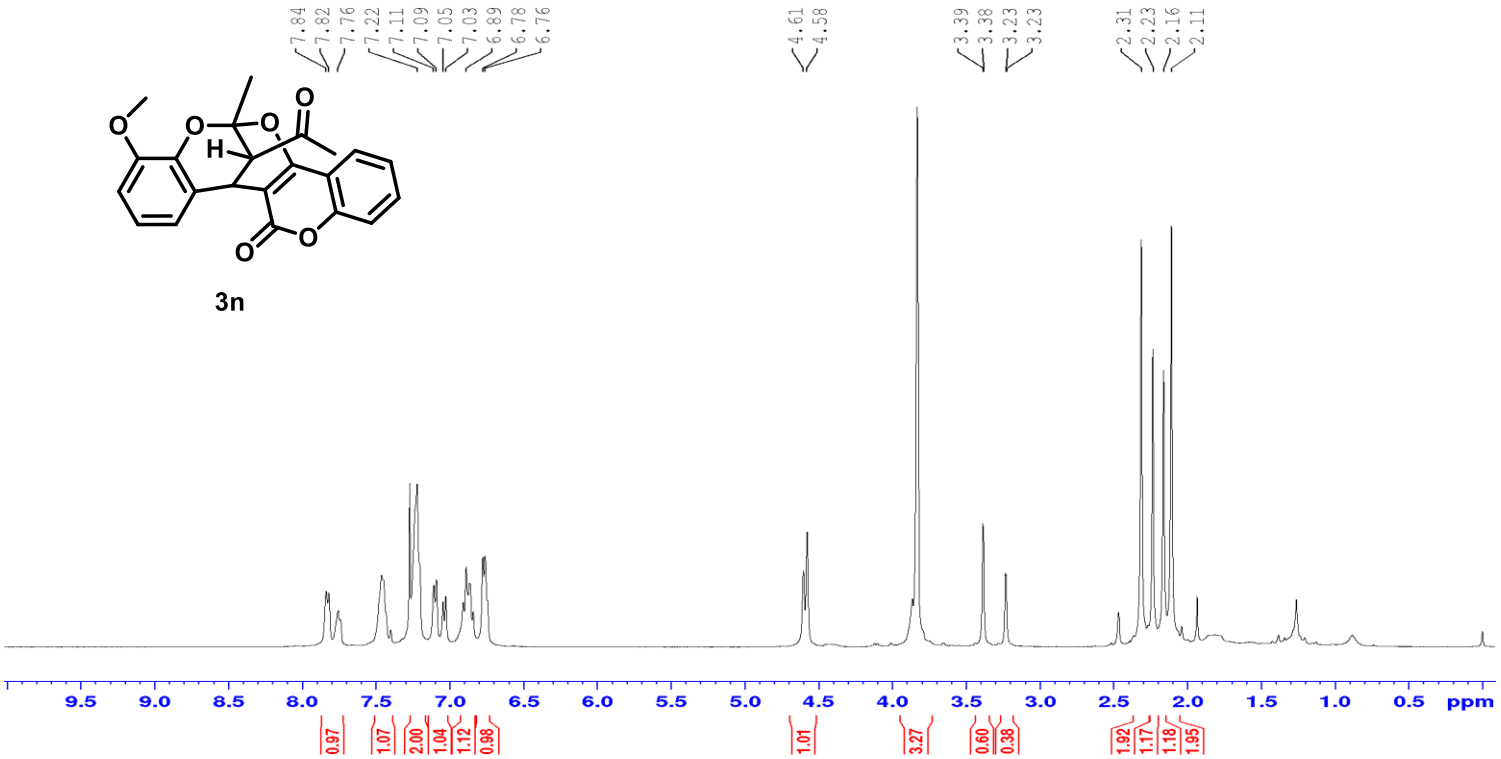
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3.38
3.23
3.23
2.31
2.23
2.16
2.11
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2.00
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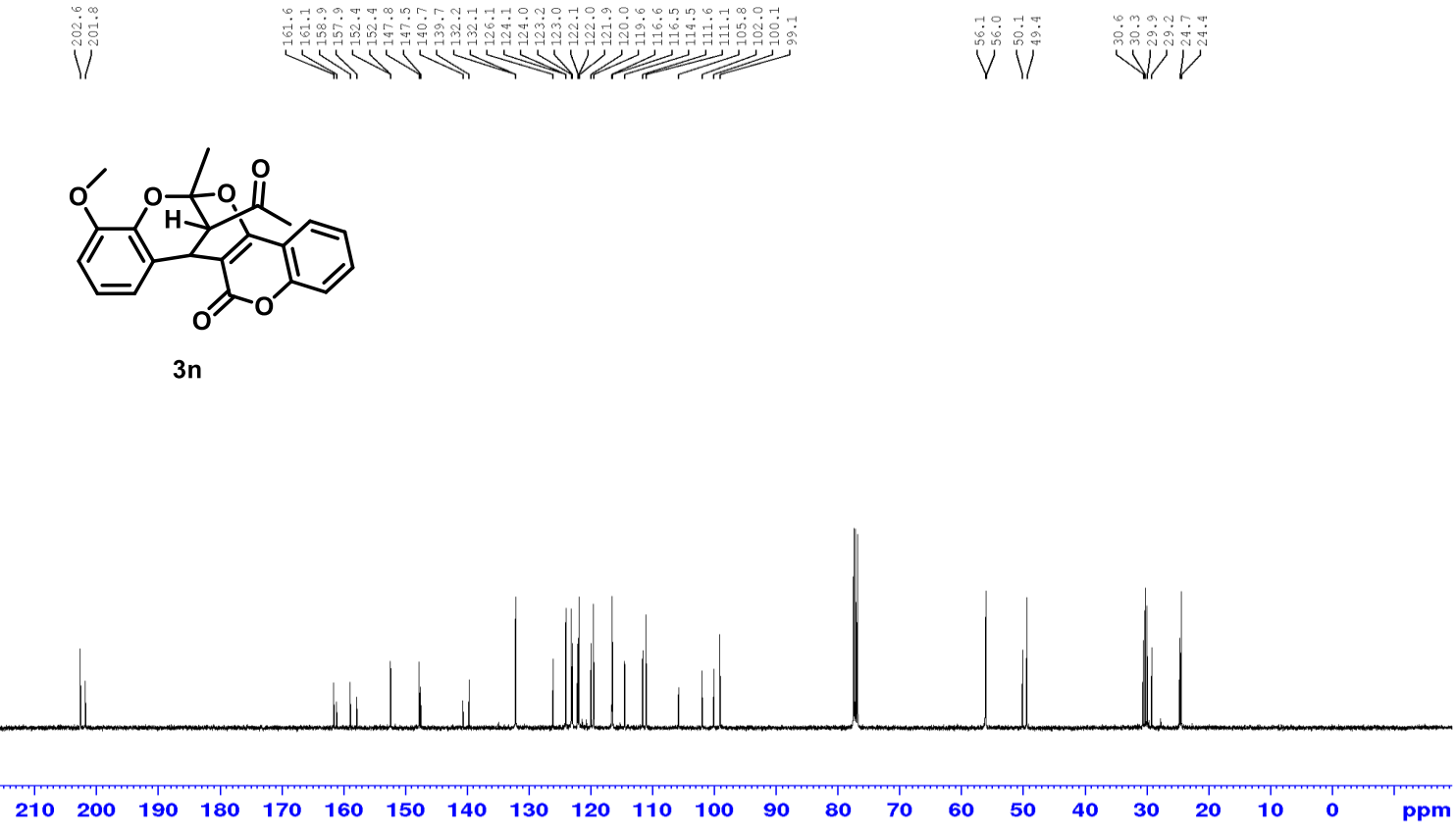
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132.1
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123.2
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121.9
120.0
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100.1
99.1
56.1
56.0
50.1
49.4
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29.2
24.7
24.4
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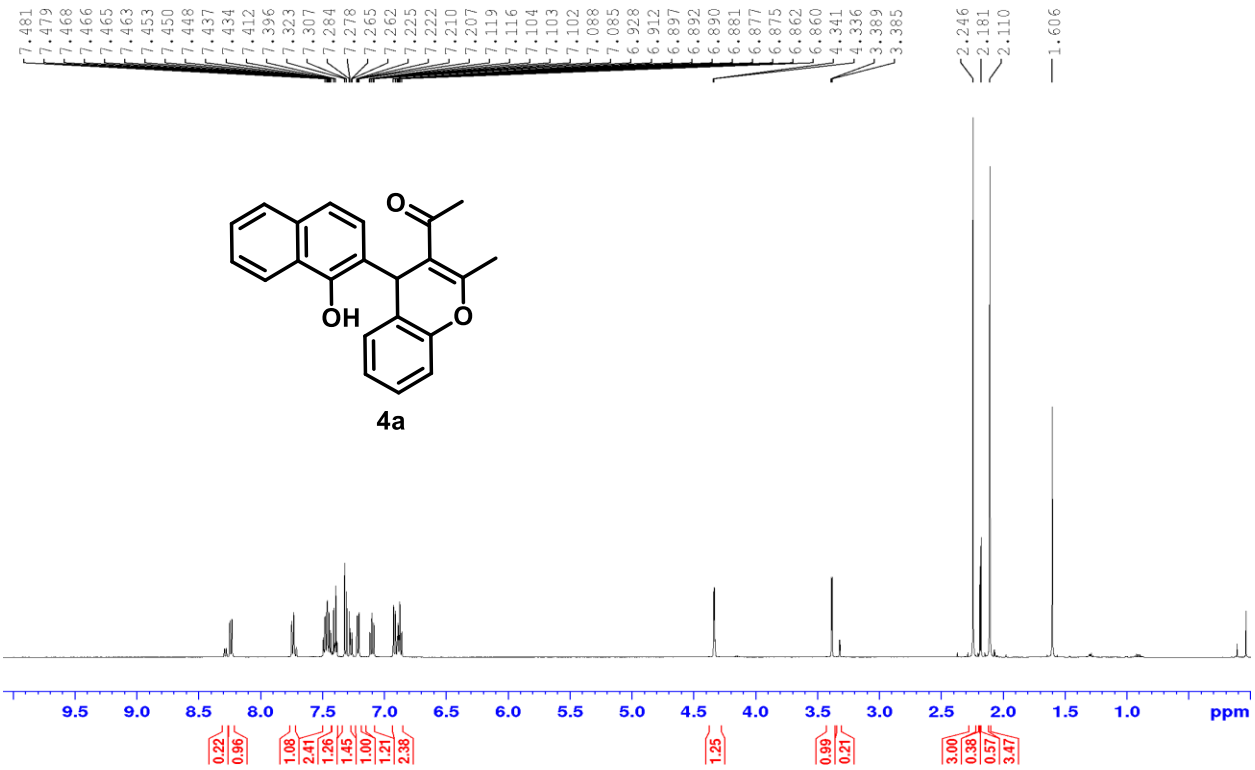
3n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7.323
7.307
7.284
7.278
7.265
7.262
7.225
7.222
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7.119
7.116
7.104
7.103
7.102
7.088
7.085
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6.912
6.897
6.892
6.890
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6.877
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3.385
2.246
2.181
2.110
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O
OH
O
4a
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
3.5
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2.0
1.5
1.0
ppm
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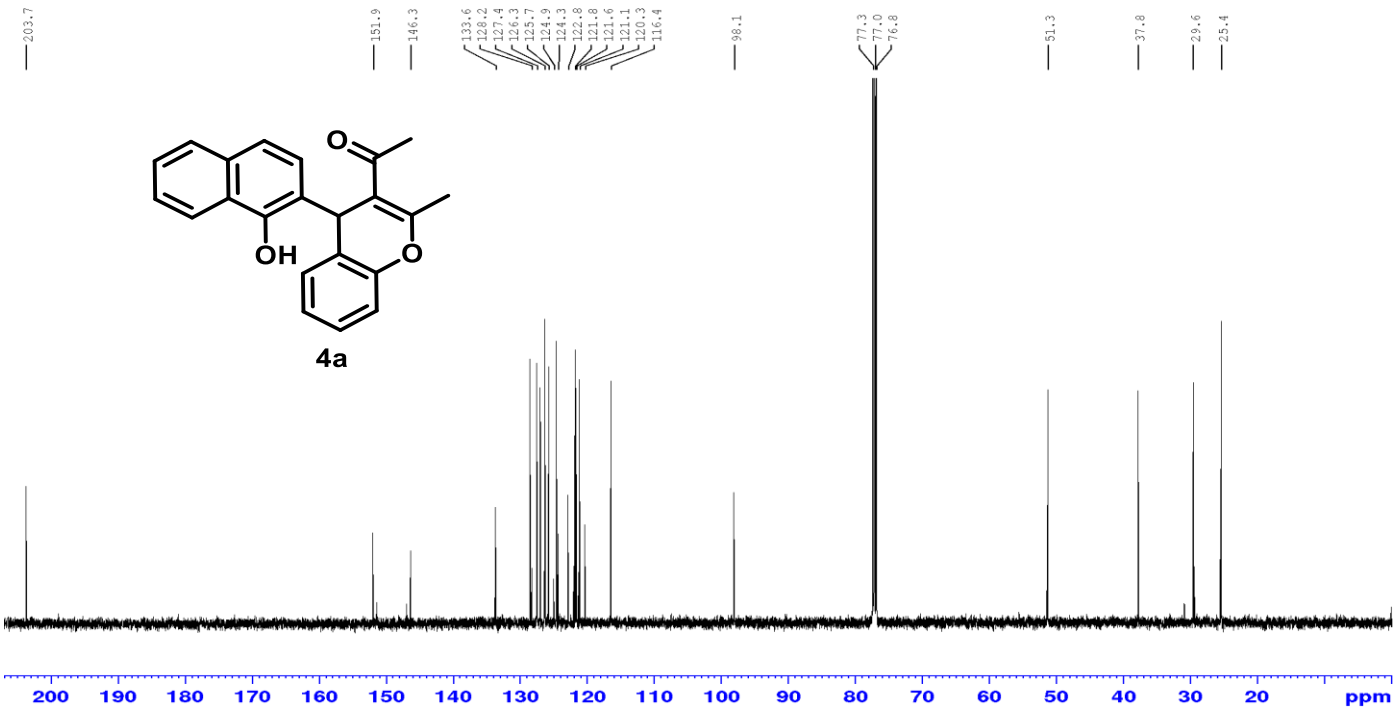
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121.6
121.1
120.3
116.4
98.1
77.3
77.0
76.8
51.3
37.8
29.6
25.4
O
OH
O
4a
200
190
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170
160
150
140
130
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110
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80
70
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50
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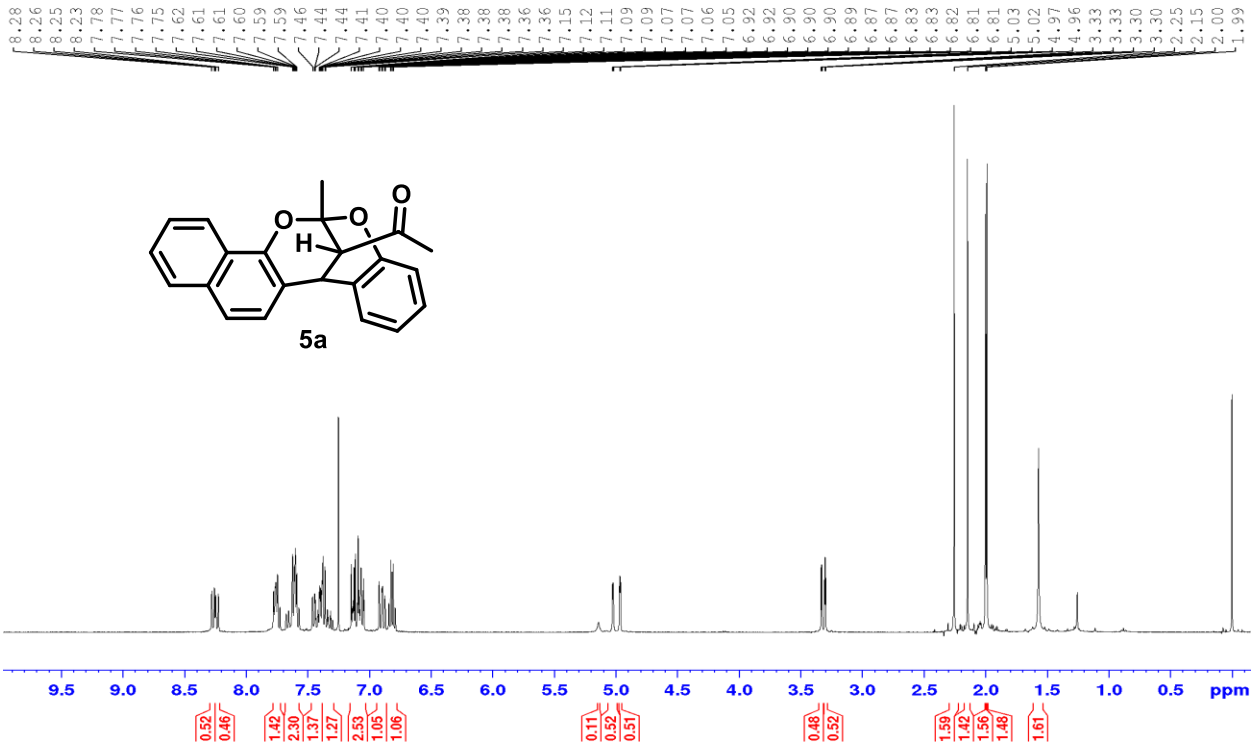
30
20
ppm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O
O
H
O
5a
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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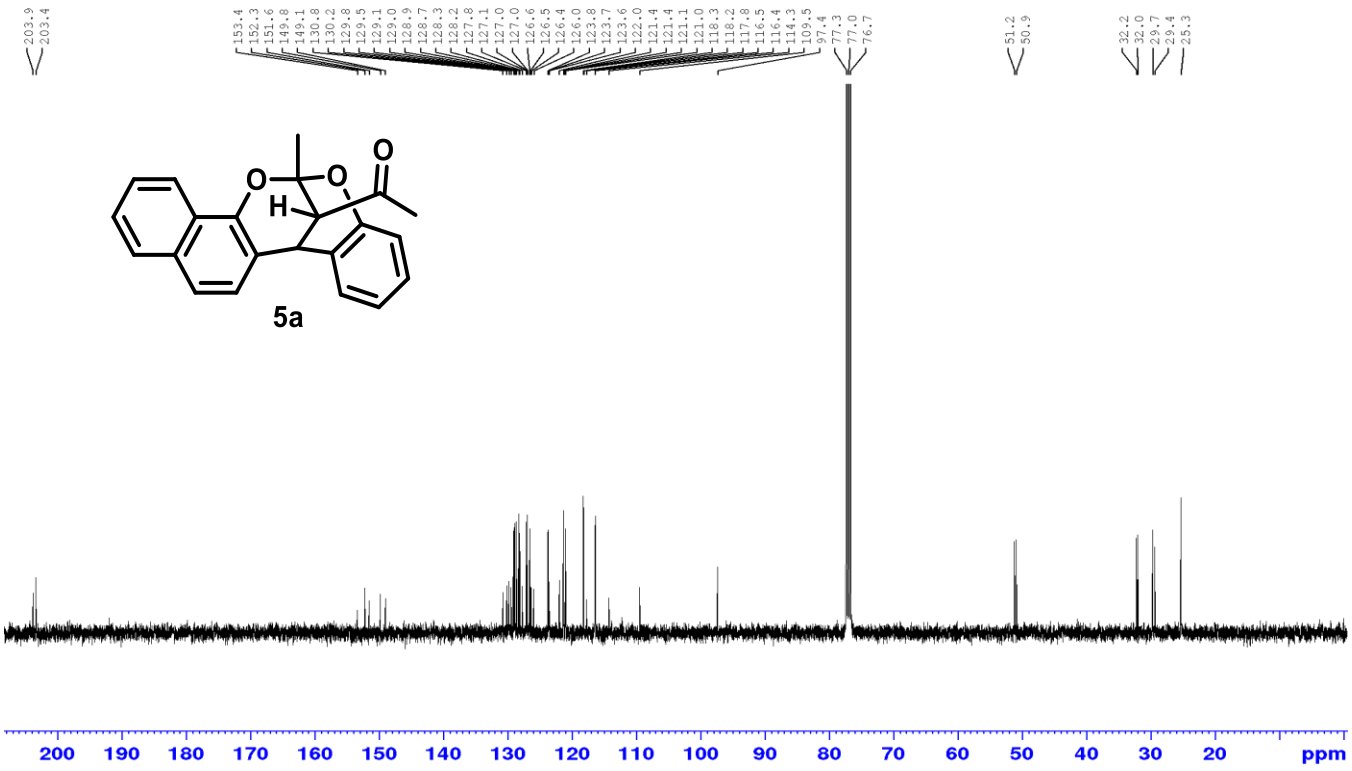
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O
O
H
O
5a
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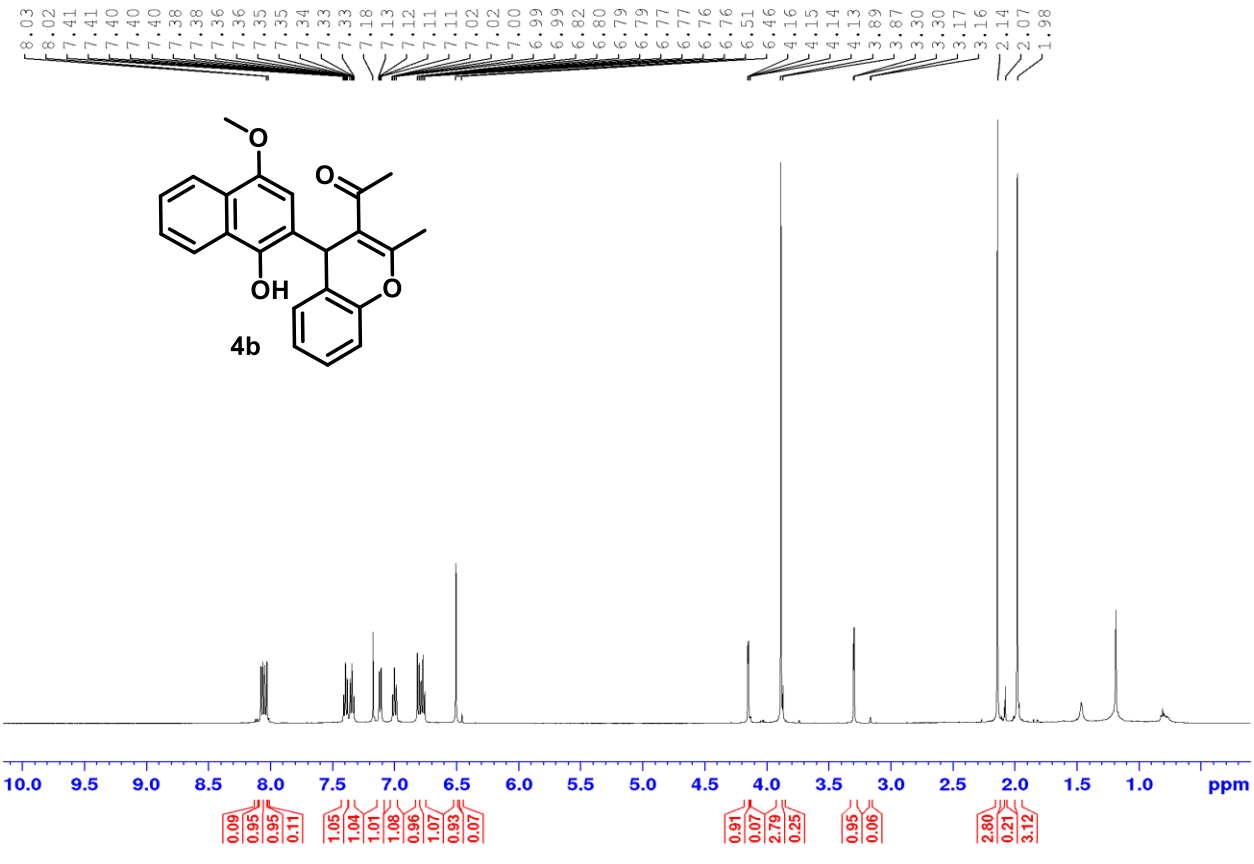
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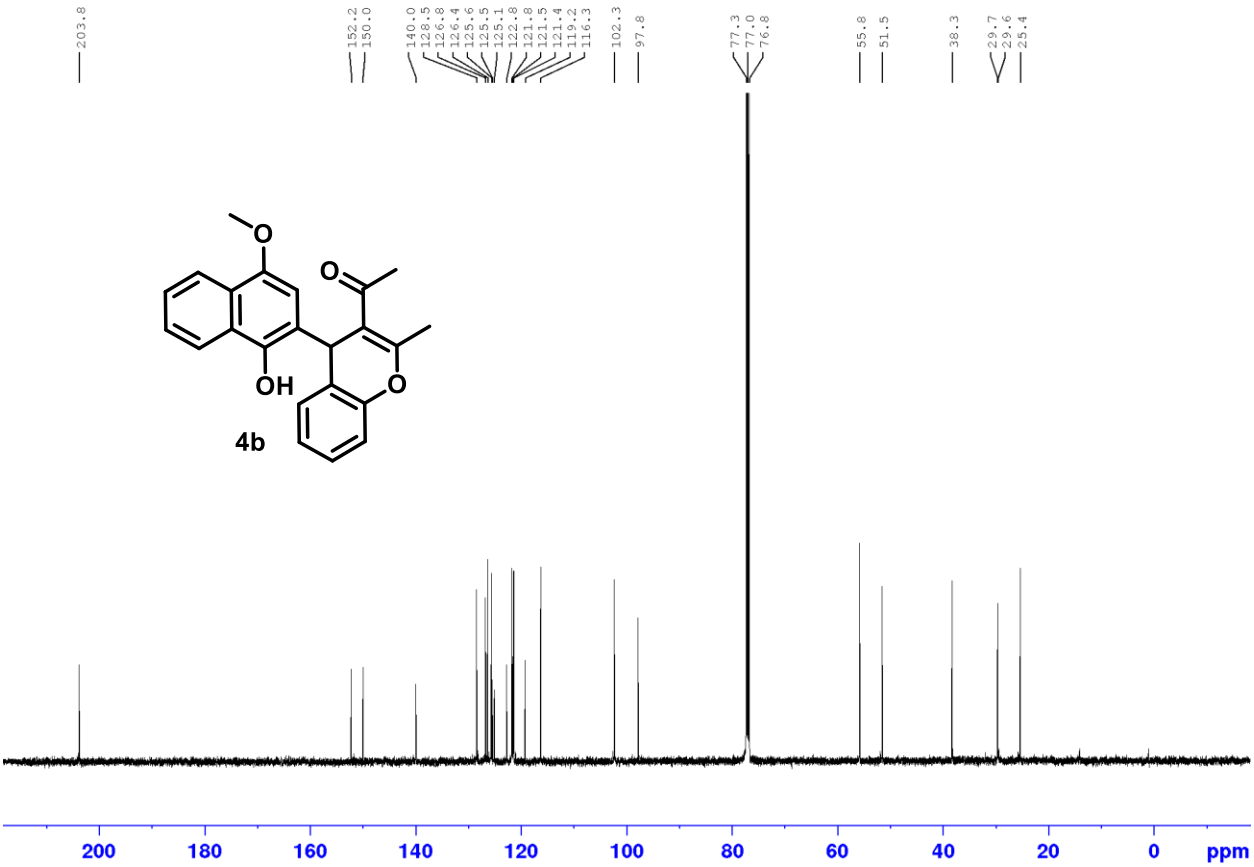
O
O
OH
O
4b
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.09 0.95 0.95 0.11 1.05 1.04 1.01 1.08 0.96 1.07 0.93 0.07 0.91 0.07 2.79 0.25 0.95 0.06 2.80 0.21 3.12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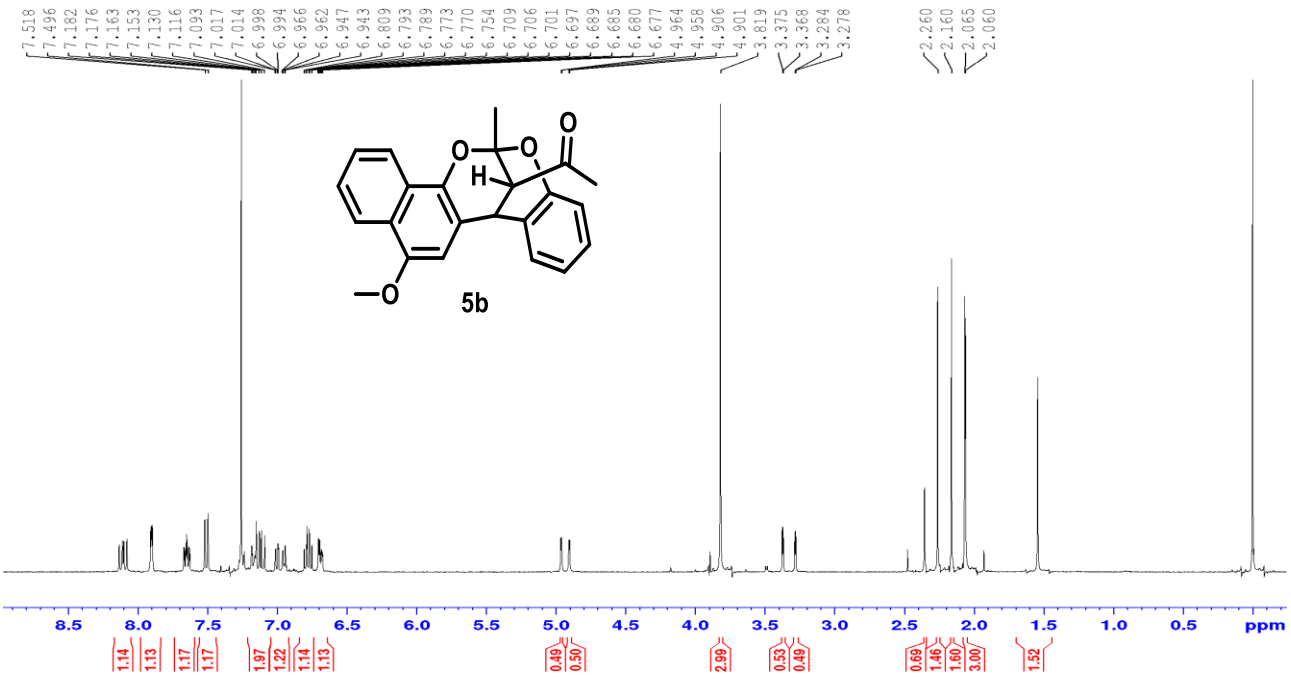
102.3 97.8
77.3 77.0 76.8
55.8 51.5
38.3
29.7 29.6 25.4
O
O
OH
O
4b
200 180 160 140 120 100 80 60 40 20 0 ppm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6.994
6.966
6.962
6.947
6.943
6.809
6.793
6.789
6.773
6.770
6.754
6.709
6.706
6.701
6.697
6.689
6.685
6.680
6.677
4.964
4.958
4.906
4.901
3.819
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3.368
3.284
3.278
2.260
2.160
2.065
2.060
O
O
H
O
O
5b
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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
ppm
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1.13
1.17
1.17
1.97
1.22
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0.68
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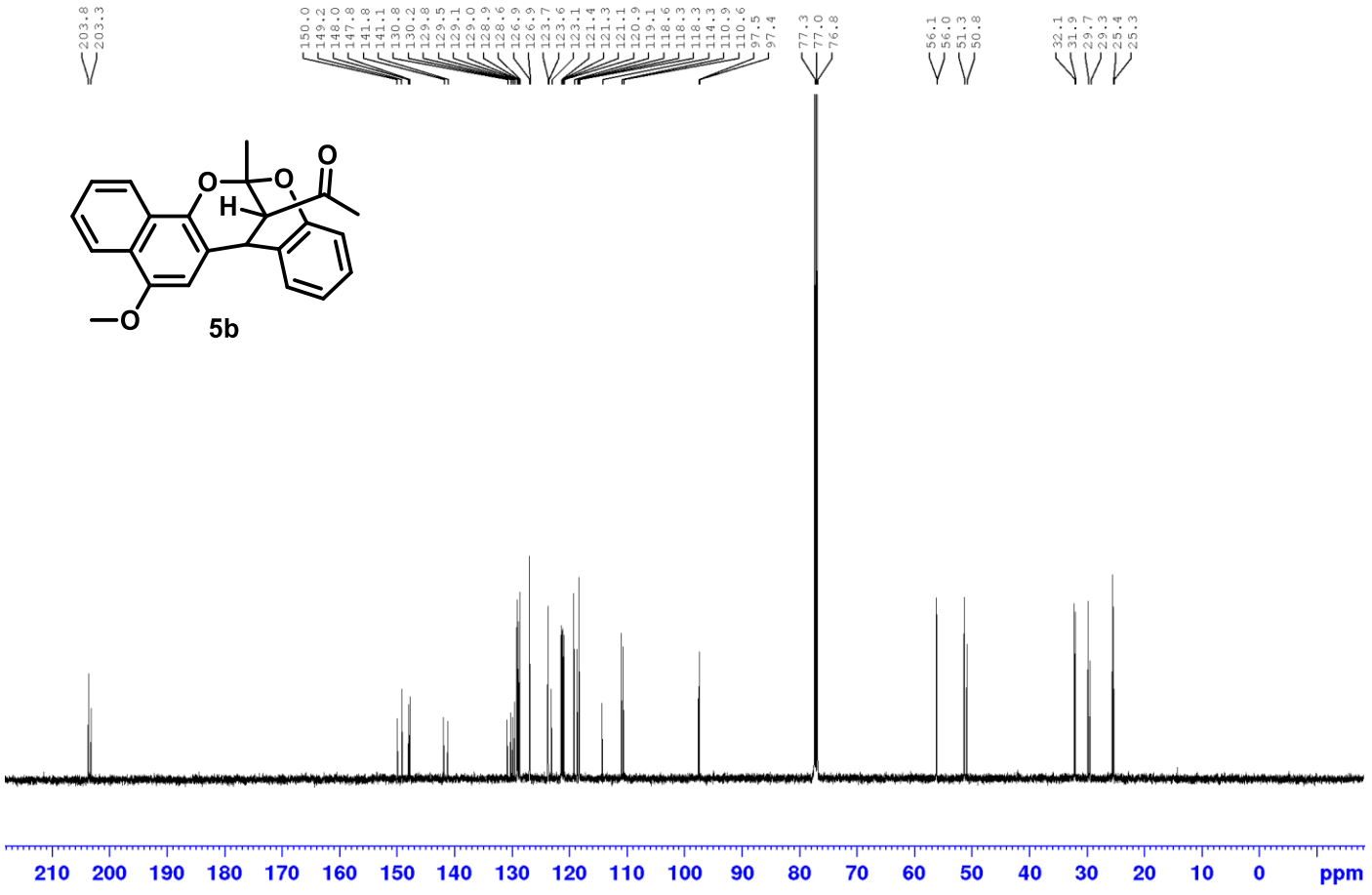
3.00
1.52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129.0
128.9
128.6
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123.6
123.1
121.4
121.3
121.1
120.9
119.1
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118.3
118.3
114.3
110.9
110.6
97.5
97.4
77.3
77.0
76.8
56.1
56.0
51.3
50.8
32.1
31.9
29.7
29.3
25.4
25.3
O
O
H
O
O
5b
210
200
190
180
170
160
150
140
130
120
110
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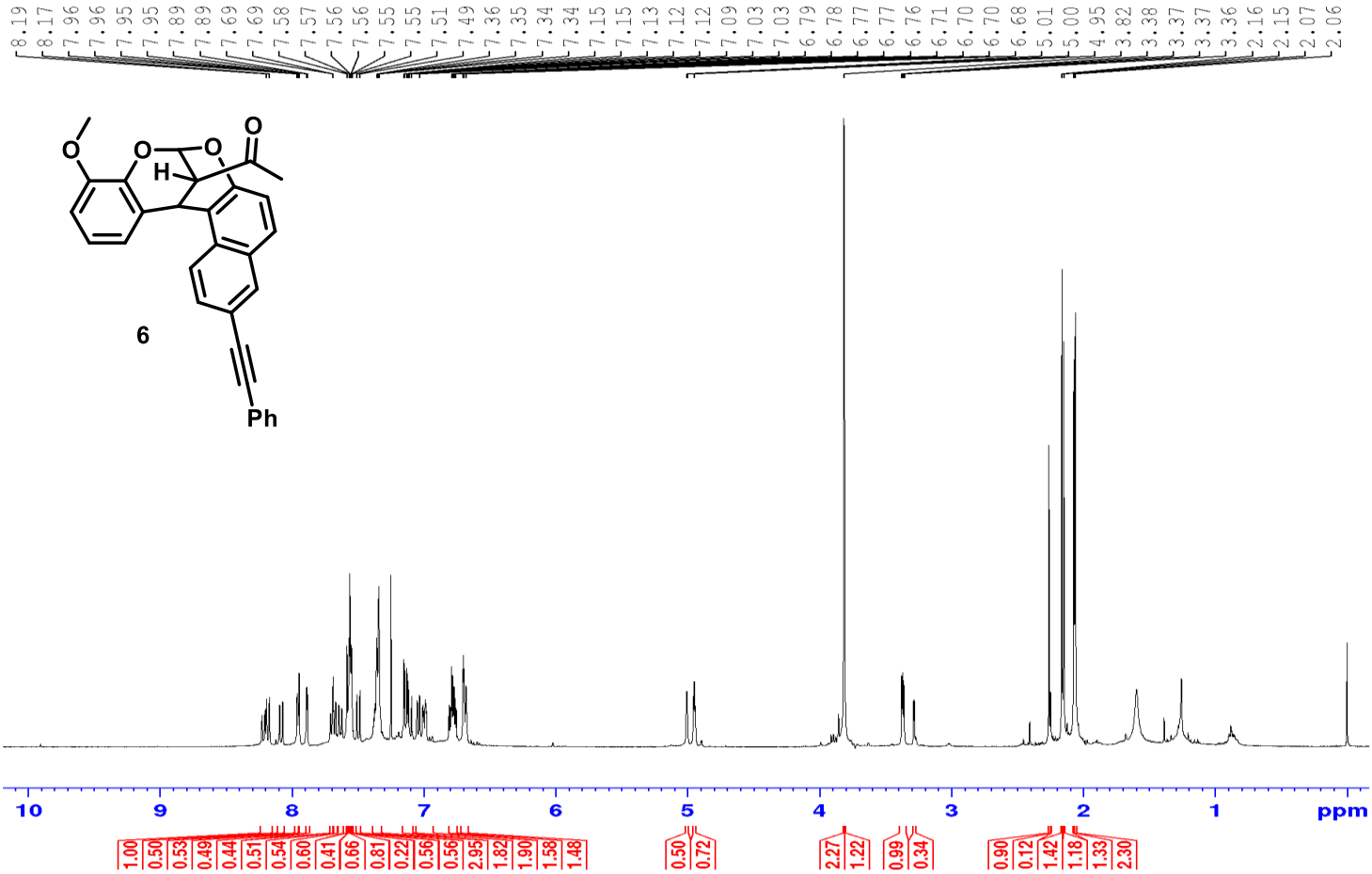
60
50
40
30
20
10
0
ppm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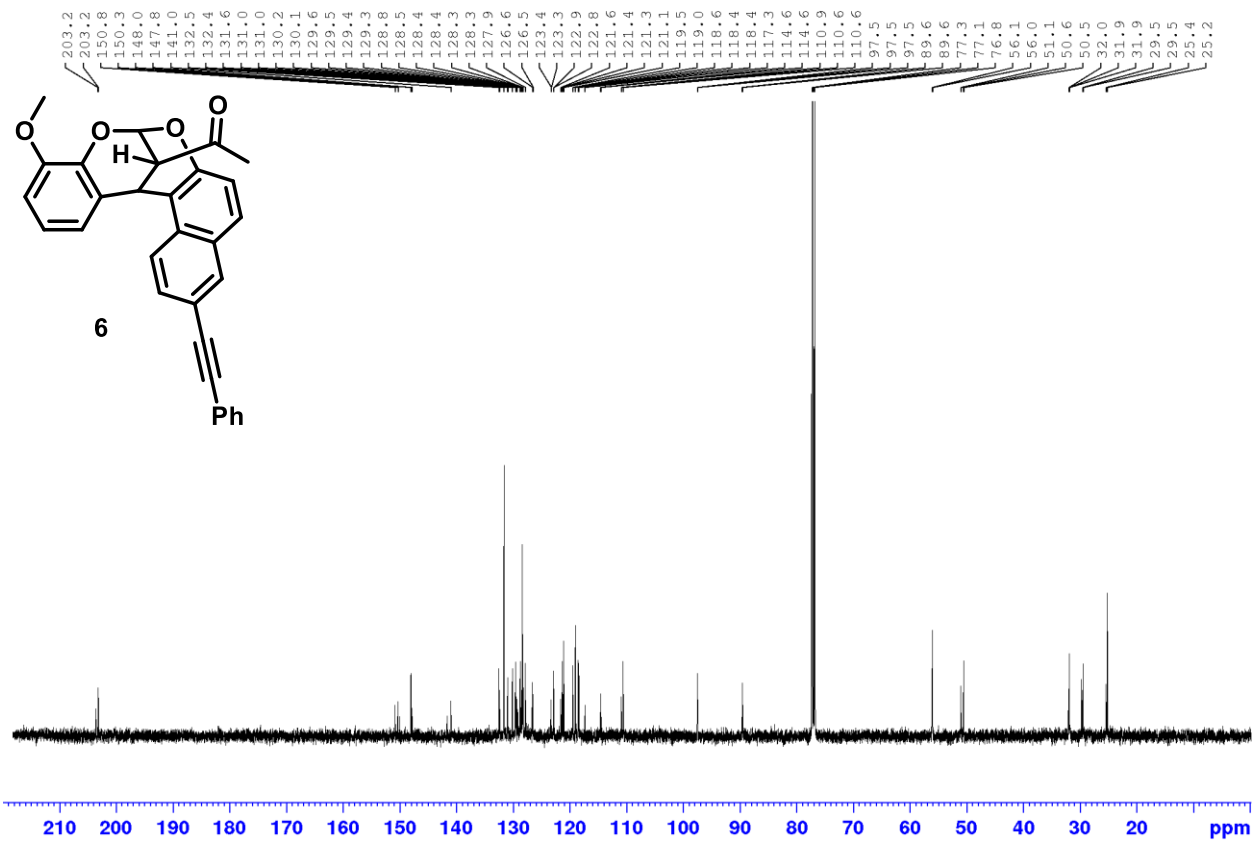
O
O
O
H
O
6
Ph
10 9 8 7 6 5 4 3 2 1 ppm
1.00 0.50 0.53 0.49 0.44 0.51 0.54 0.60 0.41 0.66 0.81 0.22 0.56 0.56 2.95 1.82 1.90 1.58 1.48 0.50 0.72 2.27 1.22 0.99 0.34 0.90 0.12 1.42 1.18 1.33 2.30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O
O
O
H
O
6
Ph
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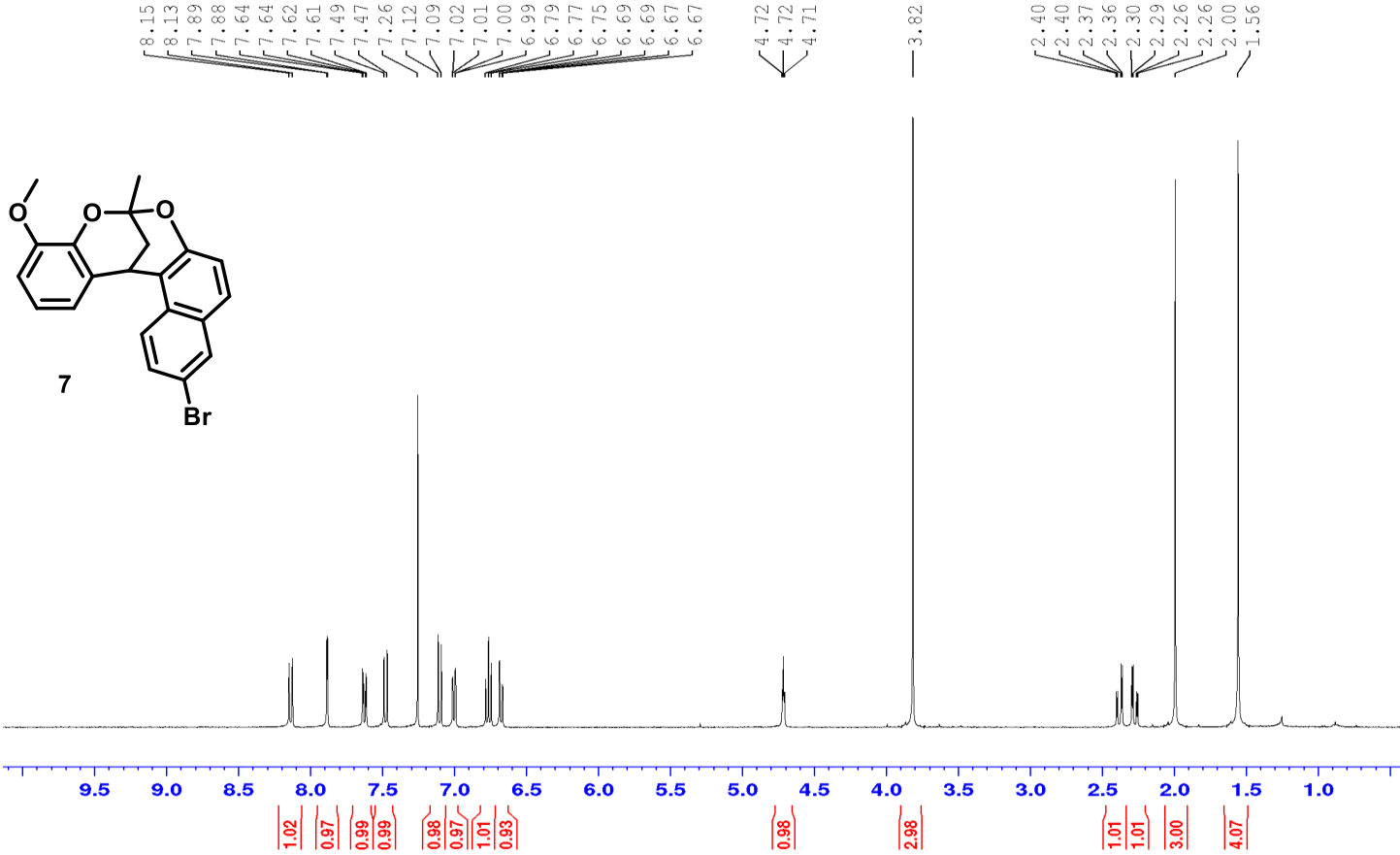
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7.09
7.02
7.01
7.00
6.99
6.79
6.77
6.75
6.69
6.69
6.67
6.67
4.72
4.72
4.71
3.82
2.40
2.40
2.37
2.36
2.30
2.29
2.26
2.26
2.00
1.56
O
O
O
7
Br
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
1.02
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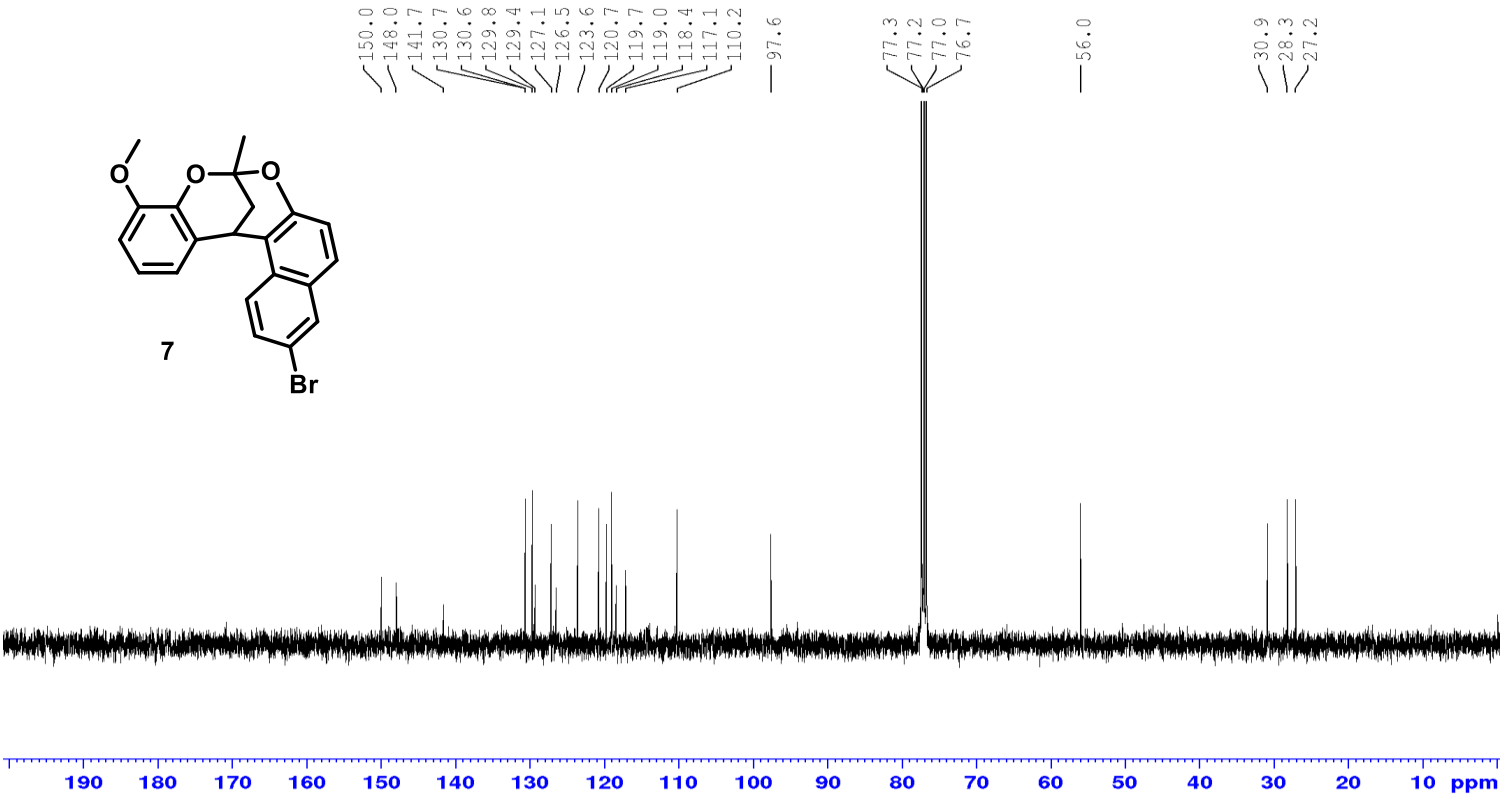
1.01
3.00
4.07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127.1
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119.7
119.0
118.4
117.1
110.2
97.6
77.3
77.2
77.0
76.7
56.0
30.9
28.3
27.2
O
O
O
7
Br
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30
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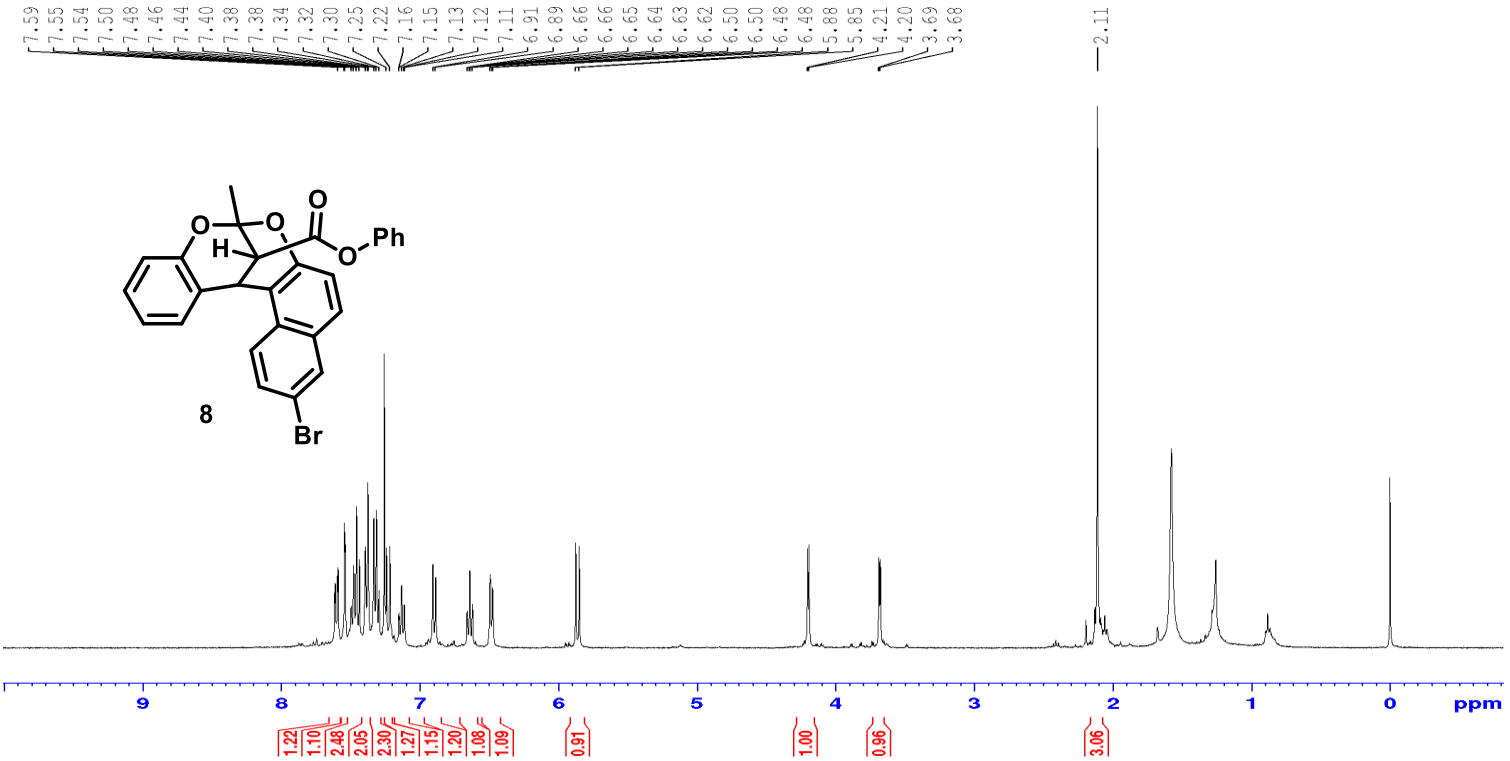
10
ppm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7.30
7.25
7.22
7.16
7.15
7.13
7.12
7.11
6.91
6.89
6.66
6.66
6.65
6.64
6.63
6.62
6.50
6.50
6.48
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5.88
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3.68
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O
O
H
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Ph
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5
4
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2
1
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ppm
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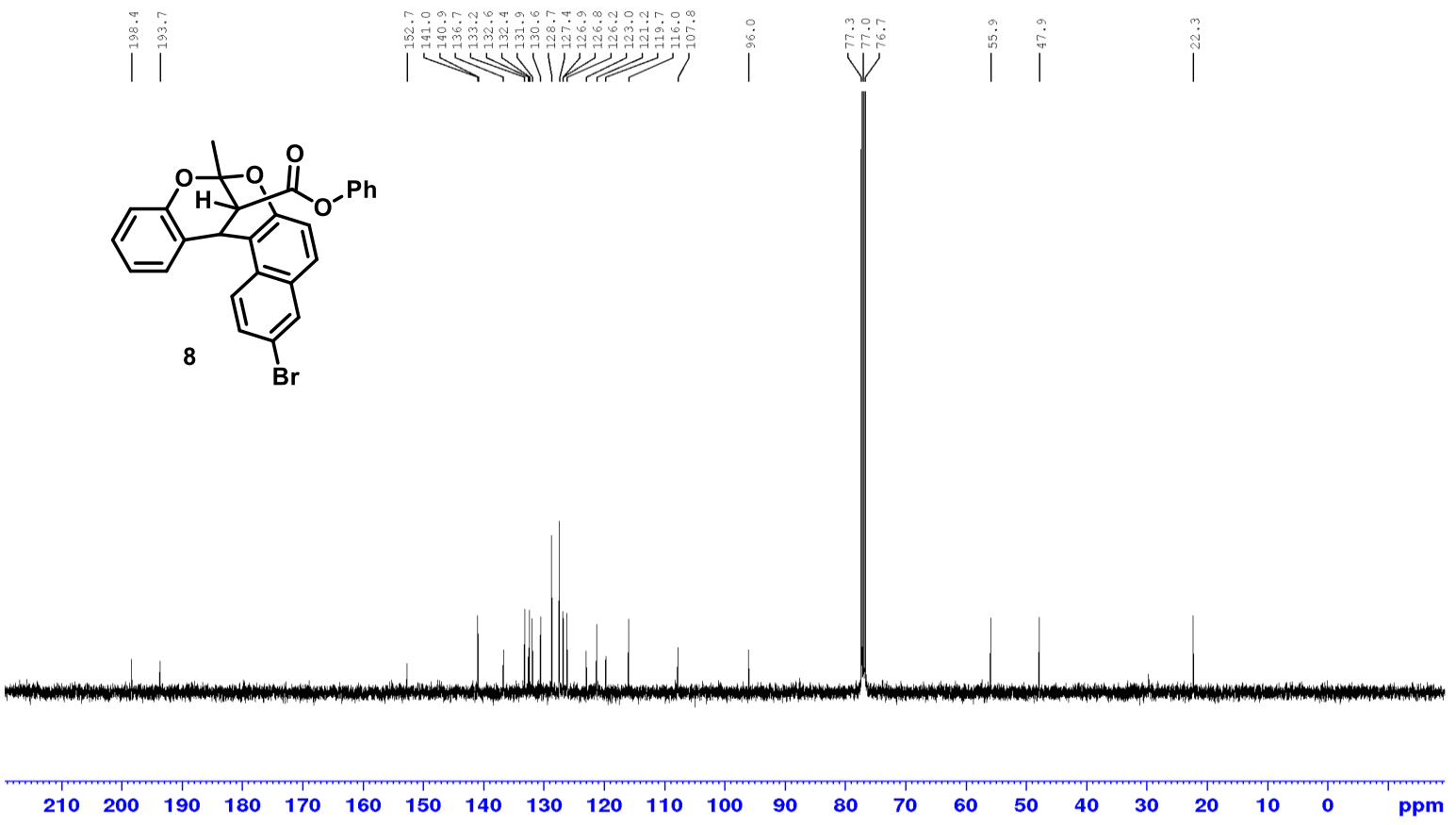
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126.8
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121.2
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116.0
107.8
96.0
77.3
77.0
76.7
55.9
47.9
22.3
O
O
H
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O
Ph
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Br
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200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

7. References

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