

SUPPORTING INFORMATION FOR

Rearrangement of Methylenebis(cyclohexane-1,3-dione) Enols Induced by

Mn(III)-Catalyzed Aerobic Oxidation

Yûki Murakami, Kazuki Hisano, and Hiroshi Nishino*

Department of Chemistry, Graduate School of Science, Kumamoto University,

Kurokami 2-39-1, Chûou-Ku, Kumamoto 860-8555, Japan

Fax: +81-96-342-3374; E-mail: nishino@kumamoto-u.ac.jp

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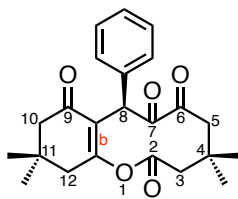
Measurements

Melting points were obtained using an MP-J3 Yanagimoto micromelting point apparatus and are uncorrected. The IR spectra were measured neat or in CHCl_3 using an IRAffinity-1S FT-IR spectrometer with the MIRacle 10 ATR accessory. All the IR data were expressed in cm^{-1} . The NMR spectra were recorded using a JNM ECX 500 FT-NMR spectrometer at 500 MHz for the ^1H and at 125 MHz for $^{13}\text{C}\{^1\text{H}\}$ with tetramethylsilane as the internal standard. The chemical shifts are reported as δ values (ppm) and the coupling constants J in Hz. The following abbreviations were used for the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; sext, sextet; m, multiplet; and brs, broad singlet for the ^1H NMR spectra. The high-resolution mass spectra using a JEOL JMS-700 MStation double-focusing mass spectrometer and the elemental analyses using a J-SCIENCE LAB JM10 for the products were performed at the Instrumental Analysis Center, Kumamoto University, Kumamoto, Japan. The X-ray analysis was performed using a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-K α radiation, and the structure was solved by direct methods and expanded using Fourier techniques.

Materials

Manganese(II) acetate tetrahydrate, $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, was purchased from Wako Pure Chemical Ind., Ltd. Dimedone was purchased from Tokyo Kasei Co., Ltd. The methylenebis(cyclohexanedione) enols **1a-o** were prepared by the condensation of dimedone with the corresponding commercially available aldehyde in the presence of piperidine.⁵ Manganese(III) acetate dihydrate, $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$, was synthesized according to our modified method.²ⁱ Flash column chromatography was performed on silica gel 60N (40-50 mm), which was purchased from Kanto Chemical Co., Inc., and preparative thin layer chromatography (TLC) on Wakogel B-10 and B-5F from Wako Pure Chemical Ind., Ltd. The solvents were commercially-available first-grade and used as received.

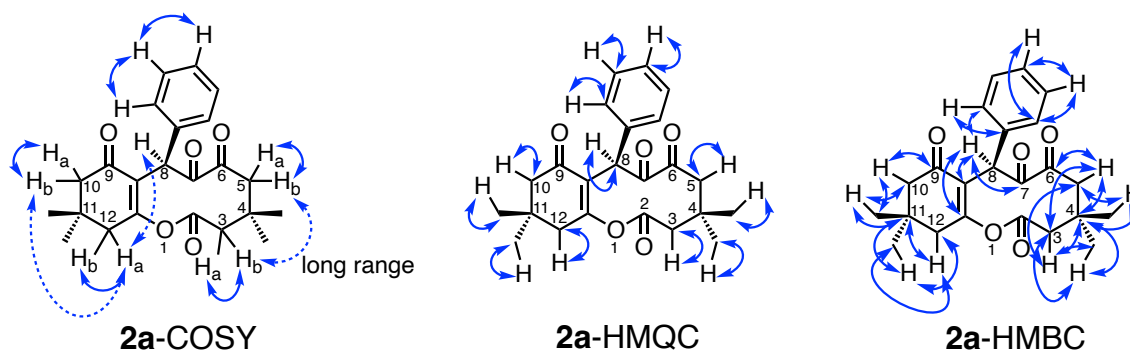
(R)-4,4,11,11-Tetramethyl-8-phenyl-4,5,8,10,11,12-hexahydro-2H-benzo[*b*]oxecine-2,6,7,9(3*H*)-tetraone (**2a**: *R* = *Ph*).



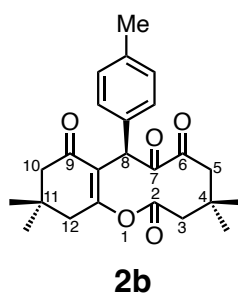
2a

Yield (85.1 mg, 44%); yellow needles (from Et_2O /hexane); mp 118–119 °C; R_f = 0.40

(EtOAc/hexane 1:4 v/v); IR ν 1763, 1709, 1676, and 1633 (C=O); ^1H NMR (500 MHz, CDCl_3) δ 7.31 (2H, t, $J = 7.6$ Hz, arom H), 7.24 (1H, t, $J = 6.8$ Hz, arom H), 7.11 (2H, dd, $J = 7.8, 1.3$ Hz, arom H), 5.32 (1H, br.t, $J = 1.2$ Hz, H-8), 3.74 (1H, d, $J = 12.2$ Hz, H_a -5), 2.86 (1H, dd, $J = 18.5, 1.7$ Hz, H_a -12), 2.73 (1H, d, $J = 18.4$ Hz, H_b -12), 2.63 (1H, d, $J = 13.8$ Hz, H_a -3), 2.30 (1H, d, $J = 16.3$ Hz, H_a -10), 2.29 (1H, dd, $J = 13.8, 1.2$ Hz, H_b -3), 2.19 (1H, dd, $J = 16.3, 1.0$ Hz, H_b -10), 1.93 (1H, dd, $J = 12.2, 1.2$ Hz, H_b -5), 1.23 (3H, s, C-4- CH_3), 1.18 (3H, s, C-4- CH_3'), 1.10 (3H, s, C-11- CH_3), 1.00 (3H, s, C-11- CH_3'); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 197.2 (C-7), 196.1 (C-6), 196.0 (C-9), 166.5 (C-2), 160.4 (C-12a), 136.4 (arom C), 129.3 (2C), 128.3 (2C), 127.3 (arom CH), 124.0 (C-8a), 50.4 (C-10), 48.6 (C-8), 46.3 (C-3), 44.9 (C-5), 42.4 (C-12), 36.5 (C-4), 33.9 (C-4- CH_3), 32.9 (C-11), 28.4 (C-11- CH_3), 27.4 (C-11- CH_3'), 24.9 (C-4- CH_3'). HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{27}\text{O}_5$ 383.1858; Found 383.1868.



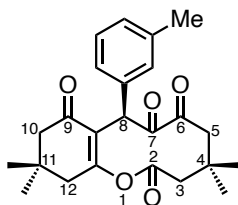
(*R*)-8-(4-Methylphenyl)-4,4,11,11-tetramethyl-4,5,8,10,11,12-hexahydro-2H-benzo[*b*]oxecine-2,6,7,9(3*H*)-tetraone (**2b**: $R = 4\text{-MeC}_6\text{H}_4$).



Yield (71.3 mg, 36%); yellow amorphous; $R_f = 0.41$ (EtOAc/hexane 1:4 v/v); IR ν 1709, 1676, and 1653 (C=O); ^1H NMR (500 MHz, CDCl_3) δ 7.12 (2H, d, $J = 7.8$ Hz, arom H), 6.99 (2H, d, $J = 7.8$ Hz, arom H), 5.28 (1H, s, H-8), 3.74 (1H, d, $J = 12.2$ Hz, H_a -5), 2.86 (1H, dd, $J = 18.3, 1.6$ Hz, H_a -12), 2.73 (1H, d, $J = 18.3$ Hz, H_b -12), 2.63 (1H, d, $J = 14.0$ Hz, H_a -3), 2.31 (3H, s, CH_3), 2.30 (1H, d, $J = 16.3$ Hz, H_a -10), 2.28 (1H, d, $J = 14.0$ Hz, H_b -3), 2.19 (1H, d, $J = 16.3$ Hz, H_b -10), 1.93 (1H, d, $J = 12.2$ Hz, H_b -5), 1.22 (3H, s, C-4- CH_3), 1.18 (3H, s, C-4- CH_3'), 1.10 (3H, s, C-11- CH_3), 1.00 (3H, s, C-11- CH_3'); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ

197.5 (C-7), 196.4 (C-6), 196.2 (C-9), 166.7 (C-2), 160.5 (C-12a), 137.0, 133.5 (arom C), 129.3 (2C), 129.2 (2C) (arom CH), 124.3 (C-8a), 50.6 (C-10), 48.4 (C-8), 46.5 (C-3), 45.1 (C-5), 42.6 (C-12), 36.6 (C-4), 34.1 (C-4-CH₃), 33.0 (C-11), 28.6 (C-11-CH₃), 27.6 (C-11-CH₃'), 25.1 (C-4-CH₃'), 21.2 (CH₃). HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₄H₂₉O₅ 397.2015. Found 397.2045.

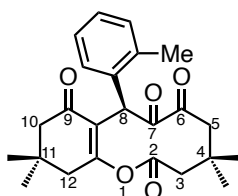
(*R*)-8-(3-Methylphenyl)-4,4,11,11-tetramethyl-4,5,8,10,11,12-hexahydro-2H-benzo[*b*]oxecine-2,6,7,9(3*H*)-tetraone (**2c**: R = 3-MeC₆H₄).



2c

Yield (70.4 mg, 35%); yellow amorphous; *R*_f = 0.31 (EtOAc/hexane 1:4 v/v); IR ν 1709, 1674, and 1653 (C=O); ¹H NMR (500 MHz, CDCl₃) δ 7.19 (1H, t, *J* = 7.6 Hz, arom H), 7.06 (1H, d, *J* = 7.6 Hz, arom H), 6.91 (1H, br. s, arom H), 6.89 (1H, d, *J* = 7.7 Hz, arom H), 5.28 (1H, br. s, H-8), 3.74 (1H, d, *J* = 12.2 Hz, H_a-5), 2.86 (1H, dd, *J* = 18.5, 1.6 Hz, H_a-12), 2.73 (1H, d, *J* = 18.5 Hz, H_b-12), 2.63 (1H, d, *J* = 13.8 Hz, H_a-3), 2.31 (3H, s, CH₃), 2.30 (1H, d, *J* = 16.4 Hz, H_a-10), 2.28 (1H, dd, *J* = 13.8, 1.2 Hz, H_b-3), 2.19 (1H, dd, *J* = 16.4, 1.0 Hz, H_b-10), 1.93 (1H, dd, *J* = 12.2, 1.2 Hz, H_b-5), 1.23 (3H, s, C-4-CH₃), 1.18 (3H, s, C-4-CH₃'), 1.10 (3H, s, C-11-CH₃), 1.01 (3H, s, C-11-CH₃'); ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 197.5 (C-7), 196.3 (C-6), 196.2 (C-9), 166.7 (C-2), 160.6 (C-12a), 138.0, 136.5 (arom C), 130.2, 128.3, 128.2, 126.3 (arom CH), 124.2 (C-8a), 50.6 (C-10), 48.7 (C-8), 46.5 (C-3), 45.1 (C-5), 42.6 (C-12), 36.7 (C-4), 34.1 (C-4-CH₃), 33.0 (C-11), 28.6 (C-11-CH₃), 27.6 (C-11-CH₃'), 25.0 (C-4-CH₃'), 21.6 (CH₃). HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₄H₂₉O₅ 397.2015. Found 397.2020.

(*R*)-8-(2-Methylphenyl)-4,4,11,11-tetramethyl-4,5,8,10,11,12-hexahydro-2H-benzo[*b*]oxecine-2,6,7,9(3*H*)-tetraone (**2d**: R = 2-MeC₆H₄).

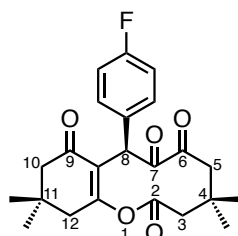


2d

Yield (66.1 mg, 33%); yellow amorphous; *R*_f = 0.45 (EtOAc/hexane 1:4 v/v); IR ν 1705, 1676, and 1653 (C=O); ¹H NMR (500 MHz, CDCl₃) δ 7.18–7.10 (3H, m, arom H), 6.86 (1H,

br. s, arom H), 5.56 (1H, s, H-8), 3.72 (1H, d, $J = 12.2$ Hz, H_a-5), 2.85 (1H, dd, $J = 18.2, 1.6$ Hz, H_a-12), 2.78 (1H, d, $J = 18.3$ Hz, H_b-12), 2.62 (1H, d, $J = 13.9$ Hz, H_a-3), 2.34 (3H, s, CH₃), 2.29 (1H, d, $J = 16.4$ Hz, H_a-10), 2.28 (1H, dd, $J = 13.9, 1.0$ Hz, H_b-3), 2.20 (1H, d, $J = 16.2$ Hz, H_b-10), 1.94 (1H, dd, $J = 12.3, 1.0$ Hz, H_b-5), 1.23 (3H, s, C-4-CH₃), 1.17 (3H, s, C-4-CH₃'), 1.11 (3H, s, C-11-CH₃), 1.04 (3H, s, C-11-CH₃'); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl₃) δ 197.5 (C-7), 196.5 (C-6), 196.4 (C-9), 166.6 (C-2), 161.0 (C-12a), 137.0, 136.2 (arom C), 130.6, 128.0, 127.4, 126.9 (arom CH), 124.6 (C-8a), 50.6 (C-10), 46.5 (C-8), 46.2 (C-3), 44.7 (C-5), 42.5 (C-12), 36.6 (C-4), 34.1 (C-4-CH₃), 33.1 (C-11), 28.4 (C-11-CH₃), 27.9 (C-11-CH₃'), 25.0 (C-4-CH₃'), 19.7 (CH₃). HRMS (ESI) m/z : [M + H]⁺ Calcd for C₂₄H₂₉O₅ 397.2015. Found 397.2036.

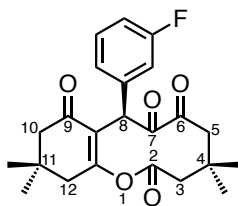
(*R*)-8-(4-Fluorophenyl)-4,4,11,11-tetramethyl-4,5,8,10,11,12-hexahydro-2H-benzo[*b*]oxecine-2,6,7,9(3H)-tetraone (**2e**: $R = 4\text{-FC}_6\text{H}_4$).



2e

Yield (87.0 mg, 44%); yellow needles (from Et₂O/hexane); mp 135 °C; $R_f = 0.36$ (EtOAc/hexane 1:4 v/v); IR ν 1701, 1686, and 1653 (C=O); ^1H NMR (500 MHz, CDCl₃) δ 7.08 (2H, dd, $J = 8.2, 8.0$ Hz, arom H), 6.99 (2H, t, $J = 8.6$ Hz, arom H), 5.31 (1H, s, H-8), 3.74 (1H, d, $J = 12.2$ Hz, H_a-5), 2.86 (1H, d, $J = 18.4$ Hz, H_a-12), 2.71 (1H, d, $J = 18.4$ Hz, H_b-12), 2.63 (1H, d, $J = 13.8$ Hz, H_a-3), 2.31 (1H, d, $J = 16.4$ Hz, H_a-10), 2.29 (1H, d, $J = 13.8$ Hz, H_b-3), 2.19 (1H, d, $J = 16.4$ Hz, H_b-10), 1.94 (1H, d, $J = 12.3$ Hz, H_b-5), 1.23 (3H, s, C-4-CH₃), 1.19 (3H, s, C-4-CH₃'), 1.10 (3H, s, C-11-CH₃), 0.99 (3H, s, C-11-CH₃'); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl₃) δ 197.1 (C-7), 196.18 (C-6), 196.17 (C-9), 166.6 (C-2), 162.0 (d, $^1J_{\text{C-F}} = 244$ Hz, arom C-F), 160.7 (C-12a), 132.4 (d, $^4J_{\text{C-F}} = 4$ Hz, arom C), 131.0 (d, $^3J_{\text{C-F}} = 9$ Hz, arom CH), 124.1 (C-8a), 115.4 (d, $^2J_{\text{C-F}} = 21$ Hz, arom CH), 50.5 (C-10), 47.9 (C-8), 46.4 (C-3), 45.1 (C-5), 42.6 (C-12), 36.7 (C-4), 34.1 (C-4-CH₃), 33.0 (C-11), 28.6 (C-11-CH₃), 27.5 (C-11-CH₃'), 25.0 (C-4-CH₃'). HRMS (ESI) m/z : [M + H]⁺ Calcd for C₂₃H₂₆O₅F 401.1764. Found 401.1768.

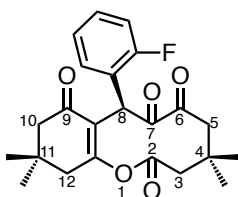
(*R*)-8-(3-Fluorophenyl)-4,4,11,11-tetramethyl-4,5,8,10,11,12-hexahydro-2H-benzo[*b*]oxecine-2,6,7,9(3H)-tetraone (**2f**: $R = 3\text{-FC}_6\text{H}_4$).



2f

Yield (84.8 mg, 42%); yellow needles (from Et₂O/hexane); mp 135–136 °C; *R*_f = 0.30 (EtOAc/hexane 1:4 v/v); IR ν 1713, 1684, and 1659 (C=O); ¹H NMR (500 MHz, CDCl₃) δ 7.27 (1H, q, *J* = 7.0 Hz, arom H), 6.94 (1H, td, *J* = 8.5, 2.4 Hz, arom CH), 6.91 (1H, t, *J* = 7.7 Hz, arom H), 6.81 (1H, dt, *J* = 10, 1.7 Hz, arom CH), 5.33 (1H, s, H-8), 3.73 (1H, d, *J* = 12.3 Hz, H_a-5), 2.86 (1H, dd, *J* = 18.4, 1.7 Hz, H_a-12), 2.74 (1H, d, *J* = 18.4 Hz, H_b-12), 2.64 (1H, d, *J* = 13.8 Hz, H_a-3), 2.32 (1H, d, *J* = 16.4 Hz, H_a-10), 2.29 (1H, d, *J* = 13.8 Hz, H_b-3), 2.21 (1H, d, *J* = 16.4 Hz, H_b-10), 1.94 (1H, d, *J* = 12.3 Hz, H_b-5), 1.23 (3H, s, C-4-CH₃), 1.19 (3H, s, C-4-CH₃'), 1.11 (3H, s, C-11-CH₃), 1.01 (3H, s, C-11-CH₃'); ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 196.7 (C-7), 196.2 (C-6), 196.0 (C-9), 166.5 (C-2), 162.7 (d, ¹*J*_{C-F} = 245 Hz, arom C-F), 161.1 (C-12a), 139.2 (d, ³*J*_{C-F} = 8 Hz, arom C), 129.8 (d, ⁴*J*_{C-F} = 8 Hz, arom CH), 125.2 (d, ⁴*J*_{C-F} = 3 Hz, arom CH), 123.6 (C-8a), 116.4 (d, ²*J*_{C-F} = 21 Hz, arom CH), 114.4 (d, ²*J*_{C-F} = 20 Hz, arom CH), 50.5 (C-10), 48.0 (C-8), 46.4 (C-3), 45.0 (C-5), 42.5 (C-12), 36.7 (C-4), 34.1 (C-4-CH₃), 33.0 (C-11), 28.6 (C-11-CH₃), 27.5 (C-11-CH₃'), 25.0 (C-4-CH₃'). HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₃H₂₆O₅F 401.1764. Found 401.1780.

(*R*)-8-(2-Fluorophenyl)-4,4,11,11-tetramethyl-4,5,8,10,11,12-hexahydro-2H-benzo[*b*]oxecine-2,6,7,9(3*H*)-tetraone (**2g**: *R* = 2-FC₆H₄).

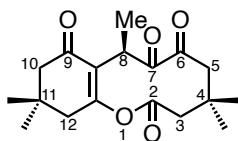


2g

Yield (84.2 mg, 42%); yellow needles (from Et₂O/hexane); mp 142–144 °C; *R*_f = 0.32 (EtOAc/hexane 1:4 v/v); IR ν 1701, 1670, and 1643 (C=O); ¹H NMR (500 MHz, CDCl₃) δ 7.26–7.22 (1H, m, arom H), 7.14–7.01 (3H, m, arom H), 5.51 (1H, s, H-8), 3.74 (1H, d, *J* = 12.3 Hz, H_a-5), 2.84 (1H, dd, *J* = 18.5, 1.7 Hz, H_a-12), 2.75 (1H, d, *J* = 18.4 Hz, H_b-12), 2.65 (1H, d, *J* = 14.0 Hz, H_a-3), 2.31 (1H, d, *J* = 16.4 Hz, H_a-10), 2.29 (1H, dd, *J* = 14.0, 0.9 Hz, H_b-3), 2.21 (1H, d, *J* = 16.4 Hz, H_b-10), 1.94 (1H, dd, *J* = 12.2, 0.9 Hz, H_b-5), 1.23 (3H, s, C-4-CH₃), 1.18 (3H, s, C-4-CH₃'), 1.10 (3H, s, C-11-CH₃), 1.00 (3H, s, C-11-CH₃'); ¹³C {¹H} NMR

(125 MHz, CDCl₃) δ 196.3 (C-7), 195.9 (C-6), 195.6 (C-9), 166.3 (C-2), 161.2 (C-12a), 161.1 (d, $^1J_{C-F}$ = 246 Hz, arom C-F), 131.3 (d, $^4J_{C-F}$ = 4 Hz, arom CH), 129.3 (d, $^3J_{C-F}$ = 9 Hz, arom CH), 124.1 (d, $^4J_{C-F}$ = 4 Hz, arom CH), 123.8 (d, $^2J_{C-F}$ = 15 Hz, arom C), 122.5 (C-8a), 115.5 (d, $^2J_{C-F}$ = 21 Hz, arom CH), 50.5 (C-10), 46.5 (C-3), 45.1 (C-5), 44.0 (C-8), 42.5 (C-12), 34.1 (C-4-CH₃), 33.1 (C-4), 33.0 (C-11), 28.5 (C-11-CH₃), 27.6 (C-11-CH₃'), 24.90 (C-4-CH₃'). HRMS (ESI) m/z : [M + H]⁺ Calcd for C₂₃H₂₆O₅F 401.1764. Found 401.1772.

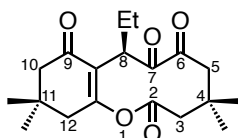
(*R*)-4,4,8,11,11-Pentamethyl-4,5,8,10,11,12-hexahydro-2*H*-benzo[*b*]oxecine-2,6,7,9(3*H*)-tetraone (**2m**: R = Me).



2m

Yield (30.6 mg, 19%); yellow needles (from Et₂O/hexane); mp 102–103 °C; R_f = 0.45 (EtOAc/hexane 1:4 v/v); IR ν 1709, 1668, and 1647 (C=O); ¹H NMR (500 MHz, CDCl₃) δ 4.08 (1H, q, J = 6.9 Hz, H-8), 3.77 (1H, d, J = 12.1 Hz, H_a-5), 2.79 (1H, d, J = 18.5 Hz, H_a-12), 2.61 (1H, d, J = 18.4 Hz, H_b-12), 2.59 (1H, d, J = 14.0 Hz, H_a-3), 2.37 (1H, d, J = 16.4 Hz, H_a-10), 2.32 (1H, d, J = 16.3 Hz, H_b-10), 2.24 (1H, d, J = 13.7 Hz, H_b-3), 1.91 (1H, d, J = 12.1 Hz, H_b-5), 1.20 (3H, d, J = 6.5 Hz, C-8-CH₃), 1.19 (3H, s, C-4-CH₃), 1.18 (3H, s, C-4-CH₃'), 1.10 (3H, s, C-11-CH₃), 1.05 (3H, s, C-11-CH₃'); ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 199.8 (C-7), 197.1 (C-6), 196.1 (C-9), 166.6 (C-2), 159.9 (C-12a), 125.6 (C-8a), 50.7 (C-10), 46.5 (C-8), 45.0 (C-3), 42.5 (C-5), 36.7 (C-12), 36.6 (C-4), 34.0 (C-4-CH₃), 33.0 (C-11), 28.5 (C-11-CH₃), 27.3 (C-11-CH₃'), 25.0 (C-4-CH₃'), 14.5 (C-8-CH₃). HRMS (ESI) m/z : [M + H]⁺ Calcd for C₁₈H₂₅O₅ 321.1702. Found 321.1700.

(*R*)-8-Ethyl-4,4,11,11-tetramethyl-4,5,8,10,11,12-hexahydro-2*H*-benzo[*b*]oxecine-2,6,7,9(3*H*)-tetraone (**2n**: R = Et).

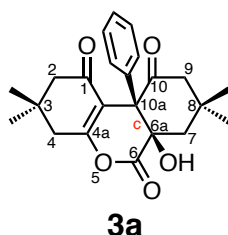


2n

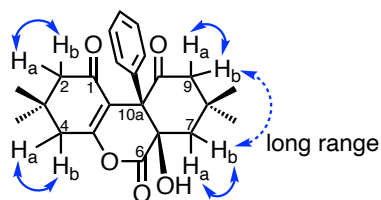
Yield (7.6 mg, 4%); yellow liquid; R_f = 0.48 (EtOAc/hexane 1:4 v/v); IR ν 1709, 1670, and 1643 (C=O); ¹H NMR (500 MHz, CDCl₃) δ 3.99 (1H, dq, J = 6.4, 1.6 Hz, H-8), 3.71 (1H, d, J = 12.2 Hz, H_a-5), 2.75 (1H, d, J = 18.5 Hz, H_a-12), 2.69 (1H, d, J = 18.5 Hz, H_b-12), 2.59 (1H, d, J = 13.8 Hz, H_a-3), 2.37 (1H, d, J = 16.1 Hz, H_a-10), 2.33 (1H, d, J = 16.2 Hz, H_b-10), 2.23

(1H, d, $J = 13.8$ Hz, H_b-3), 1.92 (1H, d, $J = 12.1$ Hz, H_b-5), 1.83–1.67 (2H, m, C-8-CH₂CH₃), 1.20 (3H, d, $J = 6.5$ Hz, C-8-CH₃), 1.17 (3H, s, C-4-CH₃), 1.10 (3H, s, C-4-CH₃'), 1.07 (3H, s, C-11-CH₃), 0.85 (3H, t, $J = 7.4$ Hz, CH₂CH₃); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 199.5 (C-7), 197.2 (C-6), 196.3 (C-9), 166.5 (C-2), 160.7 (C-12a), 124.0 (C-8a), 50.8 (C-10), 46.5 (C-8), 45.2 (C-3), 42.9 (C-5), 42.3 (C-12), 36.6 (C-4), 34.0 (C-4-CH₃), 33.0 (C-11), 28.4 (C-11-CH₃), 27.7 (C-11-CH₃'), 25.1 (C-4-CH₃'), 22.0 (CH₂CH₃), 11.4 (CH₂CH₃). HRMS (ESI) m/z : [M + H]⁺ Calcd for C₁₉H₂₇O₅ 335.1858. Found 335.1857.

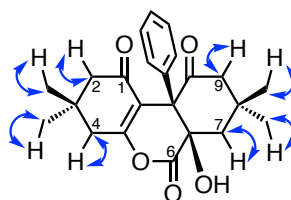
(6*aR*, 10*aS*)-6*a*-Hydroxy-3,3,8,8-tetramethyl-10*a*-phenyl-2,3,4,6*a*,7,8,9,10*a*-octahydro-1*H*-benzo[*c*]chromene-1,6,10-trione (**3a**: R = Ph).



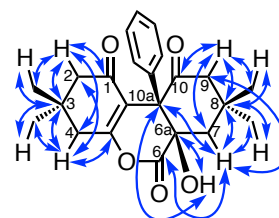
Yield (81.9 mg, 43% based on **1a**); colorless microcrystals (from EtOH); mp 258 °C; $R_f = 0.28$ (EtOAc/CHCl₃ 1:19 v/v); IR ν 3500–3300 (OH), 1801, 1728, 1655, and 1628 (C=O); ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.31–7.29 (2H, m, arom H), 7.24–7.20 (3H, m, arom H), 6.51 (1H, s, OH), 2.73 (1H, d, $J = 18.3$ Hz, H_a-4), 2.65 (1H, d, $J = 18.3$ Hz, H_b-4), 2.44 (1H, d, $J = 15.5$ Hz, H_a-2), 2.42 (1H, d, $J = 12.5$ Hz, H_a-9), 2.37 (1H, d, $J = 15.5$ Hz, H_b-2), 2.17 (1H, d, $J = 14.3$ Hz, H_a-7), 2.10 (1H, dd, $J = 12.5, 2.0$ Hz, H_b-9), 1.78 (1H, dd, $J = 14.3, 2.0$ Hz, H_b-7), 1.134 (3H, s, CH₃), 1.131 (3H, s, Me), 1.01 (3H, s, CH₃), 1.00 (3H, s, CH₃); ¹³C{¹H} NMR (125 MHz, DMSO-*d*₆) δ 202.1 (C-10), 197.1 (C-1), 169.5 (C-6), 167.3 (C-4a), 134.8 (arom C), 130.5 (2C), 127.6, 127.5 (2C) (arom CH), 117.9 (C-10b), 79.1 (C-6a), 58.1 (C-10a), 52.8 (C-9), 50.4 (C-2), 43.8 (C-7), 40.3 (C-4), 37.4 (C-8), 33.7 (C-8-CH₃), 32.6 (C-3), 28.6 (C-8-CH₃'), 27.7 (C-3-CH₃), 27.6 (C-3-CH₃'). HRMS (ESI) m/z : [M + H]⁺ Calcd for C₂₃H₂₇O₅ 383.1858. Found 383.1847.



3a-COSY

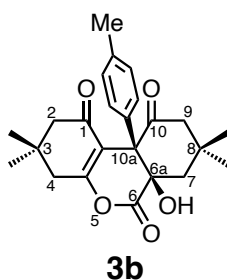


3a-HMQC



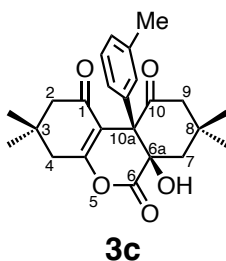
3a-HMBC

(6*aR*, 10*aS*)-6*a*-Hydroxy-10*a*-(4-methylphenyl)-3,3,8,8-tetramethyl-2,3,4,6*a*,7,8,9,10*a*-octahydro-1*H*-benzo[*c*]chromene-1,6,10-trione (**3b**: R = 4-MeC₆H₄).



Yield (77.3 mg, 39%); colorless microcrystals (from EtOH); mp 250–251 °C; $R_f = 0.25$ (EtOAc/CHCl₃ 1:19 v/v); IR ν 3500–3300 (OH), 1794, 1730, 1659, and 1634 (C=O); ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.18 (2H, d, $J = 9.5$ Hz, arom H), 7.06 (2H, d, $J = 8.3$ Hz, arom H), 6.44 (1H, s, OH), 2.73 (1H, d, $J = 18.1$ Hz, H_a-4), 2.63 (1H, d, $J = 18.2$ Hz, H_b-4), 2.43 (1H, d, $J = 15.8$ Hz, H_a-2), 2.40 (1H, d, $J = 11.9$ Hz, H_a-9), 2.35 (1H, d, $J = 16.0$ Hz, H_b-2), 2.24 (3H, s, arom-CH₃), 2.16 (1H, d, $J = 14.3$ Hz, H_a-7), 2.09 (1H, dd, $J = 12.4, 1.9$ Hz, H_b-9), 1.76 (1H, dd, $J = 14.5, 1.8$ Hz, H_b-7), 1.13 (3H, s, CH₃), 1.12 (3H, s, CH₃), 1.02 (3H, s, CH₃), 1.00 (3H, s, CH₃); ¹³C{¹H} NMR (125 MHz, DMSO-*d*₆) δ 202.1 (C-10), 197.0 (C-1), 169.5 (C-6), 167.1 (C-4a), 136.6, 131.7 (arom C), 130.4 (2C), 128.1 (2C) (arom CH), 118.0 (C-10b), 79.2 (C-6a), 57.9 (C-10a), 52.8 (C-9), 50.4 (C-2), 43.8 (C-7), 40.3 (C-4), 37.4 (C-8), 33.8 (C-8-CH₃), 32.6 (C-3), 28.8 (C-8-CH₃'), 27.7 (C-3-CH₃), 27.6 (C-3-CH₃'), 21.1 (arom-CH₃). HRMS (ESI) m/z : [M + H]⁺ Calcd for C₂₄H₂₉O₅ 397.2015. Found 397.2010.

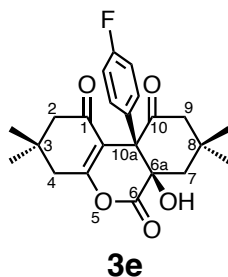
(6*aR*, 10*aS*)-6*a*-Hydroxy-10*a*-(3-methylphenyl)-3,3,8,8-tetramethyl-2,3,4,6*a*,7,8,9,10*a*-octahydro-1*H*-benzo[*c*]chromene-1,6,10-trione (**3c**: R = 3-MeC₆H₄).



Yield (86.1 mg, 44%); colorless microcrystals (from EtOH); mp 261 °C; $R_f = 0.33$ (EtOAc/CHCl₃ 1:19 v/v); IR ν 3500–3300 (OH), 1801, 1730, 1653, and 1628 (C=O); ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.12 (1H, br. s, arom H), 7.08–6.98 (3H, m, arom H), 6.42 (1H, s, OH), 2.68 (1H, d, $J = 18.4$ Hz, H_a-4), 2.62 (1H, d, $J = 18.4$ Hz, H_b-4), 2.39 (1H, d, $J = 16.1$ Hz, H_a-2), 2.38 (1H, d, $J = 12.2$ Hz, H_a-9), 2.34 (1H, d, $J = 16.0$ Hz, H_b-2), 2.20 (3H, s, arom-CH₃), 2.14 (1H, d, $J = 14.3$ Hz, H_a-7), 2.06 (1H, dd, $J = 12.2, 1.5$ Hz, H_b-9), 1.73 (1H, dd, $J = 14.2, 1.4$ Hz, H_b-7), 1.10 (6H, s, CH₃ × 2), 0.99 (3H, s, CH₃), 0.98 (3H, s, CH₃); ¹³C{¹H} NMR (125 MHz, DMSO-*d*₆) δ 202.1 (C-10), 197.1 (C-1), 169.6 (C-6), 167.2 (C-4a), 136.1, 134.7 (arom C), 131.5, 128.2, 127.4, 127.2 (arom CH), 118.1 (C-10b), 79.1 (C-6a), 58.1 (C-10a), 52.9 (C-

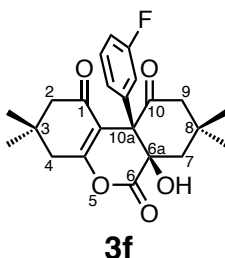
9), 50.4 (C-2), 43.8 (C-7), 40.3 (C-4), 37.4 (C-8), 33.8 (C-8- $\underline{\text{C}}\text{H}_3$), 32.6 (C-3), 28.5 (C-8- $\underline{\text{C}}\text{H}_3'$), 27.8 (C-3- $\underline{\text{C}}\text{H}_3$), 27.7 (C-3- $\underline{\text{C}}\text{H}_3'$), 22.0 (arom- $\underline{\text{C}}\text{H}_3$). Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{O}_5$: C, 72.71; H, 7.12. Found; C, 72.52; H, 7.20.

(6*aR*,10*aS*)-10*a*-(4-Fluorophenyl)-6*a*-hydroxy-3,3,8,8-tetramethyl-2,3,4,6*a*,7,8,9,10*a*-octahydro-1*H*-benzo[*c*]chromene-1,6,10-trione (**3e**: R = 4-FC₆H₄).



Yield (100.0 mg, 50%); colorless microcrystals (from EtOH); mp 262 °C; $R_f = 0.25$ (EtOAc/CHCl₃ 1:19 v/v); IR ν 3500–3300 (OH), 1801, 1730, 1653, and 1628 (C=O); ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.32–7.27 (2H, m, arom H), 7.04–6.99 (2H, m, arom H), 6.56 (1H, s, OH), 2.73 (1H, d, $J = 18.1$ Hz, H_a-4), 2.62 (1H, d, $J = 18.2$ Hz, H_b-4), 2.43 (1H, d, $J = 16.1$ Hz, H_a-2), 2.38 (1H, d, $J = 12.5$ Hz, H_a-9), 2.33 (1H, d, $J = 16.0$ Hz, H_b-2), 2.14 (1H, d, $J = 14.3$ Hz, H_a-7), 2.08 (1H, dd, $J = 12.4, 2.0$ Hz, H_b-9), 1.75 (1H, dd, $J = 14.3, 1.9$ Hz, H_b-7), 1.10 (3H, s, CH₃), 1.09 (3H, s, CH₃), 1.00 (3H, s, CH₃), 0.99 (3H, s, CH₃); ¹³C{¹H} NMR (125 MHz, DMSO-*d*₆) δ 202.0 (C-10), 197.1 (C-1), 169.3 (C-6), 167.6 (C-4a), 161.8 (d, ¹ $J_{\text{C-F}}$ = 243 Hz, arom C-F), 132.7 (d, ³ $J_{\text{C-F}}$ = 7.5 Hz, arom CH), 130.6 (d, ⁴ $J_{\text{C-F}}$ = 2.5 Hz, arom C), 117.6 (C-10b), 114.1 (d, ² $J_{\text{C-F}}$ = 21.3 Hz, arom CH), 79.1 (C-6a), 57.7 (C-10a), 52.7 (C-9), 50.3 (C-2), 43.7 (C-7), 40.2 (C-4), 37.5 (C-8), 33.7 (C-8- $\underline{\text{C}}\text{H}_3$), 32.5 (C-3), 28.8 (C-8- $\underline{\text{C}}\text{H}_3'$), 27.7 (C-3- $\underline{\text{C}}\text{H}_3$), 27.6 (C-3- $\underline{\text{C}}\text{H}_3'$). Anal. Calcd for $\text{C}_{23}\text{H}_{25}\text{FO}_5$: C, 68.99; H, 6.29. Found: C, 68.73; H, 6.24.

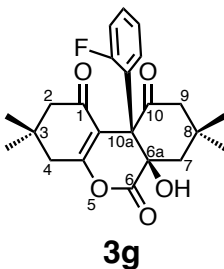
(6*aR*,10*aS*)-10*a*-(3-Fluorophenyl)-6*a*-hydroxy-3,3,8,8-tetramethyl-2,3,4,6*a*,7,8,9,10*a*-octahydro-1*H*-benzo[*c*]chromene-1,6,10-trione (**3f**: R = 3-FC₆H₄).



Yield (106.7 mg, 53%); colorless needles (from EtOH); mp 243–244 °C; $R_f = 0.29$ (EtOAc/CHCl₃ 1:19 v/v); IR ν 3500–3300 (OH), 1801, 1730, 1653, and 1628 (C=O); ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.23 (1H, q, $J = 7.7$ Hz, arom H), 7.16 (1H, dt, $J = 12.1, 2.1$ Hz, arom

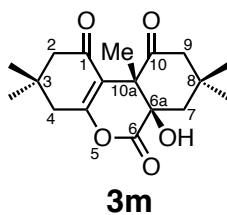
H), 7.04 (1H, td, $J = 8.6, 2.5$ Hz, arom H), 7.01 (1H, d, $J = 9.0$ Hz, arom H), 6.65 (1H, s, OH), 2.72 (1H, d, $J = 18.1$ Hz, H_a-4), 2.63 (1H, d, $J = 18.3$ Hz, H_b-4), 2.43 (1H, d, $J = 16.1$ Hz, H_a-2), 2.39 (1H, d, $J = 12.3$ Hz, H_a-9), 2.34 (1H, d, $J = 16.2$ Hz, H_b-2), 2.15 (1H, d, $J = 14.4$ Hz, H_a-7), 2.09 (1H, dd, $J = 12.4, 1.7$ Hz, H_b-9), 1.76 (1H, dd, $J = 14.3, 1.5$ Hz, H_b-7), 1.10 (6H, s, CH₃ × 2), 0.99 (3H, s, CH₃), 0.98 (3H, s, CH₃); ¹³C{¹H} NMR (125 MHz, DMSO-*d*₆) δ 201.8 (C-10), 197.2 (C-1), 169.3 (C-6), 167.8 (C-4a), 161.4 (d, $^1J_{C-F} = 239$ Hz, arom C-F), 137.5 (d, $^3J_{C-F} = 9$ Hz, arom C), 129.3 (d, $^3J_{C-F} = 9$ Hz, arom CH), 125.4 (d, $^4J_{C-F} = 3$ Hz, arom CH), 118.6 (d, $^2J_{C-F} = 24$ Hz, arom CH), 117.5 (C-10b), 114.6 (d, $^2J_{C-F} = 20$ Hz, arom CH), 79.0 (C-6a), 58.0 (C-10a), 52.7 (C-9), 50.3 (C-2), 43.7 (C-7), 40.3 (C-4), 37.5 (C-8), 33.7 (C-8-CH₃), 32.6 (C-3), 28.6 (C-8-CH₃'), 27.7 (C-3-CH₃), 27.6 (C-3-CH₃'). Anal. Calcd for C₂₃H₂₅FO₅: C, 68.99; H, 6.29. Found: C, 69.00; H, 6.20.

(6*a**R*, 10*a**S*)-10*a*-(2-Fluorophenyl)-6*a*-hydroxy-3,3,8,8-tetramethyl-2,3,4,6*a*,7,8,9,10*a*-octahydro-1*H*-benzo[*c*]chromene-1,6,10-trione (**3g**: *R* = 2-FC₆H₄).



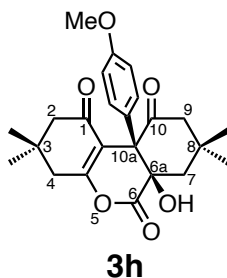
Yield (91.0 mg, 46%); colorless microcrystals (from EtOH); mp 234–235 °C; $R_f = 0.25$ (EtOAc/CHCl₃ 1:19 v/v); IR ν 3500–3300 (OH), 1792, 1740, 1663, and 1624 (C=O); ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.32–7.24 (2H, m, arom H), 7.03–6.97 (2H, m, arom H), 6.41 (1H, s, OH), 2.64 (2H, s, H-4), 2.41 (1H, d, $J = 12.7$ Hz, H_a-9), 2.31 (2H, s, H-2), 2.13 (1H, d, $J = 14.6$ Hz, H_a-7), 2.09 (1H, dd, $J = 12.6, 2.1$ Hz, H_b-9), 1.76 (1H, dd, $J = 14.3, 2.0$ Hz, H_b-7), 1.11 (3H, s, CH₃), 1.08 (3H, s, CH₃), 0.98 (3H, s, CH₃), 0.97 (3H, s, CH₃); ¹³C{¹H} NMR (125 MHz, DMSO-*d*₆) δ 199.5 (C-10), 196.0 (C-1), 169.3 (C-6), 167.4 (C-4a), 161.5 (d, $^1J_{C-F} = 250$ Hz, arom C-F), 132.6 (d, $J_{C-F} = 3$ Hz, arom CH), 130.1 (d, $^3J_{C-F} = 9$ Hz, arom CH), 123.4 (d, $^4J_{C-F} = 3$ Hz, arom CH), 122.1 (d, $^2J_{C-F} = 11$ Hz, arom C), 117.0 (d, $^2J_{C-F} = 26$ Hz, arom CH), 116.3 (C-10b), 79.4 (C-6a), 58.4 (d, $^3J_{C-F} = 5$ Hz, C-10a), 52.3 (C-9), 50.7 (C-2), 44.1 (C-7), 40.7 (C-4), 36.8 (C-8), 33.5 (C-8-CH₃), 32.2 (C-3), 28.6 (C-8-CH₃'), 27.7 (C-3-CH₃ × 2). Anal. Calcd for C₂₃H₂₅FO₅: C, 68.99; H, 6.29. Found: C, 68.98; H, 6.24.

(6*a**R*, 10*a**S*)-6*a*-Hydroxy-3,3,8,8,10*a*-pentamethyl-2,3,4,6*a*,7,8,9,10*a*-octahydro-1*H*-benzo[*c*]chromene-1,6,10-trione (**3m**: *R* = Me).



Yield (24.0 mg, 15%); colorless microcrystals (from Et₂O); mp 195–196 °C; *R*_f = 0.19 (EtOAc/CHCl₃ 1:9 v/v); IR ν 3500–3300 (OH), 1794, 1724, 1659, and 1639 (C=O); ¹H NMR (500 MHz, DMSO-*d*₆) δ 6.32 (1H, s, OH), 2.67 (1H, d, *J* = 17.9 Hz, H_a-4), 2.55 (1H, d, *J* = 17.5 Hz, H_b-4), 2.39 (1H, d, *J* = 16.0 Hz, H_a-2), 2.32 (1H, d, *J* = 16.9 Hz, H_b-2), 2.31 (1H, d, *J* = 12.0 Hz, H_a-9), 2.07 (1H, d, *J* = 14.3 Hz, H_a-7), 1.97 (1H, dd, *J* = 12.1, 1.8 Hz, H_b-9), 1.67 (1H, dd, *J* = 14.4, 1.9 Hz, H_b-7), 1.15 (3H, s, CH₃), 1.08 (3H, s, CH₃), 1.05 (3H, s, CH₃), 1.02 (3H, s, CH₃), 1.00 (3H, s, CH₃); ¹³C{¹H} NMR (125 MHz, DMSO-*d*₆) δ 204.9 (C-10), 196.5 (C-1), 169.5 (C-6), 165.7 (C-4a), 118.8 (C-10b), 79.3 (C-6a), 51.7 (C-9), 50.4 (C-10a), 50.3 (C-2), 42.4 (C-7), 40.3 (C-4), 37.7 (C-8), 33.7 (C-8-CH₃), 32.6 (C-3), 28.2 (C-8-CH₃'), 27.9 (C-3-CH₃), 27.6 (C-3-CH₃'), 16.6 (CH₃). Anal. Calcd for C₁₈H₂₄O₅•0.4H₂O: C, 66.00; H, 7.63. Found: C, 66.09; H, 7.54.

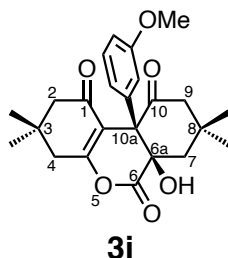
(6*aR*,10*aS*)-6*a*-Hydroxy-10*a*-(4-methoxyphenyl)-3,3,8,8-tetramethyl-2,3,4,6*a*,7,8,9,10*a*-octahydro-1*H*-benzo[*c*]chromene-1,6,10-trione (**3h**: *R* = 4-MeOC₆H₄).



Yield (52.0 mg, 25%); colorless needles (from EtOH); mp 268–269 °C; *R*_f = 0.19 (EtOAc/CHCl₃ 1:19 v/v); IR ν 3500–3300 (OH), 1801, 1728, 1653, and 1632 (C=O); ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.17 (2H, dt, *J* = 9.1, 3.3 Hz, arom H), 6.74 (2H, dt, *J* = 9.1, 3.2 Hz, arom H), 6.40 (1H, s, OH), 3.67 (3H, s, OCH₃), 2.71 (1H, d, *J* = 18.1 Hz, H_a-4), 2.60 (1H, d, *J* = 18.1 Hz, H_b-4), 2.40 (1H, d, *J* = 15.9 Hz, H_a-2), 2.36 (1H, d, *J* = 12.3 Hz, H_a-9), 2.31 (1H, d, *J* = 16.0 Hz, H_b-2), 2.12 (1H, d, *J* = 14.3 Hz, H_a-7), 2.04 (1H, dd, *J* = 12.3, 1.8 Hz, H_b-9), 1.73 (1H, dd, *J* = 14.4, 1.8 Hz, H_b-7), 1.10 (3H, s, CH₃), 1.09 (3H, s, CH₃), 1.01 (3H, s, CH₃), 0.97 (3H, s, CH₃); ¹³C{¹H} NMR (125 MHz, DMSO-*d*₆) δ 201.8 (C-10), 196.4 (C-1), 168.9 (C-6), 166.6 (C-4a), 158.2 (arom C), 131.3 (2C) (arom CH), 125.8 (arom C), 117.4 (C-10b), 112.2 (2C) (arom CH), 78.9 (C-6a), 57.0 (C-10a), 54.9 (OCH₃), 52.6 (C-9), 49.8 (C-2), 43.7 (C-7), 40.2 (C-4), 36.9 (C-8), 33.2 (C-8-CH₃), 32.0 (C-3), 28.3 (C-8-CH₃'), 27.2 (C-3-CH₃), 27.0 (C-

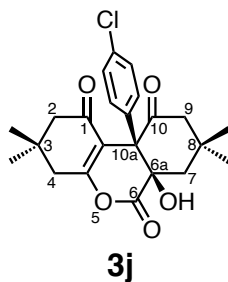
3- $\underline{\text{C}}\text{H}_3$ '). HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{24}\text{H}_{28}\text{O}_6\text{Na}$ 435.1784 ($\text{M} + \text{Na}$). Found 435.1808.

(6*aR*,10*aS*)-6*a*-Hydroxy-10*a*-(3-methoxyphenyl)-3,3,8,8-tetramethyl-2,3,4,6*a*,7,8,9,10*a*-octahydro-1*H*-benzo[*c*]chromene-1,6,10-trione (**3i**; $R = 3\text{-MeOC}_6\text{H}_4$).



Yield (34.7 mg, 17%); colorless microcrystals (from EtOH); mp 246–247 °C; $R_f = 0.30$ (EtOAc/ CHCl_3 1:9 v/v); IR ν 3500–3300 (OH), 1801, 1728, 1653, and 1628 (C=O); ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 7.09 (1H, t, $J = 8.1$ Hz, arom H), 6.91 (1H, t, $J = 2.1$ Hz, arom H), 6.80–6.75 (2H, m, arom H), 6.49 (1H, s, OH), 3.64 (3H, s, OCH_3), 2.63 (2H, br. s, H-4), 2.37 (1H, d, $J = 12.7$ Hz, H_a -9), 2.35 (2H, br. s, H-2), 2.13 (1H, d, $J = 14.3$ Hz, H_a -7), 2.06 (1H, dd, $J = 12.2, 2.0$ Hz, H_b -9), 1.73 (1H, dd, $J = 14.4, 1.9$ Hz, H_b -7), 1.09 (6H, s, $\text{CH}_3 \times 2$), 0.97 (3H, s, CH_3), 0.95 (3H, s, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $\text{DMSO-}d_6$) δ 202.1 (C-10), 197.2 (C-1), 169.6 (C-6), 167.2 (C-4a), 158.6, 136.7 (arom C), 128.4, 122.0 (arom CH), 118.3 (C-10b), 117.1, 112.3 (arom CH), 79.0 (C-6a), 58.1 (C-10a), 54.9 (OCH_3), 52.9 (C-9), 50.4 (C-2), 43.8 (C-7), 40.3 (C-4), 37.4 (C-8), 33.7 (C-8- $\underline{\text{C}}\text{H}_3$), 32.6 (C-3), 28.4 (C-8- $\underline{\text{C}}\text{H}_3$ '), 27.9 (C-3- $\underline{\text{C}}\text{H}_3$), 27.8 (C-3- $\underline{\text{C}}\text{H}_3$ '). Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{O}_6$: C, 69.89; H, 6.84. Found: C, 69.66; H, 7.05.

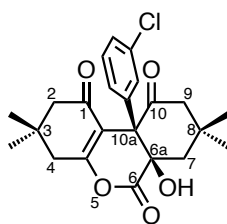
(6*aR*,10*aS*)-10*a*-(4-Chlorophenyl)-6*a*-hydroxy-3,3,8,8-tetramethyl-2,3,4,6*a*,7,8,9,10*a*-octahydro-1*H*-benzo[*c*]chromene-1,6,10-trione (**3j**; $R = 4\text{-ClC}_6\text{H}_4$).



Yield (63.7 mg, 31%); colorless microcrystals (from EtOH); mp 264–265 °C; $R_f = 0.28$ (EtOAc/ CHCl_3 1:19 v/v); IR ν 3500–3300 (OH), 1800, 1730, 1655, and 1634 (C=O); ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 7.25–7.21 (4H, m, arom H), 6.56 (1H, s, OH), 2.68 (1H, d, $J = 18.2$ Hz, H_a -4), 2.58 (1H, d, $J = 18.2$ Hz, H_b -4), 2.38 (1H, d, $J = 16.0$ Hz, H_a -2), 2.33 (1H, d, $J = 12.4$ Hz, H_a -9), 2.29 (1H, d, $J = 16.0$ Hz, H_b -2), 2.10 (1H, d, $J = 14.3$ Hz, H_a -7), 2.04 (1H, dd,

$J = 12.4, 1.5$ Hz, H_b-9), 1.72 (1H, dd, $J = 14.3, 1.5$ Hz, H_b-7), 1.06 (3H, s, CH_3), 1.05 (3H, s, CH_3), 0.96 (3H, s, CH_3), 0.94 (3H, s, CH_3); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO- d_6) δ 201.8 (C-10), 197.0 (C-1), 169.3 (C-6), 167.7 (C-4a), 133.6, 132.6 (arom C), 132.5 (2C), 127.4 (2C) (arom CH), 117.4 (C-10b), 79.0 (C-6a), 57.8 (C-10a), 52.6 (C-9), 50.3 (C-2), 43.6 (C-7), 40.2 (C-4), 37.5 (C-8), 33.7 (C-8- \underline{CH}_3), 32.5 (C-3), 28.8 (C-8- \underline{CH}_3'), 27.7 (C-3- \underline{CH}_3), 27.6 (C-3- \underline{CH}_3'). HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{23}H_{26}O_5Cl$ 417.1469. Found 417.1481.

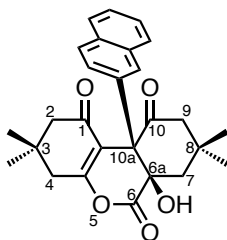
(6a*R*,10a*S*)-10a-(3-Chlorophenyl)-6a-hydroxy-3,3,8,8-tetramethyl-2,3,4,6a,7,8,9,10a-octahydro-1*H*-benzo[*c*]chromene-1,6,10-trione (**3k**: $R = 3-ClC_6H_4$).



3k

Yield (47.3 mg, 23%); colorless microcrystals (from EtOH); mp 262–263 °C; $R_f = 0.32$ (EtOAc/ $CHCl_3$ 1:19 v/v); IR ν 3500–3300 (OH), 1798, 1730, 1657, and 1630 (C=O); 1H NMR (500 MHz, DMSO- d_6) δ 7.50 (1H, t, $J = 1.9$ Hz, arom H), 7.37 (1H, dq, $J = 7.9, 1.1$ Hz, arom H), 7.32 (1H, t, $J = 7.9$ Hz, arom H), 7.19 (1H, dt, $J = 7.9, 1.4$ Hz, arom H), 6.77 (1H, s, OH), 2.81 (1H, d, $J = 18.4$ Hz, H_a-4), 2.74 (1H, d, $J = 18.2$ Hz, H_b-4), 2.51 (1H, d, $J = 16.3$ Hz, H_a-2), 2.47 (1H, d, $J = 12.4$ Hz, H_a-9), 2.45 (1H, d, $J = 16.0$ Hz, H_b-2), 2.24 (1H, d, $J = 14.3$ Hz, H_a-7), 2.18 (1H, dd, $J = 12.2, 1.9$ Hz, H_b-9), 1.84 (1H, dd, $J = 14.4, 1.6$ Hz, H_b-7), 1.19 (3H, s, CH_3), 1.18 (3H, s, CH_3), 1.08 (6H, s, $CH_3 \times 2$); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO- d_6) δ 201.8 (C-10), 197.2 (C-1), 169.2 (C-6), 167.8 (C-4a), 137.1, 132.1 (arom C), 131.7, 129.4, 127.9, 127.7 (arom CH), 117.3 (C-10b), 79.0 (C-6a), 58.0 (C-10a), 52.6 (C-9), 50.3 (C-2), 43.6 (C-7), 40.6 (C-4), 37.5 (C-8), 33.6 (C-8- \underline{CH}_3), 32.6 (C-3), 28.5 (C-8- \underline{CH}_3'), 27.8 (C-3- \underline{CH}_3), 27.7 (C-3- \underline{CH}_3'). Anal. Calcd for $C_{23}H_{25}O_5Cl$: C, 66.26; H, 6.04. Found: C, 66.24; H, 6.12.

(6a*R*,10a*S*)-6a-Hydroxy-3,3,8,8-tetramethyl-10a-(naphthalen-2-yl)-2,3,4,6a,7,8,9,10a-octahydro-1*H*-benzo[*c*]chromene-1,6,10-trione (**3l**: $R = 2$ -naphthyl).

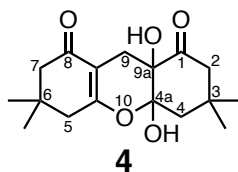


3l

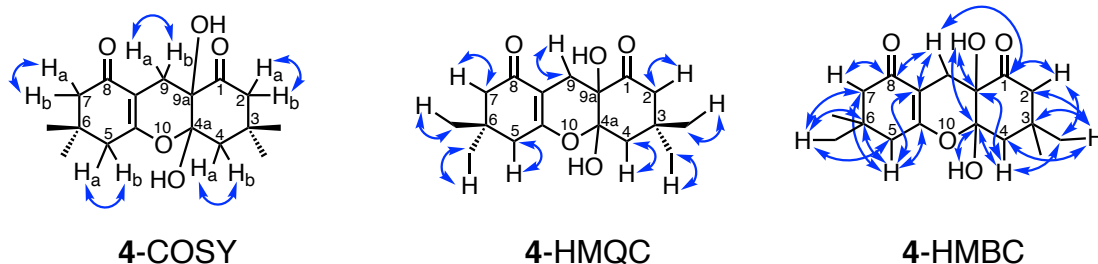
Yield (22.4 mg, 10%); colorless microcrystals (from EtOH); mp 219–220 °C; $R_f = 0.34$

(EtOAc/CHCl₃ 1:19 v/v); IR ν 3500–3300 (OH), 1780, 1730, 1653, and 1636 (C=O); ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.76 (1H, d, *J* = 7.9 Hz, arom H), 7.73 (1H, d, *J* = 7.8 Hz, arom H), 7.67 (1H, d, *J* = 9.0 Hz, arom H), 7.62 (1H, br. s, arom H), 7.52 (1H, dd, *J* = 8.8, 1.7 Hz, arom H), 7.43–7.37 (2H, m, arom H), 6.55 (1H, s, OH), 2.74 (1H, d, *J* = 18.2 Hz, H_a-4), 2.63 (1H, d, *J* = 18.2 Hz, H_b-4), 2.44 (1H, d, *J* = 16.0 Hz, H_a-2), 2.40 (1H, d, *J* = 12.6 Hz, H_a-9), 2.34 (1H, d, *J* = 16.0 Hz, H_b-2), 2.16 (1H, d, *J* = 14.3 Hz, H_a-7), 2.08 (1H, dd, *J* = 12.3, 1.6 Hz, H_b-9), 1.75 (1H, dd, *J* = 14.2, 1.3 Hz, H_b-7), 1.11 (3H, s, CH₃), 1.08 (3H, s, CH₃), 0.99 (3H, s, CH₃), 0.97 (3H, s, CH₃); ¹³C {¹H} NMR (125 MHz, DMSO-*d*₆) δ 202.4 (C-10), 197.2 (C-1), 169.5 (C-6), 167.7 (C-4a), 133.0, 132.7, 132.5 (arom C), 130.4, 128.5, 127.9, 127.5, 126.8, 126.0, 125.9 (arom CH), 117.7 (C-10b), 79.6 (C-6a), 58.4 (C-10a), 52.9 (C-9), 50.4 (C-2), 43.8 (C-7), 40.6 (C-4), 37.5 (C-8), 33.7 (C-8-CH₃), 32.6 (C-3), 28.7 (C-8-CH₃'), 27.8 (C-3-CH₃), 27.7 (C-3-CH₃'). HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₇H₂₈O₅Na 455.1834 (M + Na). Found 455.1845.

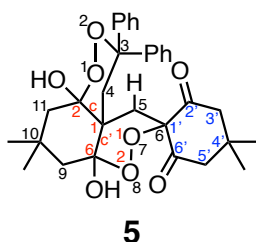
4a,9a-Dihydroxy-3,3,6,6-tetramethyl-3,4,4a,5,6,7,9,9a-octahydro-1H-xanthene-1,8(2H)-dione (4).



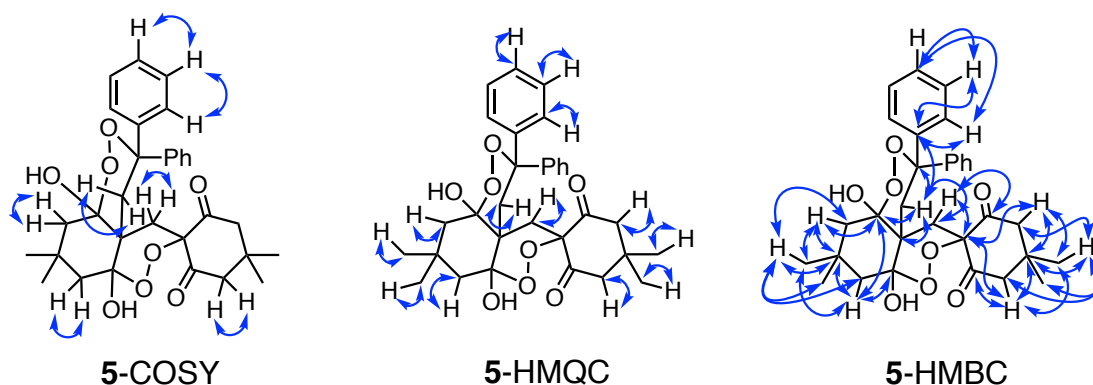
Yield (10.2 mg, 7%); colorless solid; *R*_f = 0.32 (EtOAc/CHCl₃ 3:2 v/v); IR ν 3700–3300 (OH), 1724 (C=O); ¹H NMR (500 MHz, DMSO-*d*₆) δ 6.97 (1H, s, OH), 5.71 (1H, s, OH), 3.00 (1H, d, *J* = 12.8 Hz, H_a-2), 2.30 (1H, d, *J* = 16.9 Hz, H_a-9), 2.27 (1H, d, *J* = 13.4 Hz, H_a-4), 2.21 (1H, d, *J* = 14.0 Hz, H_a-7), 2.17 (1H, d, *J* = 16.5 Hz, H_a-5), 2.07 (1H, d, *J* = 13.0 Hz, H_b-7), 2.06 (1H, d, *J* = 16.5 Hz, H_b-5), 2.06 (1H, d, *J* = 16.9 Hz, H_b-9), 1.80 (1H, d, *J* = 12.9 Hz, H_b-2), 1.75 (1H, d, *J* = 13.6 Hz, H_b-4), 1.03 (3H, s, C-3-CH₃), 1.00 (3H, s, C-6-CH₃), 0.97 (3H, s, C-6-CH₃'), 0.95 (3H, s, C-3-CH₃'); ¹³C {¹H} NMR (125 MHz, DMSO-*d*₆) δ 209.0 (C-1), 197.5 (C-8), 165.6 (C-10a), 108.9 (C-8a), 100.7 (C-4a), 72.4 (C-9a), 50.8 (C-7), 49.4 (C-2), 42.6 (C-4), 42.0 (C-5), 33.6 (C-3-CH₃), 32.7, 32.5 (C-3, C-6), 29.3 (C-6-CH₃), 28.2 (C-3-CH₃'), 27.6 (C-6-CH₃'), 21.7 (C-9). HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₇H₂₅O₅ 309.1702. Found 309.1710.



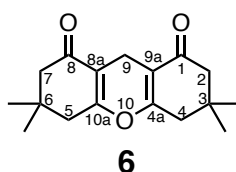
8a,11a-Dihydroxy-4',4',10,10-tetramethyl-3,3-diphenylhexahydro-5H,10H-spiro[benzo[2,1-c:6,1-c']bis([1,2]dioxine)-6,1'-cyclohexane]-2',6'-dione (5) (1:1 diastereomer mixture).



Yield (167.3 mg, 62%); colorless microcrystals (from EtOH); mp 185 °C; $R_f = 0.28$ (EtOAc/CHCl₃ 1:19 v/v); IR ν 3535, 3500–3300 (OH), 1713 (C=O); ¹H NMR (500 MHz, CDCl₃) δ 8.07 (1H, broad s, arom *ortho*-H), 7.48 (1H, broad s, arom *ortho*-H), 7.36 (2H, d, $J = 7.7$ Hz, arom *ortho*-H), 7.29 (4H, t, $J = 7.8$ Hz, arom *meta*-H), 7.23 (2H, t, $J = 7.1$ Hz, arom *para*-H), 4.05 (1H, s, OH), 3.67 (1H, broad s, OH), 2.92 (1H, d, $J = 14.2$ Hz, H_a-4), 2.78 (1H, d, $J = 14.3$ Hz, H_b-4), 2.70 (1H, d, $J = 14.8$ Hz, H_a-9), 2.04 (1H, d, $J = 15.2$ Hz, H_a-11), 2.03 (1H, dd, $J = 15.4, 1.9$ Hz, H_a-3'), 1.98 (1H, dd, $J = 15.0, 1.9$ Hz, H_b-3'), 1.86 (1H, d, $J = 13.3$ Hz, H_a-5), 1.82 (1H, d, $J = 13.3$ Hz, H_a-5'), 1.77 (1H, d, $J = 13.2$ Hz, H_b-5), 1.74 (1H, d, $J = 14.2$ Hz, H_b-9), 1.65 (1H, d, $J = 16.5$ Hz, H_b-11), 1.62 (1H, d, $J = 13.9$ Hz, H_b-5'), 1.17 (3H, s, CH₃), 1.02 (3H, s, CH₃), 0.93 (3H, s, CH₃), 0.91 (3H, s, CH₃); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 204.0 (2C) (C-2' and C-6'), 144.1, 142.9 (arom C), 128.7 (4C), 128.4, 127.3, 125.7 (4C) (arom CH), 106.2, 103.4, (100.7 (diastereomer)) (C-8a, C-11a), 84.8, 83.9 (C-3, C-6), 50.3 (C-9 or C-11), 48.7 (C-3' or C-5'), 44.0 (C-11 or C-9), 41.1 (C-5' or C-3'), 39.1 (C-5), 36.0 (C-4a), 35.1 (C-10-C_aH₃), 32.4 (C-10-C_bH₃), 32.0 (C-10), 30.1 (C-4'), 29.4 (C-4'-C_aH₃), 28.1 (C-4), 26.6 (C-4'-C_bH₃). HRMS (ESI) m/z : [M + Na]⁺ Calcd for C₃₁H₃₆O₈Na 559.2308 (M + Na). Found 559.2290. Anal. Calcd for C₃₁H₃₆O₈•0.25H₂O: C, 68.81; H, 6.80. Found: C, 68.91; H, 7.14.



*3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (6).*¹



Yield (137.4 mg, quant.); $R_f = 0.10$ (CHCl_3); IR ν 1688, 1659 ($\text{C}=\text{O}$); ^1H NMR (500 MHz, CDCl_3) δ 2.88 (2H, s, H-9), 2.36 (4H, s, H-2 and H-7), 2.29 (4H, s, H-4 and H-5), 1.11 (12H, s, $\text{CH}_3 \times 4$); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 197.4 (C-1 and C-8), 162.8 (C-4a and C-10a), 111.0 (C-8a and C-9a), 50.4 (C-2 and C-7), 40.6 (C-4 and C-5), 31.9 (C-3 and C-6), 28.2 ($\text{CH}_3 \times 4$), 15.3 (C-9).

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X-ray crystallographic data of **2a**: empirical formula $C_{23}H_{26}O_5$; formula weight 382.44; yellow needles from Et_2O /hexane; orthorhombic; space group $P2_12_12_1$; $a = 5.7862(3)$, $b = 11.7906(8)$, $c = 30.043(2)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 2049.6(2)$ Å³, $Z = 4$; $D_{\text{calcd}} = 1.239$ g/cm³; $F(000) = 816.0$; $R = 0.0490$; $R_w = 0.1320$; GOF = 1.009. X-ray coordinates were deposited with the Cambridge Crystallographic Data Centre: CCDC 2120597.

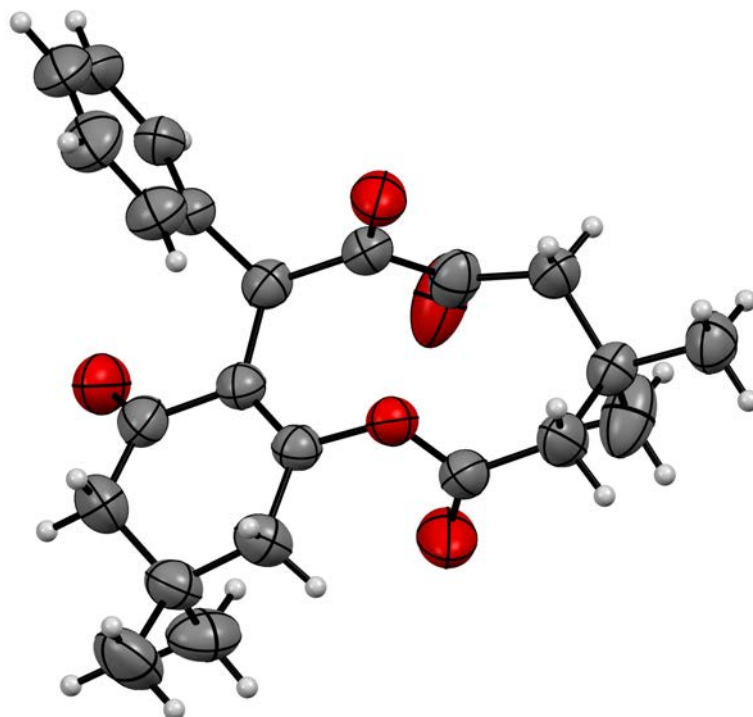
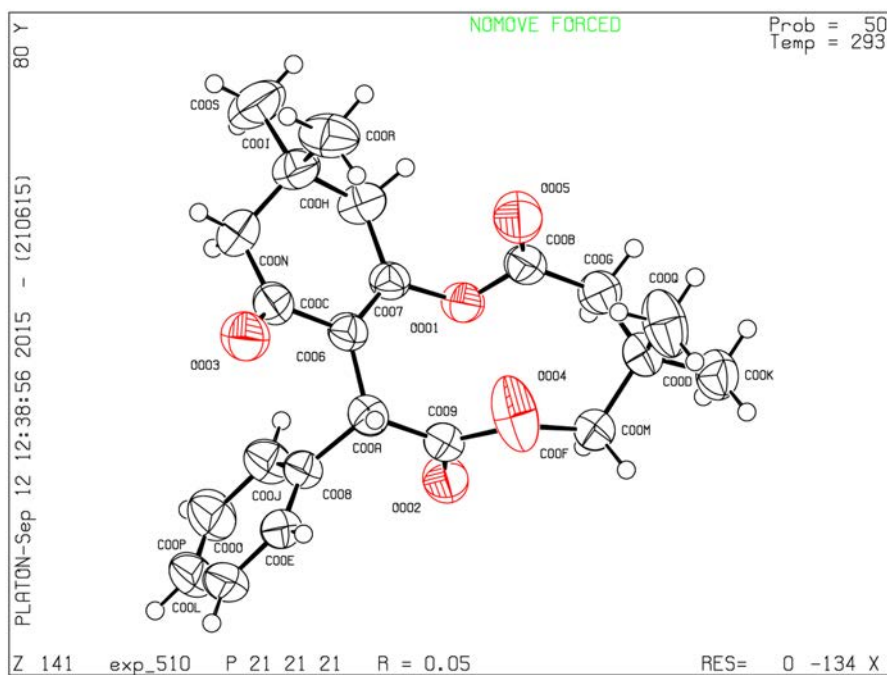


Figure 1. Crystal Structure of **2a**

X-ray crystallographic data of **3a**: empirical formula $C_{23}H_{26}O_5$; formula weight 382.44; colorless cubs from EtOH; monoclinic; space group $P12_1/n_1$; $a = 9.69831(18)$, $b = 17.6296(4)$, $c = 11.3966(2)$ Å, $\alpha = 90.00^\circ$, $\beta = 99.9315(18)^\circ$, $\gamma = 90.00^\circ$, $V = 1919.36(6)$ Å³, $Z = 4$; $D_{\text{calcd}} = 1.323$ g/cm³; $F(000) = 816.0$; $R = 0.0383$; $R_w = 0.0999$; GOF = 1.035. X-ray coordinates were deposited with the Cambridge Crystallographic Data Centre: CCDC 2120608.

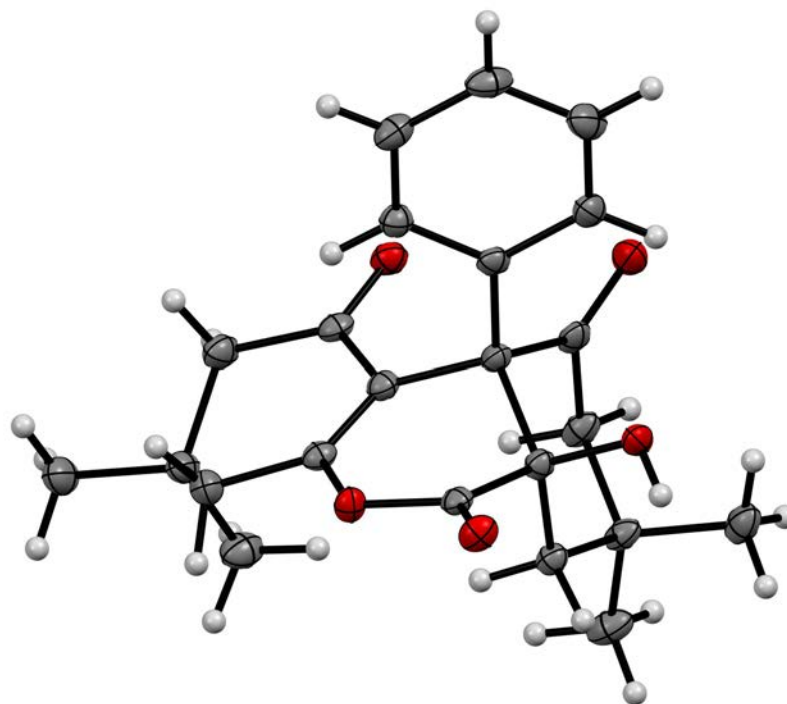
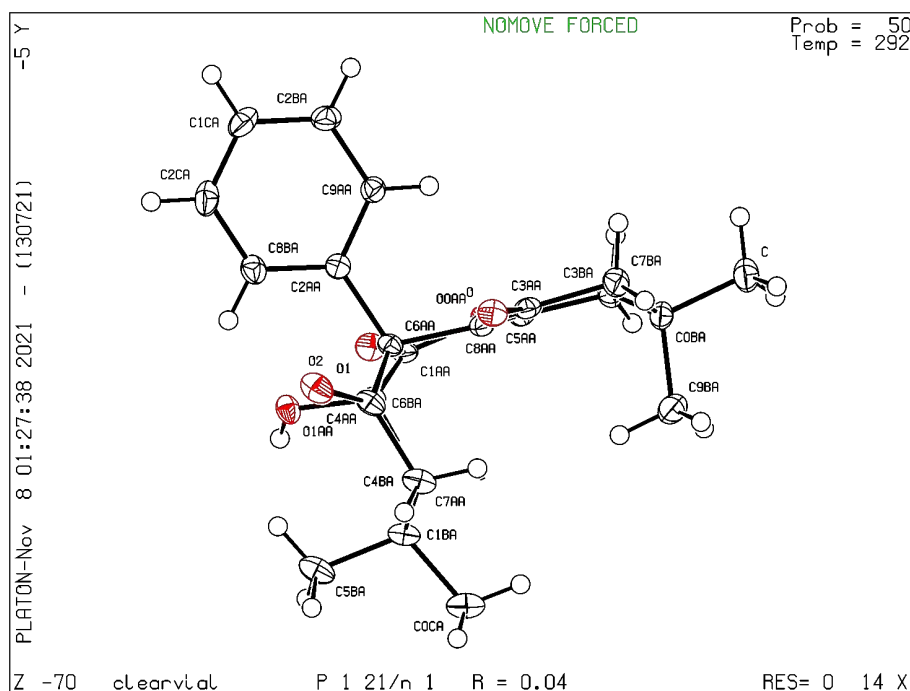
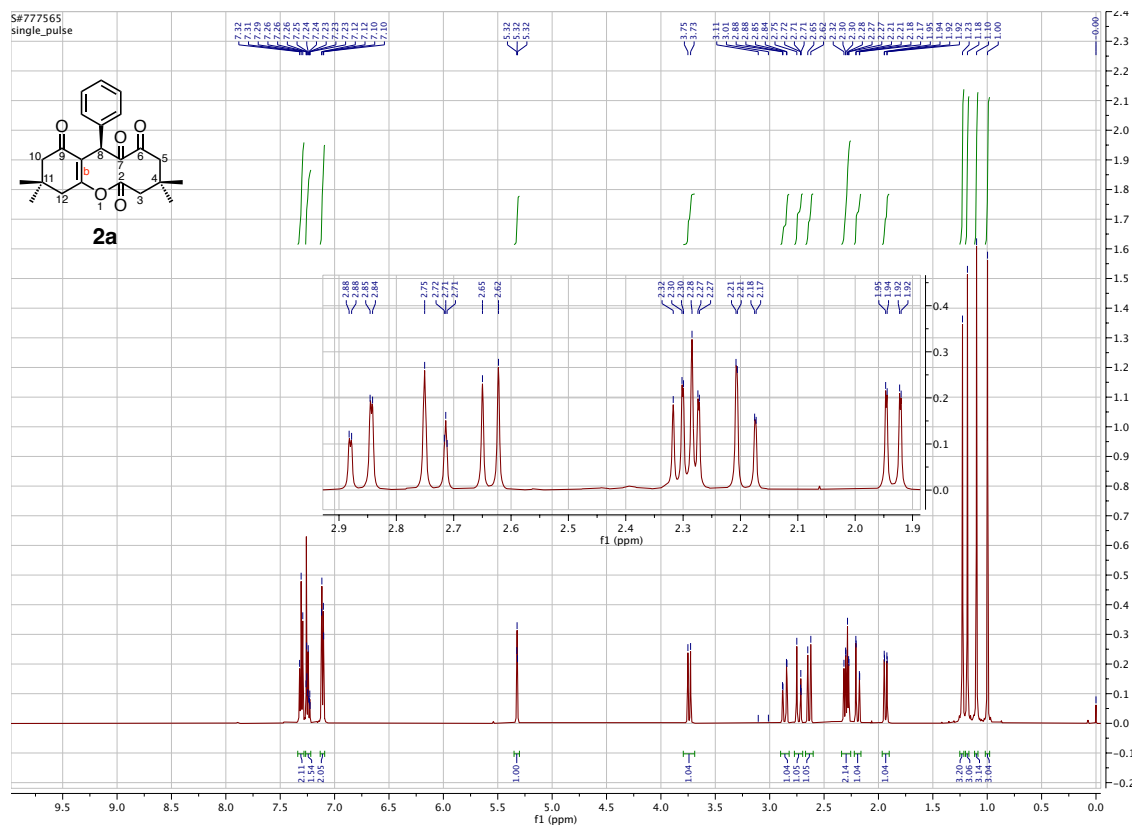
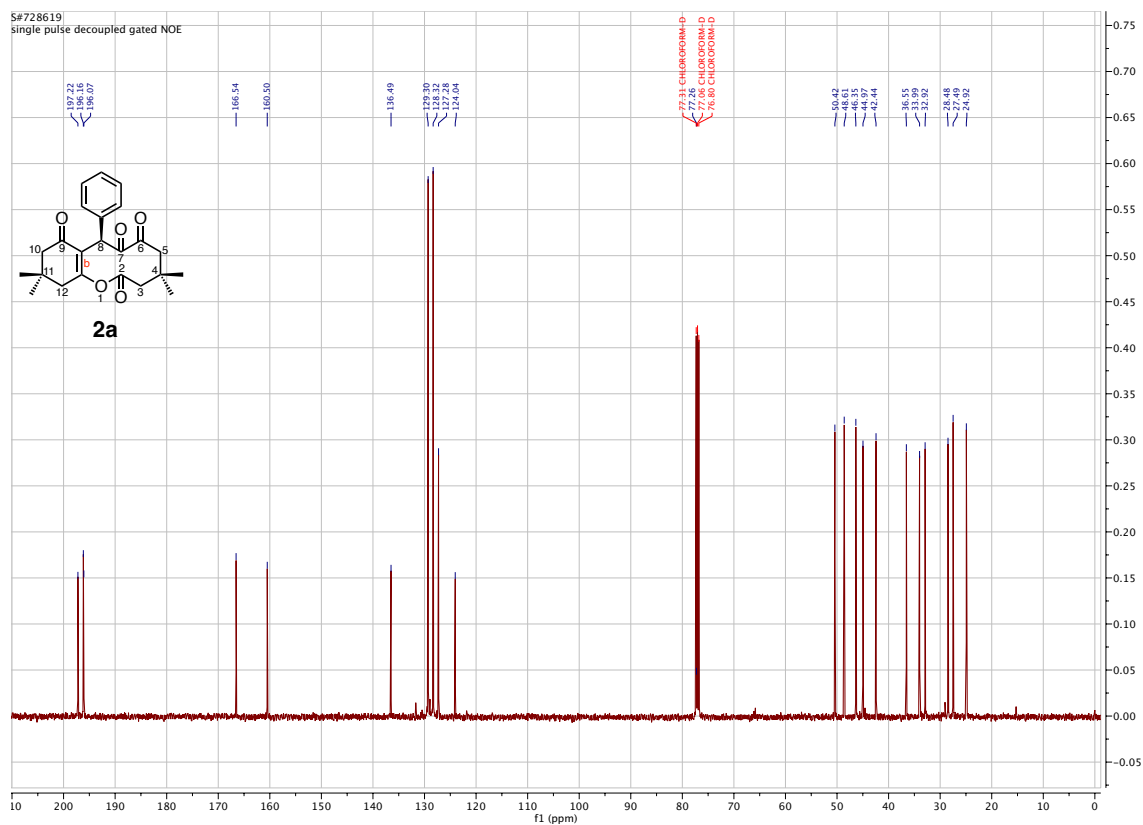


Figure 2. Crystal Structure of **3a**

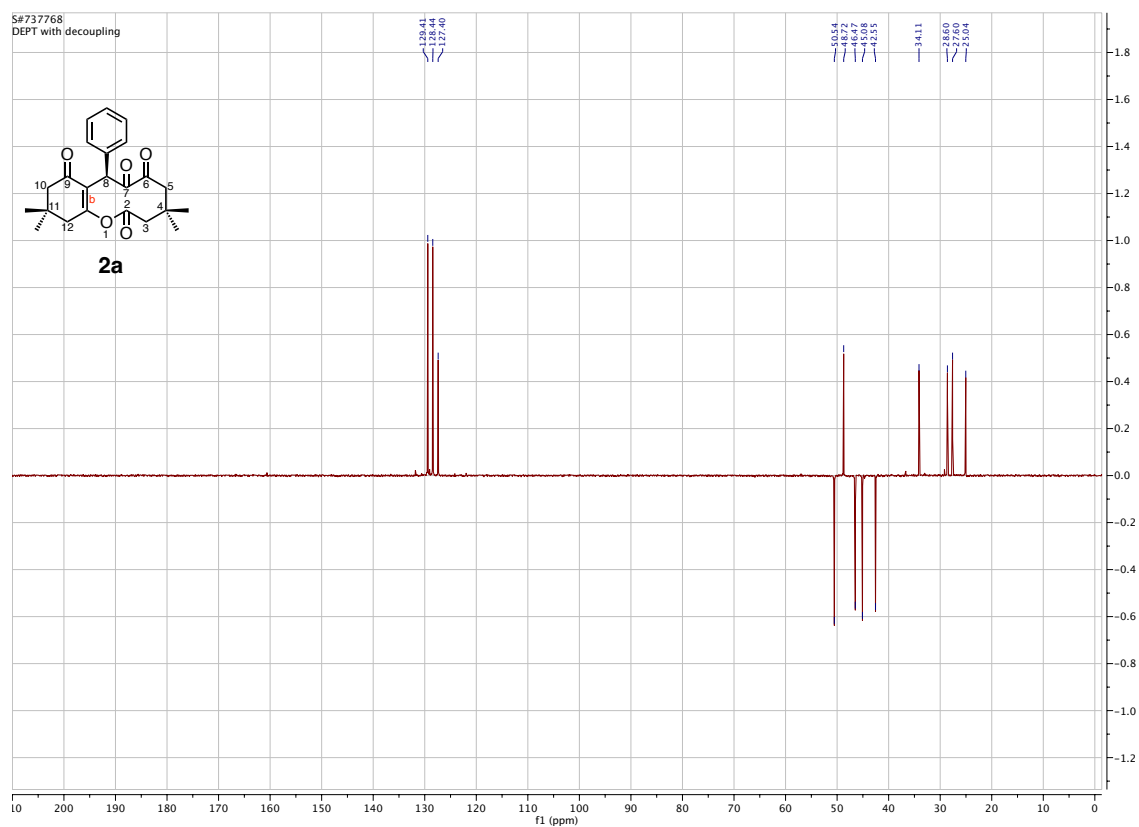
Spectral charts of **2a–g**, **m**, **n**, **3a–c**, **e–m**, and **4–6** as follows:
 ^1H NMR spectrum (500 MHz) using CDCl_3 of **2a**



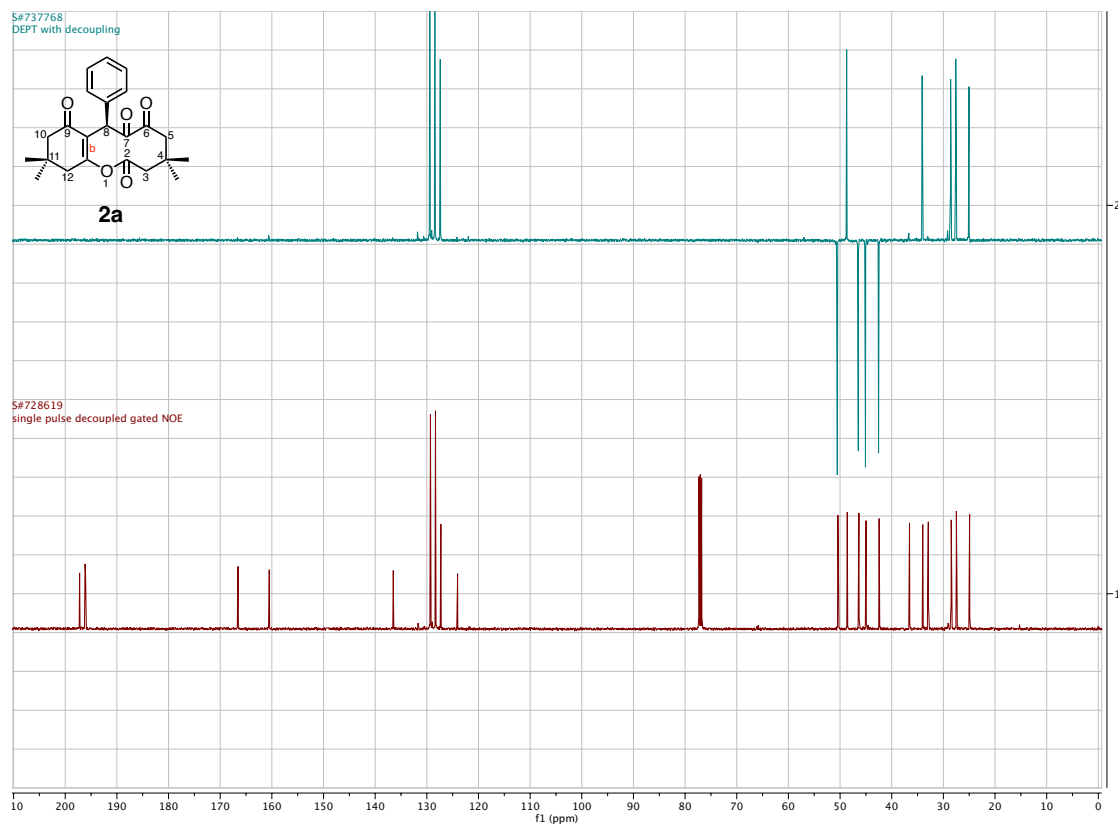
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz) using CDCl_3 of **2a**



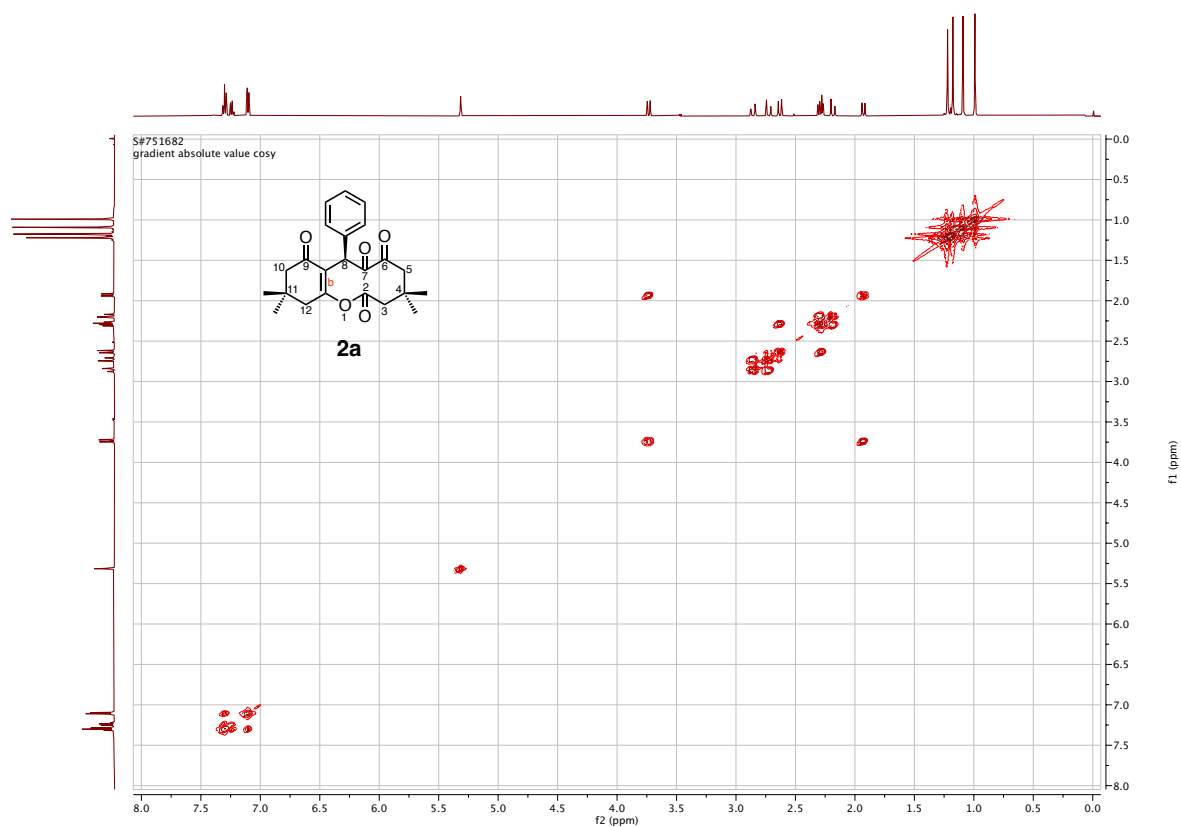
DEPT spectrum using CDCl₃ of **2a**



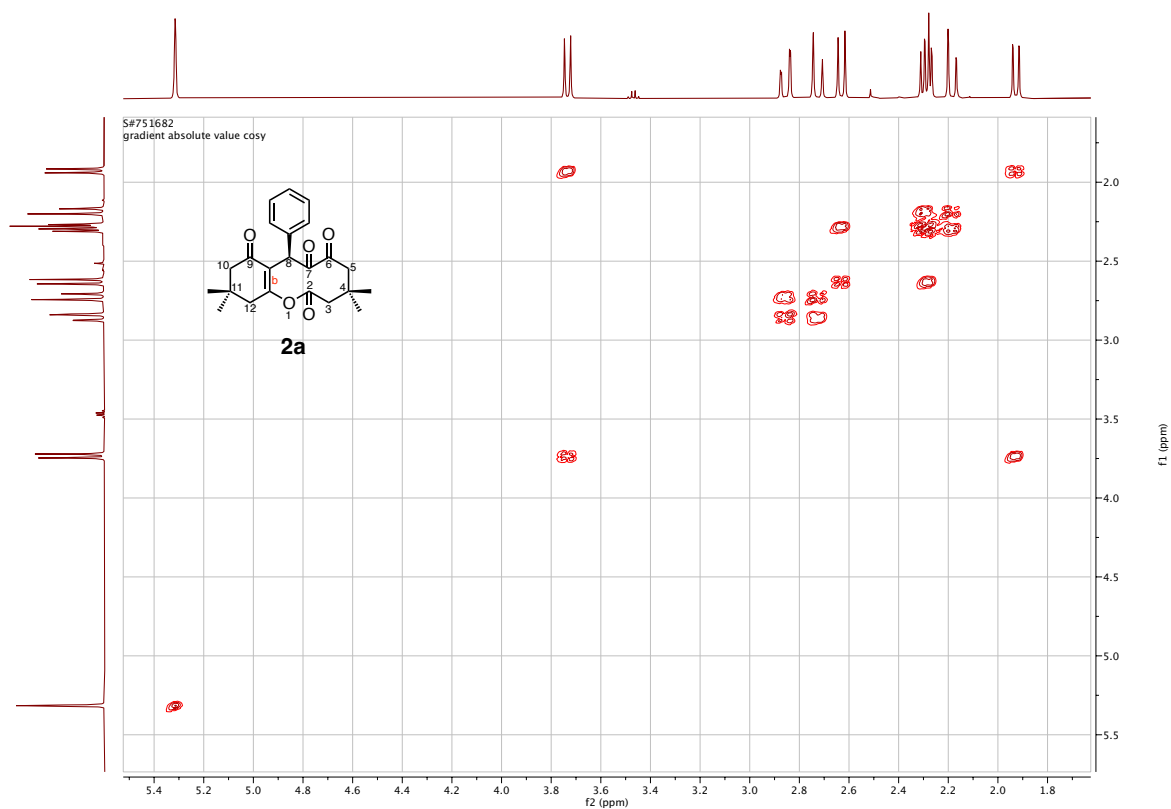
¹³C{¹H} NMR (125 MHz) (lower) and DEPT (upper) spectra using CDCl₃ of **2a**



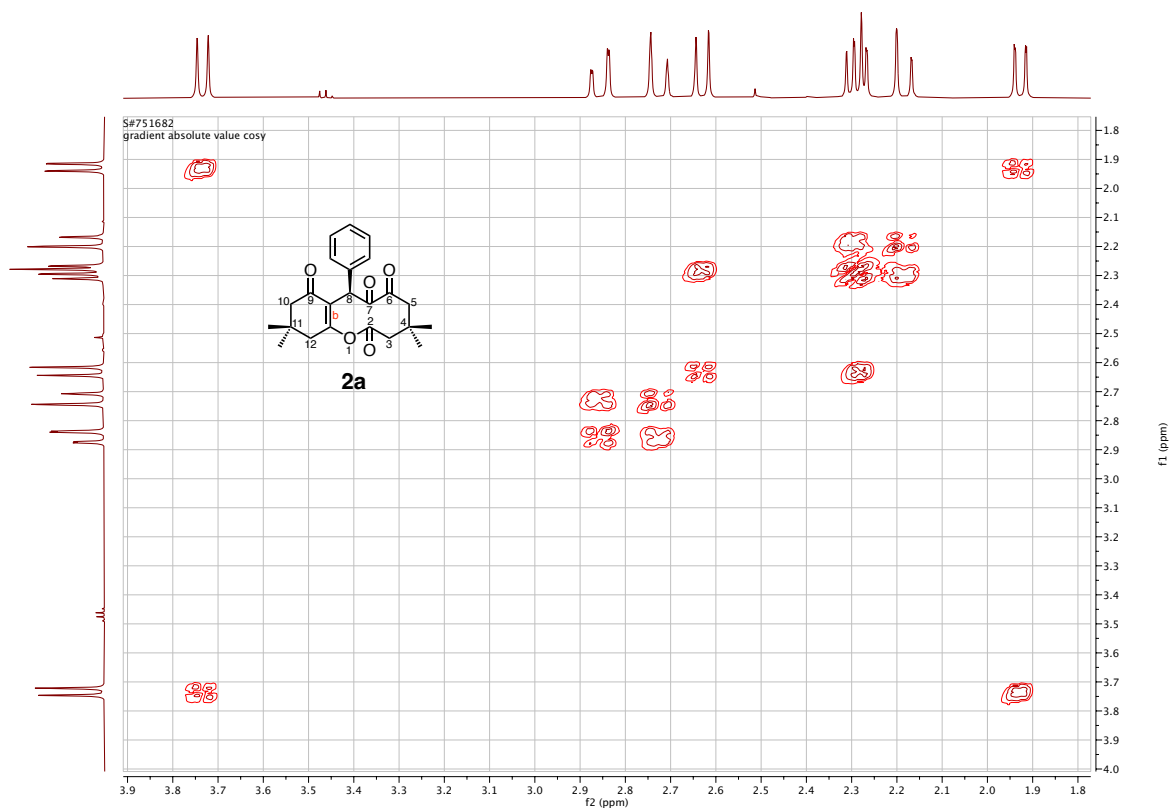
COSY spectrum using CDCl₃ of **2a**



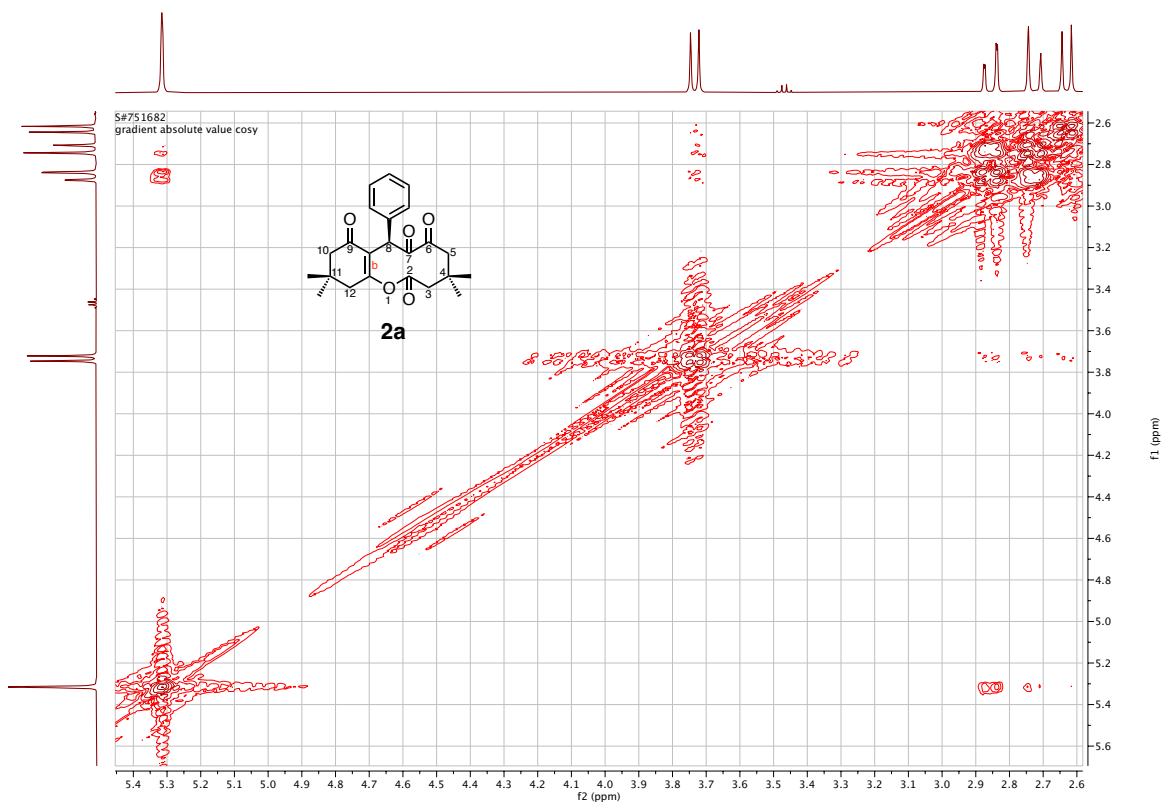
Expansion for COSY spectrum using CDCl₃ of **2a**



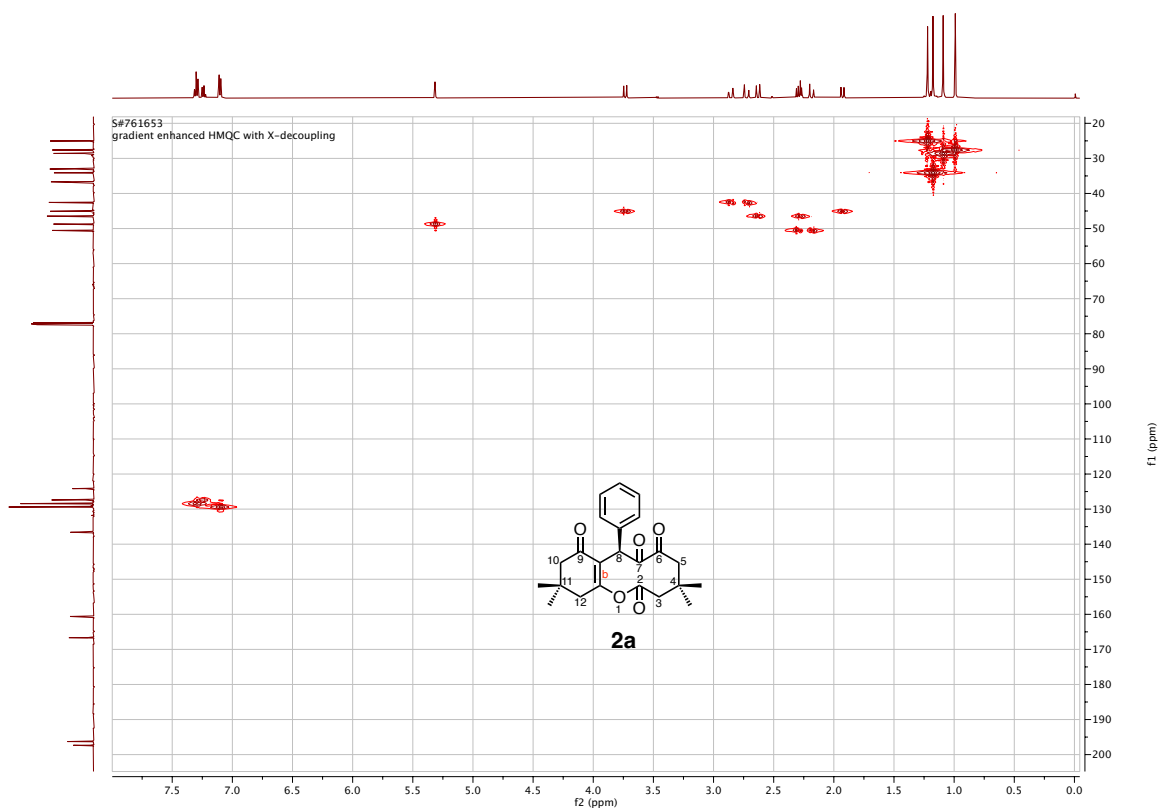
Expansion for COSY spectrum using CDCl₃ of **2a**



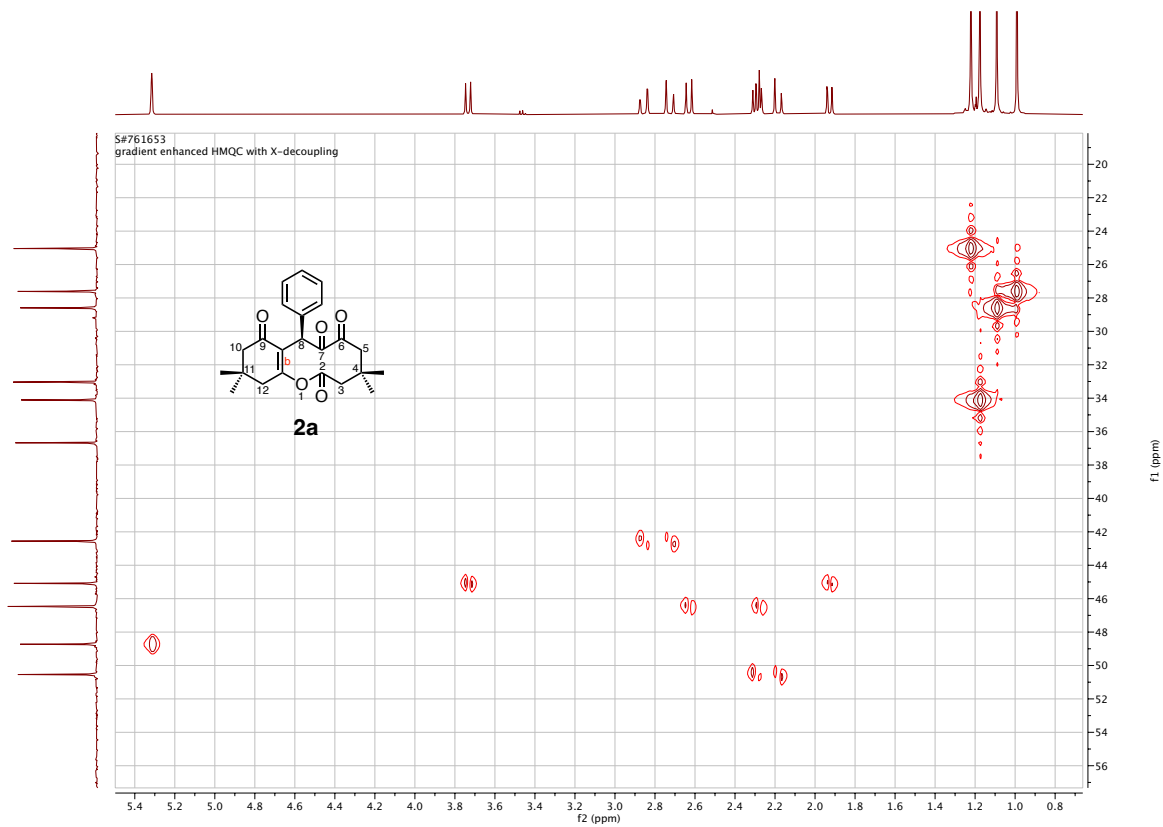
Expansion for COSY spectrum using CDCl₃ of **2a**



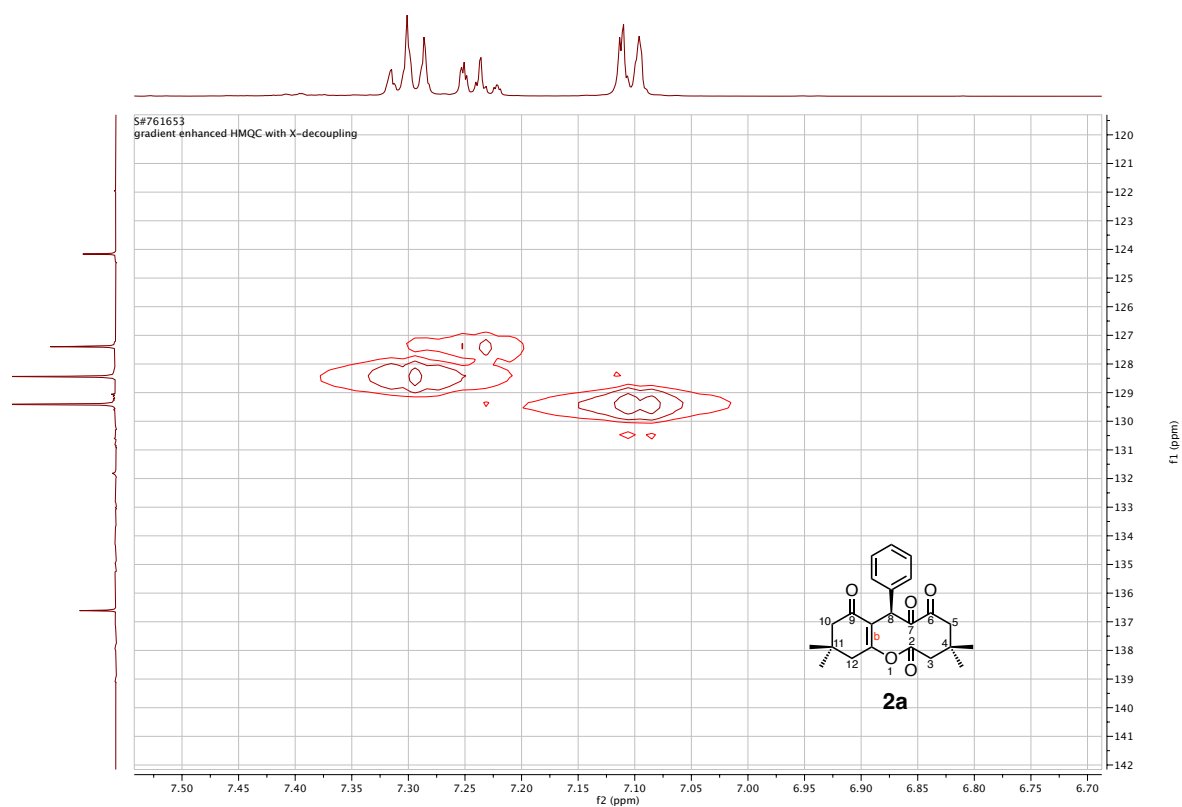
HMQC spectrum using CDCl₃ of 2a



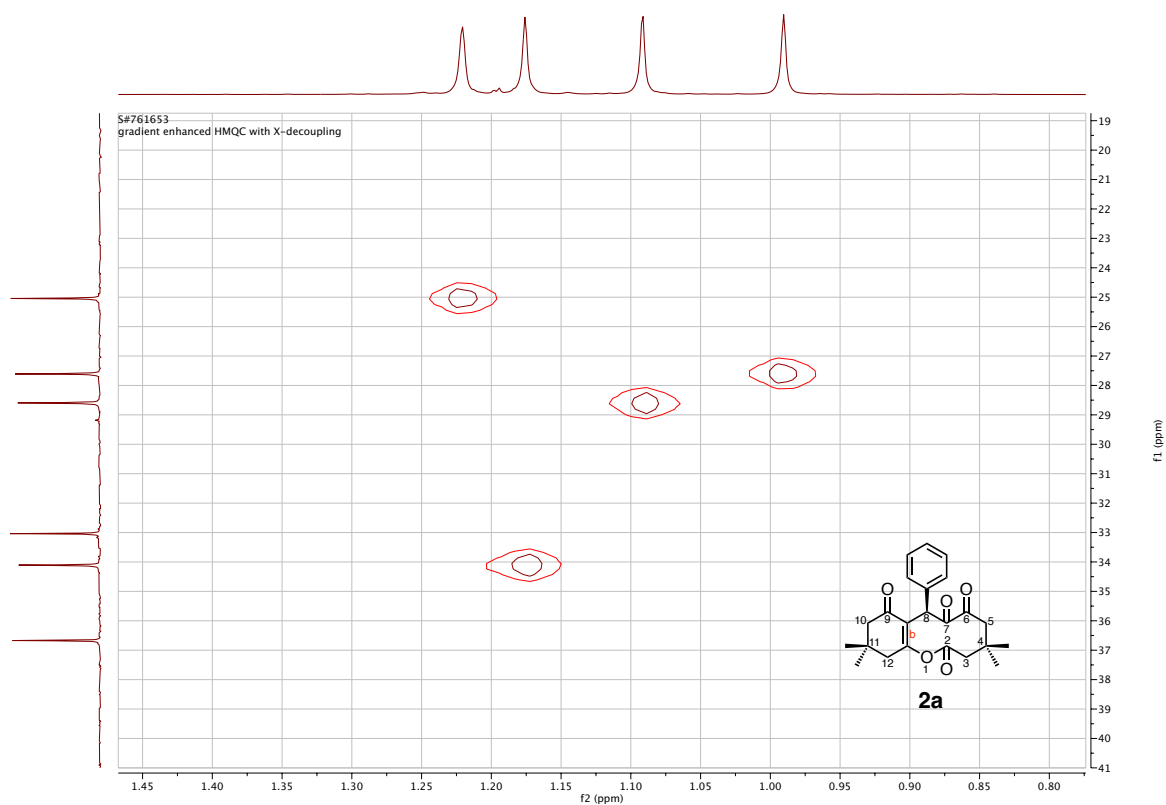
Expansion for HMQC spectrum using CDCl₃ of 2a



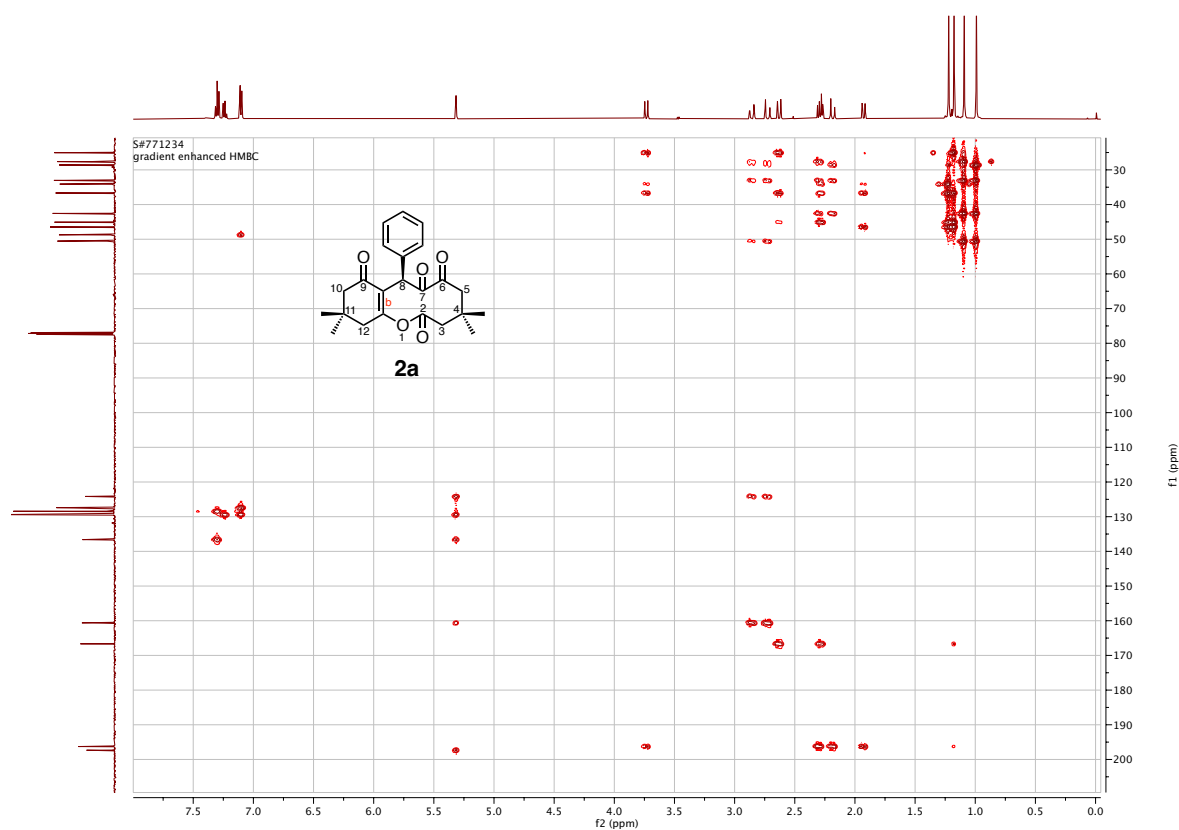
Expansion for HMQC spectrum using CDCl₃ of **2a**



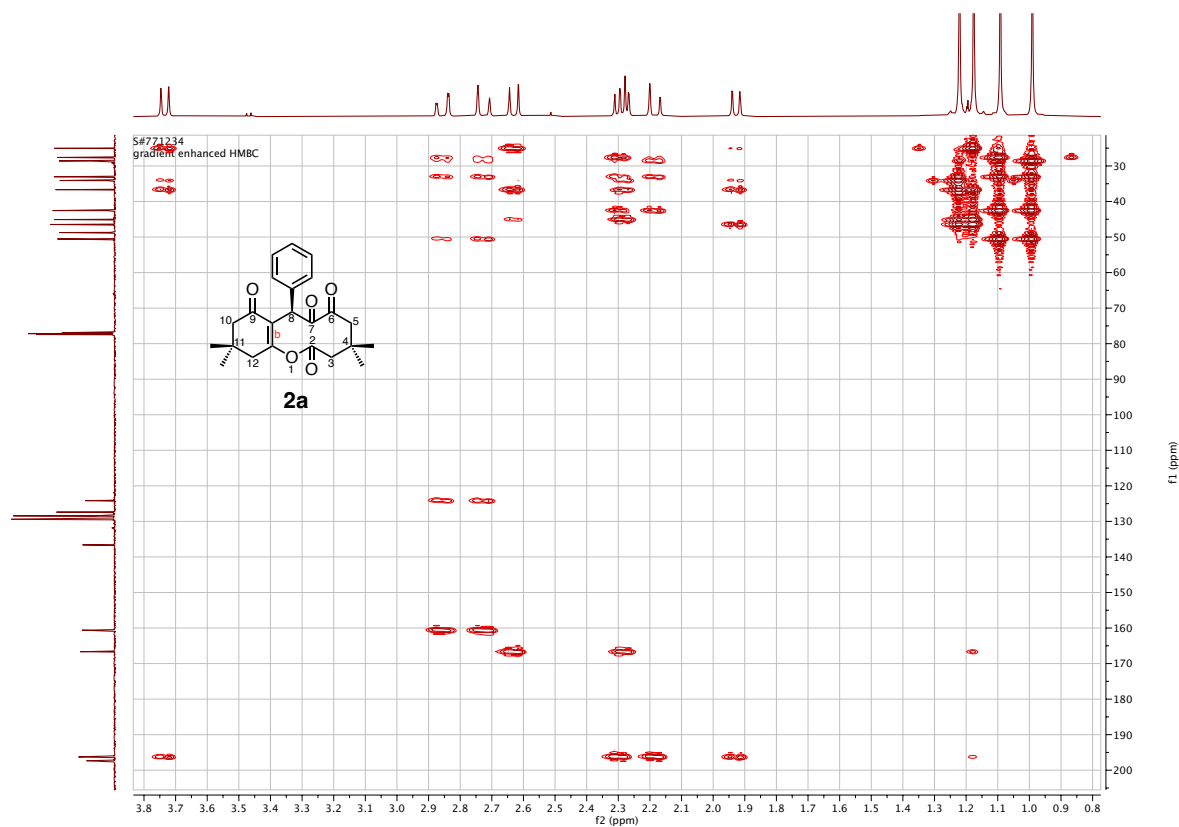
Expansion for HMQC spectrum using CDCl₃ of **2a**



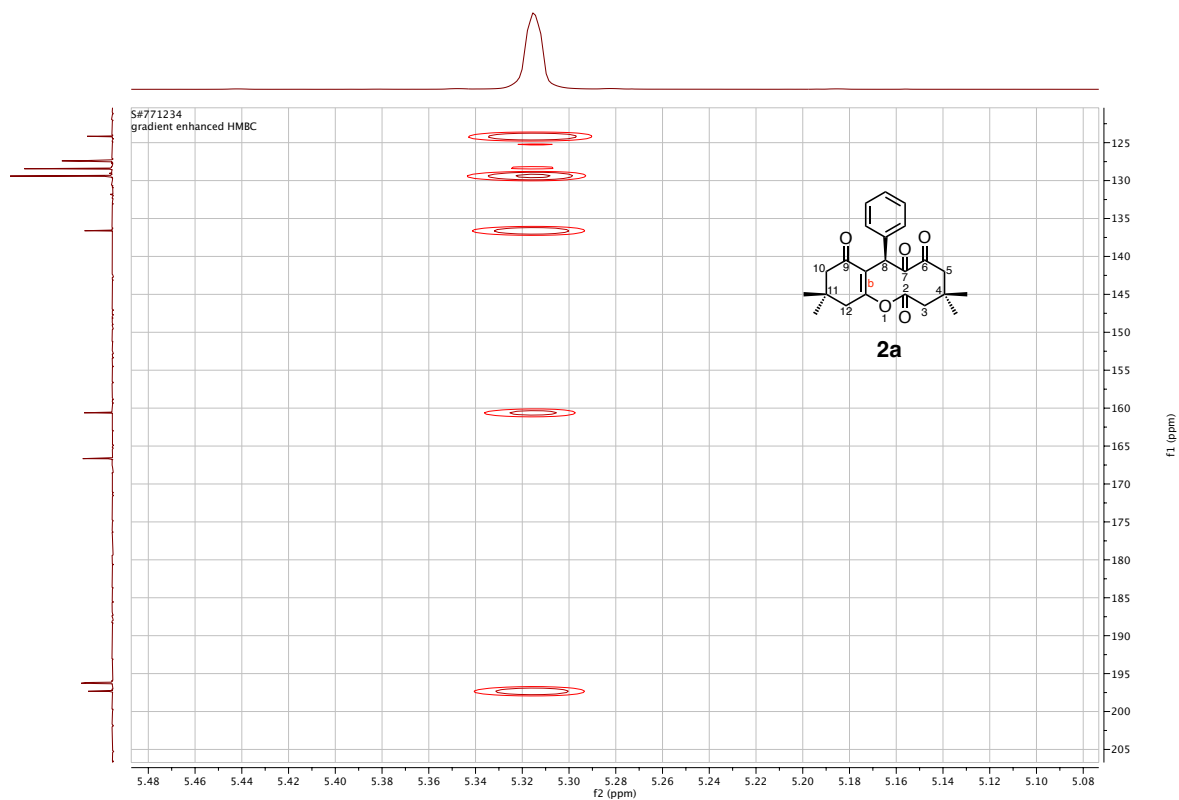
HMBC spectrum using CDCl₃ of **2a**



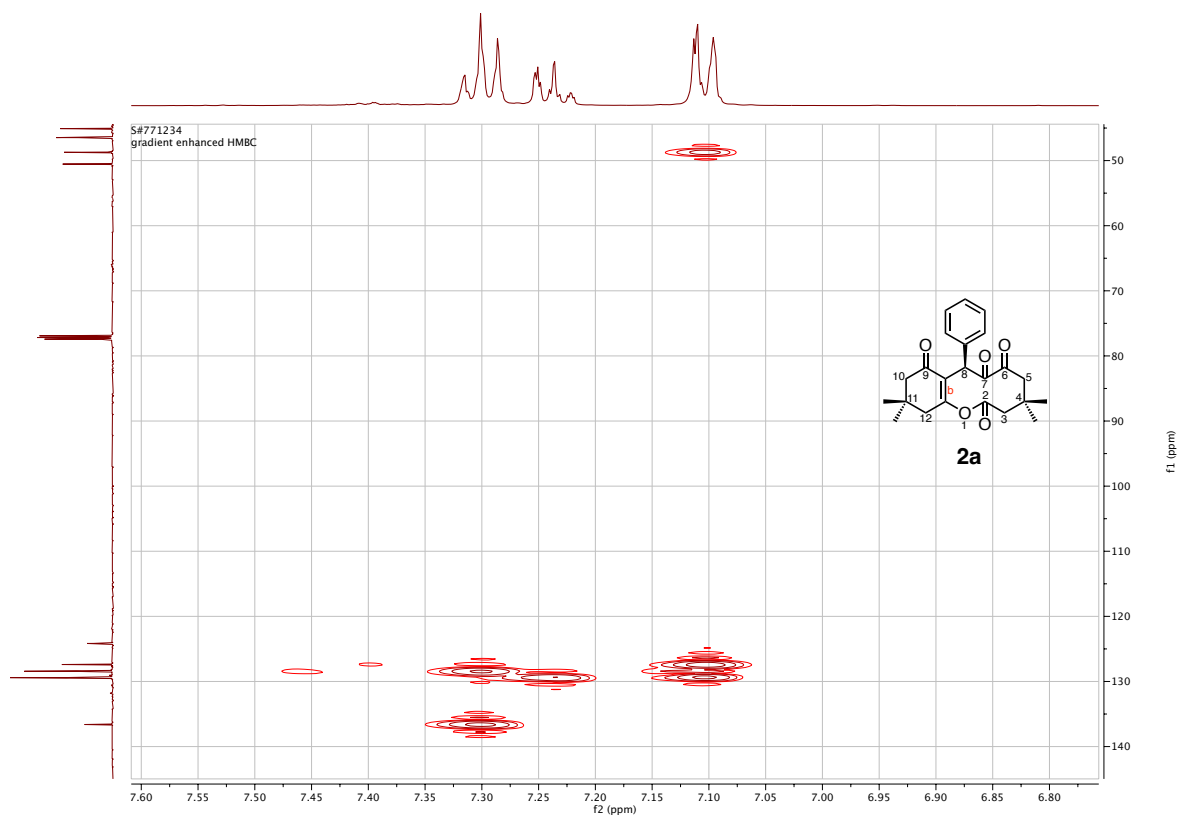
Expansion for HMBC spectrum using CDCl₃ of **2a**



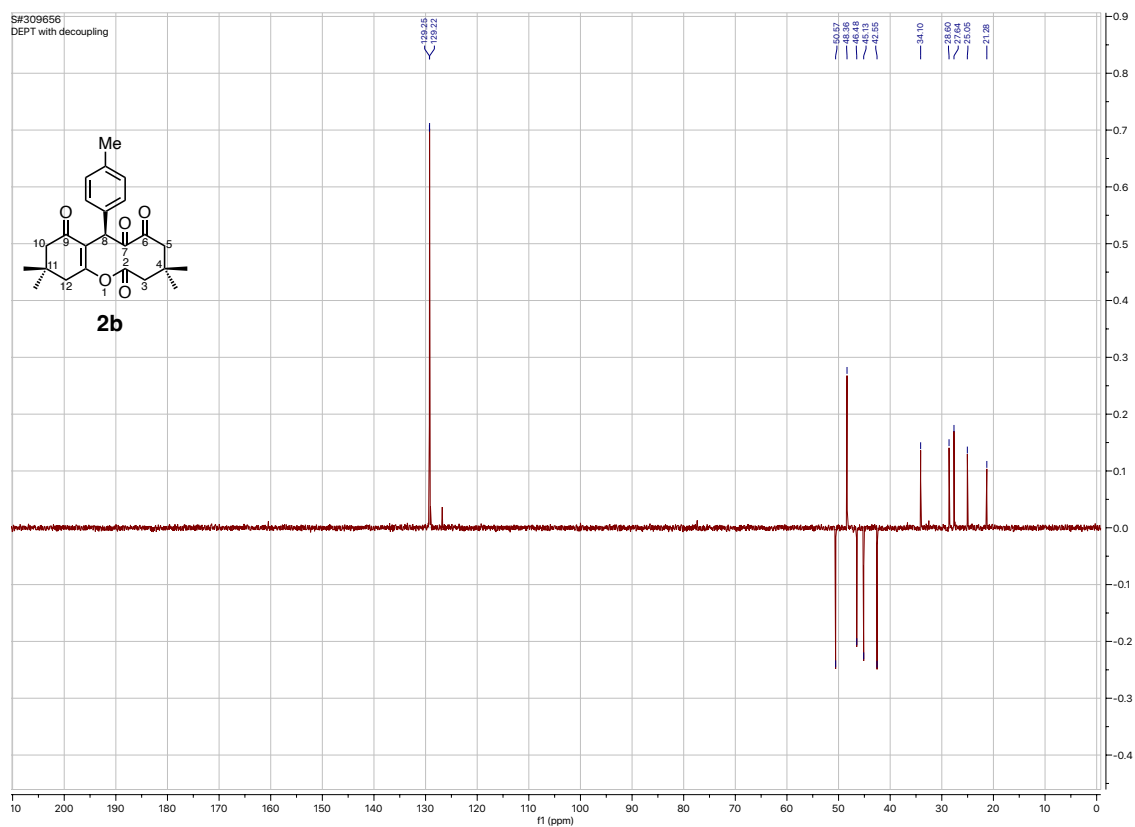
Expansion for HMBC spectrum using CDCl₃ of **2a**



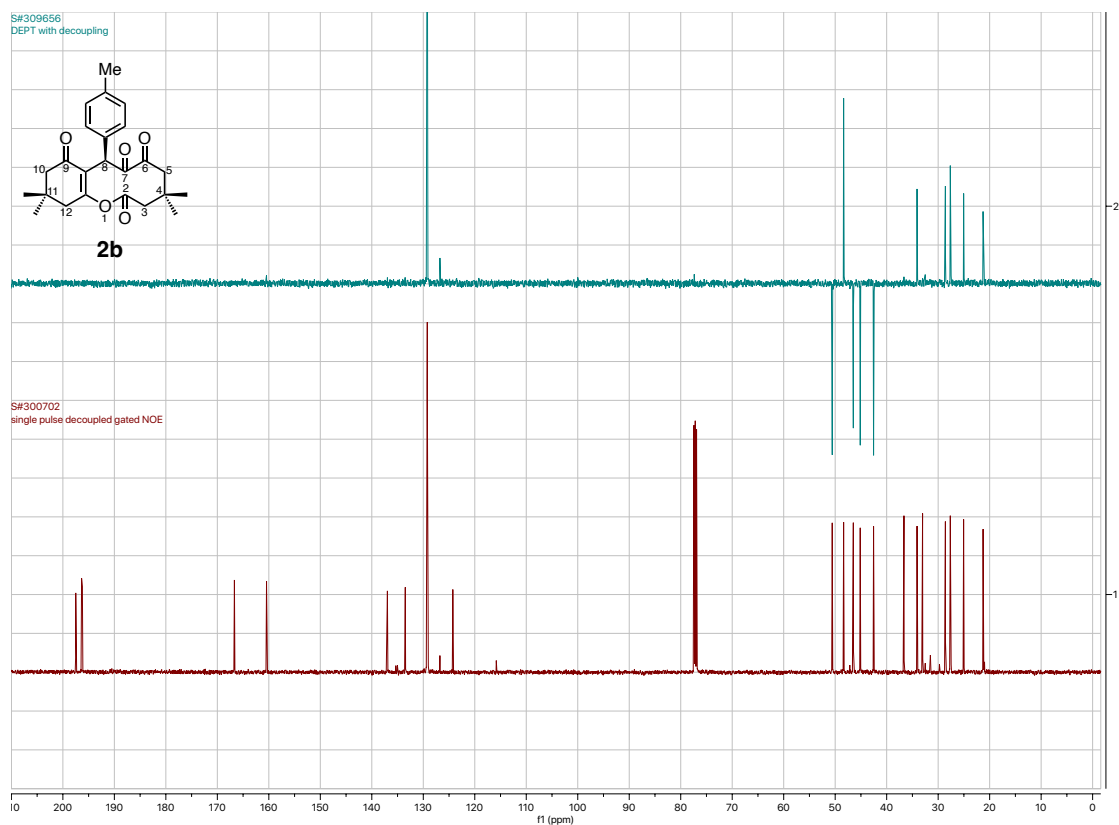
Expansion for HMBC spectrum using CDCl₃ of **2a**



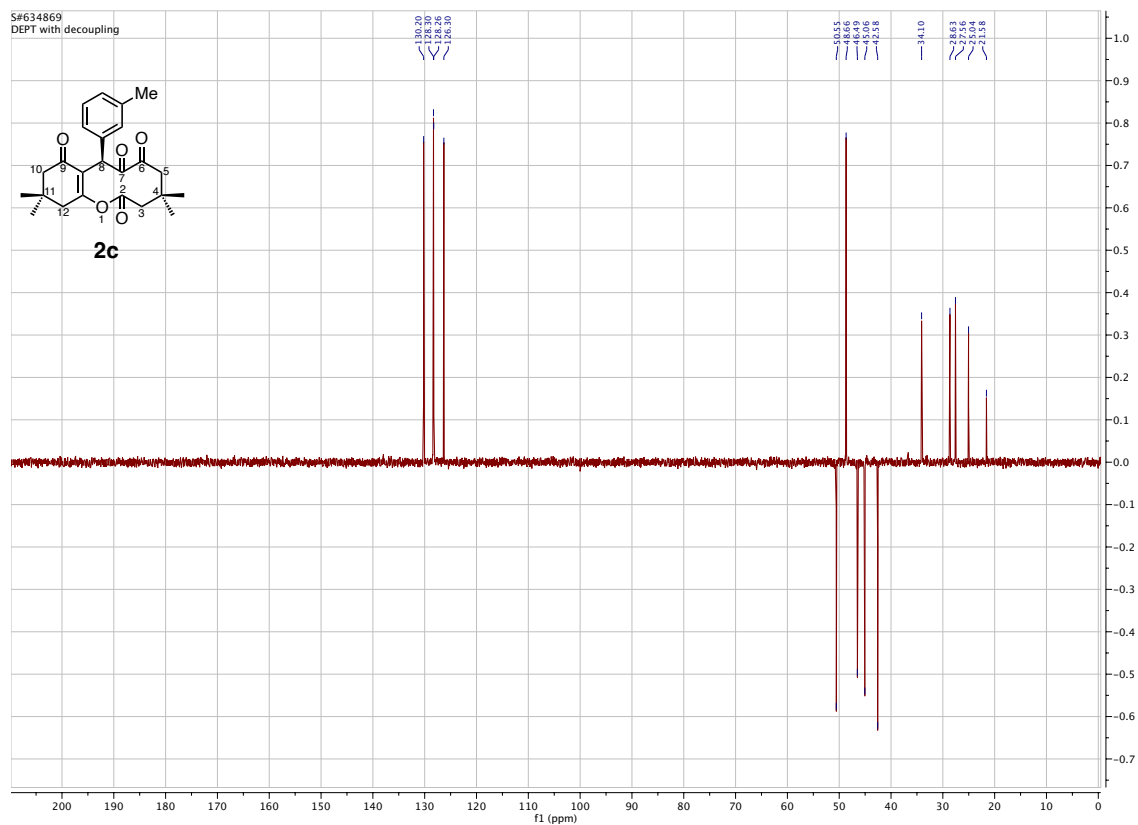
DEPT spectrum using CDCl₃ of **2b**



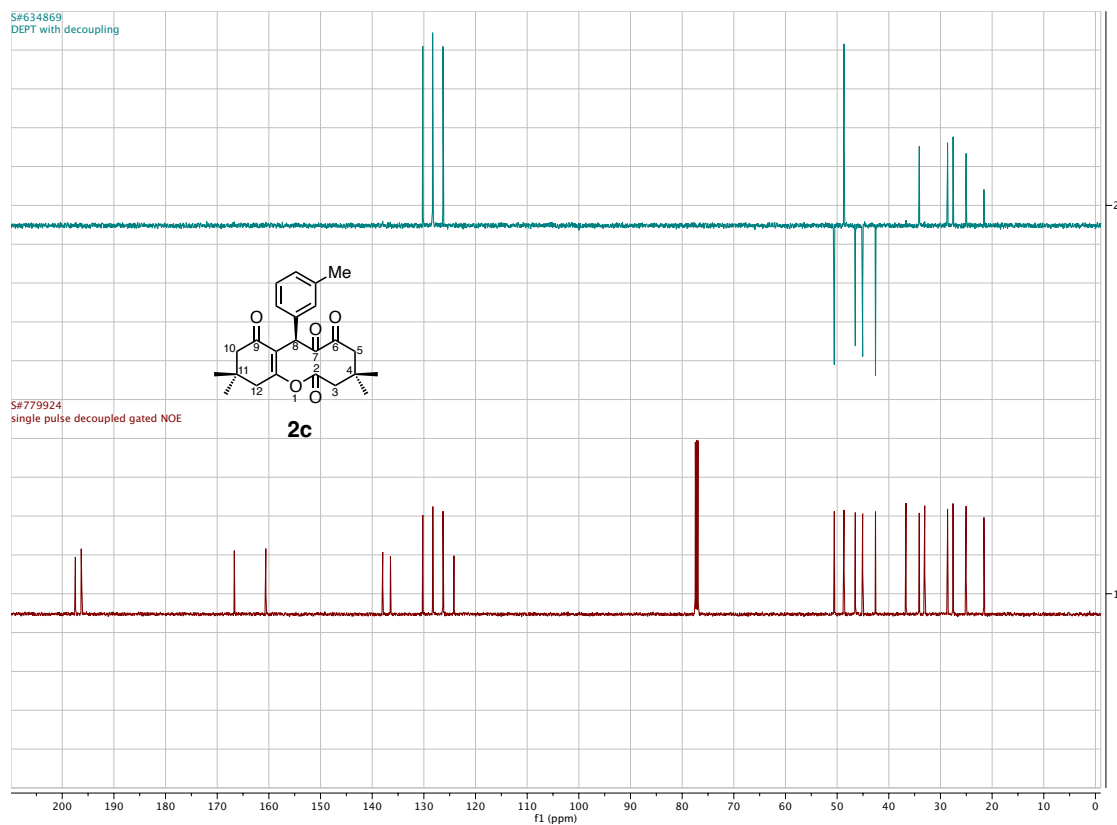
¹³C{¹H} NMR (125 MHz) (lower) and DEPT (upper) spectra using CDCl₃ of **2b**



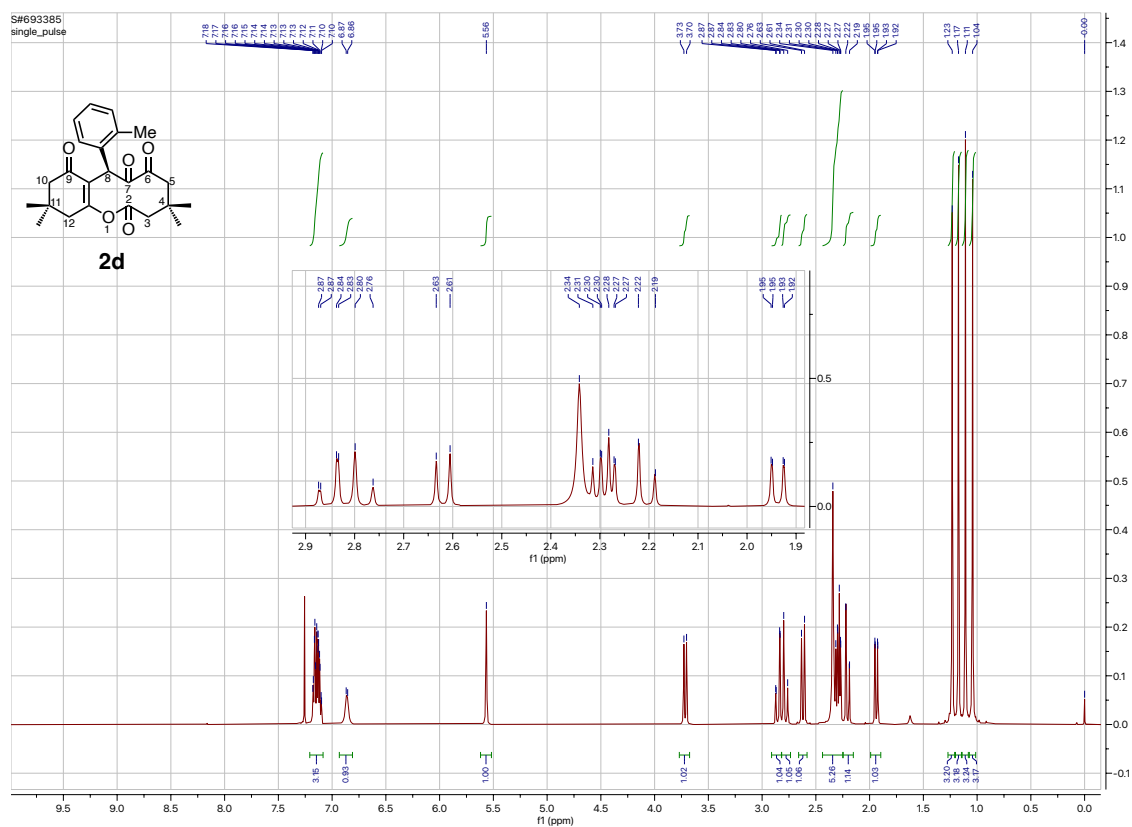
DEPT spectrum using CDCl₃ of **2c**



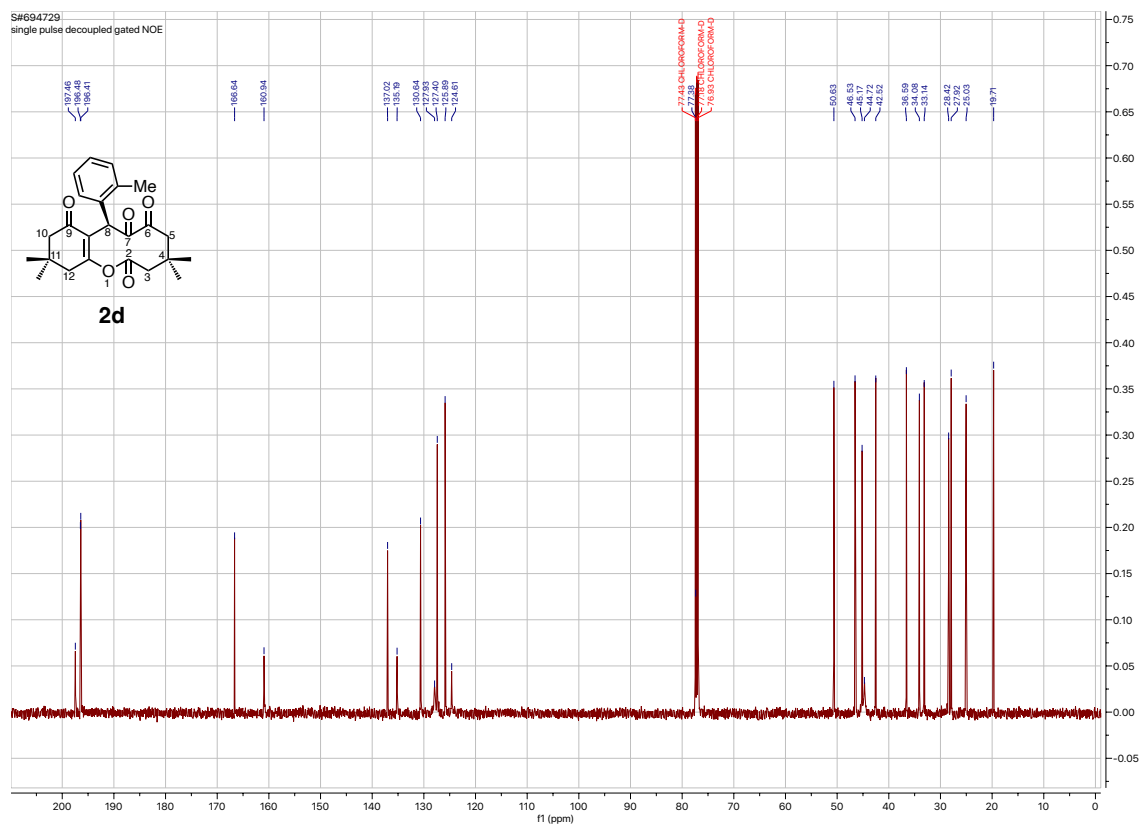
¹³C{¹H} NMR (125 MHz) (lower) and DEPT (upper) spectra using CDCl₃ of **2c**



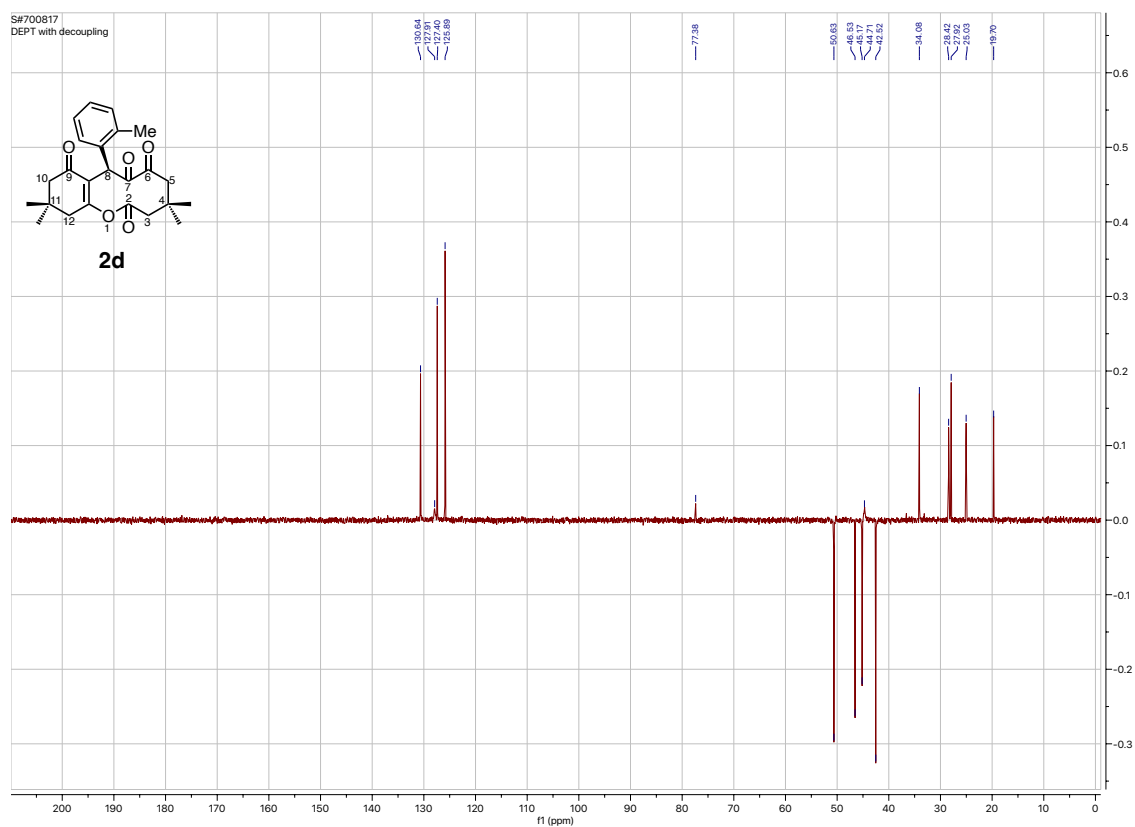
^1H NMR spectrum (500 MHz) using CDCl_3 of **2d**



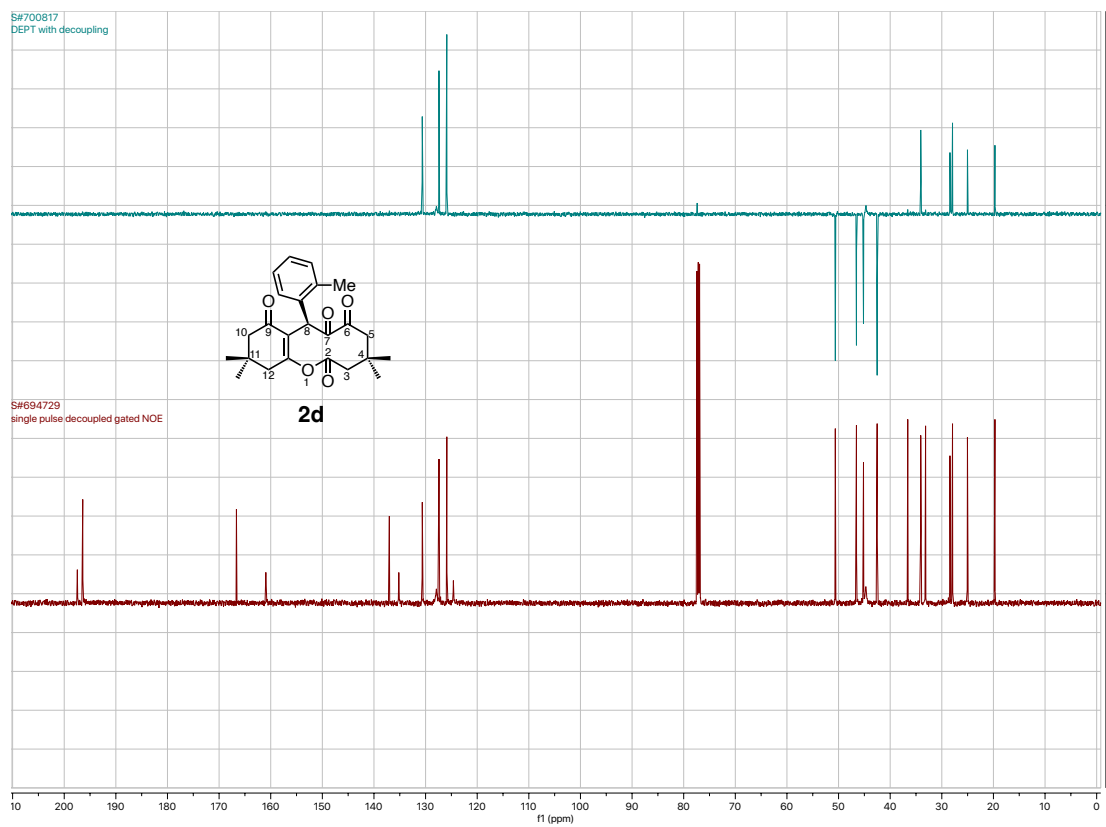
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz) using CDCl_3 of **2d**



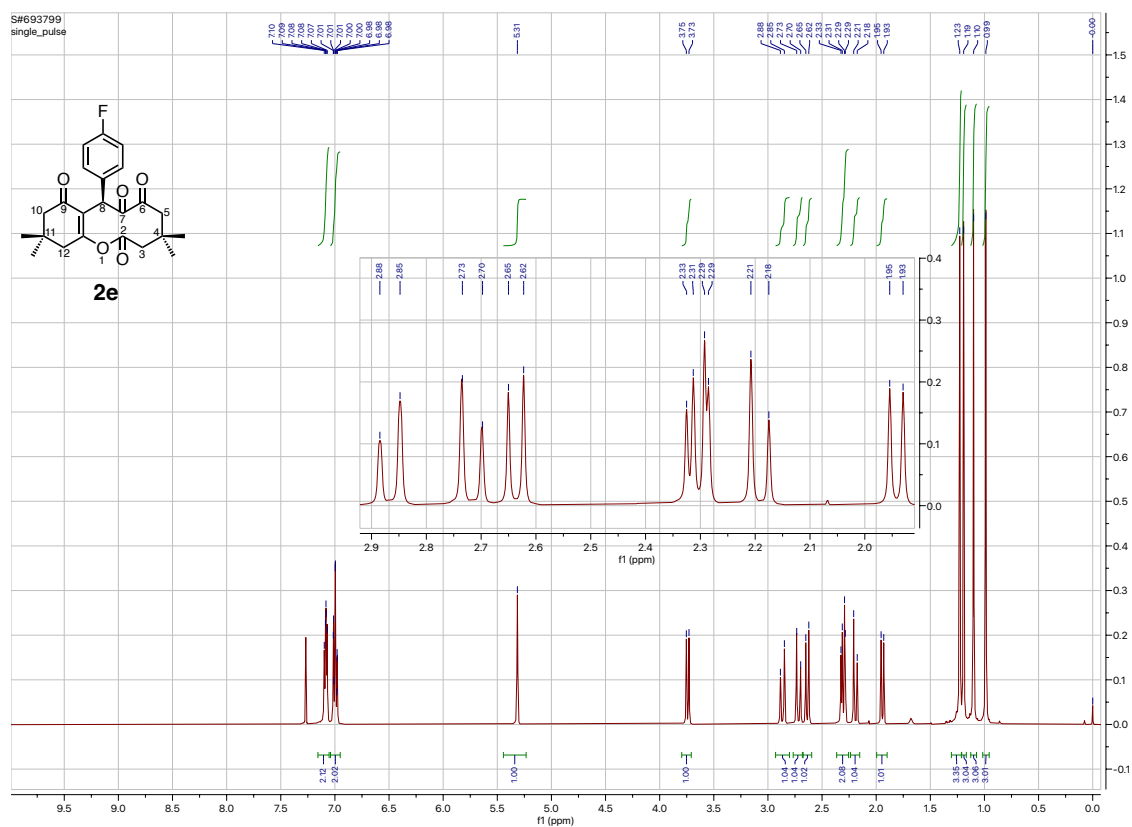
DEPT spectrum using CDCl₃ of **2d**



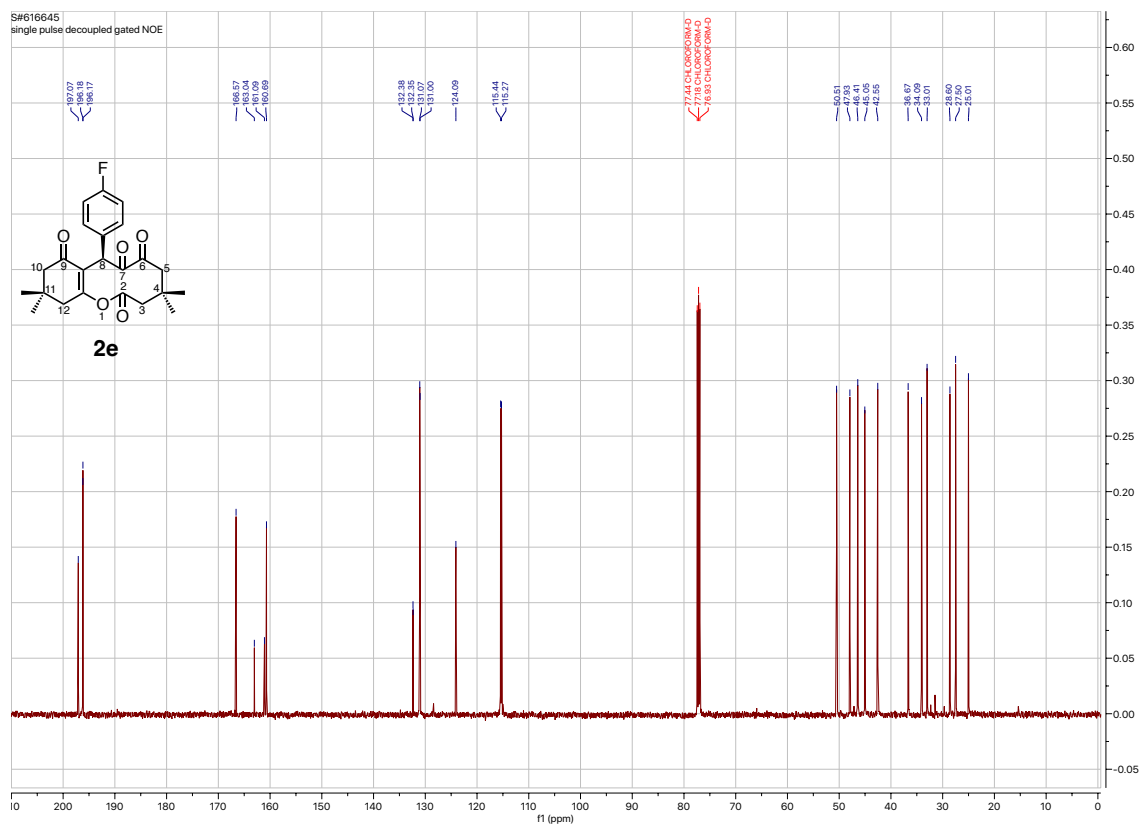
¹³C{¹H} NMR (125 MHz) (lower) and DEPT (upper) spectra using CDCl₃ of **2d**



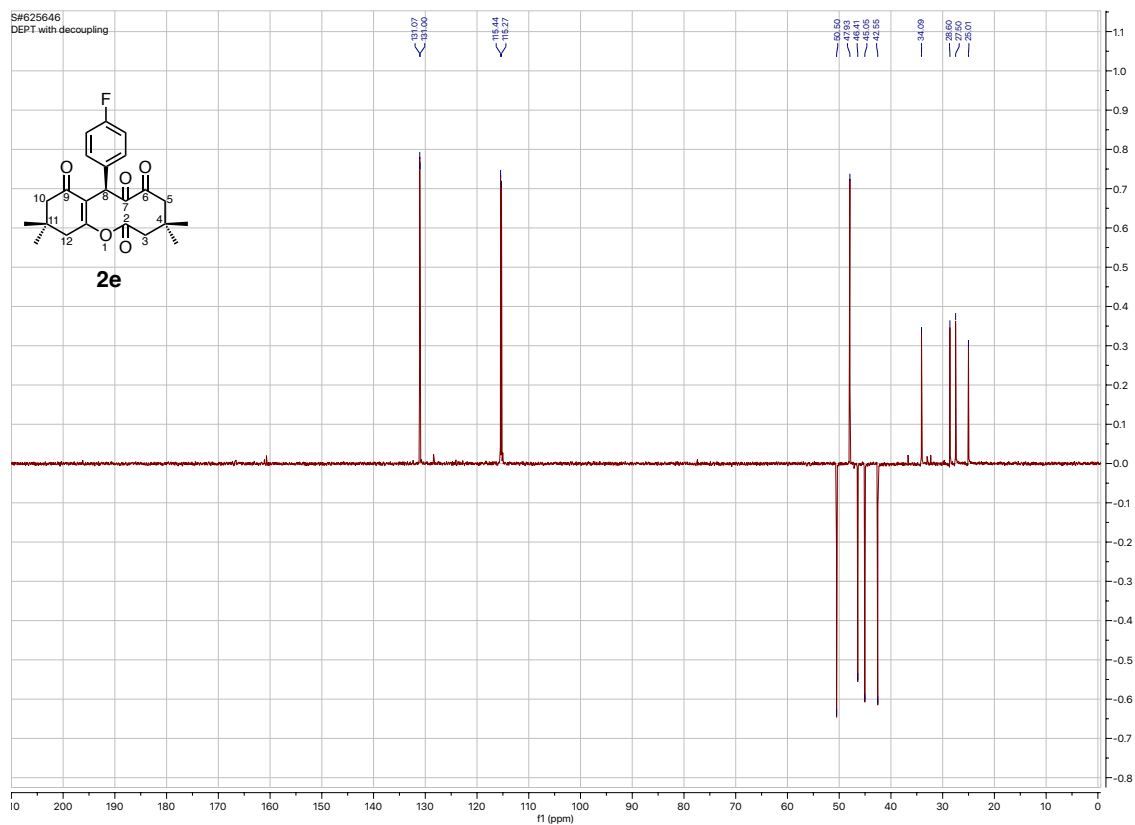
^1H NMR spectrum (500 MHz) using CDCl_3 of **2e**



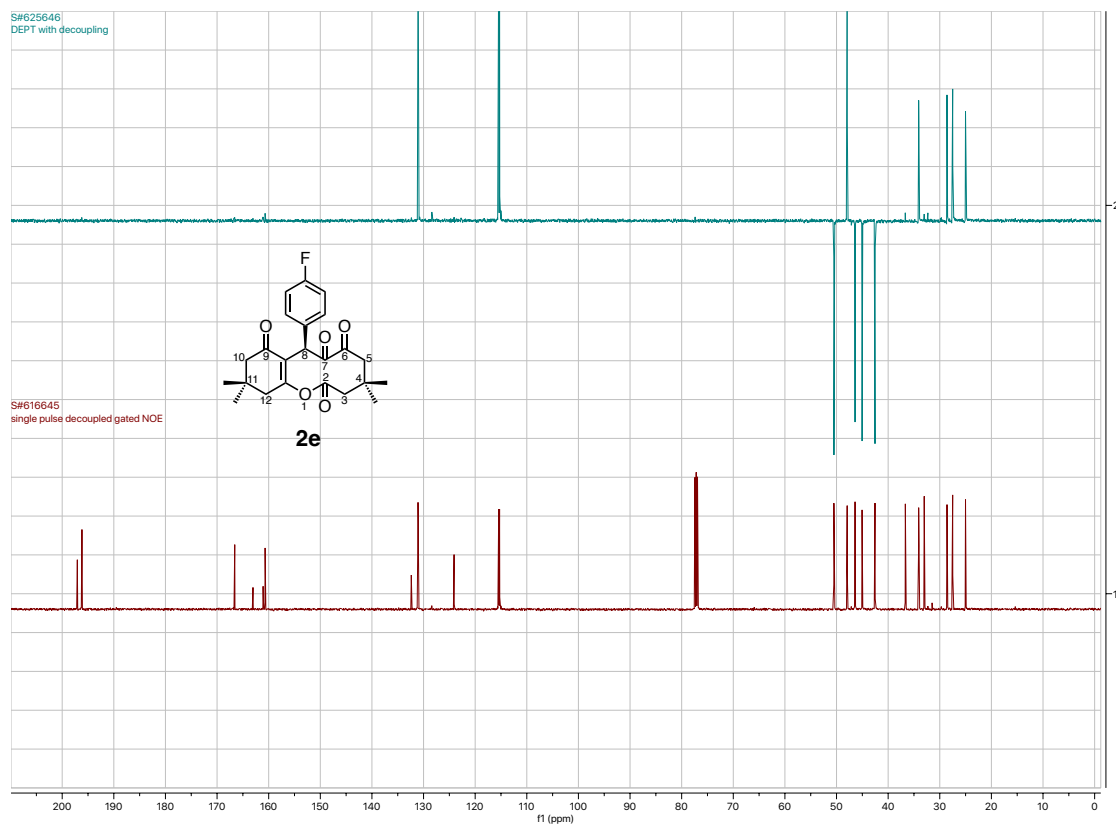
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz) using CDCl_3 of **2e**



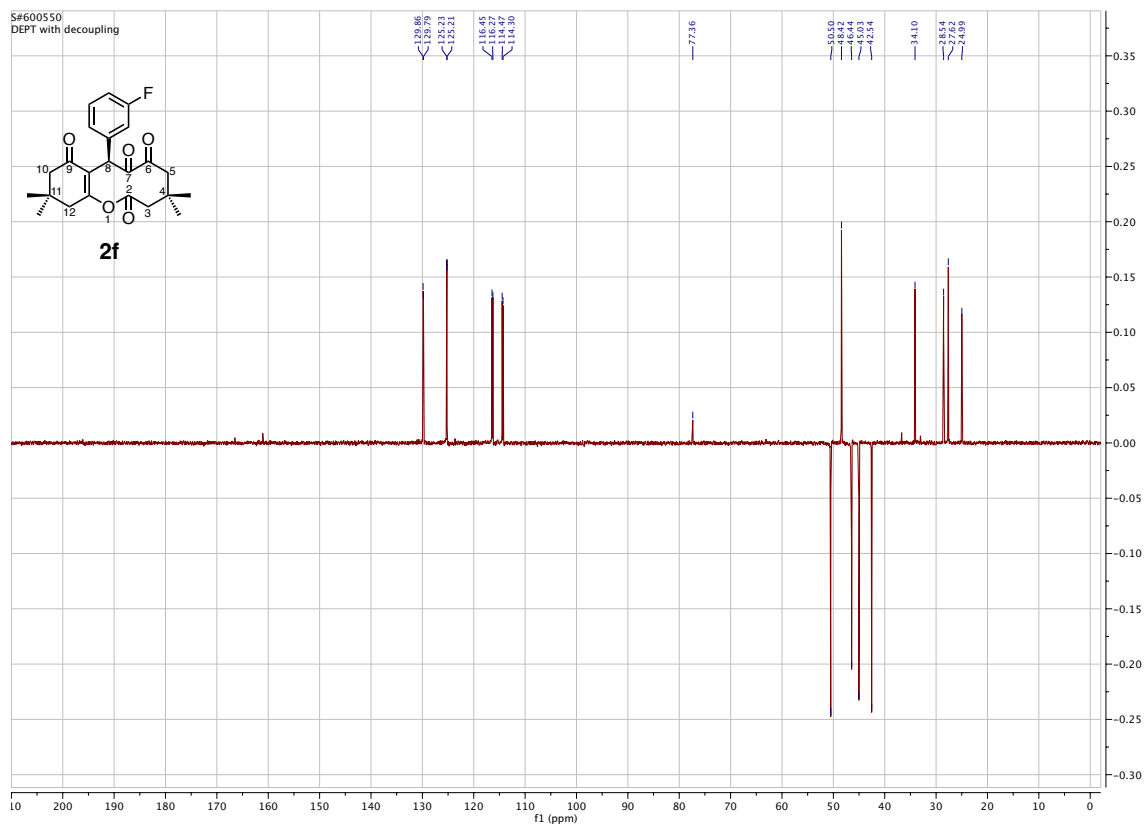
DEPT spectrum using CDCl₃ of **2e**



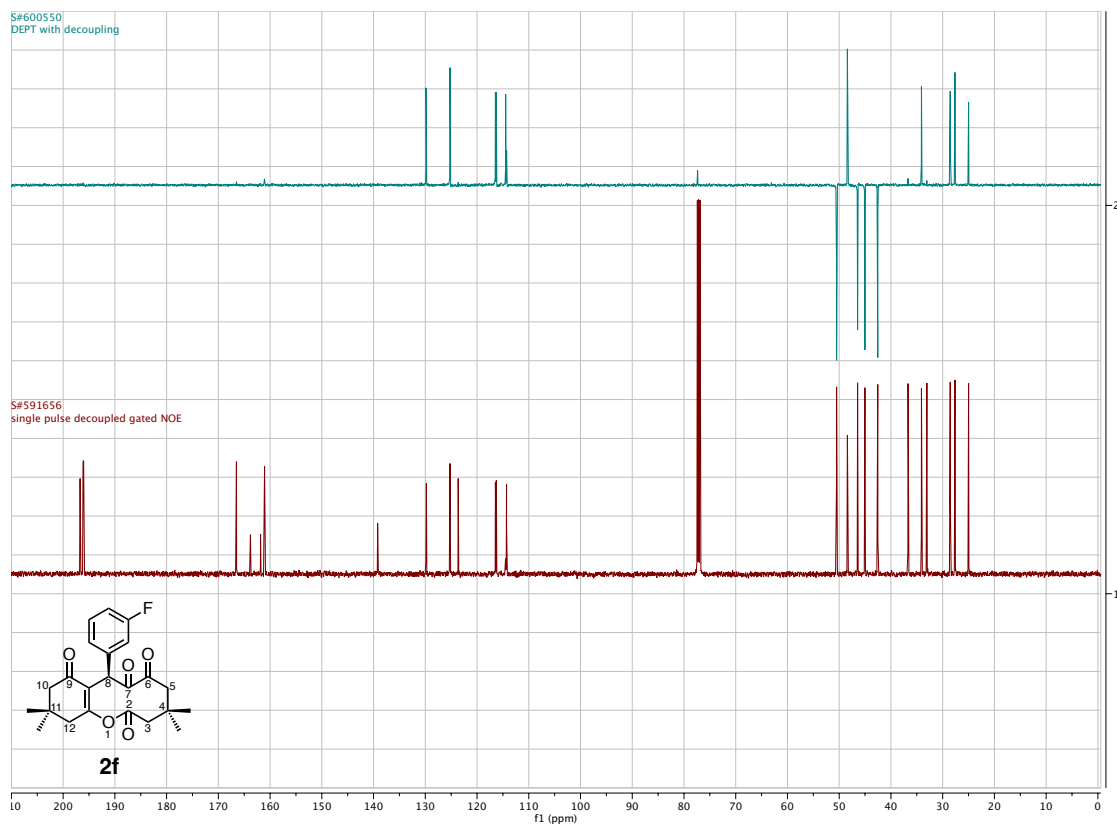
¹³C{¹H} NMR (125 MHz) (lower) and DEPT (upper) spectra using CDCl₃ of **2e**



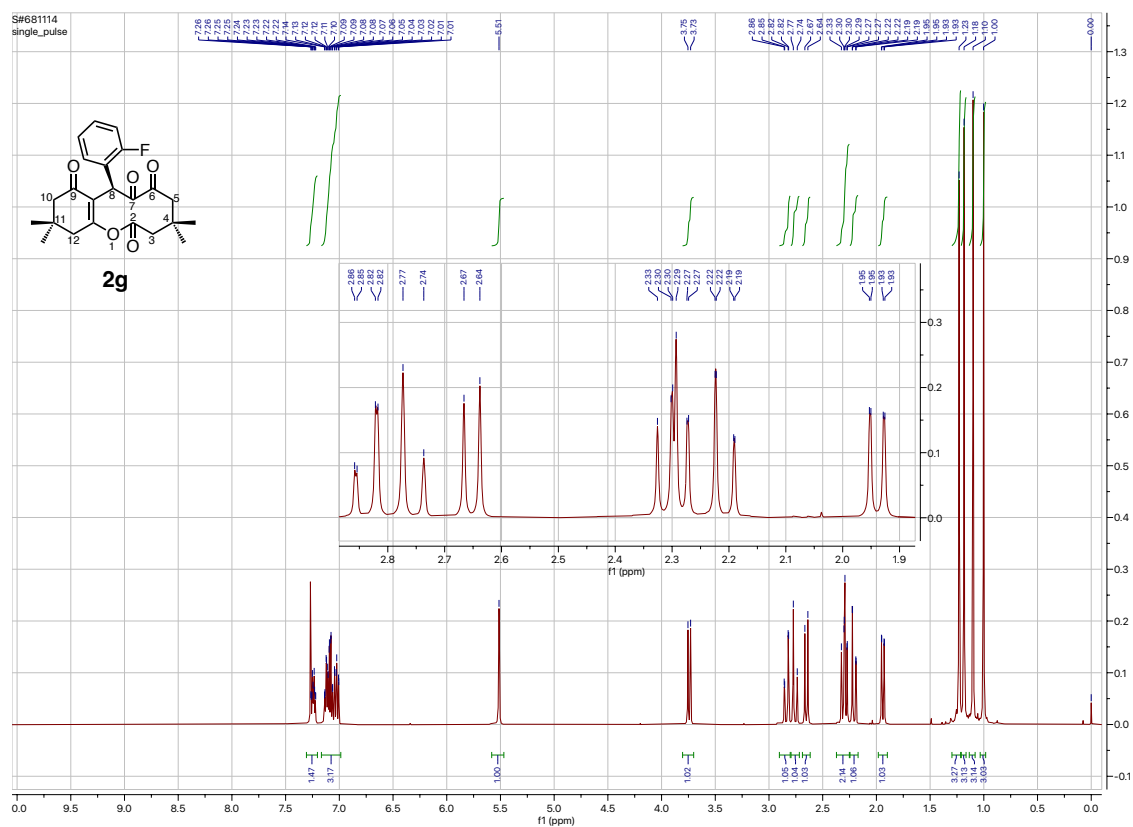
DEPT spectrum using CDCl₃ of **2f**



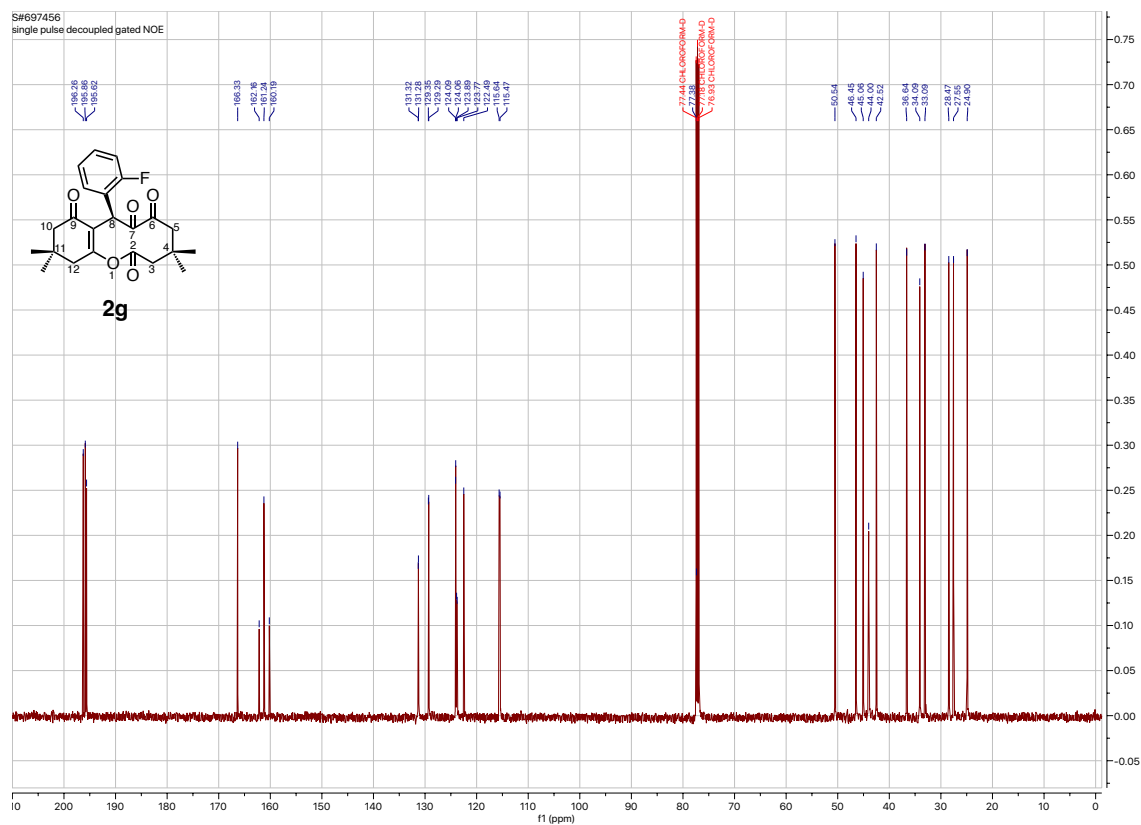
¹³C{¹H} NMR (125 MHz) (lower) and DEPT (upper) spectra using CDCl₃ of **2f**



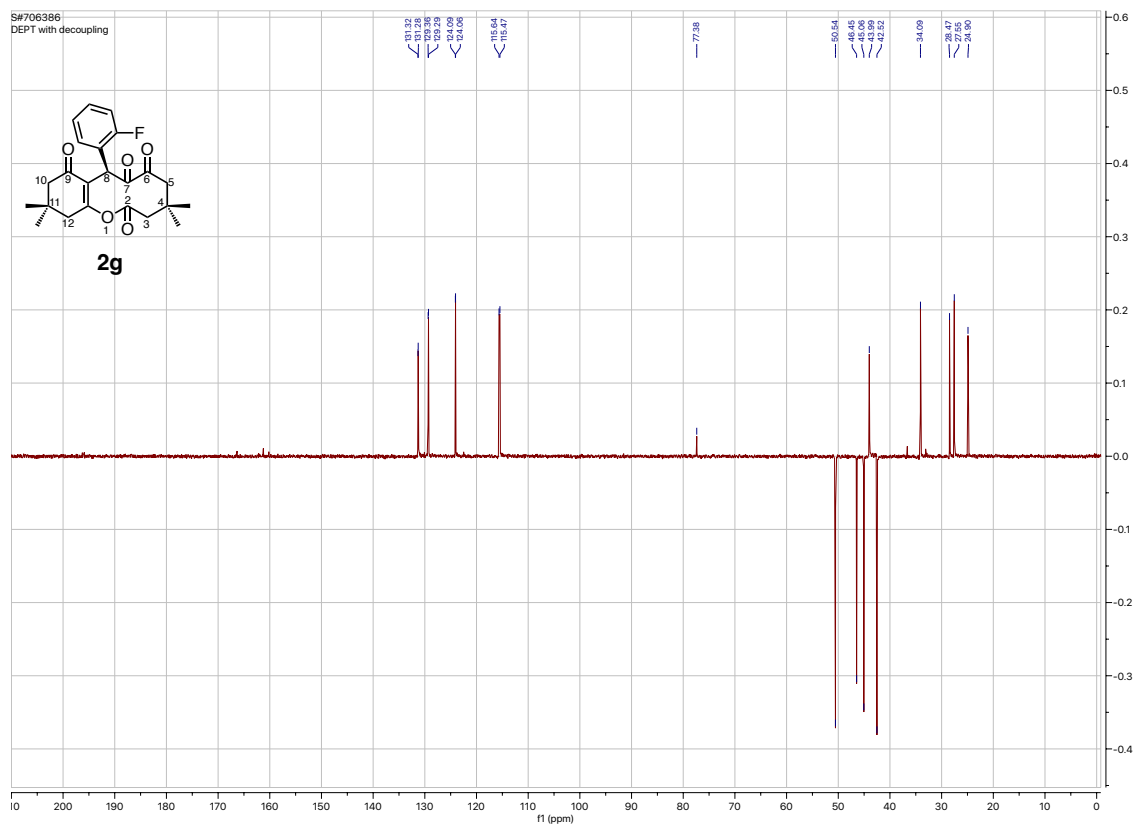
^1H NMR spectrum (500 MHz) using CDCl_3 of **2g**



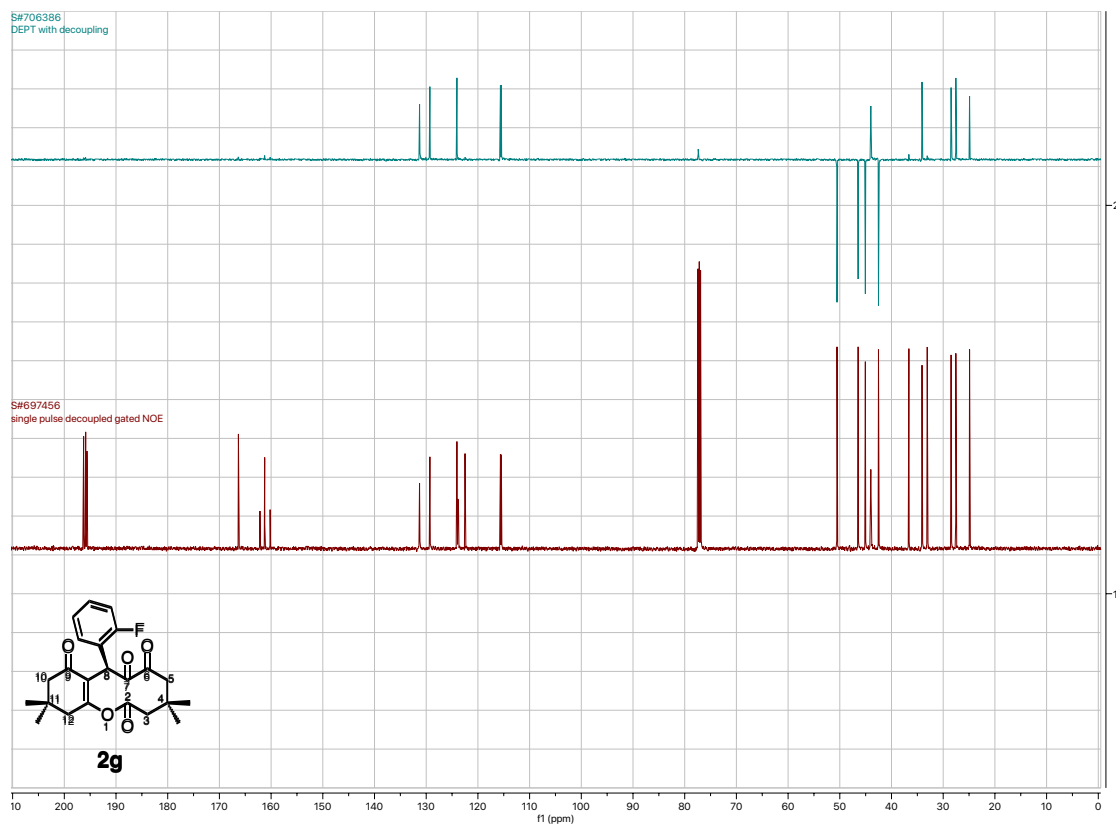
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz) using CDCl_3 of **2g**



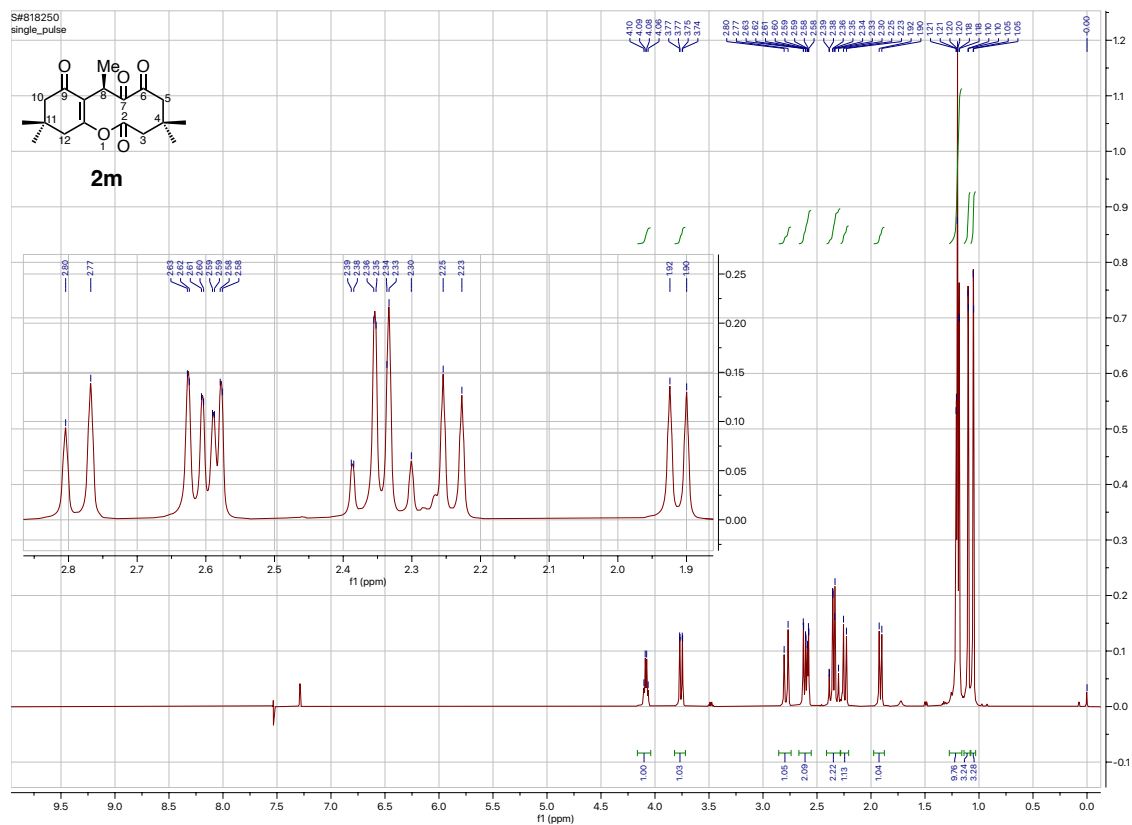
DEPT spectrum using CDCl₃ of **2g**



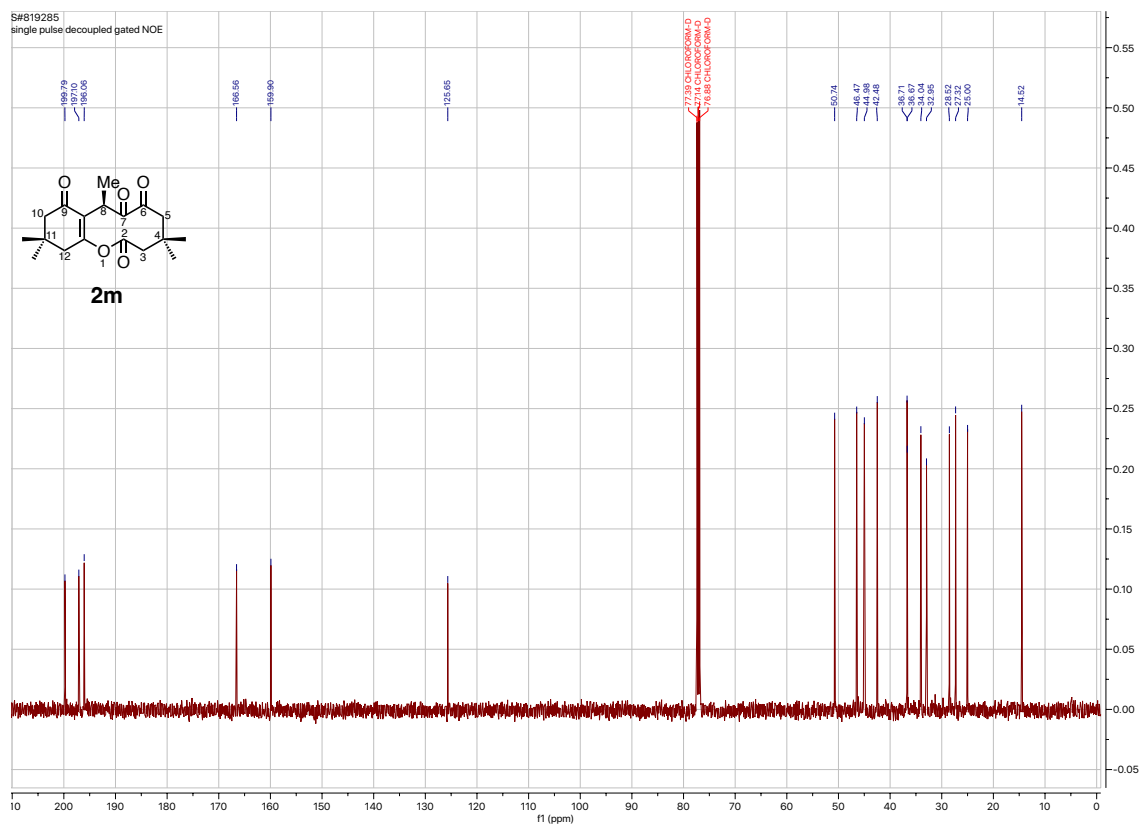
¹³C{¹H} NMR (125 MHz) (lower) and DEPT (upper) spectra using CDCl₃ of **2g**



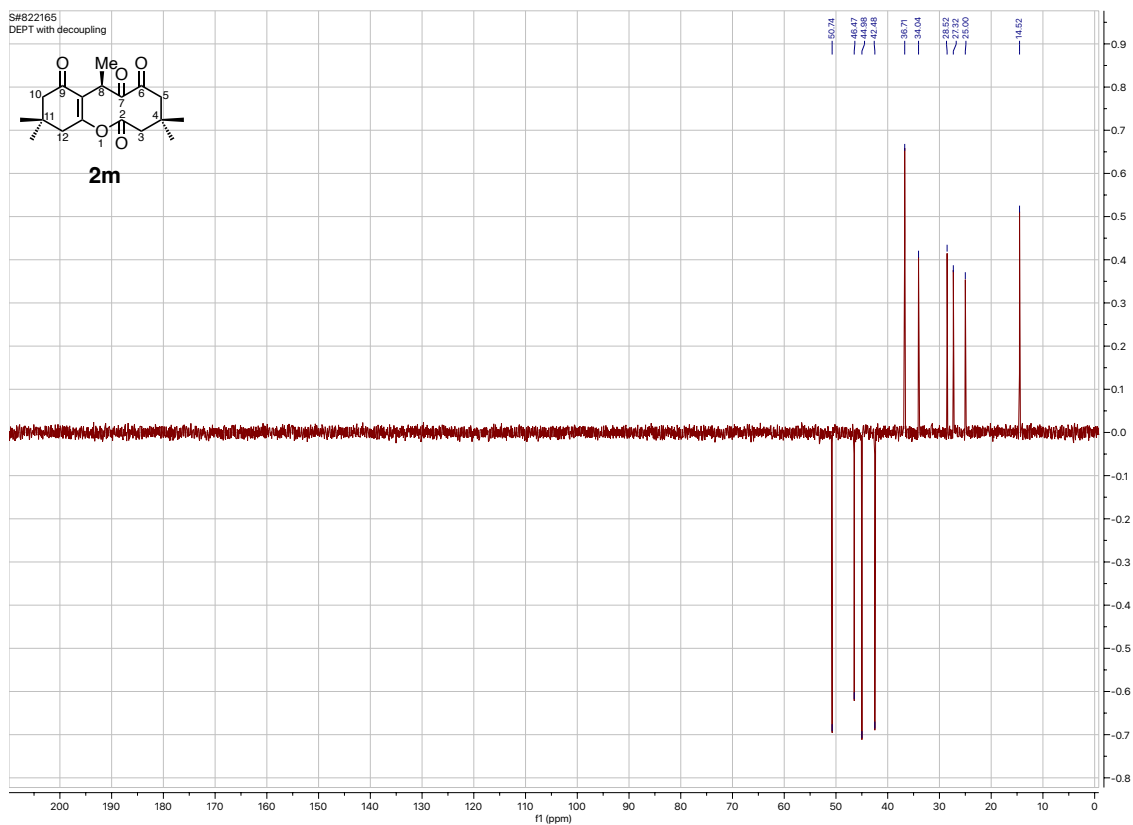
^1H NMR spectrum (500 MHz) using CDCl_3 of **2m**



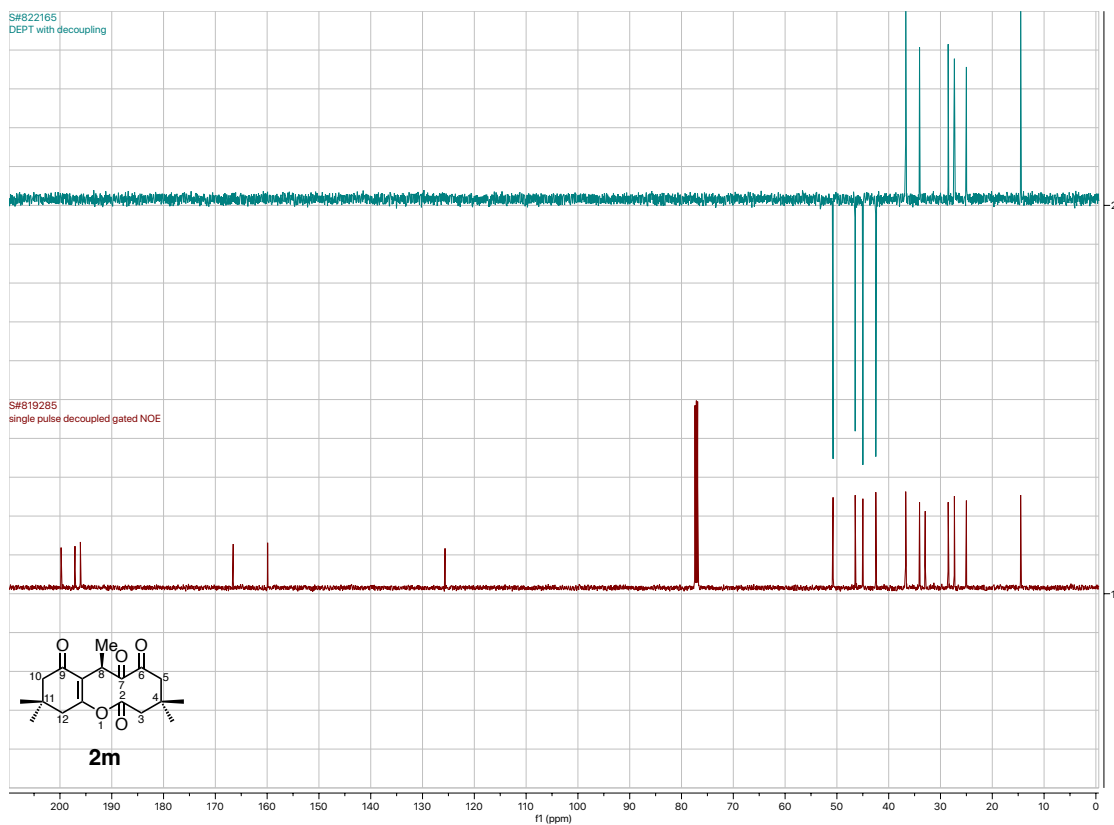
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz) using CDCl_3 of **2m**



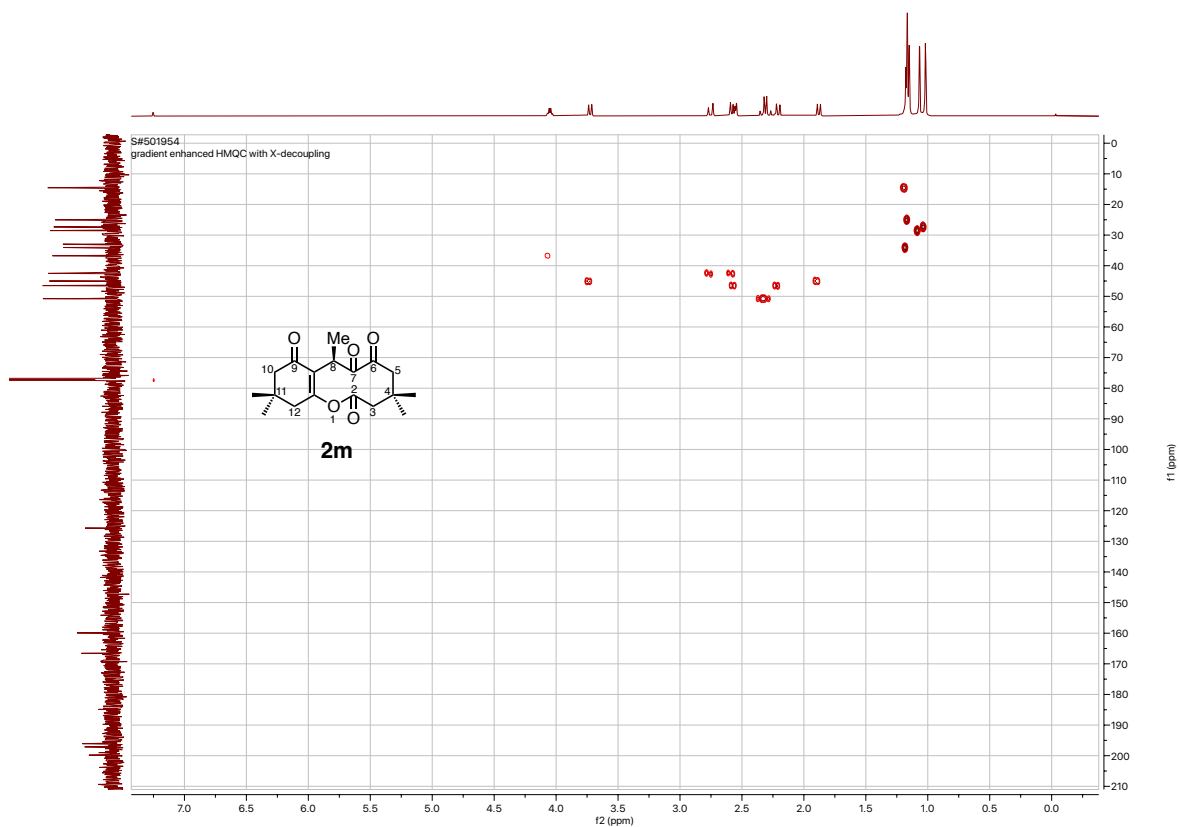
DEPT spectrum using CDCl₃ of **2m**



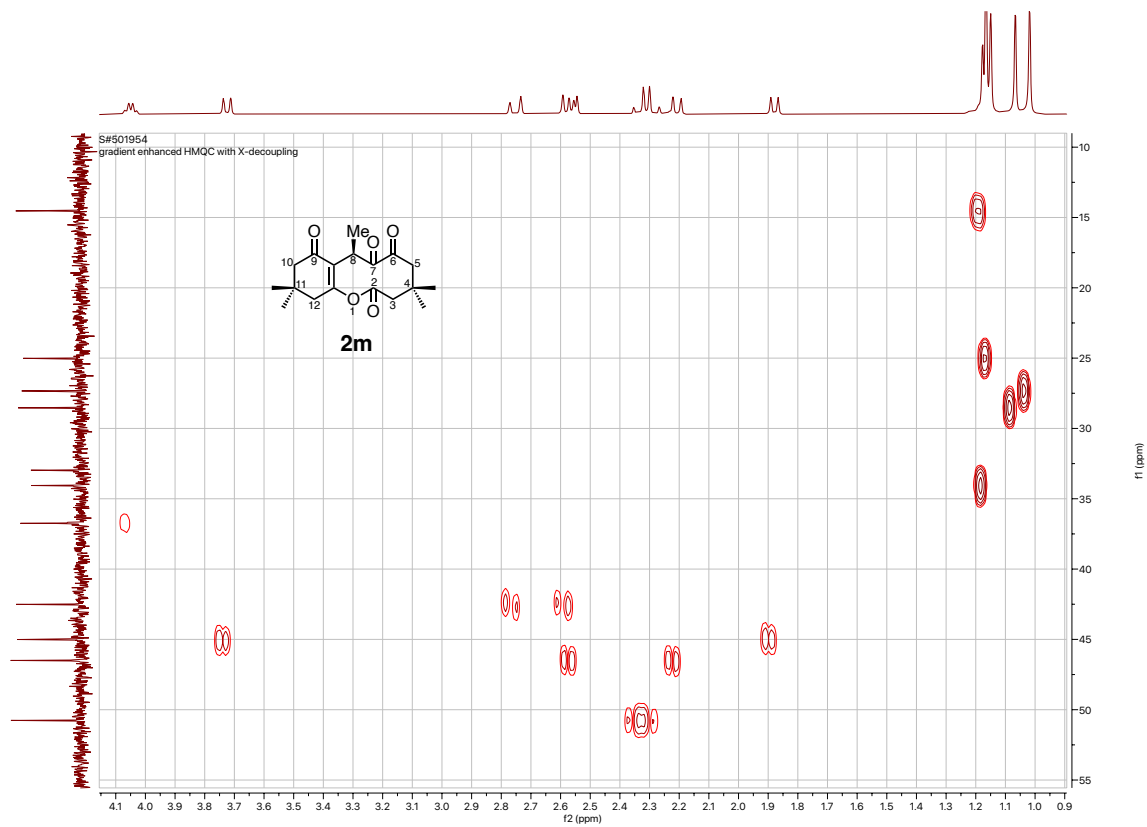
¹³C{¹H} NMR (125 MHz) (lower) and DEPT (upper) spectra using CDCl₃ of **2m**



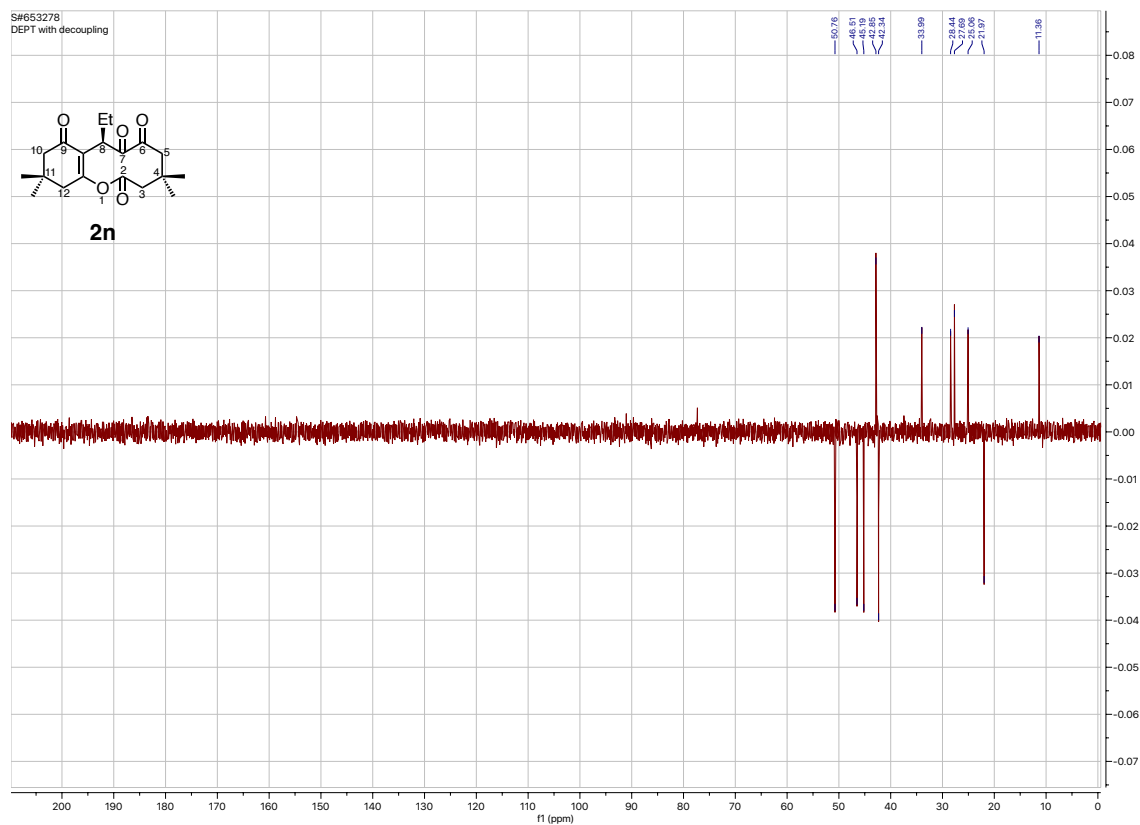
HMQC spectrum using CDCl₃ of **2m**



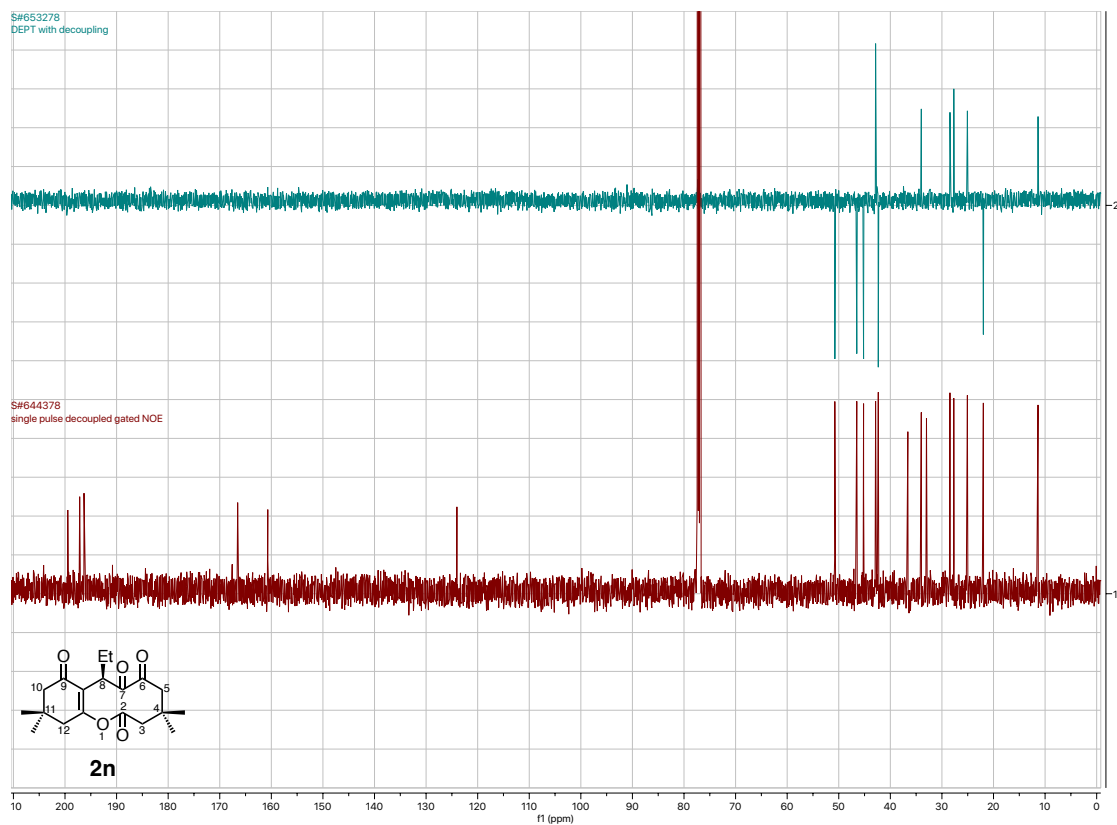
Expansion for HMQC spectrum using CDCl₃ of **2m**



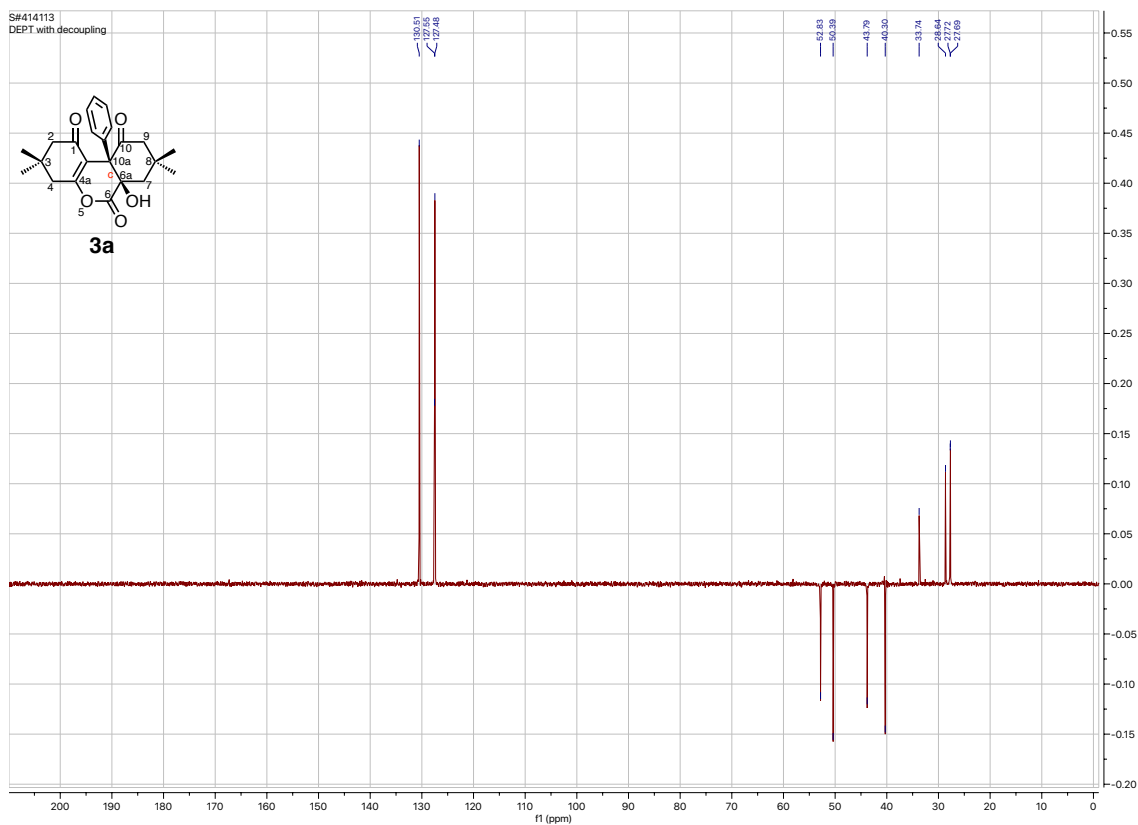
DEPT spectrum using CDCl₃ of **2m**



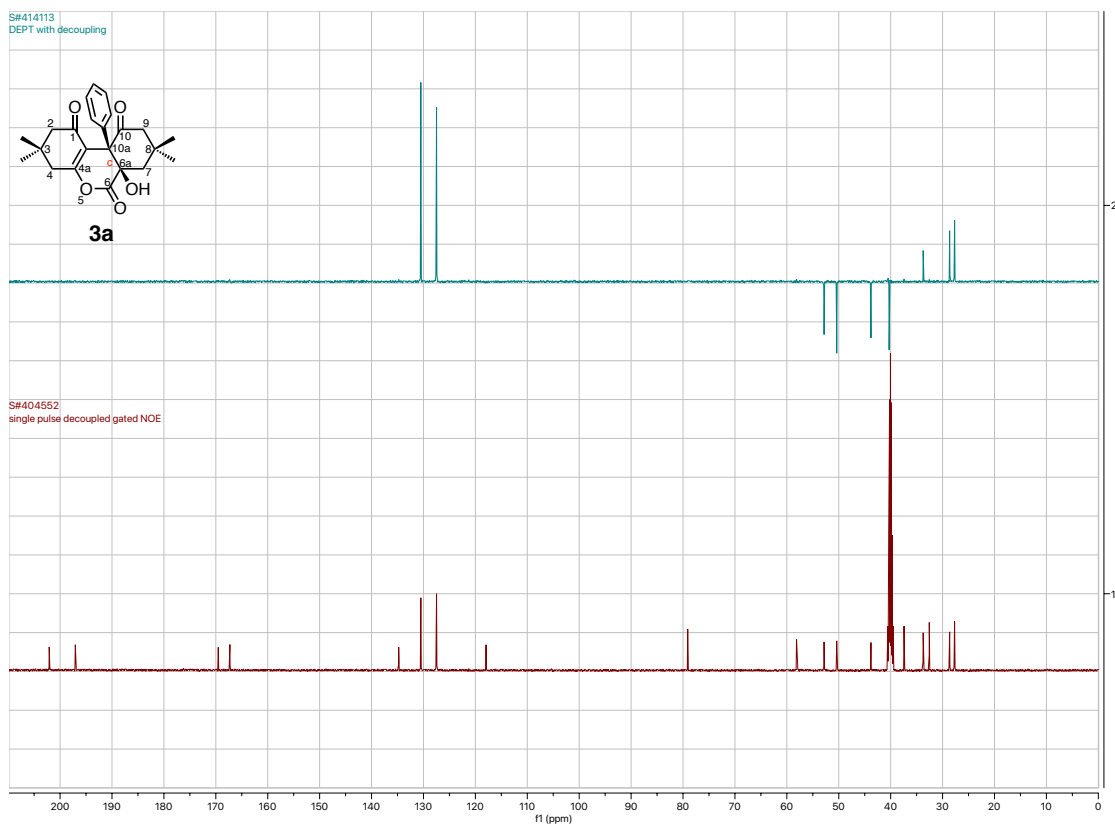
¹³C{¹H} NMR (125 MHz) (lower) and DEPT (upper) spectra using CDCl₃ of **2m**



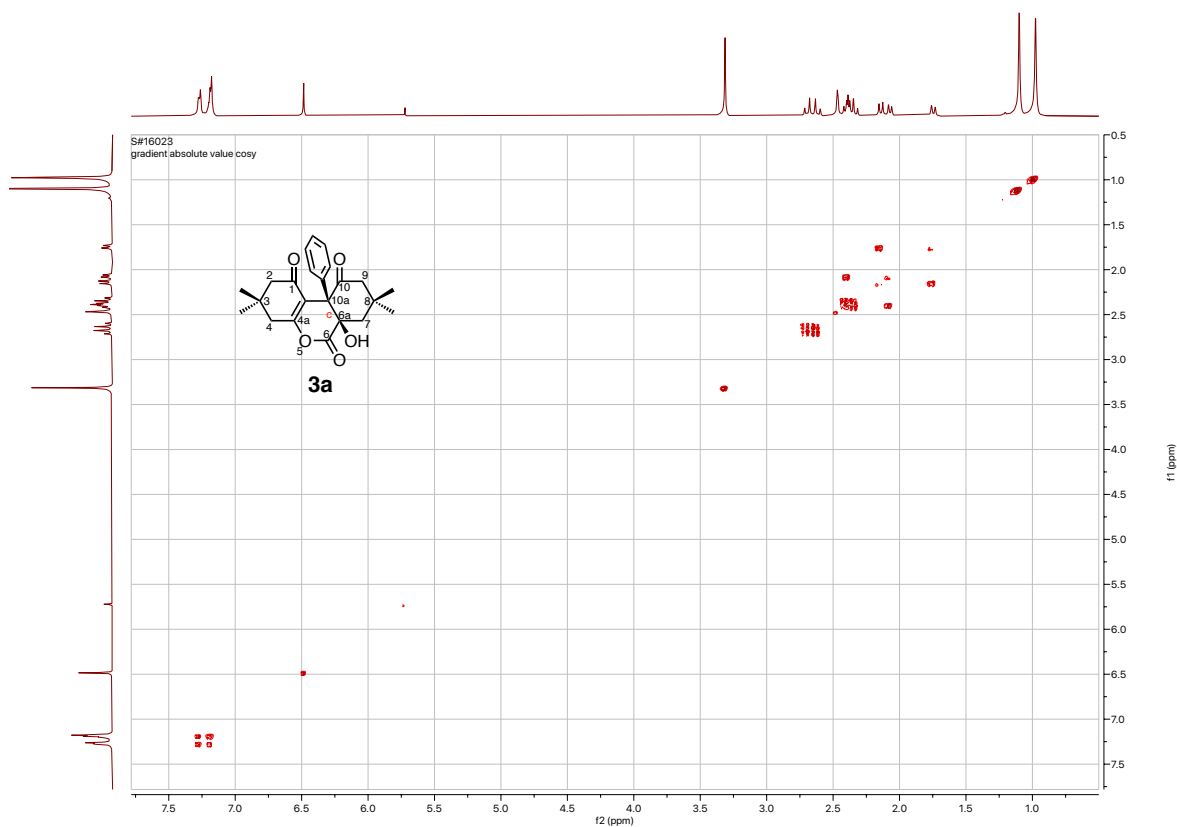
DEPT spectrum using DMSO-*d*₆ of **3a**



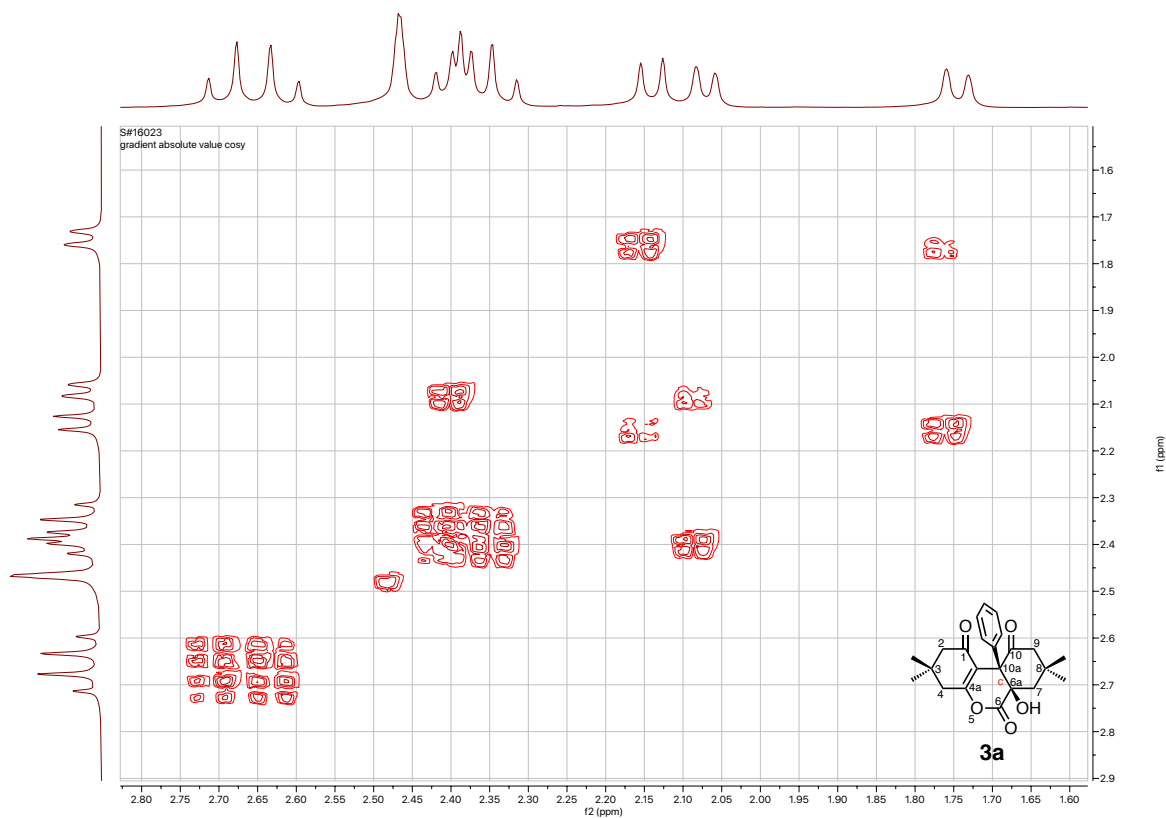
¹³C{¹H} NMR (125 MHz) (lower) and DEPT (upper) spectra using DMSO-*d*₆ of **3a**



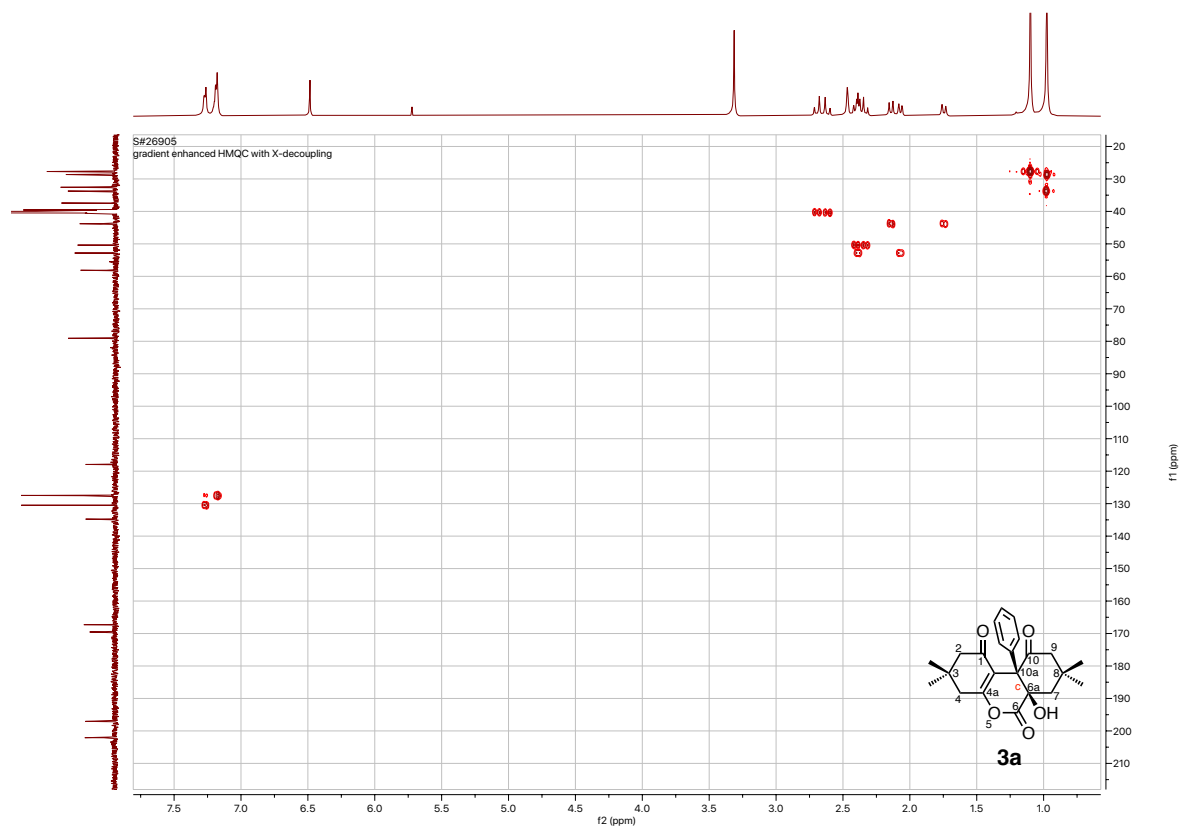
COSY spectrum using DMSO-*d*₆ of **3a**



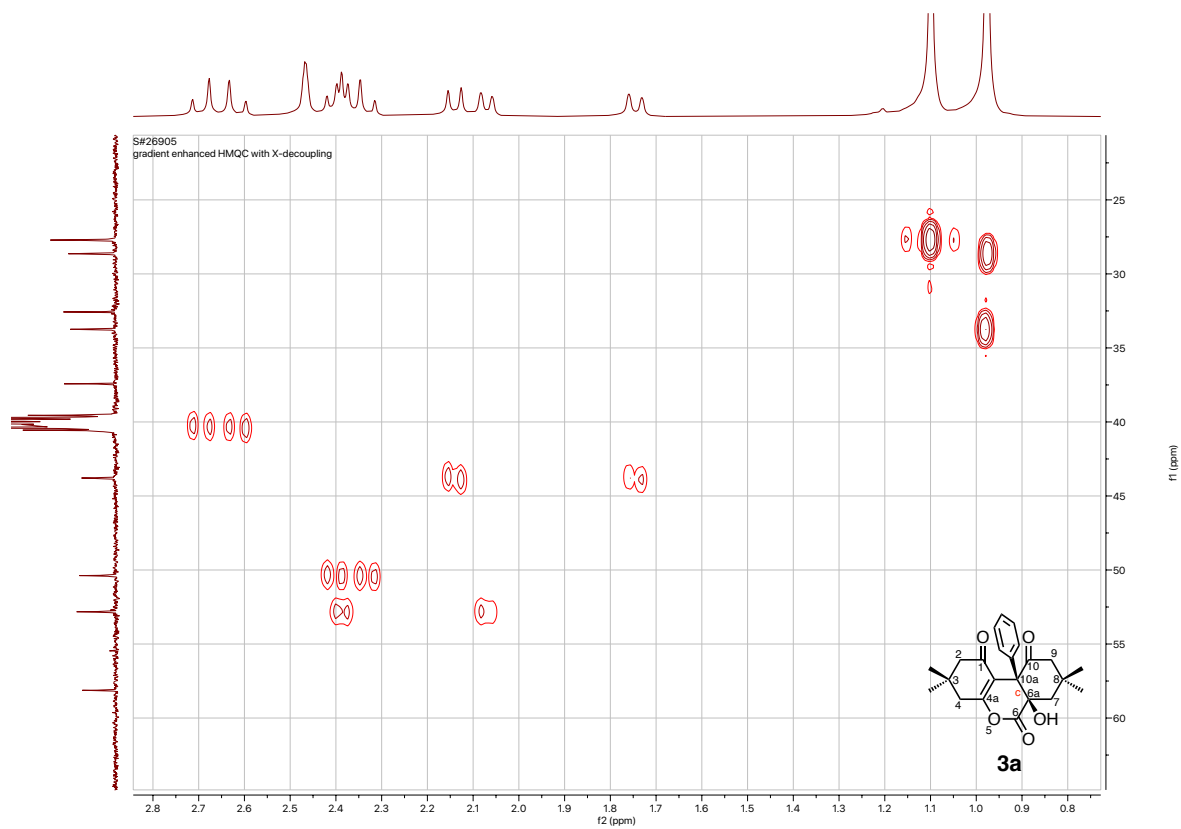
Expansion for COSY spectrum using DMSO-*d*₆ of **3a**



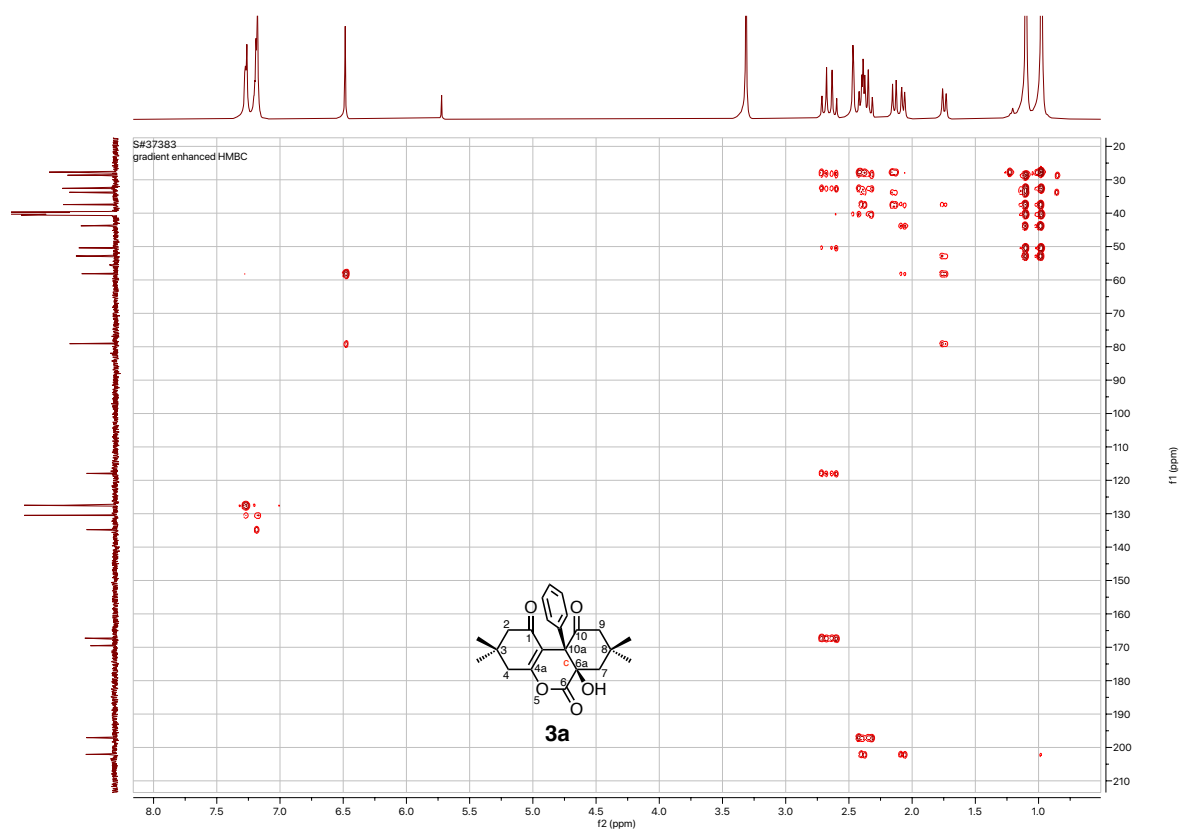
HMQC spectrum using DMSO-*d*₆ of **3a**



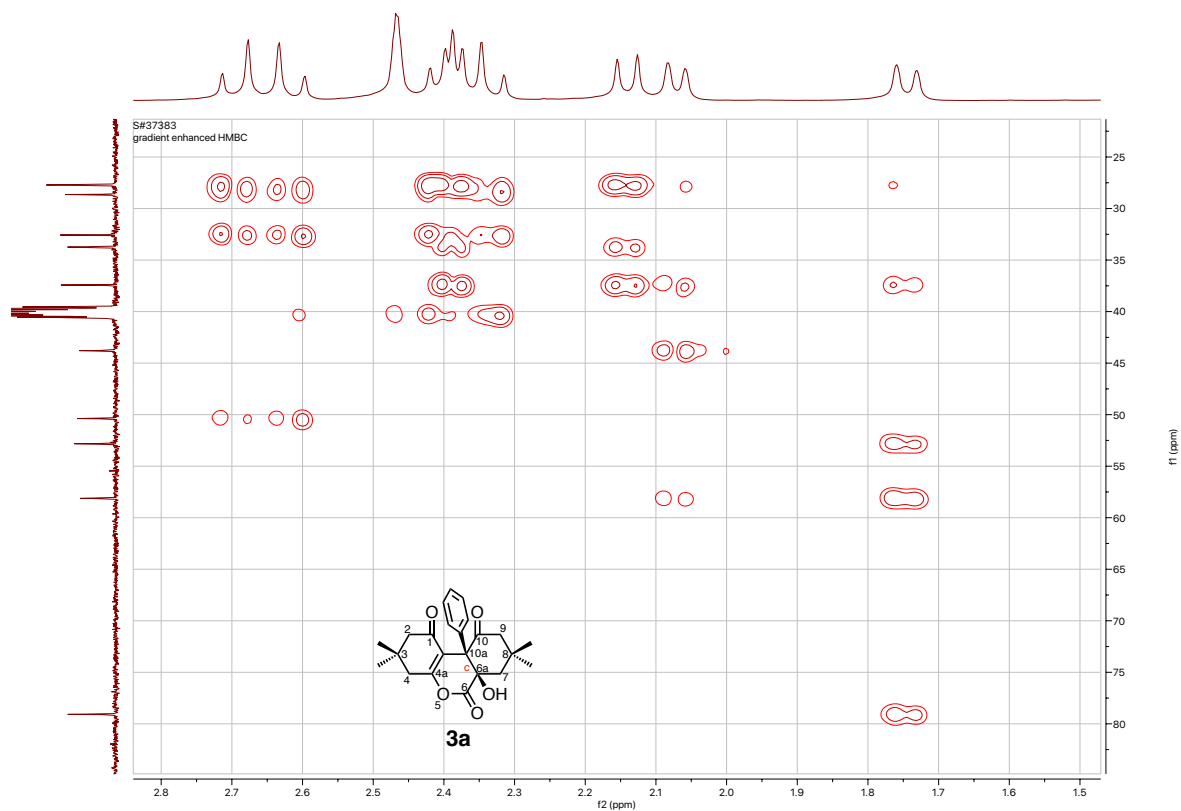
Expansion for HMQC spectrum using DMSO-*d*₆ of **3a**



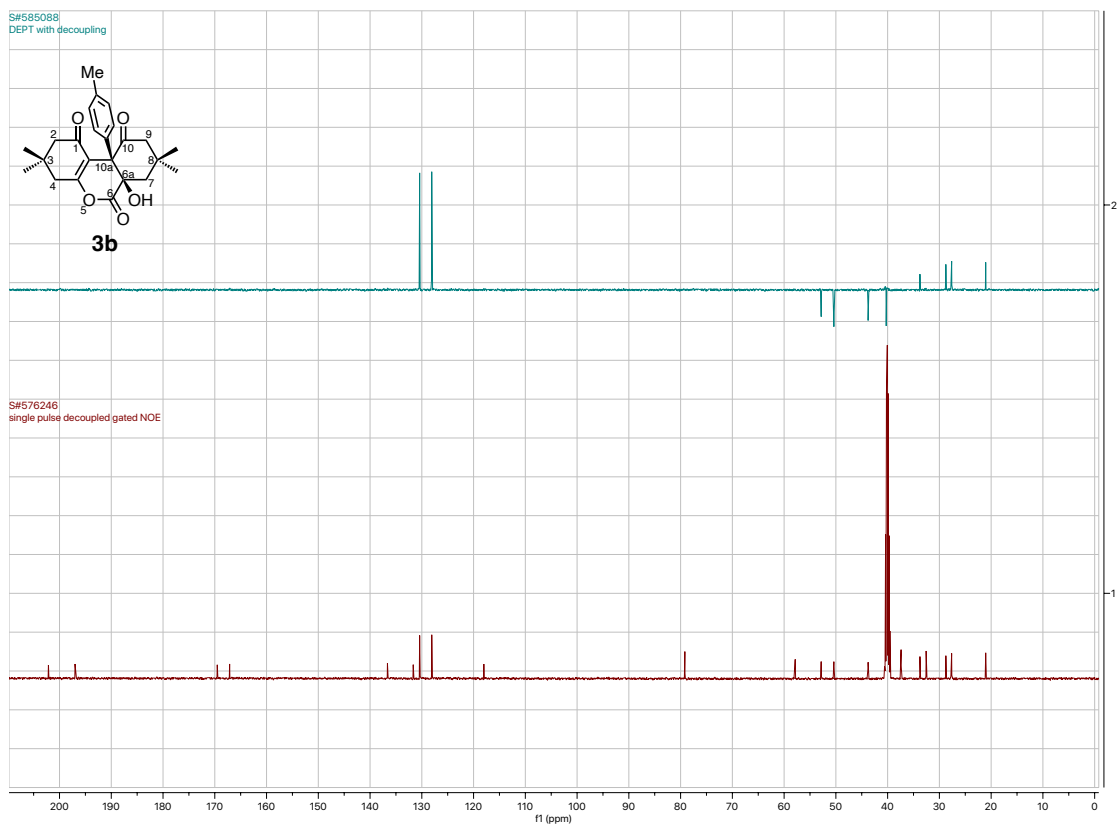
HMBC spectrum using DMSO-*d*₆ of **3a**



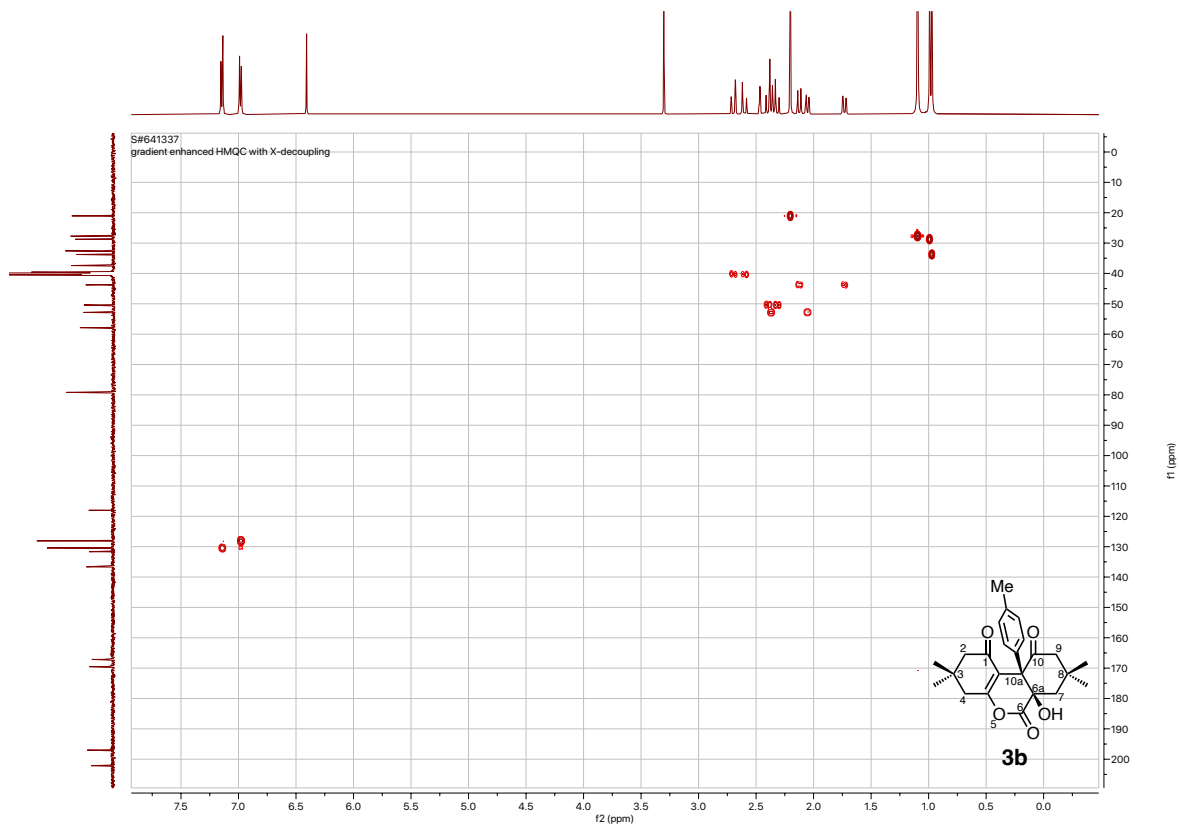
Expansion for HMBC spectrum using DMSO-*d*₆ of **3a**



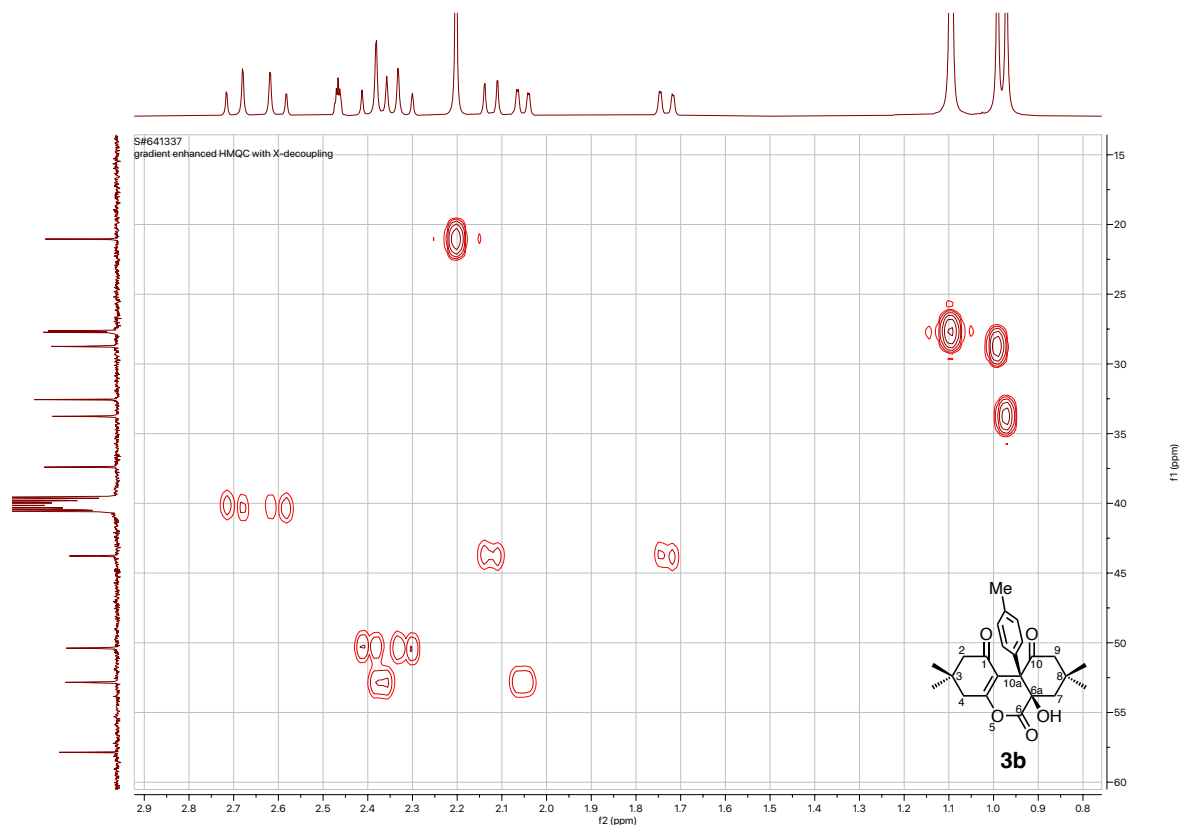
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) (lower) and DEPT (upper) spectra using $\text{DMSO-}d_6$ of **3b**



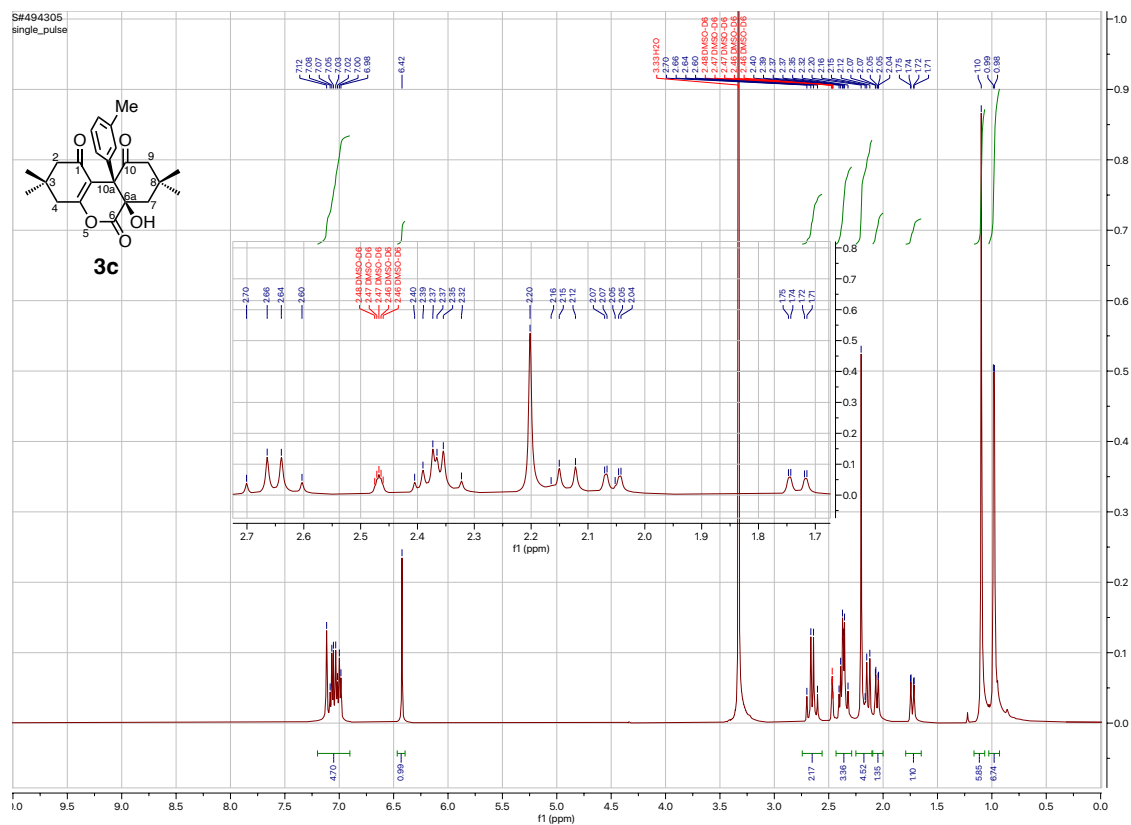
HMQC spectrum using $\text{DMSO-}d_6$ of **3b**



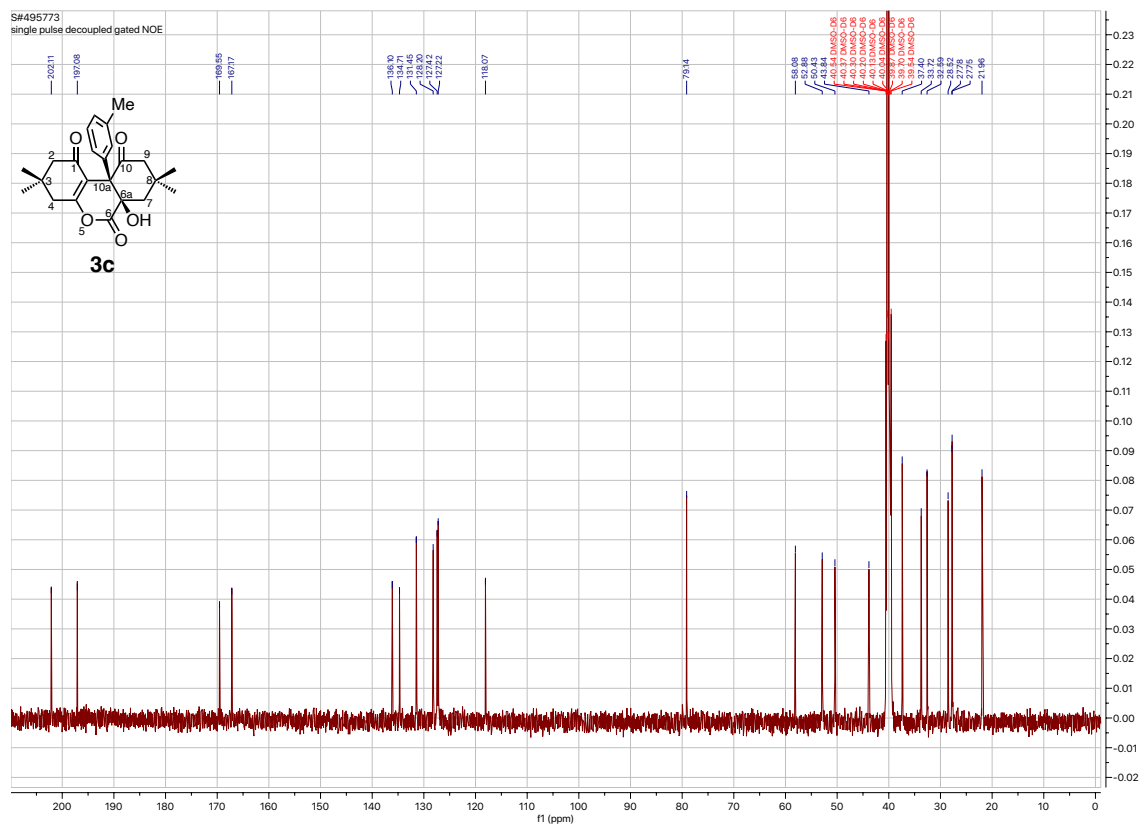
Expansion for HMQC spectrum using DMSO-*d*₆ of **3b**



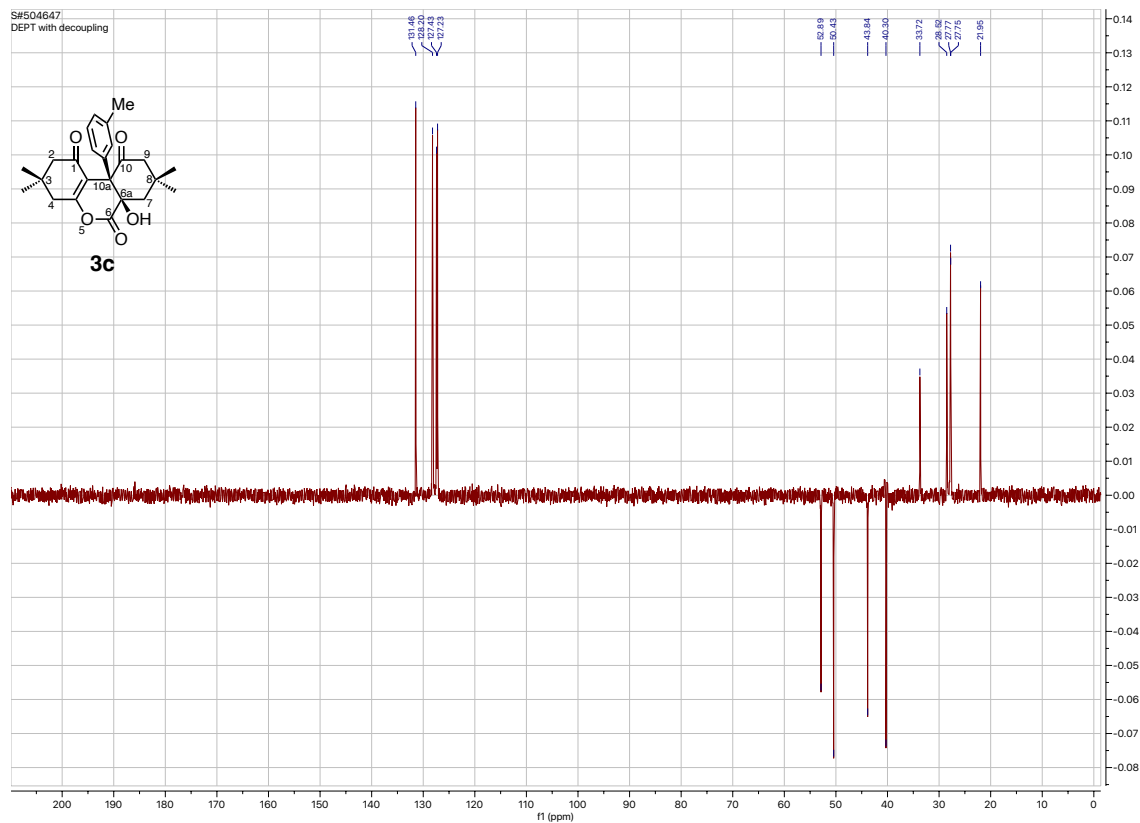
¹H NMR spectrum (500 MHz) using DMSO-*d*₆ of **3c**



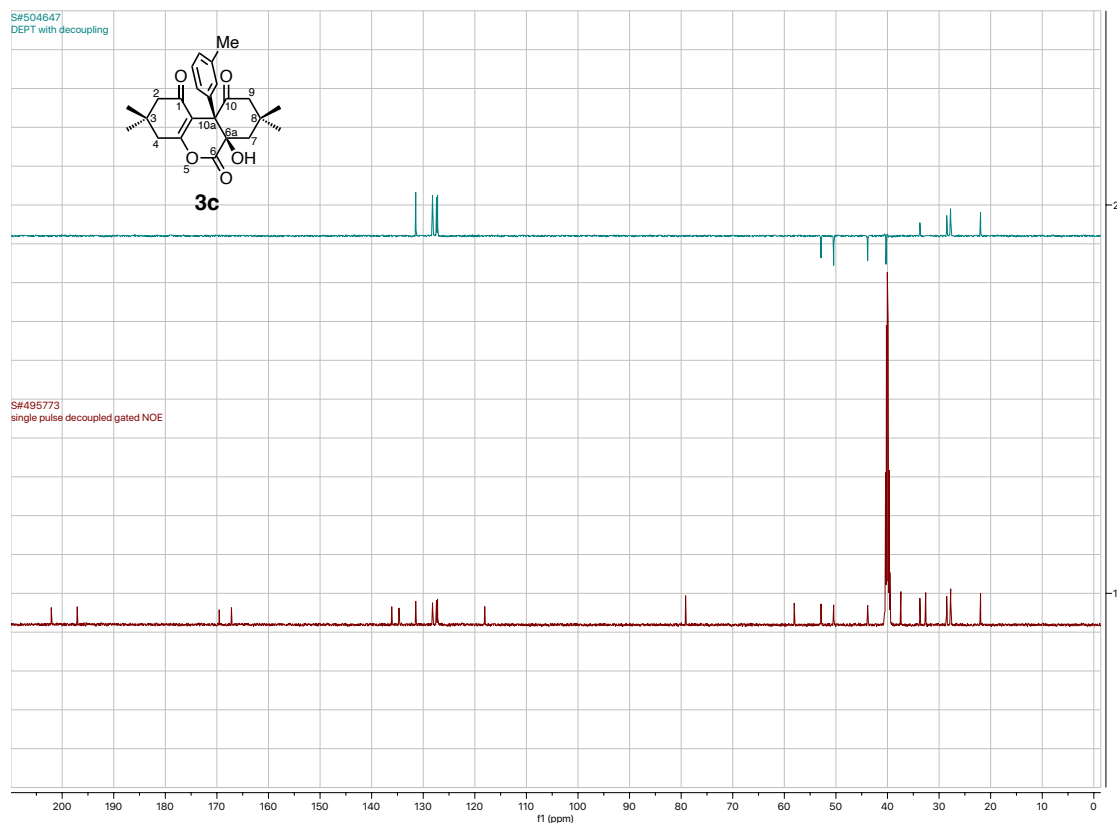
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz) using $\text{DMSO-}d_6$ of **3c**



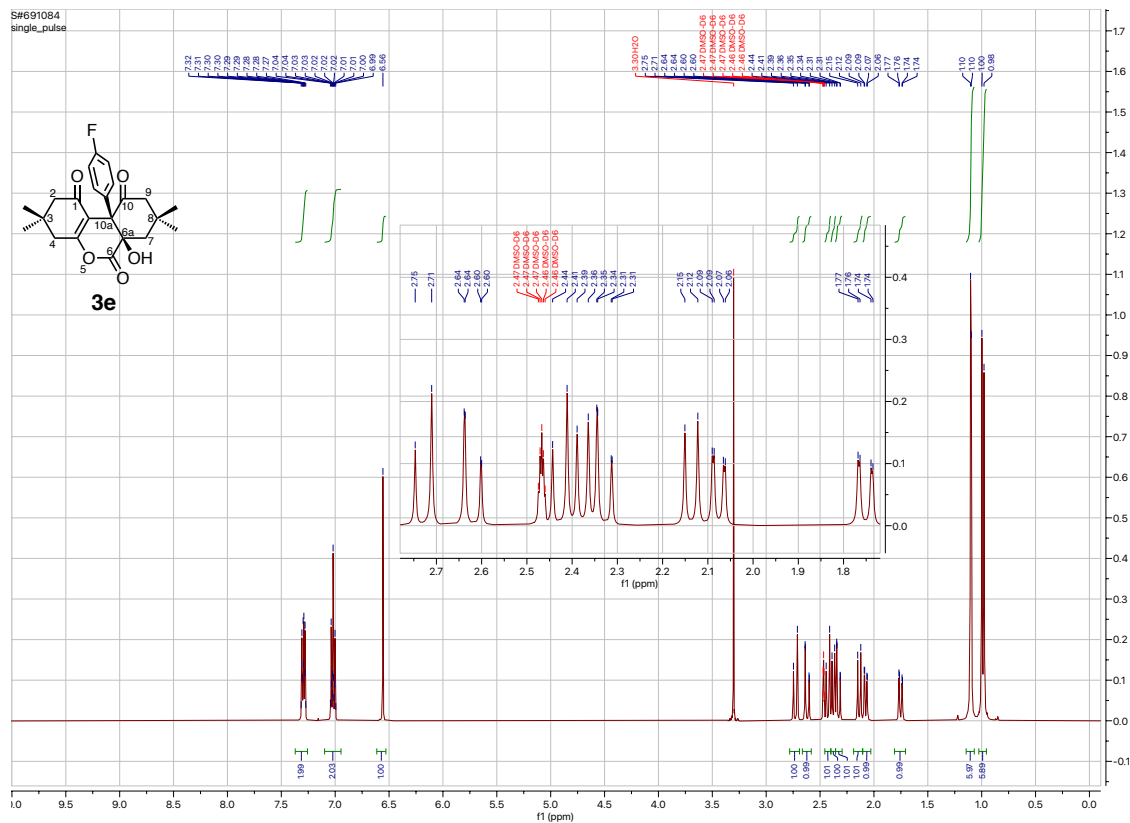
DEPT spectrum using $\text{DMSO-}d_6$ of **3c**



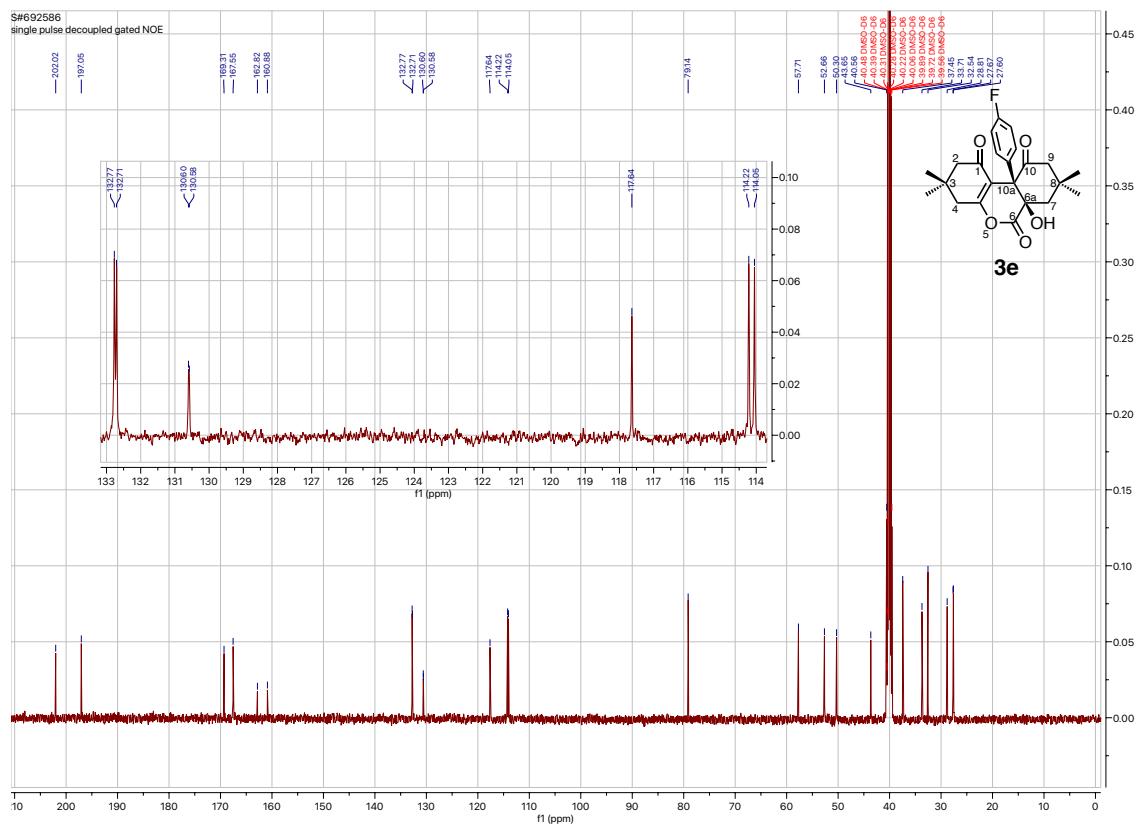
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) (lower) and DEPT (upper) spectra using $\text{DMSO-}d_6$ of **3c**



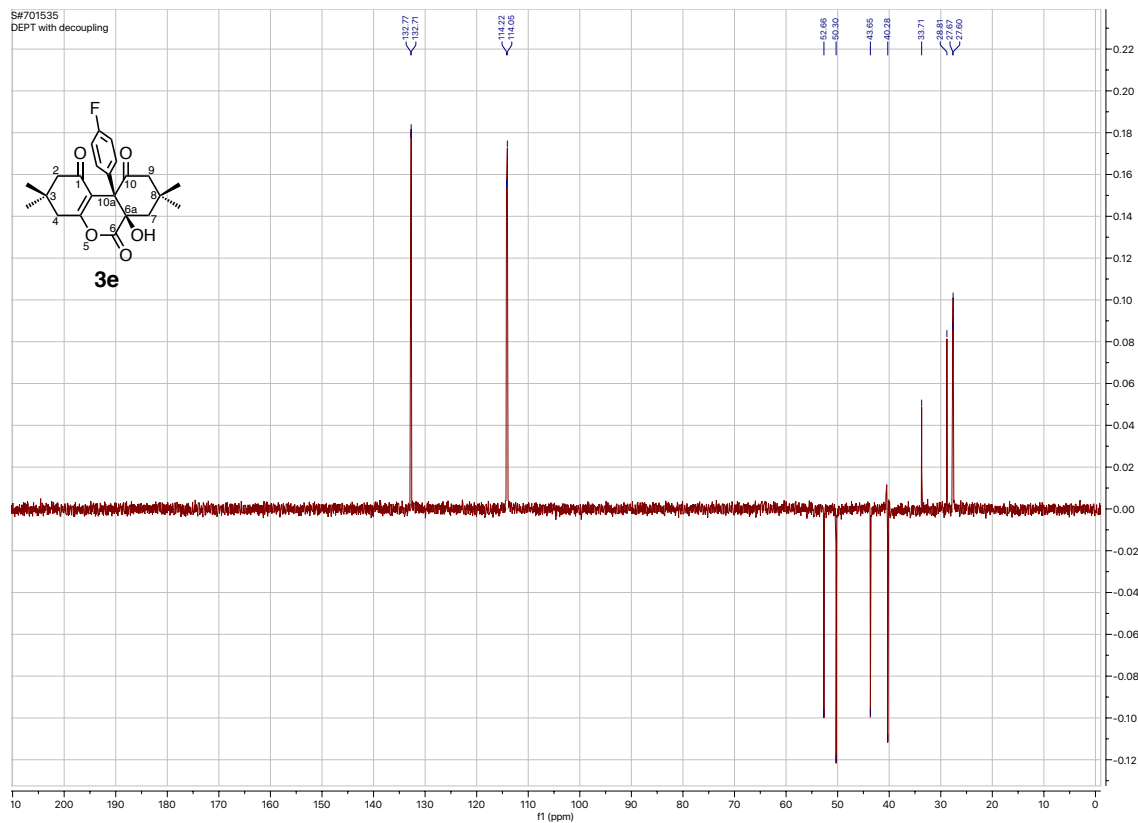
^1H NMR spectrum (500 MHz) using $\text{DMSO-}d_6$ of **3e**



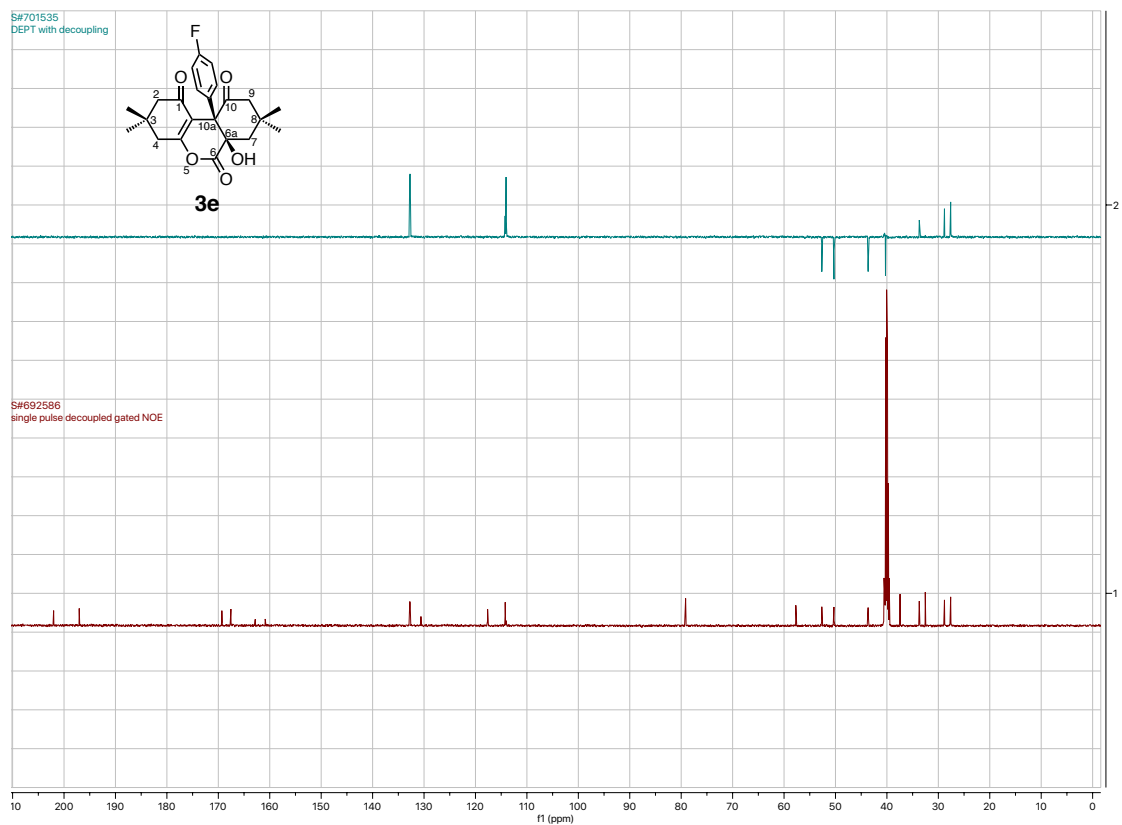
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz) using $\text{DMSO-}d_6$ of **3e**



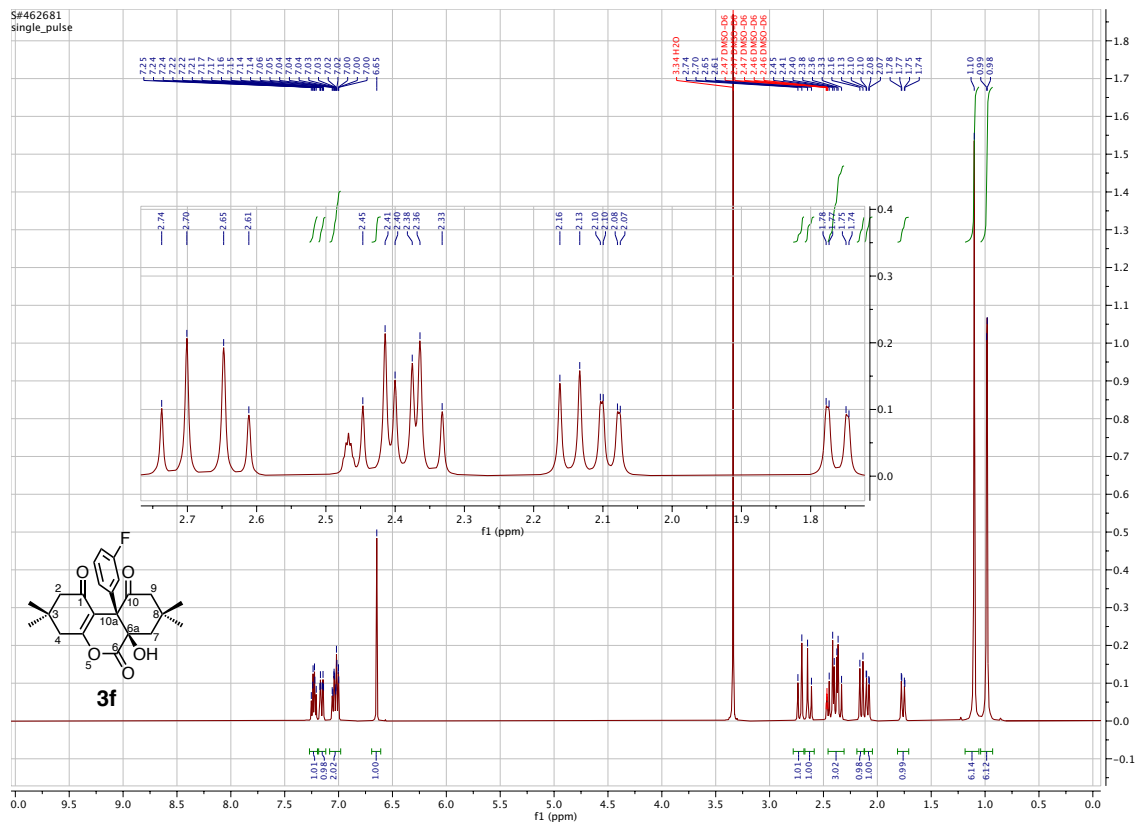
DEPT spectrum using $\text{DMSO-}d_6$ of **3e**



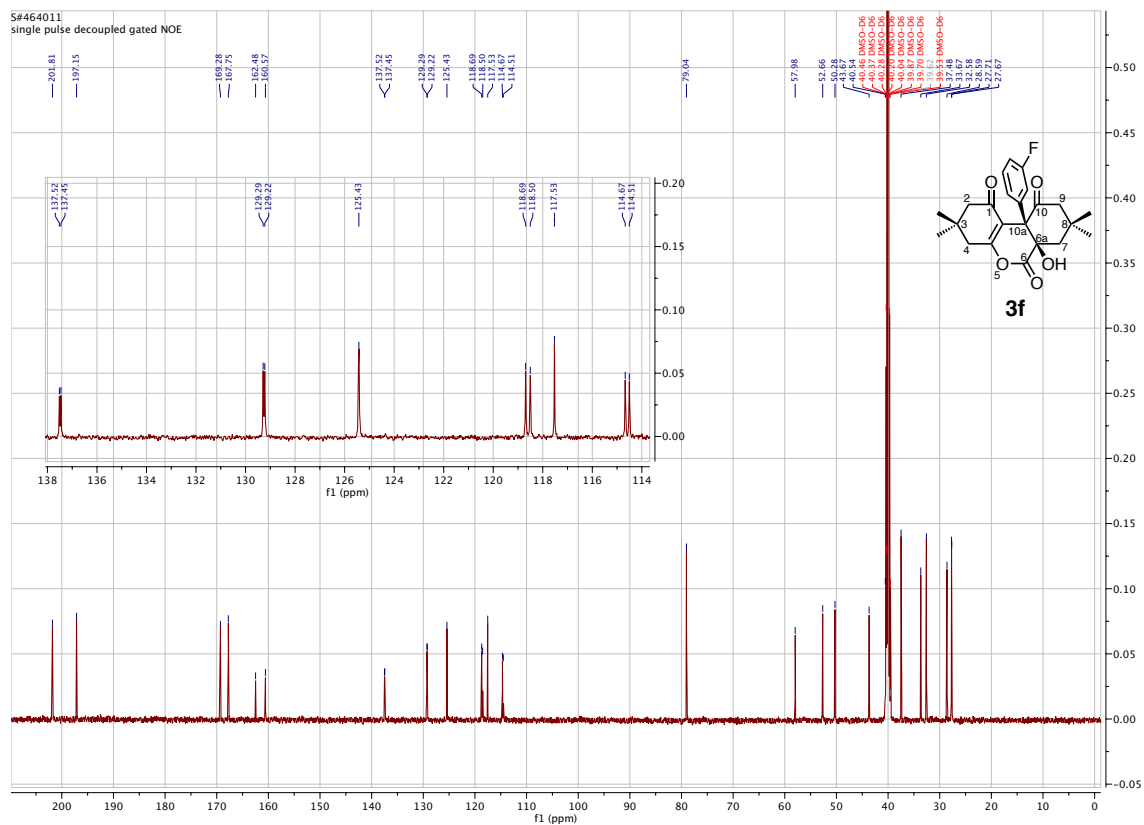
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) (lower) and DEPT (upper) spectra using $\text{DMSO-}d_6$ of **3e**



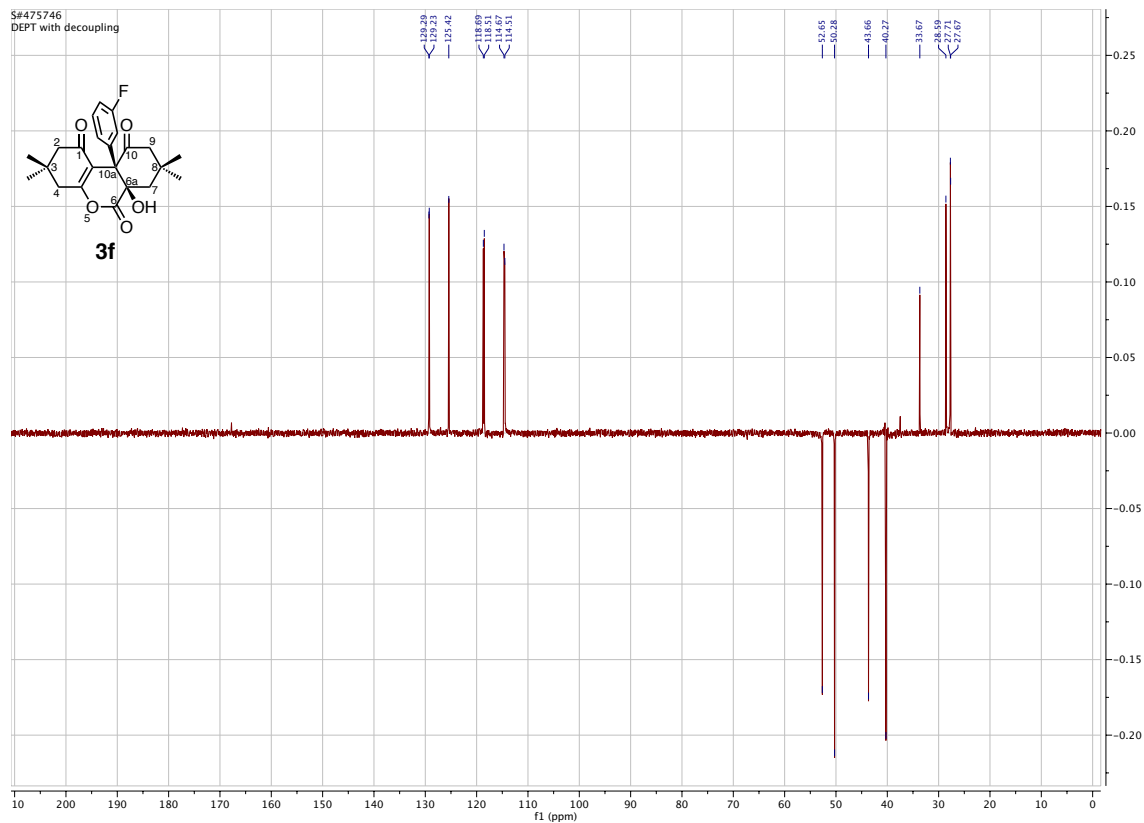
^1H NMR spectrum (500 MHz) using $\text{DMSO-}d_6$ of **3f**



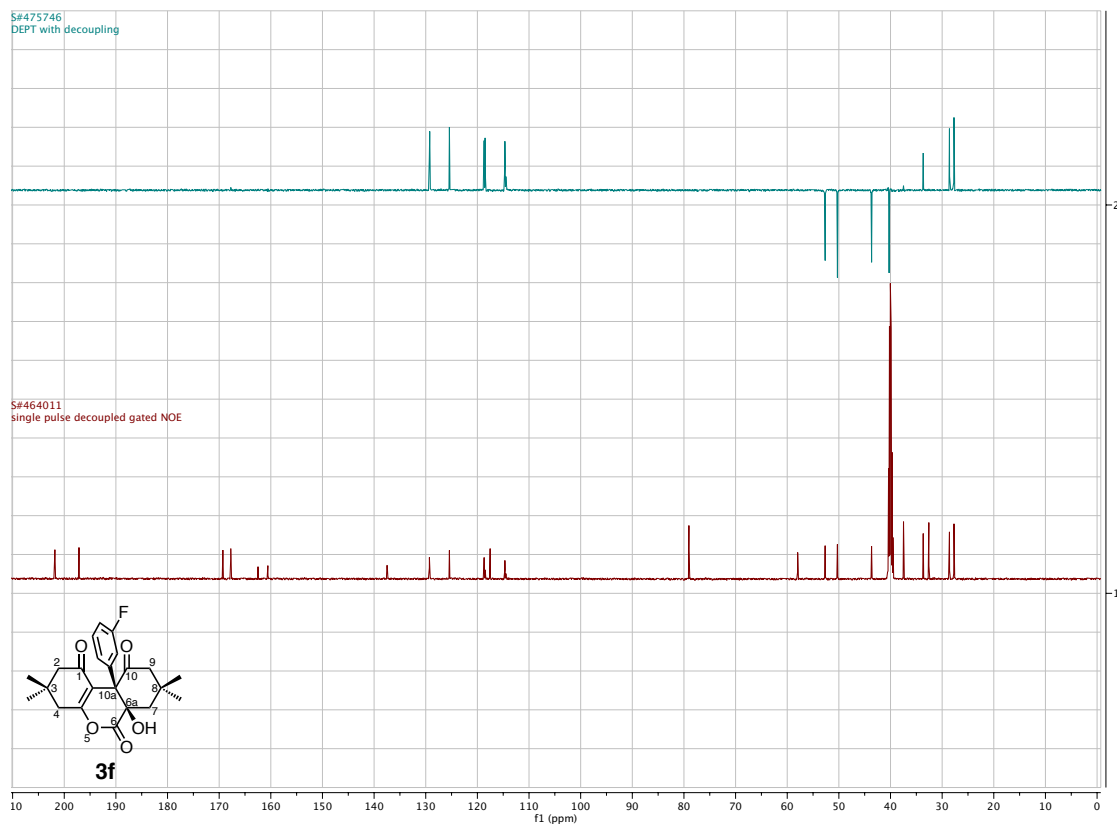
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz) using $\text{DMSO-}d_6$ of **3f**



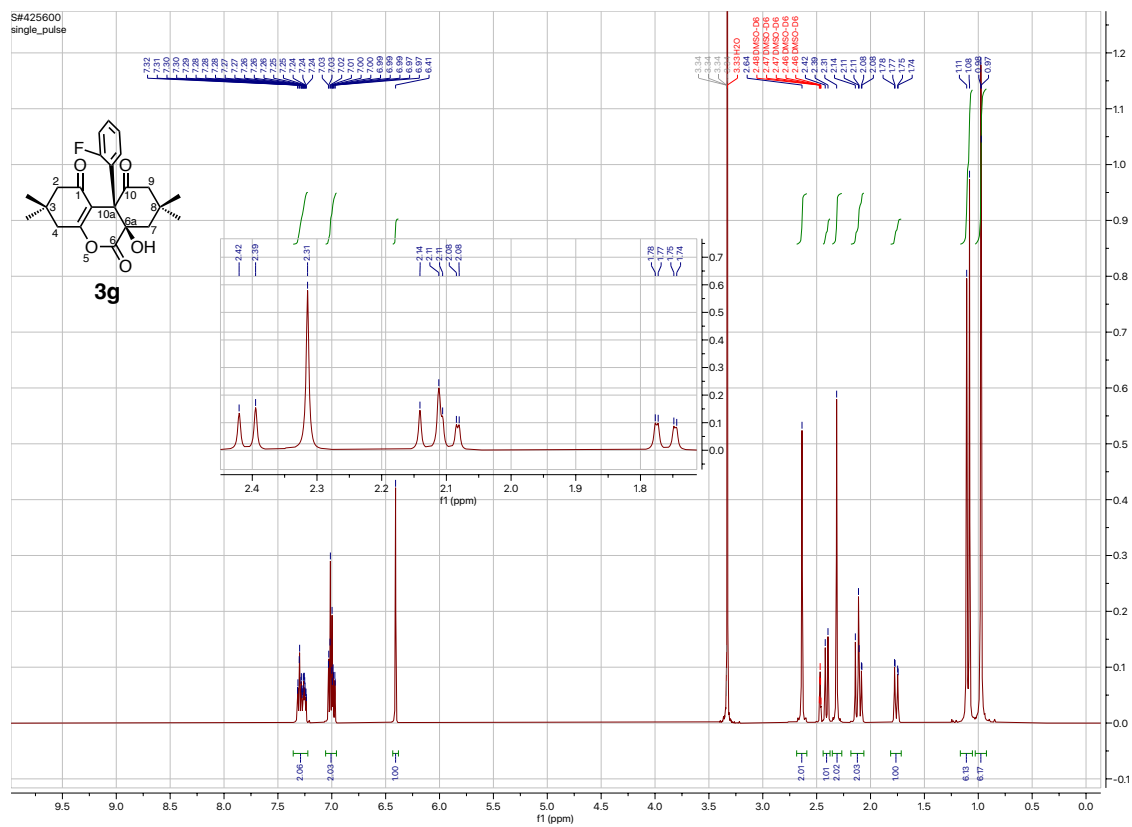
DEPT spectrum using $\text{DMSO-}d_6$ of **3f**



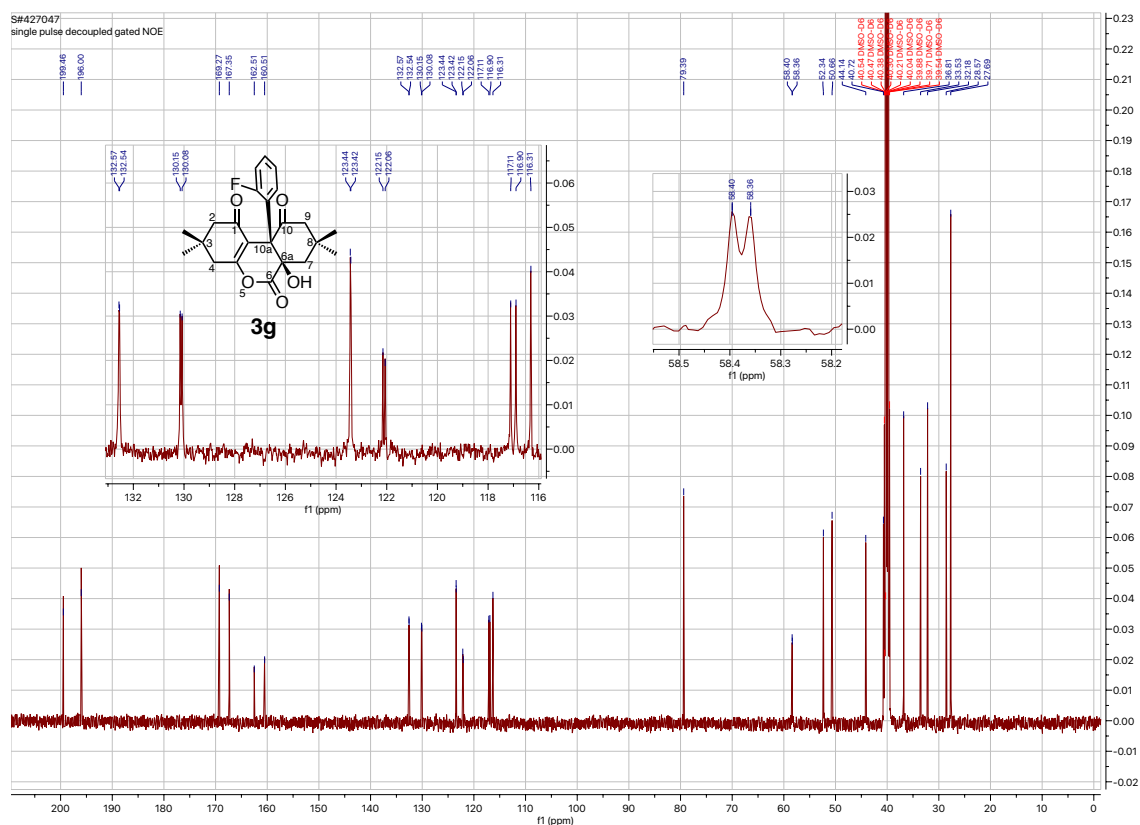
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) (lower) and DEPT (upper) spectra using $\text{DMSO-}d_6$ of **3f**



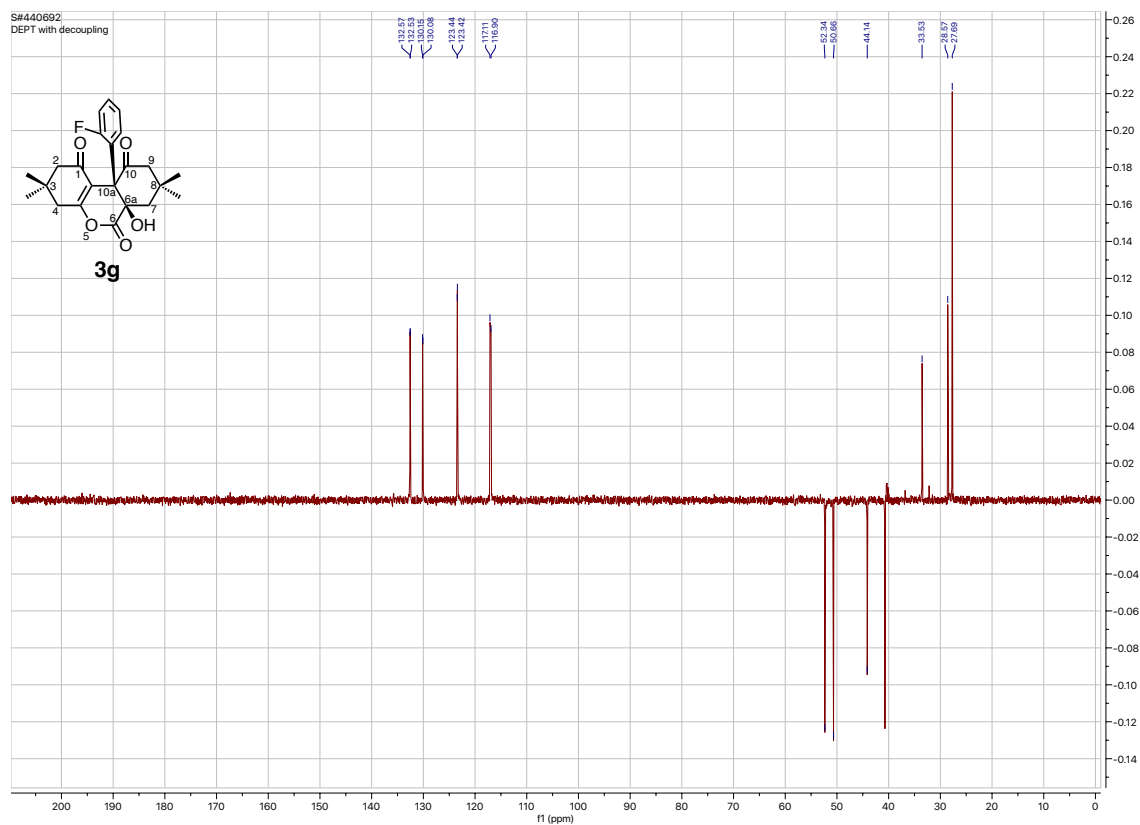
^1H NMR spectrum (500 MHz) using $\text{DMSO-}d_6$ of **3g**



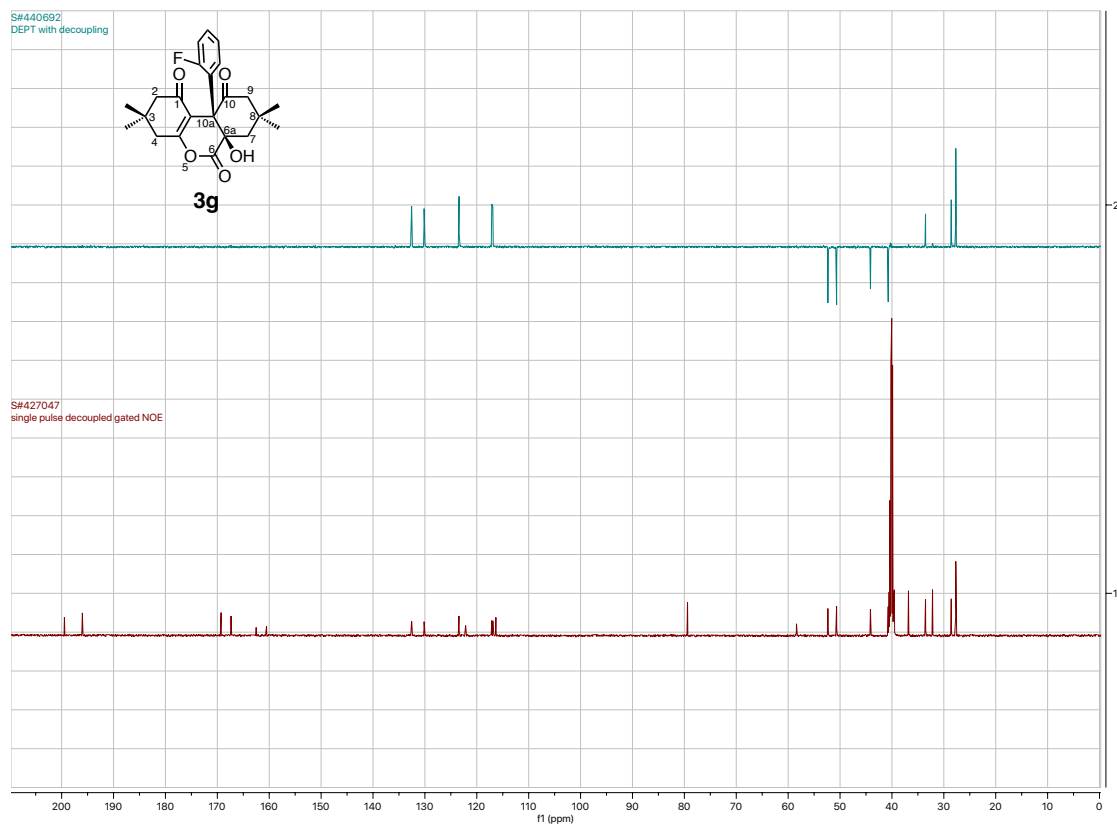
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz) using $\text{DMSO-}d_6$ of **3g**



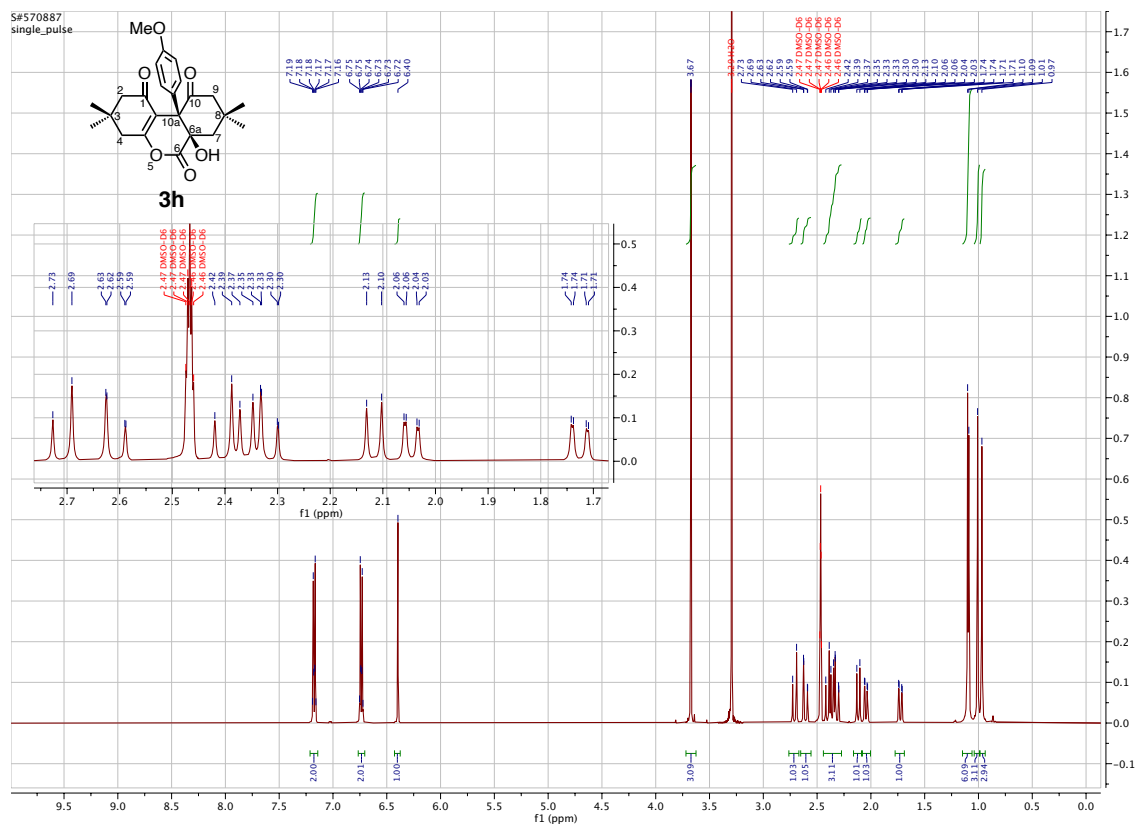
DEPT spectrum using $\text{DMSO-}d_6$ of **3g**



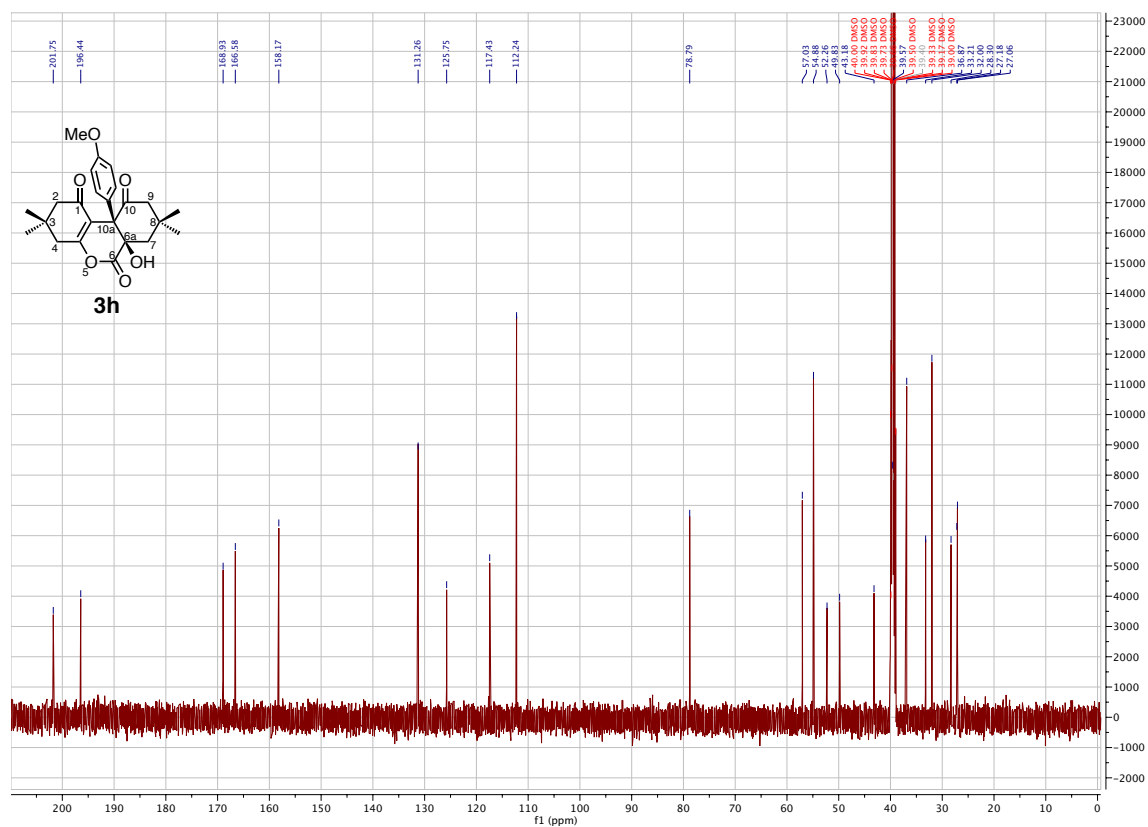
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) (lower) and DEPT (upper) spectra using $\text{DMSO-}d_6$ of **3g**



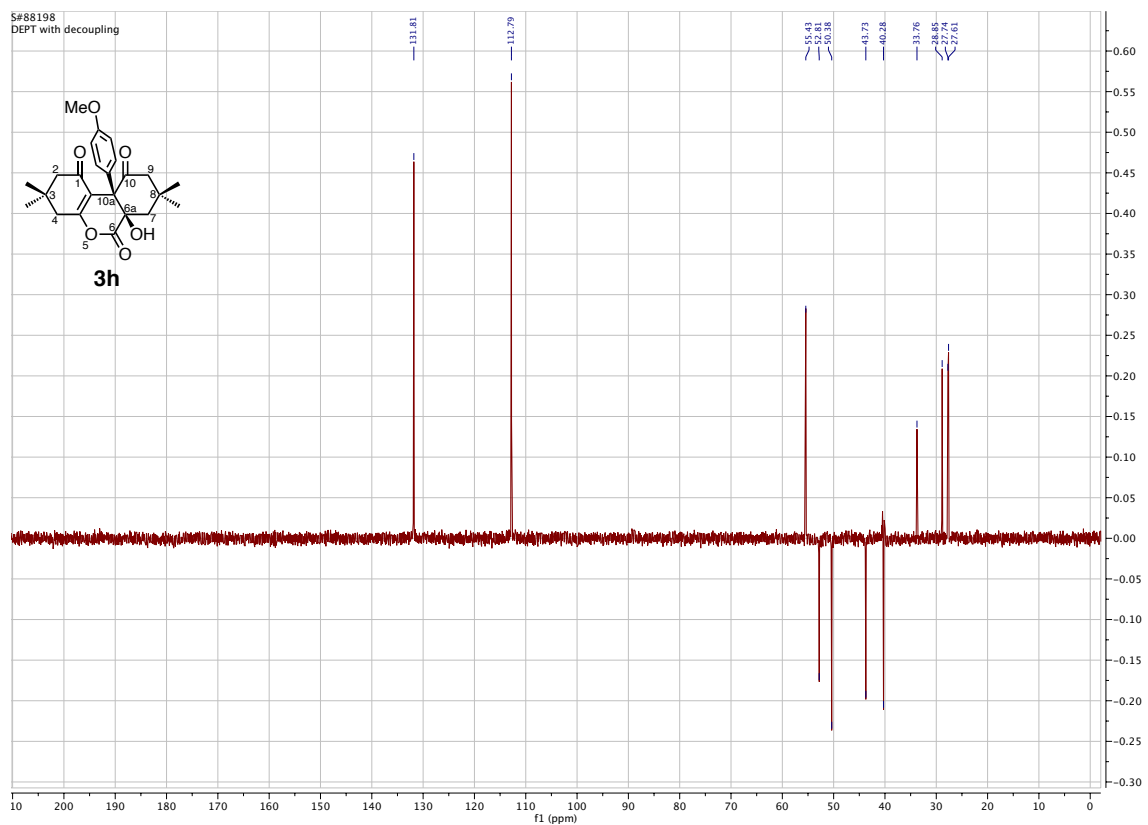
^1H NMR spectrum (500 MHz) using $\text{DMSO-}d_6$ of **3h**



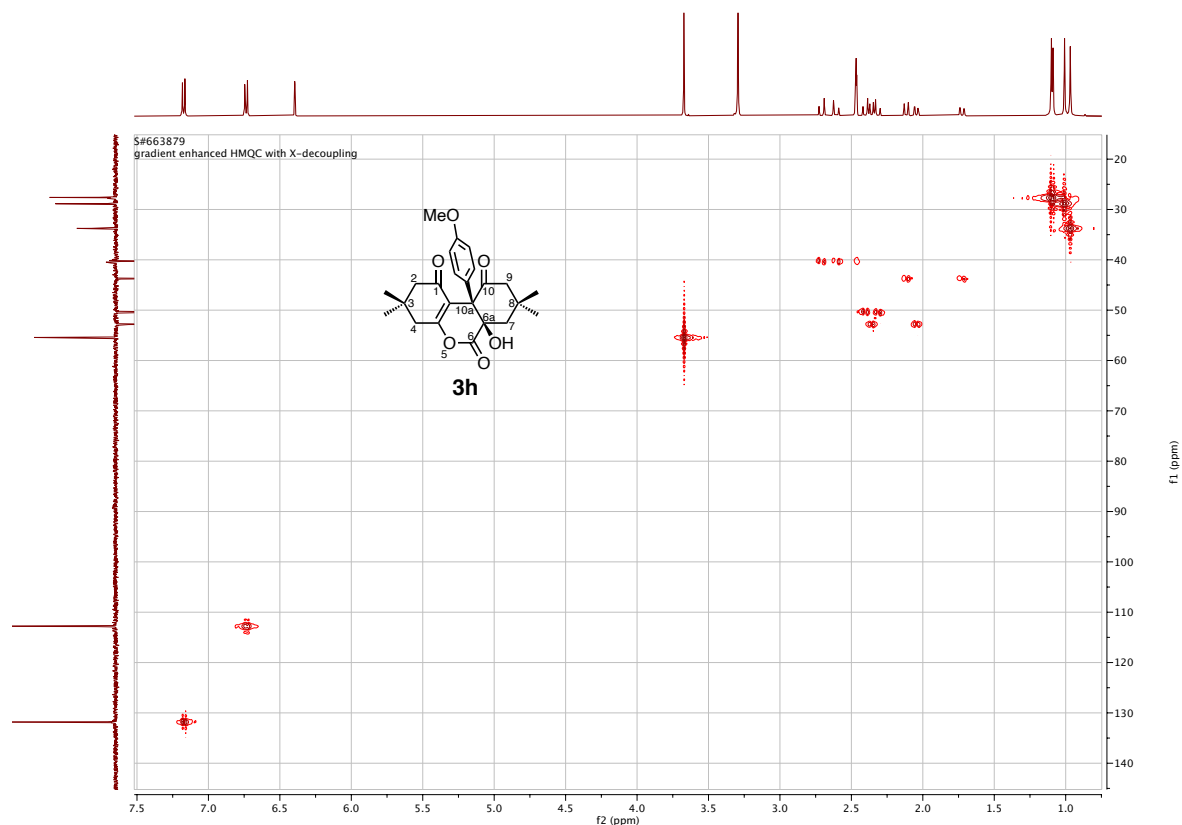
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz) using $\text{DMSO-}d_6$ of **3h**



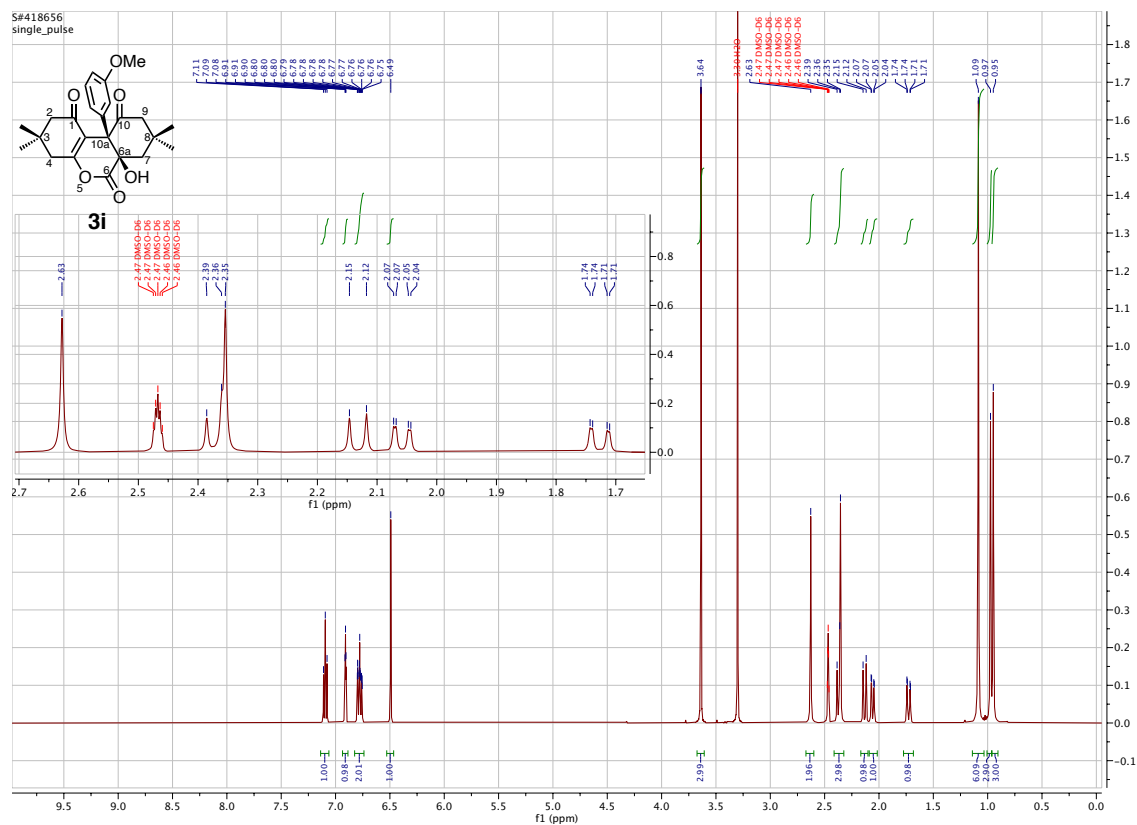
DEPT spectrum using $\text{DMSO-}d_6$ of **3h**



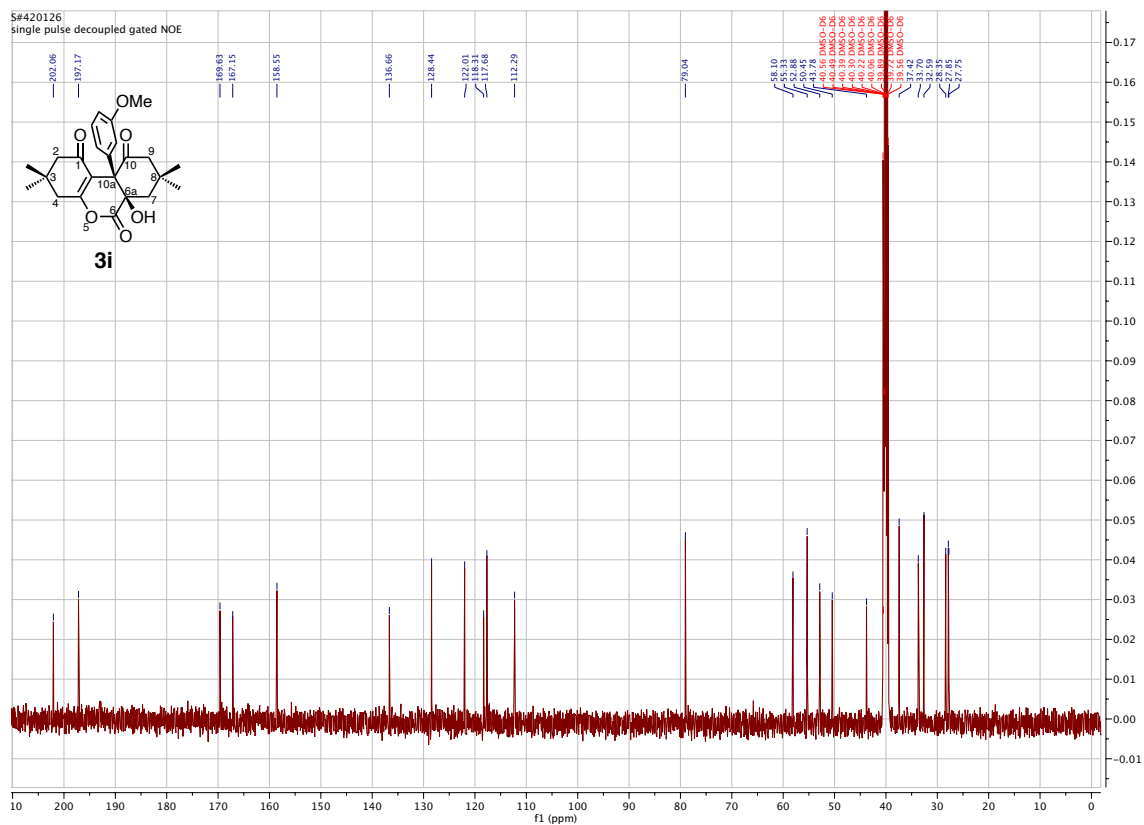
HMQC spectrum using DMSO-*d*₆ of **3h**



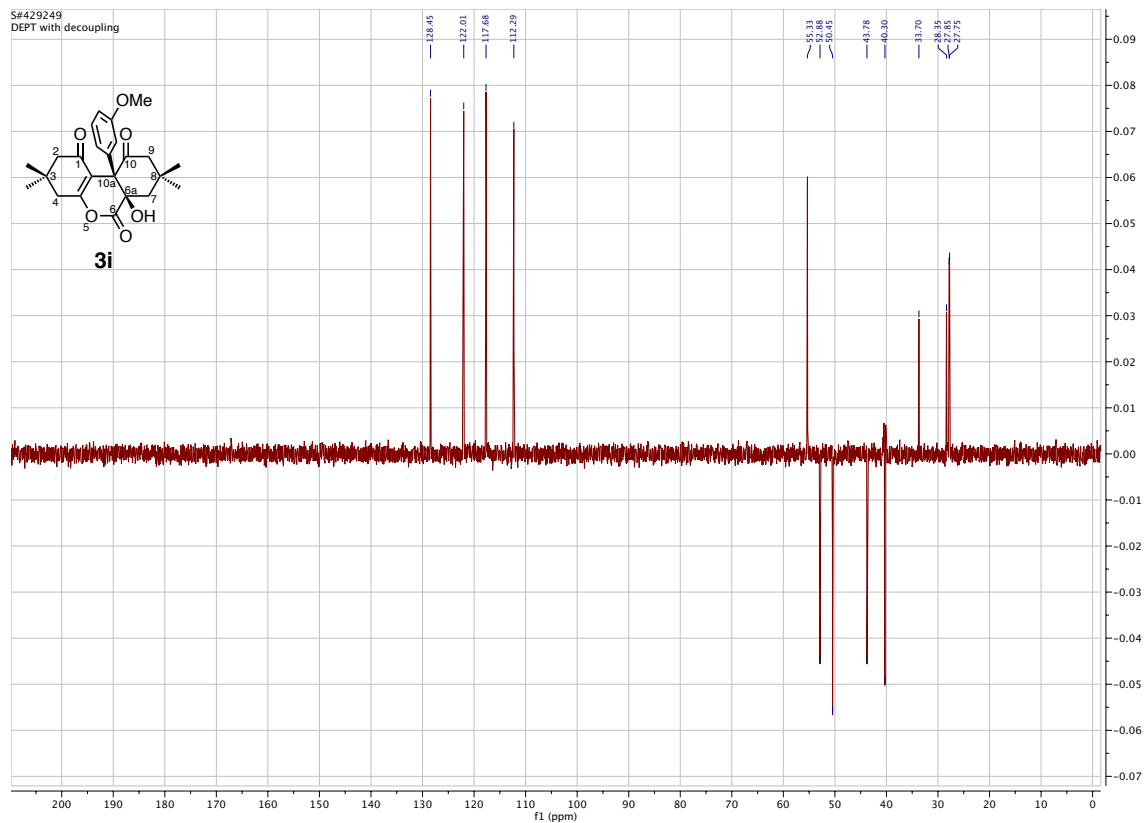
¹H NMR spectrum (500 MHz) using DMSO-*d*₆ of **3i**



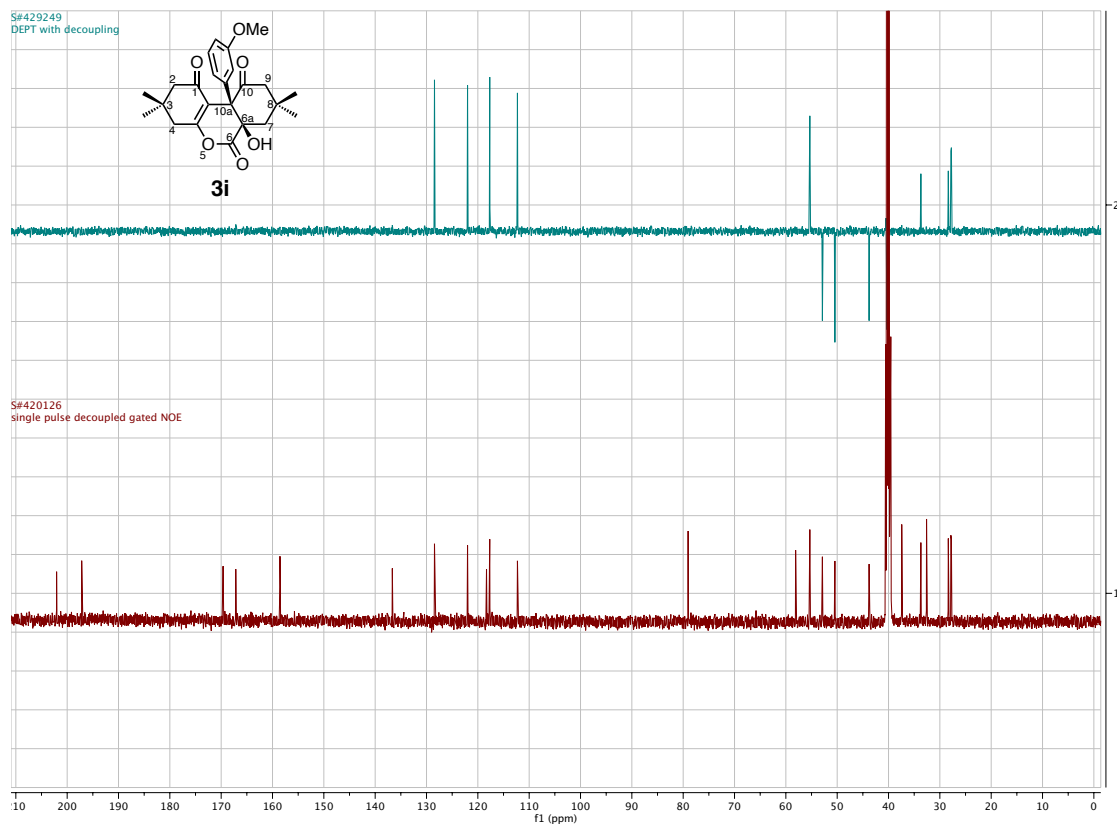
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz) using $\text{DMSO-}d_6$ of **3i**



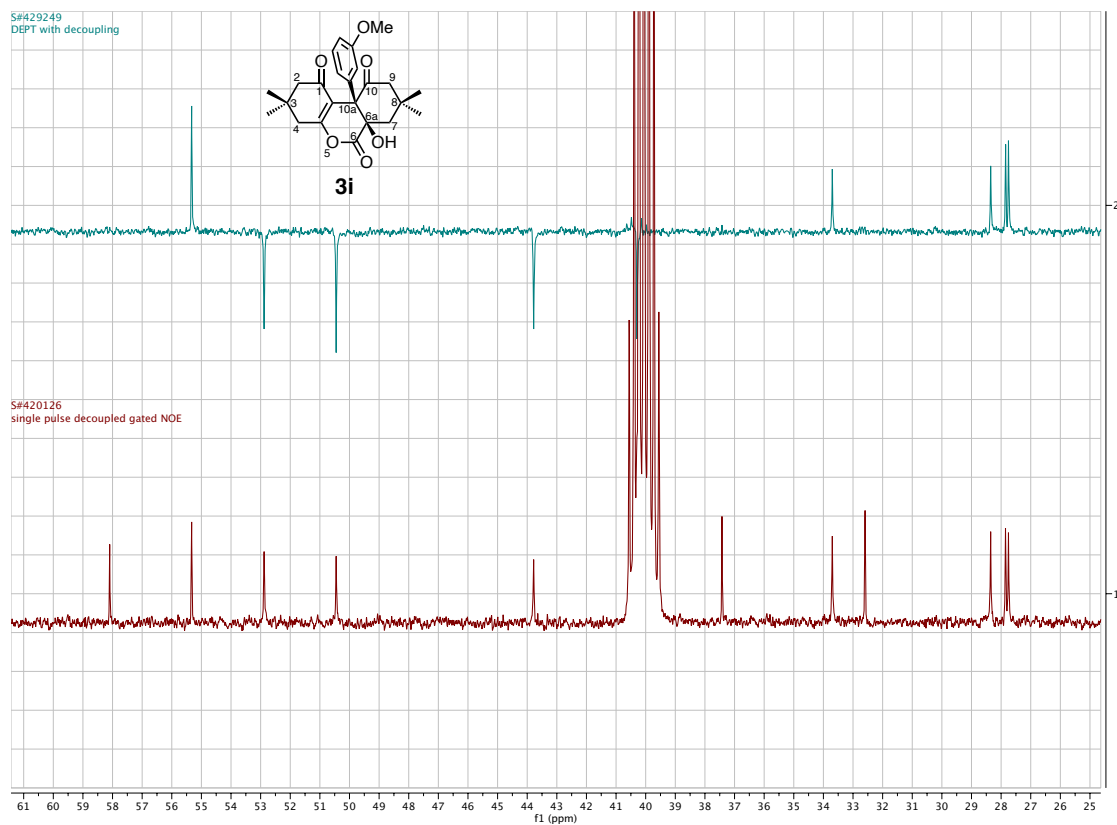
DEPT spectrum using $\text{DMSO-}d_6$ of **3i**



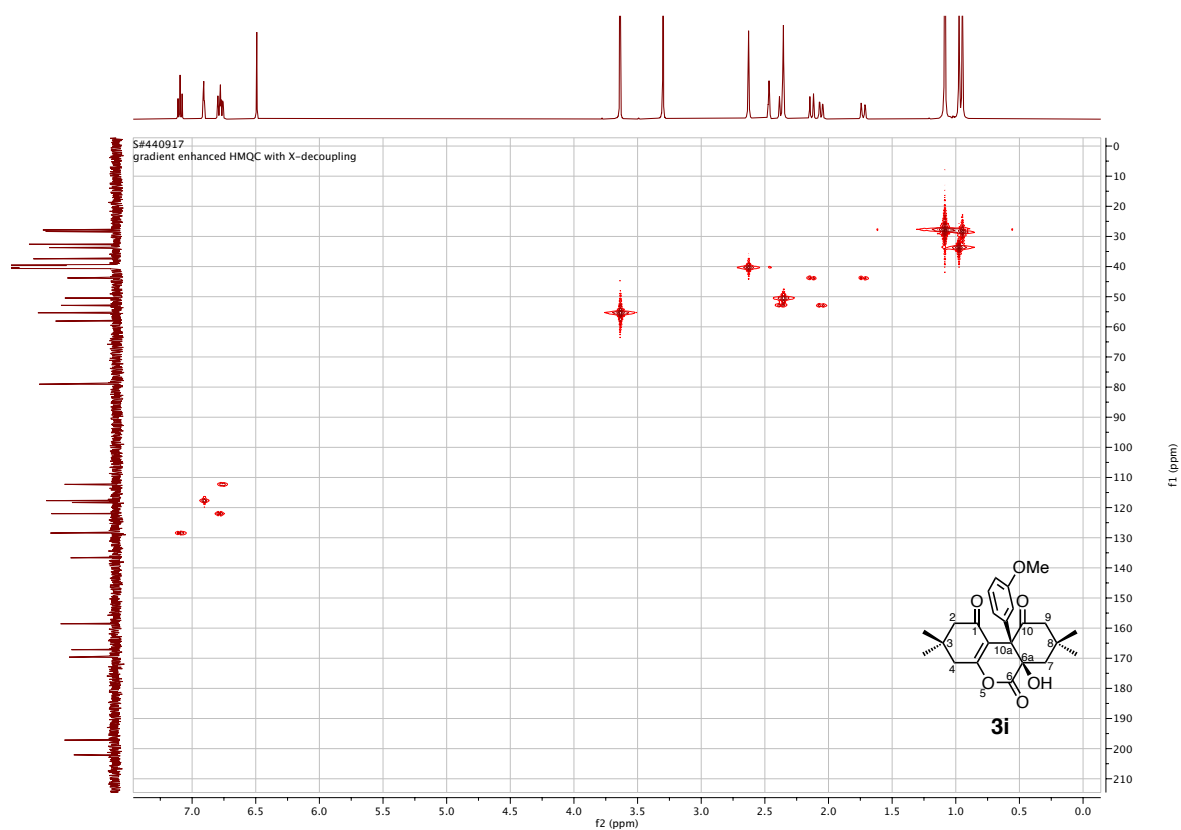
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) (lower) and DEPT (upper) spectra using $\text{DMSO-}d_6$ of **3i**



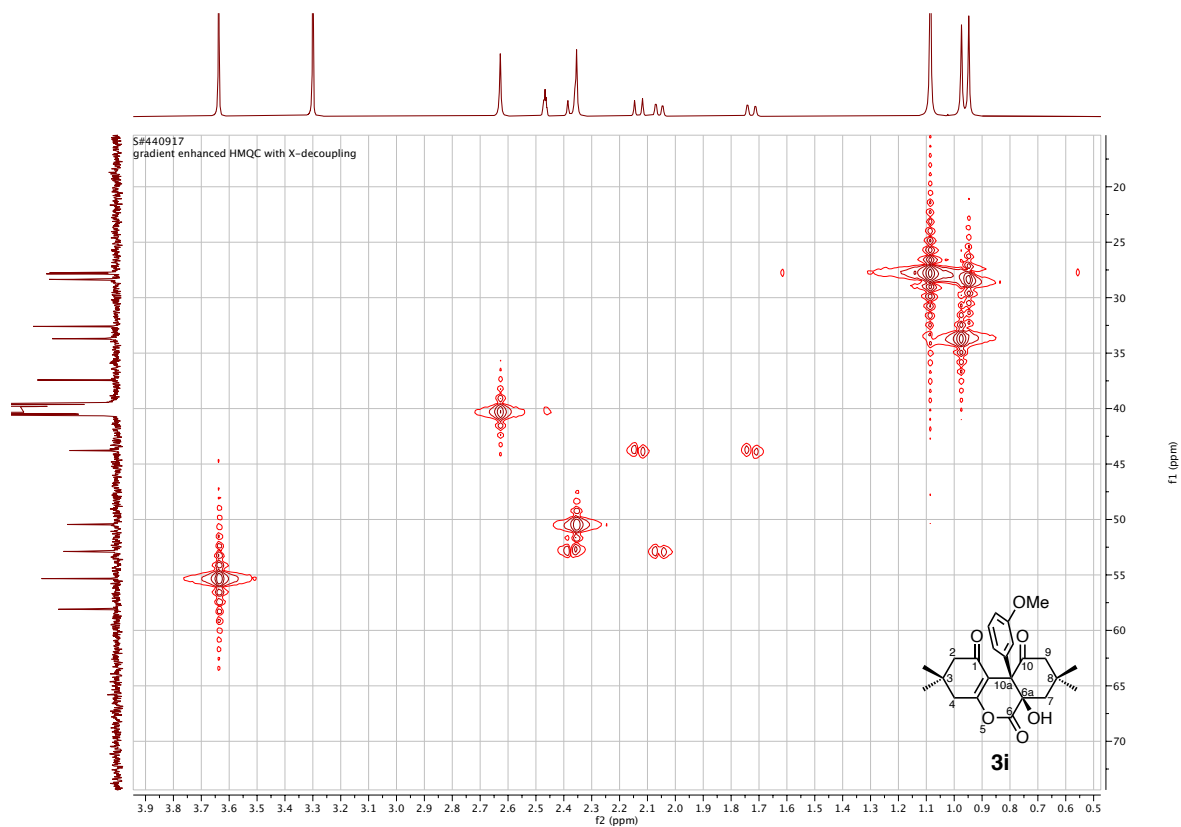
Expansion for $^{13}\text{C}\{^1\text{H}\}$ NMR (lower) and DEPT (upper) spectra using $\text{DMSO-}d_6$ of **3i**



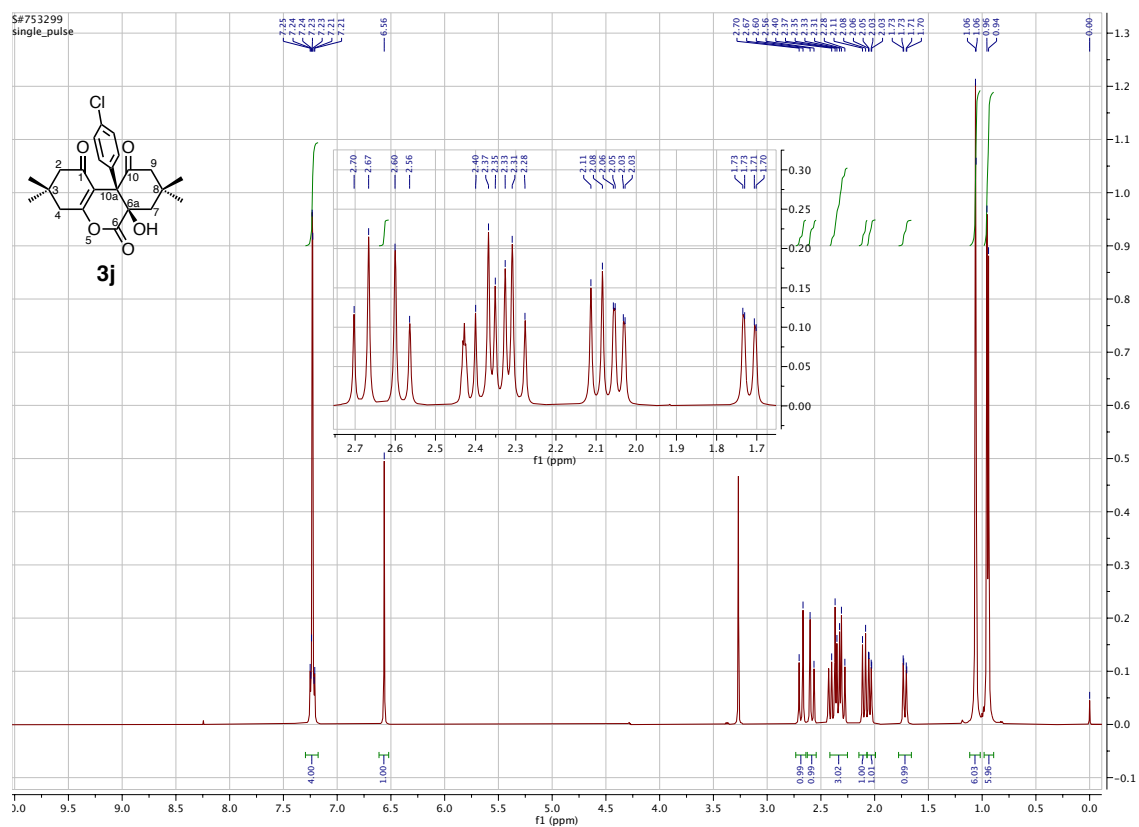
HMQC spectrum using DMSO-*d*₆ of **3i**



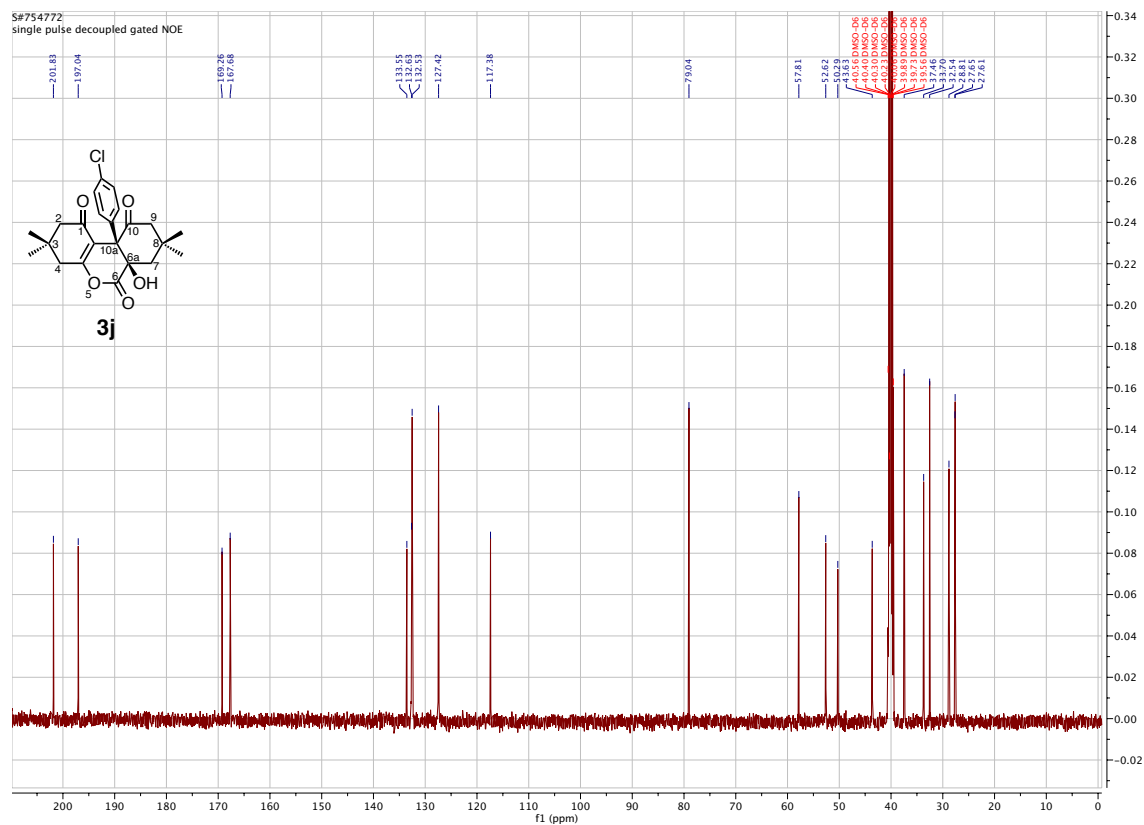
Expansion for HMQC spectrum using DMSO-*d*₆ of **3i**



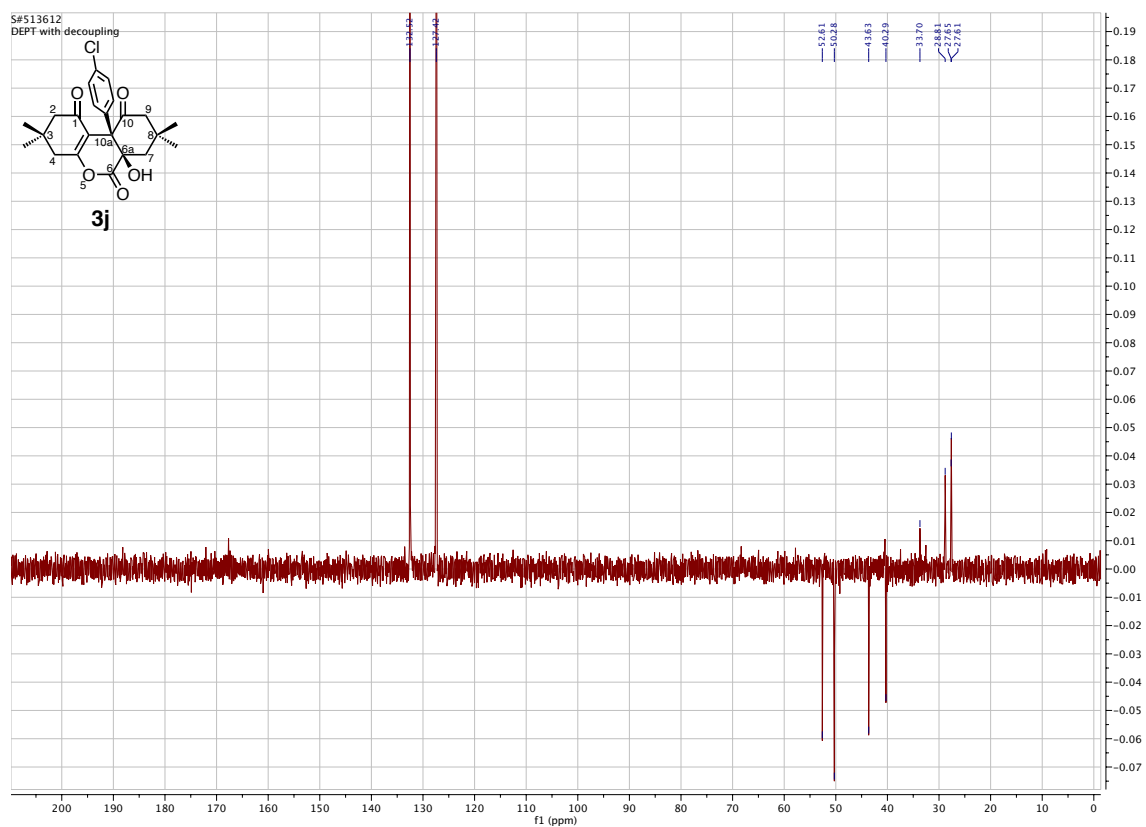
^1H NMR spectrum (500 MHz) using $\text{DMSO-}d_6$ of **3j**



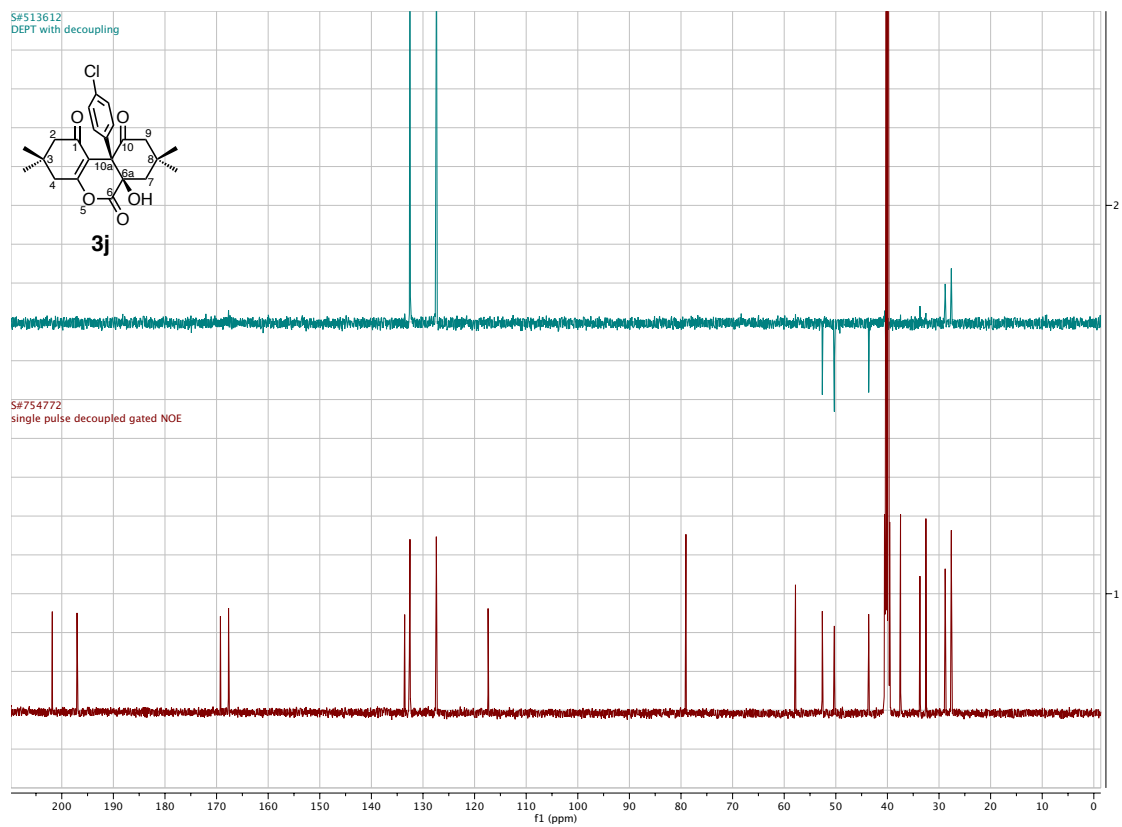
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz) using $\text{DMSO-}d_6$ of **3j**



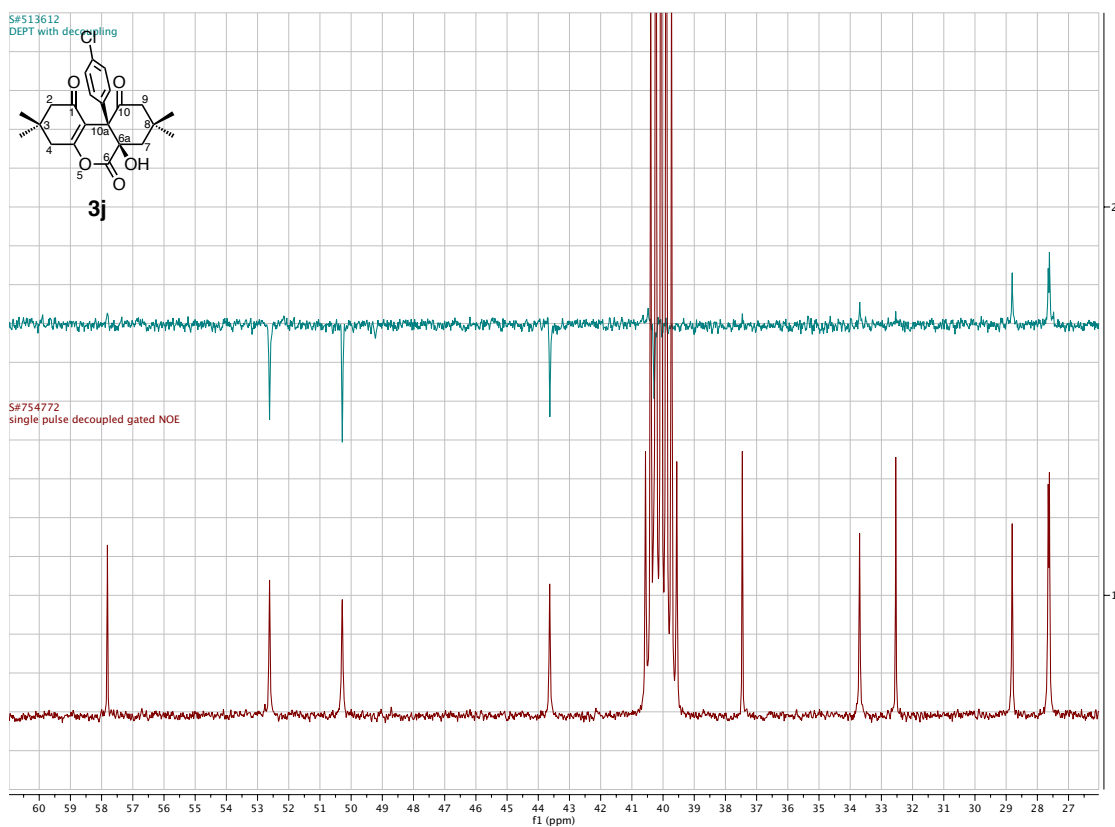
DEPT spectrum using DMSO-*d*₆ of **3j**



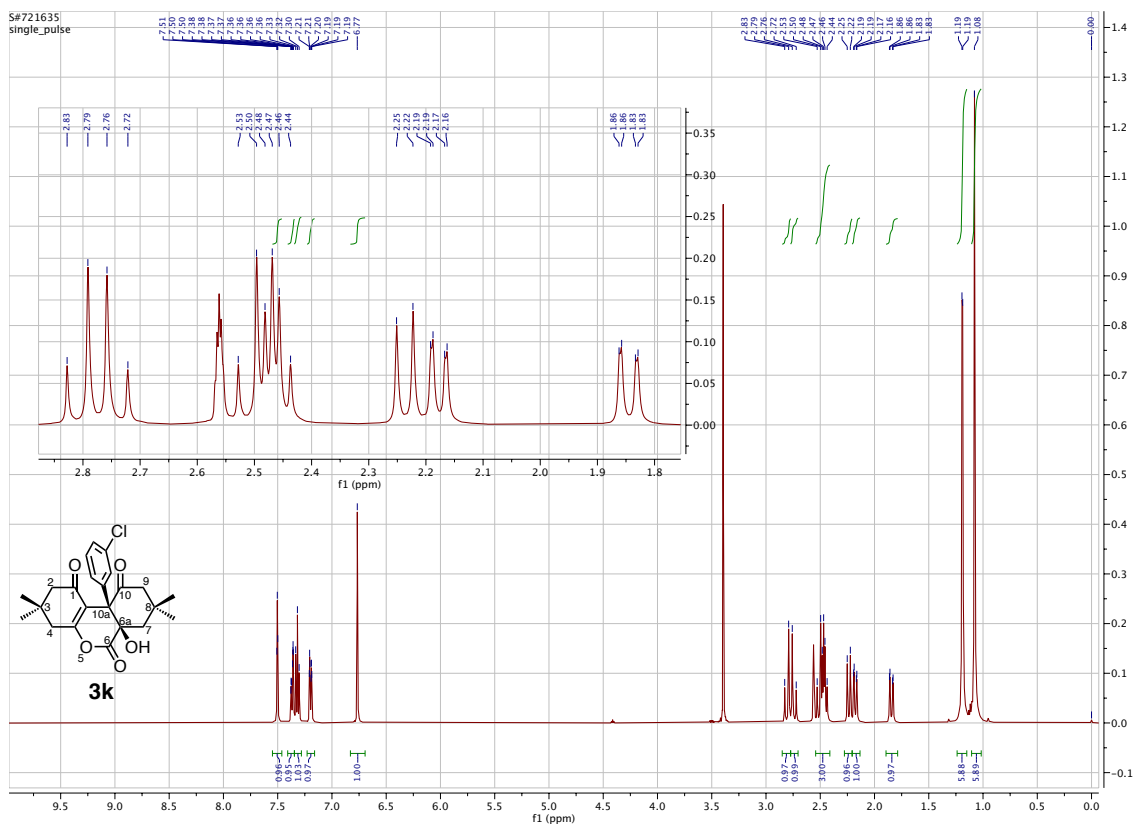
¹³C{¹H} NMR (125 MHz) (lower) and DEPT (upper) spectra using DMSO-*d*₆ of **3j**



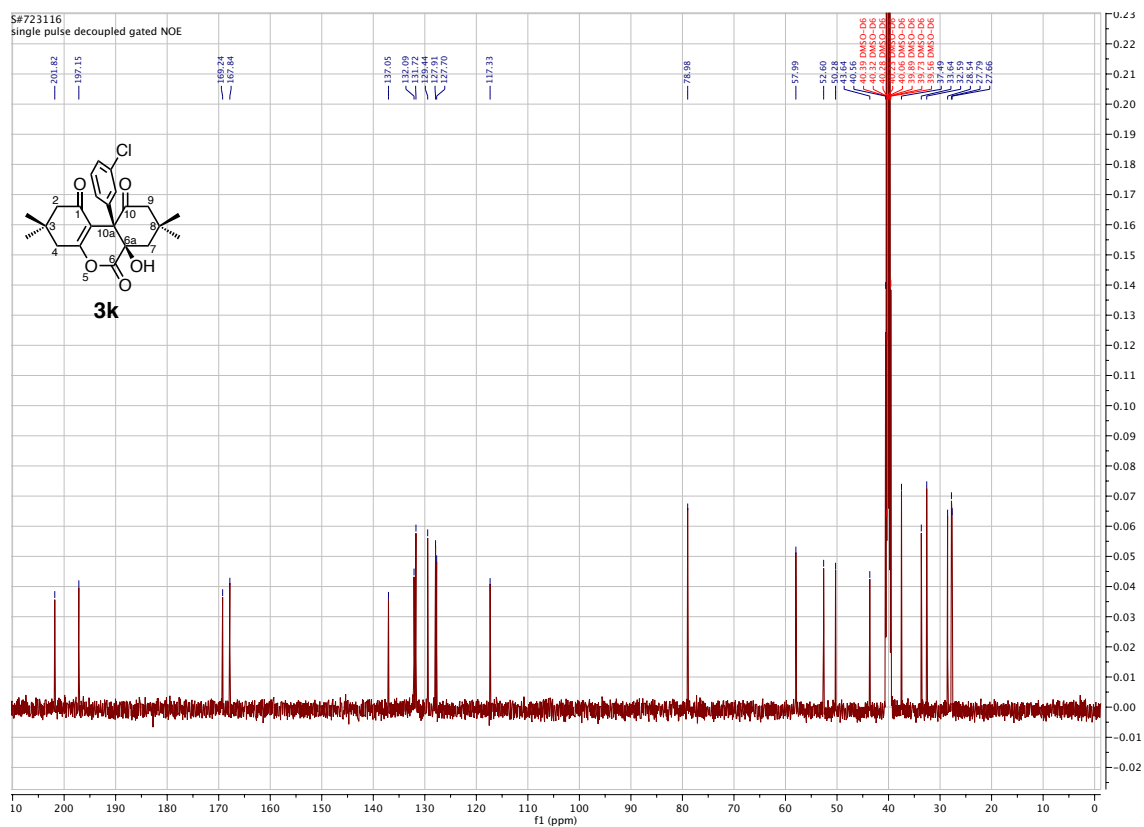
Expansion for $^{13}\text{C}\{^1\text{H}\}$ NMR (lower) and DEPT (upper) spectra using $\text{DMSO-}d_6$ of **3j**



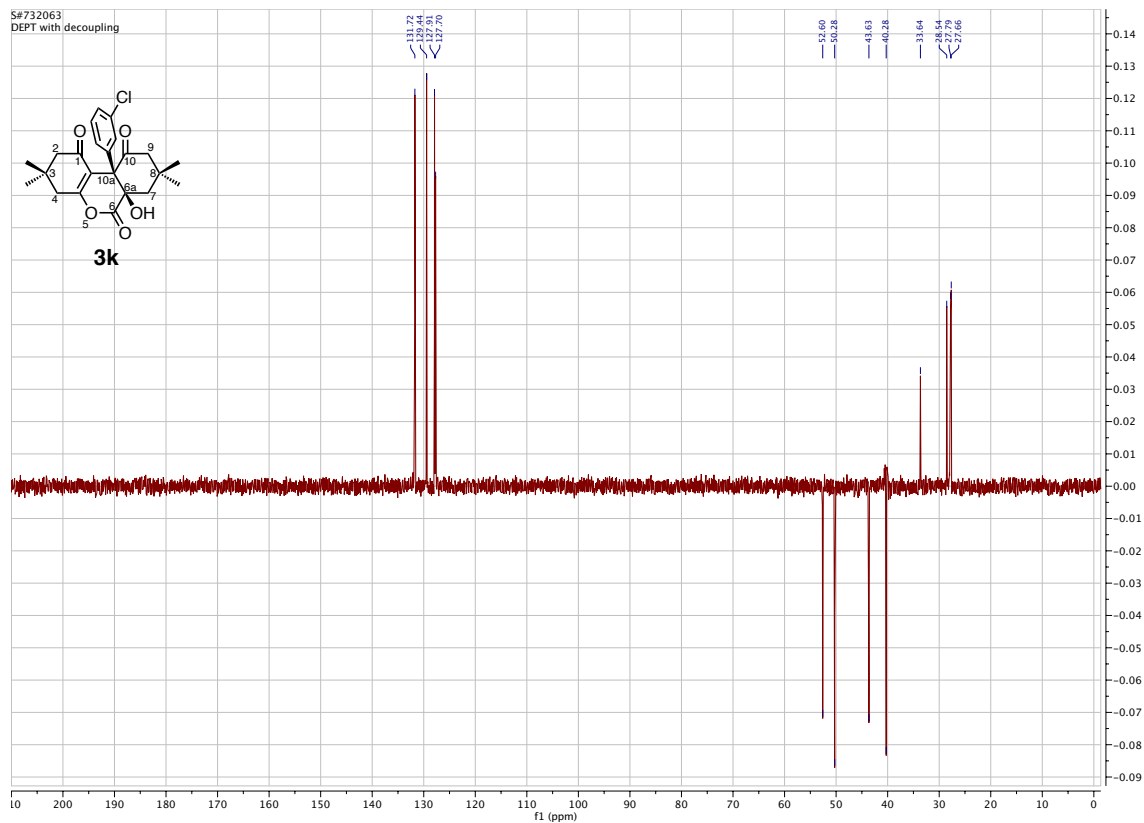
^1H NMR spectrum (500 MHz) using $\text{DMSO-}d_6$ of **3k**



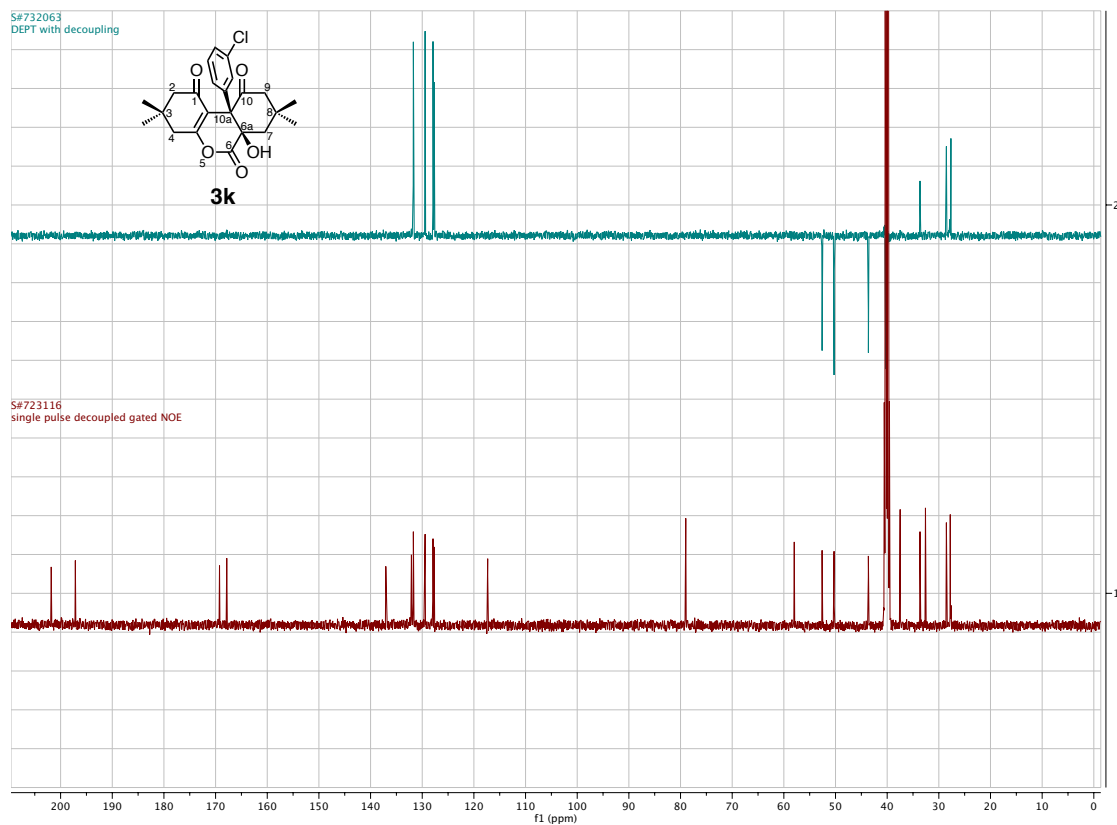
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz) using $\text{DMSO-}d_6$ of **3k**



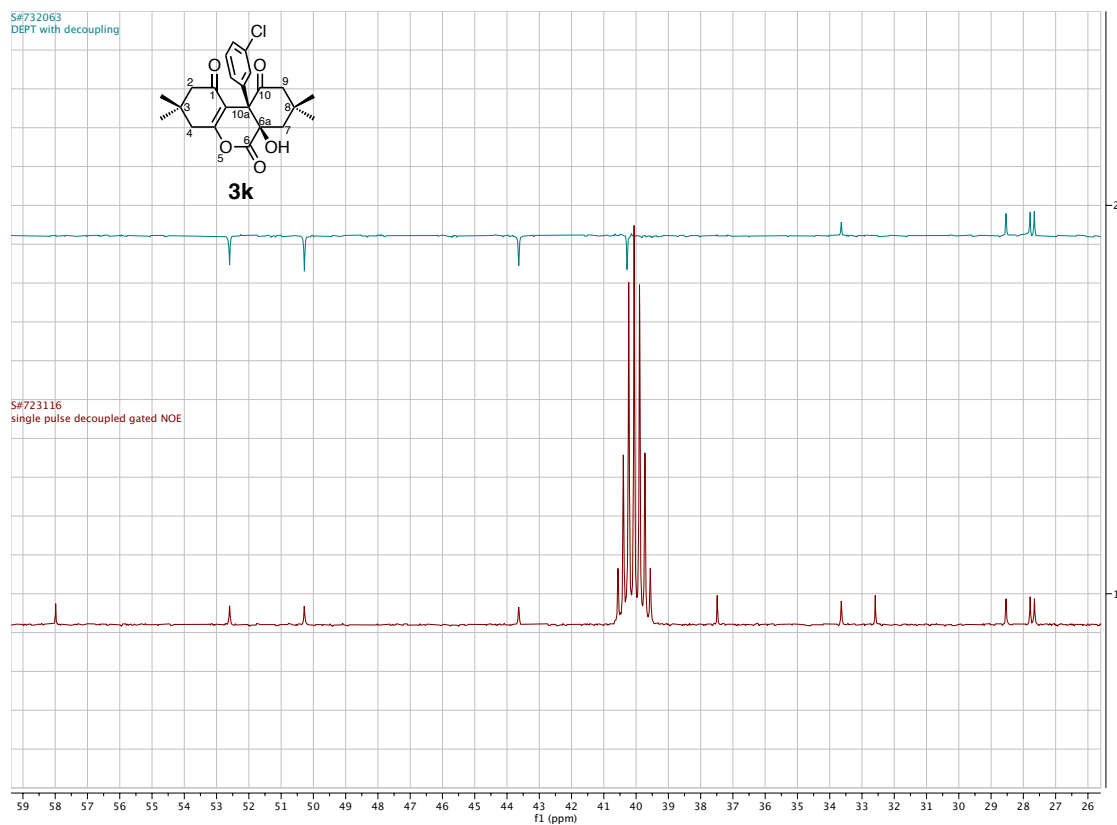
DEPT spectrum using $\text{DMSO-}d_6$ of **3k**



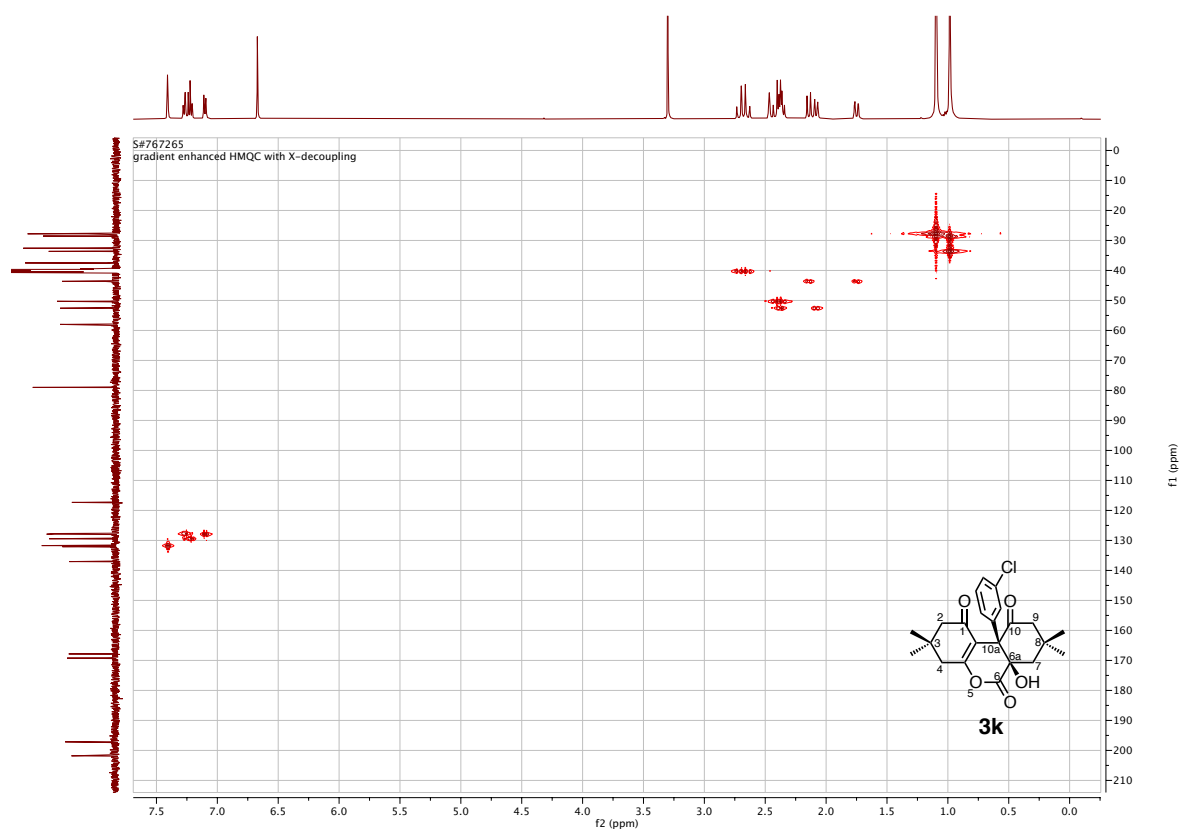
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) (lower) and DEPT (upper) spectra using $\text{DMSO-}d_6$ of **3k**



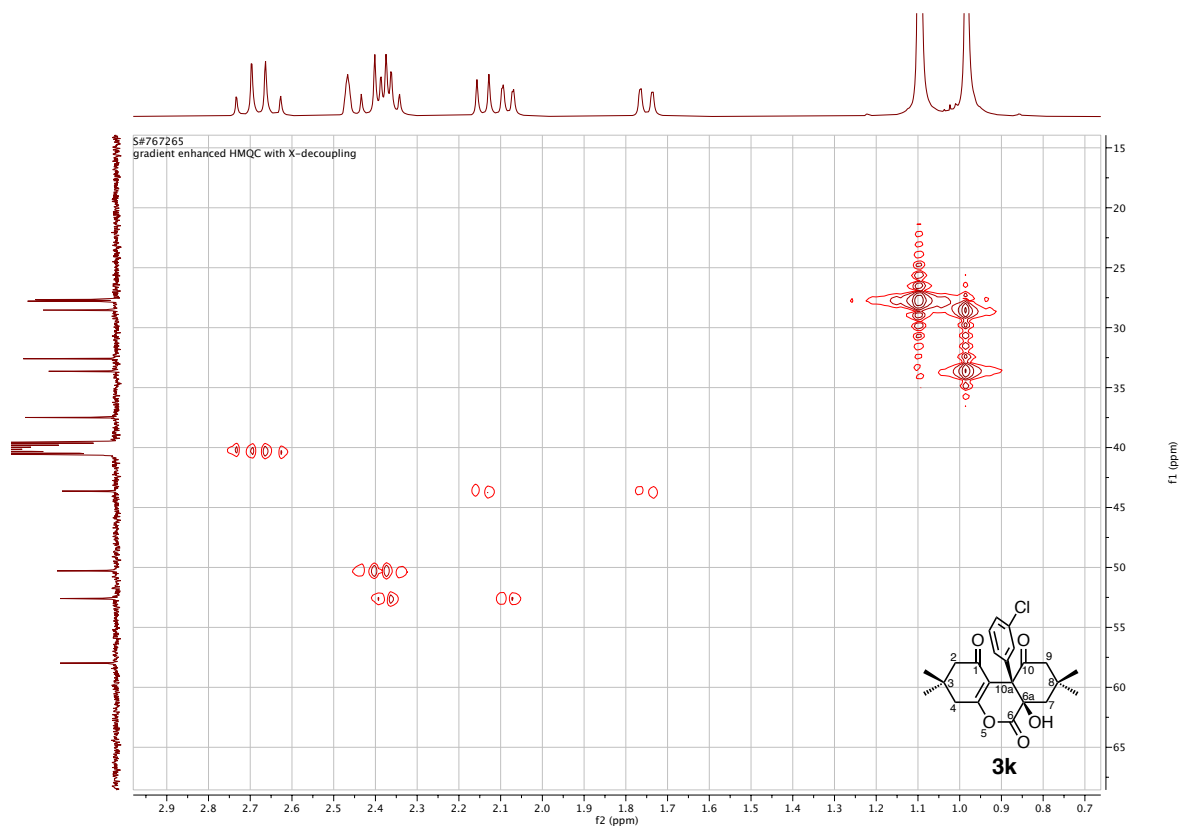
Expansion for $^{13}\text{C}\{^1\text{H}\}$ NMR (lower) and DEPT (upper) spectra using $\text{DMSO-}d_6$ of **3k**



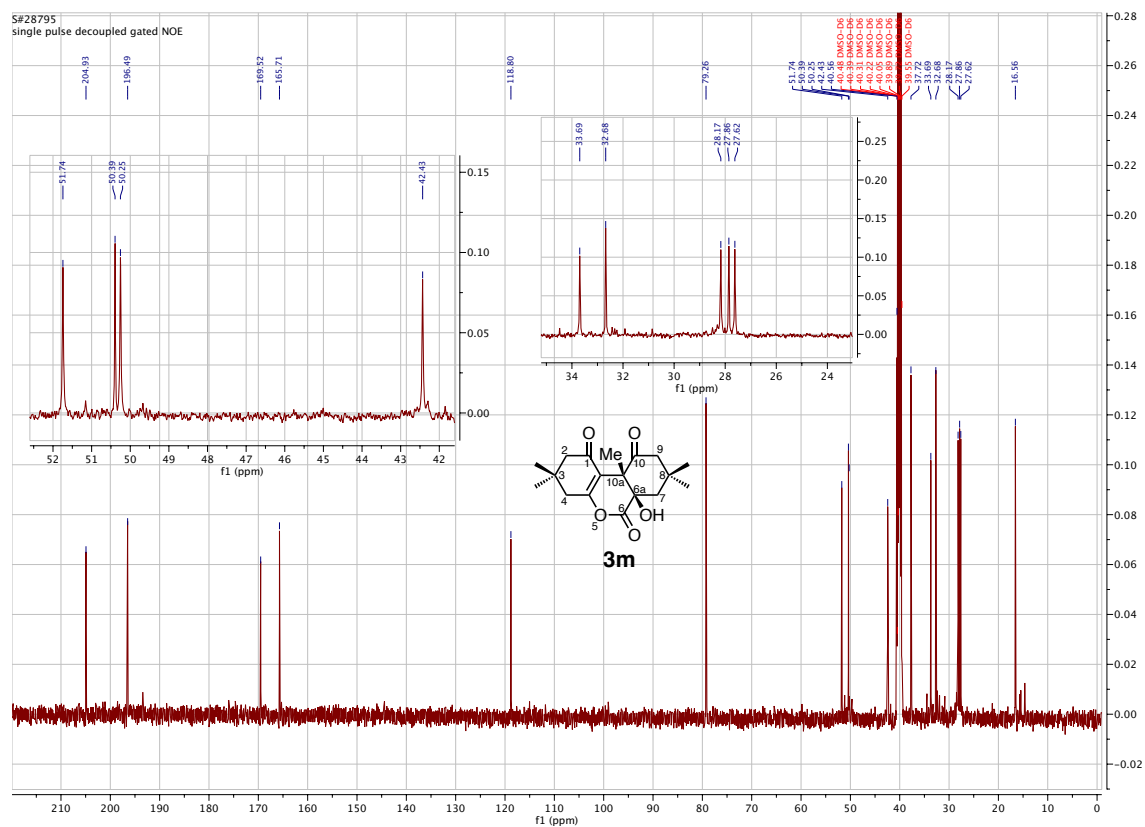
HMQC spectrum using DMSO-*d*₆ of **3k**



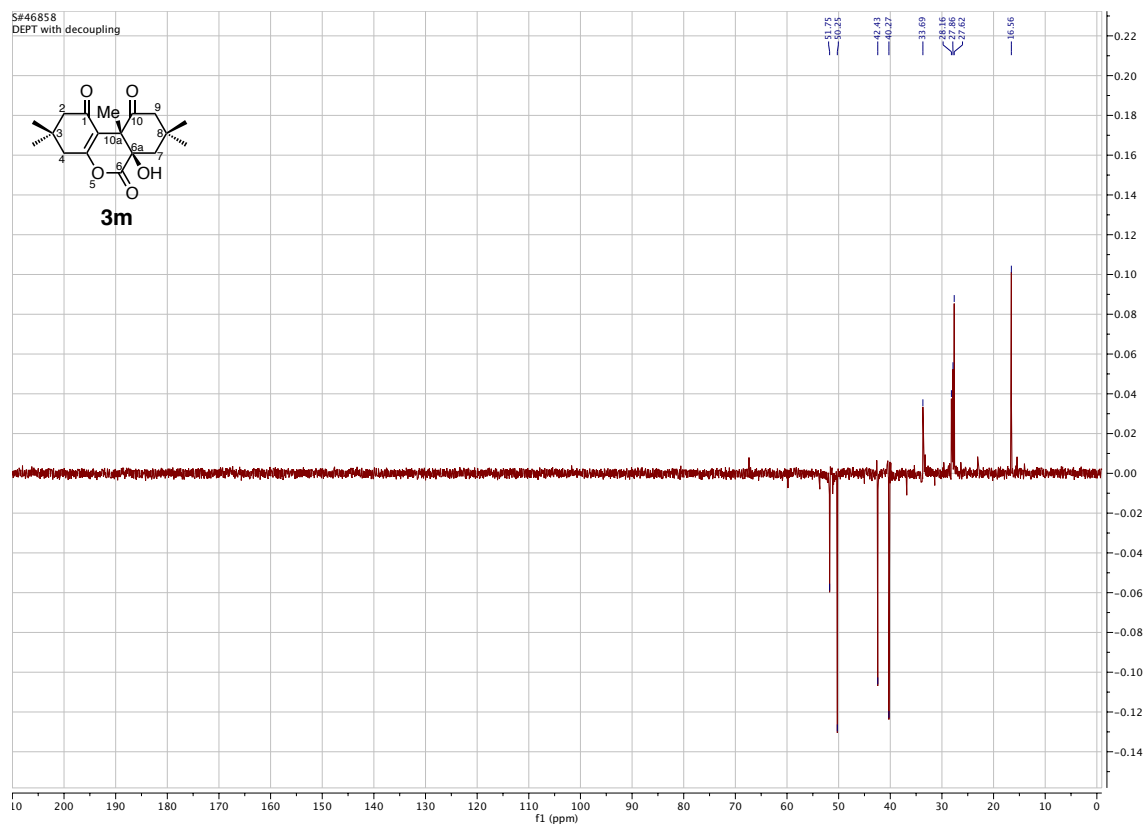
Expansion for HMQC spectrum using DMSO-*d*₆ of **3k**



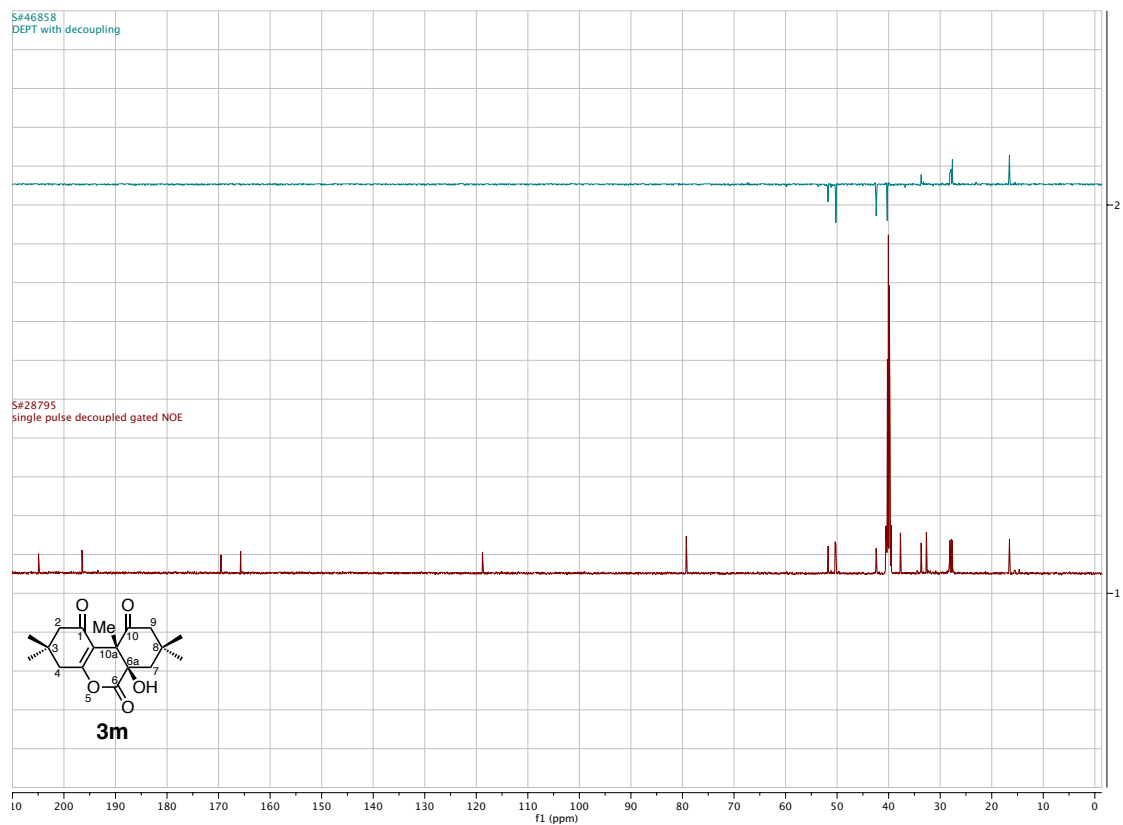
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz) using $\text{DMSO-}d_6$ of **3m**



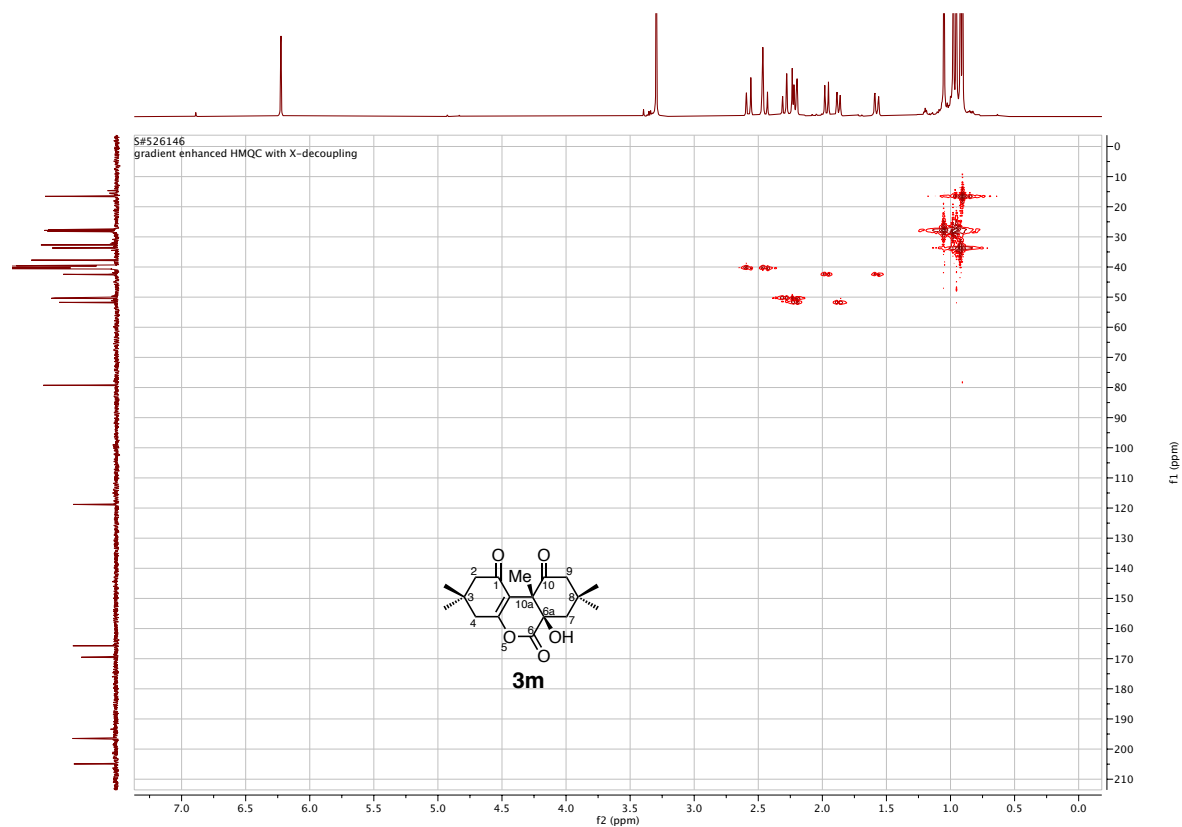
DEPT spectrum using $\text{DMSO-}d_6$ of **3m**



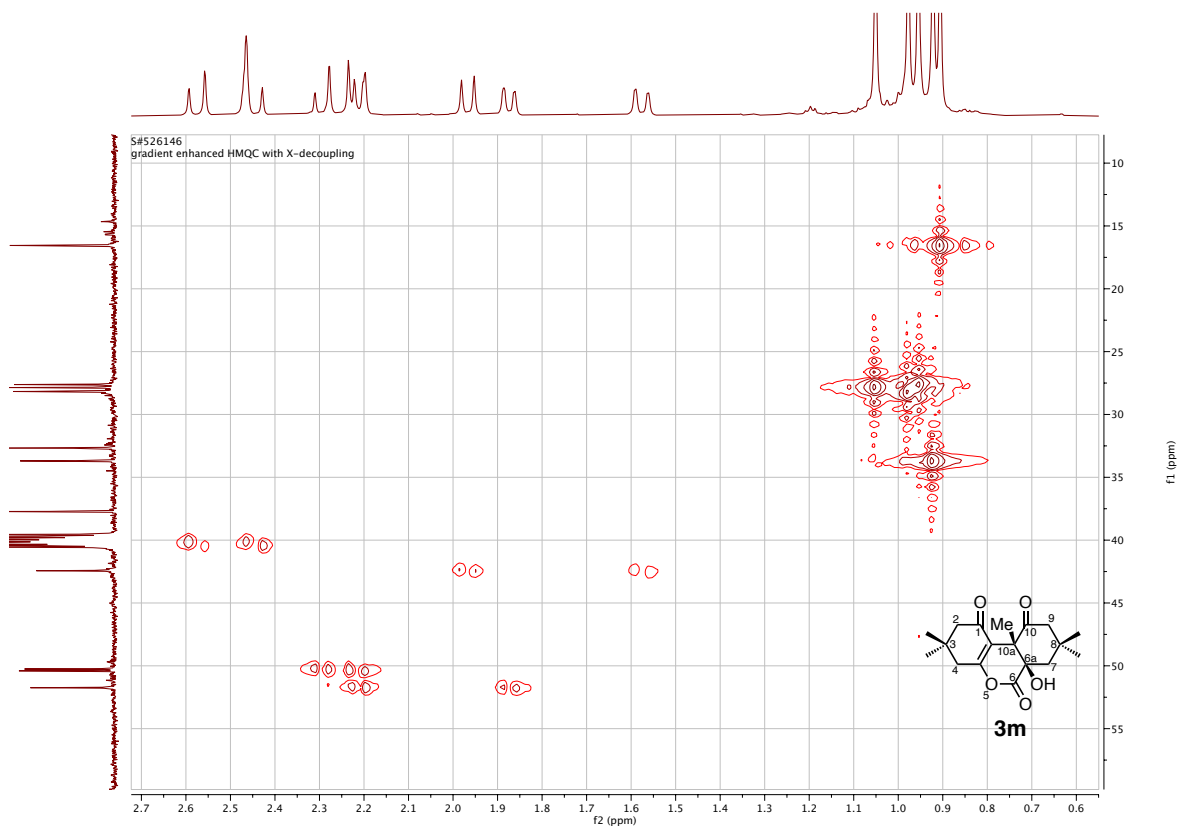
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) (lower) and DEPT (upper) spectra using $\text{DMSO-}d_6$ of **3m**



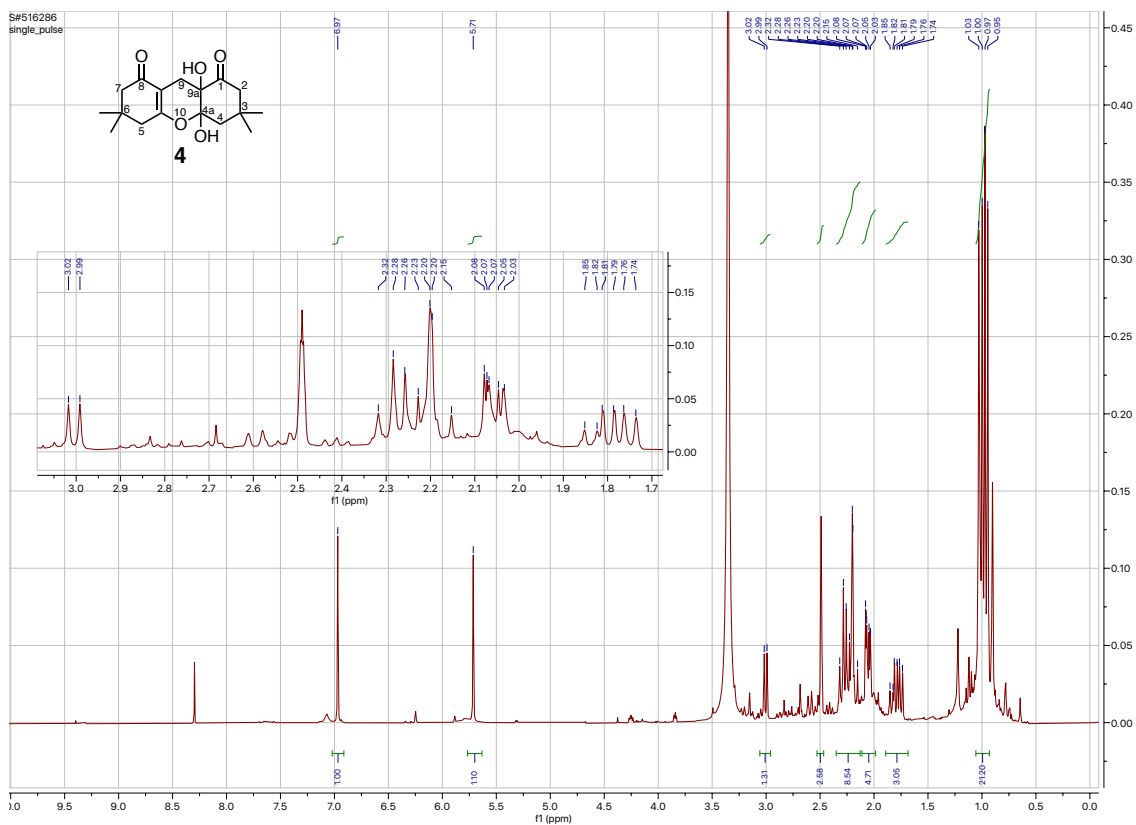
HMQC spectrum using $\text{DMSO-}d_6$ of **3m**



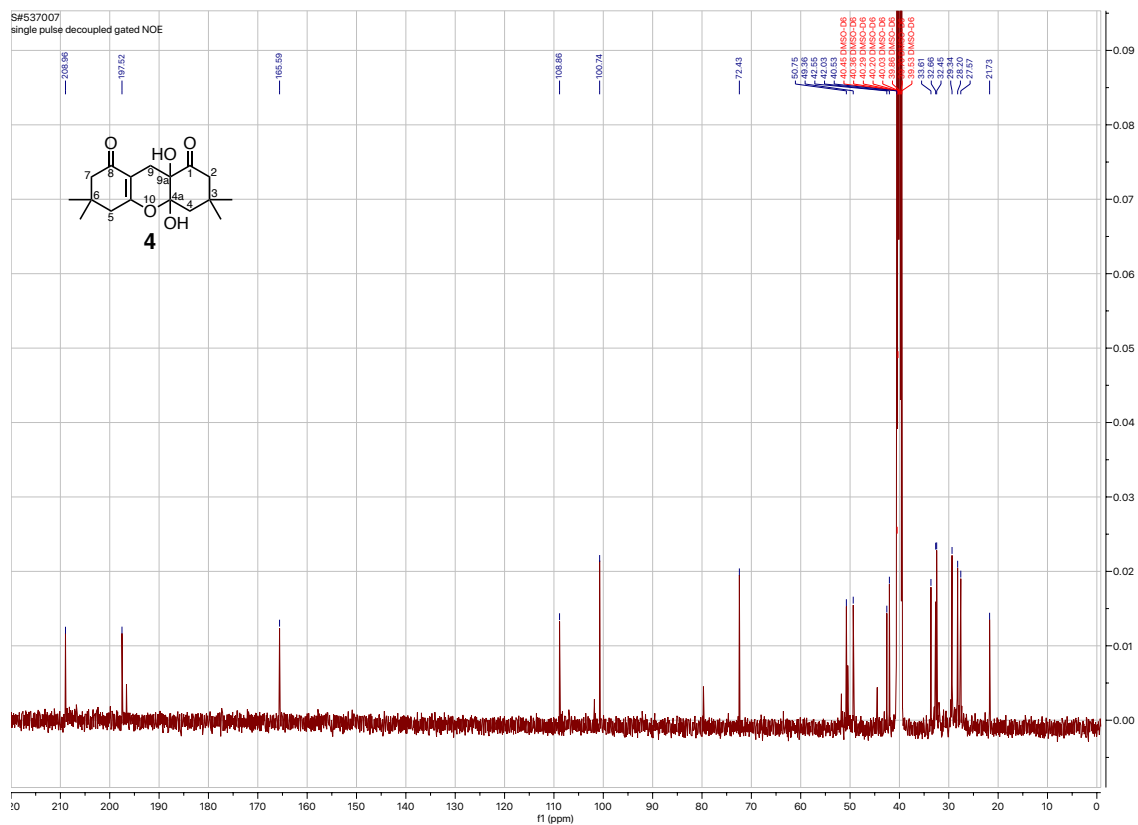
Expansion for HMQC spectrum using DMSO-*d*₆ of **3m**



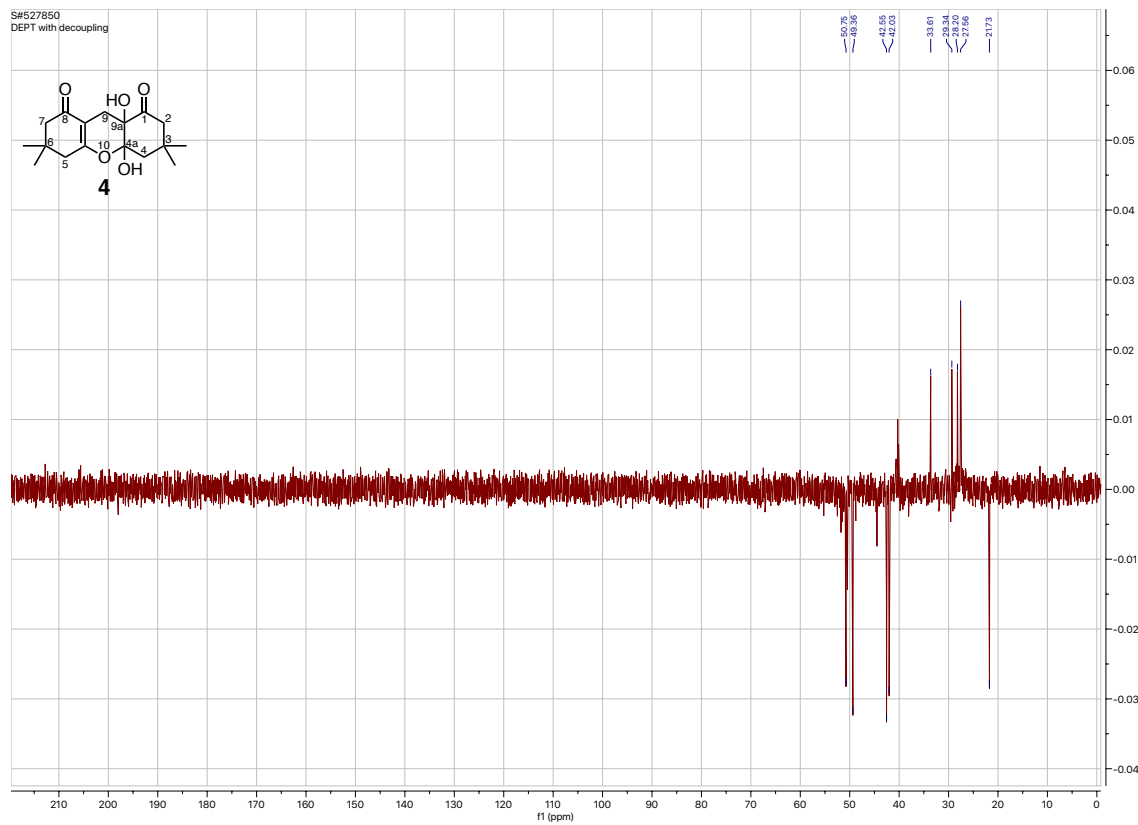
¹H NMR spectrum (500 MHz) using DMSO-*d*₆ of **4**



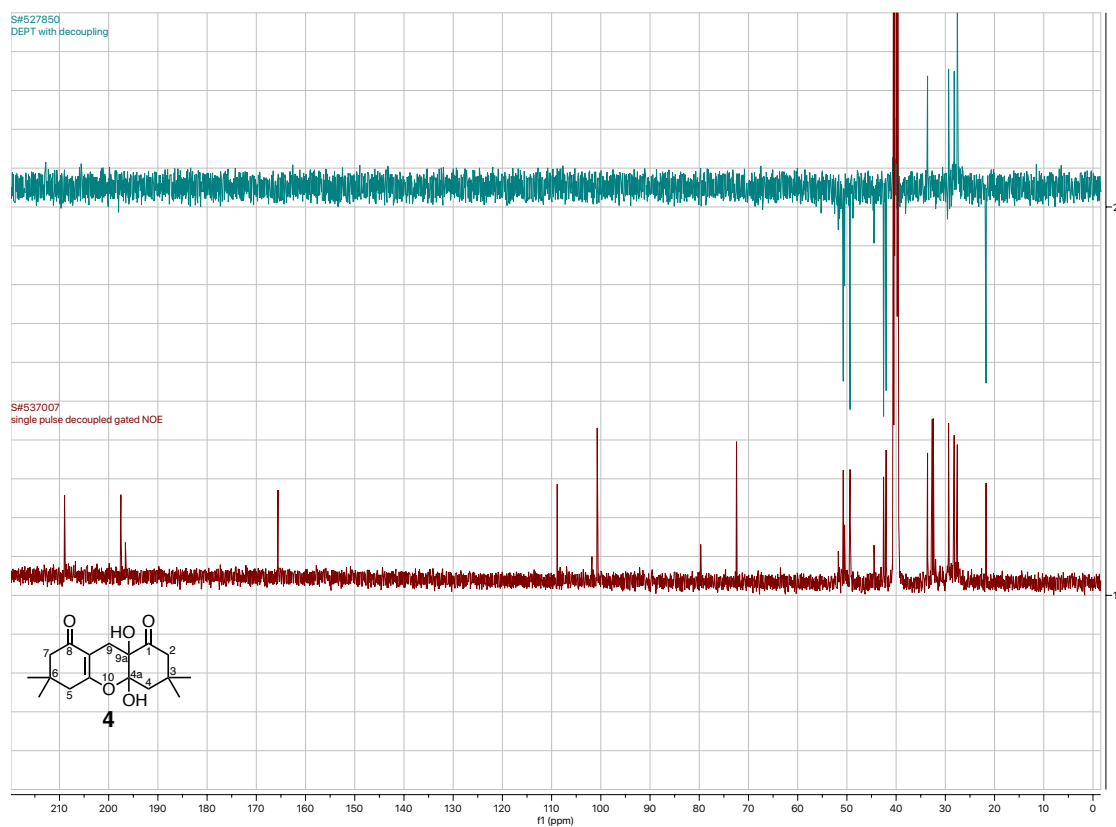
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz) using $\text{DMSO-}d_6$ of **4**



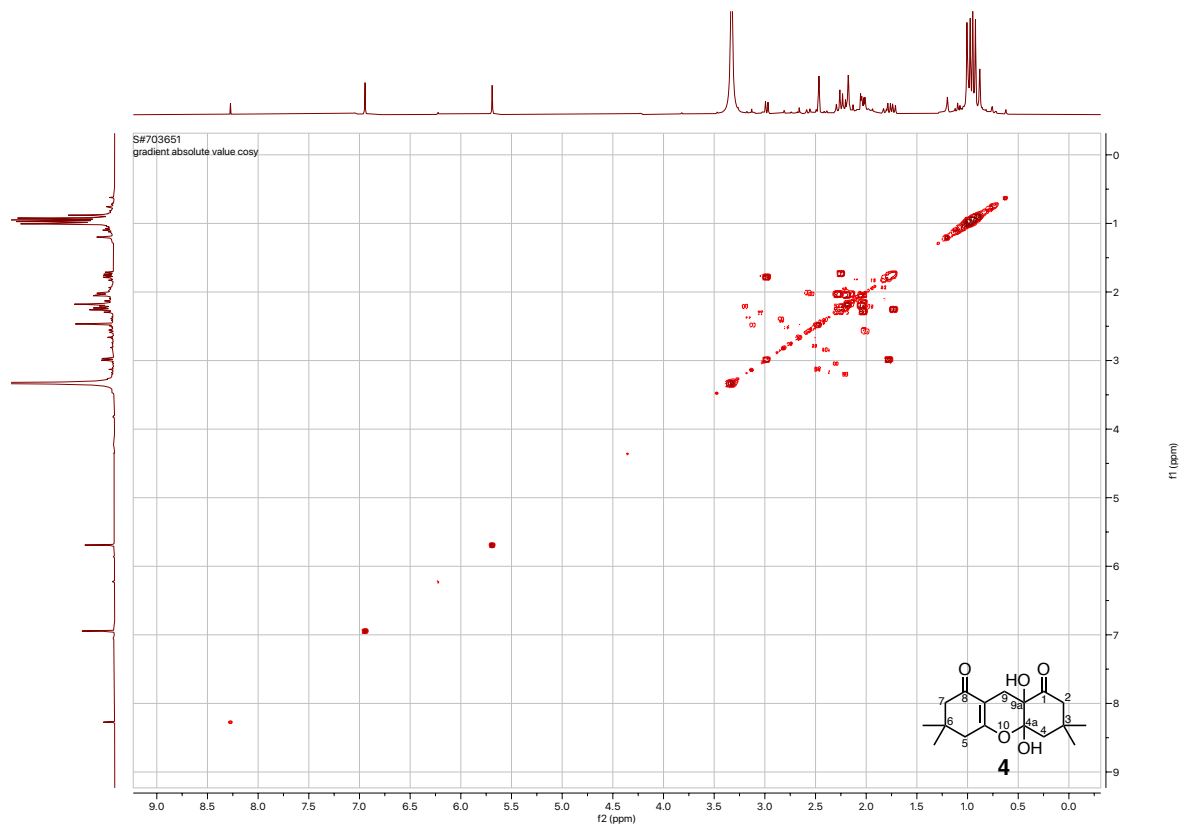
DEPT spectrum using $\text{DMSO-}d_6$ of **4**



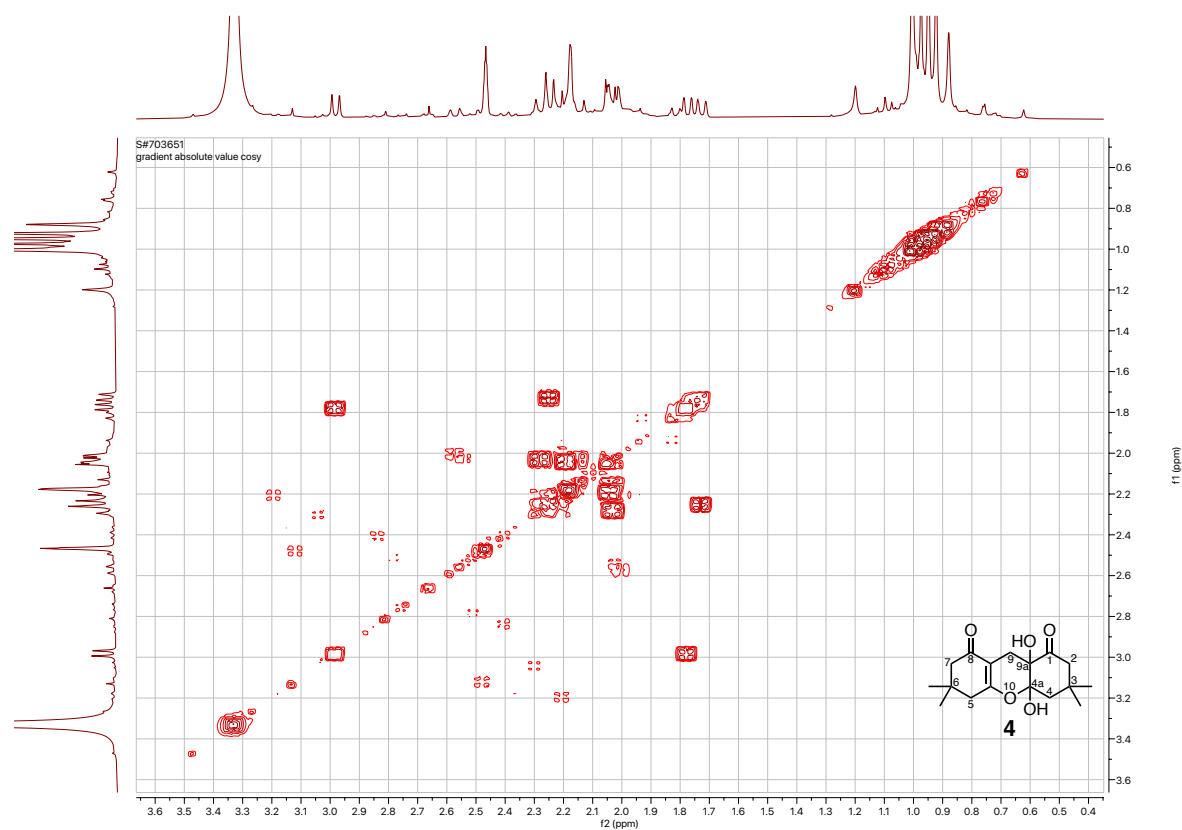
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) (lower) and DEPT (upper) spectra using $\text{DMSO-}d_6$ of **4**



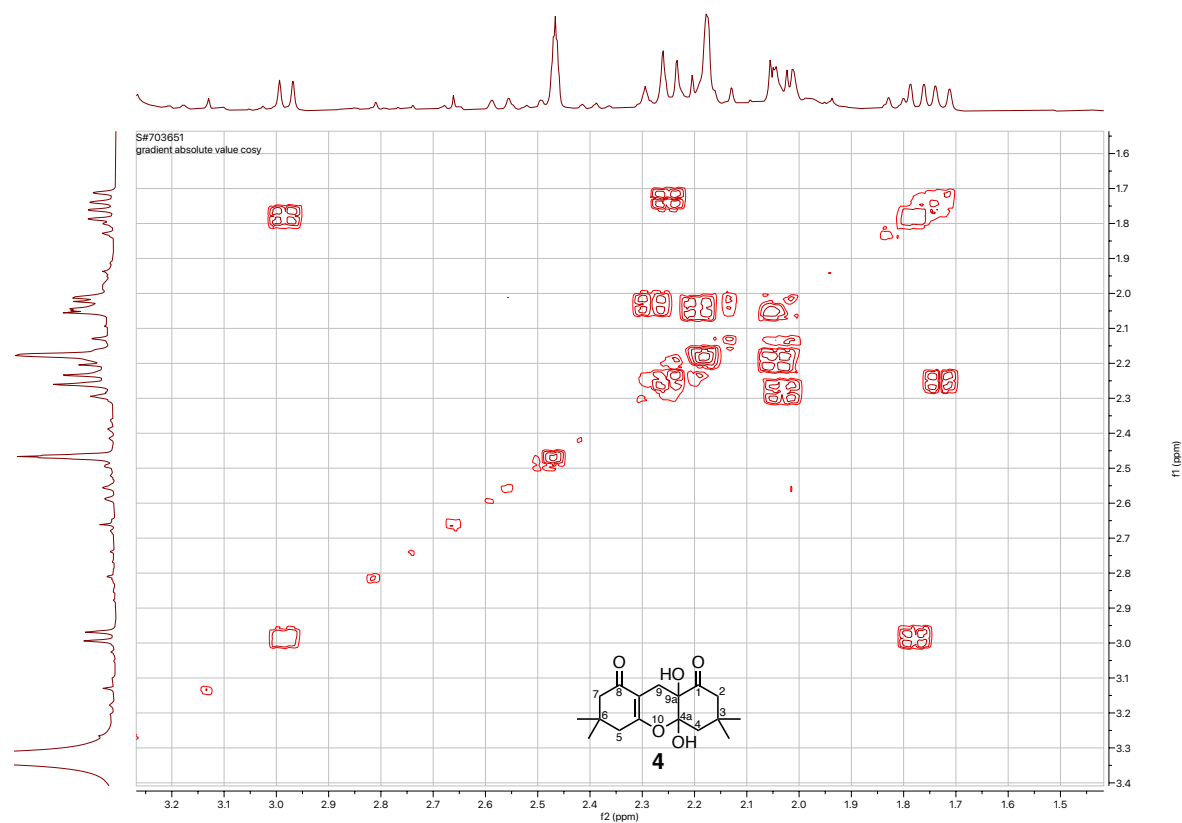
COSY spectrum using $\text{DMSO-}d_6$ of **4**



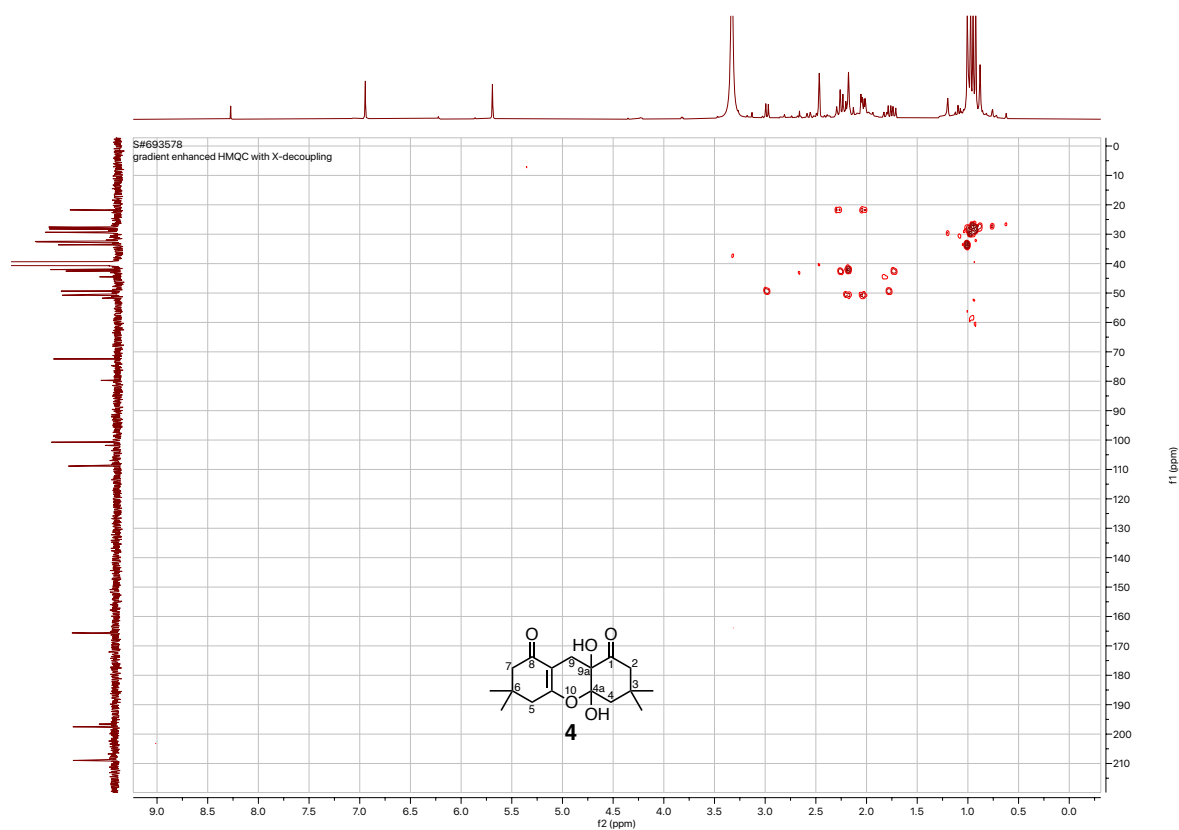
Expansion for COSY spectrum using DMSO- d_6 of **4**



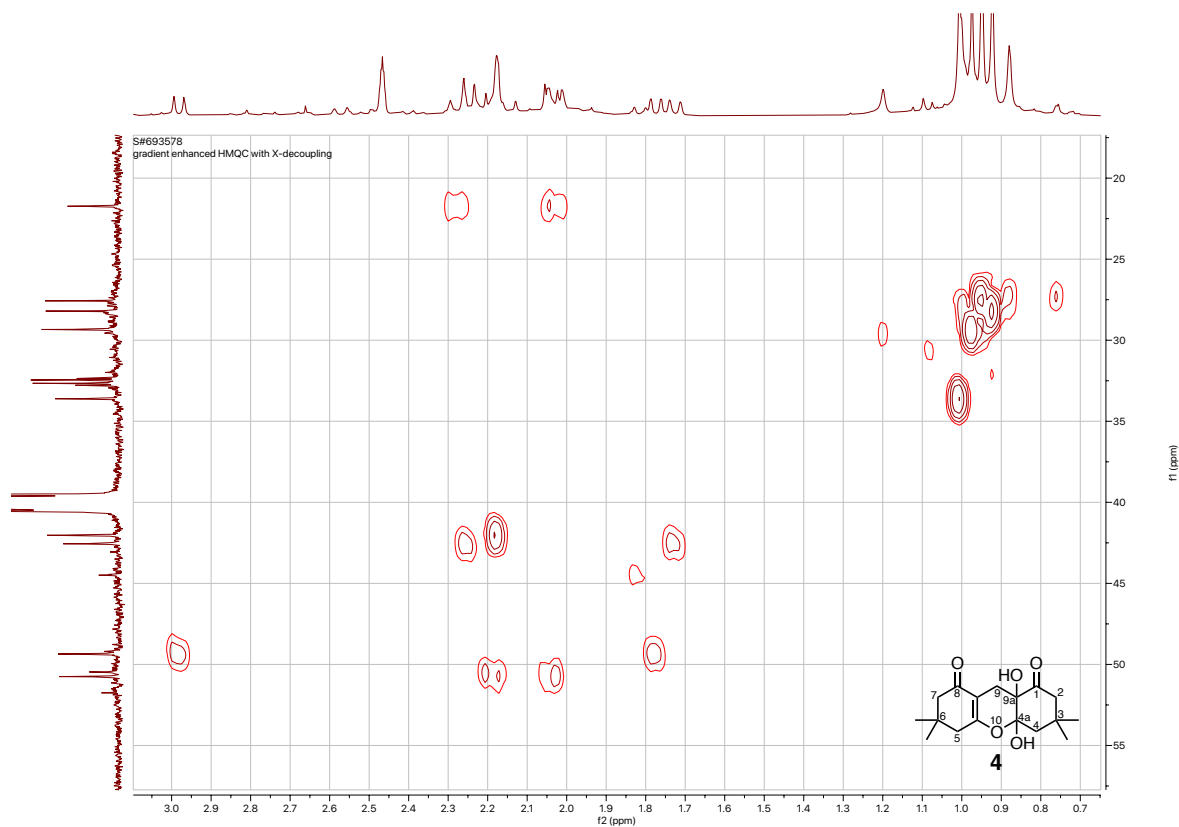
Expansion for COSY spectrum using DMSO- d_6 of **4**



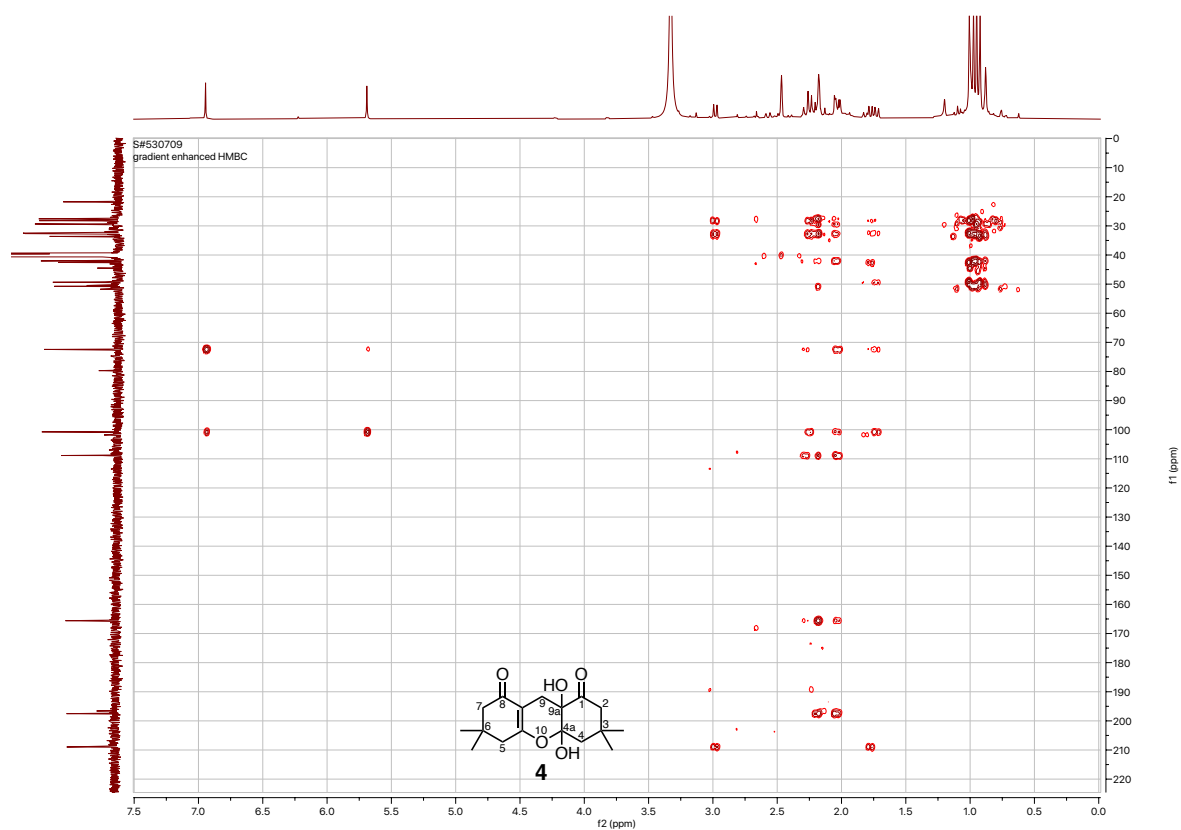
HMQC spectrum using DMSO-*d*₆ of **4**



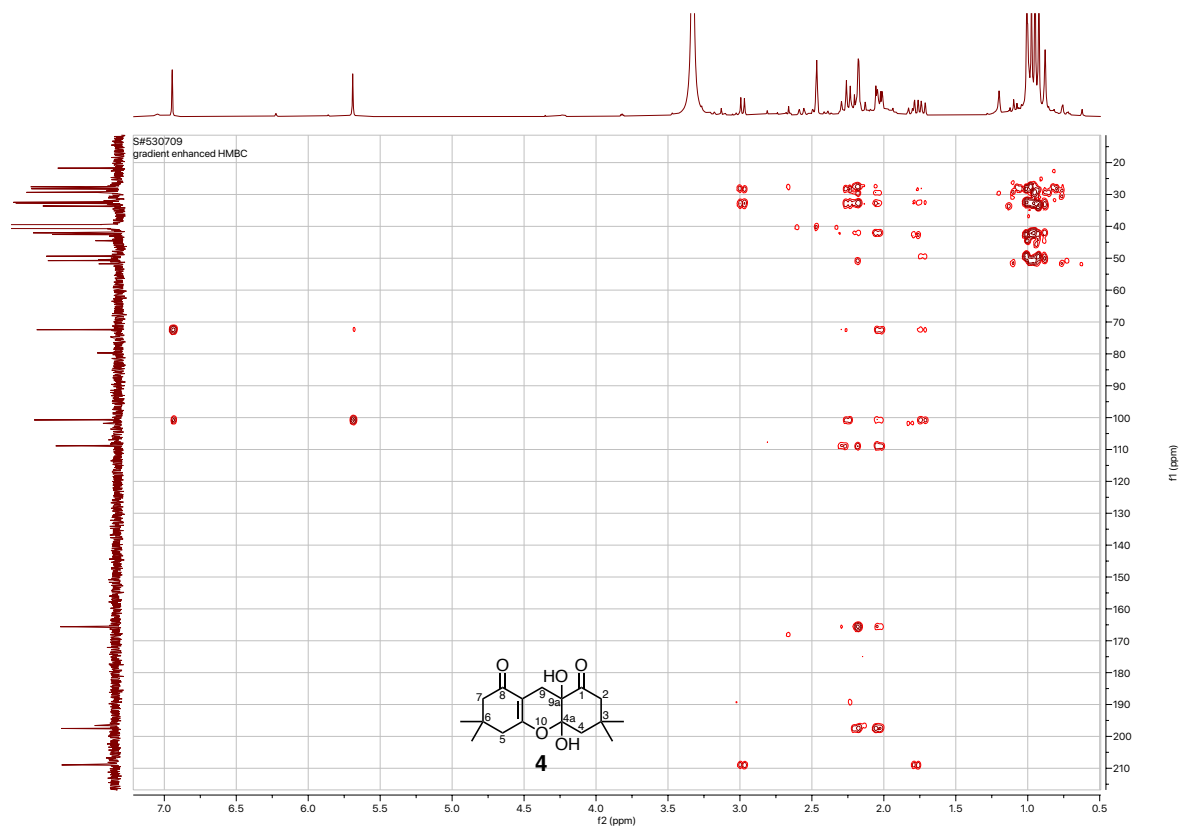
Expansion for HMQC spectrum using DMSO-*d*₆ of **4**



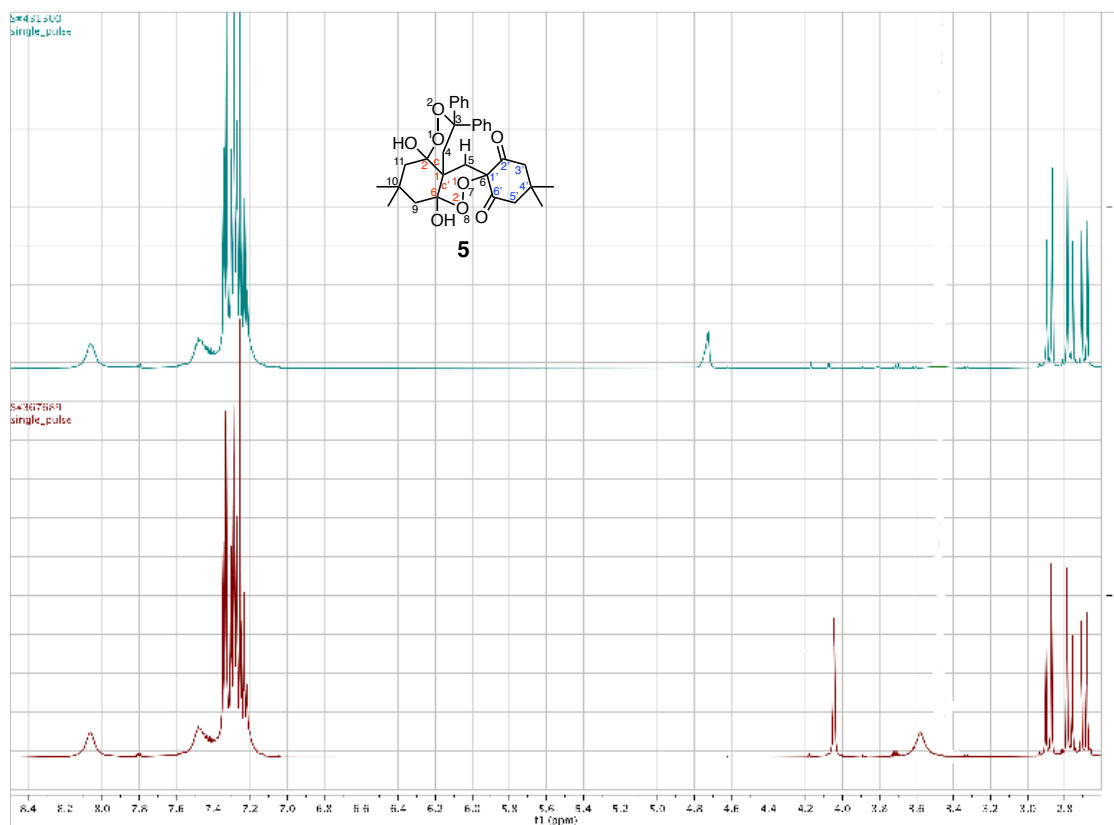
HMBC spectrum using DMSO-*d*₆ of **4**



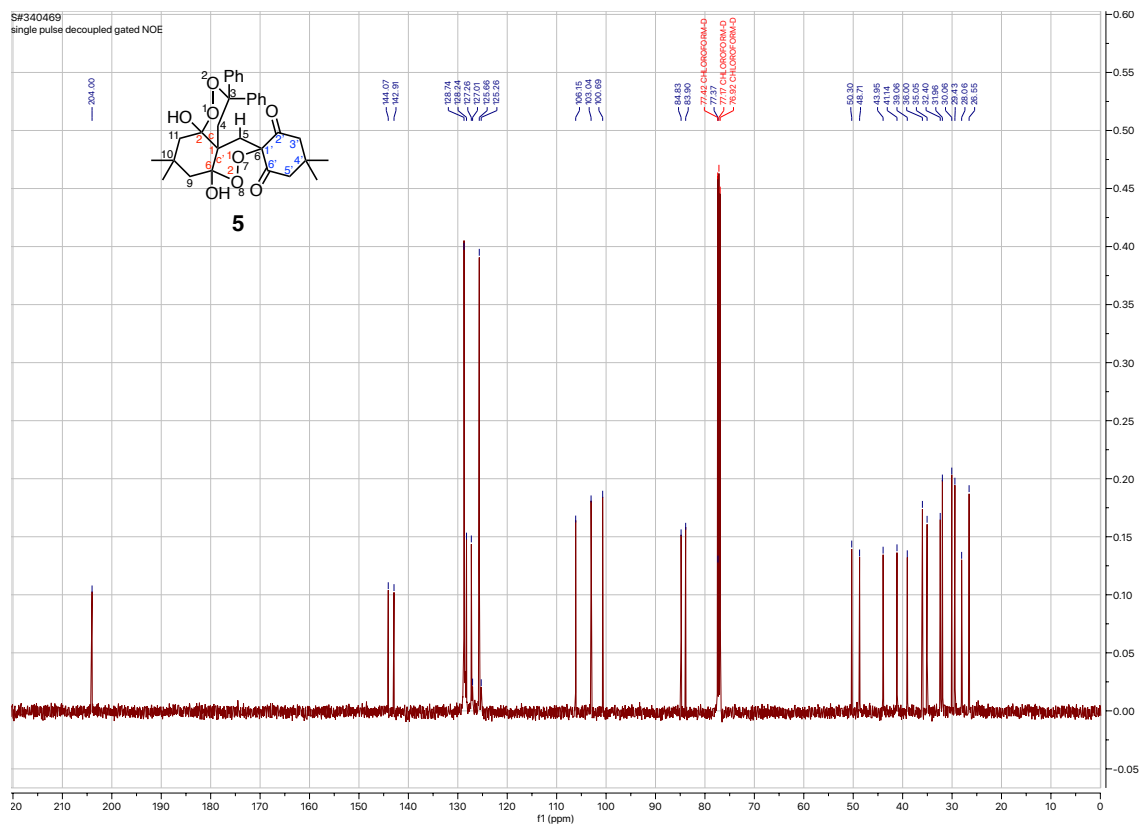
Expansion for HMBC spectrum using DMSO-*d*₆ of **4**



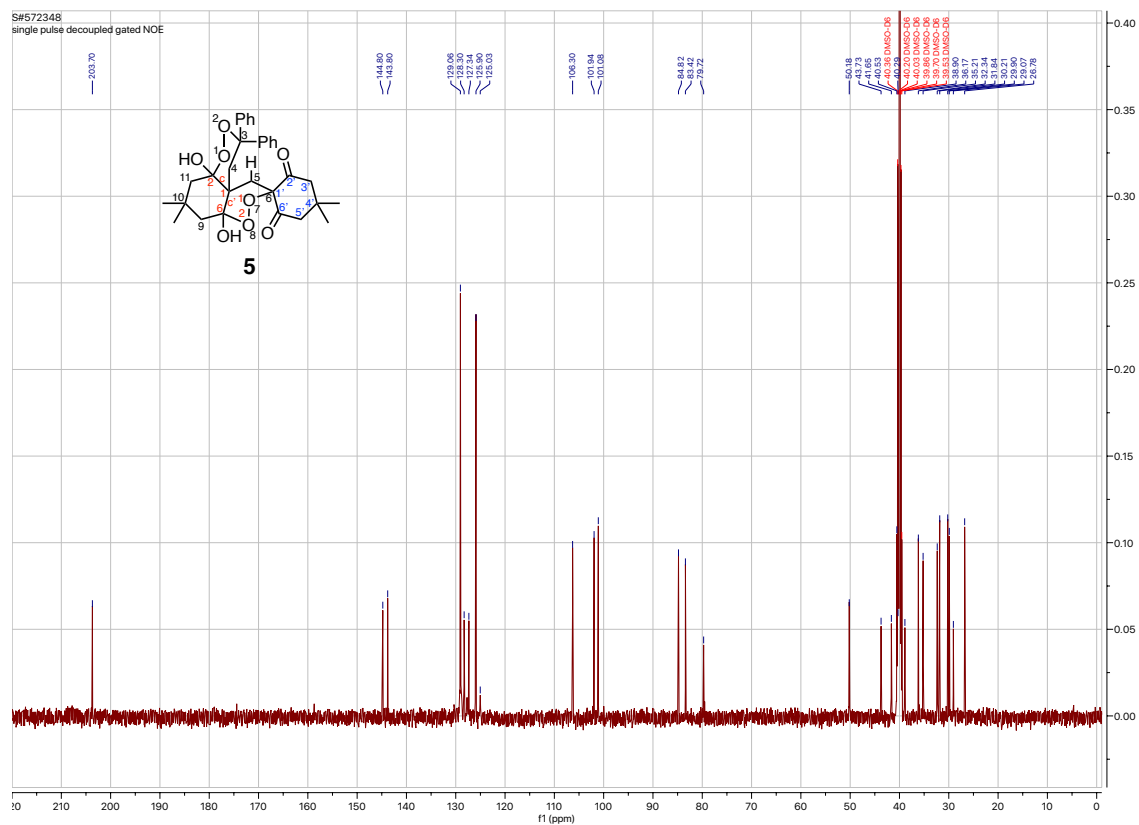
^1H NMR spectrum (500 MHz) for addition of D_2O to **5** in CDCl_3



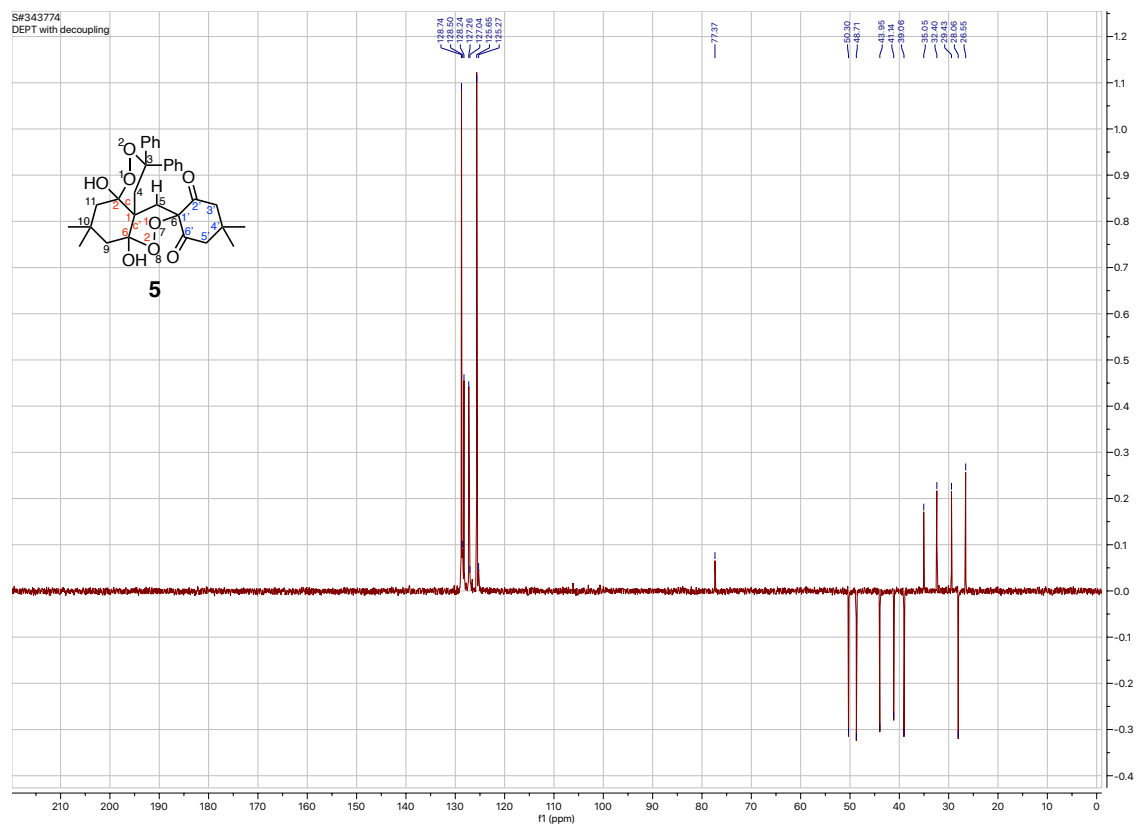
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz) using CDCl_3 of **5**



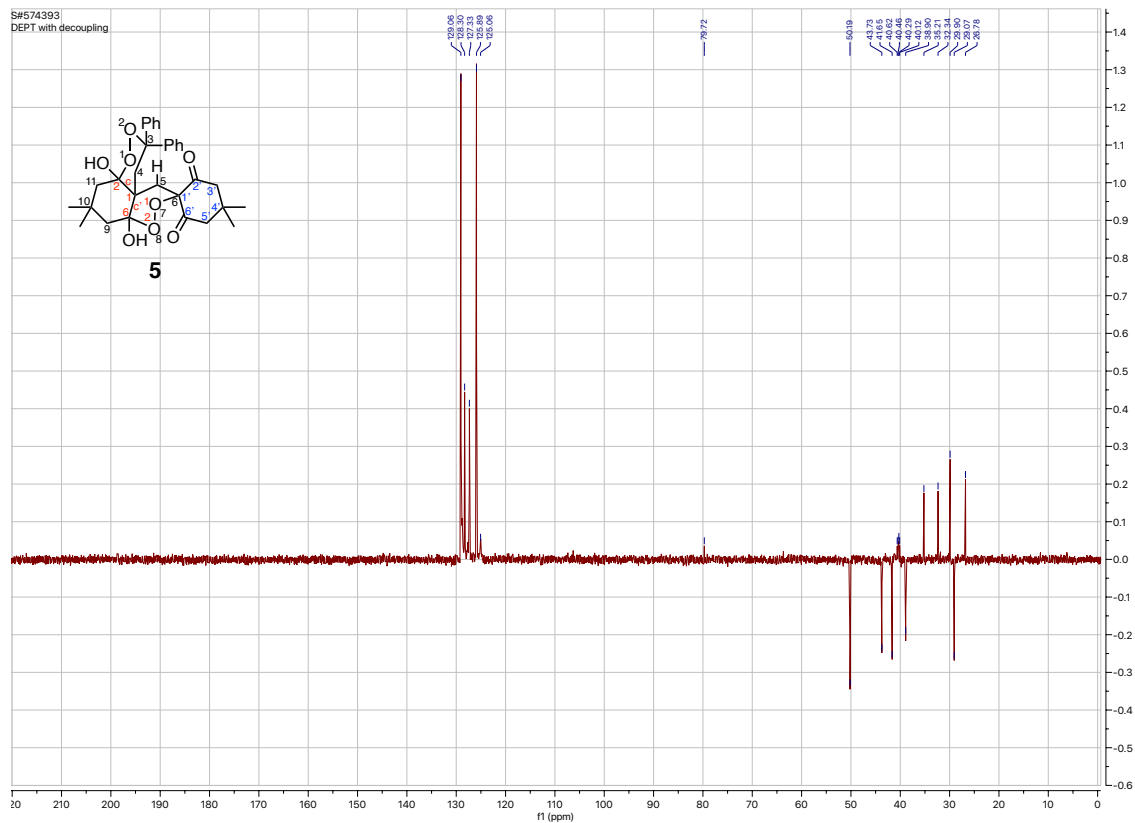
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz) using $\text{DMSO-}d_6$ of **5**



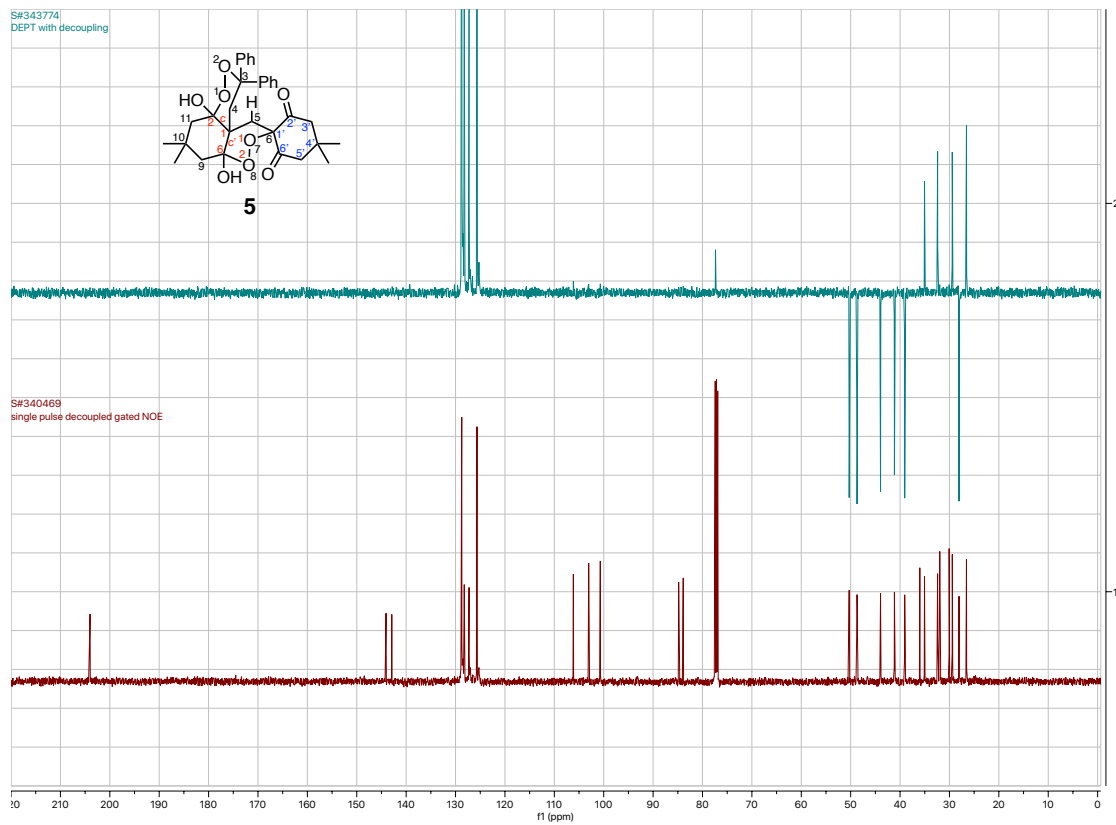
DEPT spectrum using CDCl_3 of **5**



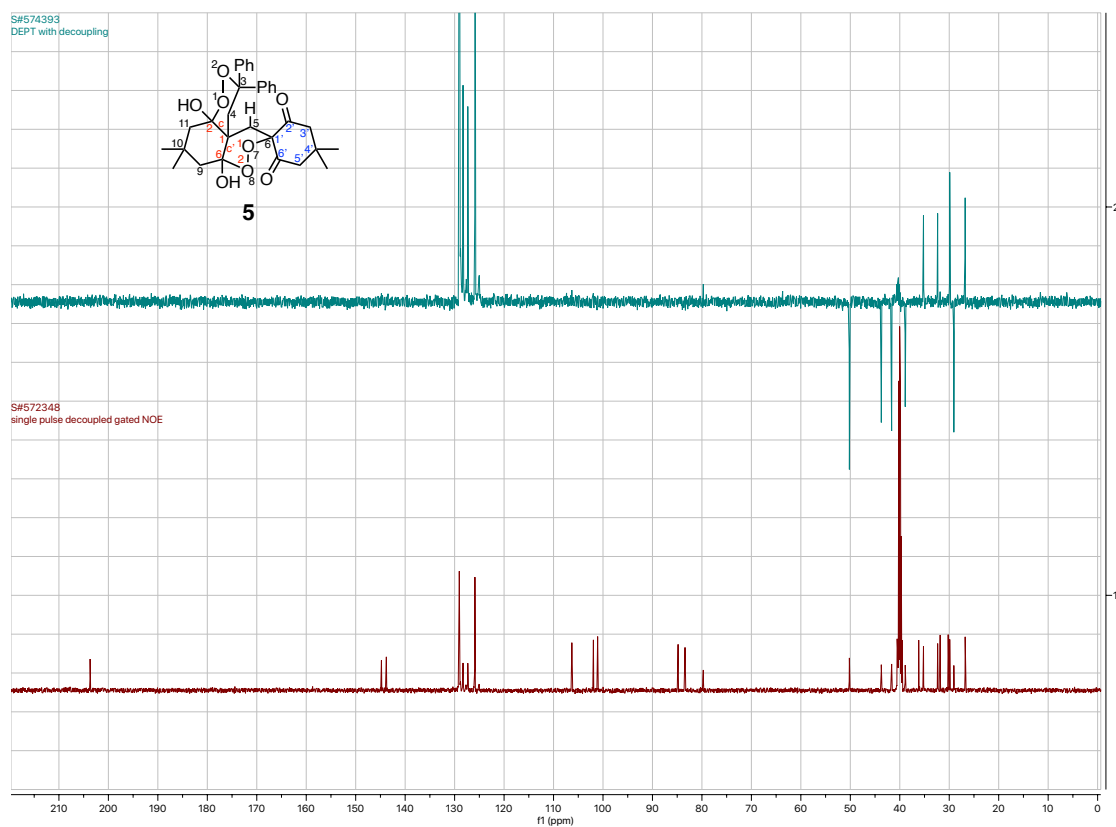
DEPT spectrum using DMSO-*d*₆ of **5**



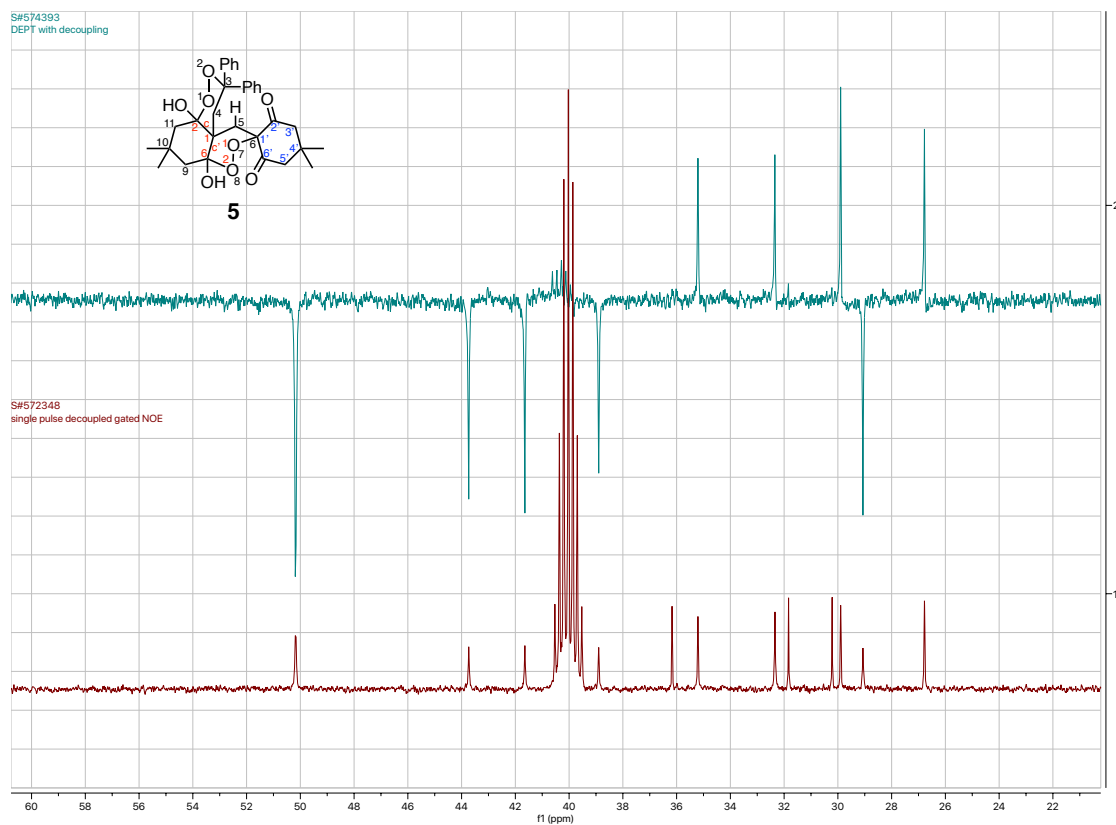
¹³C{¹H} NMR (125 MHz) (lower) and DEPT (upper) spectra using CDCl₃ of **5**



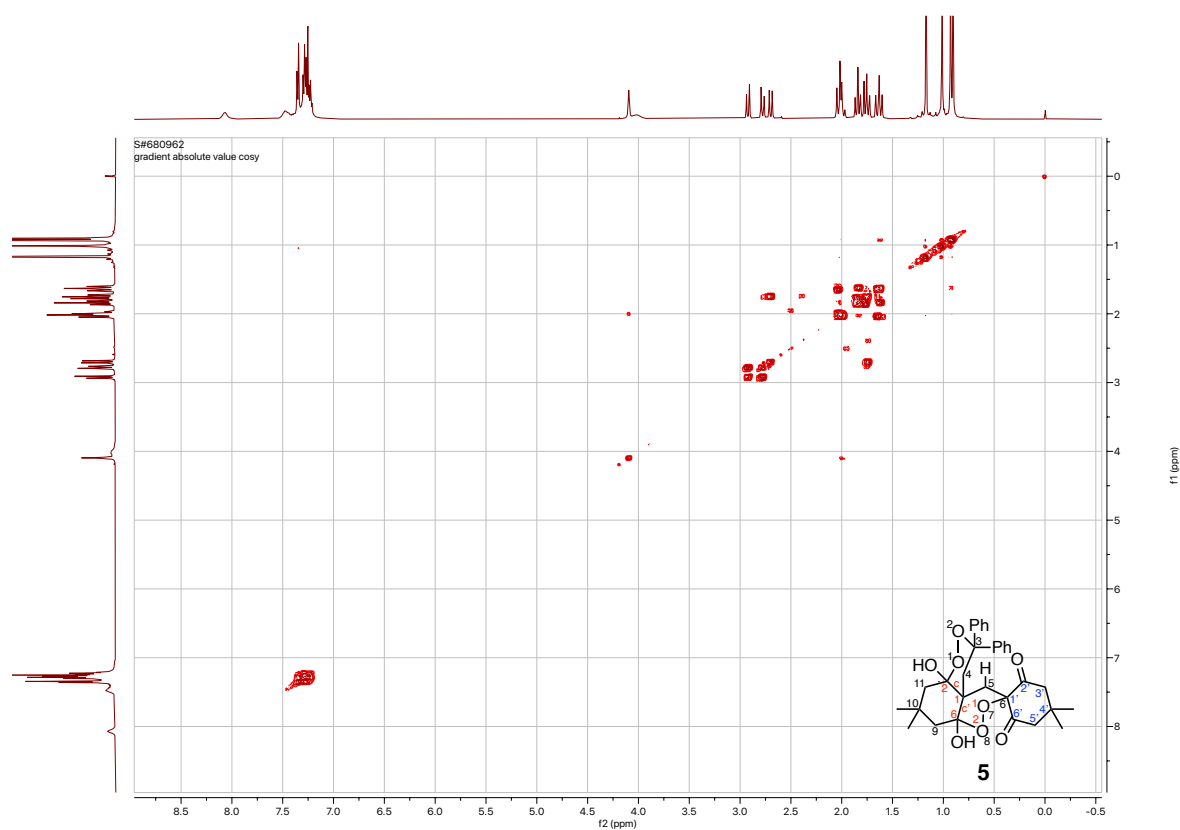
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) (lower) and DEPT (upper) spectra using $\text{DMSO-}d_6$ of **5**



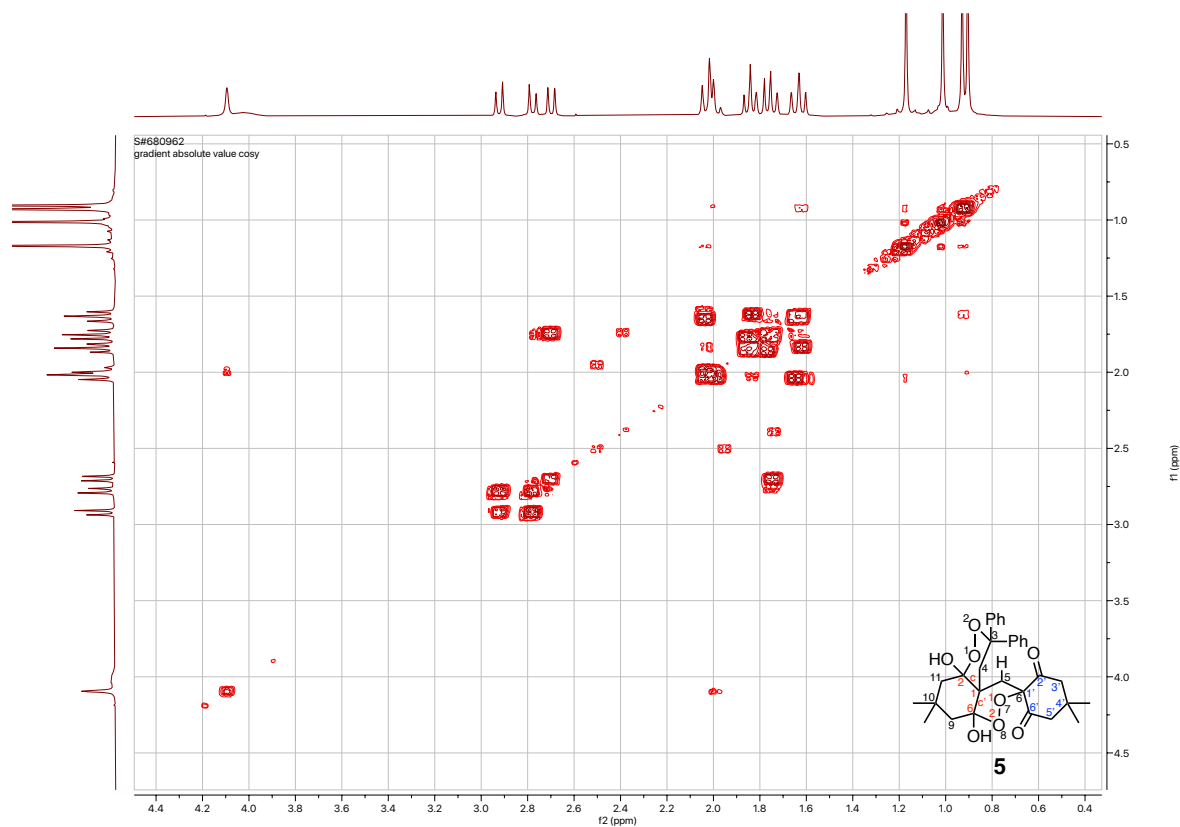
Expansion for $^{13}\text{C}\{^1\text{H}\}$ NMR (lower) and DEPT (upper) spectra using $\text{DMSO-}d_6$ of **5**



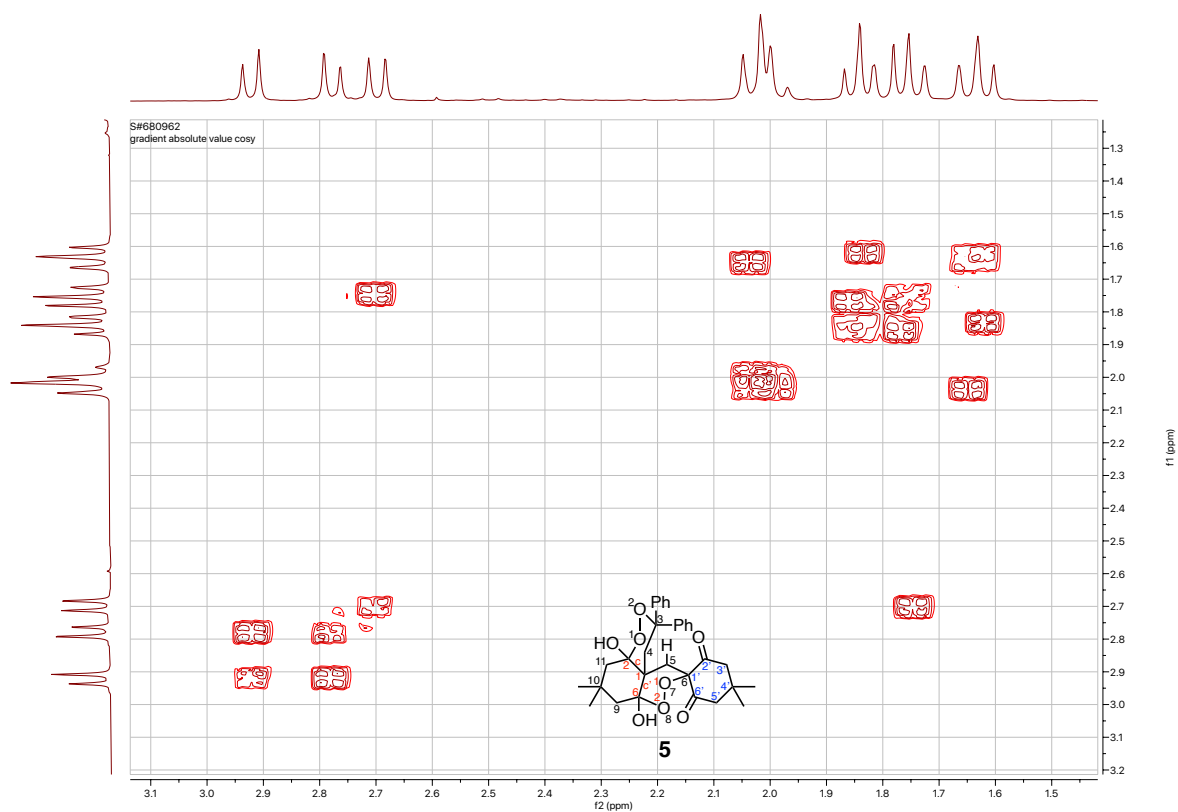
COSY spectrum using CDCl₃ of **5**



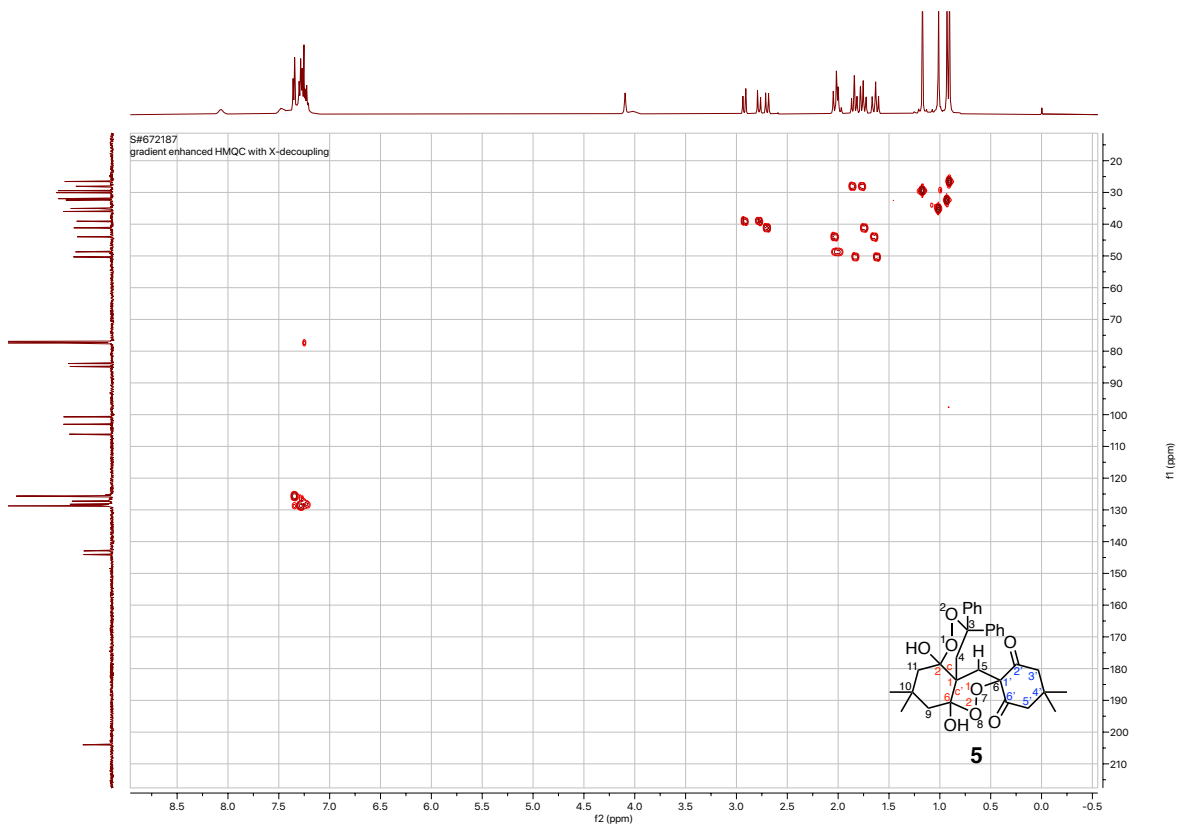
Expansion for COSY spectrum using CDCl₃ of **5**



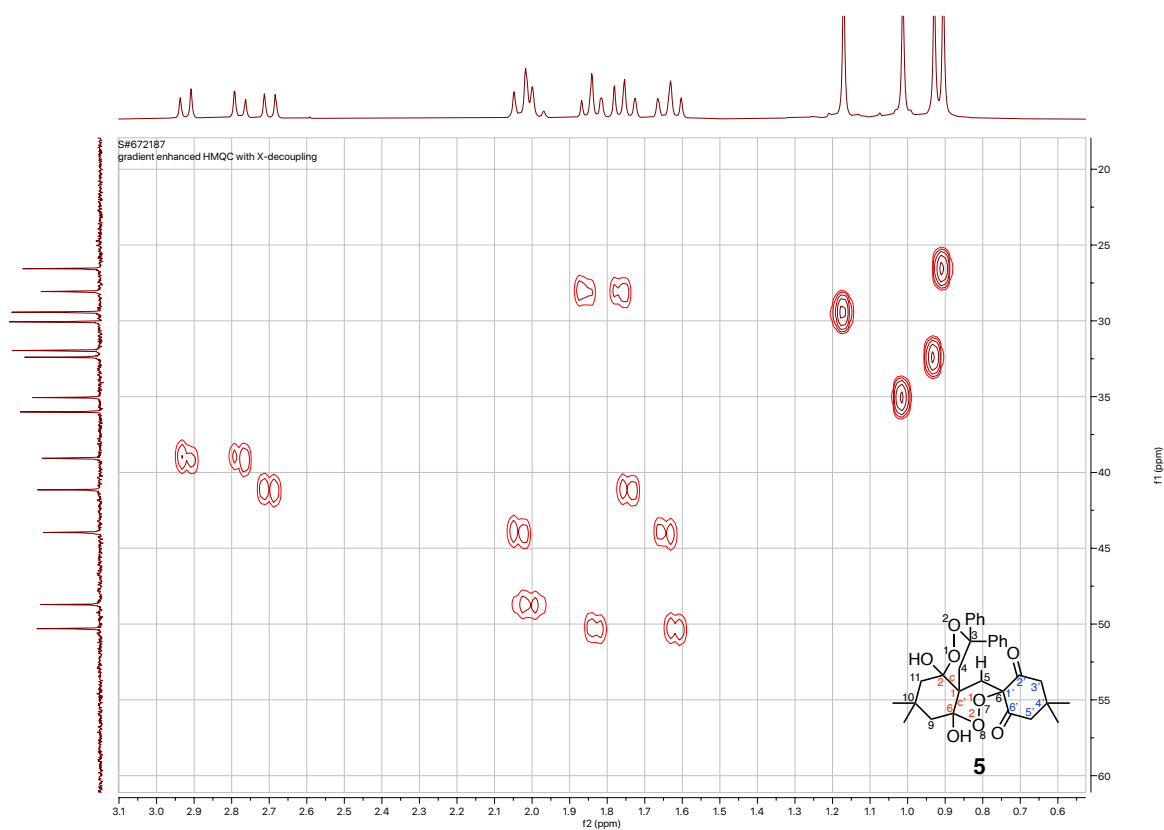
Expansion for COSY spectrum using CDCl₃ of **5**



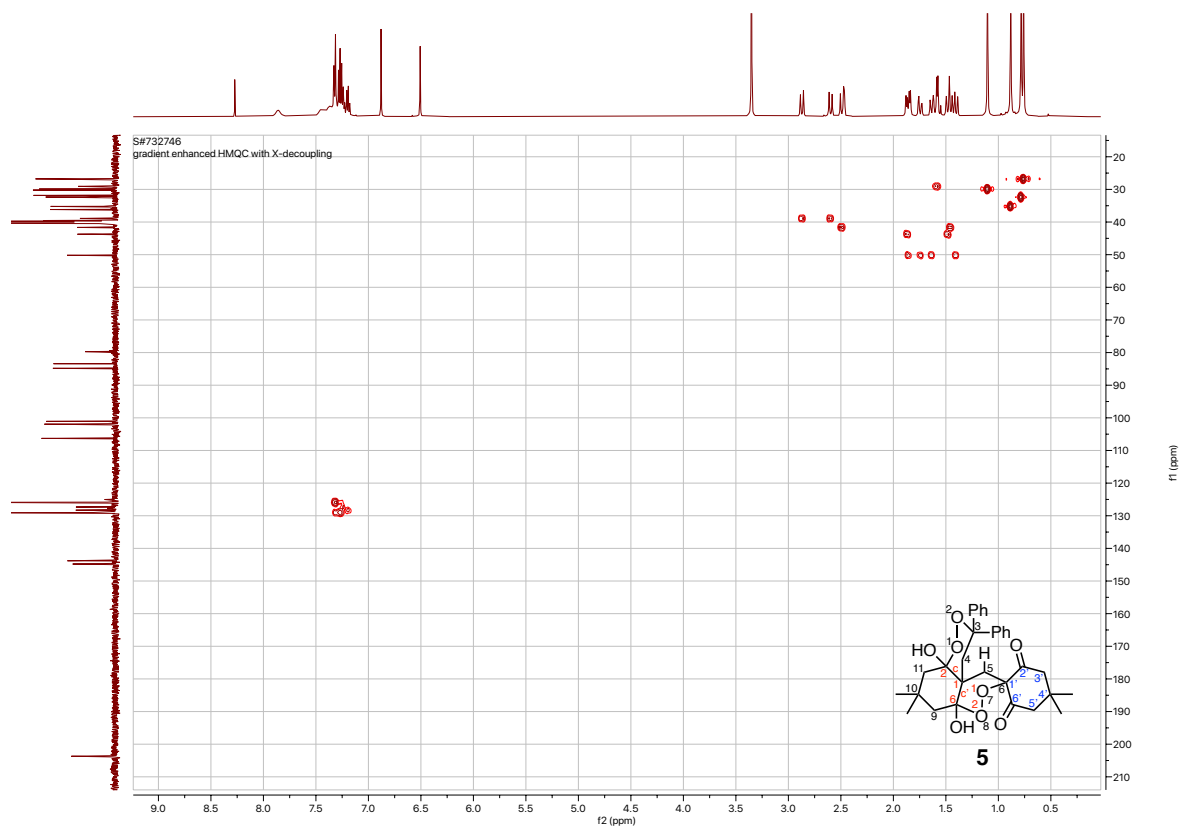
HMQC spectrum using CDCl₃ of **5**



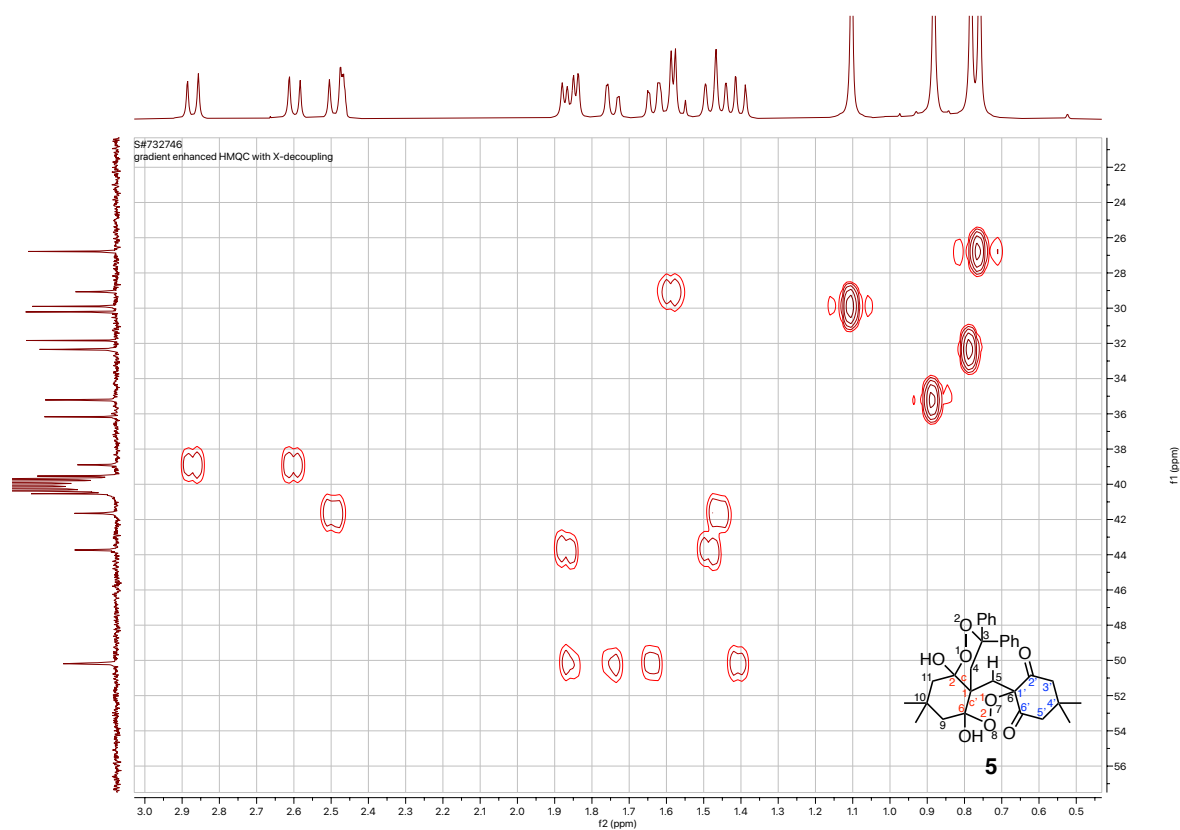
Expansion for HMQC spectrum using CDCl₃ of **5**



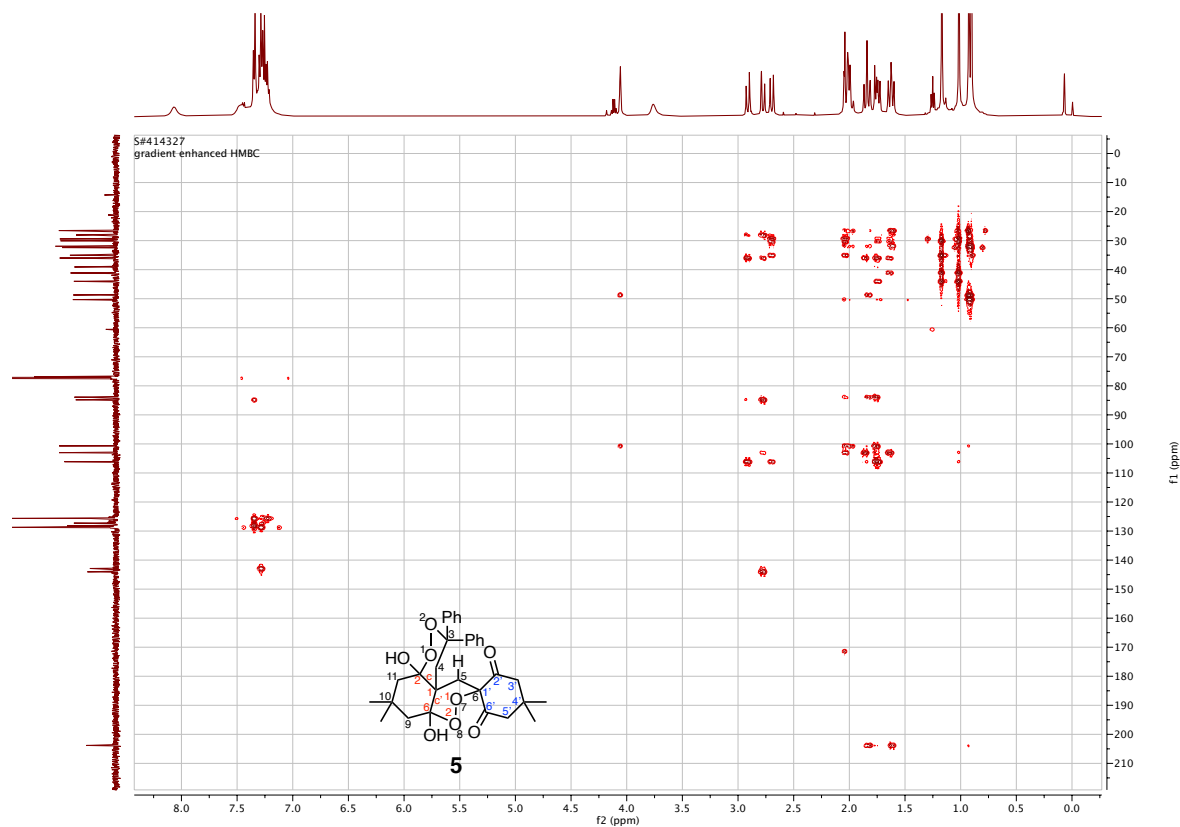
HMQC spectrum using DMSO-*d*₆ of **5**



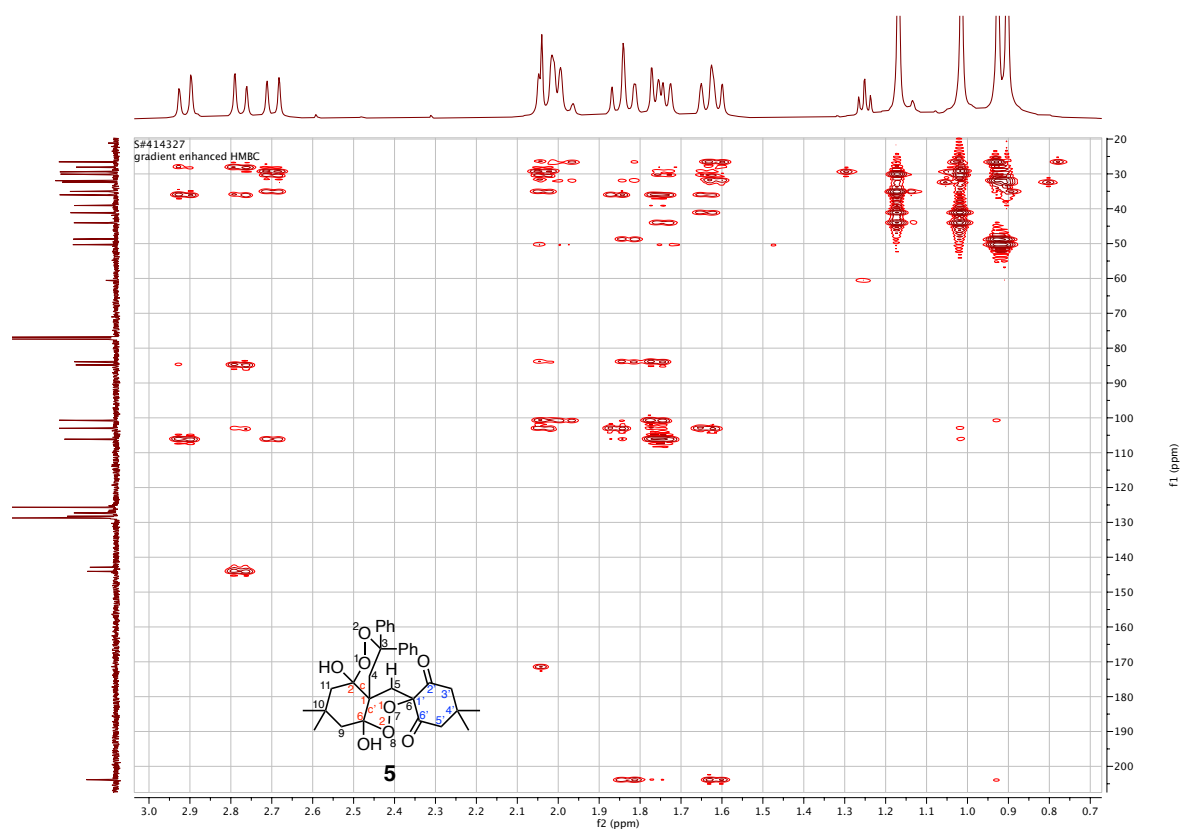
Expansion for HMQC spectrum using DMSO-*d*₆ of **5**



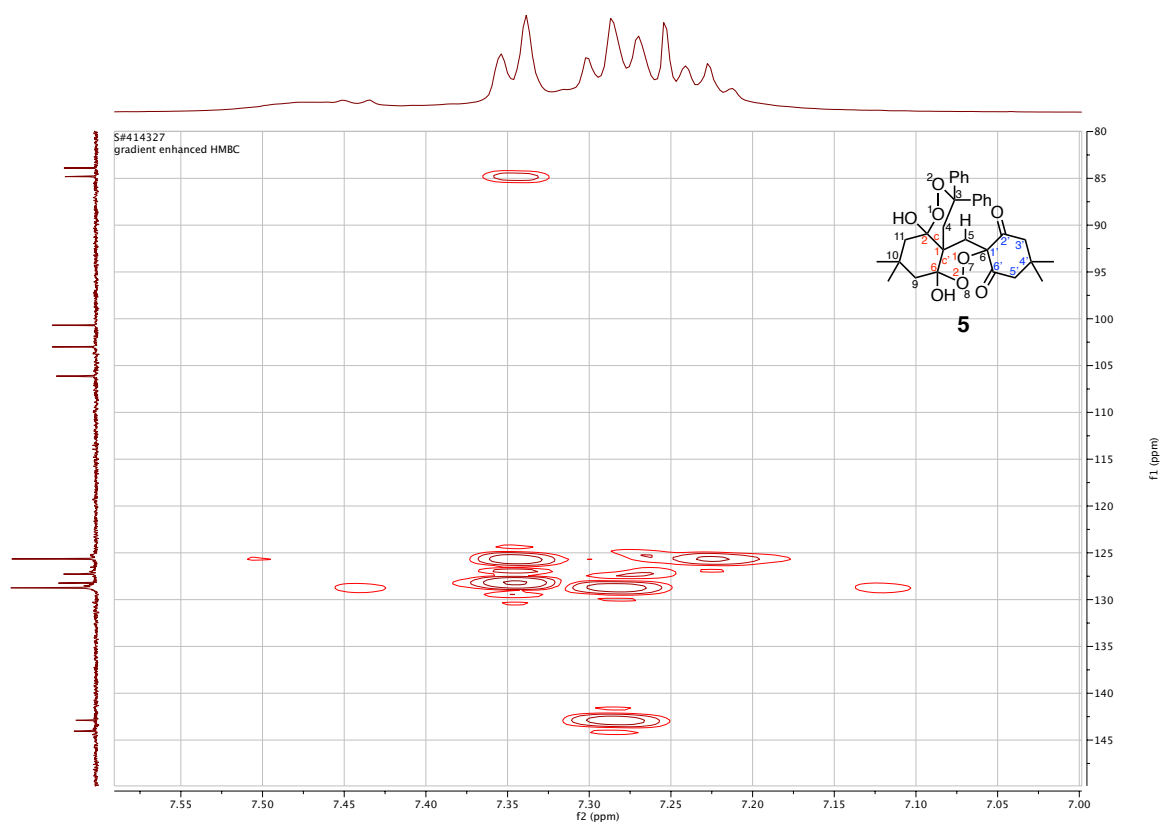
HMBC spectrum using CDCl₃ of **5**



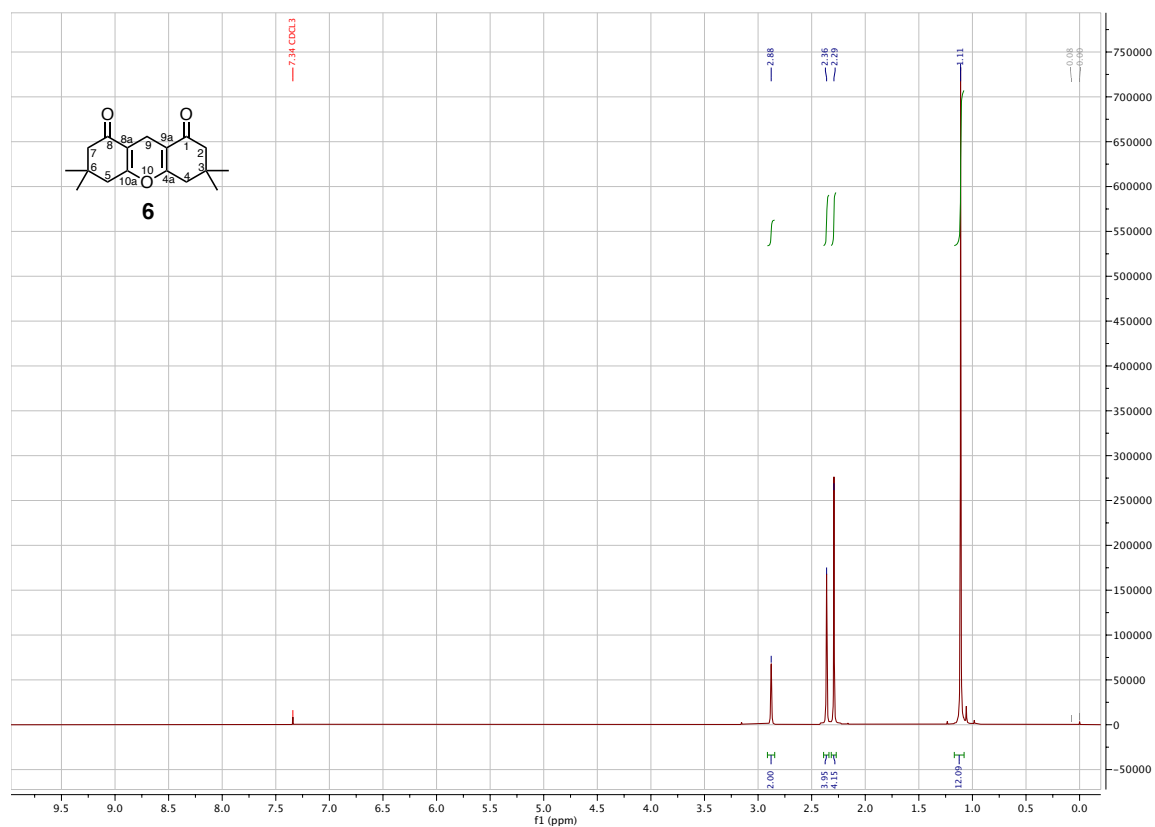
Expansion for HMBC spectrum using CDCl₃ of **5**



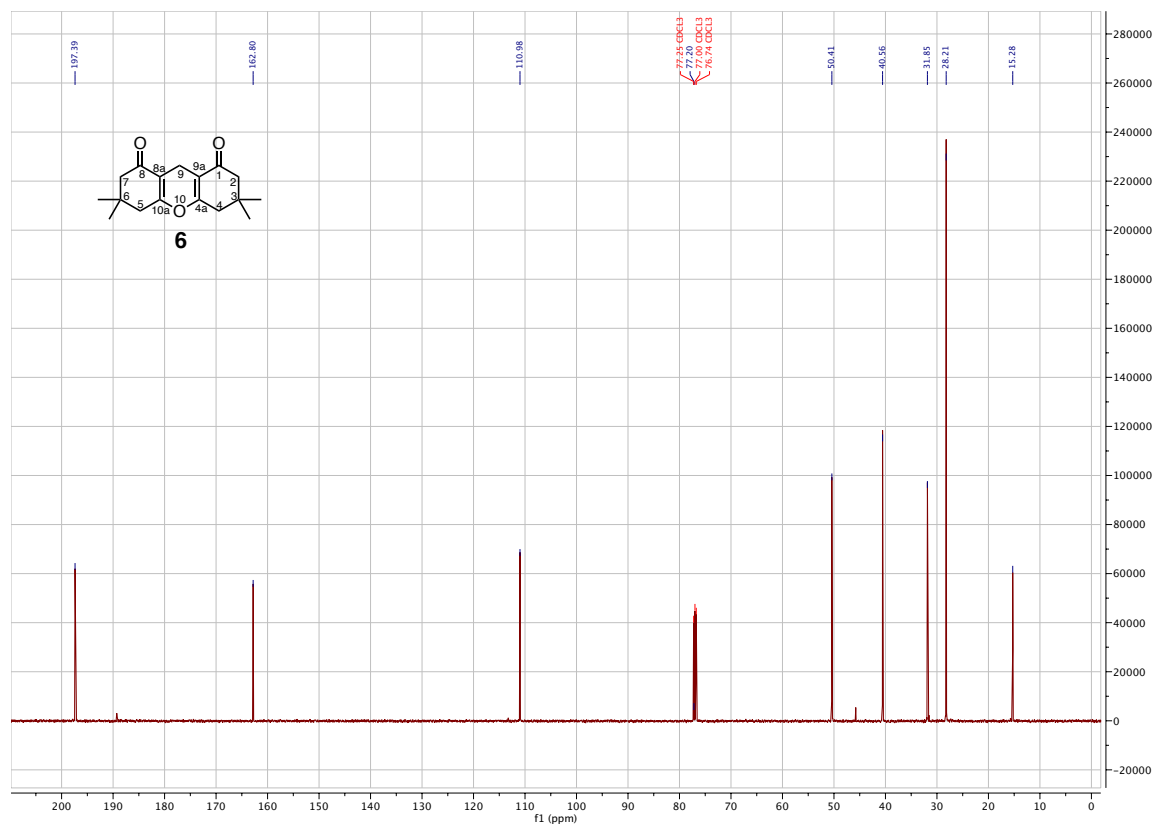
Expansion for HMBC spectrum using CDCl₃ of **5**



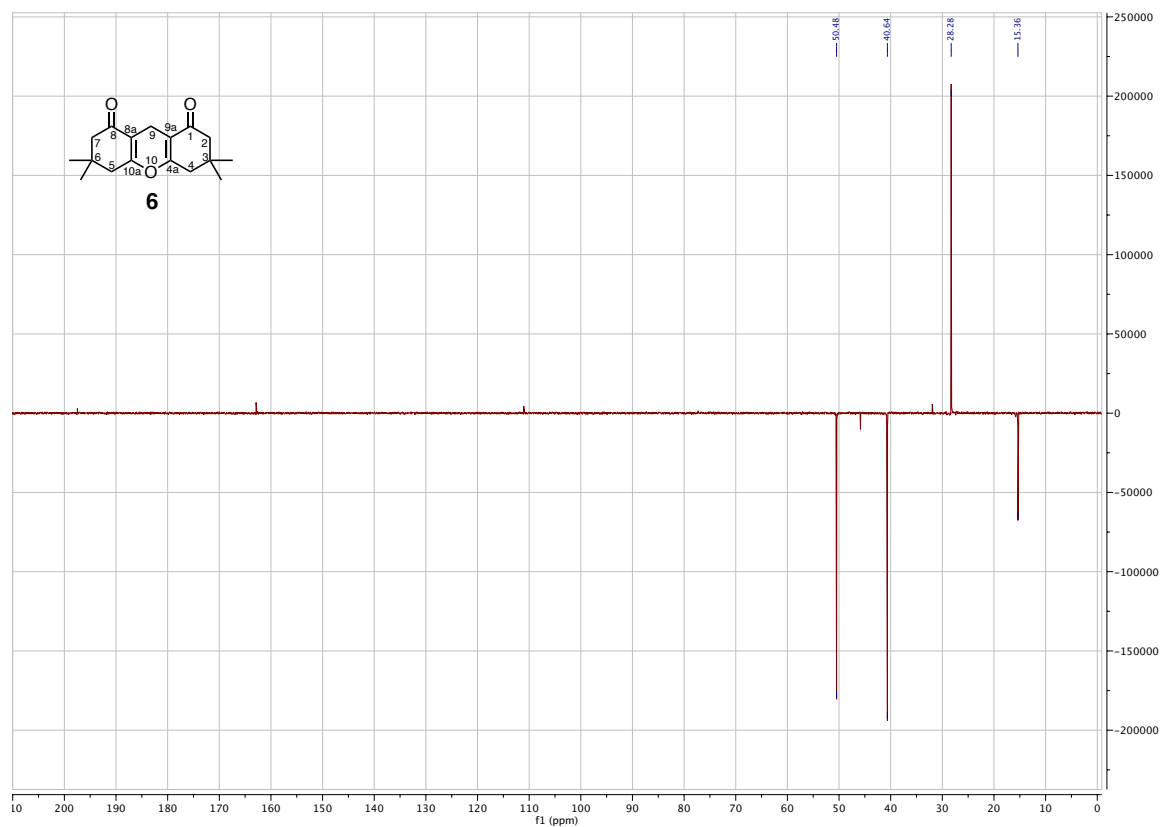
^1H NMR spectrum (500 MHz) using CDCl_3 of **6**



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz) using CDCl_3 of **6**



DEPT spectrum using CDCl₃ of **6**



¹³C{¹H}NMR (125 MHz) (lower) and DEPT (upper) spectra in CDCl₃ of **6**

