Supporting Information

Silver-Catalyzed Cyclization of α-Imino-Oxy Acids to Fused Tetralone Derivatives

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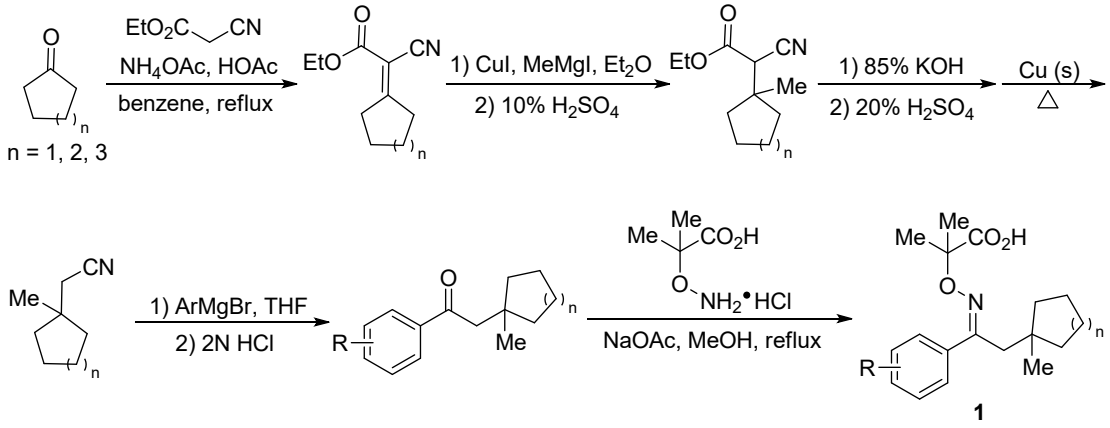
General information:

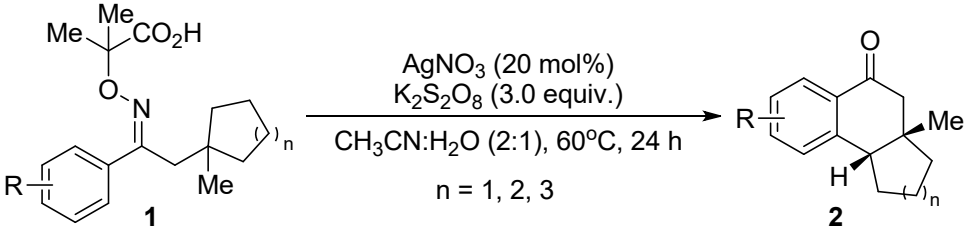
^{1}H, and ^{13}C were recorded at Bruker 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR). Chemical shifts were reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm, 77.0 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br (broad). Coupling constants were reported in Hertz (Hz). Infrared spectra were obtained with a AVATAR 360 FT-IR spectrometer. Melting points were measured with a XT-4 melting point apparatus without correction.

Materials: All commercially available reagents and solvent were used without further purification. Analytical thin layer chromatography was performed on 0.25 mm silica gel plates. Silica gel (200-300 mesh) was used for flash chromatography. α-Imino-oxy acids were prepared according to the literatures.[1]

The route for the preparation of α-Imino-oxy acids:

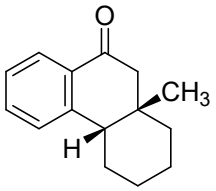


General Procedure for the Intramolecular Radical Relay Cyclization of α-Imino-Oxy Acids:



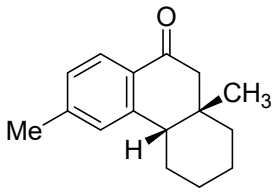
To a 10 mL Schenk flask charged with α-imino-oxy acids **1** (0.2 mmol), $AgNO_3$ (6.8 mg, 0.04 mmol), and $K_2S_2O_8$ (162 mg, 0.6 mmol) were added CH_3CN (1.0 mL) and distilled H_2O (0.5 mL) *via* a syringe. Then, the reaction mixture was vigorously stirred at 60 °C for 24 h. After the reaction was complete, the mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and washed with saturated brine (15 mL), dried over anhydrous $MgSO_4$, and then concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent) to afford the desired products **2**.

10a-methyl-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (2a)[2]



Colorless oil, 98% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.87 (s, 3H), 1.26–1.49 (m, 5H), 1.56–1.62 (m, 1H), 1.72–1.74 (m, 2H), 2.05 (dd, *J* = 17.6 Hz, 1.2 Hz, 1H), 2.44–2.48 (m, 1H), 2.97 (d, *J* = 17.2 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.21 (dt, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.42 (dt, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.2, 148.0, 133.9, 130.6, 129.1, 126.6, 126.3, 47.7, 44.3, 39.0, 35.0, 32.9, 28.7, 25.9, 21.7; **IR** (KBr) ν 2926, 2861, 1682, 1598, 1453, 1299, 1274, 1241, 1207 cm^{-1}.

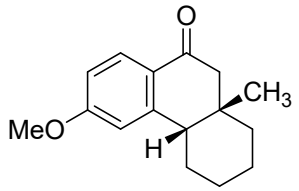
6,10a-Dimethyl-2,3,4,4a,10,10a-hexahydrophenanthren-9(1*H*)-one (2b) [2]



White solid, 93% yield, mp 82–84 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.93 (s, 3H), 1.32–1.55 (m, 5H), 1.64 (d, *J* = 12.0 Hz, 1H), 1.79 (d, *J* = 8.8 Hz, 2H), 2.08 (d, *J* = 17.2 Hz, 1H), 2.37 (s, 3H), 2.45–2.48 (m, 1H), 3.01 (d, *J* = 17.2 Hz, 1H), 7.02 (s, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ

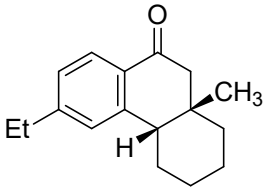
198.9, 148.1, 144.6, 129.6, 128.3, 127.4, 126.8, 47.7, 44.2, 39.0, 35.0, 32.9, 28.7, 25.9, 21.7; **IR** (KBr) ν 2925, 2860, 1677, 1607, 1447, 1412, 1311, 1294, 1277 cm^{-1}.

4-cyclohexyl-7-methylbenzo[e][1,2,3]oxathiazine 2,2-dioxide (2c)



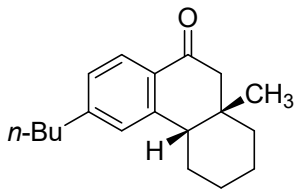
Colorless oil, 84% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.93 (s, 3H), 1.32–1.54 (m, 5H), 1.63 (d, *J* = 12.0 Hz, 1H), 1.79 (d, *J* = 11.2 Hz, 2H), 2.06 (d, *J* = 17.2 Hz, 1H), 2.44–2.48 (m, 1H), 2.98 (d, *J* = 17.2 Hz, 1H), 3.84 (s, 3H), 6.68 (s, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 163.9, 150.6, 129.2, 124.3, 113.1, 112.5, 55.3, 48.2, 44.0, 38.9, 35.0, 32.8, 28.7, 25.9, 21.7; **IR** (KBr) ν 2927, 2860, 1679, 1605, 1445, 1412, 1384, 1315, 1295, 1257 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{20}NaO_2^+$ 267.1356, found 267.1360.

4-cyclohexyl-8-methylbenzo[e][1,2,3]oxathiazine 2,2-dioxide (2d)



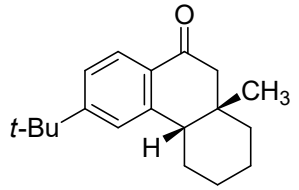
Colorless oil, 91% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.94 (s, 3H), 1.25 (t, *J* = 8.0 Hz, 3H), 1.34–1.55 (m, 5H), 1.62–1.66 (m, 1H), 1.78–1.81 (m, 2H), 2.09 (dd, *J* = 17.2 Hz, 1.2 Hz, 1H), 2.47–2.51 (m, 1H), 2.66 (q, *J* = 15.2 Hz, 7.6 Hz, 2H), 3.01 (d, *J* = 17.2 Hz, 1H), 7.04 (s, 1H), 7.11 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.9, 150.8, 148.2, 128.5, 128.3, 126.8, 126.2, 47.8, 44.3, 39.0, 35.0, 32.9, 28.9, 28.8, 26.0, 21.7, 14.9; **IR** (KBr) ν 2970, 2862, 1718, 1436, 1366, 1226 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{22}NaO^+$ 265.1563, found 265.1571.

6-butyl-10a-methyl-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (2e)



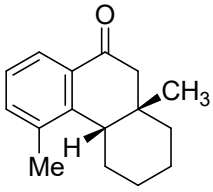
Colorless oil, 85% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.2 Hz, 3H), 0.94 (s, 3H), 1.31–1.44 (m, 5H), 1.50–1.69 (m, 5H), 1.78–1.81 (m, 2H), 2.09 (dd, *J* = 17.2 Hz, 1.2 Hz, 1H), 2.47–2.50 (m, 1H), 2.62 (t, *J* = 7.6 Hz, 2H), 3.01 (d, *J* = 17.2 Hz, 1H), 7.03 (s, 1H), 7.10 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.9, 149.6, 148.1, 128.9, 128.5, 126.8, 126.7, 47.8, 44.3, 39.1, 35.8, 35.0, 33.1, 33.0, 28.8, 26.0, 22.4, 21.8, 13.9; **IR** (KBr) ν 2925, 1681, 1601, 1445, 1362, 1240 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{26}NaO^+$ 293.1876, found 293.1887.

6-(tert-butyl)-10a-methyl-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (2f) [2]



White solid, 96% yield, mp 56–58 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.95 (s, 3H), 1.32 (s, 9H), 1.37–1.53 (m, 5H), 1.63–1.66 (m, 1H), 1.79–1.81 (m, 2H), 2.09 (dd, *J* = 17.2 Hz, 1.2 Hz, 1H), 2.49–2.52 (m, 1H), 3.02 (d, *J* = 17.2 Hz, 1H), 7.20 (d, *J* = 1.6 Hz, 1H), 7.31 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.0, 157.5, 147.9, 128.2, 126.4, 125.7, 123.7, 48.1, 44.3, 39.1, 35.1, 33.1, 31.0, 28.8, 26.0, 21.8; **IR** (KBr) ν 2967, 2926, 2865, 1728, 1680, 1604, 1436, 1410, 1228, 1216 cm^{-1}.

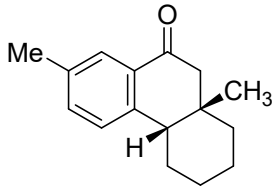
5,10a-dimethyl-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (2g) [2]



Colorless oil, 83% yield; Major regioisomer; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.90 (s, 3H), 1.29–1.54 (m, 5H), 1.62–1.69 (m, 1H), 1.78–1.83 (m, 2H), 2.10 (d, *J* = 17.6 Hz, 1H), 2.36 (s, 3H), 2.64–2.68 (m, 1H), 3.08 (d, *J* = 17.6 Hz, 1H), 7.18 (t, *J* = 7.6 Hz,

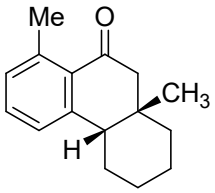
1H), 7.35 (d, J = 7.2 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.6, 145.9, 135.9, 135.8, 130.9, 125.8, 125.0, 44.4, 43.6, 39.3, 34.7, 29.7, 28.9, 26.0, 21.7, 18.7; **IR** (KBr) ν 2971, 1736, 1436, 1362, 1228, 1217 cm^{-1}.

7,10a-dimethyl-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (2g')



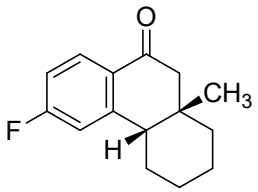
Minor regioisomer; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.93 (s, 1.51H), 1.29–1.54 (m, 2.52H), 1.62–1.69 (m, 0.48H), 1.78–1.83 (m, 1.00H), 2.10 (d, J = 17.6 Hz, 0.53H), 2.35 (s, 1.50H), 2.48–2.51 (m, 0.51H), 3.02 (d, J = 17.2 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 7.31 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.80 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.4, 145.2, 136.0, 134.8, 130.4, 129.0, 126.8, 47.3, 44.4, 39.0, 35.0, 32.9, 28.7, 25.9, 21.8, 20.8; **IR** (KBr) ν 2965, 1721, 1436, 1363, 1228, 1217 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{20}NaO^+$ 251.1406, found 251.1407.

8,10a-dimethyl-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (2h)



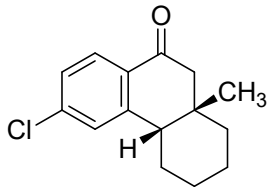
Colorless oil, 52% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.95 (s, 3H), 1.33–1.64 (m, 5H), 1.62–1.64 (m, 1H), 1.79 (d, J = 10.8 Hz, 2H), 2.09 (d, J = 17.2 Hz, 1H), 2.50–2.53 (m, 1H), 2.62 (t, J = 7.6 Hz, 2H), 2.64 (s, 3H), 3.05 (d, J = 17.2 Hz, 1H), 7.06–7.09 (m, 2H), 7.32 (t, J = 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.9, 149.4, 141.0, 132.6, 130.3, 129.1, 127.4, 48.9, 45.9, 38.8, 34.4, 33.2, 28.9, 26.0, 23.4, 21.7; **IR** (KBr) ν 2924, 1717, 1607, 1445, 1422, 1365, 1294, 1277 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{20}NaO^+$ 251.1406, found 251.1409.

6-fluoro-10a-methyl-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (2i) [2]



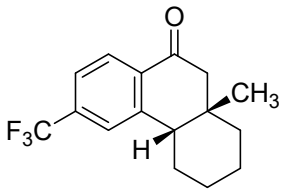
White solid, 78% yield, mp 53–55 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.94 (s, 3H), 1.33–1.55 (m, 5H), 1.62–1.66 (m, 1H), 1.74–1.81 (m, 2H), 2.10 (dd, *J* = 17.2 Hz, 0.8 Hz, 1H), 2.49–2.52 (m, 1H), 3.00 (d, *J* = 17.2 Hz, 1H), 6.90 (dd, *J* = 9.2 Hz, 2.4 Hz, 1H), 6.95 (dt, *J* = 8.4 Hz, 2.4 Hz, 1H), 8.02 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.5, 166.1 (d, $J_{C\text{-}F}$ = 251.8 Hz), 151.2 (d, $J_{C\text{-}F}$ = 8.4 Hz), 129.9 (d, $J_{C\text{-}F}$ = 9.5 Hz), 127.3, 115.3 (d, $J_{C\text{-}F}$ = 21.0 Hz), 114.0 (d, $J_{C\text{-}F}$ = 21.9 Hz), 47.9, 44.1, 38.8, 35.0, 32.6, 28.6, 25.8, 21.6; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -104.39 (s, 1F); **IR** (KBr) ν 2971, 1729, 1436, 1365, 1228, 1216 cm^{-1}.

6-chloro-10a-methyl-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (2j) [2]



White solid, 85% yield, mp 65–67 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.94 (s, 3H), 1.34–1.57 (m, 5H), 1.64–1.68 (m, 1H), 1.81 (d, *J* = 8.4 Hz, 2H), 2.12 (dd, *J* = 17.2 Hz, 0.8 Hz, 1H), 2.48–2.56 (m, 1H), 3.02 (d, *J* = 17.2 Hz, 1H), 7.24–7.27 (m, 2H), 7.94 (d, *J* = 8.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.0, 149.7, 140.0, 129.1, 129.0, 128.4, 126.9, 47.7, 44.1, 38.8, 35.0, 32.7, 28.6, 25.8, 21.6; **IR** (KBr) ν 2970, 2874, 1739, 1686, 1591, 1445, 1365, 1228, 1215 cm^{-1}.

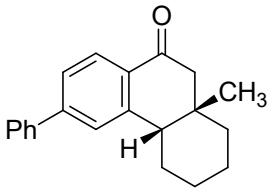
10a-methyl-6-(trifluoromethyl)-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (2k) [2]



White solid, 77% yield, mp 101–103 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.94 (s, 3H), 1.36–1.50 (m, 4H), 1.55–1.59 (m, 1H), 1.65–1.69 (m, 1H), 1.81–1.86 (m, 2H), 2.18 (dd, *J* = 17.6 Hz, 1.2 Hz, 1H), 2.59–2.62 (m, 1H), 3.06 (d, *J* = 17.2 Hz, 1H), 7.51–7.54 (m, 2H), 8.09 (d, *J* = 8.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.1, 148.5,

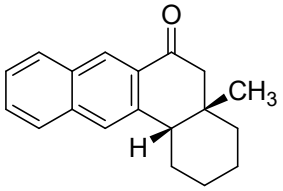
135.0 (q, $J_{C\text{-}F}$ = 32.1 Hz), 133.0, .127.4, 126.2 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.6 (q, $J_{C\text{-}F}$ = 271.3 Hz), 123.2 (q, $J_{C\text{-}F}$ = 3.6 Hz), 47.7, 44.2, 38.9, 34.9, 32.8, 28.6, 25.8, 21.6; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -63.13 (s, 3F); **IR** (KBr) ν 2968, 1718, 1436, 1374, 1216, 1122 cm^{-1}.

10a-methyl-6-phenyl-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (2l)



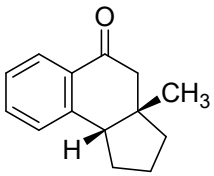
White solid, 89% yield, mp 113–115 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.99 (s, 3H), 1.40–1.59 (m, 5H), 1.65–1.69 (m, 1H), 1.81–1.90 (m, 2H), 2.15 (dd, *J* = 17.2 Hz, 0.8 Hz, 1H), 2.61 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.07 (d, *J* = 17.2 Hz, 1H), 7.37–7.41 (m, 1H), 7.44–7.48 (m, 3H), 7.52 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.62–7.64 (m, 2H), 8.07 (d, *J* = 8.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.8, 148.5, 146.4, 140.0, 129.4, 128.8, 128.1, 127.6, 127.3, 127.2, 125.2, 48.0, 44.3, 39.0, 35.0, 33.0, 28.8, 25.9, 21.7; **IR** (KBr) ν 2970, 1729, 1686, 1448, 1366, 1228, 1216, 1206 cm^{-1}; **HRMS** (ESI) m/z: $[M+K]^+$ calcd for $C_{21}H_{22}KO^+$ 329.1302, found 329.1304.

4a-methyl-1,3,4,4a,5,12b-hexahydrotetraphen-6(2H)-one (2m)



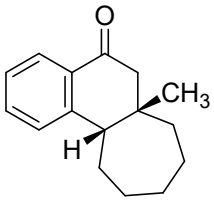
White solid, 88% yield, mp 65–67 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.98 (s, 3H), 1.46–1.58 (m, 4H), 1.66 (d, *J* = 11.2 Hz, 1H), 1.74 (d, *J* = 9.2 Hz, 1H), 1.85–1.87 (m, 1H), 2.06 (d, *J* = 12.0 Hz, 1H), 2.23 (d, *J* = 17.2 Hz, 1H), 3.17 (d, *J* = 17.6 Hz, 1H), 3.31–3.34 (m, 1H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.86 (t, *J* = 4.8 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 8.15–8.18 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.2, 146.3, 136.4, 130.9, 129.0, 128.0, 126.8, 126.5, 124.8, 122.6, 43.7, 43.6, 39.6, 35.3, 31.3, 28.8, 26.1, 21.9; **IR** (KBr) ν 2970, 1738, 1436, 1366, 1229, 1115 cm^{-1}; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{21}O^+$ 265.1587, found 265.1579.

3a-methyl-2,3,3a,4-tetrahydro-1H-cyclopenta[a]naphthalen-5(9bH)-one (2n)



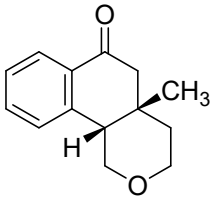
Colorless oil, 72% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.11 (s, 3H), 1.67 (t, *J* = 7.2 Hz, 2H), 1.78–1.88 (m, 3H), 2.26–2.35 (m, 2H), 2.70 (d, *J* = 16.4 Hz, 1H), 2.86–2.93 (m, 1H), 7.23–7.30 (m, 2H), 7.49 (dt, *J* = 7.2 Hz, 0.8 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.9, 145.6, 133.7, 130.3, 129.6, 126.6, 126.3, 49.9, 46.2, 44.3, 40.1, 34.0, 25.6, 22.3; **IR** (KBr) ν 2970, 1716, 1438, 1368, 1216, 1112 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{16}NaO^+$ 223.1093, found 223.1084.

6a-methyl-6,6a,7,8,9,10,11,11a-octahydro-5H-cyclohepta[a]naphthalen-5-one (2o) [2]



Colorless oil, 95% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.00 (s, 3H), 1.35–1.42 (m, 1H), 1.46–1.56 (m, 2H), 1.64–1.75 (m, 4H), 1.88–1.94 (m, 2H), 1.88–1.94 (m, 2H), 1.97–2.04 (m, 1H), 2.31 (dd, *J* = 16.4 Hz, 0.8 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.51 (dt, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.4, 149.2, 133.9, 130.5, 130.1, 126.2, 125.9, 50.8, 48.3, 42.2, 37.7, 33.3, 30.5, 30.3, 27.1, 21.2; **IR** (KBr) ν 2970, 2925, 1736, 1688, 1446, 1366, 1228, 1218, 1206 cm^{-1}.

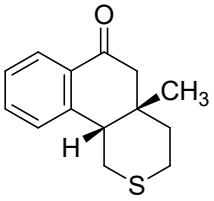
4a-methyl-3,4,4a,5-tetrahydro-1H-benzo[h]isochromen-6(10bH)-one (2p)



White solid, 78% yield, mp 90–92 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.04 (s, 3H), 1.44 (d, *J* = 14.0 Hz, 1H), 1.77–1.85 (m, 1H), 2.22 (dd, *J* = 17.2 Hz, 1.2 Hz, 1H), 2.91 (dd, *J* = 11.6 Hz, 1.2 Hz, 1H), 3.21 (d, *J* = 17.2 Hz, 1H), 3.44 (t, *J* = 12.0 Hz, 1H), 3.71 (dt, *J* = 12.4 Hz, 2.0 Hz, 1H), 3.87–3.95 (m, 2H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.35 (dt, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.53 (dt, *J* = 7.6 Hz, 1.2 Hz, 1H), 8.03 (dd, *J* = 8.0 Hz,

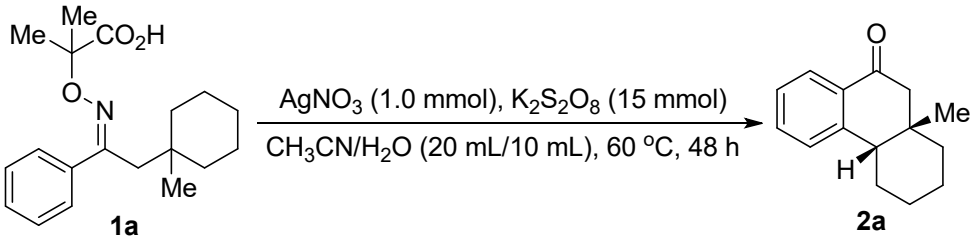
0.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 141.5, 134.1, 131.4, 129.8, 127.3, 126.9, 69.8, 63.9, 46.7, 43.3, 38.1, 33.0, 28.3; **IR** (KBr) ν 2952, 1689, 1436, 1415, 1287, 1261, 1225, 1110 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{16}NaO_2^+$ 239.1043, found 239.1032.

4a-methyl-3,4,4a,5-tetrahydro-1H-benzo[h]isothiochromen-6(10bH)-one (2q)



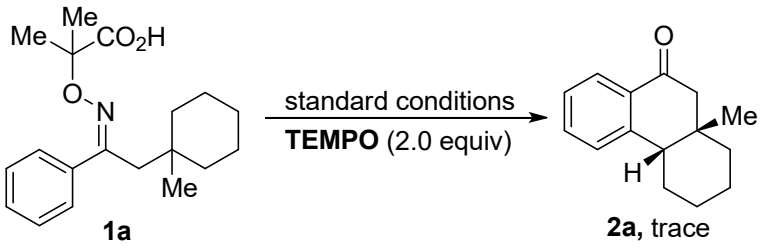
Colorless oil, 40% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.08 (s, 3H), 1.96 (d, *J* = 15.2 Hz, 1H), 2.29–2.41 (m, 2H), 2.97 (d, *J* = 17.6 Hz, 1H), 3.03–3.09 (m, 3H), 3.18 (dt, *J* = 14.4 Hz, 2.8 Hz, 1H), 3.45 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.2 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.7, 142.2, 135.0, 130.4, 128.6, 128.3, 127.6, 54.0, 46.8, 45.3, 42.5, 36.3, 33.7, 27.0; **IR** (KBr) ν 2970, 1736, 1436, 1366, 1228, 1112 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{16}NaOS^+$ 255.0814, found 255.0820.

The procedure for the gram-scale reaction:



To a 100 mL Schenk flask charged with α-imino-oxy acids **1a** (5 mmol, 1.59 g), $AgNO_3$ (170 mg, 1.0 mmol), and $K_2S_2O_8$ (2.43 g, 15 mmol) were added CH_3CN (20 mL) and distilled H_2O (10 mL) *via* a syringe. Then, the reaction mixture was vigorously stirred at 60 °C for 48 h. After the reaction was complete, the mixture was diluted with water (100 mL) and extracted with ethyl acetate (3 × 100 mL). The organic layers were combined and washed with a saturated brine (150 mL), dried over anhydrous $MgSO_4$, and then concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent) to afford the desired products **2a** in 95% yield (1.02 g) as colorless oil.

The Procedure for the radical inhibition experiment:



1a **2a,** trace

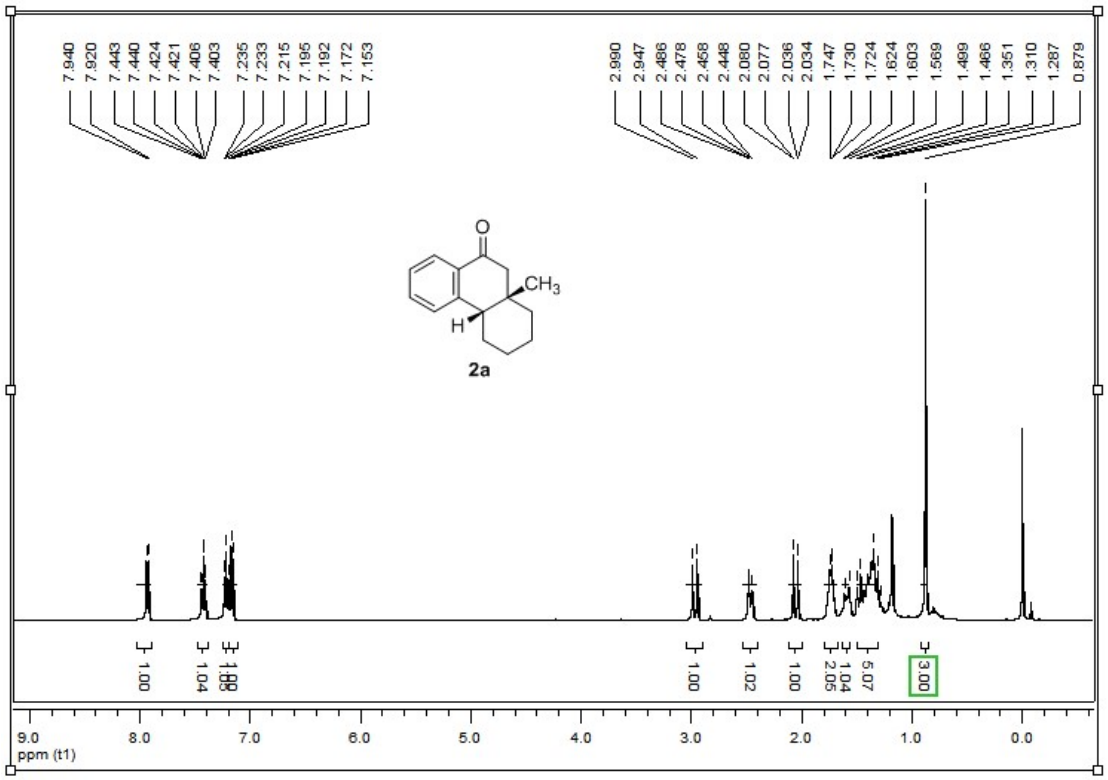
To a 10 mL Schenk flask charged with α-imino-oxy acids **1a** (0.2 mmol), $AgNO_3$ (6.8 mg, 0.04 mmol), $K_2S_2O_8$ (162 mg, 0.6 mmol), and TEMPO (62.5 mg, 0.4 mmol) were added CH_3CN (1.0 mL) and distilled H_2O (0.5 mL) *via* a syringe. Then, the reaction mixture was vigorously stirred at 60 ^oC for 24 h. After the reaction was complete, the mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and washed with a saturated brine (15 mL), dried over anhydrous $MgSO_4$, and then concentrated in vacuo. The target product **2a** was not detected by TLC, but the raw materials **1a** almost disappeared.

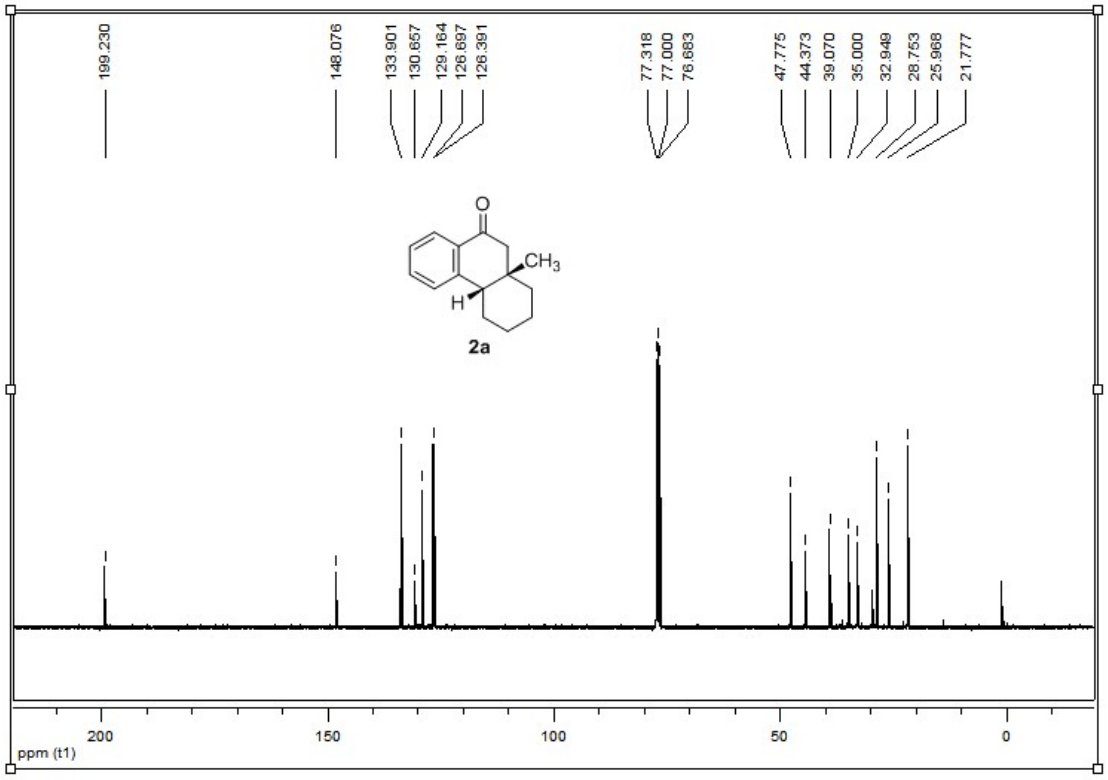
Reference:

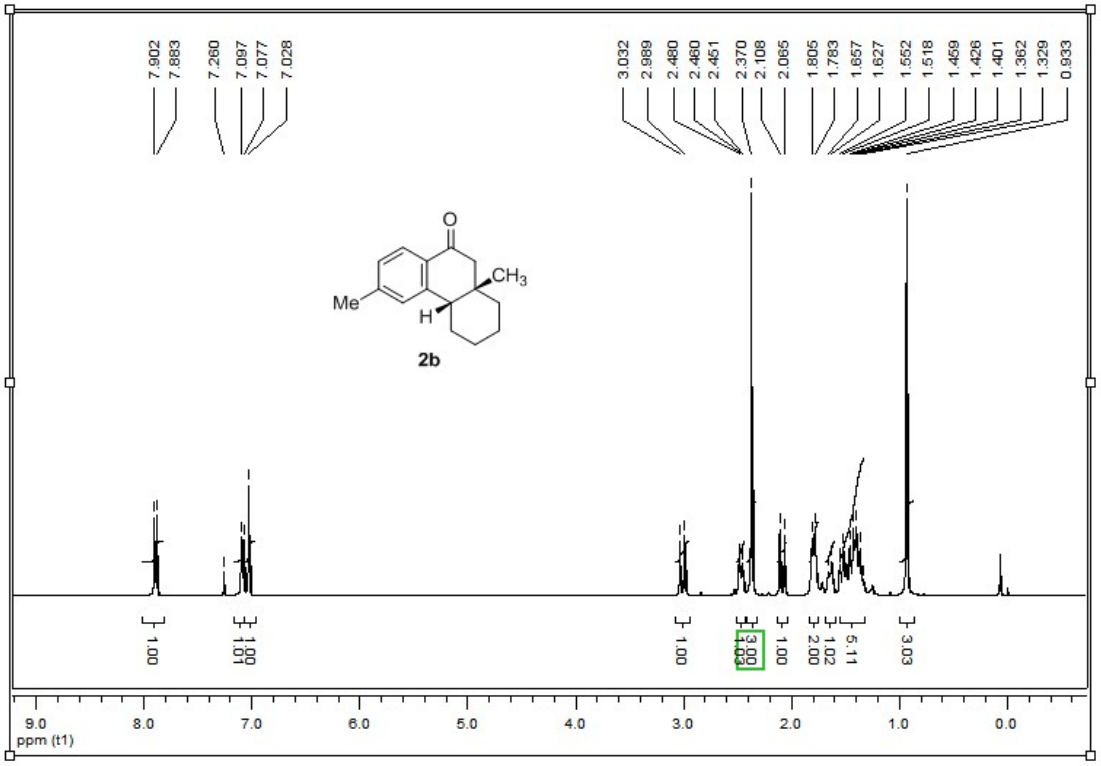
[1] (a) M. T. Liu, J. Ho, J. K. Liu, R. Purakait, U. N. Morzan, L. Ahmed, V. S. Batista, H. Matsunami and K. Ryan, *Org. Biomol. Chem.*, 2018, **16**, 2541. (b) L. Fang, S. Fan, W. Wu, T. Li and J. Zhu, *Chem. Commun.*, 2021, **57**, 7386. (c) F. Le Vaillant, M. Garreau, S. Nicolai, G. Gryn'ova, C. Corminboeuf and J. Waser, *Chem. Sci.*, 2018, **9**, 5883.

[2] (a) W. Shu, A. Lorente, E. Gómez-Bengoa and C. Nevado, *Nat. Commun.*, 2017, **8**, 13832. (b) W. Shu and C. Nevado, *Angew. Chem., Int. Ed.*, 2017, **56**, 1881.

Copies of NMR spectra of the products:



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2.065
1.805
1.783
1.657
1.627
1.552
1.518
1.459
1.426
1.401
1.362
1.329
0.933
O
CH3
Me
H
2b
1.00
1.01
1.00
3.09
1.00
2.00
1.02
5.11
3.03
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
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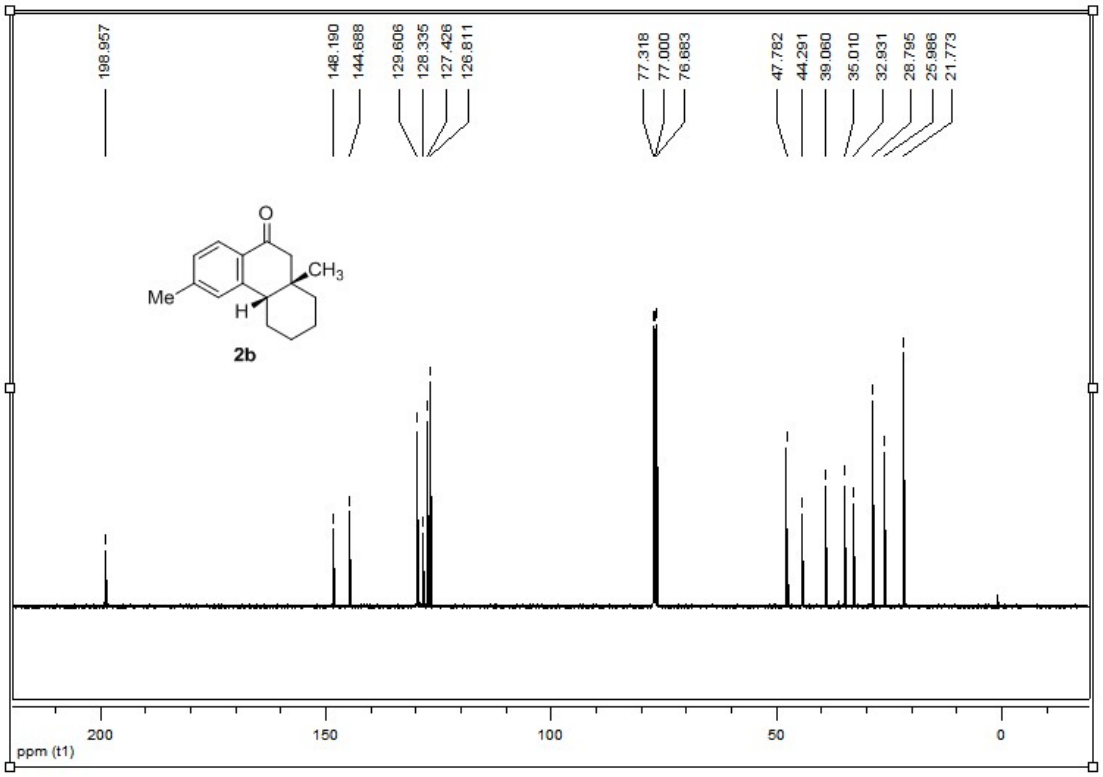
0.0
ppm (t1)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39.060
35.010
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25.986
21.773
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CH3
Me
H
2b
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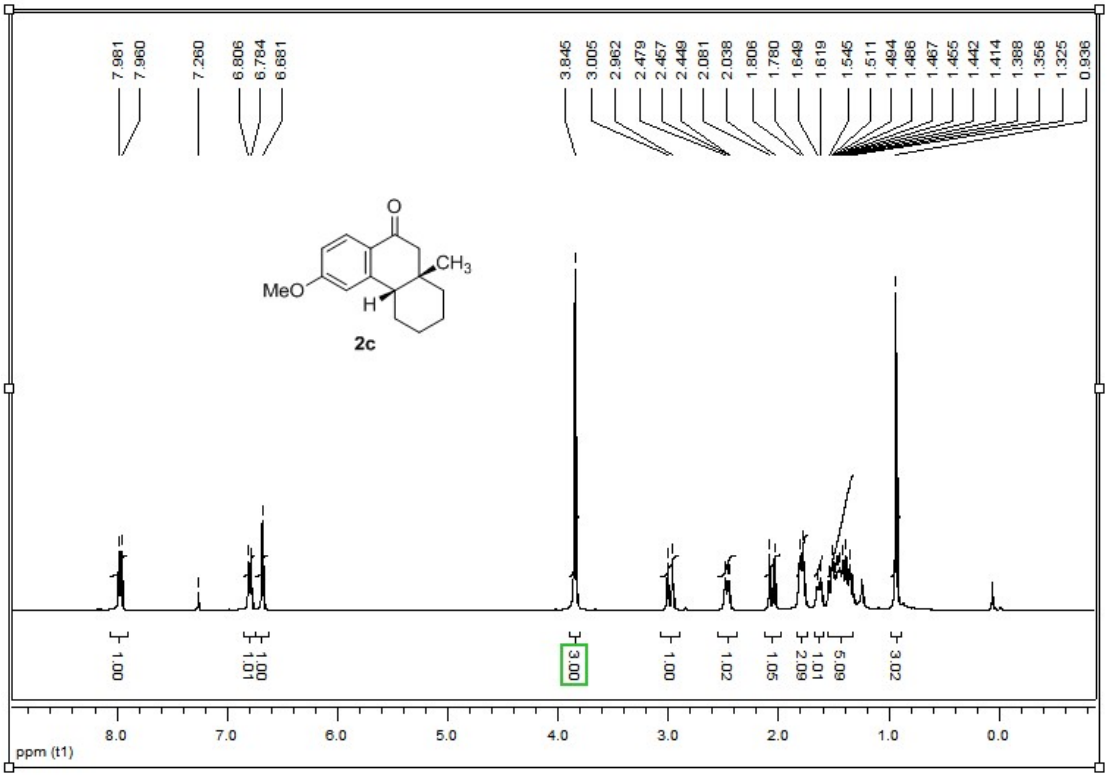
150
100
50
0
ppm (t1)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2.449
2.081
2.038
1.806
1.780
1.649
1.619
1.545
1.511
1.494
1.486
1.467
1.455
1.442
1.414
1.388
1.356
1.325
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MeO
H
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1.00
1.01
3.00
1.00
1.02
1.06
2.09
1.01
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7.0
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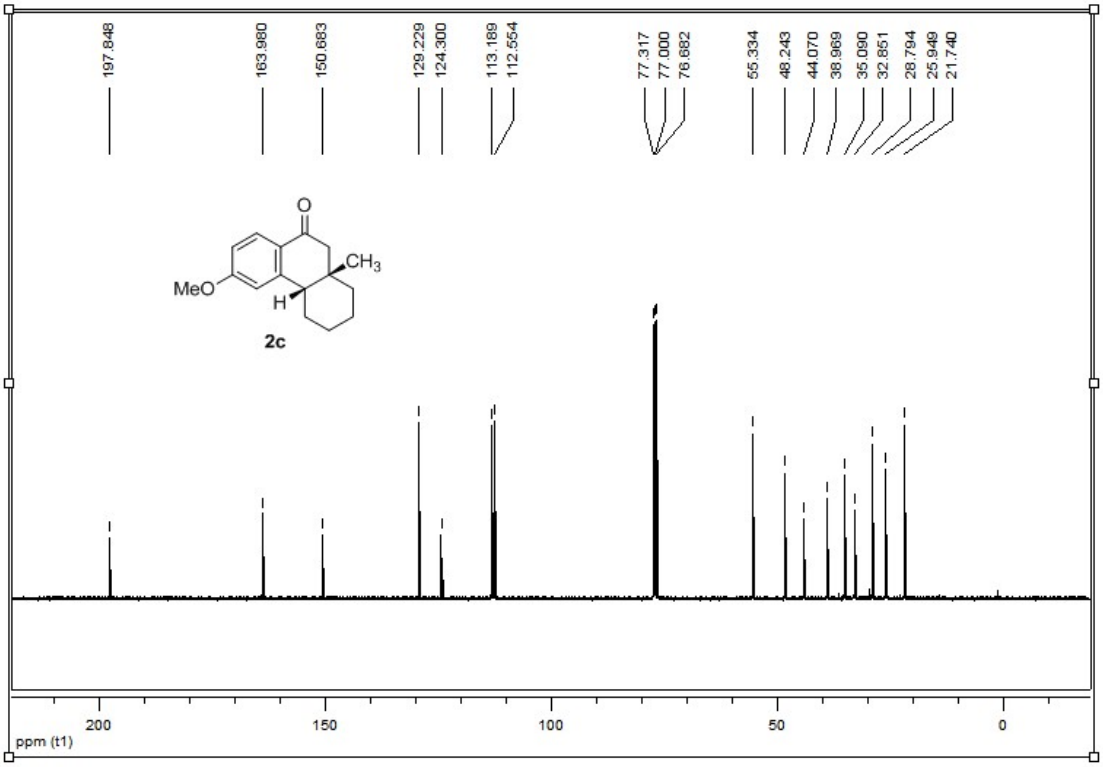
ppm (t1)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38.969
35.090
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28.794
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21.740
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MeO
H
2c
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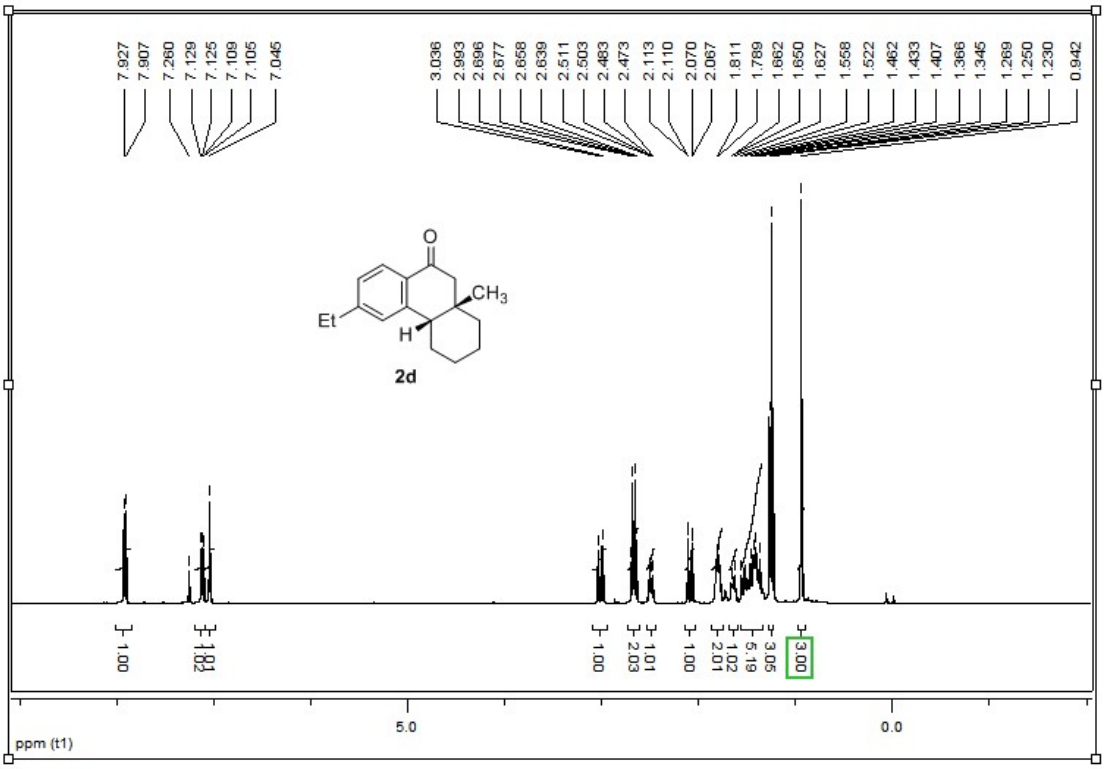
50
0
ppm (t1)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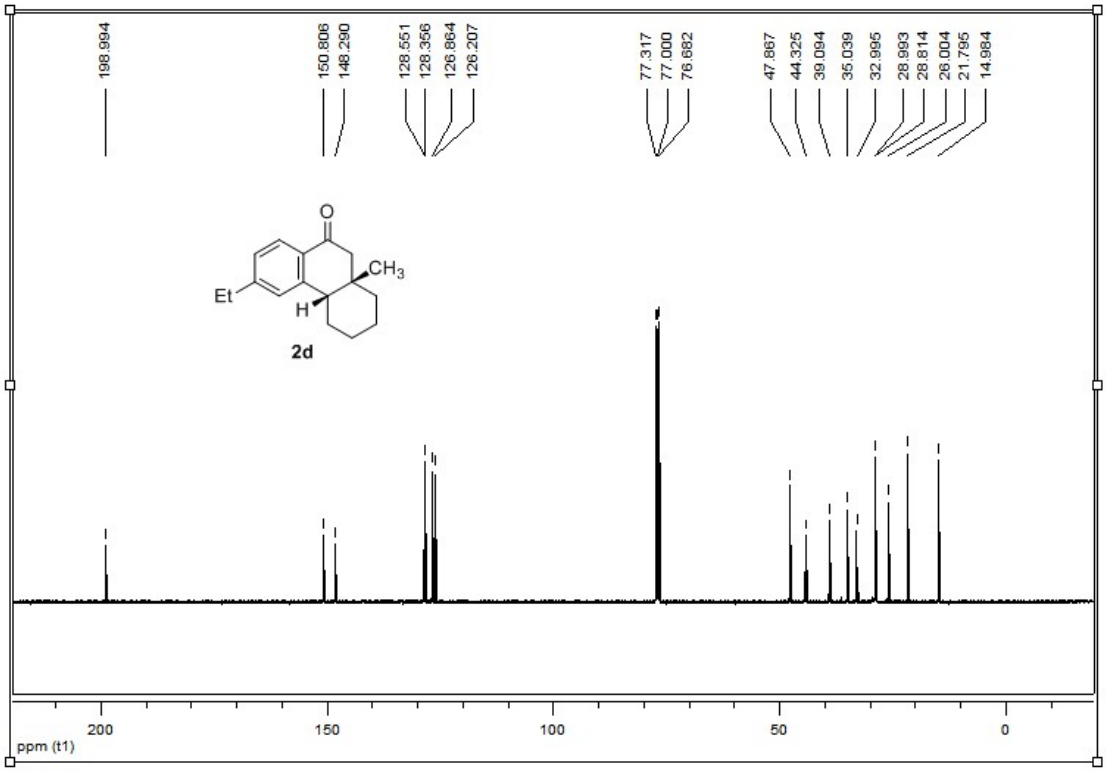
ppm (t1)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39.094
35.039
32.995
28.993
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Et
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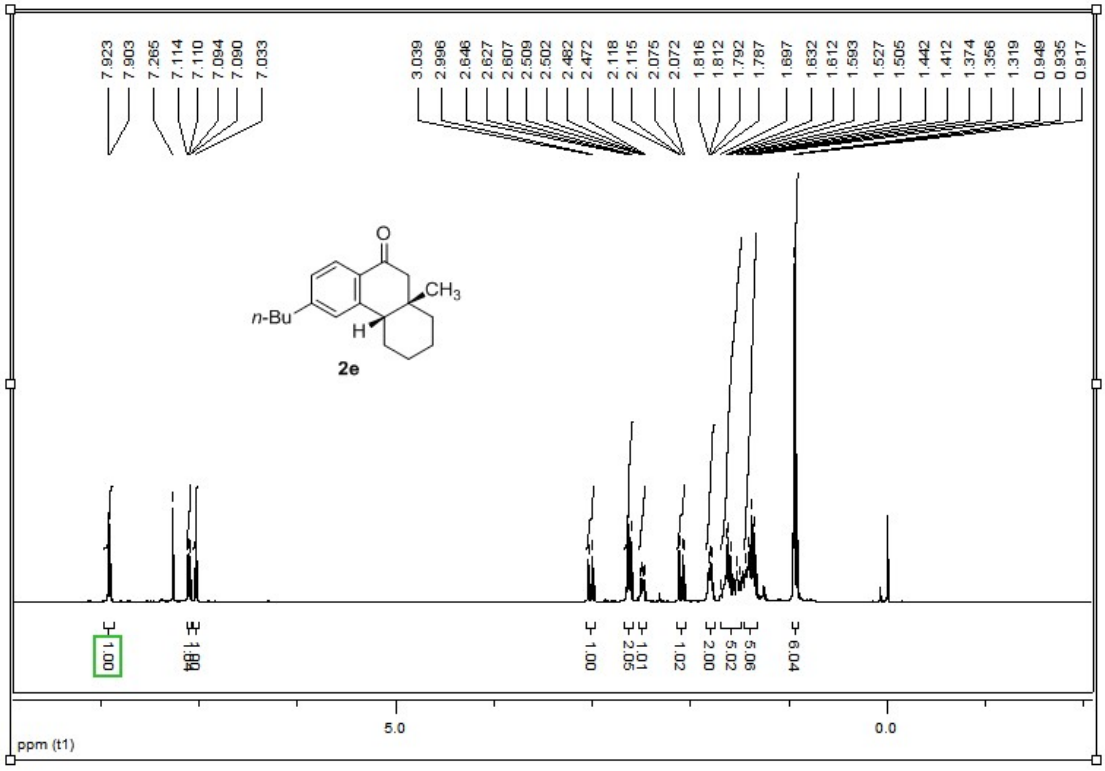
ppm (t1)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H
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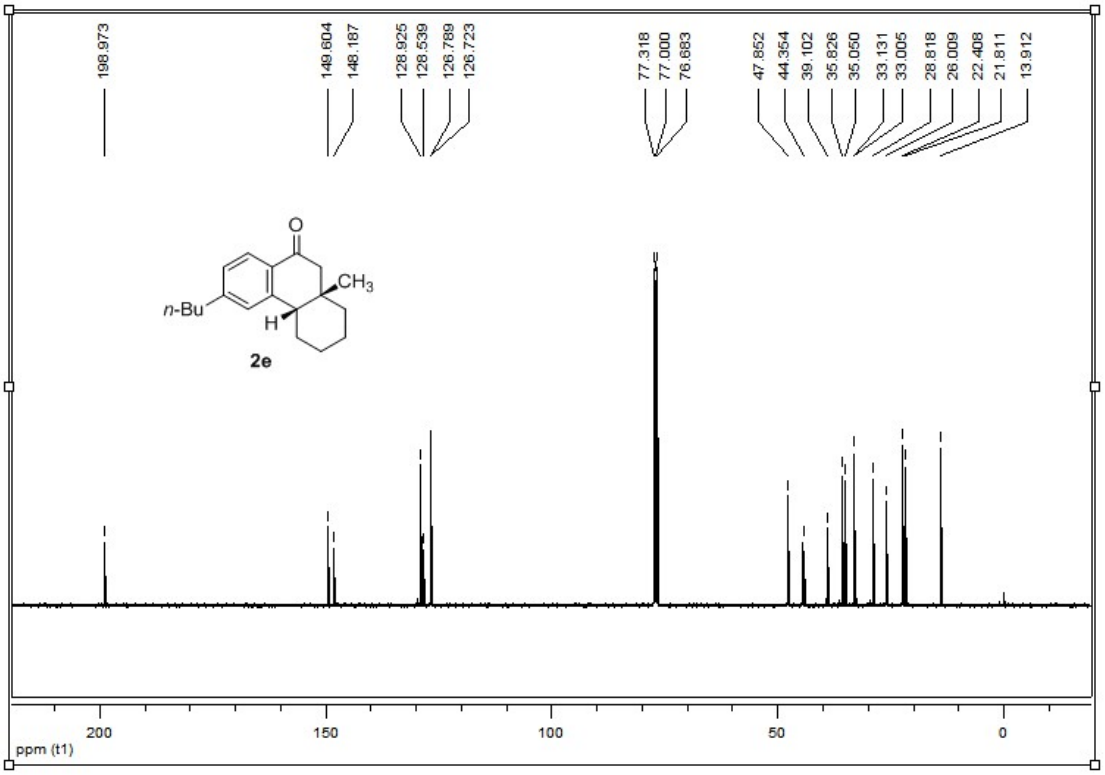
ppm (t1)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35.050
33.131
33.005
28.818
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n-Bu
H
2e
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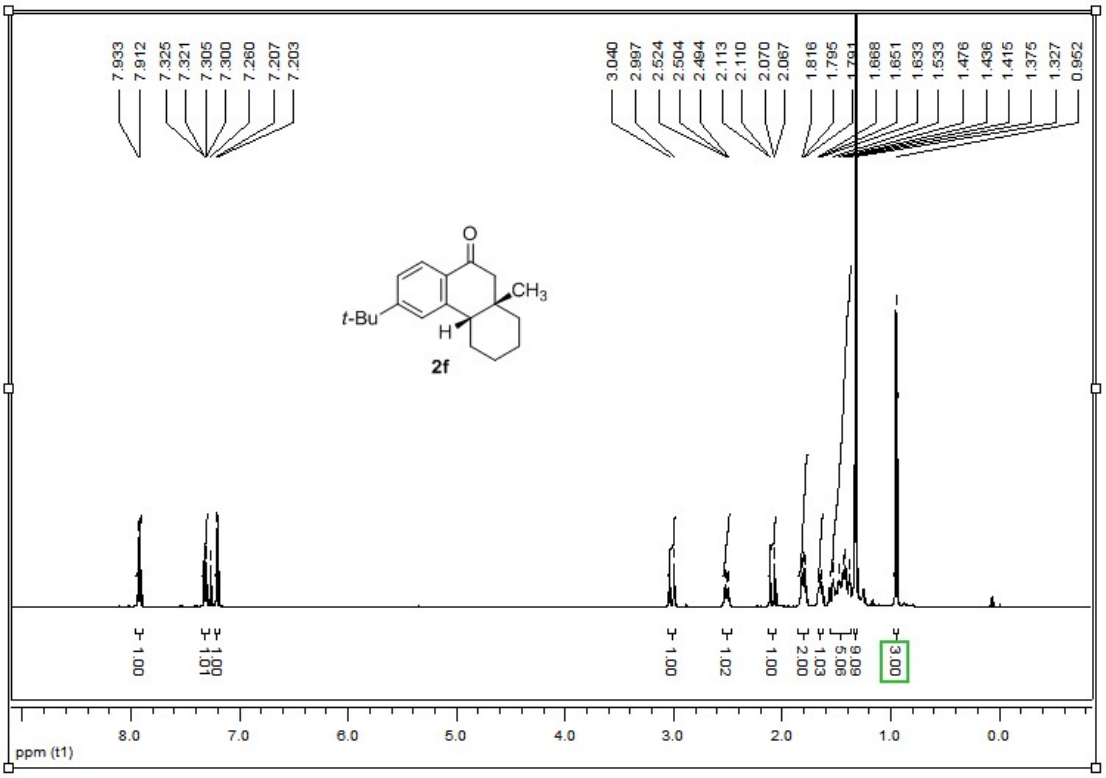
ppm (t1)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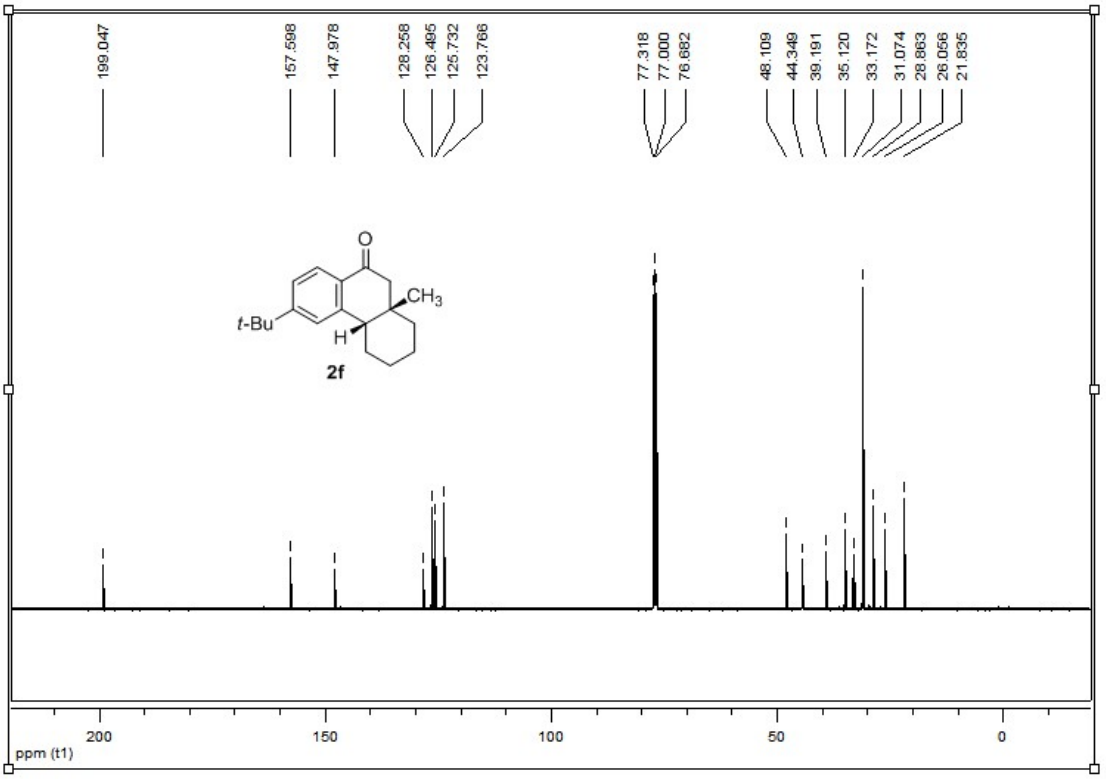
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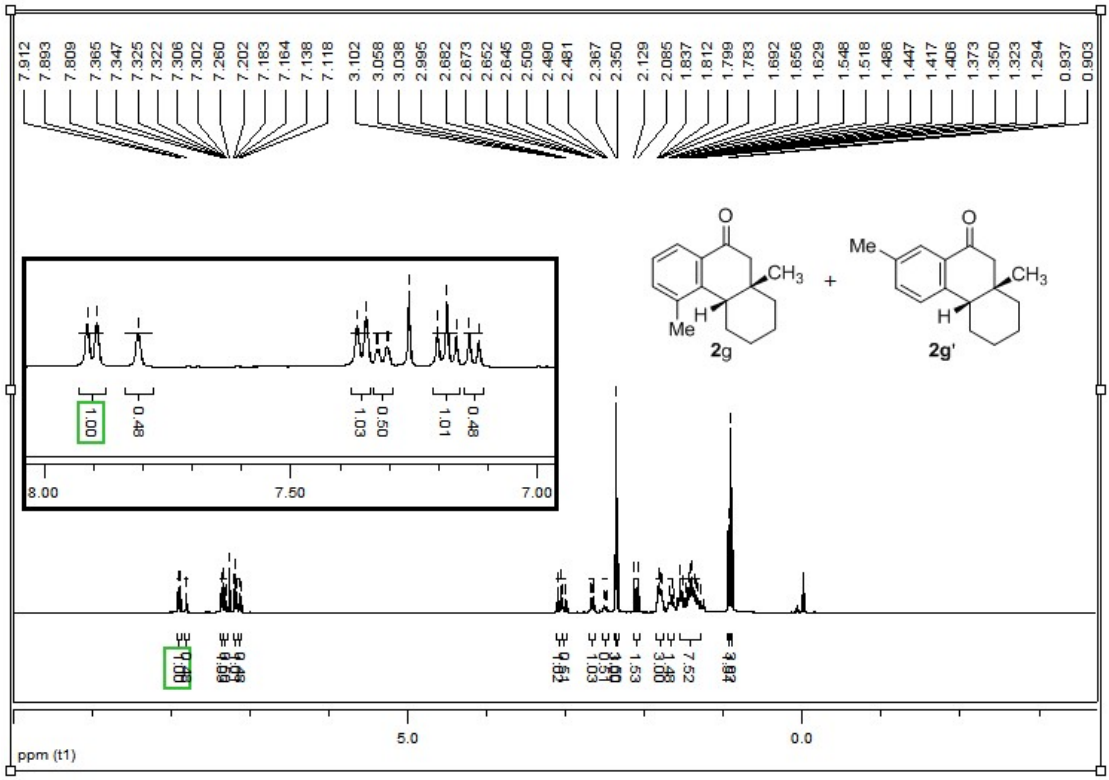
50
0
ppm (t1)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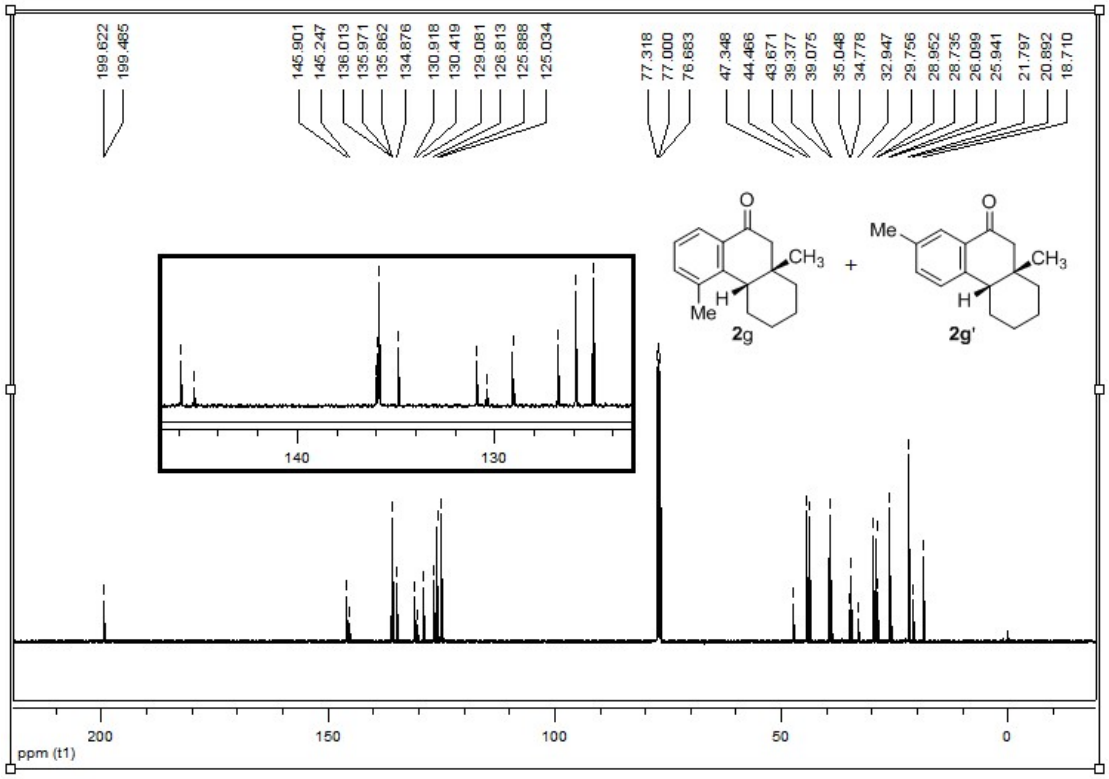
2g'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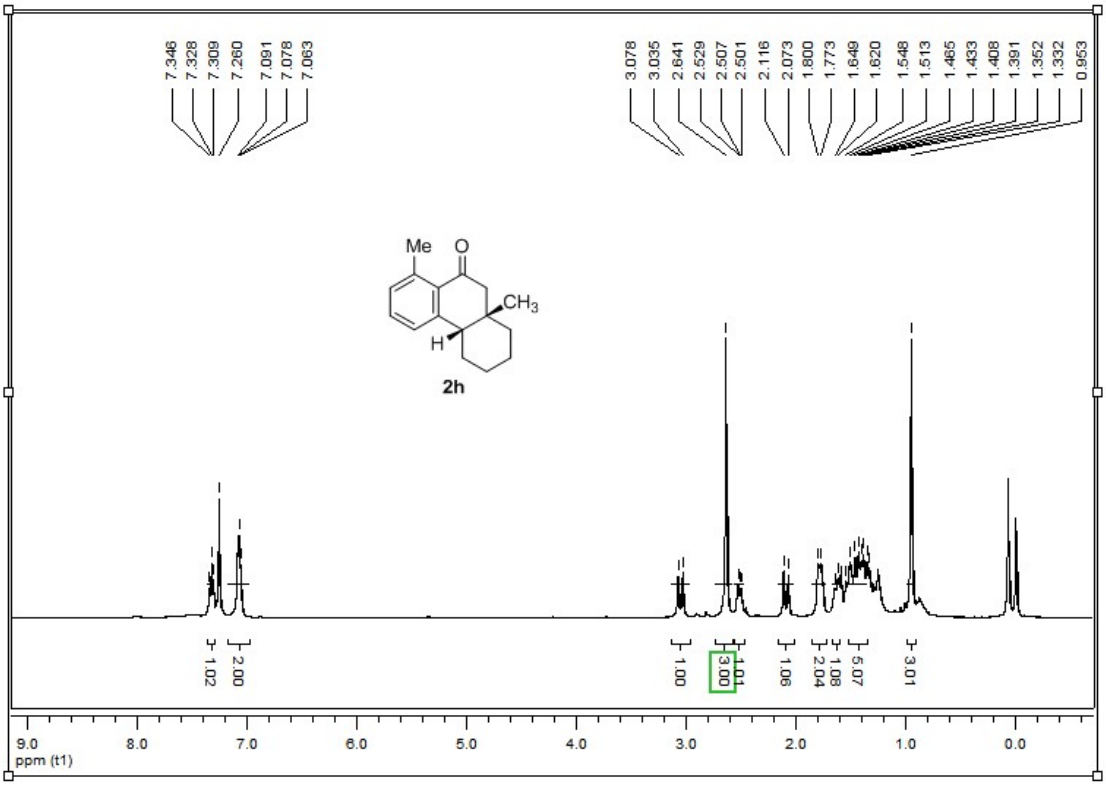
2g
2g'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7.260
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7.063
3.078
3.035
2.641
2.529
2.507
2.501
2.116
2.073
1.800
1.773
1.649
1.620
1.548
1.513
1.465
1.433
1.408
1.391
1.352
1.332
0.953
Me
O
CH3
H
2h
2.02
1.00
3.00
1.01
1.06
2.04
1.08
6.07
3.01
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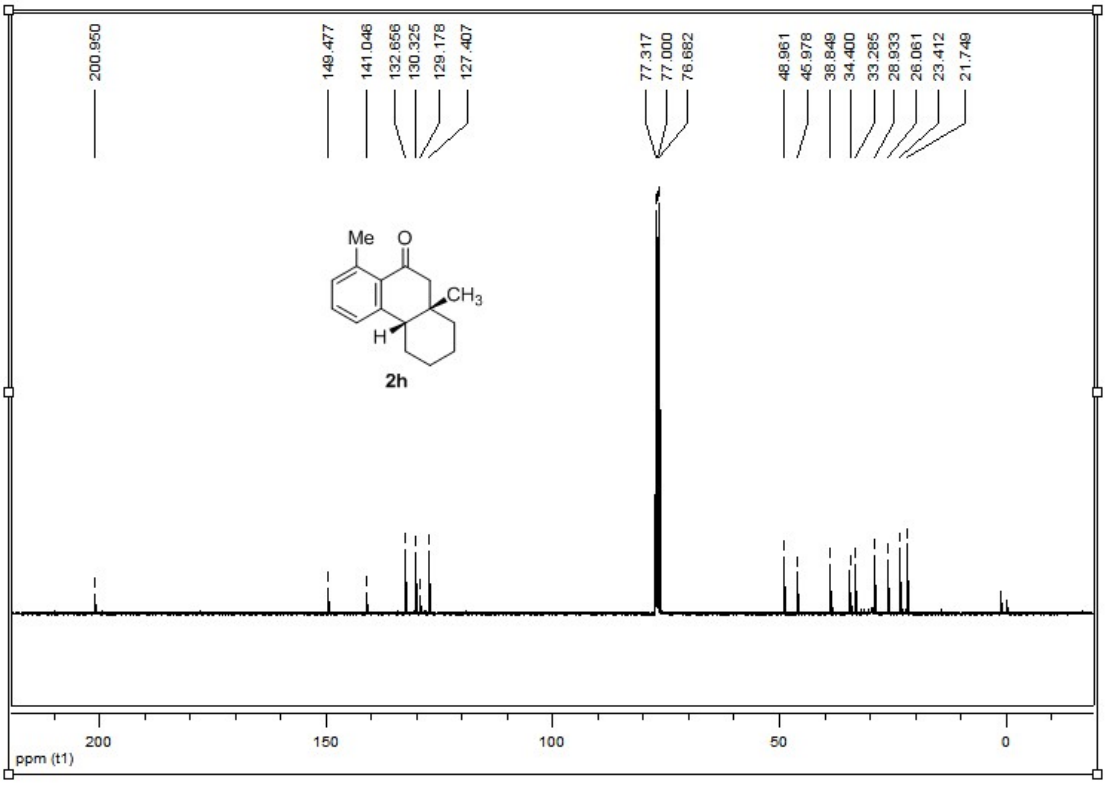
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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141.046
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130.325
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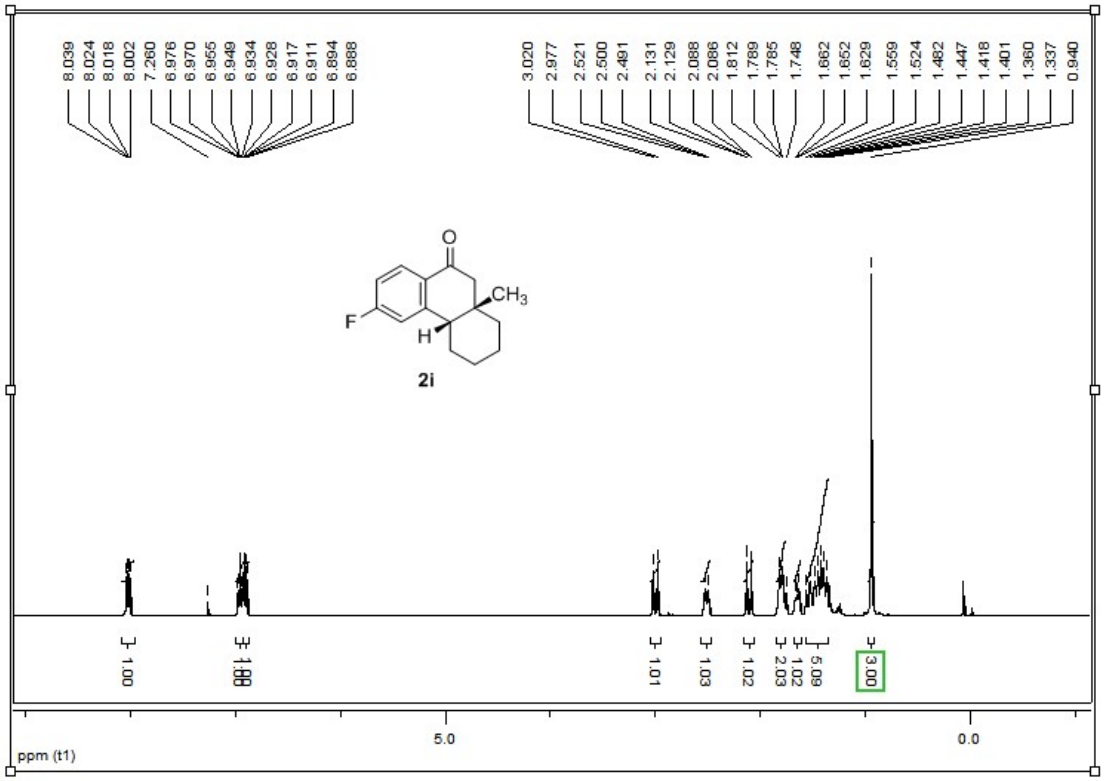
127.407
77.317
77.000
76.682
48.961
45.978
38.849
34.400
33.285
28.933
26.061
23.412
21.749
Me
O
CH3
H
2h
200
150
100
50
0
ppm (t1)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8.018
8.002
7.260
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6.955
6.949
6.934
6.928
6.917
6.911
6.894
6.888
3.020
2.977
2.521
2.500
2.491
2.131
2.129
2.088
2.086
1.812
1.789
1.785
1.748
1.662
1.652
1.629
1.559
1.524
1.482
1.447
1.418
1.401
1.360
1.337
0.940
O
CH3
F
H
2i
1.00
3.18
1.01
1.03
1.02
2.03
5.09
3.00
5.0
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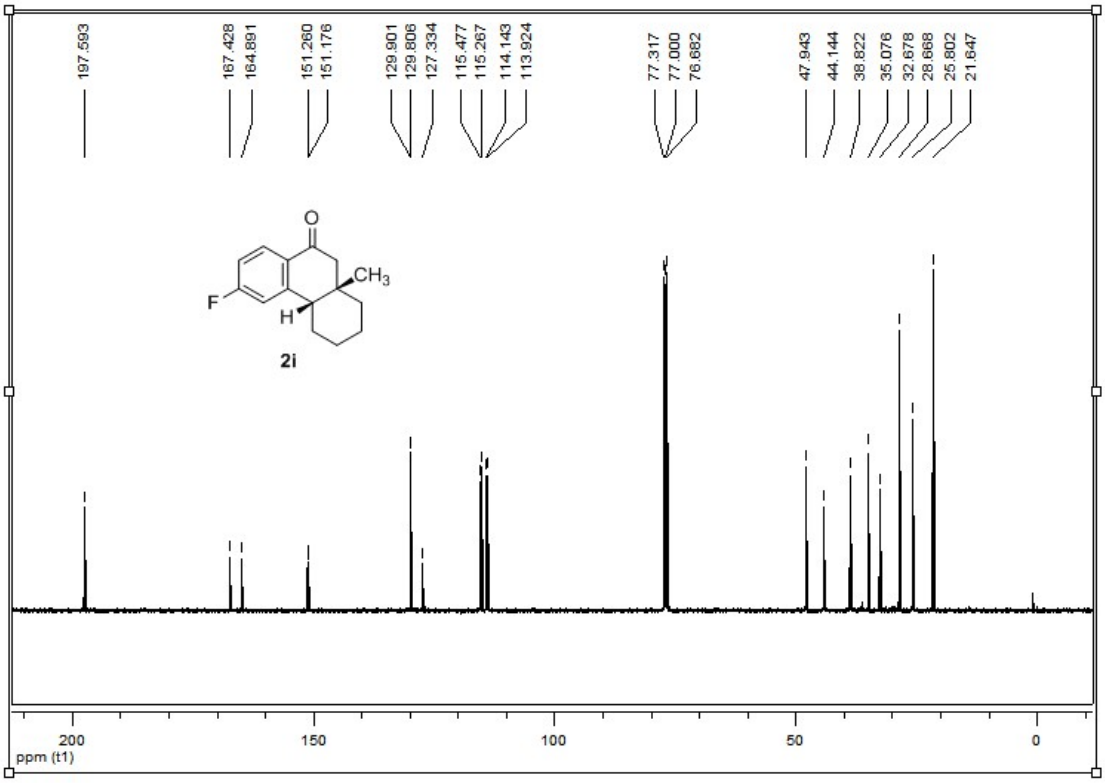
ppm (t1)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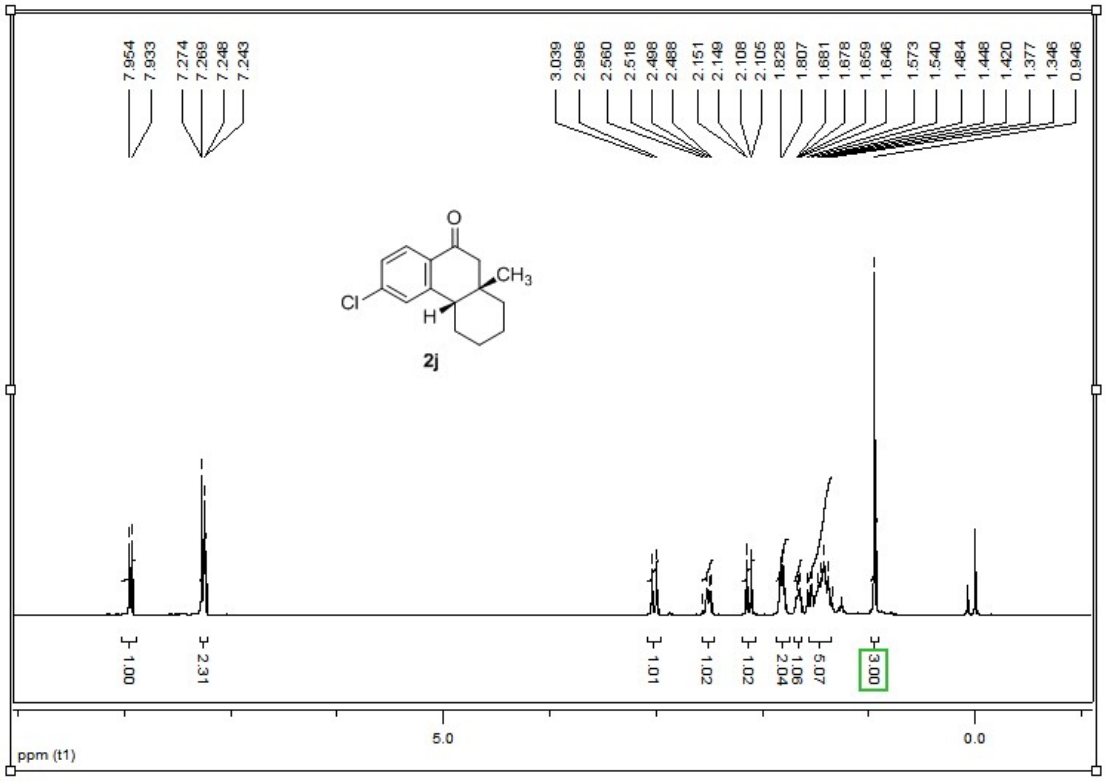
167.428
164.891
151.260
151.176
129.901
129.806
127.334
115.477
115.267
114.143
113.924
77.317
77.000
76.682
47.943
44.144
38.822
35.076
32.678
28.868
25.802
21.647
O
CH3
F
H
2i
200
150
100
50
0
ppm (t1)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7.933
7.274
7.269
7.248
7.243
3.039
2.996
2.560
2.518
2.498
2.488
2.151
2.149
2.108
2.105
1.828
1.807
1.681
1.678
1.659
1.646
1.573
1.540
1.484
1.448
1.420
1.377
1.346
0.946
O
CH3
Cl
H
2j
1.00
2.31
1.01
1.02
1.02
2.04
1.06
5.07
3.00
5.0
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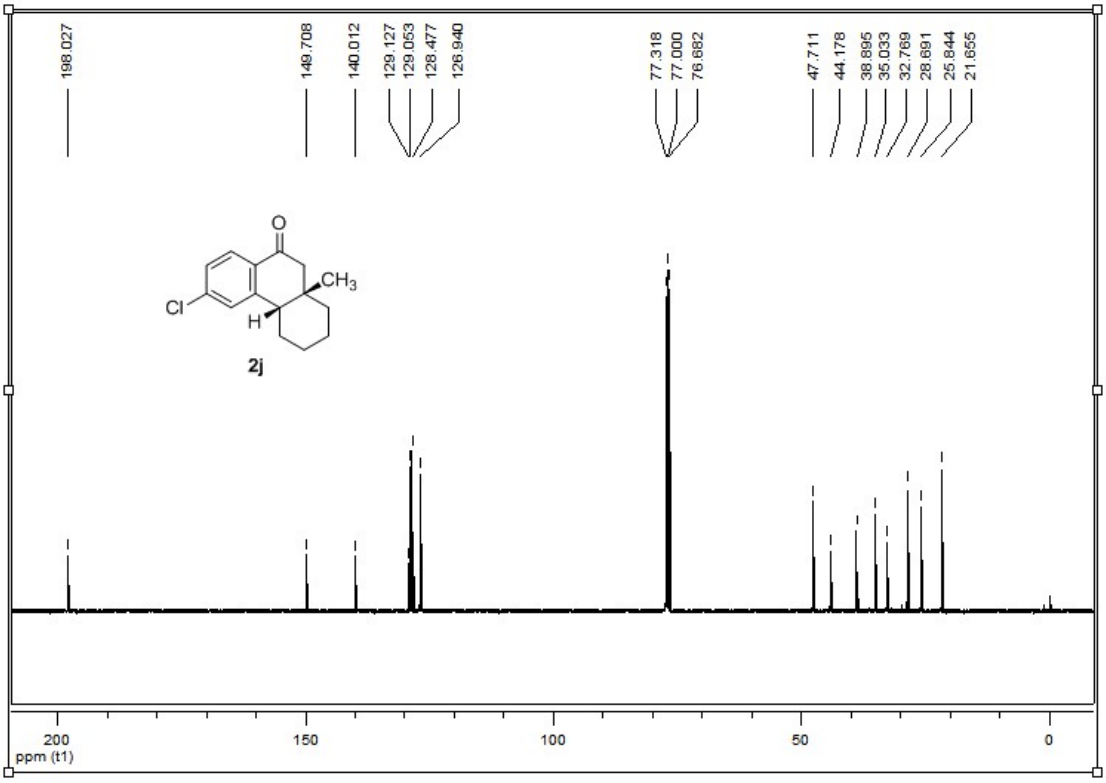
ppm (t1)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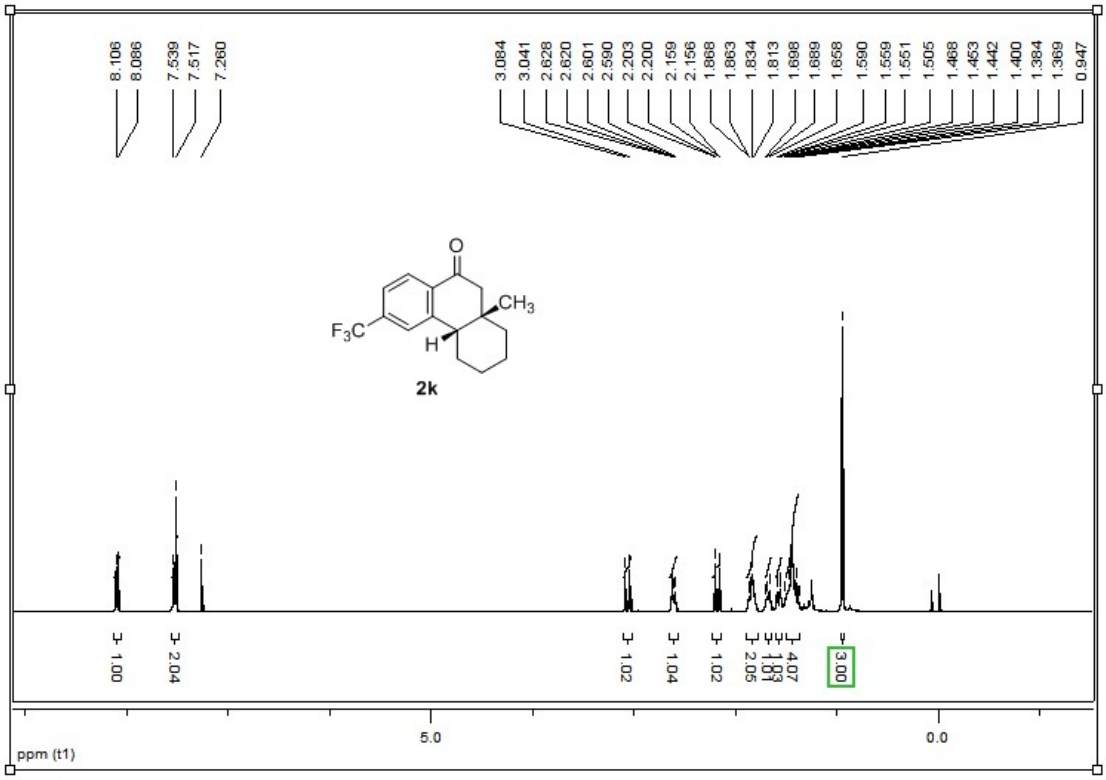
129.053
128.477
126.940
77.318
77.000
76.682
47.711
44.178
38.895
35.033
32.769
28.691
25.844
21.655
O
CH3
Cl
H
2j
200
150
100
50
0
ppm (t1)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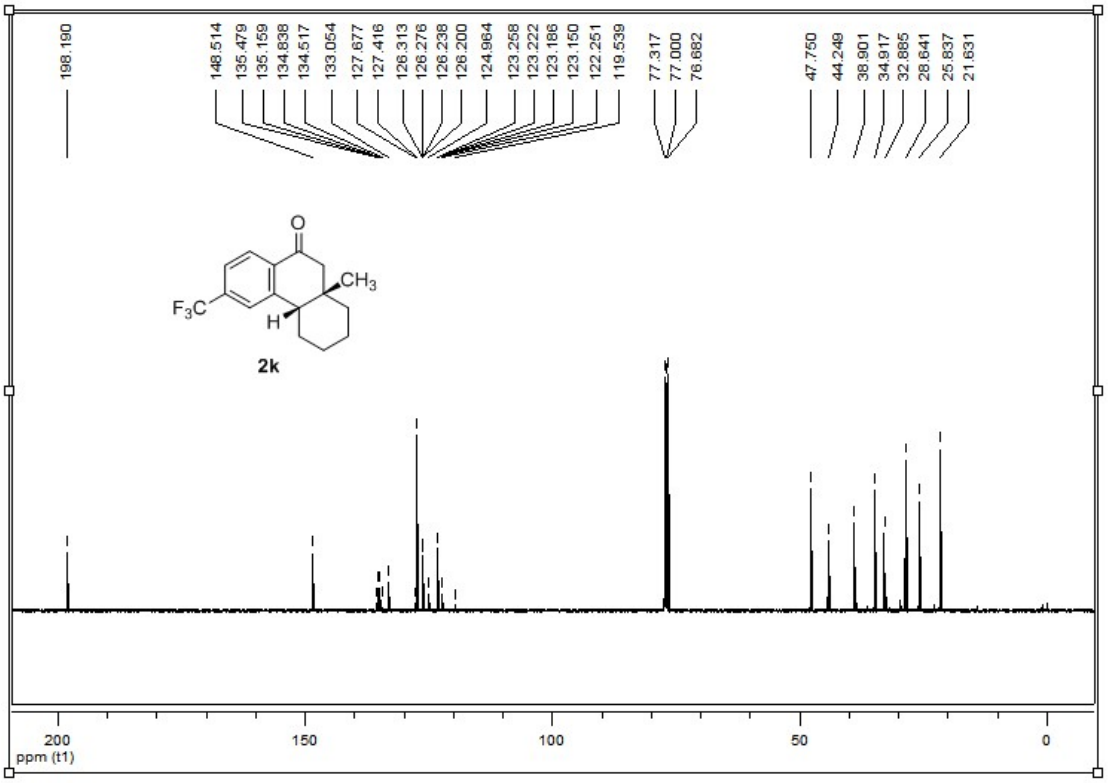
8.086
7.539
7.517
7.260
3.084
3.041
2.628
2.620
2.601
2.590
2.203
2.200
2.159
2.156
1.868
1.863
1.834
1.813
1.698
1.689
1.658
1.590
1.559
1.551
1.505
1.468
1.453
1.442
1.400
1.384
1.369
0.947
O
CH3
F3C
H
2k
1.00
2.04
1.02
1.04
1.02
2.05
1.83
4.07
3.00
5.0
0.0
ppm (t1)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135.479
135.159
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134.517
133.054
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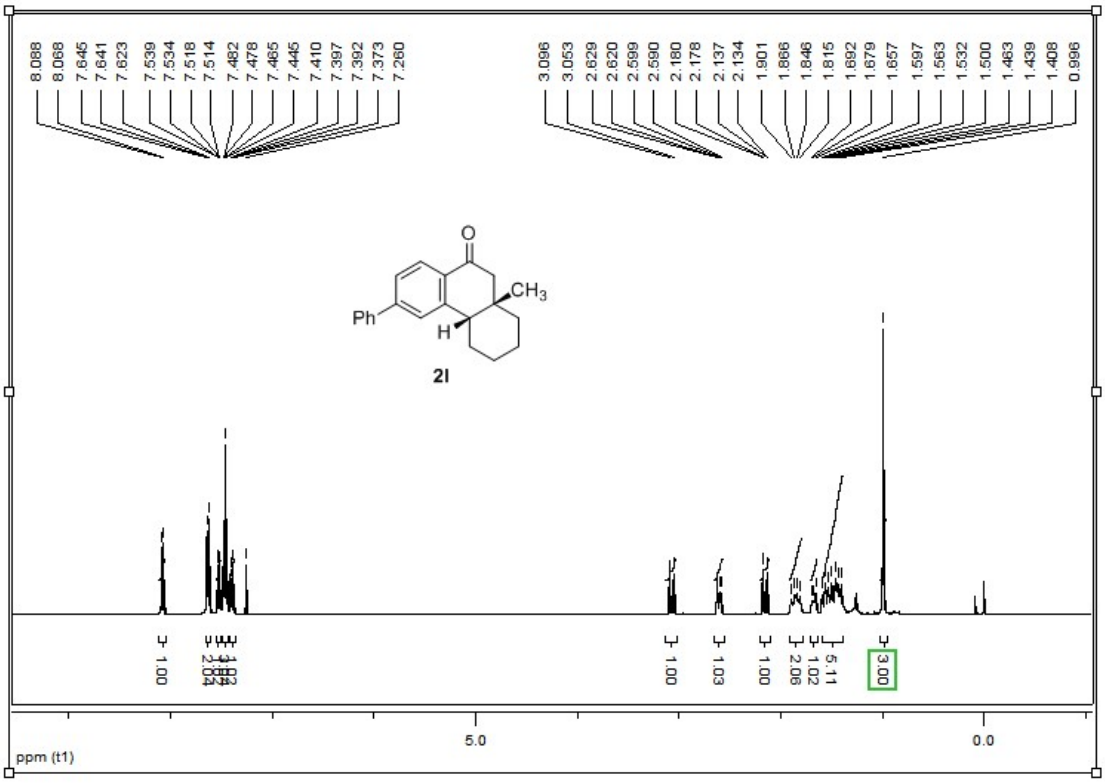
126.313
126.276
126.238
126.200
124.964
123.258
123.222
123.186
123.150
122.251
119.539
77.317
77.000
76.682
47.750
44.249
38.901
34.917
32.885
28.641
25.837
21.631
O
CH3
F3C
H
2k
200
150
100
50
0
ppm (t1)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7.534
7.518
7.514
7.482
7.478
7.465
7.445
7.410
7.397
7.392
7.373
7.260
3.096
3.053
2.629
2.620
2.599
2.590
2.180
2.178
2.137
2.134
1.901
1.866
1.846
1.815
1.692
1.679
1.657
1.597
1.563
1.532
1.500
1.483
1.439
1.408
0.996
O
CH3
Ph
H
2l
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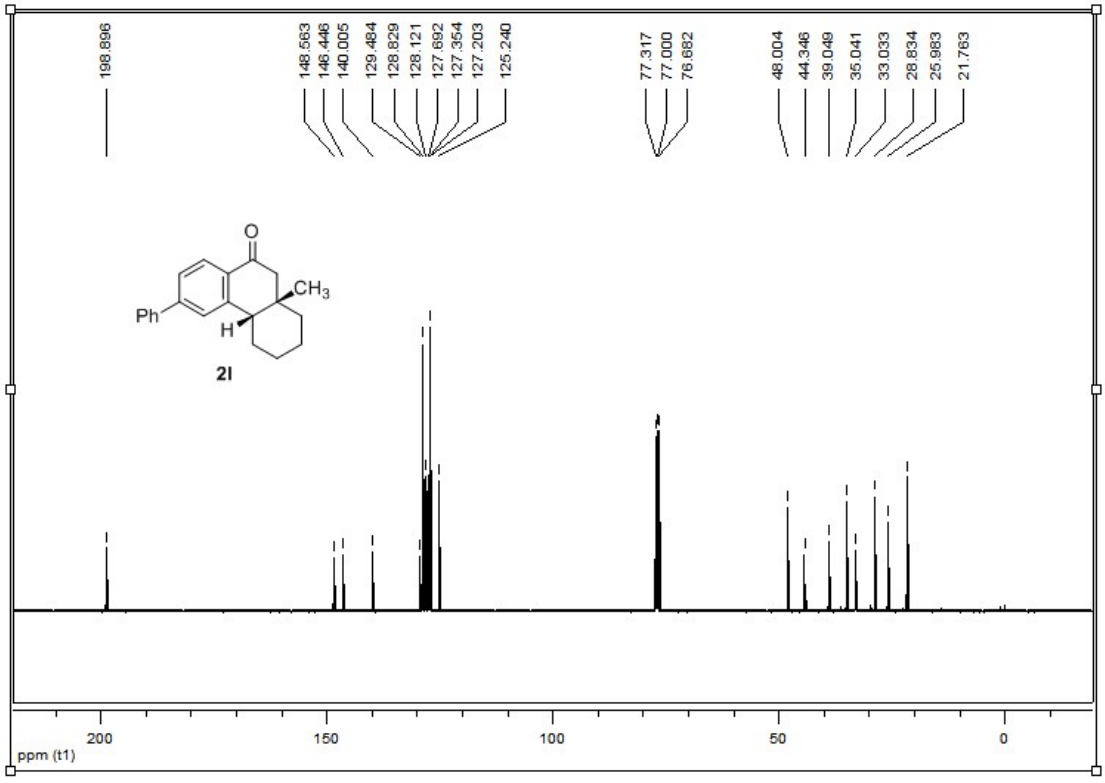
1.03
1.00
2.06
1.02
5.11
3.00
5.0
0.0
ppm (t1)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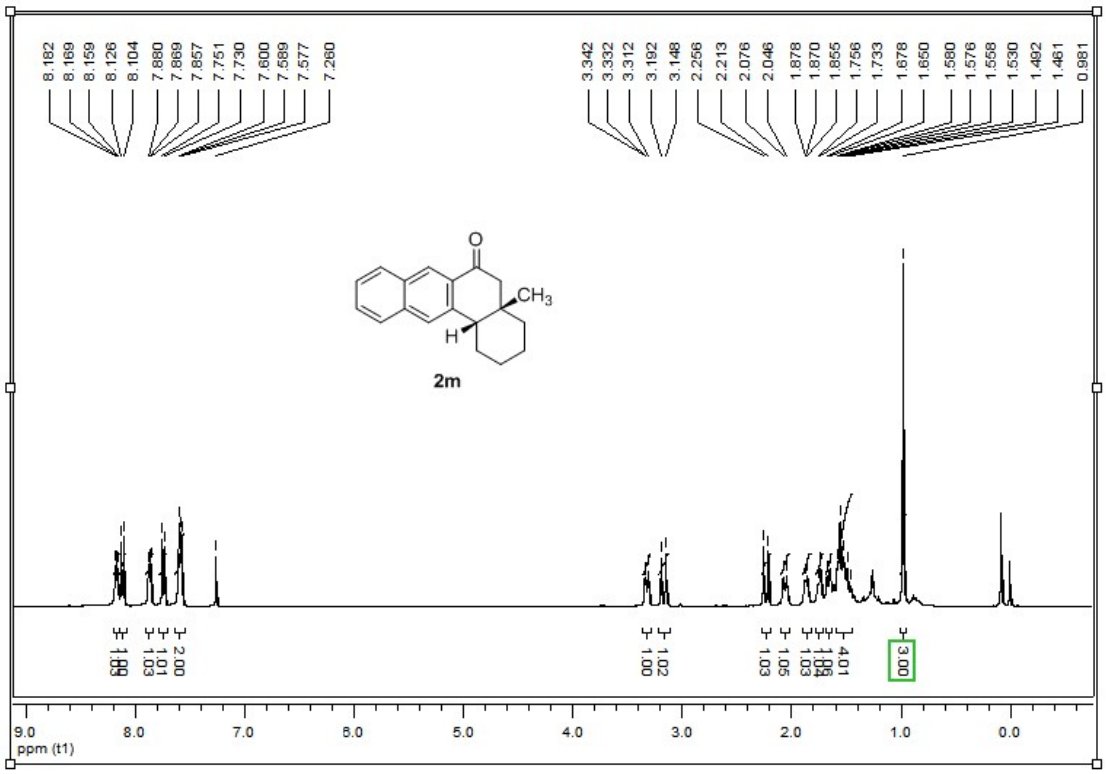
127.692
127.354
127.203
125.240
77.317
77.000
76.682
48.004
44.346
39.049
35.041
33.033
28.834
25.983
21.763
O
CH3
Ph
H
2l
200
150
100
50
0
ppm (t1)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8.169
8.159
8.126
8.104
7.880
7.869
7.857
7.751
7.730
7.600
7.589
7.577
7.260
3.342
3.332
3.312
3.192
3.148
2.256
2.213
2.076
2.046
1.878
1.870
1.855
1.756
1.733
1.678
1.650
1.580
1.576
1.558
1.530
1.492
1.461
0.981
O
CH3
H
2m
1.09
1.03
1.01
2.00
1.00
1.02
1.03
1.05
1.03
1.03
1.01
3.00
9.0
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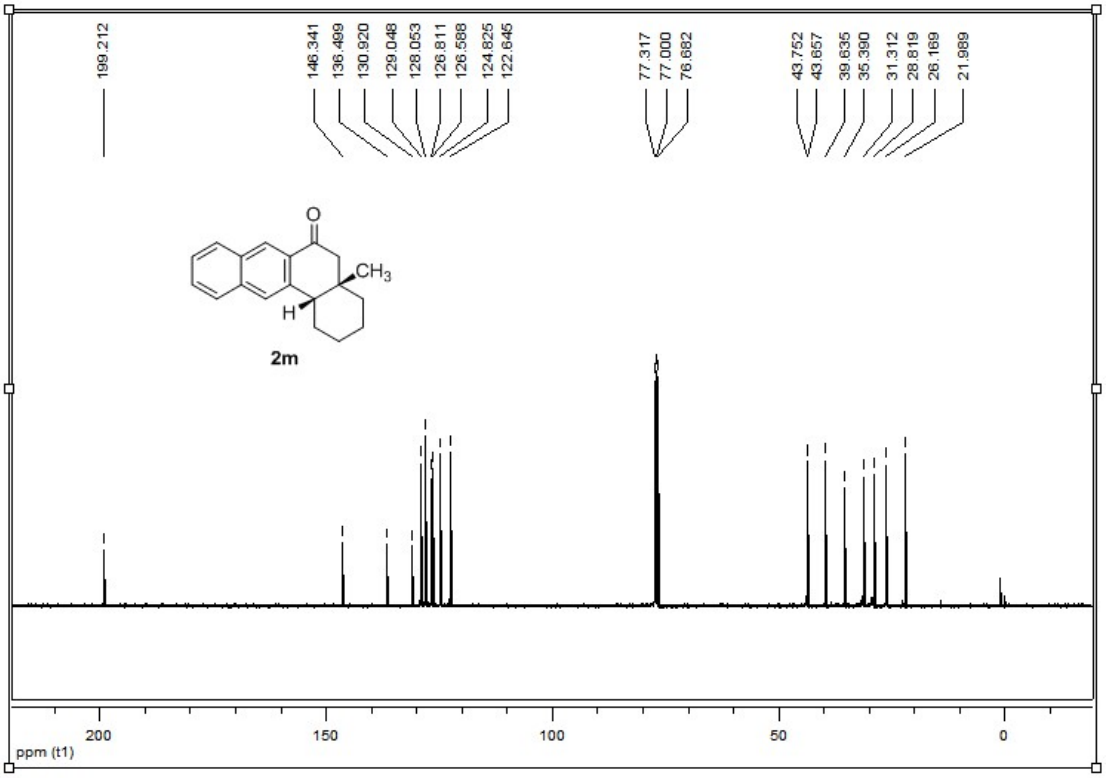
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


199.212
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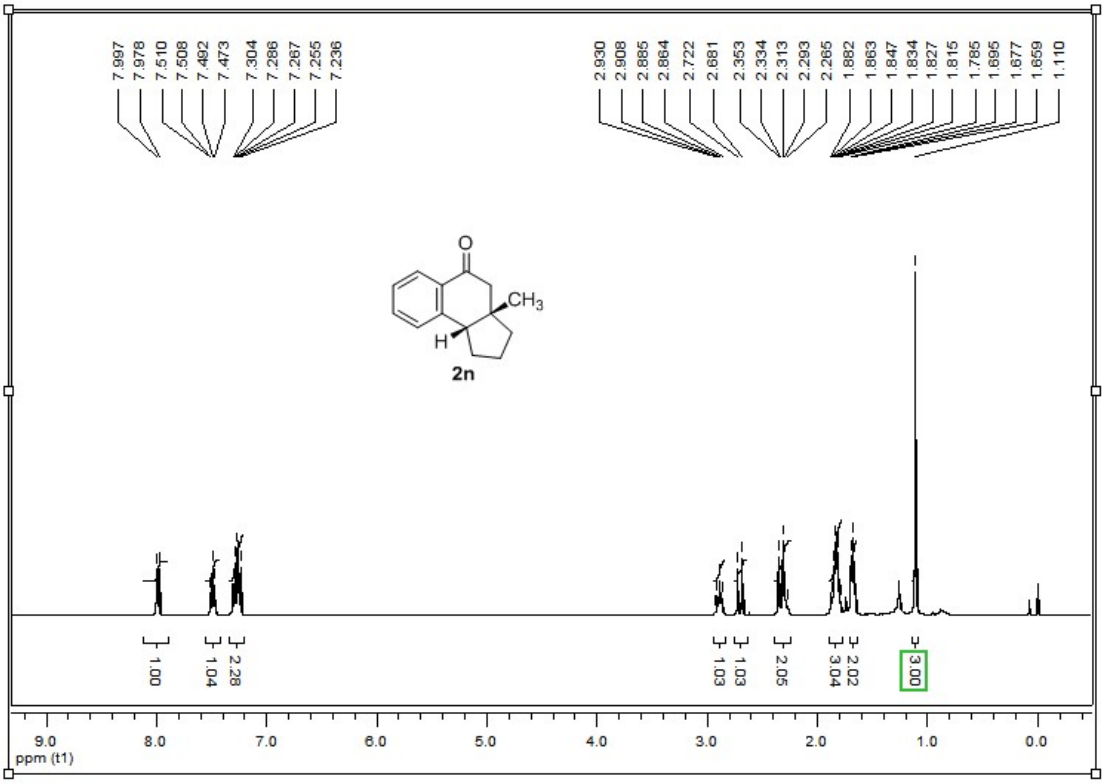
130.920
129.048
128.053
126.811
126.588
124.825
122.645
77.317
77.000
76.682
43.752
43.657
39.635
35.390
31.312
28.819
26.169
21.989
O
CH3
H
2m
200
150
100
50
0
ppm (t1)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7.508
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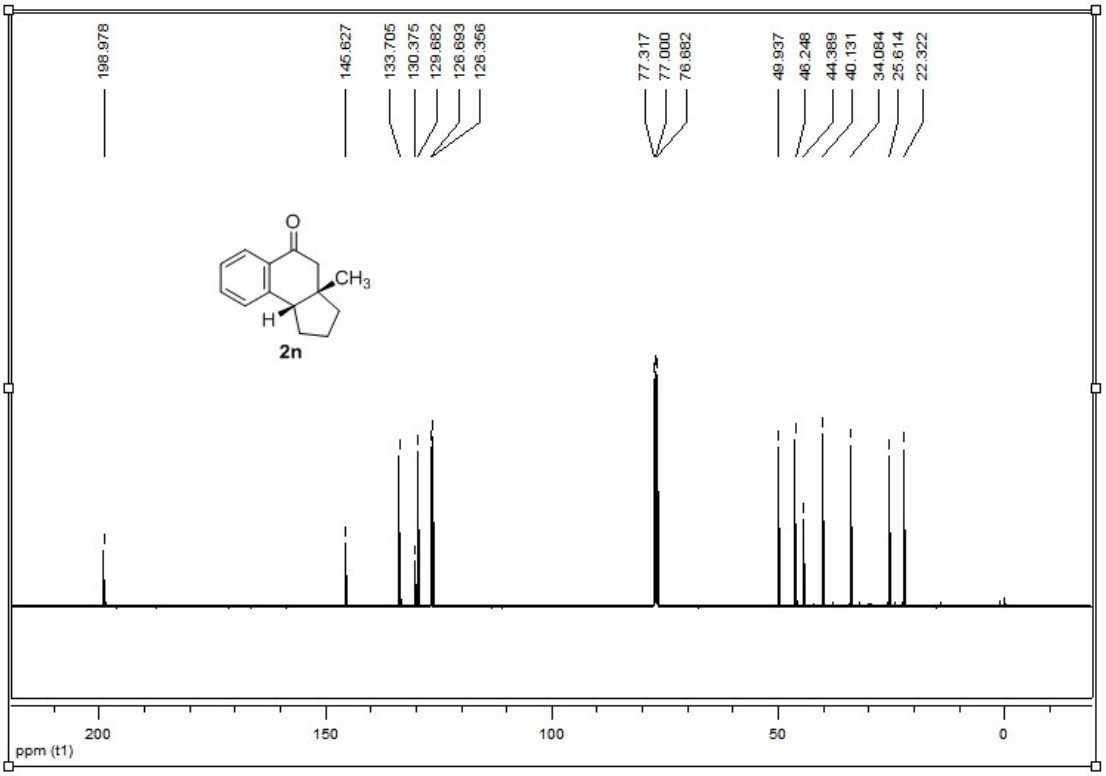
7.473
7.304
7.286
7.267
7.255
7.236
2.930
2.908
2.885
2.864
2.722
2.681
2.353
2.334
2.313
2.293
2.265
1.882
1.863
1.847
1.834
1.827
1.815
1.785
1.695
1.677
1.659
1.110
O
CH3
H
2n
1.00
1.04
2.28
1.03
1.03
2.05
3.04
2.02
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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129.682
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126.356
77.317
77.000
76.682
49.937
46.248
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40.131
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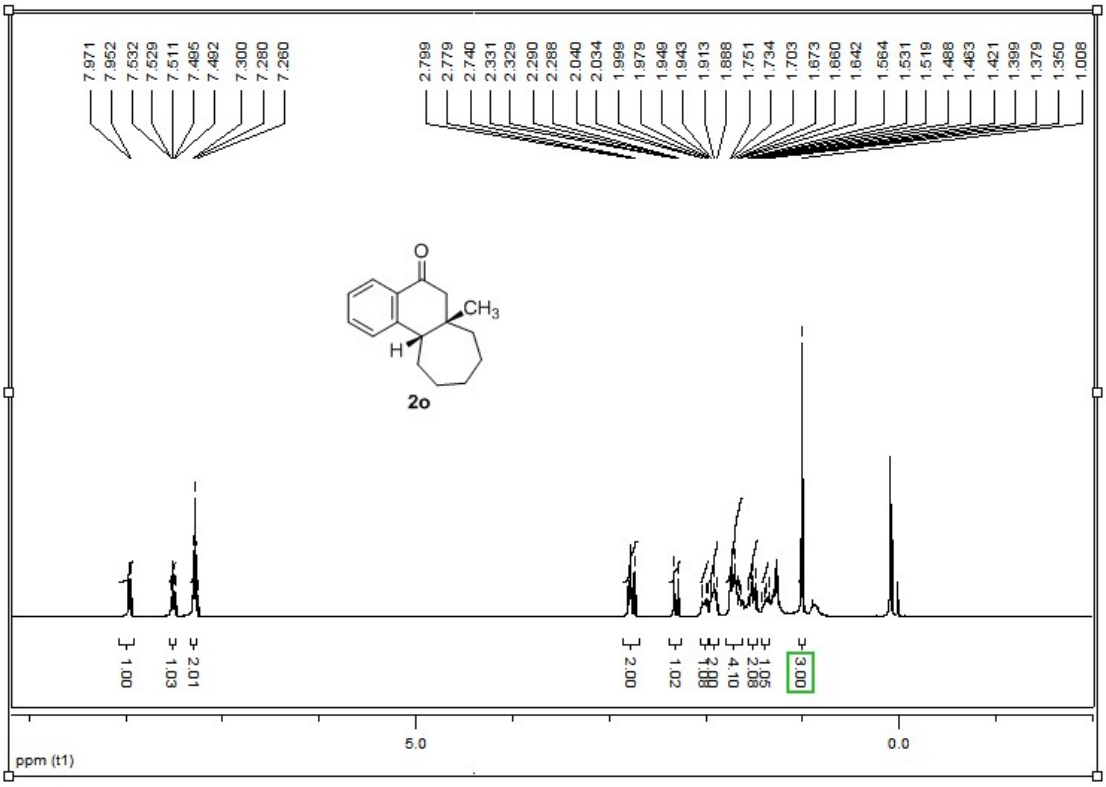
25.614
22.322
O
CH3
H
2n
200
150
100
50
0
ppm (t1)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7.511
7.495
7.492
7.300
7.280
7.260
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2.779
2.740
2.331
2.329
2.290
2.288
2.040
2.034
1.999
1.979
1.949
1.943
1.913
1.888
1.751
1.734
1.703
1.673
1.660
1.642
1.564
1.531
1.519
1.488
1.463
1.421
1.399
1.379
1.350
1.008
O
CH3
H
2o
1.00
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1.02
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3.00
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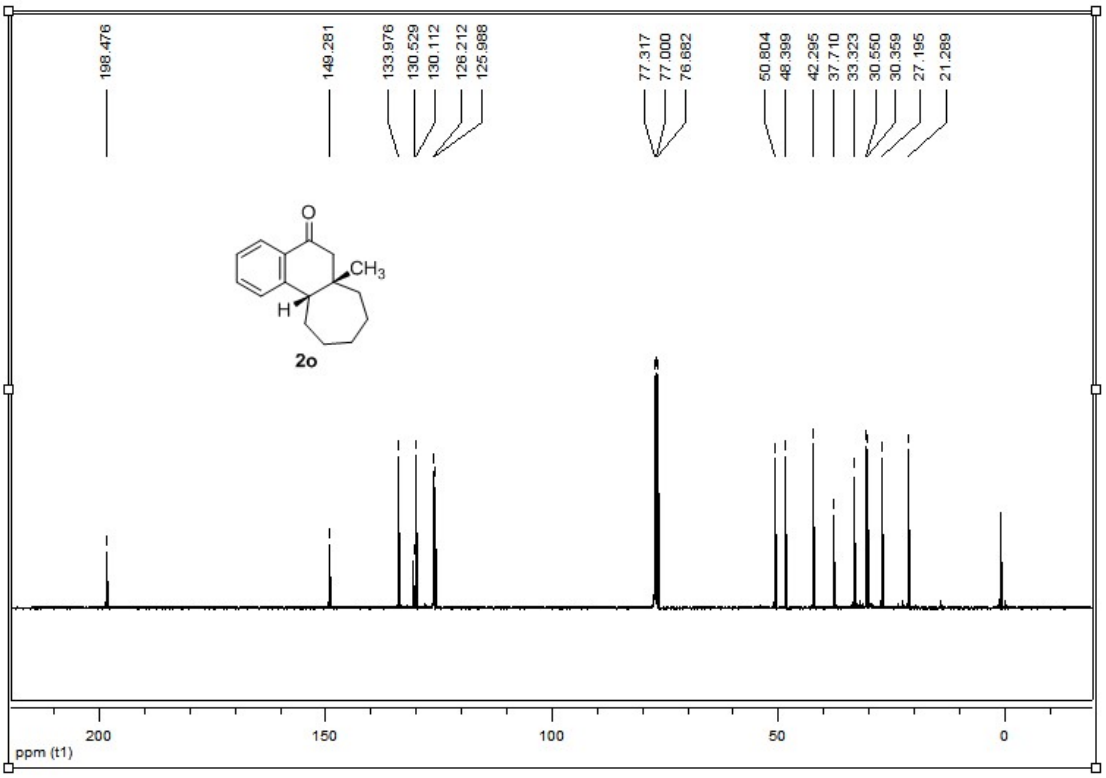
ppm (t1)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125.988
77.317
77.000
76.682
50.804
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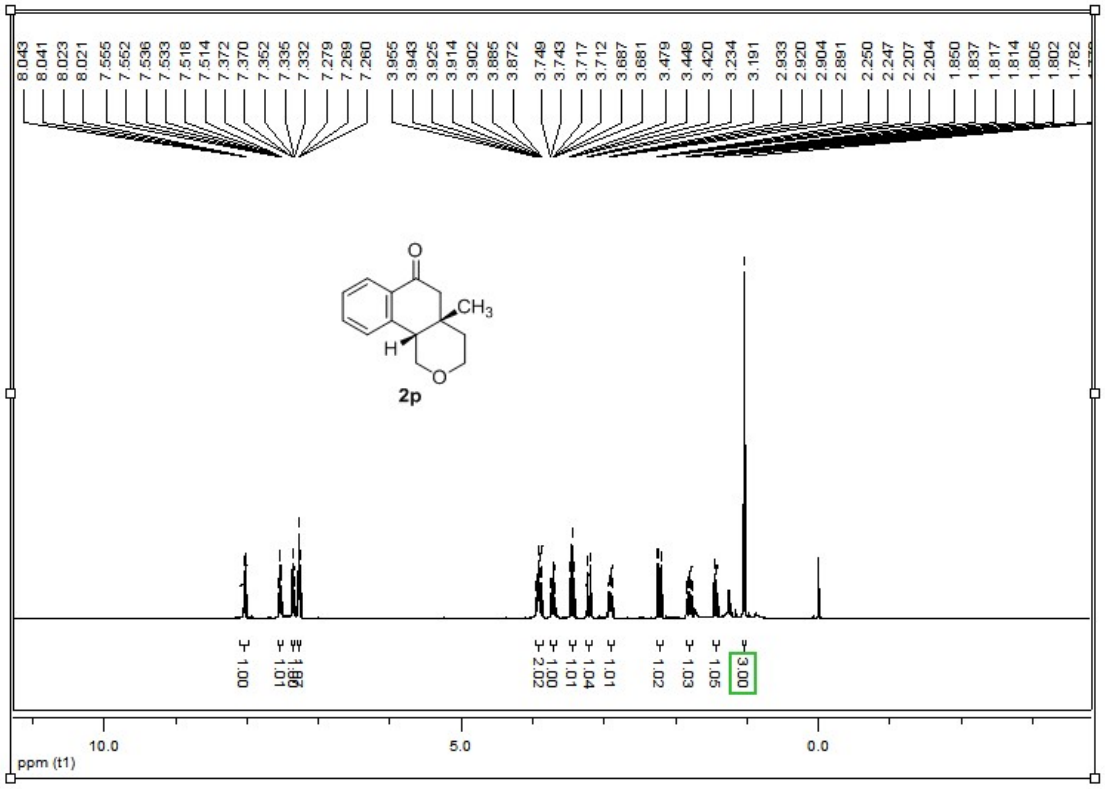
42.295
37.710
33.323
30.550
30.359
27.195
21.289
O
CH3
H
2o
200
150
100
50
0
ppm (t1)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8.021
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7.533
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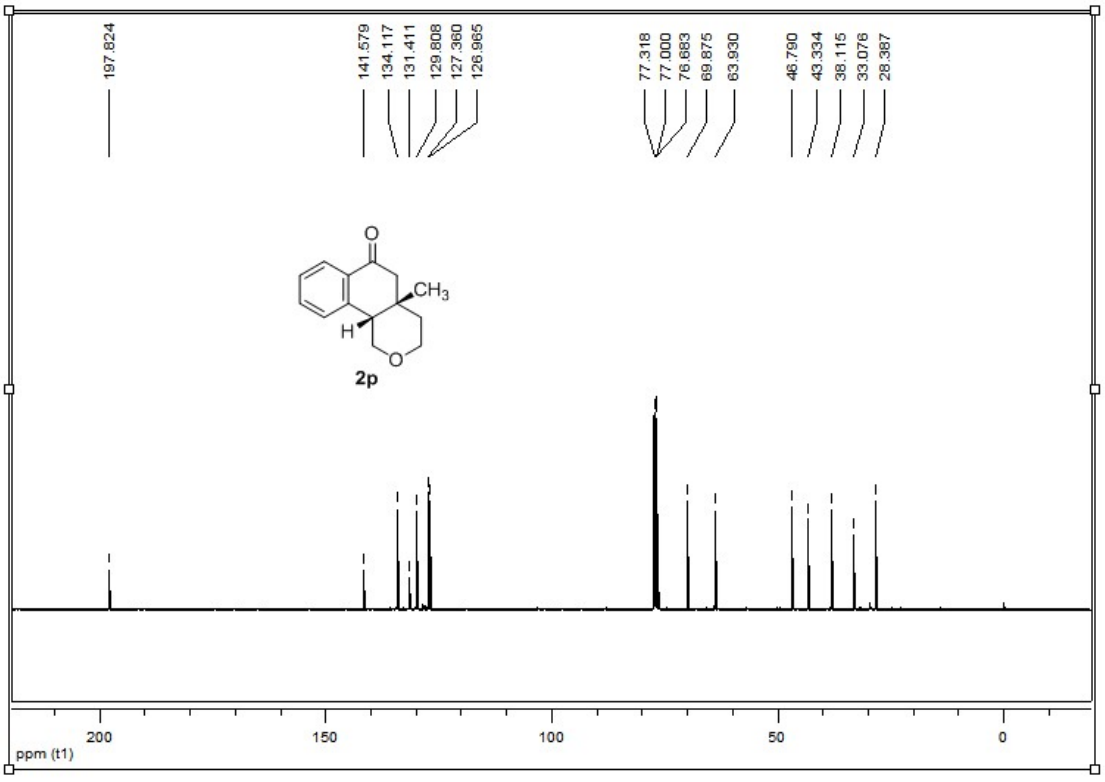
7.514
7.372
7.370
7.352
7.335
7.332
7.279
7.269
7.260
3.955
3.943
3.925
3.914
3.902
3.885
3.872
3.749
3.743
3.717
3.712
3.687
3.681
3.479
3.449
3.420
3.234
3.191
2.933
2.920
2.904
2.891
2.250
2.247
2.207
2.204
1.850
1.837
1.817
1.814
1.805
1.802
1.782
O
CH3
H
O
2p
1.00
1.01
1.06
2.02
1.00
1.01
1.04
1.01
1.02
1.03
1.05
3.00
10.0
5.0
0.0
ppm (t1)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127.360
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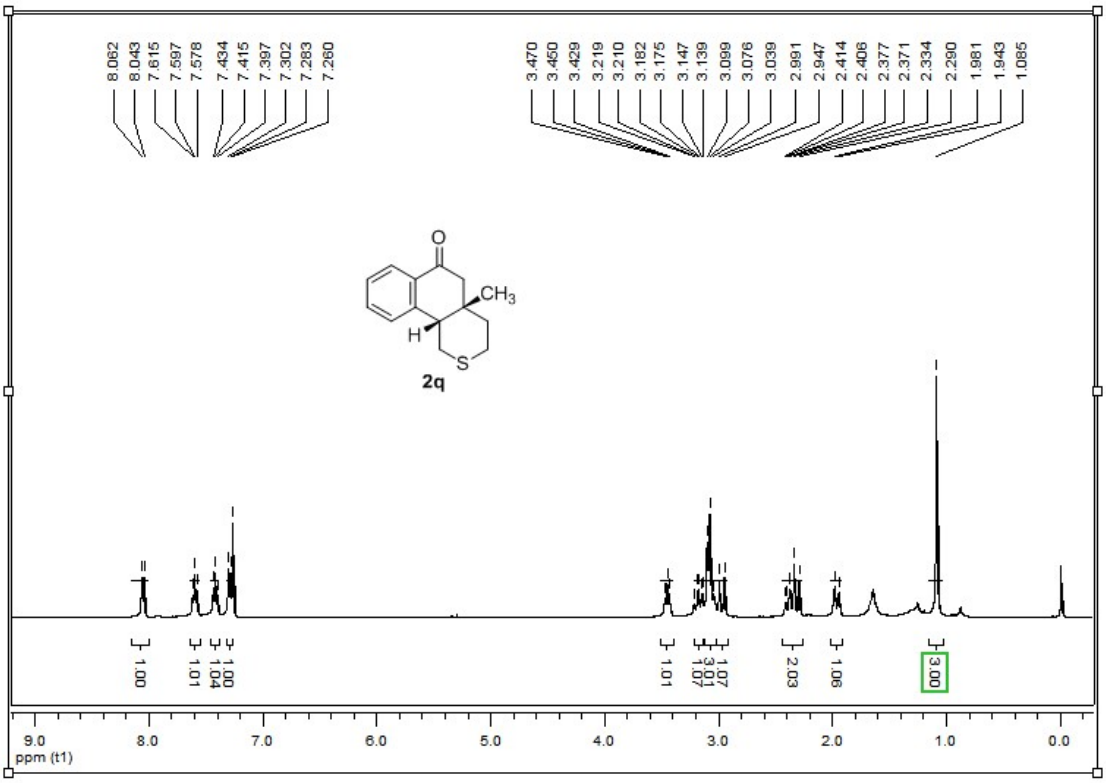
77.000
76.683
69.875
63.930
46.790
43.334
38.115
33.076
28.387
O
CH3
H
O
2p
200
150
100
50
0
ppm (t1)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7.283
7.260
3.470
3.450
3.429
3.219
3.210
3.182
3.175
3.147
3.139
3.099
3.076
3.039
2.991
2.947
2.414
2.406
2.377
2.371
2.334
2.290
1.981
1.943
1.085
O
CH3
H
S
2q
1.00
1.01
1.04
1.00
1.01
1.07
1.07
2.03
1.06
3.00
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7.0
6.0
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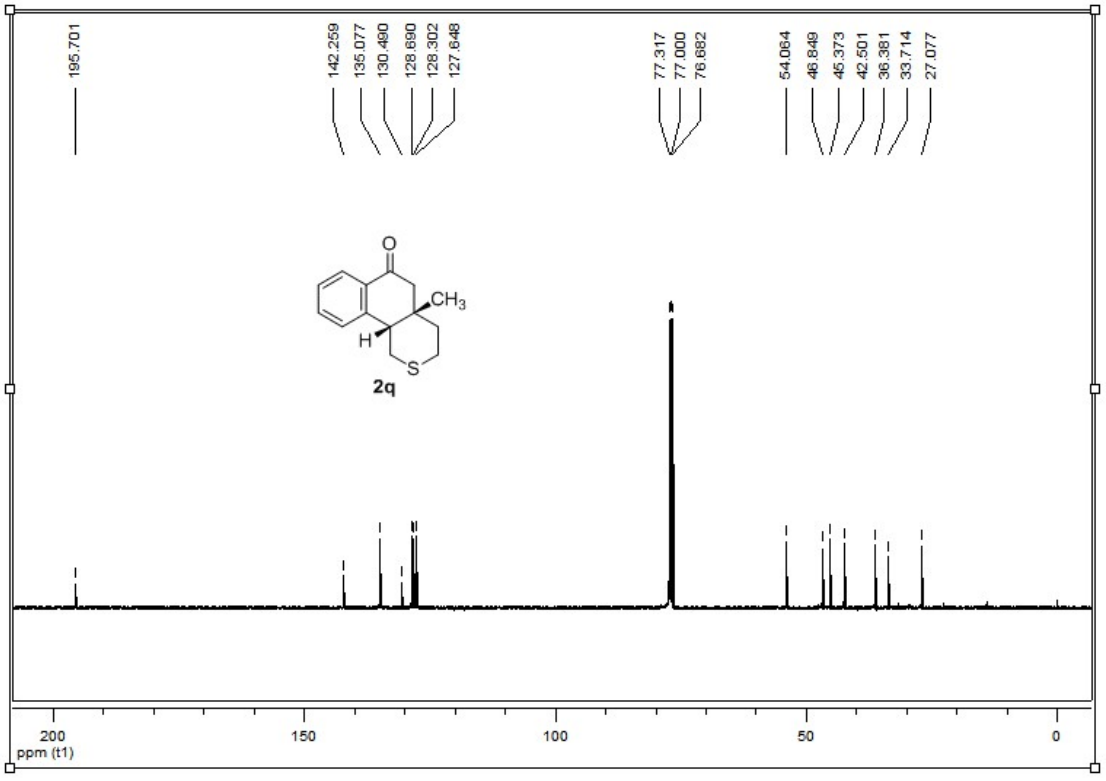
2.0
1.0
0.0
ppm (t1)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128.302
127.648
77.317
77.000
76.682
54.064
46.849
45.373
42.501
36.381
33.714
27.077
O
CH3
H
S
2q
200
150
100
50
0
ppm (t1)