Supporting Information for

Catalytic Dehydrogenative Dual Functionalization of Ethers: Dealkylation–Oxidation–Bromination Accompanied by C–O Bond via Aerobic Oxidation of Bromide

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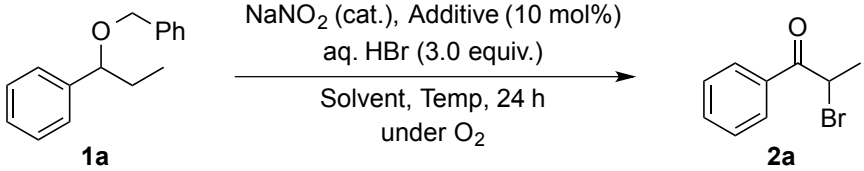
1. General Methods. ^{1}H NMR spectra were measured on a JEOL ECS-400 (400 MHz) spectrometer at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; sep = septet; m = multiplet; br = broad), coupling constant (Hz), integration, and assignment. ^{13}C NMR spectra were measured on a JEOL ECS-400 (100 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuterochloroform at 77.0 ppm). High-resolution mass spectra were recorded by Thermo Fisher Scientific Exactive Orbitrap mass spectrometers. Infrared (IR) spectra were recorded on a JASCO FT/IR 4100 spectrometer. Single crystal X-ray diffraction data were collected at 173K on a Bruker SMART APEX II CCD diffractometer with Mo Kα (λ = 0.71073) radiation and graphite monochromator. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60GF254 0.25 mm) were used. The products were purified by neutral column chromatography on silica gel (Kanto Chemical Co., Inc. silica gel 60N, Prod. No. 37560-84; Merck silica gel 60, Prod. No. 1.09385.9929). Visualization was accomplished by UV light (254 nm), anisaldehyde, $KMnO_4$, and phosphomolybdic acid. In experiments that required dry solvents were distilled in prior to use.

2. General Procedure for Catalytic Dehydrogenative Dual Functionalization of Ethers (1) (Scheme 1, Table 1, Table 2, and Table 3).

To a solution of **1a** (113.2 mg, 0.50 mmol), $NaNO_2$ (3.5 mg, 0.050 mmol), and 4-nitrobenzenesulfonamide (10.1 mg, 0.050 mmol) in MeCN (3.0 mL) was added 48% aq. HBr (169.7 μL, 1.5 mmol) at 0 °C under oxygen atmosphere (1 atm). After stirred at the same temperature for 30 min, the reaction mixture was stirred at 60 °C for 24 h. Saturated Na_2SO_3 aqueous solution (10 mL) was added to the mixture, and the product was extracted with AcOEt (20 mL × 3). The organic phase was washed with brine (20 mL) and dried over Na_2SO_4. The organic phase concentrated under reduced pressure, and the crude products was purified by column chromatography (eluent: hexane/AcOEt = 30/1) to give the desired products **2a** (99.5 mg, 93 % yield).

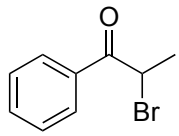
Table S1. Screening for DDF of **1a** via aerobic oxidation of bromide.



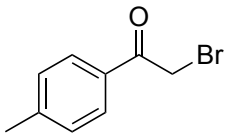
1a **2a**

Entry	$NaNO_2$ (mol%)	Additive	Solvent	Temp. (ºC)	Yield (%)
1	20	-	$CHCl_3$	50	10 (70)[a]
2	20	-	AcOEt	50	64 (28)[b]
3	20	-	MeCN	50	55 (42)[c]
4	10	-	MeCN	60	82 (11)[c]
5	10	$PhCONH_2$	MeCN	60	71 (15)[d]
6	10	*p*-$NO_2C_6H_4CONH_2$	MeCN	60	87 (5)[c]
7	10	*p*-$CF_3C_6H_4CONH_2$	MeCN	60	87
8	10	3,4-$(NO_2)_2C_6H_3CONH_2$	MeCN	60	83
9	10	$C_6F_5CONH_2$	MeCN	60	51 (24)[d]
10	10	*p*-$NO_2C_6H_4SO_2NH_2$	MeCN	60	93
11	10	*p*-$NO_2C_6H_4SO_2NHMe$	MeCN	60	63 (11)[c]
12[e]	10	*p*-$NO_2C_6H_4SO_2NH_2$	MeCN	60	68 (4)[c]
13	-	*p*-$NO_2C_6H_4SO_2NH_2$	MeCN	60	0
14[f]	10	*p*-$NO_2C_6H_4SO_2NH_2$	MeCN	60	0

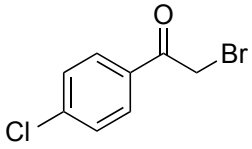
[a]Number in brackets indicates yield of (α-bromopropyl)benzene. [b]Number in brackets indicates recovery of **1a**. [c]Number in brackets indicates yield of propiophenone. [d]Number in brackets indicates yield of α,α-dibromopropiophenone. [e]HBr (2.0 equiv.) was used. [f]The reaction was carried out in air.



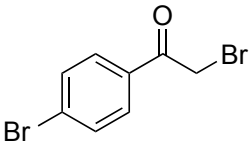
2-Bromo-1-phenylpropan-1-one (2a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (d, *J* = 6.9 Hz, 3H), 5.30 (q, *J* = 6.9 Hz, 1H), 7.45-7.52 (m, 2H), 7.56-7.63 (m, 1H), 8.00-8.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1, 41.4, 128.7 (2C), 128.9 (2C), 133.7, 134.0, 193.3. IR (neat) 2978, 1685, 1345, 1236, 1160 cm^{-1}. MS (ESI) calcd for $C_9H_{10}BrO$ $[M+H]^+$ 212.9910, found 212.9912.



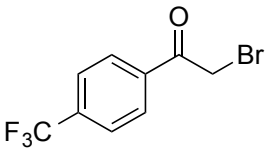
2-Bromo-1-(*p*-tolyl)ethan-1-one (2b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 4.43 (s, 2H), 7.26-7.32 (m, 2H), 7.85-7.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 31.0, 129.0 (2C), 129.5 (2C), 131.4, 145.0, 190.9. IR (neat) 2952, 1690, 1391, 1285, 1180 cm^{-1}.



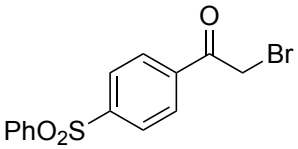
2-Bromo-1-(4-chlorophenyl)ethan-1-one (2c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.42 (s, 2H), 7.44-7.50 (m, 2H), 7.91-7.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.4, 129.2 (2C), 130.3 (2C), 132.2, 140.5, 190.2. IR (neat) 2954, 1693, 1400, 1283, 1197 cm^{-1}.



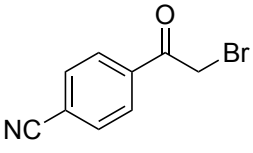
2-Bromo-1-(4-bromophenyl)ethan-1-one (2d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.42 (s, 2H), 7.60-7.65 (m, 2H), 7.82-7.87 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.5, 129.2, 130.3 (2C), 132.1 (2C), 132.5, 190.3. IR (neat) 2952, 1693, 1395, 1284, 1194 cm^{-1}.



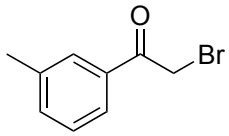
2-Bromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one (2e): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.46 (s, 2H), 7.77 (d, J = 8.2 Hz, 2H), 8.10 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.3, 123.4 (q, $J_{C–F}$ = 274.0 Hz), 125.9 (q, $J_{C–F}$ = 3.8 Hz, 2C), 129.3 (2C), 135.1 (q, $J_{C–F}$ = 32.6 Hz), 136.6, 190.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ –63.2. IR (neat) 2947, 1700, 1411, 1326, 1110 cm^{-1}. MS (APPI) calcd for $C_9H_7BrF_3O$ $[M+H]^+$ 266.9627, found 266.9629.



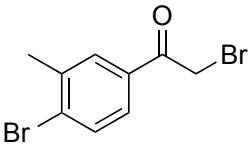
2-Bromo-1-(4-(phenylsulfonyl)phenyl)ethan-1-one (2f): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.44 (s, 2H), 7.51-7.58 (m, 2H), 7.59-7.65 (m, 1H), 7.94-7.99 (m, 2H), 8.02-8.07 (m, 2H), 8.07-8.11 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.3, 127.8 (2C), 128.0 (2C), 129.5 (2C), 129.7 (2C), 133.8, 137.2, 140.4, 146.0, 190.1. IR (neat) 2953, 1708, 1399, 1298, 1155 cm^{-1}. MS (APCI) calcd for $C_{14}H_{12}BrO_3S$ $[M+H]^+$ 338.9685, found 338.9687.



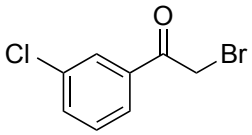
4-(2-Bromoacetyl)benzonitrile (2g): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.45 (s, 2H), 7.79-7.85 (m, 2H), 8.07-8.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.0, 117.1, 117.6, 129.4 (2C), 132.6 (2C), 136.8, 190.1. IR (neat) 2940, 2224, 1706, 1387, 1272, 1193 cm^{-1}. MS (APCI) calcd for C_9H_7BrNO $[M+H]^+$ 223.9706, found 223.9710.



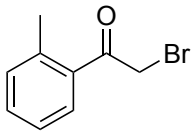
2-Bromo-1-(*m*-tolyl)ethan-1-one (2h (X = H)): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 4.45 (s, 2H), 7.32-7.44 (m, 2H), 7.73-7.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 31.1, 126.1, 128.6, 129.3, 133.9, 134.7, 138.7, 191.4. IR (neat) 2945, 1679, 1392, 1283, 1153 cm^{-1}. MS (APCI) calcd for $C_9H_{10}BrO$ $[M+H]^+$ 212.9910, found 212.9908.



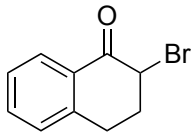
2-Bromo-1-(4-bromo-3-methylphenyl)ethan-1-one (2h (X = Br)): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H), 4.41 (s, 2H), 7.62-7.69 (m, 2H), 7.83-7.86 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.0, 30.5, 127.6, 130.9, 131.7, 132.87, 132.95, 138.9, 190.7. IR (neat) 2947, 1693, 1385, 1272, 1177 cm^{-1}. MS (APCI) calcd for $C_9H_9Br_2O$ $[M+H]^+$ 290.0915, found 290.9015.



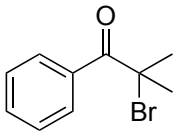
2-Bromo-1-(3-chlorophenyl)ethan-1-one (2i): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.43 (s, 2H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.56-7.62 (m, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.96 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.5, 127.0, 128.9, 130.2, 133.9, 135.2, 135.4, 190.1. IR (neat) 2941, 1684, 1420, 1261, 1192 cm^{-1}. MS (APCI) calcd for C_8H_7BrClO $[M+H]^+$ 232.9363, found 232.9367.



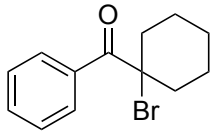
2-Bromo-1-(*o*-tolyl)ethan-1-one (2j): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52 (s, 3H), 4.42 (s, 2H), 7.25-7.32 (m, 2H), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H), 7.63-7.69 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 33.7, 125.8, 129.0, 132.30, 132.34, 134.3, 139.7, 194.1. IR (neat) 2965, 1680, 1383, 1260, 1186 cm^{-1}. MS (APCI) calcd for $C_9H_{10}BrO$ $[M+H]^+$ 212.9910, found 212.9911.



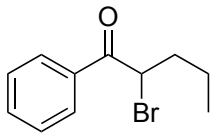
2-Bromo-3,4-dihydronaphthalen-1(2*H*)-one (2k): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41-2.58 (m, 2H), 2.92 (dt, *J* = 17.3, 4.5 Hz, 1H), 3.31 (ddd, *J* = 17.3, 10.0, 4.8 Hz, 1H), 4.73 (dd, *J* = 4.8, 4.1 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.52 (td, *J* = 7.8, 1.4 Hz, 1H), 8.08 (dd, *J* = 7.8, 1.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.0, 31.8, 50.4, 127.0, 128.6, 128.7, 129.8, 134.1, 142.9, 190.5. IR (neat) 2946, 1680, 1454, 1303, 1195 cm^{-1}. MS (APCI) calcd for $C_{10}H_{10}BrO$ $[M+H]^+$ 224.9910, found 224.9909.



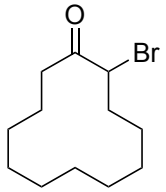
2-Bromo-2-methyl-1-phenylpropan-1-one (2l): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 6H), 7.40-7.47 (m, 2H), 7.50-7.57 (m, 1H), 8.11-8.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.5 (2C), 60.3, 128.1 (2C), 130.1 (2C), 132.4, 134.8, 196.9. IR (neat) 2928, 1674, 1387, 1268, 1167 cm^{-1}.



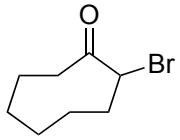
(1-Bromocyclohexyl)(phenyl)methanone (2m): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32-1.44 (m, 1H), 1.46-1.64 (m, 3H), 1.72-1.87 (m, 2H), 2.11-2.25 (m, 2H), 2.27-2.38 (m, 2H), 7.38-7.45 (m, 2H), 7.49-7.55 (m, 1H), 8.04-8.10 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.5 (2C), 24.9, 38.2 (2C), 67.9, 128.1 (2C), 129.8 (2C), 132.0, 135.8, 197.5. IR (neat) 2934, 1675, 1446, 1245, 1181 cm^{-1}. MS (APCI) calcd for $C_{13}H_{16}BrO$ $[M+H]^+$ 267.0379, found 267.0377.



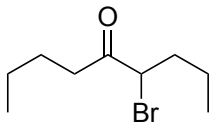
2-Bromo-1-phenylpentan-1-one (2n): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, *J* = 7.5 Hz, 3H), 1.37-1.51 (m, 1H), 1.51-1.65 (m, 1H), 2.06-2.25 (m, 2H), 5.16 (dd, *J* = 8.0, 6.6 Hz, 1H), 7.45-7.52 (m, 2H), 7.60 (tt, *J* = 7.6, 1.4 Hz, 1H), 7.99-8.05 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 20.8, 35.4, 47.0, 128.75 (2C), 128.81 (2C), 133.6, 134.5, 193.3. IR (neat) 2961, 1684, 1448, 1272, 1210 cm^{-1}. MS (ESI) calcd for $C_{11}H_{14}BrO$ $[M+H]^+$ 241.0223, found 241.0225.



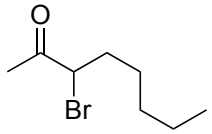
2-Bromocyclododecan-1-one (2o): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13-1.46 (m, 14H), 1.51-1.65 (m, 1H), 1.82-2.06 (m, 2H), 2.24-2.38 (m, 1H), 2.71 (ddd, *J* = 16.8, 11.2, 3.6 Hz, 1H), 2.81 (ddd, *J* = 16.8, 6.4, 3.6 Hz, 1H), 4.39 (dd, *J* = 11.8, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 22.4, 23.7 (2C), 23.9, 24.0, 25.1, 25.3, 33.5, 35.2, 51.6, 205.6. IR (neat) 2929, 1711, 1469, 1362, 1243, 1140 cm^{-1}. MS (APCI) calcd for $C_{12}H_{22}BrO$ $[M+H]^+$ 261.0849, found 261.0847.



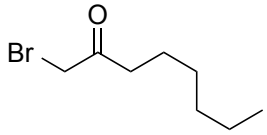
2-Bromocyclooctan-1-one (2p): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10-1.24 (m, 1H), 1.34-1.47 (m, 1H), 1.50-1.63 (m, 2H), 1.63-1.84 (m, 3H), 1.88-1.99 (m, 1H), 2.26-2.46 (m, 3H), 2.88 (td, *J* = 12.4, 4.0 Hz, 1H), 4.28 (dd, *J* = 11.2, 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.9, 25.3, 26.5, 28.7, 32.6, 36.1, 54.3, 208.7. IR (neat) 2929, 1702, 1466, 1327, 1213, 1147 cm^{-1}. MS (APCI) calcd for $C_8H_{14}BrO$ $[M+H]^+$ 205.0223, found 205.0223.



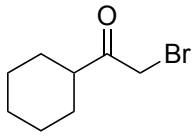
4-Bromononan-5-one (2q): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (dt, *J* = 10.5, 7.5 Hz, 6H), 1.27-1.42 (m, 3H), 1.42-1.59 (m, 1H), 1.54-1.65 (m, 2H), 1.85-2.03 (m, 2H), 2.58-2.77 (m, 2H), 4.26 (dd, *J* = 8.2, 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 13.8, 20.6, 22.2, 26.0, 35.4, 38.7, 53.5, 204.5. IR (neat) 2959, 1714, 1464, 1380, 1259, 1042 cm^{-1}. MS (APCI) calcd for $C_9H_{18}BrO$ $[M+H]^+$ 221.0536, found 221.0535.



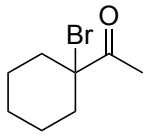
3-Bromooctan-2-one (2r–2º): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 6.8 Hz, 3H), 1.24-1.40 (m, 5H), 1.41-1.54 (m, 1H), 1.85-2.06 (m, 2H), 2.36 (s, 3H), 4.23 (dd, *J* = 8.2, 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.3, 26.0, 26.9, 31.1, 33.5, 54.4, 202.2. IR (neat) 2929, 1718, 1465, 1358, 1232, 1147 cm^{-1}. MS (APCI) calcd for $C_8H_{16}BrO$ $[M+H]^+$ 207.0379, found 207.0380.



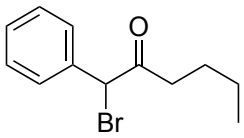
1-Bromooctan-2-one (2r–1º): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.23-1.36 (m, 6H), 1.57-1.66 (m, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 3.89 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.4, 23.8, 28.7, 31.5, 34.3, 39.8, 202.2. IR (neat) 2928, 1715, 1464, 1377, 1174 cm^{-1}. MS (APCI) calcd for $C_8H_{16}BrO$ $[M+H]^+$ 207.0379, found 207.0385.



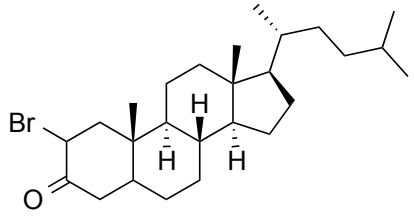
2-Bromo-1-cyclohexylethan-1-one (2s–1º): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14-1.46 (m, 5H), 1.64-1.73 (m, 1H), 1.75-1.84 (m, 2H), 1.84-1.93 (m, 2H), 2.71 (tt, *J* = 11.2, 3.4 Hz, 1H), 3.97 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4 (2C), 25.6, 28.7 (2C), 33.4, 48.0, 204.6. IR (neat) 2929, 1708, 1448, 1394, 1246, 1144 cm^{-1}. MS (APCI) calcd for $C_8H_{14}BrO$ $[M+H]^+$ 205.0223, found 205.0228.



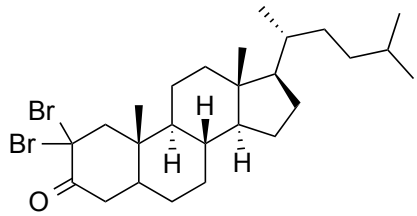
1-(1-Bromocyclohexyl)ethan-1-one (2s–3º): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27-1.41 (m, 1H), 1.52-1.66 (m, 3H), 1.70-1.85 (m, 2H), 1.88-2.06 (m, 2H), 2.09-2.21 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.2, 24.1, 24.8 (2C), 36.4 (2C), 71.3, 202.9. IR (neat) 2935, 1709, 1446, 1354, 1227, 1189 cm^{-1}. MS (APCI) calcd for $C_8H_{14}BrO$ $[M+H]^+$ 205.0223, found 205.0222.



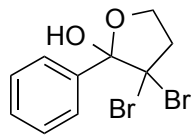
1-Bromo-1-phenylhexan-2-one (2t): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, *J* = 7.5 Hz, 3H), 1.19-1.31 (m, 2H), 1.50-1.60 (m, 3H), 2.55 (dt, *J* = 17.4, 7.3 Hz, 1H), 2.61 (dt, *J* = 17.4, 7.6 Hz, 1H), 7.30-7.39 (m, 3H), 7.39-7.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 22.0, 26.1, 38.8, 55.7, 128.8 (2C), 129.0 (2C), 129.1, 135.3, 201.6. IR (neat) 2957, 1724, 1454, 1363, 1259, 1122 cm^{-1}. MS (APCI) calcd for $C_{12}H_{16}BrO$ $[M+H]^+$ 255.0379, found 255.0380.



(8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-2-Bromo-10,13-dimethyl-17-((*R*)-5-methylhexan-2-yl)hexadecahydro-3*H*-cyclopenta[*a*]phenanthren-3-one (2u (X = H)): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.67 (s, 3H), 0.72-0.82 (m, 1H), 0.860 (d, *J* = 6.6 Hz, 3H), 0.863 (d, *J* = 6.6 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.93-1.19 (m, 9H), 1.08 (s, 3H), 1.19-1.45 (m, 8H), 1.45-1.66 (m, 4H), 1.66-1.75 (m, 1H), 1.75-1.90 (m, 2H), 2.00 (dt, *J* = 13.2, 3.2 Hz, 1H), 2.34-2.48 (m, 2H), 2.63 (dd, *J* = 13.2, 6.4 Hz, 1H), 4.76 (dd, *J* = 13.6, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 12.1, 18.6, 21.5, 22.5, 22.8, 23.7, 24.1, 27.9, 28.1, 28.3, 31.4, 34.8, 35.7, 36.0, 38.9, 39.4, 39.6, 42.5, 43.9, 47.4, 51.6, 53.5, 54.6, 56.0, 56.1, 201.2. IR (neat) 2927, 1720, 1442, 1378, 1186 cm^{-1}. MS (APCI) calcd for $C_{27}H_{46}BrO$ $[M+H]^+$ 465. 2727, found 465.2720.



(8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-2,2-Dibromo-10,13-dimethyl-17-((*R*)-5-methylhexan-2-yl)hexadecahydro-3*H*-cyclopenta[*a*]phenanthren-3-one (2u (X = Br)): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.67 (s, 3H), 0.63-0.73 (m, 1H), 0.861 (d, *J* = 6.6 Hz, 3H), 0.865 (d, *J* = 6.6 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.92-1.18 (m, 8H), 1.24 (s, 3H), 1.18-1.61 (m, 12H), 1.61-1.74 (m, 2H), 1.76-1.89 (m, 1H), 1.95-2.04 (m, 1H), 2.33 (dd, *J* = 15.3, 3.2 Hz, 1H), 2.73 (d, *J* = 15.8 Hz, 1H), 3.07 (t, *J* = 14.9 Hz, 1H), 3.24 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.1, 13.3, 18.6, 21.4, 22.5, 22.8, 23.8, 24.1, 27.98, 28.07, 28.13, 31.3, 34.3, 35.7, 36.1, 38.8, 39.1, 39.5, 39.7, 42.6, 46.5, 55.3, 55.9, 56.1, 62.5, 66.3, 195.1. IR (neat) 2932, 1731, 1444, 1384, 1169 cm^{-1}. MS (APCI) calcd for $C_{27}H_{45}Br_2O$ $[M+H]^+$ 543.1832, found 543.1834.



3,3-Bibromo-2-phenyltetrahydrofuran-2-ol (4a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.07 (ddd, *J* = 13.8, 7.1, 2.0 Hz, 1H), 3.25 (s, 1H), 3.46 (dt, *J* = 13.8, 9.5 Hz, 1H), 4.12 (ddd, *J* = 9.5, 8.3, 2.0 Hz, 1H), 4.29 (ddd, *J* = 9.5, 8.3, 7.1 Hz, 1H), 7.38-7.44 (m, 3H), 7.79-7.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.0, 65.1, 67.5, 105.7, 127.5 (2C), 127.6 (2C), 129.4, 138.2. IR (neat) 3368, 1440, 1398, 1257, 1022 cm^{-1}. MS (ESI) calcd for $C_{10}H_{10}Br_2NaO_2$ $[M+Na]^+$ 342.8940, found

342.8954.

Crystal data of 4a: Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1531429. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

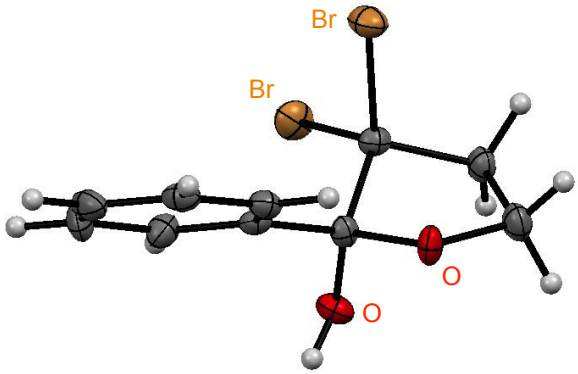
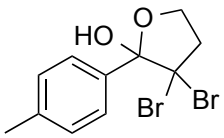


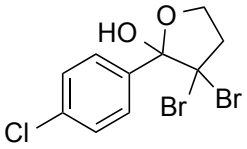
Figure S1. ORTEP drawing of **4a**.

Formula	$C_{10}H_{10}Br_2O_2$
Formula Weight	322.00
Temperature	173 K
Wavelength	0.71073 Å
Crystal System	Monoclinic
Space Group	P 1 21/c 1
Unit Cell Dimensions	a = 20.362(2) Å α = 90.00 º
	b = 6.3138(7) Å β = 95.2864(16) º
	c = 16.3787(18) Å γ = 90.00 º
Volume	2096.7(4) $Å^3$
Z Value	8
Calculated Density	2.040 g cm^{-3}
Absorption coeficiente	7.702 mm^{-1}
F(000)	1248
Crystal size	0.20×0.20×0.10 mm^3
Theta Range for Data Collection	2.4977-27.2970
Index Ranges	$-23 \leq h \leq 26$, $-6 \leq k \leq 8$, $-16 \leq l \leq 21$
Reflections Collected	4737
Independent Reflections	4737 [R(int) = 0.0000]
Completeness to Theta = 27.462º	98.7%
Refinement Method	Full-matrix least-squares on F^2

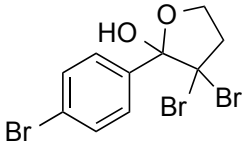
Data/ Restraints/ Parameters	4737/0/255
Goodness-of-Fit onF^2	1.040
Final R Indices [I>2sigma(I)]	R_1 = 0.0357 and wR_2 = 0.0572
R Indices (All Data)	R_1 = 0.0642 and wR_2 = 0.0635
Largest Diff. Peak and Hole	0.491 and –0.554 e^-/ $Å^3$



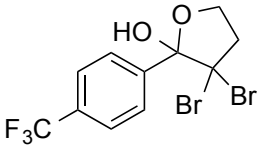
3,3-Dibromo-2-(*p*-tolyl)tetrahydrofuran-2-ol (4b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 3.06 (ddd, *J* = 13.6, 7.0, 1.8 Hz, 1H), 3.21 (s, 1H), 3.45 (dt, *J* = 13.6, 9.4 Hz, 1H), 4.11 (ddd, *J* = 9.4, 8.2, 1.8 Hz, 1H), 4.27 (ddd, *J* = 9.4, 8.2, 7.0 Hz, 1H), 7.17-7.23 (m, 2H), 7.66-7.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 46.9, 65.0, 67.9, 105.8, 127.4 (2C), 128.3 (2C), 135.2, 139.3. IR (neat) 3361, 1441, 1393, 1266, 1025 cm^{-1}. MS (ESI) calcd for $C_{11}H_{13}Br_2O_2$ $[M+H]^+$ 334.9277, found 334.9276.



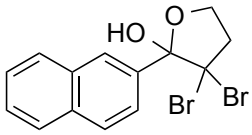
3,3-Dibromo-2-(4-chlorophenyl)tetrahydrofuran-2-ol (4c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.04 (ddd, *J* = 13.6, 7.0 Hz, 1H), 3.41 (dt, *J* = 13.6, 9.5 Hz, 1H), 3.53 (s, 1H), 3.98-4.06 (m, 1H), 4.20-4.29 (m, 1H), 7.31-7.38 (m, 2H), 7.68-7.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.8, 65.2, 67.0, 105.4, 127.7 (2C), 129.0 (2C), 135.5, 136.6. IR (neat) 3384, 1439, 1343, 1251, 1012 cm^{-1}. MS (APCI) calcd for $C_{10}H_{10}Br_2ClO_2$ $[M+H]^+$ 354.8731, found 354.8727.



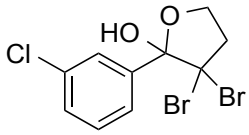
3,3-Dibromo-2-(4-bromophenyl)tetrahydrofuran-2-ol (4d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.04 (ddd, *J* = 13.6, 6.8, 1.7 Hz, 1H), 3.38 (s, 1H), 3.42 (dt, *J* = 13.6, 9.4 Hz, 1H), 4.02-4.10 (m, 1H), 4.22-4.31 (m, 1H), 7.48-7.54 (m, 2H), 7.63-7.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.8, 65.3, 67.0, 105.4, 123.9, 129.3 (2C), 130.7 (2C), 137.1. IR (neat) 3337, 1441, 1392, 1262, 1009 cm^{-1}. MS (APCI) calcd for $C_{10}H_{10}Br_3O_2$ $[M+H]^+$ 398.8225, found 398.8222.



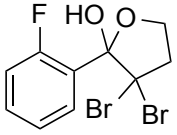
3,3-Dibromo-2-(4-(trifluoromethyl)phenyl)tetrahydrofuran-2-ol (4e): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.07 (ddd, *J* = 14.0, 7.2, 2.0 Hz, 1H), 3.44 (s, 1H), 3.44 (dt, *J* = 14.0, 9.6 Hz, 1H), 4.03-4.12 (m, 1H), 4.29 (ddd, *J* = 9.6, 8.6, 7.2 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.8, 65.5, 66.4, 105.3, 123.9 (q, $J_{C–F}$ = 276.5 Hz), 124.5 (q, $J_{C–F}$ = 3.8 Hz, 2C), 128.1 (2C), 131.4 (q, $J_{C–F}$ = 33.4 Hz), 141.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ –62.6. IR (neat) 3341, 1406, 1325, 1116, 1056, 1012 cm^{-1}. MS (APCI) calcd for $C_{11}H_{10}Br_2F_3O_2$ $[M+H]^+$ 388.8994, found 388.8989.



3,3-Dibromo-2-(naphthalen-2-yl)tetrahydrofuran-2-ol (4f): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.02-3.11 (m, 1H), 3.46 (dt, *J* = 13.8, 9.4 Hz, 1H), 3.64 (s, 1H), 4.05-4.13 (m, 1H), 4.24-4.35 (m, 1H), 7.45-7.54 (m, 2H), 7.76-7.94 (m, 4H), 8.26 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.0, 65.2, 67.6, 105.8, 124.9, 126.2, 126.7, 127.1, 127.2, 127.6, 128.7, 132.3, 133.6, 135.6. IR (neat) 3243, 1436, 1356, 1223, 1190 cm^{-1}. MS (APCI) calcd for $C_{14}H_{13}Br_2O_2$ $[M+H]^+$ 370.9277, found 370.9275.

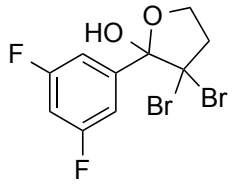


3,3-Dibromo-2-(3-chlorophenyl)tetrahydrofuran-2-ol (4g): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.07 (ddd, *J* = 13.5, 6.8, 1.8 Hz, 1H), 3.18 (s, 1H), 3.45 (dt, *J* = 13.5, 9.4 Hz, 1H), 4.10-4.19 (m, 1H), 4.30 (ddd, *J* = 9.4, 8.2, 6.8 Hz, 1H), 7.30-7.36 (m, 1H), 7.36-7.42 (m, 1H), 7.71 (dt, *J* = 7.5, 1.4 Hz, 1H), 7.80 (t, *J* = 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.9, 65.4, 66.7, 105.1, 125.7, 127.9, 128.9, 129.5, 133.6, 140.1. IR (neat) 3370, 1436, 1376, 1247, 1044 cm^{-1}. MS (APCI) calcd for $C_{10}H_{10}Br_2ClO_2$ $[M+H]^+$ 354.8731, found 354.8725.

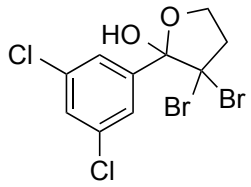


3,3-Dibromo-2-(2-fluorophenyl)tetrahydrofuran-2-ol (4h): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.05 (ddd, *J* = 13.8, 6.8, 2.1 Hz, 1H), 3.44 (dt, *J* = 13.8, 9.4 Hz, 1H), 4.17 (d, *J* = 9.8 Hz, 1H), 4.22 (td, *J* = 8.2, 2.1 Hz, 1H), 4.32 (ddd, *J* = 9.4, 8.2, 6.8 Hz, 1H), 7.07-7.22 (m, 2H), 7.34-7.43 (m, 1H),

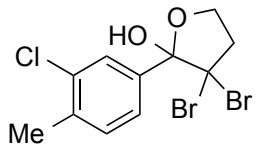
7.74 (td, J = 8.2, 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.7, 65.9, 68.3, 106.4 (d, $J_{C–F}$ = 3.8 Hz), 116.3 (d, $J_{C–F}$ = 24.0 Hz), 123.3 (d, $J_{C–F}$ = 2.9 Hz), 124.3 (d, $J_{C–F}$ = 9.6 Hz), 131.3 (d, $J_{C–F}$ = 5.8 Hz), 131.4, 160.2 (d, $J_{C–F}$ = 248.1 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ –109.9. IR (neat) 3360, 1445, 1360, 1279, 1027 cm^{-1}. MS (APCI) calcd for $C_{10}H_{10}Br_2FO_2$ $[M+H]^+$ 338.9026, found 338.9018.



3,3-Dibromo-2-(3,5-difluorophenyl)tetrahydrofuran-2-ol (4i): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.06 (ddd, J = 14.0, 6.8, 1.6 Hz, 1H), 3.41 (s, 1H), 3.43 (dt, J = 14.0, 9.6 Hz, 1H), 4.07-4.15 (m, 1H), 4.29 (ddd, J = 9.6, 8.4, 6.8 Hz, 1H), 6.85 (tt, J = 9.0, 2.4 Hz, 1H), 7.29-7.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.7, 65.6, 66.0, 104.82 (t, $J_{C–F}$ = 25.8 Hz), 104.83 (t, $J_{C–F}$ = 2.9 Hz), 111.0 (dd, $J_{C–F}$ = 20.0, 7.6 Hz, 2C), 141.9 (t, $J_{C–F}$ = 9.1 Hz), 163.4 (dd, $J_{C–F}$ = 251.8, 12.4 Hz, 2C). ^{19}F NMR (471 MHz, $CDCl_3$) δ –109.4. IR (neat) 3338, 1600, 1436, 1326, 1114, 1051 cm^{-1}. MS (DART) calcd for $C_{10}H_9Br_2F_2O_2$ $[M+H]^+$ 356.8932, found 356.8935.



3,3-Dibromo-2-(3,5-dichlorophenyl)tetrahydrofuran-2-ol (4j): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.06 (ddd, J = 13.6, 6.8, 1.6 Hz, 1H), 3.42 (td, J = 13.6, 9.6 Hz, 1H), 3.48 (s, 1H), 4.07-4.15 (m, 1H), 4.24-4.33 (m, 1H), 7.39 (t, J = 2.0 Hz, 1H), 7.66 (d, J = 2.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.7, 65.6, 66.0, 104.7, 126.3 (2C), 129.5 (2C), 134.2, 141.3. IR (neat) 3363, 1567, 1417, 1363, 1254, 1060 cm^{-1}. MS (APCI) calcd for $C_{10}H_9Br_2Cl_2O_2$ $[M+H]^+$ 388.8341, found 388.8337.

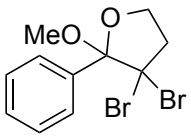


3,3-Dibromo-2-(3-chloro-4-methylphenyl)tetrahydrofuran-2-ol (4k): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 3.04 (ddd, J = 13.8, 6.8, 2.0 Hz, 1H), 3.41 (dt, J = 13.8, 9.6 Hz, 1H), 3.55 (s, 1H), 4.00-4.10 (m, 1H), 4.20-4.31 (m, 1H), 7.23 (d, J = 8.4 Hz, 1H), 7.56 (dd, J = 8.4, 2.0 Hz, 1H), 7.74 (d, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 46.8, 65.2, 67.1, 105.2, 125.7, 128.2, 130.0, 133.6, 137.27, 137.29. IR (neat) 3357, 1436, 1389, 1253, 1051 cm^{-1}. MS (APCI)

calcd for $C_{11}H_{12}Br_2ClO_2$ $[M+H]^+$ 368.8887, found 368.8882.

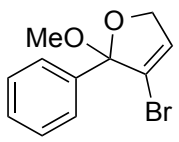
3. Transformation of 4a into Substituted Furan Derivartives (Scheme 2).

To a solution of **4a** (2.77 g, 8.62 mmol) in MeOH (40 mL) was added conc. H_2SO_4 (91.7 μL, 1.72 mmol) at 0 °C and the reaction mixture was stirred at room temperature for 1 h. Saturated $NaHCO_3$ aqueous solution (30 mL) was added to the mixture, and volatile solvents were removed under reduced pressure. The residue was extracted with AcOEt (30 mL × 3), and then the organic phase was washed with brine (50 mL) and dried over Na_2SO_4. The organic phase concentrated under reduced pressure, and the crude products was purified by column chromatography (eluent: hexane/AcOEt=30:1) to give the desired product **9** (2.67 g, 92% yield).



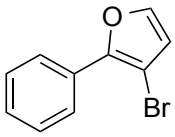
3,3-Dibromo-2-methoxy-2-phenyltetrahydrofuran (9): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.08 (ddd, *J* = 13.5, 7.3, 2.1 Hz, 1H), 3.12 (s, 3H), 3.45 (dt, *J* = 13.5, 9.6 Hz, 1H), 4.00-4.08 (m, 1H), 4.26-4.35 (m, 1H), 7.38-7.44 (m, 3H), 7.72-7.78 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.1, 51.4, 64.8, 67.9, 108.4, 127.5 (2C), 128.3, 129.1 (2C), 134.7. IR (neat) 2935, 1449, 1273, 1117, 1040 cm^{-1}. MS (APCI) calcd for $C_{11}H_{12}Br_2O_2$ $[M+H]^+$ 333.9199, found 333.9199.

To a solution of **9** (67.2 mg, 0.20 mmol) in THF (1.25 mL) was added *t*-BuOK (33.7 mg, 0.30 mmol) in THF (0.50 mL) at room temperature. The reaction mixture was stirred at 80 °C for 3 h. Saturated NH_4Cl aqueous solution (10 mL) was added to the mixture, and the product was extracted with AcOEt (10 mL × 3). The organic phase was washed with brine (20 mL) and dried over Na_2SO_4. The organic phase concentrated under reduced pressure. The pure product **10** was gave without further purification (47.3 mg, 98% yield).



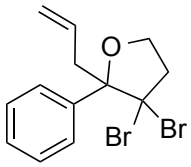
3-Bromo-2-methoxy-2-phenyl-2,5-dihydrofuran (10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.34 (s, 3H), 4.78 (d, *J* = 1.8 Hz, 2H), 6.41 (t, *J* = 1.8 Hz, 1H), 7.31-7.39 (m, 3H), 7.50-7.56 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 49.7, 74.7, 112.8, 119.5, 126.4 (2C), 127.9 (2C), 128.6, 130.2, 139.7. IR (neat) 2928, 1449, 1270, 1190, 1044 cm^{-1}. MS (APCI) calcd for $C_{11}H_{12}BrO_2$ $[M+H]^+$ 255.0015, found 255.0017.

To a solution of **10** (47.3 mg, 0.20 mmol) in MeCN (1.7 mL) was added *p*-TsOH•H_2O (38.0 mg, 0.20 mmol) at room temperature. The reaction mixture was stirred at room temperature for 30 min. Saturated $NaHCO_3$ aqueous solution (10 mL) was added to the mixture, and the product was extracted with AcOEt (10mL × 3). The organic phase was washed with brine (20 mL) and dried over Na_2SO_4. The organic phase concentrated under reduced pressure, and the crude products was purified by column chromatography (eluent: hexane/AcOEt=50:1) to give the desired product **11** (43.5 mg, >99% yield).



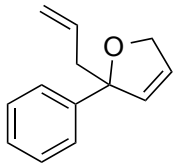
3-Bromo-2-phenylfuran (11): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53 (d, *J* = 2.0 Hz, 1H), 7.30-7.36 (m, 1H), 7.39-7.46 (m, 3H), 7.93-7.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 95.9, 116.2, 125.5 (2C), 128.0, 128.5 (2C), 129.7, 141.7, 148.9. IR (neat) 3057, 1480, 1373, 1186, 1056 cm^{-1}. MS (APCI) calcd for $C_{10}H_8BrO$ $[M+H]^+$ 222.9753, found 222.9752.

To a solution of **9** (67.2 mg, 0.20 mmol) in CH_2Cl_2 (0.40 mL) was added allyltrimethylsilane (63.8 μL, 0.40 mmol) and BF_3-OEt_2 (50.5 μL, 0.20 mmol) at –78 °C under argon atmosphere, and the reaction mixture stirred at room temperature for 16 h. Saturated $NaHCO_3$ aqueous solution (10 mL) was added to the mixture, and the product was extracted with AcOEt (10mL × 3). The organic phase was washed with brine (20 mL) and dried over Na_2SO_4. The organic phase concentrated under reduced pressure, and the crude products was purified by column chromatography (eluent: hexane/AcOEt =50:1) to give the desired product **12** (62.7 mg, 92% yield).



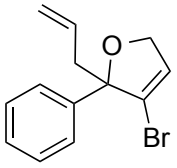
2-Allyl-3,3-dibromo-2-phenyltetrahydrofuran (12): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (dd, *J* = 14.6, 7.4 Hz, 1H), 3.12-3.37 (m, 3H), 4.10 (td, *J* = 9.2, 3.2 Hz, 1H), 4.24-4.33 (m, 1H), 4.92-5.03 (m, 2H), 5.39-5.52 (m, 1H), 7.29-7.40 (m, 3H), 7.63-7.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.0, 49.2, 64.1, 70.7, 90.9, 118.3, 125.9 (2C), 127.6 (2C), 127.7, 133.3, 141.3. IR (neat) 2892, 1640, 1447, 1270, 1063 cm^{-1}. MS (APCI) calcd for $C_{13}H_{15}Br_2O$ $[M+H]^+$ 344.9484, found 344.9491.

To a solution of **12** (58.5 mg, 0.17 mmol) in Et_2O (0.42 mL) was added MeLi (250 μL, 0.25 mmol) dropwise at –78 °C under argon atmosphere, and the reaction mixture was stirred at same temperature for 4 h. H_2O (10 mL) was added to the mixture, and the product was extracted with Et_2O (10mL × 3). The organic phase was washed with brine (20 mL) and dried over Na_2SO_4. The organic phase concentrated under reduced pressure, and the crude products was purified by column chromatography (eluent: hexane/Et_2O =30:1) to give the desired product **13** (28.5 mg, 91% yield).



2-Allyl-2-phenyl-2,5-dihydrofuran (13): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 (dd, *J* = 14.4, 7.5 Hz, 1H), 2.71 (dd, *J* = 14.4, 6.8 Hz, 1H), 4.68-4.80 (m, 2H), 5.01-5.11 (m, 2H), 5.67-5.80 (m, 1H), 5.91 (dt, *J* = 6.2, 1.6 Hz, 1H), 6.01 (dt, *J* = 6.2, 2.5 Hz, 1H), 7.20-7.26 (m, 1H), 7.30-7.36 (m, 2H), 7.36-7.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.0, 75.3, 93.0, 117.7, 124.9 (2C), 126.0, 126.8, 128.2 (2C), 132.2, 133.7, 145.4. IR (neat) 2848, 1640, 1446, 1261, 1057 cm^{-1}. MS (APCI) calcd for $C_{13}H_{15}O$ $[M+H]^+$ 187.1117, found 187.1116.

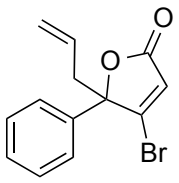
To a solution of **12** (86.5 mg, 0.25 mmol) in THF (1.7 mL) was added *t*-BuOK (42.1 mg, 0.375 mmol) at room temperature, and the reaction mixture was stirred at 80 °C for 2 h. Saturated NH_4Cl aqueous solution (10 mL) was added to the mixture, and the product was extracted with Et_2O (10mL × 3). The organic phase was washed with brine (20 mL) and dried over Na_2SO_4. The organic phase concentrated under reduced pressure, and the crude products was purified by column chromatography (eluent: hexane/Et_2O =50:1) to give the desired product **14** (63.3 mg, 96% yield).



2-Allyl-3-bromo-2-phenyl-2,5-dihydrofuran (14): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.81 (dd, *J* = 14.6, 6.6 Hz, 1H), 2.91 (dd, *J* = 14.6, 7.3 Hz, 1H), 4.68 (dd, *J* = 13.0, 1.8 Hz, 1H), 4.77 (dd, *J* = 13.0, 1.8 Hz, 1H), 5.09-5.16 (m, 1H), 5.17-5.25 (m, 1H), 5.75-5.88 (m, 1H), 6.05 (t, *J* = 1.8 Hz, 1H), 7.25-7.32 (m, 1H), 7.32-7.39 (m, 2H), 7.47-7.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

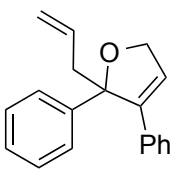
41.7, 74.8, 92.7, 118.7, 122.8, 125.8 (2C), 126.5, 127.6, 128.1 (2C), 132.6, 142.5. IR (neat) 2850, 1628, 1446, 1342, 1209, 1065 cm^{-1}. MS (APCI) calcd for $C_{13}H_{14}BrO$ $[M+H]^+$ 265.0223, found 265.0218.

To a solution of **14** (53.0 mg, 0.20 mmol) and silica gel (129.9 mg) in CH_2Cl_2 (1.2 mL) was added PCC (129.9 mg, 0.60 mmol) under argon atmosphere, and the reaction mixture was stirred at 40 °C for 21 h. To the solution was added PCC (43.3 mg, 0.20 mmol), and then the reaction mixture was stirred at 40 °C for 9 h. The mixture was filtered through Celite® and washed with a mixture of CH_2Cl_2 and Et_2O (1/4) (10 mL × 3). The filtrate was washed with brine (20 mL) and dried over Na_2SO_4. The organic phase concentrated under reduced pressure, and the crude products was purified by column chromatography (eluent: hexane/AcOEt =10:1) to give the desired product **15** (44.7 mg, 80% yield).



5-Allyl-4-bromo-5-phenylfuran-2(5*H*)-one (15): ^1H NMR (400 MHz, $CDCl_3$) δ 3.02 (dd, *J* = 14.8, 7.6 Hz, 1H), 3.09 (dd, *J* = 14.8, 6.8 Hz, 1H), 5.17-5.32 (m, 2H), 5.58-5.72 (m, 1H), 6.29 (s, 1H), 7.35-7.48 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.7, 91.7, 121.3, 121.6, 125.5 (2C), 128.7 (2C), 129.0, 129.1, 136.0, 154.8, 169.9. IR (neat) 2926, 1745, 1600, 1447, 1251, 1193 cm^{-1}. MS (APCI) calcd for $C_{13}H_{12}BrO_2$ $[M+H]^+$ 279.0015, found 279.0009.

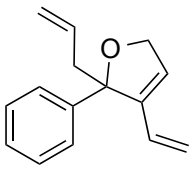
A solution of **14** (53.0 mg, 0.20 mmol), $PhB(OH)_2$ (61.0 mg, 0.50 mmol), and $PdCl_2(PPh_3)_2$ (14.0 mg, 0.020 mmol) in DMF (4.0 mL) was stirred at room temperature for 30 min. 2 M K_2CO_3 aqueous solution (0.80 mL) was added to the reaction mixture, and the mixture was stirred at 60 °C for 4 h. H_2O (10 mL) was added to reaction mixture, and extracted with Et_2O (10 mL × 3). The organic phase was washed with brine (20 mL) and dried over Na_2SO_4. The organic phase concentrated under reduced pressure, and the crude products was purified by column chromatography (eluent: hexane/Et_2O =30:1) to give the desired product **16** (50.4 mg, 96% yield).



2-Allyl-2,3-diphenyl-2,5-dihydrofuran (16): ^1H NMR (400 MHz, $CDCl_3$) δ 2.92 (ddt, *J* = 14.4,

7.6, 1.2 Hz, 1H), 3.04 (ddt, *J* = 14.4, 6.6, 1.2 Hz, 1H), 4.81 (dd, *J* = 14.0, 2.0 Hz, 1H), 4.91 (dd, *J* = 14.0, 2.0 Hz, 1H), 4.98-5.07 (m, 2H), 5.87 (m, 1H), 6.22 (t, *J* = 2.0 Hz, 1H), 7.02-7.07 (m, 2H), 7.15-7.23 (m, 3H), 7.24-7.28 (m, 1H), 7.28-7.36 (m, 2H), 7.39-7.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.3, 74.6, 93.1, 118.0, 124.3, 126.2 (2C), 127.4 (2C), 127.5, 127.6, 128.1 (2C), 128.3 (2C), 133.6, 133.8, 143.9, 144.3. IR (neat) 2843, 1445, 1205, 1068, 913 cm^{-1}. MS (APCI) calcd for $C_{19}H_{19}O$ $[M+H]^+$ 263.1430, found 263.1420.

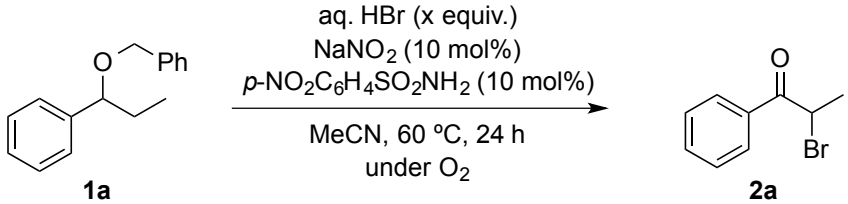
To a solution of **14** (53.0 mg, 0.20 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.05 mmol) in toluene (1.0 mL) was added tributylvinyltin (70.1 μL, 0.24 mmol) at room temperature, and then the reaction mixture was stirred at 100 °C for 4 h. The reaction mixture was cooled to room temperature and distilled with Et_2O (10 ml). The organic phase was washed with brine (10 mL) and dried over Na_2SO_4. The organic phase concentrated under reduced pressure, and the crude products was purified by column chromatography (eluent: hexane/Et_2O =30:1) to give the desired product **17** (38.0 mg, 90% yield).



2-Allyl-2-phenyl-3-vinyl-2,5-dihydrofuran (17): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.89 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.97 (dd, *J* = 14.4, 6.8 Hz, 1H), 4.72 (dq, *J* = 14.4, 1.2 Hz, 1H), 4.80 (dq, *J* = 14.4, 1.2 Hz, 1H), 5.04-5.10 (m, 2H), 5.11-5.24 (m, 2H), 5.77-5.90 (m, 1H), 6.02 (s, 1H), 6.22 (ddd, *J* = 17.8, 11.2, 1.2 Hz, 1H), 7.22-7.28 (m, 1H), 7.30-7.36 (m, 2H), 7.40-7.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.7, 74.3, 92.3, 117.0, 117.8, 124.8, 125.9 (2C), 127.3, 128.2 (2C), 128.8, 133.6, 142.4, 144.3. IR (neat) 2841, 1446, 1195, 1069, 909 cm^{-1}. MS (APCI) calcd for $C_{15}H_{17}O$ $[M+H]^+$ 213.1274, found 213.1266.

4. Mechanistic Studies for Catalytic Dehydrogenative Dual Functionalization of Ethers (1).

4.1. Fluctuation of catalytic dehydrogenative dual functionalization products by amount of aq. HBr (Figure S1).



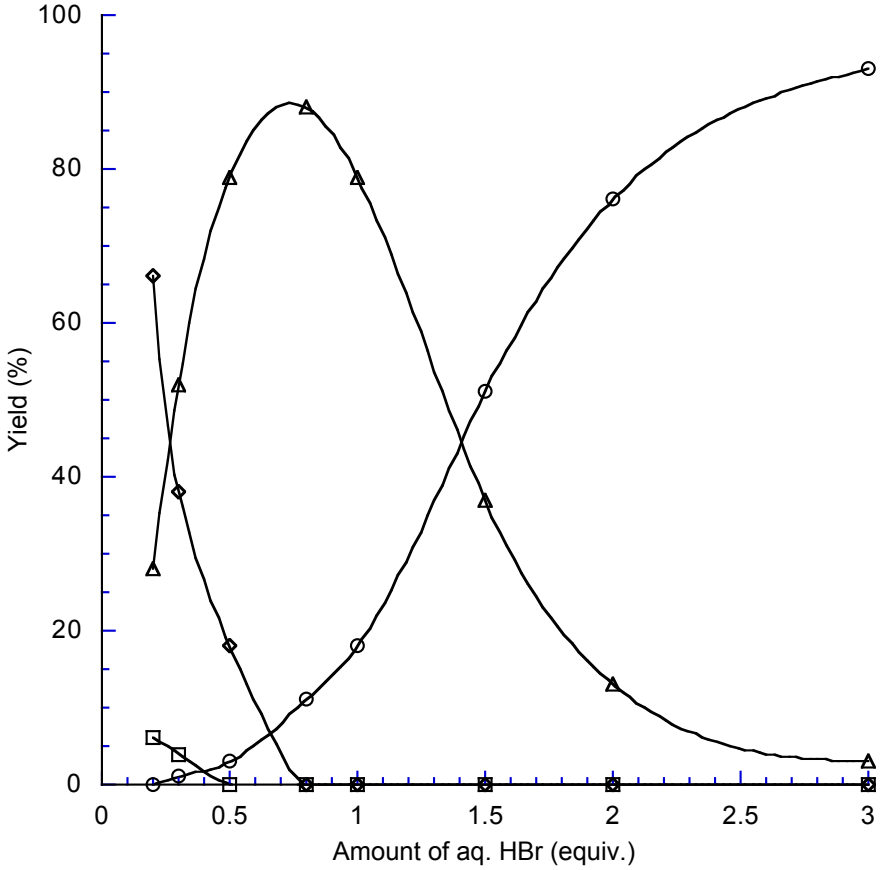
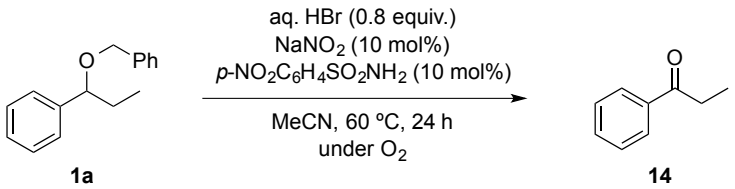


Figure S1. Plot of percentage yield (%) of products for the DDF of **1a** versus equivalent amount of aq. HBr (equiv.). ◇: **1a**. □: α-ethyl-benzyl alcohol (**1ab**). △: propiophenone (**14**). ○: **2a**.

4.2. Reactivity of each reaction by varying amounts of aq. HBr and existence of sulfonamide catalyst (Scheme S1, Eqs S1–S3).

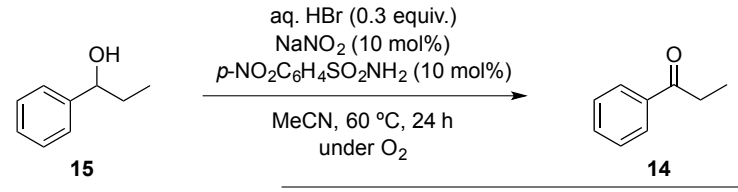
A) Dealkylation–Oxidation of Ether (1a)



1a **14** (S1)

	Yield of **14** (%)
	86 (7)[a]
without *p*-$NO_2C_6H_4SO_2NH_2$	88 (11)[a]

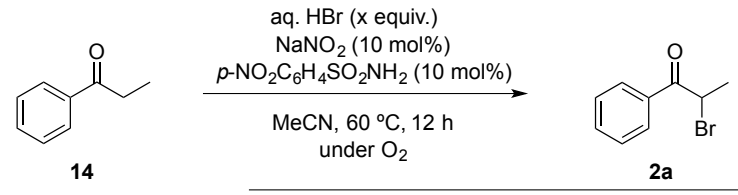
B) Oxidation of Alcohol (15)



15 **14** (S2)

	Yield of **14** (%)[b]
	82 (7)
without *p*-$NO_2C_6H_4SO_2NH_2$	77 (6)

C) α–Bromination of Ketone (14)



14 **2a** (S3)

x	Yield of **2a** (%)[c]
1.0	14 (82)
2.0	72 (28)
3.0	99 (1)
3.0 (without *p*-$NO_2C_6H_4SO_2NH_2$)	66 (33)

Scheme S1. Mechanistic studies of DDF of ethers via aerobic oxidation of bromide. [a]Number in brackets indicated yield of **2a**. [b]Number in brackets indicates recovery of **15**. [c]Number in brackets indicates recovery of **14**.

4.3. ^{1}H-NMR titration experiments for *p*-NO_2-$C_6H_4SO_2NH_2$ with Br_2 in CD_3CN (Figure S2).

NMR tube was charged with *p*-NO_2-$C_6H_4SO_2NH_2$ (4.7 mg, 0.023 mmol) in CD_3CN (750 μL) at room temperature. To the solution, Br_2 was added so that the molecular ratio of bromine and *p*-NO_2-$C_6H_4SO_2NH_2$ ([Br_2]/[*p*-NO_2-$C_6H_4SO_2NH_2$]) becomes 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0, 10.0, 20.0, and 30.0. All the ^{1}H-NMR spectra were measured on a JEOL ECS-500 spectrometer and chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (cyclohexane at 1.44 ppm).

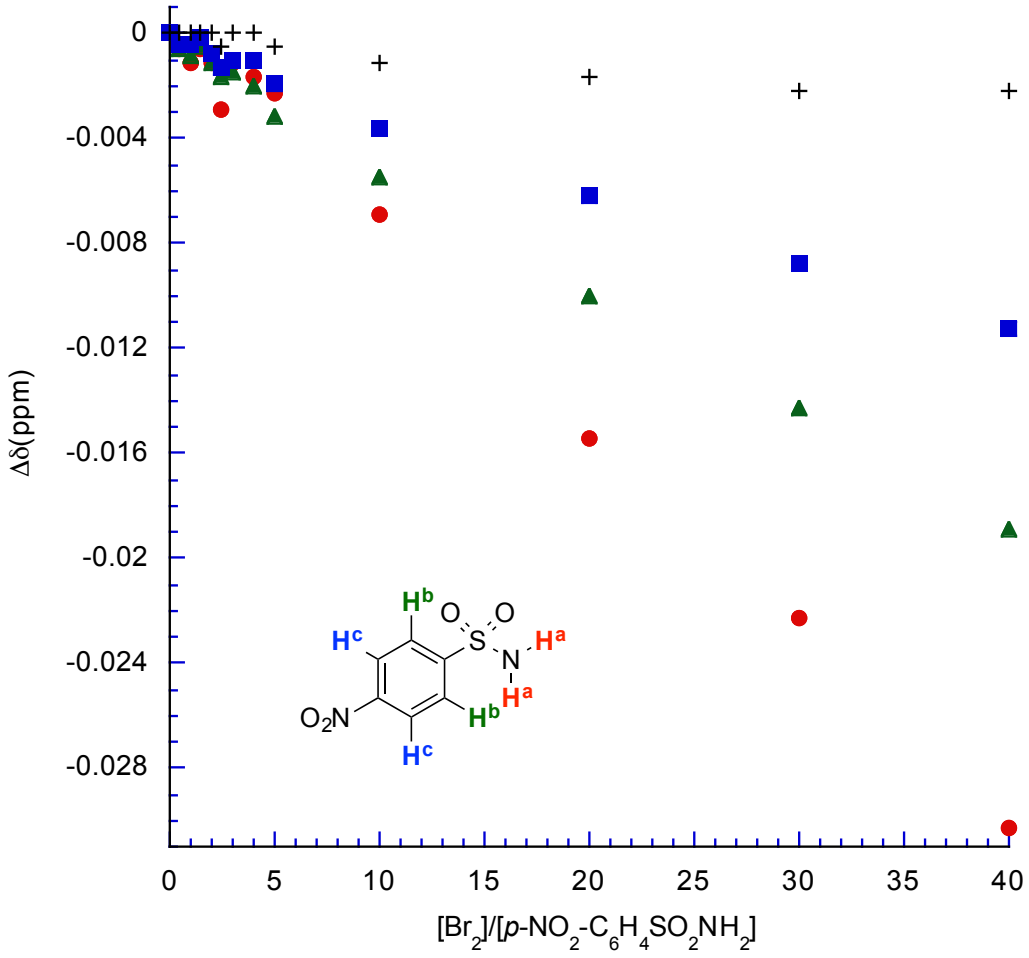
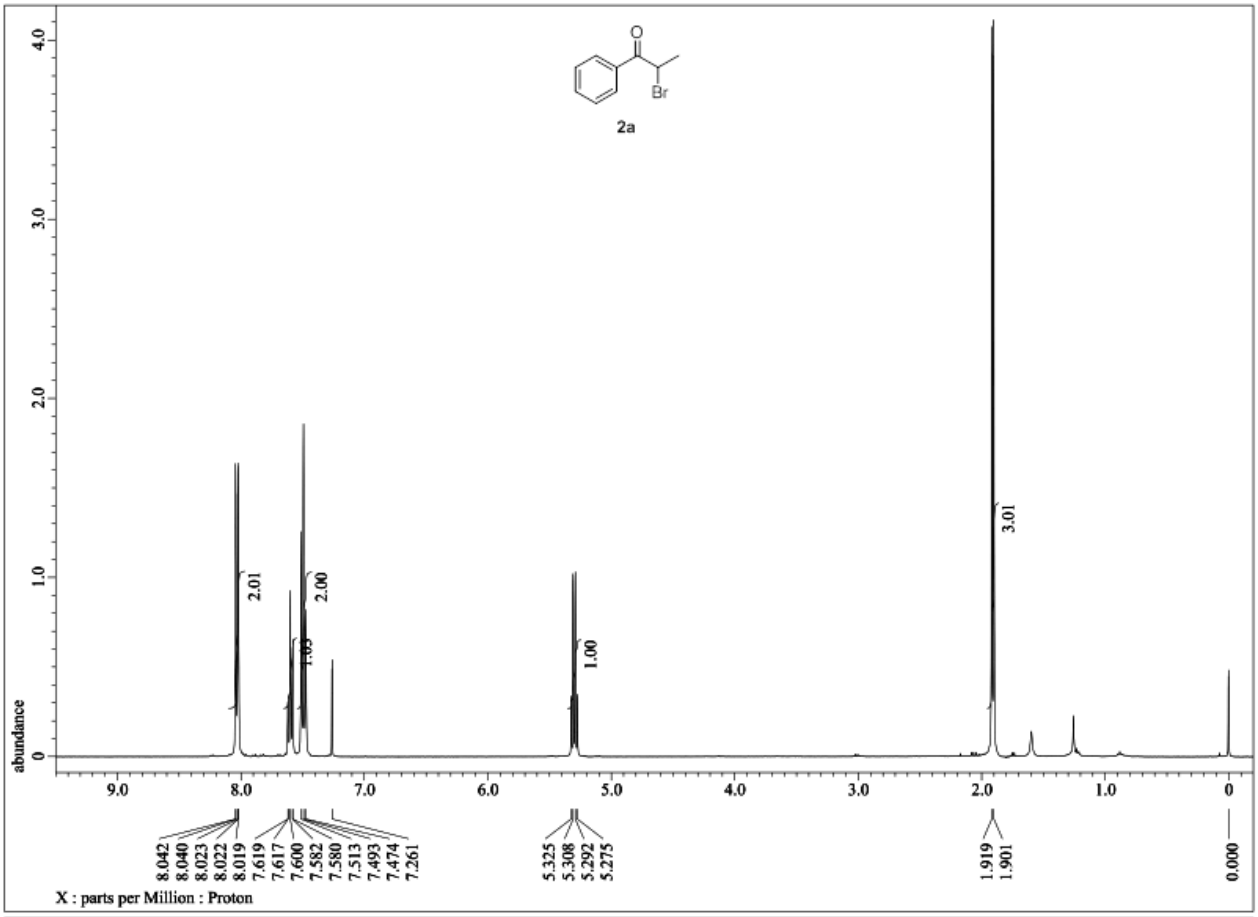
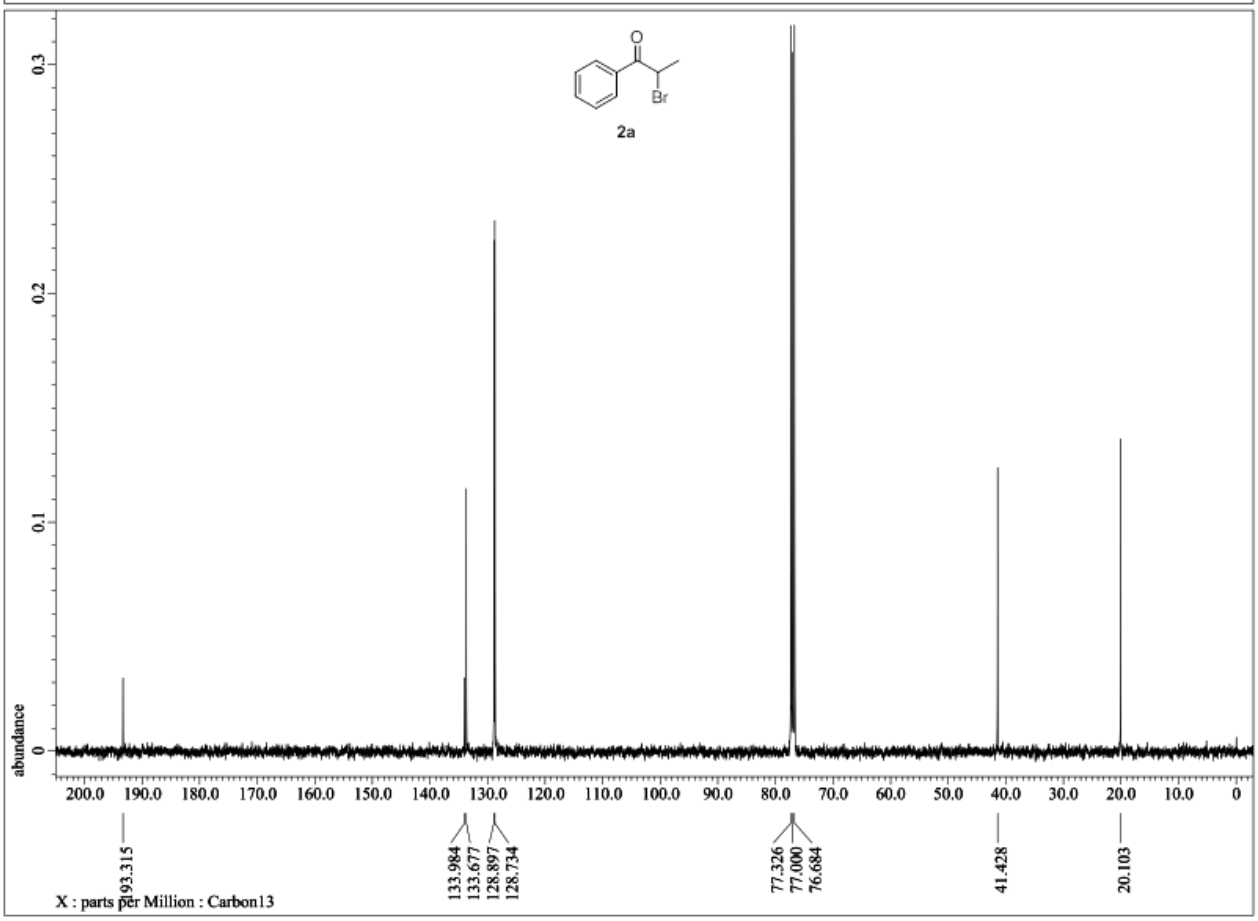
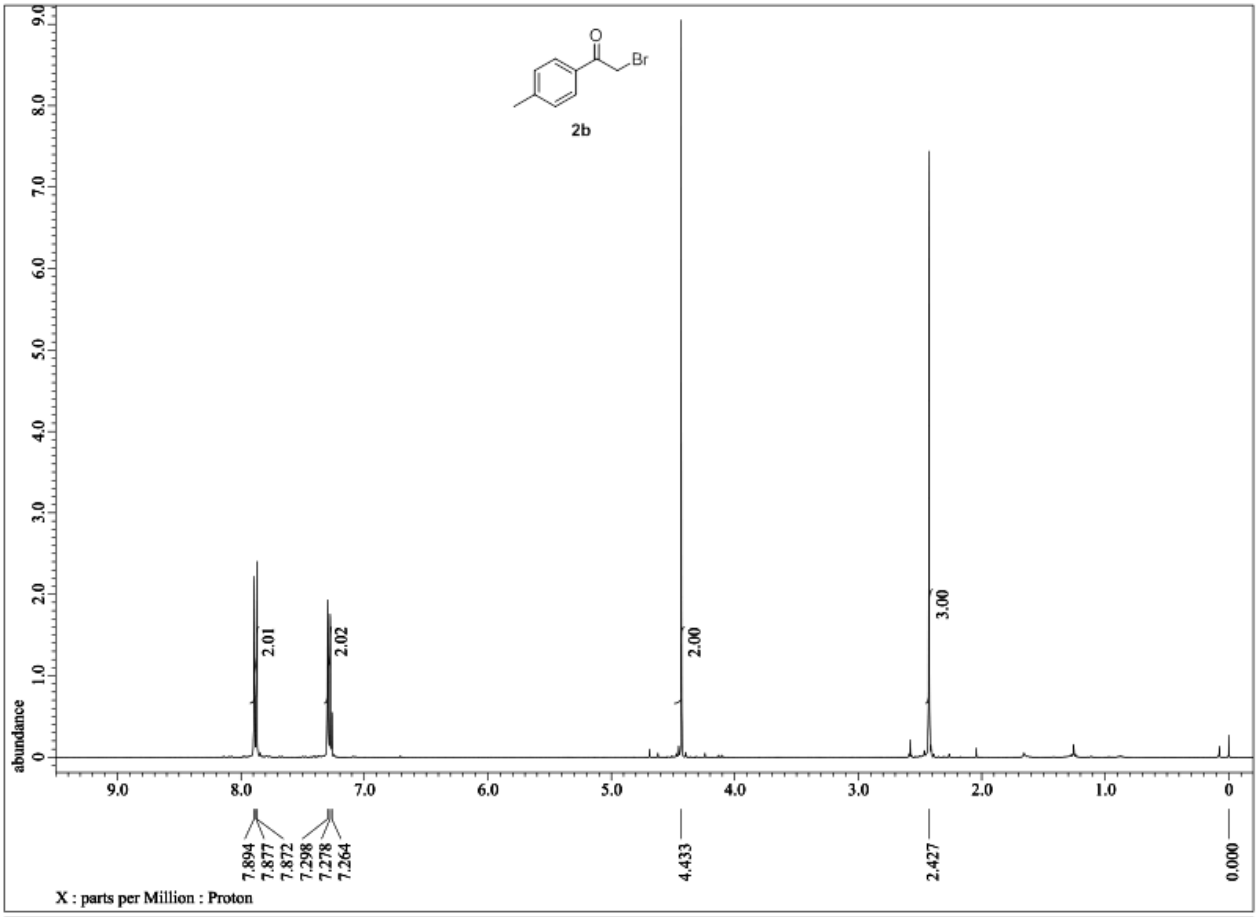
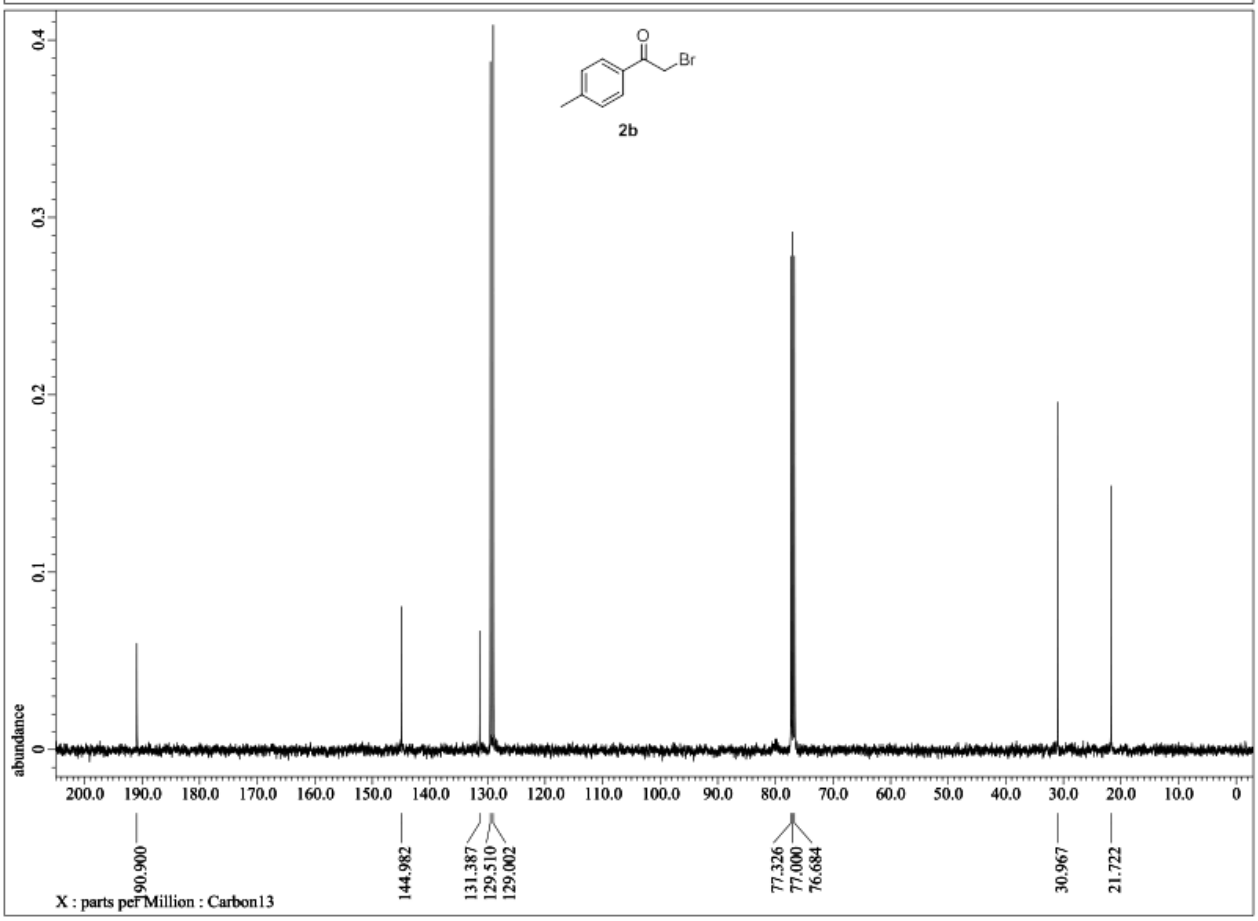


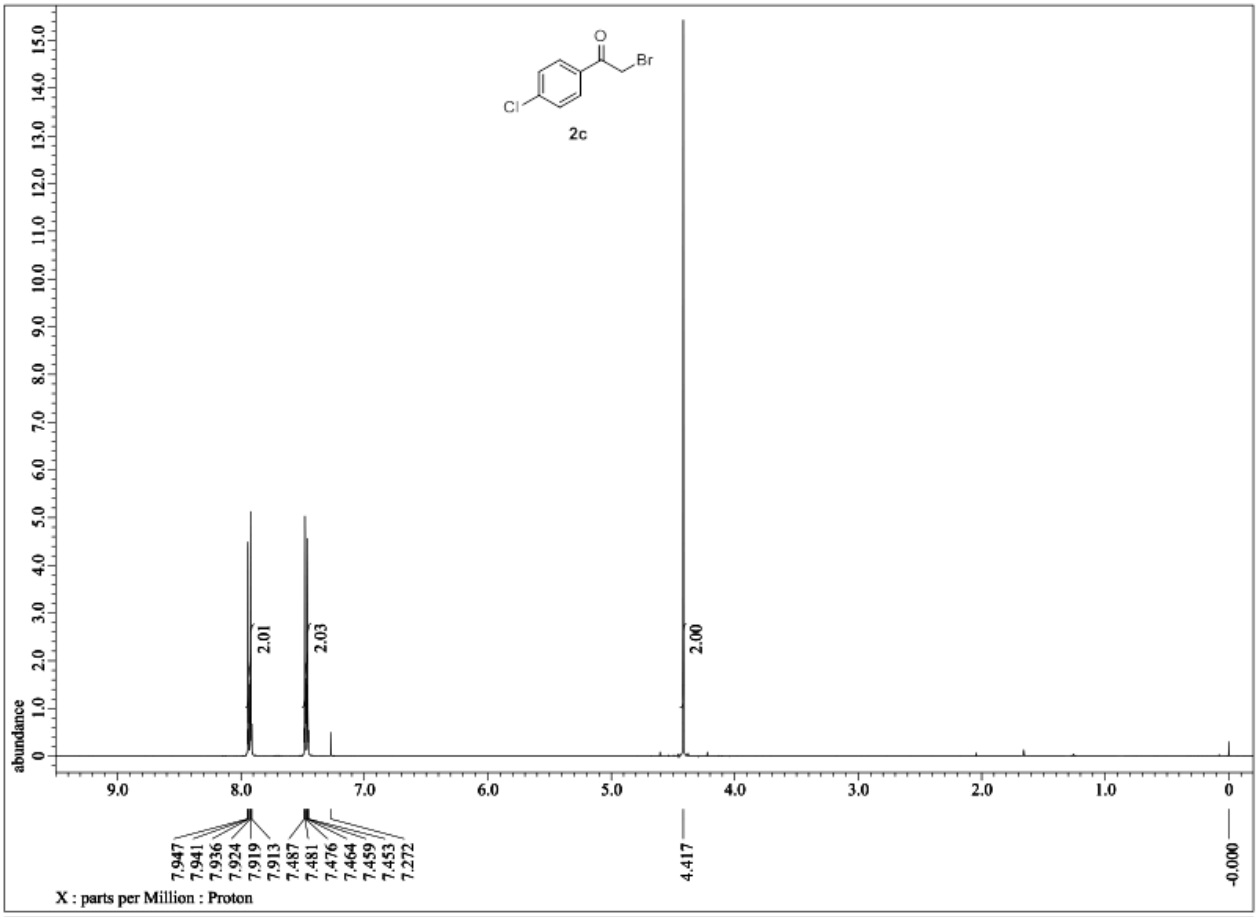
Figure S2. ^{1}H-NMR data for titration of *p*-NO_2-$C_6H_4SO_2NH_2$ with Br_2. Plot of variation of change in chemical shift (Δδ) versus [Br_2]/[*p*-NO_2-$C_6H_4SO_2NH_2$]: H^a (red ●), H^b (green ▲), H^c (bule ■), CH_3CN (brack, +).

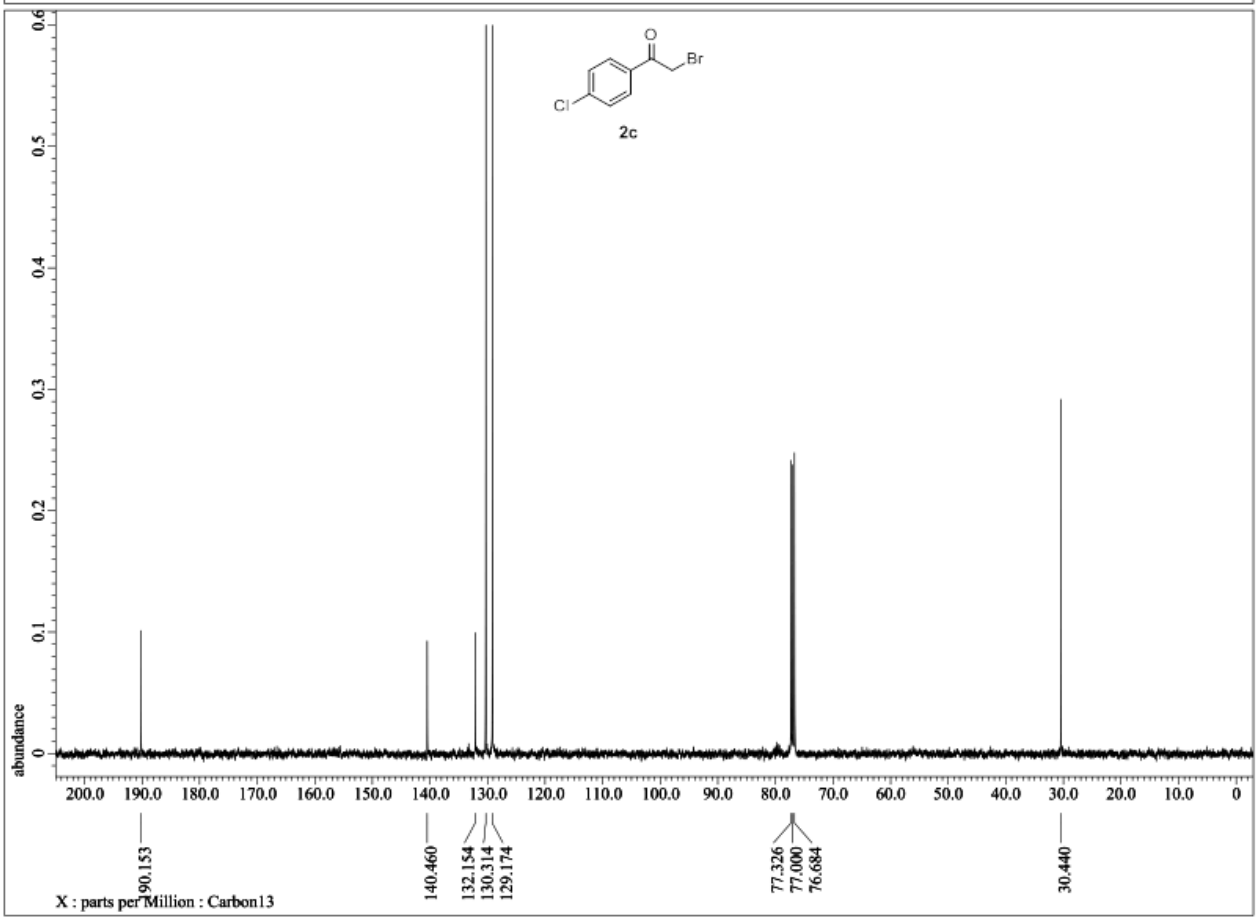

2a
abundance
X : parts per Million : Proton
8.042
8.040
8.023
8.022
8.019
7.619
7.617
7.600
7.582
7.580
7.513
7.493
7.474
7.261
5.325
5.308
5.292
5.275
1.919
1.901
0.000
2.01
2.00
1.00
3.01

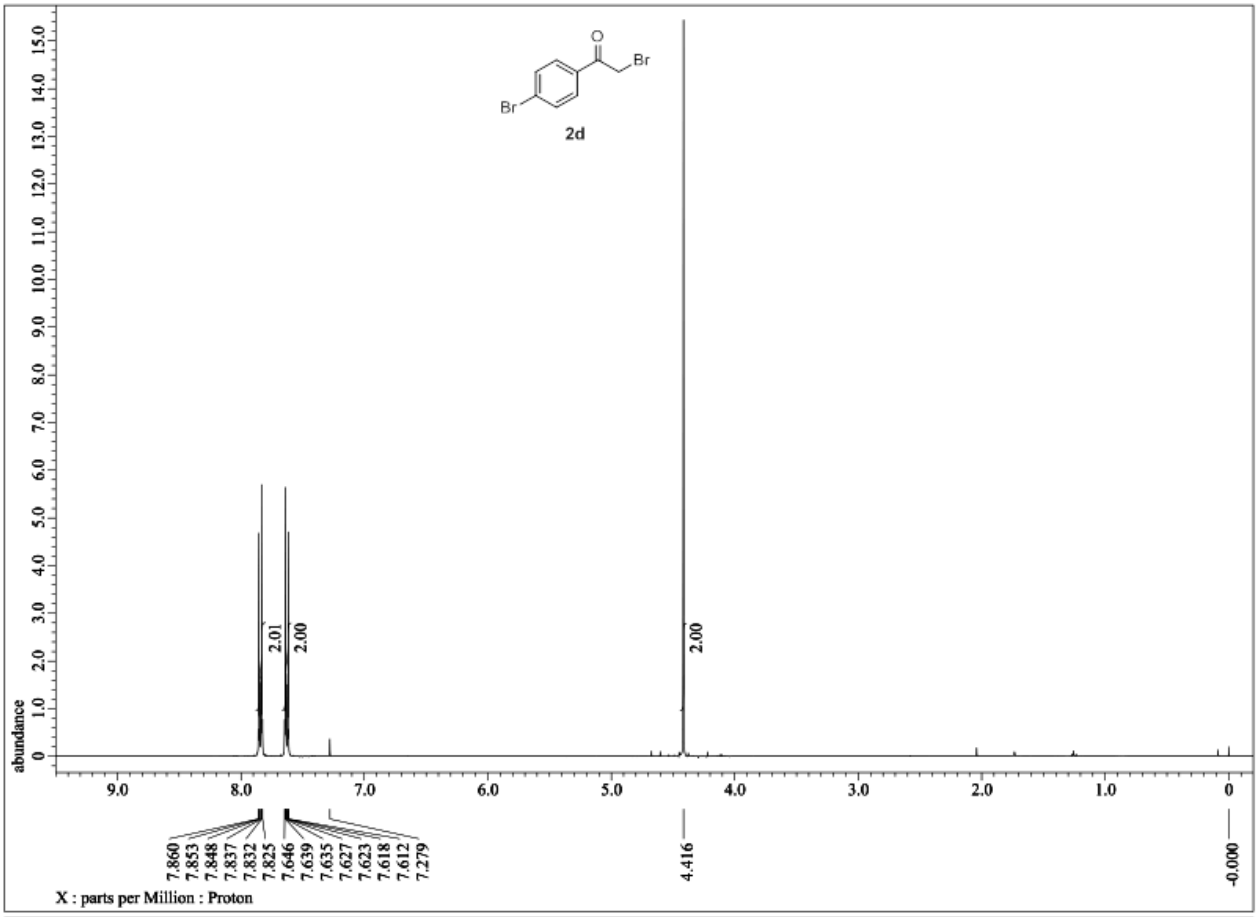

2a
abundance
X : parts per Million : Carbon13
193.315
133.984
133.677
128.897
128.734
77.326
77.000
76.684
41.428
20.103

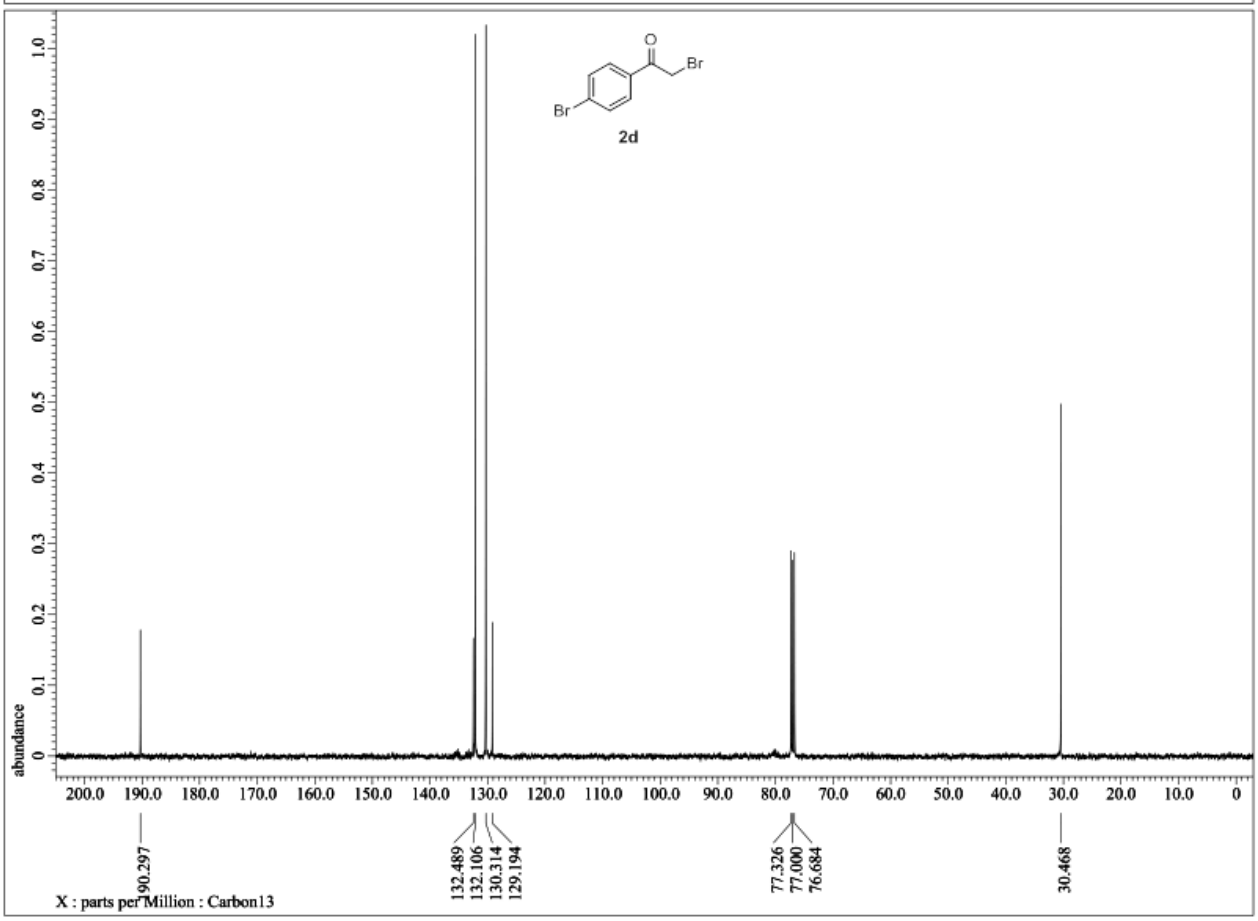

O
Br
2b
abundance
2.01
2.02
2.00
3.00
7.894
7.877
7.872
7.298
7.278
7.264
4.433
2.427
0.000
X : parts per Million : Proton

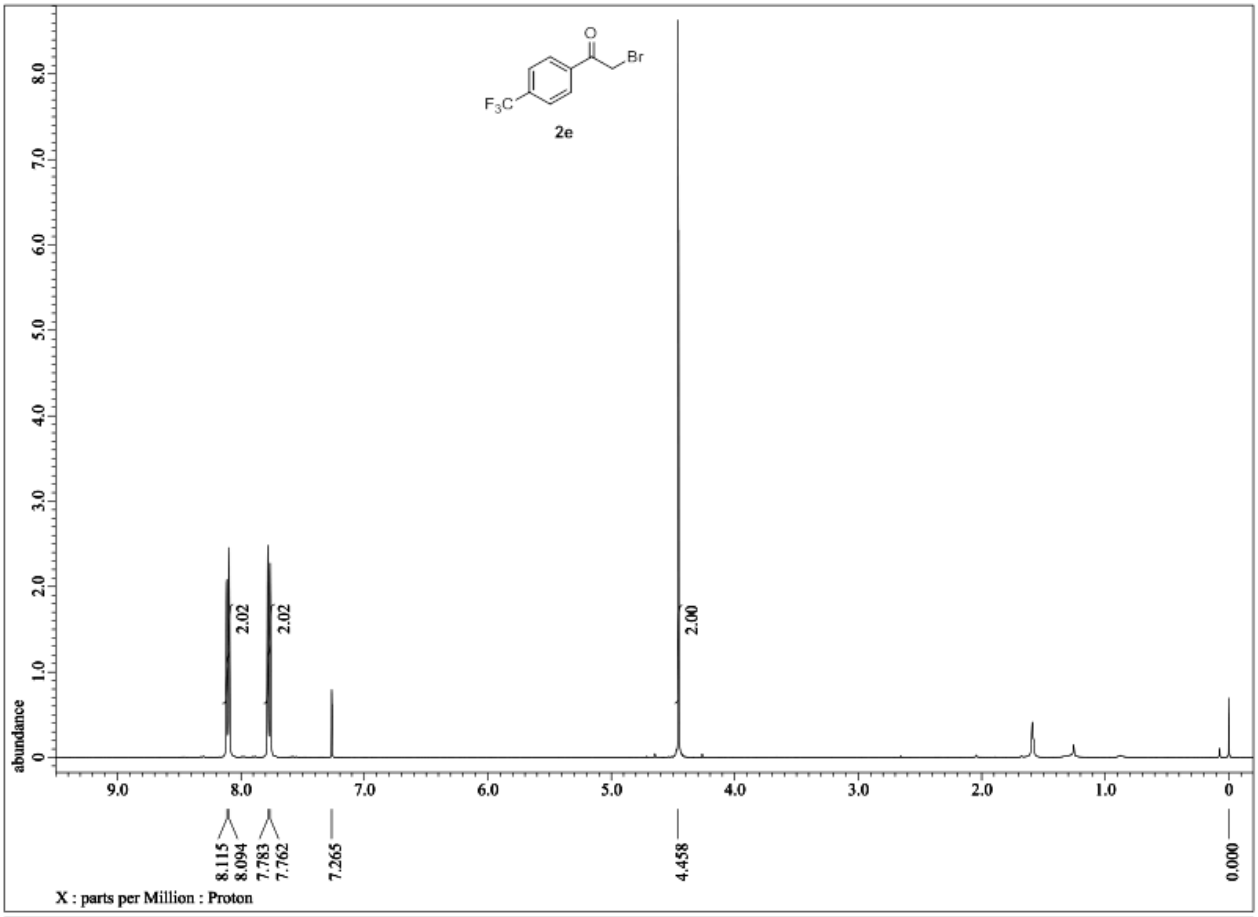

O
Br
2b
abundance
190.900
144.982
131.387
129.510
129.002
77.326
77.000
76.684
30.967
21.722
X : parts per Million : Carbon13

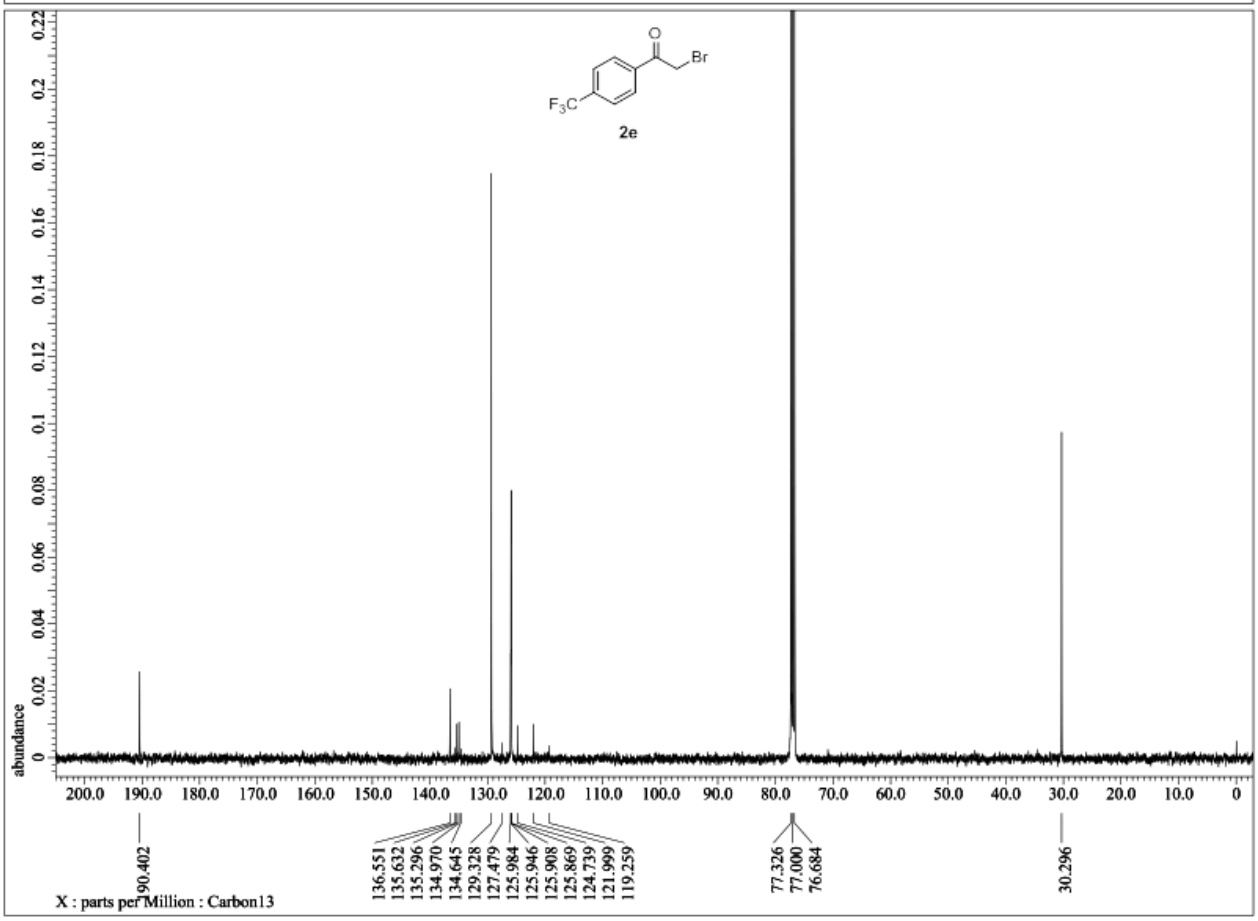

O
Br
Cl
2c
abundance
2.01
2.03
2.00
7.947
7.941
7.936
7.924
7.919
7.913
7.487
7.481
7.476
7.464
7.459
7.453
7.272
4.417
-0.000
X : parts per Million : Proton

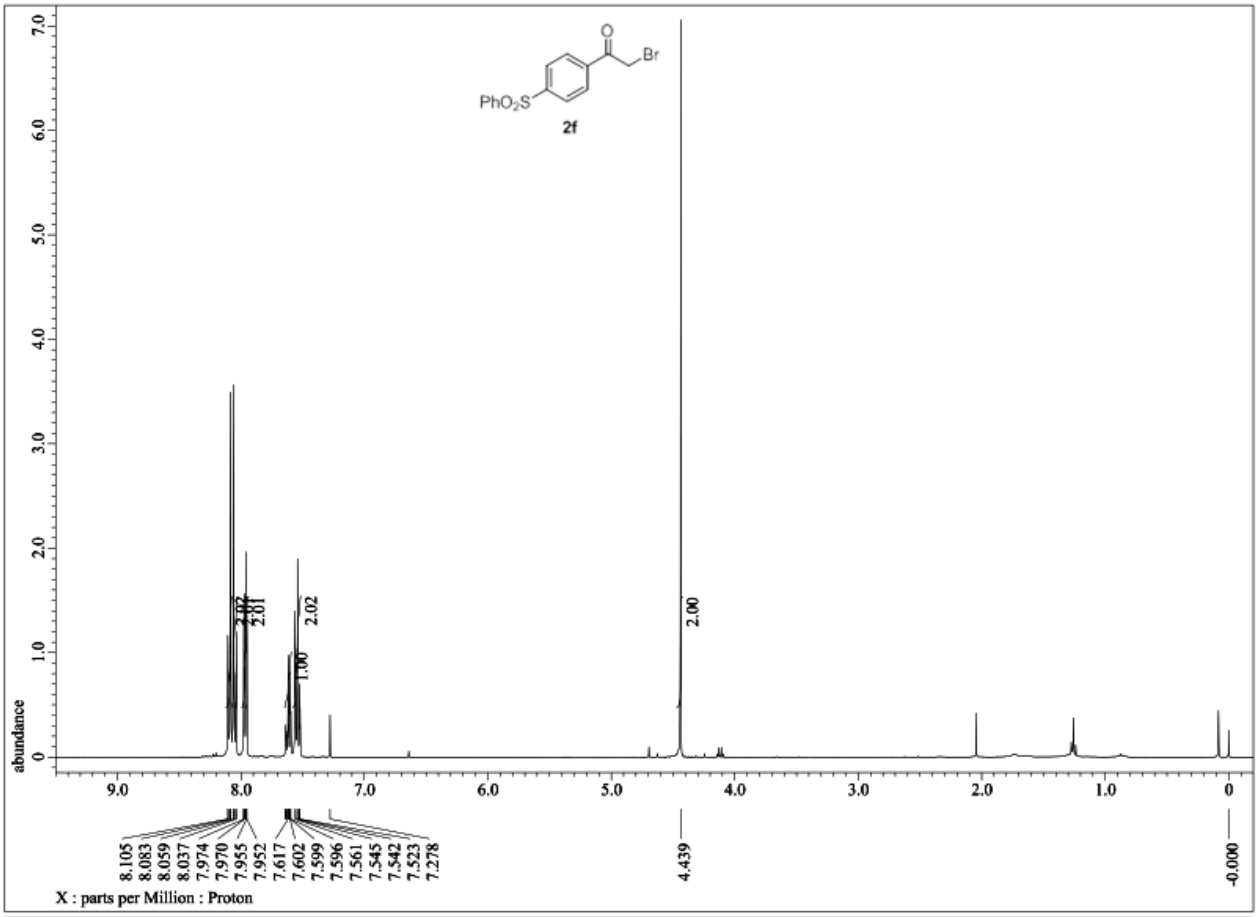

O
Br
Cl
2c
abundance
90.153
140.460
132.154
130.314
129.174
77.326
77.000
76.684
30.440
X : parts per Million : Carbon13


2d
abundance
2.01
2.00
2.00
7.860
7.853
7.848
7.837
7.832
7.825
7.646
7.639
7.635
7.627
7.623
7.618
7.612
7.279
4.416
-0.000
X : parts per Million : Proton


2d
abundance
90.297
132.489
132.106
130.314
129.194
77.326
77.000
76.684
30.468
X : parts per Million : Carbon13


O
Br
F3C
2e
abundance
2.02
2.02
2.00
8.115
8.094
7.783
7.762
7.265
4.458
0.000
X : parts per Million : Proton


O
Br
F3C
2e
abundance
190.402
136.551
135.632
135.296
134.970
134.645
129.328
127.479
125.984
125.946
125.908
125.869
124.739
121.999
119.259
77.326
77.000
76.684
30.296
X : parts per Million : Carbon13


PhO2S
Br
O
2f
abundance
X : parts per Million : Proton
8.105
8.083
8.059
8.037
7.974
7.970
7.955
7.952
7.617
7.602
7.599
7.596
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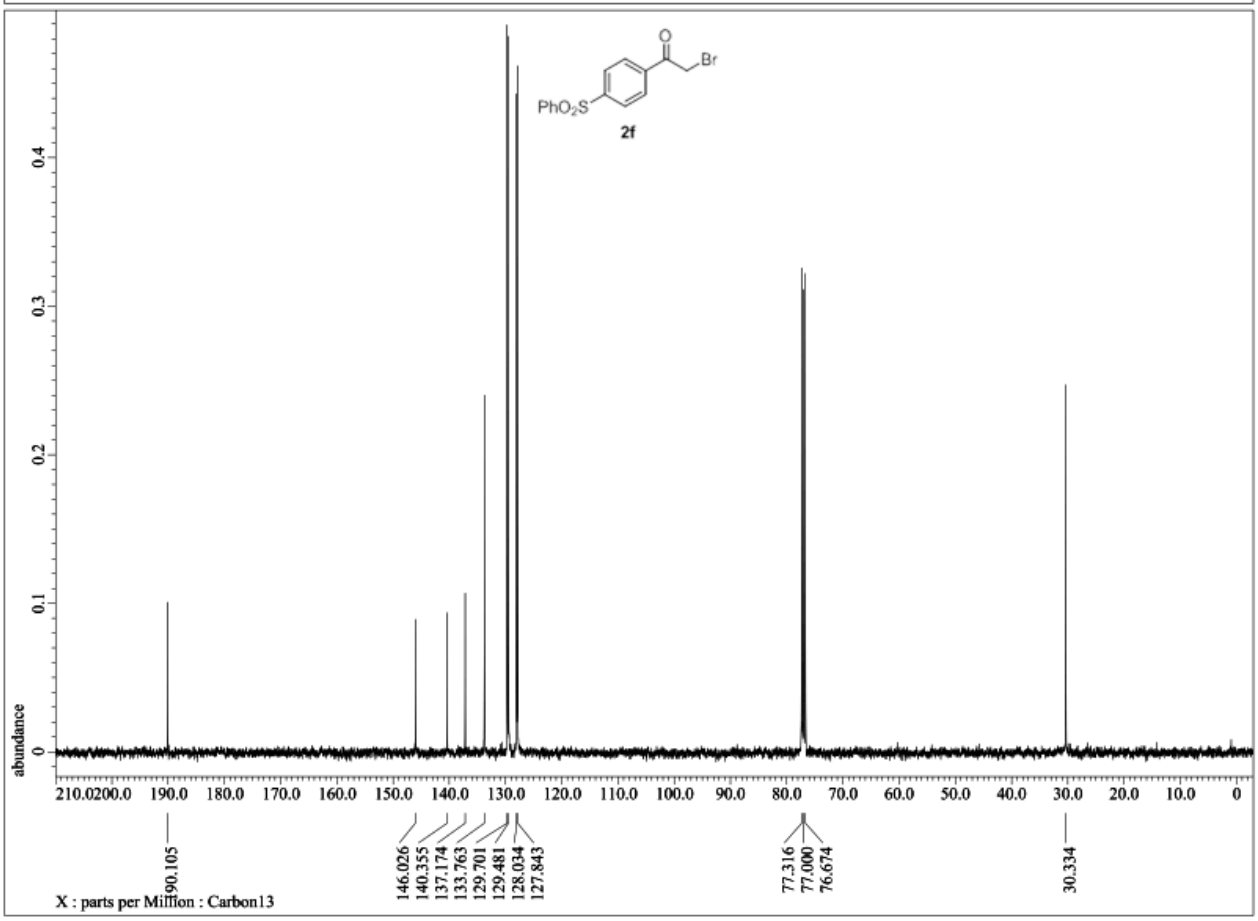
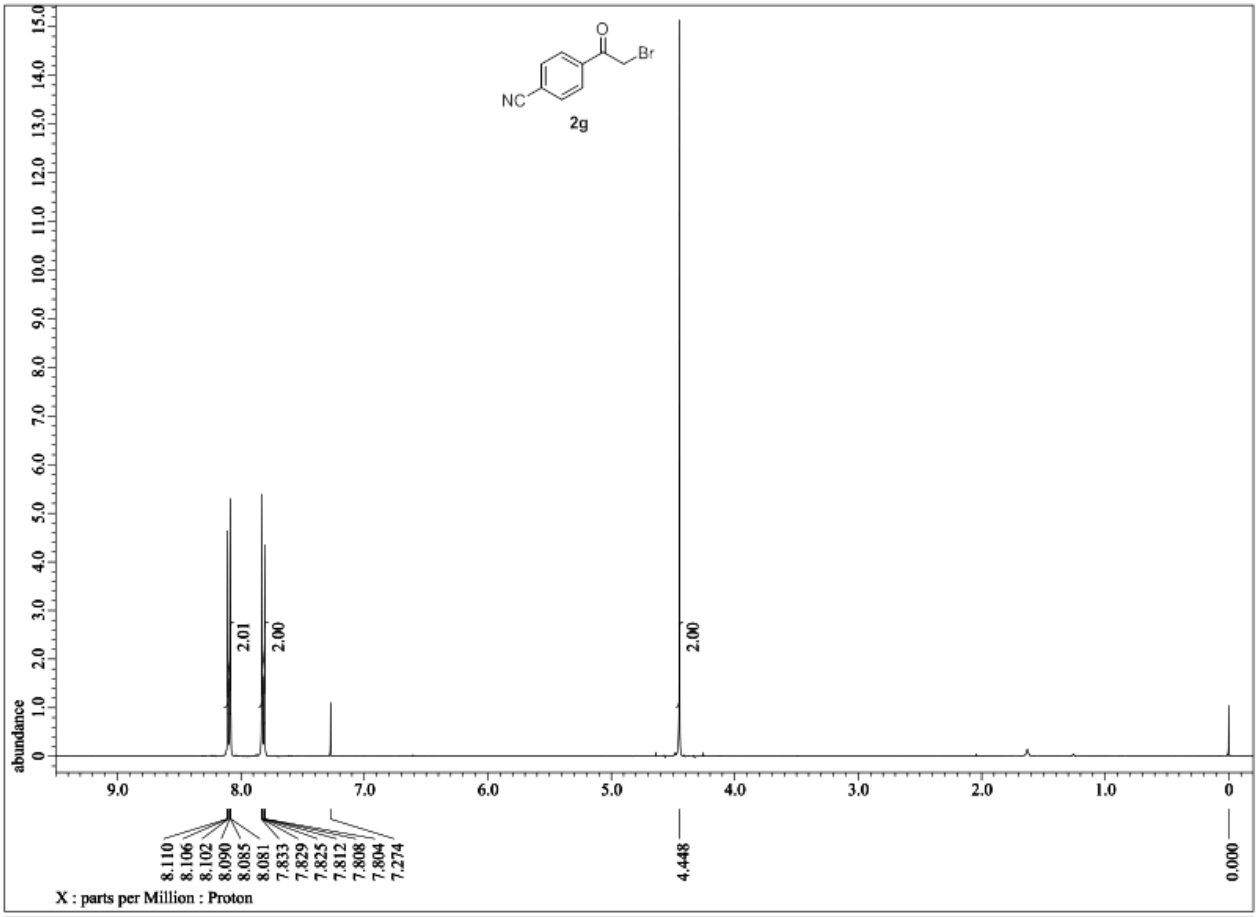
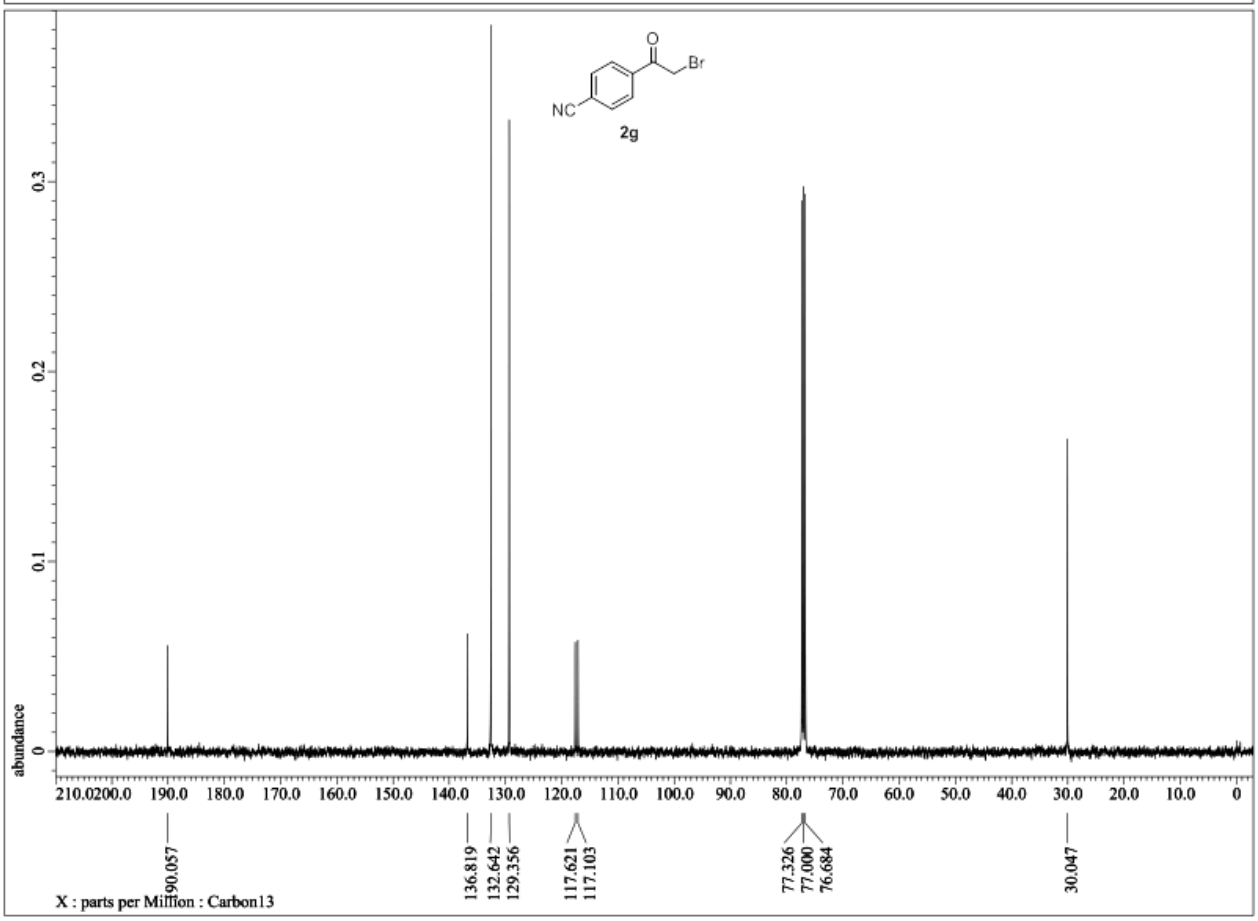
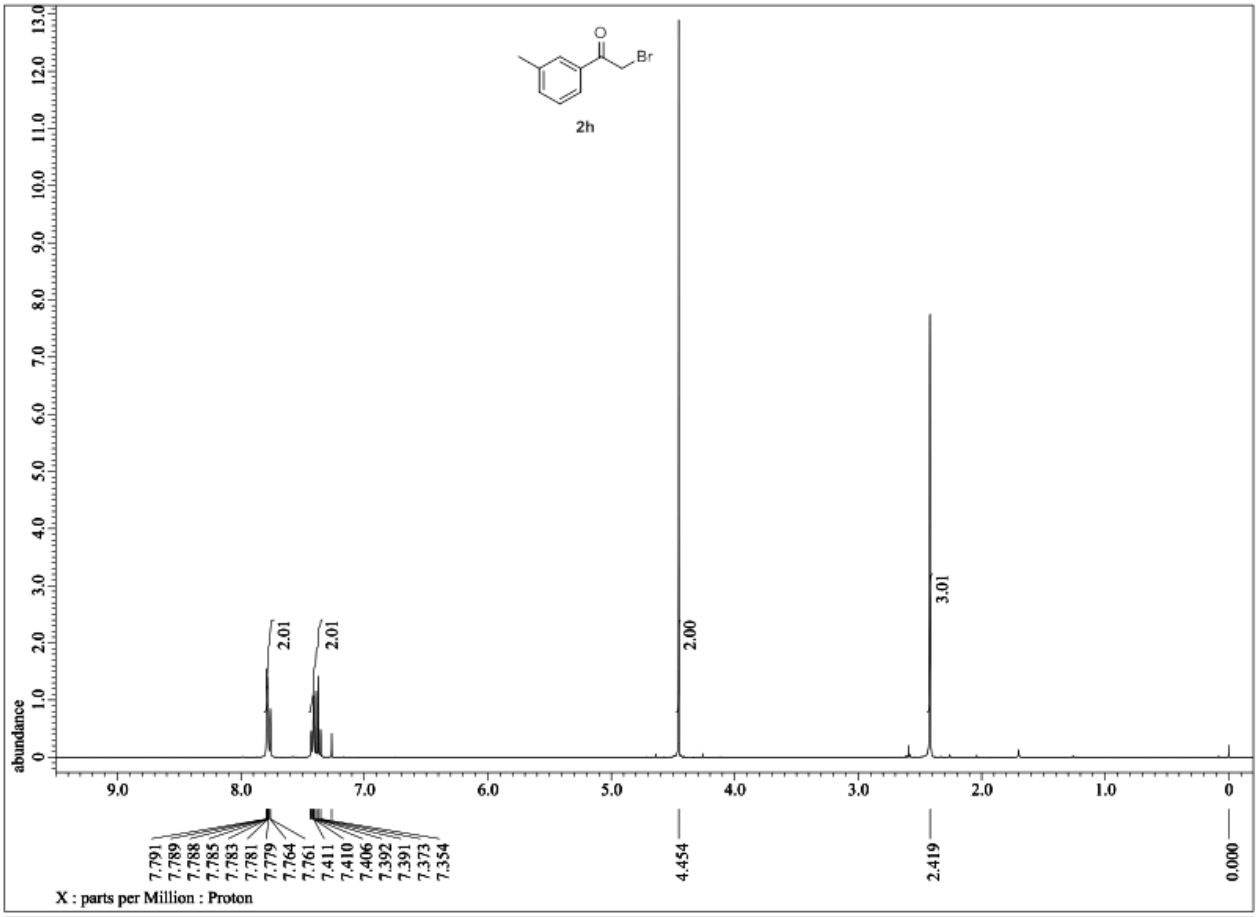
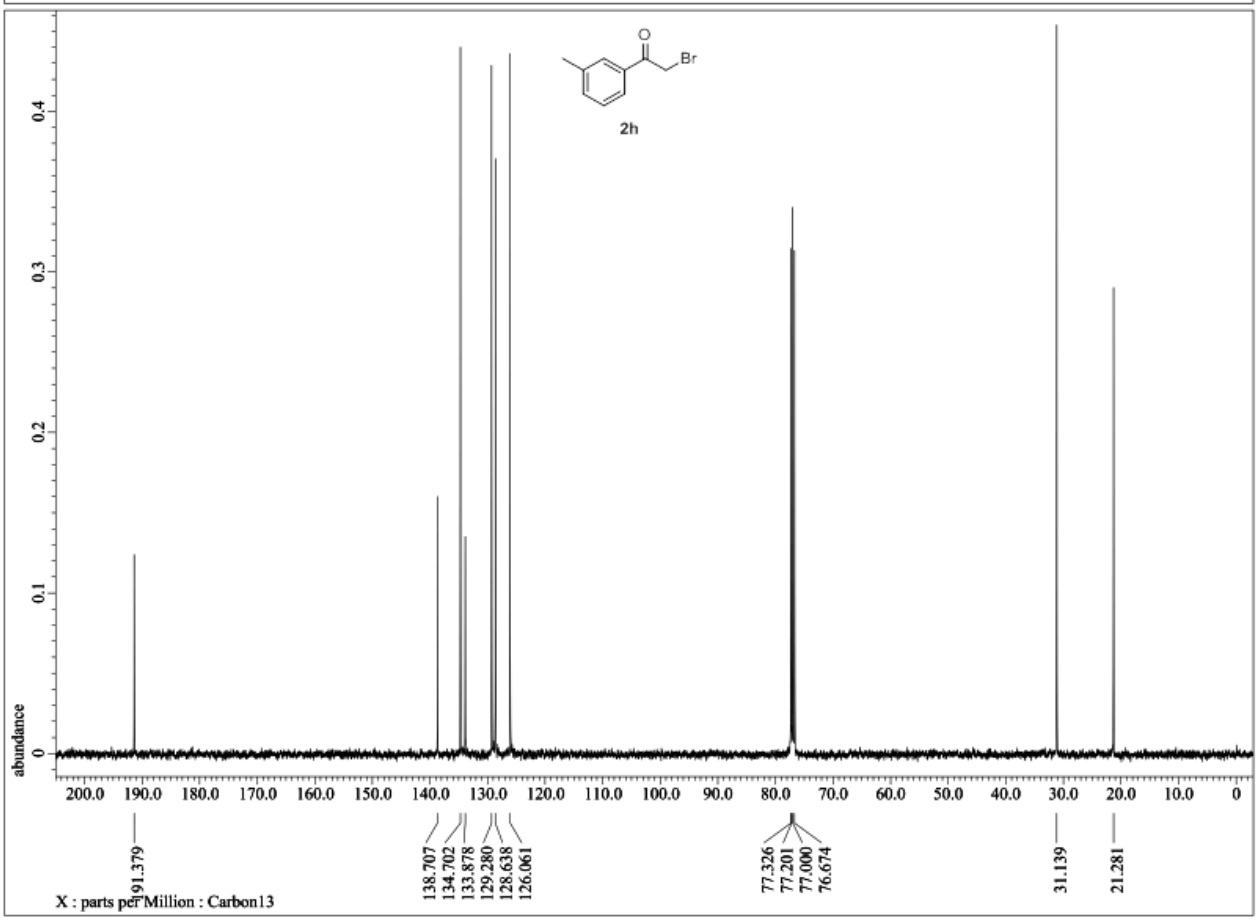
7.545
7.542
7.523
7.278
4.439
-0.000

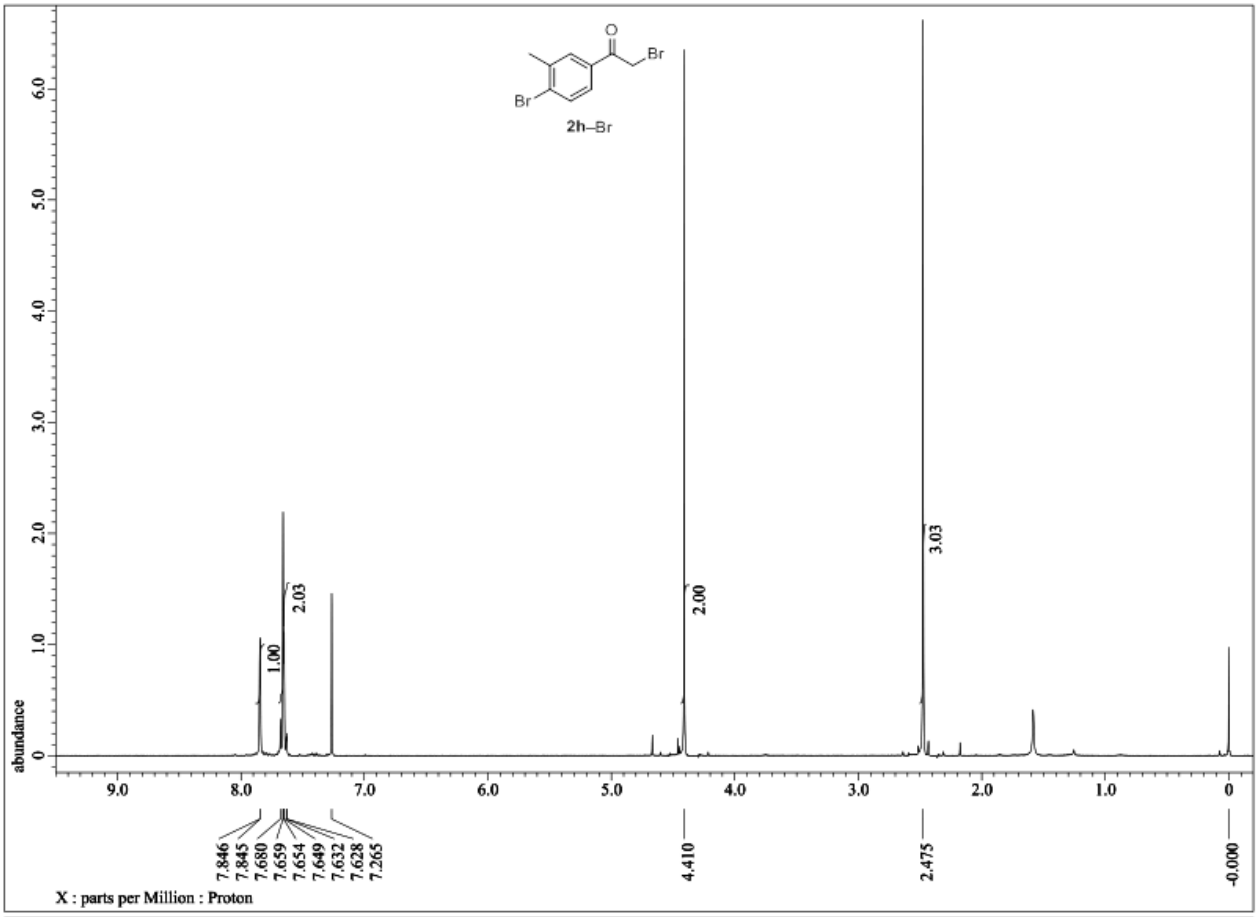

PhO2S
Br
O
2f
abundance
X : parts per Million : Carbon13
190.105
146.026
140.355
137.174
133.763
129.701
129.481
128.034
127.843
77.316
77.000
76.674
30.334

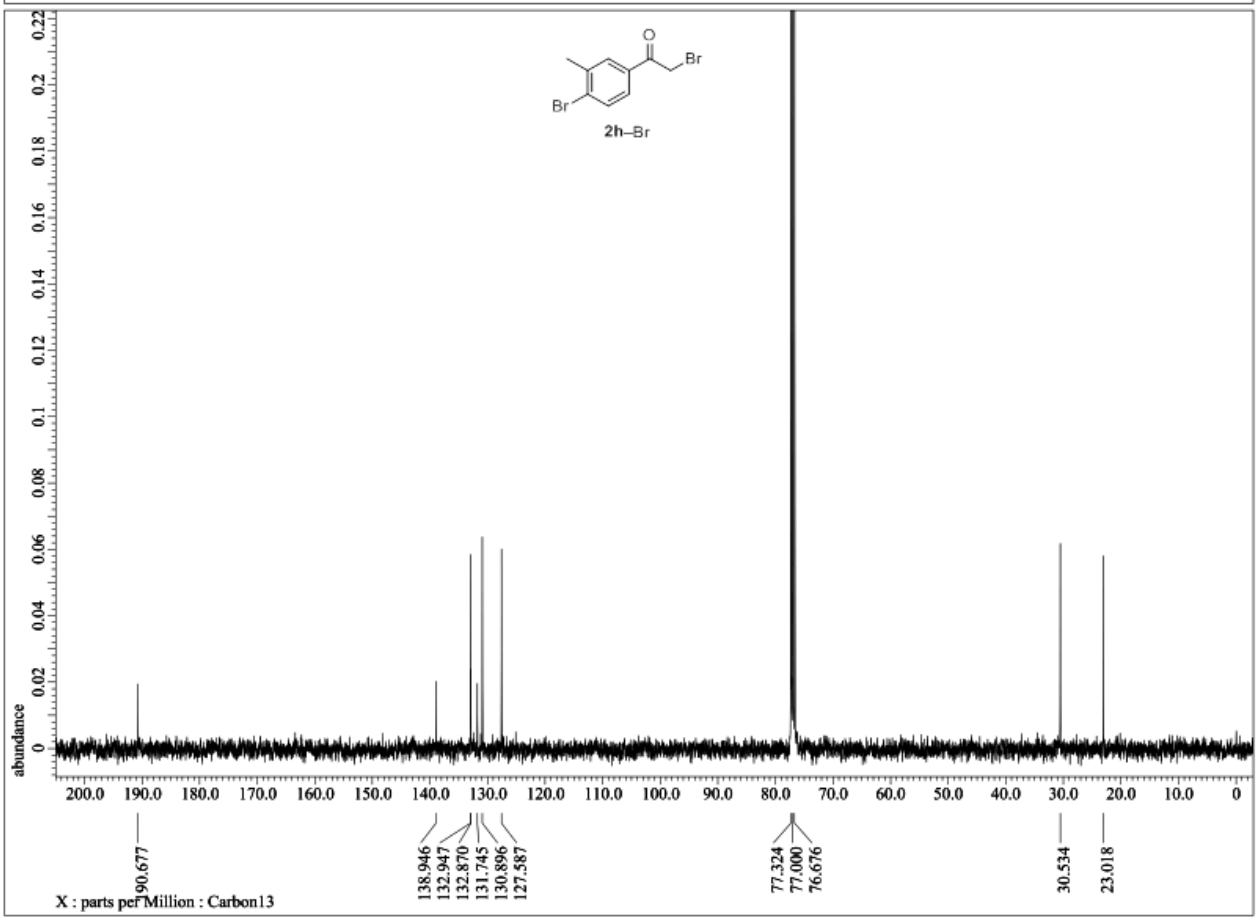

O
Br
NC
2g
abundance
2.01
2.00
2.00
8.110
8.106
8.102
8.090
8.085
8.081
7.833
7.829
7.825
7.812
7.808
7.804
7.274
4.448
0.000
X : parts per Million : Proton

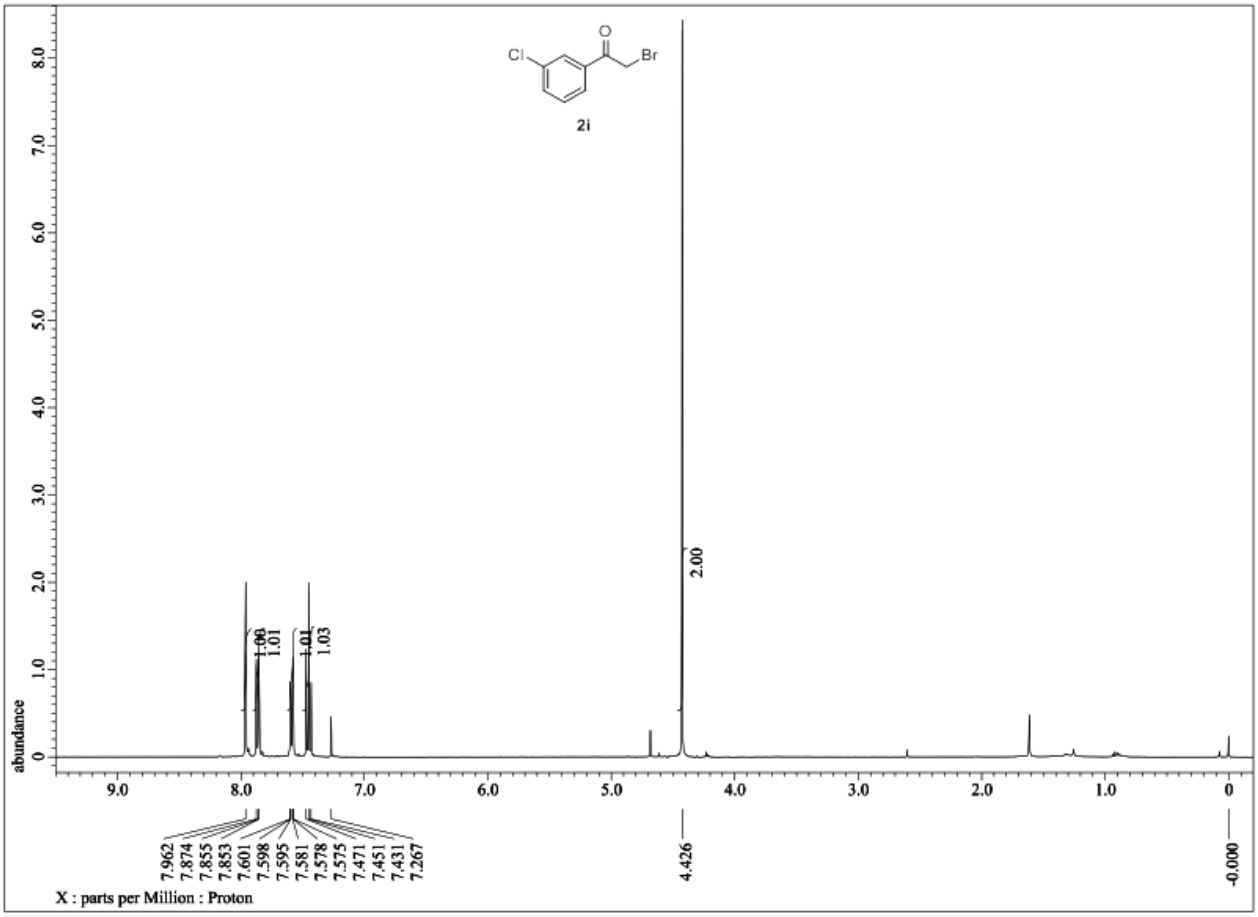

O
Br
NC
2g
abundance
190.057
136.819
132.642
129.356
117.621
117.103
77.326
77.000
76.684
30.047
X : parts per Million : Carbon13

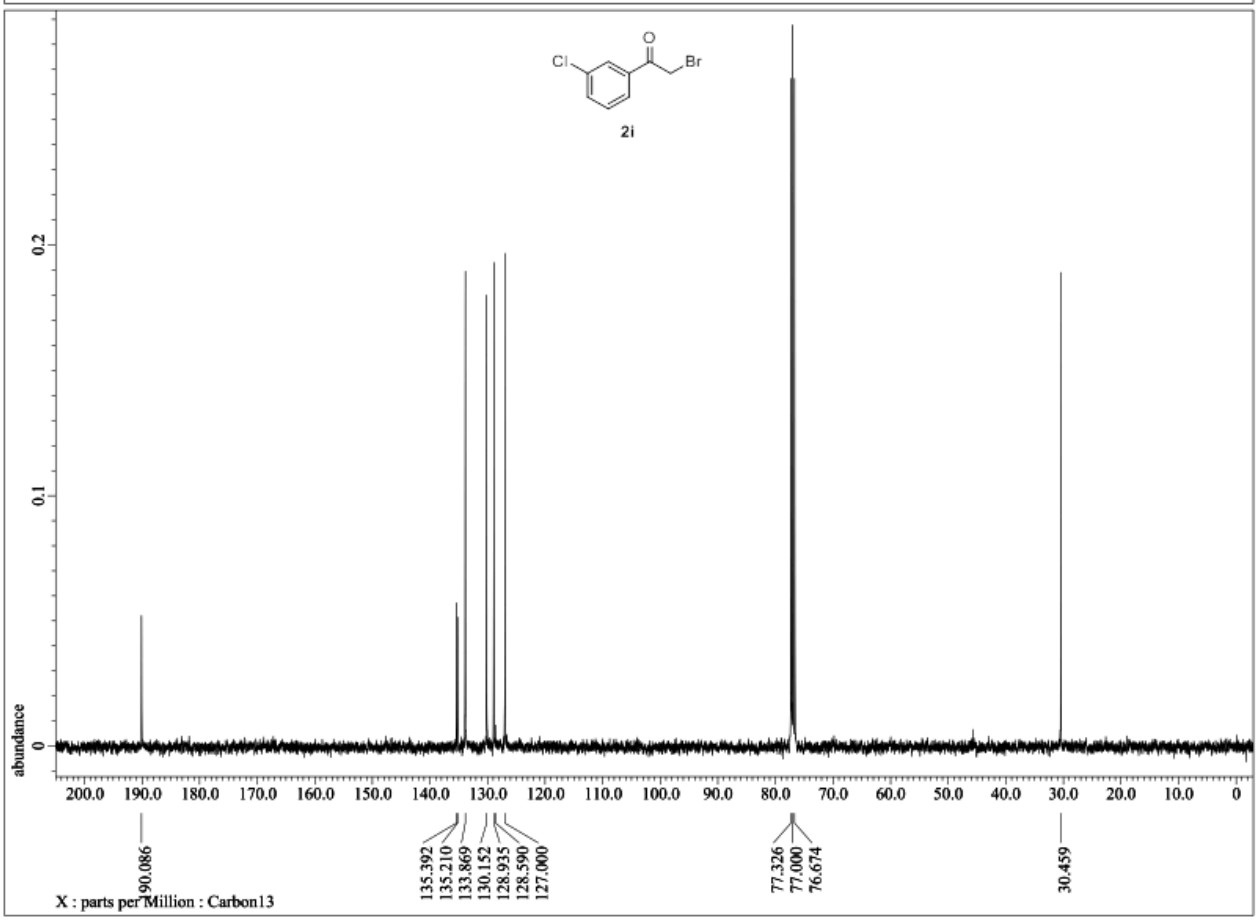

O
Br
2h
abundance
2.01
2.01
2.00
3.01
7.791
7.789
7.788
7.785
7.783
7.781
7.779
7.764
7.761
7.411
7.410
7.406
7.392
7.391
7.373
7.354
4.454
2.419
0.000
X : parts per Million : Proton

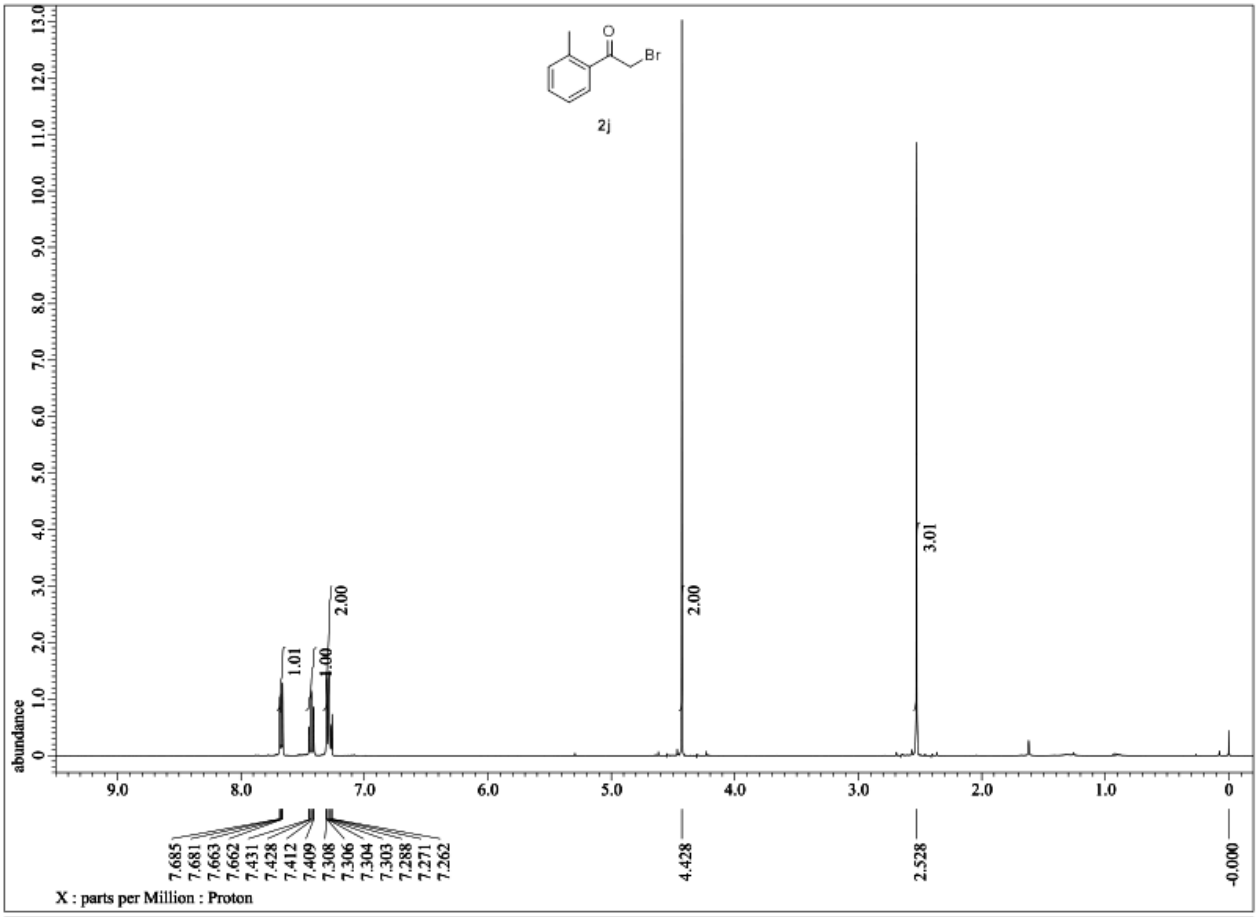

O
Br
2h
abundance
191.379
138.707
134.702
133.878
129.280
128.638
126.061
77.326
77.201
77.000
76.674
31.139
21.281
X : parts per Million : Carbon13

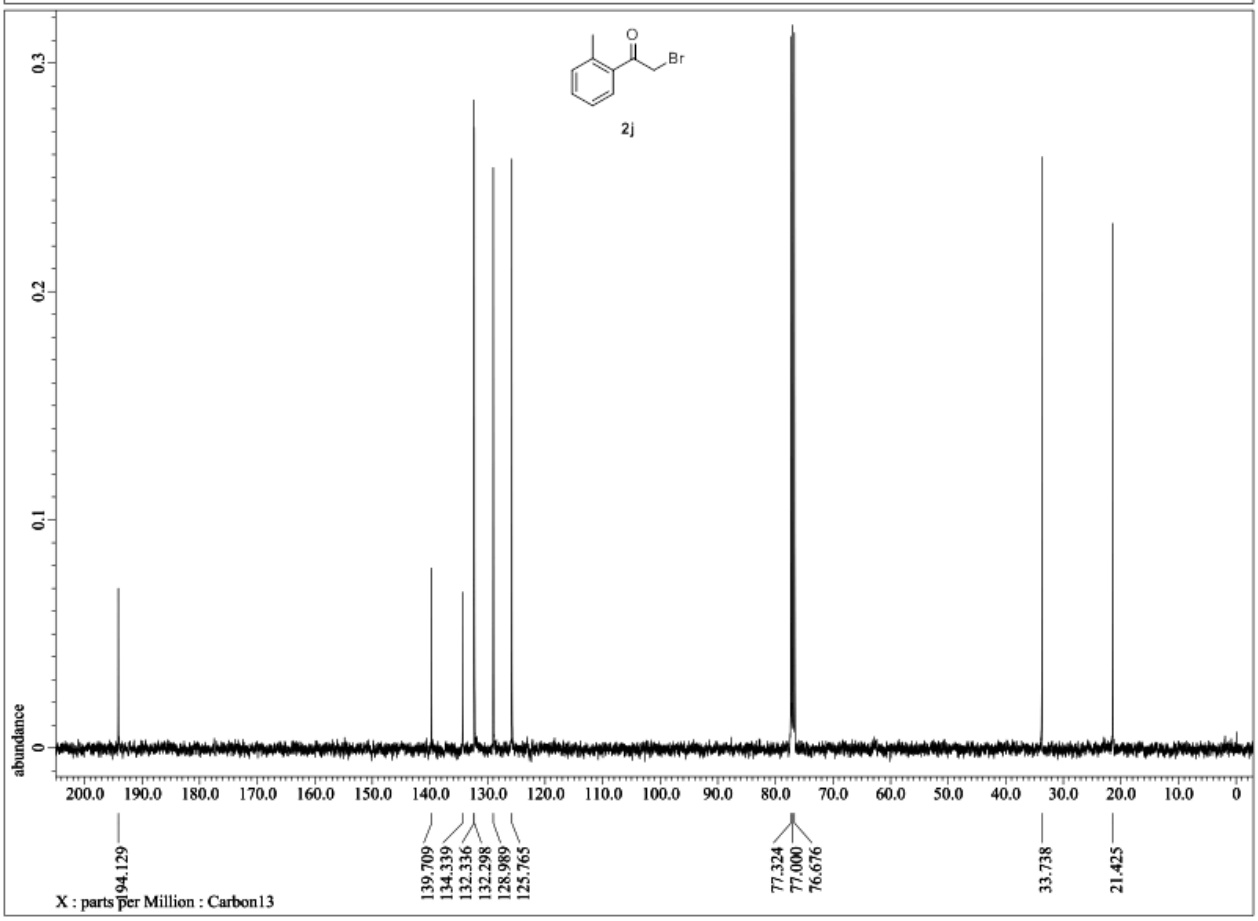

O
Br
Br
2h–Br
abundance
1.00
2.03
2.00
3.03
7.846
7.845
7.680
7.659
7.654
7.649
7.632
7.628
7.265
4.410
2.475
-0.000
X : parts per Million : Proton

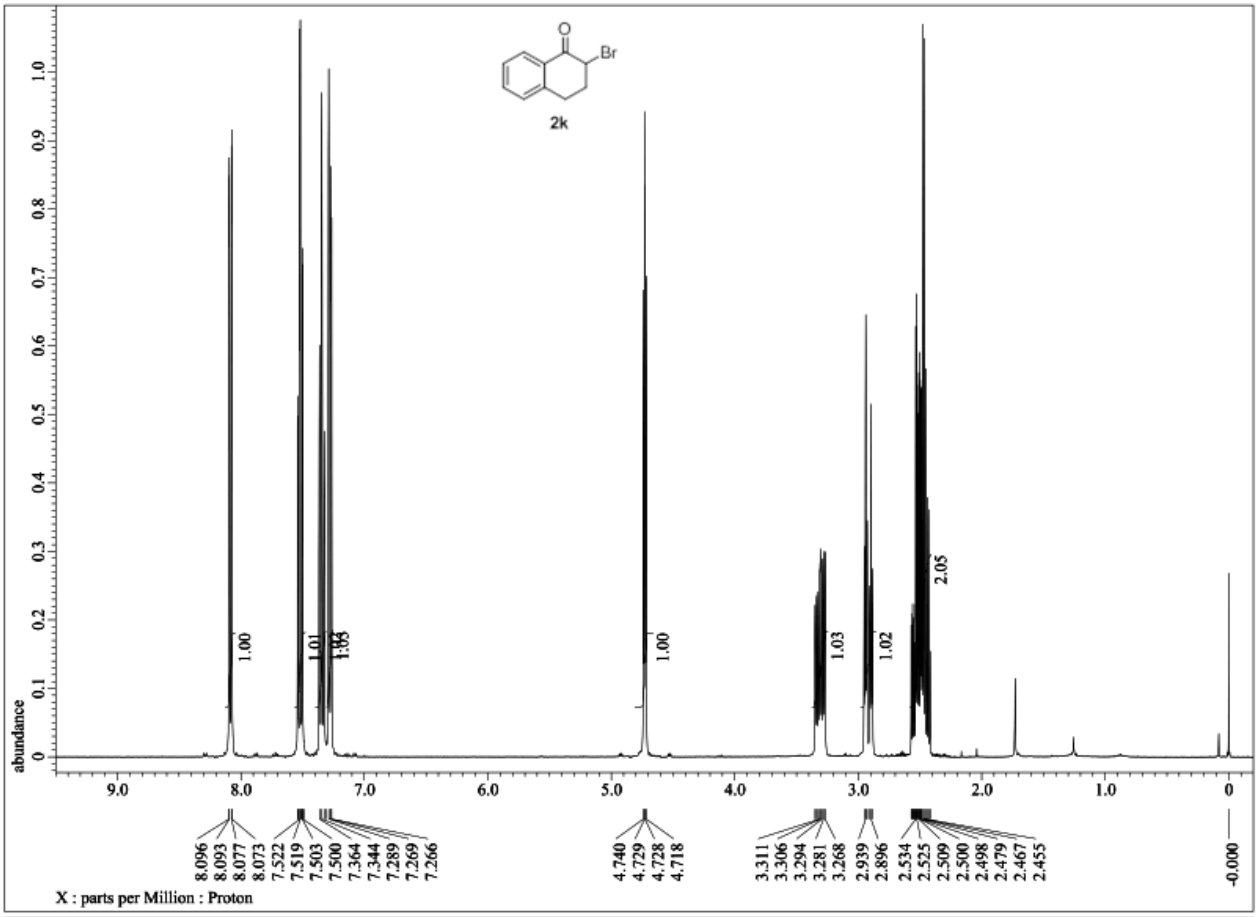

O
Br
Br
2h–Br
abundance
190.677
138.946
132.947
132.870
131.745
130.896
127.587
77.324
77.000
76.676
30.534
23.018
X : parts per Million : Carbon13

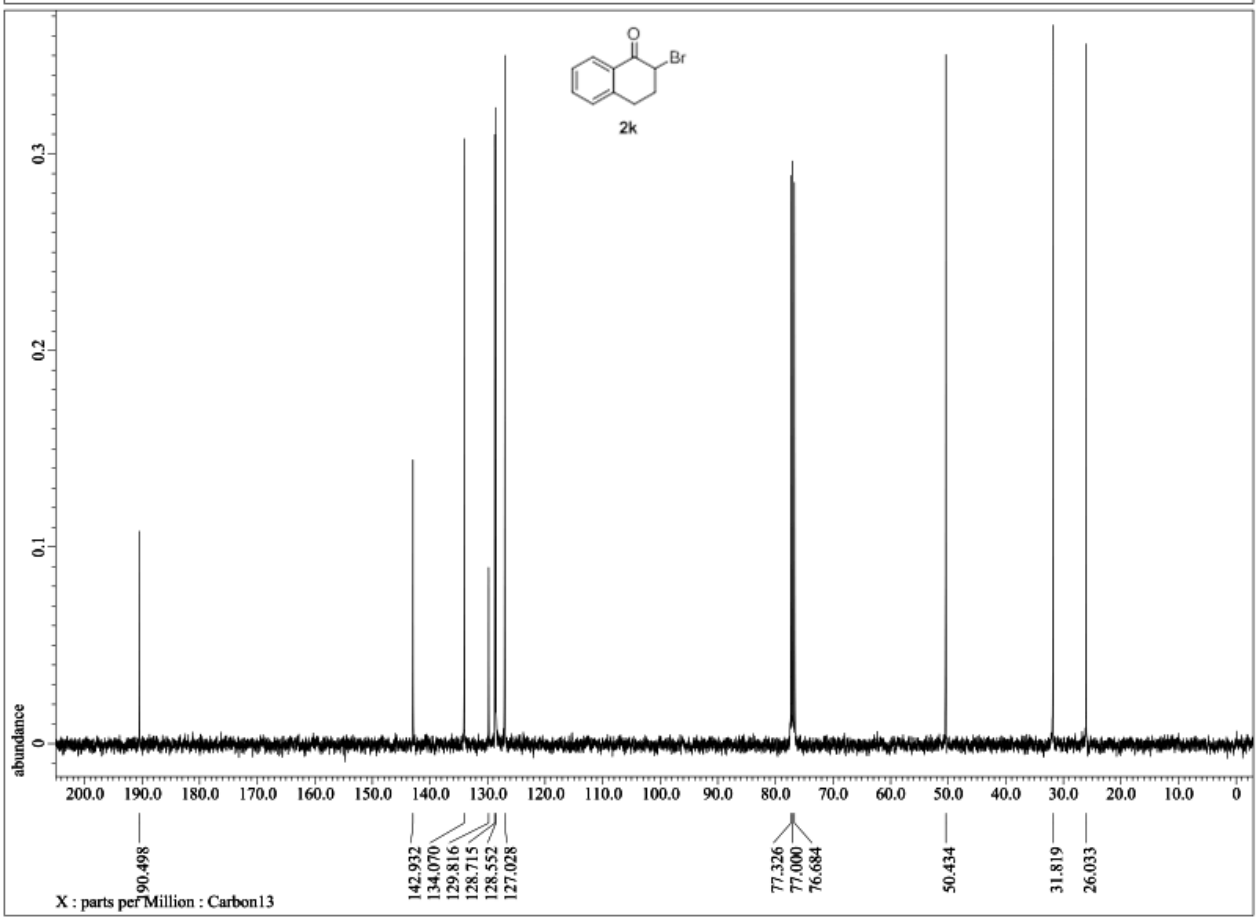

Cl
O
Br
2i
abundance
2.00
1.00
1.01
1.01
1.03
7.962
7.874
7.855
7.853
7.601
7.598
7.595
7.581
7.578
7.575
7.471
7.451
7.431
7.267
4.426
-0.000
X : parts per Million : Proton

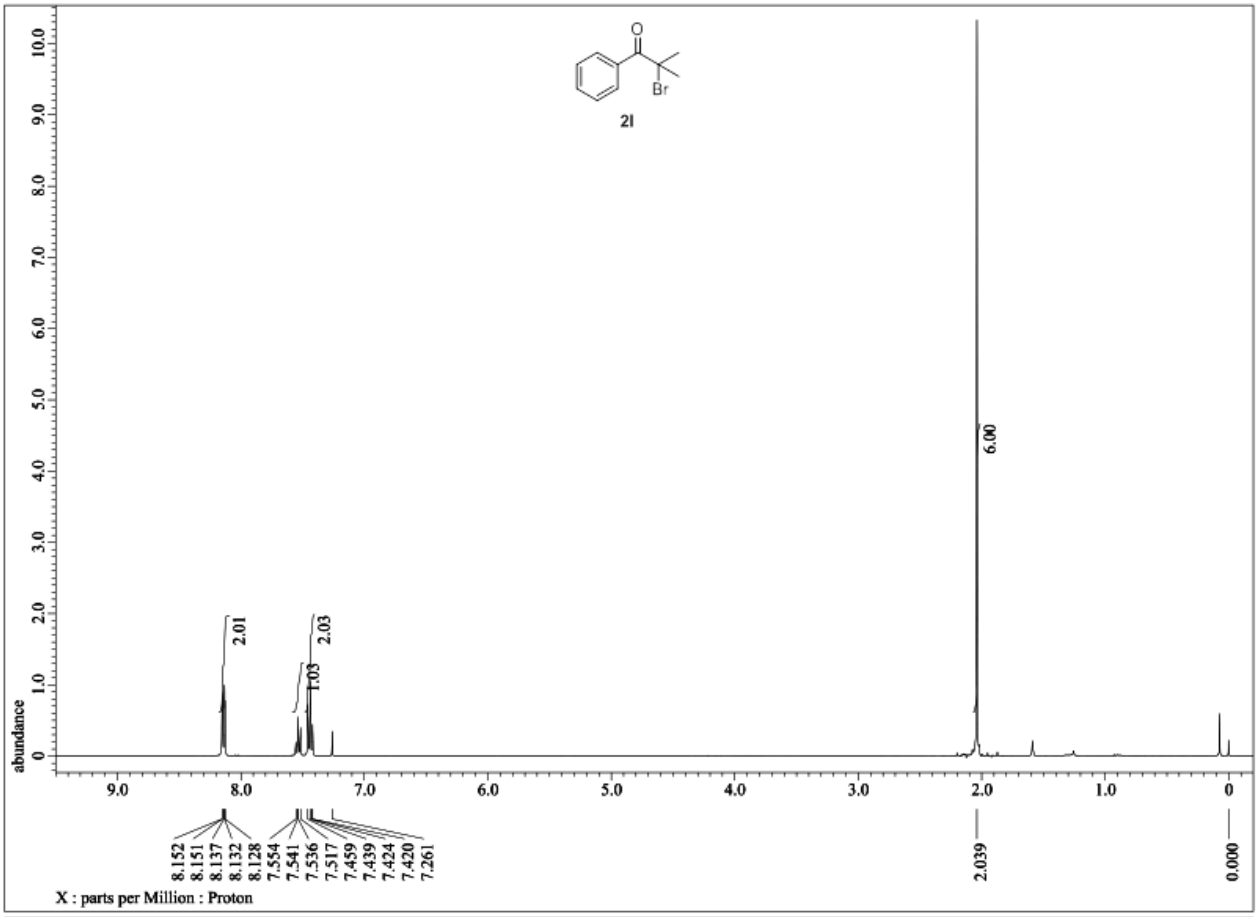

Cl
O
Br
2i
abundance
90.086
135.392
135.210
133.869
130.152
128.935
128.590
127.000
77.326
77.000
76.674
30.459
X : parts per Million : Carbon13

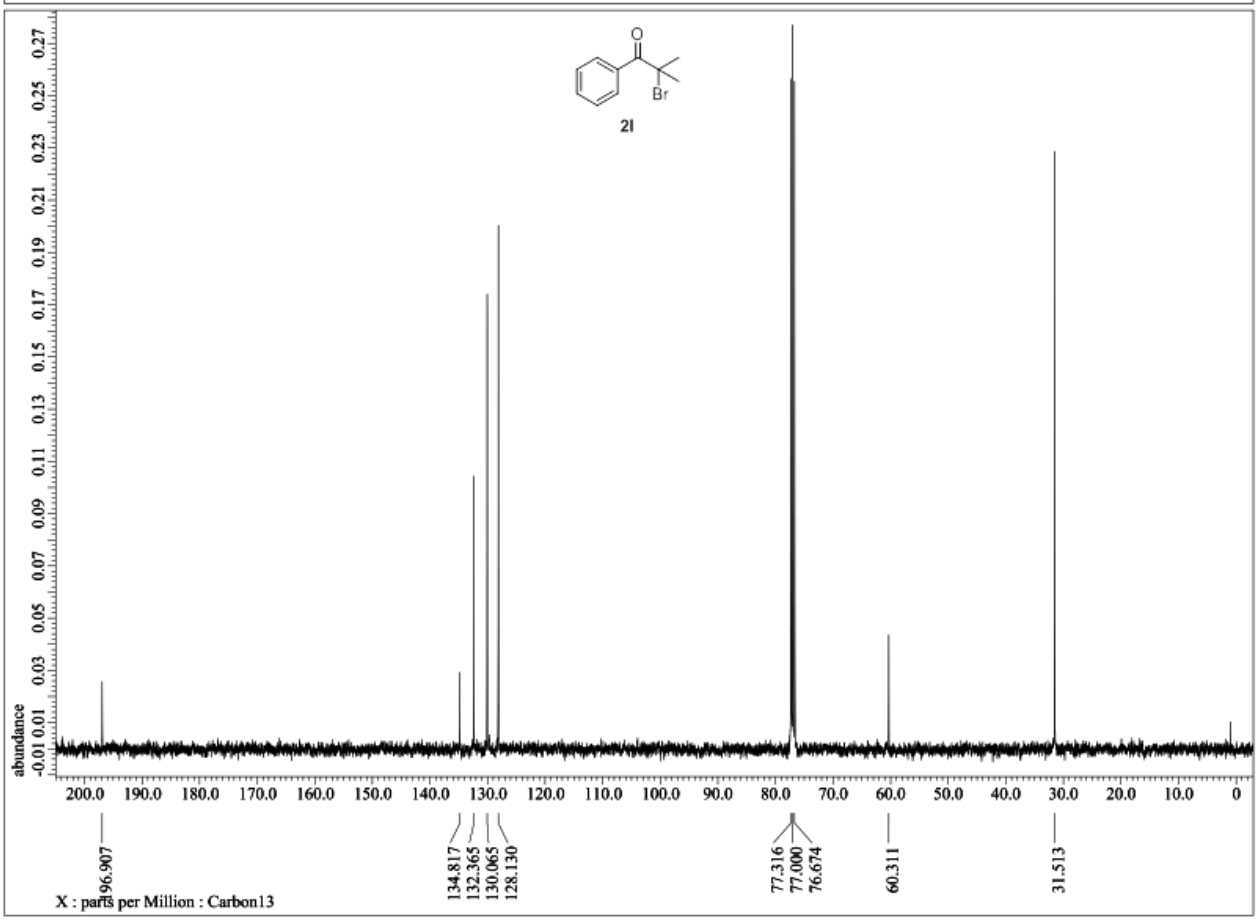

2j
abundance
1.01
1.00
2.00
2.00
3.01
7.685
7.681
7.663
7.662
7.431
7.428
7.412
7.409
7.308
7.306
7.304
7.303
7.288
7.271
7.262
4.428
2.528
-0.000
X : parts per Million : Proton

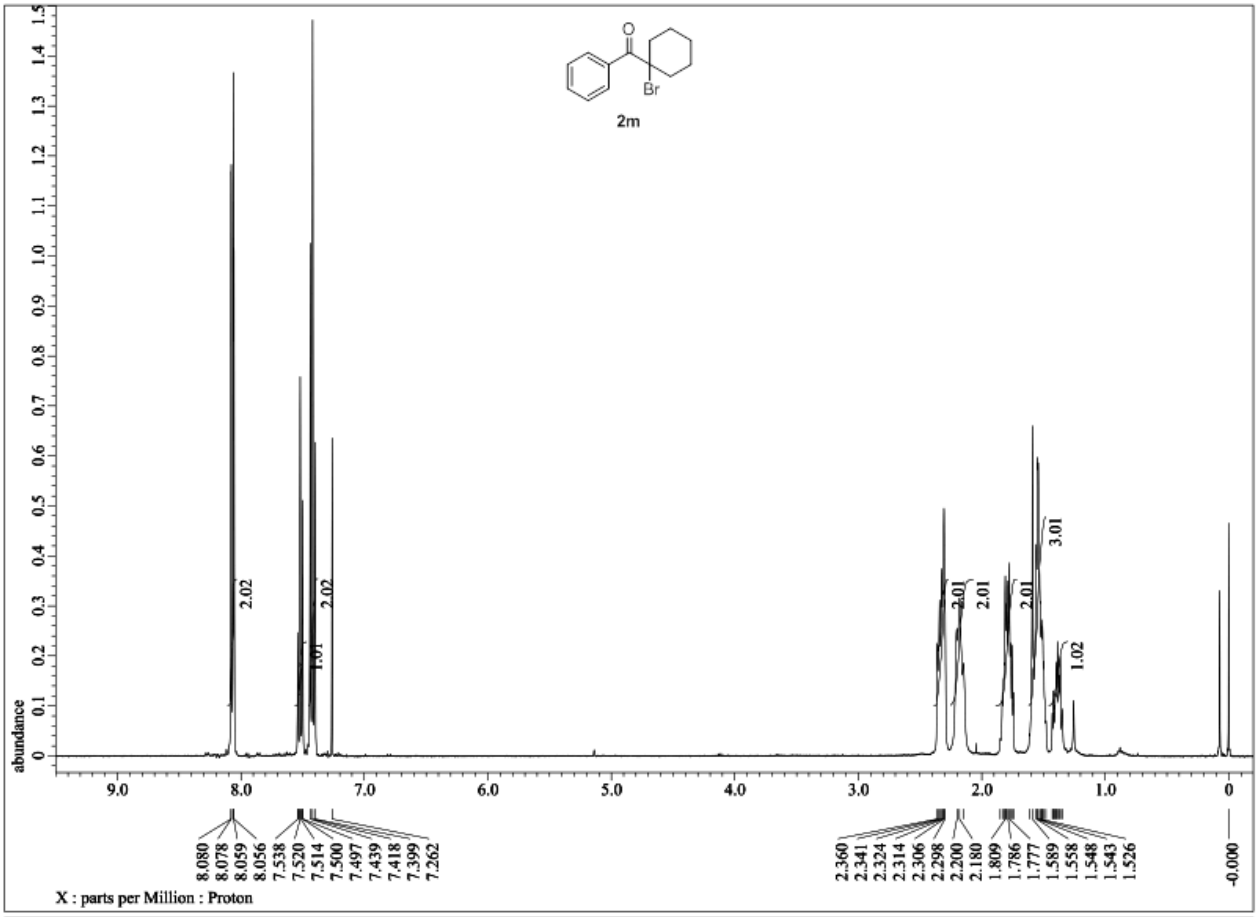

2j
abundance
194.129
139.709
134.339
132.336
132.298
128.989
125.765
77.324
77.000
76.676
33.738
21.425
X : parts per Million : Carbon13

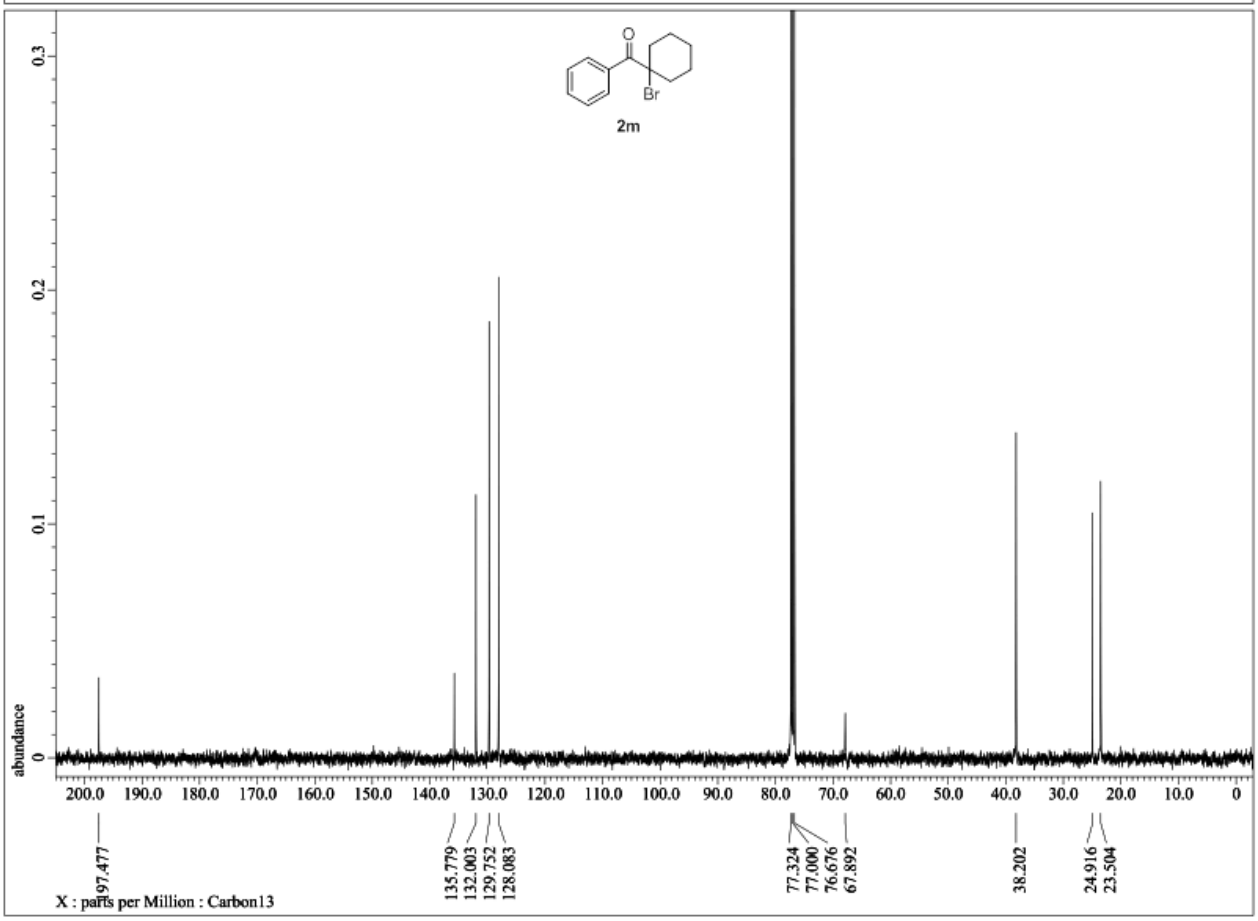

O
Br
2k
abundance
1.00
1.01
1.03
1.00
1.03
1.02
2.05
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.096
8.093
8.077
8.073
7.522
7.519
7.503
7.500
7.364
7.344
7.289
7.269
7.266
4.740
4.729
4.728
4.718
3.311
3.306
3.294
3.281
3.268
2.939
2.896
2.534
2.525
2.509
2.500
2.498
2.479
2.467
2.455
-0.000
X : parts per Million : Proton

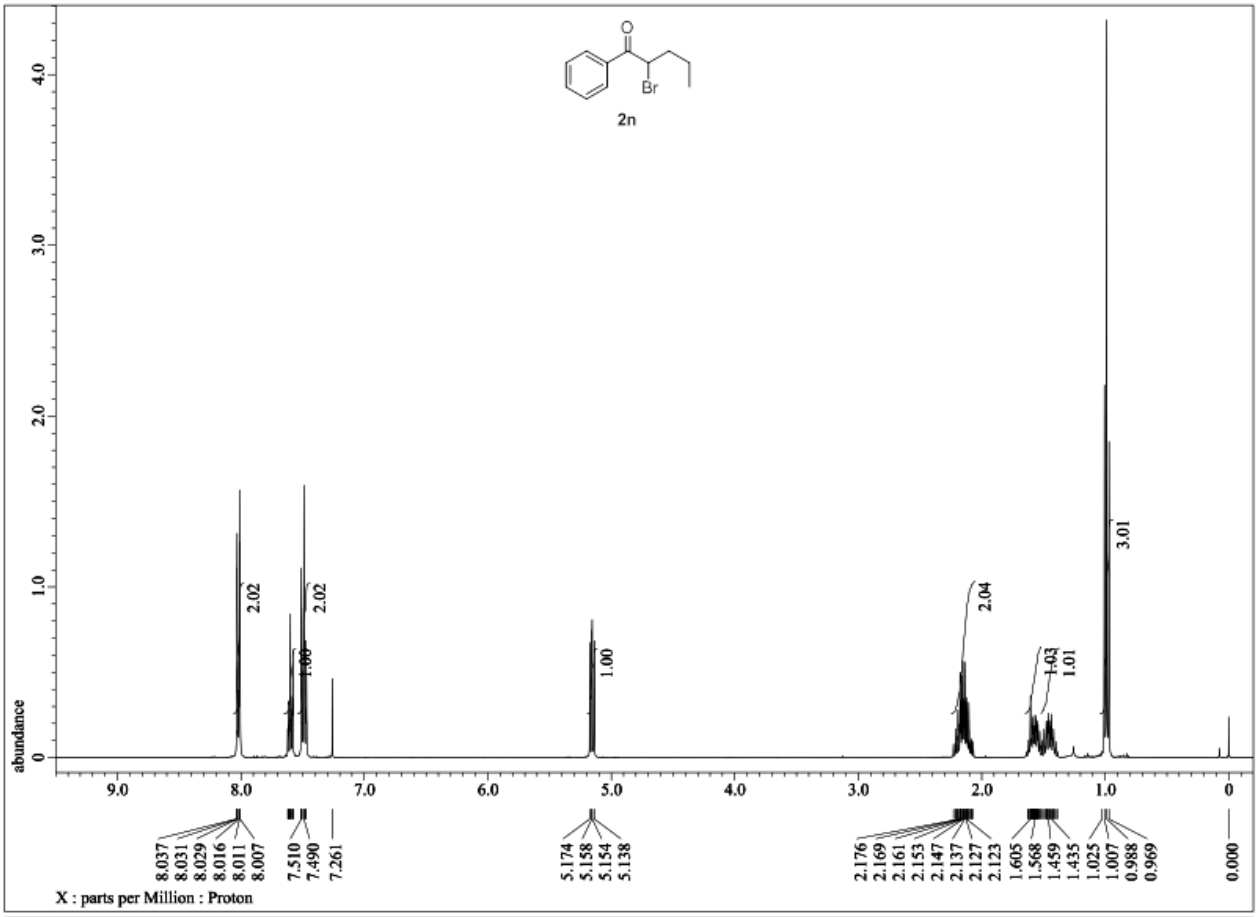

O
Br
2k
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
190.498
142.932
134.070
129.816
128.715
128.552
127.028
77.326
77.000
76.684
50.434
31.819
26.033
X : parts per Million : Carbon13

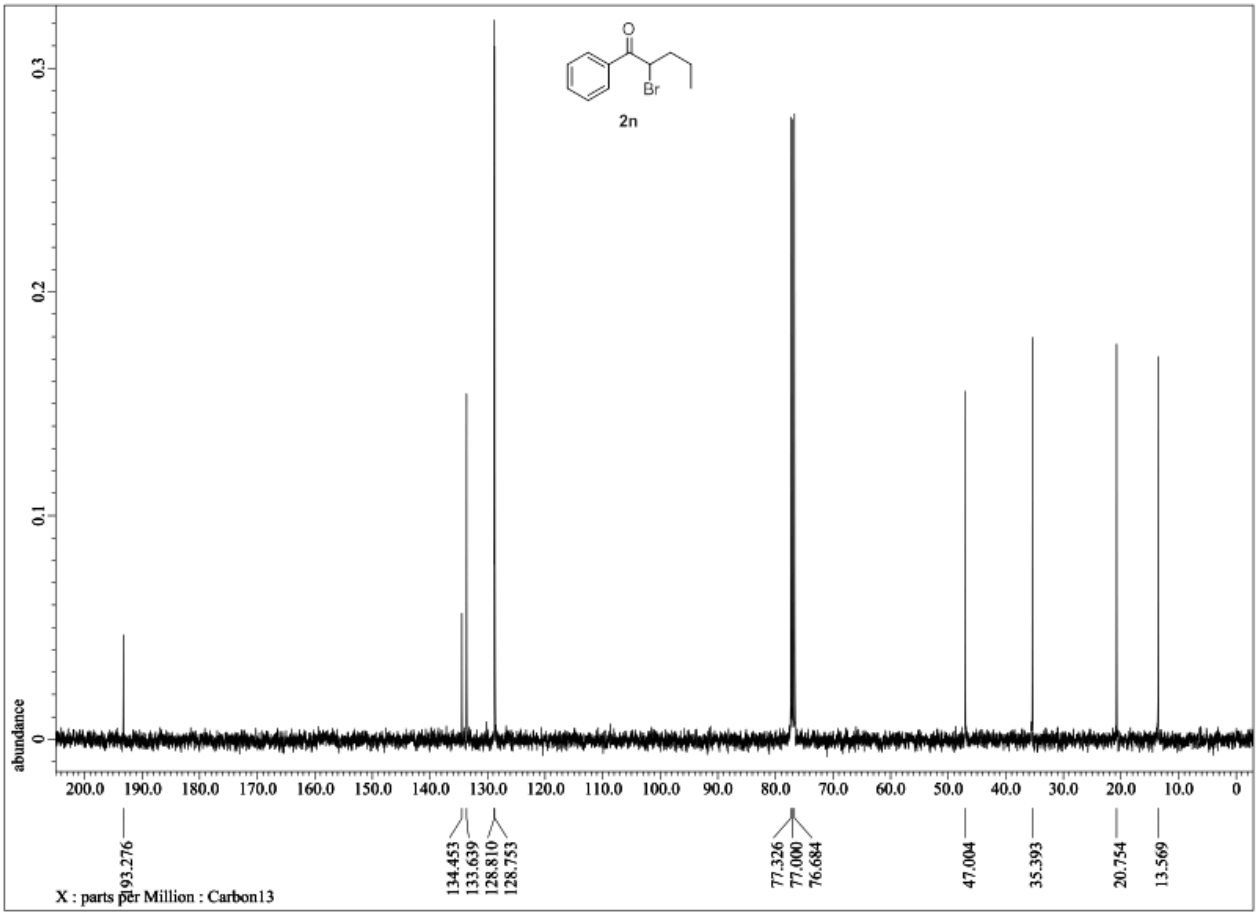

2l
abundance
X : parts per Million : Proton
2.01
2.03
1.03
6.00
8.152
8.151
8.137
8.132
8.128
7.554
7.541
7.536
7.517
7.459
7.439
7.424
7.420
7.261
2.039
0.000

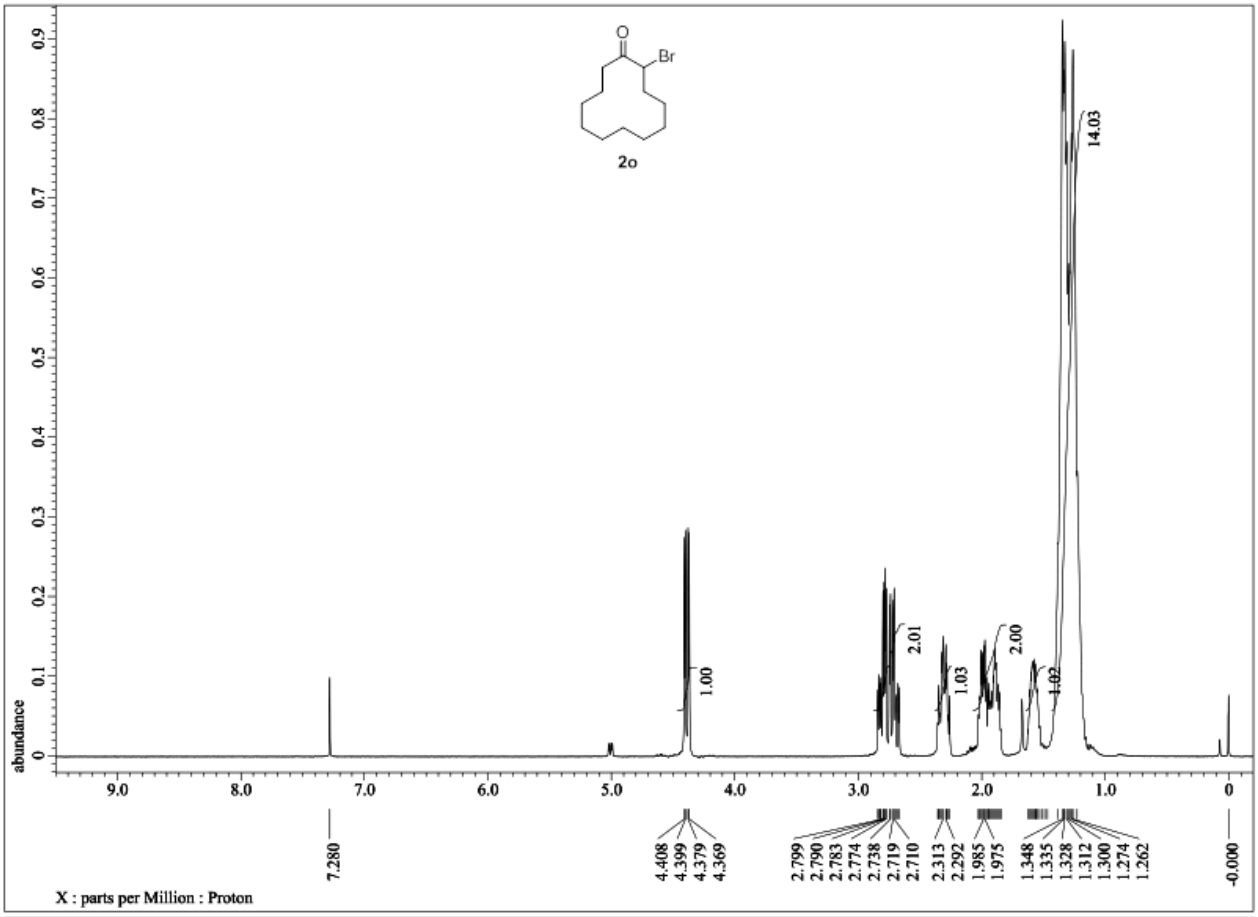

2l
abundance
X : parts per Million : Carbon13
196.907
134.817
132.365
130.065
128.130
77.316
77.000
76.674
60.311
31.513

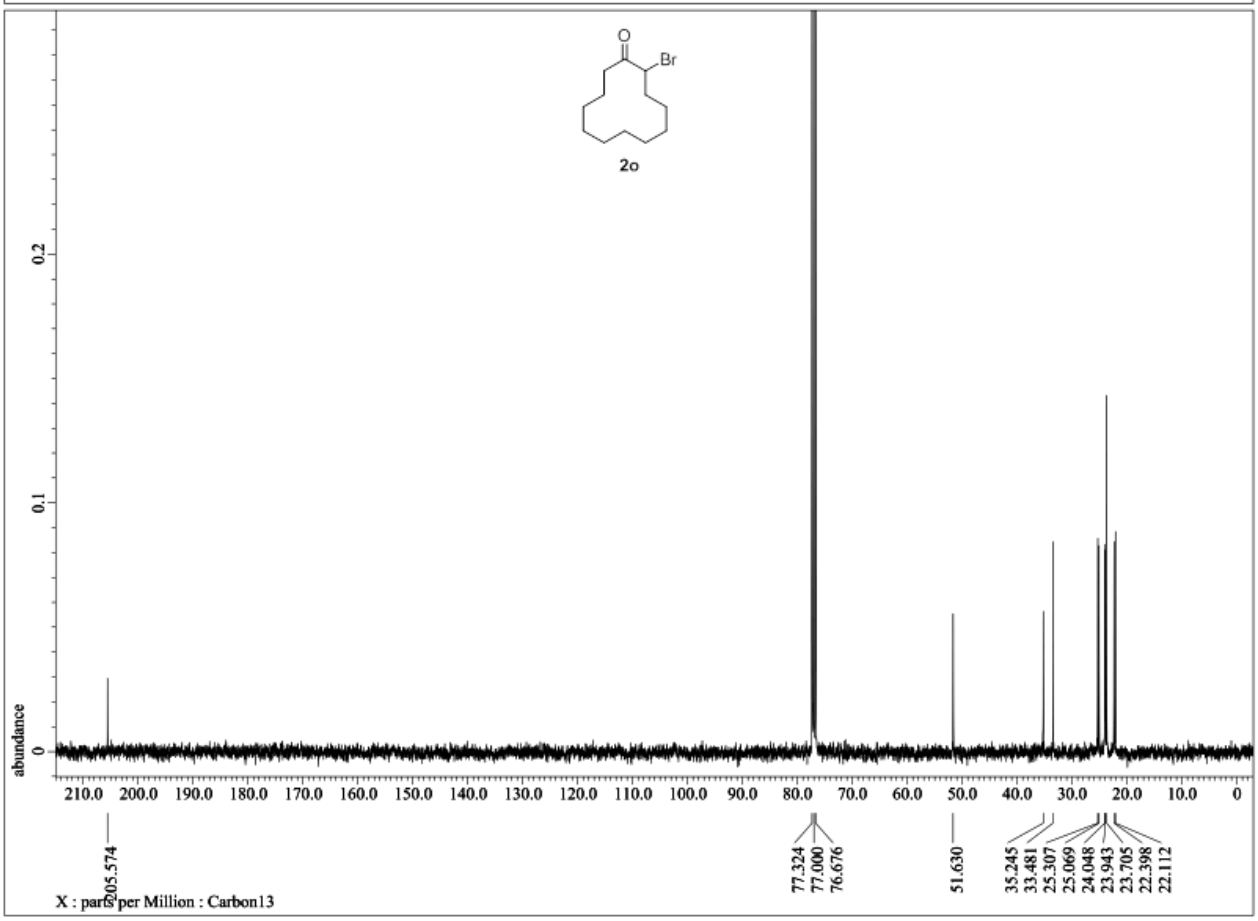

O
Br
2m
abundance
2.02
2.02
1.01
2.01
2.01
2.01
3.01
1.02
8.080
8.078
8.059
8.056
7.538
7.520
7.514
7.500
7.497
7.439
7.418
7.399
7.262
2.360
2.341
2.324
2.314
2.306
2.298
2.200
2.180
1.809
1.786
1.777
1.589
1.558
1.548
1.543
1.526
-0.000
X : parts per Million : Proton

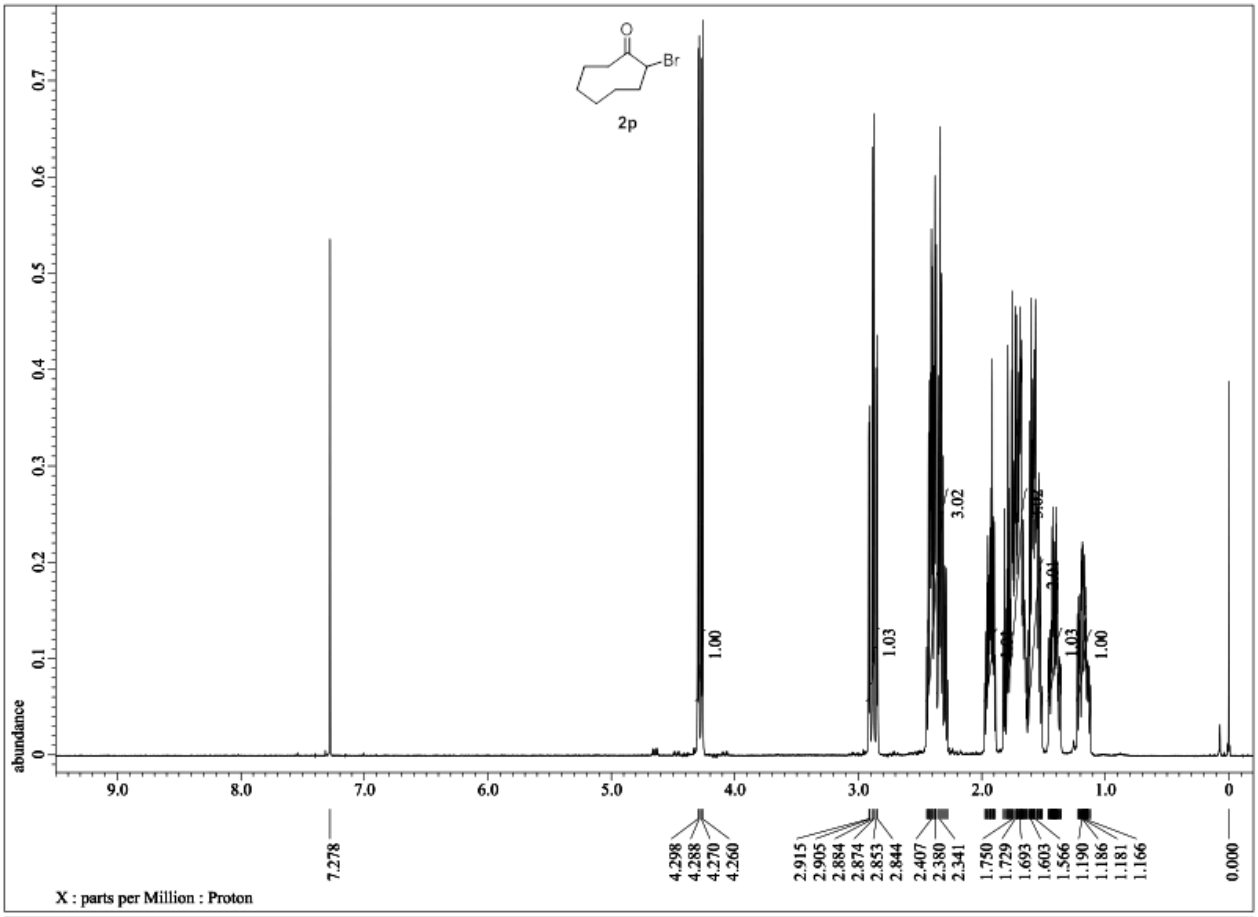

O
Br
2m
abundance
197.477
135.779
132.003
129.752
128.083
77.324
77.000
76.676
67.892
38.202
24.916
23.504
X : parts per Million : Carbon13

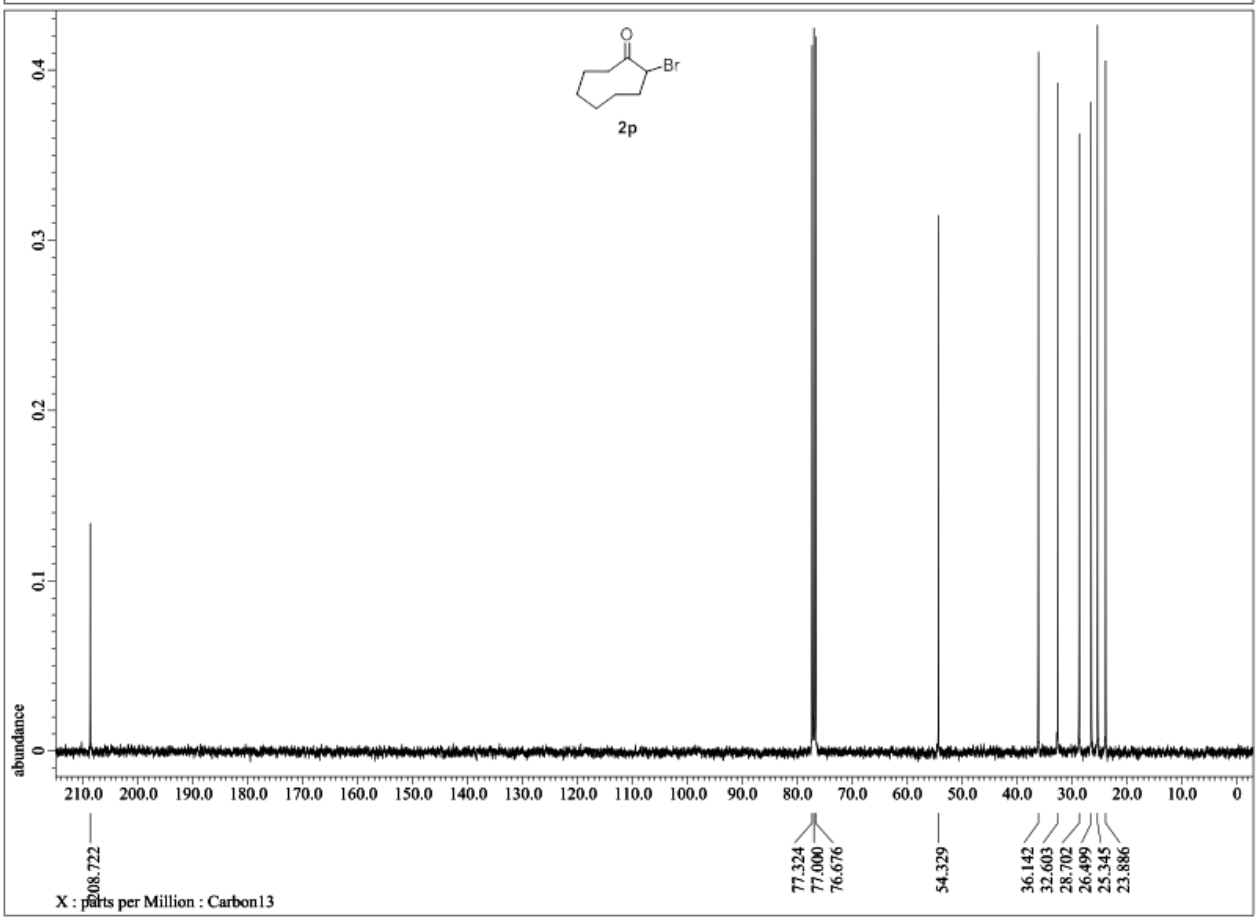

O
Br
2n
abundance
X : parts per Million : Proton
2.02
2.02
1.00
2.04
1.03
1.01
3.01
8.037
8.031
8.029
8.016
8.011
8.007
7.510
7.490
7.261
5.174
5.158
5.154
5.138
2.176
2.169
2.161
2.153
2.147
2.137
2.127
2.123
1.605
1.568
1.459
1.435
1.025
1.007
0.988
0.969
0.000

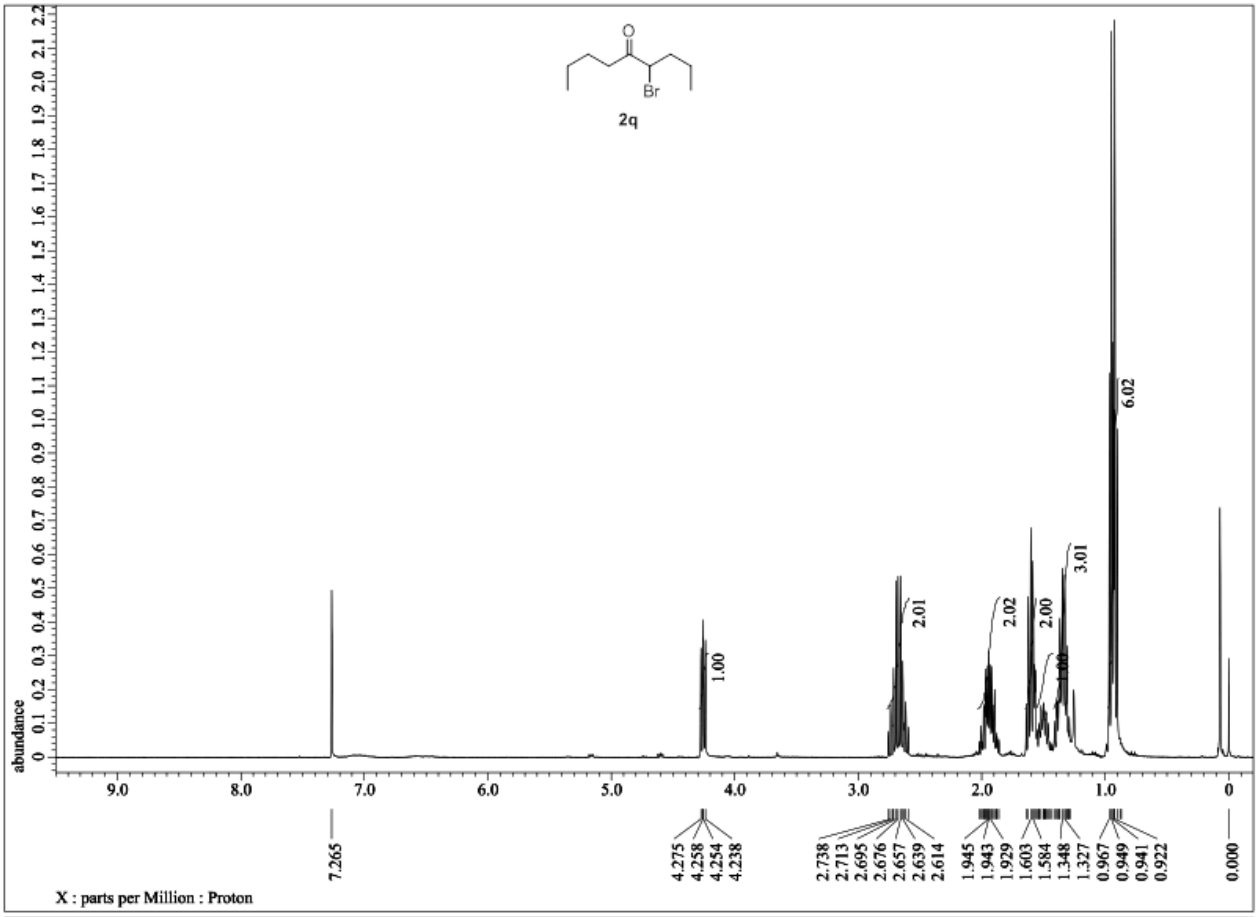

O
Br
2n
abundance
X : parts per Million : Carbon13
193.276
134.453
133.639
128.810
128.753
77.326
77.000
76.684
47.004
35.393
20.754
13.569

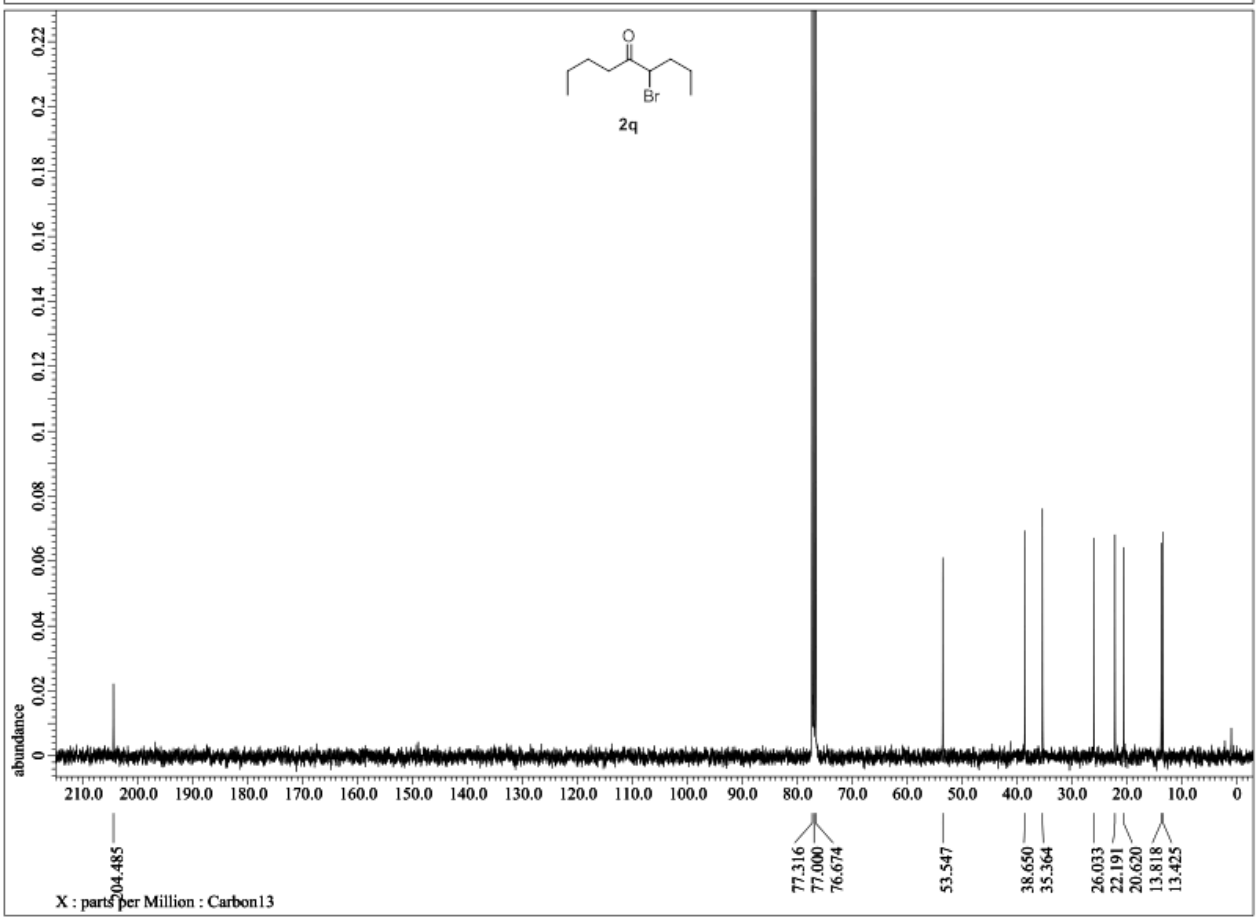

O
Br
2o
14.03
2.01
2.00
1.03
1.02
1.00
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.280
4.408
4.399
4.379
4.369
2.799
2.790
2.783
2.774
2.738
2.719
2.710
2.313
2.292
1.985
1.975
1.348
1.335
1.328
1.312
1.300
1.274
1.262
-0.000
X : parts per Million : Proton

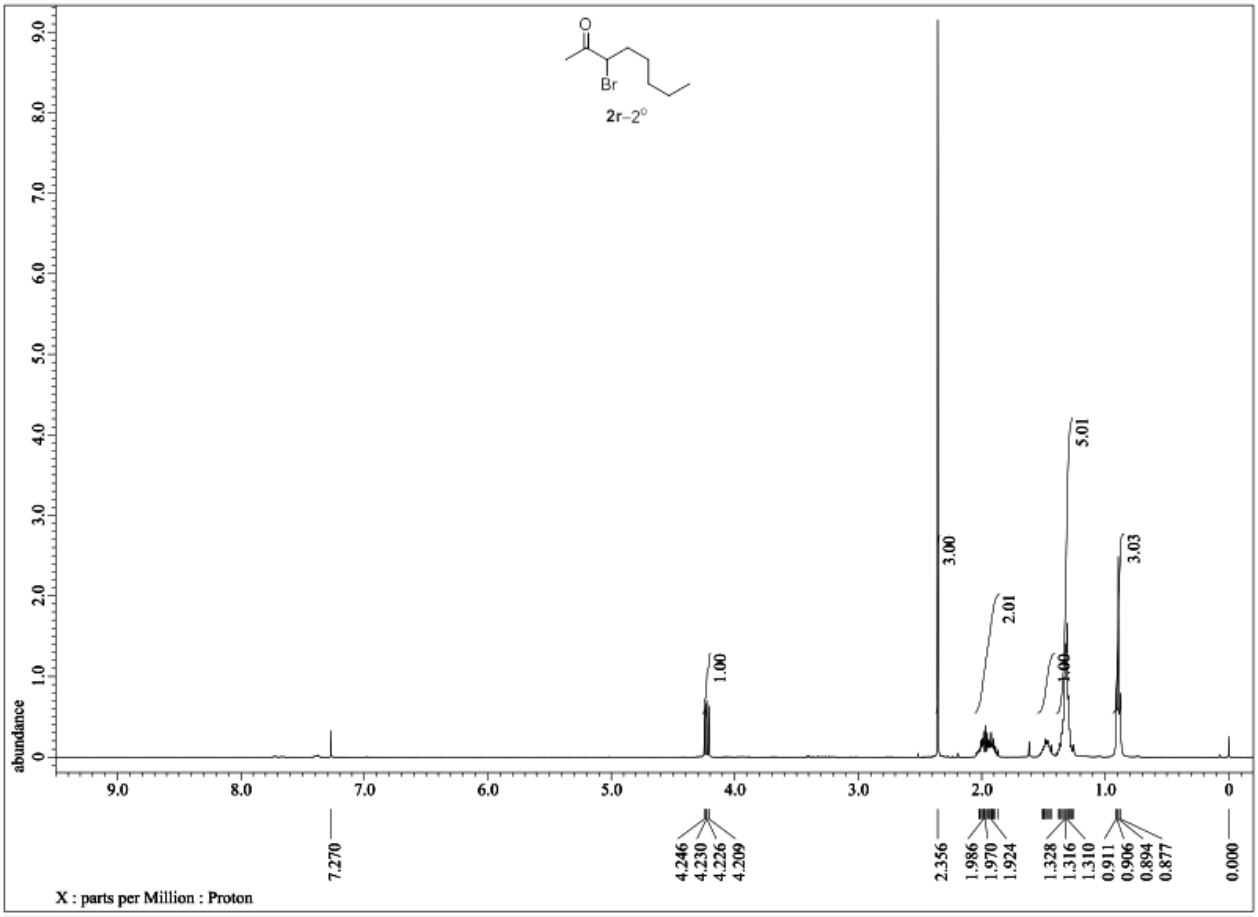

O
Br
2o
abundance
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
205.574
77.324
77.000
76.676
51.630
35.245
33.481
25.307
25.069
24.048
23.943
23.705
22.398
22.112
X : parts per Million : Carbon13

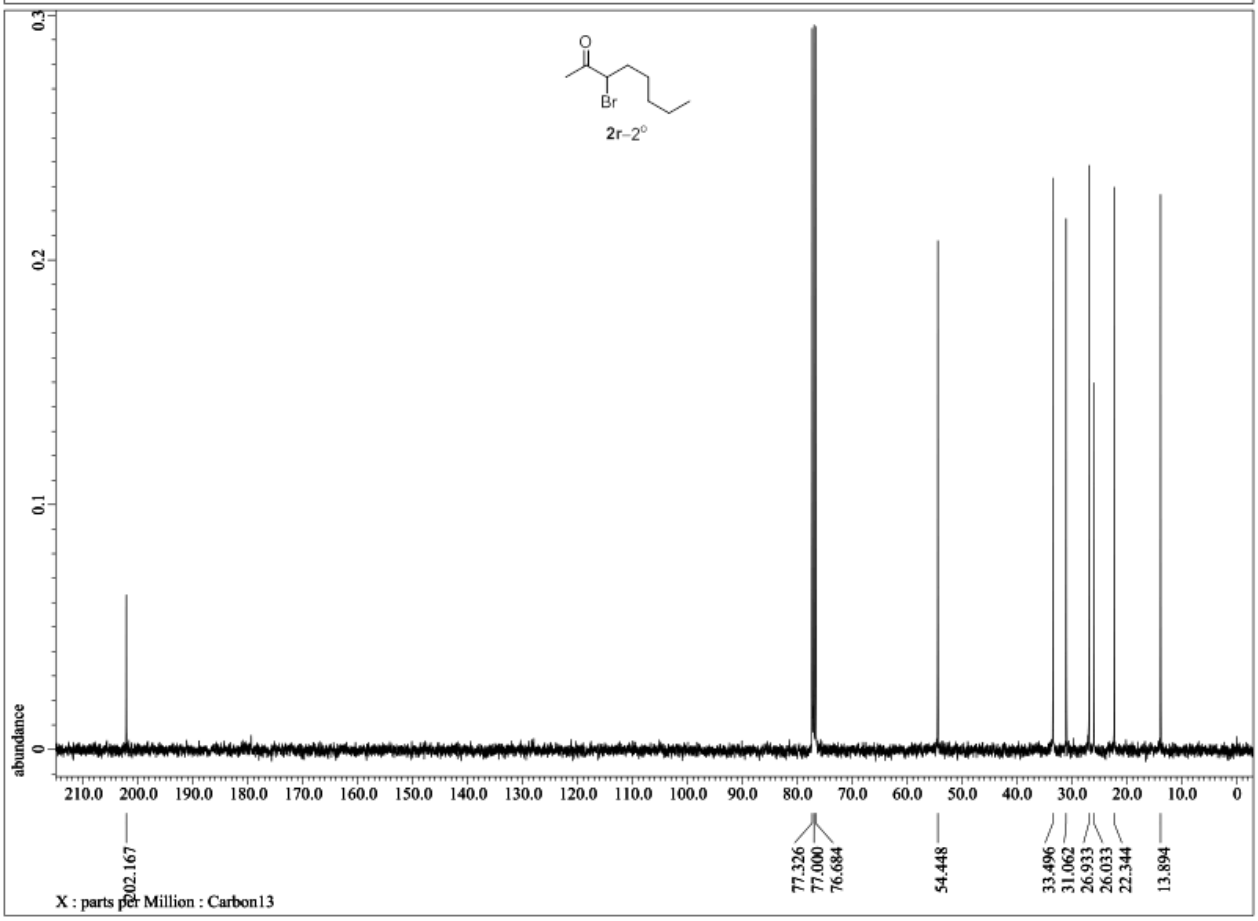

O
Br
2p
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.00
1.03
3.02
1.03
1.00
7.278
4.298
4.288
4.270
4.260
2.915
2.905
2.884
2.874
2.853
2.844
2.407
2.380
2.341
1.750
1.729
1.693
1.603
1.566
1.190
1.186
1.181
1.166
0.000
X : parts per Million : Proton

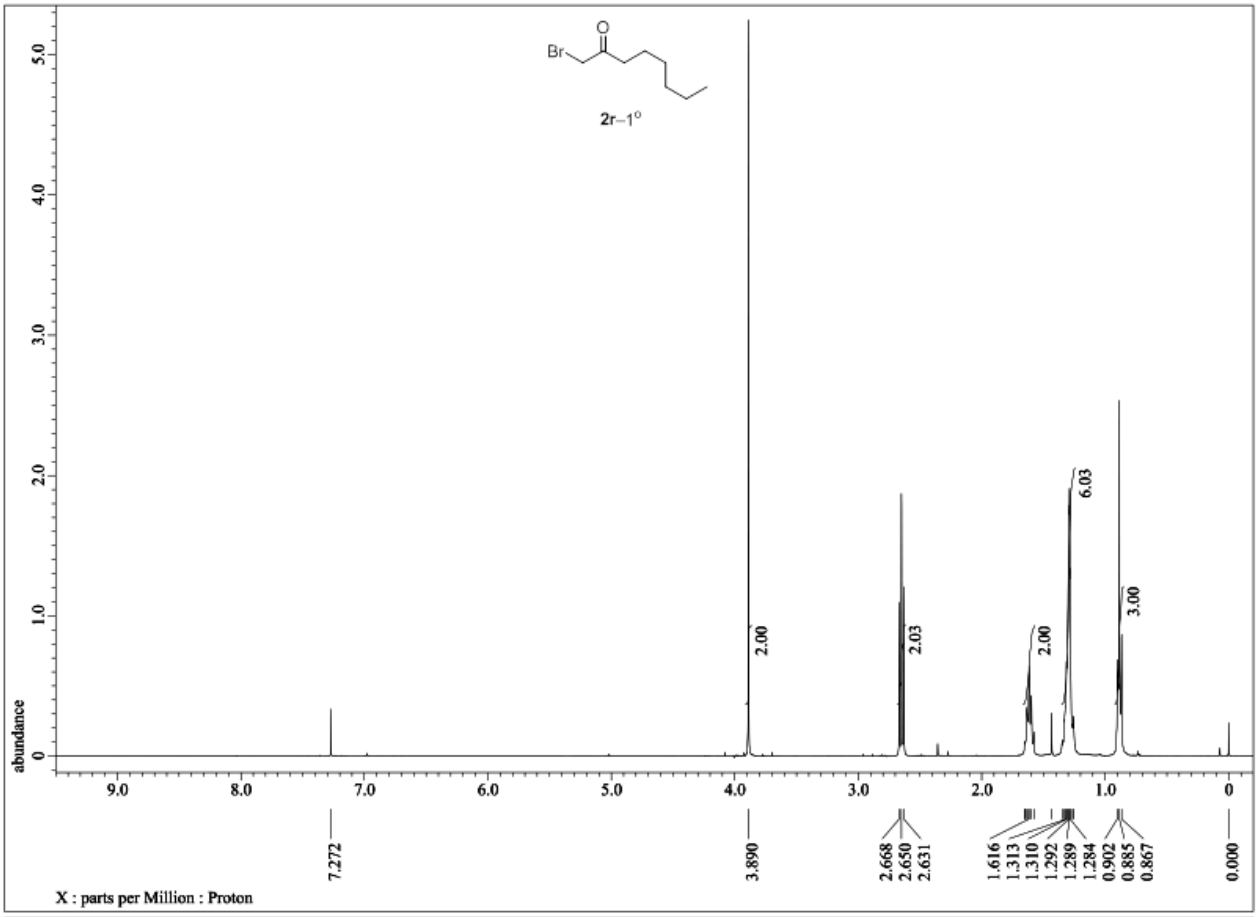

O
Br
2p
abundance
0
0.1
0.2
0.3
0.4
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
208.722
77.324
77.000
76.676
54.329
36.142
32.603
28.702
26.499
25.345
23.886
X : parts per Million : Carbon13

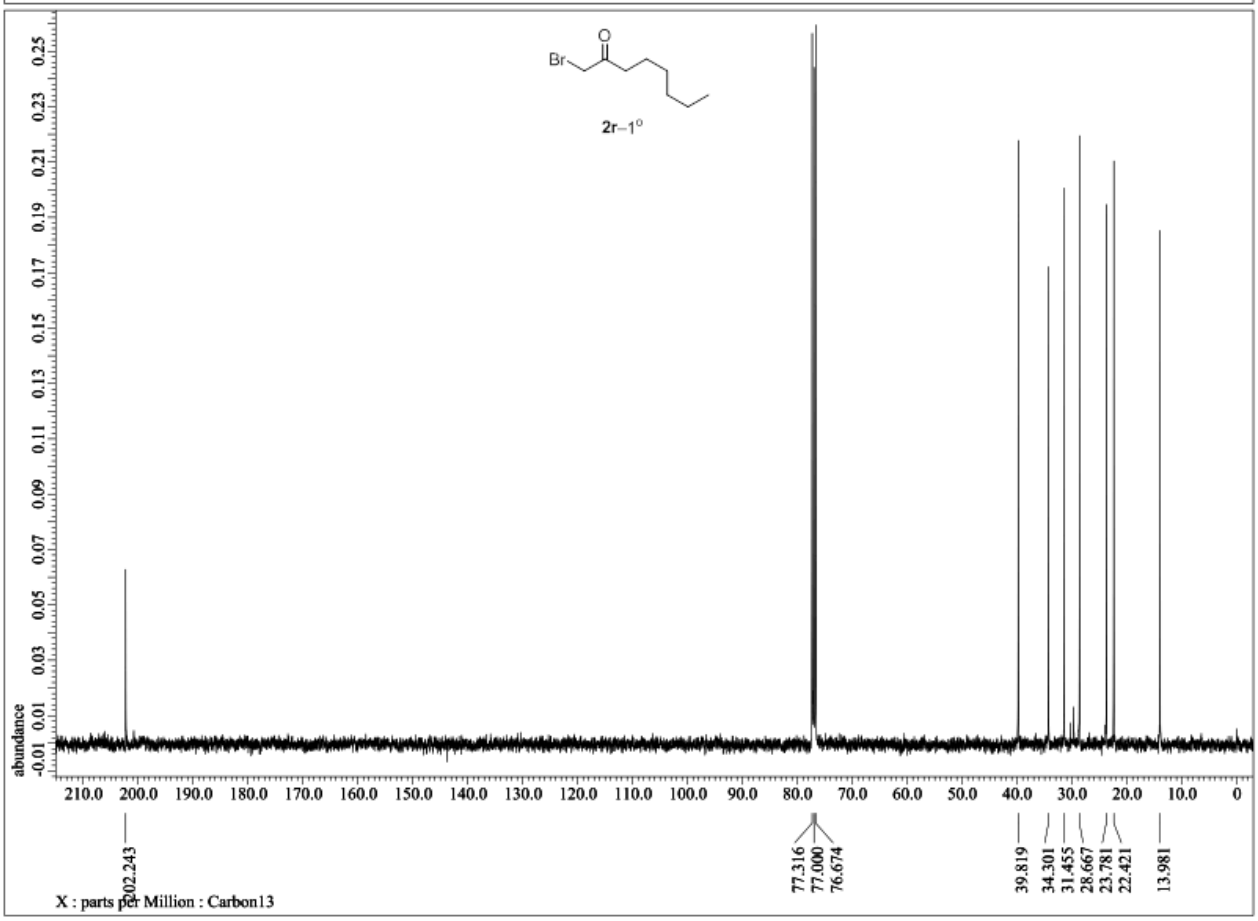

O
Br
2q
abundance
1.00
2.01
2.02
2.00
1.00
3.01
6.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.265
4.275
4.258
4.254
4.238
2.738
2.713
2.695
2.676
2.657
2.639
2.614
1.945
1.943
1.929
1.603
1.584
1.348
1.327
0.967
0.949
0.941
0.922
0.000
X : parts per Million : Proton

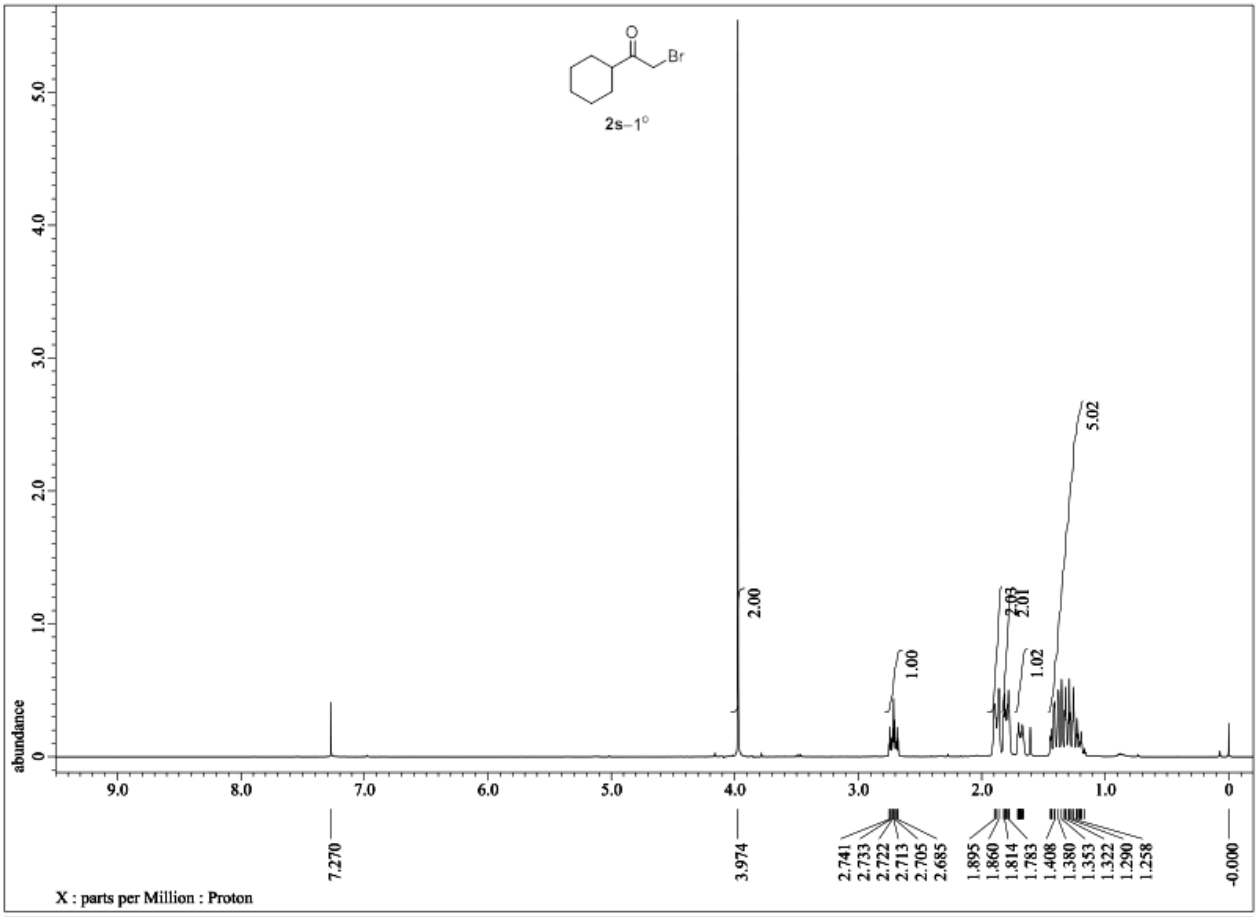

O
Br
2q
abundance
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
204.485
77.316
77.000
76.674
53.547
38.650
35.364
26.033
22.191
20.620
13.818
13.425
X : parts per Million : Carbon13

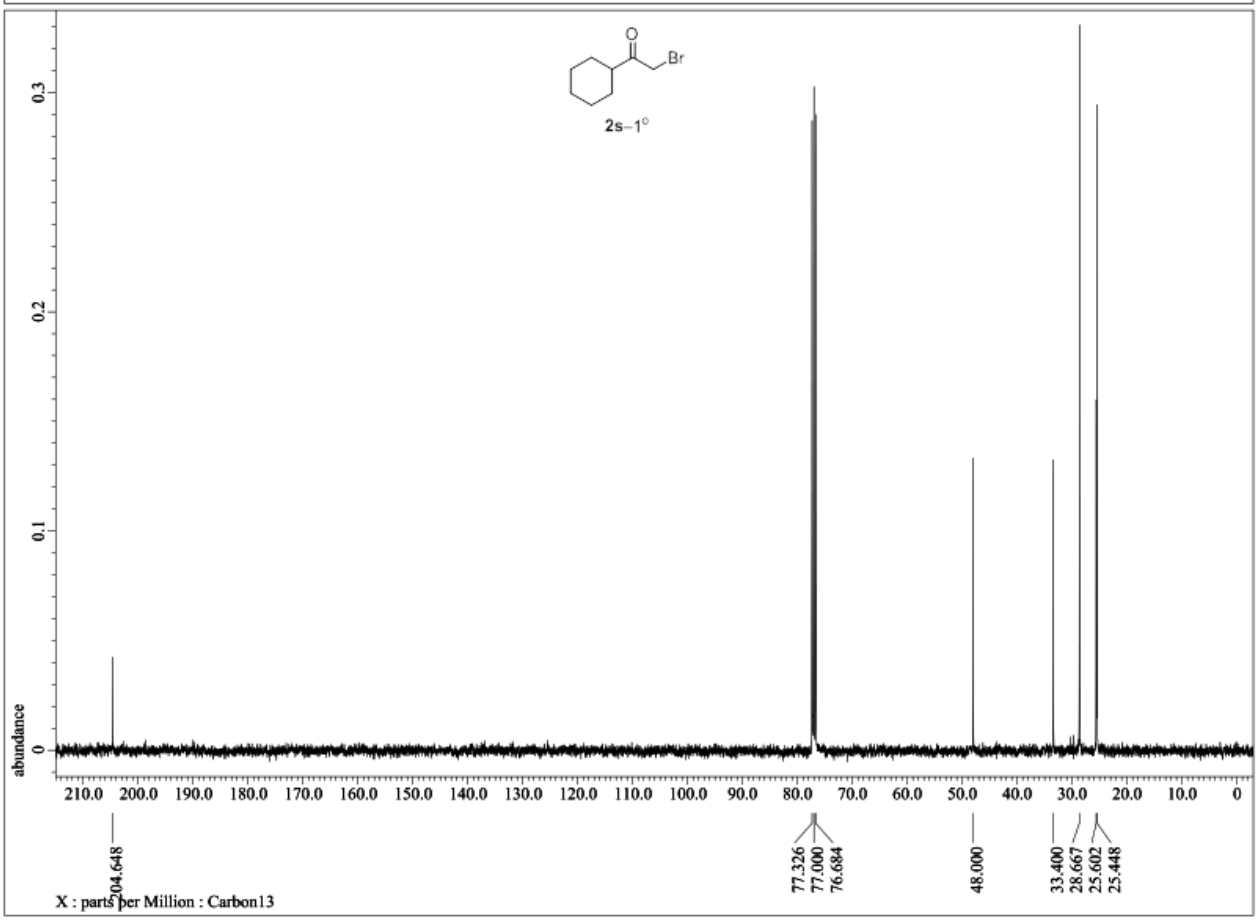

O
Br
2r–2°
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.00
3.00
2.01
1.00
5.01
3.03
7.270
4.246
4.230
4.226
4.209
2.356
1.986
1.970
1.924
1.328
1.316
1.310
0.911
0.906
0.894
0.877
0.000
X : parts per Million : Proton

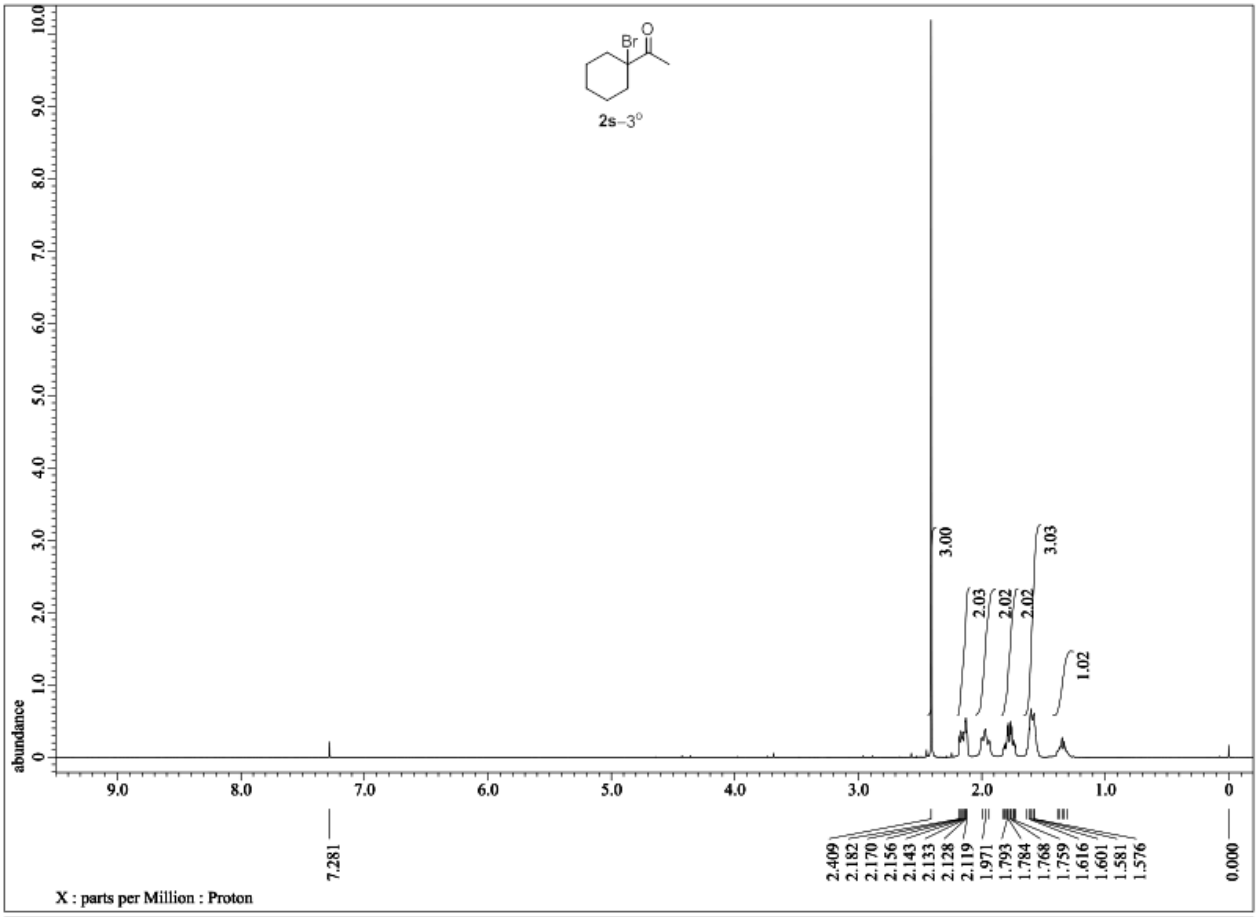

O
Br
2r–2°
abundance
0.3
0.2
0.1
0
202.167
77.326
77.000
76.684
54.448
33.496
31.062
26.933
26.033
22.344
13.894
X : parts per Million : Carbon13

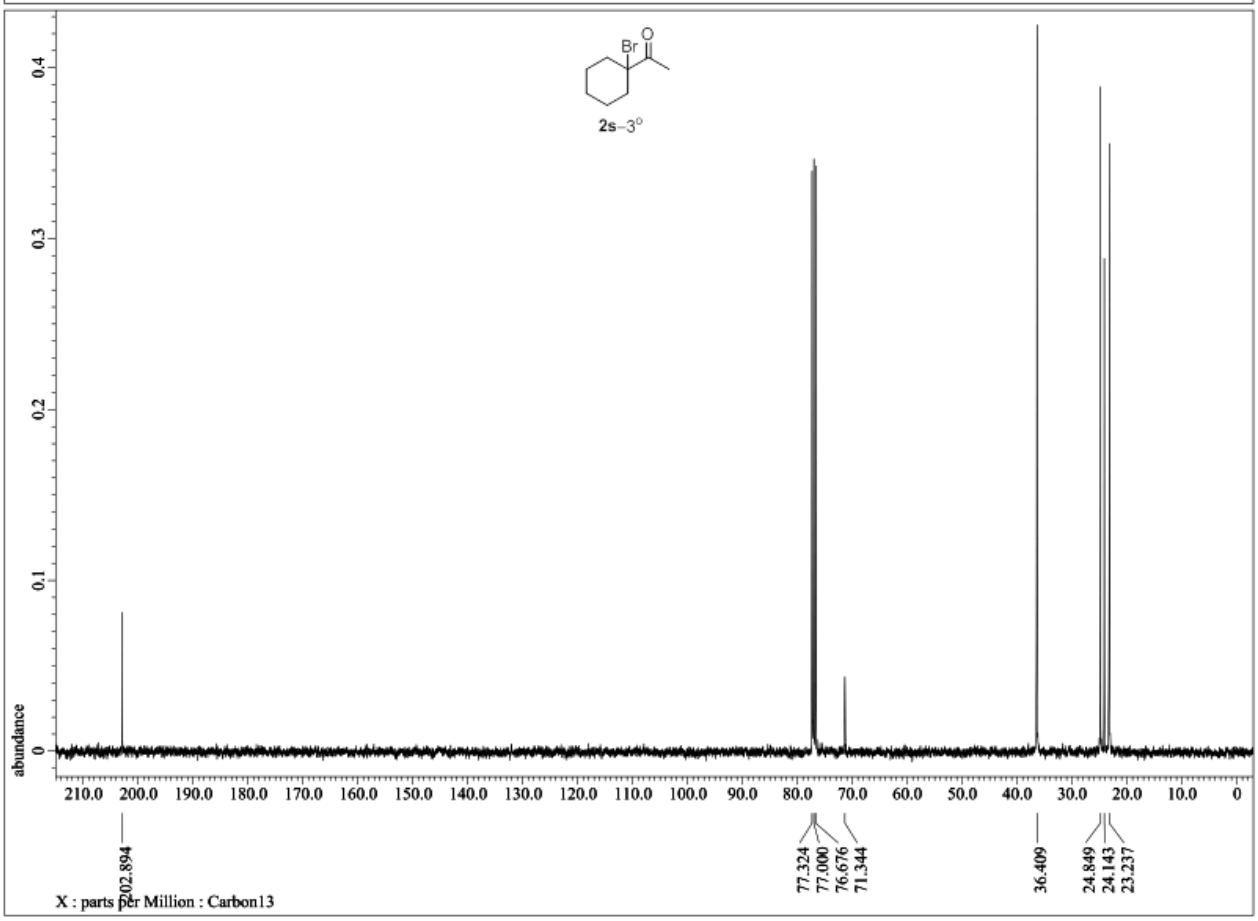

Br
O
2r–1°
abundance
X : parts per Million : Proton
2.00
2.03
2.00
6.03
3.00
7.272
3.890
2.668
2.650
2.631
1.616
1.313
1.310
1.292
1.289
1.284
0.902
0.885
0.867
0.000

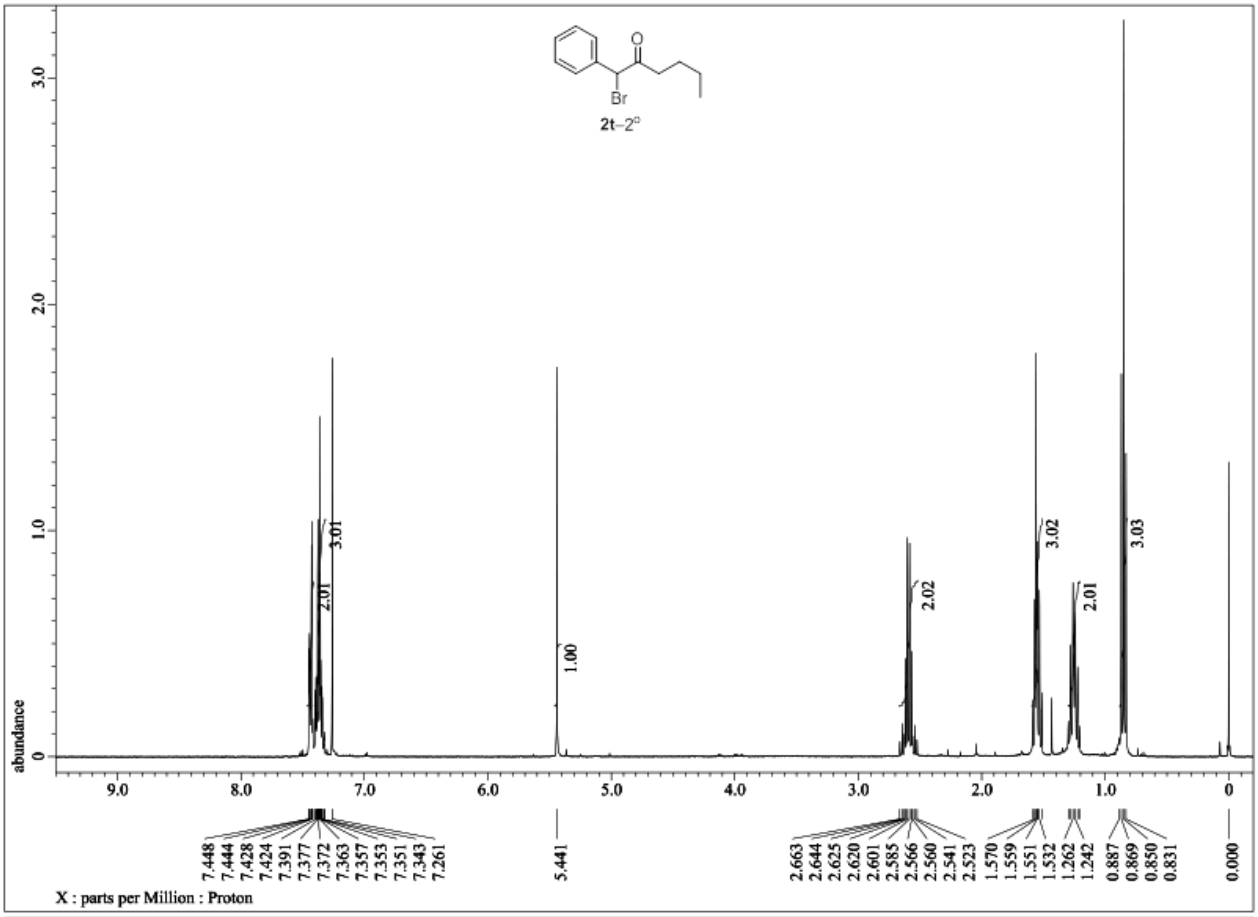

Br
O
2r–1°
abundance
X : parts per Million : Carbon13
202.243
77.316
77.000
76.674
39.819
34.301
31.455
28.667
23.781
22.421
13.981

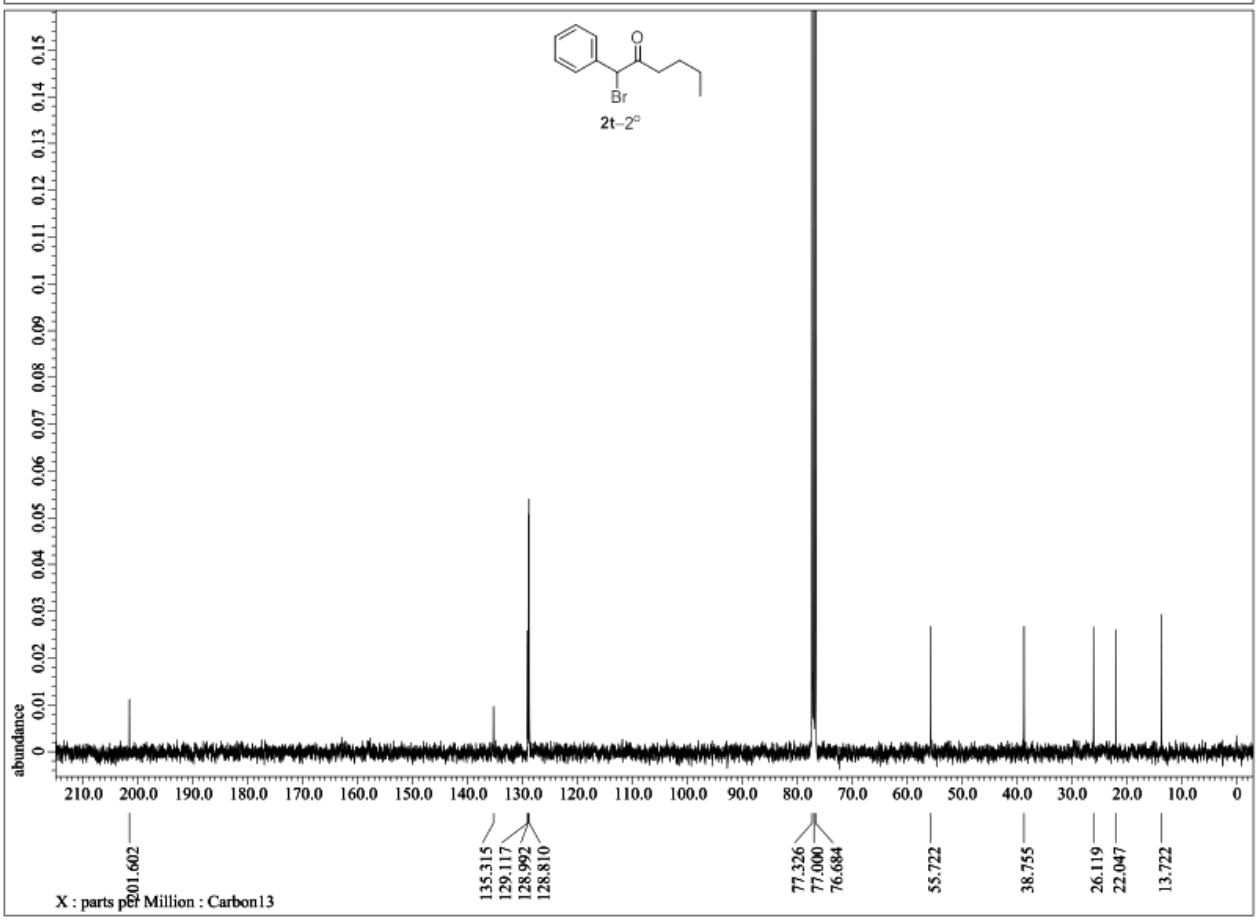

O
Br
2s–1°
abundance
5.0
4.0
3.0
2.0
1.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.00
1.00
1.02
5.02
7.270
3.974
2.741
2.733
2.722
2.713
2.705
2.685
1.895
1.860
1.814
1.783
1.408
1.380
1.353
1.322
1.290
1.258
-0.000
X : parts per Million : Proton

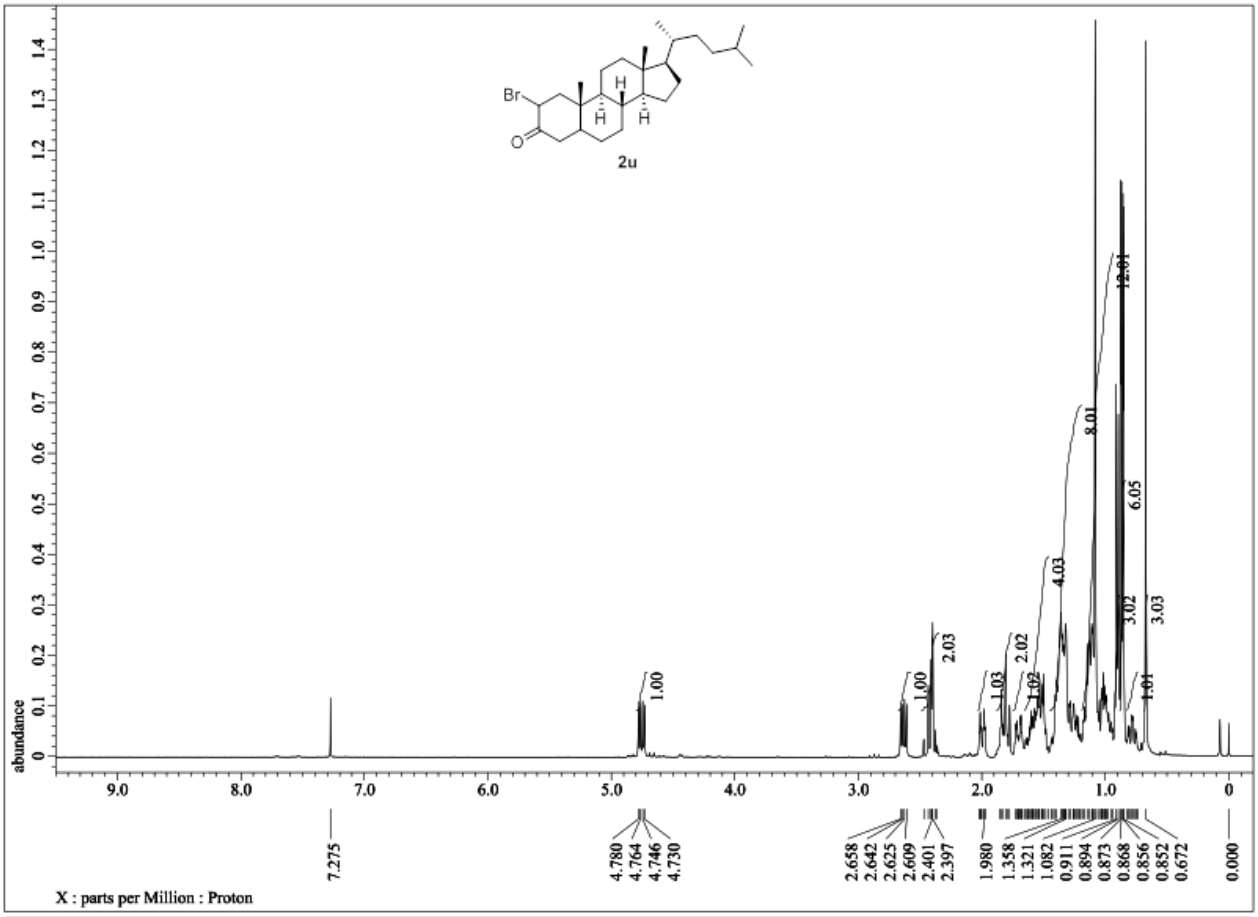

O
Br
2s–1°
abundance
0.3
0.2
0.1
0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
204.648
77.326
77.000
76.684
48.000
33.400
28.667
25.602
25.448
X : parts per Million : Carbon13

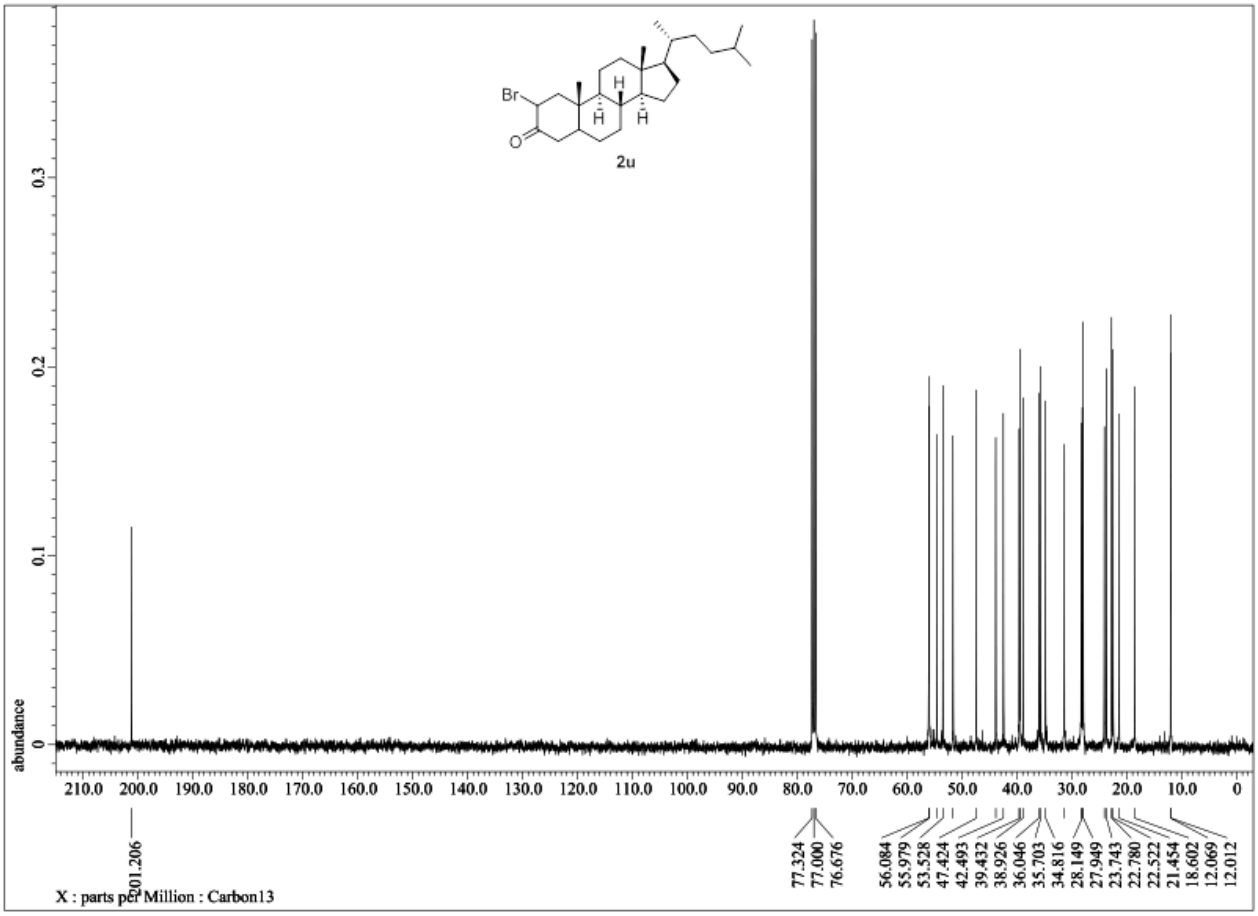

Br
O
2s–3°
abundance
X : parts per Million : Proton
3.00
2.03
2.02
2.02
3.03
1.02
7.281
0.000

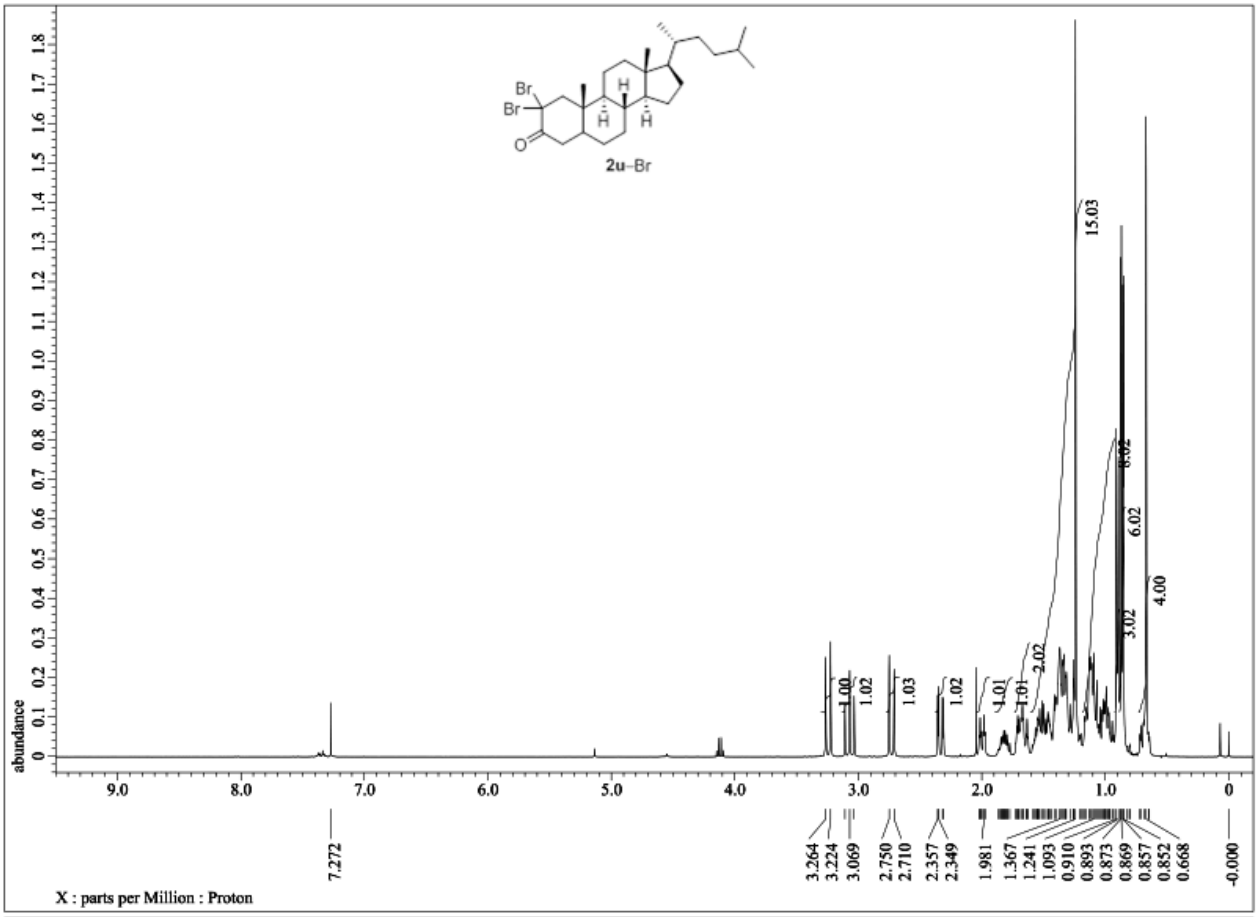

Br
O
2s–3°
abundance
X : parts per Million : Carbon13
202.894
77.324
77.000
76.676
71.344
36.409
24.849
24.143
23.237

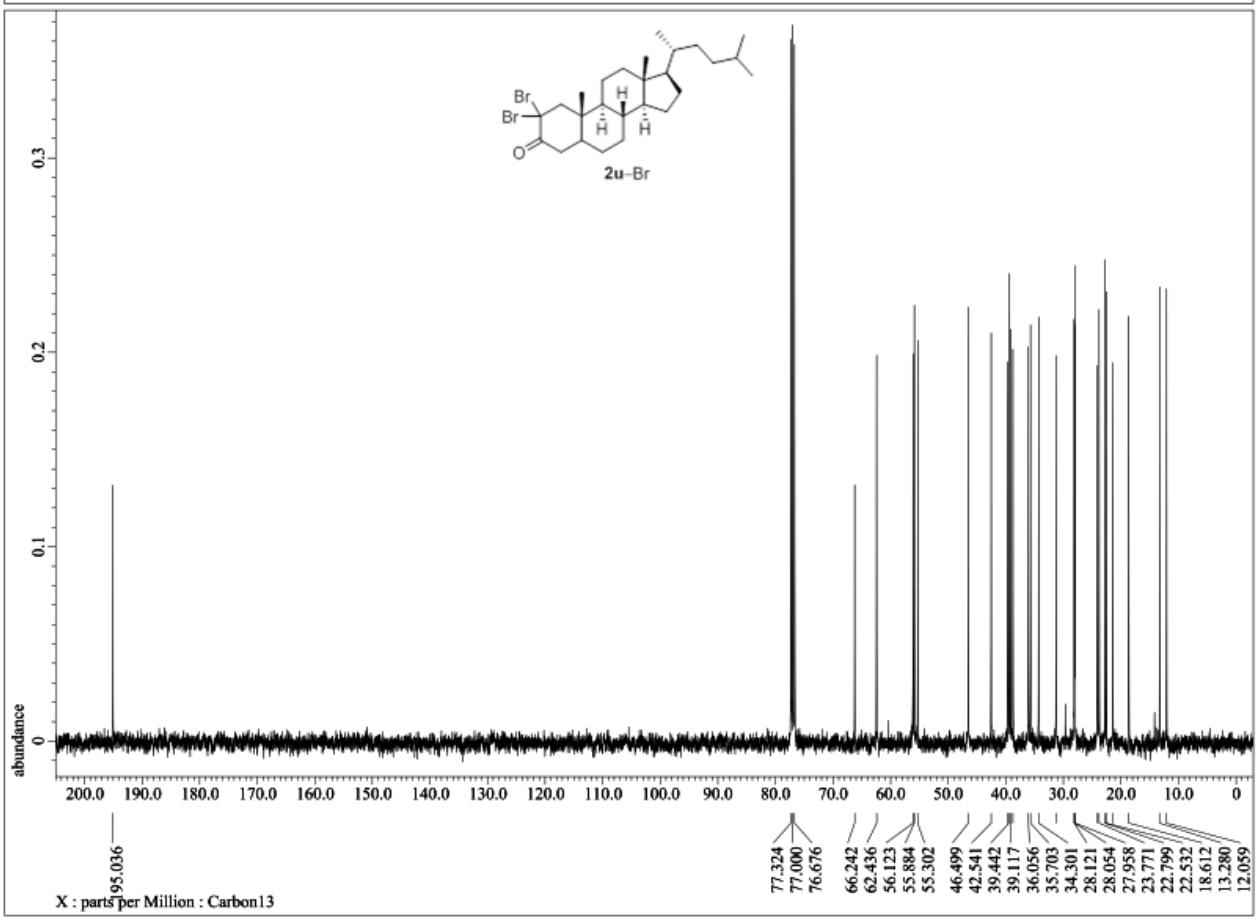

2t–2°
abundance
X : parts per Million : Proton
7.448
7.444
7.428
7.424
7.391
7.377
7.372
7.363
7.357
7.353
7.351
7.343
7.261
5.441
2.663
2.644
2.625
2.620
2.601
2.585
2.566
2.560
2.541
2.523
1.570
1.559
1.551
1.532
1.262
1.242
0.887
0.869
0.850
0.831
0.000

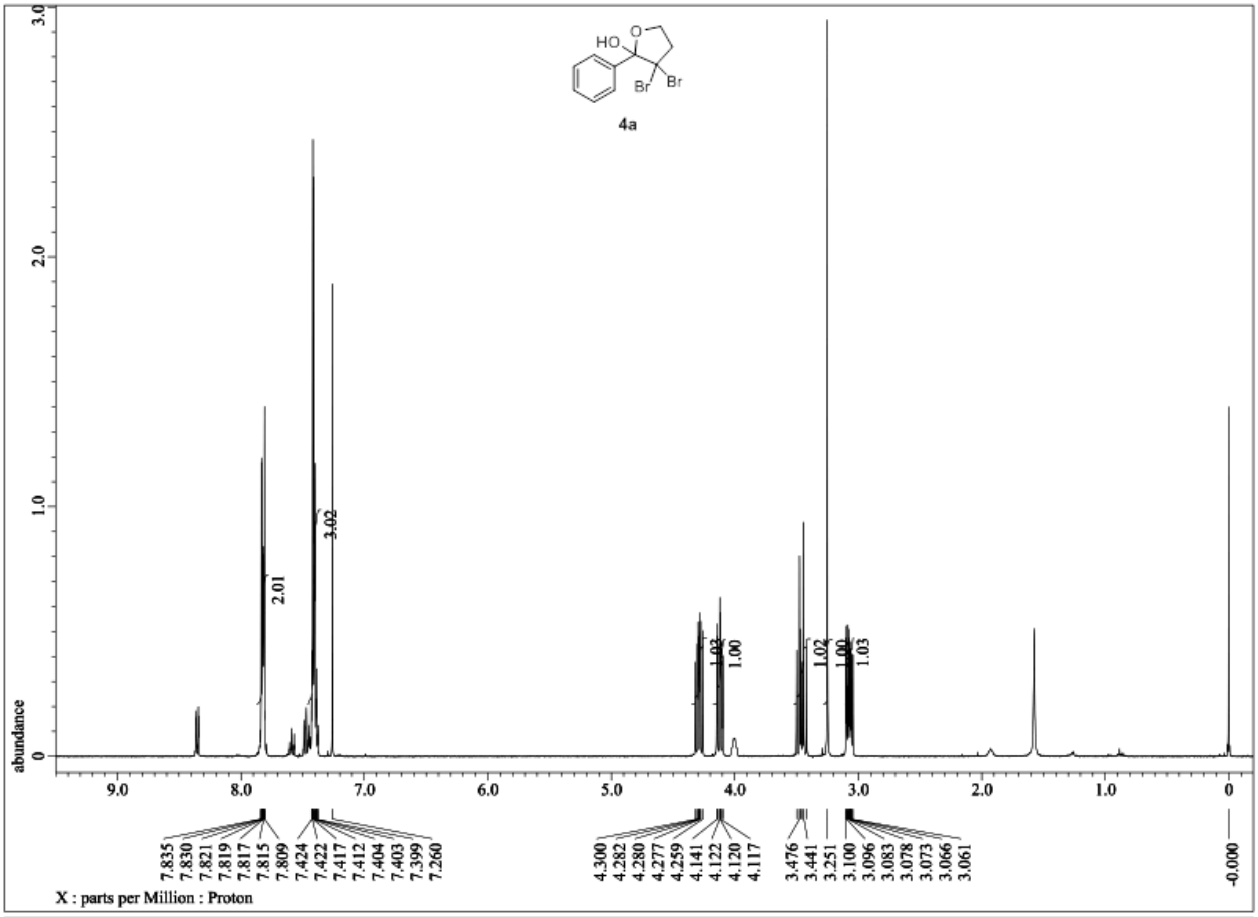

2t–2°
abundance
X : parts per Million : Carbon13
201.602
135.315
129.117
128.992
128.810
77.326
77.000
76.684
55.722
38.755
26.119
22.047
13.722

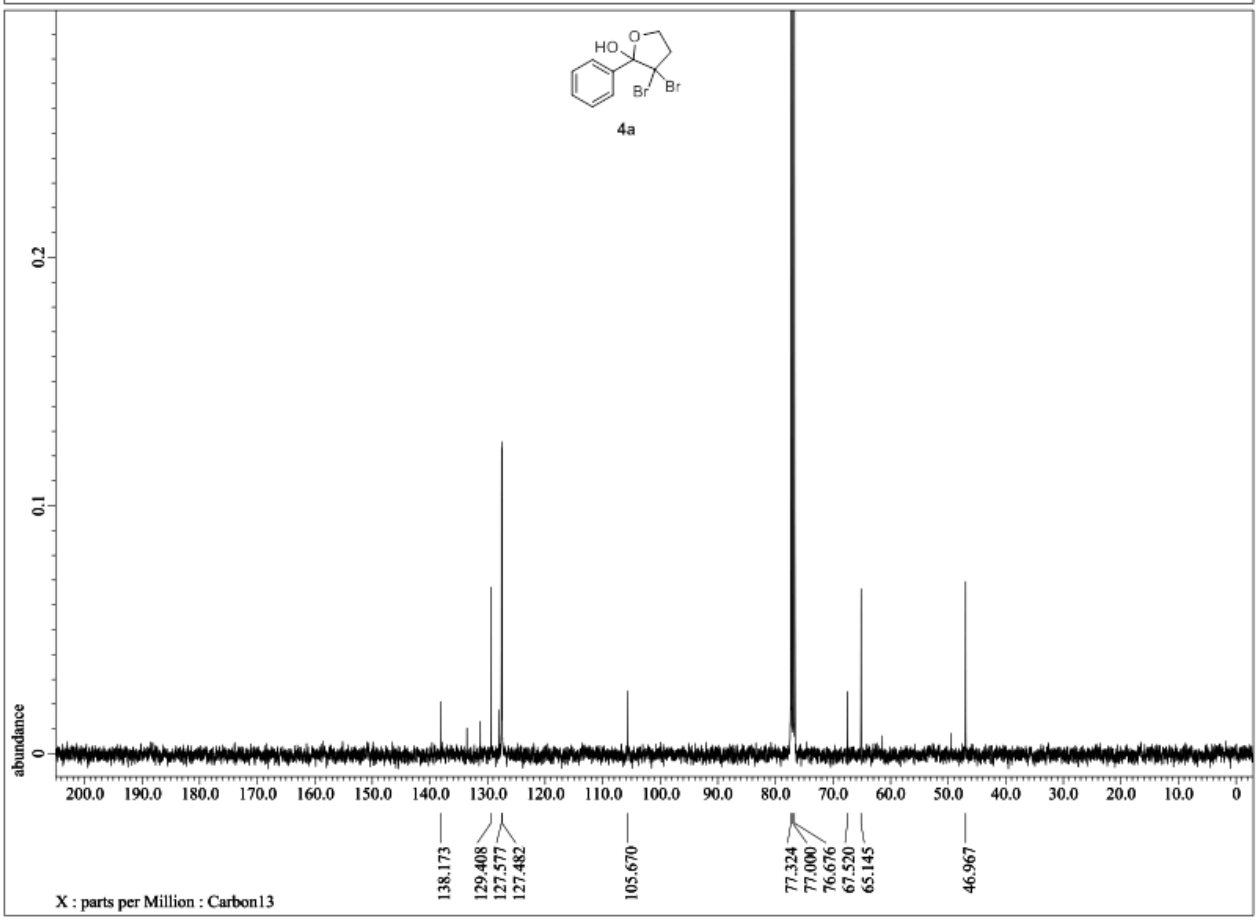

Br
H
H
H
O
2u
abundance
X : parts per Million : Proton
7.275
4.780
4.764
4.746
4.730
2.658
2.642
2.625
2.609
2.401
2.397
1.980
1.358
1.321
1.082
0.911
0.894
0.873
0.868
0.856
0.852
0.672
0.000
1.00
2.03
1.00
1.03
2.02
1.02
4.03
8.01
12.01
6.05
3.02
3.03
1.01

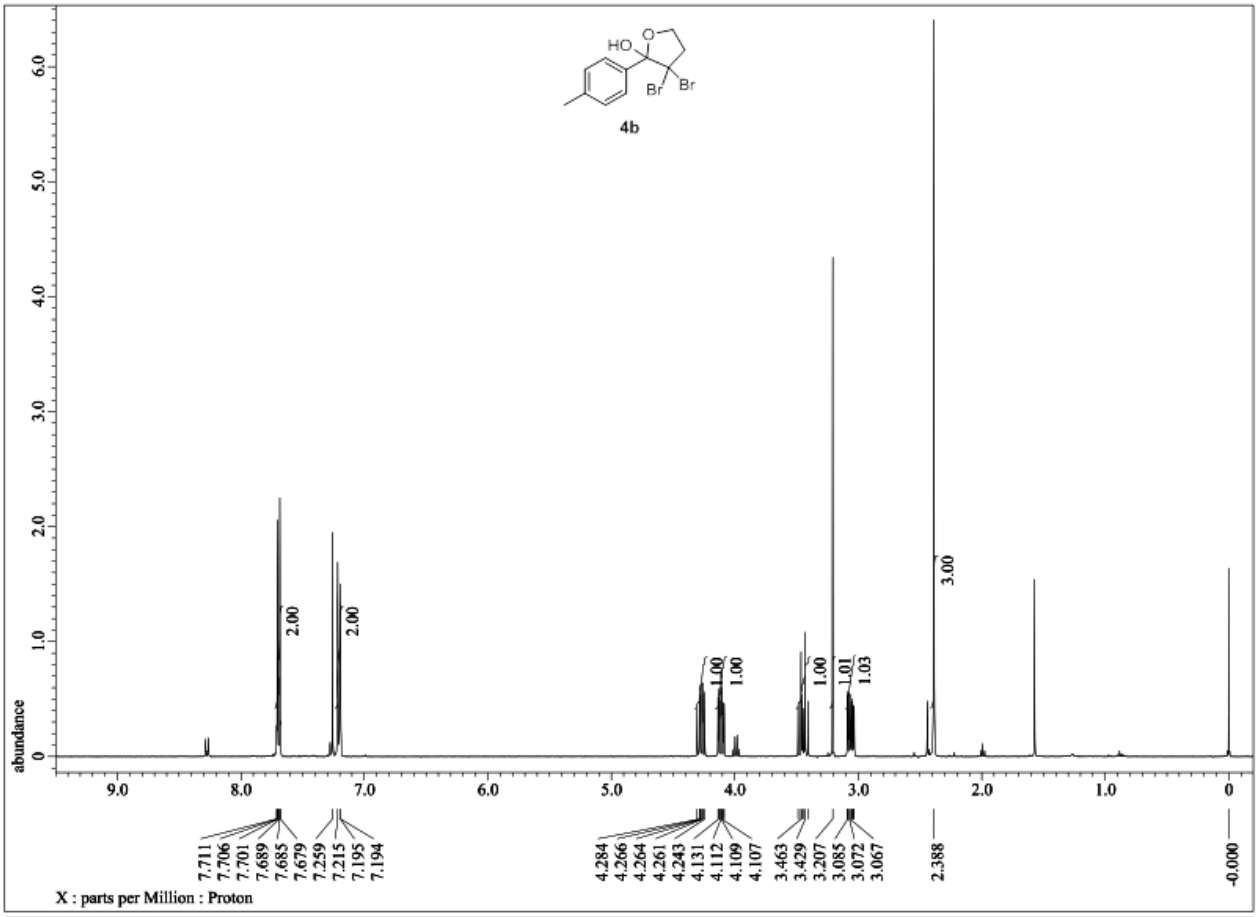

Br
H
H
H
O
2u
abundance
X : parts per Million : Carbon13
201.206
77.324
77.000
76.676
56.084
55.979
53.528
47.424
42.493
39.432
38.926
36.046
35.703
34.816
28.149
27.949
23.743
22.780
22.522
21.454
18.602
12.069
12.012

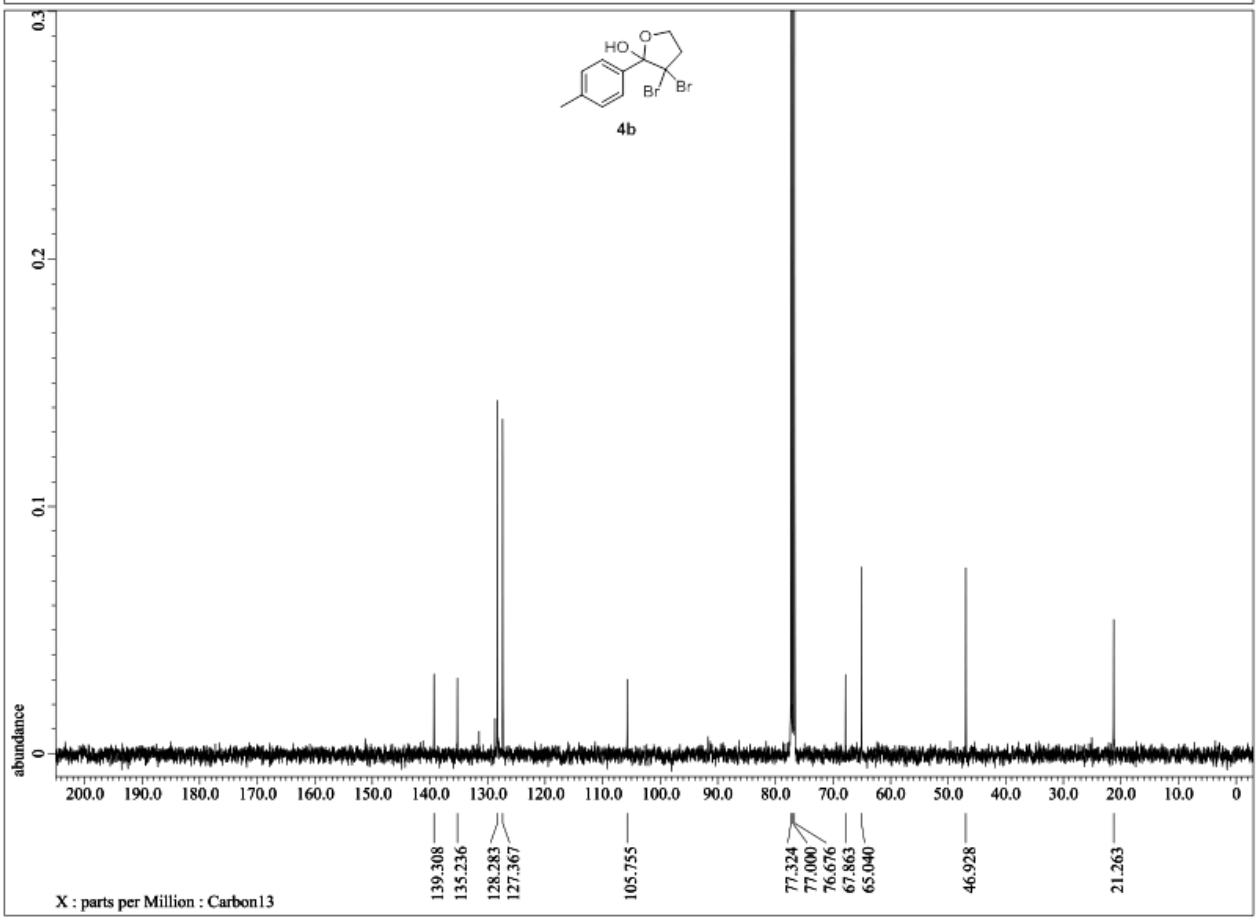

Br
Br
O
H
H
H
2u–Br
abundance
X : parts per Million : Proton
7.272
3.264
3.224
3.069
2.750
2.710
2.357
2.349
1.981
1.367
1.241
1.093
0.910
0.893
0.873
0.869
0.857
0.852
0.668
-0.000
15.03
6.02
4.00
3.02
2.02
1.03
1.02
1.00
1.01

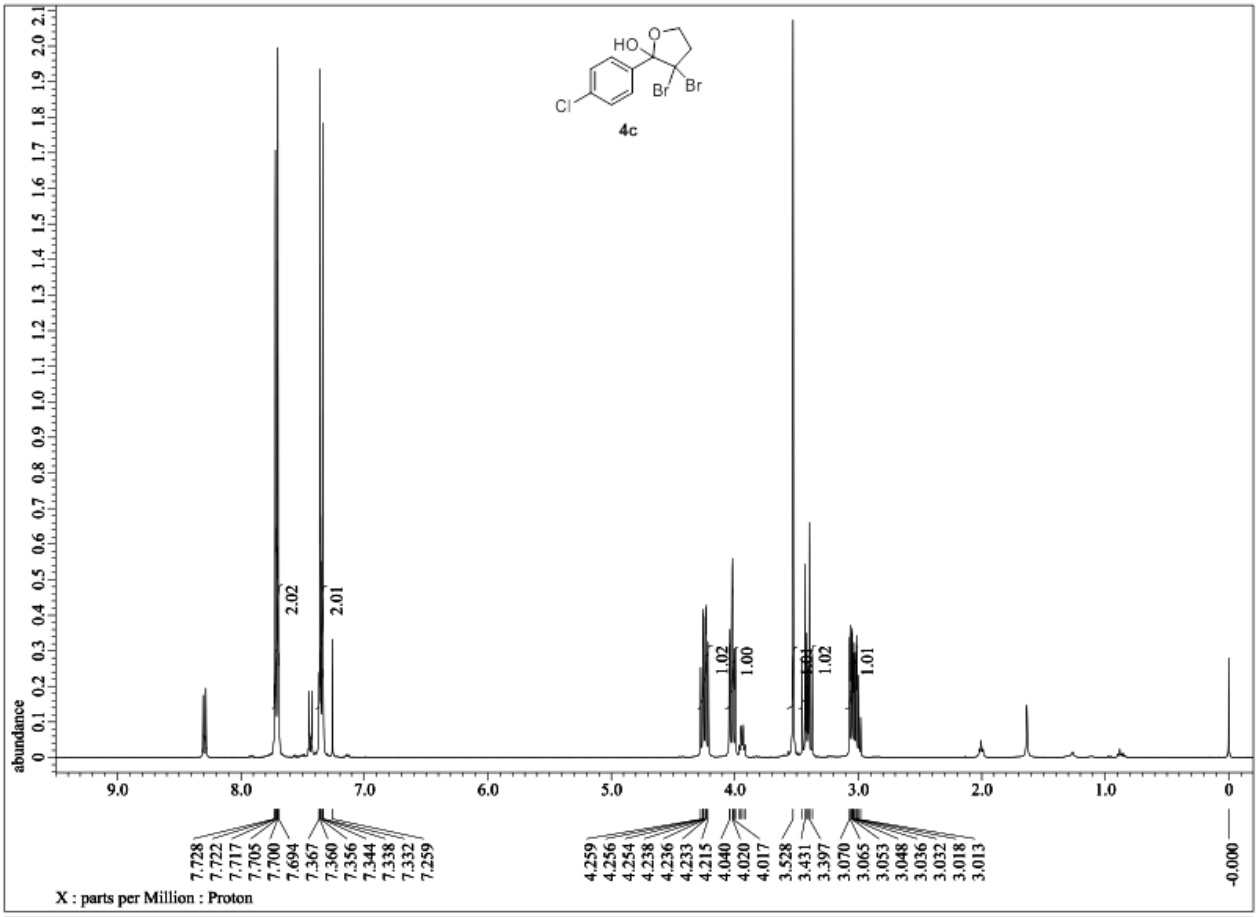

Br
Br
O
H
H
H
2u–Br
abundance
X : parts per Million : Carbon13
195.036
77.324
77.000
76.676
66.242
62.436
56.123
55.884
55.302
46.499
42.541
39.442
39.117
36.056
35.703
34.301
28.121
28.054
27.958
23.771
22.799
22.532
18.612
13.280
12.059

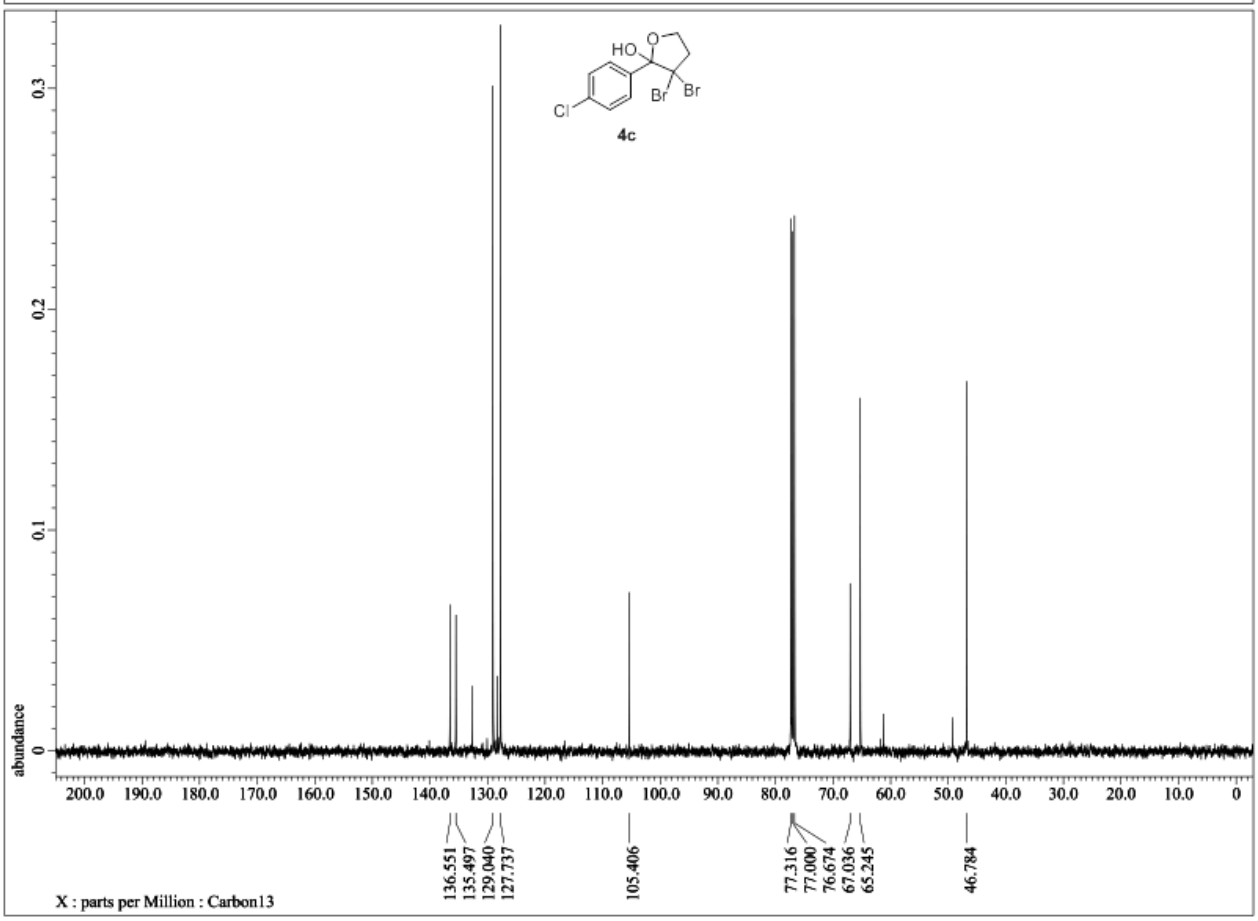

HO
O
Br
Br
4a
abundance
3.0
2.0
1.0
0
2.01
3.02
1.00
1.02
1.00
1.03
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.835
7.830
7.821
7.819
7.817
7.815
7.809
7.424
7.422
7.417
7.412
7.404
7.403
7.399
7.260
4.300
4.282
4.280
4.277
4.259
4.141
4.122
4.120
4.117
3.476
3.441
3.251
3.100
3.096
3.083
3.078
3.073
3.066
3.061
-0.000
X : parts per Million : Proton

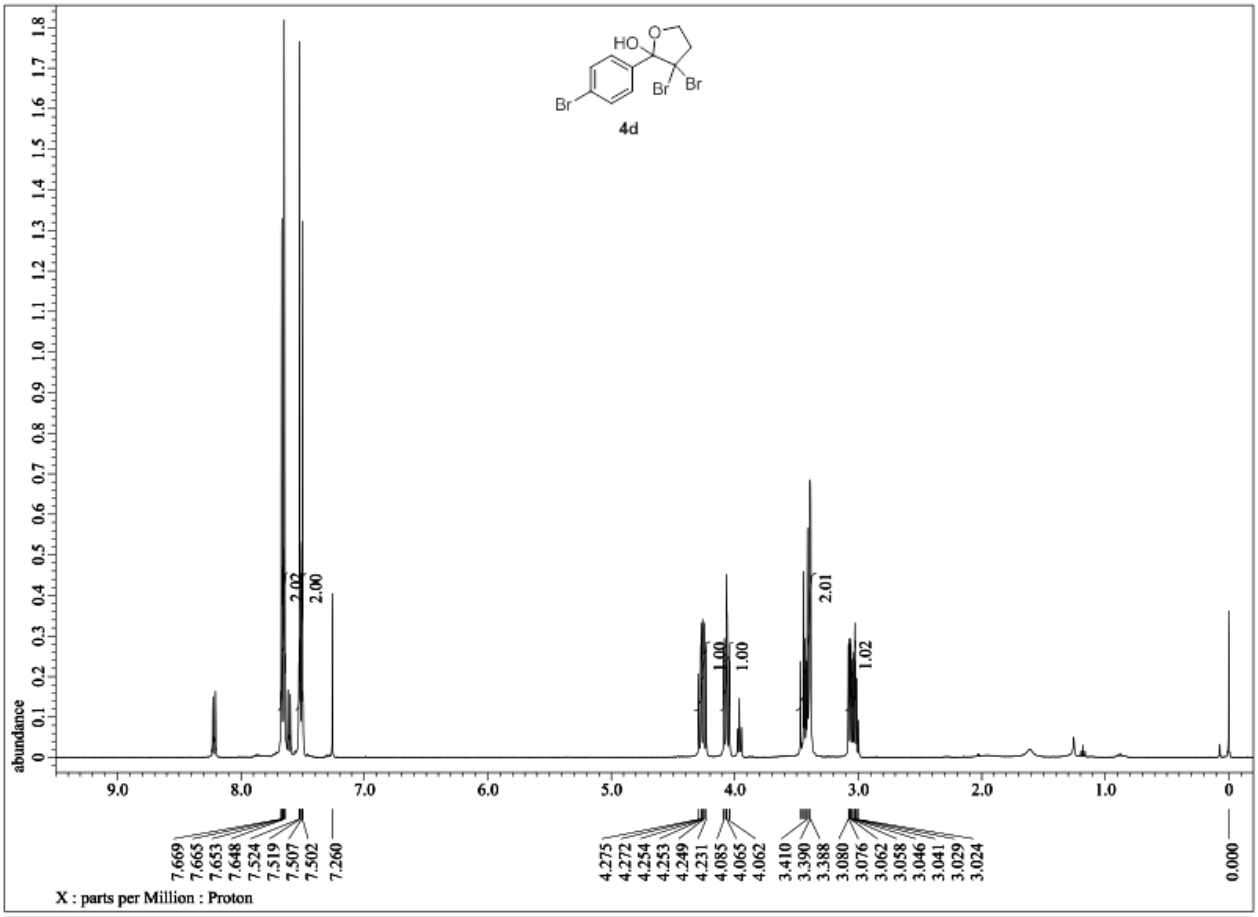

HO
O
Br
Br
4a
abundance
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
138.173
129.408
127.577
127.482
105.670
77.324
77.000
76.676
67.520
65.145
46.967
X : parts per Million : Carbon13

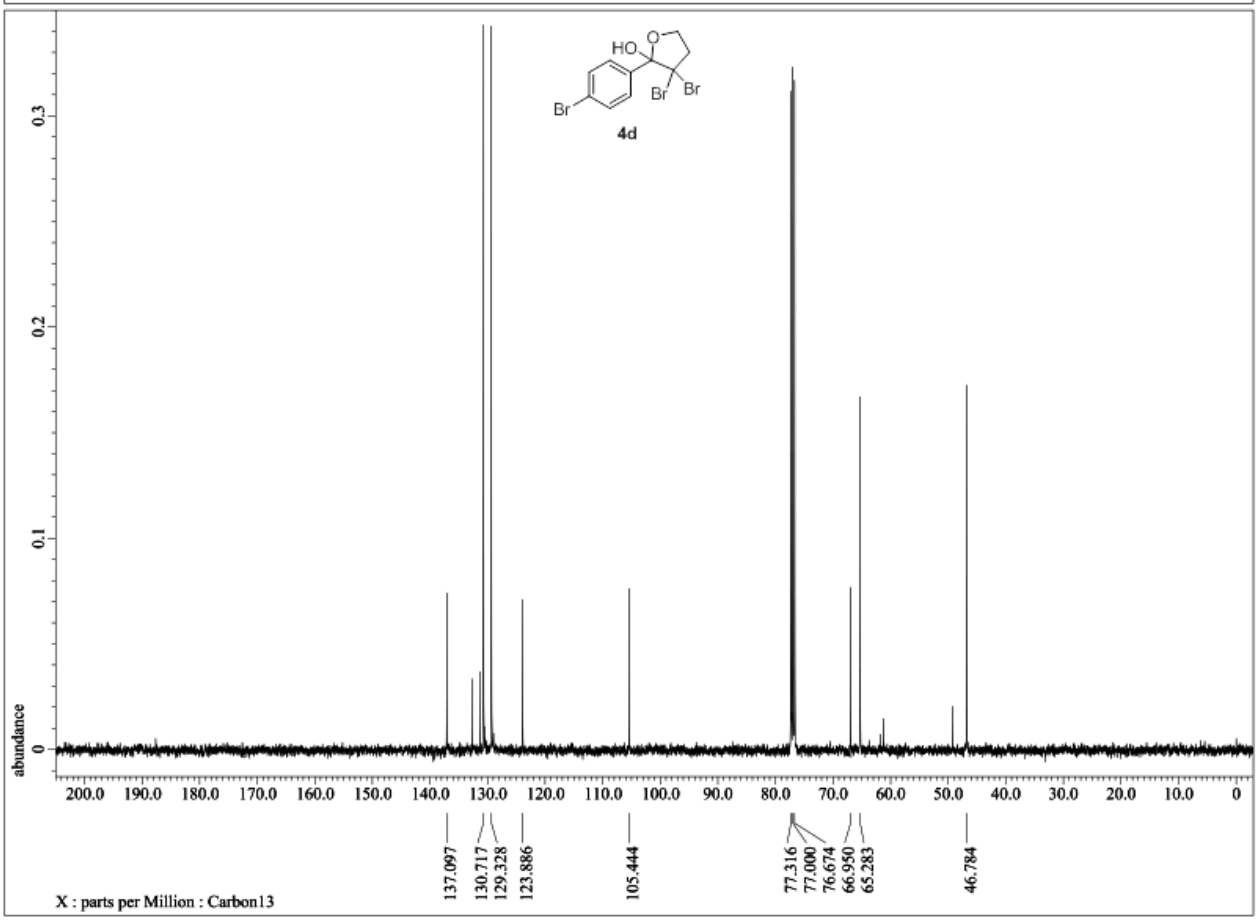

HO
O
Br
Br
4b
abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
2.00
2.00
1.00
1.00
1.00
1.01
1.03
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.711
7.706
7.701
7.689
7.685
7.679
7.259
7.215
7.195
7.194
4.284
4.266
4.264
4.261
4.243
4.131
4.112
4.109
4.107
3.463
3.429
3.207
3.085
3.072
3.067
2.388
-0.000
X : parts per Million : Proton

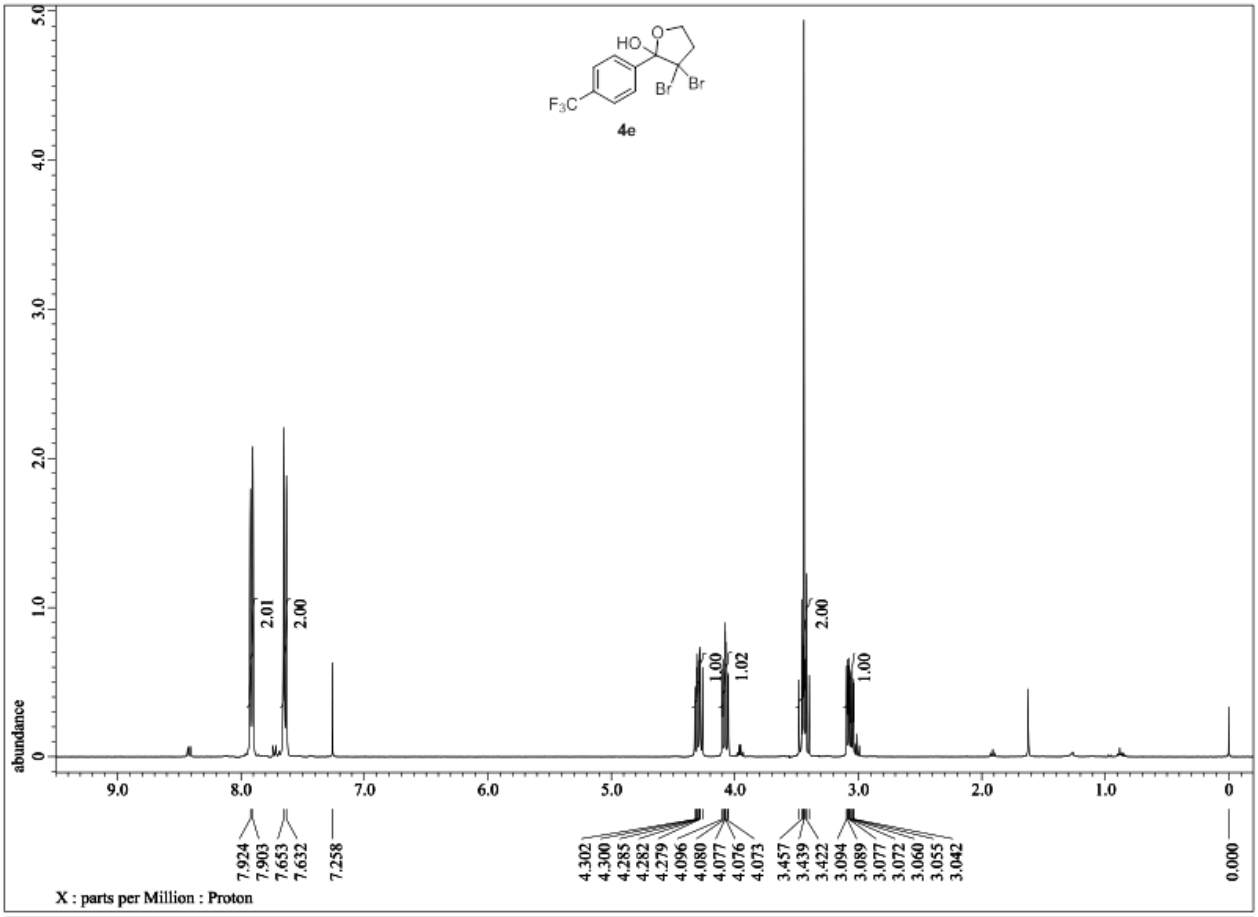

HO
O
Br
Br
4b
abundance
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
139.308
135.236
128.283
127.367
105.755
77.324
77.000
76.676
67.863
65.040
46.928
21.263
X : parts per Million : Carbon13

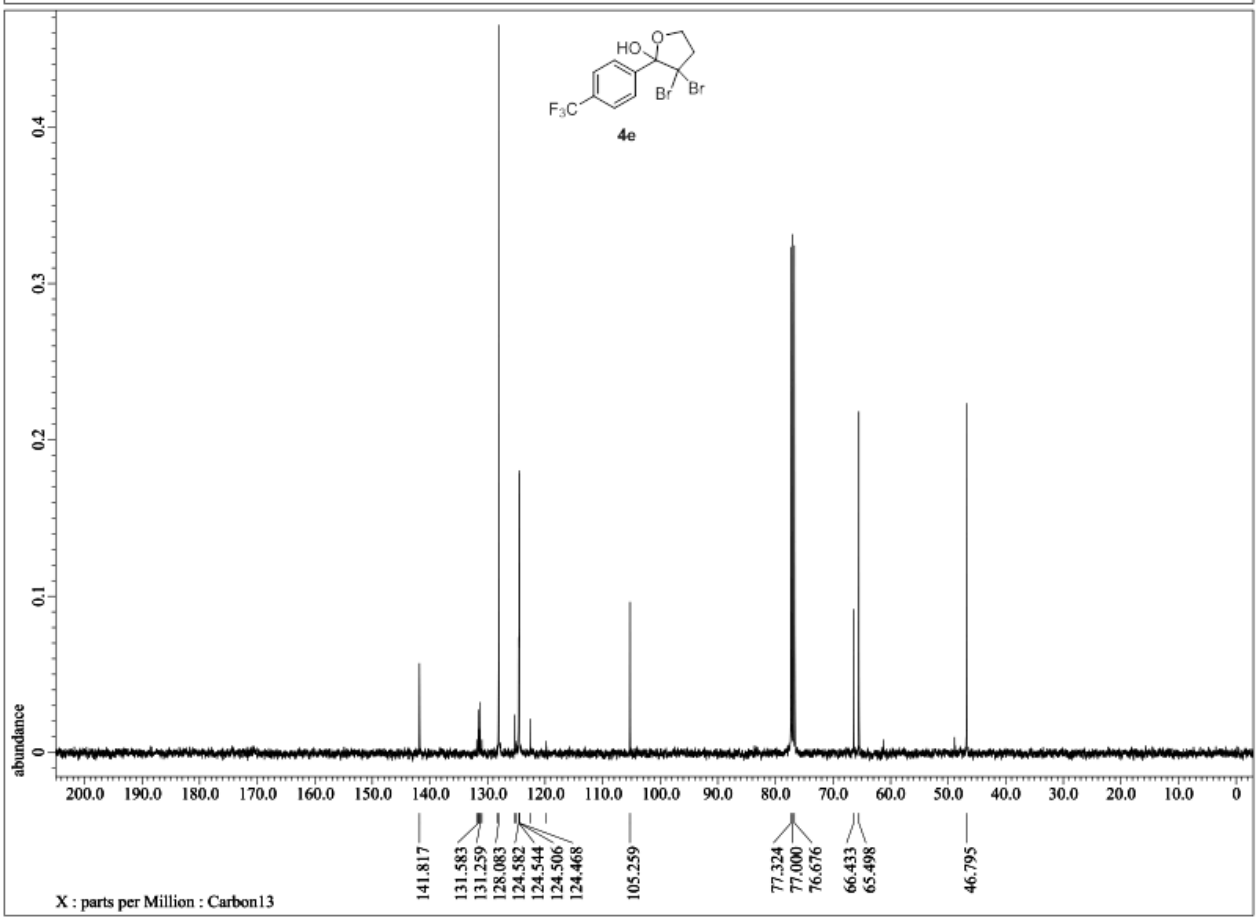

HO
O
Br
Br
Cl
4c
abundance
2.02
2.01
1.02
1.00
1.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.728
7.722
7.717
7.705
7.700
7.694
7.367
7.360
7.356
7.344
7.338
7.332
7.259
4.259
4.256
4.254
4.238
4.236
4.233
4.215
4.040
4.020
4.017
3.528
3.431
3.397
3.070
3.065
3.053
3.048
3.036
3.032
3.018
3.013
-0.000
X : parts per Million : Proton

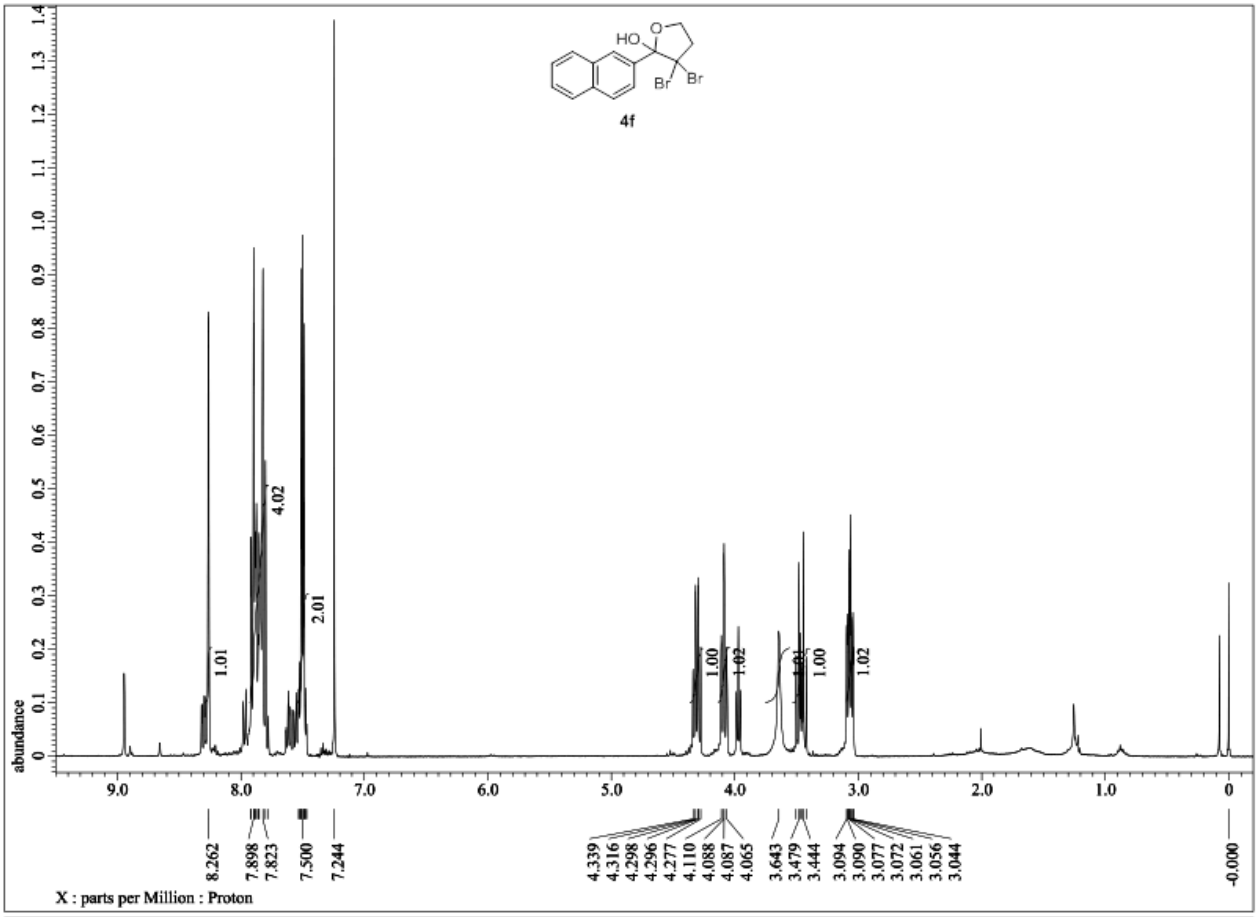

HO
O
Br
Br
Cl
4c
abundance
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
136.551
135.497
129.040
127.737
105.406
77.316
77.000
76.674
67.036
65.245
46.784
X : parts per Million : Carbon13

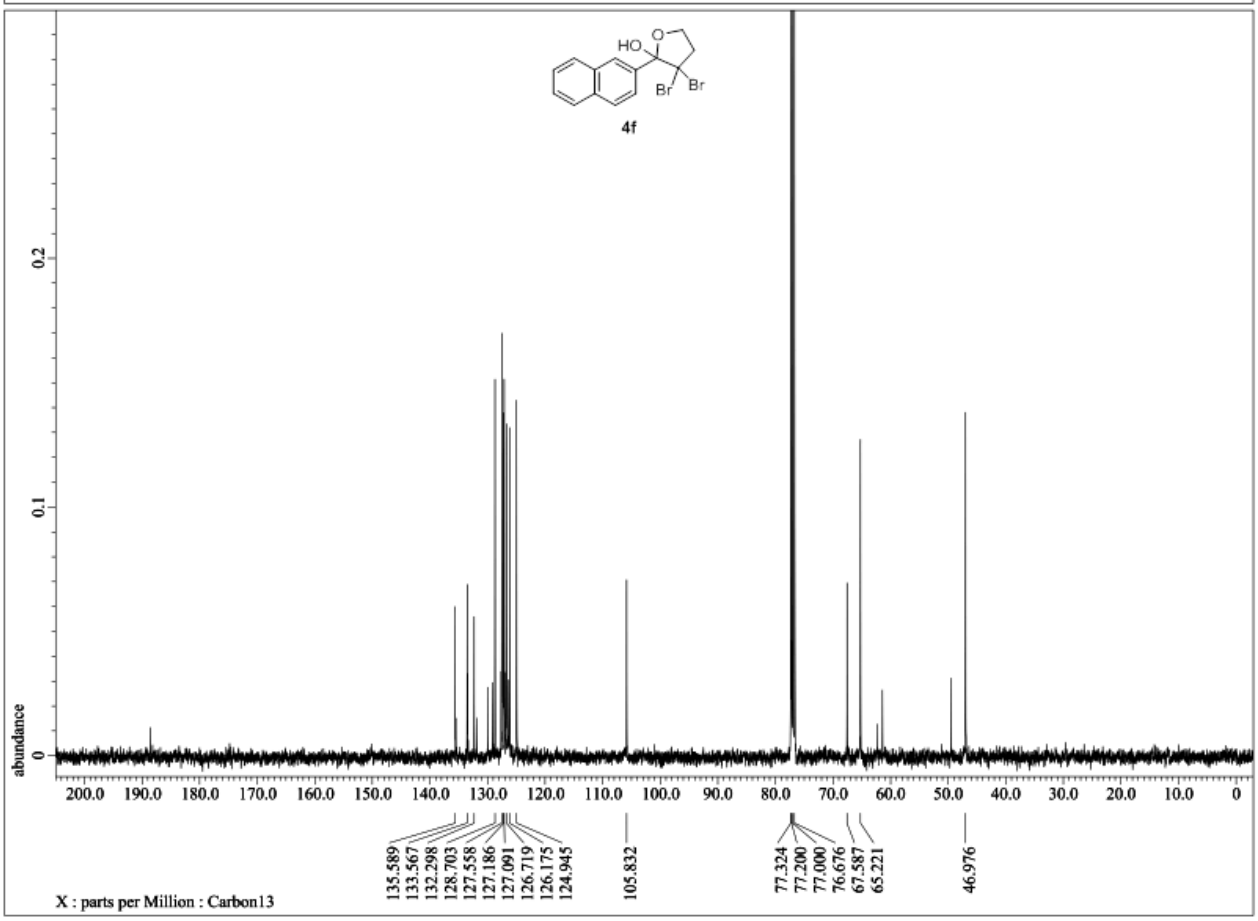

HO
O
Br
Br
Br
4d
abundance
2.02
2.00
1.00
1.00
2.01
1.02
7.669
7.665
7.653
7.648
7.524
7.519
7.507
7.502
7.260
4.275
4.272
4.254
4.253
4.249
4.231
4.085
4.065
4.062
3.410
3.390
3.388
3.080
3.076
3.062
3.058
3.046
3.041
3.029
3.024
0.000
X : parts per Million : Proton

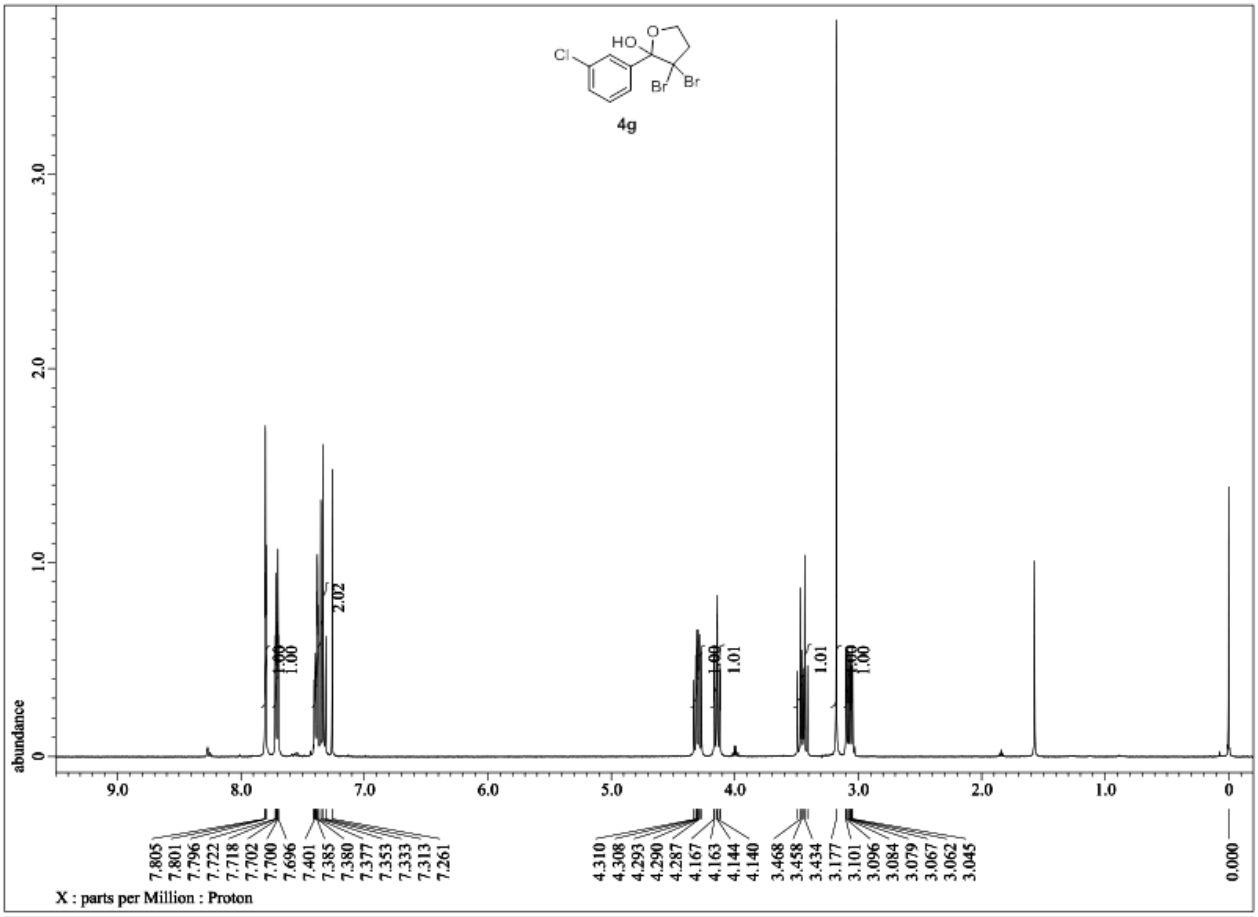

HO
O
Br
Br
Br
4d
abundance
137.097
130.717
129.328
123.886
105.444
77.316
77.000
76.674
66.950
65.283
46.784
X : parts per Million : Carbon13

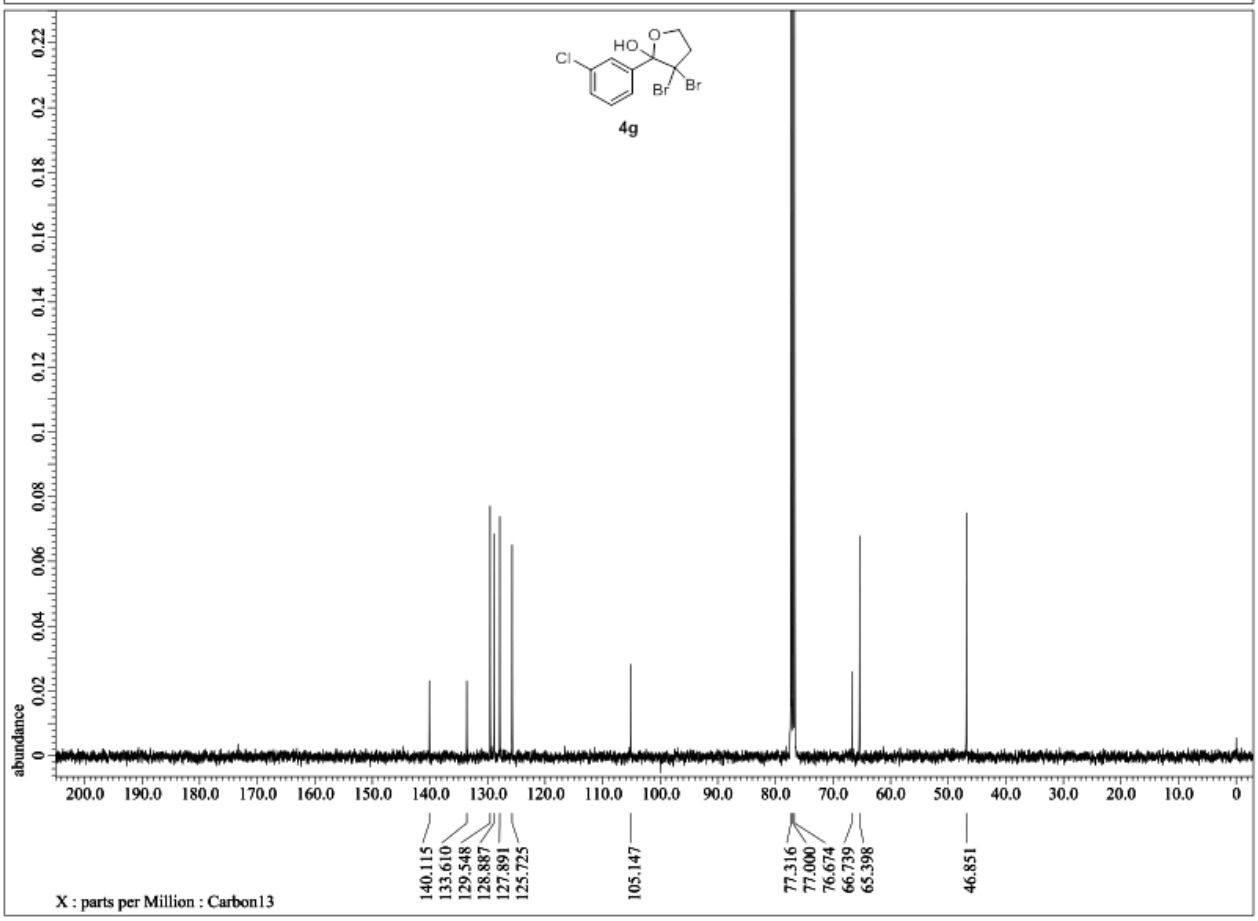

HO
O
Br
Br
F3C
4e
abundance
5.0
4.0
3.0
2.0
1.0
0
2.01
2.00
1.00
1.02
2.00
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.924
7.903
7.653
7.632
7.258
4.302
4.300
4.285
4.282
4.279
4.096
4.080
4.077
4.076
4.073
3.457
3.439
3.422
3.094
3.089
3.077
3.072
3.060
3.055
3.042
0.000
X : parts per Million : Proton

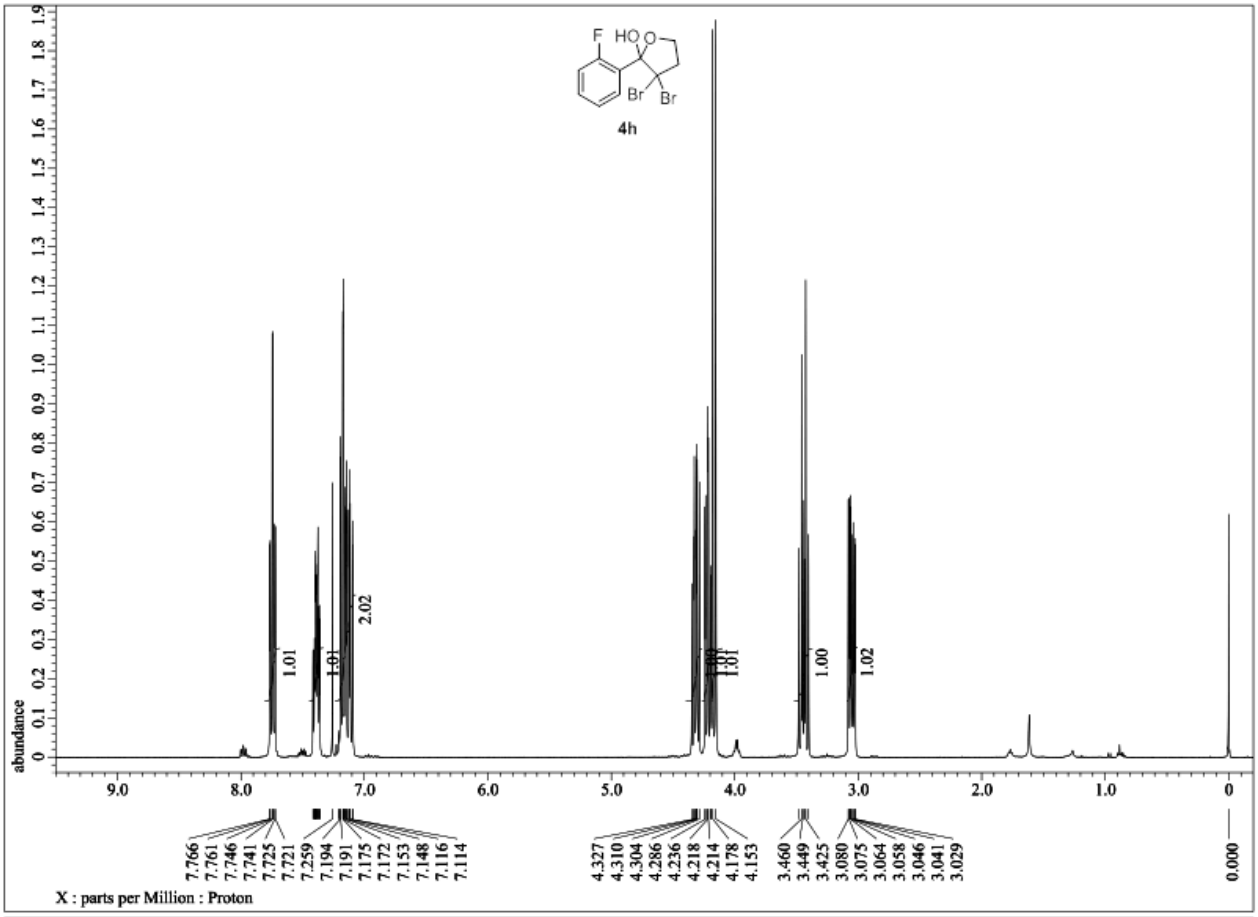

HO
O
Br
Br
F3C
4e
abundance
0.4
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
141.817
131.583
131.259
128.083
124.582
124.544
124.506
124.468
105.259
77.324
77.000
76.676
66.433
65.498
46.795
X : parts per Million : Carbon13

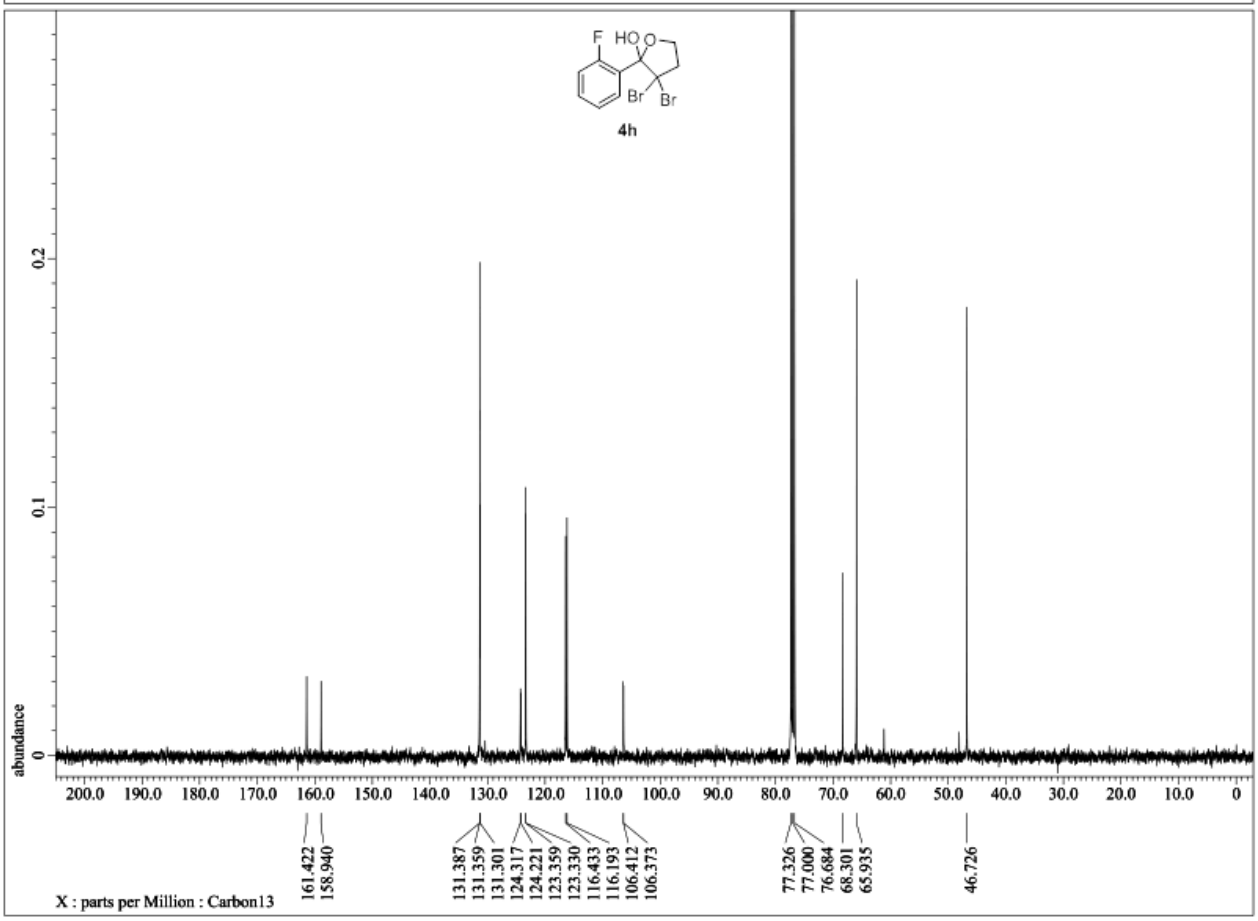

HO
O
Br
Br
4f
abundance
1.01
4.02
2.01
1.00
1.02
1.01
1.00
1.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.262
7.898
7.823
7.500
7.244
4.339
4.316
4.298
4.296
4.277
4.110
4.088
4.087
4.065
3.643
3.479
3.444
3.094
3.090
3.077
3.072
3.061
3.056
3.044
-0.000
X : parts per Million : Proton

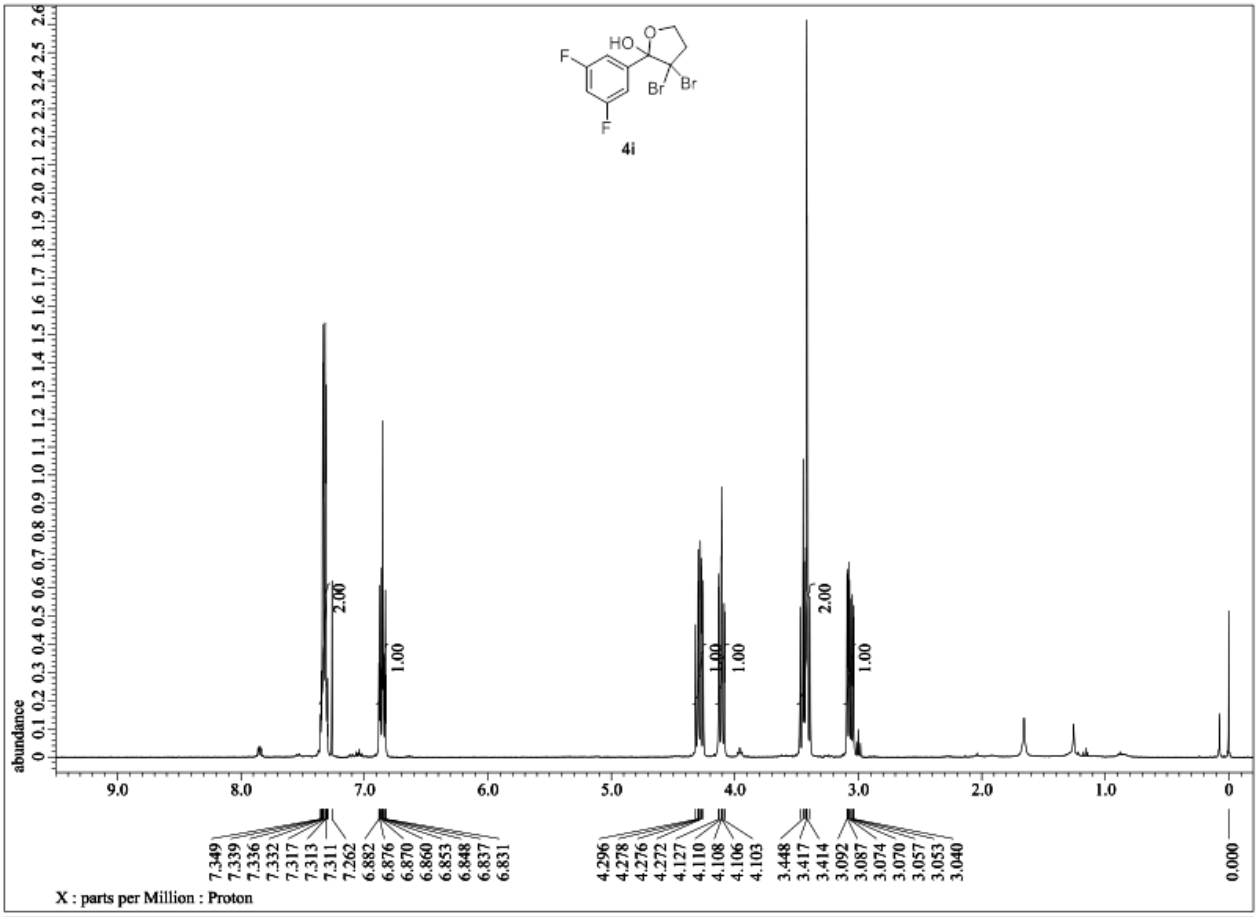

HO
O
Br
Br
4f
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
135.589
133.567
132.298
128.703
127.558
127.186
127.091
126.719
126.175
124.945
105.832
77.324
77.200
77.000
76.676
67.587
65.221
46.976
X : parts per Million : Carbon13

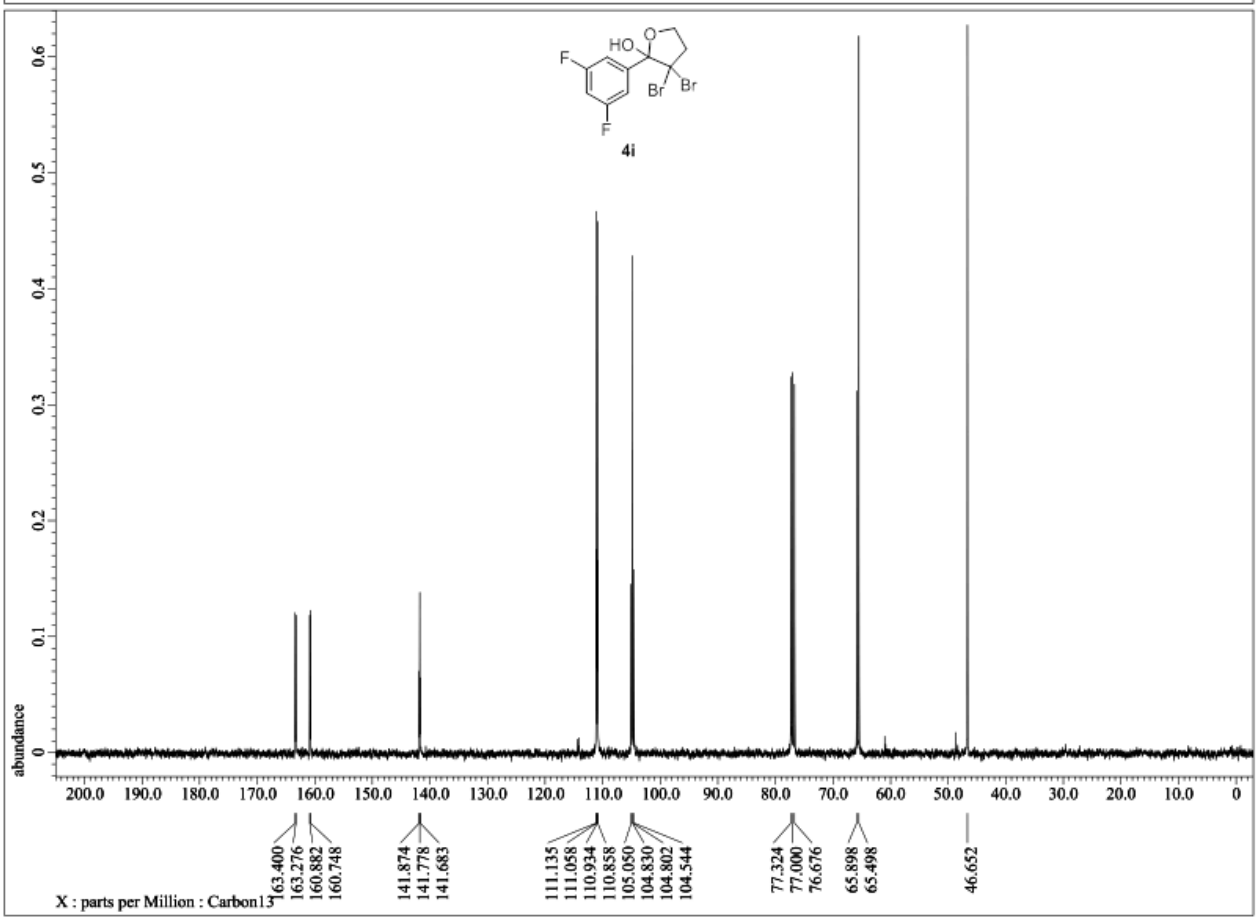

HO
O
Cl
Br
Br
4g
abundance
X : parts per Million : Proton
7.805
7.801
7.796
7.722
7.718
7.702
7.700
7.696
7.401
7.385
7.380
7.377
7.353
7.333
7.313
7.261
4.310
4.308
4.293
4.290
4.287
4.167
4.163
4.144
4.140
3.468
3.458
3.434
3.177
3.101
3.096
3.084
3.079
3.067
3.062
3.045
0.000

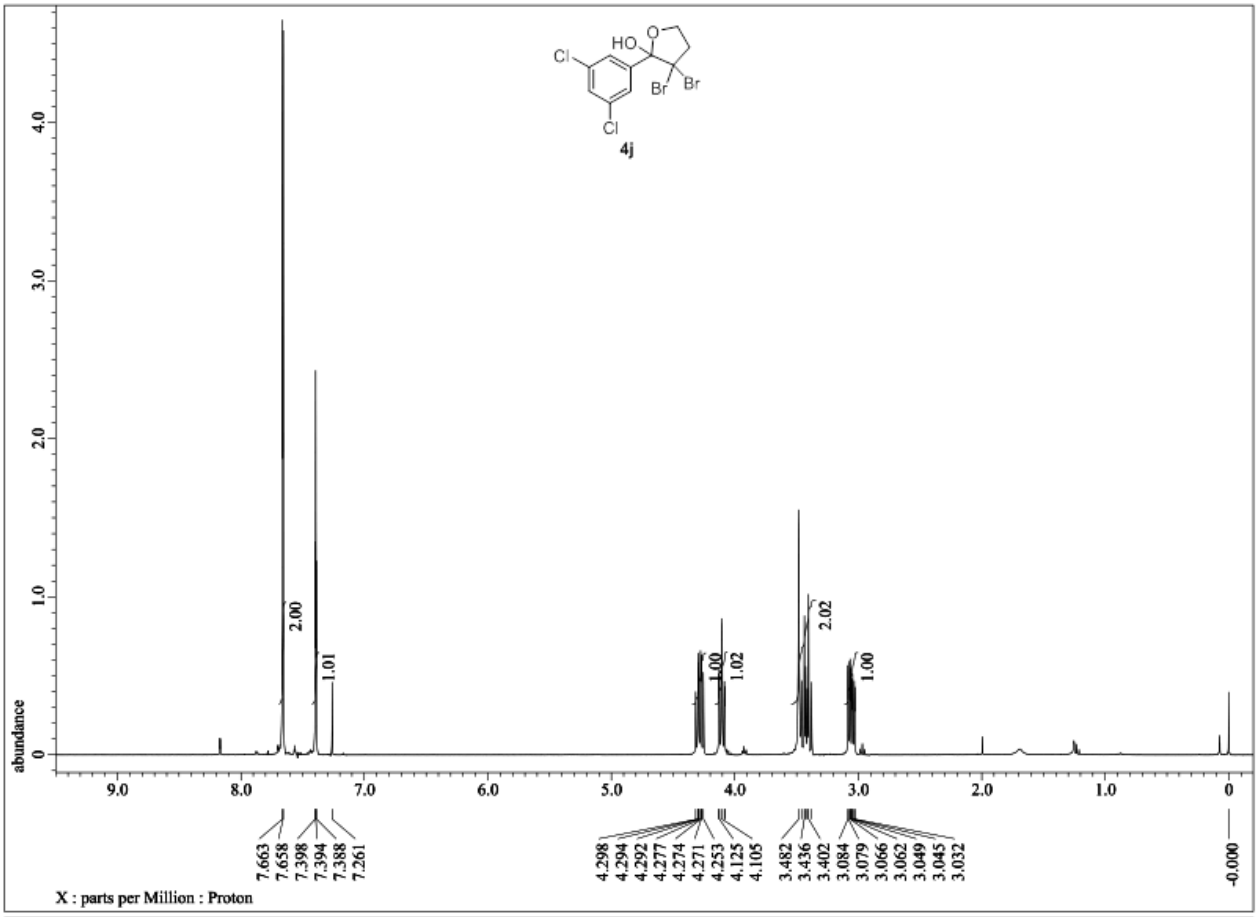

HO
O
Cl
Br
Br
4g
abundance
X : parts per Million : Carbon13
140.115
133.610
129.548
128.887
127.891
125.725
105.147
77.316
77.000
76.674
66.739
65.398
46.851

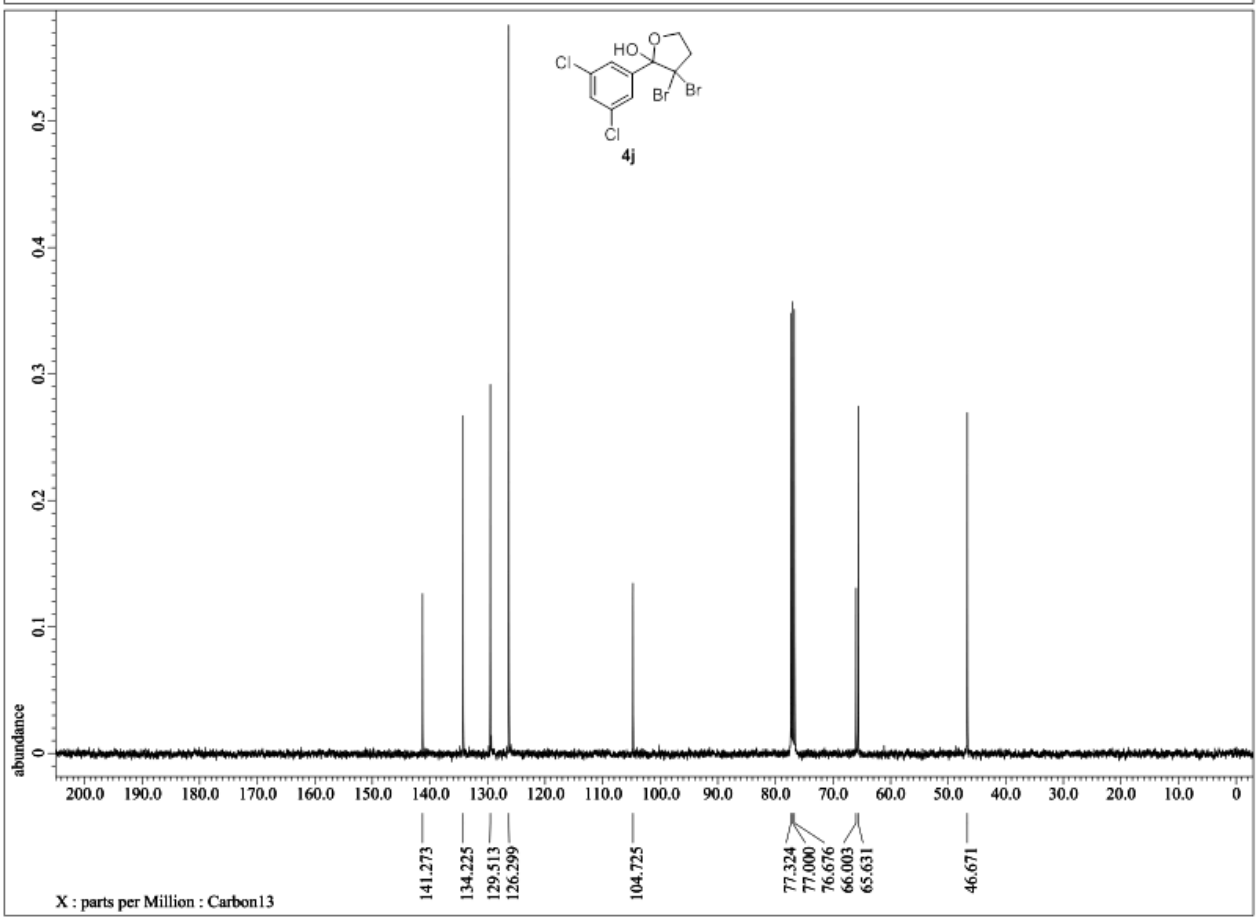

F
HO
O
Br
Br
4h
abundance
1.01
1.01
2.02
1.01
1.00
1.02
7.766
7.761
7.746
7.741
7.725
7.721
7.259
7.194
7.191
7.175
7.172
7.153
7.148
7.116
7.114
4.327
4.310
4.304
4.286
4.236
4.218
4.214
4.178
4.153
3.460
3.449
3.425
3.080
3.075
3.064
3.058
3.046
3.041
3.029
0.000
X : parts per Million : Proton

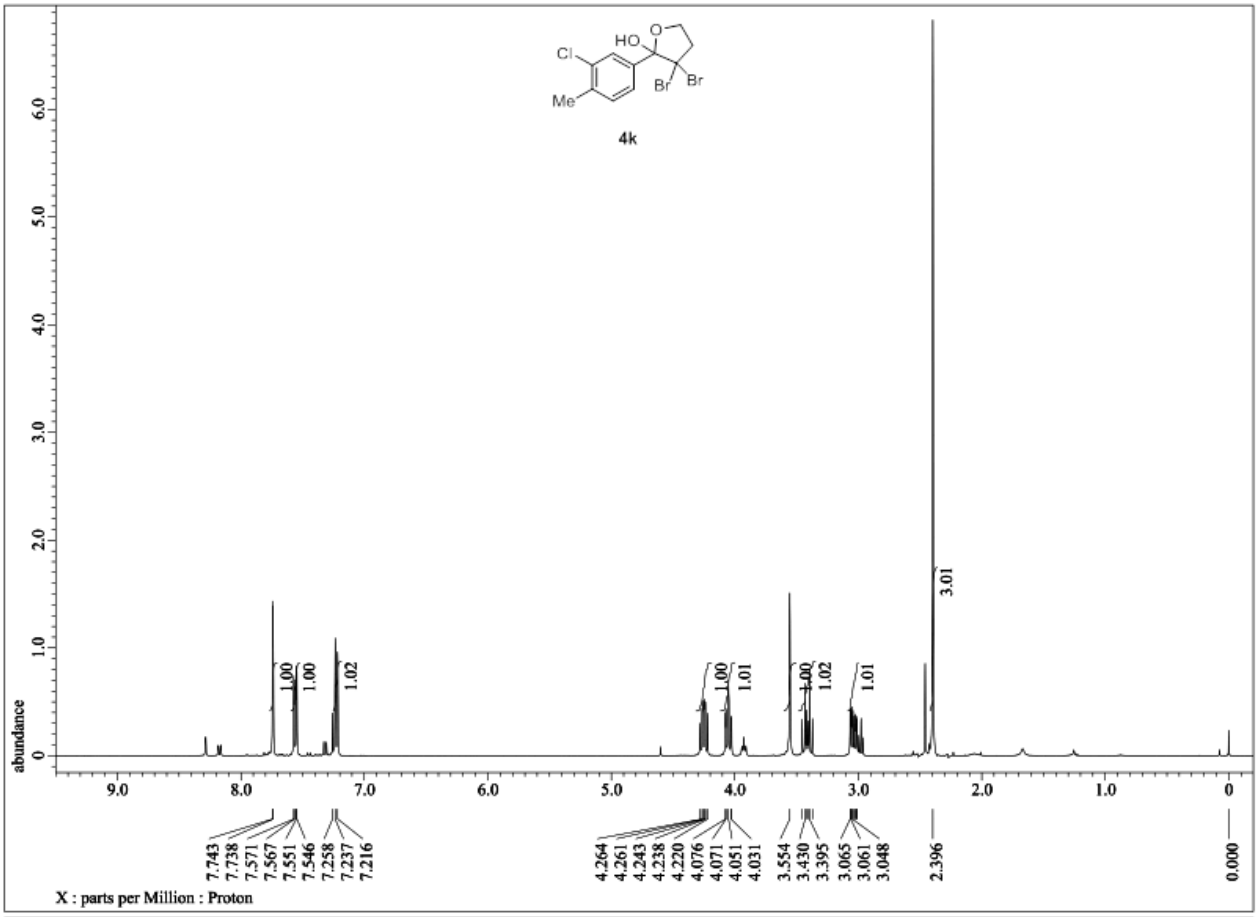

F
HO
O
Br
Br
4h
abundance
161.422
158.940
131.387
131.359
131.301
124.317
124.221
123.359
123.330
116.433
116.193
106.412
106.373
77.326
77.000
76.684
68.301
65.935
46.726
X : parts per Million : Carbon13

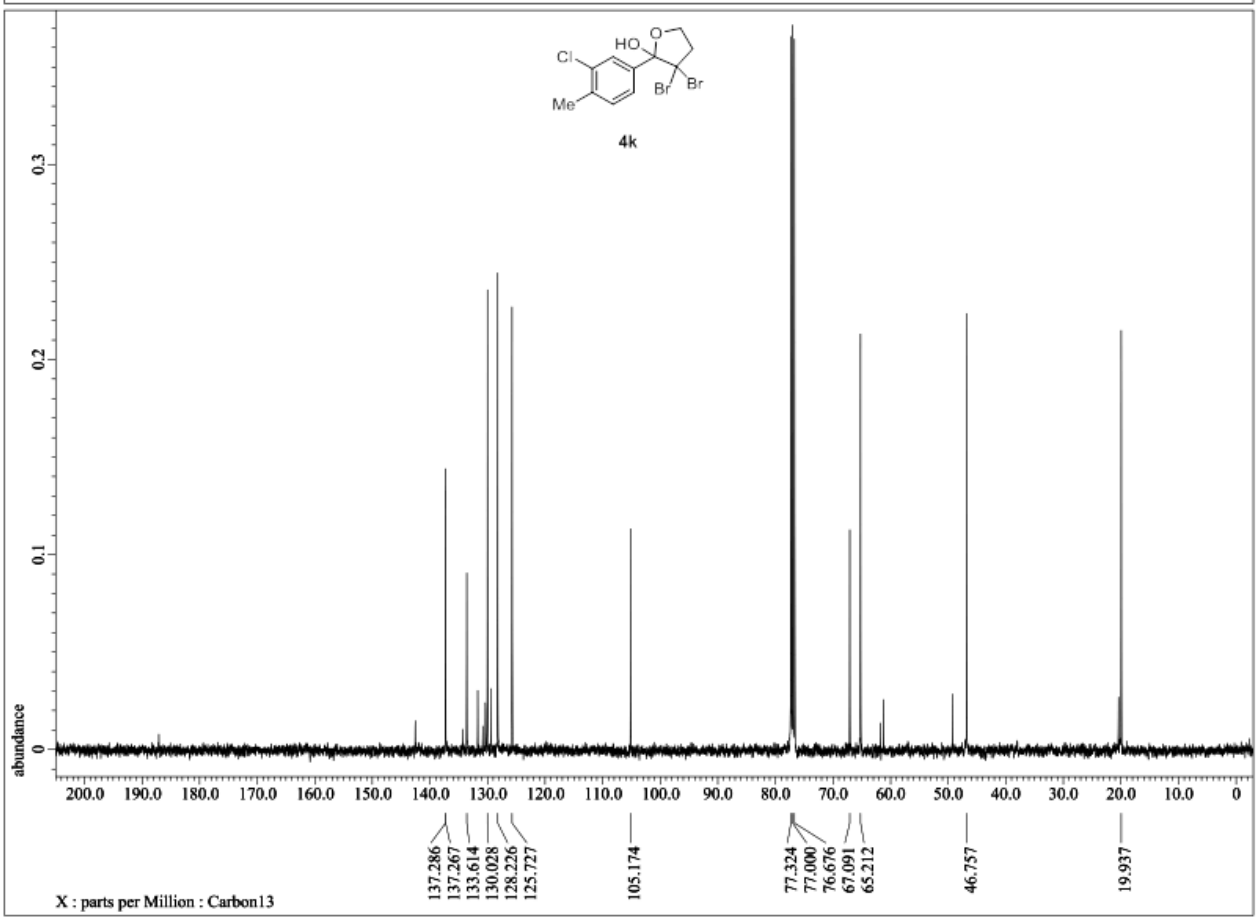

HO
O
F
Br
Br
F
4i
abundance
2.00
1.00
1.00
1.00
2.00
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.349
7.339
7.336
7.332
7.317
7.313
7.311
7.262
6.882
6.876
6.870
6.860
6.853
6.848
6.837
6.831
4.296
4.278
4.276
4.272
4.127
4.110
4.108
4.106
4.103
3.448
3.417
3.414
3.092
3.087
3.074
3.070
3.057
3.053
3.040
0.000
X : parts per Million : Proton

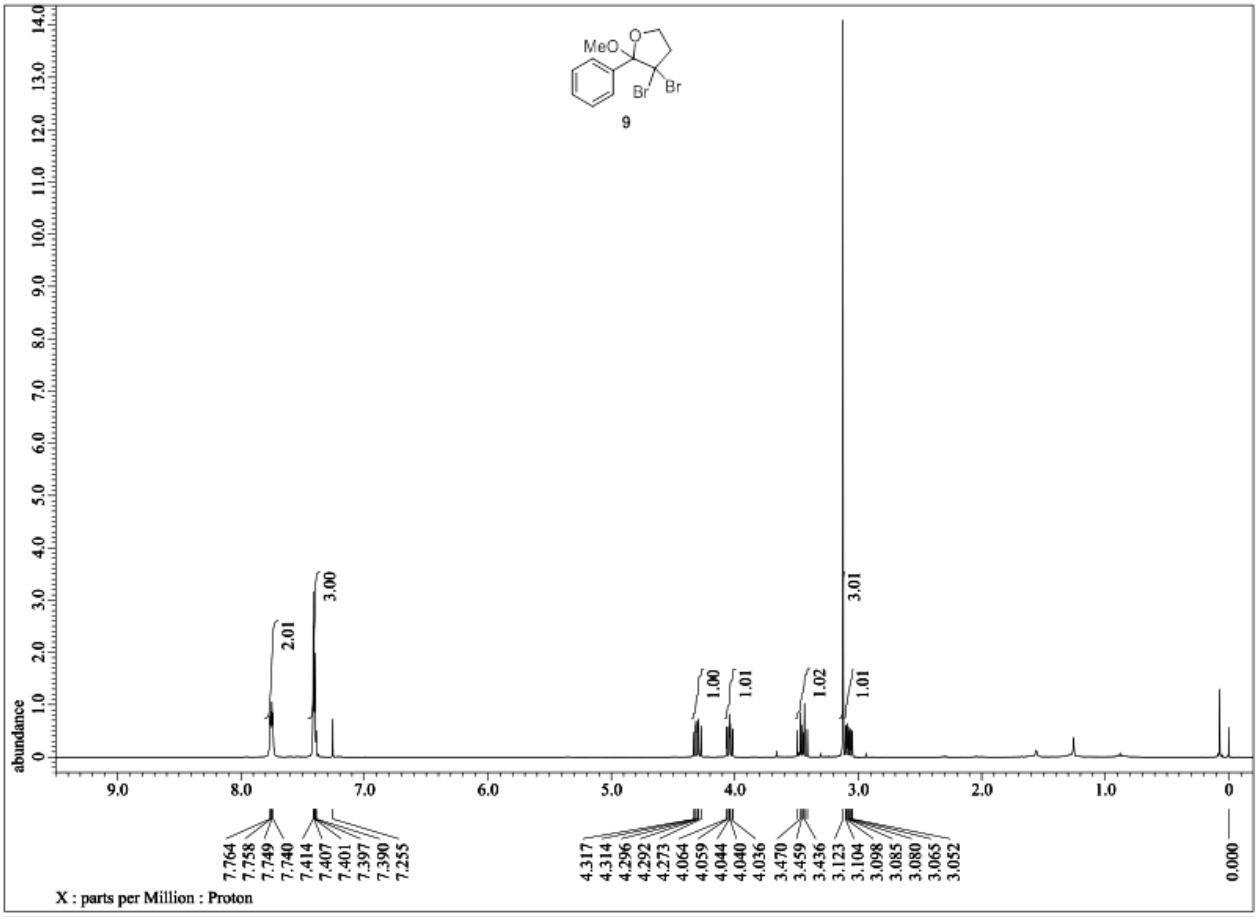

HO
O
F
Br
Br
F
4i
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
163.400
163.276
160.882
160.748
141.874
141.778
141.683
111.135
111.058
110.934
110.858
105.050
104.830
104.802
104.544
77.324
77.000
76.676
65.898
65.498
46.652
X : parts per Million : Carbon13

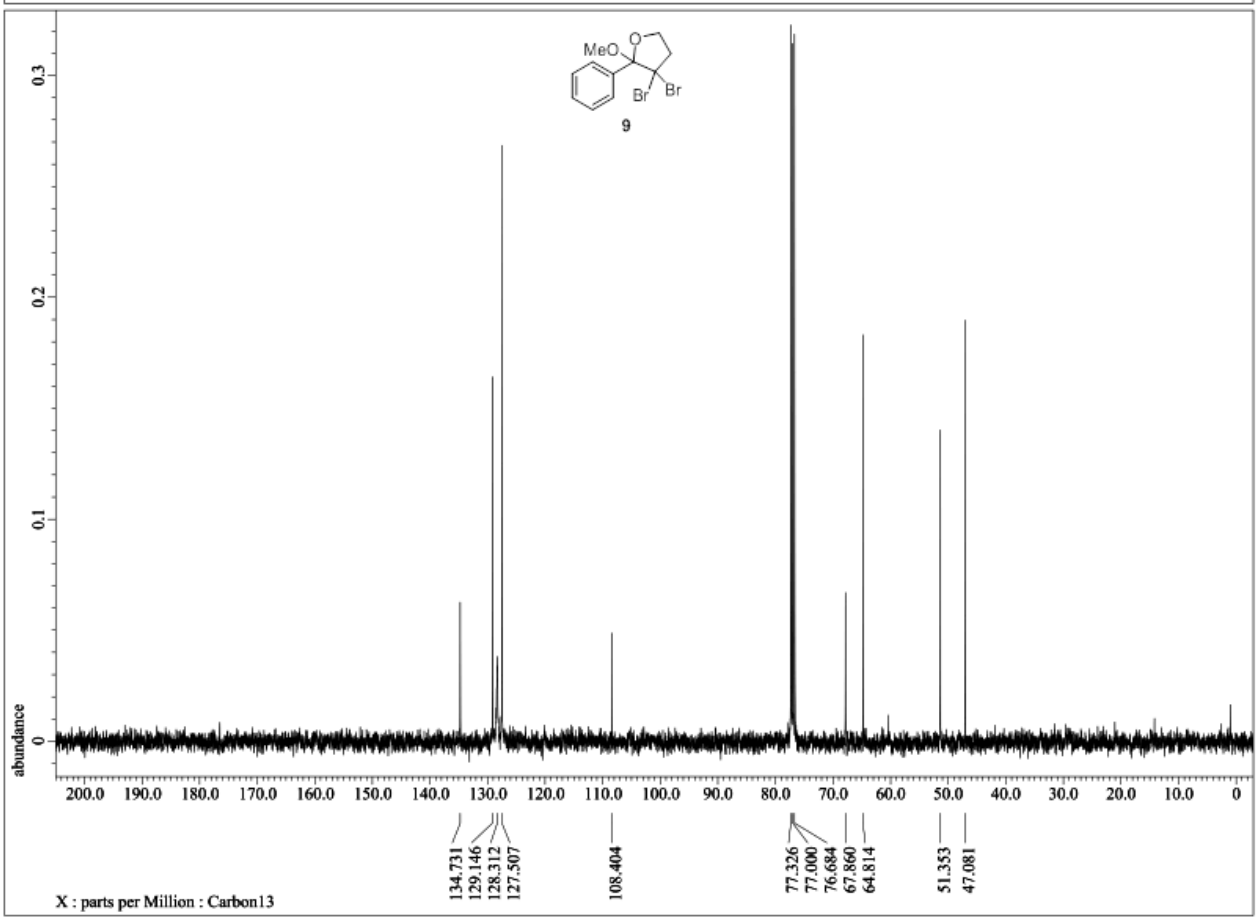

HO
O
Cl
Br
Br
Cl
4j
abundance
4.0
3.0
2.0
1.0
0
2.00
1.01
1.00
1.02
2.02
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.663
7.658
7.398
7.394
7.388
7.261
4.298
4.294
4.292
4.277
4.274
4.271
4.253
4.125
4.105
3.482
3.436
3.402
3.084
3.079
3.066
3.062
3.049
3.045
3.032
-0.000
X : parts per Million : Proton

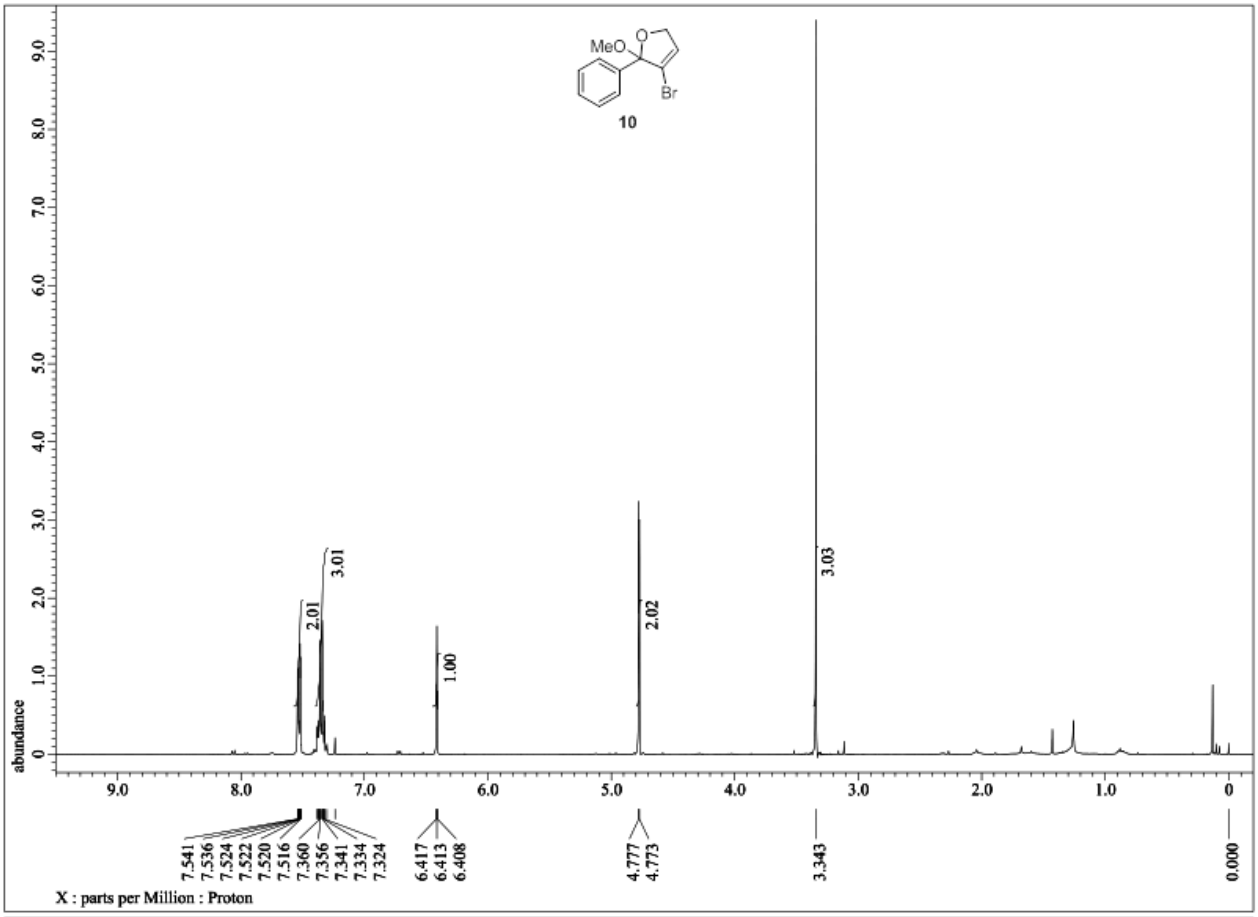

HO
O
Cl
Br
Br
Cl
4j
abundance
0.5
0.4
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
141.273
134.225
129.513
126.299
104.725
77.324
77.000
76.676
66.003
65.631
46.671
X : parts per Million : Carbon13

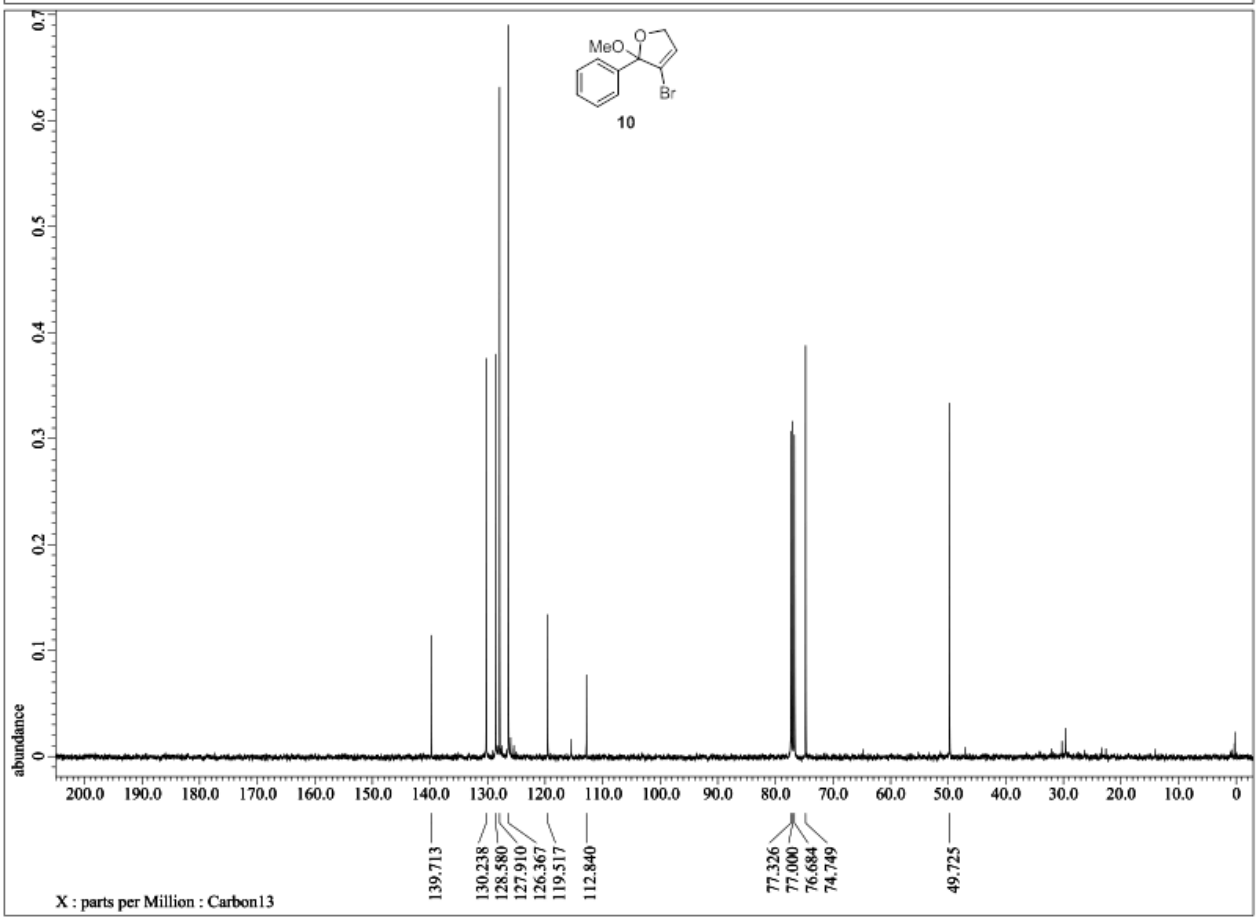

HO
O
Cl
Br
Br
Me
4k
abundance
X : parts per Million : Proton
7.743
7.738
7.571
7.567
7.551
7.546
7.258
7.237
7.216
4.264
4.261
4.243
4.238
4.220
4.076
4.071
4.051
4.031
3.554
3.430
3.395
3.065
3.061
3.048
2.396
0.000

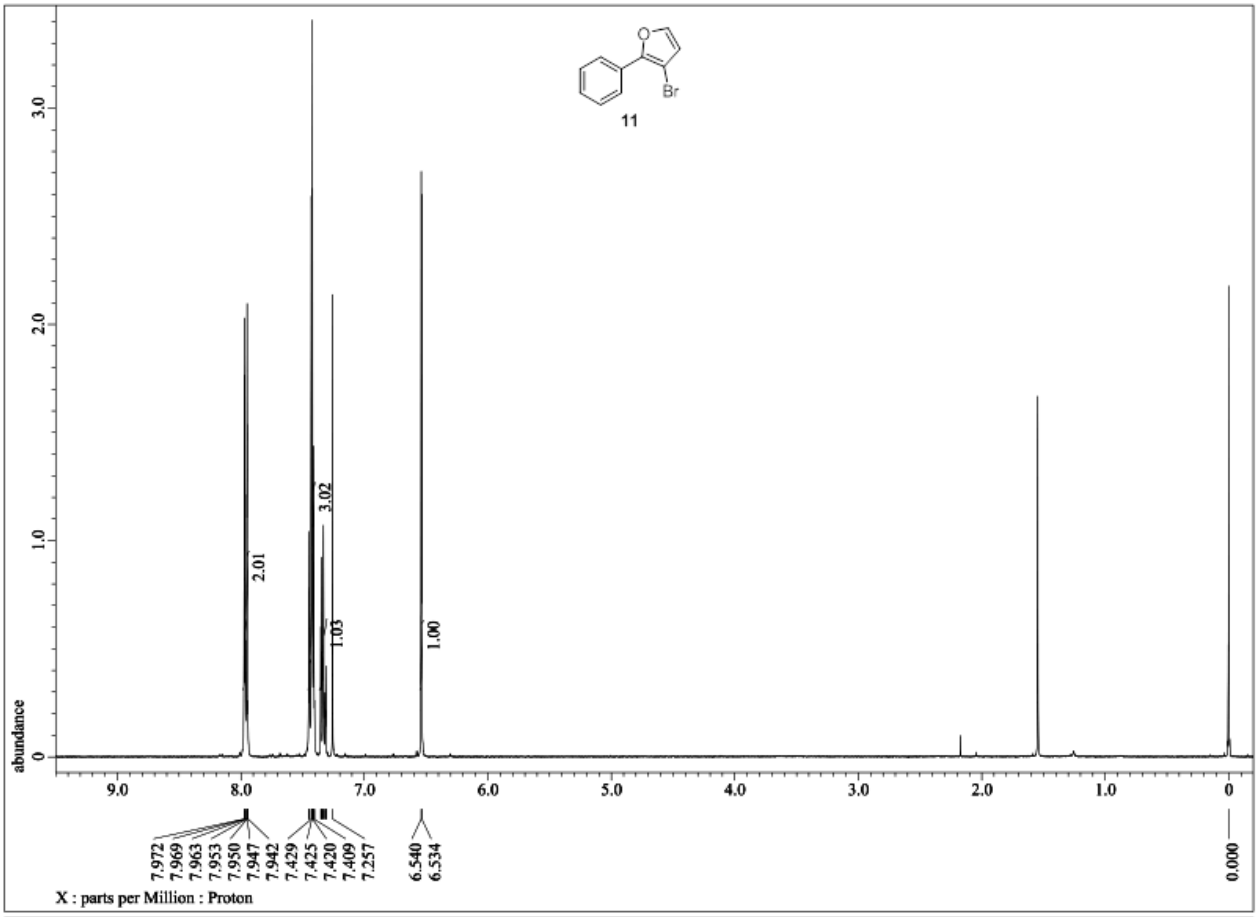

HO
O
Cl
Br
Br
Me
4k
abundance
X : parts per Million : Carbon13
137.286
137.267
133.614
130.028
128.226
125.727
105.174
77.324
77.000
76.676
67.091
65.212
46.757
19.937

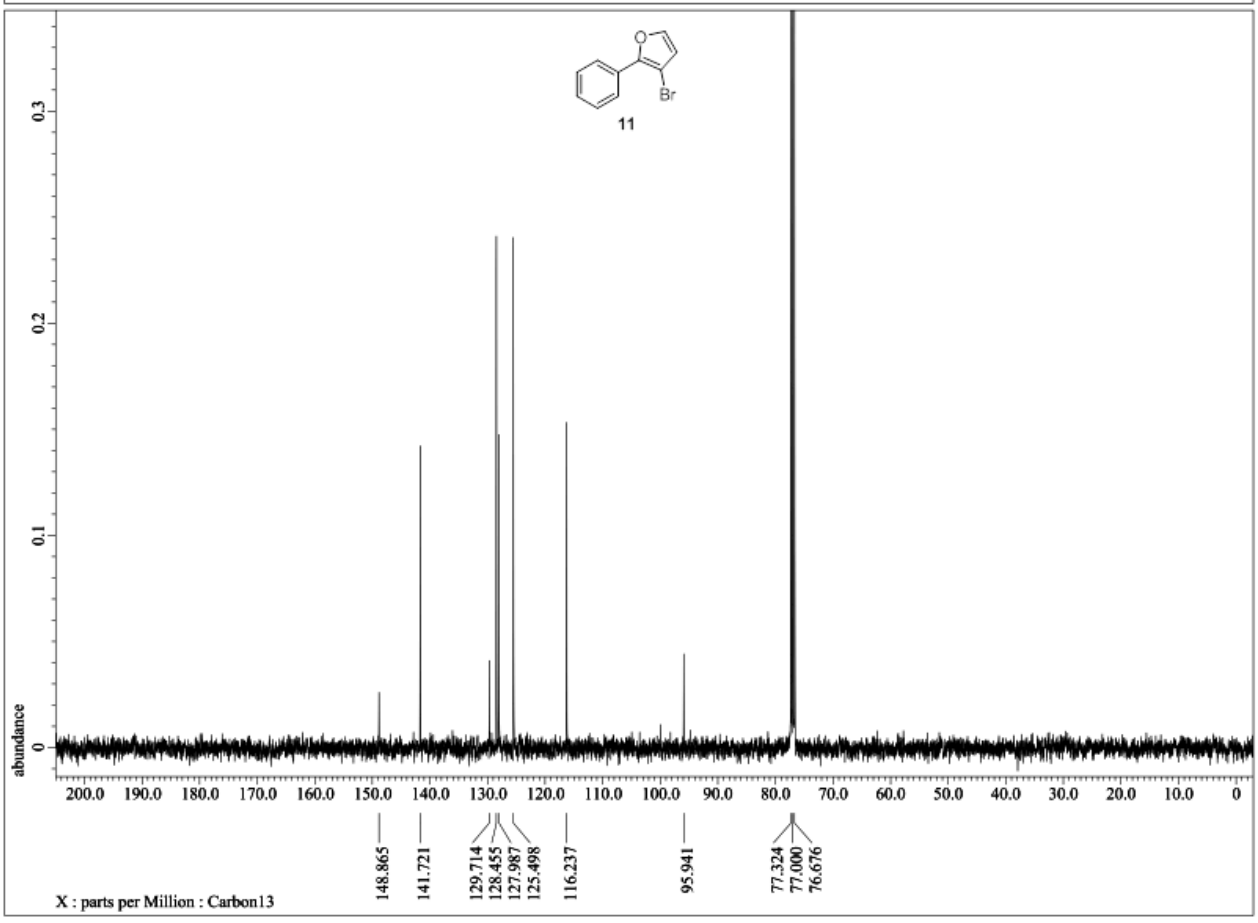

MeO
O
Br
Br
9
abundance
2.01
3.00
1.00
1.01
1.02
1.01
3.01
7.764
7.758
7.749
7.740
7.414
7.407
7.401
7.397
7.390
7.255
4.317
4.314
4.296
4.292
4.273
4.064
4.059
4.044
4.040
4.036
3.470
3.459
3.436
3.123
3.104
3.098
3.085
3.080
3.065
3.052
0.000
X : parts per Million : Proton

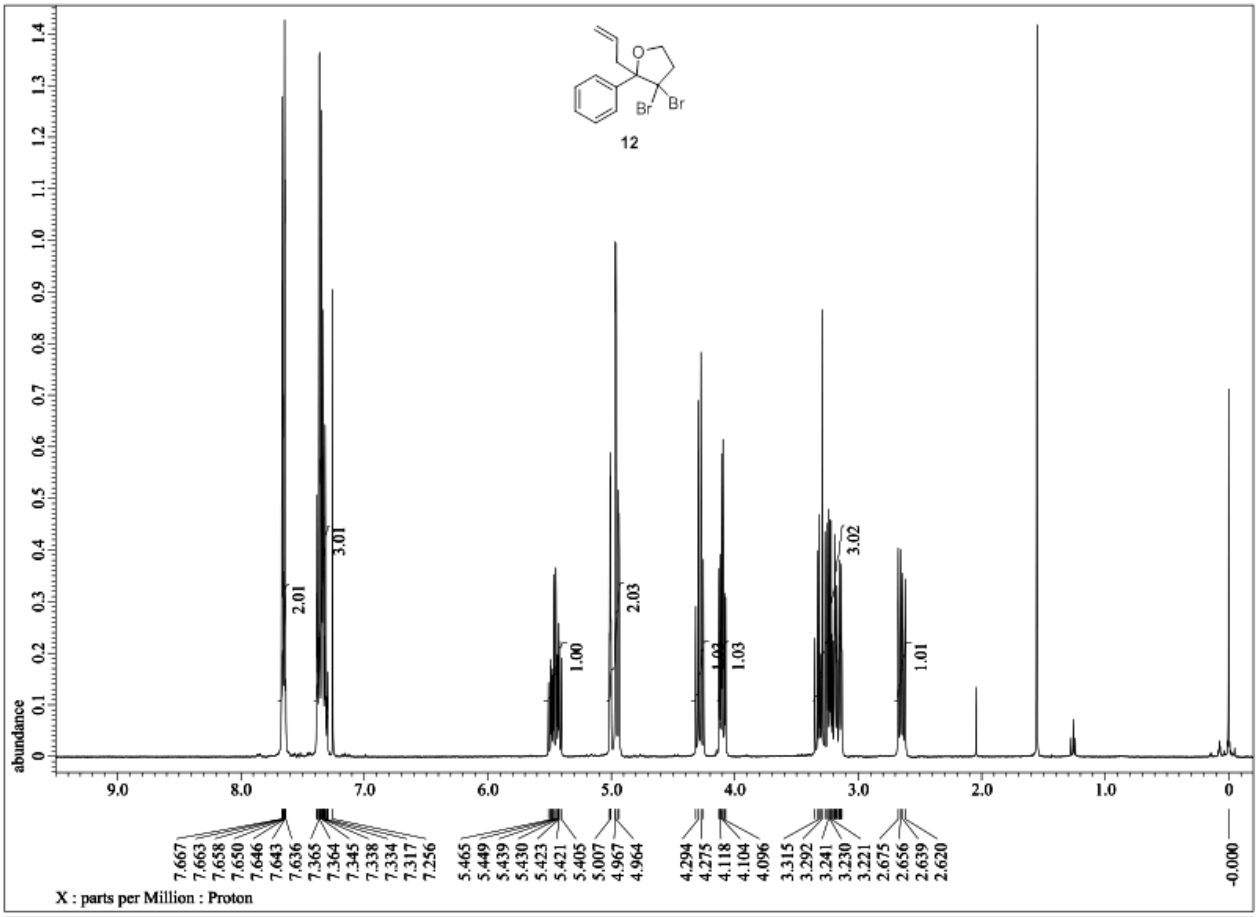

MeO
O
Br
Br
9
abundance
134.731
129.146
128.312
127.507
108.404
77.326
77.000
76.684
67.860
64.814
51.353
47.081
X : parts per Million : Carbon13

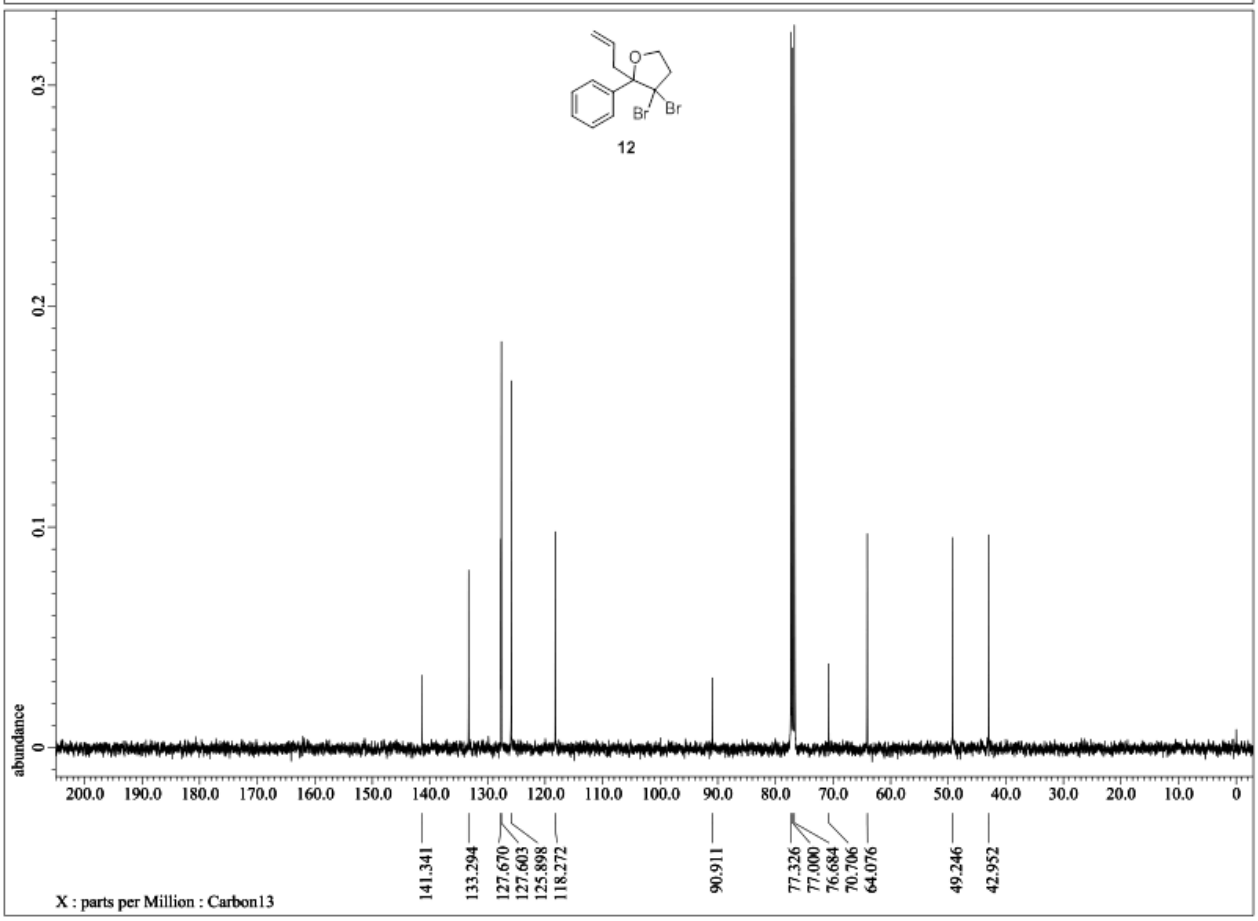

MeO
O
Br
10
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.01
3.01
1.00
2.02
3.03
7.541
7.536
7.524
7.522
7.520
7.516
7.360
7.356
7.341
7.334
7.324
6.417
6.413
6.408
4.777
4.773
3.343
0.000
X : parts per Million : Proton

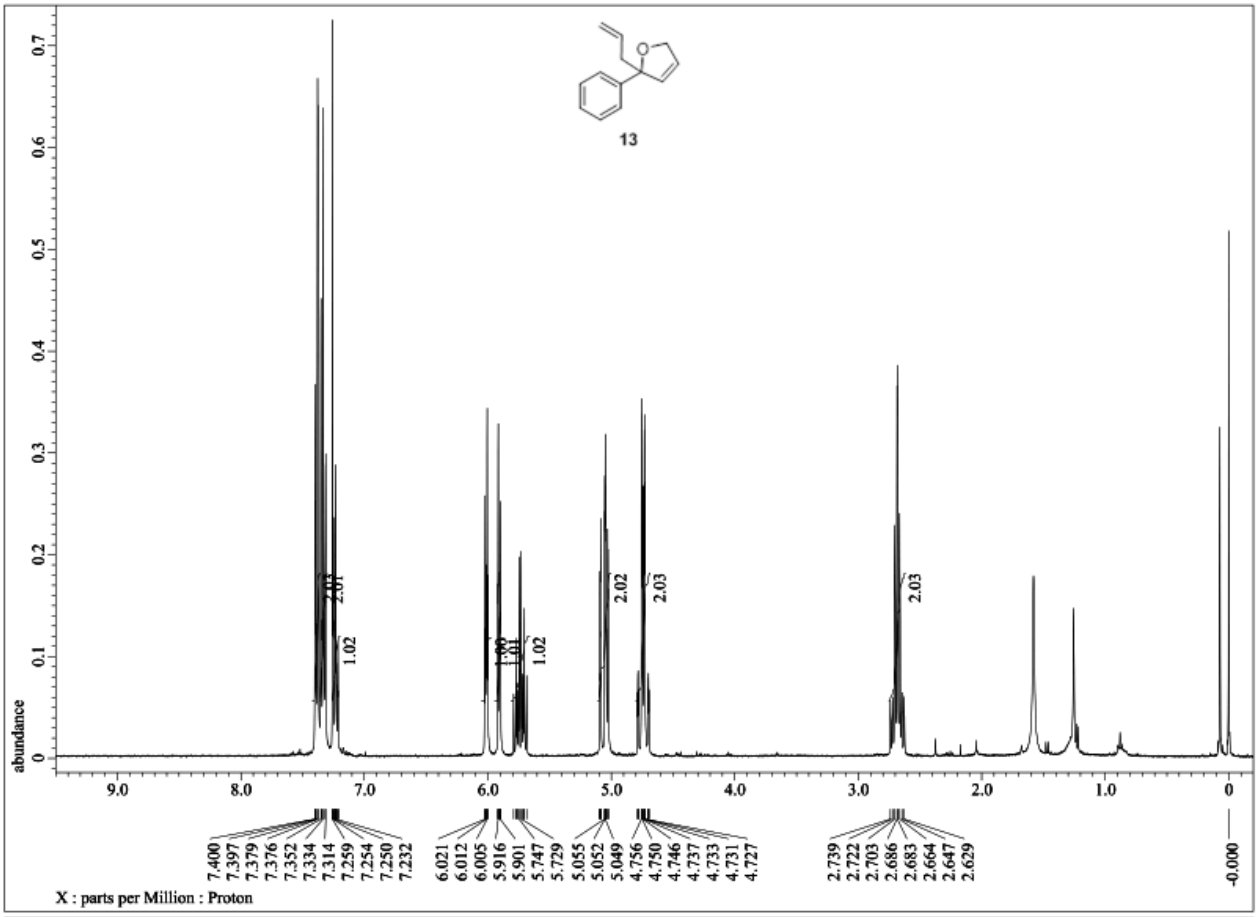

MeO
O
Br
10
abundance
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
139.713
130.238
128.580
127.910
126.367
119.517
112.840
77.326
77.000
76.684
74.749
49.725
X : parts per Million : Carbon13

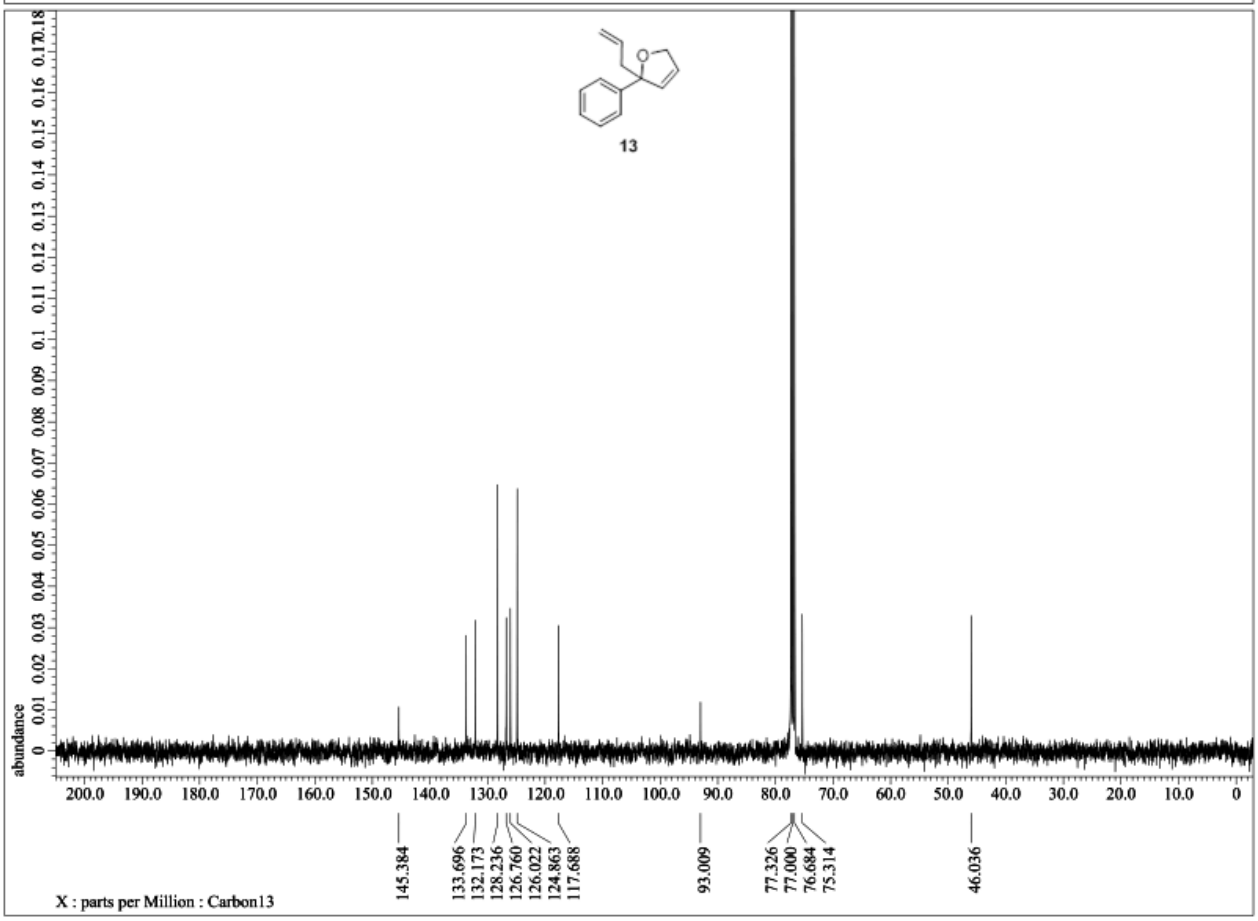

11
abundance
2.01
3.02
1.03
1.00
7.972
7.969
7.963
7.953
7.950
7.947
7.942
7.429
7.425
7.420
7.409
7.257
6.540
6.534
0.000
X : parts per Million : Proton

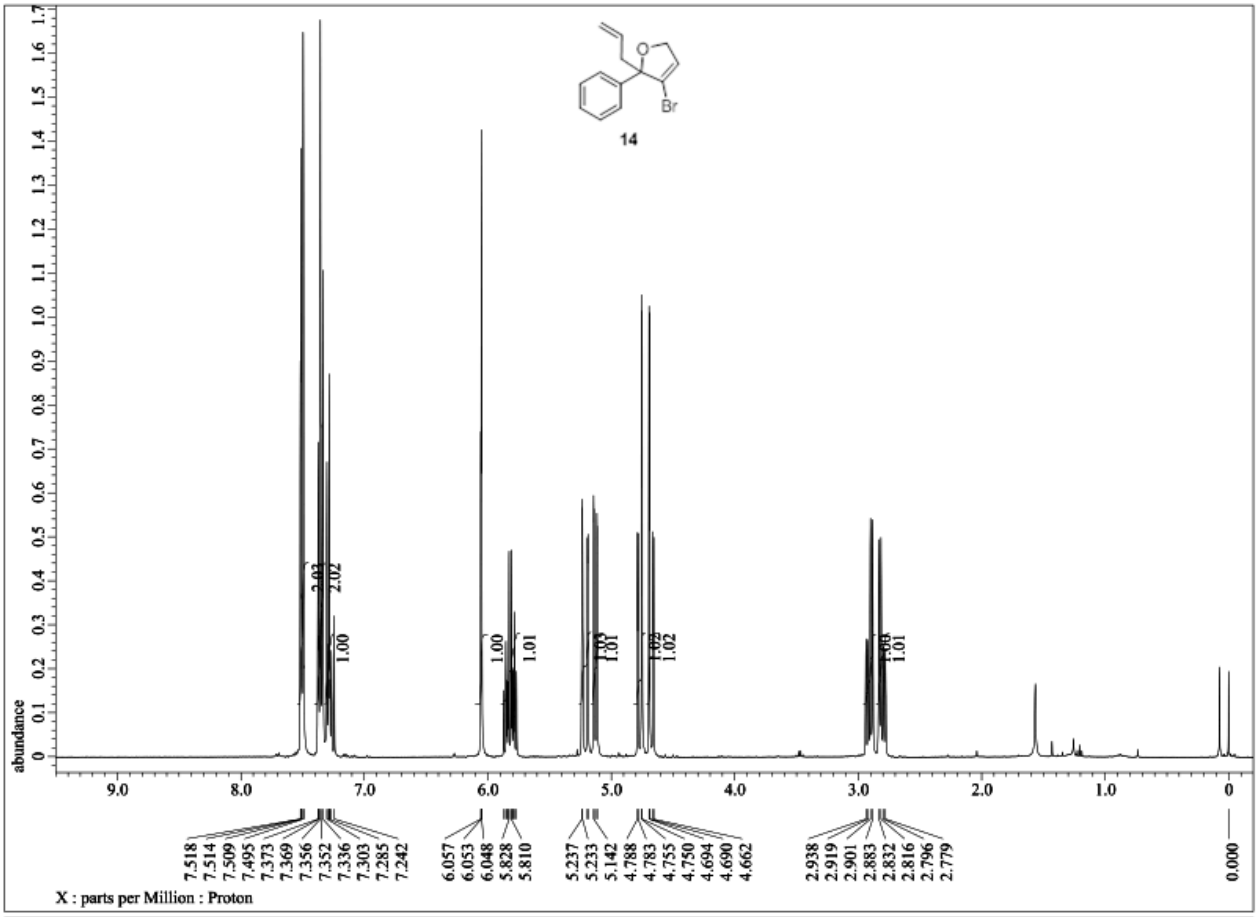

11
abundance
148.865
141.721
129.714
128.455
127.987
125.498
116.237
95.941
77.324
77.000
76.676
X : parts per Million : Carbon13

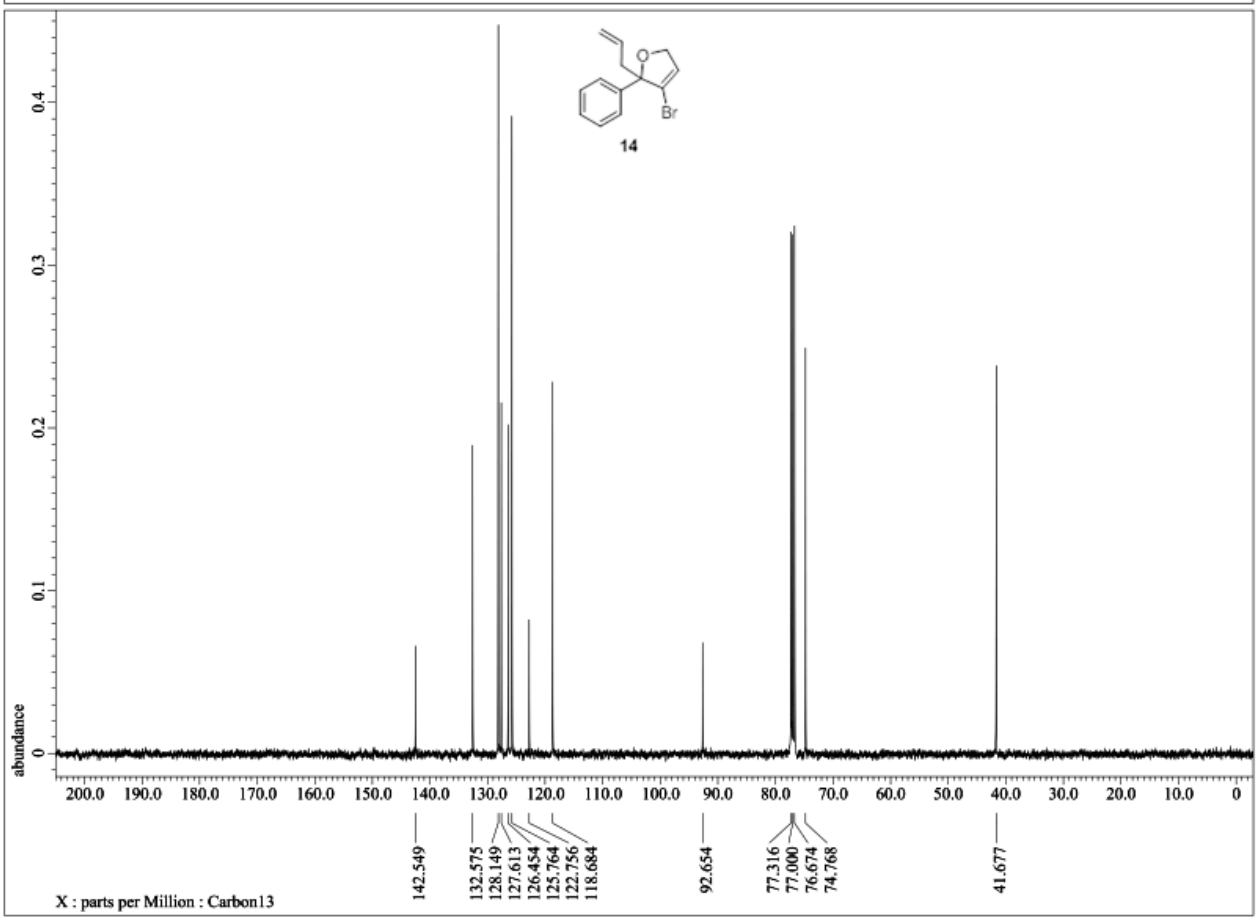

12
Br
Br
O
abundance
2.01
3.01
1.00
2.03
1.03
1.02
3.02
1.01
7.667
7.663
7.658
7.650
7.646
7.643
7.636
7.365
7.364
7.345
7.338
7.334
7.317
7.256
5.465
5.449
5.439
5.430
5.423
5.421
5.405
5.007
4.967
4.964
4.294
4.275
4.118
4.104
4.096
3.315
3.292
3.241
3.230
3.221
2.675
2.656
2.639
2.620
-0.000
X : parts per Million : Proton

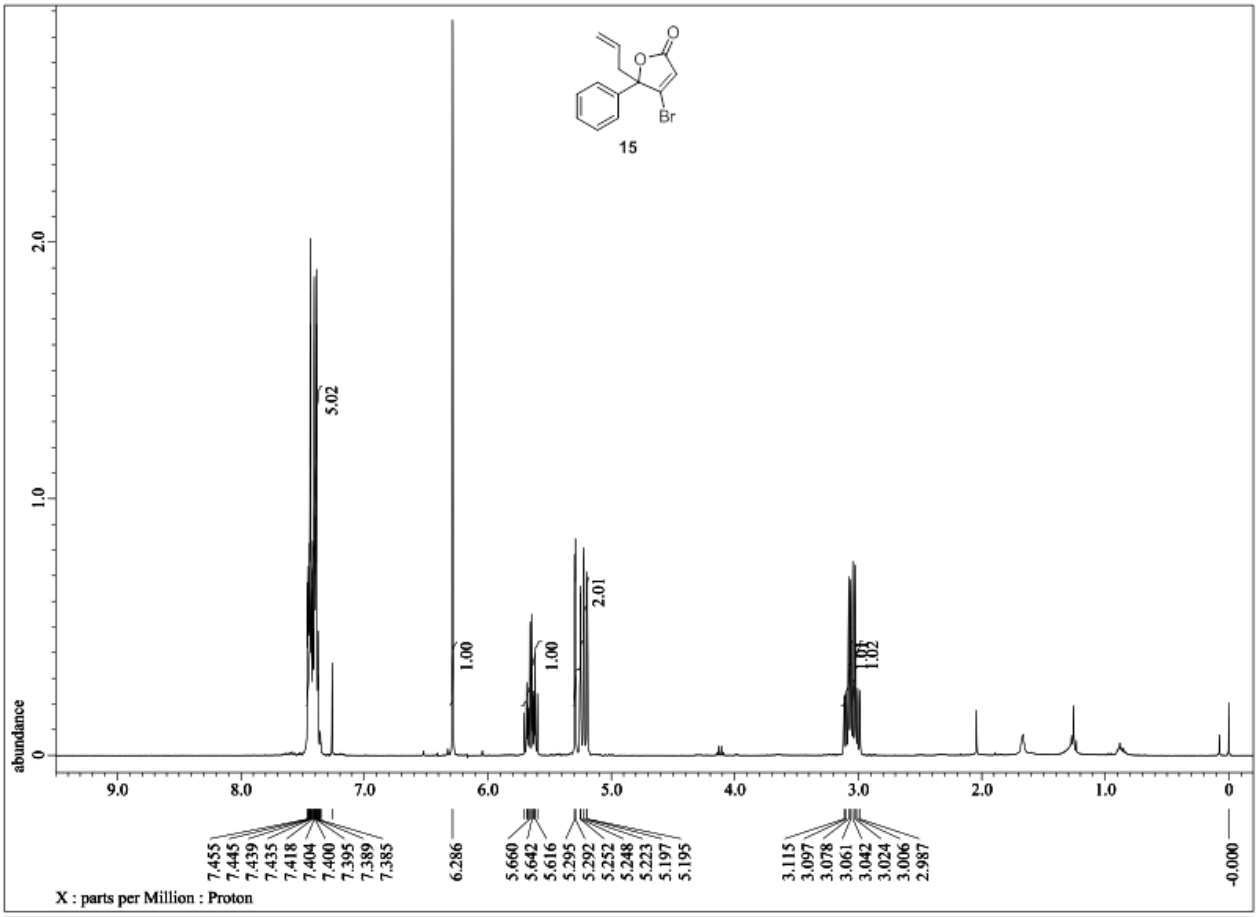

12
Br
Br
O
abundance
141.341
133.294
127.670
127.603
125.898
118.272
90.911
77.326
77.000
76.684
70.706
64.076
49.246
42.952
X : parts per Million : Carbon13

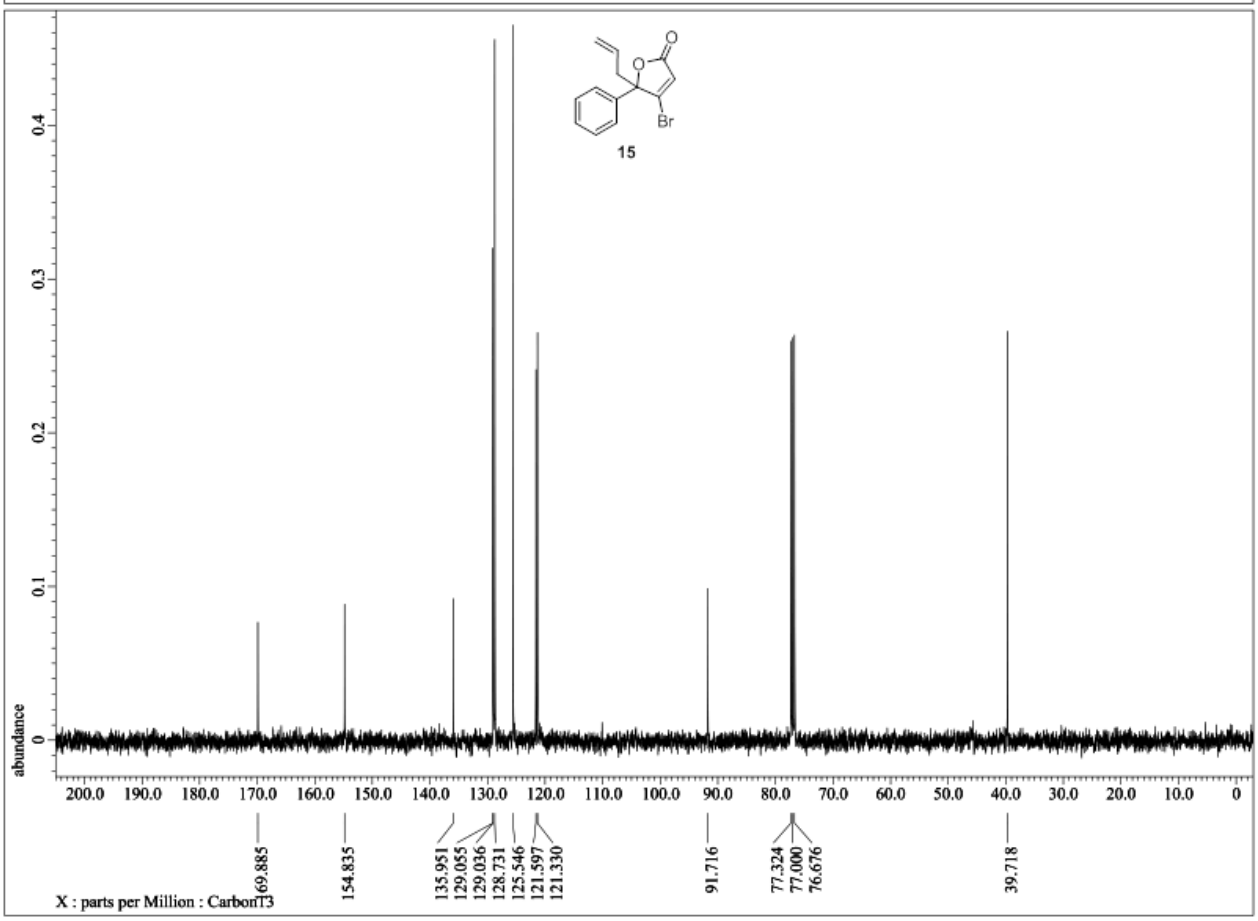

13
abundance
2.03
2.01
1.02
1.00
1.01
1.02
2.02
2.03
2.03
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.400
7.397
7.379
7.376
7.352
7.334
7.314
7.259
7.254
7.250
7.232
6.021
6.012
6.005
5.916
5.901
5.747
5.729
5.055
5.052
5.049
4.756
4.750
4.746
4.737
4.733
4.731
4.727
2.739
2.722
2.703
2.686
2.683
2.664
2.647
2.629
-0.000
X : parts per Million : Proton

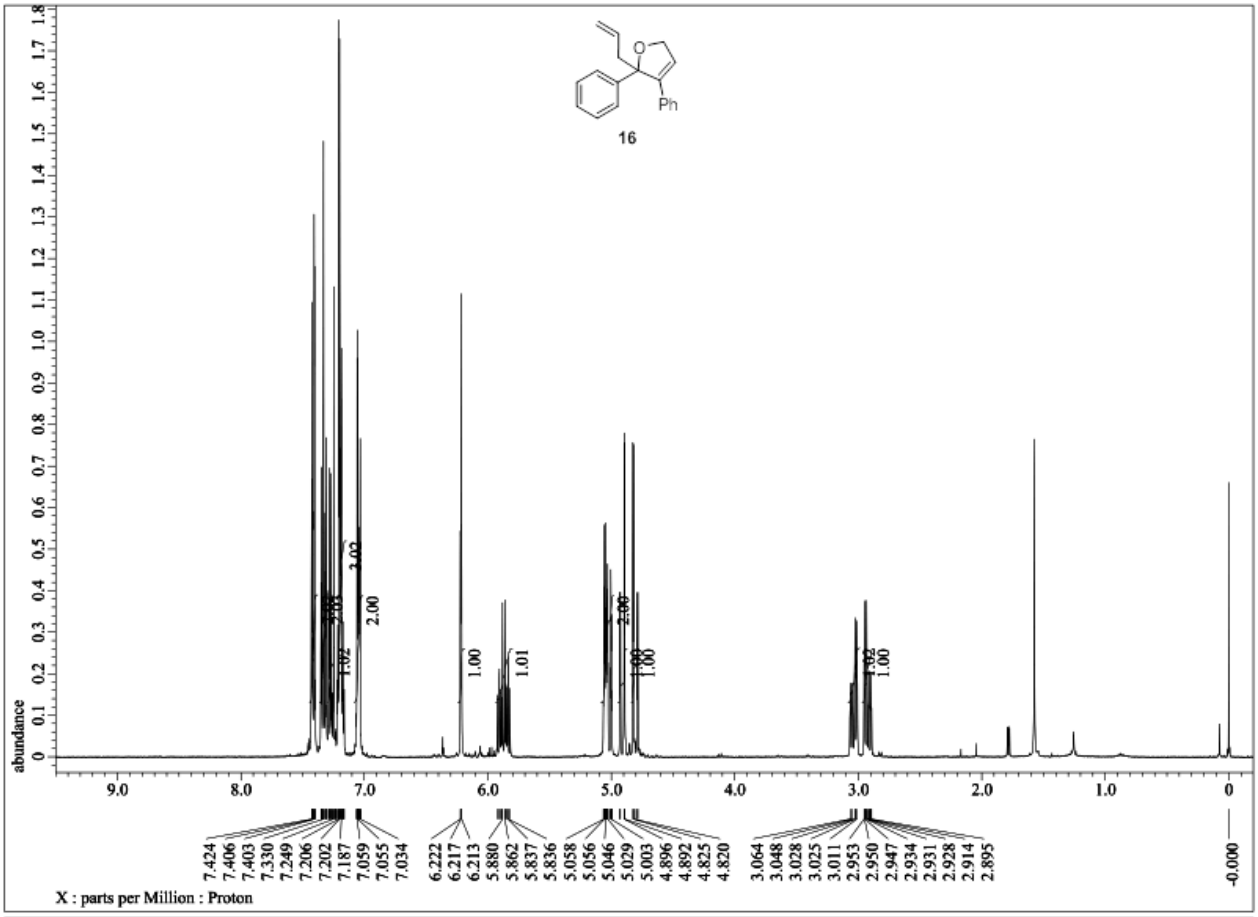

13
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
145.384
133.696
132.173
128.236
126.760
126.022
124.863
117.688
93.009
77.326
77.000
76.684
75.314
46.036
X : parts per Million : Carbon13

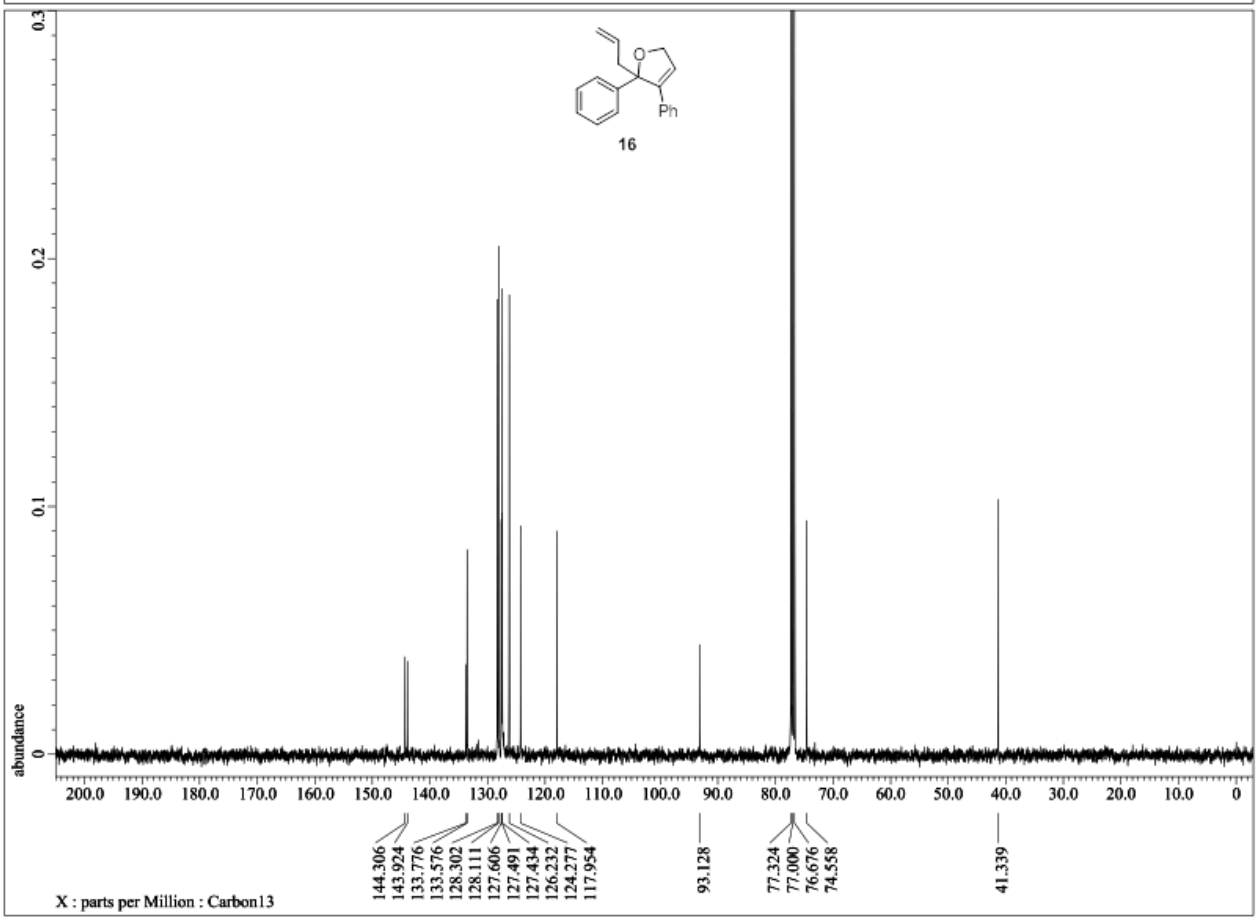

14
Br
abundance
X : parts per Million : Proton

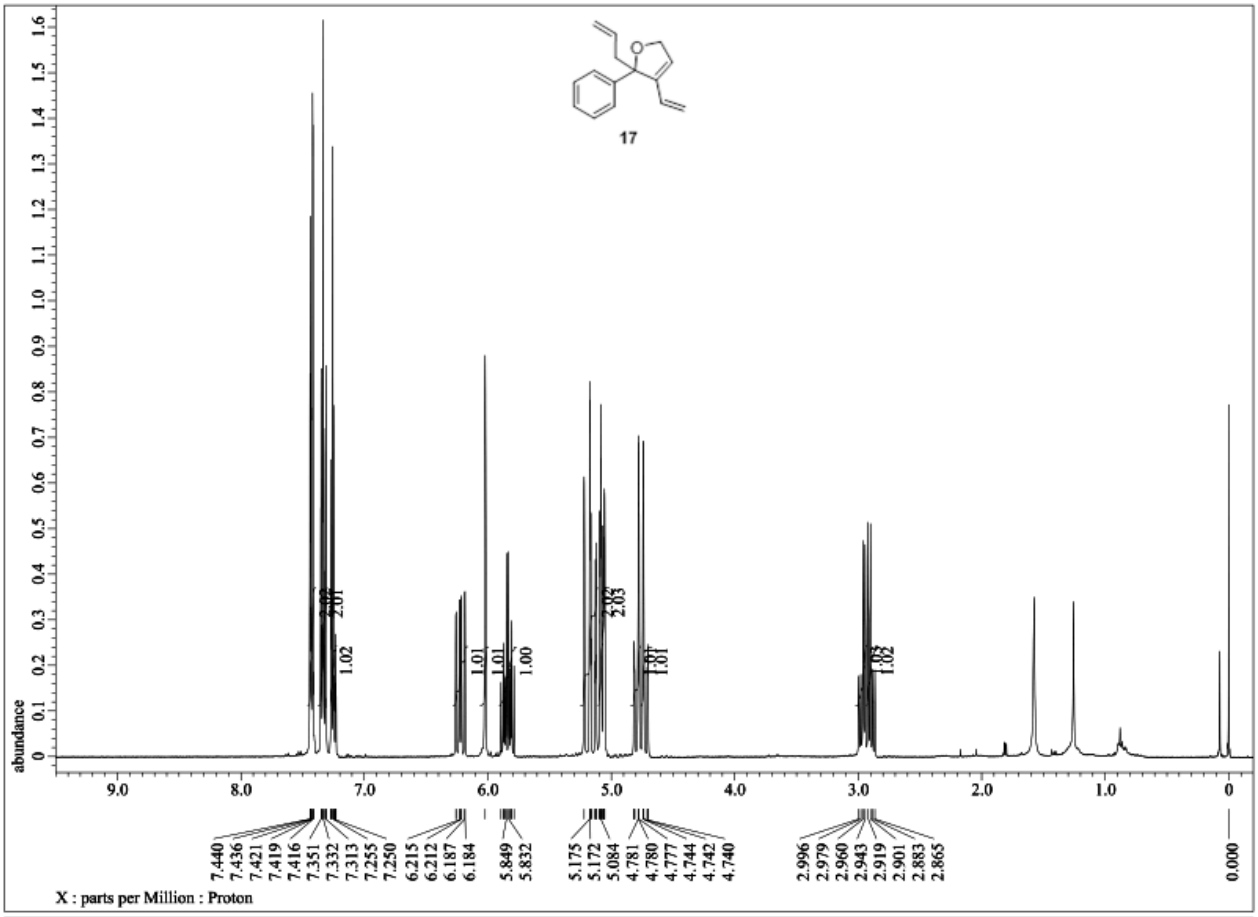

14
Br
abundance
X : parts per Million : Carbon13

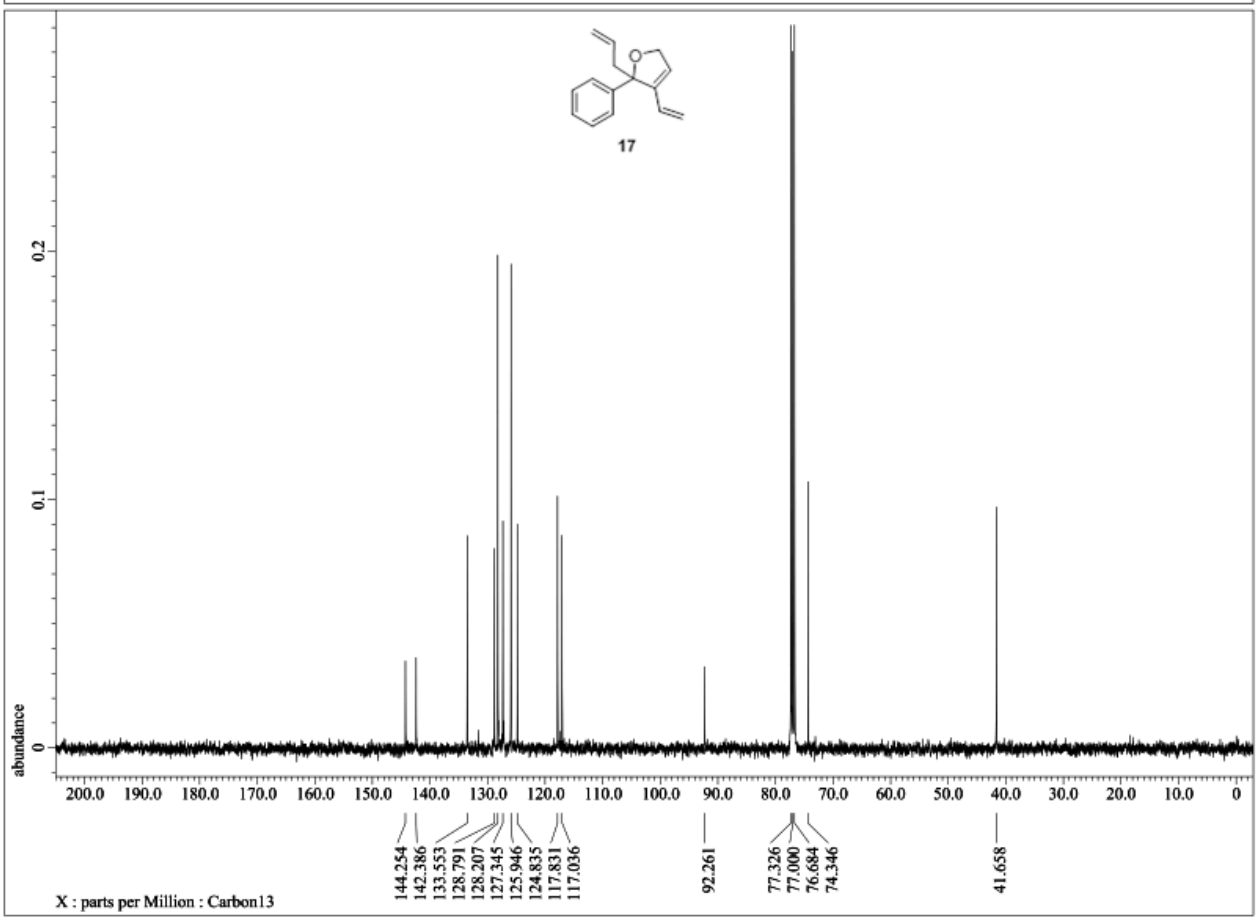

15
Br
abundance
5.02
1.00
1.00
2.01
1.01
1.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.455
7.445
7.439
7.435
7.418
7.404
7.400
7.395
7.389
7.385
6.286
5.660
5.642
5.616
5.295
5.292
5.252
5.248
5.223
5.197
5.195
3.115
3.097
3.078
3.061
3.042
3.024
3.006
2.987
-0.000
X : parts per Million : Proton


15
Br
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
69.885
154.835
135.951
129.055
129.036
128.731
125.546
121.597
121.330
91.716
77.324
77.000
76.676
39.718
X : parts per Million : Carbon13


16
Ph
abundance
X : parts per Million : Proton


16
Ph
abundance
X : parts per Million : Carbon13


17
abundance
X : parts per Million : Proton


17
abundance
X : parts per Million : Carbon13