Supporting information

The Mechanism of 1, 4 Alkyl Group Migration in Hypervalent Halonium ylides: The Stereochemical Course

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General Information

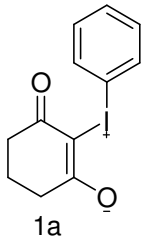
NMR spectra were recorded on a Bruker Avance DRX-500 (500 MHz) or DPX-400 instrument at 25^0C. Column chromatography was carried out using Silicycle Silica-P Flash silica gel (40-63 μm). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. All reactions were done under positive pressure of argon unless otherwise stated. Acetonitrile was dried by refluxing over calcium hydride, pentane was dried over sodium metal. (*R*)-(+)-α-Methylbenzyl alcohol was obtained from Alfa-Aesar. NMR solvents (Cambridge isotopes laboratories) were used without purification. Melting points were recorded on Fisher Johns apparatus and are uncorrected. FTIR spectra were recorded using KBr pellets on a Varian 1000 FTIR instrument at 25^0C. HRMS of all new compounds were recorded on a Thermo-Finnigan LTQ FT spectrometer. Chiral HPLCs were recorded on a Gilson HPLC. Chiral GCs were carried out using a HP 5890 gas chromatographer.

Starting Materials:

Both 1,3-cyclohexanedione (**1a)** and 5,5-dimethyl-1,3-cyclohexanedione phenyliodonium (**1b)** ylides are known and prepared by a slightly modified literature procedure.[1]

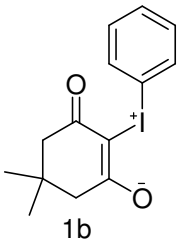
General Preparative Procedure (Phenyliodonium ylides 1a and 1b):

To a solution of cyclic the 1, 3-dione (14 mmol) in 30 mL methanol, added at room temperature, 20 mL of a 10% aq solution of KOH, followed by addition of a solution of diacetoxy iodobenzene (15 mmol) in 40 mL methanol. The reaction mixture was stirred for 2 hrs at room temperature and then quenched with ice cold water. The resulting white precipitate was filtered and mother liquor was extracted with dichloromethane, then washed with water, dried over anhydrous sodium sulfate, filtered and concentrated in vaccuo. The resultant white solid was mixed with the first crop and the mixture recrystallized from DCM/Hexanes.



1a

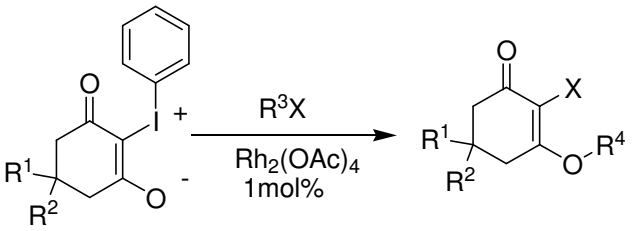
1a Pale yellow solid (95%) mp 128-130 ^{0}C (lit [2] 128-132 ^{0}C). ^{1}H-NMR (400MHz $CDCl_3$) δ: 7.78-7.26 (m, 5H), 2.54 (t, *J = 6.36 Hz*, 4H), 1.88 (q, *J* = 6.5Hz, 2H); ^{13}C-NMR (75MHz, $CDCl_3$) δ: 189.2, 133.8, 131.5, 131.3, 111.6, 96.7, 37.0, 21.0; IR: v_{max} (neat)/cm^{-1} KBr. 2940, 2390, 1470, 1348, 1260, 1138, 992 .



1b

1b White solid (quant) mp 132-133 ^{0}C (lit [2] 132-134 ^{0}C). ^{1}H-NMR (400MHz $CDCl_3$) δ: 7.81-7.26 (m, 5H), 2.42 (s, 4H), 1.05 (s, 6H); ^{13}C-NMR (75MHz, $CDCl_3$) δ: 188.4, 133.8, 131.6, 131.4, 111.9, 94.6, 50.8, 32.0, 28.2; IR: v_{max} (neat)/cm^{-1} KBr. 2955, 2360, 1530, 1469, 1361, 1329.

General Procedure for the Rreactions of 1,3-Dicarbonyl Phenyl Iodonium Ylides 1a and 1b With Benzyl, Allyl and Aryl Halides using $Rh_2(OAc)_4$ Catalysis

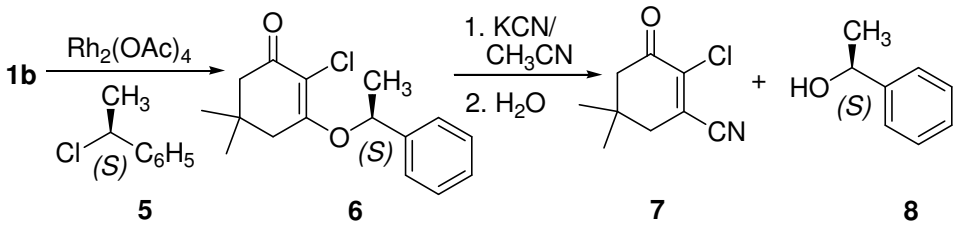


$R^1 = R^2 = H$ = 1a, $R^1 = R^2 = CH_3$ = 1b, X = Cl, Br

To the flamed dried flask containing 0.01 mol of $Rh_2(OAc)_4$ and 10mmol of alkyl, allyl or aryl halide was added, 1mmol of ylide[1]. The semi-heterogenous reaction mixture was stirred at room temperature

overnight (~12hrs). At the end of this time a solution was obtained. The resulting green solution was subjected to column chromatography to give, the corresponding products (**3a** to **3w**).

Procedure for the Reaction of 2-chloro-5,5-dimethyl-3-((*S*)-1-phenyl-ethoxy)-cyclohex-2-enone (3k) with KCN/18-crown-6

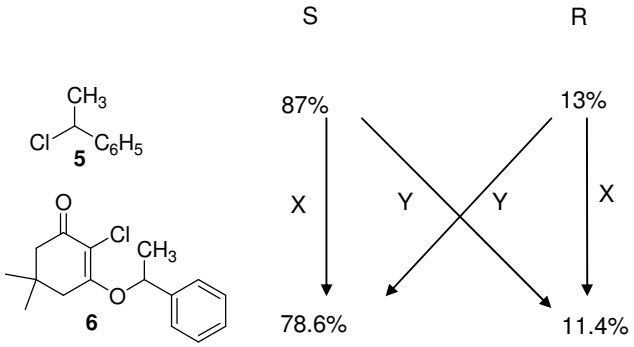


To the solution of 184 mg (0.66 mmol) (**6, 3k**) in 30mL of acetonitrile was added 128 mg of KCN (1.98 mmol, 3eq) and 76 mg of 18-crown-6 (0.198 mmol, 0.5eq) at room temperature.The Reaction mixture was refluxed overnight, quenched with water, and extracted with ethyl acetate. And the ethyl acetate extracts were dried over sodium sulfate, filtered and purified using flash column chromatography (20% EtOAc/hexanes) to yield a colorless liquid **8** (60 mg)(75 %). $[\alpha]_D^{25}$ -23.6 (*c* 1, $CHCl_3$). (lit [3] $[\alpha]_D^{25}$ -44.0, neat).

Calculation of % Retention of Configuration.

Assuming the percentage of retention of configuration be X and inversion be Y. On the basis of chiral chromatographic results.

Amount of (*S*) chloride (**5**) is found to be 87%
Amount of (*R*) chloride (**5**) is found to be 13%
Amount of (*S*) product (**6**) is found to be 78.6%
Amount of (*R*) product (**6**) is found to be 21.4%

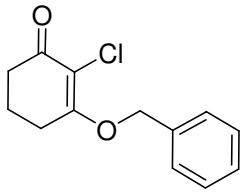


After setting up the equation as follows:

87X + 13Y = 78.6 **eq (1)**
X + Y = 1 **eq (2)**

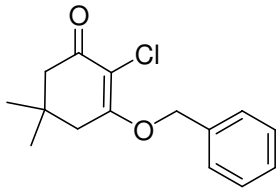
After solving equation 1 and 2,
X = 88.6% (Retention) and Y = 11.4% (Inversion)

3-Benzyloxy-2-chloro-cyclohex-2-enone **(3a)**



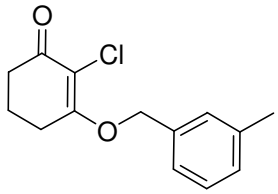
3a: White solid (70%) mp. 100-101 ^{0}C (lit [4] 98-99 ^{0}C) . ^{1}H-NMR (400MHz $CDCl_3$) δ: 7.41-7.26 (m, 5H), 5.25 (s, 2H), 2.69 (t, *J* = 6.1Hz, 2H), 2.48 (t, *J* = 6.1Hz, 2H), 1.99 (p, *J* = 6.4Hz, 2H); ^{13}C-NMR (75MHz, $CDCl_3$) δ: 191.3, 170.9, 135.4, 128.9, 128.5,126.7, 112.6, 70.6, 36.6, 27.0, 20.2 ; IR: v_{max} (neat)/cm^{-1} KBr. 2946, 2889, 1654, 1589, 1455, 1369, 1290, 1257, 1192, 1154.

3-Benzyloxy-2-chloro-5,5-dimethyl-cyclohex-2-enone **(3b)**



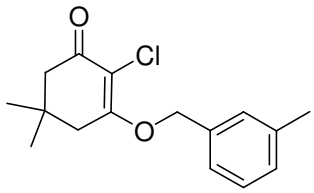
3b: White solid (73%) mp. 98-99 ^{0}C (lit [4] 92-93 ^{0}C). ^{1}H-NMR (400MHz $CDCl_3$) δ: ^{1}H-NMR (400MHz $CDCl_3$) δ: 7.41-7.26 (m, 5H), 5.20 (s, 2H), 2.51 (s, 2H), 2.30 (s, 2H), 1.00 (s, 6H); ^{13}C-NMR (75MHz, $CDCl_3$) δ: 191.3, 169.0, 135.5, 128.8, 128.5,126.7, 111.5, 70.5, 50.4, 40.5, 32.1 28.1; IR: v_{max} (neat)/cm^{-1} KBr 2960, 1666, 1594, 1355, 1297, 1241, 1220, 1051.

2-Chloro-3-(3-methyl-benzyloxy)-cyclohex-2-enone **(3c)**



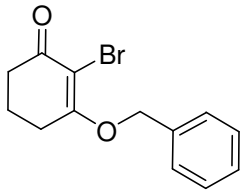
3c: White solid (62%) mp. 103-104 ^{0}C (lit [4] 117-118 ^{0}C). ^{1}H-NMR (400MHz $CDCl_3$) δ: 7.26 (dd, *J* = 8.0, 1H) 7.15-7.12 (m, 3H), 5.19 (s, 2H), 2.69 (t, *J* = 6.1Hz, 2H), 2.46 (t, *J* = 6.1Hz, 2H), 2.35 (s, 3H), 2.00 (q, *J* = 6.4Hz, 2H); ^{13}C-NMR (75MHz, $CDCl_3$) δ: 191.3, 170.5, 138.6, 135.4, 129.3, 128.7, 127.3, 123.8, 112.4, 70.7, 36.6, 27.0, 21.44, 20.2 ; IR: v_{max} (neat)/cm^{-1} KBr. 2960, 1666, 1594, 1456, 1401, 1351, 1350, 1305, 1266, 1199, 1077, 1015.

***2-Chloro-5,5-dimethyl-3-(3-methyl-benzyloxy)-cyclohex-2-enone* (3d)**



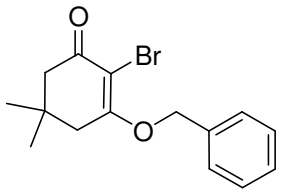
3d: White solid (70%) mp. 111-112 ^{0}C (lit [4] 115-116 ^{0}C). ^{1}H-NMR (400MHz, $CDCl_3$) δ: 7.25 (dd, *J* = 8.0,7.5 Hz, 1H) 7.16-7.12 (m, 3H), 5.19 (s, 2H), 2.51 (s, 2H), 2.36 (s, 2H), 2.34 (s, 3H), 1.02 (s, 6H); ^{13}C-NMR (75MHz, $CDCl_3$) δ: 191.3, 169.6, 138.5, 135.3, 129.1, 128.6, 127.2, 123.6, 111.4, 70.5, 50.2, 40.4, 32.0, 28.0, 21.3 ; IR: v_{max} (neat)/cm^{-1} KBr. 3028, 2966, 2860, 1661, 1598, 1470, 1362, 1303, 1248, 1176, 1054.

***3-Benzyloxy-2-bromo-cyclohex-2-enone* (3e)**



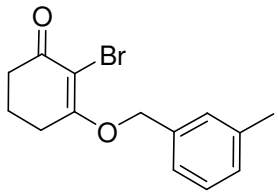
3e: White solid (22%) mp. 105-106 ^{0}C (lit [4] 104-105 ^{0}C). ^{1}H-NMR (400MHz $CDCl_3$) δ: 7.42-7.26 (m, 5H), 5.26 (s, 2H), 2.69 (t, *J* = 6.1Hz, 2H), 2.53 (t, *J* = 6.1Hz, 2H), 2.00 (q, *J* = 6.4Hz, 2H); ^{13}C-NMR (75MHz, $CDCl_3$) δ: 191.3, 172.4, 135.4, 128.9, 128.5, 126.6, 104.0, 70.6, 36.7, 27.5, 20.5 ; IR: v_{max} (neat)/cm^{-1} KBr. 2969, 1655, 1580, 1489, 1456, 1369, 1276, 1256, 1192, 1156, 1081, 1027.

***3-Benzyloxy-2-bromo-5,5-dimethyl-cyclohex-2-enone* (3f)**



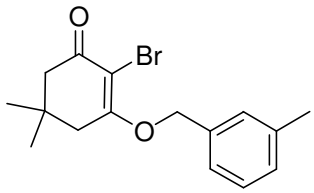
3f: White solid (35%) mp. 114-115 ^{0}C (lit [4] 102-103 ^{0}C). ^{1}H-NMR (400MHz $CDCl_3$) δ: 7.41-7.26 (m, 5H), 5.24 (s, 2H), 2.51 (s, 2H), 2.37 (s, 2H), 1.00 (s, 6H); ^{13}C-NMR (75MHz, $CDCl_3$) δ: 191.3, 169.0, 135.5, 128.8, 128.5,126.7, 103.5, 70.5, 50.4, 40.5, 32.1, 28.1; IR: v_{max} (neat)/cm^{-1} KBr. 3056, 2967, 1657, 1587, 1461, 1349, 1280, 1249, 1170, 1038.

***2-Bromo-3-(3-methyl-benzyloxy)-cyclohex-2-enone* (3g)**



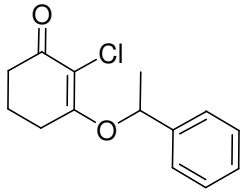
3g White solid (30%) mp. 122-123 ^{0}C. ^{1}H-NMR (400MHz, $CDCl_3$) δ: 7.26 (m, 1H) 7.16-7.13 (m, 3H), 5.20 (s, 2H), 2.66 (t, *J* = 6.1Hz, 2H), 2.49 (t, *J* = 6.1Hz, 2H), 2.35 (s, 3H), 1.98 (q, *J* = 6.4Hz, 2H); ^{13}C-NMR (75MHz, $CDCl_3$) δ: 191.3, 172.7, 138.6, 135.3, 129.2, 128.7, 127.3, 123.8, 103.9, 70.7, 36.7, 27.4, 21.4, 20.5 ; IR: v_{max} (neat)/cm^{-1} KBr. HRMS (ESI): *m/z* Calcd. for $C_{15}H_{14}O_2Br$ $[M+H]^+$: 295.03282, found : 295.03314.

***2-Bromo-5,5-dimethyl-3-(3-methyl-benzyloxy)-cyclohex-2-enone* (3h)**



3h: White solid (35%) mp. 110-111 ^{0}C. ^{1}H-NMR (400MHz, $CDCl_3$) δ: 7.26 (m, 1H) 7.16-7.12 (m, 3H), 5.20 (s, 2H), 2.51 (s, 2H), 2.37 (s, 2H), 2.35 (s, 3H), 1.02 (s, 6H); ^{13}C-NMR (75MHz, $CDCl_3$) δ: 191.0, 170.7, 138.6, 135.5, 129.2, 128.7, 127.3, 123.6, 103.0, 70.6, 50.5, 41.1, 32.3, 28.1, 21.4 ; IR: v_{max} (neat)/cm^{-1} KBr. 2958, 2927, 1664, 1589, 1465, 1369, 1353, 1295, 1240. HRMS (ESI): *m/z* Calcd. for $C_{16}H_{19}O_2Br$ $[M+H]^+$: 323.0641, found : 323.0651.

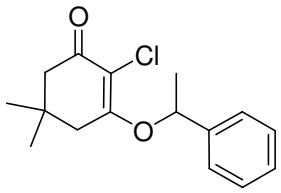
***2-Chloro-3-(1-phenyl-ethoxy)-cyclohex-2-enone* (3i)**



3i: white solid (53%) mp 145-146 ^{0}C (^{1}H-NMR (400MHz $CDCl_3$) δ: 7.38-7.26 (m, 5H), 5.46 (q, *J* = 6.4 Hz, 1H), 2.68-2.64 (m, 1H), 2.42-2.36 (m, 3H), 1.93-1.91 (m, 1H), 1.91-1.80 (m, 1H), 1.65 (d, *J* = 6.4 Hz, 3H) ; ^{13}C-NMR (75MHz, $CDCl_3$) δ: 191.4, 170.4, 141.8, 129.0, 128.2,125.0, 113.0, 81.3, 71.5, 36.7, 27.3, 24.7, 20.3; IR: v_{max} (neat)/cm^{-1} KBr. 2960, 1668, 1593, 1452,

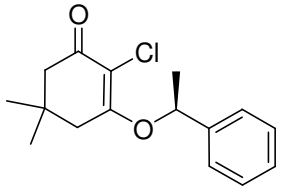
1359, 1295, 1244, 1065, 921, 762, 701. HRMS (ESI): *m/z* Calcd. for $C_{14}H_{15}O_2Cl$ $[M+Na]^+$: 273.0653, found : 273.0654.

2-Chloro-5,5-dimethyl-3-(1-phenyl-ethoxy)-cyclohex-2-enone **(3j)**



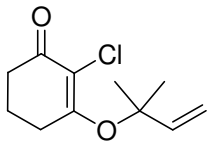
3j: White solid (58%) mp. 155-156 ^{0}C. (^{1}H-NMR (400MHz $CDCl_3$) δ: 7.37-7.27 (m, 5H), 5.44 (q, *J* = 6.4 Hz, 1H), 2.50-2.47 (m, 1H), 2.32-2.23 (m, 3H), 1.64 (d, *J* = 6.3Hz, 3H), 1.01 (s, 3H), 0.74 (s, 3H) ; ^{13}C-NMR (75MHz, $CDCl_3$) δ: 191.2, 168.6, 141.9, 129.0, 128.3,125.1, 112.4, 77.7,5.5, 40.9, 32.1, 28.5, 27.4, 24.6; IR: v_{max} (neat)/cm^{-1} KBr. 2960, 1668, 1592, 1452, 1359, 1294, 1243, 1064, 921, 762. HRMS (ESI): *m/z* Calcd. for $C_{16}H_{19}O_2Cl$ $[M+Na]^+$: 301.0966, found : 301.0964.

2-Chloro-5,5-dimethyl-3-((S)-1-phenyl-ethoxy)-cyclohex-2-enone **(6, 3k)**



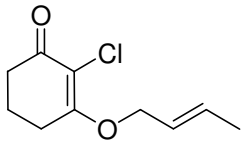
3k: White solid (58%) mp. 155-156 ^{0}C. (^{1}H-NMR (400MHz $CDCl_3$) δ: 7.37-7.27 (m, 5H), 5.44 (q, *J* = 6.4 Hz, 1H), 2.50-2.47 (m, 1H), 2.32-2.23 (m, 3H), 1.64 (d, *J* = 6.3Hz, 3H), 1.01 (s, 3H), 0.74 (s, 3H) ; ^{13}C-NMR (75MHz, $CDCl_3$) δ: 191.2, 168.6, 141.9, 129.0, 128.3,125.1, 112.4, 77.7,5.5, 40.9, 32.1, 28.5, 27.4, 24.6; IR: v_{max} (neat)/cm^{-1} KBr. 2960, 1668, 1592, 1452, 1359, 1294, 1243, 1064, 921, 762. HRMS (ESI): *m/z* Calcd. for $C_{16}H_{19}O_2Cl$ $[M+Na]^+$: 301.0966, found : 301.0964. $[\alpha]_D^{25}$ +104.4 (*c* 1.8, $CHCl_3$). HPLC (Chiralpak AD-H, *i*-PrOH/Hexane = 1/49, flow rate = 2.0 mL/min) t_R = 9.4 min(*R*), t_R = 10.7 min(*S*) **(6, 3k)**.

2-Chloro-3-(1,1-dimethyl-allyloxy)-cyclohex-2-enone **(3l)**



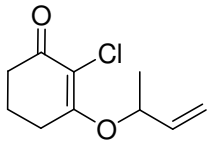
3l: Colorless oil (56%). ^{1}H-NMR (400MHz, $CDCl_3$) δ: 5.87-5.82, (m, 1H), 5.11-5.01 (m, 2H), 2.81-2.76 (m, 2H), 2.60-2.55 (m, 2H), 1.91-1.86(m, 1H), 1.74-1.70 (m, 1H), 1.14 (s, 6H); ^{13}C-NMR (75MHz, $CDCl_3$) δ: 201.4, 178.8, 142.7, 115.4, 40.3, 34.2, 23.5, 16.7 ; IR: v_{max} (neat)/cm^{-1} KBr.: 2977, 2937, 1710, 1463, 1415, 1265, 1137, 1029, 929. HRMS (EI): *m/z* Calcd. for $C_{11}H_{15}O_2Cl$ [M$^+$]: 214.0762, found : 214.0761

3-[(But-2-enyl)oxy]-2-chloro-cyclohex-2-enone **(3m)**



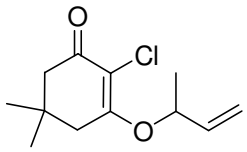
3m: Colorless oil (37%) ^{1}H-NMR (400MHz, $CDCl_3$) δ: 5.63-5.54 (m, 1H), 5.30-5.19 (m, 1H), 3.07-3.02 (m, 2H), 2.83 (d, *J* = 8.19 Hz, 2H), 2.61-2.53 (m, 2H), 2.12-2.05 (m, 1H), 1.85-1.78 (m, 1H), 1.61 (d, *J* = 6.43 Hz, 3H); ^{13}C-NMR (75MHz, $CDCl_3$) δ: 200.5, 176.4, 132.0, 123.2,122.6, 102.1, 76.7, 36.9, 31.5, 31.2, 18.0, 17.3 ; IR: v_{max} (neat)/cm^{-1} KBr.: 2977, 2937, 1710, 1463, 1415, 1265, 1137, 1029, 929. HRMS (EI): *m/z* Calcd. for $C_{10}H_{13}O_2Cl$ [M$^+$]: 200.0604, found : 200.0603

2-Chloro-3-(1-methyl-allyloxy)-cyclohex-2-enone **(3n)**



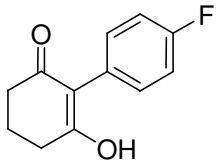
3n: White solid (60%) mp. 70-71 ^{0}C. ^{1}H-NMR (400MHz, $CDCl_3$) δ: 5.80-5.71 (m, 1H), 5.14-5.09 (m, 2H), 3.22 (m, 1H), 2.91-2.87 (m, 2H), 2.81-2.73 (m, 2H), 2.10-2.04 (m, 1H), 1.84-1.60 (m, 1H), 1.12 (d, *J* = 6.43 Hz, 3H); ^{13}C-NMR (75MHz, $CDCl_3$) δ: 199.2, 198.9, 136.2, 117.8, 87.0, 45.0, 38.0, 37.8, 17.4, 15.5 ; IR: v_{max} (neat)/cm^{-1} KBr.: 2977, 2937, 1710, 1463, 1415, 1265, 1137, 1029, 929. HRMS (EI): *m/z* Calcd. for $C_{10}H_{13}O_2Cl$ [M$^+$]: 200.0604, found : 200.0604

***2-Chloro-5,5-dimethyl-3-(1-methyl-allyloxy)-cyclohex-2-enone* (3o)**



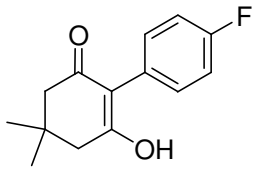
3o: White solid (60%) mp. 64-65 ^{0}C. ^{1}H-NMR (400MHz, $CDCl_3$) δ: 5.73-5.66 (m, 1H), 5.08-5.03 (m, 2H), 3.13 (m, 1H), 2.73-2.67 (m, 4H), 1.08 (s, 3H), 1.06 (d, *J* = 6.43 Hz, 3H), 0.86 (s, 3H); ^{13}C-NMR (75MHz, $CDCl_3$) δ: 199.2, 198.7, 136.3, 117.7, 100.1, 71.5, 51.5, 51.3, 45.1, 30.4, 29.2, 27.4, 15.6 ; IR: v_{max} (neat)/cm^{-1} KBr.: 2977, 2937, 1710, 1463, 1415, 1265, 1137, 1029, 929. HRMS (EI): *m/z* Calcd. for $C_{12}H_{17}O_2Cl$ [M$^+$]: 228.0917, found : 228.0914

***2-(4-Fluoro-phenyl)-cyclohexane-1,3-dione* (3p)**



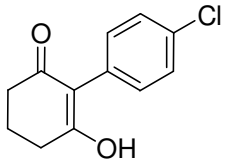
3p: White solid (22%) mp. 173-175 ^{0}C (lit [5]184 ^{0}C) . ^{1}H-NMR (400MHz, CD_3OD) δ: 7.15 (m, 2H) 7.02(m, 2H), 2.54 (t, *J* = 6.3Hz, 4H), 2.05 (q, *J* = 6.6 Hz, 2H); ^{13}C-NMR (75MHz, CD_3OD) δ: 132.5, 132.4, 114.0, 113.8, 32.8, 20.3; IR: v_{max} (neat)/cm^{-1} KBr 3459, 2963, 1594, 1460, 1397, 1310, 1234, 1000, 897.

***2-(4-Fluoro-phenyl)-5,5-dimethyl-cyclohexane-1,3-dione* (3q)**



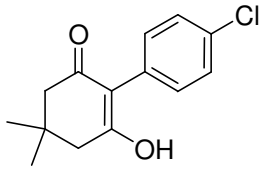
3q: White solid (30%) mp. 180-182 ^{0}C. ^{1}H-NMR (400MHz, CD_3OD) δ: 7.15 (m, 2H) 7.02(m, 2H), 2.43 (s, 4H), 1.15 (s, 6H); ^{13}C-NMR (75MHz, CD_3OD) δ: 132.4, 132.3, 114.1, 113.8, 31.3, 27.0; IR: v_{max} (neat)/cm^{-1} KBr 3423, 2963, 2625, 1627, 1597, 1487, 1397, 1332, 1254, 1027, 916, 826. HRMS (ESI): *m/z* Calcd. for $C_{14}H_{15}O_2F$ [M+H]$^+$: 235.1128, found : 235.1129.

***2-(4-chloro-phenyl)-cyclohexane-1,3-dione* (3r)**



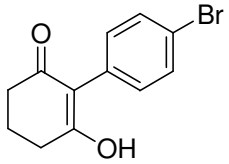
3r: White solid (41%) mp. 190-192 ^{0}C (lit [6] 220-223 ^{0}C). ^{1}H-NMR (400MHz, CD_3OD) δ: 7.2 (d, *J* = 8.19 Hz, 2H) 7.12(d, *J* = 8.19 Hz, 2H), 2.54 (t, *J* = 6.4Hz, 4H), 2.04 (q, *J* = 6.6Hz, 2H); ^{13}C-NMR (75MHz, CD_3OD) δ: 132.3, 127.3, 31.3, 27.0 ; IR: v_{max} (neat)/cm^{-1} KBr. 3471, 2943, 1608, 1570, 1488, 1387, 1359, 1297, 1163, 1128, 987, 825.

***2-(4-Chloro-phenyl)-5,5-dimethyl-cyclohexane-1,3-dione* (3s)**



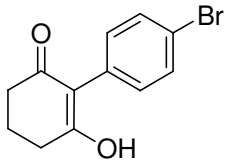
3s: White solid (41%) mp. 190-192 ^{0}C. ^{1}H-NMR (400MHz, CD_3OD) δ: 7.30 (d, *J* = 7.41 Hz, 2H) 7.14 (d, *J* = 7.43 Hz, 2H), 2.43 (s, 4H), 1.14 (s, 6H); ^{13}C-NMR (75MHz, CD_3OD) δ: 132.2, 127.4, 31.4, 27.0 ; IR: v_{max} (neat)/cm^{-1} KBr.3434, 2928, 2393, 1567, 1509, 1367, 1315, 1257, 1148, 10228, 833. HRMS (ESI): *m/z* Calcd. for $C_{14}H_{15}O_2Cl$ $[M+H]^+$: 343.0189, found : 343.0189.

***2-(4-bromo-phenyl)-cyclohexane-1,3-dione* (3t)**



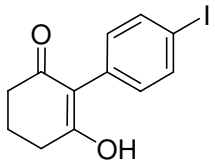
3t: White solid (27%) mp. 170-171 ^{0}C. ^{1}H-NMR (400MHz, CD_3OD) δ: 7.45 (d, *J* = 1.4, 2H) 7.08(d, *J* = 1.5, 2H), 2.54 (t, *J* = 6.4Hz, 4H), 2.05 (q, *J* = 6.6Hz, 2H); ^{13}C-NMR (75MHz, CD_3OD) δ: 132.6, 130.3, 31.3, 20.3 ; IR: v_{max} (neat)/cm^{-1} KBr. 3450, 2950, 1609, 1594, 1556, 1483, 1376, 1191, 1070, 1027, 815. HRMS (ESI): *m/z* Calcd. for $C_{12}H_{11}O_2Br[M+H]^+$: 267.0015, found : 267.0015.

***2-(4-Bromo-phenyl)-5,5-dimethyl-cyclohexane-1,3-dione* (3u)**



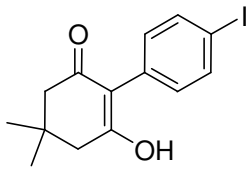
3u: White solid (37%) mp. 188-189 ^{0}C. ^{1}H-NMR (400MHz, CD_3OD) δ: 7.45 (d, *J* = 8.43, 2H) 7.09 (d, *J* = 8.45, 2H), 2.43 (s, 4H), 1.14 (s, 6H); ^{13}C-NMR (75MHz, CD_3OD) δ: 132.5, 130.3, 31.3, 27.0; IR: v_{max} (neat)/cm^{-1} KBr. 3465, 2959, 1612, 1571, 1483, 1333, 1294, 1254, 1026,819. HRMS (ESI): *m/z* Calcd. for $C_{12}H_{11}O_2Br$ $[M+H]^+$: 295.0328, found : 295.0329.

***2-(4-iodo-phenyl)-cyclohexane-1,3-dione* (3v)**

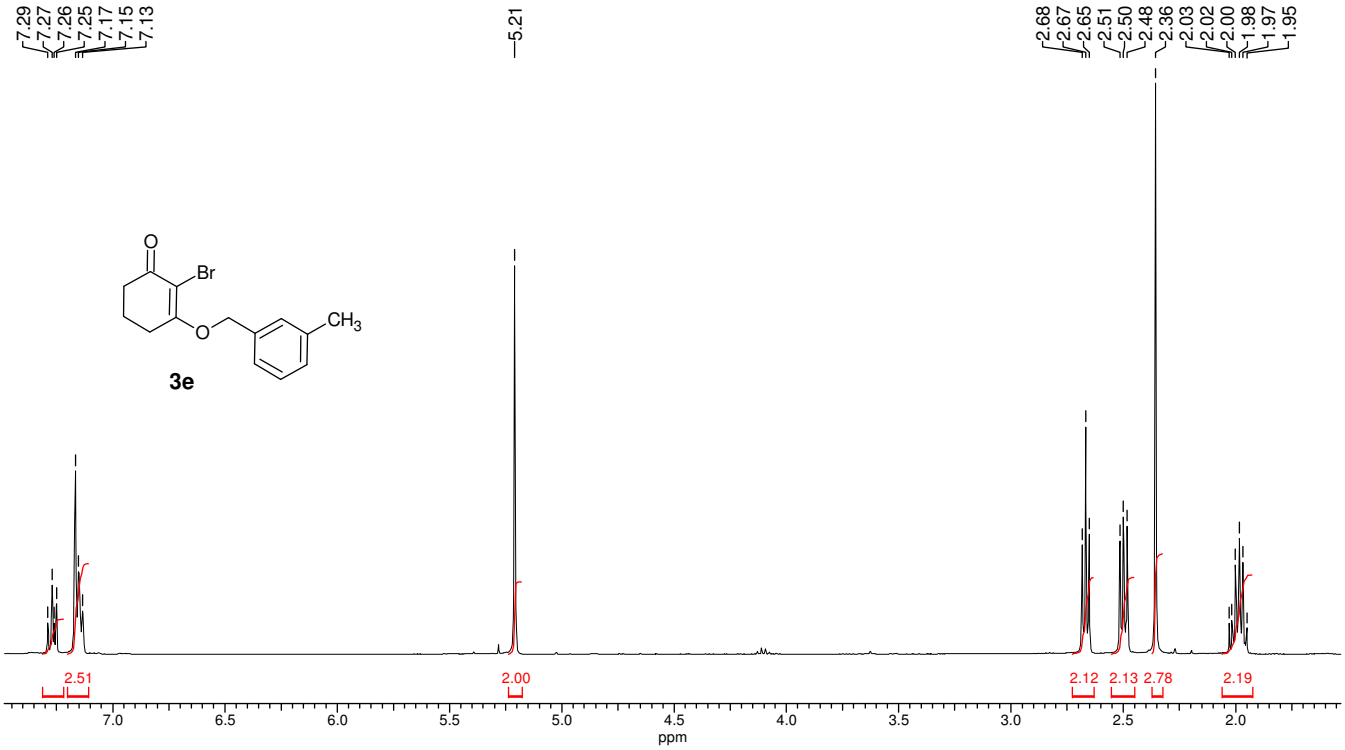


3v: White solid (30%) mp. 215-216 ^{0}C. ^{1}H-NMR (400MHz, CD_3OD) δ: 7.29 (d, *J* = 8.3 Hz, 2H) 7.13, (d, *J* = 8.4 Hz, 2H), 2.54 (t, *J* = 6.4Hz, 4H), 2.04 (q, *J* = 6.6Hz, 2H); ^{13}C-NMR (75MHz, CD_3OD) δ: 132.5, 132.4, 114.0, 113.8, 32.9, 20.3; IR: v_{max} (neat)/cm^{-1} KBr. 3435, 2926, 2641, 1613, 1590, 1550, 1450, 1375, 1334, 1259, 1165, 987, 813. HRMS (ESI): *m/z* Calcd. for $C_{12}H_{11}O_2I$ $[M+H]^+$: 314.9876, found : 314.9876.

***2-(4-Iodo-phenyl)-5,5-dimethyl-cyclohexane-1,3-dione* (3w)**



3w: White solid (38%) mp. 230-232 ^{0}C. ^{1}H-NMR (400MHz, CD_3OD) δ: 7.65 (d, *J* = 8.3 Hz, 2H) 6.95(d, *J* = 8.3 Hz, 2H), 2.42 (s, 4H), 1.14 (s, 6H); ^{13}C-NMR (75MHz, CD_3OD) δ: 136.5, 132.8, 31.3, 27.0; IR: v_{max} (neat)/cm^{-1} KBr pellet: 3465, 2952, 1616, 1571, 1488, 1388, 1297, 1257, 1164, 1128, 987, 825. HRMS (ESI): *m/z* Calcd. for $C_{14}H_{15}O_2I$ $[M+H]^+$: 343.0189, found : 343.0189.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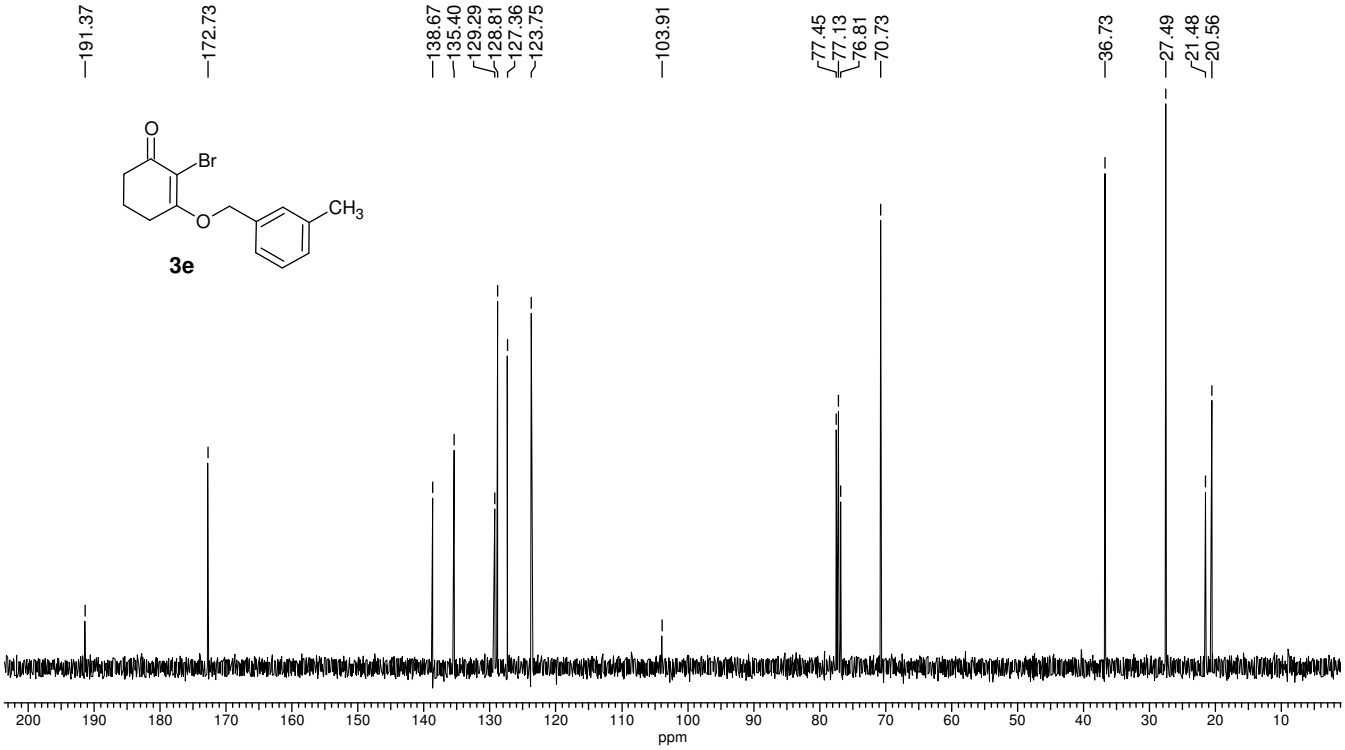
7.26
7.25
7.17
7.15
7.13
5.21
2.68
2.67
2.65
2.51
2.50
2.48
2.36
2.03
2.02
2.00
1.98
1.97
1.95
O
Br
O
CH3
3e
2.51
2.00
2.12
2.13
2.78
2.19
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm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138.67
135.40
129.29
128.81
127.36
123.75
103.91
77.45
77.13
76.81
70.73
36.73
27.49
21.48
20.56
O
Br
O
CH3
3e
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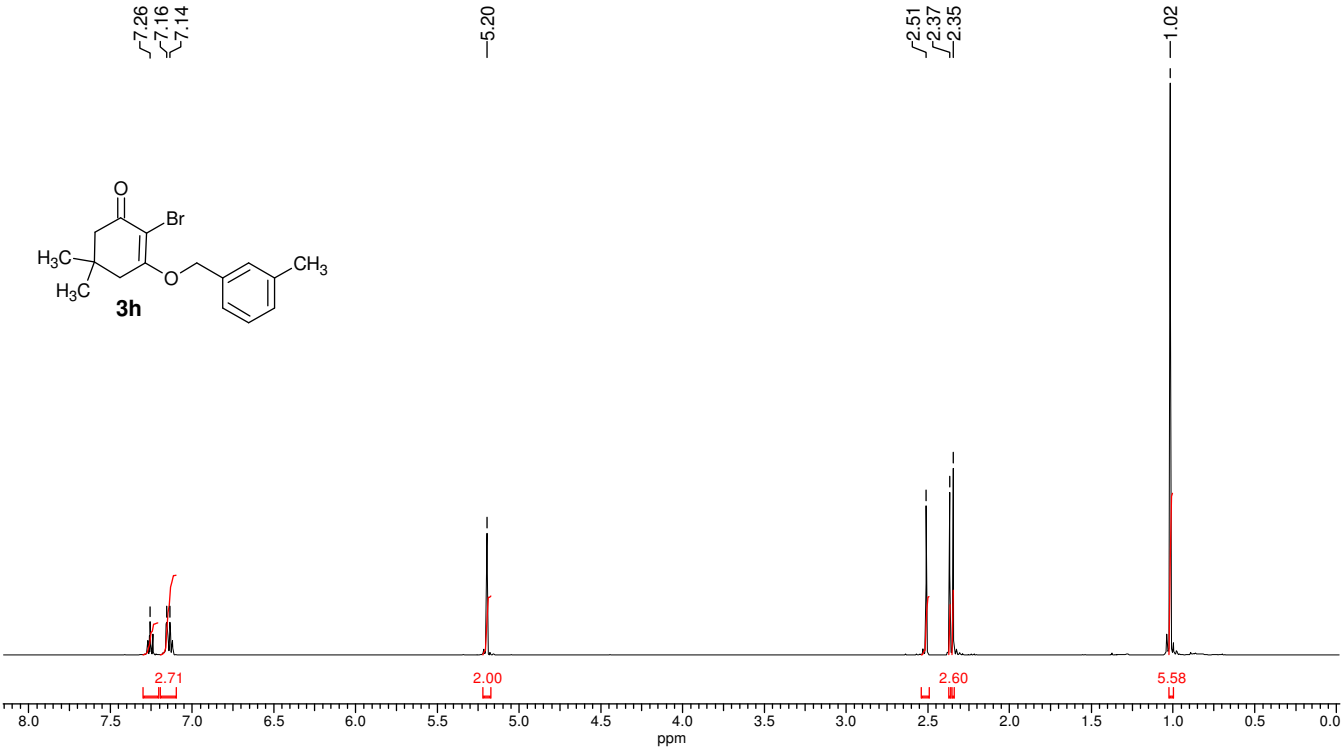
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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1.02
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Br
H3C
H3C
O
CH3
3h
2.71
2.00
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8.0
7.5
7.0
6.5
6.0
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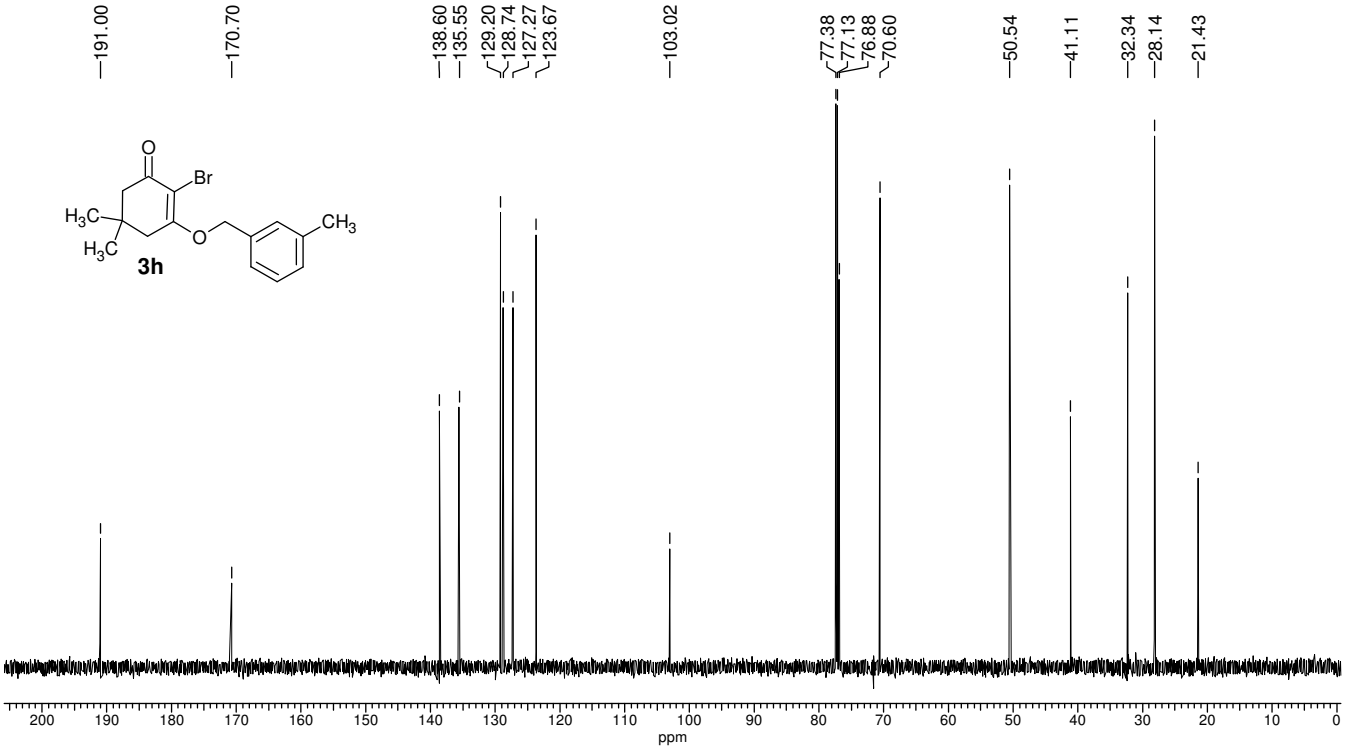
ppm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135.55
129.20
128.74
127.27
123.67
103.02
77.38
77.13
76.88
70.60
50.54
41.11
32.34
28.14
21.43
O
Br
H3C
H3C
O
CH3
3h
200
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100
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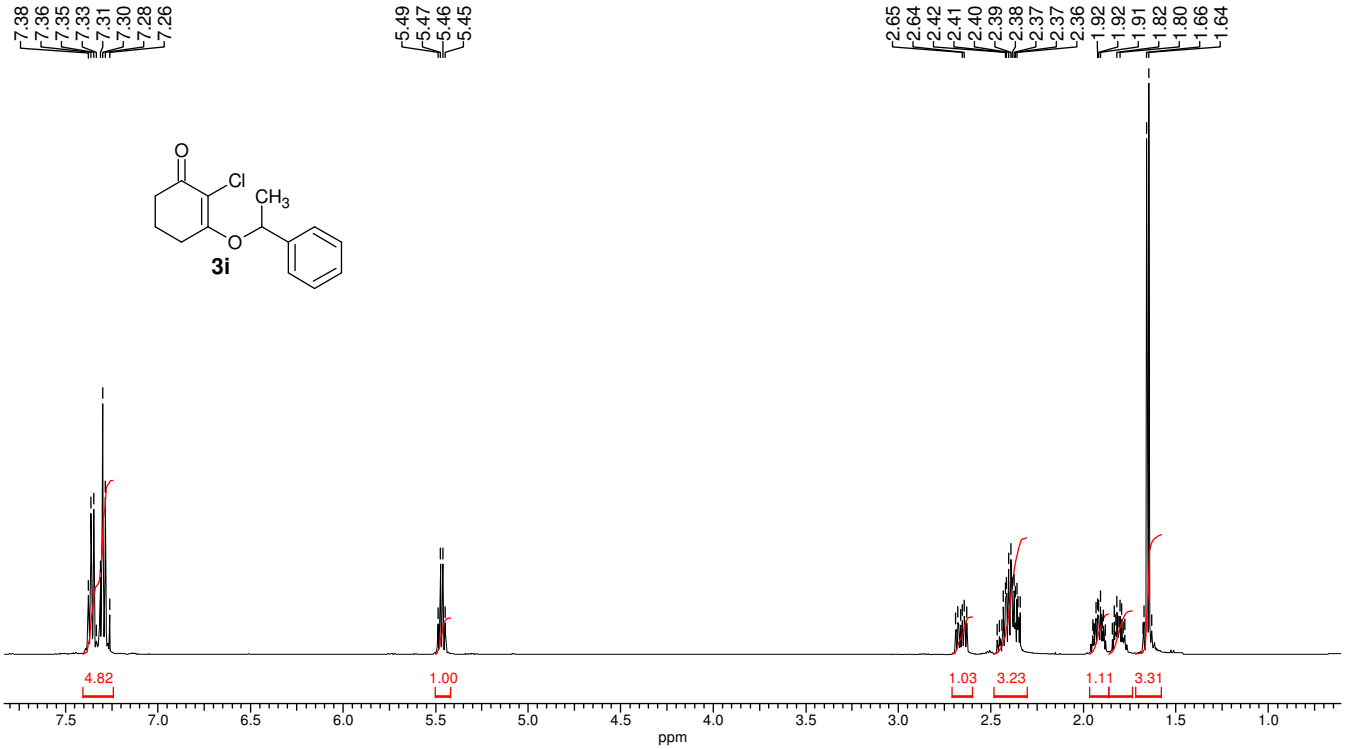
ppm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7.33
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7.26
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5.46
5.45
2.65
2.64
2.42
2.41
2.40
2.39
2.38
2.37
2.37
2.36
1.92
1.92
1.91
1.82
1.80
1.66
1.64
O
Cl
CH3
O
3i
4.82
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1.03
3.23
1.11
3.31
7.5
7.0
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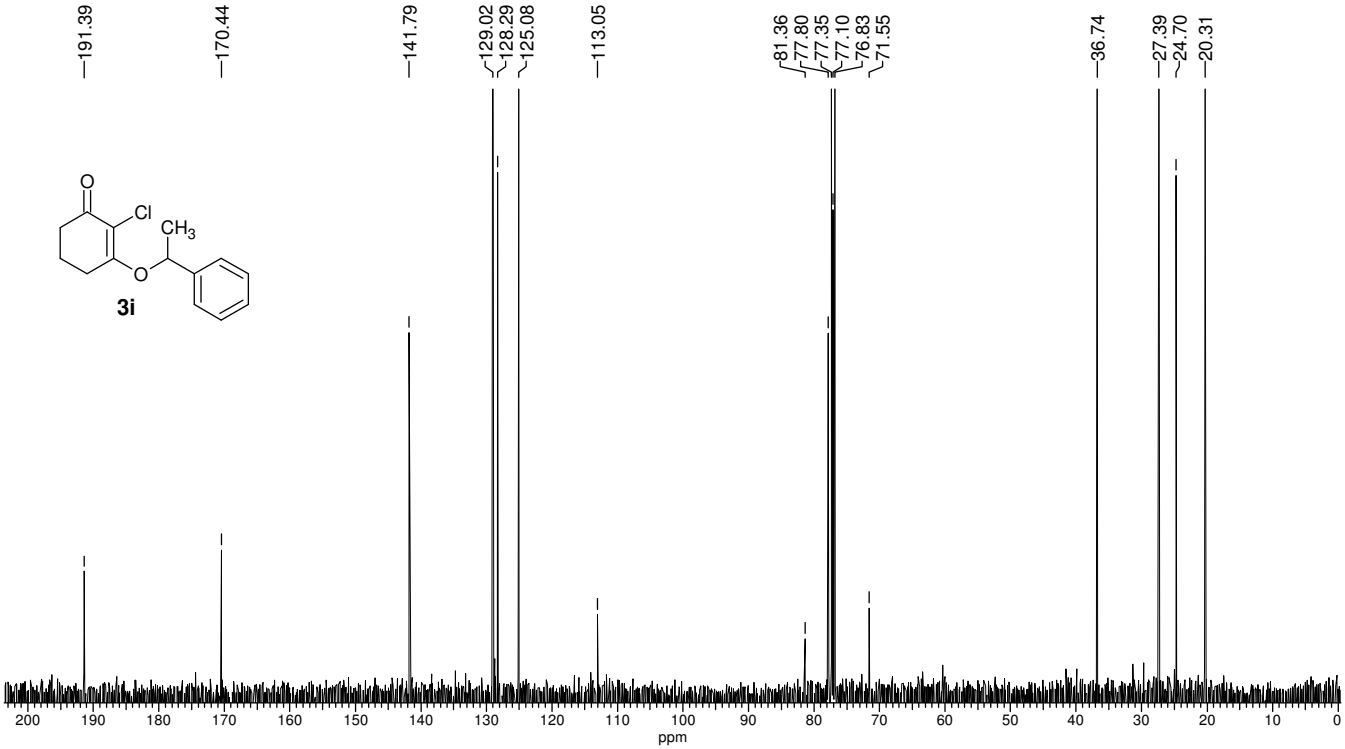
ppm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125.08
113.05
81.36
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77.35
77.10
76.83
71.55
36.74
27.39
24.70
20.31
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CH3
O
3i
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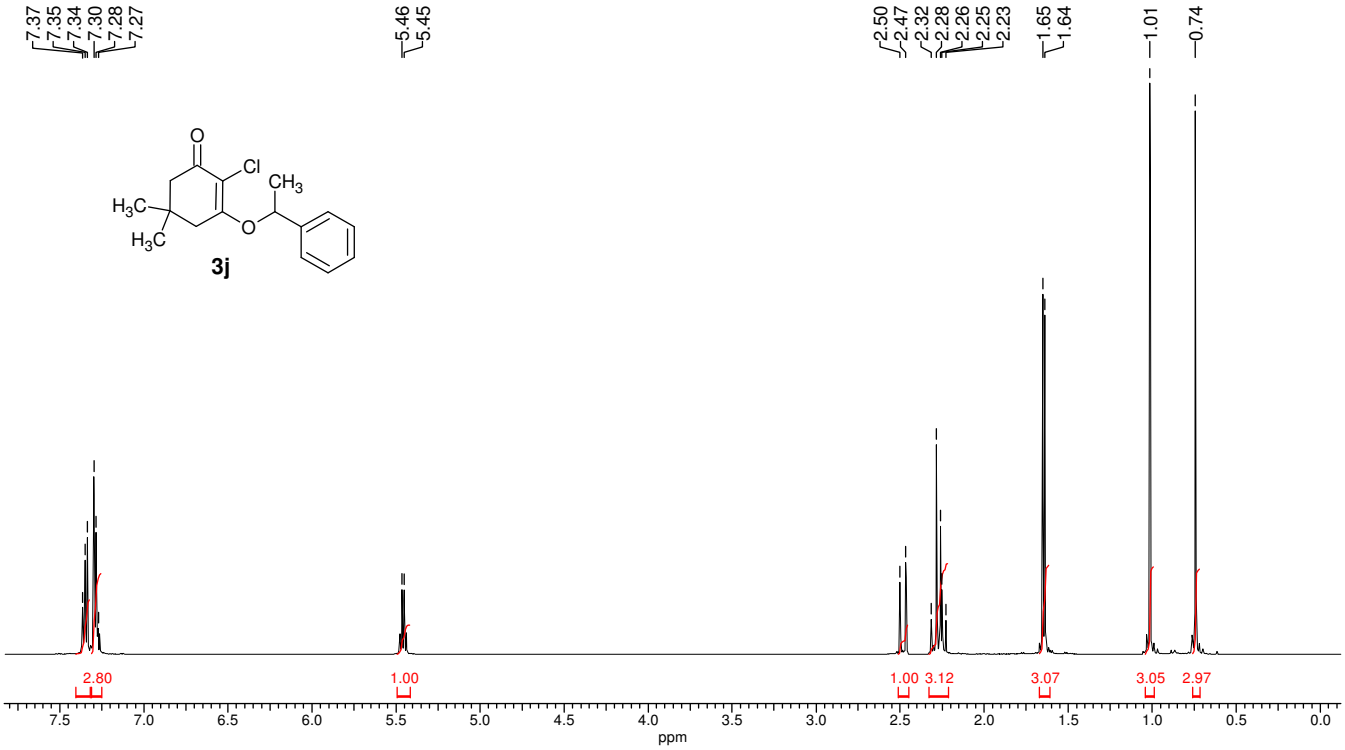
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5.45
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2.47
2.32
2.28
2.26
2.25
2.23
1.65
1.64
1.01
0.74
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Cl
CH3
H3C
H3C
O
3j
2.80
1.00
1.00
3.12
3.07
3.05
2.97
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6.5
6.0
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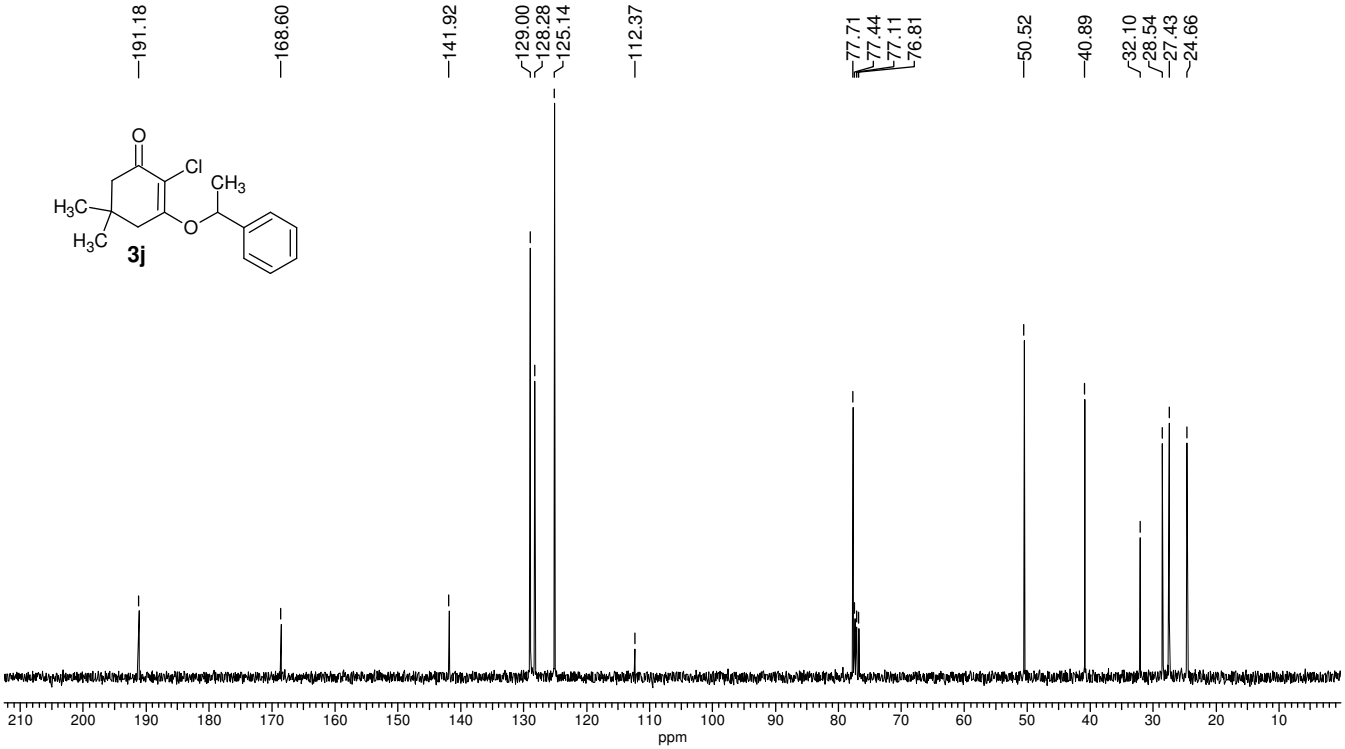
ppm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125.14
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76.81
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40.89
32.10
28.54
27.43
24.66
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Cl
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H3C
H3C
O
3j
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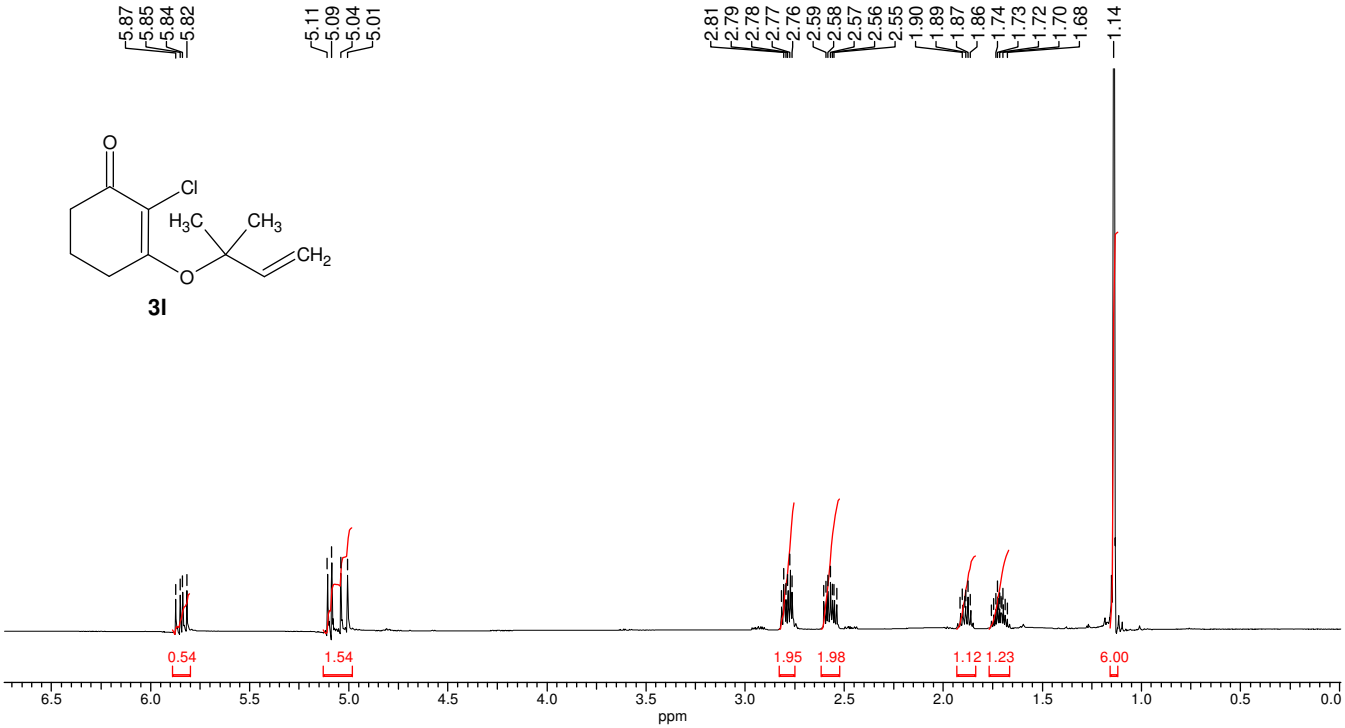
10
ppm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CH2
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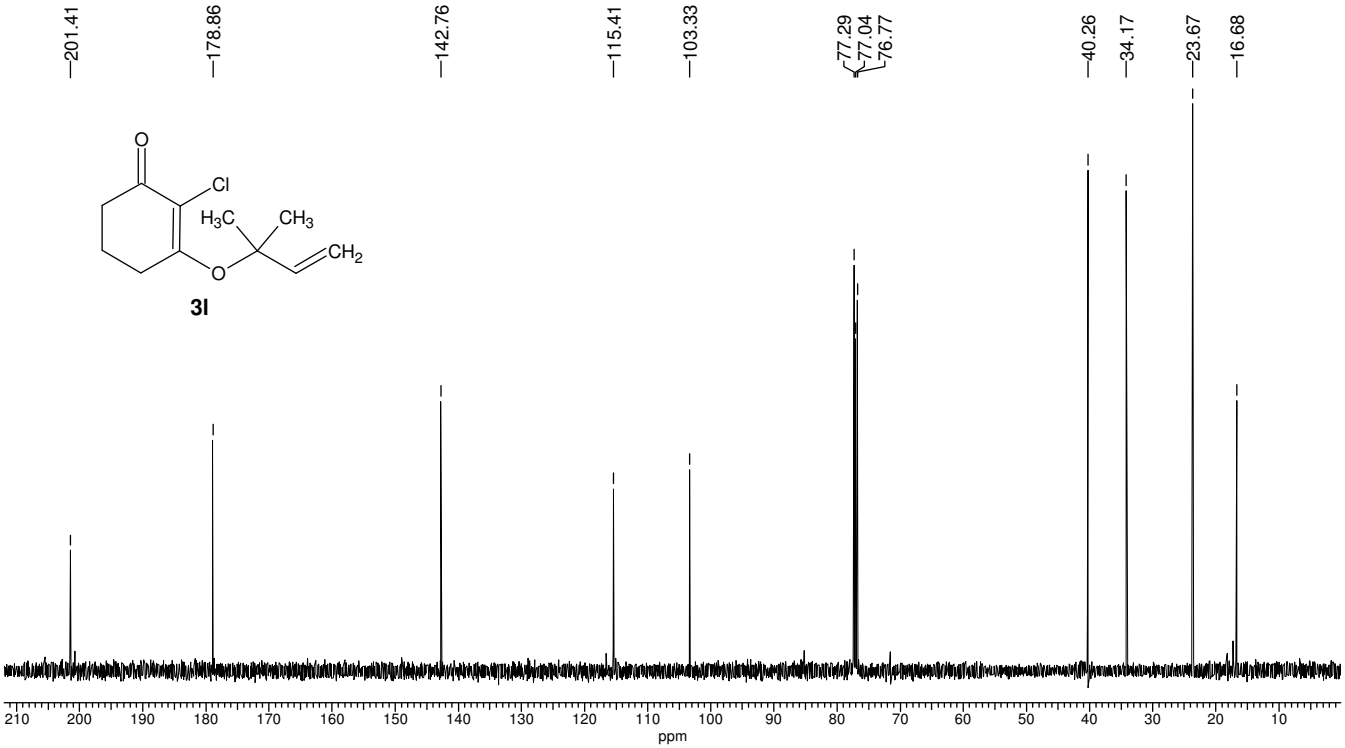
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CH2
O
3l
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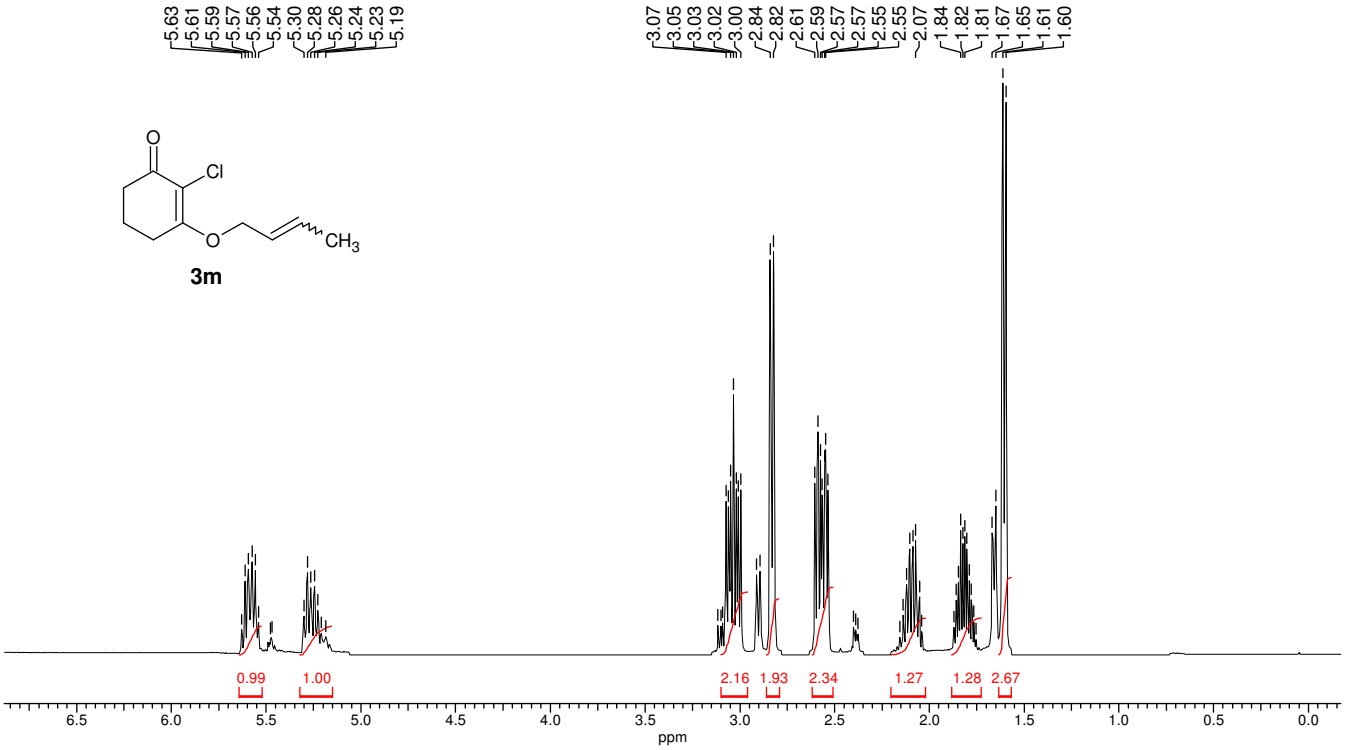
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5.19
3.07
3.05
3.03
3.02
3.00
2.84
2.82
2.61
2.59
2.57
2.57
2.55
2.55
2.07
1.84
1.82
1.81
1.67
1.65
1.61
1.60
O
Cl
O
CH3
3m
0.99
1.00
2.16
1.93
2.34
1.27
1.28
2.67
6.5
6.0
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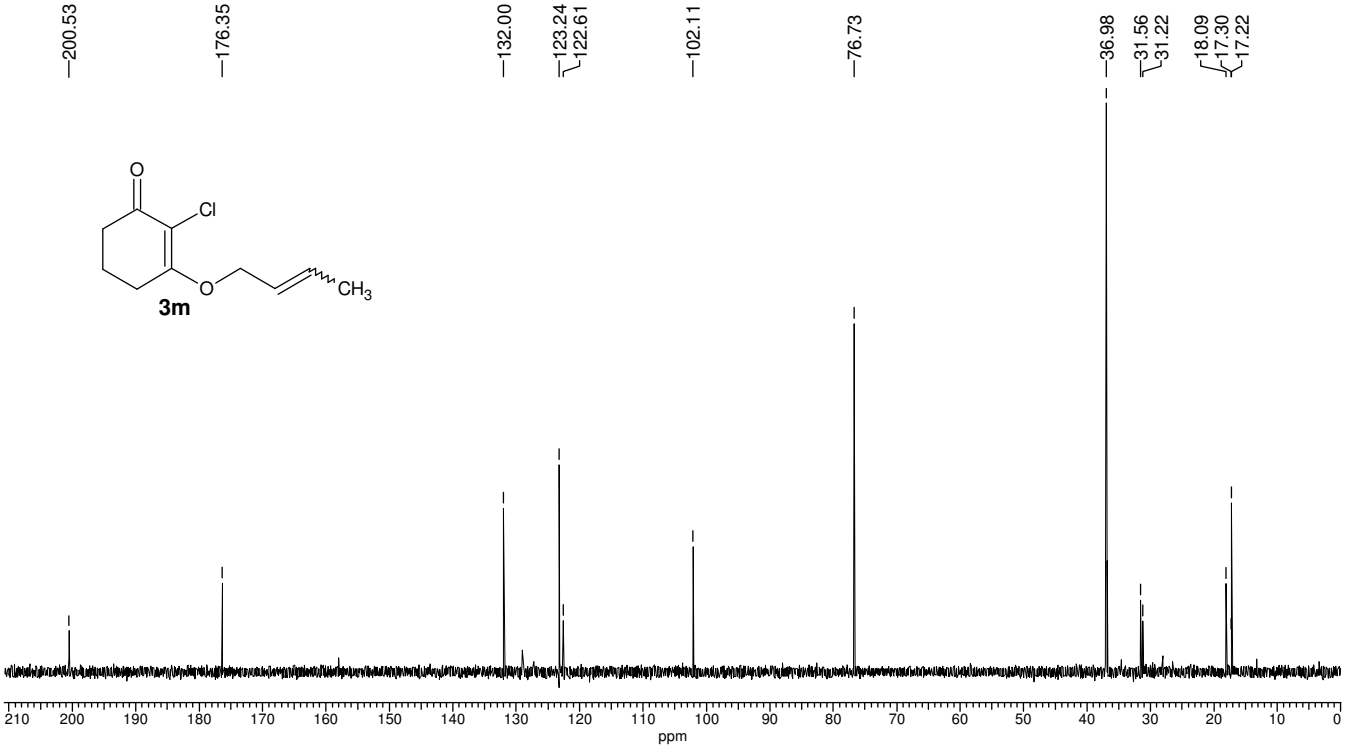
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176.35
132.00
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76.73
36.98
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31.22
18.09
17.30
17.22
O
Cl
O
CH3
3m
210
200
190
180
170
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140
130
120
110
100
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80
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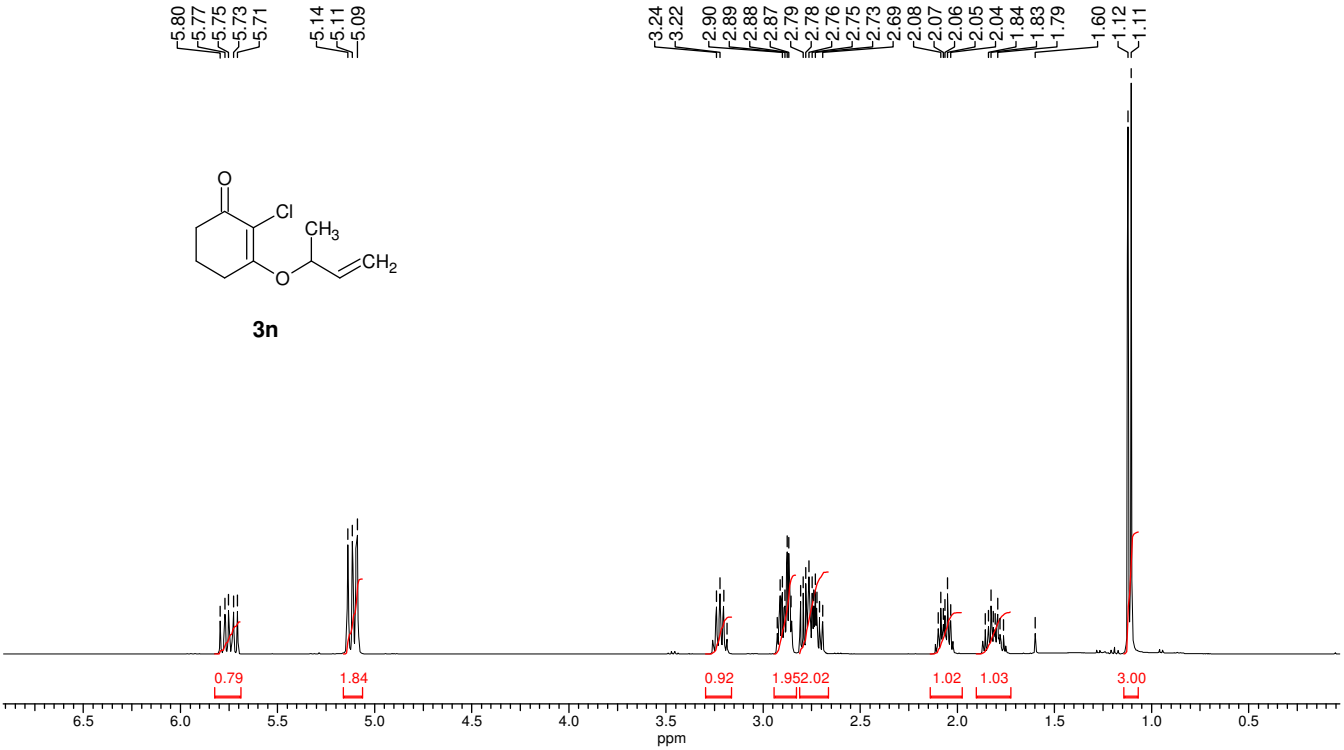
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5.11
5.09
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3.22
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2.89
2.88
2.87
2.79
2.78
2.76
2.75
2.73
2.69
2.08
2.07
2.06
2.05
2.04
1.84
1.83
1.79
1.60
1.12
1.11
O
Cl
CH3
CH2
O
3n
0.79
1.84
0.92
1.95
2.02
1.02
1.03
3.00
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
1.0
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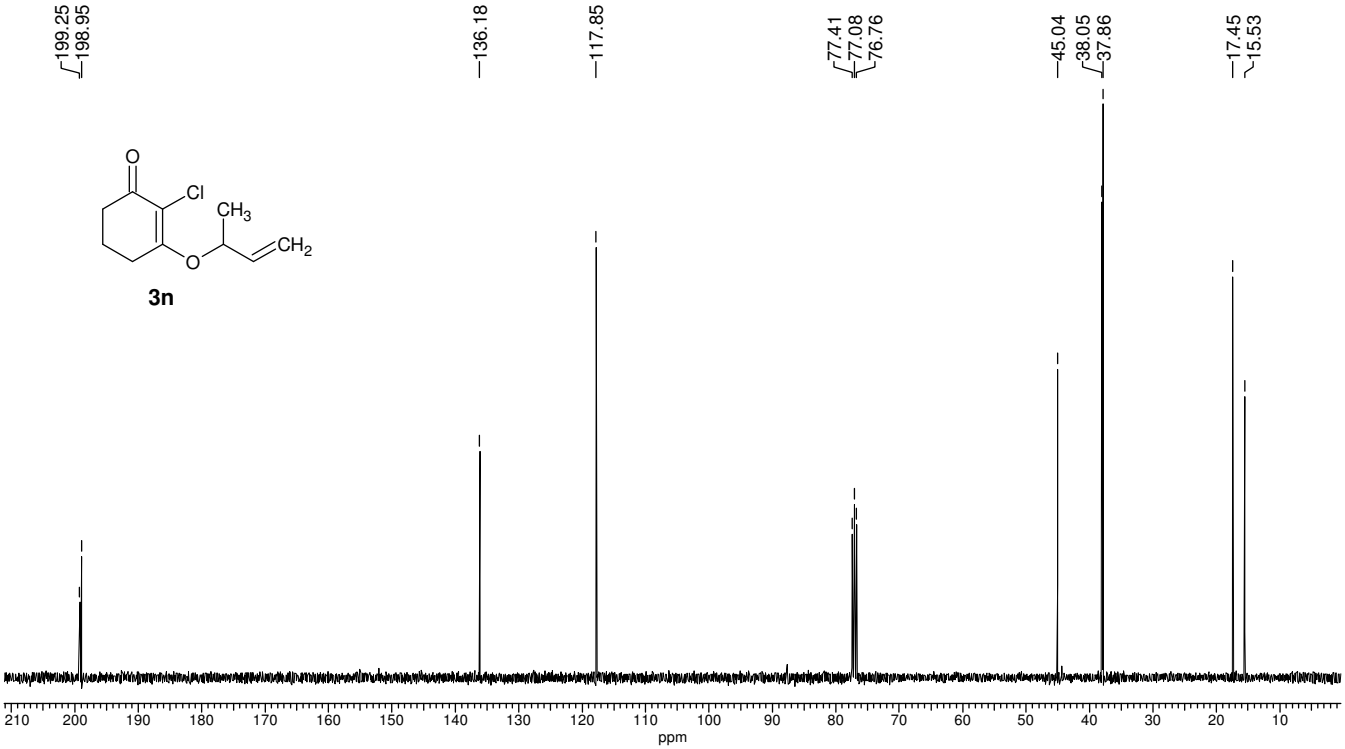
ppm


199.25
198.95
136.18
117.85
77.41
77.08
76.76
45.04
38.05
37.86
17.45
15.53
O
Cl
CH3
CH2
O
3n
210
200
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180
170
160
150
140
130
120
110
100
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80
70
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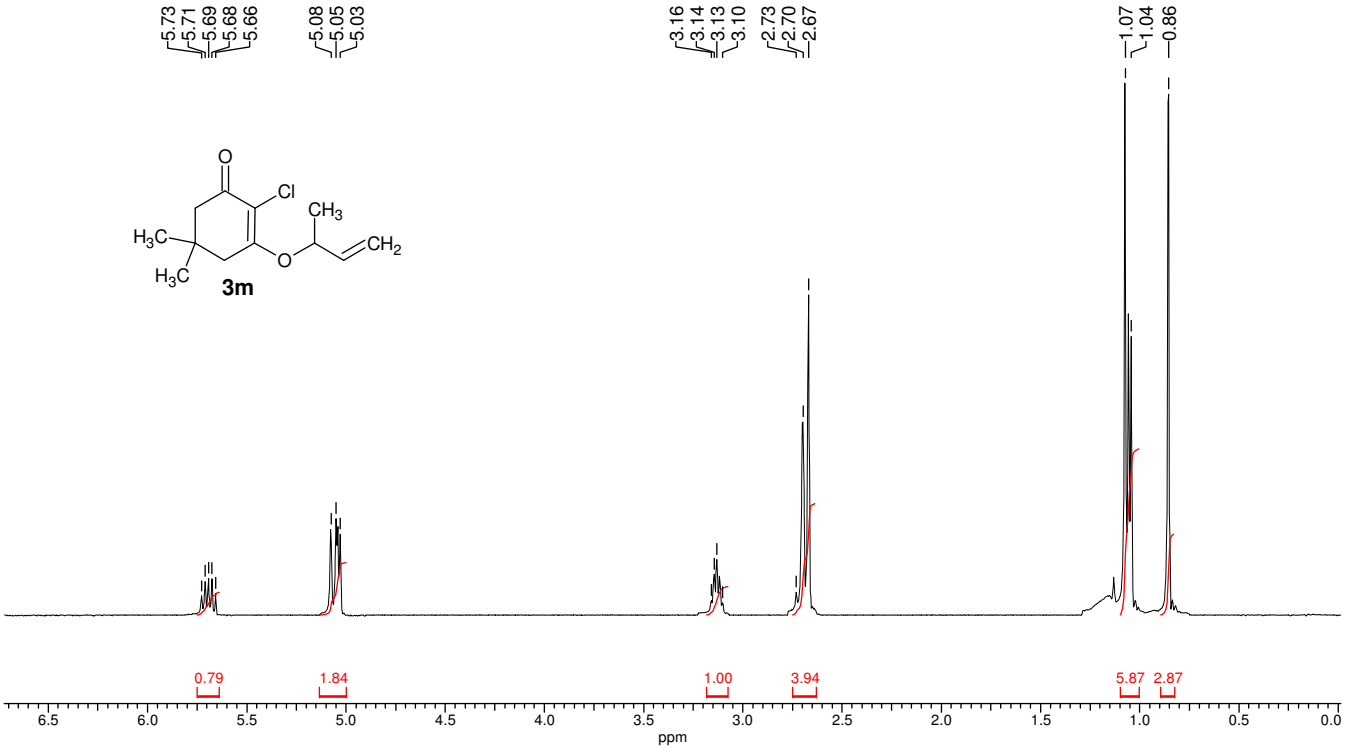
40
30
20
10
ppm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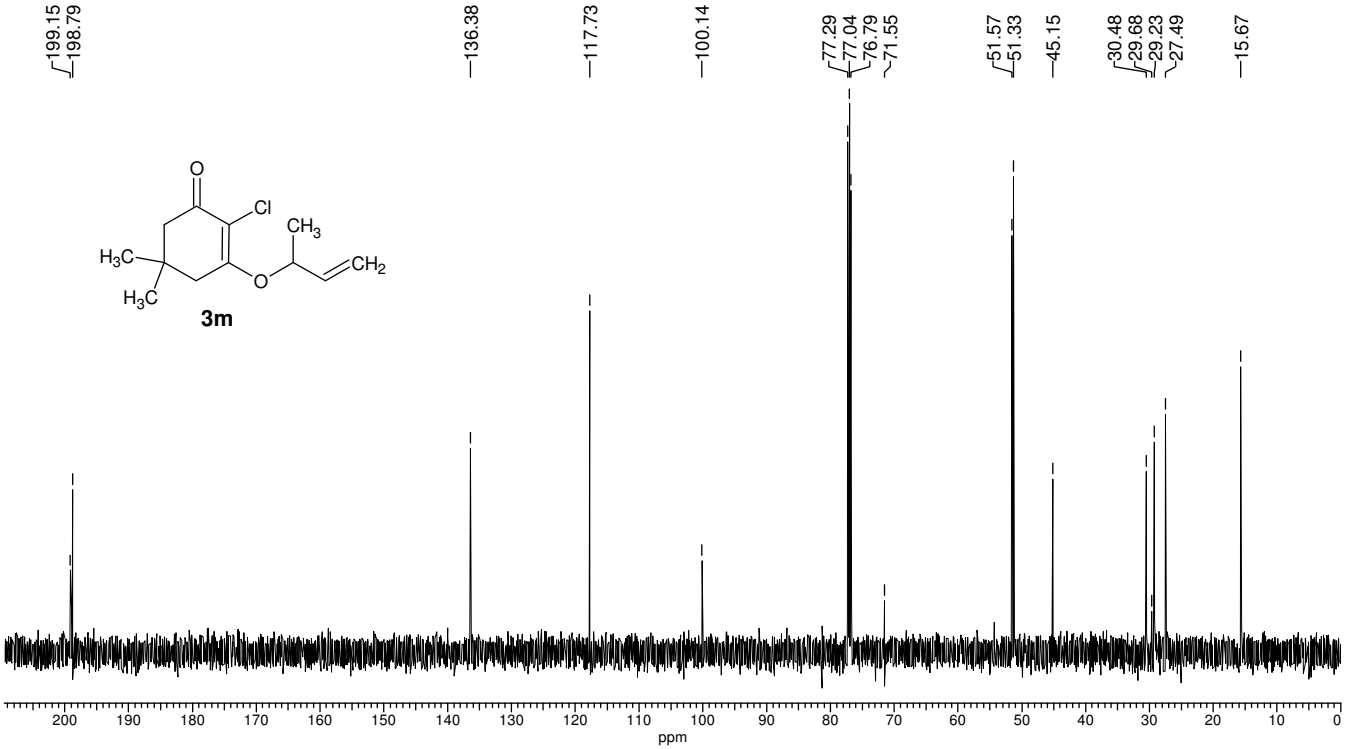
5.71
5.69
5.68
5.66
5.08
5.05
5.03
3.16
3.14
3.13
3.10
2.73
2.70
2.67
1.07
1.04
0.86
O
Cl
CH3
H3C
CH2
O
H3C
3m
0.79
1.84
1.00
3.94
5.87
2.87
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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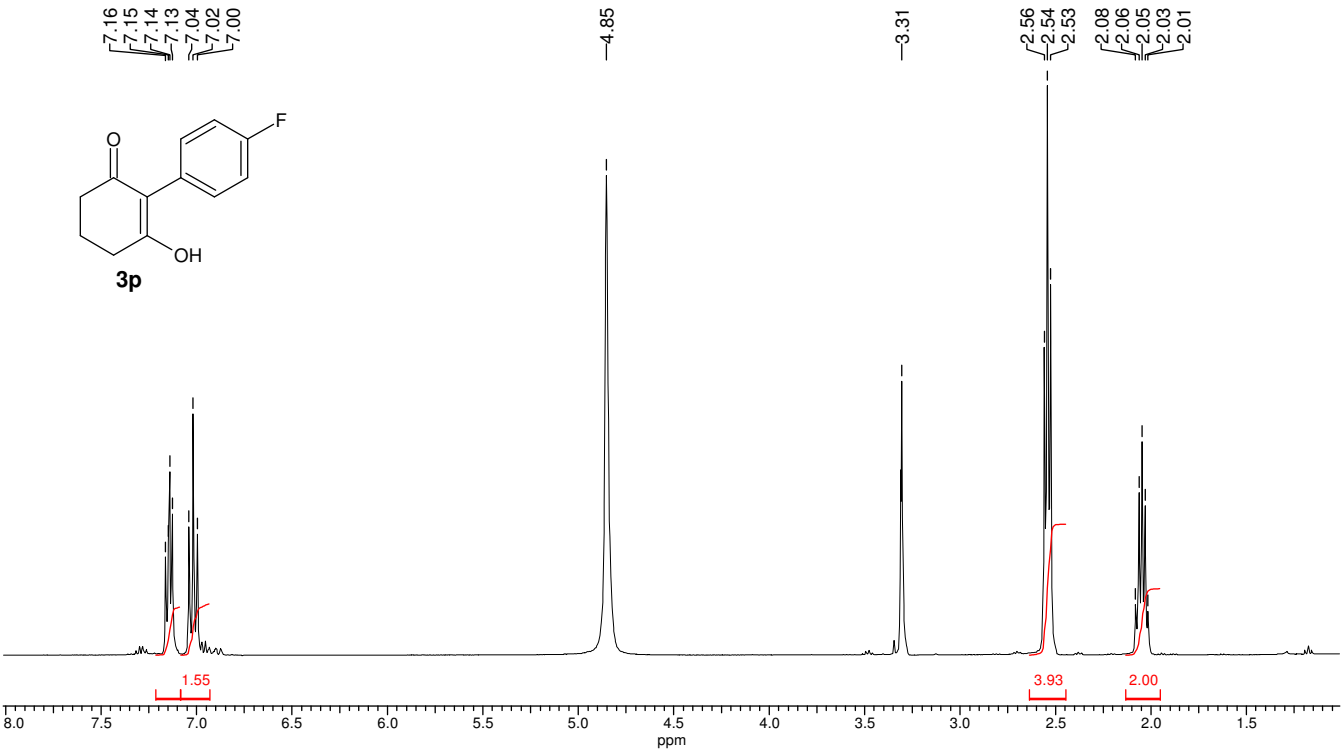
198.79
136.38
117.73
100.14
77.29
77.04
76.79
71.55
51.57
51.33
45.15
30.48
29.68
29.23
27.49
15.67
O
Cl
CH3
H3C
CH2
O
H3C
3m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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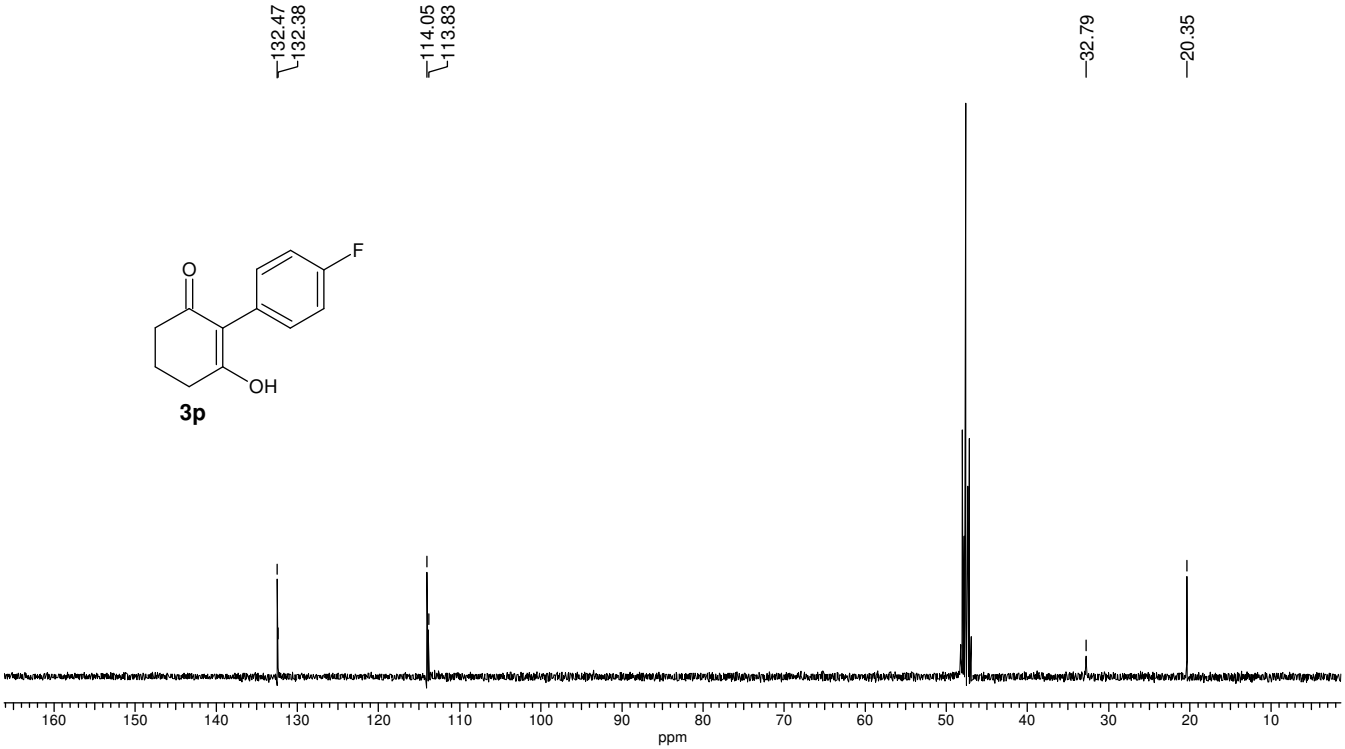
7.14
7.13
7.04
7.02
7.00
4.85
3.31
2.56
2.54
2.53
2.08
2.06
2.05
2.03
2.01
O
F
OH
3p
1.55
3.93
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


132.47
132.38
114.05
113.83
32.79
20.35
O
F
OH
3p
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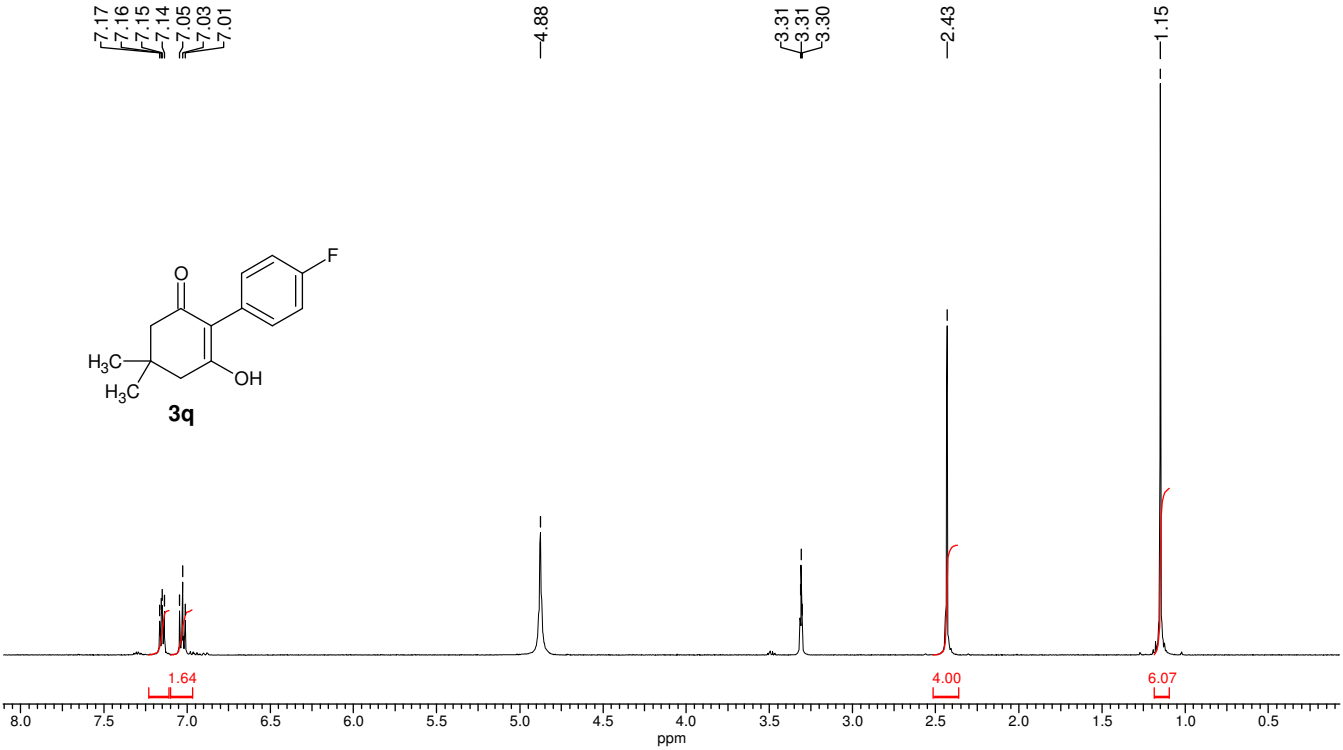
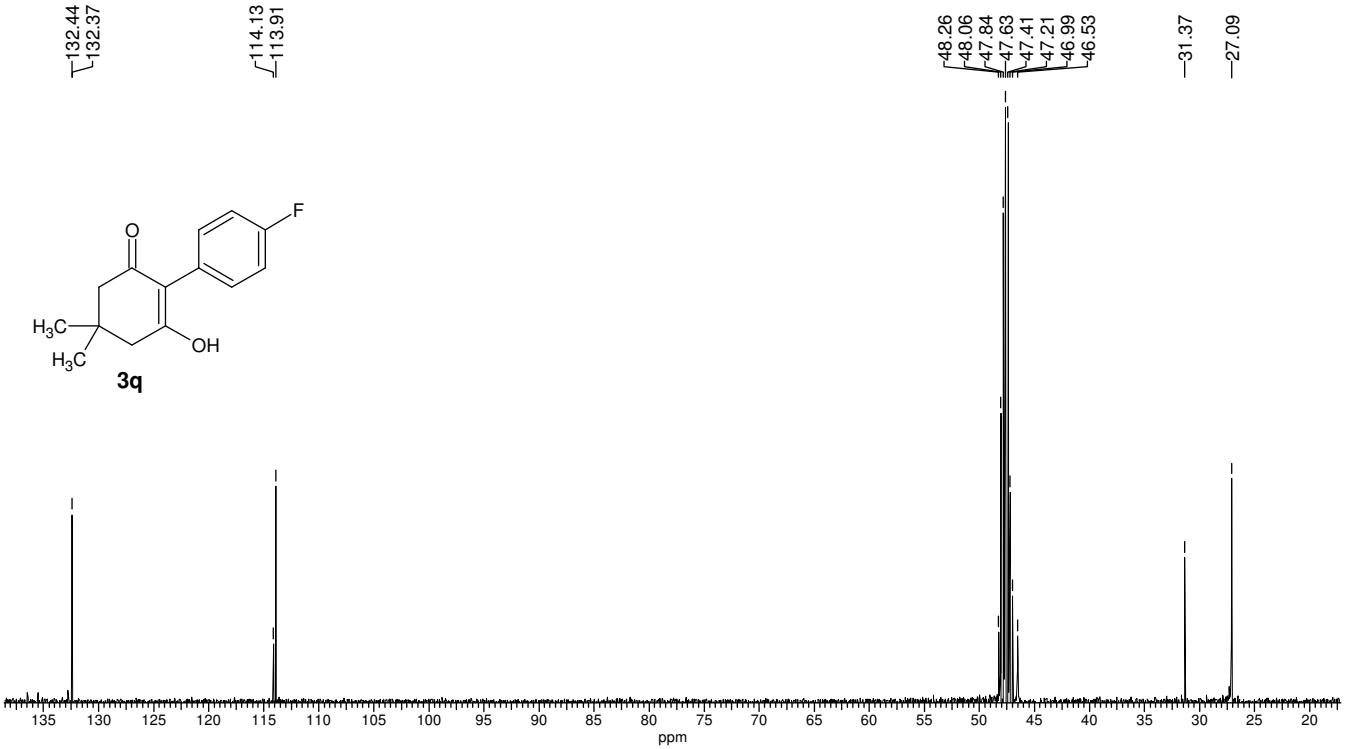
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.17
7.16
7.15
7.14
7.05
7.03
7.01
4.88
3.31
3.31
3.30
2.43
1.15
F
O
H3C
H3C
OH
3q
1.64
4.00
6.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm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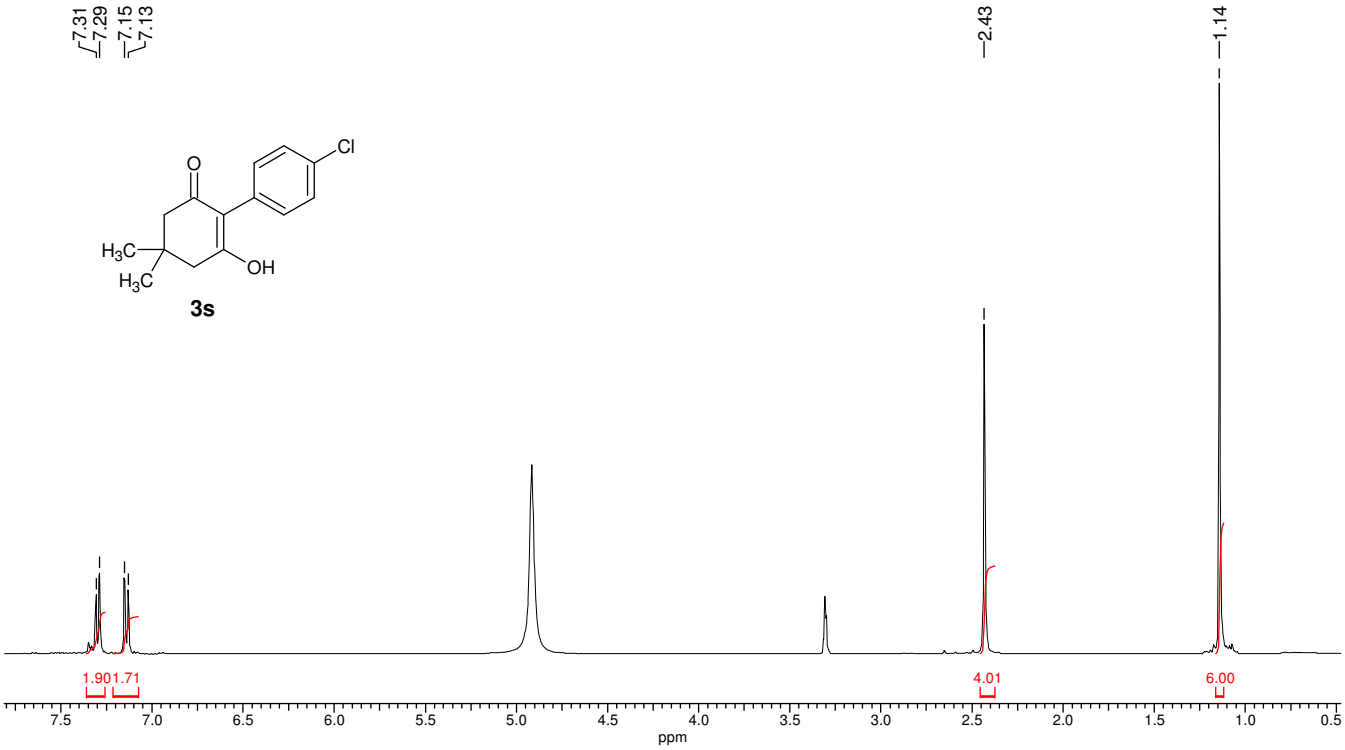
132.37
114.13
113.91
48.26
48.06
47.84
47.63
47.41
47.21
46.99
46.53
31.37
27.09
F
O
H3C
H3C
OH
3q
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
ppm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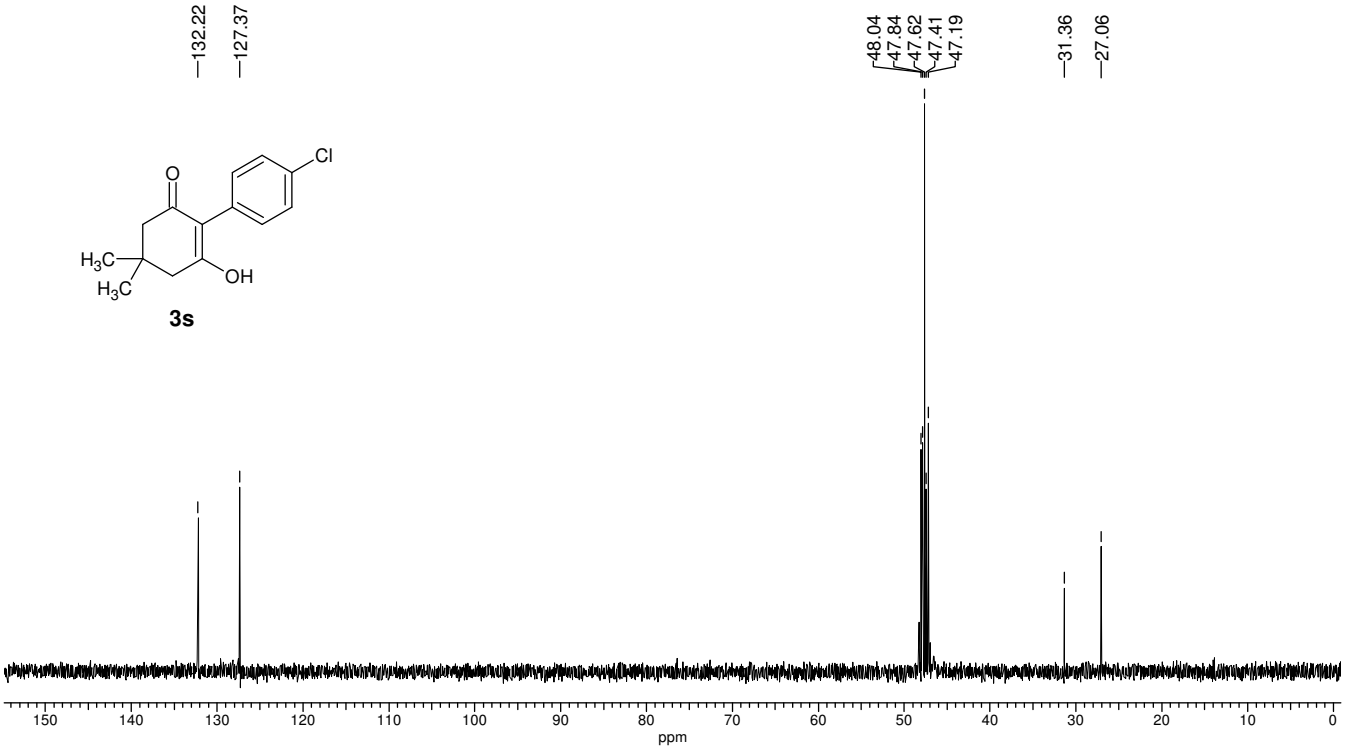
7.29
7.15
7.13
2.43
1.14
Cl
O
H3C
H3C
OH
3s
1.90
1.71
4.01
6.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm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127.37
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47.84
47.62
47.41
47.19
31.36
27.06
Cl
O
H3C
H3C
OH
3s
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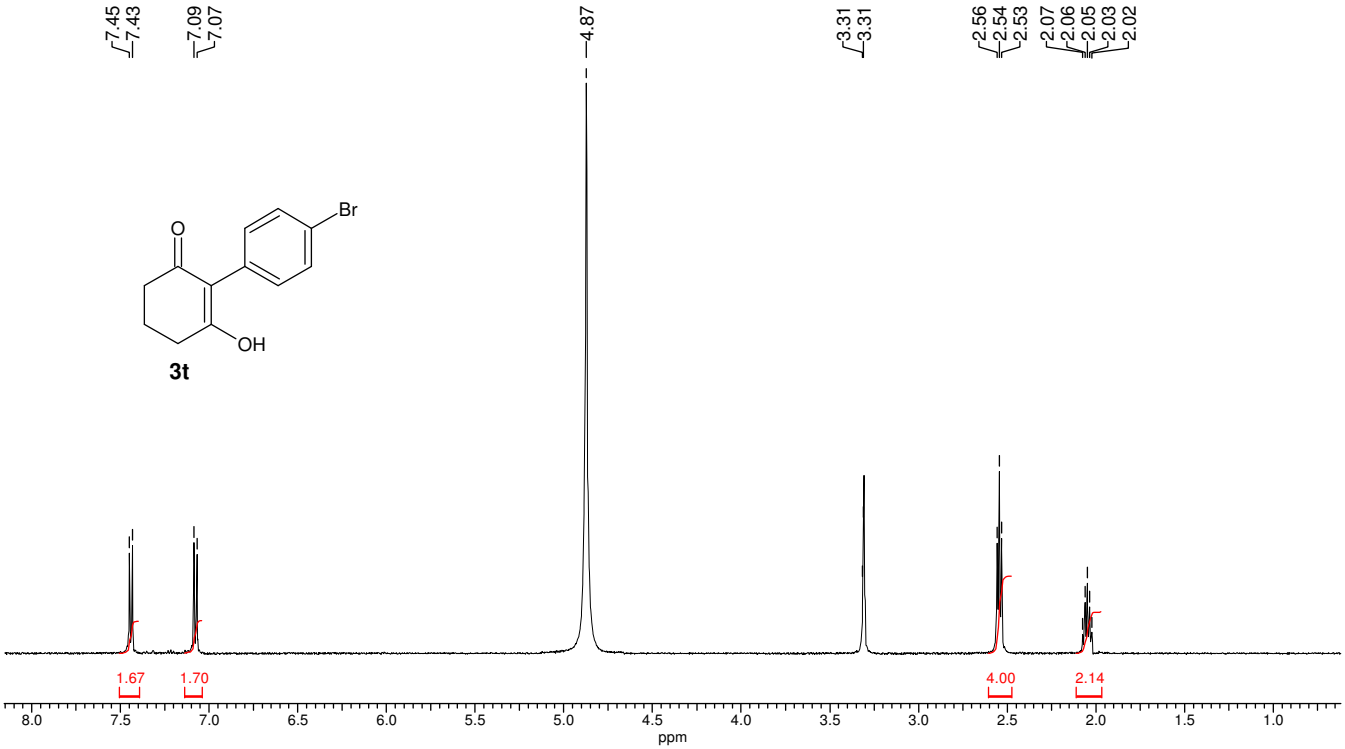
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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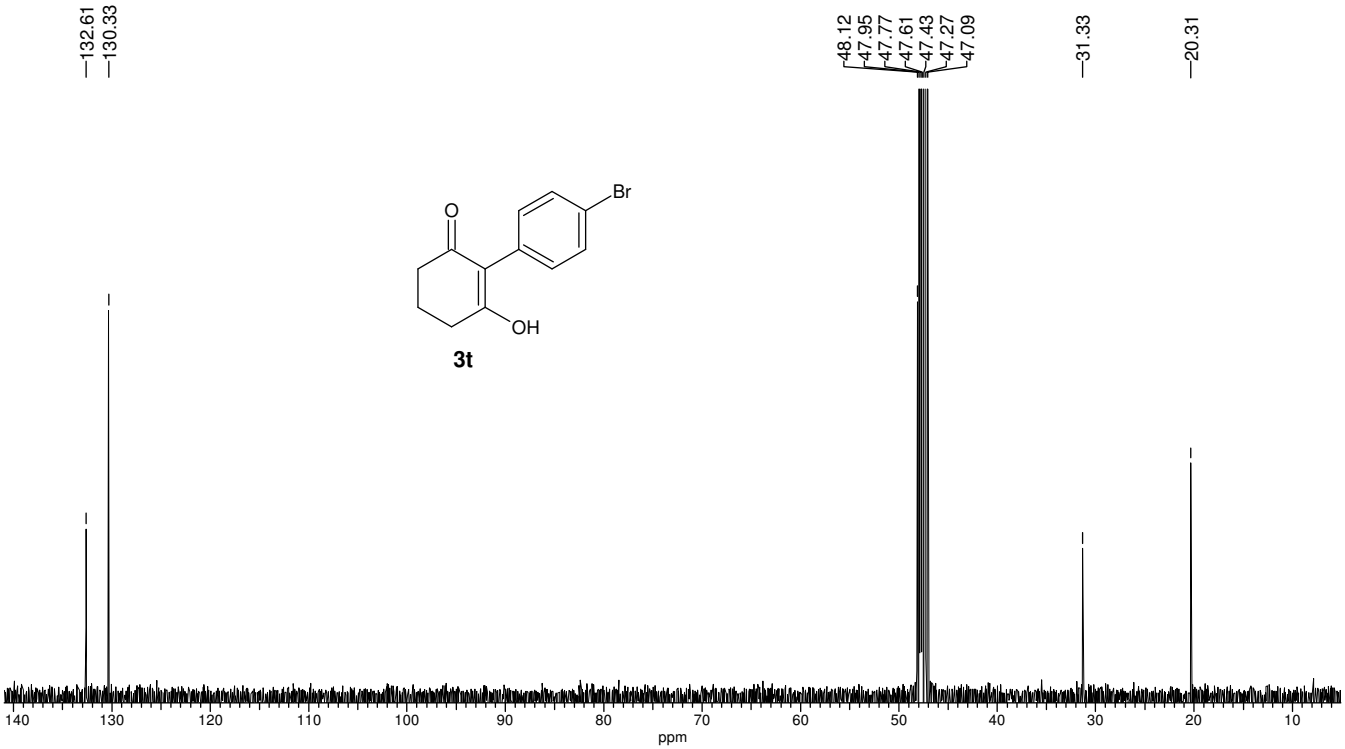
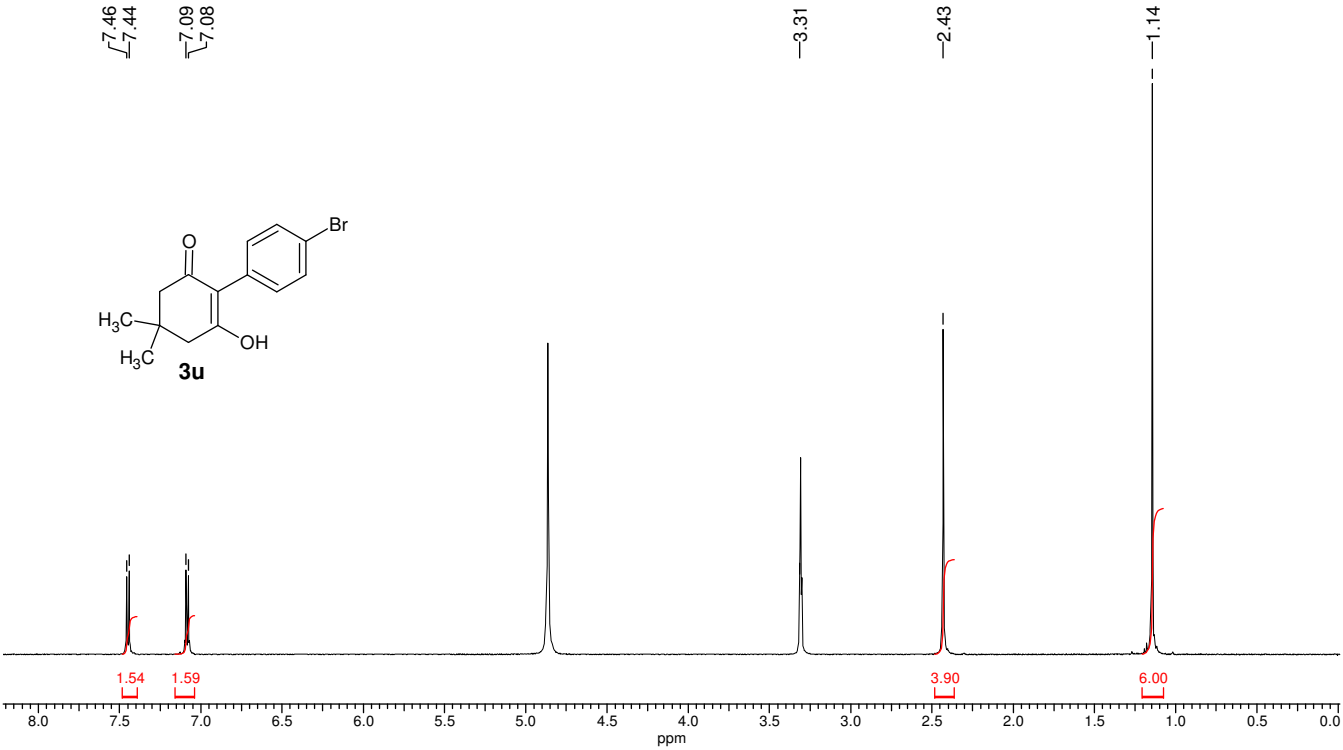
7.07
4.87
3.31
3.31
2.56
2.54
2.53
2.07
2.06
2.05
2.03
2.02
Br
O
OH
3t
1.67
1.70
4.00
2.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


132.61
130.33
48.12
47.95
47.77
47.61
47.43
47.27
47.09
31.33
20.31
Br
O
OH
3t
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.46
7.44
7.09
7.08
3.31
2.43
1.14
Br
O
H3C
H3C
OH
3u
1.54
1.59
3.90
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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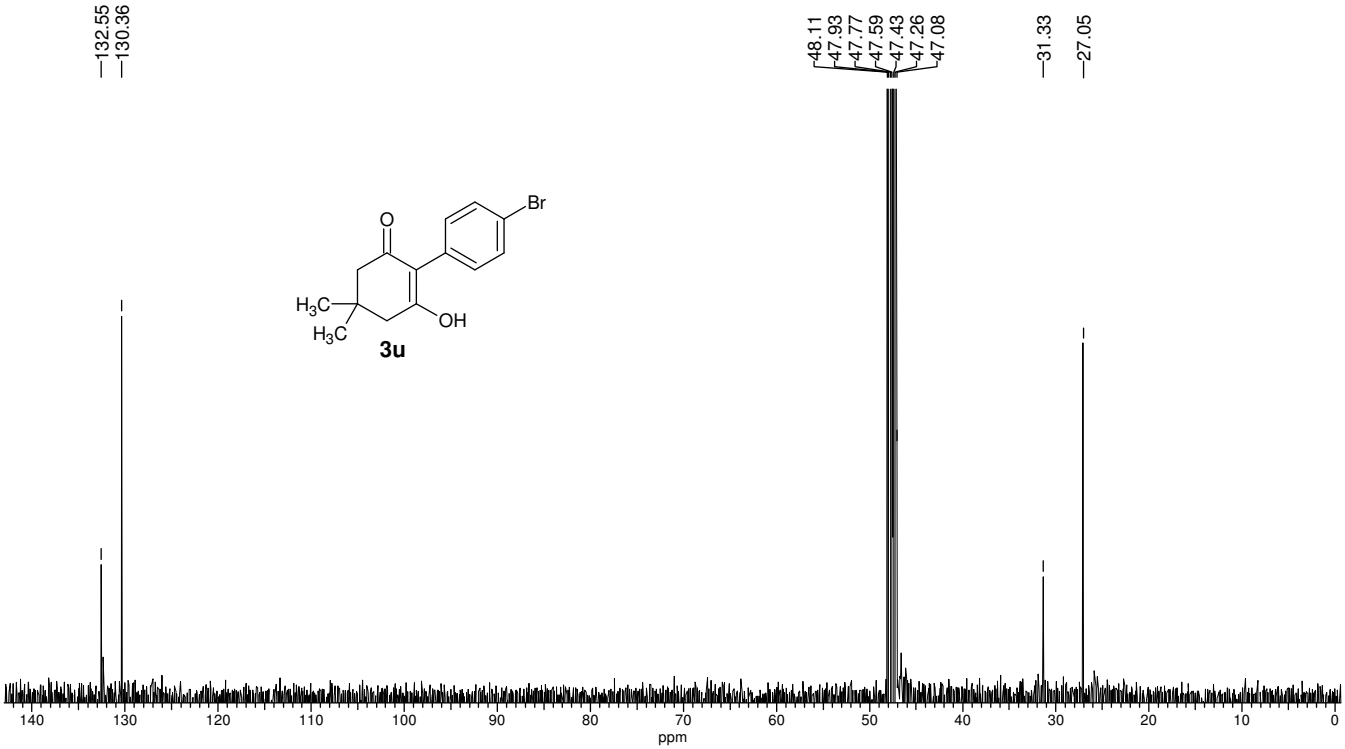
132.55
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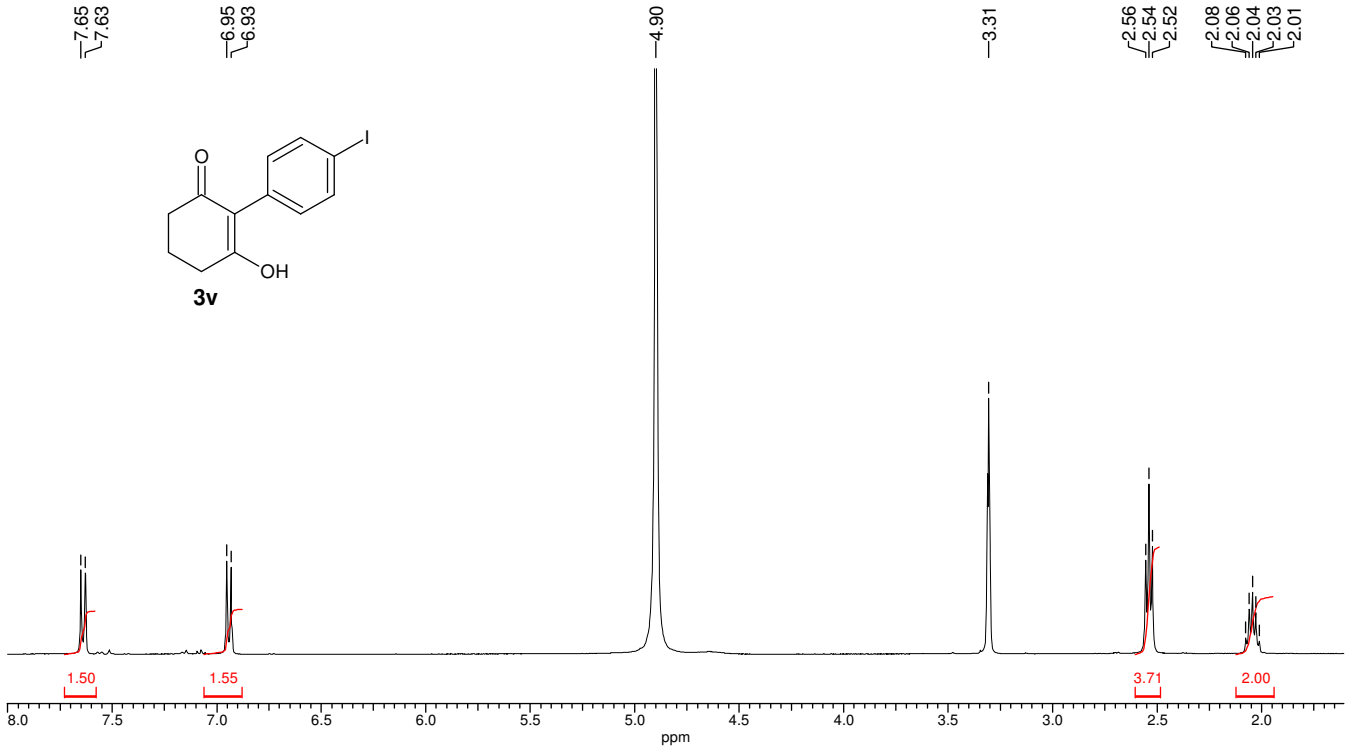
47.93
47.77
47.59
47.43
47.26
47.08
31.33
27.05
Br
O
H3C
H3C
OH
3u
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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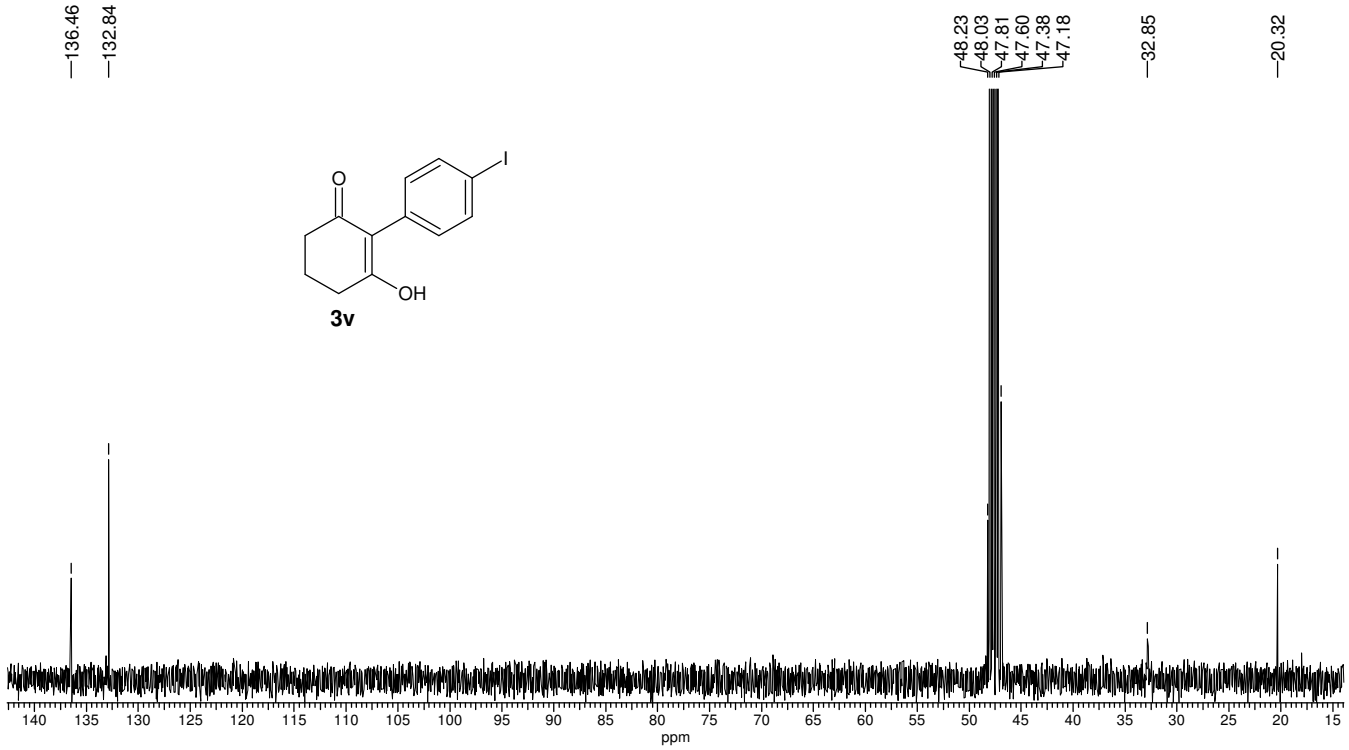
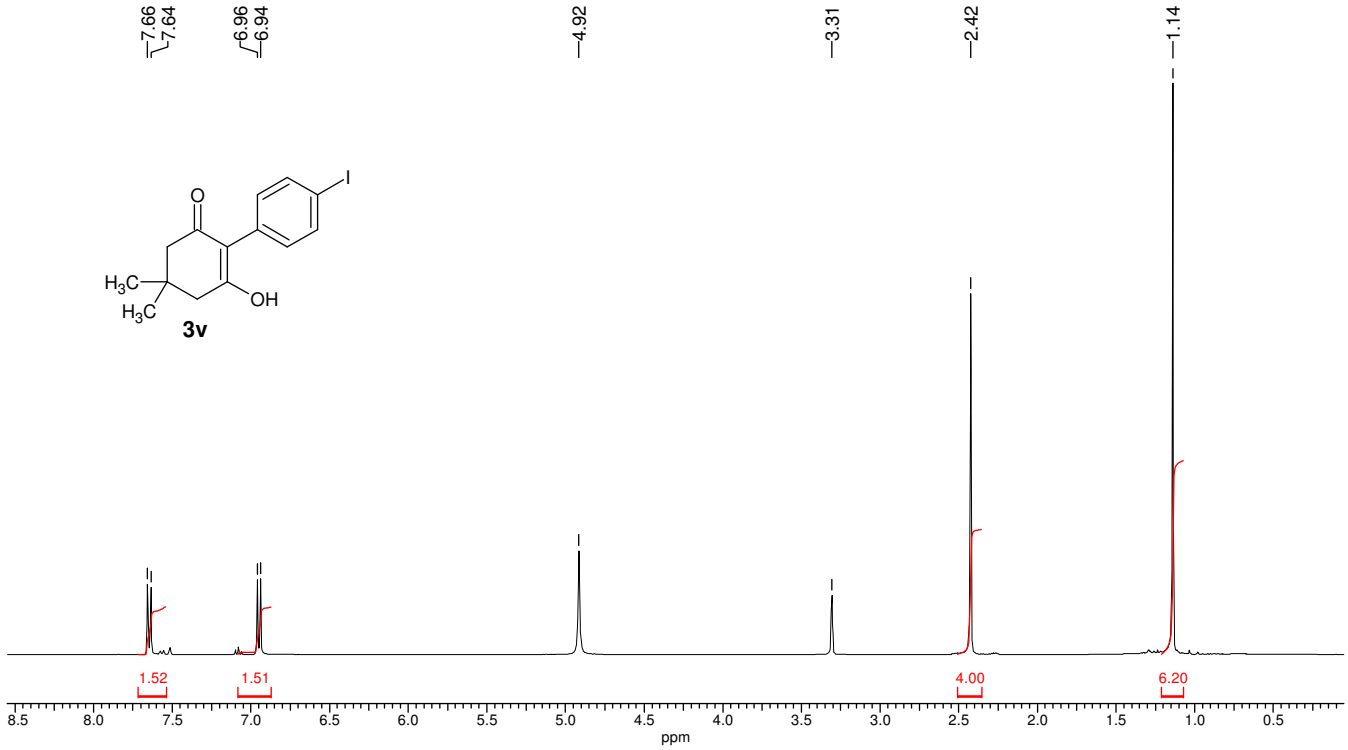
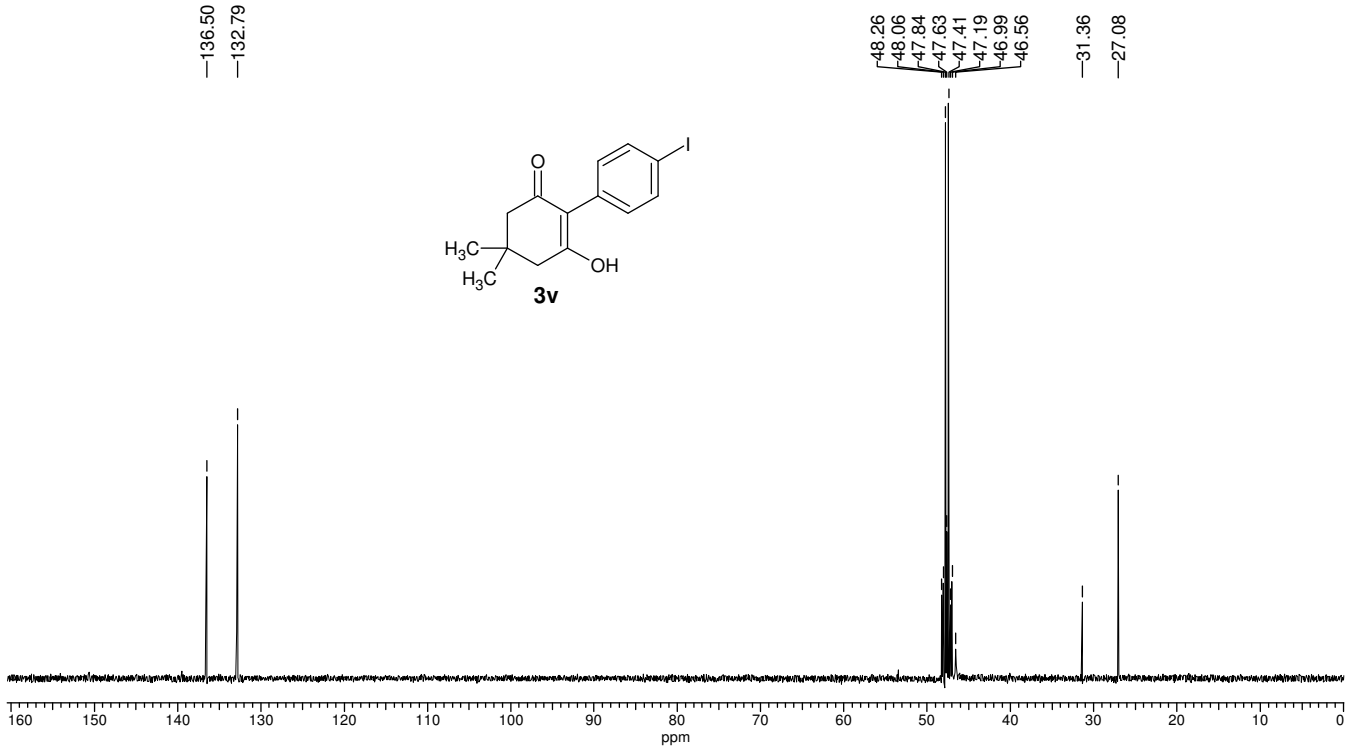
7.63
6.95
6.93
4.90
3.31
2.56
2.54
2.52
2.08
2.06
2.04
2.03
2.01
O
I
OH
3v
1.50
1.55
3.71
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm


136.46
132.84
48.23
48.03
47.81
47.60
47.38
47.18
32.85
20.32
O
I
OH
3v
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
ppm


7.66
7.64
6.96
6.94
4.92
3.31
2.42
1.14
O
I
H3C
H3C
OH
3v
1.52
1.51
4.00
6.20
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


136.50
132.79
48.26
48.06
47.84
47.63
47.41
47.19
46.99
46.56
31.36
27.08
O
I
H3C
H3C
OH
3v
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Computation results: [7]

***Table* 1**

Cartesian Coordinates of all Stationary Points Found in the Potential Energy Surface of the Transition state in gas phase (c).
(B3LYP/6-31G (d,p))

Standard orientation:

Center Number	Atom	Cartesian Coordinates (A^0) X	Y	Z
1	C	1.319031	0.205754	-1.171376
2	C	1.400723	0.621518	0.184332
3	C	1.777599	- 0.220725	1.307327
4	C	2.280331	- 1.619399	0.933481
5	C	2.871196	- 1.691952	-0.476771
6	C	1.866491	- 1.181482	-1.511861
7	O	0.774840	0.893208	-2.066541
8	Cl	0.792886	2.212341	0.528094
9	C	-1.587849	1.763245	-1.140545
10	C	-2.038672	0.588200	-0.521210
11	C	-2.655893	0.624411	0.762192
12	C	-3.154241	-0.531172	1.335901
13	C	-3.034950	-1.755751	0.660597
14	C	-2.406305	-1.822600	-0.589134
15	C	-1.900265	-0.671072	-1.171548
16	C	1.700117	0.123873	2.483983
17	H	1.427347	-2.308648	1.019777
18	H	3.000885	-1.915663	1.701095
19	H	3.171101	-2.718747	-0.714353
20	H	3.779986	-1.079076	-0.521526
21	H	1.014567	-1.872515	-1.586297
22	H	2.304778	-1.118744	-2.512859
23	H	-1.717520	2.720939	-0.651965
24	H	-1.216678	1.755930	-2.153781
25	H	-2.729192	1.573851	1.283516
26	H	-3.627394	-0.494631	2.311656
27	H	-3.420825	- 2.661444	1.118807
28	H	-2.305962	-2.777639	-1.094988
29	H	-1.382968	-0.703907	-2.124531

***Table* 2**

Vibrational frequencies of transition state in gas phase (c).
(B3LYP/6-31G (d,p))

Frequencies --	-150.5655	19.1226	27.7134
Frequencies --	66.4640	85.7484	103.3441
Frequencies --	135.2932	151.1279	214.7916
Frequencies --	241.2972	271.0250	295.9056
Frequencies --	323.4636	351.8588	393.9120
Frequencies --	439.2105	448.2252	482.3840
Frequencies --	527.4660	536.5402	544.1305
Frequencies --	591.6692	599.6230	617.6786
Frequencies --	624.9101	678.4381	690.4341
Frequencies --	776.4574	829.4228	841.4643
Frequencies --	851.0393	871.5947	914.9784
Frequencies --	919.2597	959.4919	979.5046
Frequencies --	987.1495	991.9066	1004.3506
Frequencies --	1008.3666	1012.6571	1045.3921
Frequencies --	1068.0803	1074.7323	1127.6067
Frequencies --	1149.5204	1191.3644	1204.1406
Frequencies --	1205.8077	1263.0134	1294.5672
Frequencies --	1334.5328	1347.2448	1348.6156
Frequencies --	1357.7496	1366.8146	1384.3684
Frequencies --	1394.7570	1472.8174	1483.7338
Frequencies --	1489.9689	1508.9519	1514.4293
Frequencies --	1544.6647	1572.6102	1604.8957
Frequencies --	1644.6926	1724.9535	3021.4679
Frequencies --	3025.3789	3044.1839	3084.4990
Frequencies --	3097.4984	3107.7323	3192.7059
Frequencies --	3200.4172	3207.4028	3211.6945
Frequencies --	3217.4539	3222.2968	3331.3870

***Table* 3**

Cartesian Coordinates of all Stationary Points Found in the Potential Energy Surface of the Transition state in condensed phase (b).
(B3LYP/6-31G (d,p))

Standard orientation:

Center Number	Atom	Coordinates (A^0) X	Y	Z
1	C	-3.438115	-0.094361	0.286469
2	C	-3.759792	1.397956	0.293090
3	C	-2.903782	2.173439	-0.706749

4	C	-1.423119	1.931544	-0.425631
5	C	-1.073446	0.467499	- 0.272405
6	C	-2.033874	-0.464164	- 0.000347
7	O	0.243485	0.304430	- 0.457238
8	Cl	-1.729374	-2.198765	0.002840
9	C	-4.298188	-0.926514	0.531623
10	C	1.027973	-0.775719	0.134264
11	C	2.466684	-0.339357	0.127081
12	C	3.321479	-0.735477	- 0.908213
13	C	4.652750	-0.320293	- 0.926141
14	C	5.141911	0.498041	0.093587
15	C	4.296780	0.898726	1.130441
16	C	2.966604	0.481238	1.145581
17	H	0.662761	-0.948406	1.150642
18	H	0.884568	-1.686449	- 0.447843
19	H	2.939963	-1.371374	- 1.703094
20	H	5.308093	-0.633567	- 1.733164
21	H	6.178402	0.821055	0.081179
22	H	4.674549	1.533286	1.926345
23	H	2.311002	0.793889	1.954575
24	H	-3.578366	1.770712	1.311916
25	H	-4.830819	1.498505	0.100418
26	H	-3.123693	3.244604	- 0.661561
27	H	-3.140371	1.840788	- 1.724962
28	H	-1.115312	2.445881	0.496537
29	H	-0.786107	2.332322	- 1.220514

***Table* 4**

Vibrational frequencies of transition state in condensed phase (b).
(B3LYP/6-31G (d,p))

Frequencies --	- 24.3725	29.6451	55.0593
Frequencies --	72.0706	94.8028	102.9710
Frequencies --	116.3935	140.6518	209.7079
Frequencies --	232.6866	266.3260	291.0942
Frequencies --	317.1488	369.0735	401.8892
Frequencies --	439.7202	450.3982	464.8231
Frequencies --	520.7116	532.0795	547.0102
Frequencies --	593.6870	619.0312	620.2777
Frequencies --	675.7258	686.1053	702.6620
Frequencies --	792.1471	816.0239	838.8943
Frequencies --	867.3890	873.1118	922.3890
Frequencies --	977.0630	982.4622	986.6379
Frequencies --	1006.0446	1018.5574	1021.2472

Frequencies --	1034.4525	1040.7297	1049.2130
Frequencies --	1069.5562	1076.4277	1134.1727
Frequencies --	1147.8104	1198.9777	1204.1089
Frequencies --	1208.9581	1262.9505	1295.3207
Frequencies --	1342.8978	1346.9277	1355.4420
Frequencies --	1364.7354	1367.1780	1399.3754
Frequencies --	1400.6575	1475.0285	1487.9207
Frequencies --	1488.3384	1508.9079	1511.9960
Frequencies --	1555.6680	1595.6843	1614.4373
Frequencies --	1645.7150	1702.2622	3021.2529
Frequencies --	3024.5073	3026.4711	3063.9500
Frequencies --	3090.5172	3098.4511	3142.7435
Frequencies --	3197.4621	3200.5268	3206.8138
Frequencies --	3219.7430	3225.7596	3267.7570

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