Supporting Information

A Titanium-Mediated Rearrangment of Cyclopropenylmethyl Acetates to *(E)*-Halodienes

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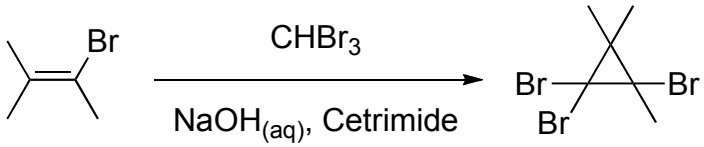
General Procedures

Unless otherwise stated all reactions were carried out under an argon or nitrogen atmosphere in flame-dried glassware. Reactions were monitored by TLC using glass-backed silica gel XHL plates (purchased from Sorbtech with UV 254, thickness 250 ⌈m) or by GC and GC/MS on an Agilent 7890 (FID detector and HP-5 column 30 m x 0.32 mm 0.25 micron, part number: 19091j-413) and Varian 3900/Saturn 2100T (ion-trap mass-selective detector and, FactorFour capillary column VF-5ms, 30m x 0.25 micrometers, Part number: cp8944) respectively. Compounds were purified using flash column chromatography with Sorbtech silica gel or by radial chromatography with a Chromatotron®. Chromatography plates employed on the Chromatotron® were 1 mm or 2 mm prepared from a mixture of calcium sulfate hemihydrate and Aldrich Silica gel (TLC standard grade, without binder, with fluorescent indicator). NMR spectra were recorded on a BrukerAvance DRX-400 (400 MHz) in $CDCl_3$ unless otherwise noted. $CDCl_3$ was stored over K_2CO_3 or 4Å molecular sieves and was purchased from Acros. Melting points are uncorrected and measure on a Thomas Hoover Unimeltcapillary melting point apparatus. IR spectra were recorded on a Thermo electron corporation Nicolet 380 FT-IR as films on NaCl plates (liquids) or in a NaCl solution cells (solids). Accurate mass measurements were recorded at the University of California, Riverside High Resolution Mass Spectrometry Facility and at the University of California, Irvine. X-ray analyses were carried out at the W.M. Keck Foundation Center for Molecular Structure in California State University, Fullerton. *n*BuLi was purchased from Strem and titrated against diphenylacetic acid prior to use. Other reagents were commercially available and used without further purification.

Synthesis of Starting Materials

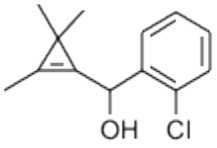


1,1,2-Tribromo-2,3,3-trimethylcyclopropane:[1] 2-bromo-3-methylbut-2-ene (10 mL, 86.15 mmol, 1.0 equiv) and bromoform (143 mL, 1637 mmol, 19 equiv) were mixed together. Solid NaOH (43.9 g, 1077 mmol, 12.5 equiv) was then dissolved in water (43 mL). The resulting NaOH solution was added to the

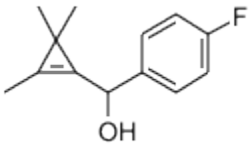
[1] Prepared according to the procedure reported by Baird and co-workers: Baird, M. S.; Hussain, H. H.; Nethercott, W. *J. Chem. Soc. Perkin Trans.* **1986**, *1*, 1845

bromoform solution followed by centrimide (1.28 g) and a condenser fitted to the flask. The mixture was then heated to 65 ^{o}C and allowed to stir at that temperature for 3 hours. After cooling, the organic layer was separated and the aqueous phase extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were washed with water (100 mL), dried ($MgSO_4$) and evaporated to dryness. The crude product was then recrystallized from hot EtOH employing charcoal to decolorize the solution. In total three crops of crystals were collected (16.0 g, 49.97 mmol, 58% yield). Spectroscopic data was in agreement with the literature[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 3H), 1.54 (3, 3H), 1.39 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 51.5, 51.0, 33.0, 27.0, 26.6, 20.9.

General preparation of cyclopropenyl alcohols: To a flame-dried Schlenk flask was added 1,1,2-tribromo-2,3,3-trimethylcyclopropane (2.0 g, 6.2 mmols, 1.0 equiv.). The flask was then evacuated and filled with argon and then diethyl ether (12 ml) was added. The resulting solution was cooled to -78^{o}C in a dry ice-acetone bath and *n*-butyllithium (11.8 ml of a 1.56 M solution in hexane, 11.8 mmols, 1.9 equiv) added dropwise. After 10 mins at -78^{o}C the reaction was warmed to -10^{o}C by replacing the dry ice-acetone bath with an ice-acetone bath. After 1 h the reaction was cooled again to -20^{o}C and the aldehyde (7.4 mmols, 1.2 equiv) added dropwise. The cooling bath was then removed and the reaction allowed to warm to rt and the reaction monitored by TLC. Reactions were generally complete in 2 h and were quenched by addition of NH_4Cl (20 ml of a saturated aqueous solution). The organic phase was separated and the aqueous phase extracted with diethyl ether (3 x 20 ml) and the combined organics dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography (90:10 hexanes: ethyl acetate) was then carried out on SiO_2 pretreated with the eluant and ~1% Et_3N.

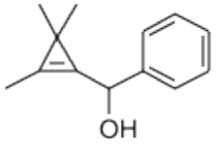


(2-chlorophenyl)(2,3,3-trimethylcycloprop-1-enyl)methanol was obtained as a clear oil (230 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.35 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.30 (dt, *J* = 2.0, 8.0 Hz, 1H), 7.22 (dt, *J* = 2.0, 8.0 Hz, 1H), 6.05 (br s, 1H), 2.19 (d, *J* = 4.0 Hz, 1H), 1.97 (d, *J* = 1.5 Hz, 3H), 1.09 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.37, 131.97, 129.40, 128.64, 127.55, 127.01, 123.97, 123.91, 67.84, 25.69, 25.29, 22.38, 8.69. IR 3598 cm^{-1}. HRMS-ESI (*m/z*): $(M + H)^{+}$calcd for $C_{13}H_{15}ClO$, 222.0811; found, 223.0876.

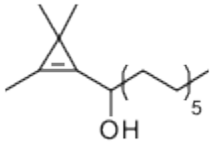


(4-fluorophenyl)(2,3,3-trimethylcycloprop-1-enyl)methanol was obtained as a pale yellow oil (560 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 12, 4 Hz, 2H), 7.09 – 7.02 (m, 2H), 5.66 (s, 1H), 2.16 (br s, 1H), 2.00 (d, *J* = 1.5 Hz, 3H), 1.13 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) 161.8 (d,

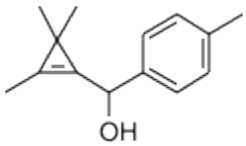
J = 242 Hz) 137.9, 128.0 (d, *J* = 8.5 Hz), 124.9, 123.8, 115.0 (d, *J* = 22 Hz) 69.9, 25.5, 21.9, 8.5. IR 3368 cm^{-1} HRMS-ESI (*m/z*): $(M - H)^+$calcd for $C_{13}H_{15}FO$, 205.1029 found, 205.1023.



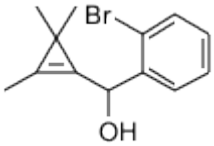
phenyl(2,3,3-trimethylcycloprop-1-enyl)methanol was obtained as a yellow oil (523 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 4H), 7.34 – 7.29 (m, 1H), 5.69 (s, 1H), 2.27 (br s, 1H), 2.02 (d, *J* = 1.5 Hz, 3H), 1.16 (s, 3H), 1.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 128.4, 127.6, 126.3, 125.0, 123.4, 70.7, 25.6, 21.9, 8.6. IR 3368 cm^{-1}. In agreement with reported data.[2]



1-(2,3,3-trimethylcycloprop-1-enyl)dodecan-1-ol was obtained as a clear oil (280 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.61 (t, *J* = 6.0 Hz, 1H), 2.01 (d, *J* = 1.5 Hz, 3H), 1.67-1.60 (m, 2H), 1.43-1.27 (m, 18H), 1.13 (s, 6H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 125.33, 121.63, 68.70, 36.56, 31.89, 29.62, 29.61, 29.58, 29.56, 29.32, 25.98, 25.71, 25.31, 22.64, 21.09, 14.00, 8.63. IR 3367 cm^{-1}. HRMS-ESI (*m/z*): $(M + H)^+$ calcd for $C_{18}H_{34}O$, 265.2526; found, 265.2523.



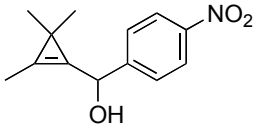
***p*-tolyl(2,3,3-trimethylcycloprop-1-enyl)methanol** was obtained as a pale yellow oil (870 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.0, 2H), 7.20 (d, *J* = 8.0, 2H), 5.65 (s, 1H), 2.39 (s, 3H), 2.03 (d, *J* = 1.4, 3H), 1.17 (s, 3H), 1.11 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) 139.22, 137.26, 129.07, 126.4, 125.04, 123.05, 70.55, 25.76, 25.54, 21.82, 21.16, 8.64. IR 3366 cm^{-1} HRMS-ESI (*m/z*): $(M + H)^+$calcd for $C_{14}H_{17}O$, 201.1274; found 201.1270.



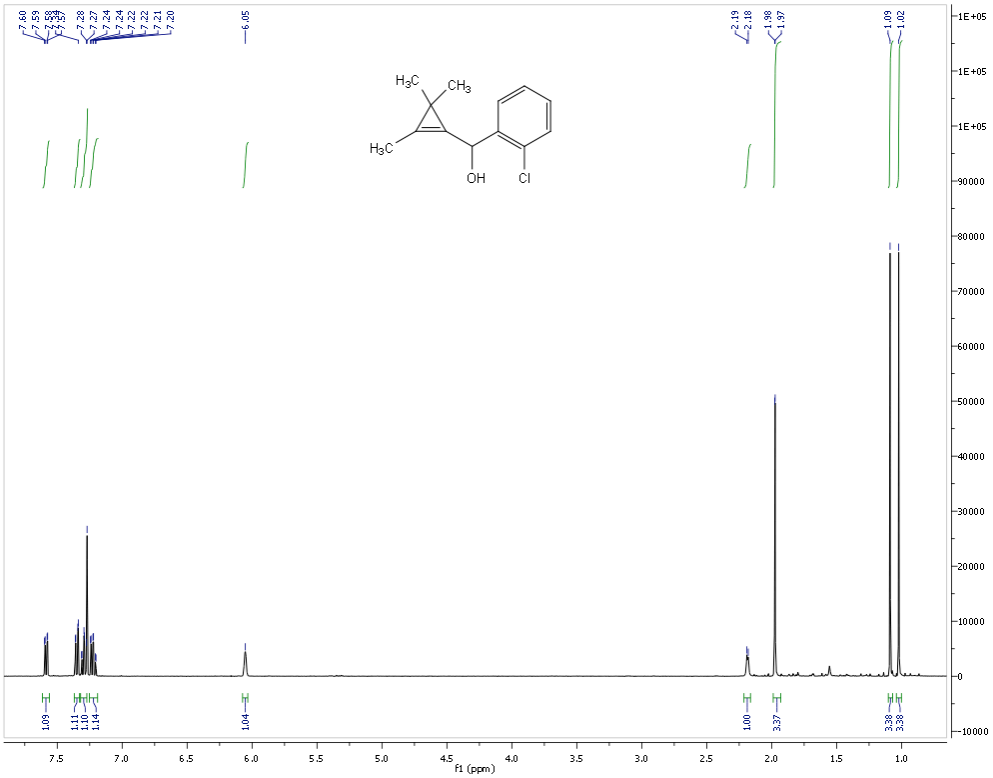
(2-bromophenyl)(2,3,3-trimethylcycloprop-1-enyl)methanol was obtained as a clear oil (1.49 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.55 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.34 (dt, *J* = 8.0, 1.5 Hz, 1H), 7.15

[2] Samah, S.; Masarwa, A.; Zohar, E.; Stanger, A.; Bertus, P.; Marek, I. *Chem.-Eur. J.* **2009**, *15*, 8449.

(dt, *J* = 8.0, 2.0 Hz, 1H), 6.03 (s, 1H) 2.36 (br s, 1H), 1.99 (d, *J* = 1.5 Hz, 3H), 1.10 (s, 3H). 1.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 132.7, 129.0, 127.8, 127.6, 124.0, 123.9, 121.9, 70.1, 25.7, 25.3, 22.3, 8.7. IR 3368, 1855, 749 cm^{-1}. HRMS-ESI (*m/z*): $(M + H)^+$calcd for $C_{13}H_{15}BrO$, 265.0223; found, 265.0226.



(4-nitrophenyl)(2,3,3-trimethylcycloprop-1-enyl)methanol was obtained as a yellow solid (800 mg, 95%). Mp: 61.0-62.0 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 9.0 Hz, 2H), 7.60 (d, *J* = 9.0 Hz, 2H), 5.80 (s, 1H), 2.20 (br s, 1H), 1.99 (d, *J* = 1.5 Hz, 3H), 1.11 (s, 3H), 1.05 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 147.4, 128.8, 125.0, 124.2, 123.7, 69.7, 25.6, 22.1, 8.6. IR 3598, 1605, 1525, 1347 cm^{-1}. HRMS-ESI (*m/z*): $(M + H)^+$calcd for $C_{13}H_{16}NO_3$, 234.1125; found, 234.1132.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1.97
1.09
1.02
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CH3
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Cl
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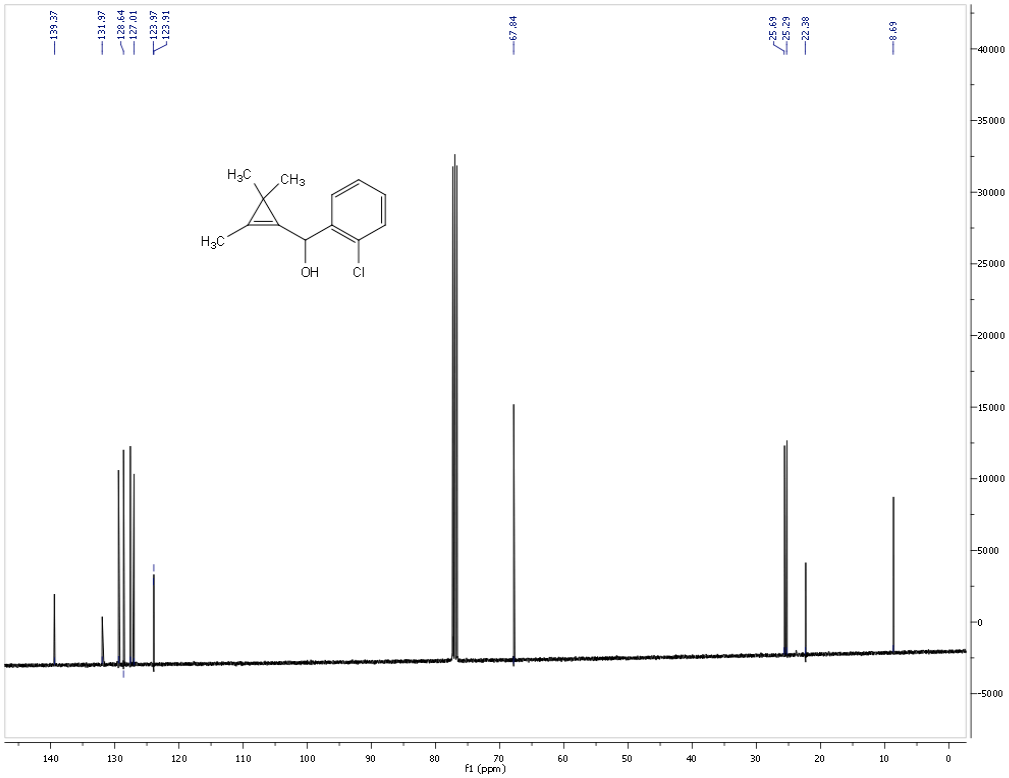
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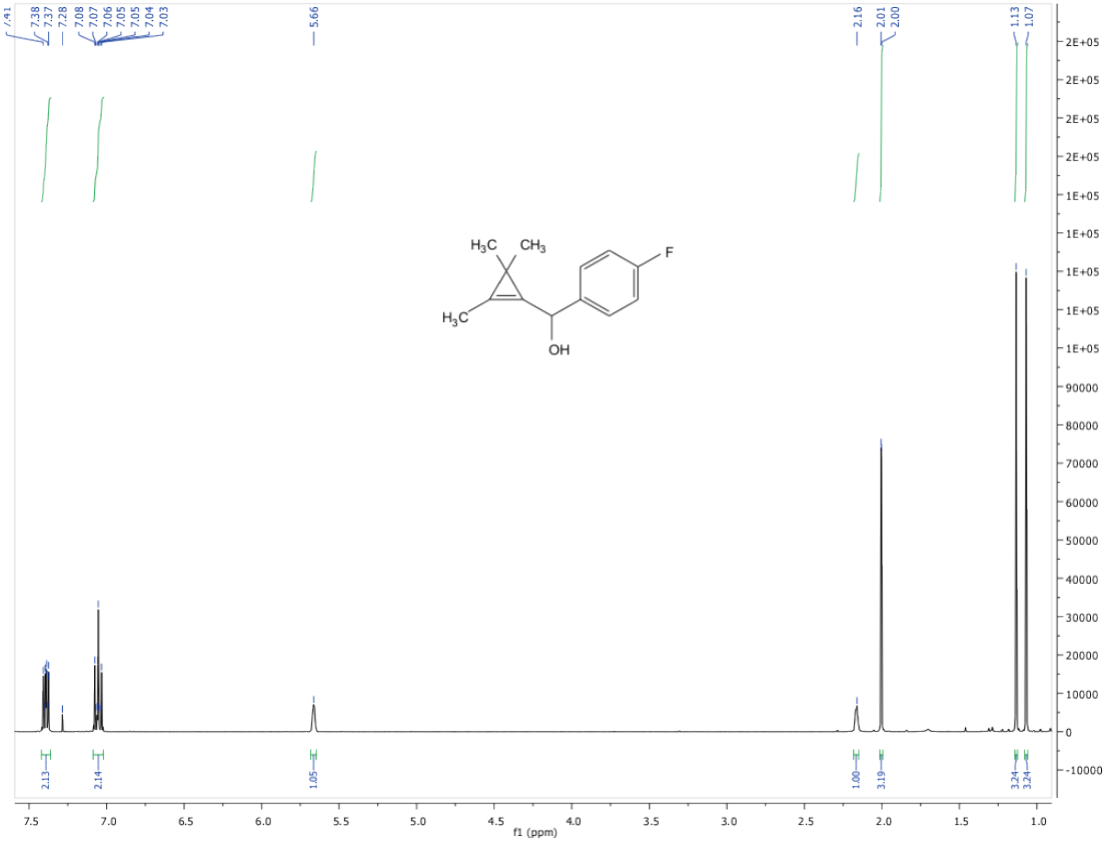
OH
Cl
f1 (ppm)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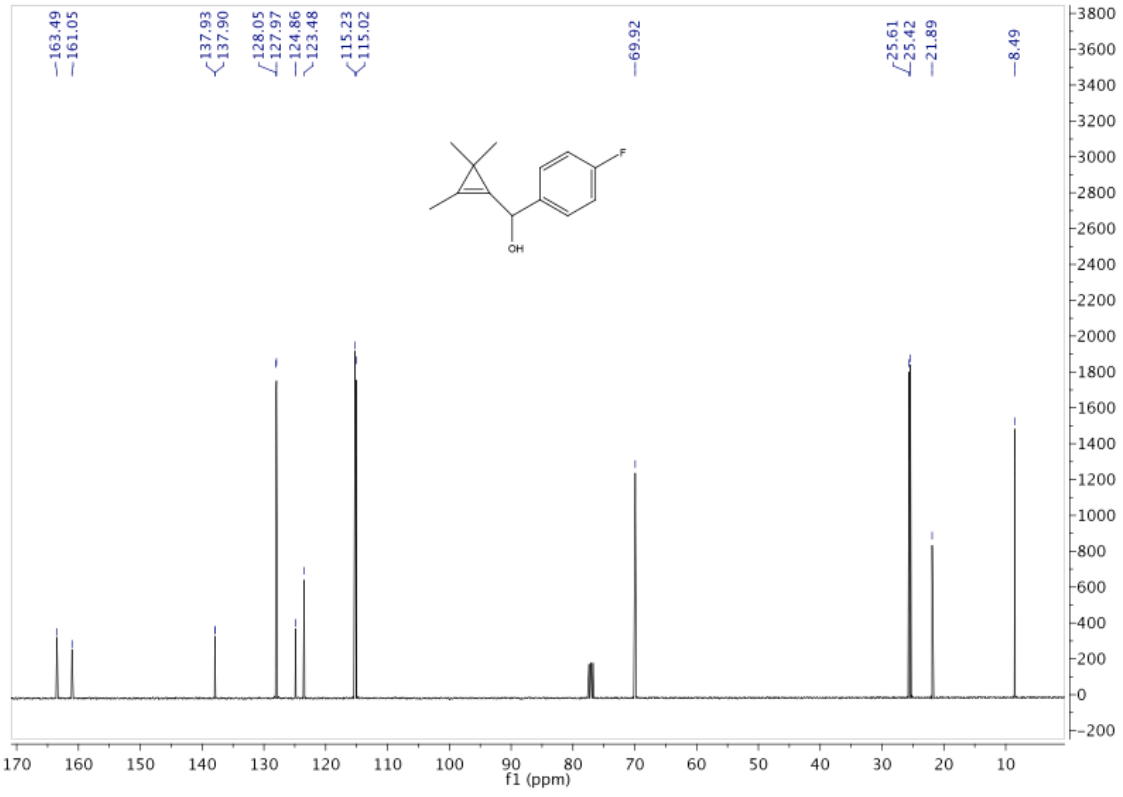
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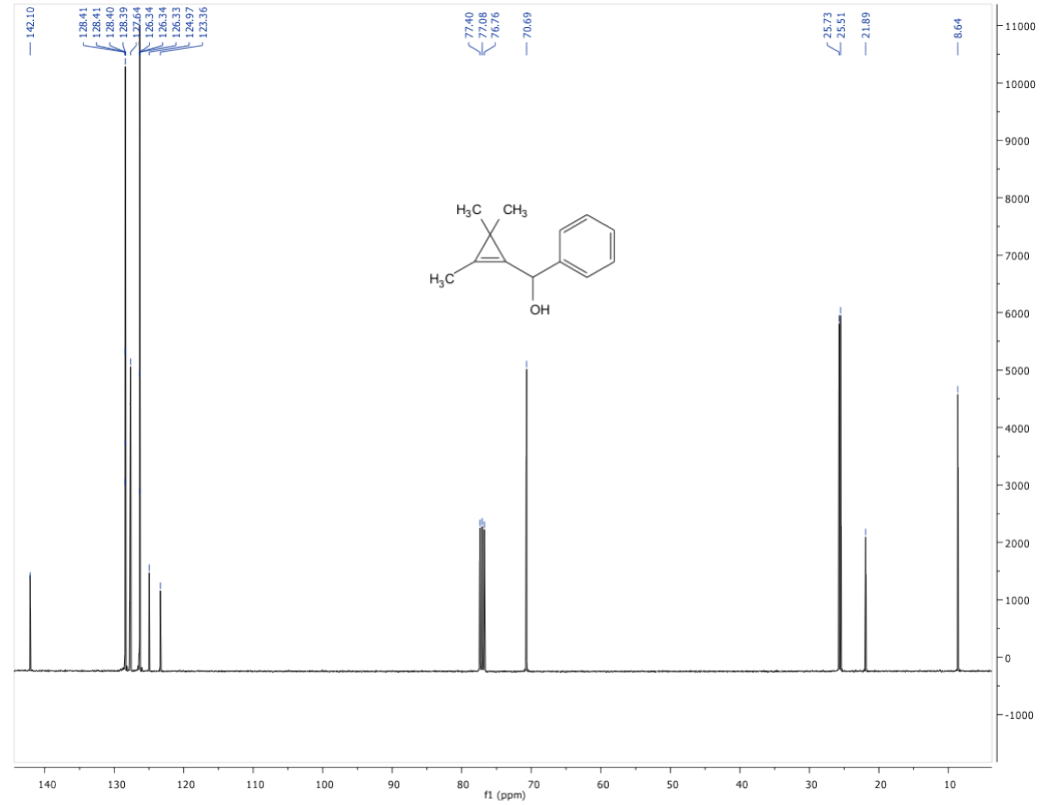
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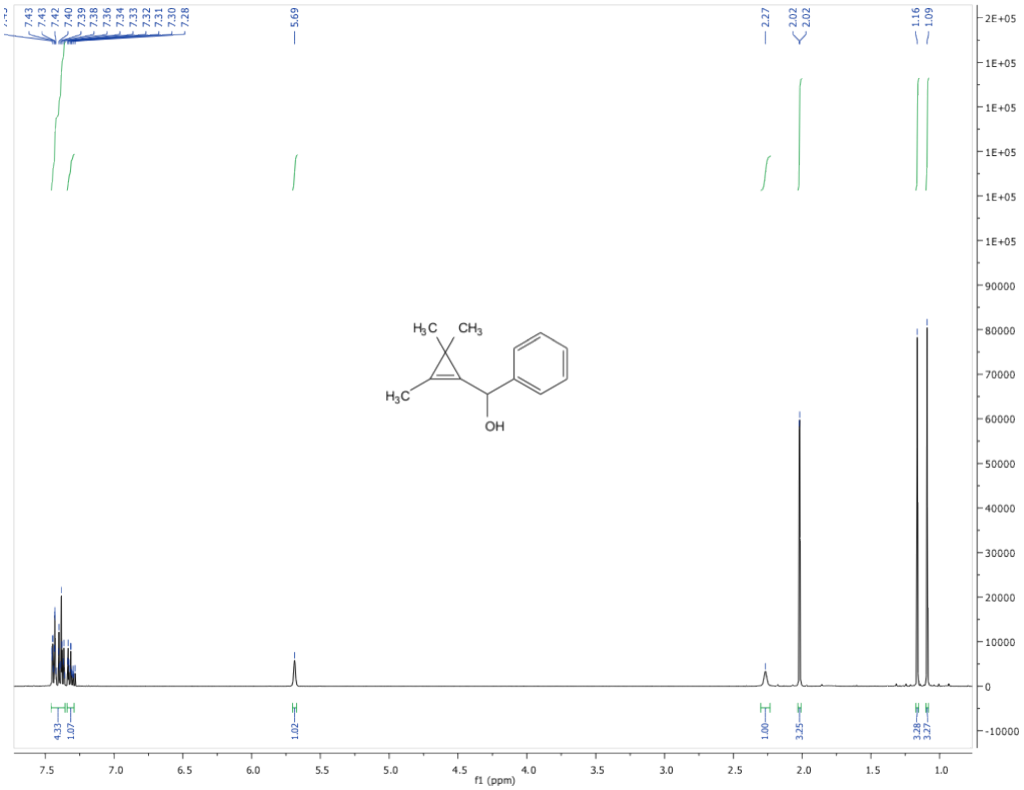
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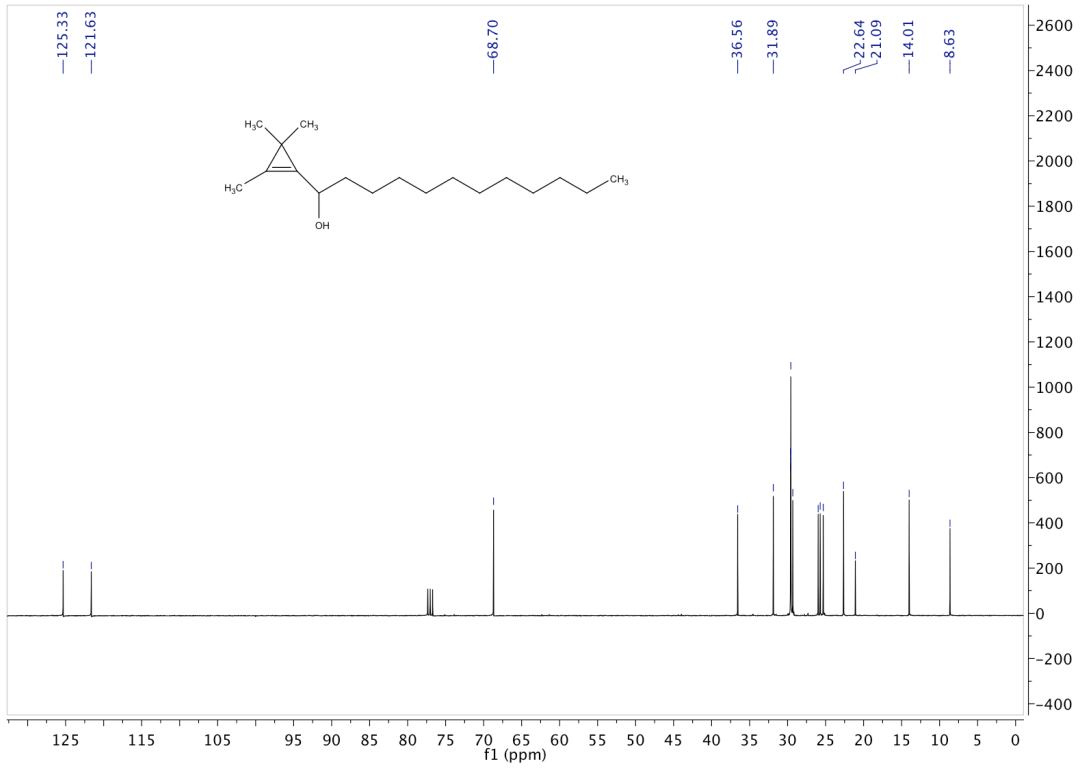
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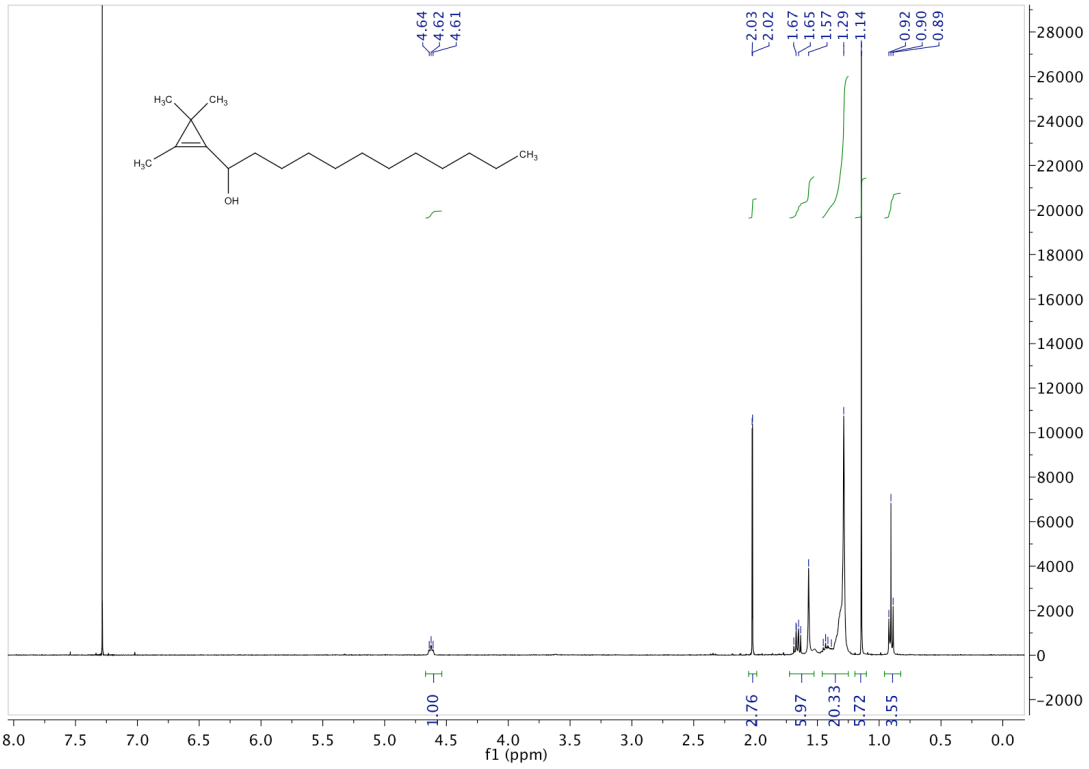
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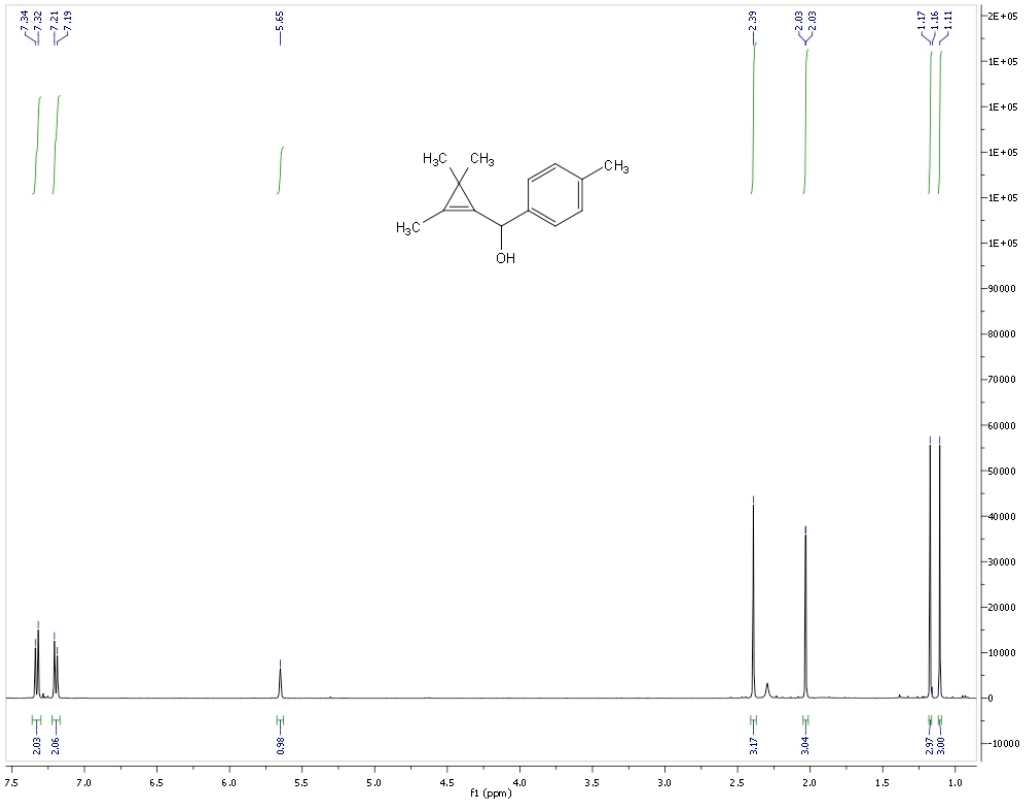
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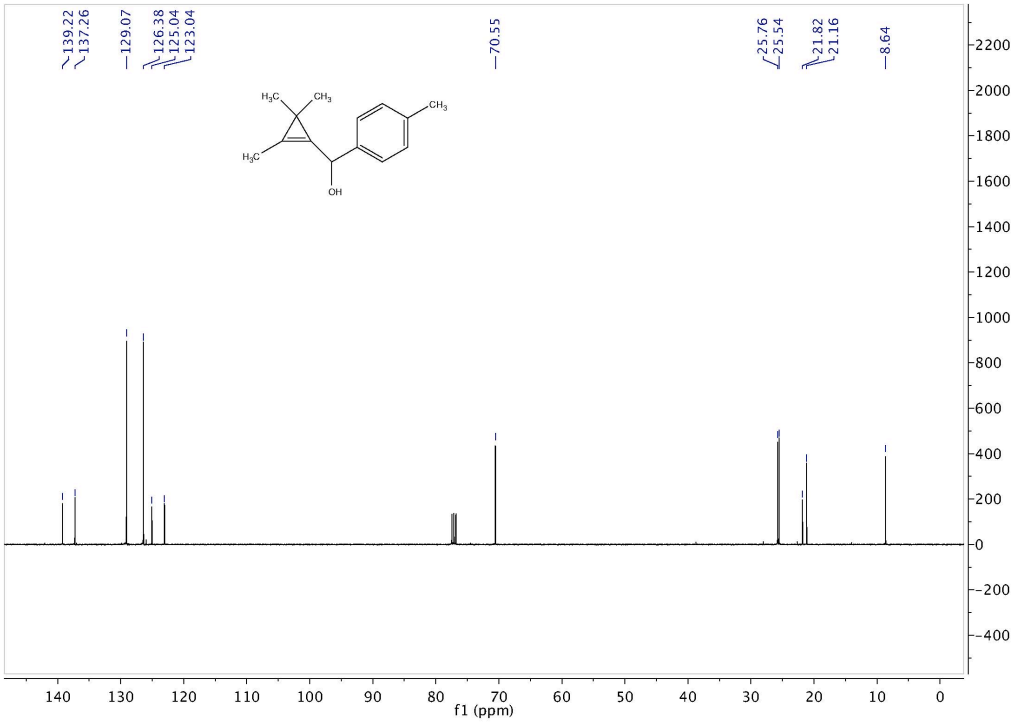
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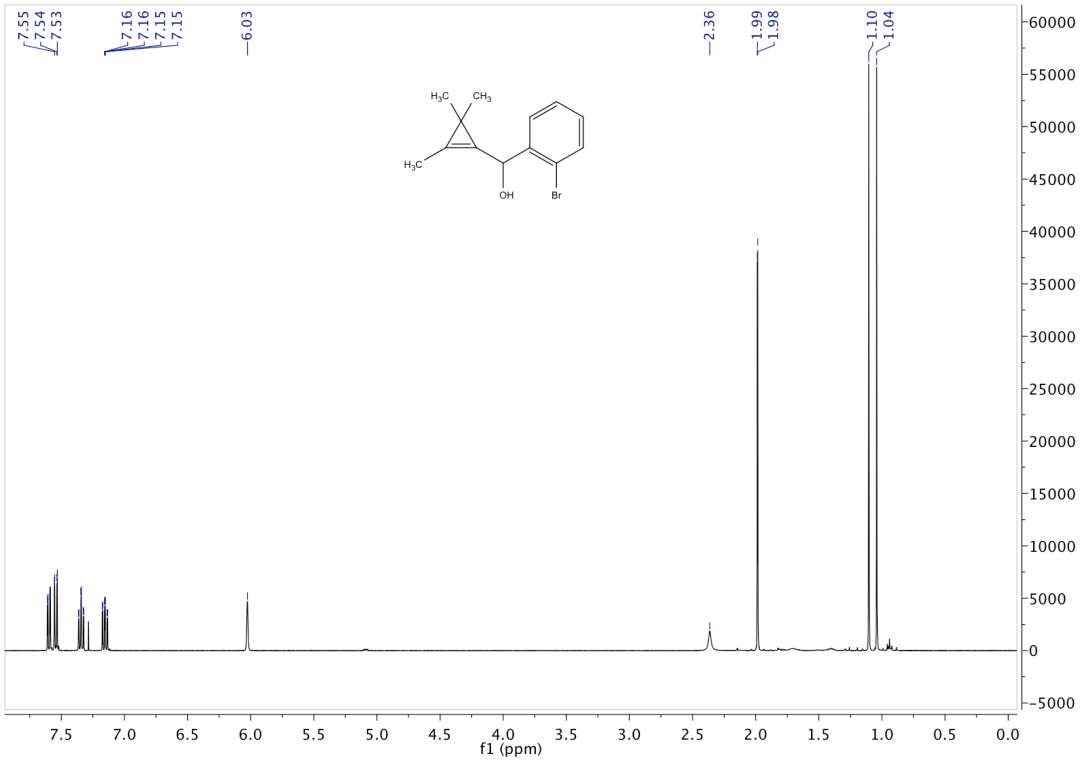
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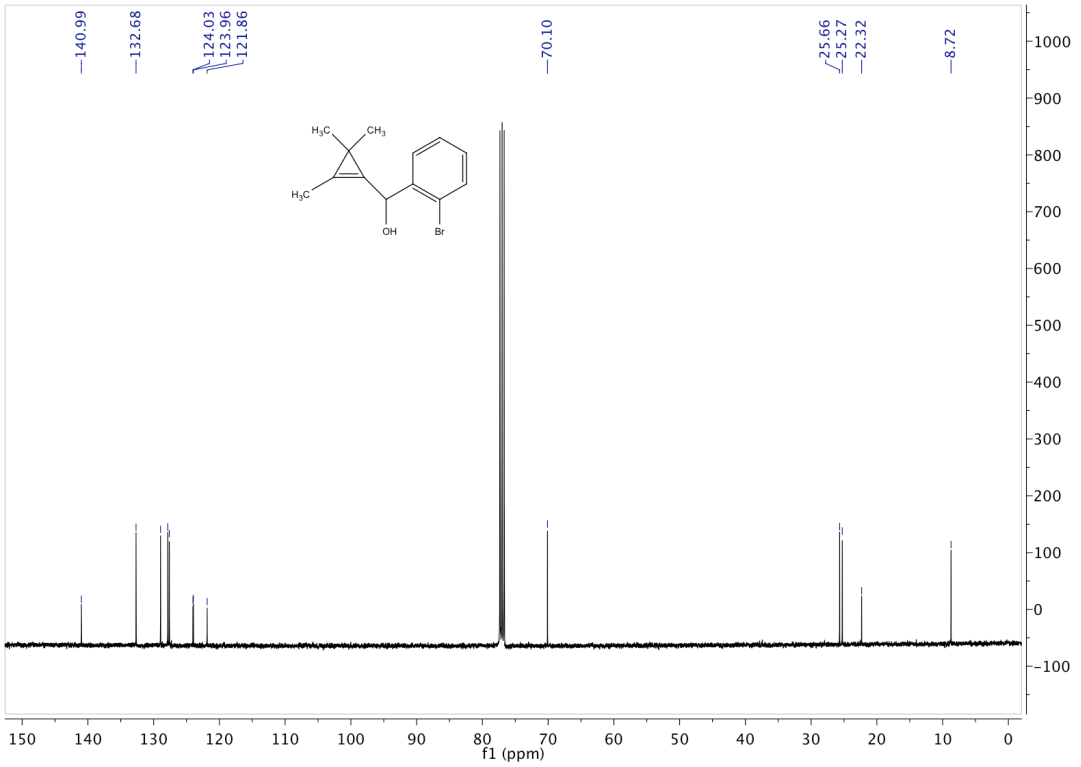
Br
f1 (ppm)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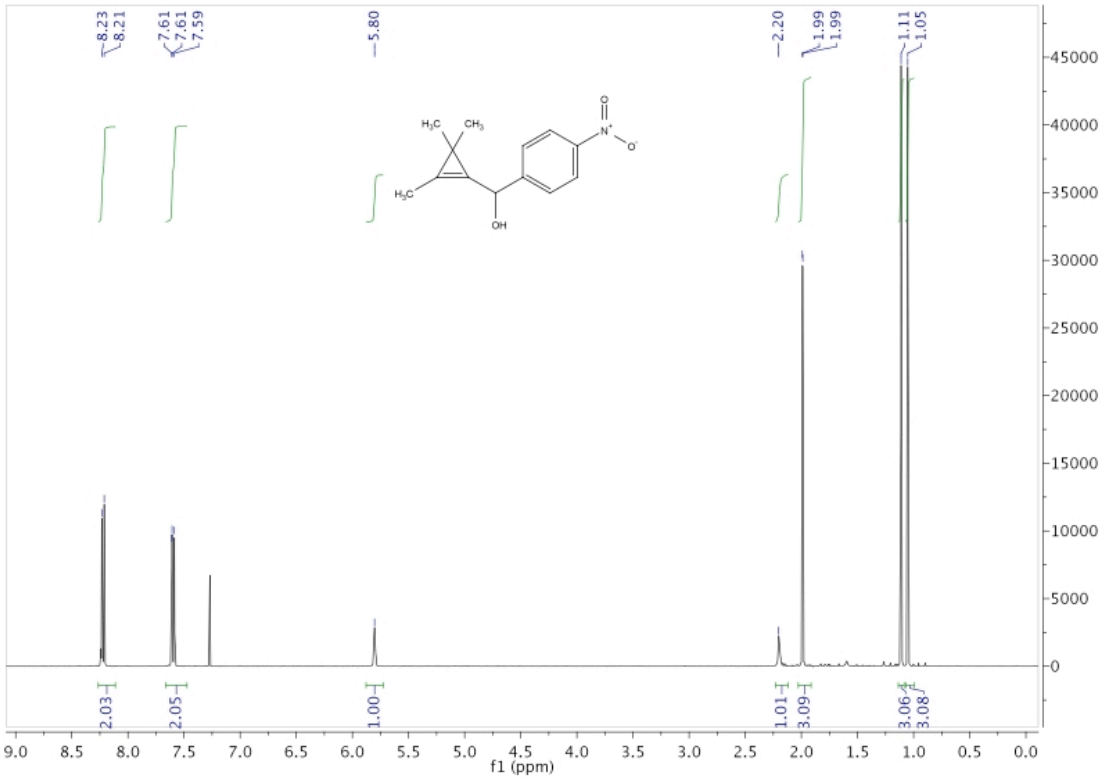
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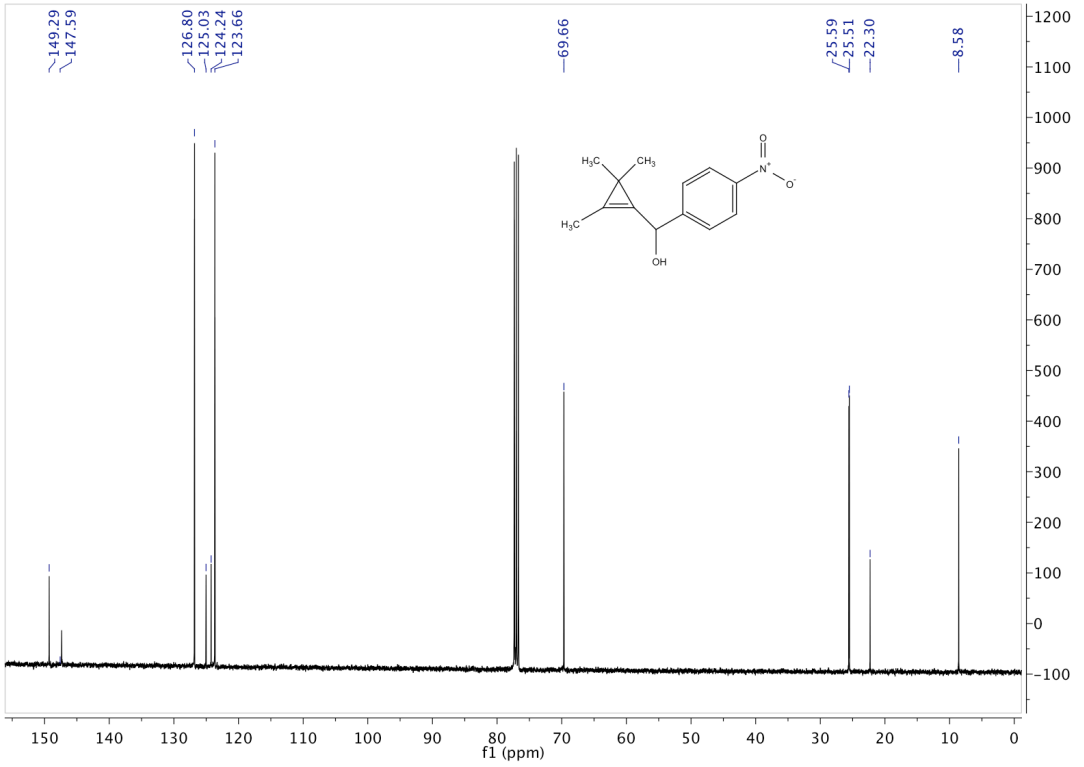
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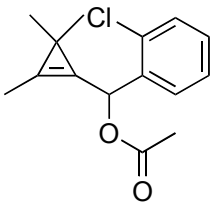
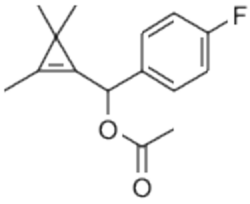
123.66
69.66
25.59
25.51
22.30
8.58
f1 (ppm)

General preparation of cyclopropenyl acetates:

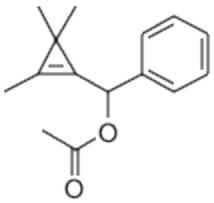
The cyclopropenyl acetate (0.79 mmol) is dissolved in pyridine (1 ml) and cooled to 0°C with an ice-bath. Acetic anhydride (0.5 ml) is then added dropwise and the ice-bath removed. After the reaction is shown to be complete by TLC (typically 1 h), it is poured into ice-water (5 ml) and diethyl ether (15 ml) added. This mixture is stirred for 30 min, the organic layer separated and the aqueous extracted with diethyl ether (3 x 10 ml). The combined organics were washed with copper sulfate (15 ml of a sat. aq. soln.), sodium bicarbonate (15 ml of a sat. aq. soln.), dried ($MgSO_4$). Evaporation to dryness in most cases gave analytically pure acetate.



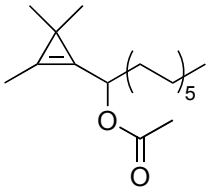
(2-chlorophenyl)(2,3,3-trimethylcycloprop-1-enyl)methanol 1d was obtained as a clear oil (28 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.42 (m, 1H), 7.39-7.37 (m, 1H), 7.29-7.25 (m, 2H), 7.01 (q, *J* = 1.5 Hz, 1H), 2.14 (s, 3H), 1.94 (d, *J* = 1.5 Hz, 3H), 1.07 (s, 3H), 1.02 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 136.1, 132.5, 129.6, 129.2, 128.3, 126.9, 125.8, 121.6, 68.9, 25.5, 25.1, 22.7, 21.0, 8.73.IR 1740 cm^{-1}. HRMS-ESI (*m/z*): $(M + H)^+$ calcd for $C_{18}H_{32}O_2$, 265.0990; found, 265.0994.



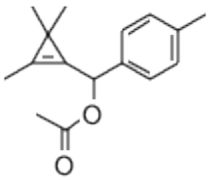
(4-fluorophenyl)(2,3,3-trimethylcycloprop-1-enyl)methylacetate 1f was obtained as a yellow oil (475 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.10 – 7.03 (m, 2H), 6.63 (d, *J* = 1.5 Hz, 1H), 2.11 (s, 3H), 1.96 (d, *J* = 1.5 Hz, 3H), 1.11 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 162.6 (d, *J* = 196 Hz), 134.2, 129.3 (d, *J* = 32 Hz), 125.74, 122.36, 115.3 (d, *J* = 84 Hz), 71.29, 25.5, 25.2, 22.4, 21.1, 8.6. IR 2922, 1758, 1203 cm^{-1}. HRMS-ESI (*m/z*): $(M + H)^+$ calcd for $C_{15}H_{18}O_2F$, 249.1285, found 249.1287.



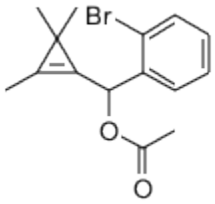
phenyl(2,3,3-trimethylcycloprop-1-enyl)methyl acetate 1b was obtained as a yellow oil (386 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.28 (m, 5H), 6.68 (s, 1H), 2.13 (s, 3H), 1.97 (d, *J* = 0.5 Hz, 3H), 1.13 (s, 3H), 1.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) 170.1, 138.3, 128.4, 128.2, 127.4, 125.4, 122.6, 71.9, 25.4, 22.4, 21.1, 8.6. IR 1743, 1230 cm^{-1}. HRMS-ESI (*m/z*): $(M + H)^+$calcd for $C_{15}H_{19}O_2$, 231.1380, found 231.1384.



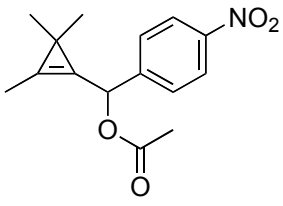
1-(2,3,3-trimethylcycloprop-1-enyl)dodecyl acetate 1g was obtained as a clear oil (280 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62 (dt, *J* = 7.0, 1.5 Hz, 1H), 2.06 (s, 3H), 1.97 (d, *J* = 1.5 Hz, 3H), 1.7-1.69 (m, 2H), 1.38-1.27 (m, 18H), 1.09 (s, 3H), 1.08 (s, 3H), 0.89 (t, *J* = 7.0 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 123.6, 122.6, 80.7, 33.4, 31.9, 29.6, 29.5, 29.5, 29.4, 29.3, 25.7, 25.6, 25.2, 22.7, 21.1, 21.7, 14.0, 8.6. IR 1744 cm^{-1}. HRMS-ESI (*m/z*): (M + H)$^+$calcd for $C_{20}H_{36}O_2$ 309.2788; found, 309.2791.



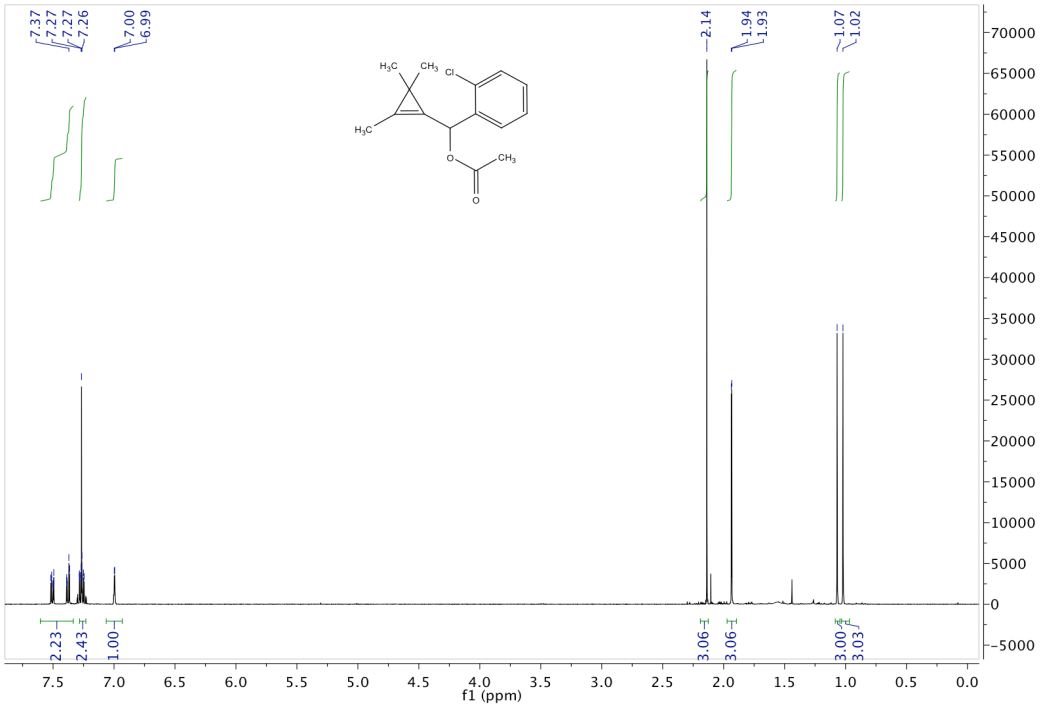
***p*-tolyl(2,3,3-trimethylcycloprop-1-enyl)methyl acetate 1c** was obtained as a pale yellow oil (440 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 2H), 7.23 – 7.11 (m, 2H), 6.63 (d, *J* = 1.5 Hz, 1H), 2.37 (d, *J* = 7.0 Hz, 3H), 2.10 (s, 3H), 2.00 – 1.95 (m, 3H), 1.12 (s, 3H), 1.07 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 170.07, 138.00, 135.34, 129.12, 127.50, 125.20, 122.60, 76.83, 71.83, 25.60, 25.29, 22.30, 21.17, 21.14, 8.64. IR 1742, 1232 cm^{-1}. HRMS-ESI (*m/z*): (M + H)$^+$calcd for $C_{16}H_{20}O_2$, 245.1542, found 245.1536.



(2-bromophenyl)(2,3,3-trimethylcycloprop-1-enyl)methyl acetate 1e was obtained as a clear oil (208 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.0 1.5 Hz 1H), 7.51 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.36 – 7.28 (m, 1H), 7.21 – 7.14 (m, 1H), 6.95 (d, *J* = 1.5 Hz, 1H), 2.14 (s, 3H), 1.94 (d, *J* = 1.5, 3H), 1.08 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.63, 137.80, 132.86, 129.43, 128.50, 127.52, 125.90, 122.42, 121.66, 71.34, 25.52, 25.14, 22.75, 21.02, 8.79. IR 2359, 1747, 1229 cm^{-1}. HRMS-ESI (*m/z*): (M + H)$^+$calcd for $C_{15}H_{18}O_2Br$, 309.0485, found, 309.0493.



(4-nitrophenyl)(2,3,3-trimethylcycloprop-1-enyl)methyl acetate 1a was obtained as a pale brown oil (67 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 6.71 (s, 1H), 2.15 (s, 3H), 1.95 (s, 3H), 1.09 (s, 3H), 1.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 147.7, 145.6, 127.8, 127.0, 123.7, 121.7, 70.7, 25.4, 25.2, 22.7, 21.0, 8.6. IR 1744, 1524, 1348, 1228 cm^{-1}. HRMS-ESI (*m/z*): (M + H)$^+$calcd for $C_{15}H_{17}NO_4$, 276.1236; found, 276.1230.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6.99
2.14
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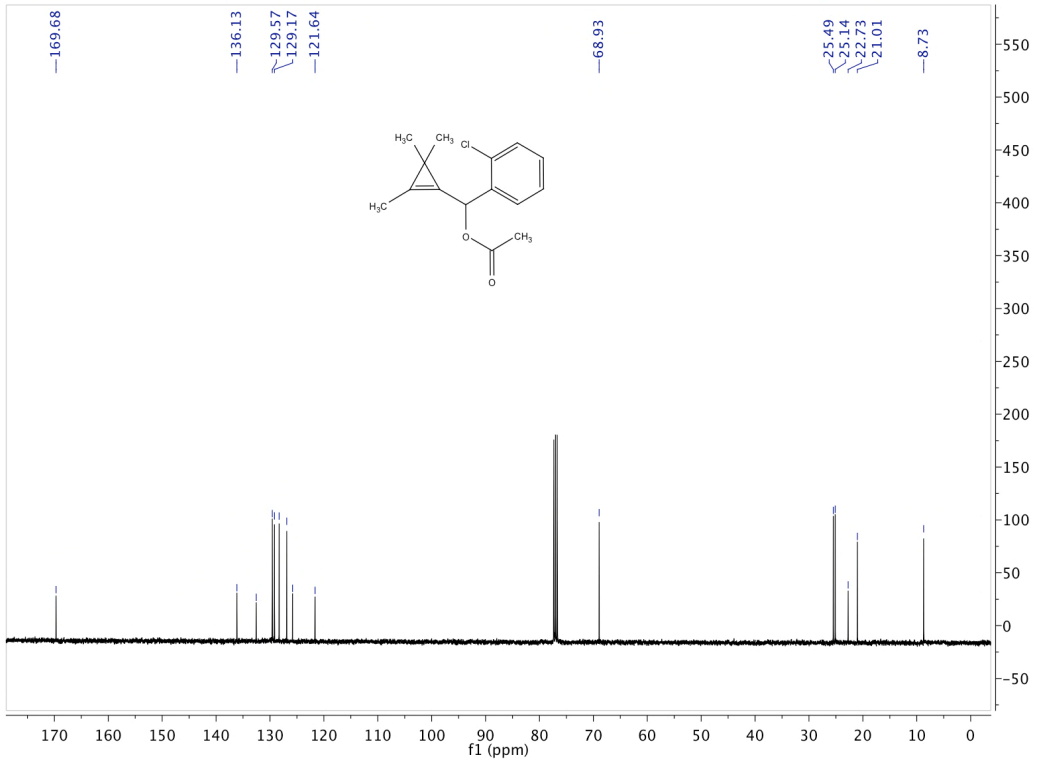
1.00
3.06
3.06
3.00
3.03
f1 (ppm)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25.14
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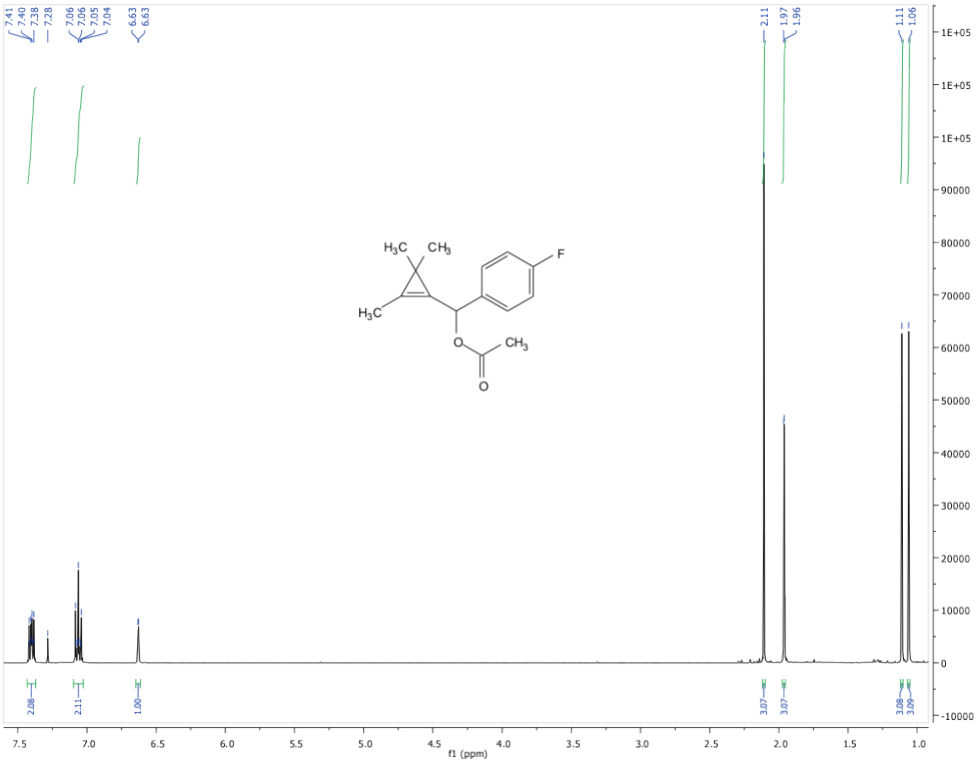
8.73
f1 (ppm)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7.06
7.05
7.04
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6.63
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1.96
1.11
1.06
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CH3
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CH3
O
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2.11
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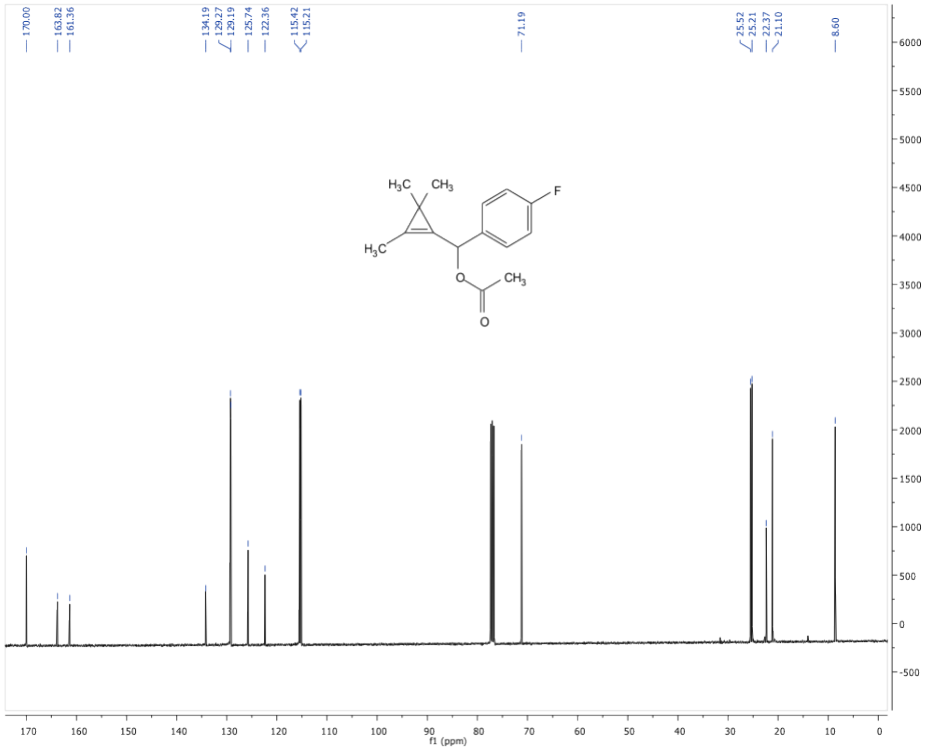
3.07
3.07
3.08
3.09
f1 (ppm)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123.19
125.74
122.36
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115.21
71.19
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F
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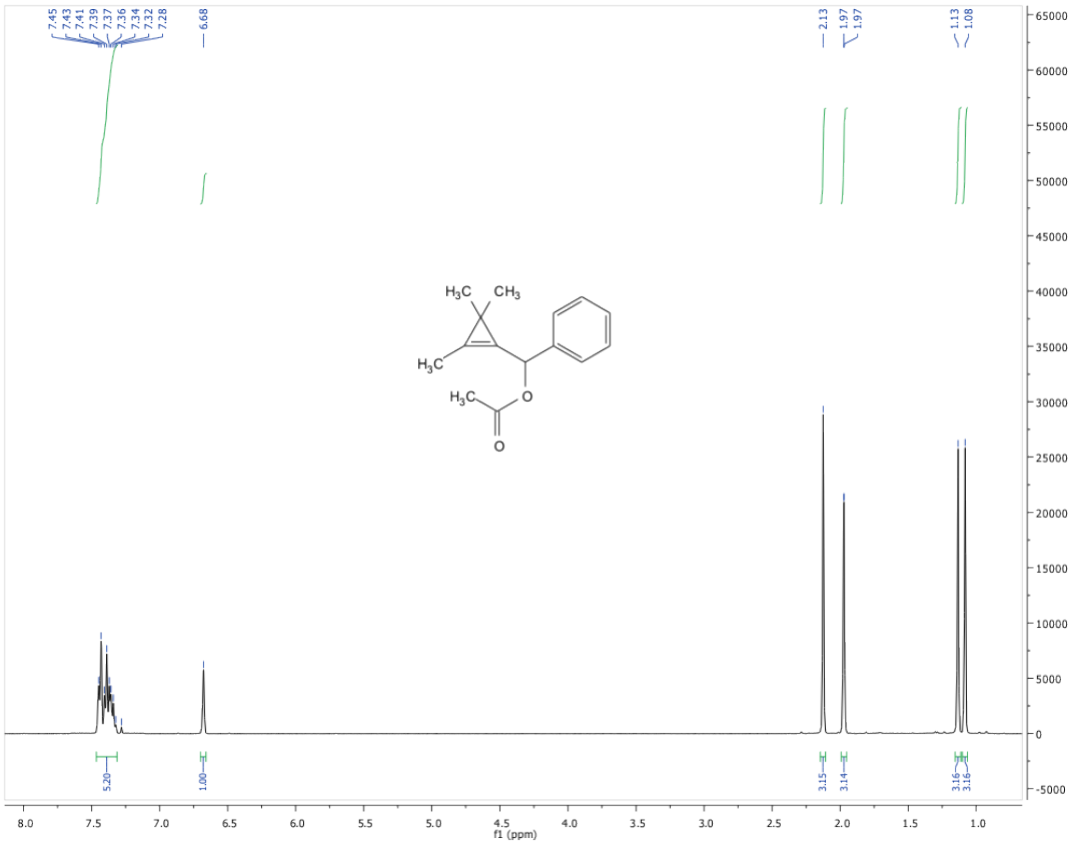
CH3
O
f1 (ppm)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7.37
7.36
7.34
7.32
7.28
6.68
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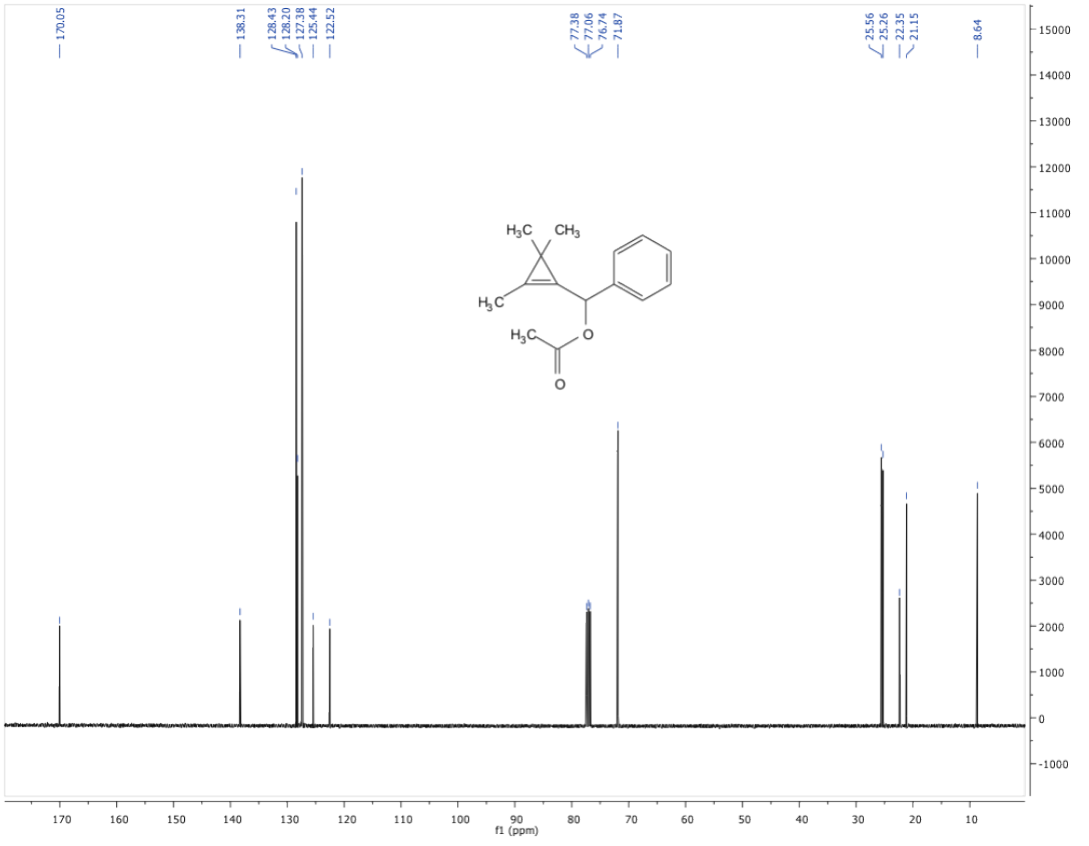
5.20
1.00
3.15
3.14
3.16
3.16
f1 (ppm)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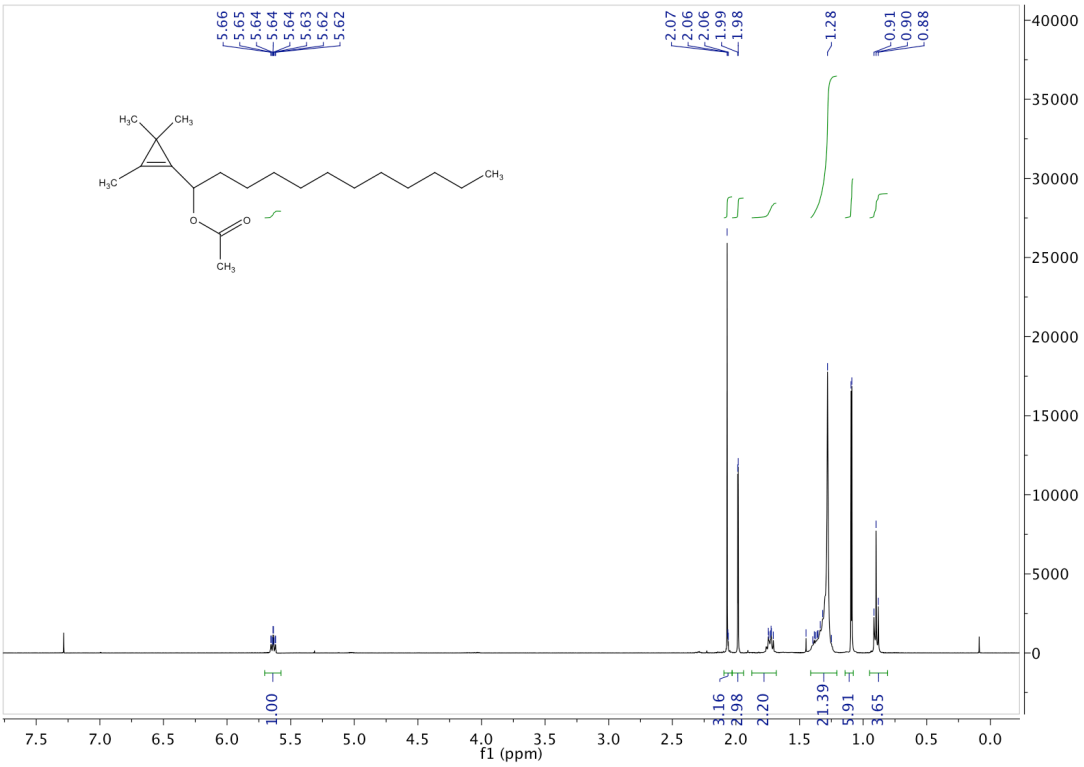
f1 (ppm)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5.64
5.63
5.62
5.62
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2.06
2.06
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1.98
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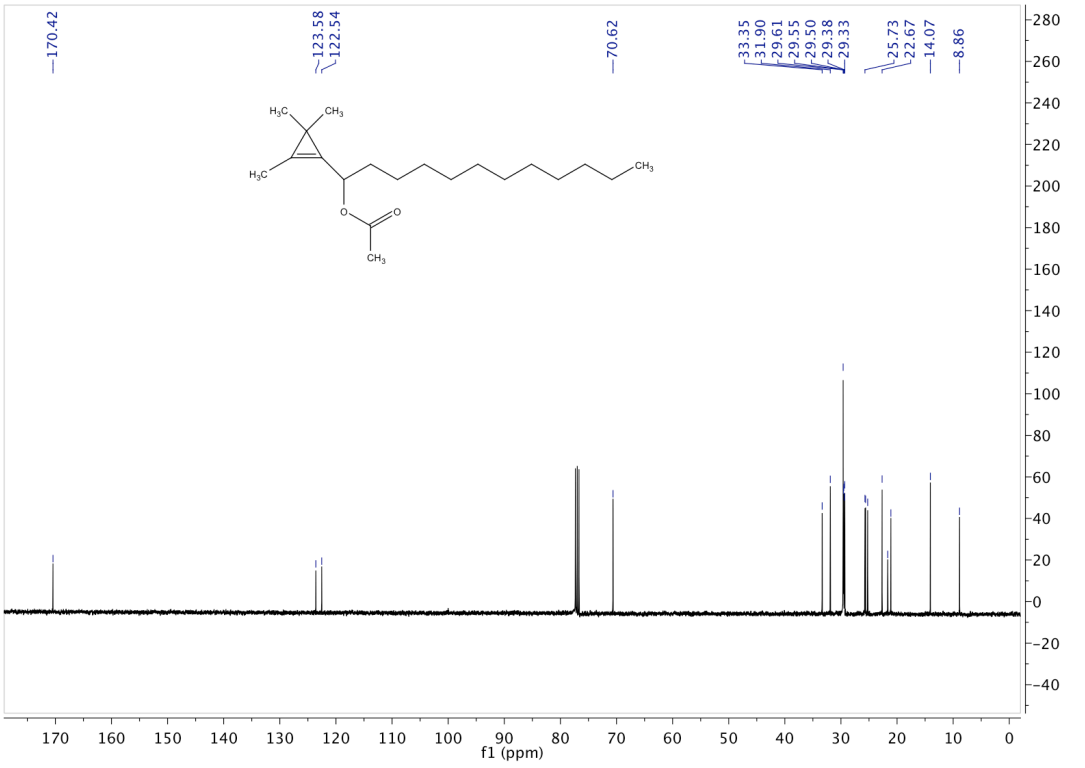
3.65
f1 (ppm)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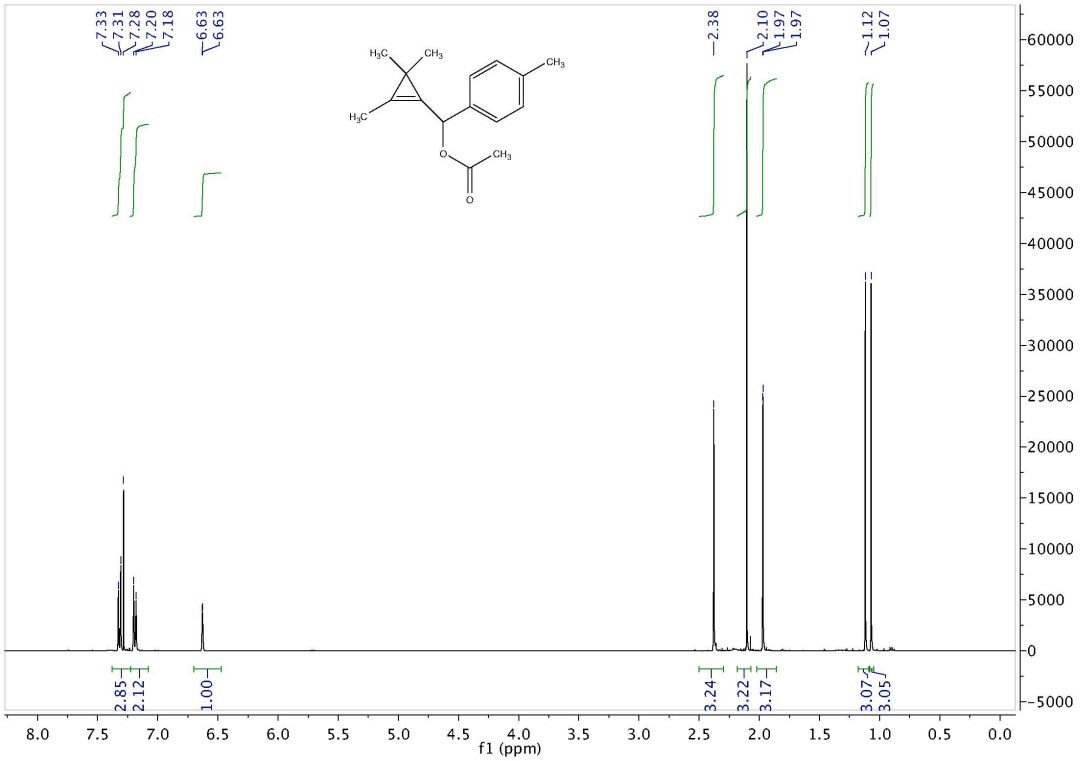
f1 (ppm)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6.63
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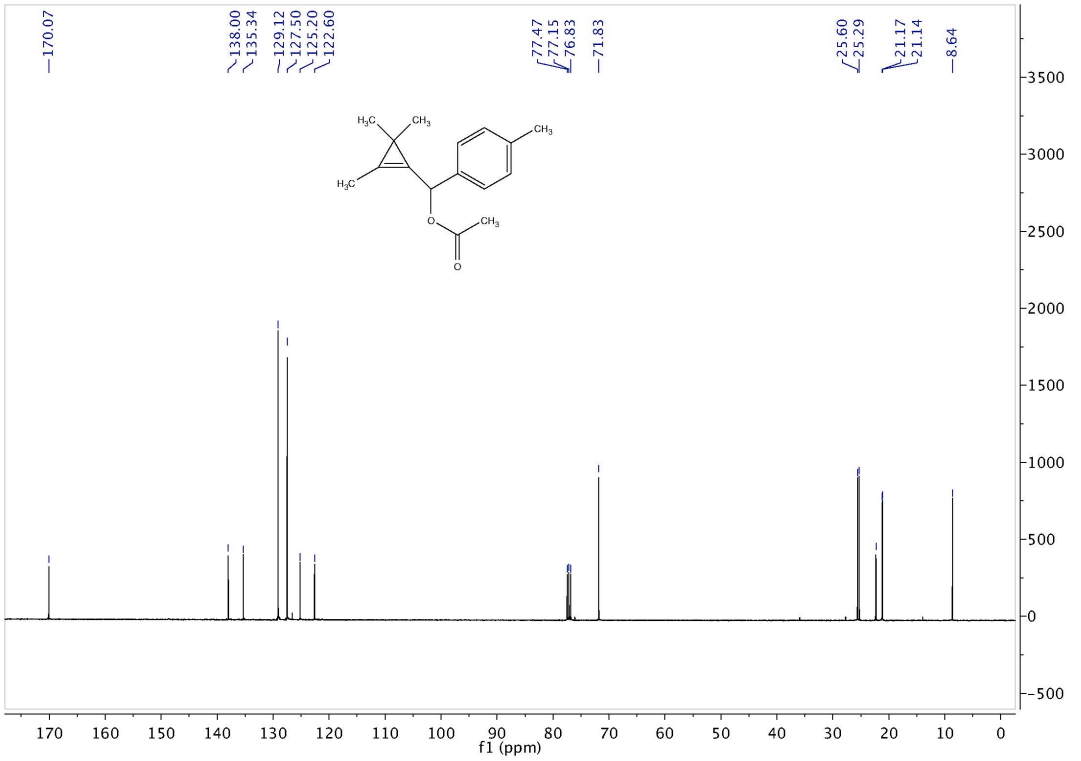
3.17
3.07
3.05
f1 (ppm)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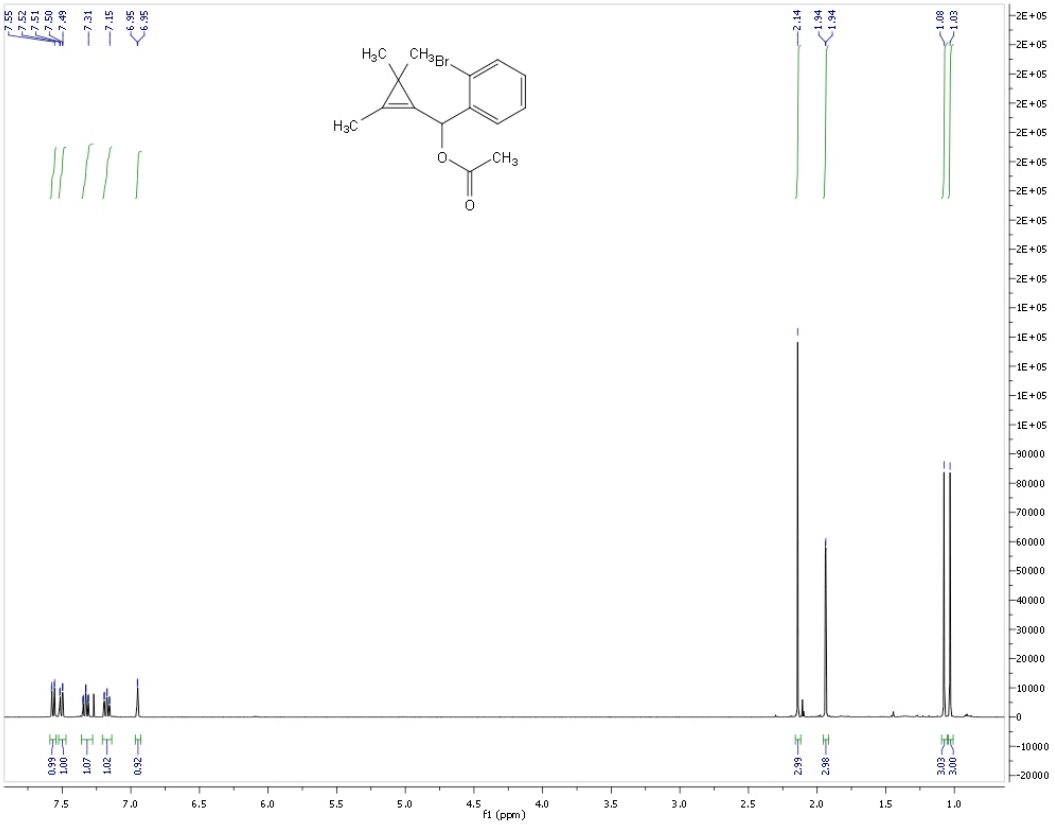
25.29
21.17
21.14
8.64
f1 (ppm)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1.94
1.08
1.03
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CH3Br
H3C
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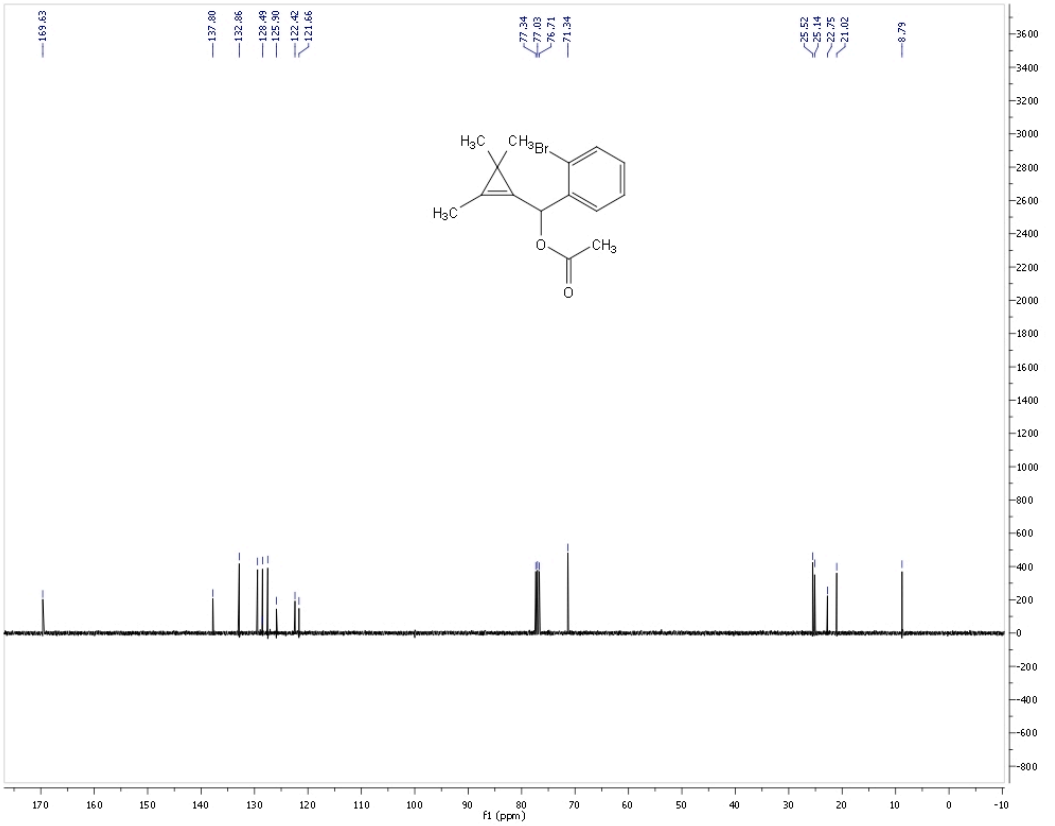
2.98
3.03
3.00
f1 (ppm)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CH3Br
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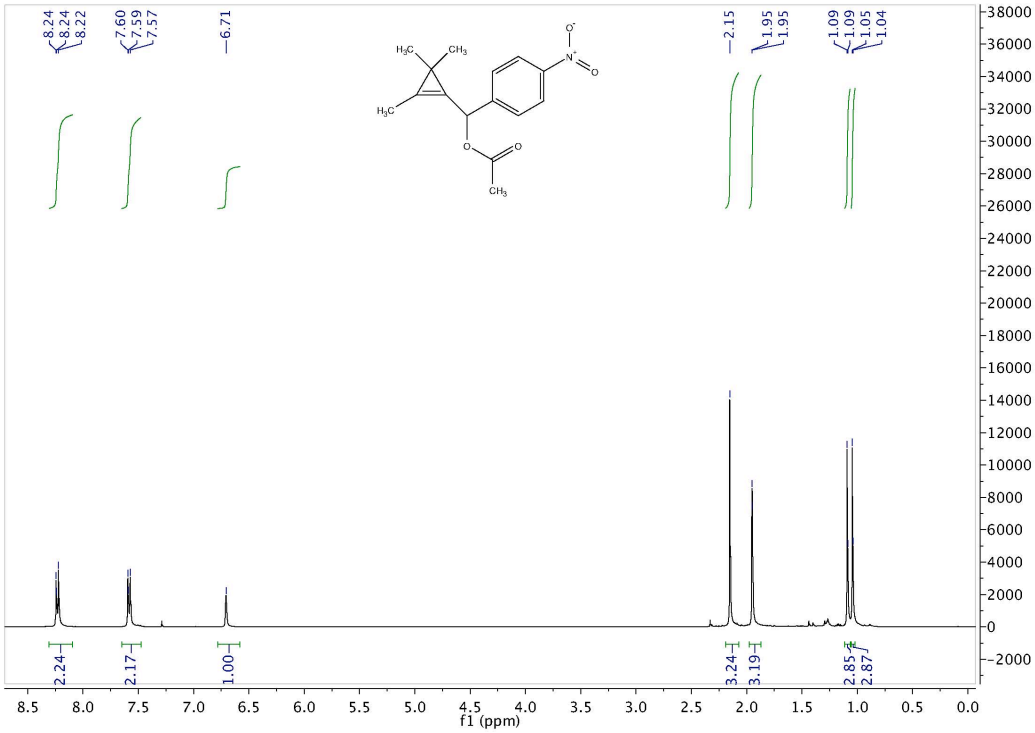
CH3
O
f1 (ppm)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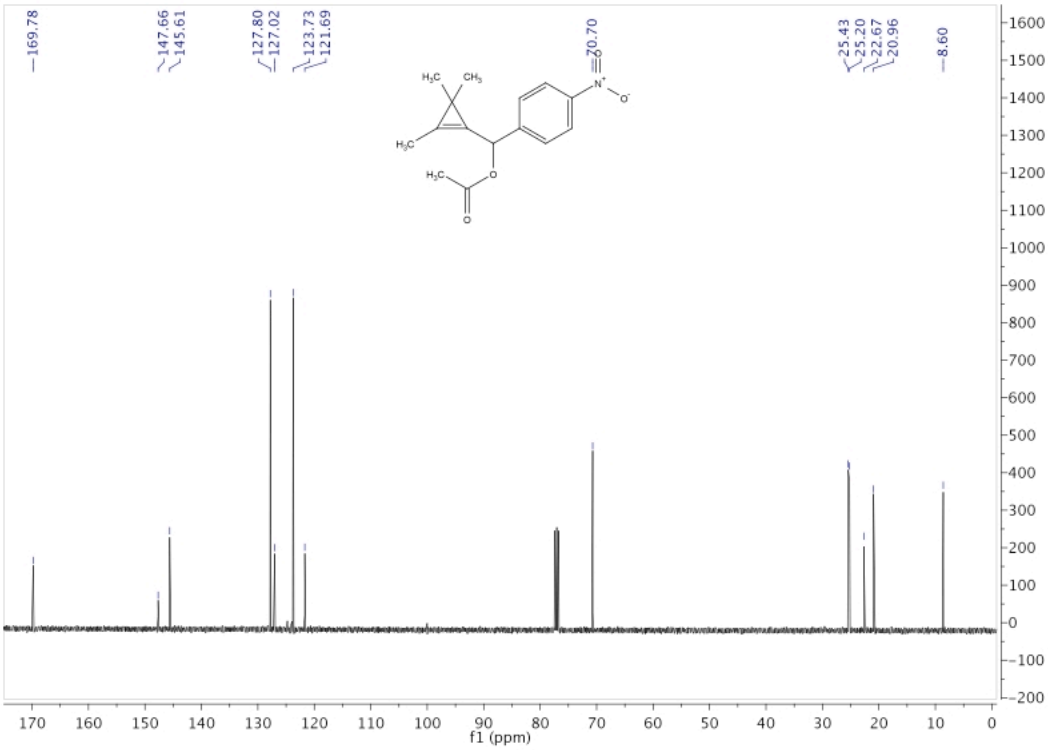
2.87
f1 (ppm)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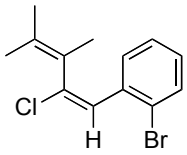
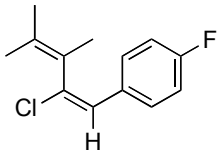
20.96
8.60
f1 (ppm)

General preparation of halo-dienes:

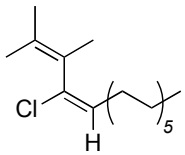
The cyclopropenyl acetate (0.17 mmol, 1.0 equiv) was weighed into a flame-dried flask purged with argon and CH_2Cl_2 (3.4 ml) added. The solution was then cooled to -78°C with a dry-ice acetone bath and $TiCl_4$ or $TiBr_4$ (0.17 ml of a 1.0 M solution in CH_2Cl_2) added dropwise. After 5 mins the reaction was quenched by the addition of MeOH:H_2O (5 ml of a 1:1 mixture) and allowed to warm to room temperature. The organic layer was separated and the aqueous extracted with CH_2Cl_2 (2 x 5 ml). The combined organics were dried ($MgSO_4$) and evaporated to dryness. Purification on SiO_2 (typically pentane or hexane on a Chromatotron ®) yielded the pure diene.



(*E*)-1-bromo-2-(2-chloro-3,4-dimethylpenta-1,3-dienyl)benzene 5e was obtained as a colorless oil (43 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.0. 1.0 Hz, 1H), 7.23 – 7.13 (m, 2H), 7.10 – 7.03 (m, 1H), 6.83 (s, 1H), 1.92 – 1.87 (m, 3H), 1.64 – 1.60 (m, 3H), 1.49 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.27, 135.93, 133.70, 132.61, 128.96, 128.63, 127.51, 126.95, 124.92, 123.45, 21.65, 20.08, 17.06. IR 1622, 1464, 1436, 1373, 1130, 1025, 802, 747 cm^{-1}. MS (EI) Calculated for $[C_{13}H_{14}BrCl]^+$: 285.6; Found: 285.6.

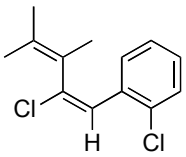


(E)-1-(2-chloro-3,4-dimethylpenta-1,3-dienyl)-4-fluorobenzene 5f was obtained as a clear colorless oil (37.4 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.17 (m, 2H), 7.04 – 6.89 (m, 2H), 6.59 (s, 1H), 1.95 – 1.86 (m, 3H), 1.74 (s, 3H), 1.64 – 1.59 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8 (d, *J* = 247 Hz), 136.14, 133.15, 131.73, 129.11, 126.50, 125.91, 115.4 (d, *J* = 21 Hz), 21.53, 19.95, 16.48. IR 1625, 1602, 1508, 1233, 1146, 829 cm^{-1}. HRMS-EI (*m/z*): $(M)^+$ calcd for $C_{13}H_{14}ClF$, 224.0768; found 224.077

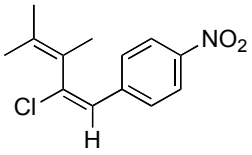


4-chloro-2,3-dimethylhexadeca-2,4-diene 5l was obtained as a clear oil (2.3:1 *E*:*Z* ratio 68 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.61 (1H, t, *J* = 7.5 Hz *major*), 5.40 (1H, t, *J* = 7.0 Hz), 2.24 (2H, q, *J* = 6.5 Hz *minor*), 1.90 (2H, q, *J* = 7.0 Hz *major*), 1.81-1.77 (6H, m *major*), 1.75-1.74 (6H, m *minor*), 1.73-1.72 (3H, m *minor*), 1.72 (3H, q, *J* = 1.5 Hz *major*) 1.35-1.28 (18H, m *major and minor*), 0.91 (t, *J* = 7.0 Hz *major and minor*). ^{13}C NMR (101 MHz,

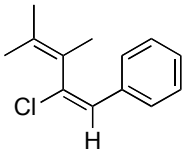
$CDCl_3$) δ 134.2, 133.0, 131.8, 130.9, 128.7, 128.3, 127.6, 125.5, 31.9, 31.9, 29.7, 29.6, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 29.3, 29.3, 29.2, 29.0, 28.6, 22.7, 21.9, 21.7, 20.2, 19.7, 17.5, 17.0, 14.1.IR 2929.2, 2854, 1465, 1373, 1132 cm^{-1}. HRMS-EI (*m/z*): M^+ calcd for $C_{18}H_{133}Cl$, 284.2271; found 284.2260.



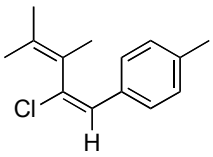
(*E*)-1-chloro-2-(2-chloro-3,4-dimethylpenta-1,3-dienyl)benzene 5d was obtained as a clear yellow oil (72 mg, 84%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.35 (m, 1H), 7.26-7.24 (m, 1H), 7.25-7.11 (m, 2H), 6.90 (s, 1H), 1.91-1.90 (m, 3H), 1.65 (d, *J*= 8.0, 1.0 Hz, 3H), 1.52-1.51 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 134.1, 133.6, 133.1, 128.7, 128.4, 126.4, 125.1, 125.0, 115.5, 21.6, 20.0, 17.0. IR 1650, 1623, 1468, 1440, 1374, 1148, 1129, 1052, 1035, 946, 929, 806, 749 cm^{-1}. HRMS-CI (*m/z*): $(M + H)^+$ calcd for $C_{13}H_{14}Cl_2$, 240.0473; found 240.0466.



(*Z*)-1-(2-chloro-3,4-dimethylpenta-1,3-dienyl)-4-nitrobenzene 5a was obtained as a pale yellow solid (120 mg, 71%). Mp: 111.0-112.1 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.68 (s, 1H), 1.91, (s, 3H), 1.74 (s, 3H), 1.58 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 142.0, 141.2, 134.0, 128.1, 126.0, 125.6, 123.8, 21.6, 20.1, 16.5. IR 1595, 1519, 1345 cm^{-1}. MS (EI) Calculated for $[C_{13}H_{14}ClNO_2]^+$: 251.7; Found: 251.9.

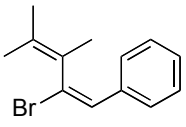


(*Z*)-(2-chloro-3,4-dimethylpenta-1,3-dienyl)benzene 5b was obtained as a clear oil (51 mg, 84%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.20 (m, 5H), 6.65 (s, 1H), 1.93-1.92 (m, 3H), 1.75 (s, 3H), 1.63 (q, *J* = 1.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 135.6, 132.9, 128.4, 127.7, 127.6, 127.2, 126.2, 21.6, 20.0, 16.5. IR 1598, 1490, 1444, 1132, 697 cm^{-1}. MS (EI) Calculated for $[C_{13}H_{15}Cl]^+$: 205.8; Found: 206.0.

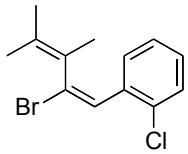


(*Z*)-1-(2-chloro-3,4-dimethylpenta-1,3-dienyl)-4-methylbenzene 5c was obtained as a clear oil (23 mg, 36%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.59 (s, 1H), 2.33 (s, 3H), 1.91-1.89 (m, 3H), 1.74 (s, 3H), 1.63 (q, *J* = 1.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 135.4, 132.8, 132.7, 129.1, 127.5, 127.4, 126.3, 21.6, 21.2, 20.0, 16.5.

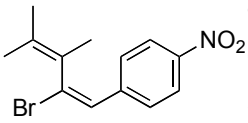
IR 1624, 1511, 1443, 1373, 1145, 952, 879, 809, 749 cm^{-1}. HRMS-CI (*m/z*): $(M + NH_4)^+$ calcd for $C_{14}H_{21}NCl$, 238.1362; found 238.1368.



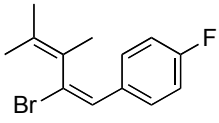
(*E*)-(2-bromo-3,4-dimethylpenta-1,3-dienyl)benzene 5h was obtained as a clear oil (26 mg, 70%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.20 (m, 5H), 6.85 (s, 1H), 1.93 (s, 3H), 1.74 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.26, 132.64, 131.41, 128.44, 128.41, 127.94, 127.47, 127.36, 21.60, 20.08, 16.65. IR 1596, 1494, 1446, 1130, 693cm^{-1}. HRMS-TOF FD (*m/z*): $(M + H)^+$calcd for $C_{13}H_{15}Br$, 250.0357; found, 250.0352.



(*E*)-1-(2-bromo-3,4-dimethylpenta-1,3-dienyl)-2-chlorobenzene 5i was obtained as a clear oil (34.0 mg, 79%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 1H), 7.25 (dd, *J* =4.0, 3.5 Hz, 1H), 7.15 (m, 3H), 1.91 (m, 3H), 1.65 (m, 3H), 1.53 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.7, 133.2, 132.9, 130.3, 129.4, 128.6, 128.5, 126.8, 126.4, 21.6, 20.2, 17.3. IR 1615, 1490, 1421, 1141, 748cm^{-1}. HRMS-TOF FD (*m/z*): $(M + H)^+$calcd for $C_{13}H_{14}BrCl$, 283.9967; found, 283.9962.

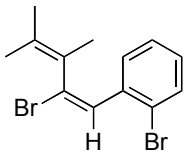


(*E*)-1-(2-bromo-3,4-dimethylpenta-1,3-dienyl)-4-nitrobenzene 5g was obtained as a yellow solid (19.2 mg, 68%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (m, 2H), 7.40 (m, 2H), 6.93 (s, 1H), 1.93 (m, 3H), 1.76 (dd, *J* = 0.9, 0.4 Hz, 3H), 1.61 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 133.6, 133.3, 129.7, 128.0, 127.4, 123.9, 21.62, 20.18, 16.70. IR 1565, 1497, 1421, 1145, 733cm^{-1}. HRMS-TOF FD (*m/z*): $(M + H)^+$calcd for $C_{13}H_{14}BrNO_2$, 295.0208; found, 295.0202.

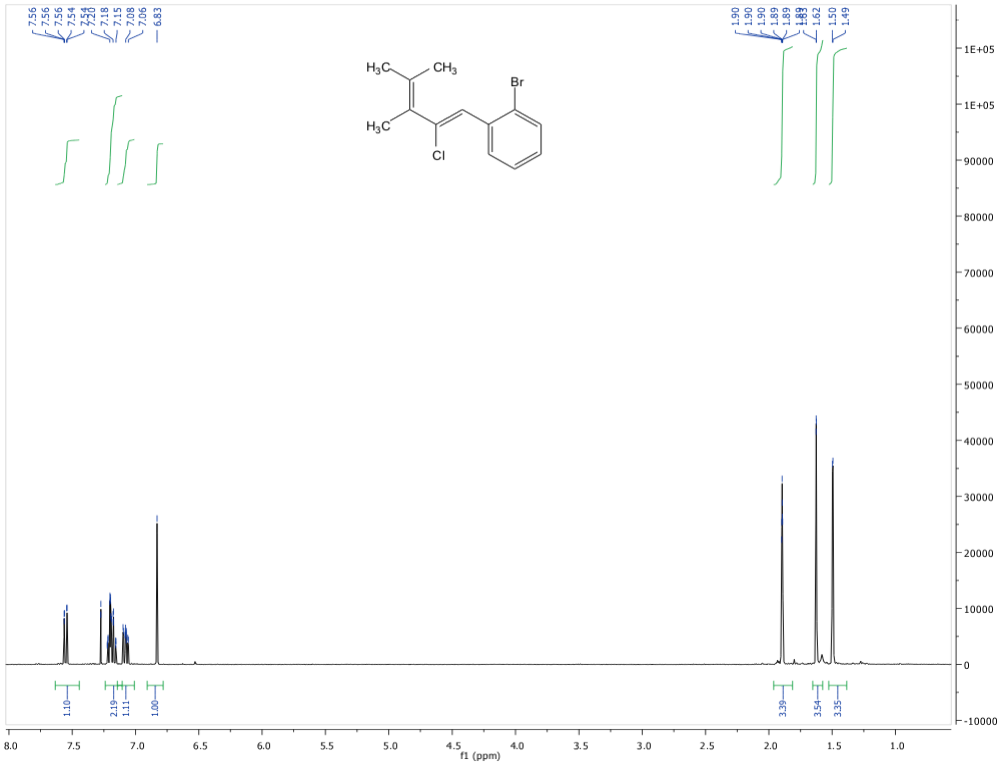


(*E*)-1-(2-bromo-3,4-dimethylpenta-1,3-dienyl)-4-fluorobenzene 5k was obtained as a clear yellow oil (41.8 mg, 68%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (m, 2H), 6.97 (dd, *J* = 9.6, 7.8 Hz, 2H), 6.81 (s, 1H), 1.90 (s, 3H), 1.74 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9 (d, *J* = 248.5 Hz), 132.85, 132.43, 130.18, 129.1, 128.0, 127.6, 115.4 (d, *J* = 22 Hz), 21.57, 20.08, 16.61. IR 1604, 1508, 1457, 1126, 688cm^{-1}. HRMS-TOF FD (*m/z*): $(M + H)^+$calcd for $C_{13}H_{14}BrF$, 268.0263; found, 268.0257.

(*E*)-1-bromo-2-(2-bromo-3,4-dimethylpenta-1,3-dienyl)benzene 5j was obtained as a clear yellow oil (42.0 mg, 70%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J*= 7.9, 1.2 Hz, 1H), 7.20 (m, 2H), 7.09 (m, 2H), 1.91 (m, 3H), 1.63



(s, 3H), 1.52 (d, J = 1.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 133.3, 132.7, 131.2, 130.3, 128.7, 128.7, 127.0, 126.6, 123.2, 21.7, 20.2, 17.4. IR 1605, 1496, 1437, 1122, 688 cm^{-1}. HRMS-TOF FD (*m/z*): $(M + H)^+$ calcd for $C_{13}H_{14}Br_2$, 327.9462; found, 327.9457.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1.89
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Cl
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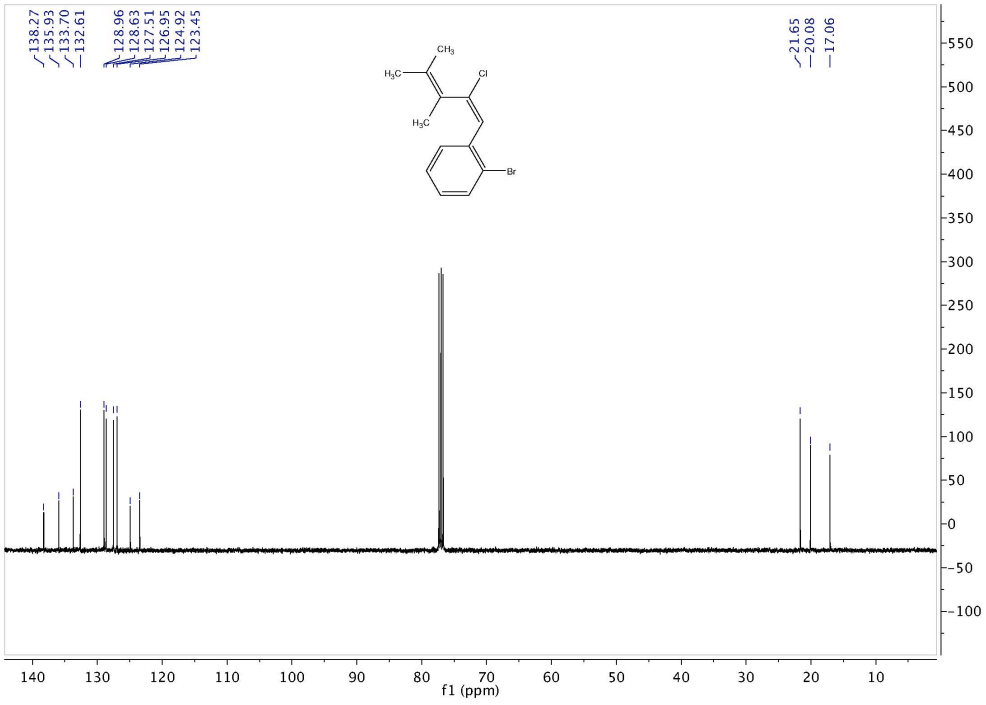
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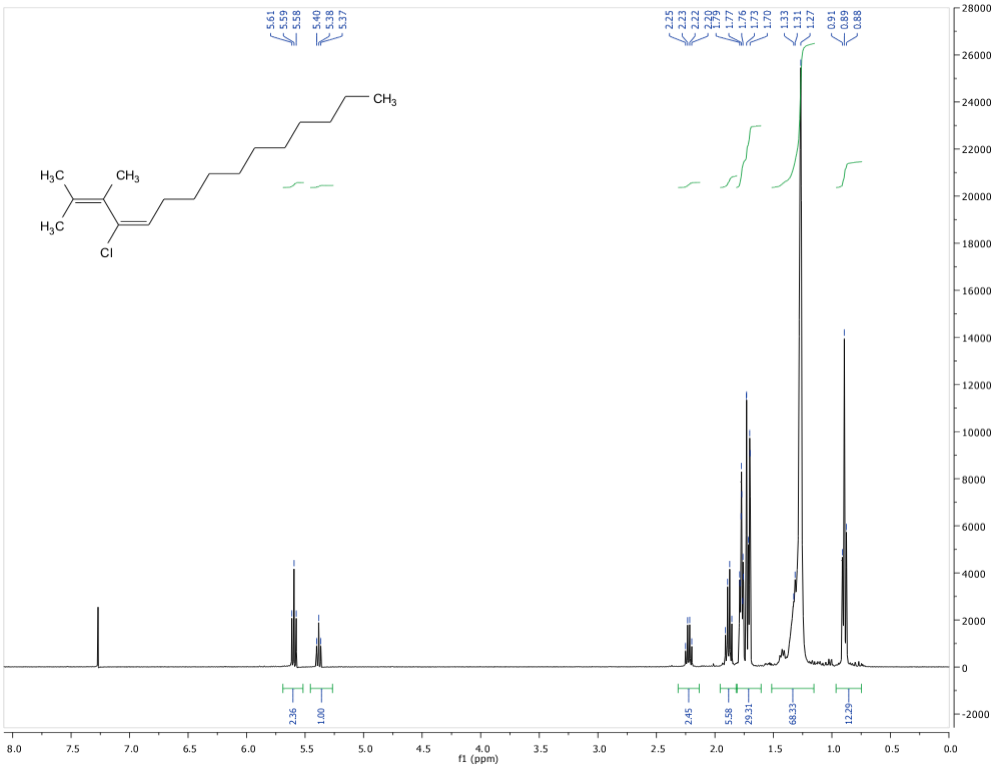
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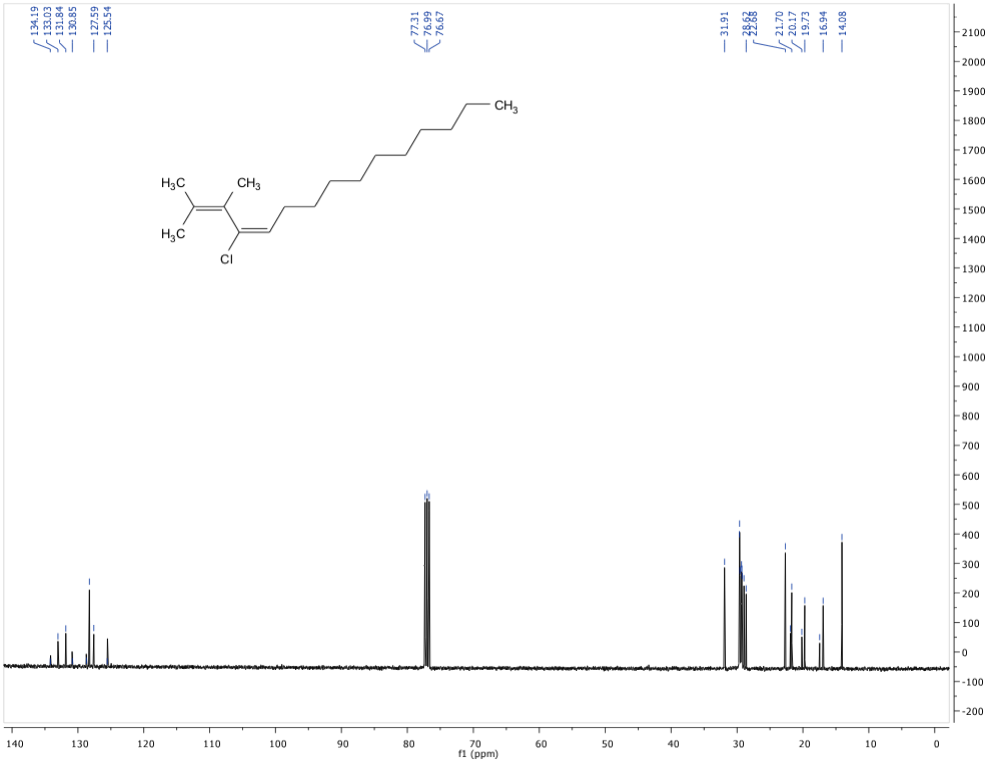
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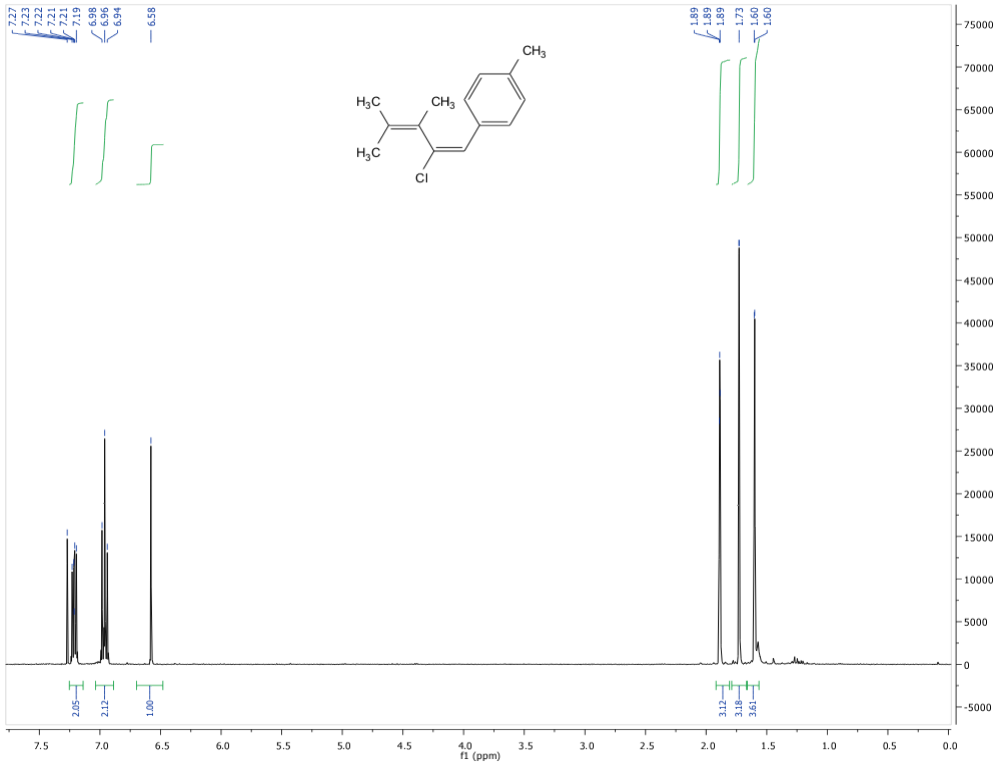
Cl
f1 (ppm)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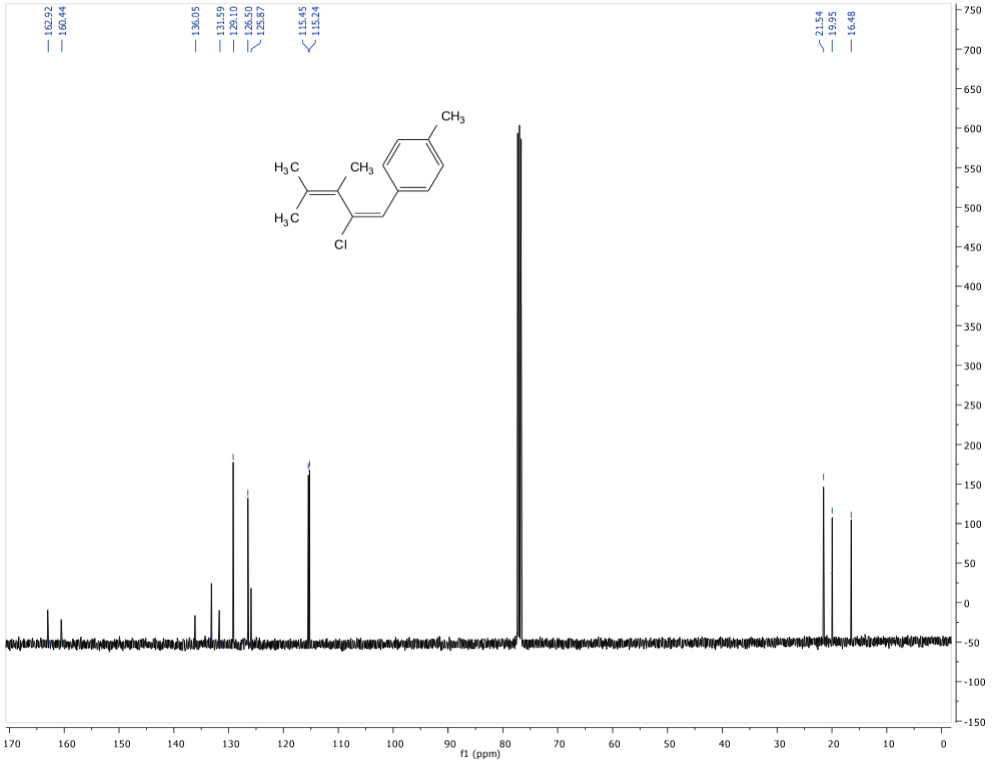
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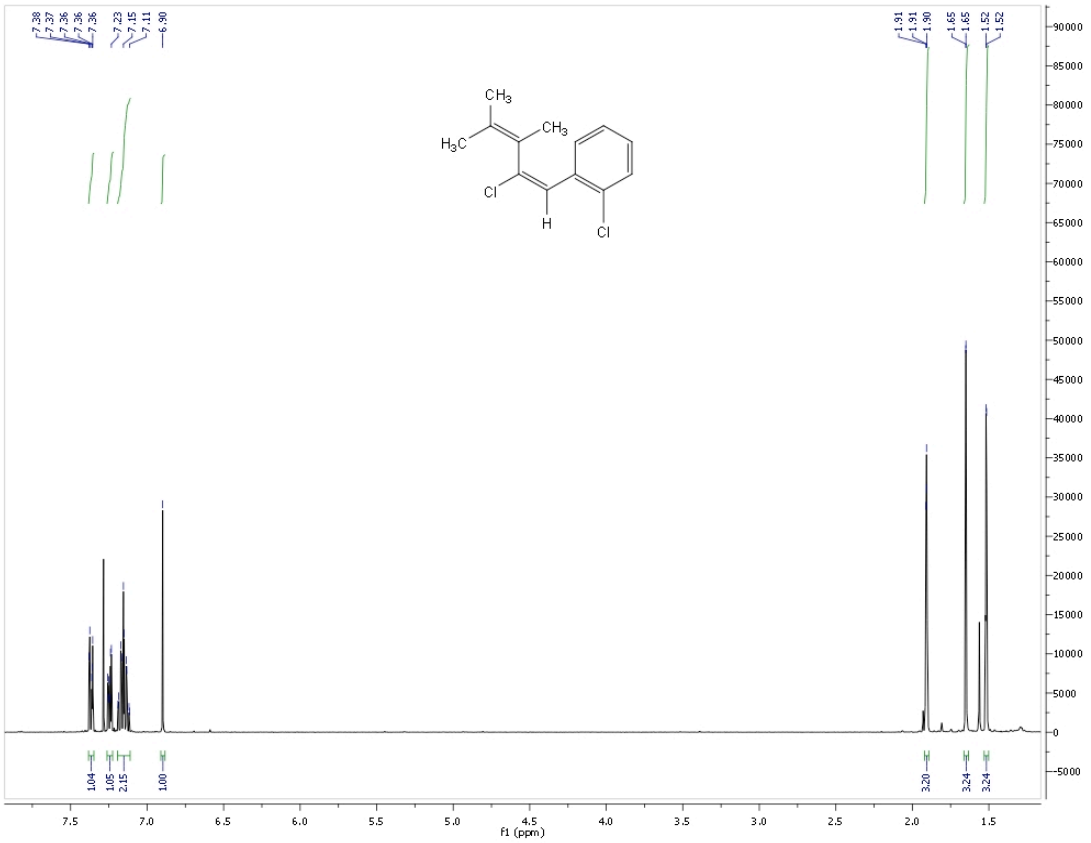
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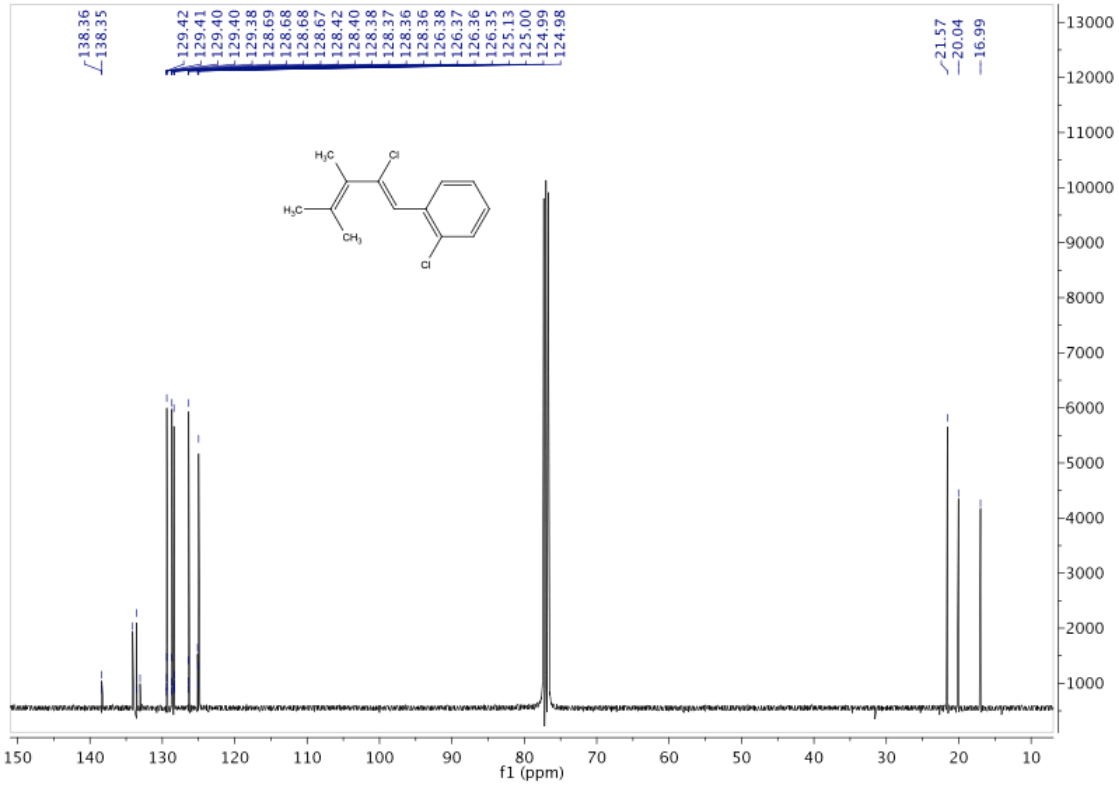
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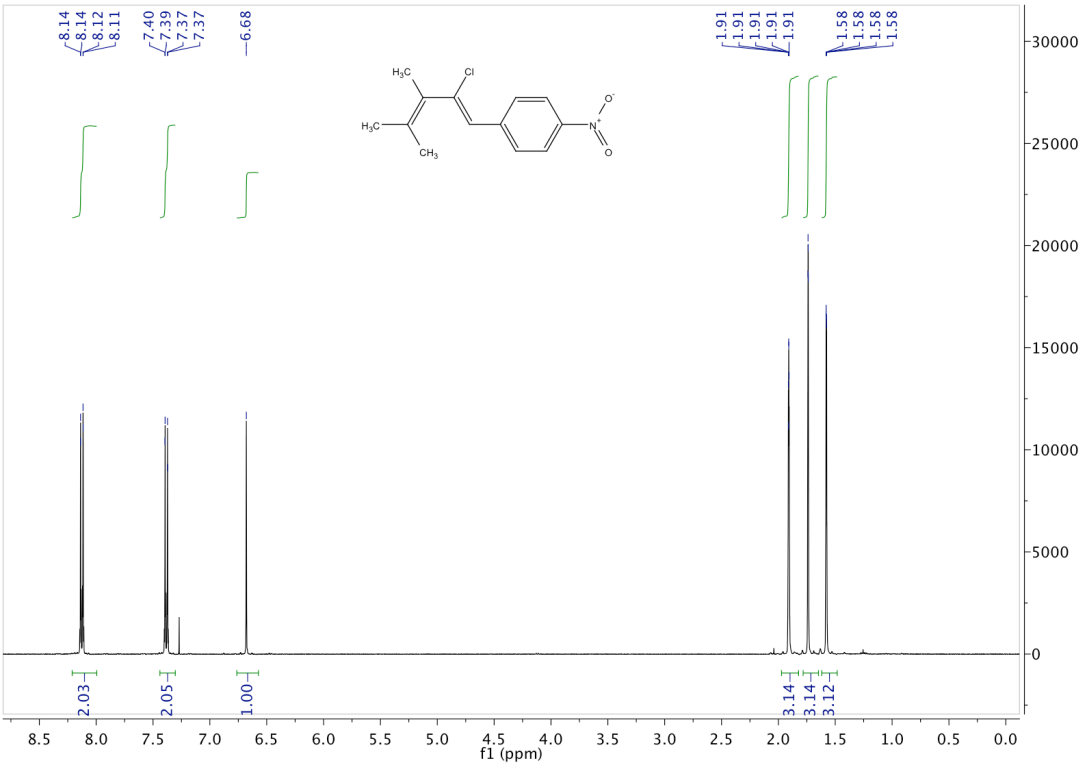
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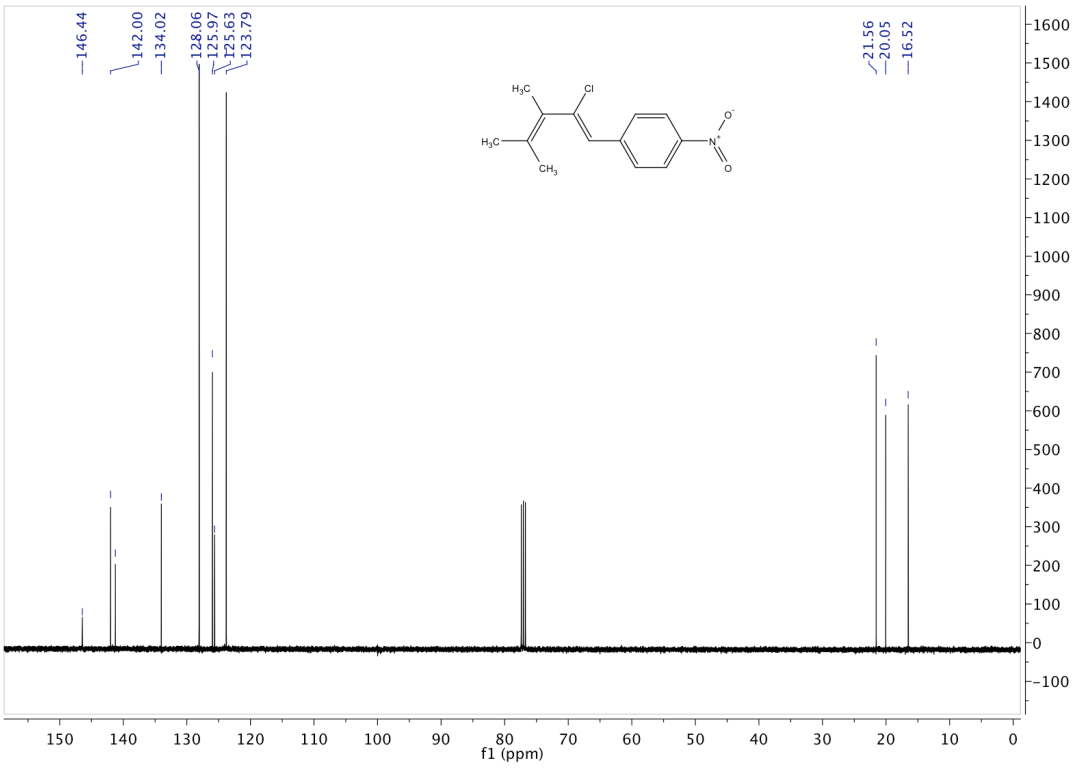
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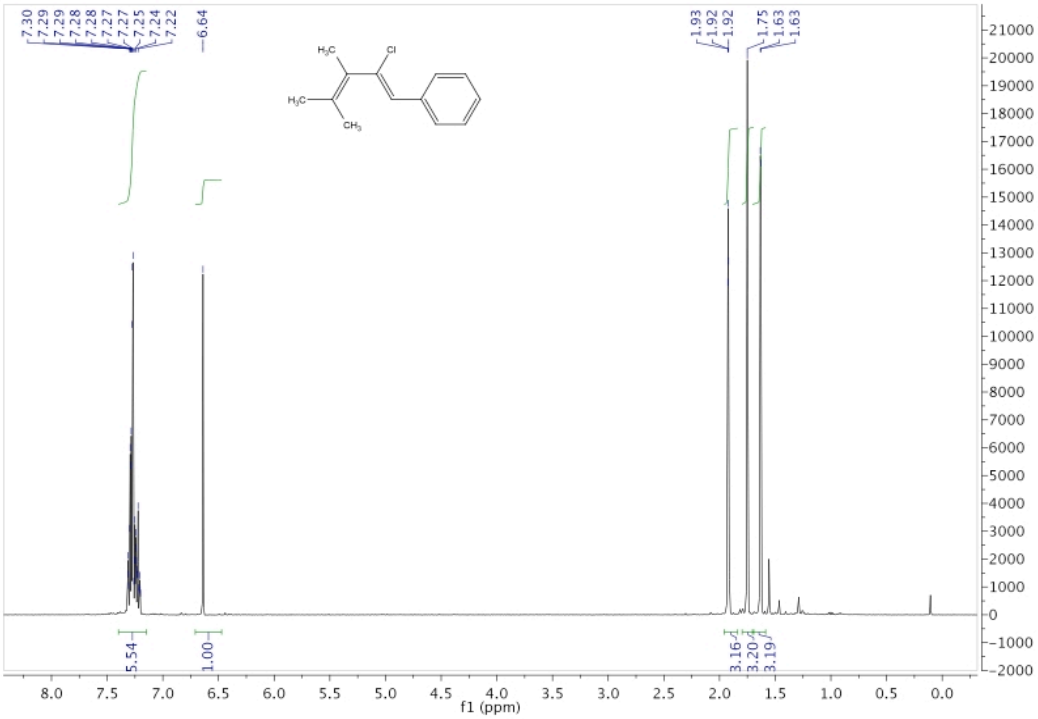
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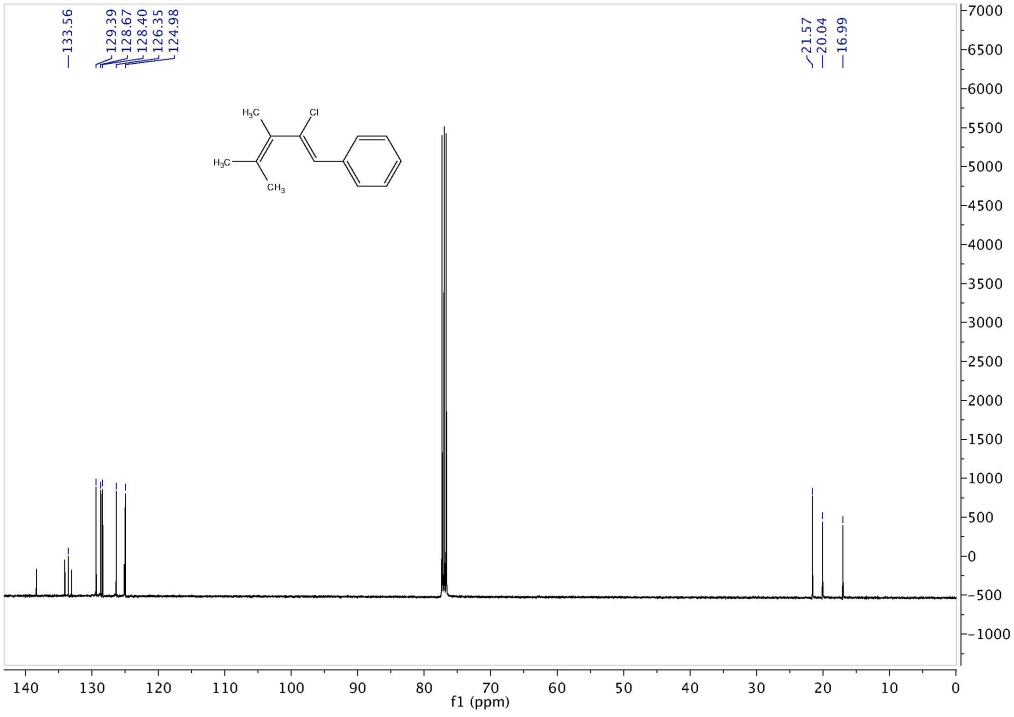
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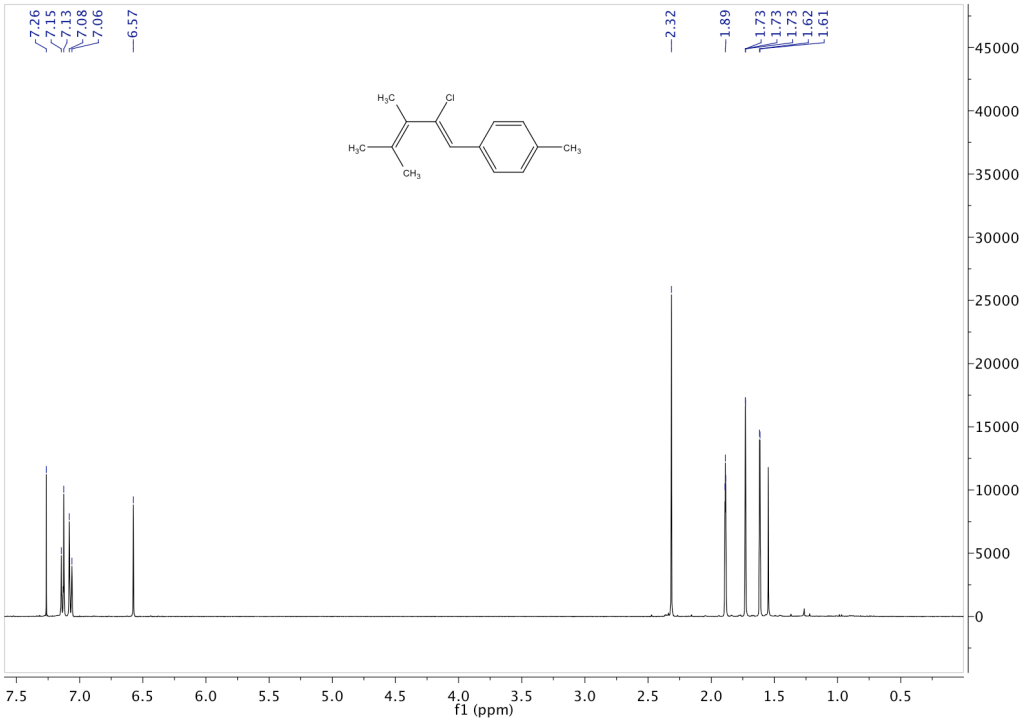
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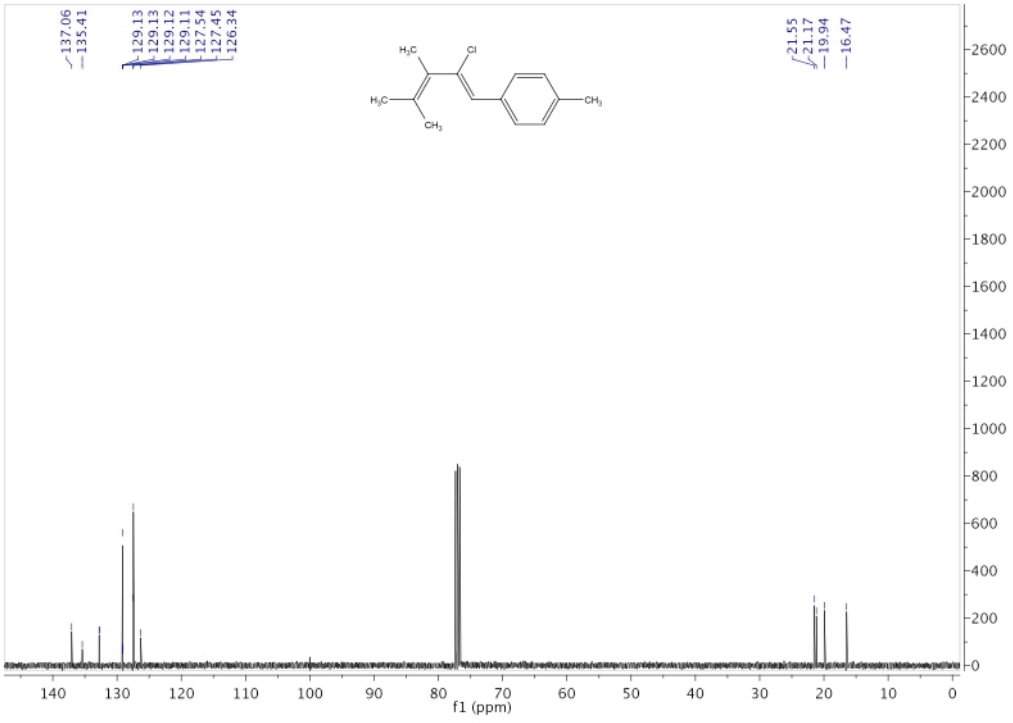
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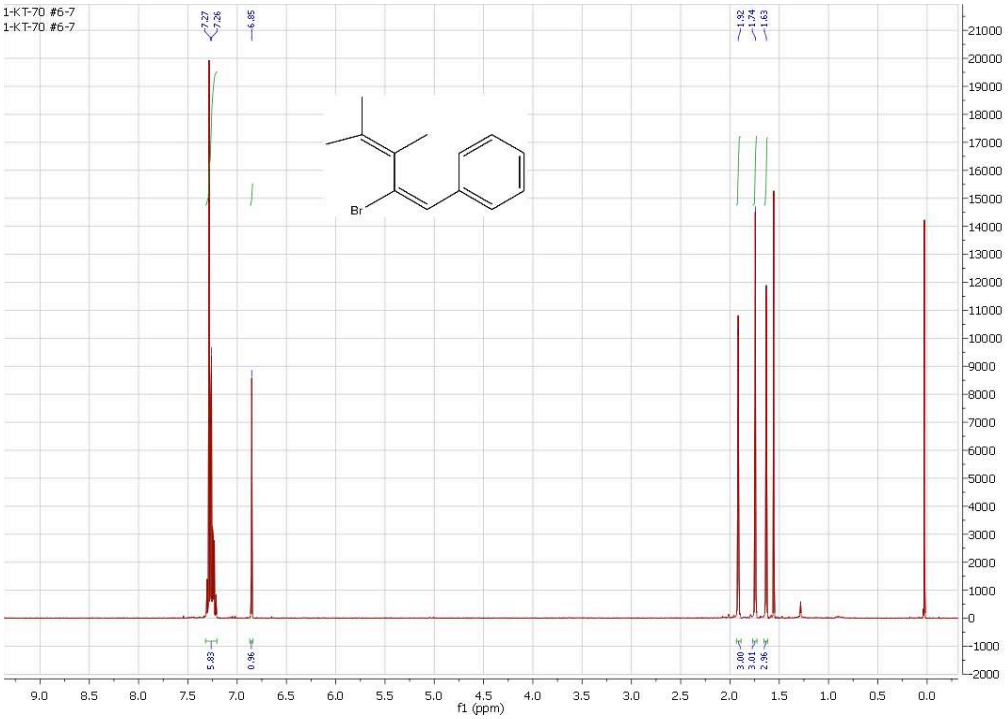
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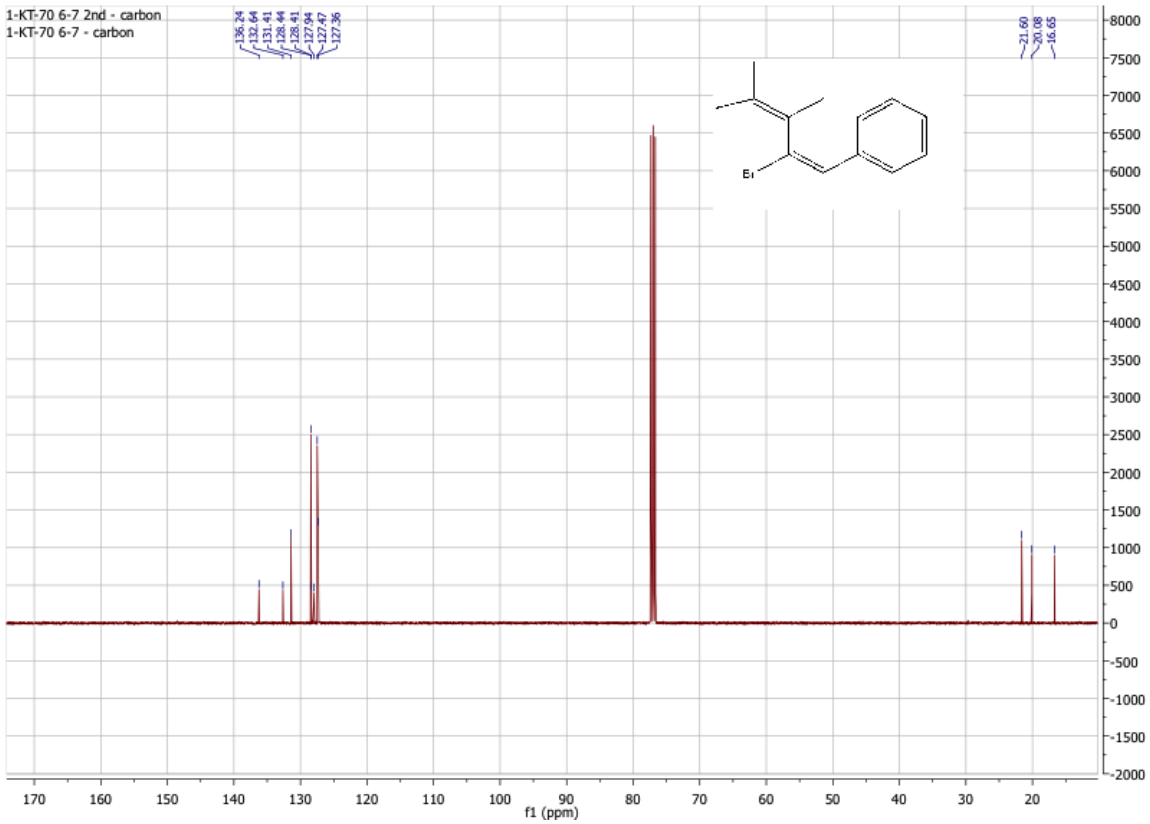
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21.60
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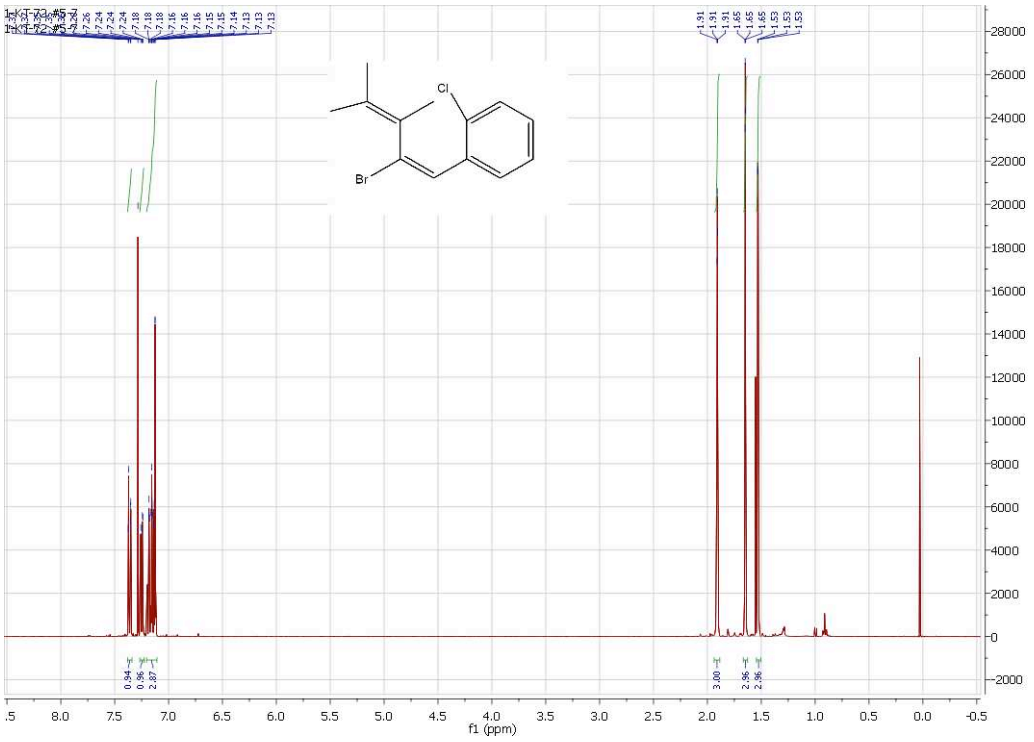
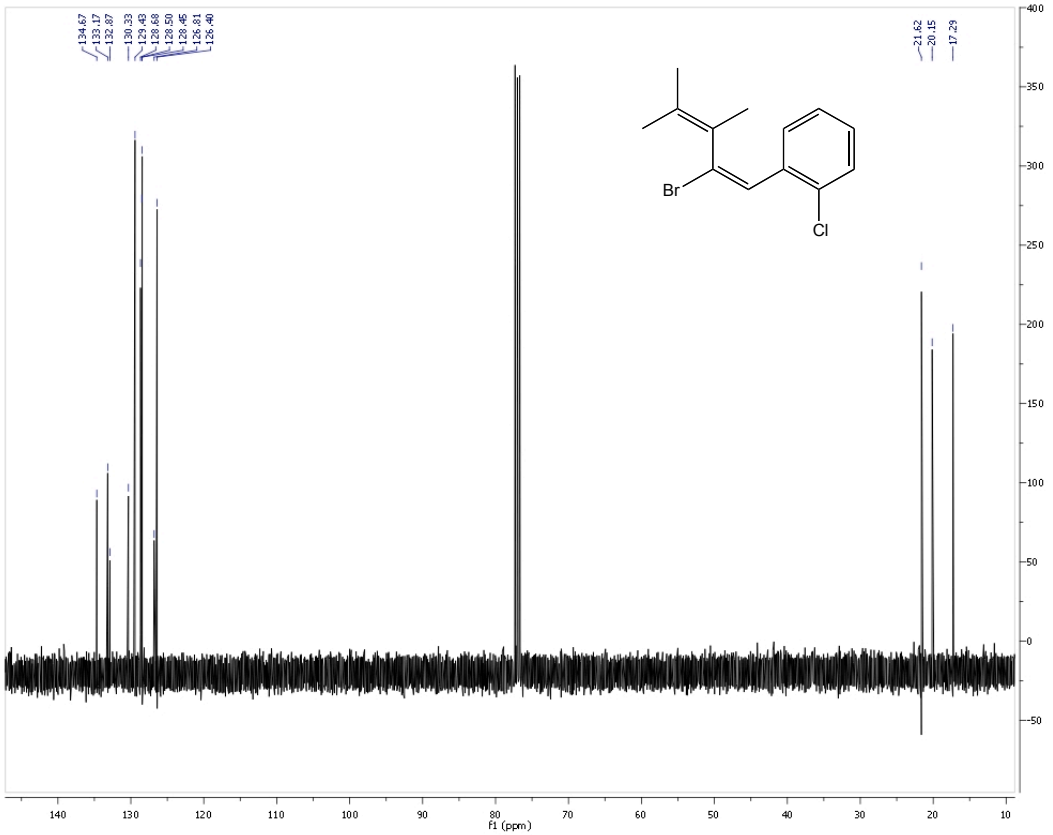
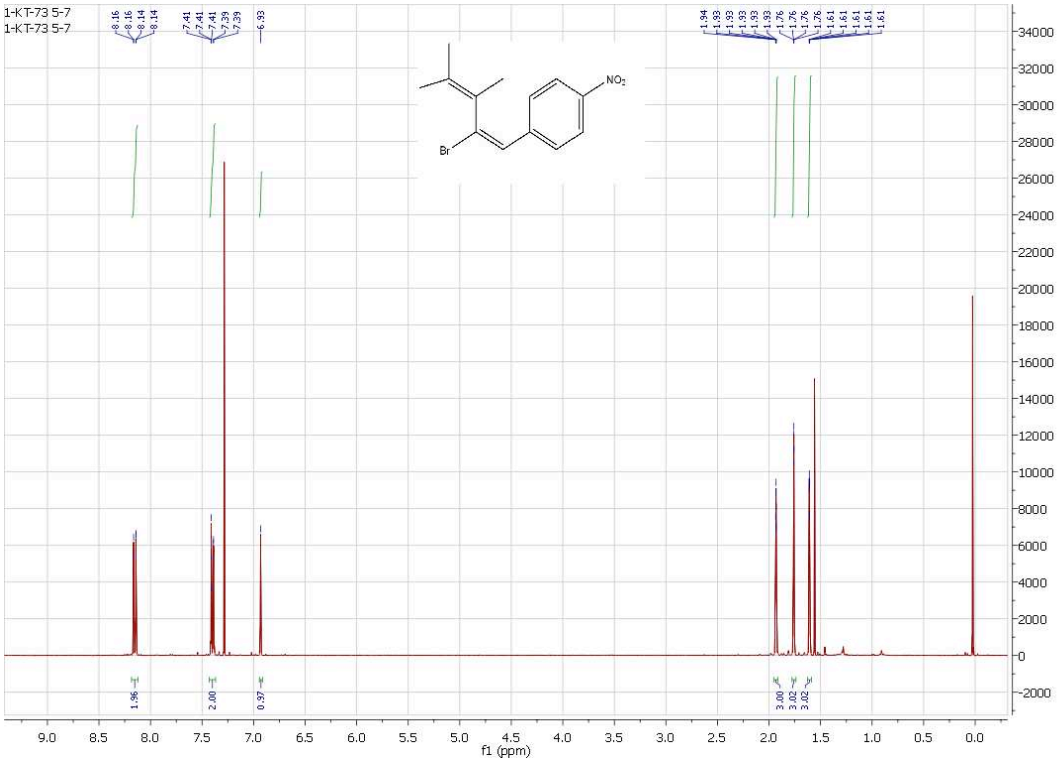
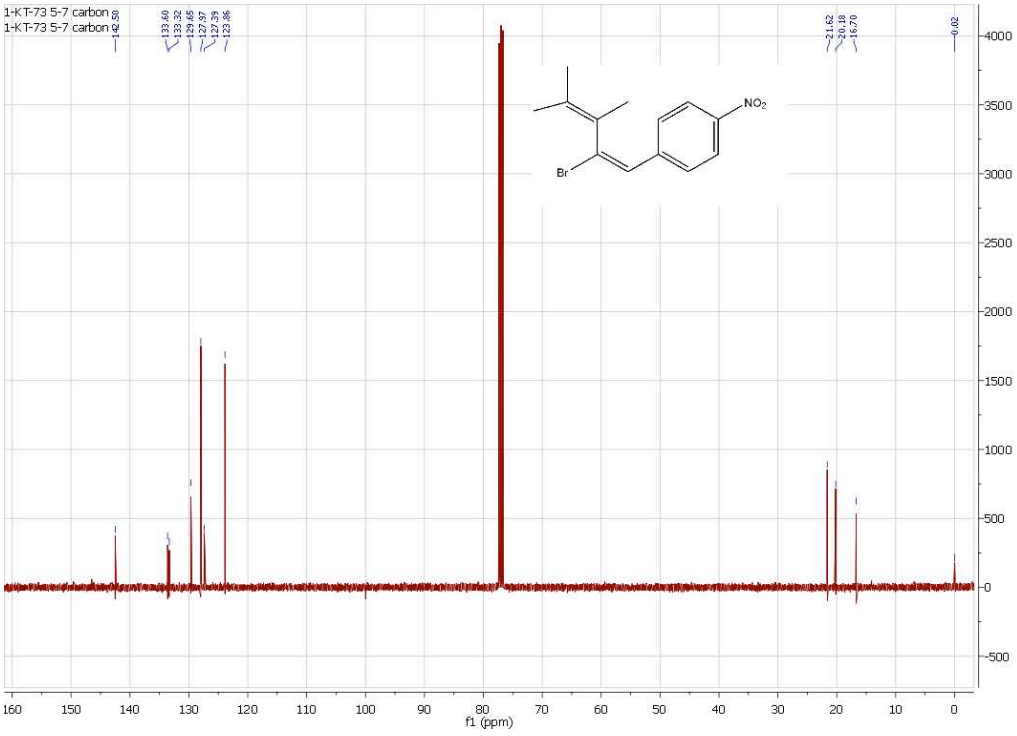
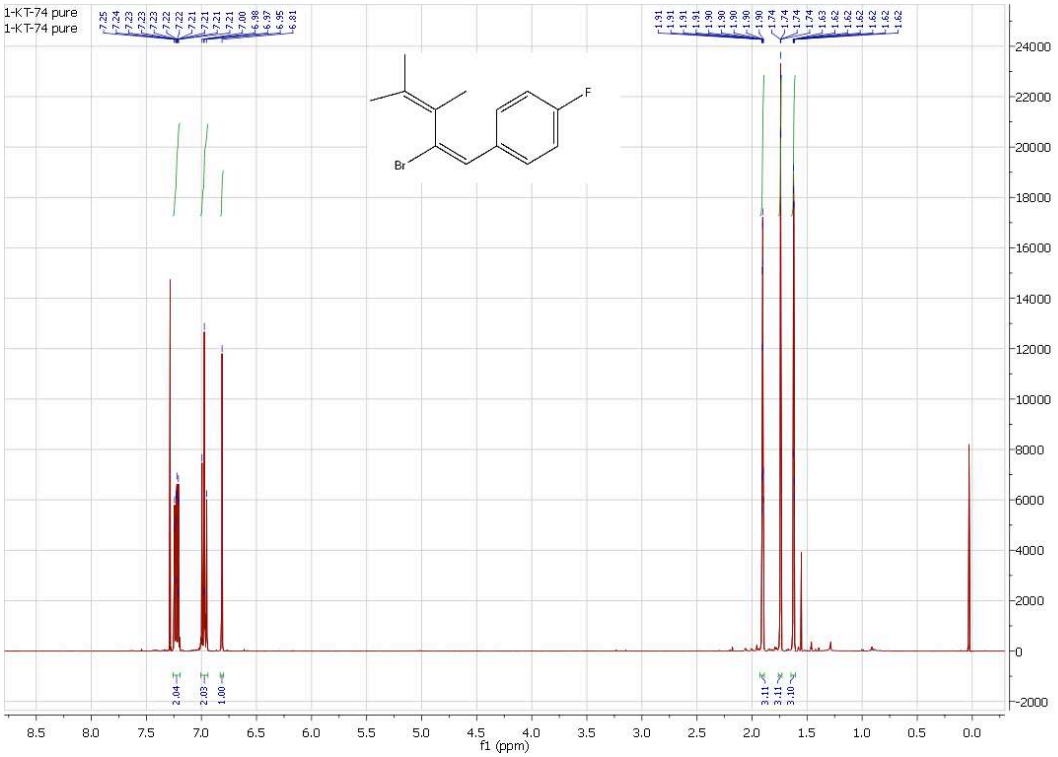
Br
f1 (ppm)

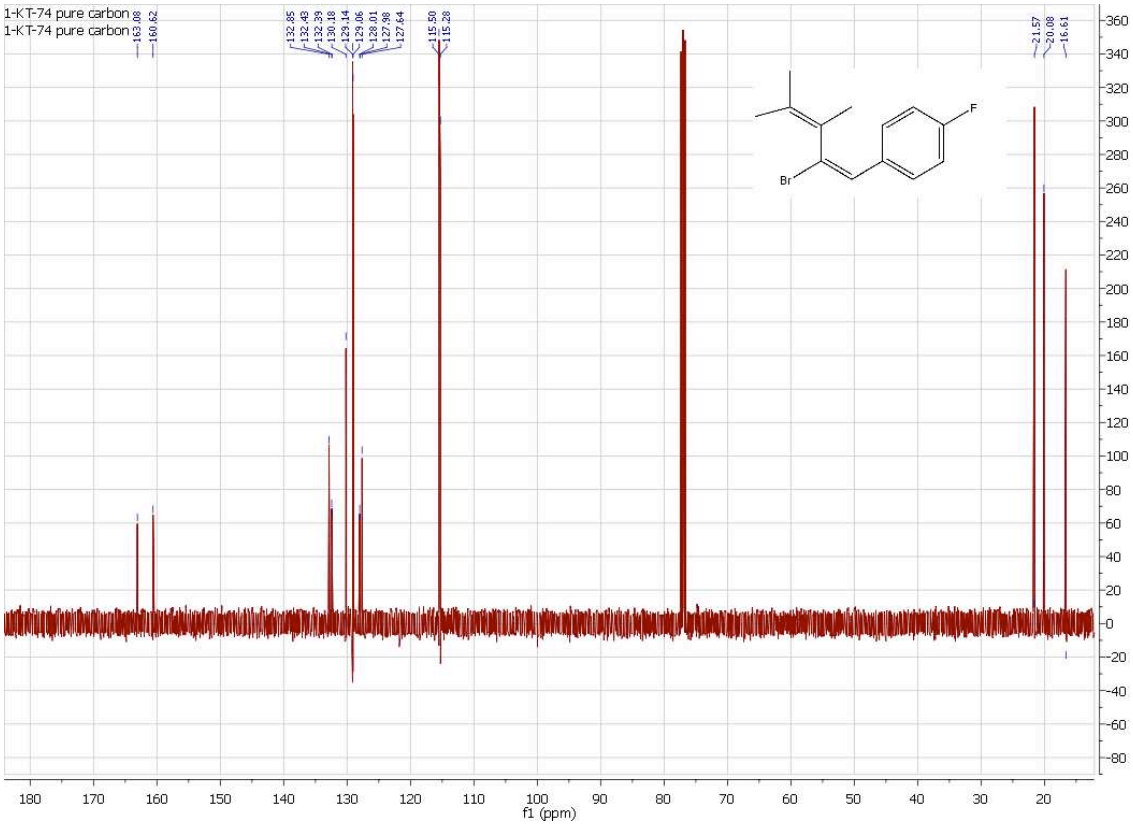

Cl
Br
f1 (ppm)

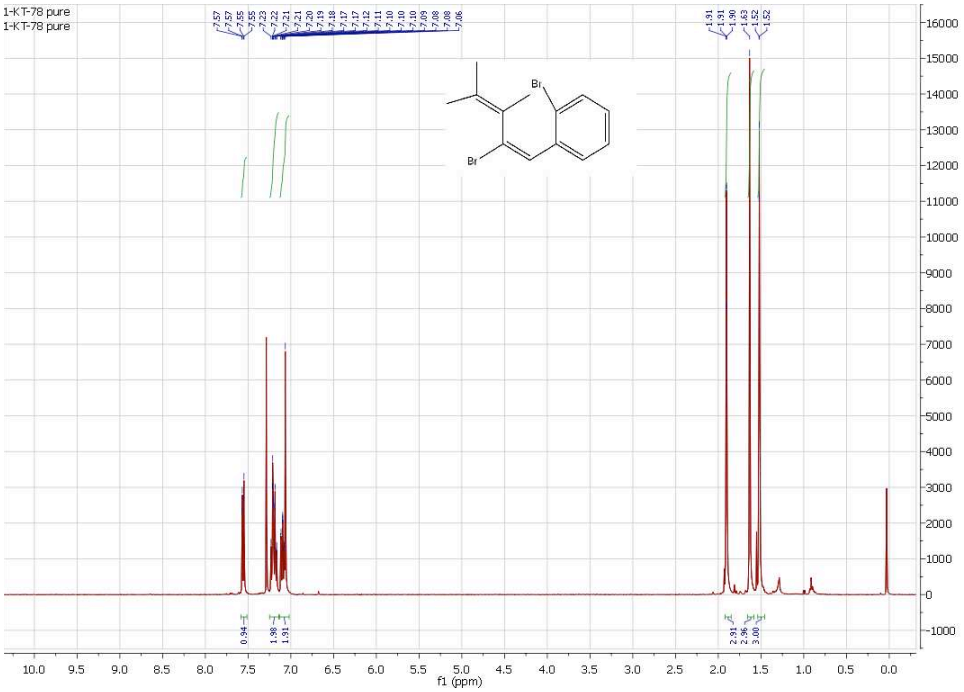

Br
Cl
f1 (ppm)

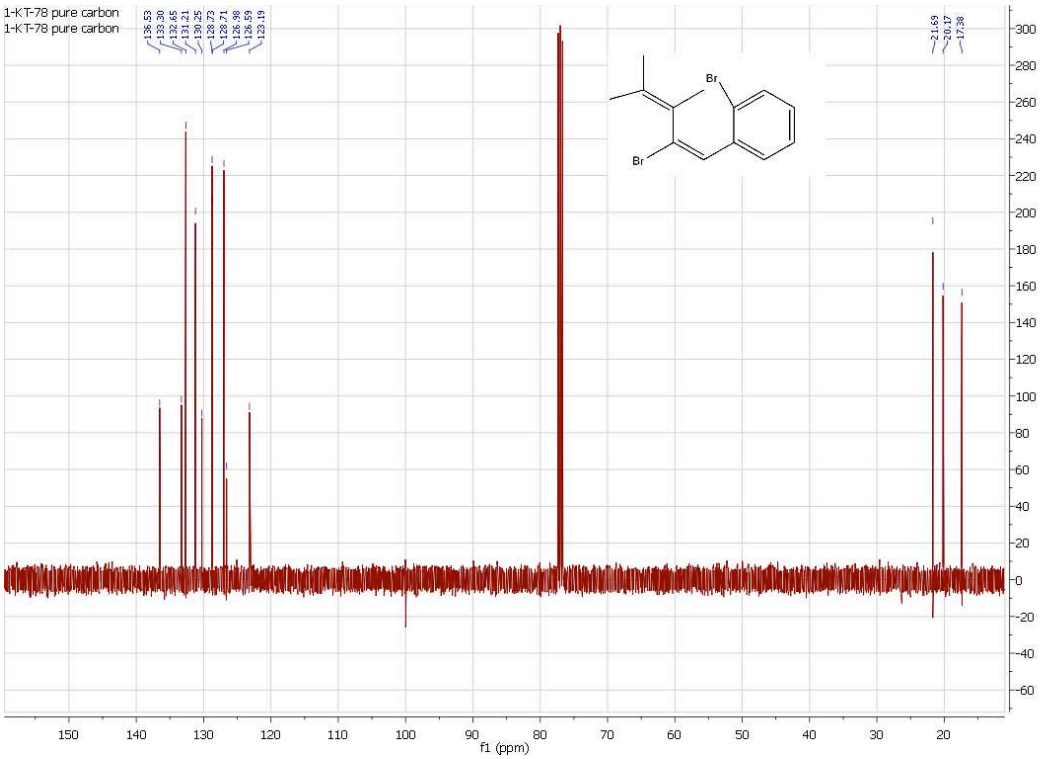

1-KT-73 5-7
1-KT-73 5-7
NO2
Br
f1 (ppm)


1-KT-73 5-7 carbon
1-KT-73 5-7 carbon
NO2
Br
f1 (ppm)


1-KT-74 pure
1-KT-74 pure
F
Br
f1 (ppm)


1-KT-74 pure carbon
1-KT-74 pure carbon
F
Br
f1 (ppm)


1-KT-78 pure
1-KT-78 pure
Br
Br
f1 (ppm)


1-KT-78 pure carbon
1-KT-78 pure carbon
Br
Br
f1 (ppm)

X-Ray Structure for 5a

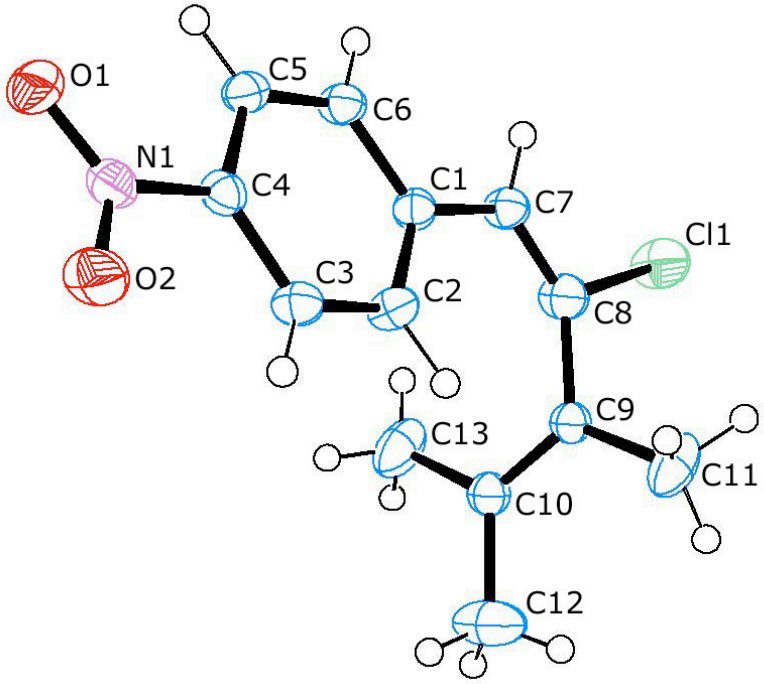


Table 1. Crystal data and structure refinement for **5a**

csuf5_0m		
Empirical formula	C13 H14 Cl N O2	
Formula weight	251.70	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 1 2/n 1	
Unit cell dimensions	a = 13.0021(13) Å	⟨= 90°.
	b = 7.2565(7) Å	®= 111.3350(10)°.
	c = 14.3625(15) Å	© = 90°.
Volume	1262.2(2) $Å^3$	
Z	4	
Density (calculated)	1.325 Mg/m^3	
Absorption coefficient	0.292 mm^{-1}	

F(000)	528
Crystal size	0.38 x 0.33 x 0.18 mm^3
Theta range for data collection	4.03 to 30.62°.
Index ranges	-18<=h<=18, -10<=k<=10, -20<=l<=14
Reflections collected	9111
Independent reflections	3699 [R(int) = 0.0172]
Completeness to theta = 30.62°	94.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3699 / 0 / 189
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0456, wR2 = 0.1272
R indices (all data)	R1 = 0.0554, wR2 = 0.1354
Largest diff. peak and hole	0.465 and -0.438 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for csuf5_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	9183(1)	2106(2)	4824(1)	22(1)
C(2)	8142(1)	1402(2)	4242(1)	27(1)
C(3)	7794(1)	1374(2)	3211(1)	26(1)
C(4)	8486(1)	2068(2)	2758(1)	23(1)
C(5)	9515(1)	2792(2)	3299(1)	26(1)
C(6)	9859(1)	2789(2)	4332(1)	25(1)
C(7)	9631(1)	2134(2)	5923(1)	26(1)
C(8)	9092(1)	1914(2)	6542(1)	31(1)
C(9)	7920(2)	1341(2)	6329(1)	23(1)
C(10)	7125(2)	2628(3)	6066(1)	26(1)
C(11)	7688(2)	-701(2)	6405(1)	40(1)
C(12)	5926(2)	2103(3)	5821(2)	53(1)
C(13)	7414(2)	4646(2)	6024(2)	47(1)
C(9B)	7902(5)	2602(9)	6302(4)	30(1)
C(10B)	7201(5)	1311(9)	6205(4)	32(1)
Cl(1)	9887(1)	1980(1)	7837(1)	43(1)
N(1)	8114(1)	2035(2)	1664(1)	28(1)

O(1)	8677(1)	2826(2)	1265(1)	38(1)
O(2)	7245(1)	1235(2)	1199(1)	39(1)

Table 3. Bond lengths [Å] and angles [°] for csuf5_0m.

C(1)-C(6)	1.4020(17)
C(1)-C(2)	1.4031(18)
C(1)-C(7)	1.4710(18)
C(2)-C(3)	1.3814(18)
C(2)-H(2A)	0.9300
C(3)-C(4)	1.3829(18)
C(3)-H(3A)	0.9300
C(4)-C(5)	1.3834(18)
C(4)-N(1)	1.4665(16)
C(5)-C(6)	1.3855(18)
C(5)-H(5A)	0.9300
C(6)-H(6A)	0.9300
C(7)-C(8)	1.3256(19)
C(7)-H(1)	0.95(2)
C(8)-C(9)	1.501(2)
C(8)-C(9B)	1.541(6)
C(8)-Cl(1)	1.7691(15)
C(9)-C(10)	1.341(3)
C(9)-C(11)	1.524(2)
C(10)-C(12)	1.516(3)
C(10)-C(13)	1.518(2)
C(11)-C(10B)	1.575(6)
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-C(10B)	1.648(7)
C(12)-H(12C)	0.9600
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(13)-C(9B)	1.605(6)
C(13)-H(13A)	0.9600
C(13)-H(13C)	0.9600
C(13)-H(13B)	0.9600
C(9B)-C(10B)	1.279(9)

N(1)-O(1)	1.2246(16)
N(1)-O(2)	1.2294(16)

C(6)-C(1)-C(2)	118.30(12)
C(6)-C(1)-C(7)	117.38(11)
C(2)-C(1)-C(7)	124.29(11)
C(3)-C(2)-C(1)	120.85(12)
C(3)-C(2)-H(2A)	119.6
C(1)-C(2)-H(2A)	119.6
C(2)-C(3)-C(4)	118.90(12)
C(2)-C(3)-H(3A)	120.6
C(4)-C(3)-H(3A)	120.6
C(3)-C(4)-C(5)	122.38(12)
C(3)-C(4)-N(1)	118.76(11)
C(5)-C(4)-N(1)	118.86(11)
C(4)-C(5)-C(6)	118.06(12)
C(4)-C(5)-H(5A)	121.0
C(6)-C(5)-H(5A)	121.0
C(5)-C(6)-C(1)	121.50(12)
C(5)-C(6)-H(6A)	119.2
C(1)-C(6)-H(6A)	119.2
C(8)-C(7)-C(1)	128.24(12)
C(8)-C(7)-H(1)	118.4(12)
C(1)-C(7)-H(1)	113.4(12)
C(7)-C(8)-C(9)	129.92(13)
C(7)-C(8)-C(9B)	122.9(2)
C(9)-C(8)-C(9B)	35.0(2)
C(7)-C(8)-Cl(1)	116.91(11)
C(9)-C(8)-Cl(1)	112.53(10)
C(9B)-C(8)-Cl(1)	112.4(2)
C(10)-C(9)-C(8)	119.04(16)
C(10)-C(9)-C(11)	123.04(17)
C(8)-C(9)-C(11)	117.91(16)
C(9)-C(10)-C(12)	120.77(18)
C(9)-C(10)-C(13)	120.46(17)
C(12)-C(10)-C(13)	118.76(17)

C(9)-C(11)-C(10B)	33.1(2)
C(9)-C(11)-H(11A)	109.5
C(10B)-C(11)-H(11A)	78.9
C(9)-C(11)-H(11B)	109.5
C(10B)-C(11)-H(11B)	134.0
H(11A)-C(11)-H(11B)	109.5
C(9)-C(11)-H(11C)	109.5
C(10B)-C(11)-H(11C)	109.6
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-C(10B)	35.5(2)
C(10)-C(12)-H(12C)	109.5
C(10B)-C(12)-H(12C)	76.7
C(10)-C(12)-H(12A)	109.5
C(10B)-C(12)-H(12A)	109.2
H(12C)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
C(10B)-C(12)-H(12B)	135.6
H(12C)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(13)-C(9B)	35.0(2)
C(10)-C(13)-H(13A)	109.5
C(9B)-C(13)-H(13A)	130.1
C(10)-C(13)-H(13C)	109.5
C(9B)-C(13)-H(13C)	115.3
H(13A)-C(13)-H(13C)	109.5
C(10)-C(13)-H(13B)	109.5
C(9B)-C(13)-H(13B)	75.4
H(13A)-C(13)-H(13B)	109.5
H(13C)-C(13)-H(13B)	109.5
C(10B)-C(9B)-C(8)	113.9(5)
C(10B)-C(9B)-C(13)	116.6(5)
C(8)-C(9B)-C(13)	129.0(4)
C(9B)-C(10B)-C(11)	115.9(6)
C(9B)-C(10B)-C(12)	111.8(5)
C(11)-C(10B)-C(12)	132.2(4)

O(1)-N(1)-O(2)	123.74(12)
O(1)-N(1)-C(4)	118.29(11)
O(2)-N(1)-C(4)	117.97(11)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (^{2}x 10^3) for csuf5_A. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^*2U11 + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	23(1)	23(1)	22(1)	-1(1)	10(1)	1(1)
C(2)	25(1)	32(1)	26(1)	-2(1)	12(1)	-5(1)
C(3)	22(1)	31(1)	26(1)	-3(1)	9(1)	-3(1)
C(4)	22(1)	27(1)	20(1)	0(1)	8(1)	4(1)
C(5)	21(1)	34(1)	24(1)	1(1)	10(1)	-1(1)
C(6)	20(1)	32(1)	24(1)	-1(1)	8(1)	-2(1)
C(7)	24(1)	31(1)	24(1)	-2(1)	9(1)	-1(1)
C(8)	28(1)	44(1)	22(1)	-1(1)	9(1)	0(1)
C(9)	27(1)	21(1)	24(1)	-2(1)	14(1)	-3(1)
C(10)	29(1)	26(1)	26(1)	-1(1)	15(1)	-2(1)
C(11)	63(1)	23(1)	46(1)	0(1)	33(1)	-4(1)
C(12)	30(1)	78(1)	53(1)	-12(1)	19(1)	-6(1)
C(13)	68(1)	26(1)	65(1)	7(1)	45(1)	5(1)
C(9B)	33(3)	32(3)	27(3)	-2(2)	14(2)	7(2)
C(10B)	38(3)	31(3)	31(3)	-6(2)	19(3)	4(2)
Cl(1)	37(1)	71(1)	22(1)	-2(1)	10(1)	-6(1)
N(1)	23(1)	37(1)	22(1)	1(1)	8(1)	6(1)
O(1)	33(1)	58(1)	26(1)	5(1)	14(1)	0(1)
O(2)	28(1)	58(1)	25(1)	-5(1)	4(1)	-5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (^{2}x 10 ^{3}) for csuf5_0m.

	x	y	z	U(eq)
H(2A)	7681	949	4553	45(5)
H(3A)	7106	895	2829	30(4)
H(5A)	9963	3267	2979	38(5)
H(6A)	10553	3251	4709	40(5)
H(1)	10405(16)	2330(20)	6200(14)	35(5)
H(11A)	7031	-839	6557	84(8)
H(11B)	8300	-1255	6926	95(10)
H(11C)	7585	-1295	5781	89(9)
H(12C)	5889	997	6174	50(6)
H(12A)	5579	1898	5115	166(18)
H(12B)	5553	3081	6019	87(9)
H(13A)	6992	5384	6311	62(6)
H(13C)	7244	5004	5341	93(9)
H(13B)	8187	4825	6394	91(9)

Computational Details

Gaussian 09[3] was used to fully optimize all the structures reported in this paper at the B3LYP level of density functional theory.[4] The 6-311G(d) basis set was chosen to describe titanium. The 6-31G(d) basis set was used for other atoms. This basis set combination will be referred to as BS1. Frequency calculations were carried out at the same level of theory as for structural optimization. To further refine the energies obtained from the B3LYP/BS1 calculations, we carried out single point energy calculations for all the structures with the larger 6-311+G(2d,p) basis set (BS2). The solvation energies were calculated using BS2 on gas phase optimized geometries with the CPCM solvation model[5] using dichloromethane as a solvent. To estimate the corresponding Gibbs free energies in solvent (ΔG), entropy corrections were calculated at the B3LYP/BS1 level and added to the solvent potential energies. We have used the solvent energies throughout the paper unless otherwise stated.

Table S1. Cartesian coordinates and total energies for all of the calculated structures

Ph
E(BS1) = -732.812878 a.u.
G(BS1) = -732.568723 a.u.
E(BS2,solvent) = -733.050411 a.u.

C	-1.71434300	-1.71737900	0.01364900
C	-1.21309900	-0.52766500	0.18203100
C	-2.72280700	-0.58936600	0.11346700
C	-3.55728200	-0.42959800	1.38497600
H	-3.81320100	0.62386700	1.56284800
H	-4.50437100	-0.98197600	1.31197400
H	-3.01875900	-0.79818400	2.26538600
C	-3.44190900	-0.09171200	-1.13983600
H	-4.37942200	-0.64039800	-1.30653900
H	-3.70138100	0.97188000	-1.05077000
H	-2.81428800	-0.21040900	-2.02946700
C	-1.55295500	-3.18577400	-0.11159200
H	-2.00955900	-3.55024100	-1.04085600
H	-0.49723200	-3.47578600	-0.10594300
H	-2.05950500	-3.70257000	0.71406100
C	-0.04841100	0.35856700	0.42108500
H	-0.08653700	0.75581800	1.44061200
C	1.29668000	-0.30175000	0.19002800
C	2.30996400	-0.18357000	1.14762200
C	1.55088700	-1.01525400	-0.98945400
C	3.55413800	-0.78280300	0.93929400

[3] M. J. Frisch, et al. *Gaussian 09*, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.
[4] a) C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; b) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett*. **1989**, *157*, 200; c) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
[5] V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995.

H	2.12533600	0.39041100	2.05151100
C	2.79455600	-1.60945400	-1.20062900
H	0.76892500	-1.10209900	-1.73855000
C	3.79837100	-1.49752500	-0.23424400
H	4.33228800	-0.68663000	1.69179000
H	2.98140200	-2.16089700	-2.11847700
H	4.76662600	-1.96324700	-0.39805200
O	-0.20482700	1.50492400	-0.48085800
C	0.22673600	2.70068100	-0.01351200
O	0.69340000	2.87302900	1.09206200
C	0.04876100	3.77475700	-1.06214300
H	-0.97802100	3.77399400	-1.44056300
H	0.29245300	4.74675400	-0.63163800
H	0.71093800	3.57316400	-1.91140600

1_Ph_Cl

E(BS1) = -3423.326578 a.u.

G(BS1) = -3423.088255 a.u.

E(BS2,solvent) = -3423.721254 a.u.

C	3.40734700	-1.36327100	1.03860400
C	2.63842000	-1.07583700	0.02824300
C	2.79241600	-2.55664500	0.33260000
C	1.65394800	-3.32517700	1.00330100
H	1.01428300	-3.82354800	0.26181800
H	2.04685100	-4.11220700	1.66093100
H	1.01964500	-2.66338500	1.60122800
C	3.67599300	-3.43786700	-0.55161500
H	4.12385500	-4.25483300	0.02957800
H	3.09609200	-3.90706600	-1.35920300
H	4.48879000	-2.86246600	-1.00868600
C	4.31491400	-0.95737700	2.13595800
H	5.30495100	-1.41273600	2.00601100
H	4.43056400	0.12962600	2.18195100
H	3.92755900	-1.30904400	3.10059600
C	2.04863100	-0.03407500	-0.85043000
H	2.30256000	-0.22500700	-1.89797500
C	2.45804200	1.37186800	-0.47894600
C	2.06067100	1.92864300	0.74441700
C	3.26042900	2.11689600	-1.34805400
C	2.46489700	3.21767400	1.08774000
H	1.42338400	1.35818400	1.41339700
C	3.67285300	3.40437400	-0.99821500
H	3.56619500	1.69166900	-2.30160500
C	3.27460100	3.95626600	0.21964400
H	2.14426700	3.64822100	2.03215700
H	4.29668800	3.97549400	-1.68004100
H	3.58797200	4.96066400	0.49051600
O	0.57131800	-0.09215700	-0.72820600
C	-0.18349300	-0.91305300	-1.42975800
O	-1.39630900	-0.94352900	-1.19600400
C	0.39776900	-1.77804400	-2.51764400
H	1.22898700	-2.38183900	-2.14304100
H	-0.38992800	-2.42612100	-2.90110500
H	0.77338800	-1.15180600	-3.33559100
Ti	-2.80030500	0.09287700	0.12915100
Cl	-1.55529000	-0.78054800	1.76178800

Cl	-2.19599900	1.88147100	-1.04634900
Cl	-4.29170700	-1.24162100	-0.79224100
Cl	-4.18077300	1.18082500	1.48305800

$TiCl_4$
E(BS1) = -2690.507239 a.u.
G(BS1) = -2690.535374 a.u.
E(BS2,solvent) = -2690.670084 a.u.

Ti	0.00014300	0.00022400	-0.00042100
Cl	-1.63886700	-1.01736600	-0.99248600
Cl	1.88034000	-0.62118800	-0.88571400
Cl	-0.23453100	2.14423400	-0.22991800
Cl	-0.00712800	-0.50596900	2.10866200

2_Ph
E(BS1) = -504.088269 a.u.
G(BS1) = -503.889511 a.u.
E(BS2,solvent) = -504.289284 a.u.

C	1.87409300	0.86860600	-0.16683800
C	1.13620800	-0.24669400	-0.07669700
C	2.66055800	-0.34147400	0.17133700
C	3.06009400	-0.61788400	1.62512100
H	3.13134100	-1.69730100	1.79457200
H	4.04301600	-0.17655500	1.82740900
H	2.34023400	-0.20080000	2.33483300
C	3.63062400	-0.89577700	-0.86670200
H	4.63295700	-0.47913600	-0.71788500
H	3.71017100	-1.98424400	-0.76196600
H	3.31155800	-0.67300400	-1.88974300
C	1.98817100	2.22866400	-0.71439000
H	2.75120800	2.24973600	-1.50401500
H	1.04142900	2.61135800	-1.10309100
H	2.35554200	2.90160400	0.07429700
C	-0.04160400	-0.95016500	-0.24281300
H	0.06353700	-2.00287600	-0.50806000
C	-1.36976000	-0.47264100	-0.07483800
C	-1.65940600	0.84512000	0.37659300
C	-2.44560700	-1.35019600	-0.38552600
C	-2.97135700	1.26949500	0.48058400
H	-0.84572100	1.50531400	0.65823000
C	-3.75710300	-0.91517100	-0.28066500
H	-2.22747300	-2.36061000	-0.72006200
C	-4.01962500	0.39241300	0.15033600
H	-3.19547800	2.27283200	0.82797400
H	-4.57628800	-1.58274800	-0.52661700
H	-5.04775900	0.73064200	0.24111200

$[TiCl_4(OAc)]^-$
E(BS1) = -2919.118366 a.u.
G(BS1) = -2919.101188 a.u.
E(BS2,solvent) = -2919.425697 a.u.

O	1.48424300	-0.00554900	1.09589100
C	2.13372900	-0.00774000	0.00601800
O	1.47605800	-0.00558200	-1.08292300
C	3.64032200	-0.00658000	-0.01119700

H	4.03583500	-0.10193800	1.00186700
H	3.99879300	-0.83085500	-0.63615700
H	3.99380400	0.92903600	-0.45888900
Ti	-0.34601900	-0.00023700	-0.00312900
Cl	-0.14956100	-2.32809000	-0.00013900
Cl	-0.13108300	2.32728900	-0.00012700
Cl	-1.71172500	0.00582700	-1.81072400
Cl	-1.69838000	0.00579400	1.81624600

3Ph

E(BS1) = -504.1061092 a.u.
G(BS1) = -503.909358 a.u.
E(BS2,solvent) = -504.3152005 a.u.

C	2.12640400	0.58860900	-0.13156900
C	0.87280700	0.40280700	-0.61912300
C	2.94952800	-0.55235400	0.03633100
C	2.51140100	-1.93374500	-0.28164400
H	3.20080700	-2.36226100	-1.02441900
H	2.63120200	-2.56075700	0.61415100
H	1.48765800	-2.00524000	-0.64696300
C	4.33264800	-0.38352100	0.55720000
H	4.30491600	0.08141600	1.55397200
H	4.87719000	-1.32675400	0.61925800
H	4.89438000	0.31995600	-0.07394600
C	2.62149600	1.98680800	0.21121700
H	3.48584100	2.26094600	-0.40419000
H	1.83513700	2.72263100	0.03649300
H	2.92287300	2.05351000	1.26239300
C	-0.32883800	0.31990100	-1.11474200
H	-0.36576500	0.39201800	-2.20770800
C	-1.61943700	0.13071000	-0.43275400
C	-1.71593600	0.05177700	0.96857500
C	-2.77987700	0.03274500	-1.21793600
C	-2.95742500	-0.12265500	1.56861500
H	-0.82302200	0.13099600	1.58336500
C	-4.02107800	-0.14213700	-0.60895400
H	-2.70922200	0.09500800	-2.30052000
C	-4.11143700	-0.22030800	0.78189100
H	-3.02976100	-0.18117300	2.65032500
H	-4.91485500	-0.21623800	-1.22048900
H	-5.07891500	-0.35588100	1.25563700

4_Ph_Cl

E(BS1) = -3423.337915 a.u.
G(BS1) = -3423.104592 a.u.
E(BS2,solvent) = -3423.74733 a.u.

C	-1.33180000	1.51798400	0.50292600
C	-2.05628500	0.40192900	0.25003800
C	-1.05417300	2.39253300	-0.57171400
C	-1.67711100	2.25524300	-1.91812000
H	-2.38212600	3.08993700	-2.05665400
H	-0.90929400	2.35980100	-2.69061600
H	-2.20959000	1.31438300	-2.05551200
C	-0.24512800	3.62243800	-0.32248900
H	0.64153100	3.40115300	0.27761300

H	0.05926700	4.10163800	-1.25437800
H	-0.85692300	4.33764100	0.25093600
C	-0.77599900	1.76097500	1.89555000
H	-1.25438700	1.09153100	2.61301800
H	0.29985900	1.55324300	1.90412400
H	-0.94454100	2.79419600	2.21758500
C	-2.81349500	-0.63836100	0.03885400
H	-2.27331600	-1.55740300	-0.19582400
C	-4.28706400	-0.70389400	0.07958300
C	-5.08173900	0.40478600	0.41929500
C	-4.91046600	-1.92188000	-0.23335200
C	-6.46832200	0.29334400	0.44268200
H	-4.60920500	1.35131800	0.66909400
C	-6.30058900	-2.02918600	-0.20933500
H	-4.30149500	-2.78301100	-0.49470500
C	-7.08247500	-0.92351100	0.12777000
H	-7.07323300	1.15568700	0.70852800
H	-6.77072800	-2.97737800	-0.45347100
H	-8.16528200	-1.00721800	0.14726200
Cl	0.40610800	-1.35091000	0.44863500
Ti	2.53539500	-0.54009700	-0.35910600
Cl	1.40965900	1.04364500	-1.62755100
Cl	2.78571200	-2.31996100	-1.66367600
Cl	4.54895000	0.39521200	-0.81238000
O	2.42870800	0.71964300	1.42113300
O	3.30050900	-1.27065700	1.38044000
C	3.00348800	-0.21862200	2.05024800
C	3.31608100	-0.14186100	3.51519500
H	2.65285600	-0.82698100	4.05593500
H	4.34464500	-0.47014000	3.69064600
H	3.17270200	0.87458200	3.88587300

5_Ph_Cl

E(BS1) = -3423.339407 a.u.
G(BS1) = -3423.106061 a.u.
E(BS2,solvent) = -3423.747895 a.u.

C	1.26798500	2.06485500	0.61880500
C	1.84716300	0.87018000	0.40650900
C	0.73272100	2.76168200	-0.50634900
C	0.89183500	2.26795700	-1.89787900
H	0.00335300	1.66327800	-2.14429900
H	0.92852000	3.10135900	-2.60583900
H	1.75603400	1.61452300	-2.02562800
C	0.15074900	4.12335200	-0.34389100
H	0.97672900	4.84010300	-0.49799500
H	-0.59972600	4.32142900	-1.11234200
H	-0.27855200	4.29964900	0.64126600
C	1.10902500	2.60260100	2.03188000
H	0.04568500	2.64913600	2.29241000
H	1.61151300	1.94609500	2.74520100
H	1.53576600	3.60659600	2.13310400
C	2.35774400	-0.31578500	0.23123900
H	1.60916500	-1.11395500	0.26472000
C	3.76252800	-0.69096000	-0.00426000
C	4.80278000	0.25458000	0.01802000
C	4.06698400	-2.03752700	-0.25689200

C	6.11666100	-0.14200200	-0.20977800
H	4.57672700	1.29910500	0.21763400
C	5.38521900	-2.43090400	-0.48534000
H	3.26655400	-2.77202800	-0.27793500
C	6.41210600	-1.48596800	-0.46234000
H	6.91348400	0.59619900	-0.18946100
H	5.60812800	-3.47565400	-0.68152300
H	7.43897600	-1.79274900	-0.63945200
Cl	-1.95038000	1.79753800	0.07771800
Ti	-2.41003900	-0.59137500	-0.24971600
Cl	-1.15969700	-0.56922300	-2.15674700
Cl	-4.49416300	-0.13425400	-0.84935600
Cl	-2.61671600	-2.84438900	-0.22610200
O	-0.62636200	-0.81583900	0.99630400
O	-2.63586700	-0.60838800	1.79703700
C	-1.38997000	-0.78585200	2.01126600
C	-0.88059600	-0.97617400	3.41075800
H	0.21019300	-0.94120000	3.43573400
H	-1.30576900	-0.21143600	4.06749400
H	-1.21944100	-1.95101900	3.77974900

$TiCl_3(OAc)$
E(BS1) = -2458.78188 a.u.
G(BS1) = -2458.768070 a.u.
E(BS2,solvent) = -2458.99343 a.u.

O	-2.68335600	-1.16555900	-0.01195200
C	-2.44439200	0.00969300	-0.00017100
O	-1.13976000	0.47711600	0.00683900
C	-3.43645400	1.14170800	0.01164200
H	-4.44958900	0.73847100	-0.00849000
H	-3.29235800	1.75143900	0.90994200
H	-3.27135900	1.79157500	-0.85407000
Ti	0.57908300	0.03596400	0.00110100
Cl	0.93693400	-1.38712300	-1.60539400
Cl	1.75149800	1.85299900	-0.32922300
Cl	1.08471500	-0.84667400	1.92876300

6_Ph_Cl
E(BS1) = -964.576512 a.u.
G(BS1) = -964.378017 a.u.
E(BS2,solvent) = -964.768820 a.u.

C	-2.22323900	0.11468800	0.42042200
C	-0.80107900	0.45452300	0.14477500
C	-2.88369700	-0.79319200	-0.33430500
C	-2.29441300	-1.45407800	-1.55996600
H	-2.15679300	-2.53237900	-1.39586700
H	-2.98955100	-1.35868900	-2.40545000
H	-1.33319300	-1.03209100	-1.85536500
C	-4.30022500	-1.24442200	-0.05916500
H	-4.96774900	-0.93295900	-0.87495700
H	-4.34499900	-2.34173700	-0.02764900
H	-4.71576100	-0.87067800	0.87760700
C	-2.80802300	0.85664800	1.60606400
H	-2.31634000	0.54668700	2.53798100
H	-2.63621400	1.93392100	1.50282200

H	-3.88223400	0.70421500	1.72048400
C	0.22288700	-0.40069800	0.32528500
H	-0.11230700	-1.37008100	0.69294600
C	1.68042600	-0.31807300	0.16443300
C	2.38133900	0.71182100	-0.49470400
C	2.43454800	-1.38116300	0.70451100
C	3.77140200	0.67678200	-0.59158300
H	1.84125600	1.53558200	-0.94082800
C	3.82298700	-1.41136700	0.61118500
H	1.91458600	-2.19227500	1.20920400
C	4.50076700	-0.37775400	-0.03840100
H	4.28791300	1.48205900	-1.10746300
H	4.37470800	-2.24253500	1.04232400
H	5.58443200	-0.39609600	-0.11680200
Cl	-0.56293200	2.14498700	-0.36766400

7_Ph_Cl

E(BS1) = -964.577187 a.u.
G(BS1) = -964.377961 a.u.
E(BS2,solvent) = -964.769576 a.u.

C	1.56344000	0.34851700	0.48890700
C	0.98057700	-0.95900700	0.08741500
C	1.90676500	1.27203600	-0.43570200
C	1.70997400	1.05485200	-1.91734700
H	1.04148800	1.82141700	-2.33326700
H	2.66708300	1.15489900	-2.44743300
H	1.29044800	0.07500000	-2.15106100
C	2.52242600	2.61170300	-0.10870000
H	3.51377900	2.69720200	-0.57490300
H	1.91289500	3.42298300	-0.53011700
H	2.63836700	2.80157100	0.95936400
C	1.76155800	0.46446100	1.98691500
H	0.79788300	0.39464800	2.50809300
H	2.37928600	-0.36603600	2.35092100
H	2.24349500	1.39630400	2.28828200
C	-0.29709200	-1.32845300	-0.10808500
H	-0.45964800	-2.37500200	-0.35605000
C	-1.53636600	-0.53918500	-0.03296700
C	-1.61274700	0.82983100	0.29164200
C	-2.74273800	-1.21828100	-0.29687300
C	-2.84286400	1.48108000	0.34871900
H	-0.70472000	1.38526500	0.49233100
C	-3.97190400	-0.56533600	-0.24146200
H	-2.70855700	-2.27579600	-0.54816200
C	-4.02856100	0.79107100	0.08280200
H	-2.87516900	2.53766700	0.60218900
H	-4.88467500	-1.11672800	-0.45102700
H	-4.98458900	1.30549900	0.12798200
Cl	2.21516700	-2.25403700	-0.04757200

8_Ph_Cl

E(BS1) = -964.565602 a.u.
G(BS1) = -964.365544 a.u.
E(BS2,solvent) = -964.7590836 a.u.

C	-1.44436500	-0.10390000	0.73888300

C	-0.28297800	-0.66262600	0.48839000
C	-2.35217900	0.34846300	-0.40295500
C	-1.74288700	0.14378300	-1.78842600
H	-2.46398700	0.42422000	-2.56095700
H	-0.85272700	0.77460700	-1.89476400
H	-1.44708300	-0.89582400	-1.94403500
C	-2.83507200	1.79047500	-0.21974600
H	-1.96881700	2.46427800	-0.22911400
H	-3.50328600	2.07323000	-1.03822400
H	-3.37122400	1.92655100	0.72189600
C	-1.90829500	0.11298100	2.16885700
H	-2.91015200	-0.30591400	2.31466600
H	-1.22313900	-0.36877900	2.87038000
H	-1.95317700	1.17995100	2.41892000
C	0.88442100	-1.22483400	0.26106700
H	0.91888100	-2.31262000	0.17144900
C	2.17823900	-0.53245900	0.10327500
C	2.30161800	0.86389400	0.21432800
C	3.33169500	-1.28595200	-0.16816500
C	3.53845900	1.48220900	0.05650800
H	1.41745000	1.45842000	0.42868800
C	4.57127500	-0.66601900	-0.32615800
H	3.25151600	-2.36710000	-0.25565000
C	4.68021300	0.72079400	-0.21501500
H	3.61485100	2.56278800	0.14636000
H	5.45162200	-1.26781100	-0.53598600
H	5.64465800	1.20595800	-0.33760800
Cl	-3.88977900	-0.73369500	-0.33771000

1TS_Ph_Cl

E(BS1) = -3423.306283 a.u.

G(BS1) = -3423.069005 a.u.

E(BS2,solvent) = -3423.706921 a.u.

C	-2.31827400	-1.58841300	-1.14254800
C	-2.40933300	-0.88537500	-0.02671300
C	-2.98317800	-2.29659700	0.00349100
C	-2.23569500	-3.43768600	0.69032300
H	-2.50355800	-3.48787700	1.75475000
H	-2.50685200	-4.40378600	0.24659900
H	-1.15104300	-3.31701100	0.60897100
C	-4.50445000	-2.44792800	0.02609000
H	-4.80918300	-3.38178400	-0.46332200
H	-4.87408100	-2.48331600	1.05893000
H	-4.99975800	-1.61573400	-0.48457700
C	-1.70716700	-1.80601300	-2.46520900
H	-2.43616300	-2.23384700	-3.16404300
H	-1.27213600	-0.89362900	-2.87999100
H	-0.89215100	-2.53471500	-2.35045500
C	-2.05158600	0.23771600	0.75895000
H	-2.22821900	0.13306400	1.82542600
C	-2.03791600	1.60701500	0.27507100
C	-2.05774200	1.91894000	-1.09854700
C	-2.00163400	2.65521000	1.21770200
C	-2.03447200	3.24458300	-1.51316400
H	-2.08542700	1.12065600	-1.83033500
C	-1.98406600	3.97967500	0.80026100

H	-1.97734100	2.41939600	2.27848800
C	-1.99752700	4.27451500	-0.56702400
H	-2.03787900	3.47920100	-2.57297500
H	-1.95156500	4.78096600	1.53191400
H	-1.97638900	5.30946000	-0.89638800
O	-0.06754400	-0.07312900	0.99037400
C	0.56925800	-0.49012200	2.02442100
O	1.80948000	-0.67348300	1.88894200
C	-0.10287400	-0.75554700	3.34311300
H	-0.87816400	-1.52009100	3.22221900
H	0.63332900	-1.09956100	4.07021500
H	-0.57765500	0.15917400	3.71491400
Ti	2.11001200	-0.15858900	-0.12639900
Cl	1.47568000	-2.36820900	-0.48039600
Cl	2.26899400	1.96799800	0.69655800
Cl	4.25616500	-0.47857200	-0.46306200
Cl	1.25259600	0.51239800	-2.09906600

2TS_Ph
E(BS1) = -504.087512 a.u.
G(BS1) = -503.888344 a.u.
E(BS2,solvent) = -504.289616 a.u.

C	2.06418500	0.86635000	-0.16766800
C	1.07850100	-0.00780500	-0.29334000
C	2.63680600	-0.37998400	0.31644300
C	2.50400700	-0.83791400	1.75656300
H	2.38795000	-1.92431300	1.81784500
H	3.43098900	-0.57475200	2.28521600
H	1.67022900	-0.35525600	2.27104800
C	3.72560100	-1.04876700	-0.49317500
H	4.70353600	-0.83461500	-0.04326100
H	3.60117600	-2.13786900	-0.47831400
H	3.74438000	-0.71118300	-1.53295000
C	2.54982500	2.11472600	-0.80718900
H	3.42790600	1.90817700	-1.43104300
H	1.77375100	2.58800200	-1.41210100
H	2.87587300	2.81331100	-0.02545200
C	-0.05810800	-0.68695100	-0.59567000
H	0.07652400	-1.63811500	-1.11355200
C	-1.40250000	-0.32504800	-0.26047700
C	-1.71209100	0.86125300	0.45281200
C	-2.45455300	-1.17920400	-0.67733600
C	-3.03159300	1.18369200	0.72153300
H	-0.90964500	1.50973500	0.79129200
C	-3.77405900	-0.84745200	-0.40492600
H	-2.21959000	-2.09090400	-1.21978100
C	-4.06258400	0.33168500	0.29310700
H	-3.27030900	2.09114200	1.26680800
H	-4.57818500	-1.49954900	-0.72989500
H	-5.09520100	0.58869800	0.51009500

3TS_Ph_Cl
E(BS1) = -3423.329325 a.u.
G(BS1) = -3423.093931 a.u.
E(BS2,solvent) = -3423.737633 a.u.

C	-0.64209000	2.55881600	0.75285400
C	-1.70297400	1.76289200	0.40731200
C	-0.16886600	3.48912200	-0.18079900
C	-0.63371700	3.51768600	-1.59226900
H	-0.74557000	4.54684300	-1.95033300
H	0.15478700	3.04280000	-2.19784300
H	-1.54731100	2.94665200	-1.75925200
C	0.91804600	4.43404700	0.20054700
H	1.86517200	3.87041500	0.16841900
H	0.99763800	5.27331000	-0.49395300
H	0.81022300	4.80489200	1.22459300
C	-0.02311000	2.42059700	2.13585200
H	-0.21853100	3.31683600	2.73842700
H	-0.43380200	1.55303400	2.65143300
H	1.05740700	2.27303000	2.05876400
C	-2.92248100	1.28968200	0.41773400
H	-3.57576100	2.05190400	0.86537400
C	-3.64783100	0.07354800	0.01984700
C	-3.03961600	-1.06845700	-0.52950800
C	-5.03907400	0.07069800	0.23600500
C	-3.81602800	-2.18003600	-0.85148500
H	-1.97409700	-1.07536500	-0.72389300
C	-5.80756400	-1.04426700	-0.08739400
H	-5.51835900	0.94922700	0.66194100
C	-5.19633900	-2.17525000	-0.63238200
H	-3.33463600	-3.05348400	-1.28183300
H	-6.87979200	-1.02900800	0.08558600
H	-5.79222000	-3.04726300	-0.88697200
Cl	0.04656000	0.10528700	-1.32459000
Ti	2.06727400	-0.79201000	-0.21052800
Cl	2.87393800	1.34541900	-0.05747500
Cl	2.77180300	-1.58003000	-2.16404400
Cl	3.70163700	-1.68159500	1.06051000
O	0.84884000	-0.60356700	1.55792800
O	0.83571200	-2.36888800	0.29172100
C	0.41790000	-1.77885800	1.34661900
C	-0.55094700	-2.45885100	2.26985400
H	-1.53281700	-2.51001700	1.78481800
H	-0.22013800	-3.48401800	2.45919600
H	-0.63743400	-1.90849000	3.20841900

3_Et

E(BS1) = -351.683136 a.u.
G(BS1) = -351.507028 a.u.
E(BS2,solvent) = -351.851771 a.u.

C	0.95440000	-0.61303400	0.09523300
C	-0.37463400	-0.51982400	0.36722100
C	1.70173900	0.58445000	-0.00081500
C	1.11478900	1.93664800	0.16973100
H	1.64473100	2.45399200	0.98322000
H	1.32286600	2.53173400	-0.73165800
H	0.04446400	1.93785600	0.37205400
C	3.15990600	0.50970000	-0.28536200
H	3.33122500	-0.00815200	-1.24063400
H	3.63224500	1.49238700	-0.32204000
H	3.66461900	-0.10691400	0.47240900

C	1.60105300	-1.97833900	-0.08491300
H	2.37620400	-2.14993800	0.67026500
H	0.85664300	-2.77036700	0.00957300
H	2.06779700	-2.06618600	-1.07221400
C	-1.64205100	-0.51595800	0.61758900
H	-1.94769900	-0.53562600	1.66825900
C	-2.75796000	-0.47225700	-0.42331800
H	-2.32819600	-0.46961400	-1.42905400
H	-3.32155300	-1.40708600	-0.31202600
C	-3.68468500	0.73379000	-0.21487600
H	-3.14896700	1.68005700	-0.34146300
H	-4.49286000	0.70227800	-0.95200600
H	-4.13686400	0.72451800	0.78237600

3TS_Et_Cl

E(BS1) = -3270.913674 a.u.
G(BS1) = -3270.700006 a.u.
E(BS2,solvent) = -3271.280732 a.u.

C	-2.38998600	1.08588000	0.98993500
C	-2.91942000	-0.09801600	0.57054600
C	-2.34429200	2.15454100	0.07626300
C	-2.68151600	1.99338200	-1.36205700
H	-3.20233000	2.87761900	-1.74550300
H	-1.72110800	1.92030000	-1.89593500
H	-3.24318700	1.08504400	-1.58014600
C	-1.99660400	3.53167000	0.53527400
H	-1.25724000	3.53593300	1.33673100
H	-1.63375600	4.14394800	-0.29297200
H	-2.91754700	4.00225300	0.91920700
C	-1.88152000	1.20459200	2.41799900
H	-2.24203800	2.12082000	2.89561600
H	-2.22204100	0.35372100	3.01181500
H	-0.78670200	1.19854500	2.42303100
C	-3.64737700	-1.15507200	0.37725800
H	-4.69974900	-1.01024400	0.65096300
C	-3.29524400	-2.51598900	-0.18754800
Cl	-0.44486500	-0.90423200	-1.08083700
Ti	1.70606000	-0.02620500	-0.35239100
Cl	0.79941700	2.09554700	-0.40114600
Cl	2.57117200	-0.38532800	-2.36669600
Cl	3.61546300	0.68331000	0.63515000
O	0.90424500	-0.41080700	1.62585400
O	2.00485800	-1.87854800	0.46233200
C	1.40620900	-1.57211600	1.55226100
C	1.34665100	-2.55157600	2.68748000
H	1.11162500	-3.54999400	2.30822500
H	2.33413500	-2.60016900	3.16125600
H	0.61056400	-2.23652900	3.42944700
H	-2.21083200	-2.60874500	-0.24961000
H	-3.66964500	-3.26482100	0.52244600
C	-3.93095300	-2.74062700	-1.56784400
H	-3.52219400	-2.03690700	-2.29922700
H	-3.70925700	-3.75481400	-1.91578700
H	-5.02071500	-2.62265900	-1.53983900

3′TS_Et_Cl

E(BS1) = -3270.914406 a.u.
G(BS1) = -3270.700600 a.u.
E(BS2,solvent) = -3271.276982 a.u.

C	-2.88633800	-0.62062800	0.37687500
C	-2.66925700	0.71669700	0.09862800
C	-2.89341300	-1.53215000	-0.67332000
C	-2.63783900	-1.17898000	-2.09952800
H	-1.76097300	-1.74404900	-2.44168000
H	-3.48609900	-1.50733400	-2.71656100
H	-2.44210700	-0.12109900	-2.26447200
C	-3.21076600	-2.97225700	-0.39336200
H	-4.23825900	-3.07333600	-0.01665700
H	-3.10935400	-3.58776400	-1.28949100
H	-2.54622800	-3.36916100	0.38208700
C	-3.08387300	-1.05175300	1.81910200
H	-2.22114800	-1.63085400	2.16687300
H	-3.18310400	-0.18209100	2.47061600
H	-3.98070000	-1.67174800	1.92778900
C	-2.91538900	1.92670400	-0.31450300
H	-3.97386300	2.06010200	-0.57053400
C	-2.03609900	3.14352400	-0.47825900
Cl	0.36112600	-2.32635300	-0.27366900
Ti	1.33715700	-0.31794800	0.12796200
Cl	-0.36397500	0.91764000	1.28284900
Cl	0.54235100	0.59959200	-1.86729700
Cl	2.16887100	-0.92664200	2.15500700
O	3.10868200	-0.69323200	-0.76674900
C	3.54237600	0.49175700	-0.51085800
O	2.75009300	1.25812700	0.11252100
C	4.91021400	0.91561200	-0.94589200
H	5.12824800	1.92316400	-0.58900900
H	5.65076500	0.20722300	-0.56087800
H	4.96296100	0.88689600	-2.03983700
H	-0.99244600	2.82908900	-0.50592800
H	-2.27663500	3.59044600	-1.45090800
C	-2.26951800	4.17252700	0.63967800
H	-1.65346700	5.05979100	0.45987400
H	-3.31722900	4.49228500	0.68675800
H	-1.99092900	3.75576500	1.61211900

$TiBr_3(OAc)$
E(BS1) = -8792.419874 a.u.
G(BS1) = -8792.407368 a.u.
E(BS2,solvent) = -8800.732222 a.u.

O	-2.14114000	0.01946200	-0.47849600
C	-2.42323500	0.01056100	0.75567500
O	-1.41171600	-0.00201400	1.56035600
C	-3.82135300	0.01364700	1.28158700
H	-4.53836000	0.02789100	0.45997500
H	-3.97457700	-0.87489500	1.90351100
H	-3.96320200	0.88877800	1.92476600
Ti	-0.09549500	0.00094600	0.04494200
Br	0.30801500	-1.93657700	-1.19117500
Br	0.33523100	1.94347200	-1.17459000
Br	1.65582300	-0.01682200	1.61846700

$[TiBr_4(OAc)]^-$
E(BS1) = -11363.95879 a.u.
G(BS1) = -11363.9495 a.u.
E(BS2,solvent) = -11375.07602 a.u.

O	-0.21327500	1.83988600	1.08792600
C	-0.30873800	2.48716600	-0.00128200
O	-0.21308900	1.83892900	-1.08987500
C	-0.57281800	3.96946500	-0.00187500
H	-0.15066500	4.43001100	0.89469800
H	-0.15947700	4.42788300	-0.90355000
H	-1.65789800	4.13040400	0.00354900
Ti	0.00743900	0.02973200	-0.00011800
Br	-2.49853400	-0.04348800	-0.00035400
Br	0.17207200	-1.41287000	1.93464900
Br	0.17203900	-1.41630000	-1.93237600
Br	2.45455600	0.53515200	-0.00070800

8_Ph_Br
E(BS1) = -3075.788519 a.u.
G(BS1) = -3075.591513 a.u.
E(BS2,solvent) = -3078.683954 a.u.

C	1.02824100	0.95909500	0.49850100
C	0.75690100	-0.44383200	0.10179800
C	1.15802300	1.93529200	-0.42792500
C	1.03101800	1.67300700	-1.90979600
H	0.19076100	2.24184500	-2.33184100
H	1.93365100	2.01442100	-2.43473700
H	0.87830900	0.61800000	-2.14217500
C	1.44665100	3.38112000	-0.10185900
H	2.39992800	3.68864700	-0.55386800
H	0.67516300	4.03015300	-0.53867600
H	1.49771300	3.59640500	0.96637800
C	1.18842400	1.12322900	1.99667700
H	0.25510300	0.86687200	2.51476400
H	1.95677200	0.43320700	2.36664400
H	1.47493900	2.13404500	2.29225200
C	-0.39740900	-1.10180100	-0.09806700
H	-0.31619100	-2.15909200	-0.33844200
C	-1.78608700	-0.61706600	-0.03242300
C	-2.17265000	0.70566700	0.26031000
C	-2.80490400	-1.56045900	-0.27270500
C	-3.51884500	1.05994000	0.31148200
H	-1.41445500	1.45816200	0.43933300
C	-4.15074700	-1.20439300	-0.22305300
H	-2.52975000	-2.58767100	-0.50016600
C	-4.51552200	0.11052300	0.07073500
H	-3.79150400	2.08715300	0.53978800
H	-4.91379300	-1.95445300	-0.41348900
H	-5.56385100	0.39350600	0.11090100
Br	2.39110400	-1.51380400	-0.02910600

7_Ph_Br
E(BS1) = -3075.777284 a.u.
G(BS1) = -3075.578597 a.u.
E(BS2,solvent) = -3078.674033 a.u.

C	-0.84879700	0.21464600	0.78833200
C	0.27625900	-0.44218200	0.61690200
C	-1.74242600	0.53804800	-0.39893200
C	-1.16332200	0.11898600	-1.74677400
H	-1.88530900	0.30903200	-2.54517900
H	-0.25611100	0.70190600	-1.95028100
H	-0.89778000	-0.93995500	-1.75868500
C	-2.19804600	1.99819700	-0.41456500
H	-1.31740100	2.64488600	-0.53015200
H	-2.87181100	2.17915200	-1.25657500
H	-2.71637400	2.28042600	0.50392100
C	-1.27123900	0.67707600	2.17227900
H	-2.29560900	0.35113000	2.38481700
H	-0.60677000	0.26242700	2.93392100
H	-1.24319400	1.77018800	2.25729000
C	1.40400100	-1.10191100	0.46555100
H	1.37300400	-2.19079800	0.54375400
C	2.73211700	-0.52182700	0.18624400
C	2.94056800	0.86555600	0.09138700
C	3.83099200	-1.37708100	0.00515700
C	4.20668000	1.37641500	-0.17866700
H	2.09943200	1.53856500	0.23518300
C	5.09995100	-0.86477900	-0.26535500
H	3.68461200	-2.45245500	0.07655100
C	5.29335700	0.51409700	-0.35922200
H	4.34922700	2.45180800	-0.24764700
H	5.93702600	-1.54416400	-0.40287600
H	6.28082800	0.91550600	-0.56978000
Br	-3.45698200	-0.57854600	-0.15566500

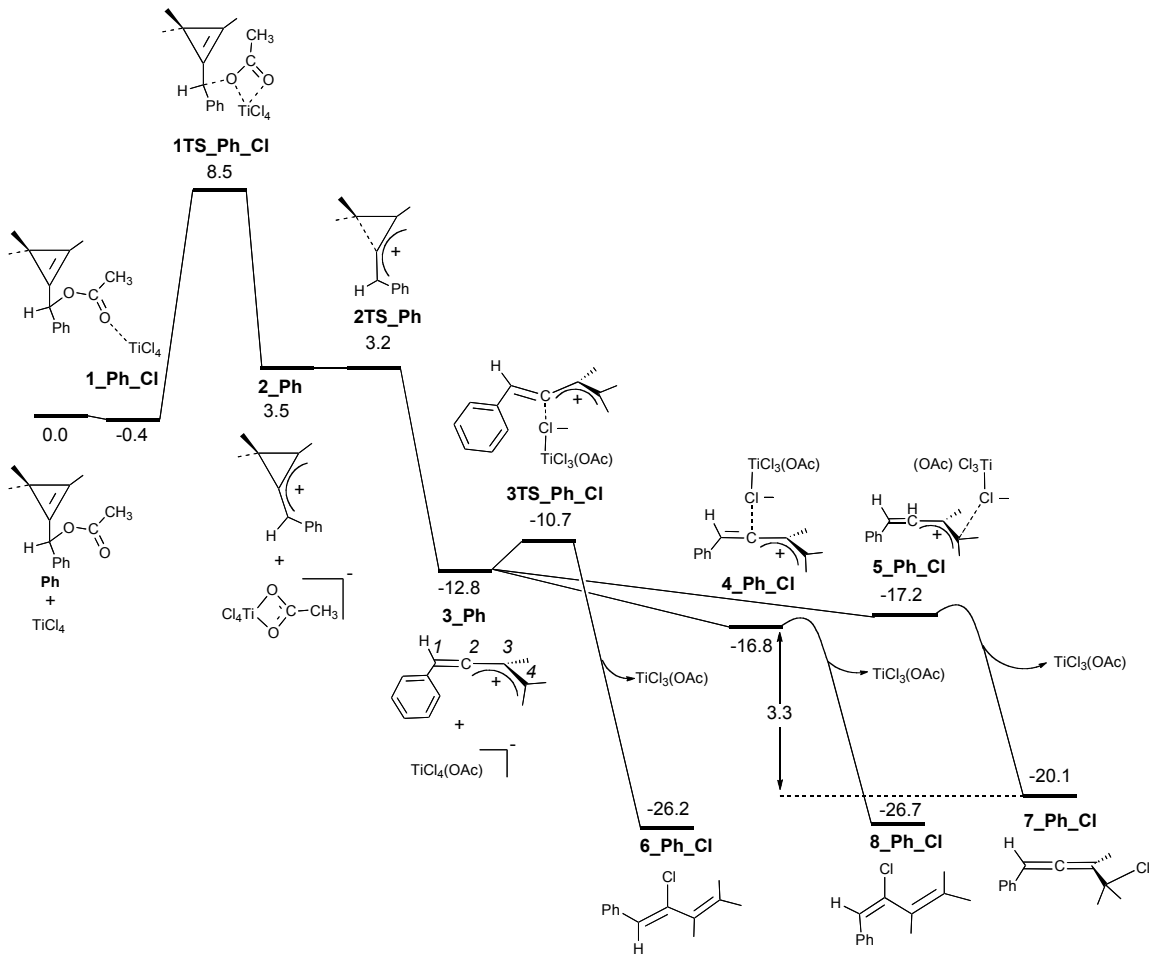


Figure S1. The DFT energy profile for the reaction of cyclopropenylmethyl acetate **1b** with $TiCl_4$ redrawn with potential energies in kcal/mol.