Supporting Information

Nickel-Catalyzed Ring-Opening Alkylative Coupling of Enone with Methylenecyclopropane in the presence of Triethylborane

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Content

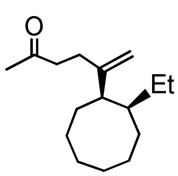
Experimental Procedure and Spectral data

I. General

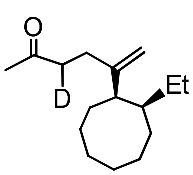
All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under dry nitrogen atmosphere by using a standard Schlenk tube or high vacuum techniques. THF was distilled over Na/benzophenone prior to use. Aldehydes were purchased and distilled or recrystallized before use. $Ni(cod)_2$,[1] **1b**,[2] **1c**,[2] **1d**,[2] **1e**,[2] **1f**,[3] **1g**,[3] **1h**,[4] **2a**,[5] **2b**,[5] **2c**,[5] **2d**,[6] **2e**,[7] **2f**[7] and **2g**,[7] were prepared according to the literature methods. The NMR spectra were recorded on a Varian Mercury-300 at ambient temperature. ^{1}H NMR spectra and ^{13}C{^{1}H} NMR spectra were measured using Me_4Si as an internal reference. All chemical shifts were recorded in ppm and all coupling constants were recorded in Hz.

II. Reductive Coupling Reaction

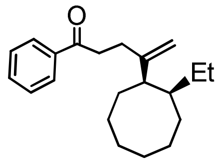
General Procedure. To a mixture of $Ni(cod)_2$ (28 mg, 0.10 mmol) and PPh_3 (53 mg, 0.20 mmol) in THF (2 mL) solution, BEt_3 (1.0 M hexane solution, 2.0 mL, 2.0 mmol), MeOH (0.08 mL, 2.0 mmol), methylenecyclopropane **2a** (136 mg, 1.0 mmol) in 1.0 mL THF solution, and enone **1a** (0.19 mL, 2.0 mmol) were added. After stirring for 16 h at room temperature, saturated NH_4Cl aq. was added to the solution. The resulting mixture was extracted with diethyl ether, dried over $MgSO_4$, filtered, and the solvent was removed using a rotary evaporator. The residue was purified by silica gel preparative TLC (ether/hexane = 1:10). Product **3aa** (191 mg, 0.81 mmol, 81%) was obtained as a colorless oil.



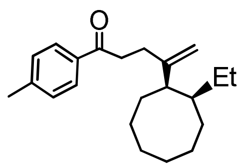
Compound **3aa**: yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.85 (t, J = 5.7 Hz, 3H, CH_3), 0.97-1.1 (m, 1H, alkyl), 1.3-1.8 (m, 14H, alkyl), 2.17 (s, 3H, CH_3), 2.2-2.3 (m, 1H, C=C-CH), 2.3-2.4 (m, 2H, alkyl), 2.5-2.7 (m, 2H, alkyl), 4.76, 4.77 (s, 2H, C=CH_2), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.7, 24.7, 25.8, 26.2, 27.2, 29.2, 29.5, 29.9, 30.2, 30.4, 39.3, 42.3, 44.3 (s, alkyl), 109.3, 152.3 (s, C=CH_2), 208.5 (C=O); HRMS (ESI) calcd for $C_{16}H_{28}O$ $[M+H]^+$ 237.2218, found 237.2220.



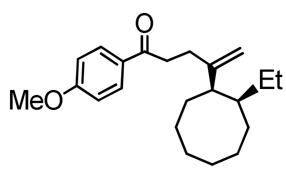
Compound **3aa-D**: yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.85 (t, J = 5.7 Hz, 3H, CH_3), 0.97-1.1 (m, 1H, alkyl), 1.3-1.8 (m, 14H, alkyl), 2.16 (s, 3H, CH_3), 2.2-2.4 (m, 3H, alkyl), 2.5-2.6 (m, 1H, alkyl), 4.75, 4.76 (s, 2H, C=CH_2), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.7, 24.8, 25.9, 26.3, 27.3, 29.2, 29.5, 29.8, 30.3, 30.4, 39.4 (s, alkyl), 42.0 (t, J = 42.0 Hz, CHD), 44.6 (s, alkyl), 109.3, 152.4 (s, C=CH_2), 208.4 (C=O).



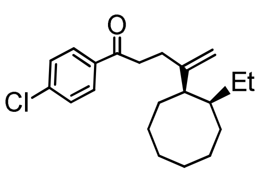
Compound **3ba**: yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.86 (t, J = 7.2 Hz, 3H, CH_3), 0.9-1.1 (m, 1H, alkyl), 1.4-1.8 (m, 15H, alkyl), 2.1-2.5 (m, 2H, alkyl), 3.1-3.2 (m, 2H, alkyl), 4.79 (s, 1H, C=CH_2), 4.85 (s, 1H, C=CH_2), 7.4-7.6 (m, 3H, Ph), 8.0 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.8, 24.7, 25.9, 26.2, 27.3, 29.2, 29.5, 30.4, 30.7, 37.4, 39.4, 44.5 (s, alkyl), 109.4 (s, C=CH_2), 128.0, 128.5, 132.9, 136.9, 152.6 (s, C=CH_2, Ph), 199.8 (s, C=O); HRMS (ESI) calcd for $C_{21}H_{30}O$ $[M+H]^+$ 299.2375, found 299.2385.



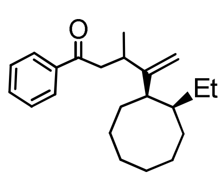
Compound **3ca**: yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.85 (t, J = 7.2 Hz, 3H, CH_3), 0.9-1.2 (m, 2H, alkyl), 1.4-1.8 (m, 13H, alkyl), 2.3-2.5 (m, 6H, alkyl), 3.0-3.2 (m, 2H, alkyl), 4.78 (s, 1H, C=CH_2), 4.84 (m, 1H, C=CH_2), 7.26 (d, J = 7.9 Hz, 2H, Ph), 7.88 (d, J = 7.9 Hz, 2H, Ph); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.7, 21.5, 24.7, 25.8, 26.2, 27.2, 29.1, 29.5, 30.4, 30.8, 37.2, 39.4, 44.5 (s, alkyl), 109.3 (s, C=C), 128.0, 129.1, 134.4, 143.5, 152.6 (s, C=C, Ph), 199.3 (C=O); HRMS (ESI) calcd for $C_{22}H_{32}O$ $[M+H]^+$ 313.2531, found 313.2492.



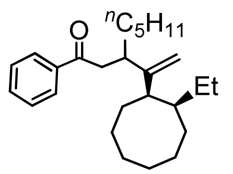
Compound **3da**: yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.85 (t, J = 7.2 Hz, 3H, CH_3), 0.9-1.1 (m, 1H, alkyl), 1.4-1.8 (m, 14H, alkyl), 2.4-2.5 (m, 3H, alkyl), 3.0-3.1 (m, 2H, alkyl), 3.88 (s, 3H, OMe), 4.78 (s, 1H, C=CH), 4.84 (m, 1H, C=CH), 6.94 (d, J = 8.8 Hz, 2H, Ph), 7.97 (d, J = 8.8 Hz, 2H, Ph); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.7, 24.7, 25.8, 26.2, 27.2, 29.2, 29.5, 30.4, 30.9, 37.0, 39.4, 44.5, 55.3 (s, alkyl), 109.3, 113.6, 130.0, 130.2, 152.7, 163.3 (s, C=C, Ph), 198.4 (C=O); HRMS (ESI) calcd for $C_{22}H_{32}O_2$ $[M+H]^+$ 329.2481, found 329.2488.



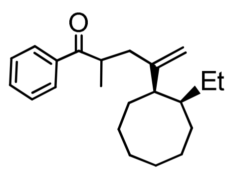
Compound **3ea**: yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.85 (t, J = 7.2 Hz, 3H, CH_3), 0.9-1.8 (m, 15H, alkyl), 2.4-2.5 (m, 3H, alkyl), 2.9-3.1 (m, 2H, alkyl), 4.79 (s, 1H, C=CH_2), 4.83 (m, 1H, C=CH_2), 7.44 (d, J = 8.7 Hz, 2H, Ph), 7.92 (d, J = 8.7 Hz, 2H, Ph); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.8, 24.8, 25.9, 26.2, 27.3, 29.2, 29.5, 30.4, 30.6, 37.3, 39.4, 44.6 (s, alkyl), 109.5, 128.8, 129.4, 135.2, 139.3, 152.5 (s, C=C, Ph), 198.5 (C=O); HRMS (ESI) calcd for $C_{21}H_{29}ClO$ $[M+H]^+$ 333.1985, found 333.1994.



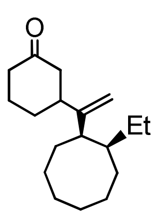
Compound **3fa**: yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.84 (t, J = 7.3 Hz, 3H, CH_3 (major diastereomer)), 0.84 (t, J = 7.6 Hz, 3H, CH_3 (minor diastereomer)), 1.0 (m, 1H, alkyl), 1.10 (d, J = 6.7 Hz, 3H, CH_3), 1.26-1.86 (m, 14H, alkyl), 2.4-2.5 (m, 1H, alkyl), 2.7-2.8 (m, 1H, alkyl), 2.9-3.0 (m, 1H, alkyl), 3.1-3.2 (m, 1H, alkyl), 4.77 (s, 1H, C=CH_2 (major diastereomer), 4.82 (s, 1H, C=CH_2 (minor diastereomer), 4.90 (s, 1H, C=CH_2 (major diastereomer), 4.98 (s, 1H, C=CH_2 (minor diastereomer), 7.4-7.5 (m, 2H, Ph), 7.5-7.6 (m, 1H, Ph), 7.9-8.0 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.4, 12.6, 12.7, 17.0, 19.5, 20.4, 21.6, 23.8, 24.0, 25.2, 25.4, 26.0, 26.1, 27.0, 27.2, 29.5, 29.6, 29.7, 29.9, 30.0, 30.6, 30.7, 31.3, 35.7, 36.1, 39.4, 39.5, 43.2, 43.8, 44.6, 45.5, 46.9 (s, alkyl), 107.6, 108.3 (s, C=C), 128.0, 128.5, 132.8, 137.3, 158.8, 158.9 (s, C=C, Ph), 199.6, 199.7 (s, C=O); HRMS (ESI) calcd for $C_{22}H_{32}O$ $[M+Na]^+$ 335.2351, found 335.2370



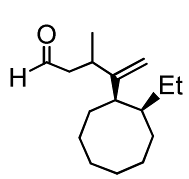
Compound **3ga**: yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.8-0.9 (m, 6H, alkyl), 0.9-2.1 (m, 23H, alkyl), 2.3-2.5 (m, 1H, alkyl), 2.6-2.7 (m, 1H, alkyl), 2.9-3.1 (m, 2H, alkyl), 4.78 (s, 1H, $C=CH_2$ (major diastereomer)), 4.82 (s, 1H, $C=CH_2$ (minor diastereomer)), 4.89 (s, 1H, $C=CH_2$ (major diastereomer)), 4.97 (s, 1H, $C=CH_2$ (minor diastereomer)), 7.4-7.5 (m, 2H, Ph), 7.5-7.6 (m, 1H, Ph), 7.9-8.0 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.4, 12.5, 14.0, 14.0, 22.6, 23.0, 23.1, 23.4, 24.7, 25.0, 25.6, 25.8, 26.1, 26.3, 26.4, 26.5, 26.6, 26.7, 26.7, 27.1, 28.5, 29.1, 30.4, 30.6, 30.9, 31.0, 31.9, 32.0, 32.0, 33.5, 33.8, 34.4, 36.1, 39.2, 41.0, 42.0, 42.5, 43.1, 46.4 (s, alkyl), 108.6, 108.7 (s, C=C), 128.0, 128.2, 128.4, 132.7, 132.8, 137.2, 137.5, 157.0, 157.5 (s, C=C, Ph), 199.7, 199.8 (C=O); HRMS (ESI) calcd for $C_{26}H_{40}O$ $[M+Na]^+$ 391.2977, found 391.2988.



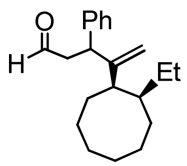
Compound **3ha**: yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.82 (t, J = 7.4 Hz, 3H, CH_3), 0.9-1.1 (m, alkyl), 1.18 (d, J = 6.8 Hz, 3H, CH_3 (major isomer)), 1.23 (d, J = 6.9 Hz, 3H, CH_3 (minor isomer)), 1.2 (m, 1H, alkyl), 1.4-1.8 (m, 14H, alkyl), 2.09 (dd, J = 15.0, 8.1 Hz, 1H, alkyl), 2.3-2.4 (m, 1H, alkyl), 2.5-2.7 (m, 1H, alkyl), 3.7-3.8 (m, 1H, alkyl), 4.72 (s 1H, $C=CH_2$ (minor diastereomer)), 4.79 (s, $C=CH_2$ (minor+major diastereomer)), 4.86 (s 1H, $C=CH_2$ (major diastereomer)), 7.5 (m, 2H, Ph), 7.5-7.69(m, 1H, Ph), 8.0 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.7, 16.9, 17.9, 24.1, 24.4, 25.5, 25.7, 26.1, 27.0, 27.1, 29.1, 29.3, 29.5, 29.7, 30.5, 39.0, 39.4, 40.4, 40.6, 42.8, 44.2 (s, alkyl), 111.3 (s, C=C), 128.1, 128.2, 128.2, 128.5, 128.6, 128.6, 132.7, 132.8, 136.4, 151.1 (s, C=C, Ph), 203.9 (C=O); HRMS (ESI) calcd for $C_{22}H_{32}O$ $[M+Na]^+$ 335.2351, found 335.2370



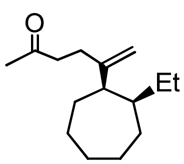
Compound **3ia**: yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.8-1.0 (m, 3H, alkyl), 1.4-1.9 (m, 16H, alkyl), 2.0-2.6 (m, 8H, alkyl), 4.85, 4.86, 4.95 (s, 2H, $C=CH_2$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.7, 12.7, 24.3, 24.3, 25.5, 25.5, 25.6, 25.7, 26.1, 26.1, 27.3, 27.4, 28.8, 29.3, 29.4, 29.5, 30.1, 30.2, 30.4, 31.1, 32.1, 39.5, 39.6, 41.2, 41.3, 43.6, 43.8, 45.2, 45.4, 47.5, 48.9 (s, alkyl), 108.9, 108.9, 156.4, 156.7 (s, $C=CH_2$), 211.5, 212.1 (s, C=O); HRMS (ESI) calcd for $C_{18}H_{30}O$ $[M+Na]^+$ 285.2194, found 285.2200.



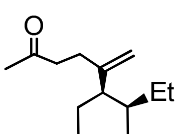
Compound **3ja**: yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.84 (t, J = 7.1 Hz, 3H, CH_3), 0.9-1.1 (m, 1H, alkyl), 1.11 (d, J = 6.3 Hz, 3H, CH_3), 1.3-1.9 (m, 16H, alkyl), 2.4-2.5 (m, 2H, alkyl), 2.6-2.7 (m, 2H, alkyl), 4.79 (s, 1H, $C=CH_2$ (major diastereomer)), 4.84 (s, $C=CH_2$ (major+minor diastereomer)), 4.93 (s, 1H, $C=CH_2$ (minor diastereomer)), 9.68 (s, 1H, CHO (major diastereomer)), 9.73 (s, 1H, CHO (minor diastereomer)); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.6, 12.7, 14.1, 20.3, 21.7, 22.6, 23.7, 23.9, 24.1, 25.3, 25.3, 25.4, 26.1, 27.0, 27.1, 29.7, 29.8, 30.0, 30.6, 30.7, 31.5, 34.5, 34.6, 39.4, 39.6, 42.9, 49.4, 51.3 (s, alkyl), 108.5, 157.6 (s, C=C), 202.5 (CHO); HRMS (ESI) calcd for $C_{16}H_{28}O$ $[M+Na]^+$ 259.2038, found 259.2044.



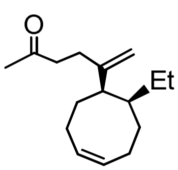
Compound **3ka**: yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.62 (t, J = 7.4 Hz, 3H, CH_3 (minor diastereomer)), 0.87 (t, J = 7.2 Hz, 3H, CH_3 (major diastereomer)), 0.9-1.7 (m, 15H, alkyl), 1.8-1.91(m, 1H, alkyl), 2.2-2.3 (m, 1H, alkyl), 2.7-2.8 (m, 1H, alkyl), 2.8-3.0 (m, 1H, alkyl), 3.8-3.9 (m, 1H, alkyl), 4.94, 5.07, 5.08 (s, 2H, $C=CH_2$), 7.1-7.3 (m, 5H, Ph), 9.66 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.3, 12.7, 23.7, 24.4, 25.0, 25.8, 26.2, 26.5, 26.9, 29.2, 29.5, 29.9, 30.3, 30.4, 30.8, 39.6, 39.7, 41.2, 45.8, 46.7, 48.4, 49.2 (s, alkyl), 109.9 (s, C=C), 126.7, 127.9,128.4, 142.3, 154.4 (s, C=C, Ph), 201.4 (s, CHO); HRMS (ESI) calcd for $C_{21}H_{30}O$ $[M+Na]^+$ 321.2194, found 321.2204.



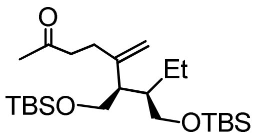
Compound **3ab**: yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.83 (t, J = 7.2 Hz, 3H, CH_3), 1.1 (m, 1H, alkyl), 1.3-1.7 (m, 12H, alkyl), 2.17 (s, 3H, CH_3), 2.2-2.4 (m, 3H, alkyl), 2.5-2.6 (m, 2H, alkyl), 4.71 (s, 1H, $C=CH_2$), 4.74 (s, 1H, $C=CH_2$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.5, 21.4, 24.7, 27.1, 28.5, 29.1, 29.8, 29.9, 30.8, 40.6, 42.2, 49.1 (s, alkyl), 108.6, 152.5 (s, C=C), 208.5 (C=O); HRMS (ESI) calcd for $C_{15}H_{26}O$ $[M+Na]^+$ 245.1881, found 245.1894



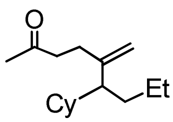
Compound **3ac**: yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.81 (t, J = 7.2 Hz, 3H, CH_3), 1.1-1.5 (m, 8H, alkyl), 1.7-1.8 (m, 3H, alkyl), 2.0-2.3 (m, 3H, alkyl), 2.16 (s, 3H, CH_3), 2.5-2.6 (m, 2H, alkyl), 4.65 (s, 1H, $C=CH_2$), 4.76 (s, 1H, $C=CH_2$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.4, 17.6, 20.3, 25.3, 26.5, 28.4, 29.1, 29.7, 37.1, 42.1, 46.4 (s, alkyl), 108.5, 151.2 (s, C=C), 208.3 (C=O); HRMS (ESI) calcd for $C_{14}H_{24}O$ $[M+Na]^+$ 231.1725, found 231.1701



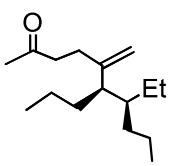
Compound **3ad**: yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.80 (t, J = 7.4 Hz, 3H, CH_3 (minor diastereomer)), 0.87 (t, J = 7.4 Hz, 3H, CH_3 (major disatereomer)), 1.2-2.0 (m, 9H alkyl), 2.16 (s, 3H, CH_3), 2.2-2.6 (m, 7H, alkyl), 4.69 (d, J = 1.4 Hz, 1H, $C=CH_2$ (minor diastereomer)), 4.71 (d, J = 1.2 Hz, 1H, $C=CH_2$ (major diastereomer)), 4.74 (s, 1H, $C=CH_2$ (minor diastereomer)), 4.76 (s, 1H, $C=CH_2$ (major diastereomer)), 5.49-5.76 (m, 2H, CH=CH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.7, 21.5, 25.1, 25.5, 29.2, 29.9, 30.5, 41.6, 42.3, 42.3, 43.2 (s, alkyl), 108.2, 127.7, 131.6, 153.0 (s, C=C), 208.7 (C=O); HRMS (ESI) calcd for $C_{16}H_{26}O$ $[M+Na]^+$ 257.1881, found 257.1861.



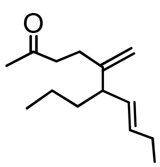
Compound **3ae**: yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.01 (s, 12H, Me_2Si), 0.86 (s, 9H, ^{t}Bu), 0.88 (s, 9H, ^{t}Bu), 1.3-1.4 (m, 1H, alkyl), 1.5-1.6 (m, 2H, alkyl), 2.15 (s, 3H, CH_3), 2.2-2.3 (m, 3H, alkyl), 2.59 (t, J = 7.8 Hz, 2H, alkyl), 3.4-3.5 (m, 1H, CH_2O), 3.5-3.6 (m, 1H, CH_2O), 3.66 (m, 2H, CH_2O), 4.78 (s, 2H, C=CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -5.6, -5.5, 11.4, 18.2, 20.2, 25.8, 29.4, 29.8, 42.1, 48.0, 62.2, 63.9 (s, alkyl), 110.1, 149.1 (s, C=C), 208.4 (C=O); HRMS (ESI) calcd for $C_{24}H_{50}O_3Si_2$ $[M+Na]^+$ 465.3196, found 465.3204.



Compound **3af**: yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.8-0.9 (m, 5H, alkyl), 1.0-1.3 (m, 7H, alkyl), 1.4-1.5 (m, 1H, alkyl), 1.6-1.8 (m, 5H, alkyl), 1.84 (m, 1H, alkyl), 2.1-2.2 (m, 2H, alkyl), 2.18 (s, 3H, CH_3), 2.60 (t, J = 6.0 Hz, 2H, alkyl), 4.70 (s, 2H, C=CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.2, 20.7, 26.5, 26.6, 26.7, 29.9, 30.8, 31.8, 32.1, 40.1, 41.6, 53.0 (s, alkyl), 109.5, 149.6 (s, C=CH_2), 208.5 (C=O); HRMS (ESI) calcd for $C_{16}H_{28}O$ $[M+Na]^+$ 259.2038, found 259.2049.

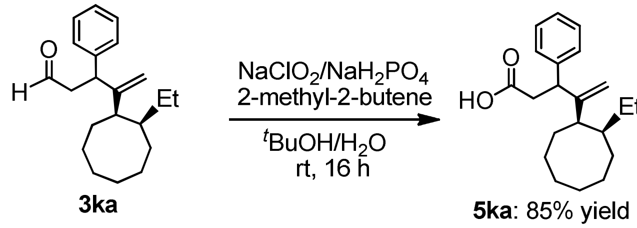


Compound **3ag**: yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.8-1.6 (m, 20H, alkyl), 1.9-2.0 (m, 1H, alkyl), 2.1-2.2 (m, 2H, alkyl), 2.18 (s, 3H, CH_3), 2.6 (m, 2H, alkyl), 4.74, 4.74 (s, 2H, C=CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.5, 14.2, 14.4, 20.0, 20.9, 21.7, 27.0, 29.9, 31.2, 32.7, 40.7, 41.8, 48.5 (s, alkyl), 109.6, 149.6 (s, C=C), 208.6 (C=O); HRMS (ESI) calcd for $C_{16}H_{30}O$ $[M+Na]^+$ 261.2194, found 261.2209



Compound **4ag**: yellowish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, J = 7.2 Hz, 3H, CH_3), 0.96 (t, J = 7.4 Hz, 3H), 1.2-1.6 (m, 3H, alkyl), 1.9-2.1 (m, 2H, alkyl), 2.1-2.2 (m, 1H, alkyl), 2.15 (s, 3H, CH_3), 2.2-2.3 (m, 2H, alkyl), 2.5-2.6 (m, 3H, alkyl), 4.68 (s, 1H, C=CH_2), 4.79 (s, 1H, C=CH_2), 5.24 (ddt, J = 15.0, 8.1, 1.5 Hz, 1H), 5.45 (dt, J = 15.0, 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.8, 14.0, 20.5, 25.5, 27.7, 29.8, 35.5, 42.0, 49.2 (a, alkyl), 108.2, 131.8, 132.2, 151.2 (s, C=C), 208.5 (C=O); HRMS (ESI) calcd for $C_{14}H_{24}O$ $[M+Na]^+$ 231.1725, found 231.1744.

III. Transformation of 3ka to carboxlic acid by oxidation



To a mixture of **3ka** (179 mg, 0.60 mmol) in ^{t}BuOH (5 mL) solution, 2-methyl-2-butene (0.25 mL, 3.36 mmol), H_2O (1 mL), $NaClO_2$ (163 mg, 1.80 mmol) and NaH_2PO_4 (108 mg, 0.90 mmol) were added. After stirring for 16 h at room temperature, the reaction mixture was extracted with ethyl acetate and H_2O at three times, dried over $MgSO_4$, filtered, and the solvent was removed using a rotary evaporator. The residue was dried under reduced pressure. Product **5ka** (161 mg, 0.51 mmol, 85%) was obtained as a white solid. Single crystals suitable for X-ray analysis was obtained by crystallization from hexane solution. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.59 (t, J = 7.3 Hz, 3H, CH_3 (minor diastereomer)), 0.84 (t, J = 7.3 Hz, 3H, CH_3 (major diastereomer)), 0.9-1.7 (m, alkyl), 1.8-1.91(m, 1H, alkyl), 2.20 (br-d, J = 11.4 Hz, 1H, alkyl), 2.67 (dd, J = 15.8, 7.0 Hz, 1H, alkyl), 2.88 (dd, J = 15.8, 8.8 Hz, 1H, alkyl), 3.81 (t, J = 8.0 Hz, 1H, alkyl), 4.94, 5.13 (s, 2H, C=CH_2), 7.2-7.3 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.6, 23.5, 25.0, 25.9, 26.4, 29.3, 30.3, 31.0, 39.5, 39.9, 41.0, 47.1 (s, alkyl), 108.9 (s, C=C), 126.7, 128.0, 128.4, 142.4, 154.7 (s, C=C, Ph), 178.5 (s, COOH); Anal. calcd for $C_{21}H_{30}O_2$; C, 80.21; H, 9.62. found C, 80.30; H, 9.50

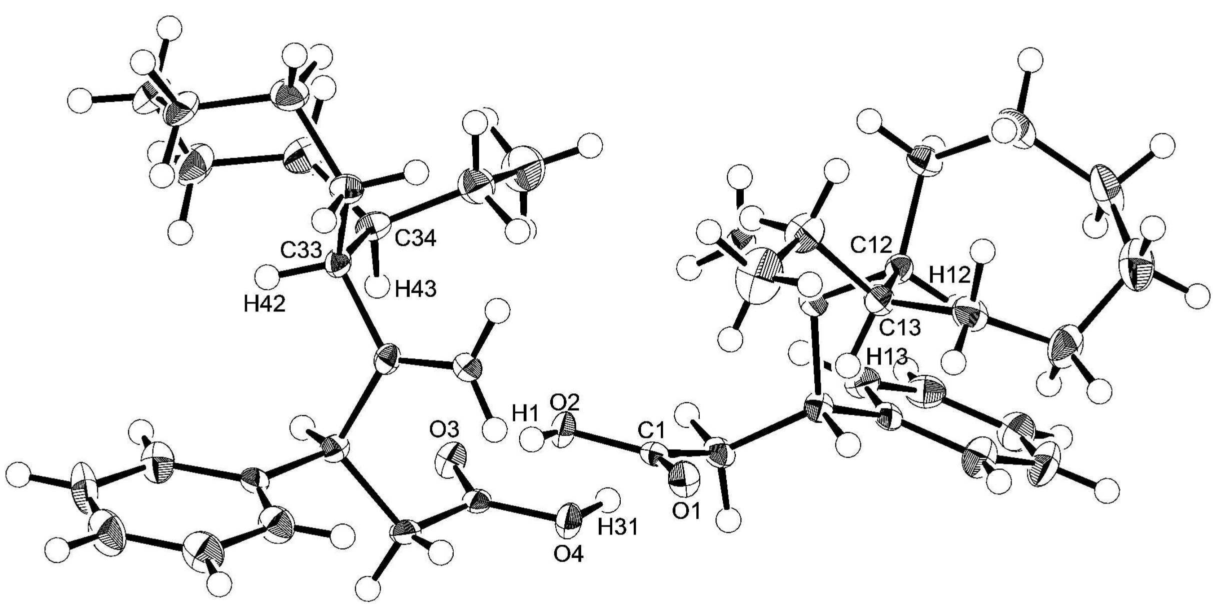


Figure S1 ORTEP drawing of **5ka** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms of H42 and H43, and H12 and H13 were mutually *syn*, respectively.

VI. References

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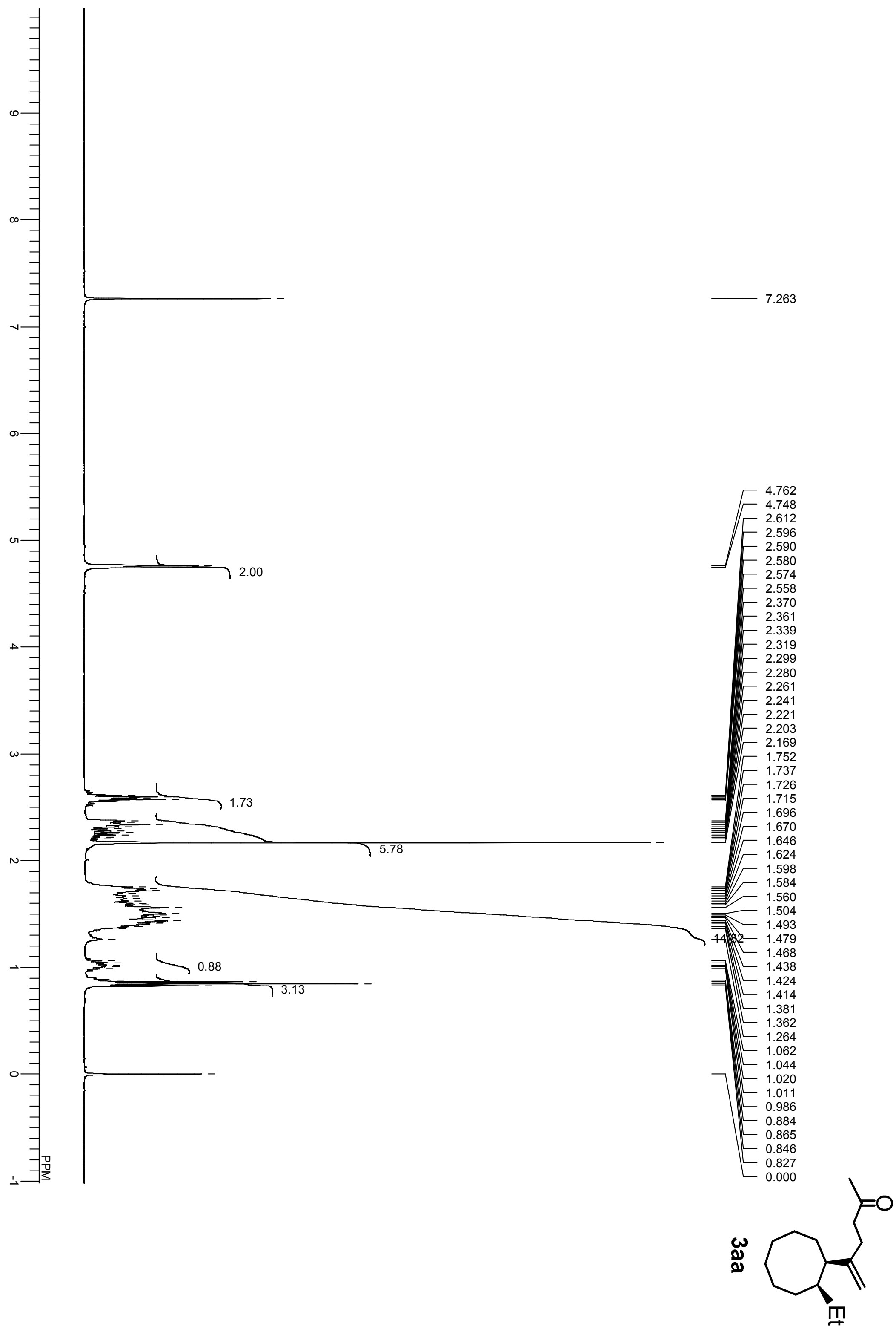
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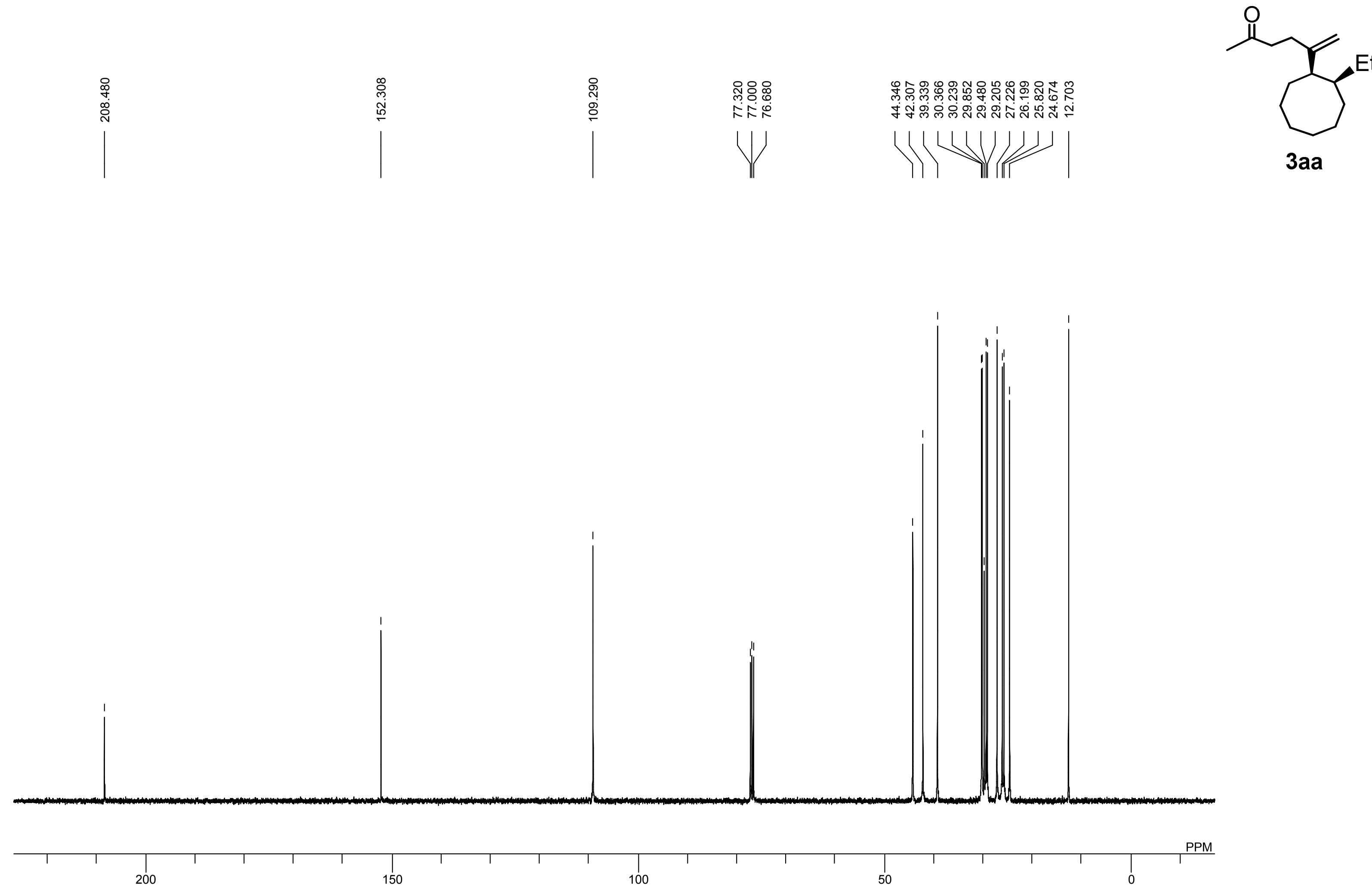
3aa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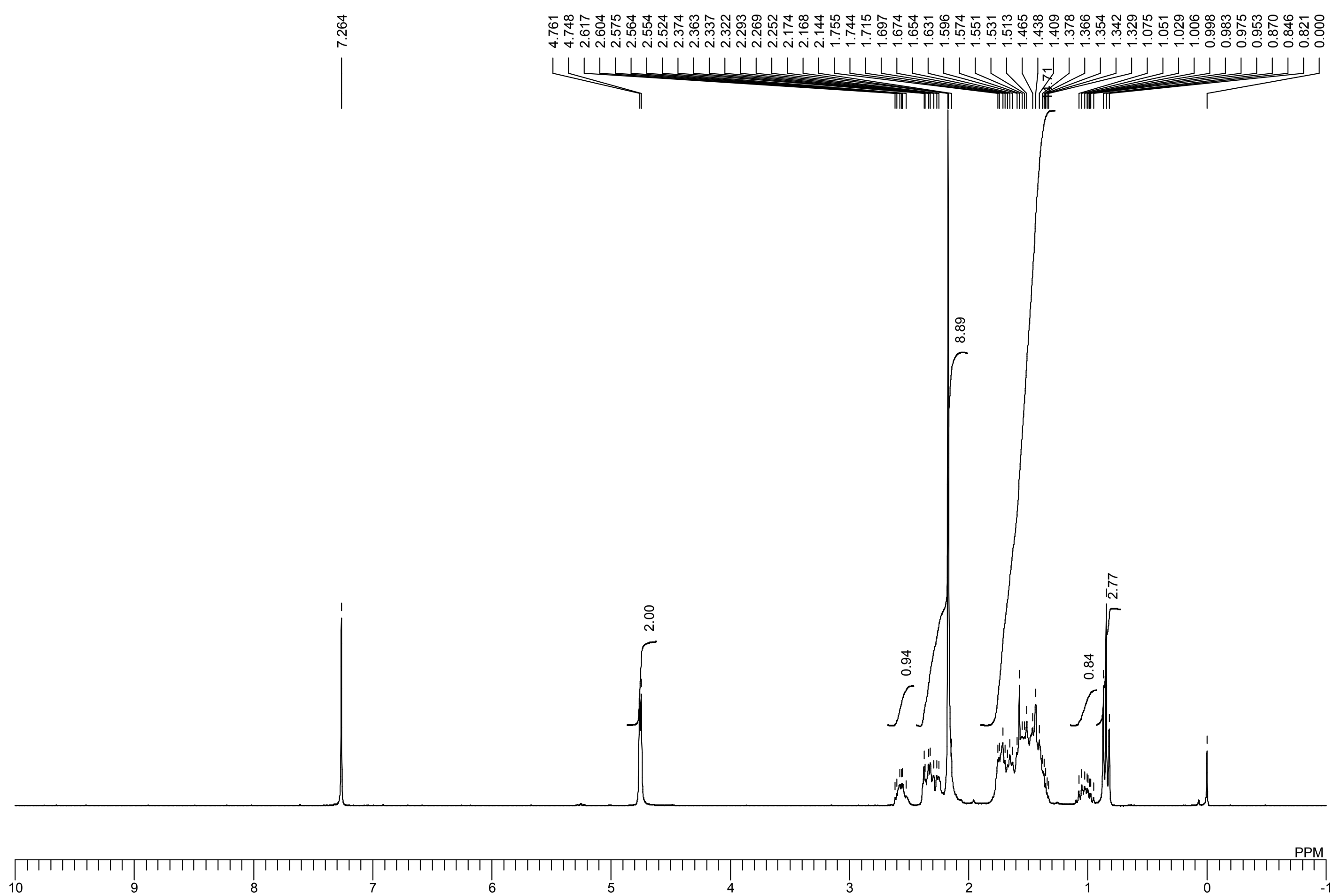
3aa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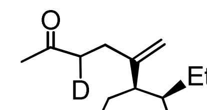
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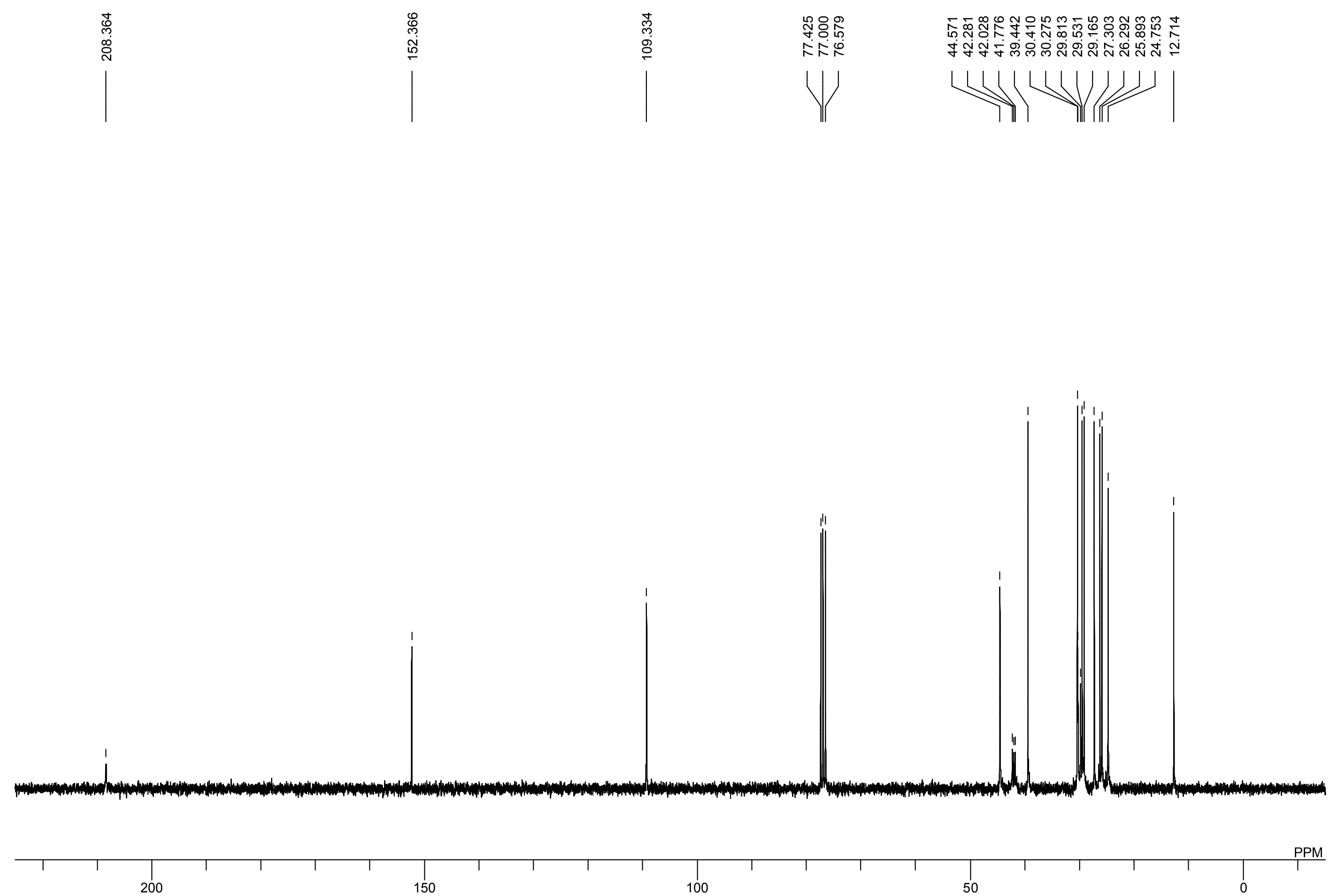
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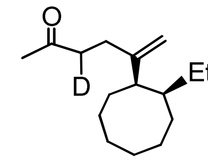
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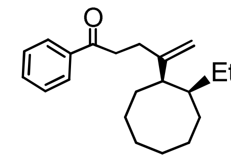

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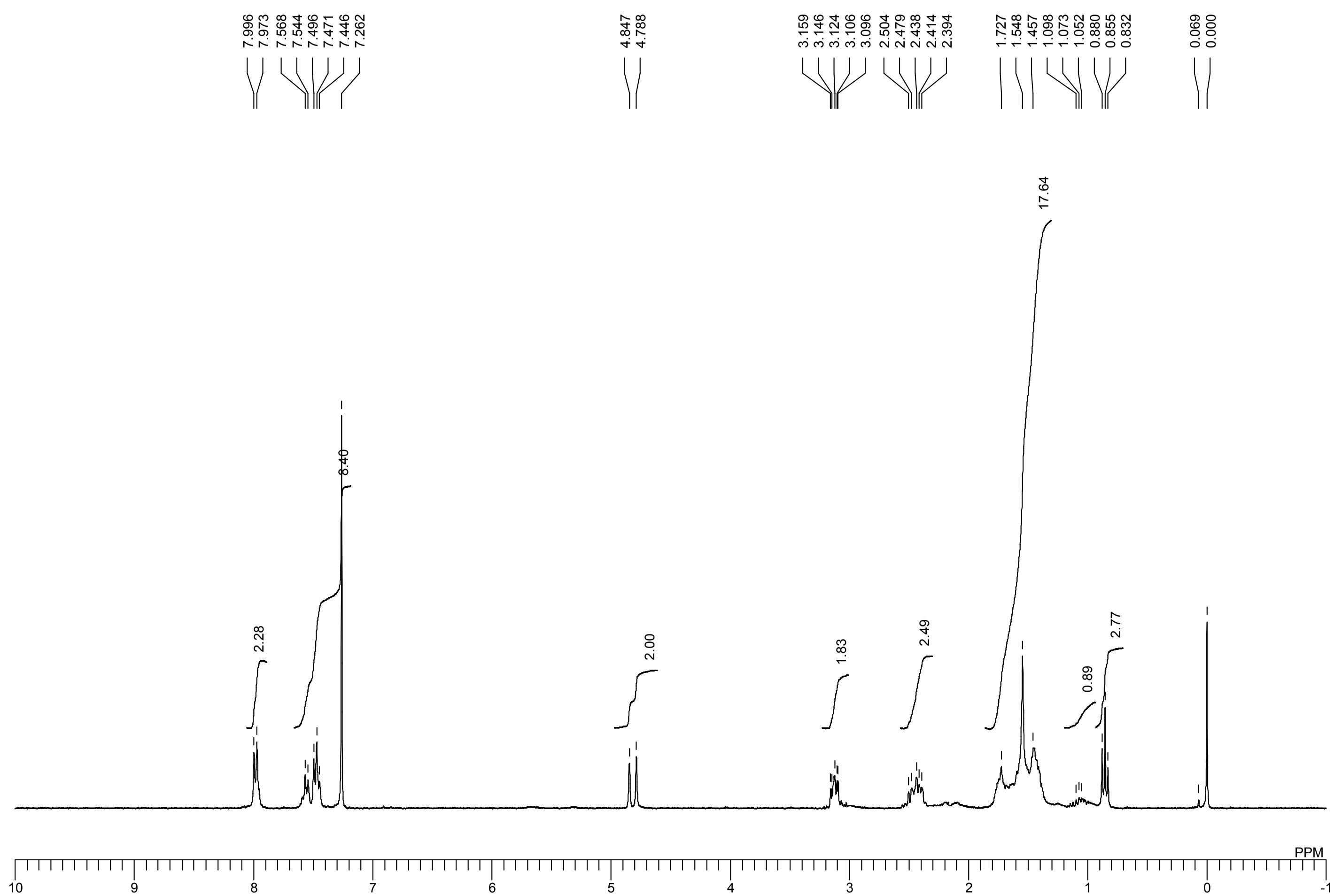
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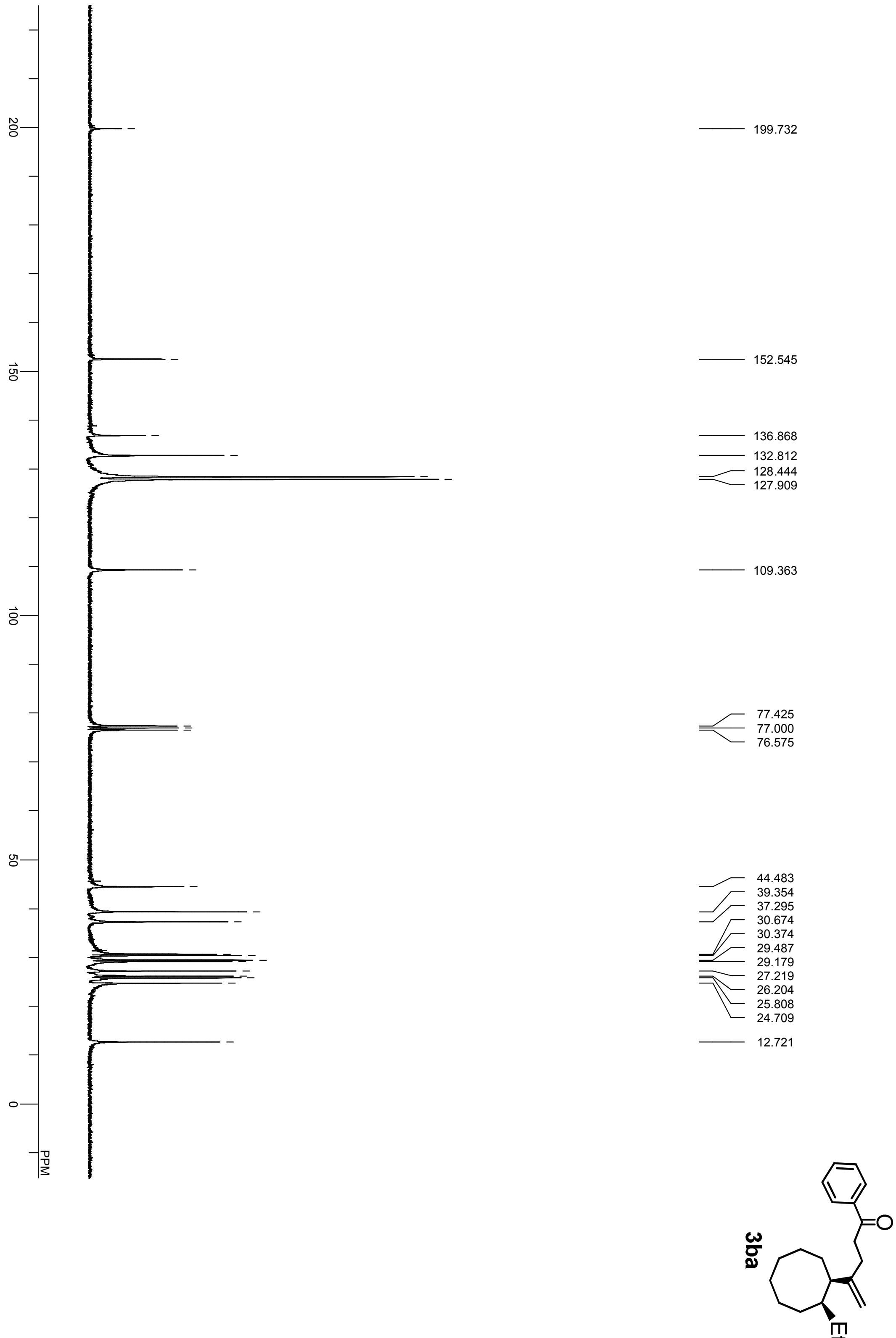
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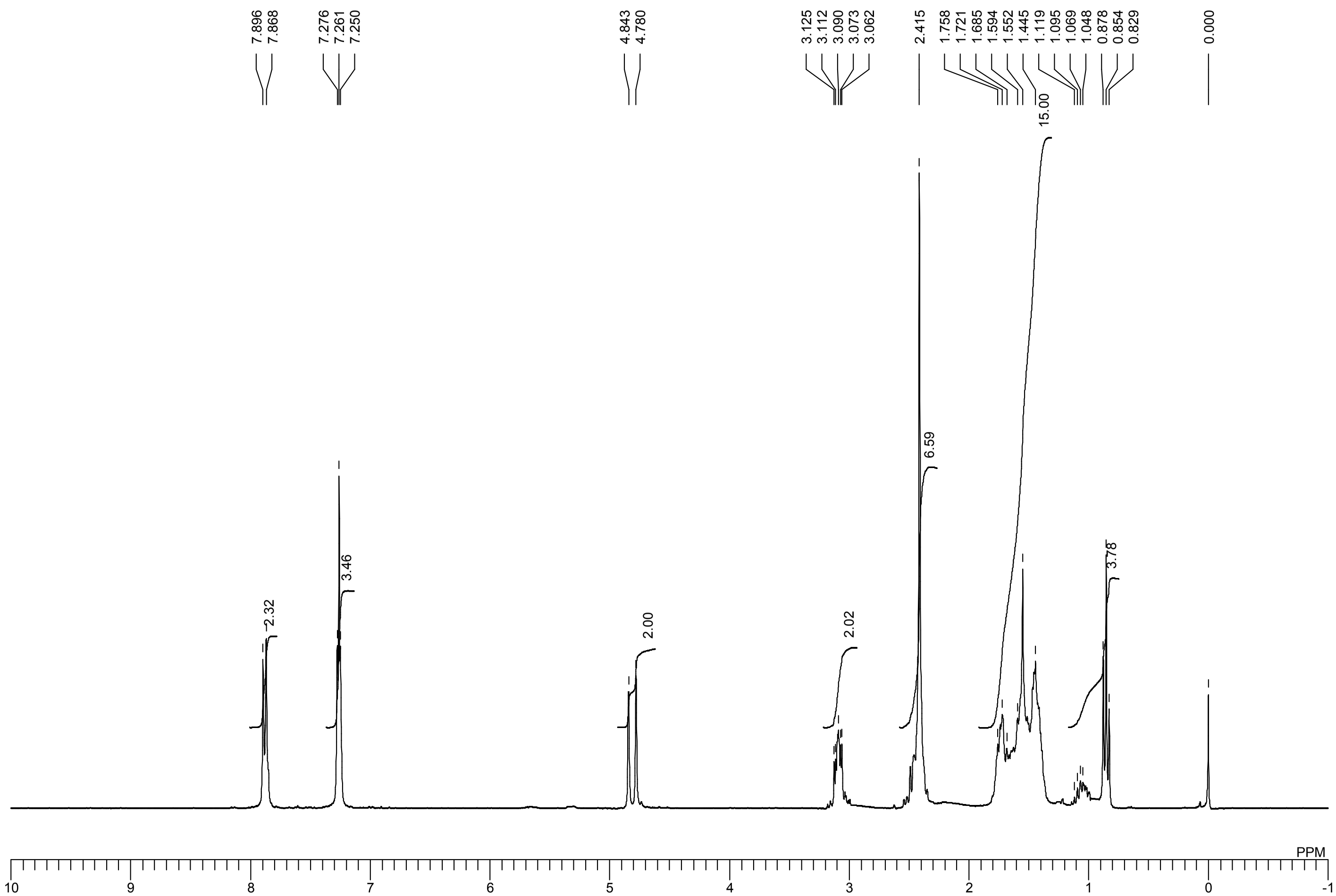
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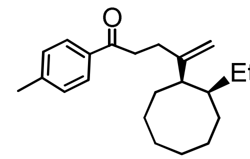
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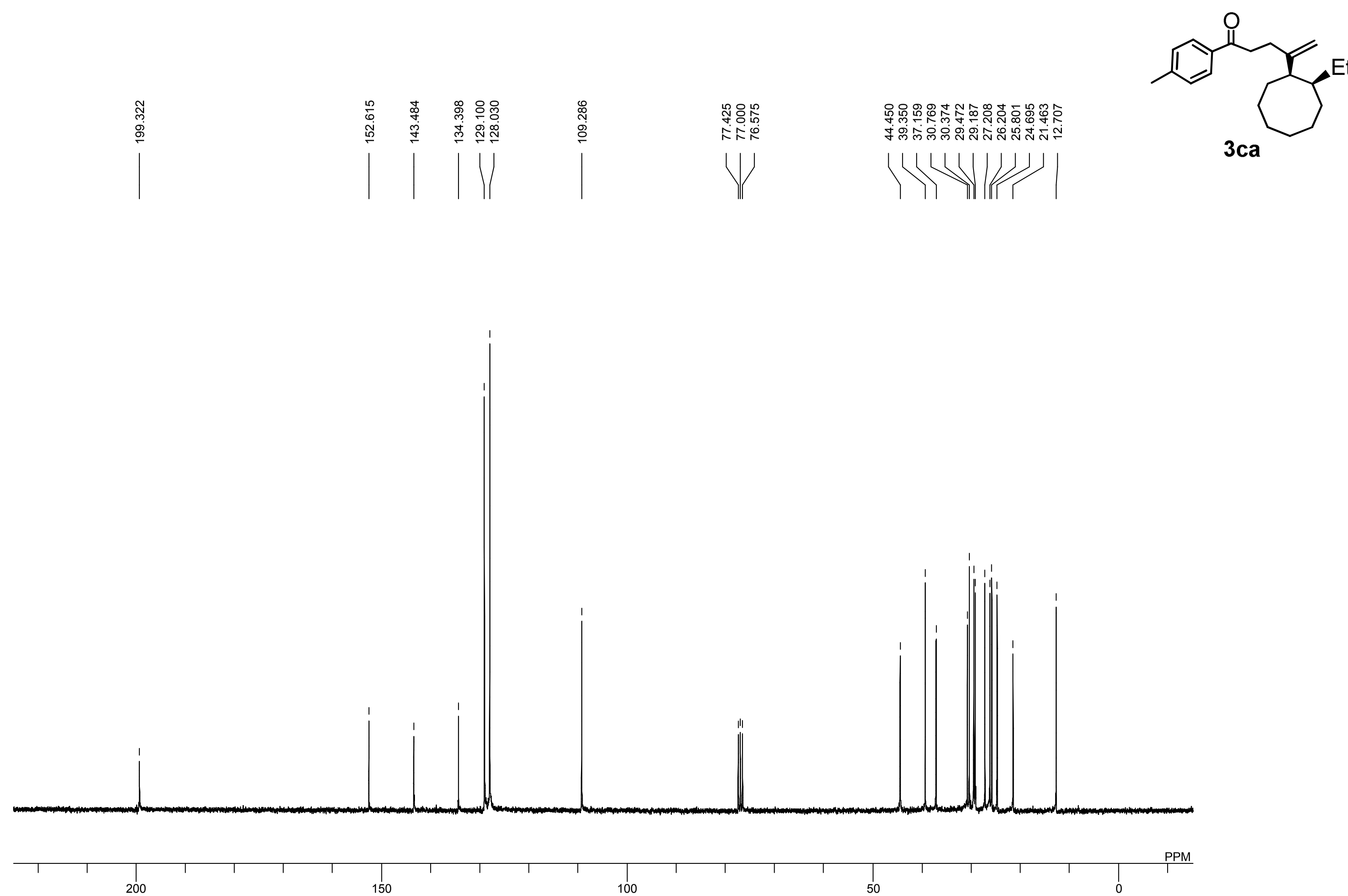
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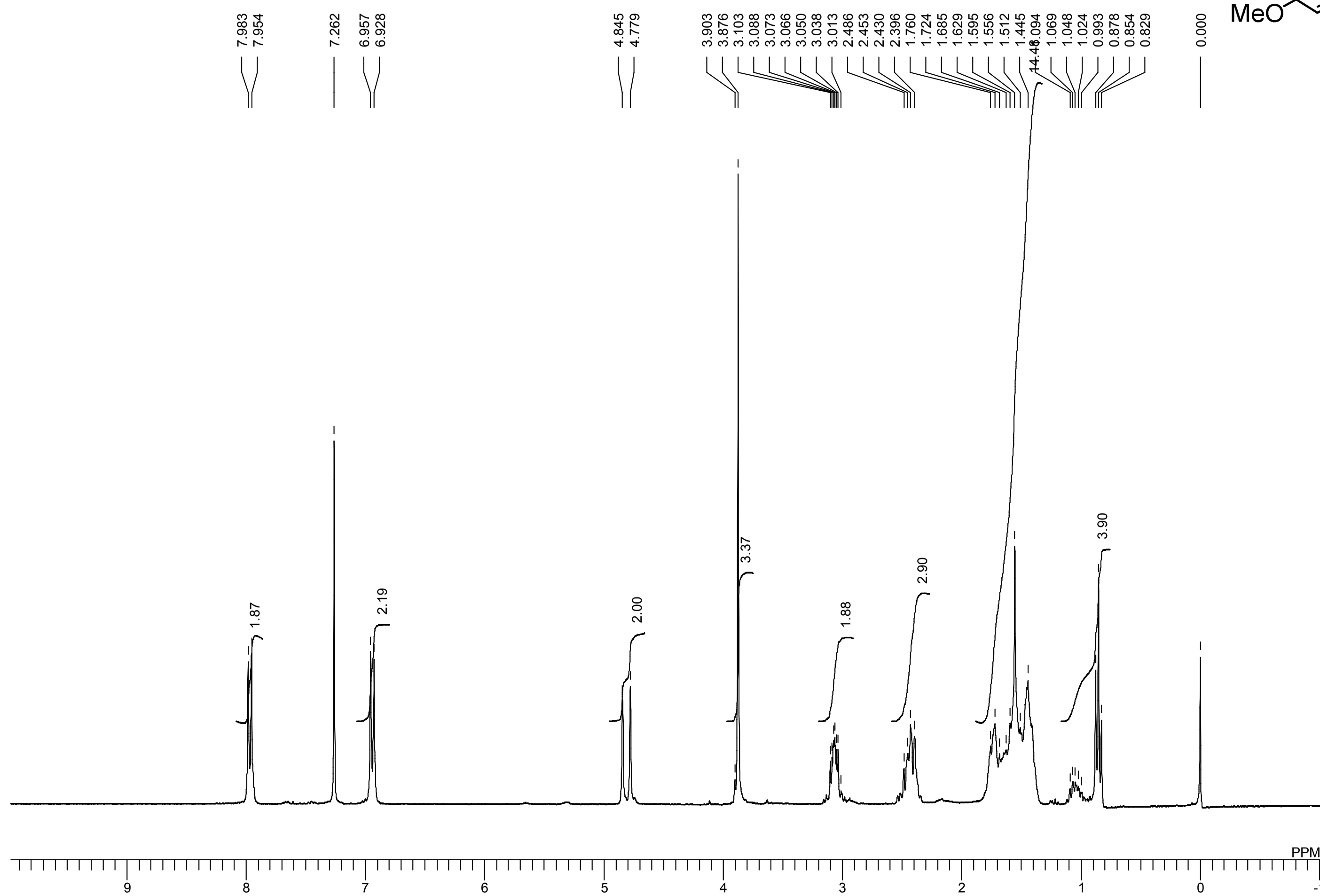
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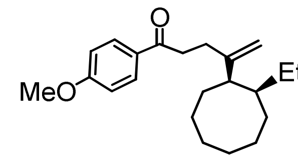
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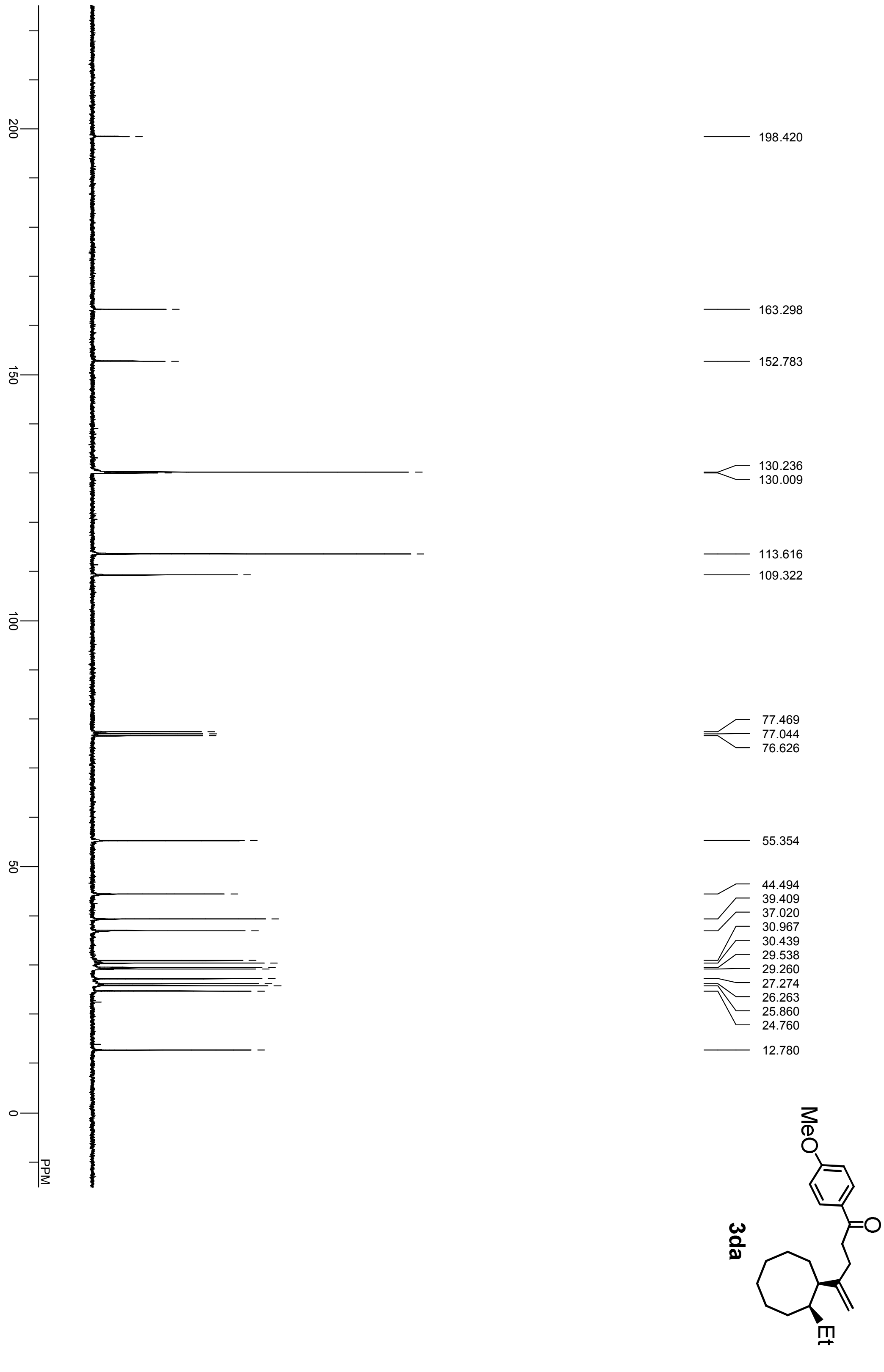
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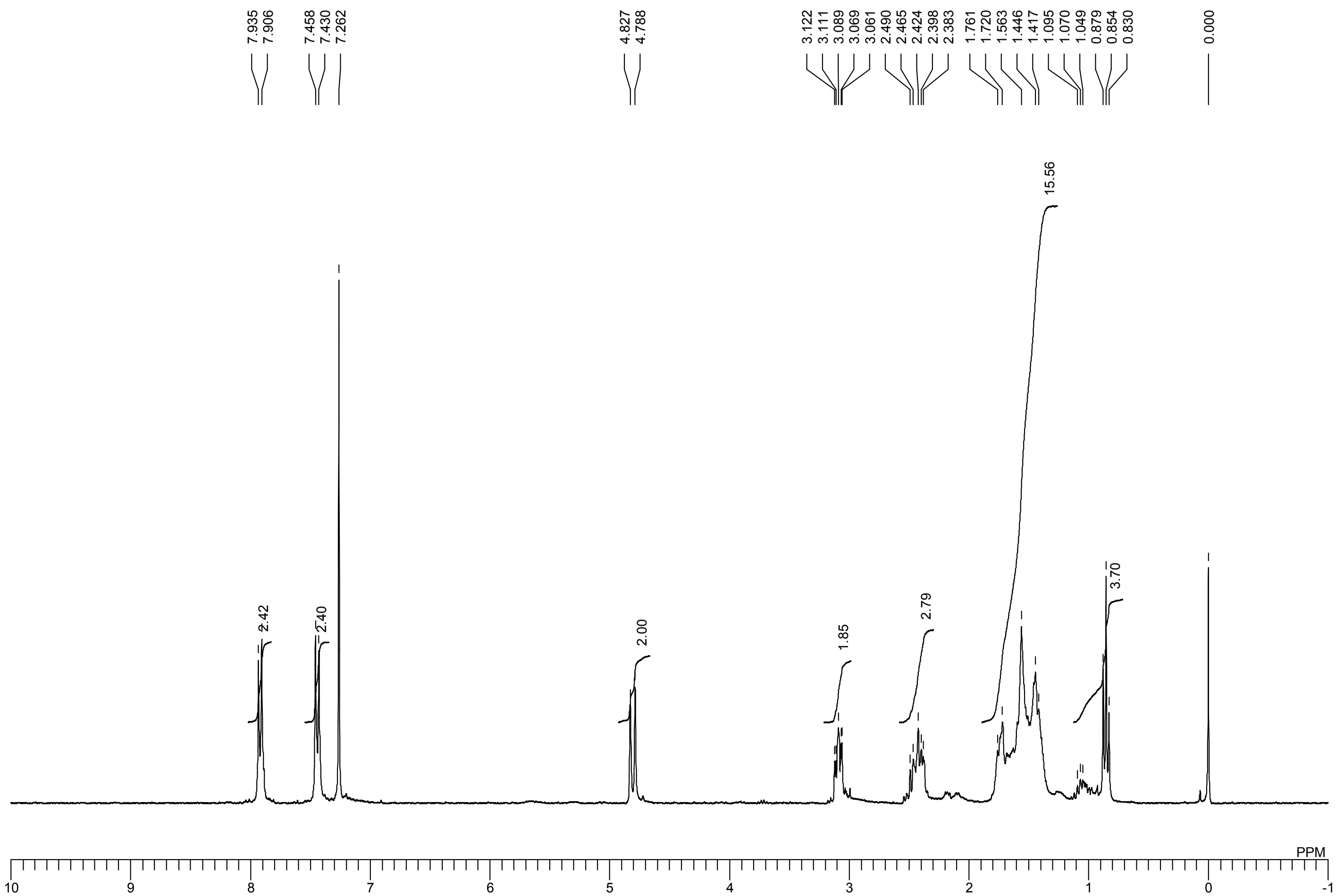
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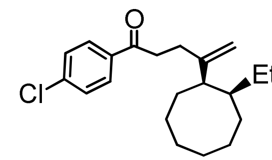
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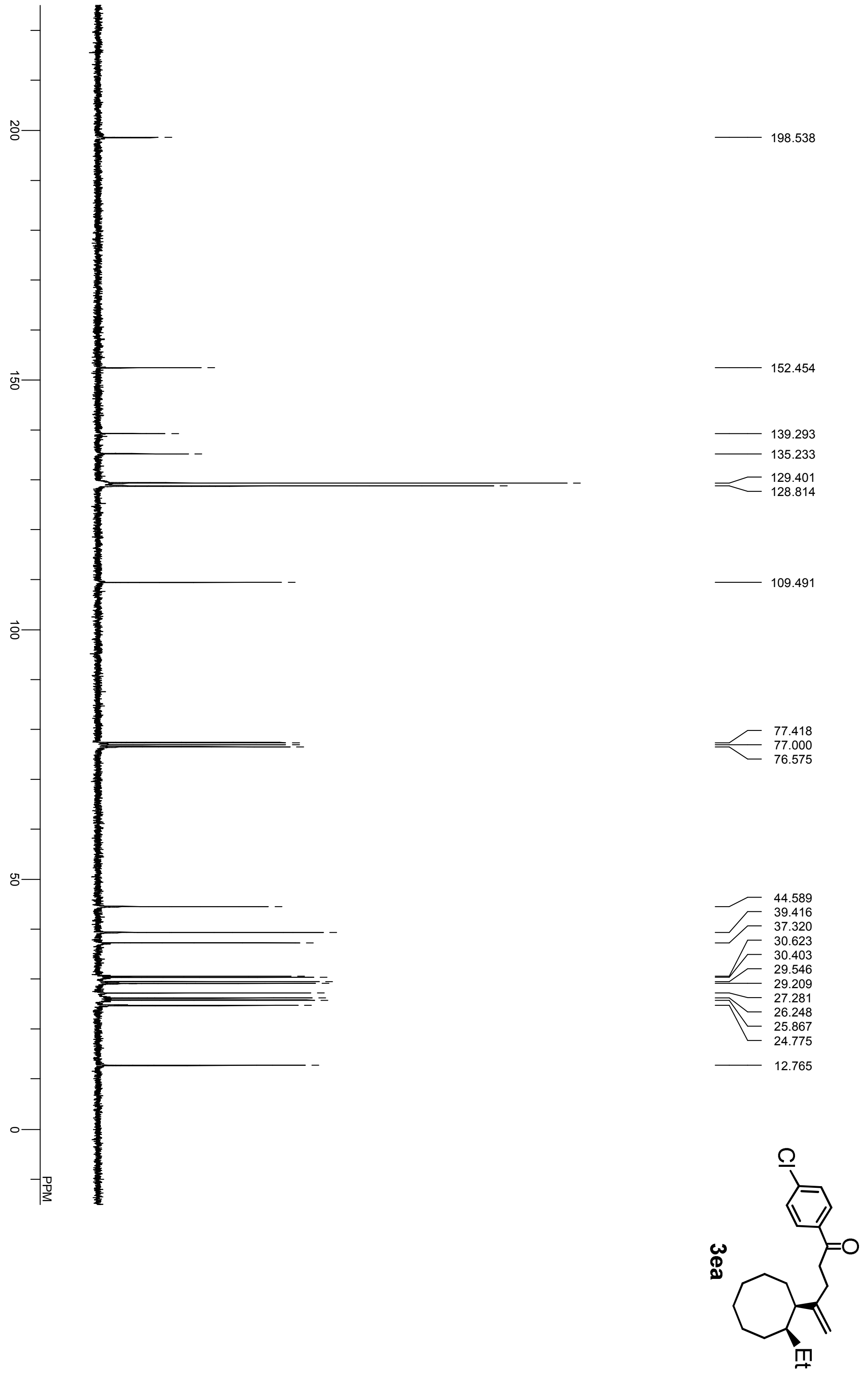
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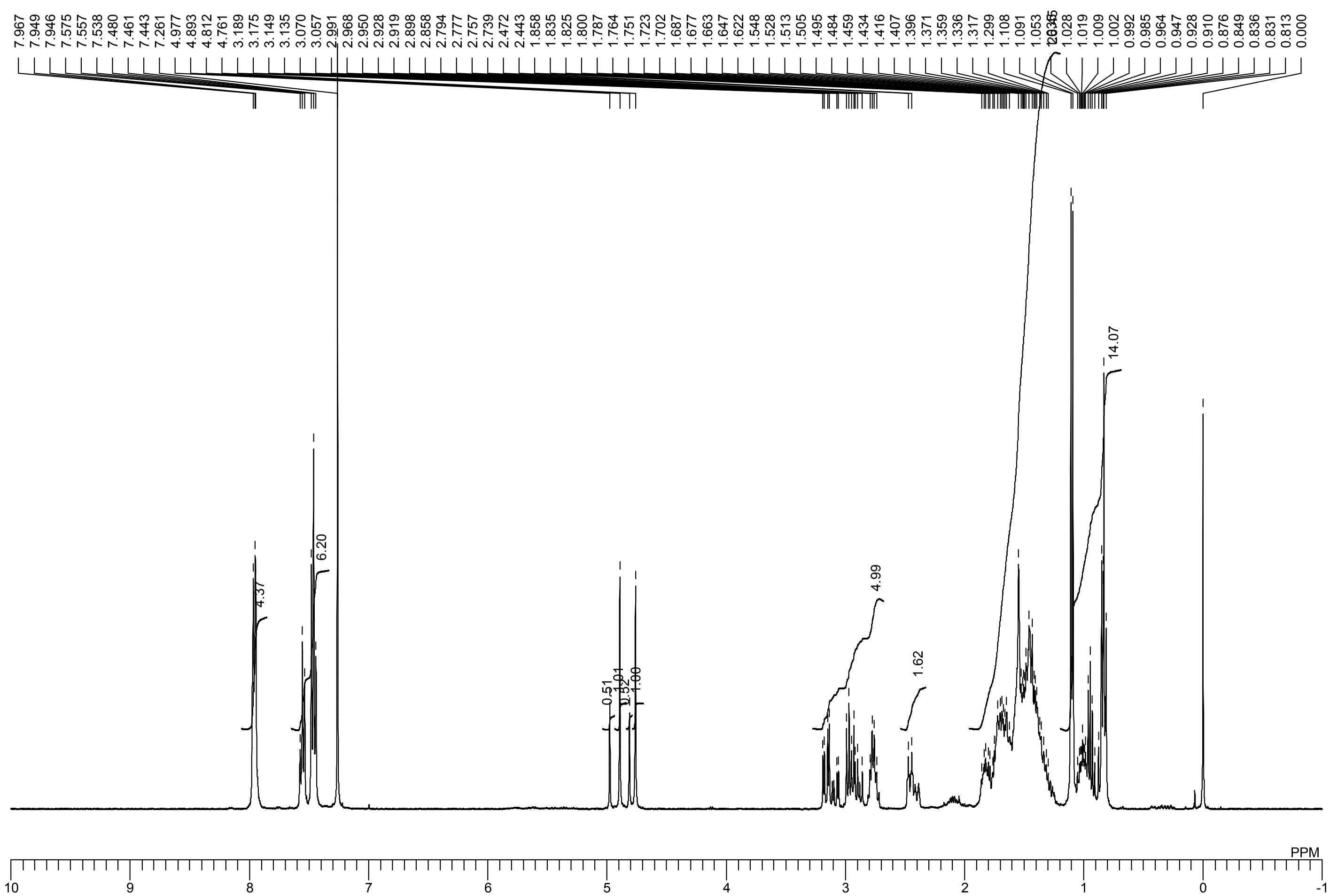
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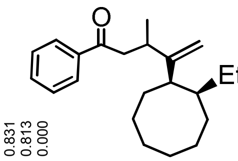
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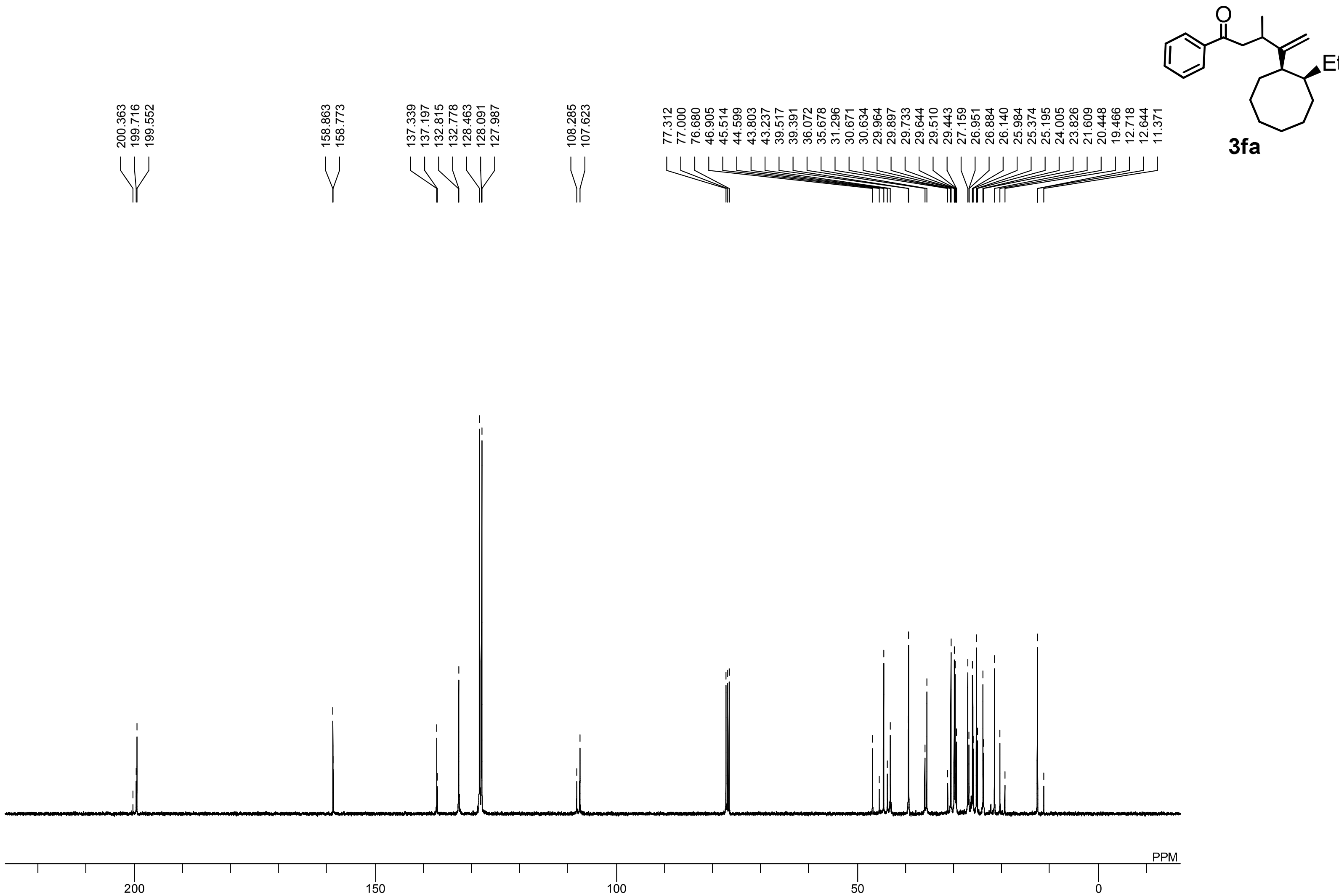
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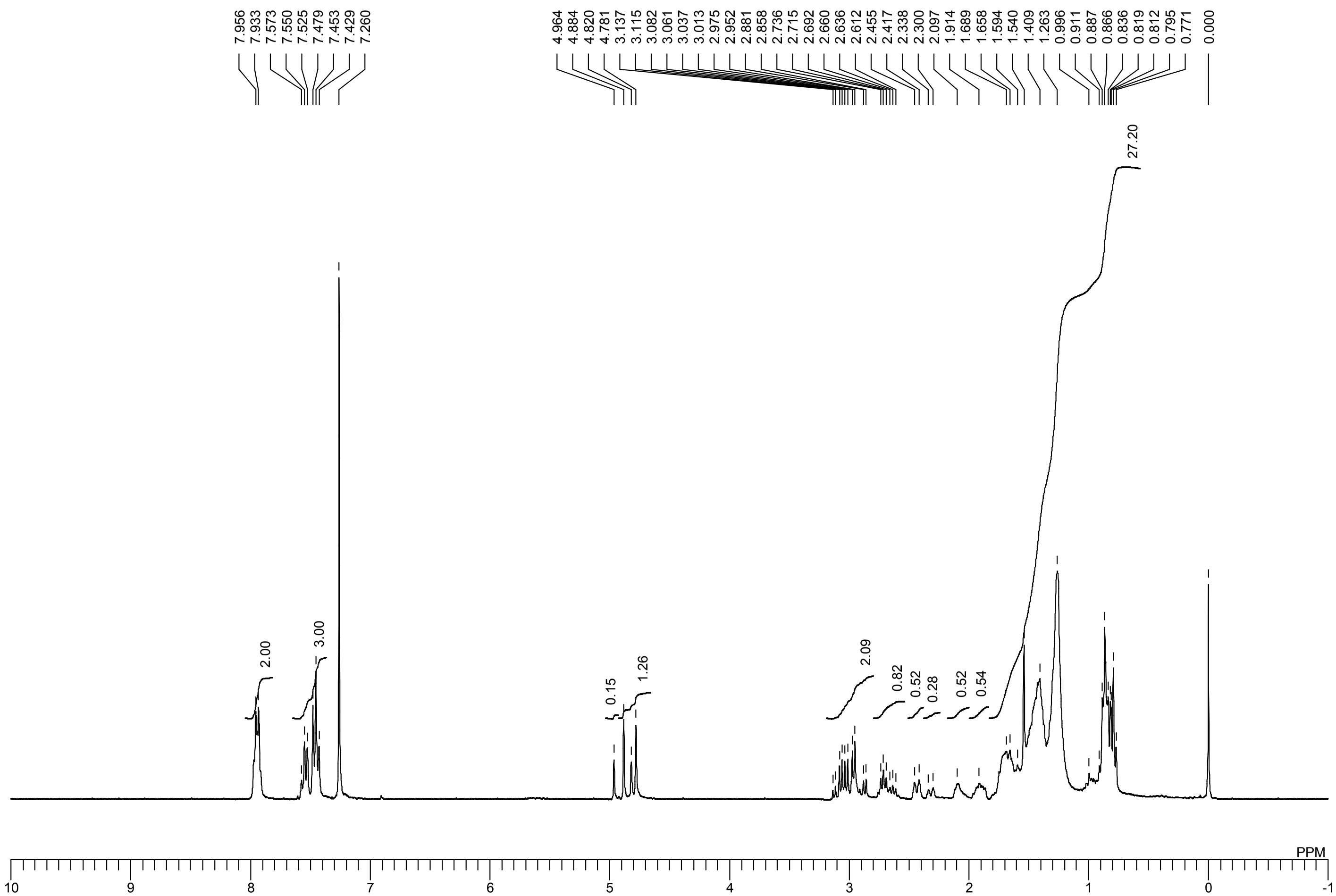
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0.52
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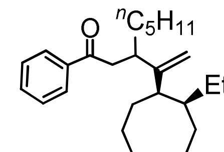
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Et

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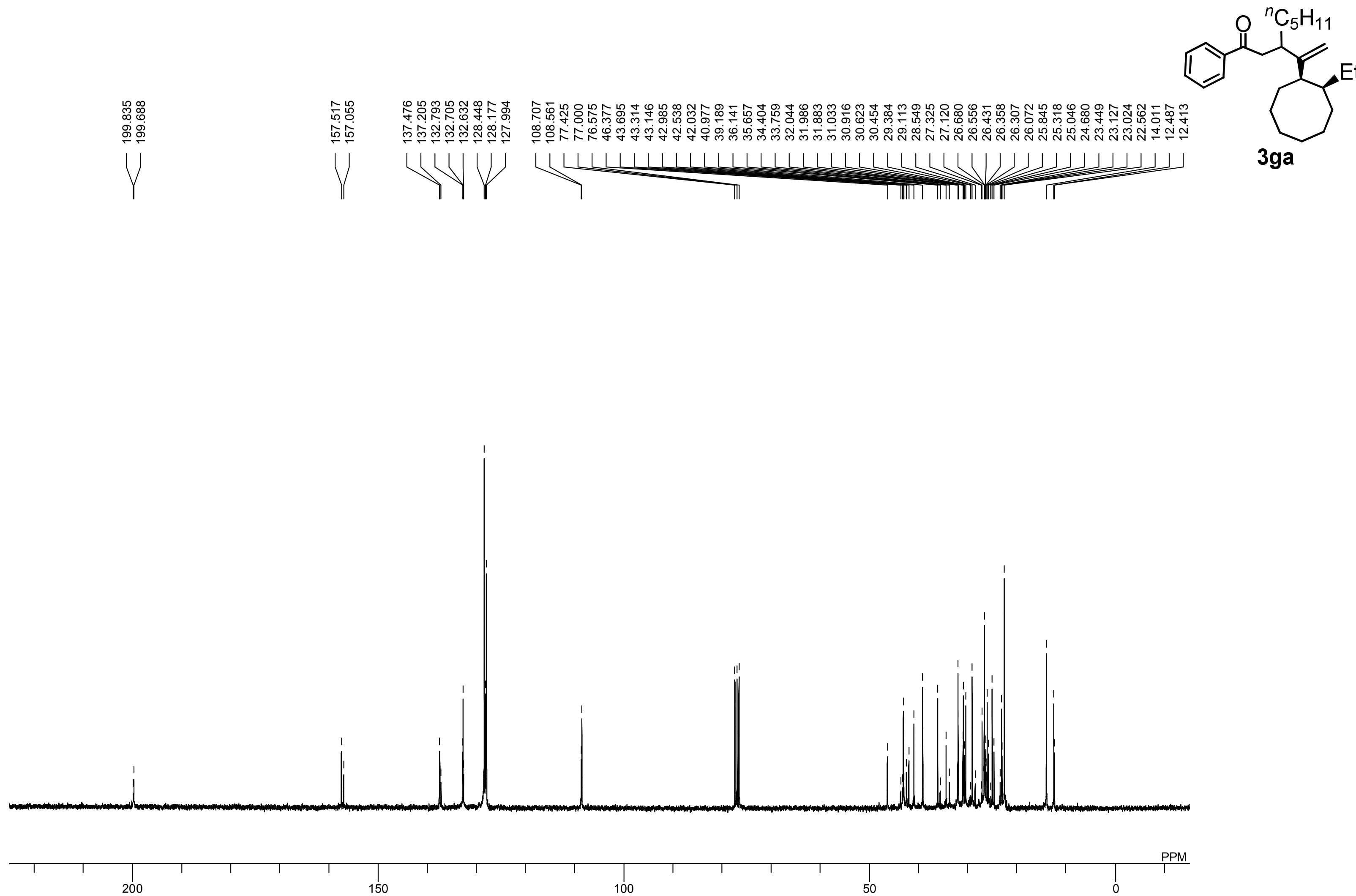
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PPM

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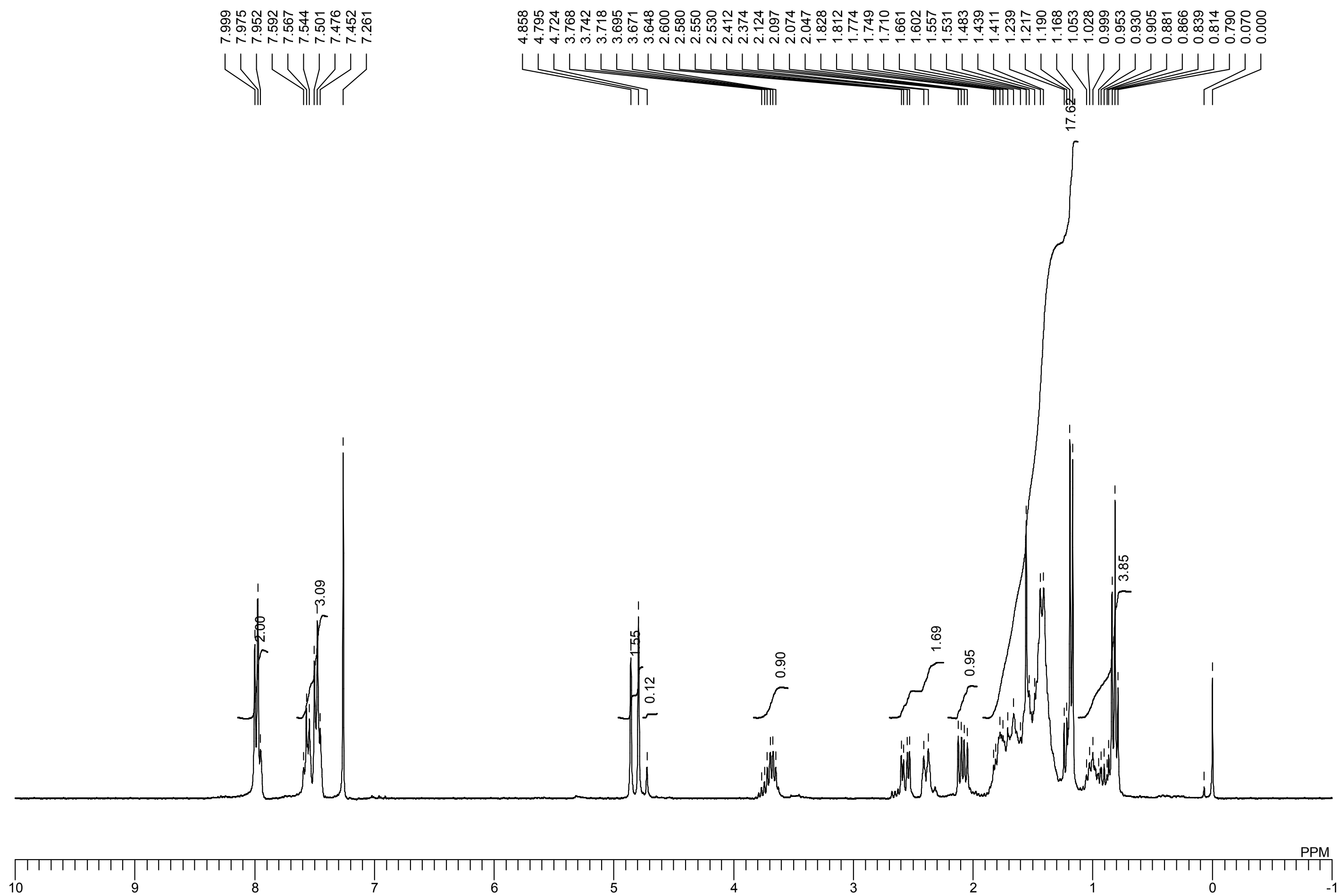
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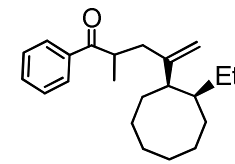
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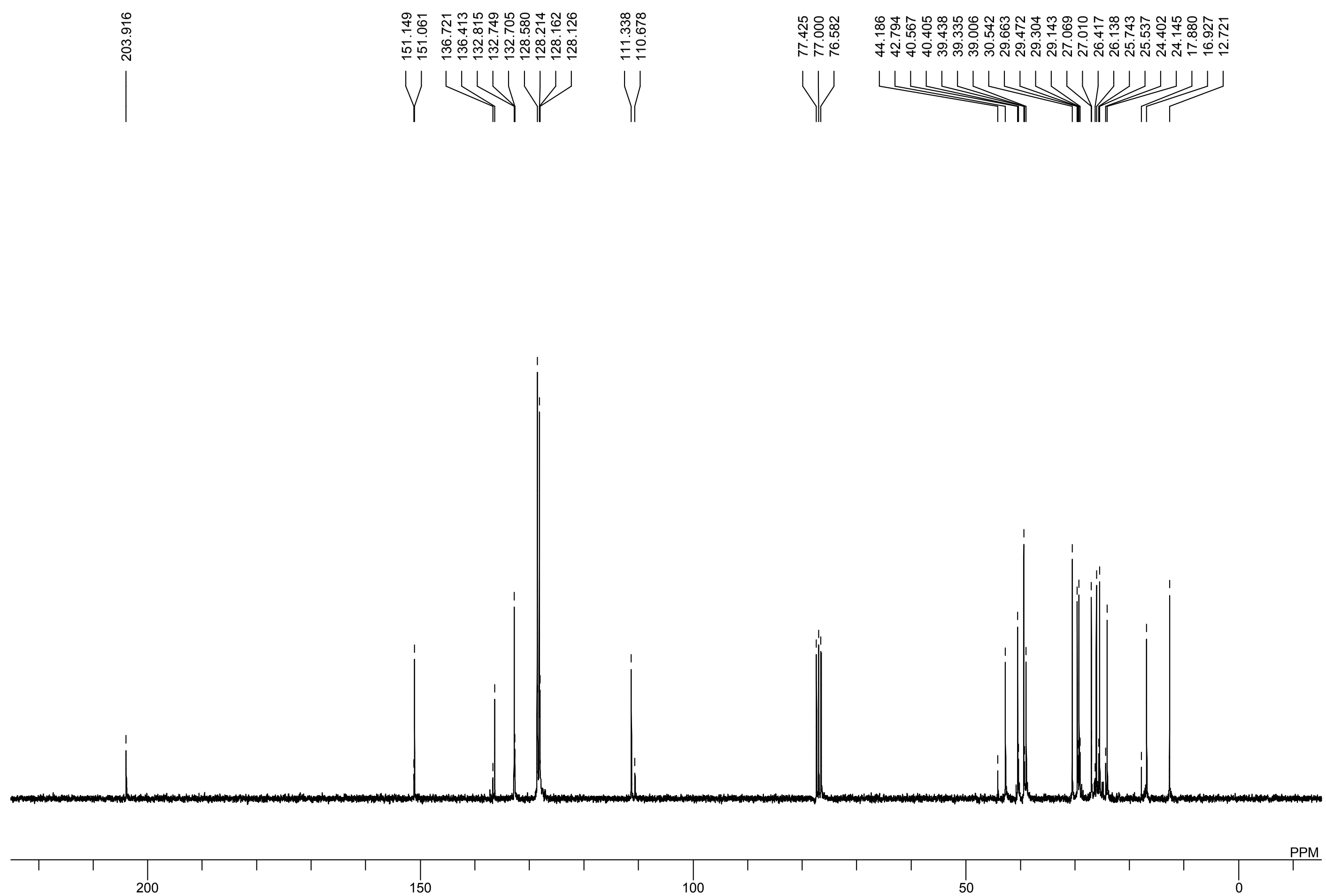

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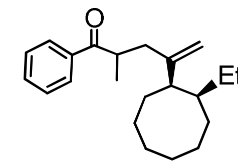

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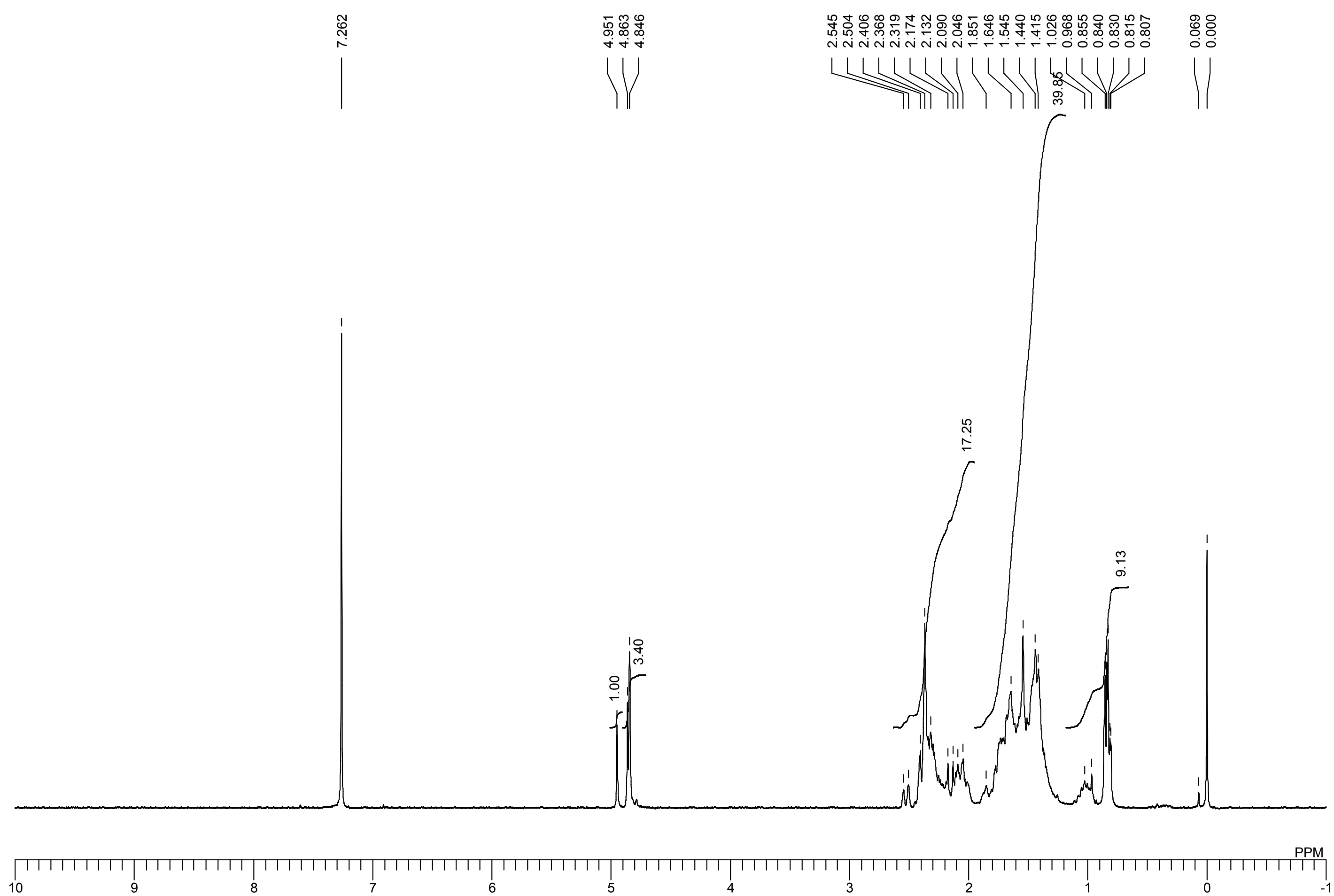
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1.545
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0.807
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1.00
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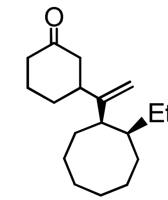
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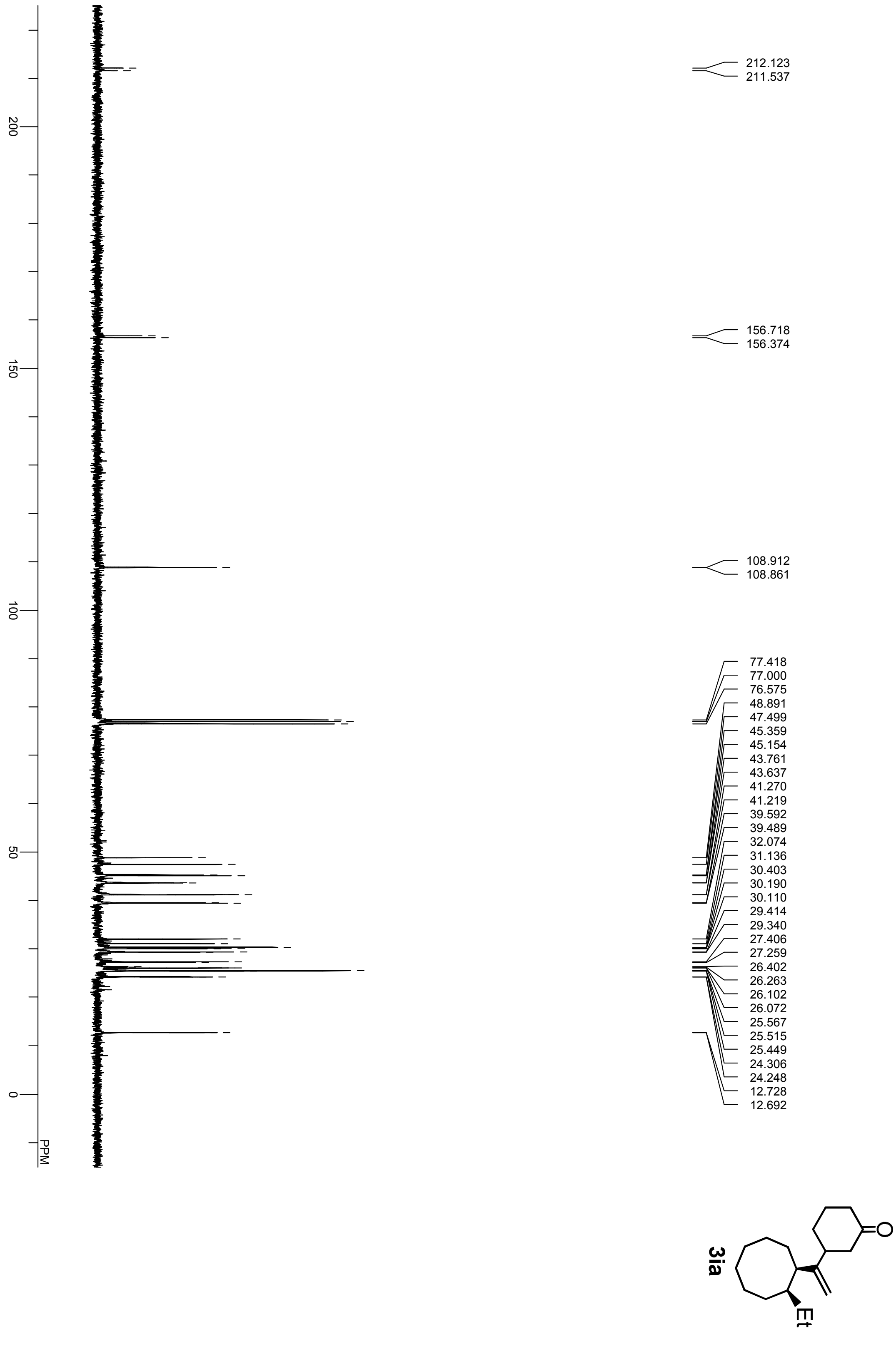
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43.761
43.637
41.270
41.219
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39.489
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31.136
30.403
30.190
30.110
29.414
29.340
27.406
27.259
26.402
26.263
26.102
26.072
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PPM
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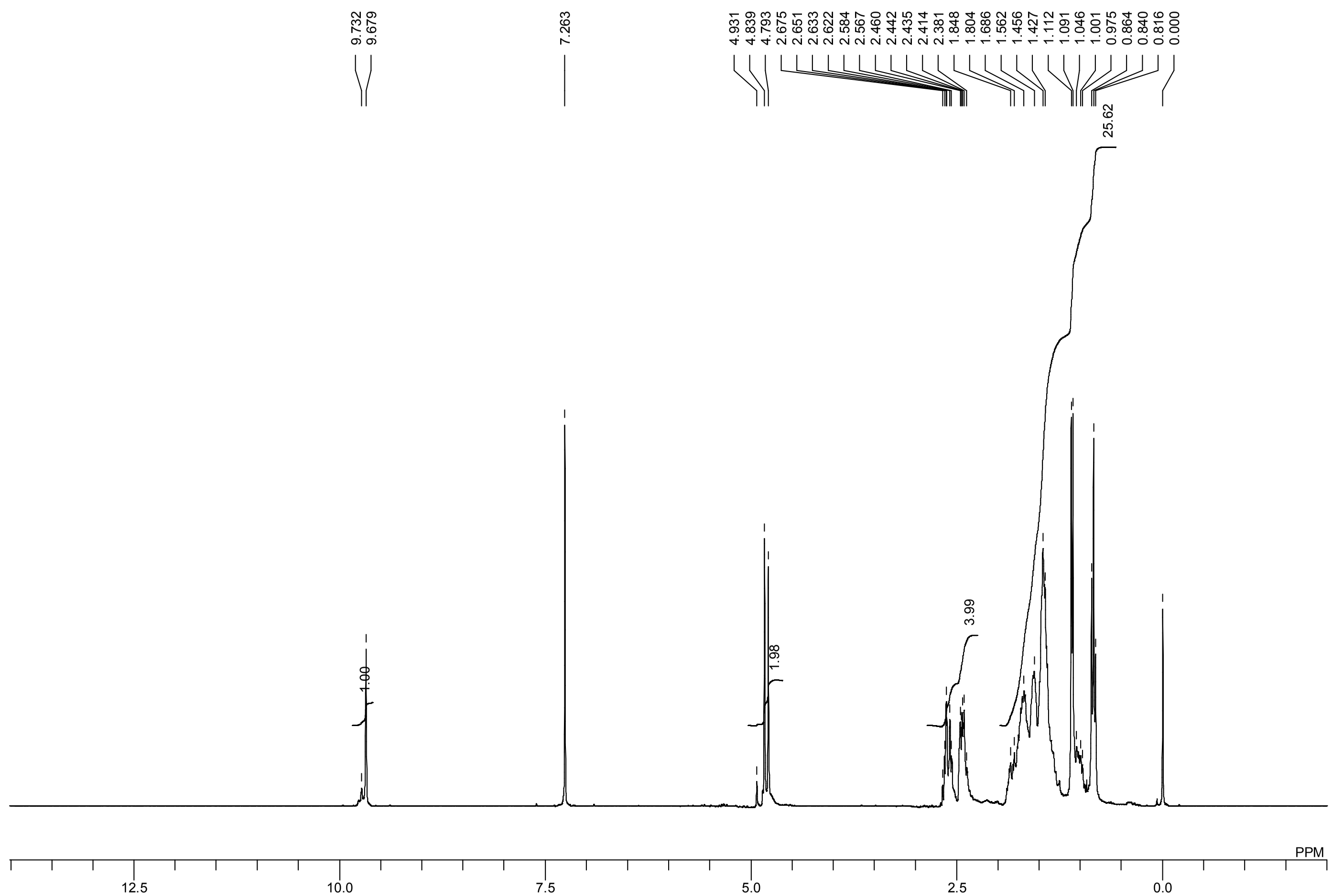
Et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0.816
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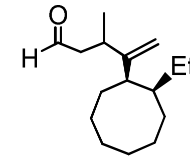
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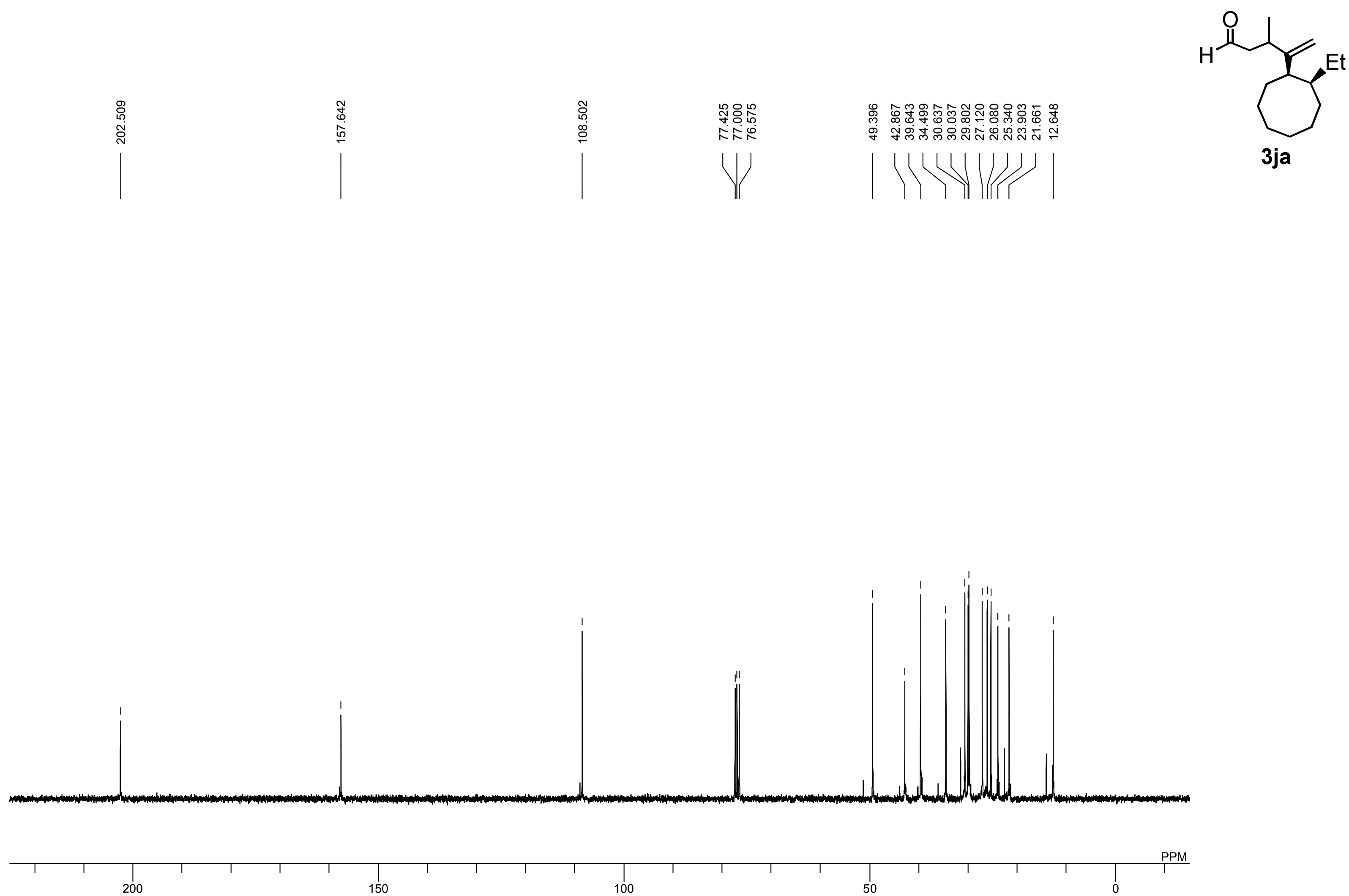
Et

3ja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29.802
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Et
3ja
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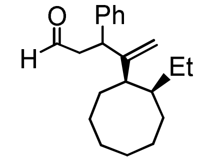
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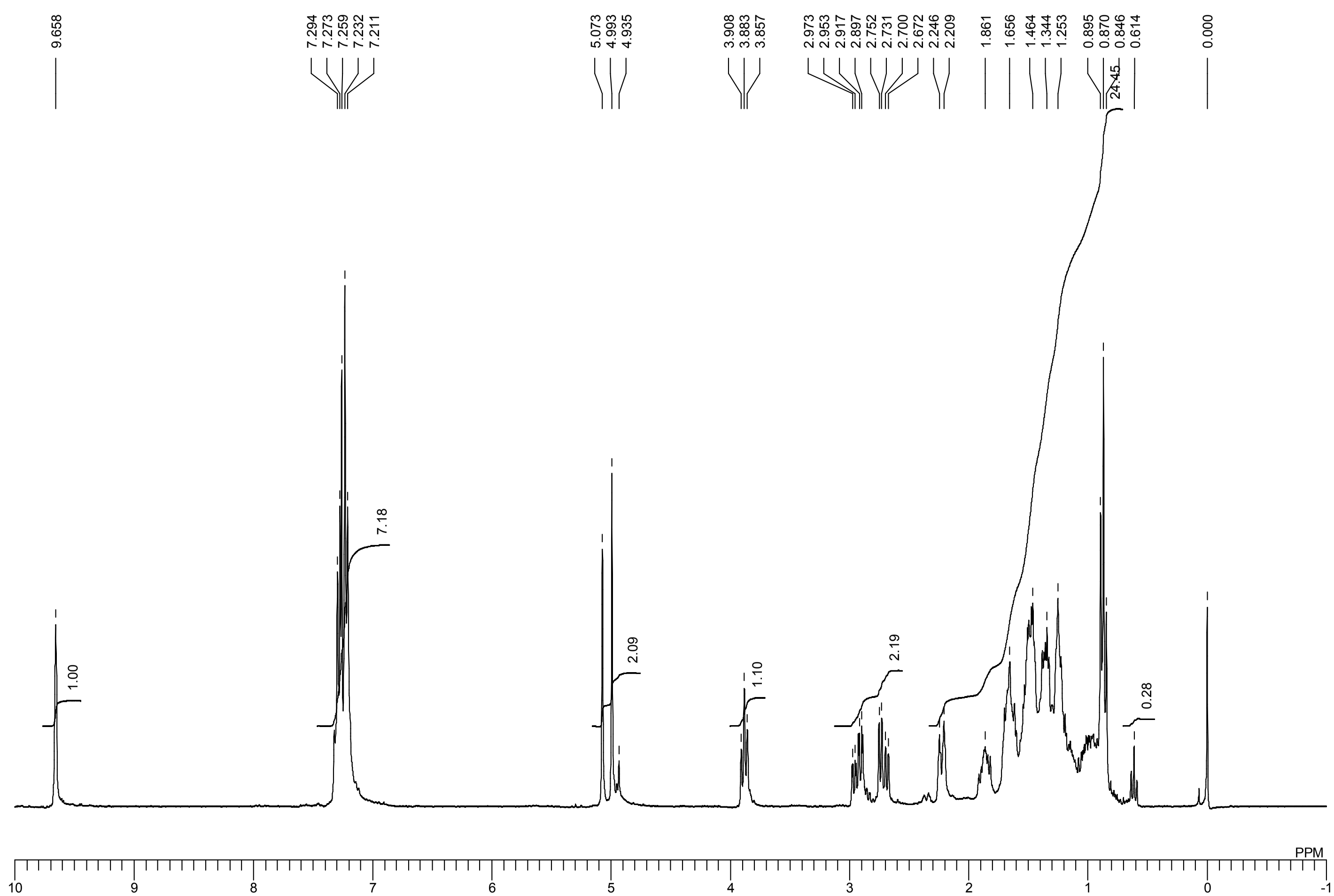
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2.973
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2.209
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1.344
1.253
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0.614
0.000
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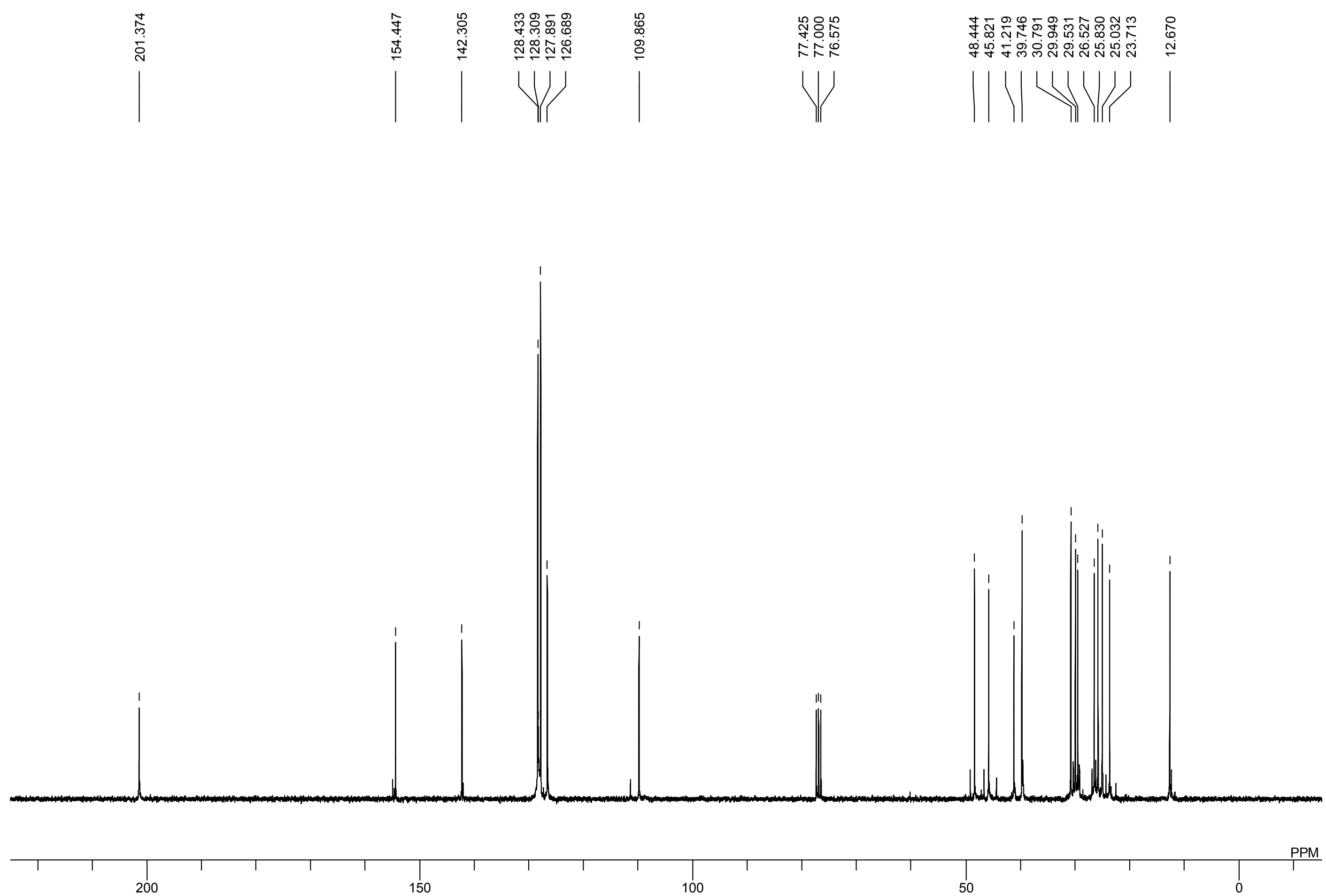
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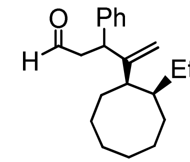
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Et

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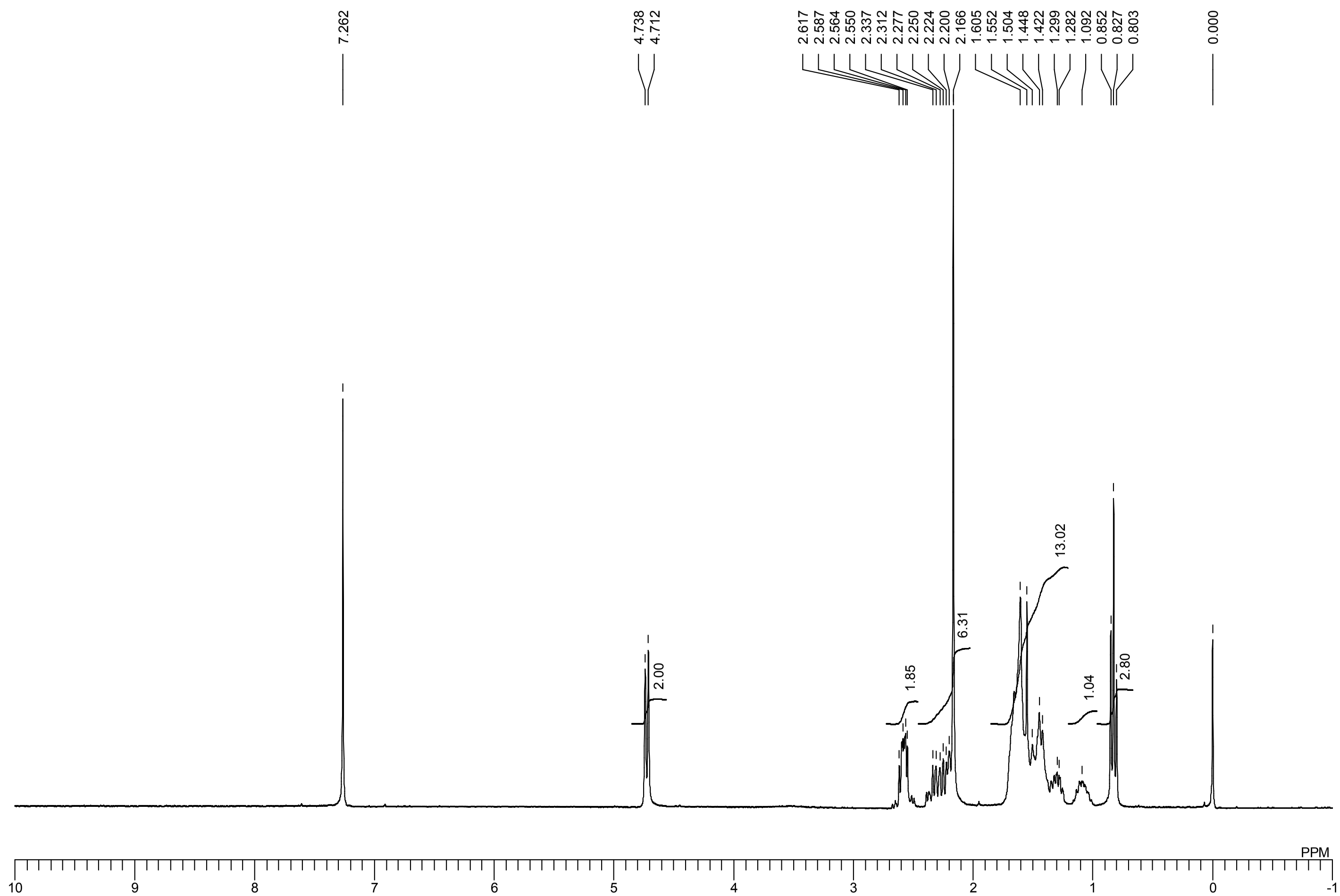
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1.299
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2.00
1.85
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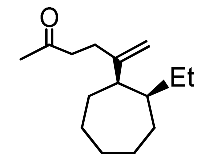
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Et

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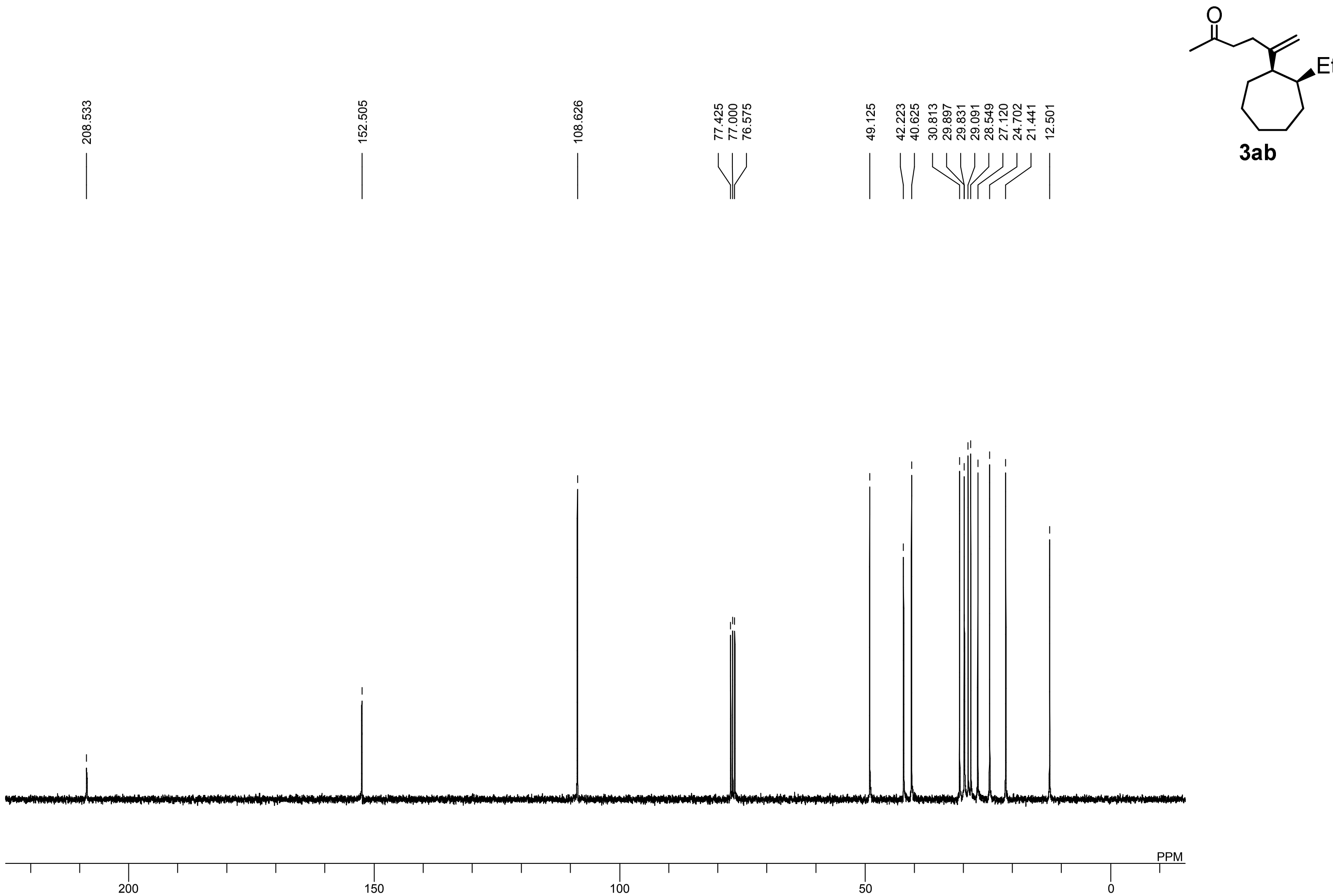
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27.120
24.702
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12.501
O
Et
3ab
PPM
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150
100
50
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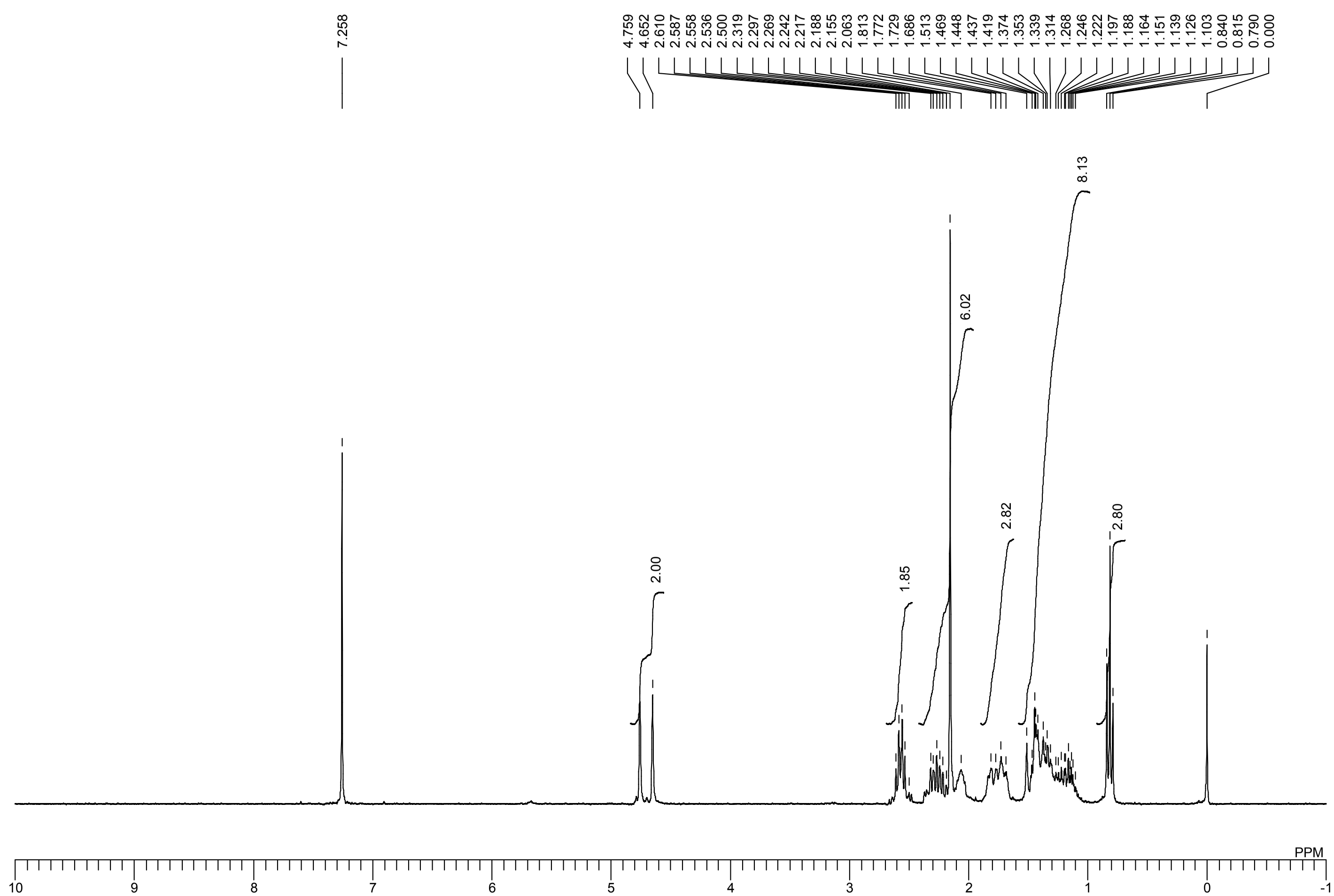

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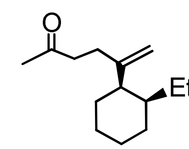

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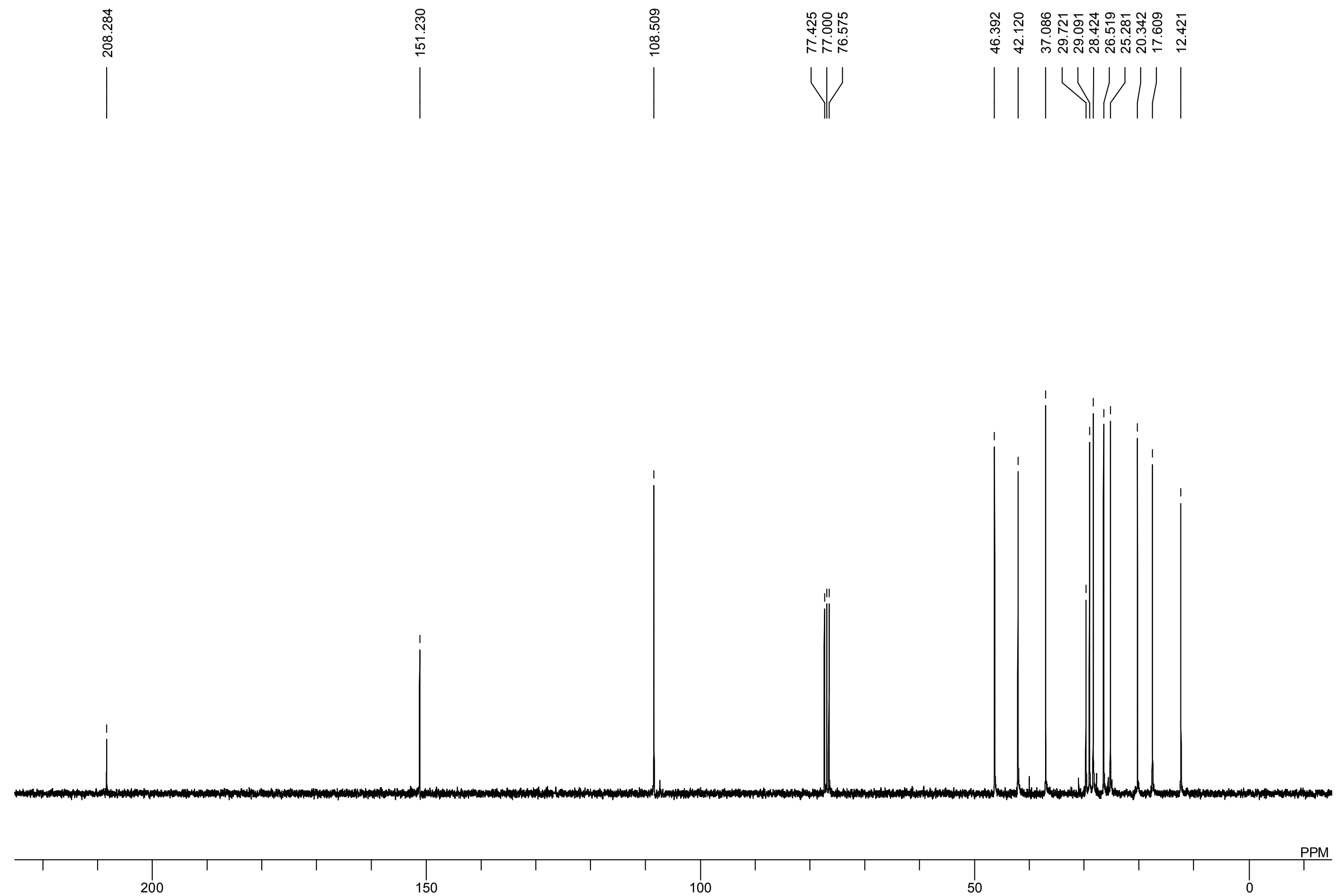
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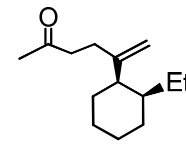
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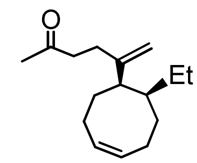

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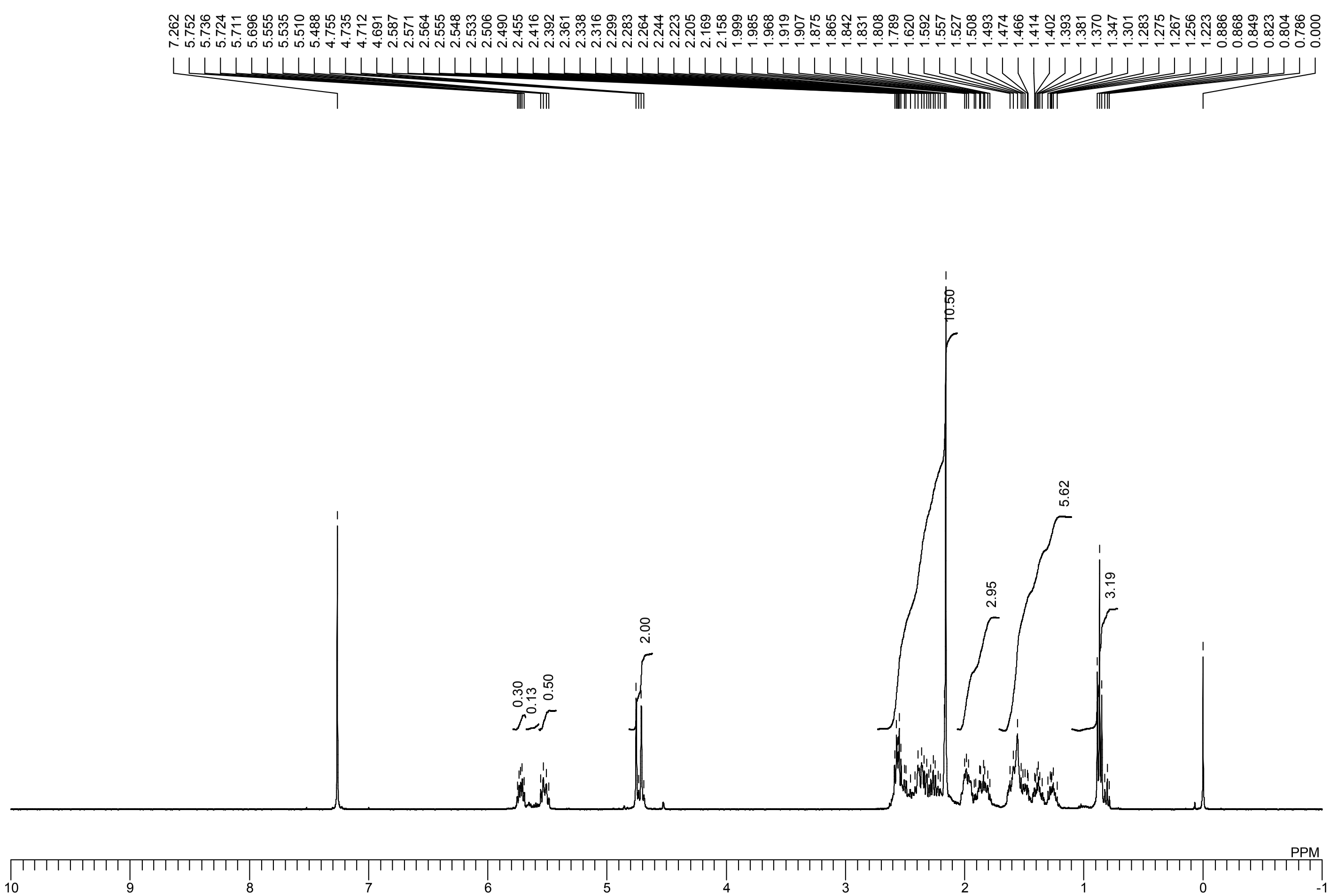
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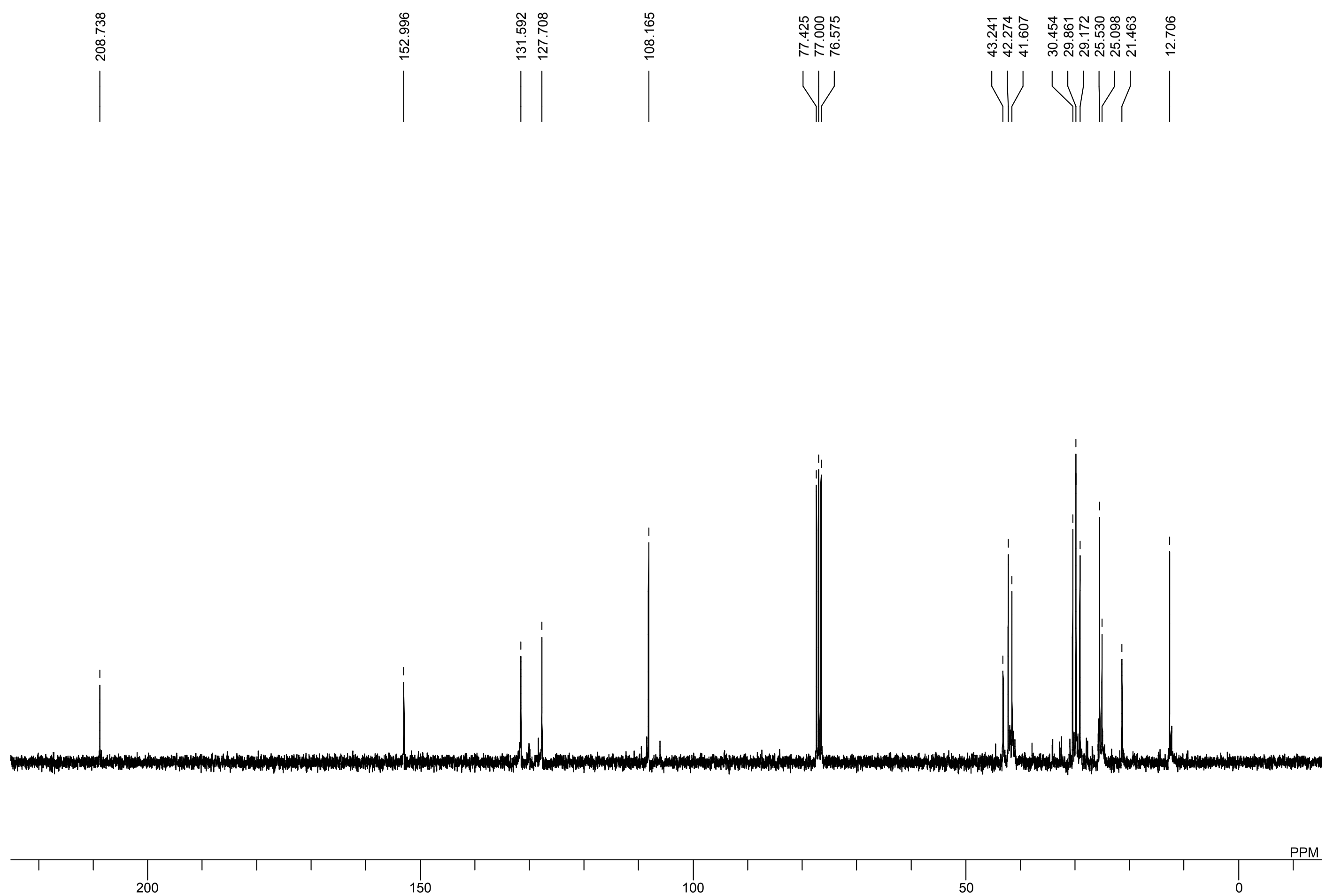
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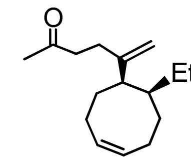
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Et

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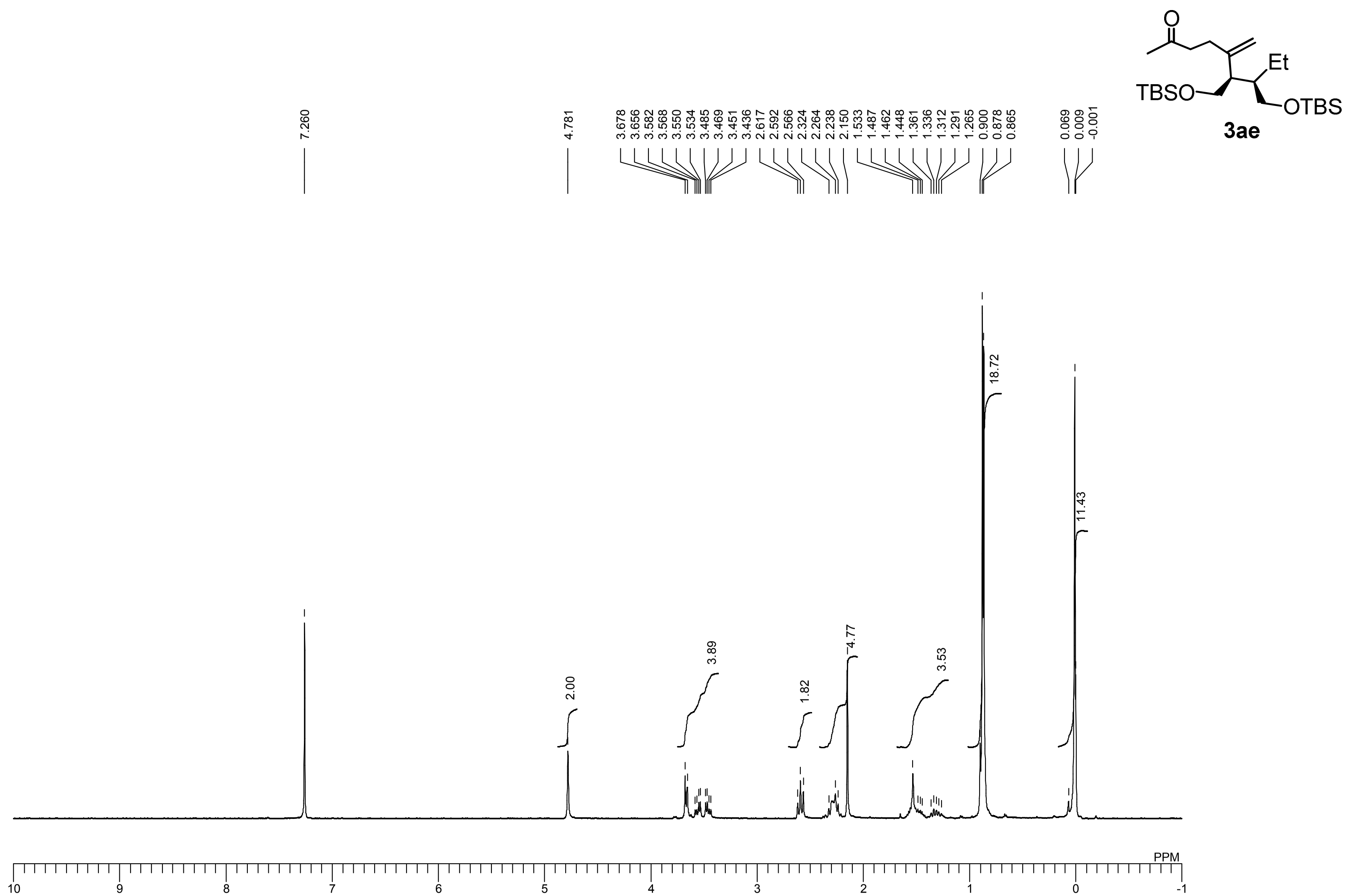
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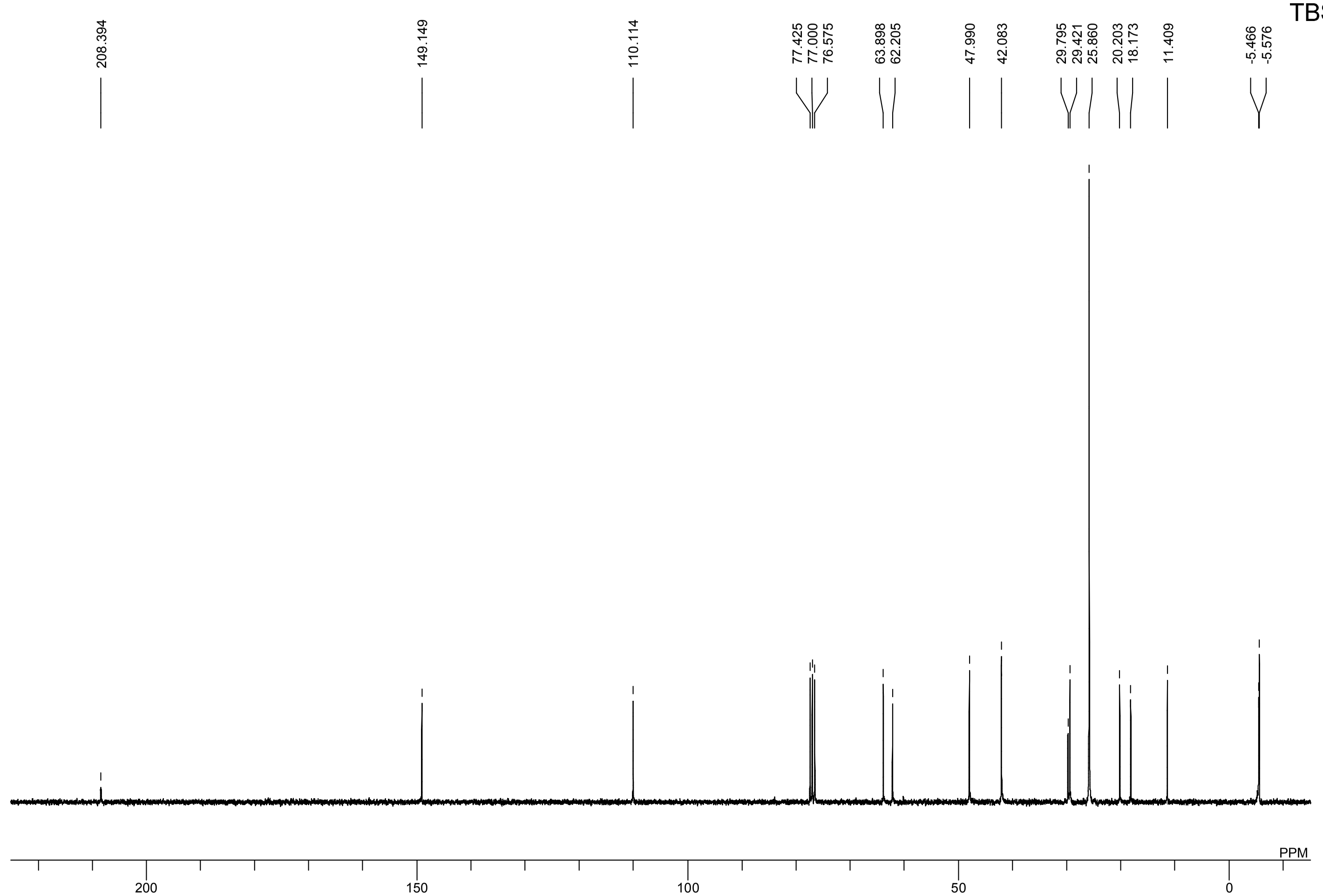
OTBS

3ae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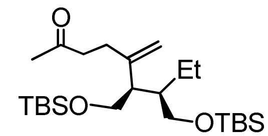
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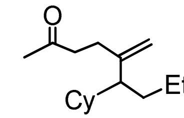
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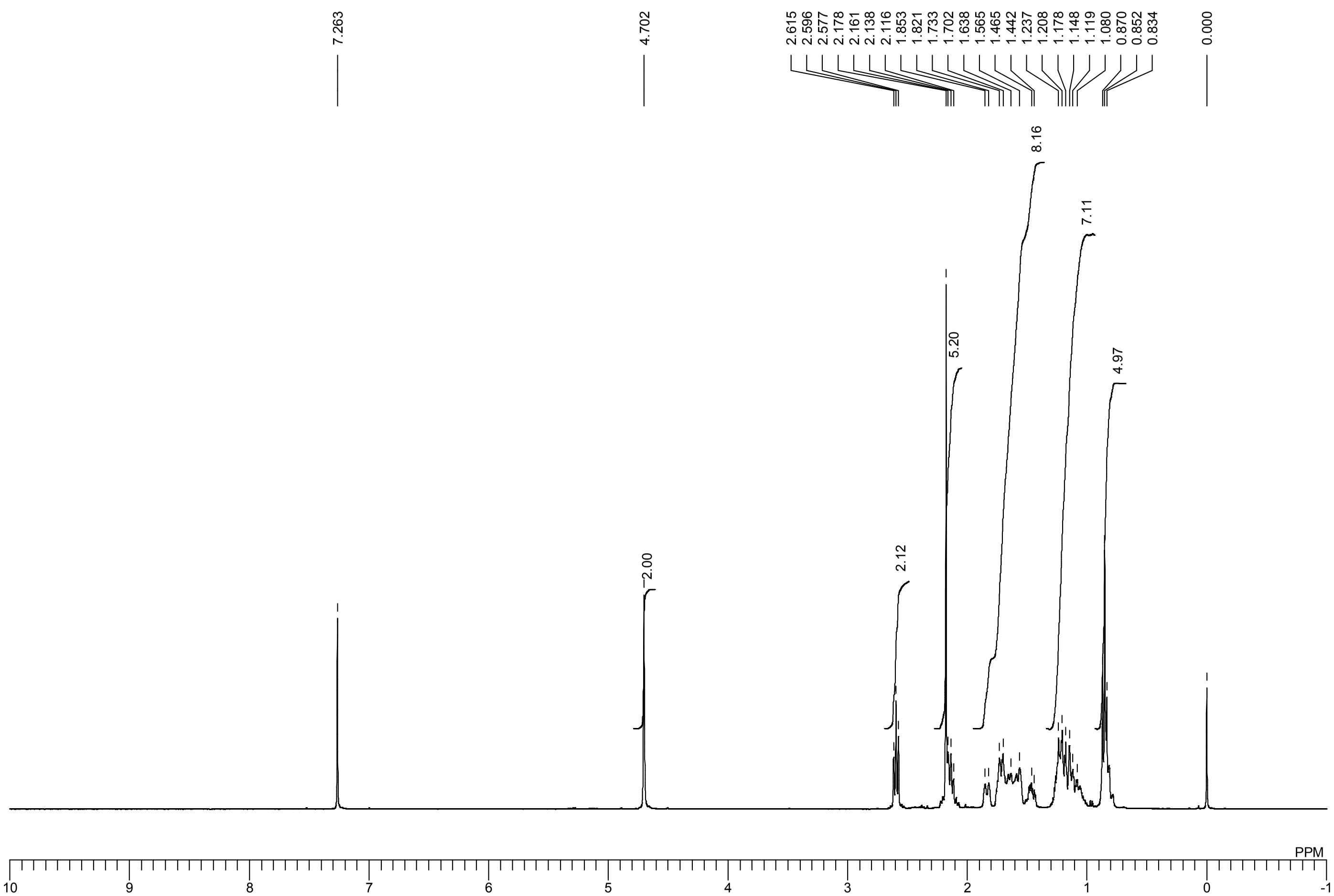
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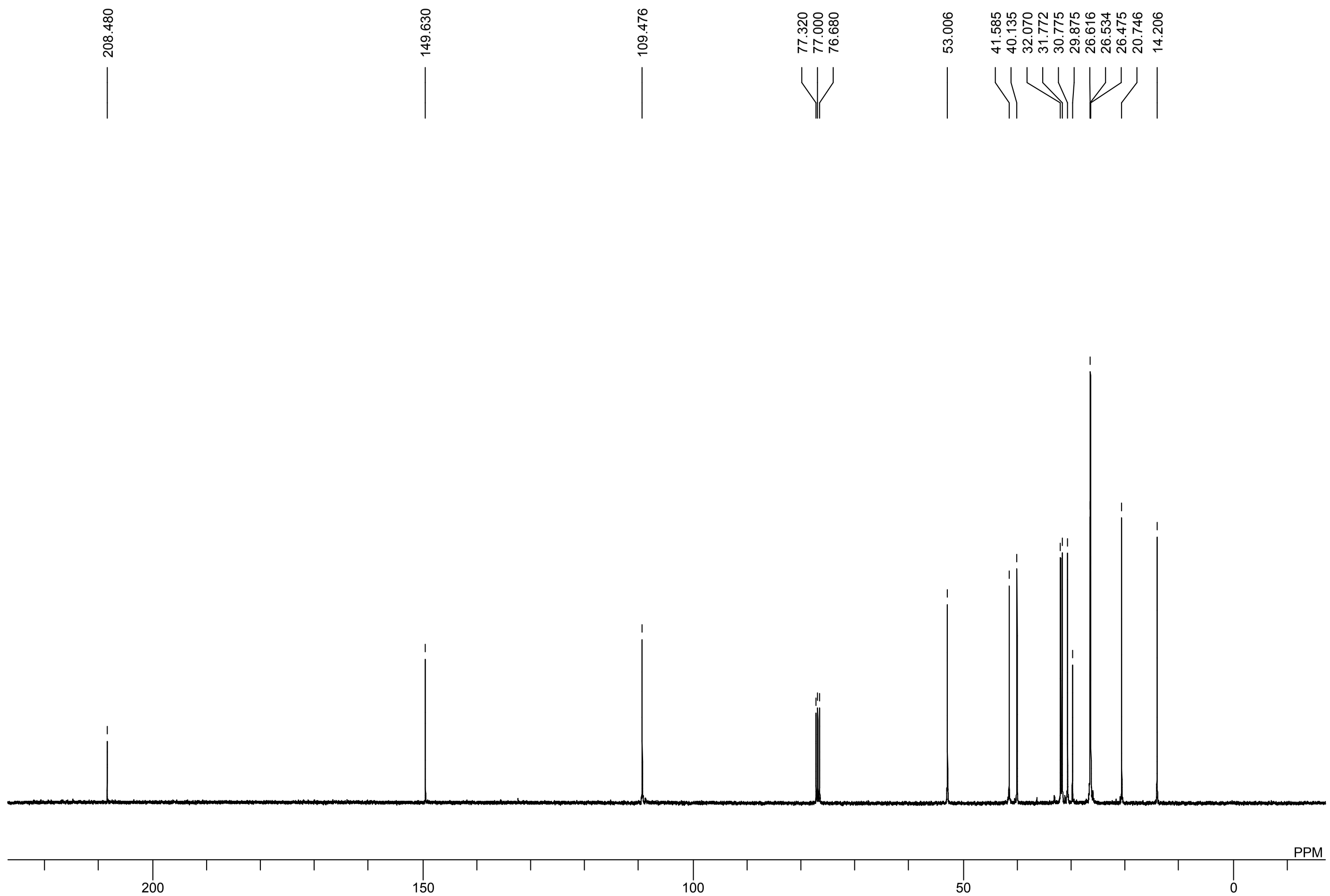
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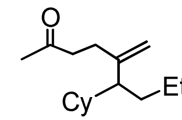
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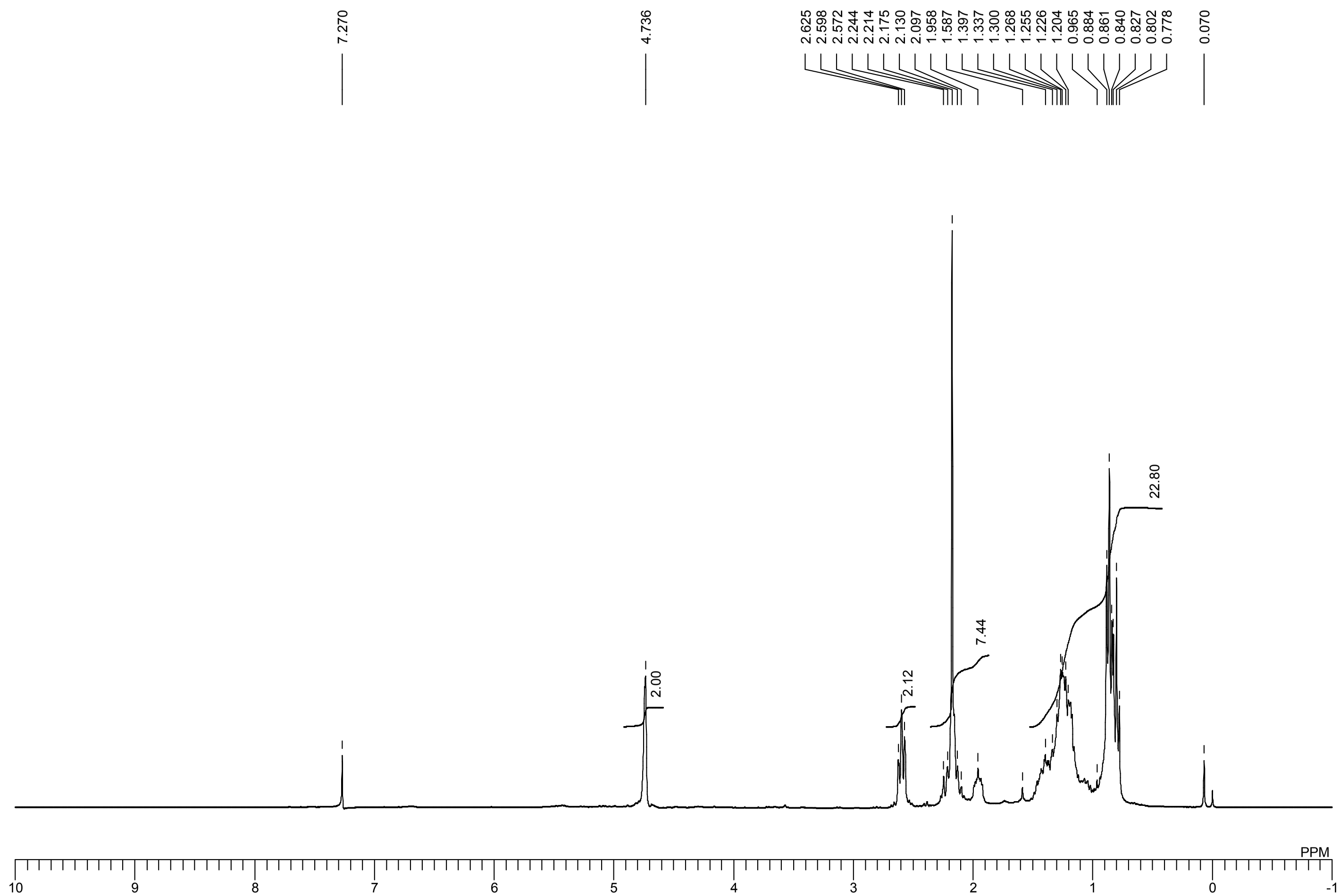
Et

3af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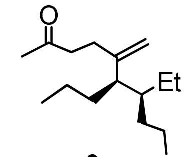
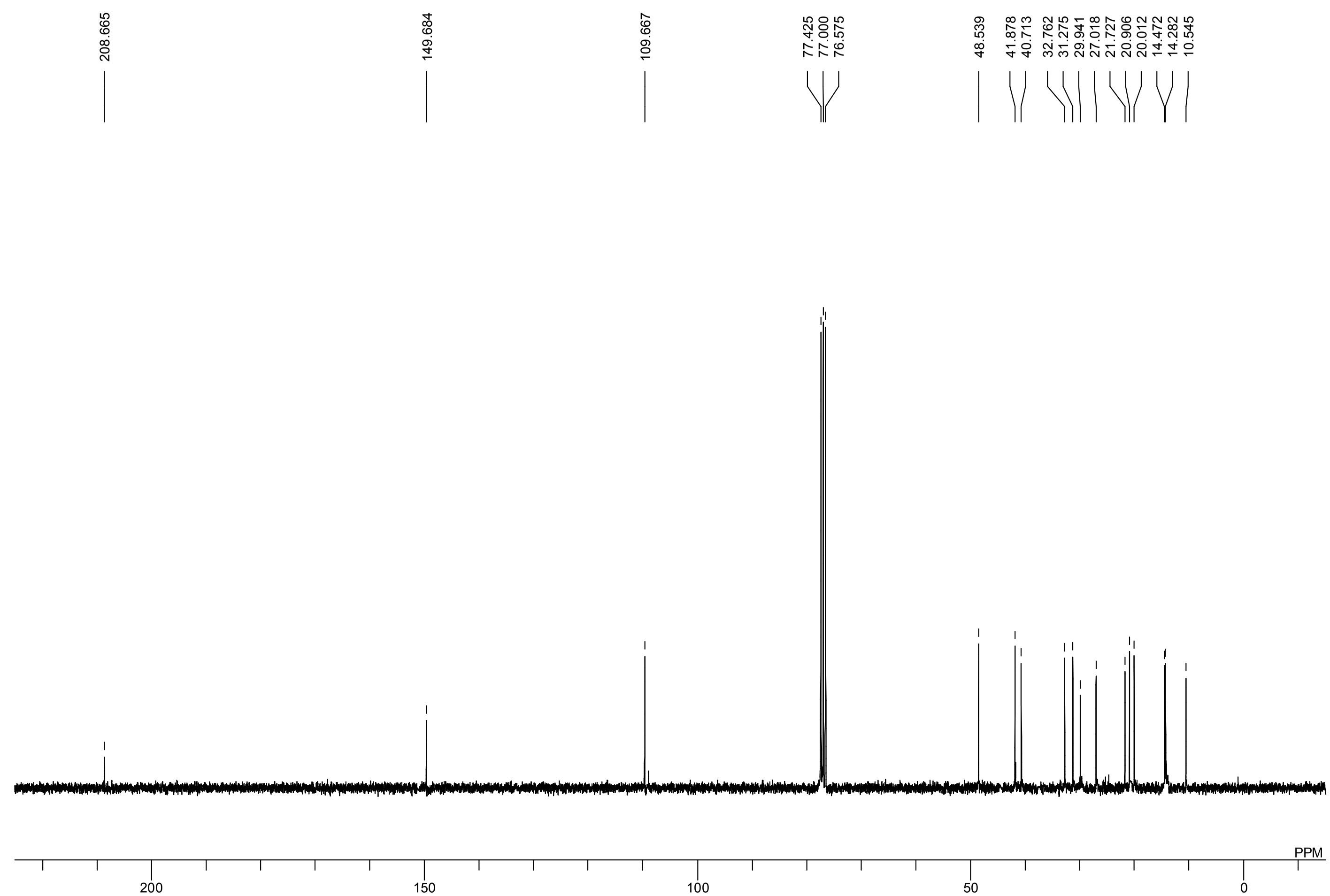
4.736
2.625
2.598
2.572
2.244
2.214
2.175
2.130
2.097
1.958
1.587
1.397
1.337
1.300
1.268
1.255
1.226
1.204
0.965
0.884
0.861
0.840
0.827
0.802
0.778
0.070
2.00
2.12
7.44
22.80
PPM
10
9
8
7
6
5
4
3
2
1
0
-1


O
Et

3ag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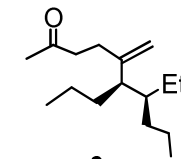
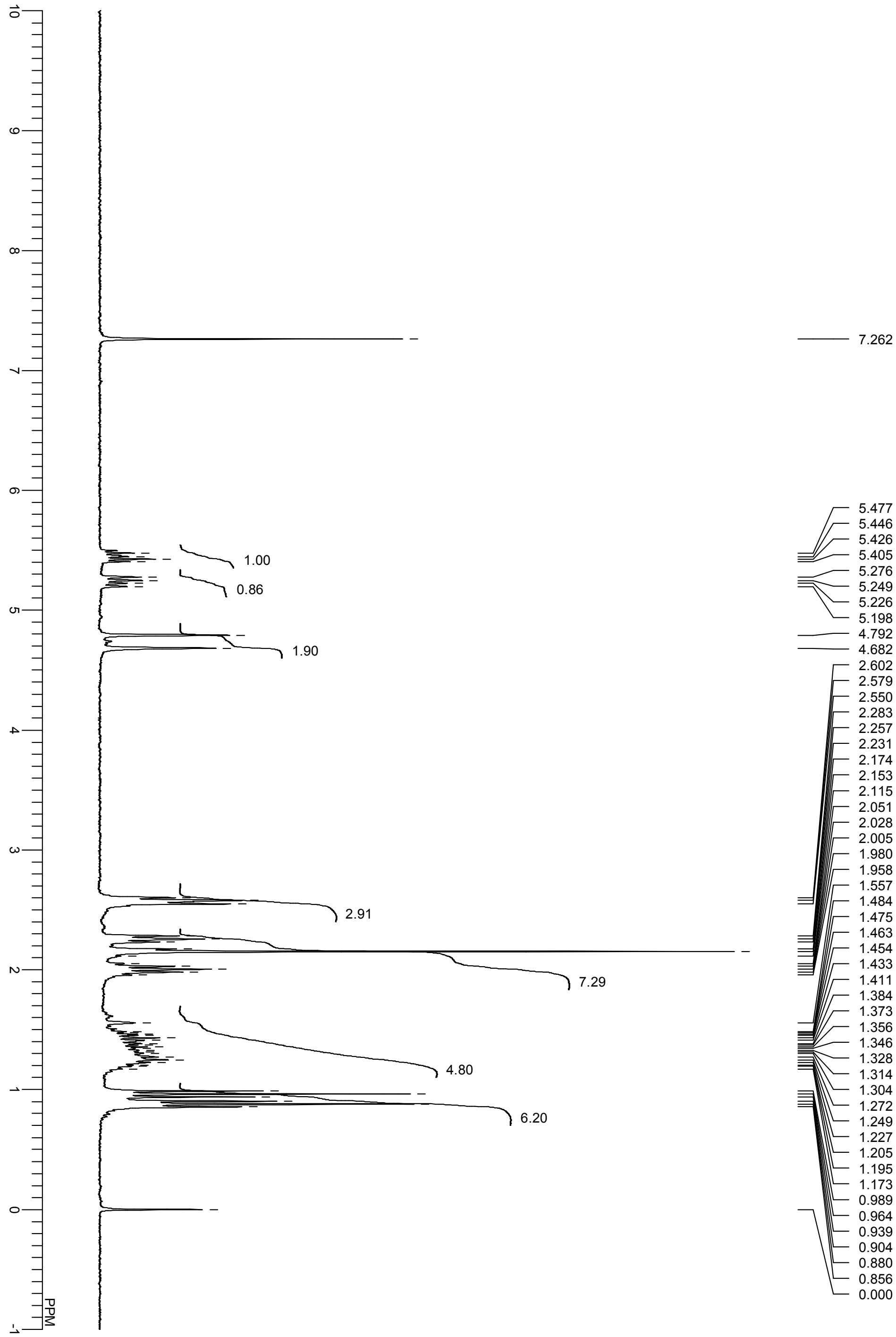
149.684
109.667
77.425
77.000
76.575
48.539
41.878
40.713
32.762
31.275
29.941
27.018
21.727
20.906
20.012
14.472
14.282
10.545
200
150
100
50
0
PPM


O
Et

3ag


PPM
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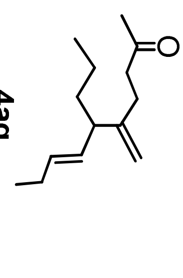
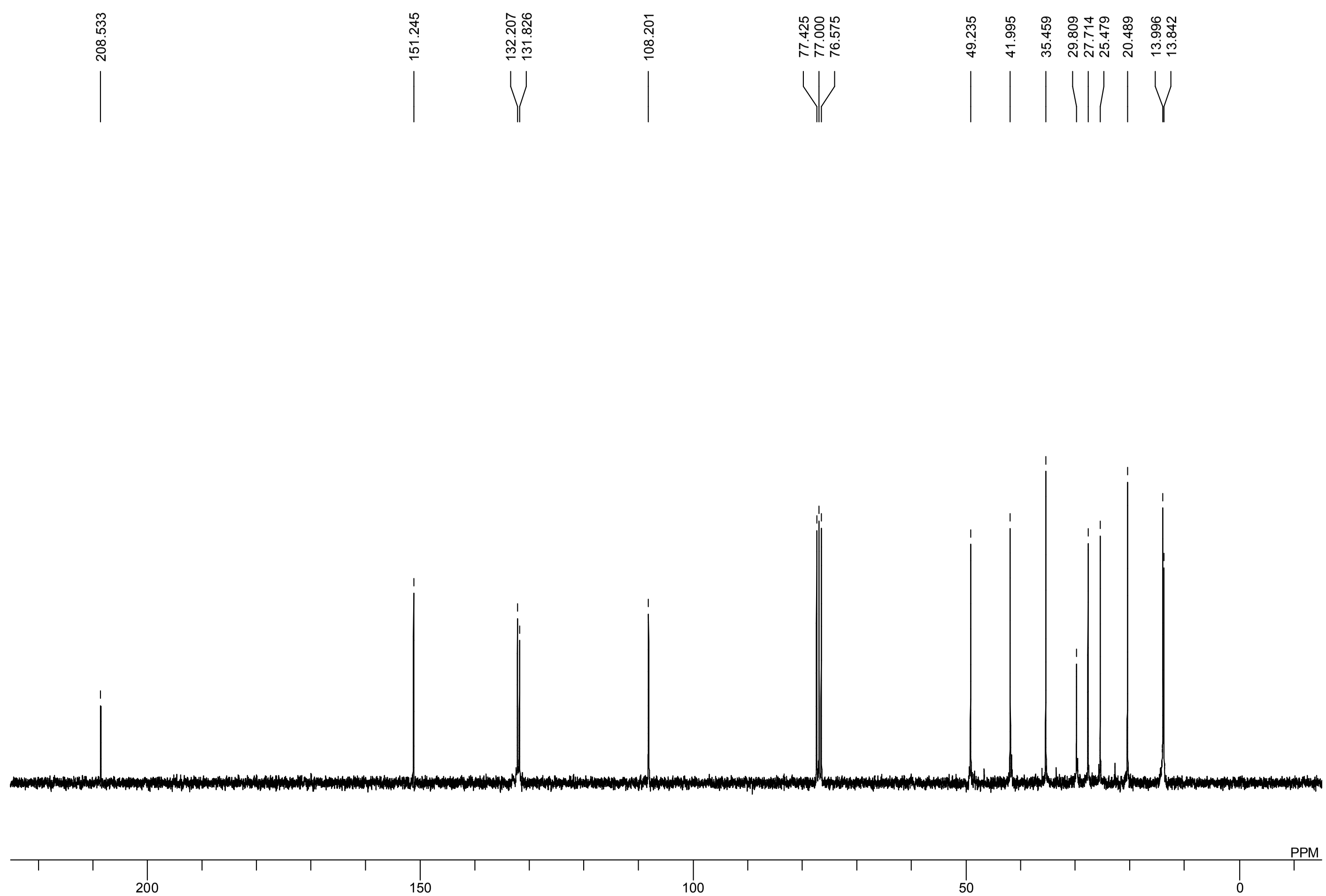
0.86
1.90
2.91
7.29
4.80
6.20
7.262
5.477
5.446
5.426
5.405
5.276
5.249
5.226
5.198
4.792
4.682
2.602
2.579
2.550
2.283
2.257
2.231
2.174
2.153
2.115
2.051
2.028
2.005
1.980
1.958
1.557
1.484
1.475
1.463
1.454
1.433
1.411
1.384
1.373
1.356
1.346
1.328
1.314
1.304
1.272
1.249
1.227
1.205
1.195
1.173
0.989
0.964
0.939
0.904
0.880
0.856
0.000



4ag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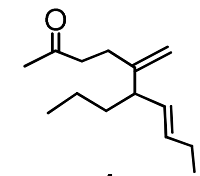
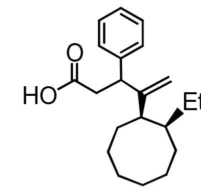
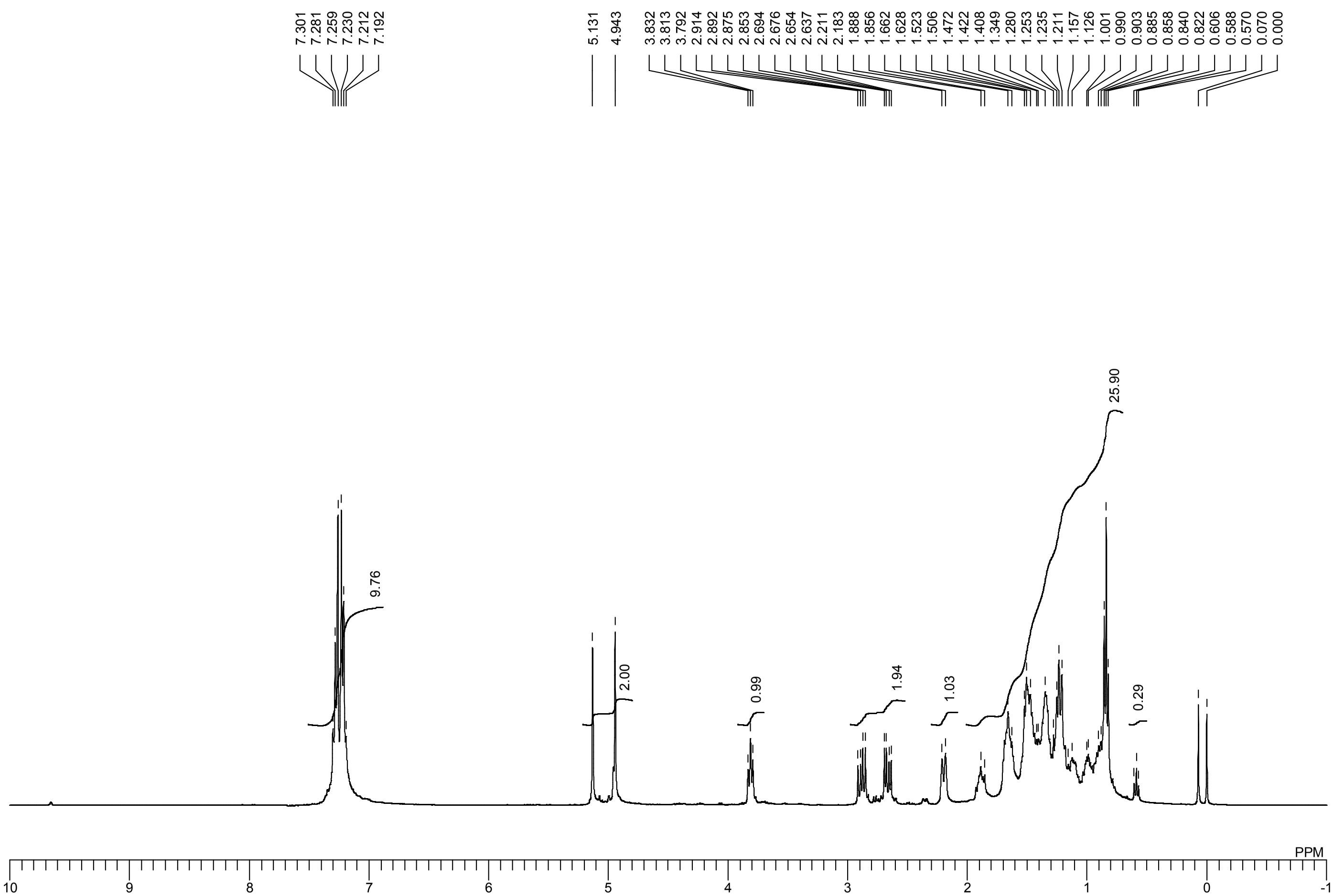
151.245
132.207
131.826
108.201
77.425
77.000
76.575
49.235
41.995
35.459
29.809
27.714
25.479
20.489
13.996
13.842
PPM
200
150
100
50
0


O

4ag


HO
O
Et

5ka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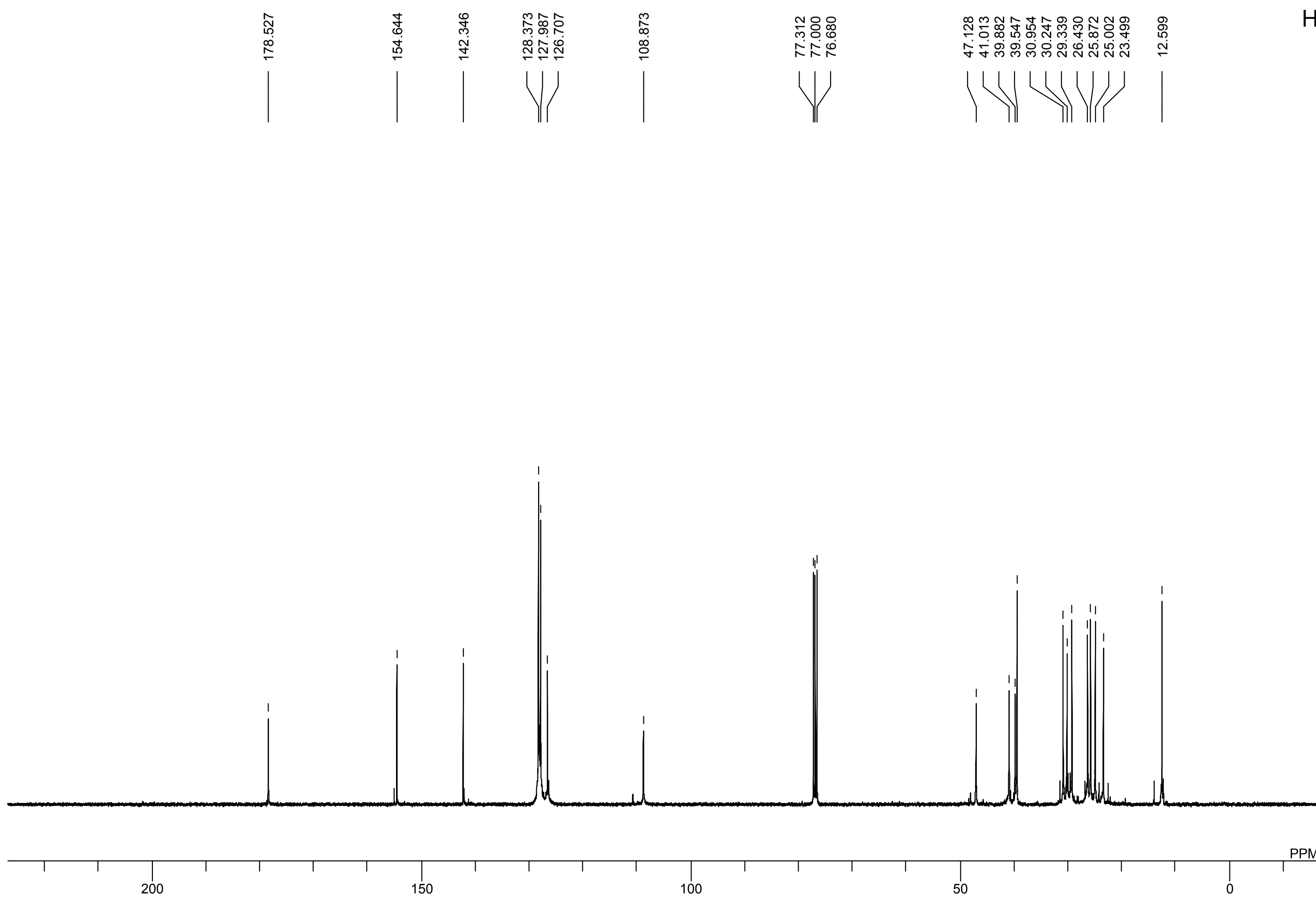
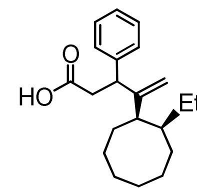
7.281
7.259
7.230
7.212
7.192
5.131
4.943
3.832
3.813
3.792
2.914
2.892
2.875
2.853
2.694
2.676
2.654
2.637
2.211
2.183
1.888
1.856
1.662
1.628
1.523
1.506
1.472
1.422
1.408
1.349
1.280
1.253
1.235
1.211
1.157
1.126
1.001
0.990
0.903
0.885
0.858
0.840
0.822
0.606
0.588
0.570
0.070
0.000
9.76
2.00
0.99
1.94
1.03
25.90
0.29
PPM
10
9
8
7
6
5
4
3
2
1
0
-1


178.527
154.644
142.346
128.373
127.987
126.707
108.873
77.312
77.000
76.680
47.128
41.013
39.882
39.547
30.954
30.247
29.339
26.430
25.872
25.002
23.499
12.599
200
150
100
50
0
PPM


HO
O
Et

5ka