Electronic Supplementary Information

Ligand-promoted palladium-catalyzed β-methylene C–H arylation of primary aldehydes

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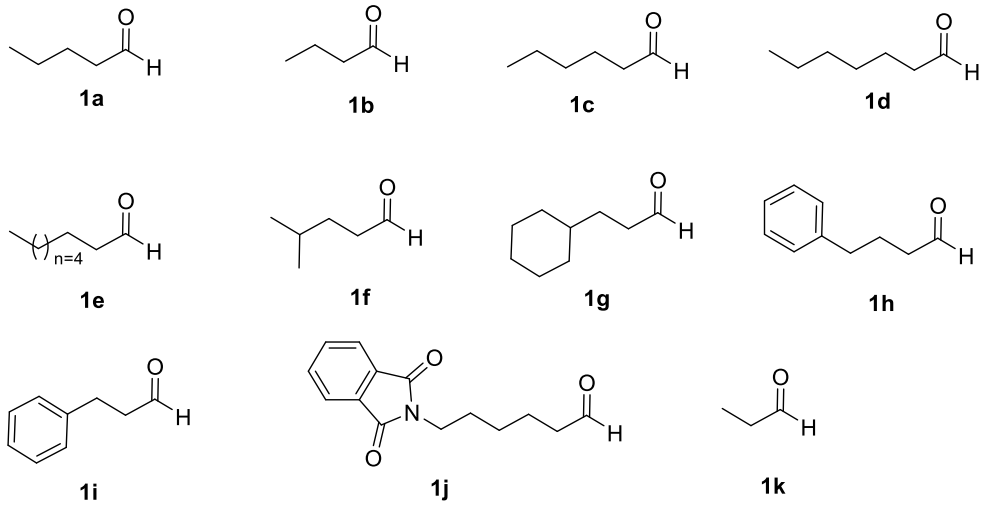
I. General Information

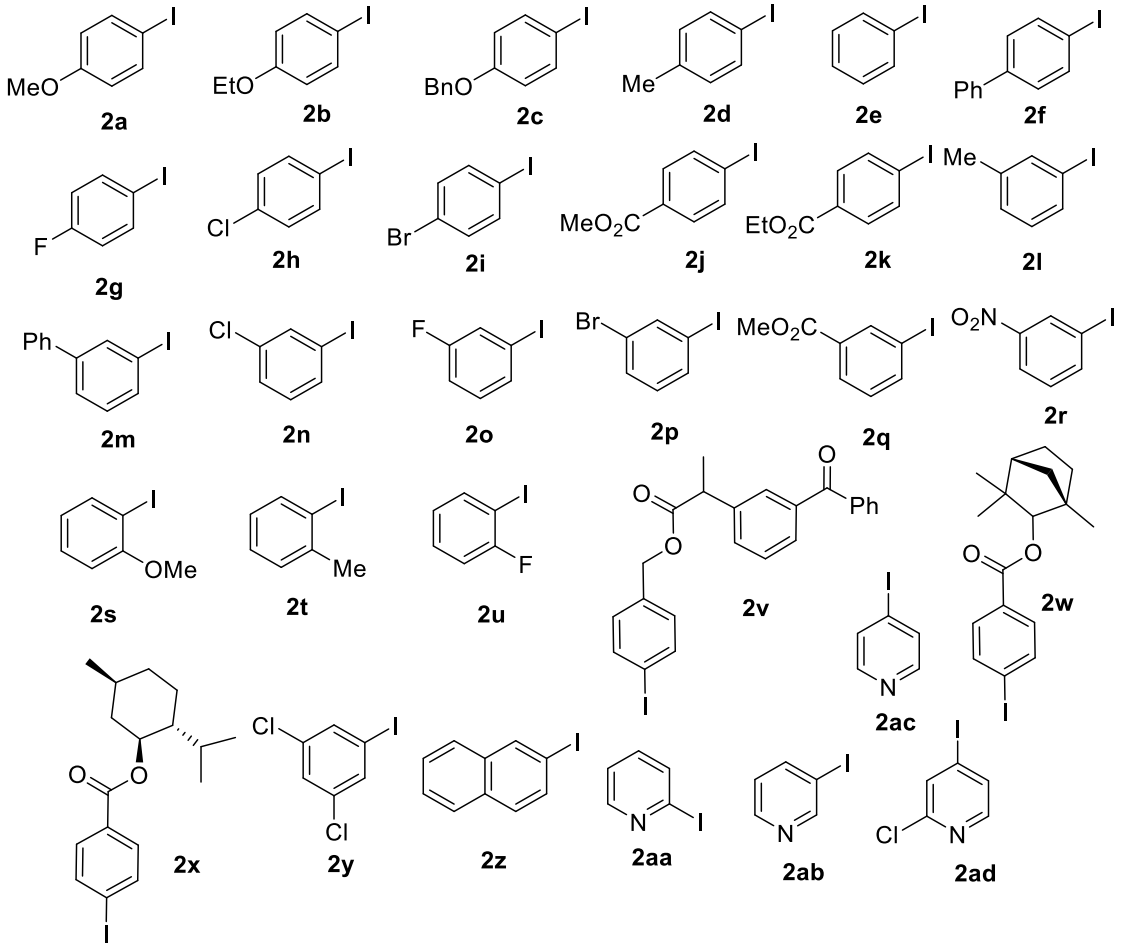
All the solvents and commercially available reagents were purchased and used directly. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light. Column chromatography was performed on EMD Silica Gel 60 (200–300 Mesh) using a forced flow of 0.5–1.0 bar. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AVANCE III–300 or 400 spectrometer. ^{1}H NMR data was reported as: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR data was reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Mass (HRMS) analysis was obtained using Agilent 6200 Accurate-Mass TOF LC/MS system with Electrospray Ionization (ESI).

II. Experimental Section

1. Starting materials:



Aliphatic aldehydes



Aryl iodides

Aliphatic aldehydes (**1)** and aryl iodides (**2a-u**) were purchased from Energy-chemical, Adamas-beta®, TCI, J&K@, Sigma-Aldrich, Chem-Impex, Chemieliva Pharmaceutical, Enamine or Oakwood chemical. Aryl iodides (**2v-x**) were prepared according to the literature procedures.[1]

2. Optimization of the reaction conditions

A 50 mL Schlenk tube was charged with 3-amino-3-methylbutanoic acid (**TDG1**), 3-(trifluoromethyl)-5-nitropyridin-2-ol (**L1**), Pd source (0.02~0.03 mmol) and AgTFA (0.3 mmol). Next, *n*-pentanal (**1a**, 22.0 μL, 0.2 mmol), 4-methoxyiodobenzene (**2a**, 93.16 mg, 0.4 mmol) and the solvents were added into the tube quickly. The reaction was then stirred vigorously at room temperature for 1.0 h before heated to 100 ˚C for 12 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (15 mL), filtered through a pad of celite, and the filtrate was then concentrated in vacuo, the crude product was analyzed by ^{1}H NMR in $CDCl_3$. Yields are based on **1a**, determined by crude ^{1}H NMR using dibromomethane as the internal standard. The residue was purified by flash chromatography on silica gel using petroleum ether/EtOAc as the eluent to yield the product **3a**.

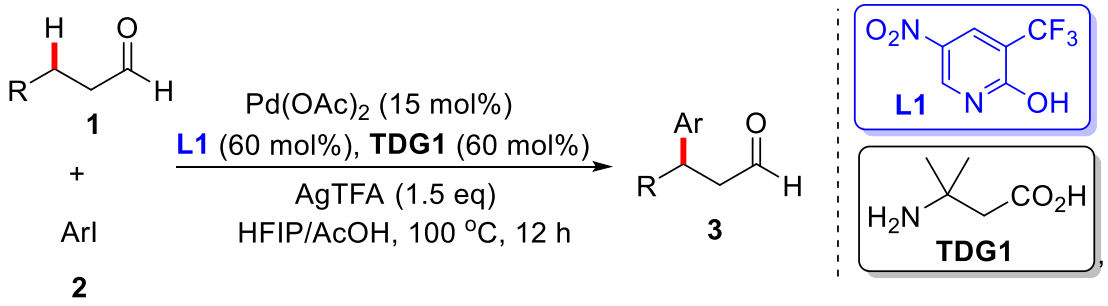
3. The investigations of 2-pyridone ligands

A 50 mL Schlenk tube was charged with 3-amino-3-methylbutanoic acid (**TDG1**, 14.06 mg, 0.12 mmol), 2-pyridone ligands (**L**, 0.12 mmol), $Pd(OAc)_2$ (6.74 mg, 0.03 mmol) and AgTFA (66.27 mg, 0.3 mmol). Next, *n*-pentanal (**1a**, 22.0 μL, 0.2 mmol), 4-methoxyiodobenzene (**2a**, 93.16 mg, 0.4 mmol) and the mixture of HFIP (1.80 mL) and HOAc (0.20 mL) were added into the tube quickly. The reaction was then stirred vigorously at room temperature for 1.0 h before heated to 100 ˚C for 12 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (15 mL), filtered through a pad of celite, and the filtrate was then concentrated in vacuo, the crude product was analyzed by ^{1}H NMR in $CDCl_3$. Yields are based on **1a**, determined by crude ^{1}H NMR using dibromomethane as the internal standard. The residue was purified by flash chromatography on silica gel using petroleum ether/EtOAc as the eluent to yield the product **3a**.

4. The investigations of transient directing groups

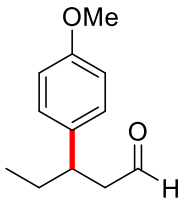
A 50 mL Schlenk tube was charged with transient directing groups (**TDG**, 0.12 mmol), 3-(trifluoromethyl)-5-nitropyridin-2-ol (25.0 mg, 0.12 mmol, **L1**), $Pd(OAc)_2$ (6.74 mg, 0.03 mmol) and AgTFA (66.27 mg, 0.3 mmol). Next, *n*-pentanal (**1a**, 22.0 μL, 0.2 mmol), 4-methoxyiodobenzene (**2a**, 93.16 mg, 0.4 mmol) and the mixture of HFIP (1.80 mL) and HOAc (0.20 mL) were added into the tube quickly. The reaction was then stirred vigorously at room temperature for 1.0 h before heated to 100 ˚C for 12 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (15 mL), filtered through a pad of celite, and the filtrate was then concentrated in vacuo, the crude product was analyzed by ^{1}H NMR in $CDCl_3$. Yields are based on **1a**, determined by crude ^{1}H NMR using dibromomethane as the internal standard. The residue was purified by flash chromatography on silica gel using petroleum ether/EtOAc as the eluent to yield the product **3a**.

5. General procedure for the scope study



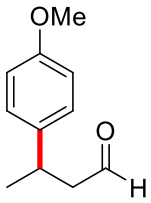
A 50 mL Schlenk tube was charged with 3-amino-3-methylbutanoic acid (**TDG1**, 14.06 mg, 0.12 mmol), 3-(trifluoromethyl)-5-nitropyridin-2-ol (25.0 mg, 0.12 mmol, **L1**), $Pd(OAc)_2$ (6.74 mg, 0.03 mmol) and AgTFA (66.27 mg, 0.3 mmol). Next, primary aldehyde (**1**, 0.2 mmol), iodobenzene (**2**, 0.4 mmol) and the mixture of HFIP (1.80 mL) and HOAc (0.20 mL) were added into the tube quickly. The reaction was then stirred vigorously at room temperature for 1.0 h before heated to 100 ˚C for 24 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (15 mL), filtered through a pad of Celite, and the filtrate was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel using petroleum ether/EtOAc as the eluent to yield the desired product **3**.

6. Data of compounds



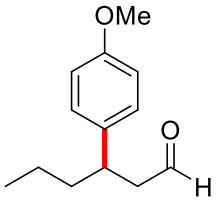
3a

Colorless oil, 26.0 mg, yield: 68% (known compound[2]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.57 (t, *J* = 2.2 Hz, 1H), 7.03 – 7.01 (m, 2H), 6.78 – 6.75 (m, 2H), 3.71 (s, 3H), 3.01 – 2.91 (m, 1H), 2.60 (dd, *J* = 7.4, 2.1 Hz, 2H), 1.66 – 1.46 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.36, 158.20, 135.64, 128.44, 113.97, 55.23, 50.40, 41.03, 29.67, 11.88.



3b

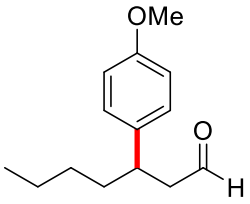
Colorless oil, 22.0 mg, yield: 62% (known compound[3]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.60 (t, *J* = 2.1 Hz, 1H), 7.07 – 7.04 (m, 2H), 6.78 – 6.75 (m, 2H), 3.69 (s, 3H), 3.29 – 3.17 (m, 1H), 2.67 – 2.49 (m, 2H), 1.20 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.17, 158.17, 137.55, 127.72, 114.04, 55.27, 51.97, 33.56, 22.43.



3c

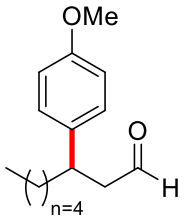
Colorless oil, 24.8 mg, yield: 60% (known compound[4]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.57 (t, *J* = 2.1 Hz, 1H), 7.05 – 7.00 (m, 2H), 6.79 – 6.74 (m, 2H), 3.71 (s, 3H), 3.11 – 3.01 (m, 1H), 2.60 (dd, *J* =

7.4, 2.1 Hz, 2H), 1.55 – 1.46 (m, 2H), 1.18 – 1.07 (m, 2H), 0.78 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.35, 157.11, 134.84, 127.32, 112.91, 54.17, 49.73, 38.02, 37.94, 19.38, 12.90.



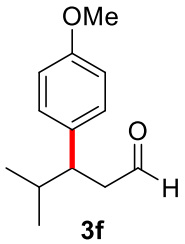
3d

Colorless oil, 25.0 mg, yield: 57% (known compound[5]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.57 (t, *J* = 2.1 Hz, 1H), 7.05 – 7.00 (m, 2H), 6.79 – 6.74 (m, 2H), 3.71 (s, 3H), 3.08 – 2.99 (m, 1H), 2.59 (dd, *J* = 7.4, 2.1 Hz, 2H), 1.59 – 1.46 (m, 2H), 1.24 – 1.02 (m, 4H), 0.75 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.39, 158.16, 135.95, 128.37, 113.97, 55.22, 50.83, 39.32, 36.52, 29.49, 22.59, 13.99.



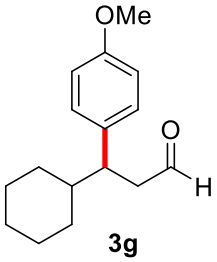
3e

Colorless oil, 28.5 mg, yield: 61%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.64 (t, *J* = 2.2 Hz, 1H), 7.12 – 7.07 (m, 2H), 6.86 – 6.81 (m, 2H), 3.78 (s, 3H), 3.16 – 3.06 (m, 1H), 2.67 (dd, *J* = 7.4, 2.2 Hz, 2H), 1.62 – 1.56 (m, 2H), 1.26 – 1.20 (m, 6H), 0.83 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.38, 158.16, 135.96, 128.35, 113.98, 55.22, 50.81, 39.35, 36.76, 31.70, 26.96, 22.51, 14.04. HRMS (ESI, *m/z*): calcd. for $C_{15}H_{23}O_2$ $[M+H]^+$: 235.1693, found: 235.1699.



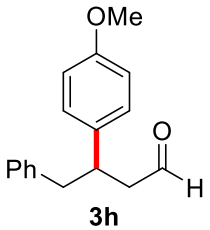
3f

Colorless oil, 17.7 mg, yield: 43%, (known compound[6]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.51 (t, *J* = 2.3 Hz, 1H), 7.01 – 6.98 (m, 2H), 6.77 – 6.74 (m, 2H), 3.71 (s, 3H), 2.86 – 2.80 (m, 1H), 2.72 – 2.63 (m, 2H), 1.81 – 1.70 (m, 1H), 0.86 (d, *J* = 6.7 Hz, 3H), 0.69 (d, *J* = 6.7 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 202.77, 158.18, 134.50, 129.17, 113.75, 55.21, 47.30, 46.16, 33.53, 20.60, 20.17.



3g

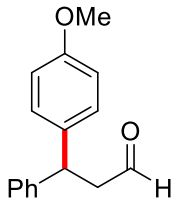
Colorless oil, 27.0 mg, yield: 55%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.51 (t, *J* = 2.2 Hz, 1H), 7.00 – 6.95 (m, 2H), 6.78 – 6.73 (m, 2H), 3.71 (s, 3H), 2.89 – 2.55 (m, 3H), 1.74 – 1.56 (m, 4H), 1.42 – 1.32 (m, 2H), 1.21 – 0.97 (m, 3H), 0.91 – 0.70 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.91, 158.13, 134.67, 129.18, 113.74, 55.20, 47.23, 45.39, 43.26, 31.11, 30.62, 26.44, 26.35. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{23}O_2$ $[M+H]^+$: 247.1693, found: 247.1690.



3h

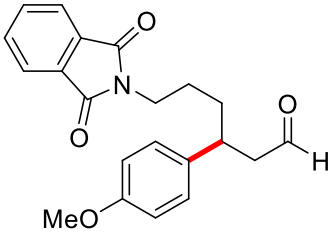
Colorless oil, 25.5 mg, yield: 50%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.49 (t, *J* = 2.0 Hz, 1H), 7.18 – 7.09 (m, 3H), 7.00 – 6.96 (m, 4H), 6.76 – 6.72 (m, 2H), 3.69 (s, 3H), 3.41 – 3.31 (m, 1H), 2.88 – 2.73 (m, 2H), 2.65 – 2.61 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.78, 157.22, 138.32, 134.15, 128.18,

127.39, 127.24, 125.23, 112.90, 54.15, 48.07, 42.45, 40.19. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{19}O_2$ $[M+H]^+$: 255.1380, found: 255.1385.



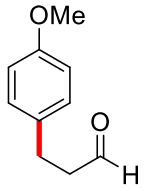
3i

Colorless oil, 21.5 mg, yield: 45% (known compound[2]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.65 (t, *J* = 1.9 Hz, 1H), 7.24 – 7.05 (m, 7H), 6.77 – 6.74 (m, 2H), 4.50 (t, *J* = 7.8 Hz, 1H), 3.69 (s, 3H), 3.05 (dd, *J* = 7.8, 1.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.26, 158.30, 143.62, 135.32, 128.73, 128.72, 127.64, 126.64, 114.12, 55.26, 49.59, 44.23.



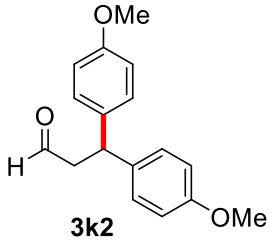
3j

Yellow oil, 42.2 mg, yield: 60%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.55 (t, *J* = 2.0 Hz, 1H), 7.75 – 7.73 (m, 2H), 7.64 – 7.61 (m, 2H), 7.04 – 6.99 (m, 2H), 6.76 – 6.72 (m, 2H), 3.69 (s, 3H), 3.55 (t, *J* = 6.8 Hz, 2H), 3.14 – 3.05 (m, 1H), 2.62 – 2.59 (m, 2H), 1.61 – 1.44 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.80, 168.38, 158.33, 135.03, 133.93, 132.07, 128.36, 123.20, 114.13, 55.21, 50.68, 38.83, 37.68, 33.73, 26.41. HRMS (ESI, *m/z*): calcd. for $C_{21}H_{22}NO_4$ $[M+H]^+$: 352.1543, found: 352.1550.



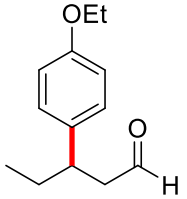
3k1

Colorless oil, 7.2 mg, yield: 22% (known compound[7]).^{1}H NMR (300 MHz, $CDCl_3$) δ 9.81 (t, *J* = 1.4 Hz, 1H), 7.13 – 7.09 (m, 2H), 6.86 – 6.81 (m, 2H), 3.78 (s, 3H), 2.90 (t, *J* = 7.4 Hz, 2H), 2.77 – 2.71 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ 201.89, 158.09, 132.34, 129.26, 114.01, 55.29, 45.58, 27.28.



3k2

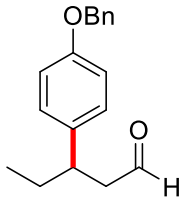
White solid, 11.5 mg, yield: 21% (known compound[8]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.72 (t, *J* = 1.9 Hz, 1H), 7.15 – 7.11 (m, 4H), 6.85 – 6.80 (m, 4H), 4.53 (t, *J* = 7.8 Hz, 1H), 3.77 (s, 6H), 3.10 (dd, *J* = 7.8, 2.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.51, 158.21, 135.70, 128.60, 114.07, 55.26, 49.77, 43.43.



3l

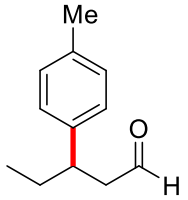
Colorless oil, 26.8 mg, yield: 65%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.58 (t, *J* = 2.2 Hz, 1H), 7.03 – 7.00 (m, 2H), 6.78 – 6.75 (m, 2H), 3.93 (q, *J* = 7.0 Hz, 2H), 3.00 –2.90 (m, 1H), 2.61 (dd, *J* = 7.4, 2.2 Hz, 2H), 1.64 – 1.49 (m, 2H), 1.33 (t, *J* = 7.0 Hz, 3H), 0.72 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$)

δ 202.47, 157.57, 135.46, 128.42, 114.50, 63.37, 50.42, 41.04, 29.68, 14.91, 11.91. HRMS (ESI, *m/z*): calcd. for $C_{13}H_{19}O_2$ $[M+H]^+$: 207.1380, found: 207.1382.



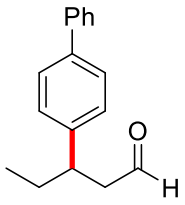
3m

Colorless oil, 33.8 mg, yield: 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (t, *J* = 2.1 Hz, 1H), 7.43 – 7.29 (m, 5H), 7.11 – 7.07 (m, 2H), 6.93 – 6.90 (m, 2H), 5.02 (s, 2H), 3.06 – 2.99 (m, 1H), 2.67 (dd, *J* = 7.3, 2.1 Hz, 2H), 1.71 – 1.54 (m, 2H), 0.80 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.38, 157.58, 137.19, 136.04, 128.68, 128.56, 128.05, 127.62, 114.98, 70.13, 50.47, 41.11, 29.74, 11.99. HRMS (ESI, *m/z*): calcd. for $C_{18}H_{21}O_2$ $[M+H]^+$: 269.1536, found: 269.1540.



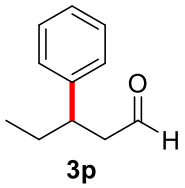
3n

Colorless oil, 21.5 mg, yield: 61% (known compound[9]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.06 – 6.98 (m, 4H), 3.02 – 2.92 (m, 1H), 2.63 – 2.61 (m, 2H), 2.25 (s, 3H), 1.65 – 1.48 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.38, 140.56, 136.09, 129.30, 127.40, 50.30, 41.42, 29.57, 21.03, 11.92.



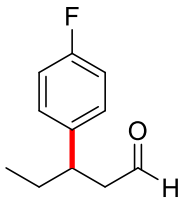
3o

Colorless oil, 33.3 mg, yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.59 – 7.52 (m, 4H), 7.44 – 7.40 (m, 2H), 7.34 – 7.30 (m, 1H), 7.26 – 7.24 (m, 2H), 3.15 – 3.09 (m, 1H), 2.75 (dd, *J* = 7.3, 1.8 Hz, 2H), 1.78 – 1.46 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.11, 142.85, 140.92, 139.56, 128.83, 128.03, 127.39, 127.24, 127.08, 50.29, 41.49, 29.59, 12.02. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{19}O$ $[M+H]^+$: 239.1430, found: 239.1435.



3p

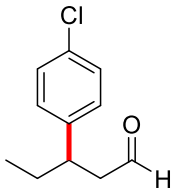
White solid, 20.0 mg, yield: 62%, (known compound[3]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (t, *J* = 2.1 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.23 – 7.17 (m, 3H), 3.12 – 3.04 (m, 1H), 2.72 (dd, *J* = 7.3, 2.1 Hz, 2H), 1.74 – 1.65 (m, 2H), 0.81 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.03, 143.67, 128.60, 127.53, 126.58, 50.22, 41.81, 29.51, 11.86.



3q

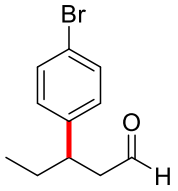
Colorless oil, 18.0 mg, yield: 50% (known compound[4]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.60 (t, *J* = 1.9 Hz, 1H), 7.10 – 7.03 (m, 2H), 6.95 – 6.89 (m, 2H), 3.06 – 2.96 (m, 1H), 2.65 – 2.62 (m, 2H), 1.68 – 1.46 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.69, 161.52 (d, *J* = 244.4 Hz), 139.30 (d, *J* = 3.3 Hz), 128.89 (d, *J* = 7.8 Hz), 115.39 (d, *J* = 21.1 Hz). 50.37, 40.97, 29.59, 11.82.



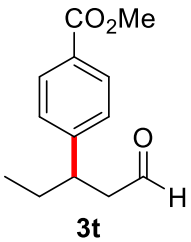
3r

Colorless oil, 20.8 mg, yield: 53% (known compound[10]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 3.05 – 2.95 (m, 1H), 2.65 – 2.62 (m, 2H), 1.65 – 1.46 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.51, 142.20, 132.22, 128.91, 128.74, 50.19, 41.05, 29.42, 11.83.



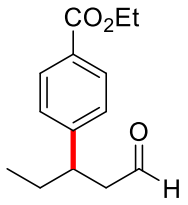
3s

Colorless oil, 29.0 mg, yield: 60% (known compound[11]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.59 (t, *J* = 1.9 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.01 – 6.98 (m, 2H), 3.02 –2.94 (m, 1H), 2.65 – 2.63 (m, 2H), 1.63 – 1.53 (m, 2H), 0.72 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.43, 142.73, 131.70, 129.30, 120.28, 50.14, 41.13, 29.37, 11.82.



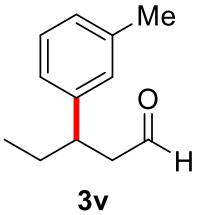
3t

Colorless oil, 29.5 mg, yield: 67% (known compound[9]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.59 (t, *J* = 1.7 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 3H), 3.13 – 3.04 (m, 1H), 2.69 – 2.66 (m, 2H), 1.71 – 1.50 (m, 2H), 0.72 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.22, 166.93, 149.22, 129.95, 128.58, 127.62, 52.04, 49.96, 41.57, 29.28, 11.81.



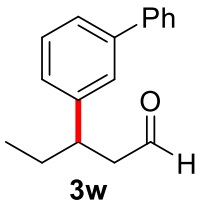
3u

Colorless oil, 25.8 mg, yield: 55%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.60 (t, *J* = 1.6 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 7.1 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.14– 3.04 (m, 1H), 2.70 – 2.67 (m, 2H), 1.69 – 1.53 (m, 2H), 1.31 (d, *J* = 7.1 Hz, 3H), 0.72 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.29, 166.46, 149.07, 129.92, 128.94, 127.57, 60.88, 49.99, 41.59, 29.30, 14.36, 11.82. HRMS (ESI, *m/z*): calcd. for $C_{14}H_{19}O_3$ $[M+H]^+$: 235.1329, found: 235.1330.



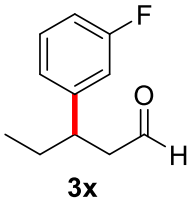
3v

Colorless oil, 21.2 mg, yield: 60% (known compound[12]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (t, *J* = 2.1 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.02 – 6.96 (m, 3H), 3.06 – 2.99 (m, 1H), 2.69 (dd, *J* = 7.4, 2.1 Hz, 2H), 2.32 (s, 3H), 1.69 – 1.60 (m, 2H), 0.80 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.39, 143.67, 138.22, 128.53, 128.38, 127.40, 124.59, 50.29, 41.83, 29.58, 21.56, 12.01.



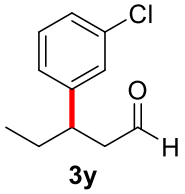
3w

Colorless oil, 29.5 mg, yield: 62%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.63 (t, *J* = 2.0 Hz, 1H), 7.52 – 7.49 (m, 2H), 7.40 – 7.25 (m, 6H), 7.11 – 7.08 (m, 1H), 3.11 – 3.06 (m, 1H), 2.70 (dd, *J* = 7.3, 1.9 Hz, 2H), 1.73 – 1.55 (m, 2H), 0.77 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.10, 144.21, 141.57, 141.20, 129.05, 128.79, 127.35, 127.24, 126.50, 126.47, 125.52, 50.26, 41.84, 29.55, 12.00. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{19}O$ $[M+H]^+$: 239.1430, found: 239.1437.



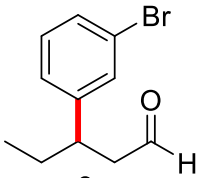
3x

Colorless oil, 18.5 mg, yield: 51%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.61 (t, *J* = 1.7 Hz, 1H), 7.23 – 7.16 (m, 1H), 6.91 – 6.81 (m, 3H), 3.08 – 2.98 (m, 1H), 2.65 (dd, *J* = 7.2, 1.7 Hz, 2H), 1.69 – 1.48 (m, 2H), 0.74 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.51, 163.10 (d, *J* = 245.8 Hz), 146.47 (d, *J* = 6.9 Hz), 130.12 (d, *J* = 8.4 Hz), 123.38 (d, *J* = 2.8 Hz), 114.37 (d, *J* = 21.1 Hz), 113.56 (d, *J* = 21.1 Hz), 50.17, 41.49 (d, *J* = 1.8 Hz), 29.43, 11.90. HRMS (ESI, *m/z*): calcd. for $C_{11}H_{14}FO$ $[M+H]^+$: 181.1023, found: 181.1030.



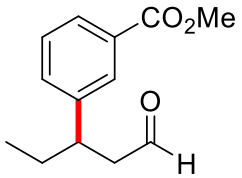
3y

Colorless oil, 22.0 mg, yield: 56% (known compound[11]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.17 – 7.10 (m, 3H), 7.00 (d, *J* = 7.2 Hz, 1H), 3.04 – 2.97 (m, 1H), 2.65 (dd, *J* = 7.2, 1.6 Hz, 2H), 1.67 – 1.50 (m, 2H), 0.74 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.30, 145.87, 134.41, 129.86, 127.61, 126.81, 125.87, 50.08, 41.37, 29.33, 11.84.



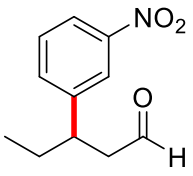
3z

Colorless oil, 24.0 mg, yield: 50%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.29 – 7.26 (m, 2H), 7.13 – 7.03 (m, 2H), 3.04 – 2.95 (m, 1H), 2.65 (dd, *J* = 7.2, 1.6 Hz, 2H), 1.66 – 1.48 (m, 2H), 0.74 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.37, 146.20, 130.53, 130.20, 129.75, 126.37, 122.73, 50.10, 41.35, 29.36, 11.88. HRMS (ESI, *m/z*): calcd. for $C_{11}H_{14}BrO$ $[M+H]^+$: 241.0223, found: 241.0225.



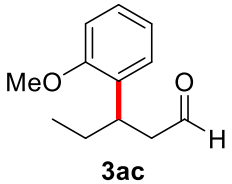
3aa

Colorless oil, 32.2 mg, yield: 73%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.60 (t, *J* = 1.8 Hz, 1H), 7.84 – 7.80 (m, 2H), 7.32 – 7.30 (m, 2H), 3.84 (s, 3H), 3.14– 3.04 (m, 1H), 2.69 (dd, *J* = 7.3, 1.8 Hz, 2H), 1.70 – 1.52 (m, 2H), 0.72 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.48, 166.06, 143.10, 131.41, 129.40, 127.64, 127.43, 126.86, 51.14, 49.10, 40.37, 28.35, 10.84. HRMS (ESI, *m/z*): calcd. for $C_{13}H_{17}O_3$ $[M+H]^+$: 221.1172, found: 221.1173.



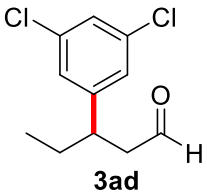
3ab

Colorless oil, 17.0 mg, yield: 41%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.64 (t, *J* = 1.4 Hz, 1H), 8.03 – 8.00 (m, 2H), 7.49 – 7.39 (m, 2H), 3.23 – 3.13 (m, 1H), 2.77 – 2.74 (m, 2H), 1.75 – 1.51 (m, 2H), 0.75 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.50, 148.51, 146.09, 134.21, 129.52, 122.24, 121.79, 50.00, 41.08, 29.27, 11.82. HRMS (ESI, *m/z*): calcd. for $C_{11}H_{14}NO_3$ $[M+H]^+$: 208.0968, found: 208.0980.



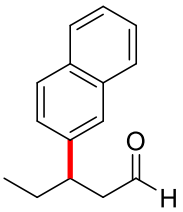
3ac

Colorless oil, 17.0 mg, yield: 44% (known compound[13]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.15 – 7.05 (m, 2H), 6.88 – 6.78 (m, 2H), 3.75 (s, 3H), 3.51 – 3.42 (m, 1H), 2.61 (d, *J* = 6.2 Hz, 2H), 1.71 – 1.54 (m, 2H), 0.75 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.15, 157.20, 131.50, 127.82, 127.44, 120.68, 110.62, 55.30, 49.19, 34.95, 27.75, 11.98.



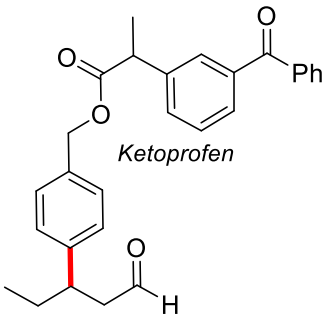
3ad

Colorless oil, 18.5 mg, yield: 40%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.15 (s, 1H), 7.00 (s, 2H), 3.04 – 2.95 (m, 1H), 2.66 (d, *J* = 7.1 Hz, 2H), 1.68 – 1.46 (m, 2H), 0.74 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.64, 147.39, 135.06, 126.88, 126.17, 49.92, 41.10, 29.18, 11.85. HRMS (ESI, *m/z*): calcd. for $C_{11}H_{13}Cl_2O$ $[M+H]^+$: 231.0338, found: 231.0348.



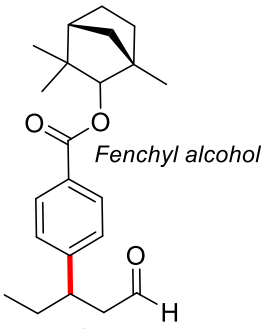
3ae

Colorless oil, 20.0 mg, yield: 47% (known compound[11]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (t, *J* = 2.0 Hz, 1H), 7.81 – 7.77 (m, 3H), 7.61 (s, 1H), 7.47 – 7.41 (m, 2H), 7.32 (dd, *J* = 8.5, 1.6 Hz, 1H), 3.29 – 3.21 (m, 1H), 2.82 – 2.79 (m, 2H), 1.82 – 1.69 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.06, 141.12, 133.58, 132.50, 128.49, 127.70, 127.69, 126.34, 126.18, 125.70, 125.60, 50.28, 41.99, 29.48, 12.02.



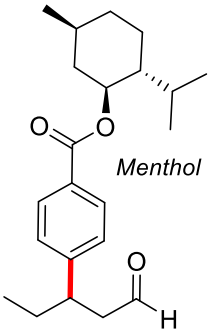
3af

Colorless oil, 43.0 mg, yield: 50%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.55 (t, *J* = 2.0 Hz, 1H), 7.70 – 7.67 (m, 3H), 7.60 – 7.58 (m, 1H), 7.50 – 7.43 (m, 2H), 7.40 – 7.31 (m, 3H), 7.11 – 7.02 (m, 4H), 5.04 – 4.95 (m, 2H), 3.76 (q, *J* = 7.2 Hz, 1H), 3.03 – 2.93 (m, 1H), 2.62 – 2.59 (m, 2H), 1.64 – 1.45 (m, 5H), 0.69 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.86, 196.48, 173.90, 143.81, 140.72, 137.89, 137.48, 134.04, 132.55, 131.56, 130.10, 129.32, 129.06, 128.58, 128.34, 128.31, 127.72, 66.41, 50.14, 45.41, 41.40, 29.44, 18.43, 11.90. HRMS (ESI, *m/z*): calcd. for $C_{28}H_{29}O_4$ $[M+H]^+$: 429.2060, found: 429.2062.



3ag

Colorless oil, 43.8 mg, yield: 64%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.61 (t, *J* = 1.7 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.22 – 7.17 (m, 2H), 4.53 (d, *J* = 1.7 Hz, 1H), 3.15 – 3.05 (m, 1H), 2.69 (dd, *J* = 7.3, 1.6 Hz, 2H), 1.90 – 1.81 (m, 1H), 1.74 – 1.55 (m, 5H), 1.49 – 1.40 (m, 1H), 1.18 – 1.11 (m, 5H), 1.03 (s, 3H), 0.77 – 0.72 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.28, 166.71, 149.04, 129.93, 129.15, 127.63, 86.61, 50.02, 48.64, 48.43, 41.62, 41.47, 39.84, 29.76, 29.32, 26.90, 25.93, 20.35, 19.51, 11.86. HRMS (ESI, *m/z*): calcd. for $C_{22}H_{31}O_3$ $[M+H]^+$: 343.2268, found: 343.2268.



3ah

Colorless oil, 39.3 mg, yield: 57%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.60 (t, *J* = 1.7 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.20 – 7.17 (m, 2H), 4.88 – 4.80 (m, 1H), 3.14 – 3.02 (m, 1H), 2.70 – 2.67 (m, 2H), 2.06 – 2.02 (m, 1H), 1.92 – 1.86 (m, 1H), 1.68 – 1.63 (m, 3H), 1.60 – 1.44 (m, 3H), 1.21 – 0.99 (m, 3H), 0.86 – 0.71 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.29, 165.92, 148.95, 129.95, 129.32, 127.55, 74.73, 50.01, 47.29, 41.62, 40.99, 34.34, 31.45, 29.31, 26.46, 23.60, 22.06, 20.81, 16.50, 11.83. HRMS (ESI, *m/z*): calcd. for $C_{22}H_{33}O_3$ $[M+H]^+$: 345.2424, found: 345.2425.

7. Computational Methods

Density functional theory (DFT) calculations were performed with the Gaussian 09 package.[14] Geometries were optimized using the M06-L functional[15] and a mixed basis set of SDD for Pd Ag, and I and 6-31G(d) for other atoms, and final geometries were verified by vibrational frequency calculations to be either energy minimum or transition state (no or one imaginary frequency, respectively). Single-point energies were computed by the PBE0-D3[16,17] functional and a mixed basis set of SDD for Pd, Ag, and I and 6-311++G(d,p) for other atoms, and the solvation model based on density (SMD)[18] for 2-propanol (eps=16.7 was set to simulate HFIP solvent). Free energies in solution (1.0 mol/L) were utilized in the discussion. Molecular visualizations were carried out in PyMOL and Multiwfn.[19]

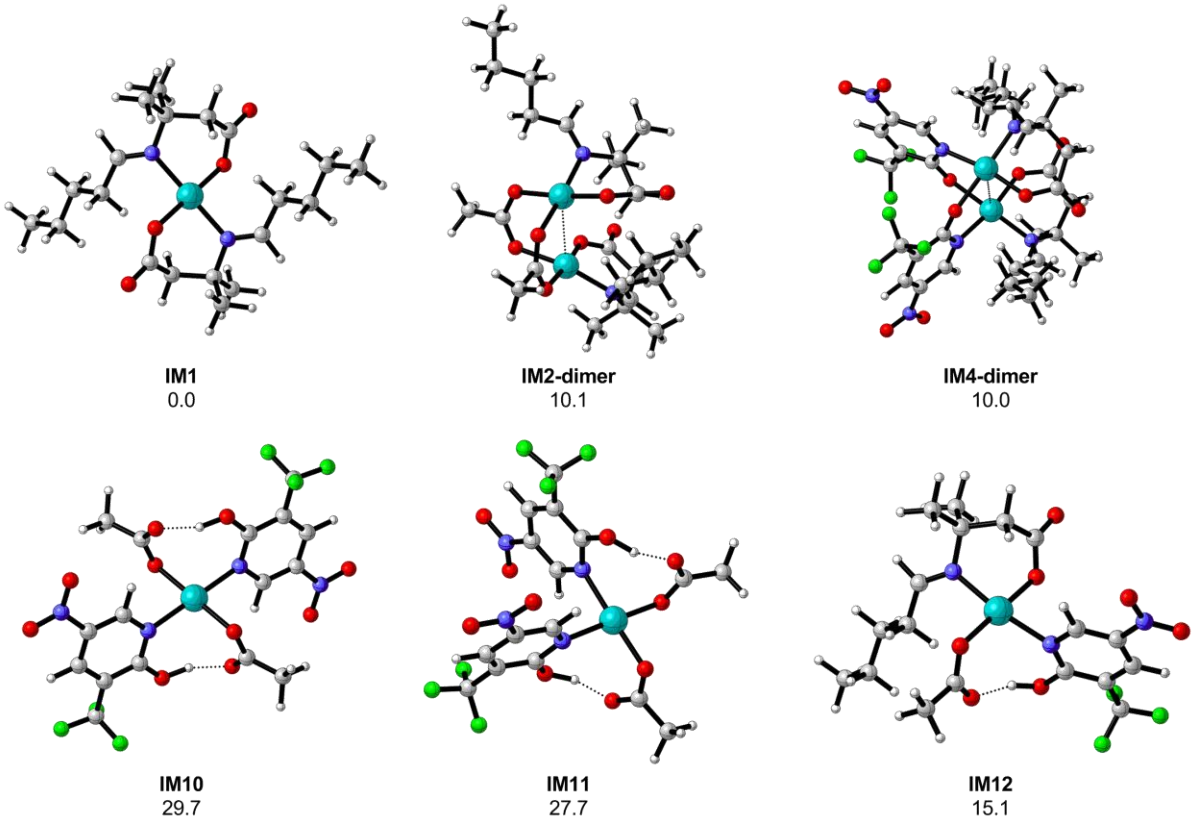


Fig. S1. Possible Pd(II) complexes derived from initiation. Energies are relative to complex **IM1** and are mass-balanced.

8. Cartesian Coordinates (Å) and Energies for the Optimized Structures

$Pd_3(OAc)_6$

PBE0(D3) SCF energy in solution: -1753.679109 a.u.

PBE0(D3) free energy in solution: -1753.429256 a.u.

Pd	-1.536450	0.895228	-0.000806
C	0.069414	2.576887	1.887539
O	-0.979746	2.499386	1.184197
O	1.145220	1.923913	1.731615
C	2.276320	-1.238483	-1.862775
O	1.676476	-2.109763	-1.169360
O	2.213961	0.021913	-1.730035
C	3.191894	-1.749803	-2.939255
C	0.027320	3.544297	3.036872
Pd	-0.000785	-1.800772	-0.000325
C	2.180368	-1.340490	1.893731
O	2.633994	-0.393247	1.186608
O	1.083182	-1.956790	1.735777
C	-0.067482	2.577623	-1.886798
O	-1.143932	1.925673	-1.730987
O	0.981708	2.498802	-1.183667
C	-0.024683	3.545696	-3.035551
C	3.033152	-1.766816	3.054954
Pd	1.537181	0.893945	0.000992
C	-2.181575	-1.338301	-1.894122
O	-2.634225	-0.390704	-1.186867
O	-1.084996	-1.955728	-1.736301
C	-3.034864	-1.763675	-3.055326
C	-2.276958	-1.237298	1.862529
O	-2.213483	0.023054	1.730087
O	-1.678251	-2.108956	1.168568
C	-3.192548	-1.748253	2.939170
H	-1.014515	3.684912	-3.473788
H	0.661827	3.164544	-3.798985
H	0.374185	4.505894	-2.696064
H	-0.373345	4.504202	2.698730
H	-0.657369	3.161704	3.801243
H	1.017681	3.684329	3.473665
H	-3.314519	-1.002389	3.727688
H	-2.820003	-2.688339	3.351660
H	-4.179143	-1.937161	2.500854
H	4.084235	-1.798402	2.756048
H	2.718641	-2.737931	3.441205
H	2.945650	-1.019199	3.850948
H	2.821379	-2.691834	-3.349049
H	3.310887	-1.005486	-3.729719
H	4.179631	-1.934613	-2.501791
H	-2.947704	-1.015443	-3.850772
H	-4.085817	-1.795407	-2.755956
H	-2.720626	-2.734539	-3.442408

IM1

PBE0(D3) SCF energy in solution: -1321.202271 a.u.

PBE0(D3) free energy in solution: -1320.721159 a.u.

C	1.265488	-2.283525	-1.240824
C	1.024404	-2.772453	0.188848
C	-0.456395	-2.990845	0.526449
H	1.547726	-3.727239	0.314995
O	1.819292	-3.000675	-2.062951
O	0.835680	-1.077853	-1.520316
Pd	0.000046	0.000059	-0.000006
H	1.448366	-2.060782	0.915424
N	-1.167006	-1.668305	0.411184
C	-1.063491	-3.983839	-0.461858
H	-0.494091	-4.919717	-0.443693
H	-2.104718	-4.221943	-0.214623
H	-1.027951	-3.593818	-1.485117
C	-0.583467	-3.483795	1.964861
H	-1.628099	-3.688471	2.229858
H	-0.018916	-4.413806	2.096336
H	-0.192592	-2.740270	2.669113
C	-2.432536	-1.617554	0.594712
H	-2.963867	-2.546925	0.850890
C	-3.264782	-0.395979	0.461957
C	-4.627694	-0.662996	-0.168779
H	-2.706469	0.350060	-0.118376
H	-3.393788	0.049507	1.461188
C	-5.433644	0.617282	-0.331689
H	-4.496854	-1.143875	-1.150728
H	-5.192151	-1.381797	0.446241
C	-6.793317	0.386195	-0.965148
H	-5.551319	1.096894	0.651345
H	-4.853770	1.329577	-0.938546
H	-7.351909	1.321969	-1.076474
H	-6.698245	-0.062300	-1.962224
H	-7.405845	-0.293098	-0.358849
N	1.167121	1.668506	-0.410961
C	0.456646	2.991215	-0.525457
C	-1.024331	2.772719	-0.188723
H	-1.447918	2.061306	-0.915770
H	-1.547582	3.727545	-0.314810
C	-1.266216	2.283310	1.240651
O	-0.835802	1.077844	1.520239
O	-1.821077	2.999928	2.062538
C	0.584366	3.485377	-1.963402
H	0.020024	4.415597	-2.094283
H	1.629116	3.690118	-2.227867
H	0.193613	2.742526	-2.668430
C	1.063471	3.983260	0.463965
H	2.104848	4.221367	0.217368
H	0.494218	4.919241	0.446400

H	1.027447	3.592299	1.486857
C	2.432634	1.617779	-0.594585
H	2.963997	2.547249	-0.850345
C	3.264833	0.396101	-0.462544
C	4.627842	0.662692	0.168156
H	3.393663	-0.048867	-1.462046
H	2.706595	-0.350233	0.117446
C	5.433888	-0.617668	0.329948
H	5.192172	1.382002	-0.446392
H	4.497142	1.142814	1.150494
C	6.793509	-0.387037	0.963679
H	4.854048	-1.330588	0.936107
H	5.551666	-1.096368	-0.653518
H	7.352071	-1.322897	1.074428
H	7.406113	0.292653	0.357900
H	6.698350	0.060790	1.961049

IM2

PBE0(D3) SCF energy in solution: -952.859797 a.u.

PBE0(D3) free energy in solution: -952.584303 a.u.

C	-2.440008	-0.827404	1.372983
C	-2.852446	-0.732371	-0.090174
C	-2.503080	0.627796	-0.701558
H	-3.936779	-0.876280	-0.150785
O	-3.264882	-0.850523	2.273067
O	-1.147265	-0.832721	1.606222
Pd	0.125664	-0.777973	0.052332
H	-2.369132	-1.524360	-0.680910
N	-1.002207	0.762253	-0.697639
C	-3.115379	1.750079	0.133736
H	-4.195203	1.592720	0.230532
H	-2.960466	2.732376	-0.328141
H	-2.691776	1.769081	1.143791
C	-2.986662	0.680644	-2.147356
H	-2.768674	1.650578	-2.611342
H	-4.071367	0.531047	-2.184682
H	-2.511624	-0.102719	-2.749036
C	-0.463019	1.846992	-1.116280
H	-1.121616	2.650054	-1.473470
C	2.185069	-2.026985	-0.514992
O	1.766959	-1.086594	-1.276492
C	1.004784	2.084424	-1.100512
C	1.527412	2.384382	0.311814
H	1.514231	1.188488	-1.480306
H	1.248229	2.916507	-1.773322
C	3.046291	2.444928	0.357379
H	1.168381	1.598218	0.994906
H	1.098025	3.328693	0.680320
C	3.576949	2.728954	1.750751
H	3.406197	3.210662	-0.346797
H	3.447296	1.487416	-0.010016
H	4.671857	2.760369	1.768143

H	3.255669	1.957775	2.461700
H	3.213006	3.692678	2.128748
O	1.506116	-2.315700	0.521943
C	3.453054	-2.743832	-0.827858
H	4.303671	-2.153477	-0.467379
H	3.479634	-3.717282	-0.332822
H	3.570113	-2.862871	-1.908446

TS1

PBE0(D3) SCF energy in solution: -952.828722 a.u.

PBE0(D3) free energy in solution: -952.556561 a.u.

C	-2.046785	-2.114340	0.192019
C	-2.732951	-1.047399	-0.658799
C	-2.636344	0.390717	-0.124672
H	-2.328737	-1.071528	-1.681445
O	-2.676269	-3.098711	0.553229
O	-0.793838	-1.934880	0.516420
Pd	0.339878	-0.330241	-0.005223
H	-3.789745	-1.327966	-0.722097
N	-1.259312	0.865475	-0.426399
C	-3.703314	1.252681	-0.789132
H	-4.689245	0.835633	-0.561800
H	-3.698166	2.284631	-0.417113
H	-3.593405	1.271230	-1.880656
C	-2.800165	0.433517	1.394425
H	-2.792741	1.468934	1.756405
H	-3.753574	-0.026920	1.677493
H	-1.997847	-0.117845	1.896114
C	-1.000741	1.994953	-0.974708
H	-1.811072	2.669697	-1.268362
C	0.408435	2.374696	-1.229738
C	1.397895	1.682795	-0.289430
H	0.507464	3.471460	-1.184020
H	0.640728	2.115657	-2.275154
C	2.994940	-1.322044	-0.241759
H	2.393844	2.004813	-0.639367
C	1.315139	2.133851	1.171842
C	1.704151	3.593319	1.376256
H	1.979442	1.496129	1.771780
H	0.304881	1.961519	1.571940
H	1.694694	3.863323	2.437991
H	2.713071	3.792161	0.992184
H	1.017372	4.278983	0.863343
O	3.126301	-0.266344	-0.937320
H	2.041374	0.467975	-0.665071
O	1.935466	-1.617587	0.385477
C	4.147843	-2.276524	-0.170528
H	4.252210	-2.781003	-1.137273
H	5.079155	-1.732295	0.009626
H	3.989202	-3.028987	0.603418

IM3

PBE0(D3) SCF energy in solution: -2452.884554 a.u.

PBE0(D3) free energy in solution: -2452.495643 a.u.

C	-1.381991	3.506462	1.261005
C	-0.320479	3.983096	0.275387
C	1.102856	3.733733	0.788659
H	-0.452114	5.060094	0.126203
O	-2.037567	4.291913	1.923206
O	-1.520292	2.201648	1.390788
Pd	-0.304940	1.030845	0.300392
H	-0.446307	3.494179	-0.703507
N	1.272819	2.243242	0.964018
C	1.293885	4.439737	2.129459
H	1.053874	5.502782	2.021155
H	2.326900	4.370252	2.489143
H	0.627122	4.028694	2.894721
C	2.120895	4.214132	-0.241024
H	3.149054	4.059100	0.109087
H	1.990627	5.286070	-0.425382
H	2.005136	3.693970	-1.200230
C	2.334333	1.797086	1.523749
H	3.099950	2.516117	1.848675
C	-2.946377	0.616367	-1.028110
C	-2.311639	-1.141455	0.435173
C	-4.210730	0.082024	-1.188786
H	-2.674324	1.544731	-1.525266
C	-3.636848	-1.681072	0.311873
C	-4.567451	-1.081023	-0.494974
H	-5.568801	-1.486539	-0.606579
N	-2.030320	0.023265	-0.259653
O	-1.422916	-1.676415	1.145976
C	-3.965124	-2.917125	1.093433
N	-5.156509	0.742416	-2.062042
O	-6.277557	0.242966	-2.156443
O	-4.776768	1.753800	-2.655984
F	-5.232781	-3.314074	0.856400
F	-3.848750	-2.713878	2.416303
F	-3.160201	-3.944675	0.768306
C	2.619723	0.363335	1.778202
C	3.306951	0.092871	3.113033
H	1.687964	-0.212204	1.707961
H	3.274877	-0.001222	0.965172
C	3.689503	-1.374060	3.254121
H	2.638120	0.387666	3.934865
H	4.204496	0.723792	3.208279
C	4.310003	-1.694865	4.600932
H	4.386294	-1.640206	2.444893
H	2.798228	-1.998260	3.089589
H	4.588120	-2.751471	4.672869
H	3.614400	-1.480435	5.421527
H	5.216445	-1.101459	4.775893
C	1.613926	0.550578	-1.901887
C	1.431604	-1.395332	-0.629996

C	2.673471	0.031821	-2.616850
H	1.243893	1.551023	-2.110023
C	2.529413	-1.964109	-1.332775
C	3.151908	-1.247122	-2.326759
H	3.995511	-1.652153	-2.877328
O	0.886418	-2.084986	0.318630
C	3.016128	-3.330159	-0.937188
N	3.302631	0.843327	-3.650414
O	4.232767	0.333911	-4.268905
O	2.862061	1.979615	-3.819584
N	1.011764	-0.133329	-0.916128
F	2.064034	-4.261444	-1.070578
F	4.061083	-3.698505	-1.702281
F	3.430478	-3.339097	0.343013
H	-0.052624	-1.749898	0.667798

IM4

PBE0(D3) SCF energy in solution: -1588.398460 a.u.

PBE0(D3) free energy in solution: -1588.094681 a.u.

C	-2.949375	-2.429027	0.236743
C	-3.477367	-1.760203	-1.021311
C	-3.988446	-0.338035	-0.768281
H	-4.305852	-2.366422	-1.402652
O	-3.518929	-3.371702	0.760109
O	-1.858698	-1.907700	0.759232
Pd	-0.961354	-0.363087	-0.140838
H	-2.698470	-1.727188	-1.797201
N	-2.807566	0.524661	-0.400248
C	-4.986784	-0.329559	0.386709
H	-5.795041	-1.041970	0.187813
H	-5.435646	0.661797	0.521150
H	-4.508937	-0.623529	1.327650
C	-4.616320	0.199877	-2.051547
H	-5.027451	1.207443	-1.918512
H	-5.441373	-0.450920	-2.360904
H	-3.883392	0.232178	-2.865857
C	-2.989038	1.776753	-0.191168
H	-4.010058	2.169714	-0.286168
C	1.824809	-1.920364	0.395295
C	1.473332	0.221811	-0.541870
C	3.198744	-1.748987	0.276858
H	1.388123	-2.823936	0.813017
C	2.870963	0.442613	-0.650730
C	3.723489	-0.559543	-0.241484
H	4.801597	-0.444348	-0.306362
N	1.012020	-0.955148	-0.012316
O	0.530935	1.022297	-0.883578
C	3.369091	1.756132	-1.162224
N	4.090140	-2.806740	0.711980
O	5.299264	-2.613692	0.582787
O	3.576823	-3.822748	1.180617
F	4.713591	1.793011	-1.187903

F	2.951075	2.772282	-0.378813
F	2.932298	2.013299	-2.407734
C	-1.905639	2.719934	0.193344
C	-1.433872	2.537054	1.642595
H	-1.046197	2.566603	-0.471738
H	-2.256832	3.748628	0.045177
C	-0.222804	3.402386	1.954898
H	-1.183080	1.475636	1.802752
H	-2.255942	2.763115	2.338796
C	0.263770	3.229541	3.382139
H	-0.470044	4.458415	1.767827
H	0.581989	3.152531	1.247713
H	1.140370	3.853205	3.587510
H	0.544872	2.187921	3.582551
H	-0.513681	3.502441	4.106967

TS2

PBE0(D3) SCF energy in solution: -1588.371765 a.u.

PBE0(D3) free energy in solution: -1588.070956 a.u.

C	2.298446	2.533553	-0.685057
C	3.418361	1.692139	-1.288226
C	4.015538	0.616311	-0.365206
H	3.063463	1.209759	-2.210624
O	2.369626	3.751556	-0.691723
O	1.271737	1.905679	-0.159093
Pd	1.038961	-0.114889	-0.070633
H	4.213506	2.388543	-1.575116
N	3.040519	-0.506070	-0.325680
C	5.373435	0.183845	-0.905182
H	6.034968	1.054639	-0.944166
H	5.860746	-0.558936	-0.261954
H	5.299803	-0.224001	-1.921014
C	4.160237	1.130068	1.067337
H	4.650324	0.381241	1.701316
H	4.766441	2.042923	1.076045
H	3.184873	1.370287	1.504251
C	3.364076	-1.736095	-0.481194
H	4.403370	-2.019069	-0.675816
C	2.313446	-2.777875	-0.416546
C	1.088809	-2.348691	0.393764
H	2.744477	-3.713047	-0.024412
H	2.017200	-3.018969	-1.449872
C	-1.479484	1.508116	0.434989
C	-1.838550	-0.708771	-0.300154
C	-2.842408	1.747878	0.453909
H	-0.748606	2.276678	0.677064
C	-3.245365	-0.477735	-0.307515
C	-3.739416	0.746298	0.071832
H	-4.806147	0.948806	0.080577
H	0.371756	-3.180550	0.289841
C	1.329880	-2.209247	1.900434
C	1.668890	-3.531659	2.578230

H	0.423555	-1.791659	2.361051
H	2.126751	-1.477568	2.101192
H	1.772525	-3.406013	3.661403
H	0.884793	-4.279471	2.404622
H	2.613129	-3.953676	2.211415
N	-0.999782	0.313781	0.076606
O	-1.322032	-1.823583	-0.627641
H	-0.042652	-1.775112	-0.266003
C	-4.146684	-1.597569	-0.724932
N	-3.335338	3.047288	0.873545
O	-4.554528	3.220396	0.841592
O	-2.506888	3.880215	1.236787
F	-5.440262	-1.222141	-0.680592
F	-3.887996	-2.006453	-1.979273
F	-4.012062	-2.668341	0.079837

TS2'

PBE0(D3) SCF energy in solution: -1588.364563 a.u.

PBE0(D3) free energy in solution: -1588.0643 a.u.

C	-2.048895	2.314040	0.924773
C	-2.725400	1.267343	1.801728
C	-3.805516	0.492278	1.042995
H	-1.987776	0.555846	2.202274
O	-2.230515	3.508188	1.095929
O	-1.309707	1.836517	-0.051009
Pd	-1.071233	-0.187121	-0.245991
H	-3.196079	1.778321	2.648681
N	-3.134299	-0.340299	-0.021434
C	-4.508079	-0.470555	1.997244
H	-4.966983	0.086128	2.821583
H	-5.302880	-1.031326	1.489574
H	-3.798855	-1.189675	2.424050
C	-4.794758	1.465273	0.405409
H	-5.655521	0.949437	-0.035884
H	-5.176224	2.152826	1.167893
H	-4.312701	2.069059	-0.370728
C	-3.856556	-0.993131	-0.848128
H	-4.949177	-0.912426	-0.783642
C	-3.274725	-1.924600	-1.849837
C	-2.228708	-2.851954	-1.221543
H	-2.826802	-1.348926	-2.674915
H	-4.083651	-2.512564	-2.297365
C	1.497037	1.370096	-0.686324
C	1.740442	-0.763131	0.312667
C	2.856211	1.606501	-0.568511
H	0.810830	2.114240	-1.085003
C	3.139620	-0.532244	0.461804
C	3.687706	0.647012	0.016524
H	4.750400	0.848778	0.111430
H	-2.150204	-3.737602	-1.871218
C	-0.820743	-2.302645	-1.053993
N	0.971205	0.215394	-0.274007

O	1.158013	-1.828643	0.688960
H	-0.070793	-1.780007	0.093323
C	3.978003	-1.596767	1.098832
N	3.410553	2.856117	-1.054060
O	4.622432	3.024677	-0.912882
O	2.635604	3.655875	-1.576651
F	5.269544	-1.217508	1.167143
F	3.570037	-1.873340	2.349670
F	3.935406	-2.746951	0.400199
H	-2.608188	-3.219135	-0.258040
H	-0.270449	-3.148516	-0.610521
C	-0.134963	-1.979784	-2.373448
H	0.919780	-1.723629	-2.226253
H	-0.168310	-2.846077	-3.051805
H	-0.597436	-1.134787	-2.900362

IM5

PBE0(D3) SCF energy in solution: -1588.405492 a.u.

PBE0(D3) free energy in solution: -1588.102561 a.u.

C	-2.089645	-2.547380	0.746000
C	-3.365173	-1.763130	1.056041
C	-4.022396	-0.939636	-0.068345
H	-4.094636	-2.493158	1.423700
O	-1.903672	-3.643955	1.238308
O	-1.236777	-1.944783	-0.062165
Pd	-1.173173	0.206033	-0.222061
H	-3.152301	-1.092888	1.902877
N	-3.200651	0.285324	-0.291430
C	-4.040373	-1.713681	-1.386176
H	-4.544953	-2.676472	-1.242715
H	-4.582726	-1.153352	-2.157198
H	-3.025277	-1.909433	-1.743266
C	-5.447442	-0.588785	0.351697
H	-6.003569	-0.073300	-0.439947
H	-5.995290	-1.510361	0.572428
H	-5.462624	0.035123	1.254014
C	-3.698086	1.435870	-0.574987
H	-4.782252	1.583299	-0.633455
C	-2.760560	2.541412	-0.873545
C	-1.359883	2.245259	-0.309400
H	-3.168186	3.500497	-0.510790
H	-2.726084	2.646211	-1.969752
C	1.653009	1.345246	-0.090576
C	1.743499	-0.977366	-0.107784
C	3.027496	1.446595	-0.044261
H	1.062118	2.253015	-0.098552
C	3.170158	-0.917521	-0.072102
C	3.813326	0.293848	-0.039343
H	4.895710	0.368034	-0.006988
H	-0.603241	2.654930	-0.997002
C	-1.171928	2.824285	1.089256
C	-0.962240	4.335360	1.087135

H	-0.312049	2.351580	1.587475
H	-2.043576	2.560995	1.708894
H	-0.882943	4.731485	2.105746
H	-0.039318	4.601729	0.555518
H	-1.789044	4.862361	0.593303
N	0.998836	0.174440	-0.128444
O	1.199983	-2.145220	-0.121300
C	3.950674	-2.201299	-0.060152
N	3.638709	2.762373	-0.003044
O	4.866887	2.809117	0.033857
O	2.889500	3.741058	-0.007226
F	5.276470	-1.946777	-0.047508
F	3.676318	-2.943368	1.023475
F	3.698548	-2.948852	-1.145750
H	0.125921	-2.165975	-0.073522

IM6

PBE0(D3) SCF energy in solution: -1081.219077 a.u.

PBE0(D3) free energy in solution: -1080.892685 a.u.

C	-0.756542	2.531579	-1.286416
C	-2.292973	2.476254	-1.260198
C	-2.902131	2.398274	0.151050
H	-2.660052	3.391393	-1.737953
O	-0.205769	3.573020	-1.630214
O	-0.130770	1.454924	-0.916832
Pd	-1.169781	-0.159424	0.007238
H	-2.660790	1.620275	-1.845946
N	-2.728045	1.000013	0.638409
C	-2.145856	3.308881	1.117523
H	-2.116090	4.330457	0.722443
H	-2.630361	3.324064	2.101958
H	-1.111379	2.970627	1.242327
C	-4.378447	2.780910	0.092363
H	-4.850578	2.802593	1.082165
H	-4.474835	3.787623	-0.327015
H	-4.943640	2.092555	-0.548106
C	-3.495370	0.444662	1.504877
H	-4.357487	0.981650	1.919201
C	-3.149577	-0.922288	1.962875
C	-2.280705	-1.639880	0.917590
H	-4.062647	-1.482284	2.230284
H	-2.596789	-0.813104	2.909769
H	-1.622875	-2.367334	1.417596
C	-3.109386	-2.348548	-0.148274
C	-3.865269	-3.569539	0.369456
H	-2.455128	-2.668651	-0.973525
H	-3.819113	-1.637075	-0.600277
H	-4.429710	-4.060956	-0.431502
H	-3.173852	-4.309536	0.792149
H	-4.582257	-3.306452	1.157396

I	0.839784	-1.867558	-0.756698
C	2.638523	-0.833822	-0.139120
C	2.750389	0.531568	-0.344162
C	3.653238	-1.588972	0.442938
C	3.928599	1.165461	0.052910
H	1.930820	1.109645	-0.773233
C	4.821228	-0.948208	0.827506
H	3.543511	-2.659125	0.601016
C	4.964944	0.431411	0.635038
H	4.014834	2.237506	-0.101451
H	5.636808	-1.501275	1.287200
O	6.144380	0.960688	1.049468
C	6.320064	2.352346	0.877075
H	5.564764	2.925839	1.432270
H	7.311534	2.579734	1.272420
H	6.275914	2.636222	-0.183560

TS3

PBE0(D3) SCF energy in solution: -1081.204122 a.u.

PBE0(D3) free energy in solution: -1080.875455 a.u.

C	-1.301351	1.847945	-2.243827
C	-2.507219	2.059522	-1.310564
C	-2.127171	2.526222	0.106714
H	-3.143273	2.824990	-1.768804
O	-1.123531	2.644015	-3.160846
O	-0.519288	0.846655	-1.979604
Pd	-0.732487	-0.267453	-0.151140
H	-3.106040	1.138607	-1.222428
N	-1.652428	1.322803	0.840539
C	-0.963863	3.516413	0.061466
H	-1.200483	4.339521	-0.621756
H	-0.760929	3.927661	1.058275
H	-0.053129	3.030805	-0.307653
C	-3.341989	3.142416	0.793627
H	-3.111387	3.529262	1.793793
H	-3.703682	3.988682	0.200722
H	-4.160006	2.416236	0.881181
C	-1.695518	1.178413	2.113540
H	-2.116631	1.957550	2.761499
C	-1.121977	-0.070081	2.678078
C	-1.201889	-1.196094	1.642779
H	-1.602086	-0.327678	3.637521
H	-0.065658	0.136722	2.922780
H	-0.489164	-1.997370	1.884526
C	-2.594049	-1.783752	1.475921
C	-3.066977	-2.568299	2.698285
H	-2.598684	-2.450865	0.602901
H	-3.317972	-0.984382	1.247933
H	-4.054092	-3.012038	2.526687

H	-2.372080	-3.383917	2.934307
H	-3.145506	-1.934097	3.590253
C	1.491017	-0.546083	-0.017169
C	2.118136	0.401177	-0.821624
C	2.010913	-0.890655	1.233101
C	3.225819	1.085760	-0.325488
H	1.711201	0.641794	-1.799948
C	3.113929	-0.204732	1.718595
H	1.565021	-1.684179	1.827424
C	3.727301	0.789614	0.946109
H	3.686207	1.847248	-0.949409
H	3.528496	-0.438389	2.696881
I	0.455833	-2.406310	-1.215834
O	4.804527	1.393179	1.510744
C	5.463573	2.381309	0.745242
H	6.291436	2.735342	1.361802
H	5.858468	1.967544	-0.193265
H	4.796433	3.223204	0.511577

IM7

PBE0(D3) SCF energy in solution: -1081.222930 a.u.

PBE0(D3) free energy in solution: -1080.892353 a.u.

C	-0.353573	1.976140	-2.242556
C	-1.355068	2.841406	-1.465583
C	-0.900406	3.141855	-0.029376
H	-1.457790	3.798730	-1.989432
O	0.557380	2.537416	-2.851442
O	-0.511746	0.690251	-2.174800
Pd	-0.791038	-0.091054	-0.193308
H	-2.346513	2.366371	-1.427194
N	-0.932237	1.845817	0.714807
C	0.534869	3.661083	0.014118
H	0.633326	4.540739	-0.630880
H	0.810160	3.939360	1.039447
H	1.244421	2.911414	-0.348730
C	-1.858891	4.147778	0.604061
H	-1.550838	4.450849	1.611968
H	-1.882793	5.056013	-0.006991
H	-2.879389	3.748560	0.656105
C	-0.998628	1.777431	1.991241
H	-1.046867	2.689413	2.599807
C	-0.988083	0.445842	2.645050
C	-1.473499	-0.637137	1.685658
H	-1.584813	0.472121	3.572463
H	0.045323	0.248222	2.971269
H	-1.106011	-1.631627	1.965813
C	-2.982804	-0.654167	1.502014
C	-3.717588	-1.190441	2.729440
H	-3.241614	-1.284056	0.639953
H	-3.347693	0.359687	1.267297
H	-4.800235	-1.198343	2.563570
H	-3.406177	-2.217988	2.951160

H	-3.525896	-0.583643	3.623157
C	1.176801	-0.334429	0.299844
C	2.058321	0.334624	-0.536815
C	1.625196	-1.110523	1.363007
C	3.425316	0.295003	-0.243816
H	1.722658	0.876048	-1.420035
C	2.985717	-1.146072	1.644688
H	0.944004	-1.707106	1.964526
C	3.892527	-0.437919	0.848701
H	4.106582	0.834613	-0.896450
H	3.364887	-1.743511	2.470965
I	-0.796120	-2.576938	-1.067940
O	5.198891	-0.538216	1.208638
C	6.139453	0.136712	0.399297
H	7.116851	-0.068752	0.839396
H	6.119562	-0.232179	-0.635745
H	5.962491	1.221811	0.394921

TS4

PBE0(D3) SCF energy in solution: -1081.204284 a.u.

PBE0(D3) free energy in solution: -1080.871953 a.u.

C	3.272116	0.300884	-1.412196
C	3.663279	-0.913002	-0.576990
C	2.645153	-2.064987	-0.553789
H	4.606331	-1.288856	-0.988849
O	4.056675	0.728003	-2.248045
O	2.111477	0.869162	-1.216703
Pd	0.568788	0.227327	-0.013844
H	3.867591	-0.601385	0.458514
N	1.556095	-1.634107	0.356181
C	2.020821	-2.284833	-1.931429
H	2.809647	-2.454547	-2.672890
H	1.359176	-3.159700	-1.926732
H	1.440623	-1.411782	-2.250661
C	3.336168	-3.341719	-0.089017
H	2.641950	-4.189161	-0.024607
H	4.108615	-3.610471	-0.816214
H	3.829975	-3.216584	0.882847
C	1.240935	-2.272002	1.418233
H	1.757891	-3.199495	1.689320
C	0.141658	-1.800695	2.295285
C	-0.266351	-0.356494	2.053330
H	0.445933	-1.929521	3.346344
H	-0.711474	-2.482983	2.162517
H	-1.249730	-0.180534	2.491888
C	0.686311	0.658154	2.711763
C	0.552174	0.619795	4.233209
H	0.450872	1.670313	2.365000
H	1.730770	0.469950	2.424153
H	1.174276	1.399821	4.684697
H	-0.483756	0.801579	4.545685
H	0.867746	-0.336983	4.667245

C	-1.374200	-0.531216	0.312585
C	-2.527791	0.250877	0.451953
C	-1.510648	-1.807062	-0.263067
C	-3.758334	-0.182460	-0.024410
H	-2.465243	1.222637	0.935610
C	-2.734956	-2.247823	-0.742304
H	-0.649823	-2.462047	-0.375438
C	-3.868453	-1.435169	-0.638615
H	-4.624000	0.464985	0.088753
H	-2.832338	-3.222484	-1.215272
I	-0.319847	2.748064	-0.365093
O	-5.016634	-1.950028	-1.141591
C	-6.173836	-1.140839	-1.069313
H	-6.971424	-1.716169	-1.542043
H	-6.448750	-0.923695	-0.027614
H	-6.036303	-0.194096	-1.609447

IM8

PBE0(D3) SCF energy in solution: -1595.625038 a.u.

PBE0(D3) free energy in solution: -1595.270227 a.u.

C	-0.622880	2.041165	-2.192778
C	-1.039642	2.889852	-0.978523
C	0.106441	3.149608	0.016155
H	-1.377054	3.859703	-1.359592
O	-0.588176	2.567275	-3.297816
O	-0.289998	0.804995	-1.956226
Pd	-0.282595	0.100780	0.055594
H	-1.885513	2.428219	-0.448526
N	0.294263	1.897681	0.816277
C	1.406317	3.449197	-0.727147
H	1.262091	4.327992	-1.365146
H	2.224300	3.658948	-0.025480
H	1.695326	2.618912	-1.379088
C	-0.261289	4.307745	0.939967
H	0.554973	4.582134	1.619347
H	-0.479002	5.191039	0.331881
H	-1.154072	4.078744	1.534505
C	0.666700	1.852954	2.043583
H	0.916093	2.778224	2.574629
C	0.759850	0.531635	2.708593
C	-0.229607	-0.459925	2.082493
H	0.620966	0.642665	3.795301
H	1.792825	0.171784	2.575740
H	0.160535	-1.485301	2.129892
C	-1.627530	-0.389489	2.666696
C	-1.681259	-0.825176	4.129462
H	-2.297239	-1.038377	2.090330
H	-2.038015	0.627163	2.561572
H	-2.714179	-0.826708	4.494156
H	-1.283424	-1.839956	4.254362
H	-1.106126	-0.162520	4.787818
C	1.601930	-0.615268	-0.068273

C	2.735096	0.181542	-0.069972
C	1.693465	-1.997185	-0.216709
C	3.993737	-0.407348	-0.229363
H	2.675786	1.260934	0.036907
C	2.944784	-2.579203	-0.373632
H	0.802285	-2.620597	-0.229892
C	4.100628	-1.790314	-0.383514
H	4.873191	0.230984	-0.241833
H	3.044291	-3.654959	-0.500071
O	5.272480	-2.459329	-0.546454
C	6.449577	-1.683484	-0.607947
H	7.267679	-2.389218	-0.762361
H	6.418991	-0.970512	-1.444174
H	6.618277	-1.129881	0.327387
O	-1.292788	-1.651486	-0.554176
C	-2.442534	-1.094686	-0.538206
O	-2.633226	0.085143	-0.184886
C	-3.650366	-1.973539	-0.867959
F	-4.152391	-2.440112	0.297244
F	-4.605147	-1.268110	-1.476664
F	-3.333606	-3.020706	-1.632802

TS5

PBE0(D3) SCF energy in solution: -1595.614798 a.u.

PBE0(D3) free energy in solution: -1595.260451 a.u.

C	3.005791	-0.523180	-1.655113
C	3.324206	-1.684284	-0.719939
C	2.190273	-2.705943	-0.524150
H	4.189941	-2.205114	-1.142788
O	3.748556	-0.274672	-2.592712
O	1.929057	0.181956	-1.424133
Pd	0.497003	-0.180191	-0.015316
H	3.628870	-1.294739	0.262870
N	1.208273	-2.079861	0.402395
C	1.452247	-2.979536	-1.834327
H	2.167601	-3.301617	-2.599262
H	0.703983	-3.771048	-1.705504
H	0.947134	-2.079617	-2.202332
C	2.767630	-4.002628	0.029358
H	1.994044	-4.760109	0.208008
H	3.463924	-4.419573	-0.704401
H	3.327795	-3.843314	0.959361
C	0.870586	-2.594596	1.525084
H	1.288742	-3.554883	1.842299
C	-0.128836	-1.935124	2.397417
C	-0.433750	-0.484852	2.048560
H	0.210764	-2.000067	3.443162
H	-1.045002	-2.545375	2.364600
H	-1.431733	-0.243962	2.419076
C	0.511209	0.545396	2.673291
C	0.345095	0.593657	4.190279
H	0.281419	1.534409	2.265416

H	1.561242	0.359296	2.411755
H	0.956977	1.399359	4.608849
H	-0.697653	0.786059	4.473525
H	0.656105	-0.337064	4.681211
C	-1.534267	-0.599085	0.277155
C	-2.448985	0.453532	0.195432
C	-1.951005	-1.892997	-0.062622
C	-3.742103	0.232312	-0.263490
H	-2.142440	1.461860	0.462334
C	-3.241283	-2.117223	-0.521554
H	-1.262184	-2.733878	-0.013133
C	-4.146961	-1.056850	-0.628031
H	-4.424718	1.074756	-0.335998
H	-3.563570	-3.112520	-0.819592
O	-5.382806	-1.375223	-1.087973
C	-6.310356	-0.318005	-1.230057
H	-7.223414	-0.770904	-1.620144
H	-6.524871	0.162389	-0.265035
H	-5.948400	0.441676	-1.936509
O	-0.027492	1.777596	-0.369111
C	0.897960	2.612488	-0.015855
O	1.936767	2.409010	0.589873
C	0.470684	4.046692	-0.386450
F	-0.594145	4.396046	0.376746
F	0.100489	4.151931	-1.670639
F	1.442983	4.931336	-0.158047

IM9

PBE0(D3) SCF energy in solution: -1595.672405 a.u.

PBE0(D3) free energy in solution: -1595.319075 a.u.

C	-2.649826	3.392918	0.722893
C	-1.168601	3.671795	0.491799
C	-0.405050	2.836506	-0.542880
H	-1.096732	4.729139	0.211257
O	-3.388803	4.310331	1.043851
O	-3.115330	2.171311	0.617900
Pd	-2.174174	0.503628	0.066822
H	-0.659316	3.579602	1.462713
N	-0.381112	1.440593	-0.012019
C	-1.126428	2.820918	-1.888796
H	-1.182107	3.841019	-2.285317
H	-0.590030	2.198817	-2.614476
H	-2.149223	2.439822	-1.796620
C	0.993831	3.415520	-0.722437
H	1.598595	2.822045	-1.418746
H	0.906294	4.423626	-1.139442
H	1.535767	3.501630	0.227303
C	0.696279	0.850864	0.354583
H	1.655590	1.362957	0.217722
C	0.742218	-0.500416	0.973487
C	2.056535	-0.754495	1.727081
H	0.611959	-1.257246	0.184302

H	-0.130552	-0.629880	1.630669
H	2.168518	0.034121	2.491363
C	1.988578	-2.099276	2.458145
C	3.220454	-2.393003	3.293506
H	1.834850	-2.900656	1.718855
H	1.091081	-2.106969	3.093700
H	3.121475	-3.342248	3.830553
H	4.120902	-2.453443	2.670649
H	3.391080	-1.606374	4.040174
C	3.242232	-0.654616	0.794704
C	4.221891	0.322446	0.961533
C	3.387335	-1.544362	-0.280876
C	5.313576	0.426764	0.098883
H	4.138107	1.021958	1.795485
C	4.464010	-1.461303	-1.145934
H	2.641651	-2.323944	-0.443901
C	5.438096	-0.471306	-0.962286
H	6.056792	1.201697	0.266360
H	4.577947	-2.153758	-1.976751
O	6.455248	-0.467658	-1.863271
C	7.454881	0.514981	-1.698173
H	8.173102	0.352920	-2.503818
H	7.040462	1.530315	-1.778286
H	7.964766	0.413516	-0.729456
O	-3.835806	-0.881371	-0.079303
C	-3.009527	-1.759593	-0.440988
O	-1.767014	-1.515944	-0.539341
C	-3.476432	-3.173077	-0.783005
F	-4.797051	-3.302391	-0.663535
F	-2.880483	-4.057779	0.034463
F	-3.126006	-3.474350	-2.043163

1a

PBE0(D3) SCF energy in solution: -271.536306 a.u.

PBE0(D3) free energy in solution: -271.426446 a.u.

C	-2.980091	-0.348661	-0.113541
C	-1.735824	0.512061	0.012515
H	-3.894223	0.255116	-0.114144
H	-2.968767	-0.931079	-1.043511
H	-3.056249	-1.062871	0.716243
C	-0.451377	-0.304304	0.015212
H	-1.700059	1.240569	-0.811064
H	-1.784796	1.109861	0.935427
C	0.802863	0.555899	0.139739
H	-0.479511	-1.030390	0.843568
H	-0.395901	-0.905518	-0.904981
H	0.915643	1.246938	-0.704792
H	0.720870	1.171028	1.051834
C	2.051818	-0.268271	0.268605
H	1.976057	-1.087897	1.032787
O	3.067825	-0.110762	-0.367068

TDG

PBE0(D3) SCF energy in solution: -402.076010 a.u.

PBE0(D3) free energy in solution: -401.942315 a.u.

C	-1.587250	-0.169149	-0.132522
C	-0.243136	-0.725635	-0.588891
C	1.008981	-0.063066	0.008917
H	-0.246527	-1.796988	-0.363736
O	-2.539153	-0.878686	0.094766
O	-1.659849	1.167598	-0.025906
H	-0.197655	-0.641646	-1.686579
N	1.015551	1.348123	-0.453826
C	0.931802	-0.048839	1.531498
H	0.828549	-1.067101	1.922179
H	1.841600	0.383991	1.967725
H	0.073986	0.536750	1.880646
C	2.254519	-0.815395	-0.450616
H	3.165074	-0.342982	-0.059572
H	2.245128	-1.856401	-0.104448
H	2.326965	-0.833427	-1.546198
H	-0.754915	1.543842	-0.214776
H	1.289020	1.383176	-1.434994
H	1.722438	1.875134	0.055339

Imine-1a

PBE0(D3) SCF energy in solution: -597.229696 a.u.

PBE0(D3) free energy in solution: -596.988173 a.u.

C	3.111003	-1.097578	-0.081560
C	2.707470	0.278963	-0.596378
C	1.511936	0.969222	0.093173
H	3.595203	0.915150	-0.515651
O	4.267663	-1.434982	0.015080
O	2.106930	-1.935458	0.229752
H	2.485946	0.185852	-1.670330
N	0.345586	0.096886	-0.141792
C	1.728800	1.008174	1.607538
H	2.654878	1.544108	1.847170
H	0.896494	1.520310	2.104332
H	1.802542	-0.002542	2.023078
C	1.374409	2.385387	-0.451399
H	0.573215	2.942788	0.049042
H	2.304983	2.939135	-0.285820
H	1.171632	2.388374	-1.529983
C	-0.763662	0.547124	-0.567425
H	-0.916978	1.619845	-0.779715
C	-1.951103	-0.327433	-0.784947
C	-3.155616	0.113381	0.046280
H	-1.681587	-1.367103	-0.559873
H	-2.226471	-0.290351	-1.851446
C	-4.394083	-0.731149	-0.216275
H	-2.896416	0.069152	1.115005
H	-3.381367	1.171295	-0.162996

C -5.590515 -0.295006 0.610245

H -4.641831 -0.685214 -1.287703

H -4.161747 -1.786593 -0.010492

H -6.471764 -0.913132 0.406908

H -5.379187 -0.364845 1.684726

H -5.862309 0.746985 0.398897

H 1.247086 -1.454399 0.103219

H_2O

PBE0(D3) SCF energy in solution: -76.384755 a.u.

PBE0(D3) free energy in solution: -76.380807 a.u.

O 0.000000 0.000000 0.119372

H 0.000000 0.757188 -0.477489

H 0.000000 -0.757188 -0.477489

L

PBE0(D3) SCF energy in solution: -864.451155 a.u.

PBE0(D3) free energy in solution: -864.387952 a.u.

C -1.628158 1.447835 0.000222

C 0.840143 1.464906 0.000025

C -1.643766 0.078732 -0.000191

H -2.539958 2.036901 0.001206

C 0.763682 0.011598 -0.000382

C -0.429676 -0.646555 -0.000168

H -0.474529 -1.732082 0.000059

N -0.445033 2.082944 -0.000081

O 1.837620 2.161459 0.000248

C 2.063991 -0.737666 -0.000083

N -2.917282 -0.608904 0.000217

O -2.889799 -1.838581 0.000671

O -3.938099 0.082696 -0.000789

F 1.851094 -2.069270 -0.000382

F 2.801953 -0.447322 -1.083627

F 2.801241 -0.447612 1.084027

H -0.412977 3.097054 0.000042

L'

PBE0(D3) SCF energy in solution: -864.440886 a.u.

PBE0(D3) free energy in solution: -864.37806 a.u.

C 1.567294 1.488493 -0.000212

C -0.713080 1.403000 -0.000160

C 1.644991 0.101613 -0.000076

H 2.475067 2.087851 -0.000283

C -0.734214 -0.007911 -0.000016

C 0.480911 -0.662752 0.000019

H 0.543231 -1.746490 0.000118

N 0.402113 2.132640 -0.000260

O -1.875582 2.058662 -0.000219

C -2.031749 -0.761009 0.000094

N 2.945190 -0.555100 -0.000044

O 2.956326 -1.785156 0.000209

O 3.941789 0.166383 0.000165

F -1.816547 -2.089528 0.000147

F -2.772888 -0.470698 1.083722

F -2.773004 -0.470801 -1.083482

H -1.652655 3.007369 -0.000329

ArI

PBE0(D3) SCF energy in solution: -357.280547 a.u.

PBE0(D3) free energy in solution: -357.192974 a.u.

C 2.592750 0.279247 -0.000071

C 1.801134 1.433083 -0.000023

C 0.418210 1.336571 0.000018

C -0.181885 0.078110 -0.000004

C 0.591580 -1.073876 -0.000057

C 1.982712 -0.977006 -0.000098

H 2.292901 2.403167 -0.000010

H -0.186584 2.239506 0.000054

H 0.124936 -2.055627 -0.000087

H 2.573366 -1.888955 -0.000166

I -2.321429 -0.078490 0.000014

O 3.936674 0.482734 -0.000074

C 4.757604 -0.665403 0.000150

H 5.786126 -0.300506 -0.000066

H 4.589601 -1.281693 0.894931

H 4.589367 -1.282154 -0.894271

Imine-3a

PBE0(D3) SCF energy in solution: -942.509354 a.u.

PBE0(D3) free energy in solution: -942.161807 a.u.

C -3.474807 0.187833 -1.200335

C -3.590920 -0.615926 0.090314

C -2.328952 -0.712722 0.970225

H -4.410767 -0.170305 0.663364

O -4.361983 0.909530 -1.592769

O -2.339557 0.025898 -1.902566

H -3.910122 -1.635260 -0.174905

N -1.312190 -1.398875 0.153420

C -1.776172 0.685774 1.262428

H -2.537301 1.300395 1.758508

H -0.894806 0.622907 1.912655

H -1.468911 1.192527 0.340234

C -2.675152 -1.426784 2.271855

H -1.829663 -1.443573 2.969968

H -3.497391 -0.908780 2.777900

H -2.990165 -2.462003 2.089238

C -0.437274 -2.169315 0.656501

H -0.410078 -2.403829 1.735610

C 0.677342 -2.711028 -0.171909

C 2.001115 -1.965432 0.114189

H 0.414966 -2.604411 -1.233093

H 0.824627 -3.782357 0.026324

C 3.108679 -2.497402 -0.802512

H	2.293638	-2.187015	1.155120
C	4.475791	-1.915870	-0.492448
H	3.137964	-3.594430	-0.721620
H	2.836725	-2.279240	-1.847034
H	5.248731	-2.339647	-1.142861
H	4.486499	-0.827697	-0.626397
H	4.767974	-2.120271	0.546164
H	-1.743528	-0.583416	-1.390249
C	1.823120	-0.468381	0.005941
C	2.126053	0.371964	1.073628
C	1.310527	0.120382	-1.159459
C	1.929174	1.751821	1.006355
H	2.527055	-0.059532	1.992798
C	1.097952	1.485129	-1.247120
H	1.049393	-0.505885	-2.014212
C	1.405208	2.312756	-0.159170
H	2.179774	2.371100	1.863485
H	0.675684	1.935068	-2.142903
O	1.152310	3.637990	-0.334181
C	1.402418	4.486635	0.764190
H	1.119386	5.490070	0.440777
H	0.799810	4.201785	1.639509
H	2.465068	4.481967	1.047752

AcOH

PBE0(D3) SCF energy in solution: -228.918680 a.u.

PBE0(D3) free energy in solution: -228.883255 a.u.

C	0.092069	0.126814	-0.000006
C	-1.387665	-0.098278	0.000002
H	-1.683072	-0.681029	-0.878569
O	0.762226	-1.053505	-0.000008
O	0.655684	1.197097	-0.000001
H	-1.683095	-0.680803	0.878714
H	1.706584	-0.817225	0.000062
H	-1.910118	0.859108	-0.000120

TFA

PBE0(D3) SCF energy in solution: -526.452222 a.u.

PBE0(D3) free energy in solution: -526.445991 a.u.

O	1.505760	-1.051609	-0.000028
C	0.932778	0.159482	-0.000154
O	1.502000	1.218462	0.000122
C	-0.595641	0.001765	-0.000071
F	-0.995135	-0.675514	-1.086844
F	-1.182347	1.195004	-0.000542
F	-0.995195	-0.674673	1.087460
H	2.469178	-0.905676	-0.000075

AgTFA

PBE0(D3) SCF energy in solution: -672.832963 a.u.

PBE0(D3) free energy in solution: -672.840973 a.u.

O	0.102835	1.147627	-0.030344

C 0.663545 0.023986 -0.038370

O 0.100309 -1.101621 -0.030128

C 2.201070 0.001326 -0.005469

F 2.692699 -0.965834 -0.791478

F 2.734200 1.162057 -0.397178

F 2.607719 -0.239364 1.256583

Ag -1.938817 -0.002801 0.002882

AgI

PBE0(D3) SCF energy in solution: -158.440555 a.u.

PBE0(D3) free energy in solution: -158.466305 a.u.

Ag 0.000000 0.000000 -1.388853

I 0.000000 0.000000 1.231624

IM2-dimer

PBE0(D3) SCF energy in solution: -1905.774466 a.u.

PBE0(D3) free energy in solution: -1905.200608 a.u.

Pd 1.194036 0.261713 -0.460840

Pd -1.492176 -1.124035 -0.750001

C -1.991633 -2.339403 1.970835

C -4.012188 -1.056382 0.827923

C -3.250912 -1.486233 2.087526

H -2.975815 -0.582286 2.653445

C 0.199745 2.138051 1.484075

C 1.338201 0.141934 2.591154

C 0.012132 0.804272 2.196741

O -1.631078 -0.082521 -2.538451

C -0.641504 0.604843 -2.943385

O 0.457410 0.802505 -2.352615

O 1.866894 -1.572949 -1.174654

C 1.090005 -2.460932 -1.643962

O -0.169557 -2.427169 -1.704370

C 1.746636 -3.707078 -2.174992

H 2.809163 -3.545499 -2.369309

H 1.640691 -4.504239 -1.430777

H 1.242181 -4.044160 -3.084148

C -0.820163 1.311184 -4.260501

H -1.655106 0.893734 -4.826853

H -1.021171 2.371354 -4.062714

H 0.100421 1.263230 -4.847748

O -1.243507 -2.274820 0.900239

O -1.675198 -3.043589 2.921984

H -3.937038 -2.043494 2.736396

C -4.343674 -2.253892 -0.061270

H -5.009656 -2.935717 0.480289

H -4.853192 -1.932059 -0.976855

H -3.446782 -2.814095 -0.345894

C -5.313989 -0.383200 1.253826

H -5.938210 -1.121267 1.767177

H -5.151484 0.445367 1.953425

H -5.885072 -0.011668 0.394274

N -3.101911 -0.140788 0.069193

C	-3.360476	1.108552	-0.067697
H	-4.298366	1.493496	0.348956
C	-2.490007	2.113505	-0.722543
H	-1.452147	1.755348	-0.741902
H	-2.804509	2.197489	-1.776127
H	-0.550836	0.106197	1.557260
H	-0.569515	0.977899	3.109766
O	0.697974	2.089427	0.270083
O	-0.094064	3.199950	2.022129
C	2.103338	1.066291	3.536670
H	1.477007	1.295435	4.405634
H	3.024186	0.604841	3.911207
H	2.358198	2.015392	3.051584
C	1.082423	-1.223625	3.216705
H	0.411909	-1.128029	4.078150
H	0.609329	-1.909339	2.505770
H	2.019814	-1.672781	3.569957
N	2.133921	-0.066751	1.326988
C	3.354725	-0.442445	1.404445
H	3.772512	-0.628629	2.404218
C	4.291055	-0.598611	0.264426
H	4.460273	-1.673733	0.094402
H	3.827575	-0.215187	-0.652681
C	-2.571846	3.483311	-0.054375
C	-1.608021	4.474626	-0.688694
H	-2.328932	3.390274	1.013025
H	-3.604653	3.865473	-0.110853
C	-1.596677	5.810859	0.029301
H	-0.599627	4.038242	-0.668644
H	-1.872635	4.609806	-1.750681
H	-0.918316	6.523073	-0.453857
H	-2.595207	6.268189	0.052716
H	-1.259616	5.680327	1.064286
C	5.627125	0.090861	0.539156
C	6.617513	-0.090821	-0.601667
H	6.064088	-0.299251	1.472336
H	5.456794	1.164393	0.712289
C	7.944976	0.598212	-0.342369
H	6.779077	-1.166238	-0.771148
H	6.171165	0.293453	-1.530667
H	8.644065	0.456749	-1.173732
H	7.811939	1.678339	-0.203199
H	8.426203	0.209227	0.563942

IM4-dimer

PBE0(D3) SCF energy in solution: -3176.851825 a.u.

PBE0(D3) free energy in solution: -3176.21002 a.u.

Pd	0.547978	-0.600074	1.334686
Pd	-0.482509	-0.657021	-1.352108
C	0.965218	-3.264126	-1.566140
C	-1.496590	-3.222088	-2.517224
C	-0.325683	-3.992856	-1.894113

H	-0.676228	-4.473108	-0.969239
C	-0.658895	-3.329601	1.590362
C	1.774324	-3.034916	2.568930
C	0.693945	-3.923283	1.939365
O	-1.046275	0.822479	1.307458
O	0.997093	0.892095	-1.344512
O	1.026158	-1.967484	-1.683900
O	1.947166	-3.920015	-1.213935
H	-0.051742	-4.815496	-2.568109
C	-1.132116	-2.543638	-3.835642
H	-0.816127	-3.299811	-4.563563
H	-2.001406	-2.019626	-4.251959
H	-0.315523	-1.824902	-3.722589
C	-2.624452	-4.217748	-2.783422
H	-2.302589	-4.904316	-3.573071
H	-2.865605	-4.827555	-1.905270
H	-3.536063	-3.718401	-3.133426
N	-1.890968	-2.152375	-1.535595
C	-2.934917	-2.291812	-0.799213
H	-3.544267	-3.187176	-0.951257
C	-3.418524	-1.351654	0.239285
H	-2.559908	-0.843495	0.680648
H	-4.039816	-0.583843	-0.255162
H	1.101034	-4.368328	1.019614
H	0.497219	-4.765986	2.614821
O	-0.840886	-2.040819	1.654073
O	-1.575249	-4.085515	1.262047
C	1.317433	-2.369467	3.864931
H	1.061832	-3.138660	4.602856
H	2.120900	-1.753082	4.286963
H	0.435720	-1.738556	3.719103
C	2.985548	-3.913945	2.875921
H	2.715805	-4.609078	3.677467
H	3.296101	-4.518701	2.016317
H	3.841105	-3.324025	3.226474
N	2.084651	-1.953369	1.570977
C	3.146250	-2.008945	0.849291
H	3.839785	-2.835602	1.030681
C	3.543331	-1.055399	-0.213260
H	2.640119	-0.658468	-0.680171
H	4.068886	-0.207938	0.261141
C	-4.217416	-2.021691	1.348162
C	-4.542141	-1.027672	2.453767
H	-3.623661	-2.854130	1.748332
H	-5.145665	-2.457417	0.944768
C	-5.347489	-1.640450	3.584362
H	-3.599151	-0.612801	2.843010
H	-5.088808	-0.169695	2.028069
H	-5.560987	-0.909835	4.372318
H	-6.308555	-2.030367	3.225080
H	-4.808436	-2.477595	4.045278
C	4.428514	-1.676403	-1.284457

C	4.637445	-0.713118	-2.443695
H	3.945645	-2.595475	-1.642040
H	5.399914	-1.970724	-0.855466
C	5.556965	-1.268765	-3.515229
H	3.655553	-0.469880	-2.877892
H	5.038140	0.241689	-2.064449
H	5.681952	-0.566726	-4.346962
H	6.554889	-1.485237	-3.112421
H	5.162323	-2.205677	-3.927928
C	-2.526572	1.478340	-1.823064
C	-1.718058	1.389270	0.396564
C	-3.302875	2.587766	-1.539655
H	-2.521729	1.043749	-2.820056
C	-2.495755	2.553662	0.701325
C	-3.282850	3.142068	-0.254729
H	-3.880474	4.021772	-0.034727
N	-1.766289	0.896824	-0.892471
C	-2.415273	3.092670	2.096759
N	-4.126114	3.166016	-2.581796
O	-4.788977	4.159785	-2.285968
O	-4.111467	2.622475	-3.687617
F	-3.173646	4.196223	2.237379
F	-1.150890	3.432923	2.421905
F	-2.840726	2.196850	3.004714
C	2.352661	1.732792	1.799754
C	1.595998	1.534056	-0.432680
C	3.005312	2.918957	1.517543
H	2.377106	1.310851	2.802041
C	2.248619	2.773482	-0.737265
C	2.949718	3.453499	0.225545
H	3.452765	4.391039	0.006979
N	1.682361	1.060171	0.862063
C	2.144729	3.283660	-2.142509
N	3.739361	3.594718	2.567336
O	4.305358	4.646094	2.269997
O	3.752992	3.069116	3.681848
F	2.740653	2.453786	-3.017874
F	2.732592	4.490130	-2.265770
F	0.861086	3.422701	-2.527214

IM10

PBE0(D3) SCF energy in solution: -2313.477464 a.u.

PBE0(D3) free energy in solution: -2313.239849 a.u.

Pd	-0.000023	0.000077	0.000007
C	2.554739	-1.332169	-0.566013
C	2.895216	0.900101	0.043391
C	3.913289	-1.571710	-0.558374
H	1.841285	-2.123406	-0.787317
C	4.299614	0.692487	0.060807
C	4.807430	-0.547257	-0.245099
H	5.875794	-0.740748	-0.240563
N	2.057287	-0.118650	-0.273338

O	2.446849	2.076926	0.359206
C	5.198813	1.838178	0.432587
N	4.401357	-2.914903	-0.846778
O	5.619701	-3.068170	-0.882808
O	3.559306	-3.793052	-1.020491
F	6.489912	1.456820	0.403738
F	5.060292	2.868627	-0.415102
F	4.932966	2.284244	1.669344
H	1.453908	2.251065	0.153194
C	-2.554855	1.332268	0.565848
C	-2.895171	-0.900104	-0.043331
C	-3.913425	1.571707	0.558205
H	-1.841440	2.123564	0.787074
C	-4.299588	-0.692593	-0.060726
C	-4.807488	0.547146	0.245049
H	-5.875864	0.740570	0.240493
N	-4.401594	2.914885	0.846466
O	-5.619947	3.068089	0.882436
O	-3.559601	3.793101	1.020131
C	-5.198701	-1.838380	-0.432415
F	-4.932807	-2.284525	-1.669135
F	-5.060115	-2.868752	0.415354
F	-6.489835	-1.457128	-0.403610
O	-2.446729	-2.076916	-0.359030
N	-2.057319	0.118759	0.273280
H	-1.453734	-2.251031	-0.153032
O	0.343627	-1.157551	1.673975
C	0.306413	-2.423500	1.432785
O	-0.149801	-2.926227	0.381664
O	-0.343602	1.157701	-1.673947
C	-0.306286	2.423652	-1.432719
O	0.149907	2.926293	-0.381563
C	0.906558	-3.308402	2.486881
H	0.243092	-4.154122	2.688005
H	1.841717	-3.726825	2.094258
H	1.120662	-2.764022	3.408475
C	-0.906373	3.308599	-2.486819
H	-1.841917	3.726431	-2.094477
H	-0.243227	4.154690	-2.687413
H	-1.119862	2.764371	-3.408645

IM11

PBE0(D3) SCF energy in solution: -2313.479049 a.u.

PBE0(D3) free energy in solution: -2313.243074 a.u.

Pd	-0.000279	1.777382	-0.000222
C	-1.022621	-0.361114	-1.838905
C	-2.225143	-0.237807	0.166357
C	-1.673435	-1.528346	-2.187220
H	-0.268977	0.076980	-2.488705
C	-2.885813	-1.453820	-0.137491
C	-2.608526	-2.096759	-1.322381
H	-3.109108	-3.021375	-1.593544

N	-1.282617	0.260539	-0.677843
O	-2.498277	0.385784	1.273974
C	-3.892294	-2.011346	0.830913
N	-1.358179	-2.171770	-3.458570
O	-1.953918	-3.214825	-3.714259
O	-0.523406	-1.624415	-4.173655
F	-4.361353	-3.194983	0.391399
F	-3.346147	-2.214396	2.038310
F	-4.941583	-1.190540	0.983766
H	-2.346746	1.419001	1.200650
C	1.022921	-0.360288	1.838980
C	2.225214	-0.237250	-0.166427
C	1.674023	-1.527289	2.187537
H	0.269256	0.077831	2.488739
C	2.886133	-1.453073	0.137632
C	2.609111	-2.095750	1.322731
H	3.109923	-3.020193	1.594057
N	1.359077	-2.170420	3.459116
O	1.955139	-3.213232	3.715060
O	0.524229	-1.623087	4.174125
C	3.892642	-2.010652	-0.830711
F	3.346552	-2.213812	-2.038100
F	4.941937	-1.189835	-0.983579
F	4.361705	-3.194245	-0.391072
O	2.498168	0.386186	-1.274193
N	1.282657	0.261108	0.677719
H	2.346352	1.419302	-1.200973
O	1.193726	3.262284	0.714127
C	2.190684	3.559566	-0.045998
O	2.571864	2.898240	-1.034686
O	-1.194817	3.261781	-0.714709
C	-2.191703	3.558961	0.045532
O	-2.572590	2.897671	1.034374
C	2.897672	4.835089	0.317667
H	3.944417	4.791286	0.009216
H	2.421554	5.663500	-0.219008
H	2.819145	5.044182	1.386981
C	-2.899031	4.834292	-0.318130
H	-2.819884	5.043850	-1.387309
H	-3.945954	4.789890	-0.010383
H	-2.423655	5.662690	0.219220

IM12

PBE0(D3) SCF energy in solution: -1817.339803 a.u.

PBE0(D3) free energy in solution: -1816.978887 a.u.

C	-0.261929	-2.677887	1.578555
C	-1.110840	-3.320534	0.486055
C	-2.542821	-2.774620	0.444120
H	-1.159693	-4.397327	0.681631
O	0.067702	-3.295080	2.578062
O	0.058917	-1.416552	1.388779
Pd	-0.613664	-0.516407	-0.293151

H	-0.644309	-3.180541	-0.501317
N	-2.479560	-1.302511	0.111483
C	-3.202976	-2.959367	1.808509
H	-3.159204	-4.014562	2.099097
H	-4.257610	-2.661032	1.796597
H	-2.685509	-2.382274	2.582295
C	-3.324504	-3.482300	-0.658165
H	-4.368001	-3.146247	-0.694131
H	-3.330347	-4.562962	-0.477994
H	-2.871253	-3.300585	-1.639651
C	-3.564211	-0.623562	0.085146
H	-4.508642	-1.146413	0.296685
C	2.247474	-0.857914	-1.004303
C	1.887007	1.118112	0.177800
C	3.606508	-0.785258	-0.769727
H	1.821036	-1.682673	-1.568417
C	3.267014	1.212127	0.484179
C	4.127996	0.251688	0.003649
H	5.193689	0.292662	0.206699
N	1.405093	0.069190	-0.531771
O	1.069826	2.045710	0.589006
C	3.761792	2.357592	1.321022
N	4.482499	-1.810923	-1.316259
O	5.681376	-1.715218	-1.065667
O	3.959911	-2.696003	-1.991743
F	5.098711	2.287236	1.475021
F	3.209014	2.346661	2.543397
F	3.480512	3.542635	0.756487
H	0.218073	2.047702	0.020386
C	-3.661316	0.826001	-0.208830
C	-4.726955	1.552409	0.604243
H	-2.680142	1.297580	-0.070213
H	-3.897726	0.927791	-1.281736
C	-4.840257	3.013115	0.190598
H	-4.485493	1.487406	1.675741
H	-5.702393	1.055022	0.481674
C	-5.867963	3.781269	1.000579
H	-5.094707	3.061670	-0.879848
H	-3.852730	3.490136	0.281767
H	-5.932805	4.827382	0.682745
H	-5.617514	3.776327	2.068601
H	-6.868079	3.341492	0.896750
O	-1.250205	0.369276	-2.055575
C	-1.193936	1.653242	-2.084595
O	-0.801535	2.388332	-1.152791
C	-1.703463	2.293625	-3.349689
H	-0.960442	2.999294	-3.733606
H	-2.599896	2.880181	-3.115536
H	-1.945750	1.555466	-4.117018

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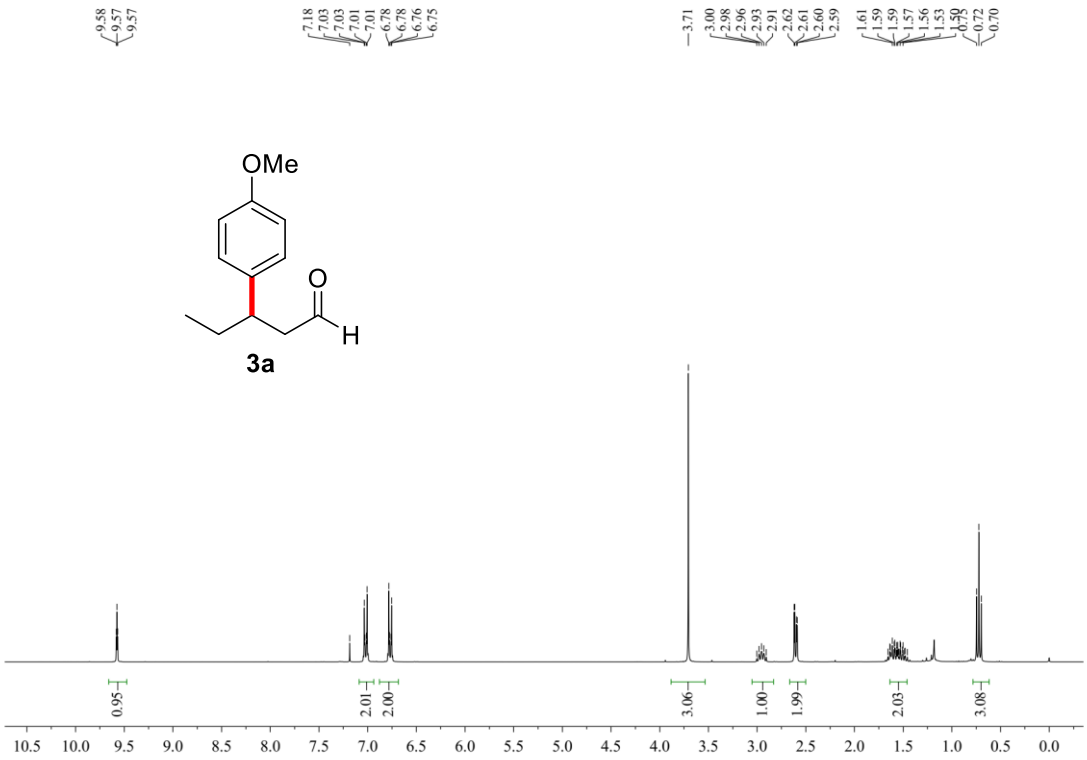
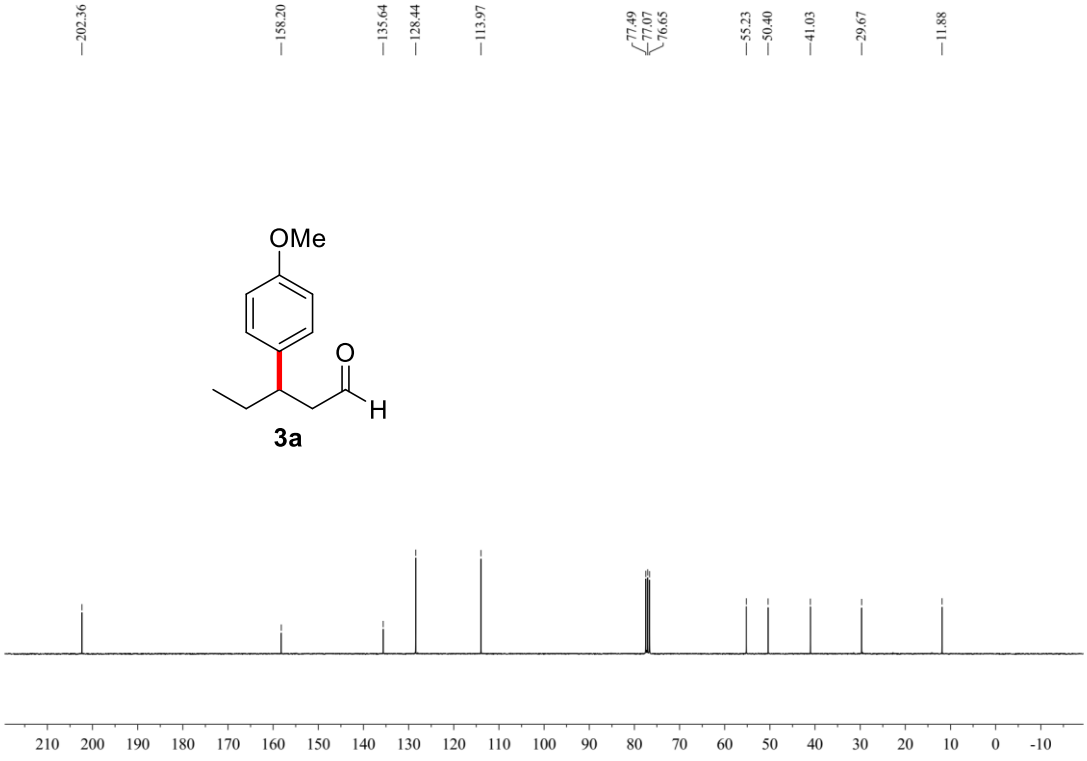
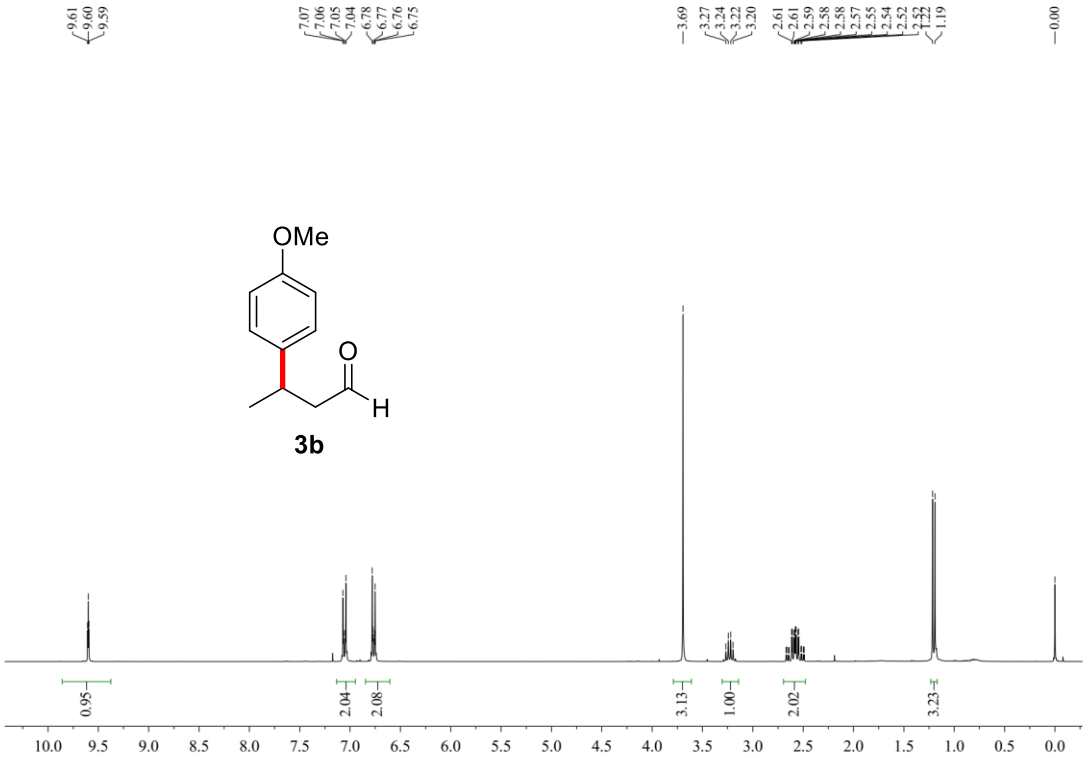
IV. ^{1}H and ^{13}C NMR Spectra



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2.54
2.52
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0.00
OMe
O
H
3b
0.95
2.04
2.08
3.13
1.00
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3.23
10.0
9.5
9.0
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8.0
7.5
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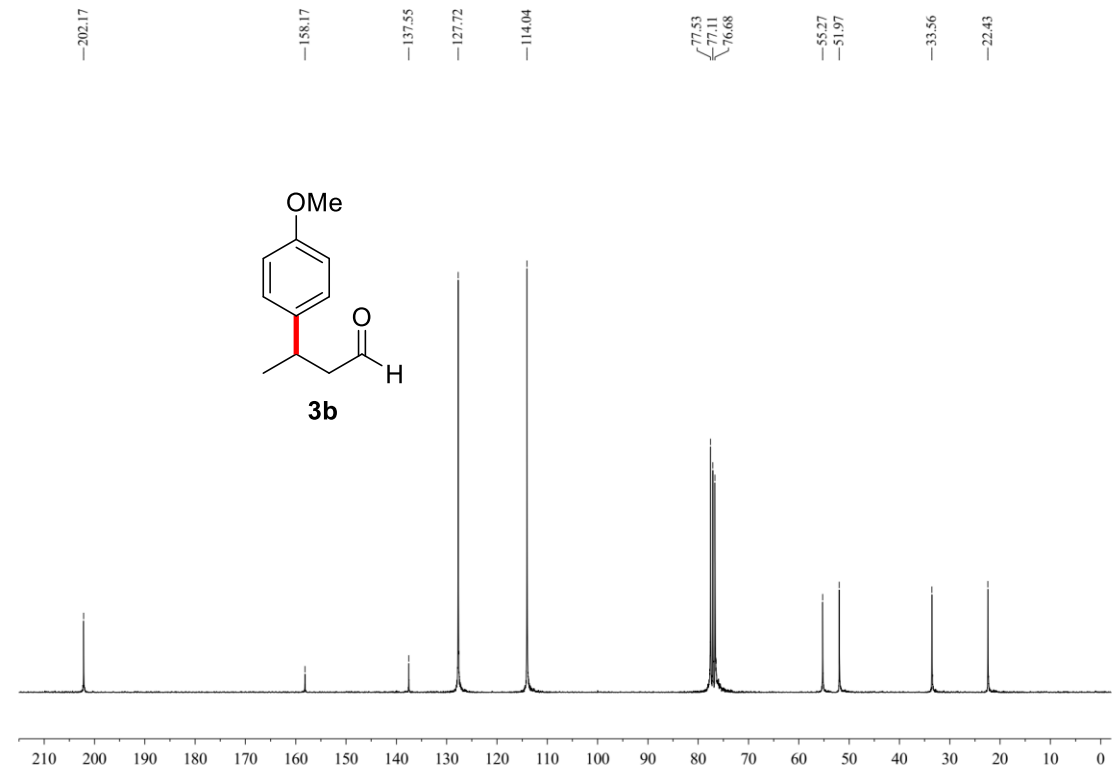
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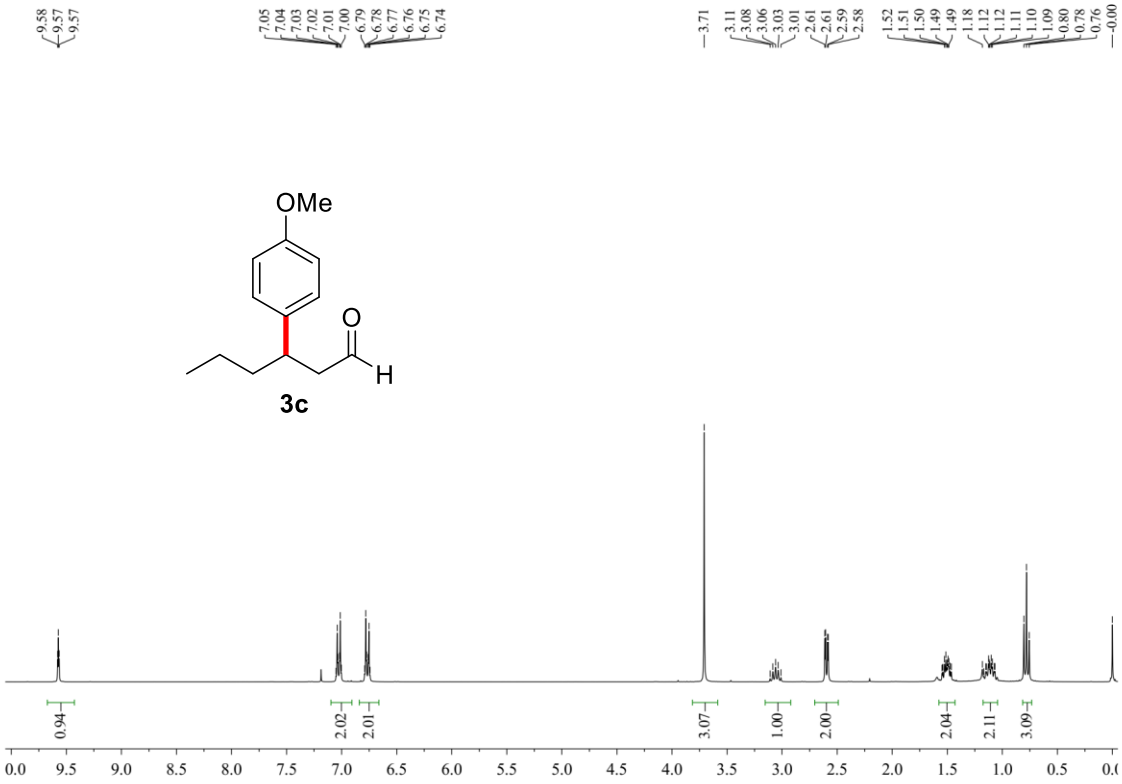
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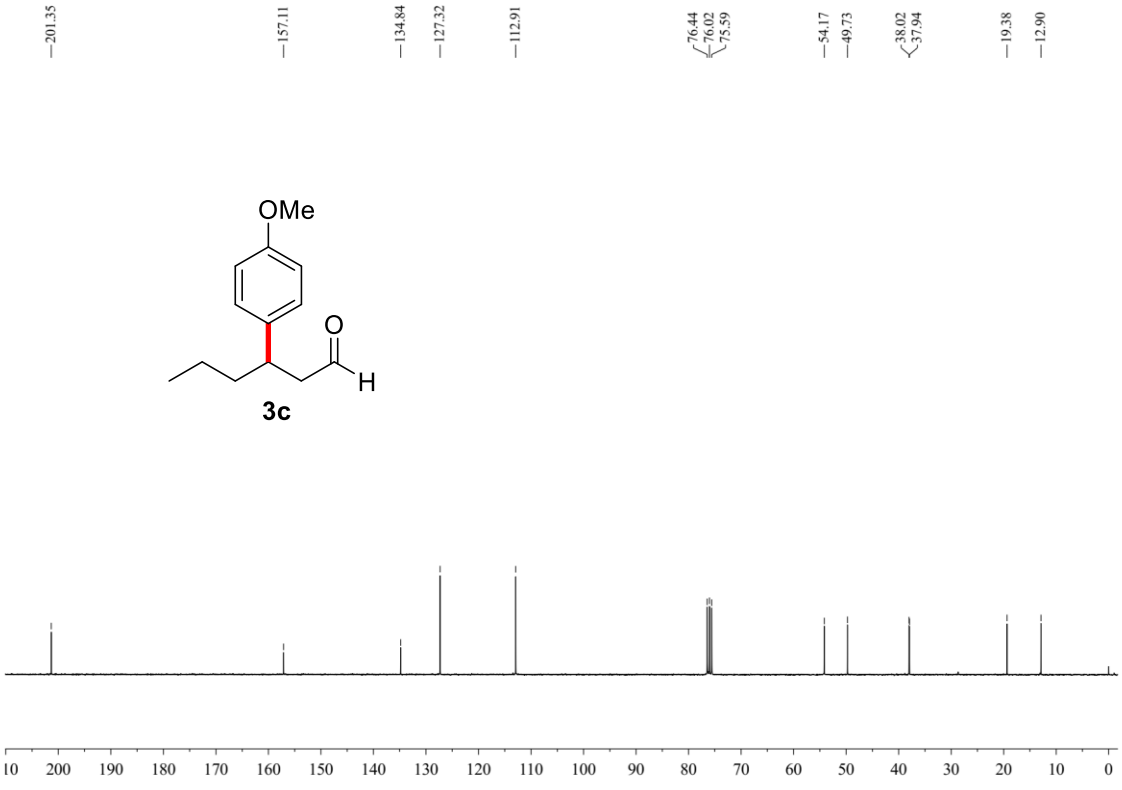
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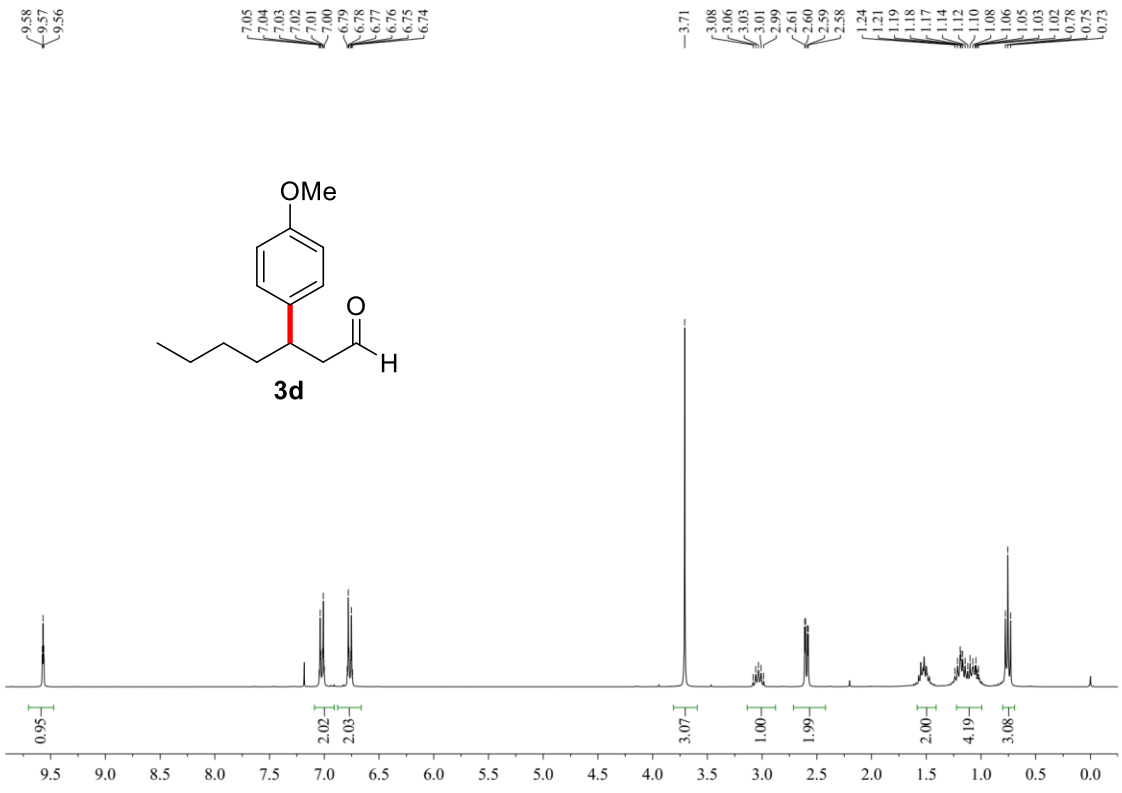
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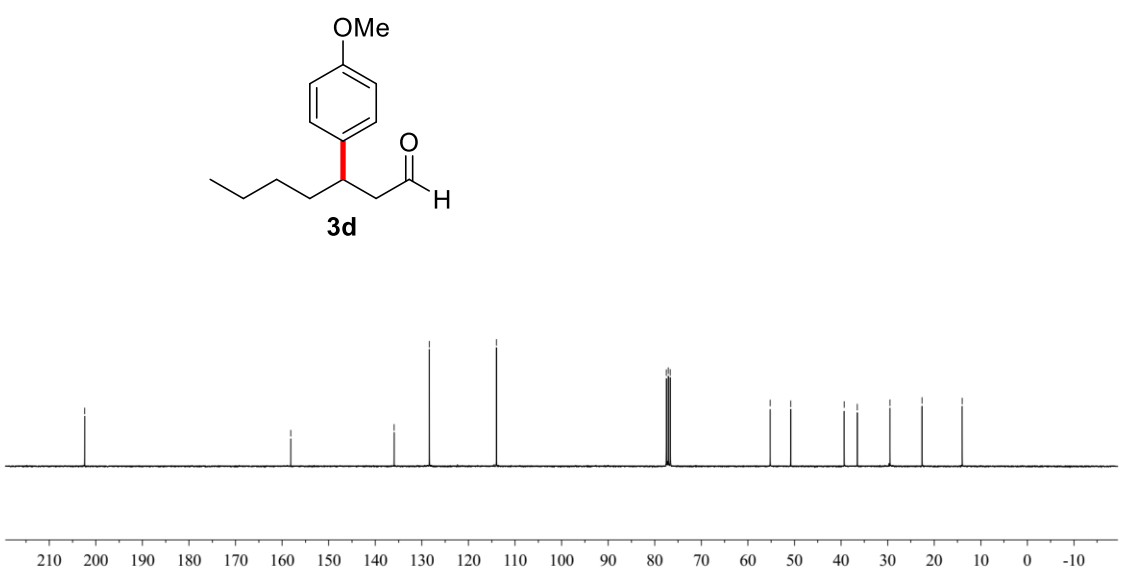
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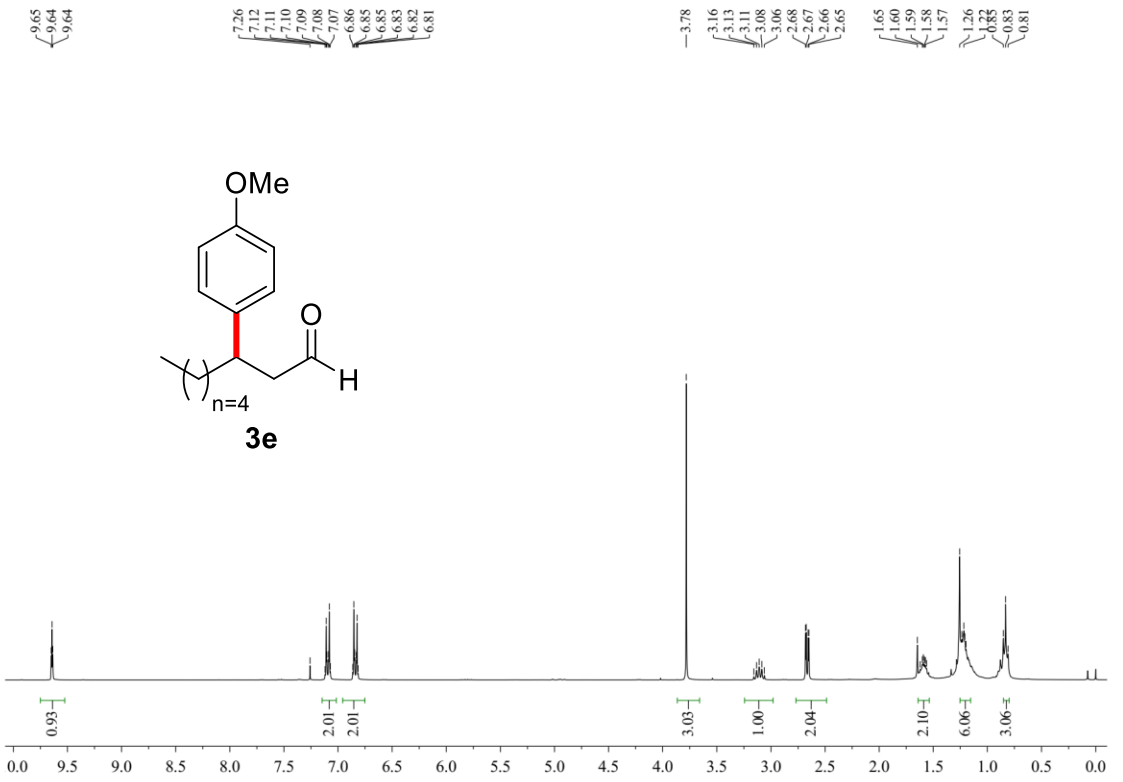
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H
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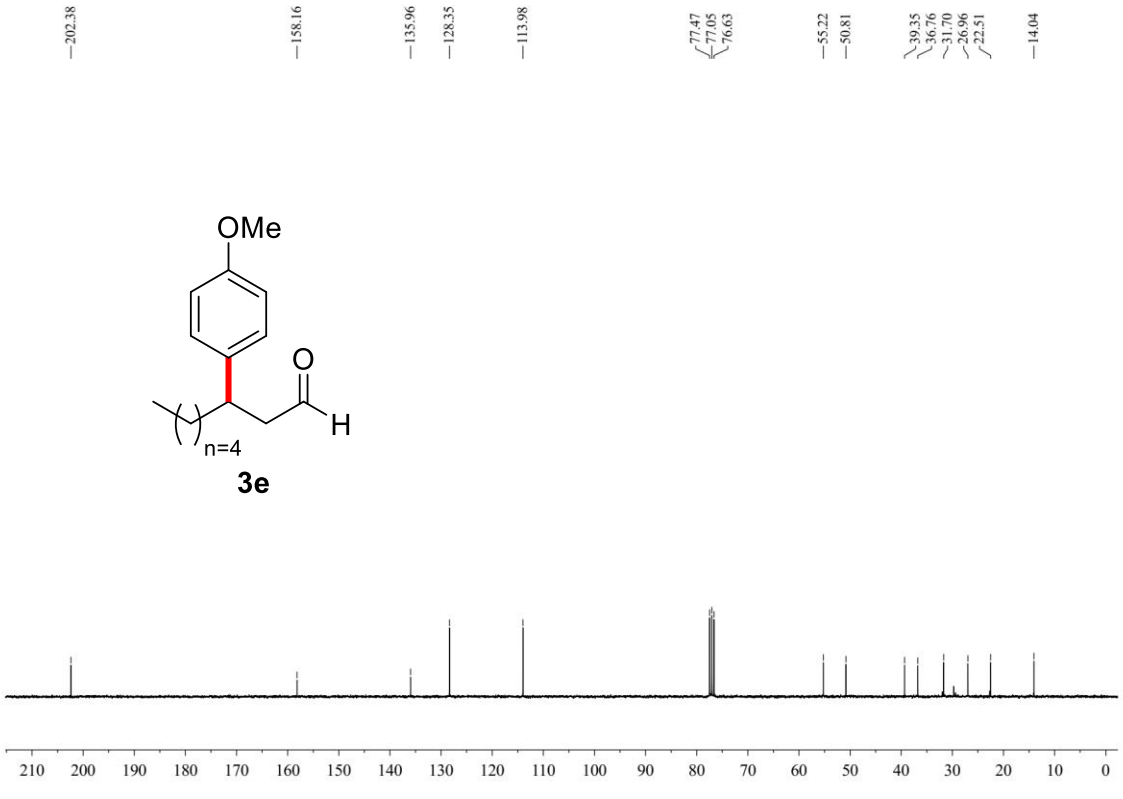
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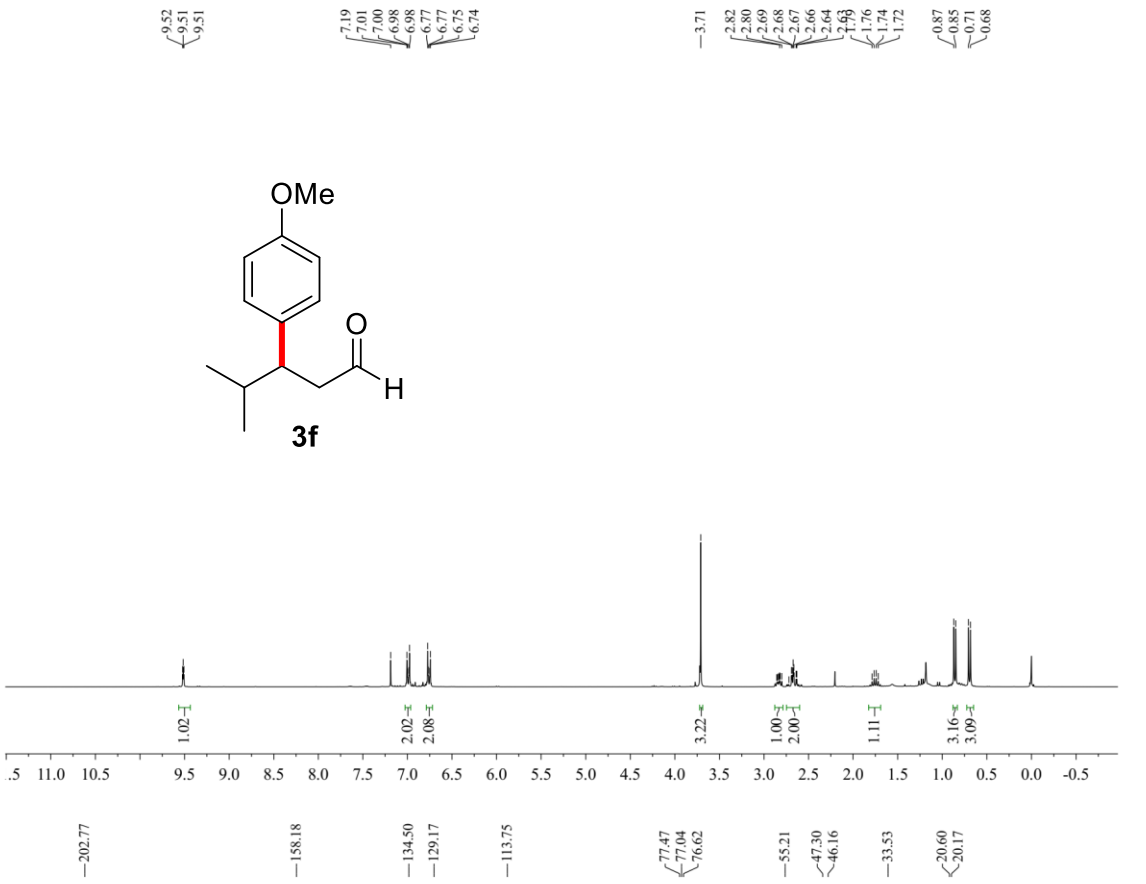
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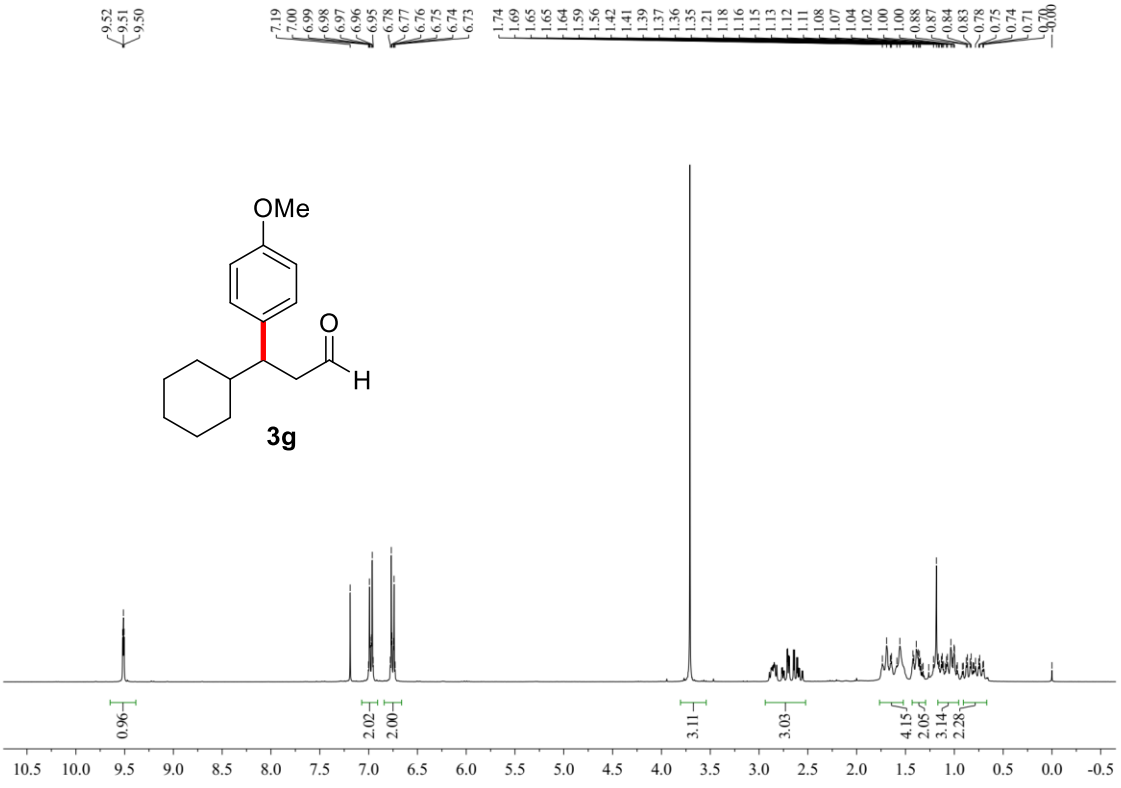
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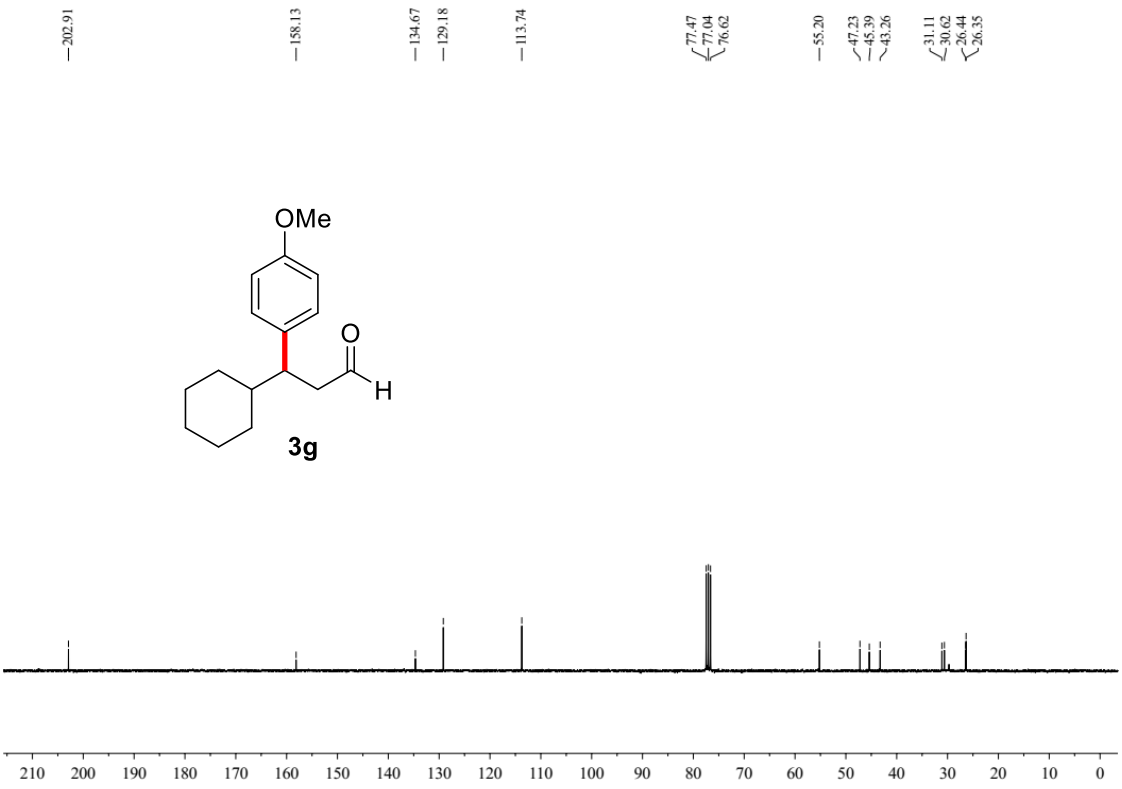
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O
H
3g
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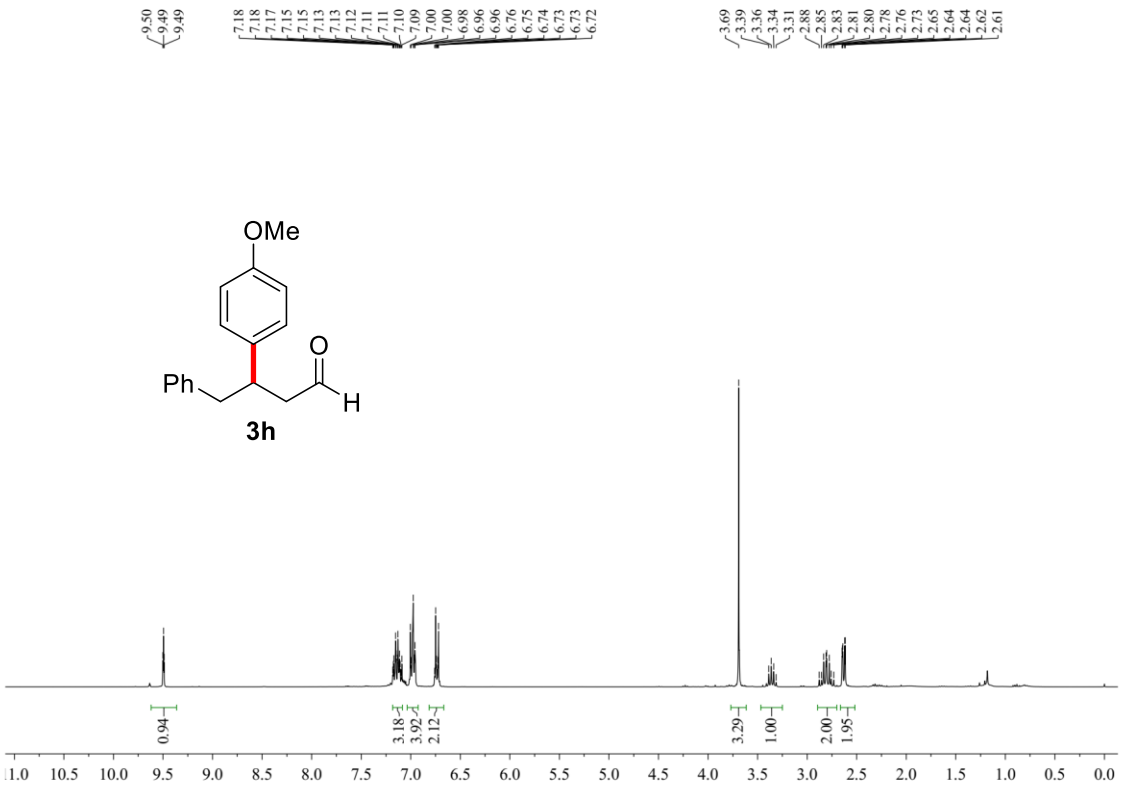
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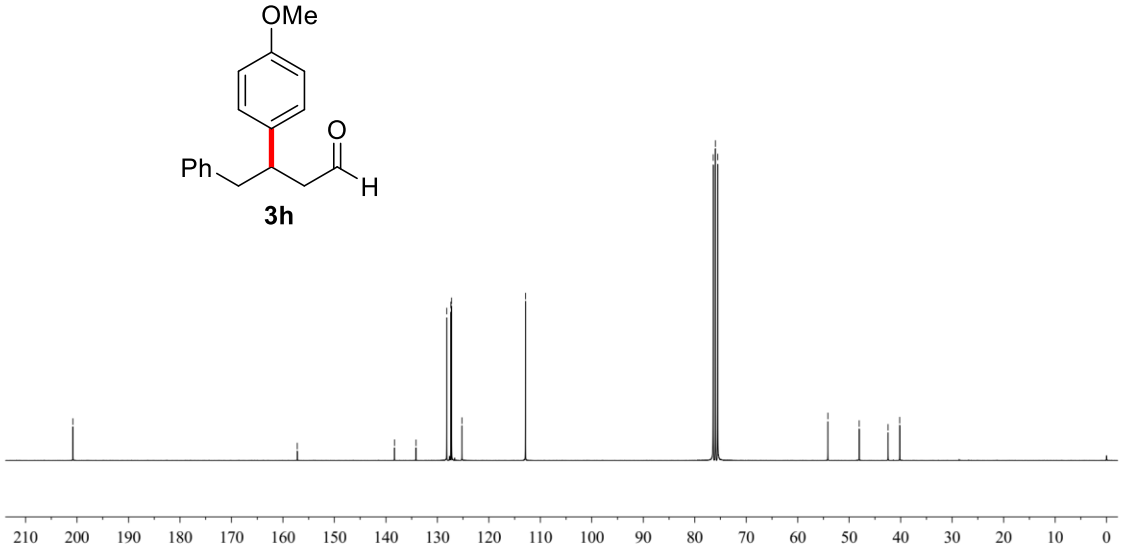
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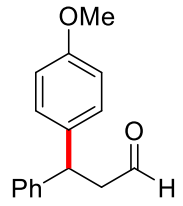
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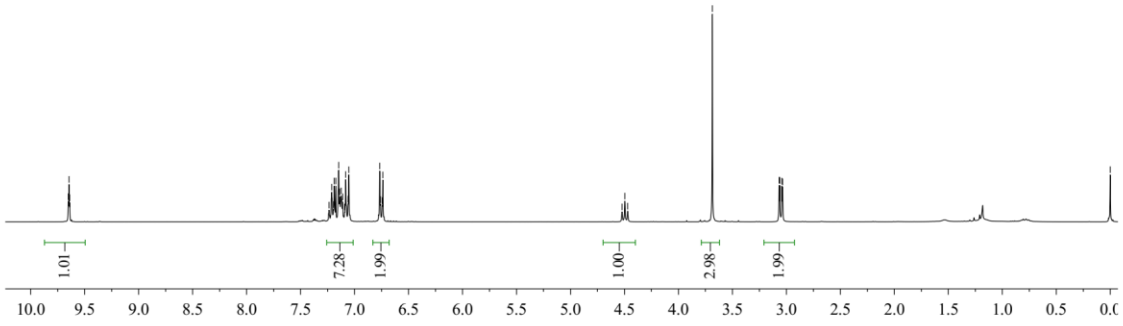
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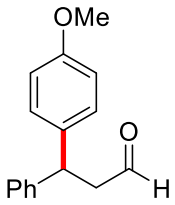
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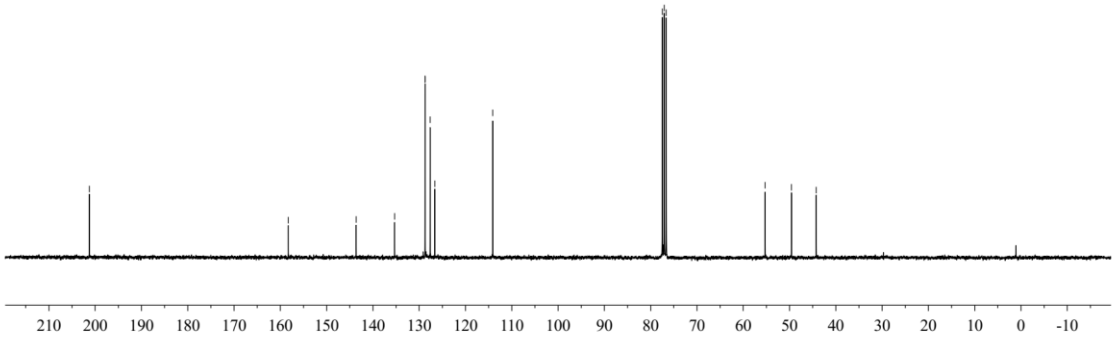
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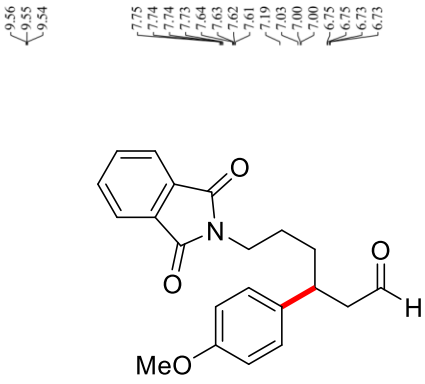
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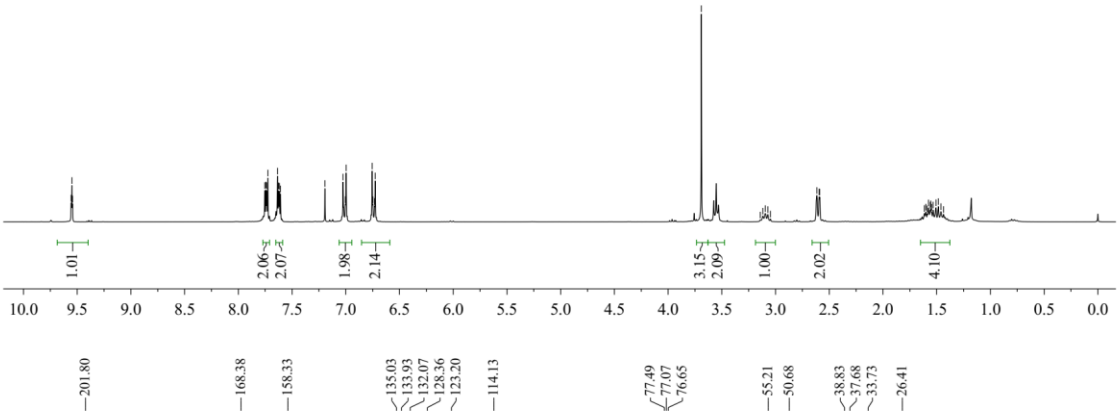
MeO

3j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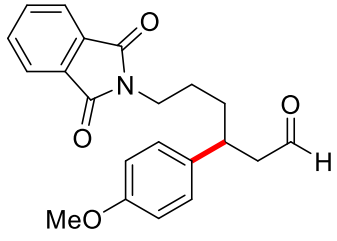
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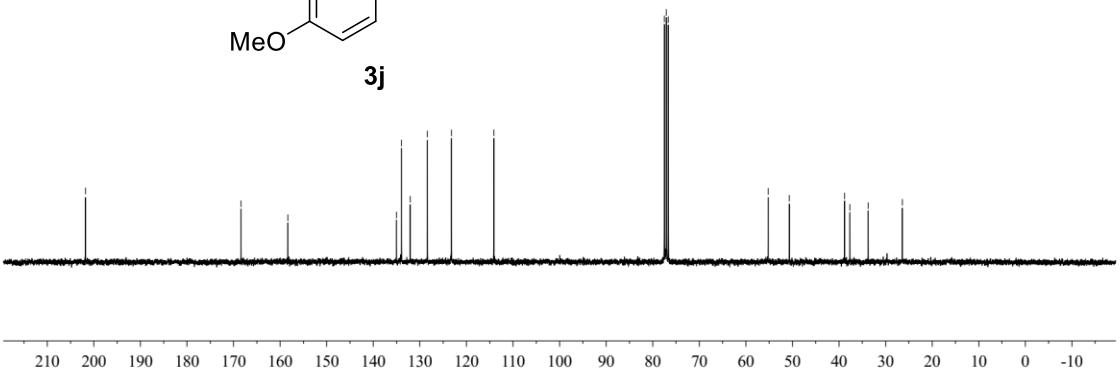
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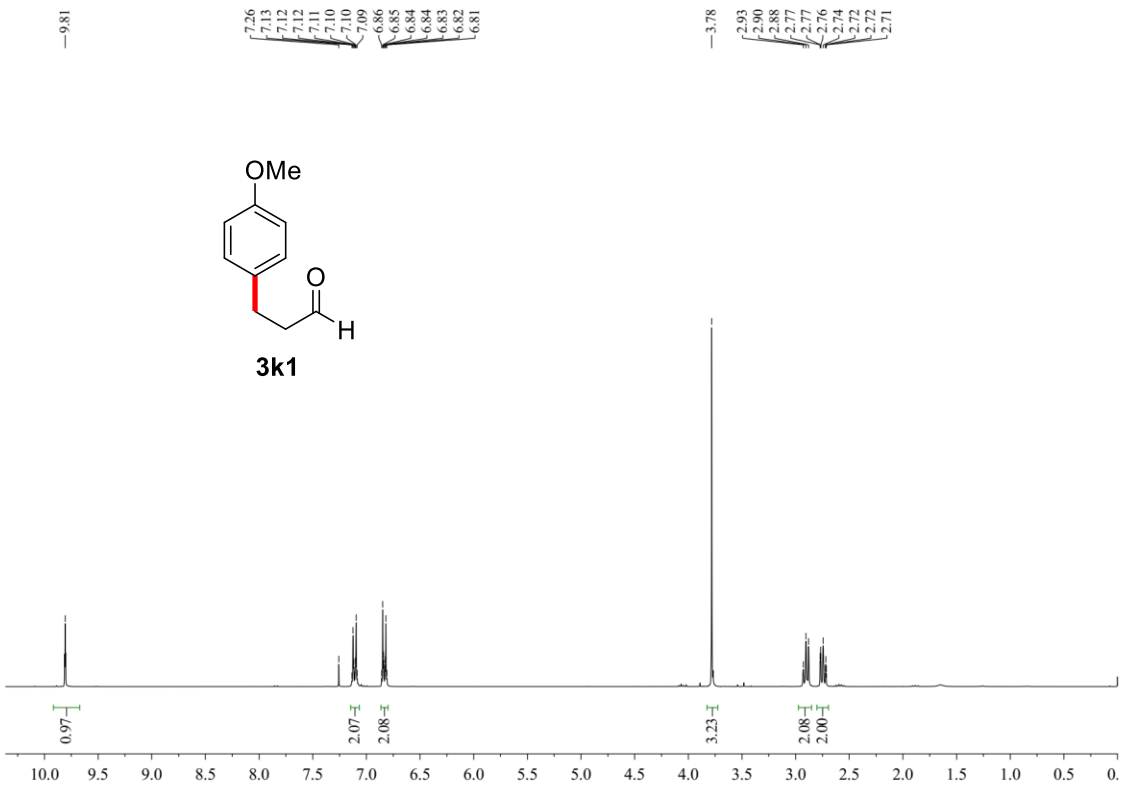
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OMe
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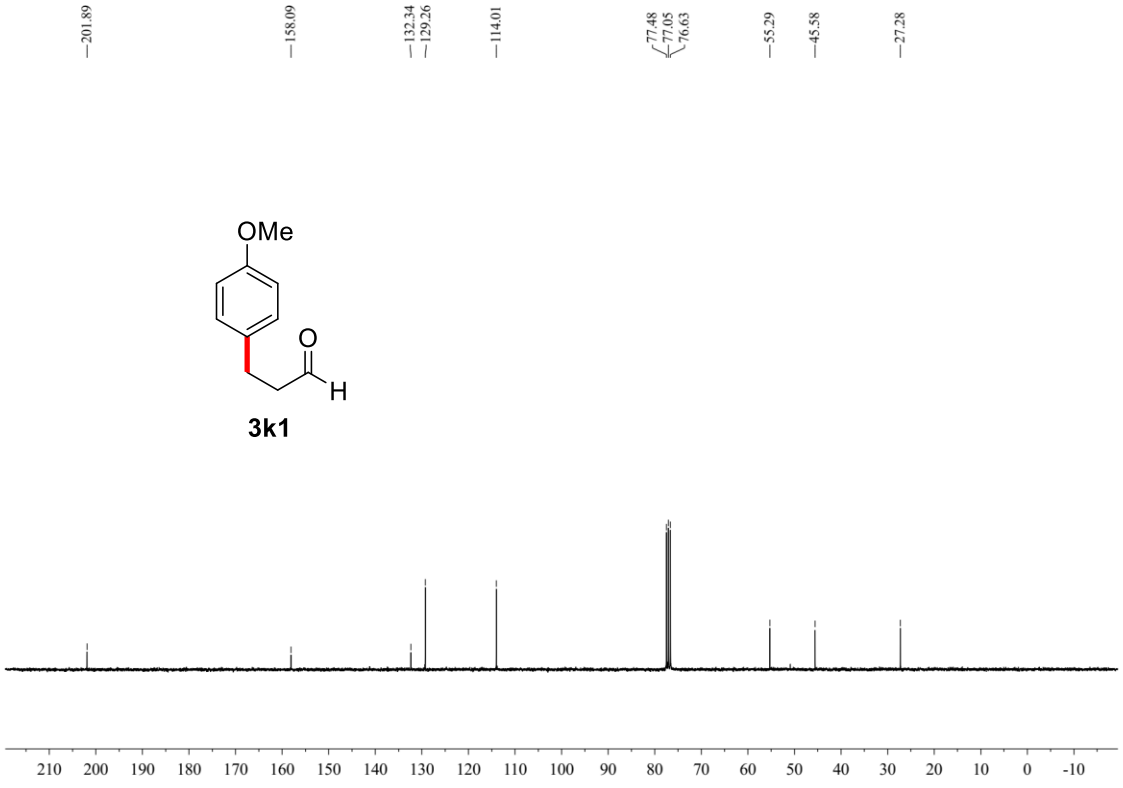
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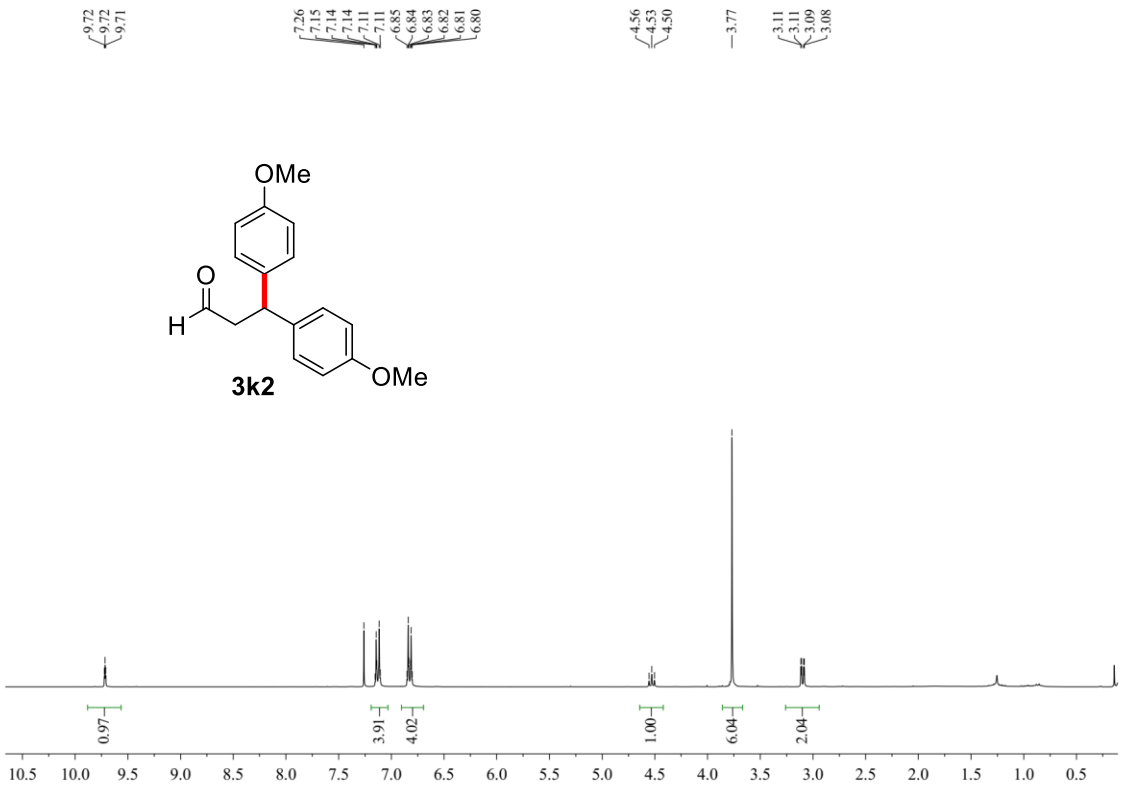
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3.11
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O
H
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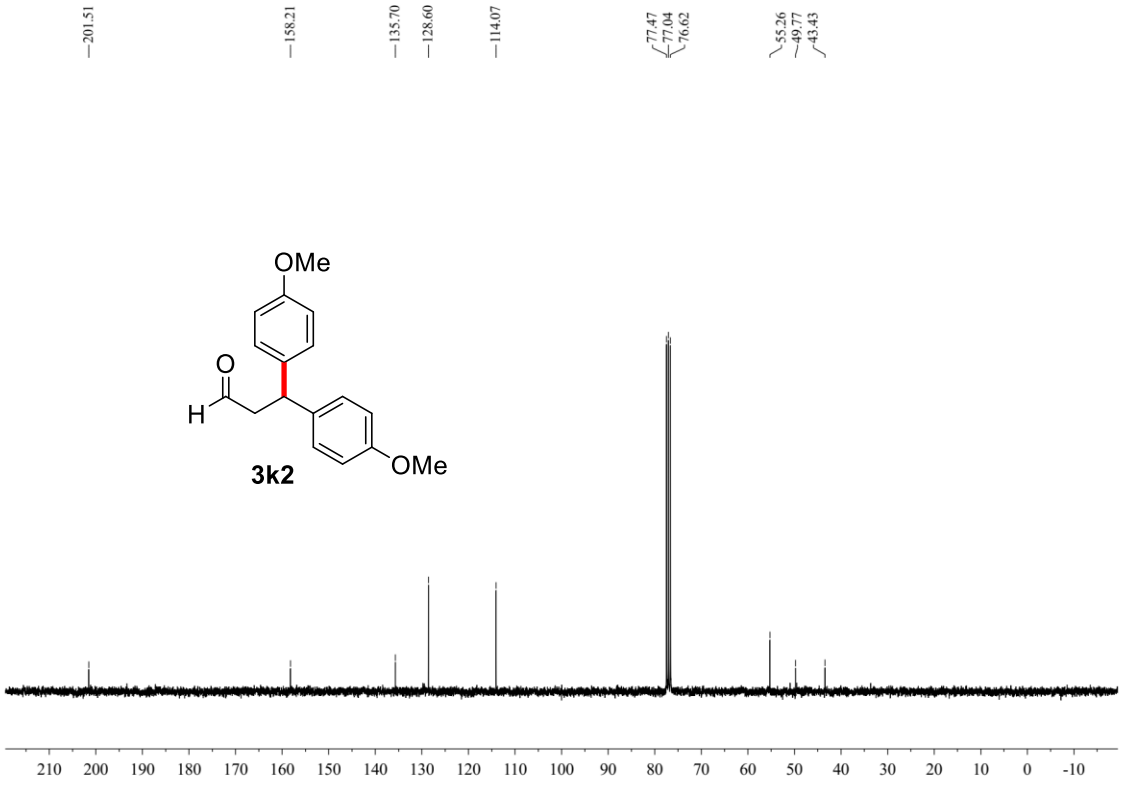
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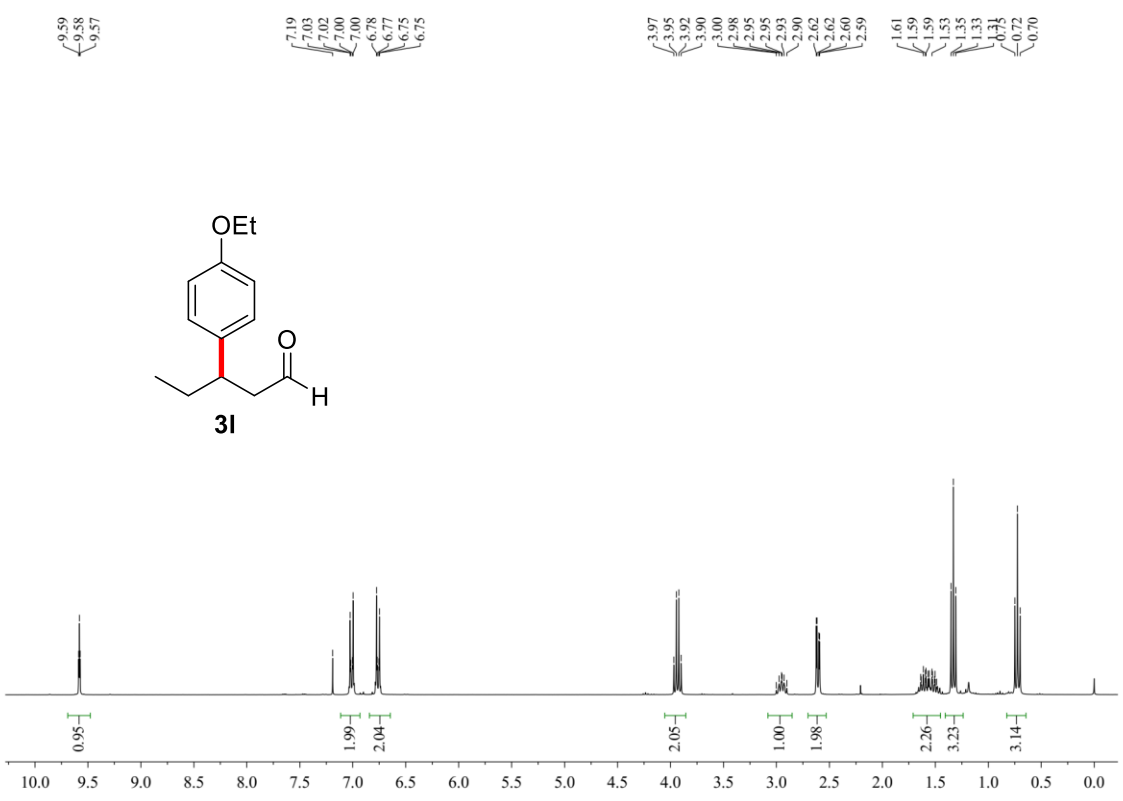
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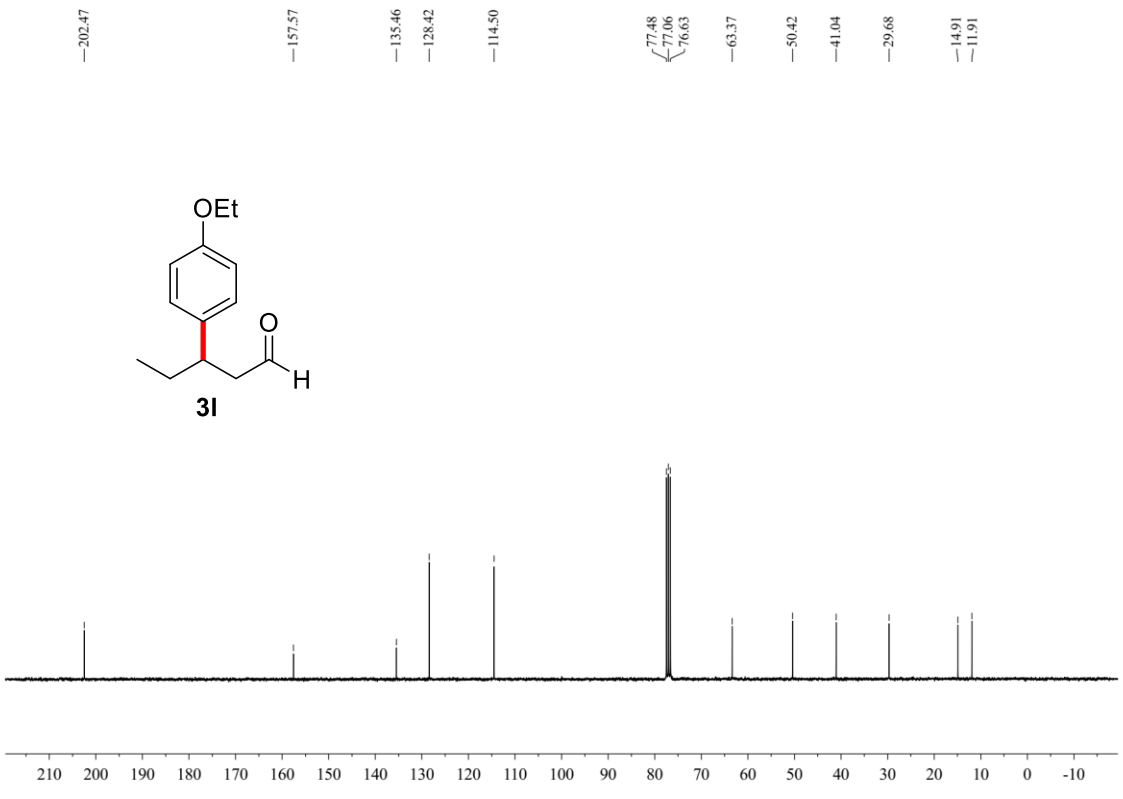
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O
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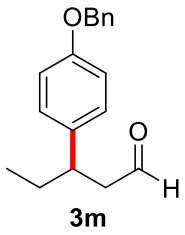
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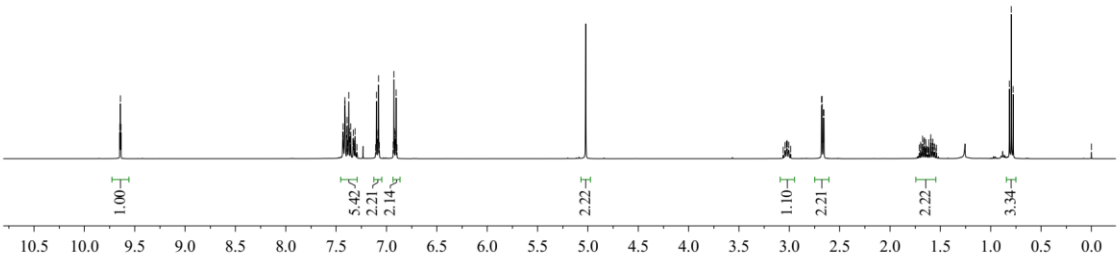
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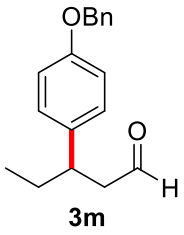
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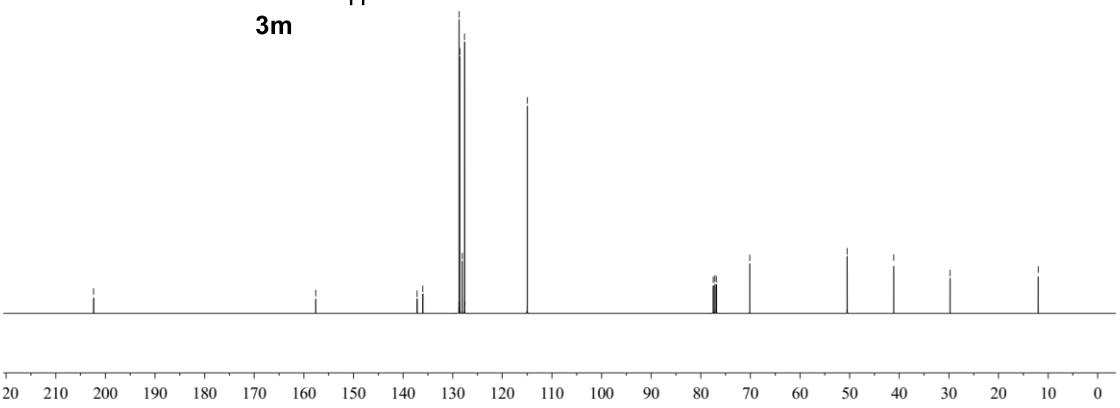
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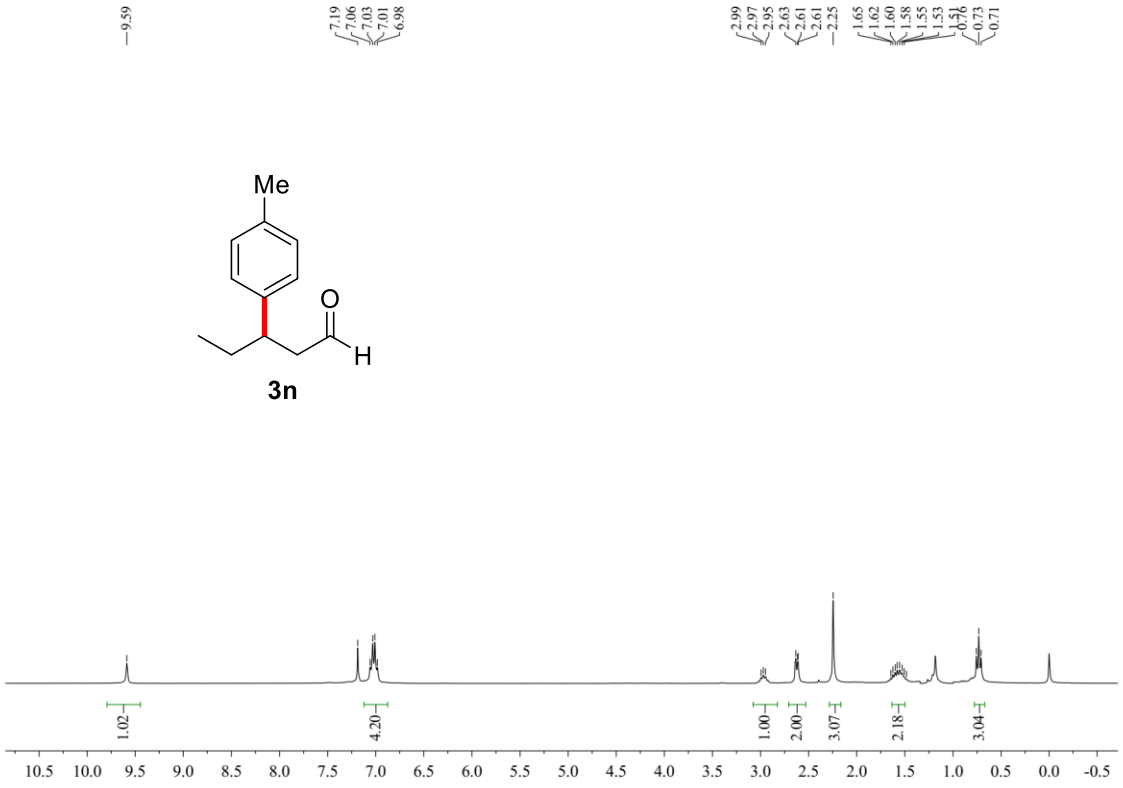
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2.00
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3.04
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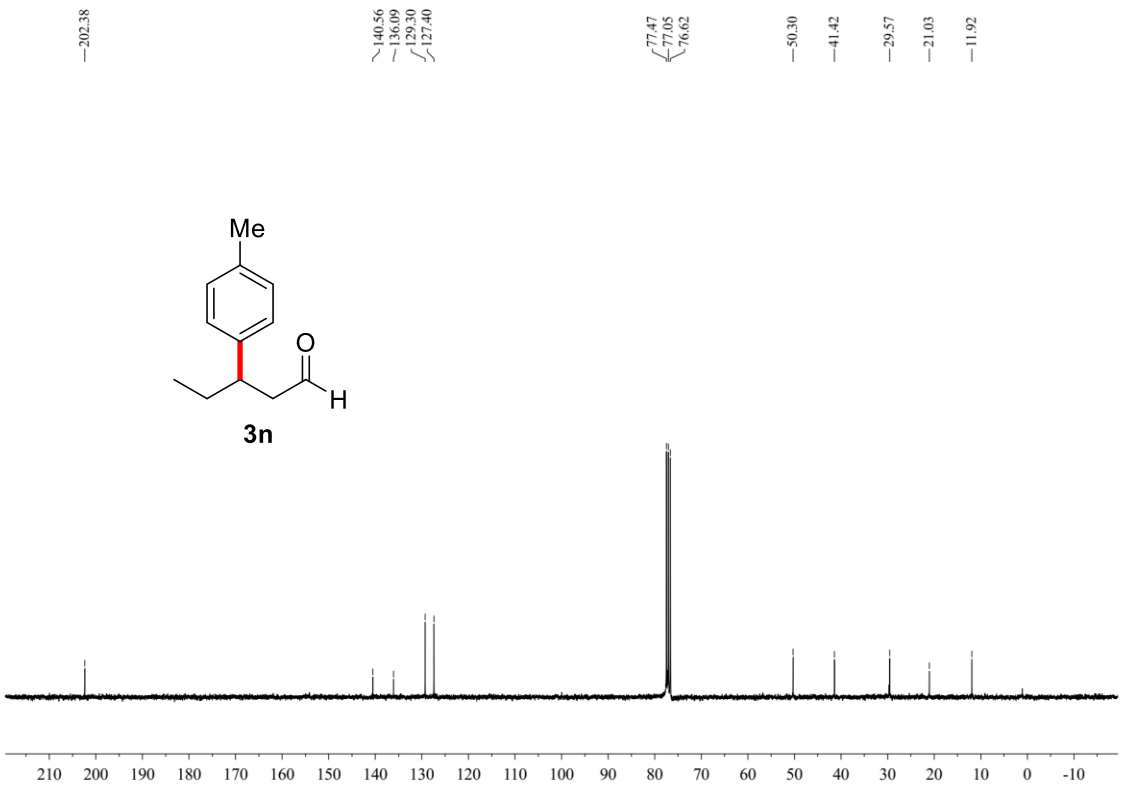
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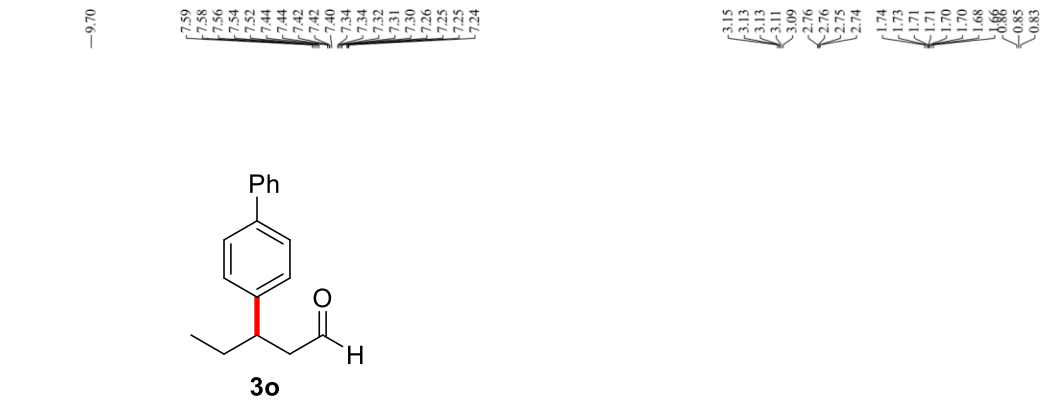
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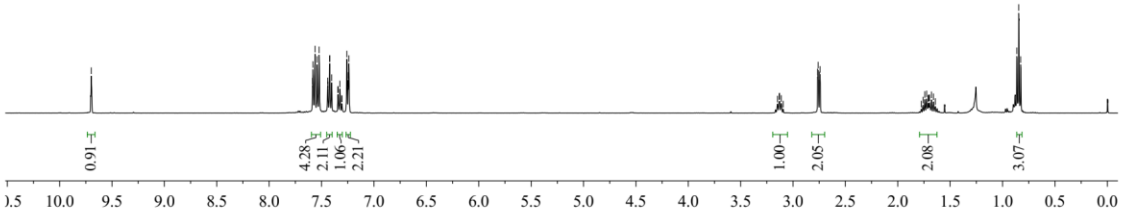
Ph
O
H

3o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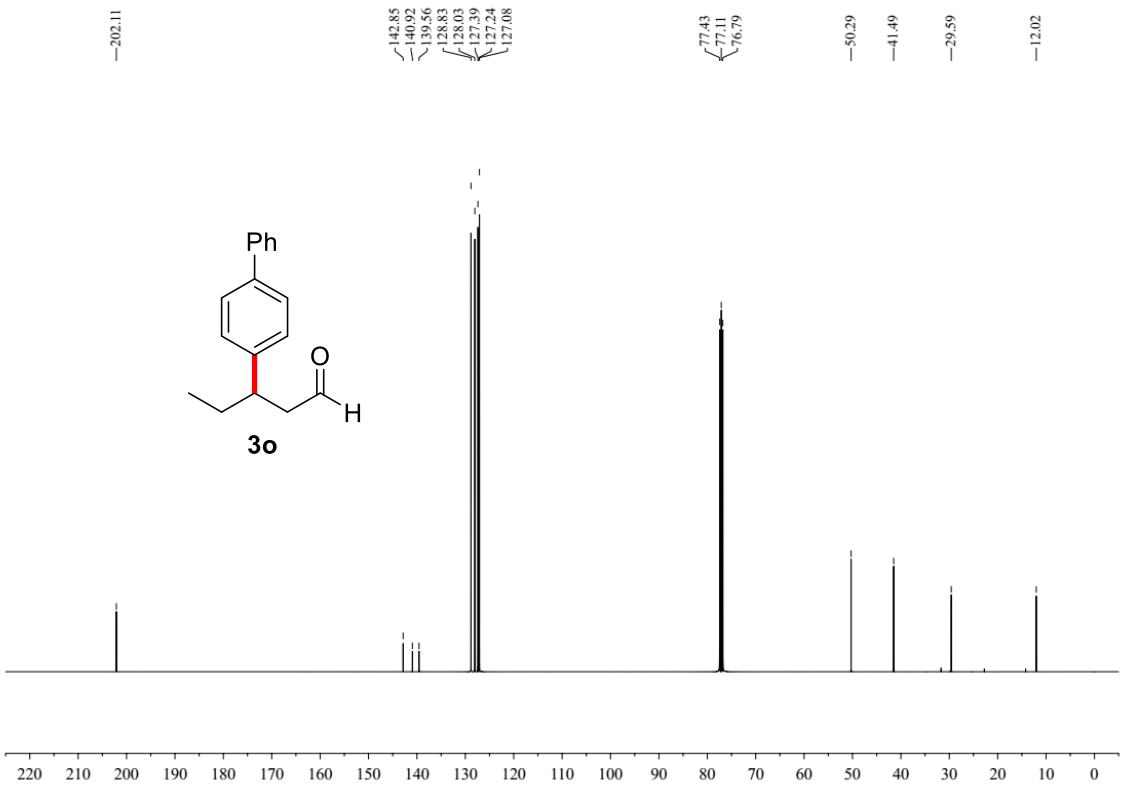
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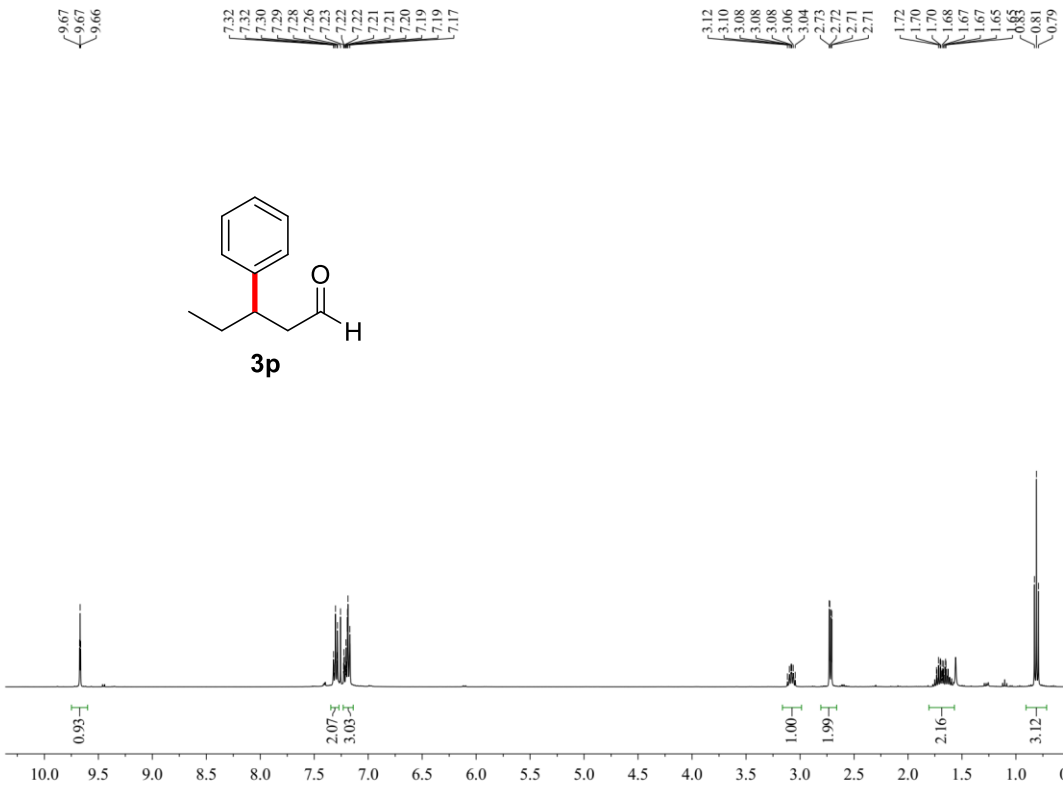
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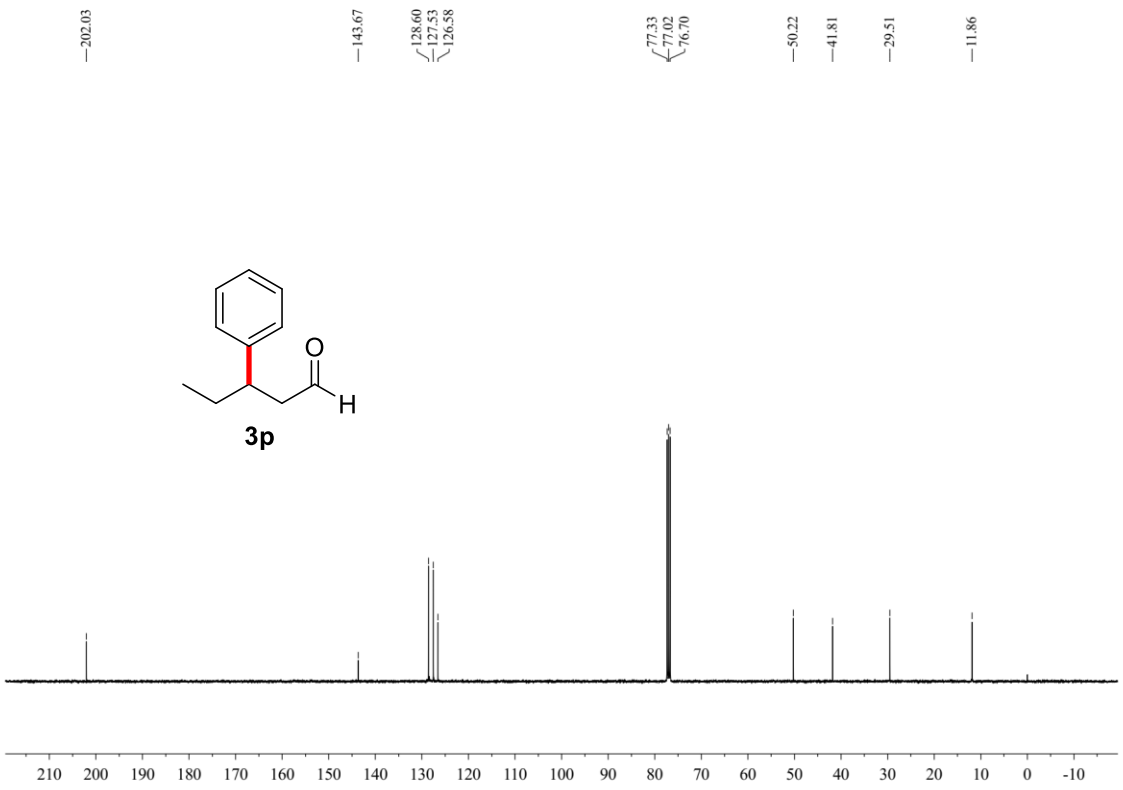
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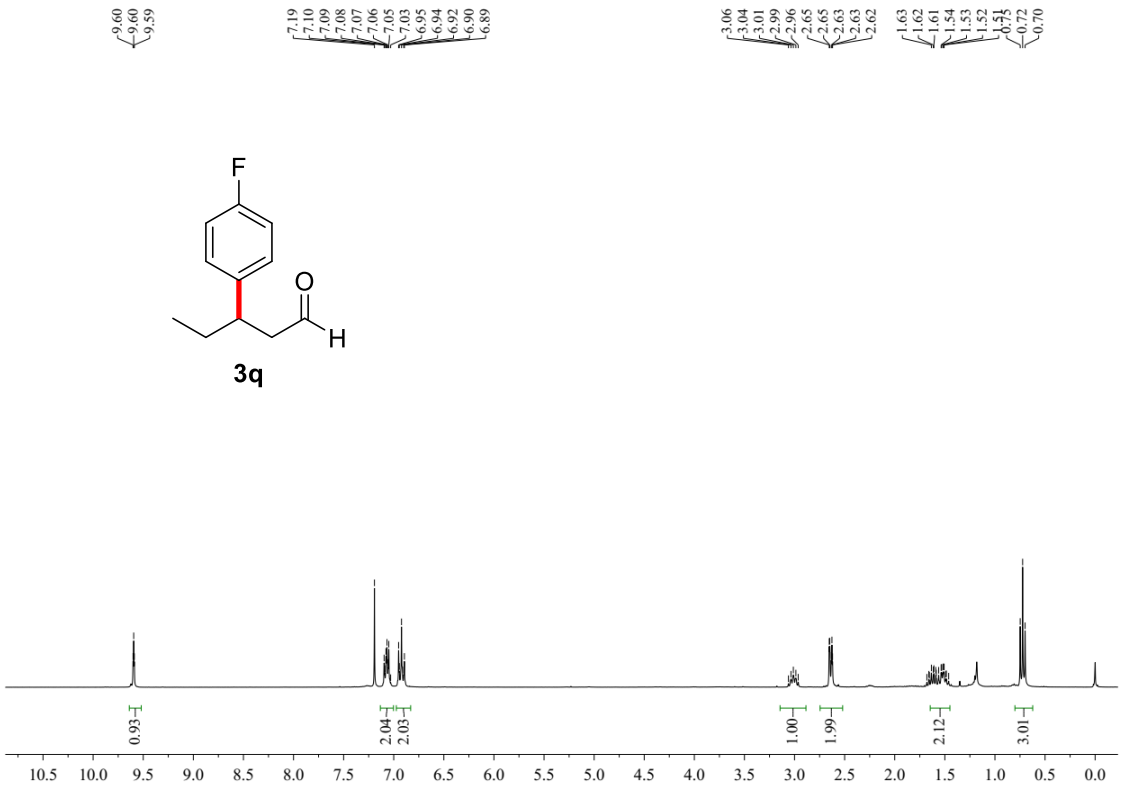
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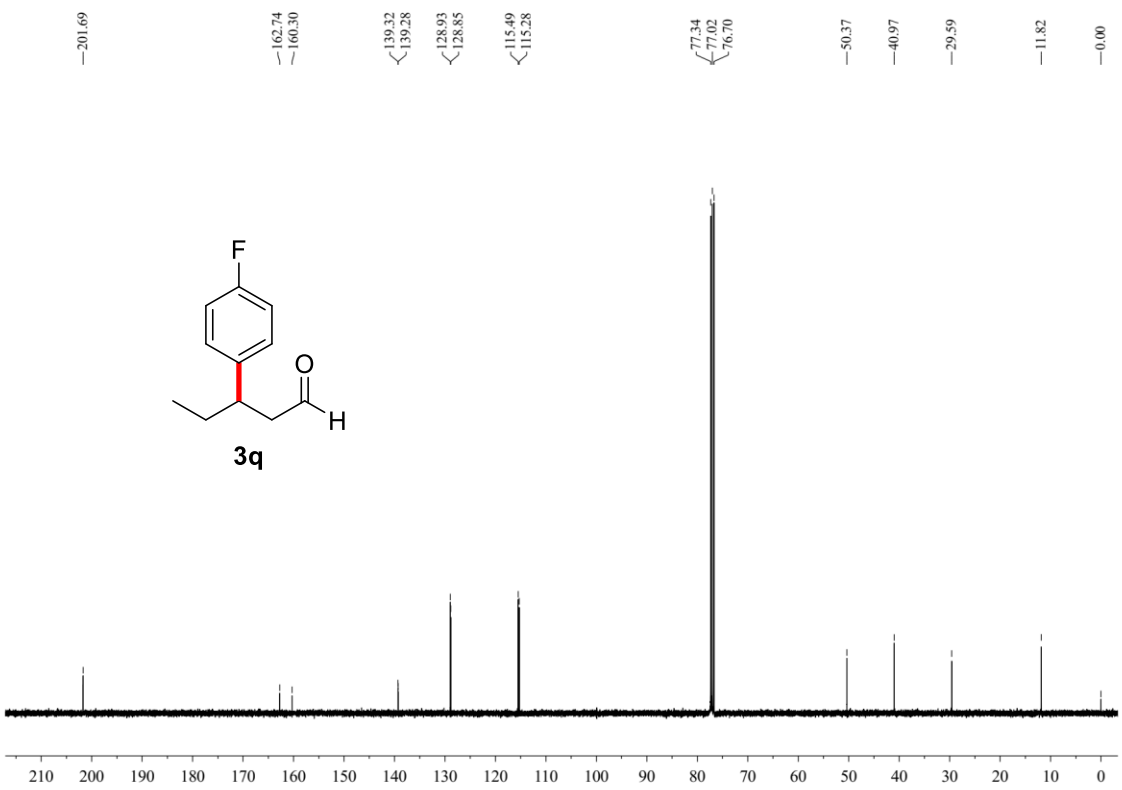
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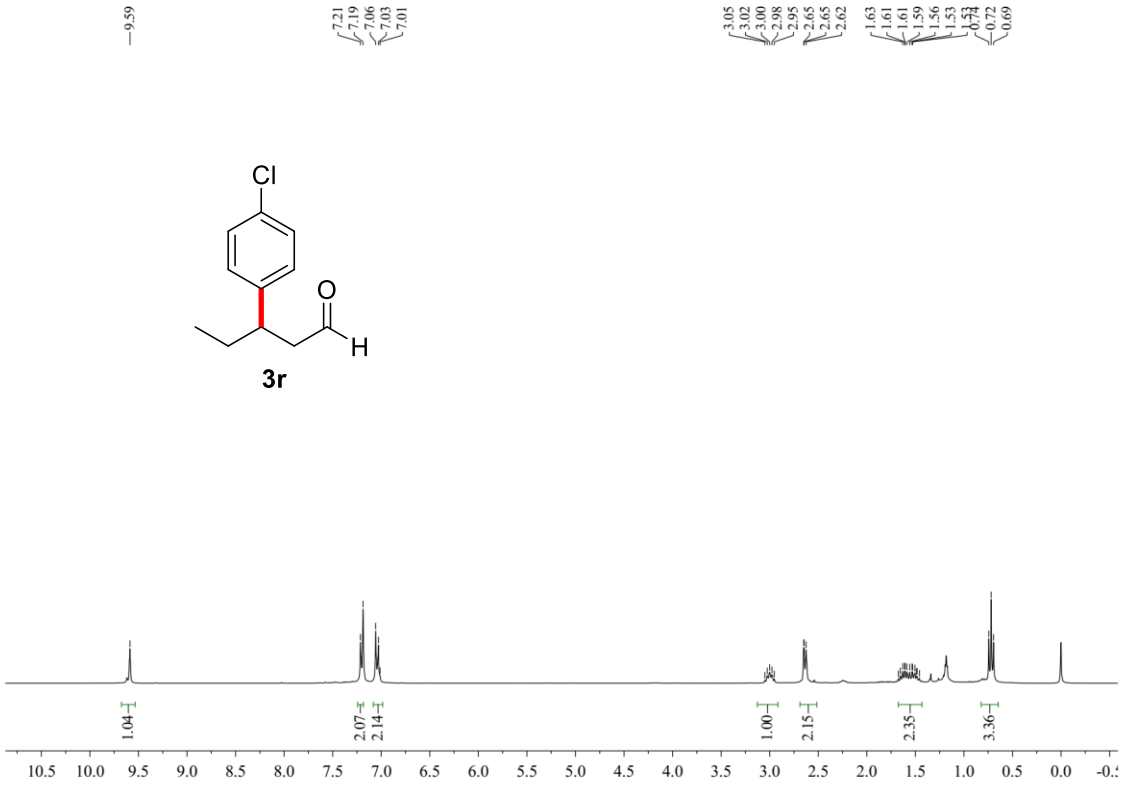
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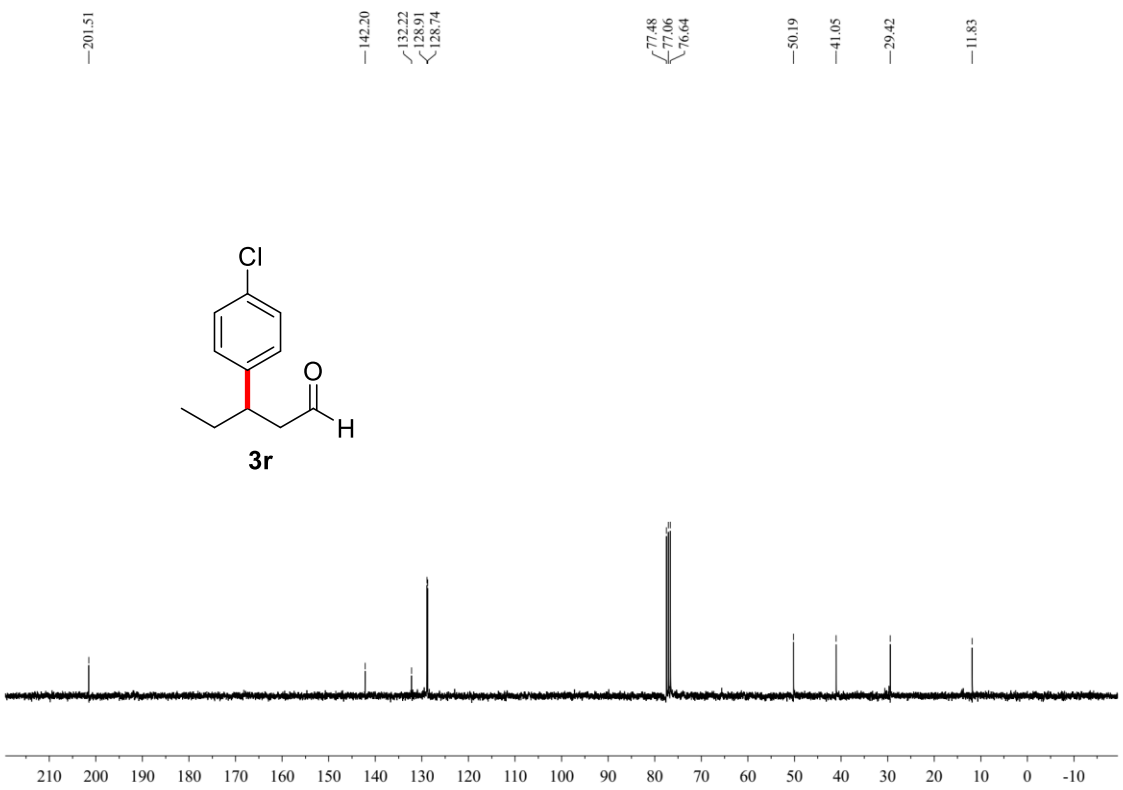
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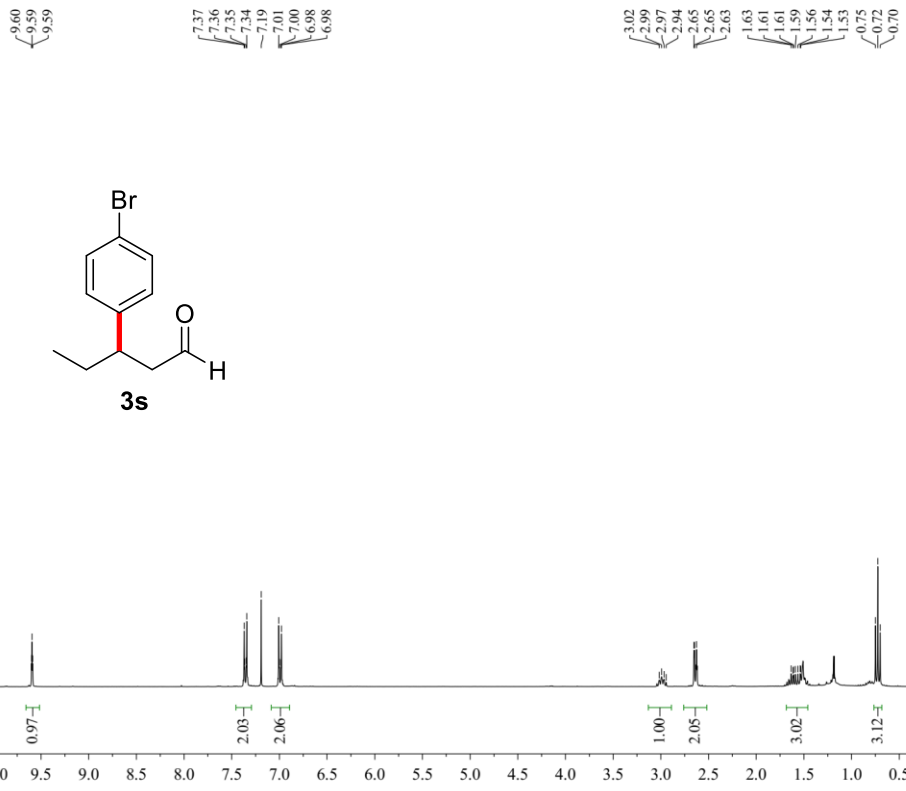
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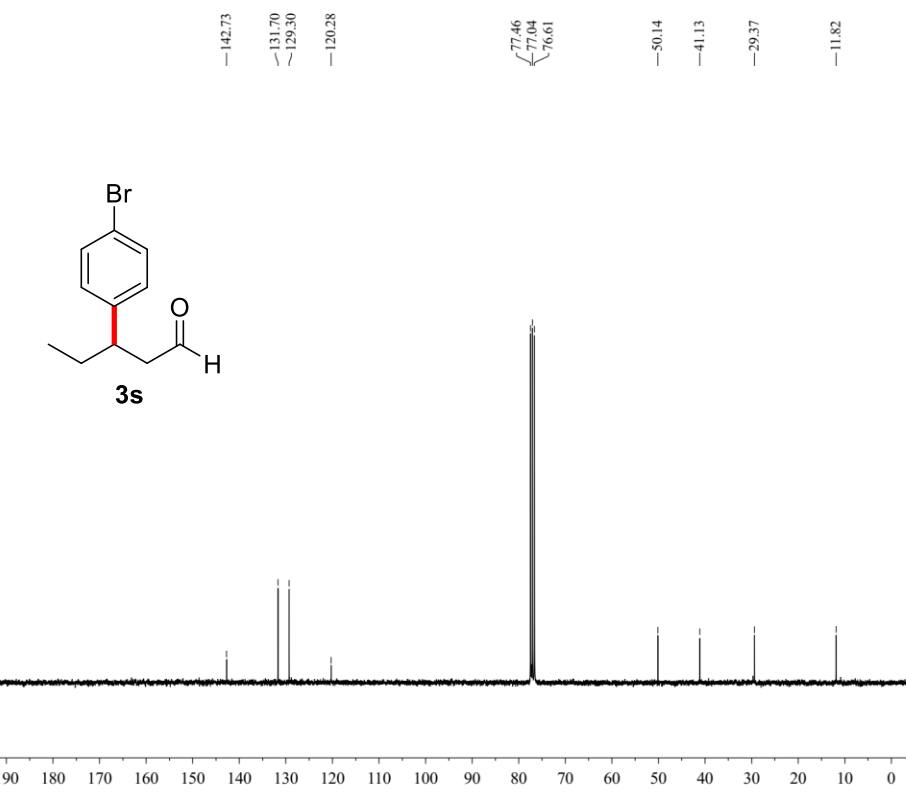
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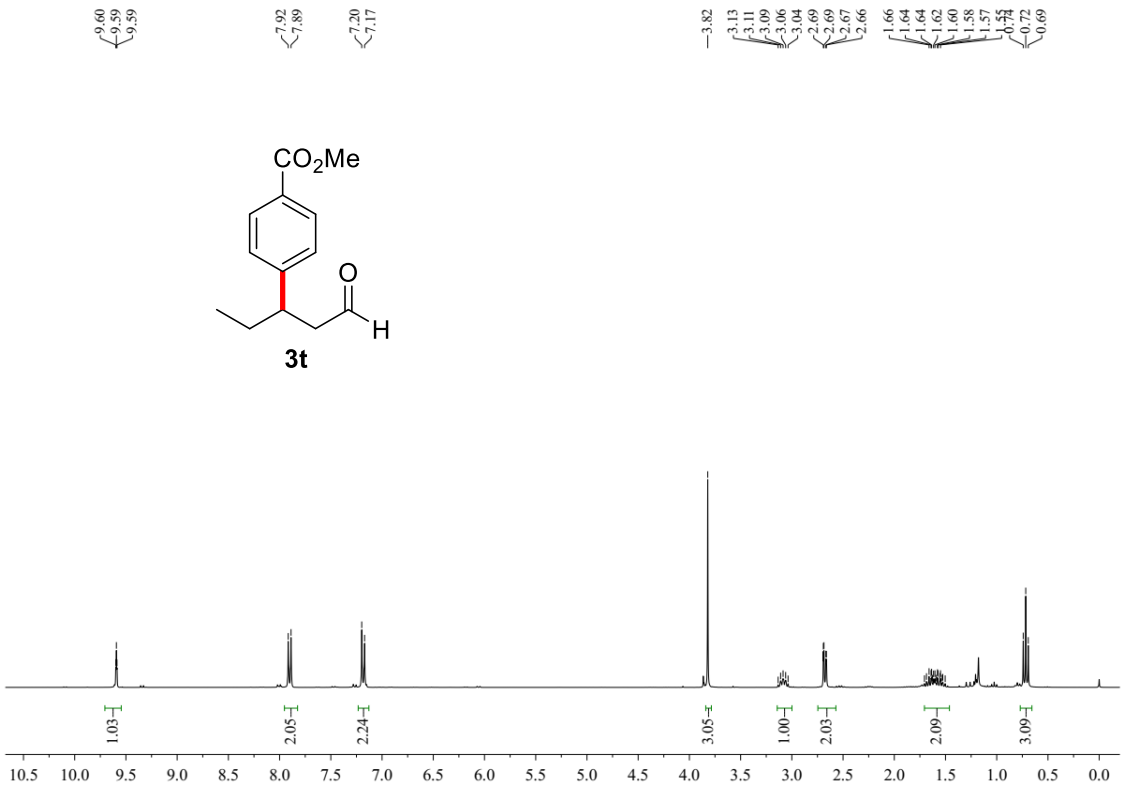
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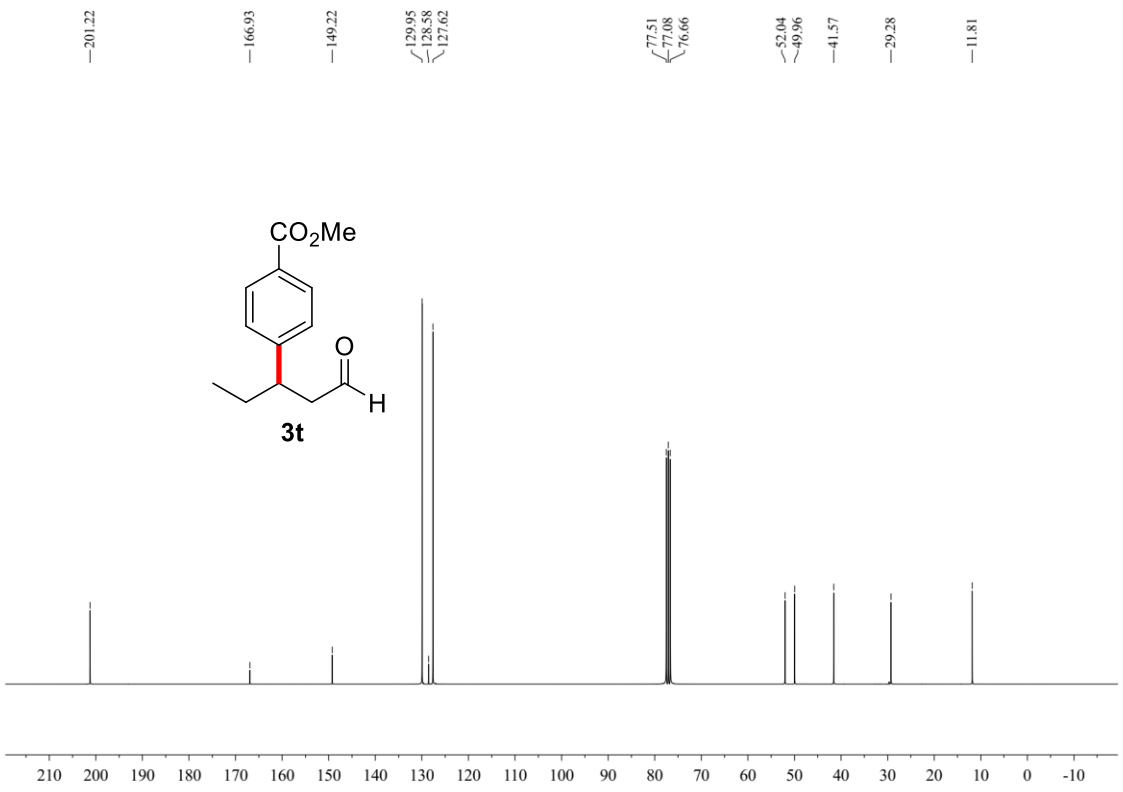
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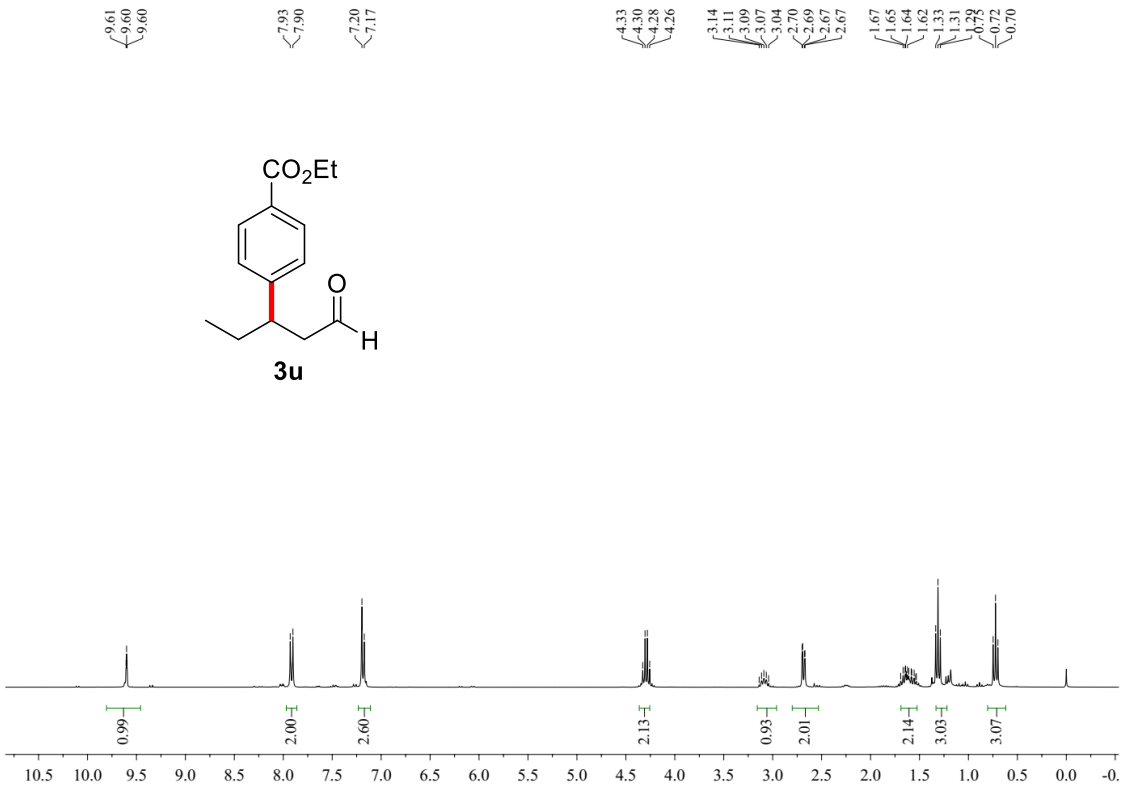
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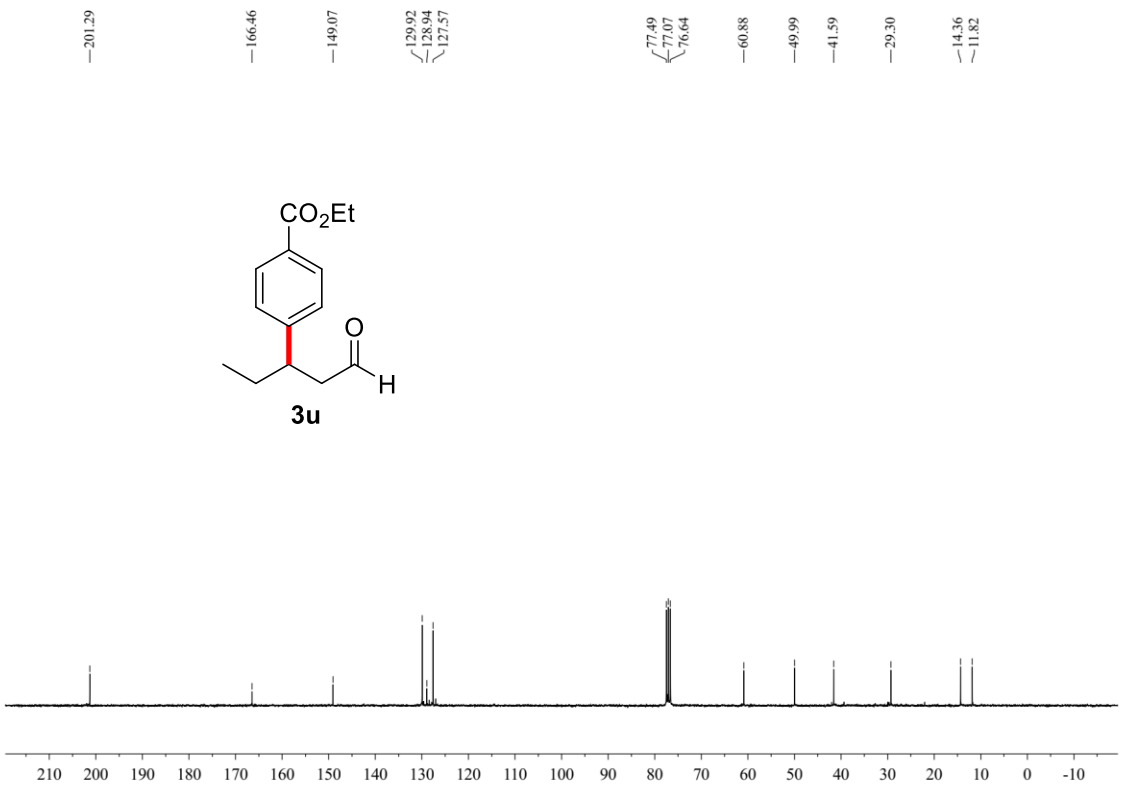
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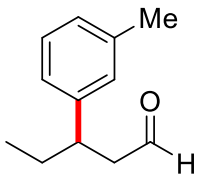

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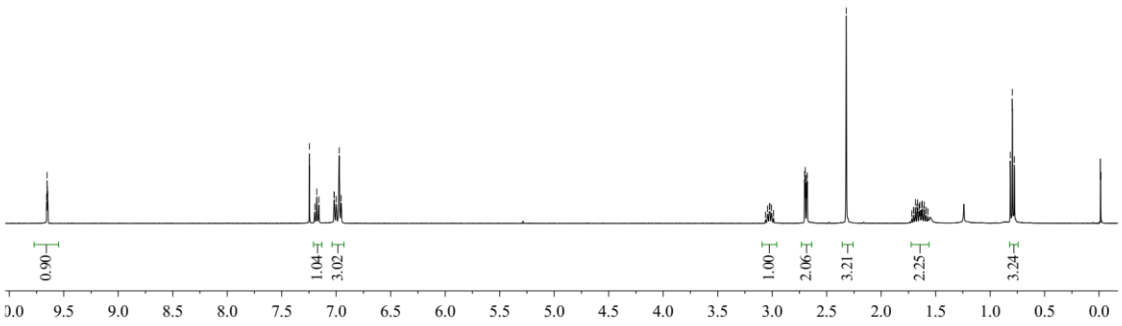

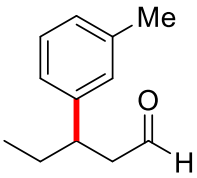

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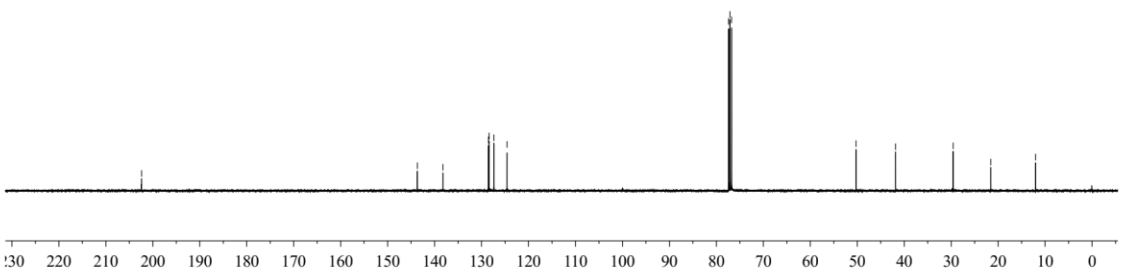

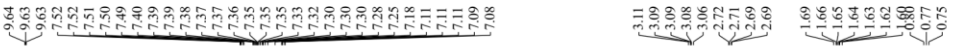
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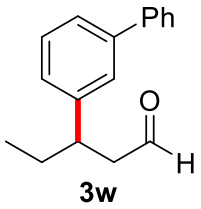
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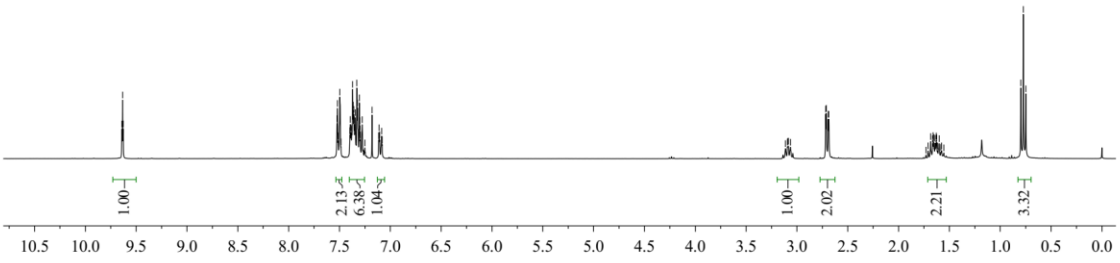
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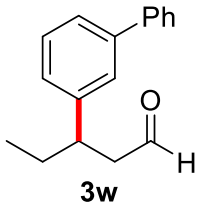
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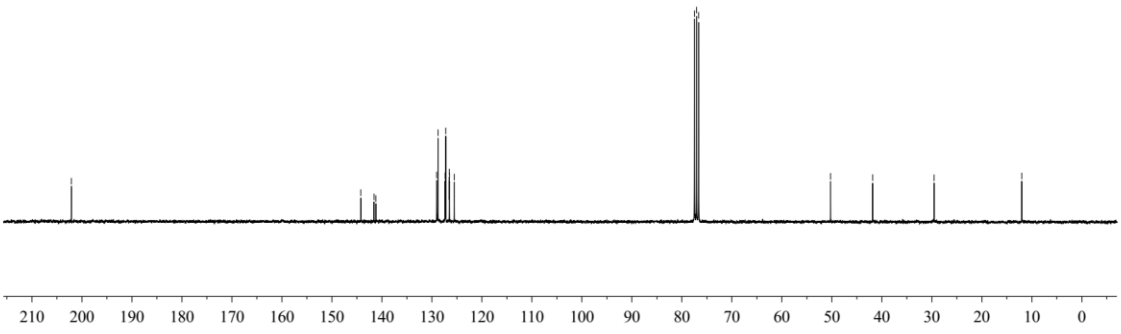
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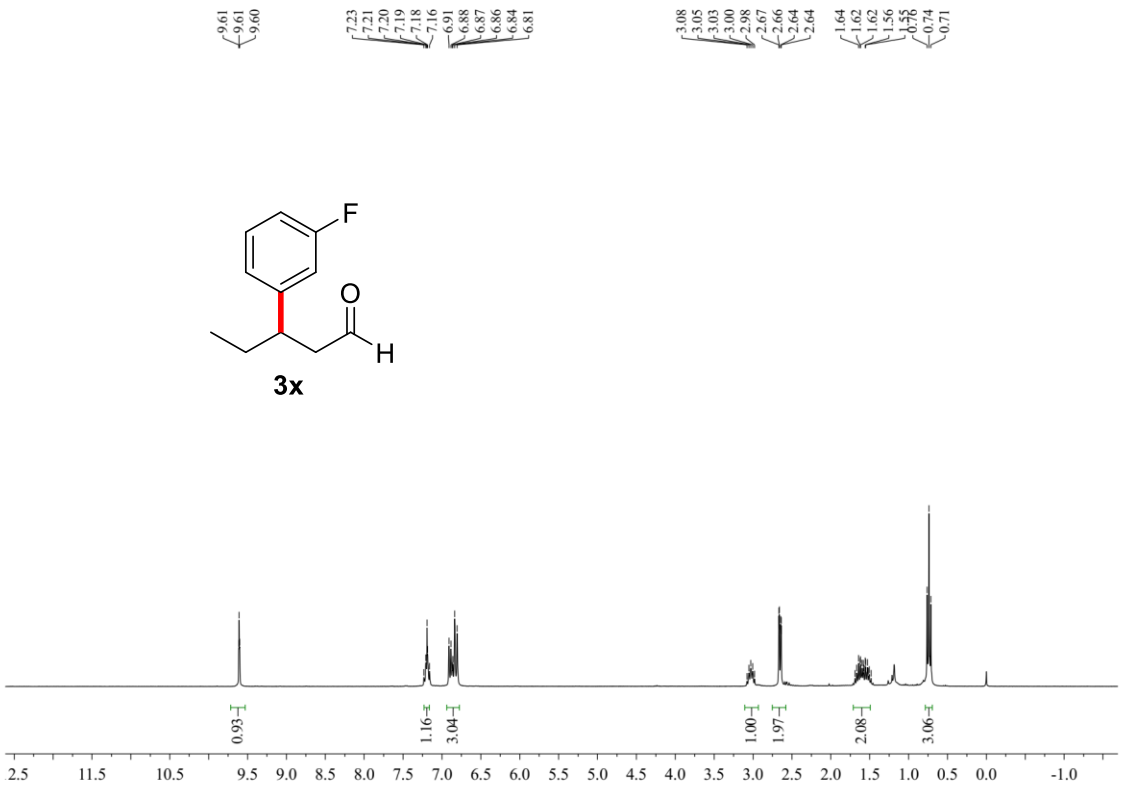
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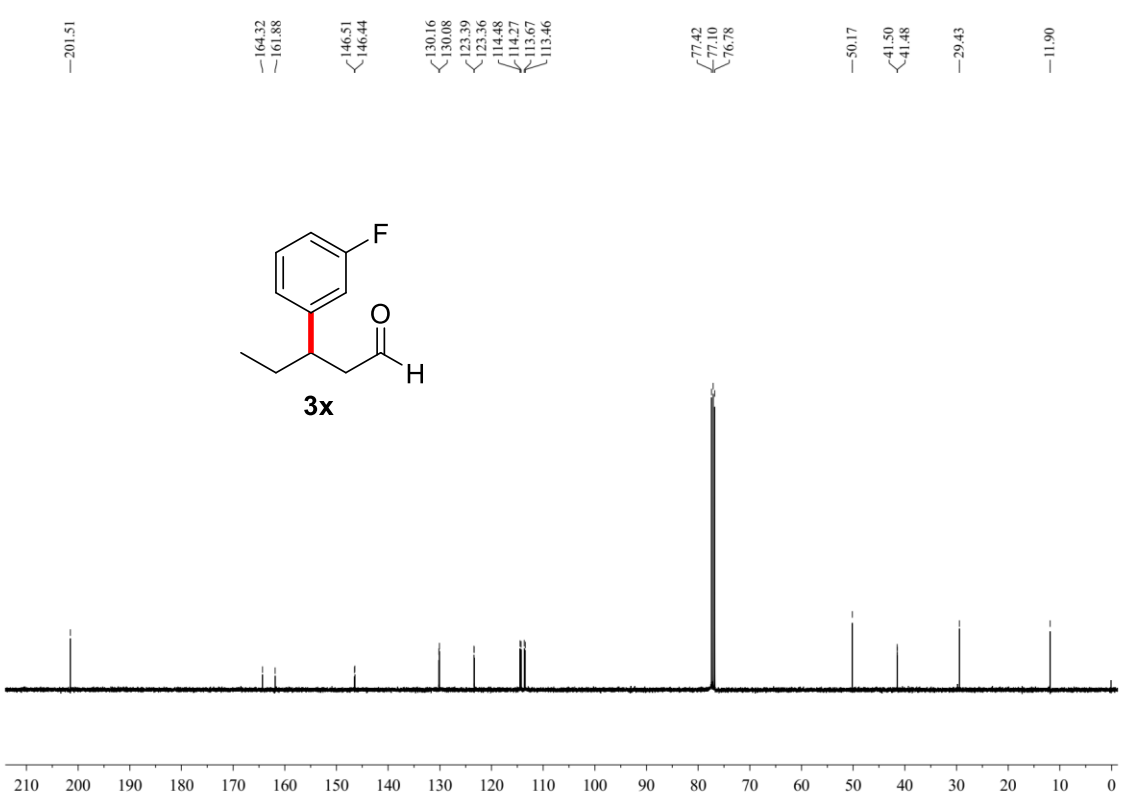
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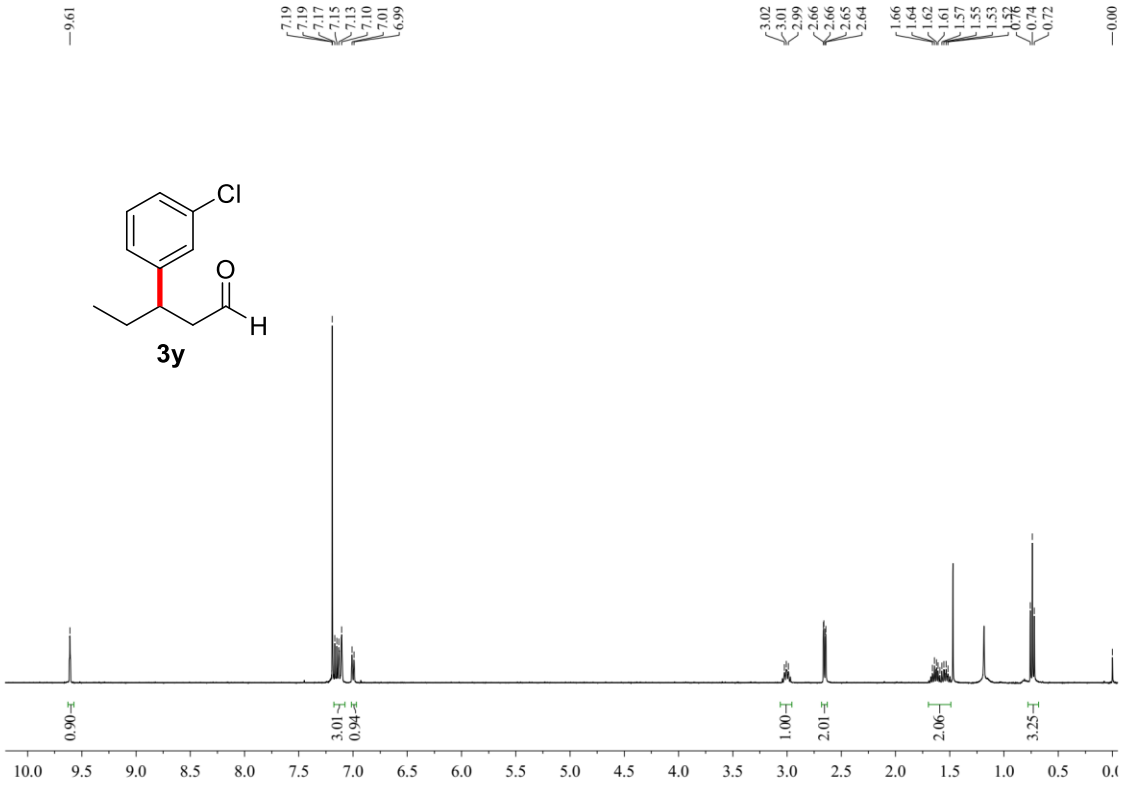
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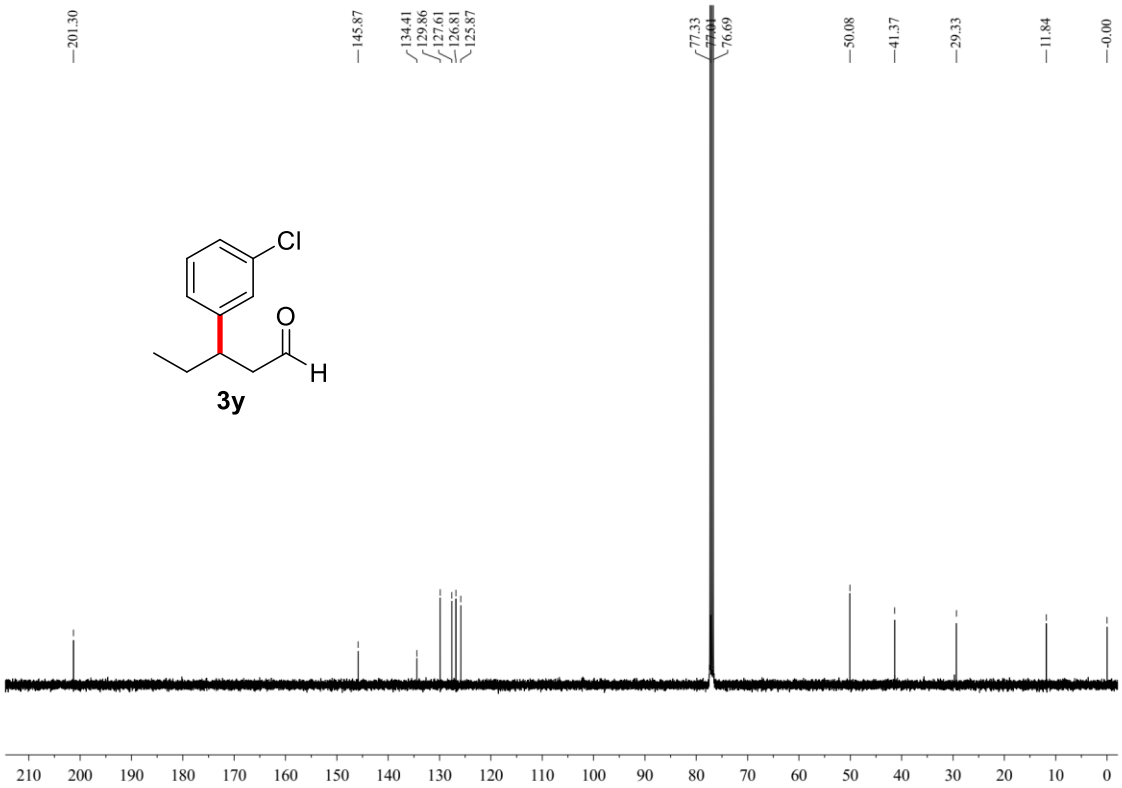
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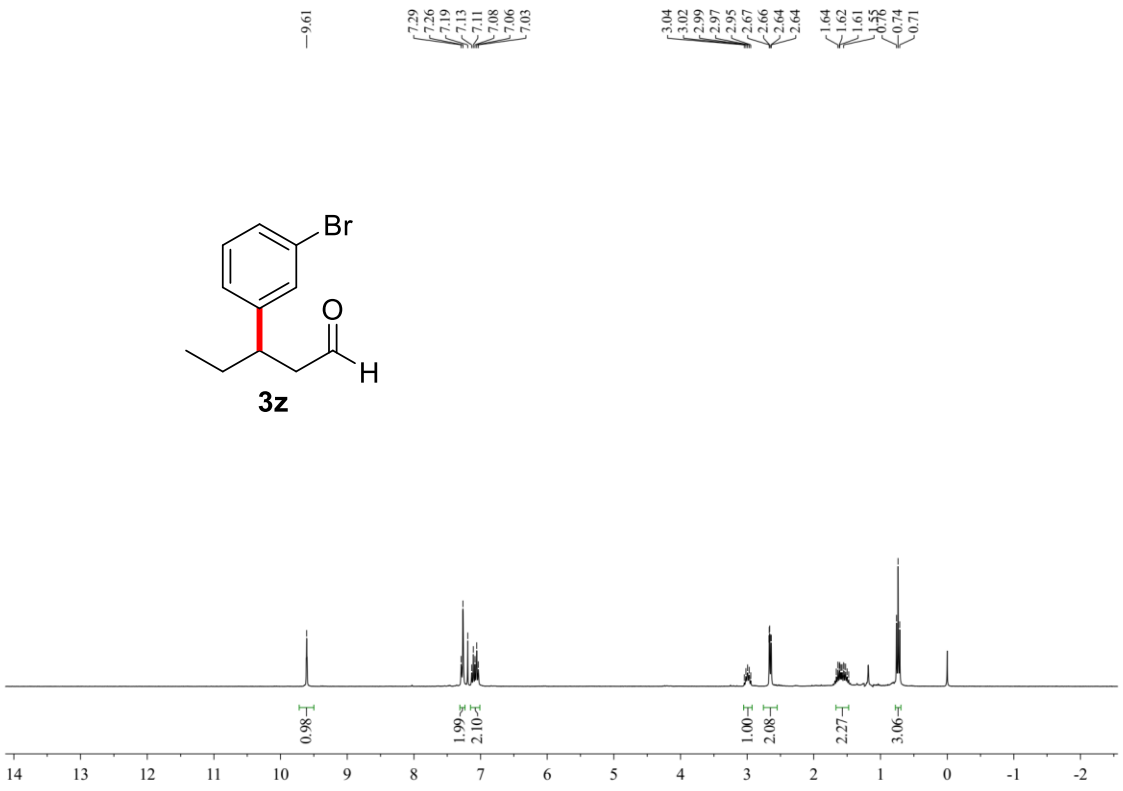
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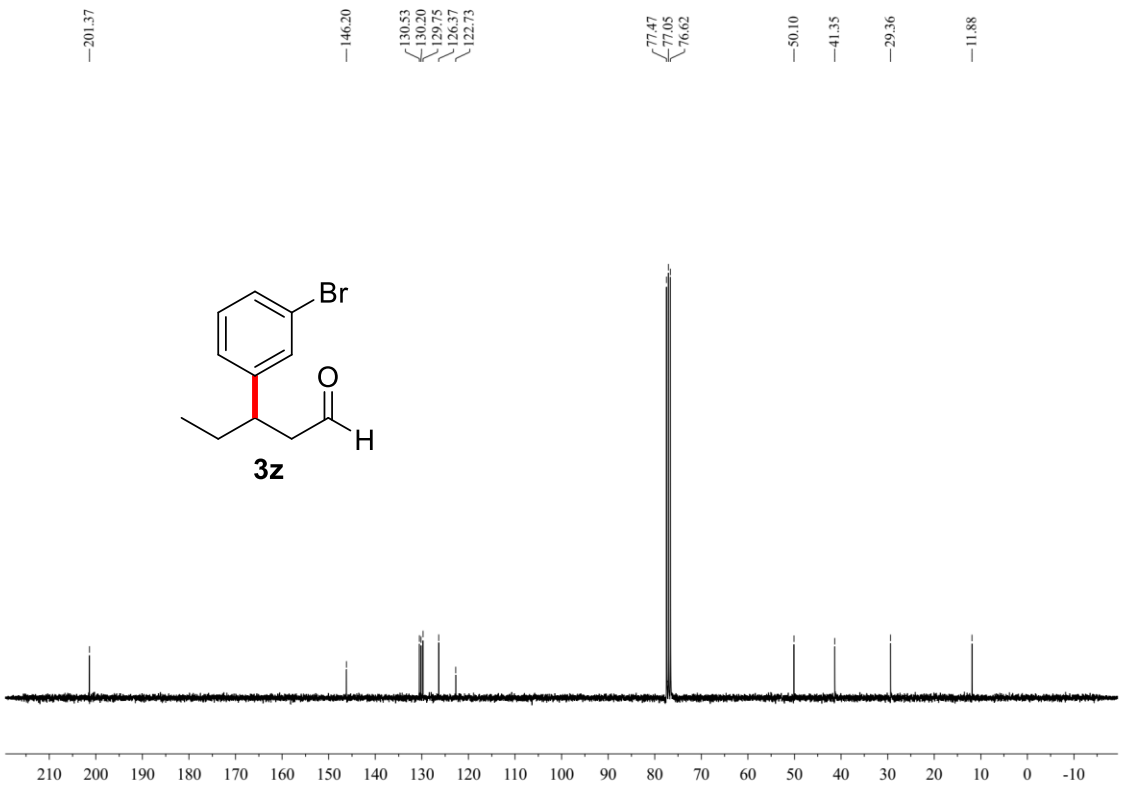
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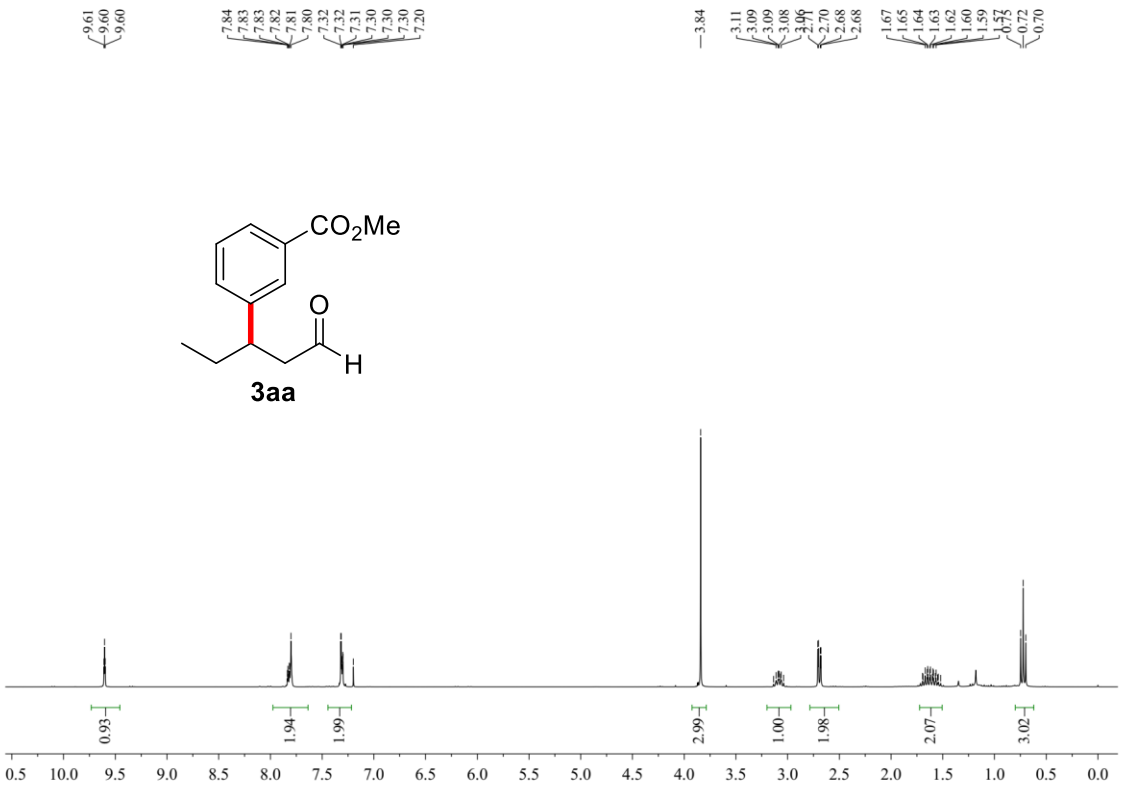
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7.30
7.20
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3.09
3.08
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2.68
1.67
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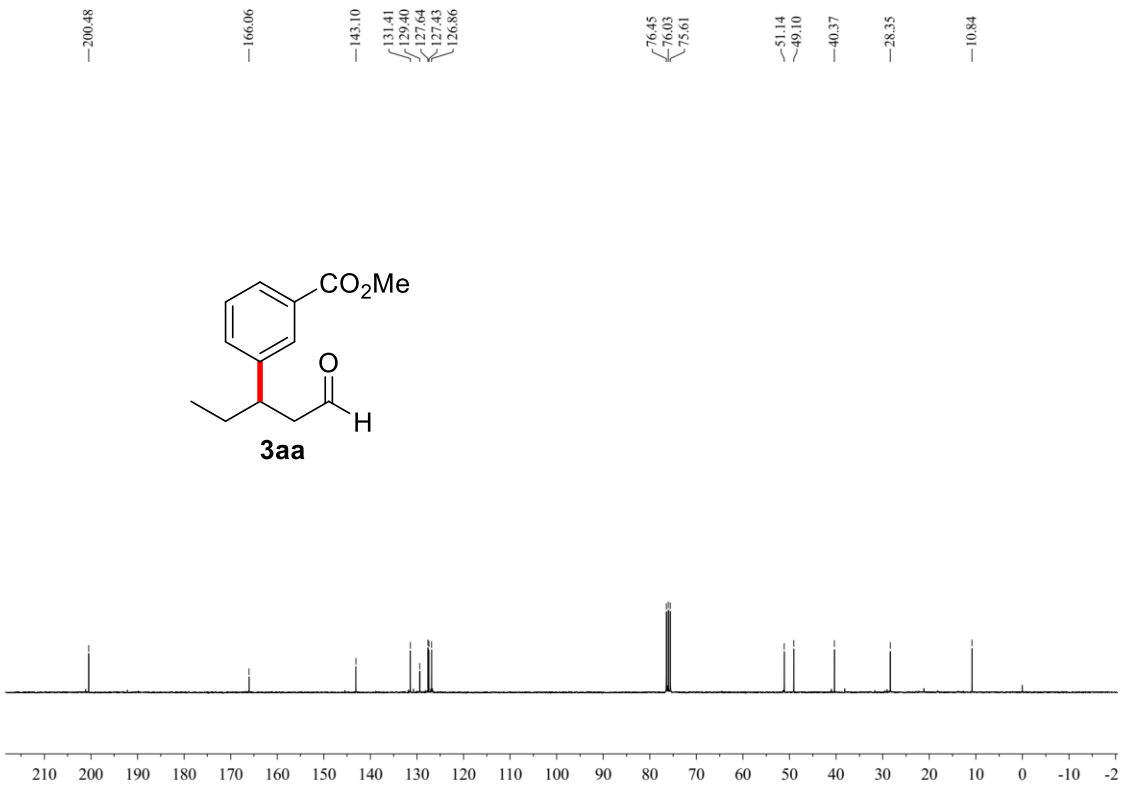
1.64
1.63
1.62
1.60
1.59
0.72
0.70
CO2Me
O
H
3aa
0.93
1.94
1.99
2.99
1.00
1.98
2.07
3.02
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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CO2Me
O
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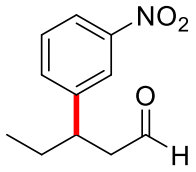
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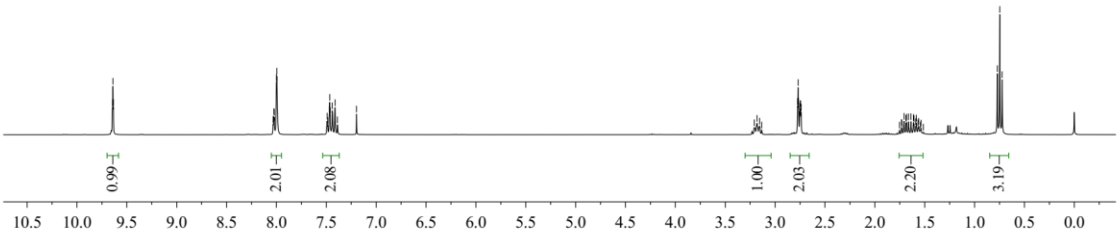
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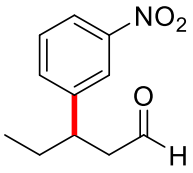
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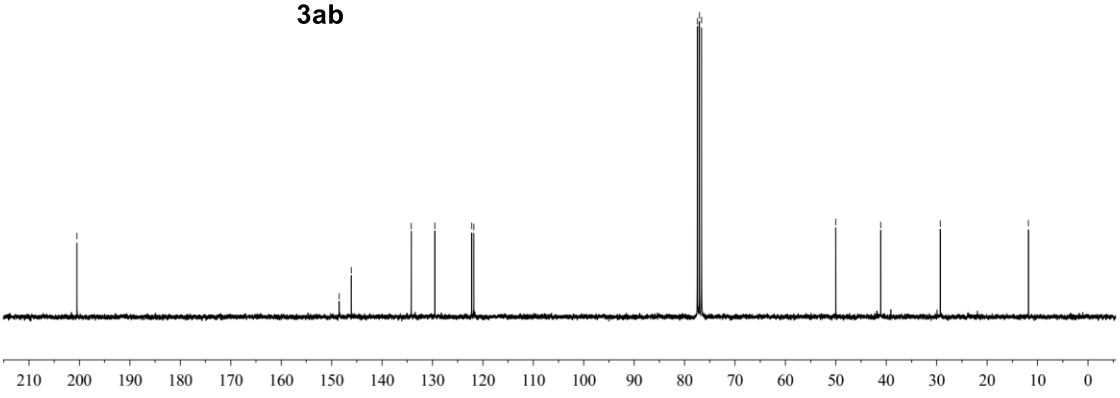
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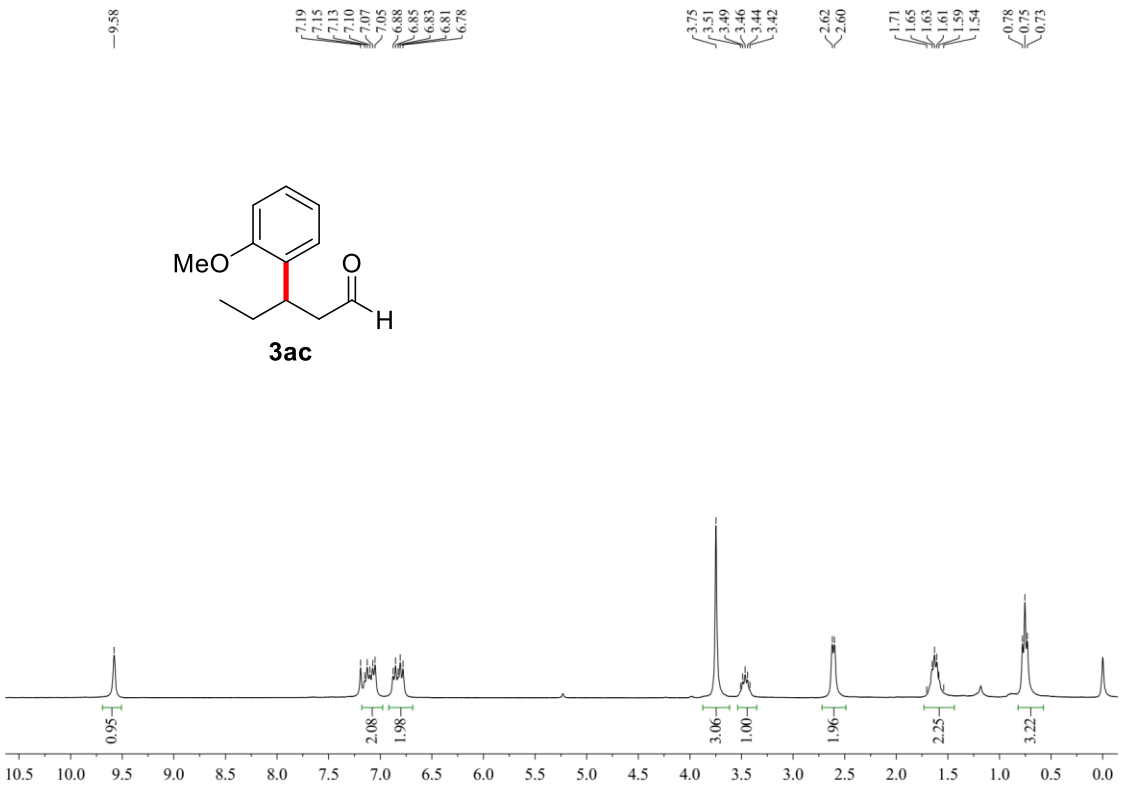
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3.51
3.49
3.46
3.44
3.42
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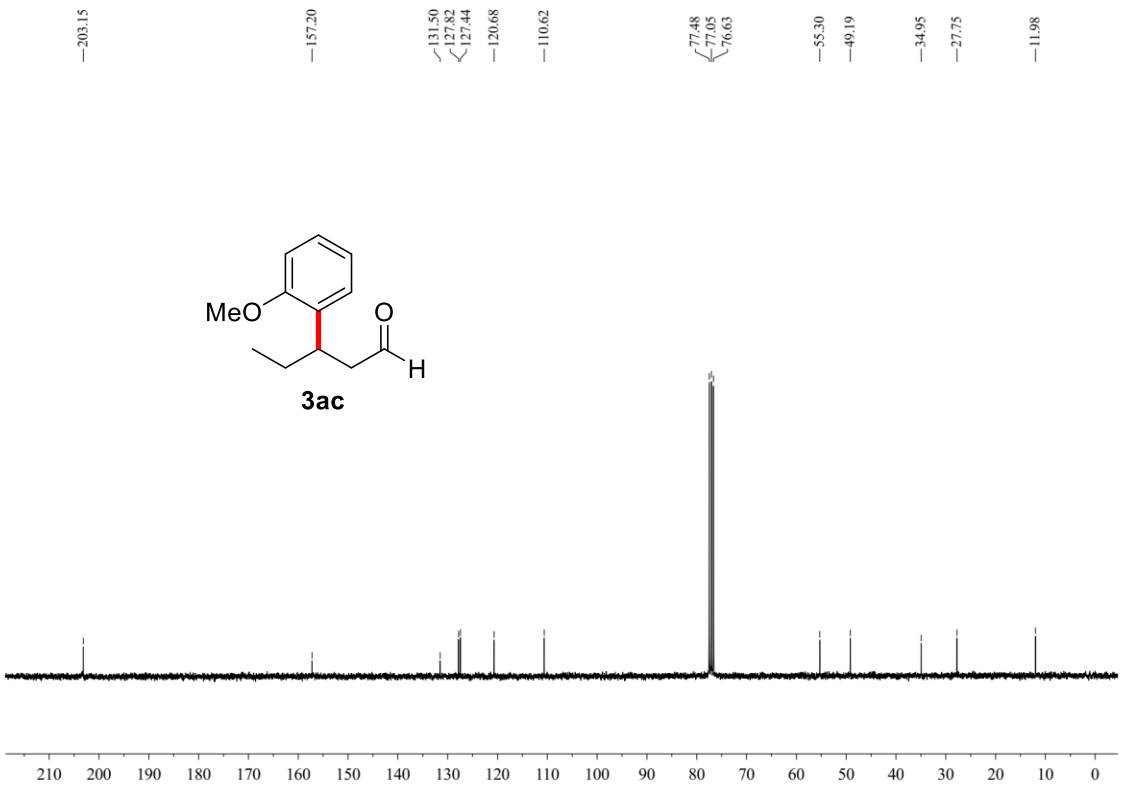
2.60
1.71
1.65
1.63
1.61
1.59
1.54
0.78
0.75
0.73
MeO
O
H
3ac
0.95
2.08
1.98
3.06
1.00
1.96
2.25
3.22
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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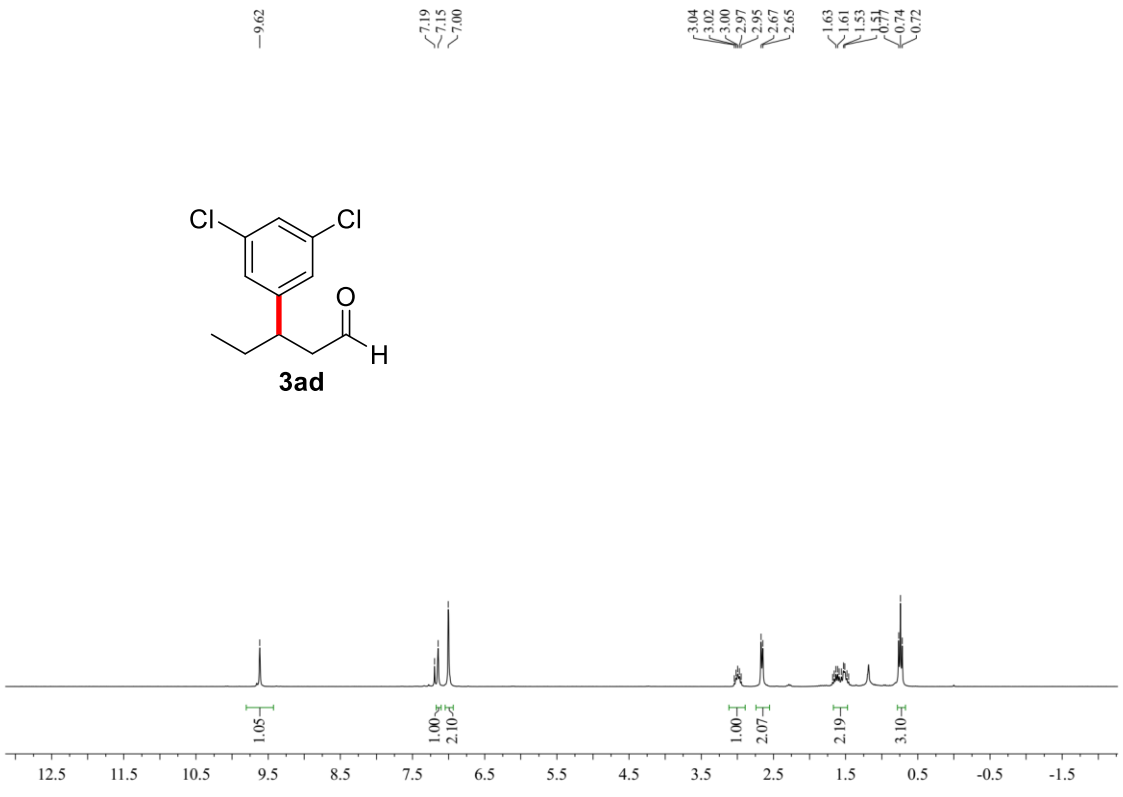
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1.61
1.53
1.51
0.77
0.74
0.72
Cl
Cl
O
H
3ad
1.05
1.00
2.10
1.00
2.07
2.19
3.10
12.5
11.5
10.5
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1.5
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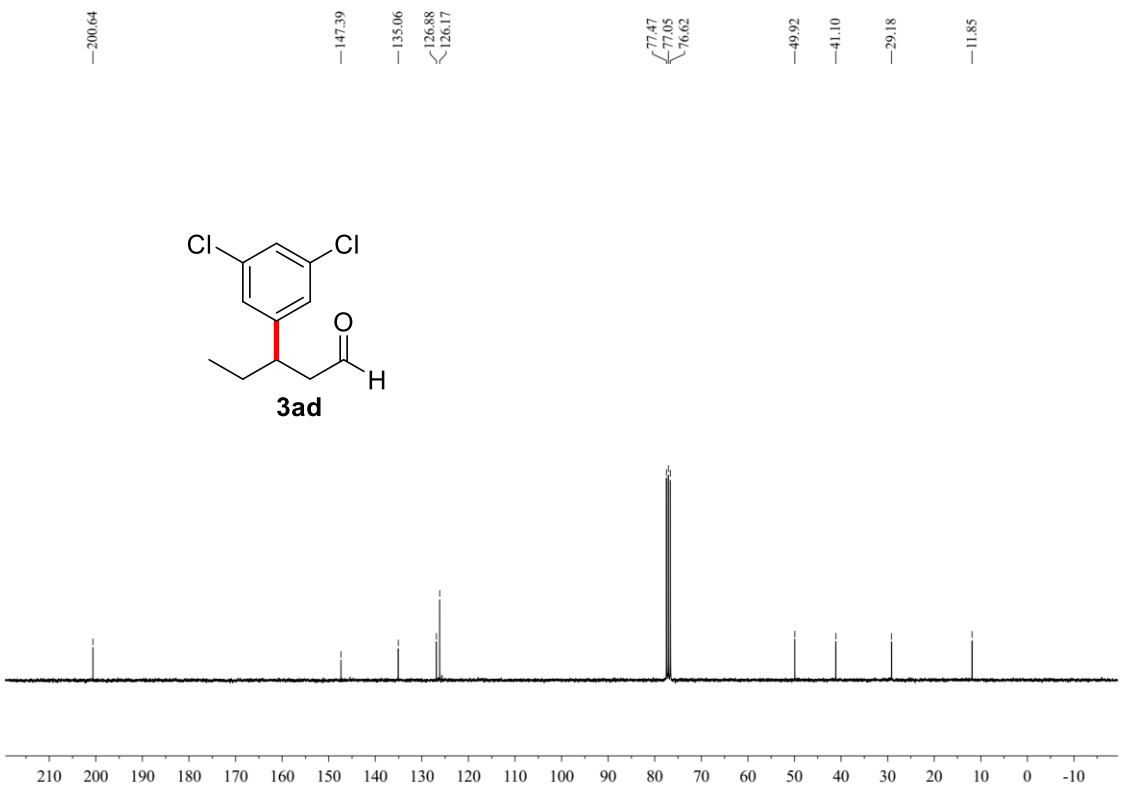
-1.5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Cl
Cl
O
H
3ad
210
200
190
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100
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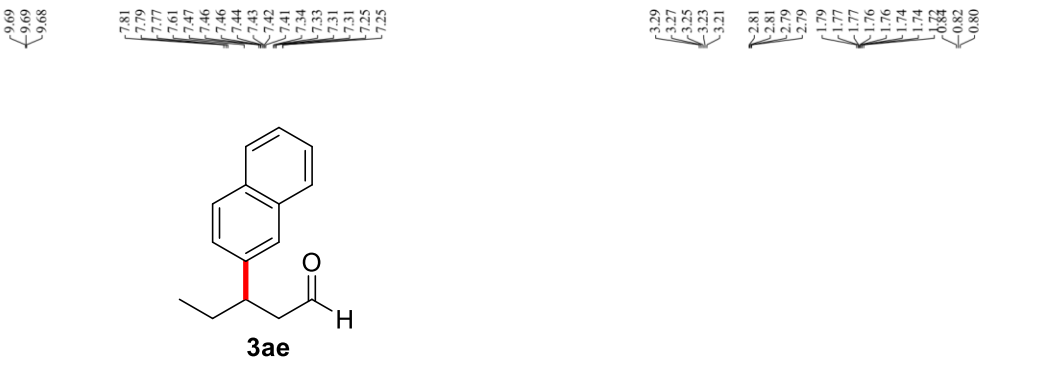
0
-10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2.81
2.79
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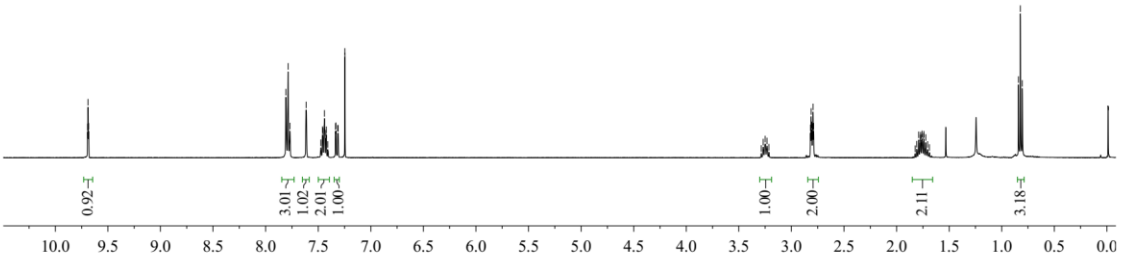
O
H

3ae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8.5
8.0
7.5
7.0
6.5
6.0
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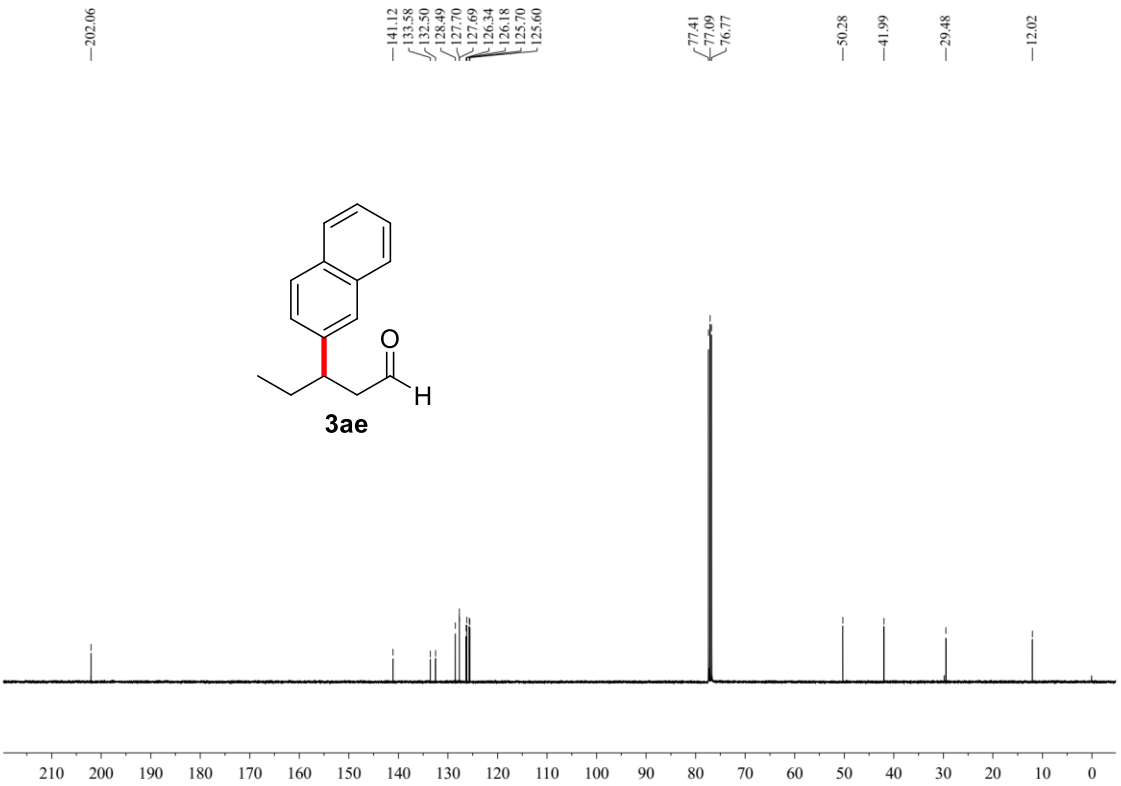
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50.28
41.99
29.48
12.02
O
H
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200
190
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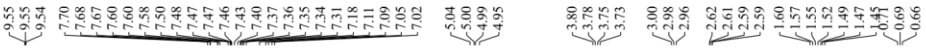
0

3ae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7.47
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7.31
7.18
7.11
7.09
7.05
7.02
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3.75
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2.62
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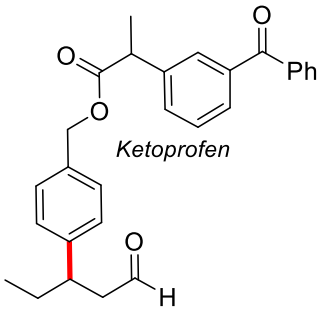
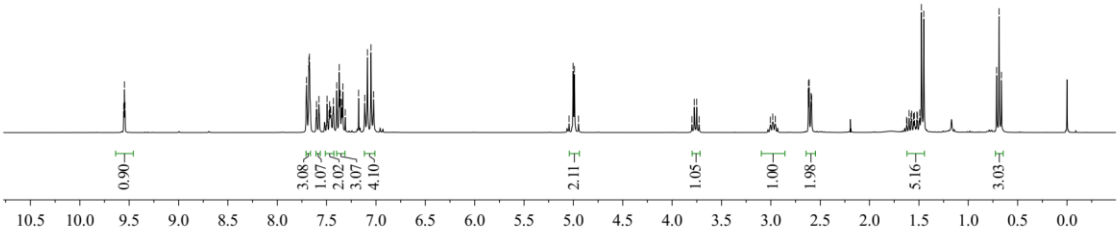

O
O
Ph
O
Ketoprofen
O
H

3af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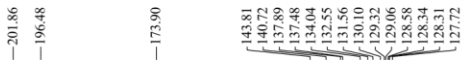
1.07
2.02
3.07
4.10
2.11
1.05
1.00
1.98
5.16
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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129.32
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128.58
128.34
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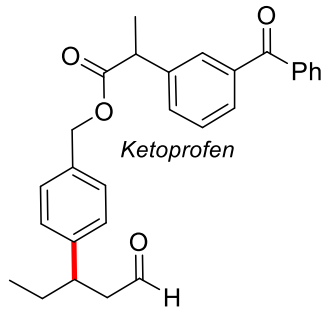
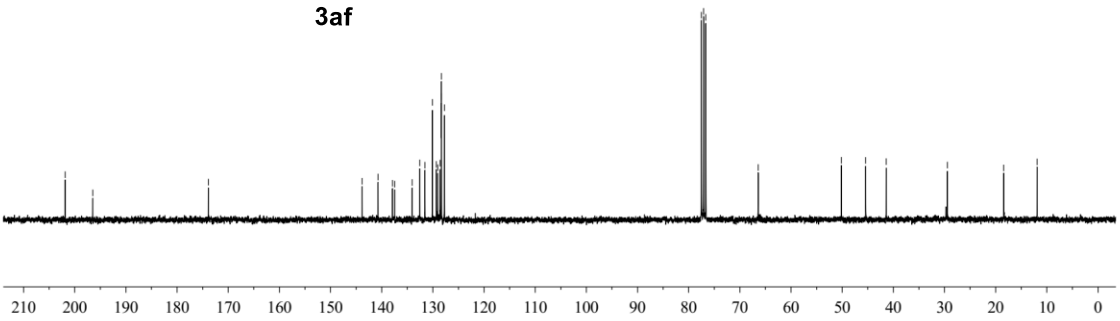
11.90


O
O
Ph
O
Ketoprofen
O
H

3af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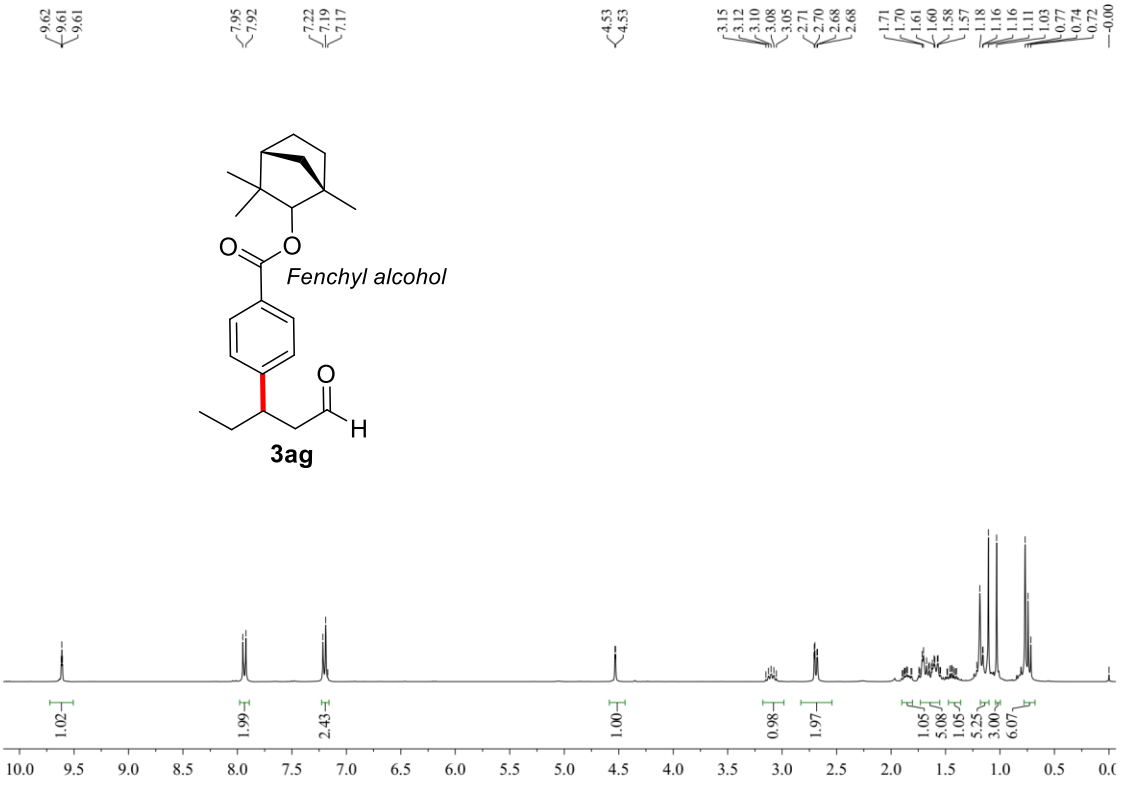
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7.17
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4.53
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3.12
3.10
3.08
3.05
2.71
2.70
2.68
2.68
1.71
1.70
1.61
1.60
1.58
1.57
1.18
1.16
1.16
1.11
1.03
0.77
0.74
0.72
0.00
O
O
Fenchyl alcohol
O
H
3ag
1.02
1.99
2.43
1.00
0.98
1.97
1.05
5.08
1.05
5.25
3.00
6.07
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9.5
9.0
8.5
8.0
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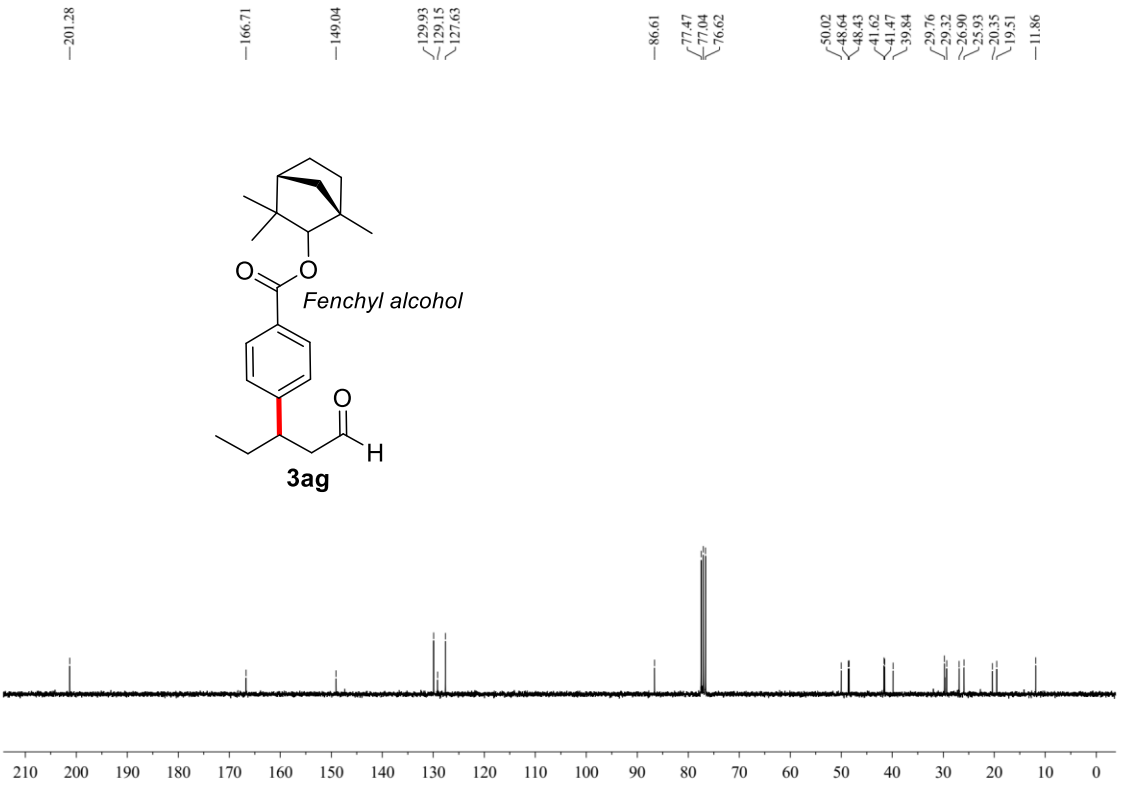
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76.62
50.02
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48.43
41.62
41.47
39.84
29.76
29.32
26.90
25.93
20.35
19.51
11.86
O
O
Fenchyl alcohol
O
H
3ag
210
200
190
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150
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70
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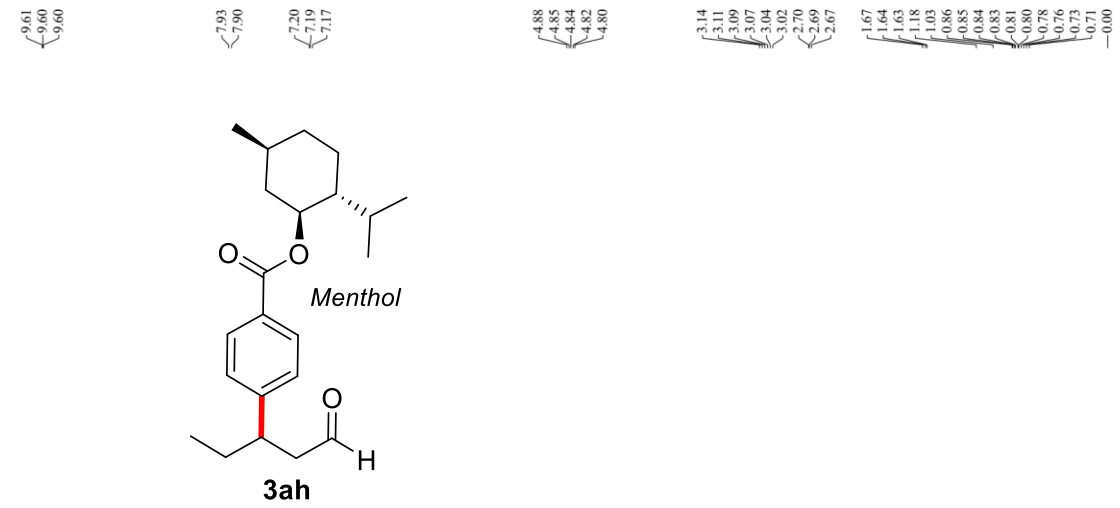
10
0


Menthol
3ah


Menthol
3ah