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Electronic Supplementary Information

CO-Enabled Rhenium Hydride Catalyst for Directed C(sp^2)-H bond Alkylation with Olefins

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General Information

All reactions were carried out under CO atmosphere unless otherwise noted. All reagents and solvents were obtained from commercial suppliers and used without further purification. Reactions were monitored by TLC on silica gel plates (GF254). ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz spectrometer, with chemical shifts (δ) referenced to the residual solvent signal (^{1}H and ^{13}C). Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; m, multiplet.

Materials

All solvents were used without further purification. $ReOCl_3(PPh_3)_2$[1] and reagents **1**[2, 3], **4**[4-6] have been prepared from according literature. $KReO_4$ was purchased from ZHUZHOUKAITE Industrial Corporation. Ltd.

Synthesis of heptahydridobis(triphenylphosphine)rhenium, $ReH_7(PPh_3)_2$

$ReOCl_3(PPh_3)_2$ (2.4 mmol, 2.0 g) was added to 30 mL dry THF and the mixture was stirred under N_2 atmosphere. $LiAlH_4$ (19 mmol, 0.71 g) was carefully added at 0 °C. After the reaction finished, the solvent was removed on a vacuum line. The residue was washed twice with absolute water (15x2 mL), twice with EtOH (15x2 mL), and twice times with Et_2O (10x2 mL). The dry residue was extracted three times with THF (10x3 mL). The volume of THF was reduced to 5 mL. Et_2O (10 mL), and hexane (10 mL) were added to induced precipitation. The beige microcrystalline $ReH_7(PPh_3)_2$ was corrected by filtering and dried under vacuum. Yield 0.94g (55 %).

$ReD_7(PPh_3)_2$ was prepared by the similar procedure, just using $LiAlD_4$ instead of $LiAlH_4$.

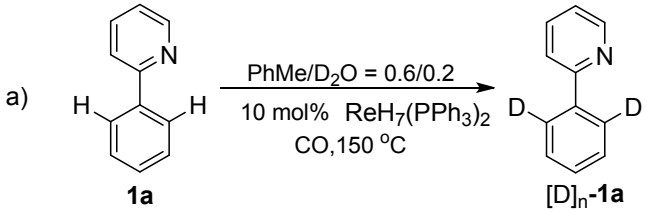
General procedure for the CO-enabled rhenium hydride compound-catalyzed C(sp^2) -H alkylation

General procedure for the rhenium hydride compound-catalyzed sp^2 C-H alkylation: the mixture of arenes **1** (0.2 mmol), unsaturated compounds **2** (0.6 mmol), $ReH_7(PPh_3)_2$ (10 mol%, 14 mg) and toluene (0.5 mL) were added into the flask. The 10 mL sealed tube was evacuated and backfilled with CO (approximate 1.5 atm). The reaction mixture was vigorously stirred at 150 °C for 20-24 h. After the reaction finished, the reaction mixture was cooled to room temperature, and the residue was purified by flash column chromatography on silica gel or preparative TLC on GF254 to afford the desired products **3**.

General procedure for the rhenium-catalyzed intramolecular reaction for constrcution of indolone framworks

In a 20 mL sealed tube, the substrates **4** (0.2 mmol), $ReH_7(PPh_3)_2$ (10 mol%, 14 mg) and toluene (0.5 mL) were placed under CO atmosphere (approximate 1.5 atm). The mixture was stirred at 150 °C for 20-24 h. After the reaction finished, the reaction mixture was cooled to room temperature and purified by preparative TLC on GF254 to afford the desired products **5**.

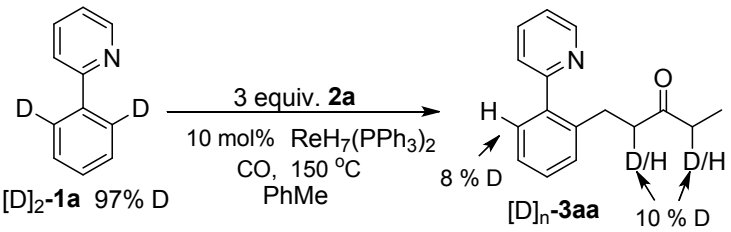
Deuterium labeling studies.



1a [D]$_n$-**1a**

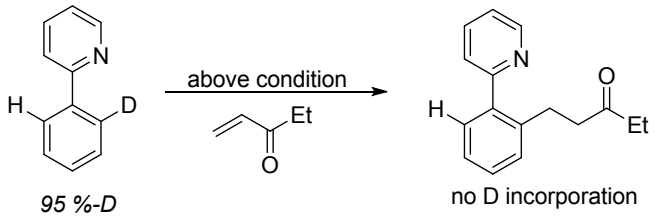
To the 3:1 mixture of PhMe and D_2O add **1a** (0.2 mmol), and were heated under standard condition for 20h. The reaction mixture was cooled to room temperature and purified by preparative TLC on GF254 to afford [D]$_n$-**1a**, which was characterized by ^{1}H NMR (400 MHz, $CDCl_3$).

b)



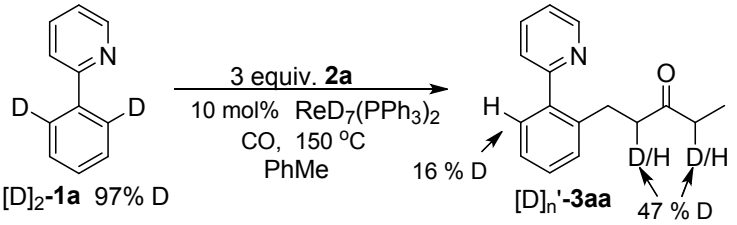
The mixture of $[D]_2$-**1a** (0.2 mmol) and **2a** (0.6 mmol) were heated under standard condition for 24h. The reaction mixture was cooled to room temperature and purified by preparative TLC on GF254 to afford $[D]_n$-**3aa**, which was characterized by ^{1}H NMR (400 MHz, $CDCl_3$).

A large negative kinetic isotope effect



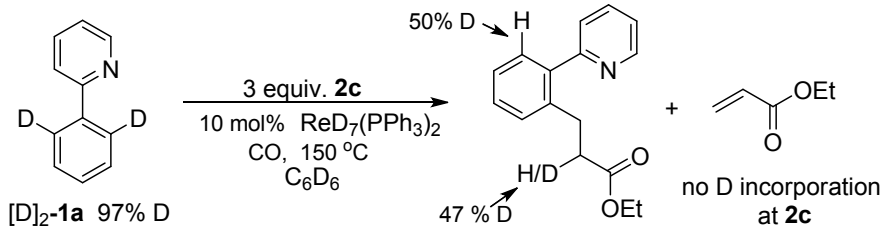
Above procedure was followed. An intramolecular competition reaction was carried out.There is no D incorporation in the product. It reveals that the deuterated species reacts faster than the undeuterated analogue where the rate constants $k_D >> k_H$. It also suggests the step of C-H activation is reversible.

c)



Above procedure was followed, using $ReD_7(PPh_3)_2$ instead of $ReH_7(PPh3)_2$.

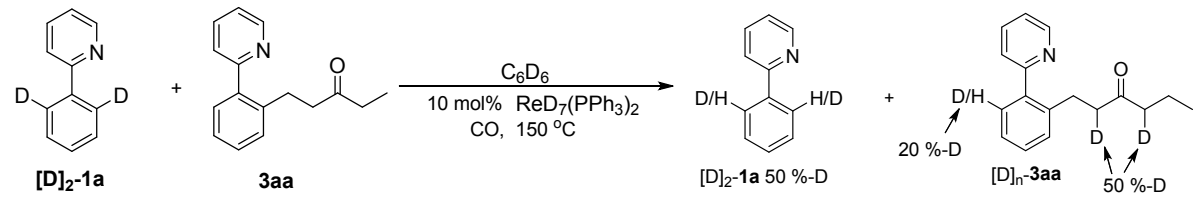
d)



$[D]_n$-**3ac**

The mixture of $[D]_2$-**1a** (0.2 mmol) and **2a** (0.6 mmol) were heated in C_6D_6 under standard condition for 24h. Then, the reaction mixture was directly characterized by ^{1}H NMR (400 MHz, C_6D_6). Following, the $[D]_n$-**3ac** was separated and characterized by ^{1}H NMR (400 MHz, d_6-acetone).

e)

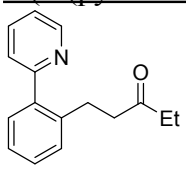


The mixture of $[D]_2$-**1a** (0.2 mmol) and **3aa** (0.1 mmol) were heated in C_6D_6 under standard condition for 24h. The reaction mixture was cooled to room temperature and purified by preparative TLC on GF254 to afford $[D]_n$-**3aa**, which was characterized by ^{1}H NMR (400 MHz, $CDCl_3$).

Characterization data of compounds

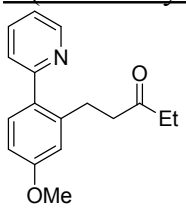
Heptahydridobis(triphenylphosphine)rhenium[7]
$ReH_7(PPh_3)_2$
Yield 55%, grey solid. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.87-7.80 (m, 12H), 7.02-6.92 (m, 18H), -4.19 (t, *J* = 18.0 Hz, 7H) ppm.

1-(2-(pyridin-2-yl)phenyl)pentan-3-one, **3aa**



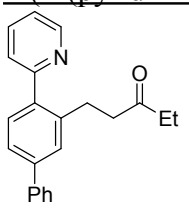
Yield 92 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71-8.66 (m, 1 H), 7.82-7.76 (m, 1 H), 7.44-7.40 (m, 1 H), 7.37-7.27 (m, 5 H), 2.95 (t, *J* = 8.0 Hz, 2 H), 2.66 (t, *J* = 8.0 Hz, 2 H), 2.32 (q, *J* = 7.2 Hz, 2 H), 0.98 (t, *J* = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.0, 159.7, 148.8, 139.9, 139.2, 136.8, 129.9, 129.8, 128.7, 126.3, 124.2, 122.0, 43.9, 35.8, 27.5, 7.80 ppm. HRMS (ESI) m/z calcd for $C_{16}H_{17}NO$ $[M+H]^+$ 240.1383; found: 240.1385.

1-(5-methoxy-2-(pyridin-2-yl)phenyl)pentan-3-one, **3ba**



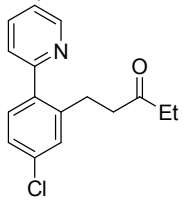
Yield 93 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.66-8.61 (m, 1 H), 7.75-7.69 (m, 1 H), 7.39-7.19 (m, 3 H), 6.85-6.79 (m, 2 H), 3.82 (s, 3 H), 2.97 (t, *J* = 7.2 Hz, 2 H), 2.67 (t, *J* = 7.6 Hz, 2 H), 2.32 (q, *J* = 7.6 Hz, 2 H), 0.99 (t, *J* = 7.6 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.0, 159.7, 159.6, 148.9, 140.9, 136.4, 133.0, 131.2, 124.0, 121.5, 115.3, 111.6, 55.3, 43.9, 35.8, 27.9, 7.80 ppm. HRMS (ESI) m/z calcd for $C_{17}H_{19}NO_2$ $[M+H]^+$ 270.1489; found: 270.1490.

1-(4-(pyridin-2-yl)-[1,1'-biphenyl]-3-yl)pentan-3-one, **3ca**



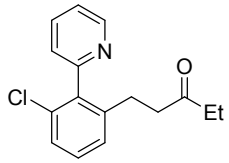
Yield 96 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71-8.67 (m, 1 H), 7.83-7.76 (m, 1 H), 7.65-7.60 (m, 2 H), 7.55-7.50 (m, 2 H), 7.49-7.41 (m, 3H), 7.40-7.32 (m, 1H), 7.32-7.26 (m, 1H), 3.04 (t, *J* = 7.6 Hz, 2 H), 2.72 (t, *J* = 7.6 Hz, 2 H), 2.33 (q, *J* = 7.2 Hz, 2 H), 0.99 (t, *J* = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.9, 159.4, 148.8, 141.5, 140.6, 139.8, 138.8, 136.8, 130.5, 128.8 (2C), 128.7, 127.5, 127.1 (2C), 125.1, 124.2, 121.9, 55.3, 44.1, 35.9, 27.7, 7.80 ppm. HRMS (ESI) m/z calcd for $C_{22}H_{21}NO$ $[M+Na]^+$ 338.1515; found: 338.1530.

1-(5-chloro-2-(pyridin-2-yl)phenyl)pentan-3-one, **3da**



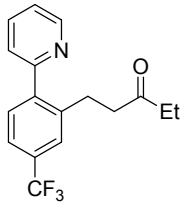
Yield 93 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.66-8.61 (m, 1 H), 7.75-7.69 (m, 1 H), 7.39-7.19 (m, 3 H), 6.85-6.79 (m, 2 H), 3.82 (s, 3 H), 2.97 (t, *J* = 7.2 Hz, 2 H), 2.67 (t, *J* = 7.6 Hz, 2 H), 2.32 (q, *J* = 7.6 Hz, 2 H), 0.99 (t, *J* = 7.6 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.0, 159.7, 159.6, 148.9, 140.9, 136.4, 133.0, 131.2, 124.0, 121.5, 115.3, 111.6, 55.3, 43.9, 35.8, 27.9, 7.80 ppm. HRMS (ESI) m/z calcd for $C_{16}H_{16}ClNO$ [M+H]+ 274.0993; found: 274.0996.

1-(3-chloro-2-(pyridin-2-yl)phenyl)pentan-3-one, **3ea**



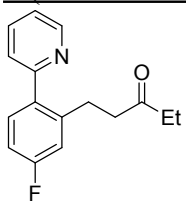
Yield 85 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.76-8.71 (m, 1 H), 7.91-7.83 (m, 1 H), 7.42-7.31 (m, 3 H), 7.31-7.25 (m, 1 H), 7.23-7.17 (m, 1 H), 2.79-2.48 (m, 4 H), 2.30 (q, *J* = 7.2 Hz, 2 H), 0.96 (t, *J* = 7.6 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.3, 156.4, 148.6, 141.8, 138.1, 137.4, 133.3, 129.7, 127.8, 127.4, 125.7, 122.9, 43.2, 35.9, 27.8, 7.7 ppm. HRMS (ESI) m/z calcd for $C_{16}H_{16}ClNO$ [M+H]+ 274.0993; found: 274.0997.

1-(2-(pyridin-2-yl)-5-(trifluoromethyl)phenyl)pentan-3-one, **3fa**



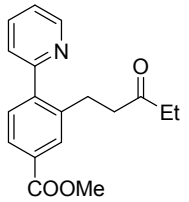
Yield 83 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71-8.66 (m, 1 H), 7.85-7.78 (m, 1 H), 7.57-7.52 (m, 2 H), 7.49-7.40 (m, 2 H), 7.35-7.30 (m, 1H), 3.82 (s, 3 H), 2.99 (t, *J* = 7.6 Hz, 2 H), 2.70 (t, *J* = 7.6 Hz, 2 H), 2.34 (q, *J* = 7.2 Hz, 2 H), 1.00 (t, *J* = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.3, 158.4, 149.1, 143.5, 140.4, 136.9, 130.6 (q, *J* = 33 Hz), 130.4, 126.8 (q, *J* = 273 Hz), 126.6 (q, *J* = 3.6 Hz), 124.1, 123.1 (q, *J* = 3.6 Hz), 122.6, 43.5, 35.9, 27.4, 7.80 ppm. HRMS (ESI) m/z calcd for $C_{17}H_{16}F_3NO$ $[M+H]^+$ 308.1257; found: 308.1260.

1-(5-fluoro-2-(pyridin-2-yl)phenyl)pentan-3-one, **3ga**



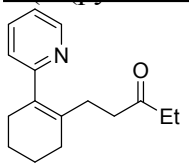
Yield 88 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.70-8.63 (m, 1 H), 7.83-7.77 (m, 1 H), 7.43-7.38 (m, 1 H), 7.36-7.26 (m, 2 H), 7.04-6.93 (m, 2 H), 2.94 (t, *J* = 7.6 Hz, 2 H), 2.68 (t, *J* = 7.2 Hz, 2 H), 2.34 (q, *J* = 7.2 Hz, 2 H), 0.99 (t, *J* = 7.6 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.5, 162.8 (d, *J* = 247.1 Hz), 158.6, 148.7, 142.0 (d, *J* = 7.6 Hz), 137.1, 135.8, 131.7 (d, *J* = 7.5 Hz), 124.4, 122.2, 116.4 (d, *J* = 19.9 Hz), 113.2 (d, *J* = 21 Hz), 43.5, 35.9, 27.4, 7.8 ppm. HRMS (ESI) m/z calcd for $C_{16}H_{16}FNO$ $[M+H]^+$ 258.1289; found: 258.1290.

Methyl-3-(3-oxopentyl)-4-(pyridin-2-yl)benzoate, **3ha**



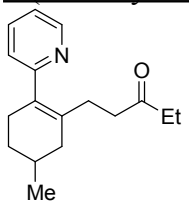
Yield 94 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.72-8.67 (m, 1 H), 8.00-7.92 (m, 2 H), 7.85-7.79 (m, 1 H), 7.47-7.40 (m, 2 H), 7.36-7.30 (m, 1H), 3.94 (s, 3H), 2.99 (t, *J* = 7.2 Hz, 2 H), 2.71 (t, *J* = 7.2 Hz, 2 H), 2.35 (q, *J* = 7.2 Hz, 2 H), 1.00 (t, *J* = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.5, 166.8, 158.7, 148.9, 144.2, 139.7, 137.0, 130.9, 130.2, 130.1, 127.4, 124.2, 122.5, 52.2, 43.6, 35.9, 27.3, 7.8 ppm. HRMS (ESI) m/z calcd for $C_{18}H_{19}NO_3$ $[M+H]^+$ 298.1438; found: 298.1439.

1-(2-(pyridin-2-yl)cyclohex-1-en-1-yl)pentan-3-one, **3ia**



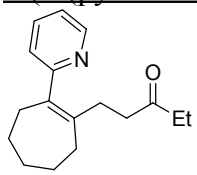
Yield 98 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.63-8.50 (m, 1 H), 7.70-7.60 (m, 1 H), 7.21-7.09 (m, 2 H), 2.55-2.43 (m, 2 H), 2.39-2.27 (m, 4 H), 2.25-2.15 (m, 2 H), 2.13-2.04 (m, 2 H), 1.81-1.64 (m, 4 H), 0.98 (t, *J* = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.4, 161.6 148.8, 136.5, 134.6, 133.4, 123.3, 121.4, 41.2, 35.7, 30.6, 28.9, 28.5, 23.0, 22.7, 7.8 ppm. HRMS (ESI) m/z calcd for $C_{16}H_{21}NO$ $[M+H]^+$ 244.1696; found: 244.1698.

1-(5-methyl-2-(pyridin-2-yl)cyclohex-1-en-1-yl)pentan-3-one, **3ja**



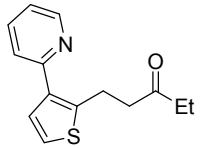
Yield 96 %, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.61-8.56 (m, 1 H), 7.71-7.65 (m, 1 H), 7.22-7.12 (m, 2 H), 2.57-2.44 (m, 2 H), 2.43-2.36 (m, 2 H), 2.33 (q, *J* = 7.2 Hz, 2H), 2.26-2.05 (m, 3 H), 1.85-1.70 (m, 3 H), 1.39-1.28 (m, 1 H), 1.01 (d, *J* = 6.0 Hz, 3 H), 0.98 (t, *J* = 7.6 Hz, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.4, 161.3, 148.5, 136.9, 134.5, 132.6, 123.5, 121.5, 41.1, 37.6, 35.7, 31.1, 30.8, 28.7, 28.4, 21.8, 7.8 ppm. HRMS (ESI) m/z calcd for $C_{17}H_{23}NO$ $[M+H]^+$ 258.1852; found: 258.1855.

1-(2-(pyridin-2-yl)cyclohept-1-en-1-yl)pentan-3-one, **3ka**



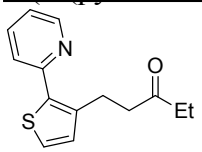
Yield 86 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.58-8.53 (m, 1 H), 7.66-7.59 (m, 1 H), 7.14-7.07 (m, 2 H), 2.55-2.48 (m, 4 H), 2.35 (q, *J* = 7.2 Hz, 2 H), 2.32-2.18 (m, 4 H), 1.87-1.77 (m, 2 H), 1.67-1.54 (m, 4 H), 1.00 (t, *J* = 7.6 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.4, 162.8, 148.8, 141.3, 139.1, 136.3, 123.0, 121.1, 41.1, 35.7, 34.6, 33.7, 32.6, 30.4, 26.9, 26.5, 7.8 ppm. HRMS (ESI) m/z calcd for $C_{17}H_{23}NO$ $[M+H]^+$ 258.1852; found: 258.1856.

1-(3-(pyridin-2-yl)thiophen-2-yl)pentan-3-one, **3la**



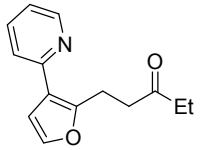
Yield 97 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.67-8.61 (m, 1 H), 7.76-7.70 (m, 1 H), 7.51-7.46 (m, 1 H), 7.29-7.11 (m, 3 H), 3.38 (t, *J* = 7.6 Hz, 2 H), 2.86 (t, *J* = 7.2 Hz, 2 H), 2.42 (q, *J* = 7.2 Hz, 2 H), 1.05 (t, *J* = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.4, 154.9, 149.2, 142.4, 136.9, 136.7, 128.6, 122.8, 122.2, 121.4, 44.1, 36.0, 23.2, 7.80 ppm. HRMS (ESI) m/z calcd for $C_{14}H_{15}NOS$ $[M+H]^+$ 246.0947; found: 246.0951.

1-(2-(pyridin-2-yl)thiophen-3-yl)pentan-3-one, **3ma**



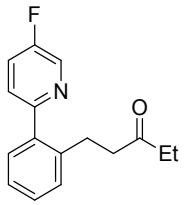
Yield 82 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.65-8.60 (m, 1 H), 7.76-7.68 (m, 1 H), 7.58-7.52 (m, 1 H), 7.32-7.28 (m, 1 H), 7.21-7.14 (m, 1H), 6.97-6.94 (m, 1 H), 3.20 (t, *J* = 7.6 Hz, 2 H), 2.79 (t, *J* = 7.6 Hz, 2 H), 2.43 (q, *J* = 7.2 Hz, 2 H), 1.05 (t, *J* = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.0, 153.1, 149.5, 139.3, 137.7, 136.8, 130.6, 125.8, 122.0, 121.6, 42.9, 36.0, 23.8, 7.8 ppm.

1-(3-(pyridin-2-yl)furan-2-yl)pentan-3-one, **3na**



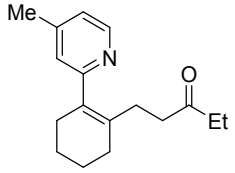
Yield 98 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.63-8.58 (m, 1 H), 7.72-7.68 (m, 1 H), 7.50-7.44 (m, 1 H), 7.36-7.32 (m, 1 H), 7.18-7.11 (m, 1H), 6.77-6.73 (m, 1 H), 3.34 (t, *J* = 7.2 Hz, 2 H), 2.87 (t, *J* = 7.2 Hz, 2 H), 2.46 (q, *J* = 7.2 Hz, 2 H), 1.06 (t, *J* = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.6, 153.6, 152.7, 149.1, 140.9, 136.9, 121.4, 121.0, 120.2, 110.3, 40.2, 35.9, 22.3, 7.8 ppm. HRMS (ESI) m/z calcd for $C_{14}H_{15}NO_2$ $[M+H]^+$ 230.1176; found: 230.1178.

1-(2-(5-fluoropyridin-2-yl)phenyl)pentan-3-one, **3oa**



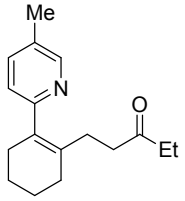
Yield 94 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.55-8.48 (m, 1 H), 7.52-7.45 (m, 1 H), 7.44-7.38 (m, 1 H), 7.36-7.25 (m, 4 H), 2.93 (t, *J* = 7.6 Hz, 2 H), 2.67 (t, *J* = 7.2 Hz, 2 H), 2.34 (q, *J* = 7.2 Hz, 2 H), 1.00 (t, *J* = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.9, 158.5 (d, *J* = 254.3 Hz), 156.0 (d, *J* = 3.1 Hz), 139.3, 139.0, 137.1 (d, *J* = 23.6 Hz), 133.5 (d, *J* = 11.2 Hz), 129.9 (d, *J* = 2.2 Hz), 128.8, 126.3, 125.0 (d, *J* = 4.5 Hz), 123.6 (d, *J* = 17.8 Hz), 43.9, 35.9, 27.4, 7.8 ppm. HRMS (ESI) m/z calcd for $C_{16}H_{16}FNO$ $[M+H]^+$ 258.1289; found: 258.1287.

1-(2-(4-methylpyridin-2-yl)cyclohex-1-en-1-yl)pentan-3-one, **3pa**



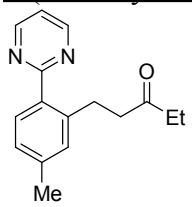
Yield 88 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.44-8.38 (m, 1 H), 6.98-6.93 (m, 2 H), 2.52-2.44 (m, 2 H), 2.37-2.27 (m, 7 H), 2.21-2.13 (m, 2 H), 2.11-2.04 (m, 2 H), 1.76-1.66 (m, 4 H), 0.98 (t, *J* = 7.6 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.6, 161.6 148.8, 147.3, 134.0, 133.7, 123.9, 122.3, 41.3, 35.7, 30.6, 28.9, 28.6, 23.0, 22.8, 21.1, 7.8 ppm. HRMS (ESI) m/z calcd for $C_{17}H_{23}NO$ $[M+H]^+$ 258.1852; found: 258.1853.

1-(2-(5-methylpyridin-2-yl)cyclohex-1-en-1-yl)pentan-3-one, **3qa**



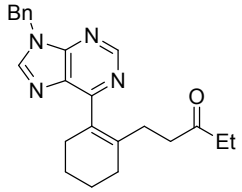
Yield 88 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.42-8.39 (m, 1 H), 7.53-7.47 (m, 1 H), 7.11-7.06 (m, 1 H), 2.53-2.46 (m, 2 H), 2.37-2.28 (m, 7 H), 2.21-2.14 (m, 2 H), 2.11-2.04 (m, 2 H), 1.76-1.67 (m, 4 H), 0.99 (t, *J* = 7.6 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.5, 158.4 148.7, 137.6, 134.7, 132.8, 130.9, 122.9, 41.1, 35.7, 30.6, 28.9, 28.5, 23.0, 22.8, 18.2, 7.8 ppm. HRMS (ESI) m/z calcd for $C_{17}H_{23}NO$ $[M+H]^+$ 258.1852; found: 258.1854.

1-(5-methyl-2-(pyrimidin-2-yl)phenyl)pentan-3-one, **3ra**



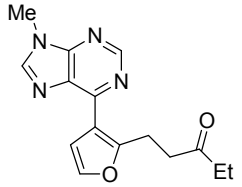
Yield 82 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.83-8.79 (m, 2 H), 7.79-7.75 (m, 1 H), 7.23-7.19 (m, 1 H), 7.16-7.10 (m, 2 H), 3.14 (t, *J* = 8.4 Hz, 2 H), 2.78 (t, *J* = 8.0 Hz, 2 H), 2.39 (q, *J* = 7.2 Hz, 2 H), 2.38 (s, 3 H), 1.03 (t, *J* = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.4, 167.2, 156.9 (2C), 140.6, 139.8, 134.9, 131.4, 130.9, 127.2, 118.4, 44.6, 35.9, 28.4, 21.3, 7.8 ppm. HRMS (ESI) m/z calcd for $C_{16}H_{18}N_2O$ $[M+H]^+$ 255.1492; found: 255.1496.

1-(2-(9-benzyl-9H-purin-6-yl)cyclohex-1-en-1-yl)pentan-3-one, **3sa**



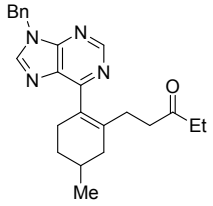
Yield 98 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.97 (s, 1 H), 8.01 (s, 1 H), 7.42-7.31 (m, 5 H), 5.45 (s, 2 H), 2.63-2.55 (m, 2 H), 2.54-2.47 (m, 2 H), 2.34-2.26 (q, *J* = 7.6 Hz, 2 H), 2.24-2.14 (m, 4 H), 1.85-1.73 (m, 4H), 0.95 (t, *J* = 7.6 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.4, 161.0, 152.5, 151.6, 143.9, 138.6, 135.0, 131.6, 129.2(2C), 128.8, 128.6, 127.9 (2C), 47.3, 41.1, 35.7, 29.5, 29.1, 29.1, 22.7, 22.6, 7.8 ppm. HRMS (ESI) m/z calcd for $C_{23}H_{26}N_4O$ $[M+H]^+$ 375.2179; found: 375.2183.

1-(3-(9-methyl-9H-purin-6-yl)furan-2-yl)pentan-3-one, **3ta**



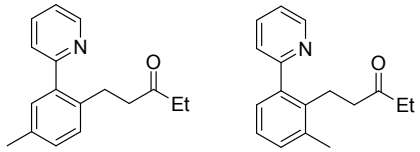
Yield 98 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.91 (s, 1 H), 8.03 (s, 1 H), 7.63-7.59 (m, 1 H), 7.43-7.40 (m, 1 H), 3.91 (s, 3 H), 3.60 (t, *J* = 7.2 Hz, 2 H), 2.93 (t, J = 7.6 Hz, 2 H), 2.48 (q, *J* = 7.2 Hz, 2 H), 1.07 (t, *J* = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.4, 158.1, 152.1, 151.3, 144.2, 141.1(2C), 130.3, 116.6, 112.2, 40.2, 35.8, 29.8, 23.2, 7.8 ppm. HRMS (ESI) m/z calcd for $C_{15}H_{16}N_4O_2$ $[M+H]^+$ 285.1346; found: 285.1347.

1-(2-(9-benzyl-9H-purin-6-yl)-5-methylcyclohex-1-en-1-yl)pentan-3-one, **3ua**



Yield 95 %, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.24 (s, 1 H), 8.35 (s, 1 H), 7.44-7.30 (m, 5 H), 5.54 (s, 2 H), 2.68-2.55 (m, 4 H), 2.35 (q, *J* = 7.2 Hz, 2 H), 2.27-2.17 (m, 2 H), 1.95-1.80 (m, 4 H), 1.49-1.36 (m, 1H), 1.02 (d, J = 5.6 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.6, 157.2, 152.7, 149.5, 147.1, 143.6, 134.1, 130.6, 129.3(2C), 129.0, 128.4 (2C), 124.1, 48.1, 40.2, 37.7, 35.8, 30.5, 29.8, 28.9, 28.1, 21.6, 7.8 ppm. HRMS (ESI) m/z calcd for $C_{24}H_{28}N_4O$ $[M+H]^+$ 389.2336; found: 389.2238.

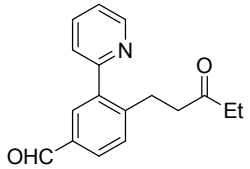
1-(methyl-2-(pyridin-2-yl)phenyl)pentan-3-one, **3va**



85 : 15

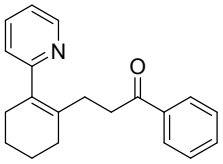
Yield 85 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71-8.67 (m, 1 H), 7.82-7.79 (m, 1 H), 7.45-7.42 (m, 1 H), 7.32-7.29 (m, 1 H), 7.18-7.16 (m, 3H), 2.91 (t, *J* = 7.6 Hz, 2 H), 2.63 (t, *J* = 7.6 Hz, 2 H), 2.35 (s, 3H), 2.32 (q, *J* = 7.6 Hz, 2 H), 0.98 (t, *J* = 7.6 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 211.1, 159.6, 148.5, 139.4, 137.1, 136.1, 135.9, 130.6, 129.7, 129.5, 124.4, 122.0, 44.0, 35.9, 27.1, 21.0, 7.80 ppm. HRMS (ESI) m/z calcd for $C_{17}H_{19}NO$ $[M+H]^+$ 254.1539; found: 254.1541.

4-(3-oxopentyl)-3-(pyridin-2-yl)benzaldehyde, **3wa**



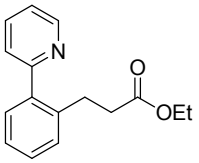
Yield 93 %, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.01 (s, 1 H), 8.73-8.69 (m, 1 H), 7.89-7.83 (m, 3 H), 7.52-7.46 (m, 2 H), 7.38-7.34 (m, 1 H), 3.04 (t, *J* = 8.0 Hz, 2 H), 2.71 (t, *J* = 8.0 Hz, 2 H), 2.34 (q, *J* = 7.6 Hz, 2 H), 0.99 (t, *J* = 7.6 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.2, 191.7, 158.2, 148.8, 146.8, 140.5, 137.4, 134.7, 131.5, 130.7, 129.6, 124.3, 122.7, 43.2, 35.9, 27.7, 7.78 ppm. HRMS (ESI) m/z calcd for $C_{17}H_{17}NO_2$ $[M+H]^+$ 268.1332; found: 268.1332.

1-phenyl-3-(2-(pyridin-2-yl)cyclohex-1-en-1-yl)propan-1-one, **3ib**



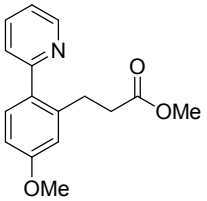
Yield 83 %, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.66-8.58 (m, 1 H), 7.91-7.85 (m, 2 H), 7.72-7.66 (m, 1 H), 7.54-7.49 (m, 1 H), 7.43-7.37 (m, 2H), 7.24-7.16 (m, 2H), 3.07 (t, *J* = 8.0 Hz, 2 H), 2.42-2.30 (m, 4 H), 2.21-2.12 (m, 2 H), 1.80-1.69 (m, 4 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.1, 161.1, 148.2, 137.4, 136.6, 135.4, 132.9 (2C), 128.5 (2C), 128.1 (2C), 123.7, 121.6, 37.6, 30.6, 29.2, 29.0, 22.9, 22.7 ppm. HRMS (ESI) m/z calcd for $C_{20}H_{21}NO$ $[M+H]^+$ 292.1696; found: 292.1696.

Ethyl-3-(2-(pyridin-2-yl)phenyl)propanoate, **3ac**[8]



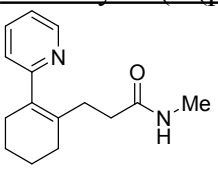
Yield 86 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.72-8.65 (m, 1 H), 7.83-7.73 (m, 1 H), 7.44-7.40 (m, 1 H), 7.36-7.24 (m, 5 H), 4.06 (q, *J* = 7.2 Hz, 2 H), 3.04 (t, *J* = 7.6 Hz, 2 H), 2.52 (t, *J* = 8.0 Hz, 2 H), 1.19 (t, *J* = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.1, 159.8, 149.0, 140.3, 138.6, 136.5, 129.9, 129.8, 128.6, 126.4, 124.1, 121.9, 60.3, 35.7, 28.4, 14.2 ppm.

Methyl 3-(5-methoxy-2-(pyridin-2-yl)phenyl)propanoate, **3bd**



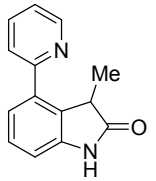
Yield 90 %, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.69-8.65 (m, 1 H), 7.80-7.73 (m, 1 H), 7.42-7.37 (m, 1 H), 7.34-7.29 (m, 1 H), 7.27-7.22 (m, 1 H), 6.87-6.81 (m, 2 H), 3.84 (s, 3 H), 3.61 (s, 3 H), 3.05 (t, *J* = 7.6 Hz, 2 H), 2.56 (t, *J* = 8.0 Hz, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.5, 159.8, 159.3, 148.7, 140.3, 136.8, 132.5, 131.4, 124.2, 121.6, 115.3, 111.7, 55.3, 51.6, 35.5, 28.7 ppm. HRMS (ESI) m/z calcd for $C_{16}H_{17}NO_3$ $[M+H]^+$ 272.1281; found: 272.1282.

N-methyl-3-(2-(pyridin-2-yl)cyclohex-1-en-1-yl)propanamide, **3ie**



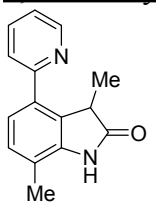
Yield 87 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.60-8.56 (m, 1 H), 7.68-7.61 (m, 1 H), 7.17-7.10 (m, 2 H), 3.60 (s, 3 H), 2.40-2.31 (m, 4 H), 2.30-2.23 (m, 2 H), 2.15-2.05 (m, 2 H), 1.78-1.67 (m, 4 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.9, 161.6 149.1, 136.3, 134.1, 133.7, 123.2, 121.3, 51.5, 32.9, 30.6, 29.5, 28.7, 23.0, 22.8 ppm. HRMS (ESI) m/z calcd for $C_{15}H_{20}N_2O$ $[M+H]^+$ 245.1648; found: 245.1650.

3-methyl-4-(pyridin-2-yl)indolin-2-one, **5a**



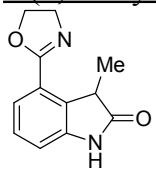
Yield 82 %, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.11 (br s, 1 NH), 8.74-8.69 (m, 1 H), 7.84-7.77 (m, 1 H), 7.62-7.57 (m, 1 H), 7.34-7.22 (m, 3 H), 6.98-6.92 (m, 1 H), 4.20 (q, *J* = 7.6 Hz, 1 H), 1.13 (d, *J* = 7.6 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 181.7, 157.5, 149.4, 142.2, 136.8 (2C), 129.7, 128.2, 122.63, 122.61, 122.4, 110.0, 41.4, 14.7 ppm. HRMS (ESI) m/z calcd for $C_{14}H_{12}N_2O$ $[M+H]^+$ 225.1022; found: 225.1026.

3,7-dimethyl-4-(pyridin-2-yl)indolin-2-one, **5b**



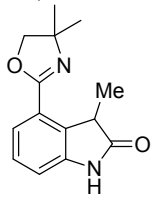
Yield 87 %, white solid; ^{1}H NMR (400 MHz, *d*^{6}-DMSO) δ = 10.48 (s br, 1 NH), 8.68-8.63 (m, 1 H), 7.90-7.83 (m, 1 H), 7.75-7.70 (m, 1 H), 7.38-7.32 (m, 1 H), 7.22-7.17 (m, 1 H), 7.14-7.09 (m, 1 H), 4.02 (q, *J* = 7.2 Hz, 1 H), 2.25 (s, 3 H), 0.97 (d, *J* = 7.6 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, *d*^{6}-DMSO) δ = 180.3, 156.9, 149.2, 141.7, 136.9, 133.7, 129.2, 128.7, 122.3, 122.2, 121.6, 119.1, 40.9, 16.5, 14.6 ppm. HRMS (ESI) m/z calcd for $C_{15}H_{14}N_2O$ $[M+H]^+$ 239.1179; found: 239.1180.

4-(4,5-dihydrooxazol-2-yl)-3-methylindolin-2-one, **5c**



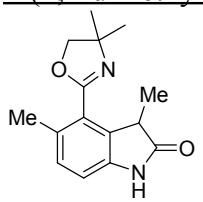
Yield 76 %, white solid; ^{1}H NMR (400 MHz, $CHCl_3$) δ = 9.36 (s br, 1 NH), 7.60-7.53 (m, 1 H), 7.29-7.21 (m, 1 H), 7.06-7.00 (m, 1 H), 4.50-4.36 (m, 2 H), 4.14-4.09 (m, 2 H), 3.86 (q, *J* = 7.6 Hz, 1H), 1.53 (d, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CHCl_3$) δ = 182.0, 163.3, 142.2, 131.5, 127.8, 124.4, 122.9, 112.4, 67.4, 55.0, 42.6, 15.9 ppm. HRMS (ESI) m/z calcd for $C_{12}H_{12}N_2O_2$ $[M+H]^+$ 217.0972; found: 217.0971.

4-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-methylindolin-2-one, **5d**



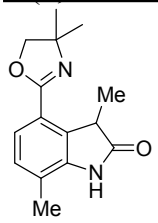
Yield 79 %, white solid; ^{1}H NMR (400 MHz, $CHCl_3$) δ = 9.14 (s br, 1 NH), 7.60-7.53 (m, 1 H), 7.26-7.20 (m, 1 H), 7.05-6.98 (m, 1 H), 4.12 (dt, *J* = 8.0, 6.4 Hz, 2 H), 3.90 (q, *J* = 7.6 Hz, 1H), 1.53 (d, *J* = 7.6 Hz, 3H), 1.40 (d, *J* = 3.2 Hz, 6 H) ppm; ^{13}C NMR (100 MHz, $CHCl_3$) δ = 182.2, 161.0, 142.2, 131.6, 127.8, 124.5, 122.9, 112.4, 79.0, 67.7, 42.5, 28.3, 28.2, 15.8 ppm. HRMS (ESI) m/z calcd for $C_{14}H_{16}N_2O_2$ $[M+H]^+$ 245.1285; found: 245.1282.

4-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3,5-dimethylindolin-2-one, **5e**



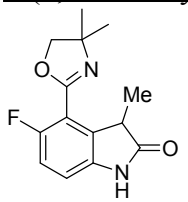
Yield 84 %, white solid; ^{1}H NMR (400 MHz, $CHCl_3$) δ = 9.21 (s br, 1 NH), 7.05 (d, *J* = 8.0 Hz, 1 H), 6.84 (d, *J* = 8.0 Hz, 1 H), 4.15 (dt, *J* = 8.4, 2.0 Hz, 2 H), 3.76 (q, *J* = 7.6 Hz, 1H), 2.39 (s, 3 H), 1.45 (d, *J* = 2.8 Hz, 6H), 1.43 (d, *J* = 7.6 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CHCl_3$) δ = 181.3, 161.3, 139.5, 131.3, 131.2, 129.8, 124.8, 111.4, 79.2, 67.8, 41.6, 28.5, 28.3, 19.6, 15.3 ppm. HRMS (ESI) m/z calcd for $C_{15}H_{18}N_2O_2$ $[M+H]^+$ 259.1441; found: 259.1444.

4-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3,7-dimethylindolin-2-one, **5f**



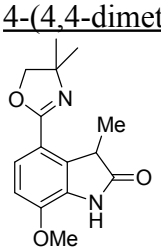
Yield 86 %, white solid; ^{1}H NMR (400 MHz, $CHCl_3$) δ = 9.88 (s br, 1 NH), 7.46 (d, *J* = 8.0 Hz, 1 H), 7.06 (d, *J* = 8.0 Hz, 1 H), 4.08 (dt, *J* = 8.4, 8.0 Hz, 2 H), 3.94 (q, *J* = 7.6 Hz, 1H), 2.35 (s, 3 H), 1.54 (d, *J* = 7.6 Hz, 3H), 1.38 (d, *J* = 3.2 Hz, 6 H) ppm; ^{13}C NMR (100 MHz, $CHCl_3$) δ = 182.7, 160.9, 140.9, 131.2, 129.1, 122.9, 122.4, 122.2, 78.8, 67.7, 42.9, 28.4, 28.3, 16.8, 16.0 ppm. HRMS (ESI) m/z calcd for $C_{15}H_{18}N_2O_2$ $[M+H]^+$ 259.1441; found: 259.1445.

4-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-5-fluoro-3-methylindolin-2-one, **5g**



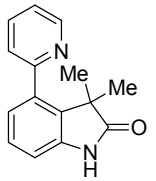
Yield 69 %, yellow solid; ^{1}H NMR (400 MHz, $CHCl_3$) δ = 9.31 (s br, 1 NH), 7.03-6.90 (m, 2 H), 4.14 (s, 2 H), 3.87 (q, *J* = 7.6 Hz, 1H), 1.47 (d, *J* = 7.6 Hz, 3H), 1.42 (d, *J* = 7.6 Hz, 6 H) ppm; ^{13}C NMR (100 MHz, $CHCl_3$) δ = 181.5, 157.2 (*J* = 2.6 Hz), 157.0 (*J* = 247.1 Hz), 137.7 (*J* = 2.6 Hz), 132.8 (*J* = 1.4 Hz), 115.3 (*J* = 24.7 Hz), 114.5 (J = 15.9 Hz), 112.4 (J = 7.7 Hz), 79.0, 68.0, 42.5 (J= 1.6 Hz), 28.4, 28.2, 15.3 ppm. HRMS (ESI) m/z calcd for $C_{14}H_{15}FN_2O_2$ $[M+H]^+$ 263.1190; found: 263.1194.

4-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-7-methoxy-3-methylindolin-2-one, **5h**



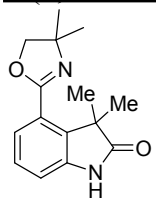
Yield 77 %, white solid; ^{1}H NMR (400 MHz, $CHCl_3$) δ = 8.12 (s br, 1 NH), 7.63 (d, *J* = 8.8 Hz, 1 H), 6.83 (d, *J* = 8.4 Hz, 1 H), 4.16-4.06 (m, 2 H), 3.92 (s, 3 H), 3.89 (q, *J* = 7.6 Hz, 1H), 1.53 (d, *J* = 7.6 Hz, 3H), 1.38 (s, 6 H) ppm; ^{13}C NMR (100 MHz, $CHCl_3$) δ = 180.5, 161.2, 146.0, 132.3, 130.6, 124.5, 116.8, 109.9, 79.1, 67.3, 55.8, 43.2, 28.3, 28.2, 16.0 ppm. HRMS (ESI) m/z calcd for $C_{15}H_{18}N_2O_3$ $[M+H]^+$ 275.1390; found: 275.1395.

3,3-dimethyl-4-(pyridin-2-yl)indolin-2-one, **5i**



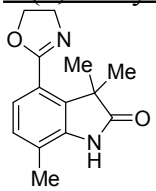
Yield 58 %, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.03 (br s, 1 NH), 8.73-8.70 (m, 1 H), 7.82-7.76 (m, 1 H), 7.42-7.38 (m, 1 H), 7.36-7.31 (m, 1 H), 7.28-7.23 (m, 1 H), 7.02-6.96 (m, 2 H), 1.33 (s, 6 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 184.4, 158.6, 148.5, 140.5, 138.4, 136.5, 133.2, 127.6, 124.3, 123.9, 122.5, 110.1, 46.3, 24.0 ppm. HRMS (ESI) m/z calcd for $C_{15}H_{14}N_2O$ $[M+H]^+$ 239.1179; found: 239.1180.

4-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3,3-dimethylindolin-2-one, **5j**



Yield 57 %, white solid; ^{1}H NMR (400 MHz, $CHCl_3$) δ = 9.46 (s br, 1 NH), 7.56-7.50 (m, 1 H), 7.29-7.19 (m, 1 H), 7.10-7.04 (m, 1 H), 4.15 (s, 2 H), 1.60 (s, 6H), 1.42 (s, 6 H) ppm; ^{13}C NMR (100 MHz, $CHCl_3$) δ = 184.6, 161.4, 141.1, 134.9, 127.6, 125.2, 124.2, 112.7, 79.1, 67.8, 46.8, 28.3, 22.3 ppm. HRMS (ESI) m/z calcd for $C_{15}H_{18}N_2O_2$ $[M+H]^+$ 259.1441; found: 259.1445.

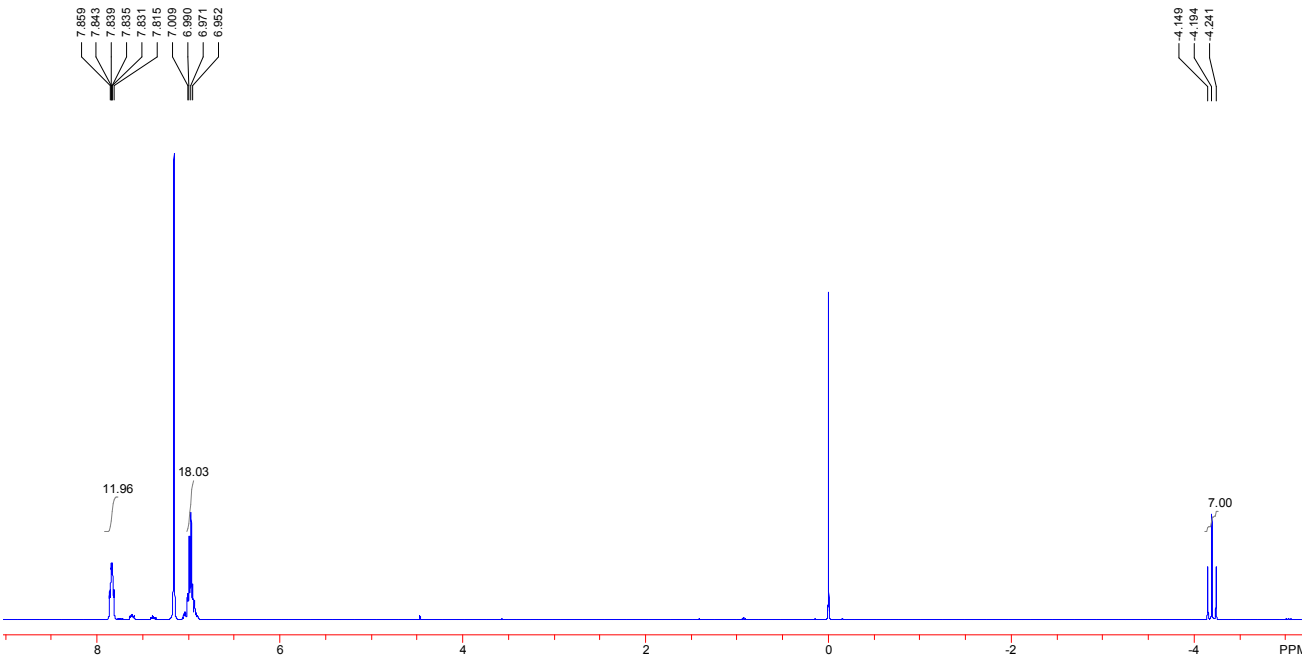
4-(4,5-dihydrooxazol-2-yl)-3,3,7-trimethylindolin-2-one, **5k**



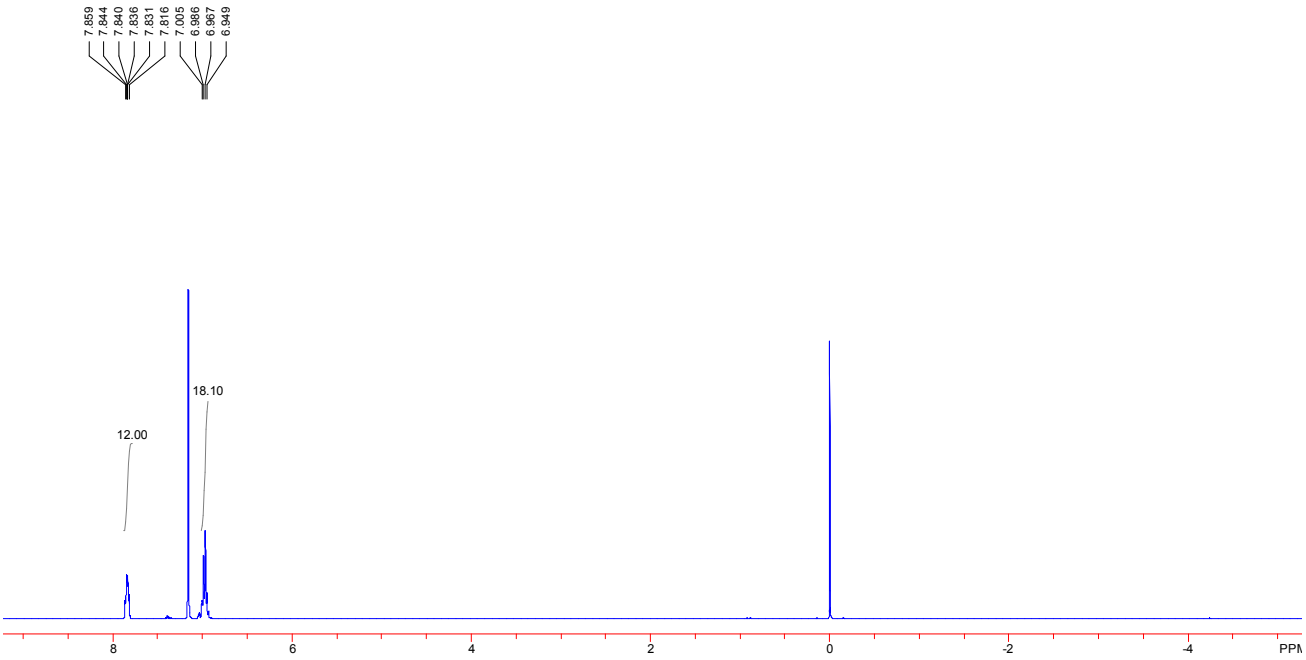
Yield 63 %, white solid; ^{1}H NMR (400 MHz, $CHCl_3$) δ = 9.35 (s br, 1 NH), 7.54 (d, *J* = 8.0 Hz, 1 H), 7.09 (d, J = 8.4 Hz, 1 H), 4.48 (t, *J* = 9.6 Hz, 2 H), 4.12 (t, *J* = 9.6 Hz, 2 H), 2.36 (s, 3H), 1.58 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CHCl_3$) δ = 184.9, 163.7, 139.7, 134.5, 128.8, 126.2, 124.1, 122.5, 67.0, 55.0, 47.2, 22.2, 16.9 ppm. HRMS (ESI) m/z calcd for $C_{13}H_{14}N_2O_2$ $[M+H]^+$ 245.1285; found: 245.1280.

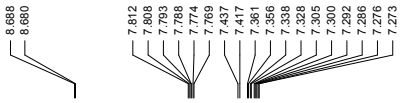
Copies ^{1}H NMR, ^{13}C NMR

$ReH_7(PCy_3)_2$



$ReD_7(PPh_3)_2$

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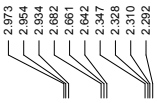
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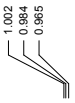
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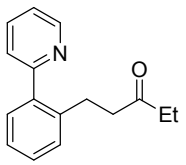
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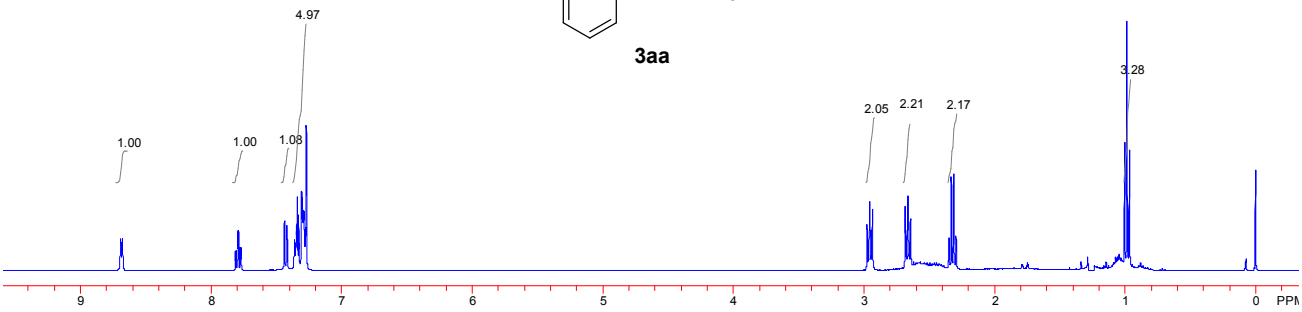
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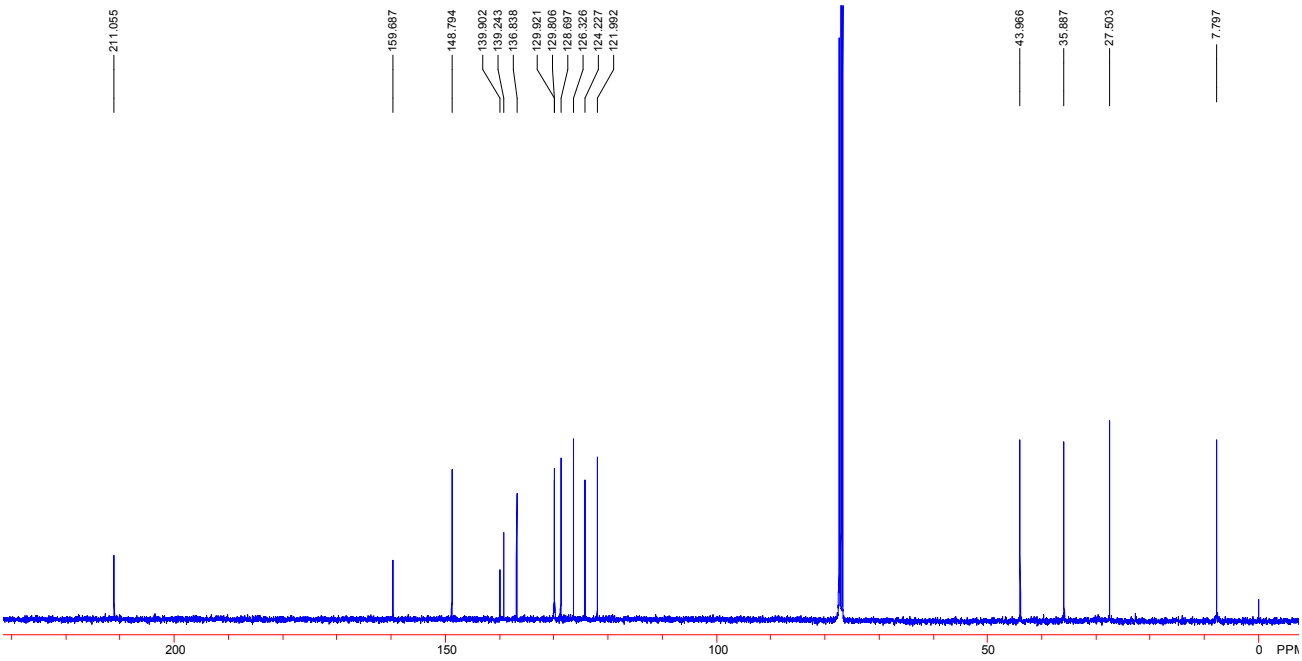
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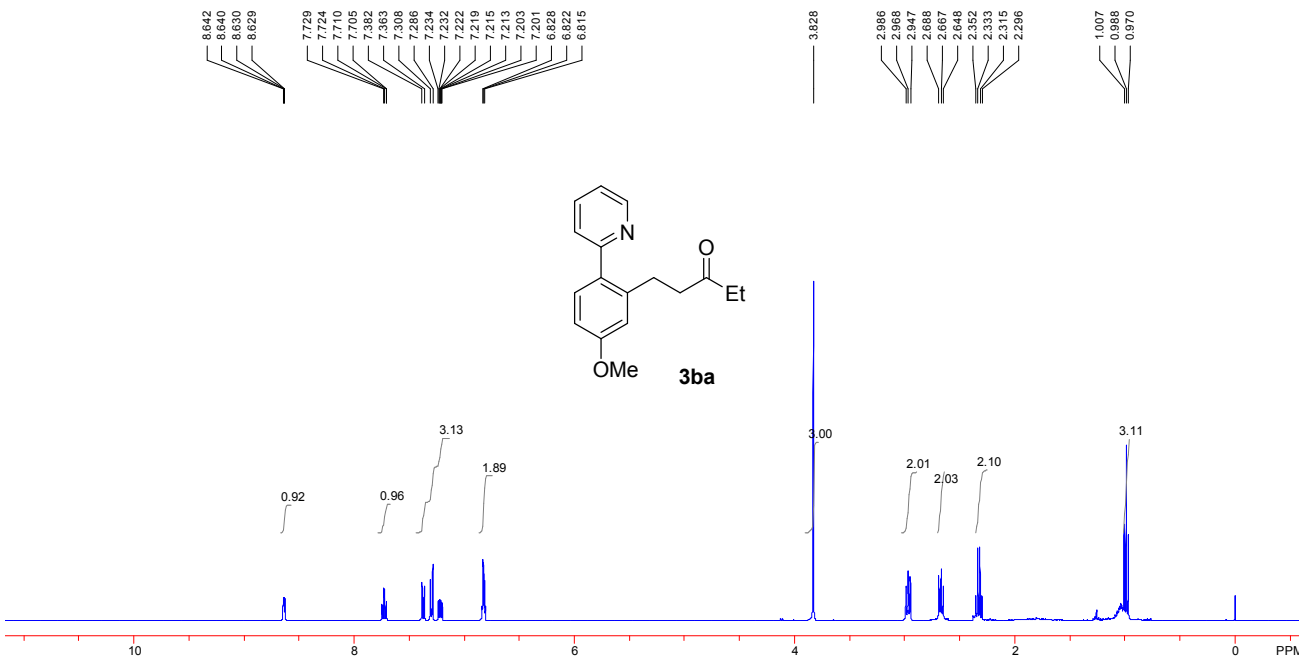
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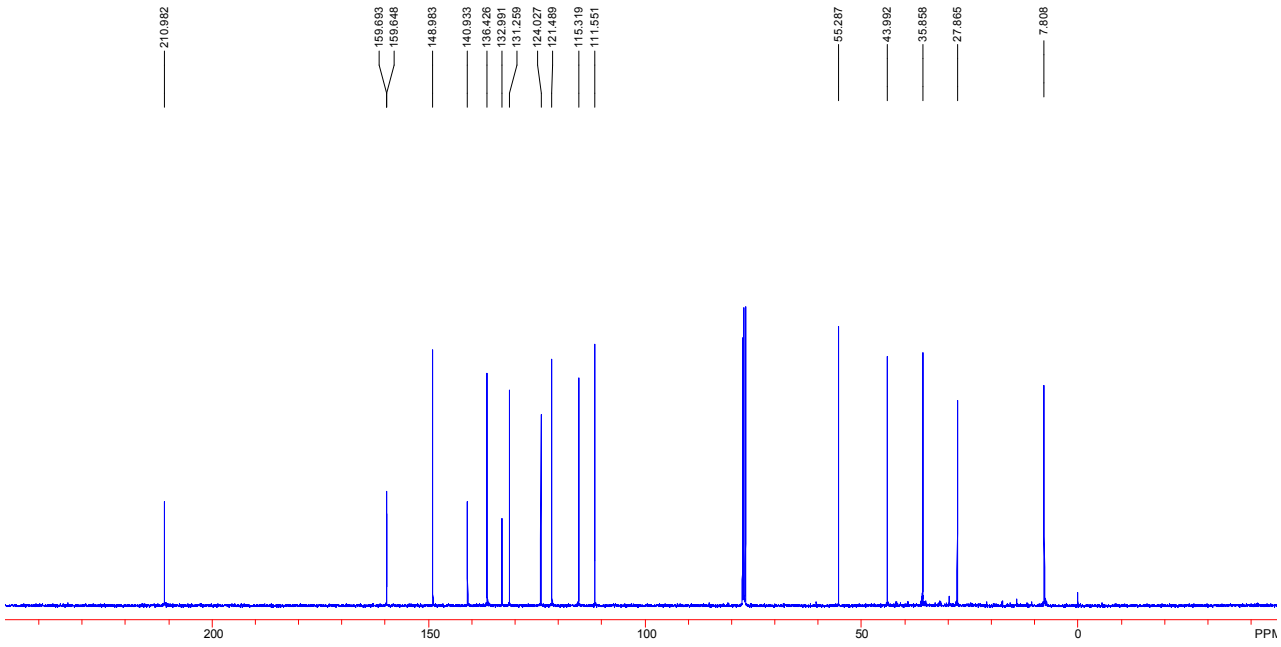
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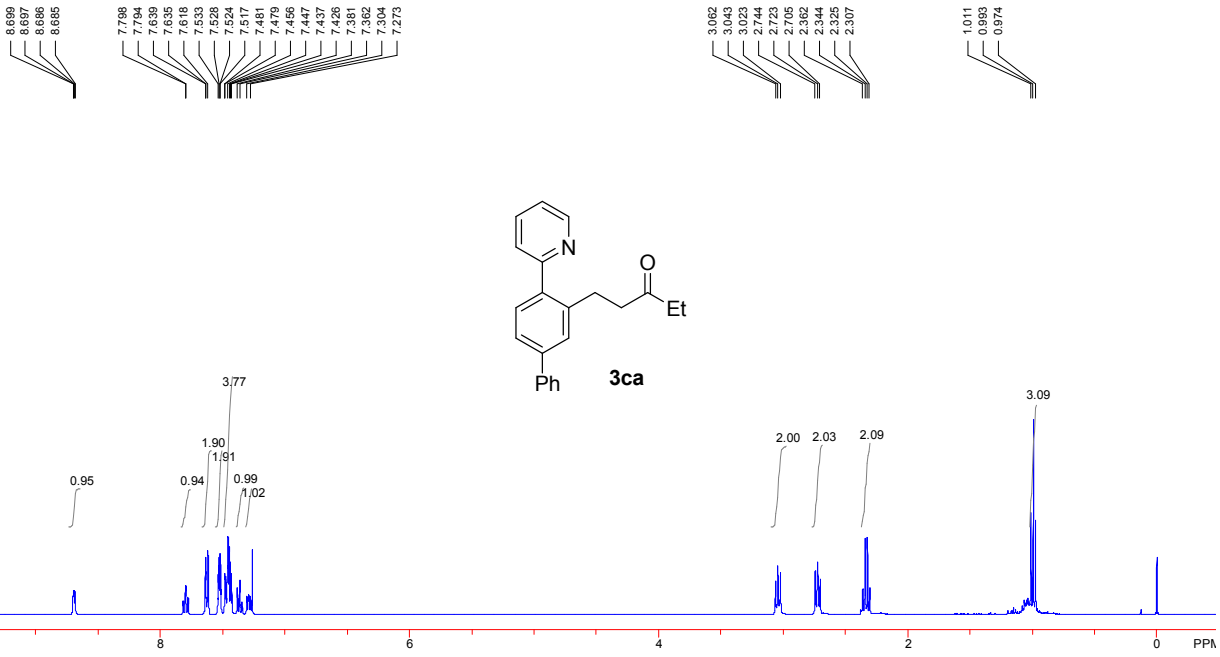
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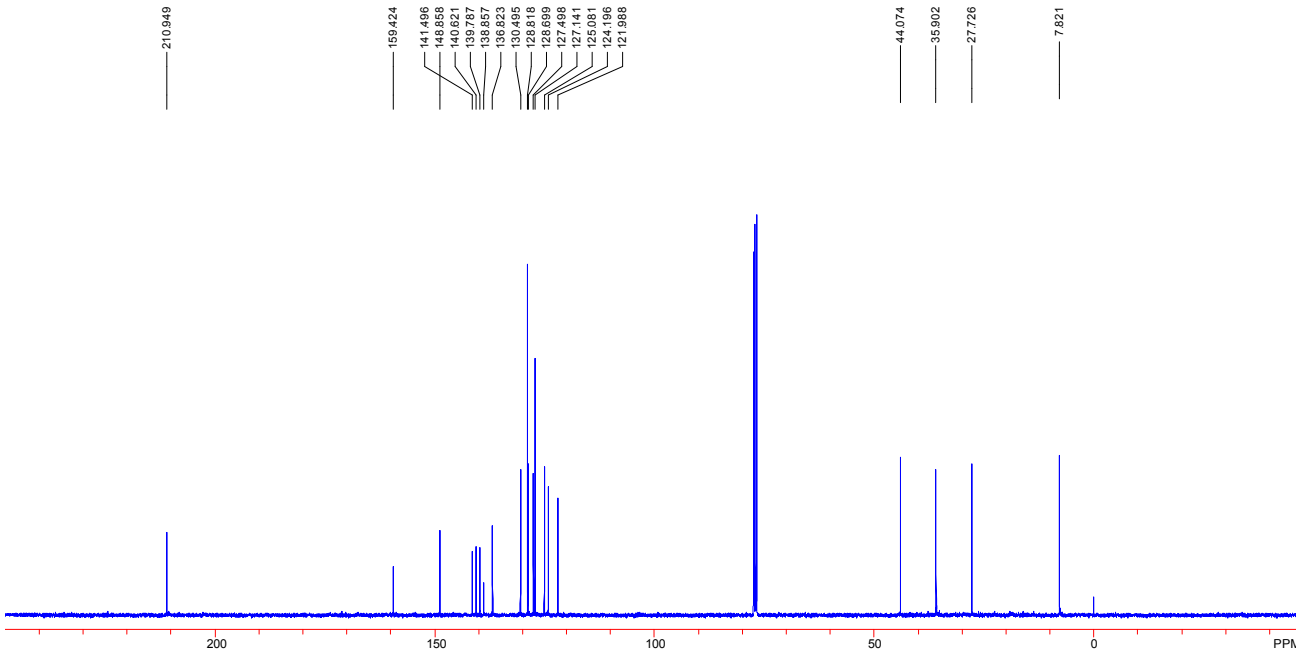
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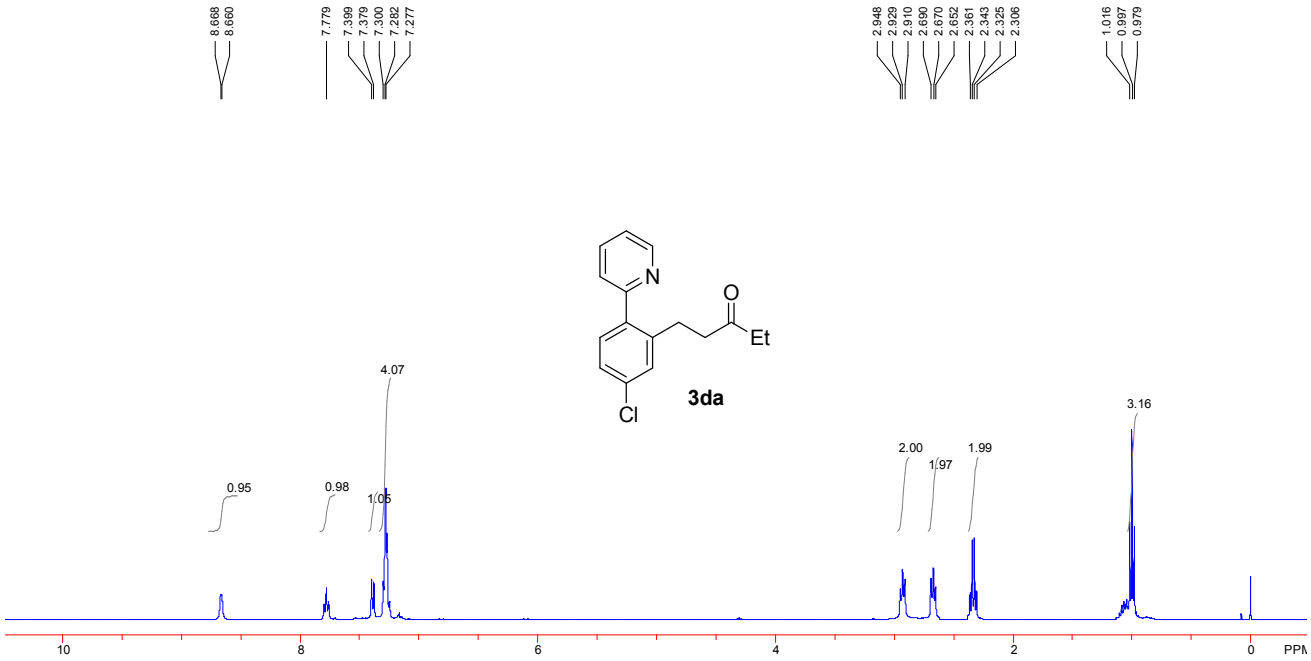
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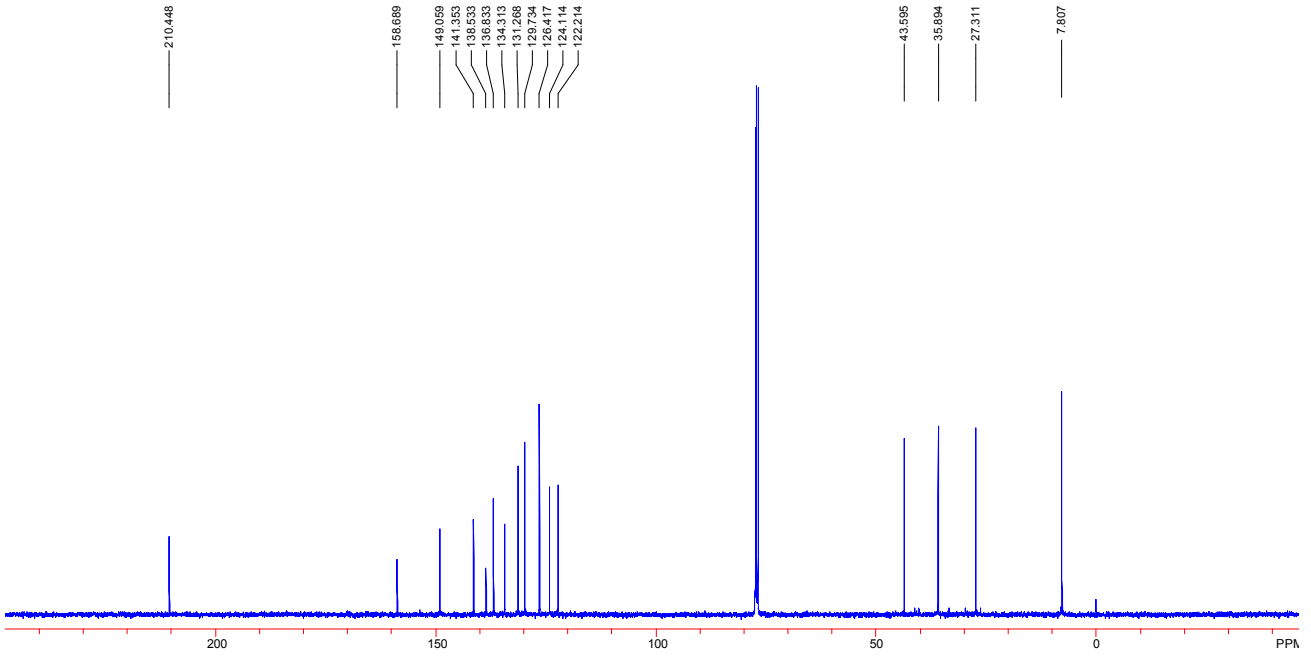
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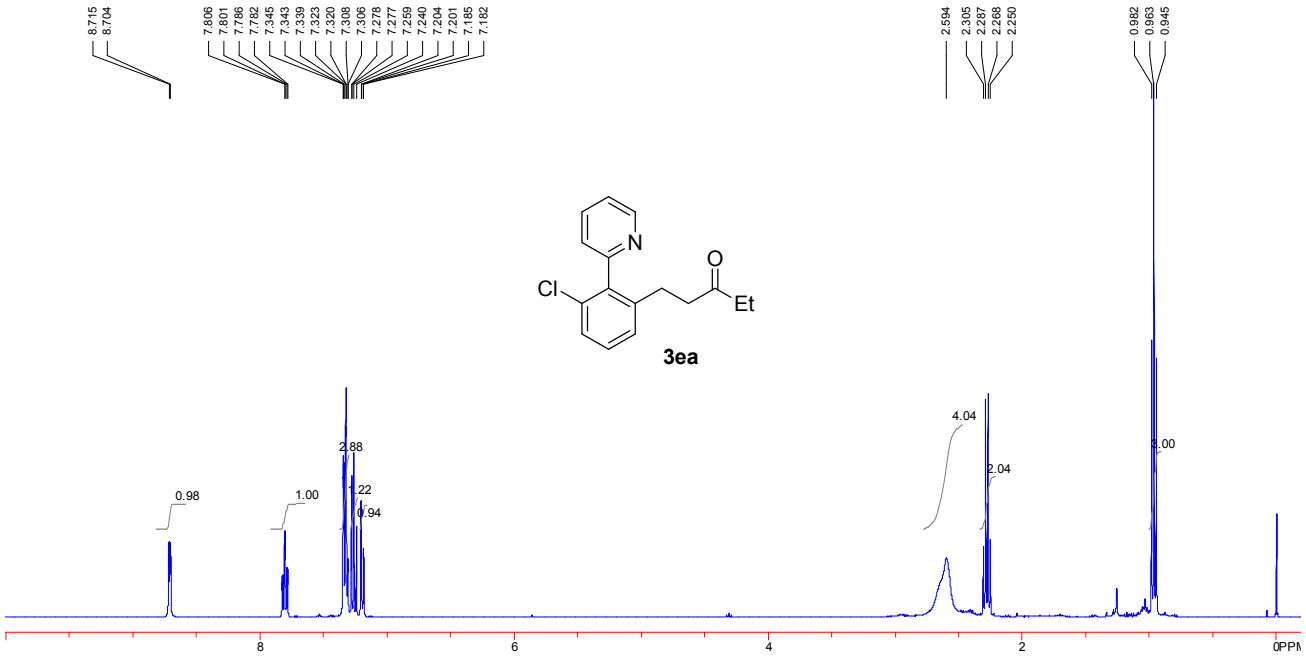
PPM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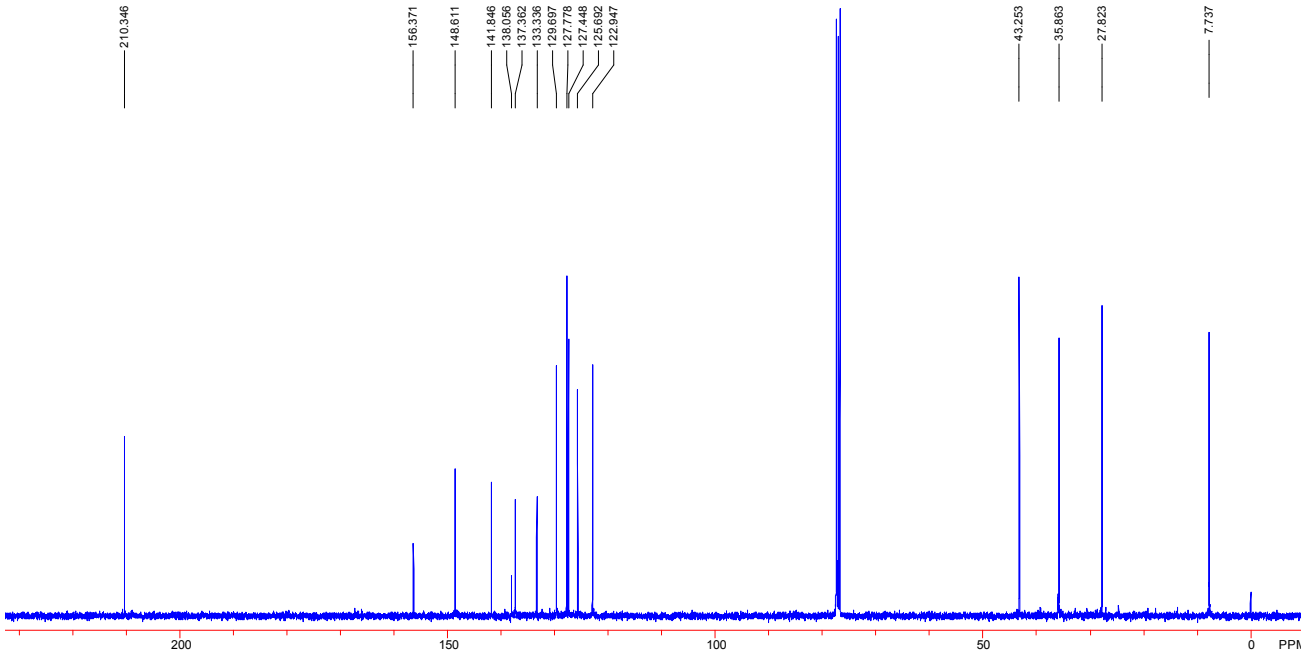
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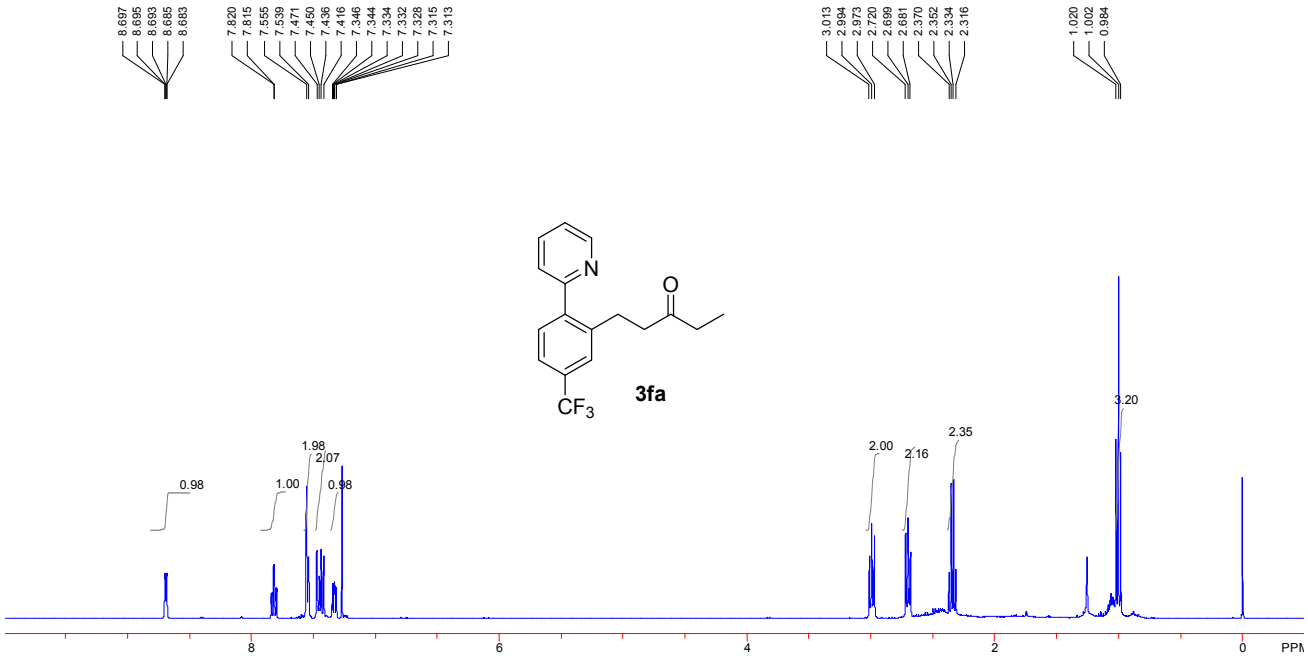
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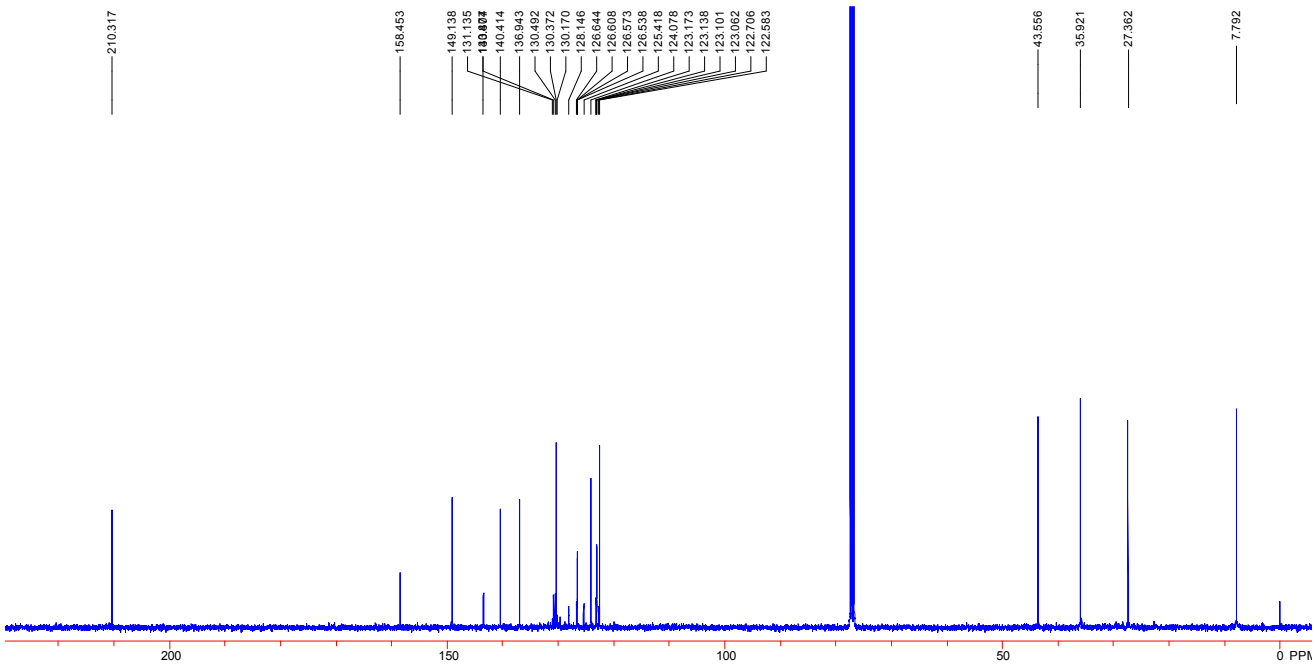
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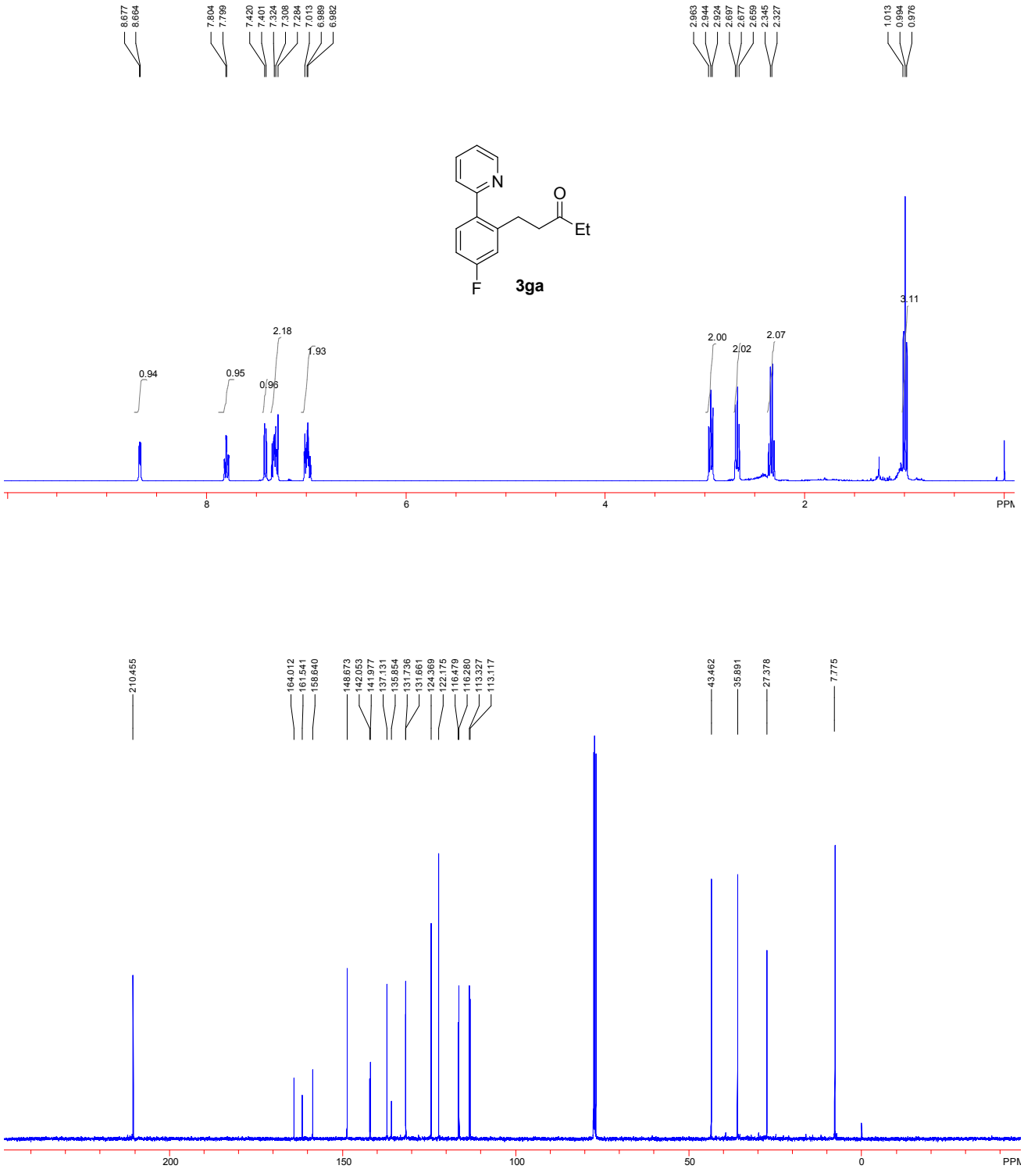
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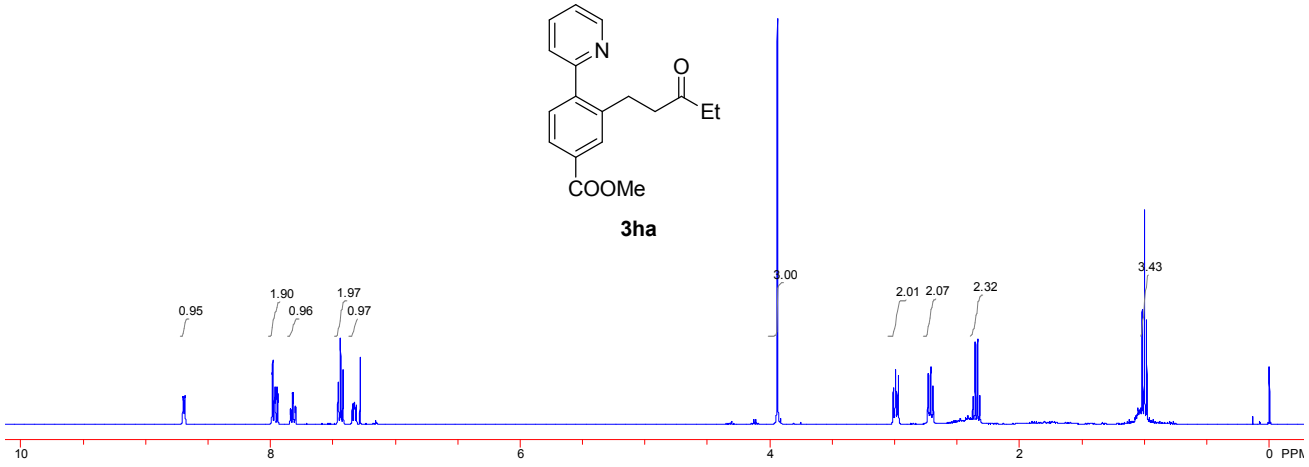
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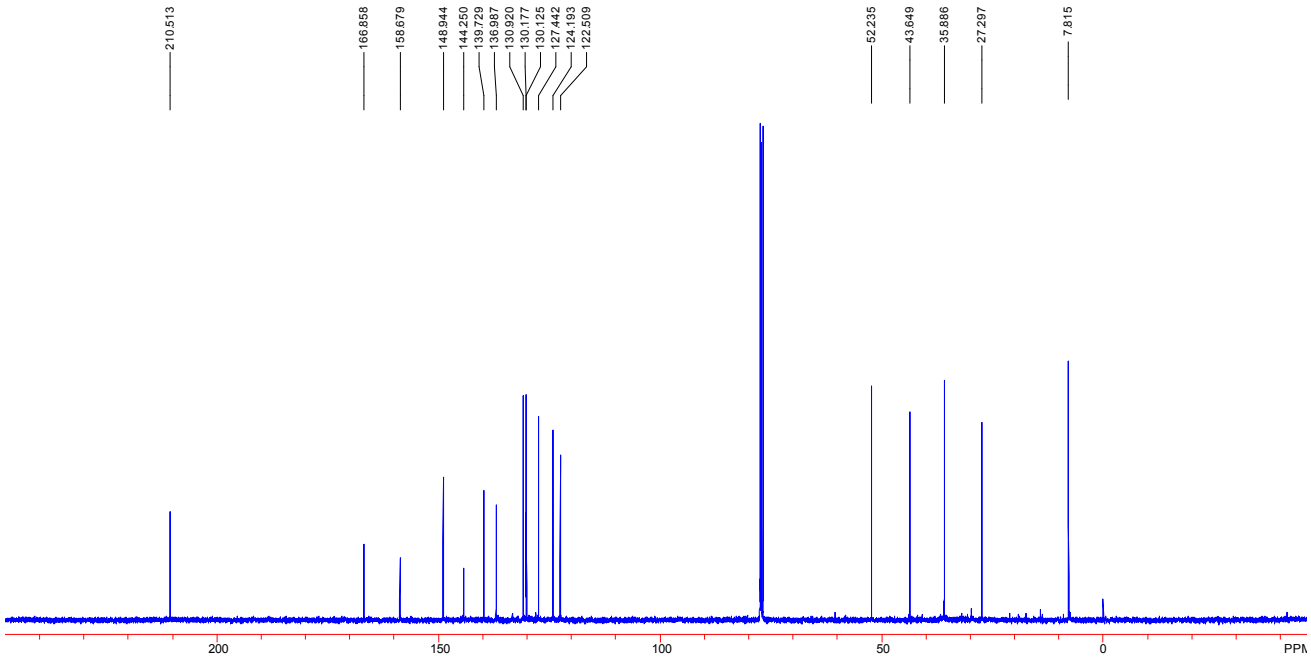
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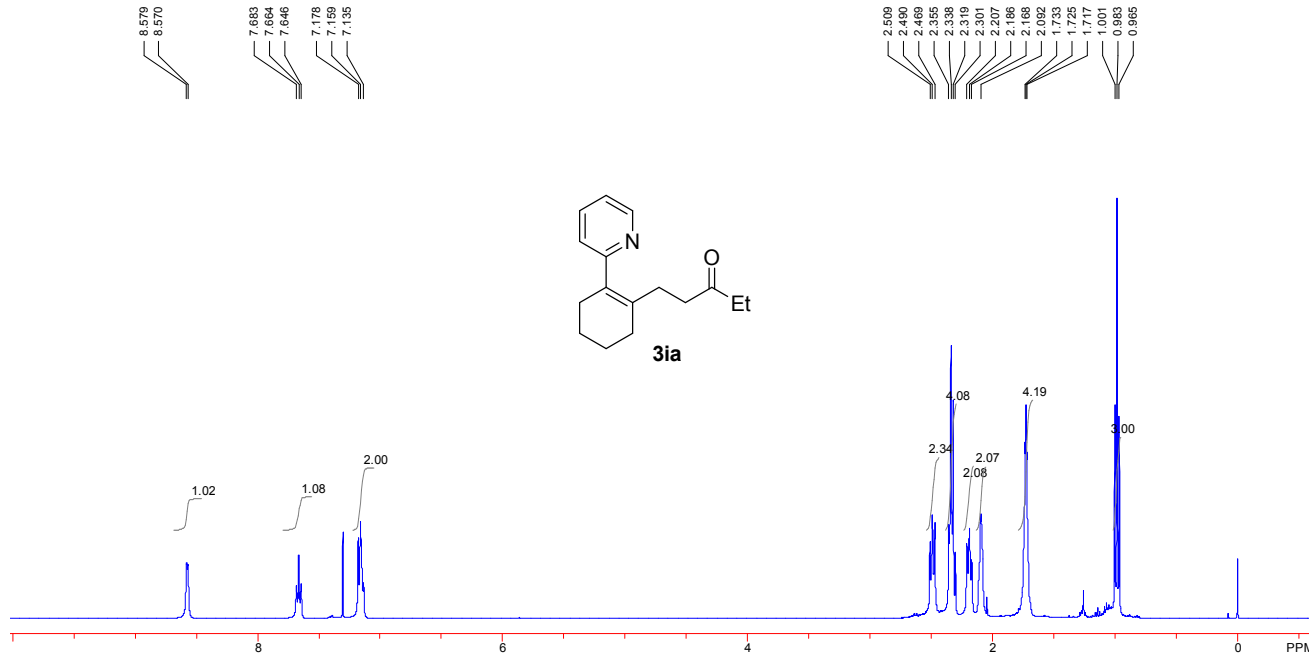
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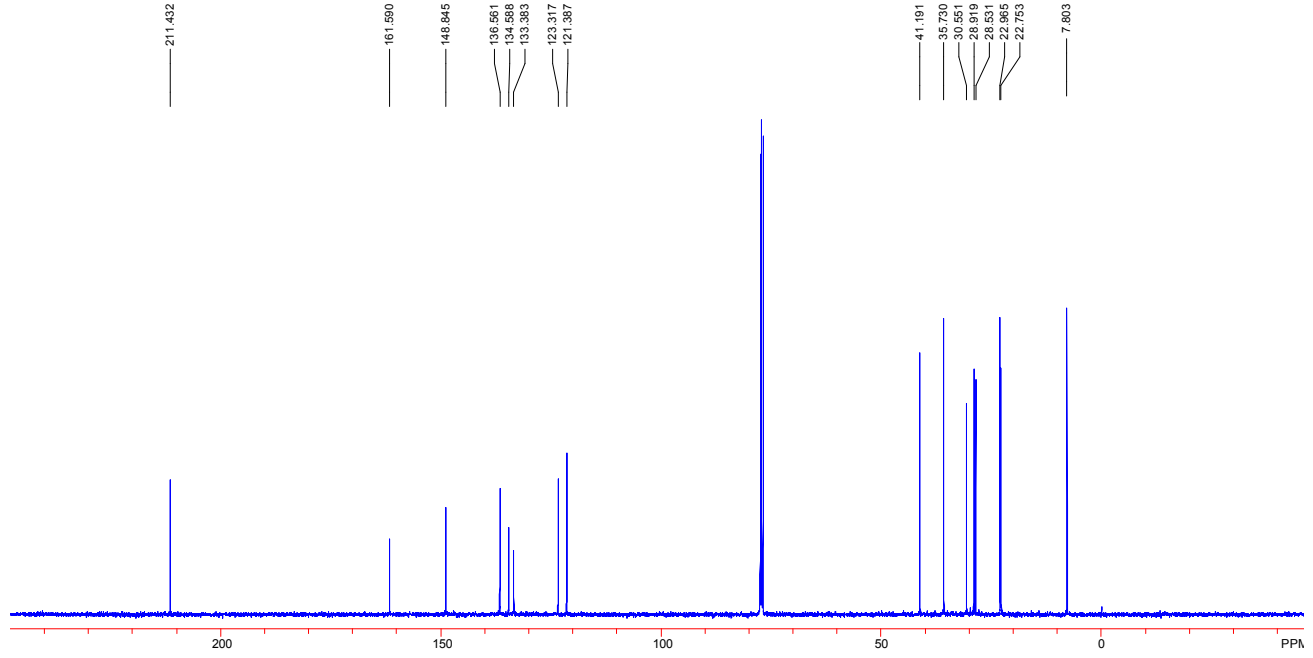
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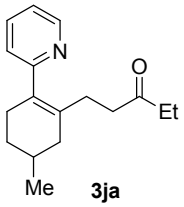
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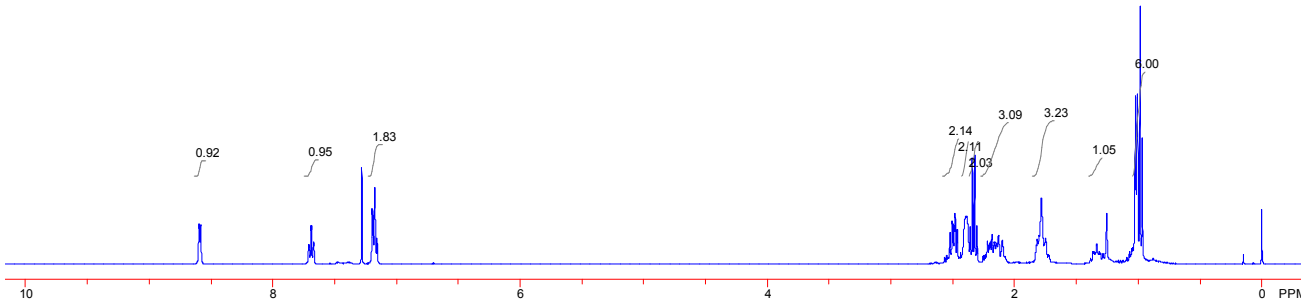
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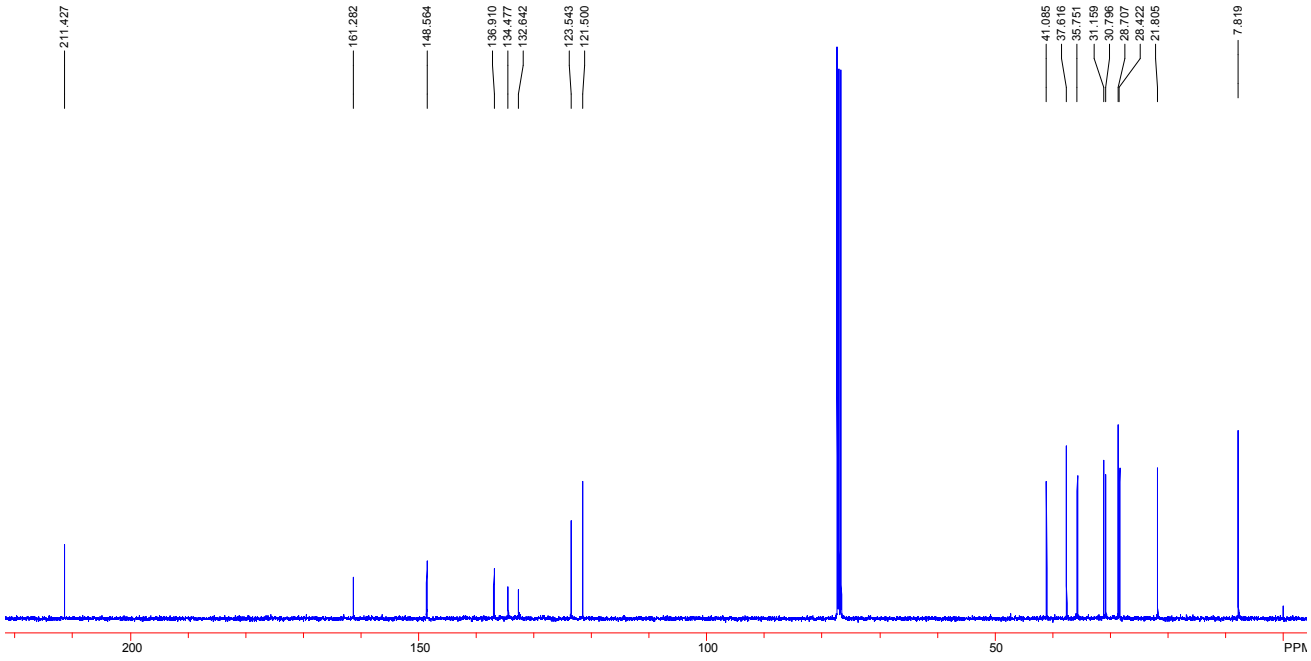
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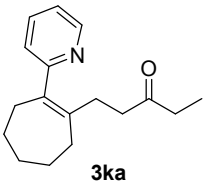
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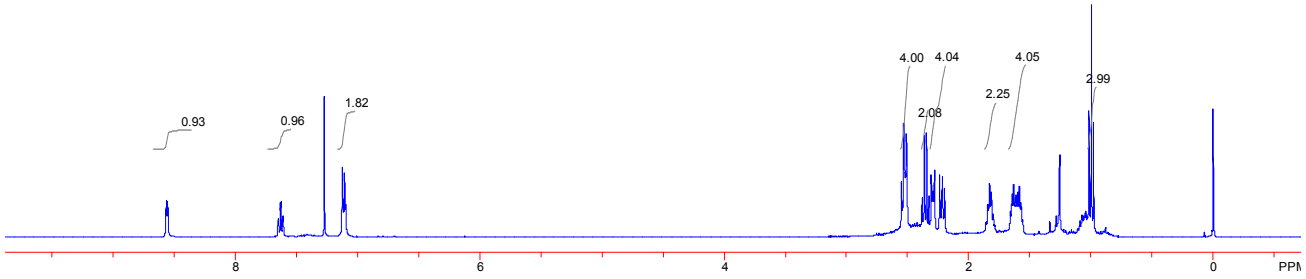
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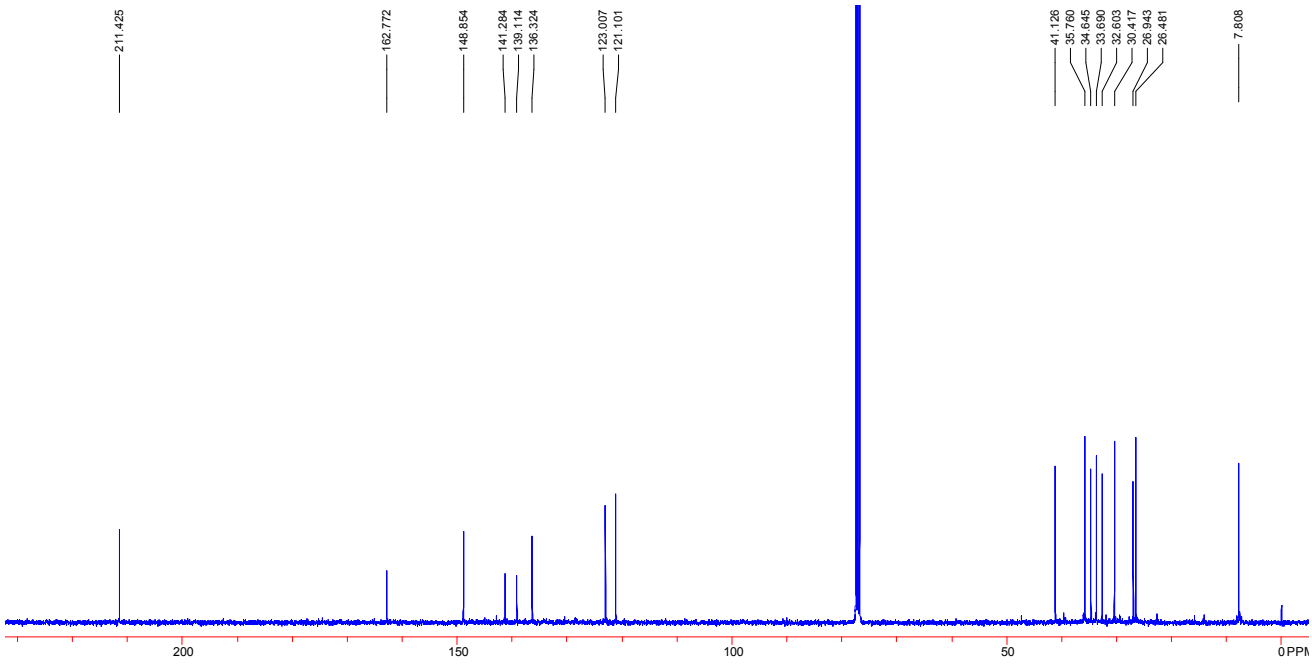
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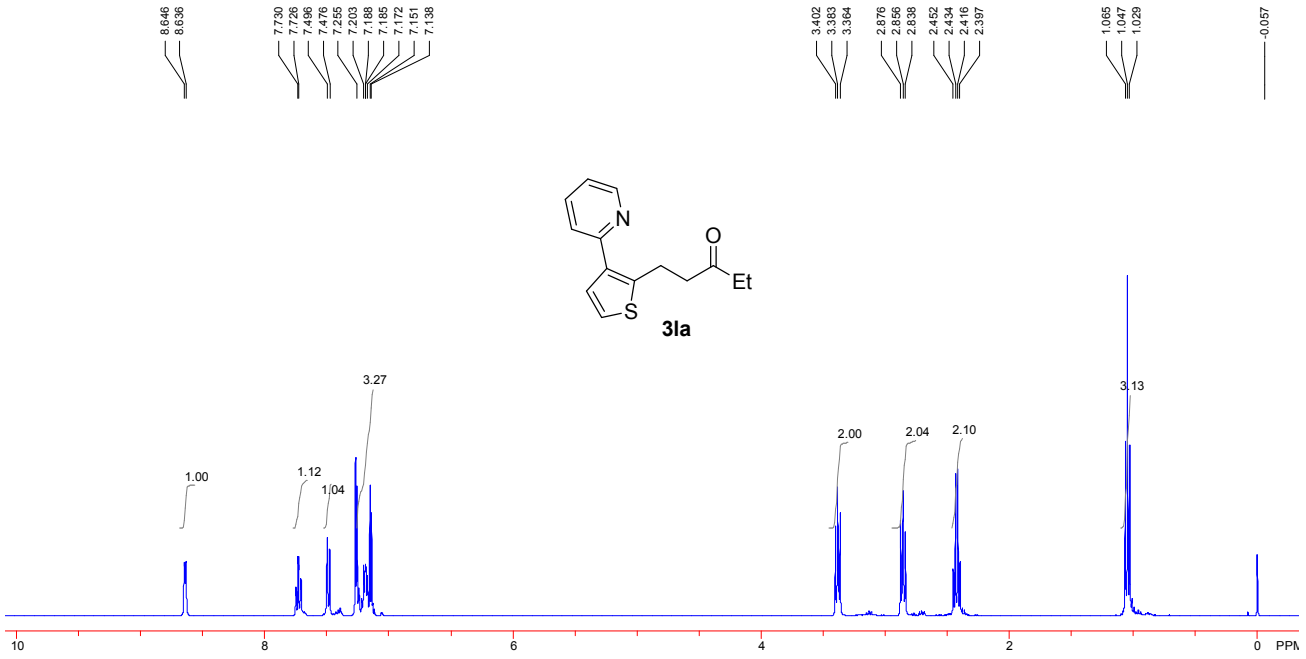
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1.047
1.029
-0.057
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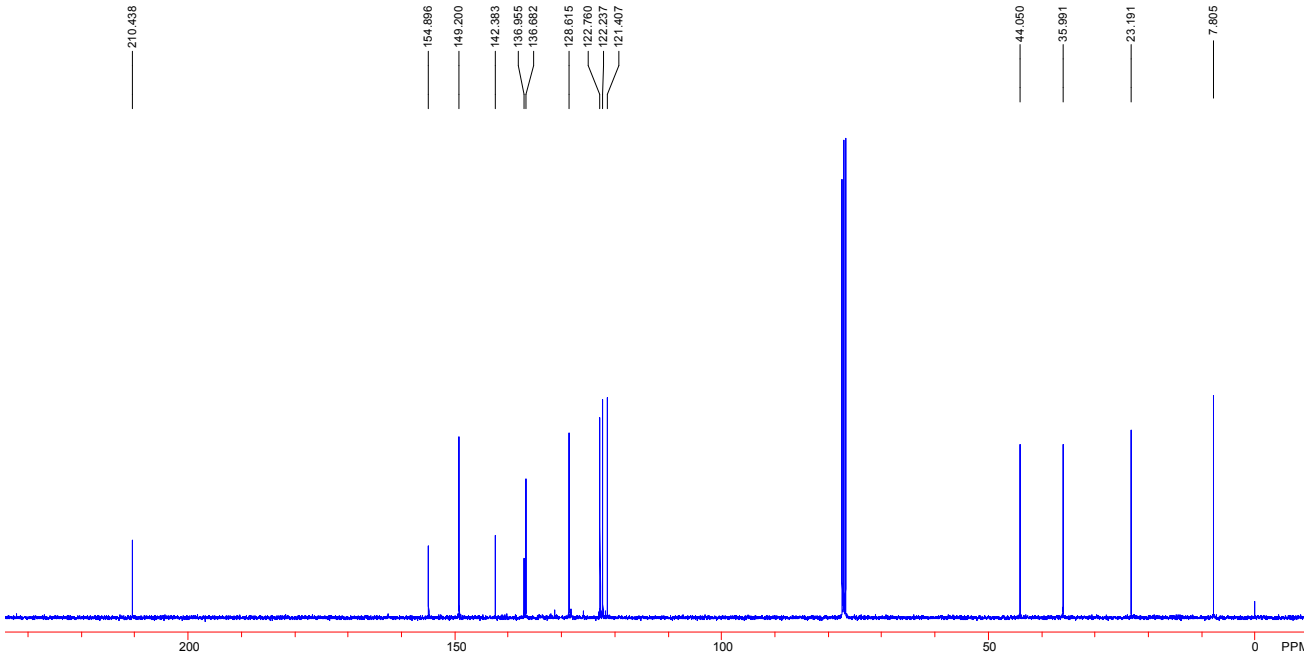
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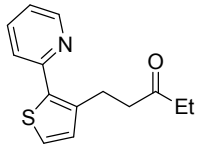
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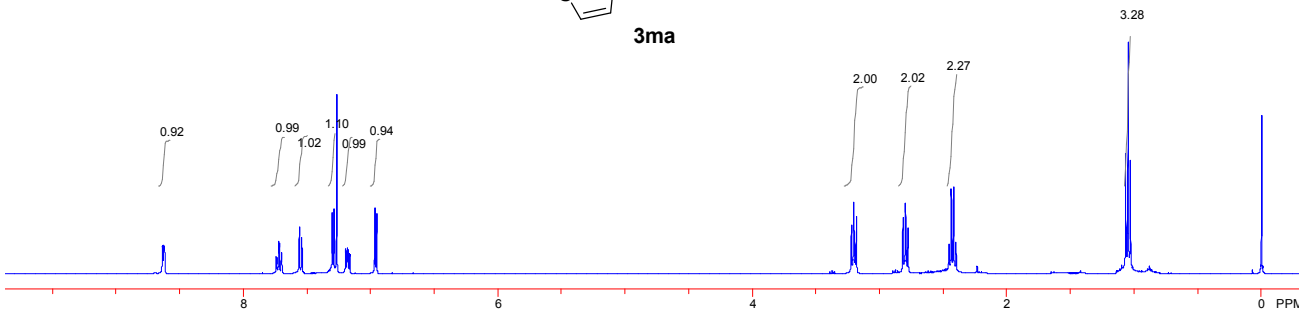
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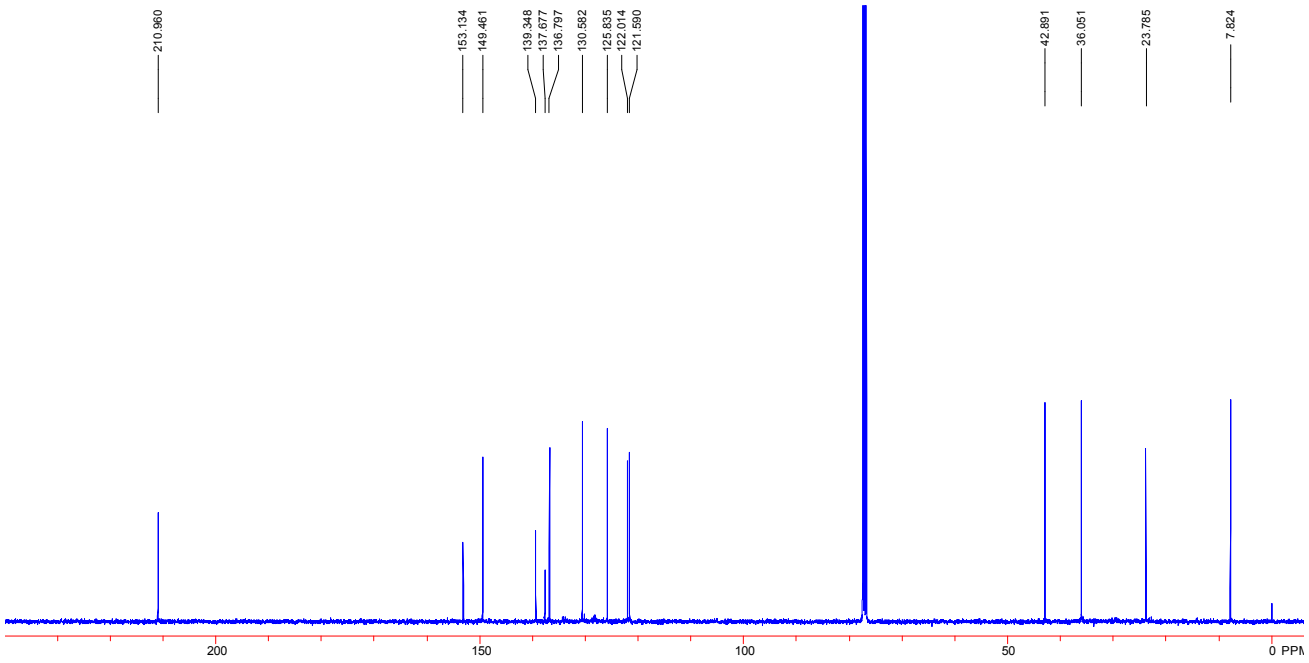
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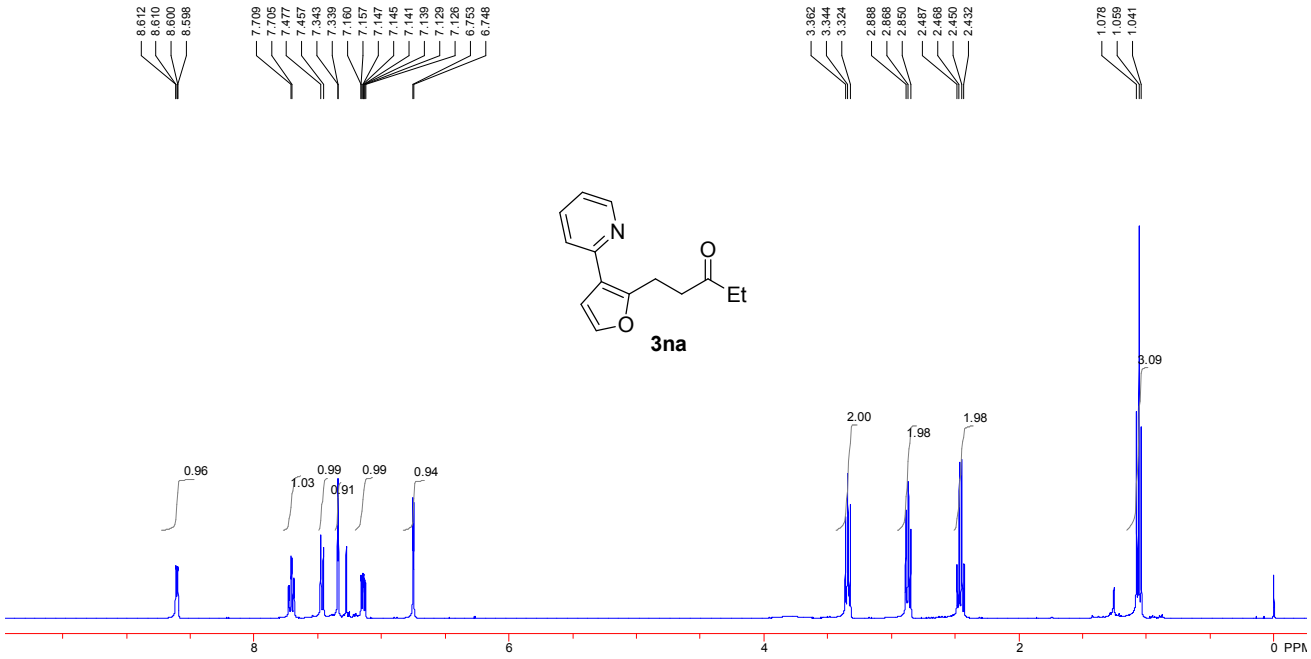
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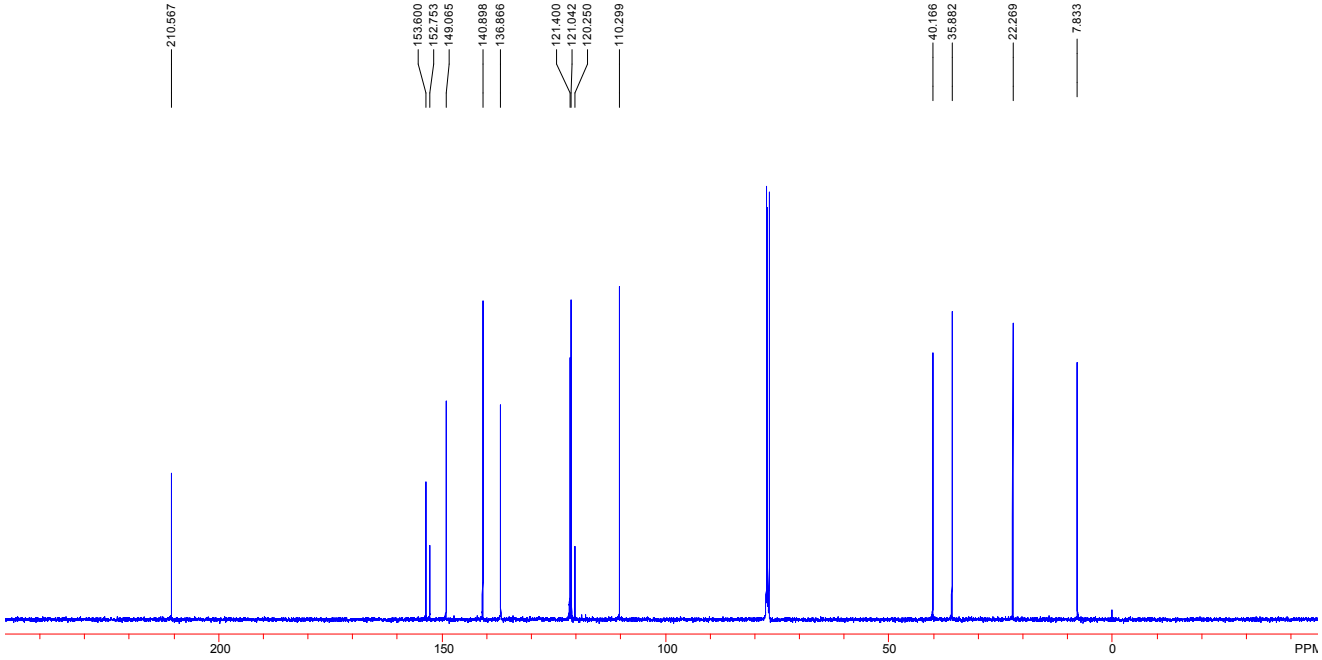
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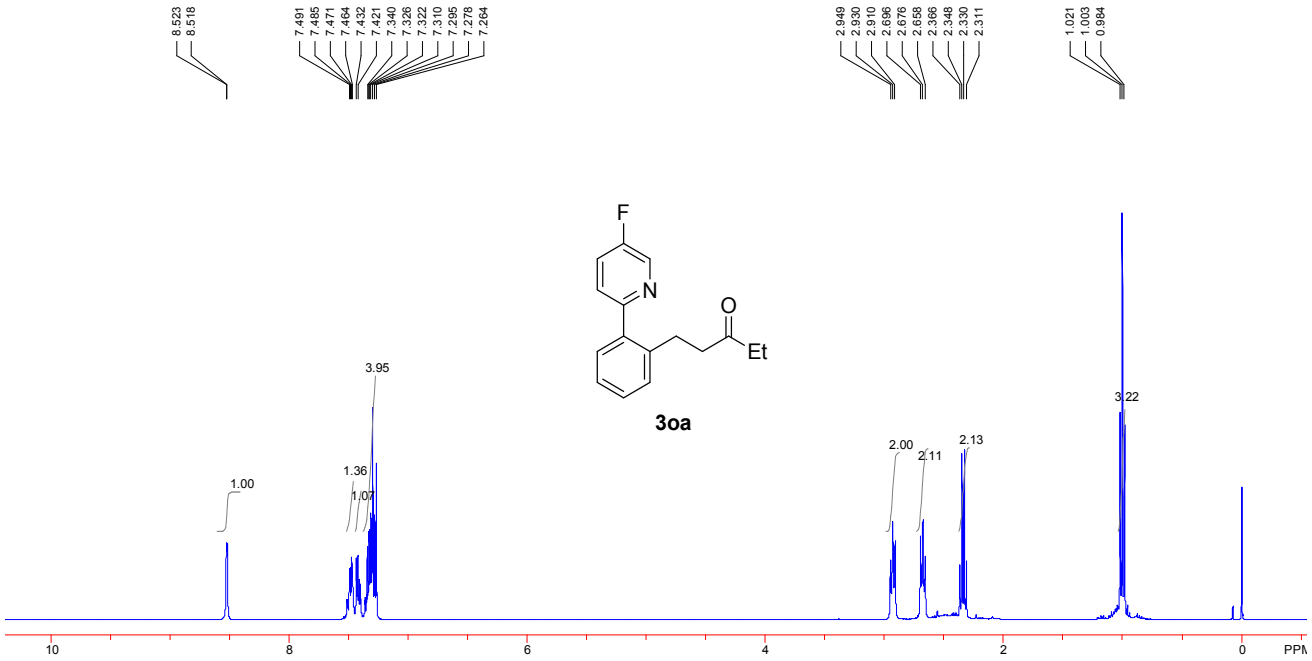
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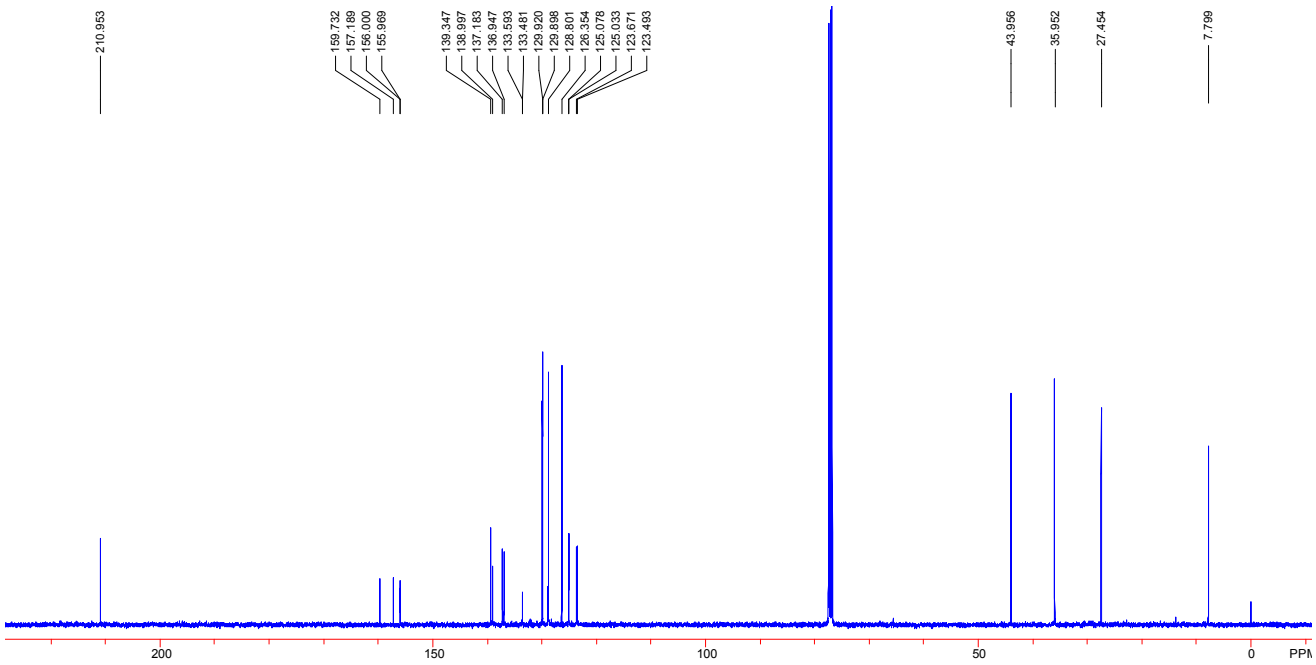
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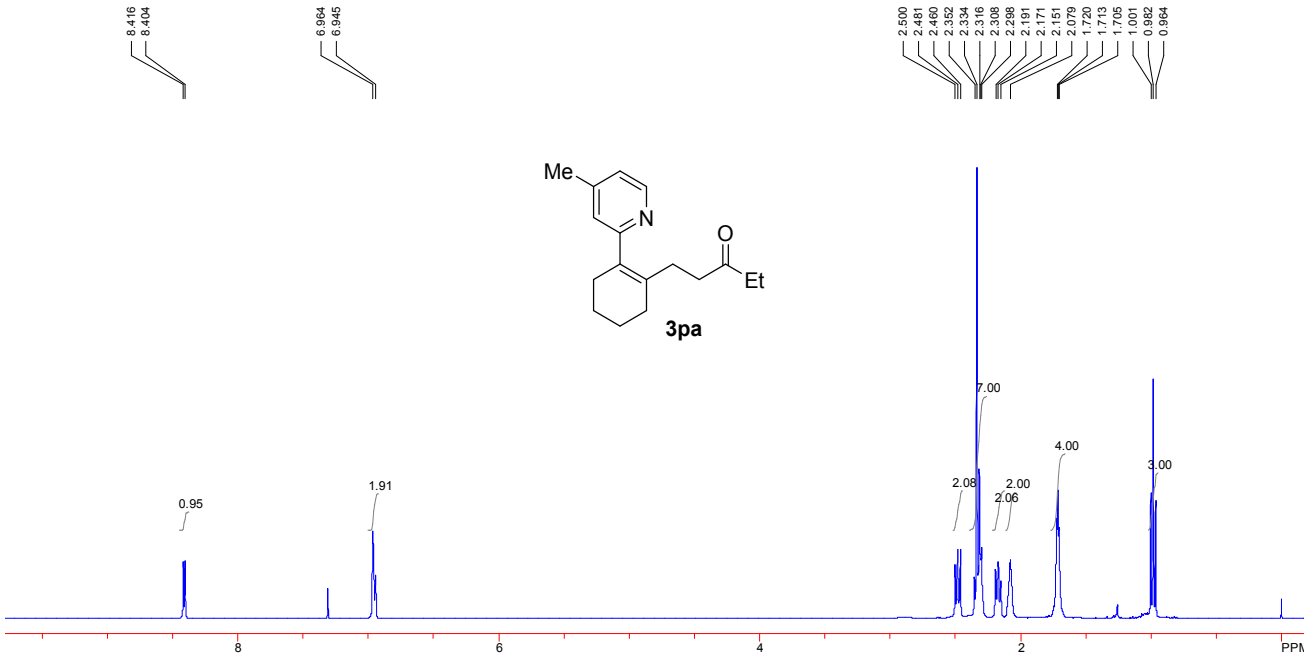
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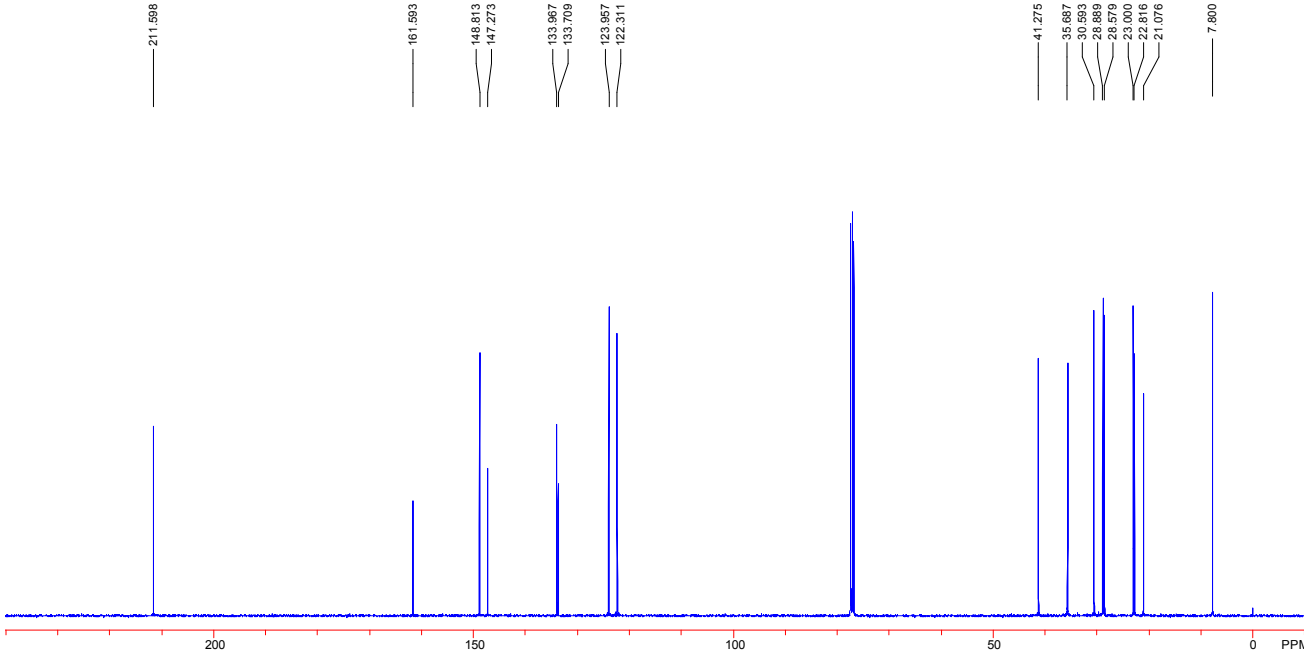
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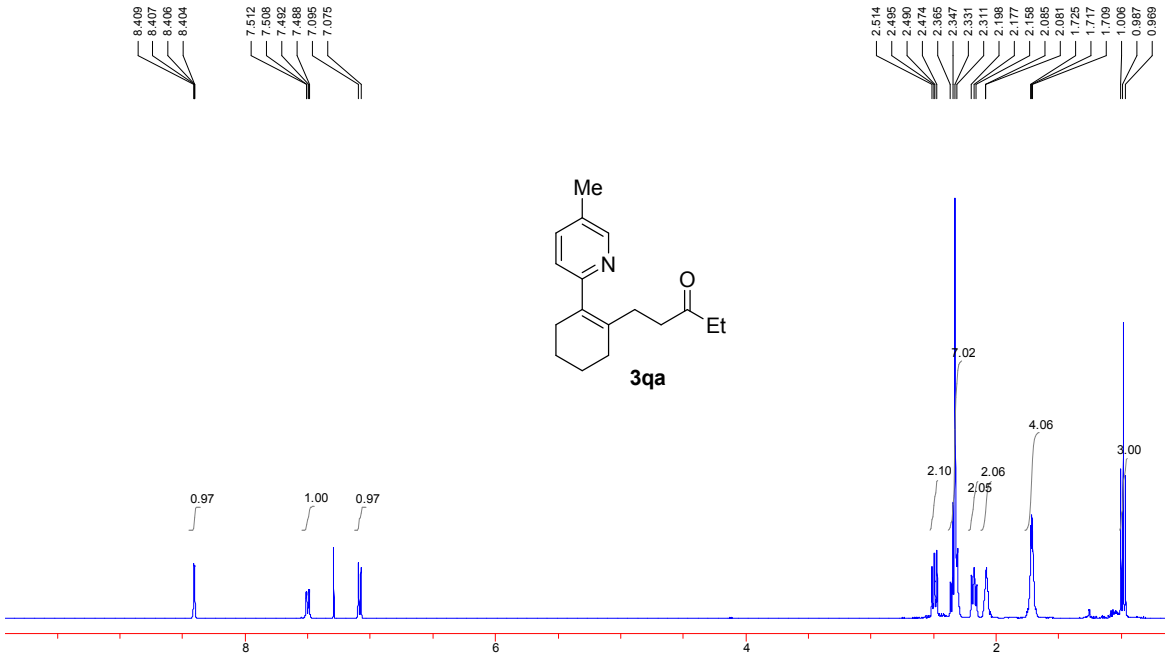
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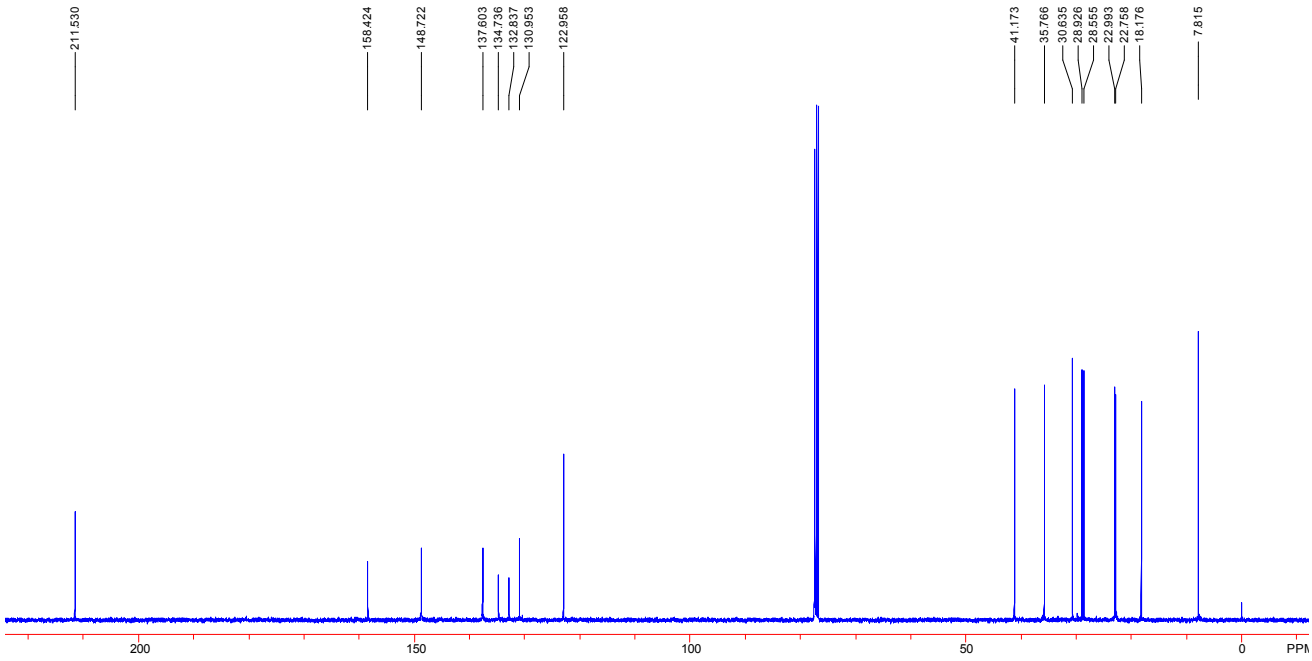
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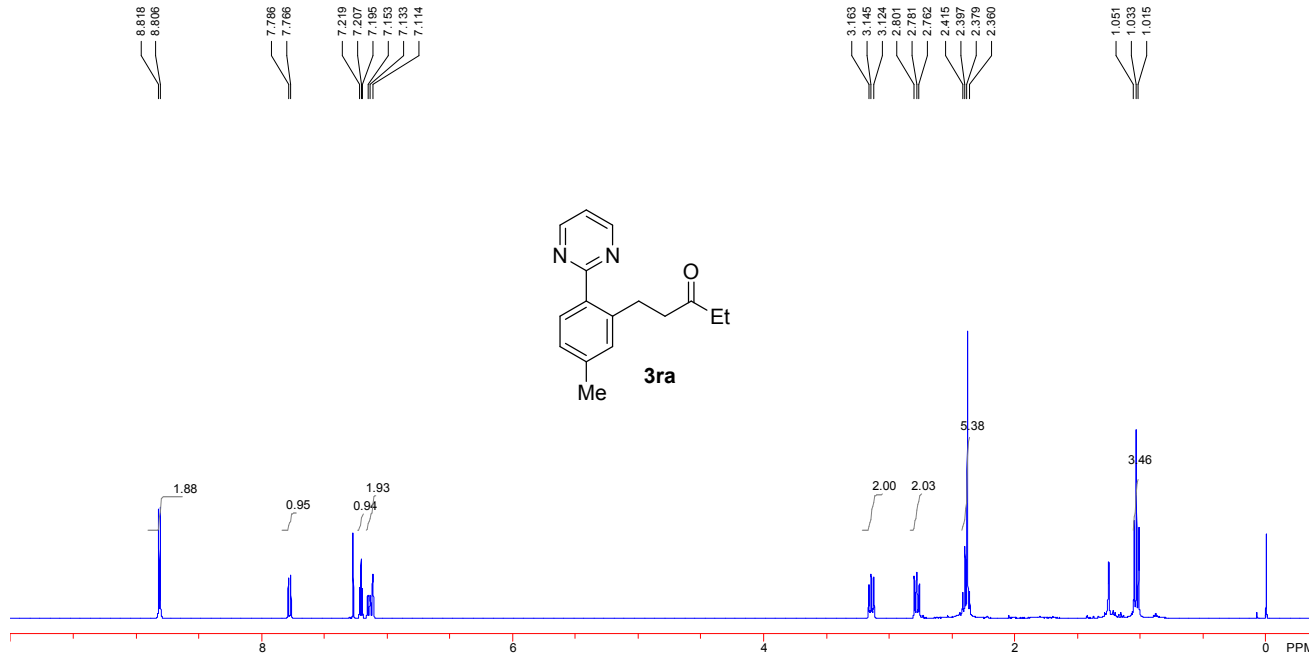
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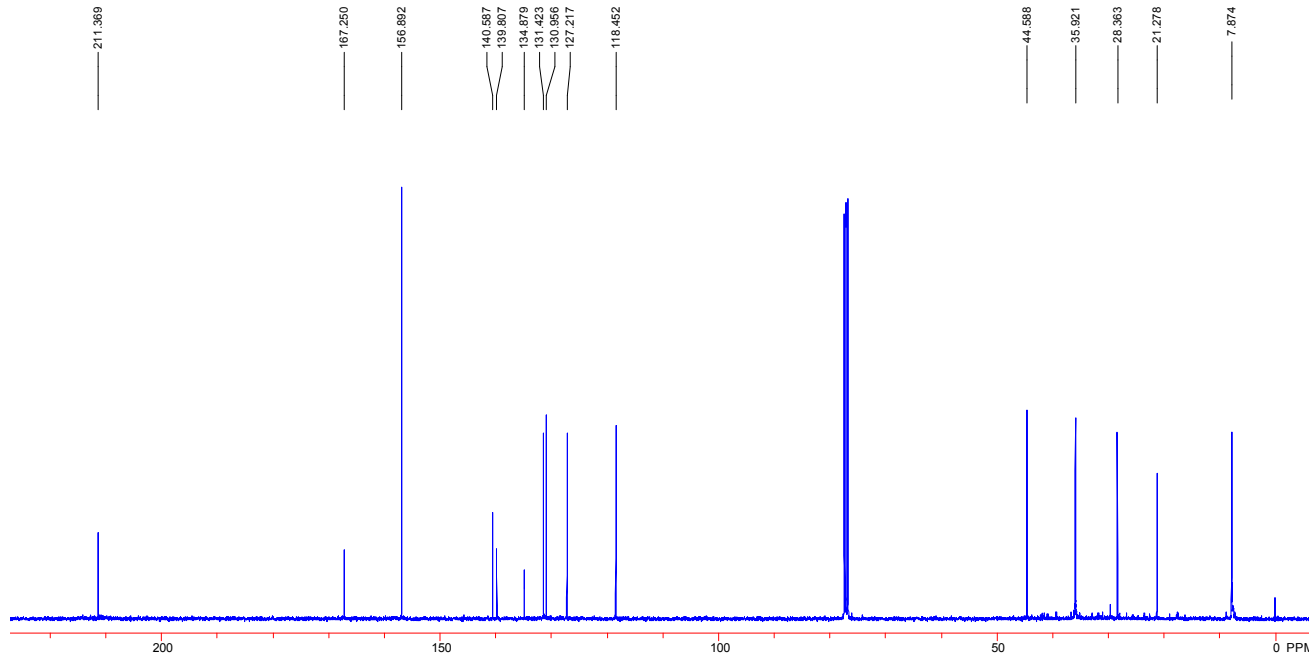
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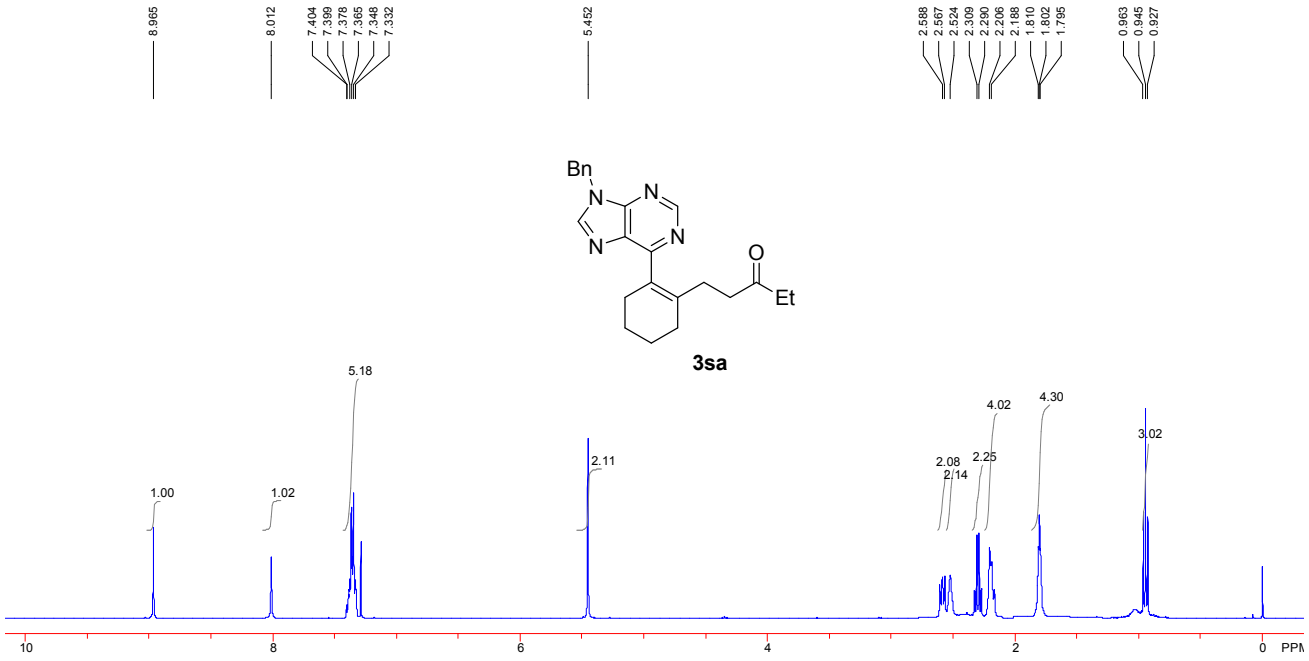
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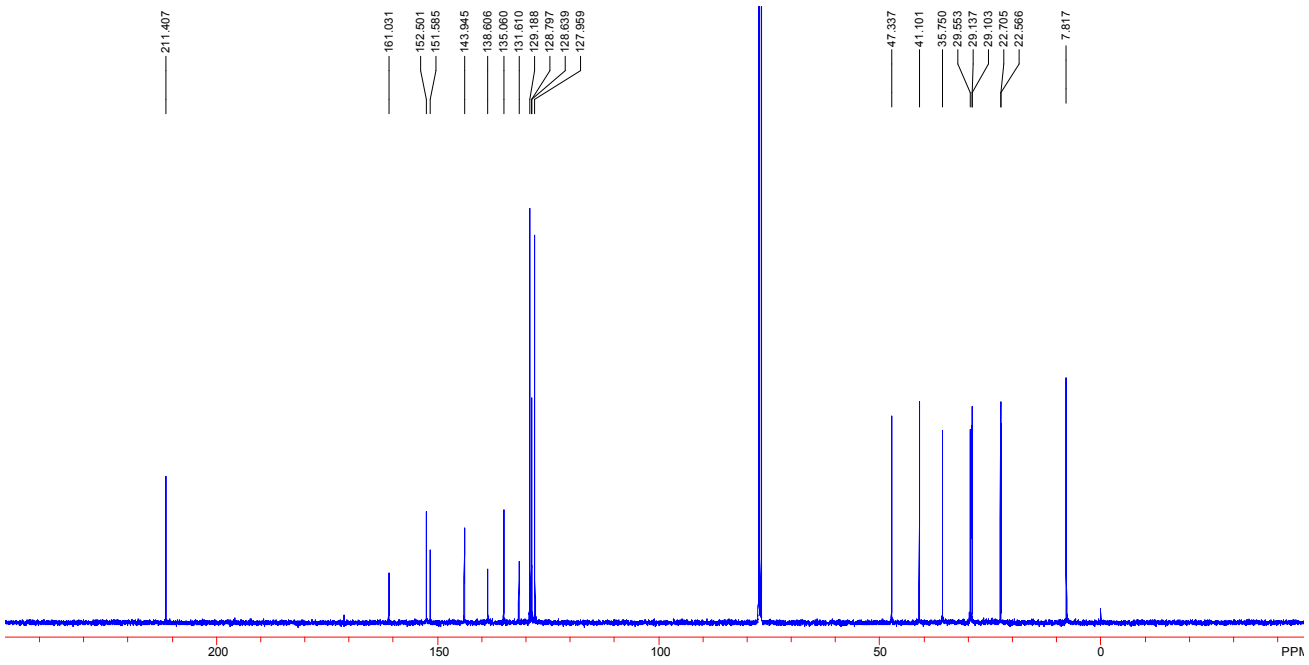
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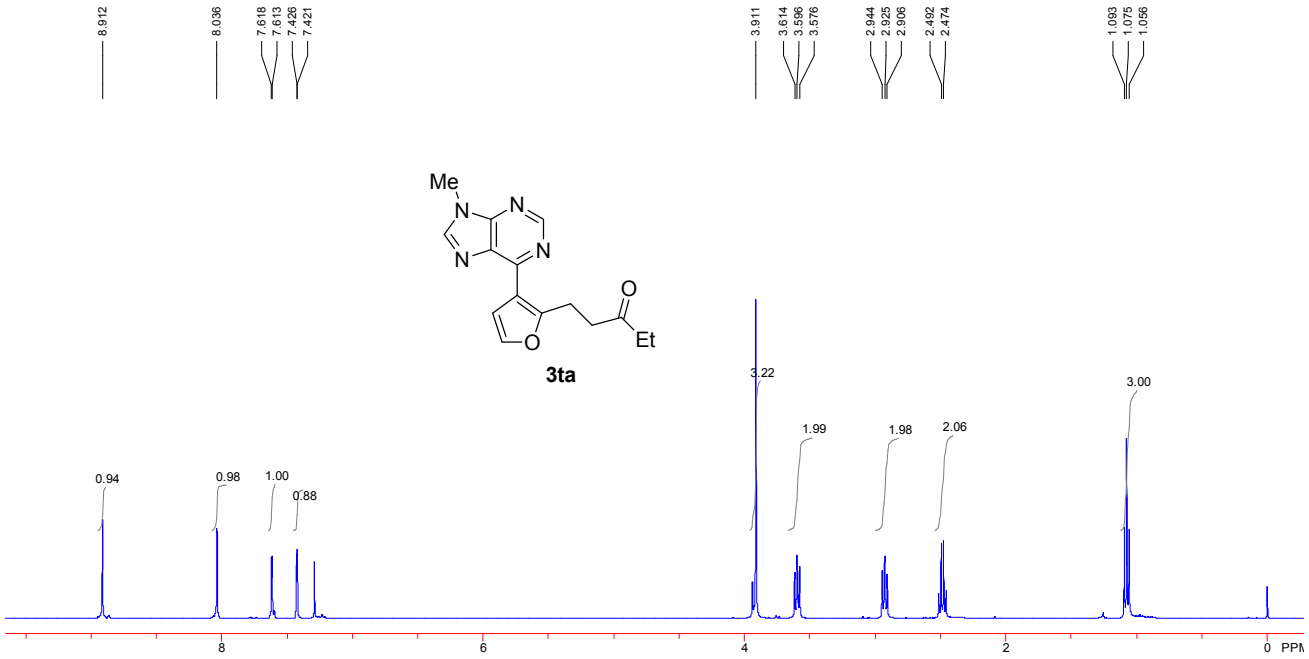
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3.576
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2.474
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1.075
1.056
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N
N
O
Et
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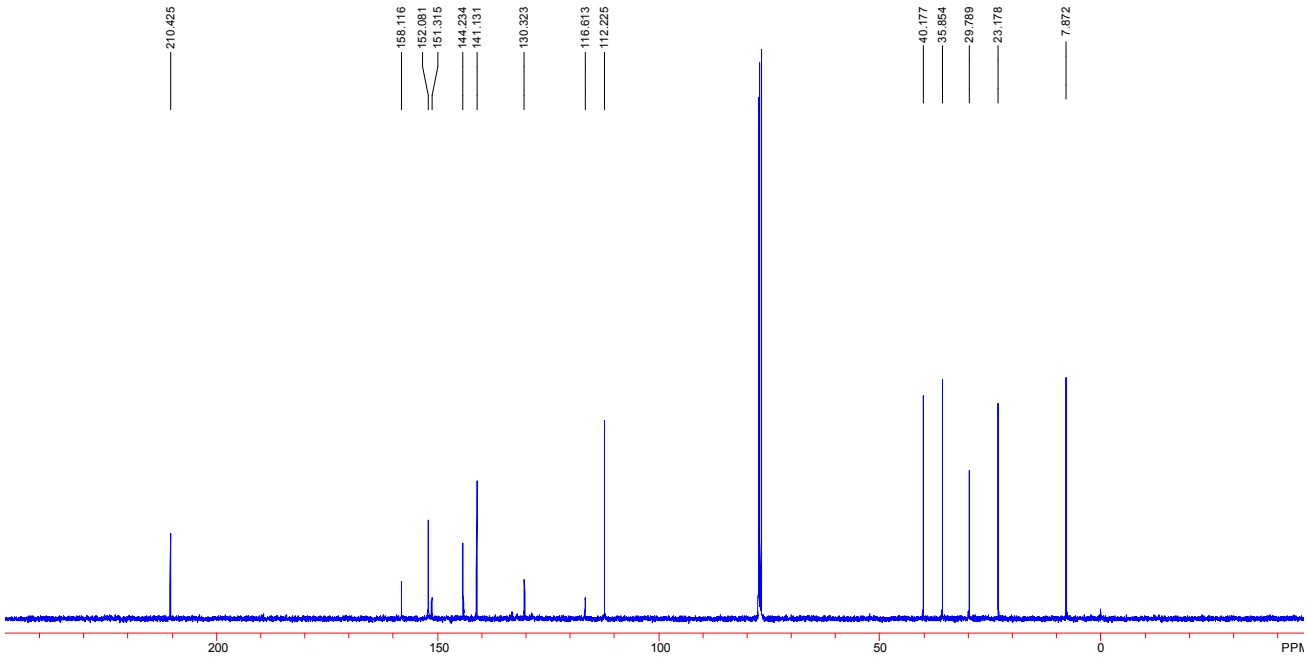
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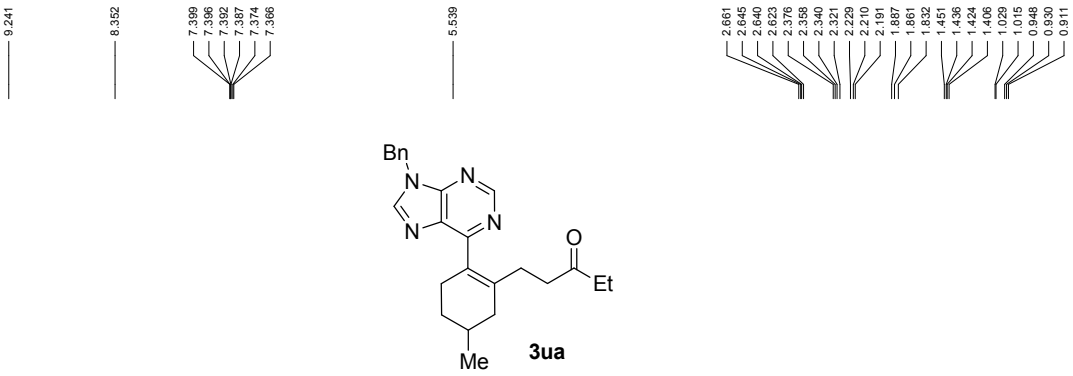
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Et
Me

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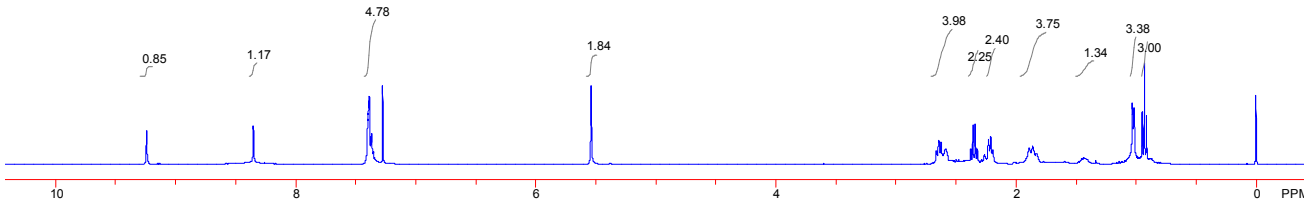
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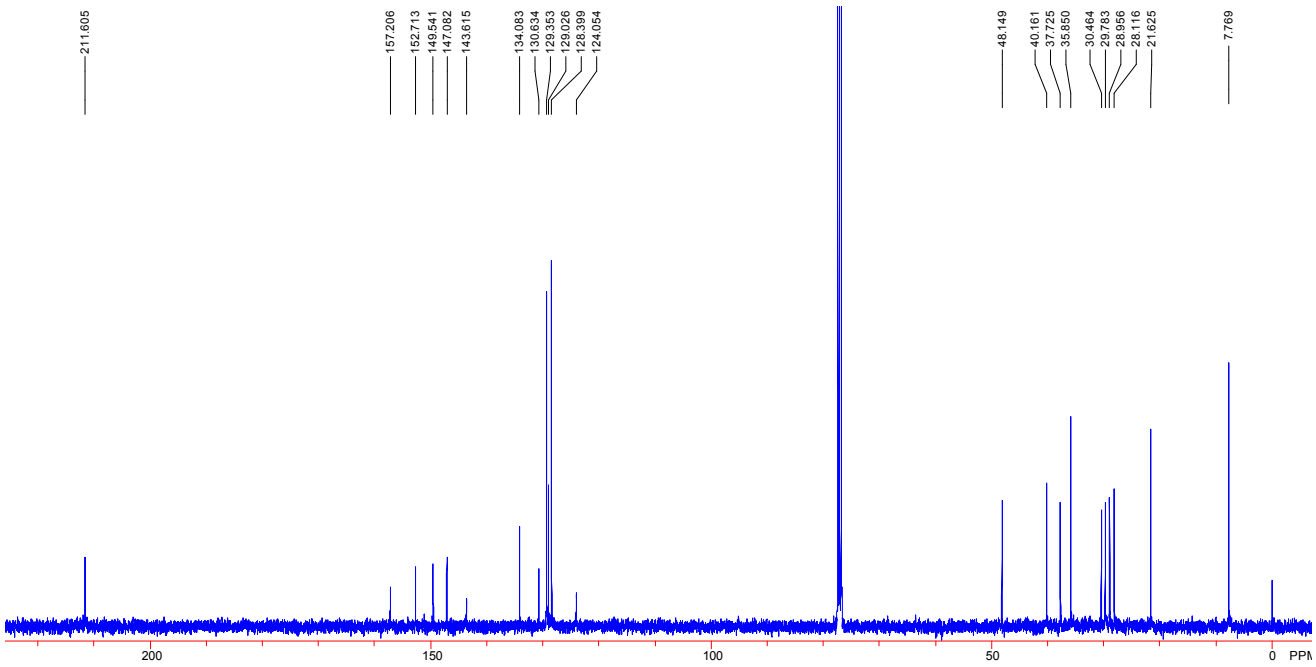
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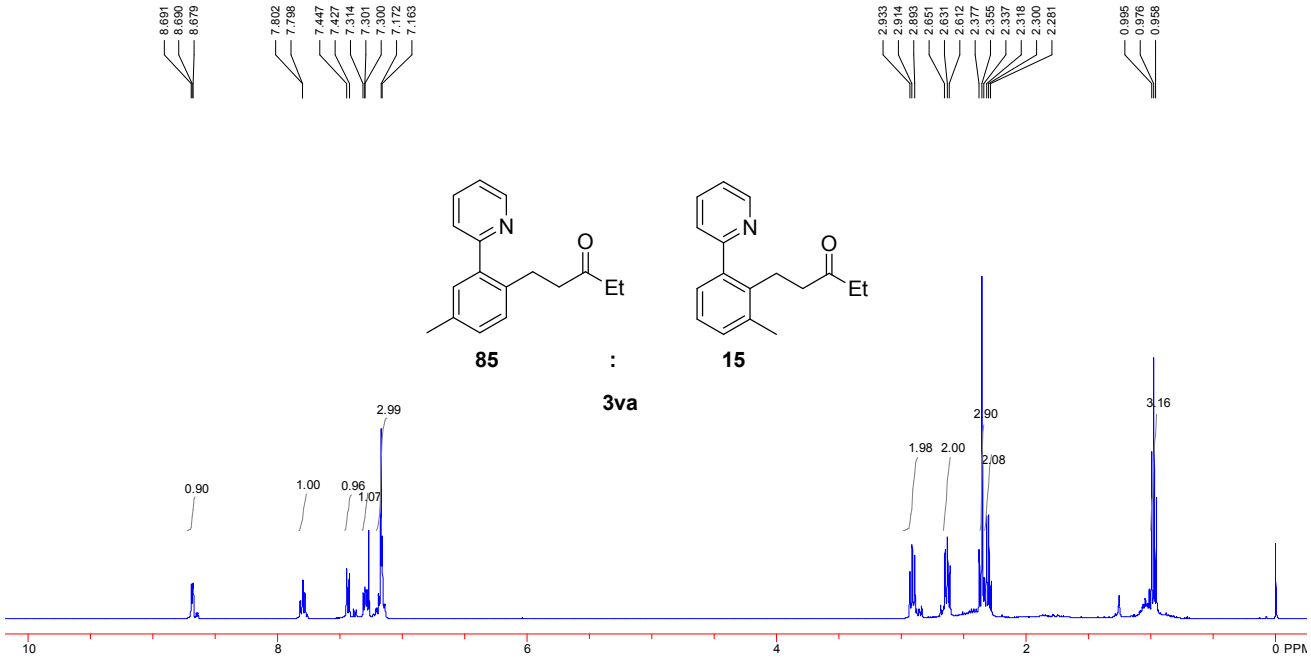
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O
Et
N
O
Et
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3va
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0.90
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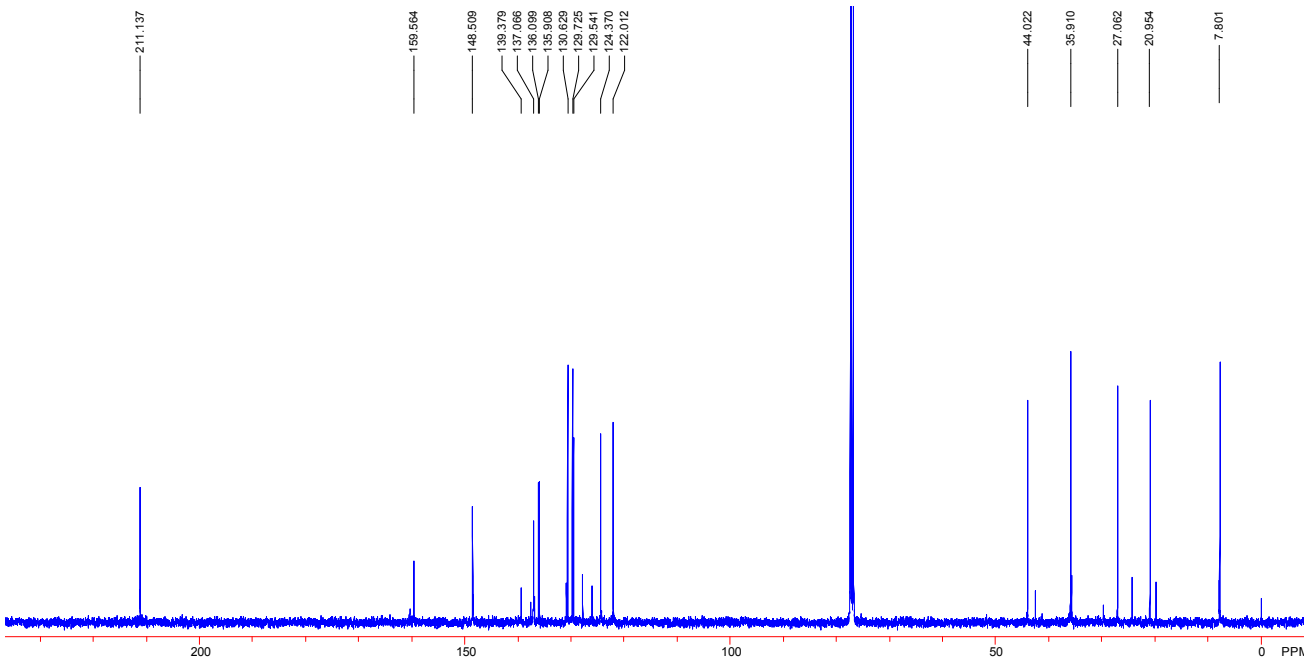
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27.062
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200
150
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50
0 PPM


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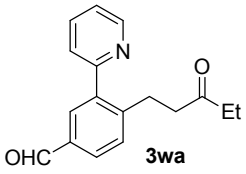
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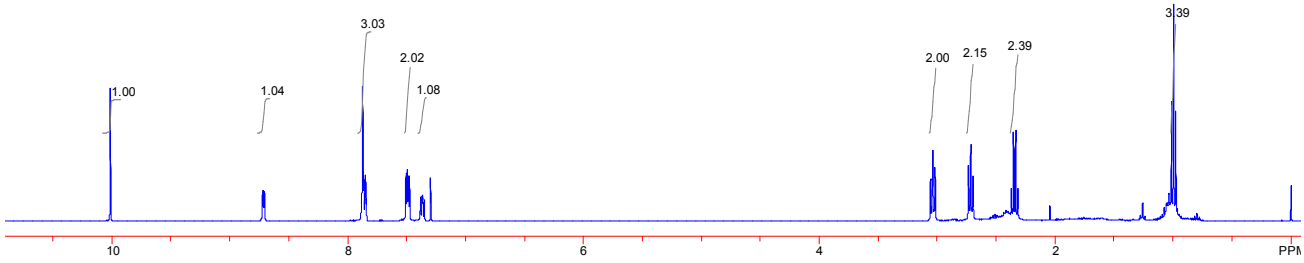
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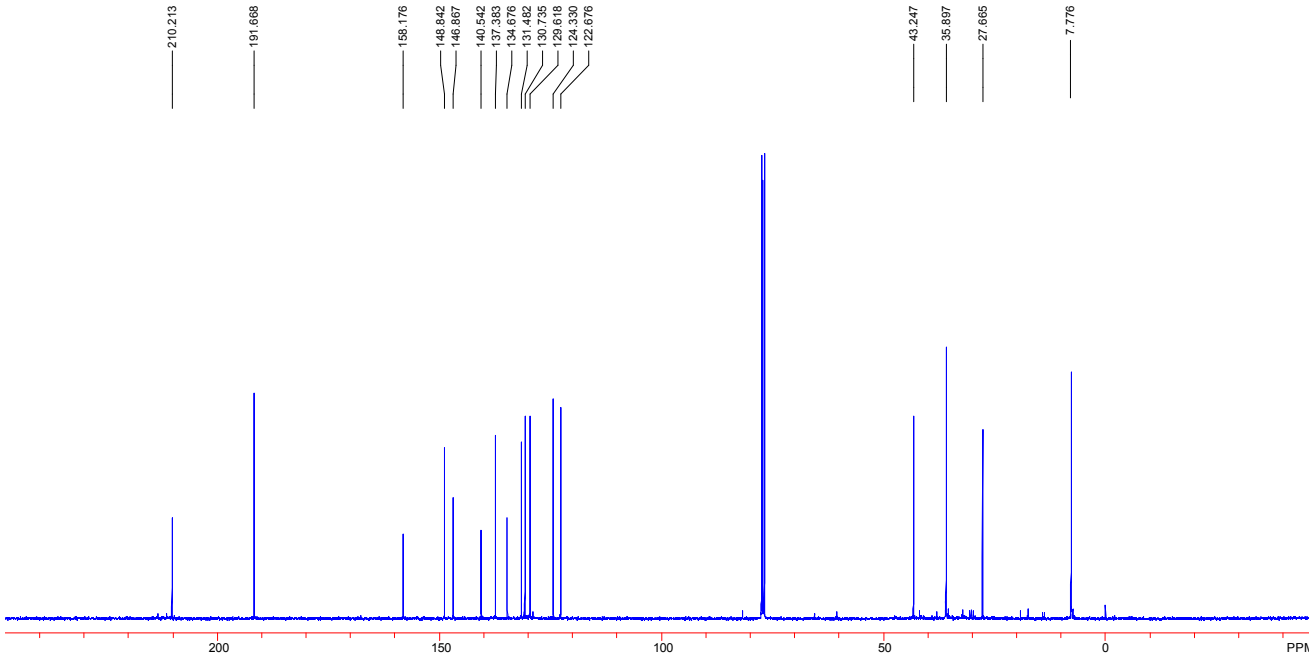
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200
150
100
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0
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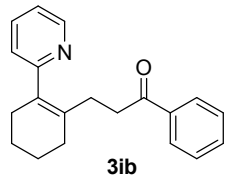
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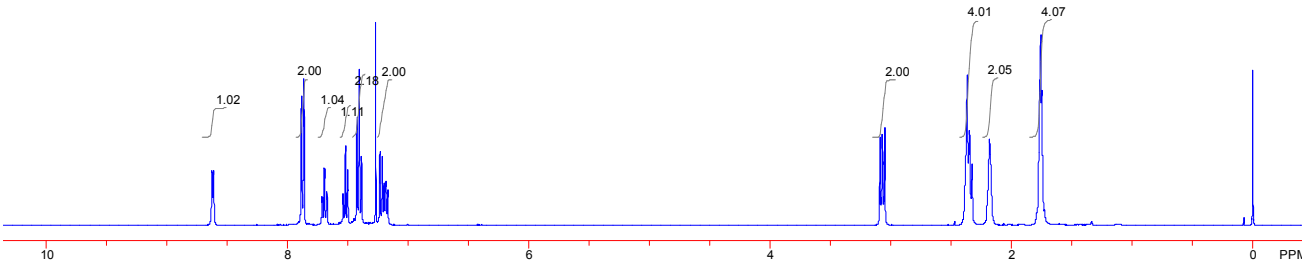
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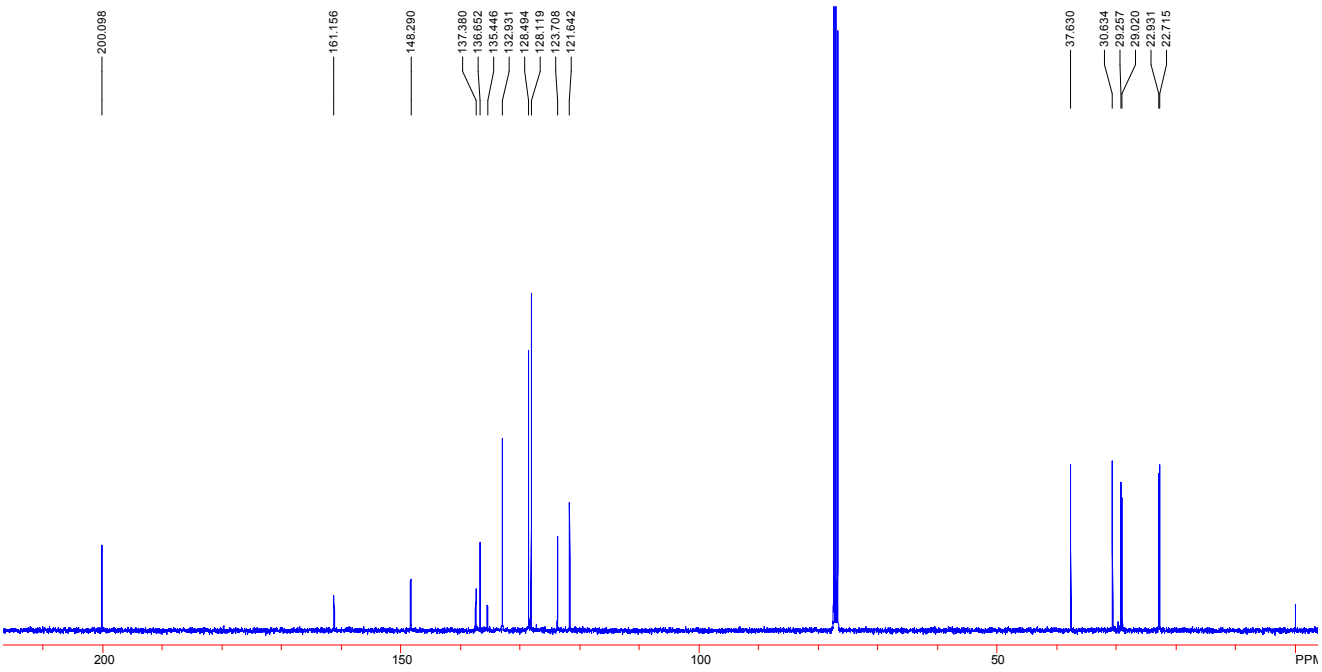
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29.257
29.020
22.931
22.715
200
150
100
50
PPM


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7.272
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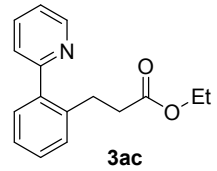
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Et

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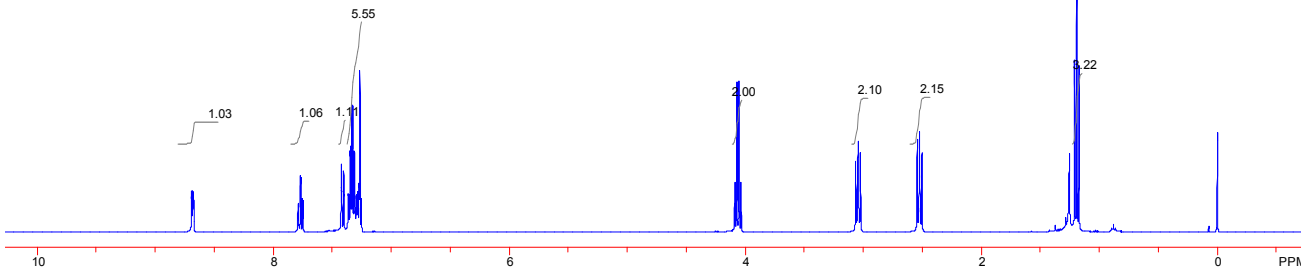
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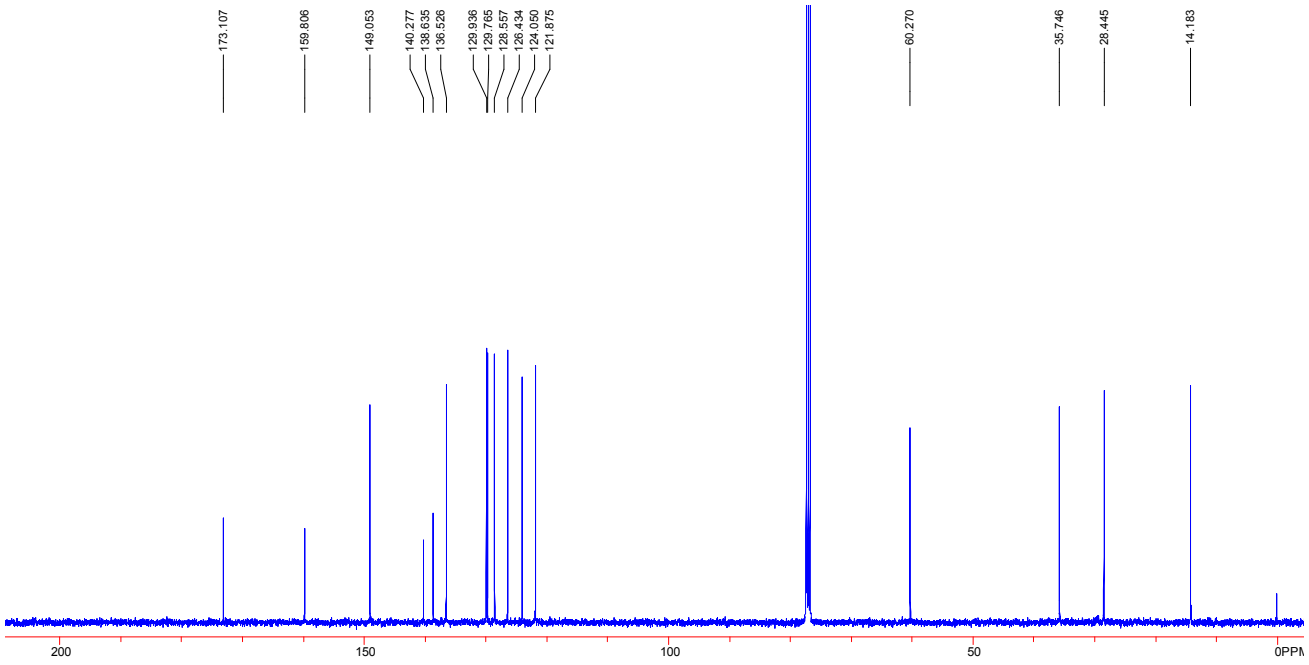
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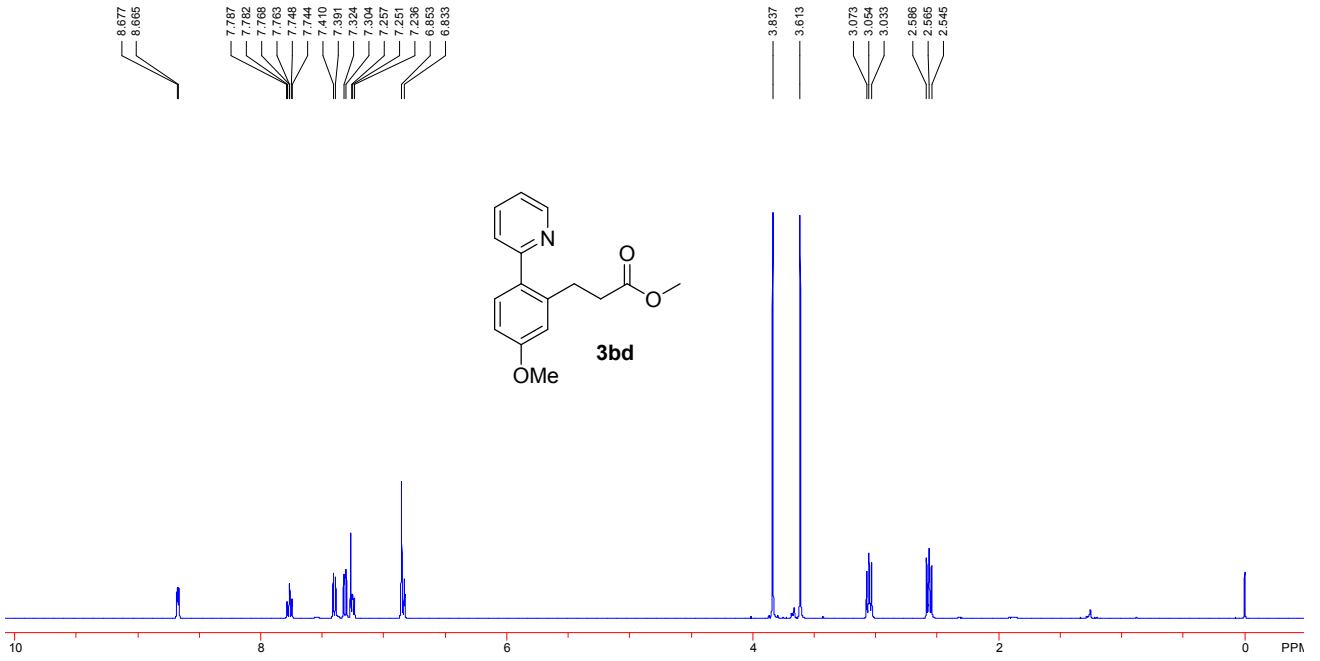
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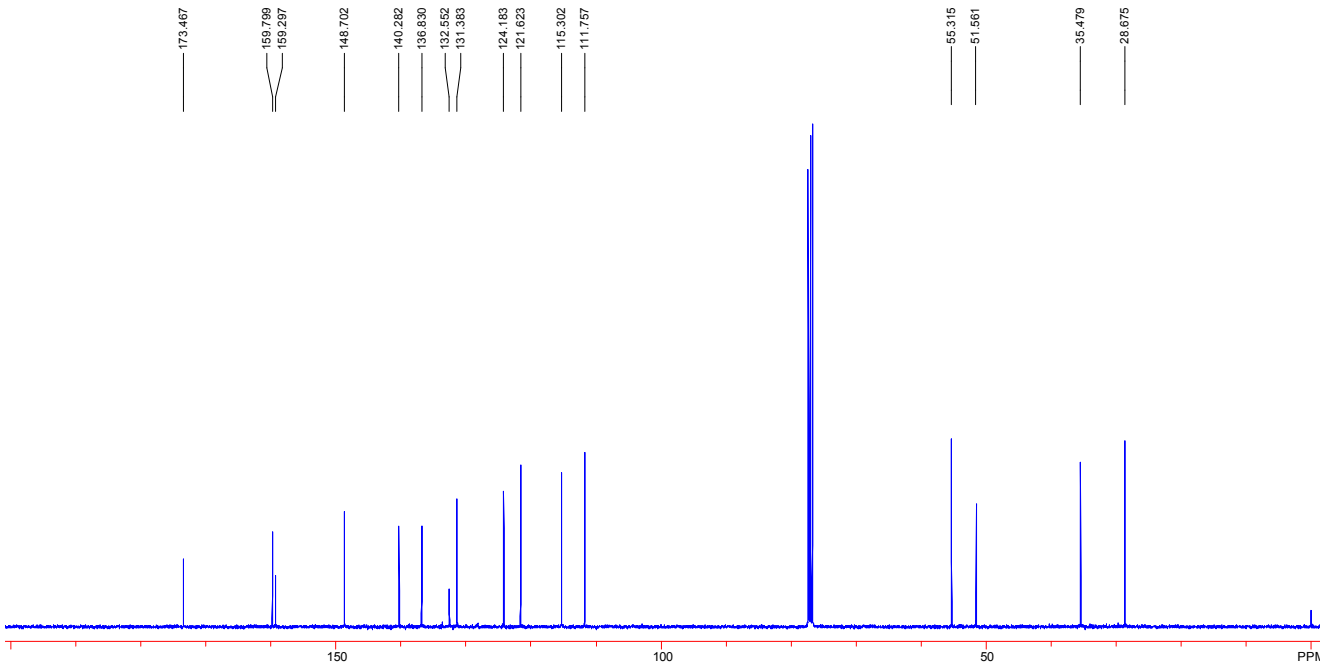
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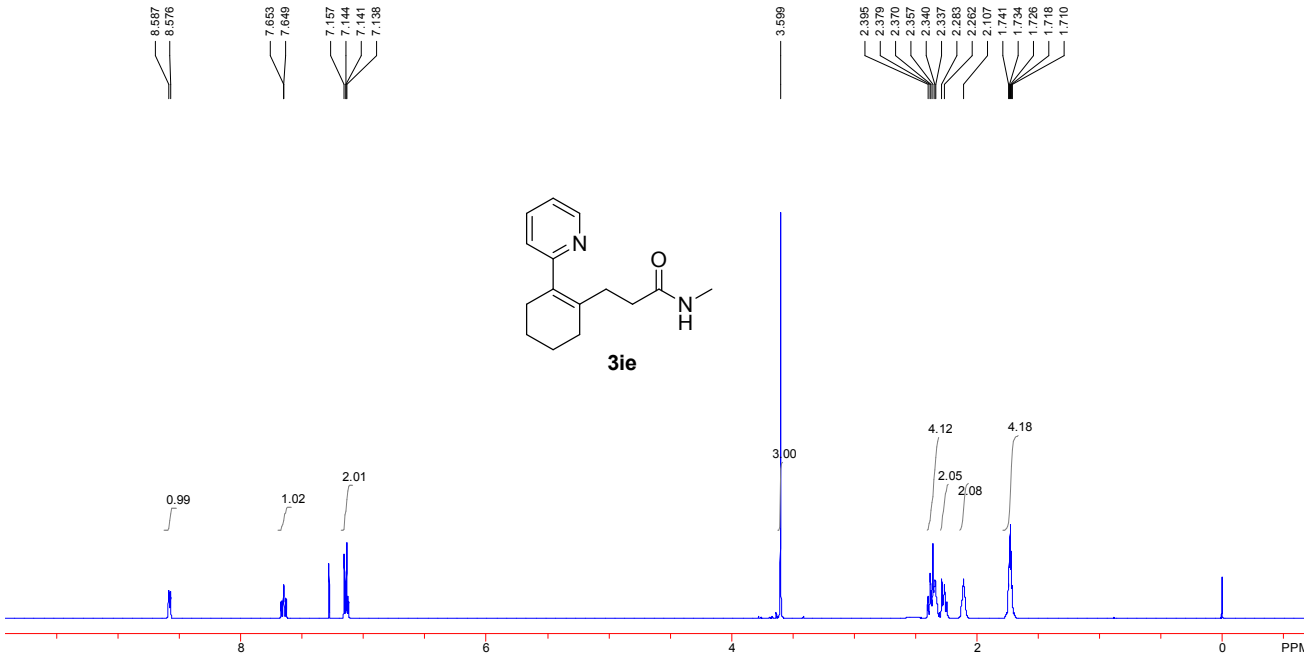
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1.734
1.726
1.718
1.710
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O
N
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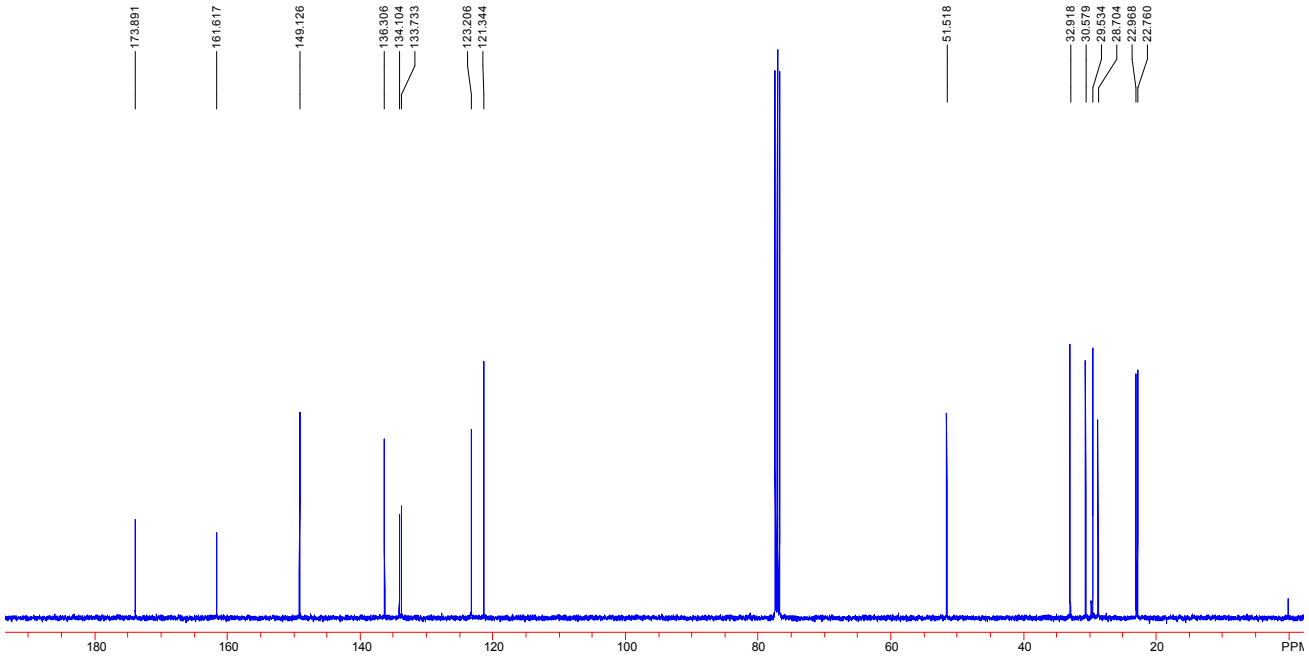
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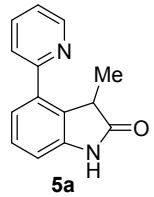
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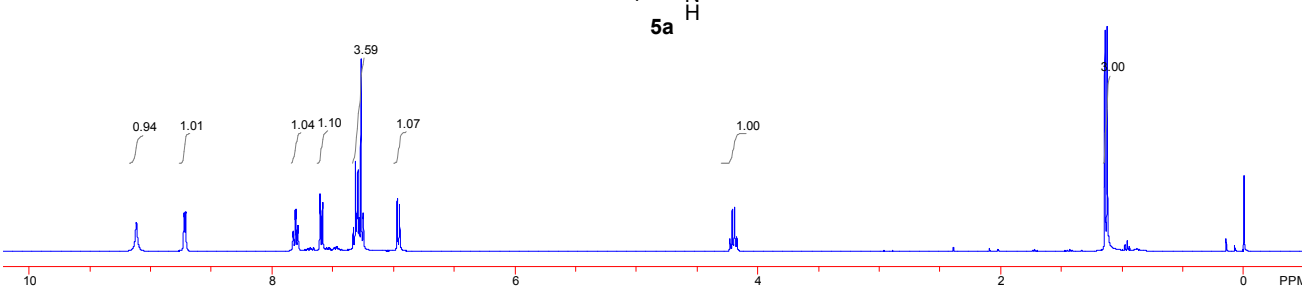
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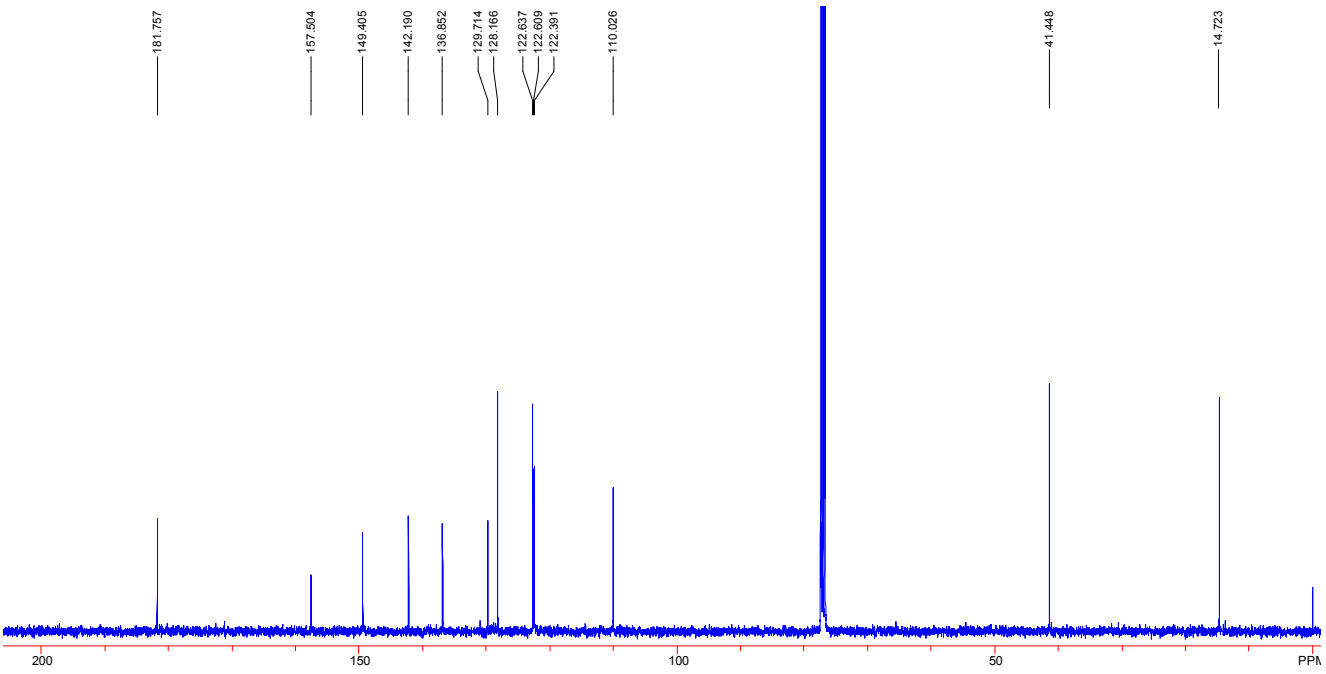
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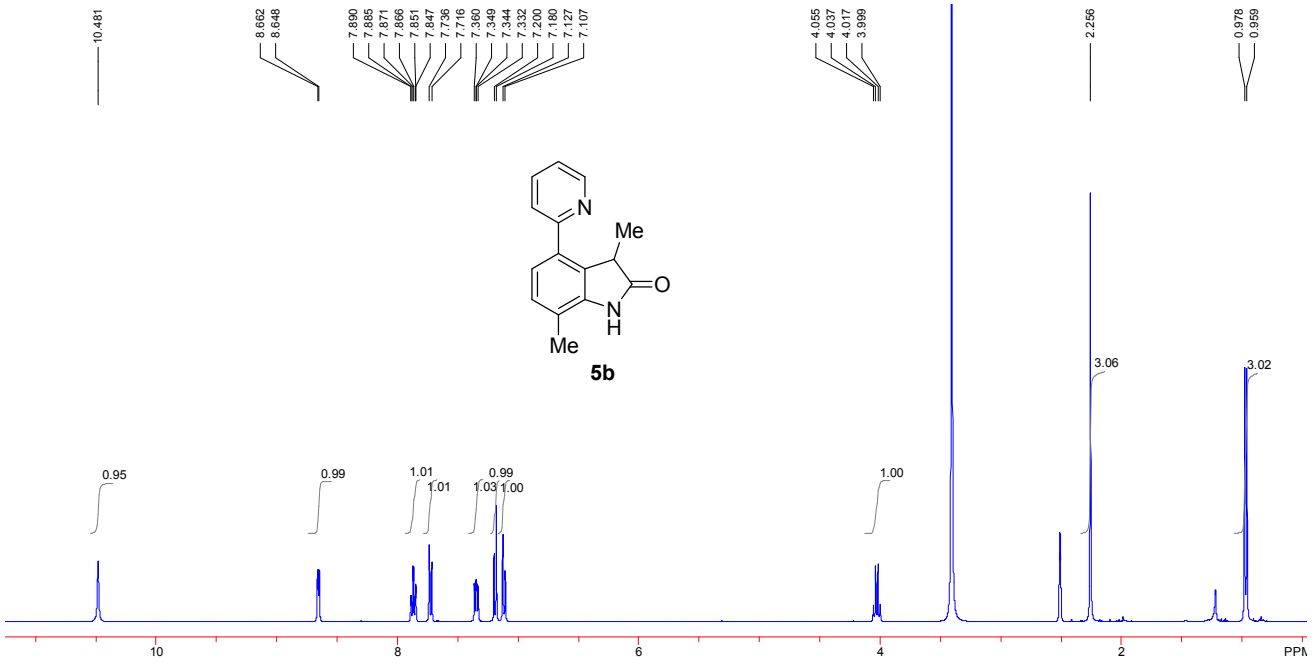
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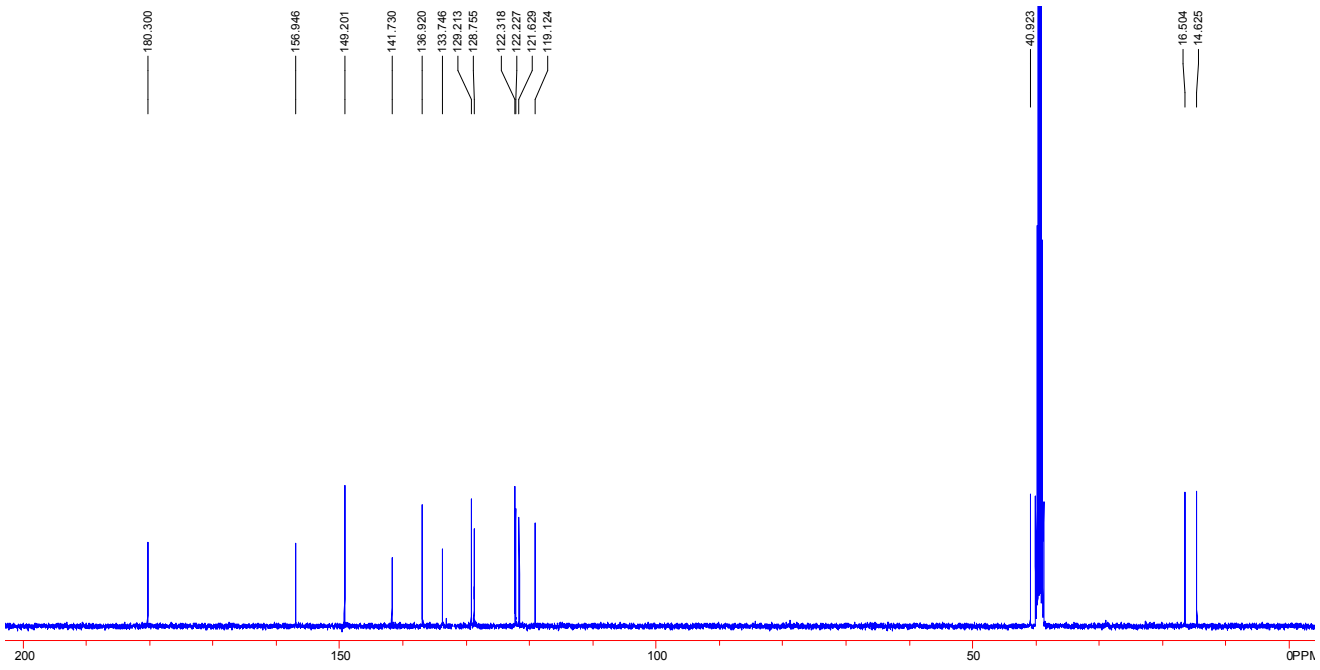
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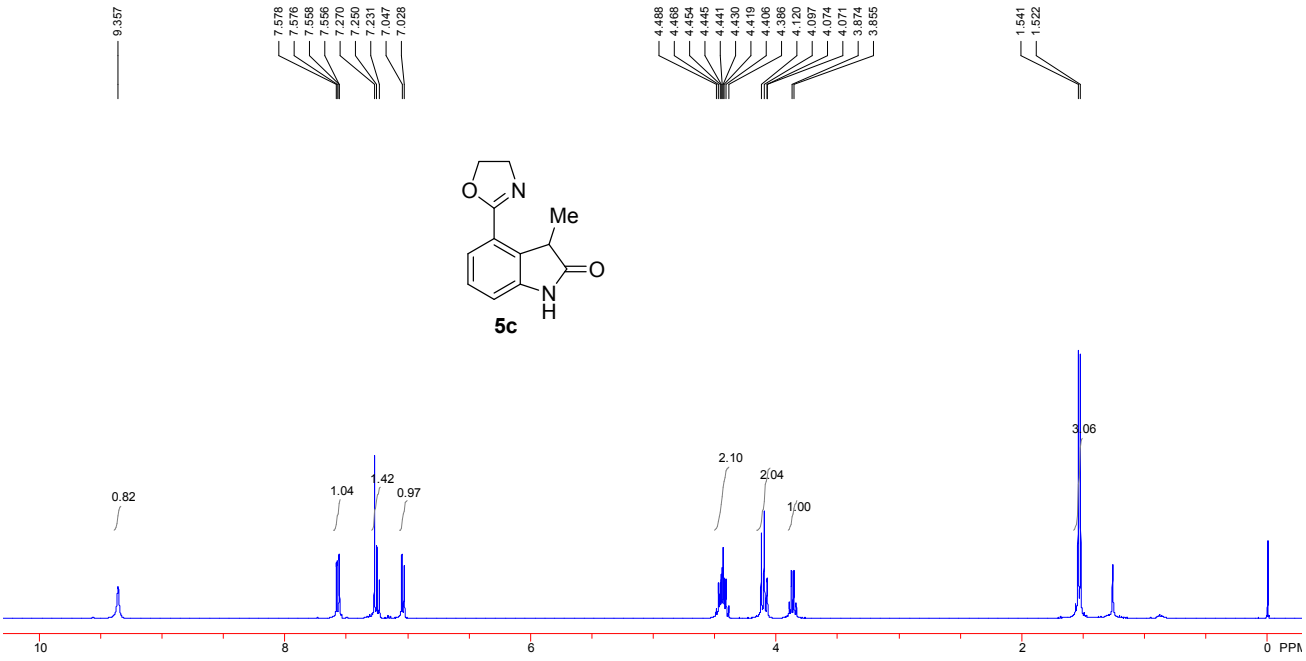
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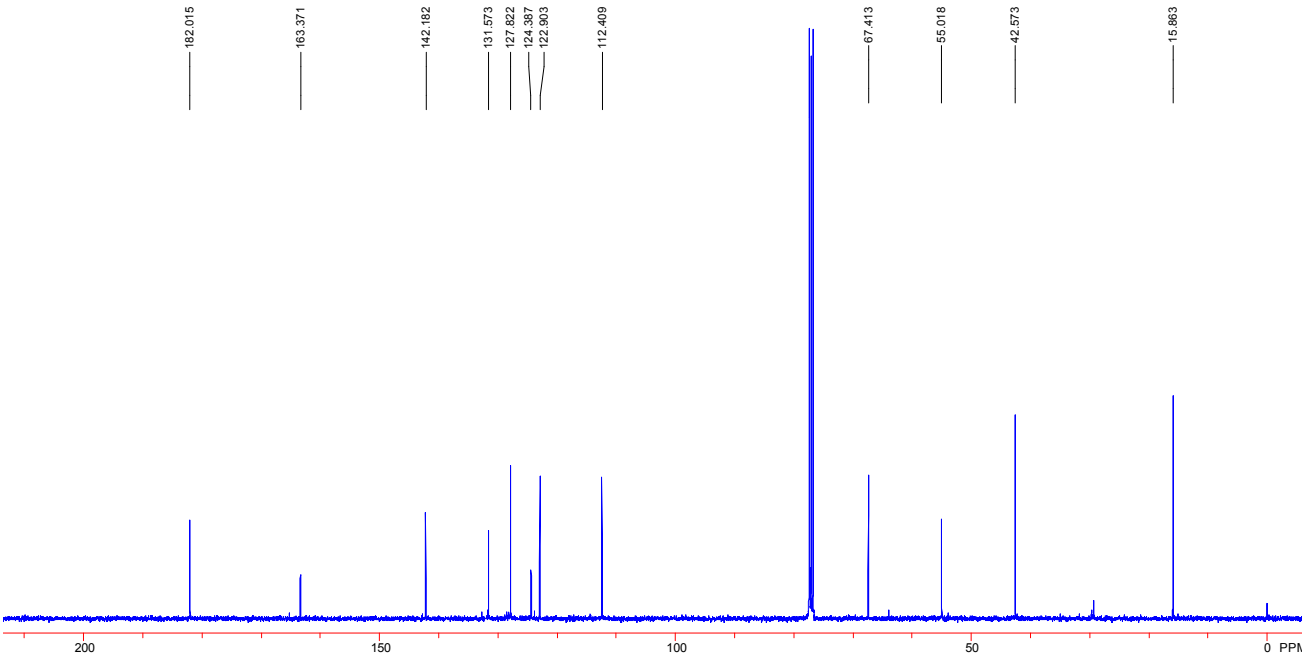
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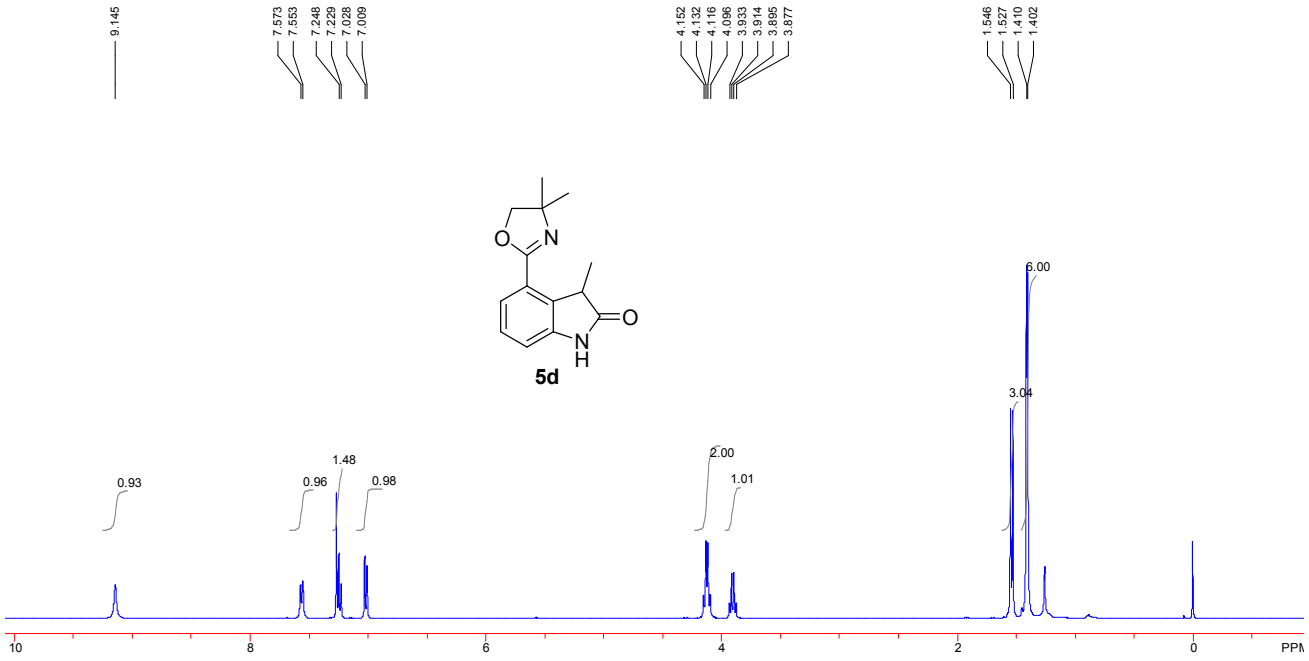
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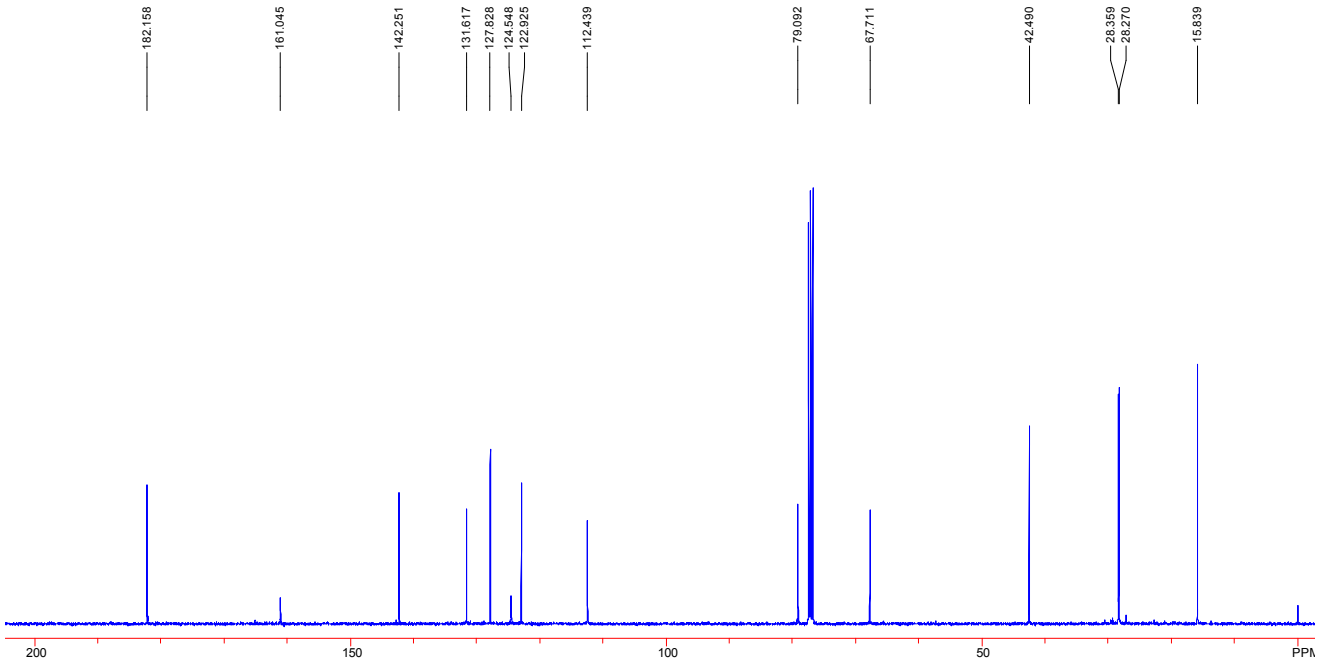
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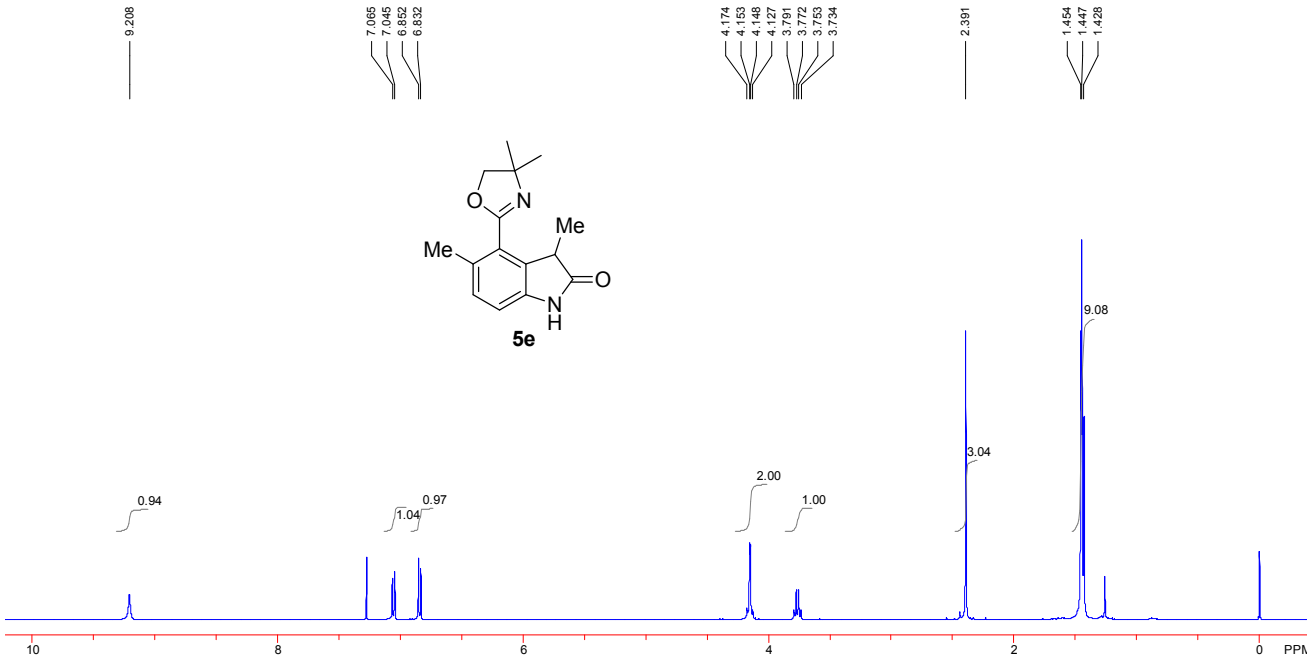
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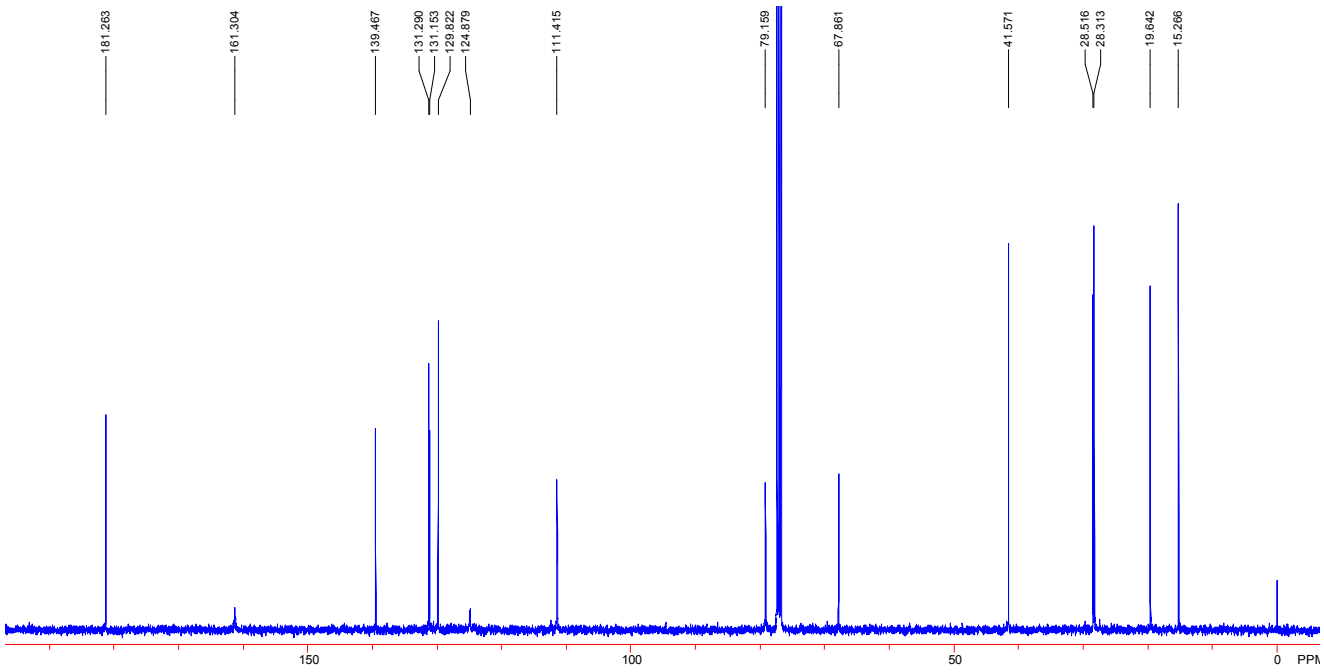
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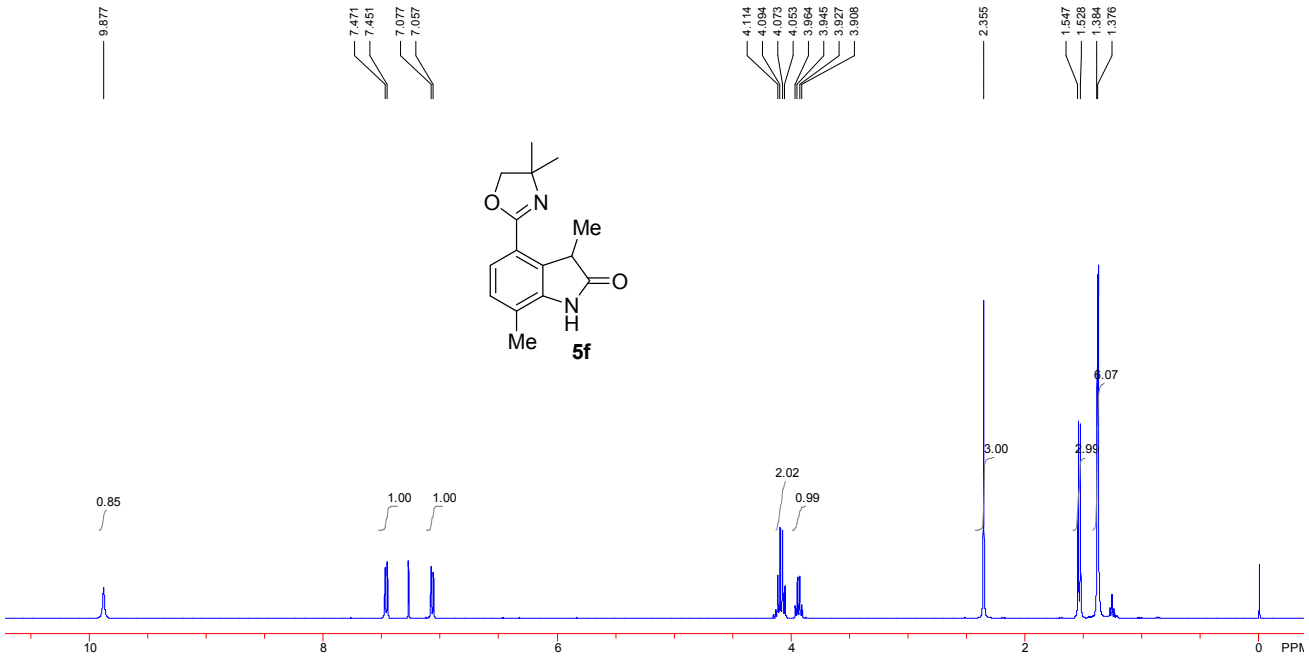
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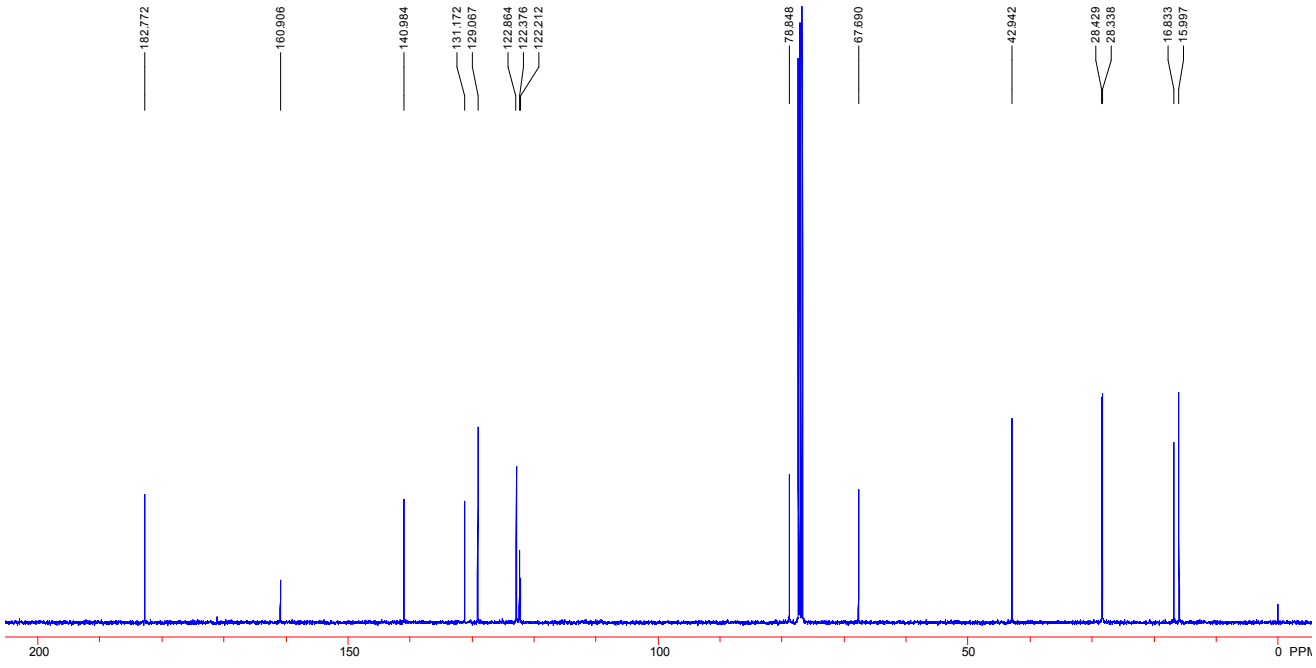
2.99
6.07
10
8
6
4
2
0
PPM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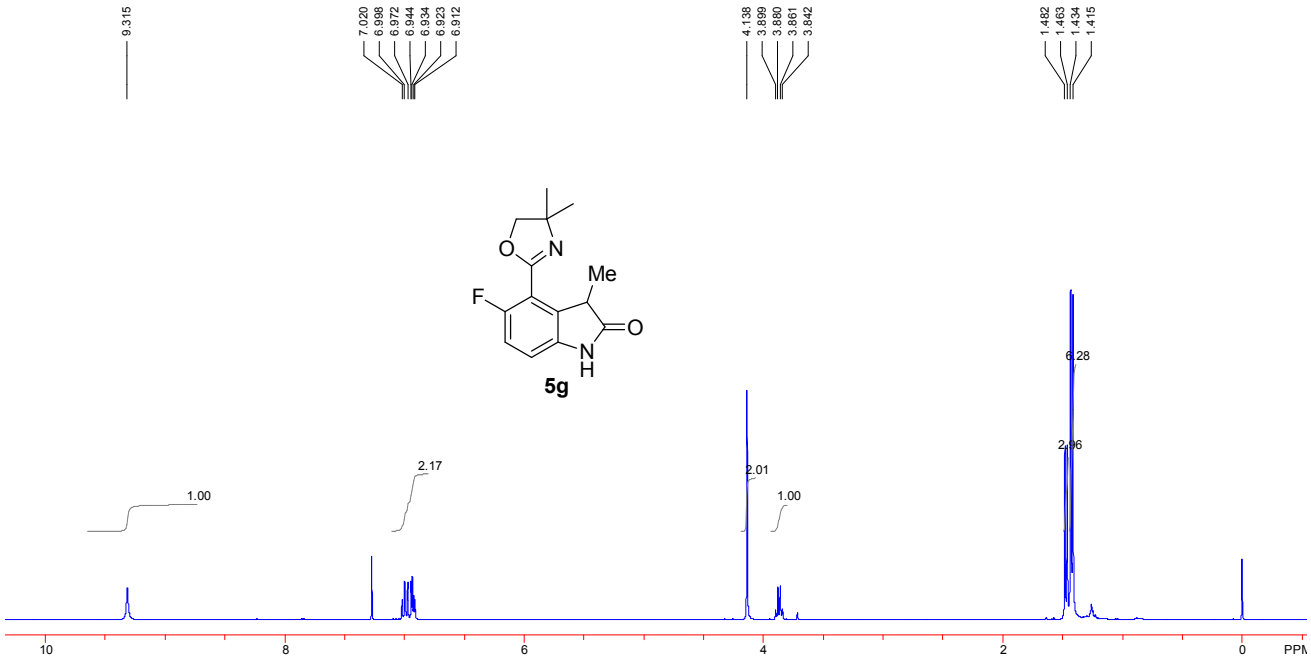
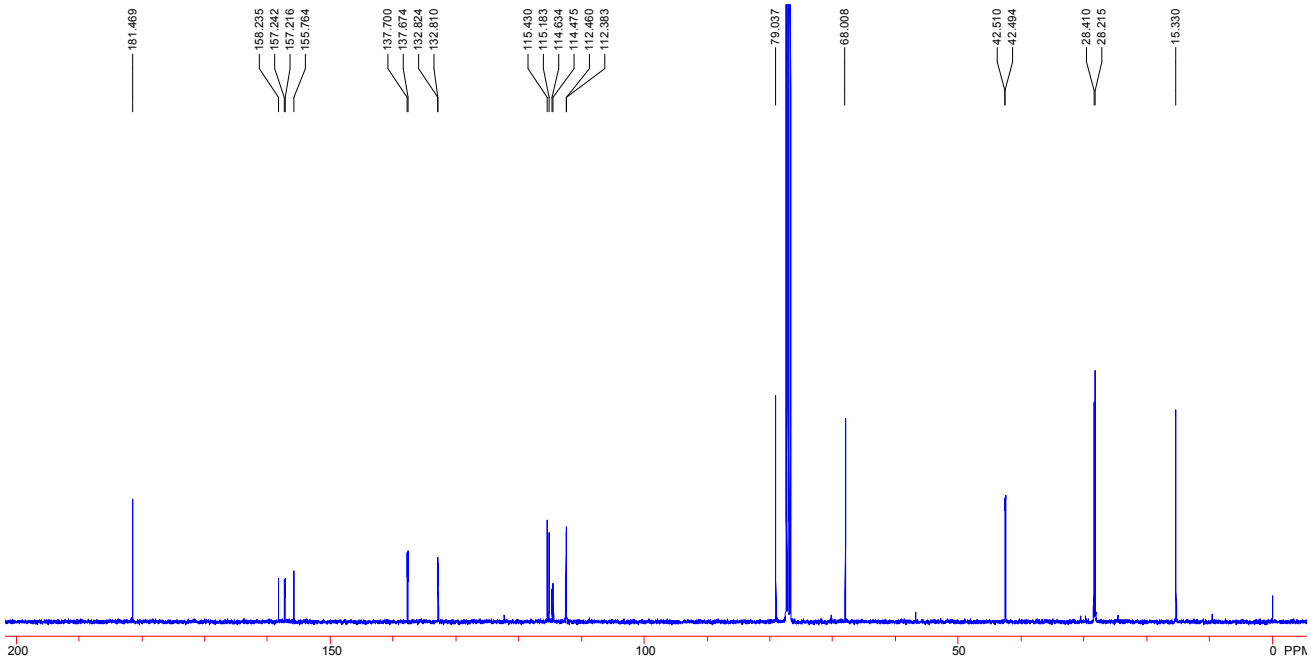
160.906
140.984
131.172
129.067
122.864
122.376
122.212
78.848
67.690
42.942
28.429
28.338
16.833
15.997
200
150
100
50
0
PPM


9.315
7.020
6.998
6.972
6.944
6.934
6.923
6.912
4.138
3.899
3.880
3.861
3.842
1.482
1.463
1.434
1.415
Me
F
O
N
O
N
H
5g
1.00
2.17
2.01
1.00
6.28
2.06
10
8
6
4
2
0
PPM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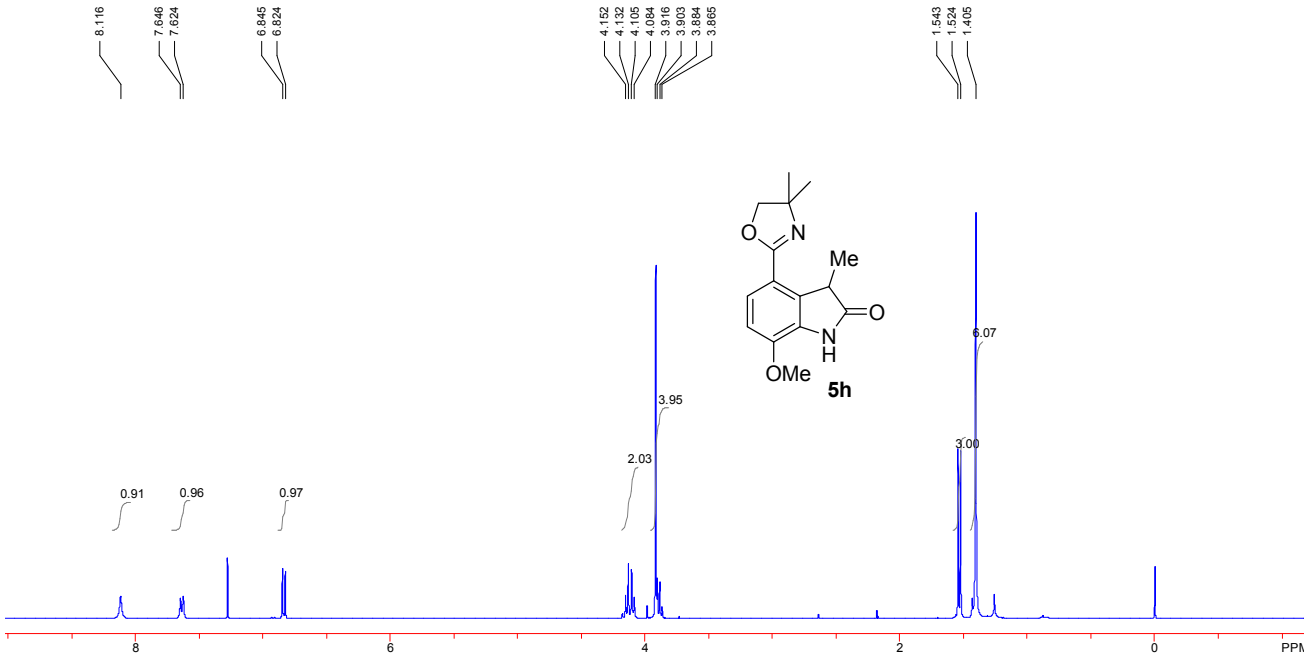
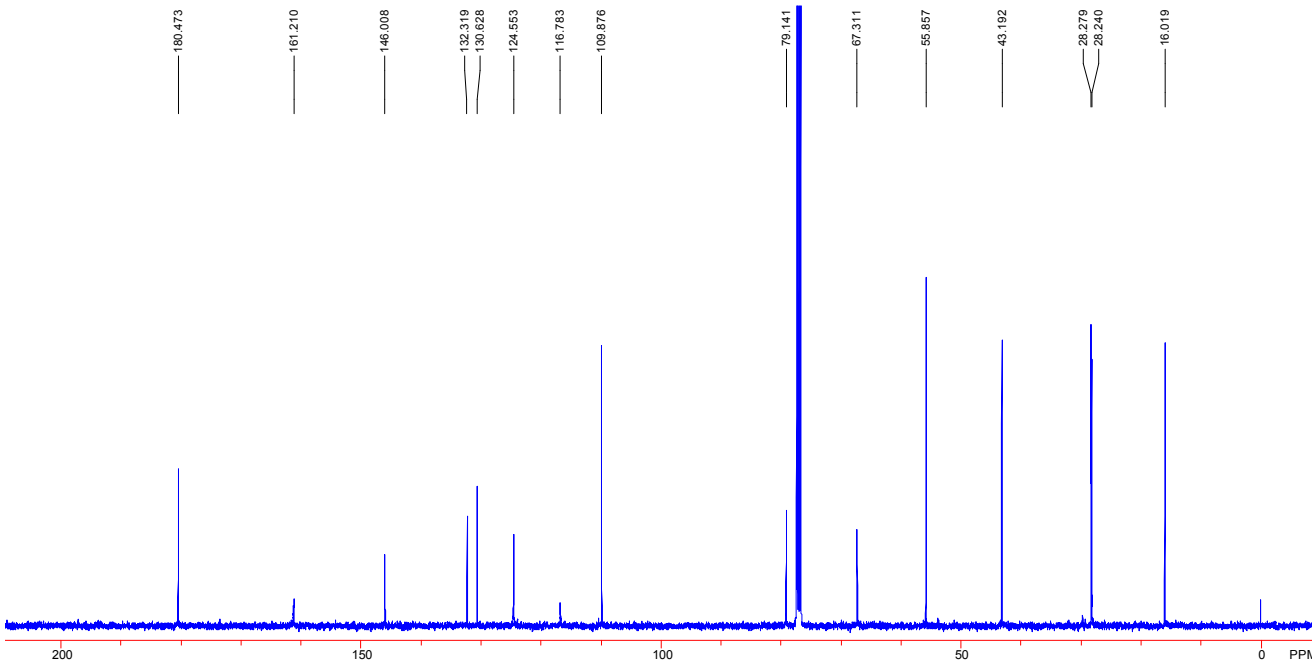
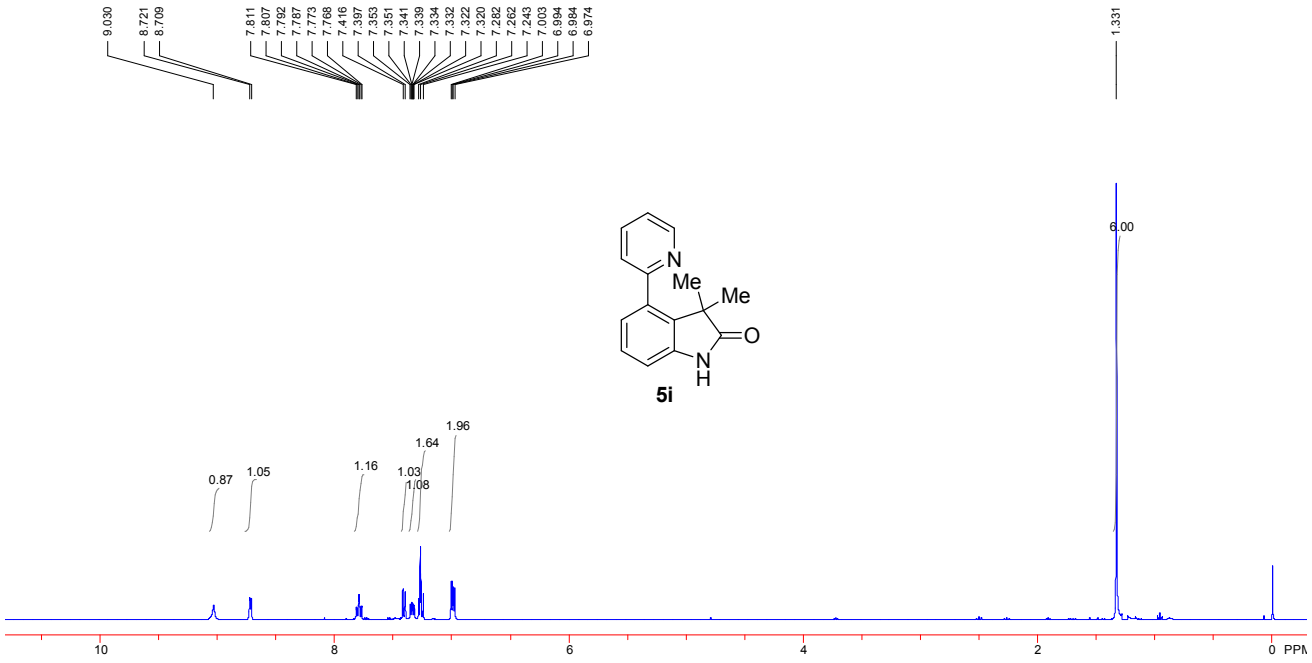
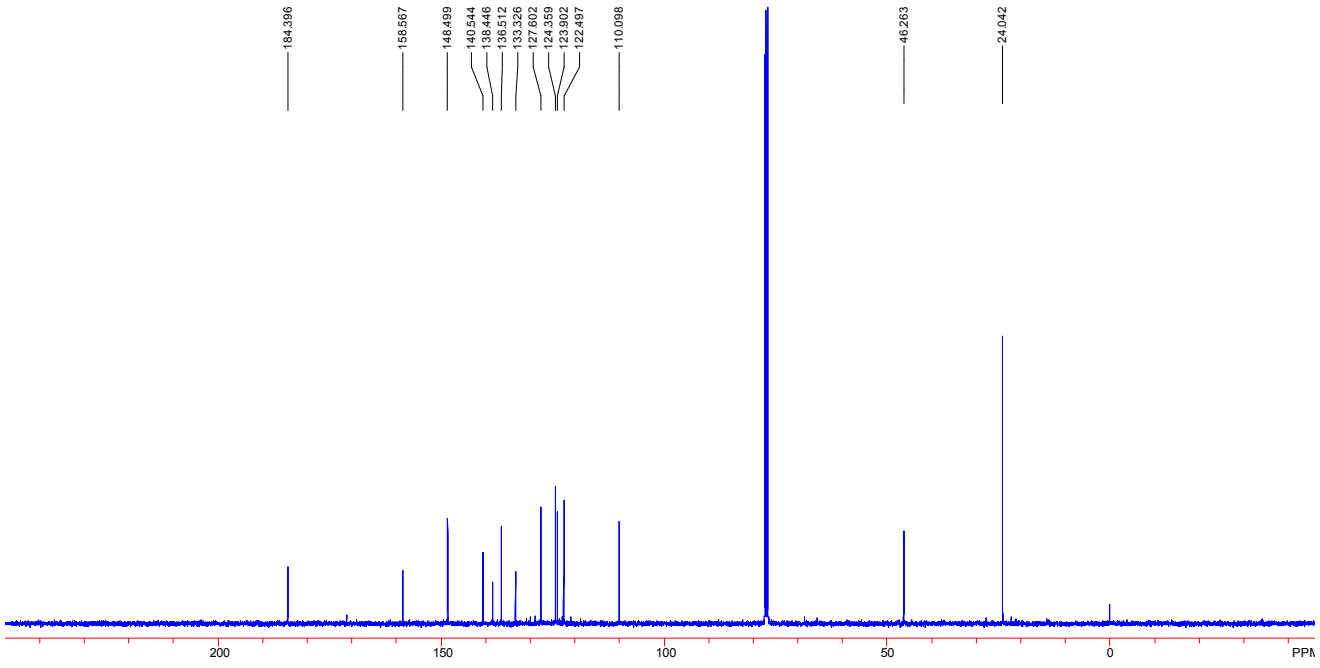
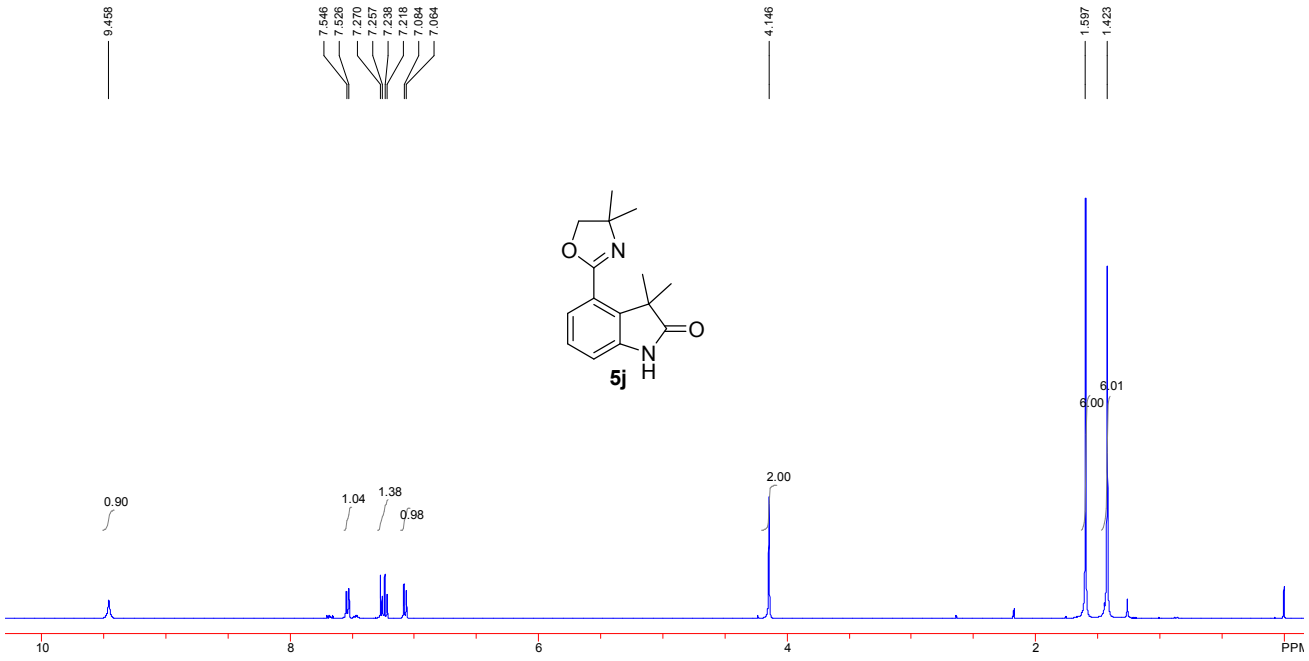
158.235
157.242
157.216
155.764
137.700
137.674
132.824
132.810
115.430
115.183
114.634
114.475
112.460
112.383
79.037
68.008
42.510
42.494
28.410
28.215
15.330
200
150
100
50
0 PPM

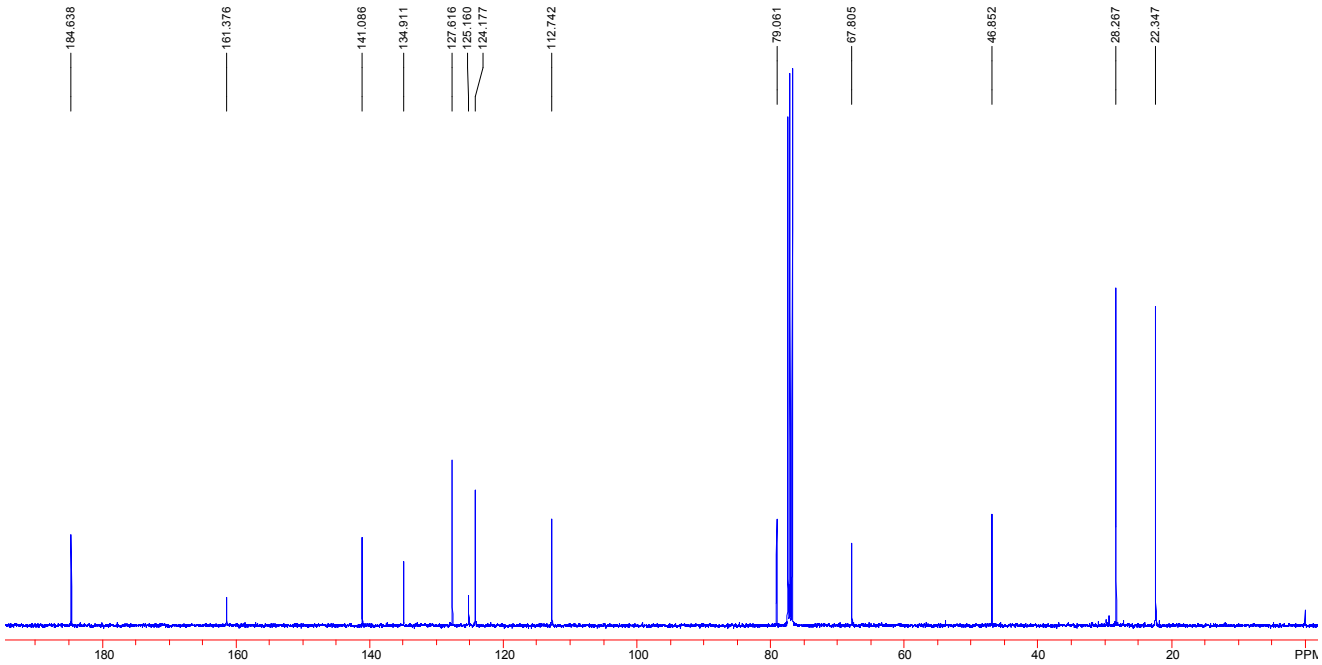

8.116
7.646
7.624
6.845
6.824
4.152
4.132
4.105
4.084
3.916
3.903
3.884
3.865
1.543
1.524
1.405
O
N
Me
O
N
H
OMe
5h
0.91
0.96
0.97
2.03
3.95
3.00
6.07
8
6
4
2
0
PPM


180.473
161.210
146.008
132.319
130.628
124.553
116.783
109.876
79.141
67.311
55.857
43.192
28.279
28.240
16.019
200
150
100
50
0
PPM


9.030
8.721
8.709
7.811
7.807
7.792
7.787
7.773
7.768
7.416
7.397
7.353
7.351
7.341
7.339
7.334
7.332
7.322
7.320
7.282
7.262
7.243
7.003
6.994
6.984
6.974
1.331
6.00
1.96
1.64
1.16
1.03
1.08
1.05
0.87
Me
Me
O
N
H
5i
10
8
6
4
2
0
PPM


184.396
158.567
148.499
140.544
138.446
136.512
133.326
127.602
124.359
123.902
122.497
110.098
46.263
24.042
200
150
100
50
0
PPM


9.458
7.546
7.526
7.270
7.257
7.238
7.218
7.084
7.064
4.146
1.597
1.423
O
N
O
N
H
5j
6.01
6.00
2.00
0.90
1.04
1.38
0.98
10
8
6
4
2
PPM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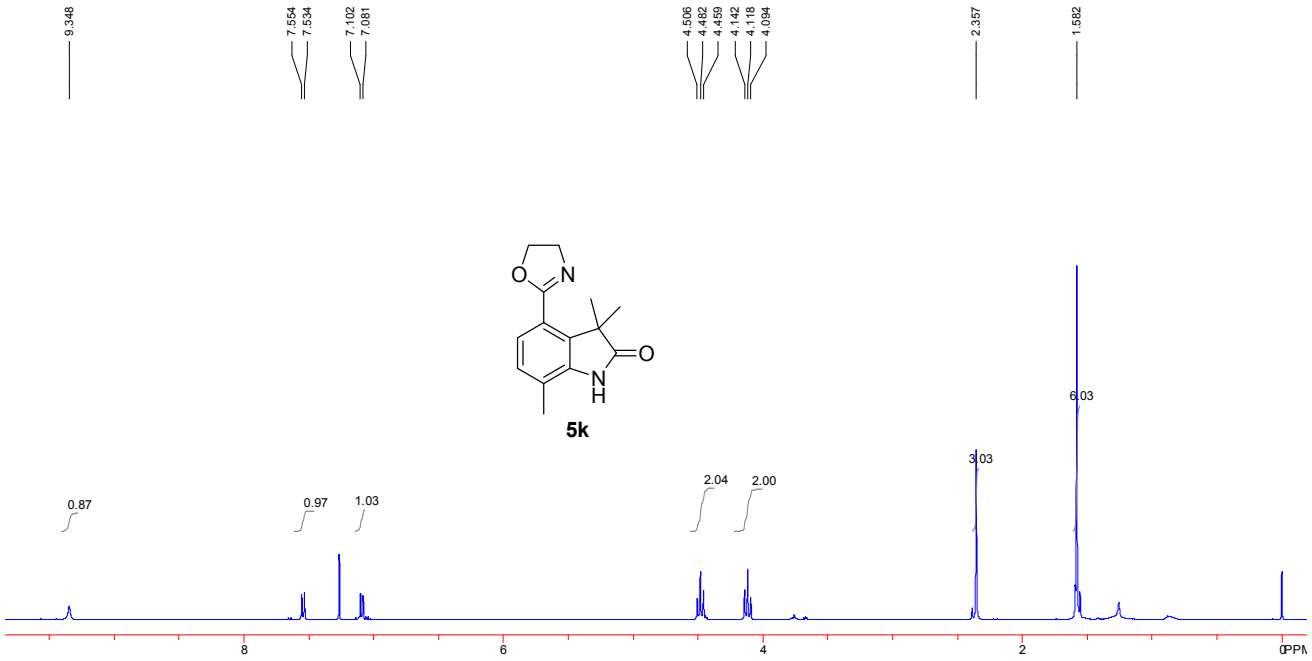
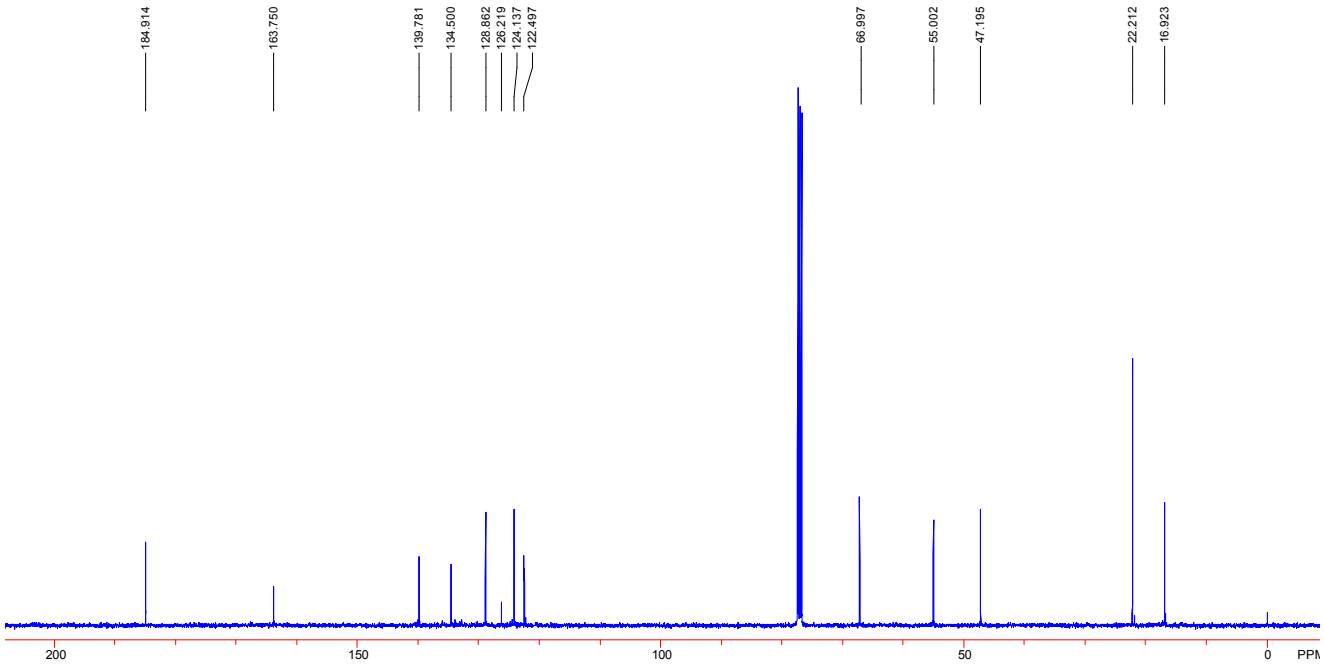
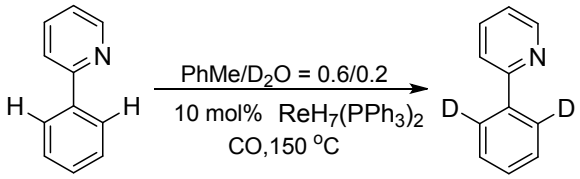
141.086
134.911
127.616
125.160
124.177
112.742
79.061
67.805
46.852
28.267
22.347
180
160
140
120
100
80
60
40
20
PPM


9.348
7.554
7.534
7.102
7.081
4.506
4.482
4.459
4.142
4.118
4.094
2.357
1.582
O
N
O
N
H
5k
0.87
0.97
1.03
2.04
2.00
3.03
6.03
8
6
4
2
0PPM

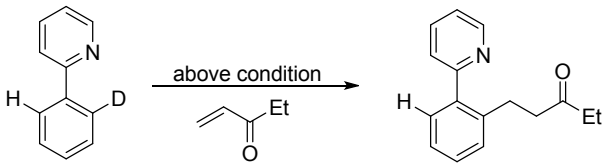

184.914
163.750
139.781
134.500
128.862
126.219
124.137
122.497
66.997
55.002
47.195
22.212
16.923
200
150
100
50
0 PPM

a)



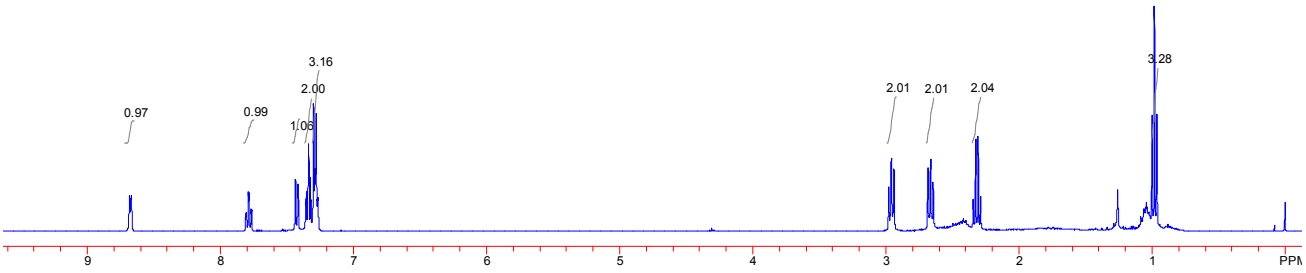
1a $[D]_n$**-1a**

KIE experiment:

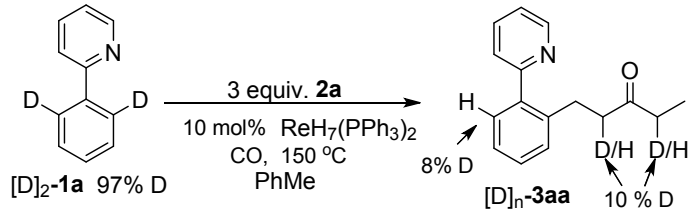


95 %-D no D incoporation

A large negative kinetic isotope effect

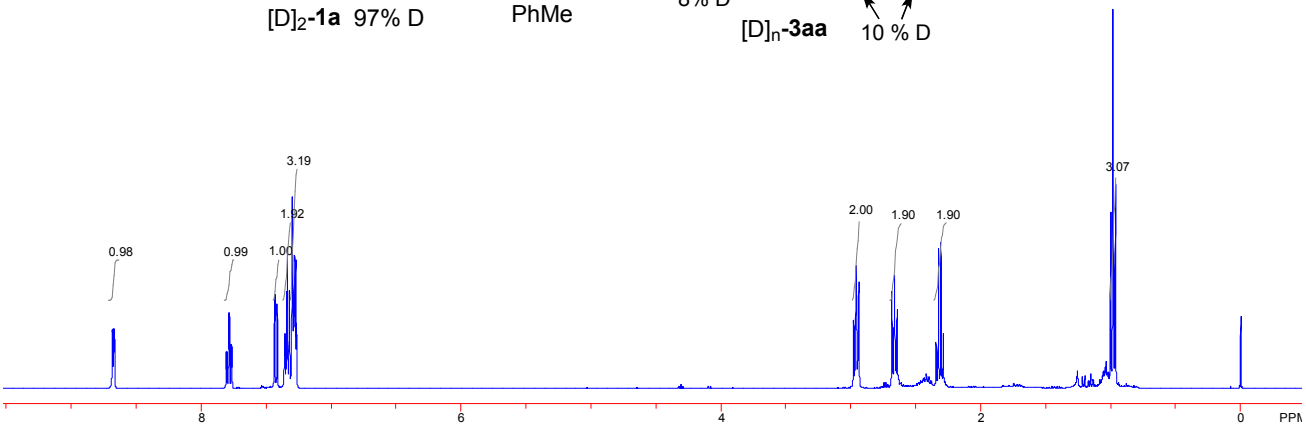


b)

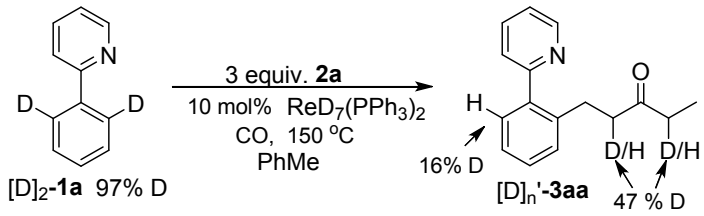


[D]$_2$-**1a** 97% D

[D]$_n$-**3aa**

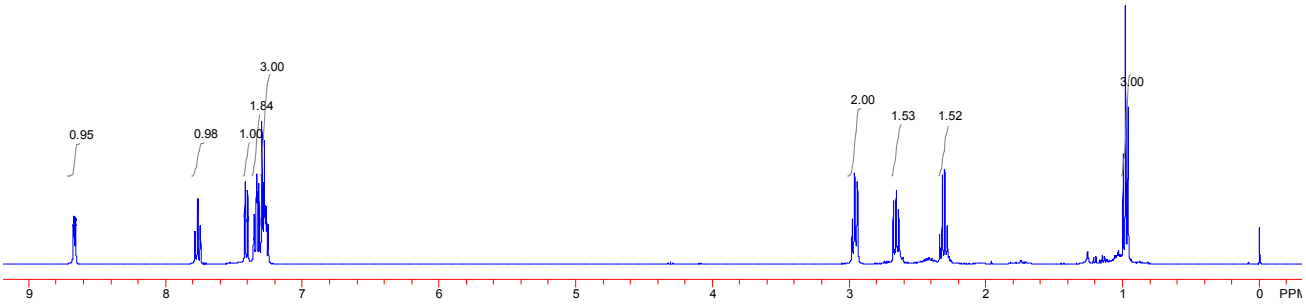


c)

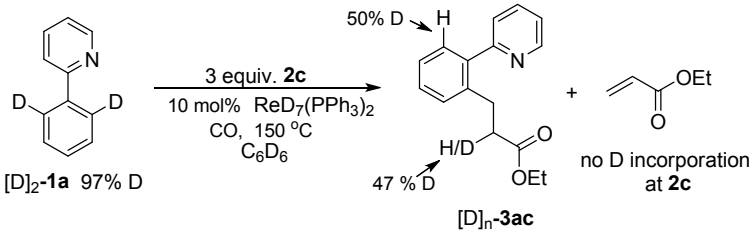


[D]$_2$-**1a** 97% D

[D]$_n$'-**3aa**



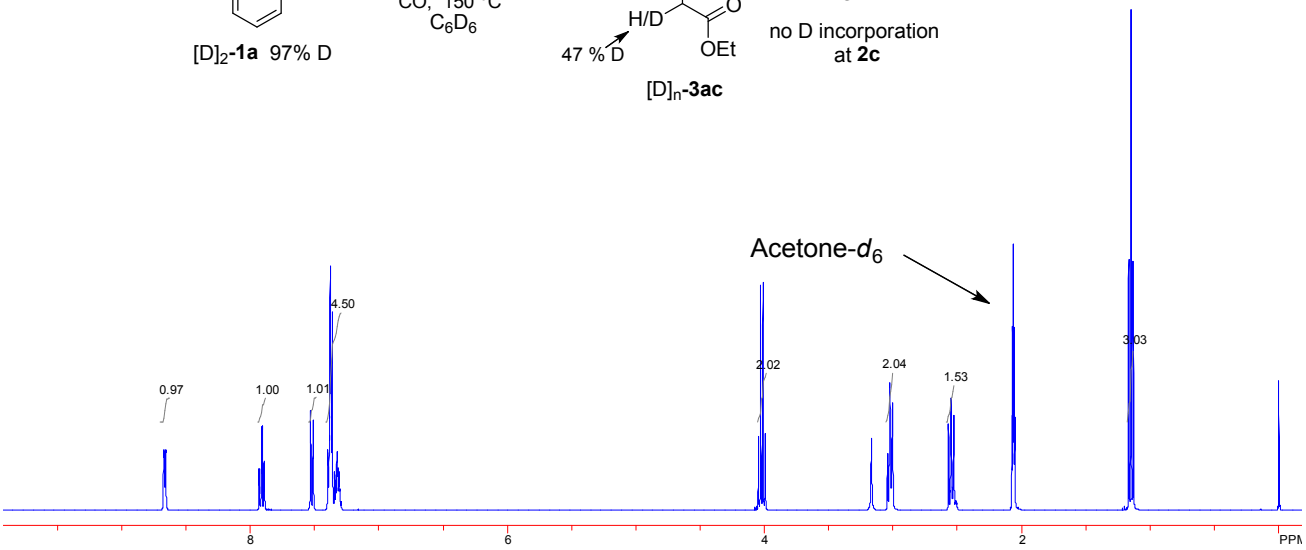
d)



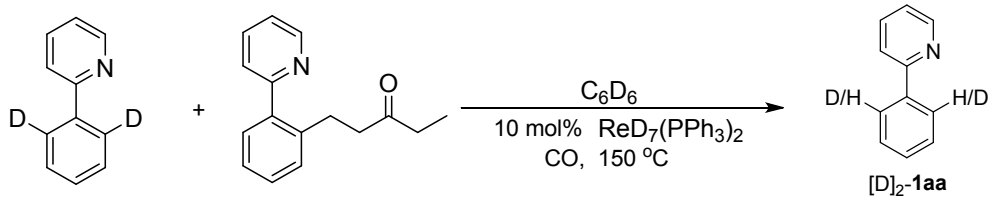
[D]$_2$-**1a** 97% D

[D]$_n$-**3ac**

no D incorporation at **2c**

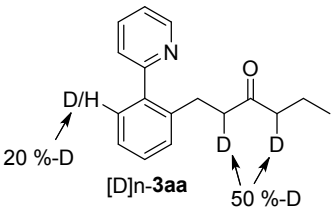


e)

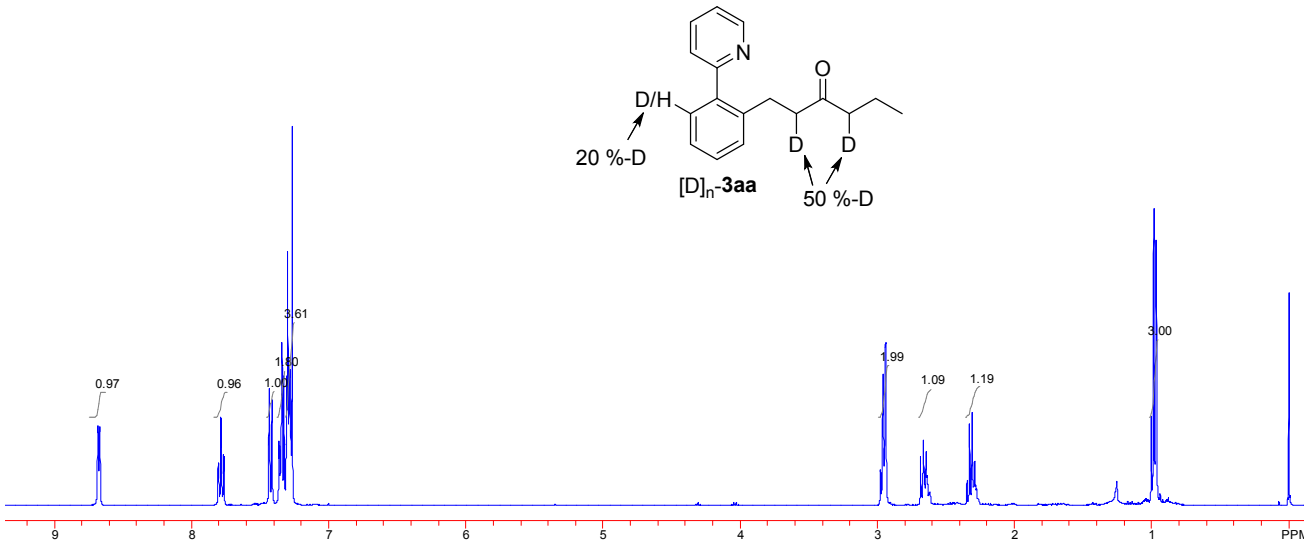


[D]$_2$-**1aa**

50 %-D



[D]n-**3aa**



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