Supporting Information

Metal-free Synthesis of β-Aminoketones by Reductive Hydroamination of Ynones

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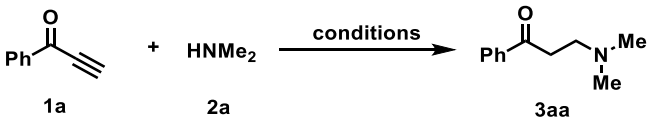
General methods:

All reactions were carried out in flame or oven-dried glassware under nitrogen atmosphere with freshly distilled dry solvents under anhydrous conditions unless otherwise indicated. Flash column chromatography was performed with silica gel (200 - 300 mesh). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining with base solution of potassium permanganate and molybdate. NMR spectra were recorded at RT on 400 MHz JEOL or BRUKER spectrometers. The residual solvent signals were taken as the reference (0.00 ppm for ^{1}H NMR spectra and 77.0 ppm for ^{13}C NMR spectra in $CDCl_3$). Chemical shift (δ) is reported in ppm, coupling constants (J) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, q = quartet and br = broad signal. HRMS (ESI) spectra were recorded on a Waters Q-Tof premier TM mass spectrometer.

Table S1. Optimization of reaction conditions[a]

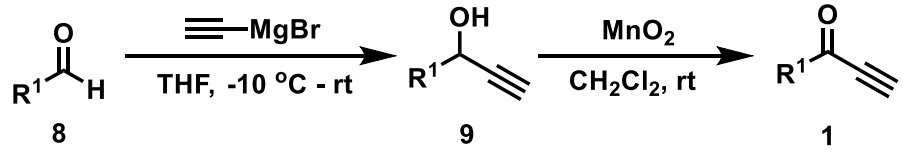


1a 2a 3aa

Entry	Reductant[b]	Solvent	Yield (%)[c]
1	$NaBH_4$	THF	6
2	$PhSiH_3$	THF	0
3	HBpin	THF	35
4	$BH_3{\cdot}NMe_3$	THF	0
5	$BH_3{\cdot}THF$	THF	0
6	HBpin	Toluene	28
7	HBpin	Hexane	31
8	HBpin	DCE	27
9	HBpin	MeCN	23
10	HBpin	MeOH	9
11	HBpin[d]	THF	64
12	**HBpin[e]**	**THF**	**88**

[a]Experiments were performed with **1a** (0.20 mmol, 1.0 equiv.), **2a** (0.30 mmol, 1.5 equiv.) and reducing agent in solvent (2.0 mL) at room temperature without inert gas protection. [b]Without other noticed, 1.5 equiv. of reduceing agent was used. [c]Isolated yields. [d]2.0 equiv. of HBpin. [e]2.5 equiv. of HBpin. HBpin = pinacolborane; THF = tetrahydrofuran; DCE = 1,2-dichloroethane.

General procedure for ynones and their spectral data[1]:

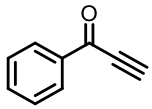


8 9 1

Ethynylmagnesium bromide (0.50 M solution in THF 12 mL, 1.2 equiv.) was added dropwise to a stirred solution of aldehyde **8** (5.0 mmol, 1.0 equiv.) in anhydrous THF (10 mL) at -10 ºC. The mixture was kept stirring at -10 ºC for 20 minutes and warmed to room temperature for additional two hours. Then the reaction mixture was quenched with saturated ammonium chloride (20 mL) and extracted with ethyl acetate for three times. The organic layers was combined and dried with anhydrous $MgSO_4$. It was evaporated under reduced pressure to give intermediate alcohol **9**, which was used in next step directly.

The crude alcohol **9** was dissolved in dichloromethane and treated with activated MnO_2 (10 equiv.). After completion of the reaction (monitored by TLC), the solid was removed by filtration of the reaction mixture through a pad of celite. Then it was extracted with ethyl acetate and dried with anhydrous Na_2SO_4. Then the reaction mixture was concentrated under reduced pressure and purified by column chromatography to give the desired ynones **1**.

1-Phenylprop-2-yn-1-one (1a):

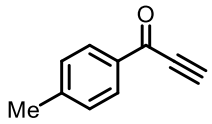


The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.38). The product was obtained as yellow solid in 86% yield (559.0 mg), m.p. 44 - 45 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 - 8.16 (m, 2H), 7.66 - 7.62 (m, 1H), 7.52 - 7.49 (m, 2H), 3.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 136.1, 134.5, 129.7, 128.7, 80.8, 80.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for C_9H_7O: 131.0497. Found:

[1] 1. J. Rong, H. Li, R. Fu, W. Sun, T.-P. Loh and Y. Jiang, *ACS Catal.*, 2020, **10**, 3664 – 3669.

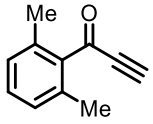
131.0495.

1-(*p*-Tolyl)prop-2-yn-1-one (1b):



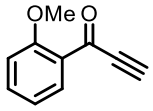
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.54). The product was obtained as yellow solid in 95% yield (684.5 mg), m.p. 35 - 36 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 - 7.95 (m, 2H), 7.21 - 7.19 (m, 2H), 3.34 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 145.7, 133.8, 129.8, 129.3, 80.4, 80.3, 21.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_9O$: 145.0653. Found: 145.0655.

1-(2,6-Dimethylphenyl)prop-2-yn-1-one (1c):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.5). The product was obtained as brown oil in 82% yield (648.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.20 (m, 1H), 7.05 (d, J = 7.6 Hz, 2H), 3.50 (s, 1H), 2.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.1, 139.5, 134.9, 130.1, 128.4, 82.7, 81.7, 19.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{11}O$: 159.0810. Found: 159.0805.

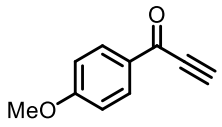
1-(2-Methoxyphenyl)prop-2-yn-1-one (1d):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.58). The product was obtained as faint yellow oil in 91% yield (728.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 - 8.05 (m, 1H), 7.57 - 7.53 (m, 1H), 7.06 - 7.00 (m, 2H), 3.93 (s, 3H), 3.39 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 160.0, 135.5, 133.2, 125.7,

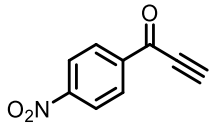
120.2, 112.1, 82.1, 79.3, 55.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_9O_2$: 161.0603. Found: 131.0600.

1-(4-Methoxyphenyl)prop-2-yn-1-one (1e):



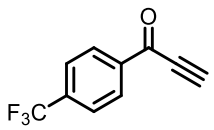
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.45). The product was obtained as yellow solid in 80% yield (640.4 mg), m.p. 72 - 73 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 - 8.12 (m, 2H), 6.97 - 6.95 (m, 2H), 3.89 (s, 3H), 3.40 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 164.7, 132.1 129.5, 113.9, 80.3, 80.1, 55.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_9O_2$: 161.0603. Found: 161.0600.

1-(4-Nitrophenyl)prop-2-yn-1-one (1f):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.55). The product was obtained as yellow solid in 79% yield (691.8 mg), m.p. 76 - 78 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 - 8.30 (m, 4H), 3.63 - 3.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 151.2, 140.2, 130.7, 124.0, 83.1, 79.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_6NO_3$: 176.0348. Found: 176.0355.

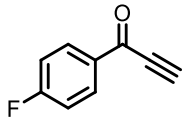
1-(4-(Trifluoromethyl)phenyl)prop-2-yn-1-one (1g):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.68). The product was obtained as yellow solid in 59% yield (584.1 mg), m.p. 65 -

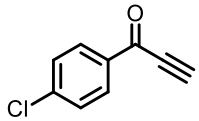
66 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 - 8.26 (m, 2H), 7.78 - 7.76 (m, 2H), 3.57 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 138.5, 135.5 (q, J = 32.5 Hz), 129.9, 125.7 (q, J = 3.7 Hz), 123.4 (q, J = 271.4 Hz), 82.1, 79.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2 (s, 3F); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_6F_3O$: 199.0371. Found: 199.0375.

1-(4-Fluorophenyl)prop-2-yn-1-one (1h):



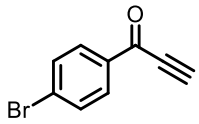
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.55). The product was obtained as yellow solid in 70% yield (518.0 mg), m.p. 43 - 44 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 - 8.17 (m, 2H), 7.17 (t, J = 8.4 Hz, 2H), 3.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 166.6 (d, J = 256.0 Hz), 132.6 (d, J = 2.9 Hz), 132.3 (d, J = 9.8 Hz), 115.9 (d, J = 22.2 Hz), 81.1, 79.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.2 (s, 1F); HRMS (ESI) m/z $[M+H]^+$: Calcd for C_9H_6FO: 149.0403. Found: 149.0403.

1-(4-Chlorophenyl)prop-2-yn-1-one (1i):



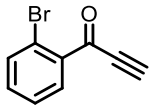
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.58). The product was obtained as yellow solid in 75% yield (615.0 mg), m.p. 94 - 95 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 3.49 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 141.2, 134.5, 130.1, 129.1, 81.3, 79.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for C_9H_6ClO: 165.0107. Found: 165.0109.

1-(4-Bromophenyl)prop-2-yn-1-one (1j):



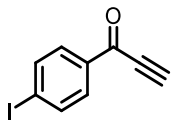
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.73). The product was obtained as yellow solid in 98% yield (1019.2 mg), m.p. 109 - 110 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.6 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 3.49 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 134.9, 132.1, 131.0, 130.1, 81.4, 79.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for C_9H_6BrO: 208.9602. Found: 208.9607.

1-(2-Bromophenyl)prop-2-yn-1-one (1k):



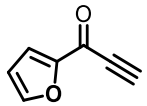
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.60). The product was obtained as faint yellow oil in 93% yield (967.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 7.6 Hz, 1H), 7.69 (d, J = 7.6 Hz, 1H), 7.48 - 7.38 (m, 2H), 3.54 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 135.7, 135.1, 133.8, 133.7, 127.3, 121.2, 81.6, 80.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for C_9H_6BrO: 208.9602. Found: 208.9597.

1-(4-Iodophenyl)prop-2-yn-1-one (1l):



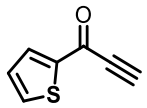
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.68). The product was obtained as yellow solid in 58% yield (742.1 mg), m.p. 117 - 118 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 - 7.82 (m, 4H), 3.48 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 138.1, 135.4, 130.8, 103.2, 81.4, 79.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for C_9H_6IO: 256.9463. Found: 256.6466.

1-(Furan-2-yl)prop-2-yn-1-one (1m):



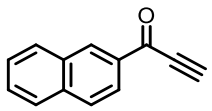
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.40). The product was obtained as yellow solid in 77% yield (462.0 mg), m.p. 44 - 45 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.35 (m, 1H), 6.54 (m, 1H), 3.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 152.6, 148.5, 122.1, 112.8, 79.5, 79.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_7H_5O_2$: 121.0290. Found: 121.0287.

1-(Thiophen-2-yl)prop-2-yn-1-one (1n):



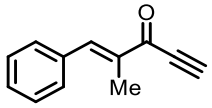
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.40). The product was obtained as yellow solid in 84% yield (571.2 mg), m.p. 39 - 40 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 3.2 Hz, 1H), 7.77 (d, J = 4.8 Hz, 1H), 7.20 - 7.18 (m, 1H), 3.40 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 144.0, 136.2, 136.0, 128.4, 79.8, 79.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for C_7H_5OS: 137.0061. Found: 137.0065.

1-(Naphthalen-2-yl)prop-2-yn-1-one (1o):



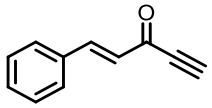
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.63). The product was obtained as yellow solid in 90% yield (810.5 mg), m.p. 91 - 92 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.13 - 8.11 (m, 1H), 8.00 - 7.98 (m, 1H), 7.89 - 7.86 (m, 2H), 7.65 - 7.59 (m, 1H), 7.57 - 7.55 (m, 1H), 3.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 136.2, 133.6, 133.3, 132.3, 129.8, 129.2, 128.6, 127.9, 127.0, 123.5, 80.7, 80.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_9O$: 181.0653. Found: 181.0655.

(*E*)-2-Methyl-1-phenylpent-1-en-4-yn-3-one (1p):



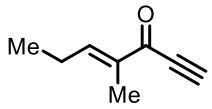
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.69). The product was obtained as yellow solid in 61% yield (518.8 mg), m.p. 43 - 44 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.43 - 7.30 (m, 5H), 3.27 (s, 1H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.0, 146.6, 137.6, 135.2, 130.1, 129.4, 128.6, 80.0, 79.7, 12.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{11}O$: 171.0810. Found: 171.0811.

(*E*)-1-Phenylpent-1-en-4-yn-3-one (1q):



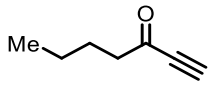
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.55). The product was obtained as brown solid in 61% yield (475.6 mg). m.p. 55 - 57 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 16.2 Hz, 1H), 7.58 - 7.56 (m, 2H), 7.47 - 7.40 (m, 3H), 6.79 (d, J = 16.1 Hz, 1H), 3.35 (d, J = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 150.0, 133.9, 131.6, 129.3, 128.9, 128.1, 80.0, 79.6,; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_9O$: 157.0653. Found: 157.0652.

(*E*)-4-Methylhept-4-en-1-yn-3-one (1r):



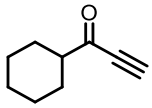
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.80). The product was obtained as yellow oil in 70% yield (427.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, J = 7.2 Hz, 1H), 3.24 (s, 1H), 2.38 - 2.30 (m, 2H), 1.80 (s, 3H), 1.13 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 153.1, 137.5, 79.6, 79.0, 22.7, 12.7, 10.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_8H_{11}O$: 123.0810. Found: 123.0811.

Hept-1-yn-3-one (1s):



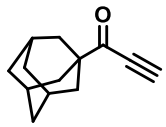
The title compound was prepared according to the general procedure (EA/PE = 1/39, R_f = 0.55). The product was obtained as colorless oil in 35% yield (192.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.19 (s, 1H), 2.52 (t, J = 7.2 Hz, 2H), 1.63 - 1.55 (m, 2H), 1.33 - 1.24 (m, 2H), 0.85 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 81.3, 78.3, 45.0, 25.7, 21.9, 13.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_7H_{11}O$: 111.0810. Found: 111.0814.

1-Cyclohexylprop-2-yn-1-one (1t):



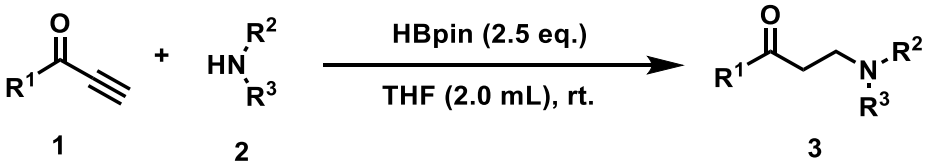
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.80). The product was obtained as brown oil in 47% yield (320.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (d, J = 6.5 Hz, 1H), 1.93 - 1.87 (m, 1H), 1.77 - 1.70 (m, 4H), 1.47 - 1.38 (m, 1H), 1.33 - 1.13 (m, 4H), 1.00 - 0.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 69.4, 43.5, 37.5, 29.8, 29.2, 26.5, 25.9, 25.8, 25.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{13}O$: 137.0966. Found: 137.0959.

1-((3r,5r,7r)-Adamantan-1-yl)prop-2-yn-1-one (1u):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.75). The product was obtained as yellow solid in 55% yield (517.8 mg). m.p. 89 - 91 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.22 (s, 1H), 2.07 (s, 3H), 1.86 (d, J = 2.5 Hz, 6H), 1.77 - 1.70 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 80.0, 46.9, 37.8, 36.5, 27.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{19}O$: 189.1279. Found: 189.1285.

General procedure for *β*-aminoketones and their spectral data:

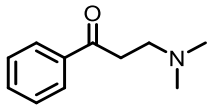


1 2 3

Method A: A tube was charged with **1** (0.20 mmol, 1.0 equiv.), **2** (0.30 mmol, 1.5 equiv.) and HBpin (0.50 mmol, 76.8 mg, 2.5 equiv.) under open-flask in THF (2.0 mL). The resulting mixture was stirred at room temperature until the **1** was consumed completely (about 4.0 hours). After completion of the reaction (monitored by TLC), the reaction solution was concentrated under reduced pressure and purified by column chromatography (dichloromethane: methanol = 9: 1) to give the desired product **3**.

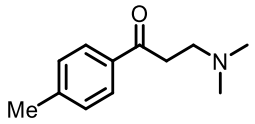
Method B: A tube was charged with **1** (0.20 mmol, 1.0 equiv.), **2** (0.30 mmol, 1.5 equiv.) under open-flask in THF (2.0 mL). The resulting mixture was stirred at room temperature until the **1** was consumed completely (about 5.0 hours). And then HBpin (0.50 mmol, 76.8 mg, 2.5 equiv.) was added directly in one portion and reacted for about 10 minutes. After completion of the reaction (monitored by TLC), the reaction solution was concentrated under reduced pressure and purified by column chromatography (dichloromethane: methanol = 9: 1) to give the desired product **3**.

3-(Dimethylamino)-1-phenylpropan-1-one (3aa):



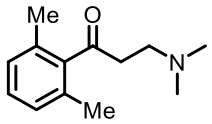
The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.25). The product was obtained as yellow solid in 88% yield (31.2 mg), m.p. 31 - 33 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 2H), 7.59 – 7.55 (m, 1H), 7.48 – 7.44(m, 2H), 3.31 (t, J = 7.3 Hz, 2H), 2.97 (t, J = 7.2 Hz, 2H), 2.44 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 136.6, 128.8, 128.2, 53.9, 45.0, 36.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{16}NO$: 178.1232. Found: 178.1233

3-(Dimethylamino)-1-(p-tolyl)propan-1-one (3ba):



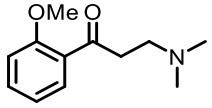
The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.30). The product was obtained as brown oil in 88% yield (33.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 2H), 7.27 – 7.24 (m, 2H), 3.25 – 3.19 (m, 2H), 2.90 – 2.84 (m, 2H), 2.40 (d, J = 6.3 Hz, 3H), 2.38 (d, J = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 144.3, 134.3, 129.5, 128.3, 54.3, 45.3, 36.4, 21.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{18}NO$: 192.1388. Found: 192.1386.

3-(Dimethylamino)-1-(2,6-dimethylphenyl)propan-1-one (3ca):



The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.25). The product was obtained as brown oil in 85% yield (34.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.13 (m, 1H), 7.01 – 6.99 (m, 2H), 2.97 – 2.93 (m, 2H), 2.82 – 2.78 (m, 2H), 2.31 (s, 6H), 2.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 142.1, 132.6, 128.8, 127.9, 53.5, 45.4, 42.7, 19.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{20}NO$: 206.1545. Found: 206.1548.

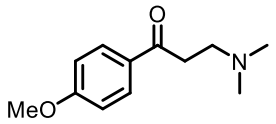
3-(Dimethylamino)-1-(2-methoxyphenyl)propan-1-one (3da):



The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.20). The product was obtained as yellow oil in 74% yield (30.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.58 (m, 1H), 7.38 – 7.33 (m, 1H), 6.91 – 6.86 (m, 2H), 3.80 (s, 3H), 3.11 – 3.07 (m, 2H), 2.64 – 2.60 (m, 2H), 2.18 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 158.5, 133.5, 130.3, 128.3, 120.7, 111.6, 55.5, 54.5, 45.5, 42.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{18}NO_2$: 208.1338.

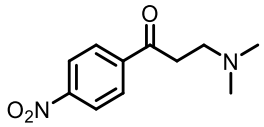
Found: 208.1342.

3-(Dimethylamino)-1-(4-methoxyphenyl)propan-1-one (3ea):



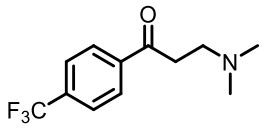
The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.20). The product was obtained as yellow solid in 78% yield (32.3 mg), m.p. 180 - 181 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.92 (m, 2H), 6.93 – 6.90 (m, 2H), 3.85 (s, 3H), 3.17 – 3.14 (m, 2H), 2.84 – 2.80 (m, 2H), 2.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 163.7, 130.5, 129.9, 113.9, 55.6, 54.4, 45.3, 36.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{18}NO_2$: 208.1338. Found: 208.1334.

3-(Dimethylamino)-1-(4-nitrophenyl)propan-1-one (3fa):



The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.25). The product was obtained as brown solid in 86% yield (38.2 mg), m.p. 190 - 191 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.29 (m, 2H), 8.12 – 8.09 (m, 2H), 3.20 (t, J = 7.2 Hz, 2H), 2.77 (t, J = 7.2 Hz, 2H), 2.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 150.4, 141.4, 129.2, 124.0, 54.0, 45.6, 37.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{15}N_2O_3$: 223.1083. Found: 223.1076.

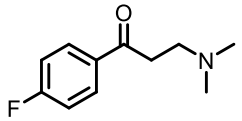
3-(Dimethylamino)-1-(4-(trifluoromethyl)phenyl)propan-1-one (3ga):



The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.35). The product was obtained as brown oil in 72 % yield

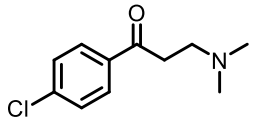
(35.3 mg), m.p. 69 - 70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 8.00 (m, 2H), 7.68 – 7.66 (m, 2H), 3.13 (t, J = 7.2 Hz, 2H), 2.72 (t, J = 7.2 Hz, 2H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 139.6, 134.4 (q, J = 32.4 Hz), 129.0, 128.4, 127.7, 125.8 (d, J = 3.5 Hz), 125.0, 122.3, 54.1, 45.5, 37.3.; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.06 (s, 3F); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{15}F_3NO$: 246.1106. Found: 246.1113.

3-(Dimethylamino)-1-(4-fluorophenyl)propan-1-one (3ha):



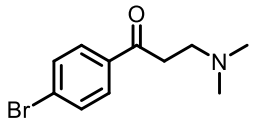
The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.40). The product was obtained as yellow oil in 88% yield (34.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.04 – 6.98 (m, 2H), 3.05 – 3.01 (m, 2H), 2.65 (t, J = 7.3 Hz, 2H), 2.18 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 167.0, 164.5, 133.4, 130.7 (d, J = 9.2 Hz), 115.7 (d, J = 22.0 Hz), 54.3, 45.5, 36.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.24 (s, 1F); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{15}FNO$: 196.1138. Found: 196.1143.

1-(4-Chlorophenyl)-3-(dimethylamino)propan-1-one (3ia):



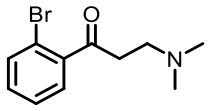
The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.30). The product was obtained as yellow solid in 82% yield (34.7 mg), m.p. 69 - 72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 2H), 7.45 – 7.41 (m, 2H), 3.12 (t, J = 7.3 Hz, 2H), 2.74 (t, J = 7.3 Hz, 2H), 2.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 139.4, 135.1, 129.4, 128.8, 54.1, 45.4, 36.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{15}ClNO$: 212.0842. Found: 212.0848.

1-(4-Bromophenyl)-3-(dimethylamino)propan-1-one (3ja):



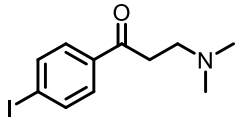
The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.30). The product was obtained as yellow solid in 84% yield (43.0 mg), m.p. 58 - 60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 2H), 7.60 – 7.57 (m, 2H), 3.14 – 3.10 (m, 2H), 2.75 (t, J = 7.3 Hz, 2H), 2.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 135.6, 132.1, 129.7, 128.4, 54.3, 45.6, 36.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{15}BrNO$: 256.0337. Found: 256.0340.

1-(2-Bromophenyl)-3-(dimethylamino)propan-1-one (3ka):



The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.25). The product was obtained as brown oil in 87% yield (44.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 1H), 7.40 – 7.37 (m, 1H), 7.36 – 7.32 (m, 1H), 7.29 – 7.24 (m, 1H), 3.10 (t, J = 7.3 Hz, 2H), 2.72 (t, J = 7.3 Hz, 2H), 2.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 141.7, 133.7, 131.7, 128.7, 128.9, 127.6, 118.7, 54.1, 45.4, 41.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{15}BrNO$: 256.0337. Found: 256.0343.

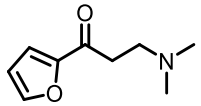
3-(Dimethylamino)-1-(4-iodophenyl)propan-1-one (3la):



The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.35). The product was obtained as yellow solid in 85% yield (51.5 mg), m.p. 82 - 85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 2H), 7.67 – 7.64 (m, 2H), 3.12 (t, J = 7.3 Hz, 2H), 2.76 (t, J = 7.3 Hz, 2H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 138.1, 136.1, 129.6, 101.3, 54.2, 45.5, 36.8; HRMS (ESI)

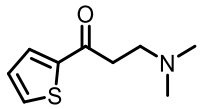
m/z $[M+H]^+$: Calcd for $C_{11}H_{15}INO$: 304.0198. Found: 304.0204.

3-(Dimethylamino)-1-(furan-2-yl)propan-1-one (3ma):



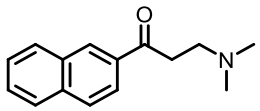
The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.40). The product was obtained as yellow solid in 80% yield (26.8 mg), m.p. 95 - 96 ºC ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 1H), 7.18 – 7.17 (m, 1H), 6.51 – 6.50 (m, 1H), 2.97 (t, J = 7.4 Hz, 2H), 2.71 (t, J = 7.3 Hz, 2H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 152.8, 146.5, 117.2, 112.4, 54.3, 45.4, 36.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{14}NO_2$: 168.1025. Found: 168.1023.

3-(Dimethylamino)-1-(thiophen-2-yl)propan-1-one (3na):



The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.40). The product was obtained as brown solid in 86% yield (31.5 mg), m.p. 178 - 180 ºC ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.67 (m, 1H), 7.58 – 7.57 (m, 1H), 7.07 (dd, J_1 = 4.9, J_2 = 3.8 Hz, 1H), 3.03 (t, J = 7.3 Hz, 2H), 2.71 (t, J = 7.3 Hz, 2H), 2.23 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 144.3, 133.9, 132.1, 128.3, 54.5, 45.5, 37.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{14}NOS$: 184.0796. Found: 184.0788.

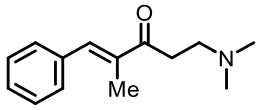
3-(Dimethylamino)-1-(naphthalen-2-yl)propan-1-one (3oa):



The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.30). The product was obtained as yellow oil in 70% yield

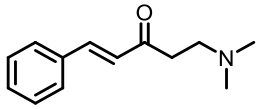
(31.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.05 – 8.02 (m, 1H), 7.98 – 7.96 (m, 1H), 7.90 – 7.86 (m, 2H), 7.63 – 7.53 (m, 2H), 3.35 – 3.31 (m, 2H), 2.87 (t, J = 7.3 Hz, 2H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 135.7, 134.2, 132.6, 129.9, 128.7, 127.9, 126.9, 123.9, 54.5, 45.5, 36.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{18}NO$: 228.1388. Found: 228.1397.

(*E*)-5-(Dimethylamino)-2-methyl-1-phenylpent-1-en-3-one (3pa):



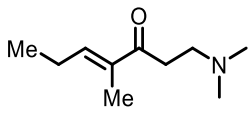
The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.20). The product was obtained as yellow solid in 85% yield (36.9 mg), m.p. 62 - 65 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 1H), 7.43 – 7.38 (m, 4H), 7.35 – 7.31 (m, 1H), 3.04 (t, J = 7.4 Hz, 2H), 2.76 – 2.73 (m, 2H), 2.32 (s, 6H), 2.05 (d, J = 1.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 139.1, 137.4, 135.9, 129.9, 128.6, 54.9, 45.5, 35.8, 13.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{20}NO$: 218.1545. Found: 218.1545.

(*E*)-5-(Dimethylamino)-1-phenylpent-1-en-3-one (3qa):



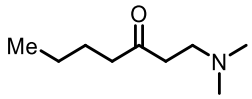
The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.30). The product was obtained as brown oil in 74% yield (34.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 3H), 7.41 – 7.38 (m, 3H), 6.75 (d, J = 16.2 Hz, 1H), 2.87 (t, J = 7.3 Hz, 2H), 2.71 (t, J = 7.3 Hz, 2H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 143.0, 134.5, 130.7, 129.1, 128.5, 126.2, 54.4, 45.5, 39.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{18}NO$: 204.1388. Found: 204.1387.

(*E*)-5-(Dimethylamino)-2-methyl-1-phenylpent-1-en-3-one (3ra):



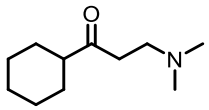
The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.25). The product was obtained as brown oil in 61% yield (20.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 – 6.73 (m, 1H), 3.36 (s, 4H), 2.78 (s, 6H), 2.31 – 2.24 (m, 2H), 1.77 – 1.76 (m, 3H)), 1.09 (t, J = 7.6 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 147.1, 136.0, 53.3, 43.6, 32.6, 29.8, 22.7, 13.0, 11.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_{20}NO$: 170.1545. Found: 170.1539.

1-(Dimethylamino)heptan-3-one (3sa):



The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.20). The product was obtained as yellow oil in 54% yield (17.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.30 (t, J = 6.8 Hz, 2H), 3.15 (t, J = 6.9 Hz, 2H), 2.78 (s, 6H), 2.48 (t, J = 7.5 Hz, 2H), 1.58 – 1.51 (m, 2H), 1.34 – 1.26 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.8, 52.4, 43.5, 42.8, 37.6, 25.7, 22.3, 13.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{20}NO$: 158.1545. Found: 158.1543.

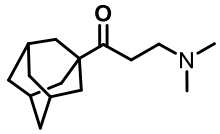
1-Cyclohexyl-3-(dimethylamino)propan-1-one (3ta):



The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.25). The product was obtained as brown oil in 67% yield (24.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 – 2.62 (m, 2H), 2.60 – 2.56 (m, 2H), 2.34 – 2.27 (m, 1H), 2.23 (s, 6H), 1.81 – 1.78 (m, 2H), 1.75 – 1.71 (m, 2H), 1.64 – 1.60 (m, 1H), 1.33 – 1.11 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.7, 53.8, 51.1, 45.3, 38.6, 28.5, 25.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{22}NO$: 184.1701. Found:

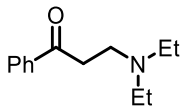
184.1707.

1-((3r,5r,7r)-Adamantan-1-yl)-3-(dimethylamino)propan-1-one (3ua):



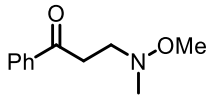
The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.25). The product was obtained as yellow oil in 75% yield (35.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.70 – 2.65 (m, 2H), 2.62 – 2.58 (m, 2H), 2.27 (s, 6H), 2.00 (s, 3H), 1.77 (d, J = 2.7 Hz, 6H), 1.67 (dd, J = 12.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.2, 53.9, 46.6, 45.3, 38.3, 36.6, 34.2, 28.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{26}NO$: 236.2014. Found: 236.2021.

3-(Diethylamino)-1-phenylpropan-1-one (3ab):



The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.20). The product was obtained as brown solid. yield: 82% (33.7 mg). m.p. 105 - 108 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.95 (m, 2H), 7.58 – 7.54 (m, 1H), 7.48 – 7.44 (m, 2H), 3.22 – 3.18 (m, 2H), 2.99 – 2.95 (m, 2H), 2.63 (q, J = 7.2 Hz, 4H), 1.08 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 137.0, 133.3, 128.8, 128.2, 47.9, 47.1, 36.2, 11.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{20}NO$: 206.1545. Found: 206.1538.

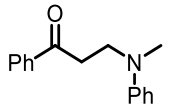
3-(Methoxy(methyl)amino)-1-phenylpropan-1-one (3ac):



The title compound was prepared according to the general procedure Method A (EA/PE = 1/9, R_f = 0.45). The product was obtained as brown oil in 88% yield (34.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 2H), 7.58 – 7.54 (m, 1H), 7.49 – 7.44 (m,

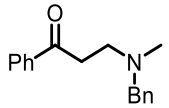
2H), 3.48 (s, 3H), 3.26 (t, J = 6.9 Hz, 2H), 3.07 (t, J = 6.9 Hz, 2H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 137.5, 133.2, 128.7, 128.2, 60.2, 55.7, 45.3, 36.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{16}NO_2$: 194.1181. Found: 194.1179.

3-(Methyl(phenyl)amino)-1-phenylpropan-1-one (3ad):



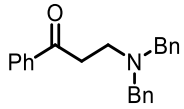
The title compound was prepared according to the general procedure Method B (EA/PE = 1/9, R_f = 0.50). The product was obtained as yellow solid in 87% yield (41.6 mg), m.p. 59 - 60 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.93 (m, 2H), 7.59 – 7.55 (m, 1H), 7.48 – 7.44 (m, 2H), 7.30 – 7.24 (m, 2H), 6.78 – 6.73 (m, 3H), 3.87 – 3.84 (m, 2H), 3.27 – 3.23 (m, 2H), 2.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 148.7, 137.0, 133.4, 129.5, 128.8, 128.2, 116.7, 112.5, 48.1, 38.7, 35.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{16}H_{18}NO$: 240.1388. Found: 240.1392

3-(Benzyl(methyl)amino)-1-phenylpropan-1-one (3ae):



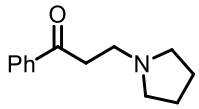
The title compound was prepared according to the general procedure Method B (MeOH/DCM = 1/9, R_f = 0.60). The product was obtained as yellow solid in 71% yield (36.0 mg), m.p. 187 - 188 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.92 (m, 2H), 7.58 – 7.54 (m, 1H), 7.47 – 7.43 (m, 2H), 7.30 – 7.29 (m, 4H), 7.25 – 7.23 (m, 1H), 3.56 (s, 2H), 3.21 – 3.18 (m, 2H), 2.91 – 2.87 (m, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 138.9, 137.1, 133.2, 129.1, 128.7, 128.4, 128.2, 127.2, 62.5, 52.6, 42.4, 37.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{20}NO$: 254.1545. Found: 254.1546.

3-(Dibenzylamino)-1-phenylpropan-1-one (3af):



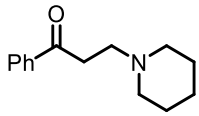
The title compound was prepared according to the general procedure Method B (EA/PE = 1/4, R_f = 0.55). The product was obtained as yellow solid in 65% yield (42.8 mg), m.p. 38 - 40 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 2H), 7.55 – 7.51 (m, 1H), 7.42 – 7.38 (m, 2H), 7.35 – 7.34 (m, 4H), 7.31 – 7.27 (m, 4H), 7.24 – 7.21 (m, 2H), 3.64 (s, 4H), 3.16 – 3.12 (m, 2H), 2.95 (t, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 139.5, 137.0, 133.1, 128.9, 128.7, 128.4, 128.2, 127.1, 58.7, 49.4, 37.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{23}H_{24}NO$: 330.1858. Found: 330.1852.

1-Phenyl-3-(pyrrolidin-1-yl)propan-1-one (3ag):



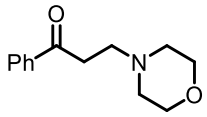
The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.20). The product was obtained as brown solid in 73% yield (29.7 mg), m.p. 155 - 156 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.93 (m, 2H), 7.55 – 7.51 (m, 1H), 7.45 – 7.41 (m, 2H), 3.27 – 3.23 (m, 2H), 2.96 – 2.92 (m, 2H), 2.63 – 2.59 (m, 4H), 1.84 – 1.79 (m, 4H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 136.1, 133.9, 128.9, 128.3, 54.2, 50.5, 36.2, 23.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{18}NO$: 204.1388. Found: 204.1385.

1-Phenyl-3-(piperidin-1-yl)propan-1-one (3ah):



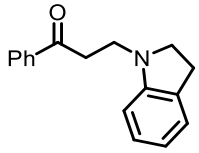
The title compound was prepared according to the general procedure Method A (EA/PE = 1/4, R_f = 0.70). The product was obtained as brown solid in 80% yield (34.7 mg), m.p. 192 - 193 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.91 (m, 2H), 7.54 – 7.50 (m, 1H), 7.44 – 7.40 (m, 2H), 3.29 – 3.25 (m, 2H), 2.89 – 2.85 (m, 2H), 2.53 (s, 4H), 1.66 – 1.61 (m, 4H), 1.47 – 1.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 136.7, 133.4, 128.8, 128.2, 54.6, 53.6, 35.8, 25.4, 23.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{20}NO$: 218.1545. Found: 218.1547.

3-Morpholino-1-phenylpropan-1-one (3ai):



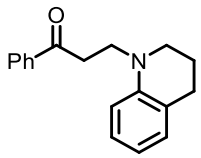
The title compound was prepared according to the general procedure Method A (MeOH/DCM = 1/9, R_f = 0.75). The product was obtained as yellow oil in 79% yield (34.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.94 (m, 2H), 7.59 – 7.54 (m, 1H), 7.48 – 7.44 (m, 2H), 3.73 – 3.71 (m, 4H), 3.22 – 3.18 (m, 2H), 2.84 (t, J = 7.4 Hz, 2H), 2.53 – 2.51 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 136.9, 133.3, 128.8, 128.2, 67.0, 53.8, 53.6, 36.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{20}NO$: 220.1338. Found: 220.1344.

3-(Indolin-1-yl)-1-phenylpropan-1-one (3aj):



The title compound was prepared according to the general procedure Method B (EA/PE = 1/9, R_f = 0.60). The product was obtained as brown oil in 85% yield (42.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 2H), 7.61 – 7.56 (m, 1H), 7.50 – 7.46 (m, 2H), 7.11 – 7.07 (m, 2H), 6.69 – 6.65 (m, 1H), 6.55 (d, J = 7.9 Hz, 1H), 3.60 (t, J = 7.1 Hz, 2H), 3.42 (t, J = 8.3 Hz, 2H), 3.28 (t, J = 7.1 Hz, 2H), 2.97 (t, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 152.0, 137.0, 133.4, 130.2, 128.8, 128.2, 127.5, 124.6, 117.8, 107.1, 53.4, 44.3, 35.9, 28.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{18}NO$: 252.1388. Found: 252.1380.

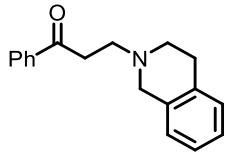
3-(3,4-Dihydroquinolin-1(2H)-yl)-1-phenylpropan-1-one (3ak):



The title compound was prepared according to the general procedure Method B (EA/PE = 1/9, R_f = 0.50). The product was obtained as yellow oil in 68% yield (36.1 mg). ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.95 (m, 2H), 7.59 – 7.55 (m, 1H), 7.49 – 7.44 (m, 2H), 7.10 – 7.06 (m, 1H), 6.98 – 6.96 (m, 1H), 6.64 – 6.59 (m, 2H), 3.79 – 3.76 (m, 2H), 3.35 – 3.32 (m, 2H), 3.30 – 3.26 (m, 2H), 2.76 (t, J = 6.4 Hz, 2H), 1.98 – 1.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 196.7, 144.0, 136.4, 133.6, 129.4, 128.7, 128.1, 127.3, 125.8 (q, J = 3.8), 51.8, 46.2, 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F); HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{18}H_{20}NO$: 266.1545. Found: 266.1543.

3-(3,4-Dihydroisoquinolin-2(1H)-yl)-1-phenylpropan-1-one (3al):



The title compound was prepared according to the general procedure Method B (EA/PE = 1/4, R_f = 0.40). The product was obtained as yellow oil in 66% yield (35.0 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.98 (m, 2H), 7.61 – 7.56 (m, 1H), 7.50 – 7.46 (m, 2H), 7.14 – 7.11 (m, 3H), 7.04 – 7.03 (m, 1H), 3.73 (s, 2H), 3.33 (t, J = 7.4 Hz, 2H), 3.05 – 3.02 (m, 2H), 2.93 (d, J = 5.6 Hz, 2H), 2.84 (t, J = 5.0 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 137.0, 134.4, 134.1, 133.3 128.8, 128.2, 126.7, 125.8, 56.2, 53.0, 51.2, 36.8, 29.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{18}H_{20}NO$: 266.1545. Found: 266.1544.

General procedure for mechanism studies:

Control experiments:

(a) A tube was charged with **1a** (0.20 mmol, 1.0 equiv.), **2a** (0.30 mmol, 1.5 equiv.), HBpin (0.50 mmol, 2.5 equiv.) and TEMPO (0.40 mmol, 2.0 equiv.) in THF (2.0 mL). The resulting mixture was stirred at room temperature until the starting material was consumed completely (about 4.0 h). The reaction solution was concentrated under reduced pressure and purified by column chromatography (dichloromethane: methanol = 9 : 1) to afford the product **3aa** as yellow solid. Yield: 87% (30.9 mg).

(b) A tube was charged with **1a** (0.20 mmol, 1.0 equiv.) and HBpin (0.50 mmol, 2.5 equiv.) in THF (2.0 mL). The reaction mixture was stirred at room temperature for 24 hours. The solution was concentrated in *vacuo*. The crude yield was detected from ^{1}H NMR using 1,1,2,2- tetrachloroethane as an internal standard (NMR yield: 0%).

(c) A tube was charged with **1a** (0.20 mmol, 1.0 equiv.), **2a** (0.30 mmol, 1.5 equiv.), HBpin (0.30 mmol, 1.5 equiv.) in THF (2.0 mL). The resulting mixture was stirred at room temperature until the starting material **1a** was consumed completely (4.0 h). The reaction solution was concentrated under reduced pressure and purified by column chromatography (dichloromethane: methanol = 9: 1) to afford the product **3aa** (35%, 12.4 mg) + **3aa'** (59%, 20.7 mg).

(d) To a flame-dried vial was added amine **4** (2.0 mmol, 1.0 equiv), HBpin (2.0 mmol, 1.0 equiv) and CH_3CN. The reaction was carried out at 120 ^{o}C for 24 hours. After the reaction was completed, removal of all the volatiles under vacuum could obtain pure product **2f-B**. Yield: 89% (575.4 mg). The base (NaO^{t}Bu, 0.05 mmol) and dibenzylamino-pinacolborane (0.30 mmol, 1.5 equiv.) were transferred into a tube under air atmosphere with methanol (2.0 mL). The ynones (0.20 mmol, 1.0 equiv.) and HBpin (0.30 mmol, 1.5 equiv.) was then added and the reaction mixture was stirred at 70 °C external temperature for 17 hours. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 9: 1) to afford the product **3af**. Yield: 75% (49.5 mg).

D-labelling experiments:

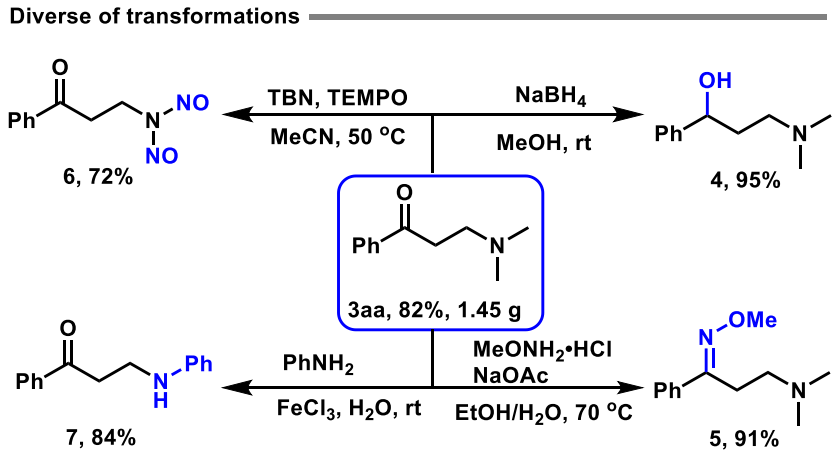
(a) A mixture of **1a** (0.20 mmol, 1.0 equiv.), **2a** (0.30 mmol, 1.5 equiv.), HBpin (0.50 mmol, 2.5 equiv.), D_2O (1.0 mmol, 5.0 equiv.) and anhydrous THF (2.0 mL) was added in an oven-dried Schlenk tube under nitrogen protection. The resulting mixture was stirred at room temperature for 4.0 hours. Then the reaction solution was concentrated under reduced pressure and purified by column chromatography (dichloromethane: methanol = 9: 1) to afford the product **3aa**. Yield: 64% (22.7 mg).

(b) A mixture of **1a** (0.20 mmol, 1.0 equiv.), **2f-*d*** (0.30 mmol, 1.5 equiv.), HBpin (0.50 mmol, 2.5 equiv.) and THF (2.0 mL) was added in an oven-dried Schlenk tube. The resulting mixture was stirred at room temperature for 4.0 hours. Then the reaction solution was concentrated under reduced pressure and purified by column chromatography (dichloromethane: methanol = 9: 1) to afford the product **3af-I**. Yield: 62% (41.1 mg).

(c) A mixture of **1a** (0.20 mmol, 1.0 equiv.), **2f-*d*** (0.30 mmol, 1.5 equiv.) and THF (2.0 mL) was added in an oven-dried Schlenk tube. The resulting mixture was stirred at room temperature for 4.0 hours. Then the reaction solution was concentrated under reduced pressure and purified by column chromatography (dichloromethane: methanol = 9: 1) to afford the product **3af'-I**. Yield: 81% (53.3 mg).

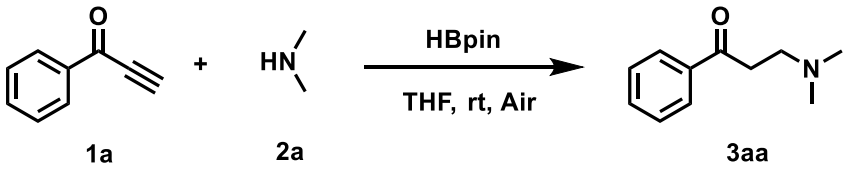
(d) A mixture of $NaBD_4$ (1.5 mmol, 62.8 mg, 3.0 equiv.), pinacol (0.5 mmol, 59.2 mg, 2.5 equiv.) and dry DCE (0.4 mL) was added in an oven-dried Schlenk tube under nitrogen protection. Then a solution of iodine (0.80 mmol, 200.0 mg, 1.6 equiv.) in dry DCE (0.4 mL) was added dropwise. The resulting mixture was stirred at room temperature for 2.0 h. Then **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.3 mmol, 1.5 equiv.) and THF (2.0 mL) was added subsequently and the reaction mixture was stirred at room temperature until the starting material was consumed completely. Then the reaction solution was concentrated under reduced pressure and purified by column chromatography (dichloromethane: methanol = 9: 1) to afford the product **3aa-I.** Yield: 67% (23.8 mg).

General procedure for applications and their spectral data:



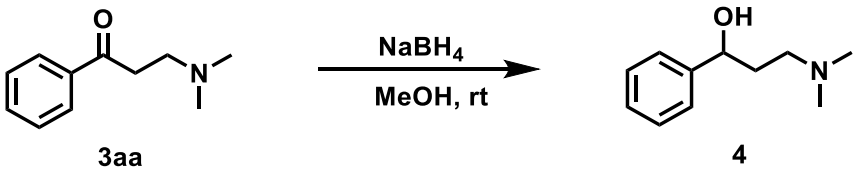
Scheme S1. Synthetic applications

Gram scale synthesis of 3aa:



A tube was charged with **1a** (10.0 mmol, 1.30 g, 1.0 equiv.), **2a** (15.0 mmol, 7.5 mL, 1.5 equiv., 2.0 M in THF), HBpin (25.0 mmol, 3.20 g, 2.5 equiv.) under open-flask in THF (100.0 mL). The resulting mixture was stirred at room temperature until the **1** was consumed completely (about 6.0 hours). After completion of the reaction (monitored by TLC), the reaction solution was concentrated under reduced pressure and purified by column chromatography (dichloromethane: methanol = 9: 1) to give the desired product **3aa** as yellow solid in 82% yield (1.45 g).

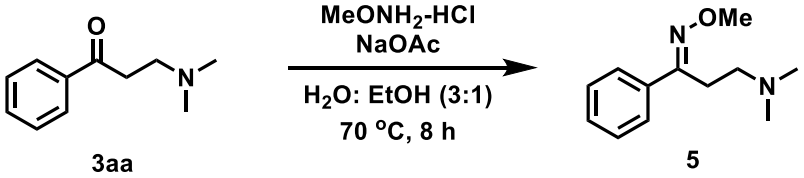
3-(Dimethylamino)-1-phenylpropan-1-ol (4):



To a solution of 3-(dimethylamino)-1-phenylpropan-l-one **3aa** (0.20 mmol, 35.5 mg, 1.0 equiv.) in MeOH (2.0 mL) was added $NaBH_4$ (0.40 mmol, 83.2 mg, 2.0 equiv.) at room temperature and the reaction mixture was stirred at the same temperature for 30 min under nitrogen atmosphere. The mixture was poured into H_2O (5 mL) and extracted

with EtOAc (10 mL). The organic layer was washed with brine (10 mL) and dried with Na_2SO_4. After removal of the solvent, the residue was subjected to column chromatography to give **4** as brown oil in 95% yield (34.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 4H), 7.25 – 7.21 (m, 1H), 6.33 (s, 1H), 4.90 (dd, J_1 = 7.5, J_2 = 4.2 Hz, 1H), 2.66 – 2.59 (m, 1H), 2.49 – 2.43 (m, 1H), 2.28 (s, 6H), 1.88 – 1.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 128.3, 127.0, 125.7, 75.5, 58.3, 45.4, 34.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{18}NO$: 180.1388. Found: 180.1383.

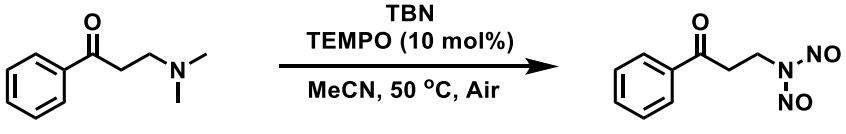
(*E*)-3-(Dimethylamino)-1-phenylpropan-1-one *O*-methyloxime (5):



3aa 5

To a 15 mL tube equipped with a stir bar was added 3-(dimethylamino)-1-phenyl-propan-l-one **3aa** (0.20 mmol, 34.5 mg, 1.0 equiv.), $MeONH_2$•HCl (0.54 mmol, 45.2 mg, 2.7 equiv.), NaOAc (0.88 mmol, 72.2 mg, 4.4 equiv.), H_2O (1.5 mL) and EtOH (0.5 mL). The flask was equipped with a reflux condenser and heated at 70°C for 8 h. After cooling to room temperature, the mixture was extracted with EtOAc (3 x 10 mL). The organic layers were combined, dried with Na_2SO_4, and concentrated. The purification was performed by flash column chromatography to afford desired pure oximes **5** as yellow oil in 91% yield (37.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.65 (m, 3H), 7.39 – 7.35 (m, 2H), 3.99 (s, 3H), 3.06 – 3.02 (m, 2H), 2.68 – 2.64 (m, 2H), 2.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 135.2, 129.5, 128.8, 126.3, 62.2, 52.3, 44.6, 24.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{19}N_2O$: 207.1497. Found: 207.1496.

***N*-Nitroso-*N*-(3-oxo-3-phenylpropyl)nitrous amide (6):**

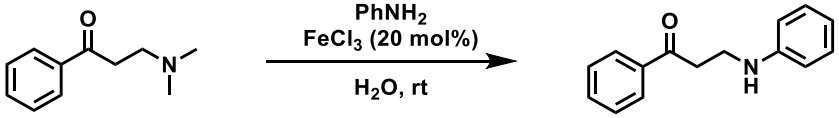


3aa 6

A tube was charged with 3-(dimethylamino)-1-phenyl-propan-l-one **3aa** (0.20 mmol,

34.5 mg, 1.0 equiv.), *t*-butyl nitrite (TBN) (0.30 mmol, 30.9 mg, 1.5 equiv.) and 2,2,6,6 -tetramethyl-1–piperid- inyloxy (TEMPO) (0.02 mmol, 3.2 mg, 10 mol %) in CH_3CN (2 mL). And the reaction mixture was stirred at 70 °C until the starting material was fully consumed (24 h). The organic layers were combined, dried with Na_2SO_4, and concentrated. The purification was performed by flash column chromatography to give **6** as yellow solid in 72% yield (29.9 mg). m.p. 71 - 73 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.97 (m, 2H), 7.65 – 7.61 (m, 1H), 7.53 – 7.49 (m, 2H), 4.84 (t, J = 6.1 Hz, 2H), 3.67 (t, J = 6.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 135.8, 134.1, 129.0, 128.3, 69.4, 35.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{10}N_3O_3$: 208.0722. Found: 208.0715.

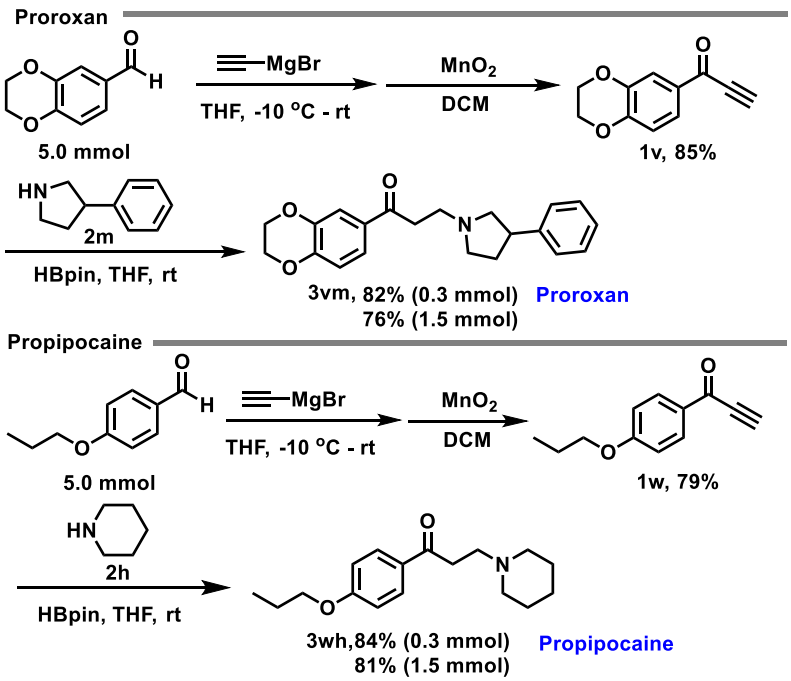
1-Phenyl-3-(phenylamino)propan-1-one (7):



3aa 7

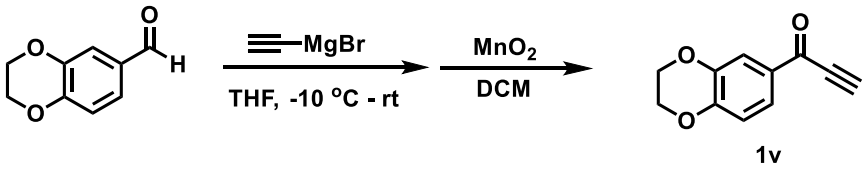
A tube was charged with 3-(dimethylamino)-1-phenyl-propan-l-one **3aa** (0.20 mmol, 34.5 mg, 1.0 equiv.), aniline (0.20 mmol, 18.7 mg, 1.0 equiv.), $FeCl_3$ (0.04 mmol, 6.5 mg, 20 mol %) in H_2O (5.0 mL). The resulting mixture was stirred at room temperature until the starting material was fully consumed. And then the mixture was extracted with EtOAc (3 x 10 mL). The organic layers were combined, dried with Na_2SO_4, and concentrated. The purification was performed by flash column chromatography to afford desired pure oximes **7** as yellow solid in 82% yield (37.0 mg). m.p. 102 - 104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.95 (m, 2H), 7.60 – 7.56 (m, 1H), 7.49 – 7.45 (m, 2H), 7.22 – 7.17 (m, 2H), 6.75 – 6.71 (m, 1H), 6.69 – 6.66 (m, 2H), 3.63 (t, J = 6.1 Hz, 2H), 3.30 (t, J = 6.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 147.7, 136.8, 133.5, 129.5, 128.8, 128.2, 117.9, 113.3, 39.0, 37.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{16}NO$: 226.1232. Found: 226.1234.

General procedures for *Proroxan* and *Propipocaine*:



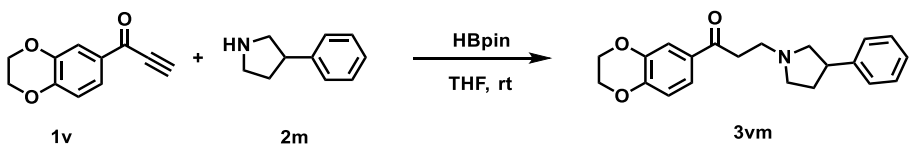
Scheme S2. Synthesis of drug molecules.

1-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)prop-2-yn-1-one (1v):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.60). The product was obtained as yellow solid in 85% yield (799.8 mg), m.p. 106 - 107 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 2H), 6.90 (d, J = 8.4 Hz, 1H), 4.32 – 4.30 (m, 2H), 4.27 – 4.25 (m, 2H), 3.38 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 149.6, 143.5, 130.3, 124.3, 119.0, 117.6, 80.4, 64.9, 64.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_9O_3$: 189.0552. Found: 189.0554.

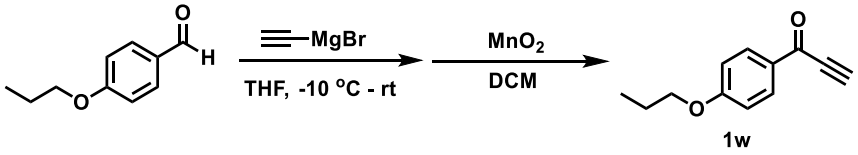
1-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-3-(3-phenylpyrrolidin-1-yl)propan-1-one(Proroxan, 3vm):



A tube was charged with **1v** (0.30 mmol, 56.5 mg, 1.0 equiv.), **2m** (0.45 mmol, 66.3

mg, 1.5 equiv.), HBpin (0.75 mmol, 96.0 mg, 2.5 equiv.) in THF (2.0 mL). And the reaction mixture was stirred until the **1v** was consumed completely. After completion of the reaction (monitored by TLC, MeOH/DCM = 1/9, R_f = 0.25), the reaction mixture was concentrated under reduced pressure and purified by column chromatography (dichloromethane: methanol = 9: 1). The product **3vm** was obtained as yellow oil in 82% yield (0.30 mmol scale, 83.0 mg) and 76% yield (1.5 mmol scale, 384.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.48 (m, 2H), 7.29 – 7.23 (m, 4H), 7.19 – 7.15 (m, 1H), 6.89 – 6.87 (m, 1H), 4.28 – 4.26 (m, 2H), 4.24 – 4.22 (m, 2H), 3.38 (p, J = 8.0 Hz, 1H), 3.19 – 3.11 (m, 3H), 3.05 – 3.00 (m, 1H), 2.98 – 2.89 (m, 2H), 2.78 – 2.72 (m, 1H), 2.62 – 2.57 (m, 1H), 2.37 – 2.28 (m, 1H), 1.94 – 1.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 148.2, 144.9, 143.5, 130.8, 128.6, 127.4, 126.4, 122.3, 117.7, 117.4, 64.8, 64.2, 62.3, 54.8, 51.3, 43.5, 37.6, 33.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{21}H_{24}NO_3$: 338.1756. Found: 338.1753.

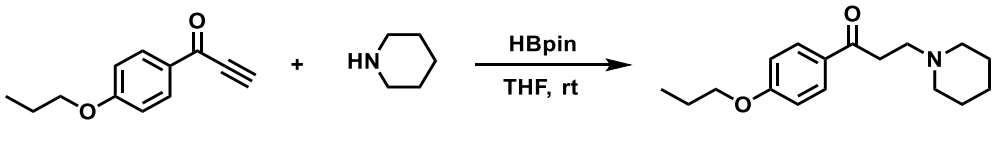
1-(4-Propoxyphenyl)prop-2-yn-1-one (1w):



1w

The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.65). The product was obtained as yellow oil in 79% yield (648.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.06 (m, 2H), 6.92 – 6.89 (m, 2H), 3.96 (t, J = 6.5 Hz, 2H), 3.40 (s, 1H), 1.80 (h, J = 7.3 Hz, 2H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 164.6, 132.3, 129.4, 114.5, 80.5, 80.3, 70.0, 22.5, 10.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{13}O_2$: 189.0916. Found: 189.0921.

3-(Piperidin-1-yl)-1-(4-propoxyphenyl)propan-1-one (Propipocaine, 3wh):

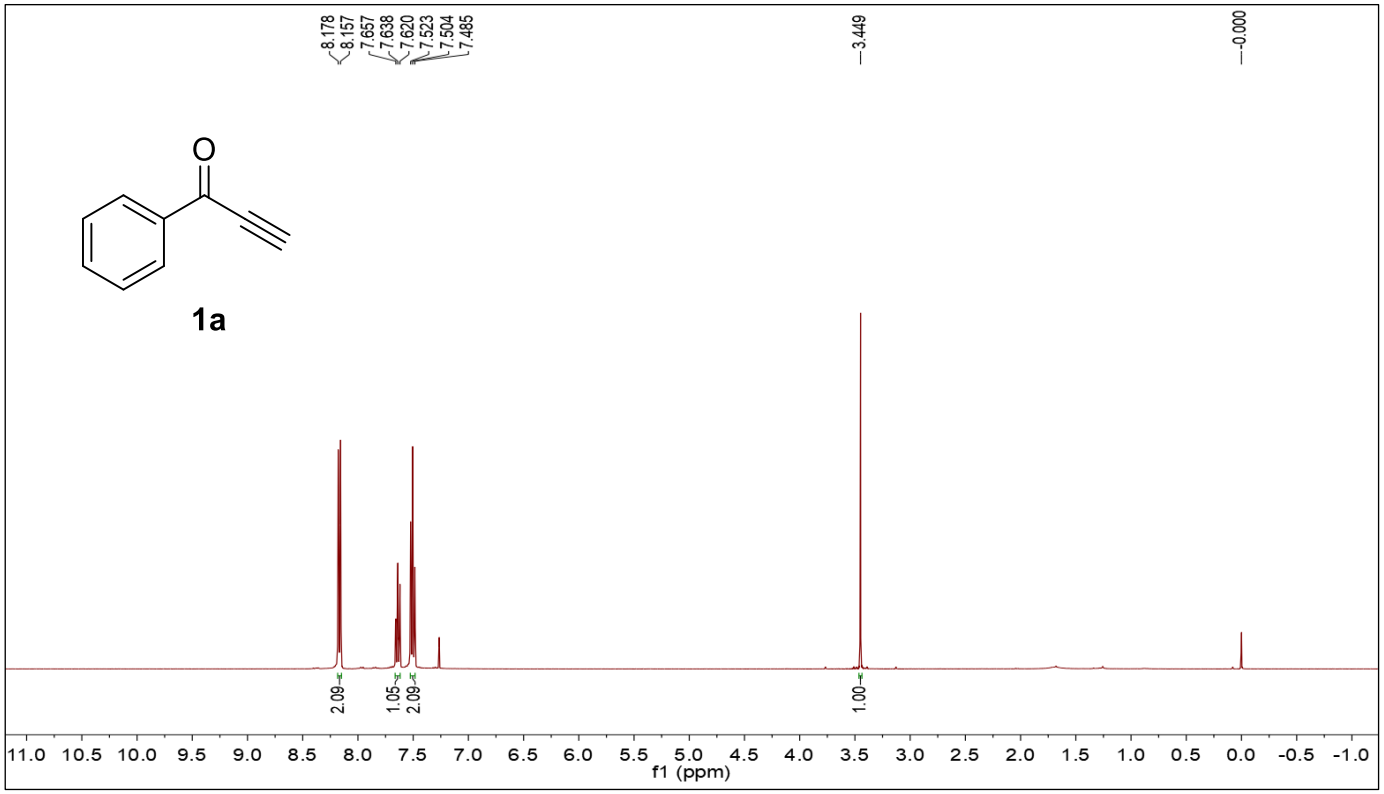


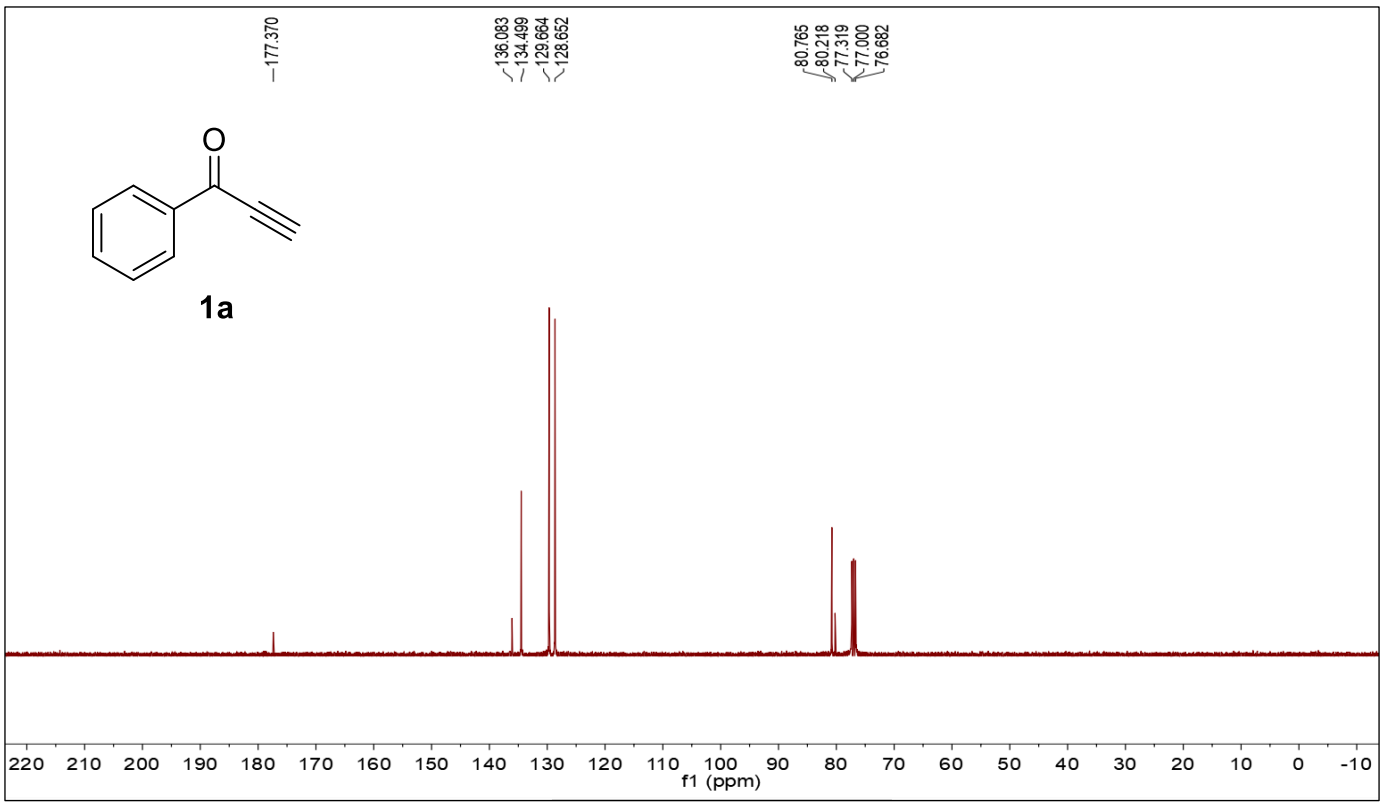
1w 2h 3wh

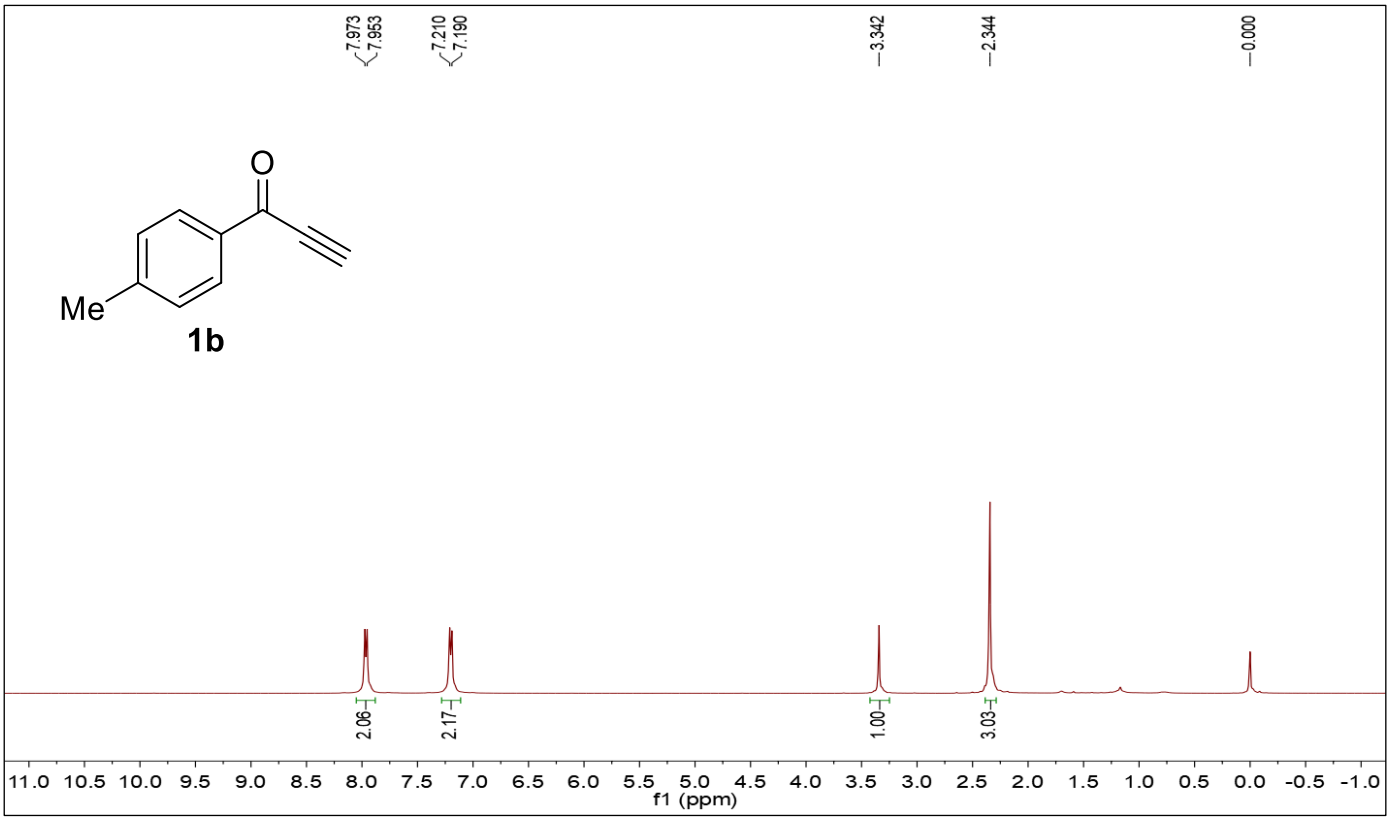
A tube was charged with **1w** (56.5 mg, 0.3 mmol, 1.0 equiv.), **2h** (38.4 mg, 0.45 mmol,

1.5 equiv.), HBpin (0.75 mmol, 96.0 mg, 2.5 equiv.) in THF (2.0 mL). And the reaction mixture was stirred until the **1v** was consumed completely. After completion of the reaction (monitored by TLC, MeOH/DCM = 1/9, R_f = 0.25), the reaction mixture was concentrated under reduced pressure and purified by column chromatography (dichloromethane: methanol = 9: 1). The product **3wh** was obtained as yellow oil in 84% yield (0.30 mmol scale, 70.0 mg) and 81% yield (1.5 mmol scale, 334.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 2H), 6.87 – 6.84 (m, 2H), 3.91 (t, J = 6.6 Hz, 2H), 3.11 – 3.07 (m, 2H), 2.75 – 2.71 (m, 2H), 2.40 (s, 4H), 1.76 (h, J = 7.4 Hz, 2H), 1.54 (p, J = 5.6 Hz, 4H), 1.41 – 1.38 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 163.2, 130.4, 129.9, 114.2, 69.8, 54.7, 54.2, 36.0, 26.0, 24.4, 22.5, 10.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{26}NO_2$: 276.1964. Found: 276.1967.

^{1}H and ^{13}C NMR spectra of ynones



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7.210
7.190
3.342
2.344
0.000
O
Me
1b
2.06
2.17
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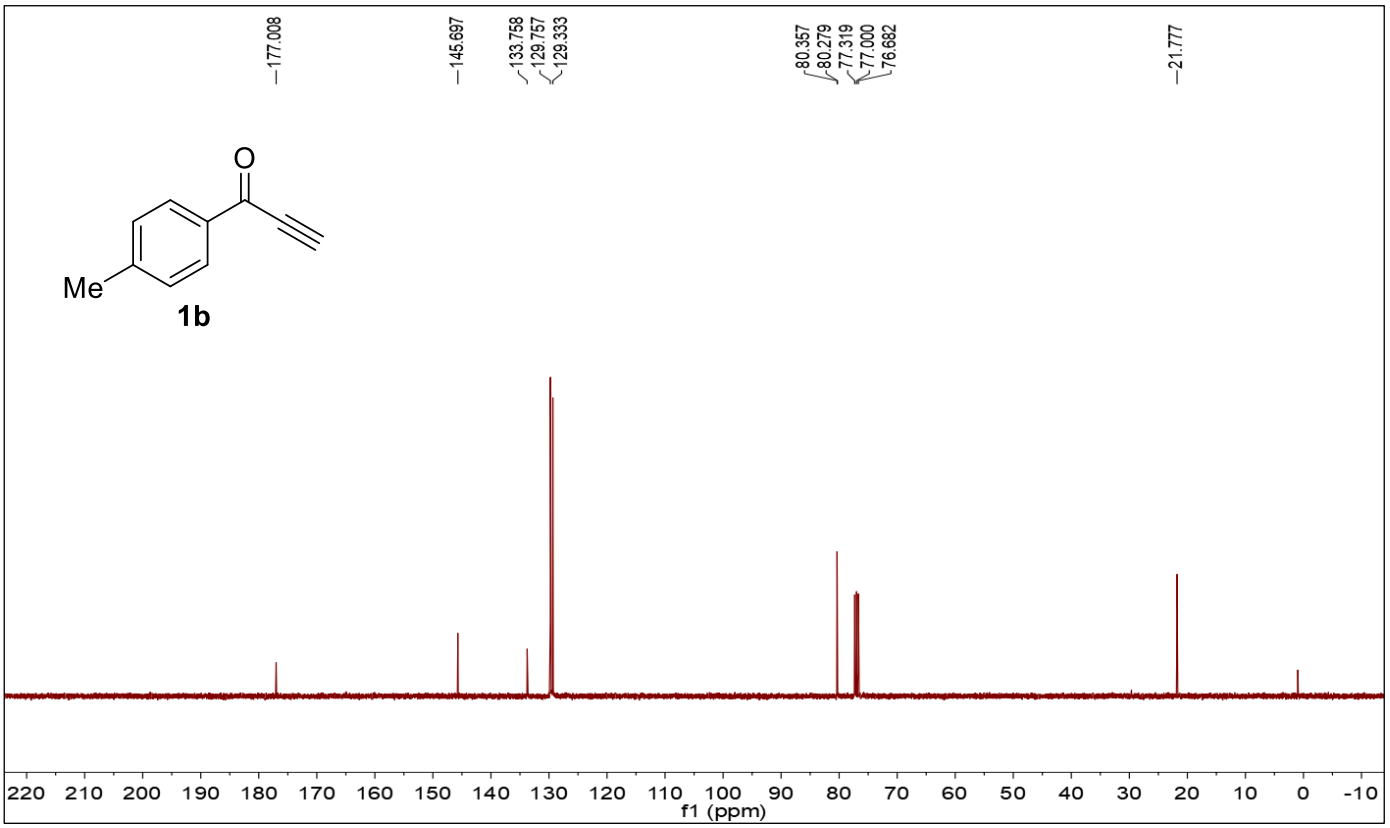
3.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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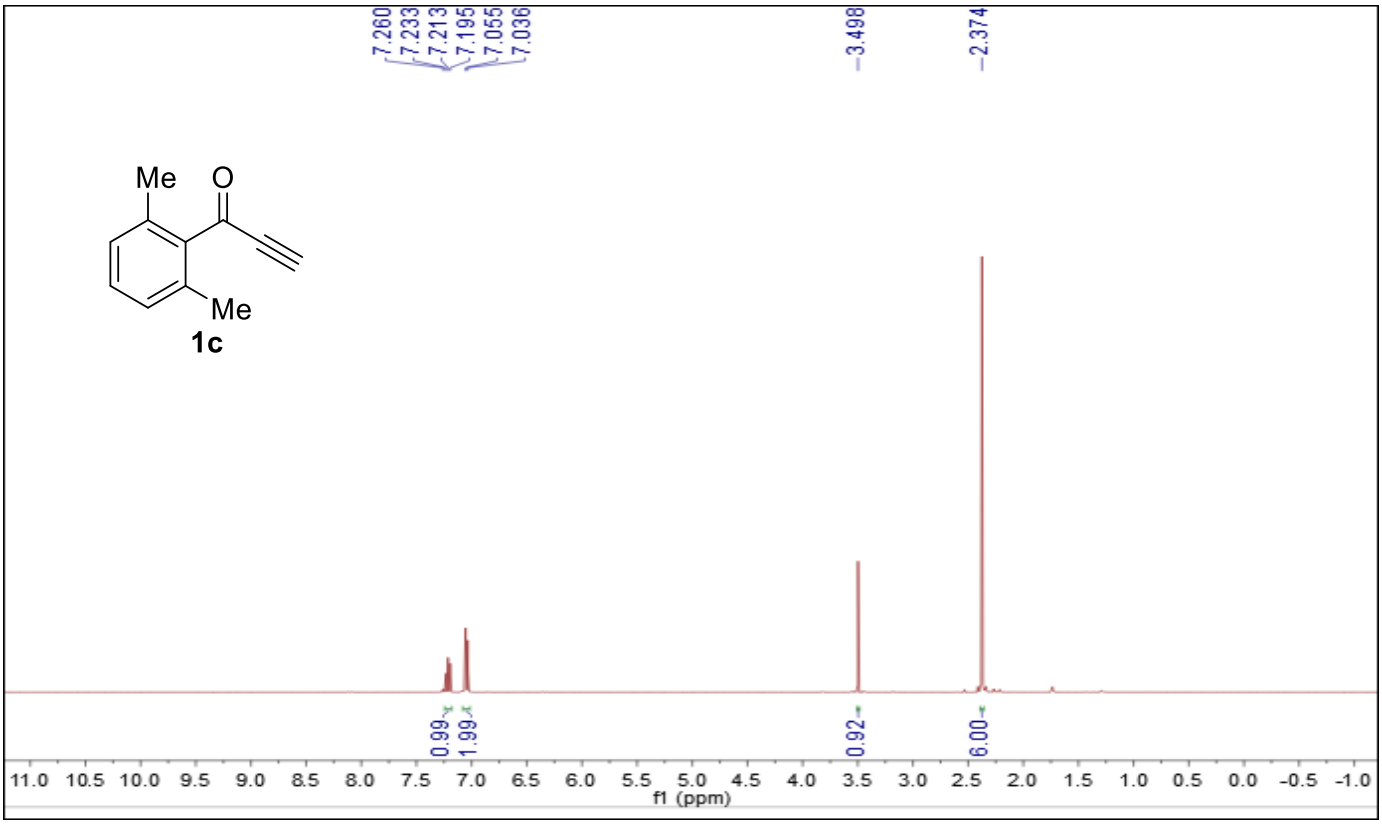
77.000
76.682
21.777
O
Me
1b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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1.99
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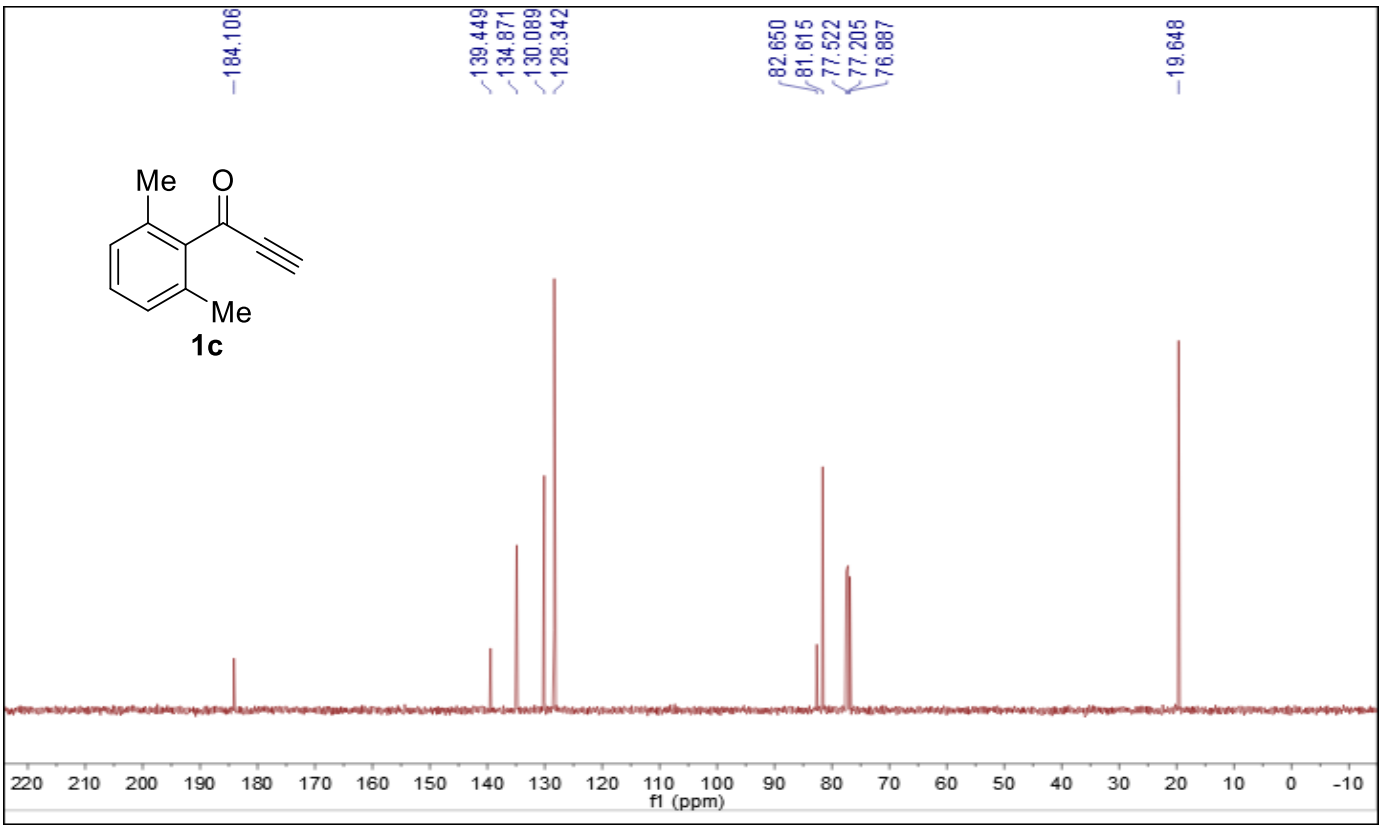
6.00
f1 (ppm)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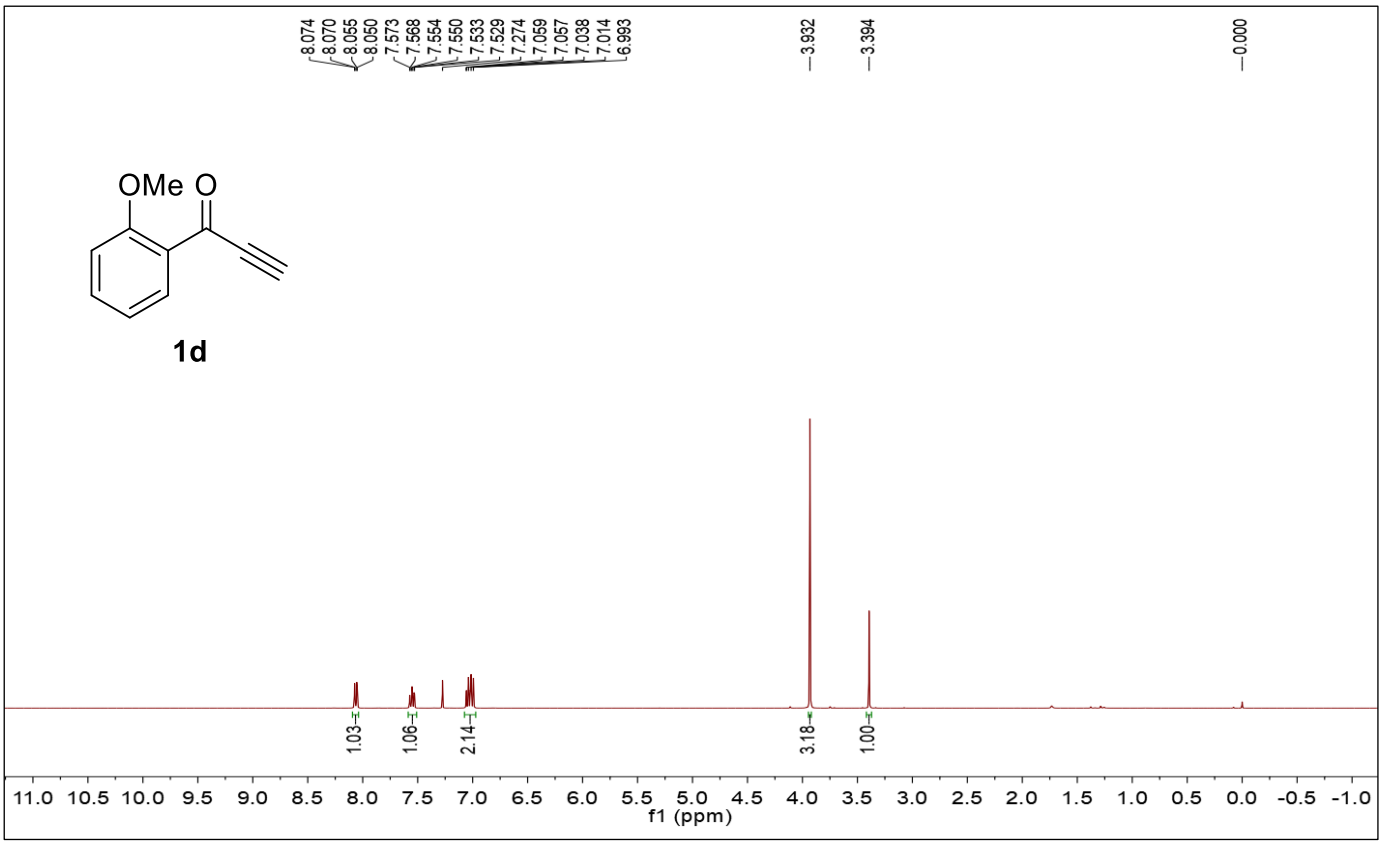
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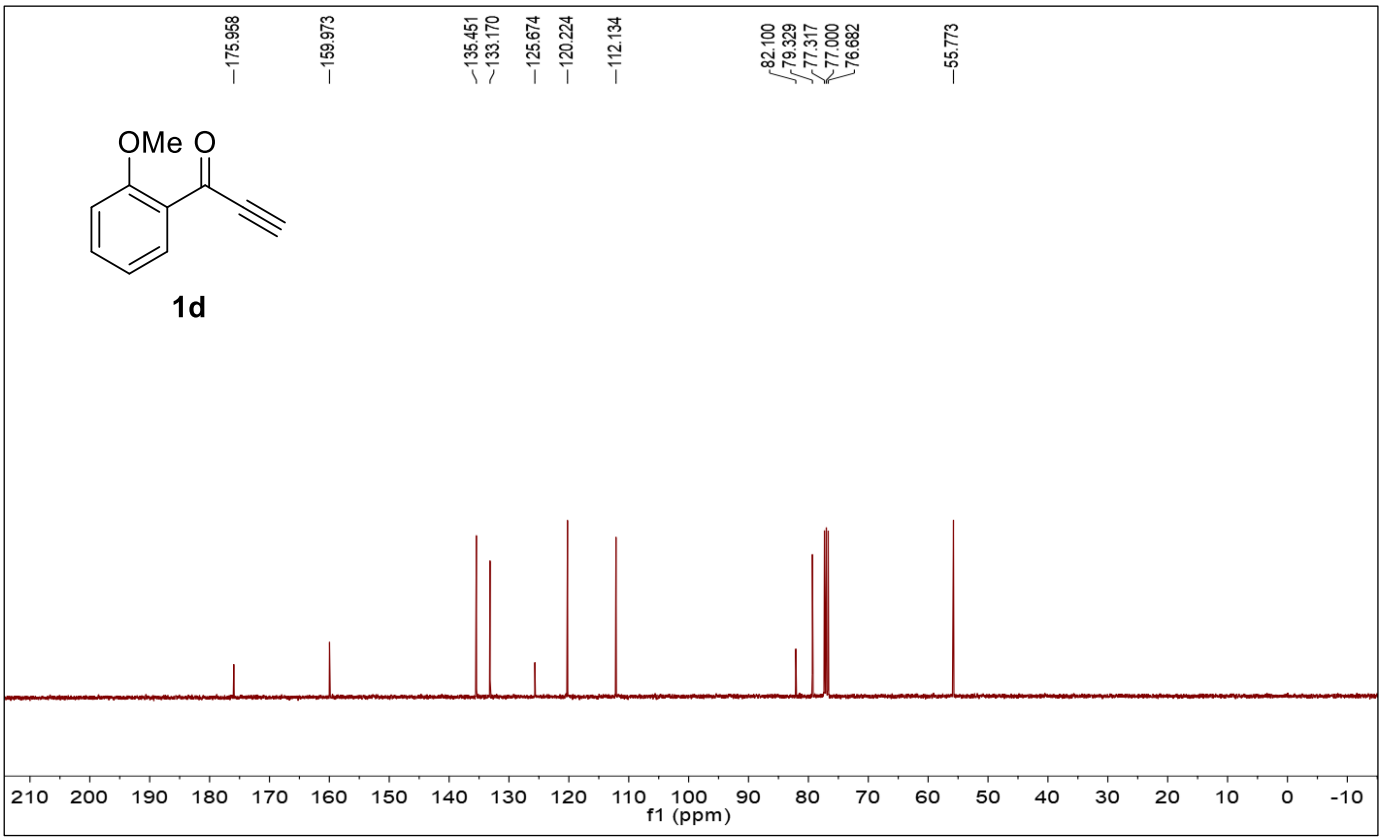
7.038
7.014
6.993
3.932
3.394
0.000
OMe O
1d
1.03
1.06
2.14
3.18
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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1d
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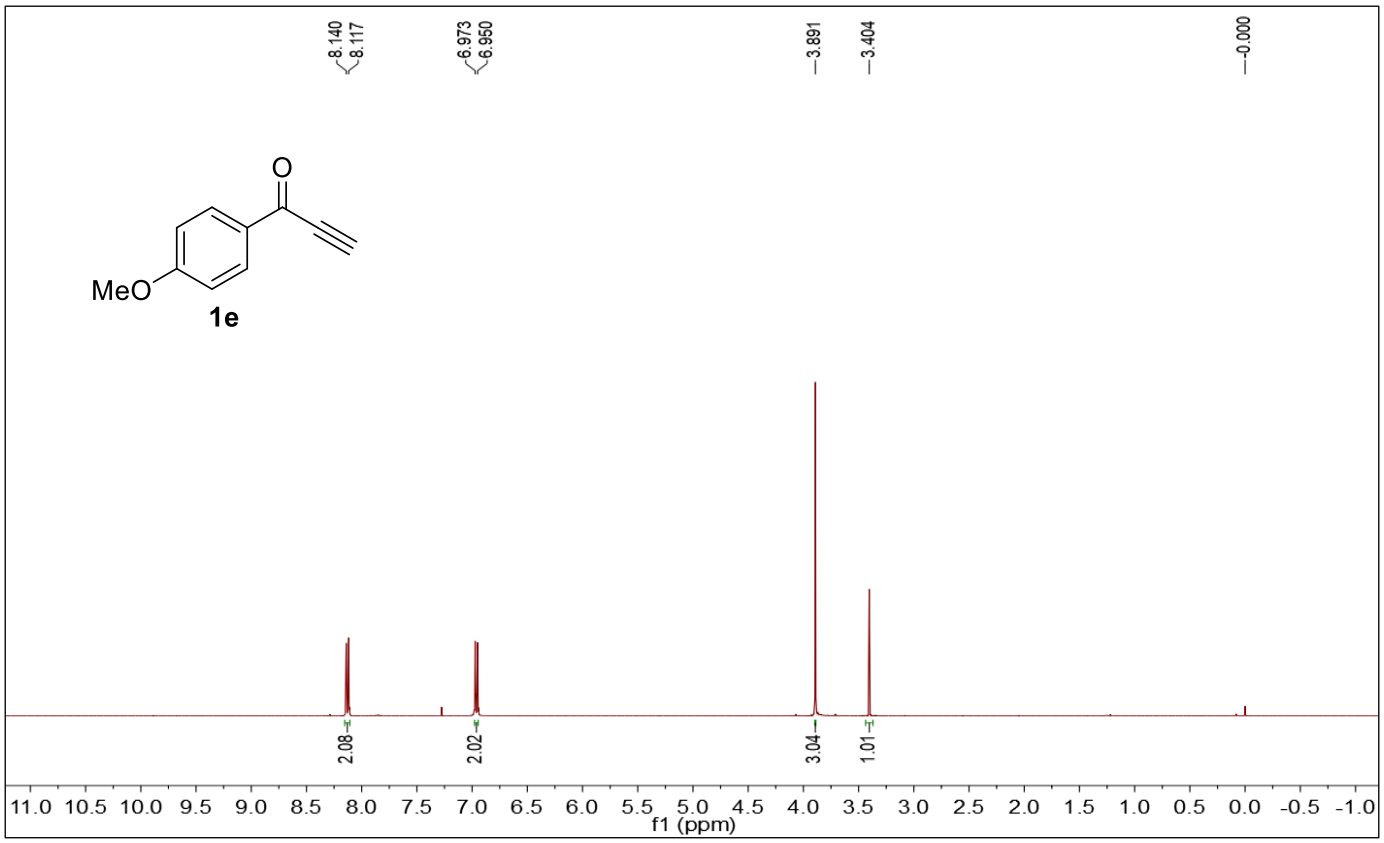
f1 (ppm)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2.08
2.02
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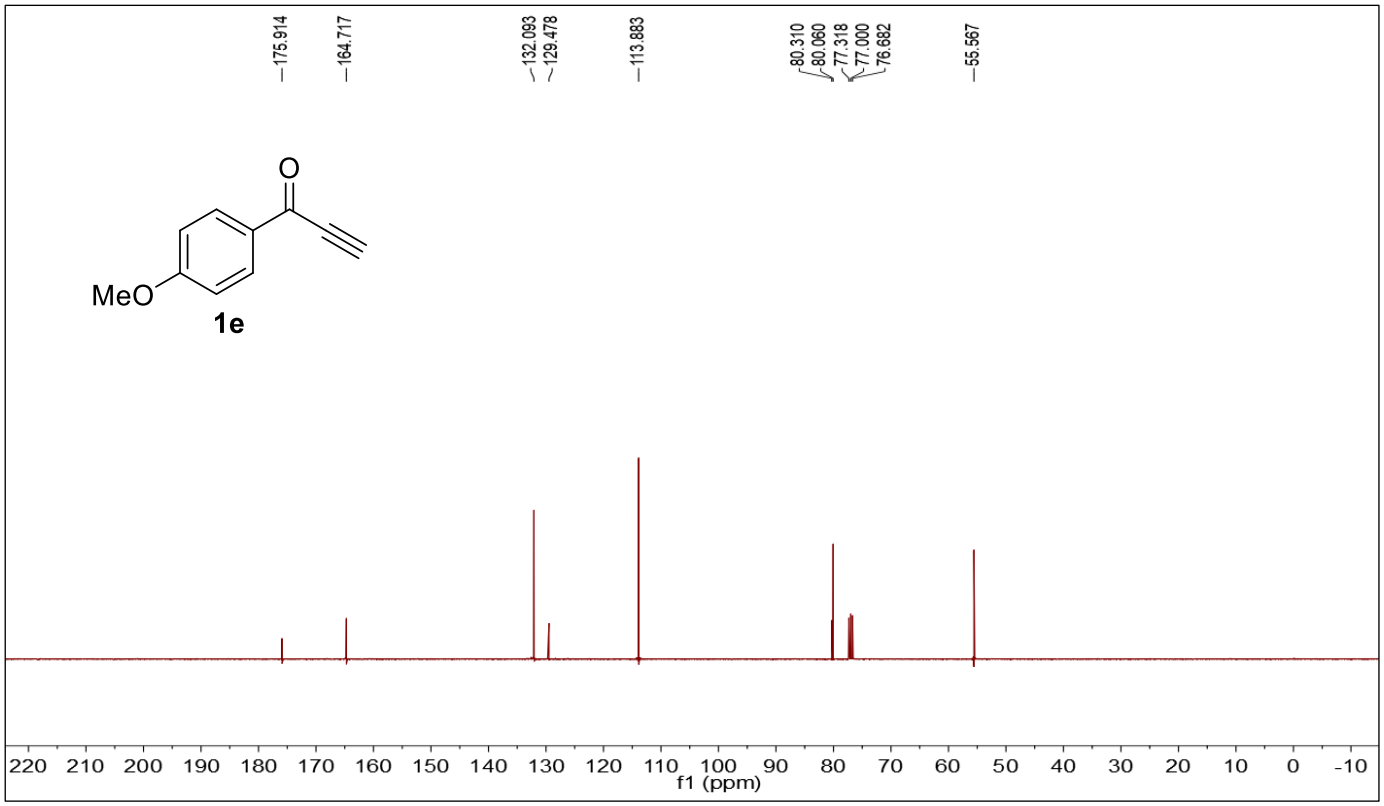
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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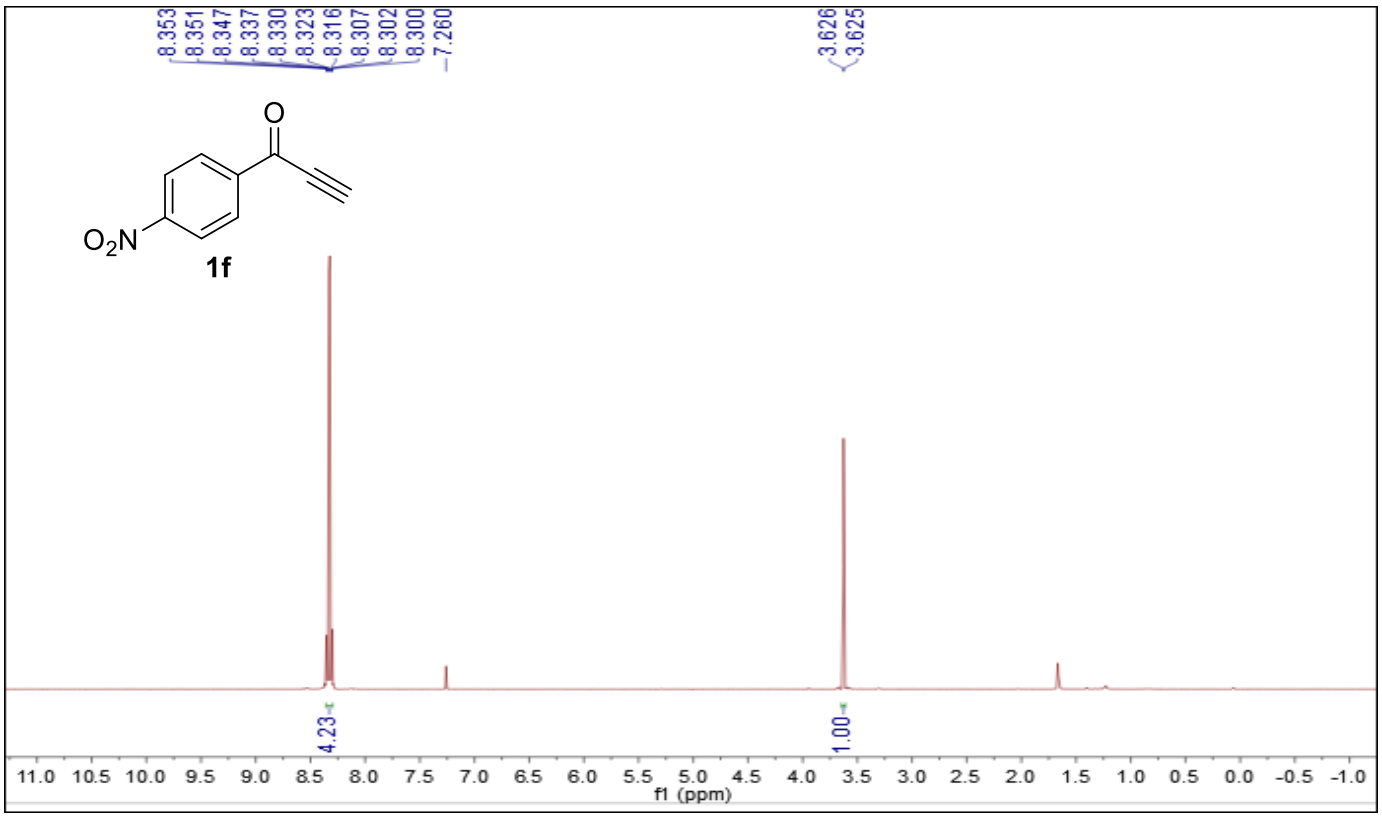
f1 (ppm)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8.323
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8.307
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8.300
7.260
3.626
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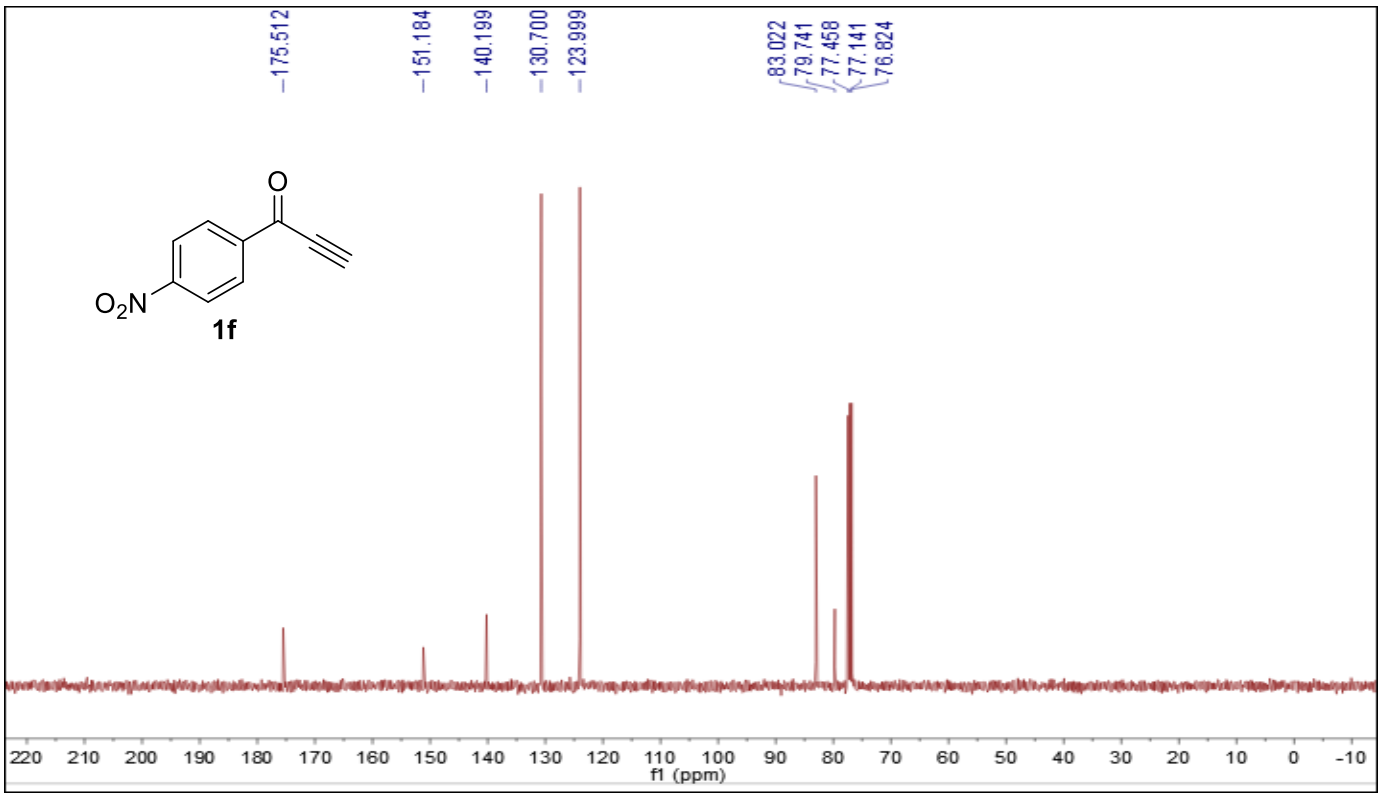
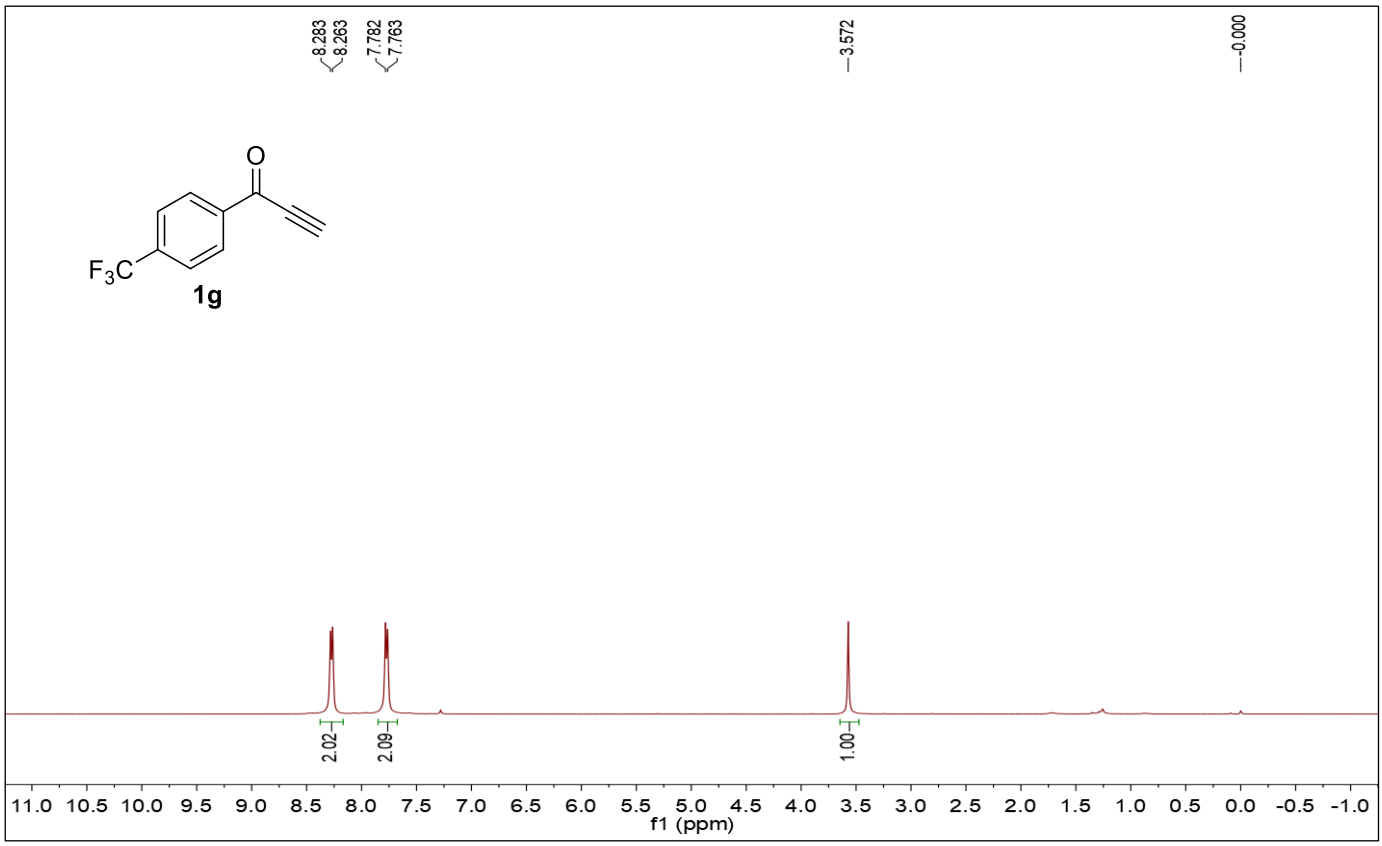
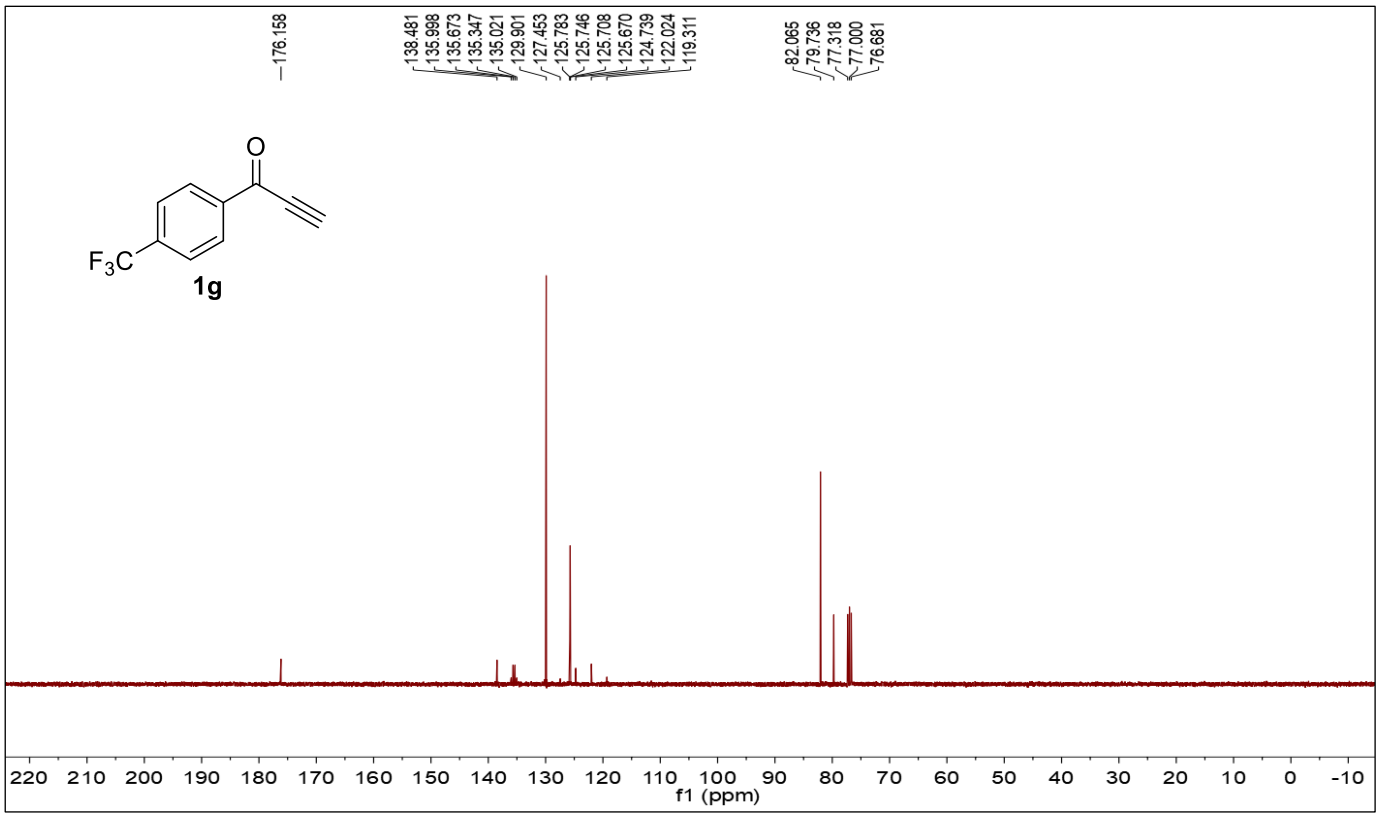
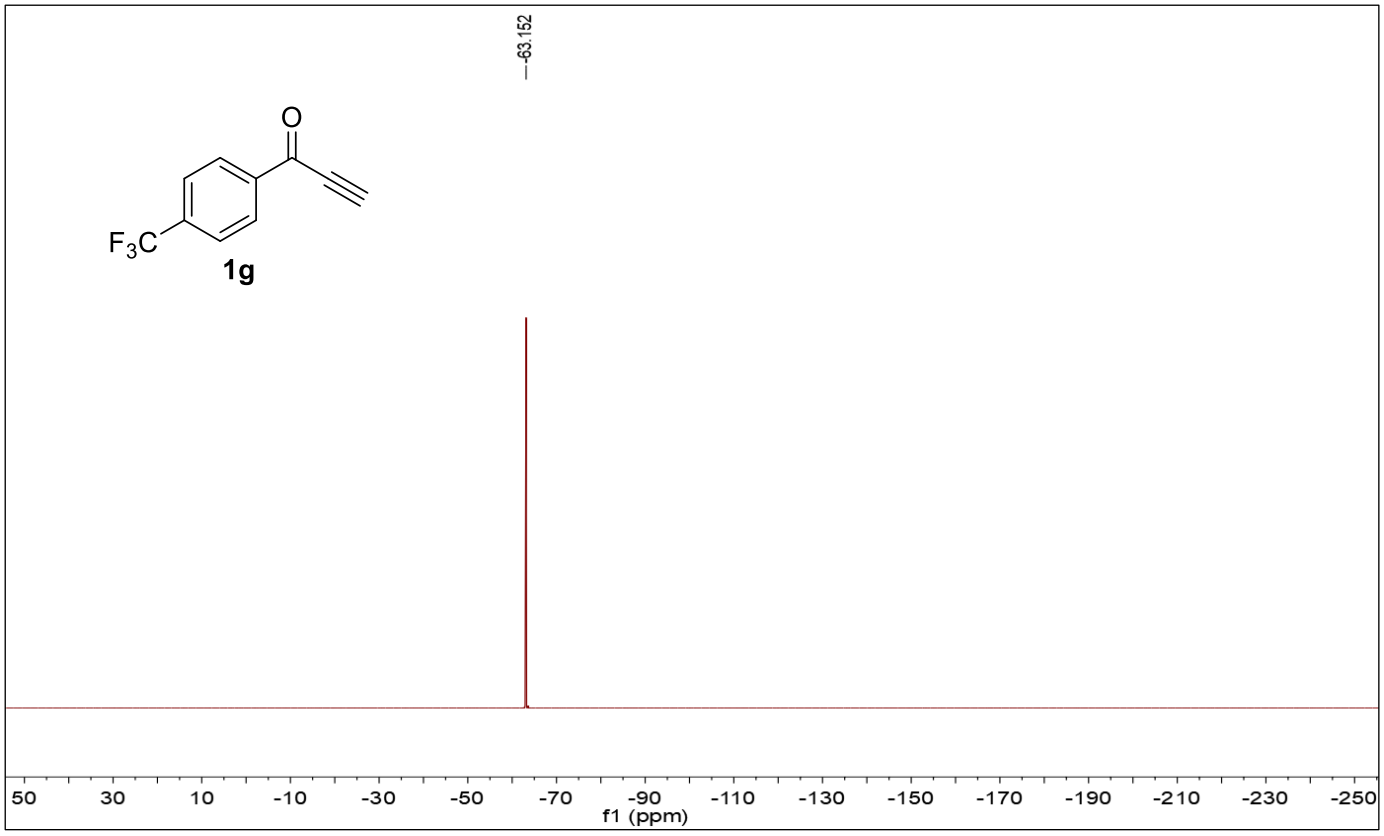
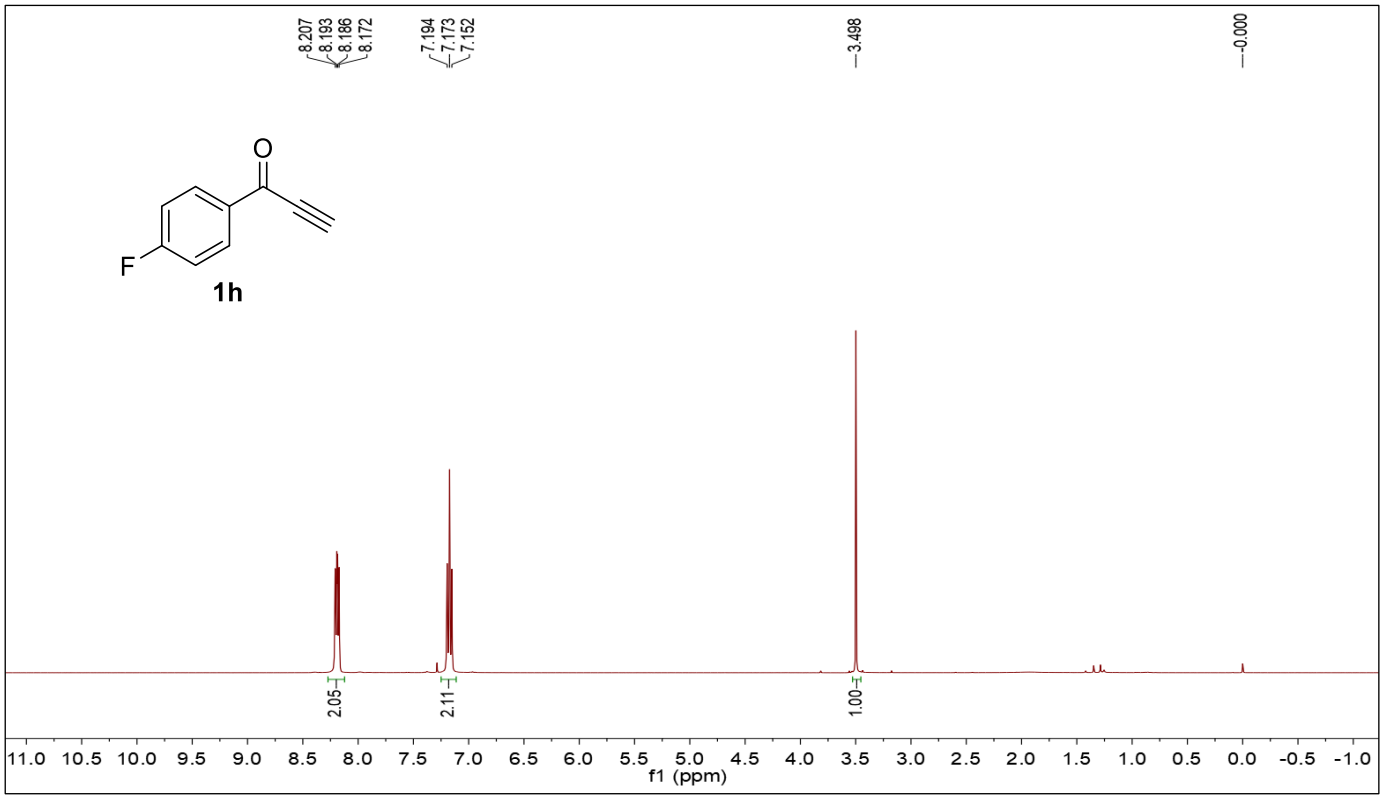
O
O2N
1f
4.23
1.00
f1 (ppm)

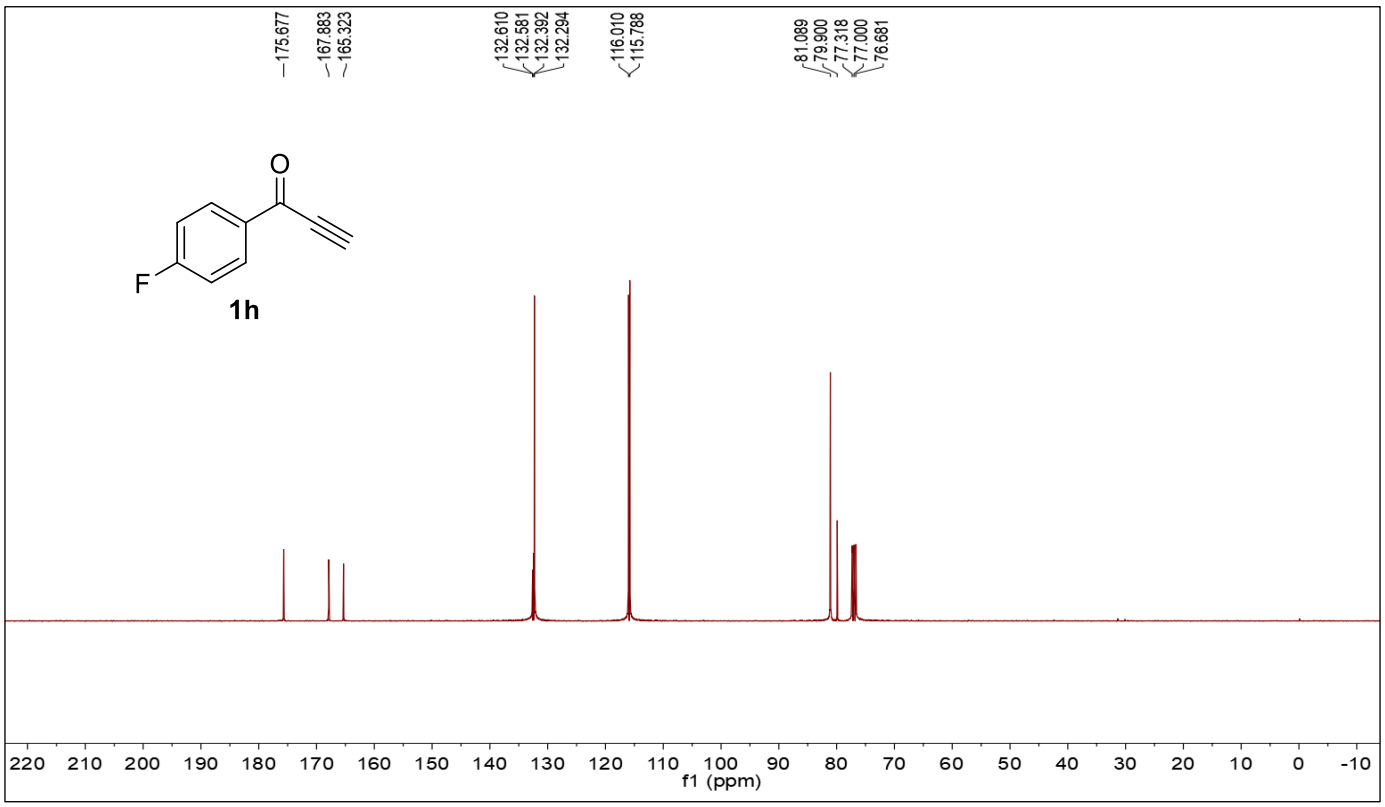

175.512
151.184
140.199
130.700
123.999
83.022
79.741
77.458
77.141
76.824
O
O2N
1f
f1 (ppm)

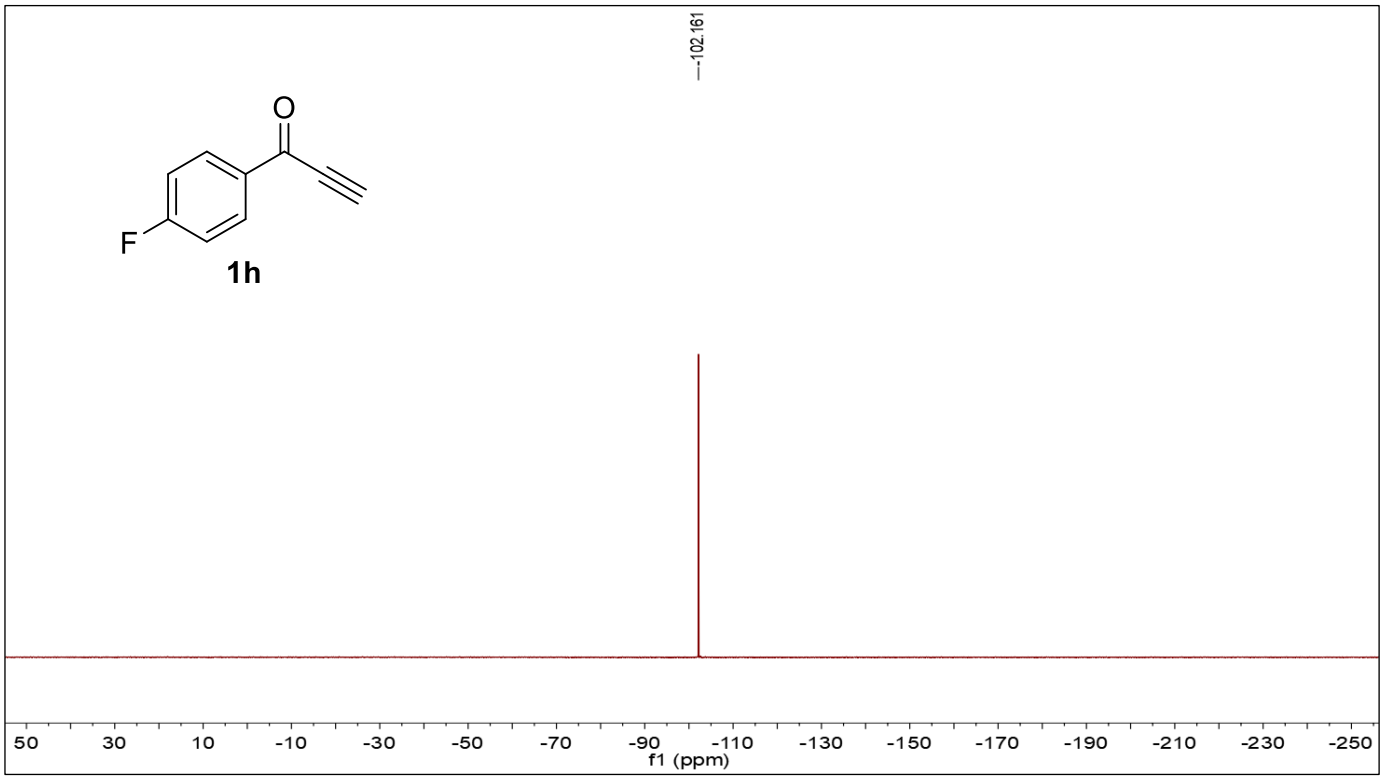

8.283
8.263
7.782
7.763
3.572
0.000
O
F3C
1g
2.02
2.09
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

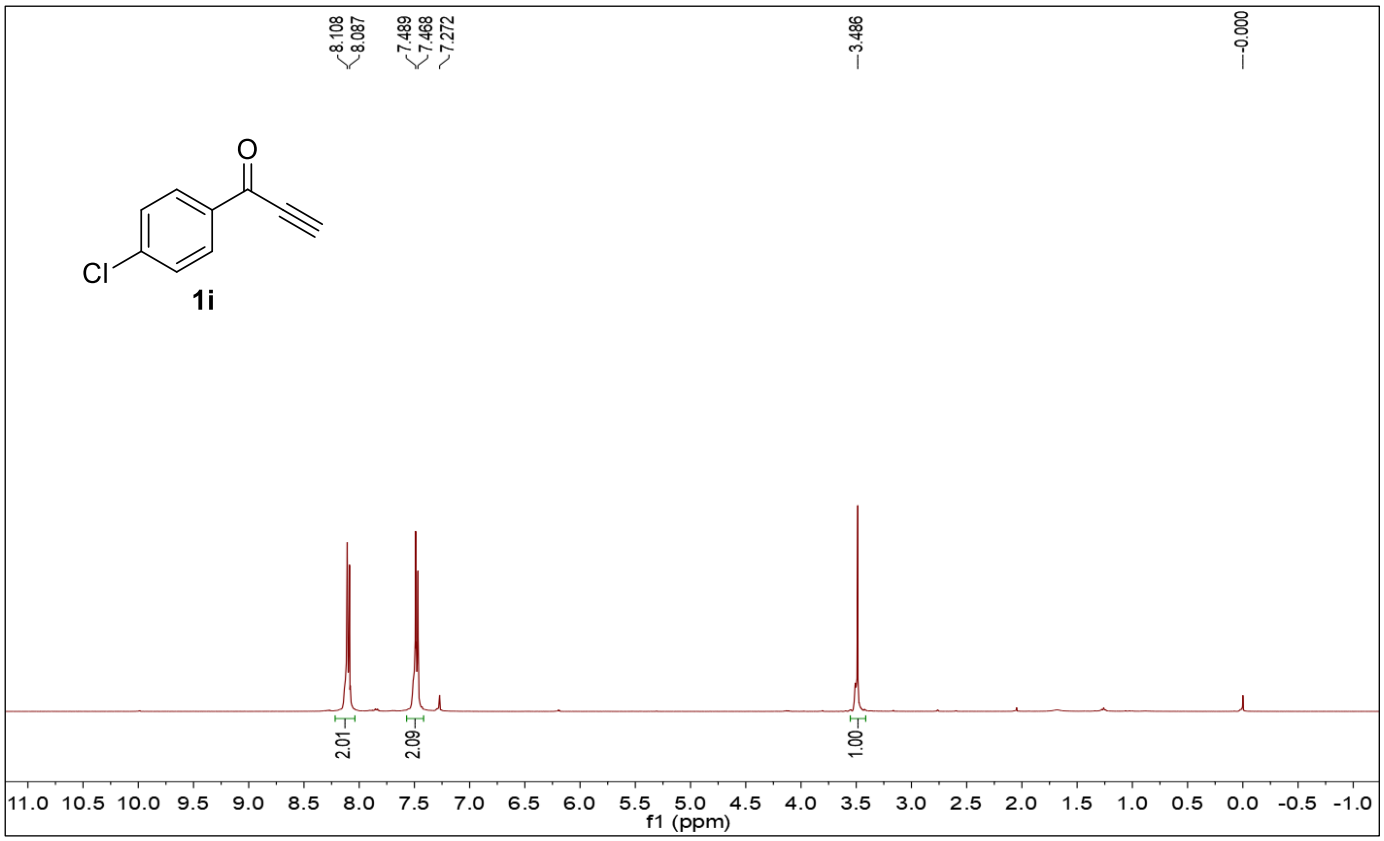

176.158
138.481
135.998
135.673
135.347
135.021
129.901
127.453
125.783
125.746
125.708
125.670
124.739
122.024
119.311
82.065
79.736
77.318
77.000
76.681
O
F3C
1g
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

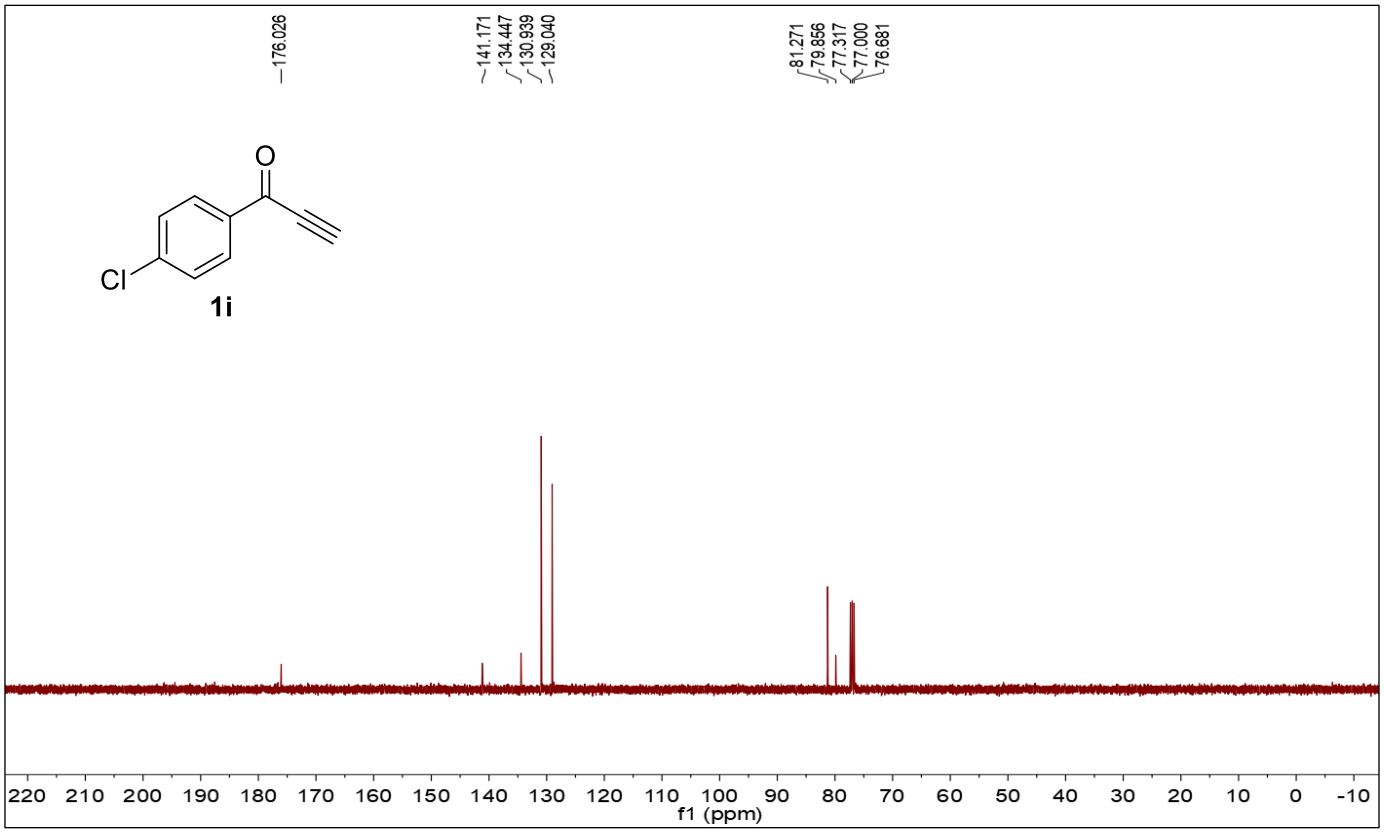

-63.152
O
F3C
1g
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
f1 (ppm)

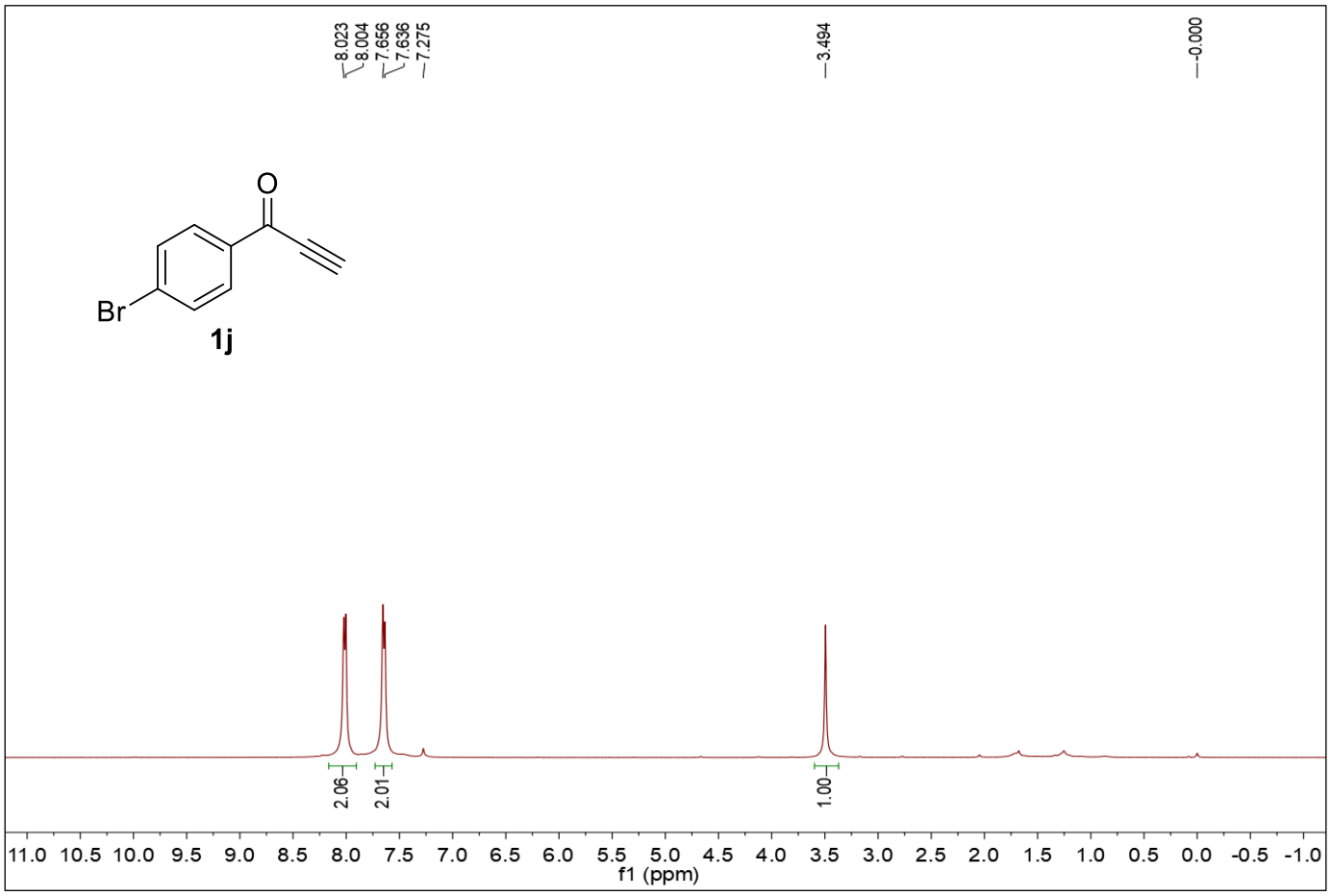

8.207
8.193
8.186
8.172
7.194
7.173
7.152
3.498
0.000
O
F
1h
2.05
2.11
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

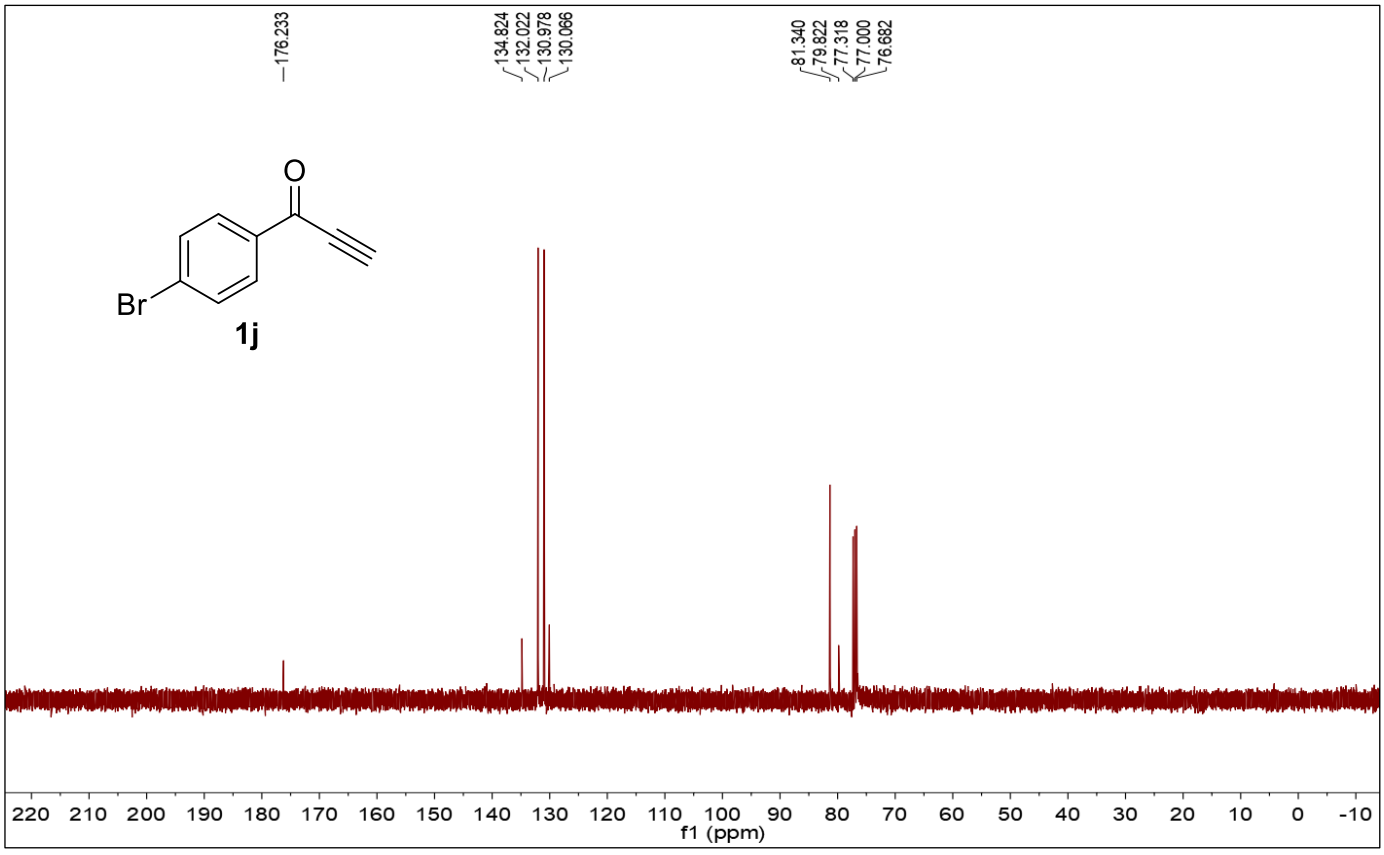

175.677
167.883
165.323
132.610
132.581
132.392
132.294
116.010
115.788
81.089
79.900
77.318
77.000
76.681
O
F
1h
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

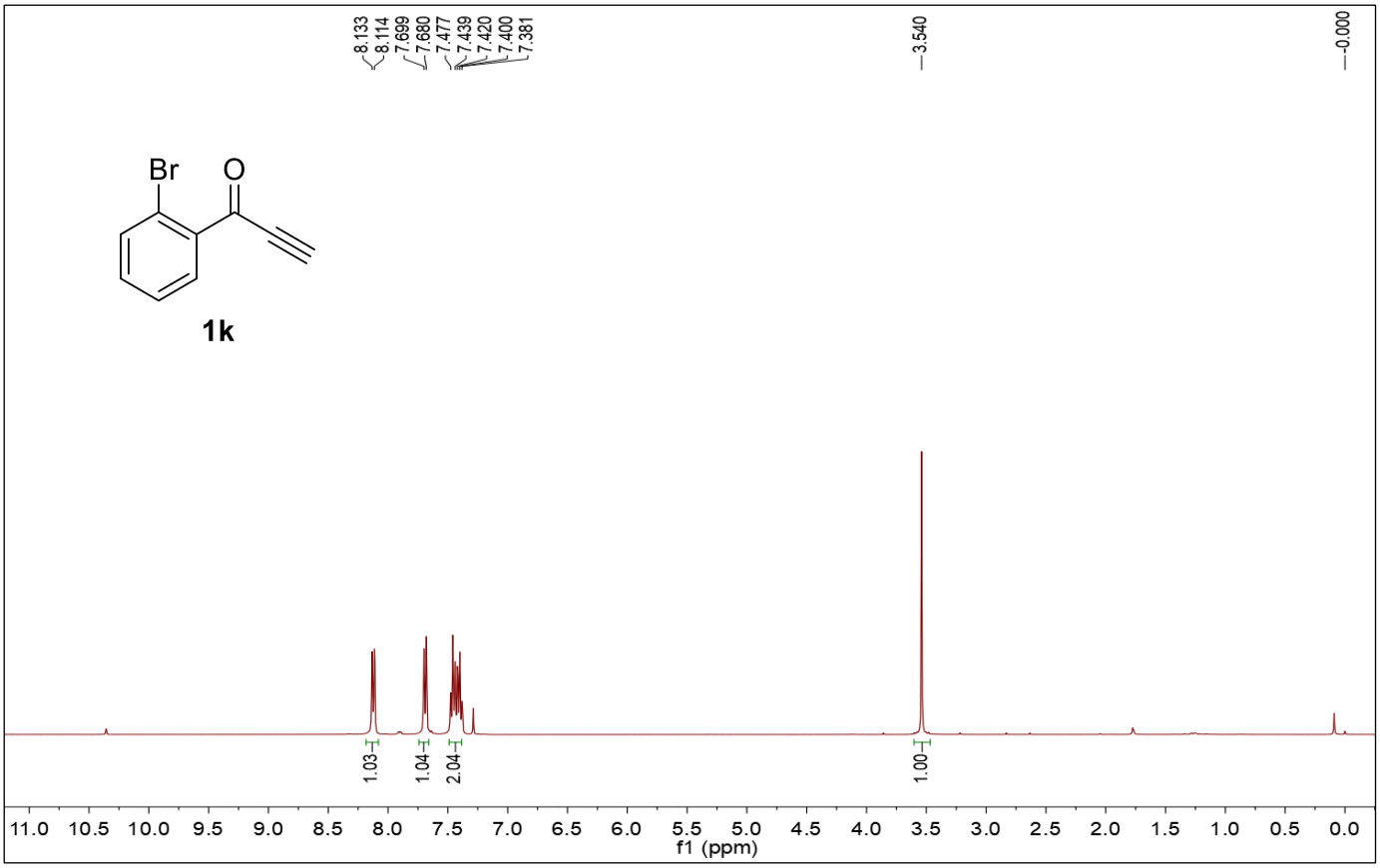

-102.161
O
F
1h
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
f1 (ppm)

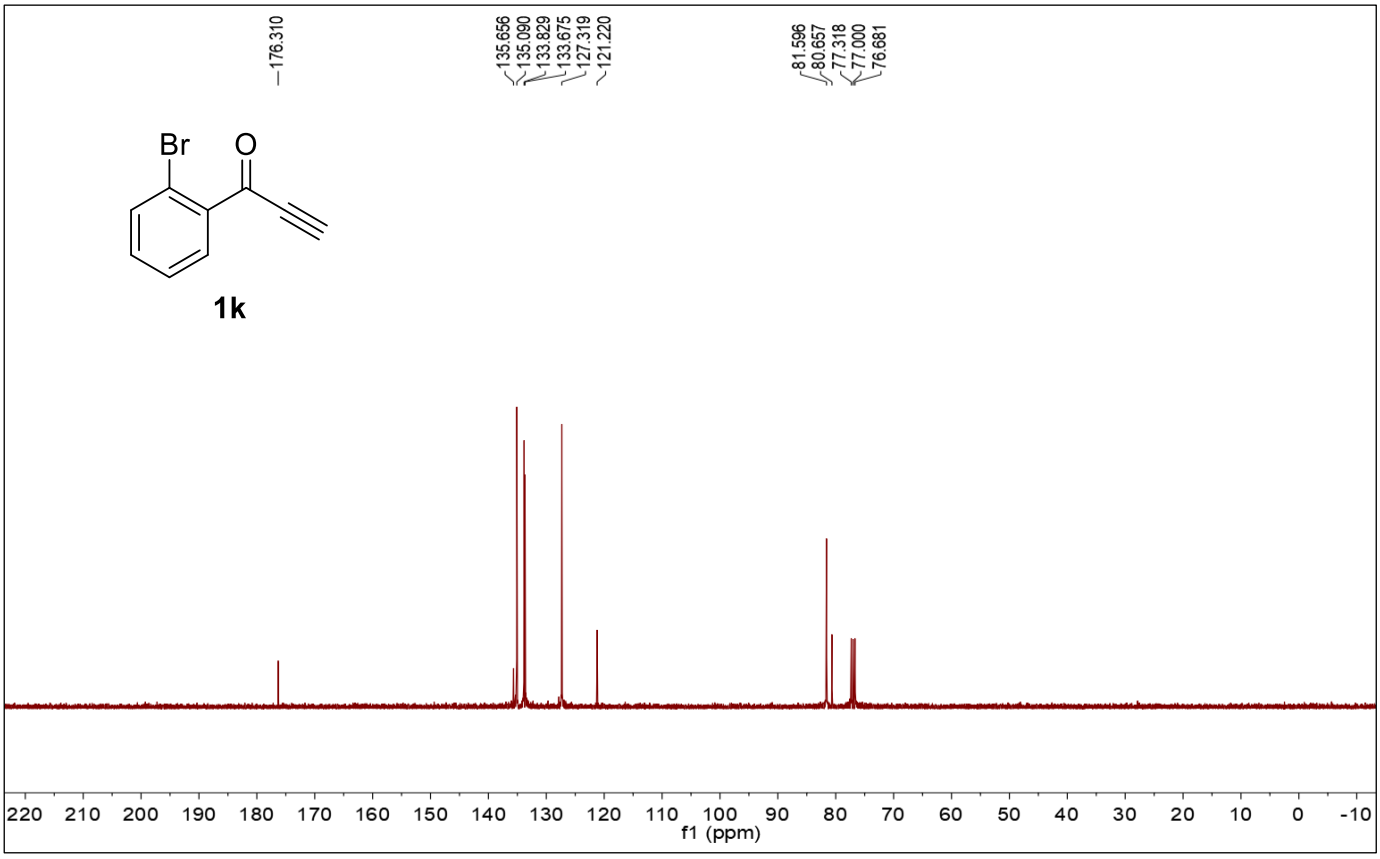

8.108
8.087
7.489
7.468
7.272
3.486
0.000
O
Cl
1i
2.01
2.09
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

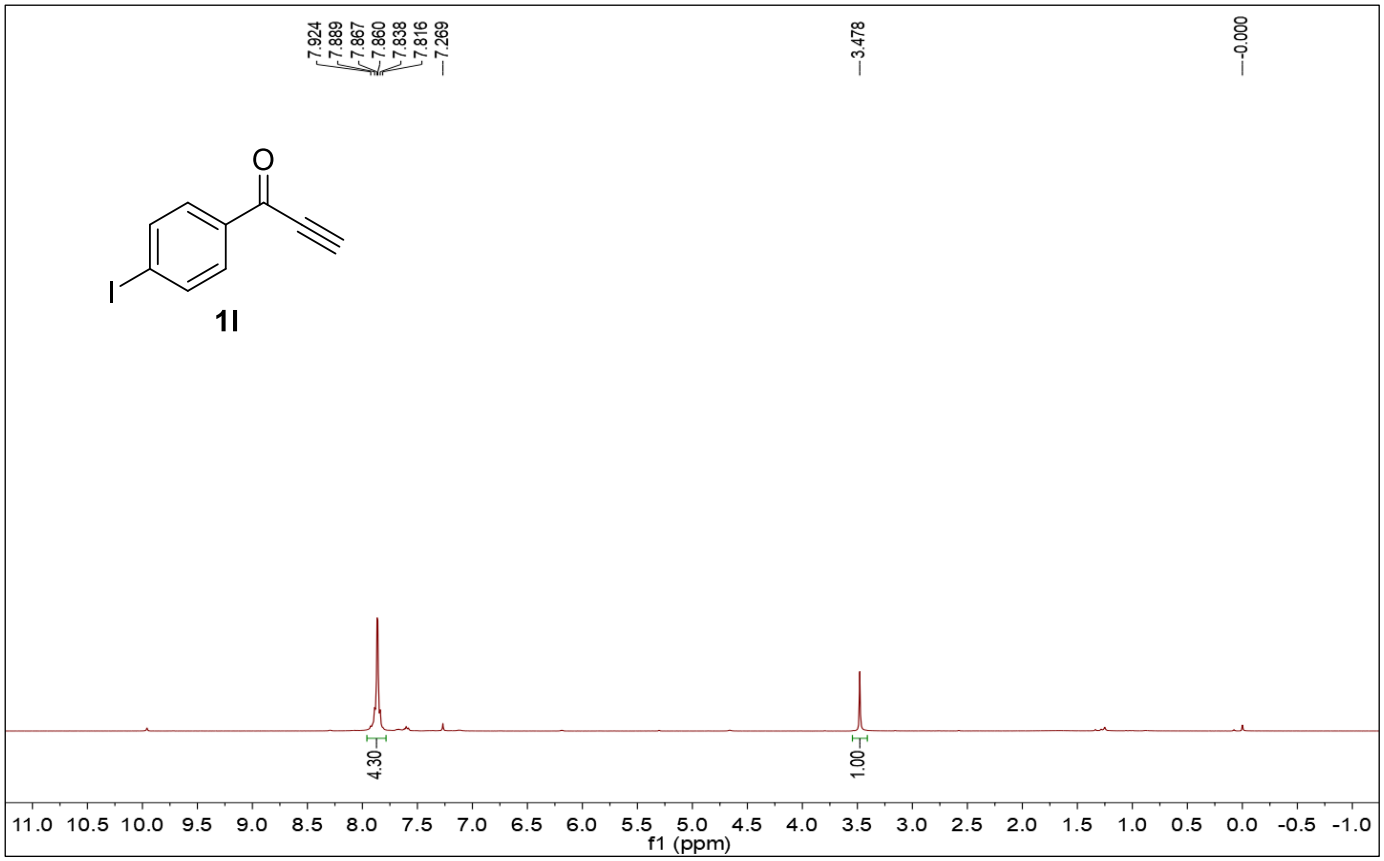

176.026
141.171
134.447
130.939
129.040
81.271
79.856
77.317
77.000
76.681
O
Cl
1i
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

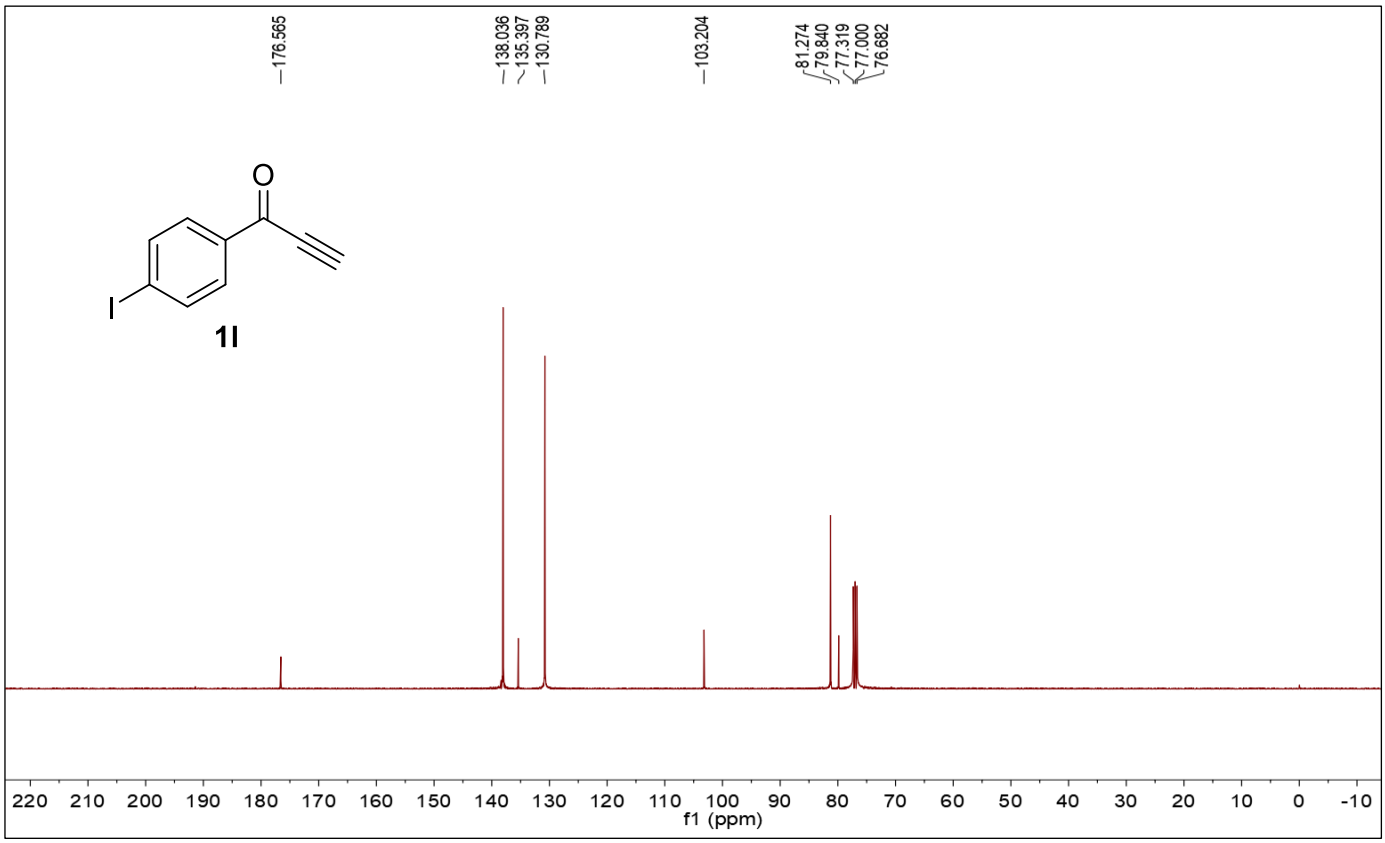

8.023
8.004
7.656
7.636
7.275
3.494
0.000
O
Br
1j
2.06
2.01
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

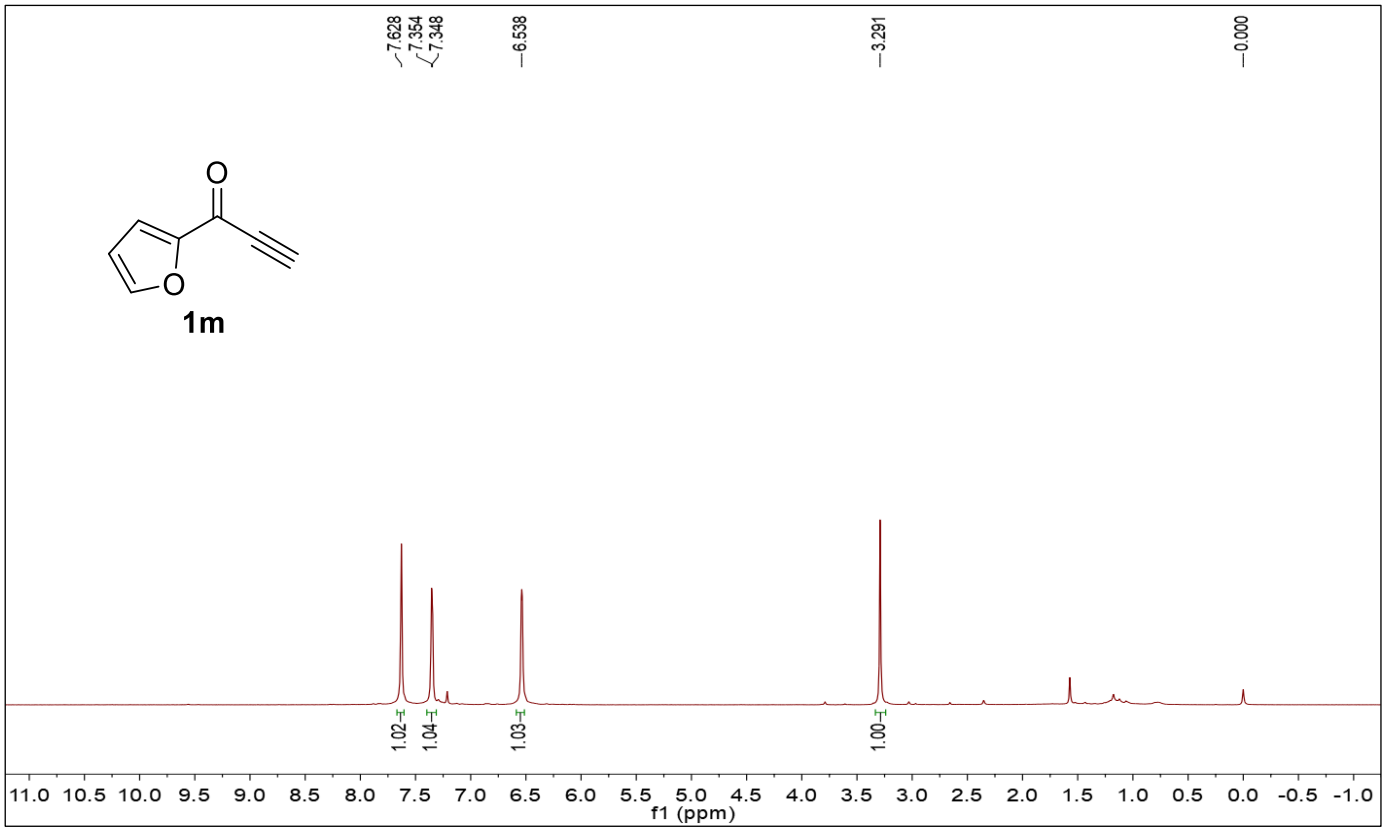

176.233
134.824
132.022
130.978
130.066
81.340
79.822
77.318
77.000
76.682
O
Br
1j
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

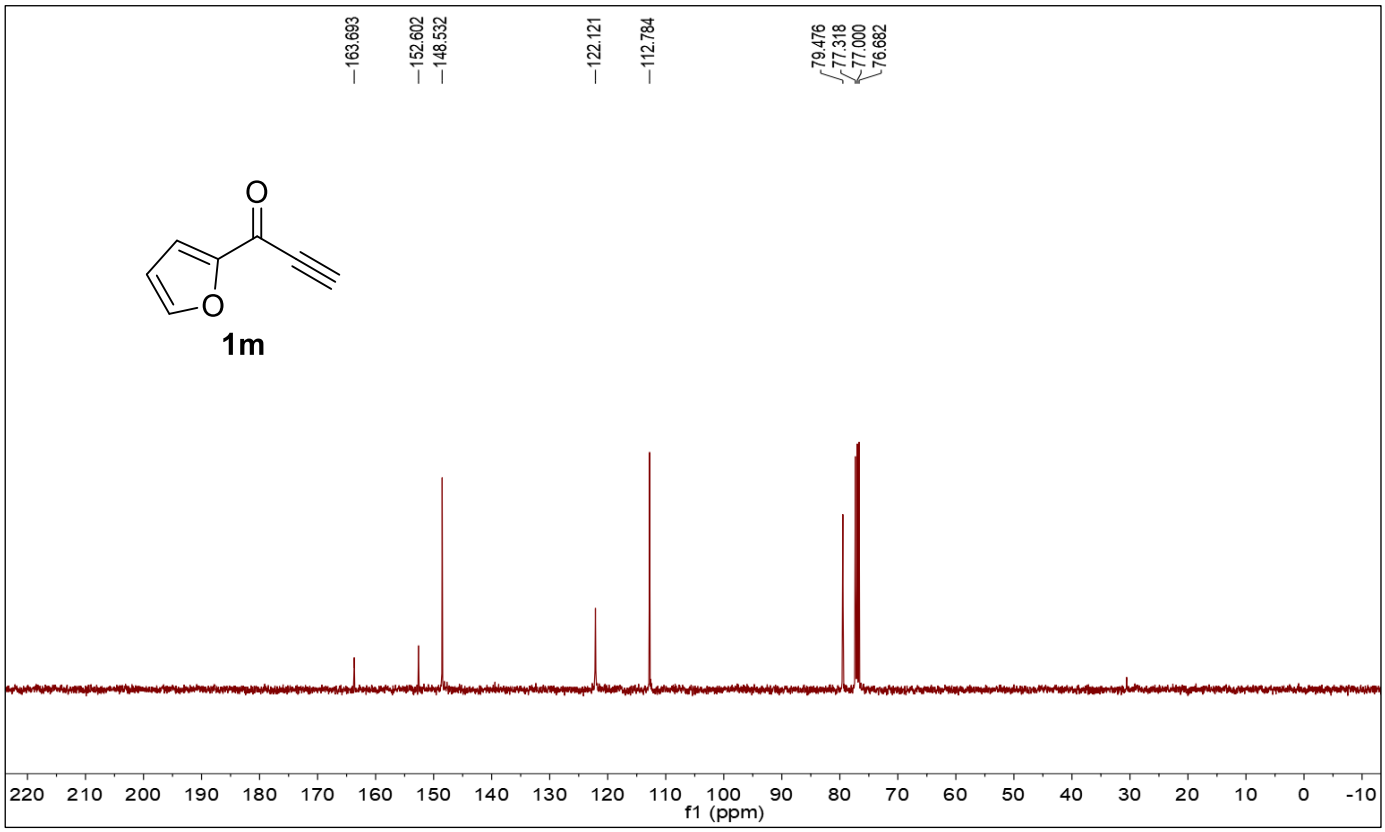

8.133
8.114
7.699
7.680
7.477
7.439
7.420
7.400
7.381
3.540
0.000
Br
O
1k
1.03
1.04
2.04
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

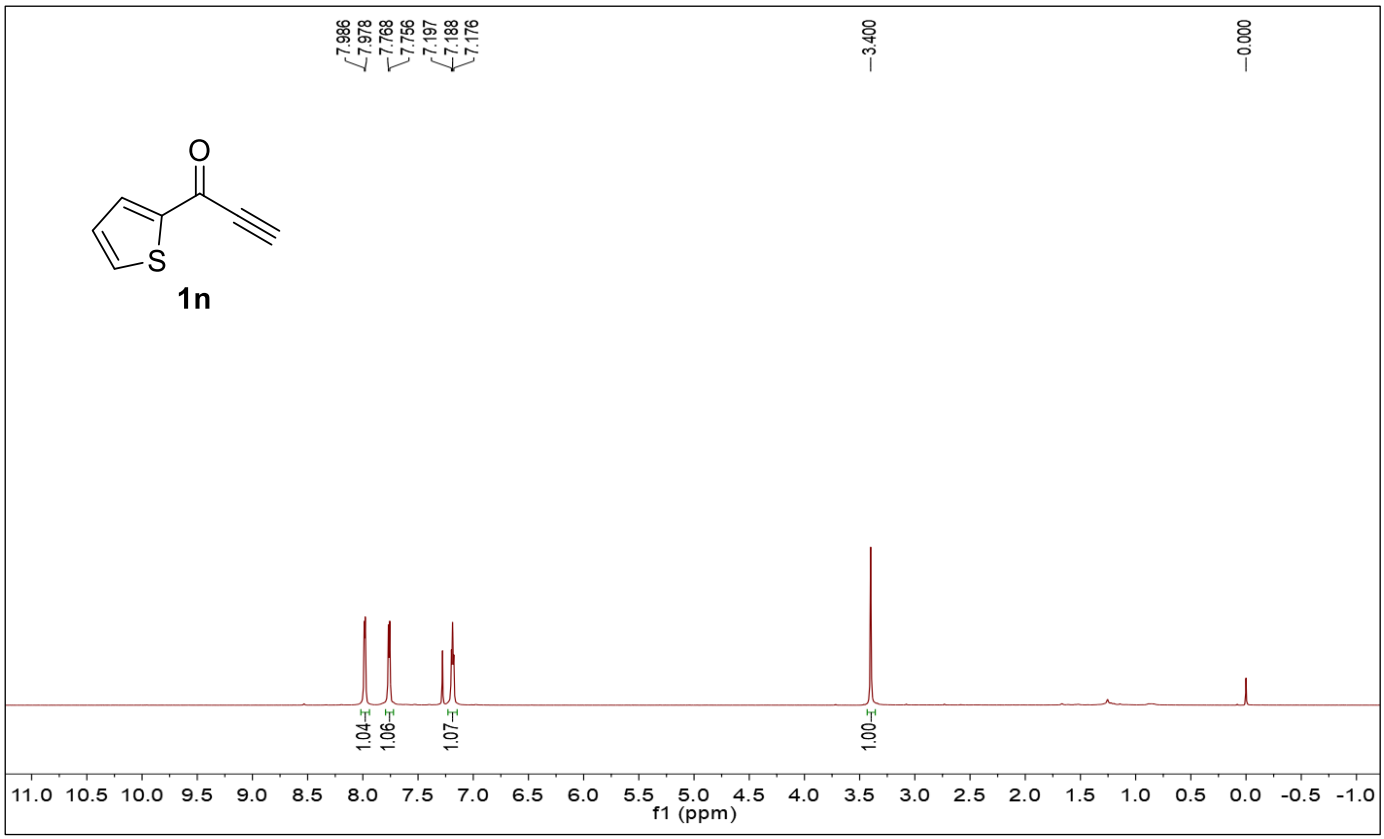

176.310
135.656
135.090
133.829
133.675
127.319
121.220
81.596
80.657
77.318
77.000
76.681
Br
O
1k
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

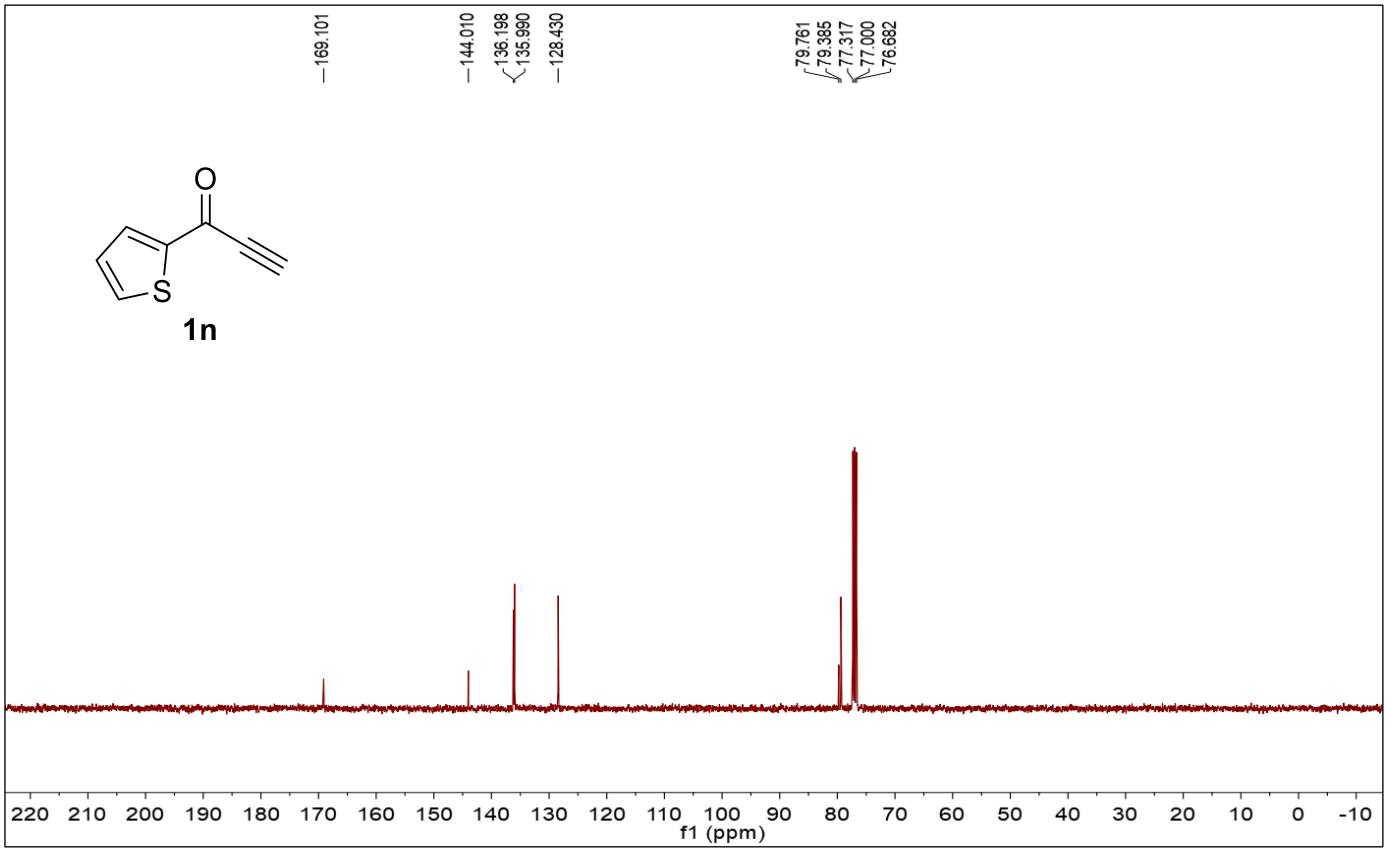

7.924
7.889
7.867
7.860
7.838
7.816
7.269
3.478
0.000
O
I
1l
4.30
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

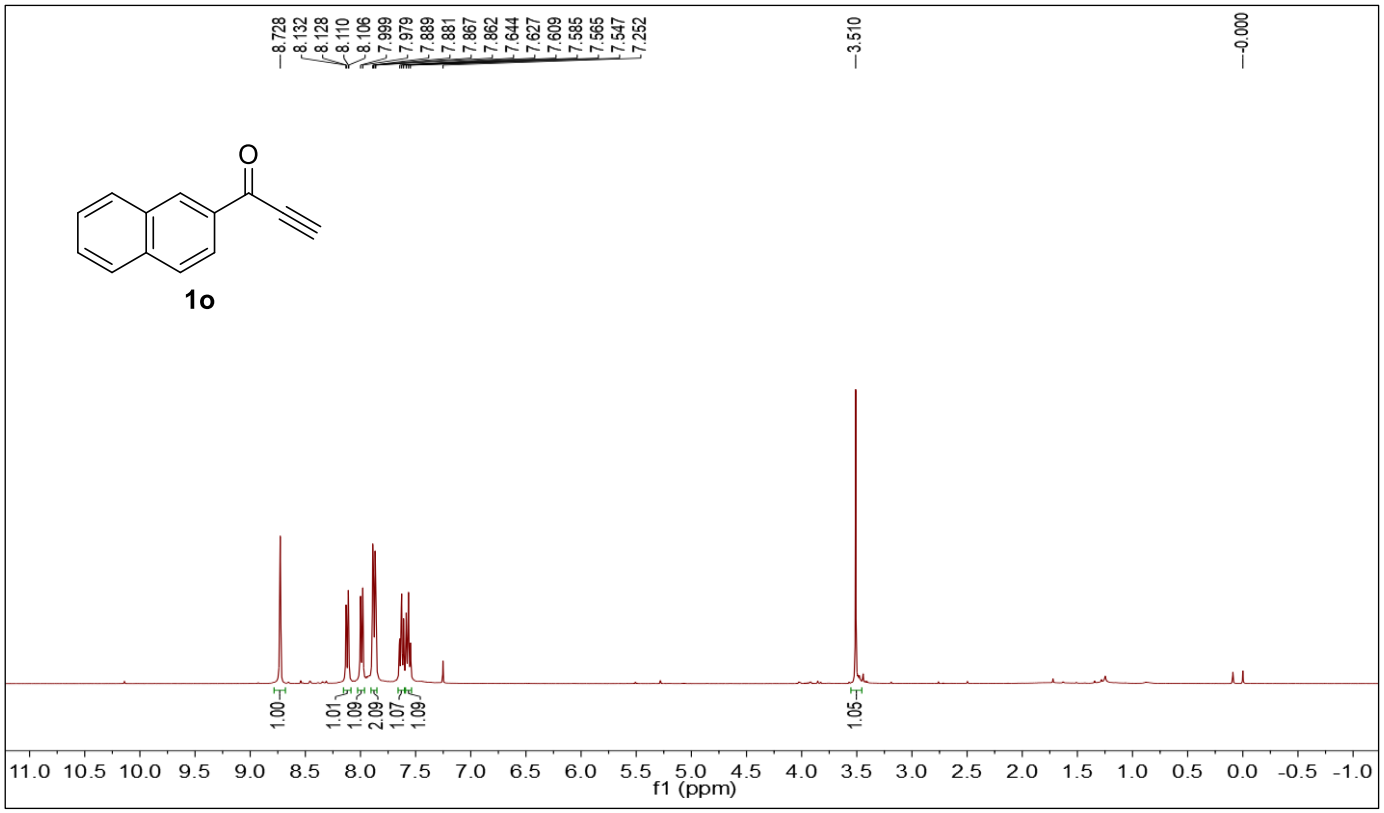

176.565
138.036
135.397
130.789
103.204
81.274
79.840
77.319
77.000
76.682
O
I
1l
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

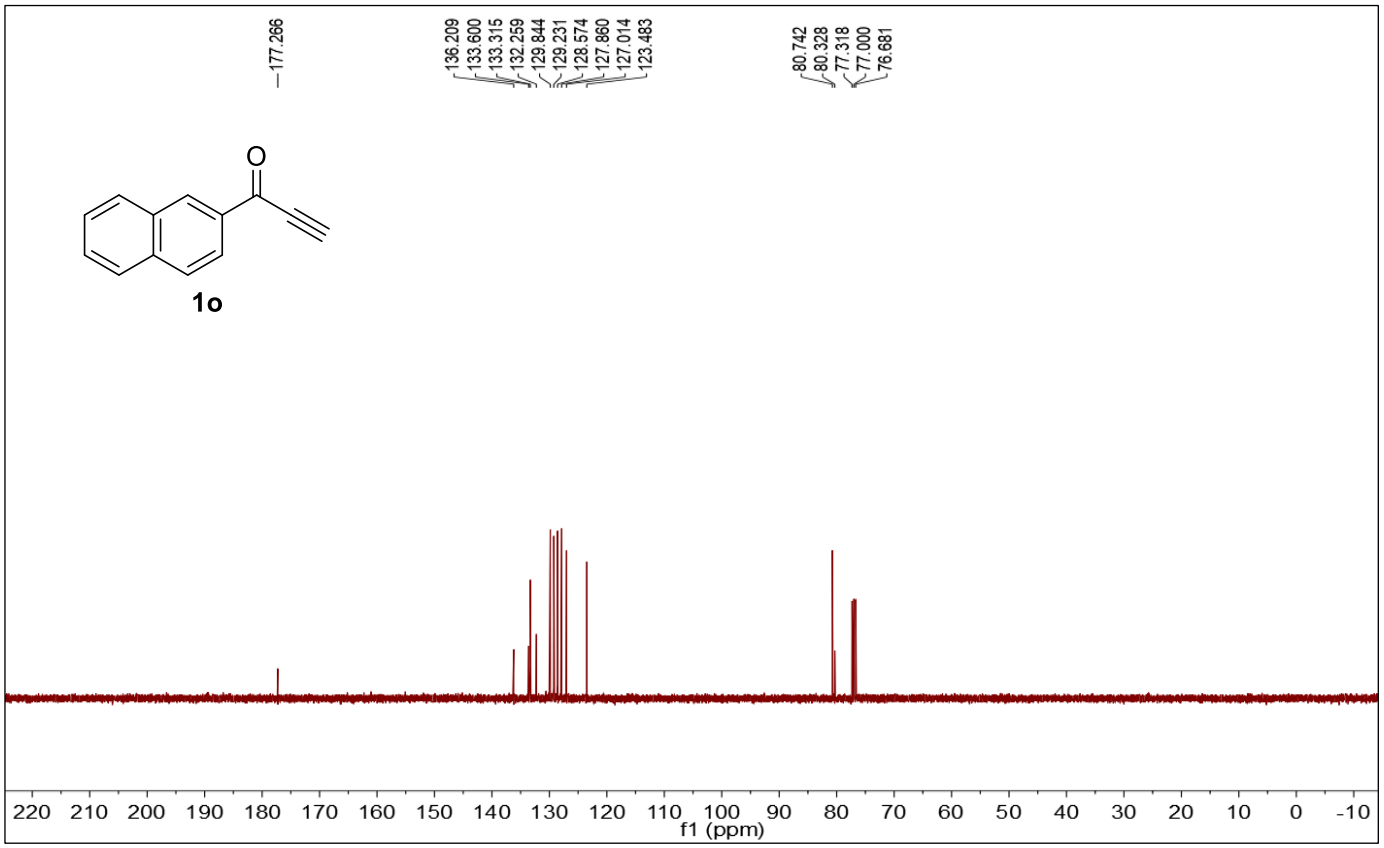

7.628
7.354
7.348
6.538
3.291
0.000
1.02
1.04
1.03
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
1m

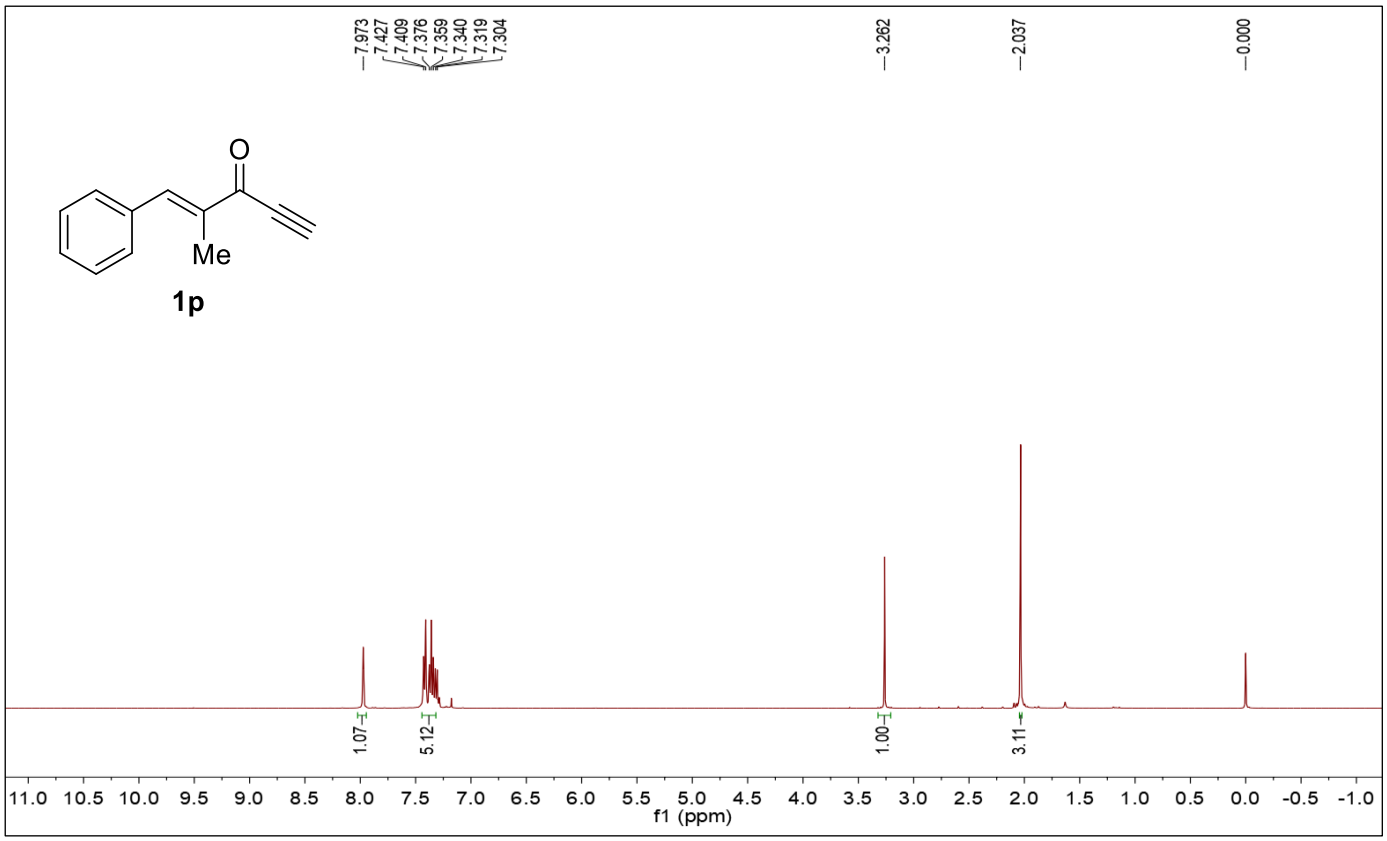

163.693
152.602
148.532
122.121
112.784
79.476
77.318
77.000
76.682
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
1m

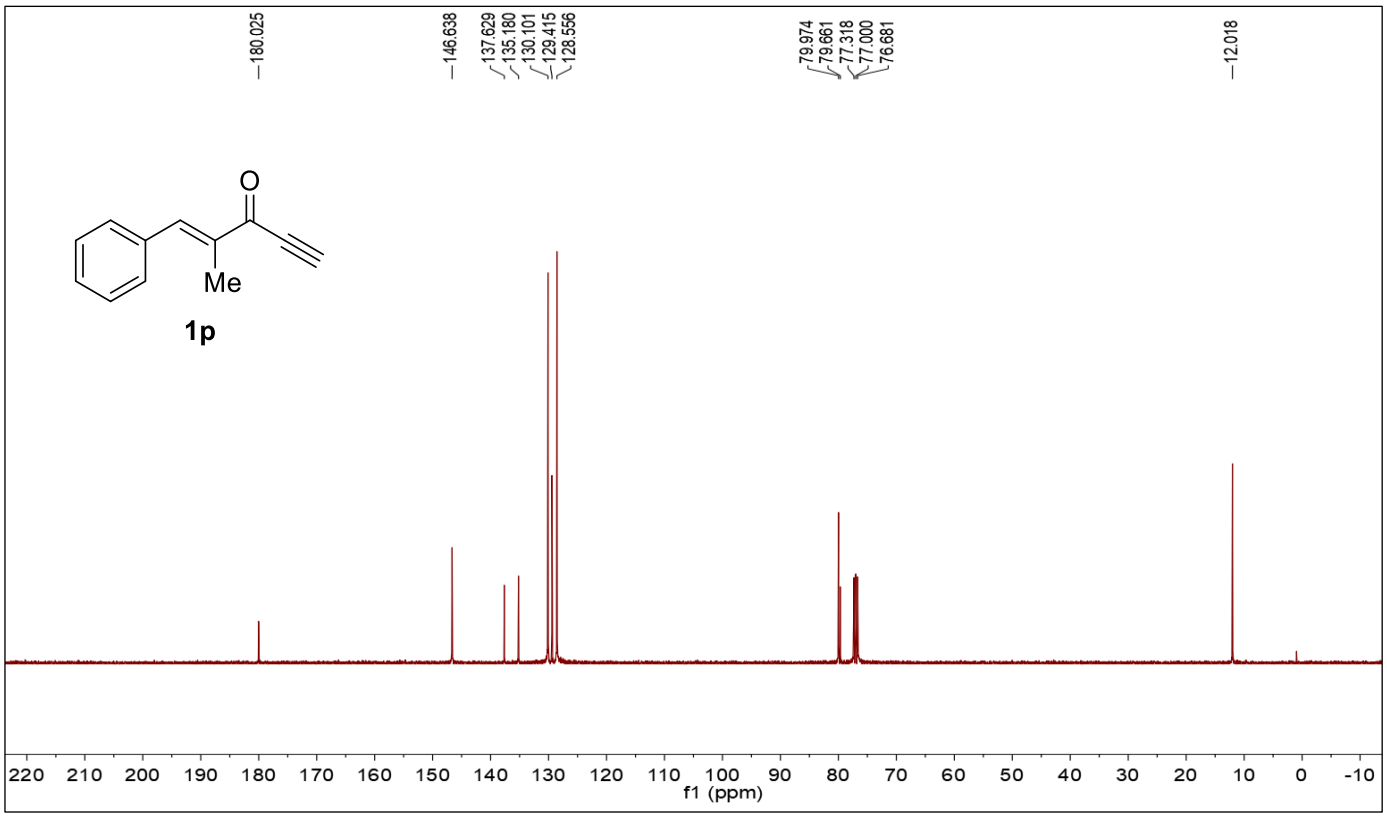

7.986
7.978
7.768
7.756
7.197
7.188
7.176
3.400
0.000
O
S
1n
1.04
1.06
1.07
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

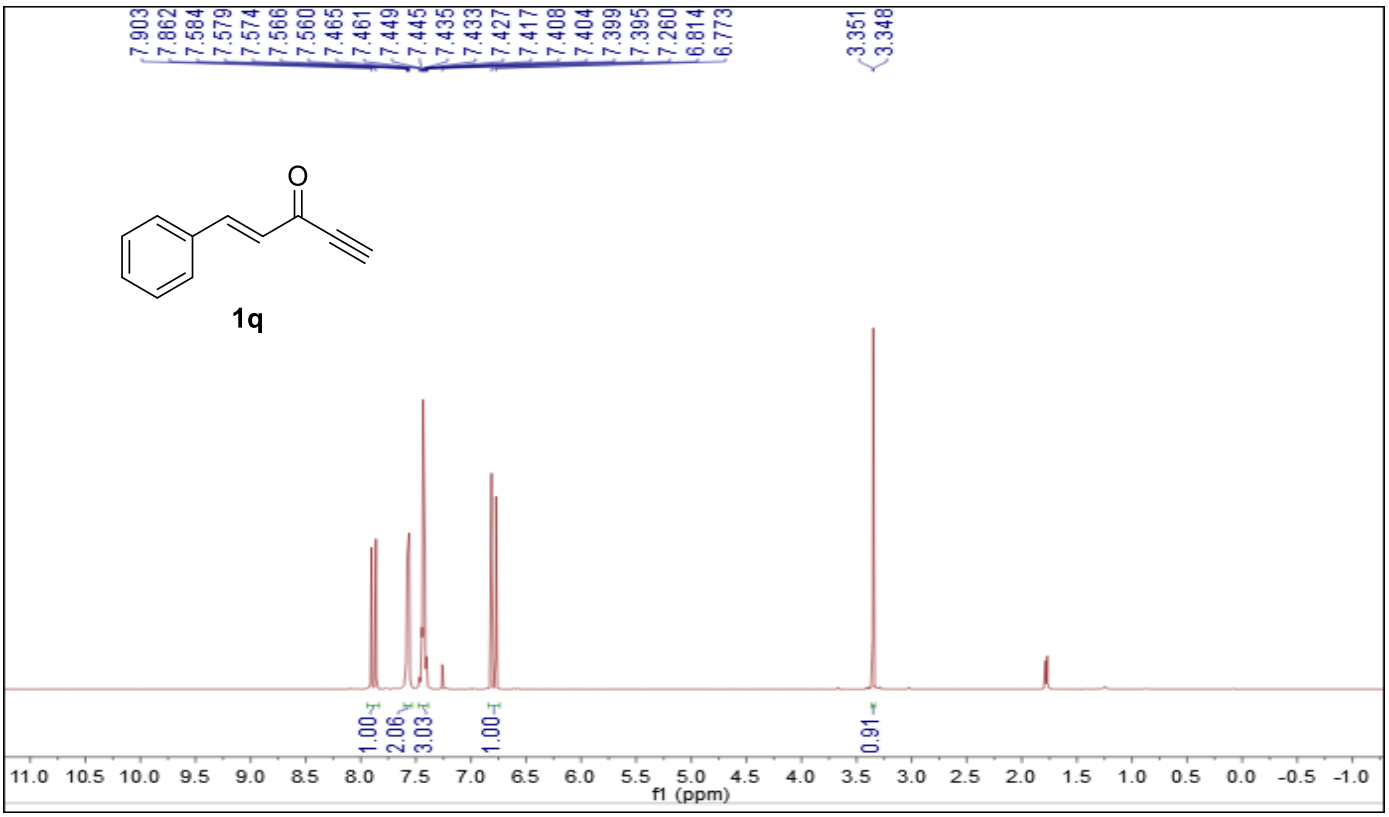

169.101
144.010
136.198
135.990
128.430
79.761
79.385
77.317
77.000
76.682
O
S
1n
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

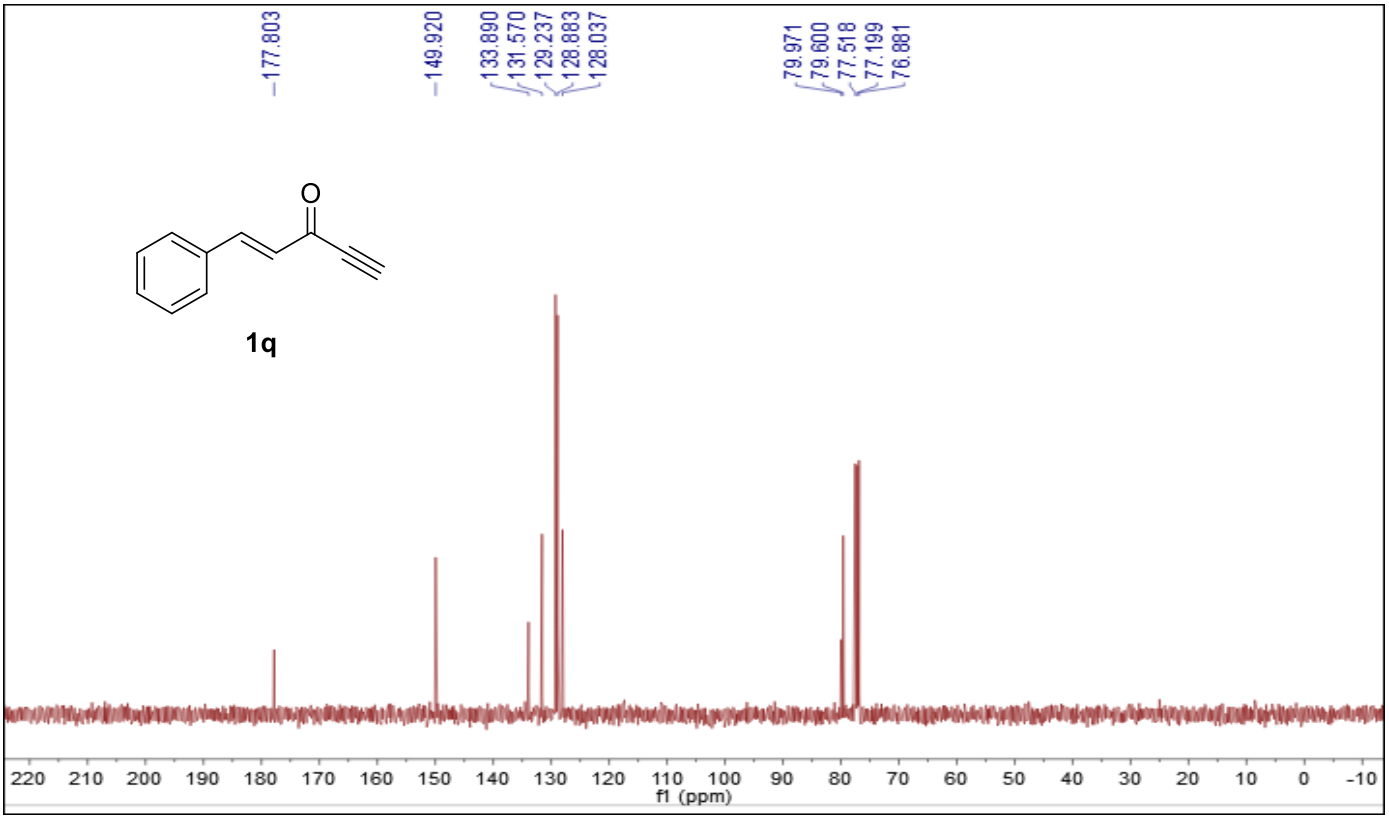

8.728
8.132
8.128
8.110
8.106
7.999
7.979
7.889
7.881
7.867
7.862
7.644
7.627
7.609
7.585
7.565
7.547
7.252
3.510
-0.000
O
1o
1.00
1.01
1.09
2.09
1.07
1.09
1.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

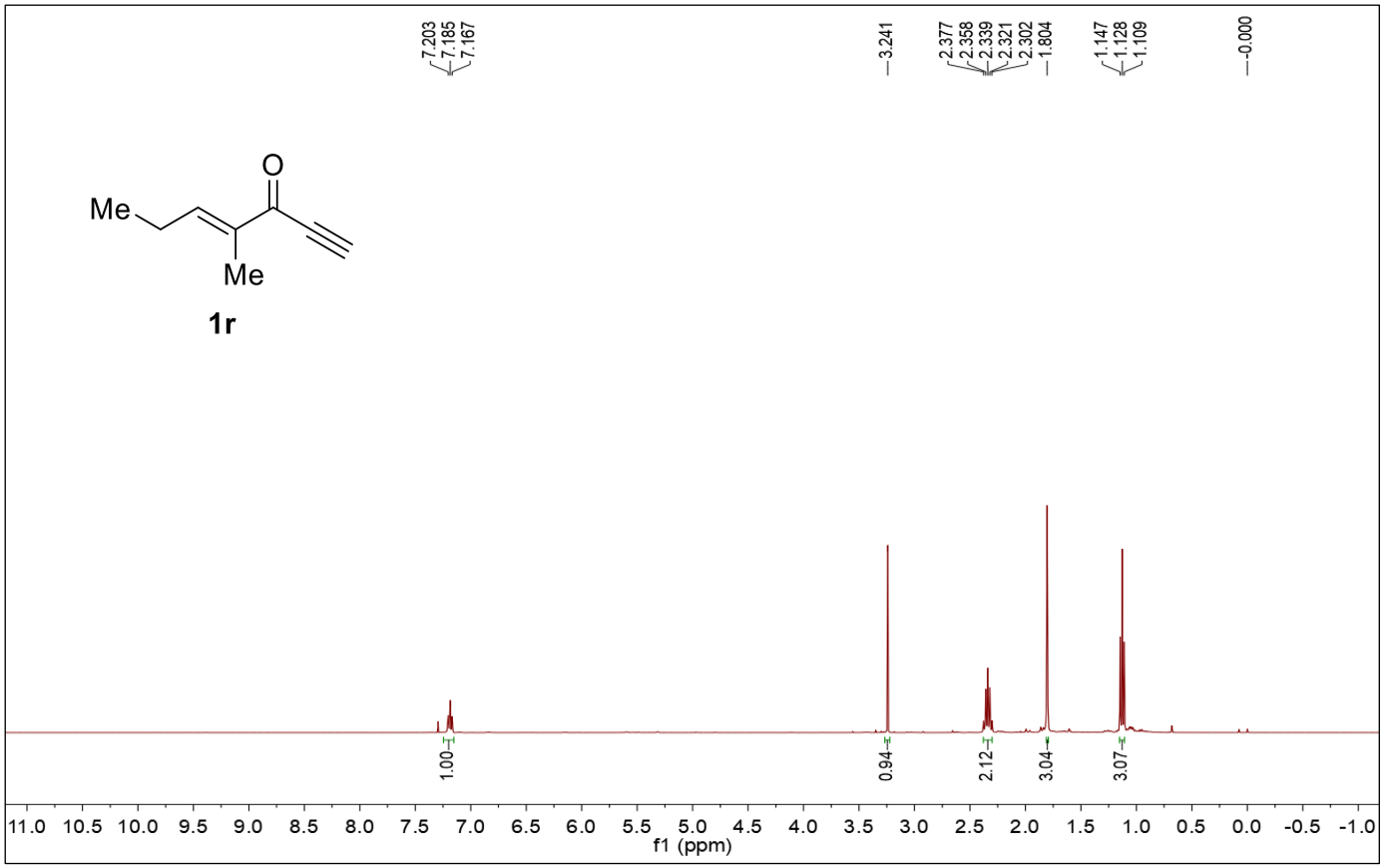

177.266
136.209
133.600
133.315
132.259
129.844
129.231
128.574
127.860
127.014
123.483
80.742
80.328
77.318
77.000
76.681
O
1o
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

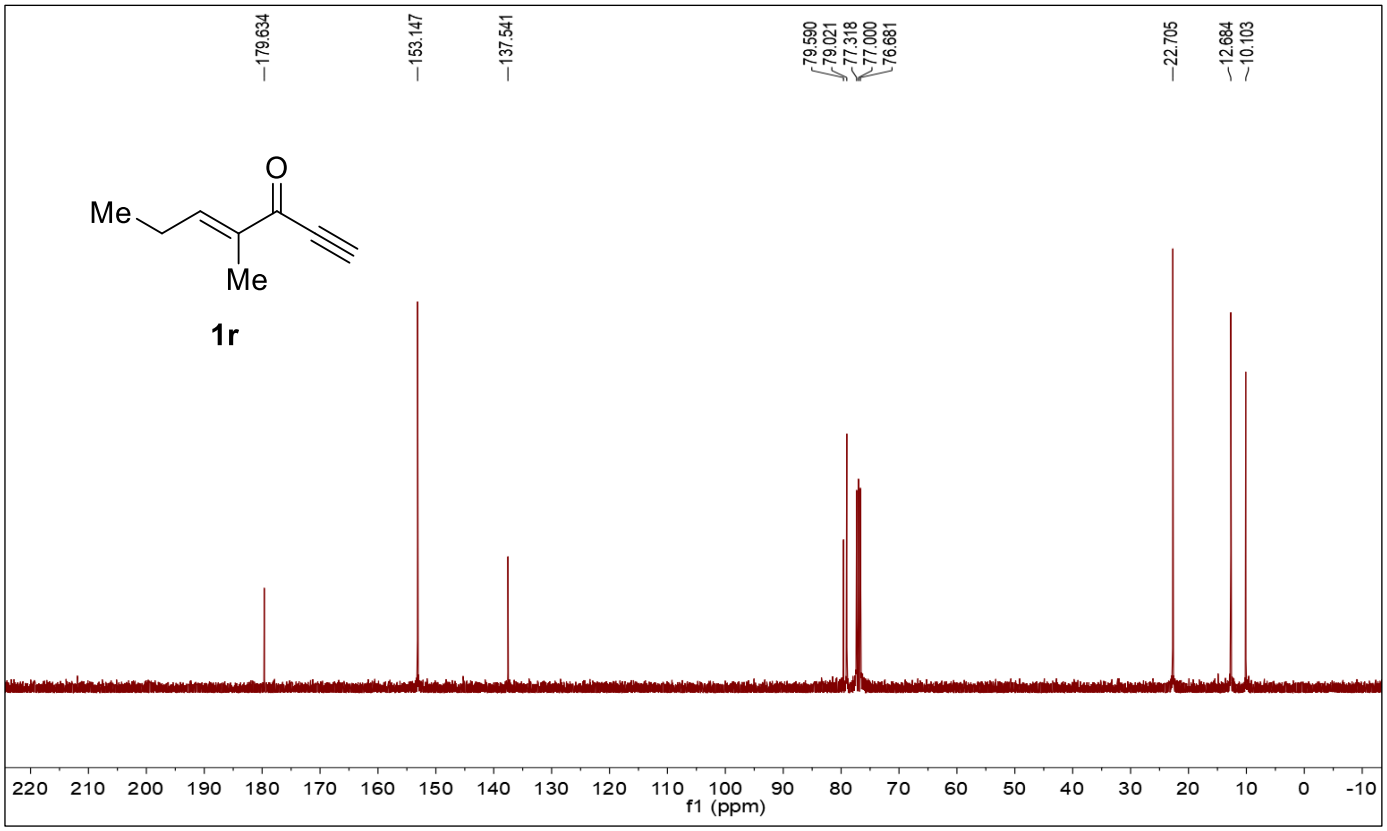

7.973
7.427
7.409
7.376
7.359
7.340
7.319
7.304
3.262
2.037
0.000
O
Me
1p
1.07
5.12
1.00
3.11
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

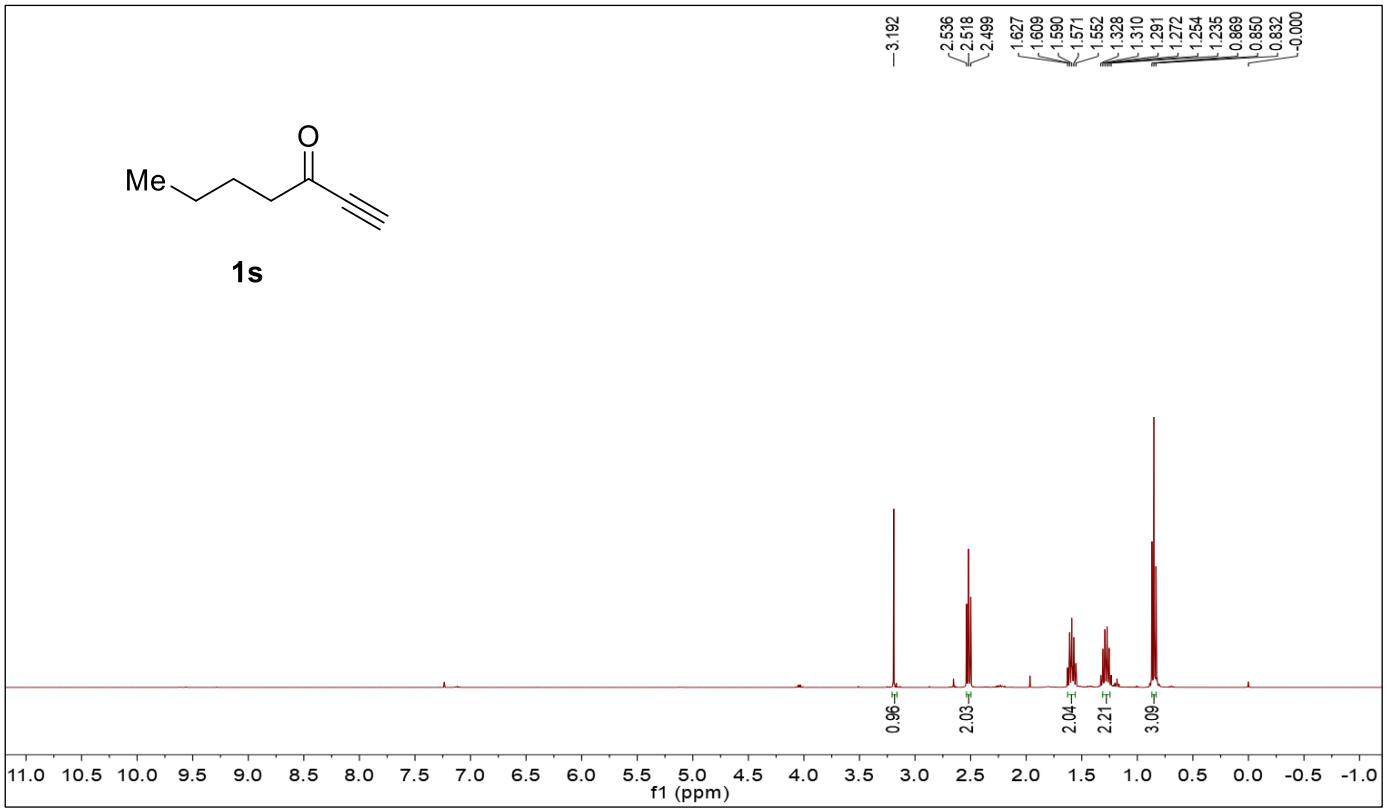

180.025
146.638
137.629
135.180
130.101
129.415
128.556
79.974
79.661
77.318
77.000
76.681
12.018
O
Me
1p
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.903
7.862
7.584
7.579
7.574
7.566
7.560
7.465
7.461
7.449
7.445
7.435
7.433
7.427
7.417
7.408
7.404
7.399
7.395
7.260
6.814
6.773
3.351
3.348
O
1q
1.00
2.06
3.03
1.00
0.91
11.0 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 -0.5 -1.0
f1 (ppm)


177.803
149.920
133.890
131.570
129.237
128.883
128.037
79.971
79.600
77.518
77.199
76.881
O
1q
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.203
7.185
7.167
3.241
2.377
2.358
2.339
2.321
2.302
1.804
1.147
1.128
1.109
-0.000
O
Me
Me
1r
1.00
0.94
2.12
3.04
3.07
11.0 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 -0.5 -1.0
f1 (ppm)


179.634
153.147
137.541
79.590
79.021
77.318
77.000
76.681
22.705
12.684
10.103
O
Me
Me
1r
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3.192
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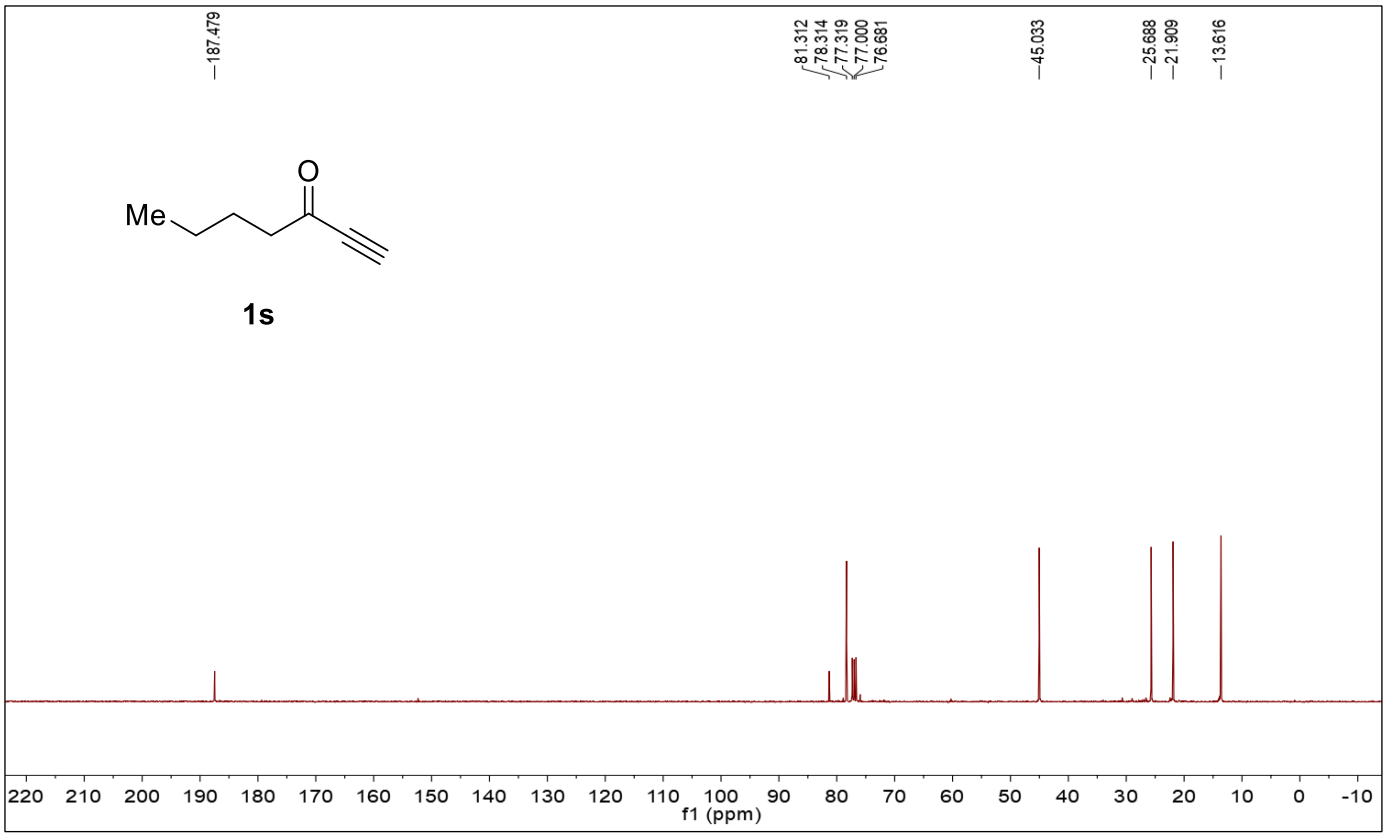
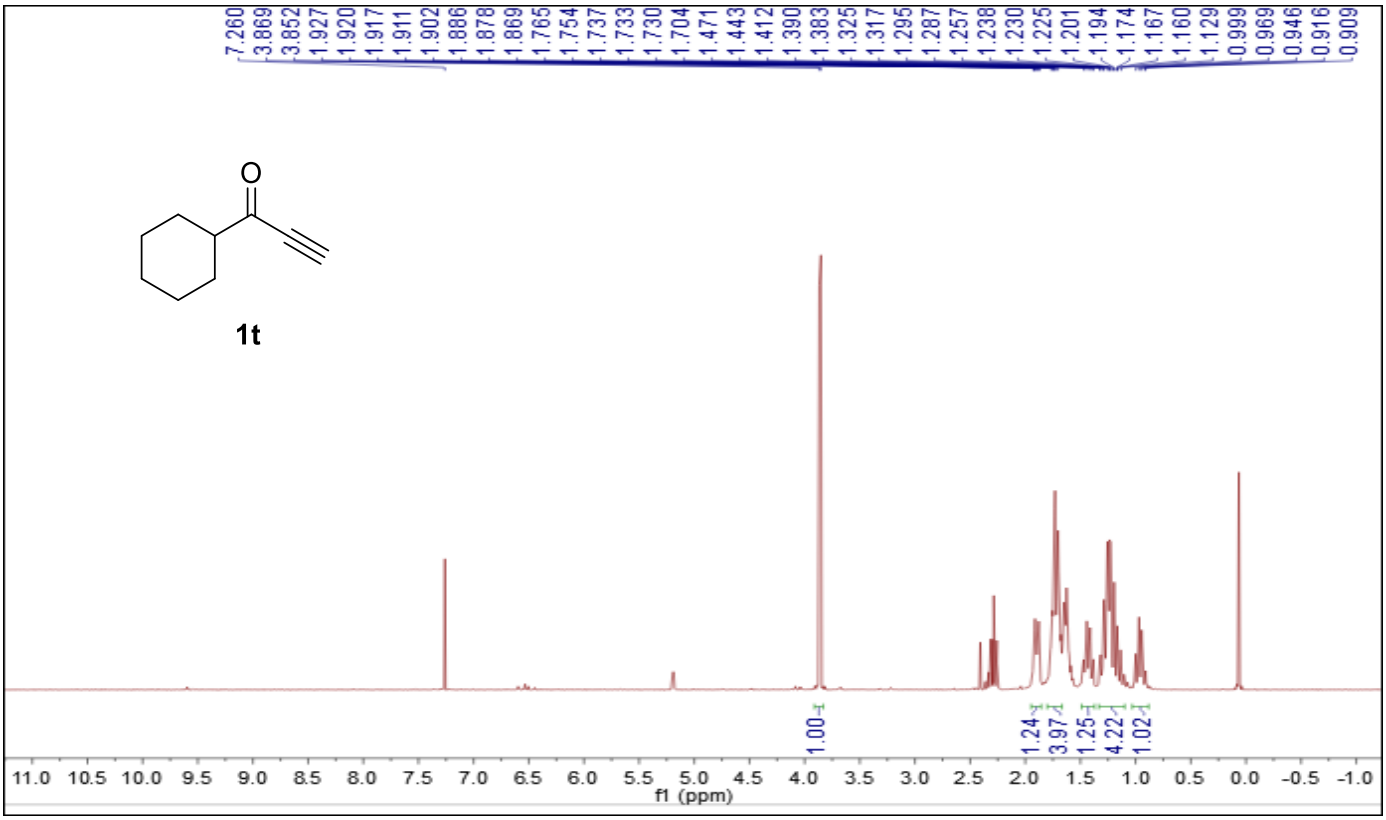
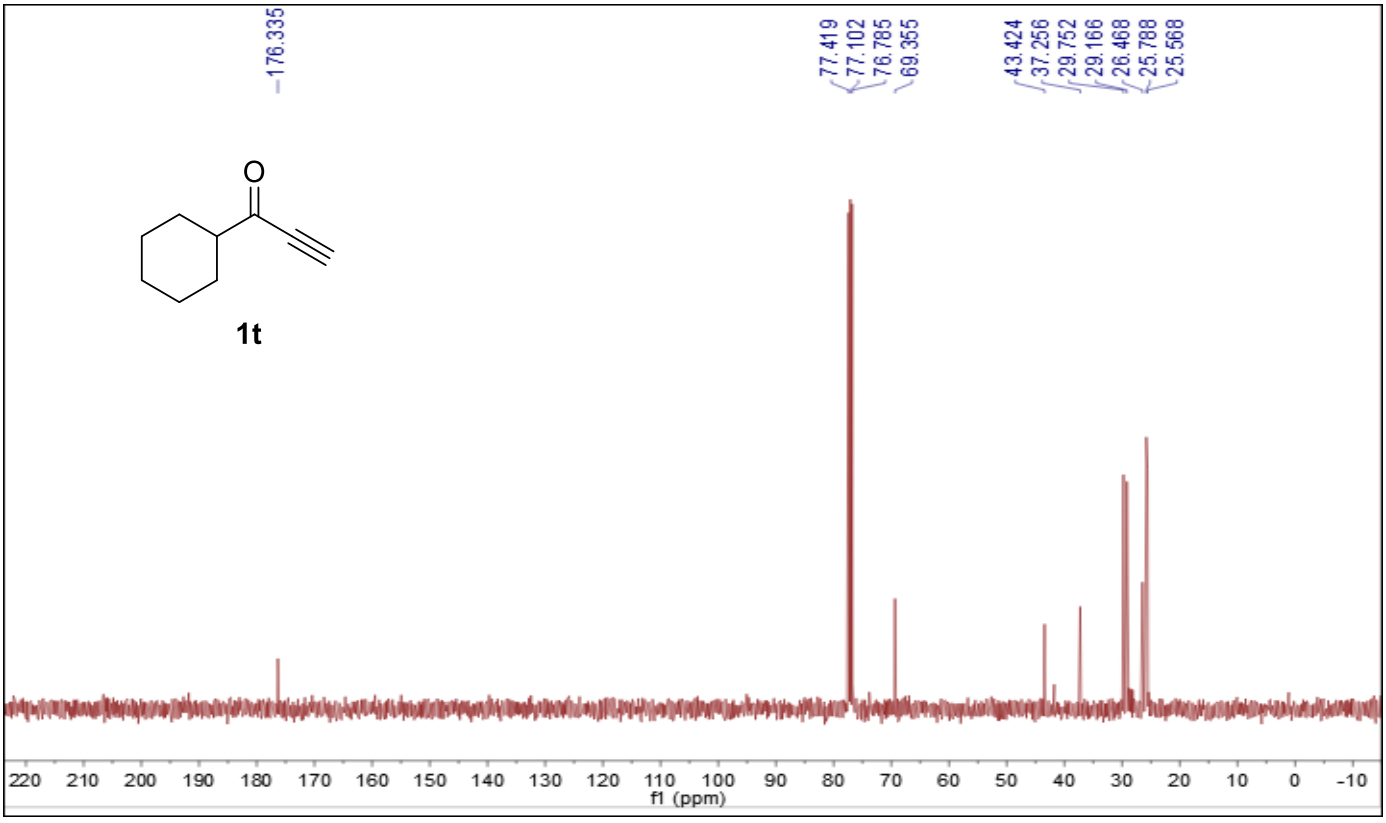
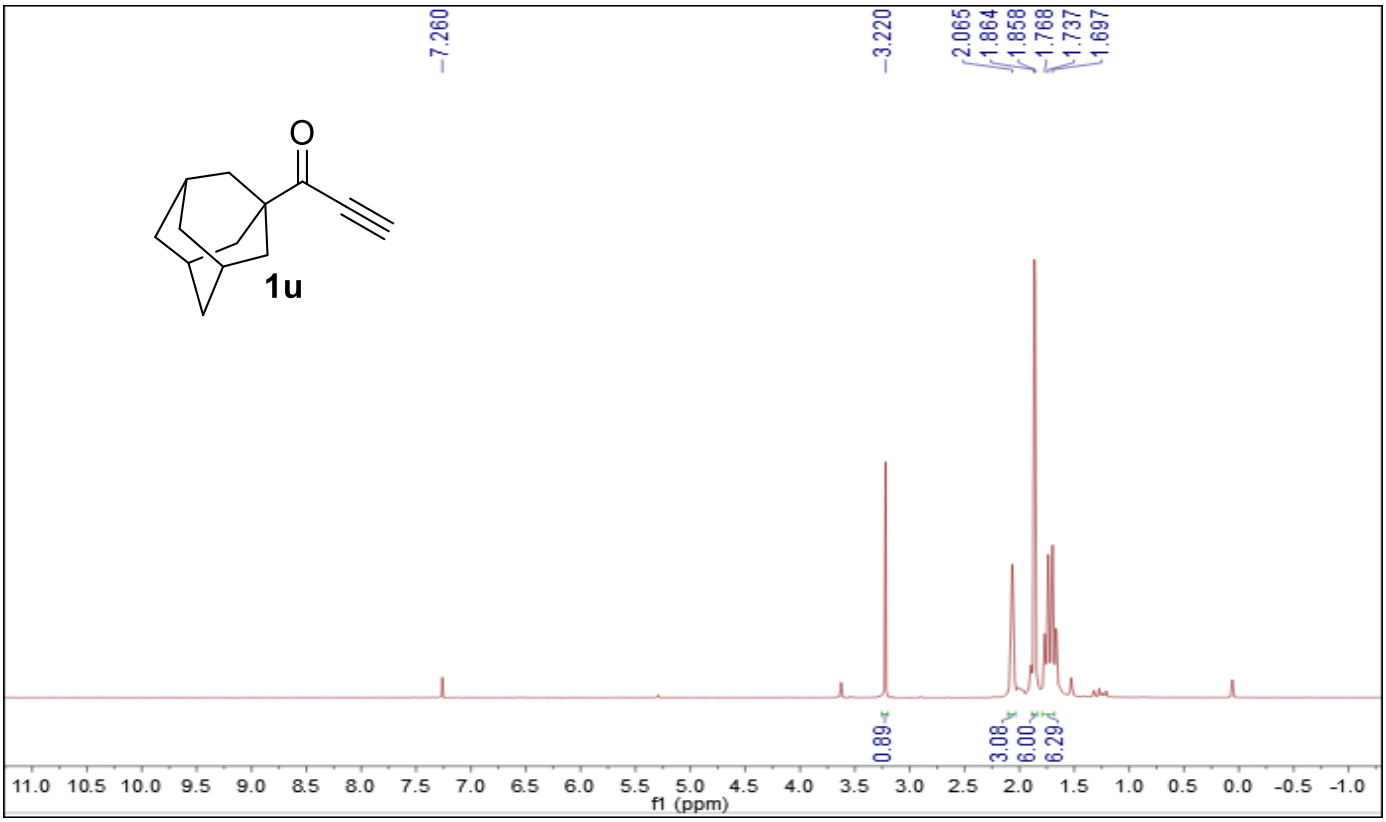
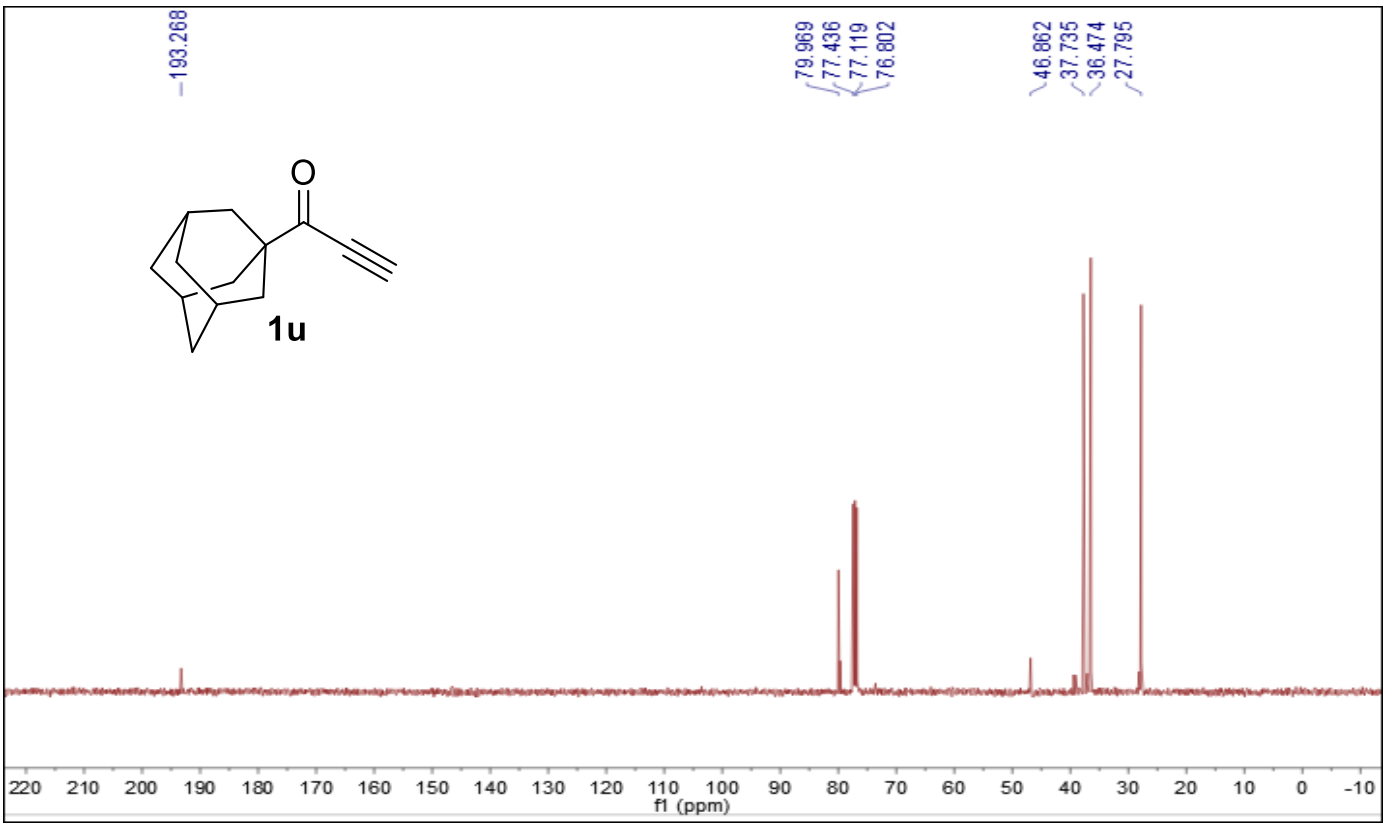
2.518
2.499
1.627
1.609
1.590
1.571
1.552
1.328
1.310
1.291
1.272
1.254
1.235
0.869
0.850
0.832
-0.000
O
Me
1s
0.96
2.03
2.04
2.21
3.09
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


187.479
81.312
78.314
77.319
77.000
76.681
45.033
25.688
21.909
13.616
O
Me
1s
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

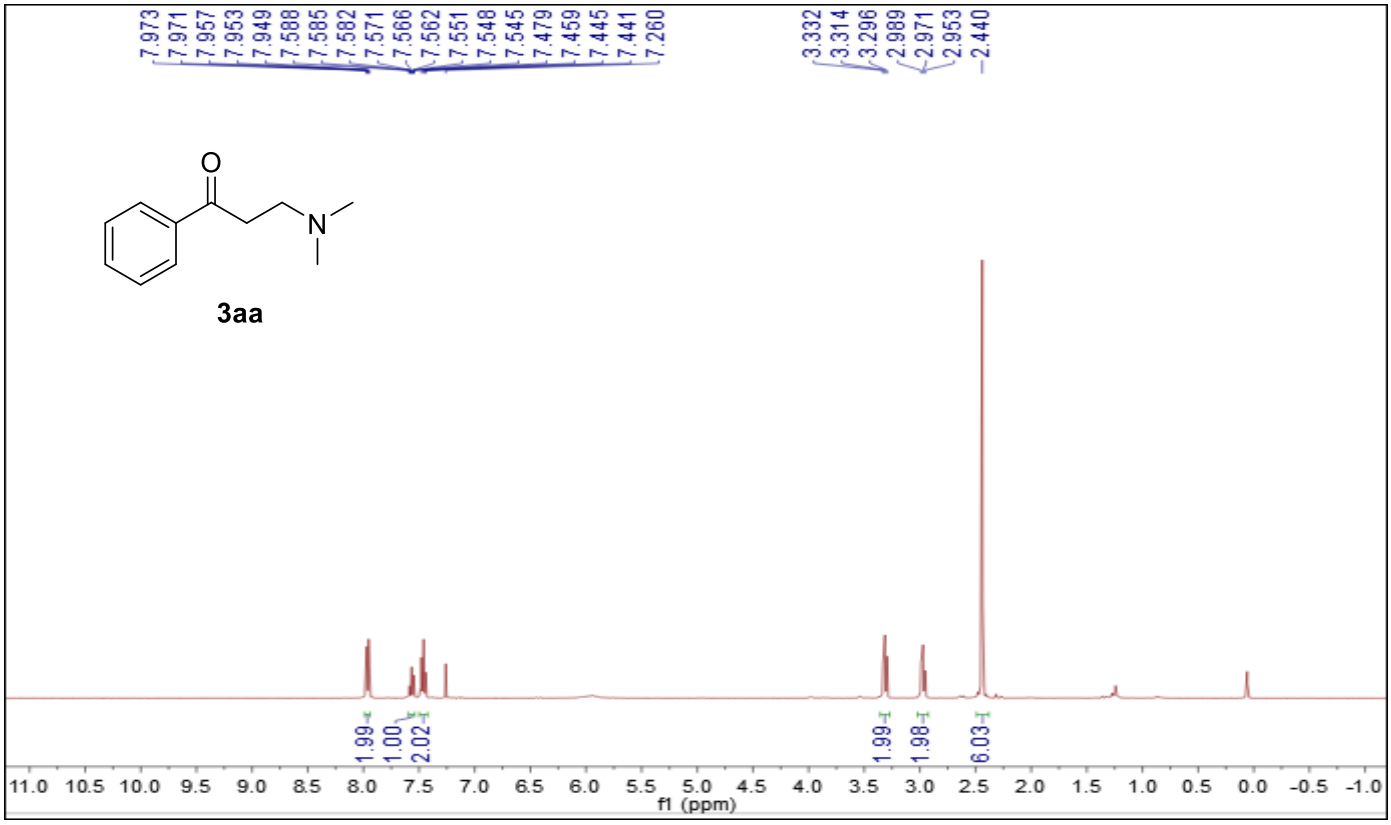

7.260
3.869
3.852
1.927
1.920
1.917
1.911
1.902
1.886
1.878
1.869
1.765
1.754
1.737
1.733
1.730
1.704
1.471
1.443
1.412
1.390
1.383
1.325
1.317
1.295
1.287
1.257
1.238
1.230
1.225
1.201
1.194
1.174
1.167
1.160
1.129
0.999
0.969
0.946
0.916
0.909
O
1t
1.00
1.24
3.97
1.25
4.22
1.02
11.0 10.5 10.0 9.5 9.0 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 -0.5 -1.0
f1 (ppm)

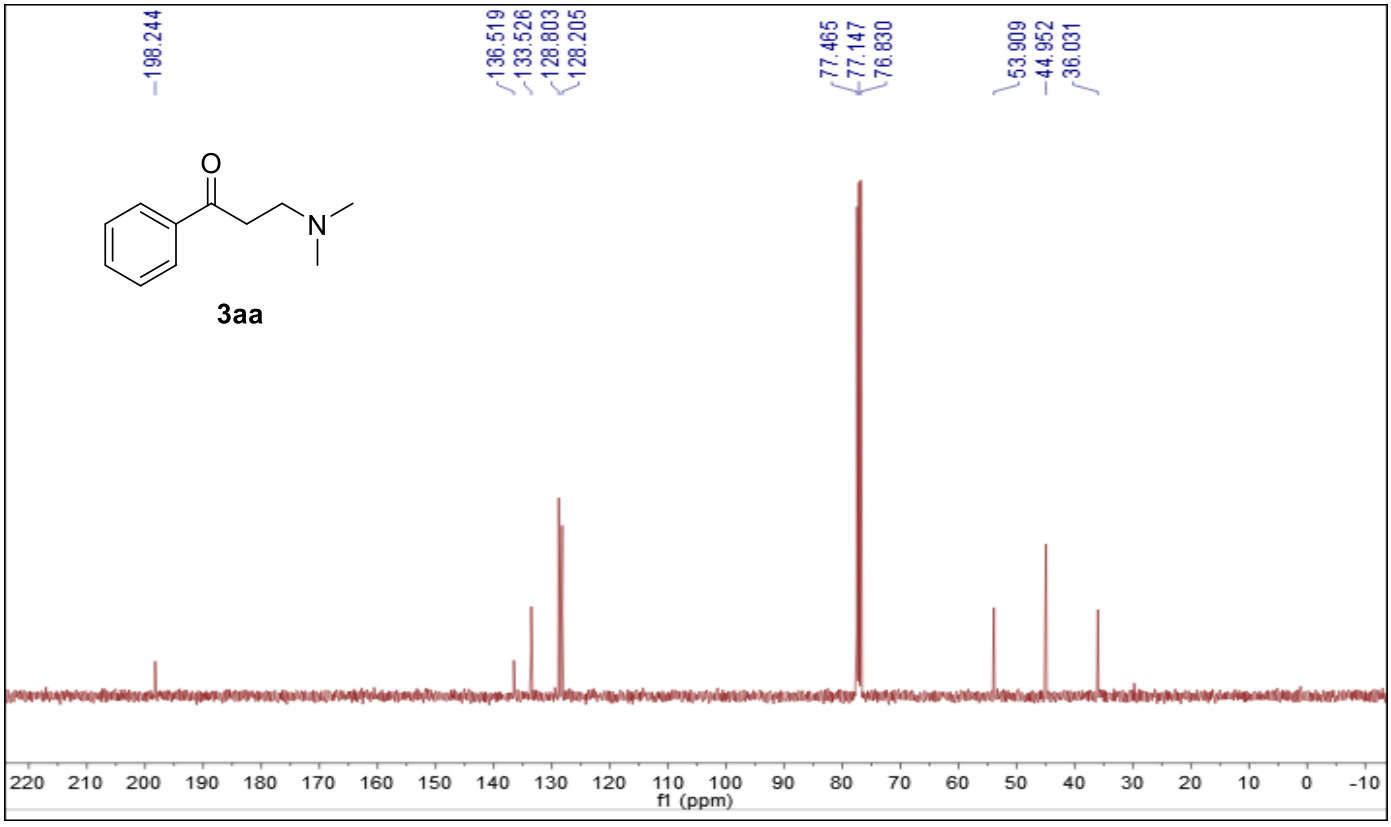

176.335
77.419
77.102
76.785
69.355
43.424
37.256
29.752
29.166
26.468
25.788
25.568
O
1t
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

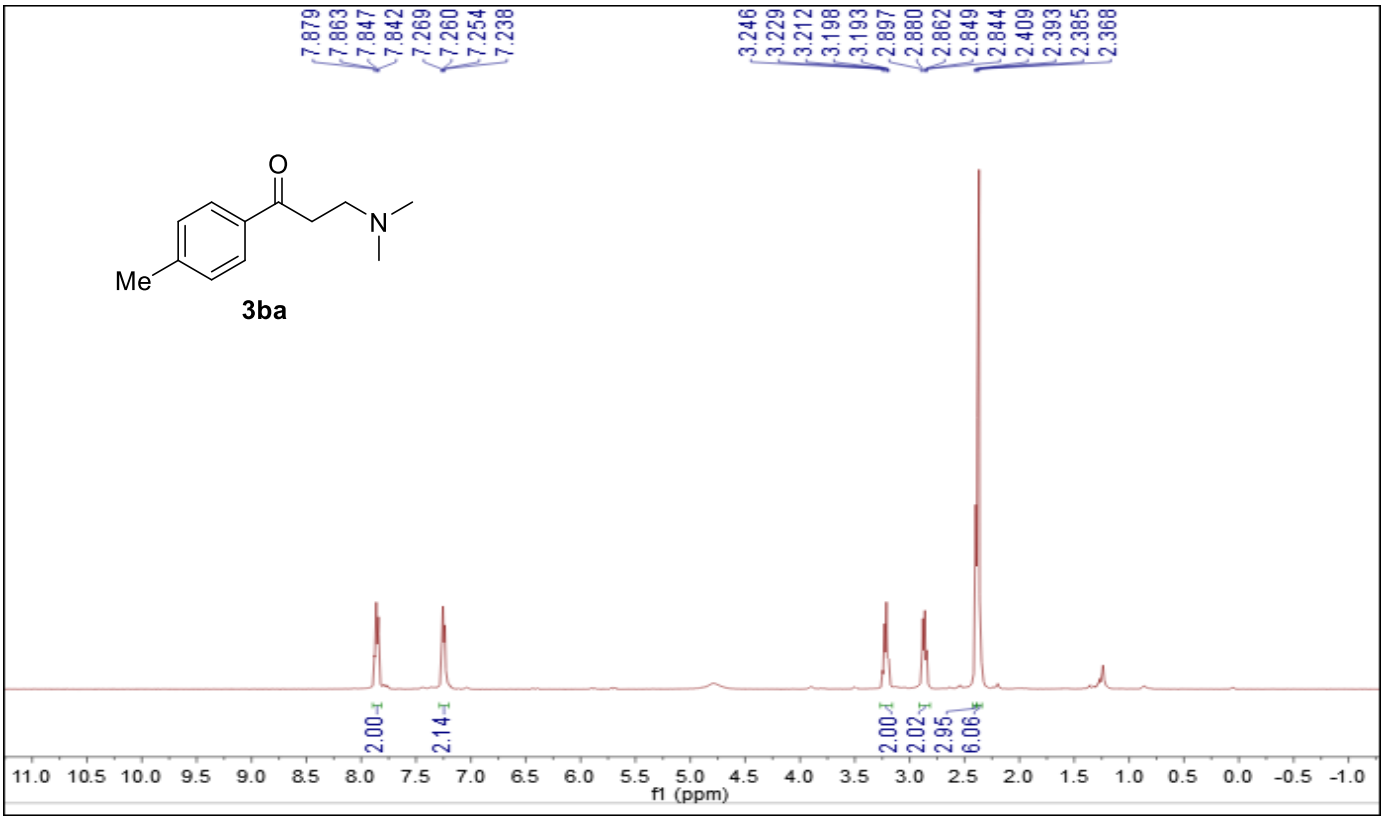

7.260
3.220
2.065
1.864
1.858
1.768
1.737
1.697
O
1u
0.89
3.08
6.00
6.29
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

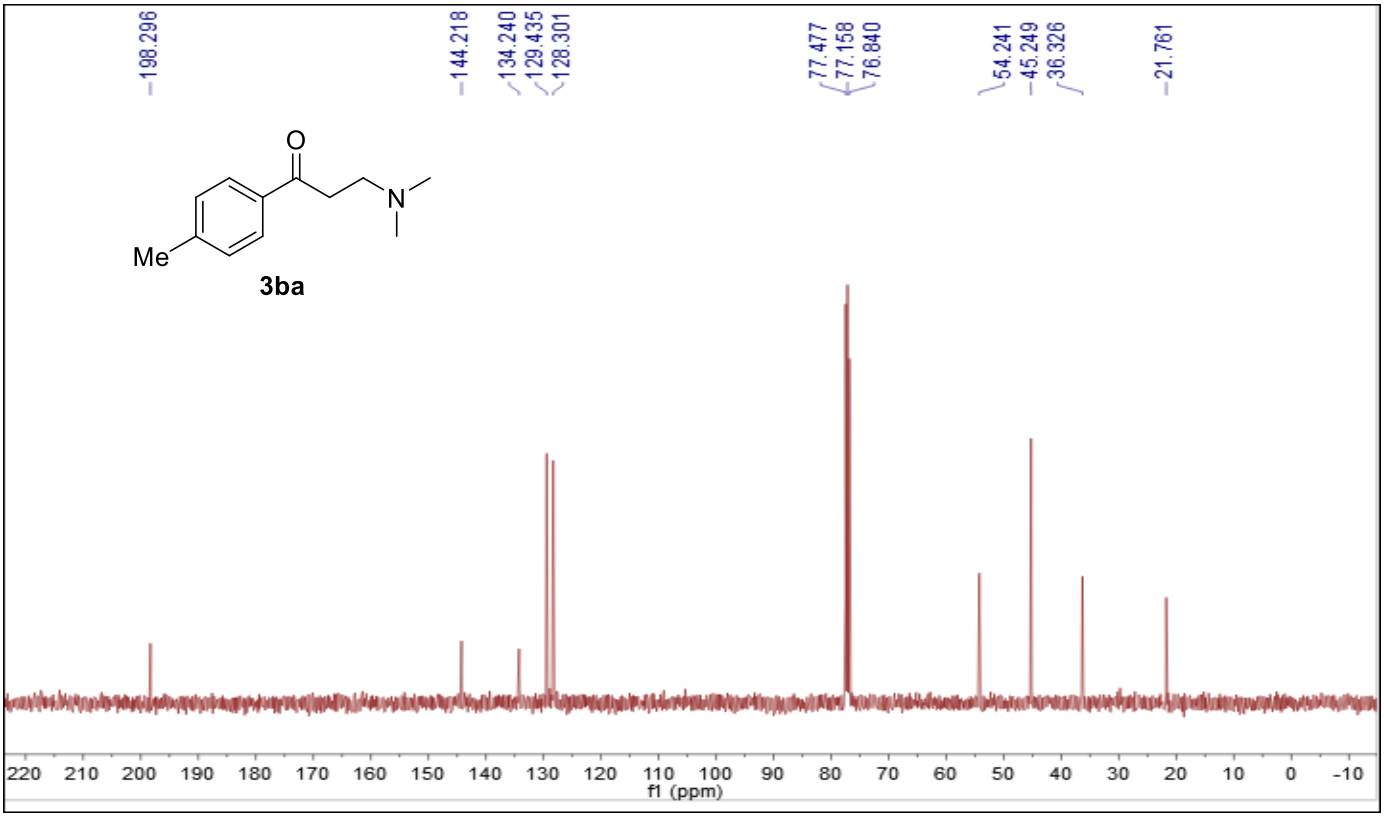

193.268
79.969
77.436
77.119
76.802
46.862
37.735
36.474
27.795
O
1u
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

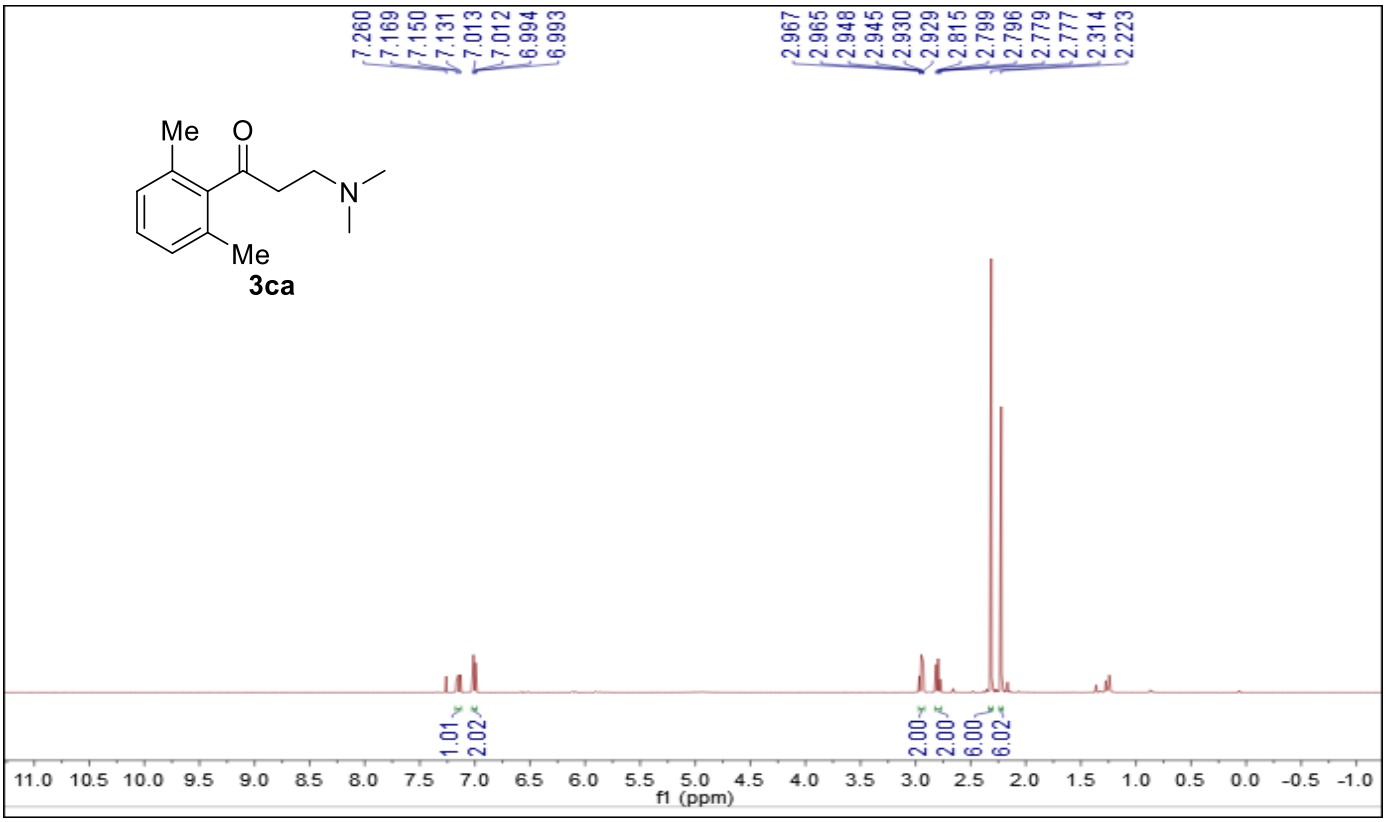
^{1}H and ^{13}C NMR spectra of *β*-aminoketones

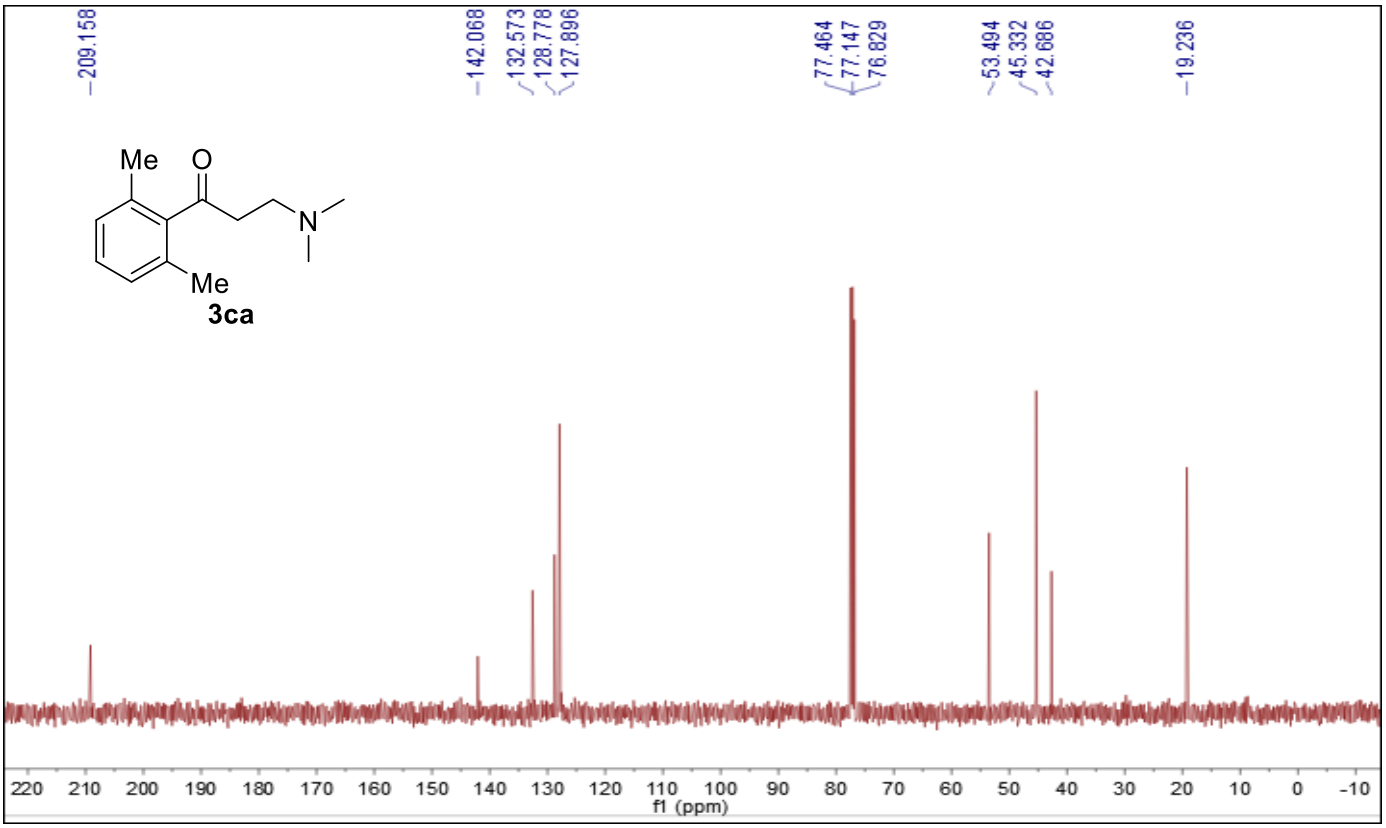


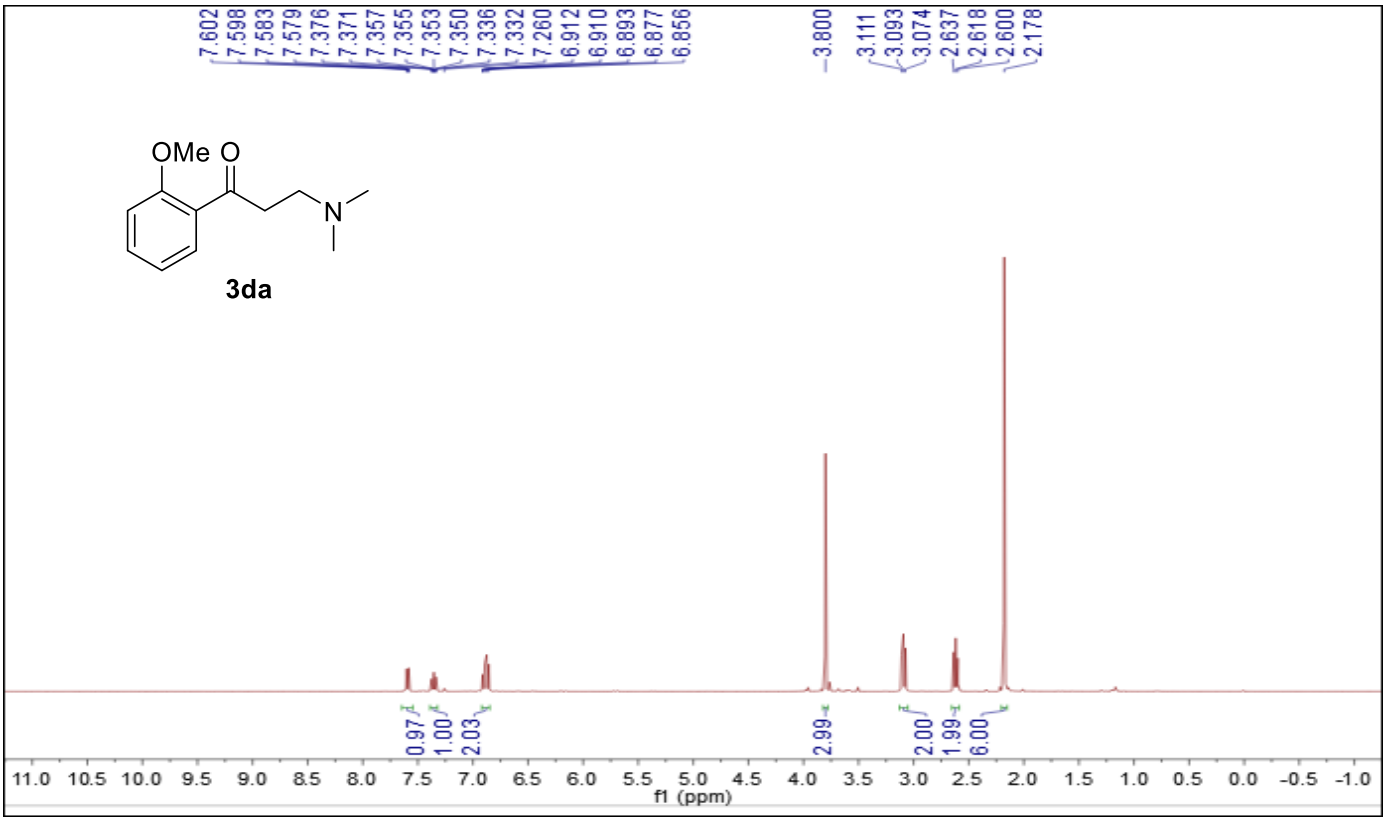


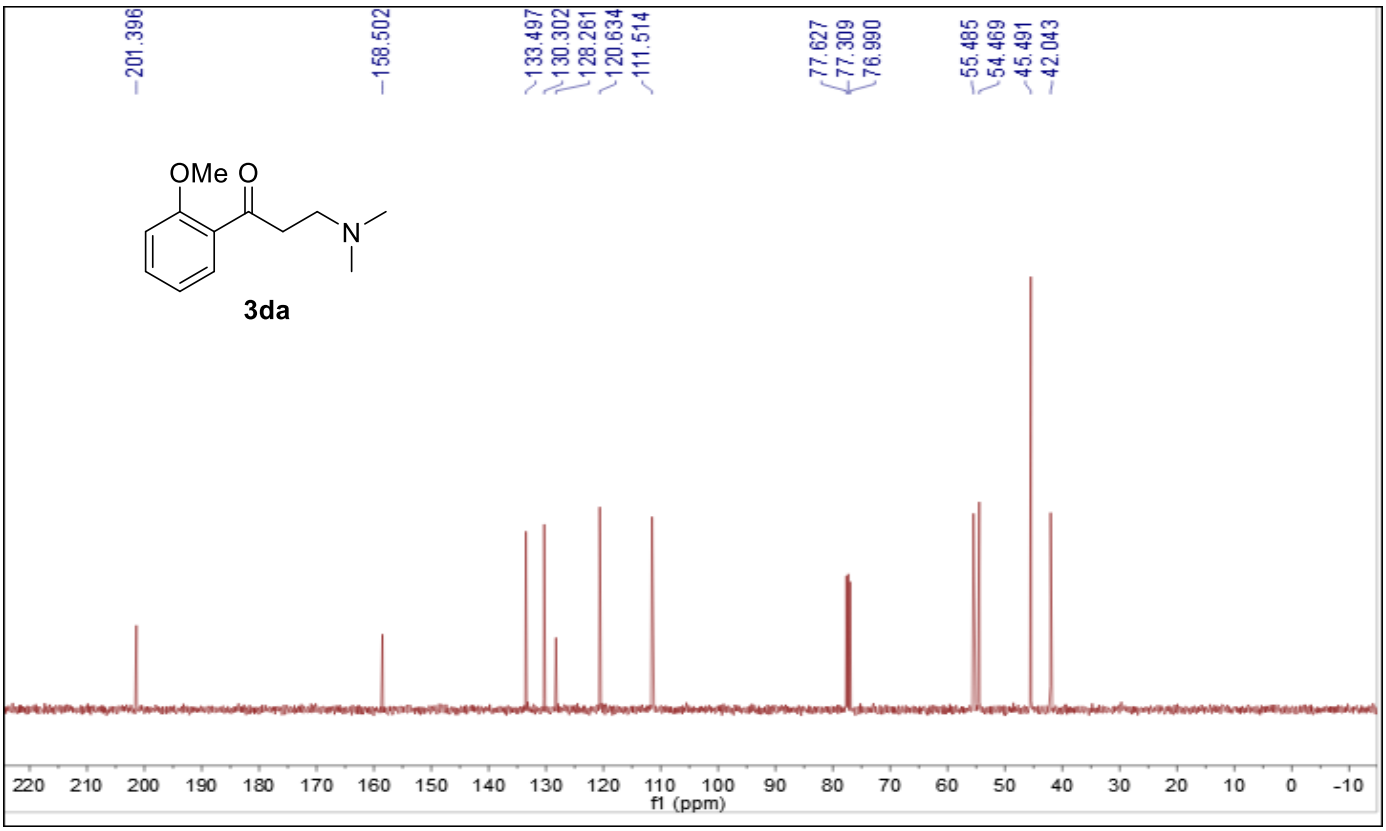

7.879
7.863
7.847
7.842
7.269
7.260
7.254
7.238
3.246
3.229
3.212
3.198
3.193
2.897
2.880
2.862
2.849
2.844
2.409
2.393
2.385
2.368
O
N
Me
3ba
2.00
2.14
2.00
2.02
2.95
6.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

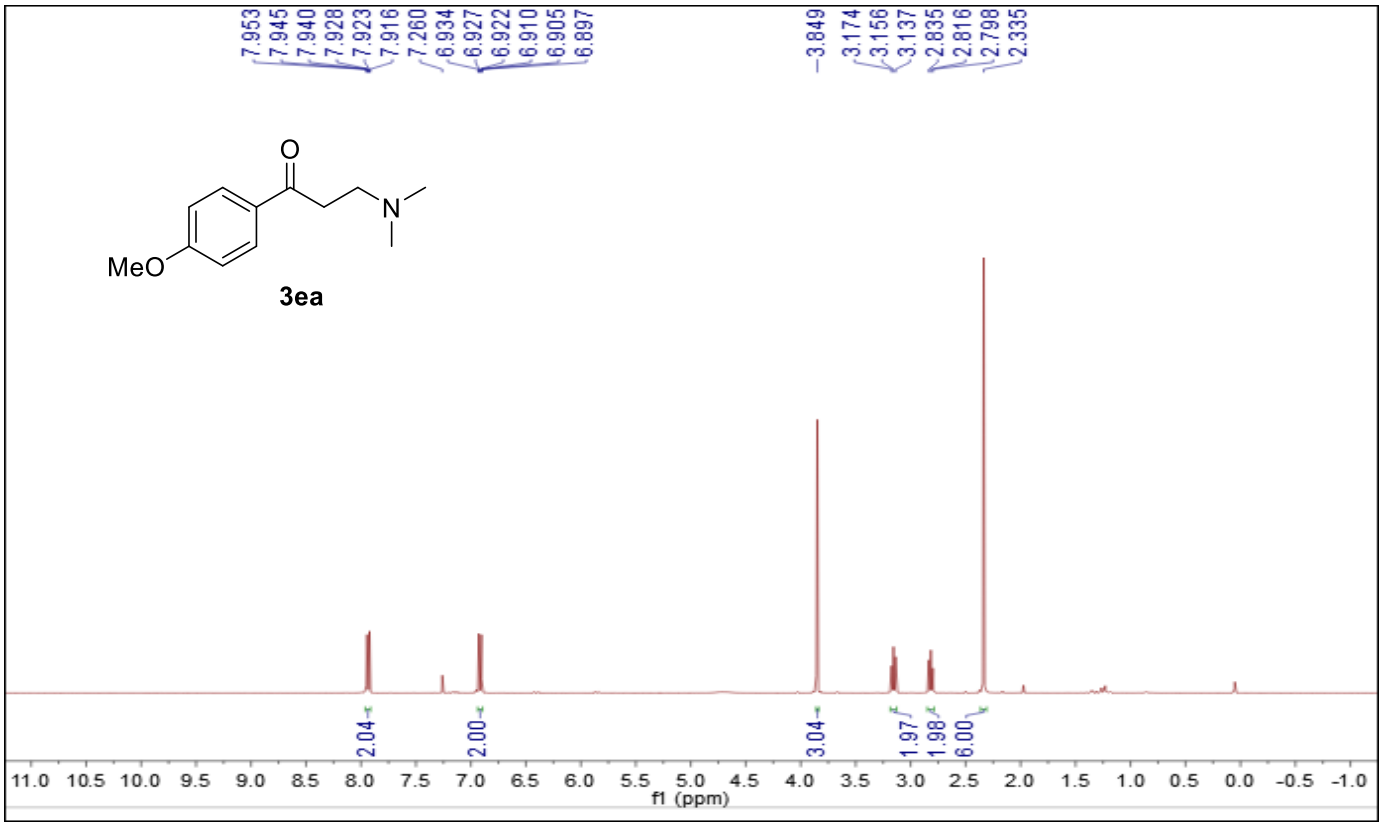

198.296
144.218
134.240
129.435
128.301
77.477
77.158
76.840
54.241
45.249
36.326
21.761
O
N
Me
3ba
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

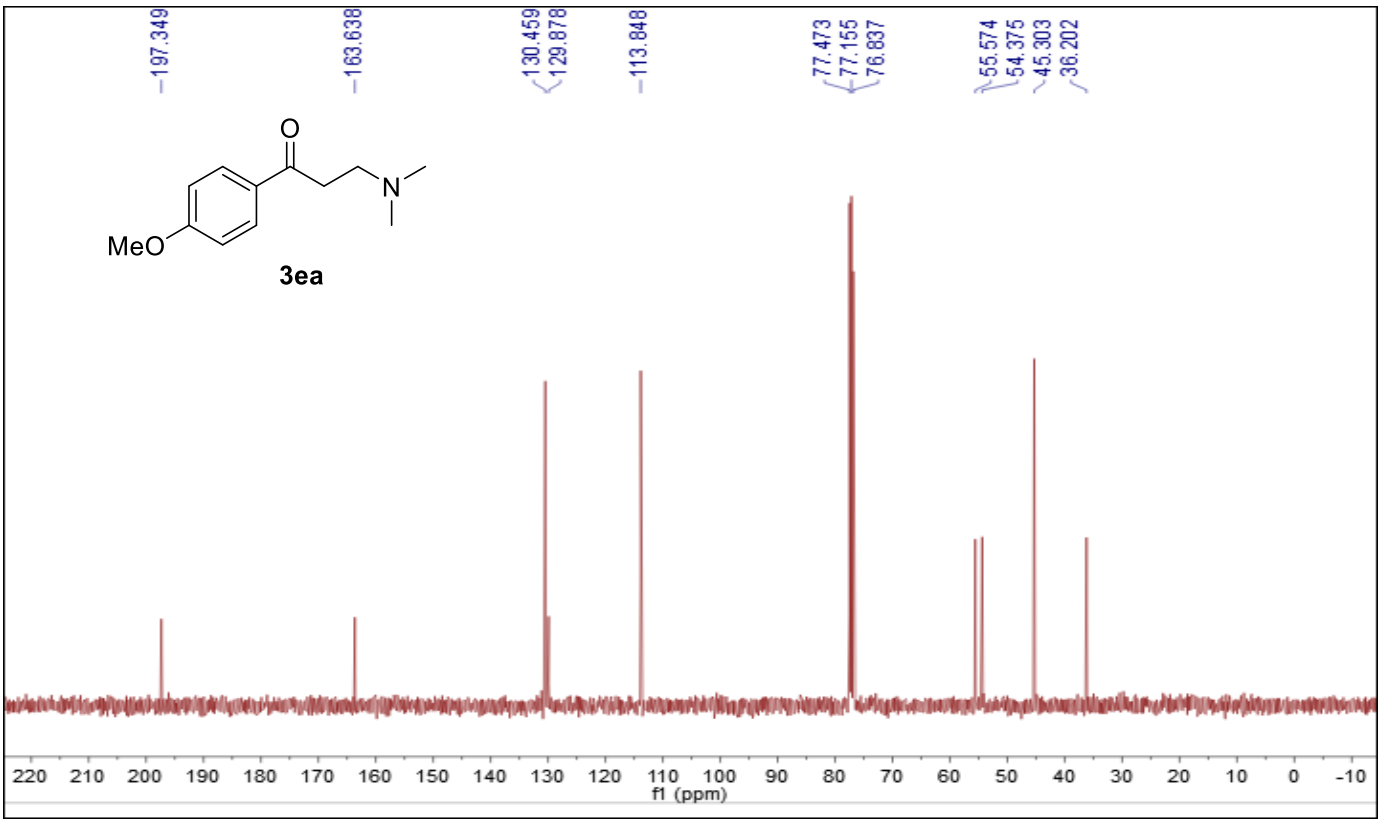

7.260
7.169
7.150
7.131
7.013
7.012
6.994
6.993
2.967
2.965
2.948
2.945
2.930
2.929
2.815
2.799
2.796
2.779
2.777
2.314
2.223
Me
O
N
Me
3ca
1.01
2.02
2.00
2.00
6.00
6.02
f1 (ppm)

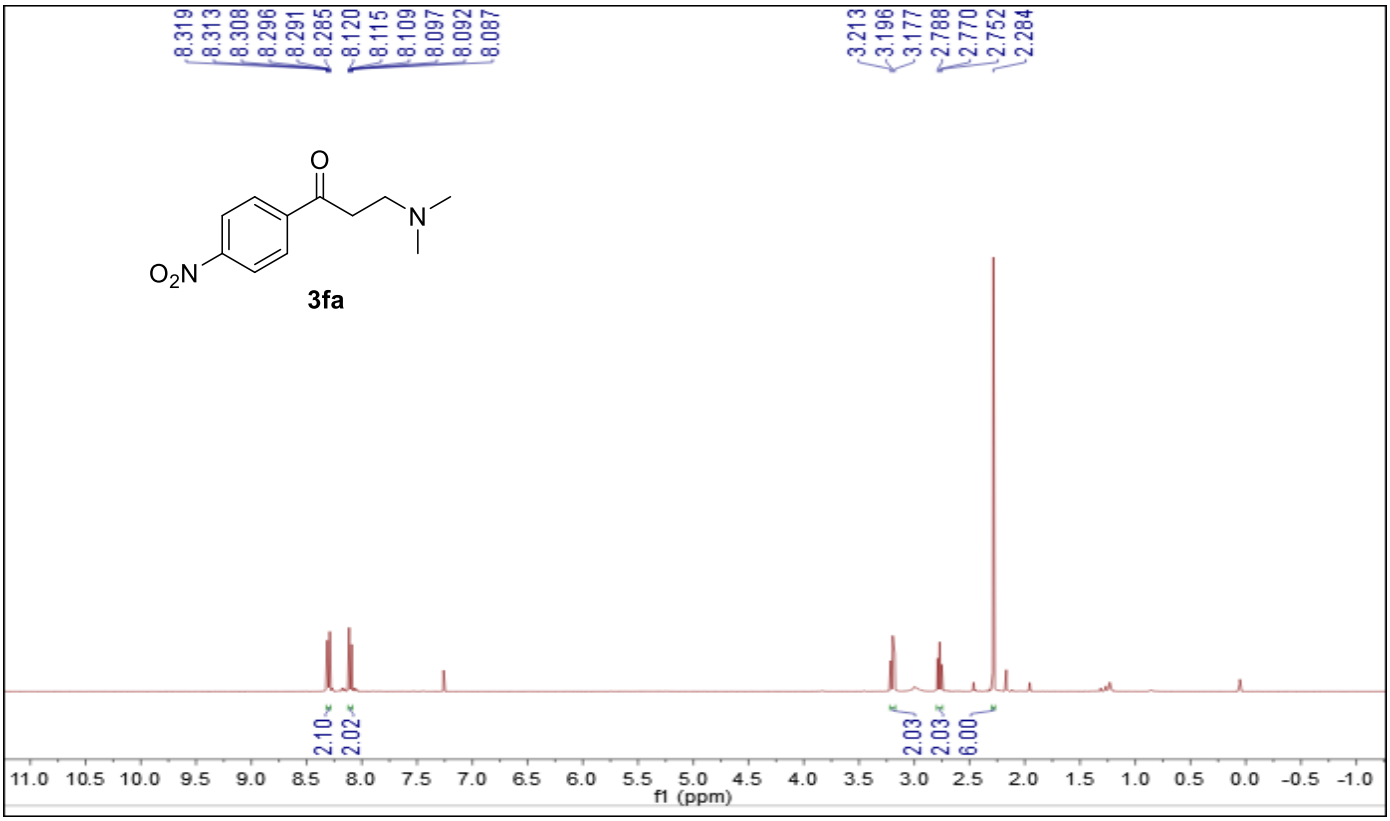

209.158
142.068
132.573
128.778
127.896
77.464
77.147
76.829
53.494
45.332
42.686
19.236
Me
O
N
Me
3ca
f1 (ppm)

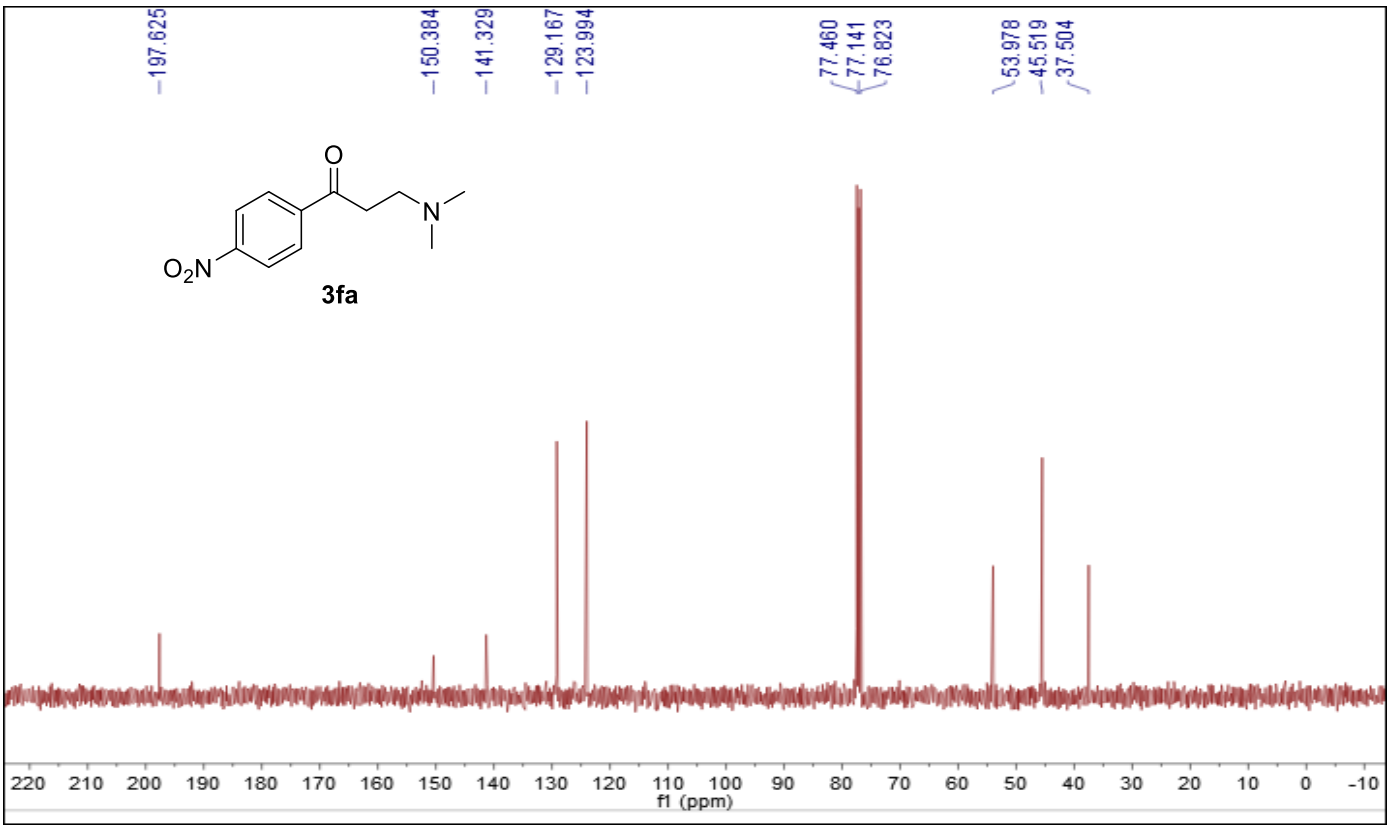

7.602
7.598
7.583
7.579
7.376
7.371
7.357
7.355
7.353
7.350
7.336
7.332
7.260
6.912
6.910
6.893
6.877
6.856
3.800
3.111
3.093
3.074
2.637
2.618
2.600
2.178
OMe O
N
3da
0.97
1.00
2.03
2.99
2.00
1.99
6.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

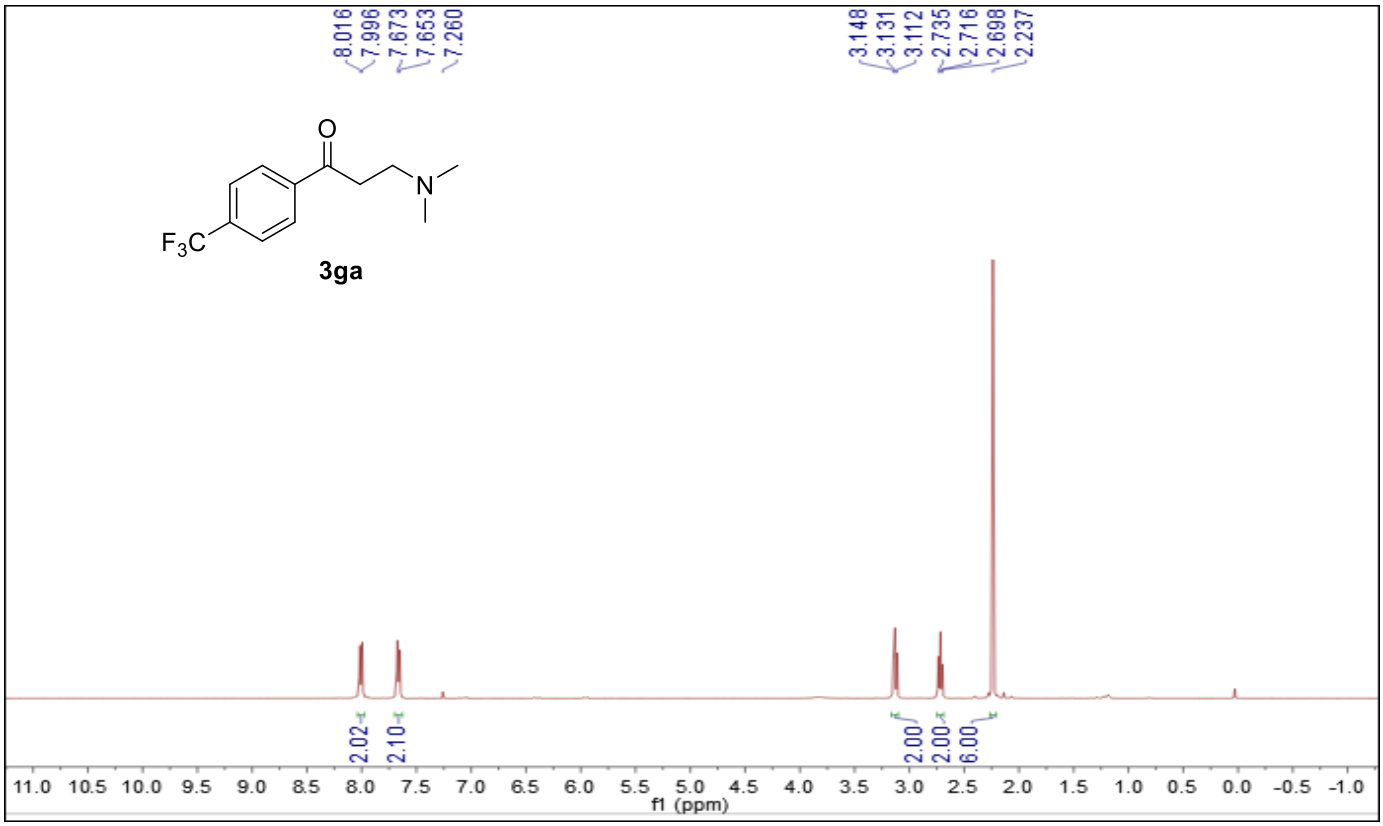

201.396
158.502
133.497
130.302
128.261
120.634
111.514
77.627
77.309
76.990
55.485
54.469
45.491
42.043
OMe O
N
3da
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

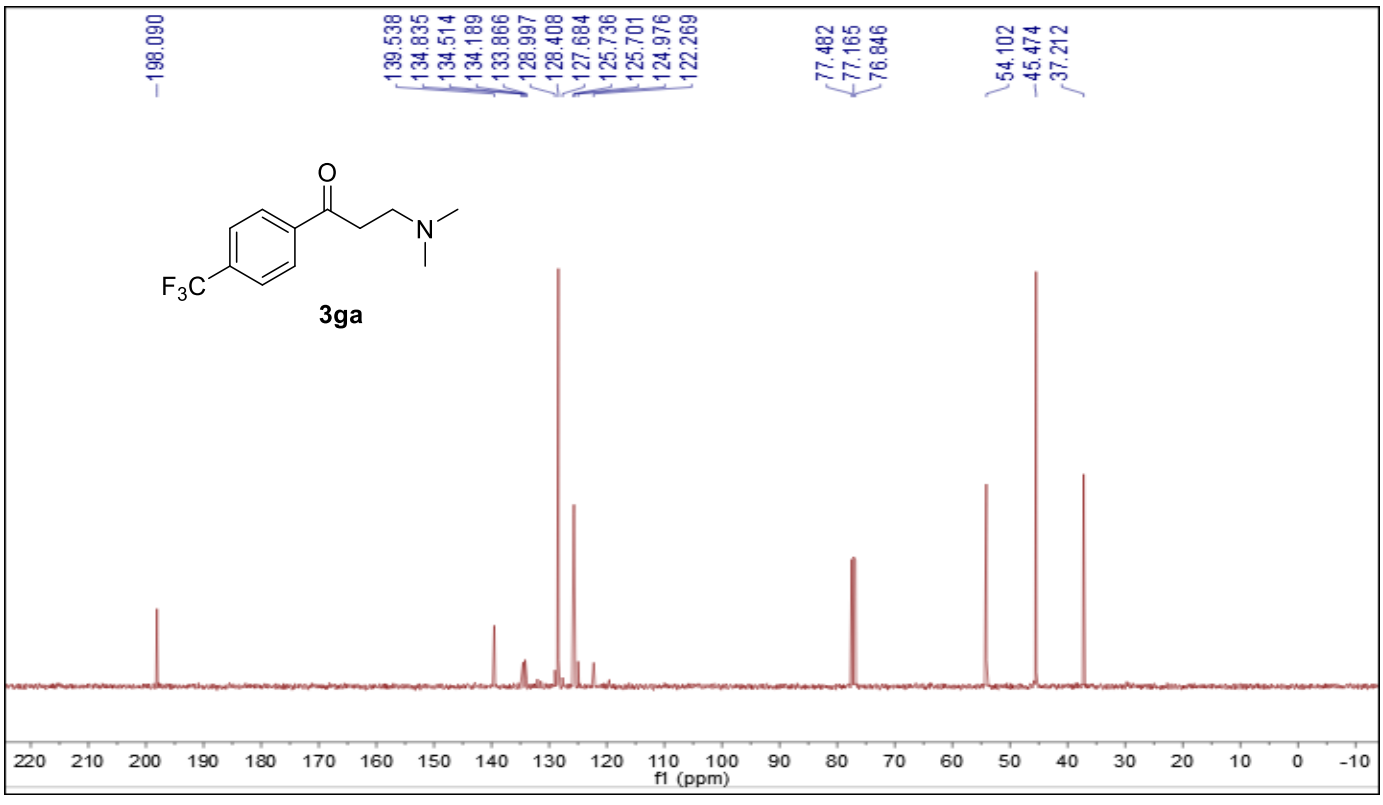

7.953
7.945
7.940
7.928
7.923
7.916
7.260
6.934
6.927
6.922
6.910
6.905
6.897
3.849
3.174
3.156
3.137
2.835
2.816
2.798
2.335
O
N
MeO
3ea
2.04
2.00
3.04
1.97
1.98
6.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

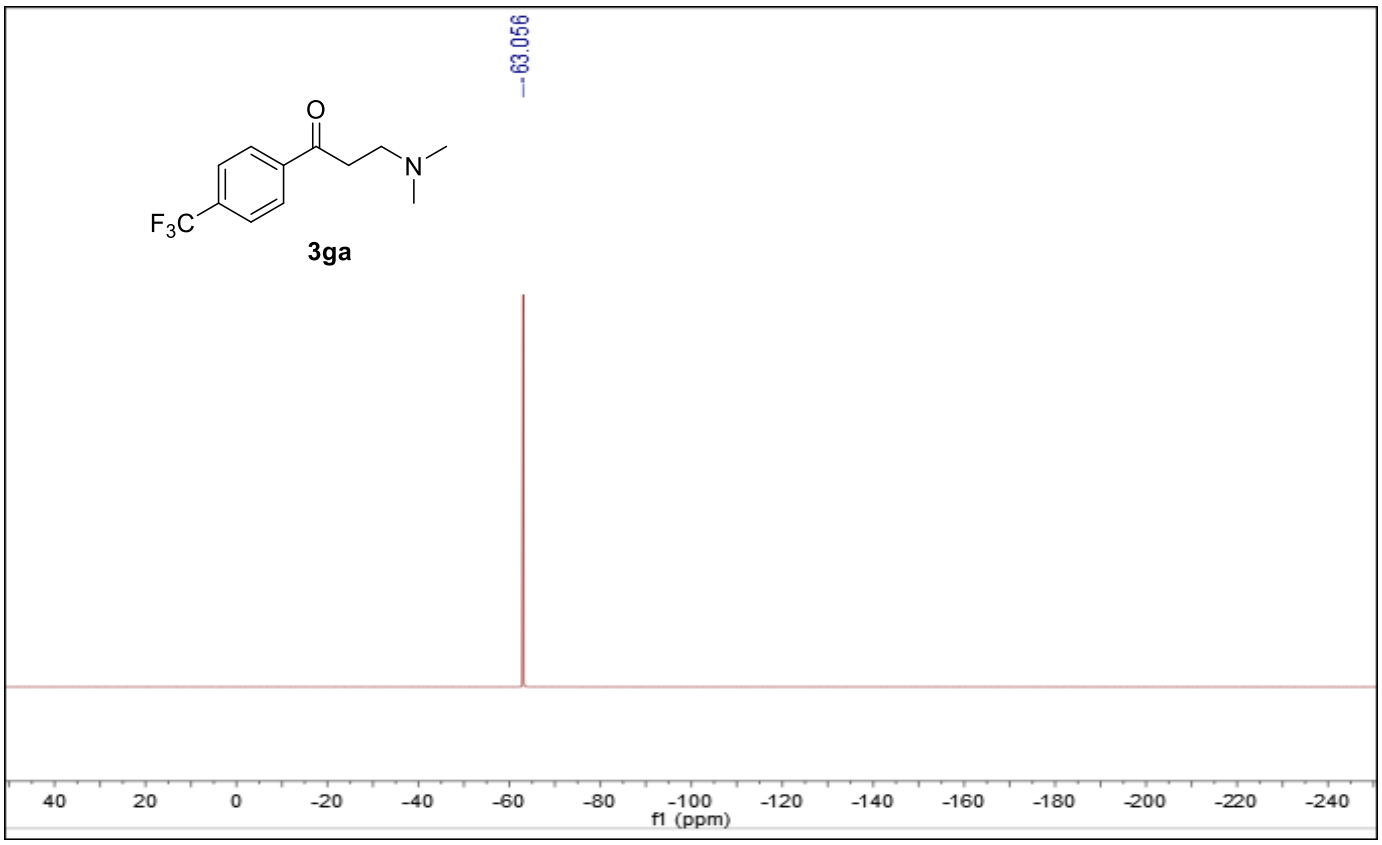

197.349
163.638
130.459
129.878
113.848
77.473
77.155
76.837
55.574
54.375
45.303
36.202
O
N
MeO
3ea
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

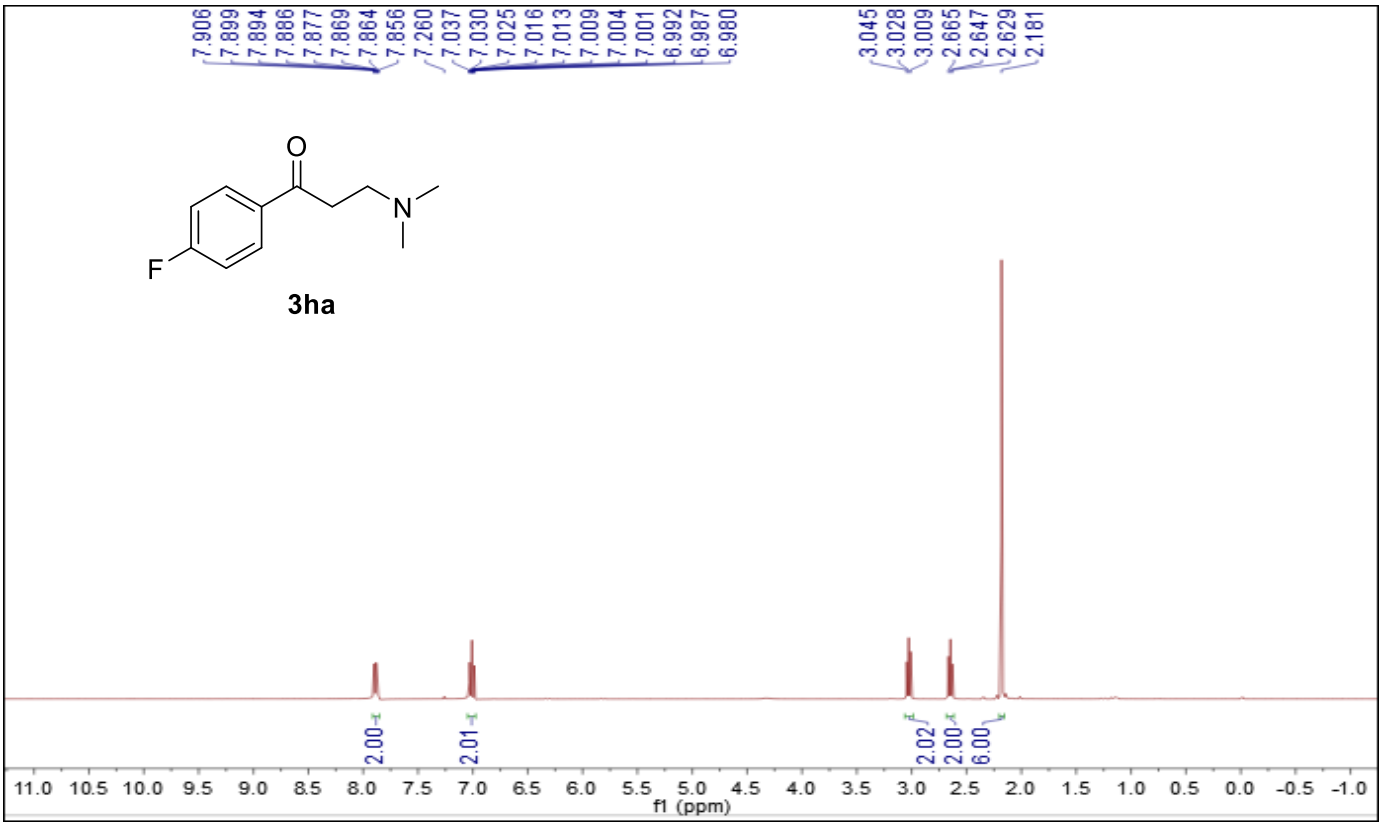

8.319
8.313
8.308
8.296
8.291
8.285
8.120
8.115
8.109
8.097
8.092
8.087
3.213
3.196
3.177
2.788
2.770
2.752
2.284
O
N
O2N
3fa
2.10
2.02
2.03
2.03
6.00
f1 (ppm)

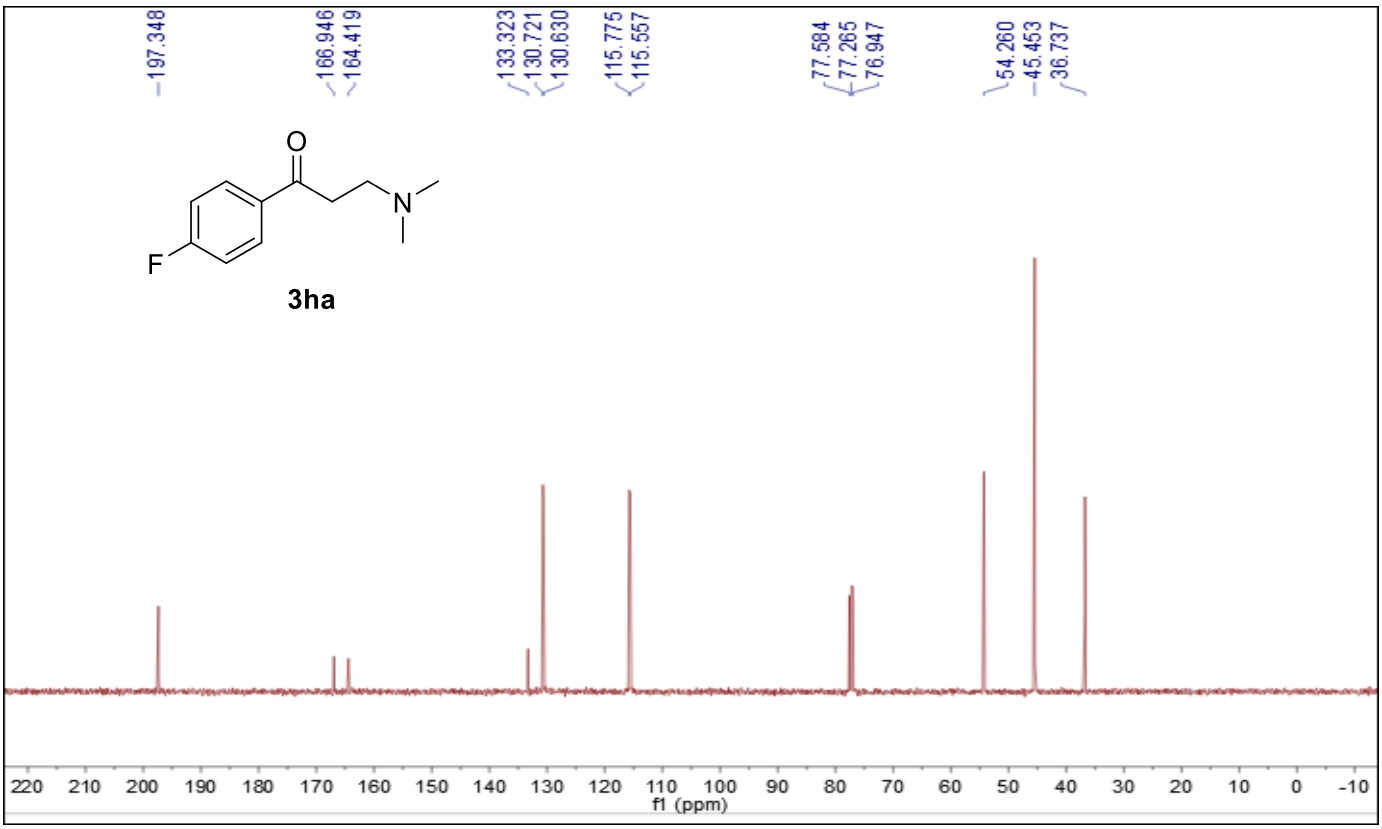

197.625
150.384
141.329
129.167
123.994
77.460
77.141
76.823
53.978
45.519
37.504
O
N
O2N
3fa
f1 (ppm)

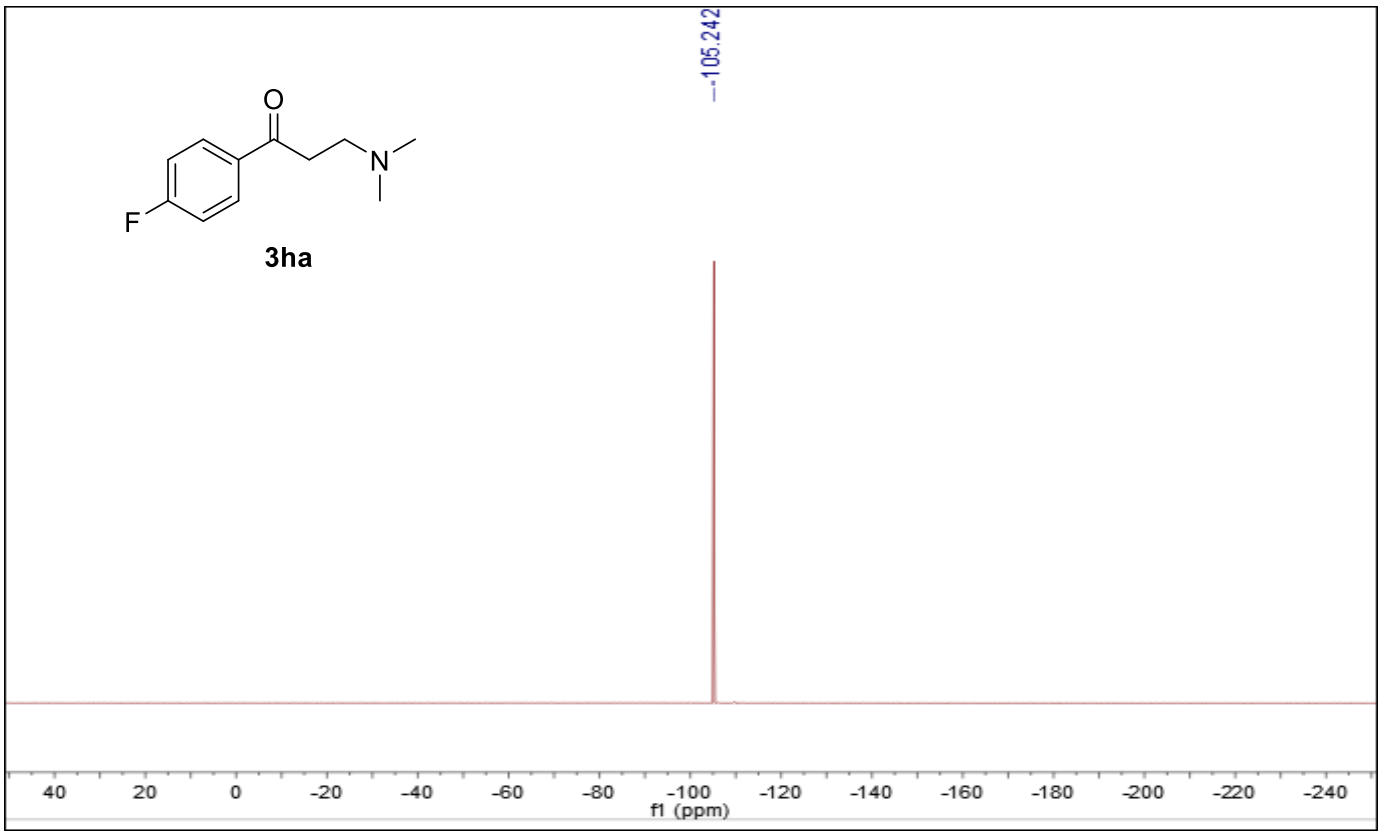

8.016
7.996
7.673
7.653
7.260
3.148
3.131
3.112
2.735
2.716
2.698
2.237
O
N
F3C
3ga
2.02
2.10
2.00
2.00
6.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

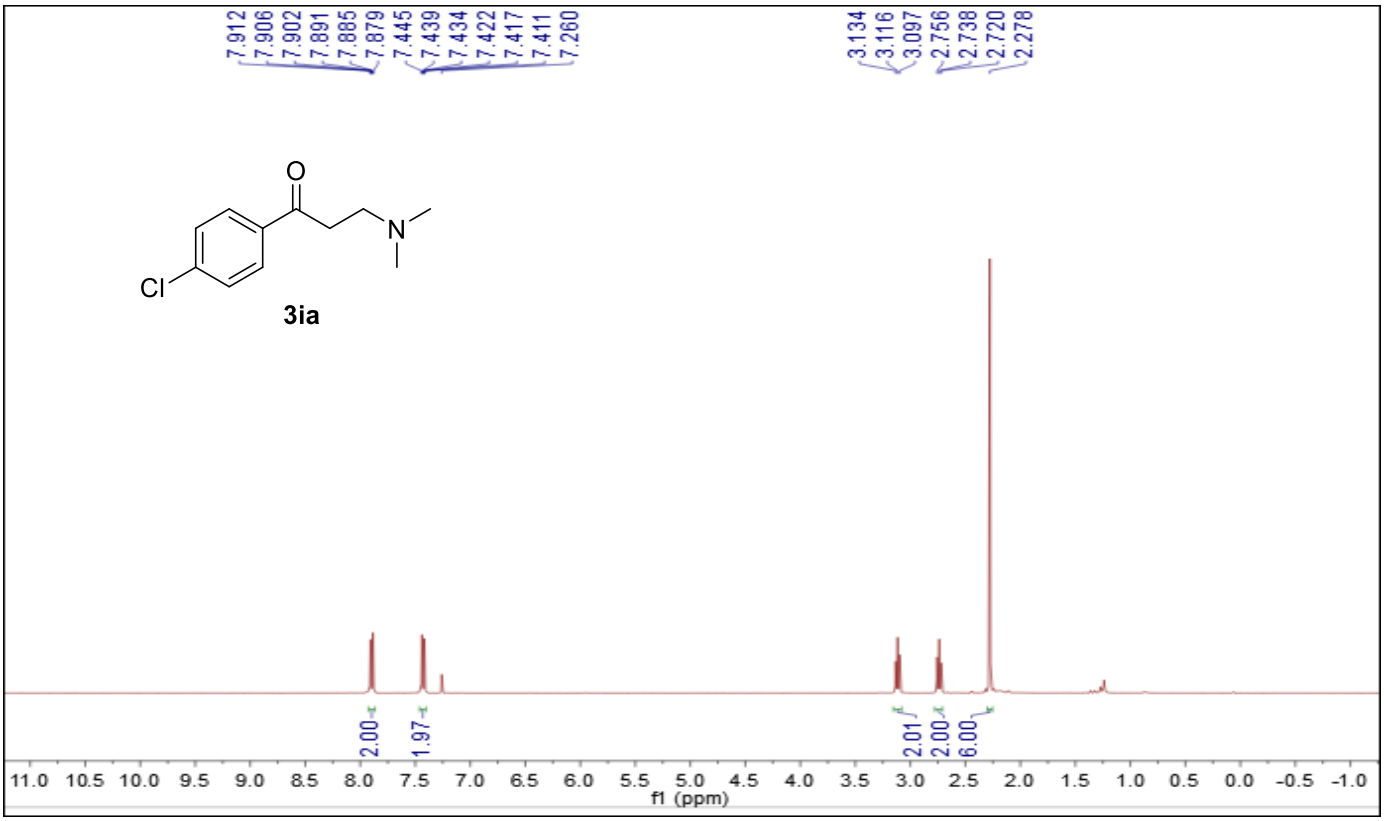

198.090
139.538
134.835
134.514
134.189
133.866
128.997
128.408
127.684
125.736
125.701
124.976
122.269
77.482
77.165
76.846
54.102
45.474
37.212
O
N
F3C
3ga
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-63.056
O
N
F3C
3ga
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)


7.906
7.899
7.894
7.886
7.877
7.869
7.864
7.856
7.260
7.037
7.030
7.025
7.016
7.013
7.009
7.004
7.001
6.992
6.987
6.980
3.045
3.028
3.009
2.665
2.647
2.629
2.181
O
N
F
3ha
2.00
2.01
2.02
2.00
6.00
11.0 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 -0.5 -1.0
f1 (ppm)


197.348
166.946
164.419
133.323
130.721
130.630
115.775
115.557
77.584
77.265
76.947
54.260
45.453
36.737
O
N
F
3ha
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-105.242
O
N
F
3ha
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)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7.902
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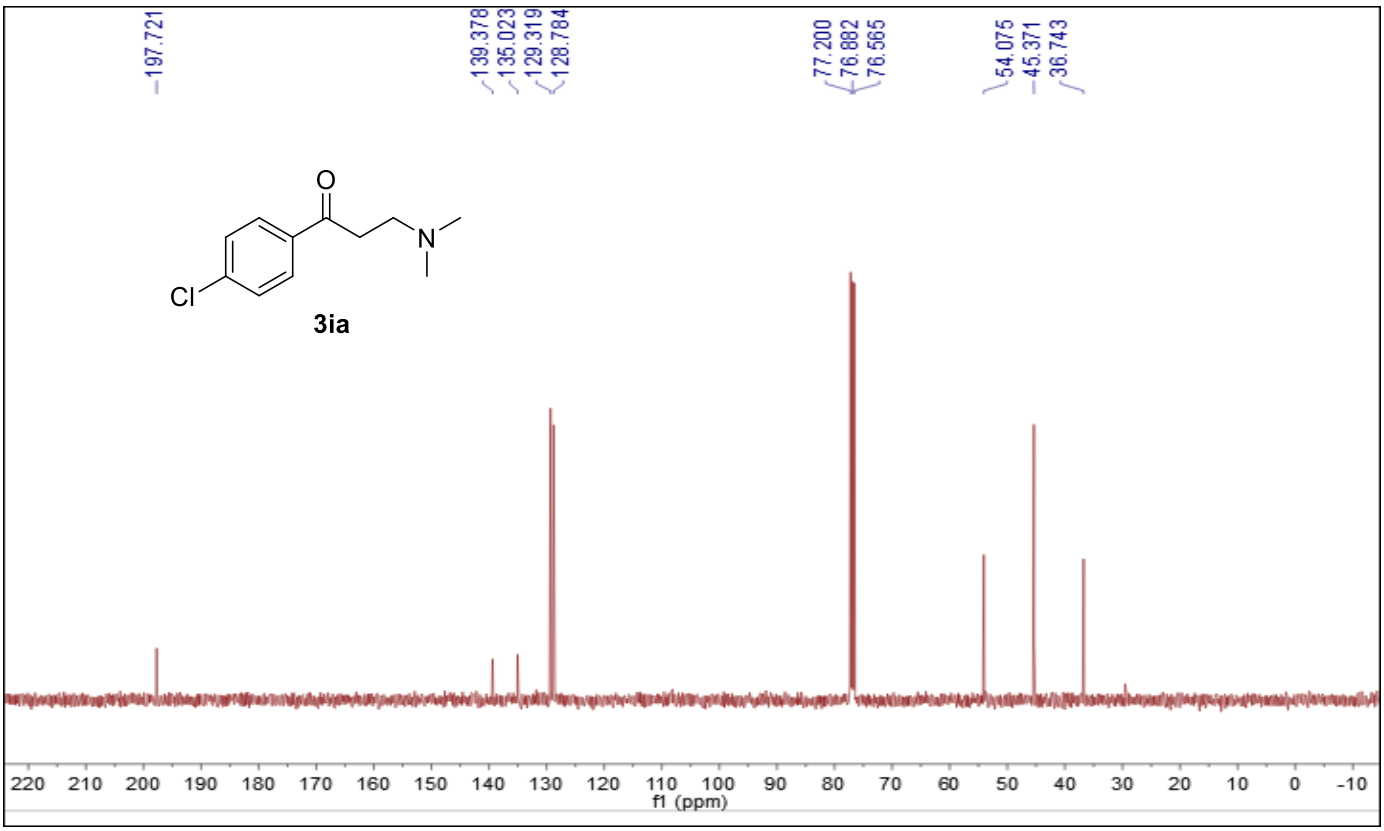
7.879
7.445
7.439
7.434
7.422
7.417
7.411
7.260
3.134
3.116
3.097
2.756
2.738
2.720
2.278
O
N
Cl
3ia
2.00
1.97
2.01
2.00
6.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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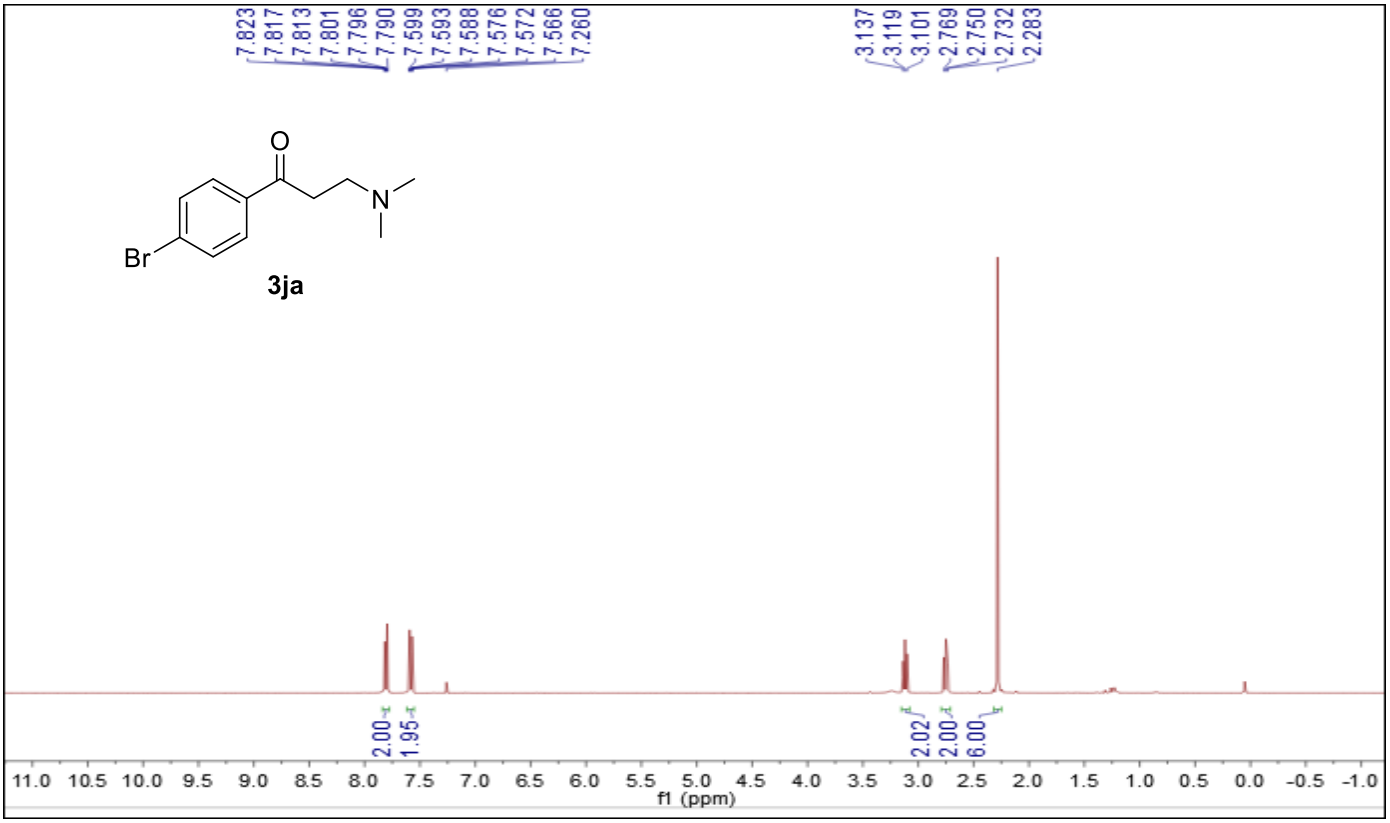
135.023
129.319
128.784
77.200
76.882
76.565
54.075
45.371
36.743
O
N
Cl
3ia
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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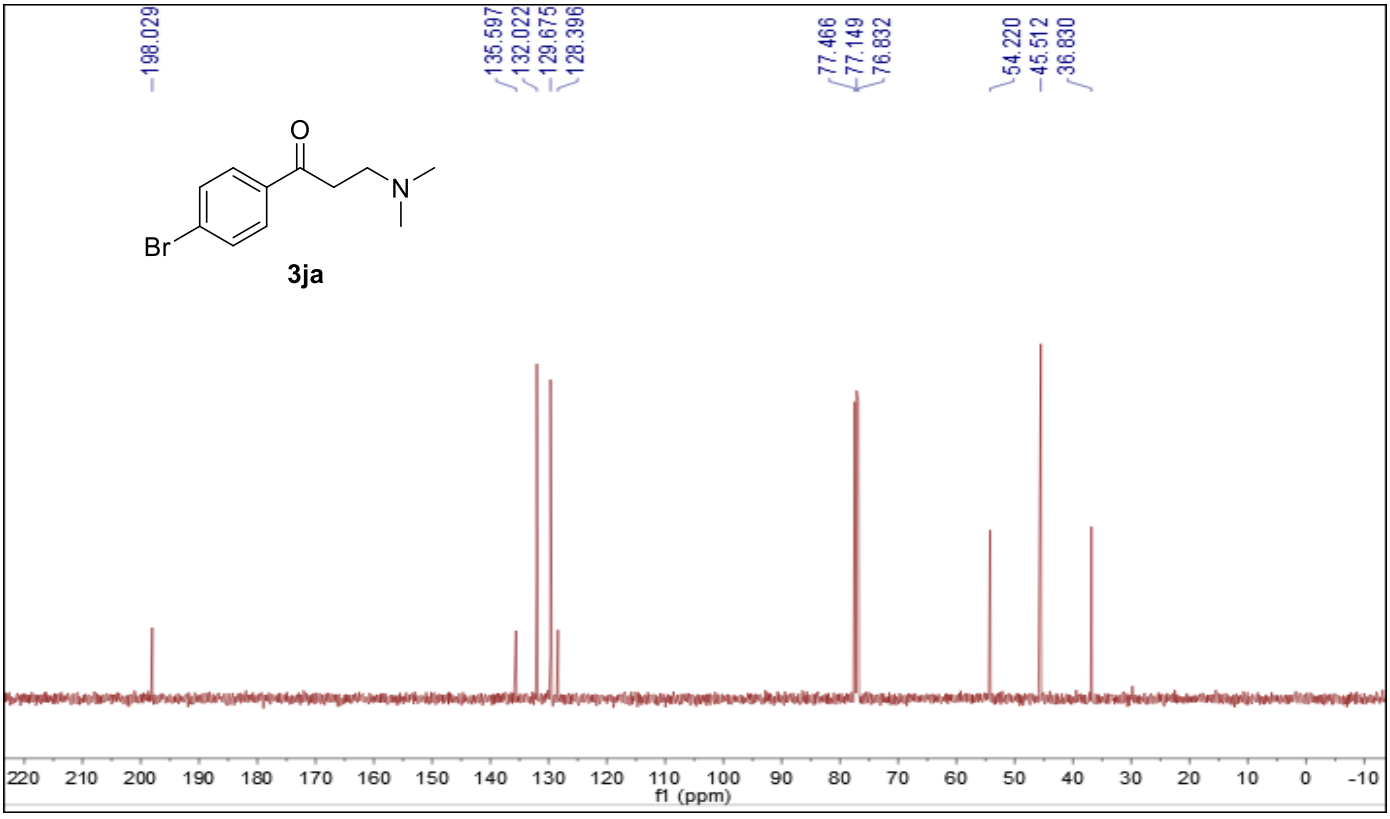
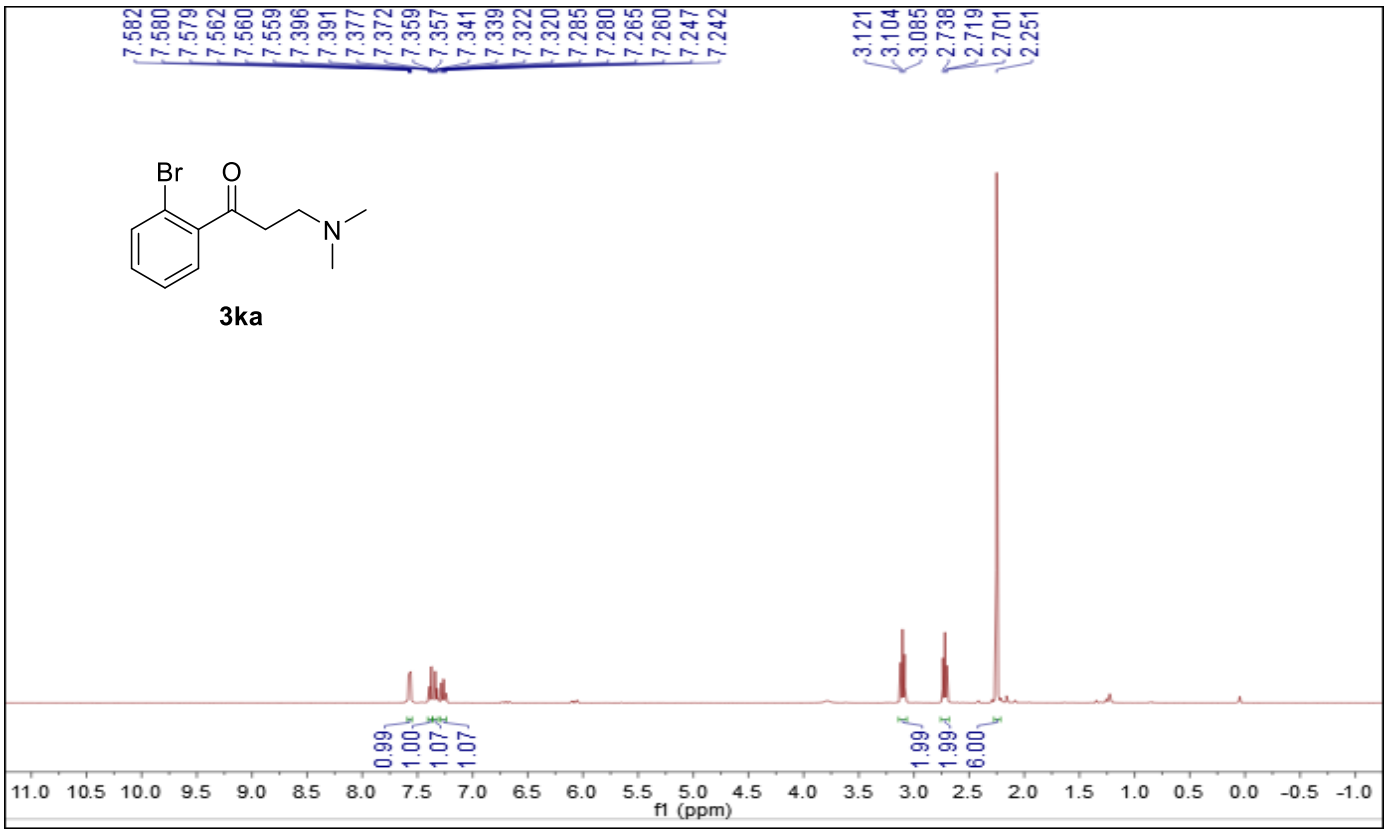
7.813
7.801
7.796
7.790
7.599
7.593
7.588
7.576
7.572
7.566
7.260
3.137
3.119
3.101
2.769
2.750
2.732
2.283
O
N
Br
3ja
2.00
1.95
2.02
2.00
6.00
f1 (ppm)


198.029
135.597
132.022
129.675
128.396
77.466
77.149
76.832
54.220
45.512
36.830
O
N
Br
3ja
f1 (ppm)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7.391
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7.372
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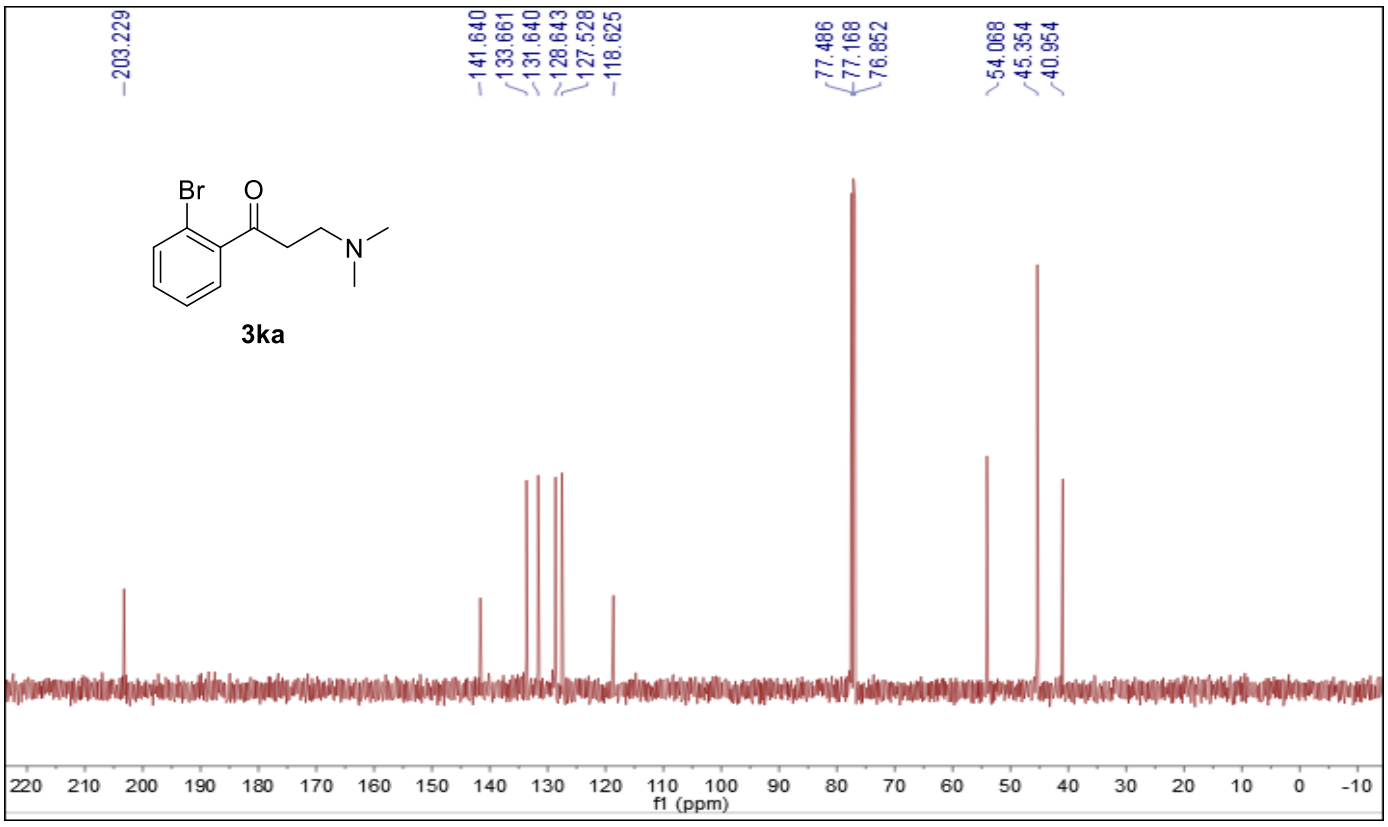
7.339
7.322
7.320
7.285
7.280
7.265
7.260
7.247
7.242
3.121
3.104
3.085
2.738
2.719
2.701
2.251
Br
O
N
3ka
0.99
1.00
1.07
1.07
1.99
1.99
6.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


203.229
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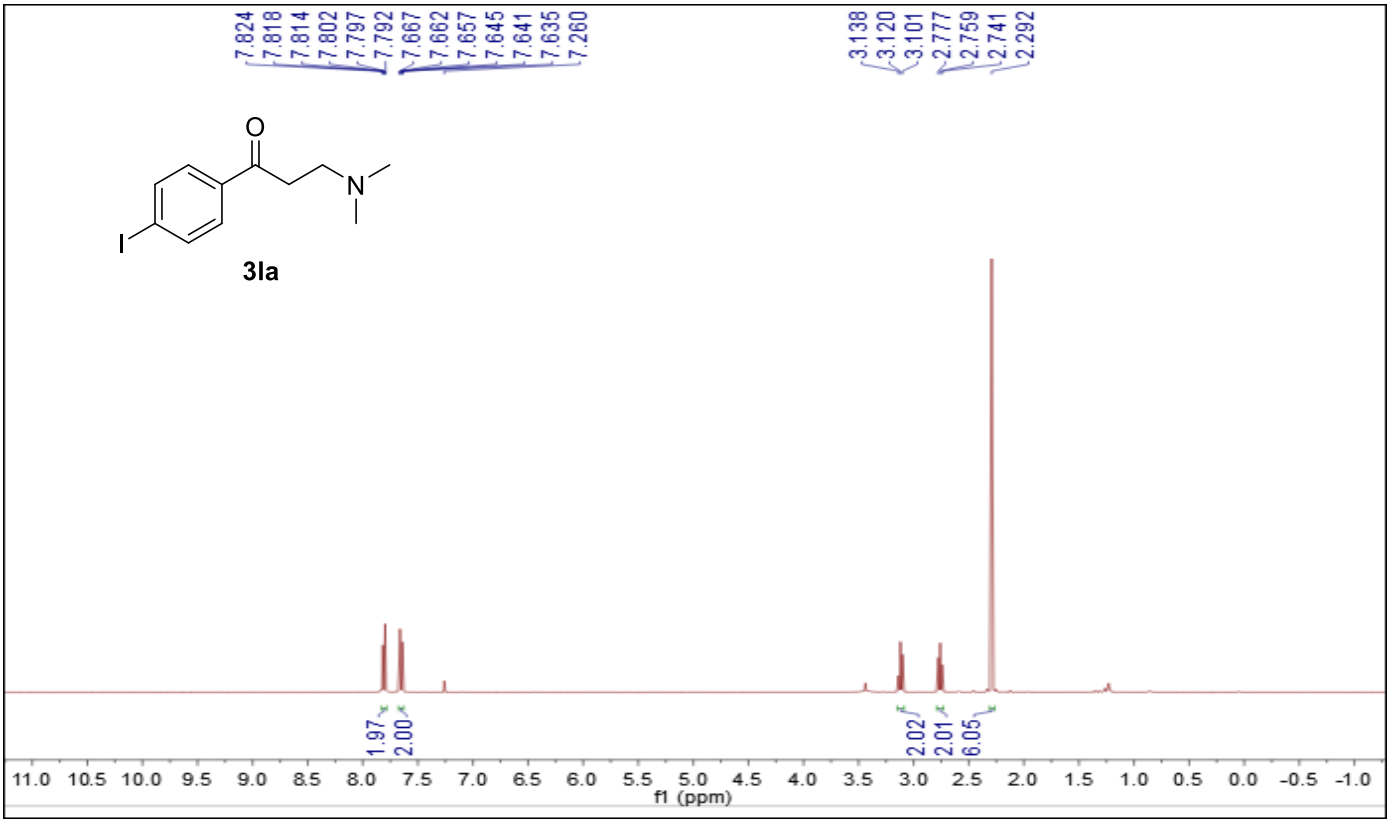
131.640
128.643
127.528
118.625
77.486
77.168
76.852
54.068
45.354
40.954
Br
O
N
3ka
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.667
7.662
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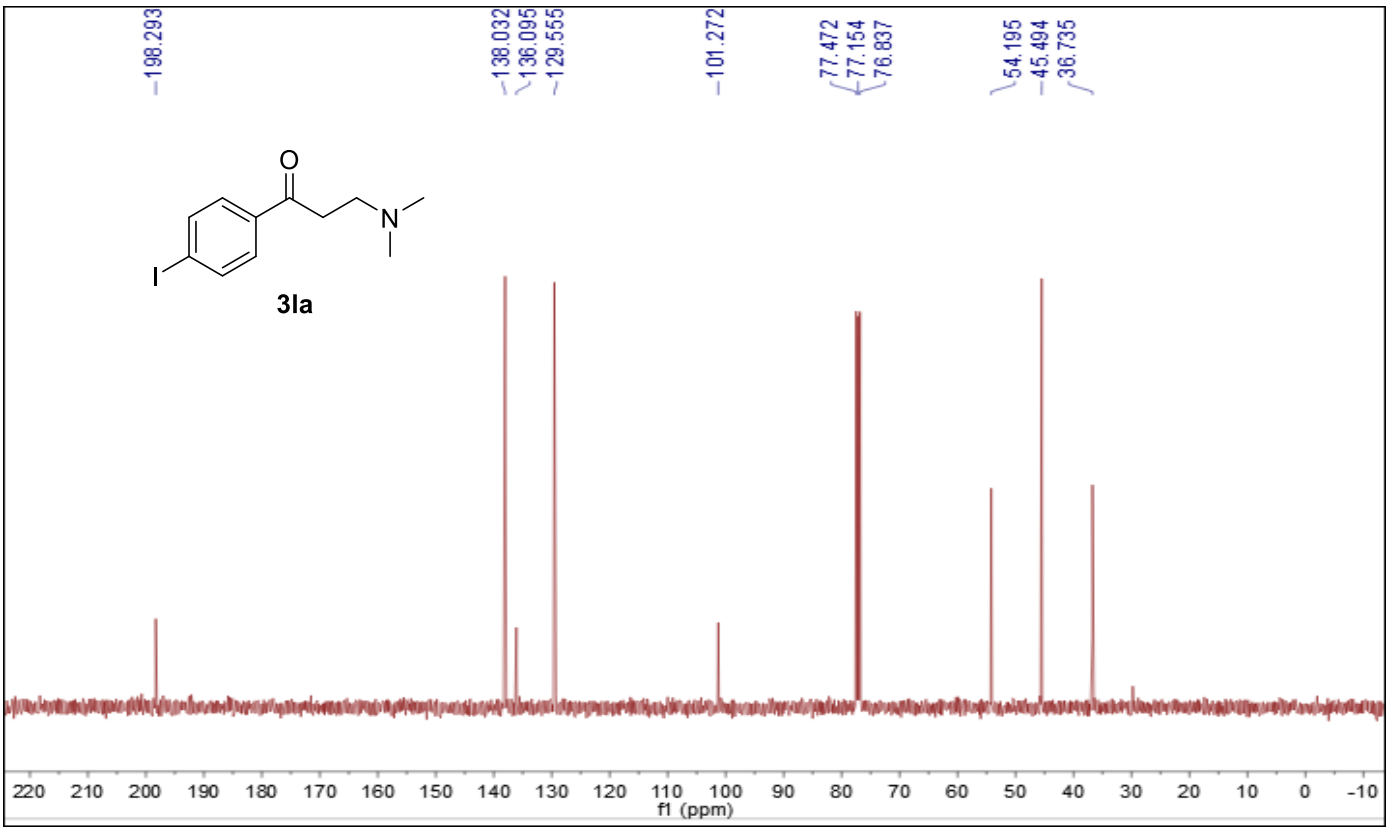
7.645
7.641
7.635
7.260
3.138
3.120
3.101
2.777
2.759
2.741
2.292
O
N
I
3Ia
1.97
2.00
2.02
2.01
6.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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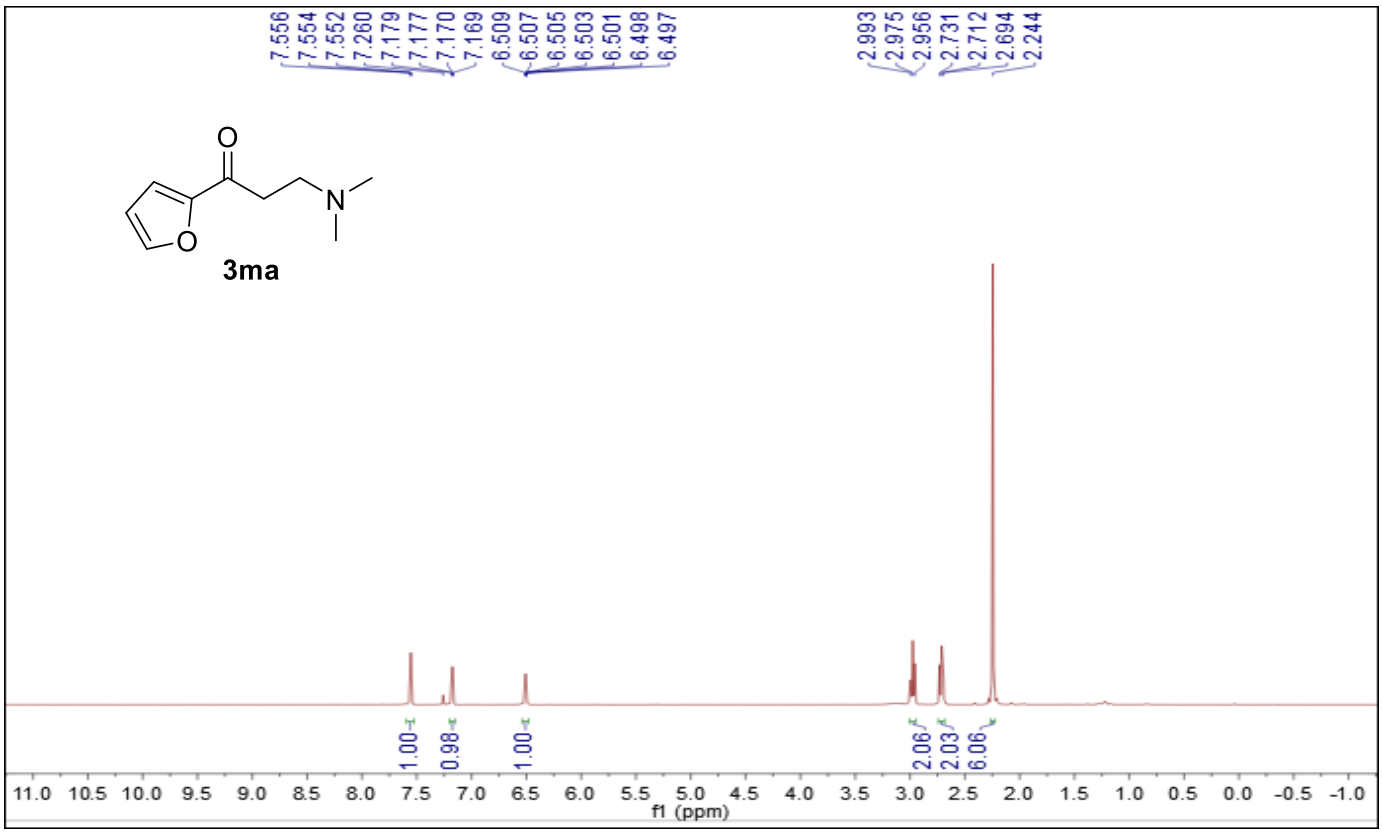
129.555
101.272
77.472
77.154
76.837
54.195
45.494
36.735
O
N
I
3Ia
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.552
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7.170
7.169
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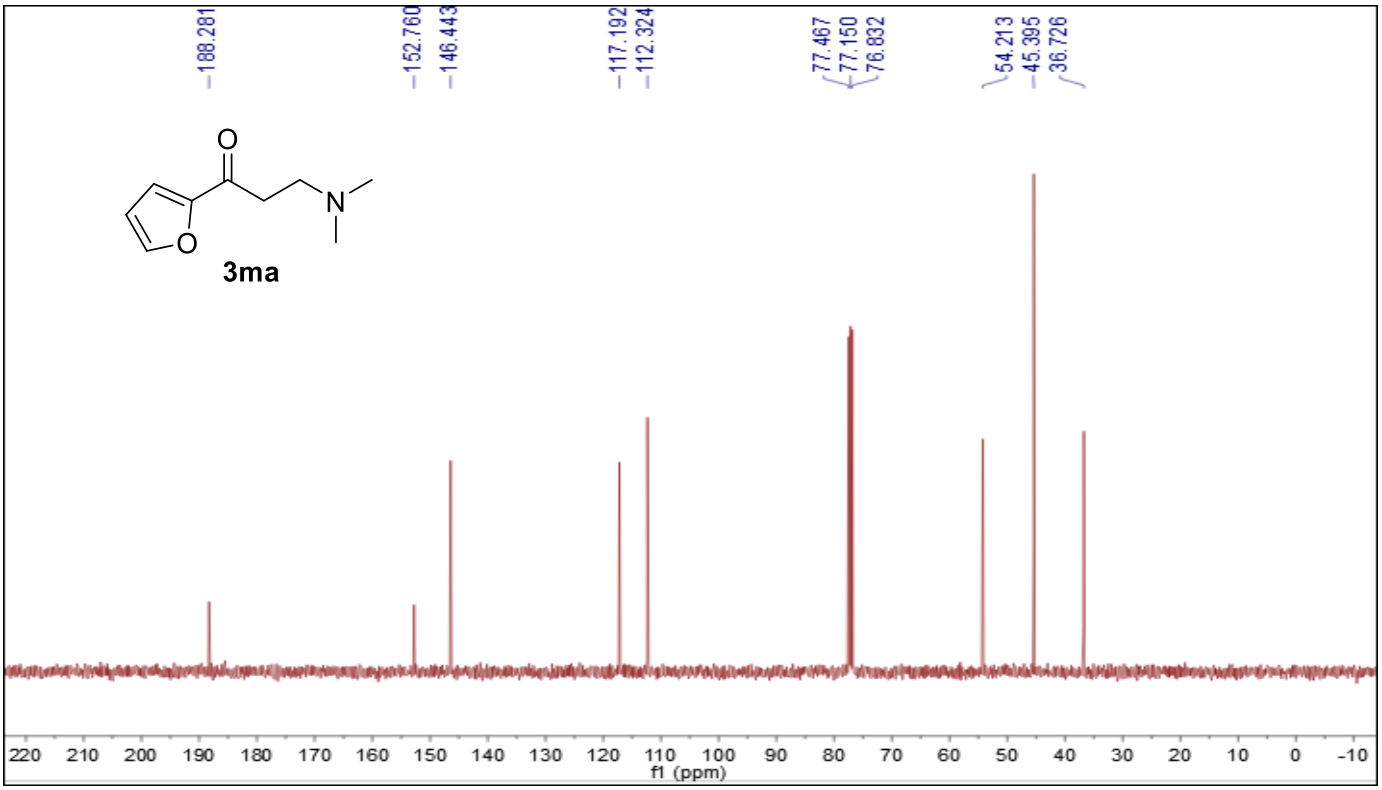
6.507
6.505
6.503
6.501
6.498
6.497
2.993
2.975
2.956
2.731
2.712
2.694
2.244
O
N
O
3ma
1.00
0.98
1.00
2.06
2.03
6.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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152.760
146.443
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77.150
76.832
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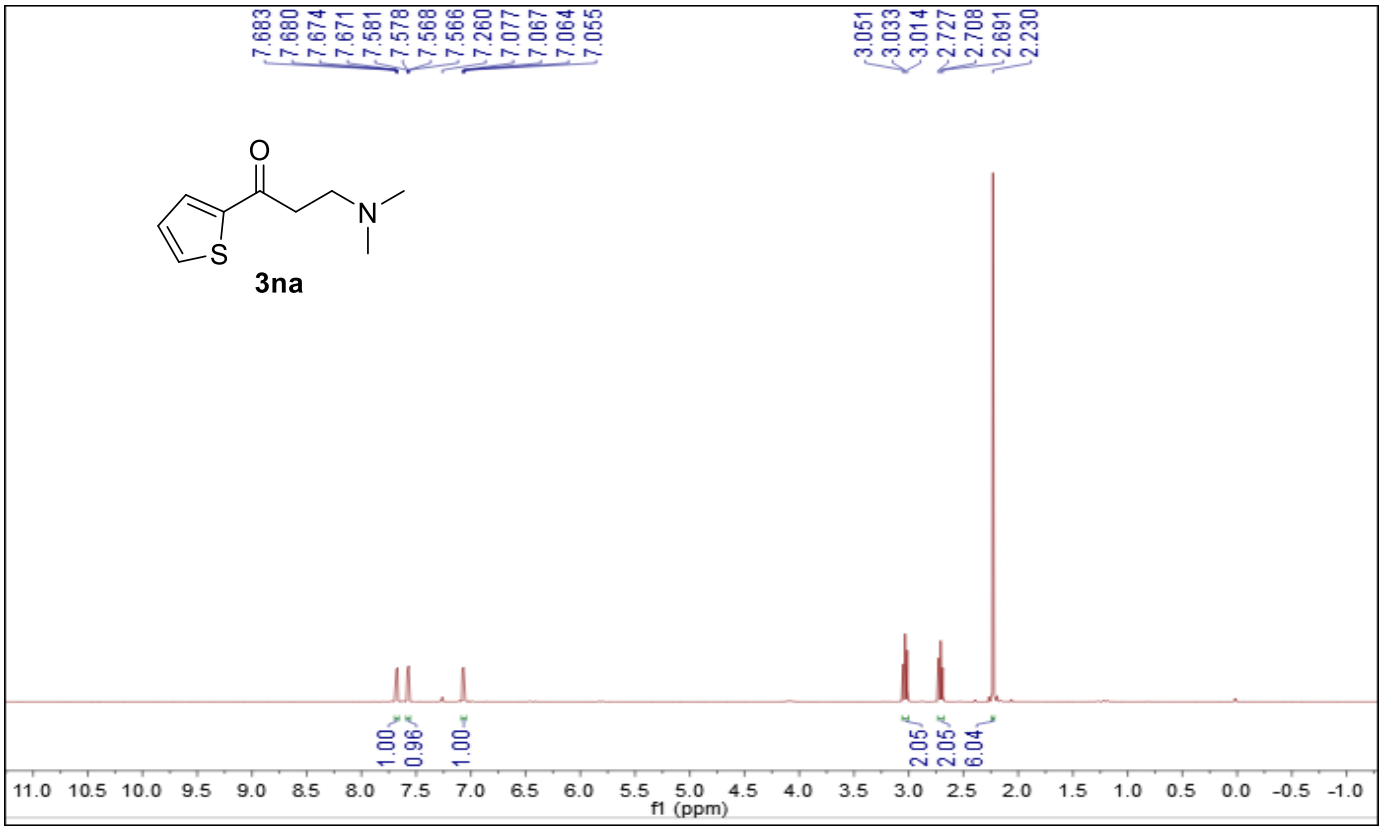
N
O
3ma
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.566
7.260
7.077
7.067
7.064
7.055
3.051
3.033
3.014
2.727
2.708
2.691
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O
N
S
3na
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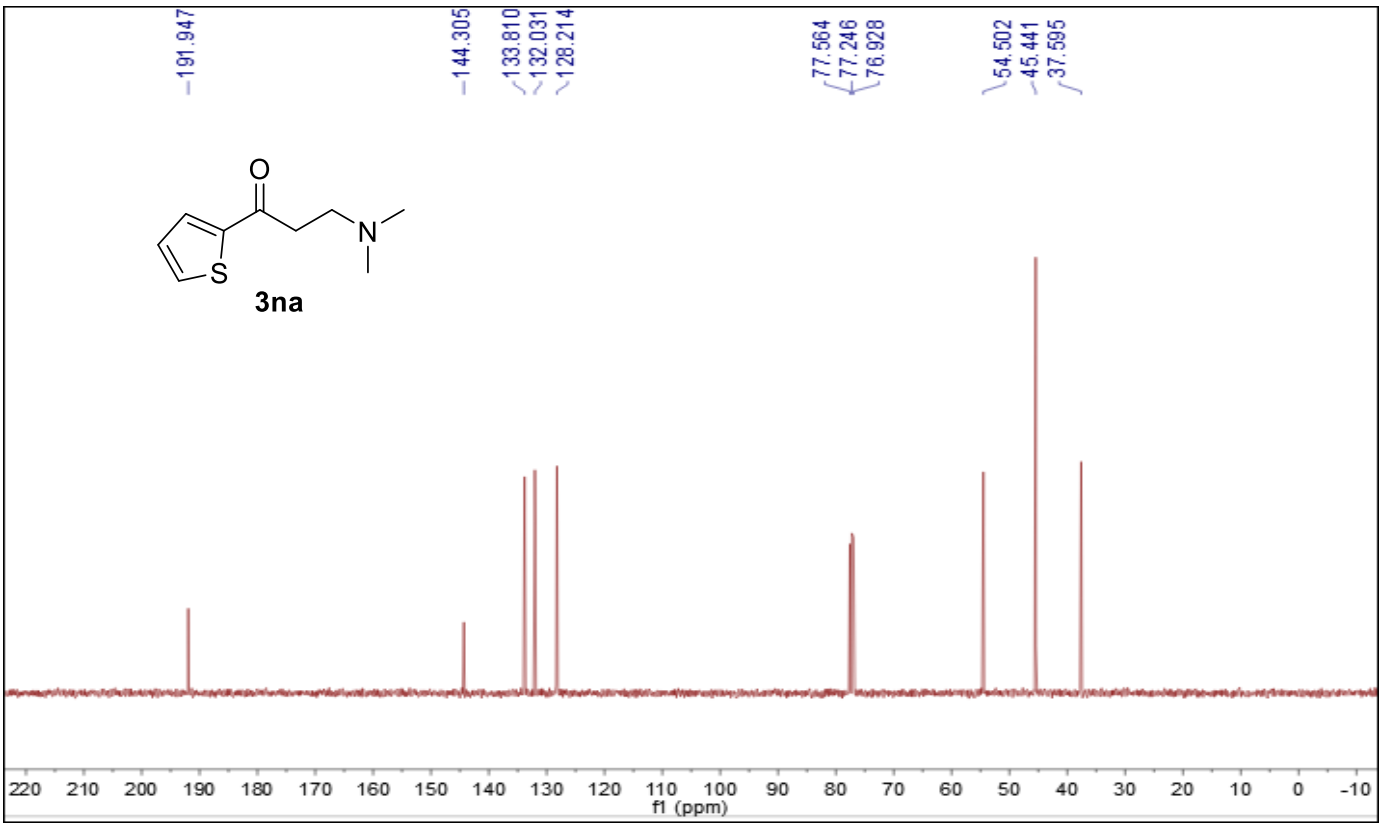
1.00
2.05
2.05
6.04
f1 (ppm)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133.810
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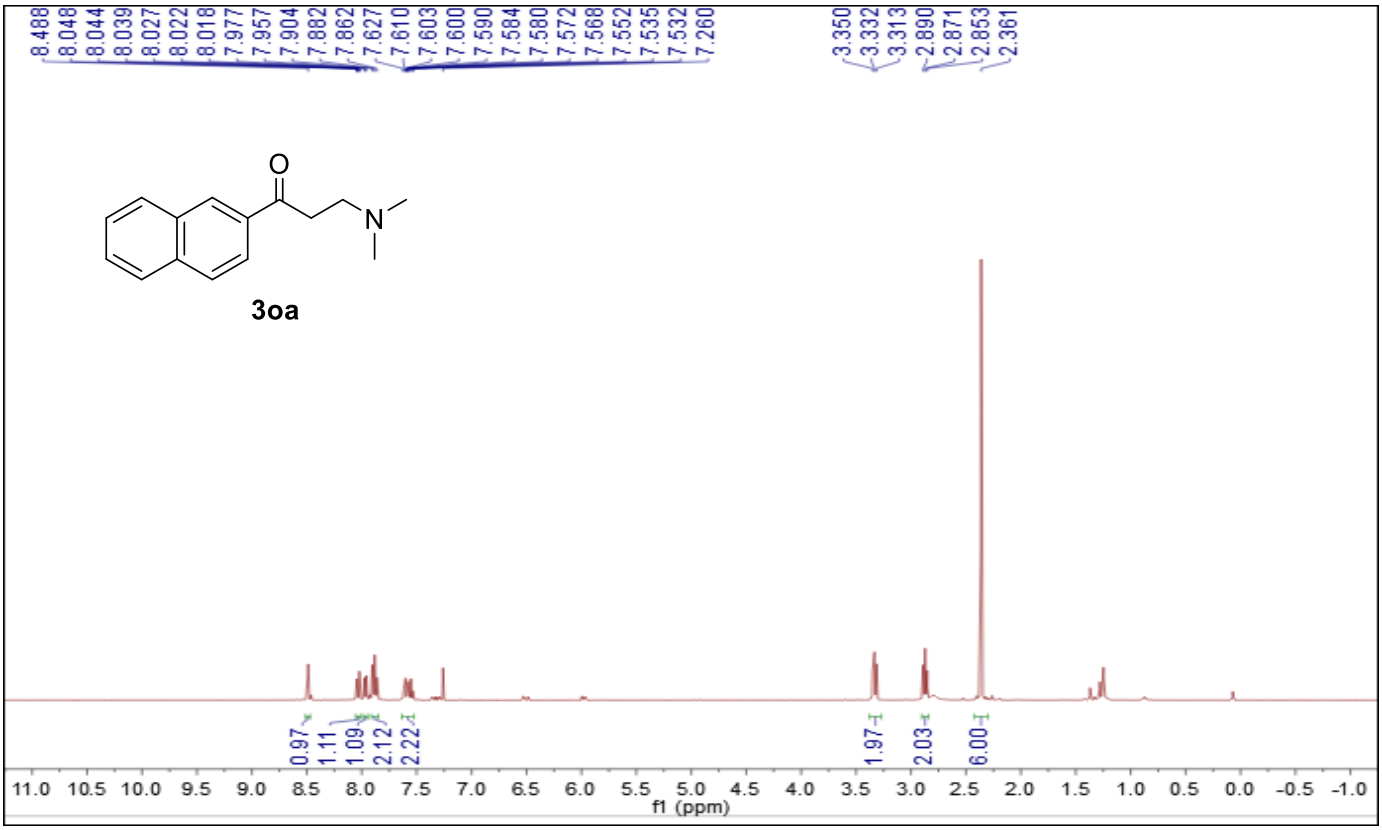
77.246
76.928
54.502
45.441
37.595
O
N
S
3na
f1 (ppm)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7.862
7.627
7.610
7.603
7.600
7.590
7.584
7.580
7.572
7.568
7.552
7.535
7.532
7.260
3.350
3.332
3.313
2.890
2.871
2.853
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N
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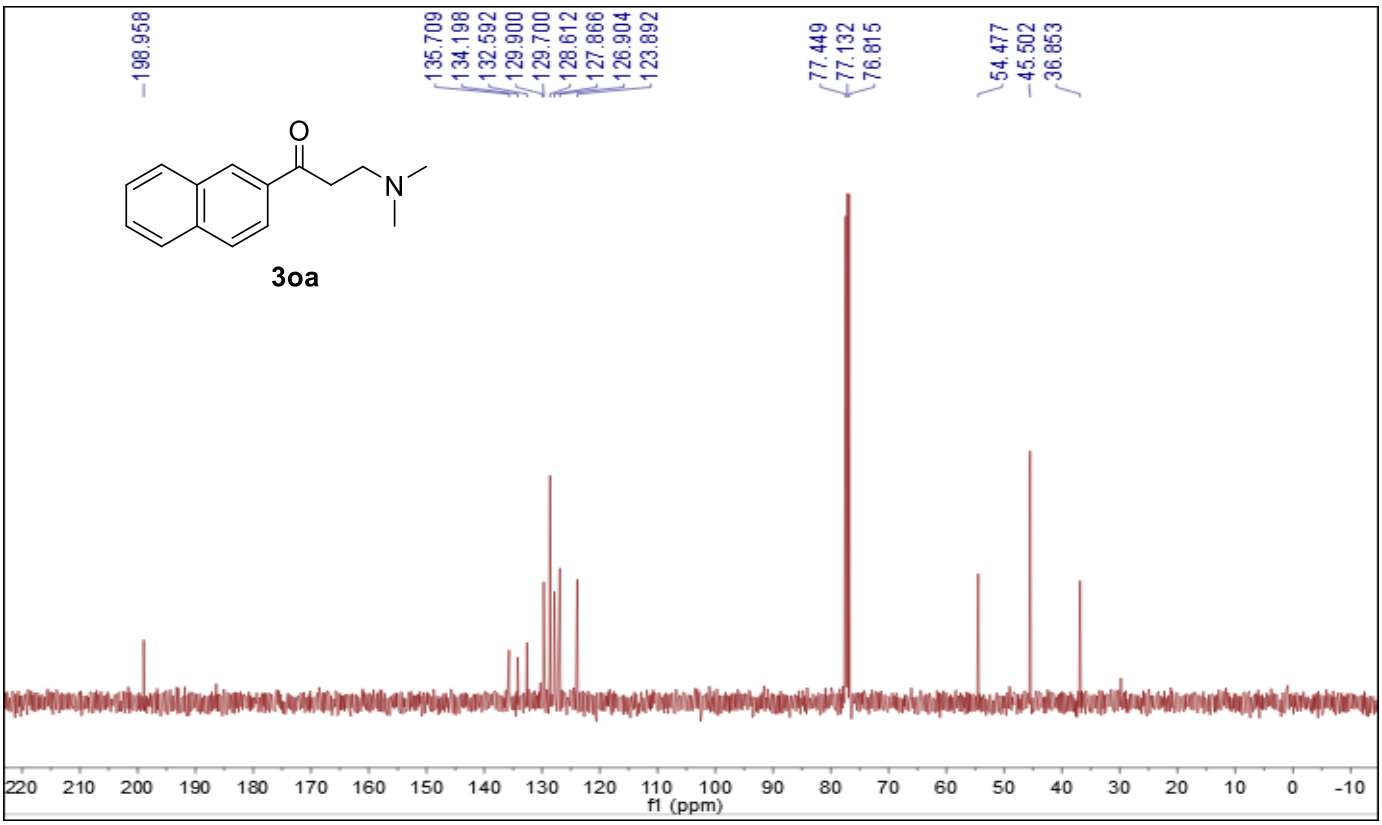
1.11
1.09
2.12
2.22
1.97
2.03
6.00
f1 (ppm)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127.866
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77.132
76.815
54.477
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36.853
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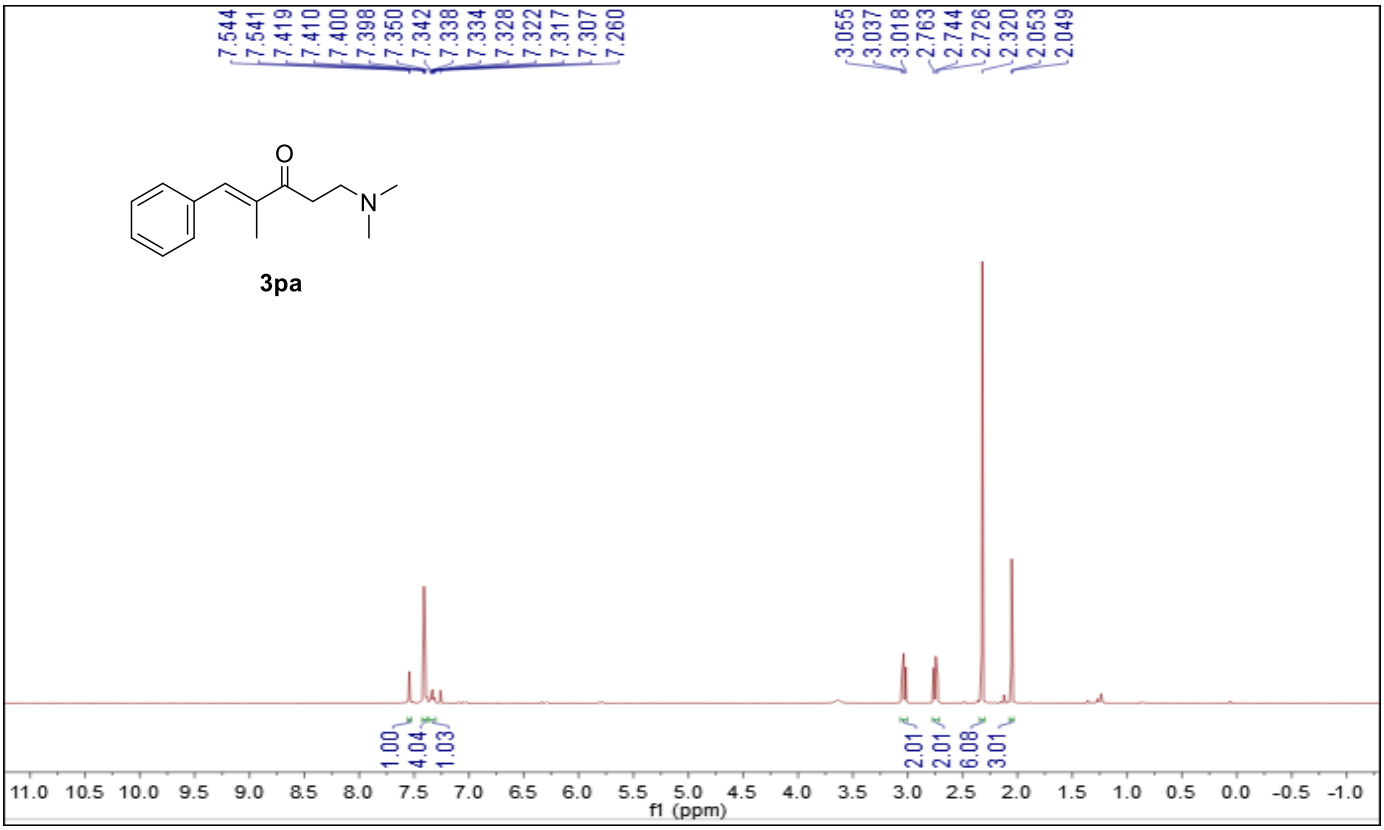
N
3oa
f1 (ppm)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7.398
7.350
7.342
7.338
7.334
7.328
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7.317
7.307
7.260
3.055
3.037
3.018
2.763
2.744
2.726
2.320
2.053
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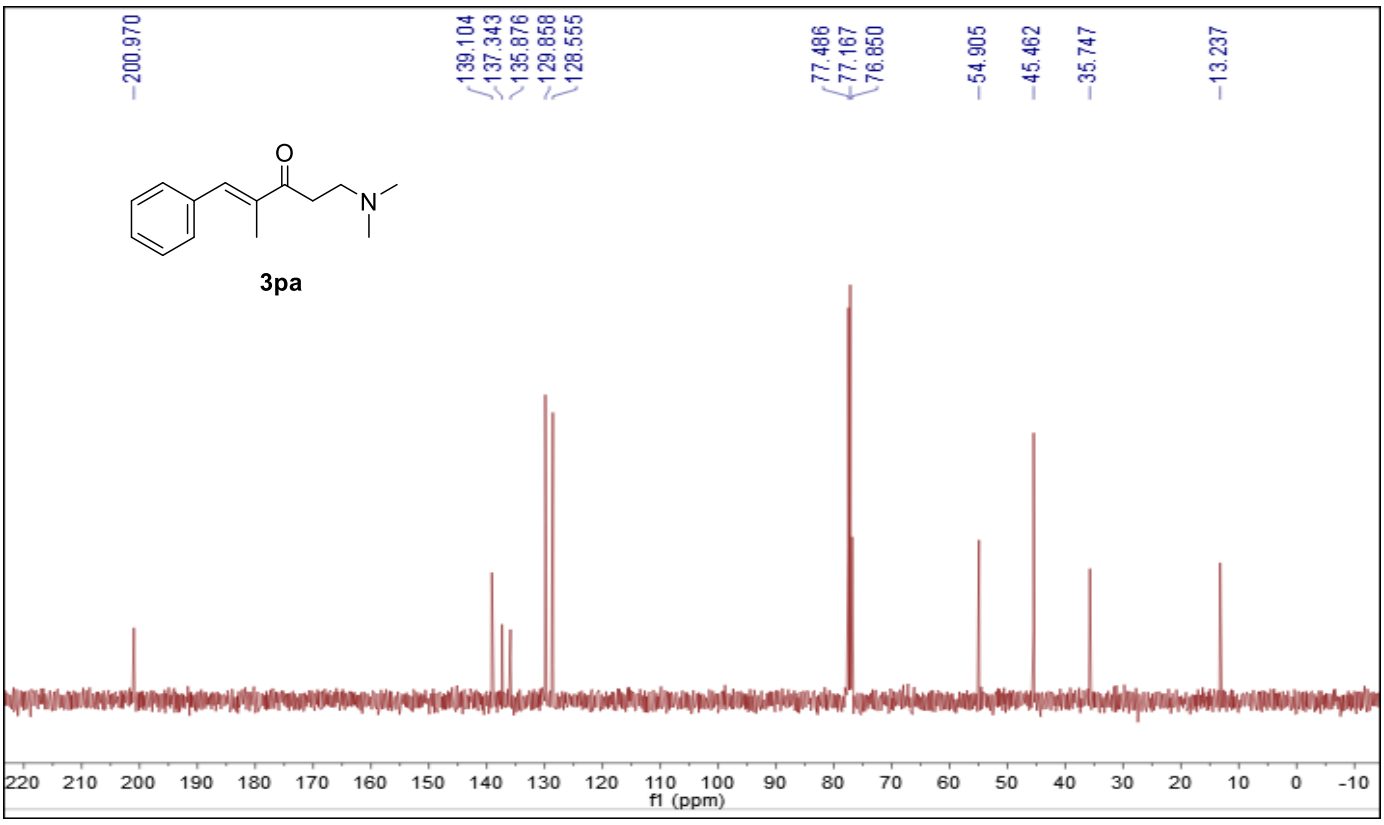
N
3pa
1.00
4.04
1.03
2.01
2.01
6.08
3.01
f1 (ppm)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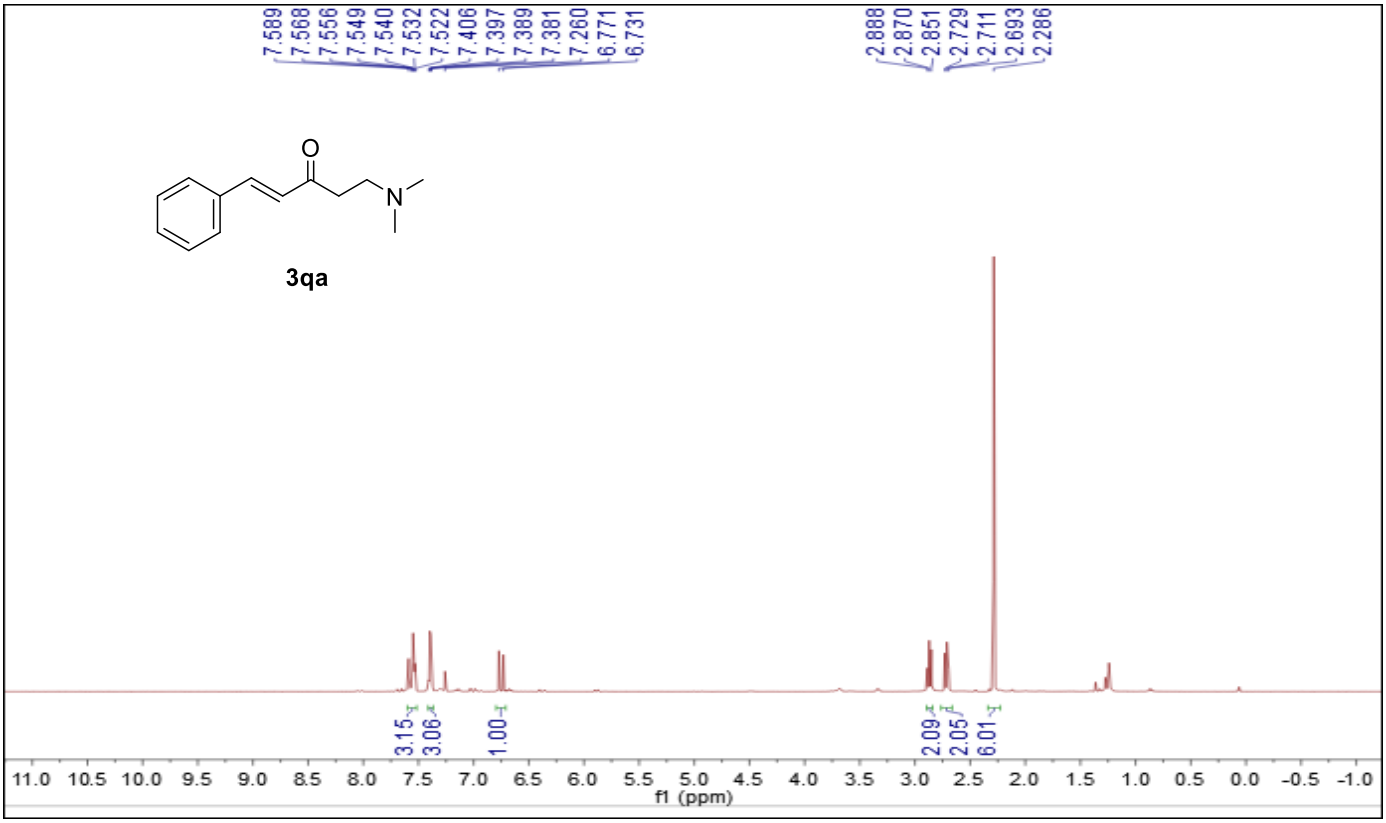
13.237
O
N
3pa
f1 (ppm)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7.556
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7.540
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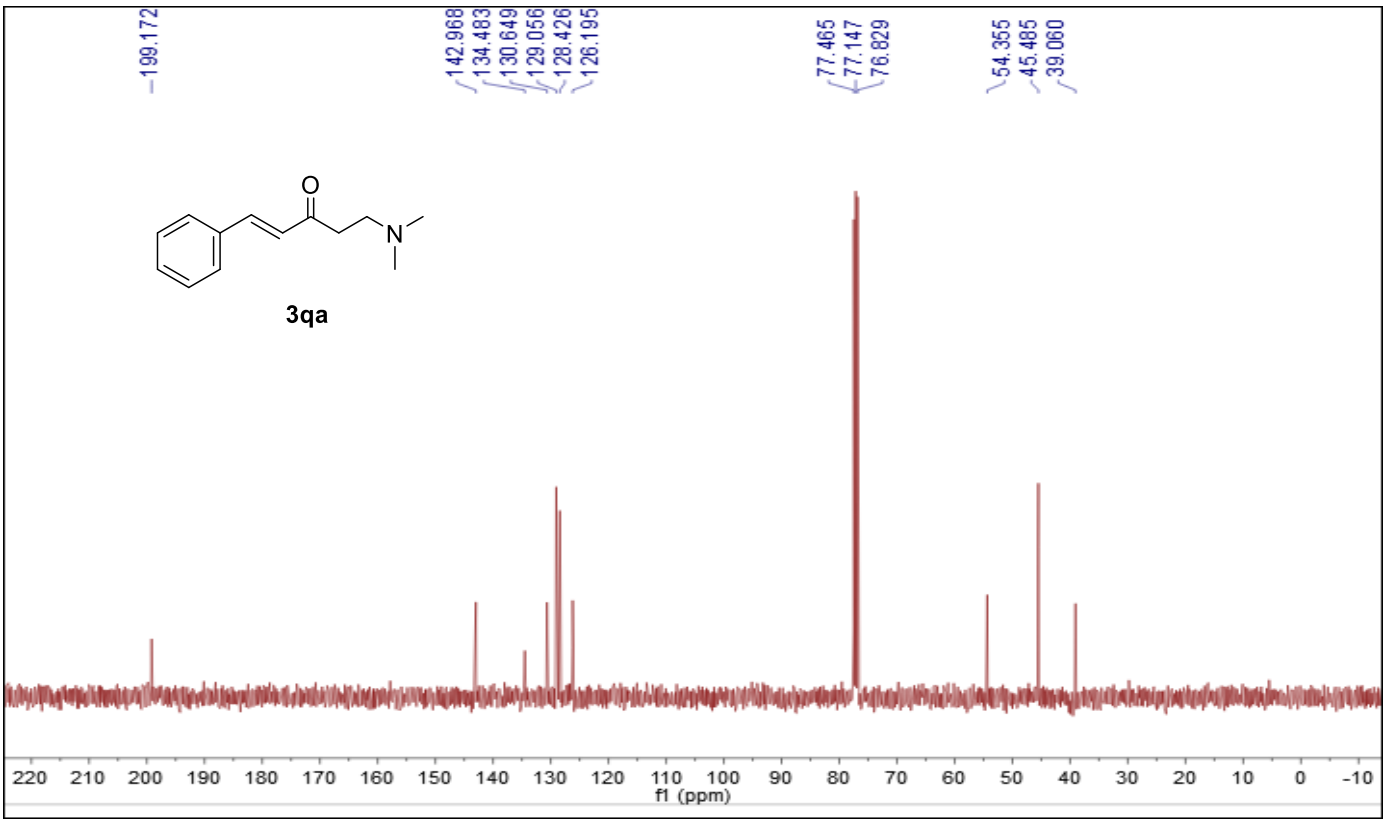
7.522
7.406
7.397
7.389
7.381
7.260
6.771
6.731
2.888
2.870
2.851
2.729
2.711
2.693
2.286
O
N
3qa
3.15
3.06
1.00
2.09
2.05
6.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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134.483
130.649
129.056
128.426
126.195
77.465
77.147
76.829
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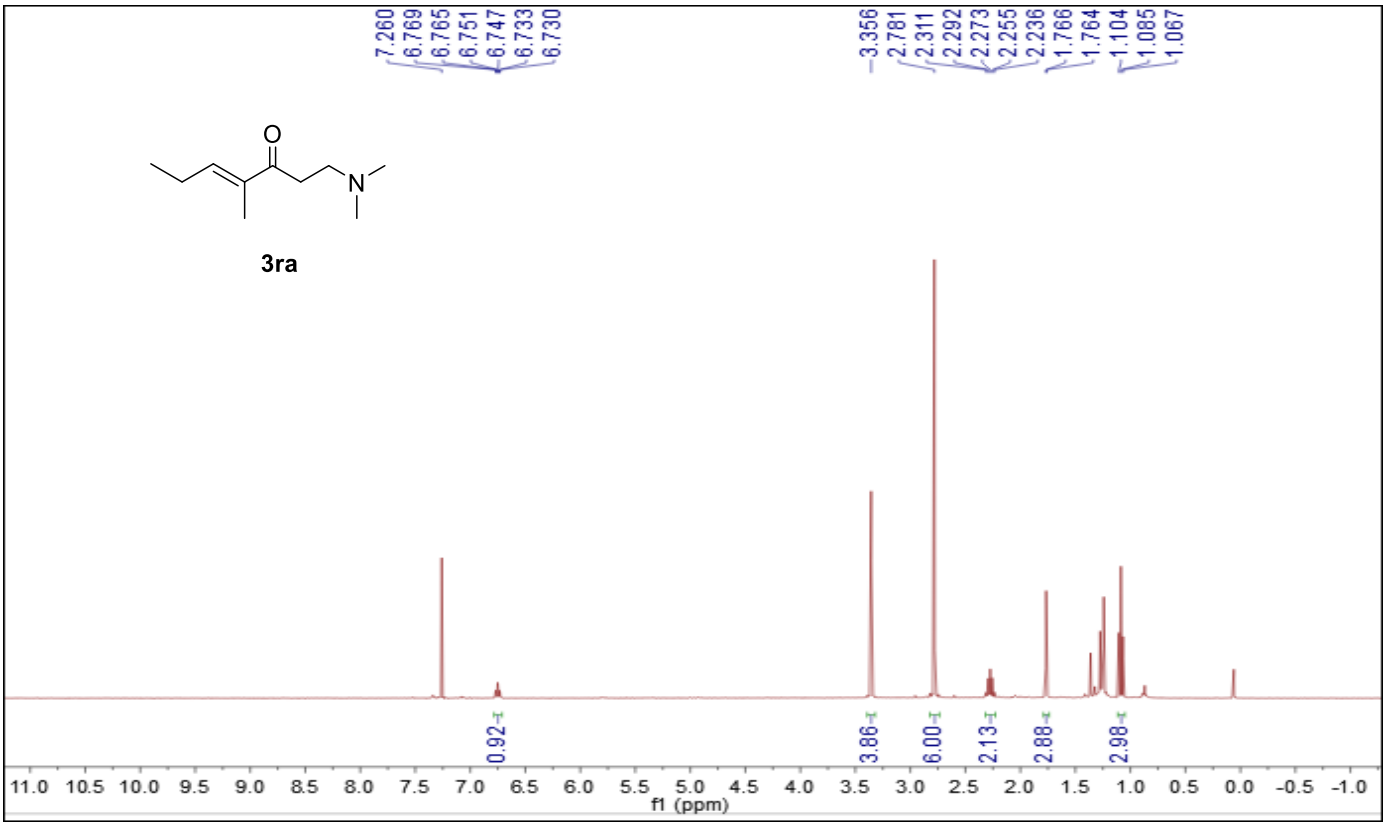
39.060
O
N
3qa
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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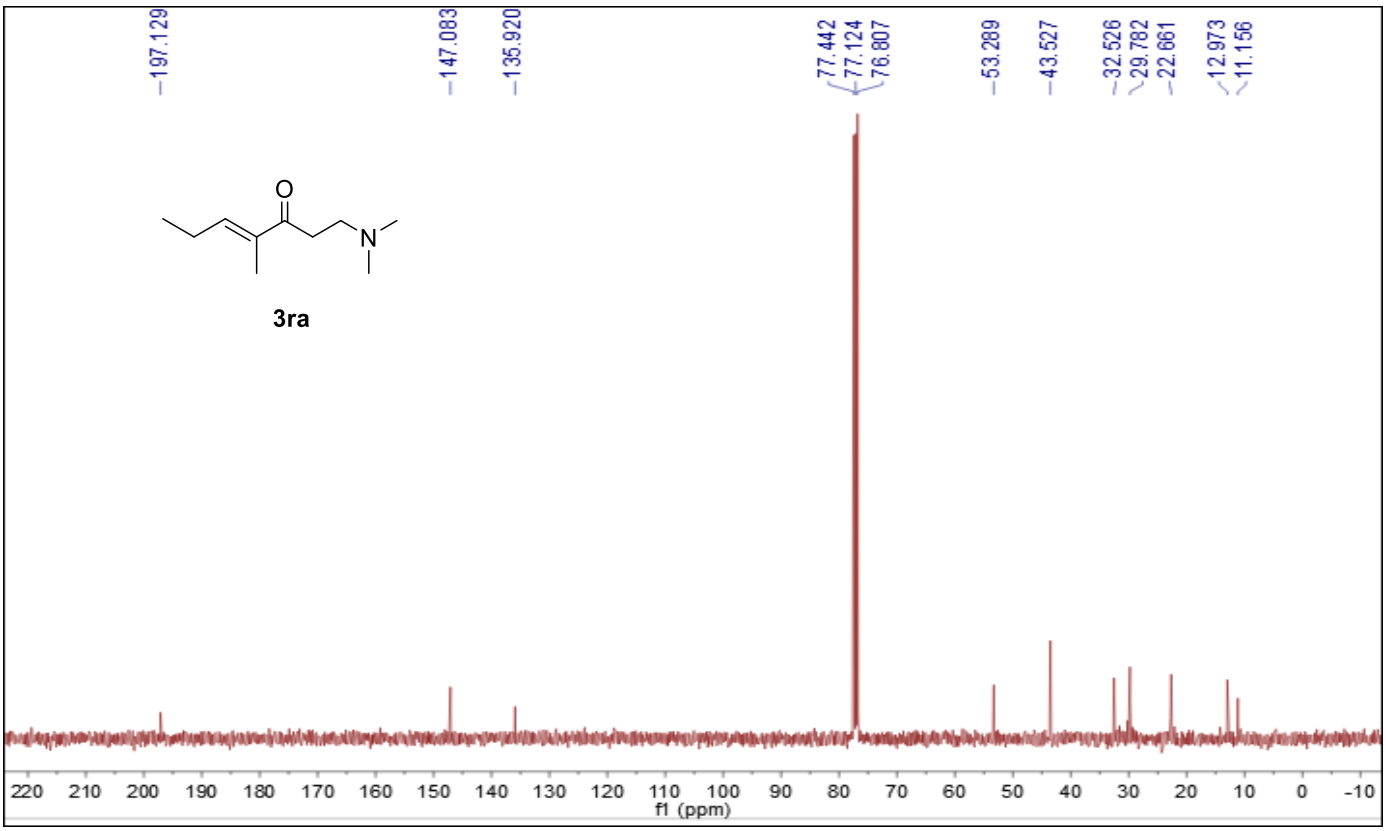
6.765
6.751
6.747
6.733
6.730
3.356
2.781
2.311
2.292
2.273
2.255
2.236
1.766
1.764
1.104
1.085
1.067
O
N
3ra
0.92
3.86
6.00
2.13
2.88
2.98
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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53.289
43.527
32.526
29.782
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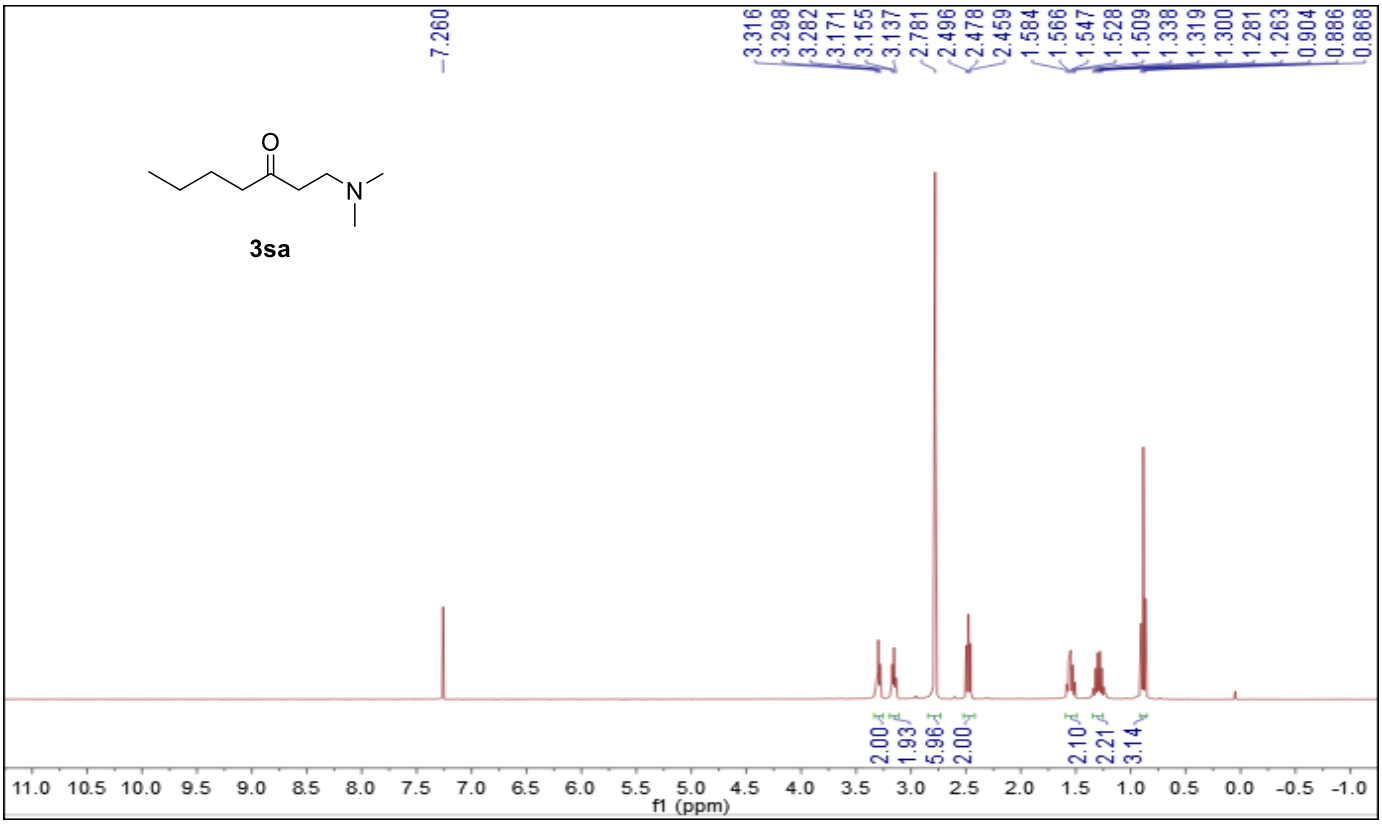
11.156
O
N
3ra
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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3.298
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3.171
3.155
3.137
2.781
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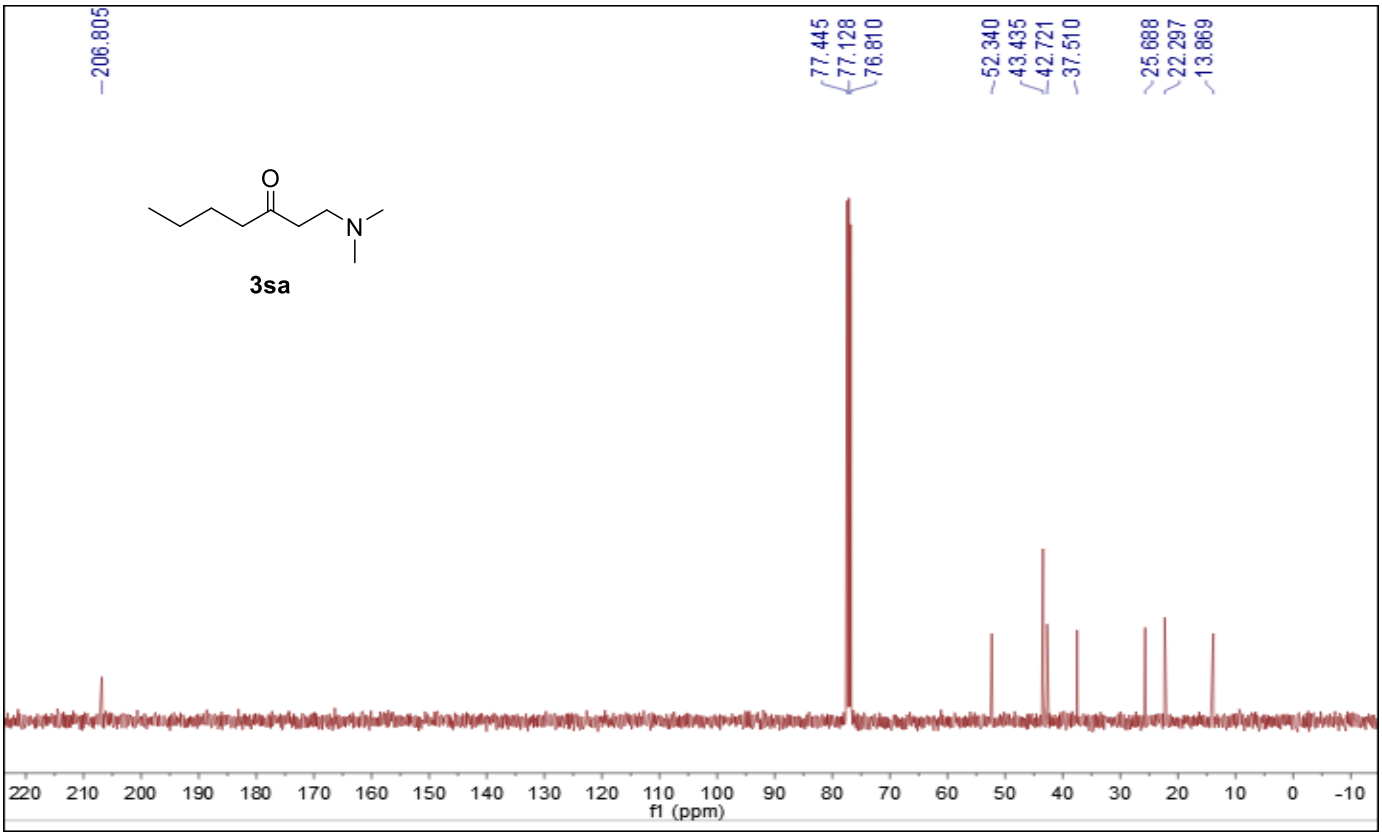
2.478
2.459
1.584
1.566
1.547
1.528
1.509
1.338
1.319
1.300
1.281
1.263
0.904
0.886
0.868
O
N
3sa
2.00
1.93
5.96
2.00
2.10
2.21
3.14
f1 (ppm)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77.128
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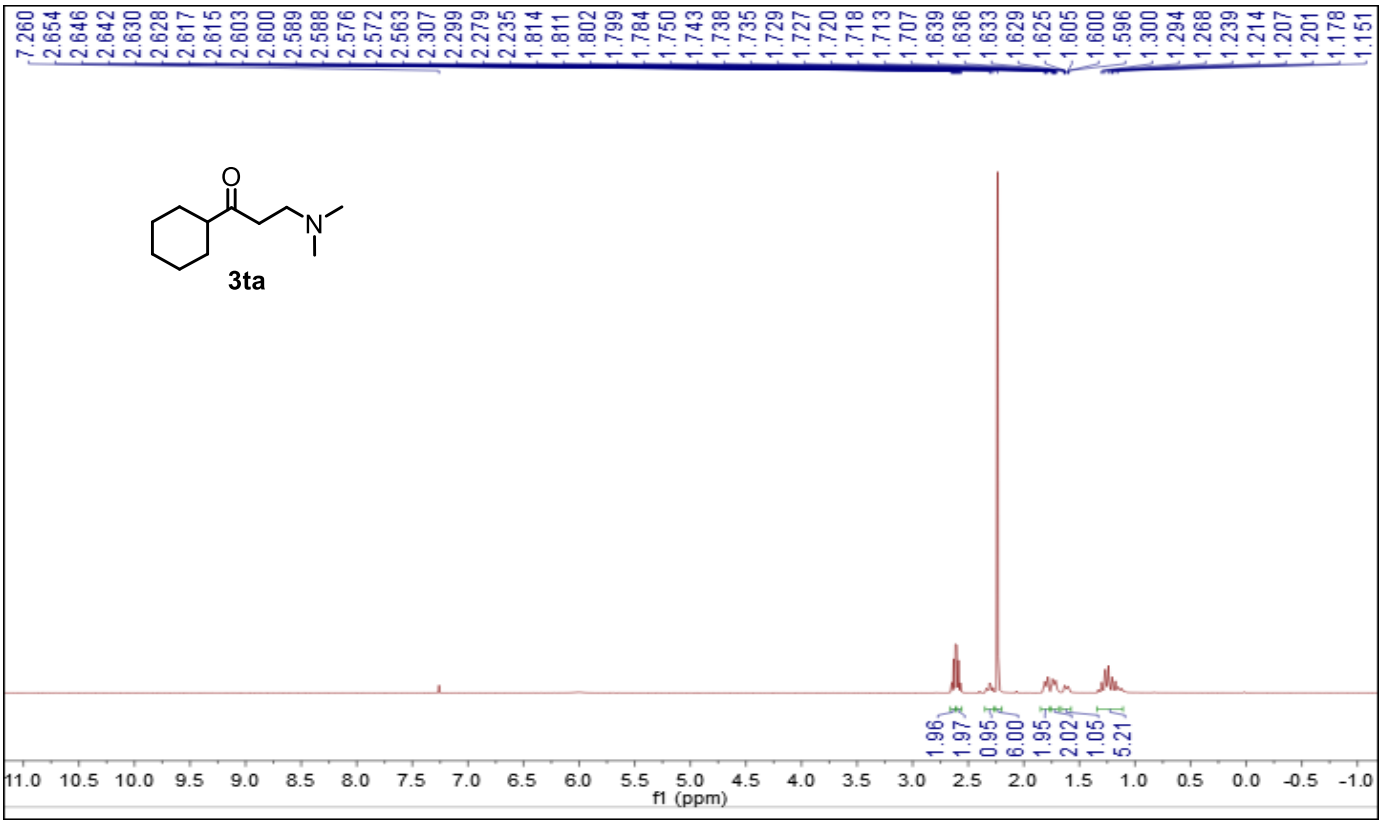
42.721
37.510
25.688
22.297
13.869
O
N
3sa
f1 (ppm)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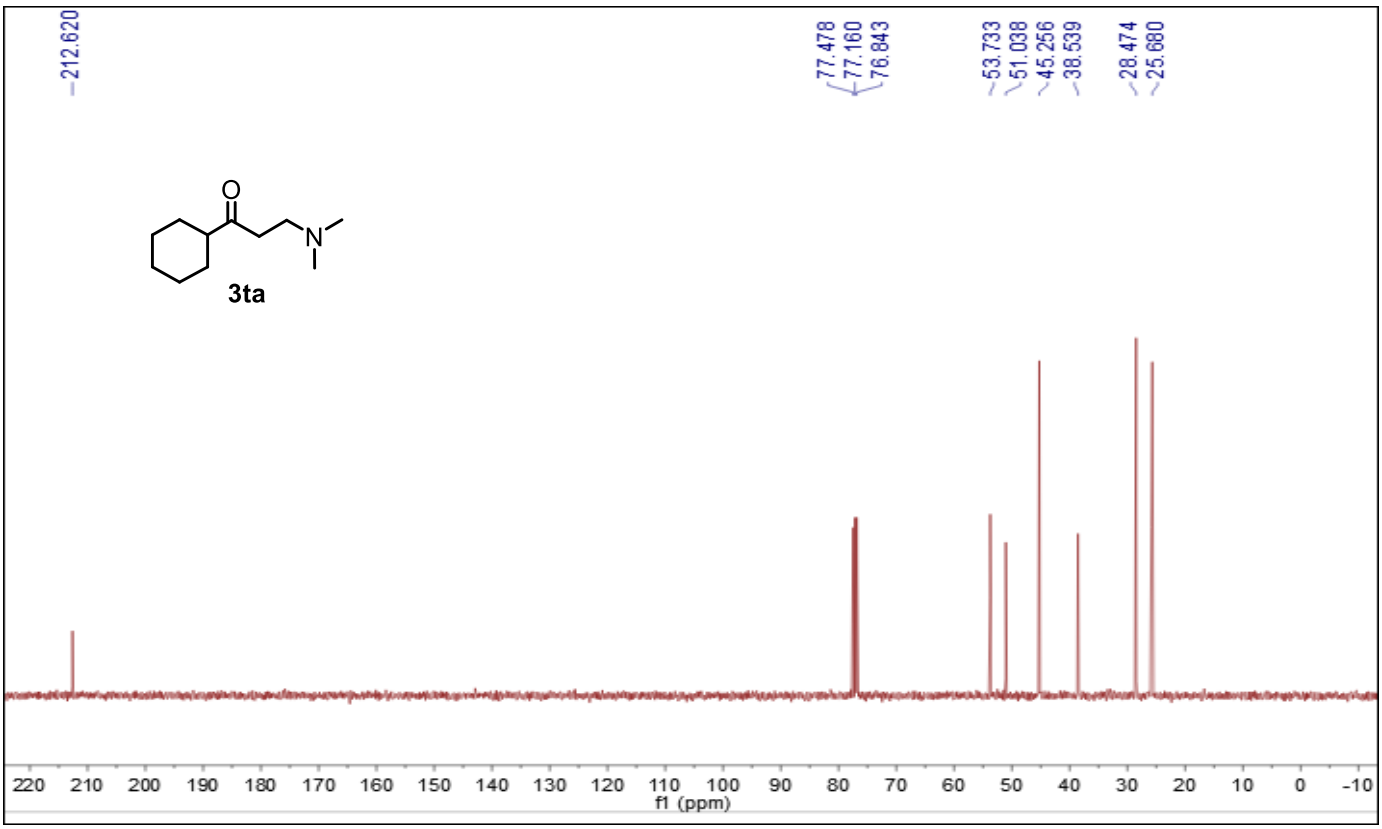
2.628
2.617
2.615
2.603
2.600
2.589
2.588
2.576
2.572
2.563
2.307
2.299
2.279
2.235
1.814
1.811
1.802
1.799
1.784
1.750
1.743
1.738
1.735
1.729
1.727
1.720
1.718
1.713
1.707
1.639
1.636
1.633
1.629
1.625
1.605
1.600
1.596
1.300
1.294
1.268
1.239
1.214
1.207
1.201
1.178
1.151
O
N
3ta
1.96
1.97
0.95
6.00
1.95
2.02
1.05
5.21
11.0 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 -0.5 -1.0
f1 (ppm)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O
N
3ta
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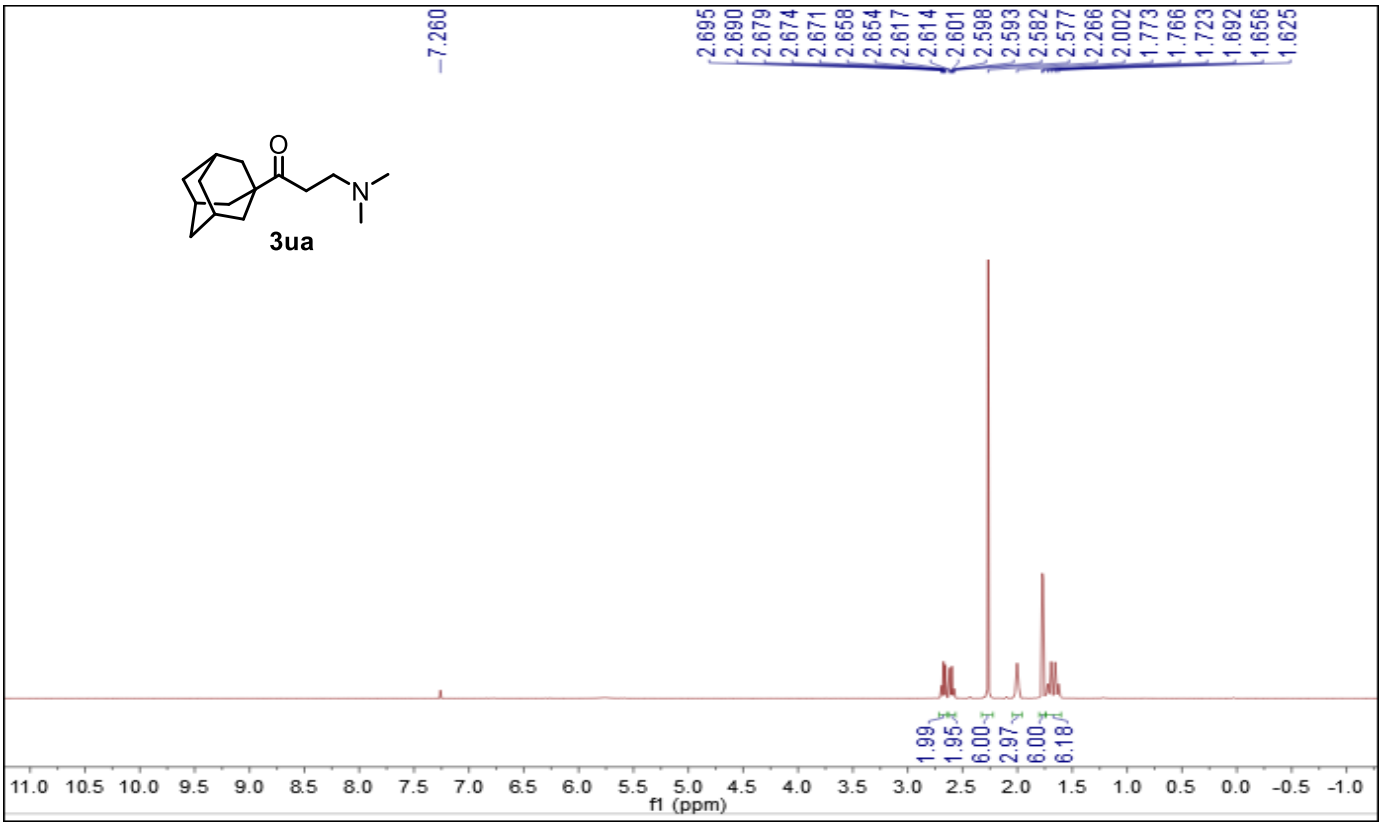
f1 (ppm)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2.654
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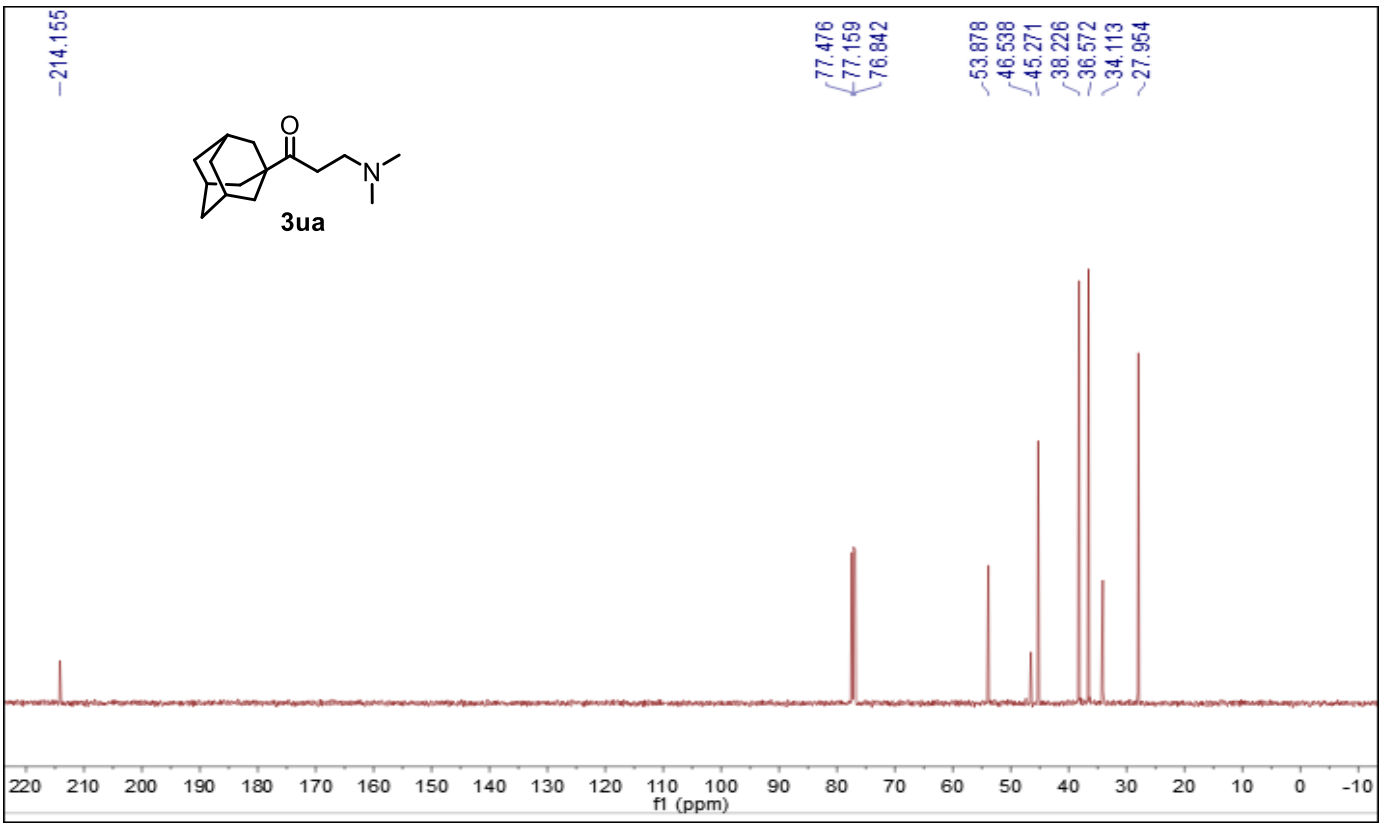
2.614
2.601
2.598
2.593
2.582
2.577
2.266
2.002
1.773
1.766
1.723
1.692
1.656
1.625
O
N
3ua
1.99
1.95
6.00
2.97
6.00
6.18
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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46.538
45.271
38.226
36.572
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27.954
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N
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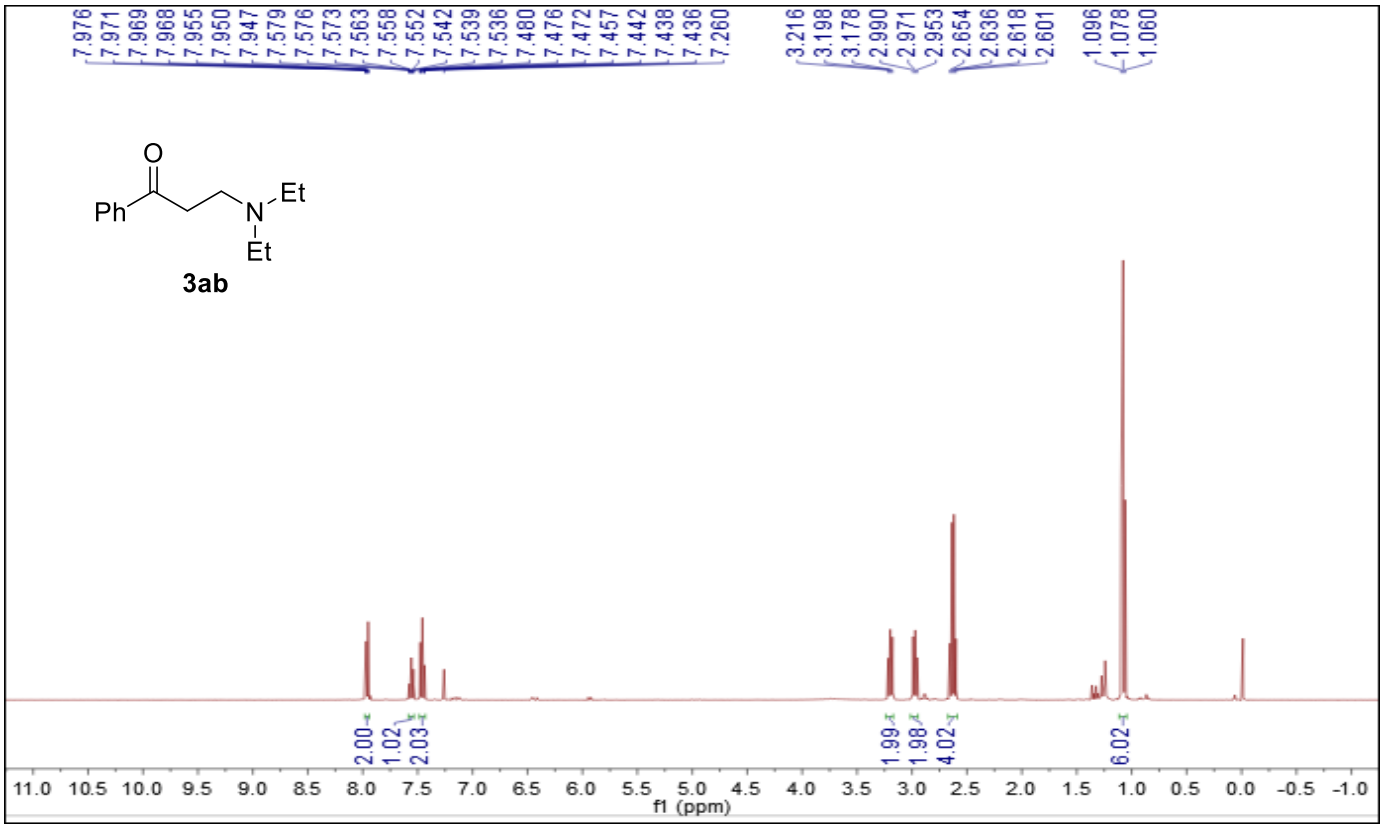
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.552
7.542
7.539
7.536
7.480
7.476
7.472
7.457
7.442
7.438
7.436
7.260
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3.198
3.178
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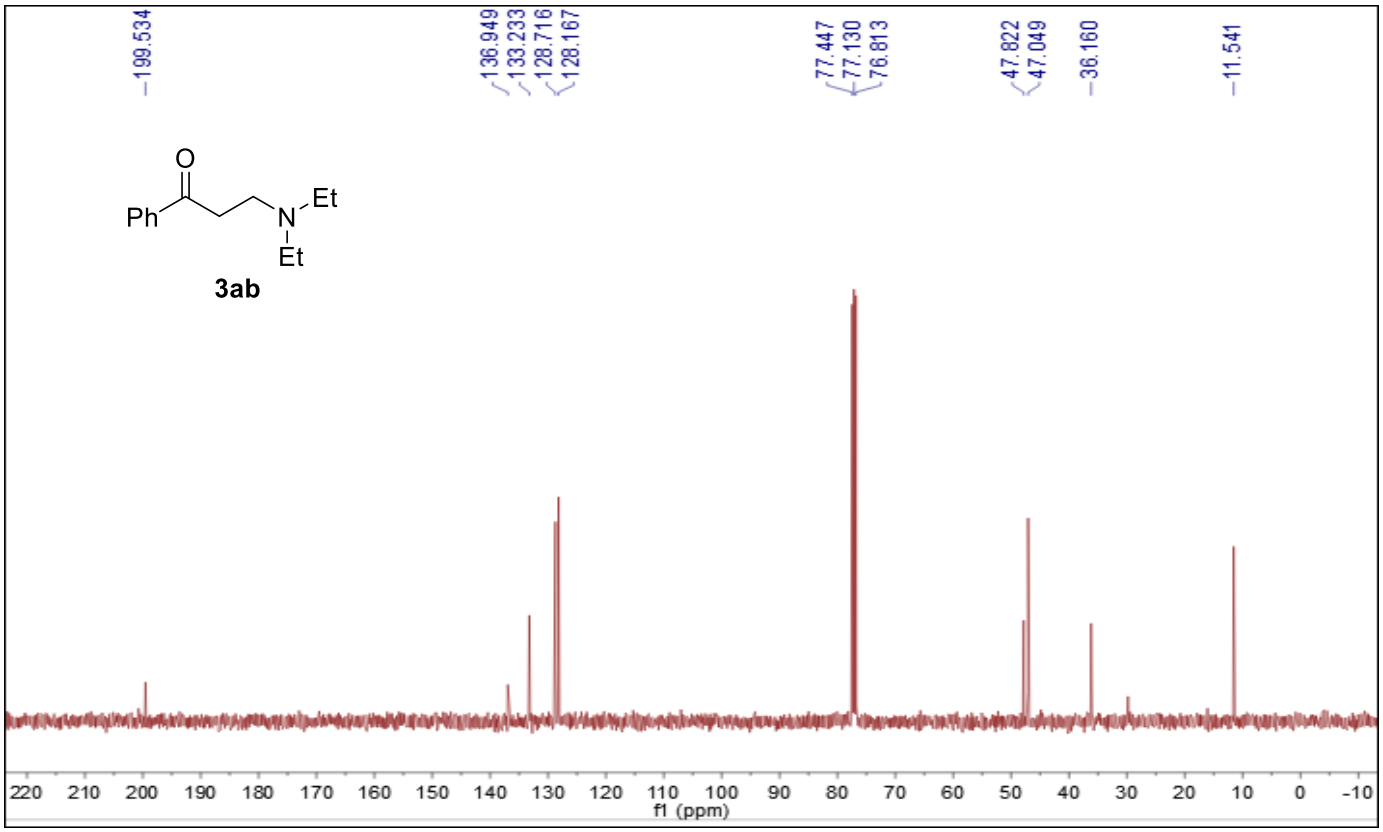
2.971
2.953
2.654
2.636
2.618
2.601
1.096
1.078
1.060
O
Ph
N
Et
Et
3ab
2.00
1.02
2.03
1.99
1.98
4.02
6.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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77.130
76.813
47.822
47.049
36.160
11.541
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Ph
N
Et
Et
3ab
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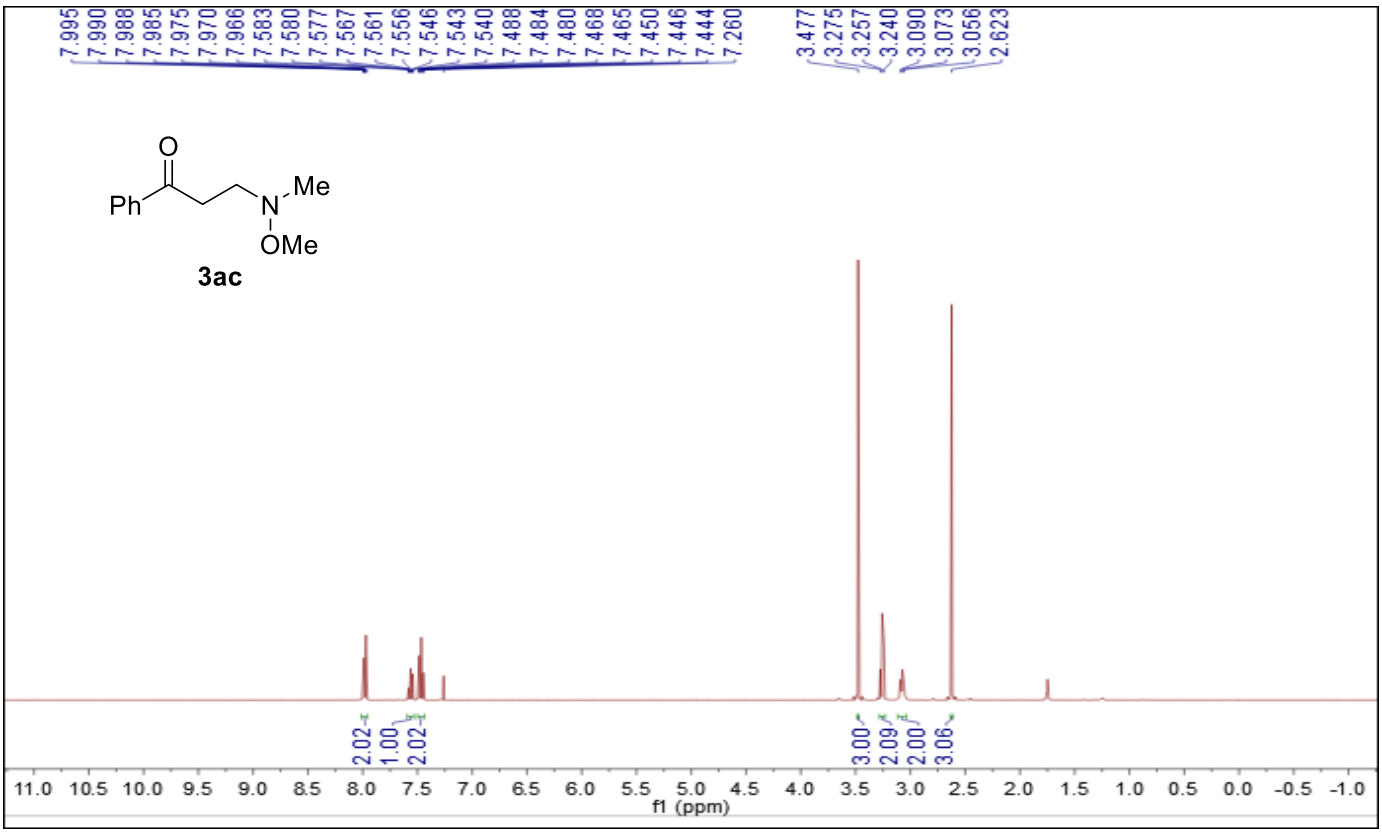
f1 (ppm)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7.543
7.540
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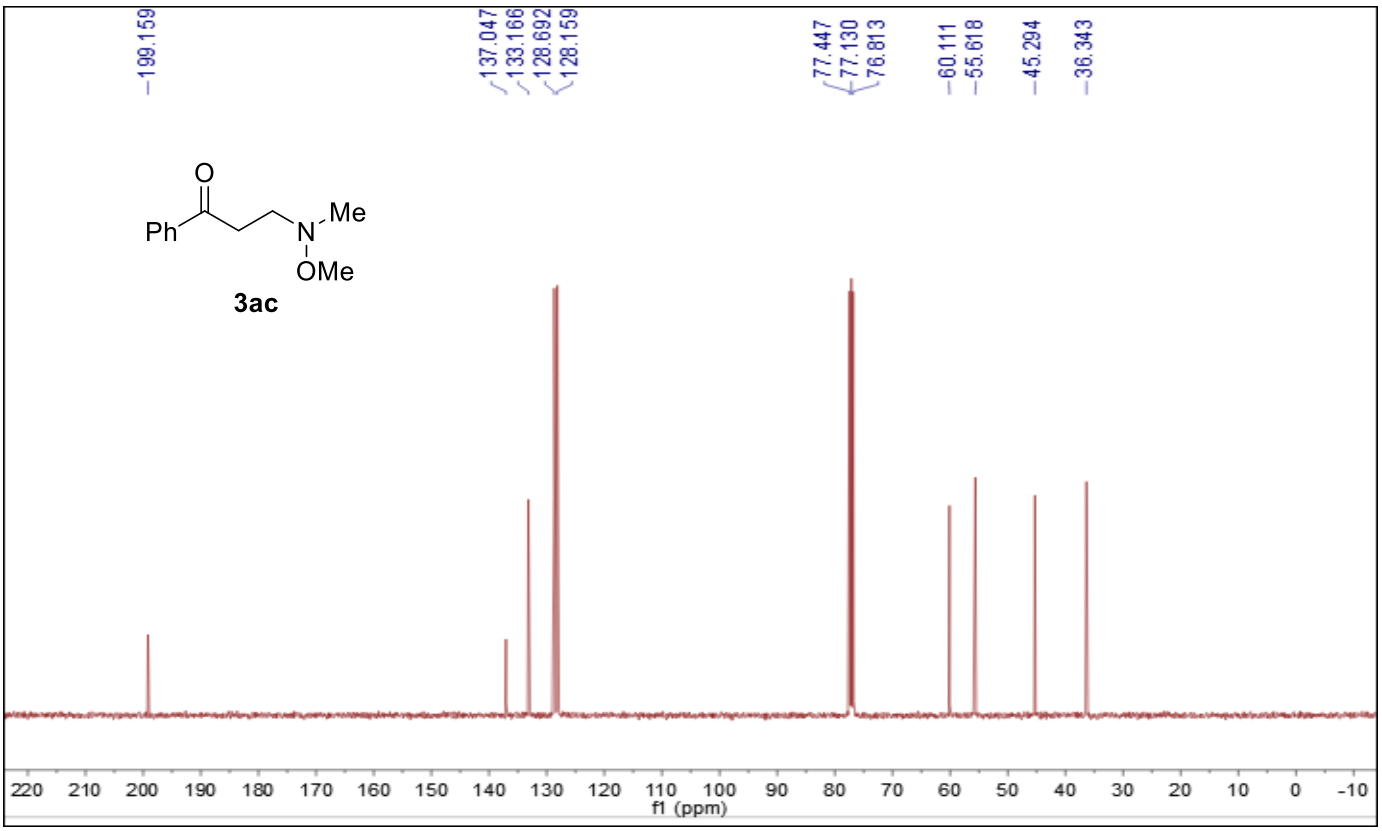
7.480
7.468
7.465
7.450
7.446
7.444
7.260
3.477
3.275
3.257
3.240
3.090
3.073
3.056
2.623
O
Ph
N
Me
OMe
3ac
2.02
1.00
2.02
3.00
2.09
2.00
3.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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128.692
128.159
77.447
77.130
76.813
60.111
55.618
45.294
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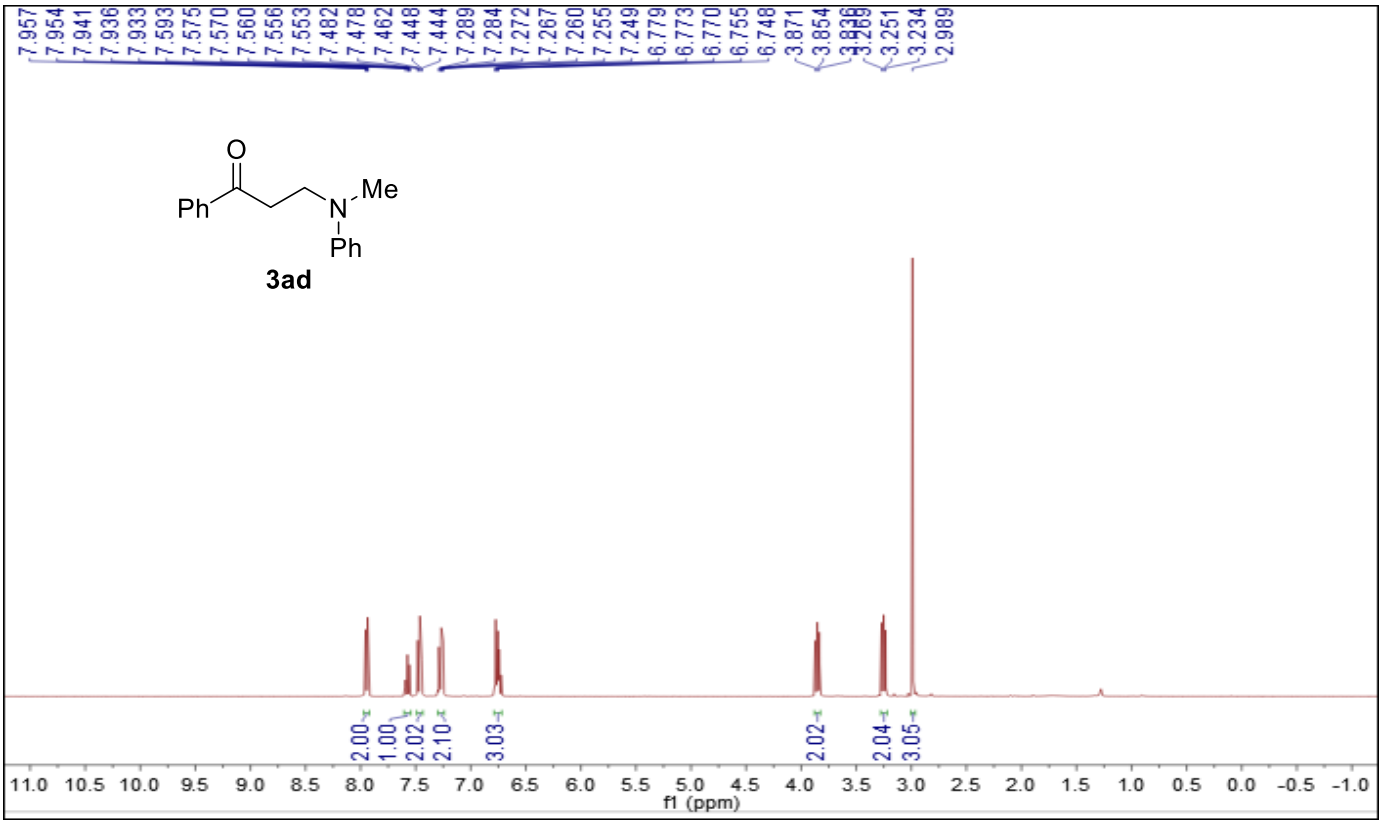
Ph
N
Me
OMe
3ac
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.462
7.448
7.444
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7.272
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7.260
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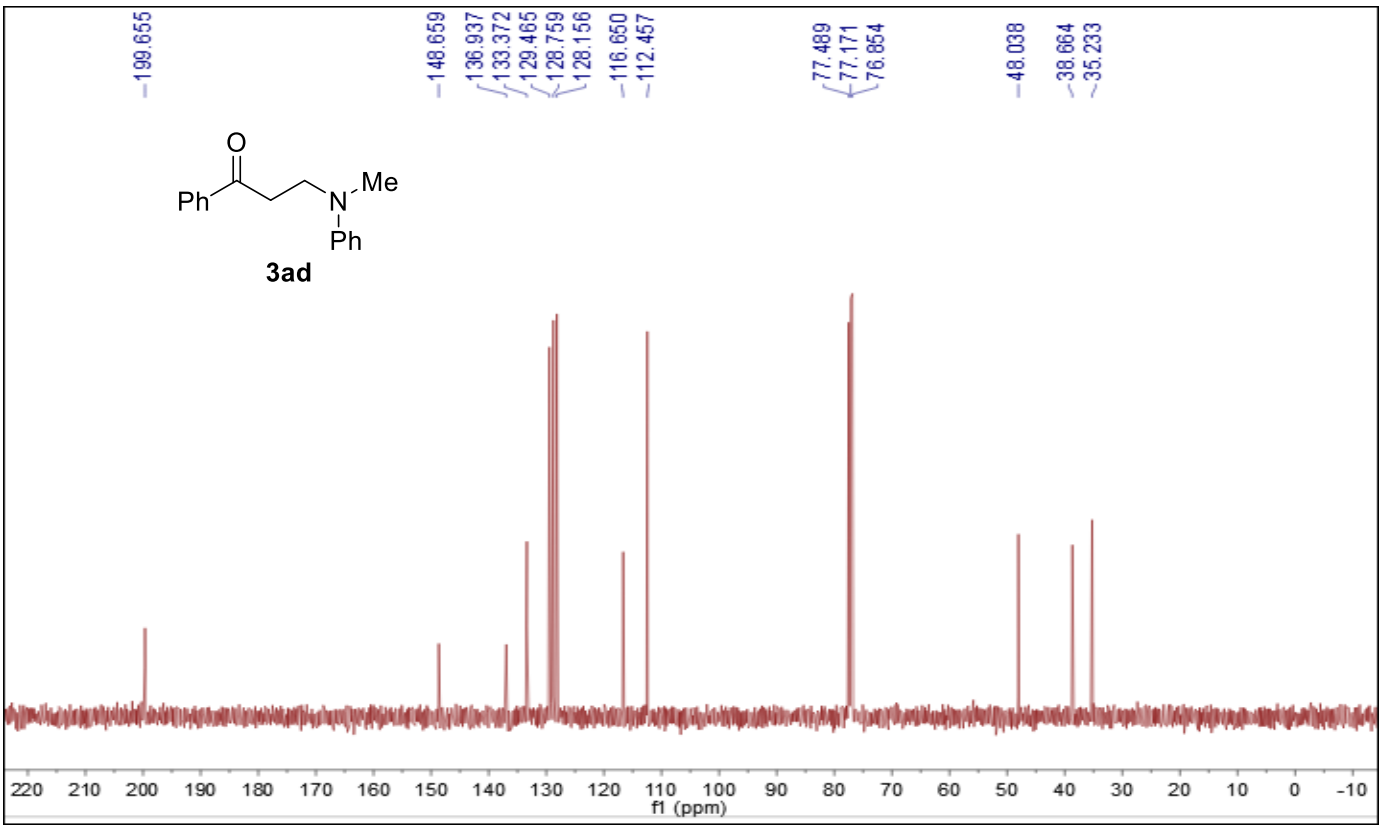
7.249
6.779
6.773
6.770
6.755
6.748
3.871
3.854
3.251
3.234
2.989
O
Ph
N
Me
Ph
3ad
2.00
1.00
2.02
2.10
3.03
2.02
2.04
3.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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77.489
77.171
76.854
48.038
38.664
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O
Ph
N
Me
Ph
3ad
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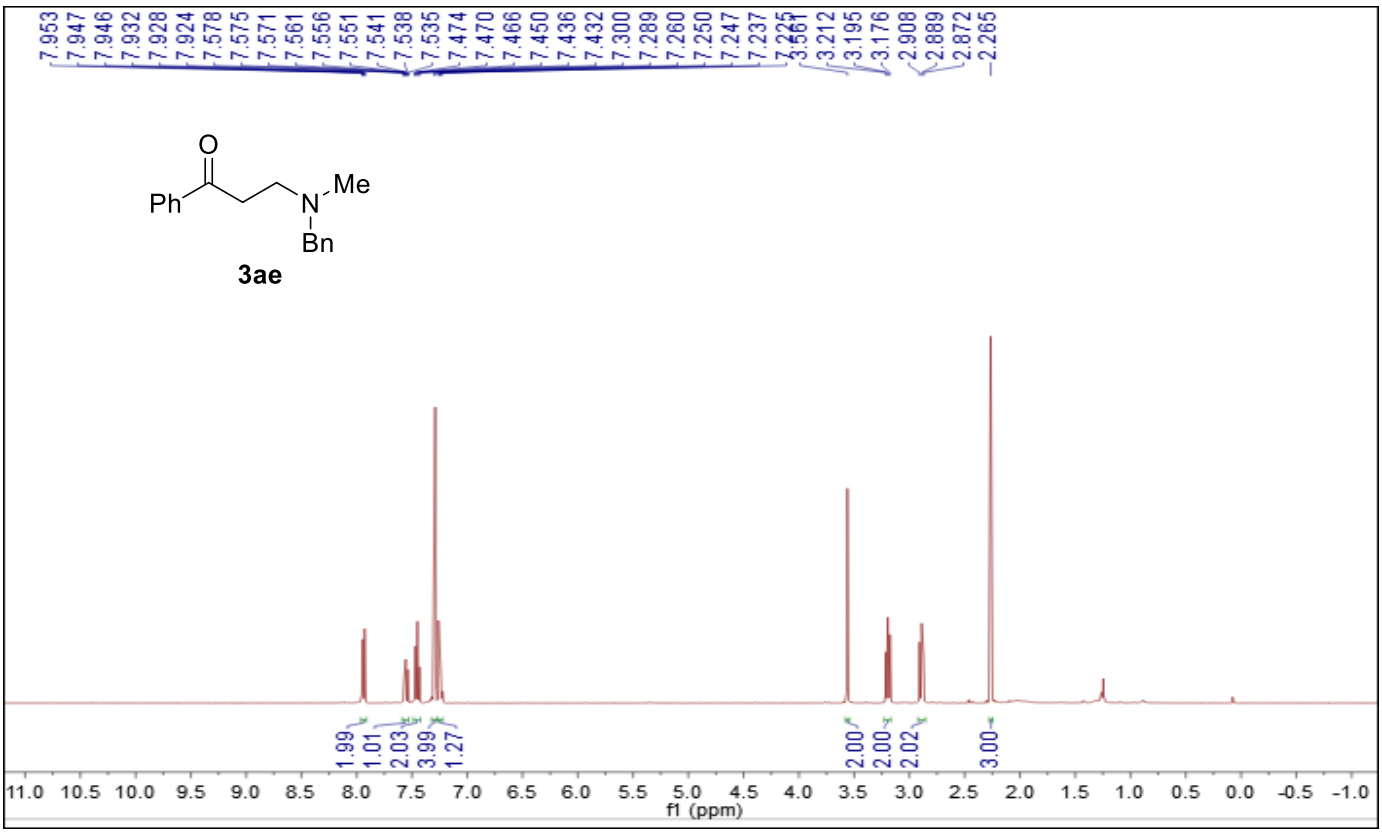
f1 (ppm)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7.541
7.538
7.535
7.474
7.470
7.466
7.450
7.436
7.432
7.300
7.289
7.260
7.250
7.247
7.237
7.225
3.561
3.212
3.195
3.176
2.908
2.889
2.872
2.265
O
Ph
N
Me
Bn
3ae
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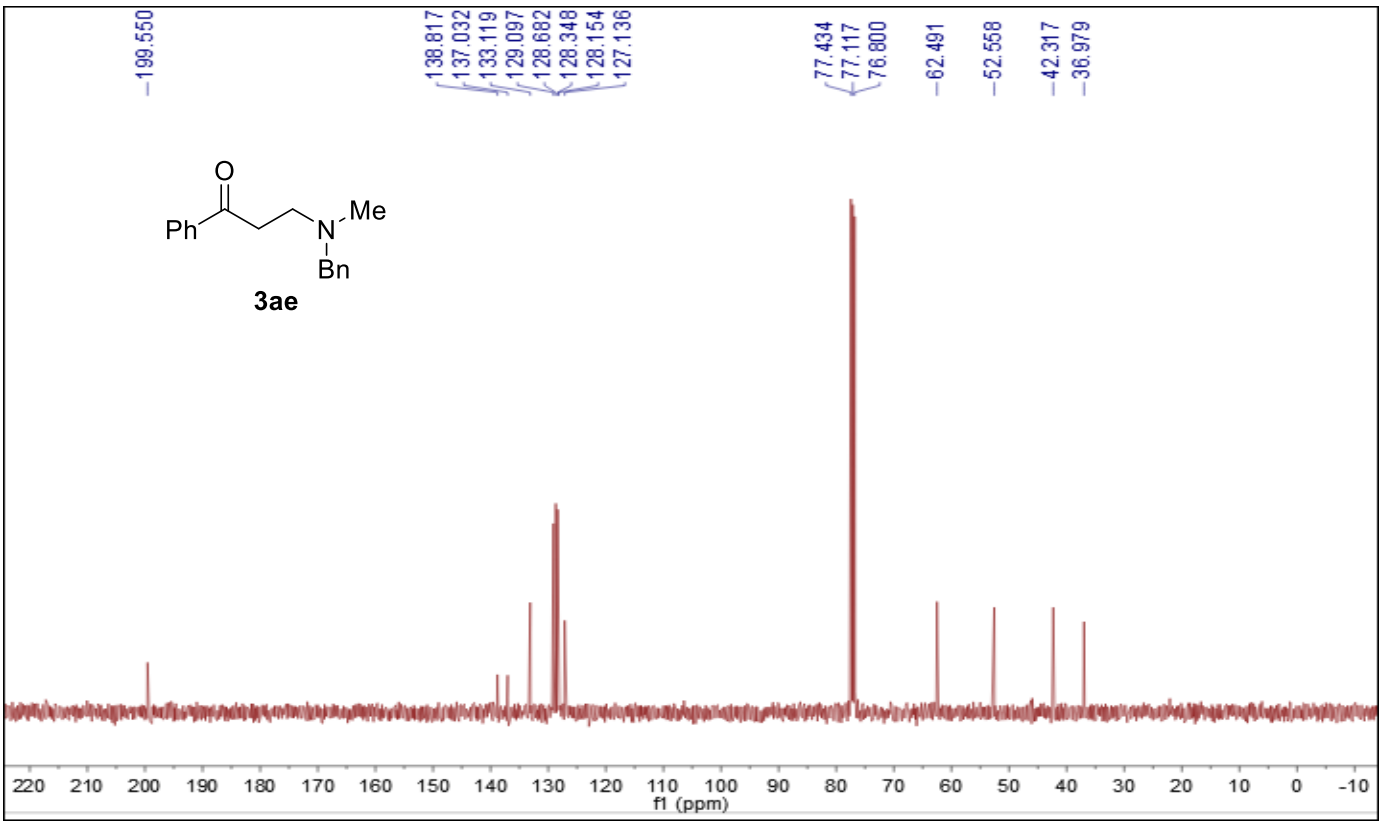
1.01
2.03
3.99
1.27
2.00
2.00
2.02
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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52.558
42.317
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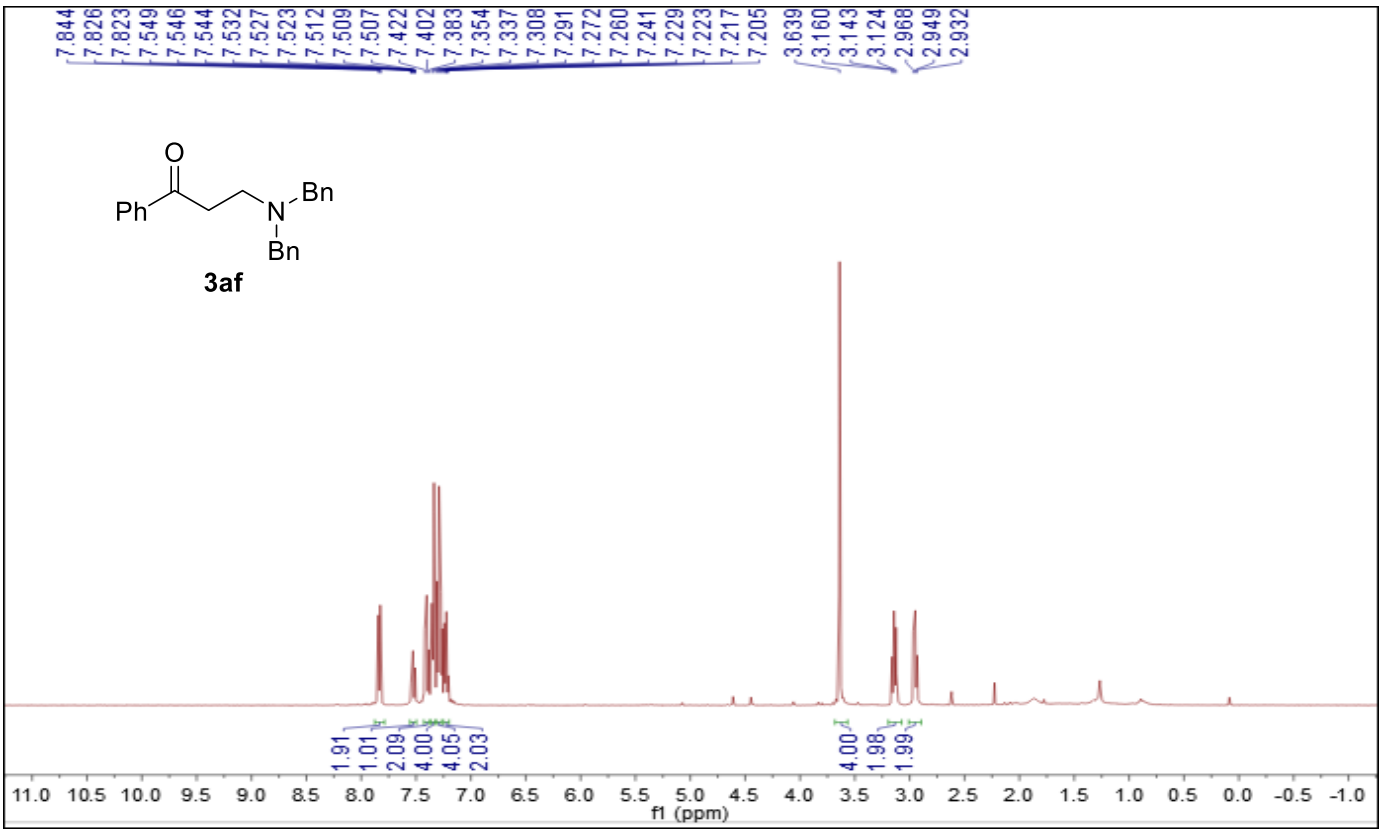
Ph
N
Me
Bn
3ae
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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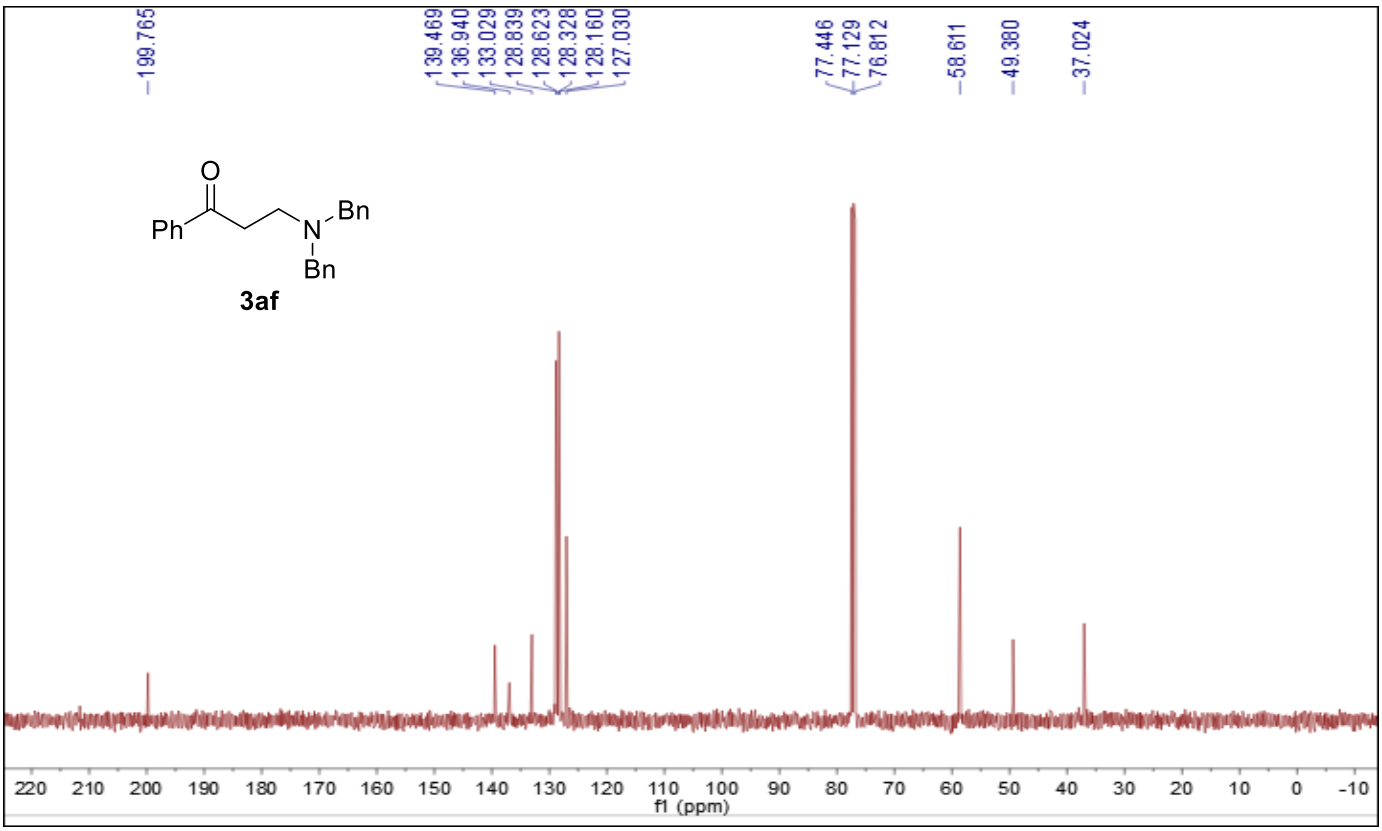
7.217
7.205
3.639
3.160
3.143
3.124
2.968
2.949
2.932
O
Ph
N
Bn
Bn
3af
1.91
1.01
2.09
4.00
4.05
2.03
4.00
1.98
1.99
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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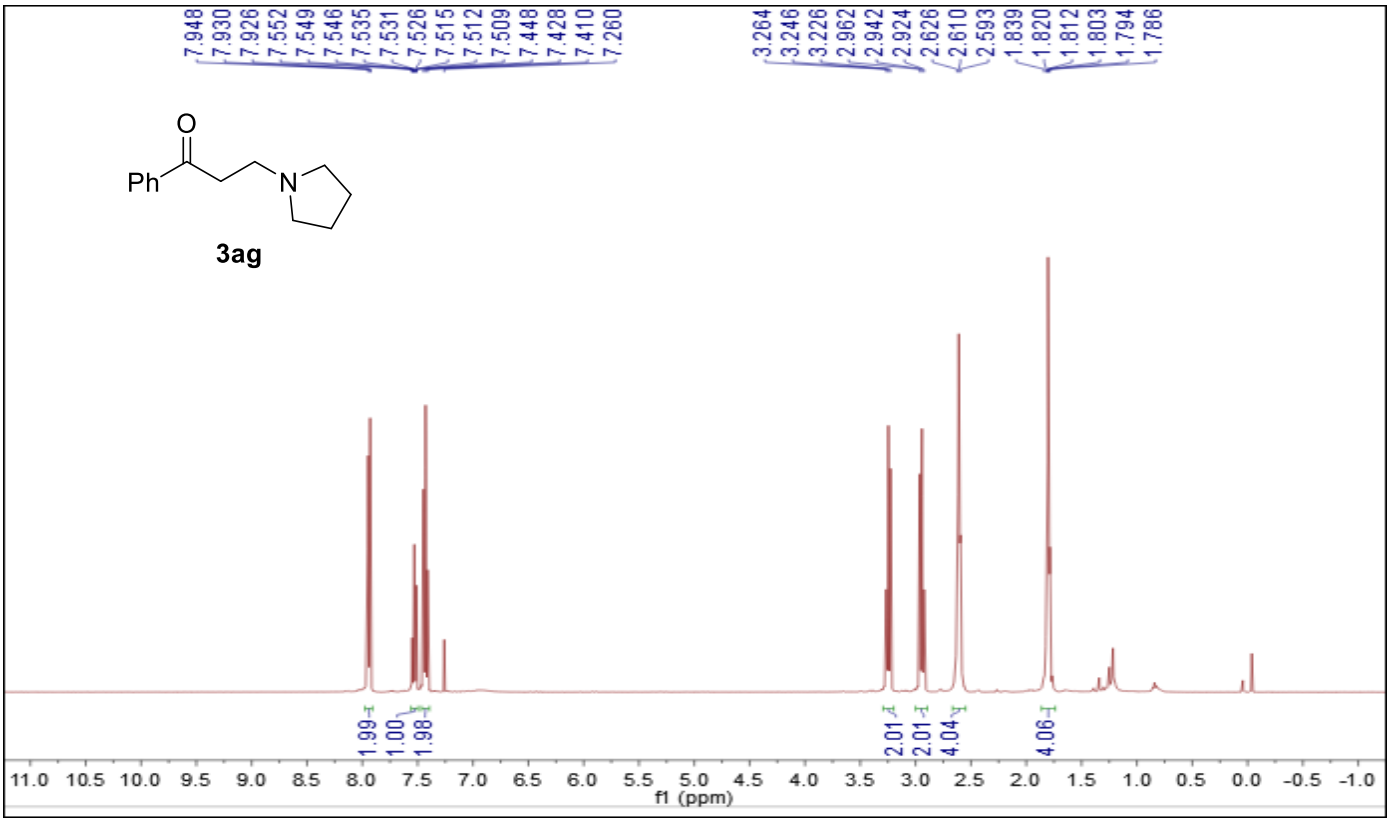
139.469
136.940
133.029
128.839
128.623
128.328
128.160
127.030
77.446
77.129
76.812
58.611
49.380
37.024
O
Ph
N
Bn
Bn
3af
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.926
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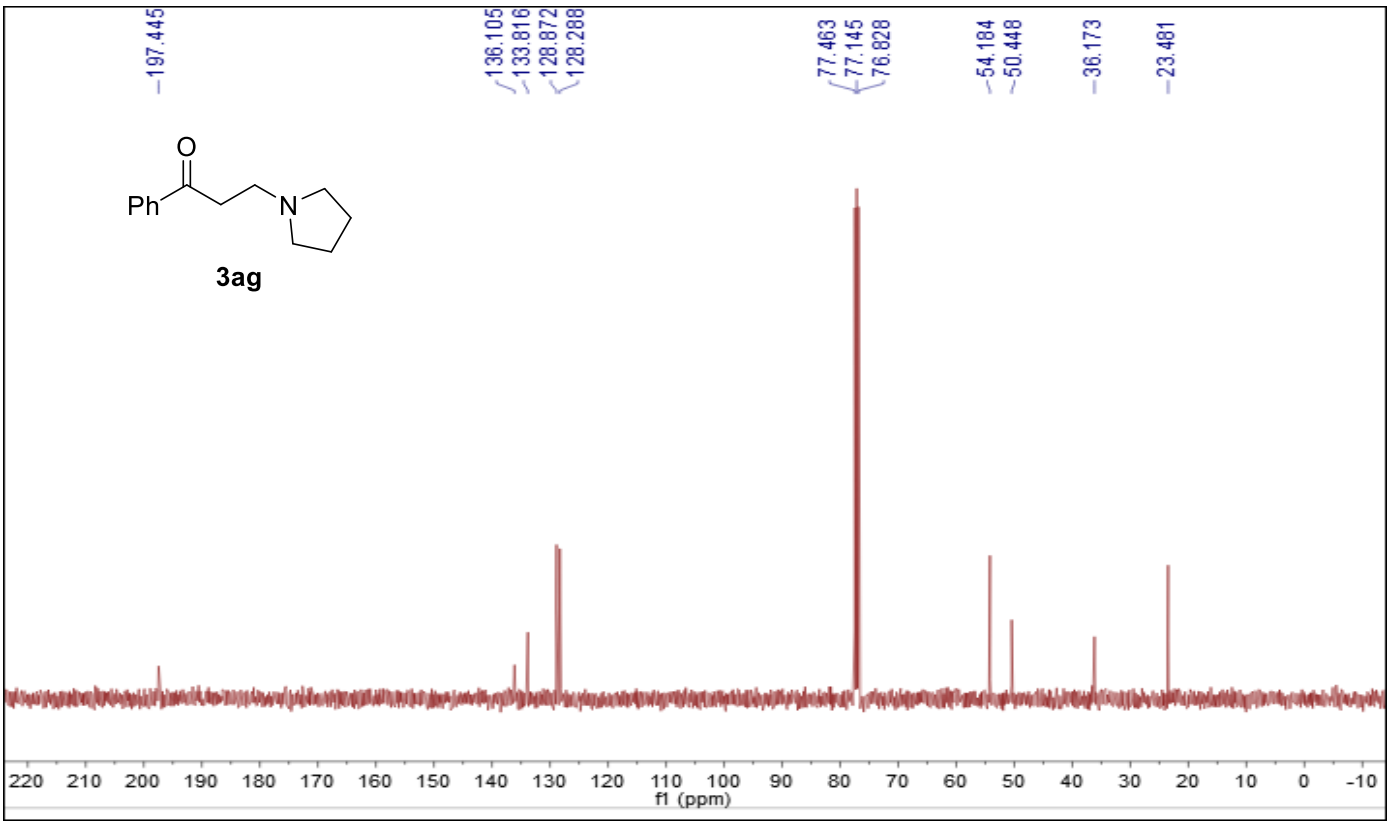
7.549
7.546
7.535
7.531
7.526
7.515
7.512
7.509
7.448
7.428
7.410
7.260
3.264
3.246
3.226
2.962
2.942
2.924
2.626
2.610
2.593
1.839
1.820
1.812
1.803
1.794
1.786
O
Ph
N
3ag
1.99
1.00
1.98
2.01
2.01
4.04
4.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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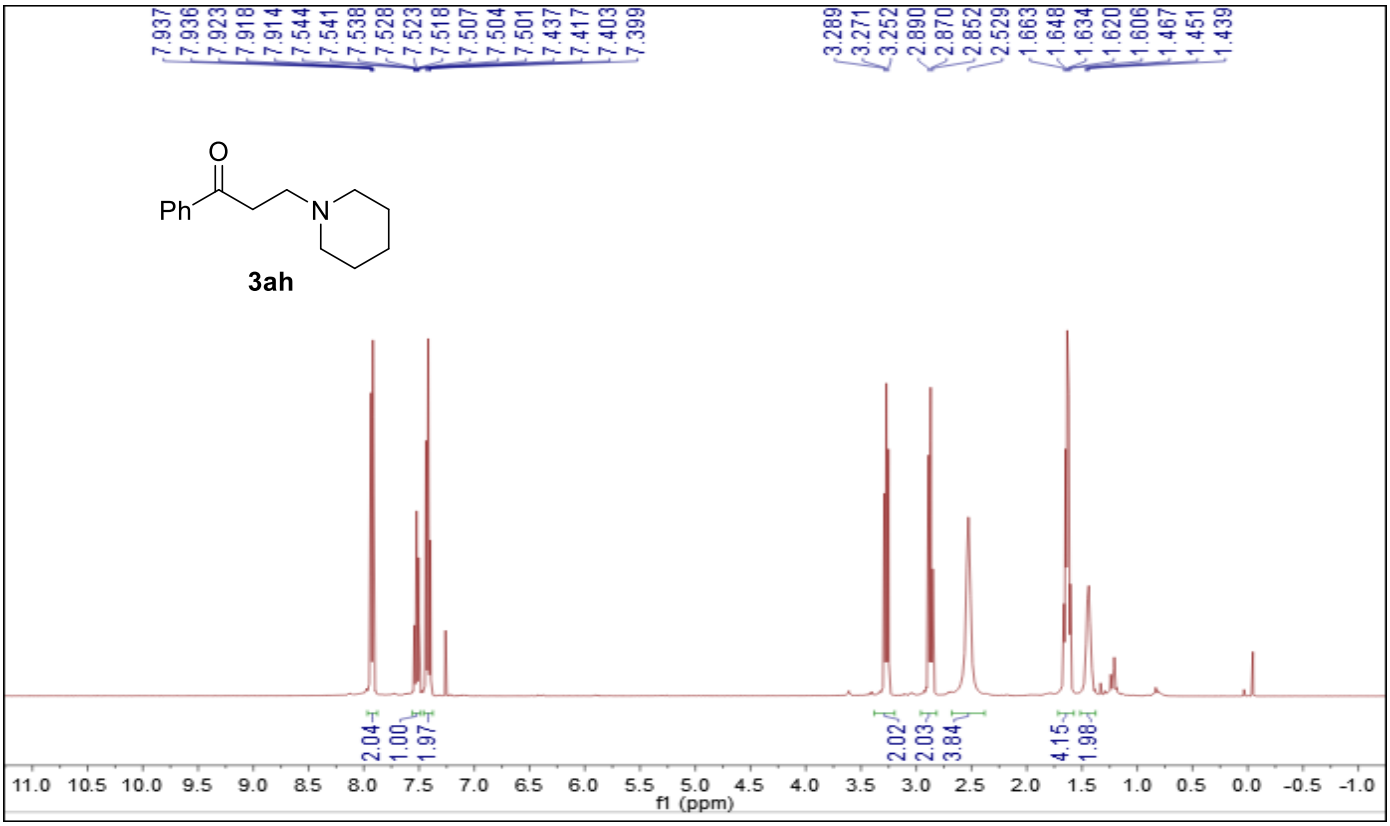
136.105
133.816
128.872
128.288
77.463
77.145
76.828
54.184
50.448
36.173
23.481
O
Ph
N
3ag
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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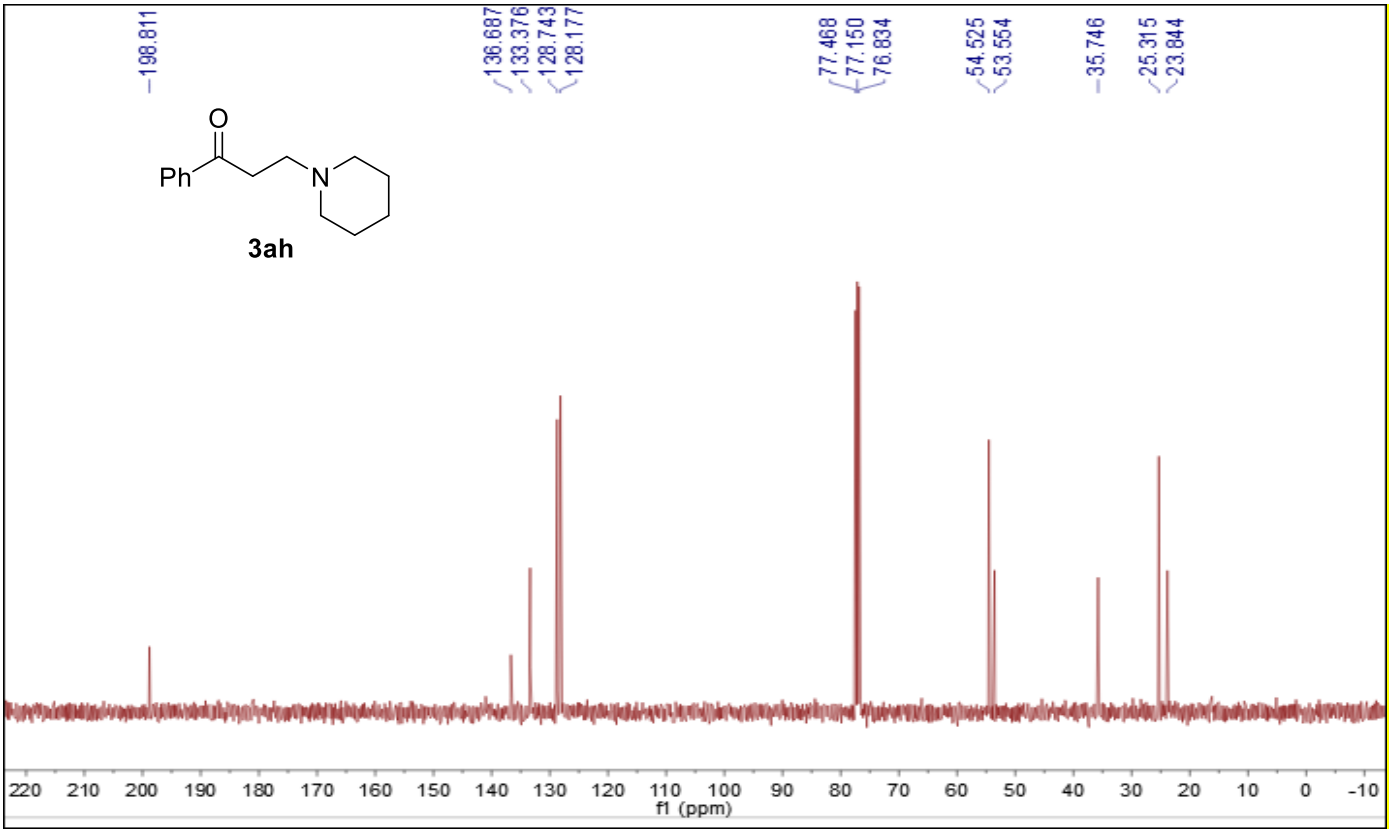
7.923
7.918
7.914
7.544
7.541
7.538
7.528
7.523
7.518
7.507
7.504
7.501
7.437
7.417
7.403
7.399
3.289
3.271
3.252
2.890
2.870
2.852
2.529
1.663
1.648
1.634
1.620
1.606
1.467
1.451
1.439
O
Ph
N
3ah
2.04
1.00
1.97
2.02
2.03
3.84
4.15
1.98
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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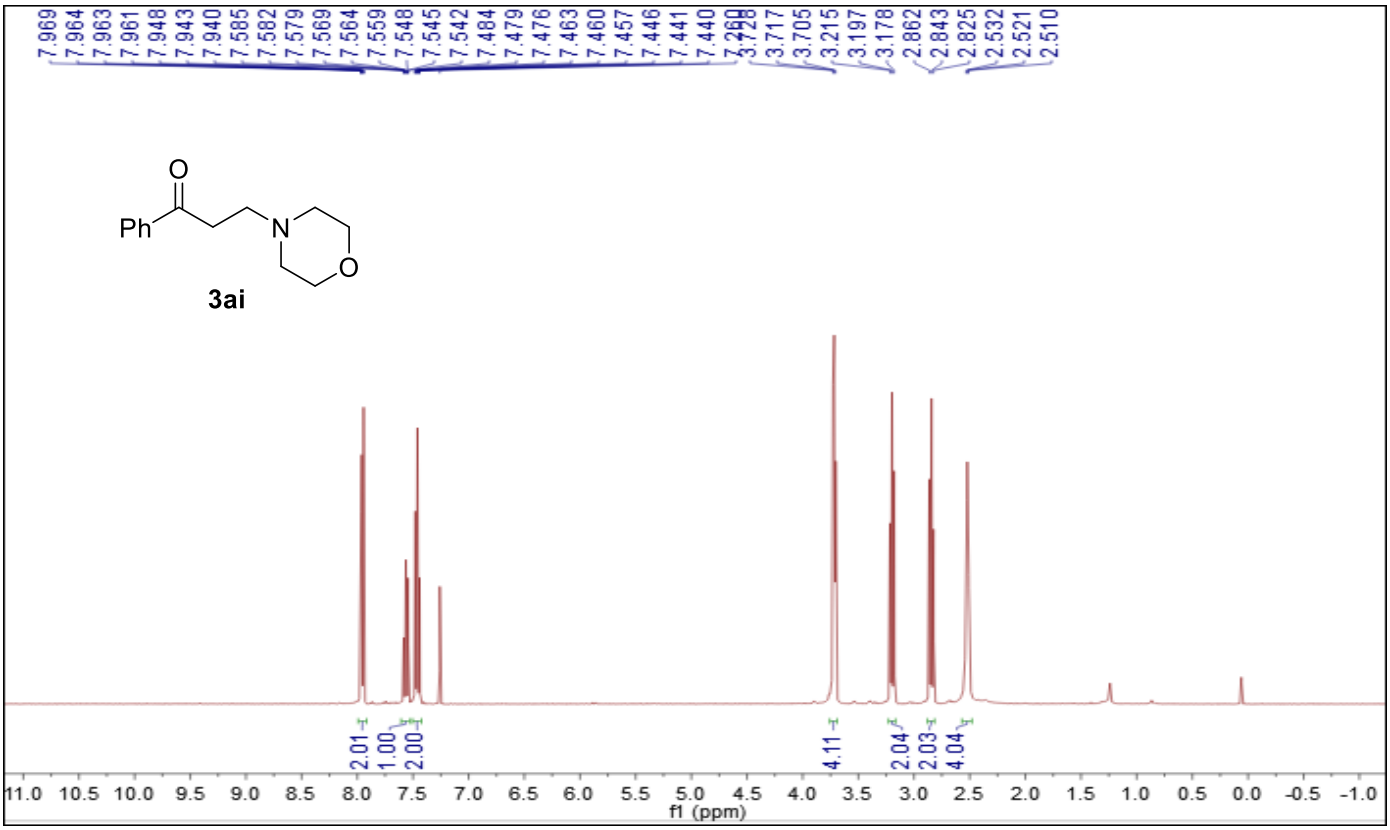
136.687
133.376
128.743
128.177
77.468
77.150
76.834
54.525
53.554
35.746
25.315
23.844
O
Ph
N
3ah
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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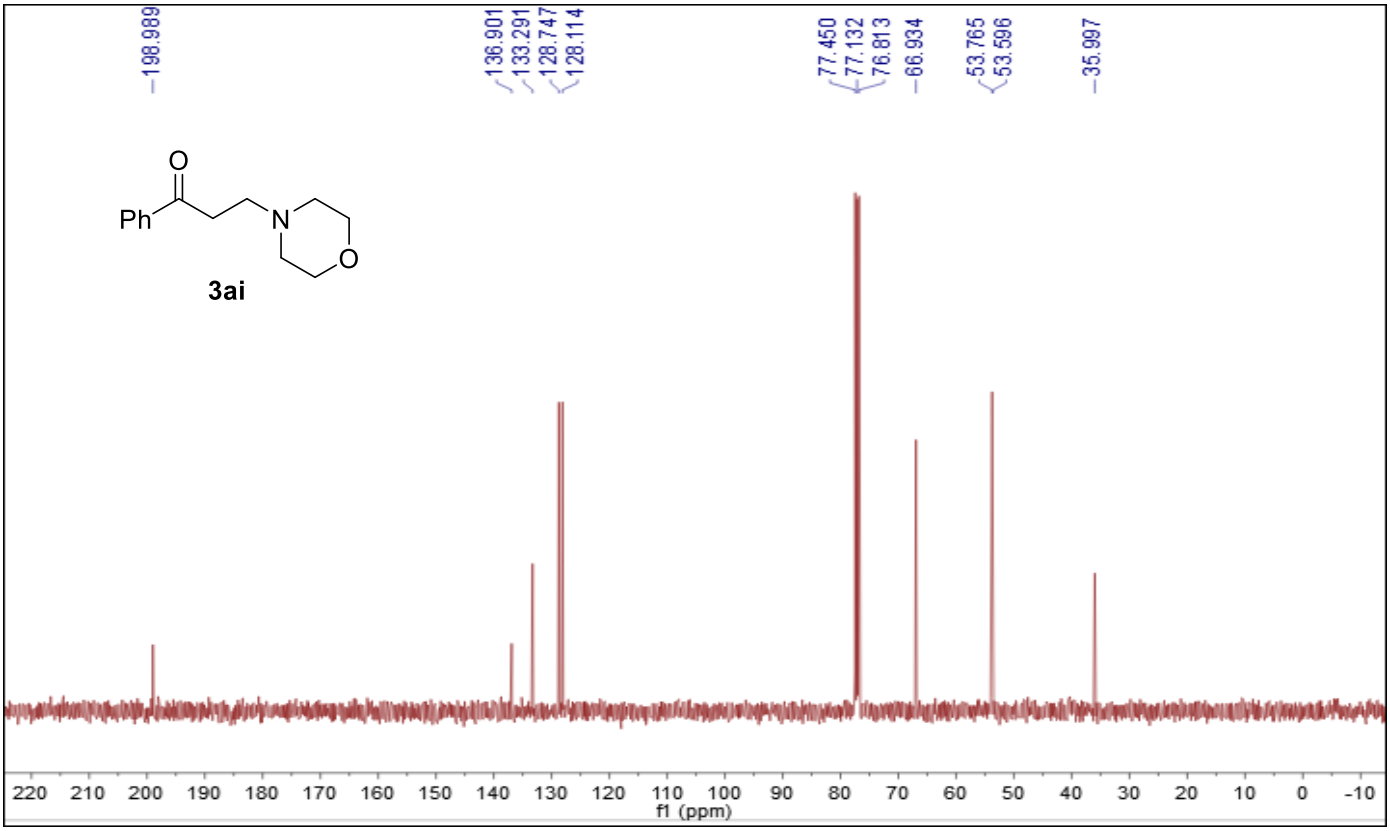
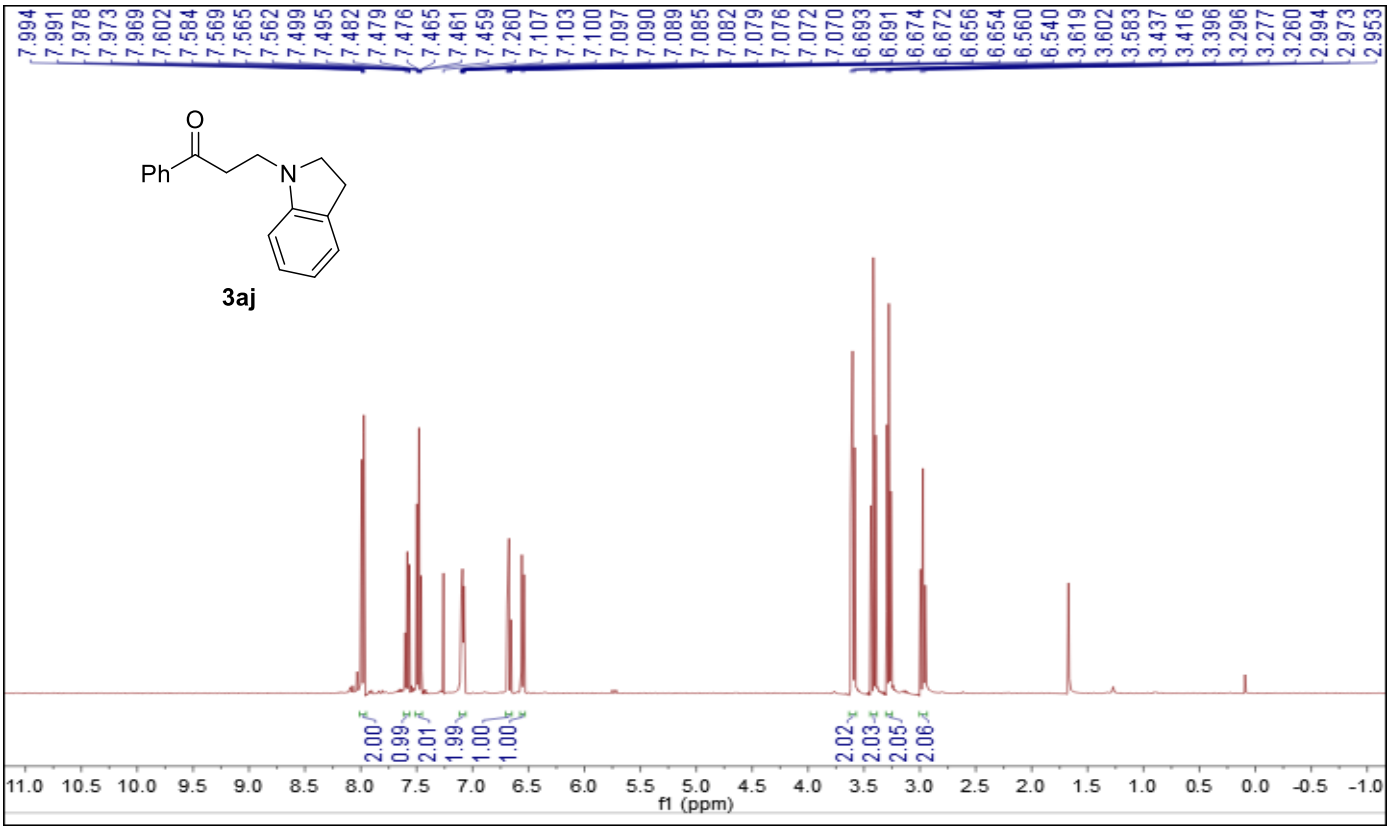
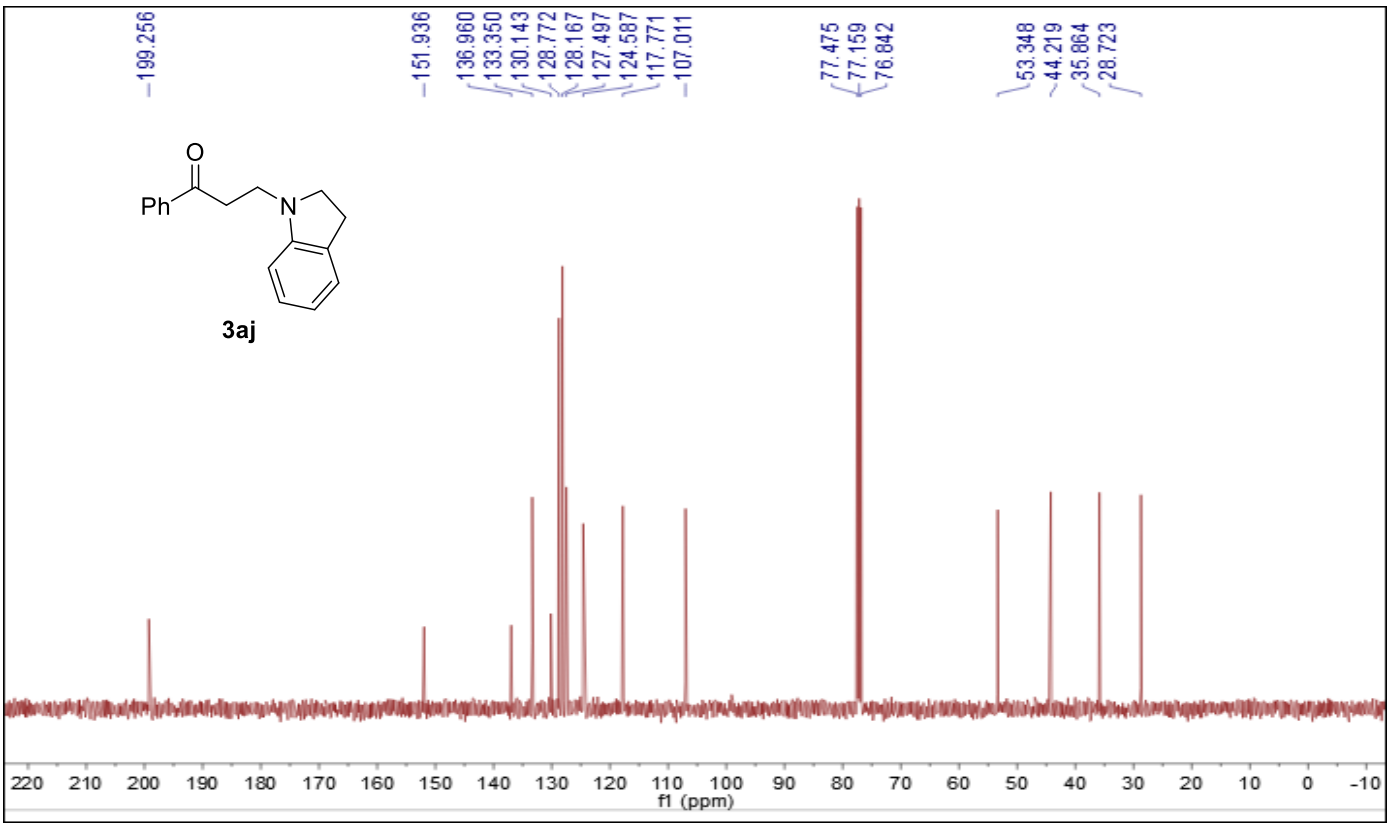
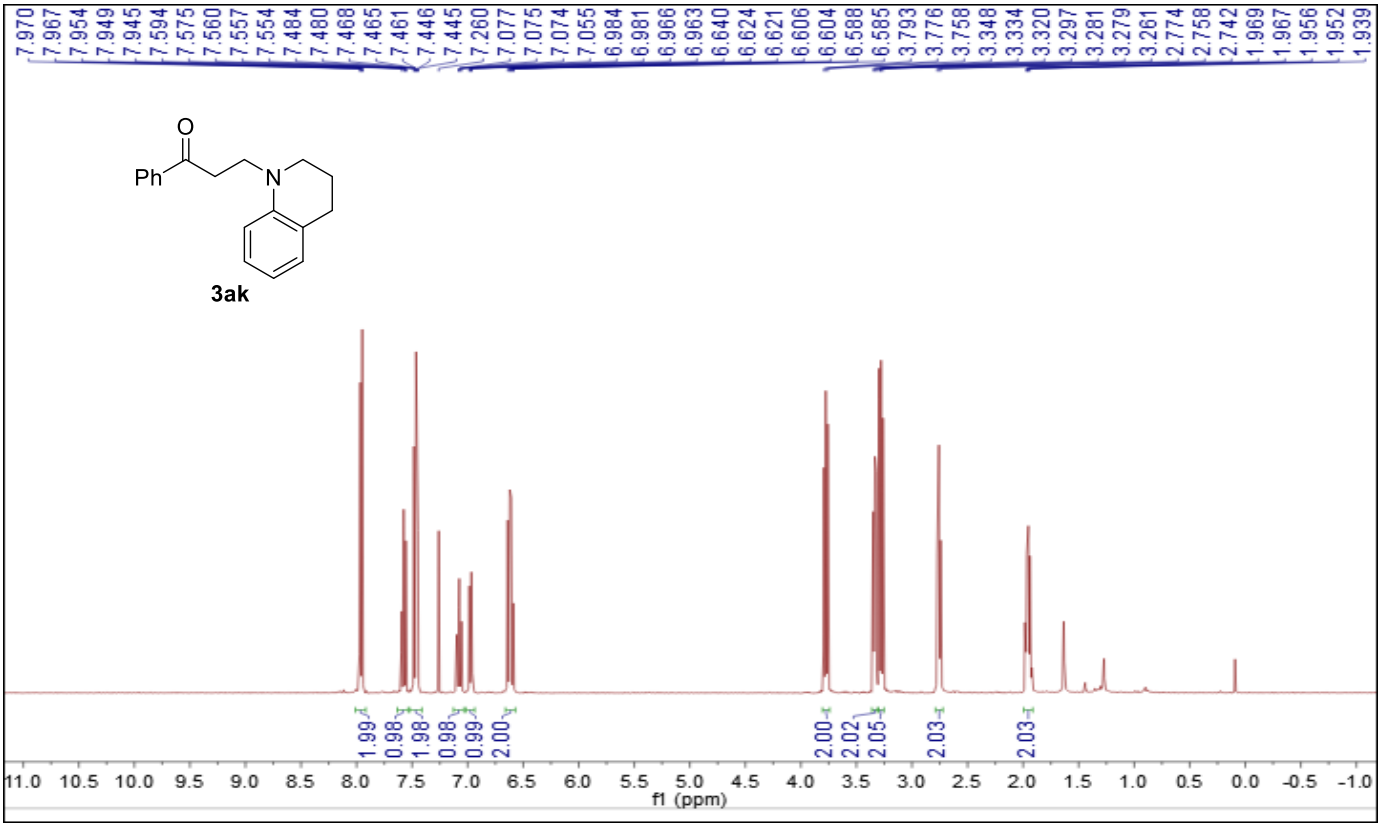
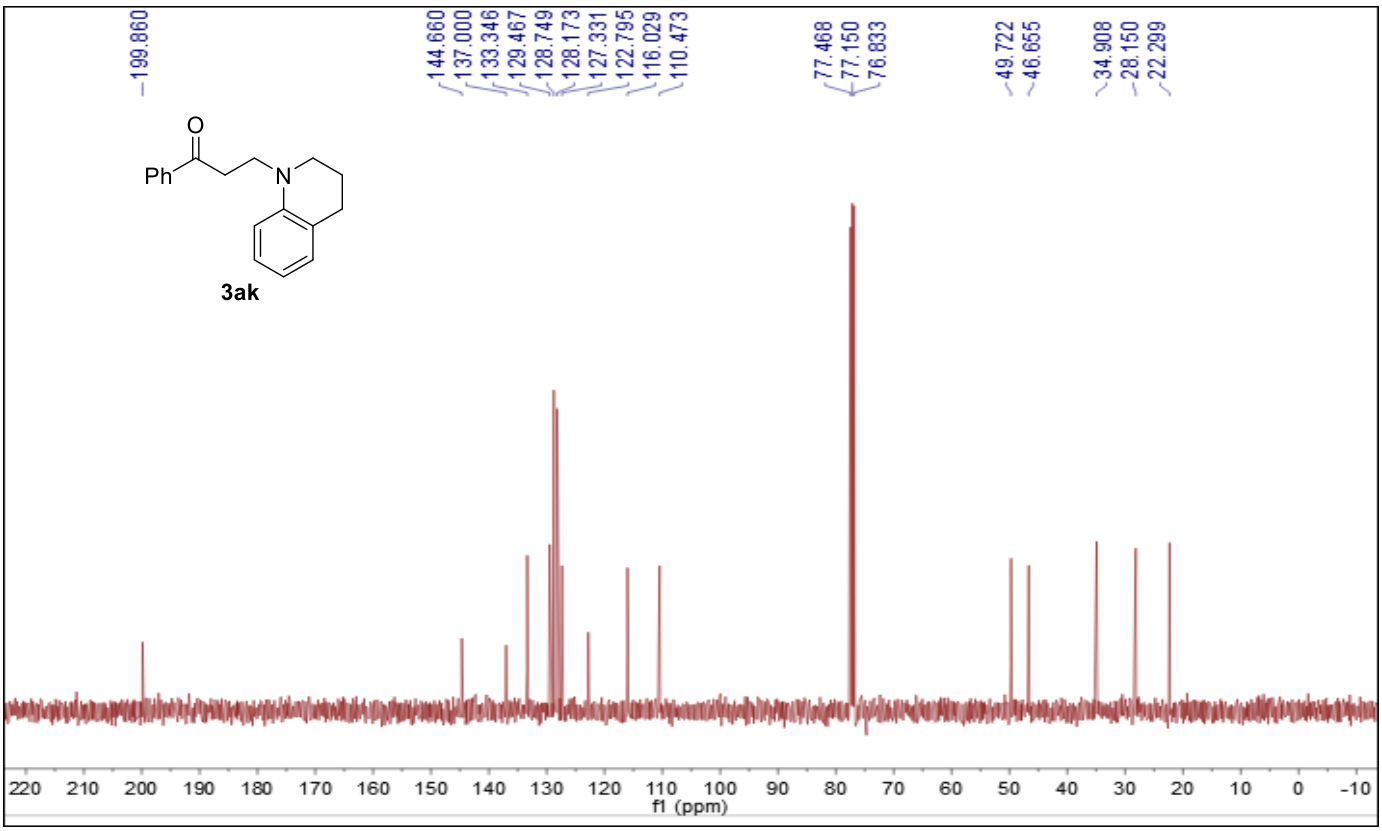
7.964
7.963
7.961
7.948
7.943
7.940
7.585
7.582
7.579
7.569
7.564
7.559
7.548
7.545
7.542
7.484
7.479
7.476
7.463
7.460
7.457
7.446
7.441
7.440
3.728
3.717
3.705
3.215
3.197
3.178
2.862
2.843
2.825
2.532
2.521
2.510
O
Ph
N
O
3ai
2.01
1.00
2.00
4.11
2.04
2.03
4.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 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 -0.5 -1.0
f1 (ppm)


198.989
136.901
133.291
128.747
128.114
77.450
77.132
76.813
66.934
53.765
53.596
35.997
O
Ph
N
O
3ai
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.994
7.991
7.978
7.973
7.969
7.602
7.584
7.569
7.565
7.562
7.499
7.495
7.482
7.479
7.476
7.465
7.461
7.459
7.260
7.107
7.103
7.100
7.097
7.090
7.089
7.085
7.082
7.079
7.076
7.072
7.070
6.693
6.691
6.674
6.672
6.656
6.654
6.560
6.540
3.619
3.602
3.583
3.437
3.416
3.396
3.296
3.277
3.260
2.994
2.973
2.953
O
Ph
N
3aj
2.00
0.99
2.01
1.99
1.00
1.00
2.02
2.03
2.05
2.06
11.0 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 -0.5 -1.0
f1 (ppm)


199.256
151.936
136.960
133.350
130.143
128.772
128.167
127.497
124.587
117.771
107.011
77.475
77.159
76.842
53.348
44.219
35.864
28.723
O
Ph
N
3aj
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.970
7.967
7.954
7.949
7.945
7.594
7.575
7.560
7.557
7.554
7.484
7.480
7.468
7.465
7.461
7.446
7.445
7.260
7.077
7.075
7.074
7.055
6.984
6.981
6.966
6.963
6.640
6.624
6.621
6.606
6.604
6.588
6.585
3.793
3.776
3.758
3.348
3.334
3.320
3.297
3.281
3.279
3.261
2.774
2.758
2.742
1.969
1.967
1.956
1.952
1.939
O
Ph
N
3ak
1.99
0.98
1.98
0.98
0.99
2.00
2.00
2.02
2.05
2.03
2.03
11.0 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 -0.5 -1.0
f1 (ppm)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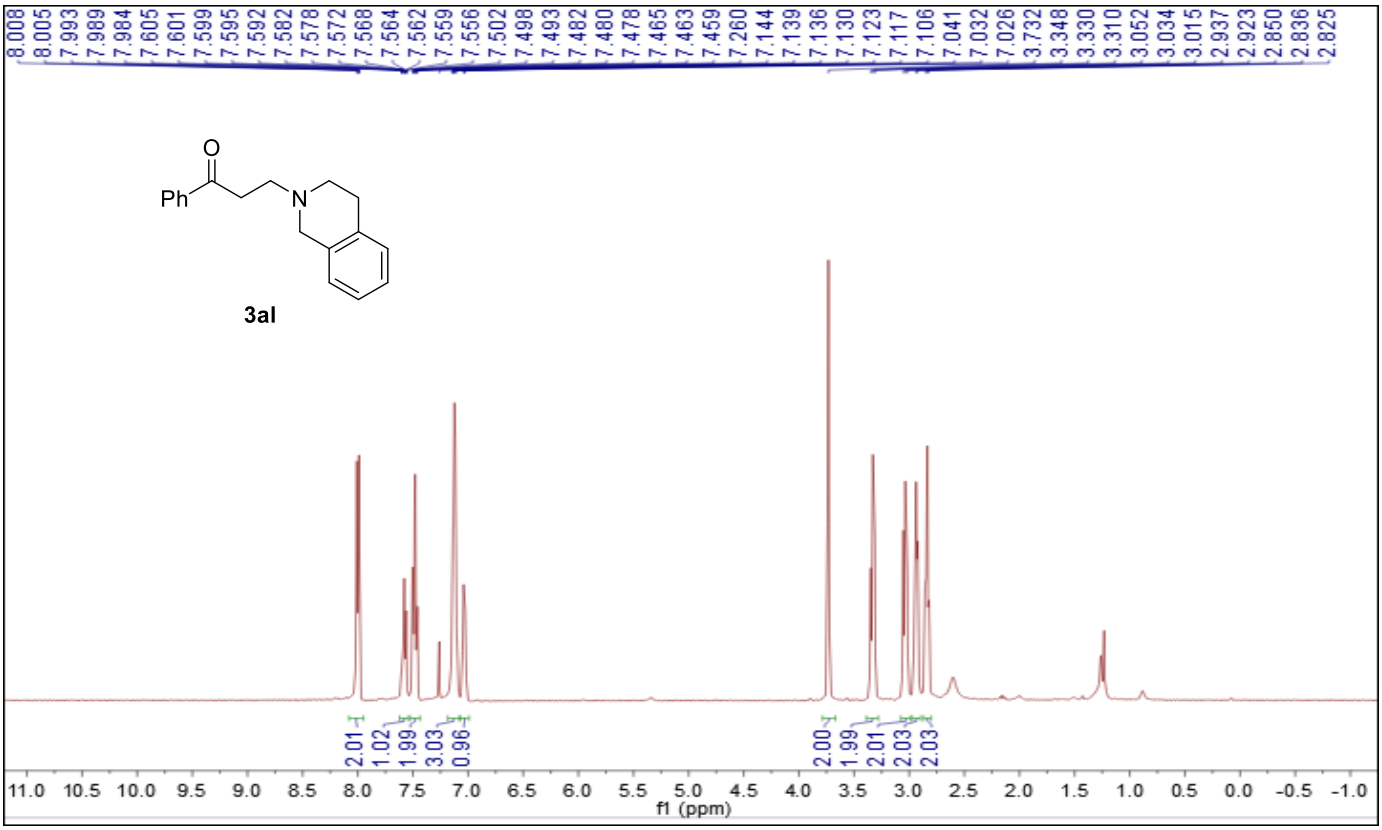
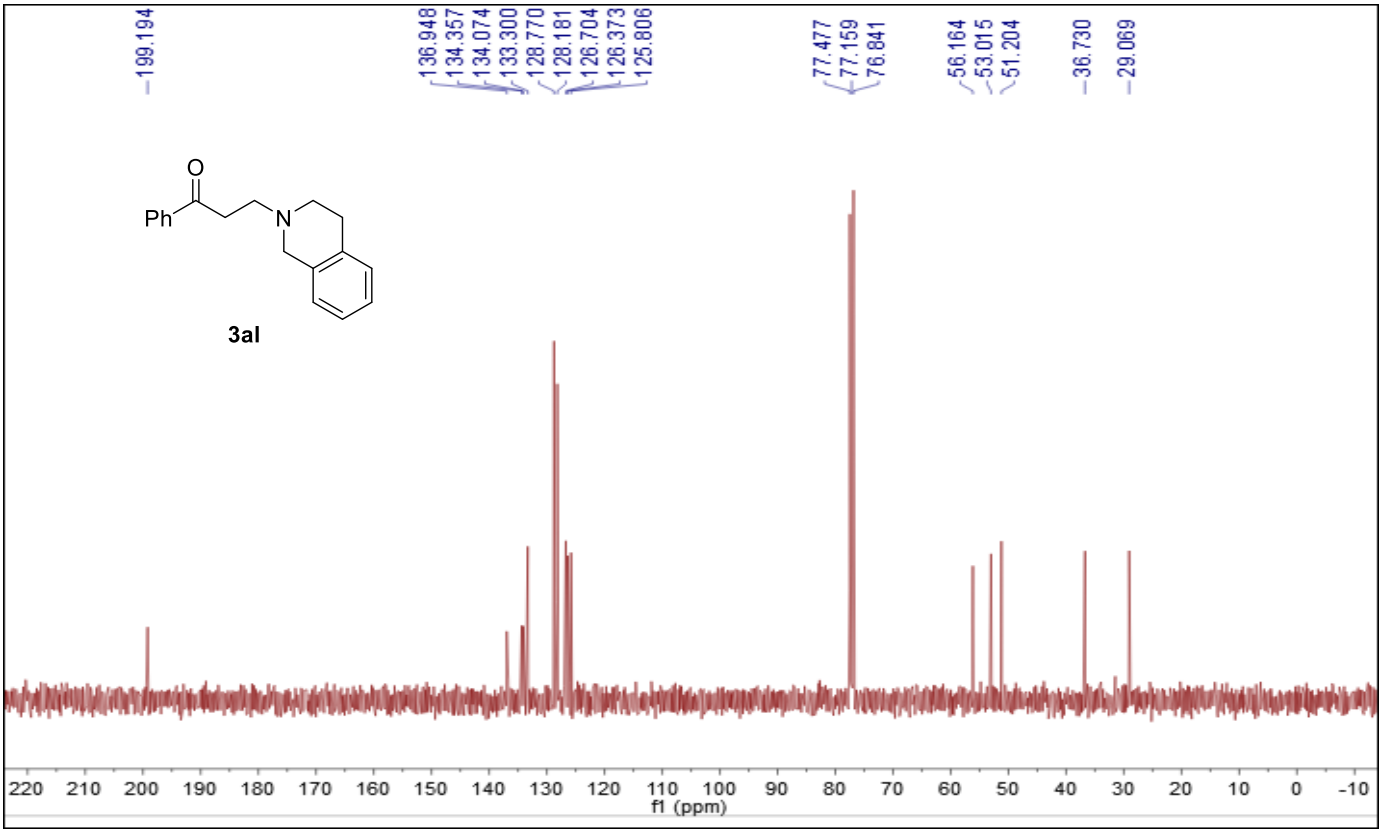
129.467
128.749
128.173
127.331
122.795
116.029
110.473
77.468
77.150
76.833
49.722
46.655
34.908
28.150
22.299
O
Ph
N
3ak
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.008
8.005
7.993
7.989
7.984
7.605
7.601
7.599
7.595
7.592
7.582
7.578
7.572
7.568
7.564
7.562
7.559
7.556
7.502
7.498
7.493
7.482
7.480
7.478
7.465
7.463
7.459
7.260
7.144
7.139
7.136
7.130
7.123
7.117
7.106
7.041
7.032
7.026
3.732
3.348
3.330
3.310
3.052
3.034
3.015
2.937
2.923
2.850
2.836
2.825
O
Ph
N
3al
2.01
1.02
1.99
3.03
0.96
2.00
1.99
2.01
2.03
2.03
11.0 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 -0.5 -1.0
f1 (ppm)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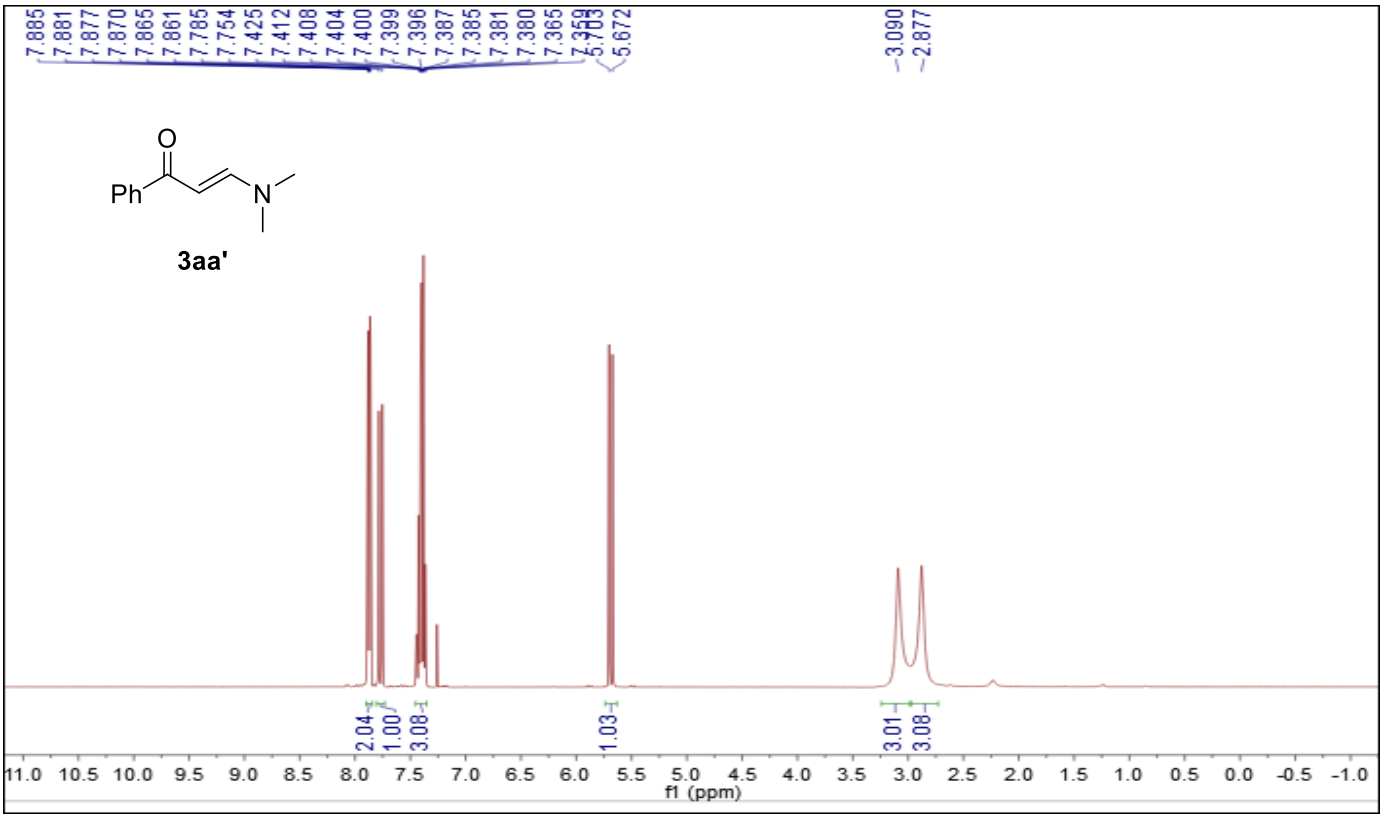
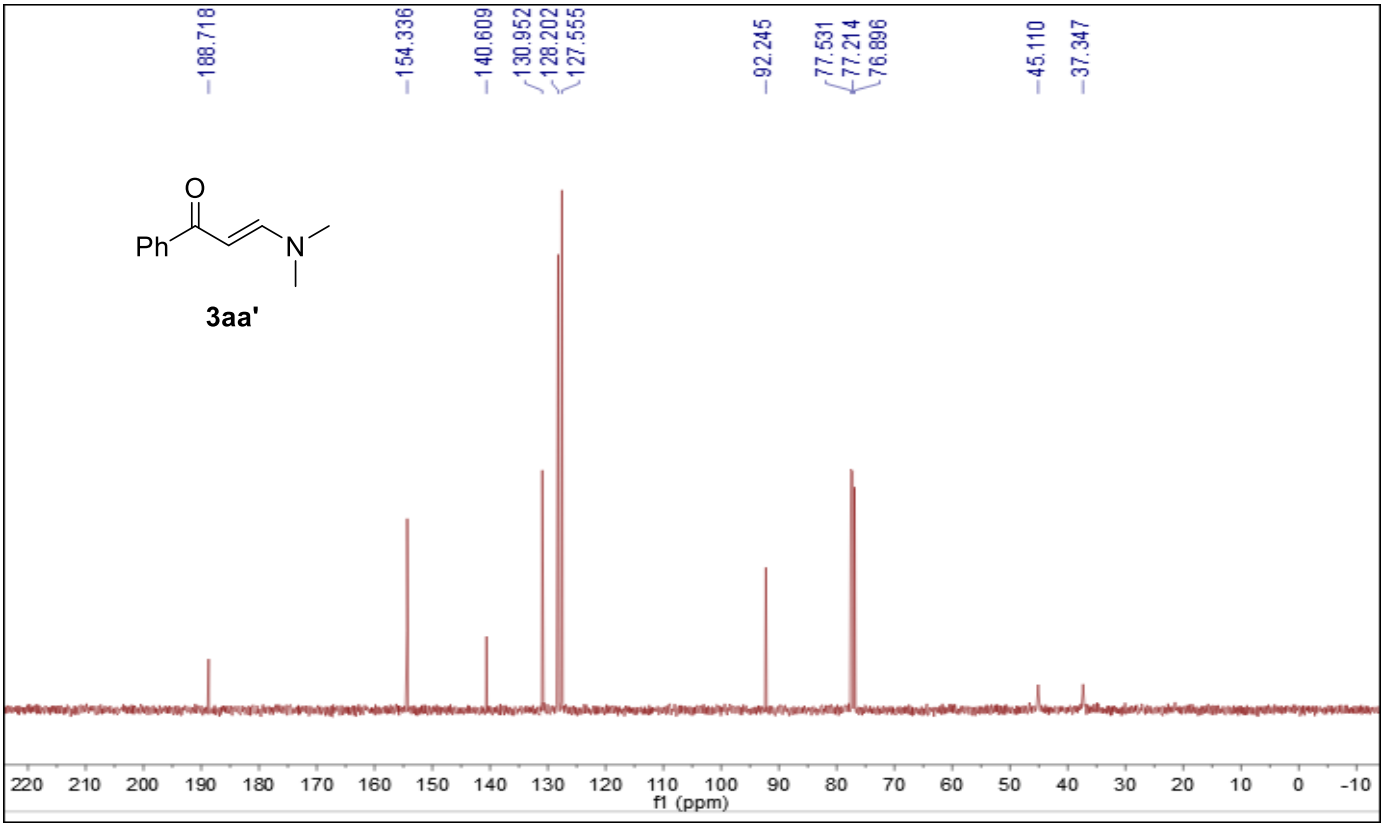
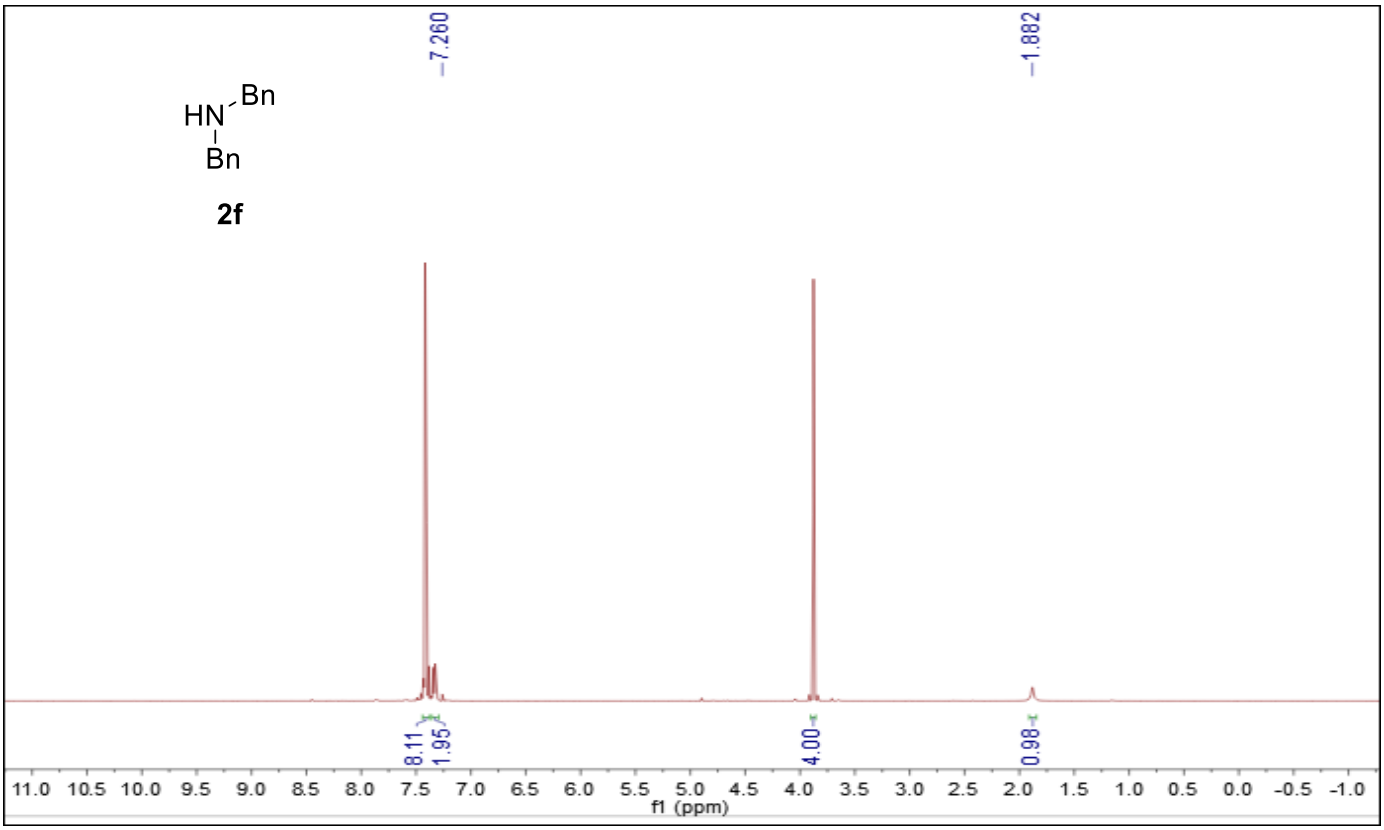
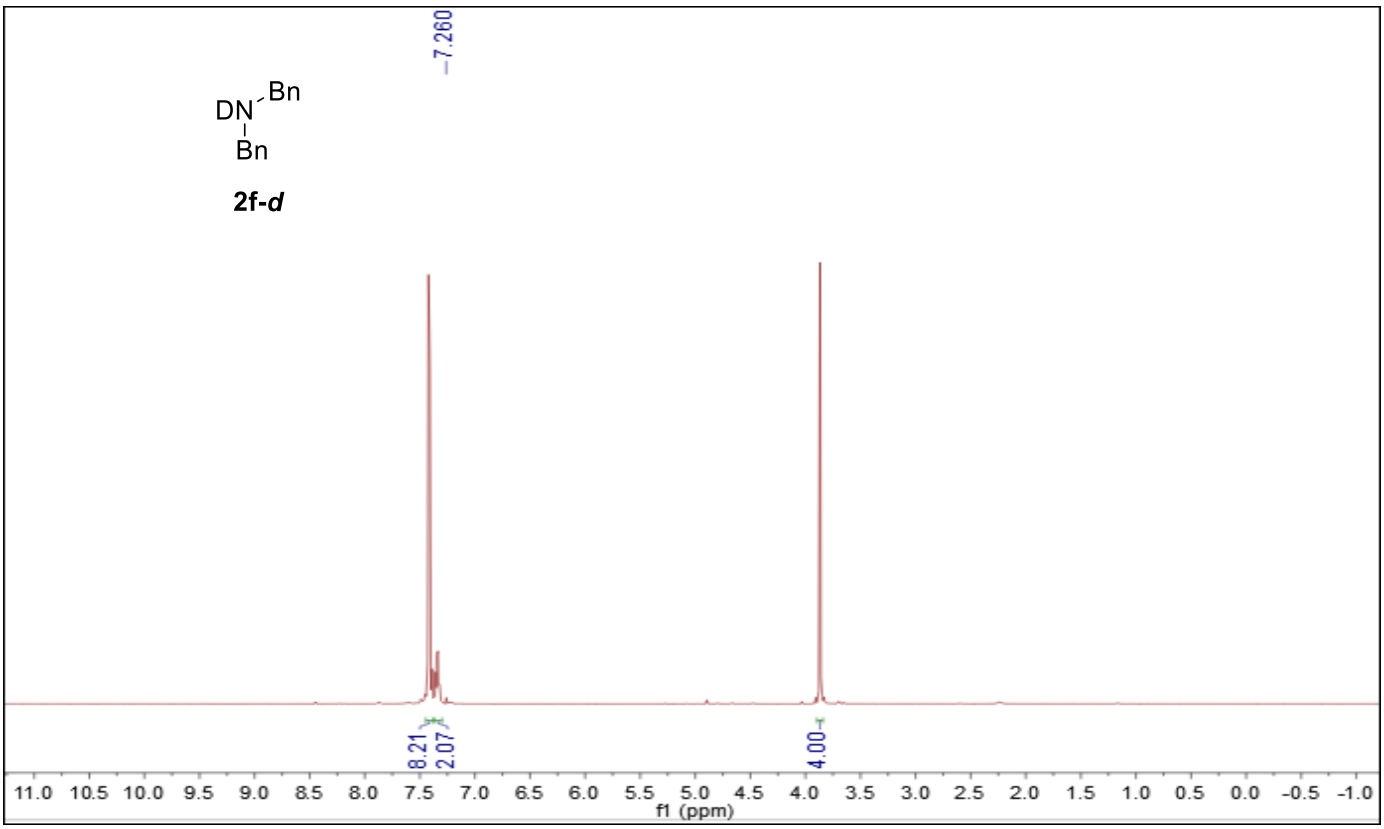
134.357
134.074
133.300
128.770
128.181
126.704
126.373
125.806
77.477
77.159
76.841
56.164
53.015
51.204
36.730
29.069
O
Ph
N
3al
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

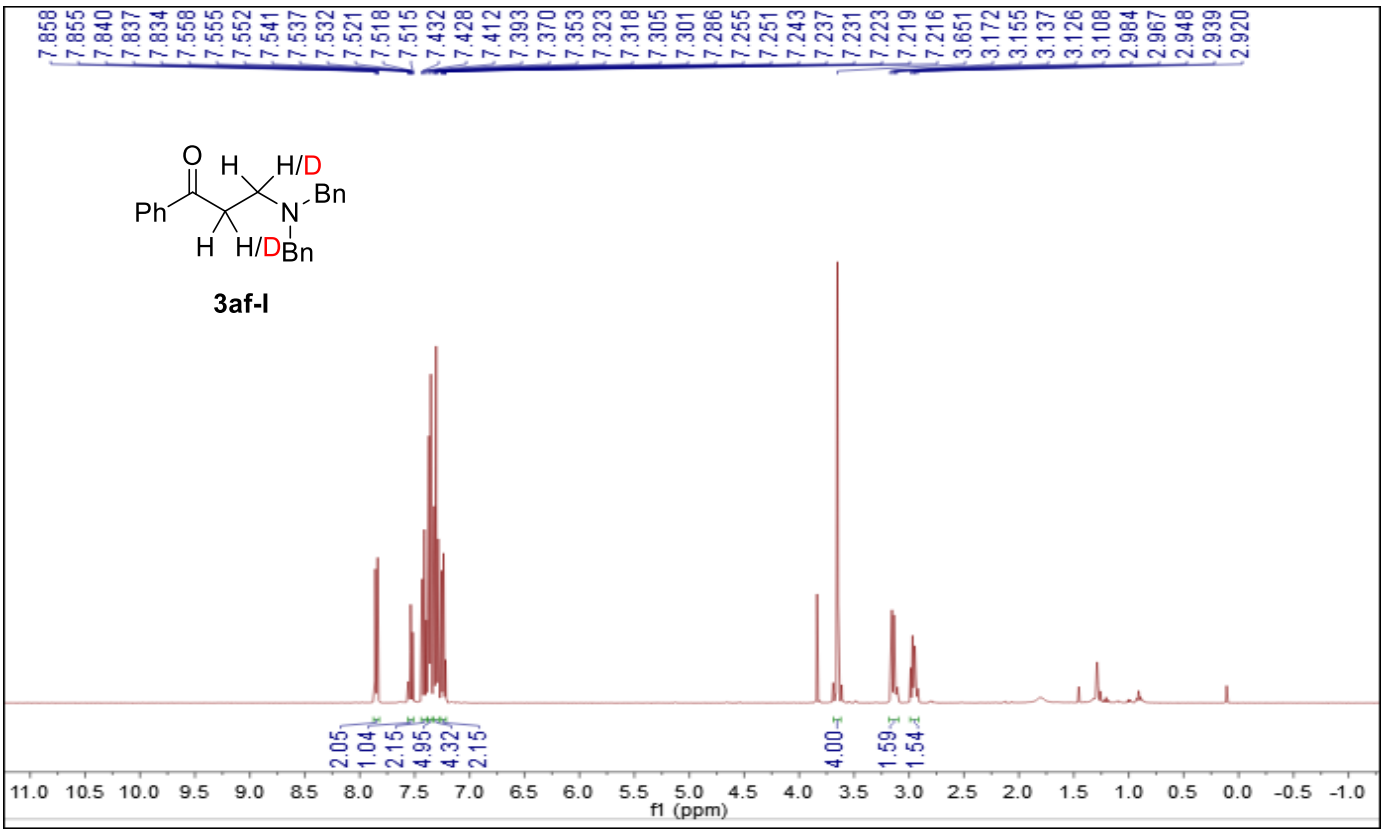
^{1}H and ^{13}C NMR spectra of mechanism studies






HN
Bn
Bn
2f
7.260
1.882
8.11
1.95
4.00
0.98
11.0 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 -0.5 -1.0
f1 (ppm)


DN
Bn
Bn
2f-d
7.260
8.21
2.07
4.00
11.0 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 -0.5 -1.0
f1 (ppm)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7.837
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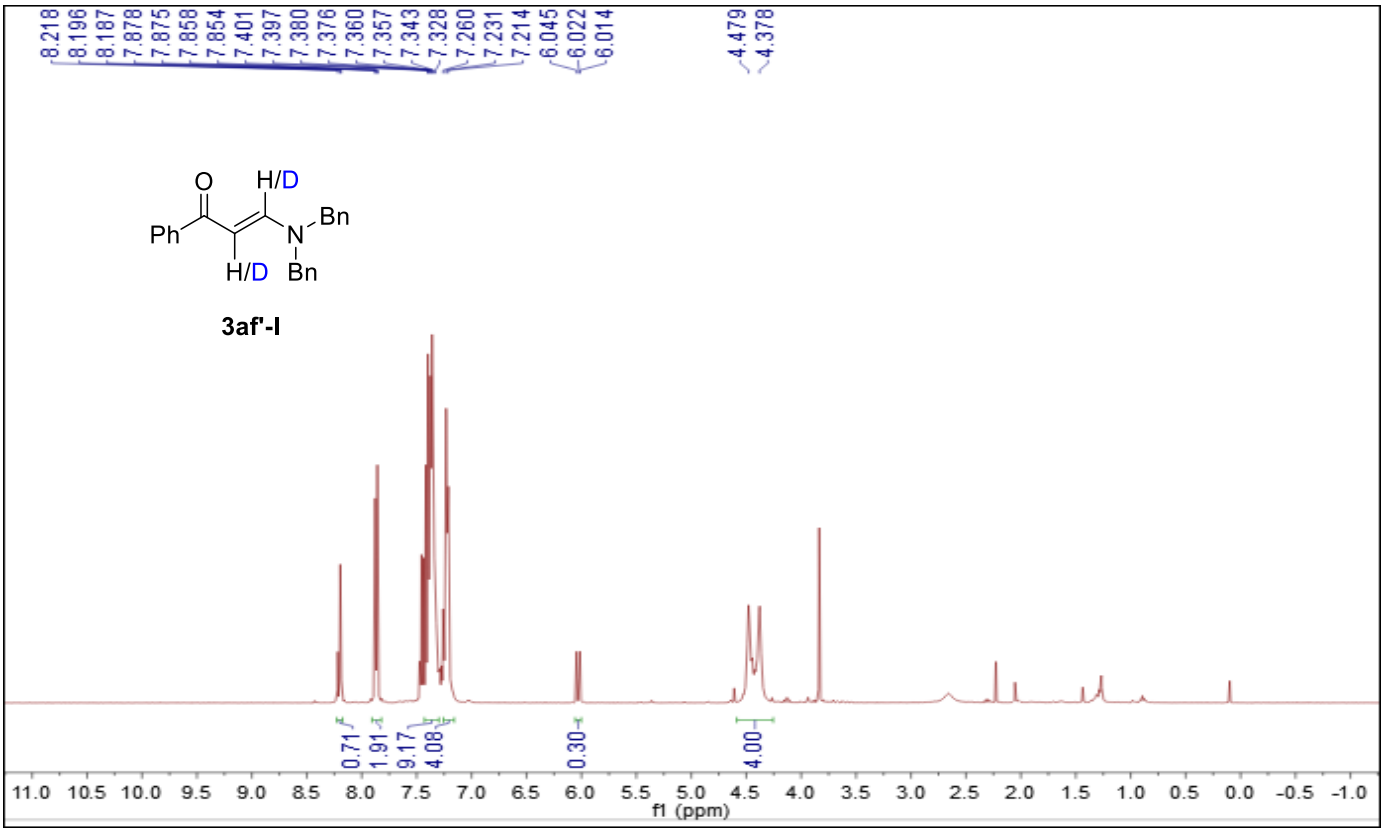
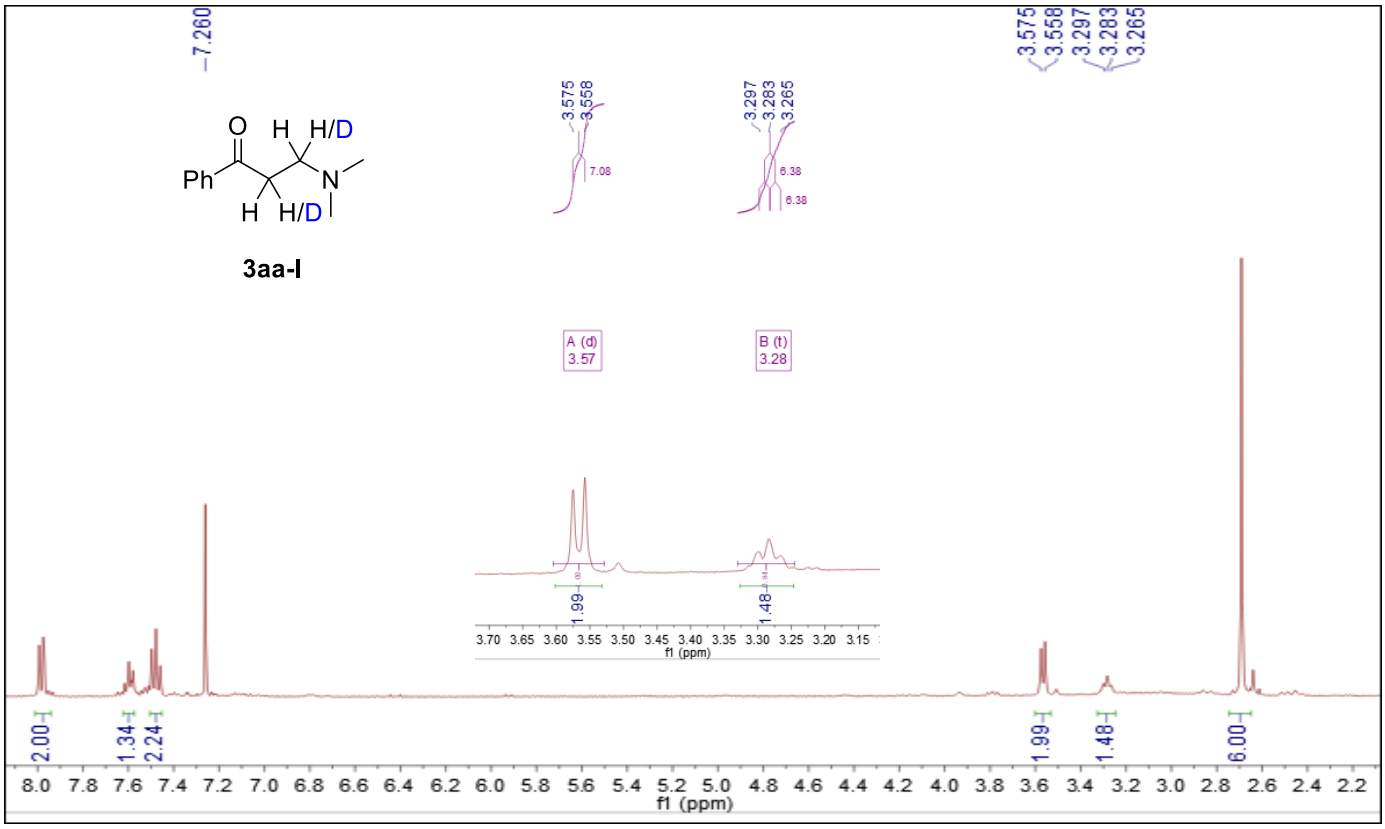
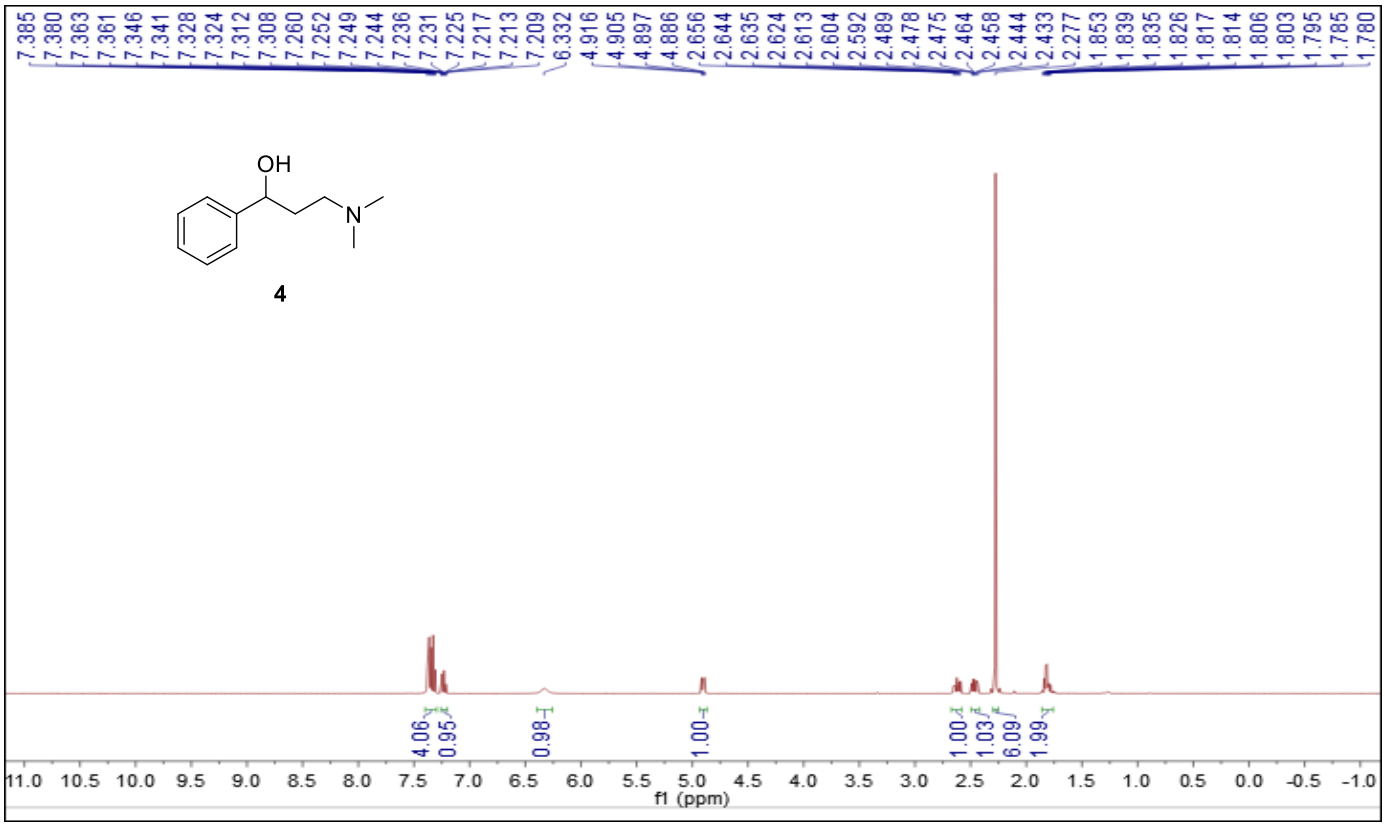
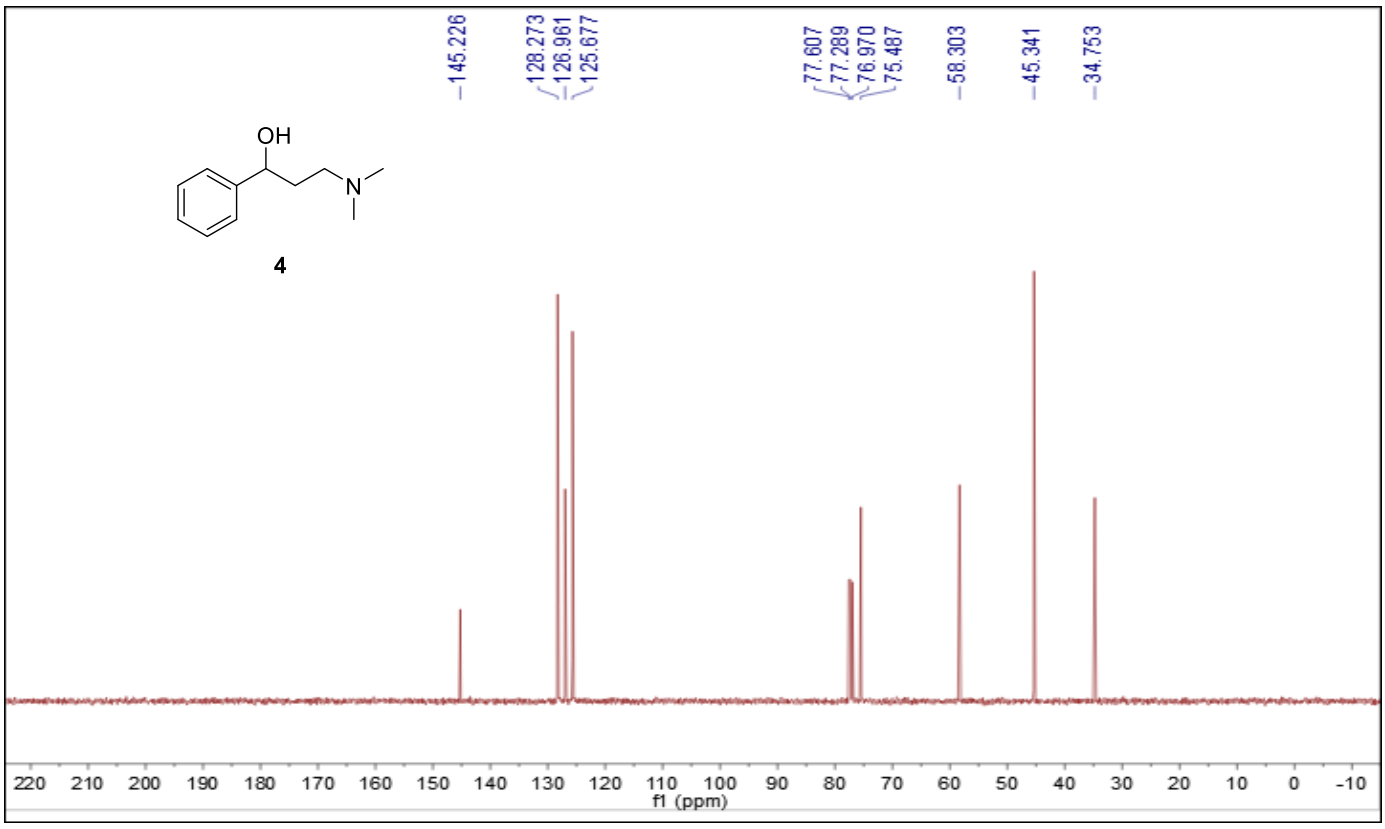
7.555
7.552
7.541
7.537
7.532
7.521
7.518
7.515
7.432
7.428
7.412
7.393
7.370
7.353
7.323
7.318
7.305
7.301
7.286
7.255
7.251
7.243
7.237
7.231
7.223
7.219
7.216
3.651
3.172
3.155
3.137
3.126
3.108
2.984
2.967
2.948
2.939
2.920
O
H
H/D
Ph
N
Bn
H
H/D
Bn
3af-l
2.05
1.04
2.15
4.95
4.32
2.15
4.00
1.59
1.54
11.0 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 -0.5 -1.0
f1 (ppm)

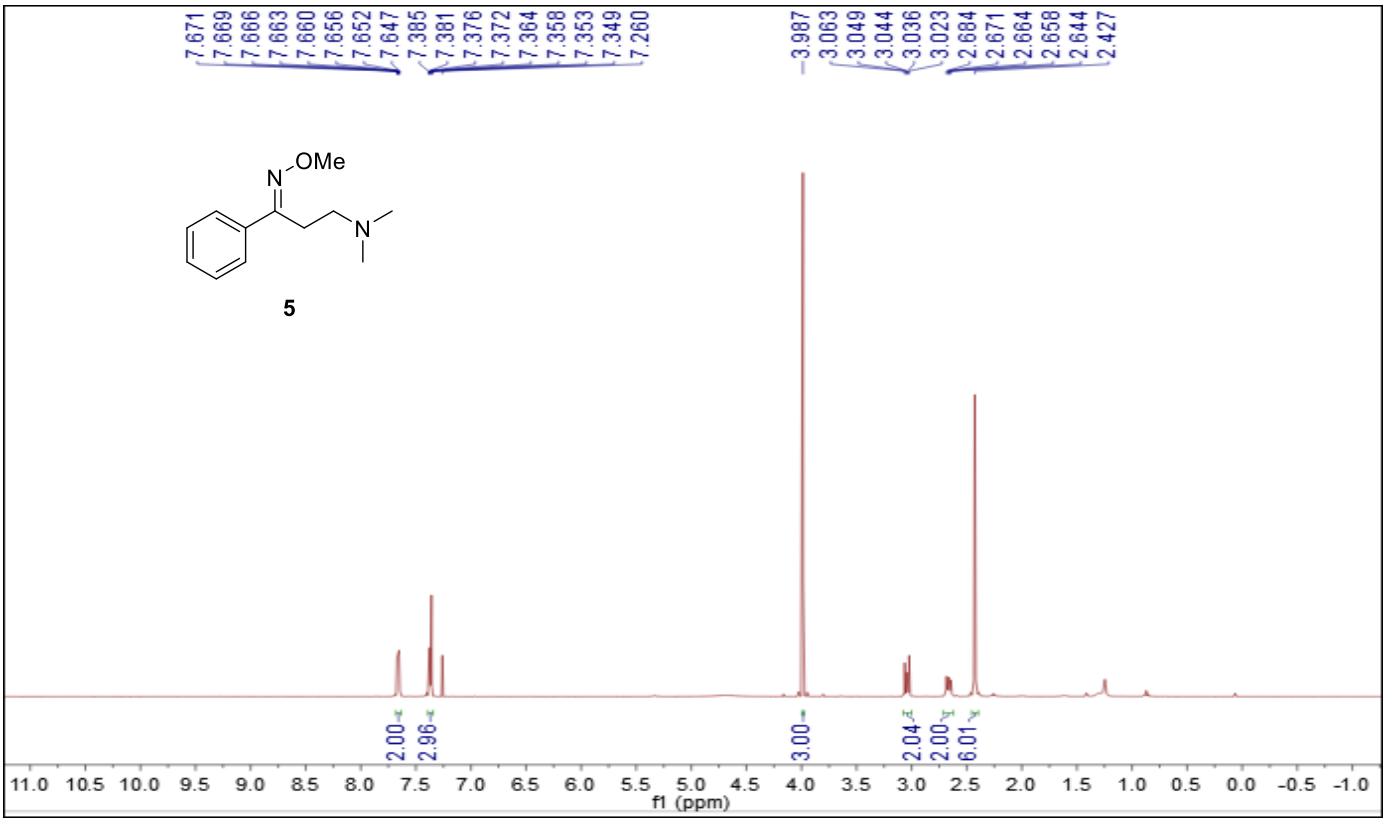

8.218
8.196
8.187
7.878
7.875
7.858
7.854
7.401
7.397
7.380
7.376
7.360
7.357
7.343
7.328
7.260
7.231
7.214
6.045
6.022
6.014
4.479
4.378
O
H/D
Ph
N
Bn
H/D
Bn
3af'-l
0.71
1.91
9.17
4.08
0.30
4.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

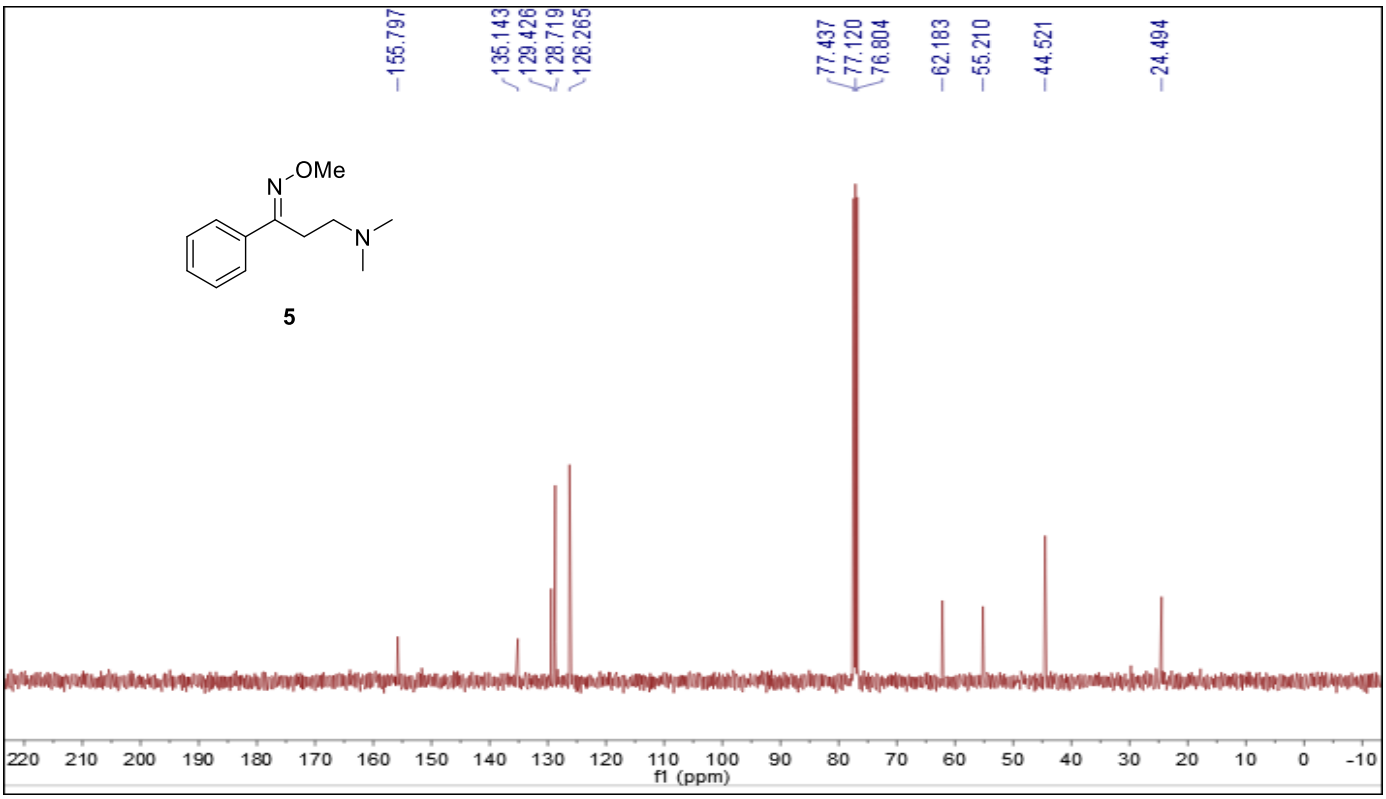

7.260
3.575
3.558
3.297
3.283
3.265
O
H
H/D
Ph
N
H
H/D
3aa-l
A (d)
3.57
B (t)
3.28
7.08
6.38
6.38
1.99
1.48
f1 (ppm)
2.00
1.34
2.24
1.99
1.48
6.00
f1 (ppm)

^{1}H and ^{13}C NMR Spectra for applications






7.671
7.669
7.666
7.663
7.660
7.656
7.652
7.647
7.385
7.381
7.376
7.372
7.364
7.358
7.353
7.349
7.260
3.987
3.063
3.049
3.044
3.036
3.023
2.684
2.671
2.664
2.658
2.644
2.427
OMe
N
N
5
2.00
2.96
3.00
2.04
2.00
6.01
f1 (ppm)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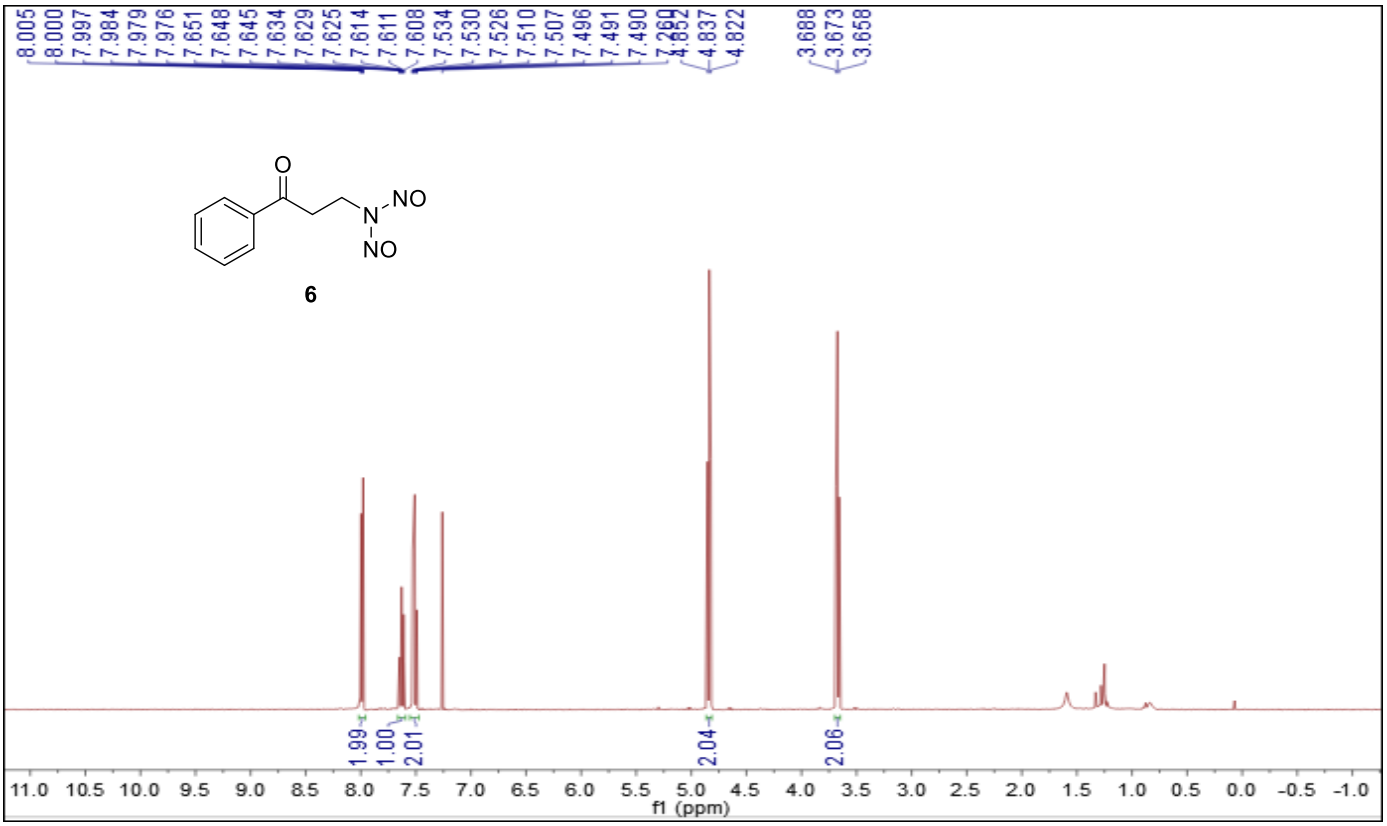
135.143
129.426
128.719
126.265
77.437
77.120
76.804
62.183
55.210
44.521
24.494
OMe
N
N
5
f1 (ppm)


8.005
8.000
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7.979
7.976
7.651
7.648
7.645
7.634
7.629
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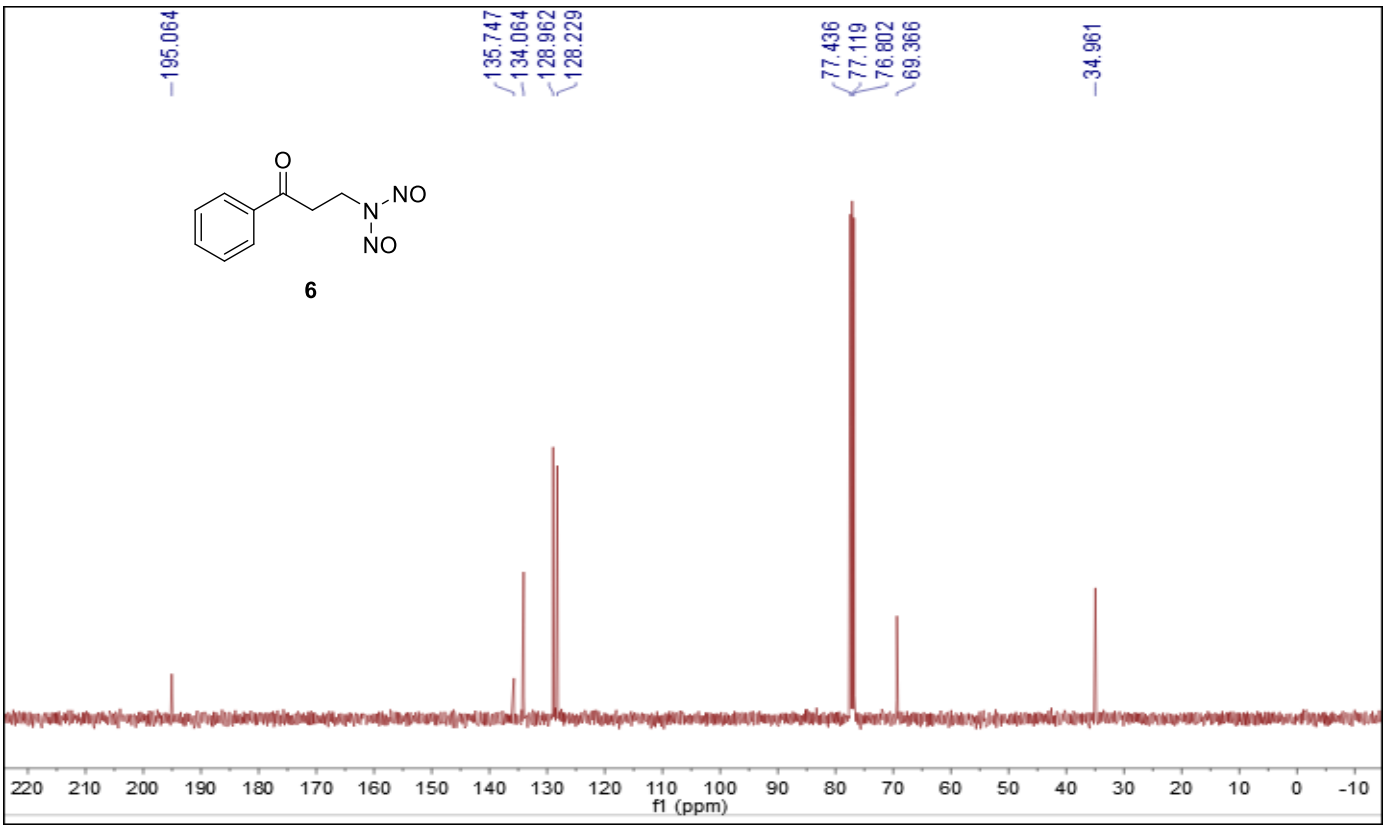
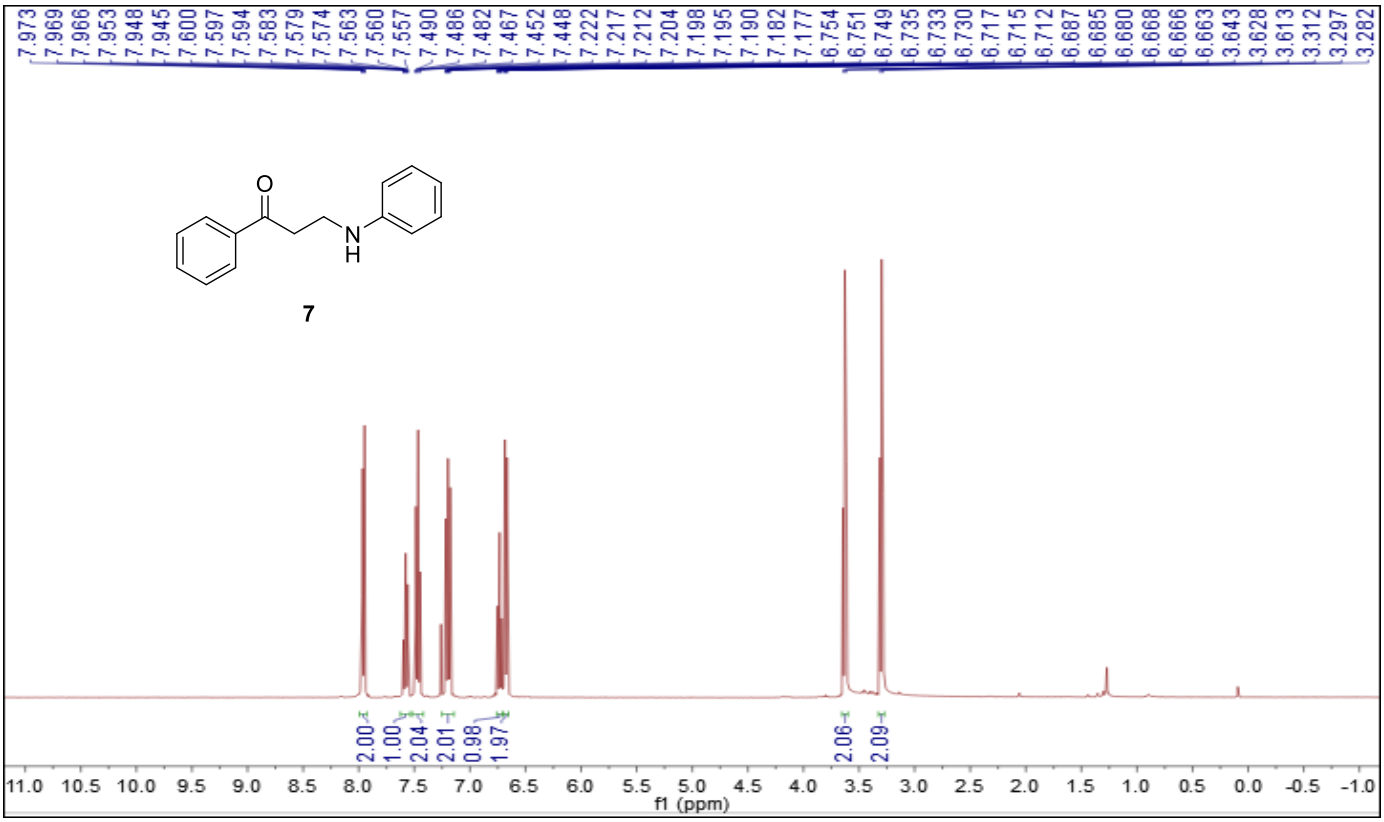
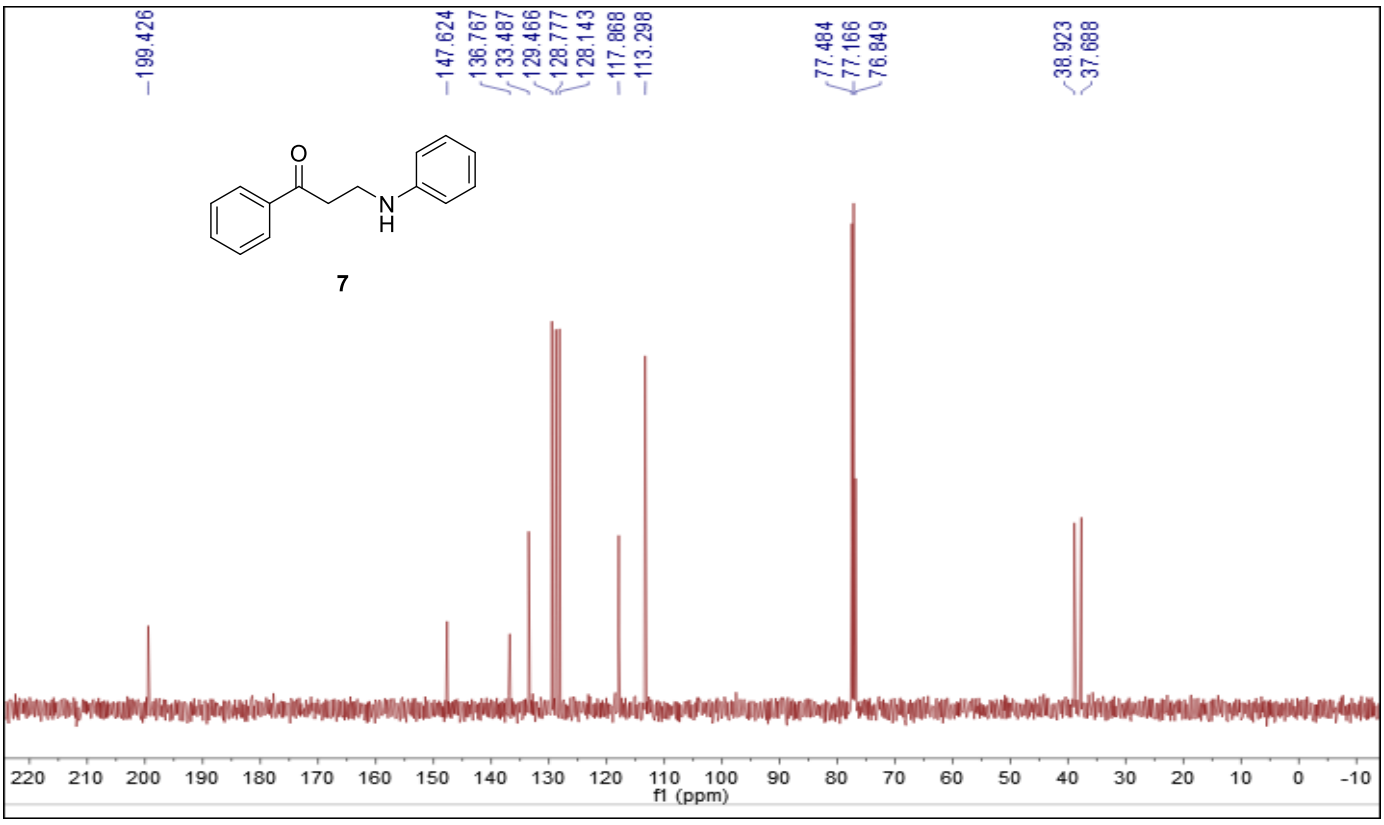
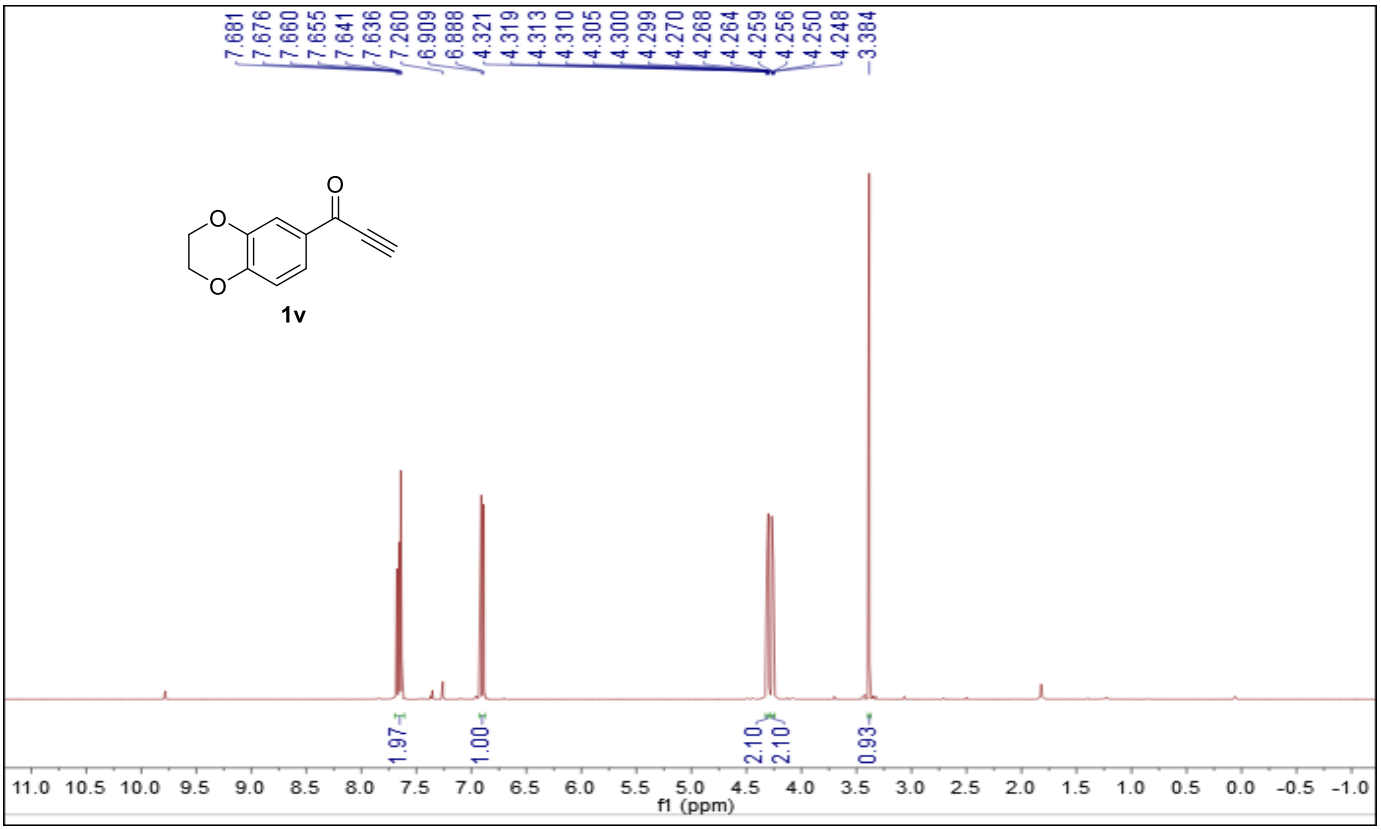
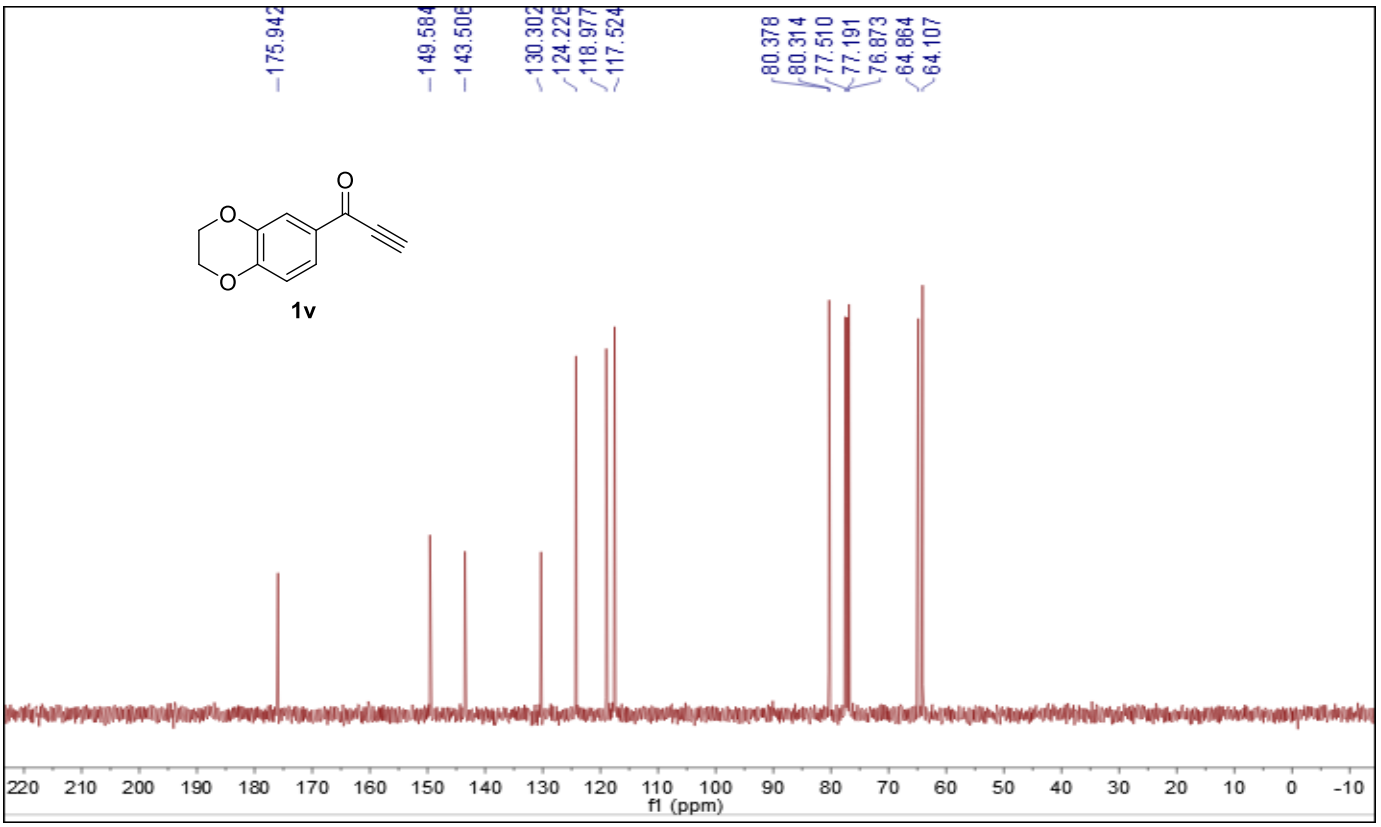
7.614
7.611
7.608
7.534
7.530
7.526
7.510
7.507
7.496
7.491
7.490
4.852
4.837
4.822
3.688
3.673
3.658
O
N
NO
NO
6
1.99
1.00
2.01
2.04
2.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

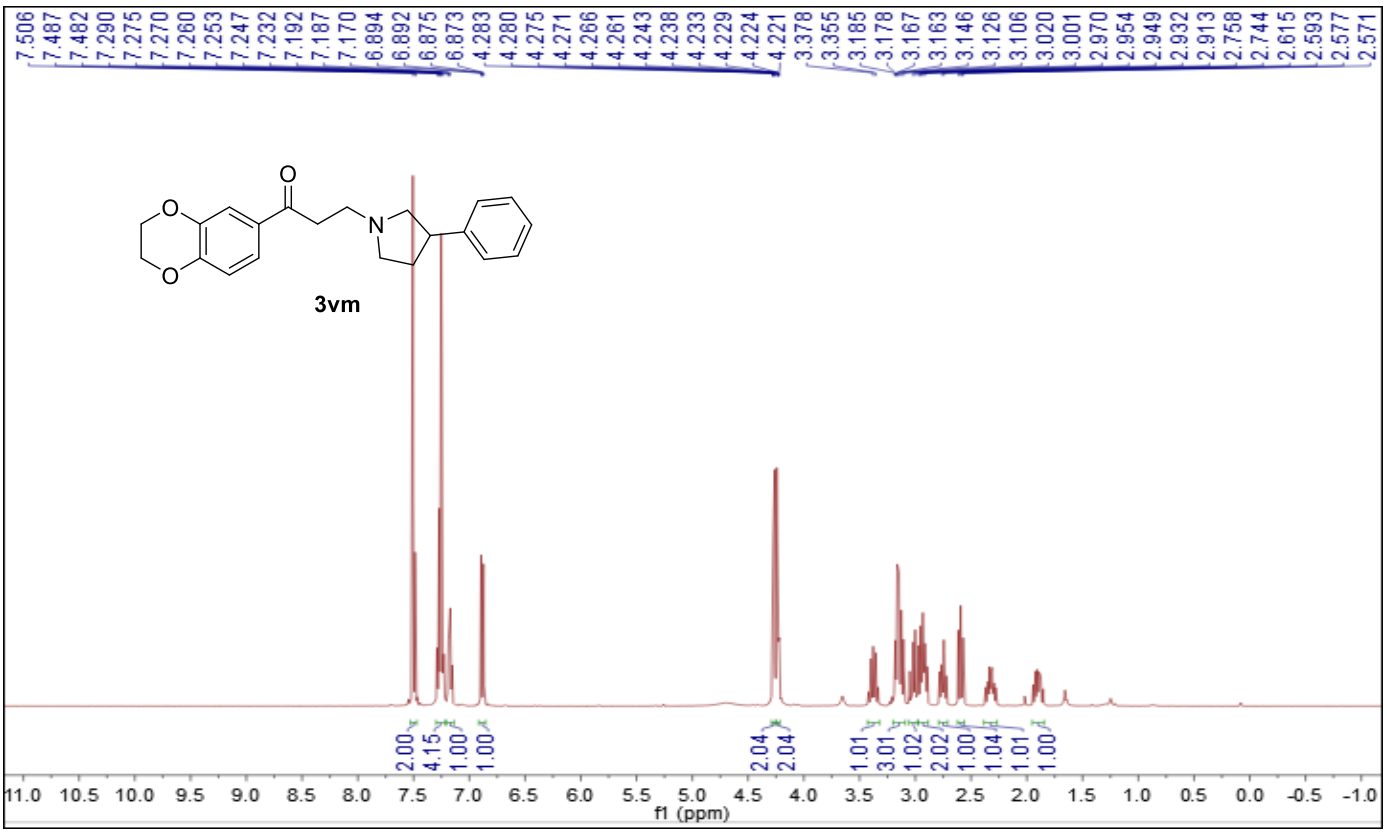

195.064
135.747
134.064
128.962
128.229
77.436
77.119
76.802
69.366
34.961
O
N
NO
NO
6
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

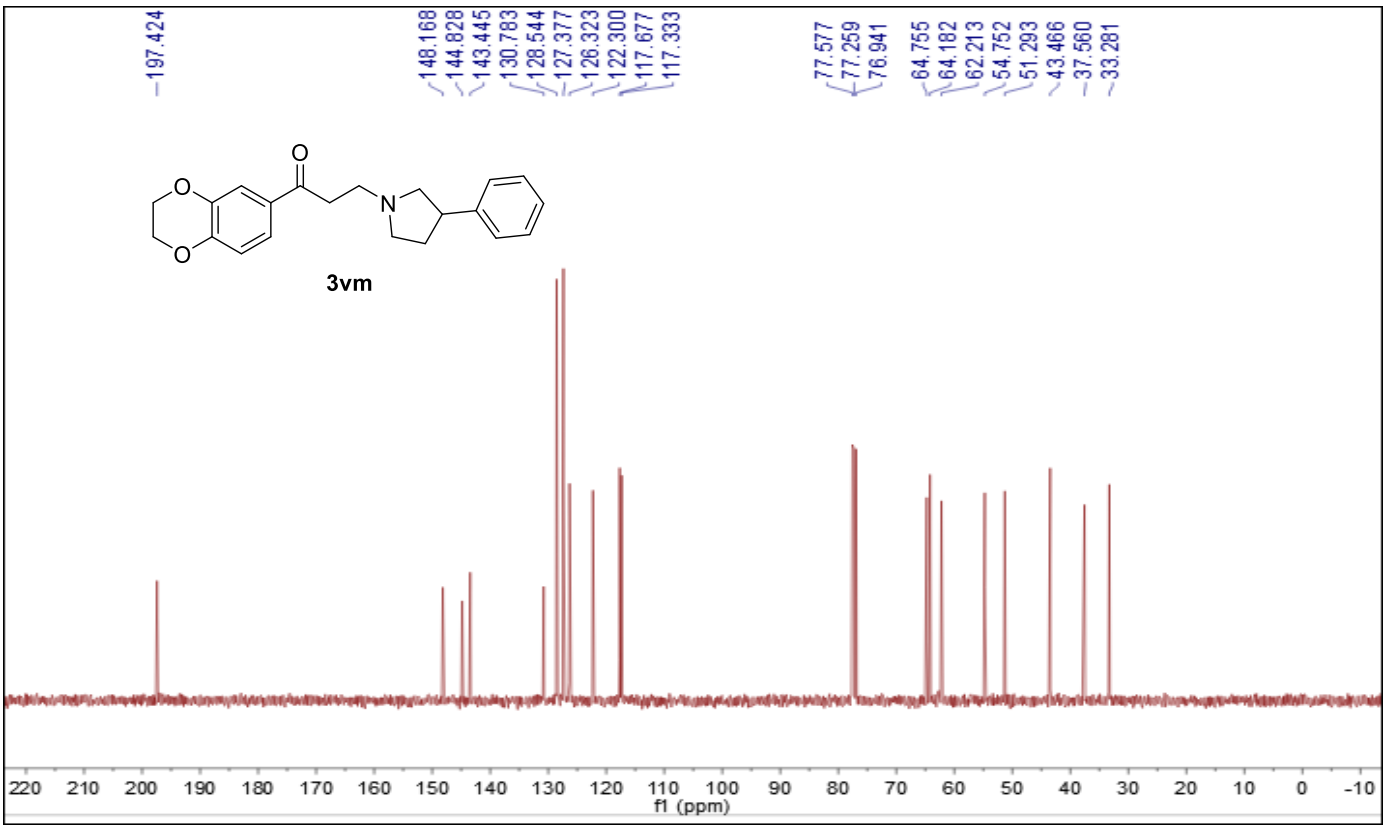

7.973
7.969
7.966
7.953
7.948
7.945
7.600
7.597
7.594
7.583
7.579
7.574
7.563
7.560
7.557
7.490
7.486
7.482
7.467
7.452
7.448
7.222
7.217
7.212
7.204
7.198
7.195
7.190
7.182
7.177
6.754
6.751
6.749
6.735
6.733
6.730
6.717
6.715
6.712
6.687
6.685
6.680
6.668
6.666
6.663
3.643
3.628
3.613
3.312
3.297
3.282
O
N
H
7
2.00
1.00
2.04
2.01
0.98
1.97
2.06
2.09
11.0 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 -0.5 -1.0
f1 (ppm)

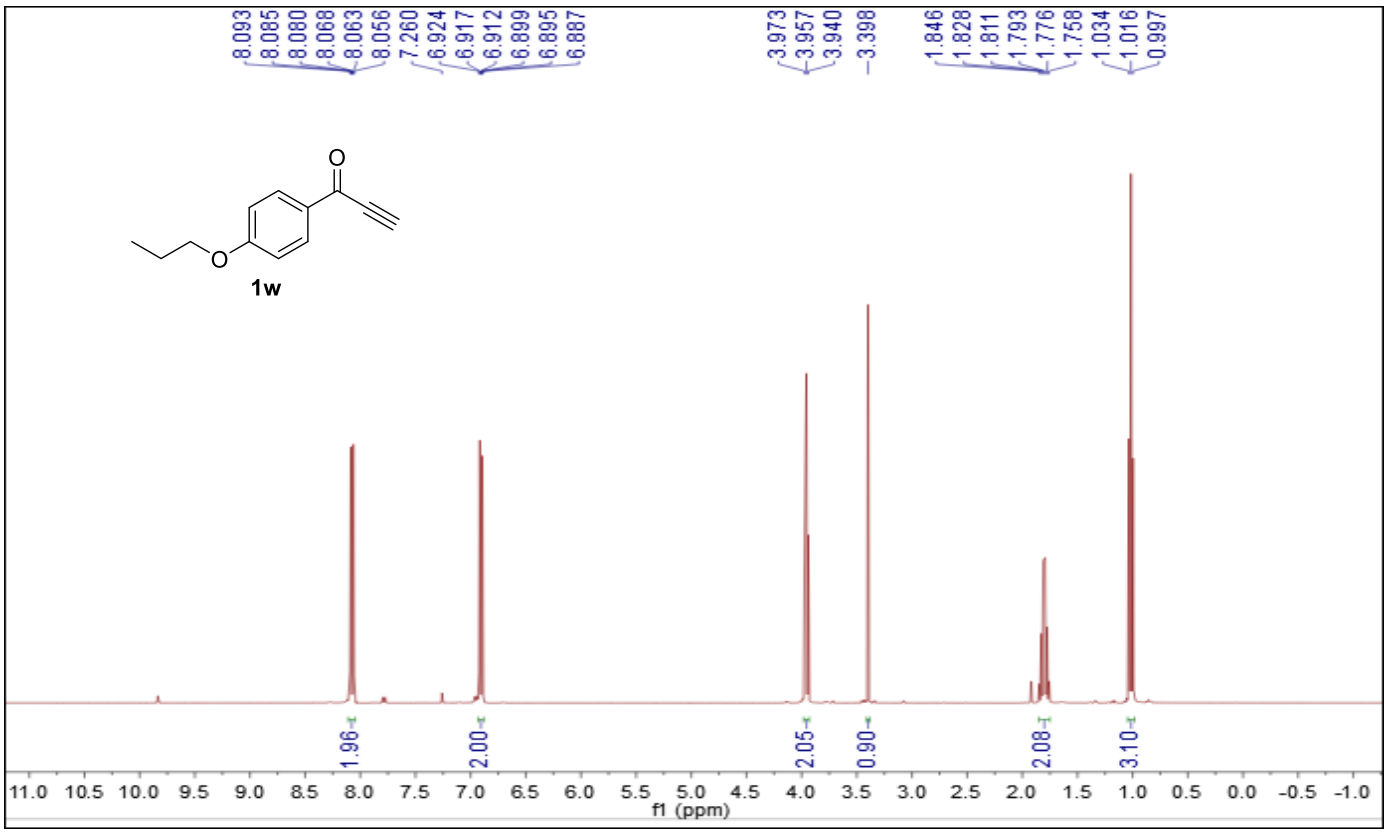

199.426
147.624
136.767
133.487
129.466
128.777
128.143
117.868
113.298
77.484
77.166
76.849
38.923
37.688
O
N
H
7
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

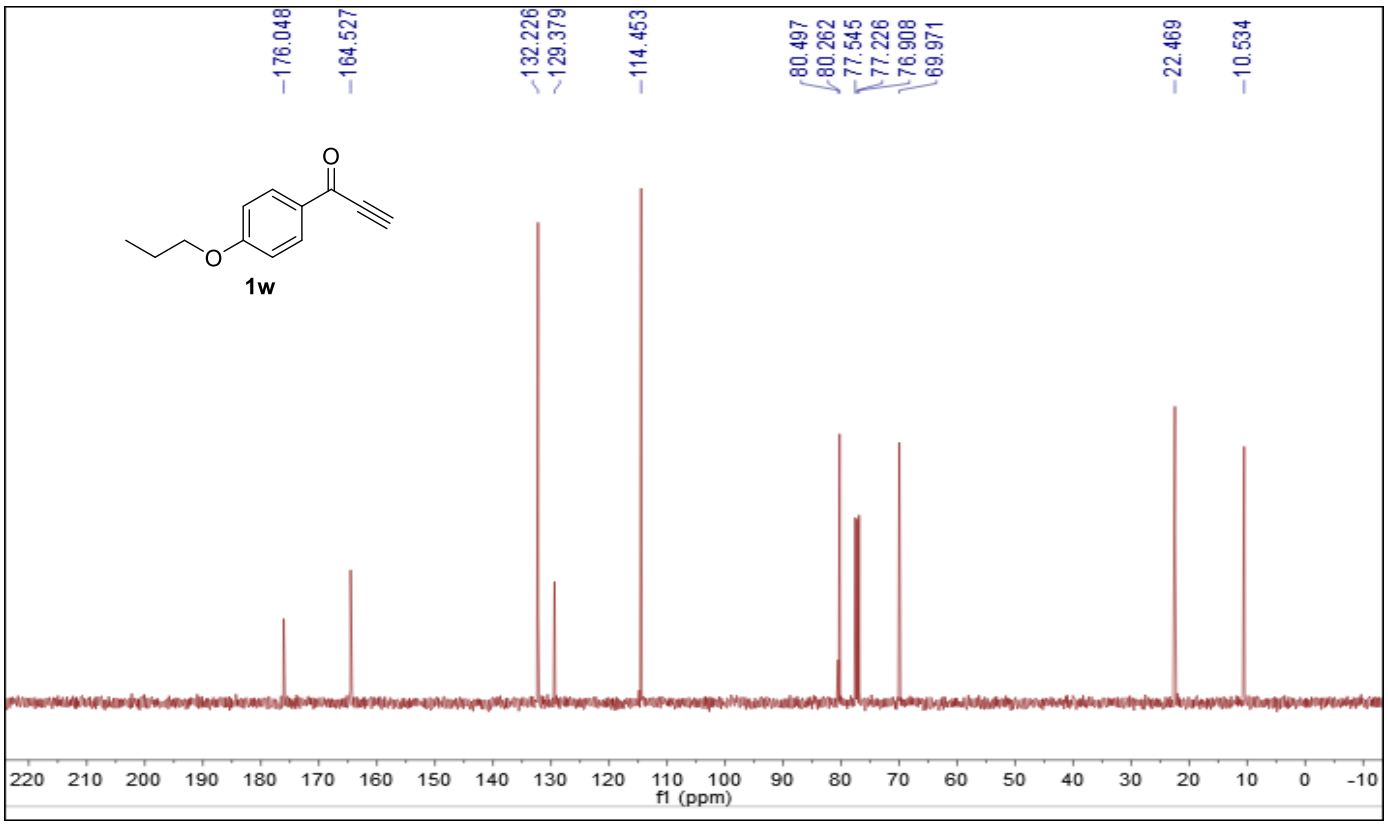

7.681
7.676
7.660
7.655
7.641
7.636
7.260
6.909
6.888
4.321
4.319
4.313
4.310
4.305
4.300
4.299
4.270
4.268
4.264
4.259
4.256
4.250
4.248
3.384
O
O
O
1v
1.97
1.00
2.10
2.10
0.93
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

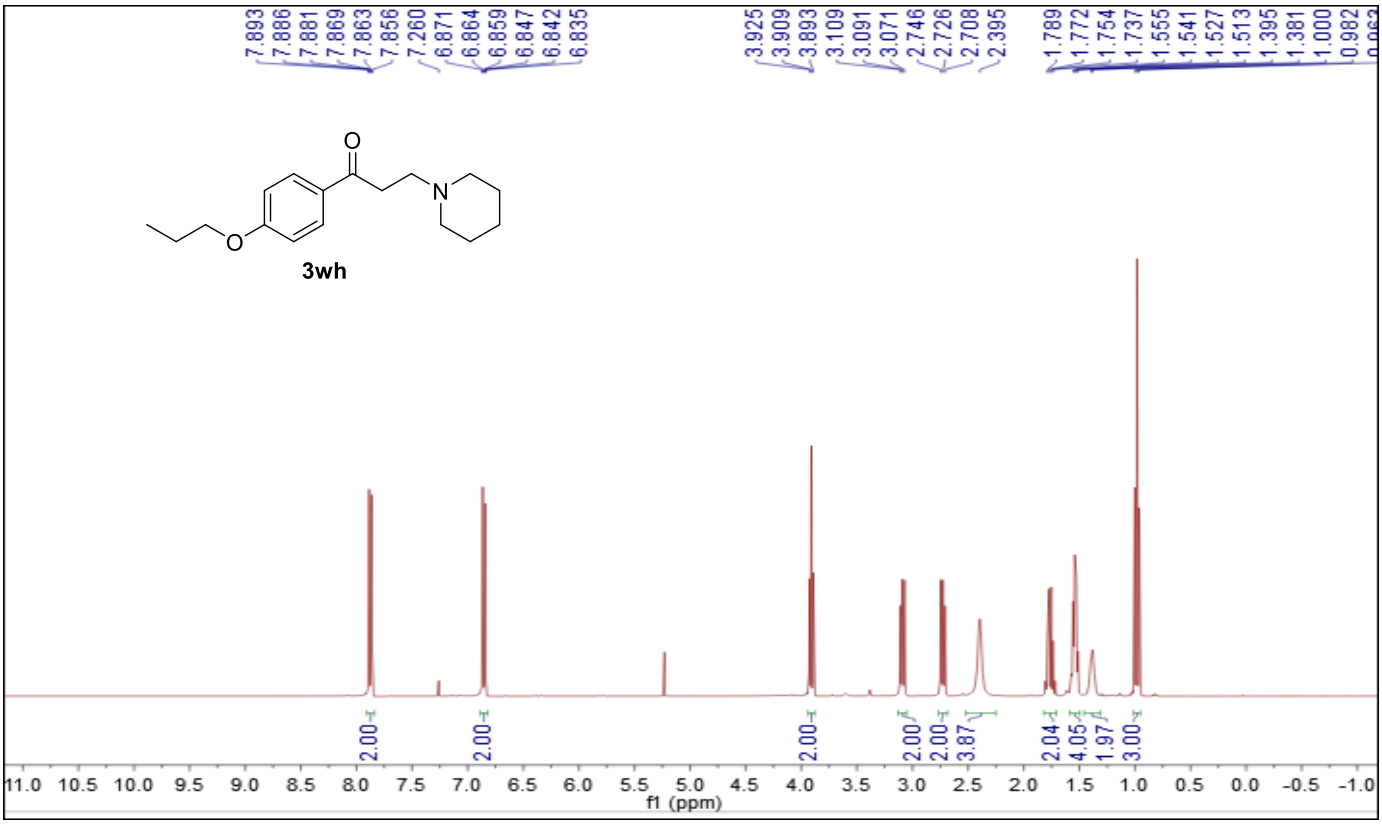

175.942
149.584
143.506
130.302
124.226
118.977
117.524
80.378
80.314
77.510
77.191
76.873
64.864
64.107
O
O
O
1v
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

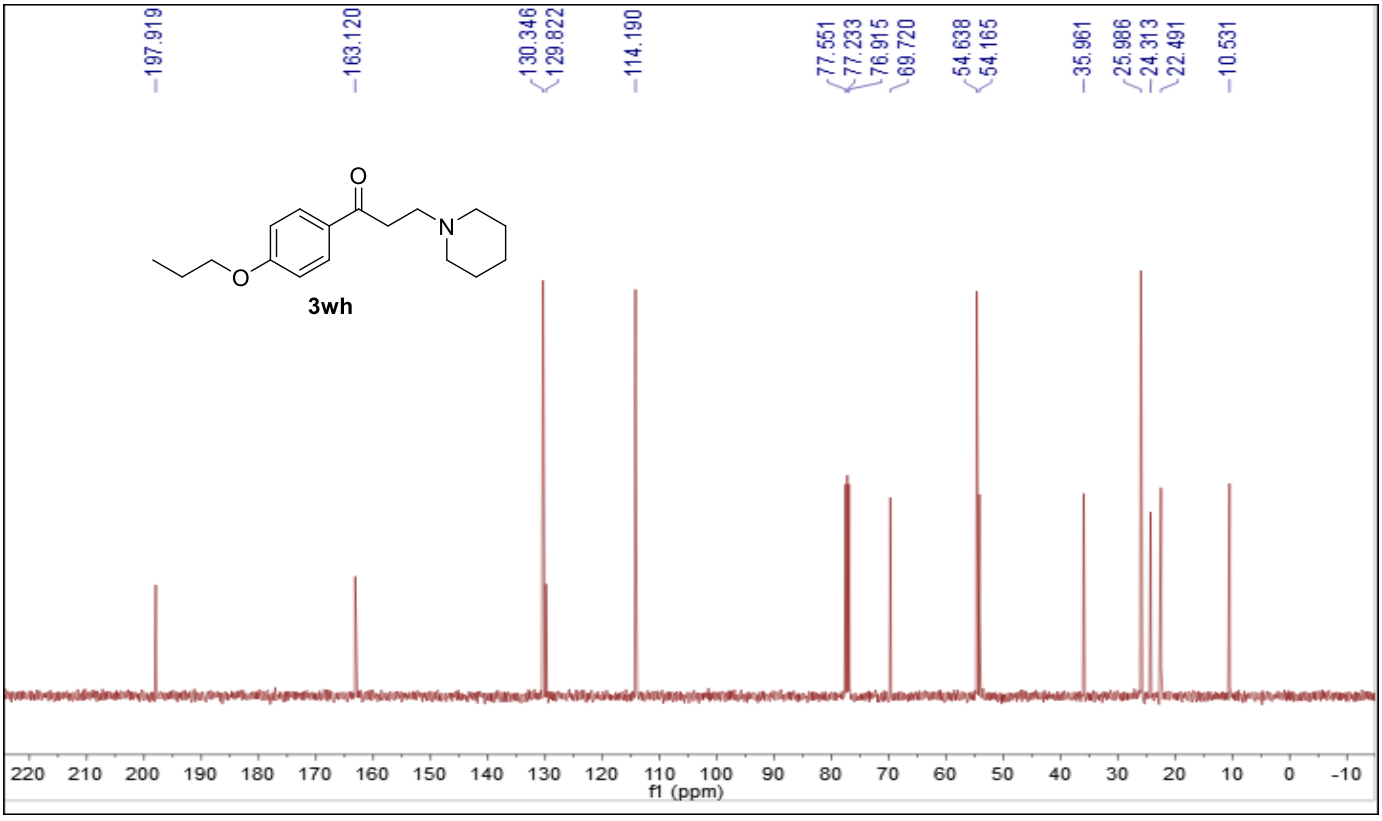

7.506
7.487
7.482
7.290
7.275
7.270
7.260
7.253
7.247
7.232
7.192
7.187
7.170
6.894
6.892
6.875
6.873
4.283
4.280
4.275
4.271
4.266
4.261
4.243
4.238
4.233
4.229
4.224
4.221
3.378
3.355
3.185
3.178
3.167
3.163
3.146
3.126
3.106
3.020
3.001
2.970
2.954
2.949
2.932
2.913
2.758
2.744
2.615
2.593
2.577
2.571
O
O
O
N
3vm
2.00
4.15
1.00
1.00
2.04
2.04
1.01
3.01
1.02
2.02
1.00
1.04
1.01
1.00
11.0 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 -0.5 -1.0
f1 (ppm)


197.424
148.168
144.828
143.445
130.783
128.544
127.377
126.323
122.300
117.677
117.333
77.577
77.259
76.941
64.755
64.182
62.213
54.752
51.293
43.466
37.560
33.281
O
O
O
N
3vm
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.093
8.085
8.080
8.068
8.063
8.056
7.260
6.924
6.917
6.912
6.899
6.895
6.887
3.973
3.957
3.940
3.398
1.846
1.828
1.811
1.793
1.776
1.758
1.034
1.016
0.997
O
O
1w
1.96
2.00
2.05
0.90
2.08
3.10
11.0 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 -0.5 -1.0
f1 (ppm)


176.048
164.527
132.226
129.379
114.453
80.497
80.262
77.545
77.226
76.908
69.971
22.469
10.534
O
O
1w
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.893
7.886
7.881
7.869
7.863
7.856
7.260
6.871
6.864
6.859
6.847
6.842
6.835
3.925
3.909
3.893
3.109
3.091
3.071
2.746
2.726
2.708
2.395
1.789
1.772
1.754
1.737
1.555
1.541
1.527
1.513
1.395
1.381
1.000
0.982
O
N
O
3wh
2.00
2.00
2.00
2.00
2.00
3.87
2.04
4.05
1.97
3.00
11.0 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 -0.5 -1.0
f1 (ppm)


197.919
163.120
130.346
129.822
114.190
77.551
77.233
76.915
69.720
54.638
54.165
35.961
25.986
24.313
22.491
10.531
O
N
O
3wh
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)