Supporting Information

Selective synthesis of β-nitrated N-heterocycles and *N*-nitroso-2-alkoxyamine aldehydes from inactivated cyclic amines promoted by ^{t}BuONO and oxoammonium salt

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Contents

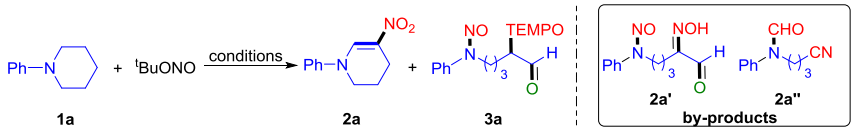
I. General experimental information

Acetone was used without further purification, and the other solvents were dried before using. *Tert*-Butyl nitrite and $BF_3 \cdot Et_2O$ were purchased from commercial source and dried before using. $T^+BF_4^-$ was synthesized with a previously described procedure.[1] *N*-Aryl cyclic amines (**1**) were prepared based on a literature procedure.[2] Melting points were recorded with a micro melting point apparatus and uncorrected. The ^1H NMR spectra were recorded at 400 MHz or 600 MHz, and the ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. The ^{19}F NMR spectra were recorded at 376 MHz or 565 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), q (quadruplet), dd (doublet of doublet), td (doublet of triplet), m (multiplet), br s (broad singlet), etc. The coupling constants *J* were given in Hz. High-resolution mass spectra (HRMS) were performed on a microTOF mass spectrometer. All the reactions were monitored by thin-layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental procedures and spectroscopic data

1. Optimization of reaction conditions

Table S1. Optimization studies on the formation of **2a** and **3a**[a]



1a 2a 3a

Entry	Oxidant (equiv.)	Additive (equiv.)	Solvent	Yield (%)[b]	
				2a	**3a**
1	$T^+BF_4^-$ (1)	-	THF	11	-
2	$T^+ClO_4^-$ (1)	-	THF	9	-
3	$T^+PF_6^-$ (1)	-	THF	9	-
4	TEMPO (1)	-	THF	trace	-
5	$T^+BF_4^-$ (0.5)	-	THF	trace	-
6	$T^+BF_4^-$ (2)	-	THF	11	-
7[c]	$T^+BF_4^-$ (1)	4 Å MS	THF	40	-
8	$T^+BF_4^-$ (1)	$B(C_6F_5)_3$ (1)	THF	9 (21)[d]	-
9	$T^+BF_4^-$ (1)	$BF_3{\cdot}Et_2O$ (1)	THF	24 (11)[d]	-
10	$T^+BF_4^-$ (1)	*p*-NBA (1)	THF	trace	-
11	$T^+BF_4^-$ (1)	$NaHCO_3$ (1)	THF	11	-
12[c]	$T^+BF_4^-$ (1)	4 Å MS+ $B(C_6F_5)_3$ (1)	THF	30 (52)[d]	-
13[c]	**$T^+BF_4^-$ (1)**	**4 Å MS + $BF_3{\cdot}Et_2O$ (1)**	**THF**	**61** (46)[d]	-
14[c,e]	$T^+BF_4^-$ (1)	4 Å MS + $BF_3{\cdot}Et_2O$ (1)	THF	57	-
15	$T^+BF_4^-$ (1)	-	acetone/H_2O = 1/9	-	15
16	$T^+BF_4^-$ (1)	-	acetone/H_2O = 1/4	-	30
17	$T^+BF_4^-$ (1)	-	acetone/H_2O = 1/1	-	42
18	$T^+BF_4^-$ (1)	-	acetone/H_2O = 4/1	-	36
19	$T^+BF_4^-$ (1)	-	H_2O	-	28
20	$T^+BF_4^-$ (2)	-	acetone/H_2O = 1/1	-	56
21	$T^+BF_4^-$ (3)	-	acetone/H_2O = 1/1	-	52
22[f]	**$T^+BF_4^-$ (2)**	-	**acetone/H_2O = 1/1**	-	**68**

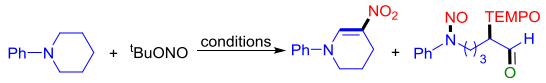
[a] Conditions: **1a** (0.2 mmol), TBN (0.6 mmol), solvent (1 mL), room temperature, air, 1 h. [b] Isolated yields. [c] 4 Å MS (100 mg). [d] $B(C_6F_5)_3/BF_3{\cdot}Et_2O$ (0.02 mmol). [e] Under O_2 (1 atm). [f] TBN (0.3 mmol).

Based on our previous studies, we commenced this work by treating 1-phenylpiperidine (**1a**) with TBN (3 equiv.) and $T^+BF_4^-$ (1 equiv.) in THF at rt under air for 1 h, from which 5-nitro-1-phenyl-1,2,3,4-tetrahydropyridine (**2a**) was obtained in a yield of 11% (Table S1, entry 1). In order to improve the efficiency of this reaction, different TEMPO salts and 2,2,6,6-tetramethyl-piperidinooxy (TEMPO) were tried, and $T^+BF_4^-$ was found to be more effective than $T^+ClO_4^-$, $T^+PF_6^-$, and TEMPO (entry 1 *vs* entries 2-4). Changing the amount of $T^+BF_4^-$ could not improve the yield of **2a** (entries 5-6). To see whether the presence of an additive could improve

this reaction, 4 Å molecular sieves (4 Å MS), $B(C_6F_5)_3$, BF_3 Ɛt$_2$O, *p*-NBA (4-nitrobenzoic acid) and $NaHCO_3$ were tried (entries 7-11). Delightfully, by using 4 Å MS, $B(C_6F_5)_3$ (0.1 equiv.) or BF_3 Ɛt$_2$O (1 equiv.) as an additive, the yield of **2a** was improved to 40%, 21% or 24%, respectively (entries 7-9). When a combination of 4 Å MS and $B(C_6F_5)_3$ (0.1 equiv)/BF_3 Ɛt$_2$O (1 equiv.) was used as the additive, **2a** was obtained in higher yields of 52% and 61%, respectively (entries 12-13). It is noted herein that the formation of acyclic by-products such as *N*-(4-(hydroxyimino)-5-oxopentyl)-*N*-phenylnitrous amide (**2a'**, 17%) and *N*-(3-cyanopropyl)-*N*-phenylformamide (**2a''**, 8%) was also detected (entry 13). Then, the reaction was run under O_2 instead of air, from which a slightly lower yield of **2a** was observed (entry 14). In another respect, when a mixture of acetone and water (v/v, 1/9) was used as the reaction medium, *N*-(5-oxo-4-((2,2,6,6-tetrame-thylpiperidin-1-yl)oxy) pent-yl)-*N*-phenylnitrous amide (**3a**) instead of **2a** was obtained in a yield of 15% (entry 15 *vs* entry 1). Following optimization with regard to different ratios of acetone with water as solvent revealed that 1/1 is the most suitable for this transformation (entry 17 *vs* entries 15-19). Considering $T^+BF_4^-$ might be used as both oxidant and substrate, the loading of $T^+BF_4^-$ was increased from 1 equiv. to 2 equiv. and 3 equiv. (entries 20-21). It turned out that using 2 equiv. of $T^+BF_4^-$ could guarantee a higher yield of **3a** (entry 20). It was also found that using 1.5 equiv. of TBN generated the optimum result (entry 22).

With entry 1 in Table S2 as model reaction conditions for the formation of **2a**, solvent effect was investigated. In dioxane or acetone lower reactivity was observed, 52% and 46% of **2a** were formed, respectively (entries 2-3). Further experiment demonstrated that also DMF is less effective solvent to lead to the formation of **2a** (31%) and **3a** (11%) (entry 4). Then, it was found that when CH_3CN was used, the reaction efficiency was dramatically reduced to afford **2a** in 9% yield (entry 5). In addition, when DMSO and chlorinated solvents such as DCM and DCE were used as the reaction medium in the reaction, turned out to be messy to give an unknown mixture, from which the desired product was not obtained (entries 6-8). On the other hand, with entry 9 as model reaction conditions for the formation of **3a**, the mixtures of different organic solvents and water (1/1) as the reaction medium were also investigated. These mixtures showed similar reactivity (entries 9-14). Among them, the mixture of acetone and water was the most effective solvent to give **3a** in a highest yield of 68% (entry 9).

Table S2. Optimization studies on the solvents for the formation of **2a** and **3a**[a]



1a **2a** **3a**

Entry	Oxidant (equiv.)	Additive (equiv.)	Solvent	Yield (%)[b]	
				2a	**3a**
1[c]	**$T^+BF_4^-$ (1)**	**4 Å MS + BF_3·Et_2O (1)**	**THF**	**61**	**-**
2[c]	$T^+BF_4^-$ (1)	4 Å MS + BF_3·Et_2O (1)	dioxane	52	-
3[c]	$T^+BF_4^-$ (1)	4 Å MS + BF_3·Et_2O (1)	acetone	46	-
4[c]	$T^+BF_4^-$ (1)	4 Å MS + BF_3·Et_2O (1)	DMF	31	11
5[c]	$T^+BF_4^-$ (1)	4 Å MS + BF_3·Et_2O (1)	CH_3CN	9	-
6[c]	$T^+BF_4^-$ (1)	4 Å MS + BF_3·Et_2O (1)	DMSO	-	-
7[c]	$T^+BF_4^-$ (1)	4 Å MS + BF_3·Et_2O (1)	DCM	-	-
8[c]	$T^+BF_4^-$ (1)	4 Å MS + BF_3·Et_2O (1)	DCE	-	-
9[d]	**$T^+BF_4^-$ (2)**	**-**	**acetone/H_2O = 1/1**	**-**	**68**
10[d]	$T^+BF_4^-$ (2)	-	dioxane/H_2O = 1/1	-	64
11[d]	$T^+BF_4^-$ (2)	-	DMF/H_2O = 1/1	-	56
12[d]	$T^+BF_4^-$ (2)	-	DMSO/H_2O = 1/1	-	51
13[d]	$T^+BF_4^-$ (2)	-	CH_3CN/H_2O = 1/1	-	50
14[d]	$T^+BF_4^-$ (2)	-	THF/H_2O = 1/1	-	61

[a] Conditions: **1a** (0.2 mmol), TBN (0.6 mmol), solvent (1 mL), room temperature, air, 1 h. [b] Isolated yields. [c] 4 Å MS (100 mg). [d] TBN (0.3 mmol).

2. A typical procedure for the synthesis of 2a the spectroscopic data of 2a-2n, 2', and 2''

To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1a**, 32 mg, 0.2 mmol), THF (1 mL), $T^+BF_4^-$ (49 mg, 0.2 mmol), *tert*-butyl nitrite (98%, 73 μL, 0.6 mmol), 4 Å molecular sieves (100 mg, activated at 500 ℃ for 5 h before use), and BF_3·Et_2O (98%, 25 μL). The resulting mixture was then stirred at room temperature under air for 1 h. Upon completion, the reaction was diluted with ethyl acetate and washed with aqueous NaCl and saturated $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (5:1) as the eluent to afford **2a** as yellow solid in 25 mg (61%). By-products **2a'** and **2a''** were also obtained as yellow/red liquid in (8 mg) 17% and (3 mg) 8%, respectively. **2b-2n, 2',** and **2''** were obtained in an analogous manner.

1 mmol scale procedure for the synthesis of 2a

To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1a**, 161 mg, 1 mmol), THF (5 mL), $T^+BF_4^-$ (243 mg, 1 mmol), *tert*-butyl nitrite (98%, 364 μL, 3 mmol), 4 Å molecular sieves (500 mg, activated at 500 ℃ for 5 h before use), and $BF_3 \cdot Et_2O$ (98%, 126 μL). The resulting mixture was then stirred at room temperature under air for 1 h. Upon completion, the reaction was diluted with ethyl acetate and washed with aqueous NaCl and saturated $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (5:1) as the eluent to afford **2a** as yellow solid in 110 mg (54%).

5-Nitro-1-phenyl-1,2,3,4-tetrahydropyridine (2a)

Eluent: petroleum ether/ethyl acetate (5:1), Yellow solid (25 mg, 61%), m.p.: 81-82 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.08-2.12 (m, 2H), 2.80 (t, *J* = 6.4 Hz, 2H), 3.70 (t, *J* = 6.4 Hz, 2H), 7.16-7.23 (m, 3H), 7.41 (t, *J* = 7.6 Hz, 2H), 8.57 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 20.5, 21.2, 46.9, 119.1, 125.3, 125.4, 129.8, 141.0, 144.6. HRMS calcd for $C_{11}H_{13}N_2O_2$: 205.0972 $[M+H]^+$, found: 205.0968.

***N*-(4-(Hydroxyimino)-5-oxopentyl)-*N*-phenylnitrous amide (2a')**[3]

Eluent: petroleum ether/ethyl acetate (5:1), red liquid (8 mg, 17%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.74-1.78 (m, 2H), 2.51 (t, *J* = 7.6 Hz, 2H), 4.04 (t, *J* = 7.6 Hz, 2H), 7.36-7.40 (m, 1H), 7.46-7.53 (m, 4H), 9.45 (br s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 18.3, 21.3, 42.8, 119.0, 126.6, 128.6, 140.3, 158.8, 189.7.

***N*-(3-Cyanopropyl)-*N*-phenylformamide (2a'')**[4]

Eluent: petroleum ether/ethyl acetate (2:1), Yellow liquid (3 mg, 8%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.93-1.97 (m, 2H), 2.38 (t, *J* = 7.2 Hz, 2H), 3.95 (t, *J* = 7.2 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H),

7.34 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 8.40 (s, 1H).

1-(4-Fluorophenyl)-5-nitro-1,2,3,4-tetrahydropyridine (2b)

Eluent: petroleum ether/ethyl acetate (5:1), Yellow solid (30 mg, 68%), m.p.: 93-94 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.08-2.10 (m, 2H), 2.79 (t, *J* = 6.4 Hz, 2H), 3.66 (t, *J* = 6.0 Hz, 2H), 7.11-7.14 (m, 4H), 8.48 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 20.5, 21.0, 47.4, 116.6 (d, $^{2}J_{C\text{-}F}$ = 23.1 Hz), 121.0 (d, $^{3}J_{C\text{-}F}$ = 8.7 Hz), 125.3, 141.0 (d, $^{4}J_{C\text{-}F}$ = 2.3 Hz), 141.1, 160.2 (d, $^{1}J_{C\text{-}F}$ = 245.1 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ: -116.4. HRMS calcd for $C_{11}H_{12}FN_2O_2$: 223.0877 $[M+H]^+$, found: 223.0868.

***N*-(4-Fluorophenyl)-*N*-(4-(hydroxyimino)-5-oxopentyl)nitrous amide (2b')**[3]

Eluent: petroleum ether/ethyl acetate (5:1), red liquid (5 mg, 10%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.71-1.75 (m, 2H), 2.49 (t, *J* = 7.6 Hz, 2H), 4.00 (t, *J* = 7.6 Hz, 2H), 7.16-7.20 (m, 2H), 7.45-7.48 (m, 2H), 9.11 (br s, 1H), 9.44 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.3, 22.3, 44.0, 116.5 (d, $^{2}J_{C\text{-}F}$ = 23.1 Hz), 122.2 (d, $^{3}J_{C\text{-}F}$ = 7.9 Hz), 137.5 (d, $^{4}J_{C\text{-}F}$ = 2.9 Hz), 160.0, 161.9 (d, $^{1}J_{C\text{-}F}$ = 246.3 Hz), 190.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ: -113.9.

1-(4-Chlorophenyl)-5-nitro-1,2,3,4-tetrahydropyridine (2c)

Eluent: petroleum ether/ethyl acetate (5:1), Yellow solid (31 mg, 65%), m.p.: 100-101 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.09-2.10 (m, 2H), 2.79 (t, *J* = 6.0 Hz, 2H), 3.66 (t, *J* = 5.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 8.50 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 20.4, 21.1, 46.9, 120.1, 126.0, 129.8, 130.7, 140.2, 143.2. HRMS calcd for $C_{11}H_{12}ClN_2O_2$: 239.0582 $[M+H]^+$, found: 239.0563.

***N*-(4-Chlorophenyl)-*N*-(4-(hydroxyimino)-5-oxopentyl)nitrous amide (2c')**[3]

Eluent: petroleum ether/ethyl acetate (5:1), red liquid (8 mg, 15%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.70-1.74 (m, 2H), 2.49 (t, *J* = 7.6 Hz, 2H), 4.00 (t, *J* = 7.6 Hz, 2H), 7.45 (br s, 4H), 9.45 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ: 19.3, 22.3, 43.4, 120.9, 129.8, 133.2, 139.9, 159.8, 190.6.

1-(4-Bromophenyl)-5-nitro-1,2,3,4-tetrahydropyridine (2d)

Eluent: petroleum ether/ethyl acetate (5:1), Yellow solid (40 mg, 71%), m.p.: 111-112 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.08-2.10 (m, 2H), 2.79 (t, J = 6.0 Hz, 2H), 3.65 (t, J = 6.0 Hz, 2H), 7.04 (dd, J_1 = 6.6 Hz, J_2 = 1.8 Hz, 2H), 7.52 (dd, J_1 = 6.6 Hz, J_2 = 1.8 Hz, 2H), 8.50 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 20.4, 21.1, 46.8, 118.3, 120.4, 126.1, 132.8, 140.0, 143.6. HRMS calcd for $C_{11}H_{12}BrN_2O_2$: 283.0077 $[M+H]^+$, found: 283.0074.

***N*-(4-Bromophenyl)-*N*-(4-(hydroxyimino)-5-oxopentyl)nitrous amide (2d')**[3]

Eluent: petroleum ether/ethyl acetate (5:1), red liquid (7 mg, 11%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.68-1.76 (m, 2H), 2.49 (t, J = 7.6 Hz, 2H), 3.99 (t, J = 7.6 Hz, 2H), 7.40 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 2H), 7.60 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 2H), 8.93, (br s, 1H), 9.45 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 19.3, 22.3, 43.3, 121.0, 121.1, 132.7, 140.4, 159.8, 190.6.

4-(5-Nitro-3,4-dihydropyridin-1(2*H*)-yl)benzonitrile (2e)

Eluent: petroleum ether/ethyl acetate (5:1), Yellow syrup (27 mg, 59%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.13-2.15 (m, 2H), 2.81 (t, J = 6.0 Hz, 2H), 3.70 (t, J = 6.0 Hz, 2H), 7.24 (dd, J_1 = 6.6 Hz, J_2 = 1.8 Hz, 2H), 7.70 (dd, J_1 = 6.6 Hz, J_2 = 1.8 Hz, 2H), 8.54 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 20.4, 21.1, 46.2, 107.6, 118.2, 118.3, 128.3, 133.9, 138.1, 147.5. HRMS calcd for $C_{12}H_{12}N_3O_2$: 230.0924 $[M+H]^+$, found: 230.0903.

***N*-(4-Cyanophenyl)-*N*-(4-(hydroxyimino)-5-oxopentyl)nitrous amide (2e')**

Eluent: petroleum ether/ethyl acetate (5:1), red liquid (7 mg, 13%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.69-1.75 (m, 2H), 2.51 (t, J = 7.6 Hz, 2H), 4.01 (t, J = 7.6 Hz, 2H), 7.67-7.69 (m, 2H), 7.78 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 2H), 8.67, (br s, 1H), 9.46 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 19.2, 22.2, 42.3, 110.4, 118.2, 118.5, 133.8, 144.7, 159.6, 190.6. HRMS calcd for $C_{12}H_{12}N_4O_3Na$: 283.0802

$[M+Na]^+$, found: 283.0824.

5-Nitro-1-(*p*-tolyl)-1,2,3,4-tetrahydropyridine (2f)

Eluent: petroleum ether/ethyl acetate (5:1), Yellow solid (11 mg, 25%), m.p.: 109-110 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.07-2.09 (m, 2H), 2.35 (s, 3H), 2.79 (t, *J* = 6.0 Hz, 2H), 3.67 (t, *J* = 6.0 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 8.55 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 20.5, 20.8, 21.2, 47.2, 119.2, 124.7, 130.3, 135.4, 141.3, 142.3. HRMS calcd for $C_{12}H_{15}N_2O_2$: 219.1128 $[M+H]^+$, found: 219.1123.

***N*-(4-(Hydroxyimino)-5-oxopentyl)-*N*-(*p*-tolyl)nitrous amide (2f')**[3]

Eluent: petroleum ether/ethyl acetate (5:1), red liquid (18 mg, 36%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.72-1.77 (m, 2H), 2.39 (s, 3H), 2.50 (t, *J* = 7.8 Hz, 2H), 4.02 (t, *J* = 7.2 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 9.44 (s, 1H), 10.01 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 19.3, 21.0, 22.3, 44.2, 120.3, 130.2, 137.9, 138.8, 159.8, 191.0.

1-(3-Fluorophenyl)-5-nitro-1,2,3,4-tetrahydropyridine (2g)

Eluent: petroleum ether/ethyl acetate (5:1), Yellow liquid (27 mg, 61%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.09-2.11 (m, 2H), 2.79 (t, *J* = 6.6 Hz, 2H), 3.67 (t, *J* = 5.4 Hz, 2H), 6.87-6.90 (m, 2H), 6.96 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.37 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 8.52 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 20.4, 21.1, 46.7, 106.2 (d, $^2J_{C\text{-}F}$ = 25.2 Hz), 111.9 (d, $^2J_{C\text{-}F}$ = 20.9 Hz), 114.2 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 126.3, 131.1 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 139.9, 146.0 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 163.4 (d, $^1J_{C\text{-}F}$ = 247.2 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ: -110.0. HRMS calcd for $C_{11}H_{12}FN_2O_2$: 223.0877 $[M+H]^+$, found: 223.0870.

***N*-(3-Cyanopropyl)-*N*-(3-fluorophenyl)formamide (2g'')**[4]

Eluent: petroleum ether/ethyl acetate (2:1), Yellow liquid (7 mg, 17%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.94-1.97 (m, 2H), 2.40 (t, *J* = 7.2 Hz, 2H), 3.95 (t, *J* = 6.8 Hz, 2H), 6.92-7.07 (m, 3H), 7.41-7.43

(m, 1H), 8.44 (s, 1H).

1-(3-Chlorophenyl)-5-nitro-1,2,3,4-tetrahydropyridine (2h)

Eluent: petroleum ether/ethyl acetate (5:1), Yellow solid (29 mg, 61%), m.p.: 100-101 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.09-2.11 (m, 2H), 2.79 (t, *J* = 6.6 Hz, 2H), 3.66 (t, *J* = 6.0 Hz, 2H), 7.05-7.07 (m, 1H), 7.16-7.18 (m, 2H), 7.33 (t, *J* = 7.8 Hz, 1H), 8.51 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 20.4, 21.1, 46.7, 116.8, 119.1, 125.1, 126.4, 130.8, 135.6, 139.9, 145.6. HRMS calcd for $C_{11}H_{12}ClN_2O_2$: 239.0582 $[M+H]^+$, found: 239.0577.

***N*-(3-Chlorophenyl)-*N*-(3-cyanopropyl)formamide (2h'')**[4]

Eluent: petroleum ether/ethyl acetate (2:1), Yellow liquid (7 mg, 16%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.93-1.97 (m, 2H), 2.40 (t, *J* = 7.6 Hz, 2H), 3.94 (t, *J* = 7.2 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 1.2 Hz, 1H), 7.32-7.39 (m, 2H), 8.41 (s, 1H).

1-(3-Bromophenyl)-5-nitro-1,2,3,4-tetrahydropyridine (2i)

Eluent: petroleum ether/ethyl acetate (5:1), Yellow solid (36 mg, 64%), m.p.: 123-124 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.08-2.10 (m, 2H), 2.79 (t, *J* = 6.6 Hz, 2H), 3.66 (t, *J* = 6.0 Hz, 2H), 7.09-7.11 (m, 1H), 7.26-7.28 (m, 1H), 7.32-7.33 (m, 2H), 8.50 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 20.4, 21.1, 46.8, 117.3, 122.0, 123.5, 126.4, 128.1, 131.0, 139.8, 145.7. HRMS calcd for $C_{11}H_{12}BrN_2O_2$: 283.0077 $[M+H]^+$, found: 283.0054.

***N*-(3-Bromophenyl)-*N*-(3-cyanopropyl)formamide (2i'')**[4]

Eluent: petroleum ether/ethyl acetate (2:1), Yellow liquid (11 mg, 21%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.91-1.98 (m, 2H), 2.40 (t, *J* = 7.2 Hz, 2H), 3.94 (t, *J* = 6.8 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.31-7.36 (m, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 8.40 (s, 1H).

1-(2-Chlorophenyl)-5-nitro-1,2,3,4-tetrahydropyridine (2j)

Eluent: petroleum ether/ethyl acetate (5:1), Yellow solid (20 mg, 42%), m.p.: 90-91 ℃. ^{1}H NMR

(600 MHz, $CDCl_3$) δ: 2.08-2.12 (m, 2H), 2.81 (t, *J* = 6.0 Hz, 2H), 3.58 (t, *J* = 6.0 Hz, 2H), 7.24-7.25 (m, 1H), 7.30 (td, J_1 = 7.2 Hz, J_2 = 1.8 Hz, 1H), 7.34 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.48 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 8.23 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 20.5, 21.1, 49.1, 124.2, 127.5, 128.3, 129.0, 130.4, 131.1, 142.5, 144.0. HRMS calcd for $C_{11}H_{12}ClN_2O_2$: 239.0582 $[M+H]^+$, found: 239.0578.

1-(Naphthalen-1-yl)-5-nitro-1,2,3,4-tetrahydropyridine (2k)

Eluent: petroleum ether/ethyl acetate (5:1), Yellow solid (26 mg, 51%), m.p.: 112-113 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.19-2.23 (m, 2H), 2.91 (br s, 2H), 3.70 (br s, 2H), 7.34-7.35 (m, 1H), 7.48-7.51 (m, 1H), 7.56-7.61 (m, 2H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.93-7.95 (m, 1H), 8.39 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 20.9, 21.3, 50.2, 122.1, 123.2, 123.5, 125.6, 127.0, 127.5, 128.6, 128.8, 128.9, 134.7, 141.9, 145.2. HRMS calcd for $C_{15}H_{15}N_2O_2$: 255.1128 $[M+H]^+$, found: 255.1123.

***N*-(3-Cyanopropyl)-*N*-(naphthalen-1-yl)formamide (2k'')**[4]

Eluent: petroleum ether/ethyl acetate (2:1), Yellow liquid (7 mg, 15%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.97-1.98 (m, 2H), 2.41-2.43 (m, 2H), 3.64-3.65 (m, 1H), 4.28 (br s, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.57-7.63 (m, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.93-7.97 (m, 2H), 8.29 (s, 1H).

4-Methyl-5-nitro-1-phenyl-1,2,3,4-tetrahydropyridine (2l)

Eluent: petroleum ether/ethyl acetate (5:1), Yellow liquid (26 mg, 60%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.26 (d, *J* = 6.6 Hz, 3H), 1.89-1.92 (m, 1H), 2.00-2.03 (m, 1H), 3.31-3.33 (m, 1H), 3.69-3.72 (m, 2H), 7.19-7.23 (m, 3H), 7.40-7.43 (m, 2H), 8.57 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 19.7, 25.4, 27.4, 43.0, 119.0, 125.4, 129.8, 129.9, 140.4, 144.5. HRMS calcd for $C_{12}H_{15}N_2O_2$: 219.1128 $[M+H]^+$, found: 219.1104.

***N*-(4-(Hydroxyimino)-3-methyl-5-oxopentyl)-*N*-phenylnitrous amide (2l')**

Eluent: petroleum ether/ethyl acetate (5:1), Red liquid (10 mg, 20%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.20 (d, *J* = 7.2 Hz, 3H), 1.82-1.85 (m, 1H), 2.11-2.14 (m, 1H), 3.23-3.25 (m, 1H), 3.78-3.83 (m, 1H), 4.07-4.11 (m, 1H), 7.35-7.38 (m, 1H), 7.45-7.50 (m, 4H), 9.40 (br s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 16.2, 27.4, 29.0, 42.4, 119.9, 127.7, 129.6, 141.2, 162.1, 191.2. HRMS calcd for $C_{12}H_{15}N_3O_3Na$: 272.1006 $[M+Na]^+$, found: 272.1020.

***N*-(3-Cyanobutyl)-*N*-phenylformamide (2l'')**[4]

Eluent: petroleum ether/ethyl acetate (2:1), Yellow liquid (3 mg, 7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.35 (d, *J* = 7.2 Hz, 3H), 1.84-1.90 (m, 2H), 2.62-2.67 (m, 1H), 3.98 (t, *J* = 7.2 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 8.40 (s, 1H).

1-(4-Fluorophenyl)-4-methyl-5-nitro-1,2,3,4-tetrahydropyridine (2m)

Eluent: petroleum ether/ethyl acetate (5:1), Yellow solid (30 mg, 64%), m.p.: 96-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.25 (d, *J* = 6.8 Hz, 3H), 1.88-1.93 (m, 1H), 1.98-2.04 (m, 1H), 3.29-3.33 (m, 1H), 3.66-3.69 (m, 2H), 7.09-7.19 (m, 4H), 8.47 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 19.7, 25.3, 27.4, 43.5, 116.6 (d, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 121.0 (d, $^{3}J_{C\text{-}F}$ = 7.7 Hz), 129.8, 140.5, 141.0 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 160.2 (d, $^{1}J_{C\text{-}F}$ = 245.1 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ: -116.4. HRMS calcd for $C_{12}H_{14}FN_2O_2$: 237.1034 $[M+H]^+$, found:237.1035.

***N*-(4-Fluorophenyl)-*N*-(4-(hydroxyimino)-3-methyl-5-oxopentyl)nitrous amide (2m')**

Eluent: petroleum ether/ethyl acetate (5:1), Red liquid (8 mg, 15%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.20 (d, *J* = 6.6 Hz, 3H), 1.80-1.85 (m, 1H), 2.09-2.13 (m, 1H), 3.21-3.25 (m, 1H), 3.75-3.80 (m, 1H), 4.05-4.10 (m, 1H), 7.16-7.18 (m, 2H), 7.45-7.47 (m, 2H), 9.40 (s, 1H), 9.55 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 16.1, 27.3, 28.9, 42.7, 116.5 (d, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 122.0 (d, $^{3}J_{C\text{-}F}$ = 7.7 Hz), 137.4 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 161.8, 161.9 (d, $^{1}J_{C\text{-}F}$ = 246.2 Hz), 191.1. ^{19}F NMR (565 MHz,

$CDCl_3$) δ: -113.7. HRMS calcd for $C_{12}H_{14}FN_3O_3Na$: 290.0911 $[M+Na]^+$, found: 290.0895.

1-(3-Chlorophenyl)-4-methyl-5-nitro-1,2,3,4-tetrahydropyridine (2n)

Eluent: petroleum ether/ethyl acetate (5:1), Yellow liquid (31 mg, 62%). ^1H NMR (400 MHz, $CDCl_3$) δ: 1.25 (d, *J* = 6.8 Hz, 3H), 1.89-1.93 (m, 1H), 1.99-2.02 (m, 1H), 3.29-3.32 (m, 1H), 3.65-3.69 (m, 2H), 7.07-7.10 (m, 1H), 7.16-7.19 (m, 2H), 7.32-7.36 (m, 1H), 8.51 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 19.7, 25.4, 27.4, 42.9, 116.8, 119.1, 125.1, 130.8, 130.9, 135.6, 139.3, 145.5. HRMS calcd for $C_{12}H_{14}ClN_2O_2$: 253.0738 $[M+H]^+$, found: 253.0739.

***N*-(3-Chlorophenyl)-*N*-(4-(hydroxyimino)-3-methyl-5-oxopentyl)nitrous amide (2n')**

Eluent: petroleum ether/ethyl acetate (5:1), Red liquid (6 mg, 11%). ^1H NMR (600 MHz, $CDCl_3$) δ: 1.21 (d, *J* = 7.2 Hz, 3H), 1.77-1.83 (m, 1H), 2.09-2.12 (m, 1H), 3.21-3.25 (m, 1H), 3.71-3.76 (m, 1H), 4.02-4.07 (m, 1H), 7.32-7.34 (m, 1H), 7.38-7.42 (m, 2H), 7.54 (s, 1H), 8.96 (br s, 1H), 9.40 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 16.2, 27.4, 29.0, 41.9, 117.3, 119.6, 127.3, 130.6, 135.4, 142.4, 161.9, 191.0. HRMS calcd for $C_{12}H_{15}ClN_3O_3$: 284.0796 $[M+H]^+$, found: 284.0794.

***N*-(3-Chlorophenyl)-*N*-(3-cyanobutyl)formamide (2n'')**[4]

Eluent: petroleum ether/ethyl acetate (2:1), Yellow liquid (3 mg, 6%). ^1H NMR (400 MHz, $CDCl_3$) δ: 1.36 (d, *J* = 6.8 Hz, 3H), 1.84-1.88 (m, 2H), 2.65-2.66 (m, 1H), 3.97 (t, *J* = 7.2 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.20 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 8.39 (s, 1H).

A typical procedure for the synthesis of 2o and the spectroscopic data of 2o and 2p

To a reaction tube equipped with a stir bar were added 1,4-diphenylpiperazine (**1o**, 48 mg, 0.2 mmol), THF (1 mL), $T^+BF_4^-$ (58 mg, 0.24 mmol), *tert*-butyl nitrite (98%, 73 μL, 0.6 mmol), and 4 Å molecular sieves (100 mg, activated at 500 ℃ for 5 h before use). The resulting mixture was then stirred at room temperature under air for 1 h. Upon completion, the reaction was diluted with ethyl acetate and washed with aqueous NaCl and saturated $NaHCO_3$ solution. The organic layer was dried

over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (5:1) as the eluent to afford **2o** as yellow solid in 23 mg (41%). **2p** was obtained in an analogous manner.

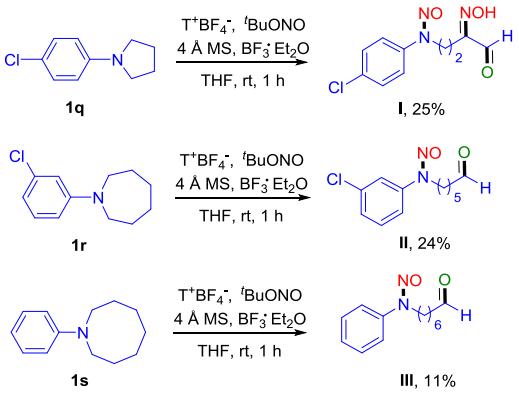
5-Nitro-1,4-diphenyl-1,2,3,4-tetrahydropyrazine (2o)

Eluent: petroleum ether/ethyl acetate (5:1), Yellow solid (23 mg, 41%), m.p.: 154-155 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 3.59 (t, *J* = 4.8 Hz, 2H), 3.76 (t, *J* = 4.8 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 7.05 (t, *J* = 7.8 Hz, 1H), 7.19-7.21 (m, 3H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 8.62 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 44.3, 48.8, 118.7, 120.4, 123.3, 125.2, 129.5, 129.88, 129.91, 130.0, 143.7, 147.1. HRMS calcd for $C_{16}H_{16}N_3O_2$: 282.1237 $[M+H]^+$, found: 282.1233.

2-Nitro-1,4-diphenyl-4,5,6,7-tetrahydro-1*H*-1,4-diazepine (2p)

Eluent: petroleum ether/ethyl acetate (5:1), Yellow solid (18 mg, 31%), m.p.: 203-204 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.14-2.17 (m, 2H), 3.70-3.79 (m, 3H), 4.38-4.41 (m, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.91 (t, *J* = 7.2 Hz, 1H), 7.20-7.24 (m, 3H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 8.31 (s, 1H). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.05 (br s, 2H), 3.65-3.80 (m, 3H), 4.36 (s, 1H), 6.83-6.87 (m, 3H), 7.24-7.31 (m, 3H), 7.44-7.45 (m, 4H), 8.22 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 24.8, 49.1, 49.3, 115.1, 120.2, 120.9, 125.9, 129.7, 129.9, 134.3, 139.3, 145.8, 146.1. HRMS calcd for $C_{17}H_{18}N_3O_2$: 296.1394 $[M+H]^+$, found: 296.1392.

Unfortunately, 1-(4-chlorophenyl)pyrrolidine, 1-(3-chlorophenyl) azepane and *N*-phenylazocane failed to give the expected β-nitrated cyclic enamines, but gave *N*-(4-chlorophenyl)-*N*-(3-(hydroxyimino)-4-oxobutyl)nitrous amide (**I**), *N*-(3-chlorophenyl)-*N*-(6-oxohexyl)nitrous amide (**II**) and *N*-(7-oxoheptyl)-*N*-phenylnitrous amide (**III**) in 25%, 24% and 11% yields, respectively (Scheme S1).



Scheme S1. Formation of I, II and III

A typical procedure for the synthesis of *N*-(4-chlorophenyl)-*N*-(3-(hydroxyimino)-4-oxobutyl) nitrous amide (I)

To a reaction tube equipped with a stir bar were added 1-(4-chlorophenyl)pyrrolidine (**1q**, 36 mg, 0.2 mmol), THF (1 mL), $T^+BF_4^-$ (49 mg, 0.2 mmol), *tert*-butyl nitrite (98%, 73 μL, 0.6 mmol), 4 Å molecular sieves (100 mg, activated at 500 ℃ for 5 h before use), and $BF_3·Et_2O$ (98%, 25 μL). The resulting mixture was then stirred at room temperature under air for 1 h. Upon completion, the reaction was diluted with ethyl acetate and washed with aqueous NaCl and saturated $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (5:1) as the eluent to afford **I** as yellow solid in 13 mg (25%).

***N*-(4-Chlorophenyl)-*N*-(3-(hydroxyimino)-4-oxobutyl)nitrous amide (I)**[3]

Eluent: petroleum ether/ethyl acetate (5:1), yellow solid (13 mg, 25%), m.p.: 144-146 ℃. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 2.56 (t, J = 7.2 Hz, 2H), 4.17 (t, J = 7.2 Hz, 2H), 7.61 (s, 4H), 9.33 (s, 1H), 13.14 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 19.4, 39.6, 121.8, 130.0, 132.3, 140.2, 156.9, 191.7.

A typical procedure for the synthesis of *N*-(3-chlorophenyl)-*N*-(6-oxohexyl)nitrous amide (II)

To a reaction tube equipped with a stir bar were added 1-(3-chlorophenyl)azepane (**1r**, 42 mg, 0.2 mmol), THF (1 mL), $T^+BF_4^-$ (49 mg, 0.2 mmol), *tert*-butyl nitrite (98%, 73 μL, 0.6 mmol), 4 Å molecular sieves (100 mg, activated at 500 ℃ for 5 h before use), and BF_3·Et_2O (98%, 25 μL). The resulting mixture was then stirred at room temperature under air for 1 h. Upon completion, the reaction was diluted with ethyl acetate and washed with aqueous NaCl and saturated $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (5:1) as the eluent to afford **II** as yellow liquid in 12 mg (24%).

***N*-(3-Chlorophenyl)-*N*-(6-oxohexyl)nitrous amide (II)**

Eluent: petroleum ether/ethyl acetate (5:1), yellow liquid (12 mg, 24%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.30-1.36 (m, 2H), 1.52-1.56 (m, 2H), 1.58-1.67 (m, 2H), 2.42-2.46 (m, 2H), 4.00 (t, *J* = 7.6 Hz, 2H), 7.32-7.35 (m, 1H), 7.41-7.42 (m, 2H), 7.56-7.57 (m, 1H), 9.75 (t, *J* = 1.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 21.4, 26.3, 26.4, 43.2, 43.6, 117.2, 119.4, 127.3, 130.6, 135.4, 142.5, 202.2. HRMS calcd for $C_{12}H_{16}ClN_2O_2$: 255.0895 $[M+H]^+$, found: 255.0887.

A typical procedure for the synthesis of and *N*-(7-oxoheptyl)-*N*-phenylnitrous amide (III)

To a reaction tube equipped with a stir bar were added 1-phenylazocane (**1s**, 38 mg, 0.2 mmol), THF (1 mL), $T^+BF_4^-$ (49 mg, 0.2 mmol), *tert*-butyl nitrite (98%, 73 μL, 0.6 mmol), 4 Å molecular sieves (100 mg, activated at 500 ℃ for 5 h before use), and BF_3·Et_2O (98%, 25 μL). The resulting mixture was then stirred at room temperature under air for 1 h. Upon completion, the reaction was diluted with ethyl acetate and washed with aqueous NaCl and saturated $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with

petroleum ether/ethyl acetate (5:1) as the eluent to afford **III** as yellow liquid in 5 mg (11%).

***N*-(7-Oxoheptyl)-*N*-phenylnitrous amide (III)**

Eluent: petroleum ether/ethyl acetate (5:1), yellow liquid (5 mg, 11%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.28-1.34 (m, 4H), 1.54-1.64 (m, 4H), 2.41 (t, *J* = 7.2 Hz, 2H), 4.03 (t, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.47-7.53 (m, 4H), 9.75 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 21.8, 26.3, 26.8, 28.6, 43.67, 43.70, 119.7, 127.4, 129.6, 141.6, 202.5. HRMS calcd for $C_{13}H_{19}N_2O_2$: 235.1441 $[M+H]^+$, found: 235.1441.

3. A typical procedure for the synthesis of 3a and the spectroscopic data of 3a-3t

To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1a**, 32 mg, 0.2 mmol), acetone (0.5 mL), H_2O (0.5 mL), $T^+BF_4^-$ (97 mg, 0.4 mmol), and *tert*-butyl nitrite (98%, 36 μL, 0.3 mmol). The resulting mixture was then stirred at room temperature under air for 1 h. Upon completion, the reaction was quenched with aqueous NaCl and extracted with ethyl acetate (5 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (20:1) as the eluent to afford **3a** as yellow liquid in 49 mg (68%). **3b-3t** were obtained in an analogous manner.

1 mmol scale procedure for the synthesis of 3a

To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1a**, 161 mg, 1 mmol), acetone (2.5 mL), H_2O (2.5 mL), $T^+BF_4^-$ (486 mg, 2 mmol), and *tert*-butyl nitrite (98%, 182 μL, 1.5 mmol). The resulting mixture was then stirred at room temperature under air for 1 h. Upon completion, the reaction was quenched with aqueous NaCl and extracted with ethyl acetate (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column

chromatography on silica-gel with petroleum ether/ethyl acetate (20:1) as the eluent to afford **3a** as yellow liquid in 224 mg (62%).

***N*-(5-Oxo-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl)-*N*-phenylnitrous amide (3a)**

Eluent: petroleum ether/ethyl acetate (20:1), Yellow liquid (49 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.11-1.13 (m, 12H), 1.32-1.44 (m, 5H), 1.58-1.74 (m, 5H), 4.02-4.12 (m, 3H), 7.35-7.39 (m, 1H), 7.45-7.53 (m, 4H), 9.79 (d, *J* = 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.1, 20.3, 20.4, 21.6, 27.4, 33.9, 34.2, 40.0, 40.1, 43.4, 60.0, 60.6, 87.6, 119.6, 127.5, 129.6, 141.3, 204.3. HRMS calcd for $C_{20}H_{32}N_3O_3$: 362.2438 $[M+H]^+$, found: 362.2438.

***N*-(4-Fluorophenyl)-*N*-(5-oxo-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl)nitrous amide (3b)**

Eluent: petroleum ether/ethyl acetate (20:1), Yellow solid (48 mg, 63%), m.p.: 40-41 ℃ H NMR (400 MHz, $CDCl_3$) δ: 1.11-1.13 (m, 12H), 1.45-1.48 (m, 5H), 1.56-1.73 (m, 5H), 3.99-4.11 (m, 3H), 7.16-7.20 (m, 2H), 7.46-7.50 (m, 2H), 9.80 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.1, 20.3, 20.4, 21.6, 27.4, 33.8, 34.2, 40.1, 43.7, 60.0, 60.5, 87.6, 116.5 (d, $^{2}J_{C\text{-}F}$ = 22.4 Hz), 121.7 (d, $^{3}J_{C\text{-}F}$ = 7.9 Hz), 137.6 (d, $^{4}J_{C\text{-}F}$ = 3.6 Hz), 161.9 (d, $^{1}J_{C\text{-}F}$ = 231.9 Hz), 204.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -114.4. HRMS calcd for $C_{20}H_{31}FN_3O_3$: 380.2344 $[M+H]^+$, found: 380.2345.

***N*-(4-Chlorophenyl)-*N*-(5-oxo-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl)nitrous amide (3c)**

Eluent: petroleum ether/ethyl acetate (20:1), Yellow solid (59 mg, 75%), m.p.: 79-80 ℃ H NMR (400 MHz, $CDCl_3$) δ: 1.11-1.13 (m, 12H), 1.30-1.33 (m, 1H), 1.45-1.48 (m, 4H), 1.54-1.75 (m, 5H), 3.99-4.12 (m, 3H), 7.16-7.20 (m, 2H), 7.46-7.50 (m, 2H), 9.80 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.1, 20.3, 20.4, 21.6, 27.4, 33.9, 34.2, 40.1, 43.1, 60.0, 60.6, 87.6, 120.5, 129.8, 133.1, 139.9, 204.2. HRMS calcd for $C_{20}H_{31}ClN_3O_3$: 396.2048 $[M+H]^+$, found: 396.2057.

***N*-(4-Bromophenyl)-*N*-(5-oxo-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl)nitrous amide (3d)**

Eluent: petroleum ether/ethyl acetate (20:1), Yellow solid (64 mg, 73%), m.p.: 64-65 ℃ H NMR (400 MHz, $CDCl_3$) δ: 1.11-1.13 (m, 12H), 1.31-1.33 (m, 1H), 1.45-1.47 (m, 4H), 1.54-1.73 (m, 5H), 3.98-4.12 (m, 3H), 7.39-7.43 (m, 2H), 7.58-7.62 (m, 2H), 9.80 (d, J = 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.0, 20.3, 20.4, 21.6, 27.4, 33.9, 34.2, 40.1, 43.0, 60.0, 60.6, 87.5, 120.75, 120.82, 132.7, 140.4, 204.2. HRMS calcd for $C_{20}H_{31}BrN_3O_3$: 440.1543 $[M+H]^+$, found: 440.1538.

***N*-(4-Cyanophenyl)-*N*-(5-oxo-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl)nitrous amide (3e)**

Eluent: petroleum ether/ethyl acetate (20:1), Yellow liquid (49 mg, 63%). H NMR (400 MHz, $CDCl_3$) δ: 1.12-1.14 (m, 12H), 1.34-1.46 (m, 5H), 1.54-1.75 (m, 5H), 3.99-4.15 (m, 3H), 7.70 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 2H), 7.79 (dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 2H), 9.82 (d, J = 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.0, 20.3, 20.4, 21.5, 27.3, 33.9, 34.2, 40.1, 42.2, 60.0, 60.6, 87.5, 110.4, 118.2, 118.3, 133.7, 144.7, 204.1. HRMS calcd for $C_{21}H_{31}N_4O_3$: 387.2391 $[M+H]^+$, found: 387.2387.

***N*-(5-Oxo-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl)-*N*-(*p*-tolyl)nitrous amide (3f)**

Eluent: petroleum ether/ethyl acetate (20:1), Yellow liquid (31 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.11-1.13 (m, 12H), 1.25-1.44 (m, 5H), 1.57-1.73 (m, 5H), 2.40 (s, 3H), 4.00-4.09 (m, 3H), 7.27 (d, J = 7.2 Hz, 2H), 7.37-7.40 (m, 2H), 9.79 (d, J = 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.1, 20.3, 20.4, 21.0, 21.6, 27.5, 33.9, 34.2, 40.1, 43.6, 60.0, 60.6, 87.6, 119.8, 130.1, 137.5, 139.0, 204.2. HRMS calcd for $C_{21}H_{34}N_3O_3$: 376.2595 $[M+H]^+$, found: 376.2590.

***N*-(5-Oxo-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl)-*N*-(*m*-tolyl)nitrous amide (3g)**

Eluent: petroleum ether/ethyl acetate (20:1), Yellow liquid (30 mg, 40%). H NMR (400 MHz,

$CDCl_3$) δ: 1.11-1.13 (m, 12H), 1.32-1.44 (m, 5H), 1.56-1.75 (m, 5H), 2.43 (s, 3H), 4.01-4.11 (m, 3H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.28-7.37 (m, 3H), 9.79 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.1, 20.3, 20.4, 21.5, 21.6, 27.5, 33.9, 34.2, 40.1, 43.5, 60.0, 60.6, 87.6, 116.8, 120.5, 128.3, 129.4, 139.7, 141.3, 204.2. HRMS calcd for $C_{21}H_{34}N_3O_3$: 376.2595 $[M+H]^+$, found: 376.2593.

_N_-(3-Fluorophenyl)-_N_-(5-oxo-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl)nitrous amide (3h)

Eluent: petroleum ether/ethyl acetate (20:1), Yellow solid (47 mg, 62%), m.p.: 55-56 ℃ H NMR (400 MHz, $CDCl_3$) δ: 1.12-1.14 (m, 12H), 1.32-1.45 (m, 5H), 1.58-1.73 (m, 5H), 3.99-4.13 (m, 3H), 7.04-7.08 (m, 1H), 7.28-7.35 (m, 2H), 7.42-7.47 (m, 1H), 9.81 (d, *J* = 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.0, 20.3, 20.4, 21.6, 27.4, 33.9, 34.2, 40.1, 42.9, 60.0, 60.6, 87.6, 106.6 (d, $^2J_{C\text{-}F}$ = 26.0 Hz), 114.0 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 114.3 (d, $^4J_{C\text{-}F}$ = 3.6 Hz), 130.9 (d, $^3J_{C\text{-}F}$ = 9.4 Hz), 142.8 (d, $^3J_{C\text{-}F}$ = 10.1 Hz), 163.2 (d, $^1J_{C\text{-}F}$ = 246.3 Hz), 204.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -110.3. HRMS calcd for $C_{20}H_{31}FN_3O_3$: 380.2344 $[M+H]^+$, found: 380.2337.

_N_-(3-Chlorophenyl)-_N_-(5-oxo-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl)nitrous amide (3i)

Eluent: petroleum ether/ethyl acetate (20:1), Yellow liquid (60 mg, 76%). H NMR (400 MHz, $CDCl_3$) δ: 1.12-1.14 (m, 12H), 1.30-1.47 (m, 5H), 1.54-1.76 (m, 5H), 3.99-4.13 (m, 3H), 7.32-7.39 (m, 1H), 7.41-7.42 (m, 2H), 7.57 (d, *J* = 0.8 Hz, 1H), 9.81 (d, *J* = 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.1, 20.3, 20.4, 21.6, 27.4, 33.9, 34.2, 40.1, 43.0, 60.0, 60.6, 87.6, 117.2, 119.4, 127.3, 130.6, 135.5, 142.4, 204.2. HRMS calcd for $C_{20}H_{31}ClN_3O_3$: 396.2048 $[M+H]^+$, found: 396.2040.

_N_-(3-Bromophenyl)-_N_-(5-oxo-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl)nitrous amide (3j)

Eluent: petroleum ether/ethyl acetate (20:1), Yellow liquid (54 mg, 61%). H NMR (400 MHz, $CDCl_3$) δ: 1.12-1.14 (m, 12H), 1.29-1.45 (m, 5H), 1.58-1.72 (m, 5H), 3.98-4.12 (m, 3H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.45-7.51 (m, 2H), 7.73 (t, *J* = 2.0 Hz, 1H), 9.81 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.1, 20.3, 20.4, 21.6, 27.4, 33.9, 34.2, 40.06, 40.10, 43.0, 60.0, 60.6, 87.6, 117.7, 122.3, 123.3, 130.2, 130.9, 142.5, 204.3. HRMS calcd for $C_{20}H_{31}BrN_3O_3$: 440.1543 $[M+H]^+$, found: 440.1541.

_N_-(3-Nitrophenyl)-_N_-(5-oxo-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl)nitrous amide (3k)

Eluent: petroleum ether/ethyl acetate (20:1), Yellow liquid (37 mg, 46%). H NMR (400 MHz, $CDCl_3$) δ: 1.12-1.14 (m, 12H), 1.26-1.45 (m, 5H), 1.56-1.78 (m, 5H), 4.07-4.15 (m, 3H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.93-7.95 (m, 1H), 8.22 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 8.41 (t, *J* = 2.0 Hz, 1H), 9.83 (d, *J* = 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.0, 20.3, 20.4, 21.6, 27.3, 33.9, 34.2, 40.1, 42.7, 60.0, 60.6, 87.5, 113.4, 121.5, 124.2, 130.6, 142.4, 149.0, 204.1. HRMS calcd for $C_{20}H_{31}N_4O_5$: 407.2289 $[M+H]^+$, found: 407.2283.

_N_-([1,1'-Biphenyl]-4-yl)-_N_-(5-oxo-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl)nitrous amide (3l)

Eluent: petroleum ether/ethyl acetate (20:1), Yellow solid (44 mg, 50%), m.p.: 84-85 ℃ H NMR (400 MHz, $CDCl_3$) δ: 1.12 (s, 12H), 1.32-1.47 (m, 5H), 1.62-1.78 (m, 5H), 4.05-4.14 (m, 3H), 7.36-7.40 (m, 1H), 7.45-7.49 (m, 2H), 7.58-7.63 (m, 4H), 7.68-7.71 (m, 2H), 9.81 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.1, 20.3, 20.4, 21.7, 27.5, 33.9, 34.3, 40.0, 40.1, 43.3, 60.0, 60.6, 87.6, 119.7, 127.0, 127.8, 128.2, 129.0, 139.9, 140.35, 140.44, 204.3. HRMS calcd for $C_{26}H_{36}N_3O_3$: 438.2751 $[M+H]^+$, found: 438.2746.

_N_-(4-Fluorophenyl)-_N_-(3-methyl-5-oxo-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl)nitrou

s amide (3m)

Eluent: petroleum ether/ethyl acetate (20:1), Yellow liquid (48 mg, 61%). H NMR (400 MHz, $CDCl_3$) δ: 1.06 (d, *J* = 6.8 Hz, 3H), 1.13 (s, 12H), 1.29-2.05 (m, 9H), 3.96-4.02 (m, 2H), 4.16-4.20 (m, 1H), 7.16-7.20 (m, 2H), 7.47-7.51 (m, 2H), 9.93 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 15.5, 17.0, 20.4, 20.5, 28.7, 34.0, 34.1, 34.3, 40.2, 40.3, 42.3, 60.0, 61.1, 90.4, 116.5 (d, $^2J_{C\text{-}F}$ = 18.6 Hz), 121.6 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 137.6 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 161.8 (d, $^1J_{C\text{-}F}$ = 247.2 Hz), 205.1. ^{19}F NMR (565 MHz, $CDCl_3$) δ: -114.4. HRMS calcd for $C_{21}H_{33}FN_3O_3$: 394.2500 $[M+H]^+$, found: 394.2495.

***N*-(4-Methoxyphenyl)-*N*-(3-methyl-5-oxo-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl)nitrous amide (3n)**

Eluent: petroleum ether/ethyl acetate (20:1), Yellow liquid (22 mg, 27%). H NMR (400 MHz, $CDCl_3$) δ: 1.05 (d, *J* = 6.8 Hz, 3H), 1.14 (s, 12H), 1.27-1.58 (m, 7H), 1.78-1.81 (m, 1H), 2.02-2.06 (m, 1H), 3.86 (s, 3H), 3.95-4.03 (m, 2H), 4.17-4.23 (m, 1H), 6.97-7.01 (m, 2H), 7.39-7.43 (m, 2H), 9.92 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 15.5, 17.1, 20.45, 20.54, 28.8, 34.0, 34.1, 34.3, 40.2, 40.3, 42.7, 55.6, 60.1, 90.5, 114.7, 121.8, 134.6, 159.1, 205.2. HRMS calcd for $C_{22}H_{36}N_3O_4$: 406.2700 $[M+H]^+$, found: 406.2696.

***N*-(3-Chlorophenyl)-*N*-(3-methyl-5-oxo-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl)nitrous amide (3o)**

Eluent: petroleum ether/ethyl acetate (20:1), Yellow liquid (47 mg, 57%). H NMR (400 MHz, $CDCl_3$) δ: 1.07 (d, *J* = 6.8 Hz, 3H), 1.14 (s, 12H), 1.35-1.54 (m, 7H), 1.80-1.83 (m, 1H), 2.05-2.09 (m, 1H), 3.97-4.02 (m, 2H), 4.17-4.22 (m, 1H), 7.32-7.36 (m, 1H), 7.39-7.44 (m, 2H), 7.58-7.59 (m, 1H), 9.94 (d, *J* = 4.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 15.5, 17.0, 20.4, 20.5, 28.7, 34.0, 34.1, 34.3, 40.17, 40.25, 41.6, 60.1, 61.0, 90.5, 117.0, 119.3, 127.2, 130.6, 135.5, 142.4, 205.1.

HRMS calcd for $C_{21}H_{33}ClN_3O_3$: 410.2205 $[M+H]^+$, found: 410.2208.

***N*-(6-Oxo-5-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)hexyl)-*N*-phenylnitrous amide (3p)**

Eluent: petroleum ether/ethyl acetate (20:1), Yellow liquid (26 mg, 35%). H NMR (600 MHz, $CDCl_3$) δ: 1.12-1.13 (m, 12H), 1.31-1.74 (m, 12H), 4.00-4.07 (m, 3H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.46-7.52 (m, 4H), 9.77 (d, *J* = 4.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 17.1, 20.3, 20.4, 22.0, 26.5, 29.5, 33.9, 34.3, 40.1, 43.6, 59.8, 60.6, 88.0, 119.8, 127.4, 129.6, 141.5, 204.4. HRMS calcd for $C_{21}H_{34}N_3O_3$: 376.2595 $[M+H]^+$, found: 376.2588.

***N*-(4-Methoxyphenyl)-*N*-(6-oxo-5-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)hexyl)nitrous amide (3q)**

Eluent: petroleum ether/ethyl acetate (20:1), Yellow liquid (16 mg, 20%). H NMR (600 MHz, $CDCl_3$) δ: 1.12-1.13 (m, 12H), 1.30-1.73 (m, 12H), 3.86 (s, 3H), 3.97-4.06 (m, 3H), 6.99 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 9.77 (d, *J* = 4.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 17.1, 20.3, 20.4, 21.9, 26.4, 29.5, 33.9, 34.3, 40.1, 44.2, 55.6, 59.8, 60.6, 88.1, 114.7, 122.0, 134.8, 159.1, 204.5. HRMS calcd for $C_{22}H_{36}N_3O_4$: 406.2700 $[M+H]^+$, found: 406.2694.

***N*-(4-Fluorophenyl)-*N*-(6-oxo-5-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)hexyl)nitrous amide (3r)**

Eluent: petroleum ether/ethyl acetate (20:1), Yellow liquid (32 mg, 41%). H NMR (400 MHz, $CDCl_3$) δ: 1.12-1.13 (m, 12H), 1.28-1.63 (m, 12H), 3.97-4.07 (m, 3H), 7.16-7.20 (m, 2H), 7.45-7.49 (m, 2H), 9.78 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 17.1, 20.3, 20.4, 21.9, 26.4, 29.4, 29.7, 33.9, 34.3, 40.1, 43.9, 59.9, 60.6, 88.0, 116.5 (d, $^2J_{C\text{-}F}$ = 23.0 Hz), 121.8 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 137.7 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 161.8 (d, $^1J_{C\text{-}F}$ = 246.2 Hz), 204.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -114.4. HRMS calcd for $C_{21}H_{33}FN_3O_3$: 394.2500 $[M+H]^+$, found: 394.2483.

***N*-(3-Fluorophenyl)-*N*-(6-oxo-5-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)hexyl)nitrous amide**

(3s)

Eluent: petroleum ether/ethyl acetate (20:1), Yellow liquid (28 mg, 36%). H NMR (400 MHz, $CDCl_3$) δ: 1.12-1.14 (m, 12H), 1.29-1.74 (m, 12H), 3.98-4.08 (m, 3H), 7.06-7.08 (m, 1H), 7.28-7.33 (m, 2H), 7.41-7.45 (m, 1H), 9.79 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 17.1, 20.3, 20.4, 21.9, 26.4, 29.4, 29.7, 33.9, 34.3, 40.1, 43.1, 59.8, 60.6, 88.0, 106.8 (d, $^2J_{C\text{-}F}$ = 26.3 Hz), 114.0 (d, $^2J_{C\text{-}F}$ = 20.9 Hz), 114.5 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 130.9 (d, $^3J_{C\text{-}F}$ = 9.9 Hz), 143.0 (d, $^3J_{C\text{-}F}$ = 9.9 Hz), 163.3 (d, $^1J_{C\text{-}F}$ = 246.2 Hz), 204.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -110.3. HRMS calcd for $C_{21}H_{33}FN_3O_3$: 394.2500 $[M+H]^+$, found: 394.2491.

***N*-(7-Oxo-6-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)heptyl)-*N*-phenylnitrous amide (3t)**

Eluent: petroleum ether/ethyl acetate (20:1), Yellow liquid (16 mg, 21%). H NMR (600 MHz, $CDCl_3$) δ: 1.12-1.14 (m, 12H), 1.28-1.71 (m, 14H), 4.00-4.06 (m, 3H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.46-7.53 (m, 4H), 9.77 (d, *J* = 4.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 17.1, 20.3, 20.4, 23.9, 26.3, 27.1, 29.7, 29.8, 33.8, 34.3, 40.1, 43.7, 59.8, 60.5, 88.3, 119.7, 127.4, 129.6, 141.6, 204.6. HRMS calcd for $C_{22}H_{36}N_3O_3$: 390.2751 $[M+H]^+$, found: 390.2749.

4. A typical procedure for the synthesis of 4a and the spectroscopic data of 4b-4d

To a reaction tube equipped with a stir bar were added *N*-(5-oxo-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl)-*N*-phenylnitrous amide (**3a**, 72 mg, 0.2 mmol), THF (2 mL), activated zinc powder (52 mg, 0.8 mmol) and NH_4Cl (32 mg, 0.6 mmol). The mixture was stirred at 50 ℃ for 4 h. Subsequently, activated zinc powder (52 mg, 0.8 mmol), NH_4Cl (32 mg, 0.6 mmol) and H_2O (2 mL) were added to the reaction mixture, and stirred at 50 ℃ for 4 h. Then, activated zinc powder (52 mg, 0.8 mmol) and NH_4Cl (32 mg, 0.6 mmol) were added to the reaction mixture, and stirred at 50 ℃ for another 4 h. Upon completion, the mixture was cooled to room temperature. The precipitate was filtered and the remaining mixture was then

extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were washed with saturated brine solution, dried over anhydrous Na_2SO_4, filtrated, and the solvent was evaporated under vacuum. The crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (20:1) as the eluent to afford **4a** as yellow liquid in 41 mg (62%). **4b-4d** were obtained in an analogous manner.

1 mmol scale procedure for the synthesis of 4a

To a reaction tube equipped with a stir bar were added *N*-(5-oxo-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl)-*N*-phenylnitrous amide (**3a**, 361 mg, 1 mmol), THF (20 mL), activated zinc powder (262 mg, 4 mmol) and NH_4Cl (160 mg, 3 mmol). The mixture was stirred at 50 ℃ for 4 h. Subsequently, activated zinc powder (262 mg, 4 mmol), NH_4Cl (160 mg, 3 mmol) and H_2O (20 mL) were added to the reaction mixture, and stirred at 50 ℃ for 4 h. Then, activated zinc powder (262 mg, 4 mmol) and NH_4Cl (160 mg, 3 mmol) were added to the reaction mixture, and stirred at 50 ℃ for another 4 h. Upon completion, the mixture was cooled to room temperature. The precipitate was filtered and the remaining mixture was the extracted with CH_2Cl_2 (20 mL × 3). The combined organic layers were washed with saturated brine solution, dried over anhydrous Na_2SO_4, filtrated, and the solvent was evaporated under vacuum. The crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (20:1) as the eluent to afford **4a** as yellow liquid in 184 mg (56%).

1-Phenyl-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-4,5,6,7-tetrahydro-1*H*-1,2-diazepine (4a)

Eluent: petroleum ether/ethyl acetate (20:1); Yellow liquid (41 mg, 62%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.14-1.21 (m, 12H), 1.47-1.56 (m, 6H), 1.74-1.77 (m, 1H), 1.90-1.97 (m, 2H), 2.08-2.11 (m, 1H), 3.28-3.33 (m, 1H), 3.89-3.93 (m, 1H), 4.53-4.56 (m, 1H), 6.88 (t, *J* = 7.2 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.26-7.29 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 17.2, 20.3, 20.5, 25.8, 27.7,

34.0, 34.8, 40.2, 53.7, 59.9, 81.8, 114.9, 120.2, 128.9, 150.3, 151.6. HRMS calcd for $C_{20}H_{32}N_3O$: 330.2540 $[M+H]^+$, found: 330.2540.

1-(4-Fluorophenyl)-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-4,5,6,7-tetrahydro-1*H*-1,2-diaze pine (4b)

Eluent: petroleum ether/ethyl acetate (20:1); Yellow liquid (35 mg, 50%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.14-1.33 (m, 12H), 1.48-1.57 (m, 6H), 1.69-1.73 (m, 1H), 1.89-1.95 (m, 2H), 2.09-2.12 (m, 1H), 3.21-3.25 (m, 1H), 3.77-3.80 (m, 1H), 4.53-4.55 (m, 1H), 6.94-6.97 (m, 2H), 7.12-7.14 (m, 2H), 7.28 (d, J = 3.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 17.2, 20.3, 20.5, 26.0, 27.6, 34.0, 34.7, 40.2, 54.8, 59.9, 81.8, 115.2 (d, $^2J_{C\text{-}F}$ = 23.0 Hz), 116.8 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 147.4, 152.1, 157.7 (d, $^1J_{C\text{-}F}$ = 237.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ: -124.5. HRMS calcd for $C_{20}H_{31}FN_3O$: 348.2446 $[M+H]^+$, found: 348.2447.

1-(4-Bromophenyl)-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-4,5,6,7-tetrahydro-1*H*-1,2-diaze pine (4c)

Eluent: petroleum ether/ethyl acetate (20:1); Yellow liquid (49 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.14-1.18 (m, 12H), 1.48-1.57 (m, 6H), 1.74-1.78 (m, 1H), 1.91-1.95 (m, 2H), 2.07-2.09 (m, 1H), 3.26-3.33 (m, 1H), 3.81-3.86 (m, 1H), 4.51-4.55 (m, 1H), 7.03-7.06 (m, 2H), 7.30 (d, J = 3.6 Hz, 1H), 7.32-7.35 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 17.2, 20.3, 20.5, 25.5, 27.6, 34.0, 34.8, 40.2, 53.7, 59.9, 81.7, 112.4, 116.4, 131.6, 149.3, 152.5. HRMS calcd for $C_{20}H_{31}BrN_3O$: 408.1645 $[M+H]^+$, found:408.1646.

1-(3-Chlorophenyl)-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-4,5,6,7-tetrahydro-1*H*-1,2-diaze pine (4d)

Eluent: petroleum ether/ethyl acetate (20:1); Yellow liquid (46 mg, 63%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.13-1.34 (m, 12H), 1.48-1.58 (m, 6H), 1.74-1.79 (m, 1H), 1.88-1.97 (m, 2H), 2.06-2.09

(m, 1H), 3.29-3.34 (m, 1H), 3.84-3.88 (m, 1H), 4.52-4.54 (m, 1H), 6.83-6.84 (m, 1H), 6.99 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.15-7.19 (m, 2H), 7.31 (d, J = 4.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 17.7, 20.3, 20.5, 25.5, 27.6, 34.0, 34.8, 40.2, 53.5, 59.9, 81.7, 112.6, 114.7, 119.9, 129.8, 134.8, 151.2, 152.7. HRMS calcd for $C_{20}H_{31}ClN_3O$: 364.2150 $[M+H]^+$, found: 364.2164.

5. A typical procedure for the synthesis of 5a and the spectroscopic data of 5b-5d

To a reaction tube equipped with a stir bar were added *N*-(5-oxo-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl)-*N*-phenylnitrous amide (**3a**, 72 mg, 0.2 mmol), AcOH/THF/H_2O (1:1:1.5, 7 mL), and zinc powder (523 mg, 8 mmol). The mixture was then stirred at 70 ℃ for 20 min. Upon completion, the mixture was cooled to room temperature. The precipitate was filtered and the remaining mixture was the extracted with EtOAc (10 mL × 3). The combined organic layers were washed with saturated brine solution and saturated $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtrated, and the solvent was evaporated under vacuum. The crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (5:1) as the eluent to afford **5a** as yellow liquid in 23 mg (60%). **5b-5d** were obtained in an analogous manner.

1 mmol scale procedure for the synthesis of 5a

To a reaction tube equipped with a stir bar were added *N*-(5-oxo-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl)-*N*-phenylnitrous amide (**3a**, 361 mg, 1 mmol), AcOH/THF/H_2O (1:1:1.5, 35 mL), and zinc powder (2.62 g, 40 mmol). The mixture was then stirred at 70 ℃ for 20 min. Upon completion, the mixture was cooled to room temperature. The precipitate was filtered and the remaining mixture was the extracted with EtOAc (20 mL × 3). The combined organic layers were washed with saturated brine solution and saturated $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtrated, and the solvent was evaporated under vacuum.

The crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (5:1) as the eluent to afford **5a** as yellow liquid in 106 mg (56%).

1-Phenyl-4,5,6,7-tetrahydro-1*H*-1,2-diazepin-4-ol (5a)

Eluent: petroleum ether/ethyl acetate (5:1); Yellow liquid (23 mg, 60%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.57-1.75 (m, 2H), 1.88-1.96 (m, 2H), 2.02-2.06 (m, 1H), 3.14-3.18 (m, 1H), 3.84-3.88 (m, 1H), 4.56-4.57 (m, 1H), 6.92 (t, *J* = 7.2 Hz, 1H), 7.12 (s, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.26-7.29 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 26.2, 31.3, 54.9, 71.3, 115.5, 120.9, 128.9, 150.7, 154.5. HRMS calcd for $C_{11}H_{15}N_2O$: 191.1179 $[M+H]^+$, found: 191.1162.

1-(4-Fluorophenyl)-4,5,6,7-tetrahydro-1*H*-1,2-diazepin-4-ol (5b)

Eluent: petroleum ether/ethyl acetate (5:1); Yellow liquid (27 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.64-1.71 (m, 1H), 1.87-2.03 (m, 4H), 3.02-3.08 (m, 1H), 3.71-3.77 (m, 1H), 4.51-4.54 (m, 1H), 6.94-6.99 (m, 2H), 7.11-7.16 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 26.4, 31.2, 56.0, 71.2, 115.3 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz), 117.8 (d, $^{3}J_{C\text{-}F}$ = 7.7 Hz), 147.8 (d, $^{4}J_{C\text{-}F}$ = 2.3 Hz), 155.2, 158.0 (d, $^{1}J_{C\text{-}F}$ = 237.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -123.4. HRMS calcd for $C_{11}H_{14}FN_2O$: 209.1085 $[M+H]^+$, found: 209.1087.

1-(4-Bromophenyl)-4,5,6,7-tetrahydro-1*H*-1,2-diazepin-4-ol (5c)

Eluent: petroleum ether/ethyl acetate (5:1); Colorless liquid (37 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.67-1.76 (m, 2H), 1.88-2.07 (m, 3H), 3.09-3.16 (m, 1H), 3.77-3.84 (m, 1H), 4.53-4.57 (m, 1H), 7.04-7.07 (m, 2H), 7.13 (d, *J* = 1.6 Hz, 1H), 7.33-7.37 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 26.1, 31.2, 54.9, 71.2, 113.1, 117.0, 131.7, 149.7, 155.3. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 1.53-1.55 (m, 1H), 1.77-1.83 (m, 2H), 1.90-1.92 (m, 1H), 3.06-3.10 (m, 1H), 3.82-3.86 (m, 1H), 4.35-4.37 (m, 1H), 5.52 (d, *J* = 5.4 Hz, 1H), 7.01 (s, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 25.9, 31.4, 54.3, 70.2, 111.5, 117.0, 131.8, 149.9,

157.4. HRMS calcd for $C_{11}H_{14}BrN_2O$: 269.0284 $[M+H]^+$, found: 269.0270.

1-(3-Chlorophenyl)-4,5,6,7-tetrahydro-1*H*-1,2-diazepin-4-ol (5d)

Eluent: petroleum ether/ethyl acetate (5:1); Yellow liquid (26 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.58-1.77 (m, 2H), 1.88-2.06 (m, 3H), 3.12-3.19 (m, 1H), 3.81-3.87 (m, 1H), 4.54-4.57 (m, 1H), 6.86-6.88 (m, 1H), 7.01 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.14-7.21 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 26.0, 31.2, 54.6, 71.2, 113.2, 115.4, 120.5, 129.9, 134.8, 151.6, 155.7. HRMS calcd for $C_{11}H_{13}ClN_2ONa$: 247.0609 $[M+Na]^+$, found: 247.0611.

6. Control Experiments

6.1. To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1a**, 32 mg, 0.2 mmol), THF (1 mL), $T^+BF_4^-$ (49 mg, 0.2 mmol), *tert*-butyl nitrite (98%, 73 μL, 0.6 mmol), 4 Å molecular sieves (100 mg, activated at 500 ℃ for 5 h before use), BF_3·Et_2O (98%, 25 μL), and BHT (88 mg, 0.4 mmol). The resulting mixture was then stirred at room temperature under air for 1 h. Subsequent TLC analysis of the resulting mixture showed that there was no desired product **2a** formed from this reaction.

6.2. To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1a**, 32 mg, 0.2 mmol), acetone (0.5 mL), H_2O (0.5 mL), $T^+BF_4^-$ (97 mg, 0.4 mmol), *tert*-butyl nitrite (98%, 36 μL, 0.3 mmol), and BHT (88 mg, 0.4 mmol). The resulting mixture was then stirred at room temperature under air for 1 h. Upon completion, the reaction was quenched with aqueous NaCl and extracted with ethyl acetate (5 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (20:1) as the eluent to afford **3a** as yellow liquid in 46 mg (64%).

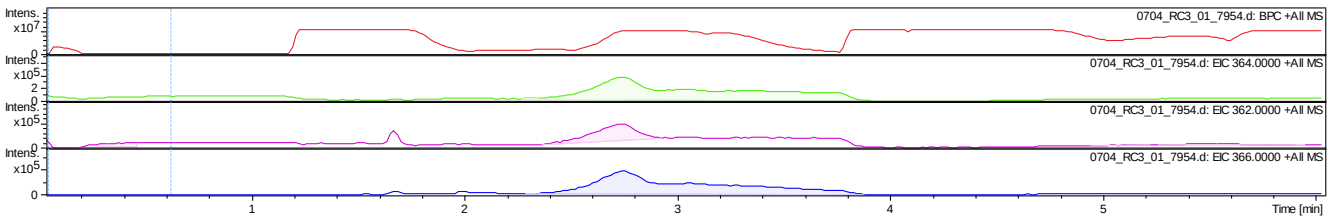
6.3. To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1a**, 32 mg, 0.2

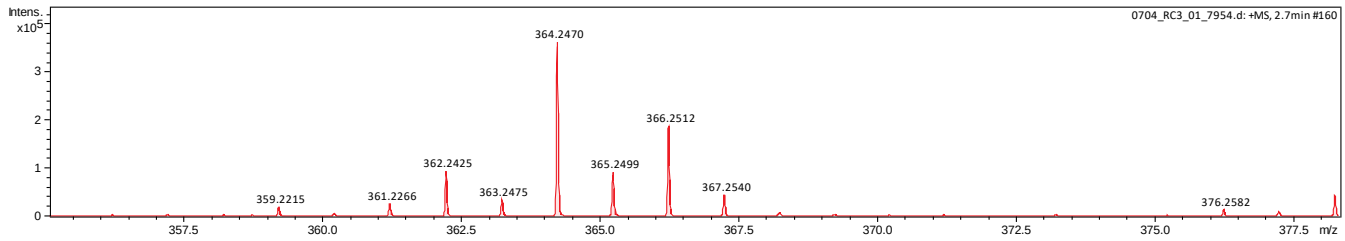
mmol), THF (1 mL), $T^+BF_4^-$ (49 mg, 0.2 mmol), *tert*-butyl nitrite (98%, 73 μL, 0.6 mmol), 4 Å molecular sieves (100 mg, activated at 500 ℃ for 5 h before use), and $BF_3 \cdot Et_2O$ (98%, 25 μL). It was then stirred at room temperature for 15 min. Subsequent HRMS analysis of the resulting mixture showed that enamine (**B**) (calcd, 182.0940; found, 182.0949) was formed.

6.4. To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1a**, 32 mg, 0.2 mmol), acetone (0.5 mL), H_2O (0.5 mL), $T^+BF_4^-$ (97 mg, 0.4 mmol), and *tert*-butyl nitrite (98%, 36 μL, 0.3 mmol). It was then stirred at room temperature for 30 min. Subsequent HRMS analysis of the resulting mixture showed that intermediate 1-phenyl-5-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2,3,4,5-tetrahydropyridin-1-ium tetrafluoroborate (**D**) (calcd, 425.2358; found, 425.2355) was formed.

6.5. To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1a**, 32 mg, 0.2 mmol), acetone (1 mL), $T^+BF_4^-$ (97 mg, 0.4 mmol), *tert*-butyl nitrite (98%, 36 μL, 0.3 mmol), and 4 Å molecular sieves (100 mg, activated at 500 ℃ for 5 h before use). The resulting mixture was then stirred at room temperature under air for 1 h. Subsequent TLC analysis of the resulting mixture showed that there was no desired product **3a** formed from this reaction.

6.6. To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1a**, 32 mg, 0.2 mmol), acetone (0.5 mL), $H_2{}^{18}O$ (0.5 mL), $T^+BF_4^-$ (97 mg, 0.4 mmol), and *tert*-butyl nitrite (98%, 36 μL, 0.3 mmol). The resulting mixture was then stirred at room temperature under air for 1 h. Upon completion, subsequent HRMS analysis of the reaction mixture showed that [$^{18}O_1$]-**3a**, [$^{18}O_2$]-**3a** and [^{16}O]-**3a** were formed in a ratio of 13.7:6.3:1 (Fig. S1).





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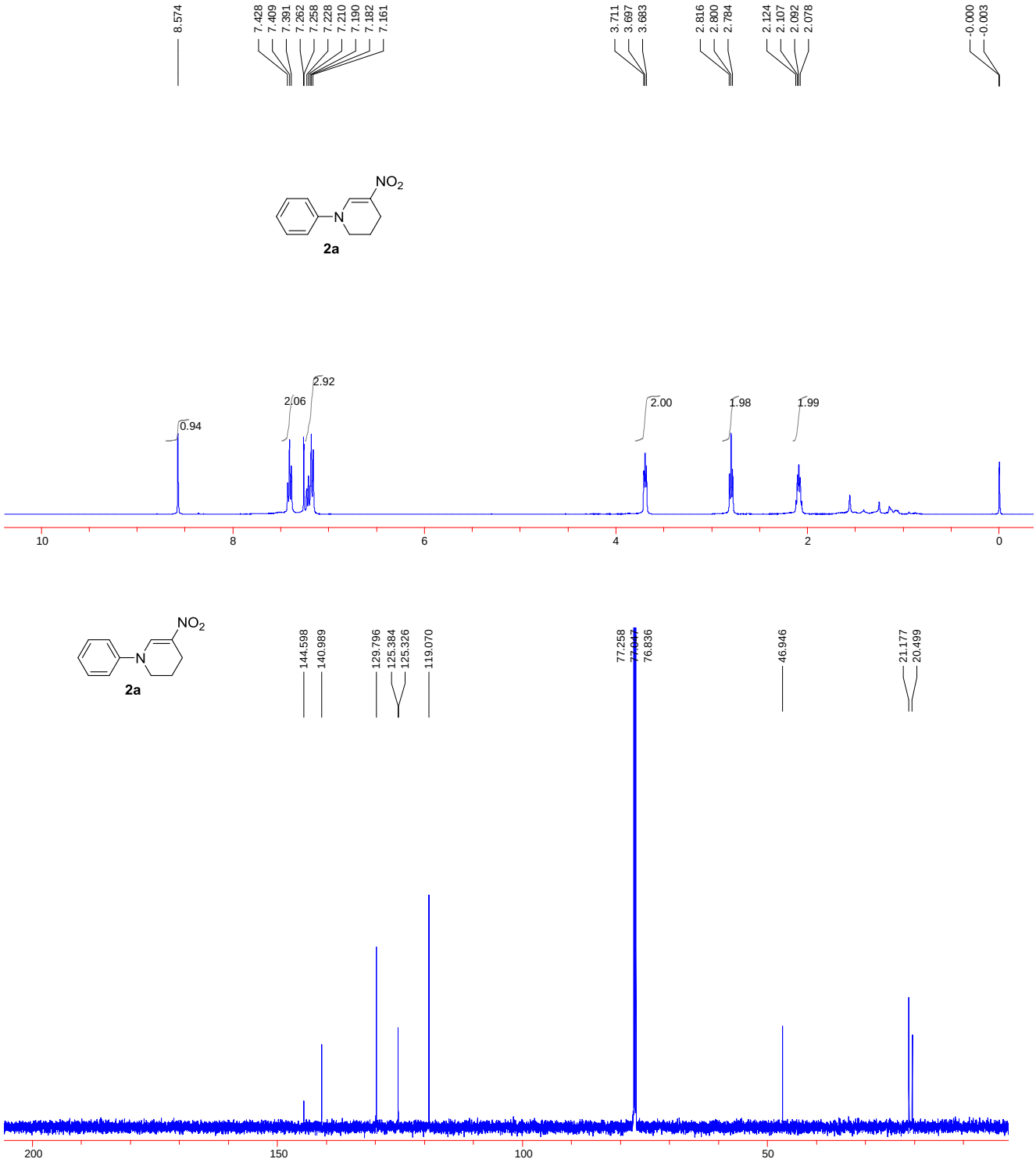
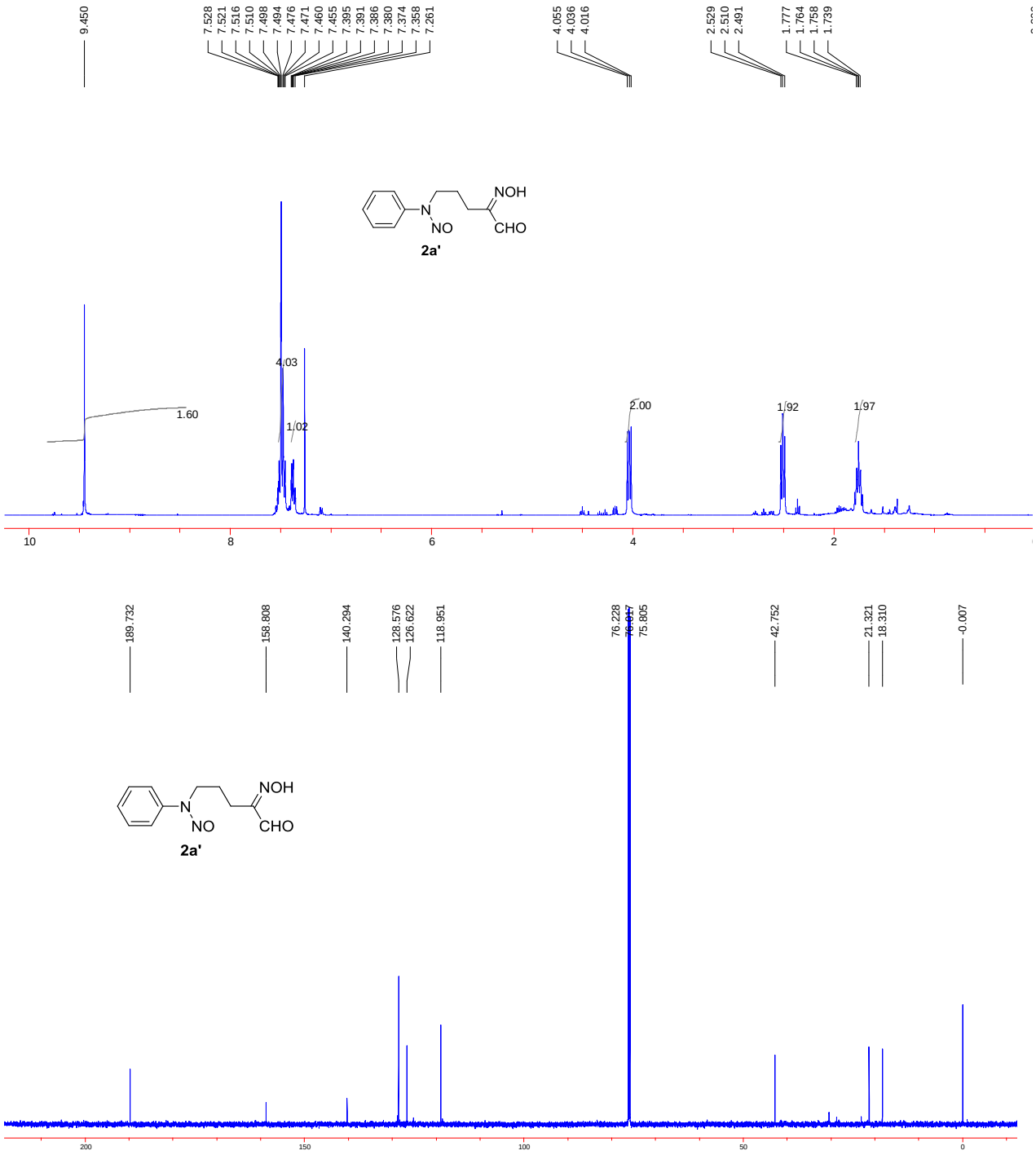
2	2.7	6049227.0	Chromatogram	183933	114.2	EIC 366.0000 +All MS	0.3
3	2.7	956292.9	Chromatogram	94498	24.3	EIC 362.0000 +All MS	0.2

Fig. S1 Copy of HRMS Spectra of the Reaction Mixture

III. Copies of the NMR spectra of 2a-2p, 2', 2'', I, II, and III

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1.97
10
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2
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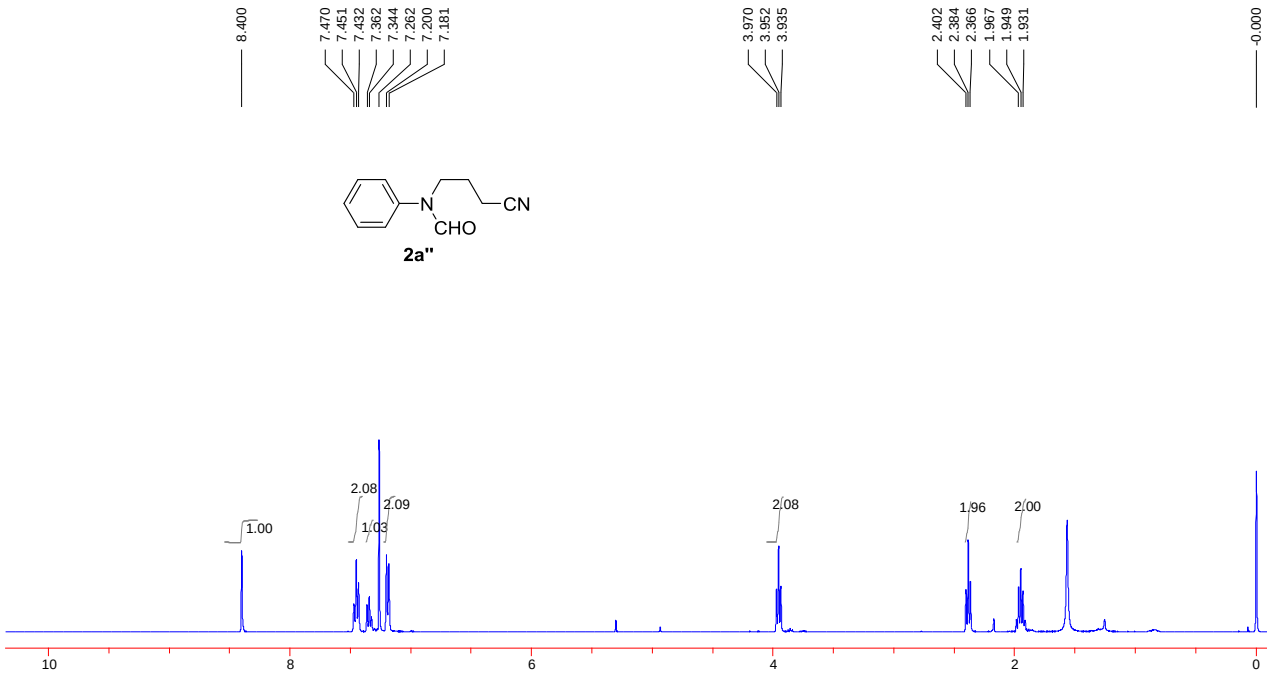
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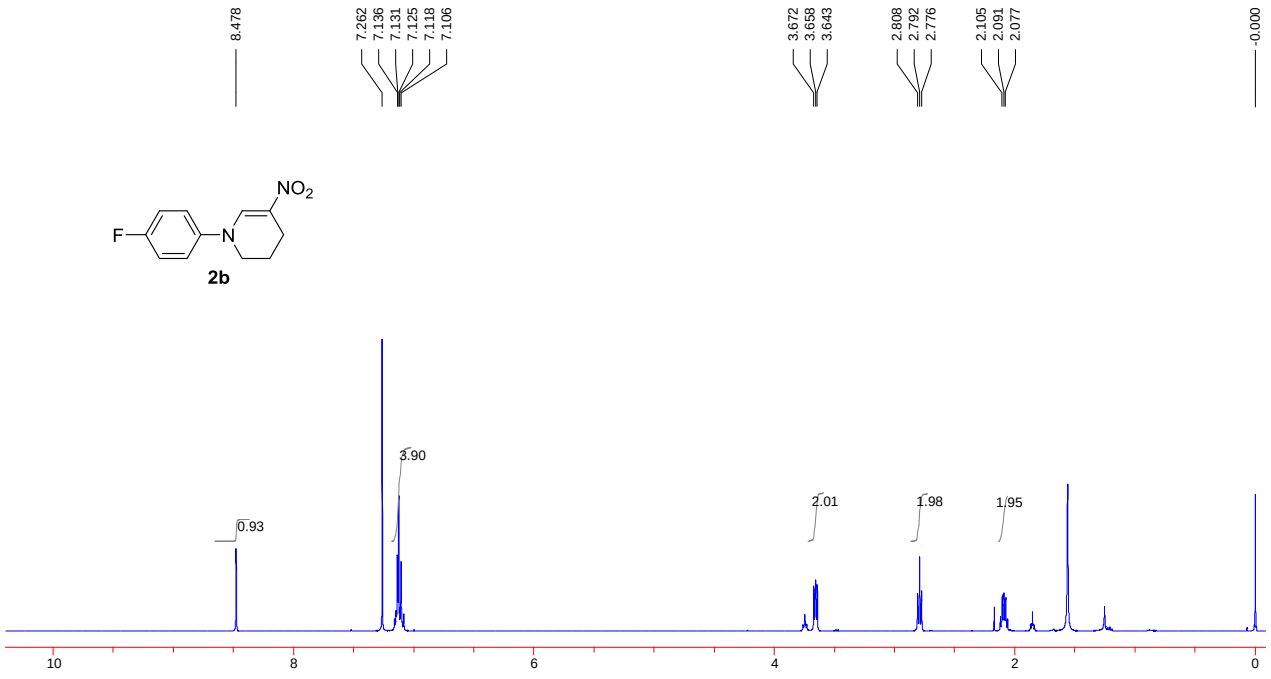
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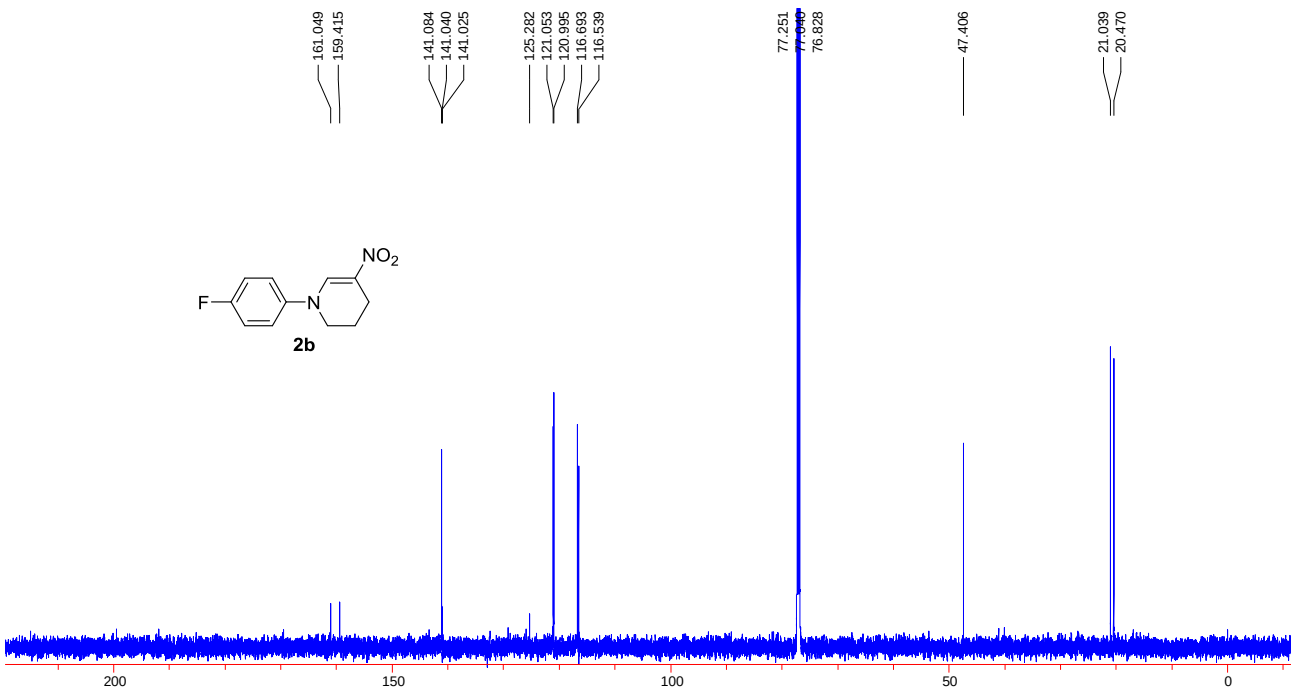
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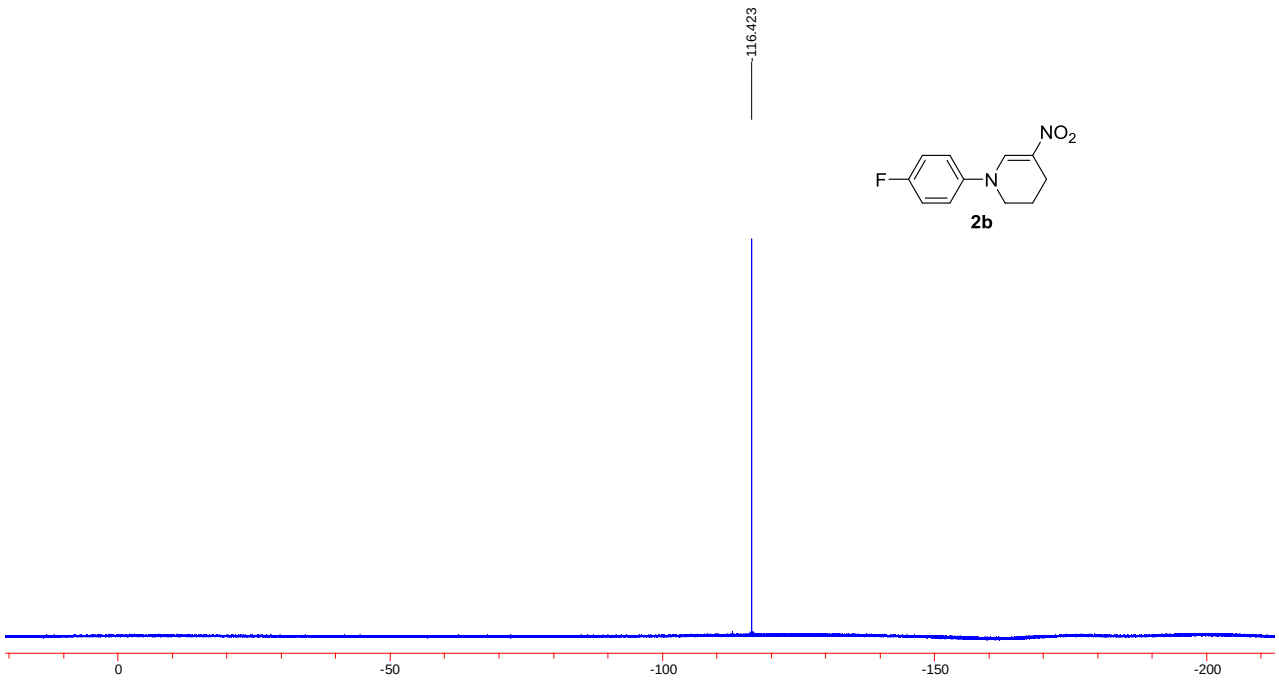
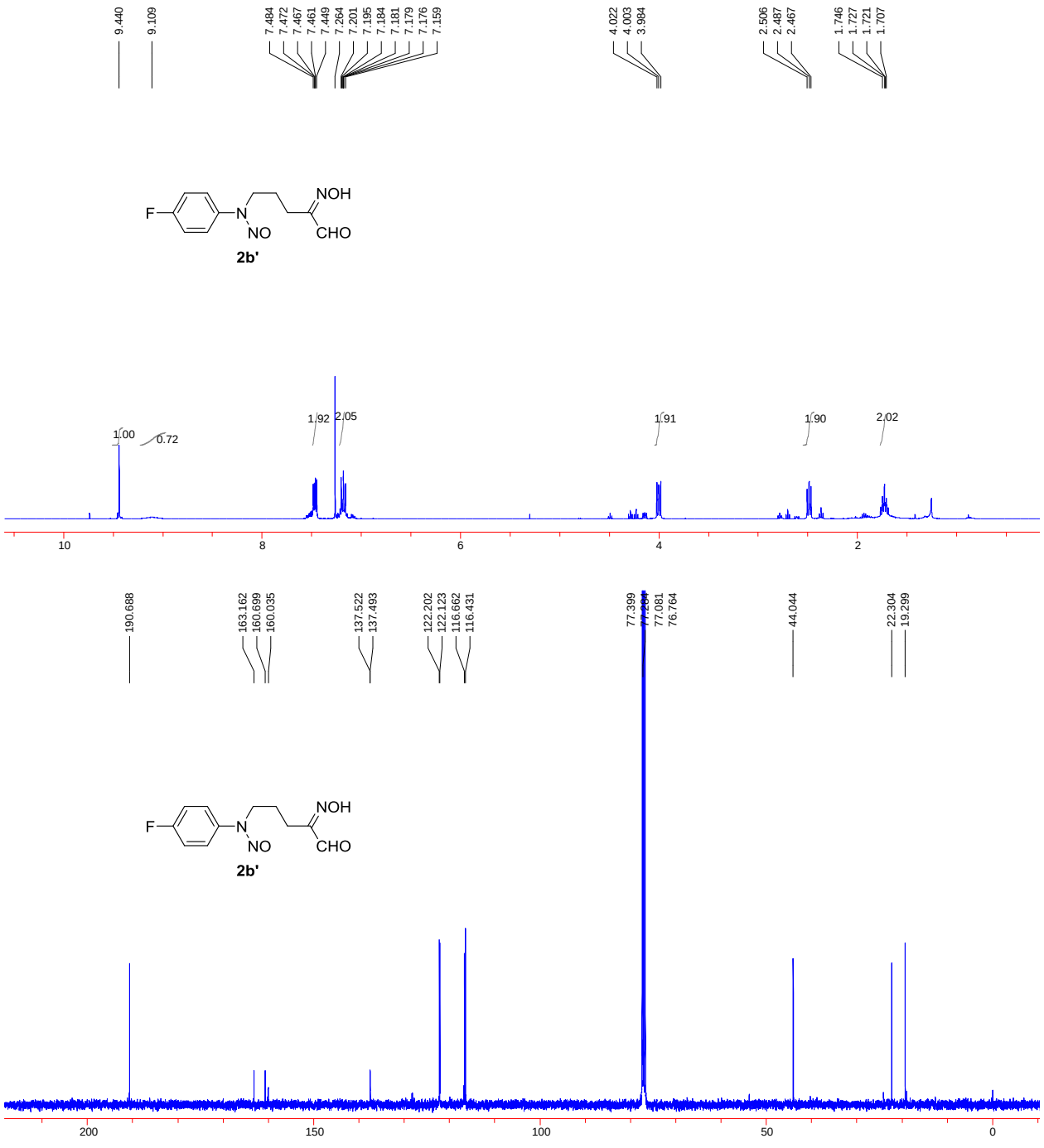


2b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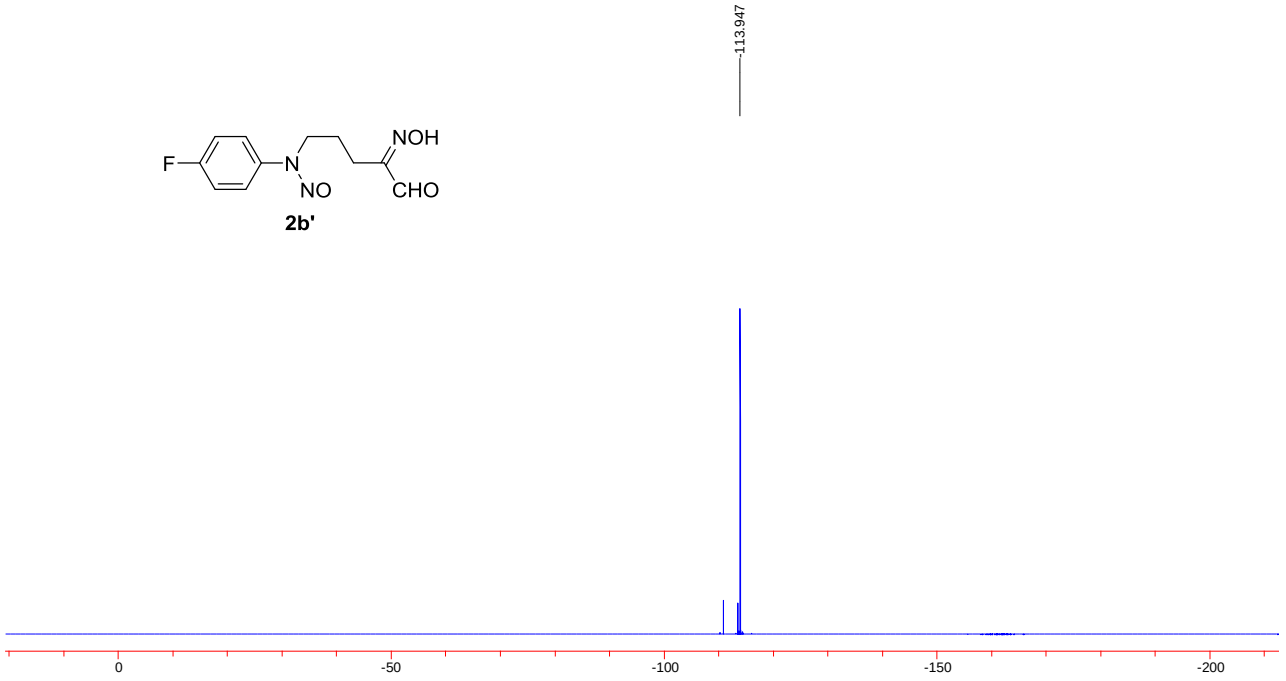
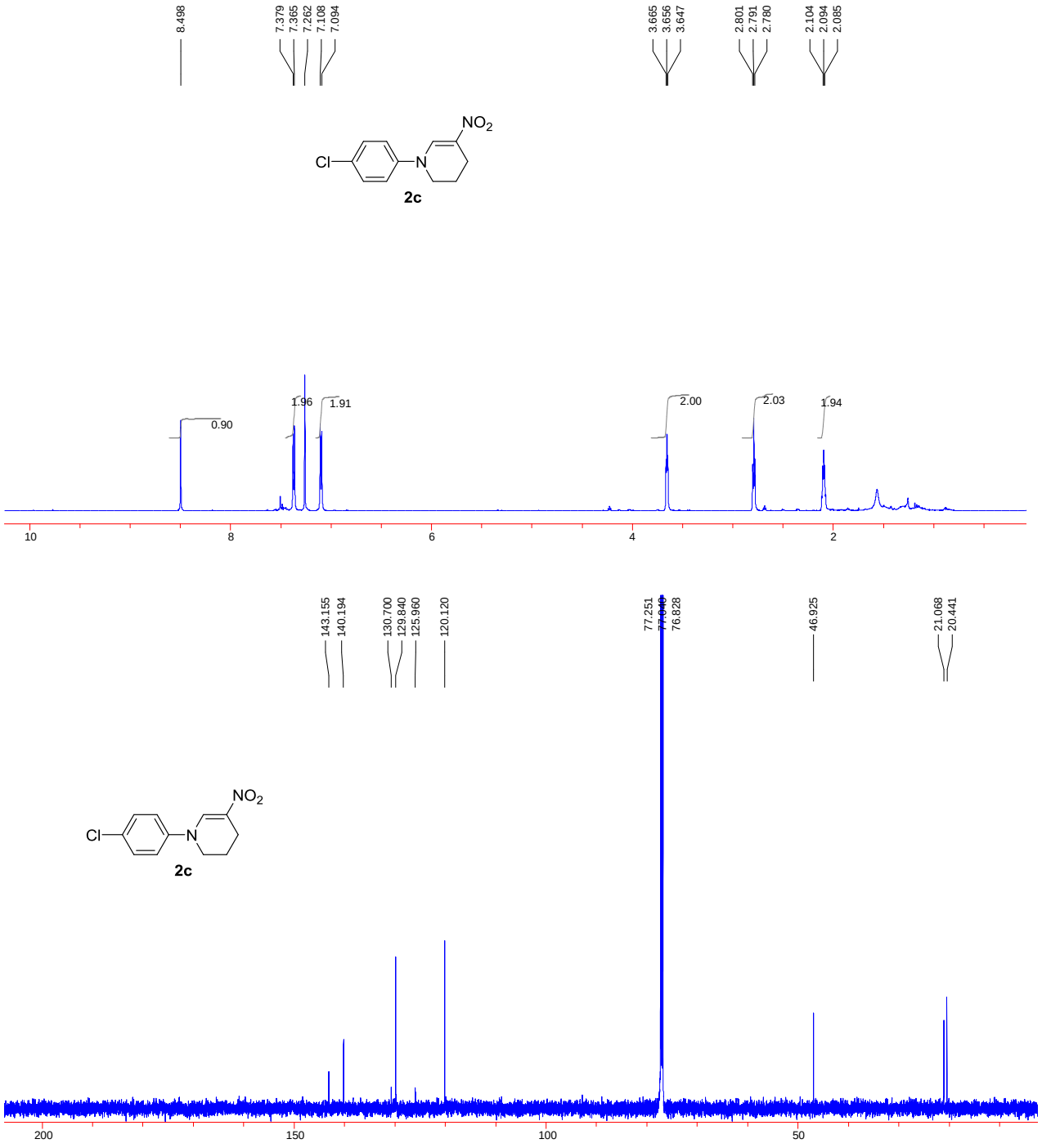


2b'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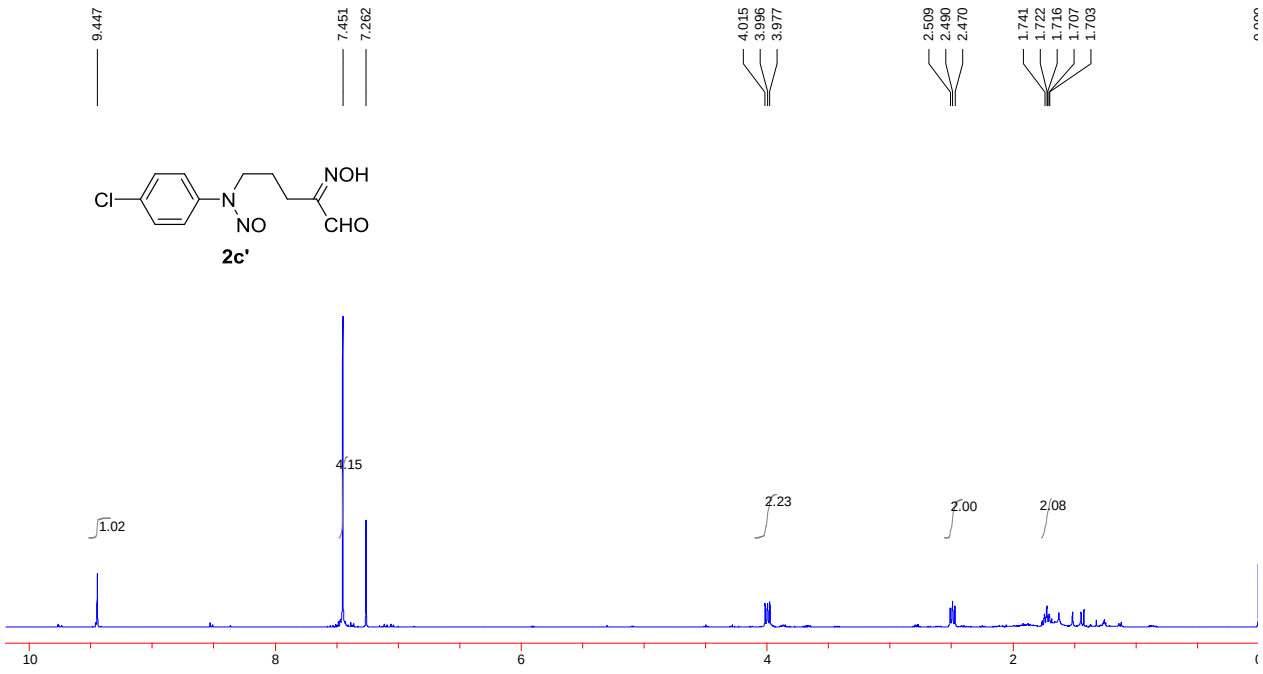
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2.08
10
8
6
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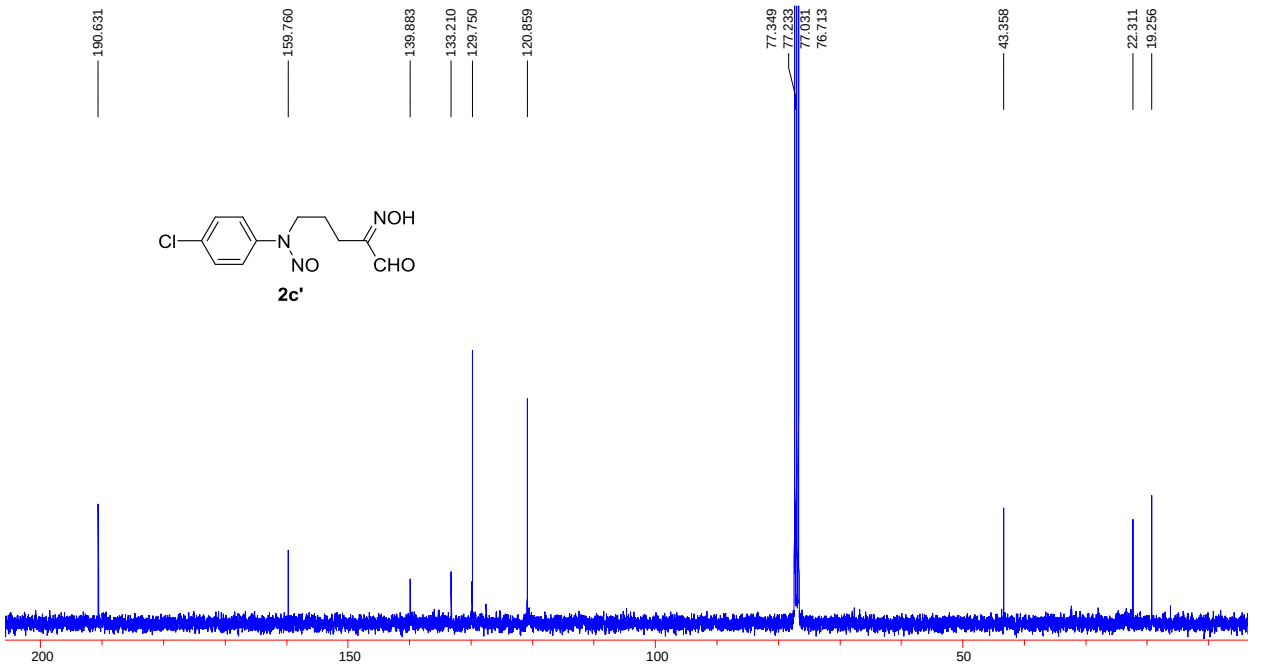
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NOH
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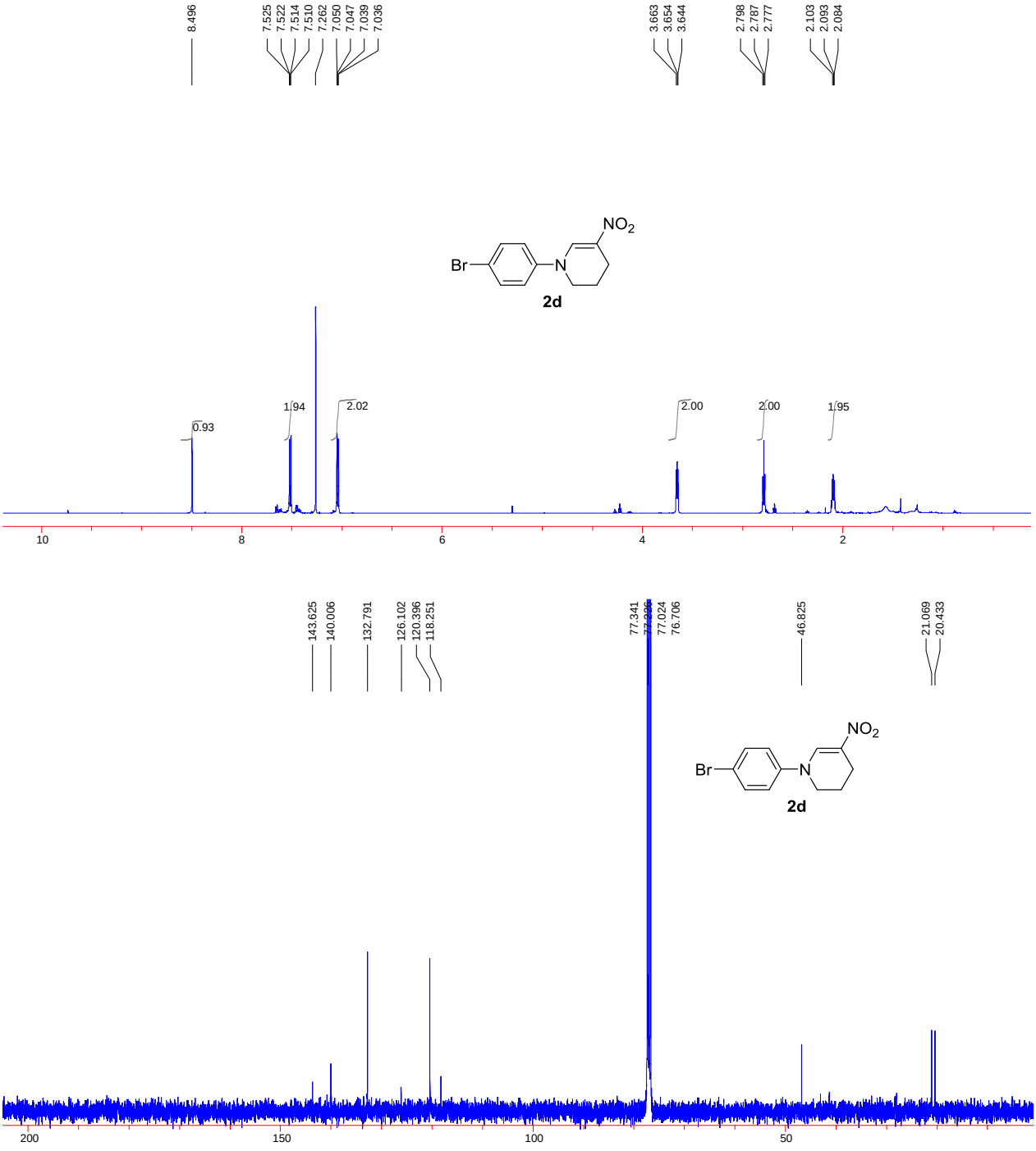
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2.787
2.777
2.103
2.093
2.084
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2.00
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46.825
21.069
20.433
NO2
Br
N
2d
200
150
100
50


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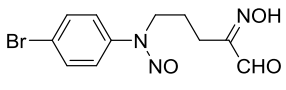
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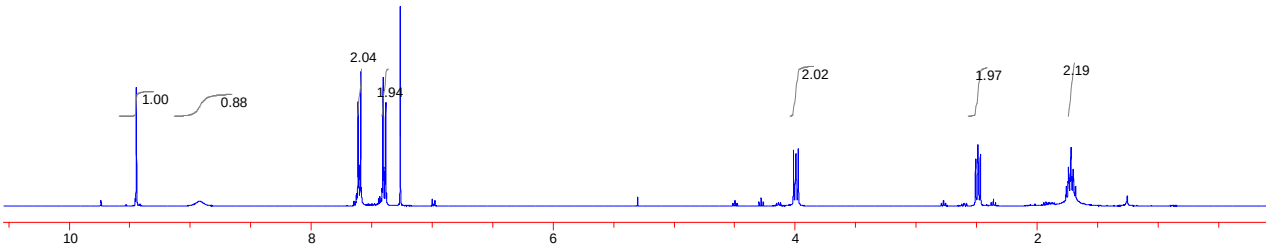
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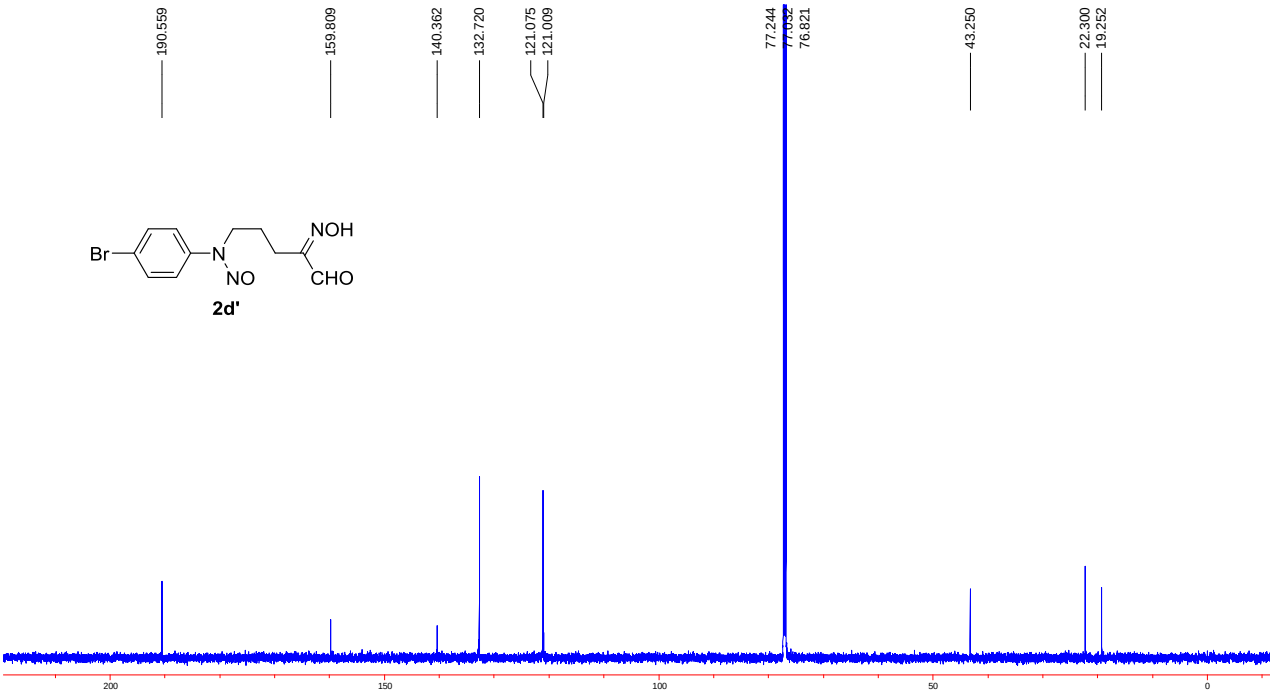
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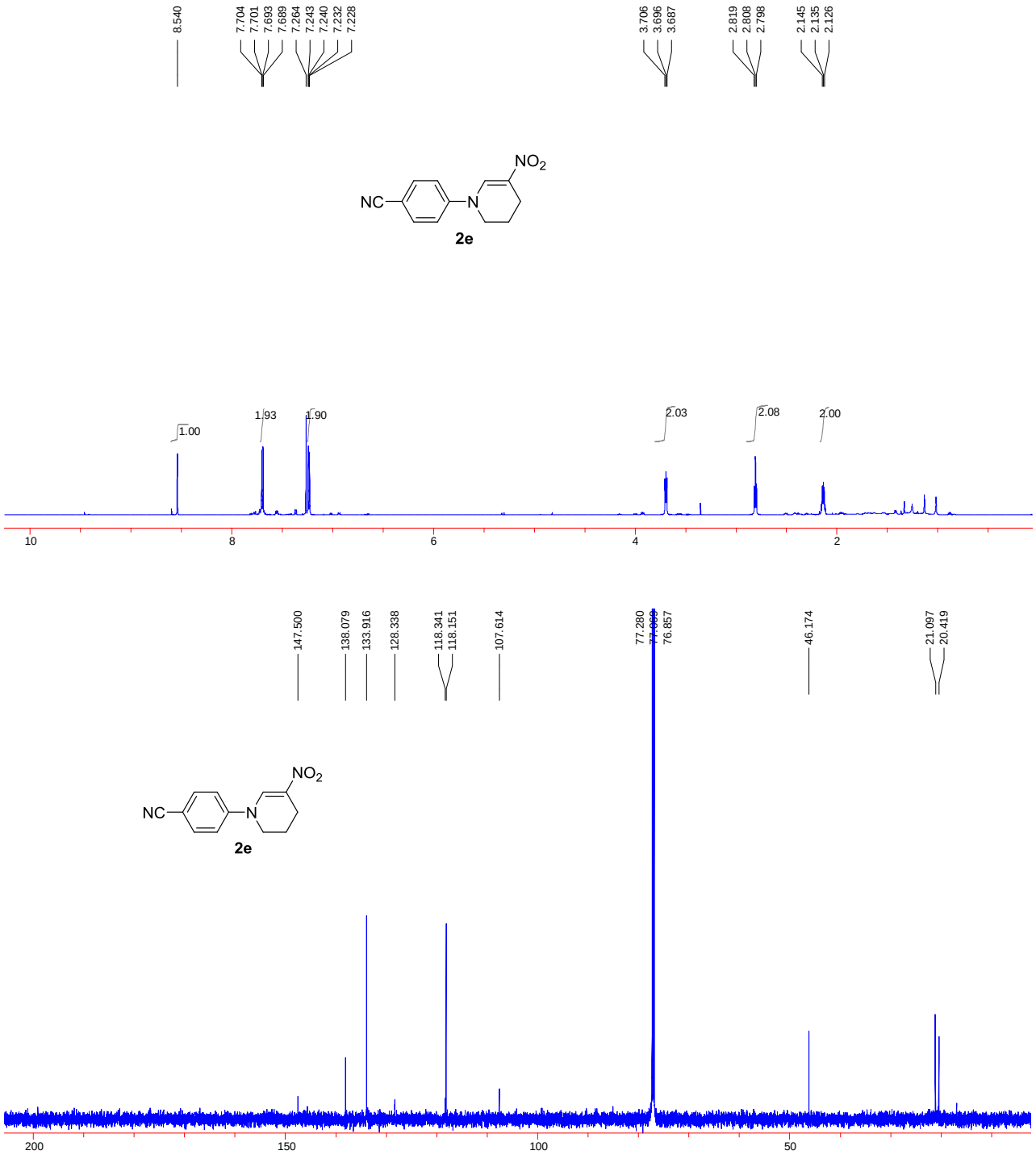
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3.696
3.687
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2.808
2.798
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2.135
2.126
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1.90
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2.08
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6
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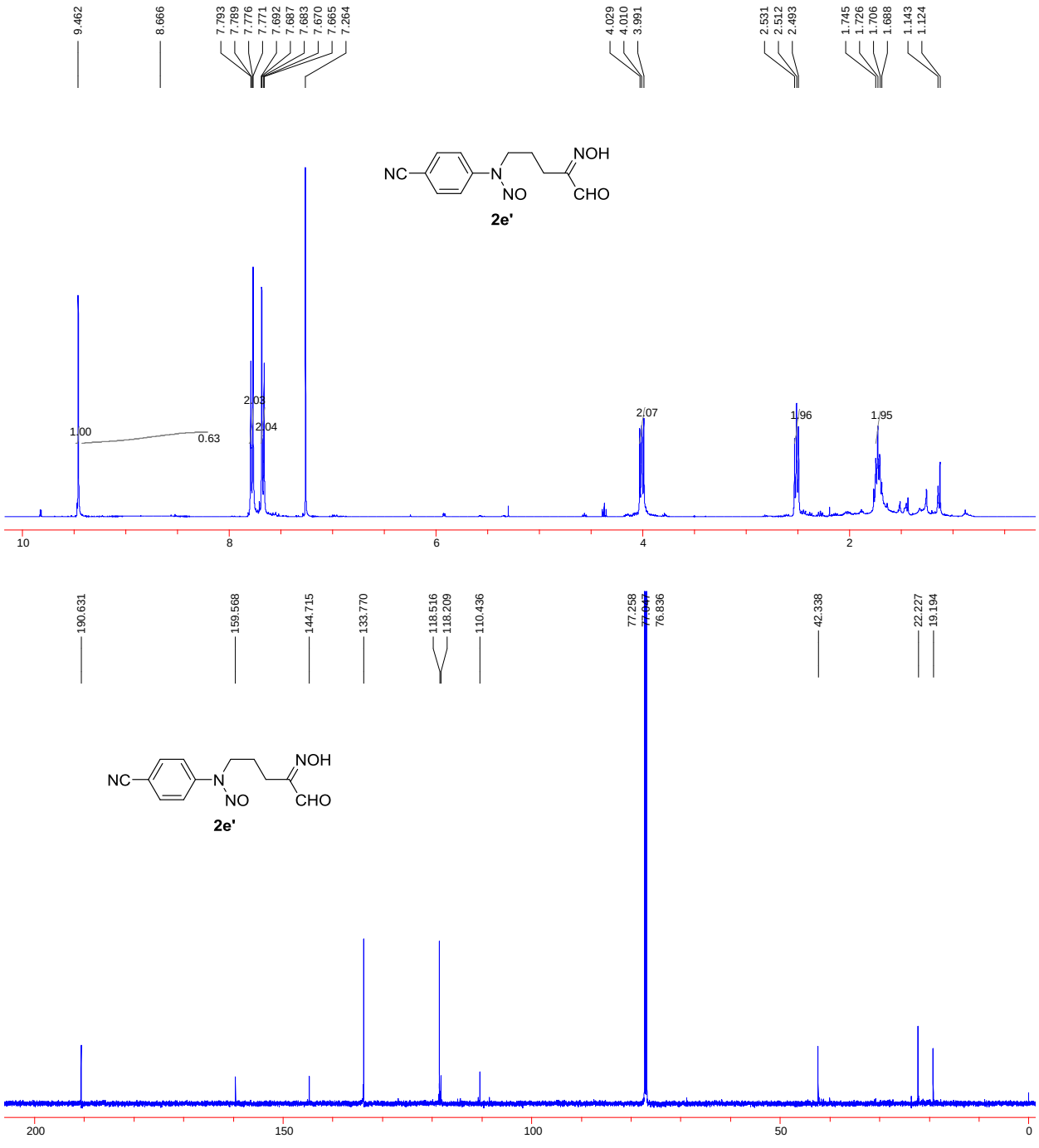
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4.010
3.991
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2.493
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1.706
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NOH
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6
4
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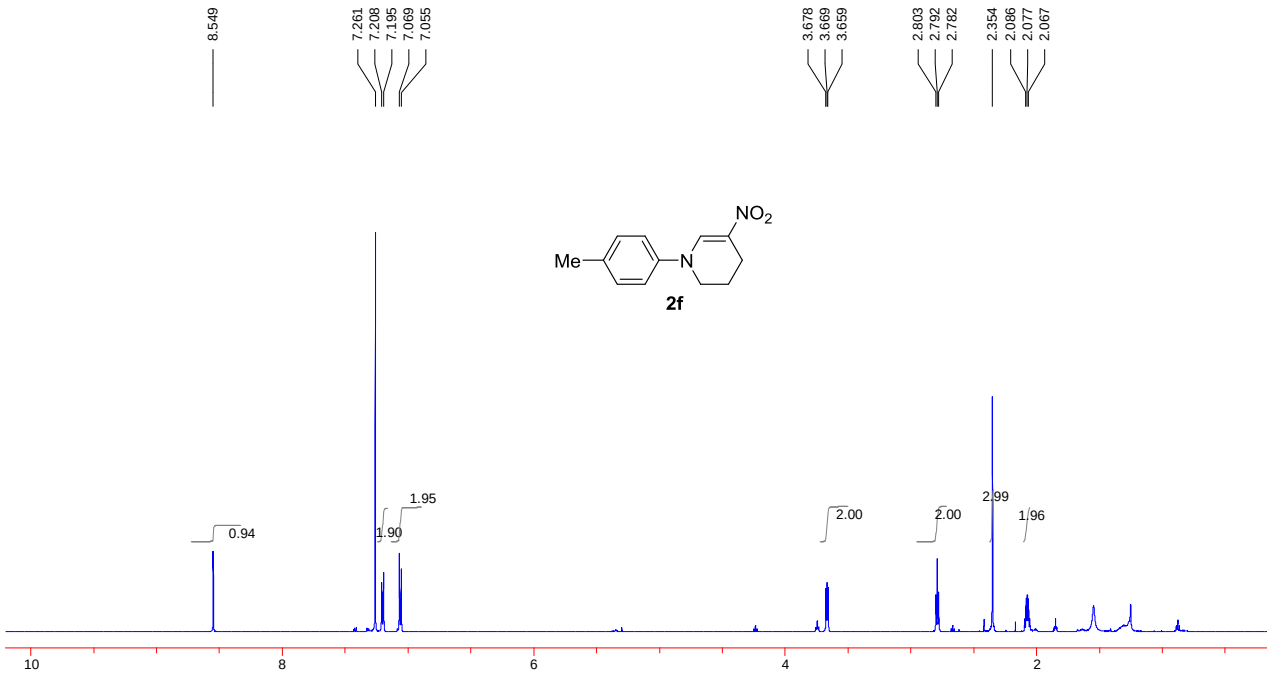
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2.086
2.077
2.067
NO2
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4
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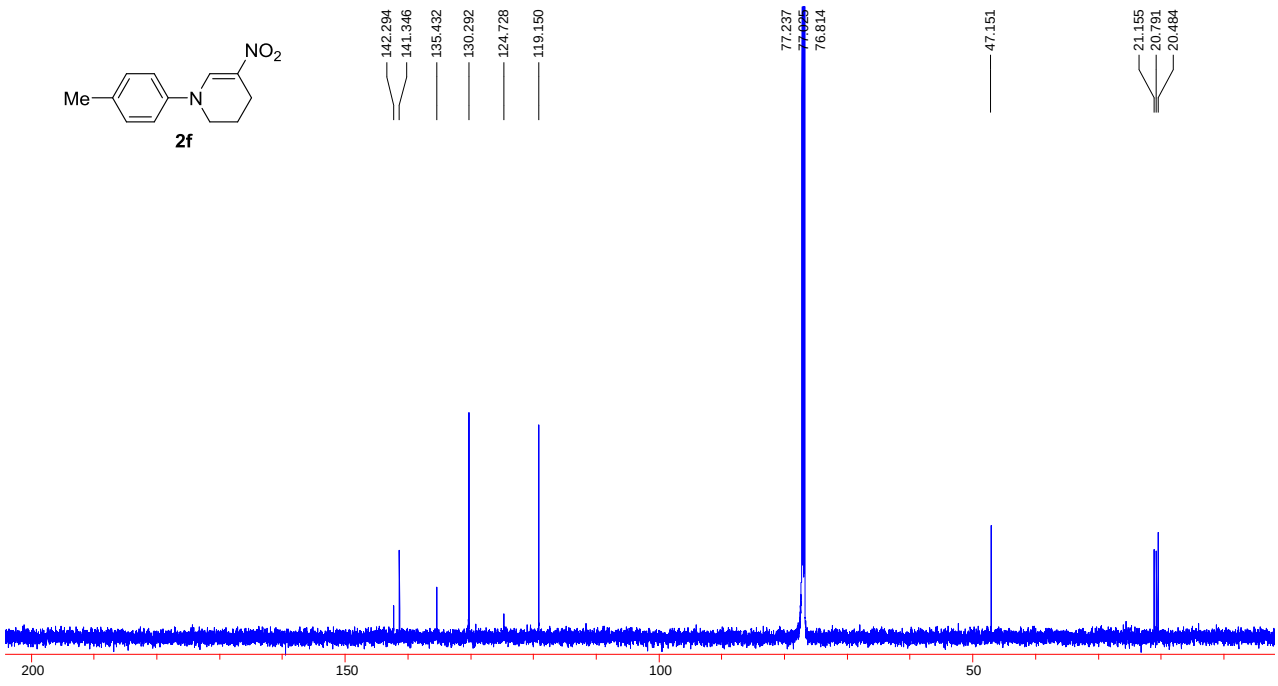
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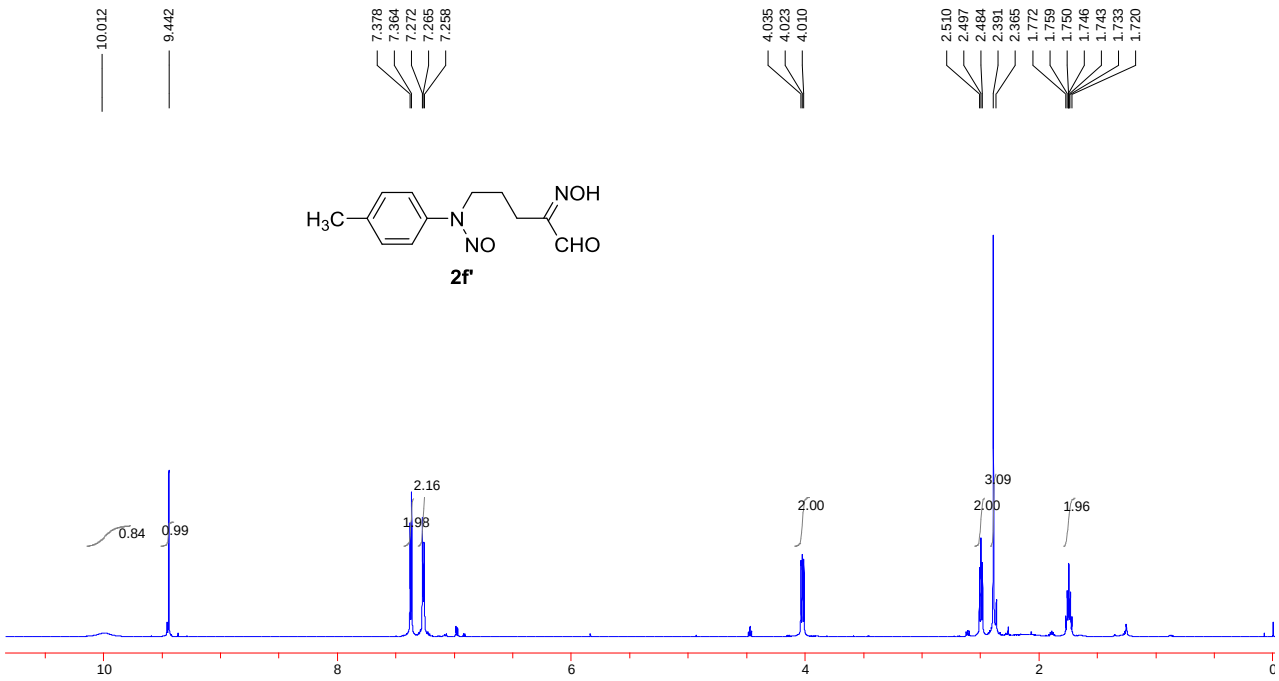
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1.750
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NO
NOH
CHO
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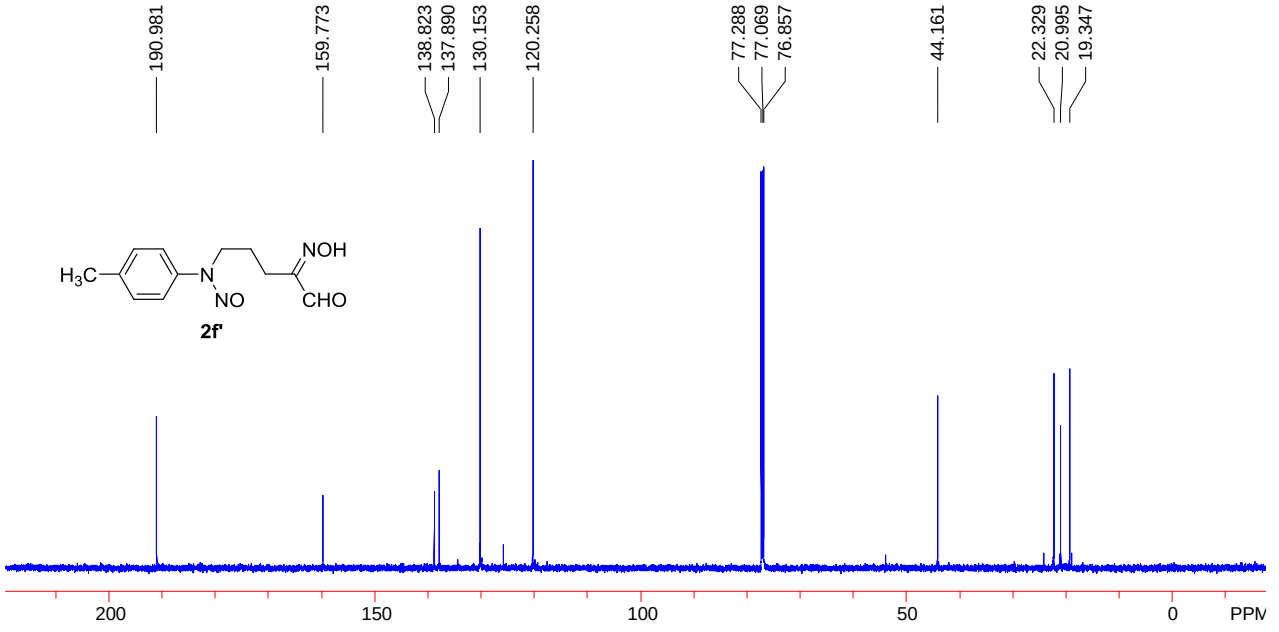
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N
NO
NOH
CHO
2f'
200
150
100
50
0
PPM


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7.358
7.266
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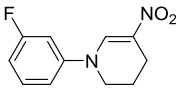
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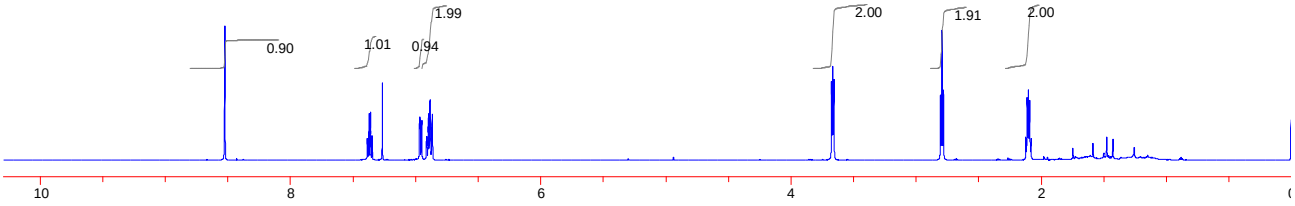
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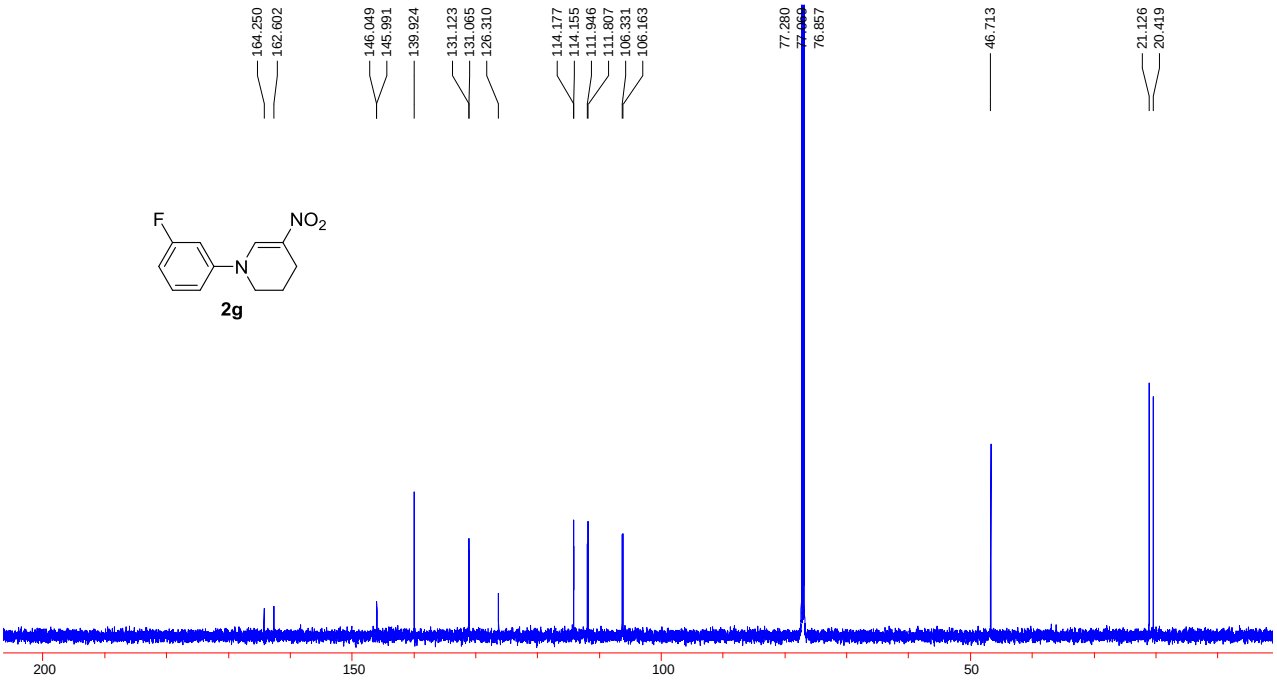
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106.331
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76.857
46.713
21.126
20.419
200
150
100
50

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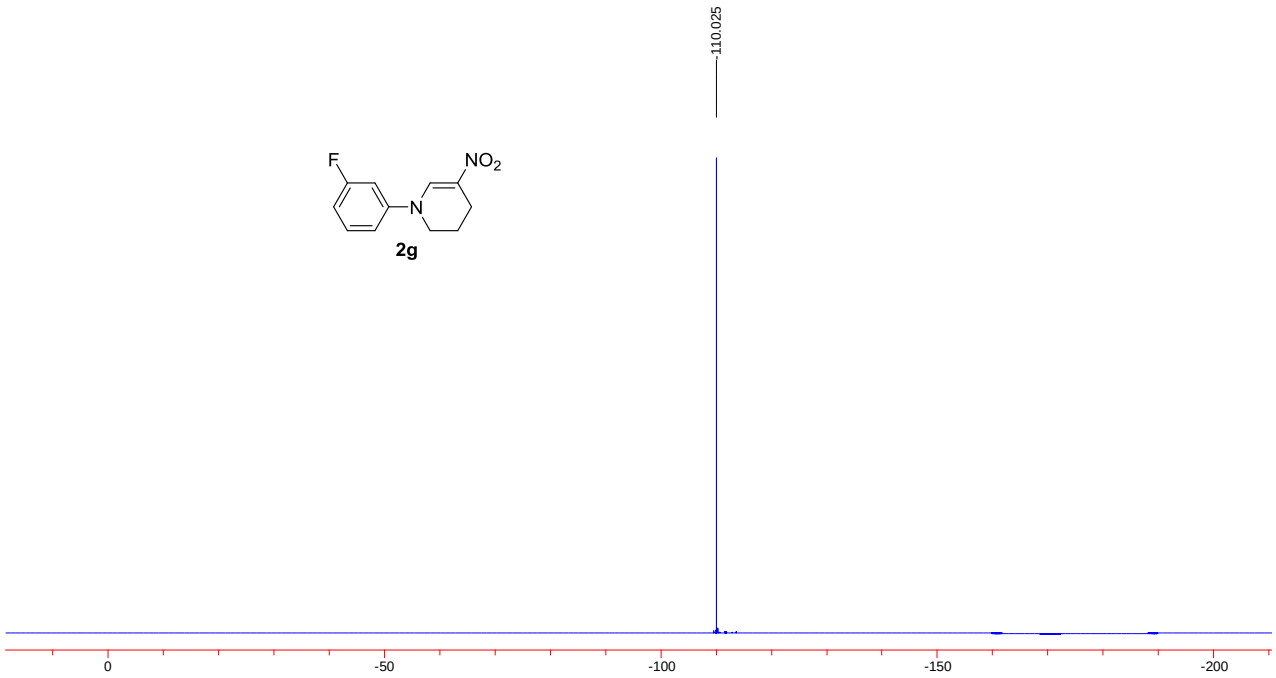
N

2g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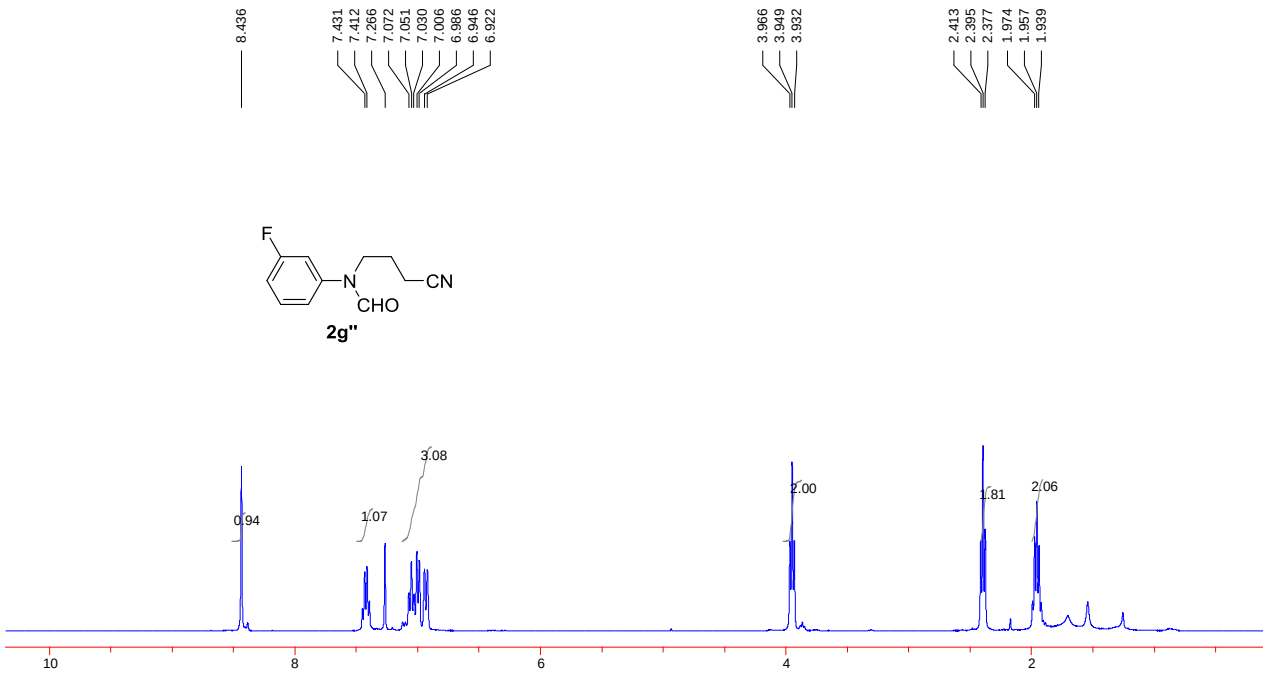
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3.932
2.413
2.395
2.377
1.974
1.957
1.939
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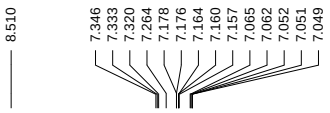
4
2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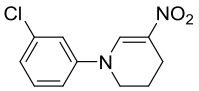
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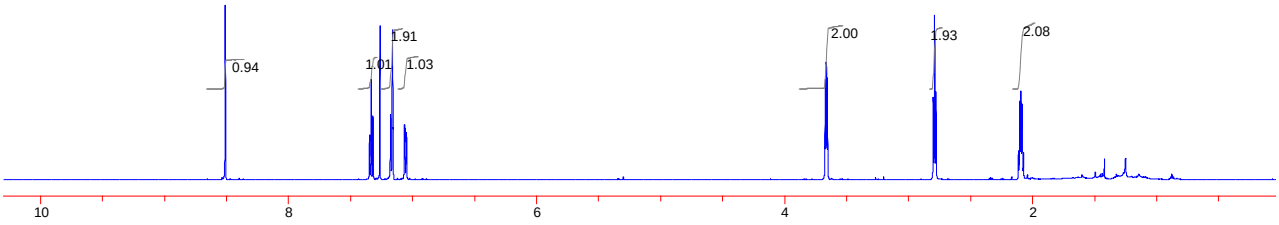
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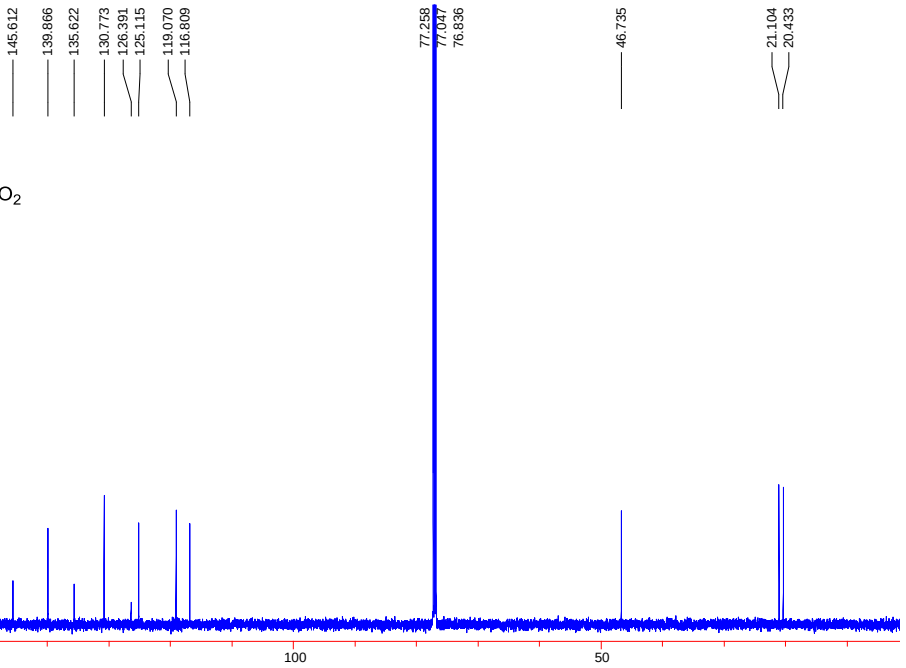
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76.836
46.735
21.104
20.433
Cl
NO2
N
200
150
100
50

2h


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7.204
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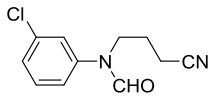
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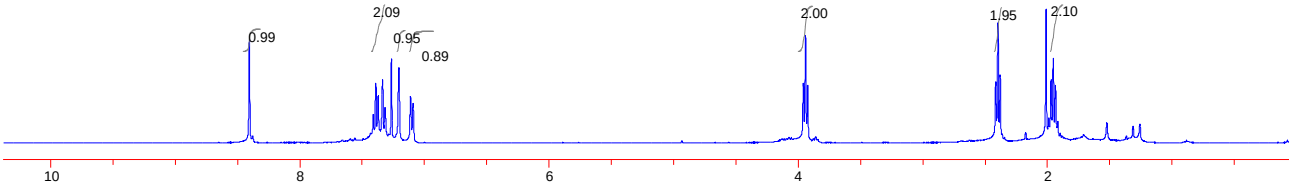
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4
2


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7.106
7.096
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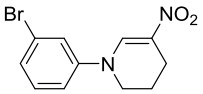
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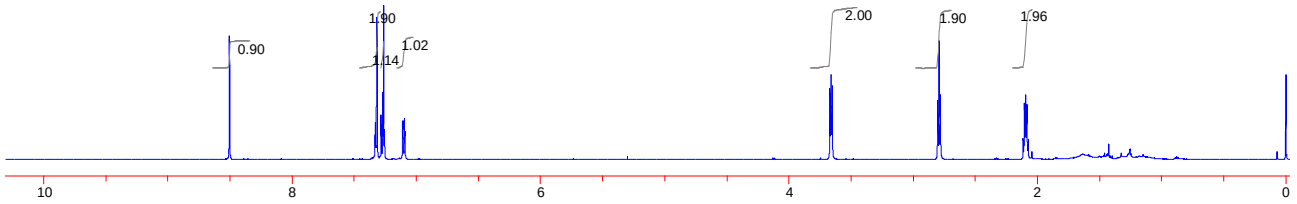
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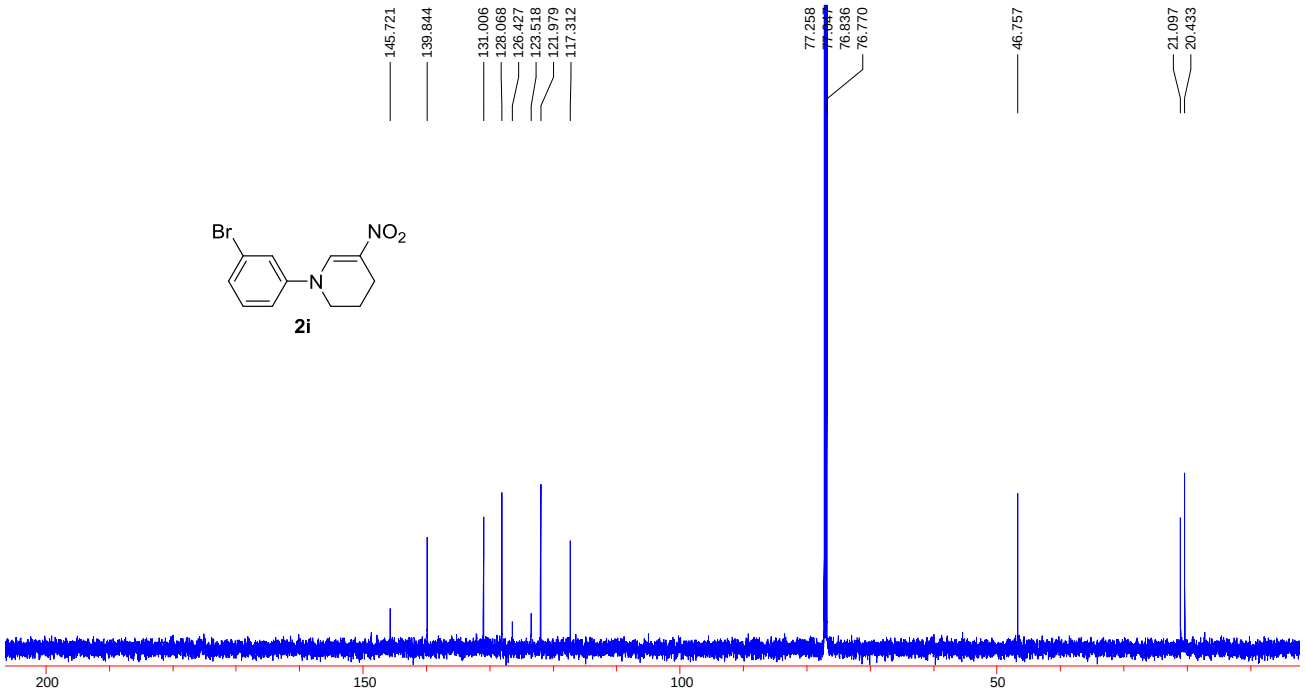
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21.097
20.433
Br
NO2
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50

2i


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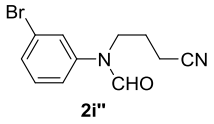
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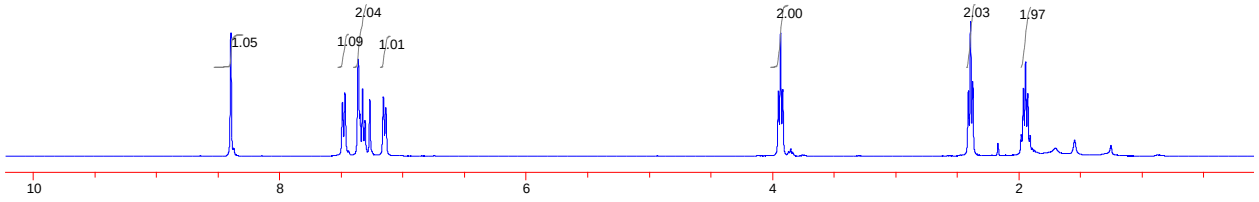
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2


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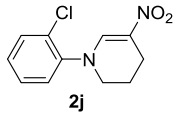
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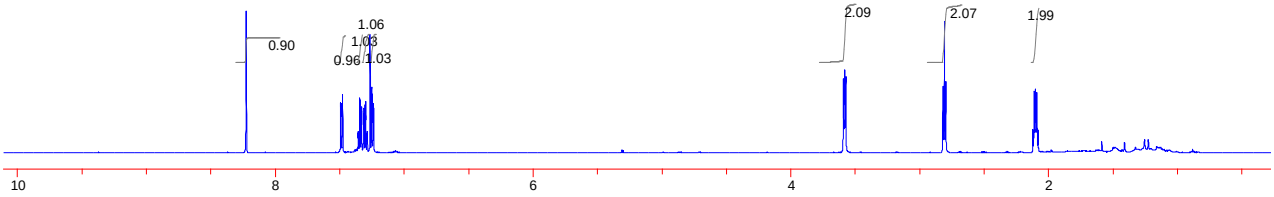
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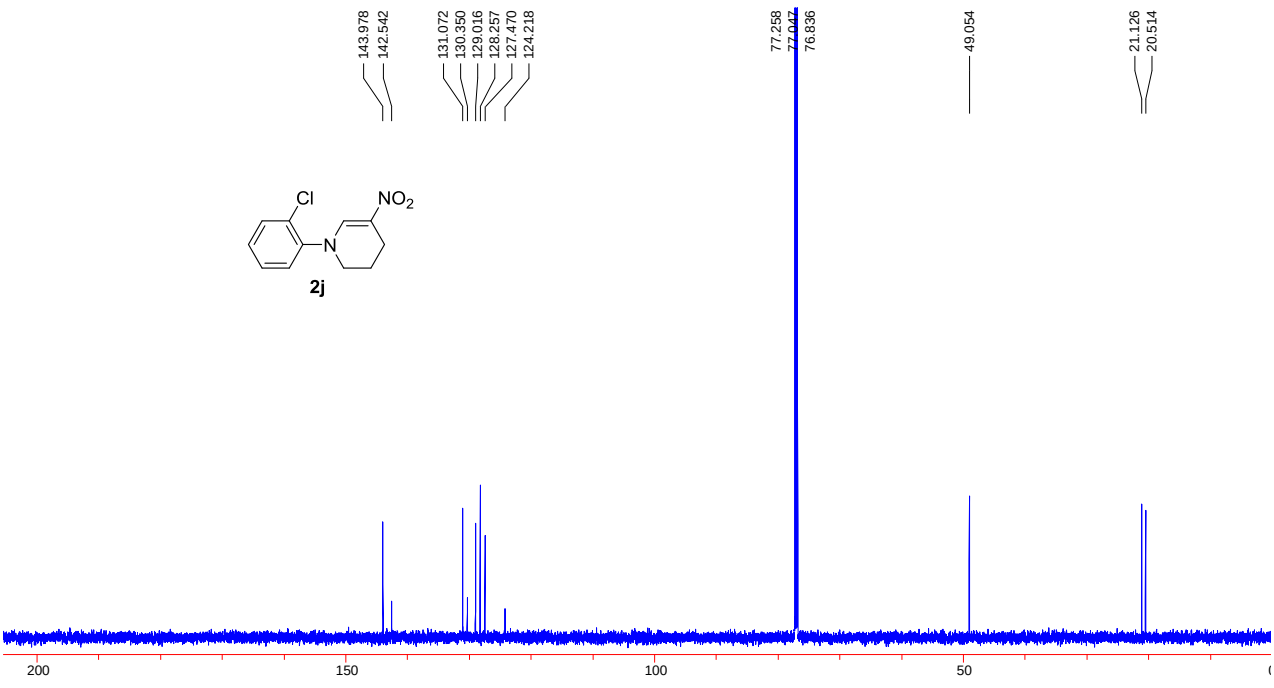
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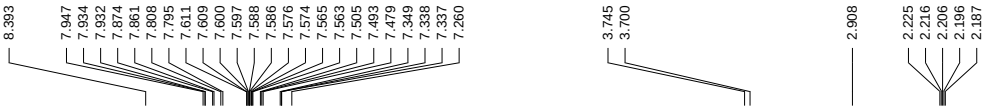
2j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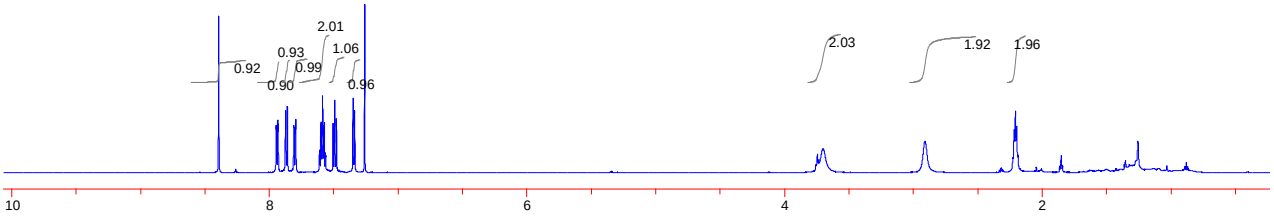
NO2
N

2k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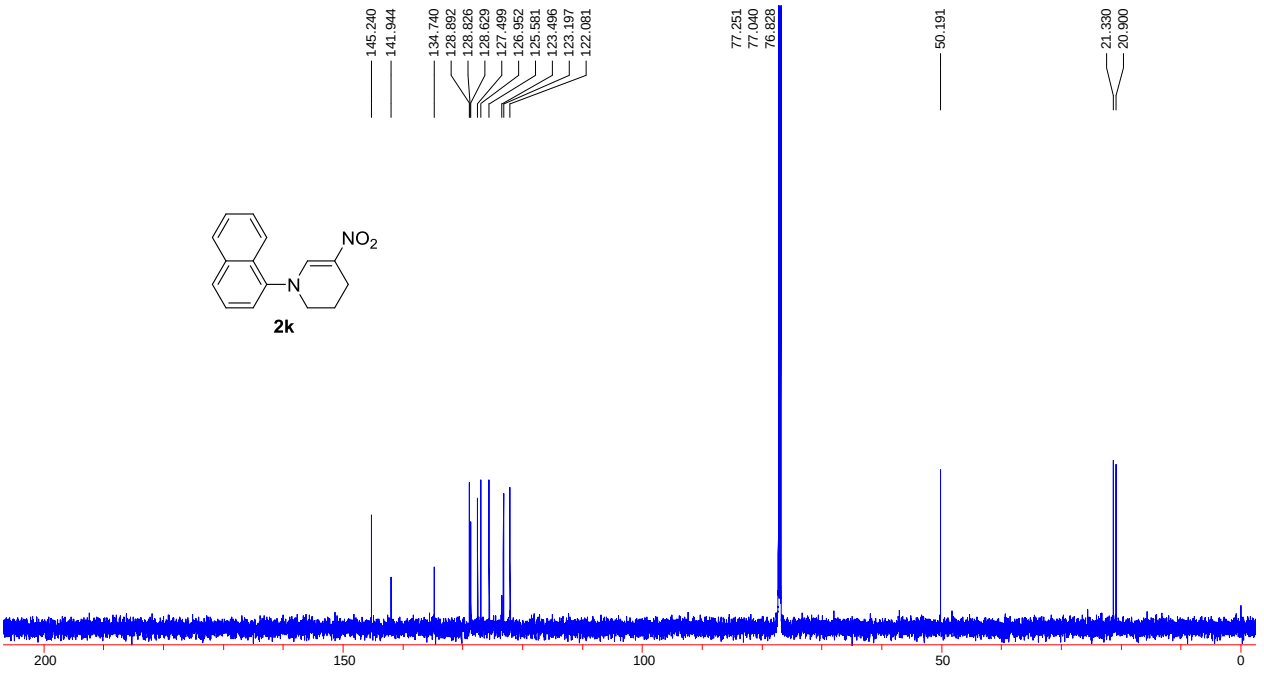
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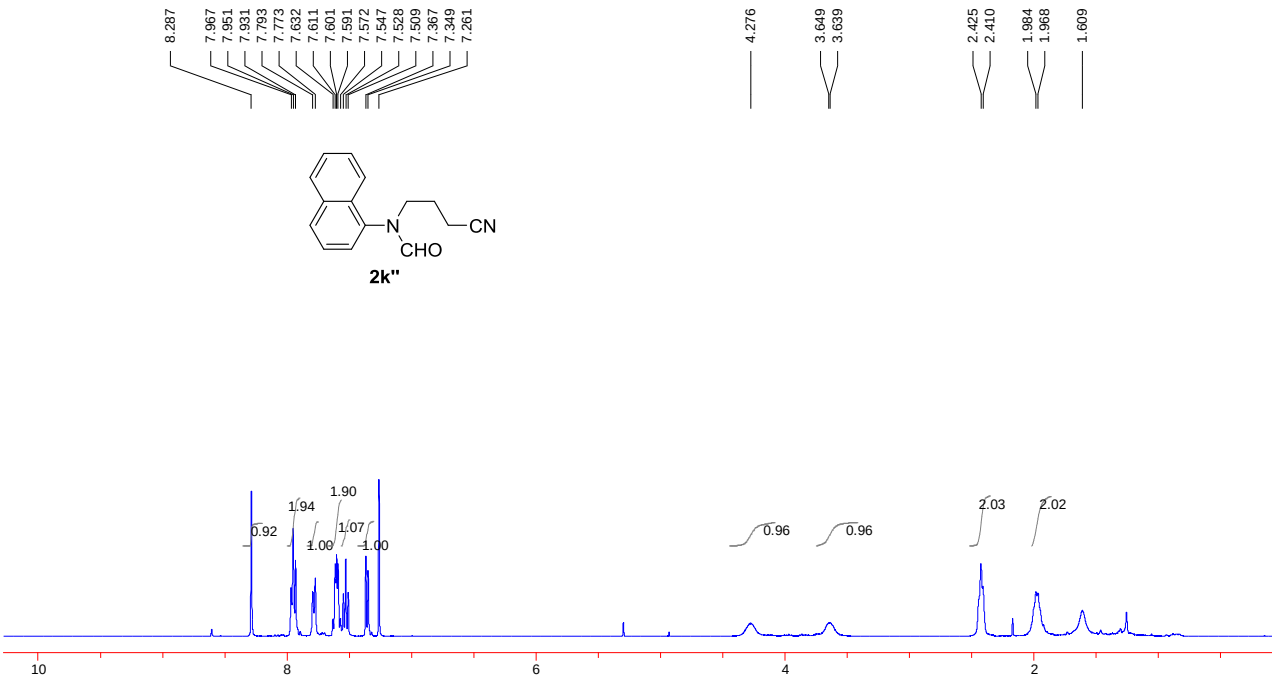
2k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7.367
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3.639
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2.410
1.984
1.968
1.609
N
CHO
CN
2k''
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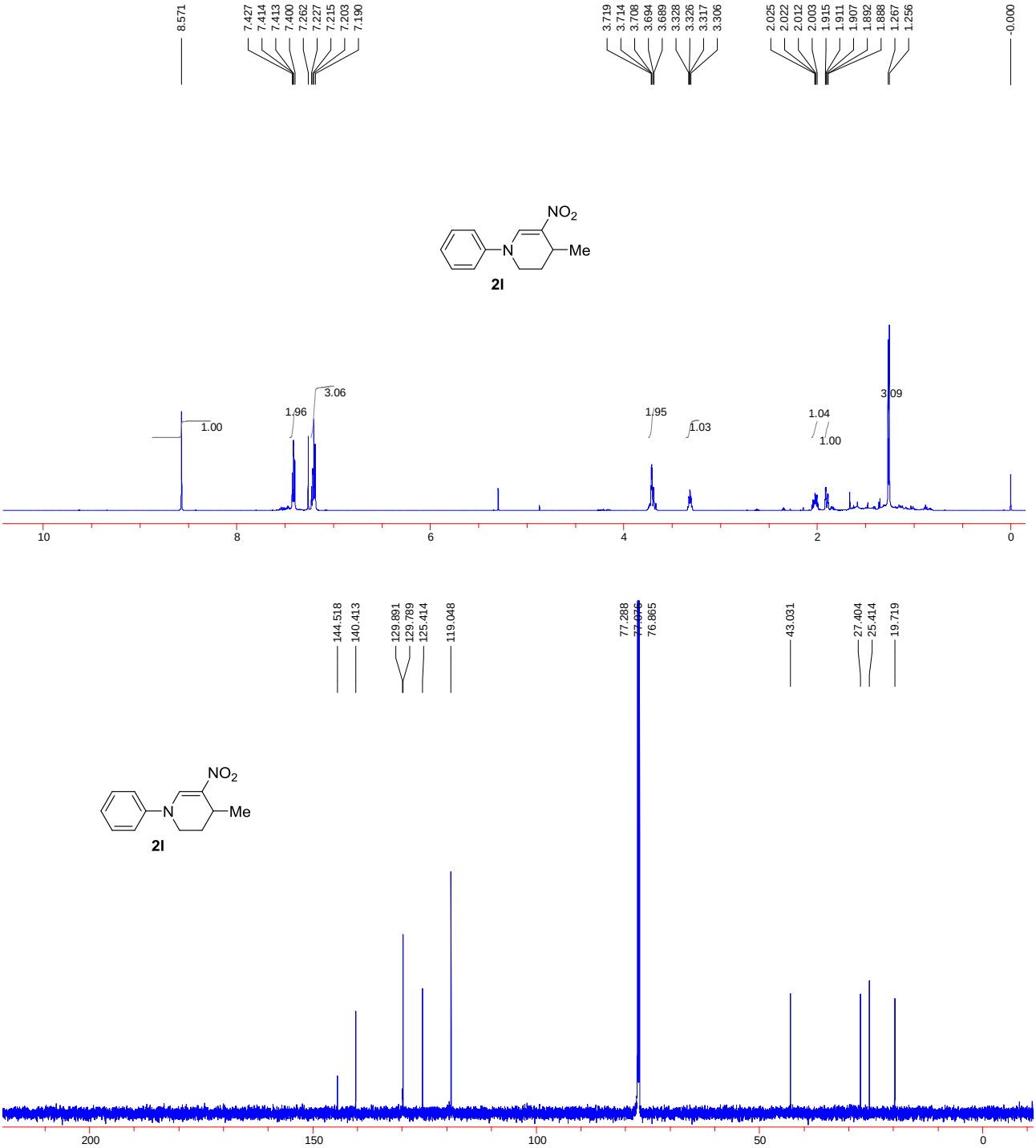
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3.689
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3.306
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2.022
2.012
2.003
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1.911
1.907
1.892
1.888
1.267
1.256
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NO2
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2l
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1.95
1.03
1.04
1.00
3.09
10
8
6
4
2
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129.891
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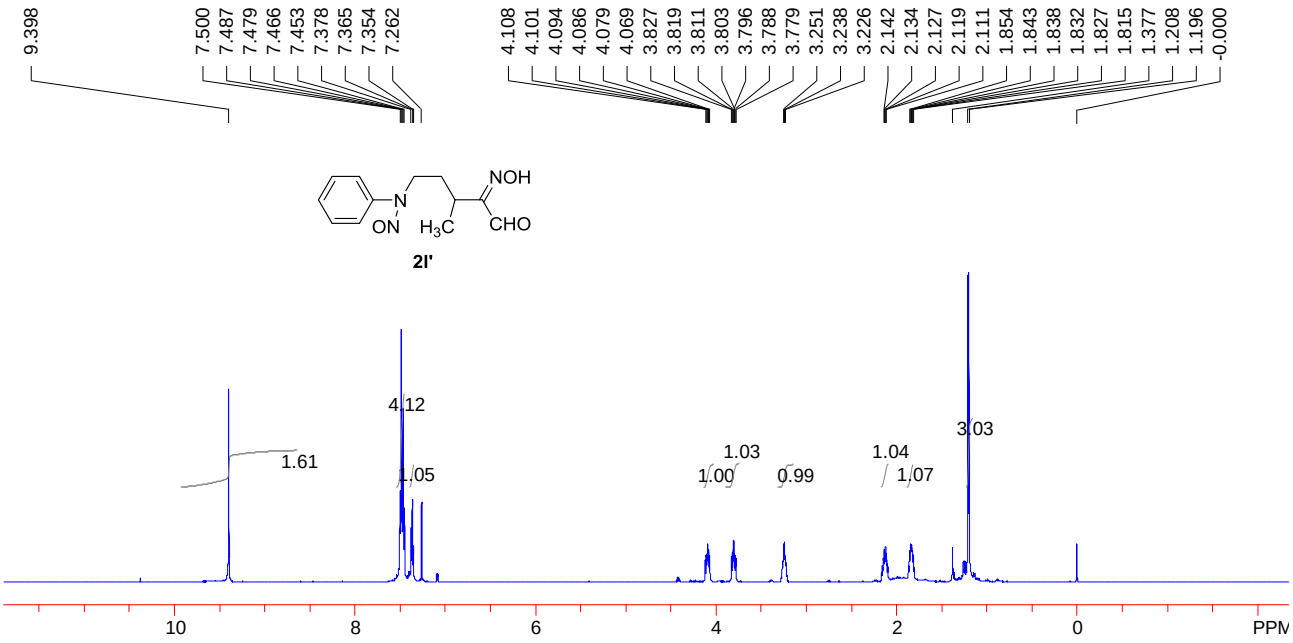
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7.365
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4.094
4.086
4.079
4.069
3.827
3.819
3.811
3.803
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3.788
3.779
3.251
3.238
3.226
2.142
2.134
2.127
2.119
2.111
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1.843
1.838
1.832
1.827
1.815
1.377
1.208
1.196
-0.000
NOH
N
ON
H3C
CHO
2l'
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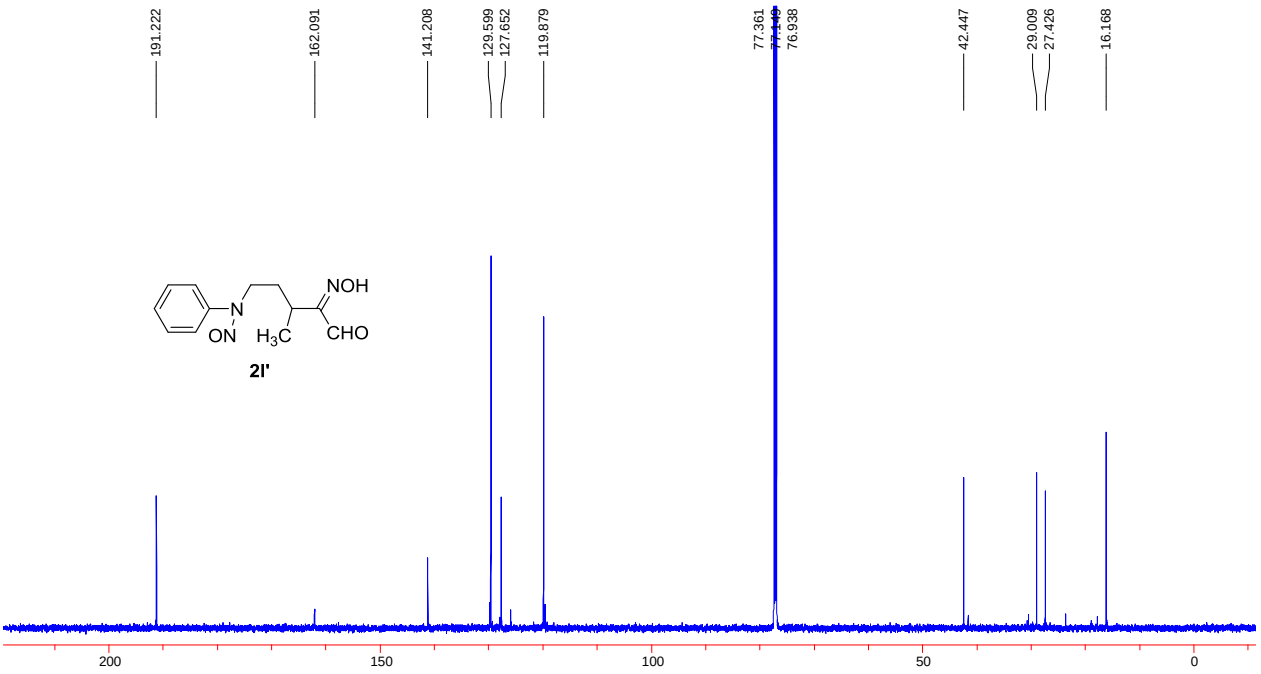
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CHO
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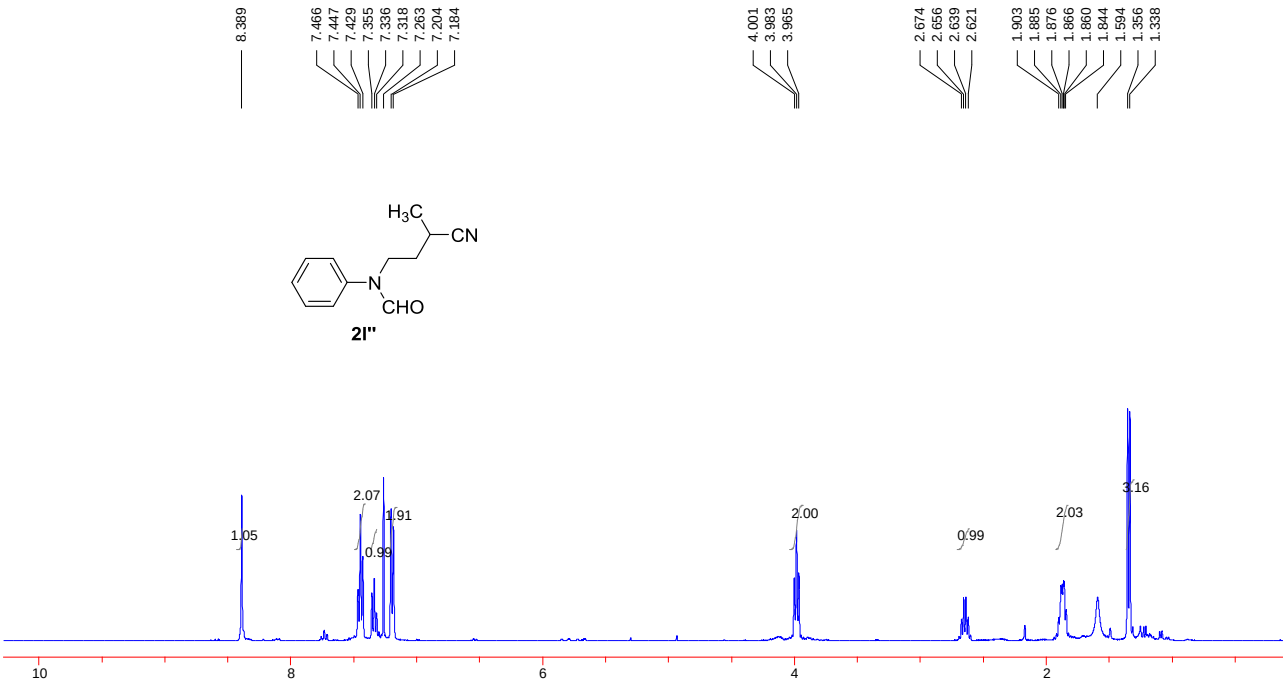
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3.965
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2.656
2.639
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1.876
1.866
1.860
1.844
1.594
1.356
1.338
H3C
CN
N
CHO
2l''
1.05
2.07
1.91
0.99
2.00
0.99
2.03
3.16
10
8
6
4
2


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7.185
7.178
7.173
7.168
7.162
7.157
7.150
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7.131
7.124
7.119
7.111
7.094
7.088
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3.679
3.672
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3.658
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2.018
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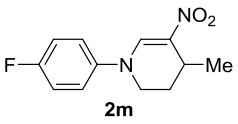
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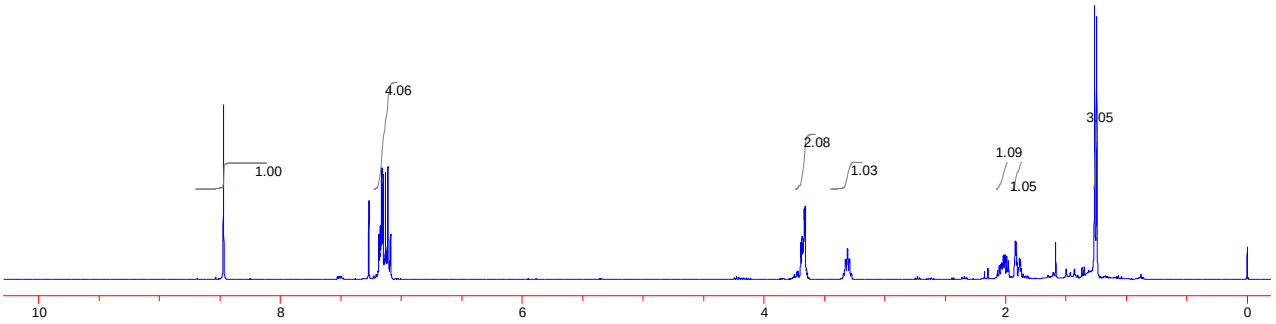
Me

2m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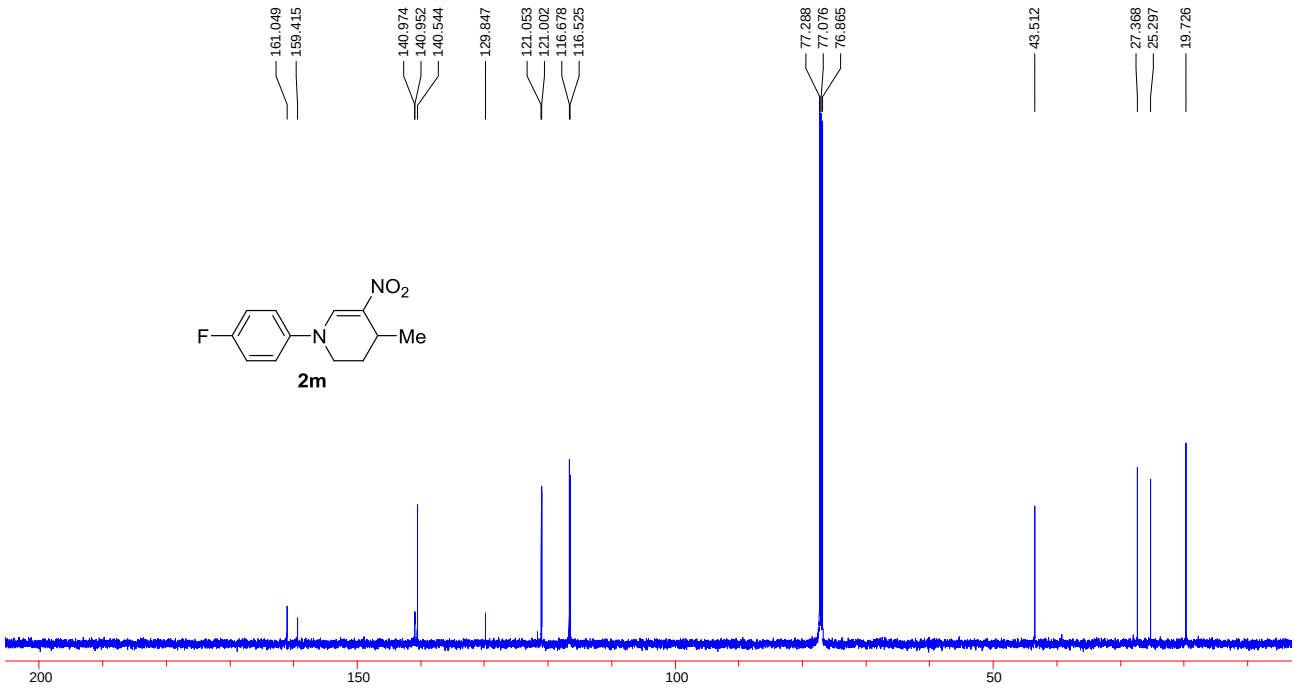
1.03
1.05
10
8
6
4
2
0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121.002
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116.525
77.288
77.076
76.865
43.512
27.368
25.297
19.726
NO2
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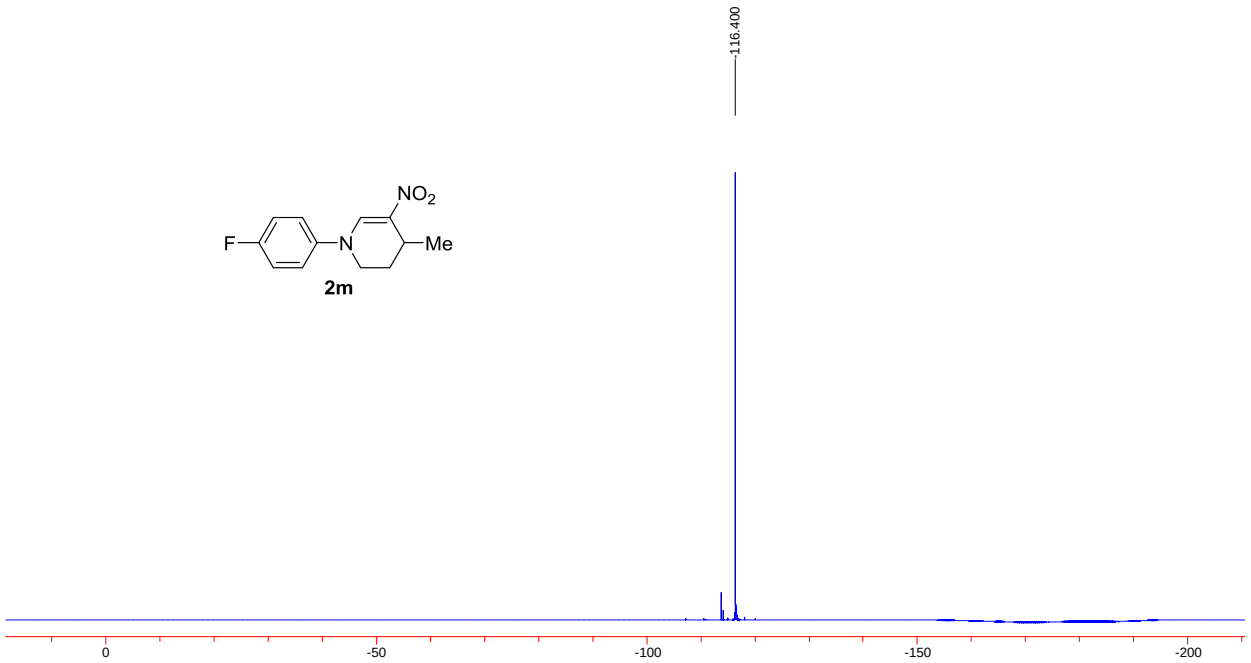
N
Me
2m
200
150
100
50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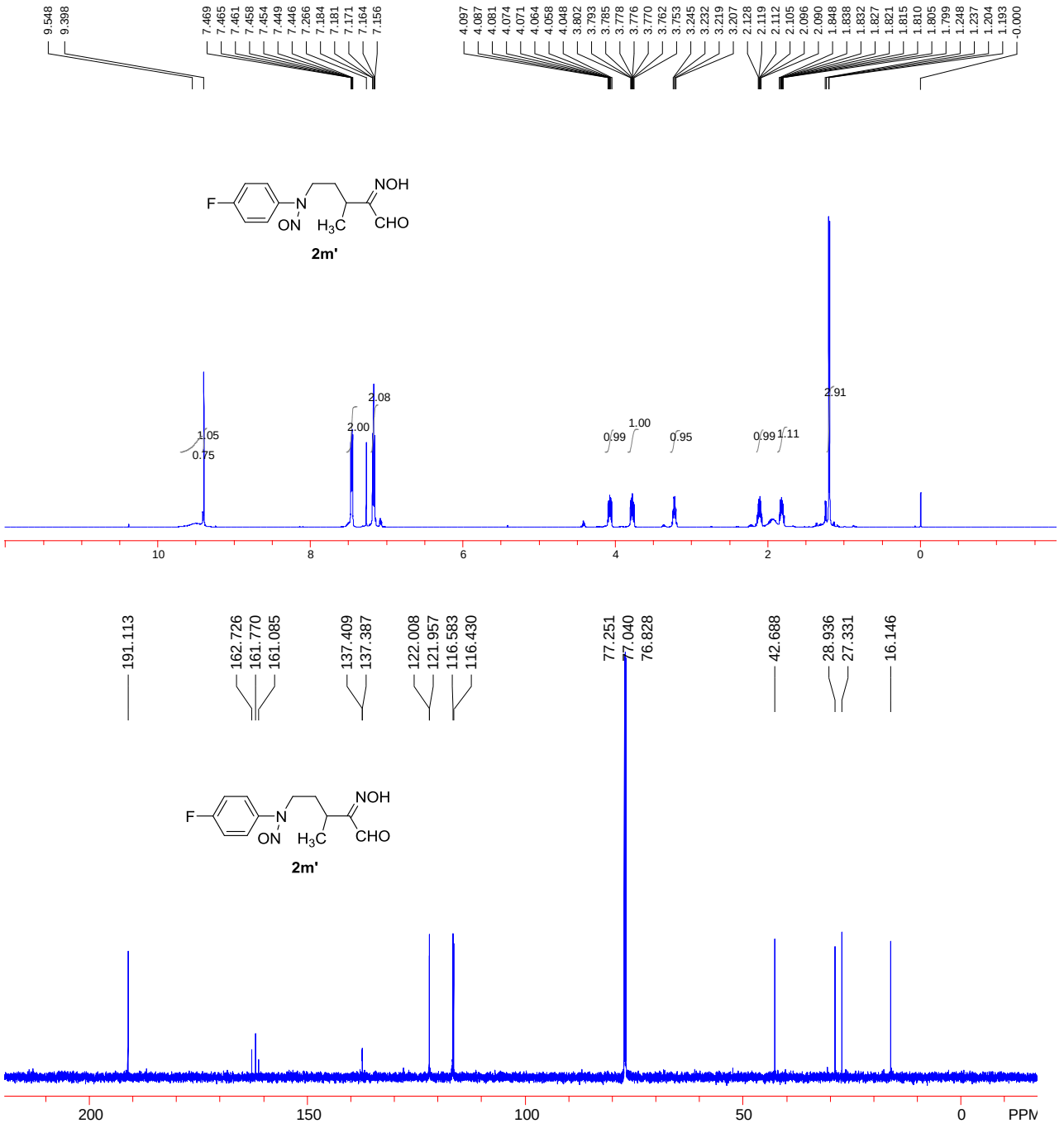
-150
-200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7.449
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7.266
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7.181
7.171
7.164
7.156
4.097
4.087
4.081
4.074
4.071
4.064
4.058
4.048
3.802
3.793
3.785
3.778
3.776
3.770
3.762
3.753
3.245
3.232
3.219
3.207
2.128
2.119
2.112
2.105
2.096
2.090
1.848
1.838
1.832
1.827
1.821
1.815
1.810
1.805
1.799
1.248
1.237
1.204
1.193
-0.000
F
N
ON
H3C
NOH
CHO
2m'
1.05
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2.08
2.00
0.99
1.00
0.95
0.99
1.11
2.91
10
8
6
4
2
0
191.113
162.726
161.770
161.085
137.409
137.387
122.008
121.957
116.583
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77.251
77.040
76.828
42.688
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F
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H3C
NOH
CHO
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100
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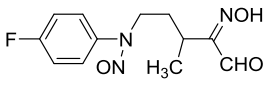
0
PPM



2m'


8.508
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7.339
7.320
7.318
7.263
7.193
7.187
7.184
7.167
7.165
7.163
7.161
7.095
7.092
7.090
7.087
7.074
7.073
7.068
7.067
3.693
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3.658
3.650
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3.320
3.307
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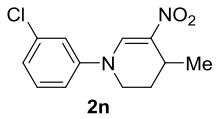
1.249


Cl
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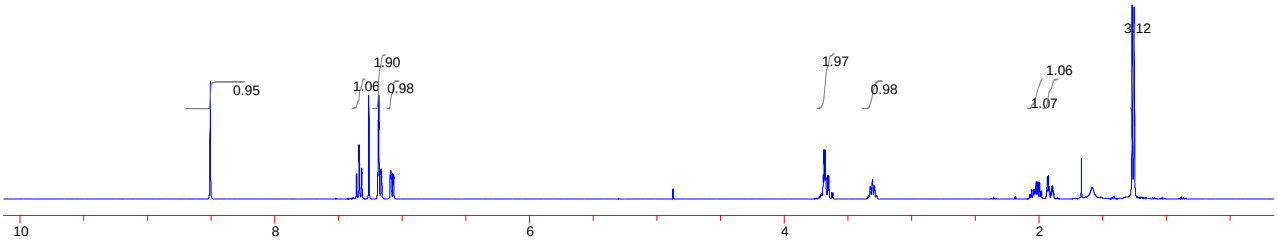
N
Me

2n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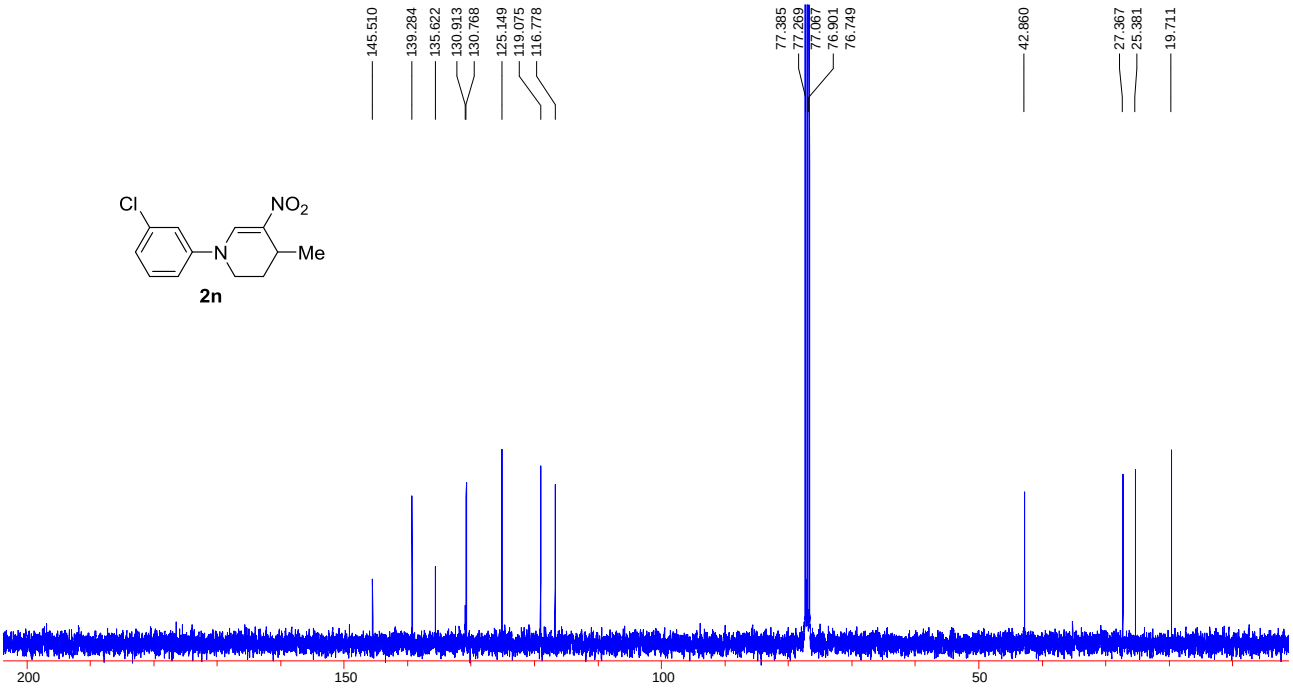
4
2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125.149
119.075
116.778
77.385
77.269
77.067
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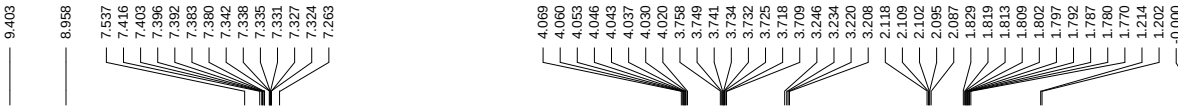
76.749
42.860
27.367
25.381
19.711
200
150
100
50

Cl
NO2
N
Me

2n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7.331
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7.324
7.263
4.069
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4.043
4.037
4.030
4.020
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3.741
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3.718
3.709
3.246
3.234
3.220
3.208
2.118
2.109
2.102
2.095
2.087
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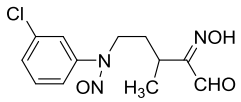
1.202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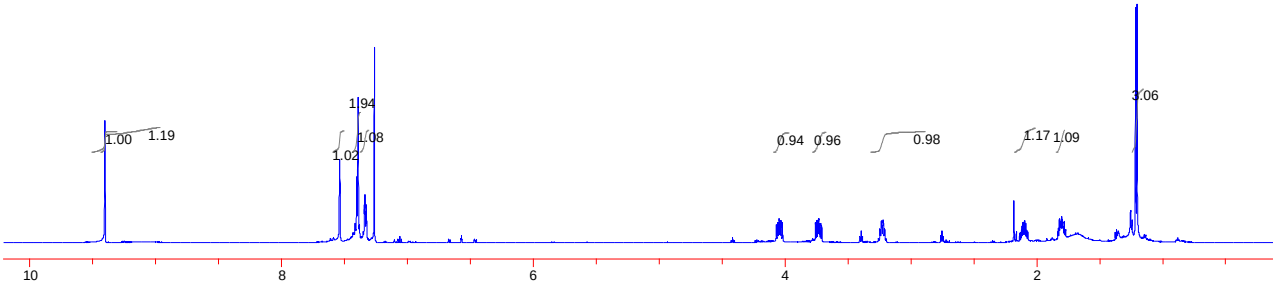
ON
H3C
NOH
CHO

2n'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0.98
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1.09
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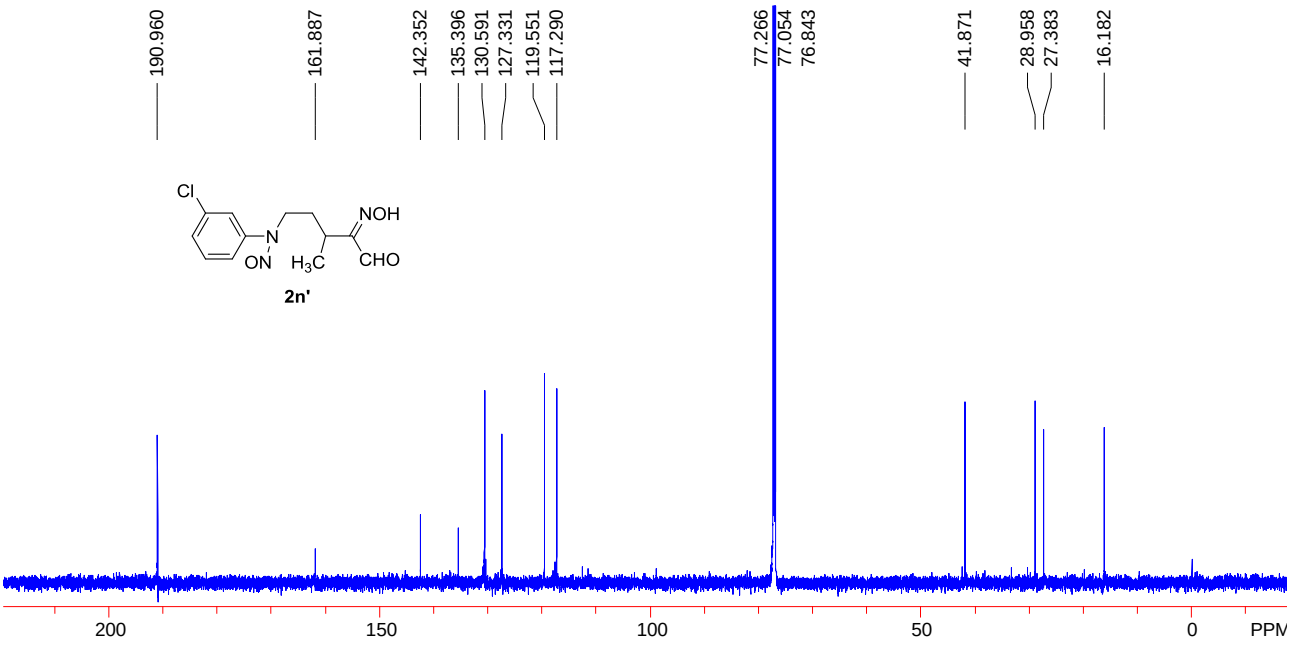
10
8
6
4
2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50
0
PPM

Cl
N
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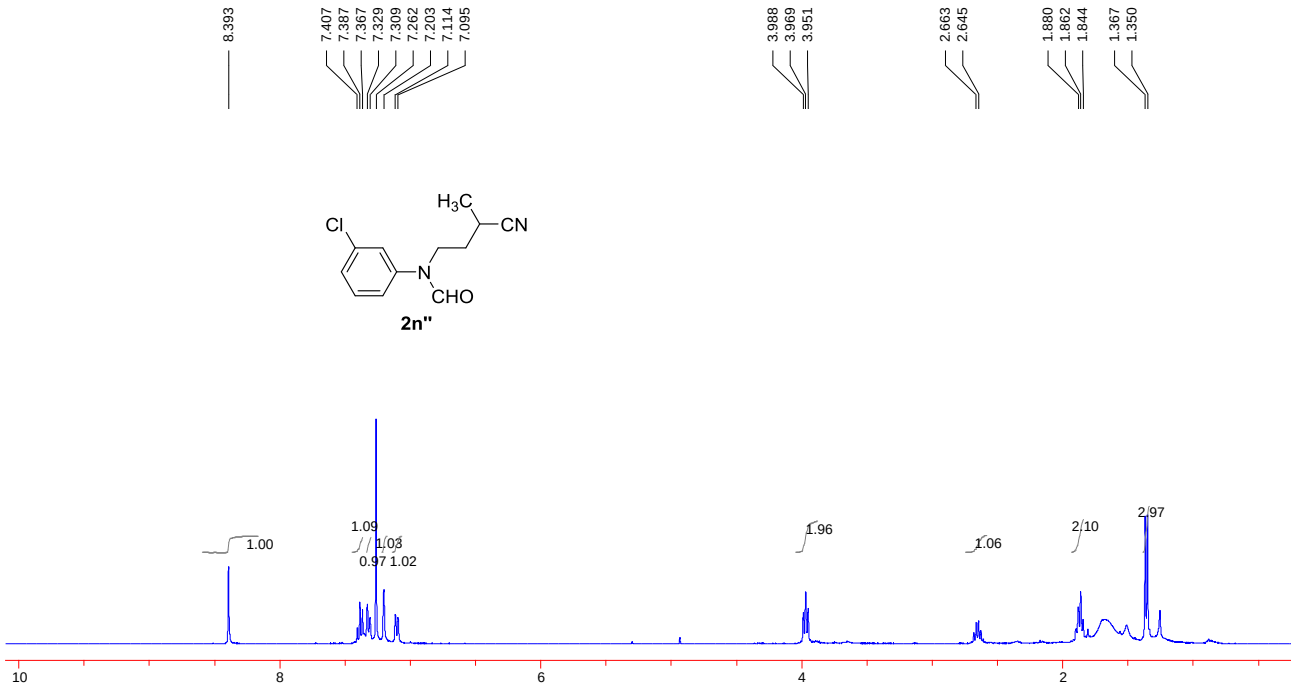
H3C
NOH
CHO

2n'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7.262
7.203
7.114
7.095
3.988
3.969
3.951
2.663
2.645
1.880
1.862
1.844
1.367
1.350
H3C
CN
Cl
N
CHO
2n''
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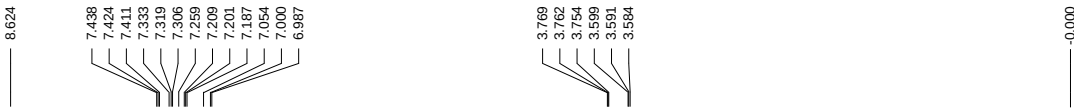
1.03
0.97 1.02
1.96
1.06
2.10
2.97
10
8
6
4
2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7.259
7.209
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3.599
3.591
3.584
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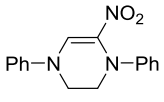
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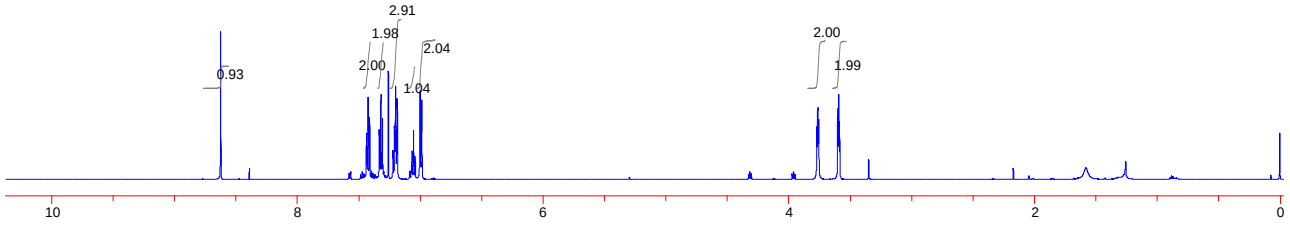
N–Ph

2o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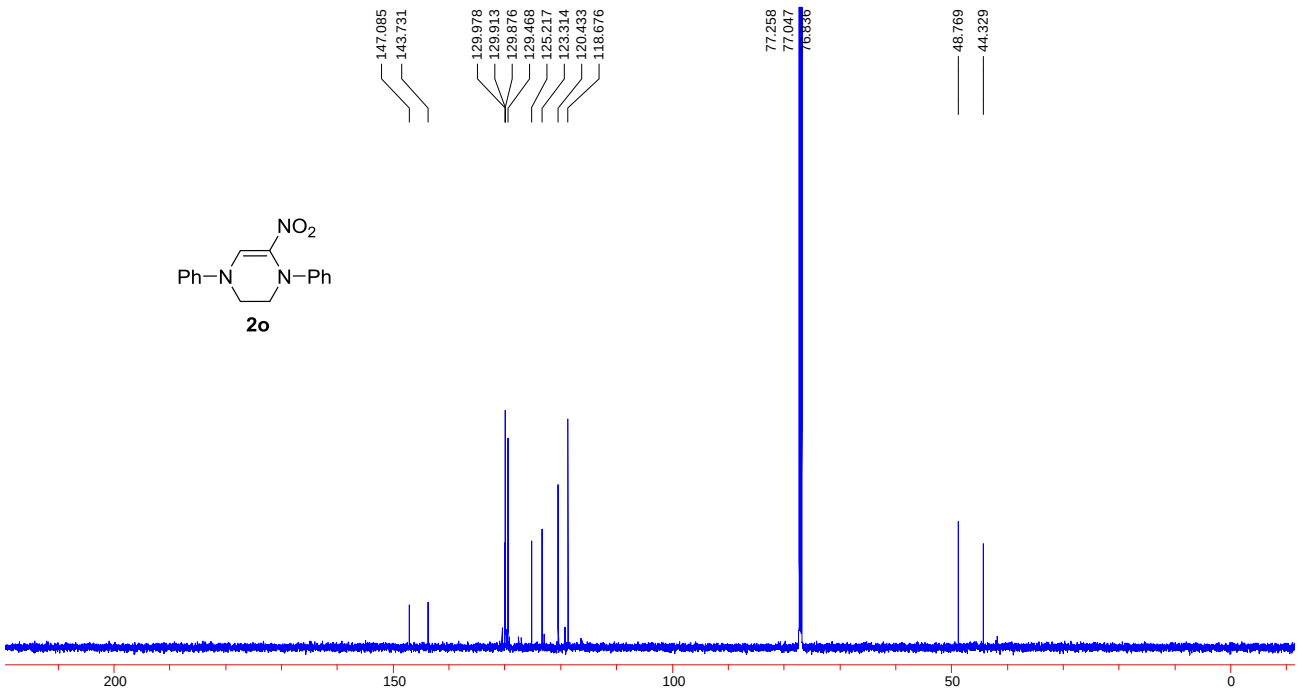
1.04
2.00
1.99
10
8
6
4
2
0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129.913
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125.217
123.314
120.433
118.676
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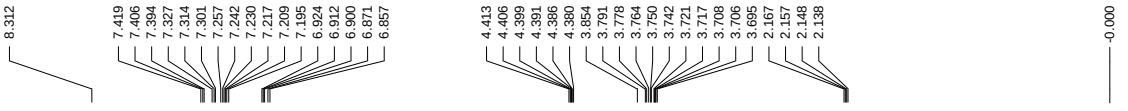
77.047
76.836
48.769
44.329
200
150
100
50
0

NO2
Ph–N
N–Ph

2o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7.314
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7.242
7.230
7.217
7.209
7.195
6.924
6.912
6.900
6.871
6.857
4.413
4.406
4.399
4.391
4.386
4.380
3.854
3.791
3.778
3.764
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2.138
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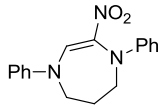
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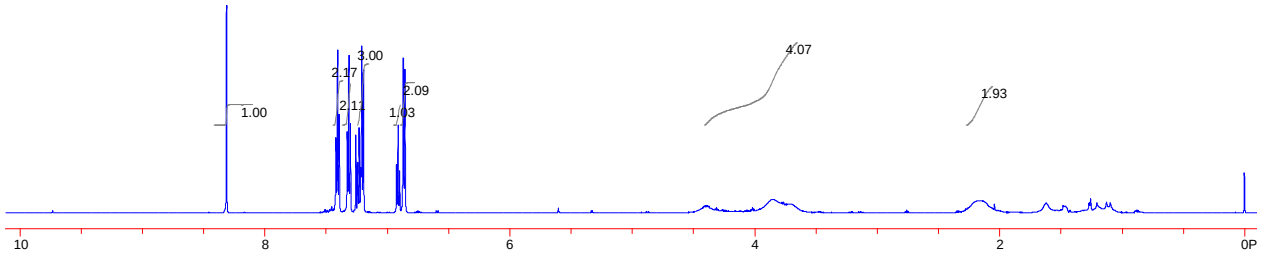
Ph
N
Ph
N

2p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1.03
2.09
4.07
1.93
10
8
6
4
2
0P


8.216
7.447
7.437
7.310
7.291
7.272
7.263
7.251
7.241
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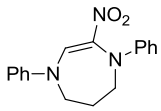
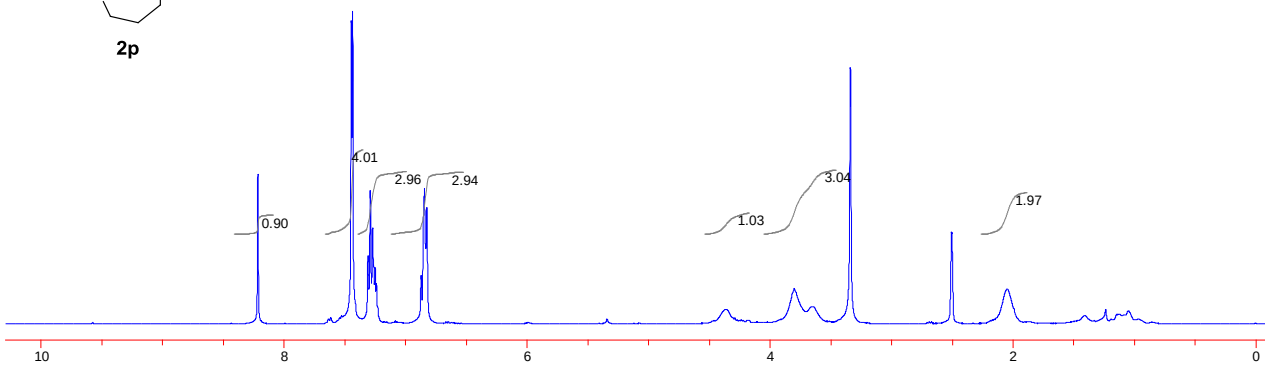
2.046


NO2
Ph
N
Ph
N

2p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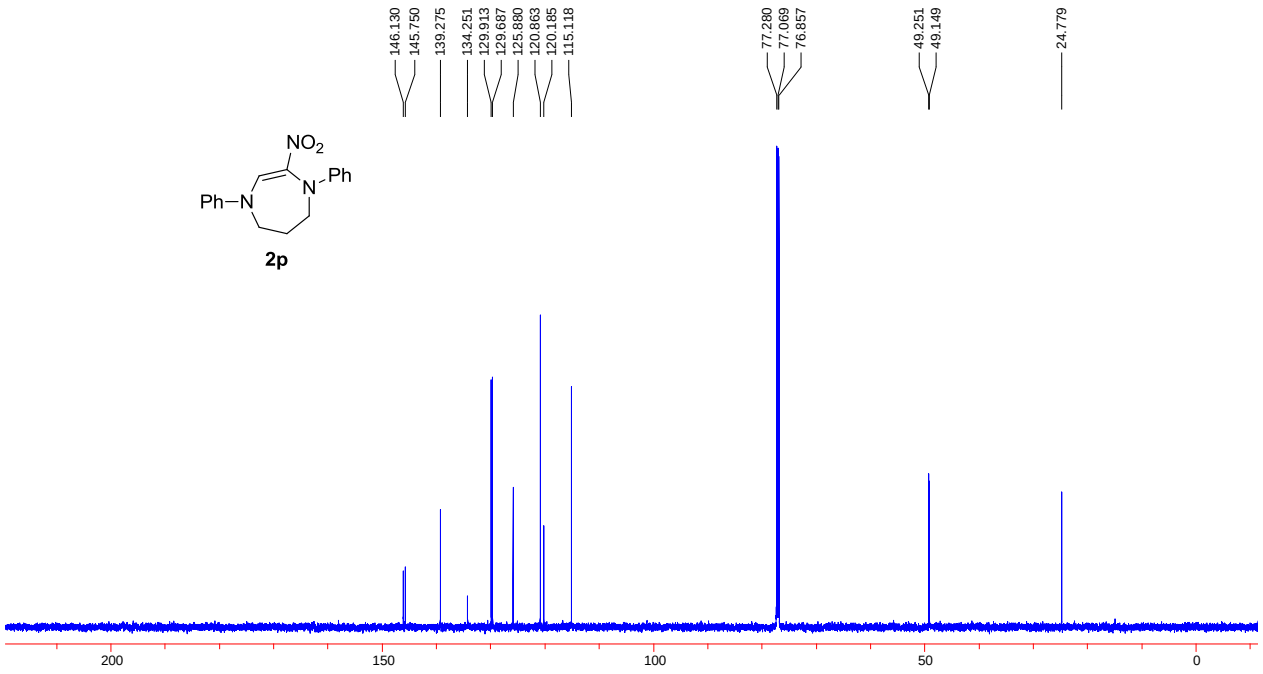
2.94
1.03
3.04
1.97
10
8
6
4
2
0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115.118
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49.149
24.779
NO2
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Ph
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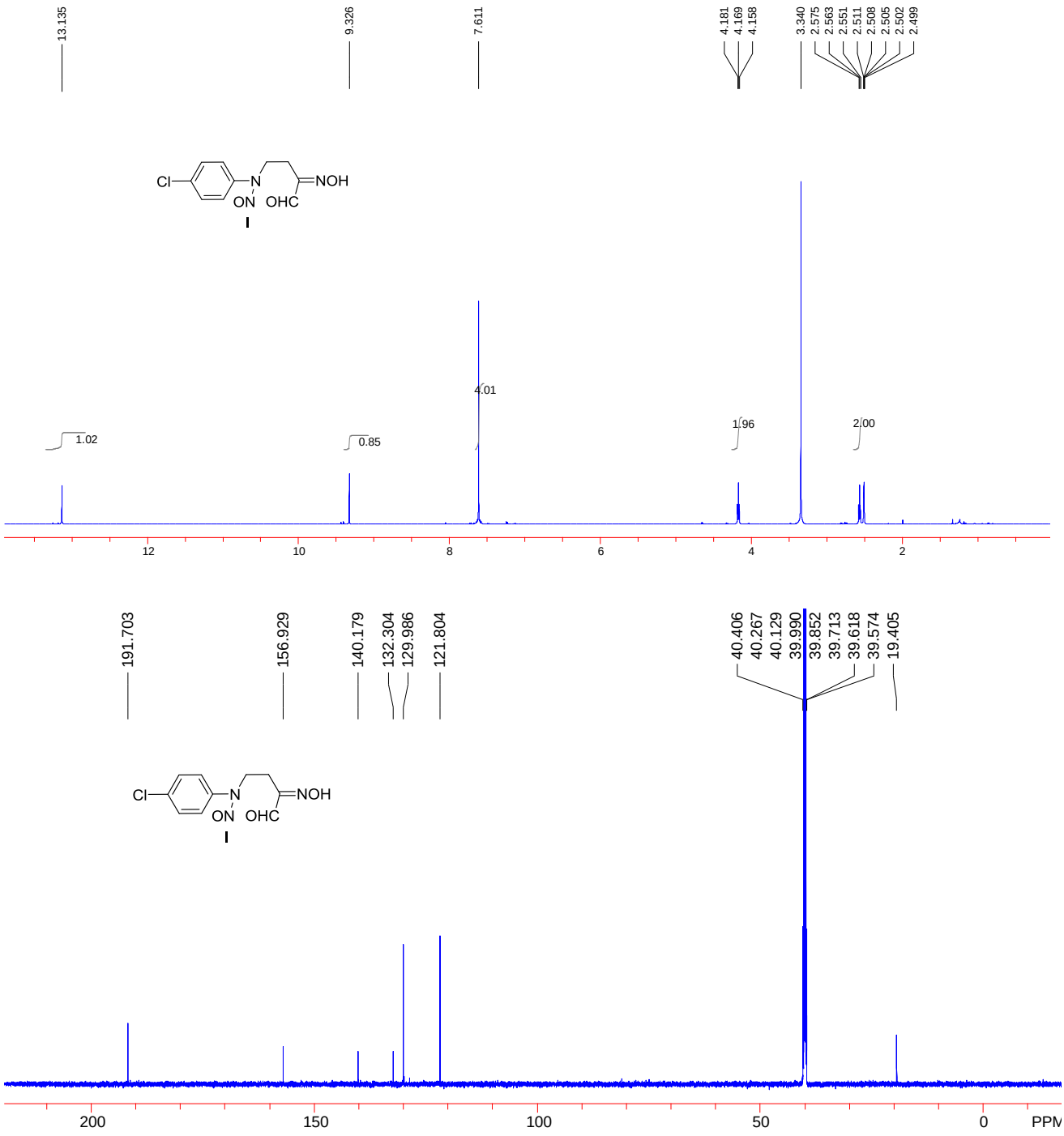
100
50
0

2p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4.158
3.340
2.575
2.563
2.551
2.511
2.508
2.505
2.502
2.499
Cl
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NOH
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OHC
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4.01
1.96
2.00
12
10
8
6
4
2
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156.929
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132.304
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40.406
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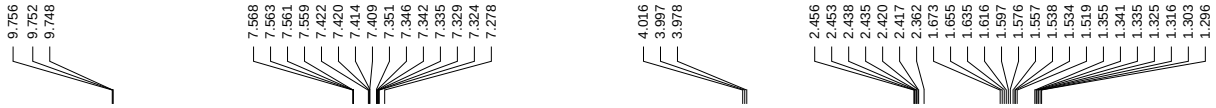
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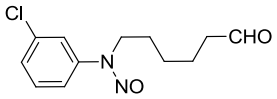
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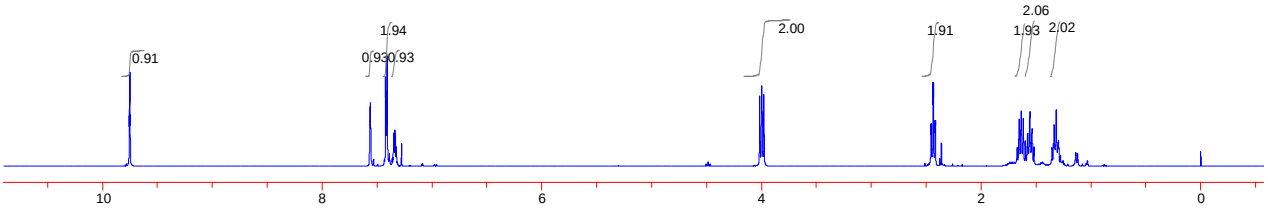
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1.93
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0


202.218
142.535
135.389
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43.563
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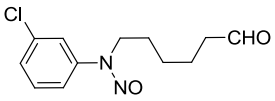
21.403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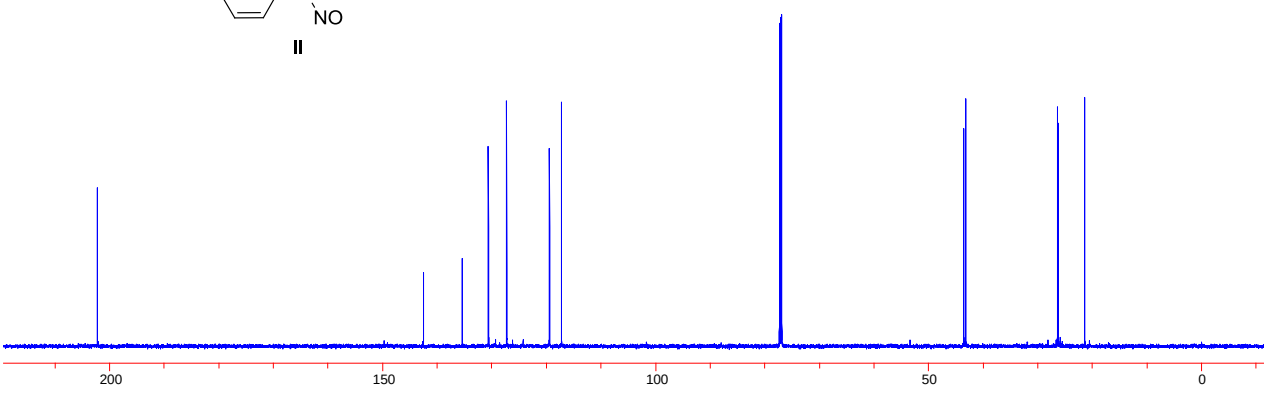
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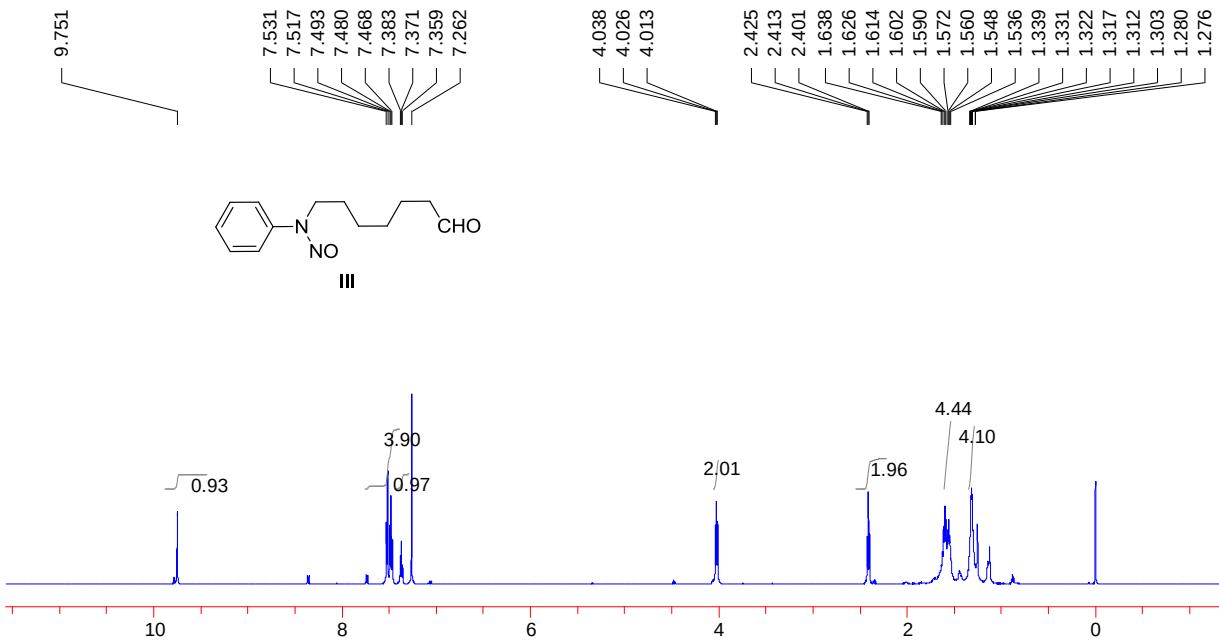
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4.013
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2.401
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1.536
1.339
1.331
1.322
1.317
1.312
1.303
1.280
1.276
N
NO
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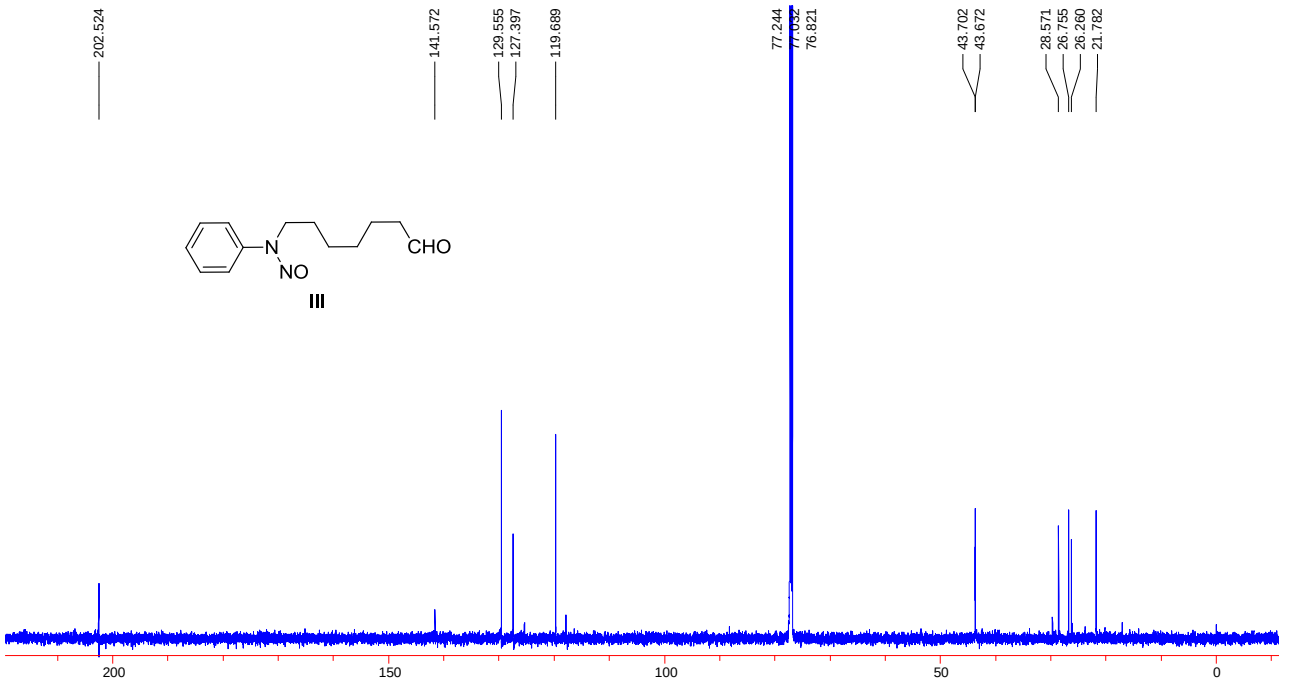
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CHO
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100
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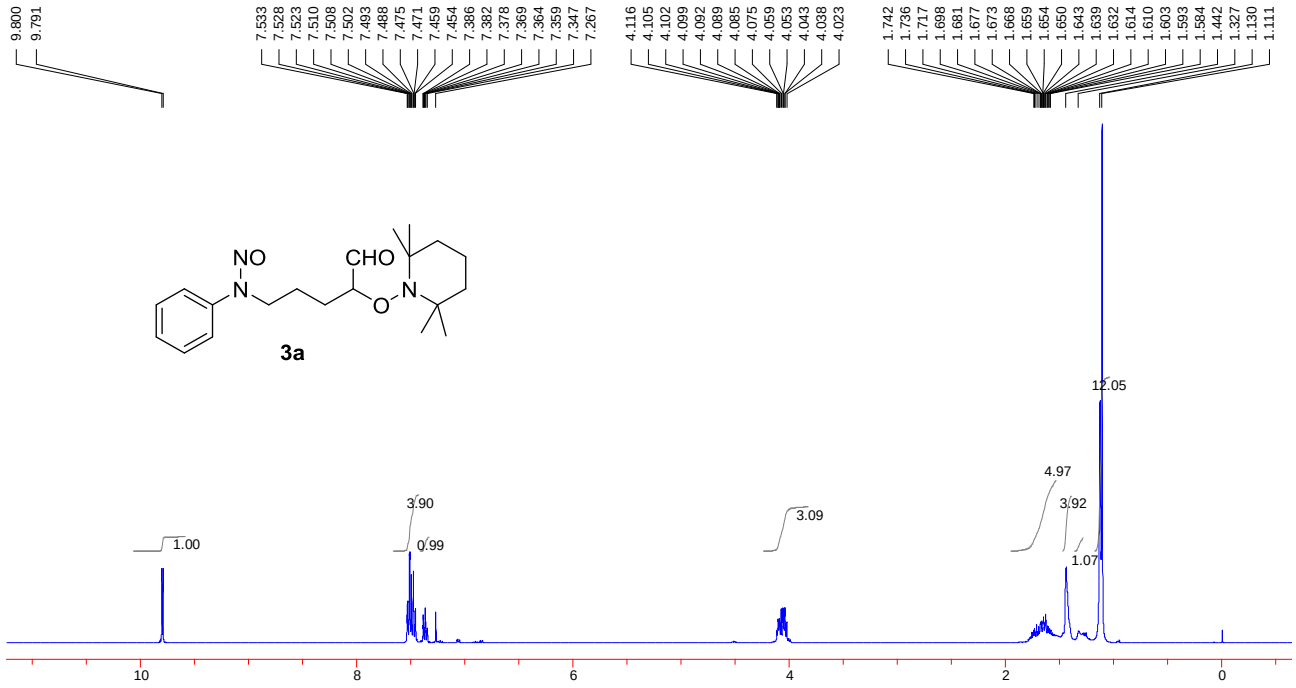
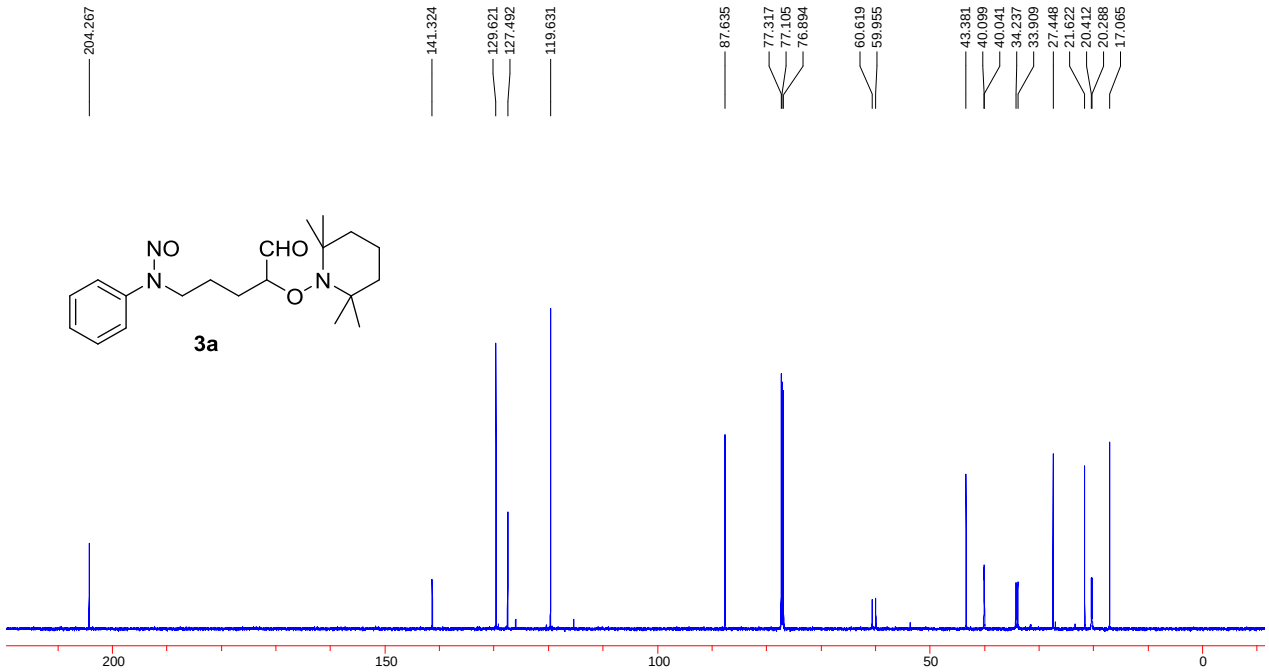
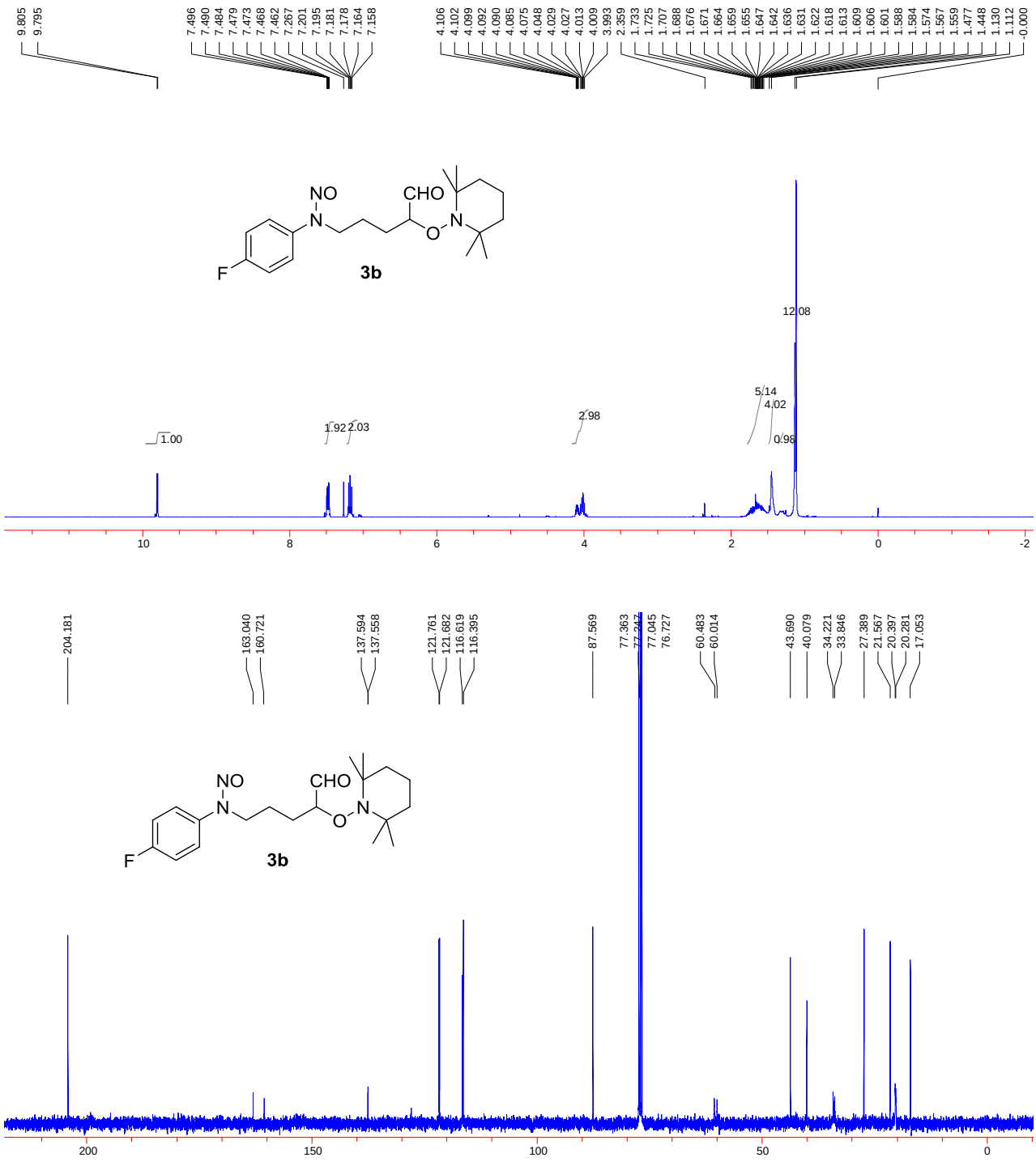
IV. Copies of the NMR spectra of 3a-3t



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7.181
7.178
7.164
7.158
4.106
4.102
4.099
4.092
4.090
4.085
4.075
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4.029
4.027
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1.725
1.707
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1.613
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1.606
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CHO
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O
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F
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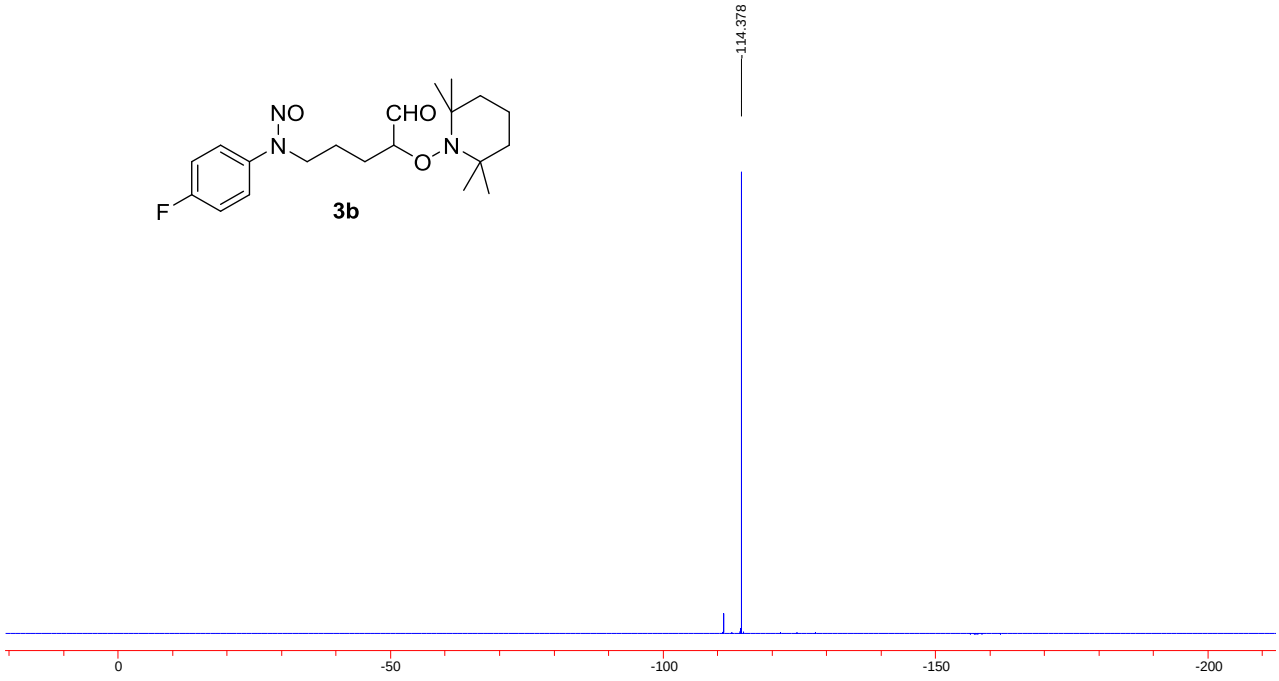
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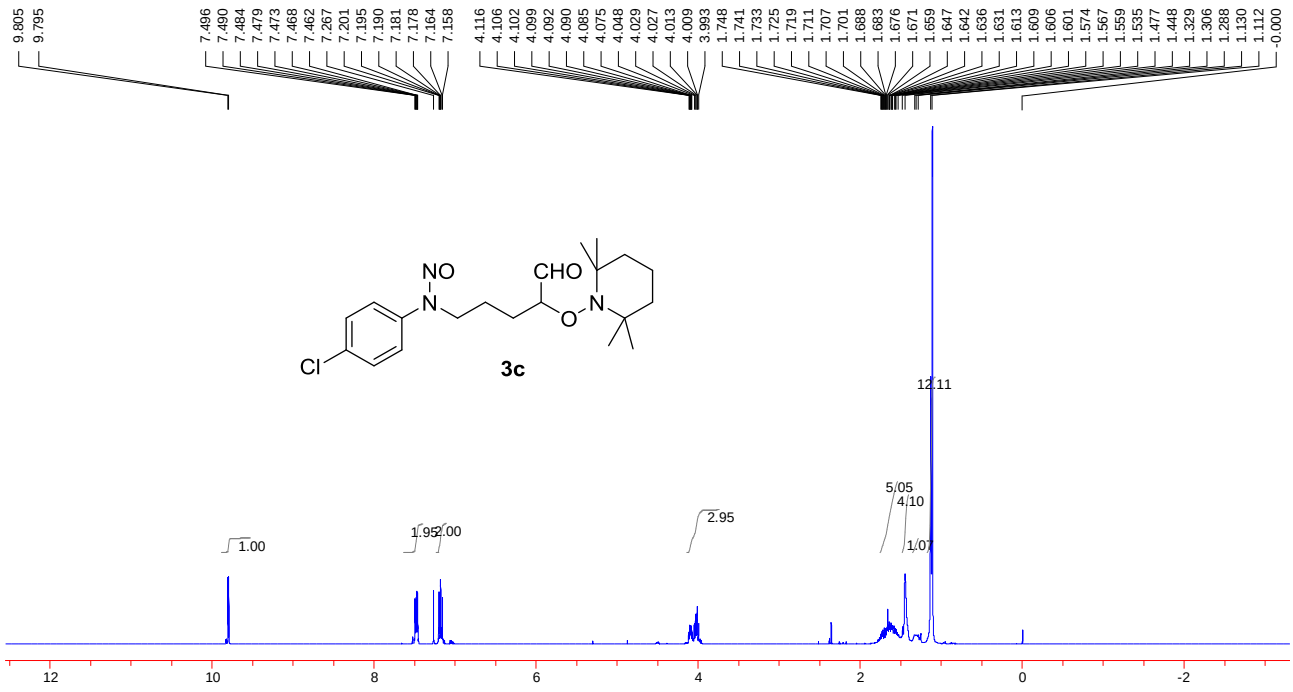
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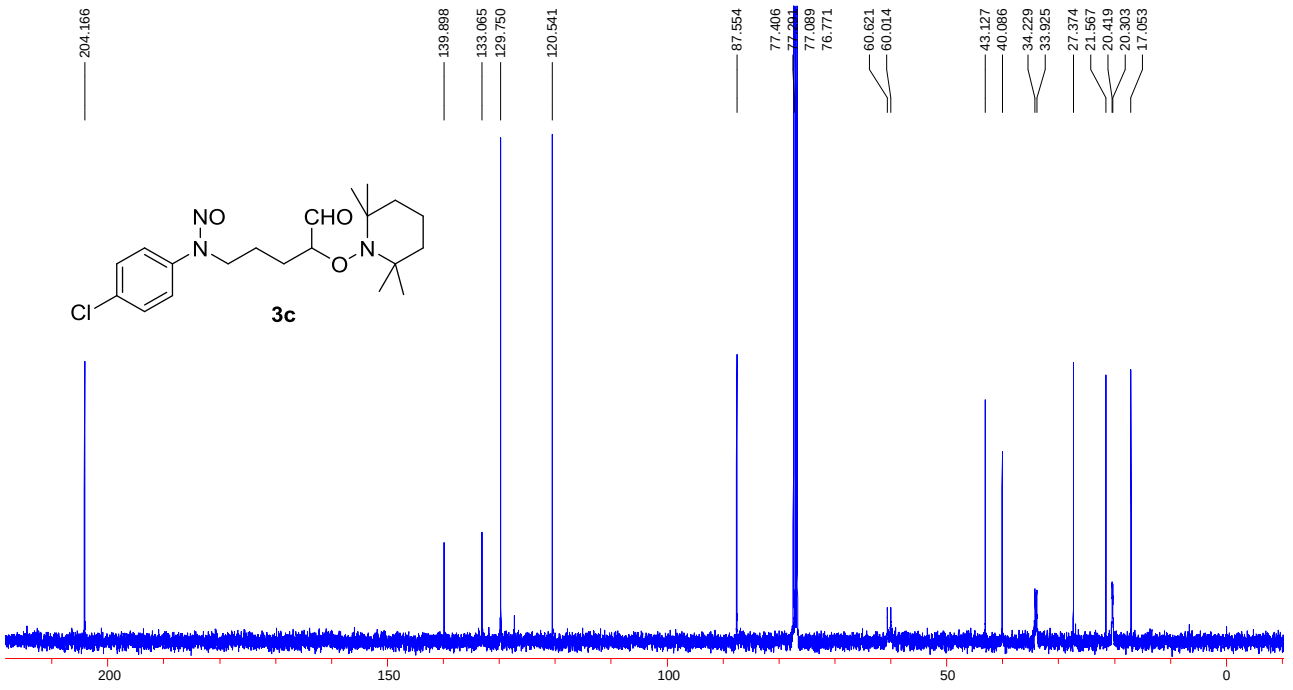
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Cl
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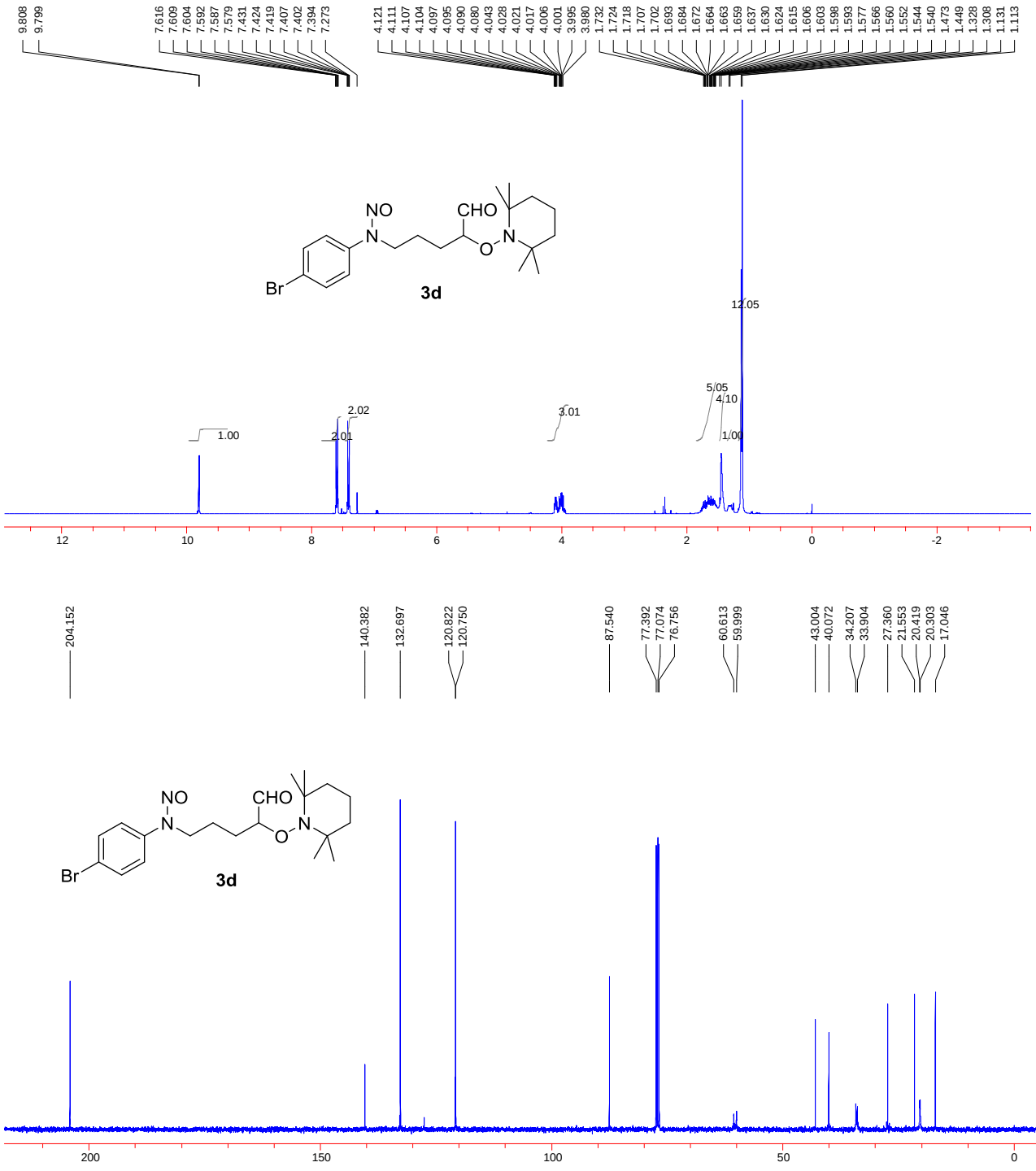
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1.00
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10
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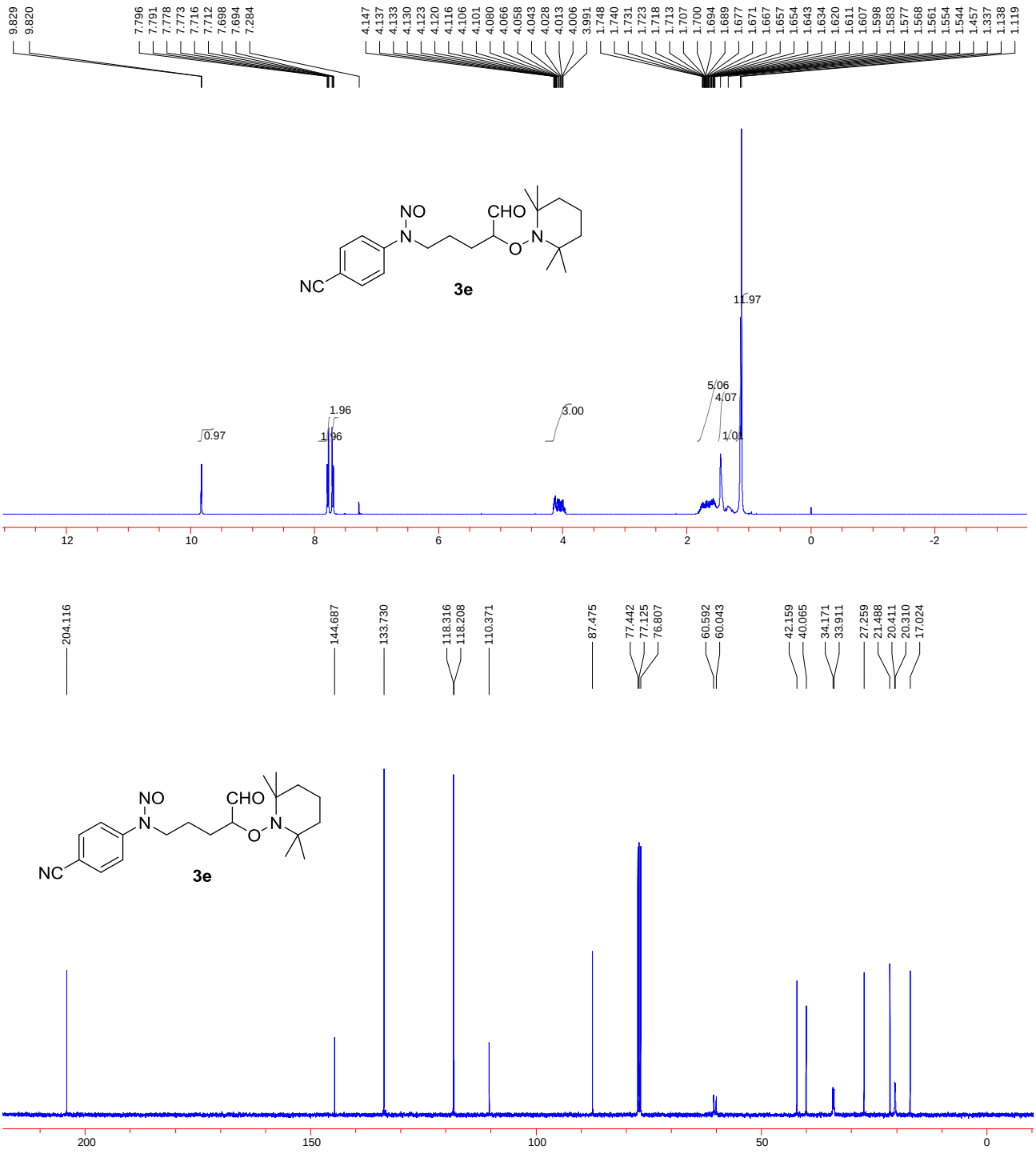
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1.01
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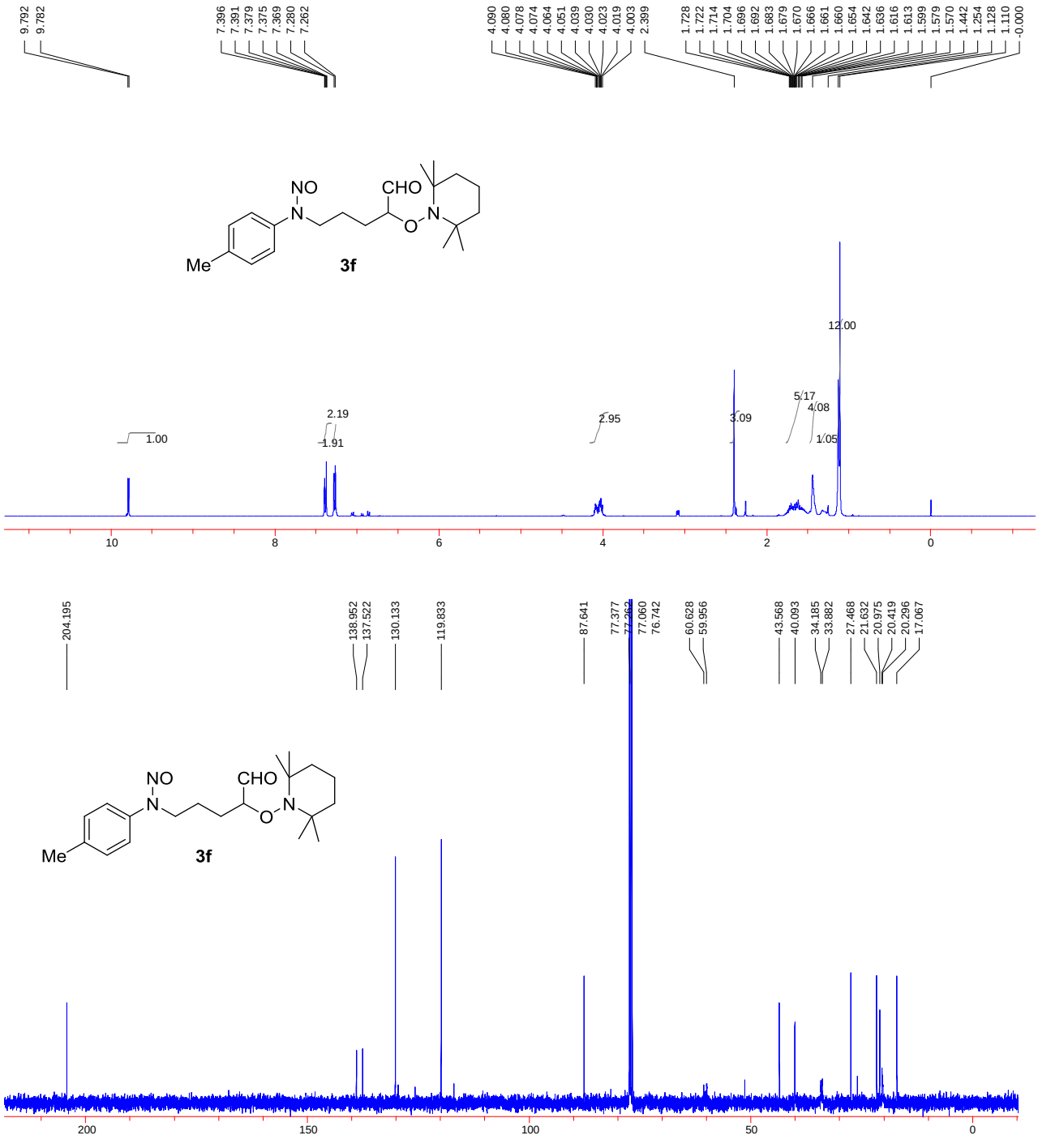
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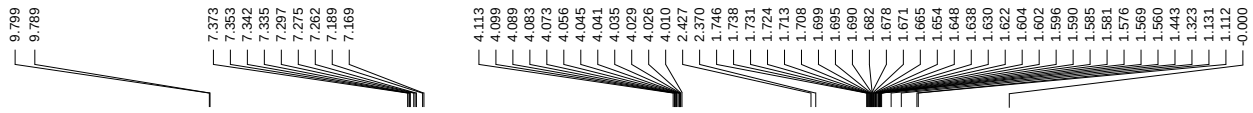
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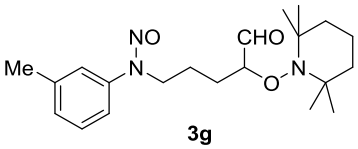
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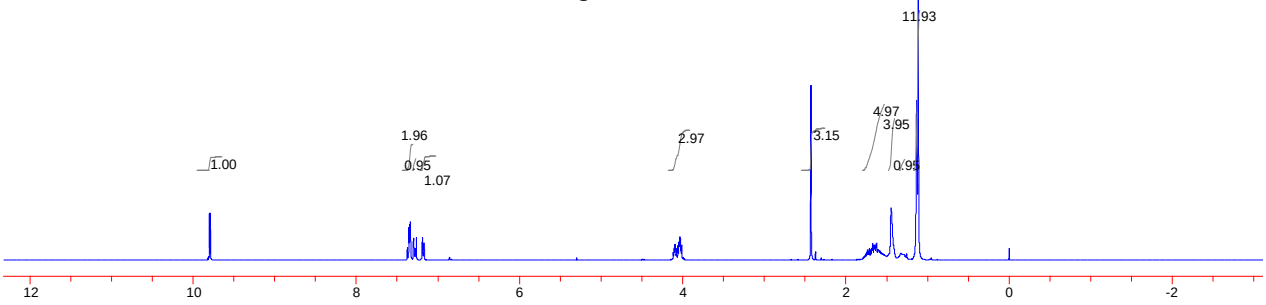
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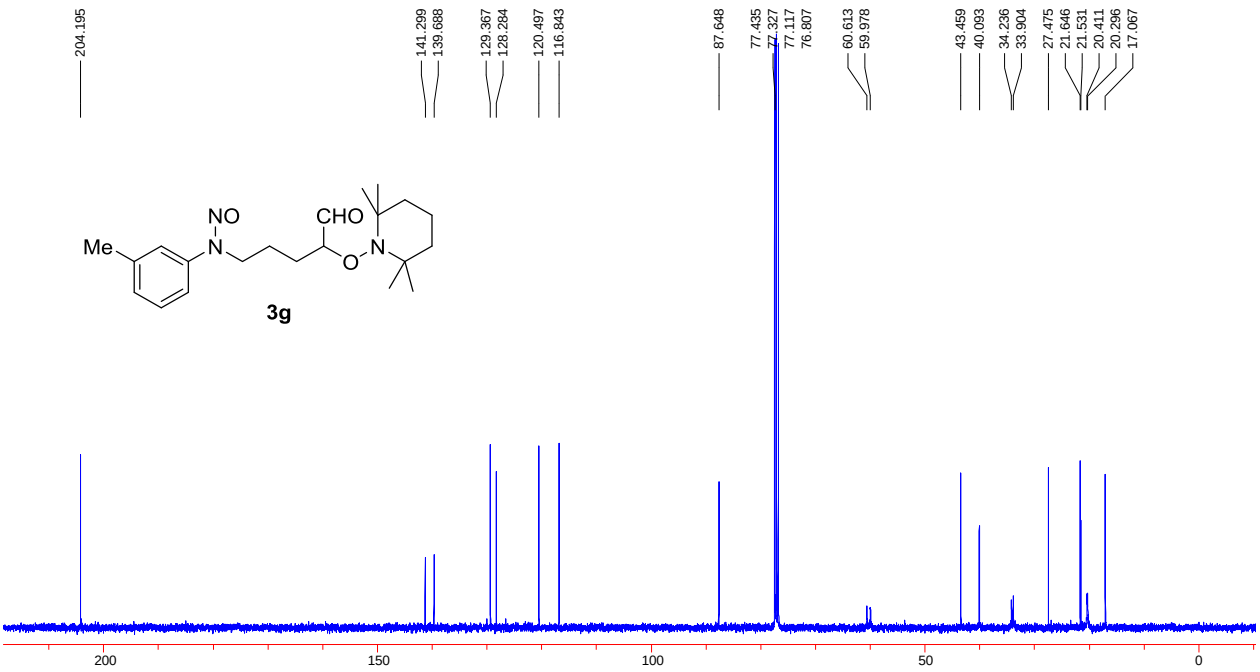
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CHO
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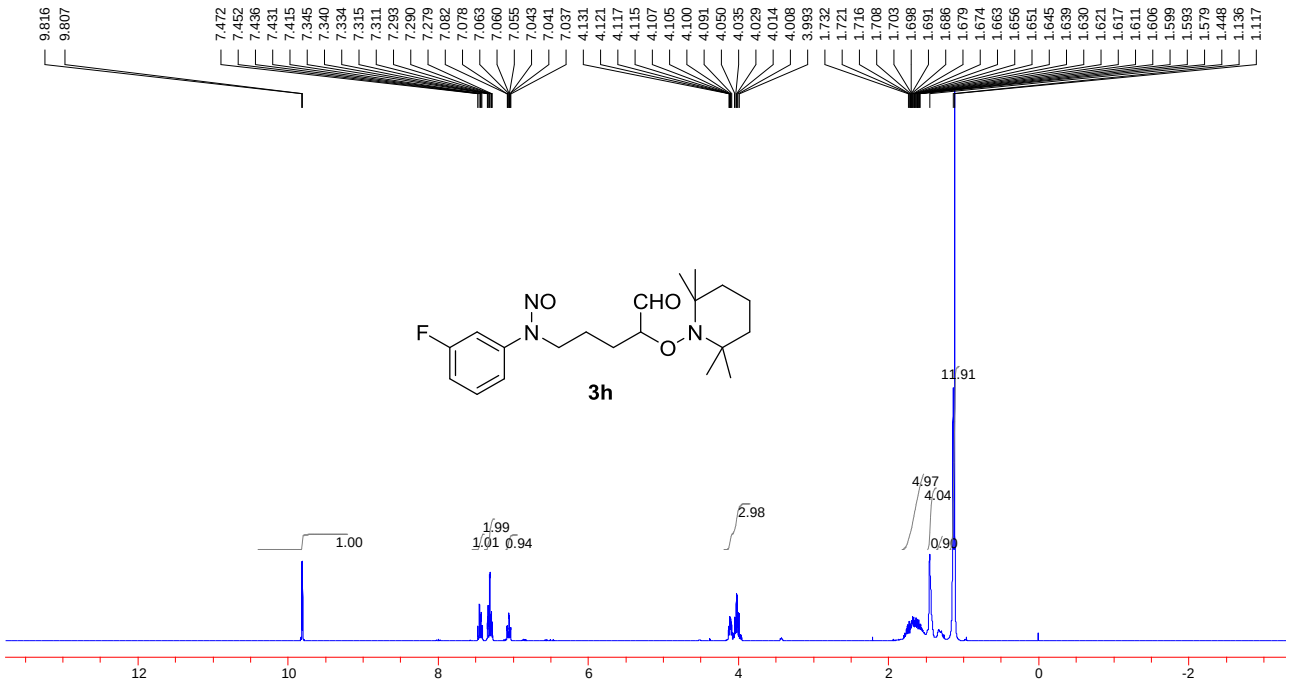
N

3g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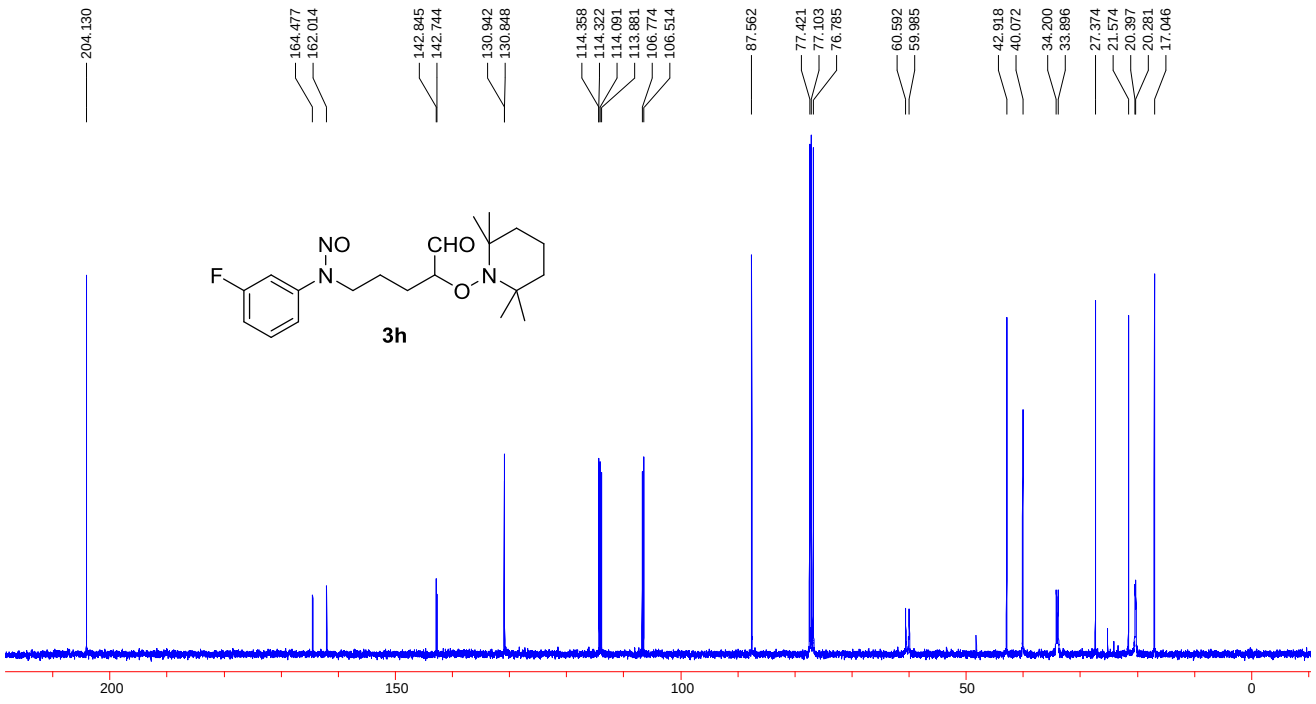
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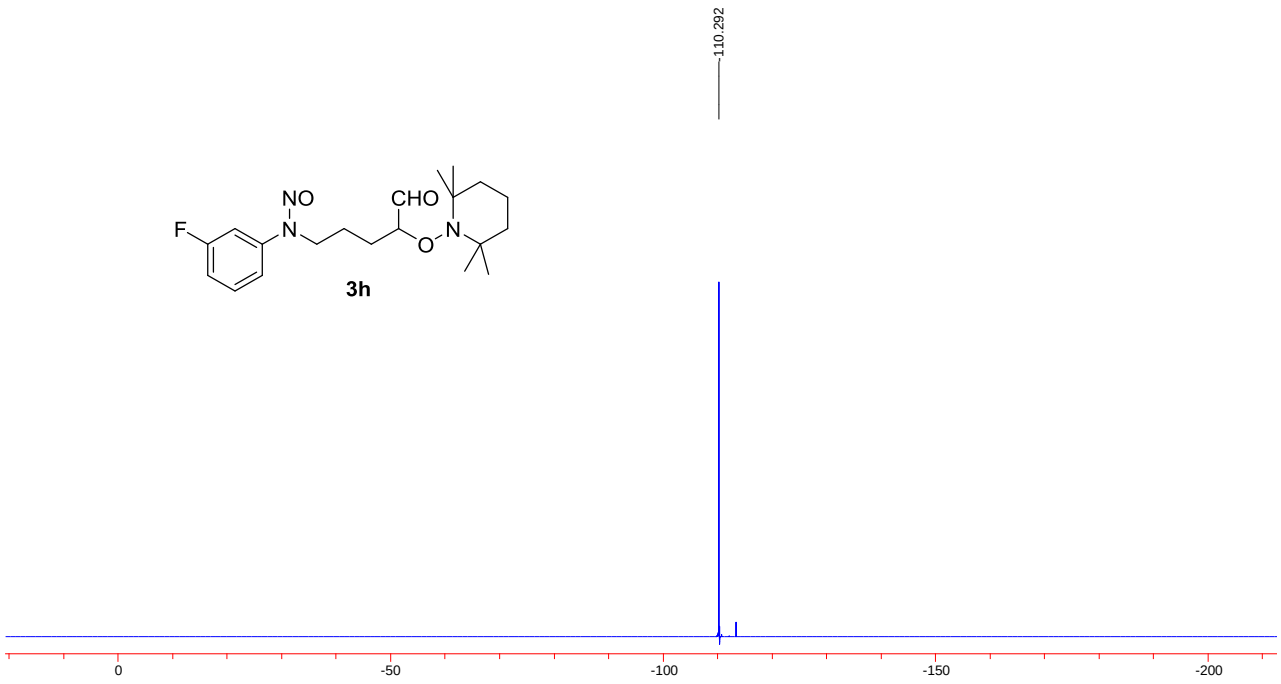

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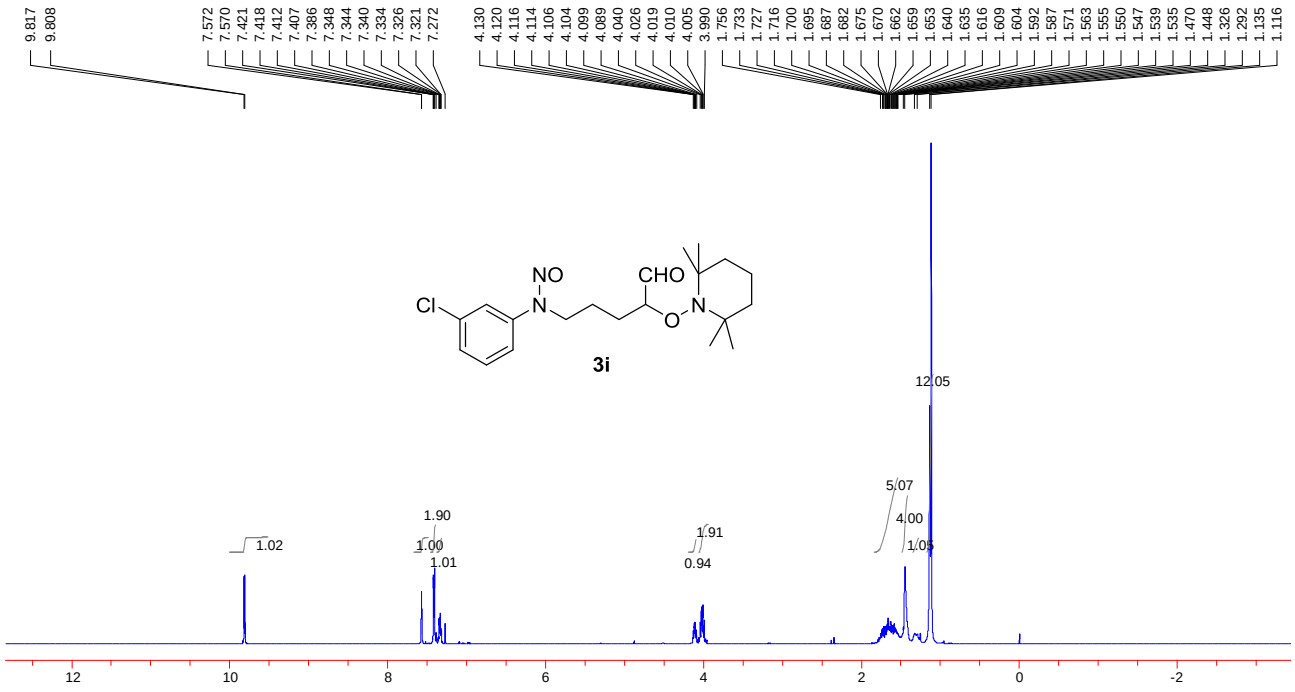
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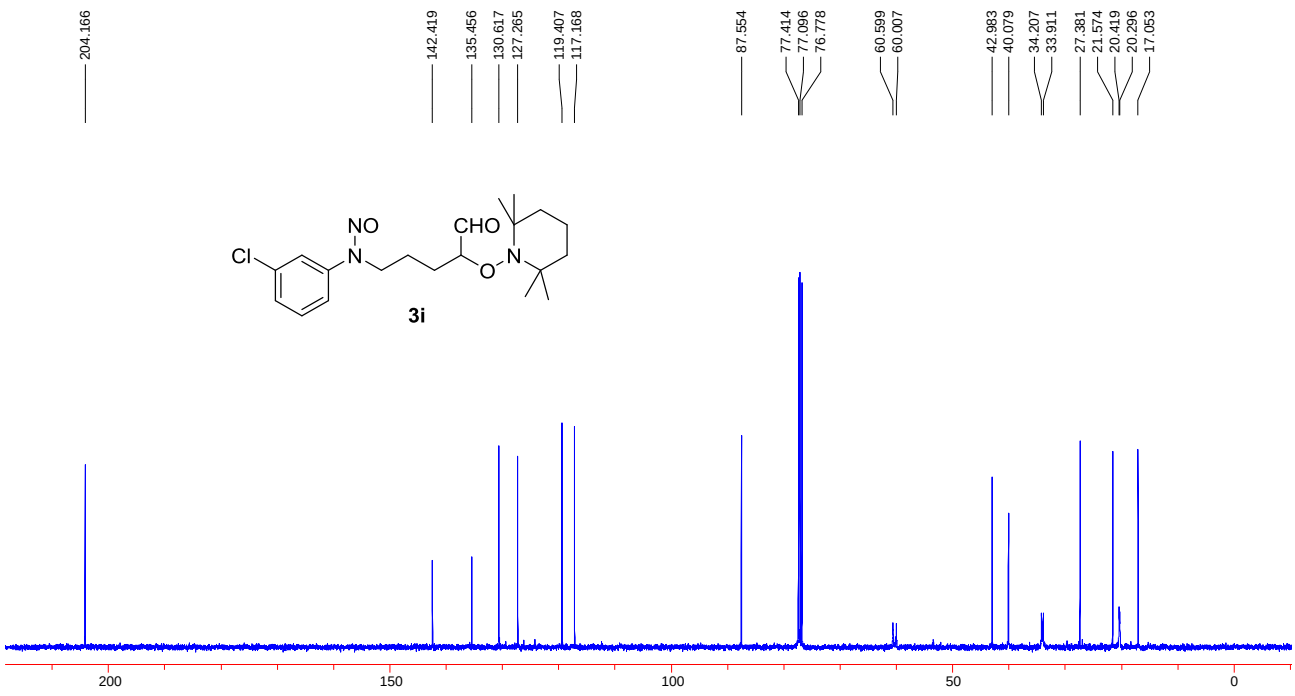
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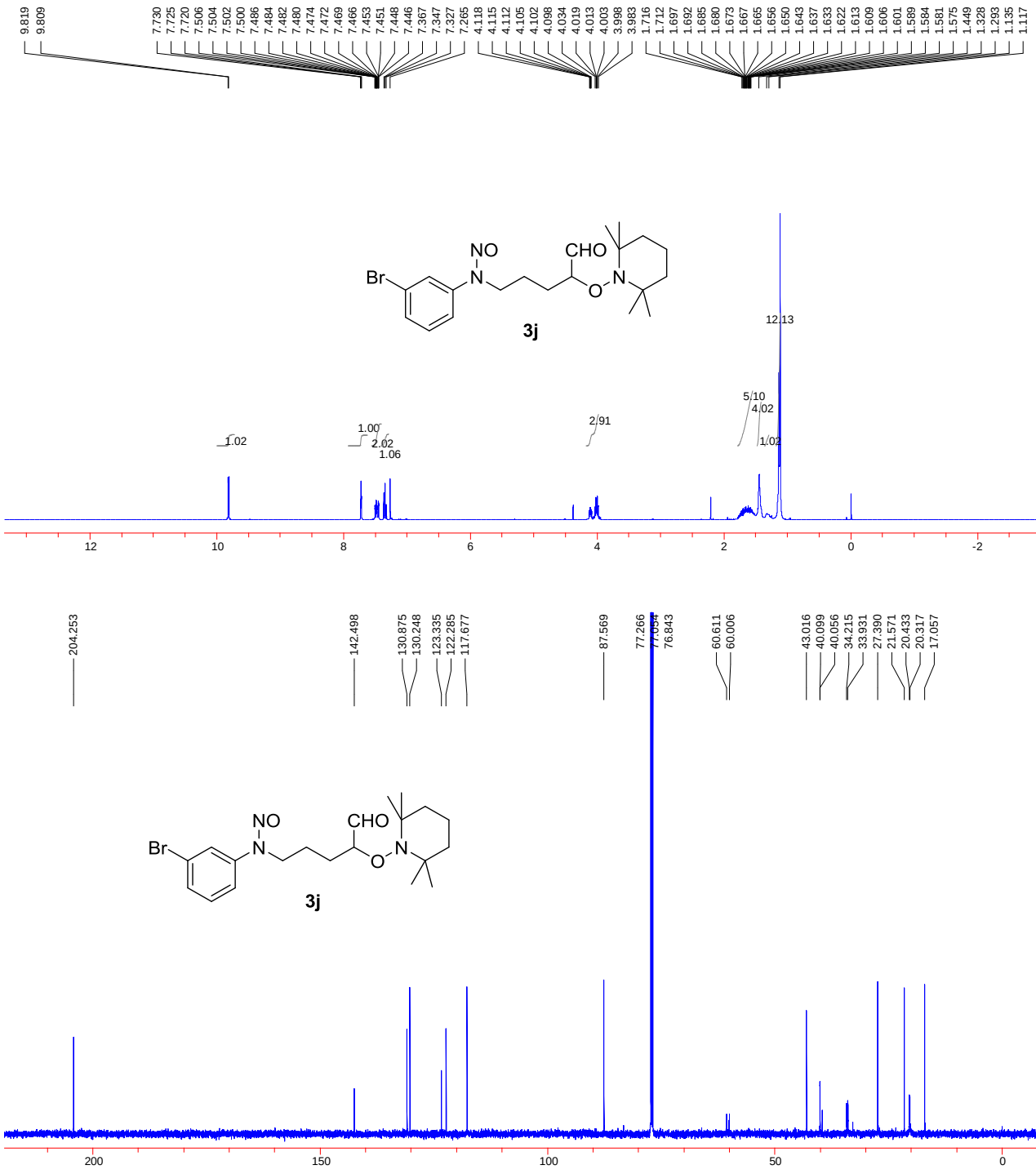
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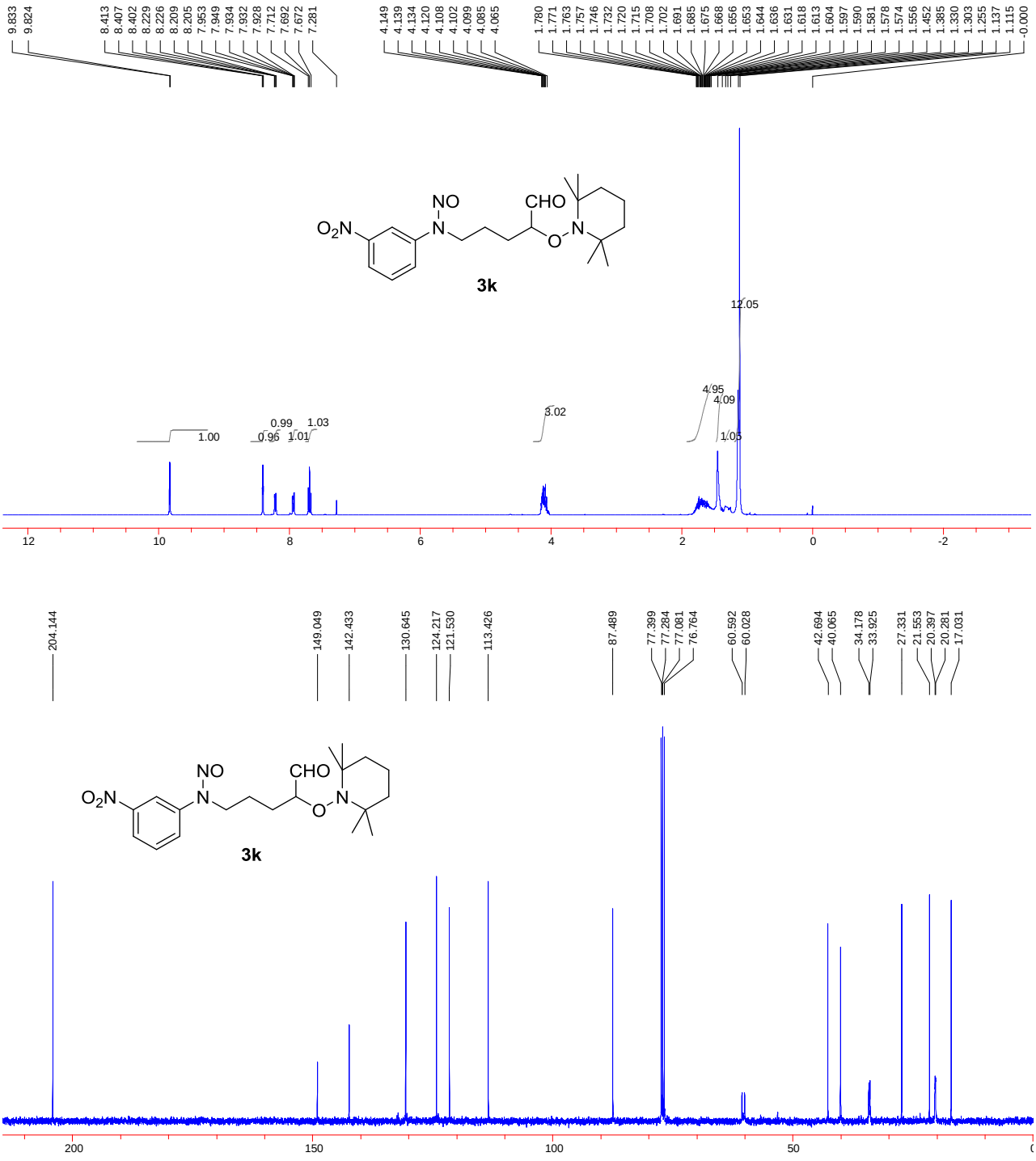
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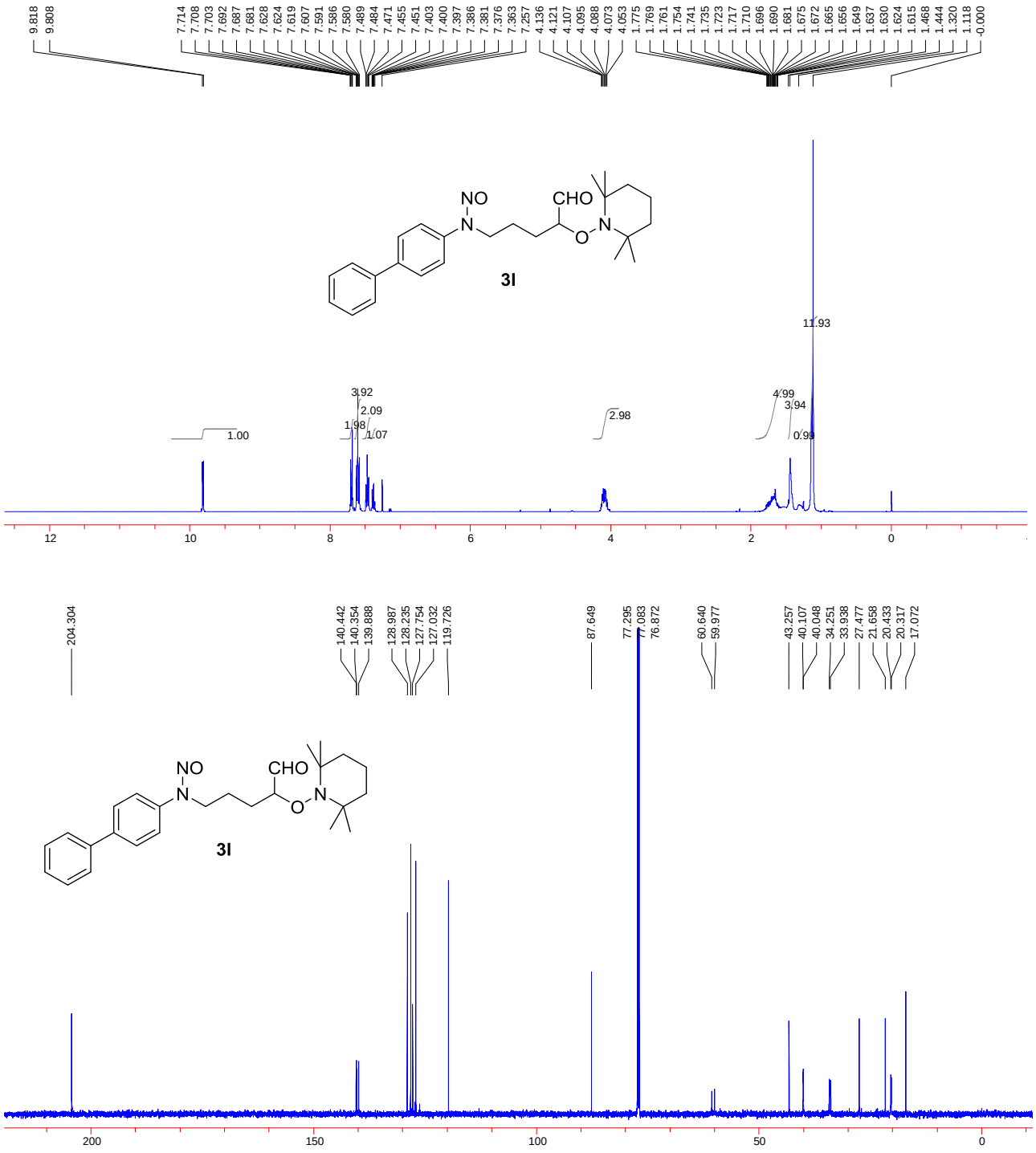
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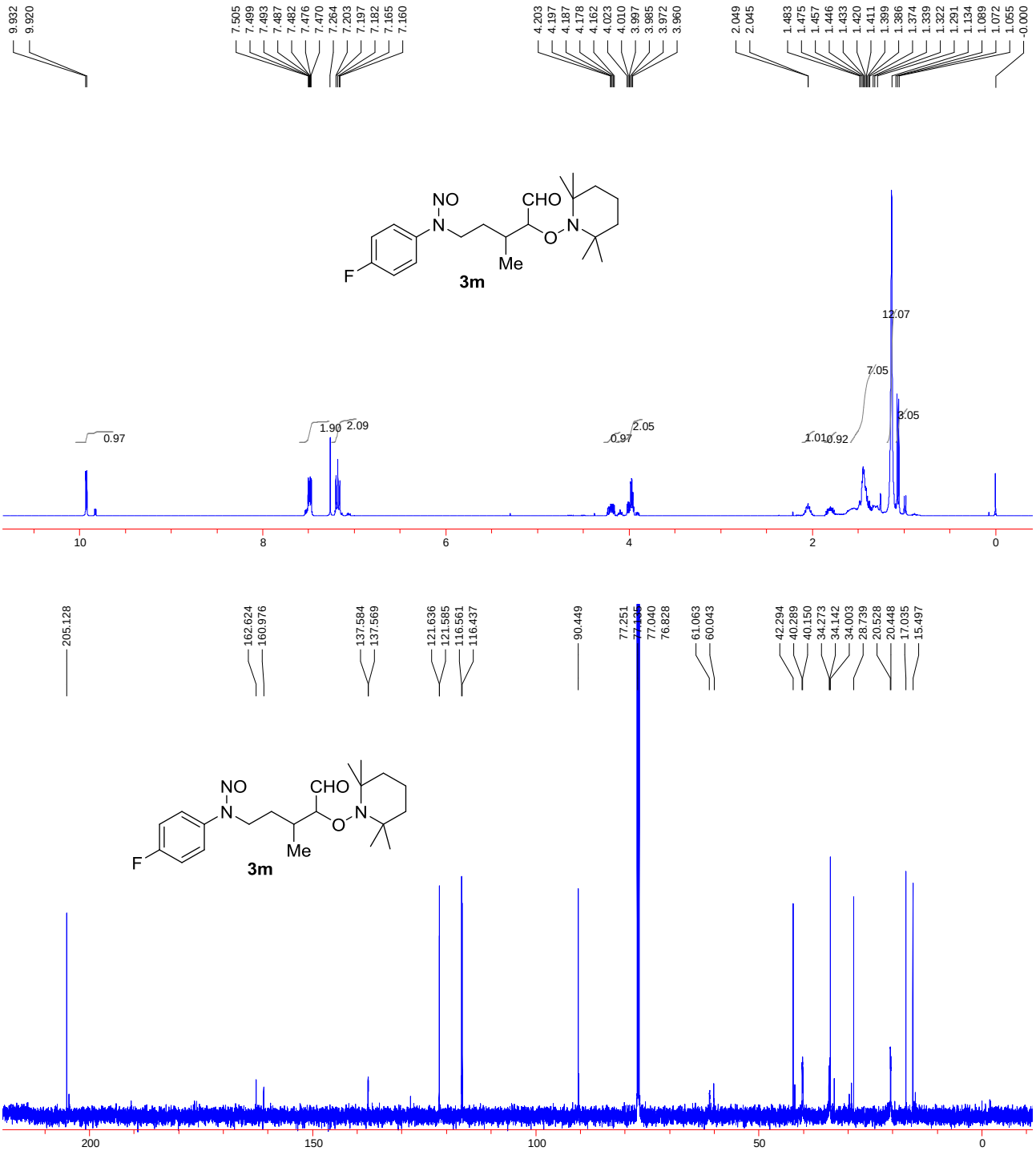
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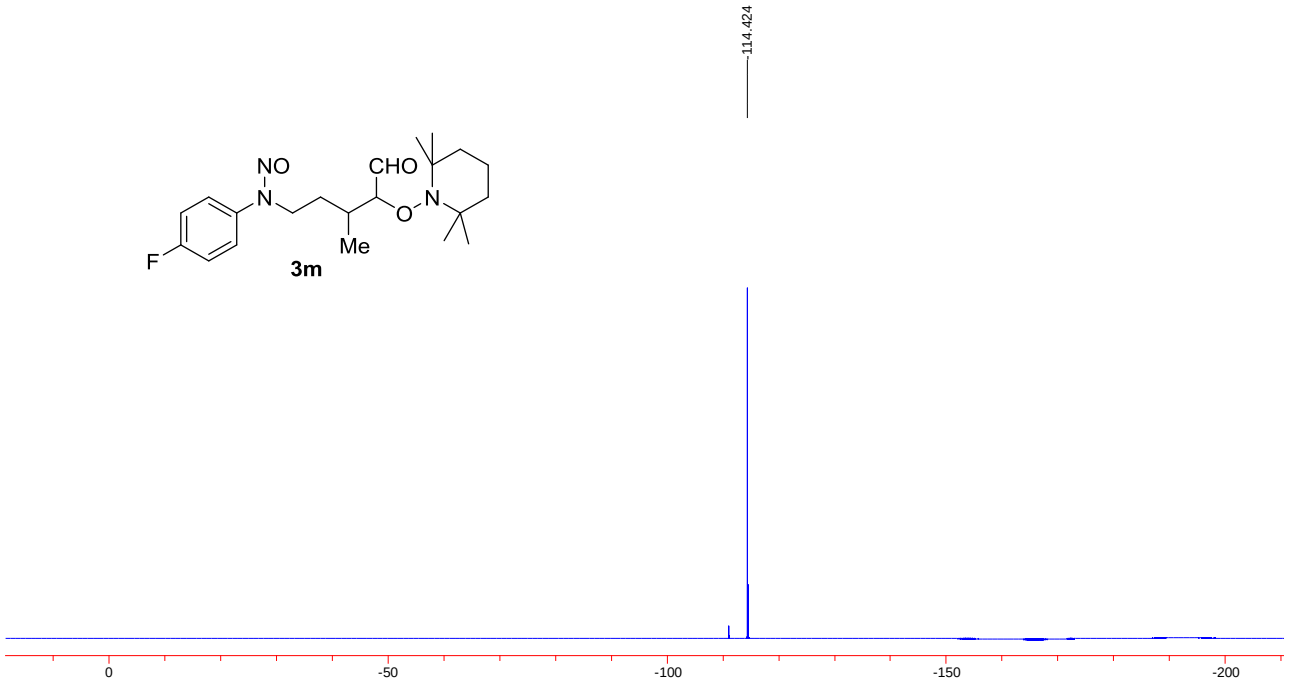
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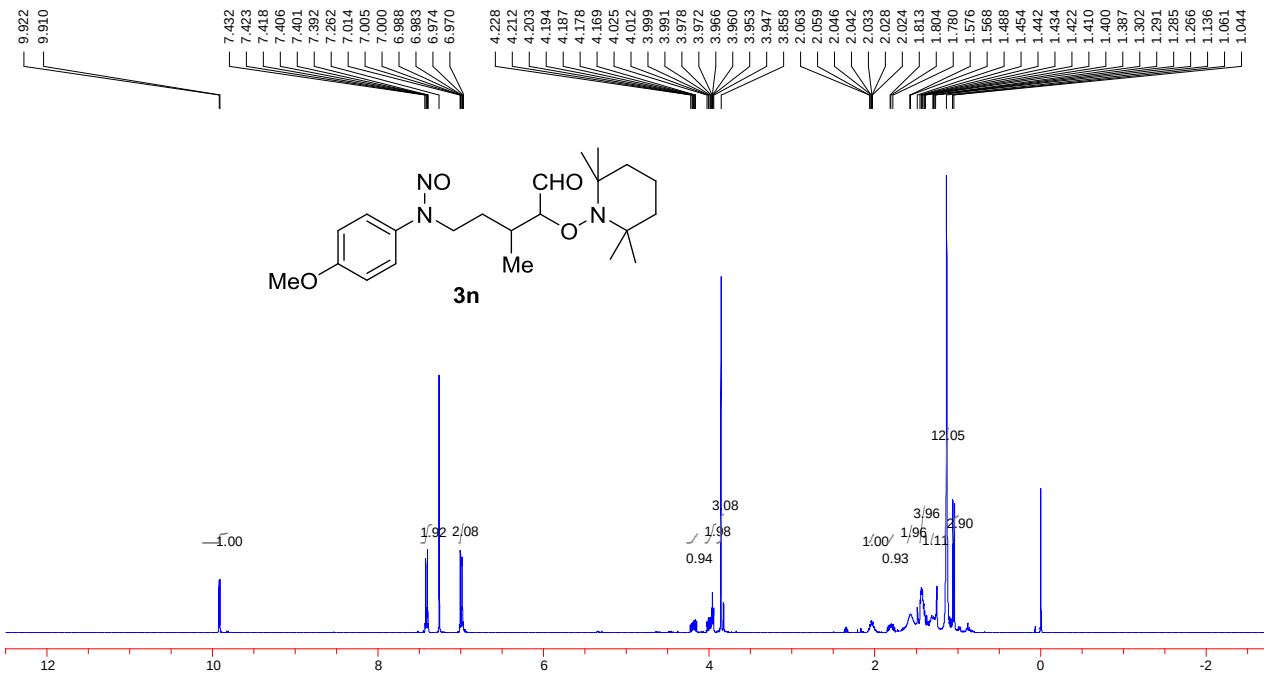
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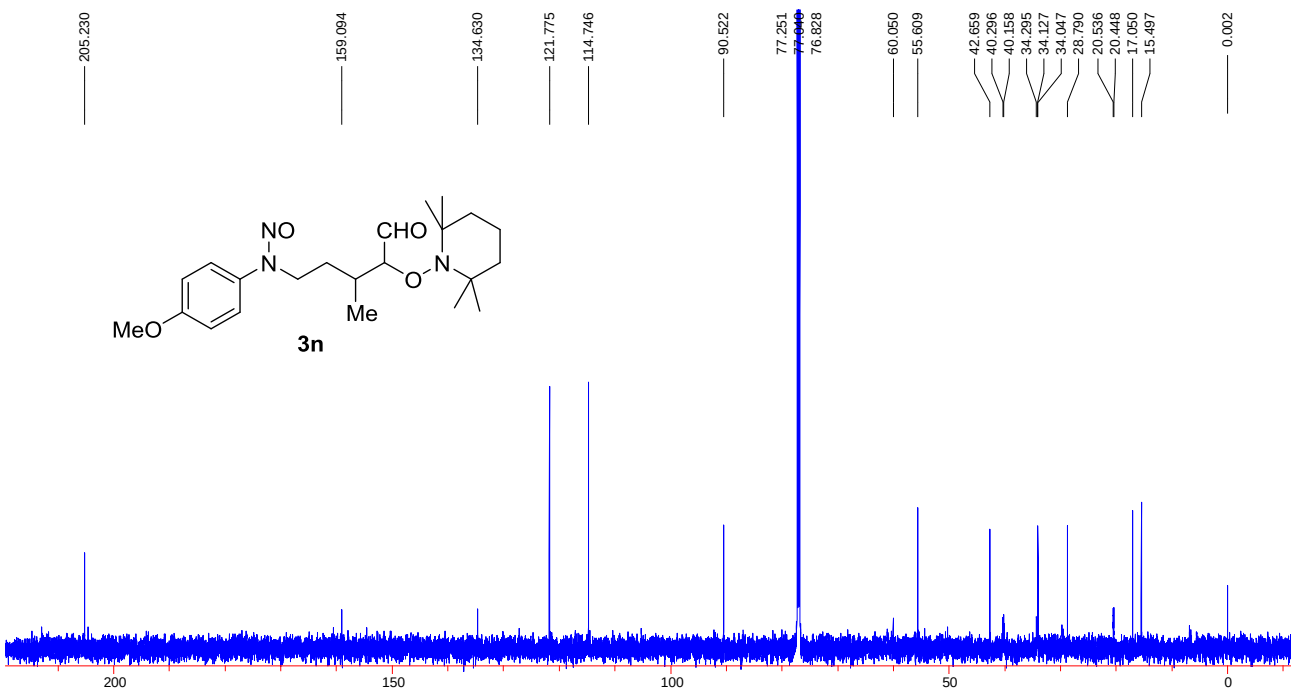
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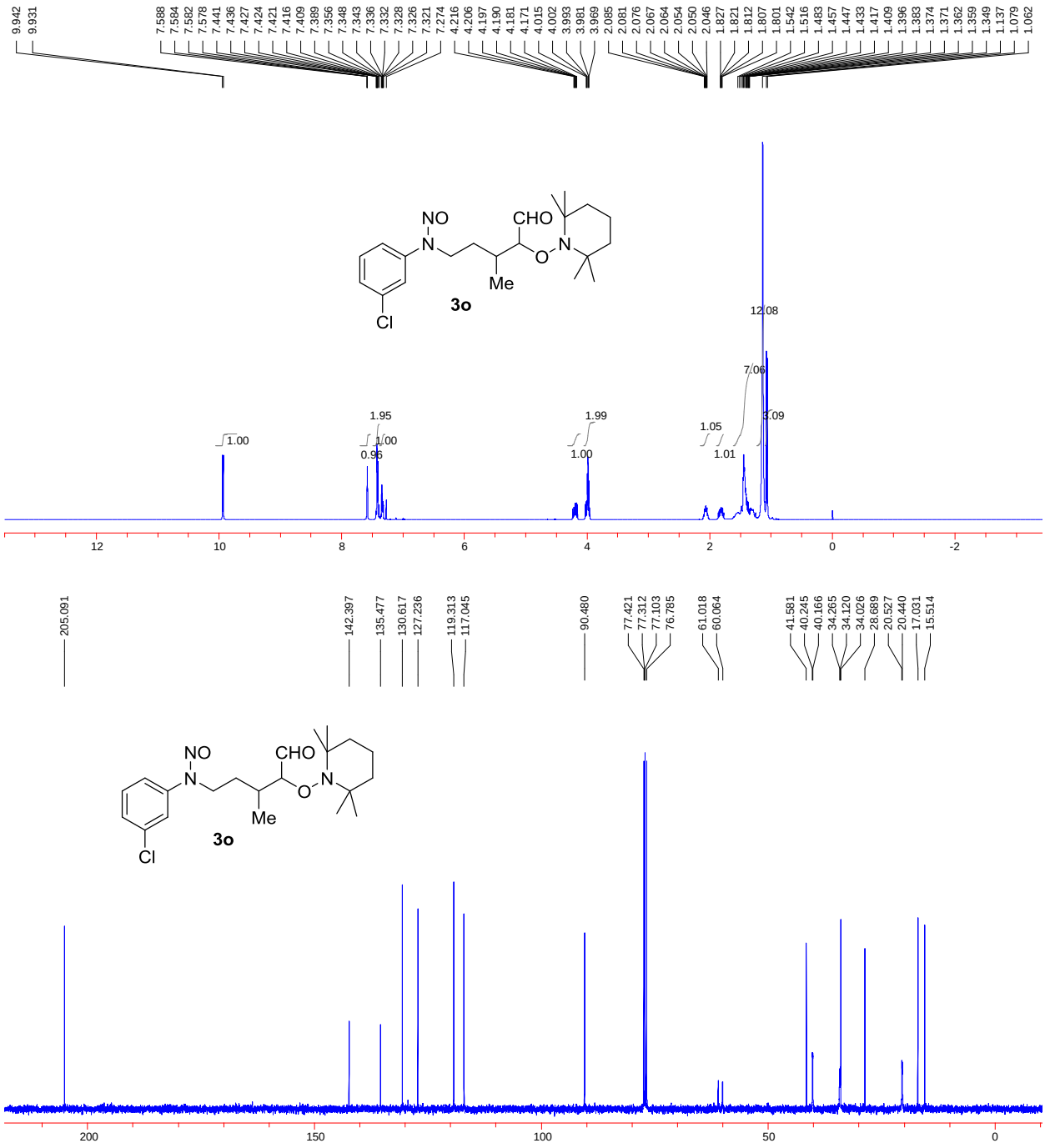
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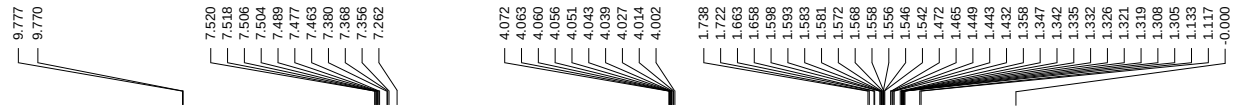
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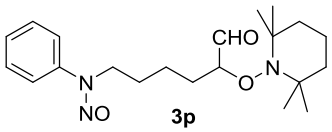
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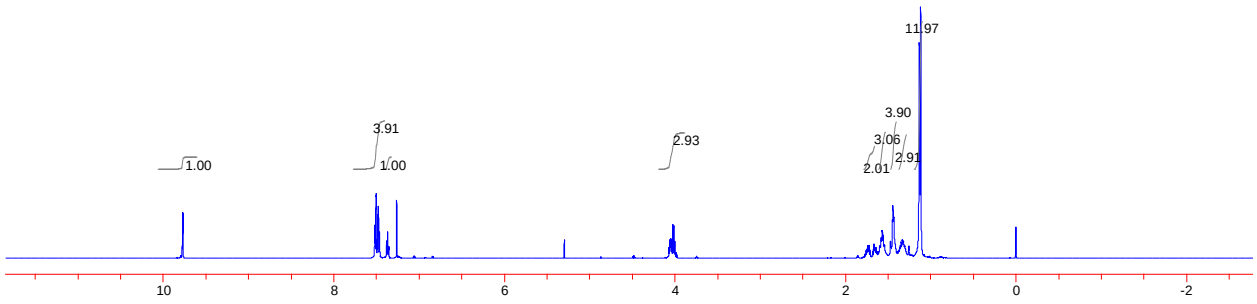
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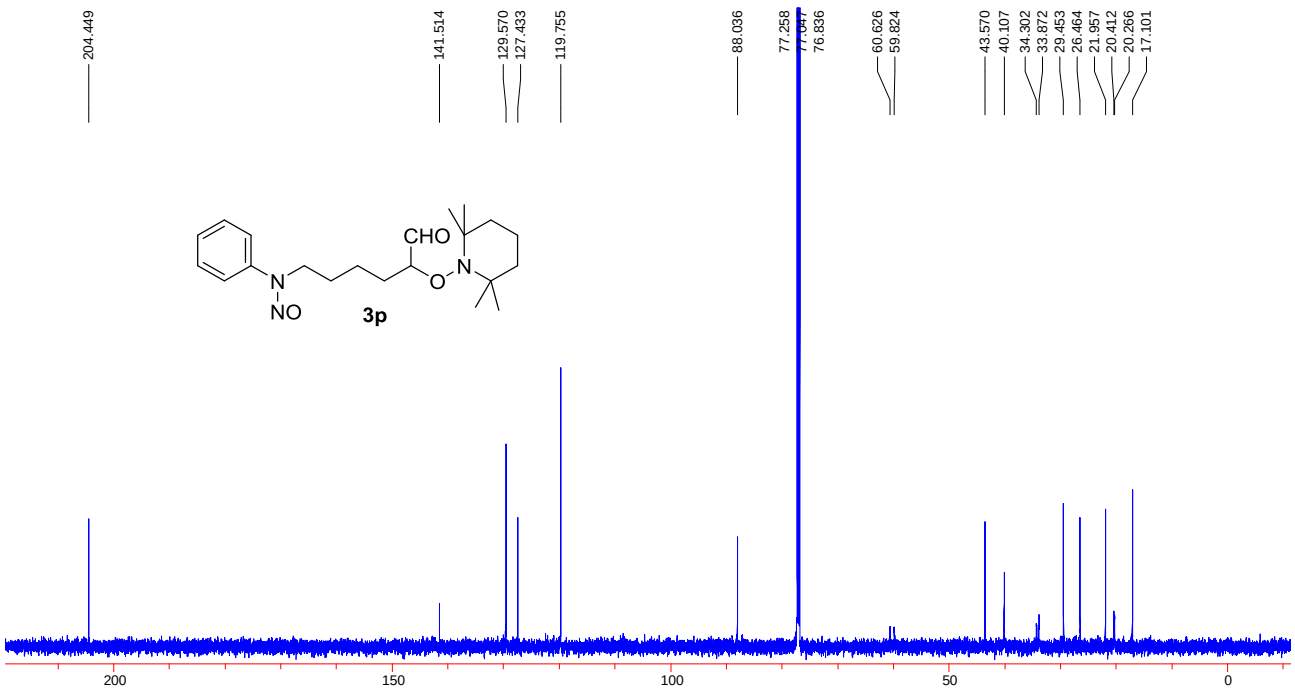
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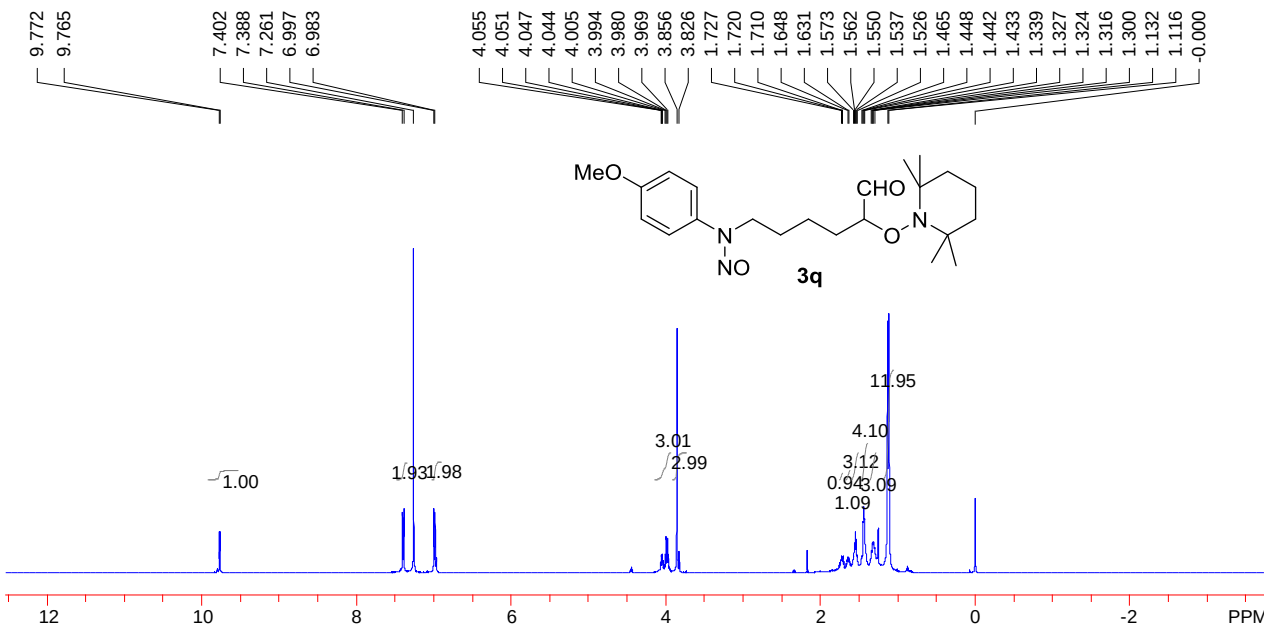
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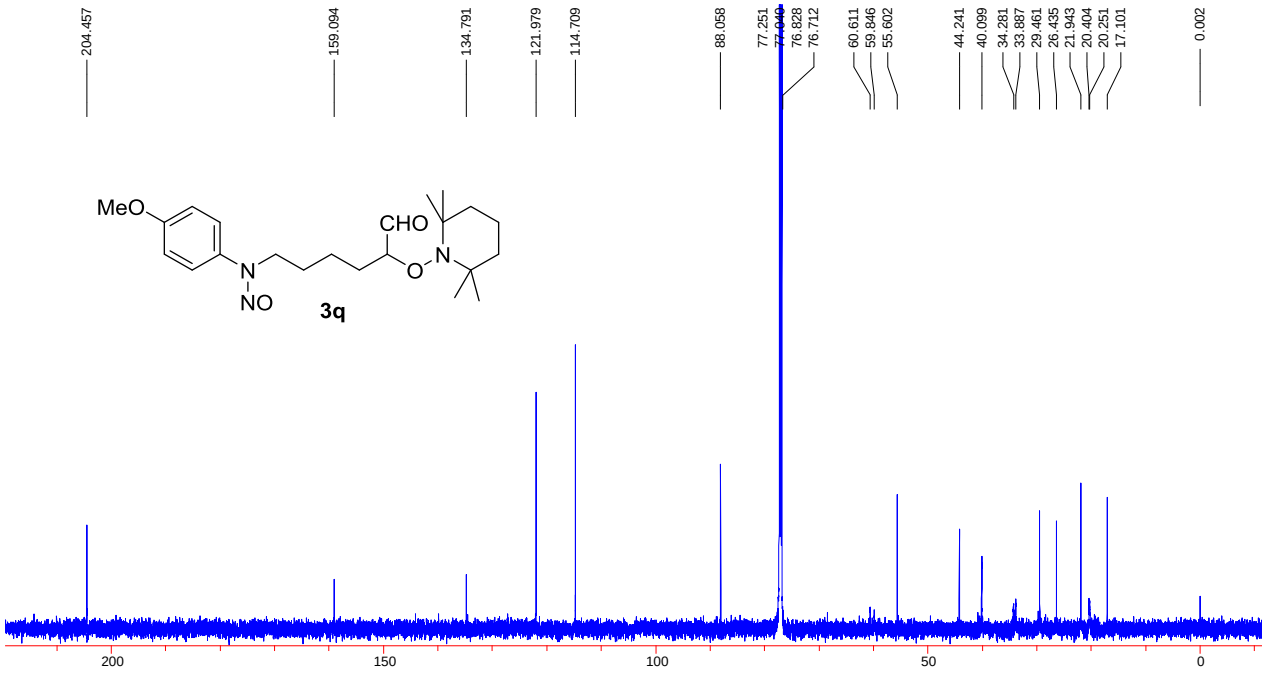
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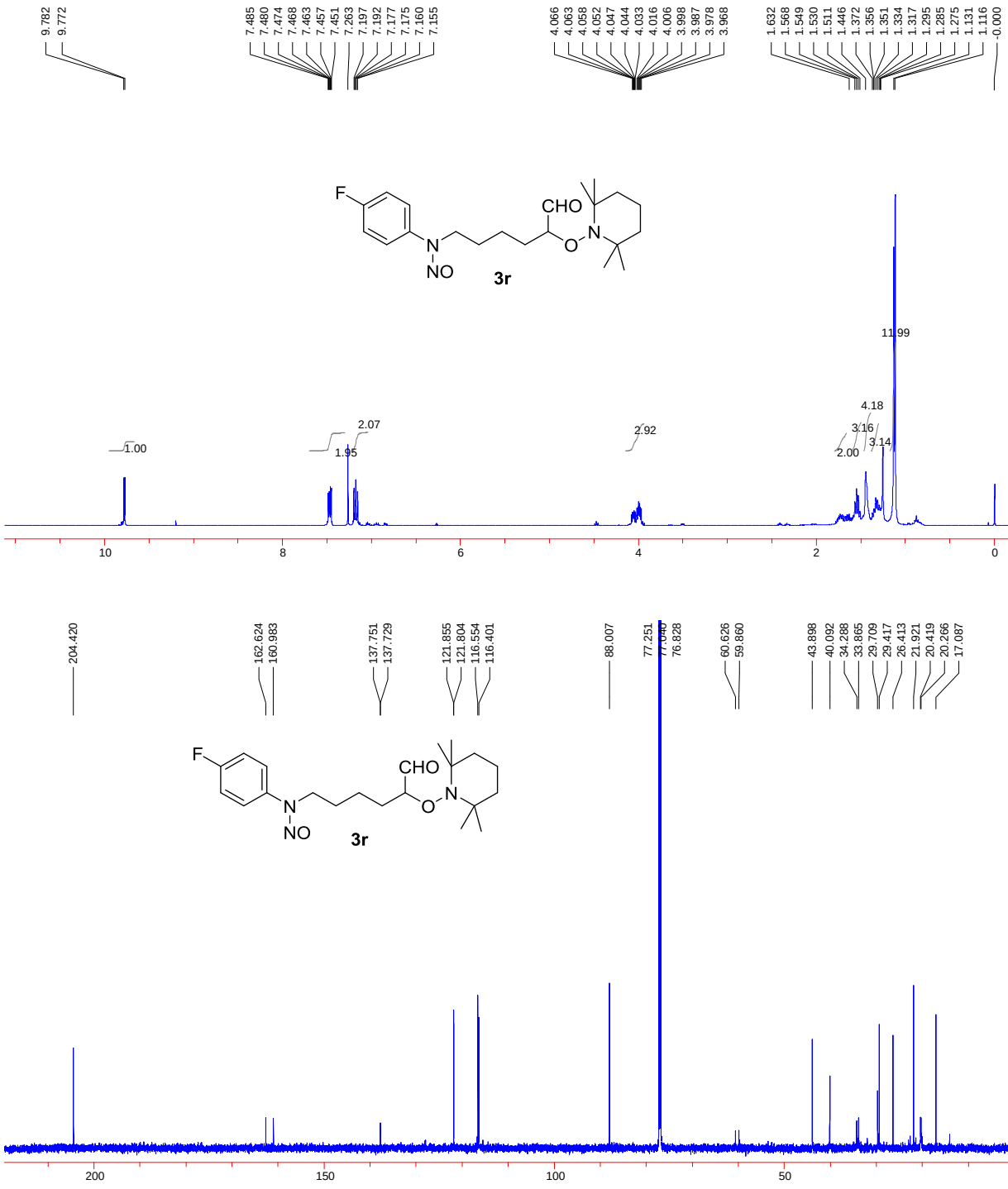
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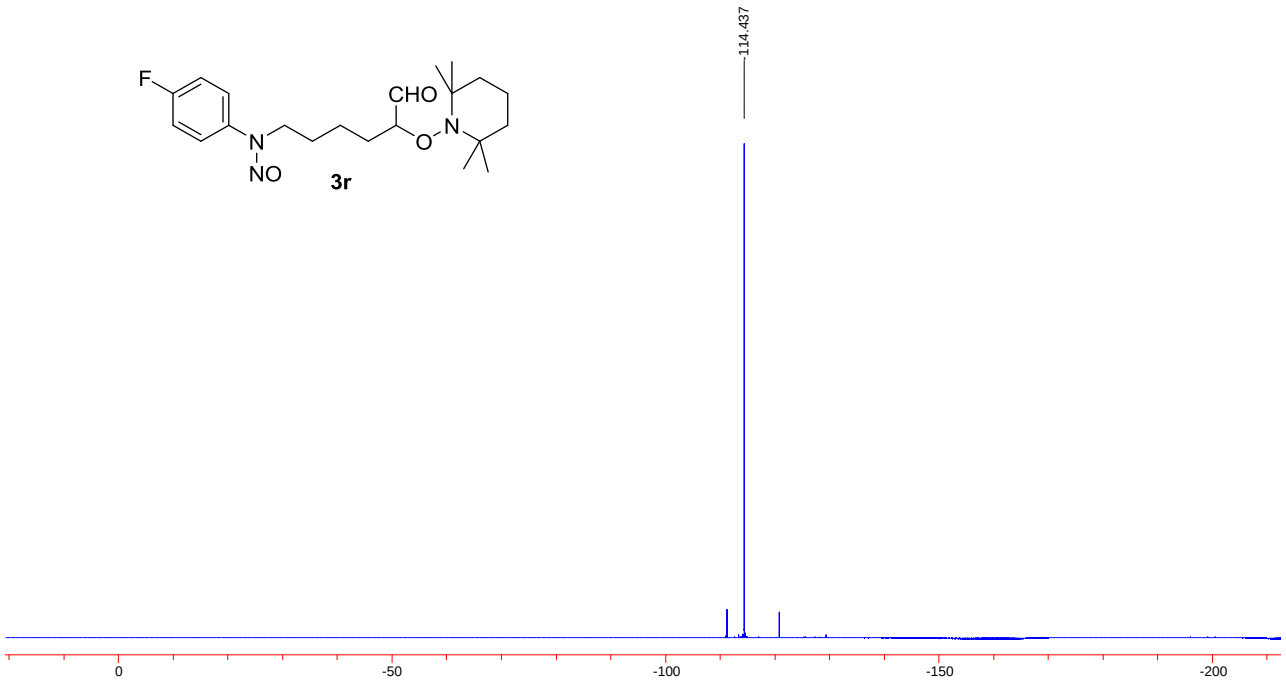
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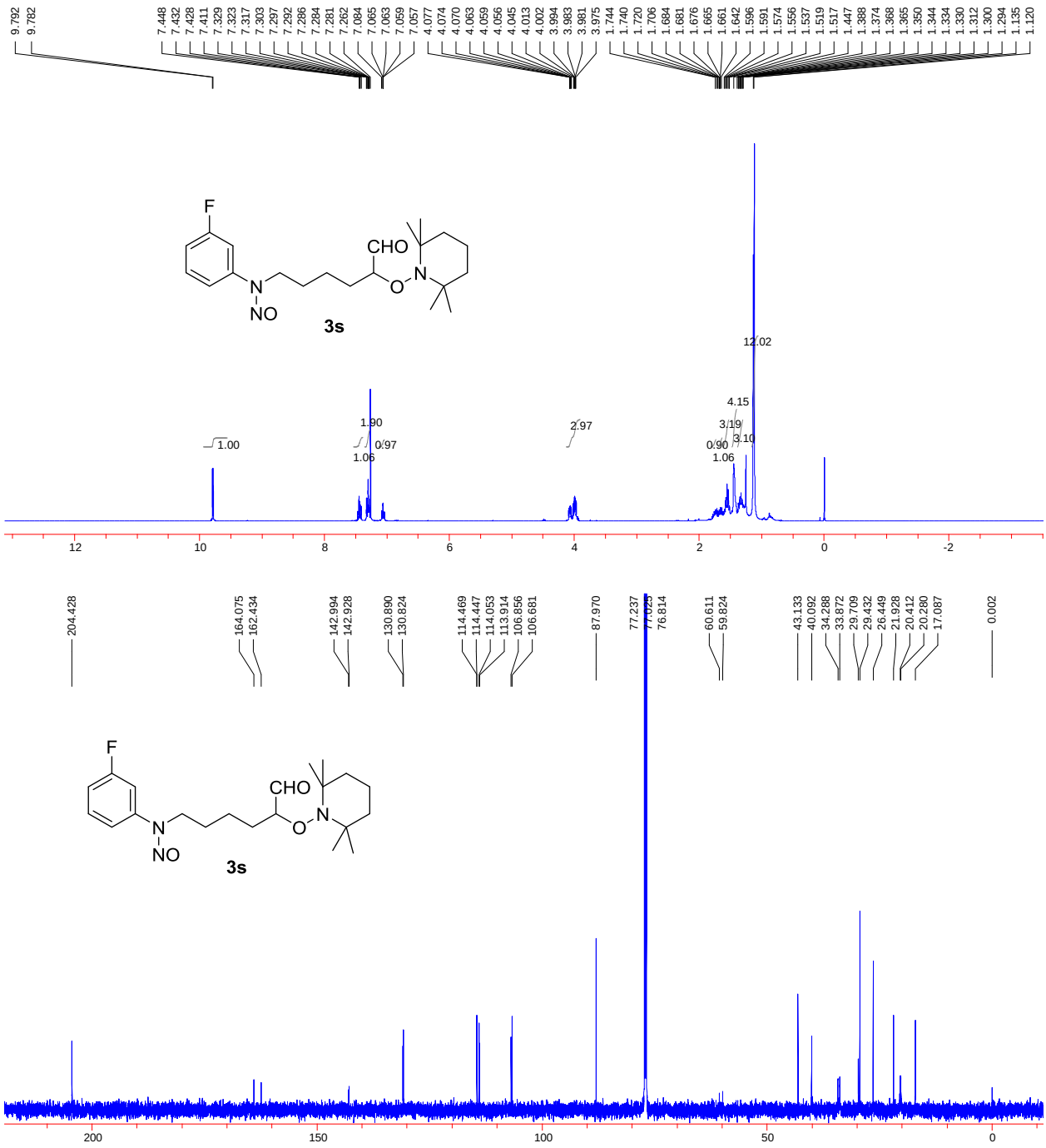
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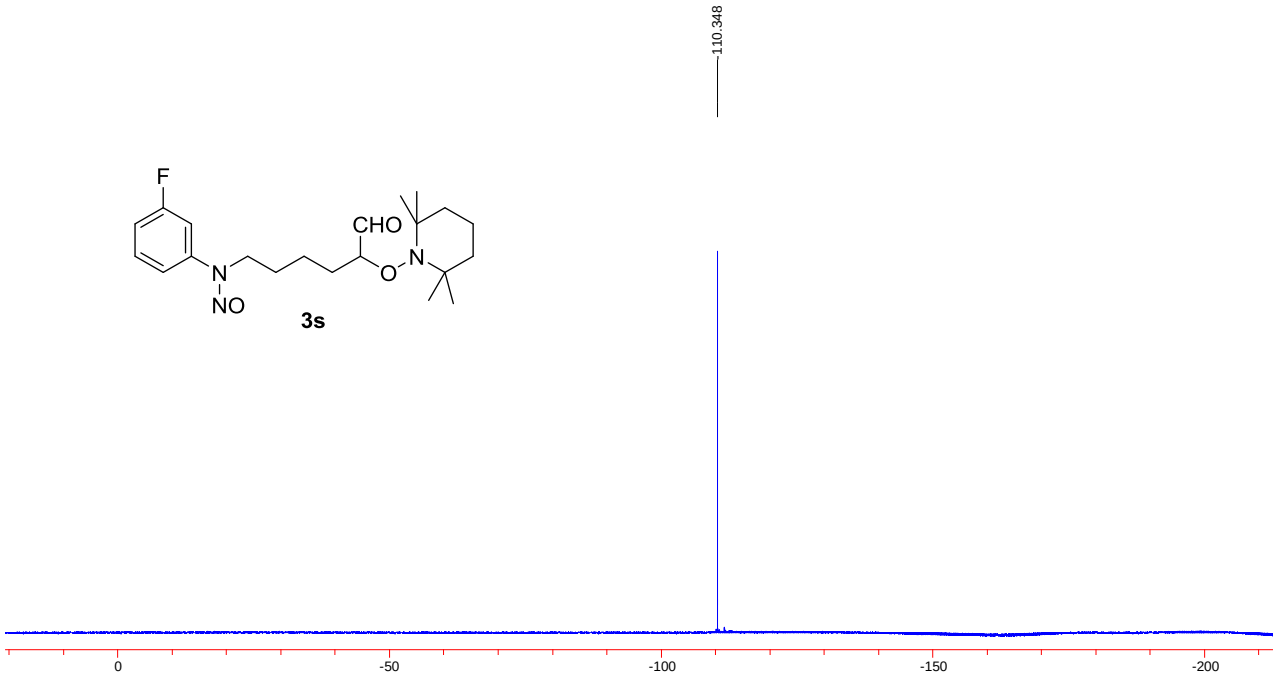
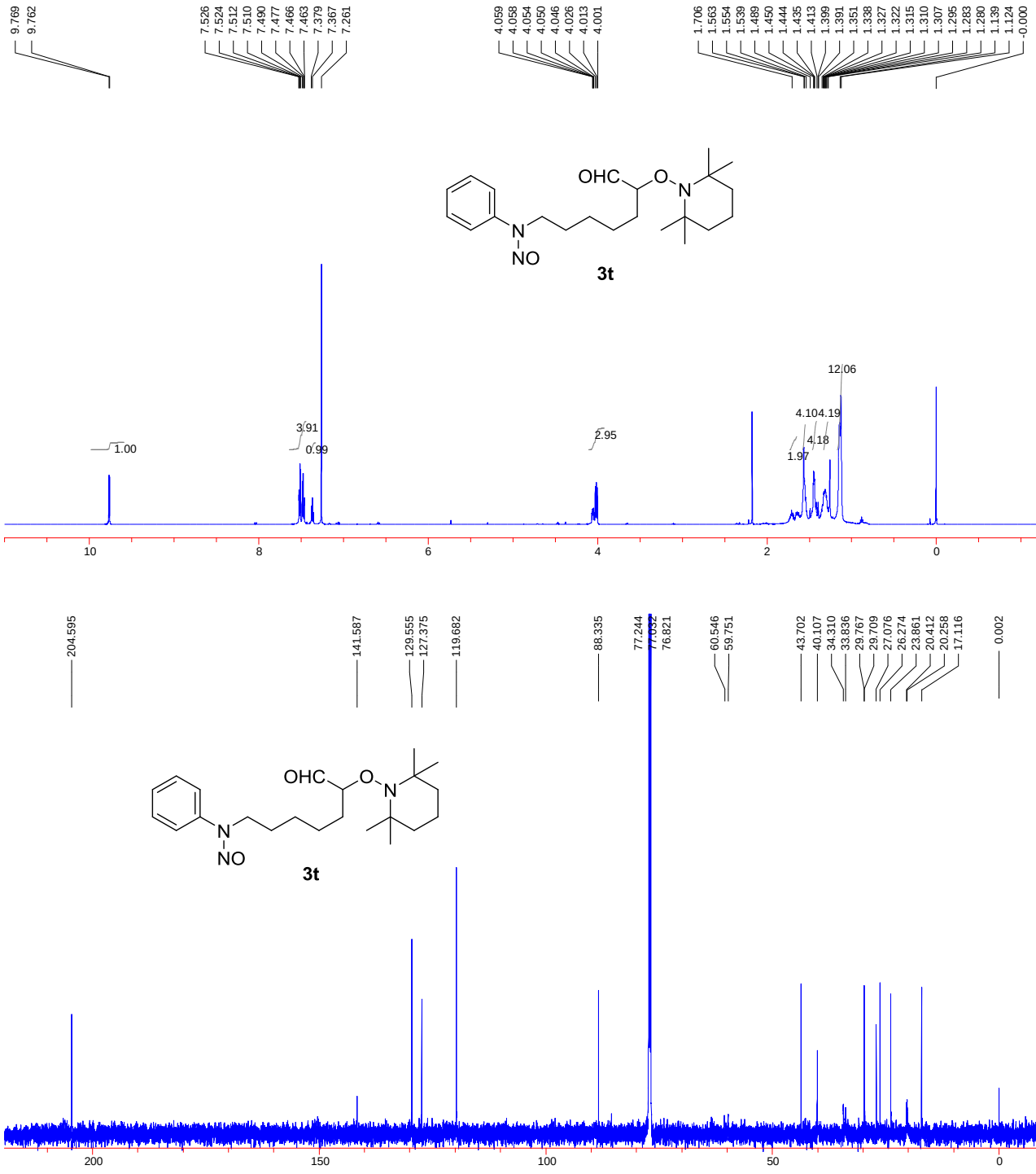
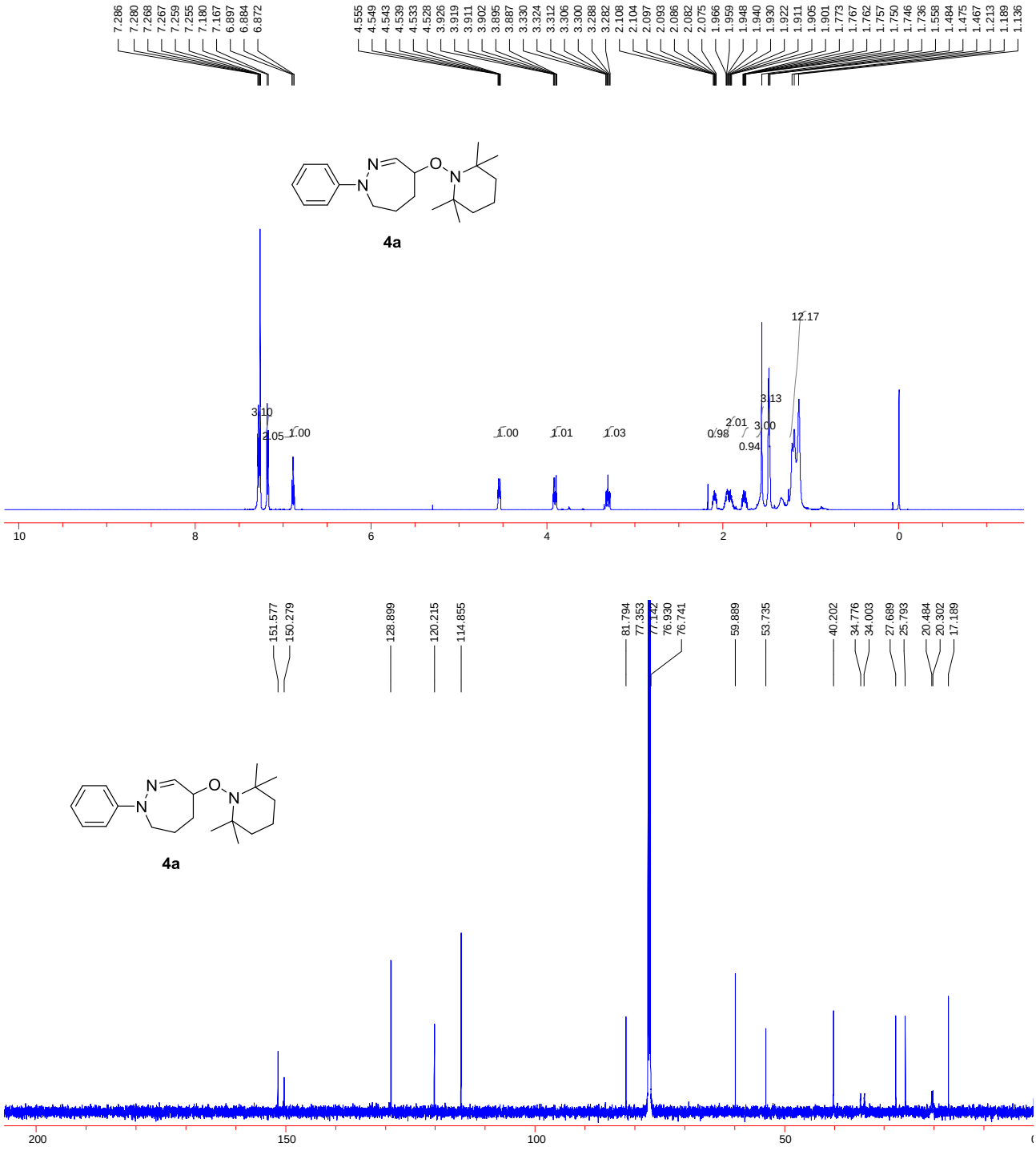
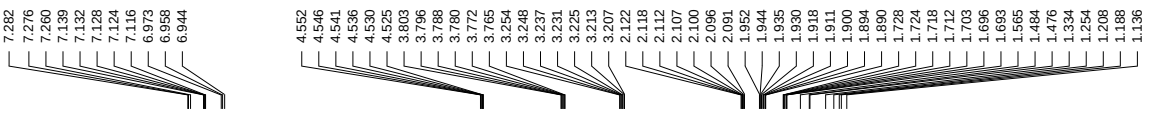
150
100
50
0

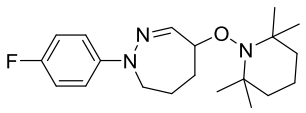

F
CHO
N
O
N
NO
3s
-110.348
0
-50
-100
-150
-200


9.769
9.762
7.526
7.524
7.512
7.510
7.490
7.477
7.466
7.463
7.379
7.367
7.261
4.059
4.058
4.054
4.050
4.046
4.026
4.013
4.001
1.706
1.563
1.554
1.539
1.489
1.450
1.444
1.435
1.413
1.399
1.391
1.351
1.338
1.327
1.322
1.315
1.310
1.307
1.295
1.283
1.280
1.139
1.124
-0.000
OHC
O
N
N
NO
3t
1.00
3.91
0.99
2.95
12.06
4.10
4.19
4.18
1.97
10
8
6
4
2
0
204.595
141.587
129.555
127.375
119.682
88.335
77.244
77.032
76.821
60.546
59.751
43.702
40.107
34.310
33.836
29.767
29.709
27.076
26.274
23.861
20.412
20.258
17.116
0.002
OHC
O
N
N
NO
3t
200
150
100
50
0

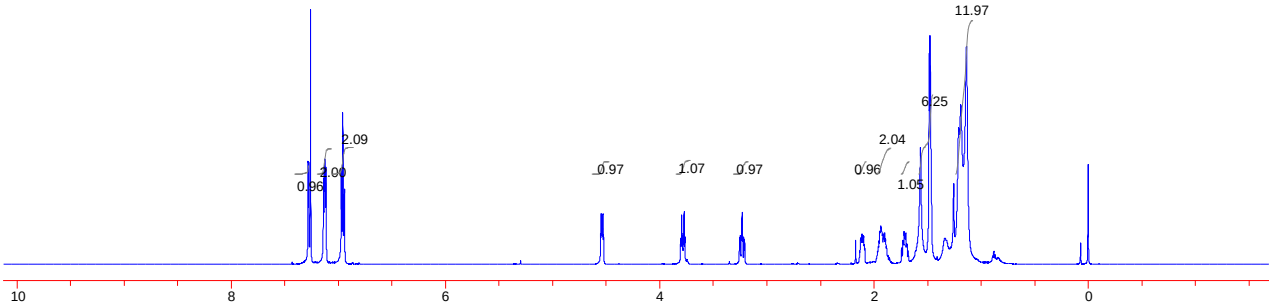
V. Copies of the NMR spectra of 4a-4d

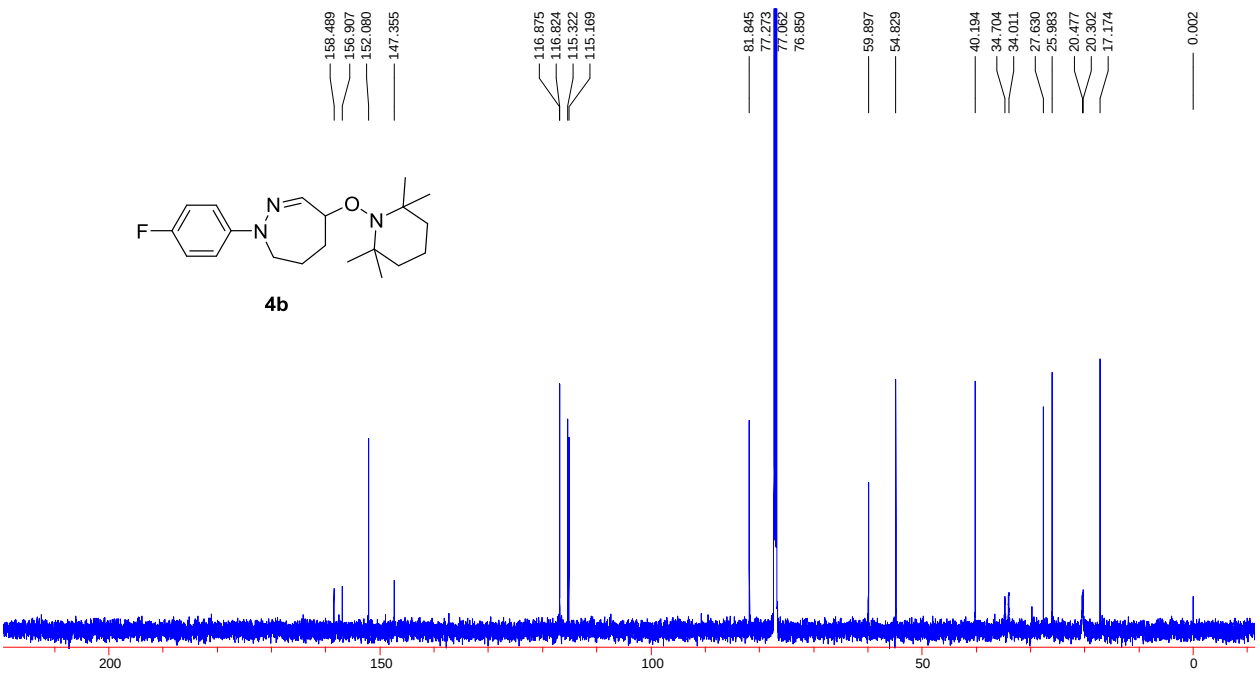



7.282
7.276
7.260
7.139
7.132
7.128
7.124
7.116
6.973
6.958
6.944
4.552
4.546
4.541
4.536
4.530
4.525
3.803
3.796
3.788
3.780
3.772
3.765
3.254
3.248
3.237
3.231
3.225
3.213
3.207
2.122
2.118
2.112
2.107
2.100
2.096
2.091
1.952
1.944
1.935
1.930
1.918
1.911
1.900
1.894
1.890
1.728
1.724
1.718
1.712
1.703
1.696
1.693
1.565
1.484
1.476
1.334
1.254
1.208
1.188
1.136


F
N
N
O
N

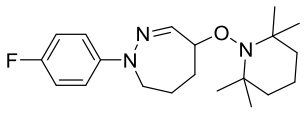
4b


11.97
6.25
2.09
2.04
2.00
0.96
0.97
1.07
0.97
0.96
1.05
10
8
6
4
2
0

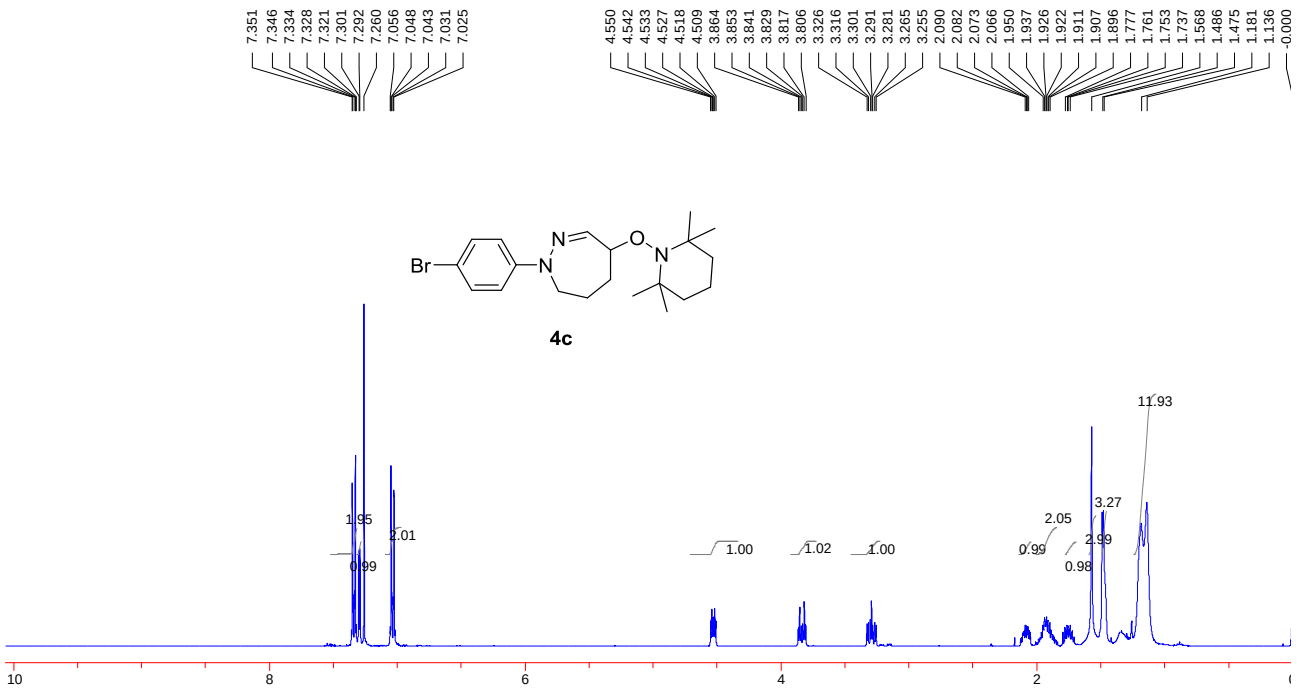

158.489
156.907
152.080
147.355
116.875
116.824
115.322
115.169
81.845
77.273
77.062
76.850
59.897
54.829
40.194
34.704
34.011
27.630
25.983
20.477
20.302
17.174
0.002
200
150
100
50
0

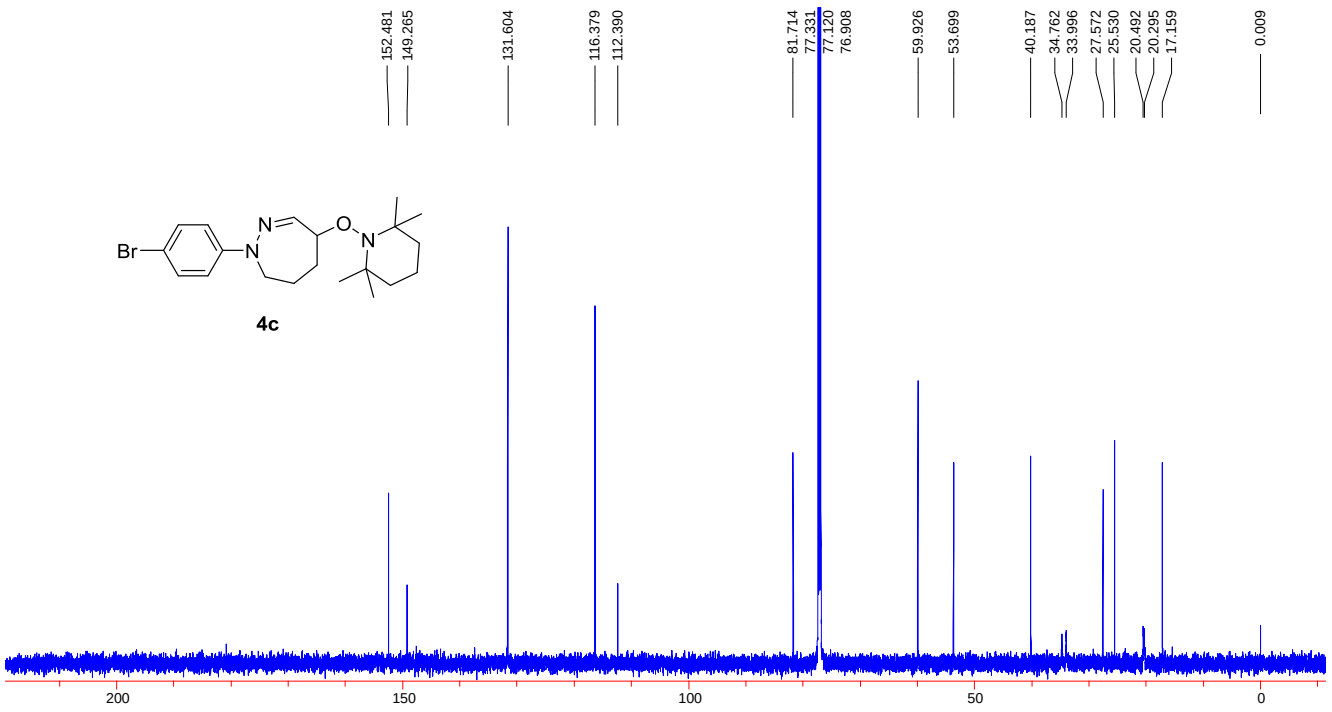
F
N
N
O
N

4b



4b


7.351
7.346
7.334
7.328
7.321
7.301
7.292
7.260
7.056
7.048
7.043
7.031
7.025
4.550
4.542
4.533
4.527
4.518
4.509
3.864
3.853
3.841
3.829
3.817
3.806
3.326
3.316
3.301
3.291
3.281
3.265
3.255
2.090
2.082
2.073
2.066
1.950
1.937
1.926
1.922
1.911
1.907
1.896
1.777
1.761
1.753
1.737
1.568
1.486
1.475
1.181
1.136
-0.000
Br
N
N
O
N
4c
11.93
3.27
2.05
2.99
1.95
2.01
1.00
1.02
1.00
0.99
0.98
0.99
10
8
6
4
2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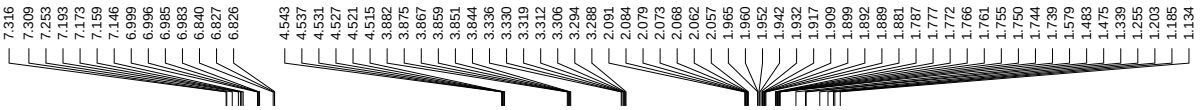
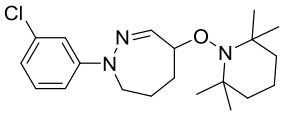
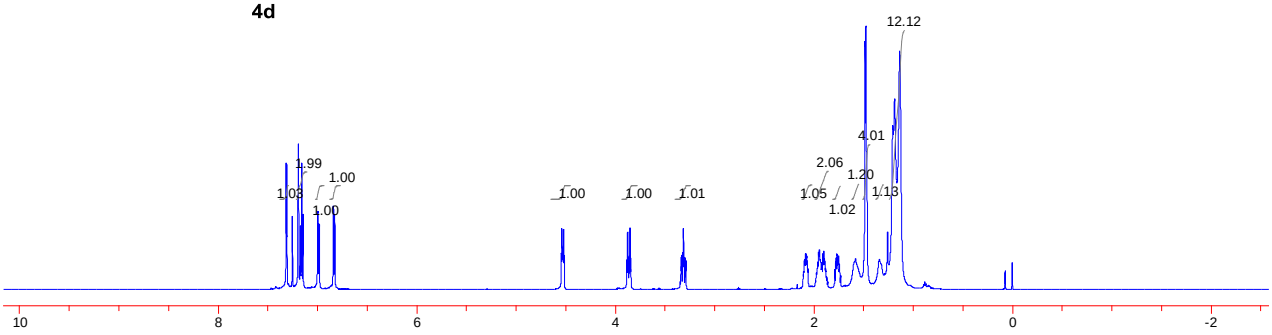
149.265
131.604
116.379
112.390
81.714
77.331
77.120
76.908
59.926
53.699
40.187
34.762
33.996
27.572
25.530
20.492
20.295
17.159
0.009
Br
N
N
O
N
4c
200
150
100
50
0

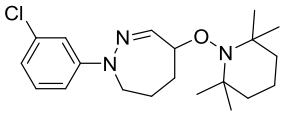

7.316
7.309
7.253
7.193
7.173
7.159
7.146
6.999
6.996
6.985
6.983
6.840
6.827
6.826
4.543
4.537
4.531
4.527
4.521
4.515
3.882
3.875
3.867
3.859
3.851
3.844
3.336
3.330
3.319
3.312
3.306
3.294
3.288
2.091
2.084
2.079
2.073
2.068
2.062
2.057
1.965
1.960
1.952
1.942
1.932
1.917
1.909
1.899
1.892
1.889
1.881
1.787
1.777
1.772
1.766
1.761
1.755
1.750
1.744
1.739
1.579
1.483
1.475
1.339
1.255
1.203
1.185
1.134


Cl
N
N
O
N

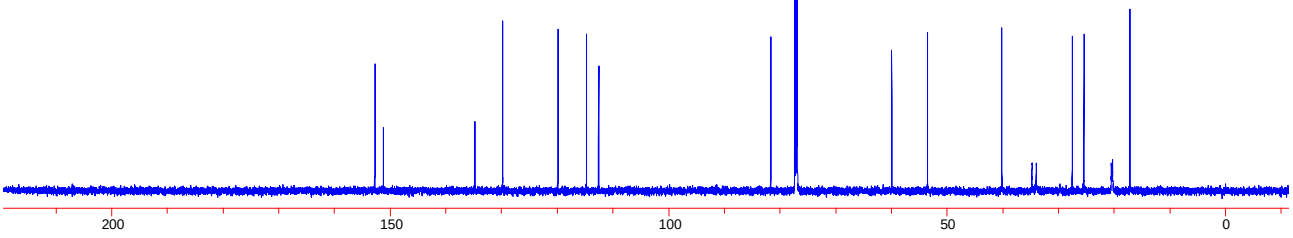
4d


12.12
4.01
2.06
1.20
1.99
1.03
1.00
1.00
1.00
1.00
1.01
1.05
1.02
1.13
10
8
6
4
2
0
-2

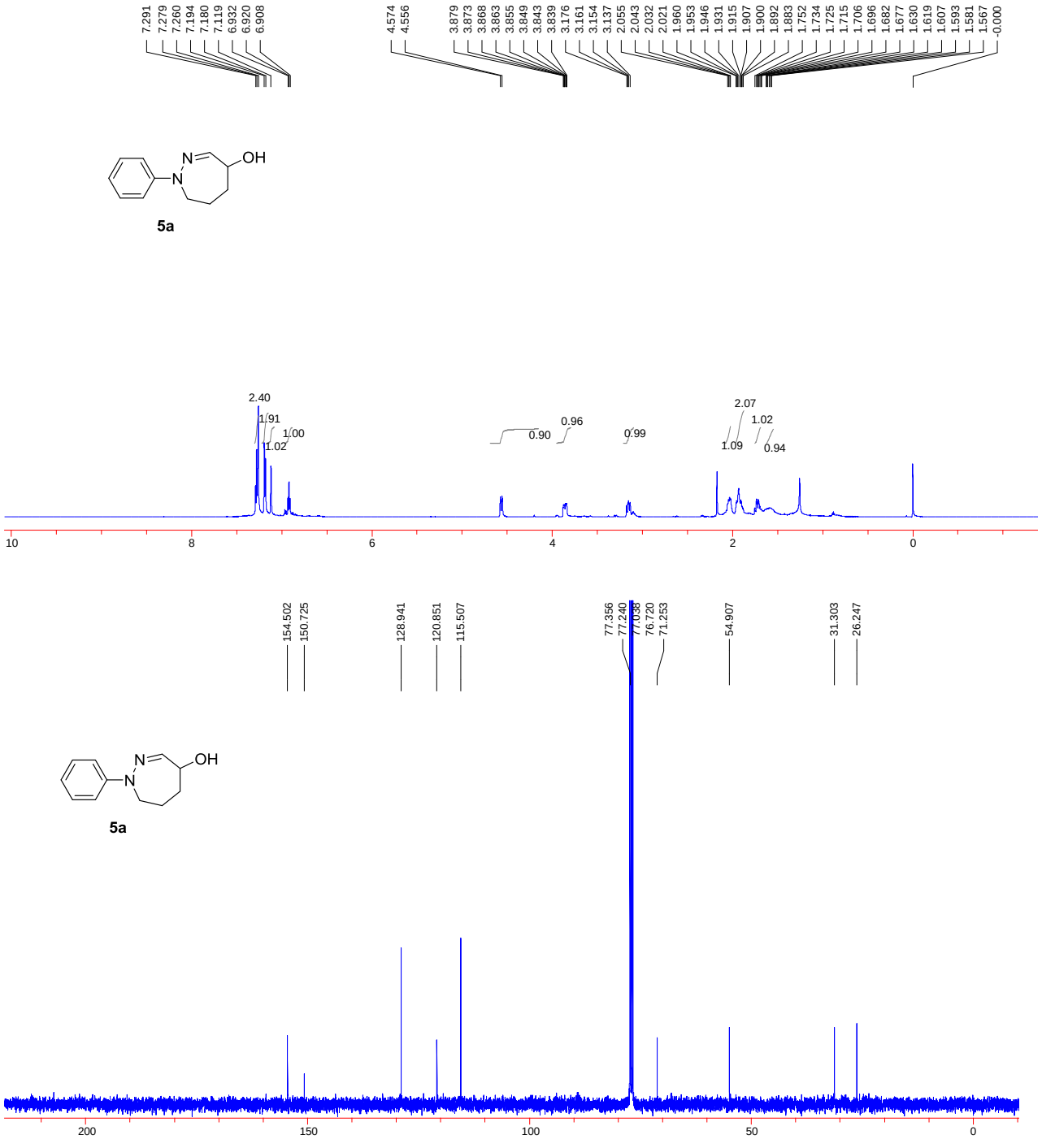

152.736
151.183
134.798
129.803
119.865
114.746
112.558
81.670
77.339
77.127
76.916
59.933
53.546
40.187
34.762
33.996
27.558
25.450
20.499
20.288
17.167

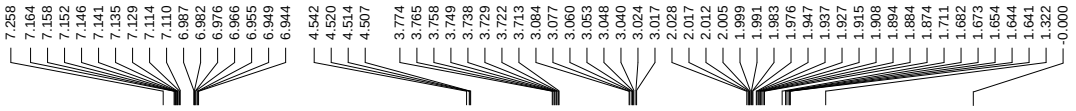

Cl
N
N
O
N

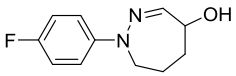
4d


200
150
100
50
0

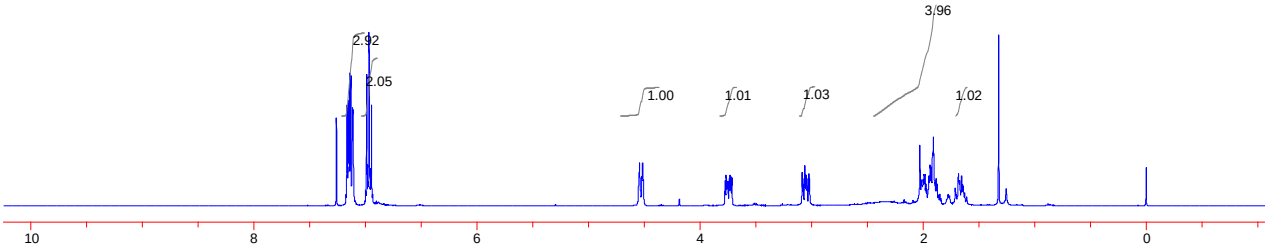
VI. Copies of the NMR spectra of 5a-5d



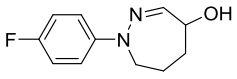

7.258
7.164
7.158
7.152
7.146
7.141
7.135
7.129
7.114
7.110
6.987
6.982
6.976
6.966
6.955
6.949
6.944
4.542
4.520
4.514
4.507
3.774
3.765
3.758
3.749
3.738
3.729
3.722
3.713
3.084
3.077
3.060
3.053
3.048
3.040
3.024
3.017
2.028
2.017
2.012
2.005
1.999
1.991
1.983
1.976
1.947
1.937
1.927
1.915
1.908
1.894
1.884
1.874
1.711
1.682
1.673
1.654
1.644
1.641
1.322
-0.000


F
N
N
OH

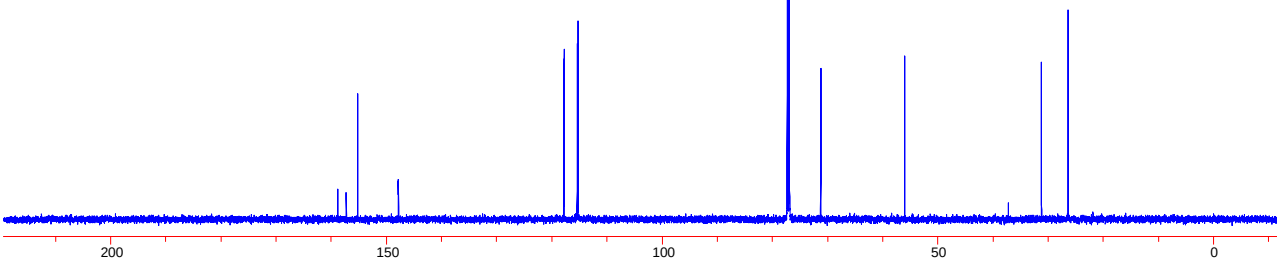
5b

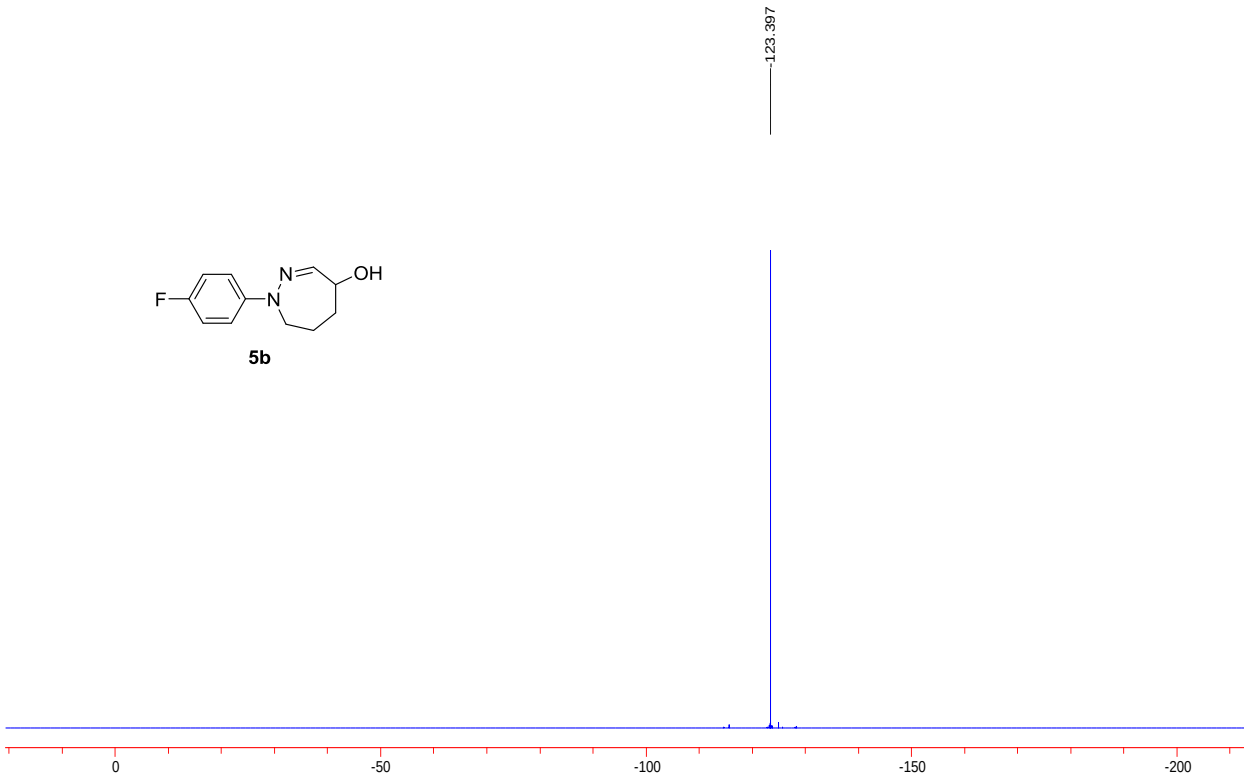

2.92
2.05
1.00
1.01
1.03
3.96
1.02
10
8
6
4
2
0


158.839
157.257
155.179
147.807
147.792
117.794
117.743
115.416
115.271
77.324
77.119
76.901
71.243
56.039
31.211
26.405

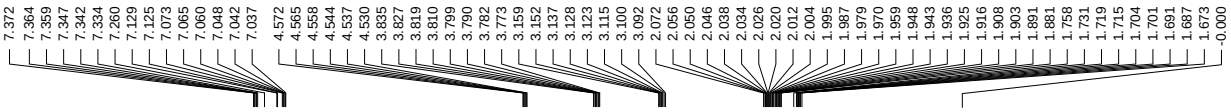

F
N
N
OH

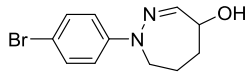
5b


200
150
100
50
0

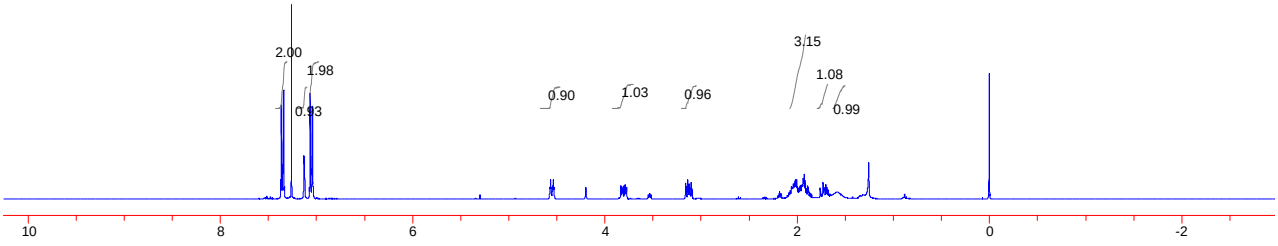


5b


7.372
7.364
7.359
7.347
7.342
7.334
7.260
7.129
7.125
7.073
7.065
7.060
7.048
7.042
7.037
4.572
4.565
4.558
4.544
4.537
4.530
3.835
3.827
3.819
3.810
3.799
3.790
3.782
3.773
3.159
3.152
3.137
3.128
3.123
3.115
3.100
3.092
2.072
2.056
2.050
2.046
2.038
2.034
2.026
2.020
2.012
2.004
1.995
1.987
1.979
1.970
1.959
1.948
1.943
1.936
1.925
1.916
1.908
1.903
1.891
1.881
1.758
1.731
1.719
1.715
1.704
1.701
1.691
1.687
1.673
-0.000


Br
N
N
OH

5c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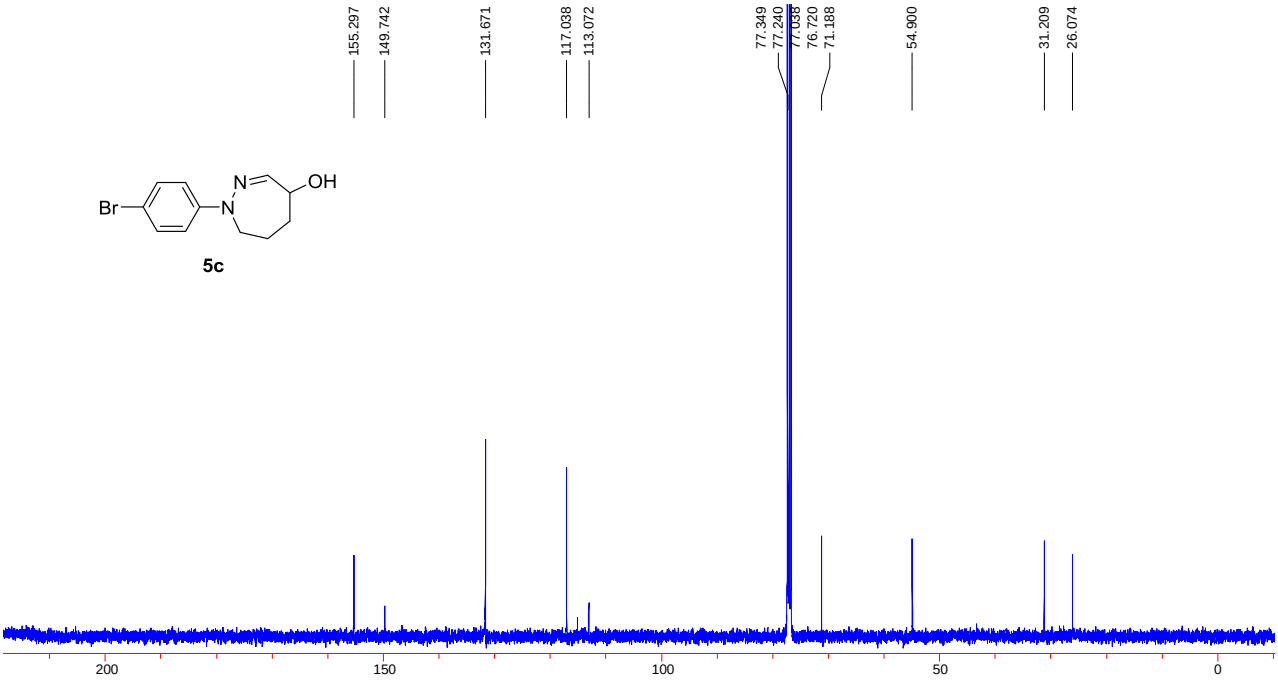
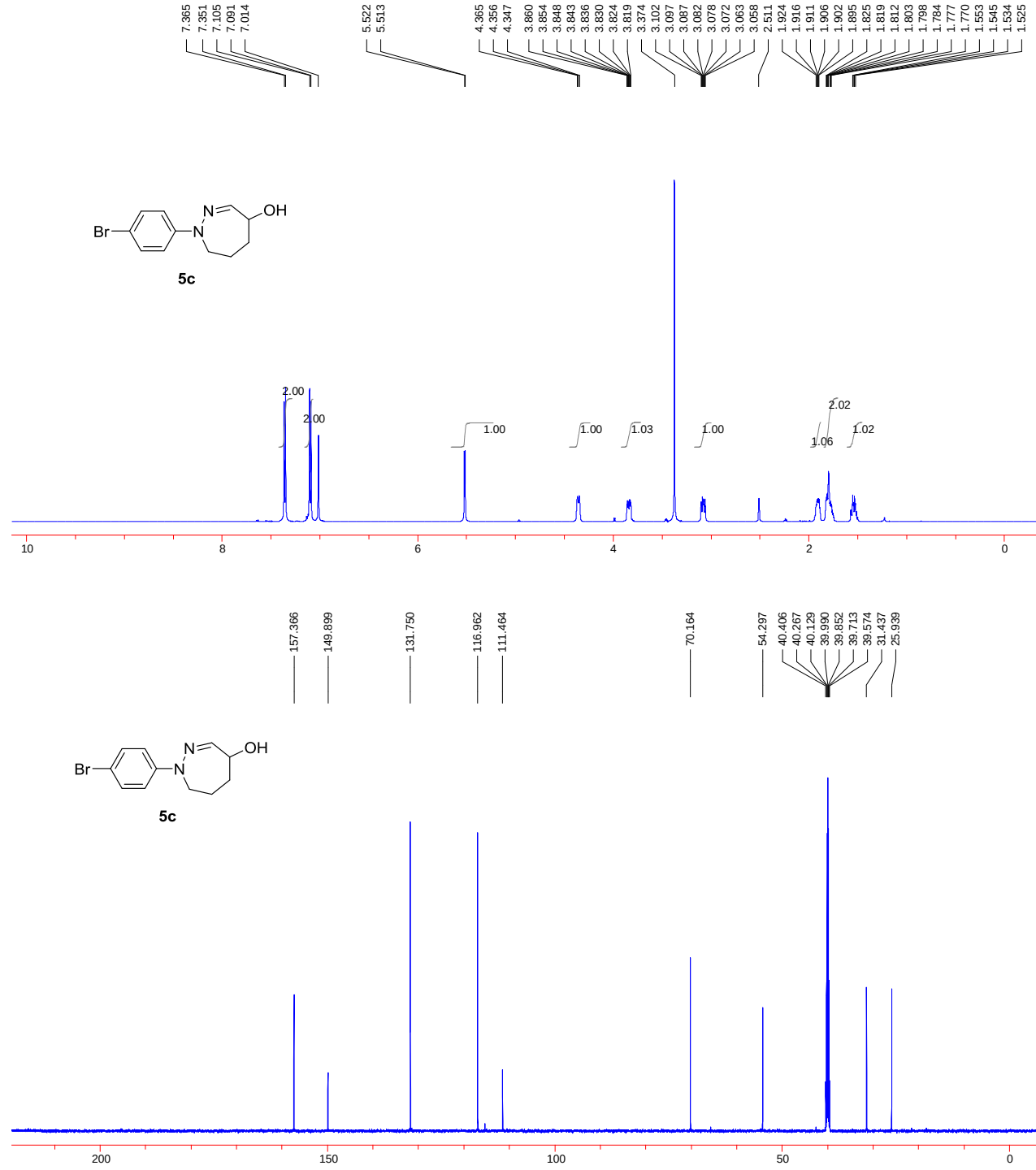
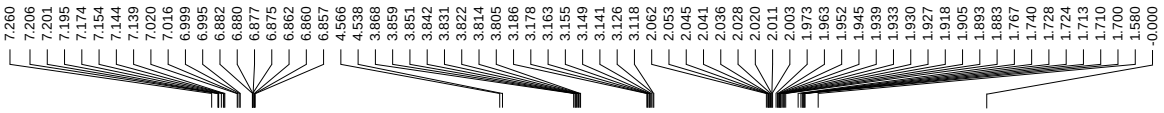
1.98
0.93
0.90
1.03
0.96
3.15
1.08
0.99
10
8
6
4
2
0
-2


155.297
149.742
131.671
117.038
113.072
77.349
77.240
77.036
76.720
71.188
54.900
31.209
26.074
200
150
100
50
0

Br
N
N
OH

5c


7.365
7.351
7.105
7.091
7.014
5.522
5.513
4.365
4.356
4.347
3.860
3.854
3.848
3.843
3.836
3.830
3.824
3.819
3.374
3.102
3.097
3.087
3.082
3.078
3.072
3.063
3.058
2.511
1.924
1.916
1.911
1.906
1.902
1.895
1.825
1.819
1.812
1.803
1.798
1.784
1.777
1.770
1.553
1.545
1.534
1.525
Br
N
N
OH
5c
2.00
2.00
1.00
1.00
1.03
1.00
2.02
1.06
1.02
10
8
6
4
2
0
157.366
149.899
131.750
116.962
111.464
70.164
54.297
40.406
40.267
40.129
39.990
39.852
39.713
39.574
31.437
25.939
Br
N
N
OH
5c
200
150
100
50
0


7.260
7.206
7.201
7.195
7.174
7.154
7.144
7.139
7.020
7.016
6.999
6.995
6.882
6.880
6.877
6.875
6.862
6.860
6.857
4.566
4.538
3.868
3.859
3.851
3.842
3.831
3.822
3.814
3.805
3.186
3.178
3.163
3.155
3.149
3.141
3.126
3.118
2.062
2.053
2.045
2.041
2.036
2.028
2.020
2.011
2.003
1.973
1.963
1.952
1.945
1.939
1.933
1.930
1.927
1.918
1.905
1.893
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1.728
1.724
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1.710
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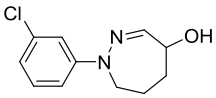
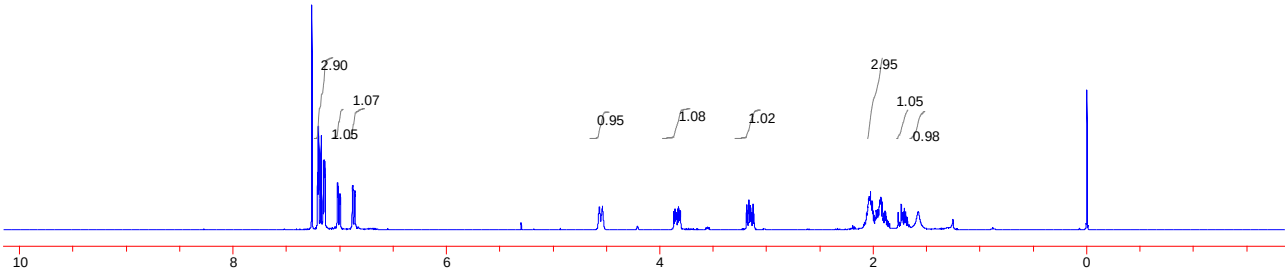
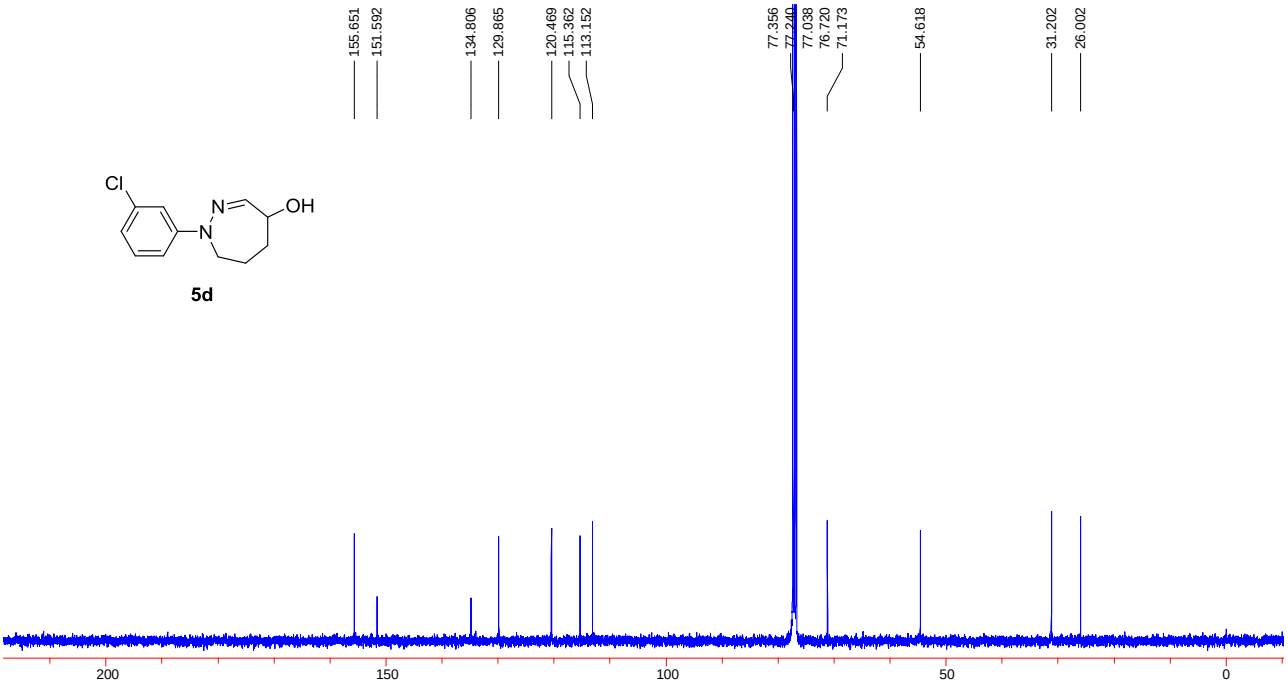
1.580
-0.000


Cl
N
N
OH

5d

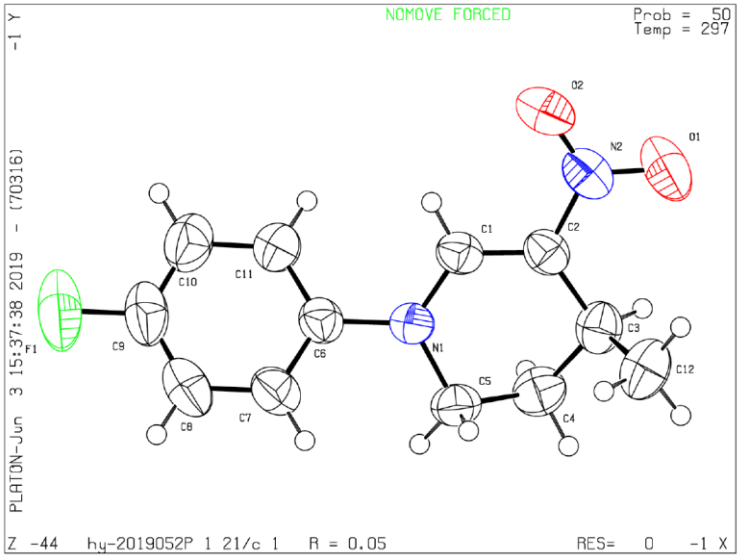

2.90
1.07
1.05
0.95
1.08
1.02
2.95
1.05
0.98
10
8
6
4
2
0


155.651
151.592
134.806
129.865
120.469
115.362
113.152
77.356
77.240
77.038
76.720
71.173
54.618
31.202
26.002
200
150
100
50
0

Cl
N
N
OH

5d

VII. X-ray Crystal Structures and Data of 2m



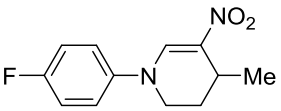


Fig. S2 X-ray structure of **2m**

X-ray structure determination. Single crystals suitable for X-ray diffraction was obtained by slow evaporation of the solvent from a Et_2O/hexane solution of **2m**. Crystal data collection and refinement parameters of **2m** are summarized in Table S1. Intensity data were collected at 296.83 K on a SuperNova Dual diffractometer using mirror-monochromated Cu Kα radiation, λ = 1.54184 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique, and refined by full-matrix least-squares procedures. Non hydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S1 Crystallographic data and structure refinement results of **2m**

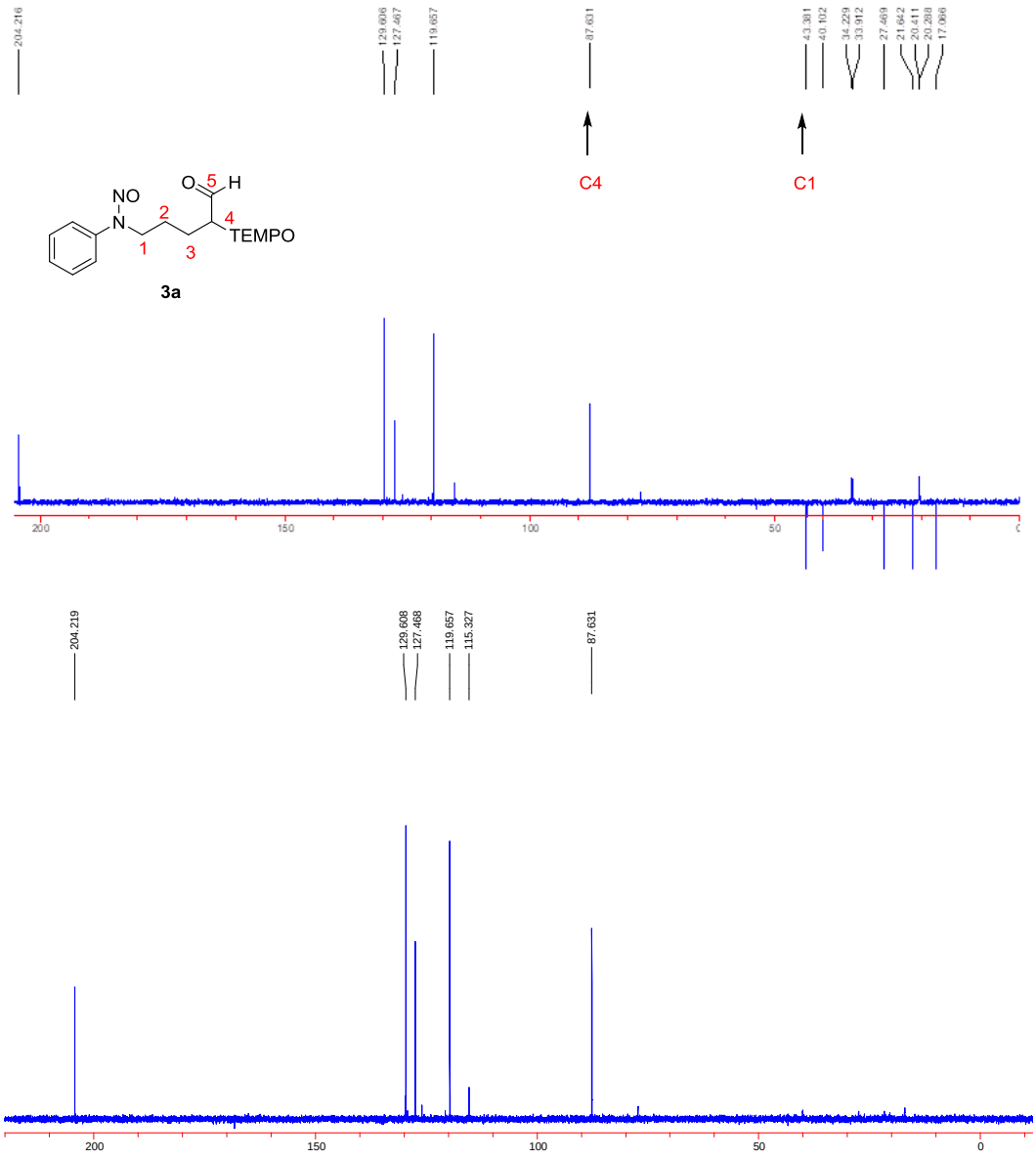
Empirical formula	$C_{12}H_{13}FN_2O_2$
Formula weight	236.24
Temp, K	296.83(10)
Crystal system	monoclinic
Space group	$P2_1/c$

a, Å	10.3361(8)
b, Å	15.5990(14)
c, Å	7.4565(5)
α (°)	90
β (°)	105.716(8)
γ (°)	90
Volume, Å^3	1157.29(16)
Z	4
d_{calc}, g cm^{-3}	1.356
λ, Å	1.54184
μ, mm^{-1}	0.878
No. of data collected	5095
No. of unique data	2223/0/155
R_{int}	0.0144
Goodness-of-fit on F^2	1.074
R_1, wR_2 ($I > 2\sigma(I)$)	0.0493, 0.1291
R_1, wR_2 (all data)	0.0649, 0.1557

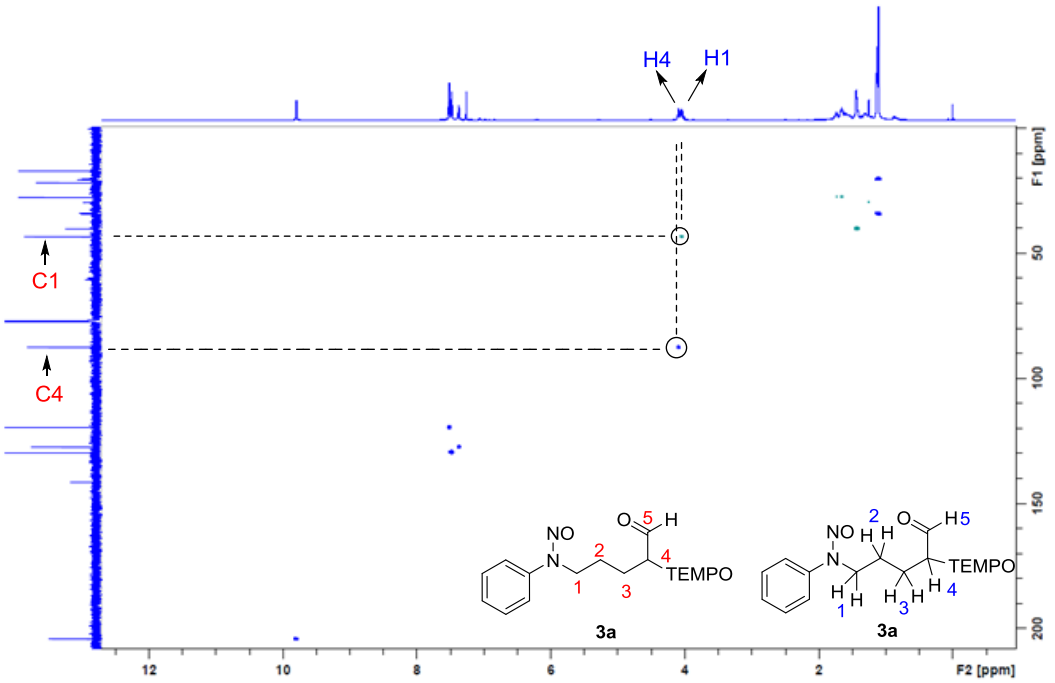
VIII. Copies of the DEPT 135, DEPT 90, C-H HSQC, H-H COSY Spectra of 3a

According to the DEPT 135 and DEPT 90 spectra of **3a** and the cross-peaks of **3a**-H4 to **3a**-C4 and **3a**-H1 to **3a**-C1 appeared on the C-H HSQC spectrum of **3a**, we could deduce that the peaks at 87.6 ppm and 43.4 ppm should be **3a**-C4 and **3a**-C1, respectively, and the peak of **3a**-H4 should on the left of the peak of **3a**-H1. In addition, the cross-peaks of **3a**-H5 to **3a**-H4 appeared on the H-H COSY spectrum of **3a** indicating that **3a**-H5 is adjacent to **3a**-H4.

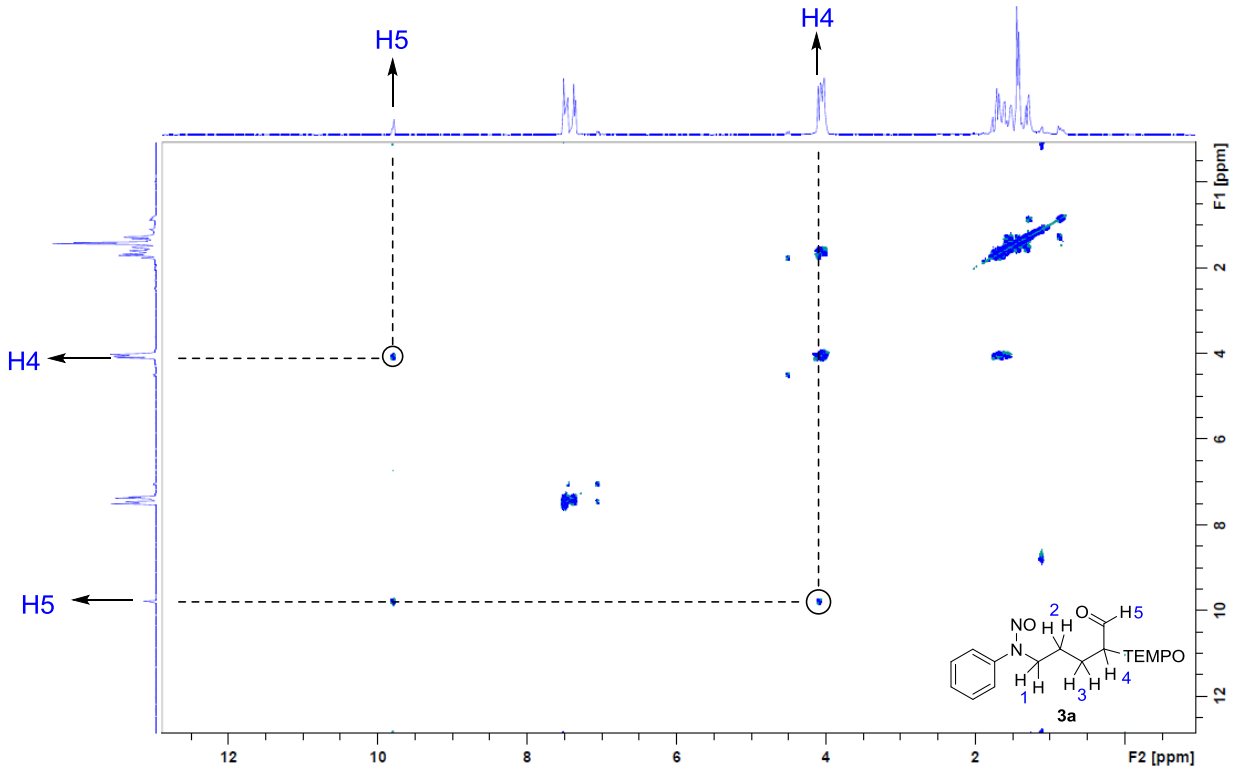
Copies of the DEPT 135 and DEPT 90 Spectra of 3a



Copy of the C-H HSQC Spectrum of 3a



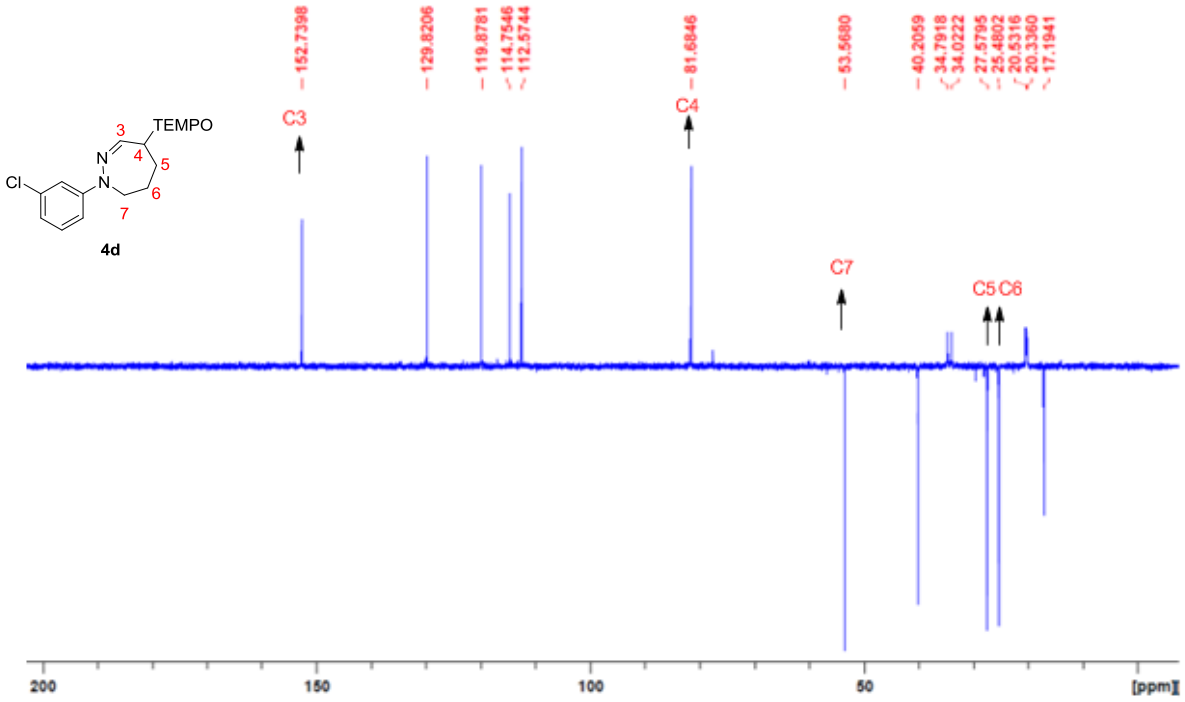
Copy of the H-H COSY Spectrum of 3a



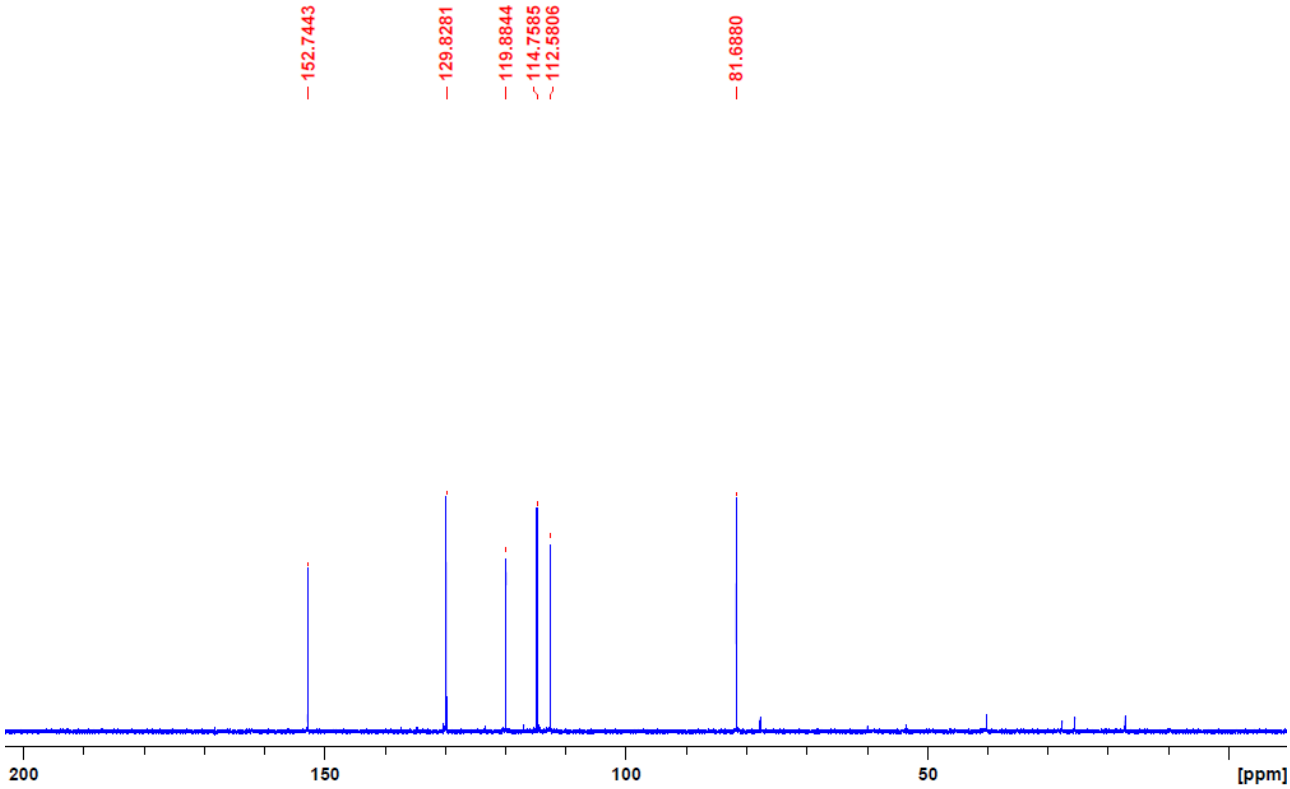
IX. (1) Copies of DEPT 135, DEPT 90, C-H HSQC, H-H COSY, C-H HMBC, TOCSY spectra of 4d

According to the DEPT 135 and DEPT 90 spectra of **4d**, the cross-peaks of **4d**-H3 to **4d**-C3, **4d**-H4 to **4d**-C4, **4d**-H5 to **4d**-C5, **4d**-H6 to **4d**-C6, and **4d**-H7 to **4d**-C7 appeared on the C-H HSQC spectrum of **4d**, and the cross-peaks of **4d**-H3 to **4d**-H4, **4d**-H4 to **4d**-H5, **4d**-H7 to **4d**-H6, and **4d**-H6 to **4d**-H5 appeared on the H-H COSY spectrum of **4d**, we could deduce that the peaks at 152.7 ppm, 81.7 ppm, 53.6 ppm, 27.6 ppm and 25.5 ppm should be **4d**-C3, **4d**-C4, **4d**-C7, **4d**-C5, and **4d**-C6, respectively. Moreover, it also suggests that **4d**-H3 and **4d**-H5 should be adjacent to **4d**-H4, **4d**-H5 should be adjacent to **4d**-H6, and **4d**-H6 should be adjacent to **4d**-H7. The cross-peaks of **4d**-C3 to **4d**-H4, **4d**-H5 and **4d**-H6, **4d**-C4 to **4d**-H3, **4d**-H5 and **4d**-H6, **4d**-C7 to **4d**-H5 and **4d**-H6, **4d**-C5 to **4d**-H3, **4d**-H4, **4d**-H7 and **4d**-H6, and **4d**-C6 to **4d**-H4, **4d**-H5 and **4d**-H7 appeared on the C-H HMBC spectrum of **4d** could further verify the above deduction. In addition, the protons of **4d**-H3, **4d**-H4, **4d**-H5, **4d**-H6, and **4d**-H7 within the same spin system can be detected in the H-H TOCSY spectrum of **4d.**

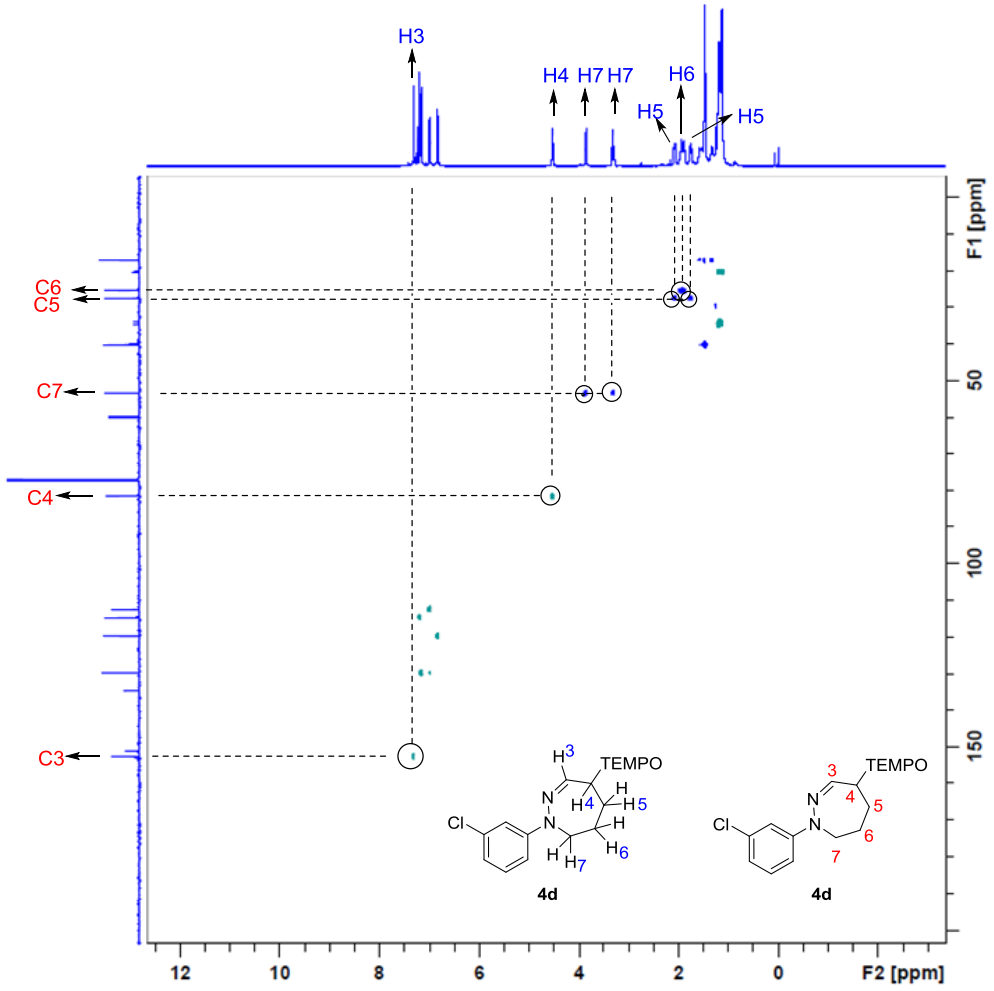
Copy of the DEPT 135 Spectrum of 4d



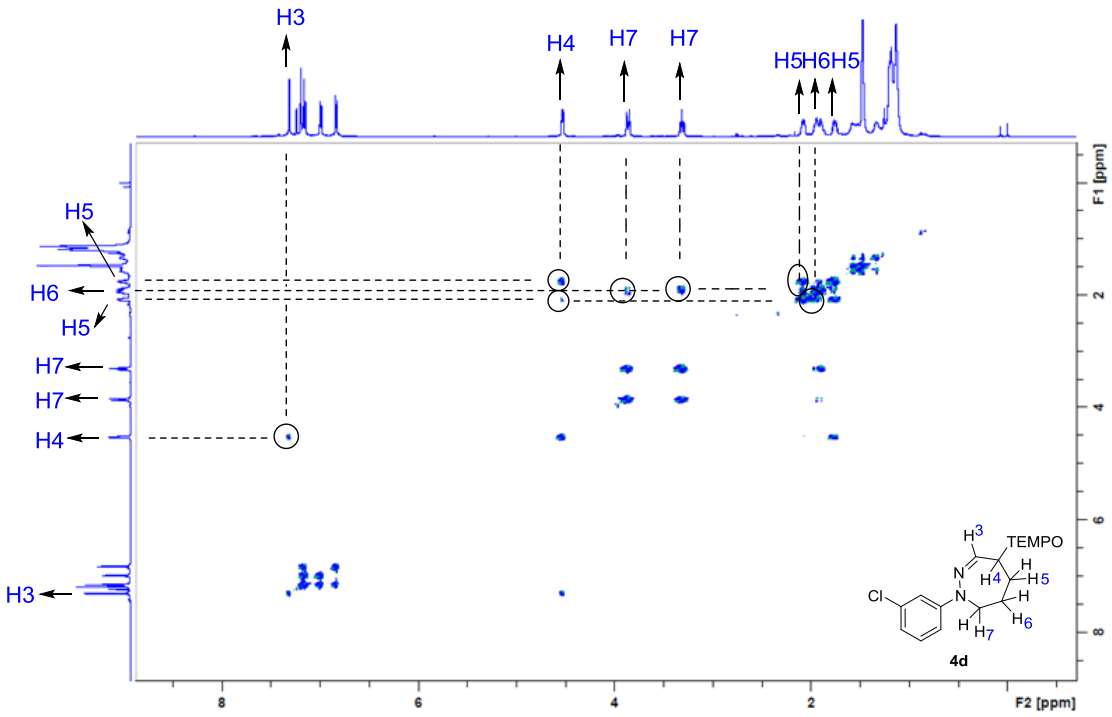
Copy of the DEPT 90 Spectrum of 4d



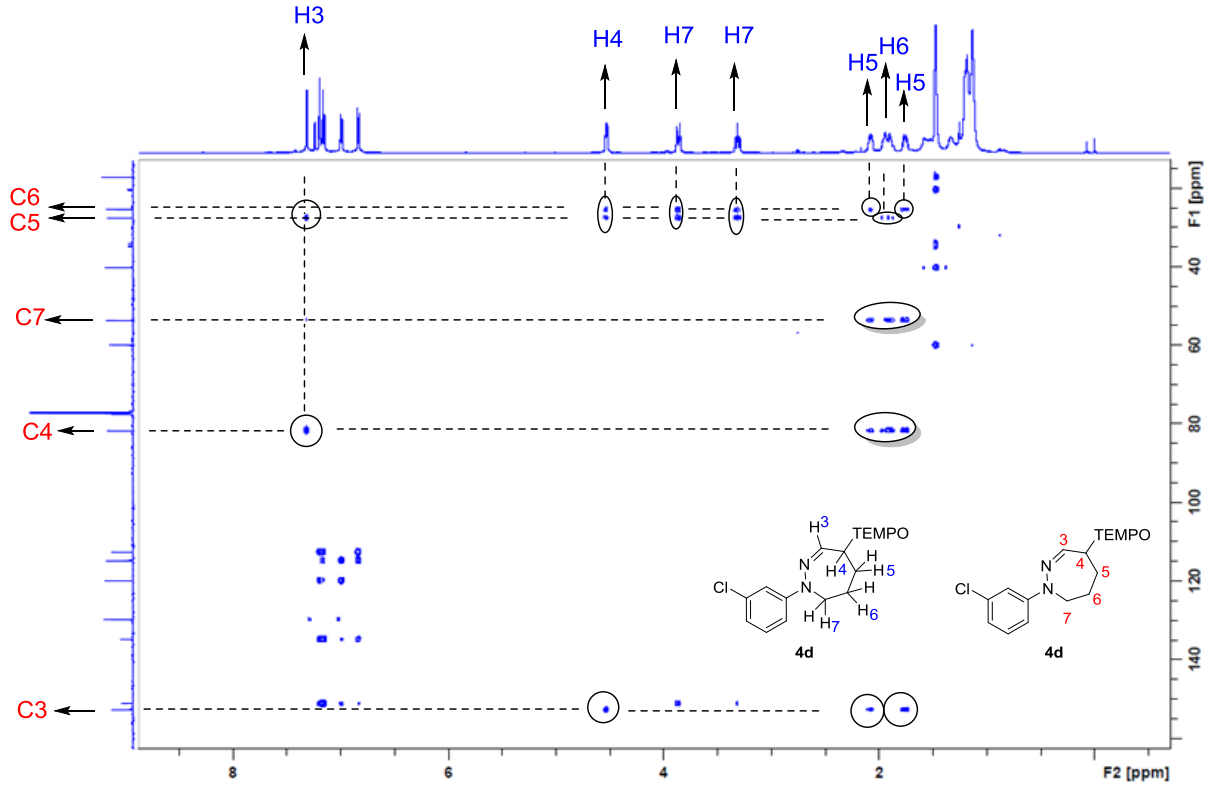
Copy of the C-H HSQC Spectrum of 4d



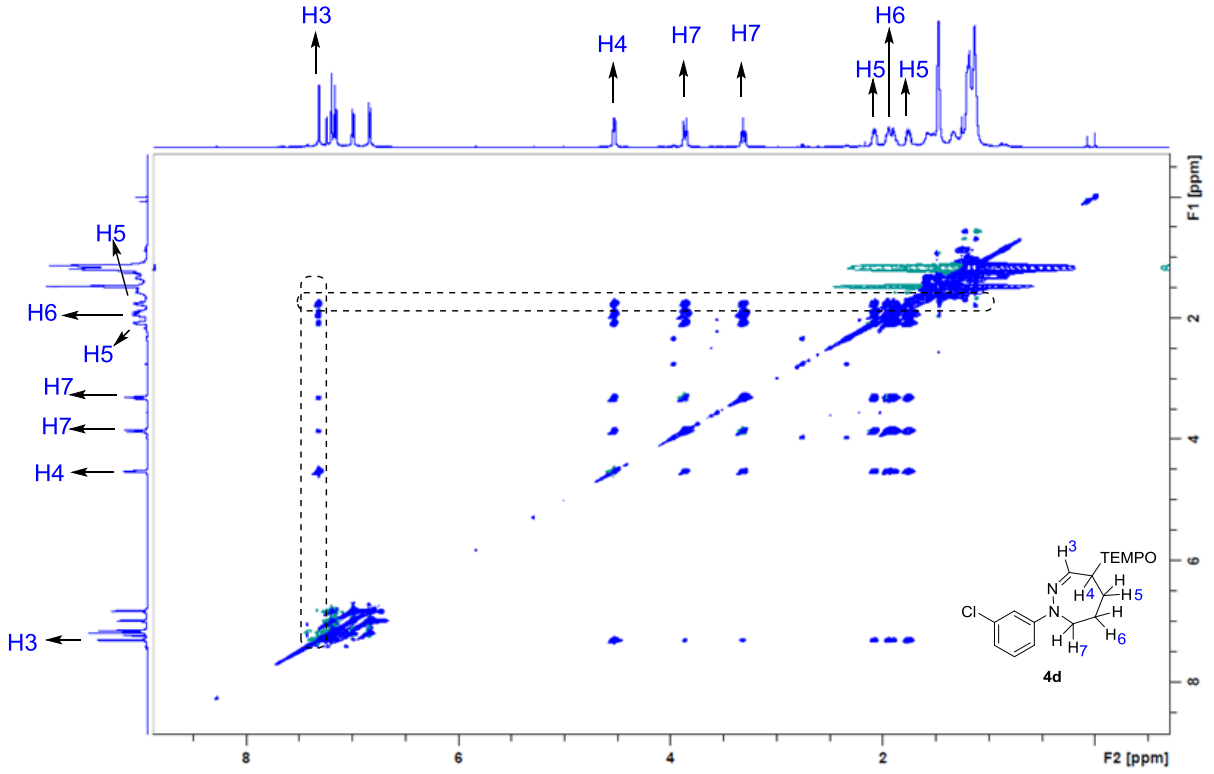
Copy of the H-H COSY Spectrum of 4d



Copy of the C-H HMBC Spectrum of 4d



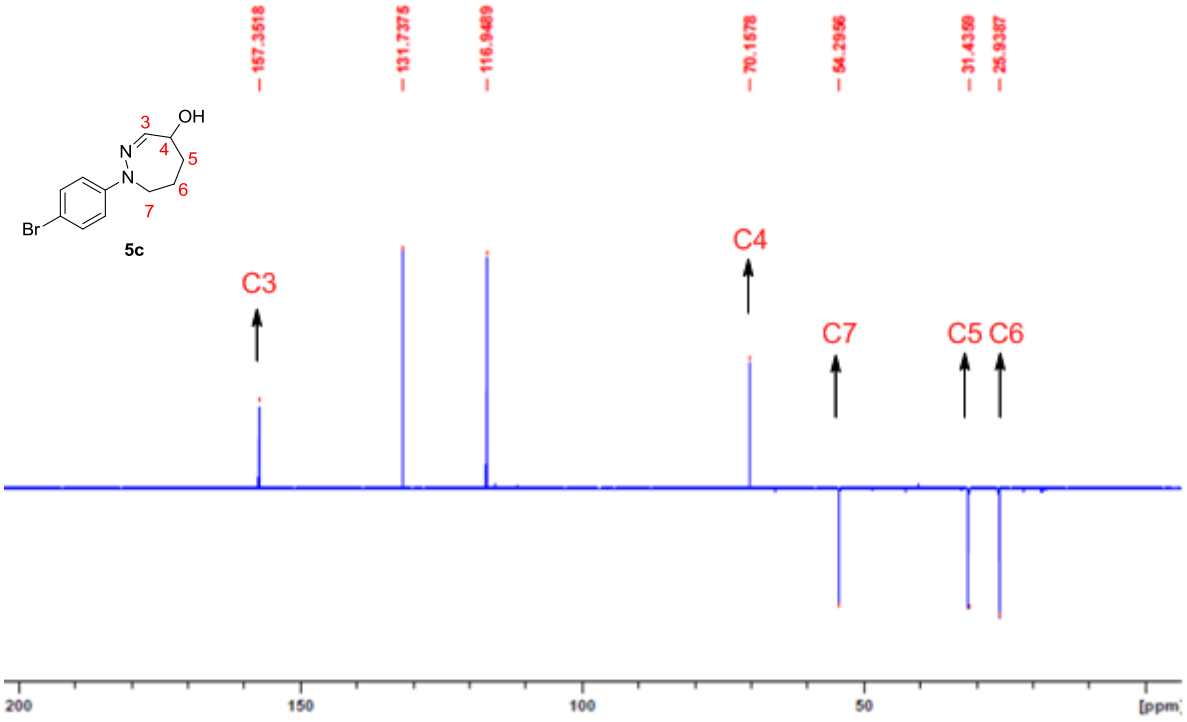
Copy of the TOCSY Spectrum of 4d



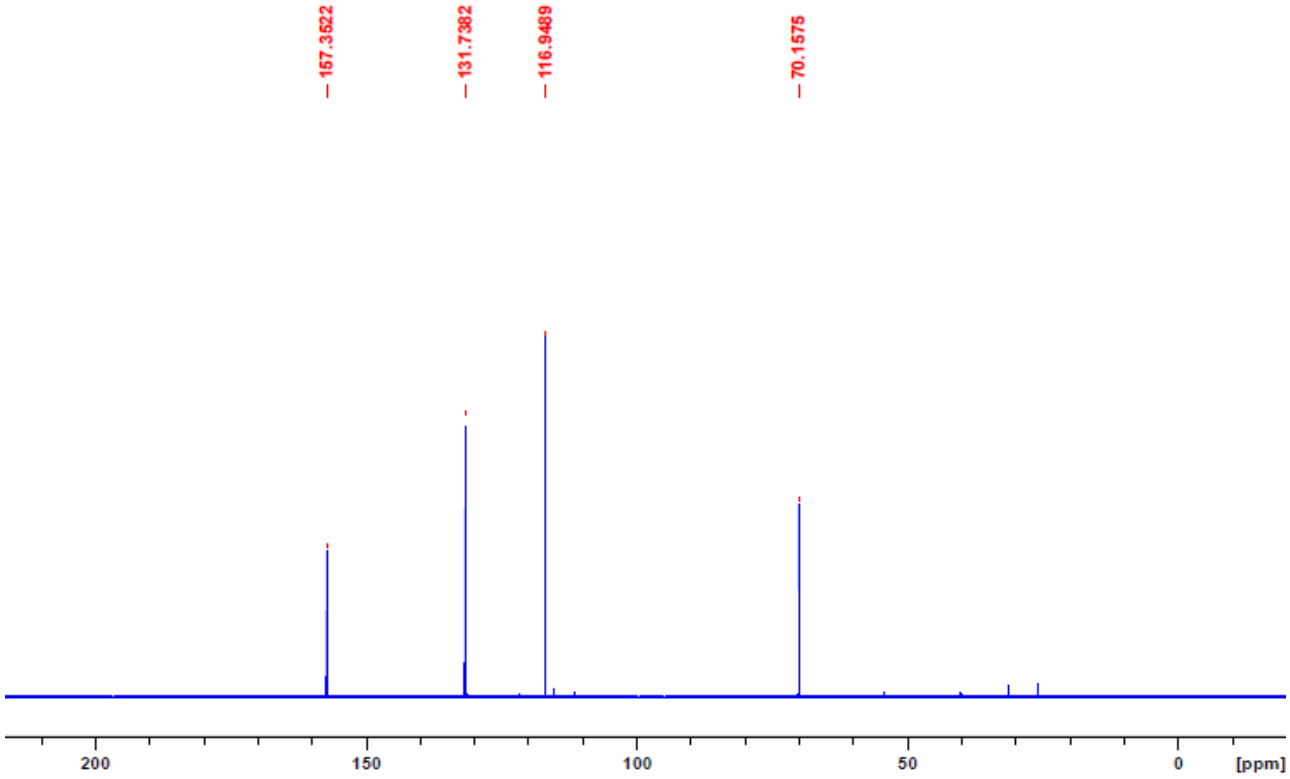
(2) Copies of DEPT 135, DEPT 90, C-H HSQC, H-H COSY, C-H HMBC, TOCSY spectra of 5c

According to the DEPT 135 and DEPT 90 spectra of **5c** the cross-peaks of **5c**-H3 to **5c**-C3, **5c**-H4 to **5c**-C4, **5c**-H5 to **5c**-C5, **5c**-H6 to **5c**-C6, and **5c**-H7 to **5c**-C7 appeared on the C-H HSQC spectrum of **5c**, and the cross-peaks of **5c**-H3 to **5c**-H4, **5c**-H4' to **5c**-H4, **5c**-H4 to **5c**-H5, **5c**-H7 to **5c**-H6, and **5c**-H6 to **5c**-H5 appeared on the H-H COSY spectrum of **5c**, we could deduce that the peaks at 157.4 ppm, 70.2 ppm, 54.3 ppm, 31.4 ppm and 25.9 ppm should be **5c**-C3, **5c**-C4, **5c**-C7, **5c**-C5 and **5c**-C6, respectively. Moreover, it also suggests that **5c**-H3 and **5c**-H5 should be adjacent to **5c**-H4, **5c**-H4' should be adjacent to **5c**-H4, **5c**-H5 should be adjacent to **5c**-H6, and **5c**-H6 should be adjacent to **5c**-H7. The cross-peaks of **5c**-C3 to **5c**-H4', **5c**-H4, and **5c**-H5, **5c**-C4 to **5c**-H3, **5c**-H4', **5c**-H5 and **5c**-H6, **5c**-C7 to **5c**-H5 and **5c**-H6, **5c**-C5 to **4d**-H3, **5c**-H4', **4d**-H4, **4d**-H7 and **4d**-H6, and **4d**-C6 to **4d**-H4, **4d**-H5, and **4d**-H7 appeared on the C-H HMBC spectrum of **5c** could further verify the above deduction. In addition, the protons of **5c**-H3, **5c**-H4', **5c**-H4, **5c**-H5, **5c**-H6, and **5c**-H7 within the same spin system can be detected in the H-H TOCSY spectrum of **5c.**

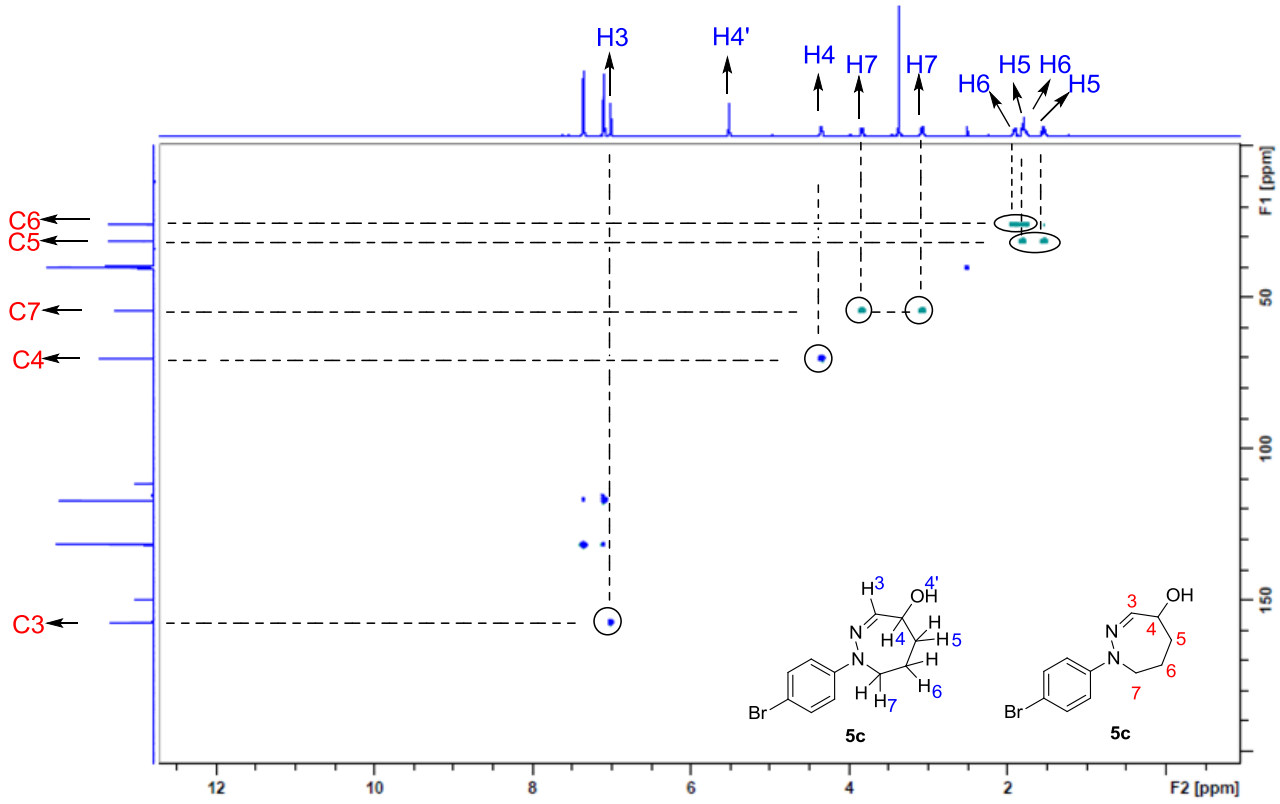
Copy of the DEPT 135 Spectrum of 5c



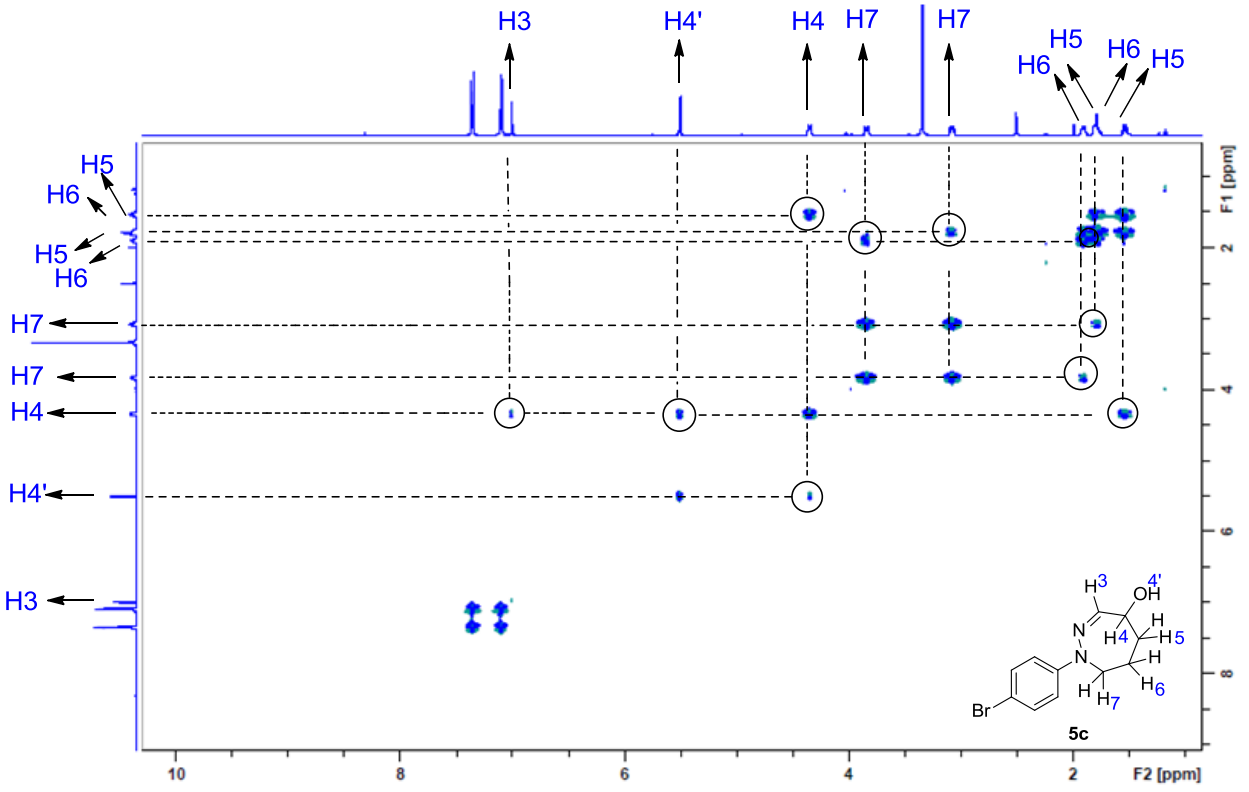
Copy of the DEPT 90 Spectrum of 5c



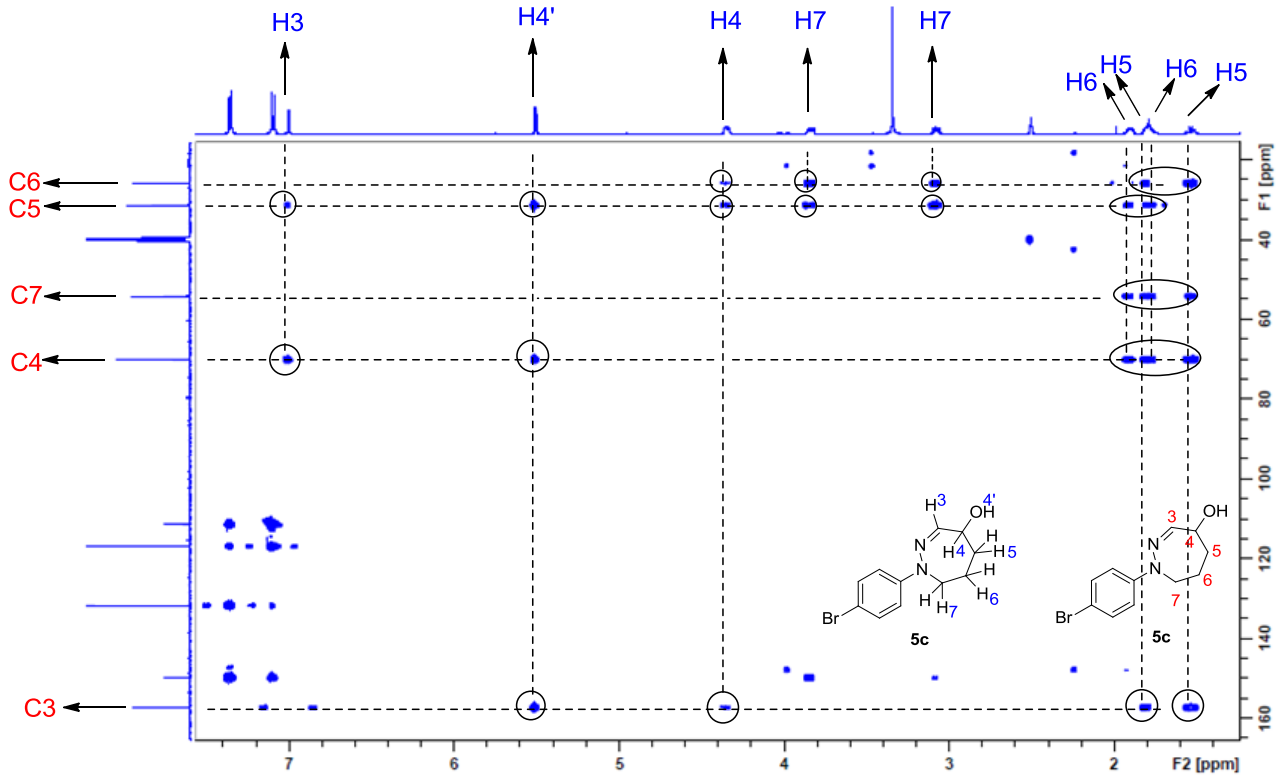
Copy of the C-H HSQC Spectrum of 5c



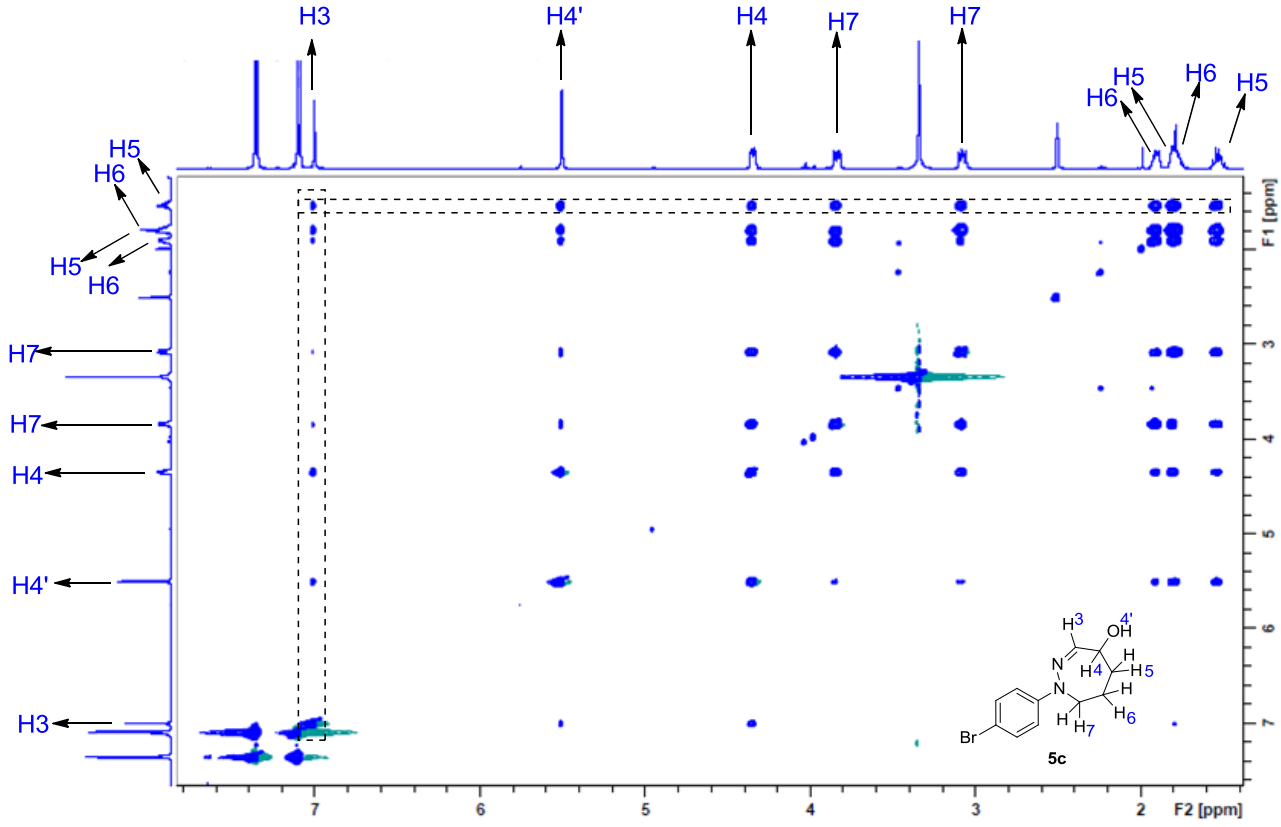
Copy of the H-H COSY Spectrum of 5c



Copy of the C-H HMBC Spectrum of 5c



Copy of the TOCSY Spectrum of 5c



X. References

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(4) Y. He, Z. Zheng, Y. Liu, J. Qiao, X. Zhang and X. Fan, *Org. Lett.*, 2019, **21**, 1676