

Electronic Supplementary Information

**One-step Construction of the Molecular Complexity by *tert*-
Butyl Nitrite (TBN)-initiated Cascade α,β -*sp*³ C-H Bond
Difunctionalization and C-N Bond Cleavage**

Kaixuan He,^[a] Pengfei Li,^[b] Shuwei Zhang,^[a] Qian Chen,^[a] Honghe Ji,
^[b] Yu Yuan^[a] and Xiaodong Jia^{*, [a]}

^[a] *School of Chemistry & Chemical Engineering, Yangzhou University, Yangzhou,
Jiangsu 225002, China*

^[b] *College of Chemistry & Chemical Engineering, Northwest Normal University,
Lanzhou, Gansu 730070, China*

jiaxd1975@163.com

ESI

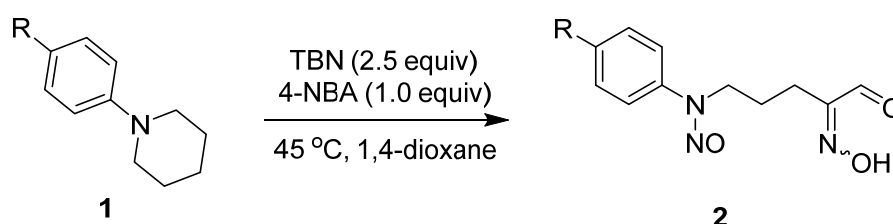
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General:

TBN were purchased from commercial source and used without further purification. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. ^1H NMR and ^{13}C NMR (400 MHz, 600MHz and 100 MHz, 150MHz respectively) spectra were recorded in CDCl_3 and d_6 -DMSO. Chemical shifts (δ) are reported in ppm using TMS as internal standard and spin-spin coupling constants (J) are given in Hz. The high resolution mass spectra (HRMS) were measured on an electrospray ionization (ESI) apparatus using time of flight (TOF) mass spectrometry.

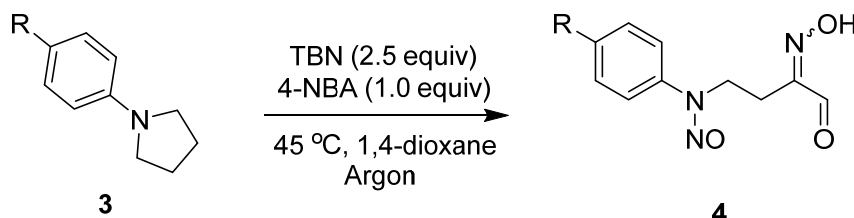
General Experimental Procedure

1. General experimental procedure for *N*-arylpiperidines



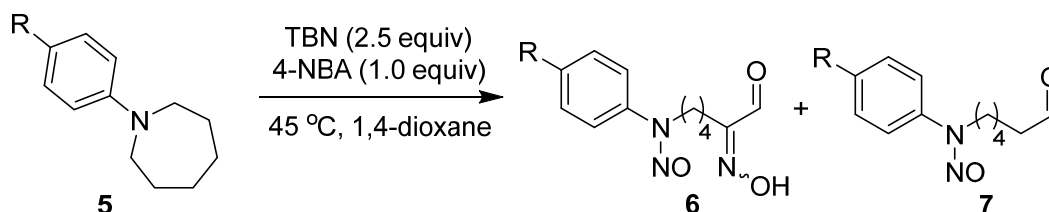
A solution of **1** (1 mmol) and 4-nitrobenzoic acid (1 mmol) in 1,4-dioxane (5 mL) was mixed fully, then TBN (2.5 eq) was added dropwise under air atmosphere. The reaction solution was stirred under 45 °C. After completion monitored by TLC (by UV visualization), the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1) to afford the products.

2. General experimental procedure for *N*-arylpyrrolines



A solution of **3** (1 mmol) and 4-nitrobenzoic acid (1 mmol) in 1,4-dioxane (5 mL) was mixed fully, then TBN (2.5 eq) was added dropwise under argon atmosphere. The reaction solution was stirred under 45 °C. After completion monitored by TLC (by UV visualization), the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1) to afford the products.

2. General experimental procedure for *N*-azepanes

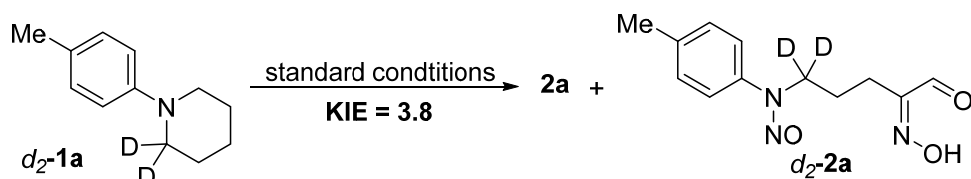


A solution of **5** (1 mmol) and 4-nitrobenzoic acid (1 mmol) in 1,4-dioxane (5 mL) was mixed

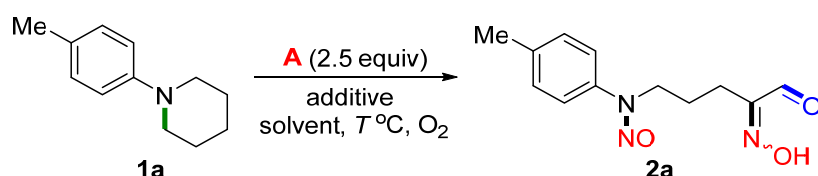
fully, then TBN (2.5 eq) was added dropwise under air atmosphere. The reaction solution was stirred under 45 °C. After completion monitored by TLC (by UV visualization), the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1) to afford the products **6** and **7** in pure form.

Measurement of KIE

The reaction of *d*₂-**1a** was performed under the standard reaction conditions, and the KIE value was obtained by ¹H NMR of the products mixture.



Optimization of the reaction conditions



Entry	Solvent	A	Additive (x equiv)	Time (h)	Yield (%) ^b
1	MeOPh	AN	TEMPO (0.1)	5	58 ^{c, d}
2	MeCN	AN	TEMPO (0.1)	5	37 ^{c, d}
3	dioxane	AN	TEMPO (0.1)	3	64 ^{c, d}
4	dioxane	AN	TEMPO (0.1)	2	63 ^{c, e}
5	dioxane	AN	TEMPO (0.1)	2	39 ^{e, f}
6	dioxane	AN	-	2	64 ^{c, e}
7	dioxane	TBN	TEMPO (0.1)	1	40 ^{c, e}
8	dioxane	IPN	-	2	62 ^{c, e}
9	dioxane	BN	-	2	65 ^{c, e}
10	dioxane	IBN	-	2	54 ^{c, e}
11	dioxane	TBN	-	2	69 ^{c, e, g}
12	dioxane	TBN	-	2	66 ^{e, f}
13	dioxane	TBN	<i>p</i> -TsOH (1)	12	trace ^{c, e}
14	dioxane	TBN	TfOH (1)	12	trace ^{c, e}
15	dioxane	TBN	^t BuCO ₂ H (1)	2	45 ^{c, e}
16	dioxane	TBN	4-PA (1)	2	42 ^{c, e}
17	dioxane	TBN	<i>o</i> -MBA (1)	1	65 ^{c, e}
18	dioxane	TBN	<i>p</i> -NBA (1)	1	78 ^{c, e}

^a AN = amyl nitrite; IPN = isopentyl nitrite; BN = butyl nitrite; IBN = isobutyl nitrite; 4-PA = 4-Picolinic acid; *o*-MBA = *o*-Methylbenzoic acid; *p*-NBA = 4-Nitrobenzoic acid ^b Isolated yield; ^c O₂ atmosphere; ^d At room temperature; ^e At 45 °C; ^f Argon atmosphere; ^g The nitrated product, 1-(4-methyl-2-nitrophenyl)piperidine, was isolated in 22% yield.

Initially, we used an *N*-arylpiperidine derivative **1a** as the representative model substrate and AN/TEMPO as the catalyst system to test this cascade C-H and C-N multifunctionalization. To our delight, in the presence of 2.5 equivalent of amyl nitrite and 10 mol % of TEMPO, the

reaction occurred smoothly, and a multifunctionalized product **2a** was isolated in 58% yield (entry 1), in which an oxime, N-NO and aldehyde functional group were constructed directly, through $\alpha,\beta\text{-sp}^3$ C-H bond difunctionalization together with the C-N bond cleavage. With this promising result in hand, a brief solvent screen was then performed (entries 1-3), and 1,4-dioxane gave the best result, leading to **2a** in 64% isolated yield. At higher reaction temperature, a comparable yield was obtained and the reaction time was shortened (entry 4). Since the alkyl nitrite could generate NO and alkoxy radicals under heat to initiate further radical reactions, we tested this C-N cleavage process under argon atmosphere. The reaction occurred smoothly, albeit resulting in only moderate yield (entry 5). This result suggested that the C-H bond activation and further C-N bond cleavage were initiated by AN, and the existence of dioxygen could accelerate the generation of active radicals.^[12] Even in the absence of TEMPO, the reaction efficiency was not affected (entry 6). Then, a series of commercially available alkyl nitrites were tested (entries 7-12), and *tert*-butyl nitrite (TBN) exhibited highest reactivity, furnishing the expected product in 69% yield (entry 11). During the investigation of these reactions, nitration on the electron-rich phenyl ring was observed, decreasing the yield of the desired product (entry 11). We hypothesized that if the electron density of the phenyl group is decreased by protonation, the nitration process might be suppressed. Consequently, addition of Brønsted acids might be beneficial to prevent the formation of the nitrated by-product. However, on the other hand, once the corresponding ammonium salt is formed, the initiated C-H bond oxidation would be hampered due to deactivation of the $\alpha\text{-sp}^3$ C-H bond. So acidic additives with proper acidity might be of great importance to inhibit the nitration process but not reduce the reactivity of the adjacent C-H bond (entries 13-18). Fortunately, after several attempts, 4-nitrobenzoic acid was proved to be competent, and the nitration was totally inhibited, delivering the desired product in 78% yield (entry 18).

Applications of the multifunctionalized products

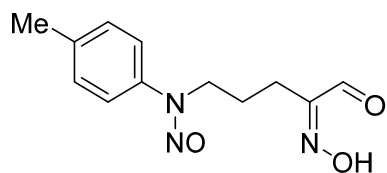
1. Condensation with phenylhydrazine, amines and hydroxylamine

A solution of **2a** (0.5 mmol) and phenylhydrazine, amines or hydroxylamine (0.5 mmol) in methanol (5 mL) was mixed fully. The reaction solution was stirred at room temperature. After completion monitored by TLC (by UV visualization), the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography eluted with petroleum ether/ ethyl acetate (v/v 6:1-4:1) to afford the products **8-11** in pure form. It is worth noting that for the reaction of cyclopropanamine, after the solvent was removed, only recrystallization from alcohol could afford the product **10** in pure form.

2. Wittig reaction of **2a**

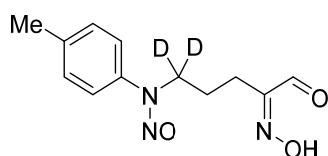
A solution of ethyl (triphenylphosphoranylidene)acetate (1 mmol) in dichloromethane (5 mL) was flushed with argon. The yellow solution is stirred at 25°C as a solution of trimethylamine (1 mmol) in 2 mL of dichloromethane is added dropwise over 5 min. After 10 min, **2a** in 2 mL of dichloromethane is added dropwise to the vigorously stirred solution. After completion monitored by TLC (by UV visualization), the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography eluted with petroleum ether/ ethyl acetate (v/v 4:1) to afford the product **12** in pure form.

Analytical data for compounds



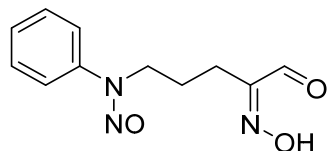
***N*-(4-(Hydroxyimino)-5-oxopentyl)-*N*-(*p*-tolyl)nitrous amide (2a)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; ^1H NMR (400 MHz, CDCl_3) δ 10.12 (s, OH, 1H), 9.43 (s, 1H), 7.36 (d, $J = 7.9$ Hz, 2H), 7.25 (d, $J = 7.9$ Hz, 2H), 4.04 (t, $J = 7.7$ Hz, 2H), 2.49 (t, $J = 7.7$ Hz, 2H), 2.38 (s, 3H), 1.79 – 1.68 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 191.0, 190.9, 159.6, 138.7, 137.9, 130.2, 130.1, 125.8, 120.2 (two ^{13}C), 44.2, 44.1, 22.3, 20.9, 19.3; HRMS (ESI): Calc'd for $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_3 + \text{Na}^+$, 272.1006; found, 272.1002.



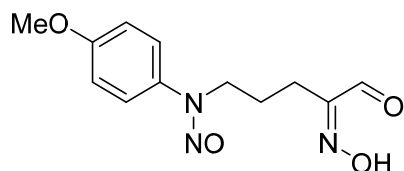
***N*-(4-(Hydroxyimino)-5-oxopentyl-1,1- d_2)-*N*-(*p*-tolyl)nitrous amide (d_2 -2a)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; ^1H NMR (400 MHz, CDCl_3) δ 10.71 (s, OH, 2H), 9.42 (s, 1H), 7.34 (d, $J = 8.5$ Hz, 2H), 7.23 (d, $J = 8.2$ Hz, 3H), 4.02 (t, $J = 7.6$ Hz, 0.46H), 2.48 (t, $J = 7.6$ Hz, 2H), 2.35 (s, 3H), 1.78 – 1.62 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 191.3, 159.6, 138.6, 138.0, 130.2, 130.1, 125.7, 120.3, 120.2, 44.4, 22.3, 22.1, 20.9, 19.3; HRMS (ESI): Calc'd for $\text{C}_{12}\text{H}_{13}\text{D}_2\text{N}_3\text{O}_3 + \text{Na}^+$, 274.1131; found, 274.1126.



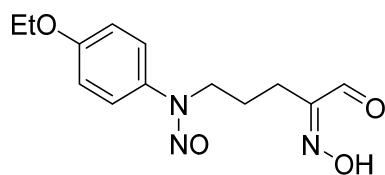
***N*-(4-(Hydroxyimino)-5-oxopentyl)-*N*-phenylnitrous amide (2b)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 6:1); red oil; ^1H NMR (400 MHz, CDCl_3) δ 10.62 (s, OH, 1H), 9.42 (s, 1H), 7.45 (m, 4H), 7.36 (t, $J = 7.5$ Hz, 1H), 4.03 (t, 2H), 2.49 (t, $J = 7.7$ Hz, 2H), 1.79 – 1.68 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 191.2, 159.5, 141.1, 129.6, 127.8, 120.1, 44.1, 22.3, 19.3. HRMS (ESI): Calc'd for $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_3 + \text{Na}^+$, 258.0849; found, 258.0847.



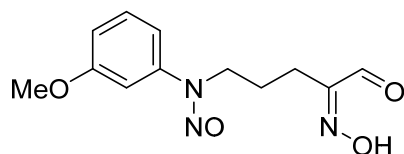
***N*-(4-(Hydroxyimino)-5-oxopentyl)-*N*-(4-methoxyphenyl)nitrous amide (2c)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 6:1); red oil; ^1H NMR (400 MHz, CDCl_3) δ 10.27 (s, OH, 1H), 9.42 (s, 1H), 7.37 (d, $J = 9.1$ Hz, 2H), 6.96 (d, $J = 9.1$ Hz, 2H), 4.00 (t, $J = 7.6$ Hz, 2H), 3.82 (s, 3H), 2.47 (t, $J = 7.6$ Hz, 2H), 1.98 – 1.60 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 191.1, 190.9, 159.6, 159.2, 134.4, 122.4, 122.1, 114.7, 114.7, 55.7, 55.5, 44.6, 22.3, 19.3. HRMS (ESI): Calc'd for $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_4 + \text{Na}^+$, 288.0960; found, 288.0951.



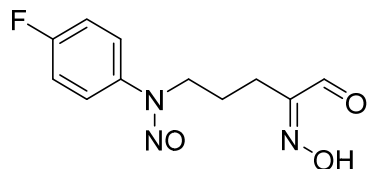
***N*-(4-Ethoxyphenyl)-*N*-(4-(hydroxyimino)-5-oxopentyl)nitrous amide (2d)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 6:1); red oil; ¹H NMR (400 MHz, CDCl₃) δ 10.55 (s, *OH*, 1H), 9.42 (s, 1H), 7.35 (d, *J* = 6.1 Hz, 2H), 6.95 (d, *J* = 6.2 Hz, 2H), 4.07 – 3.96 (m, 4H), 2.47 (t, 2H), 1.78 – 1.65 (m, 2H), 1.40 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 191.1, 159.6, 158.6, 134.2, 127.2, 122.3, 115.2, 63.9, 44.7, 22.3, 19.3, 14.7; HRMS (ESI): Calc'd for C₁₃H₁₇N₃O₄ + Na⁺, 302.1111; found, 302.1108.



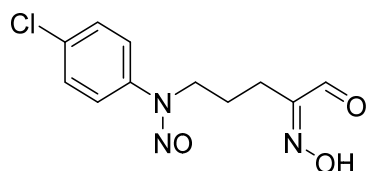
***N*-(4-(Hydroxyimino)-5-oxopentyl)-*N*-(3-methoxyphenyl)nitrous amide (2e)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 6:1); red oil; ¹H NMR (400 MHz, CDCl₃) δ 9.97 (s, *OH*, 1H), 9.43 (s, 1H), 7.35 (t, *J* = 8.2 Hz, 1H), 7.09 (s, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 8.3, 1.5 Hz, 1H), 4.00 (t, *J* = 8.0 Hz, 2H), 3.83 (s, 3H), 2.49 (t, *J* = 7.7 Hz, 2H), 1.78 – 1.68 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 190.8, 160.4, 159.7, 142.3, 130.3, 113.2, 111.8, 105.9, 55.5, 43.8, 22.3, 19.3; HRMS (ESI): Calc'd for C₁₂H₁₅N₃O₄ + Na⁺, 288.0955; found, 288.0958.



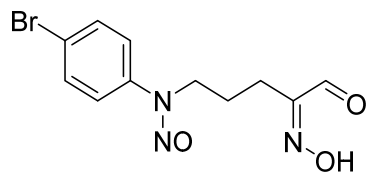
***N*-(4-Fluorophenyl)-*N*-(4-(hydroxyimino)-5-oxopentyl)nitrous amide (2f)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; ¹H NMR (400 MHz, CDCl₃) δ 10.54 (s, *OH*, 1H), 9.41 (s, 1H), 7.44 (m, 2H), 7.13 (m, 2H), 4.00 (t, *J* = 7.9 Hz, 2H), 2.46 (t, *J* = 7.7 Hz, 2H), 1.78 – 1.64 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 191.2, 162.0 (d, *J*_{C-F} = 248.2 Hz), 159.5, 137.3 (d, *J*_{C-F} = 3.1 Hz), 122.4 (d, *J*_{C-F} = 8.5 Hz), 116.5 (d, *J*_{C-F} = 23.0 Hz), 44.4, 22.2, 19.2; HRMS (ESI): Calc'd for C₁₁H₁₂FN₃O₄ + Na⁺, 276.0755; found, 276.0755.



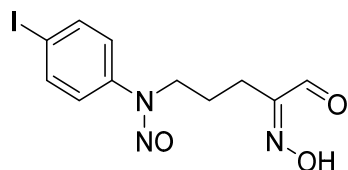
***N*-(4-Chlorophenyl)-*N*-(4-(hydroxyimino)-5-oxopentyl)nitrous amide (2g)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; ¹H NMR (400 MHz, CDCl₃) δ 10.55 (s, *OH*, 1H), 9.41 (s, 1H), 7.45 – 7.36 (m, 4H), 3.99 (t, *J* = 7.6 Hz, 2H), 2.46 (t, *J* = 7.7 Hz, 2H), 1.77 – 1.63 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 191.2, 159.5, 139.6, 133.4, 129.7, 121.1, 43.8, 22.2, 19.2; HRMS (ESI): Calc'd for C₁₁H₁₂ClN₃O₄ + Na⁺, 292.0459; found, 276.0755.



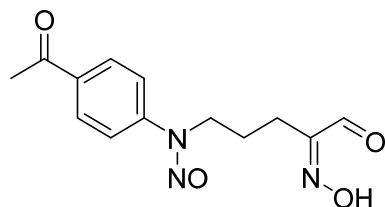
***N*-(4-Bromophenyl)-*N*-(4-(hydroxyimino)-5-oxopentyl)nitrous amide (2h)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; ¹H NMR (400 MHz, CDCl₃) δ 10.36 (s, *OH*, 1H), 9.41 (s, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 3.98 (t, *J* = 7.6 Hz, 2H), 2.46 (t, *J* = 7.7 Hz, 2H), 1.77 – 1.63 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 191.2, 191.1, 159.5, 140.1, 132.8, 132.7, 127.7, 121.2, 43.6, 22.2, 19.3. HRMS (ESI): Calc'd for C₁₁H₁₂BrN₃O₄ + Na⁺, 335.9954; found, 335.9950.



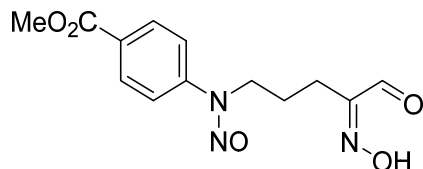
***N*-(4-(Hydroxyimino)-5-oxopentyl)-*N*-(4-iodophenyl)nitrous amide (2i)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; ¹H NMR (400 MHz, CDCl₃) δ 10.27 (s, *OH*, 1H), 9.42 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 3.98 (t, *J* = 7.6 Hz, 2H), 2.47 (t, *J* = 7.7 Hz, 2H), 1.76 – 1.65 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 191.0, 159.5, 140.8, 138.6, 121.3, 92.3, 43.4, 22.2, 19.3; HRMS (ESI): Calc'd for C₁₁H₁₂IN₃O₄ + Na⁺, 383.9816; found, 383.9813.



***N*-(4-Acetylphenyl)-*N*-(4-(hydroxyimino)-5-oxopentyl)nitrous amide (2j)**

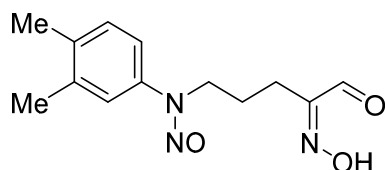
Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 4:1); light yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 10.74 (s, *OH*, 1H), 9.43 (s, 1H), 8.05 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 4.02 (t, 2H), 2.63 (s, 3H), 2.49 (t, *J* = 7.6 Hz, 2H), 1.77 – 1.64 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 197.9, 191.1, 159.4, 145.0, 135.2, 130.1, 118.3, 42.8, 26.6, 22.3, 19.2; HRMS (ESI): Calc'd for C₁₃H₁₅N₃O₄ + Na⁺, 300.0960; found, 300.0972.



Methyl 4-((4-(hydroxyimino)-5-oxopentyl)(nitroso)amino)benzoate (2k)

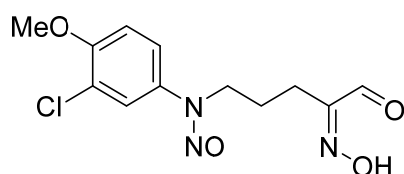
Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; ¹H NMR (400 MHz, CDCl₃) δ 9.57 (s, *OH*, 1H), 9.44 (s, 1H), 8.13 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 4.01 (t, *J* = 7.6 Hz, 2H), 2.63 (s, 3H), 2.50 (t, *J* = 7.6 Hz, 2H), 1.76 – 1.67 (m, 2H); ¹³C

NMR (101 MHz, CDCl₃) δ 190.7, 166.4, 159.6, 144.8, 131.4, 131.2, 128.6, 118.2, 117.9, 52.4, 42.7, 41.4, 22.6, 22.3, 19.2, 15.2; HRMS (ESI): Calc'd for C₁₃H₁₅N₃O₅ + Na⁺, 316.0909; found, 316.0926.



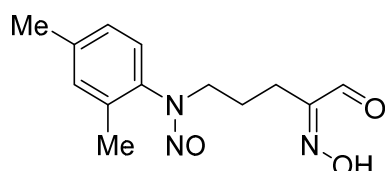
***N*-(3,4-Dimethylphenyl)-*N*-(4-(hydroxyimino)-5-oxopentyl)nitrous amide (2l)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 6:1); red oil; ¹H NMR (400 MHz, CDCl₃) δ 10.64 (s, OH, 1H), 9.43 (s, 1H), 7.26 (s, 1H), 7.17 (m, 2H), 4.01 (t, *J* = 7.6 Hz, 2H), 2.48 (t, *J* = 7.7 Hz, 2H), 2.29 (s, 3H), 2.26 (s, 3H), 1.78 – 1.68 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 191.2, 159.6, 138.9, 138.1, 136.7, 130.5, 121.7, 117.8, 44.4, 22.3, 19.9, 19.3 (two ¹³C); HRMS (ESI): Calc'd for C₁₃H₁₇N₃O₃ + Na⁺, 286.1162; found, 286.1157.



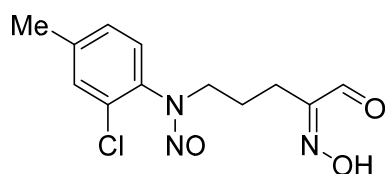
***N*-(3-Chloro-4-methoxyphenyl)-*N*-(4-(hydroxyimino)-5-oxopentyl)nitrous amide (2m)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; ¹H NMR (400 MHz, CDCl₃) δ 10.45 (s, OH, 1H), 9.41 (s, 1H), 7.51 (d, *J* = 2.6 Hz, 1H), 7.31 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.98 (d, *J* = 8.9 Hz, 1H), δ 3.96 (t, *J* = 7.6 Hz, 2H), 3.90 (s, 3H), 2.45 (t, *J* = 7.7 Hz, 2H), 1.75 – 1.63 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 191.1, 159.5, 154.7, 134.6, 123.4, 122.8, 120.0, 112.4, 56.5, 44.3, 22.3, 19.3; HRMS (ESI): Calc'd for C₁₂H₁₄ClN₃O₄ + Na⁺, 322.0565; found, 322.0561.



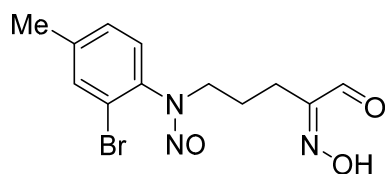
***N*-(2,4-Dimethylphenyl)-*N*-(4-(hydroxyimino)-5-oxopentyl)nitrous amide (2n)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 6:1); red oil; ¹H NMR (400 MHz, CDCl₃) δ 10.91 (s, OH, 1.5H), 9.44 (s, 0.6H), 9.39 (s, 1H), 7.17 – 7.01 (m, 5H), 6.83 (d, *J* = 7.9 Hz, 1H), 4.53 – 4.42 (m, 0.8H), 4.36 – 4.26 (m, 0.8H), 3.95 – 3.87 (m, 2H), 2.60 (t, *J* = 7.8 Hz, 1.4H), 2.50 – 2.41 (m, 2H), 2.35 (s, 3H), 2.30 (s, 2.3H), 2.16 (s, 3H), 1.99 – 1.86 (m, 3.6H), 1.75 – 1.59 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 191.4, 191.4, 159.5 (two ¹³C), 139.9, 139.6, 137.4, 135.1, 134.2, 132.3, 131.8, 127.8, 127.6, 126.4, 125.9, 54.2, 46.9, 24.3, 22.1, 21.1 (two ¹³C), 19.5, 19.2, 17.9, 17.7; HRMS (ESI): Calc'd for C₁₃H₁₇N₃O₃ + Na⁺, 286.1162; found, 286.1152.



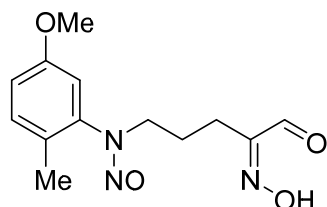
***N*-(2-Chloro-4-methylphenyl)-*N*-(4-(hydroxyimino)-5-oxopentyl)nitrous amide
(2o)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; ^1H NMR (400 MHz, CDCl_3) δ 10.35 (s, *OH*, 1H), 10.25 (s, *OH*, 1H), 9.44 (s, 0.5H), 9.39 (s, 1H), 7.35 (s, 1H), 7.31 – 7.24 (m, 1.6H), 7.18 (d, $J = 8.0$ Hz, 1H), 7.16 – 7.09 (m, 0.7H), 6.95 (d, $J = 8.0$ Hz, 0.6H), 4.63 – 4.25 (m, 1.7H), 4.01 – 3.90 (m, 2H), 2.62 (t, $J = 7.8$ Hz, 1.3H), 2.47 – 2.40 (m, 2H), 2.38 (s, 3H), 2.33 (s, 1.9H), 1.96 – 1.84 (m, 1.3H), 1.70 – 1.59 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 191.3, 191.2, 159.7, 159.7, 141.8, 141.6, 135.9, 132.5, 131.2, 131.0, 130.9, 130.7, 128.9, 128.7, 128.6 (two ^{13}C), 53.5, 46.3, 24.2, 22.2, 21.0, 21.0, 19.4, 19.2; HRMS (ESI): Calc'd for $\text{C}_{12}\text{H}_{14}\text{ClN}_3\text{O}_3 + \text{Na}^+$, 306.0616; found, 306.0612.



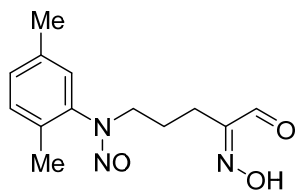
***N*-(2-Bromo-4-methylphenyl)-*N*-(4-(hydroxyimino)-5-oxopentyl)nitrous amide
(2p)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; ^1H NMR (400 MHz, CDCl_3) δ 10.10 (s, *OH*, 0.6H), 9.99 (s, *OH*, 1H), 9.45 (s, 0.6H), 9.40 (s, 1H), 7.54 (s, 1H), 7.48 (s, 0.6H), 7.26 – 7.20 (m, 2H), 7.20 – 7.12 (m, 1H), 6.93 (d, $J = 8.0$ Hz, 0.6H), 4.69 – 4.55 (m, 0.7H), 4.35 – 4.23 (m, 0.8H), 3.98 – 3.88 (m, 2H), 2.63 (t, $J = 7.9$ Hz, 1.2H), 2.48 – 2.41 (m, 2H), 2.39 (s, 3H), 2.34 (s, 1.8H), 1.99 – 1.85 (m, 1.6H), 1.72 – 1.57 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 191.2, 191.1, 159.7, 159.6, 141.9, 141.7, 137.4, 134.4, 134.3, 134.1, 129.3, 129.2, 129.1, 128.8, 120.7, 120.5, 53.4, 46.4, 24.2, 22.1, 20.9, 20.9, 19.4, 19.2; HRMS (ESI): Calc'd for $\text{C}_{12}\text{H}_{14}\text{BrN}_3\text{O}_3 + \text{Na}^+$, 350.0111; found, 350.0111.



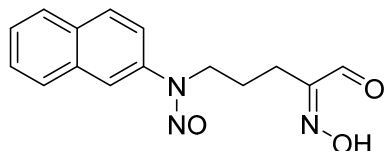
***N*-(4-(Hydroxyimino)-5-oxopentyl)-*N*-(5-methoxy-2-methylphenyl)nitrous amide
(2q)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; ^1H NMR (600 MHz, CDCl_3) δ 10.87 (s, *OH*, 1H), 9.45 (s, 0.4H), 9.41 (s, 1H), 7.31 – 7.25 (m, 0.4H), 7.22 (d, $J = 8.4$ Hz, 1H), 7.16 (d, $J = 8.6$ Hz, 0.4H), 7.14 (s, 1H), 6.97 – 6.89 (m, 1.4H), 6.87 (d, $J = 8.4$ Hz, 0.4H), 6.81 (s, 0.4H), 4.43 (t, $J = 6.9$ Hz, 0.8H), 3.96 (t, $J = 7.5$ Hz, 2H), 3.81 (s, 3H), 3.73 (s, 1.2H), 2.65 – 2.60 (m, 0.9H), 2.44 (t, $J = 7.8$ Hz, 2H), 2.32 (s, 3H), 2.27 (s, 1.3H), 1.92 – 1.83 (m, 0.9H), 1.73 – 1.61 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 191.4, 191.4, 159.8, 151.8, 151.4, 131.5, 131.1, 130.6, 130.6, 129.5, 129.3, 128.4, 125.4, 120.7, 113.9, 112.1, 112.0, 55.8 (two ^{13}C), 55.2, 53.8, 46.3, 24.0, 22.2, 20.2, 19.5, 19.2; HRMS (ESI): Calc'd for $\text{C}_{13}\text{H}_{17}\text{N}_3\text{O}_4 + \text{Na}^+$, 302.1111; found, 302.1104.



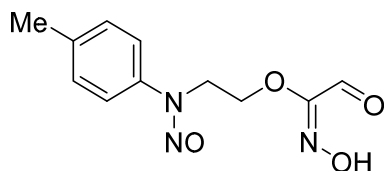
***N*-(2,5-Dimethylphenyl)-*N*-(4-(hydroxyimino)-5-oxopentyl)nitrous amide (2r)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; ¹H NMR (400 MHz, CDCl₃) δ 10.30 (s, *OH*, 0.8H), 10.15 (s, 1H), 9.46 (s, 0.7H), 9.42 (s, 1H), 7.24 (d, *J* = 9.2 Hz, 0.6H), 7.21 (s, 0.7H), 7.16 (m, 1.6H), 7.11 (d, *J* = 7.9 Hz, 0.7H), 7.04 (s, 1H), 6.77 (s, 0.6H), 4.55 – 4.44 (m, 0.7H), 4.36 – 4.26 (m, 0.7H), 3.95 – 3.86 (m, 2H), 2.62 (t, *J* = 7.8 Hz, 1.4H), 2.51 – 2.43 (m, 2H), 2.35 (s, 3H), 2.30 (s, 2H), 2.16 (s, 3H), 1.98 – 1.87 (m, 3H), 1.74 – 1.62 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 191.1, 191.0, 159.7, 159.6, 139.7, 137.0, 136.9, 136.8, 132.2, 131.4, 131.3, 130.9, 130.6, 130.2, 127.2, 126.6, 54.0, 46.6, 24.3, 22.1, 20.8, 19.5, 19.2, 17.5, 17.3; HRMS (ESI): Calc'd for C₁₃H₁₇N₃O₃ + Na⁺, 286.1162; found, 286.1155.



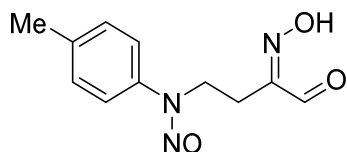
***N*-(4-(Hydroxyimino)-5-oxopentyl)-*N*-(naphthalen-2-yl)nitrous amide (2t)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 6:1); red oil; ¹H NMR (400 MHz, CDCl₃) δ 10.00 (s, *OH*, 1H), 9.44 (s, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.89 – 7.83 (m, 2H), 7.82 – 7.74 (m, 2H), 7.56 – 7.46 (m, 2H), 4.13 (t, *J* = 7.6 Hz, 2H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.89 – 1.74 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 191.0, 159.7, 138.8, 133.4, 132.3, 129.8, 128.2, 127.8, 127.2, 126.5, 118.8, 117.2, 43.7, 22.4, 19.4; HRMS (ESI): Calc'd for C₁₅H₁₅N₃O₃ + Na⁺, 308.1006; found, 308.0996.



2-(Nitroso(*p*-tolyl)amino)ethyl *N*-hydroxy-2-oxoacetimidate (2u)

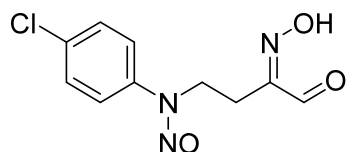
Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; ¹H NMR (400 MHz, CDCl₃) δ 9.37 (s, *OH*, 1H), 9.10 (s, 1H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 4.59 (t, *J* = 5.4 Hz, 2H), 4.29 (t, *J* = 5.3 Hz, 2H), 2.36 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 185.4, 152.4, 139.3, 137.9, 130.0, 120.7, 67.1, 45.8, 21.0; HRMS (ESI): Calc'd for C₁₁H₁₃N₃O₄ + Na⁺, 274.0798; found, 274.0788.



***N*-(3-(Hydroxyimino)-4-oxobutyl)-*N*-(*p*-tolyl)nitrous amide (4a)**

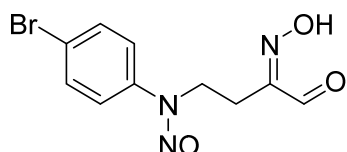
Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red solid; ¹H NMR (400 MHz, *d*₆-DMSO) δ 13.10 (s, *OH*, 1H), 9.30 (s, 1H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 4.11 (t, *J* = 6.5 Hz, 2H), 2.53 (t, *J* = 6.5 Hz, 2H), 2.33 (s, 3H); ¹³C NMR (101

MHz, d_6 -DMSO) δ 191.6, 156.9, 138.9, 137.5, 130.4, 120.3, 20.9, 19.4 (one ^{13}C lost for overlap by); HRMS (ESI): Calc'd for $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_3 + \text{Na}^+$, 258.0849; found 258.0845.



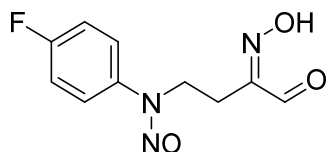
***N*-(4-Chlorophenyl)-*N*-(3-(hydroxyimino)-4-oxobutyl)nitrous amide (4b)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); yellow solid; ^1H NMR (400 MHz, d_6 -DMSO) δ 13.12 (s, OH, 1H), 9.29 (s, 1H), 7.57 (s, 4H), 4.13 (t, $J = 6.4$ Hz, 2H), 2.53 (t, $J = 6.4$ Hz, 2H); ^{13}C NMR (101 MHz, d_6 -DMSO) δ 191.6, 156.8, 140.1, 132.2, 129.9, 121.7, 39.6, 19.4; HRMS (ESI): Calc'd for $\text{C}_{10}\text{H}_{10}\text{ClN}_3\text{O}_3 + \text{Na}^+$, 278.0308; found, 278.0319.



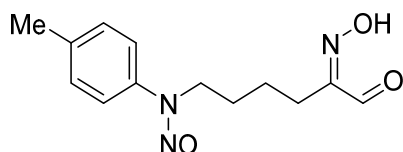
***N*-(4-Bromophenyl)-*N*-(3-(hydroxyimino)-4-oxobutyl)nitrous amide (4c)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red solid; ^1H NMR (400 MHz, d_6 -DMSO) δ 13.11 (s, OH, 1H), 9.29 (s, 1H), 7.70 (d, $J = 7.2$ Hz, 2H), 7.52 (d, $J = 7.2$ Hz, 2H), 4.13 (t, $J = 6.1$ Hz, 2H), 2.52 (t, $J = 6.0$ Hz, 2H); ^{13}C NMR (101 MHz, d_6 -DMSO) δ 191.7, 156.9, 140.5, 132.8, 122.0, 120.5, 39.5, 19.4; HRMS (ESI): Calc'd for $\text{C}_{10}\text{H}_{10}\text{BrN}_3\text{O}_3 + \text{H}^+ - \text{HNO}_2$, 252.9971; found, 252.9976.



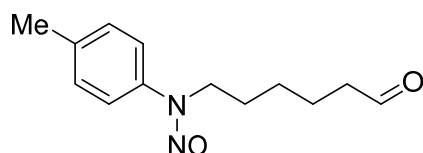
***N*-(4-Fluorophenyl)-*N*-(3-(hydroxyimino)-4-oxobutyl)nitrous amide (4d)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red solid; ^1H NMR (400 MHz, d_6 -DMSO) δ 13.12 (s, OH, 1H), 9.29 (s, 1H), 7.57 – 7.59 (m, 2H), 7.35 (t, $J = 7.5$ Hz, 2H), 4.13 (t, $J = 6.0$ Hz, 2H), 2.53 (t, $J = 6.0$ Hz, 2H); ^{13}C NMR (101 MHz, d_6 -DMSO) δ 191.6, 161.6 (d, $J_{\text{C-F}} = 244.7$ Hz), 156.9, 137.7 (d, $J_{\text{C-F}} = 3.0$ Hz), 122.7 (d, $J_{\text{C-F}} = 8.6$ Hz), 116.7 (d, $J_{\text{C-F}} = 22.9$ Hz), 39.7, 19.4; HRMS (ESI): Calc'd for $\text{C}_{10}\text{H}_{10}\text{FN}_3\text{O}_3 + \text{Na}^+$, 262.0598; found, 262.0591.



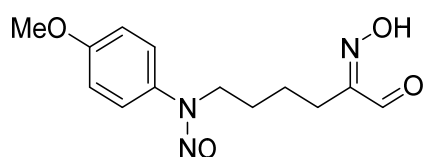
***N*-(5-(Hydroxyimino)-6-oxohexyl)-*N*-(p-tolyl)nitrous amide (6a)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; ^1H NMR (400 MHz, CDCl_3) δ 10.62 (s, OH, 1H), 9.41 (s, 1H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.24 (d, $J = 7.8$ Hz, 2H), 4.02 (t, $J = 7.2$ Hz, 2H), 2.46 (t, $J = 7.2$ Hz, 2H), 2.37 (s, 3H), 1.59 – 1.41 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 191.4, 160.3, 138.8, 137.7, 130.1, 120.1, 44.1, 26.2, 22.9, 21.1, 21.0; HRMS (ESI): Calc'd for $\text{C}_{13}\text{H}_{17}\text{N}_3\text{O}_3 + \text{Na}^+$, 286.1162; found, 286.1162.



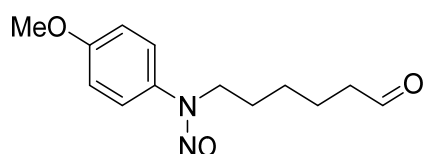
***N*-(6-Oxohexyl)-*N*-(*p*-tolyl)nitrous amide (7a)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.69 (s, 1H), 7.34 (d, $J = 8.3$ Hz, 2H), 7.23 (d, $J = 8.1$ Hz, 2H), 3.97 (t, 2H), 2.40 – 2.31 (m, 5H), 1.61 – 1.46 (m, 4H), 1.31 – 1.20 (m, 2H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 202.2, 139.0, 137.4, 130.1, 130.0, 119.8, 43.6, 43.5, 26.4, 26.2, 21.4, 20.9; HRMS (ESI): Calc'd for $\text{C}_{13}\text{H}_{18}\text{N}_2\text{O}_2 + \text{Na}^+$; 257.1260; found, 257.1256.



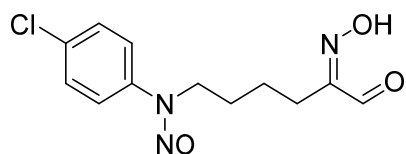
***N*-(5-(Hydroxyimino)-6-oxohexyl)-*N*-(4-methoxyphenyl)nitrous amide (6b)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.10 (s, *OH*, 1H), 9.42 (s, 1H), 7.38 (d, $J = 7.5$ Hz, 2H), 6.97 (d, $J = 8.2$ Hz, 2H), 4.01 (t, $J = 6.0$ Hz, 2H), 3.83 (s, 3H), 2.47 (t, $J = 6.3$ Hz, 2H), 1.49 (m, 10.5 Hz, 4H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 191.2, 160.5, 159.1, 134.5, 127.1, 122.1, 114.8, 114.7, 55.6, 44.5, 26.2, 22.9, 21.1; HRMS (ESI): Calc'd for $\text{C}_{13}\text{H}_{17}\text{N}_3\text{O}_4 + \text{Na}^+$; 302.1111; found, 302.1105.



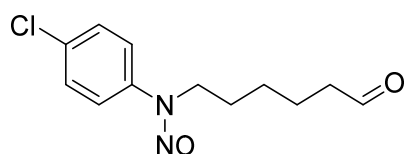
***N*-(4-Methoxyphenyl)-*N*-(6-oxohexyl)nitrous amide (7b)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.67 (s, 1H), 7.34 (d, $J = 7.4$ Hz, 2H), 6.93 (d, $J = 7.5$ Hz, 2H), 3.94 (t, $J = 6.8$ Hz, 2H), 3.79 (s, 3H), 2.35 (t, $J = 6.8$ Hz, 2H), 1.59 – 1.44 (m, 4H), 1.30 – 1.17 (m, 2H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 202.2, 159.0, 134.6, 127.1, 121.8, 114.6, 55.5, 44.1, 43.5, 26.4, 26.1, 21.4. HRMS (ESI): Calc'd for $\text{C}_{13}\text{H}_{18}\text{N}_2\text{O}_3 + \text{Na}^+$; 273.1210; found, 273.1205.



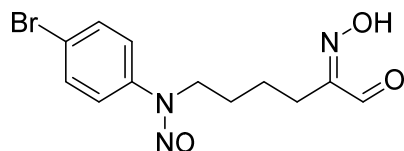
***N*-(4-Chlorophenyl)-*N*-(5-(hydroxyimino)-6-oxohexyl)nitrous amide (6c)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.18 (s, *OH*, 1H), 9.42 (s, 1H), 7.48 – 7.30 (m, 4H), 4.02 (t, $J = 5.9$ Hz, 2H), 2.46 (t, $J = 6.2$ Hz, 2H), 1.58 – 1.37 (m, 4H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 191.3, 160.4, 139.8, 133.3, 129.7, 120.9, 43.6, 26.1, 22.8, 21.1; HRMS (ESI): Calc'd for $\text{C}_{12}\text{H}_{14}\text{ClN}_3\text{O}_3 + \text{Na}^+$, 306.0616; found, 306.061.



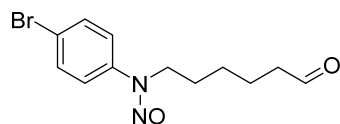
***N*-(4-Chlorophenyl)-*N*-(6-oxohexyl)nitrous amide (7c)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; ¹H NMR (400 MHz, CDCl₃) δ 9.67 (s, 1H), 7.44 – 7.34 (m, 4H), 3.94 (t, *J* = 6.3 Hz, 2H), 2.36 (t, *J* = 6.5 Hz, 2H), 1.61 – 1.42 (m, 4H), 1.29 – 1.17 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 202.1, 139.9, 132.9, 129.6, 120.6, 43.5, 43.2, 26.4, 26.2, 21.3; HRMS (ESI): Calc'd for C₁₂H₁₅ClN₂O₂ + Na⁺, 277.0714; found, 277.0709.



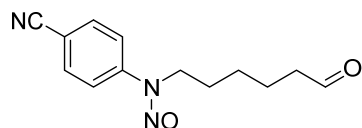
***N*-(4-Bromophenyl)-*N*-(5-(hydroxyimino)-6-oxohexyl)nitrous amide (6d)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; ¹H NMR (400 MHz, CDCl₃) δ 9.62 (s, *OH*, 1H), 9.43 (s, 1H), 7.58 (d, *J* = 5.7 Hz, 2H), 7.39 (d, *J* = 5.7 Hz, 2H), 4.00 (t, *J* = 6.3 Hz, 2H), 2.48 (t, *J* = 5.4 Hz, 2H), 1.58 – 1.41 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 191.0, 160.5, 140.3, 132.7, 121.0, 43.4, 26.1, 22.9, 21.0 (one ¹³C signal lost for overlap). HRMS (ESI): Calc'd for C₁₂H₁₄BrN₃O₃ + Na⁺; 350.0111; found, 350.0109.



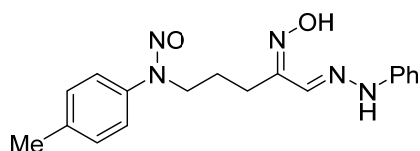
***N*-(4-Bromophenyl)-*N*-(6-oxohexyl)nitrous amide (7d)**

Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; ¹H NMR (400 MHz, CDCl₃) δ 9.71 (s, 1H), 7.56 (d, *J* = 6.7 Hz, 2H), 7.38 (d, *J* = 6.9 Hz, 2H), 3.96 (t, *J* = 6.6 Hz, 2H), 2.40 (t, *J* = 6.7 Hz, 2H), 1.64 – 1.46 (m, 4H), 1.32 – 1.21 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 202.0, 140.4, 132.6, 120.8, 120.7, 43.5, 43.1, 26.4, 26.2, 21.4; HRMS (ESI): Calc'd for C₁₂H₁₅BrN₂O₂ + Na⁺, 321.0209; found, 321.0203.



***N*-(4-Cyanophenyl)-*N*-(6-oxohexyl)nitrous amide (7e)**

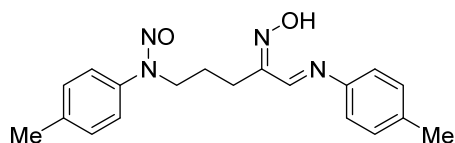
Purified by silica gel column chromatography eluted with petroleum ether/acetone (v/v 5:1); red oil; ¹H NMR (400 MHz, CDCl₃) δ 9.69 (s, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 3.96 (t, *J* = 6.4 Hz, 2H), 2.39 (t, *J* = 6.5 Hz, 2H), 1.63 – 1.44 (m, 4H), 1.26 (t, *J* = 7.3 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 202.0, 144.8, 133.6, 118.4, 118.2, 110.2, 43.4, 42.3, 26.3, 26.2, 21.3; HRMS (ESI): Calc'd for C₁₃H₁₅N₃O₂ + Na⁺, 268.1056; found, 268.1044.



***N*-(4-(Hydroxyimino)-5-(2-phenylhydrazono)pentyl)-*N*-(*p*-tolyl)nitrous amide (8)**

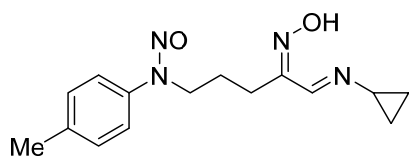
Purified by silica gel column chromatography eluted with petroleum ether/ ethyl acetate (v/v 3:1); red solid; ¹H NMR (400 MHz, *d*₆-DMSO) δ 11.23 (s, *NH*, 1H), 10.36 (s, *OH*, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.40 (s, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.17 (t, *J* = 7.8 Hz, 2H), 6.90 (d, *J* = 7.7 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 4.08 (m, 2H), 2.54 – 2.45 (m, 2H), 2.31 (s, 3H), 1.70 – 1.59 (m, 2H); ¹³C NMR (101

MHz, d_6 -DMSO) δ 156.9, 145.2, 139.0, 137.5, 135.1, 130.4, 129.5, 120.4, 119.6, 112.4, 43.6, 23.5, 21.1, 20.9; HRMS (ESI): Calc'd for $C_{18}H_{21}N_5O_2 + Na^+$, 362.1588; found, 362.1592.



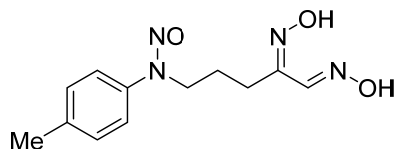
***N*-(4-(Hydroxyimino)-5-(*p*-tolylimino)pentyl)-*N*-(*p*-tolyl)nitrous amide (9)**

Purified by silica gel column chromatography eluted with petroleum ether/ ethyl acetate (v/v 6:1); red oil; 1H NMR (400 MHz, $CDCl_3$) δ 9.79 (brs, *OH*, 1H), 8.03 (s, 1H), 7.39 (d, $J = 8.5$ Hz, 2H), 7.21 (d, $J = 8.2$ Hz, 2H), 7.16 (d, $J = 8.1$ Hz, 2H), 7.05 (d, $J = 8.3$ Hz, 2H), 4.10 – 4.03 (m, 2H), 2.81 – 2.74 (m, 2H), 2.36 (s, 3H), 2.34 (s, 3H), 1.91 – 1.81 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 156.6, 148.0, 139.1, 137.4, 136.8, 130.0, 129.8, 121.0, 120.0, 44.1, 22.8, 21.0, 20.9, 20.7; HRMS (ESI): Calc'd for $C_{19}H_{22}N_4O_2 + Na^+$, 361.1635; found, 361.1649.



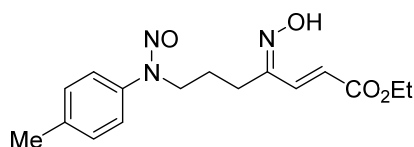
***N*-(5-(Cyclopropylimino)-4-(hydroxyimino)pentyl)-*N*-(*p*-tolyl)nitrous amide (10)**

Purified by recrystallization from alcohol; light yellow solid; 1H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.36 (d, $J = 8.5$ Hz, 2H), 7.24 (d, $J = 7.9$ Hz, 2H), 4.12 – 3.85 (m, 2H), 3.03 – 2.85 (m, 1H), 2.71 – 2.49 (m, 2H), 2.38 (s, 3H), 1.83 – 1.66 (m, 2H), 1.06 – 0.79 (m, 4H); ^{13}C NMR (101 MHz, d_6 -DMSO) δ 157.8, 156.9, 139.0, 137.5, 130.3, 120.8, 43.5, 41.5, 22.9, 20.9, 20.5, 9.4; HRMS (ESI): Calc'd for $C_{15}H_{20}N_4O_2 + Na^+$, 311.1484; found, 311.1495.



***N*-(4,5-Bis(hydroxyimino)pentyl)-*N*-(*p*-tolyl)nitrous amide (11)**

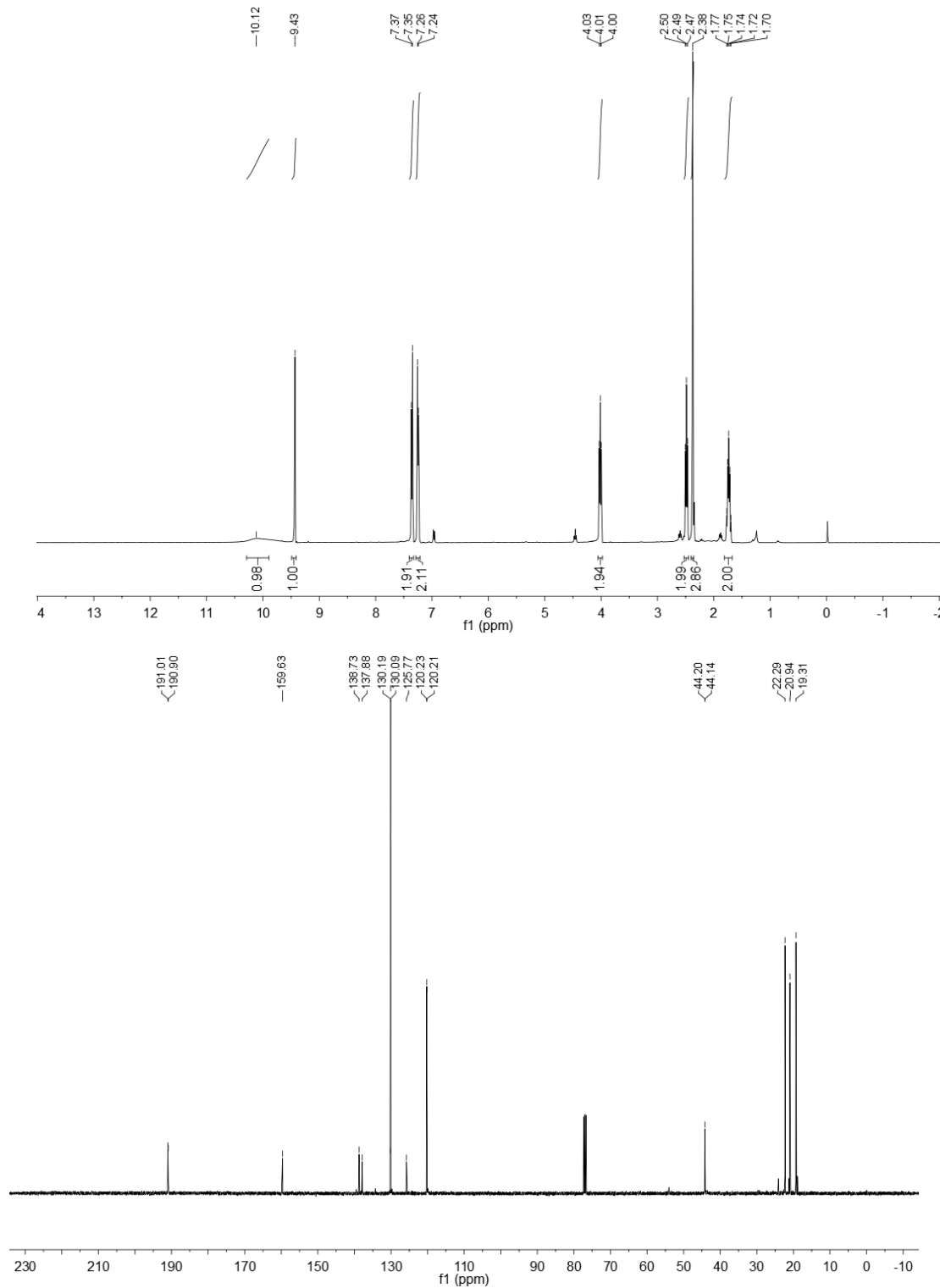
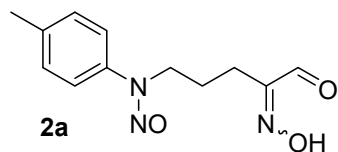
Purified by silica gel column chromatography eluted with petroleum ether/ ethyl acetate (v/v 4:1); light yellow solid; 1H NMR (400 MHz, d_6 -DMSO) δ 11.59 (s, *OH*, 1H), 11.44 (s, *OH*, 1H), 7.55 (s, 1H), 7.44 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 8.3$ Hz, 2H), 4.11 – 3.87 (m, 2H), 2.50 – 2.36 (m, 2H), 2.32 (s, 3H), 1.73 – 1.47 (m, 2H); ^{13}C NMR (101 MHz, d_6 -DMSO) δ 154.8, 147.1, 139.0, 137.6, 130.5, 120.8, 43.9, 23.1, 21.3, 20.9; HRMS (ESI): Calc'd for $C_{12}H_{16}N_4O_3 + Na^+$, 287.1115; found, 287.1124.

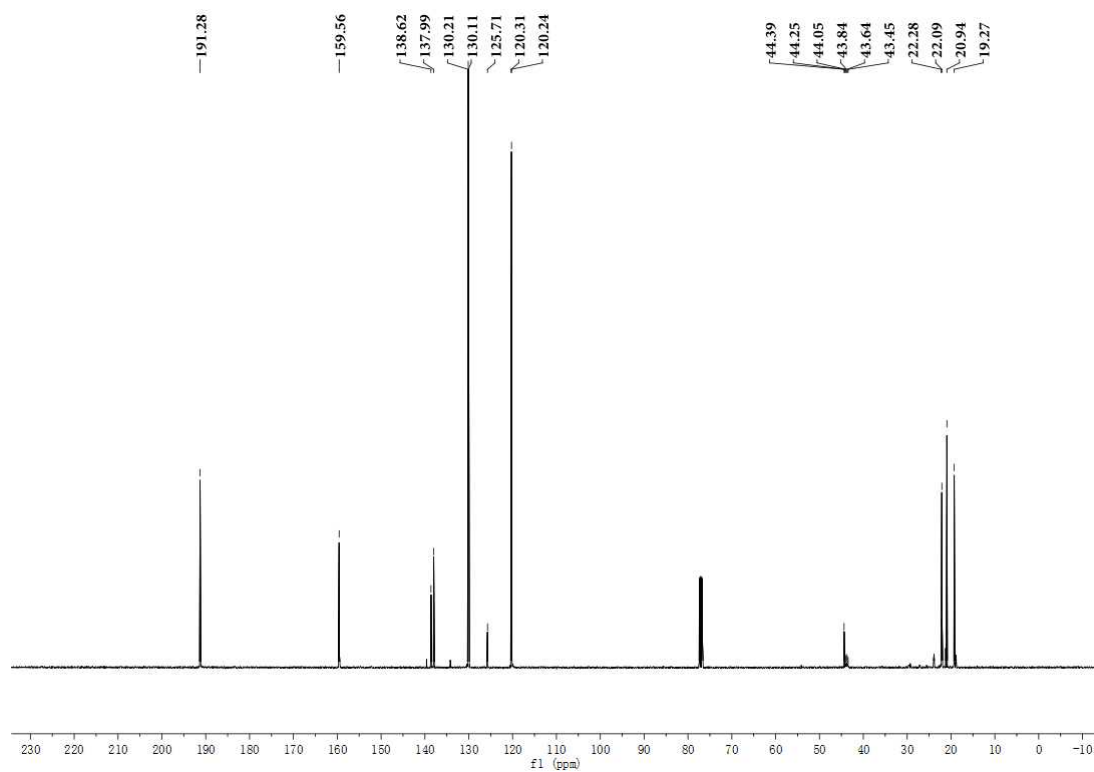
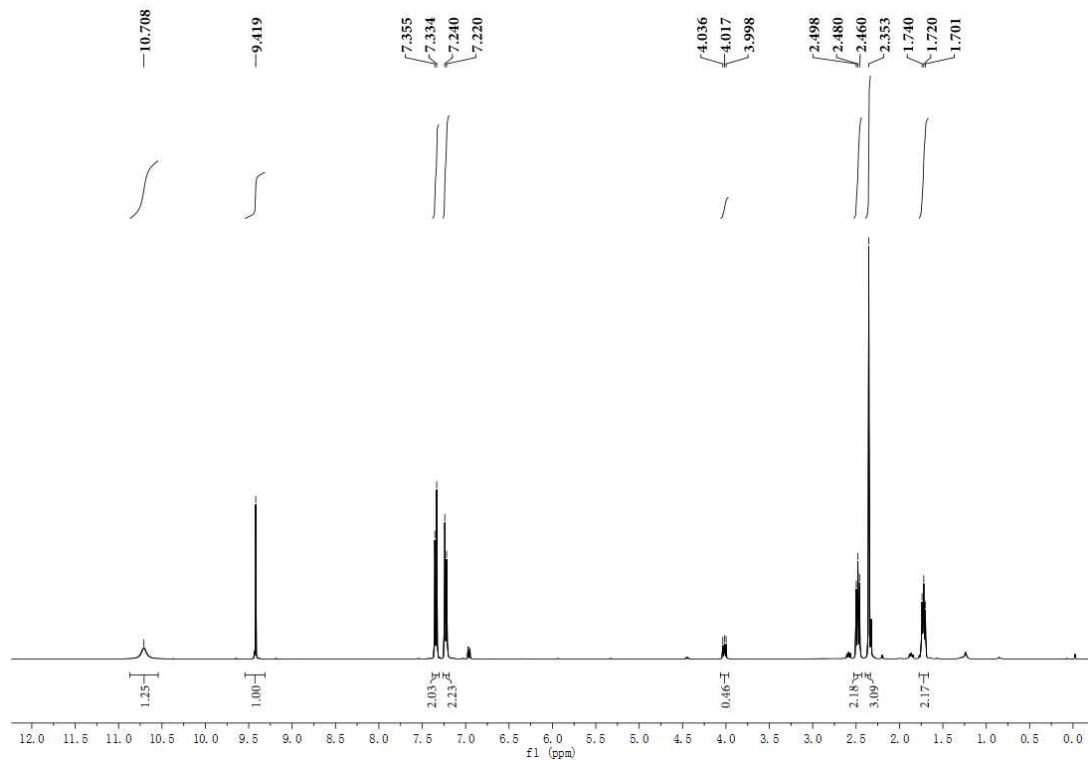
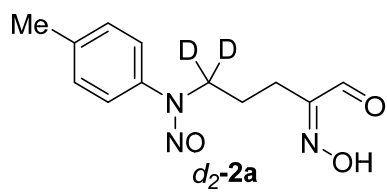


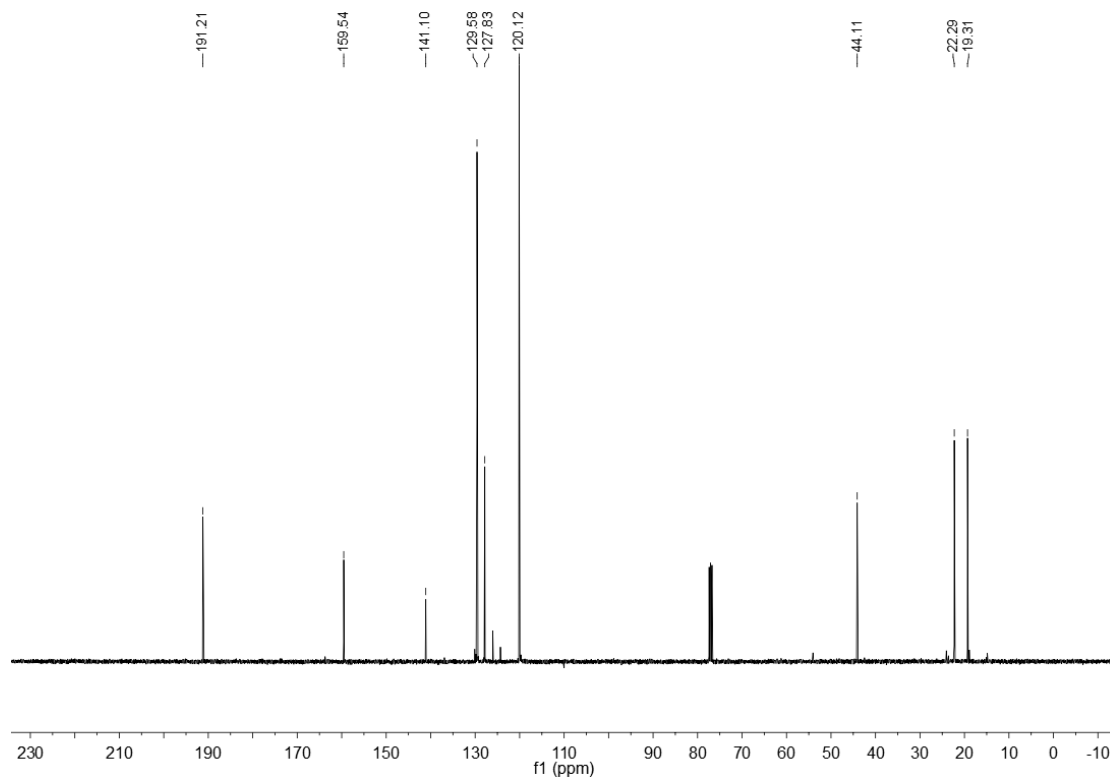
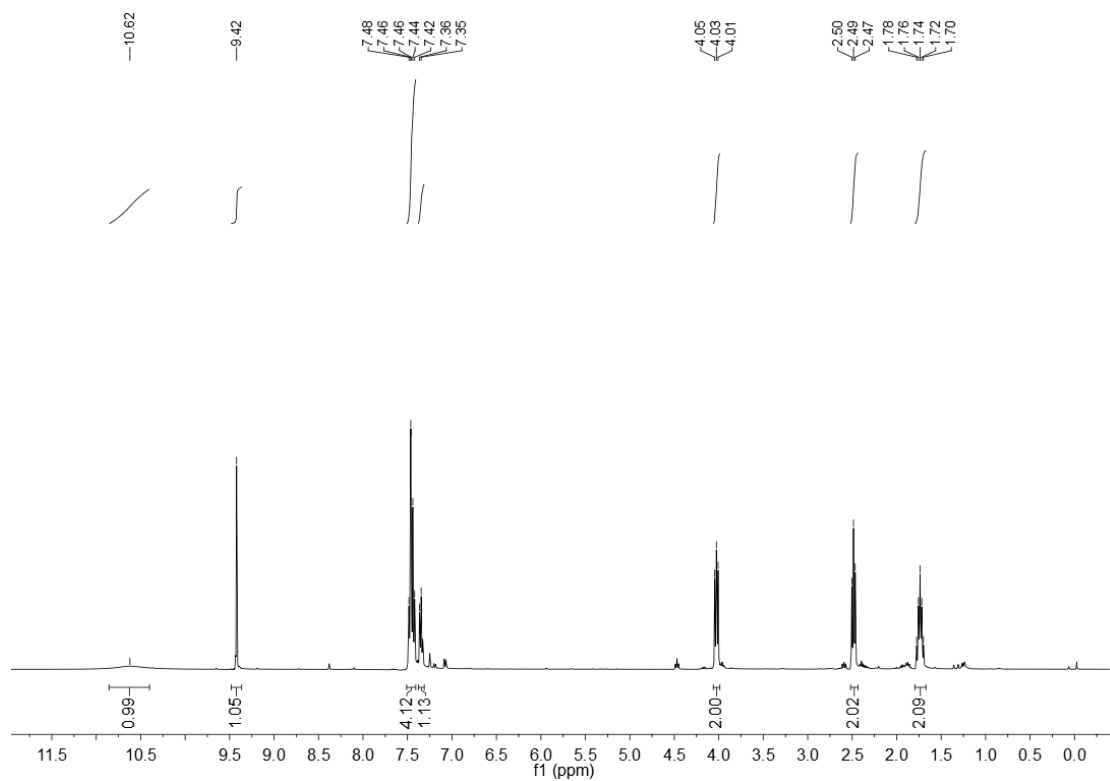
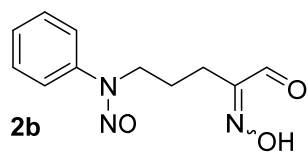
Ethyl 4-(hydroxyimino)-7-(nitroso(*p*-tolyl)amino)hept-2-enoate (12)

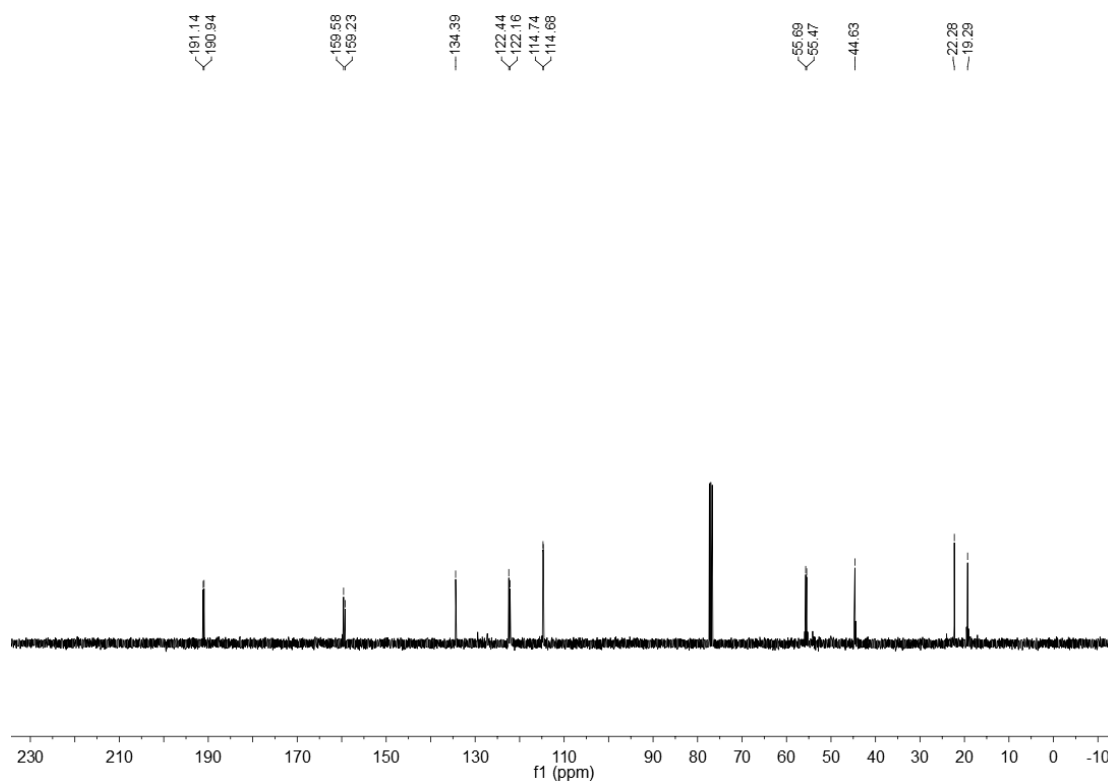
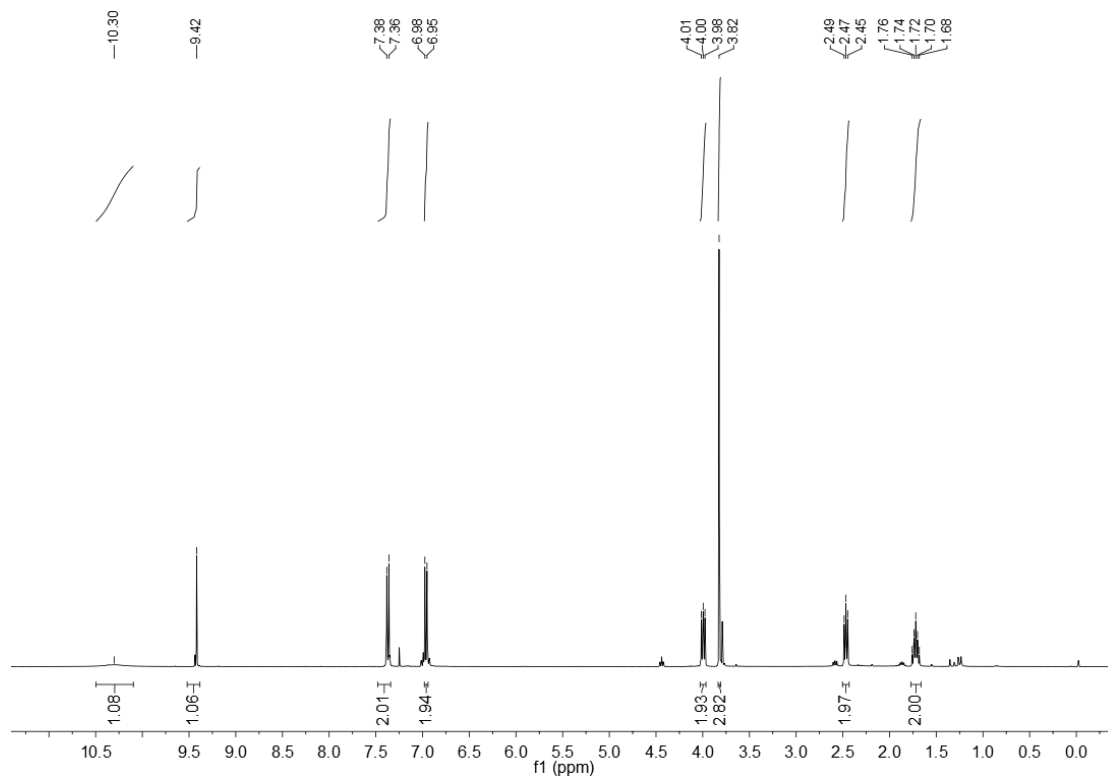
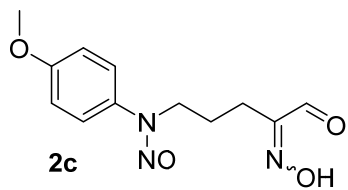
Purified by silica gel column chromatography eluted with petroleum ether/ ethyl acetate (v/v 4:1); light yellow solid; 1H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, *OH*, 1H), 7.36 (d, $J = 8.5$ Hz, 2H), 7.29 – 7.21 (m, 3H), 6.09 (d, $J = 16.2$ Hz, 1H), 4.22 (q, $J = 7.1$ Hz, 2H), 4.11 – 4.00 (m, 2H), 2.57 – 2.47 (m, 2H), 2.38 (s, 3H), 1.80 – 1.69 (m, 2H), 1.30 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, d_6 -DMSO) δ 166.3, 156.5, 141.6, 139.0, 137.6, 130.4, 121.6, 120.7, 60.7, 43.5, 23.0, 21.3, 20.9, 14.5; HRMS (ESI): Calc'd for $C_{16}H_{21}N_3O_4 + Na^+$, 342.1424; found, 342.1430.

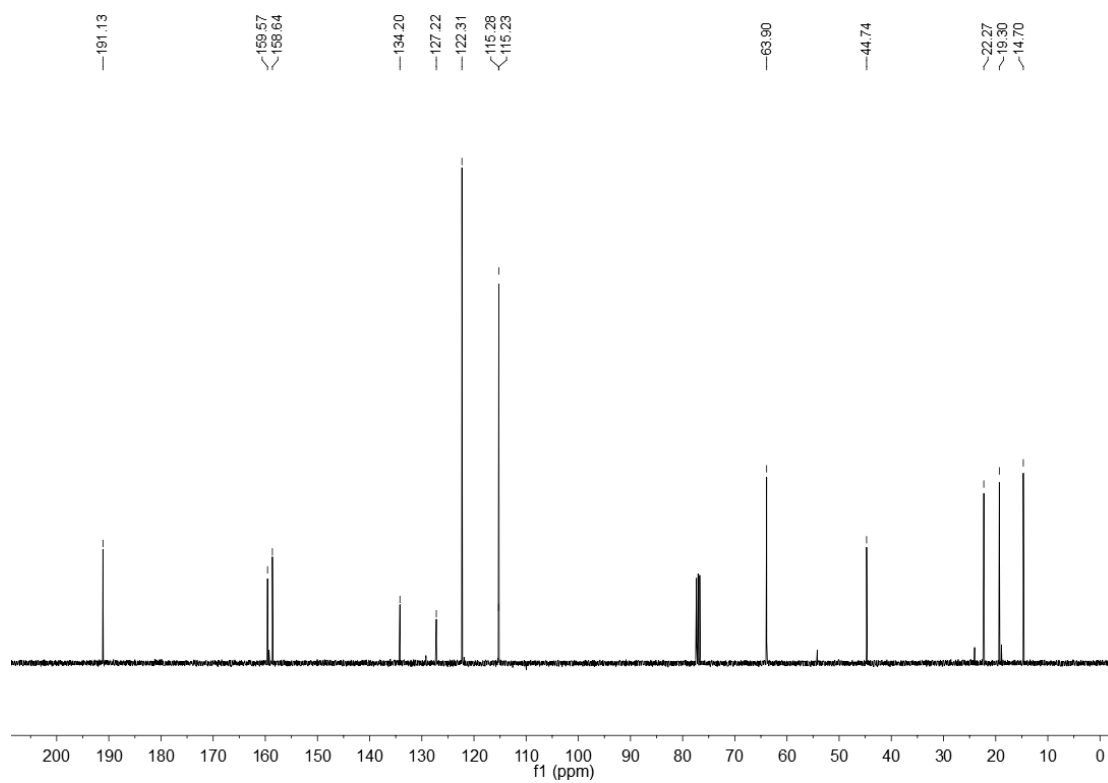
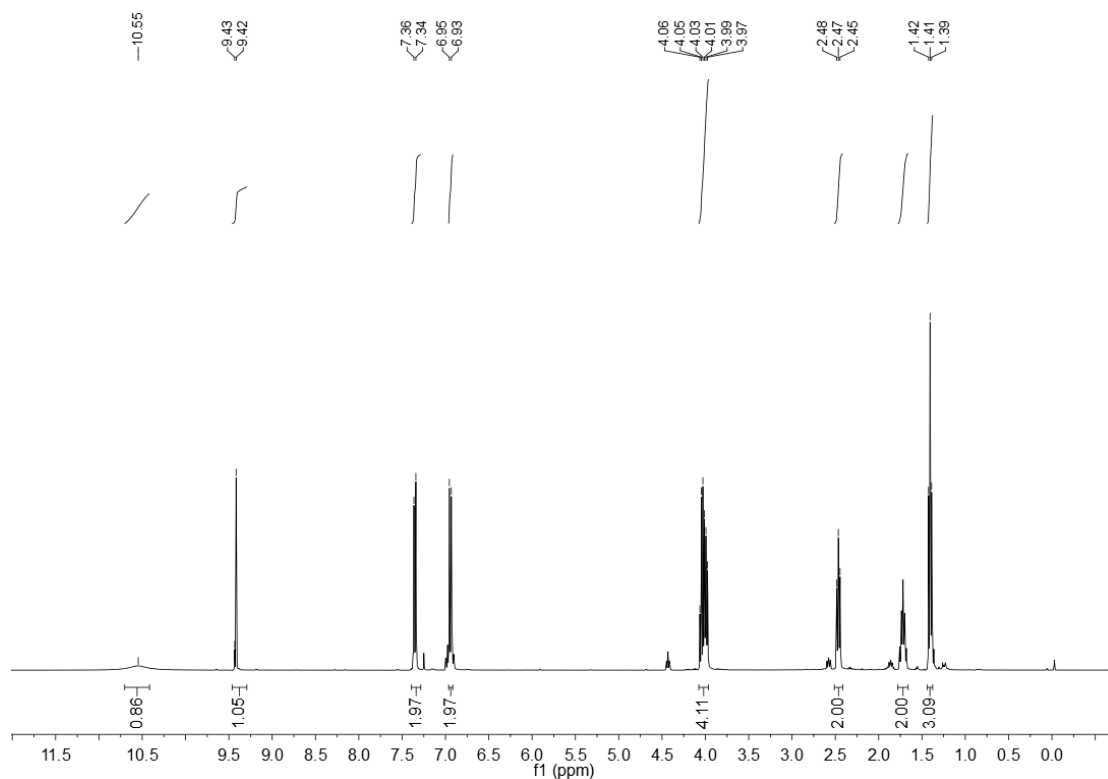
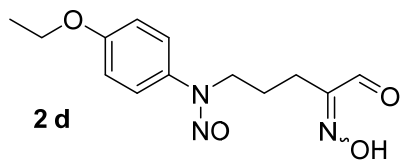
¹H and ¹³C spectra

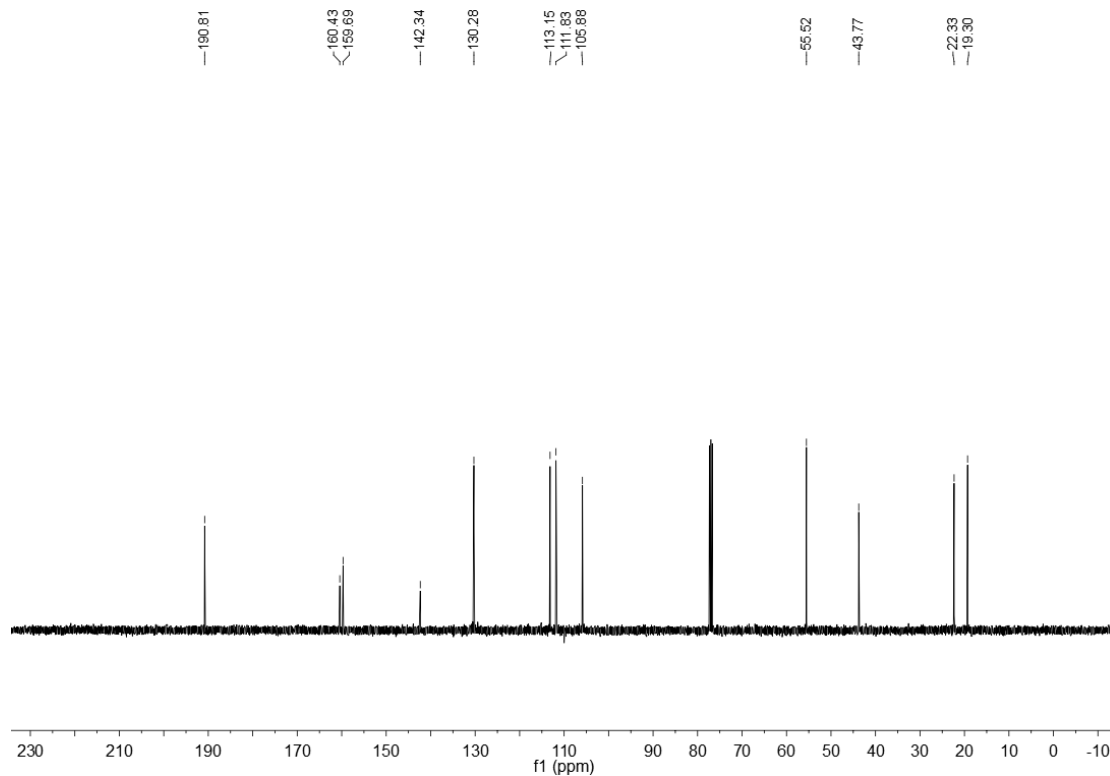
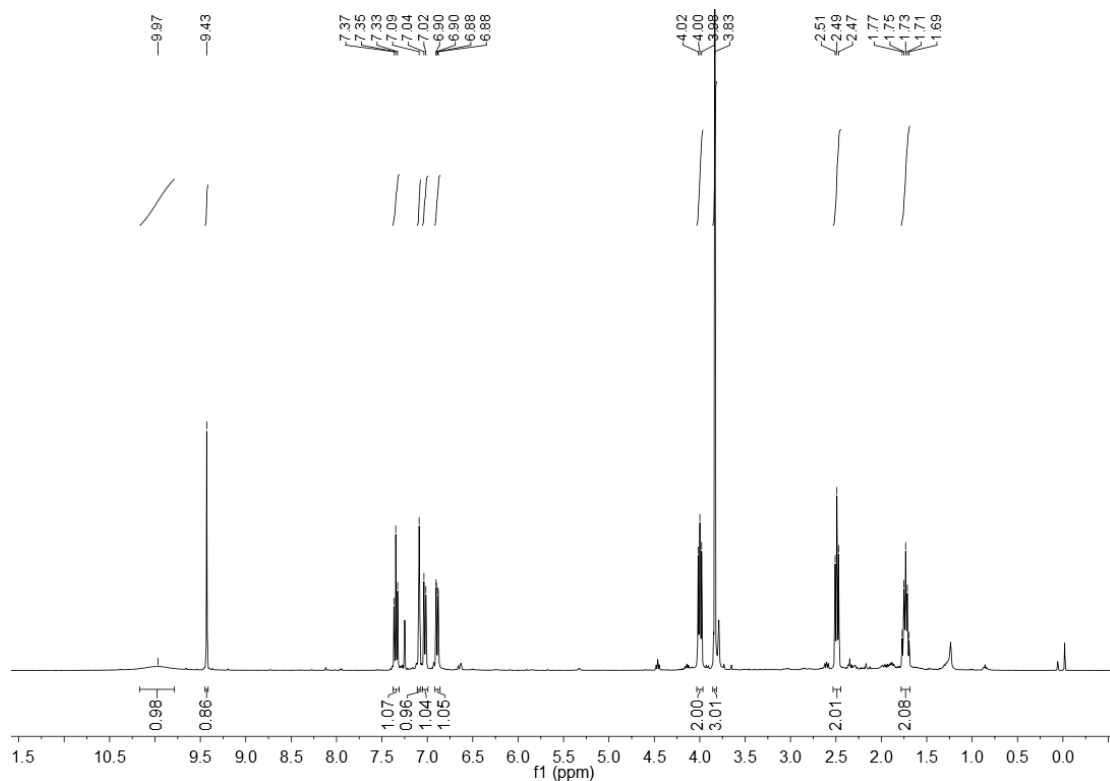
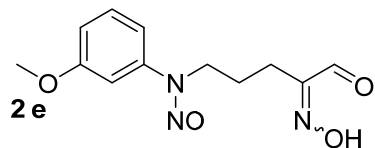


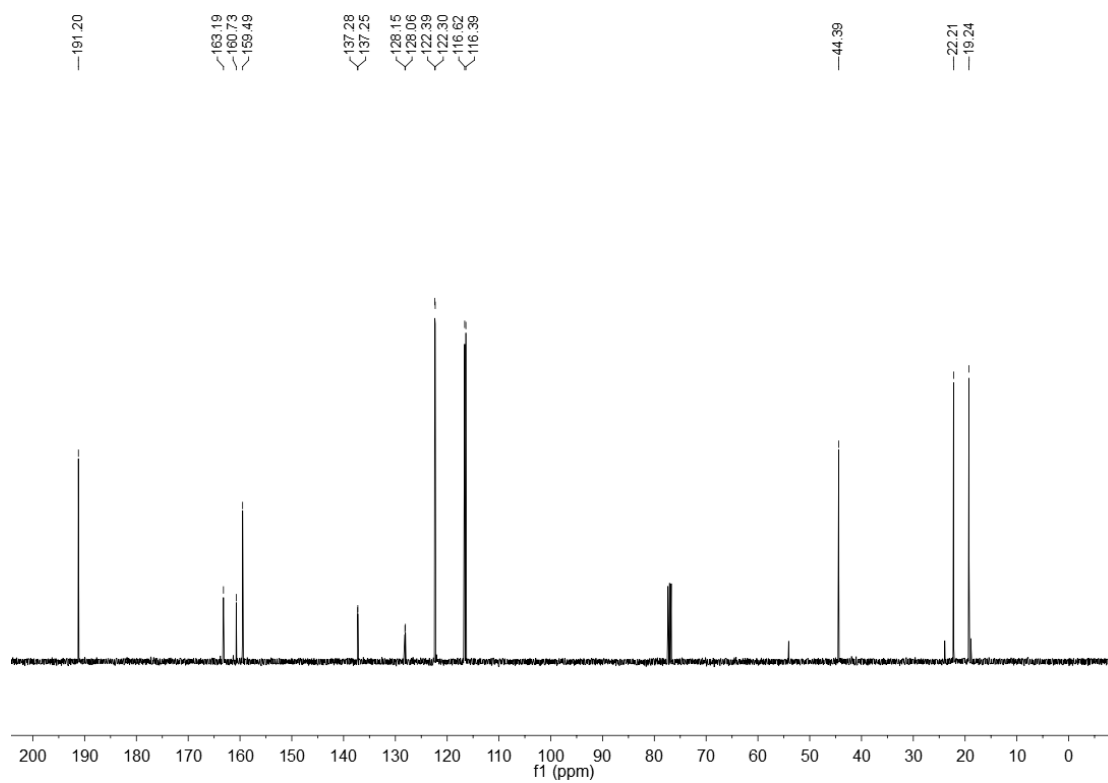
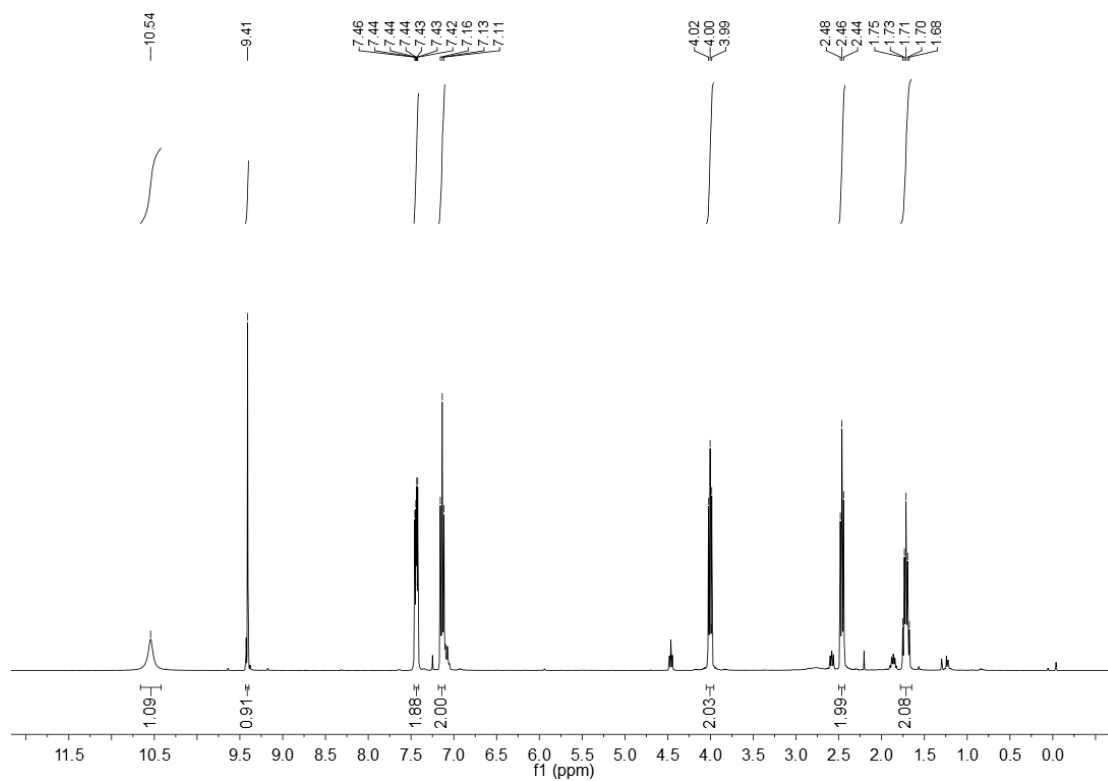
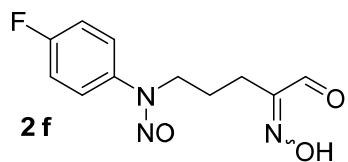


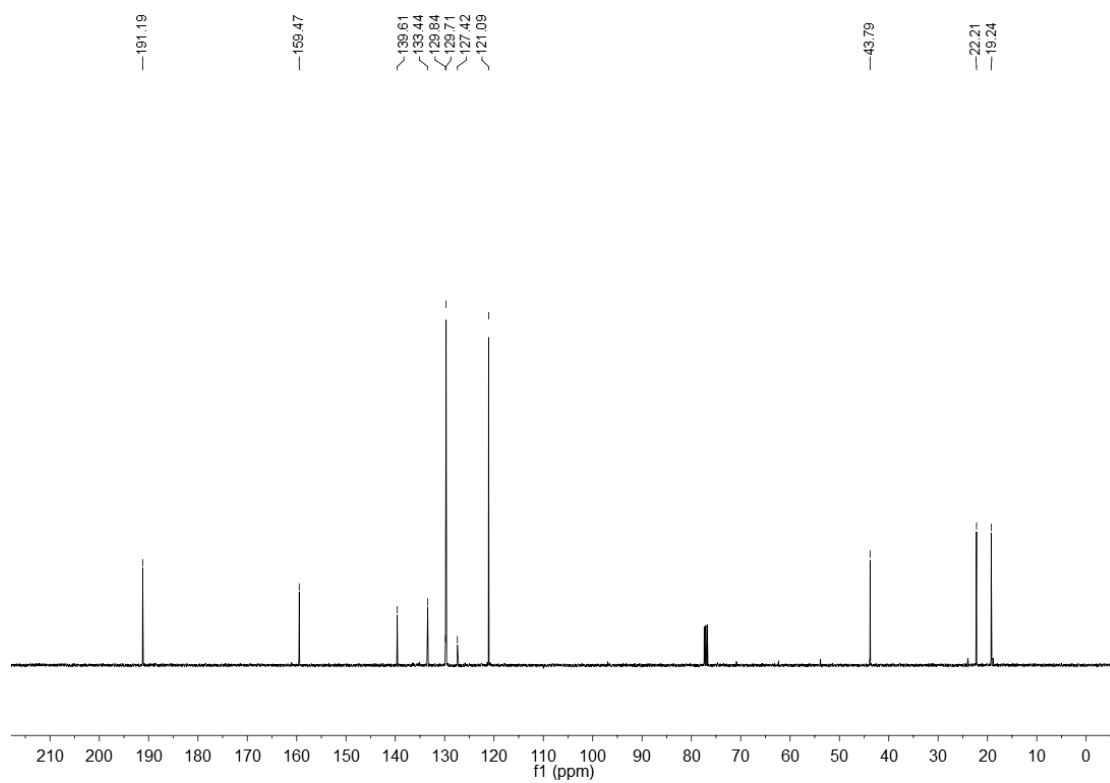
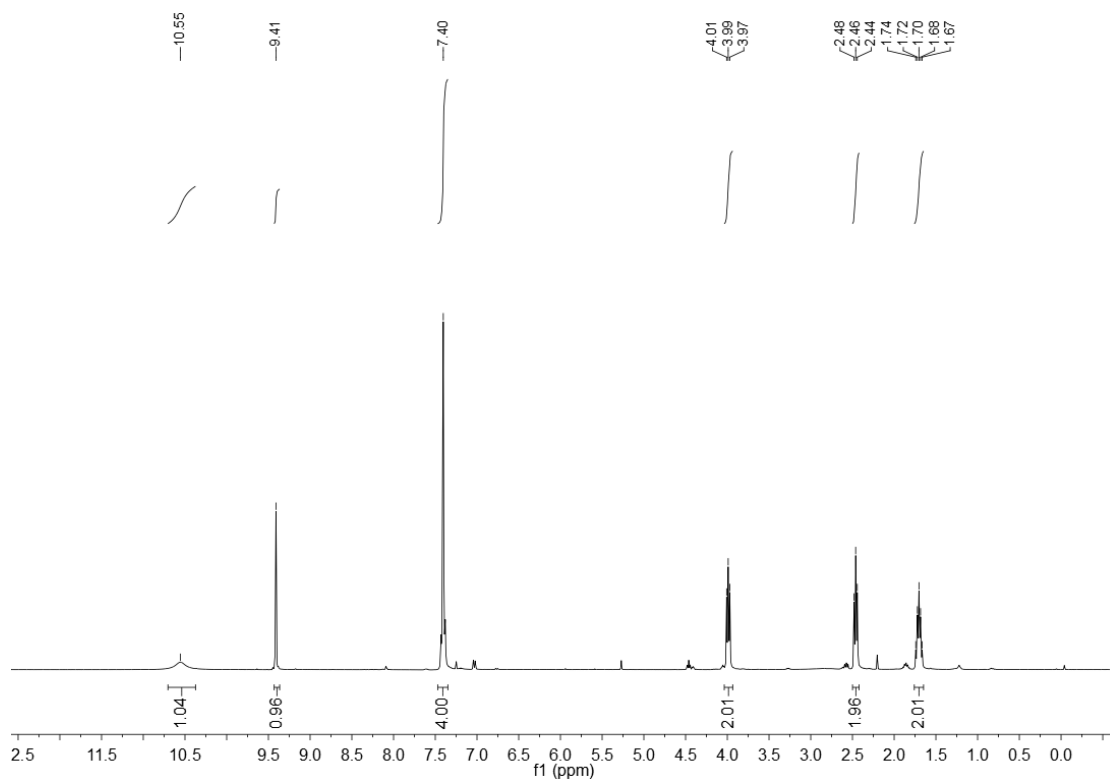
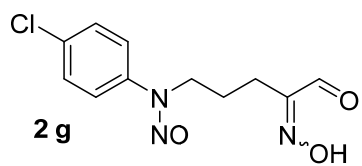


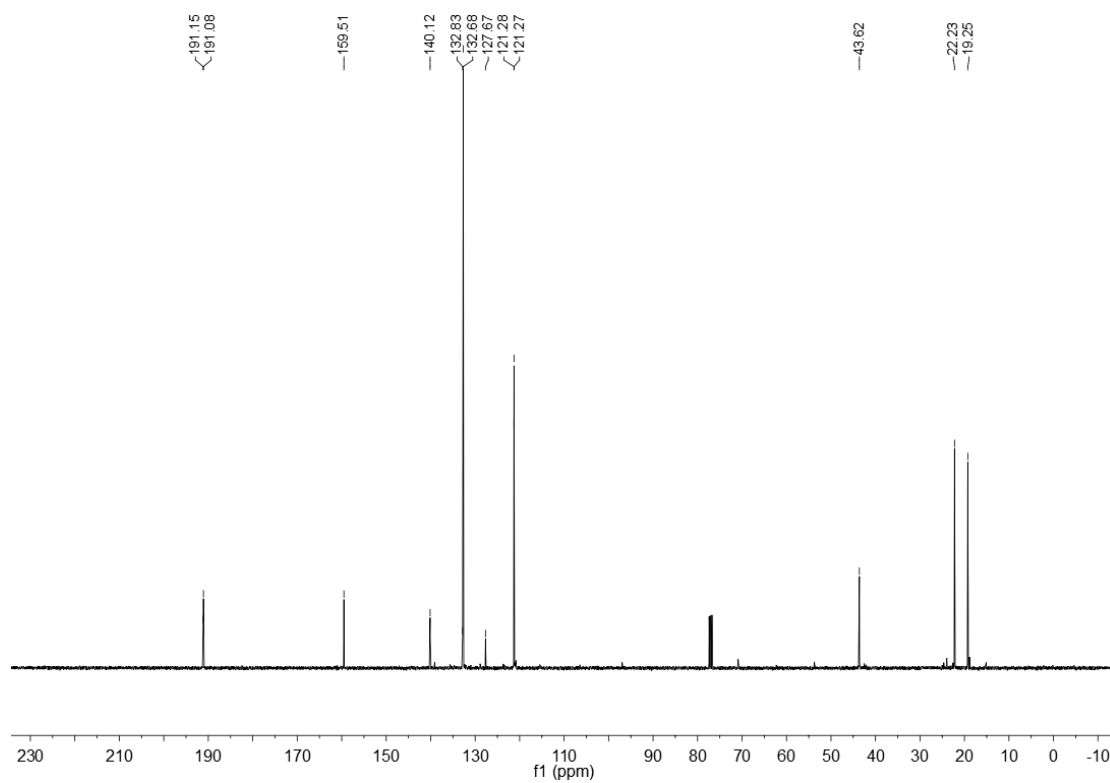
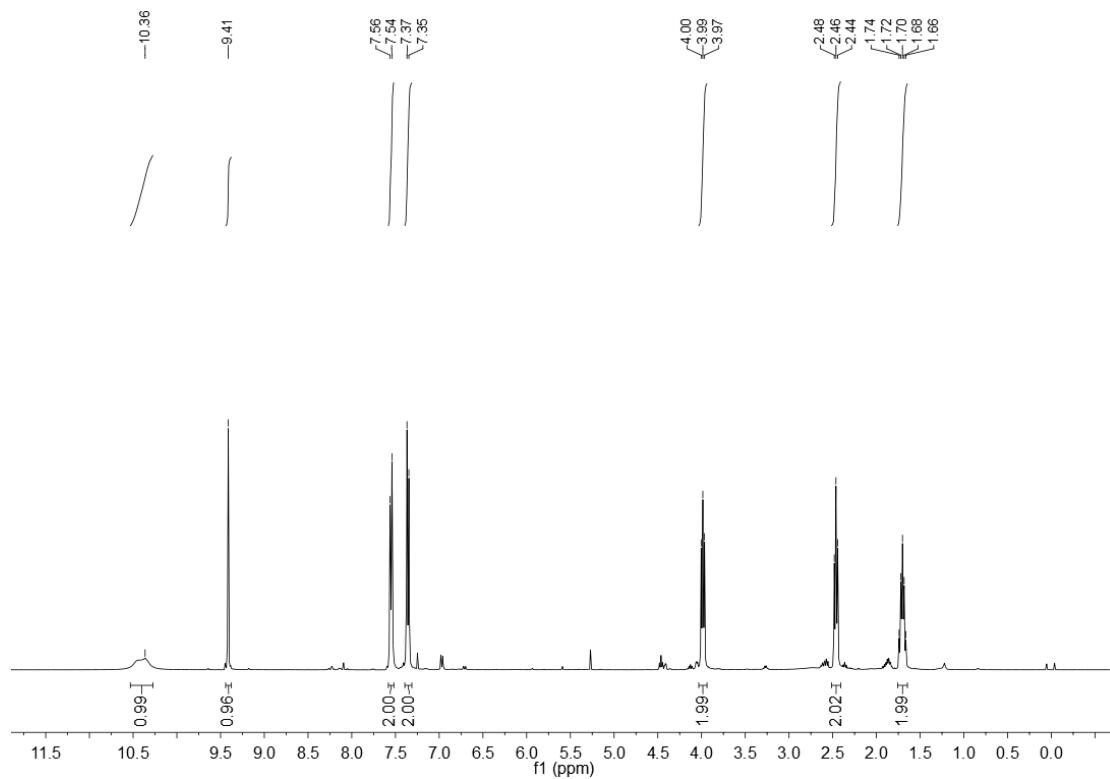
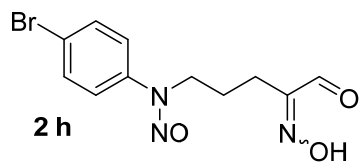


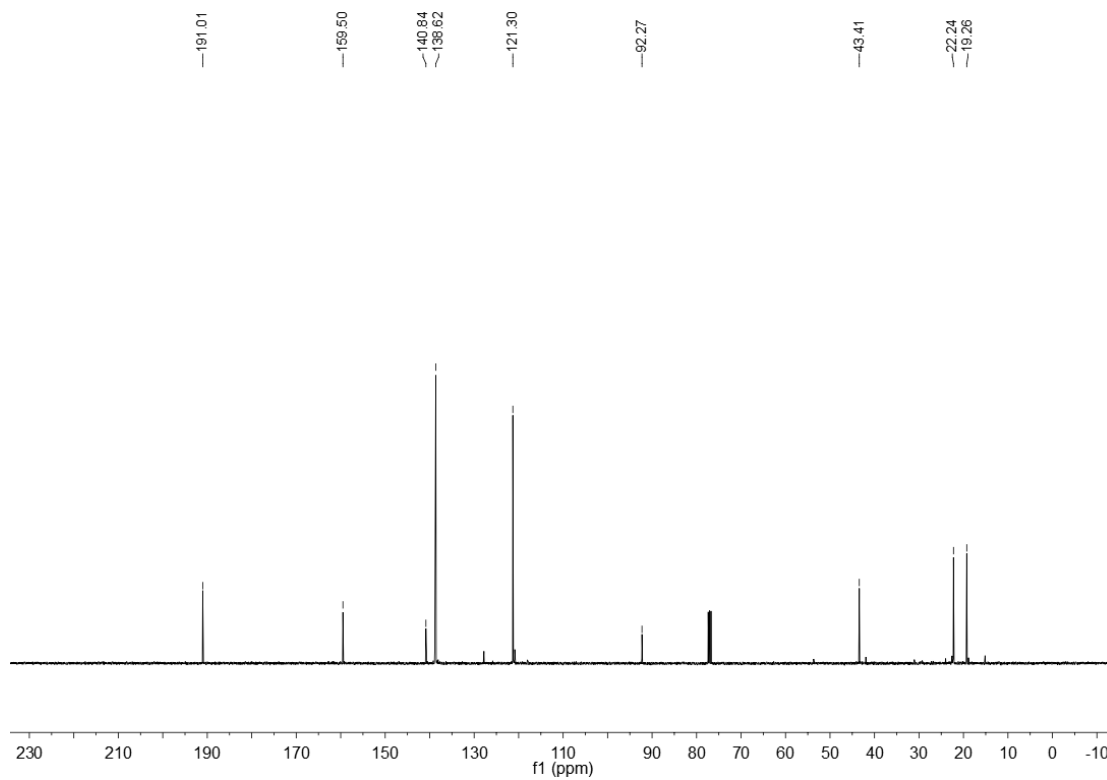
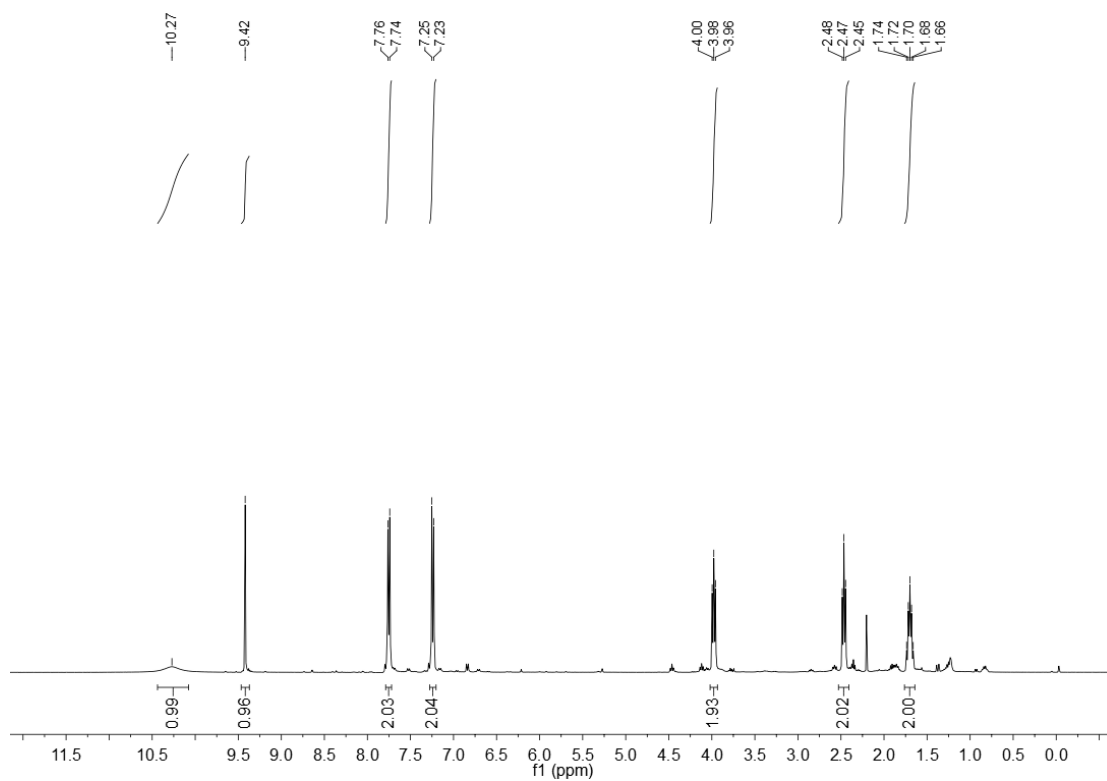
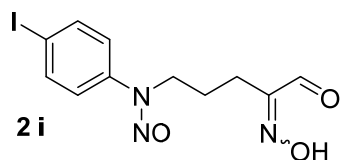


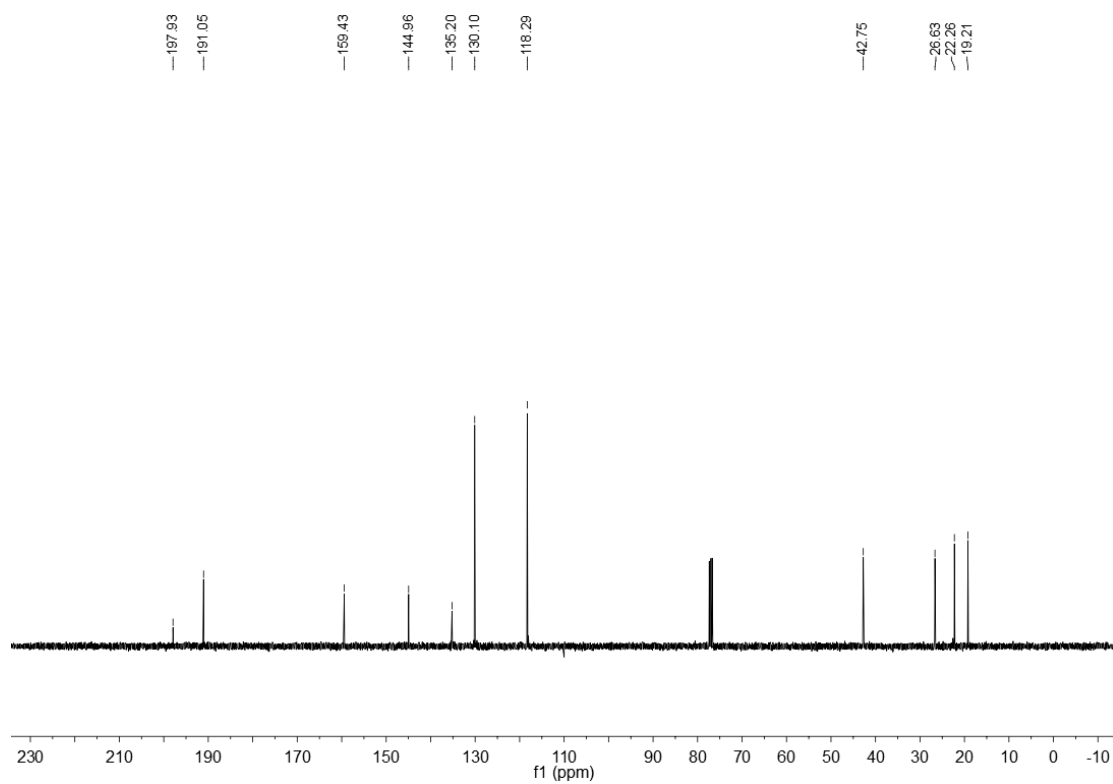
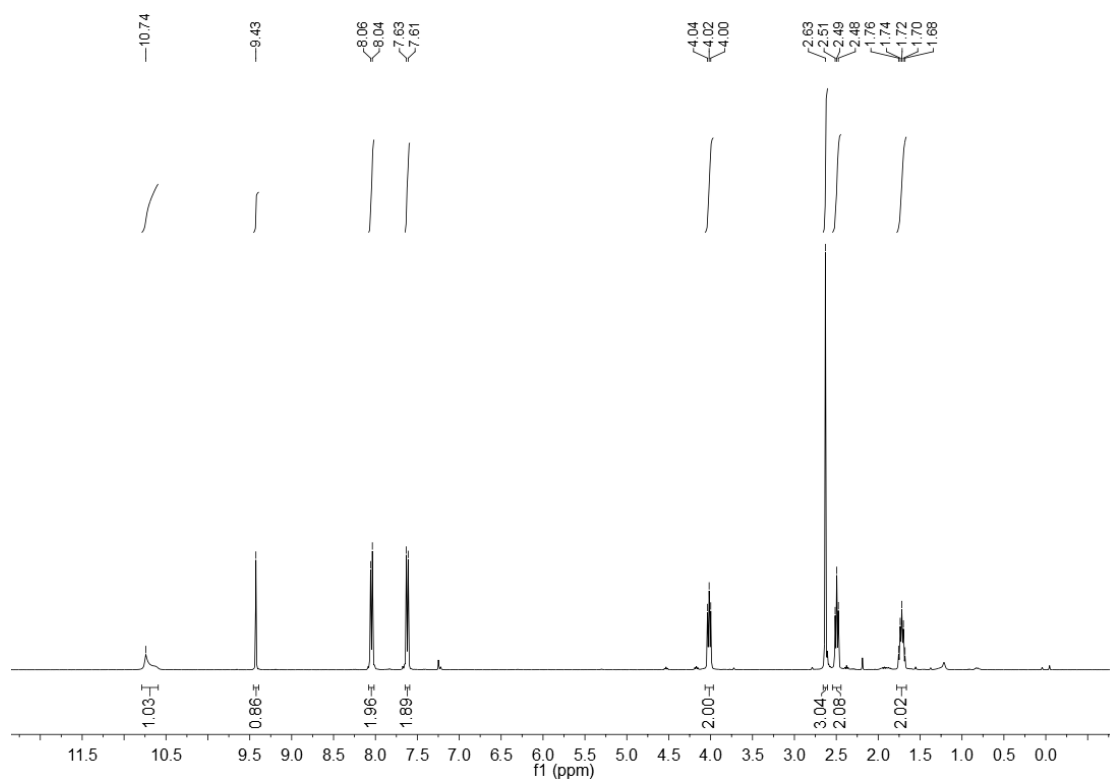
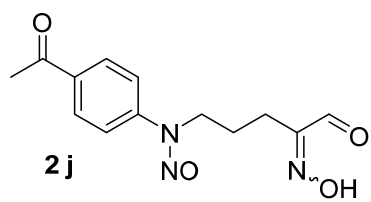


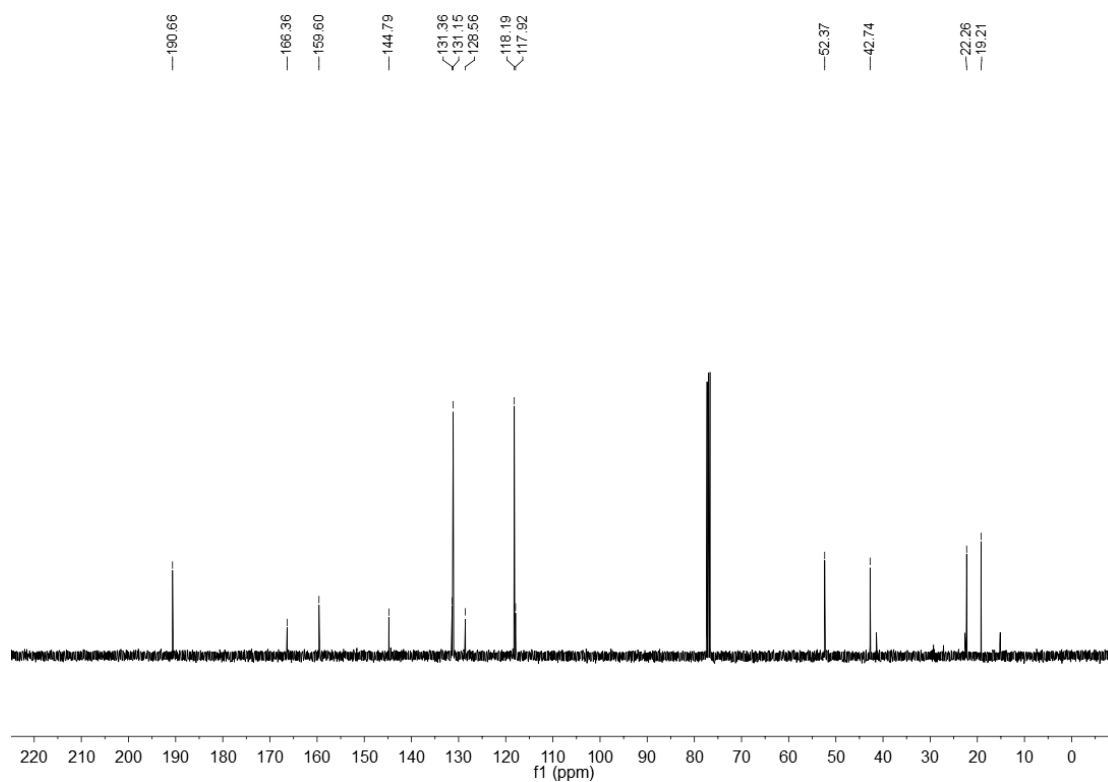
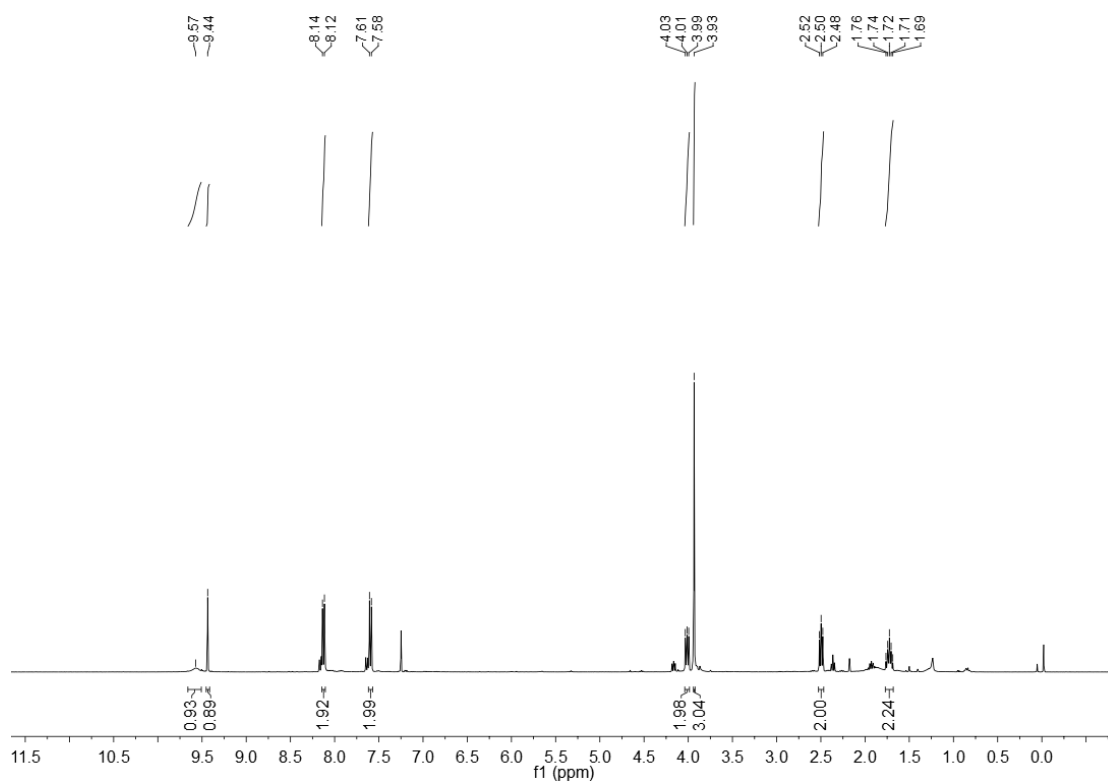
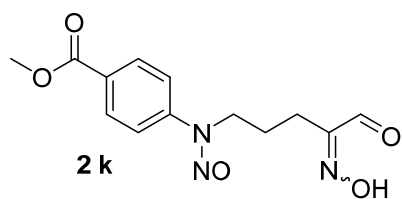


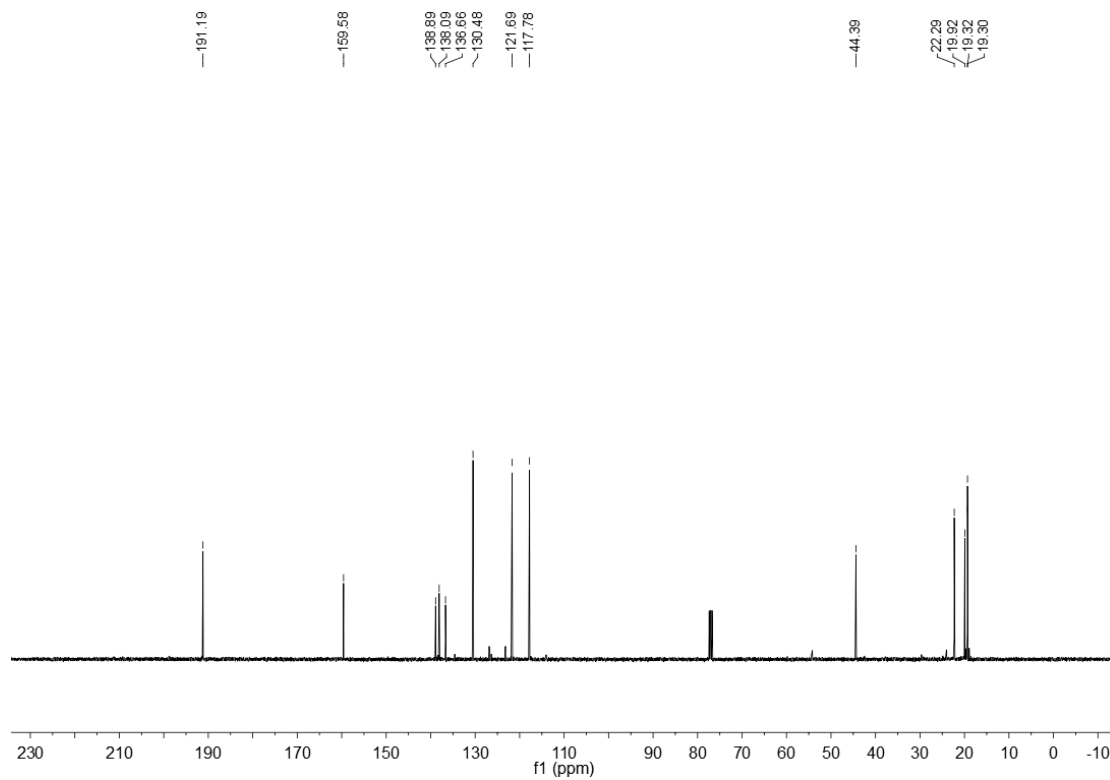
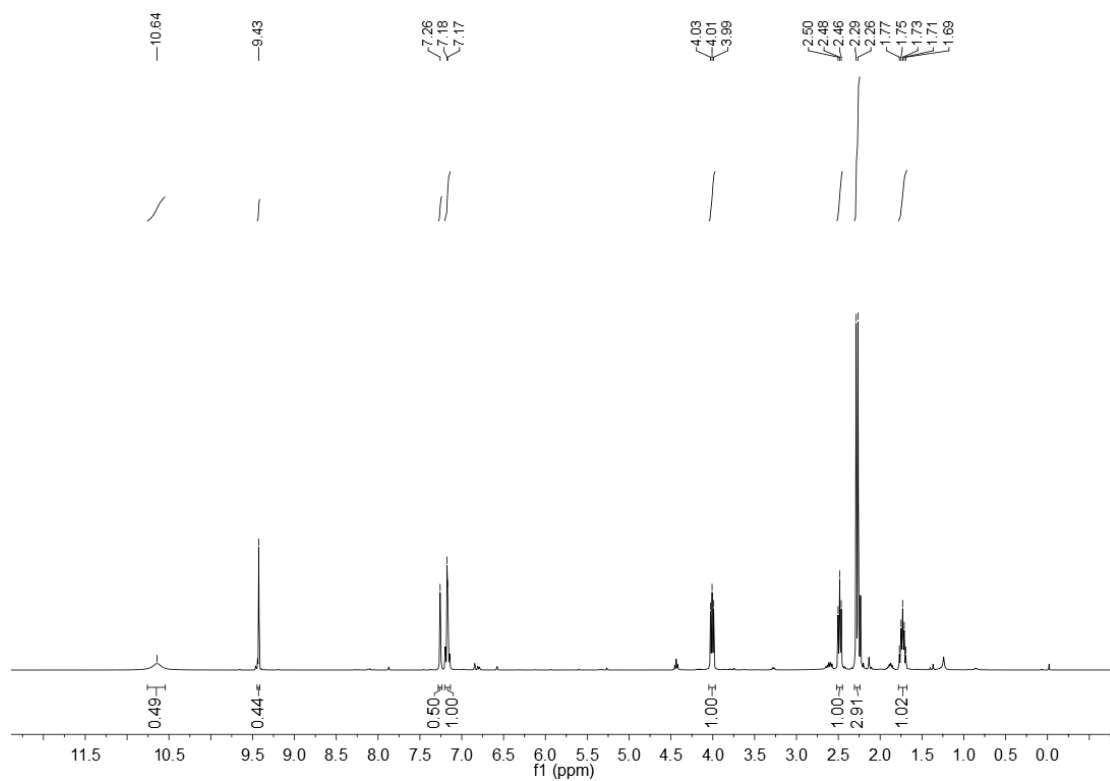
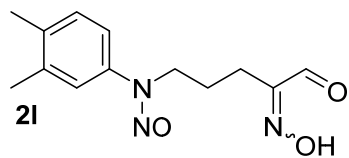


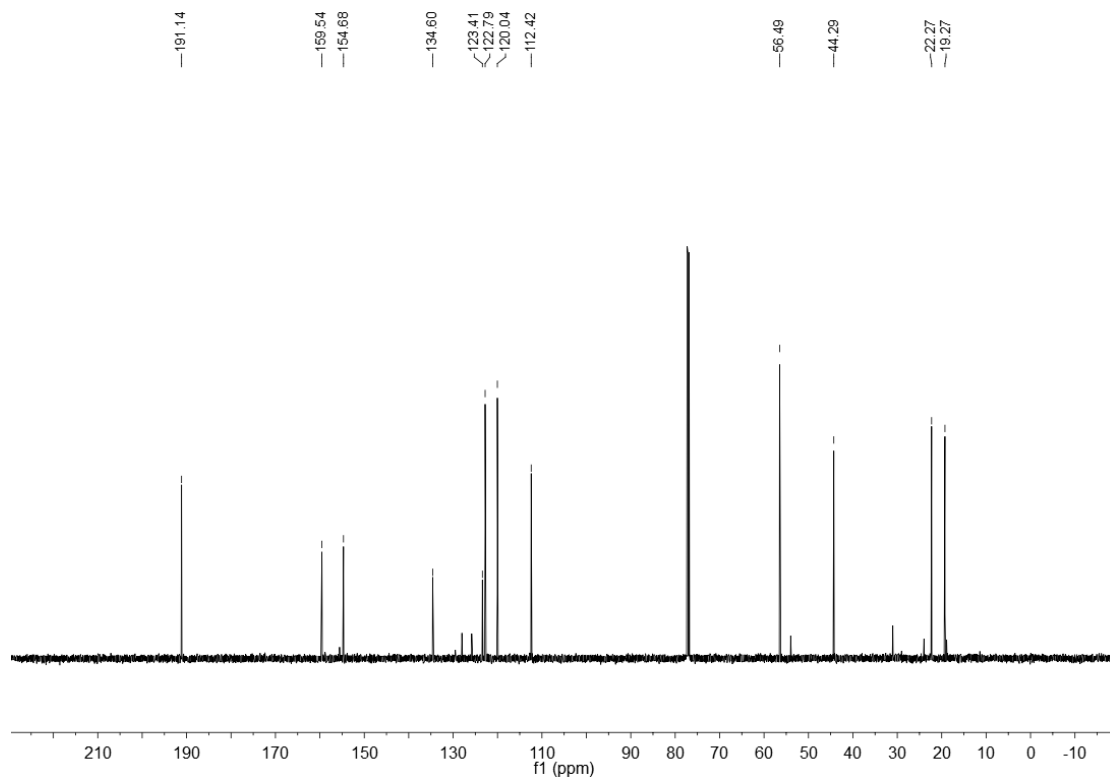
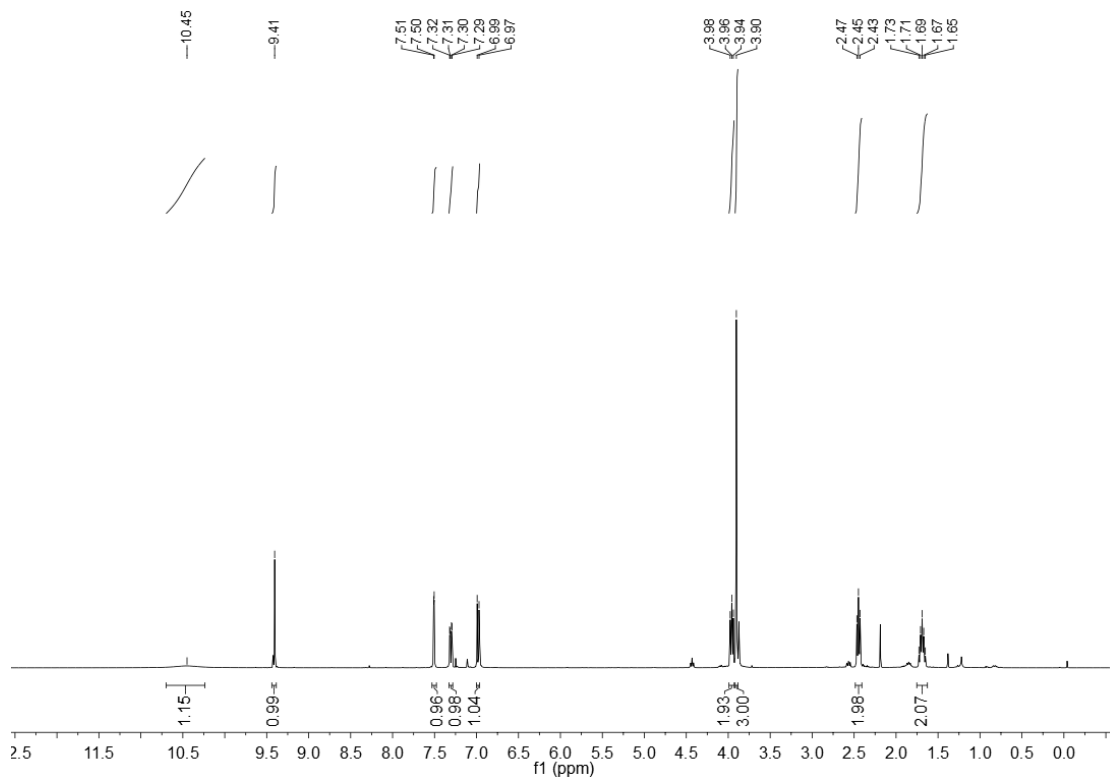
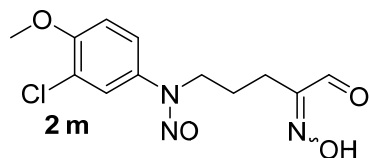


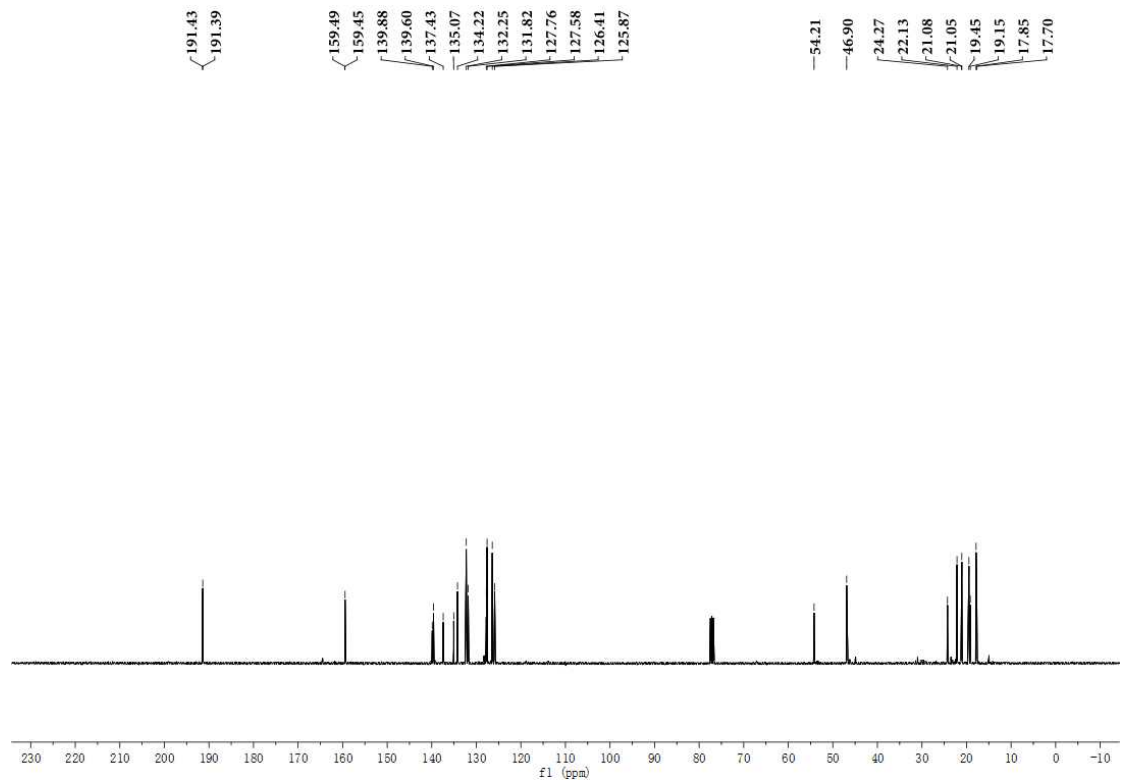
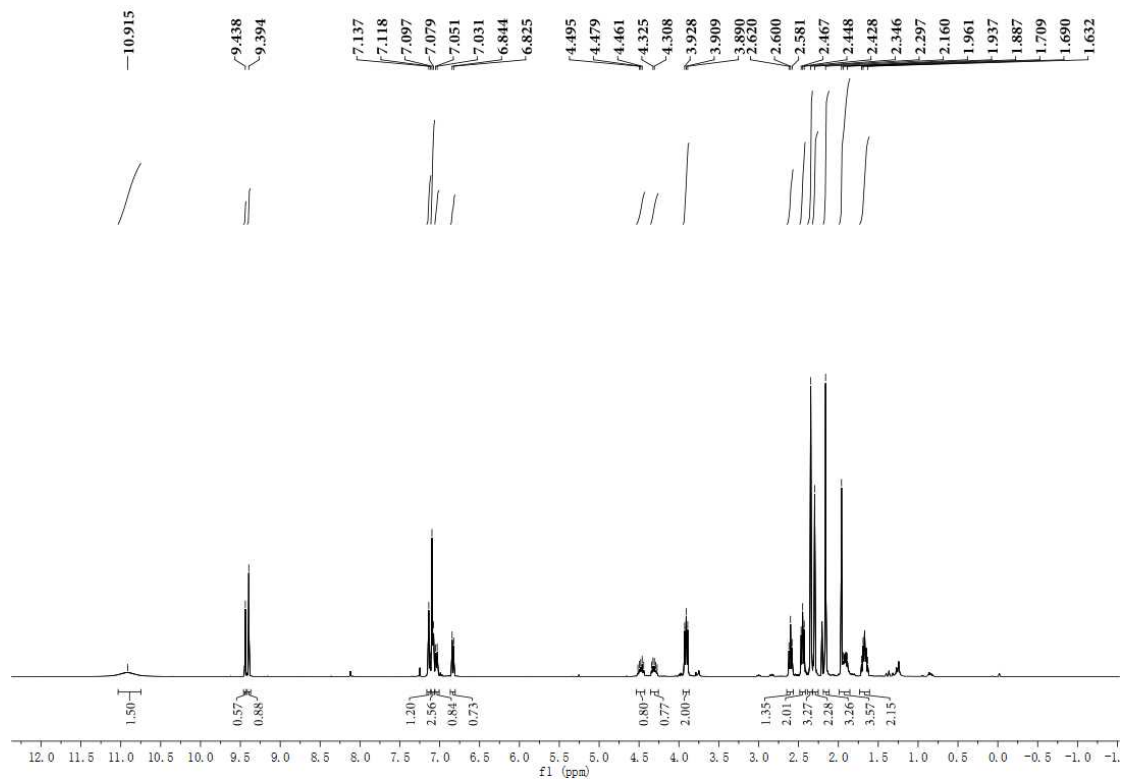
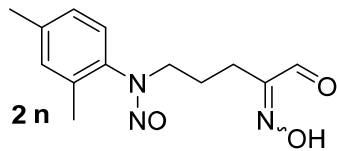


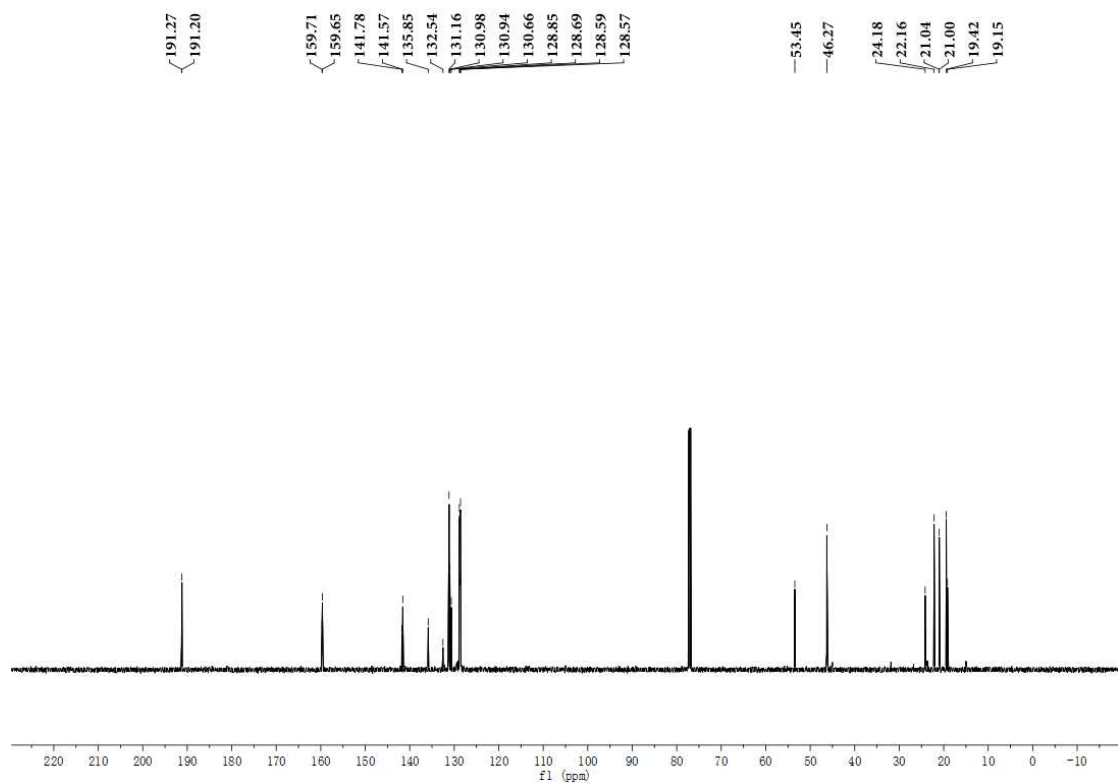
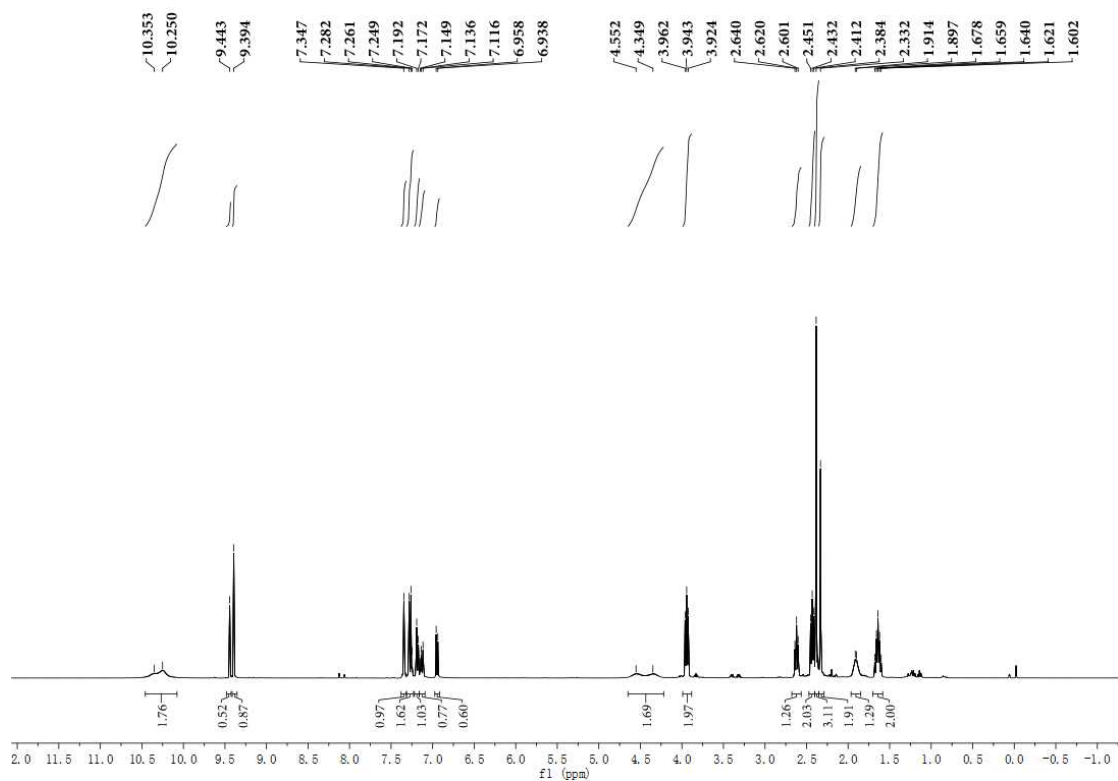
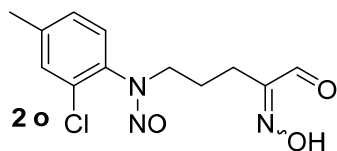


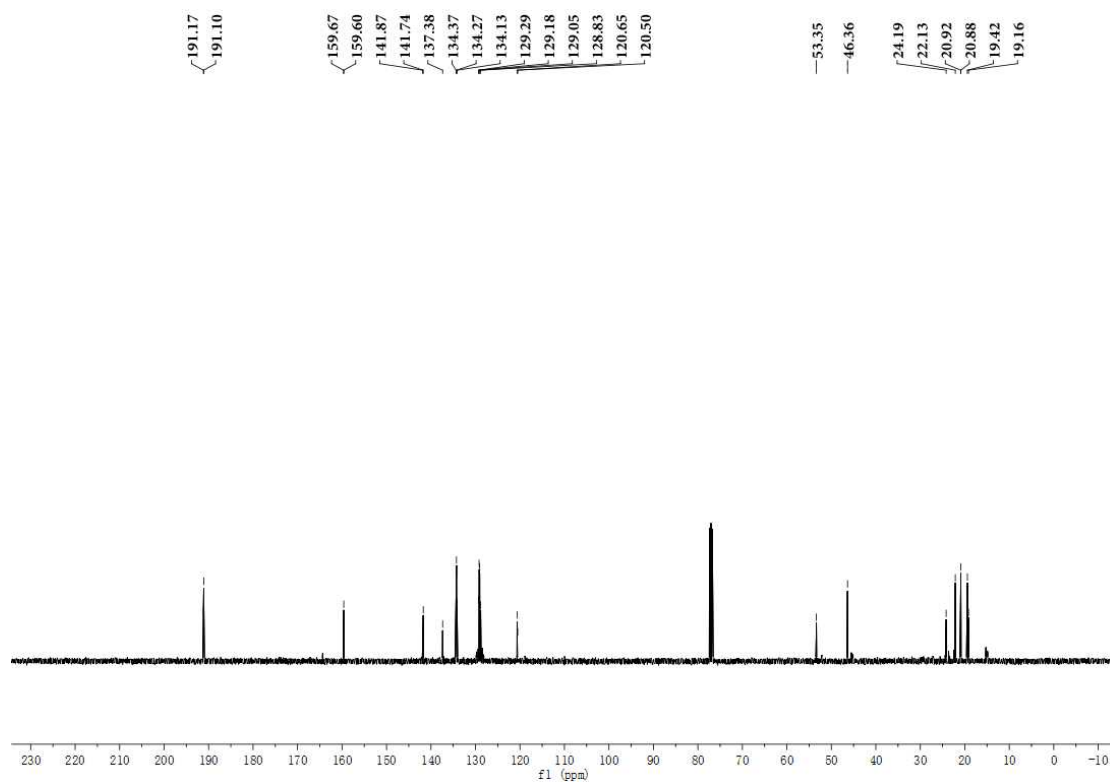
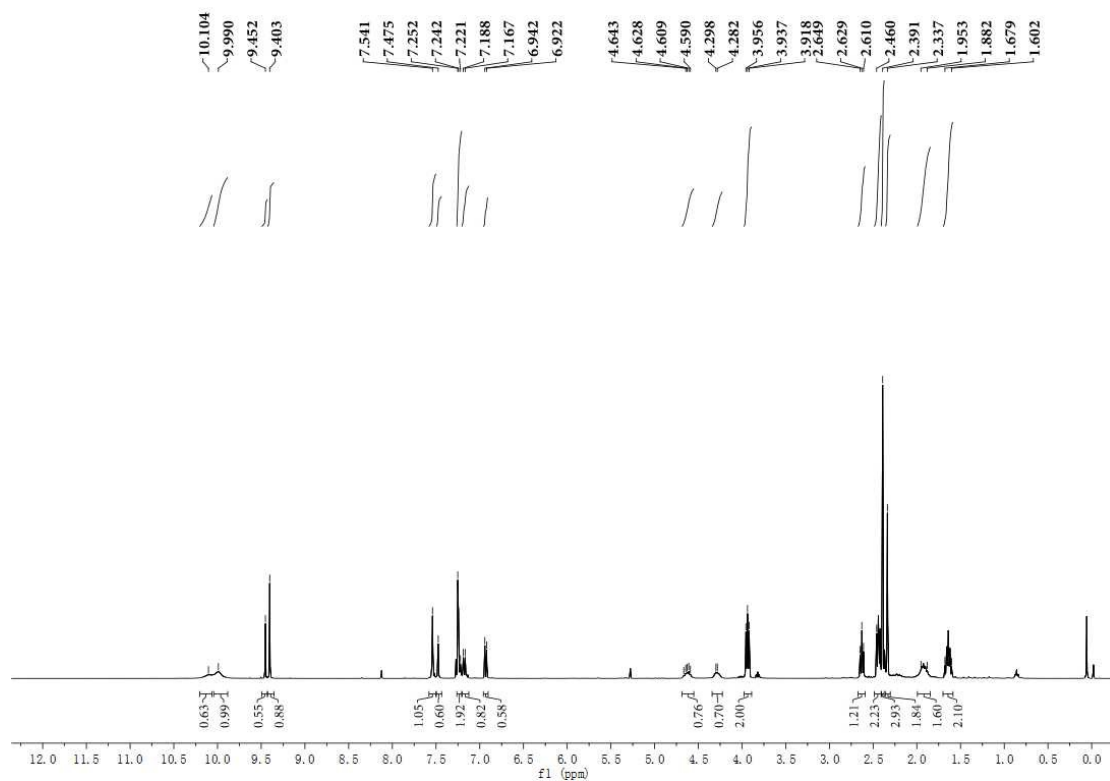
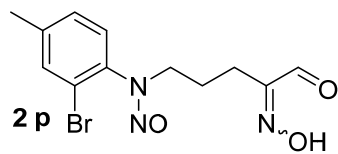


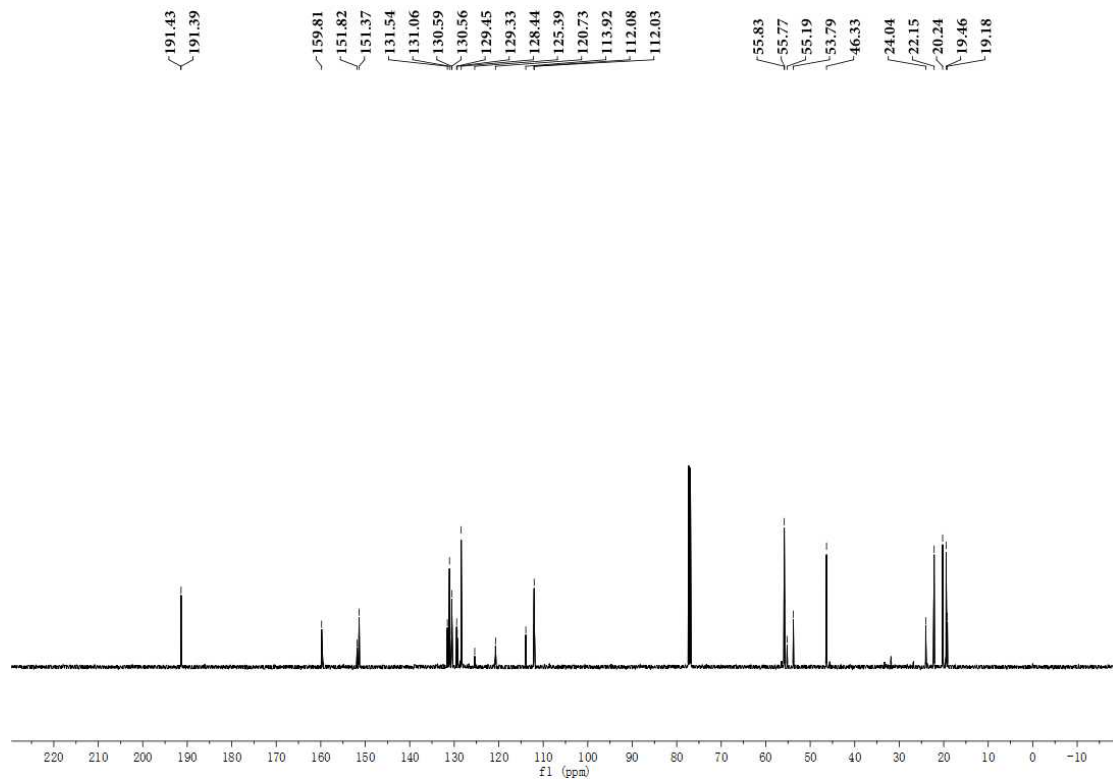
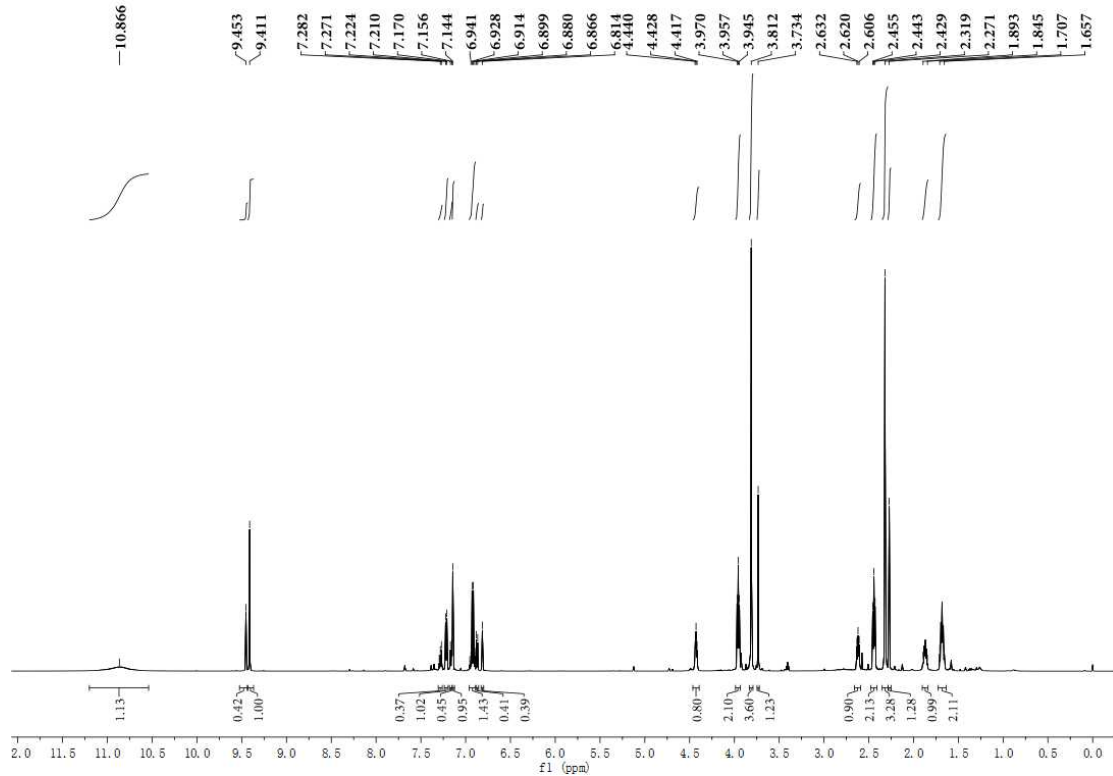
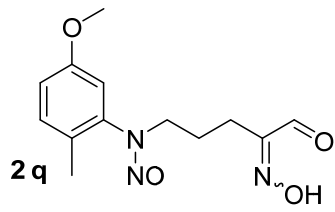


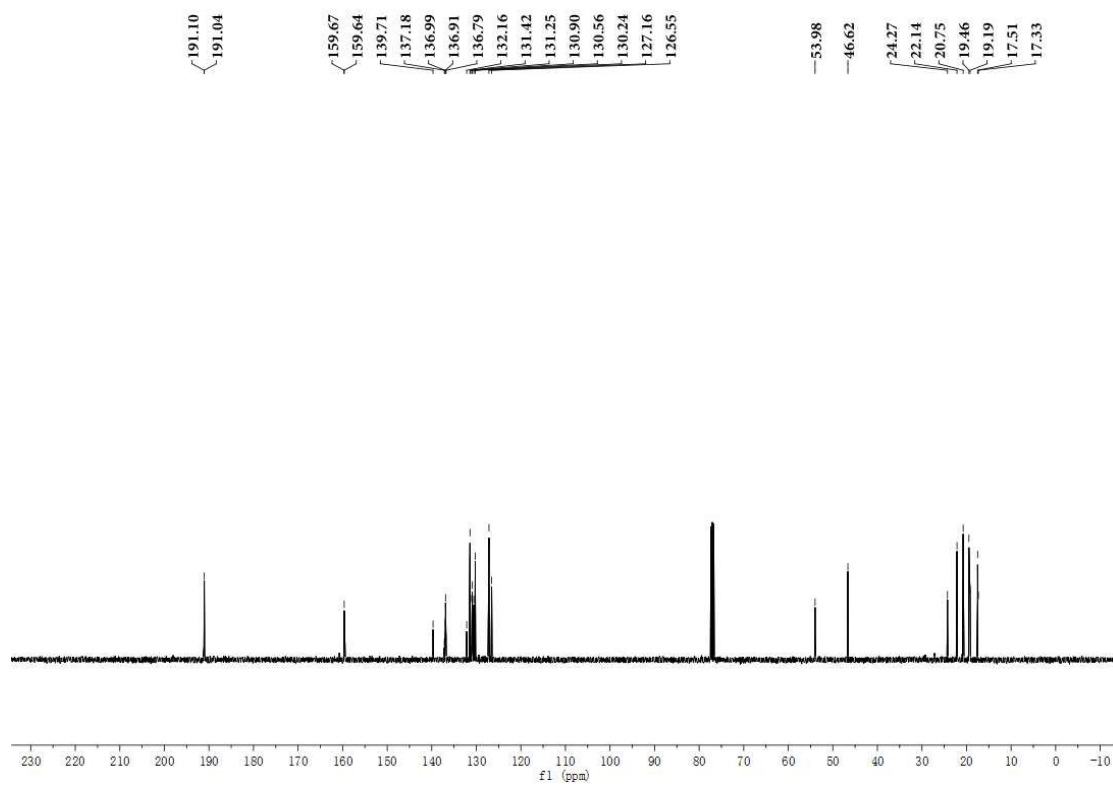
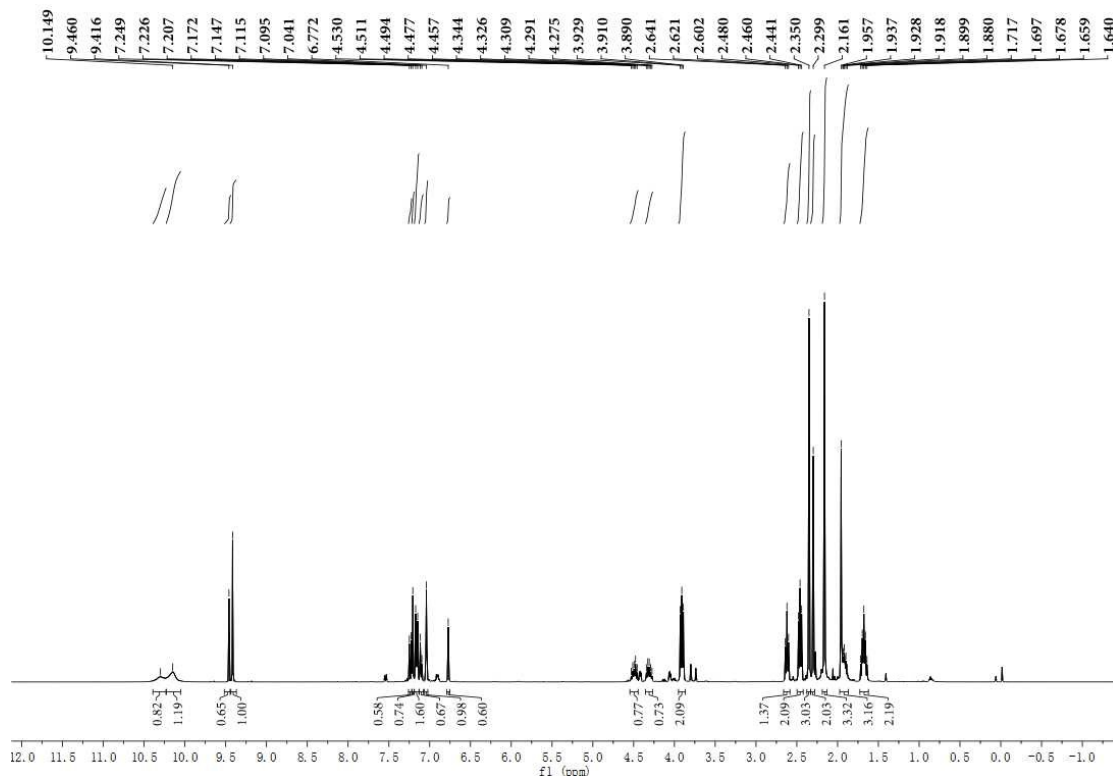
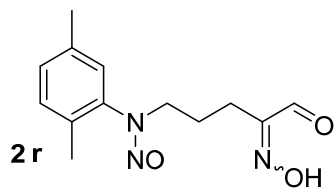


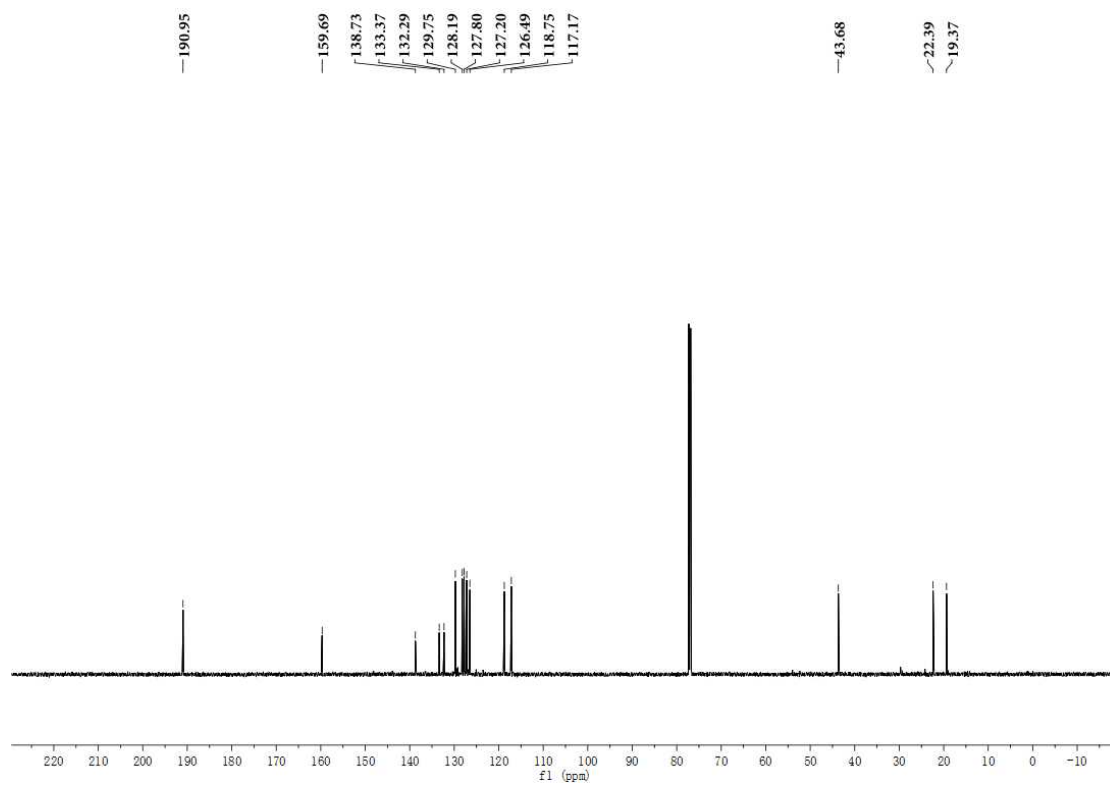
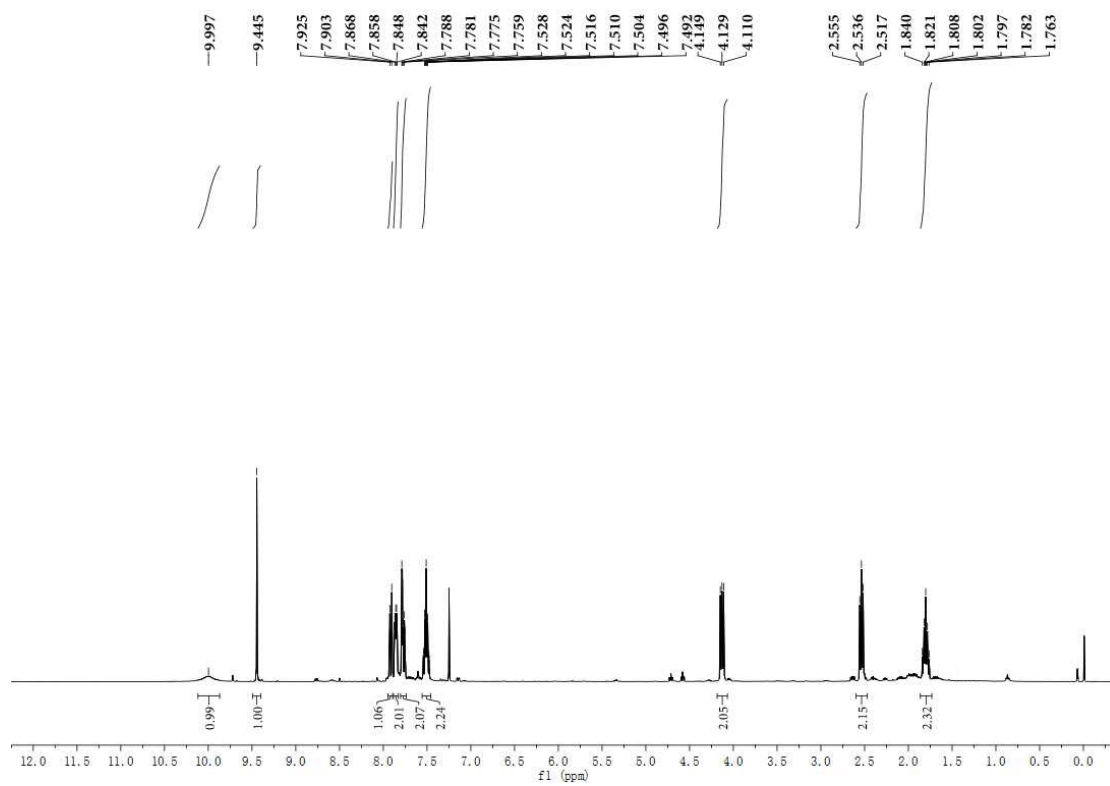
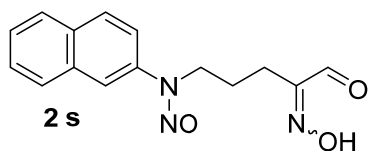


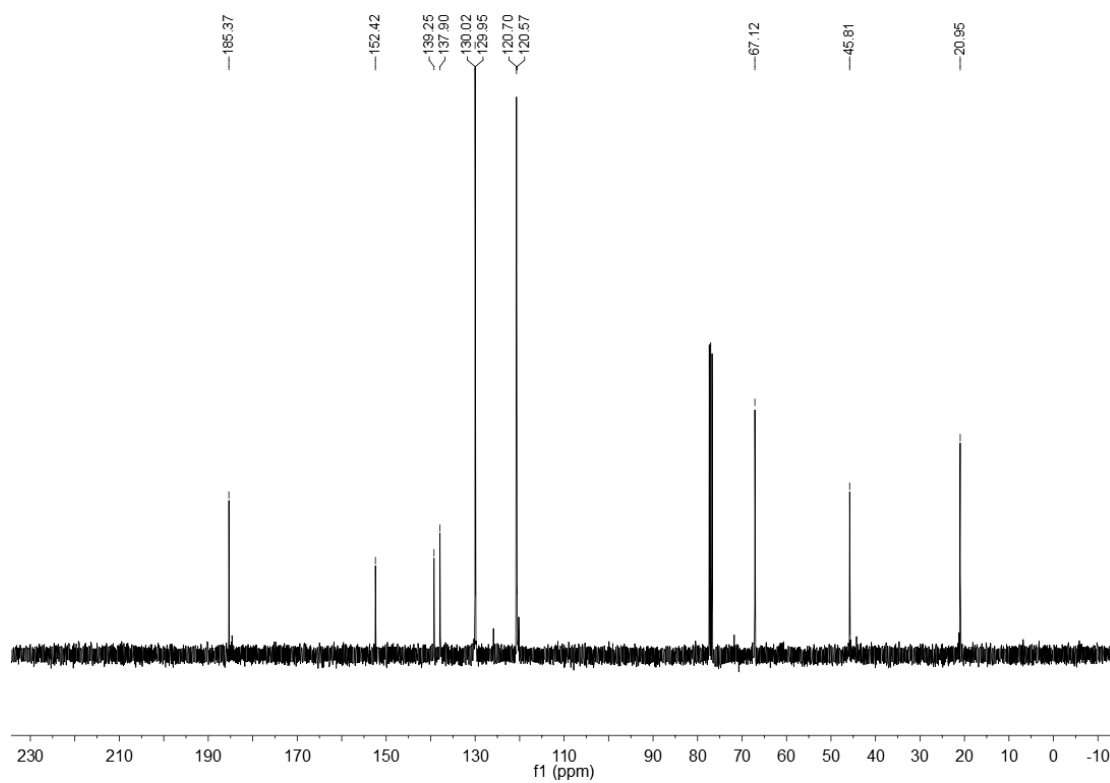
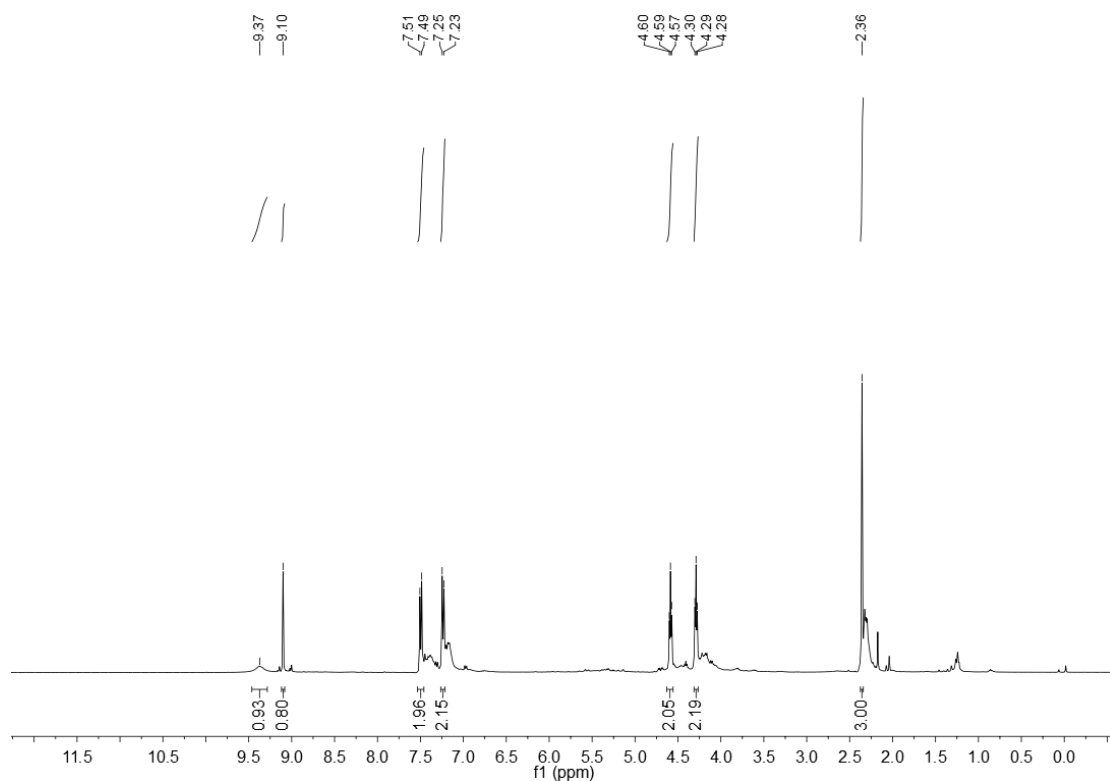
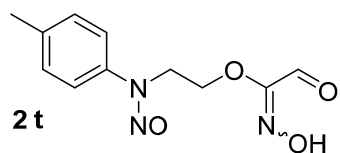


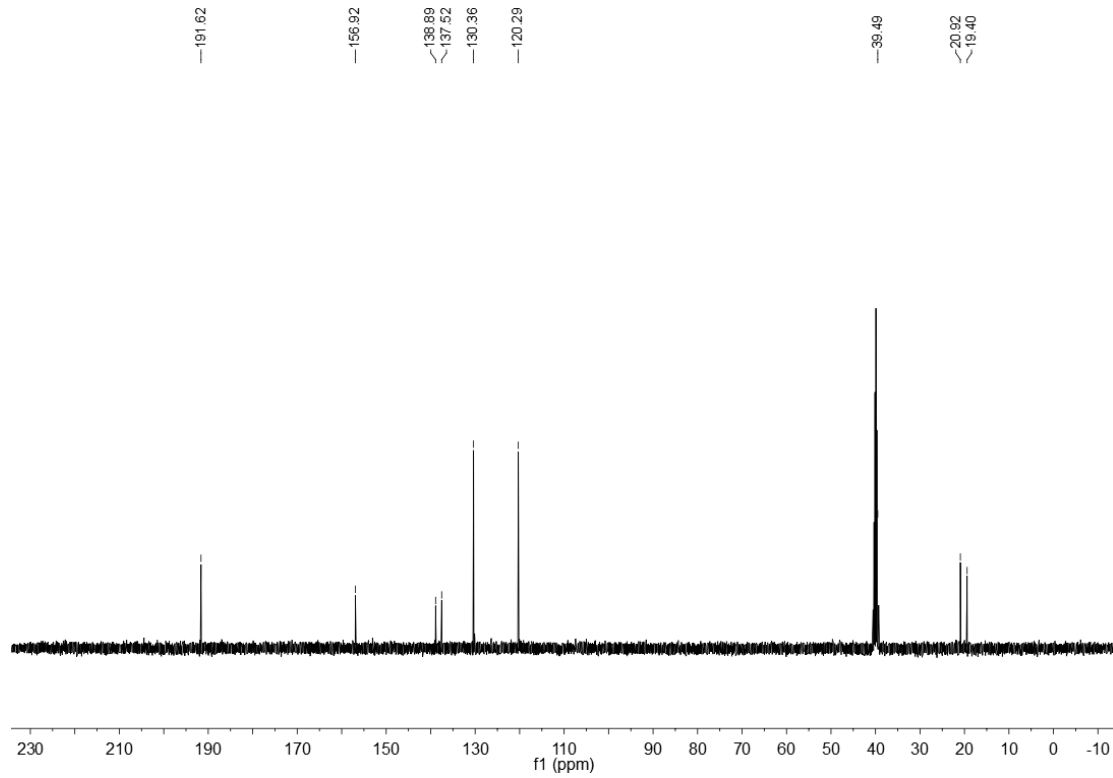
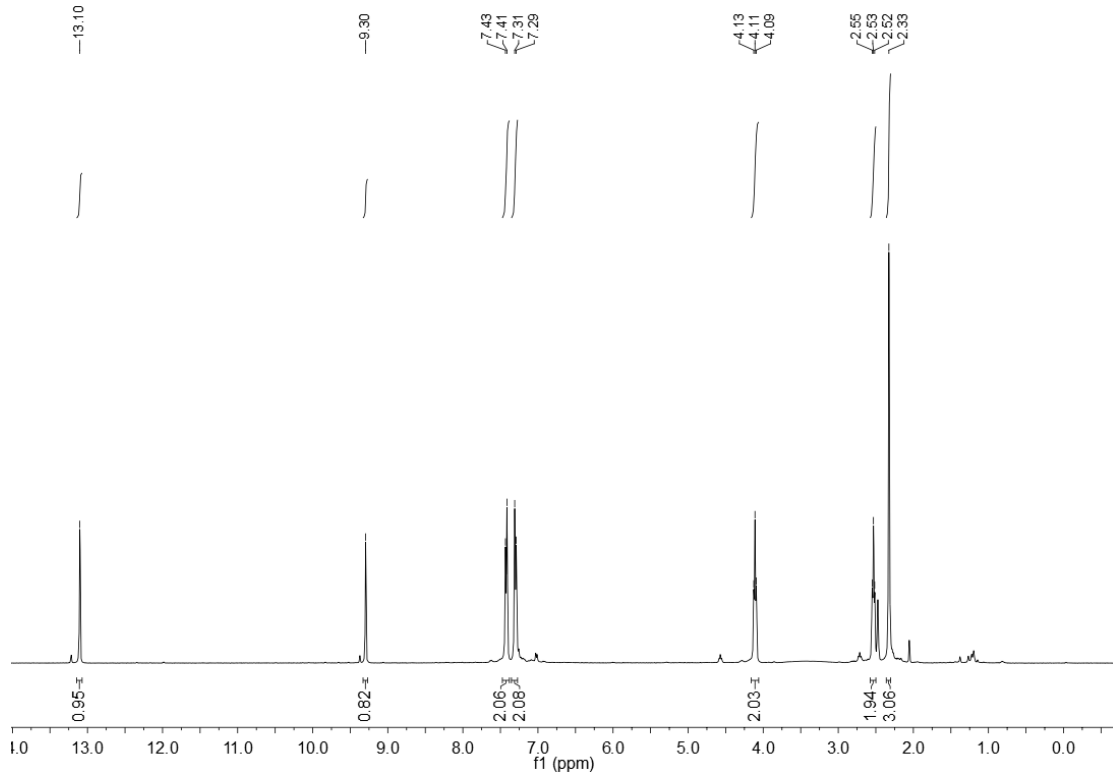
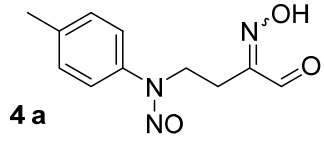


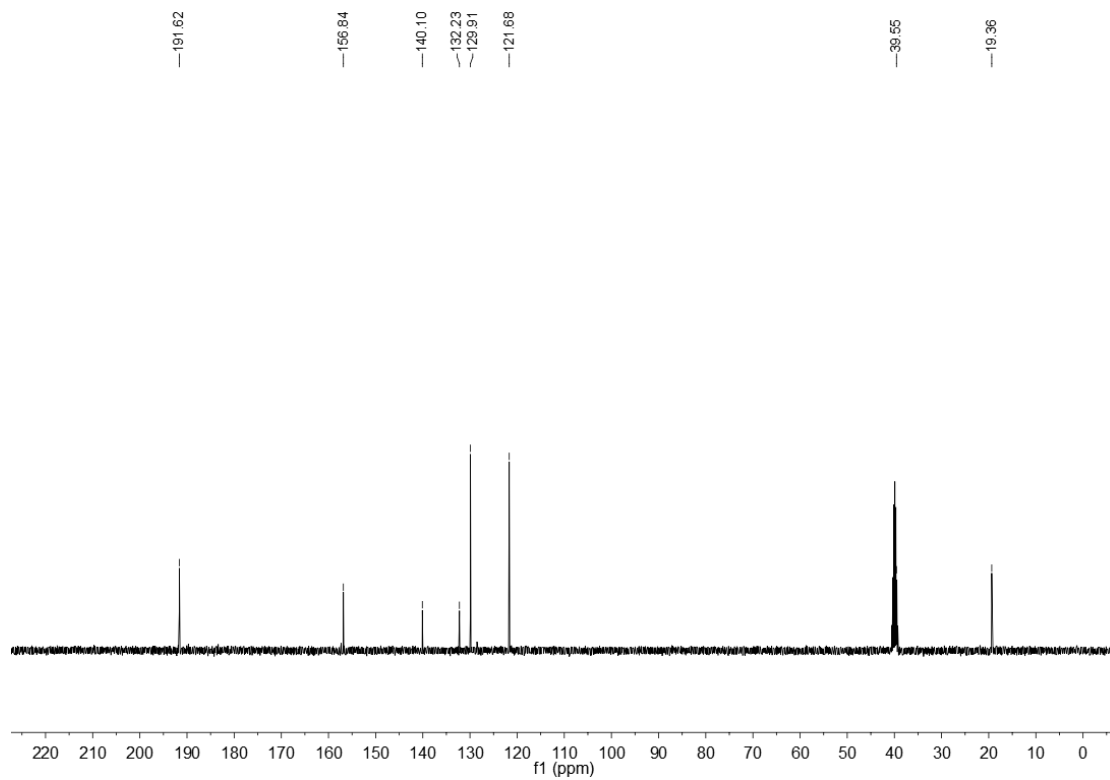
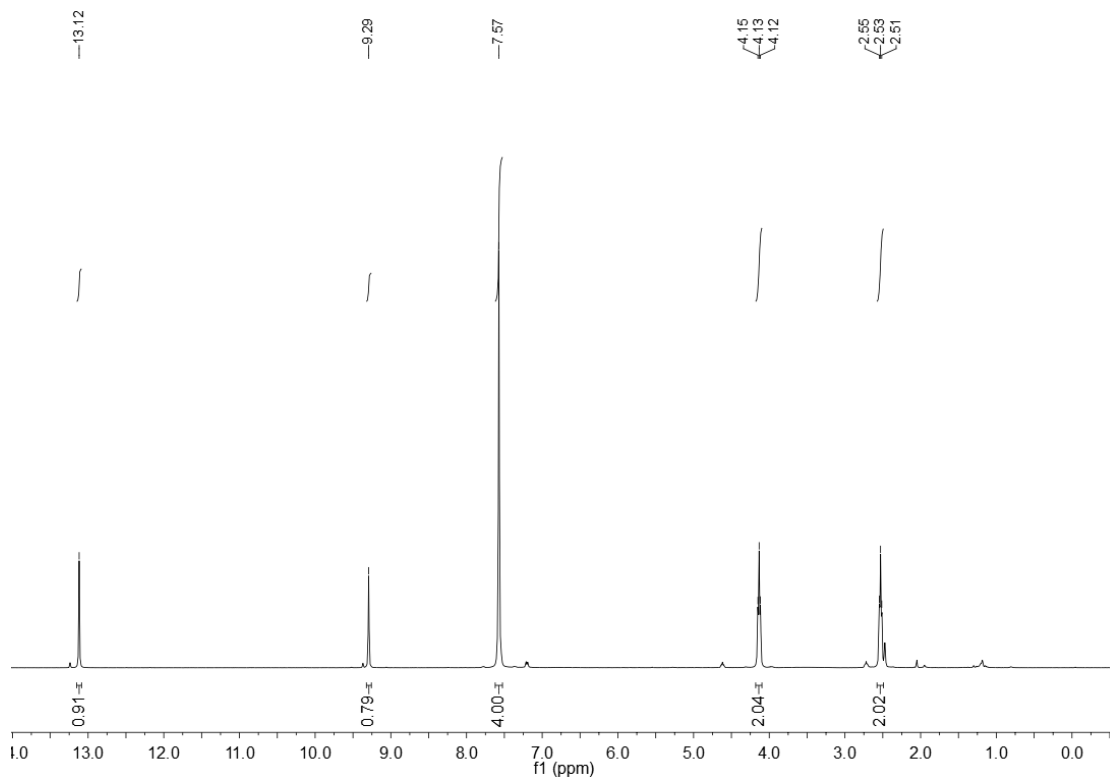
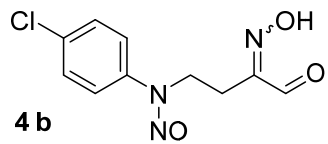


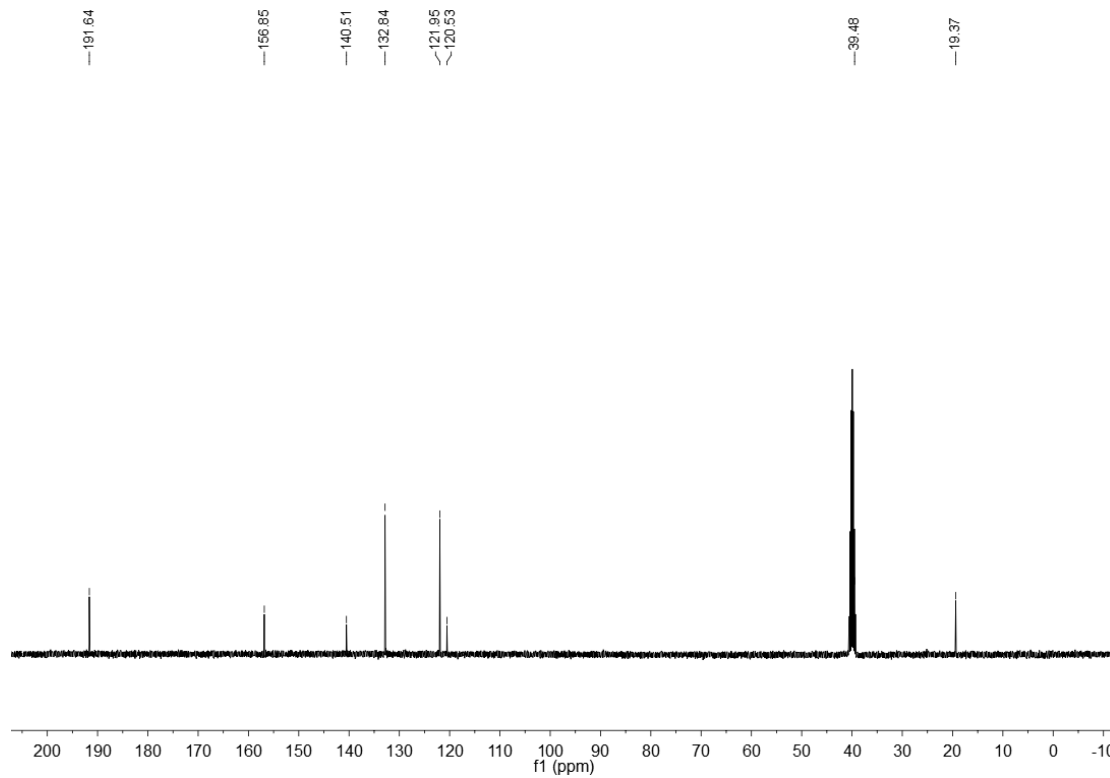
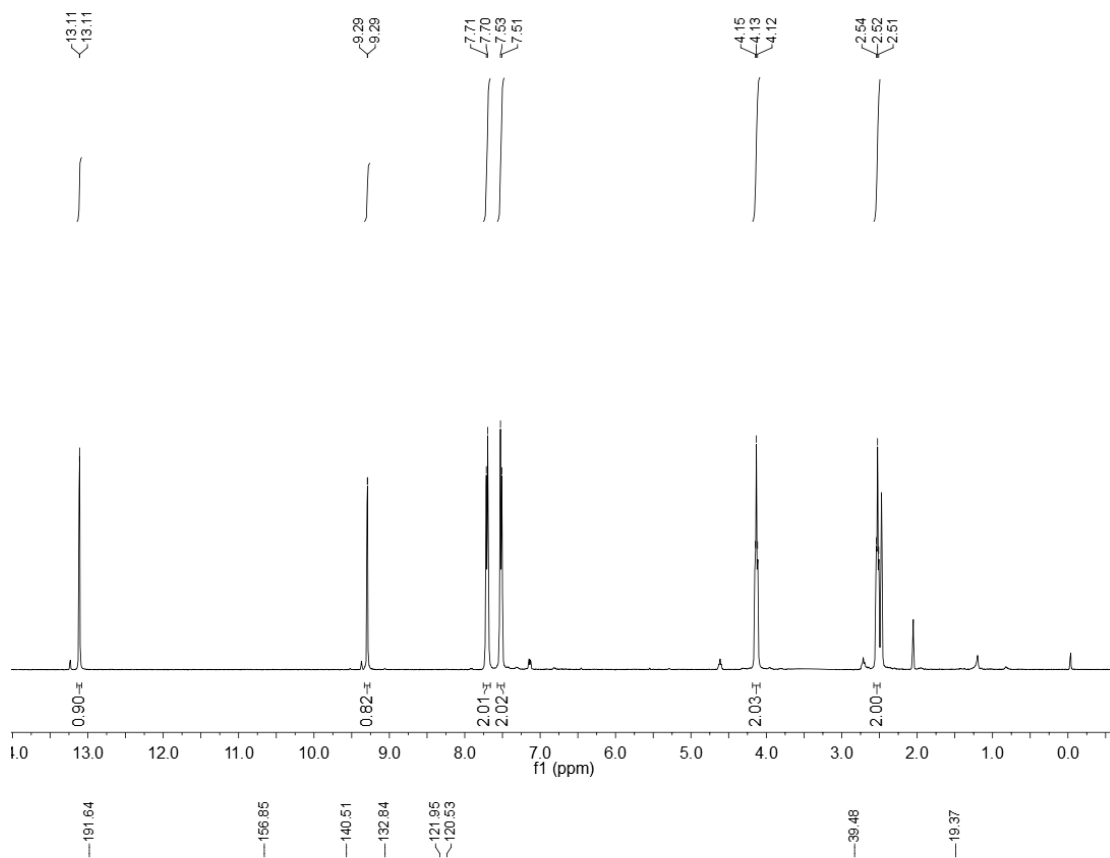
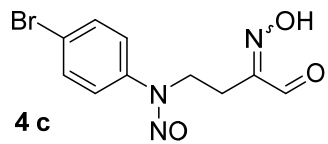


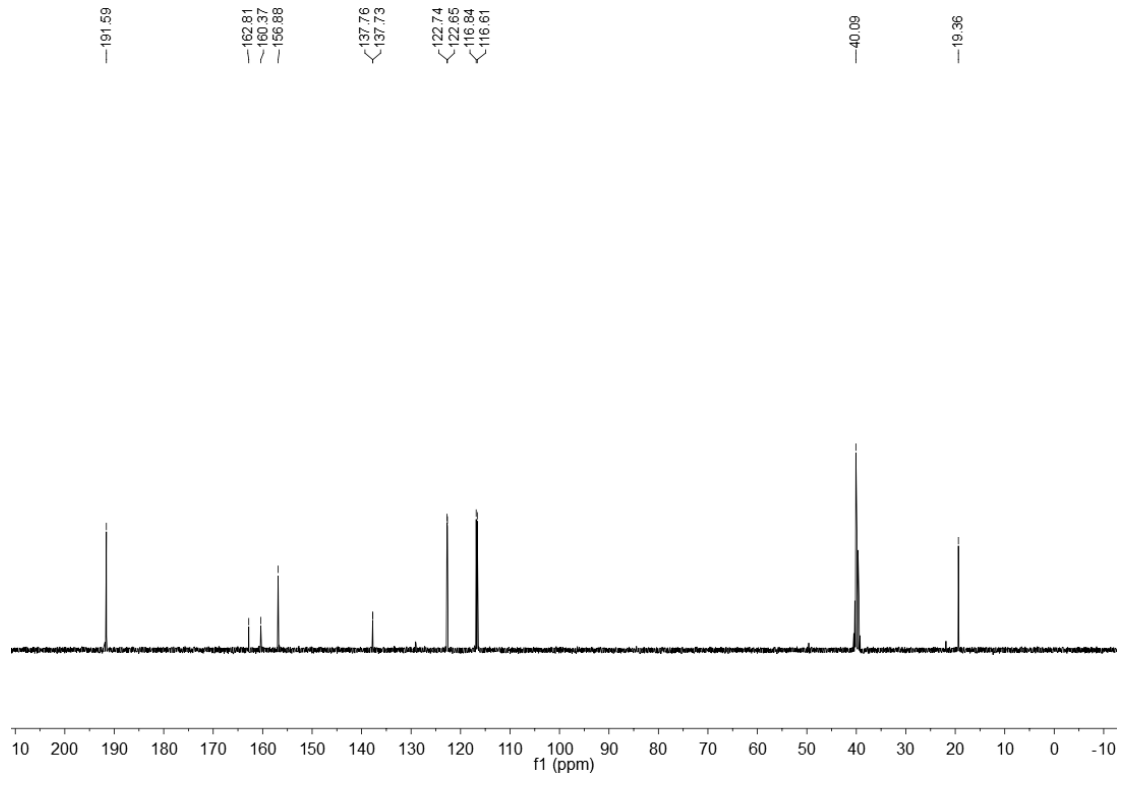
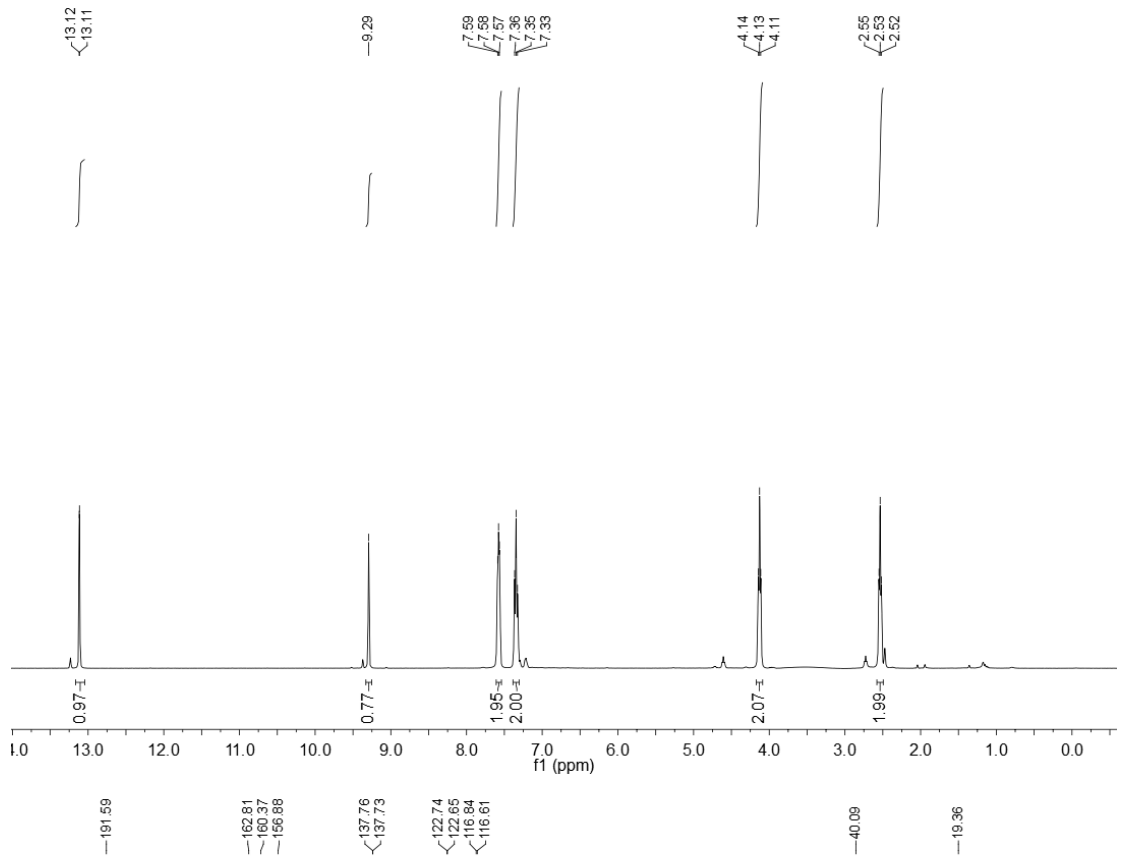
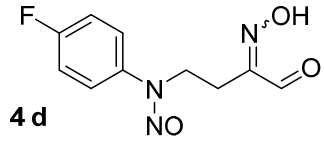


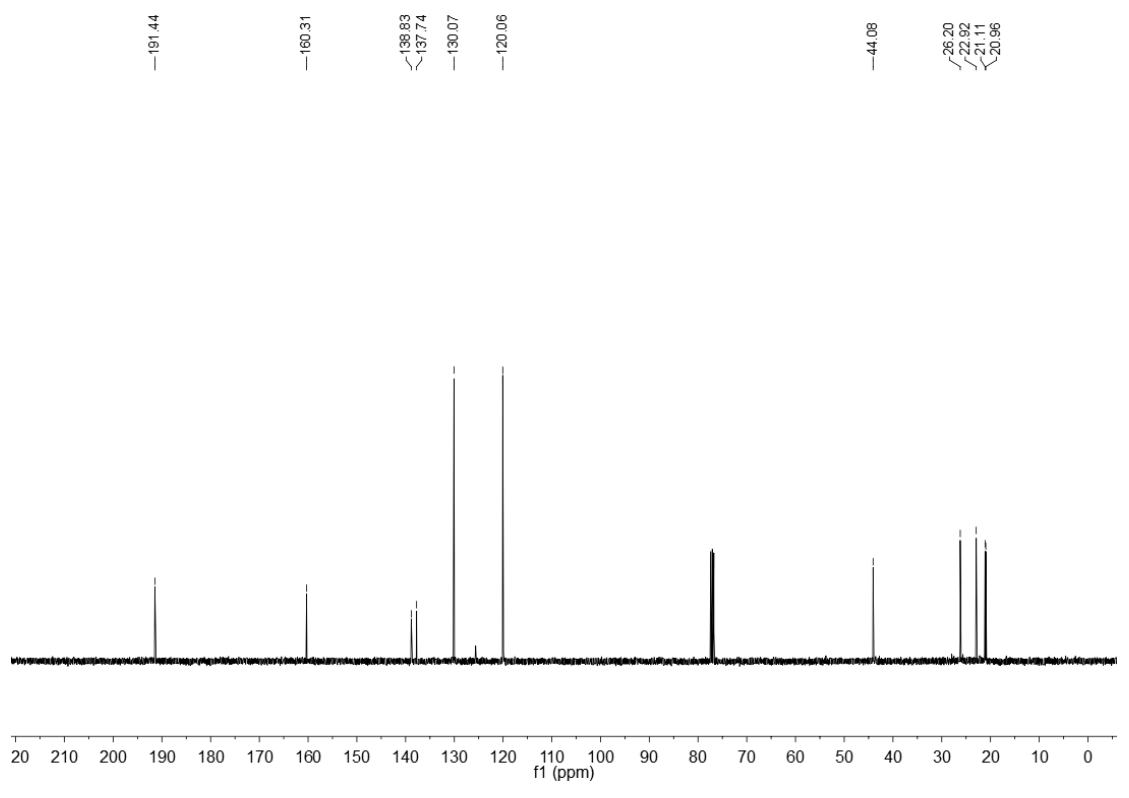
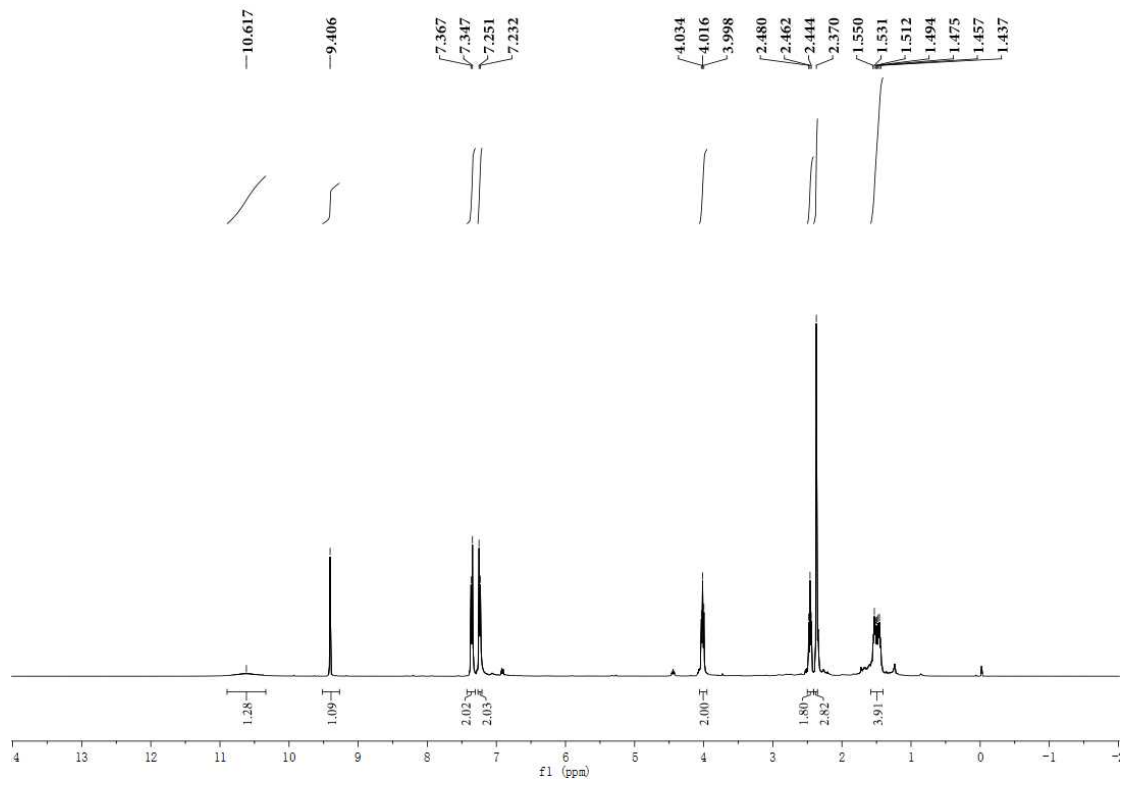
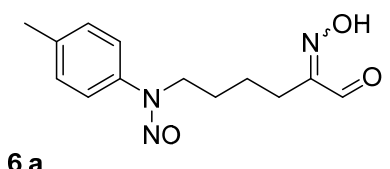


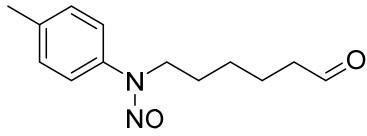




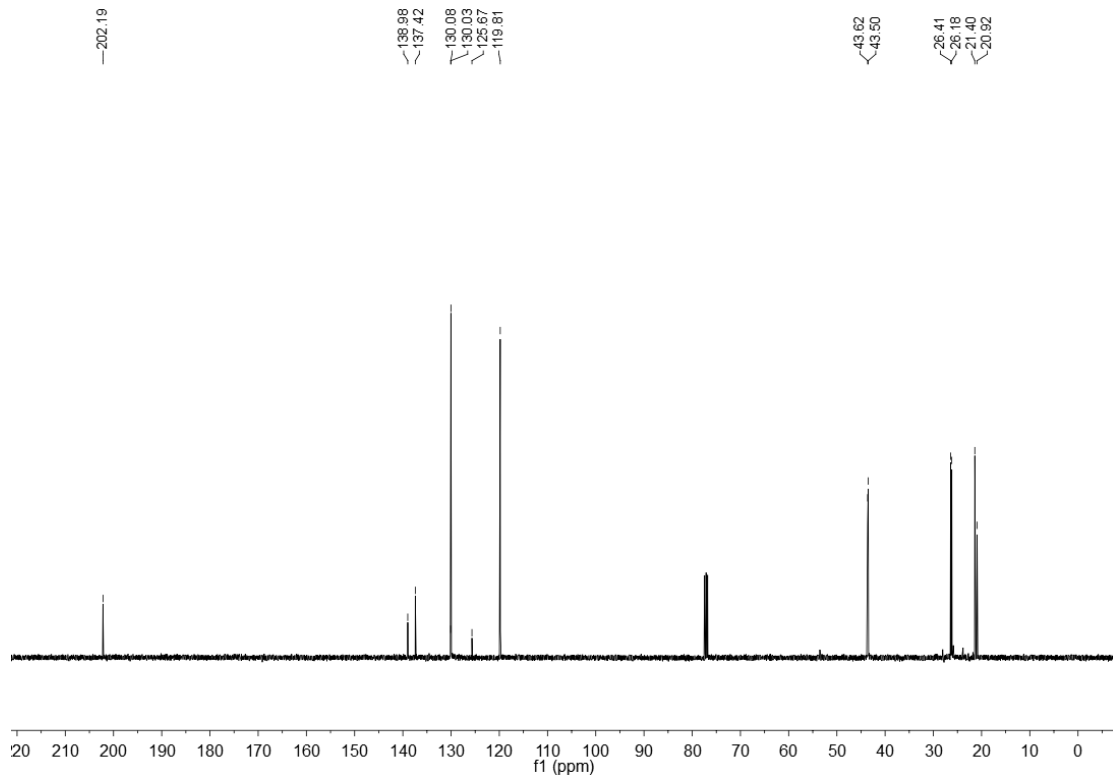
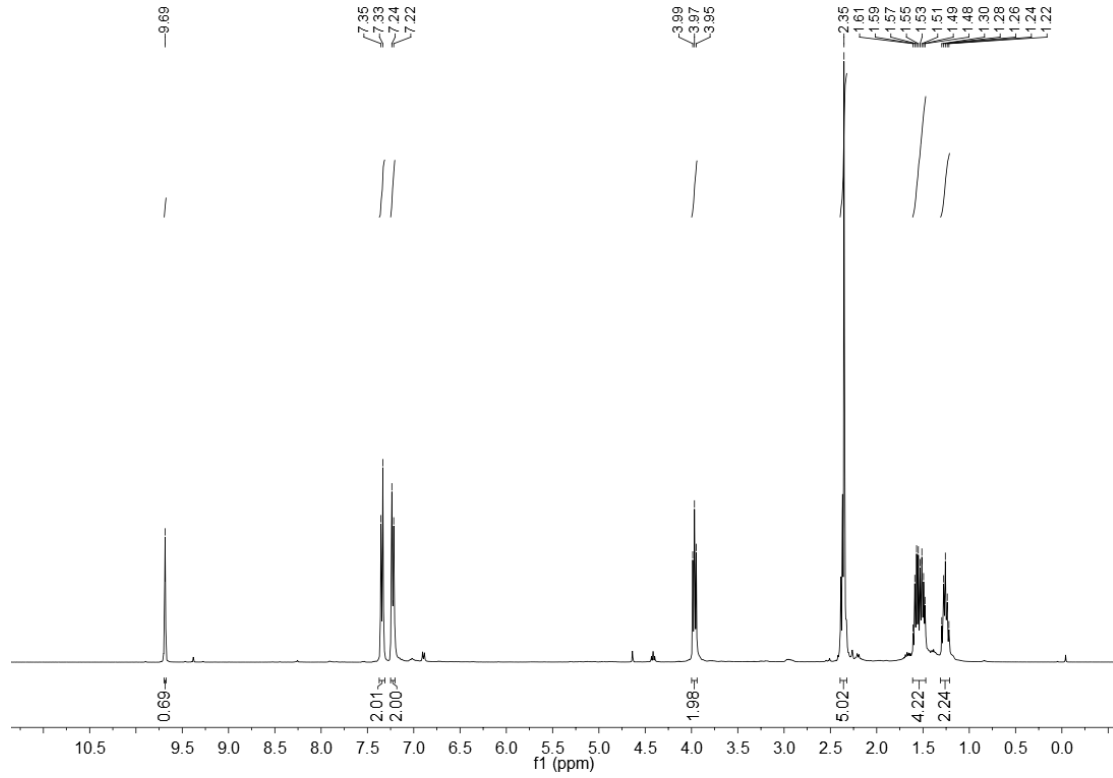


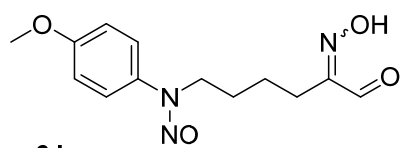




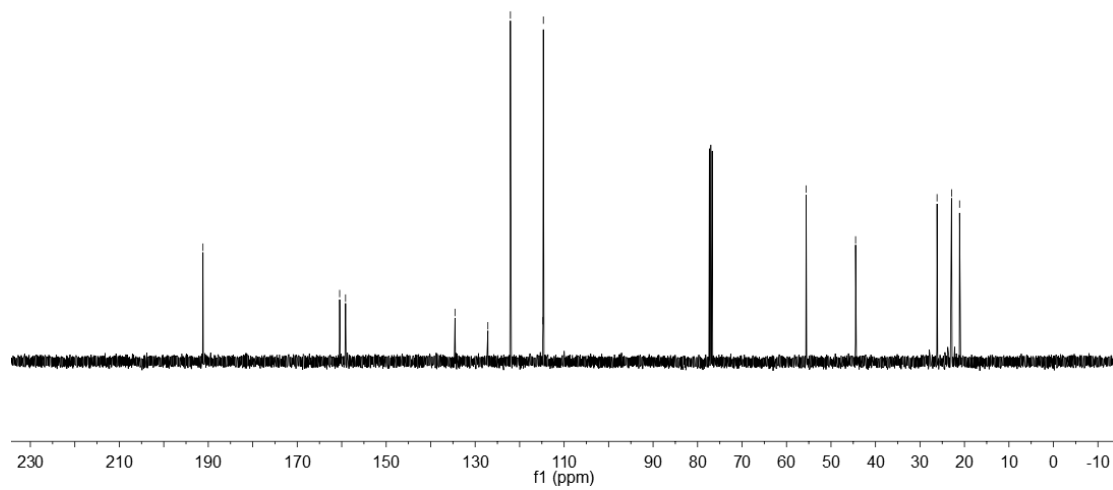
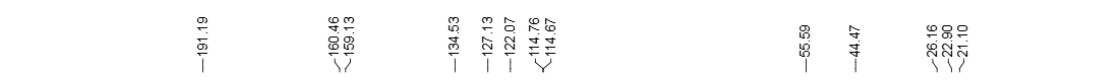
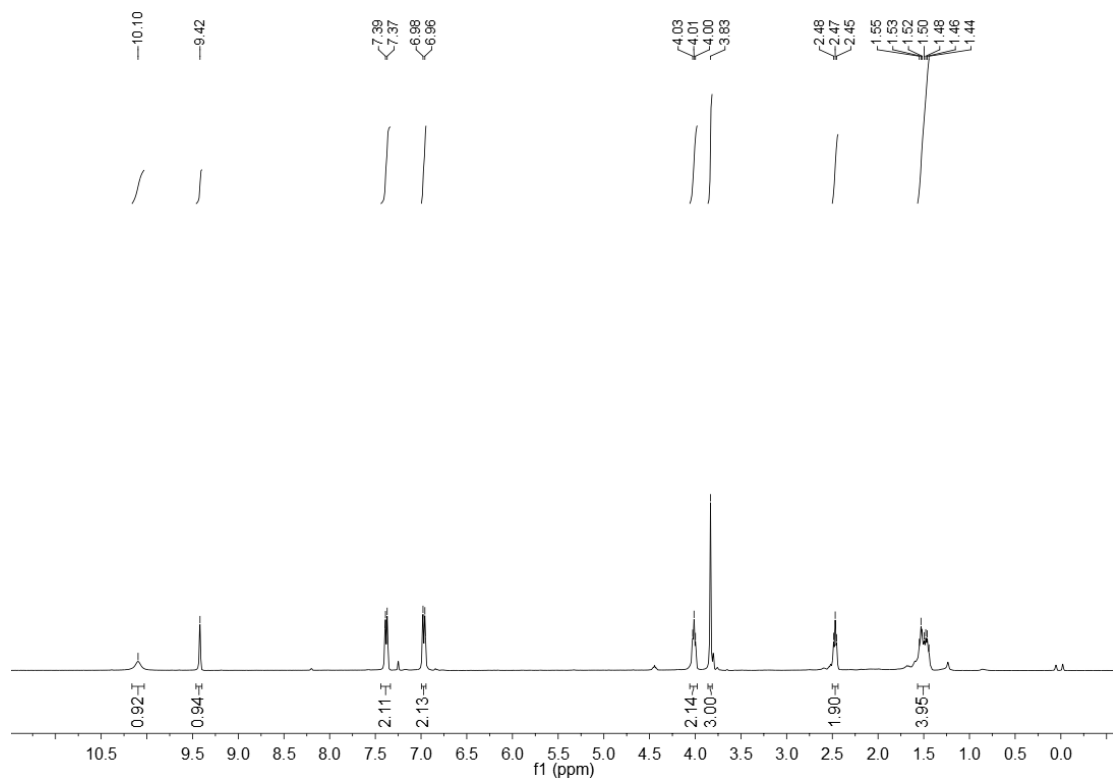


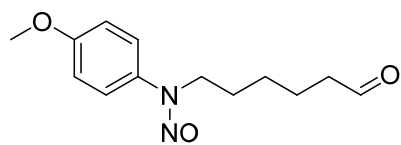
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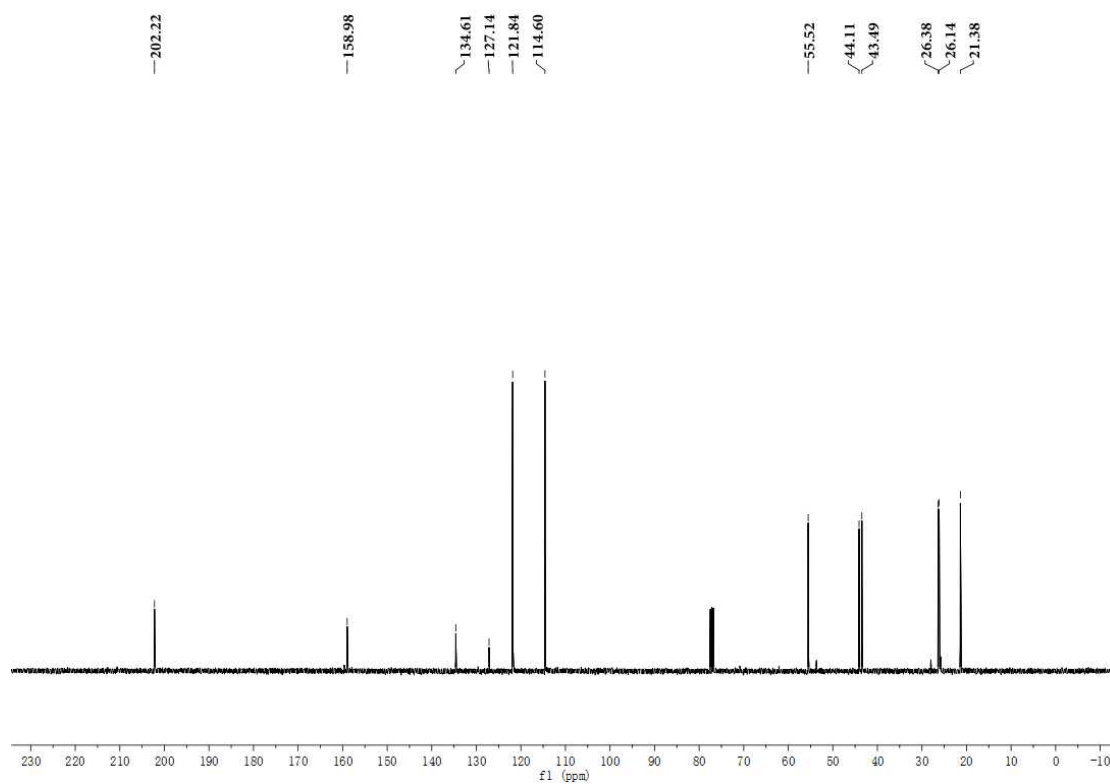
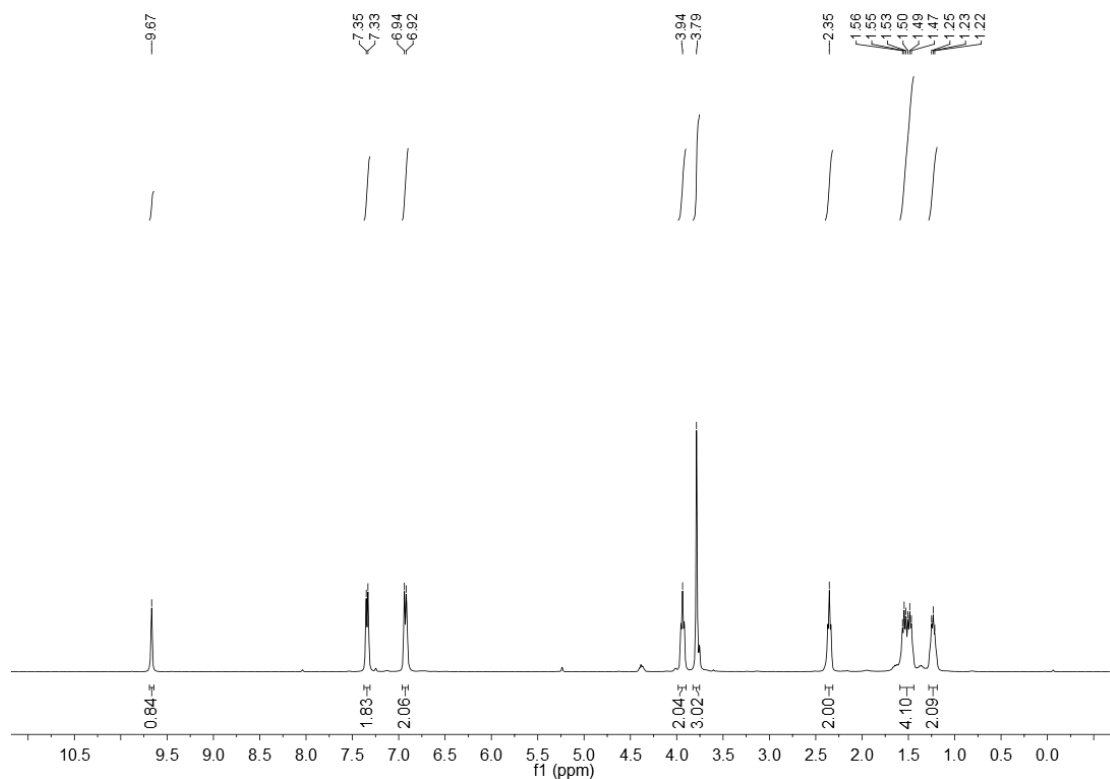


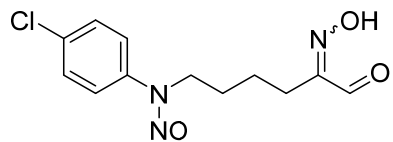
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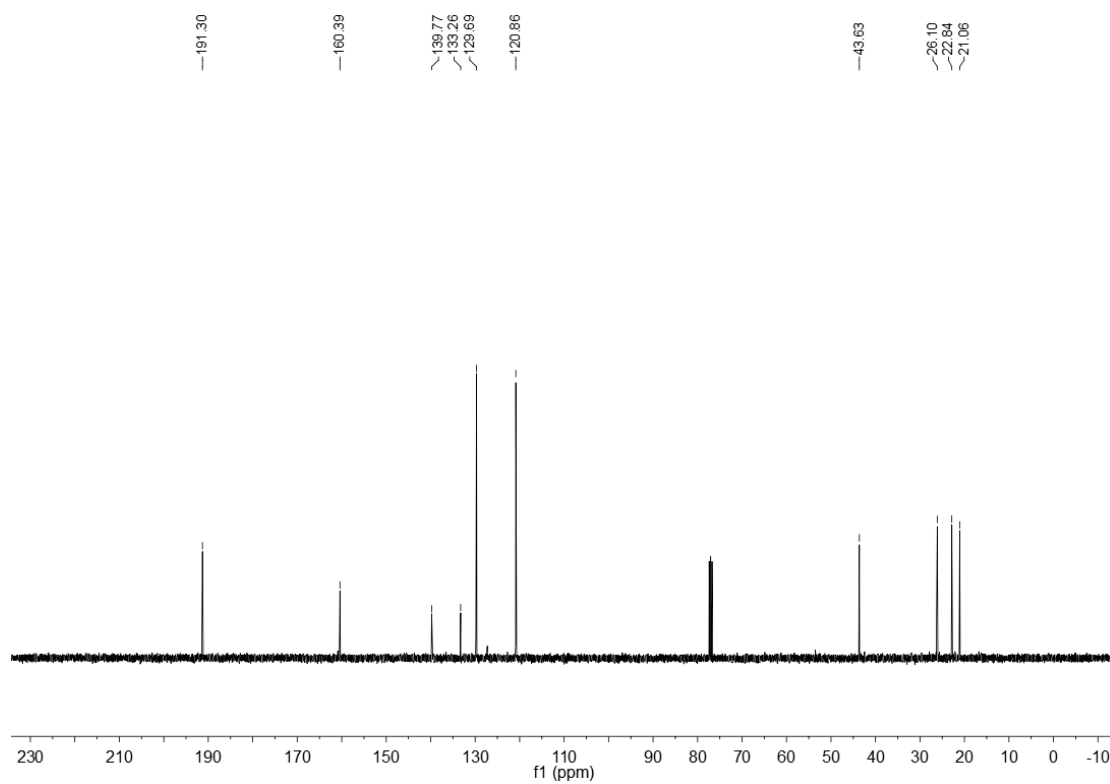
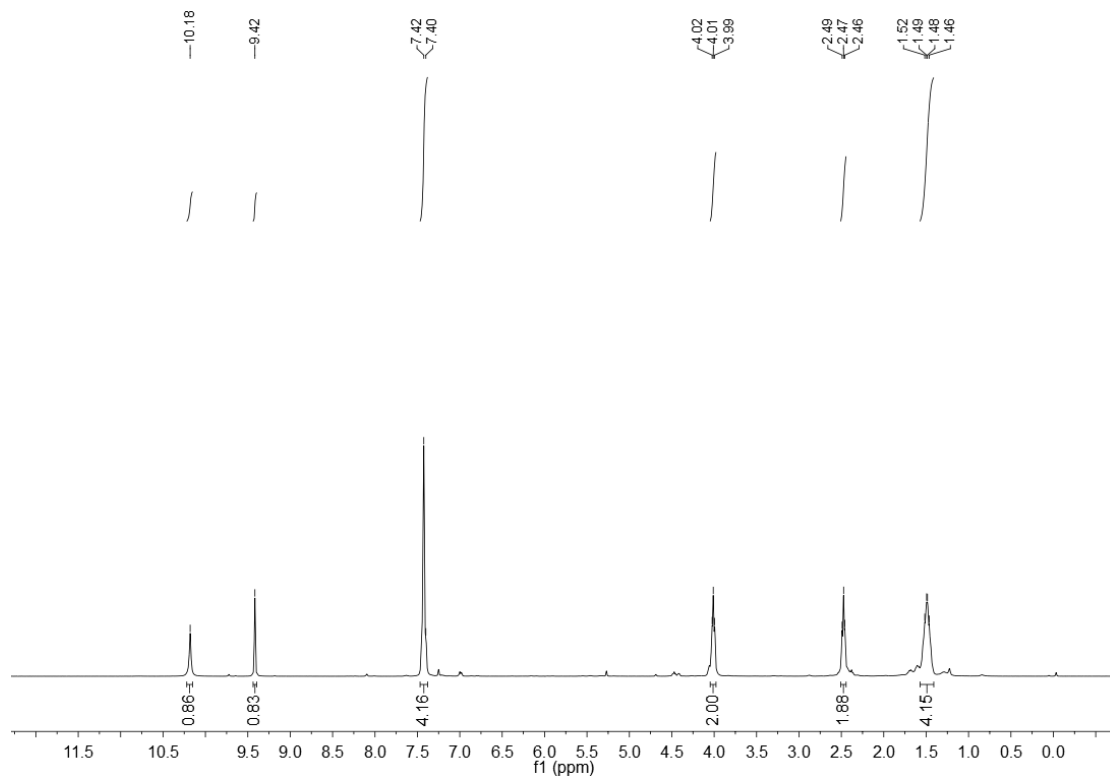


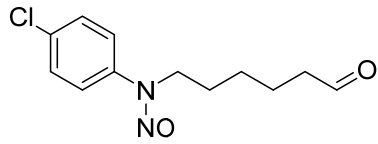
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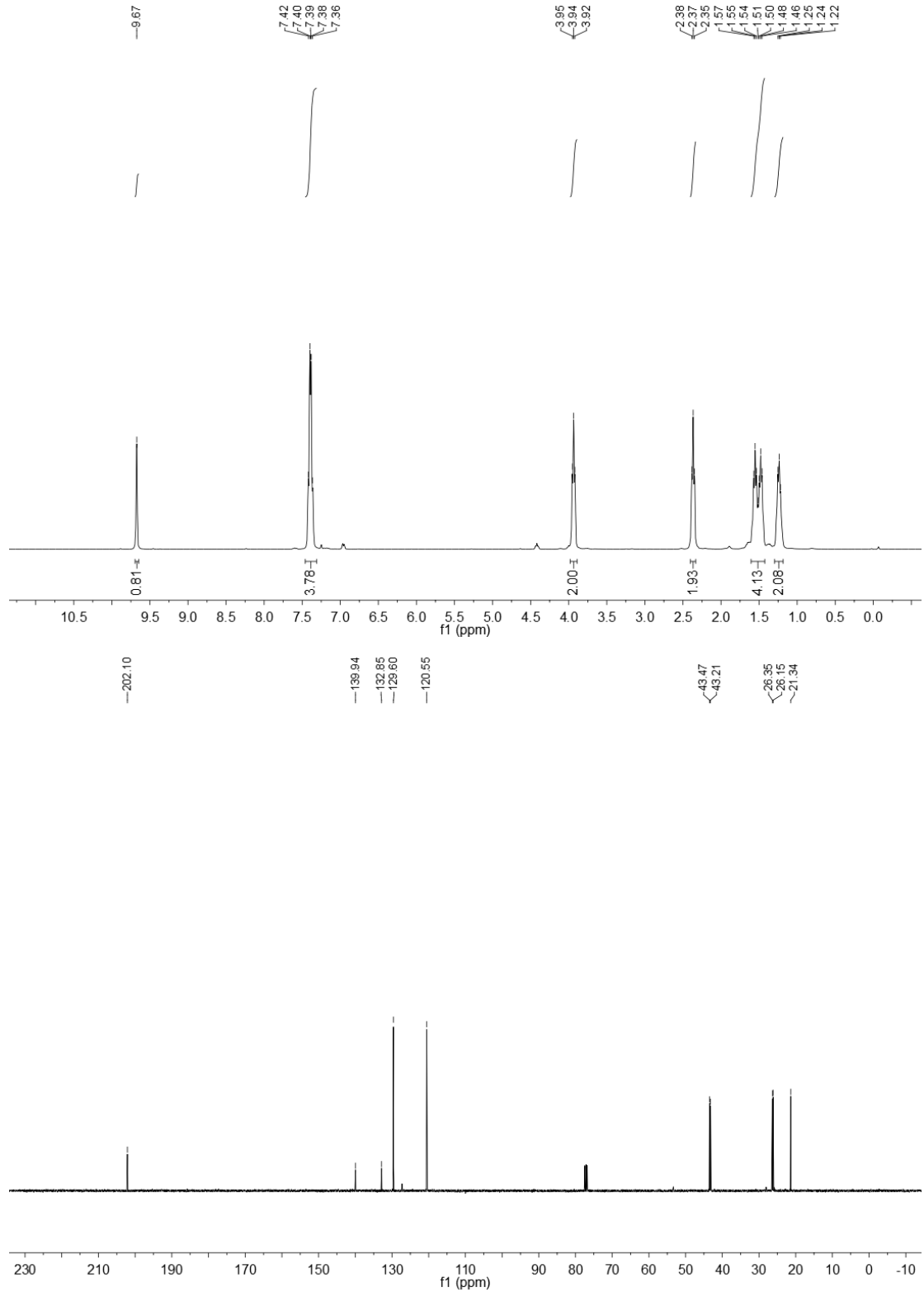


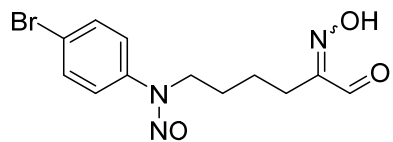
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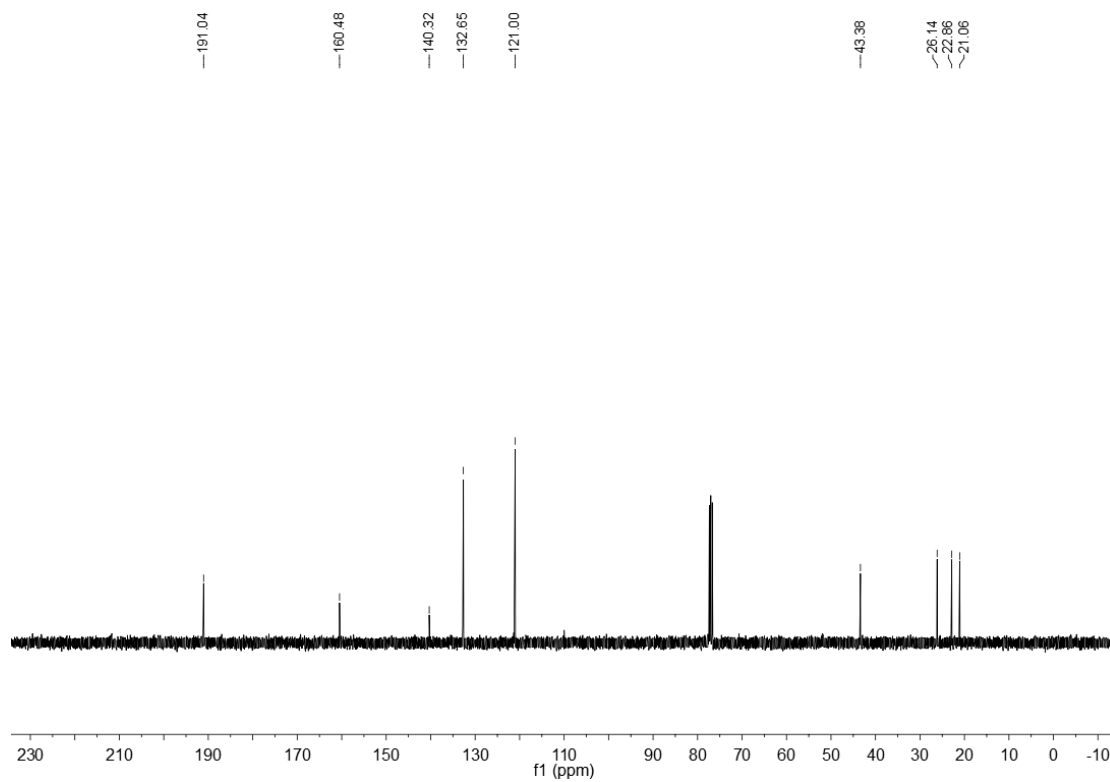
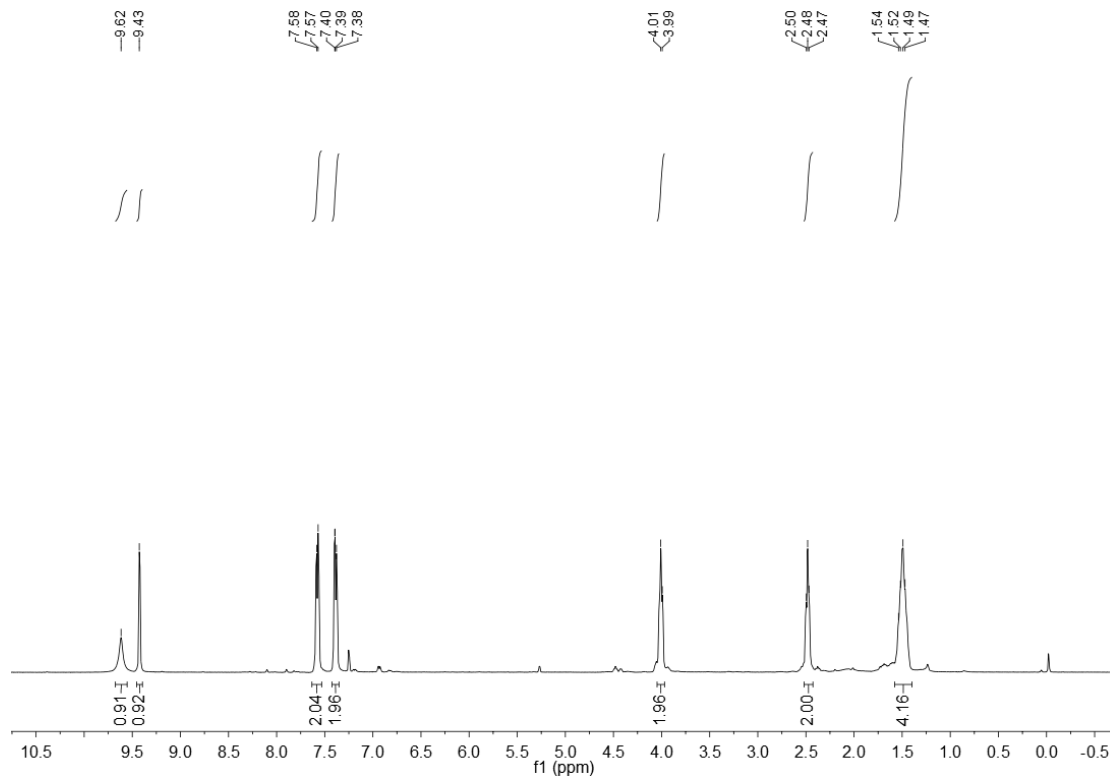


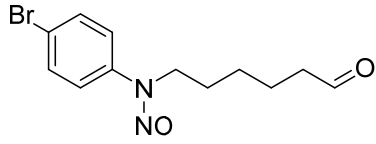
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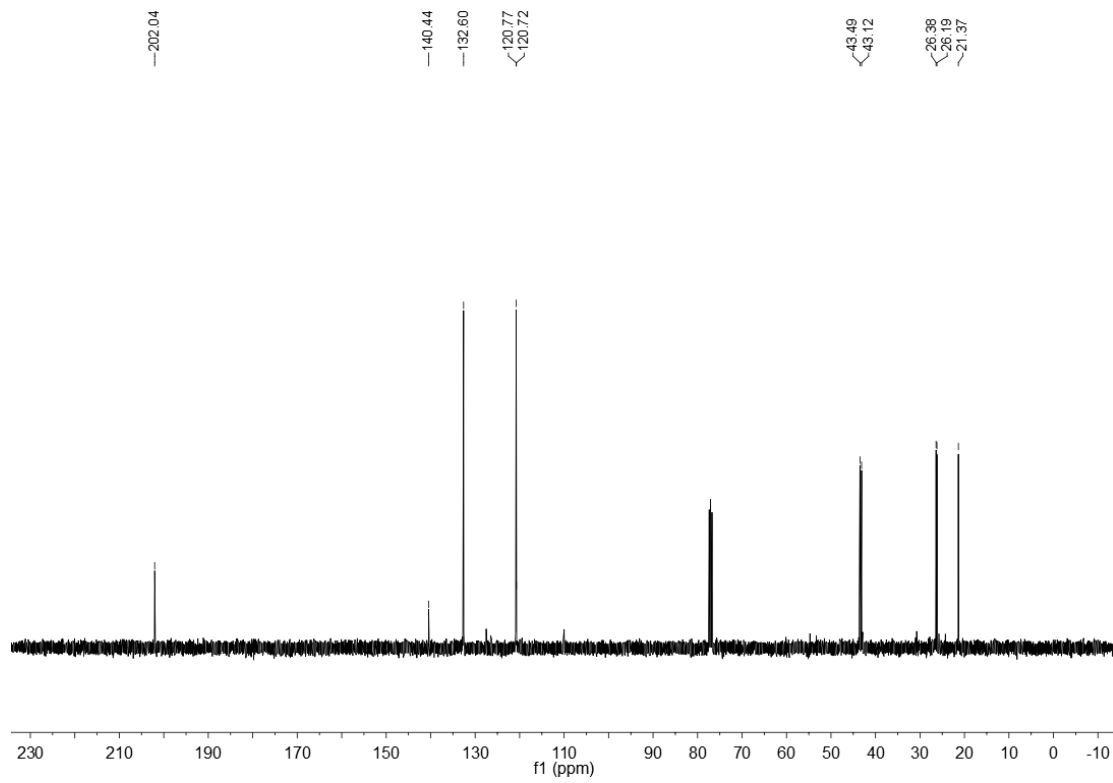
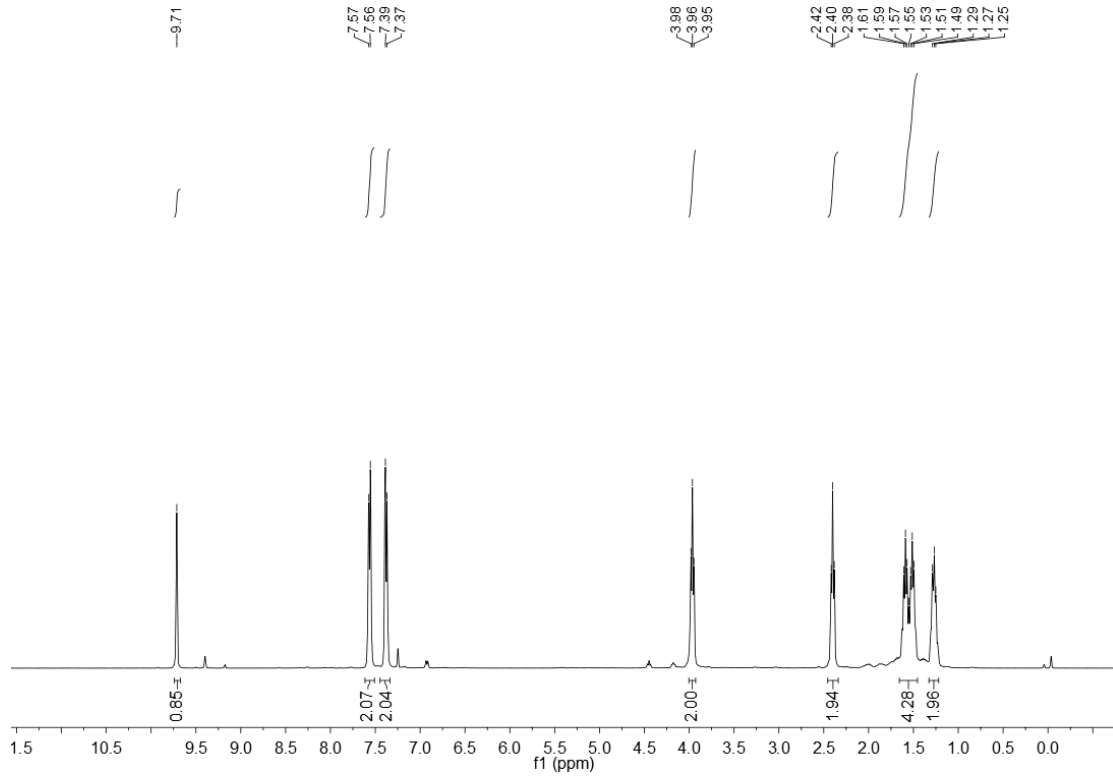


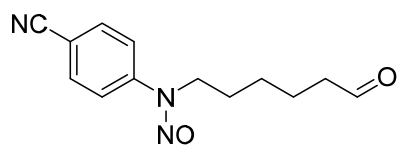
6d





7 d





7d

