Supporting Information

Modular Construction of Functionalized Anilines via Switchable C–H and N–Alkylation of Traceless N–Nitrosoanilines with Olefins

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A. General Information

^{1}H and ^{13}C NMR spectra were recorded on BRUKER DRX-400 spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); dt (doublets of triplet); dq (doublets of quartet). Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.0, triplet). Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS–QP 5000 spectrometer. HRMS was carried out on a MAT 95XP (Thermo).

B. General procedure

1) Synthesis of N-Nitrosamine Substrates:

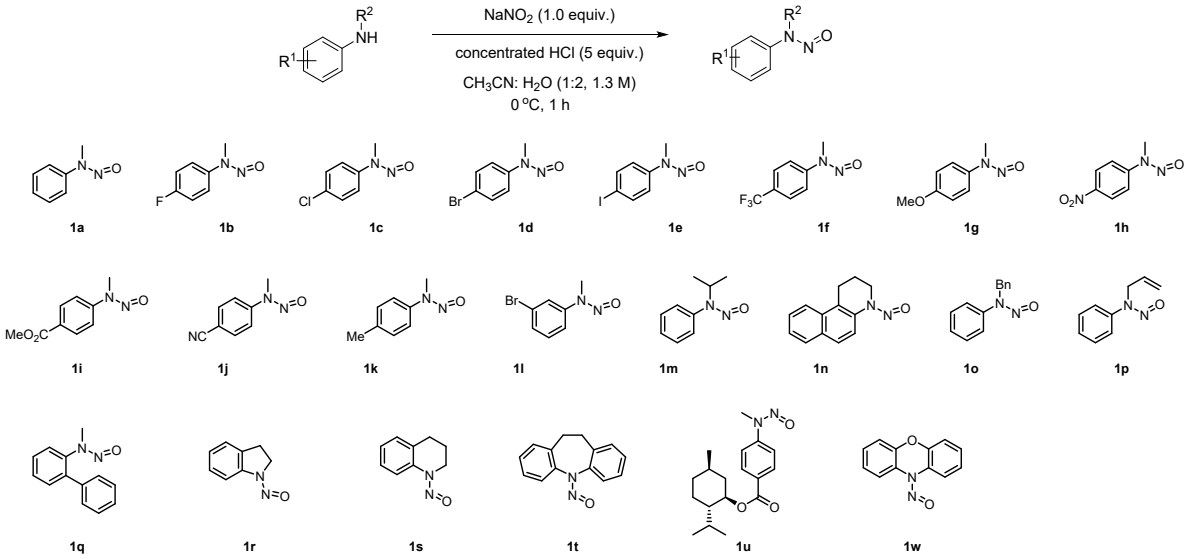
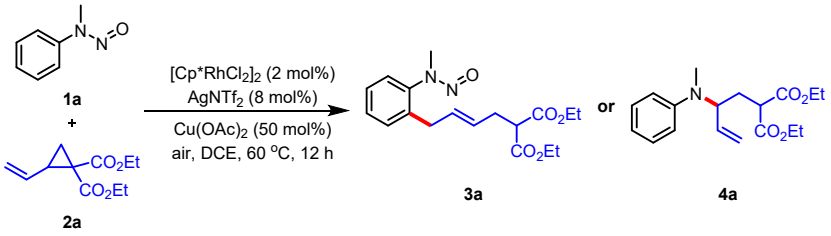


Figure S1. Synthesis of N-Nitrosamine Substrates.

A mixture of aniline (e.g., N-ethylaniline, 1.0 g, 10 mmol), concentrated HCl (1.3 ml, 5.0 equiv.) and ice (5.0 g) was placed in a round bottomed flask and stirred at low temperature. To this mixture was added an aqueous solution (13 mL) of $NaNO_2$ (0.7 g, 10 mmol) over the course of 5 to 10 min. The reaction was allowed to proceed for at least 1 h. The mixture was then extracted with DCM. The organic phase was washed with saturated brine solution, dried and dehydrated, and the solvent was removed under reduced pressure.[1]

2) Optimization of reaction conditions for sequential C-H/C-C activation versus N-N/C-C activation:



Entry	Variations from standard conditions	Yield[b] (%) 3a	4a
1	**None**	**90**	n.r.
2	$PdCl_2$ or $[IrCp^*Cl_2]_2$ instead of $[RhCp^*Cl_2]_2$	n.r.	n.r.
3	**$[Cp^*Co(CO)I_2]$** instead of $[RhCp^*Cl_2]_2$	0	**70**[c]
4[c]	AgOAc instead of $Cu(OAc)_2$	60	63[c]
5[c]	Without $Cu(OAc)_2$	<10	<10[c]
6[c]	NaOAc instead of $Cu(OAc)_2$	<10	80[c]
7[c]	HOAc instead of $Cu(OAc)_2$	<10	12[c]
8	$Cu(OAc)_2$ (30 mol%)	85	-[c]
9	$Cu(OAc)_2$ (5 mol%)	70	-[c]
10[c]	Addition of Cs_2CO_3 or PivOH (30 mol%)	85, 80	45, 30[c]
11[c]	HFIP or ^{t}Amyl-OH as the solvent	81, 77	n.r.[c]
12[c]	N_2 instead of air	20	65[c]
13[c]	rt instead of 60 °C	70	69[c]
14[c]	80 °C instead of 60 °C	89	70[c]
15[c]	120 °C instead of 60 °C	88	69[c]

[a] Standard conditions: **1a** (0.20 mmol), **2a** (0.50 mmol), $[Cp^*RhCl_2]_2$ (2 mol%) or $[Cp^*Co(CO)I_2]$ (2 mol%), $AgNTf_2$ (8 mol%), $Cu(OAc)_2$ (30 mol%), 60 °C, DCE (1 mL) under air for 12 h.

[b] Isolated yield.

[c] $[Cp^*RhCl_2]_2$ as catalyst for **3a**; for **4a,** $[Cp^*Co(CO)I_2]$ was used as catalyst, with NaOAc instead of $Cu(OAc)_2$.

3) General procedure for C–H Alkylation of N-nitroso anilines:

An oven-dried 10 mL Schlenk Tube was charged with N-nitrosamine substrate **1** (0.20 mmol), $[RhCp^*Cl_2]_2$ (2 mol%), $AgNTf_2$ (8 mol%) and $Cu(OAc)_2$ (50 mol%) in sequence, followed by addition of Olefins **2** or **5** or **6** (0.50 mmol) in DCE (1.0 mL) through syringe. The resulting reaction mixture was stirred at 60°C for 12 h and then diluted with CH_2Cl_2 and filtered through diatomite. Removing the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired products.

4) General procedure for N-Alkylation of N-nitroso anilines:

An oven-dried 10 mL Schlenk Tube was charged with N-nitrosamine substrate **1** (0.20 mmol), $[Cp^*Co(CO)I_2]$ (2 mol%), $AgNTf_2$ (8 mol%) and NaOAc (50 mol%) in sequence, followed by addition of Olefins **2** or **5** or **6** (0.50 mmol) in DCE (1.0 mL) through syringe. The resulting reaction mixture was stirred under air at 60°C for 12 h and then diluted with CH_2Cl_2 and filtered through diatomite. Removing the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired products.

C. Synthetic applications and mechanistic studies

1) Synthesis of *ortho* C–H alkenylated anilines via selective reductions:

The obtained C–H alkylated N-nitroso anilines could be readily reduced by iron or zinc with ammonium chloride, affording to secondary anilines or hydrazines, respectively (Figure S2). Notably, these obtained functionalized anilines and hydrazines are otherwise difficult to access by other procedures (**Figure S2**).

i) An oven-dried Schlenk tube with a magnetic stir bar was charged with C–H alkylated N-nitroso aniline products (0.1 mmol, 1.0 equiv.), Fe powder (22.5 mg, 4.0 equiv.), NH_4Cl (16.0 mg, 3.0 equiv.), and 75% ethanol aqueous solution (1 mL). The mixture was stirred at 80 °C for 12 h. After being cooled to room temperature, the mixture was extracted with CH_2Cl_2 and then washed and dried. The solution was concentrated by vacuum and separated on a silica gel column using petroleum ether/ CH_2Cl_2 (20:1, v/v) as eluent to give the corresponding reduction products.

ii) An oven-dried Schlenk tube with a magnetic stir bar was charged with C–H alkylated N-nitroso anilines (0.1 mmol, 1.0 equiv.), Zn powder (12.8 mg, 2.0 equiv.), NH_4Cl (6.5 mg, 1.2 equiv.), and 75% methanol aqueous solution (1 mL). The mixture was stirred at 80 °C for 12 h. After being cooled to room temperature, the mixture was extracted with CH_2Cl_2 and then washed and dried. The solution was concentrated by vacuum and separated on a silica gel column using petroleum ether/EtOAc (10:1, v/v) as eluent to give the corresponding reduced hydrazine product **6a''**.

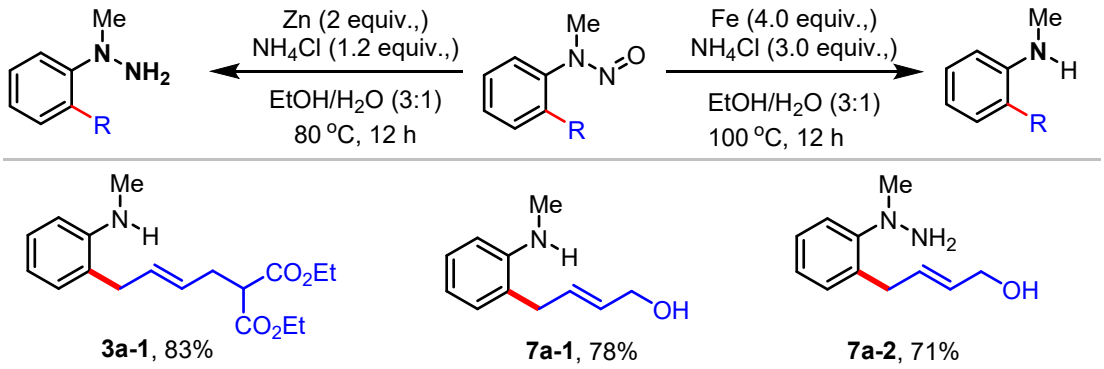


Figure S2. Selective reduction of N-nitroso aniline products

2) Pd/C catalyzed debenzylation & reductive amination cascade:

Pd/C could serve as a versatile catalyst for the debenzylation of N-Bn anilines, and followed by reductive amination of carbonyls cascade, leading to tetrahydroquinoline product, as demonstrated in transformed **7r** to **7r'** (**Figure S3**).

An oven-dried Schlenk tube with a magnetic stir bar was charged with **7r** (28.2 mg, 0.1 mmol, 1.0 equiv.), 5% Pd/C (40.0 mg), $NaH_2PO_2 \cdot H_2O$ (42.4 mg, 4.0 equiv.) and 75% methanol aqueous solution (2 mL) under an N_2 atmosphere. The mixture was stirred at 140 °C for 24 h. After being cooled to room temperature, the solution was filtered through a celite pad and washed with 10-20 mL of CH_2Cl_2. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to give tetrahydroquinoline **7r'**.

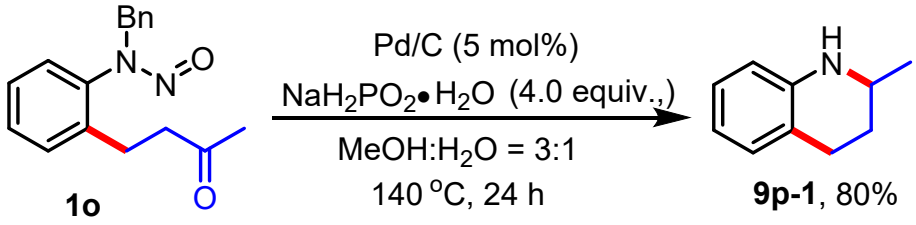


Figure S3. Reductive amination cascade: construction of tetrahydroquinoline

3) N-Nitroso anilines enabled indoles synthesis with olefins:

Transition-metal catalyzed nitrogen functionality assisted C–H activation with alkynes has emerged as powerful platforms for the rapid construction of indole skeletons, while the use of internal oxidizing, traceless directing groups enabled indoles synthesis remained under explored.

During the exploration of N-nitroso anilines assisted C–H activation with various olefins, intriguingly, indole product **11a** was obtained with styrene **10a** under this Rh(III) catalysis. Significantly, this transformation proceed smoothly without Cu(II) salt, which indicated that N-nitroso aniline serve as an internal oxidizing directing group for the indole synthesis, through multiple dehydrogenative coupling. Further optimization and synthetic potential are underway.

It was proposed that acetate salt assisted this N-nitroso anilines enabled C–H activation under Rh(III) catalysis, leading to 5-membered rhodacycle intermediate.

Subsequent olefin insertion followed by β-H elimination to afford *ortho*-olefin N-nitroso aniline **1a-C**. Further re-insertion of Rh(III) into olefin gave **1a-D**, which underwent key C–N bond reductive elimination to release the desired indole product **11a**, and regenerated the reactive Rh(III) catalyst. Simultaneously, HNO was released from N-nitroso moiety, which decomposed to N_2O and H_2O. It was anticipated that the combination of internal oxidizing N-nitroso and air enabled this multiple dehydrogenative coupling for the indole synthesis with styrenes (**Figure S4**).

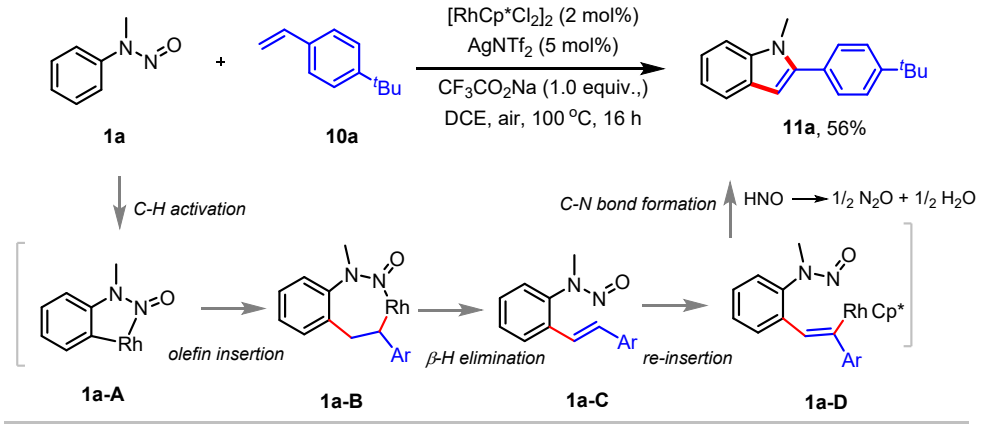


Figure S4. N-Nitroso enabled indole synthesis via dehydrogenative coupling with styrenes

4) N-Nitroso as traceless DG enabled C–H amidation:

Catalytic C–H addition reaction to polar C–N bond provided one step-economy platform for the synthesis of nitrogen-containing functional skeletons, which omitted the use of organometallic reagents or halides. (For selected reviews, (a) D. A. Colby, A. S. Tsai, R. G. Bergman, J. A. Ellman, *Acc. Chem. Res*., 2012, **45**, 814-825. (b) X.-S. Zhang, K. Chen, Shi, Z.-J. *Chem. Sci*., 2014, **5**, 2146-2159. (c) L. Yang, H. Huang, *Chem. Rev*., 2015, **115**, 3468−3517.)

Herein, we demonstrated that N-nitroso could assist C–H amidation with isocyanates, affording to 2-aminobenamides (**Figure S5**), which serve as key structural motifs in biologically active molecules. Further work towards optimization and synthetic application are underway.

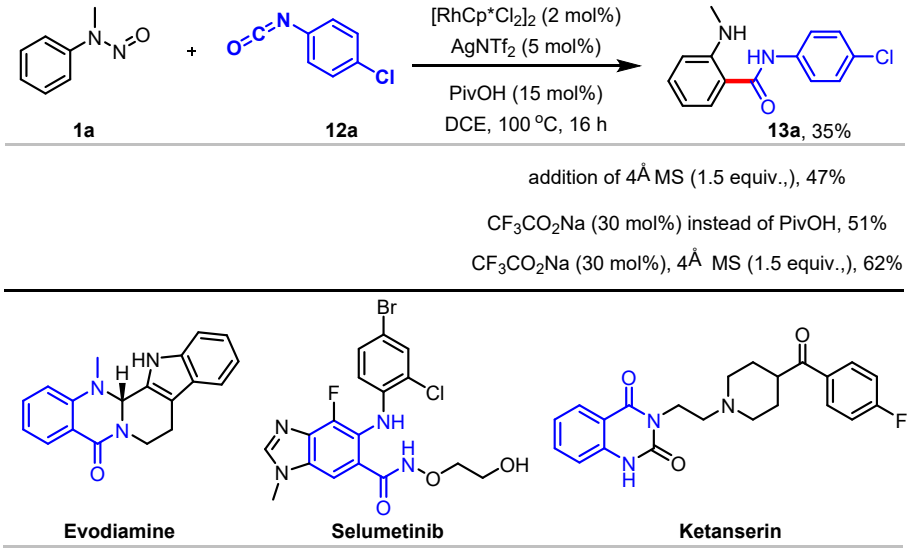


Figure S5. N-Nitroso enabled C–H addition reaction to polar C–N bond of isocyanates

5) Mechanistic study

(i) Control experiments:

To elucidate the key role of N-nitroso for the selective functionalization of anilines, we first subjected N-methyl aniline **1a' and 2a** as the substrates under the standard conditions using Rh(III) or Co(III) catalysis. The results revealed that no desired *ortho* C-H alkylated aniline product **3a'** was observed with **2a** under Rh(III) catalysis, while about 30% N-alkylated aniline product **4a** was obtained under Co(III) catalysis. These observation might support the critical role of N-nitroso functionality (**Figure S6**).

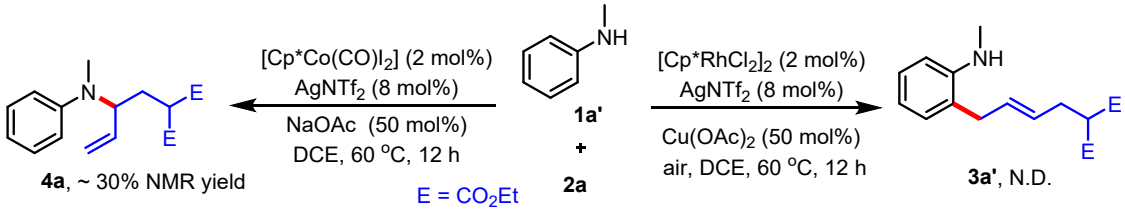
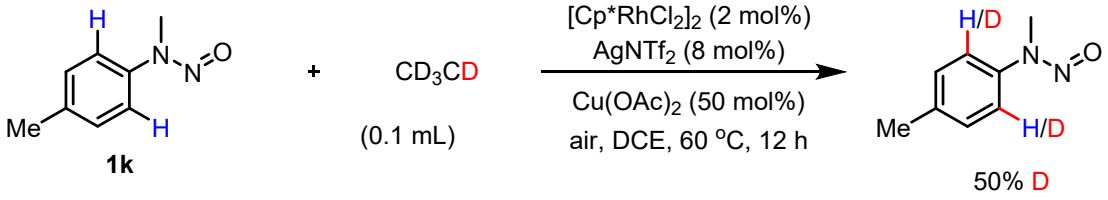


Figure S6. Control experiments

(ii) H/D exchange experiments

An oven-dried Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$

(1.2 mg, 2.0 mol%), $AgNTf_2$ (3.1 mg, 8 mol%), $Cu(OAc)_2$ (9.2 mg, 50 mol%), **1k** (0.1 mmol, 1.0 equiv.), CD_3OD (0.1 mL) and DCE (0.5 mL) under an N_2 atmosphere. The mixture was stirred at 60 °C for 12 h and then diluted with 3 mL of CH_2Cl_2. The solution was filtered through a celite pad and washed with 15-20 mL of CH_2Cl_2. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 20/1, v/v) to provide $[D_n]$-**1k**. The deuterated ratio was calculated from ^1H NMR analysis (**Figure S7**).



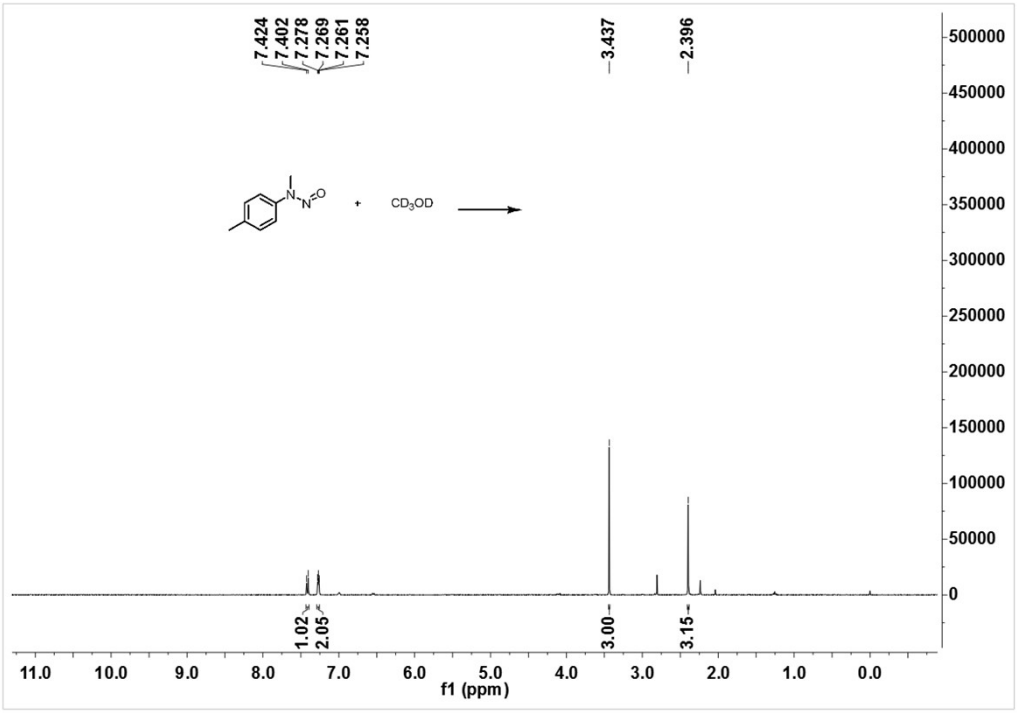
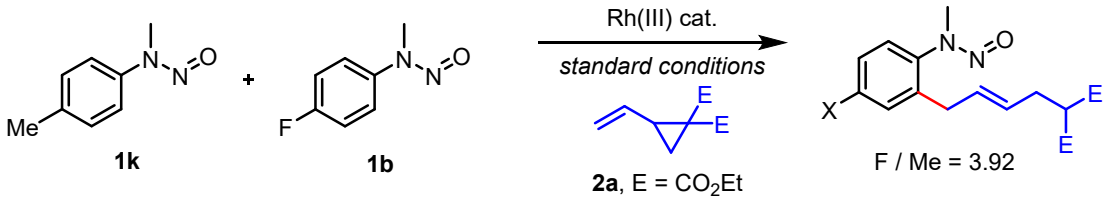


Figure S7. H/D exchange experiments

(iii) Competing experiments

To a 20 mL test tube with a stirring bar, N-methylnitrous amide **1b** (0.2 mmol, 1

equiv) and **1k** (0.2 mmol, 1 equiv), vinylcyclopropane **2a** (0.2 mmol, 1 equiv), $[Cp^*RhCl_2]_2$ (2.0 mol%), $AgNTf_2$ (3.1 mg, 8 mol%), $Cu(OAc)_2$ (50 mol%), DCE (1 mL) were added under air, and the mixture was stirred at 60 °C for 12 hours. After cooling down, the volatiles were removed and the mixture was purified by flash chromatography of silica gel. The product **3b** and **3k** were isolated and combined. The ratio of **3b**/**3k** = (14.77-3)/3 = 3.92 was determined by ^{1}H NMR analysis (**Figure S8**).



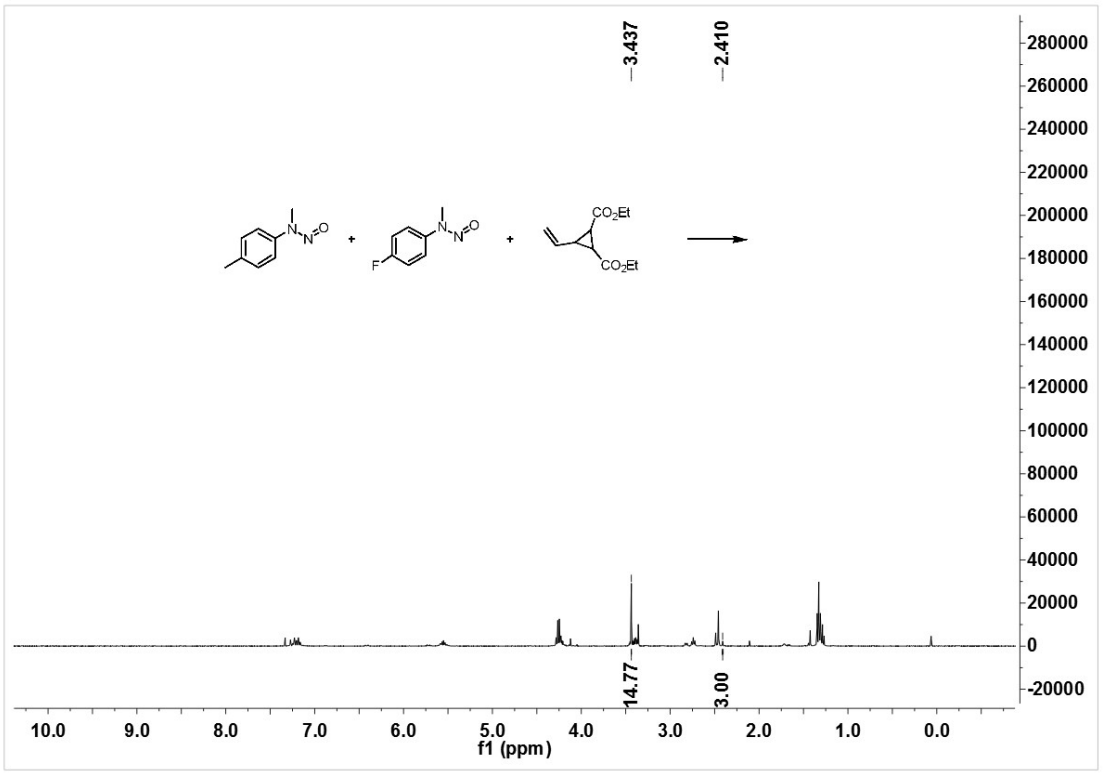
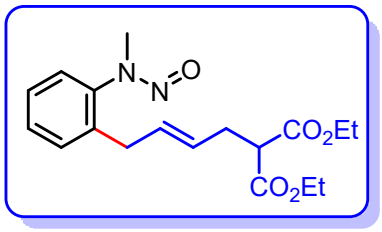
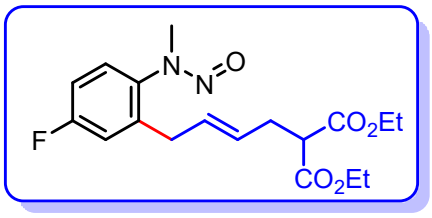


Figure S8. Competing experiments

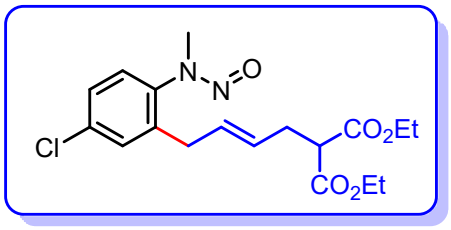
D. Characterization data for the obtained products:



Diethyl (*E*)-2-(4-(2-(methyl(nitroso)amino)phenyl)but-2-en-1-yl)malonate (3a), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33(m, 3H), 7.22 (d, J = 7.6 Hz, 1H), 5.53-5.45 (m, 2H), 4.18 (q, J = 7.2 Hz, 4H), 3.40 (s, 3H), 3.37-3.34 (m, 2H), 2.67 (t, J = 6.8 Hz, 2H), 2.60-2.55 (m, 1H), 1.25 (t, J = 7.2 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.9, 141.2, 136.7, 130.6, 129.7, 129.4, 127.3, 126.9, 125.9, 61.5, 51.7, 35.5, 29.3, 26.7, 14.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{25}N_2O_5$: 349.1758, Found: 349.1762.

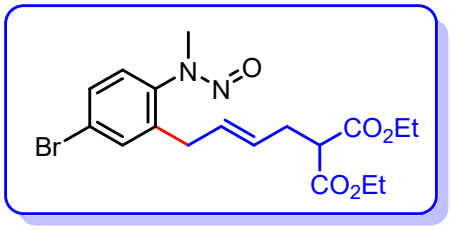


Diethyl (*E*)-2-(4-(5-fluoro-2-(methyl(nitroso)amino)phenyl)but-2-en-1-ylmalonate (3b), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.18 (m, 1H), 7.08-6.98 (m, 2H), 5.55-5.46 (m, 2H), 3.38-3.35 (m, 3H), 3.32 (d, J = 3.6 Hz, 2H), 2.67-2.62 (m, 2H), 2.60-2.54 (m, 1H), 1.25 (t, J = 7.2 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.8, 162.7 (d, J = 248 Hz), 139.6, 137.3, 128.7, 127.7, 121.1, 117.0, 114.3, 113.4, 61.5, 51.5, 35.6, 29.2, 26.6, 14.0. **^{19}F NMR (300 MHz, $CDCl_3$)** δ -111.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{24}FN_2O_5$: 367.1664, Found: 367.1668.

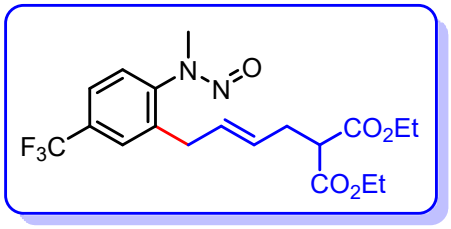


Diethyl (*E*)-2-(4-(5-chloro-2-(methyl(nitroso)amino)phenyl)but-2-en-1-yl)malonate (3c), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.31 (m, 2H), 7.17-7.15 (m, 1H), 5.53-5.47 (m, 2H), 4.20-4.16 (m, 2H), 3.38-3.36 (m, 3H), 3.34-3.32 (m, 2H), 2.67-2.60 (m, 2H), 2.57-2.54 (m, 1H), 1.27-1.23 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.8,

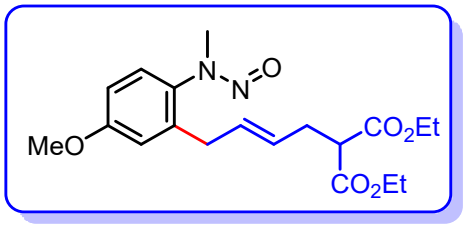
138.6, 135.1, 130.5, 128.8, 127.7, 127.5, 127.1, 61.4, 51.5, 35.4, 29.1, 26.7, 14.0. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{18}H_{24}ClN_2O_5$: 383.1368, Found: 383.1373.



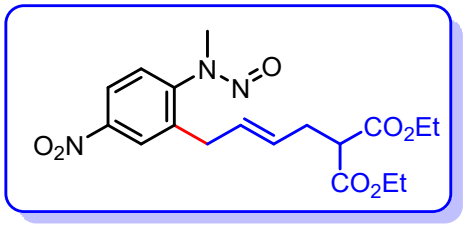
Diethyl (*E*)-2-(4-(5-bromo-2-(methyl(nitroso)amino)phenyl)but-2-en-1-yl)malona -te (3d), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.46 (m, 2H), 7.09 (dd, J = 2.0 Hz, 8.4 Hz, 1H), 5.51-5.47 (m, 2H), 4.21-4.15 (m, 4H), 3.36 (t, J = 3.6 Hz, 3H), 3.33-3.31 (m, 2H), 2.67-2.61 (m, 2H), 2.57-2.54 (m, 1H), 1.27-1.23 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.8, 168.8, 140.2, 138.9, 133.5, 128.8, 127.7, 127.3, 123.2, 61.4, 51.5, 35.4, 29.1, 26.7, 14.0. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{18}H_{24}BrN_2O_5$: 427.0863, Found: 427.0866.



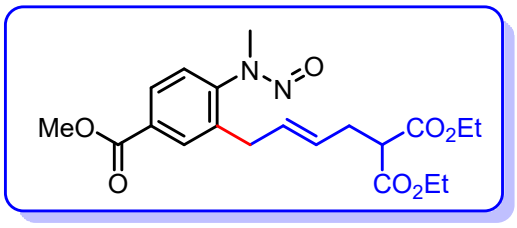
Diethyl (*E*)-2-(4-(2-(methyl(nitroso)amino)-5-(trifluoromethyl)phenyl)but-2-en-1- -yl)malonate (3e), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (t, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 1H), 5.50 (dd, J = 4.0 Hz, 9.6 Hz, 2H), 4.21-4.10 (m, 4H), 3.44-3.40 (m, 2H), 3.38-3.33 (m, 2H), 2.66 (t, J = 7.2 Hz, 2H), 2.60-2.54 (m, 1H), 1.25 (t, J = 7.2 Hz, 6H).; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.8, 143.9, 137.7, 128.8, 128.6 (q, J = 4.0 Hz), 127.9, 127.76, 126.1 (q, J = 4.0 Hz), 124.4, 124.37, 61.5, 51.9, 35.2, 31.6, 29.4, 26.7, 14.0. **^{19}F NMR (300 MHz, $CDCl_3$)** δ -62.7. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{19}H_{24}F_3N_2O_5$: 417.1632, Found: 417.1636.



Diethyl (*E*)-2-(4-(5-methoxy-2-(methyl(nitroso)amino)phenyl)but-2-en-1-yl)malonate (3f), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 8.4 Hz, 1H), 6.89-6.84 (m, 2H), 5.57-5.44 (m, 2H), 4.21-4.15 (m, 4H), 3.85 (s, 3H), 3.36 (d, J = 4.0 Hz, 3H), 3.33-3.30 (m, 2H), 2.67 (t, J = 6.8 Hz, 2H), 2.59 (t, J = 7.2 Hz, 1H), 1.28-1.24 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ. 168.8, 138.3, 134.3, 129.4, 127.3, 127.0, 115.5, 112.3, 110.5, 61.4, 55.5, 55.6, 35.8, 29.4, 26.6, 14.0. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{19}H_{27}N_2O_6$: 379.1864, Found: 379.1869.

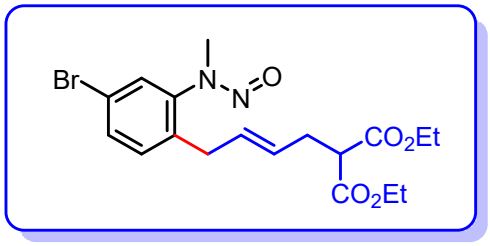


Diethyl (*E*)-2-(4-(2-(methyl(nitroso)amino)-5-nitrophenyl)but-2-en-1-yl)malonate (3g), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27-8.20 (m, 2H), 7.41 (d, J = 8.8 Hz, 1H), 5.62-5.46 (m, 2H), 4.25-4.09 (m, 4H), 3.49 (d, J = 8.8 Hz, 1H), 3.42 (s, 2H), 3.39-3.37 (m, 2H), 2.69-2.64 (m, 2H), 2.62-2.60 (m, 1H), 1.28-1.22 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.8, 146.1, 138.4, 129.8, 128.1, 126.1, 125.9, 122.5, 61.6, 51.4, 35.0, 29.5, 26.8, 14.0. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{18}H_{24}N_3O_7$: 394.1609, Found: 394.1613.

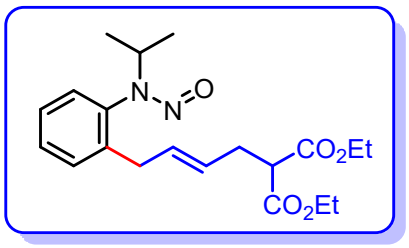


Diethyl (*E*)-2-(4-(5-(methoxycarbonyl)-2-(methyl(nitroso)amino)phenyl)but-2-en-1-yl)malonate (3h), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-8.00 (m, 2 H), 7.31-7.28 (m, 1H), 5.57-5.45 (m, 2H), 4.21-4.15 (m, 4H), 3.95-3.94 (m, 3H), 3.43-3.39 (m, 3 H),

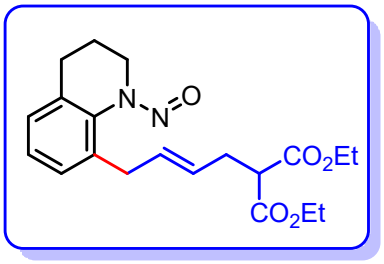
3.36-3.31 (m, 2H), 2.68-2.65 (m, 2H), 2.60-2.57 (m, 1H), 1.27-1.21 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.8, 144.7, 136.8, 132.0, 129.1, 128.6, 127.5, 125.6, 61.5, 52.4, 51.6, 35.2, 29.4, 26.7, 14.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{27}N_2O_7$: 407.1813, Found: 407.1816.



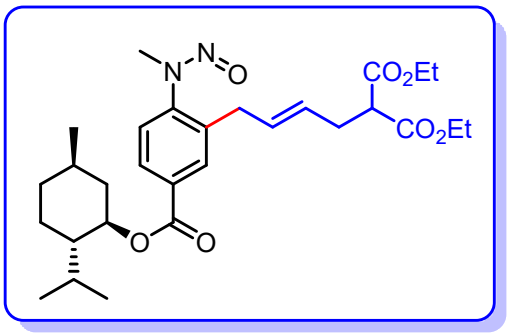
Diethyl (*E*)-2-(4-(4-bromo-2-(methyl(nitroso)amino)phenyl)but-2-en-1-yl)malonate (3i), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.40 (s, 1H), 7.26 (d, J = 8.0 Hz, 1H), 5.48 (s, 3H), 4.19 (dd, J = 12.9, 6.2 Hz, 5H), 3.36 (d, J = 12.1 Hz, 4H), 3.32 (s, 2H), 2.65 (s, 2H), 2.60 (d, J = 8.6 Hz, 1H), 1.26 (t, J = 6.5 Hz, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.8, 142.16 (s, 1H), 135.7, 132.3, 132.0, 129.0, 128.8, 127.4, 120.1, 61.5, 51.5, 35.3, 28.9, 26.6, 14.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{24}BrN_2O_5$: 427.0863, Found: 427.0866.



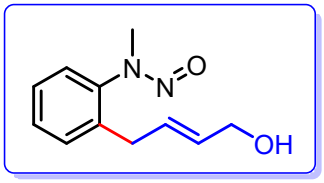
Diethyl (*E*)-2-(4-(2-(isopropyl(nitroso)amino)phenyl)but-2-en-1-yl)malonate (3j), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 2 H), 6.90-6.87 (m, 1H), 5.51-5.47 (m, 2H), 4.21-4.15 (m, 4H), 3.10-2.91 (m, 1H), 2.70-2.67 (m, 2H), 2.57-2.54 (m, 1H), 1.60 (t, J = 6.4 Hz, 3H), 1.50-1.46 (m, 3H), 1.27-1.23 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ. 168.8, 168.8, 138.6, 136.6, 129.6, 129.6, 128.8, 127.2, 126.9, 126.8, 61.4, 56.8, 51.9, 51.8, 47.4, 31.6, 22.8, 21.6, 19.5, 14.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{29}N_2O_5$: 377.2071, Found: 377.2075.



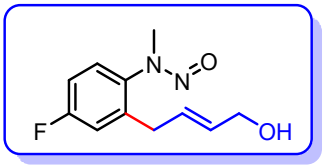
Diethyl (*E*)-2-(4-(1-nitroso-1,2,3,4-tetrahydroquinolin-8-yl)but-2-en-1-yl)malonate (3k), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.14 (m, 2H), 7.07 (d, *J* = 6.8 Hz, 1H), 5.65-5.58 (m, 1H), 5.54-5.38 (m, 1H), 4.21-4.11 (m, 4H), 3.90 (dd, *J* = 6.4 Hz, 12.8 Hz, 2H), 3.44 (d, *J* = 6.4 Hz, 1H), 3.37-3.30 (m, 2H), 2.71-2.63 (m, 2H), 2.59-2.54 (m, 2H), 2.00-1.93 (m, 2H), 1.26-1.20 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 168.9, 168.8, 131.8, 130.9, 129.8, 129.7, 128.8, 127.2, 126.6, 126.2, 126.2, 61.3, 61.3, 51.2, 43.6, 31.7, 27.7, 22.5, 14.0. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{20}H_{27}N_2O_5$: 375.1914, Found: 375.1919.



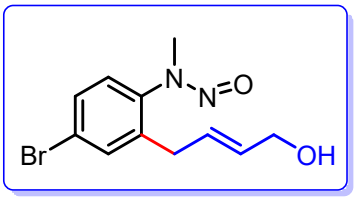
Diethyl 2-((*E*)-4-(5-((((1*R*, 2*S*, 5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)-2-(methyl(nitroso)amino)phenyl)but-2-en-1-yl)malonate (3l), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 1.6 Hz, 1H), 8.01 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 5.55-5.46 (m, 2H), 4.95 (td, *J* = 10.8 Hz, 4.4 Hz, 1H), 4.23-4.16 (m, 4H), 3.43 (d, *J* = 5.2 Hz, 2H), 3.40 (s, 3H), 2.67 (t, *J* = 6.0 Hz, 2H), 2.60-2.55 (m, 4H), 2.12 (d, *J* = 12.0 Hz, 1H), 1.96-1.91 (m, 1H), 1.74 (d, *J* = 11.6 Hz, 2H), 1.55 (s, 1H), 1.26 (t, *J* = 7.2 Hz, 6H), 1.23-1.15 (m, 2H), 1.14-1.08 (m, 2H), 0.93 (t, *J* = 6.0 Hz, 6H), 0.8 (d, *J* = 2.8 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 168.8, 165.1, 144.6, 136.7, 132.0, 131.5, 129.1, 128.5, 127.4, 125.5, 75.3, 61.5, 51.6, 47.2, 40.9, 35.2, 34.2, 31.4, 29.5, 26.7, 26.6, 23.7, 22.0), 20.6, 16.6, 14.0. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{29}H_{43}N_2O_7$: 531.3065, Found: 531.3068.



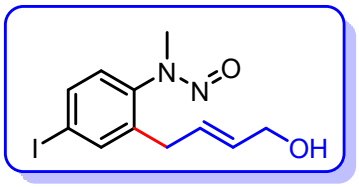
(*E*)-N-(2-(4-Hydroxybut-2-en-1-yl)phenyl)-N-methylnitrous amide (7a), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 3H), 7.23 (d, J = 7.6 Hz, 1H), 5.72-5.67 (m, 1H), 5.62-5.58 (m, 1H), 4.05 (d, J = 4.8 Hz, 2H), 3.37 (s, 3H), 3.31 (d, J = 5.6 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 141.2, 136.2, 131.3, 131.1, 129.5, 129.5, 127.6, 126.1, 63.2, 35.7, 34.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{15}N_2O_2$: 207.1128, Found: 207.1134.



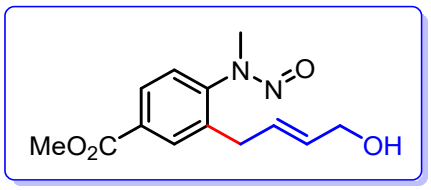
(*E*)-N-(4-Fluoro-2-(4-hydroxybut-2-en-1-yl)phenyl)-N-methylnitrous amide (7b), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.19 (m, 1H), 7.09-7.02 (m, 2H), 5.68-5.63 (m, 2H), 4.07-4.06 (m, 2H), 3.33 (s, 3H), 3.27 (d, J = 6.4 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 162.6 (d, J = 248 Hz), 139.1, 139.0, 132.0, 131.2, 130.9, 128.5, 128.2, 128.0, 127.9, 127.8, 127.6, 127.5, 117.6, 117.5, 117.4, 117.3, 116.3, 116.1, 114.6, 114.5, 114.3, 113.4, 113.2, 62.9, 35.7, 34.3. **^{19}F NMR (300 MHz, $CDCl_3$) δ** -111.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{14}FN_2O_2$: 225.1034, Found: 225.1037.



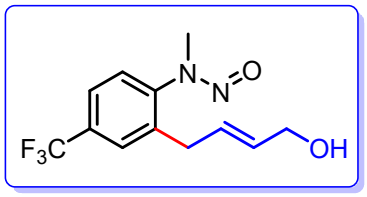
(*E*)-N-(4-Bromo-2-(4-hydroxybut-2-en-1-yl)phenyl)-N-methylnitrous amide (7c), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.49 (m, 2H), 7.12 (d, J = 8.0 Hz, 1H), 5.68-5.65 (m, 2H), 4.10 (d, J = 4.8 Hz, 2H), 3.35 (s, 3H), 3.3 (d, J = 6.0 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 140.2, 138.4, 133.9, 132.0, 130.7, 128.5, 127.5, 123.2, 63.1, 35.5, 34.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{14}BrN_2O_2$: 285.0233, Found: 285.0238.



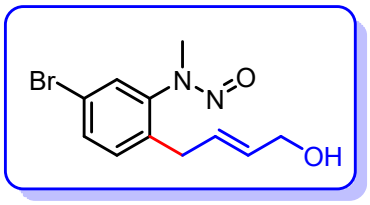
(*E*)-N-(2-(4-Hydroxybut-2-en-1-yl)-4-iodophenyl)-N-methylnitrous amide (7d), ^{1}H NMR (400 MHz, $CDCl_3$) ***δ*** 7.71-7.68 (m, 2H), 6.96 (d, *J* = 8.0 Hz, 1H), 5.69-5.61 (m, 2H), 4.10-4.04 (m, 2H), 3.33 (s, 3H), 3.26 (d, *J* = 6.4 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 139.9, 138.4, 136.7, 131.9, 128.4, 127.5, 125.0, 63.0, 35.4, 34.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{14}IN_2O_2$: 333.0094, Found: 333.0098.



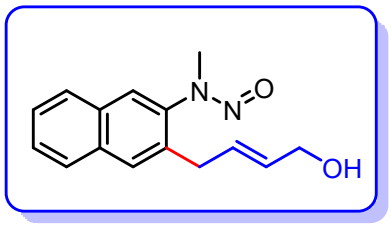
Methyl (*E*)-3-(4-hydroxybut-2-en-1-yl)-4-(methyl(nitroso)amino)benzoate (7e), ^{1}H NMR (400 MHz, $CDCl_3$) ***δ*** 8.05-8.01 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 5.74-5.69 (m, 1H), 5.65-5.60 (m, 1H), 4.07 (d, *J* = 4.0 Hz, 2H), 3.94 (s, 3H), 3.40-3.39 (m, 2H), 3.38 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 166.1, 144.7, 136.2, 132.5, 130.8, 130.7, 128.4, 125.7, 125.3, 63.0, 52.4, 35.3, 34.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{17}N_2O_4$: 265.1183, Found: 265.1188.



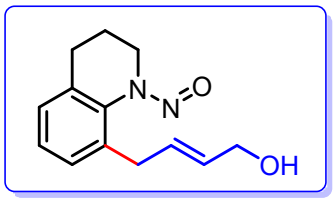
(*E*)-N-(2-(4-Hydroxybut-2-en-1-yl)phenyl)-N-methylnitrous amide (7f), ^{1}H NMR (400 MHz, $CDCl_3$) ***δ*** 7.64 (d, *J* = 6.8 Hz, 1H), 7.43-7.34 (m, 1H), 7.25 (s, 1H), 5.86-5.79 (m, 1H), 5.72-5.66 (m, 1H), 4.14 (d, *J* = 5.2 Hz, 2H), 3.42-3.39 (m 3H), 3.28 (d, *J* = 6.0 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 149.5, 132.1, 131.3, 128.3, 128.3, 128.20 (q, *J* = 4.0 Hz), 126.40 (q, *J* = 4.0 Hz), 126.3, 125.2 (q, *J* = 4.0 Hz), 123.1, 108.8, 99.9, 63.2, 34.4, 30.4. **^{19}F NMR (300 MHz, $CDCl_3$)** ***δ*** -60.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{14}F_3N_2O_2$: 275.1002, Found: 275.1007.



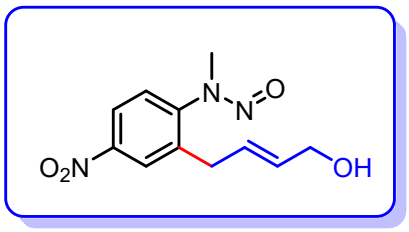
(*E*)-N-(5-Bromo-2-(4-hydroxybut-2-en-1-yl)phenyl)-N-methylnitrous amide (7g), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.14 (d, *J* = 1.6 Hz, 2H), 7.28 (d, *J* = 2.8 Hz, 1H), 5.71-5.60 (m, 2H), 4.08-4.06 (m, 2H), 3.41 (s, 3H), 3.28 (d, *J* = 6.0 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 142.1, 135.2, 134.2, 133.5, 132.4, 132.3, 131.6, 131.4, 128.9, 128.7, 128.5, 127.4 125.9, 124.9, 120.3, 63.0, 35.4, 34.0. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{11}H_{14}BrN_2O_2$: 285.0233, Found: 285.0238.



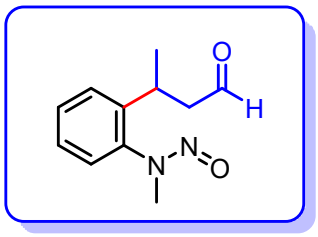
(*E*)-N-(3-(4-Hydroxybut-2-en-1-yl)naphthalen-2-yl)-N-methylnitrous amide (7h), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.84 (m, 2H), 7.48-7.46 (m, 2H), 7.45-7.41 (m, 1H), 7.37-7.35 (m, 1H), 5.75-5.68 (m, 2H), 5.64-5.55 (m, 2H), 4.11-4.02 (m, 2H), 3.43 (s, 3H), 3.35-3.31 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 135.3, 133.2, 131.4, 130.1, 129.5, 128.2, 127.8, 127.8, 126.3, 122.2, 63.2, 36.2, 34.6. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{15}H_{17}N_2O_2$: 257.1285, Found: 257.1288.



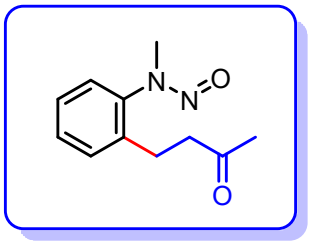
(*E*)-4-(1-Nitroso-1,2,3,4-tetrahydroquinolin-8-yl)but-2-en-1-ol (7i), ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (t, *J* = 7.6 Hz, 2H), 6.59 (t, *J* = 7.2 Hz, 1H), 5.86-5.77 (m, 1H), 5.73-5.66 (m, 1H), 4.11 (d, *J* = 5.6 Hz, 2H), 3.33 (t, *J* = 6.0 Hz, 2H), 3.20 (d, *J* = 6.0 Hz, 2H), 2.79 (t, *J* = 6.4 Hz, 2H), 1.95-1.89 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 142.5, 130.5, 129.9, 127.9, 127.4, 123.0, 121.6, 116.7, 63.3, 42.2, 34.3, 27.3, 22.0. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{13}H_{17}N_2O_2$: 233.1285, Found: 233.1287.



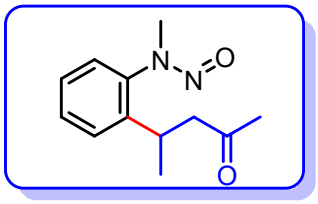
(*E*)-N-(2-(4-Hydroxybut-2-en-1-yl)-4-nitrophenyl)-N-methylnitrous amide (7j), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28-8.23 (m, 2H), 7.39-7.01 (m, 1H), 5.78-5.62 (m, 2H), 4.14-4.12 (m, 2H), 3.44 (d, J = 10.8 Hz, 2H), 3.41 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 147.5, 146.1, 137.8, 132.8, 127.5, 126.3, 126.2, 122.7, 62.9, 35.1, 34.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{14}N_3O_4$: 252.0979, Found: 252.0983.



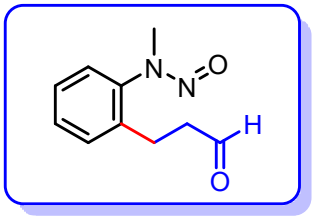
5,6-Dihydro-[1,1'-biphenyl]-3(4H)-one (9a), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.47-7.39 (m, 2H), 7.45 (td, J = 2.0 Hz, 9.6 Hz, 1H), 7.33 (dd, J = 0.8 Hz, 8.0 Hz, 1H), 3.46 (s, 3H), 3.36-3.26 (m, 1H), 2.87-2.81 (m, 1H), 2.70-2.64 (m, 1H), 1.25 (d, J = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.5, 142.1, 140.5, 129.8, 127.4, 127.1, 126.2, 51.4, 35.7, 28.1, 22.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{15}N_2O_2$: 207.1128, Found: 207.1131.



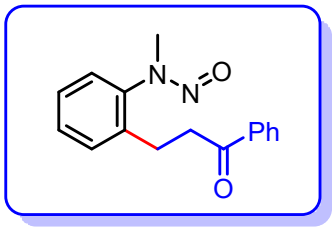
4-(2-(Methylamino)phenyl)butan-2-one (9b), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 3H), 7.21 (d, J = 7.2 Hz, 1H), 3.41 (s, 3H), 2.81-2.78 (m, 2H), 2.72-2.69 (m, 2H), 2.01 (s, 3H).; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 207.1, 137.3, 130.7, 129.5, 127.4, 126.0, 99.9, 44.4, 35.5, 29.9, 25.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{15}N_2O_2$: 207.1128, Found: 207.1131.



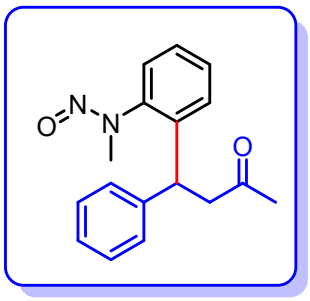
4-(2-(Methylamino)phenyl)pentan-2-one (9c), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44-7.39 (m, 2H), 7.34-7.30 (m, 1H), 7.20 (d, J = 7.6 Hz, 1H)3.48 (s, 3H), 3.28-3.19 (m, 1H), 2.88 (dd, J = 7.6 Hz, 17.2 Hz, 1H), 2.67 (dd, J = 6.8 Hz, 17.2 Hz, 1H), 2.03 (s, 3H), 1.21 (d, J = 6.8 Hz, 3H), **^{13}C NMR (100 MHz, $CDCl_3$)** δ 206.6, 142.7, 140.5, 129.6, 127.0, 126.7, 126.1, 51.0, 35.6, 30.1, 29.1, 22.0. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{12}H_{17}N_2O_2$: 221.1285, Found: 221.1289.



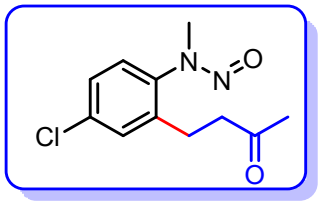
3-(2-(Methylamino)phenyl)propanal (9d), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.73 (s, 1H), 7.40-7.34 (m, 3H), 7.15 (d, J = 7.6 Hz, 1H), 3.41 (s, 3H), 2.87-2.82 (m, 2H), 2.77-2.73 (m, 2H).; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.5, 141.1, 136.6, 130.6, 129.4, 127.6, 125.8, 44.7, 35.4, 23.7. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{10}H_{13}N_2O_2$: 193.0972, Found: 193.0975.



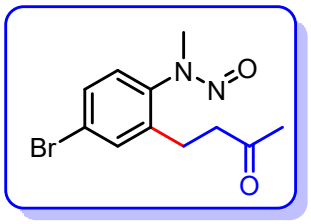
3-(2-(Methylamino)phenyl)-1-phenylpropan-1-one (9e), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91-7.86 (m, 2H), 7.46-7.41 (m, 4H), 7.38-7.34 (m, 1H), 7.24 (dd, J = 0.8 Hz, 7.6 Hz, 1H), 3.44 (s, 3H), 3.25 (t, J = 7.6 Hz, 2H), 3.00 (t, J = 8.0 Hz, 2H).; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.5, 141.2, 137.5, 136.5, 133.1, 130.7, 129.4, 128.5, 127.9, 127.4, 125.9, 39.7, 35.5, 25.8. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{16}H_{17}N_2O_2$: 269.1285, Found: 269.1288.



4-(2-(Methylamino)phenyl)-4-phenylbutan-2-one (9f), **^{1}H NMR (400 MHz, $CDCl_3$)** ***δ*** 7.48-7.44 (m, 2H), 7.38-7.33 (m, 1H), 7.23 (t, *J* = 7.2 Hz, 2H) , 7.16 (t, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 7.2Hz, 2H), 4.65 (t, *J* = 7.2Hz, 1H), 3.26-3.20 (m, 1H), 3.15 (s, 3H), 3.12-3.08 (m, 1H), 2.07 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 206.0, 142.4, 141.2, 140.3, 129.5, 128.6, 128.3, 127.7, 127.6, 126.7, 49.6, 40.5, 35.4, 30.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{19}N_2O_2$: 283.1441, Found: 283.1446.

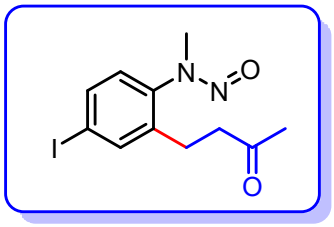


4-(5-Chloro-2-(methylamino)phenyl)butan-2-one (9g), **^{1}H NMR (400 MHz, $CDCl_3$)** ***δ*** 7.37 (d, *J* = 2.4 Hz, 1H), 7.20 (dd, *J* = 2.4 Hz, 8.4 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 3.39 (s, 3H), 2.77-2.70 (m, 4H), 2.11 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 206.6, 139.8, 139.3, 135.1, 130.6, 127.6, 127.2, 44.1, 35.4, 29.9, 25.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{14}ClN_2O_2$: 241.0738, Found: 241.0743.

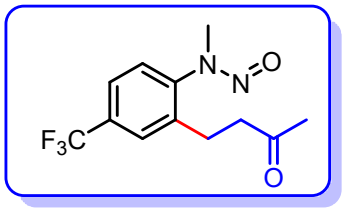


Methyl (*E*)-4-methyl-3-((3-oxo-3-phenylprop-1-en-1-yl)amino)benzoate (9h), **^{1}H NMR (400 MHz, $CDCl_3$)** ***δ*** 7.50 (d, *J* = 2.4 Hz, 1H), 7.68 (dd, *J* = 2.0 Hz, 8.4 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 3.36 (s, 3H), 2.70 (dd, *J* = 4.0 Hz, 6.4 Hz, 4H), 2.09 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 206.6, 140.2, 139.5, 133.5, 130.5, 127.3, 123.0, 43.9, 35.3, 29.8, 25.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{14}BrN_2O_2$:

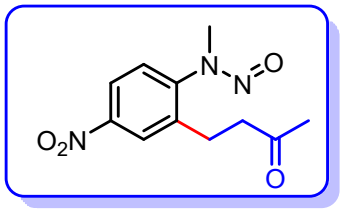
285.0233, Found: 285.0237.



4-(5-Iodo-2-(methylamino)phenyl)butan-2-one (9i), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 2.0 Hz, 1H), 7.67 (dd, *J* = 2.0 Hz, 8.4 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 3.38 (s, 3H), 2.71 (t, *J* = 2.8 Hz, 4H), 2.11 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 206.6, 141.0, 139.6, 136.9, 136.6, 127.4, 94.8, 44.2, 35.3, 29.9, 25.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{14}IN_2O_2$: 333.0094, Found: 333.0096.

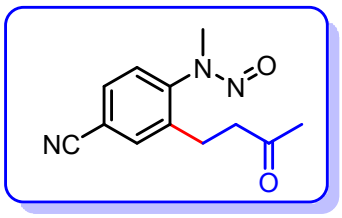


4-(2-(Methylamino)-5-(trifluoromethyl)phenyl)butan-2-one (9j), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 3.43(s, 3H), 2.87-2.83 (m, 2H), 2.77-2.73 (m, 2H), 2.12 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 206.5, 144.0, 138.3, 131.1 (q, *J* = 32.0 Hz), 127.9, 127.8, 127.8, 127.8, 126.1, 124.5, 124.5, 124.4, 124.4, 122.2 (q, *J* = 270.0 Hz), 44.1, 35.2, 29.8, 25.3. **^{19}F NMR (300 MHz, $CDCl_3$) δ** -114.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{14}F_3N_2O_2$: 275.1002, Found: 275.1005.

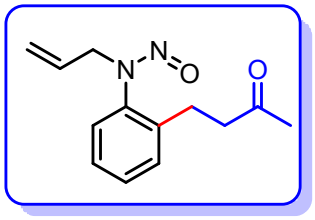


(*E*)-4-(2-(Methylamino)-5-nitrophenyl)butan-2-one (9k), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.04 (m, 1H), 6.57 (d, *J* = 9.6 Hz, 2H), 3.72 (t, *J* = 6.8 Hz, 2H), 3.07 (s, 3H), 2.77 (t, *J* = 6.8 Hz, 2H), 2.18 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 206.7 152.9, 137.1, 126.3, 126.2, 110.6, 110.2, 46.9, 40.4, 38.9, 30.4. HRMS (ESI-TOF) m/z: [M

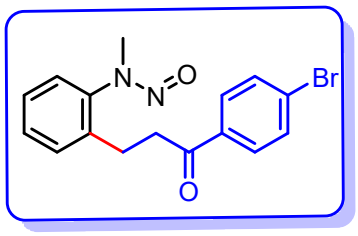
+ H]$^+$ Calcd for $C_{11}H_{14}N_3O_4$: 252.0979, Found: 252.0983.



4-(Methylamino)-3-(3-oxobutyl)benzonitrile (9l), ^{1}H NMR (400 MHz, CDCl3) δ 7.71 (d, *J* = 2.0 Hz, 1H), 7.62 (dd, *J* = 2.0 Hz, 8.4 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 3.43 (s, 3H), 2.88-2.83 (m, 2H), 2.77-2.73 (m, 2H), 2.13 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$) *δ*** 206.3, 144.8, 138.8, 134.8, 131.1, 126.2, 117.8, 113.1, 43.8, 35.0, 29.9, 25.2. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{12}H_{14}N_3O_2$: 232.1081, Found: 232.1086.

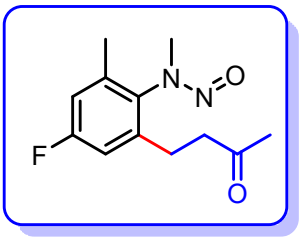


4-(2-(Allylamino)phenyl)butan-2-one (9m), ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.40-7.36 (m, 2H), 7.33-7.31 (m, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 5.78-5.68 (m, 1H), 5.31-5.26 (m, 1H), 5.20-5.17 (m, 1H), 4.51 (d, *J* = 6.4 Hz, 2H), 2.79-2.75 (m, 2H), 2.73-2.69 (m, 2H), 2.10 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$) *δ*** 207.3, 140.0, 138.0, 130.6, 129.5, 129.3, 127.2, 126.8, 120.0, 50.4, 44.7, 29.9, 25.4. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{13}H_{17}N_2O_2$: 233.1285, Found: 233.1288.

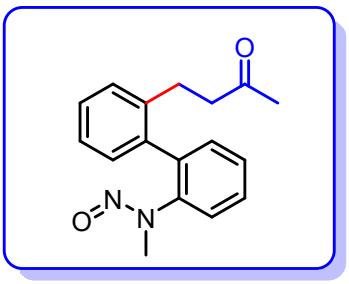


1-(4-Bromophenyl)-3-(2-(methylamino)phenyl)propan-1-one (9n), ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.75 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.47-7.43(m, 2H), 7.41-7.35 (m, 2H), 7.25-7.20 (m, 2H), 3.44 (s, 3H), 3.21 (t, *J* = 7.2 Hz, 2H), 2.95 (t, *J* = 7.9 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$) *δ*** 197.6, 141.2, 137.2, 135.2, 131.9, 131.3,

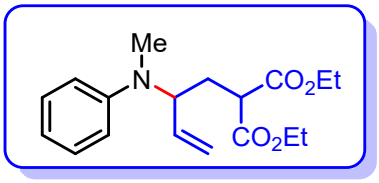
130.8, 129.5, 129.4, 128.3, 127.7, 127.5, 125.9, 39.8, 35.5, 25.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}BrN_2O_2$: 347.0390, Found: 347.0393.



4-(5-Fluoro-3-methyl-2-(methylamino)phenyl)butan-2-one (9o), ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92-6.90 (m, 2H), 3.34 (s, 3H), 2.80-2.72 (m, 1H), 2.68 (t, J = 6.4 Hz, 2H), 2.59-2.51(m, 1H), 2.13 (s, 3H), 2.10 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 207.1, 136.7, 133.1, 130.2, 128.2, 127.8, 127.4, 126.3, 122.2, 44.8, 36.1, 29.9, 25.7. **^{19}F NMR (300 MHz, $CDCl_3$) δ** -111.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{16}FN_2O_2$: 239.1190, Found: 239.1196.

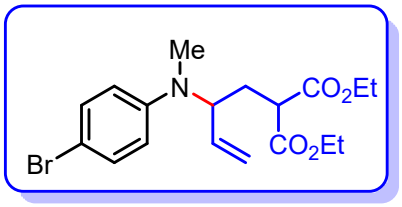


N-Methyl-N-(2'-(3-oxobutyl)-[1,1'-biphenyl]-2-yl)nitrous amide (9p), ^{1}H NMR (400 MHz, CDCl3) δ 7.48 (d, J = 7.6 Hz, 1H), 7.41-7.38 (m, 1H), 7.37-7.33 (m, 4H), 7.32-7.28 (m, 1H), 7.19 (dd, J = 2.0 Hz, 8.0 Hz, 2H), 2.86 (s, 3H), 2.76-2.73 (m, 4H), 2.18 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 207.2, 139.3, 129.7, 129.2, 128.9, 128.5, 128.1, 127.8, 44.8, 35.6, 29.9, 25.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{19}N_2O_2$: 283.1441, Found: 283.1445.

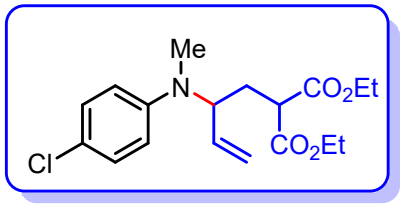


Diethyl 2-(2-(methyl(phenyl)amino)but-3-en-1-yl)malonate (4a), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.16 (m, 2H), 6.78 (d, J = 8.3 Hz, 2H), 6.72 (t, J = 7.2 Hz, 1H), 5.80 (m, 1H), 5.15 (t, J = 14.5 Hz, 3H), 4.43 (dd, J = 13.5 Hz, 6.9 Hz, 2H), 4.27–3.92

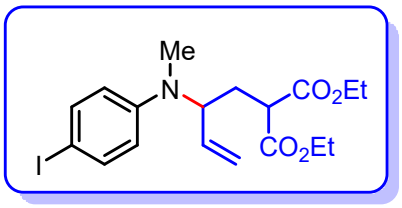
(m, 5H), 3.42 (t, J = 7.2 Hz, 1H), 2.71 (s, 4H), 2.30 (t, J = 7.5 Hz, 2H), 1.18 (dt, J = 11.5 Hz, 7.1 Hz, 7H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 169.3, 150.2, 136.0, 129.0, 117.2, 116.5, 113.6, 61.4, 58.2, 48.9, 31.3, 30.5, 13.9. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{18}H_{26}NO_4$: 320.1856, Found: 320.1857.



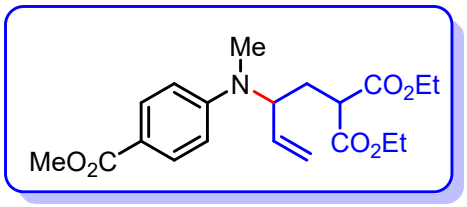
Diethyl 2-(2-((4-bromophenyl)(methyl)amino)but-3-en-1-yl)malonate (4b), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.06 (m, 2H), 6.64 (d, J = 9.1 Hz, 2H), 5.77 (m, 1H), 5.15 (ddt, J = 28.3 Hz, 17.4 Hz, 1.3 Hz, 2H), 4.41–4.26 (m, 1H), 4.27–3.99 (m, 4H), 3.37 (t, J = 7.3 Hz, 1H), 2.68 (s, 3H), 2.50–2.17 (m, 2H), 1.19 (dt, J = 10.9 Hz, 7.1 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 169.2, 169.0, 149.2, 135.5, 131.6, 116.7, 115.1, 109.0, 61.4, 58.3, 48.8, 31.3, 30.4, 13.8, 13.8. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{18}H_{25}BrNO_4$: 398.0961, Found: 398.0966.



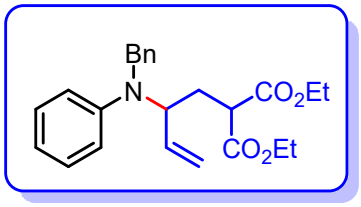
Diethyl 2-(2-((4-chlorophenyl)(methyl)amino)but-3-en-1-yl)malonate (4c), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, J = 9.0 Hz, 2H), 6.68 (d, J = 9.1 Hz, 2H), 5.76 (m, 1H), 5.14 (dd, J = 24.2 Hz, 14.0 Hz, 2H), 4.36 (dd, J = 13.5 Hz, 7.0 Hz, 1H), 4.26–3.83 (m, 4H), 3.37 (t, J = 7.3 Hz, 1H), 2.67 (s, 3H), 2.28 (t, J = 7.5 Hz, 2H), 1.18 (dt, J = 10.6 Hz, 7.1 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 169.2, 169.1, 135.6, 128.9, 128.7, 128.1, 125.2, 121.9, 116.7, 114.7, 61.4, 58.5, 48.8, 31.4, 30.4, 13.8, 13.8. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{18}H_{25}ClNO_4$: 354.1467, Found: 354.1469.



Diethyl 2-(2-((4-iodophenyl)(methyl)amino)but-3-en-1-yl)malonate (4d), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.6 Hz, 2H), 6.54 (d, J = 8.8 Hz, 2H), 6.06–5.53 (m, 1H), 5.15 (dd, J = 25.4 Hz, 14.0 Hz, 2H), 4.38 (dd, J = 13.4 Hz, 6.2 Hz, 1H), 4.26–3.89 (m, 4H), 3.35 (t, J = 7.3 Hz, 1H), 2.67 (s, 3H), 2.52–2.18 (m, 2H), 1.18 (dt, J = 11.2 Hz, 7.0 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 169.2, 169.0, 149.7, 137.5, 135.6, 116.8, 115.6, 78.1, 61.5, 58.0, 48.8, 31.2, 30.5, 13.9, 13.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{25}INO_4$: 446.0823, Found: 446.0827.

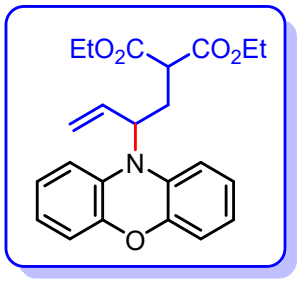


Diethyl 2-(2-((4-(methoxycarbonyl)phenyl)(methyl)amino)but-3-en-1-yl)malonate (4e), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 9.0 Hz, 2H), 6.64 (d, J = 9.0 Hz, 2H), 5.71 (m, 1H), 5.40–4.89 (m, 2H), 4.64–4.38 (m, 1H), 4.03 (m, 4H), 3.77 (d, J = 1.8 Hz, 3H), 3.24 (dd, J = 8.4 Hz, 6.2 Hz, 1H), 2.71 (s, 3H), 2.40–2.12 (m, 2H), 1.09 (dt, J = 18.0 Hz, 7.2 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 169.0, 167.1, 153.3, 135.4, 131.2, 117.8, 116.9, 111.4, 61.5, 57.2, 51.4, 48.7, 31.4, 30.4, 13.8, 13.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{28}NO_6$: 378.1911, Found: 378.1915.

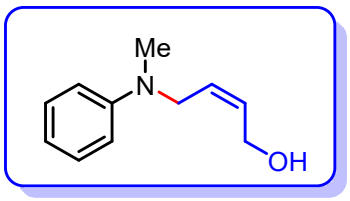


Diethyl 2-(2-(benzyl(phenyl)amino)but-3-en-1-yl)malonate (4f), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, J = 6.8 Hz, 4H), 7.20–6.97 (m, 3H), 6.77 (d, J = 8.4 Hz, 2H), 6.69 (t, J = 7.3 Hz, 1H), 5.90–5.60 (m, 1H), 5.33–5.06 (m, 2H), 4.48 (d, J = 7.0 Hz,

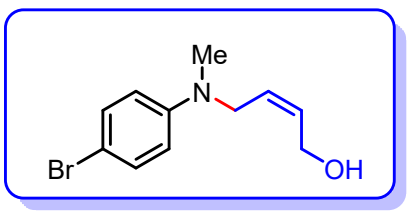
1H), 4.39 (d, J = 5.3 Hz, 2H), 4.17–4.00 (m, 4H), 3.49 (t, J = 7.3 Hz, 1H), 2.27 (qd, J = 14.2 Hz, 7.0 Hz, 2H), 1.19 (td, J = 7.0 Hz, 1.8 Hz, 6H).; **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 169.2, 148.8, 139.4, 136.1, 128.9, 128.3, 126.6, 126.4, 117.8, 117.5, 115.0, 61.4, 59.0, 49.8, 48.9, 30.6, 13.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{30}NO_4$: 396.2169, Found: 396.2175.



Diethyl 2-(2-(10*H*-phenoxazin-10-yl)but-3-en-1-yl)malonate (4g), **^{1}H NMR (400 MHz, $CDCl_3$)** ***δ*** 6.84–6.78 (m, 2H), 6.78–6.73 (m, 4H), 6.66 (d, J = 7.6 Hz, 2H), 6.02 (m, 1H), 5.31 (dt, J = 5.2, 2.4 Hz, 2H), 4.55–4.47 (m, 1H), 4.16–3.92 (m, 4H), 3.55 (dd, J = 10.3 Hz, 5.1 Hz, 1H), 2.79 (m, 2H), 1.16 (t, J = 7.2 Hz, 3H), 1.04 (t, J = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 169.2, 168.9, 147.7, 135.4, 134.2, 123.4, 121.8, 116.9, 115.7, 115.0, 61.5, 58.0, 48.6, 29.1, 13.8, 13.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{26}NO_5$: 396.1805, Found: 396.1808.

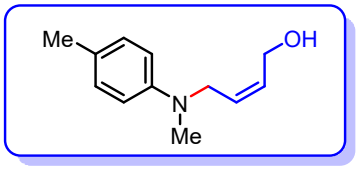


(*Z*)-4-(Methyl(phenyl)amino)but-2-en-1-ol (8a),[3] **^{1}H NMR (400 MHz, $CDCl_3$)** ***δ*** 7.25 (dd, J = 8.6, 7.2 Hz, 2H), 6.74-6.70 (m, 3H), 5.86–5.60 (m, 2H), 4.11 (d, J = 4.0 Hz, 2H), 3.94 (d, J = 4.2 Hz, 2H), 2.95 (s, 3H).; **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 149.2, 130.8, 129.0, 126.9, 116.4, 112.4, 62.8, 53.9, 37.9.

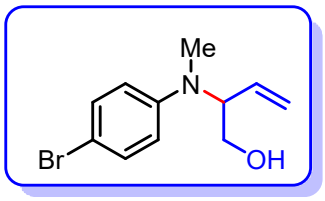


(*Z*)-4-((4-Bromophenyl)(methyl)amino)but-2-en-1-ol (8b), **^{1}H NMR (400 MHz,**

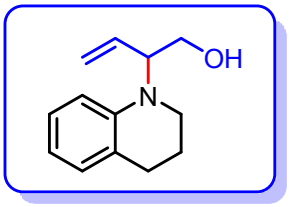
$CDCl_3$) δ 7.27 (dd, J = 6.5, 4.5 Hz, 2H), 6.56 (d, J = 9.0 Hz, 2H), 5.92 – 5.41 (m, 2H), 4.14 (s, 2H), 3.90 (d, J = 4.1 Hz, 2H), 2.92 (s, 3H).; **^{13}C NMR (100 MHz, $CDCl_3$) δ** 131.7, 131.0, 126.5, 113.9, 62.9, 53.9, 38.2. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{11}H_{15}BrNO$: 256.0332, Found: 256.0337.



(*Z*)-4-(Methyl (*p*-tolyl)amino)but-2-en-1-ol (8c), **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.88 (d, J = 9.0 Hz, 2H), 6.64 (d, J = 9.0 Hz, 2H), 5.72 (dd, J = 4.9, 3.5 Hz, 2H), 4.14 (d, J = 2.5 Hz, 2H), 3.99 (s, 2H), 3.84 (s, 3H), 3.02 (s, 3H).; **^{13}C NMR (100 MHz, $CDCl_3$) δ** 167.4, 152.3, 131.3, 131.0, 125.7, 117.1, 110.7, 62.8, 53.4, 51.4, 38.0. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C12H18NO: 192.1383, Found: 192.1386.

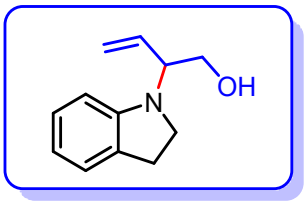


2-((4-Bromophenyl)(methyl)amino)but-3-en-1-ol (8d), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.18 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 5.94–5.56 (m, 1H), 5.19 (dd, J = 38.4 Hz, 14.0 Hz, 2H), 4.36 (dd, J = 14.0 Hz, 5.8 Hz, 1H), 3.90–3.68 (m, 2H), 2.78 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 149.5, 132.7, 128.9, 118.2, 116.0, 63.6, 61.8, 31.9. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{11}H_{15}BrNO$: 256.0332, Found: 256.0337.

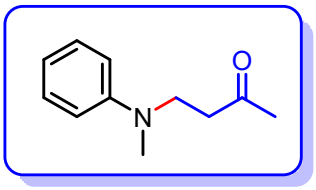


2-(3,4-Dihydroquinolin-1(2*H*)-yl)but-3-en-1-ol (8e), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.05 (t, J = 7.8 Hz, 1H), 6.98 (d, J = 6.9 Hz, 1H), 6.78 (d, J = 8.3 Hz, 1H), 6.64 (dd, J = 7.3 Hz, 6.6 Hz, 1H), 5.82 (m, 1H), 5.24 (m, 2H), 4.60–4.47 (m, 1H), 3.92–3.77 (m, 2H), 3.21 (t, J = 5.8 Hz, 2H), 2.76 (td, J = 15.8 Hz, 6.4 Hz, 2H), 2.07–1.88 (m, 2H);

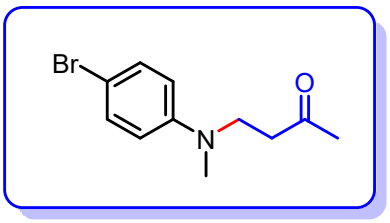
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 133.3, 129.3, 127.0, 124.0, 117.9, 116.8, 111.9, 61.4, 60.9, 42.3, 28.2, 22.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{18}NO$: 204.1383, Found: 204.1387.



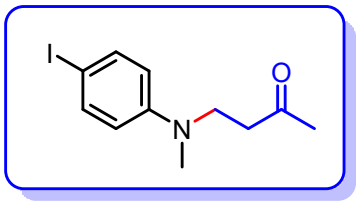
2-(Indolin-1-yl)but-3-en-1-ol (8f), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (dd, J = 14.9 Hz, 7.1 Hz, 2H), 6.78 – 6.64 (m, 1H), 6.55 (d, J = 7.9 Hz, 1H), 5.90 (m, 1H), 5.48 (dd, J = 26.1 Hz, 13.8 Hz, 2H), 4.59 (t, J = 8.2 Hz, 1H), 4.15 (dd, J = 8.5 Hz, 7.6 Hz, 2H), 3.81 (dd, J = 7.4 Hz, 4.5 Hz, 2H), 3.41 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 151.1, 132.2, 132.1, 127.2, 124.6, 121.2, 119.2, 118.2, 107.9, 69.0, 61.9, 59.9, 47.1, 28.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{16}NO$: 190.1226, Found: 190.1228.



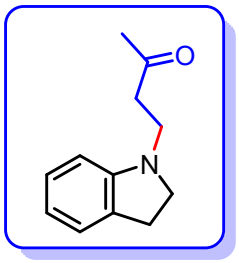
4-(Methyl(phenyl)amino)butan-2-one (10a),[2] **^{1}H NMR (400 MHz, $CDCl_3$)** δ7.25-7.21 (m, 2H), 6.72-6.69 (m, 3H), 3.63 (t, J = 6.8 Hz,2H), 2.92 (s, 3H), 2.70 (t, J = 6.8 Hz,2H), 2.15 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 208.0, 148.6, 129.3, 116.6, 112.4, 47.3, 40.3, 38.5, 30.6.



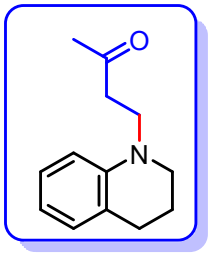
4-((4-Bromophenyl)(methyl)amino)butan-2-one (10b), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.26 (m, 2H), 6.55-6.53 (m, 2H), 6.31 (d, J = 8.8 Hz, 2H), 3.58 (t, J = 6.8 Hz, 2H), 2.88 (s, 3H), 2.67 (t, J = 6.8 Hz, 2H), 2.14 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 207.5, 147.5, 131.7, 113.8, 108.4, 47.1, 40.0, 38.4, 30.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{15}BrNO$: 256.0332, Found: 256.0337.



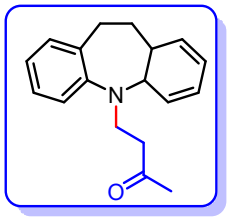
4-((4-Iodophenyl)(methyl)amino)butan-2-one (10c), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31 (d, J = 8.8 Hz, 2H), 6.31 (d, J = 8.8 Hz, 2H), 6.72-6.69 (m, 3H), 3.45 (t, J = 6.8 Hz, 2H), 2.75 (s, 3H), 2.54 (t, J = 7.2 Hz,2H), 2.00 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 207.5, 148.0, 137.6, 114.4, 46.9, 40.0, 38.3, 30.5. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{11}H_{15}INO$: 304.0193, Found: 304.0198.



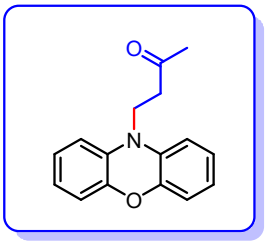
4-(Indolin-1-yl)butan-2-one (10d), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.08-7.05 (m, 2H), 6.66 (t, J = 7.6 Hz, 1H), 6.50 (d, J = 8 Hz, 1H), 3.39(t, J = 6.8 Hz, 2H), 3.30 (t, J = 8.4 Hz, 2H), 2.95 (t, J = 8.4 Hz, 2H), 2.73 (t, J = 6.8 Hz, 2H), 2.20 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 207.7, 151.9, 130.0, 127.3, 124.5, 117.8, 106.9, 53.2, 43.9, 41.1, 30.3, 28.6. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{12}H_{16}NO$: 190.1226, Found: 190.1225.



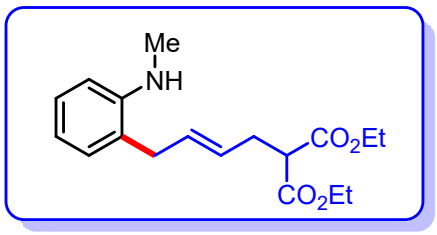
4-(3,4-Dihydroquinolin-1(2*H*)-yl)butan-2-one (10e), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.05 (t, J = 7.8 Hz, 1H), 6.95 (d, J = 7.2 Hz, 1H), 6.64-6.48 (m, 2H), 3.57 (t, J = 7.0 Hz, 2H), 3.27 (t, J = 5.6 Hz, 2H), 2.75-2.72 (m, 4H), 2.17 (s, 3H), 1.97-1.91 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 208.2, 144.6, 129.3, 127.1, 122.7, 116.0, 110.4, 49.6, 45.9, 40. 0, 30.6, 28.0, 22.2. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{13}H_{18}NO$: 204.1383, Found: 204.1386.



4-(4a,10,11,11a-Tetrahydro-5*H*-dibenzo[b,f]azepin-5-yl)butan-2-one (10f), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.15-7.13 (m, 2H), 7.08-7.03(m, 3H), 6.92 (td, J = 1.2 Hz, 7.2 Hz, 2H), 4.03 (t, J = 6.8 Hz, 2H), 3.12 (s, 3H), 2.70 (t, J = 7.2 Hz, 2H), 2.07 (s, 2H), 1.43-1.33 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 207.6, 147.9, 134.3, 129.9, 126.5, 122.7, 119.8, 45.4, 42.4, 32.1, 30.1, 29.7. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{18}H_{22}NO$: 268.1696, Found: 268.1698.

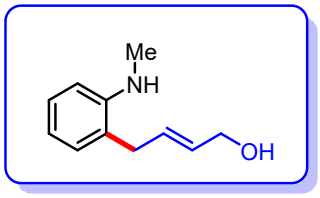


4-(10*H*-Phenoxazin-10-yl)butan-2-one (10g), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.80 (m, 2H), 6.72–6.60 (m, 4H), 6.47 (d, J = 7.2 Hz, 2H), 3.91–3.77 (m, 2H), 2.90–2.66 (m, 2H), 2.22 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 207.1, 145.0, 132.7, 123.7, 121.1, 115.5, 111.1, 38.6, 37.9, 30.5. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{16}H_{16}NO_2$: 254.1176, Found: 254.1179.

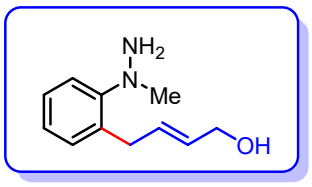


Diethyl (*E*)-2-(4-(2-(methylamino)phenyl)but-2-en-1-yl)malonate (3a-1), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.17 (t, J = 7.0 Hz, 1H), 7.04 (d, J = 7.0 Hz, 1H), 6.67 (t, J = 6.8 Hz, 1H), 6.62 (d, J = 8.0 Hz, 1H), 5.56 (dd, J = 12.0, 5.4 Hz, 1H), 5.51 – 5.43 (m, 1H), 4.21 (q, J = 6.8 Hz, 4H), 3.85 (s, 1H), 3.44 (s, 1H), 3.29 (d, J = 6.6 Hz, 2H), 2.86 (d, J = 11.4 Hz, 3H), 2.76 (t, J = 7.2 Hz, 2H), 1.27 (t, J = 7.2 Hz, 6H).; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 169.0, 147.1, 130.5, 129.0, 127.5, 126.7, 124.3, 116.8, 109.7,

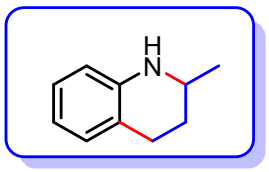
61.5, 51.7, 30.7, 29.7, 26.8, 14.0. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{18}H_{26}NO_4$: 320.1856, Found: 320.1858.



(*E*)-4-(2-(Methylamino)phenyl)but-2-en-1-ol (7a-1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (td, J = 7.9, 1.4 Hz, 1H), 7.04 (d, J = 7.4 Hz, 1H), 6.71 (td, J = 7.4, 1.0 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 5.90–5.77 (m, 1H), 5.75–5.54 (m, 1H), 4.12 (dd, J = 5.6, 1.2 Hz, 2H), 3.27 (d, J = 6.0 Hz, 2H), 2.86 (d, J = 3.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 147.1, 130.6, 129.7, 129.5, 127.8, 123.7, 117.2, 110.0, 63.3, 34.5, 30.8. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{11}H_{16}NO$: 178.1226, Found: 178.1229.

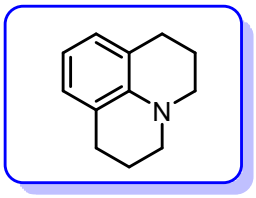


(*E*)-4-(2-(1-Methylhydrazinyl)phenyl)but-2-en-1-ol (7a-2), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.08 (m, 1H), 7.02 (dd, J = 9.9 Hz, 3.6 Hz, 1H), 6.70 (m, 1H), 6.62 (dd, J = 7.8 Hz, 4.6 Hz, 1H), 5.79 (dd, J = 7.2 Hz, 2.0 Hz, 1H), 5.71–5.58 (m, 1H), 4.05 (dd, J = 5.6 Hz, 1.0 Hz, 2H), 3.23 (d, J = 6.0 Hz, 2H), 2.82 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 147.0, 130.5, 129.4, 128.9, 127.6, 123.7, 117.1, 117.0, 109.9, 63.1, 57.9, 34.4, 30.7, 30.5, 29.9. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{11}H_{17}N_2O$: 193.1335, Found: 193.1336.

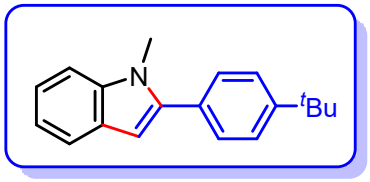


2-Methyl-1,2,3,4-tetrahydroquinoline (9p-1),[4] **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.95 (dd, J = 9.6 Hz, 3.8 Hz, 2H), 6.60 (td, J = 7.4 Hz, 0.8 Hz, 1H), 6.55–6.37 (m, 1H), 3.39 (m, 1H), 3.08–2.48 (m, 1H), 2.37–1.77 (m, 1H), 1.58 (m, 1H), 1.21 (d, J = 6.4 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 144.7, 129.2, 126.6, 121.0 116.9, 113.9, 47.1, 30.1,

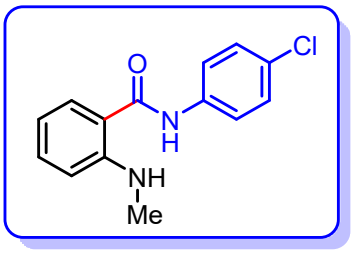
26.5, 22.5.



2,3,6,7-Ttrahydro-1*H*,5*H*-pyrido[3,2,1-ij]quinoline (13), ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96-6.92 (m, 2H), 6.67-6.63 (m, 1H), 3.28-3.26 (m, 4H), 2.93-2.89 (m, 4H), 2.15–2.09 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 142.8, 126.8, 121.4, 115.6, 49.9, 27.5, 22.0.



2-(4-(*tert*-Butyl)phenyl)-1-methyl-1*H*-indole (13a), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 1H), 7.44 (s, 4H), 7.36 (d, J = 8.0 Hz, 1H), 7.26-7.25 (m, 1H), 7.17-7.15 (m, 1H), 6.55 (s, 1H), 3.73 (s, 3H).; **^{13}C NMR (100 MHz, $CDCl_3$) δ** 150.9, 141.6, 138.3, 129.9, 129.0, 128.0, 125.4, 121.5, 120.3, 119.8, 109.5, 101.3, 34.7, 31.3, 31.2.



N-(4-Chlorophenyl)-2-(methylamino)benzamide (15a), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (brs, 1H), 7.54-7.50 (m, 2H), 7.46 (dd, J = 1.2 Hz, 7.6 Hz, 1H), 7.40-7.36 (m, 2H), 7.34-7.31 (m, 2H), 6.72 (d, J = 8.4 Hz, 1H), 6.67-6.63 (m, 1H), 2.88 (s, 3H).; **^{13}C NMR (100 MHz, $CDCl_3$) δ** 168.0, 150.9, 136.5, 133.5, 129.4, 129.0, 127.1, 121.7, 114.7, 111.5, 29.7.

E. References

1. B. Liu, Y. Fan, Y. Gao, C. Sun, C. Xu, J. Zhu, *J. Am. Chem. Soc*., **2013**, *135*,

468−473.

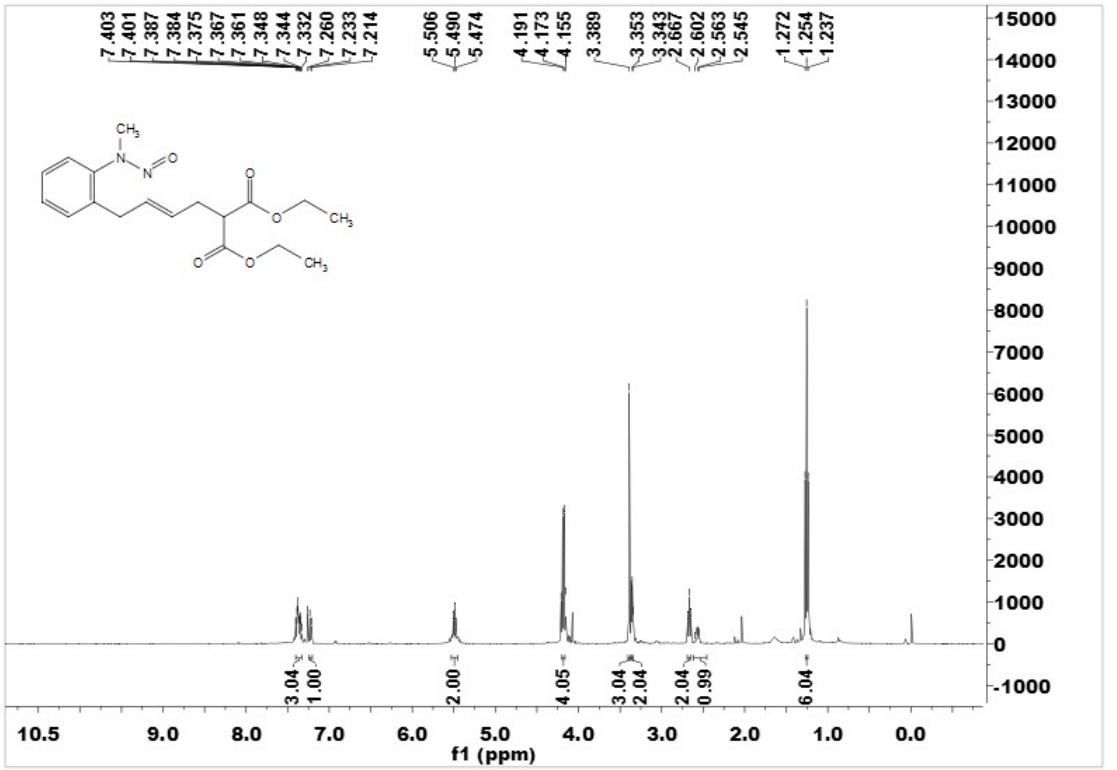
2. H. Firouzabadi, N. Iranpoor, A. A. Jafari, *Adv. Synth. Catal.*, **2005**, *347*, 655–661.

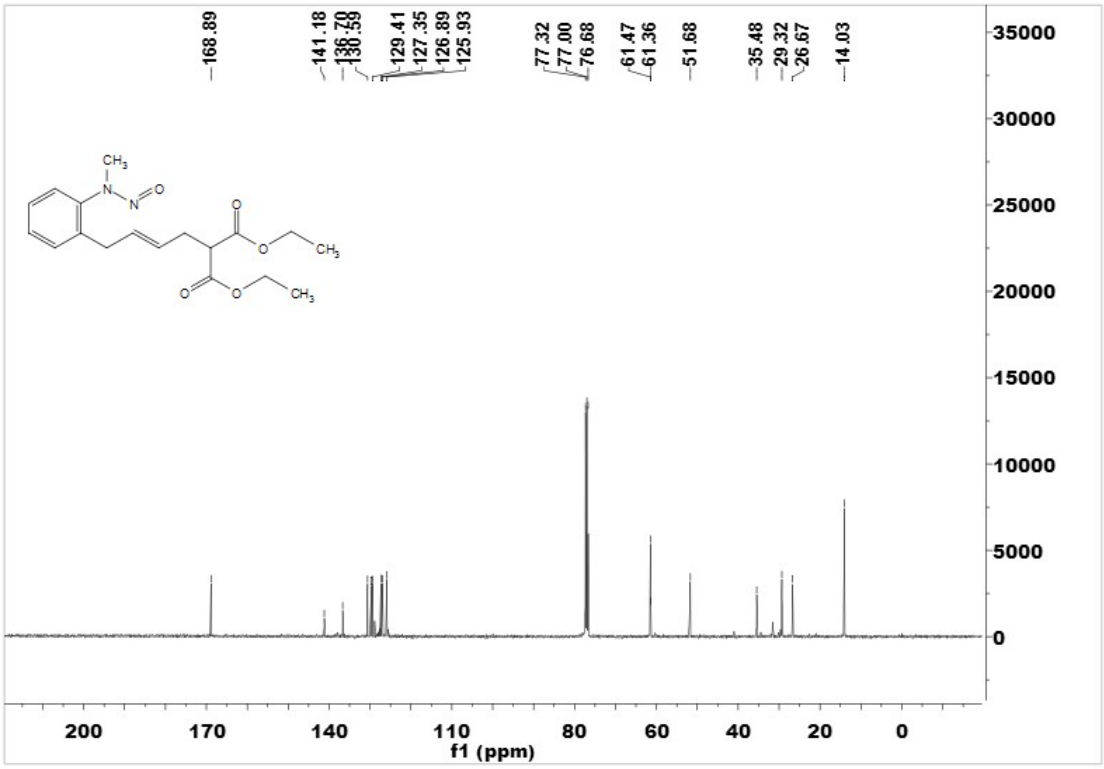
3. W. Guo, L. M-Rodríguez, R. Kuniyil, E. Martin, E. C. Escudero-Adán, F. Maseras, A. W. Kleij, *J. Am. Chem. Soc*., **2016**, *138*, 11970−11978.

4. L. Tao, Y. Ren, C.Li, H. Li, X. Chen, L. Liu, Q. Yang, *ACS Catal*. **2020**, *10*, 1783−1791.

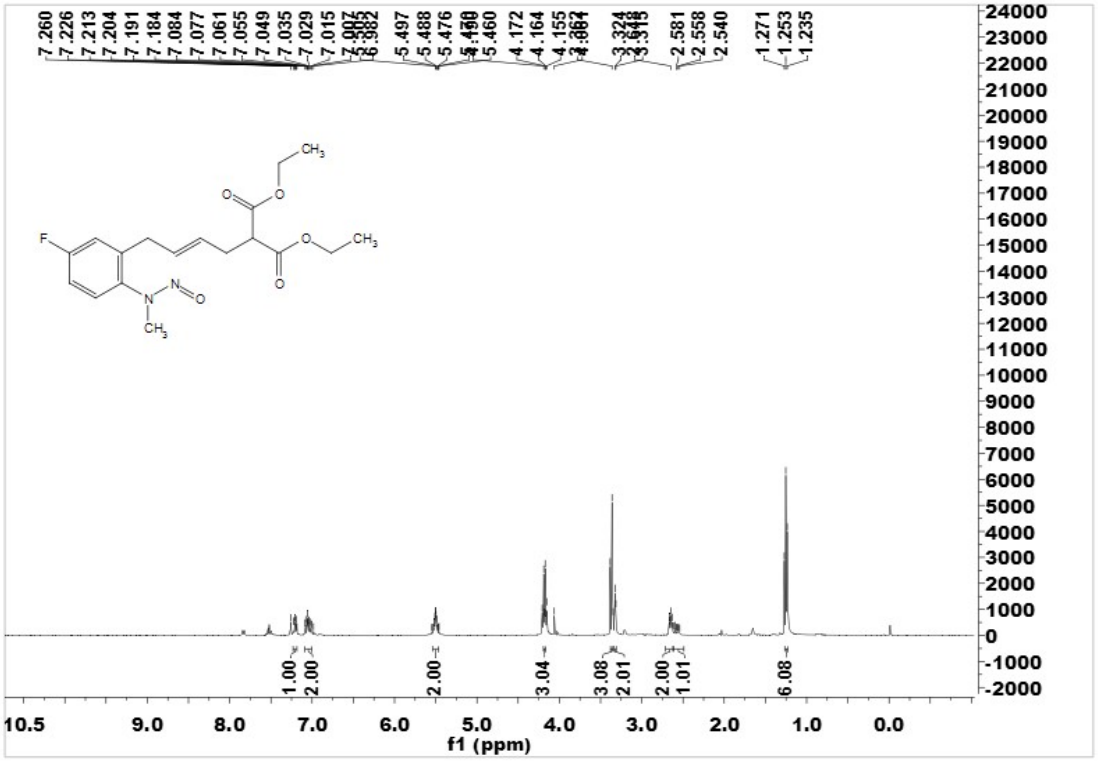
F. NMR Spectrum of the obtained products

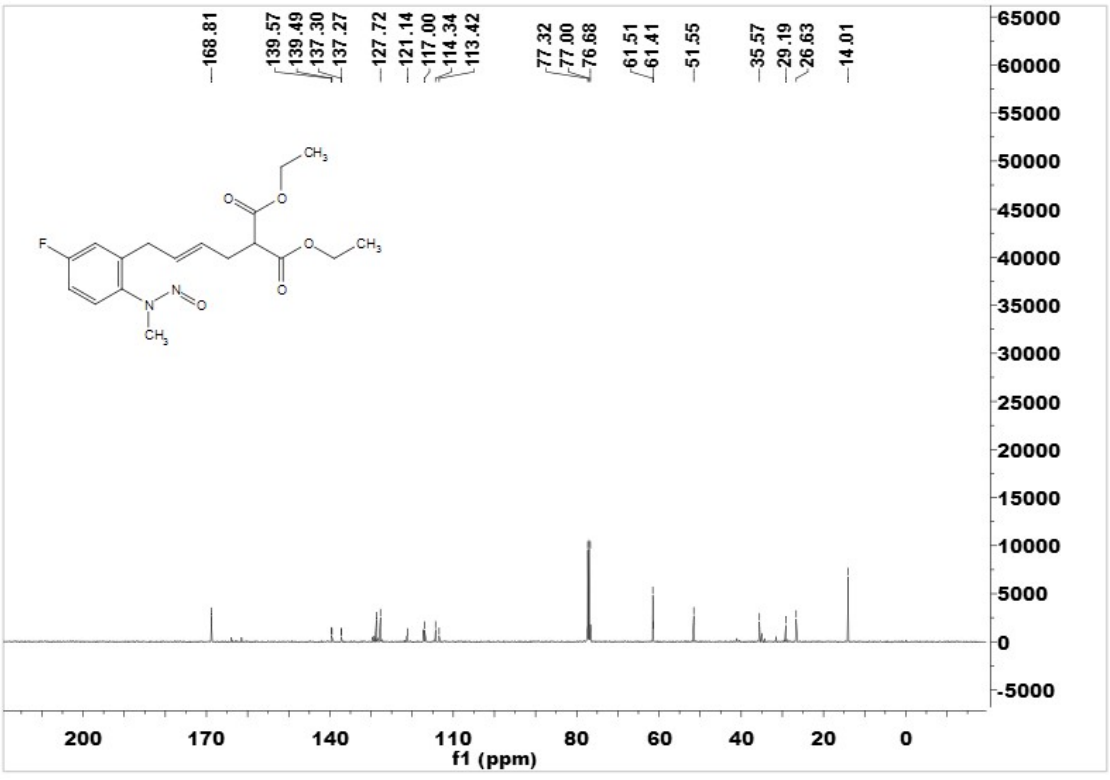
Diethyl (*E*)-2-(4-(2-(methyl(nitroso)amino)phenyl)but-2-en-1-yl)malonate (3a)



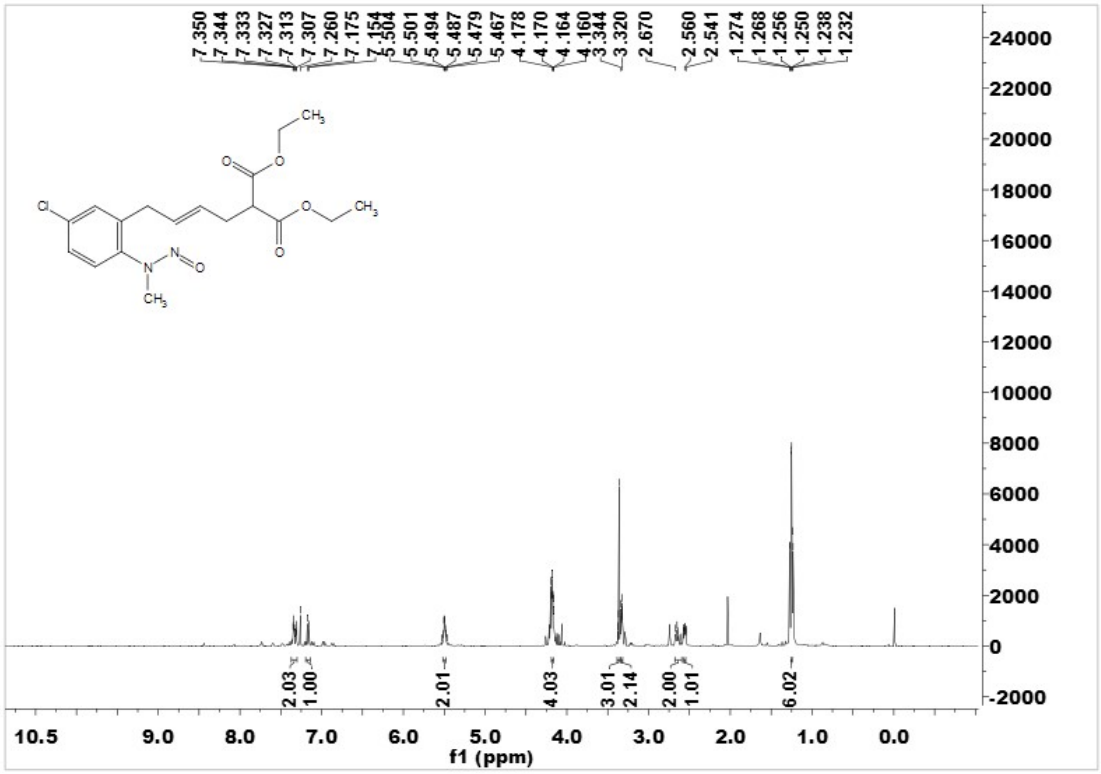


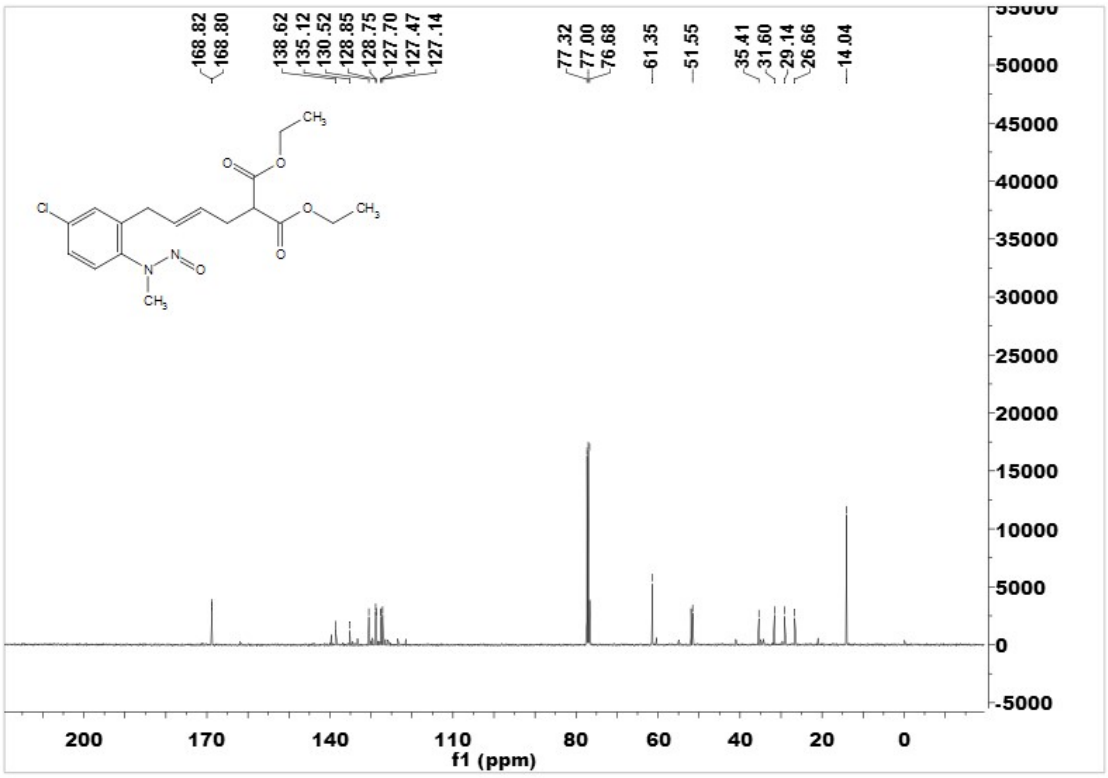
Diethyl (*E*)-2-(4-(5-fluoro-2-(methyl(nitroso)amino)phenyl)but-2-en-1-ylmalonate (3b)



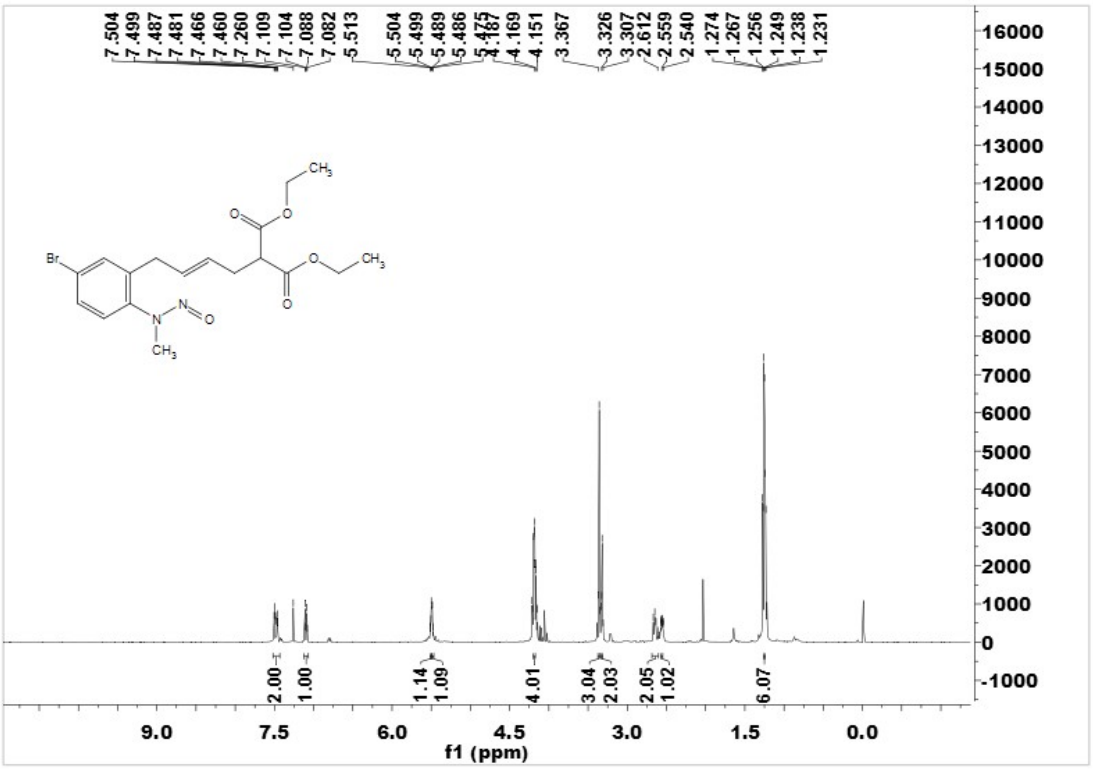


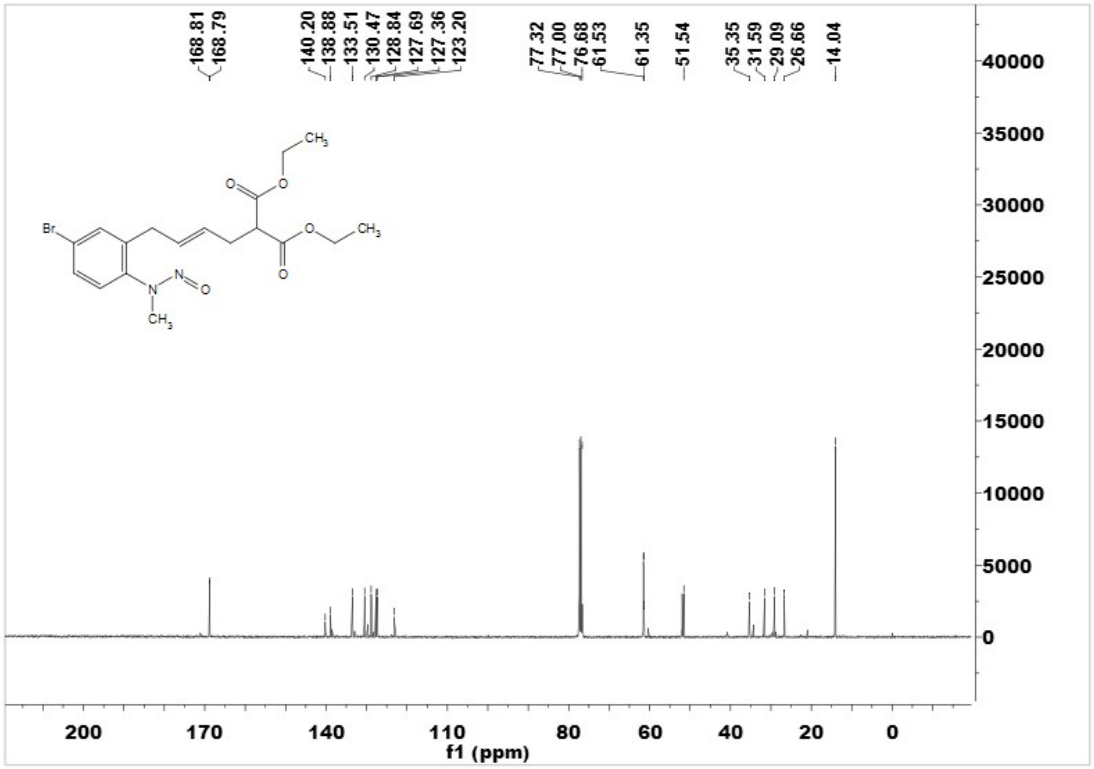
Diethyl (*E*)-2-(4-(5-chloro-2-(methyl(nitroso)amino)phenyl)but-2-en-1-yl)malonate (3c)



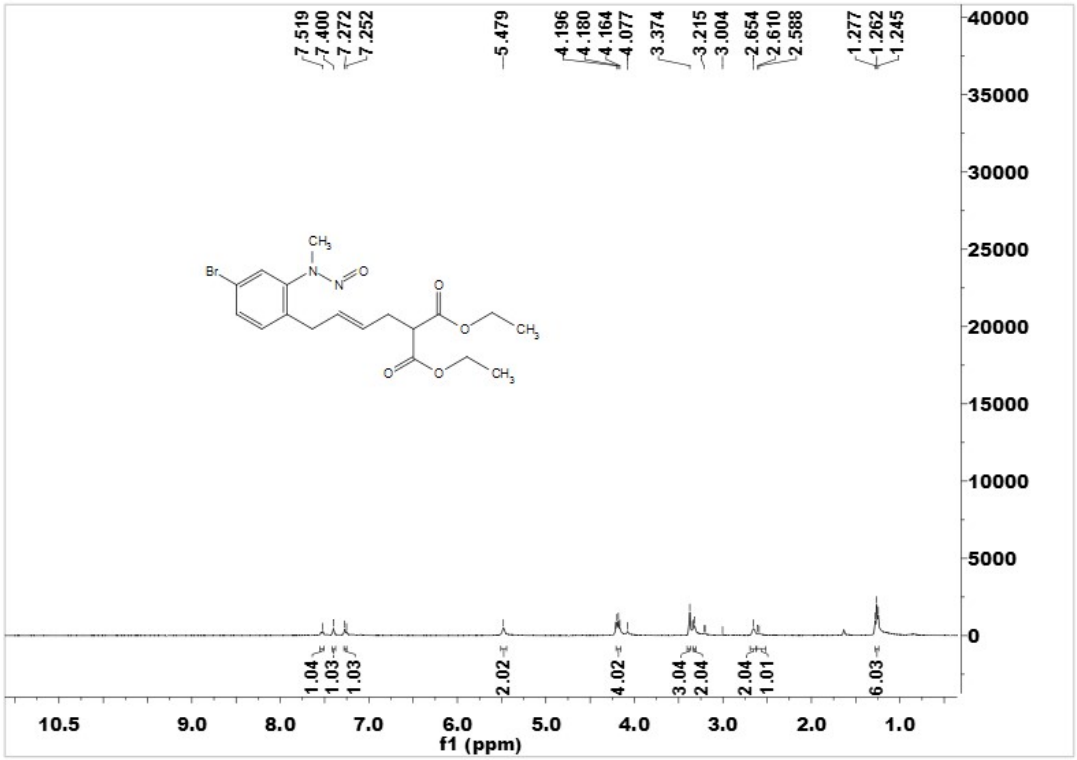


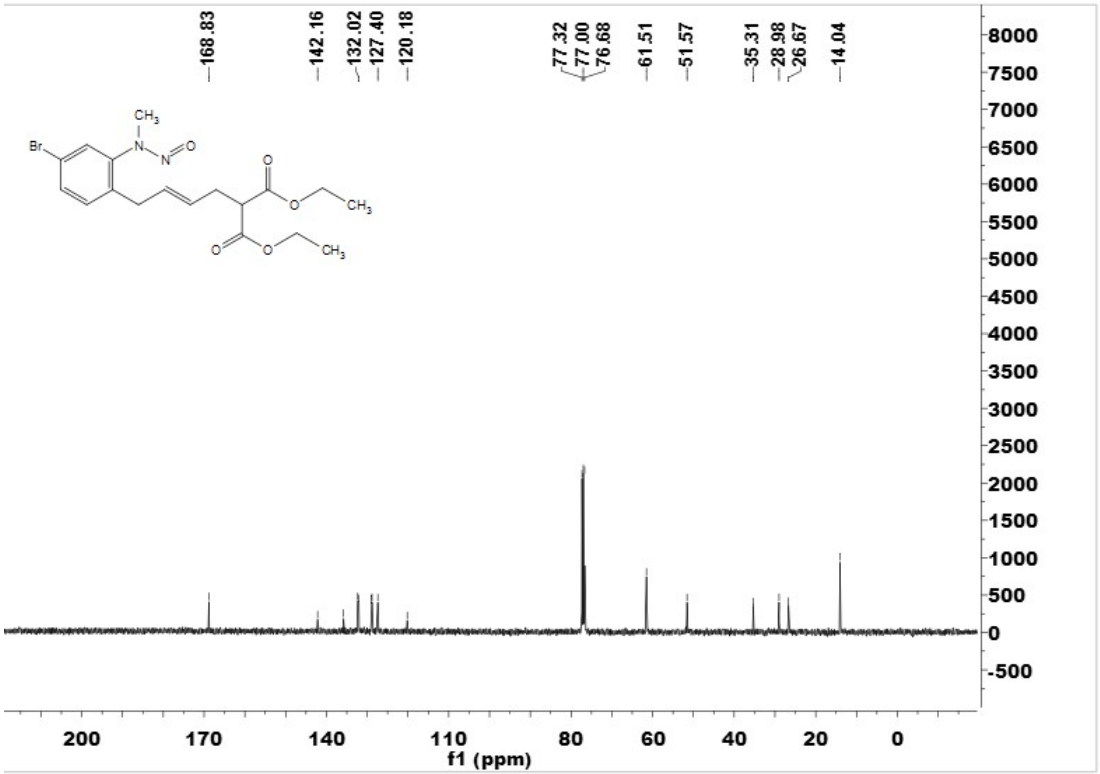
Diethyl (*E*)-2-(4-(5-bromo-2-(methyl(nitroso)amino)phenyl)but-2-en-1-yl) malonate (3d)



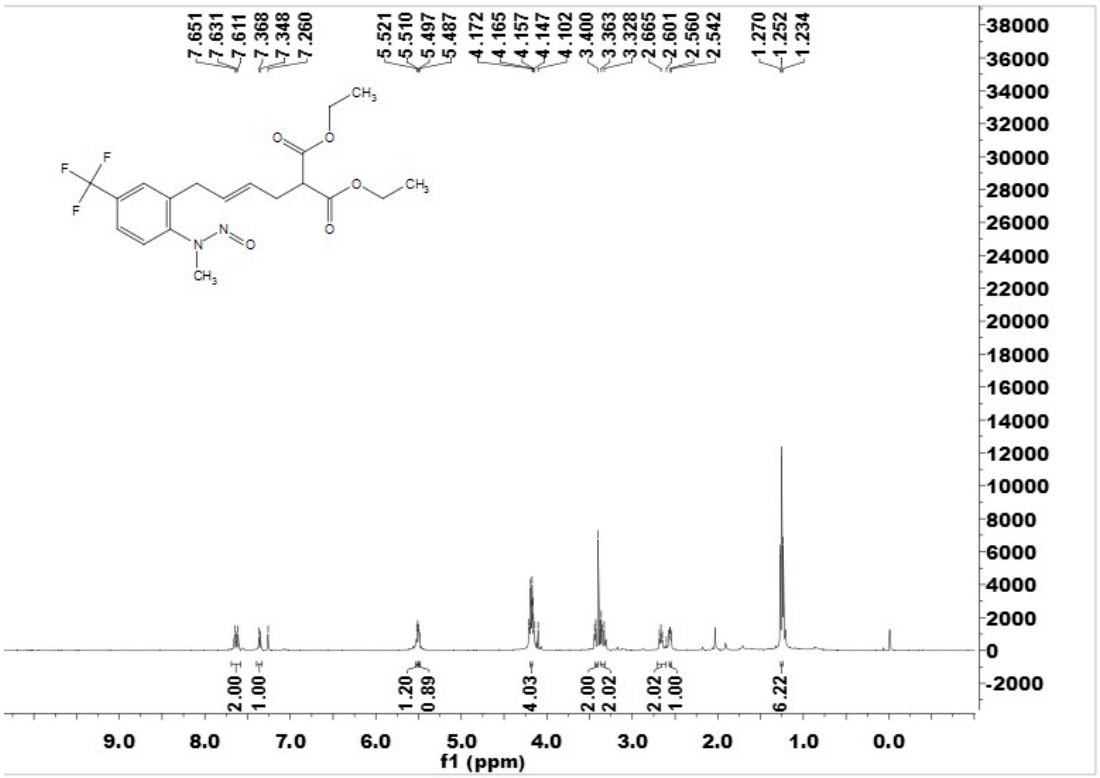


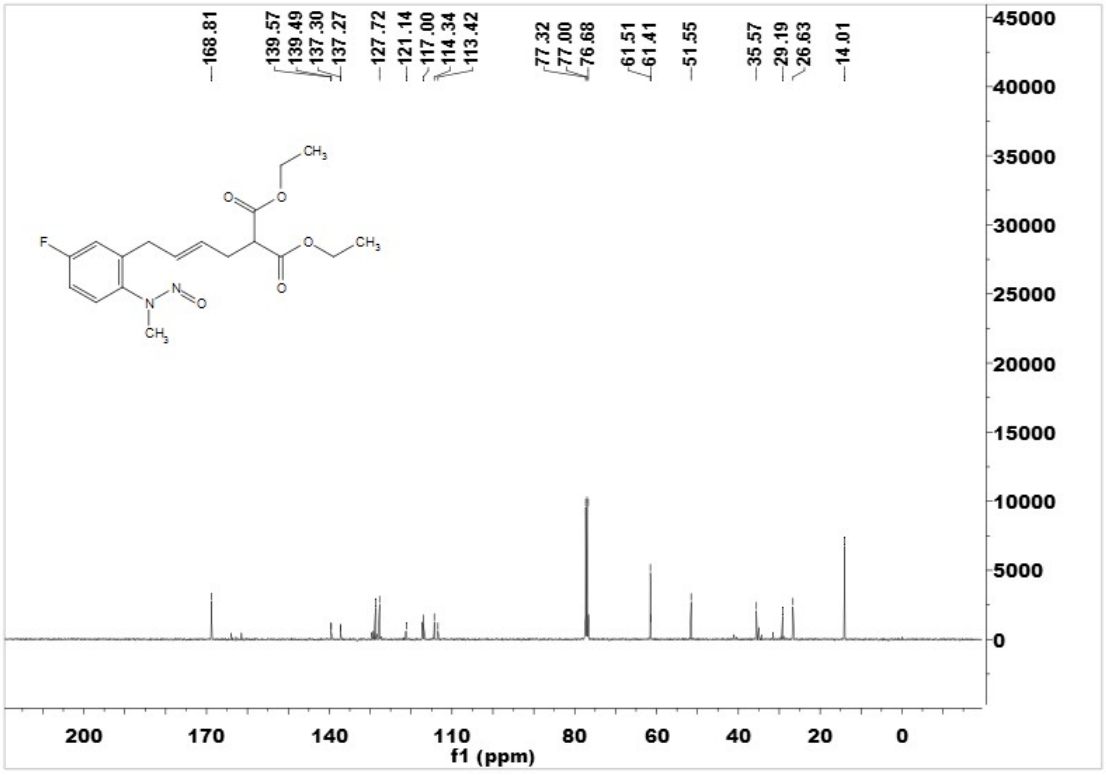
Diethyl (*E*)-2-(4-(4-bromo-2-(methyl(nitroso)amino)phenyl)but-2-en-1-yl)malonate (3e)

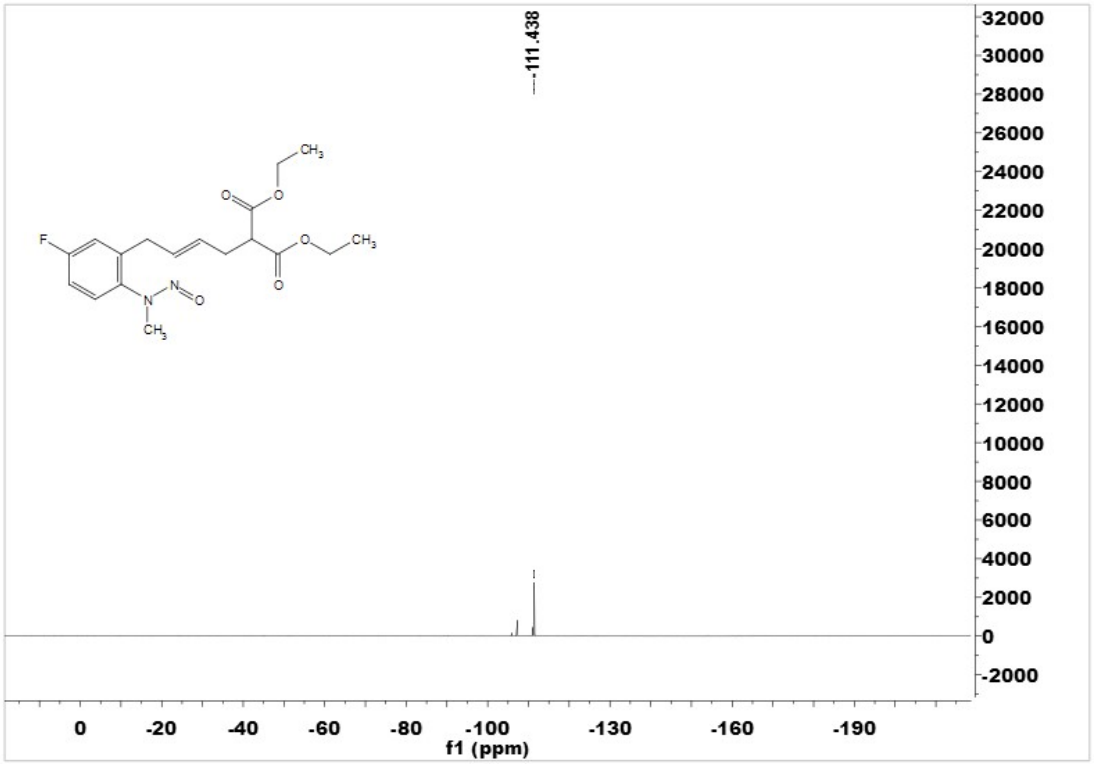




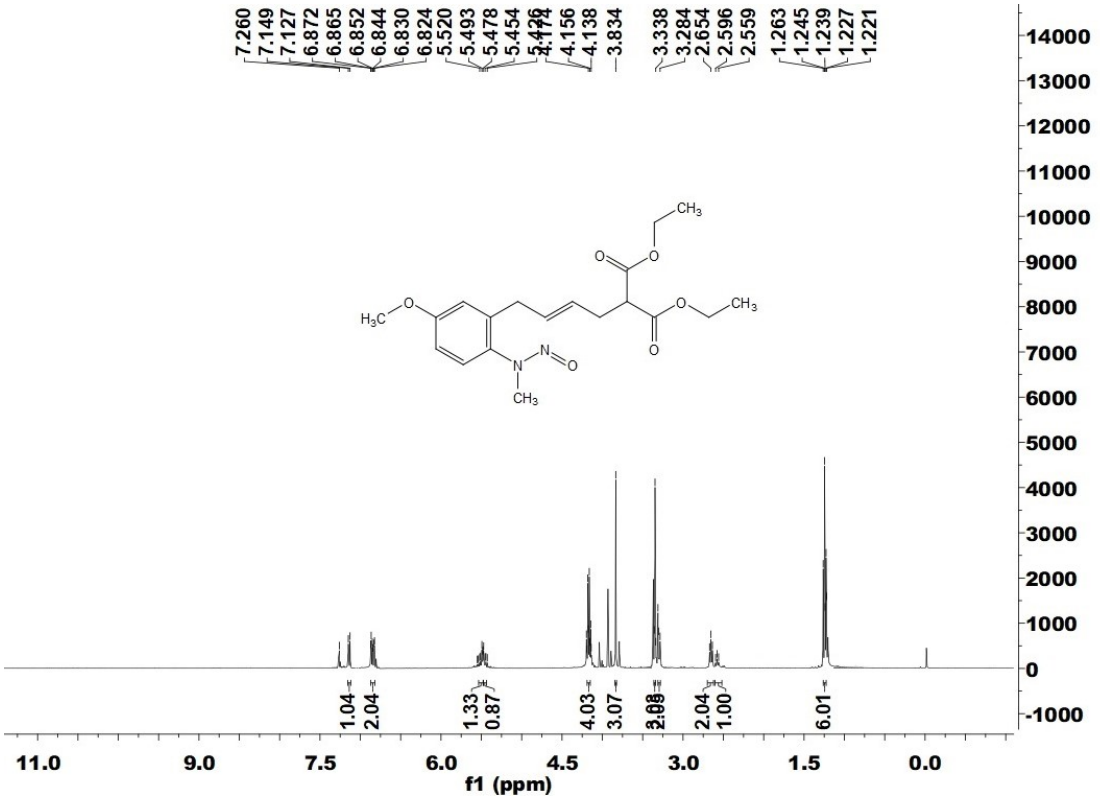
Diethyl (*E*)-2-(4-(2-(methyl(nitroso)amino)-5-(trifluoromethyl)phenyl)but-2-en-1-yl)malonate (3f)

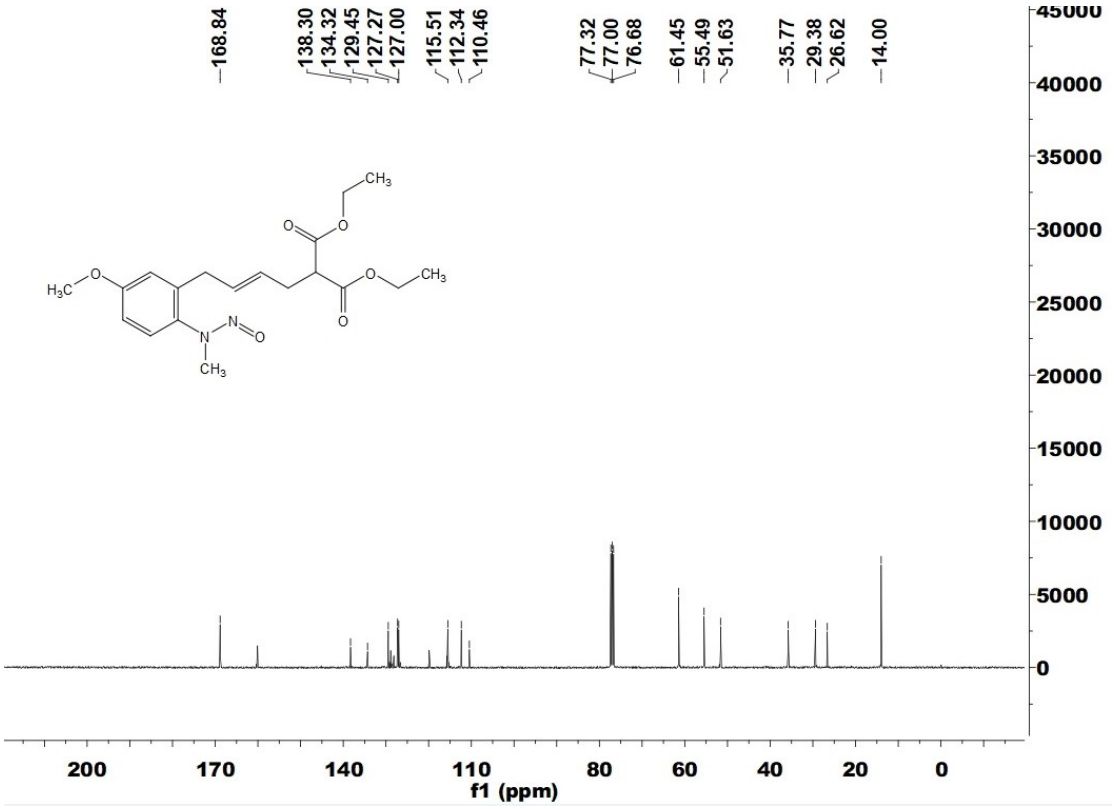




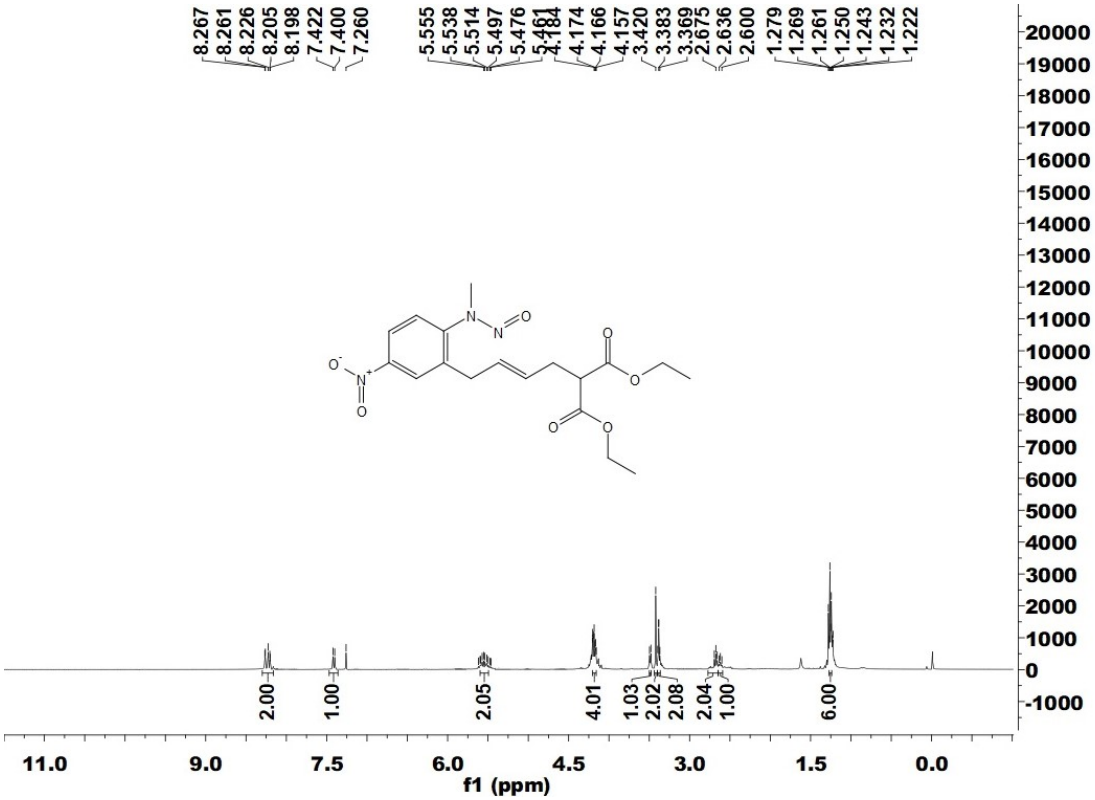


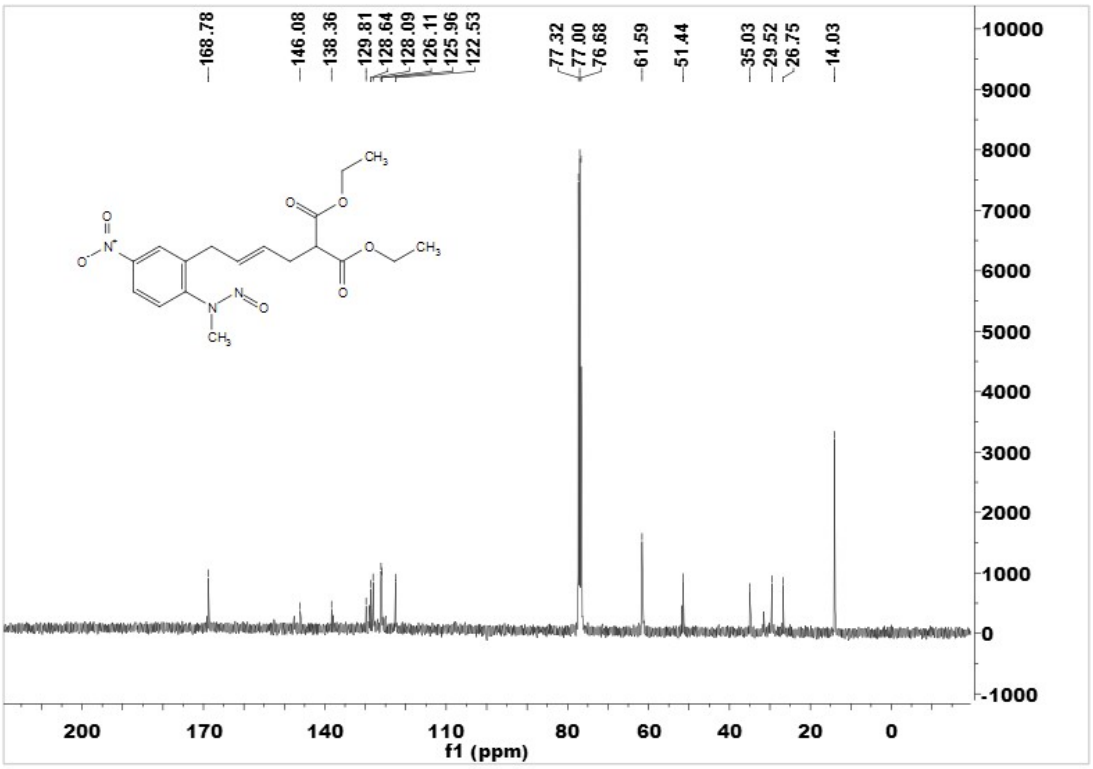
Diethyl (*E*)-2-(4-(5-methoxy-2-(methyl(nitroso)amino)phenyl)but-2-en-1-yl)malonate (3g)



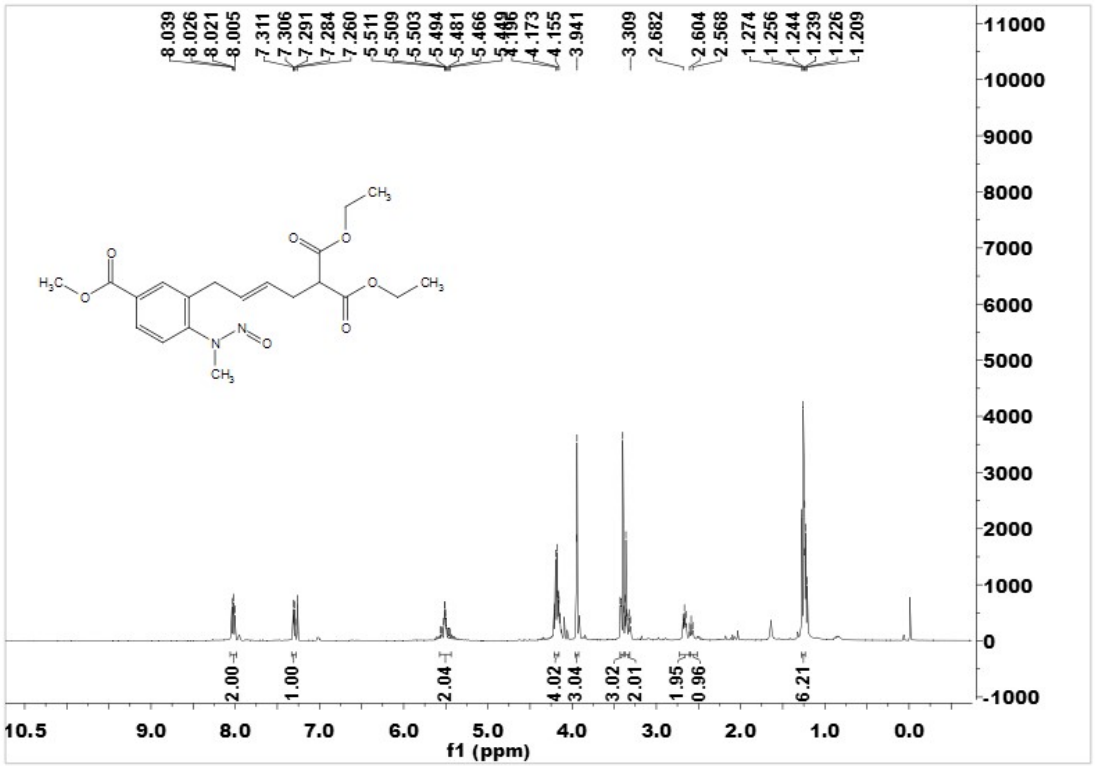


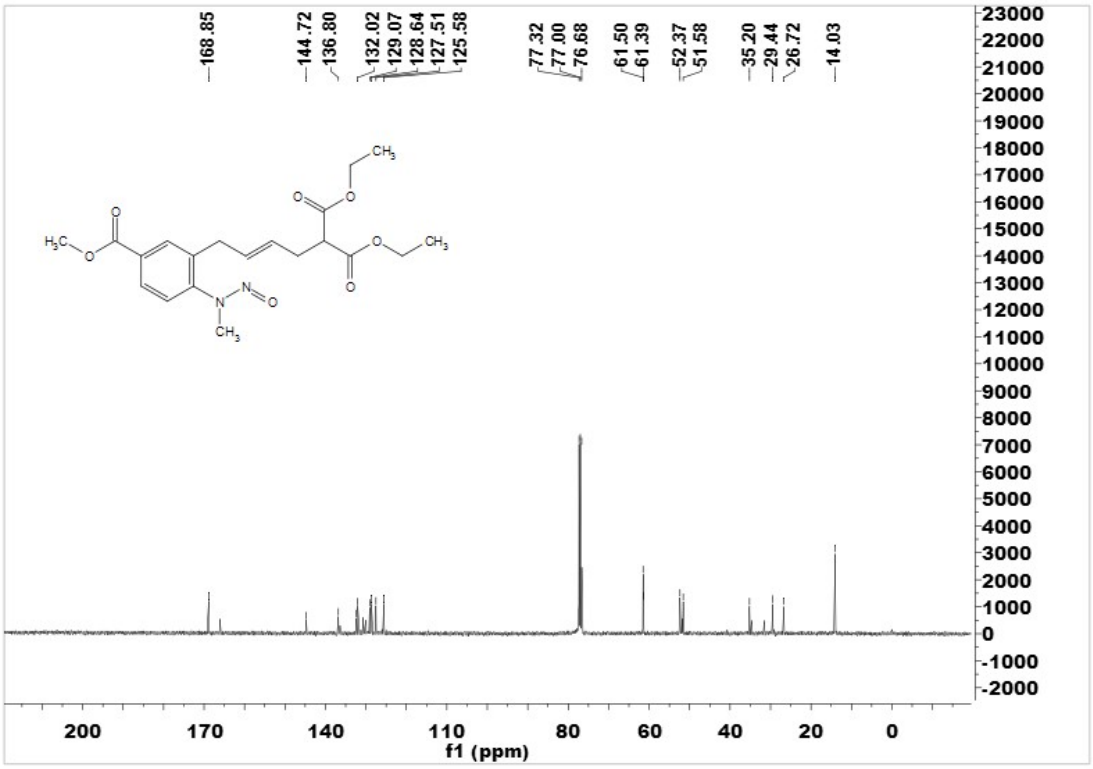
Diethyl (*E*)-2-(4-(2-(methyl(nitroso)amino)-5-nitrophenyl)but-2-en-1-yl)malonate (3h)



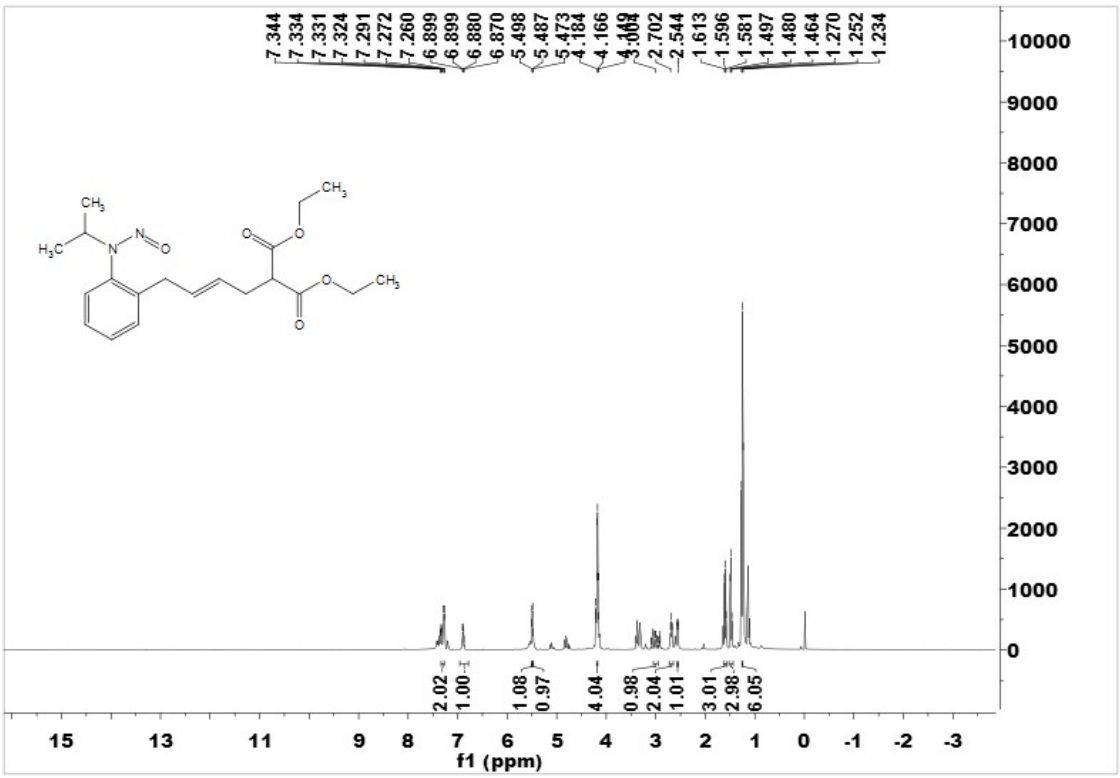


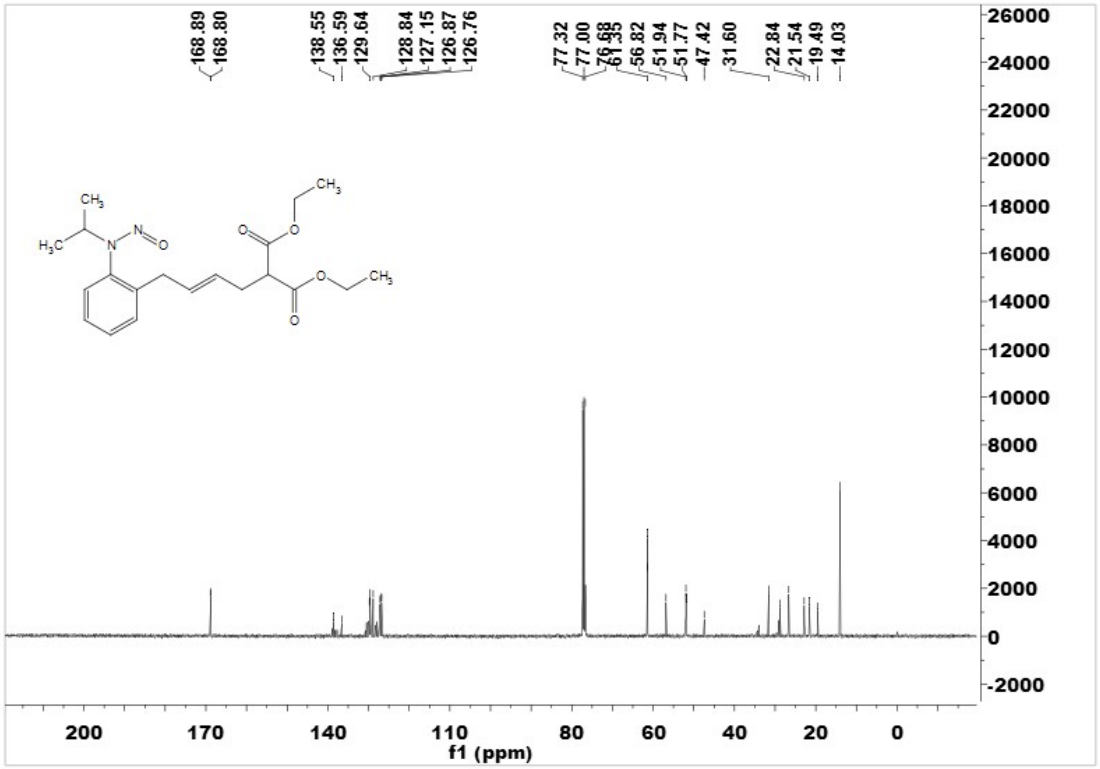
Diethyl (*E*)-2-(4-(5-(methoxycarbonyl)-2-(methyl(nitroso)amino)phenyl) but-2-en-1-yl)malonate (3i)



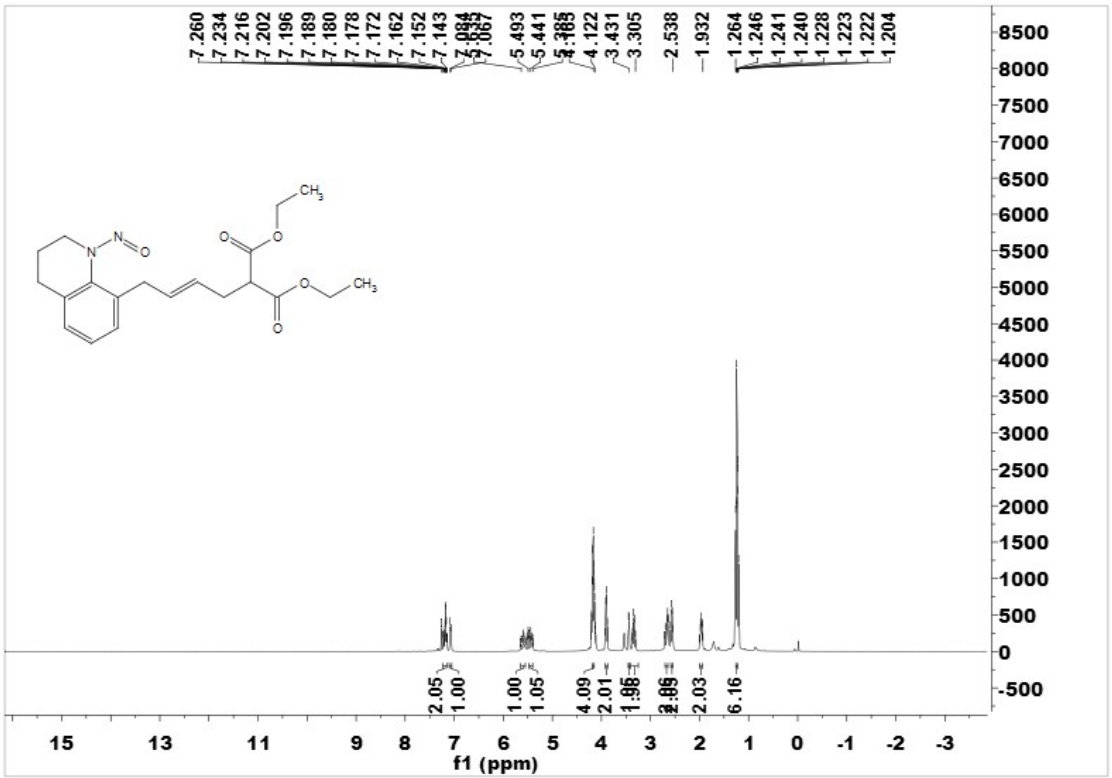


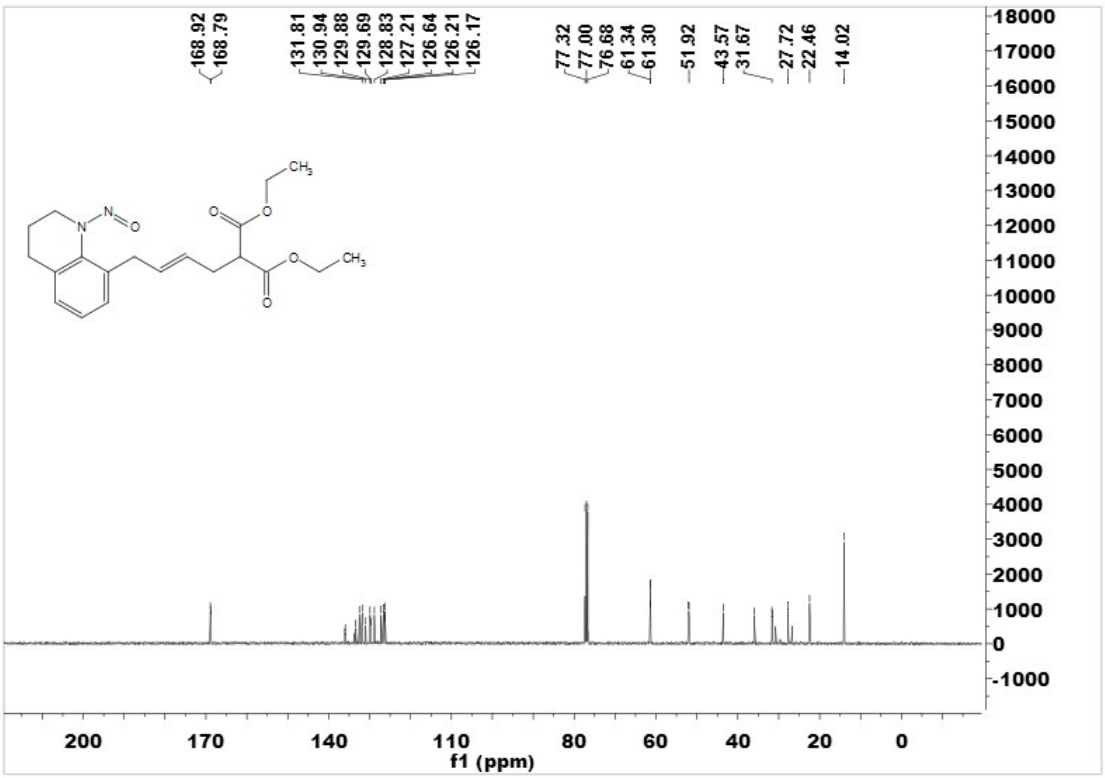
Diethyl (*E*)-2-(4-(2-(isopropyl(nitroso)amino)phenyl)but-2-en-1-yl)malonate (3j)



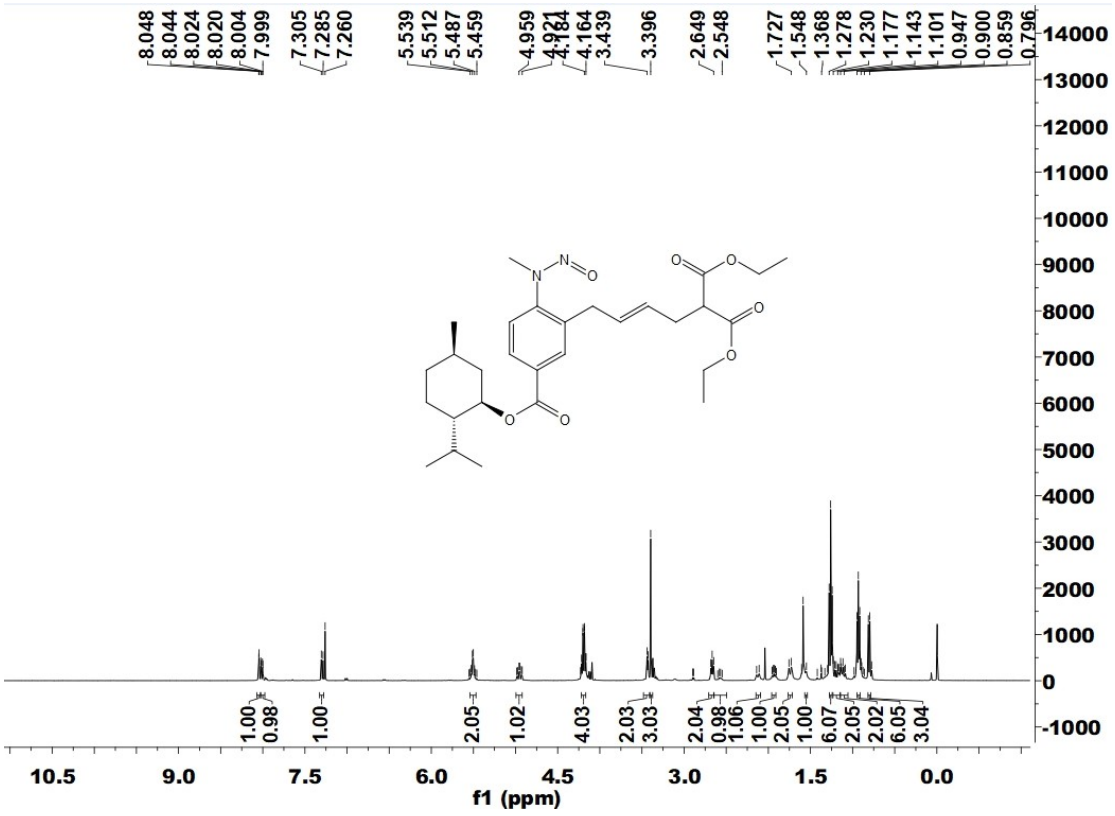


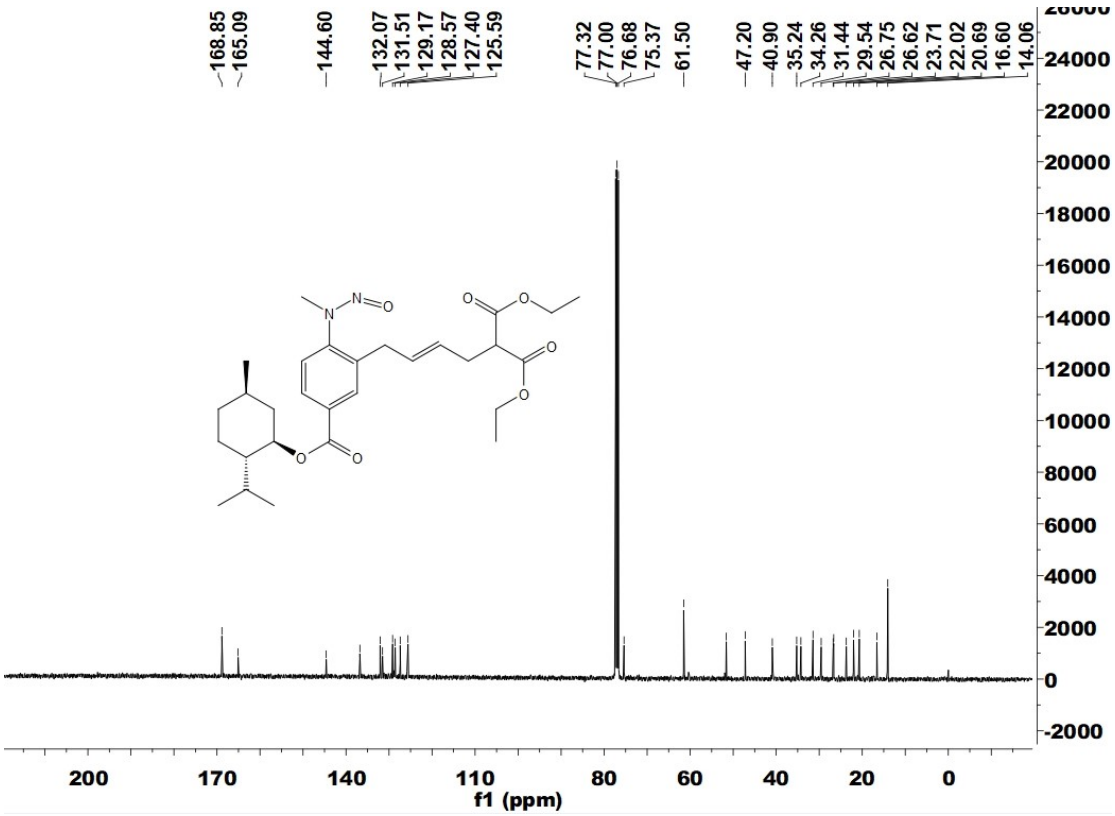
Diethyl (*E*)-2-(4-(1-nitroso-1,2,3,4-tetrahydroquinolin-8-yl)but-2-en-1-yl)malonate (3k)



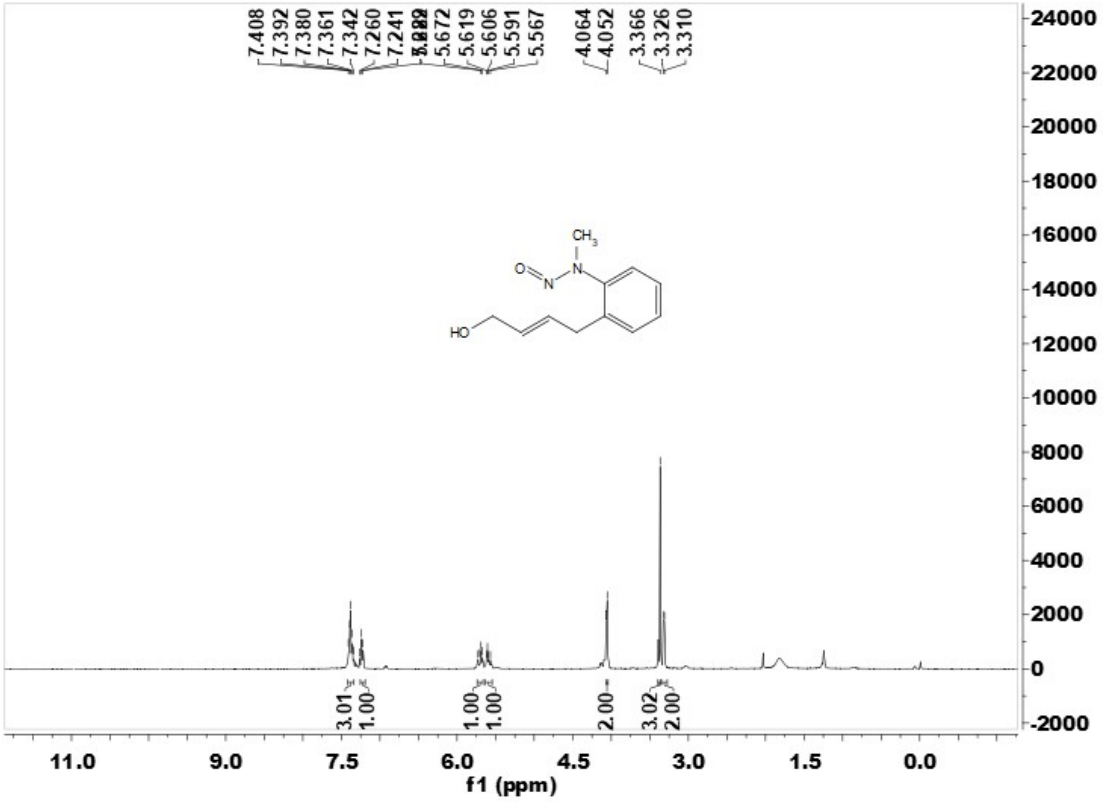


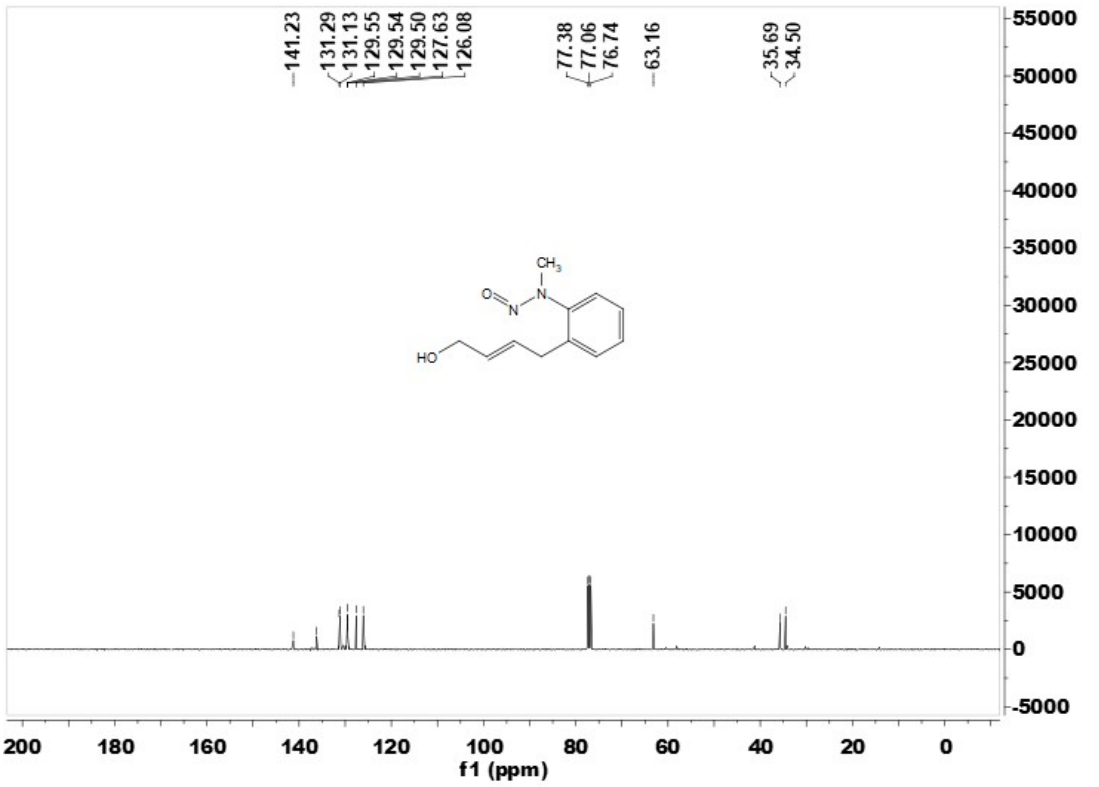
Diethyl 2-((*E*)-4-(5-((((1*R*, 2*S*, 5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)-2-(methyl(nitroso)amino)phenyl)but-2-en-1-yl)malonate (3l)



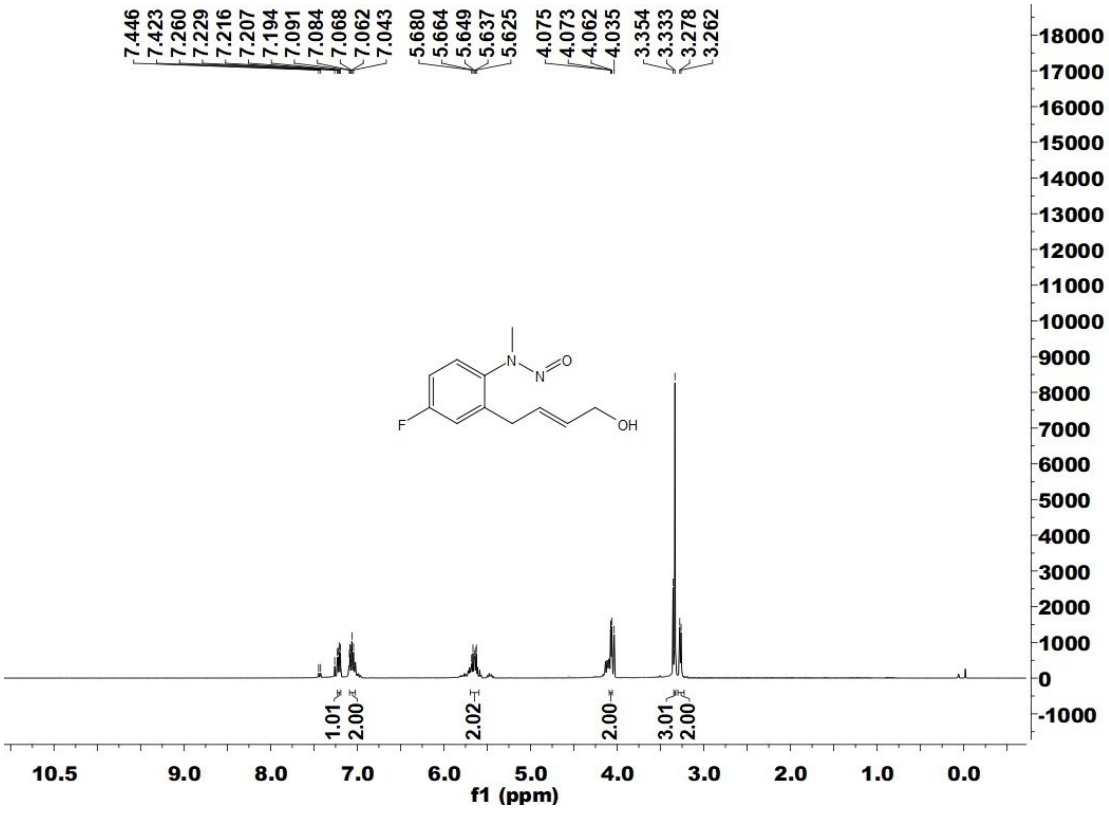


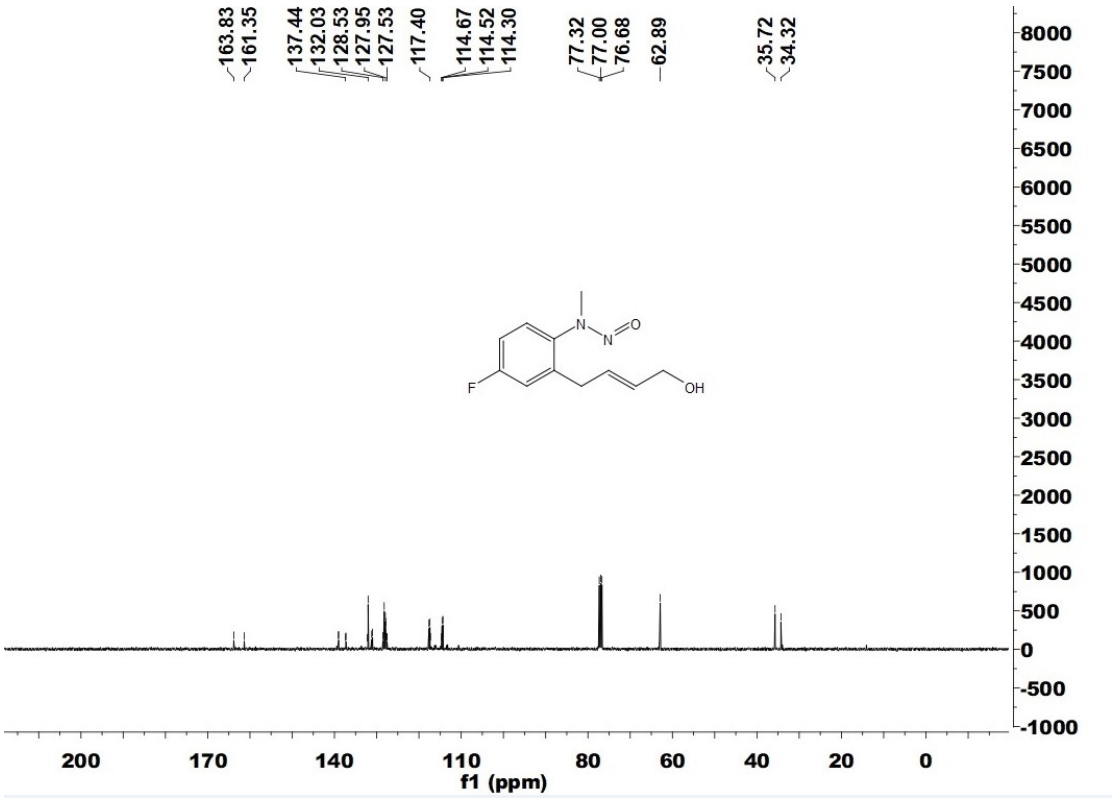
(*E*)-N-(2-(4-Hydroxybut-2-en-1-yl)phenyl)-N-methylnitrous amide (7a)

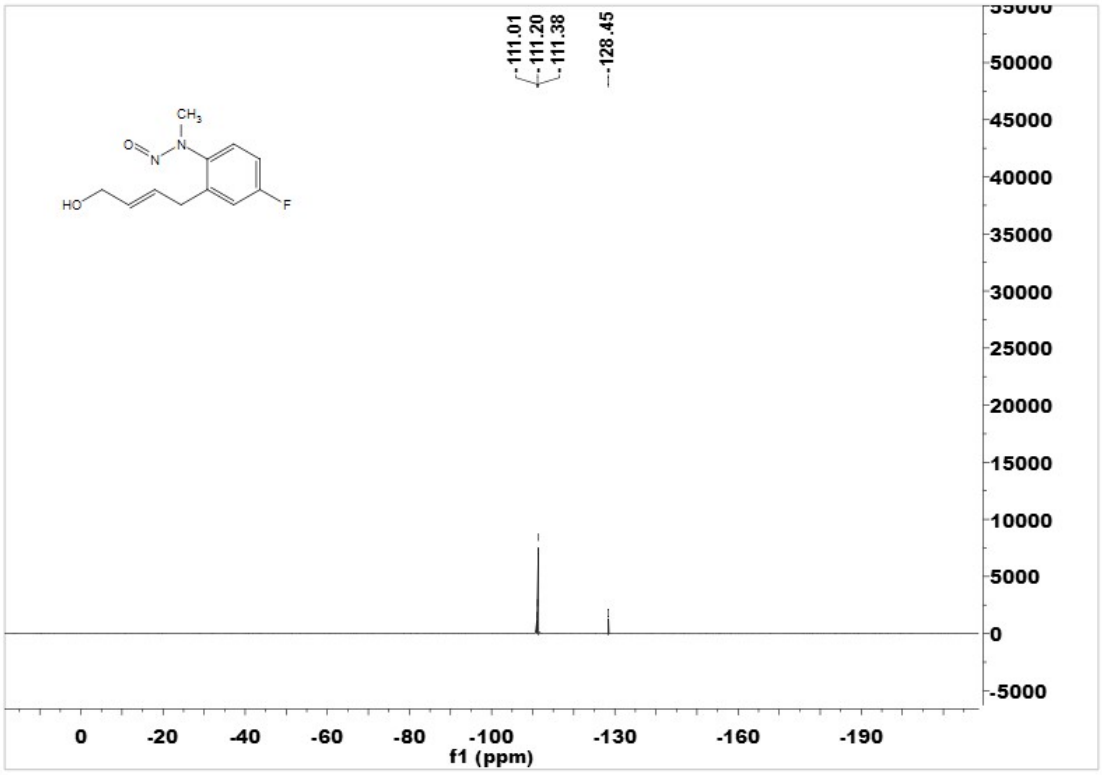




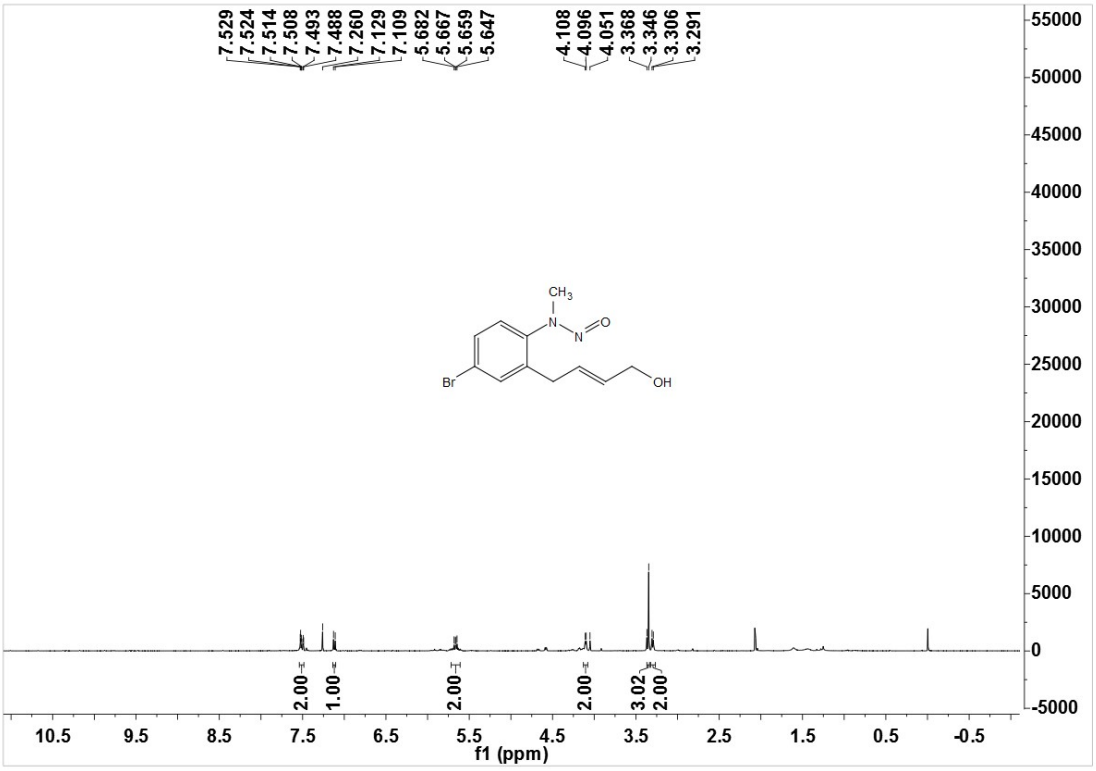
(*E*)-N-(4-Fluoro-2-(4-hydroxybut-2-en-1-yl)phenyl)-N-methylnitrous amide (7b)

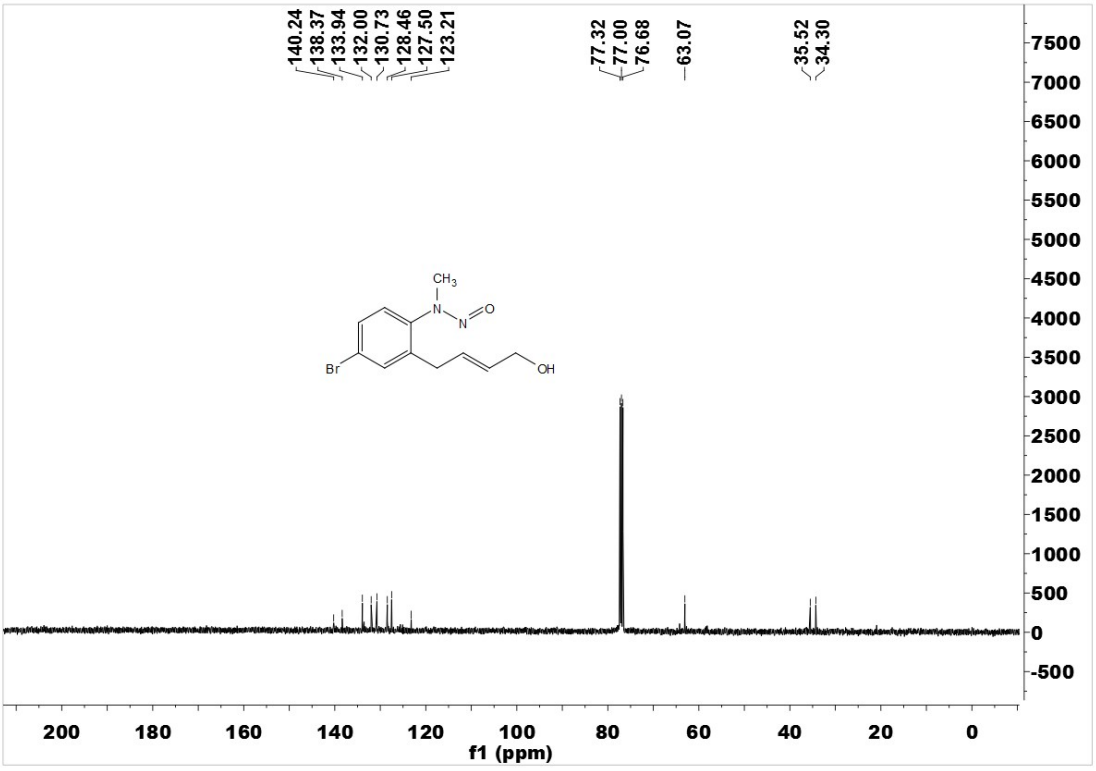



163.83
161.35
137.44
132.03
128.53
127.95
127.53
117.40
114.67
114.52
114.30
77.32
77.00
76.68
62.89
35.72
34.32
F
OH
f1 (ppm)

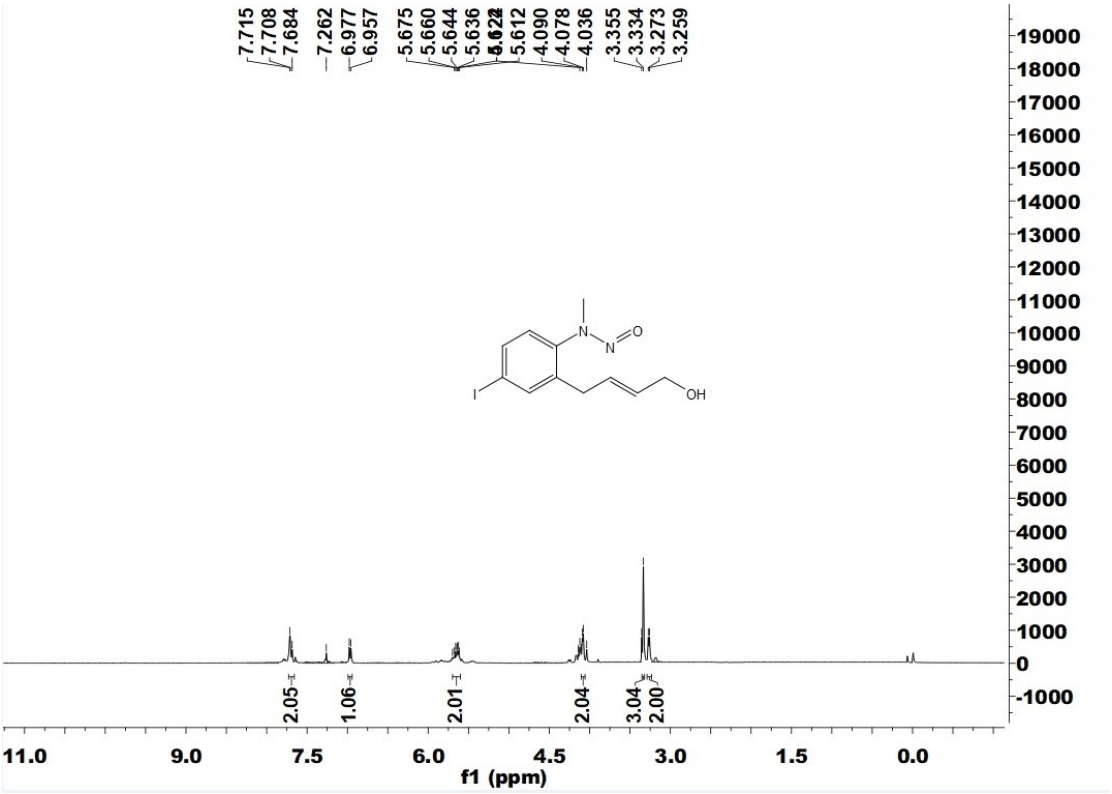

111.01
111.20
111.38
128.45
CH3
HO
F
f1 (ppm)

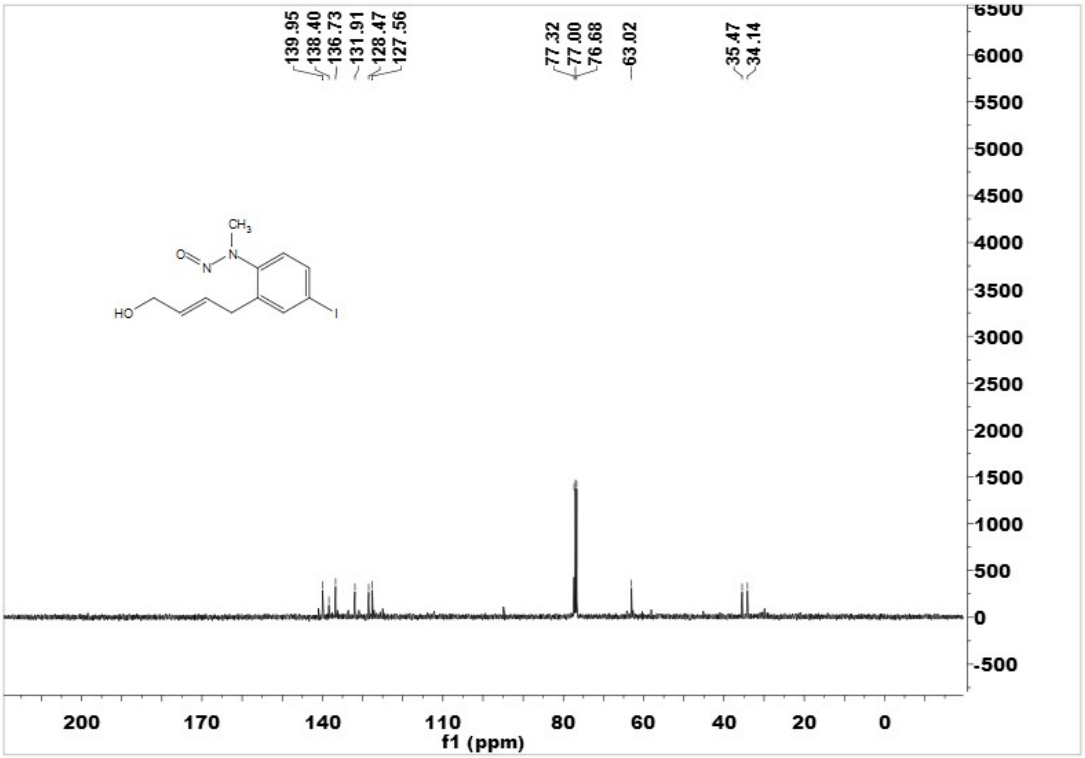
(*E*)-N-(4-Bromo-2-(4-hydroxybut-2-en-1-yl)phenyl)-N-methylnitrous amide (7c)



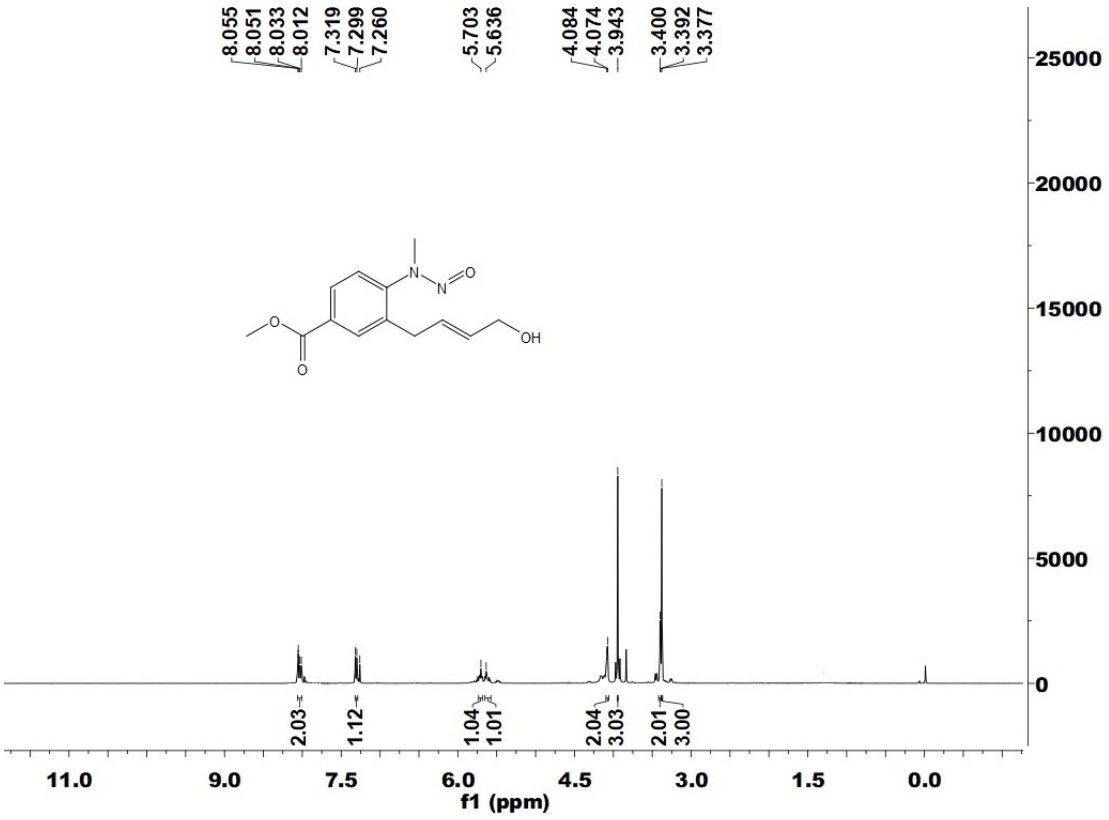


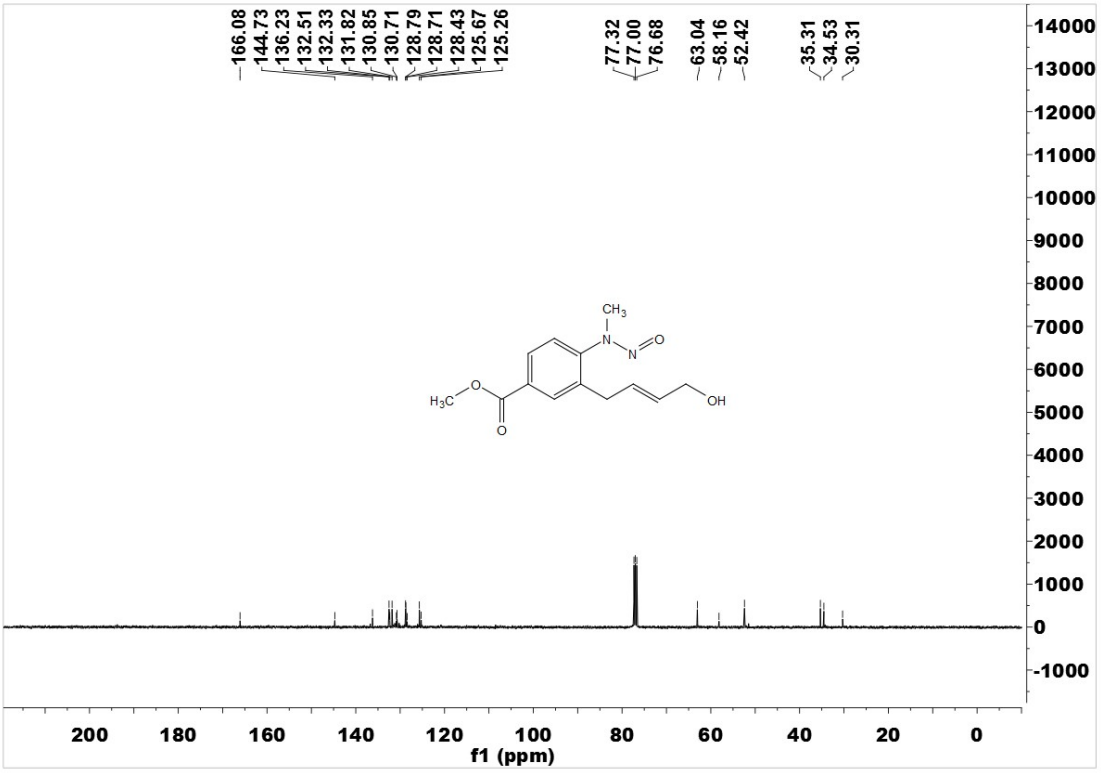
(*E*)-N-(2-(4-Hydroxybut-2-en-1-yl)-4-iodophenyl)-N-methylnitrous amide (7d)



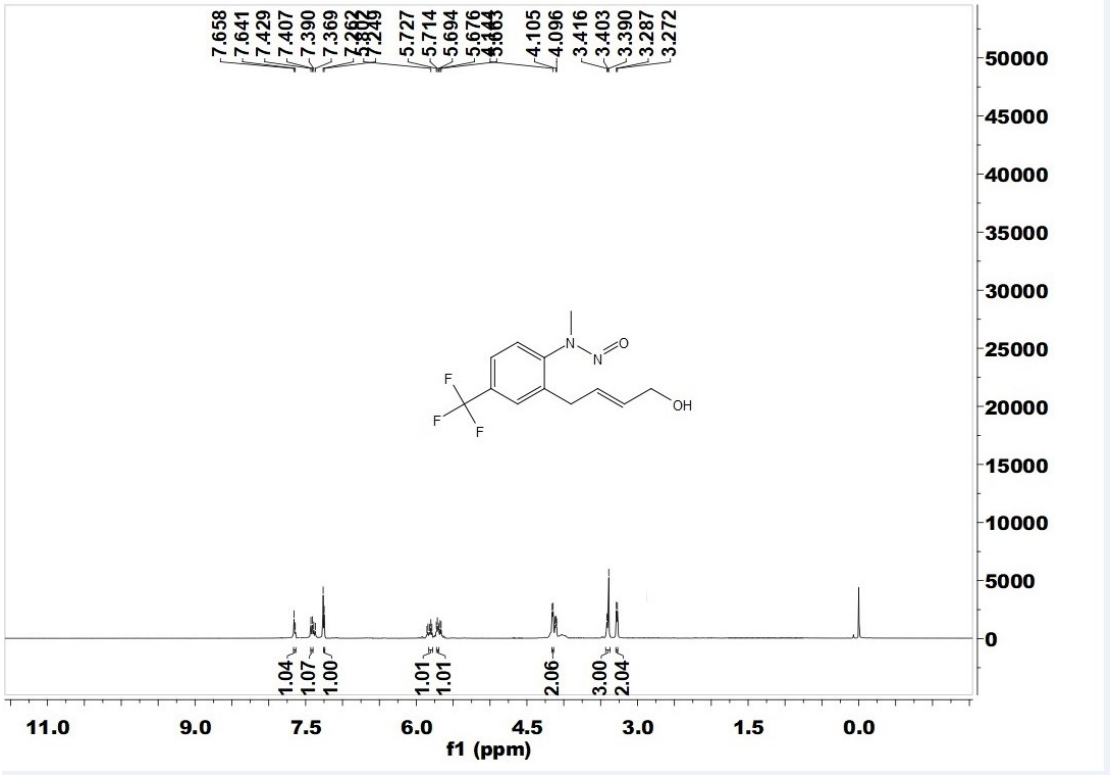


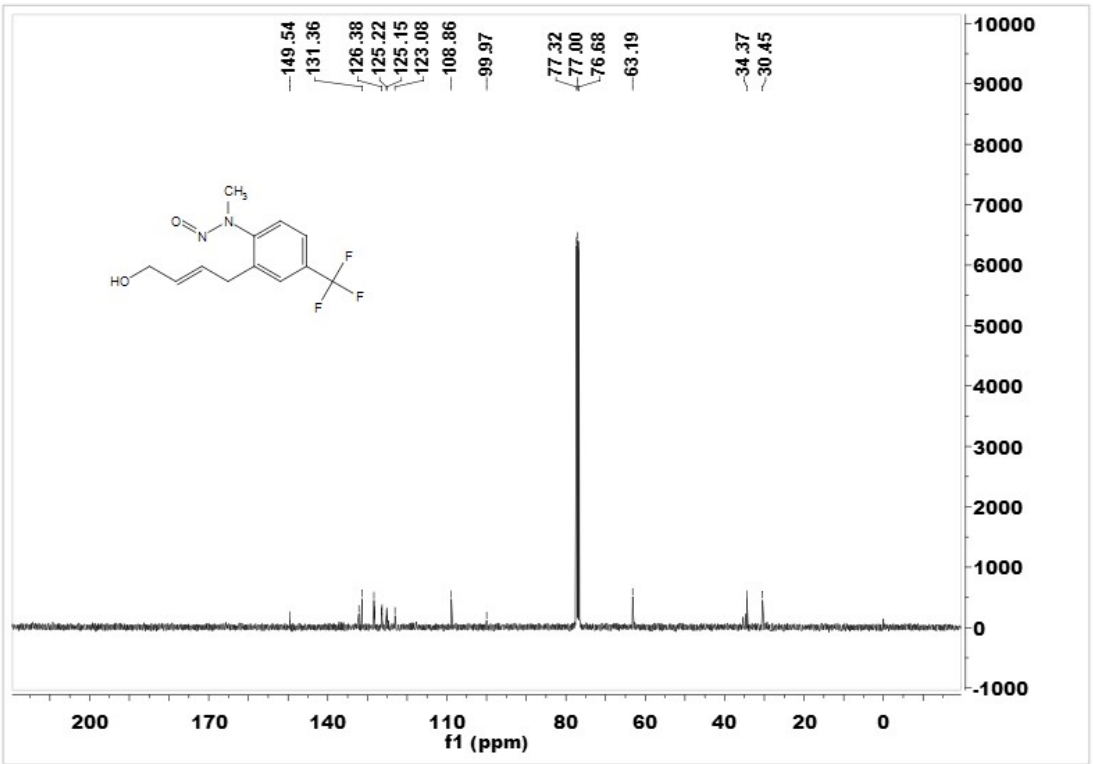
Methyl (*E*)-3-(4-hydroxybut-2-en-1-yl)-4-(methyl(nitroso)amino)benzoate (7e)

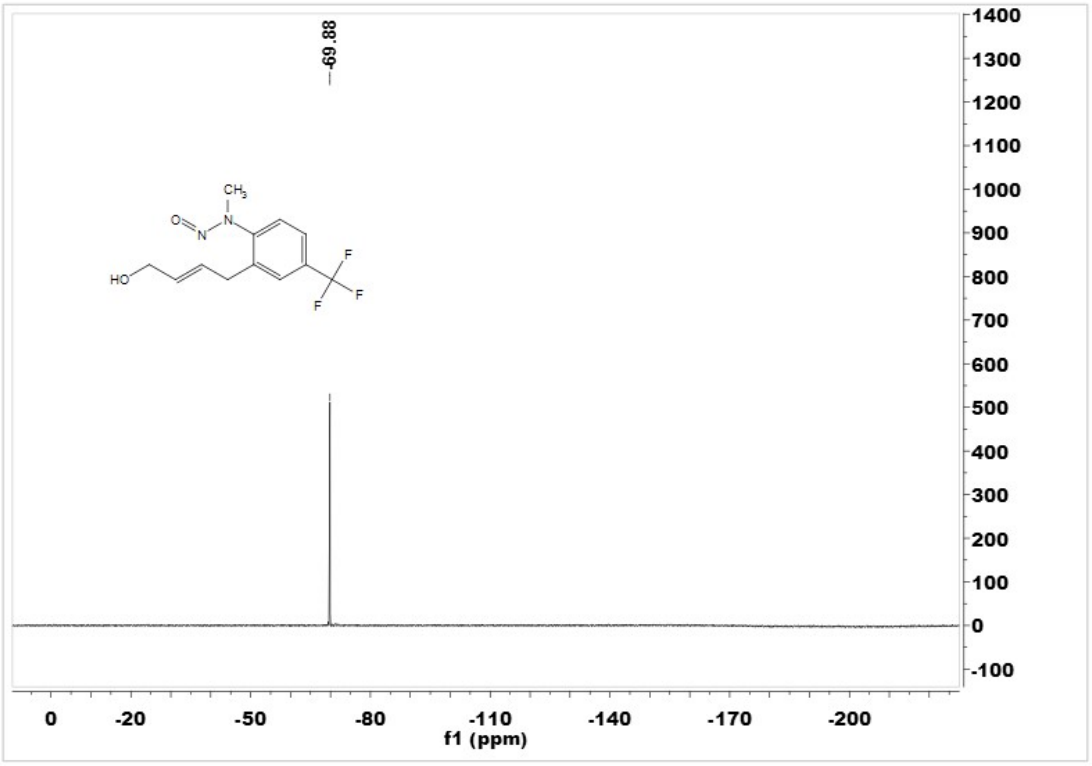




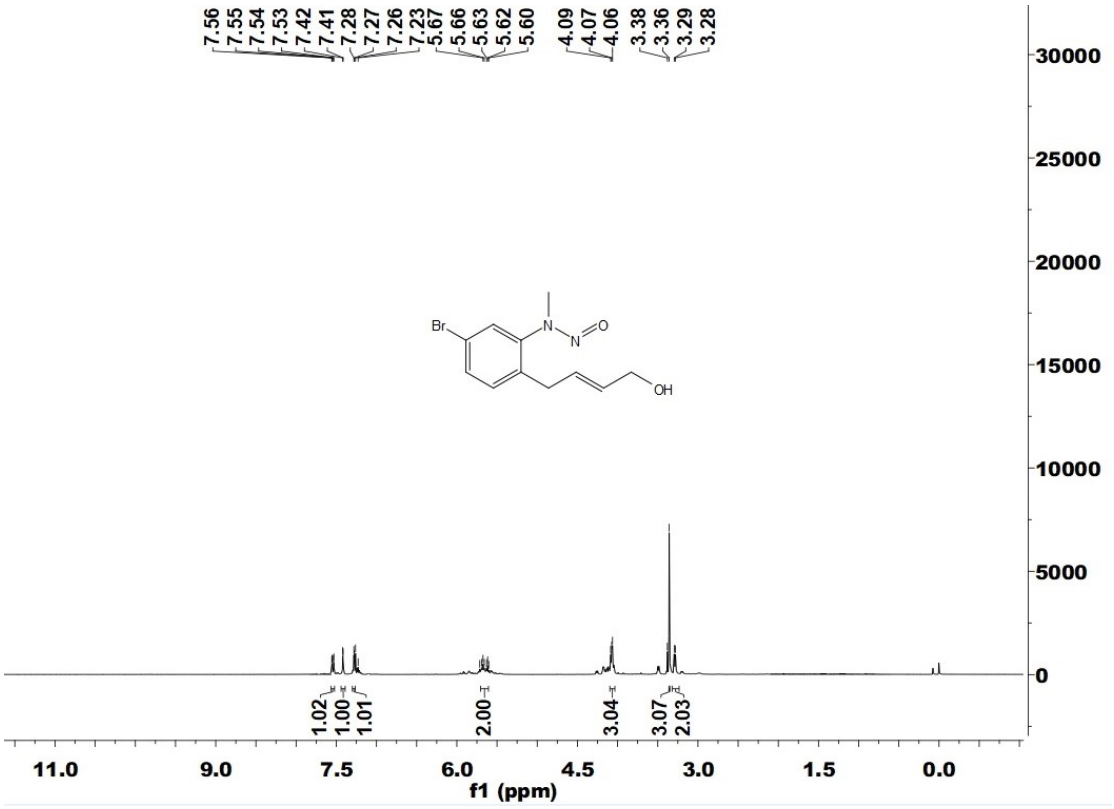
(*E*)-N-(2-(4-Hydroxybut-2-en-1-yl)phenyl)-N-methylnitrous amide (7f)

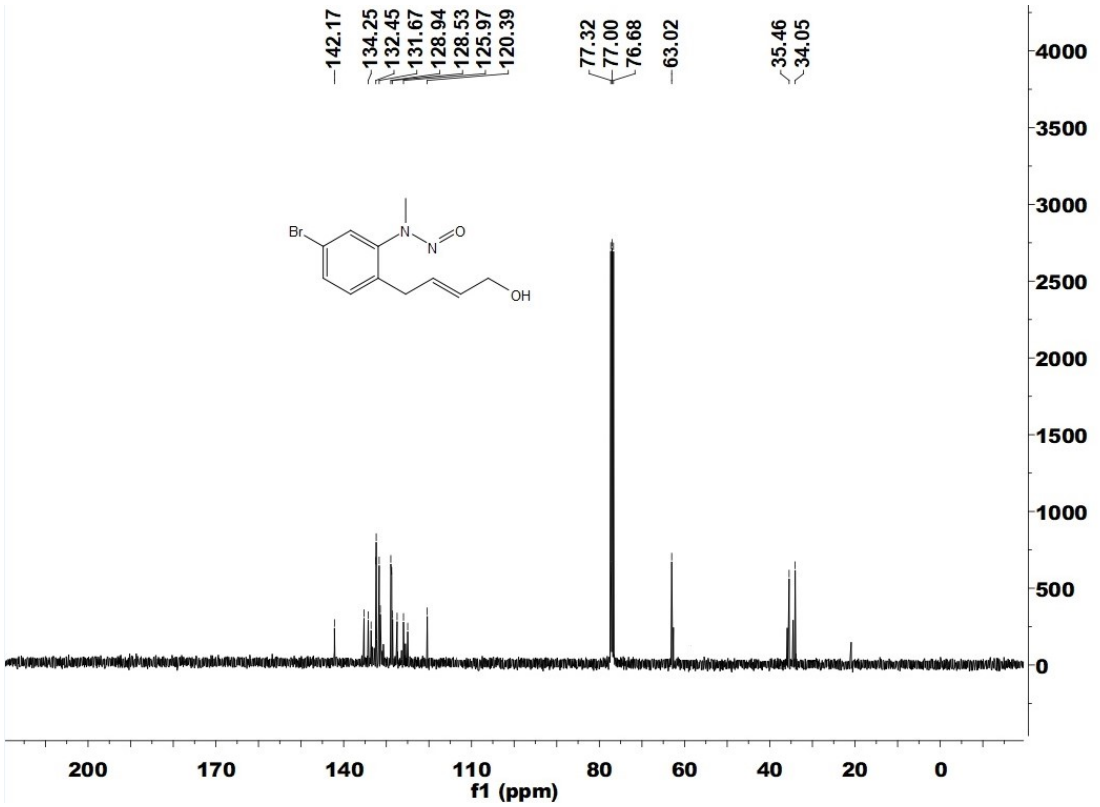




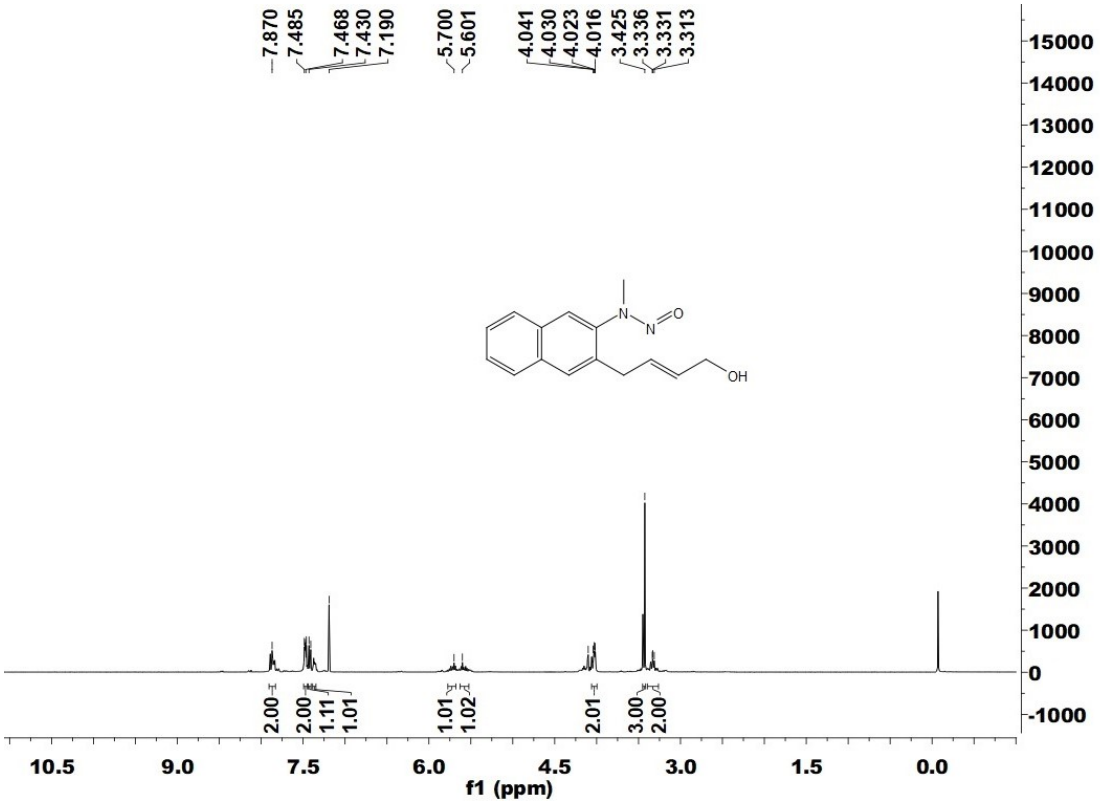


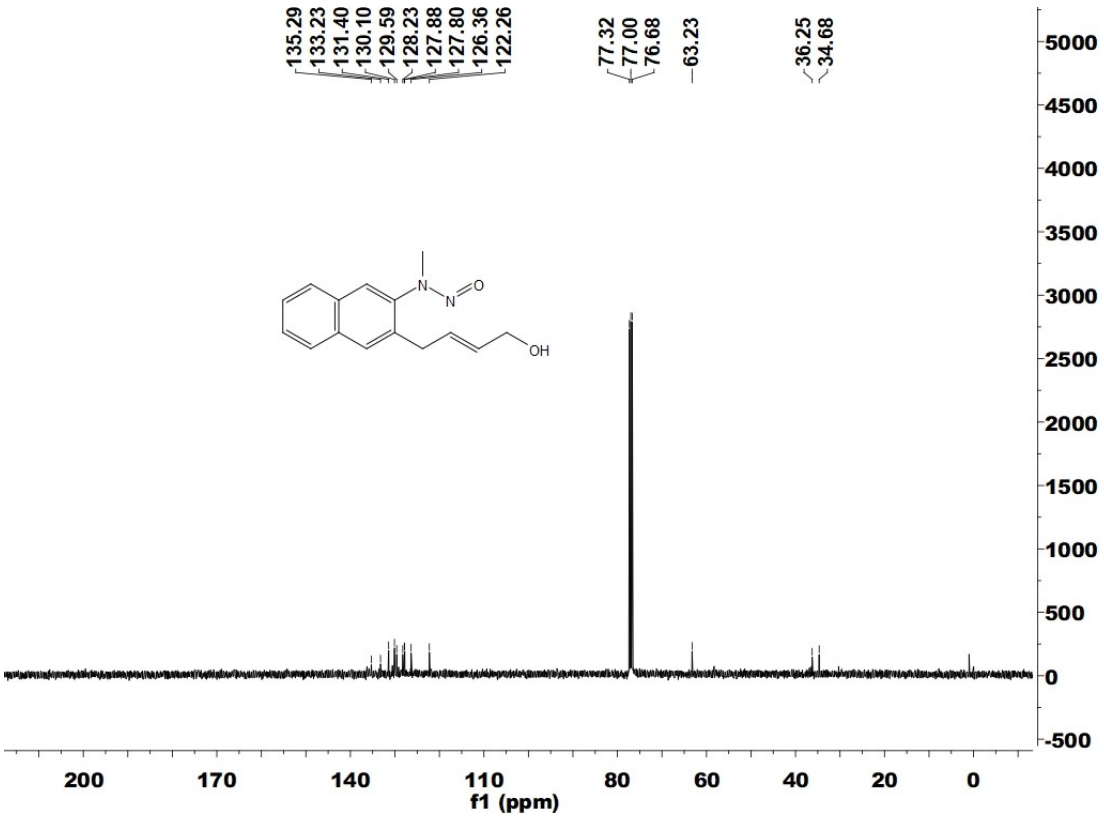
(*E*)-N-(5-Bromo-2-(4-hydroxybut-2-en-1-yl)phenyl)-N-methylnitrous amide (7g)



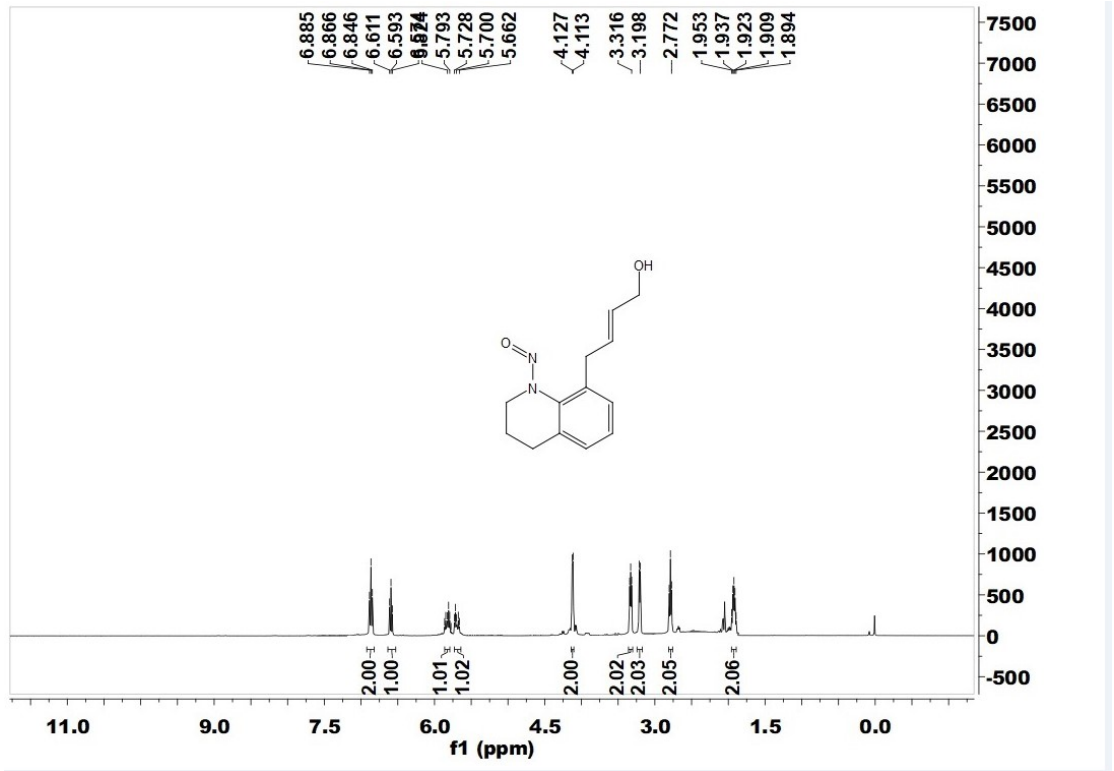


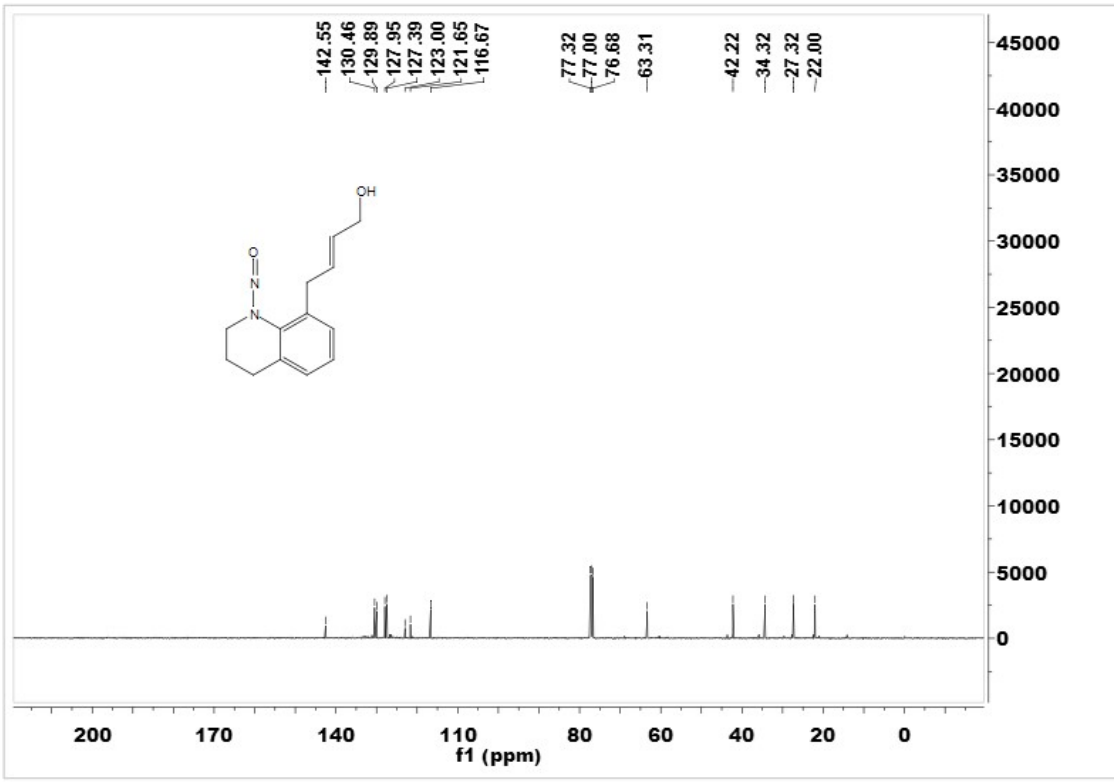
(*E*)-N-(3-(4-Hydroxybut-2-en-1-yl)naphthalen-2-yl)-N-methylnitrous amide (7h)



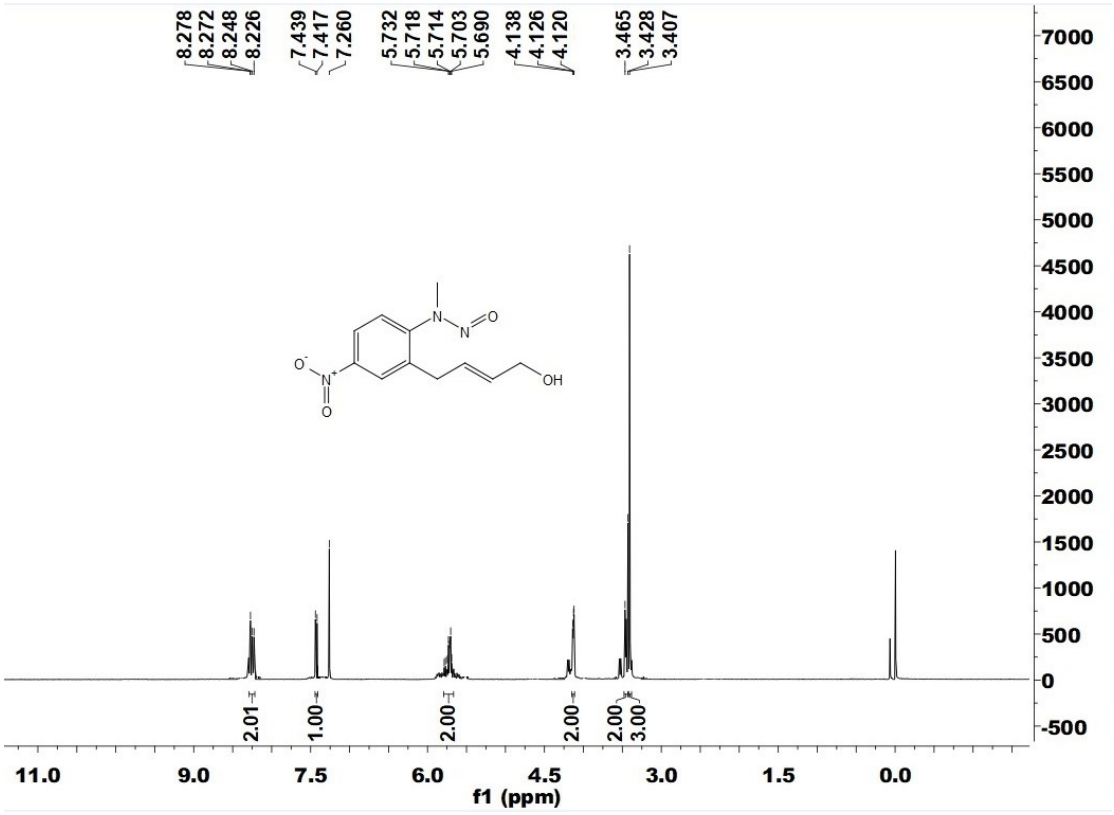


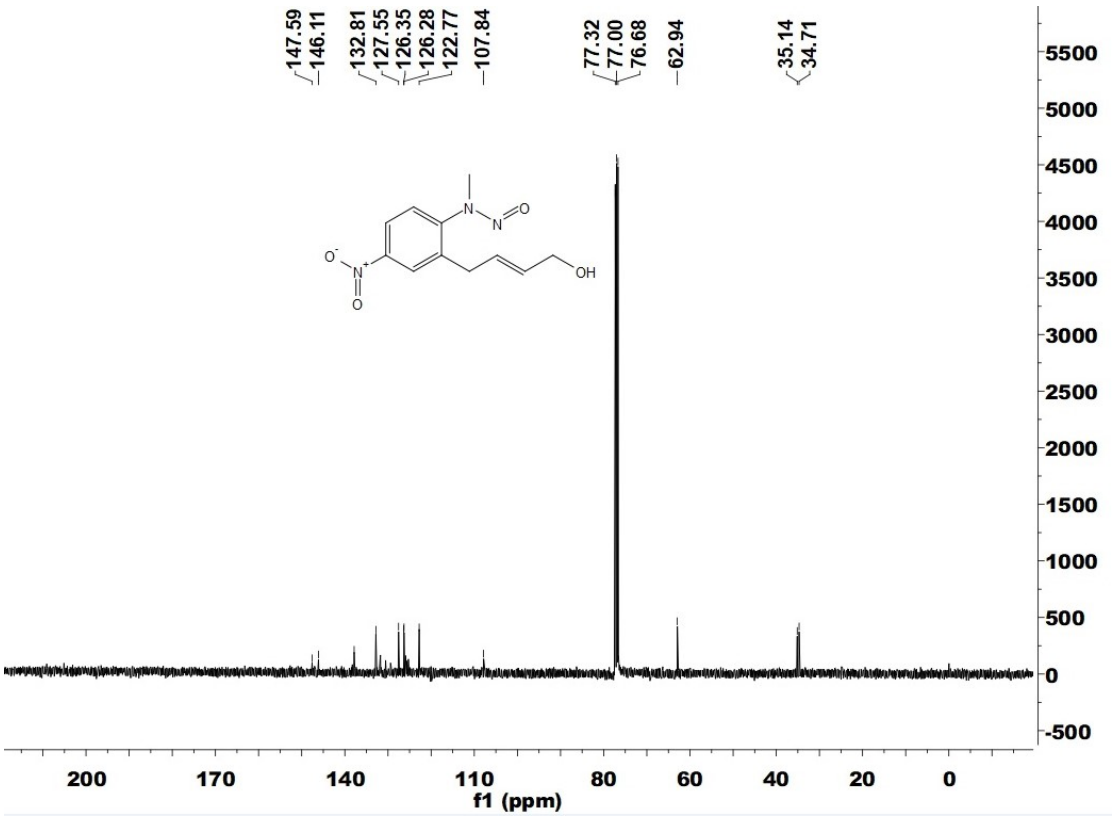
(*E*)-4-(1-Nitroso-1,2,3,4-tetrahydroquinolin-8-yl)but-2-en-1-ol (7i)



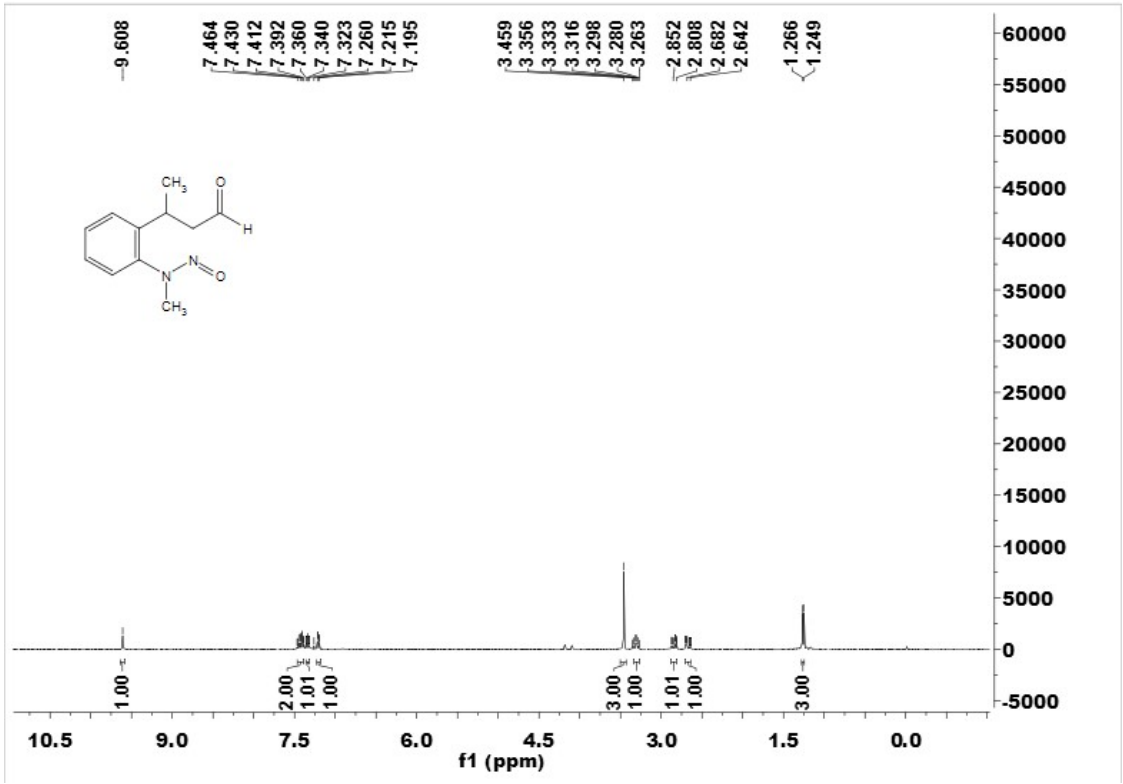


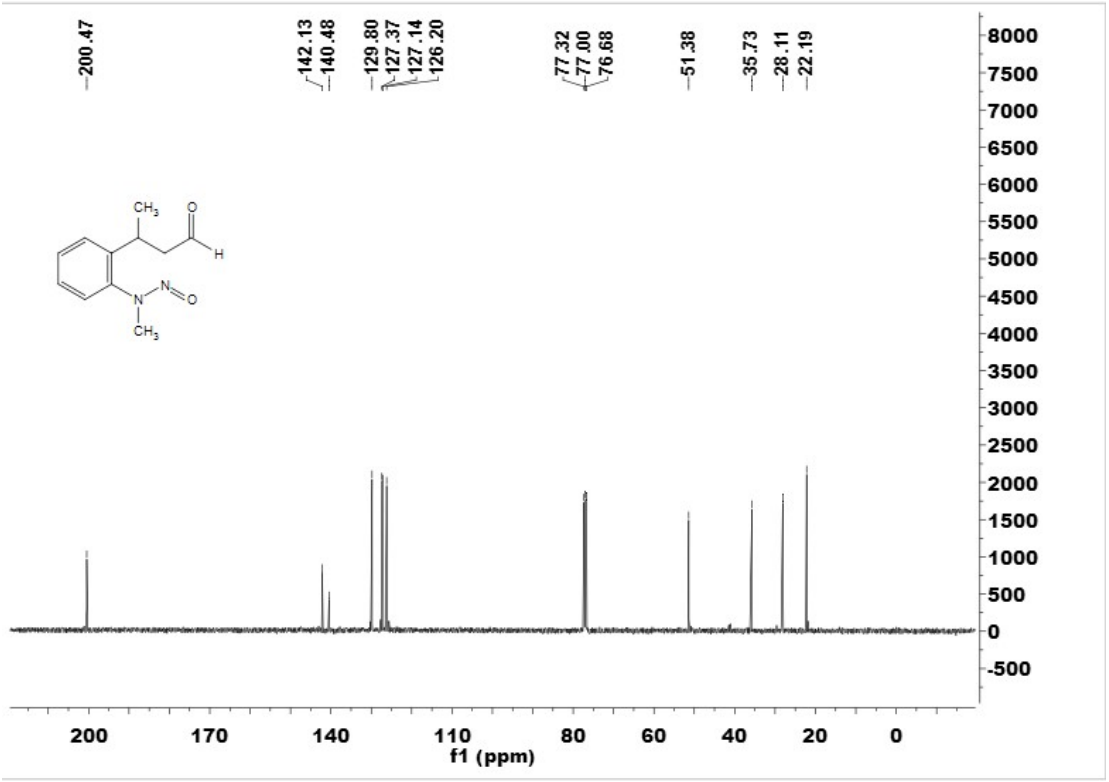
(*E*)-*N*-(2-(4-Hydroxybut-2-en-1-yl)-4-nitrophenyl)-N-methylnitrous amide (7j)



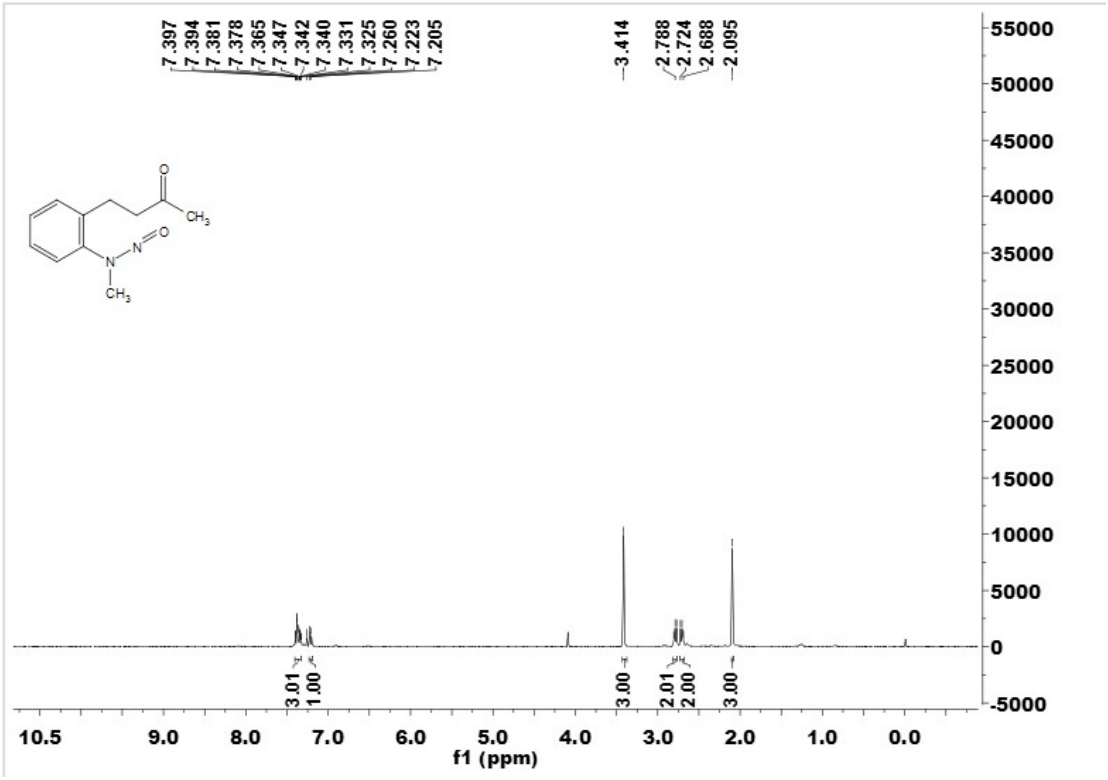


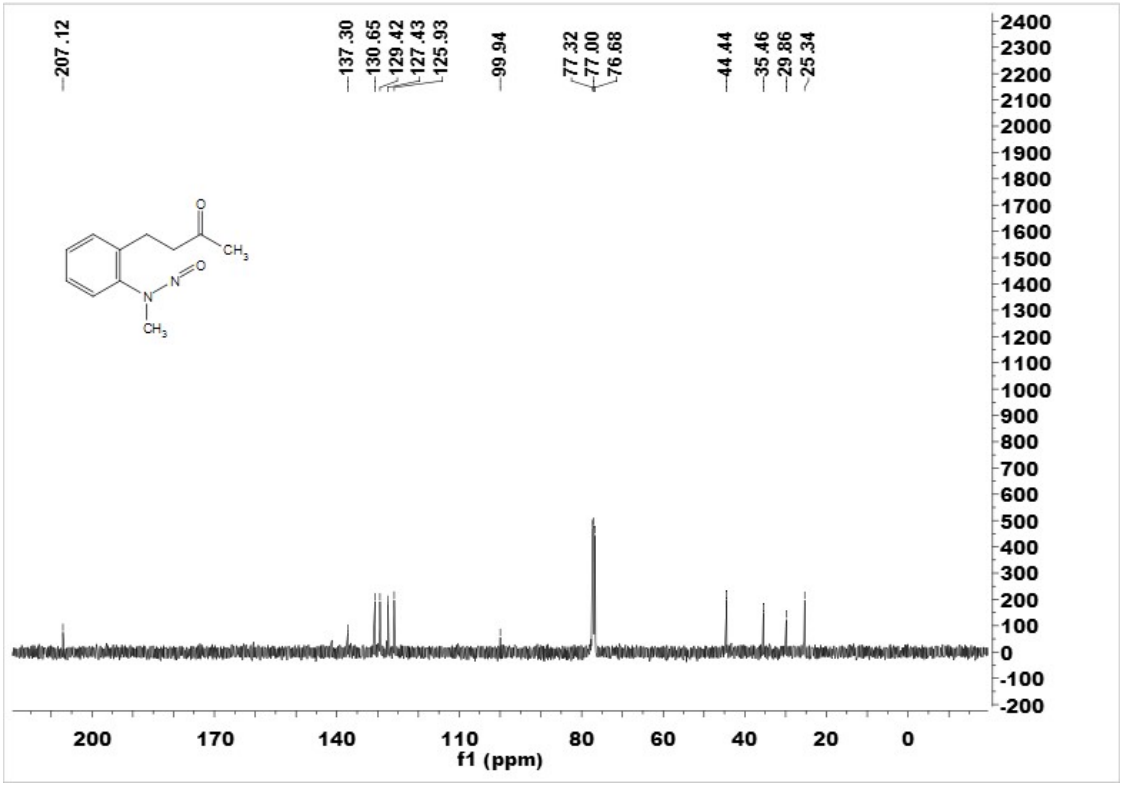
5,6-Dihydro-[1,1'-biphenyl]-3(4*H*)-one (9a)



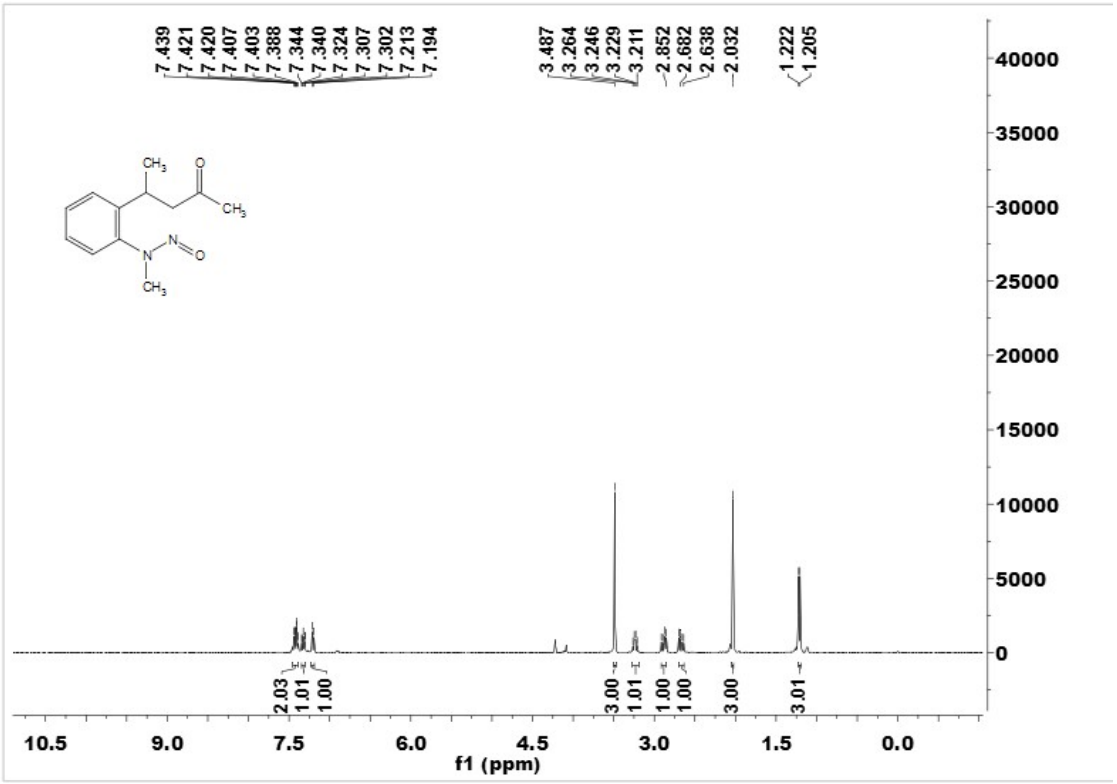


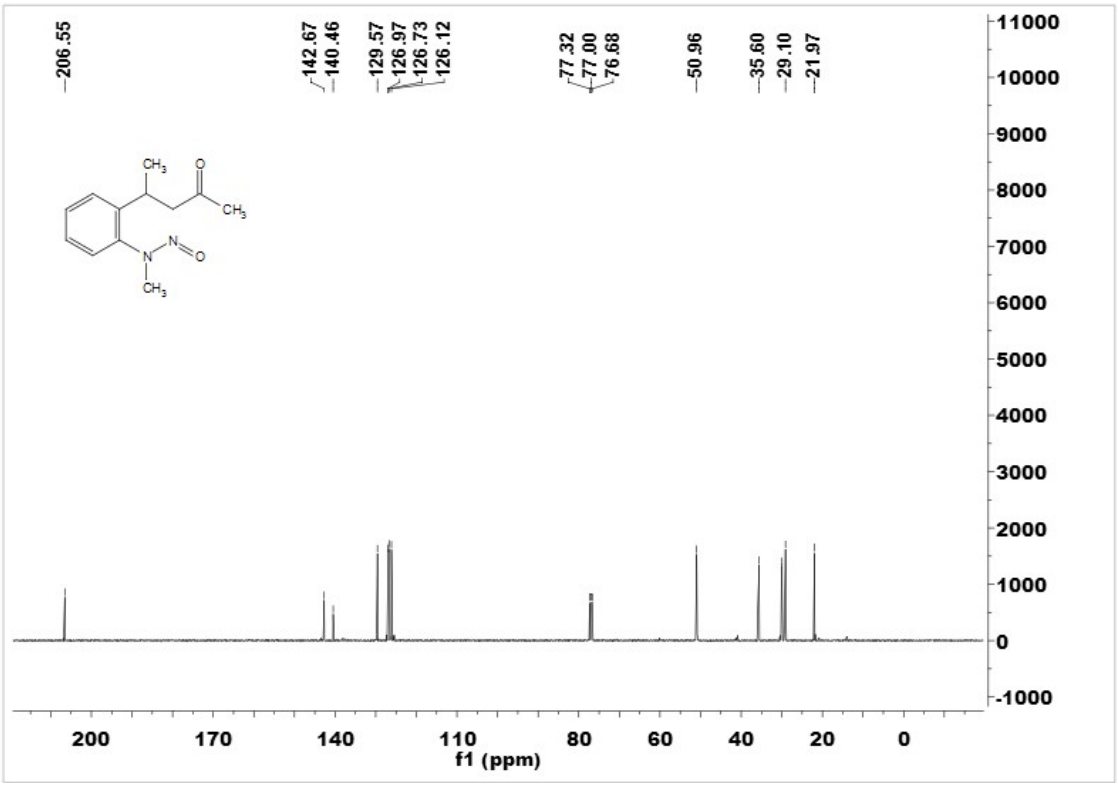
4-(2-(Methylamino)phenyl)butan-2-one (9b)



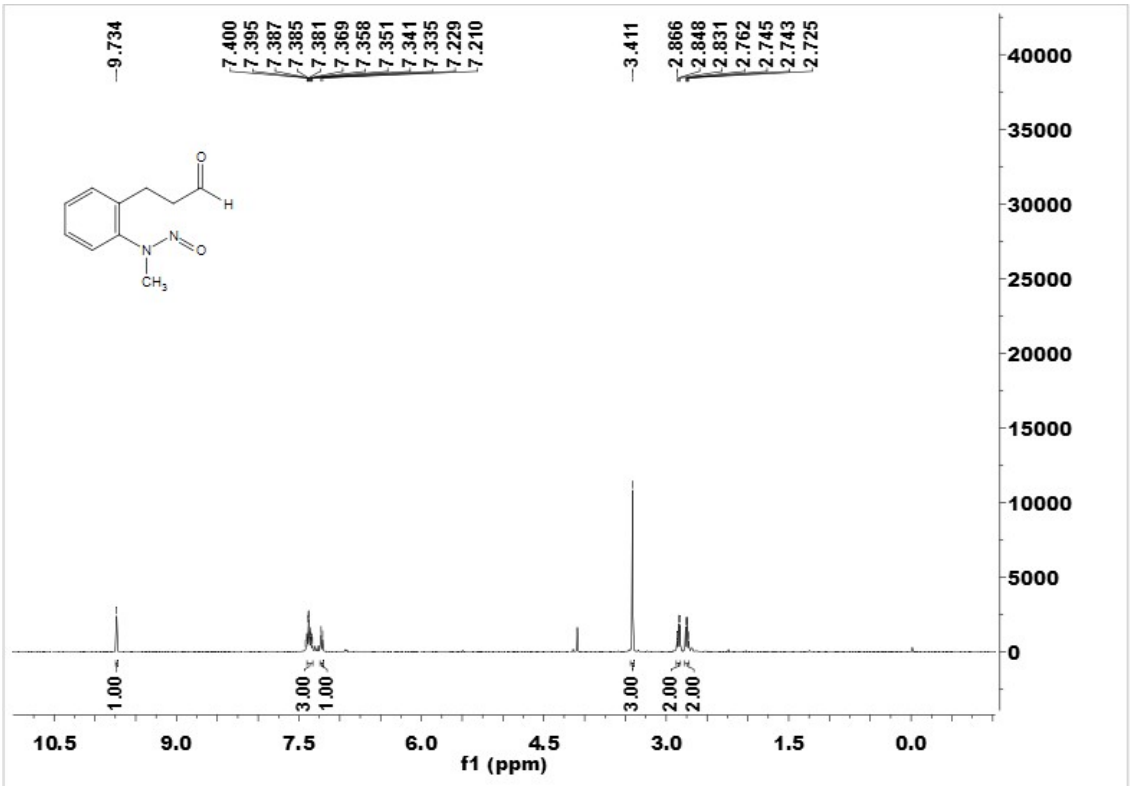


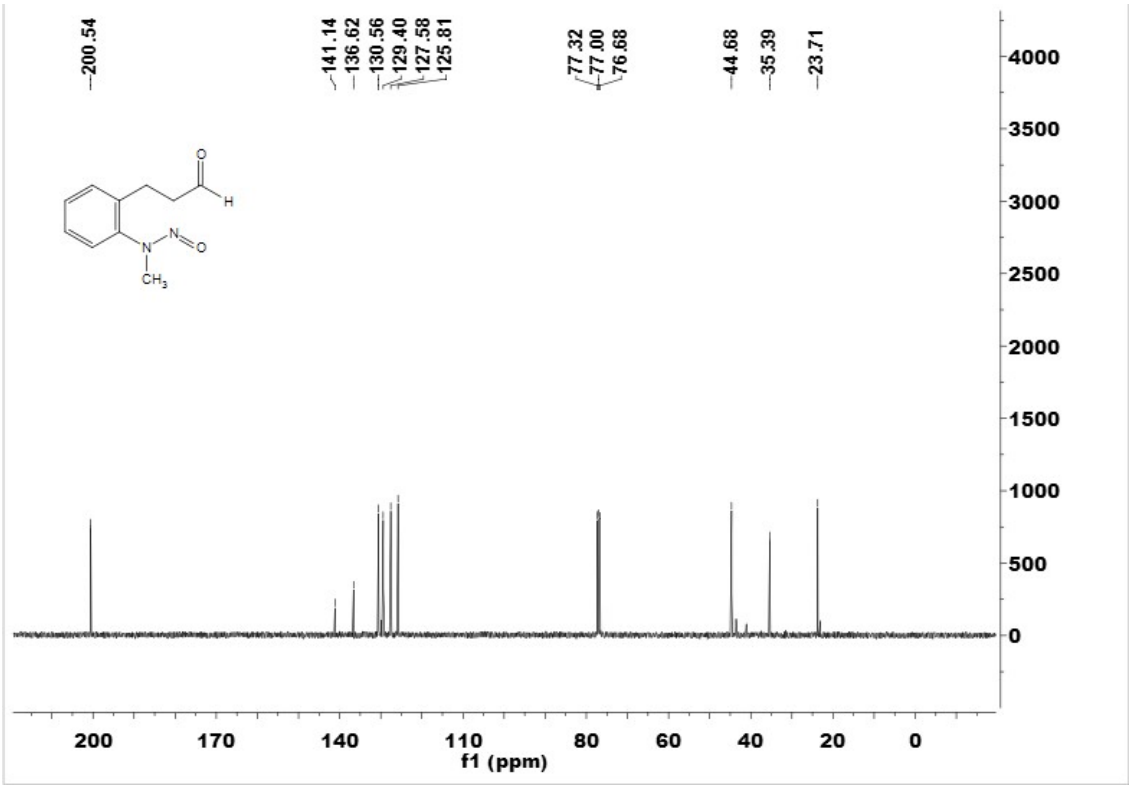
4-(2-(Methylamino)phenyl)pentan-2-one (9c)



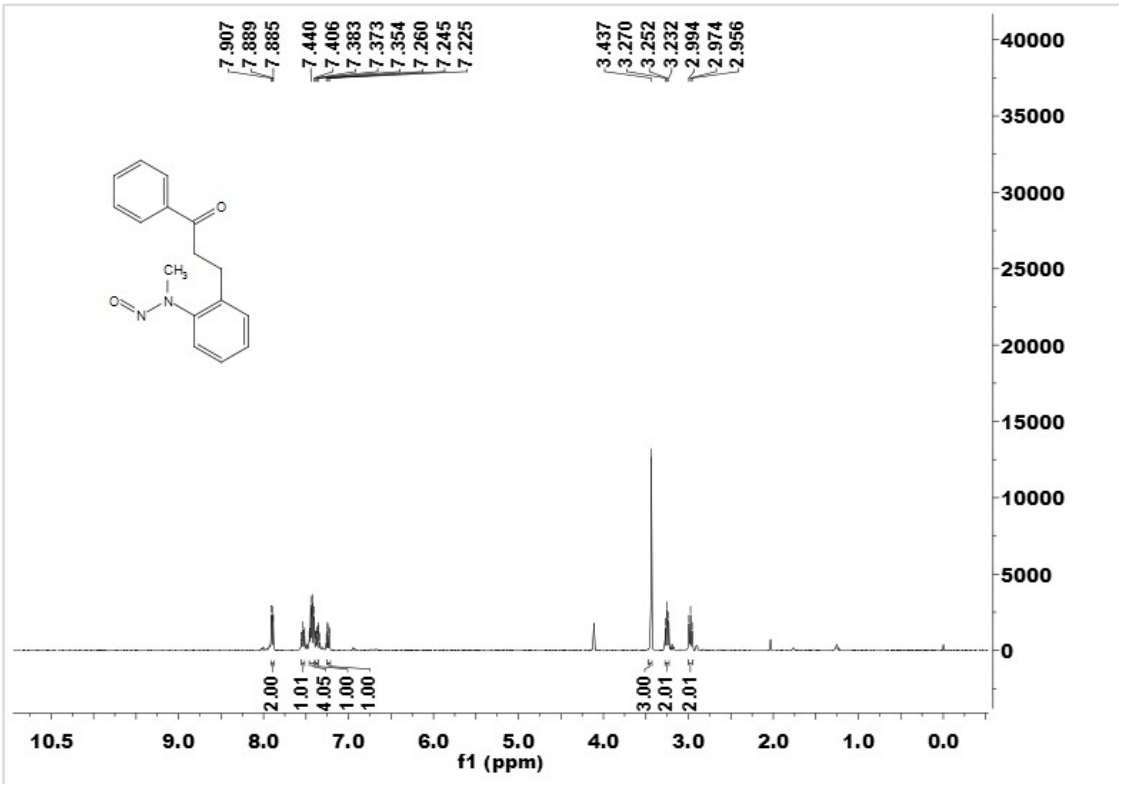


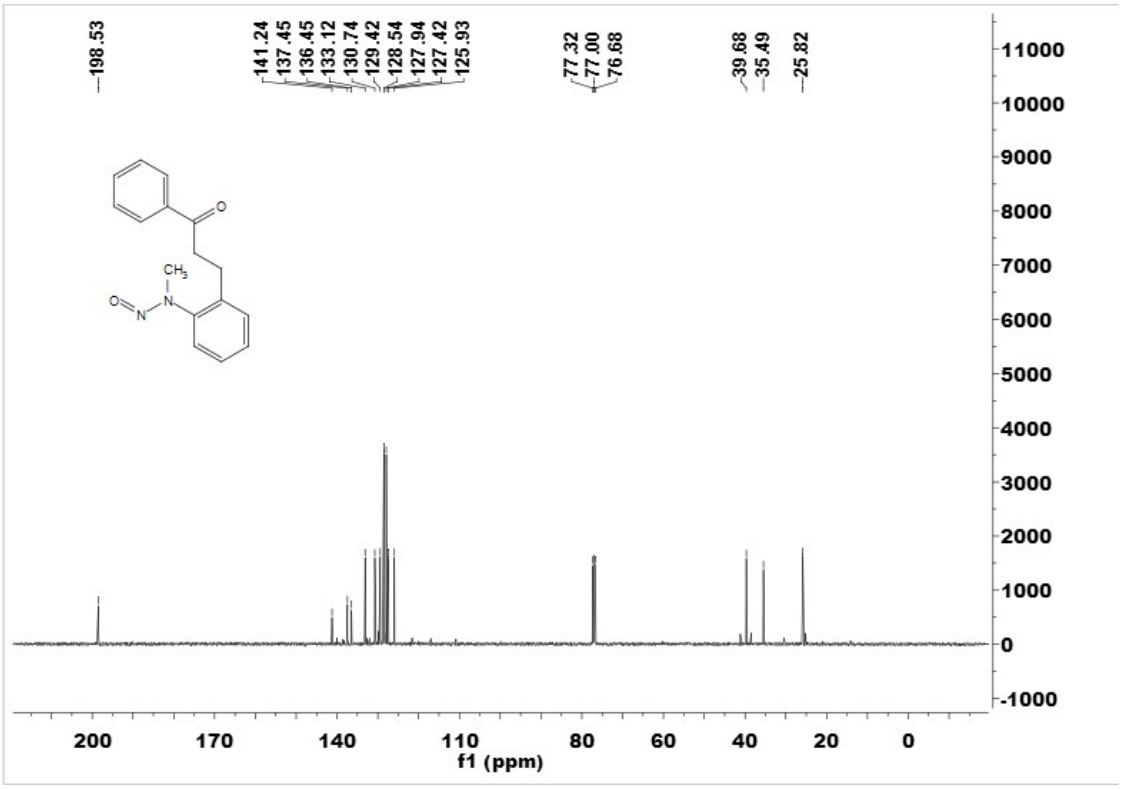
3-(2-(Methylamino)phenyl)propanal (9d),



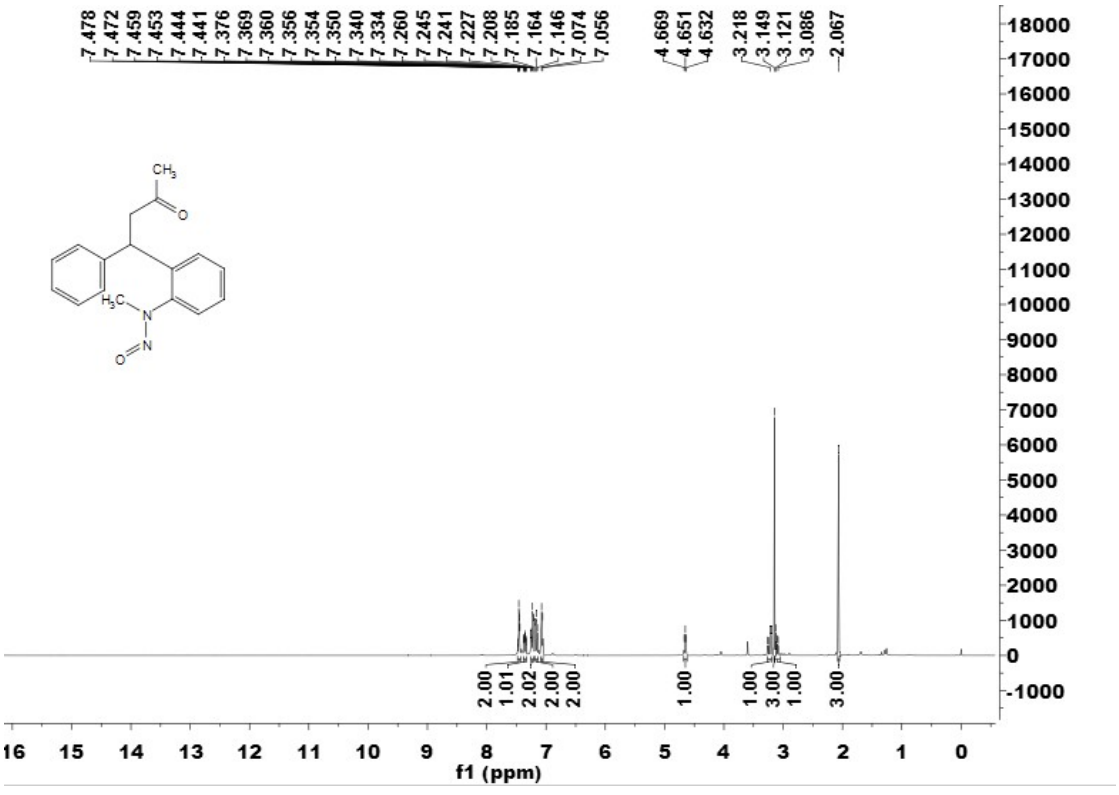


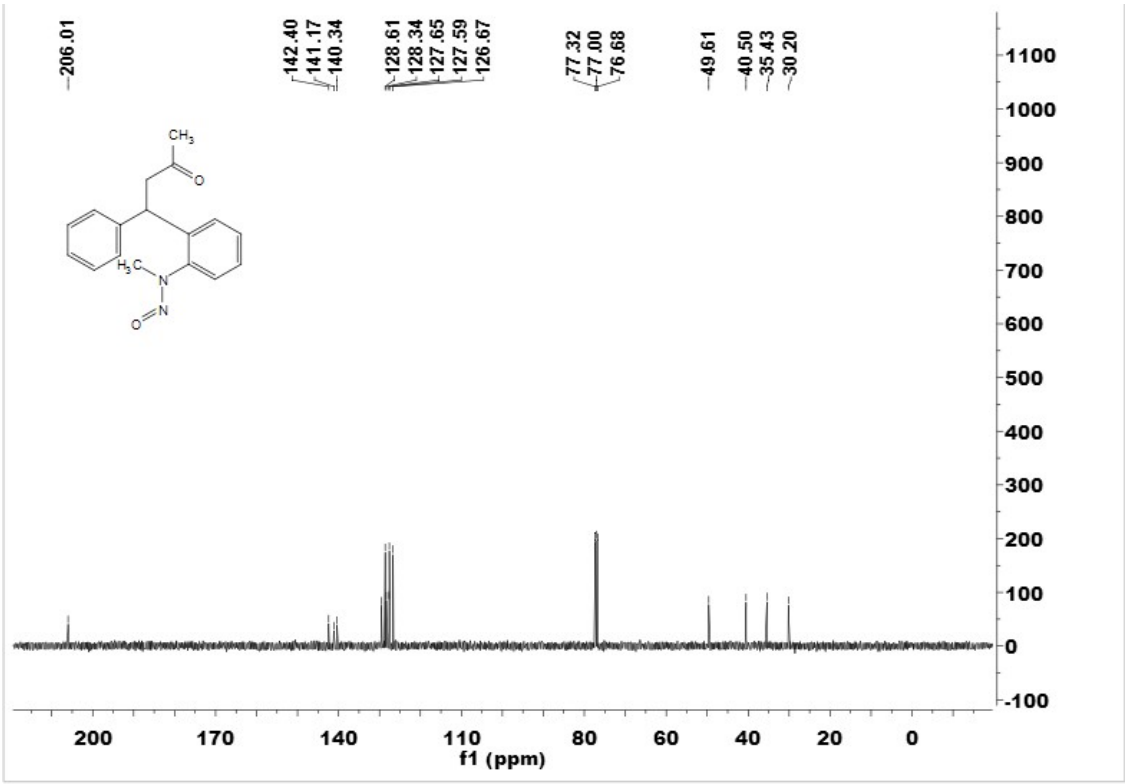
3-(2-(Methylamino)phenyl)-1-phenylpropan-1-one(9e)



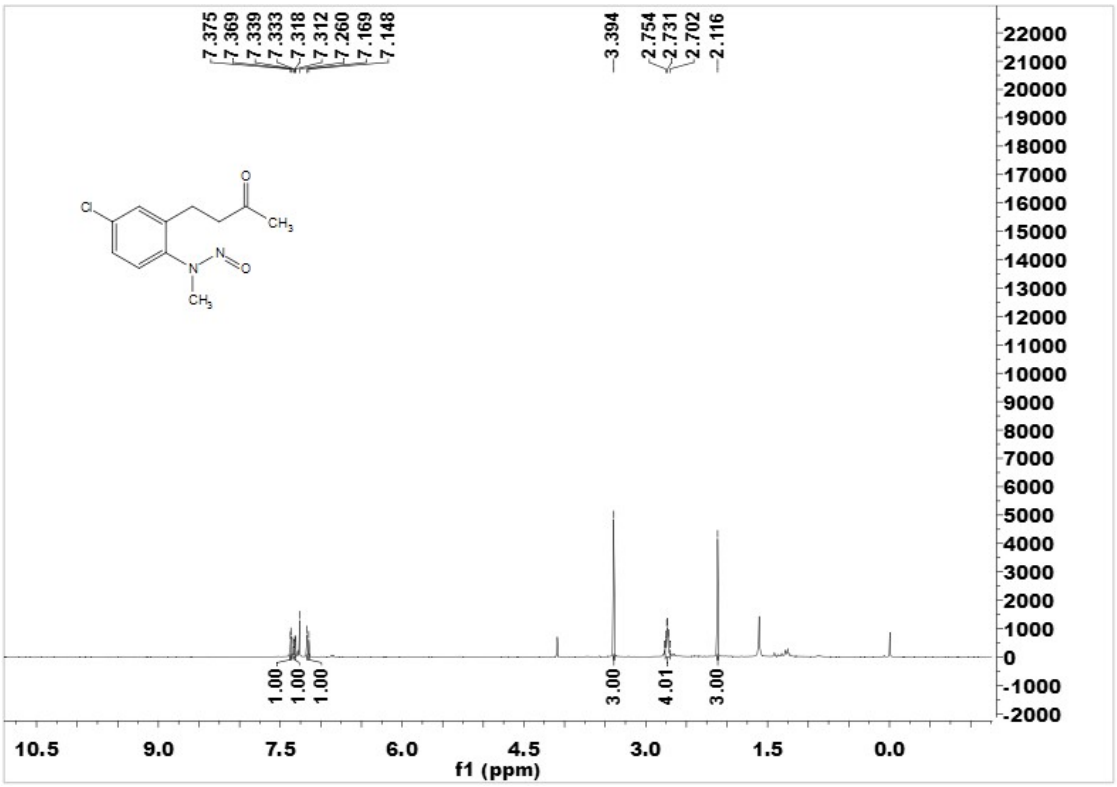


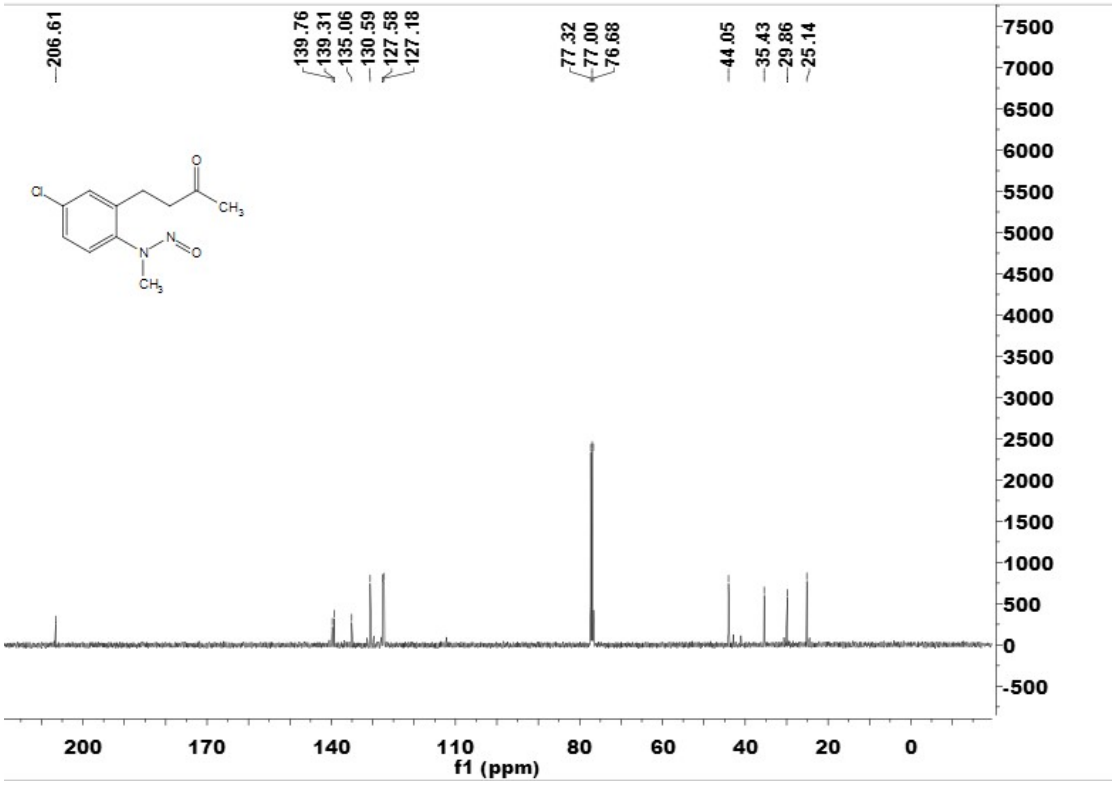
4-(2-(Methylamino)phenyl)-4-phenylbutan-2-one (9f)



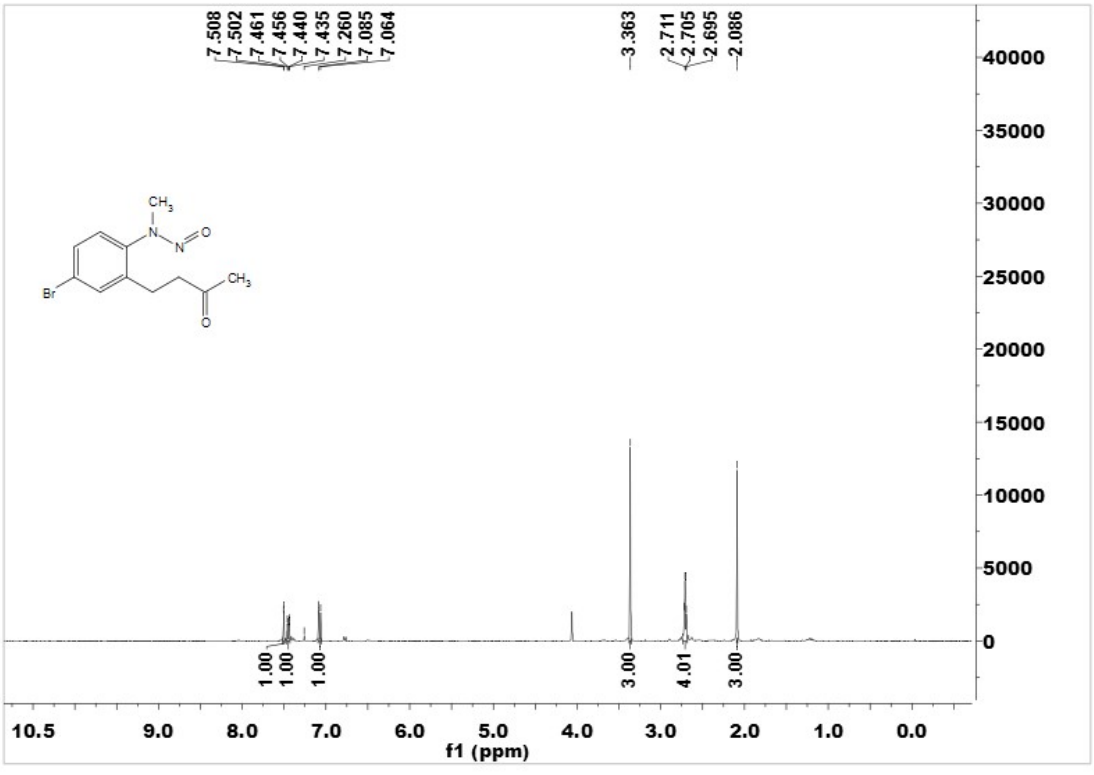


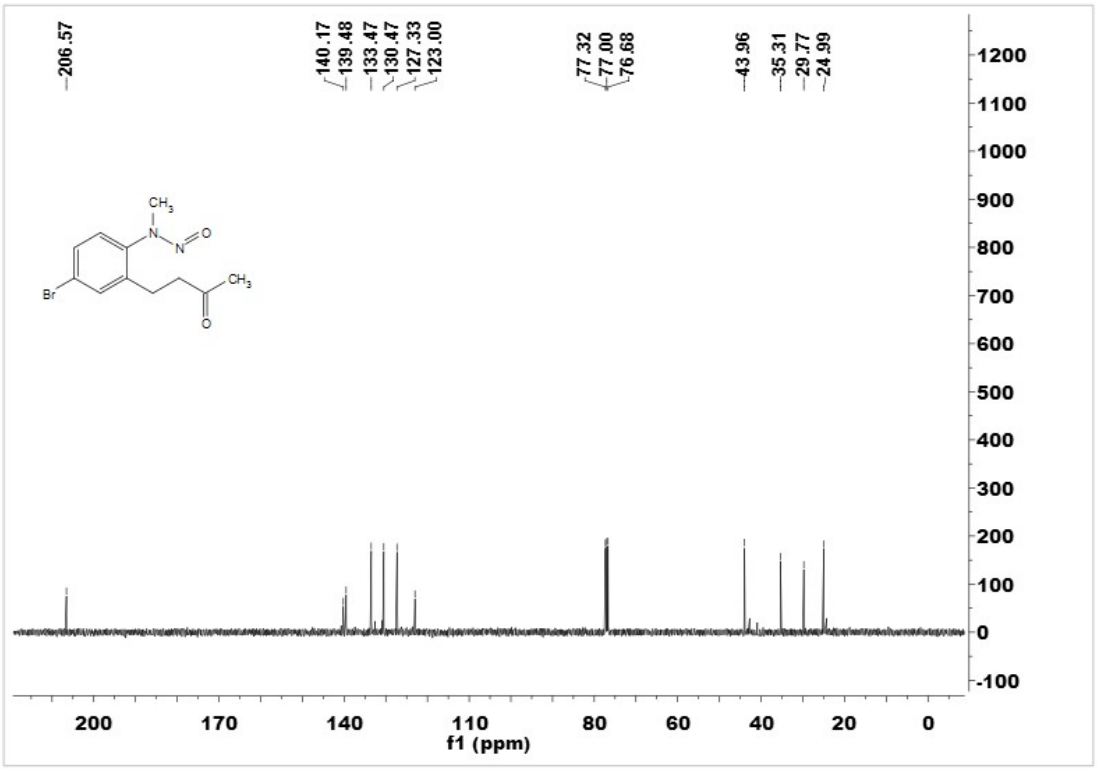
4-(5-Chloro-2-(methylamino)phenyl)butan-2-one (9g)



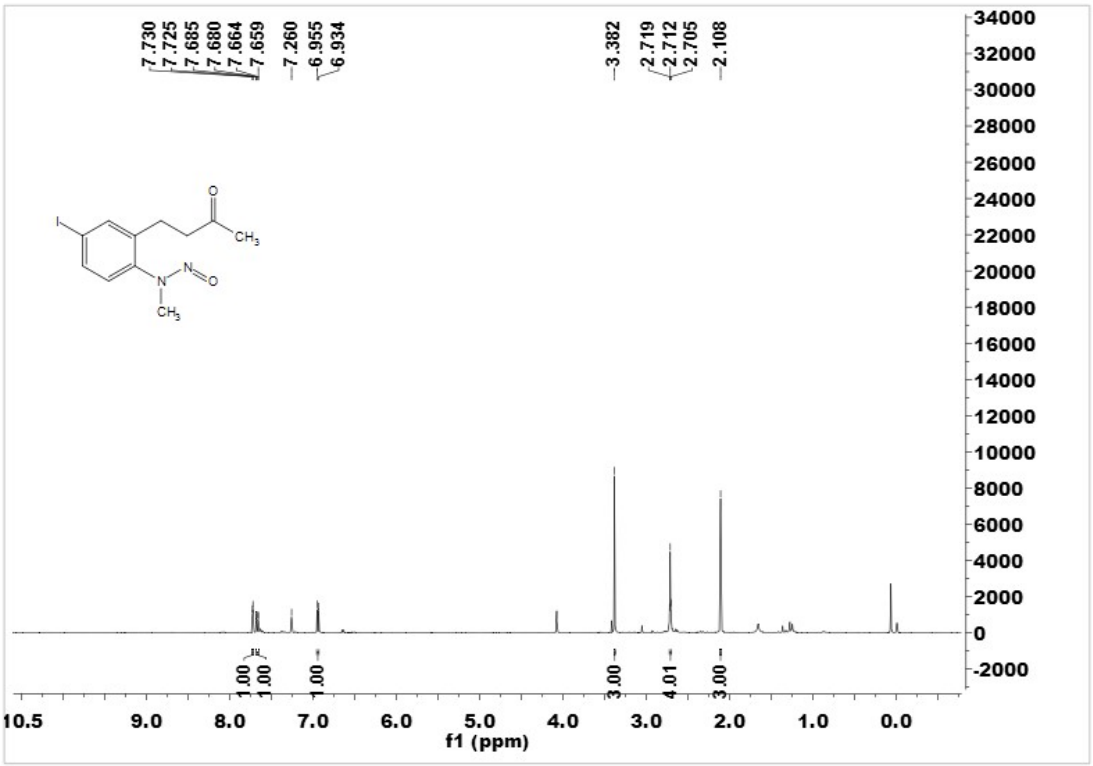


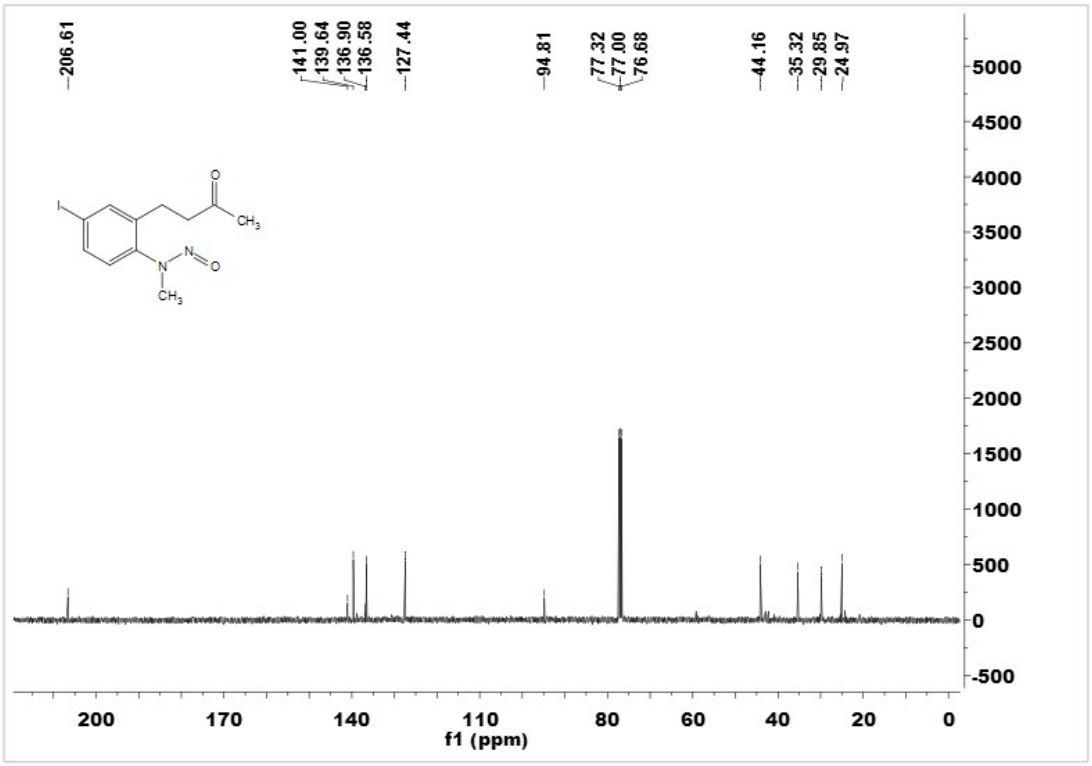
Methyl (*E*)-4-methyl-3-((3-oxo-3-phenylprop-1-en-1-yl)amino)benzoate (9h)



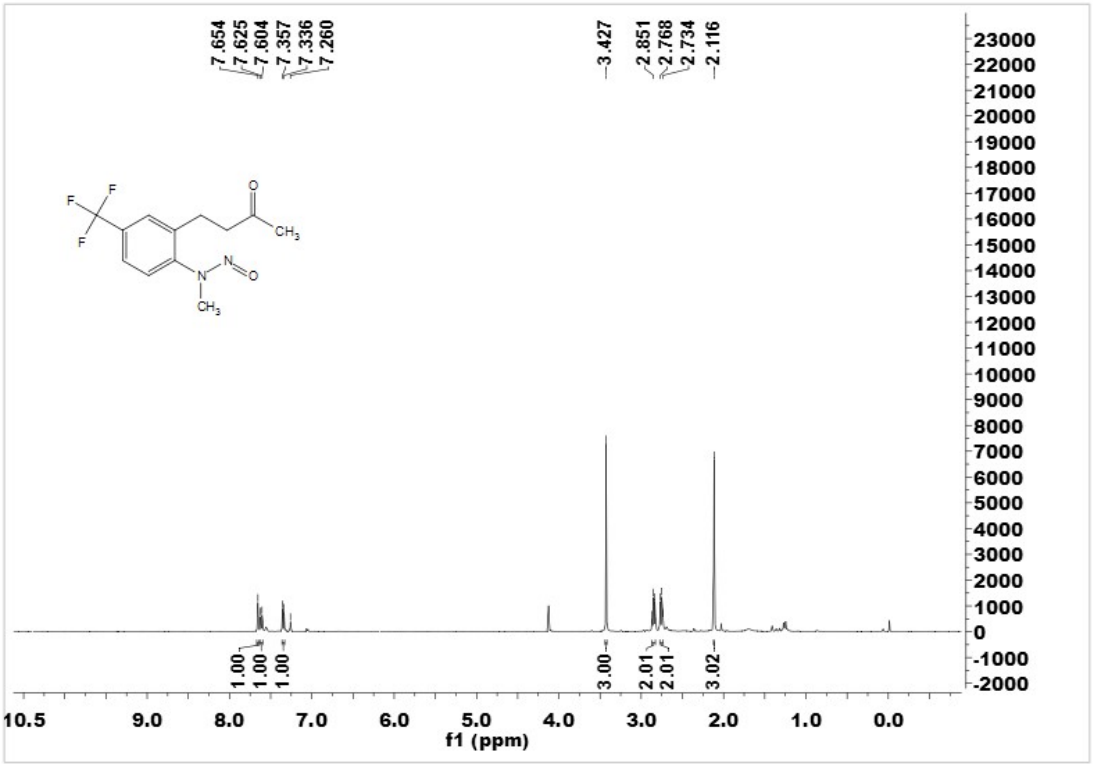


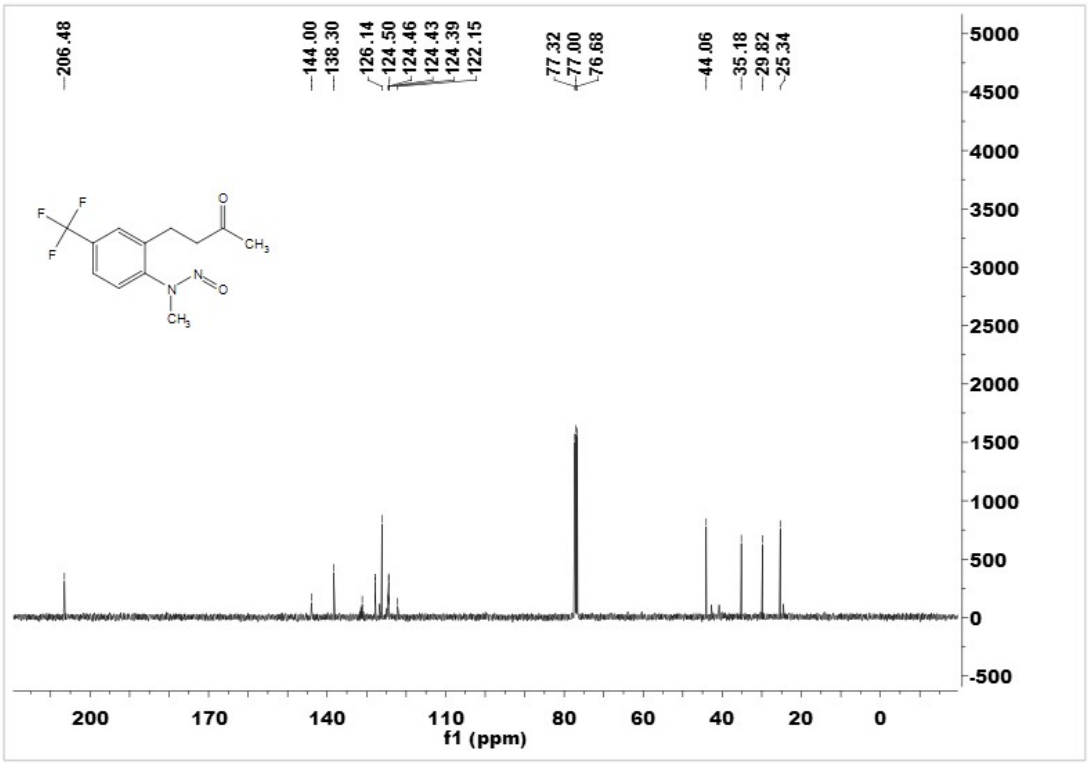
4-(5-Iodo-2-(methylamino)phenyl)butan-2-one (9i)





4-(2-(Methylamino)-5-(trifluoromethyl)phenyl)butan-2-one (9j)

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77.32
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29.82
25.34
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4500
4000
3500
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500
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-500
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170
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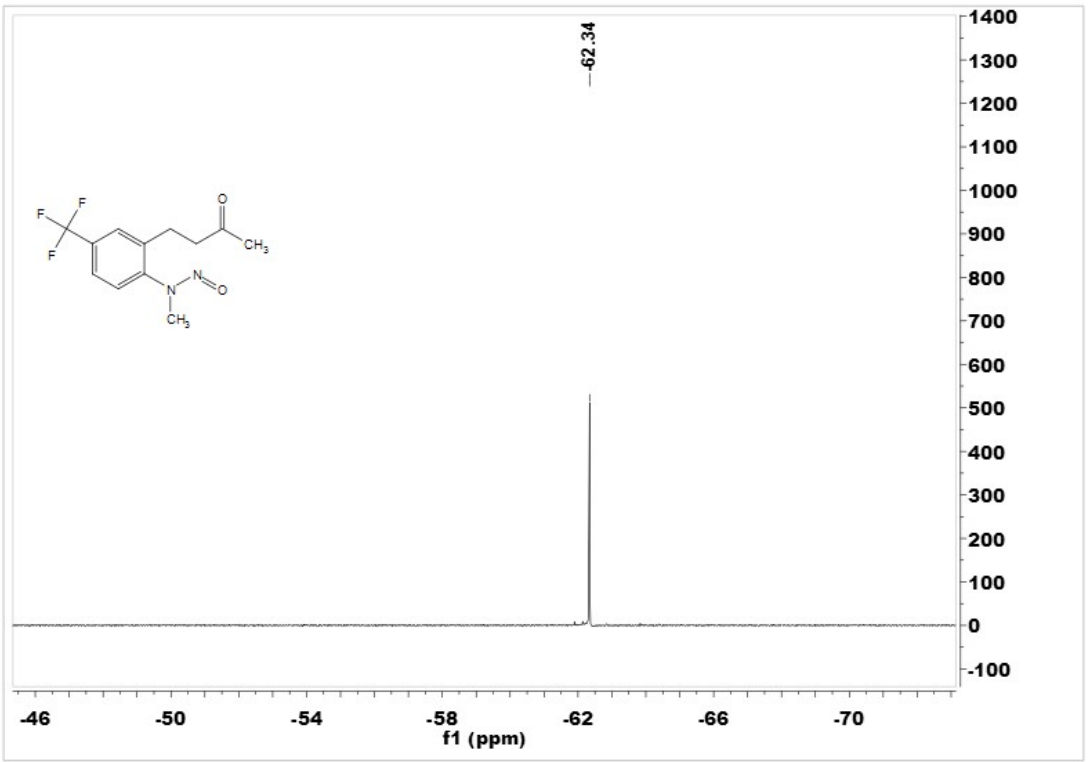
110
80
60
40
20
0
f1 (ppm)


62.34
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700
600
500
400
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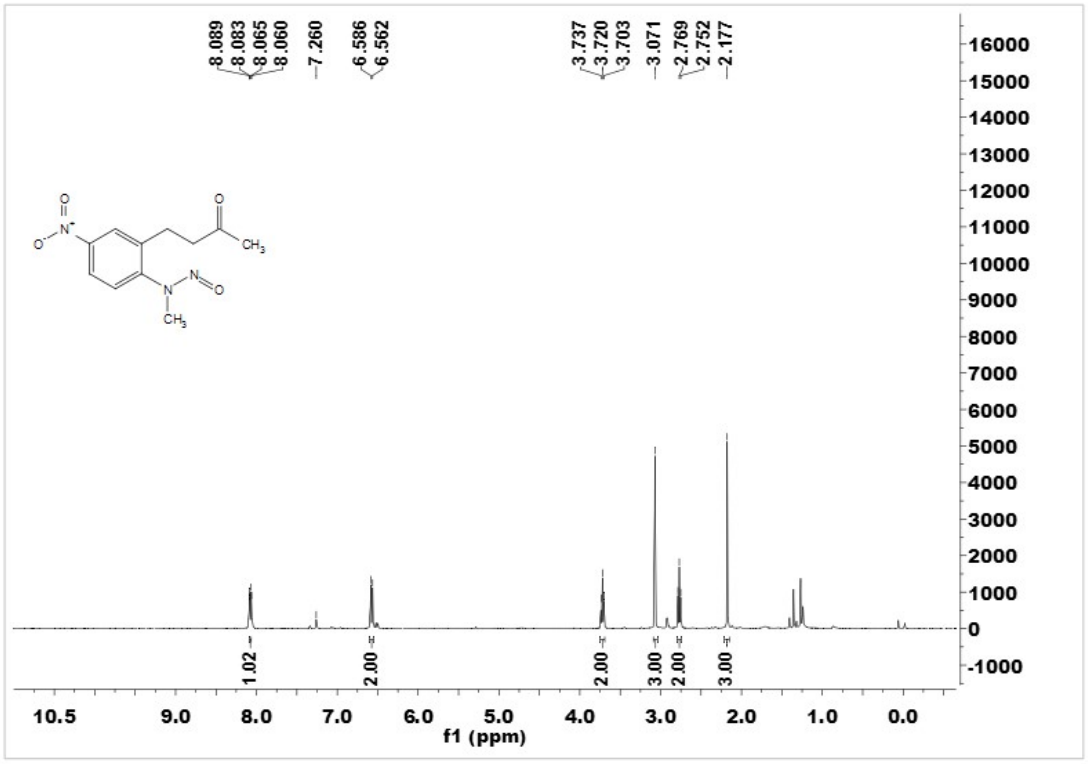
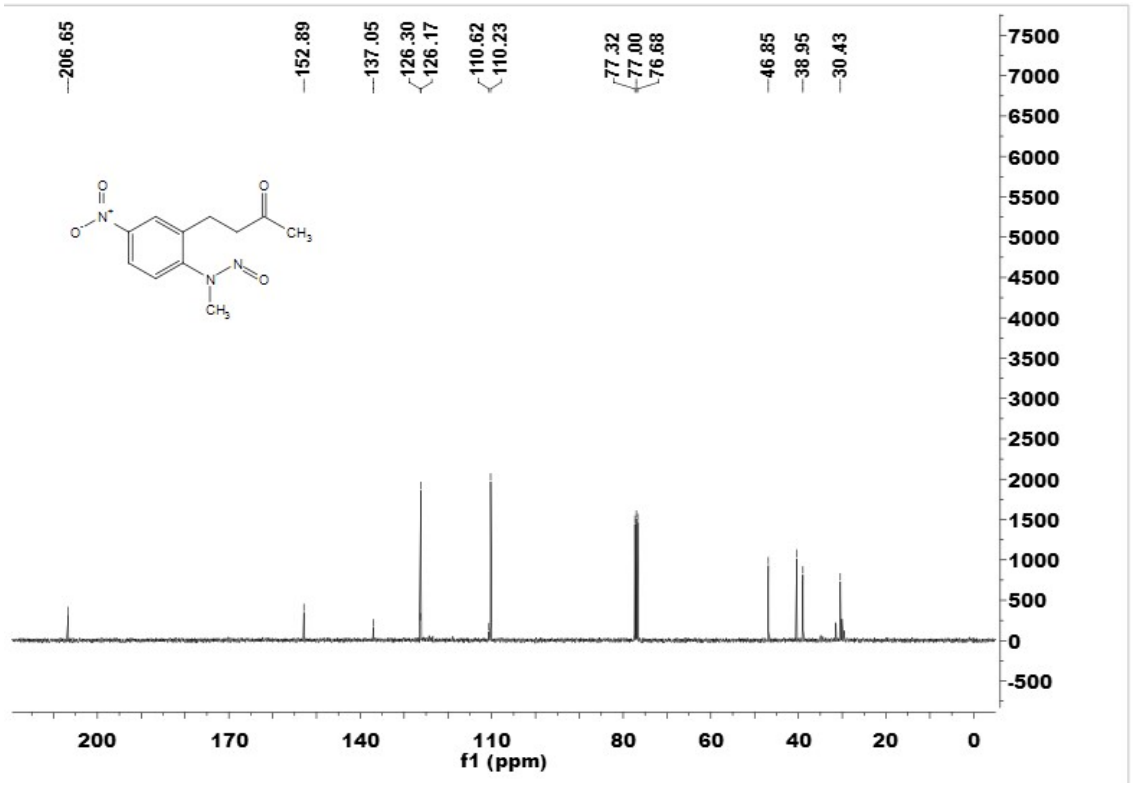
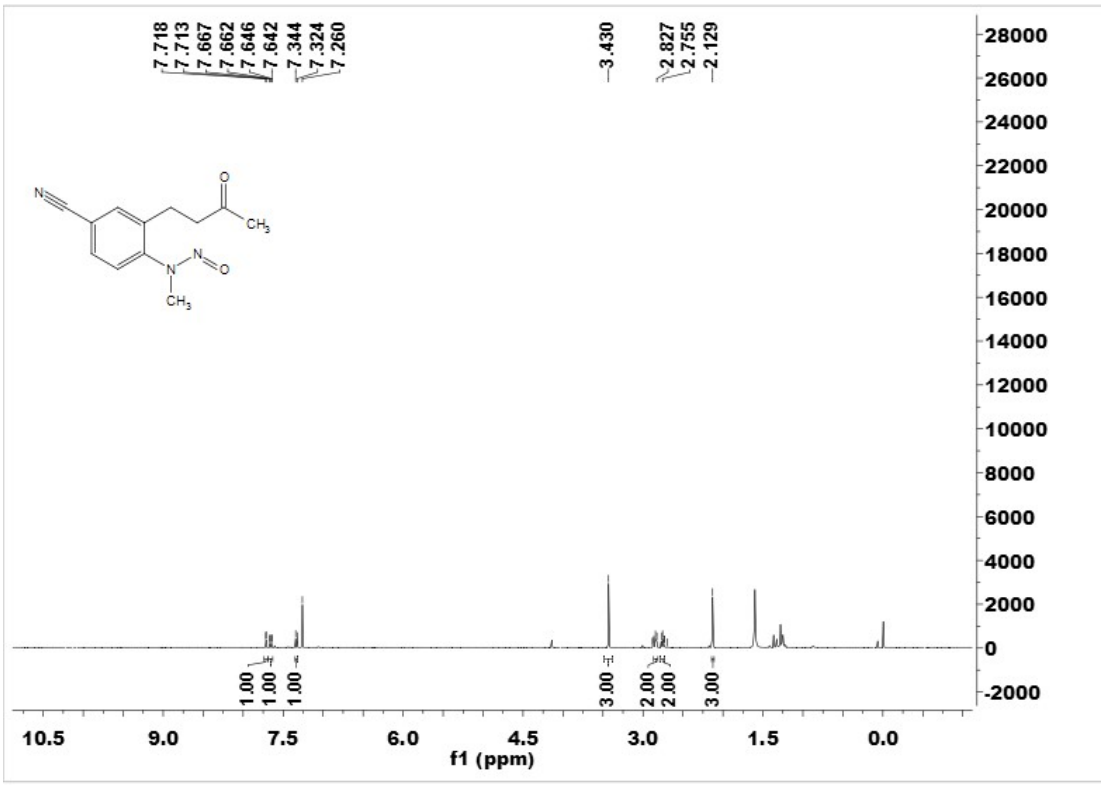
200
100
0
-100
-46
-50
-54
-58
-62
-66
-70
f1 (ppm)

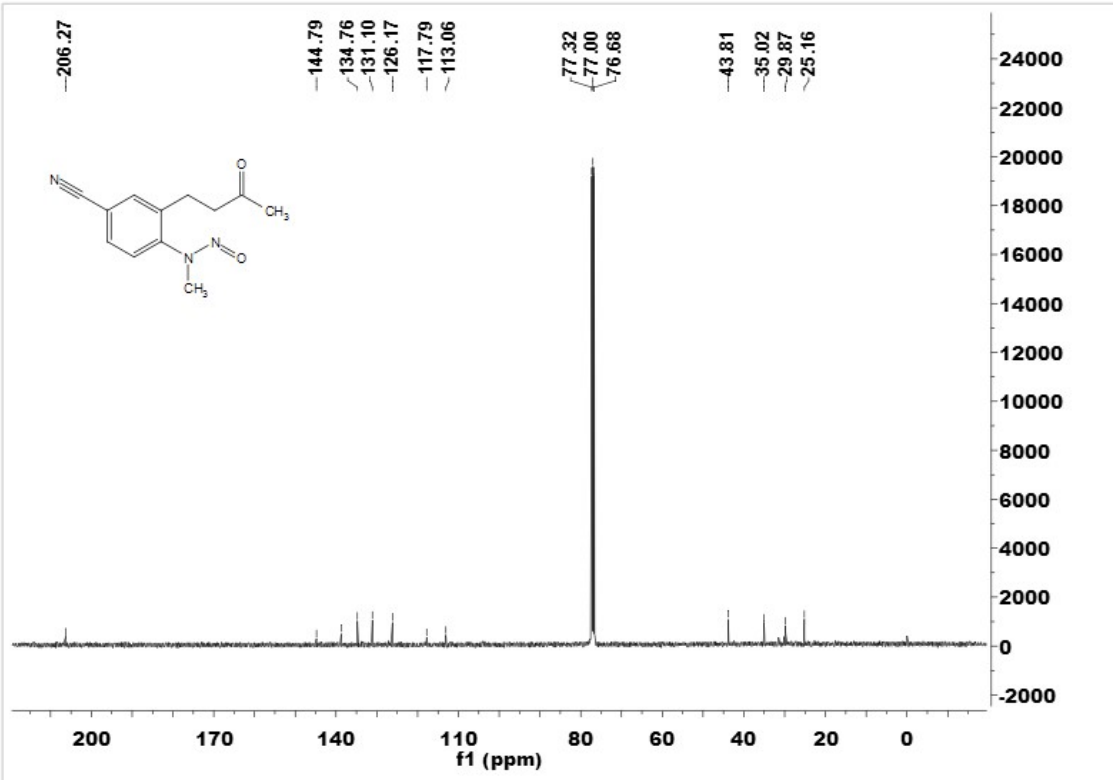
(*E*) 4-(2-(Methylamino)-5-nitrophenyl)butan-2-one (9k)



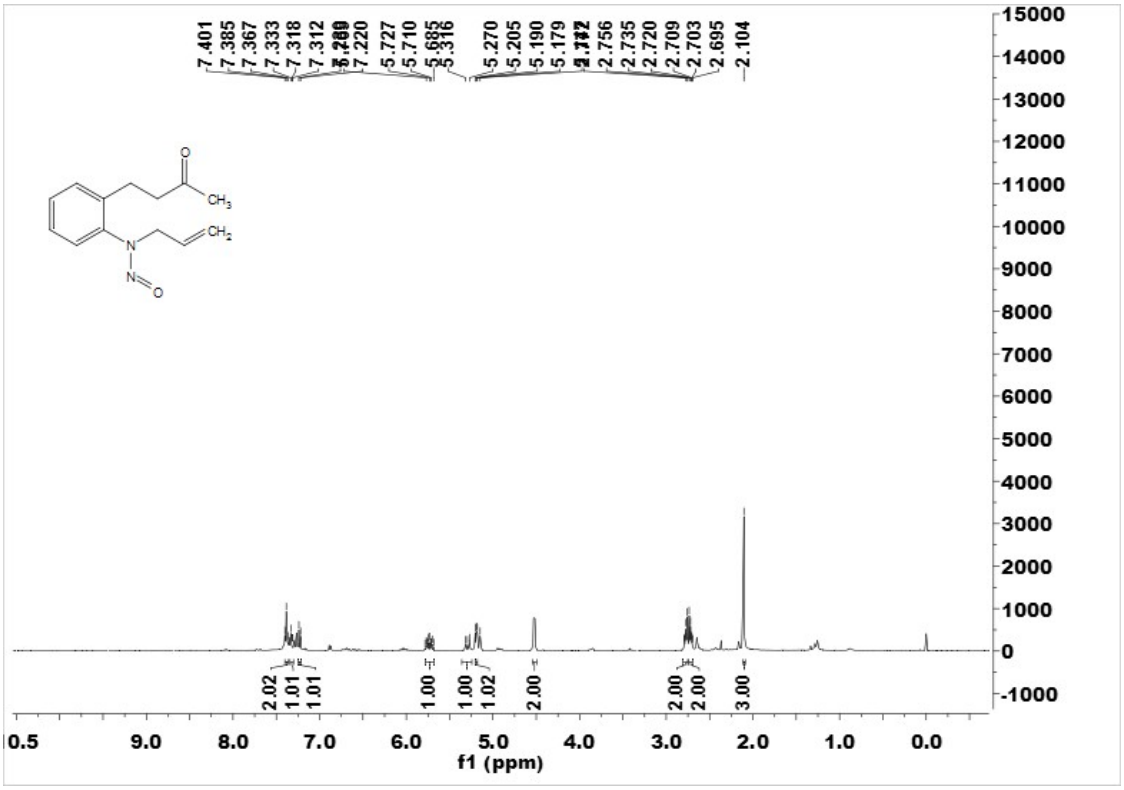


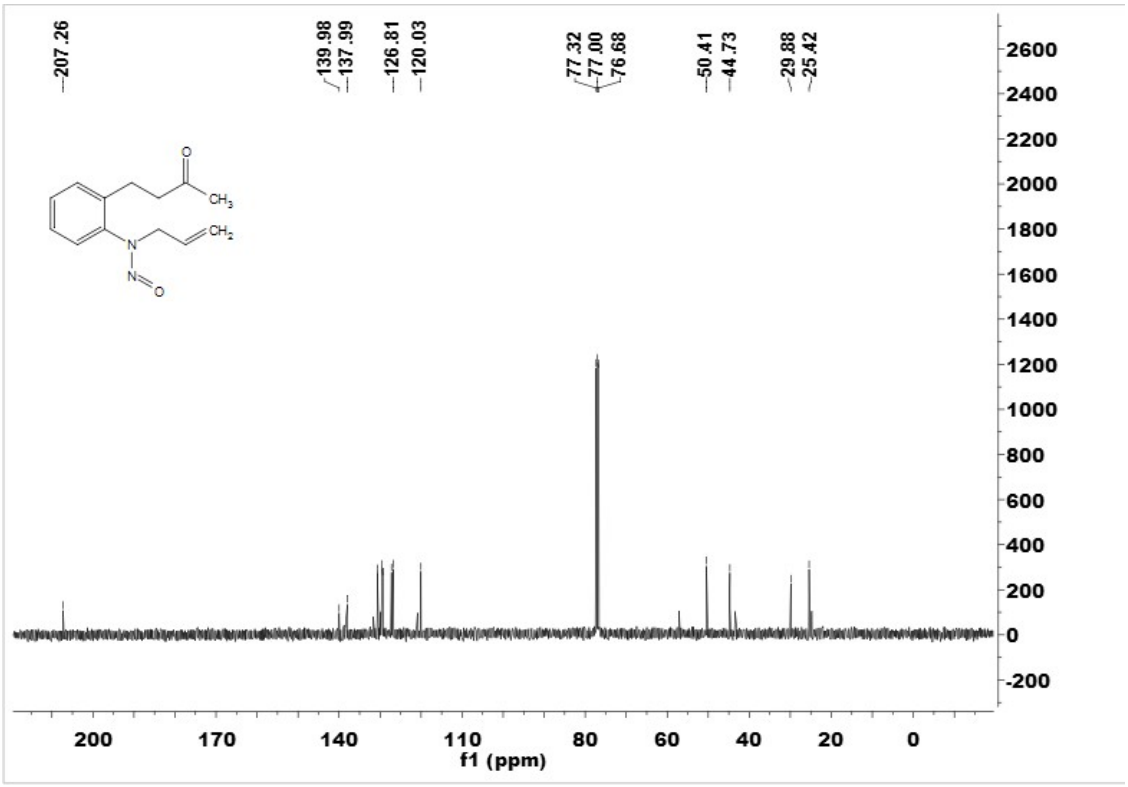
N-(4-Cyano-2-(3-oxobutyl)phenyl)-N-methylnitrous amide (9l)



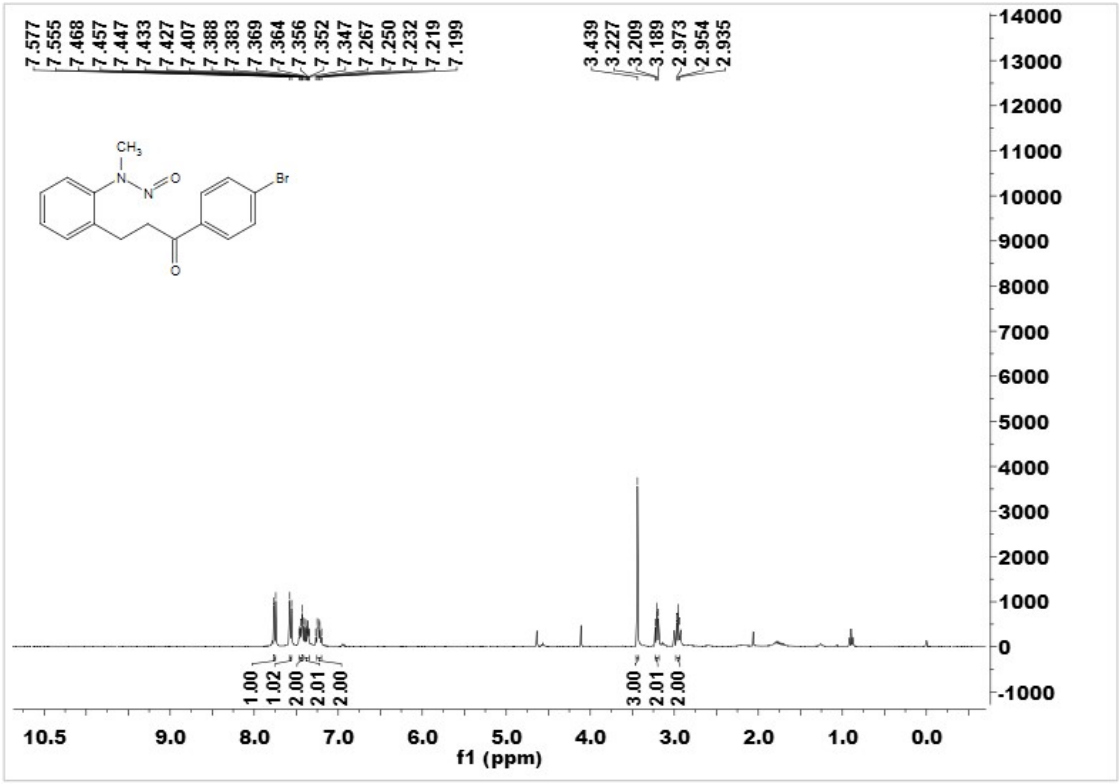


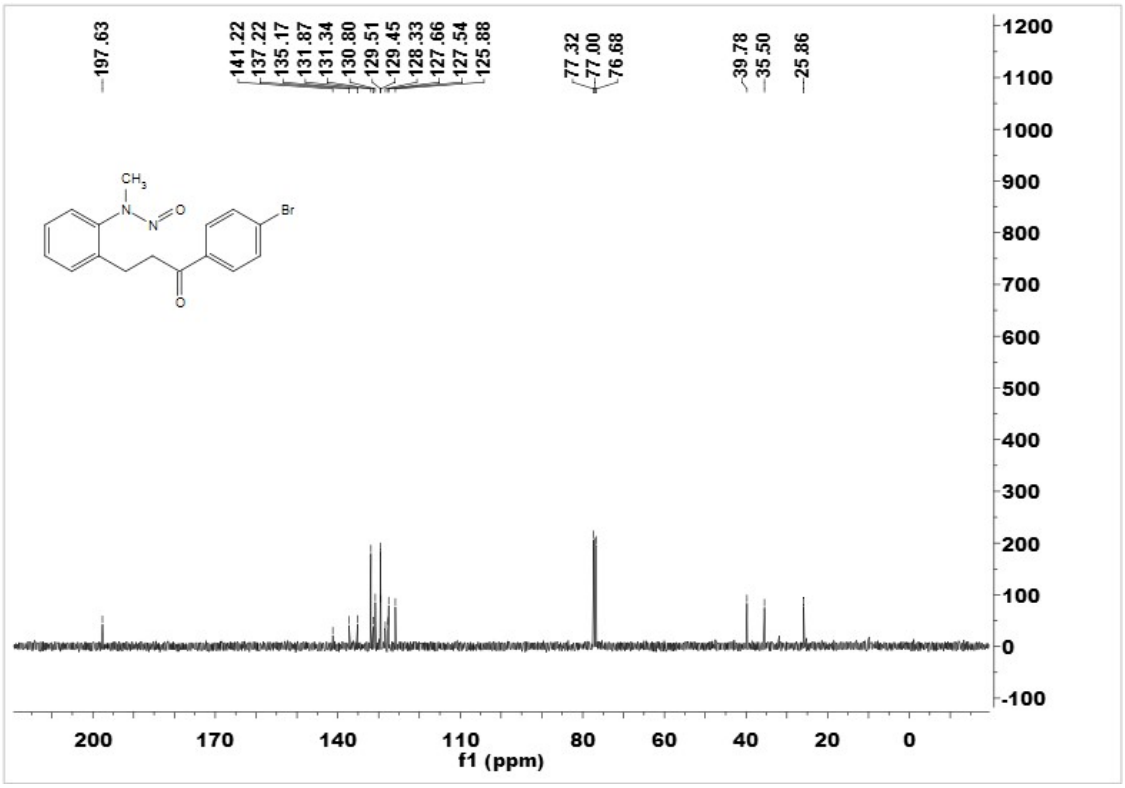
4-(5-Chloro-2-(methylamino)phenyl)butan-2-one (9m)



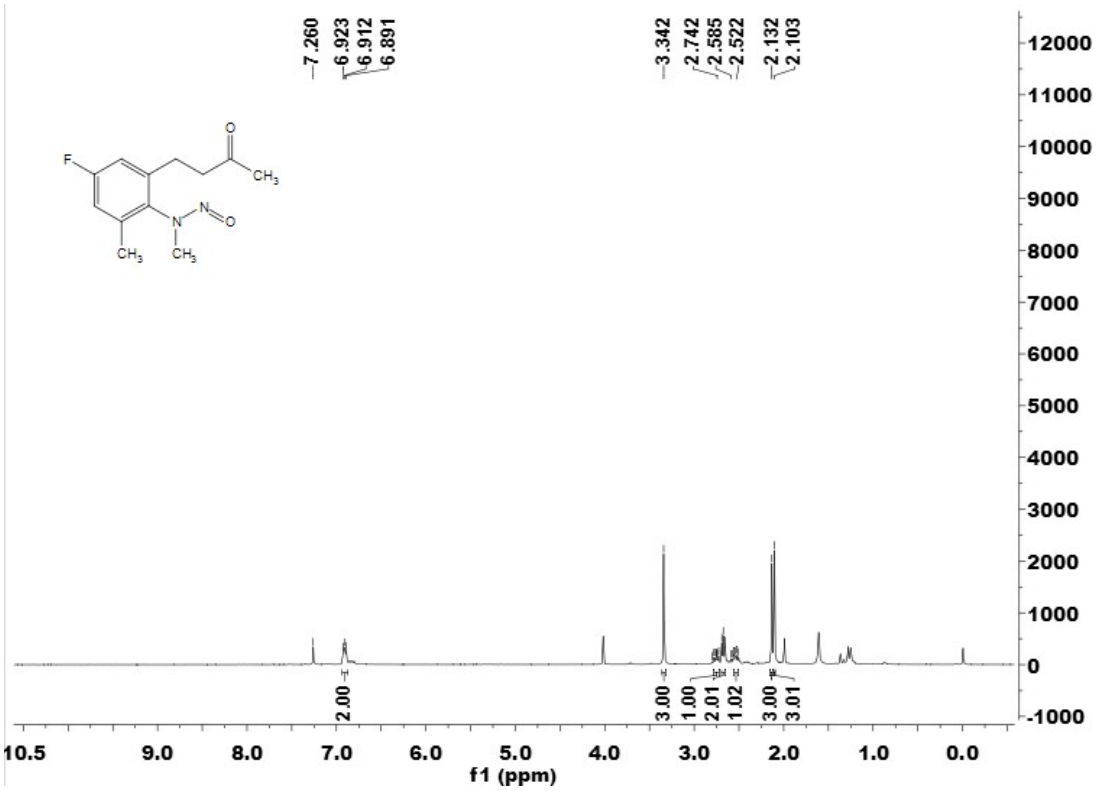


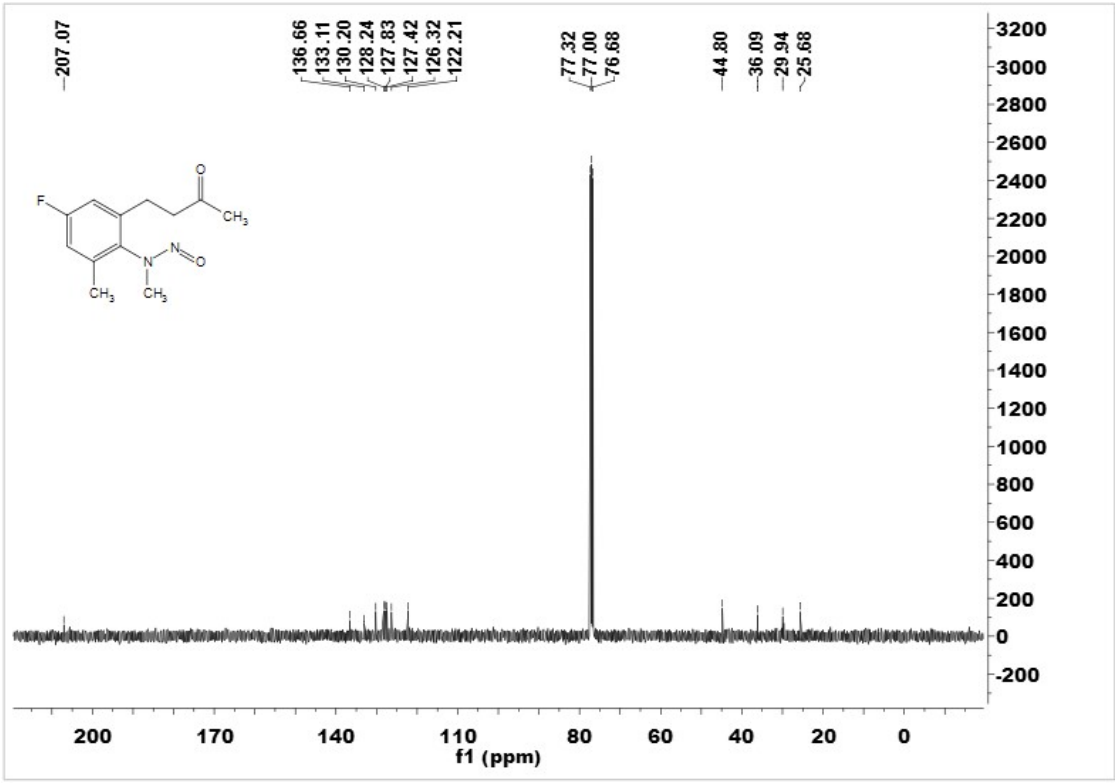
N-(2-(3-(4-Bromophenyl)-3-oxopropyl)phenyl)-N-methylnitrous amide (9n)

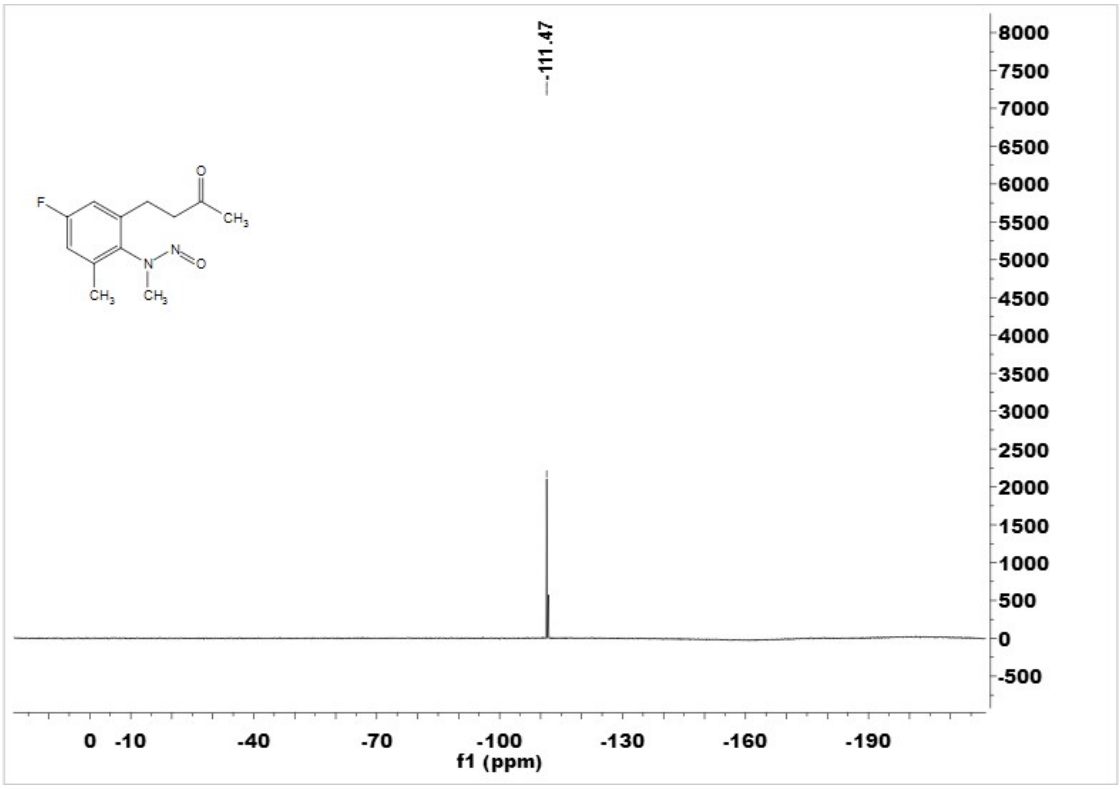




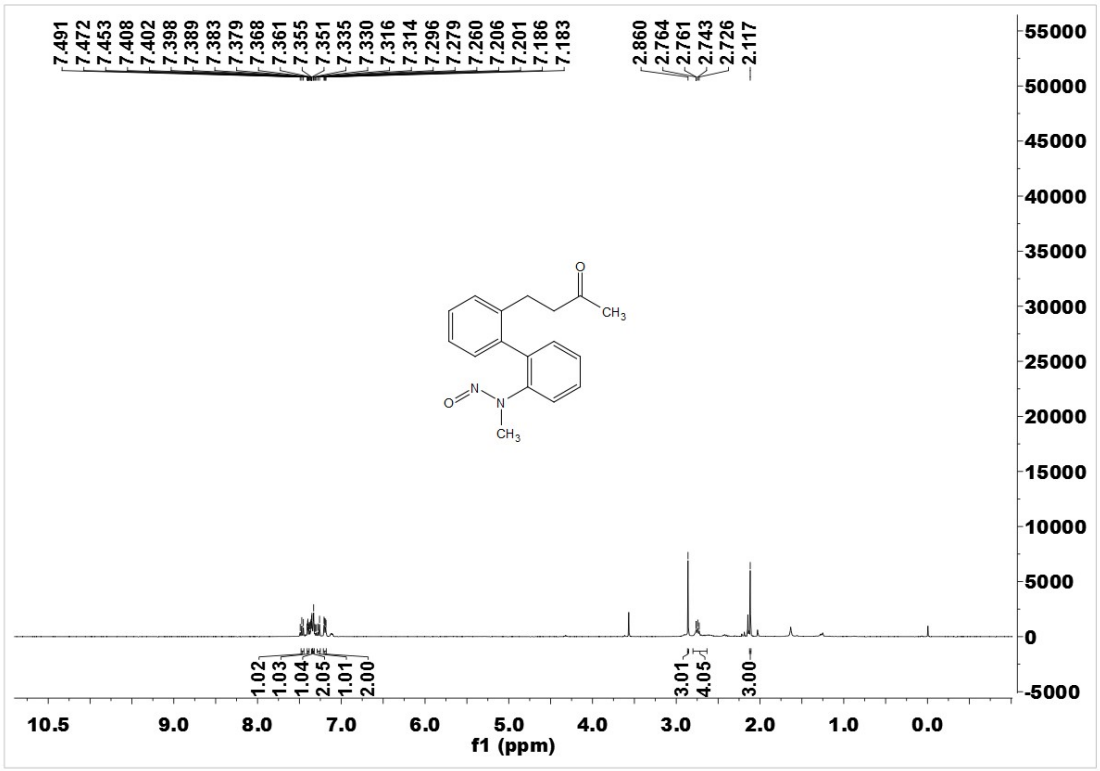
N-(4-Fluoro-2-methyl-6-(3-oxobutyl)phenyl)-N-methylnitrous amide (9o)

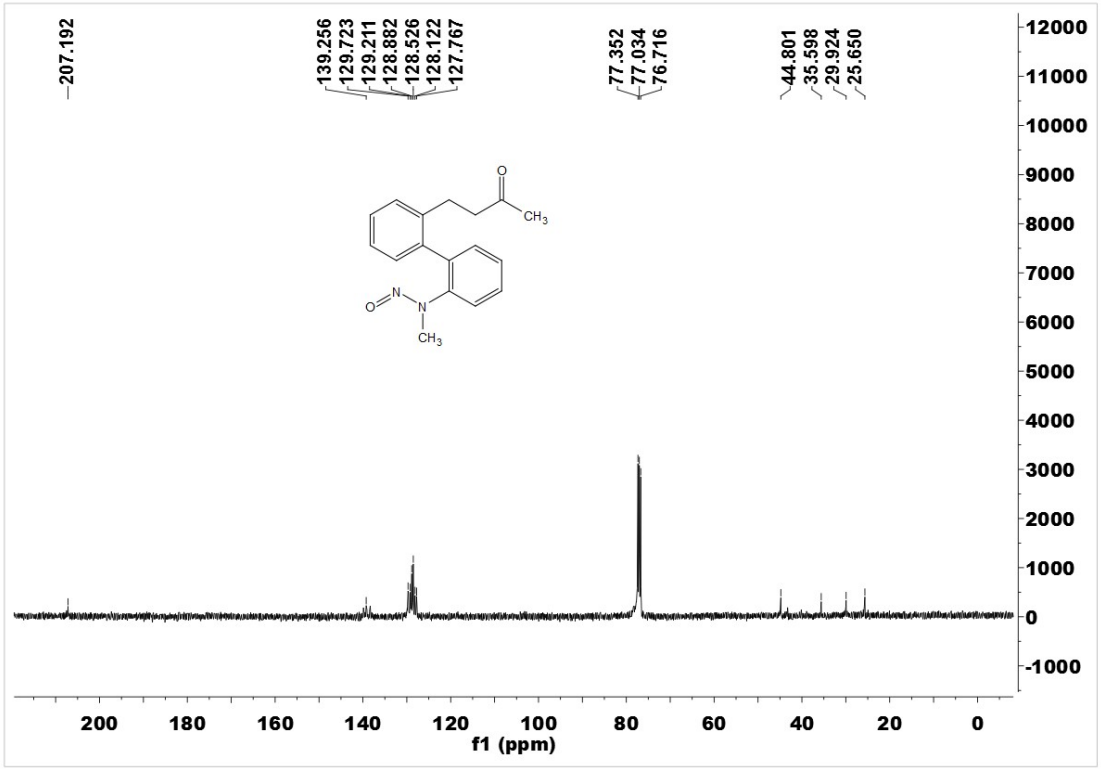




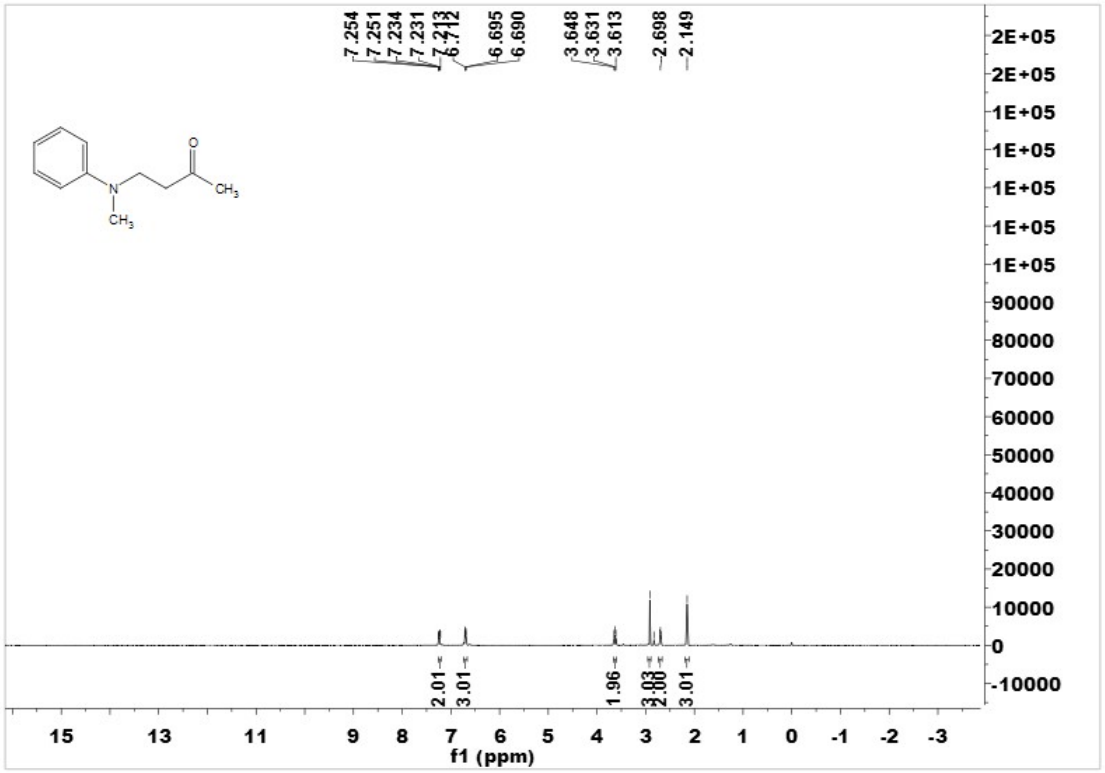


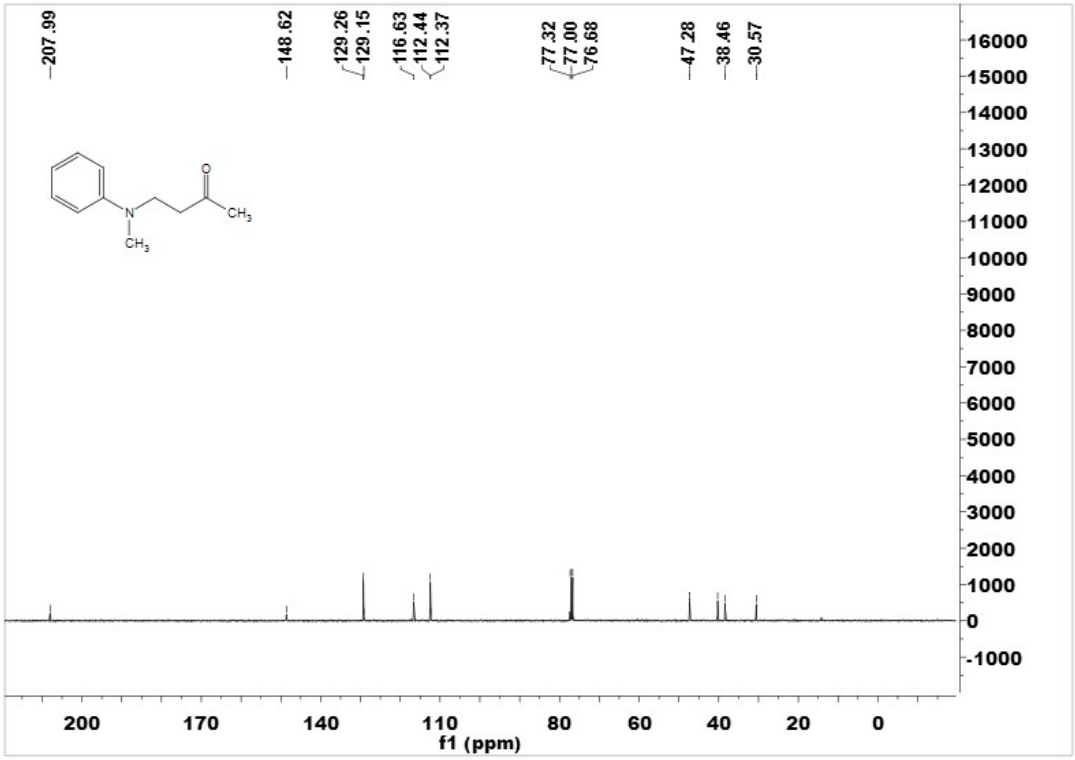
N-Methyl-N-(2'-(3-oxobutyl)-[1,1'-biphenyl]-2-yl)nitrous amide (9p)



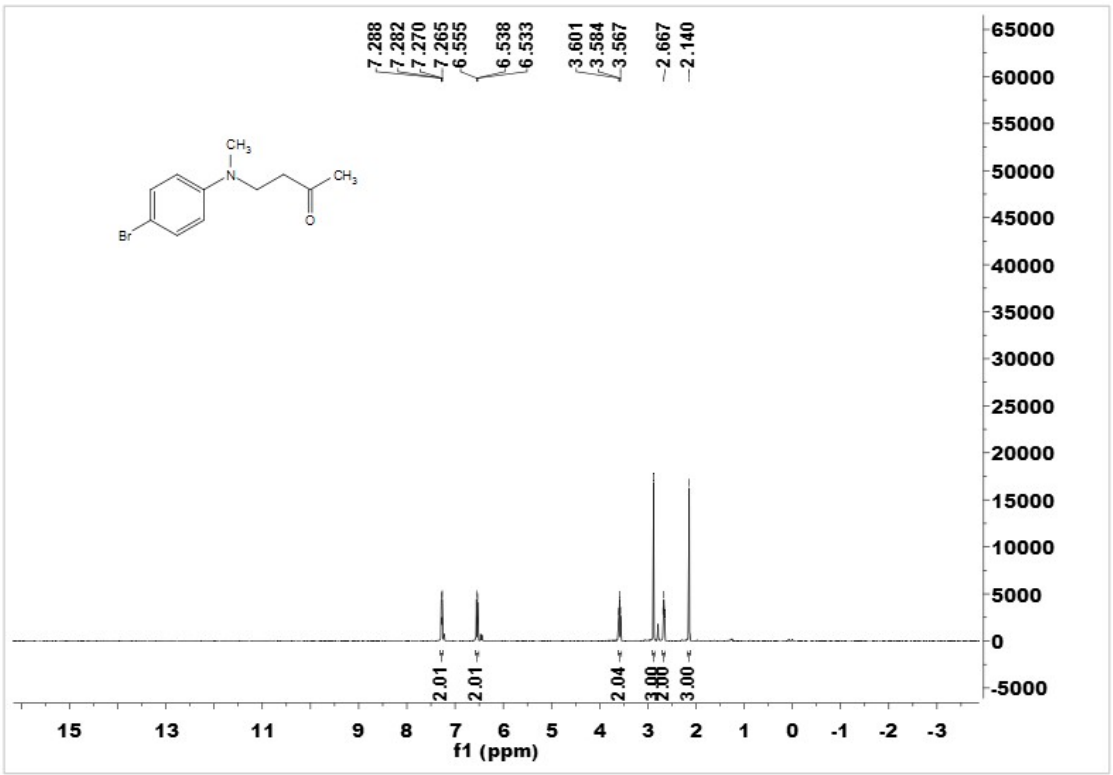


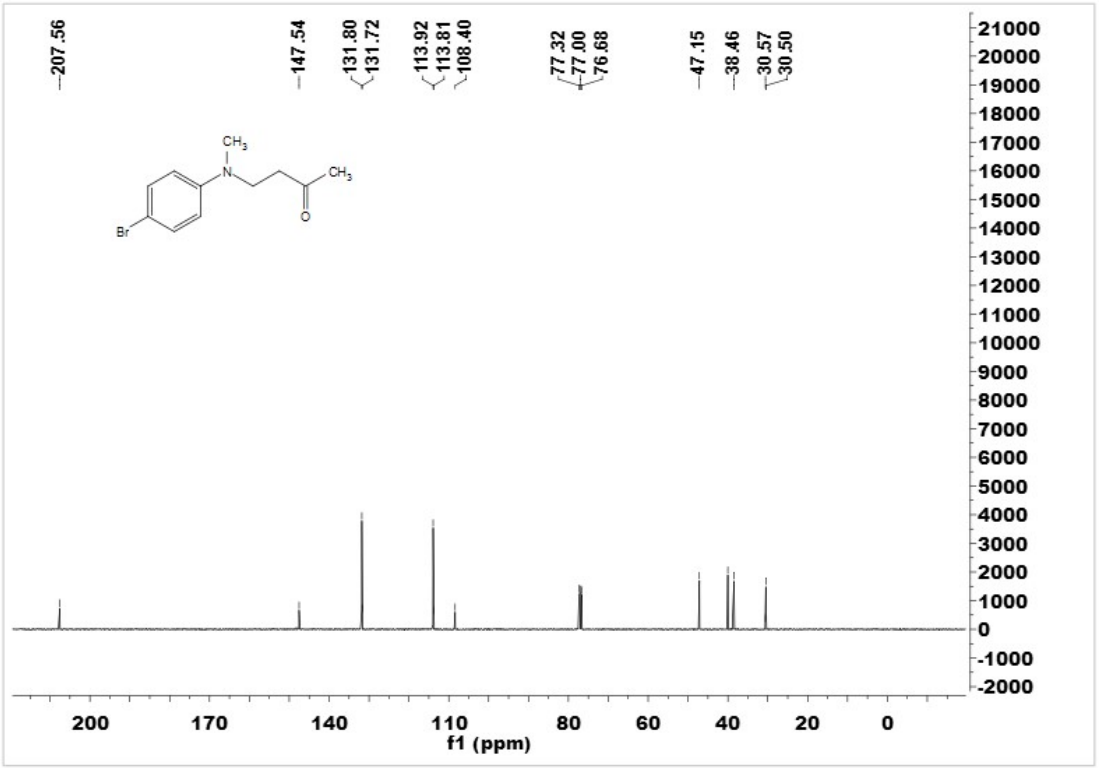
4-(Methyl(phenyl)amino)butan-2-one (10a)



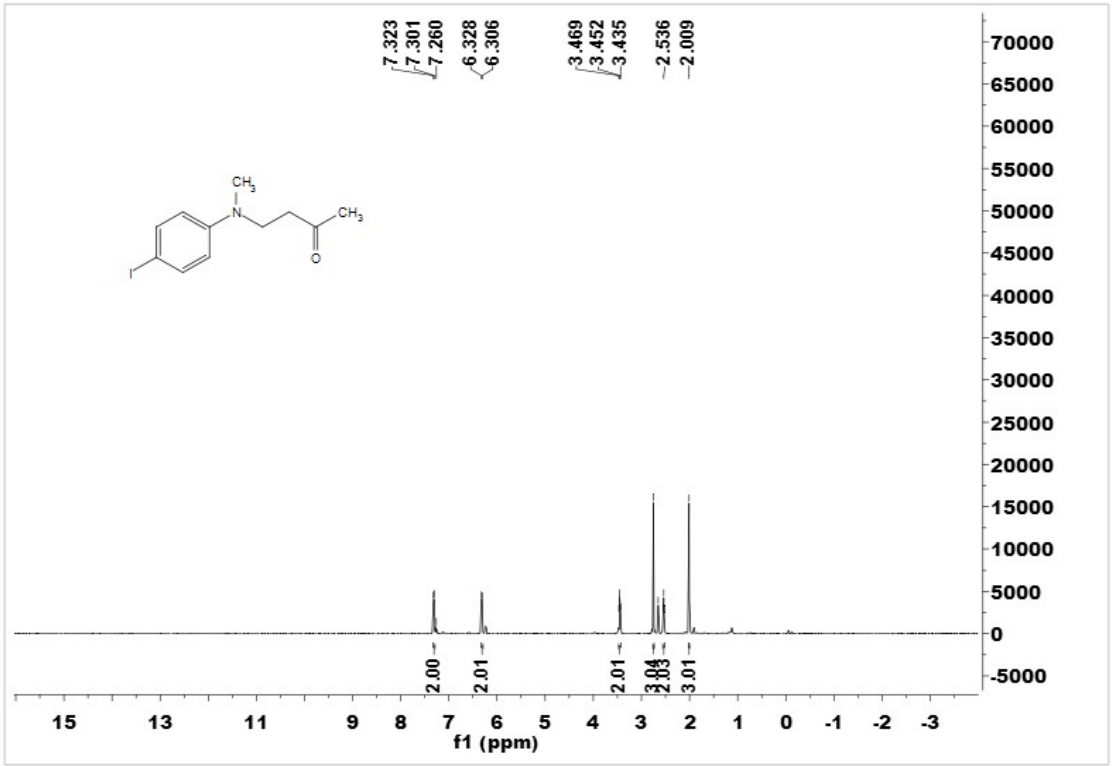


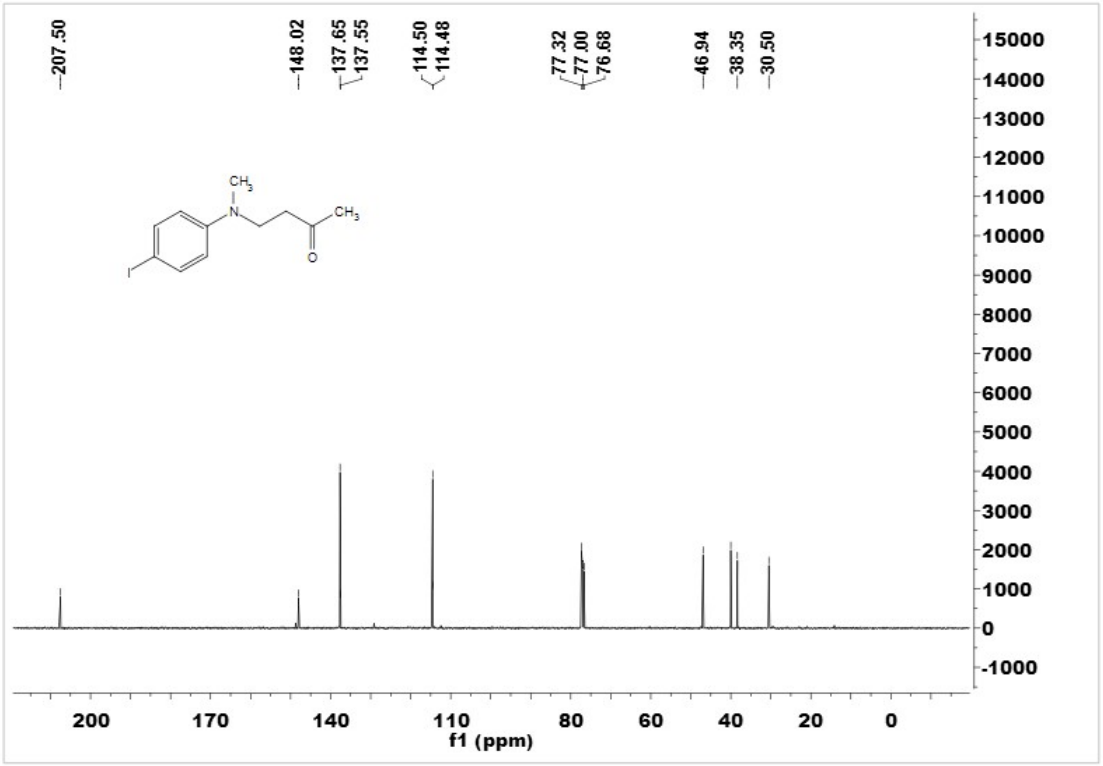
4-((4-Bromophenyl)(methyl)amino)butan-2-one (10b)



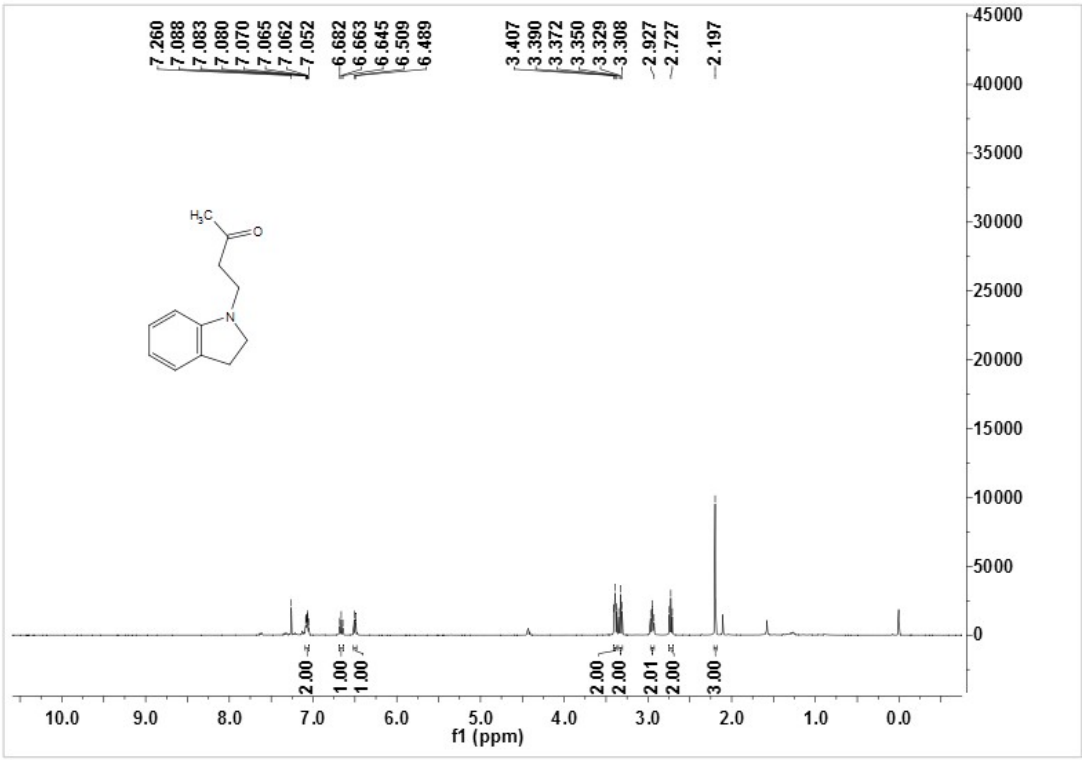


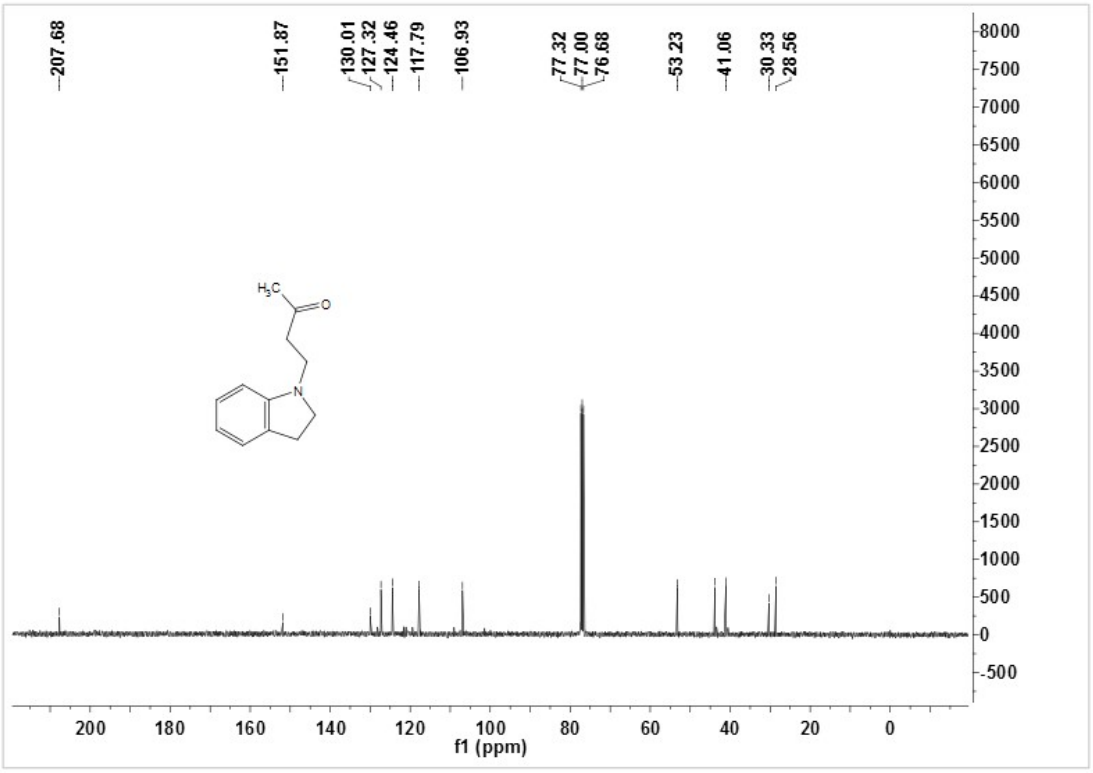
4-((4-Iodophenyl)(methyl)amino)butan-2-one (10c)



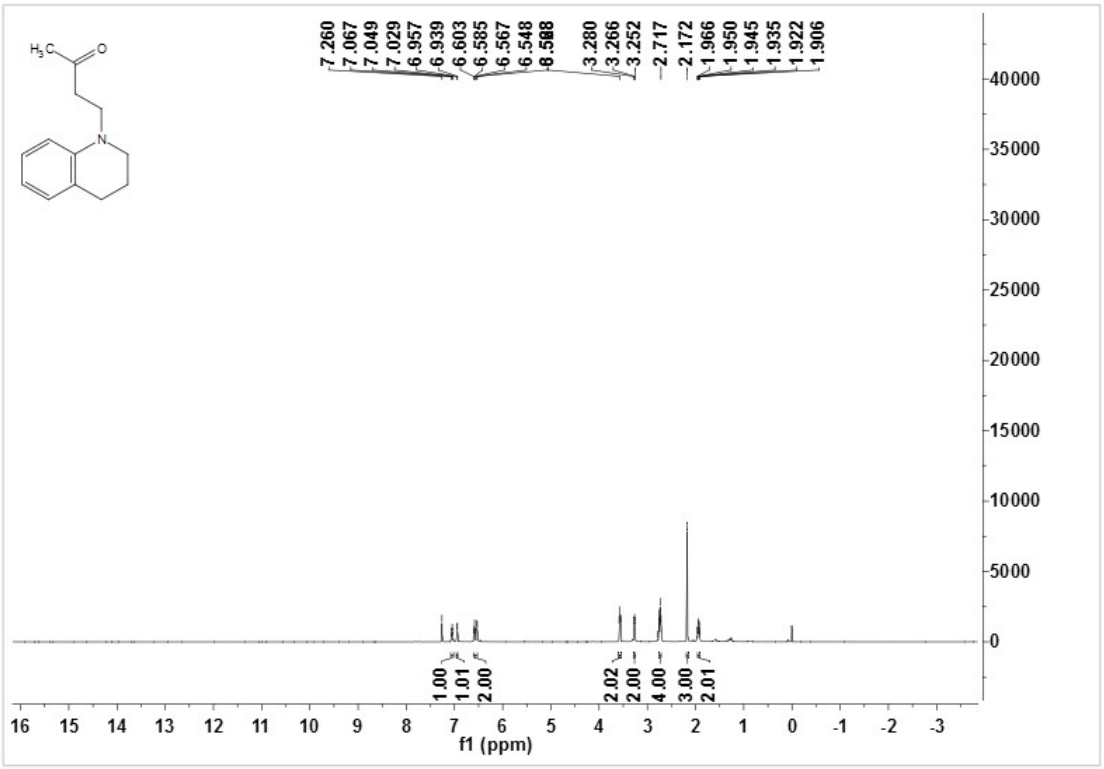


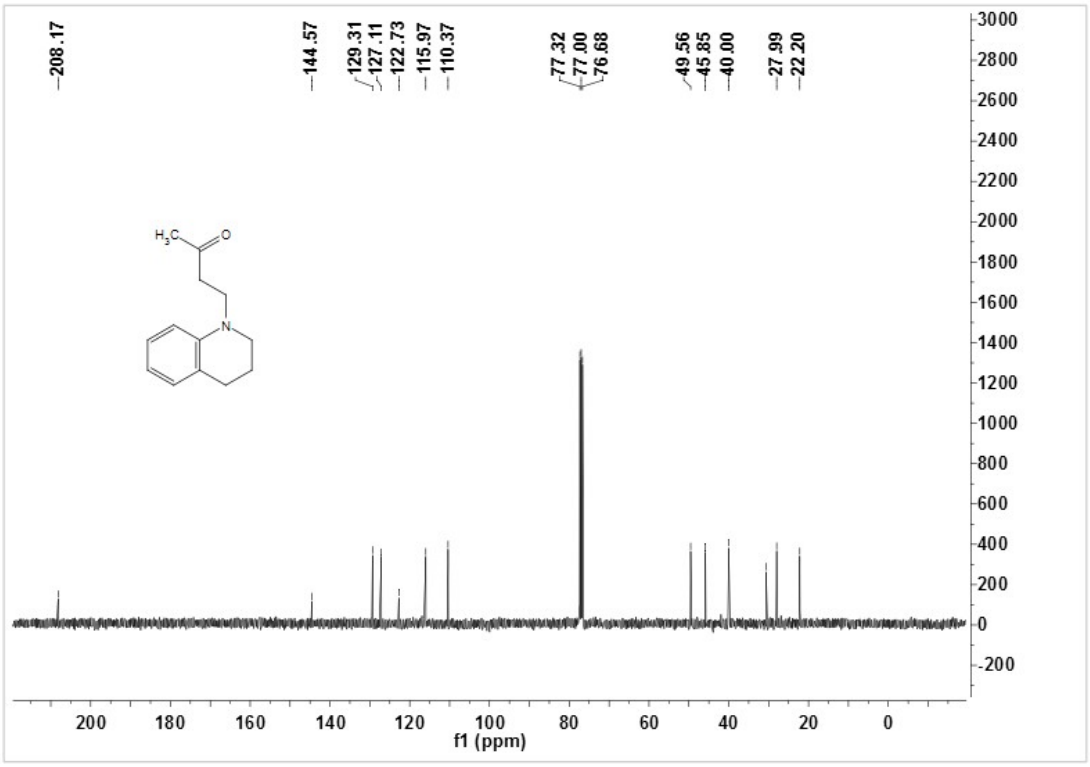
4-(Indolin-1-yl)butan-2-one (10d)



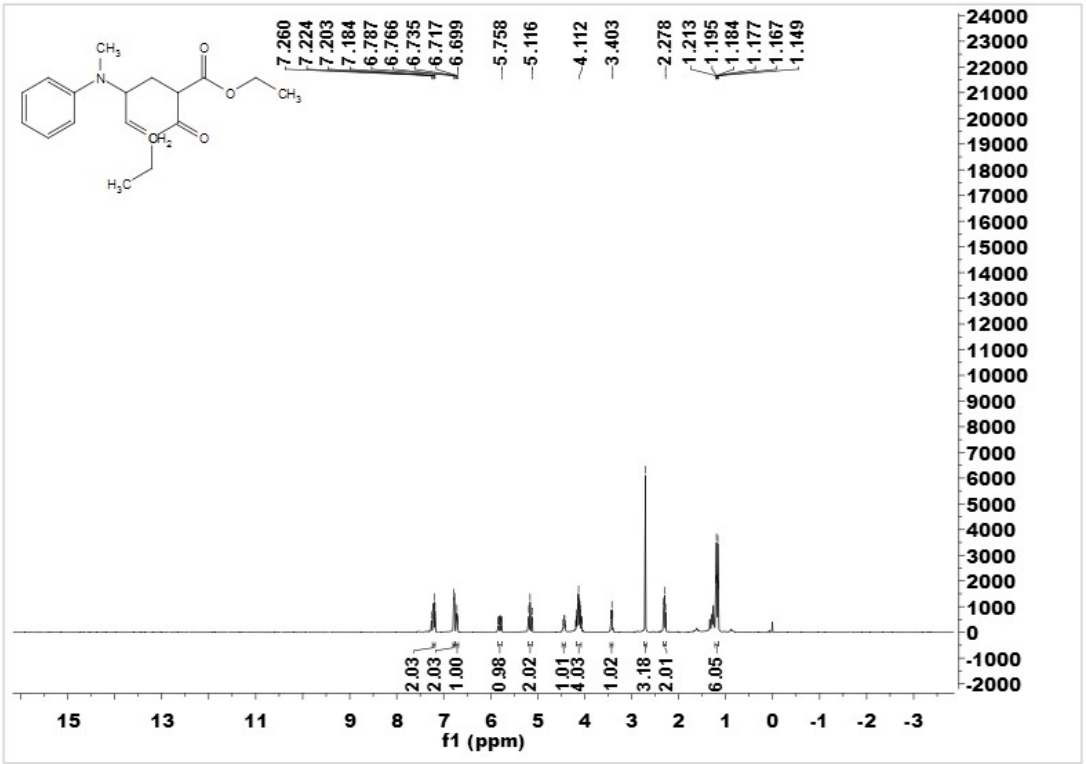


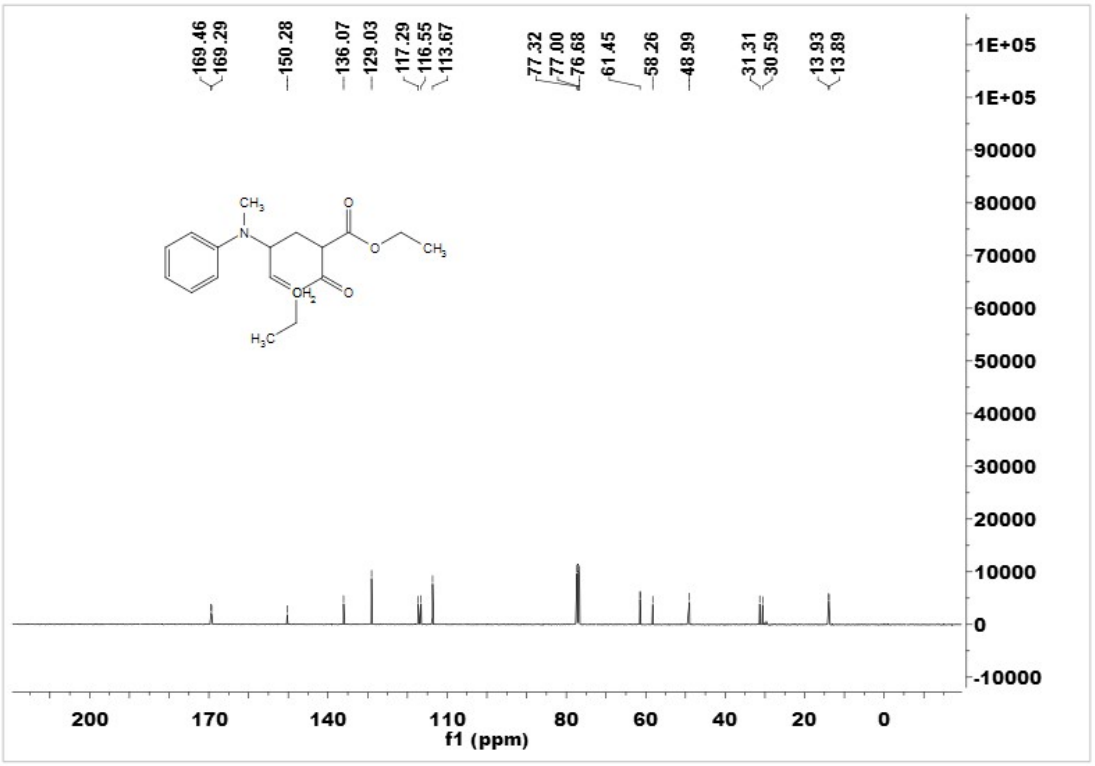
4-(3,4-Dihydroquinolin-1(2*H*)-yl)butan-2-one (10e)





Diethyl 2-(2-(methyl(phenyl)amino)but-3-en-1-yl)malonate (4a)





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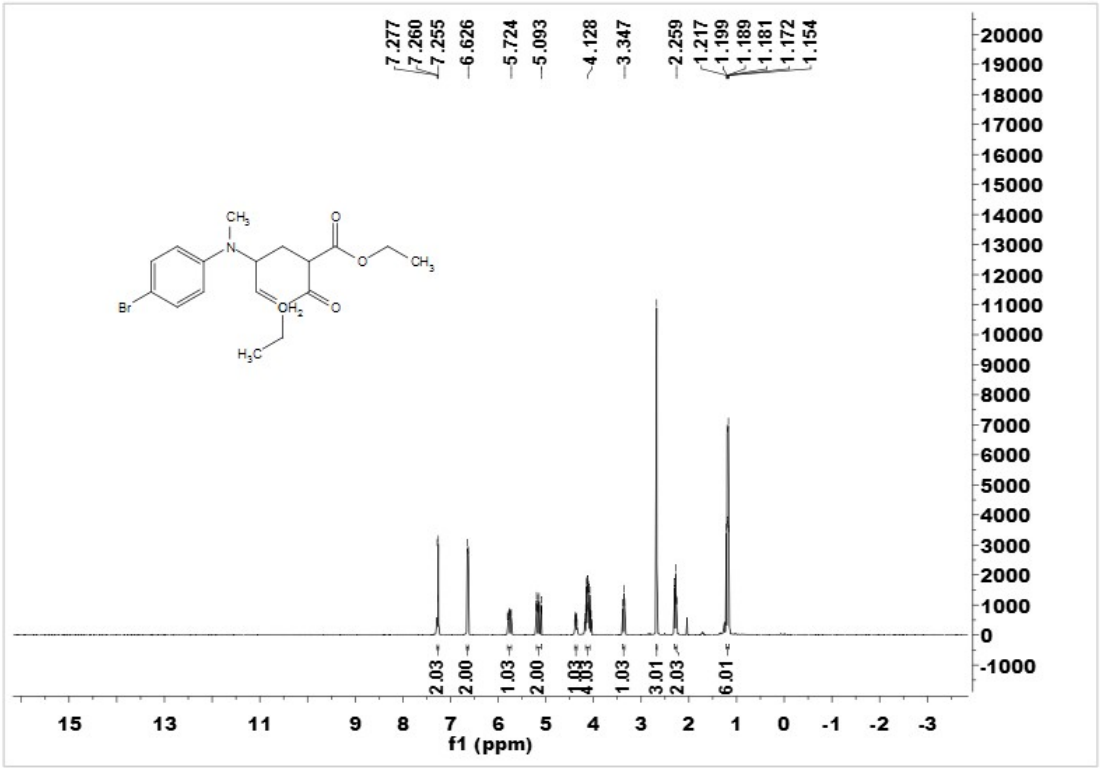
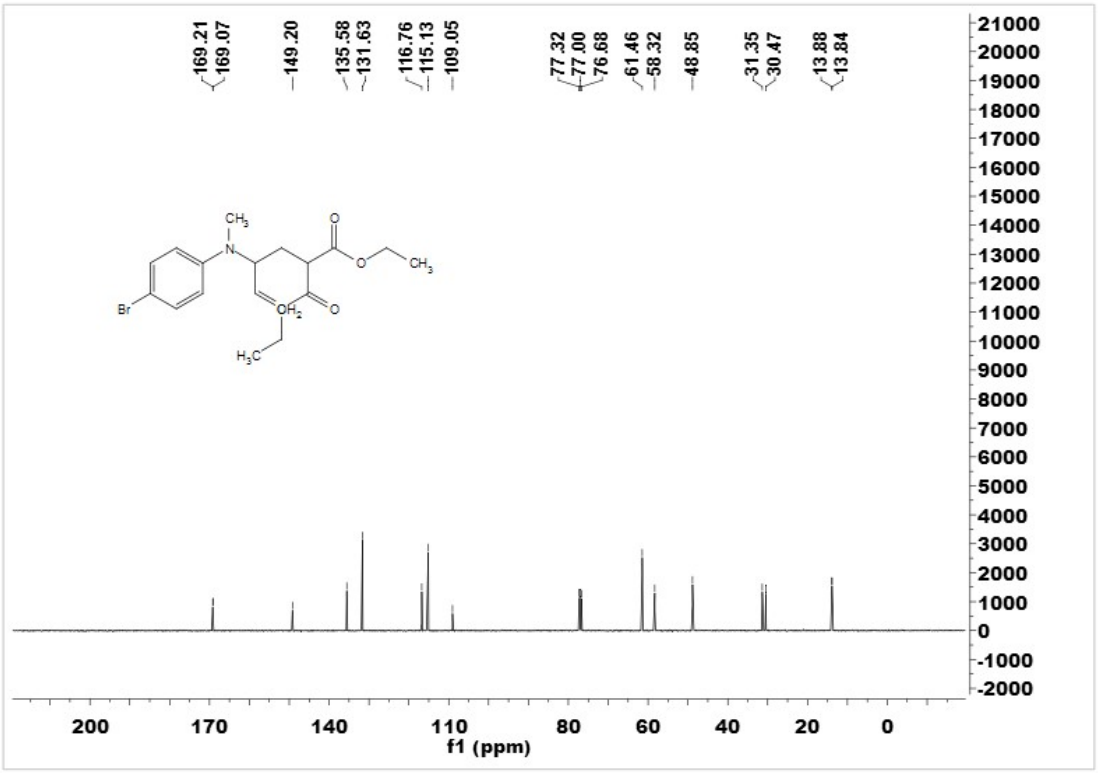
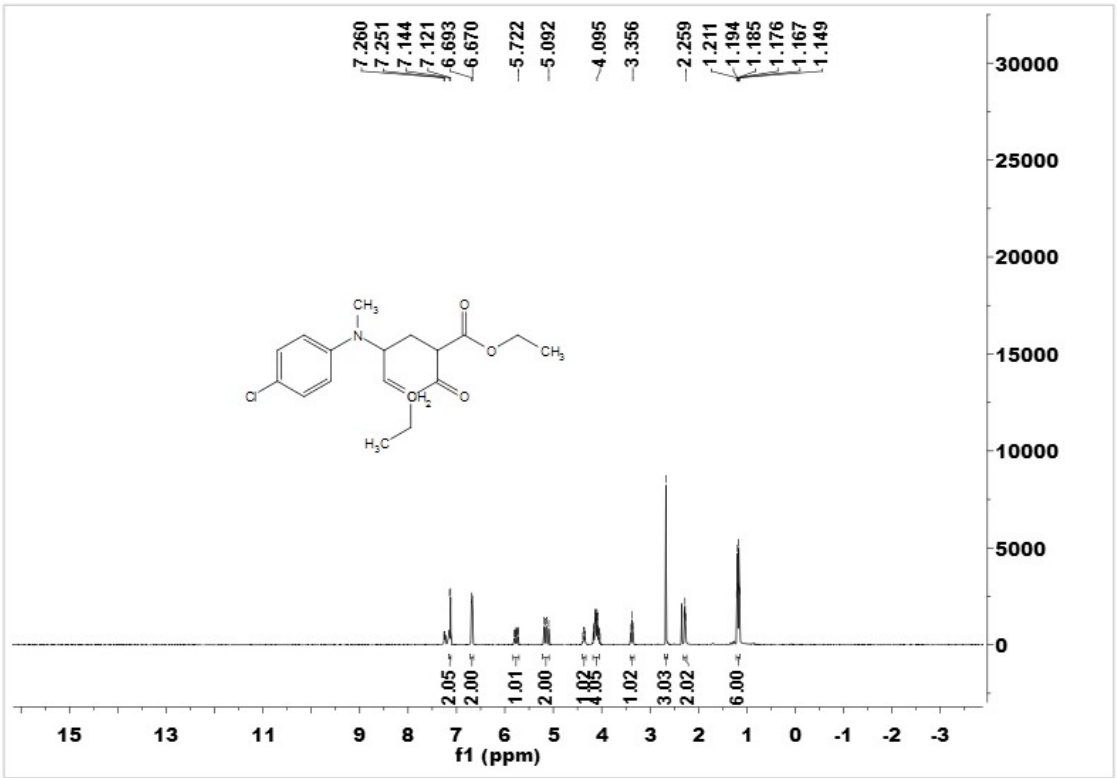
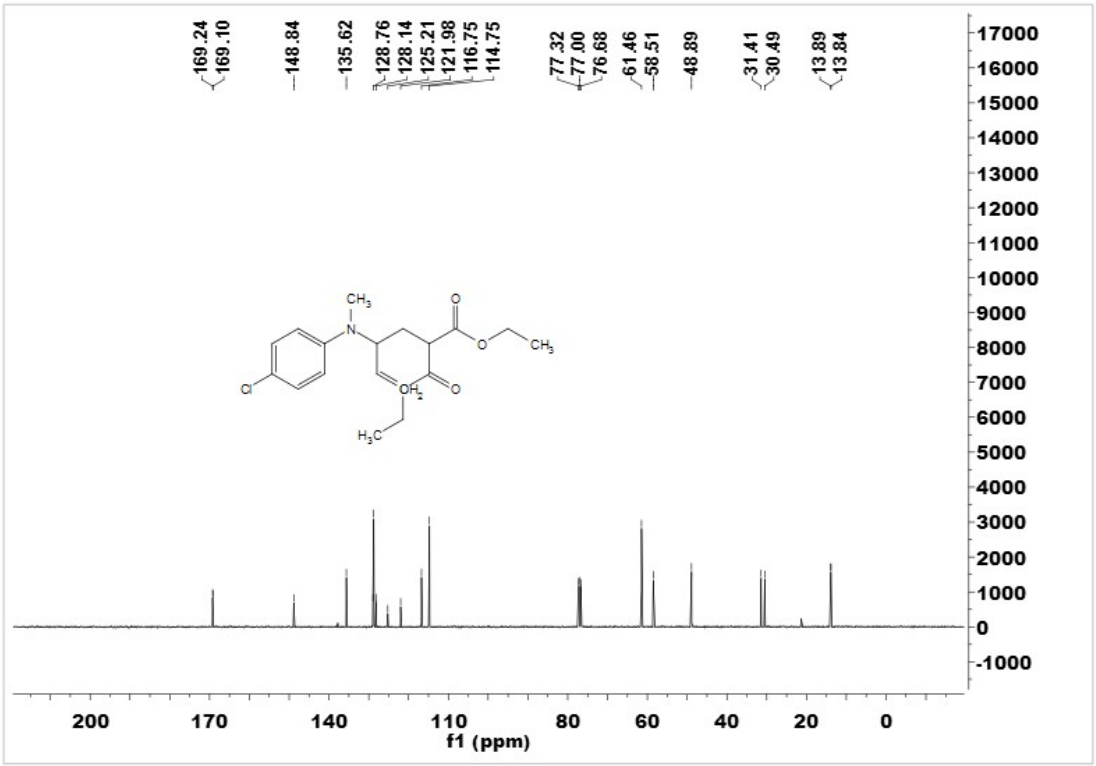


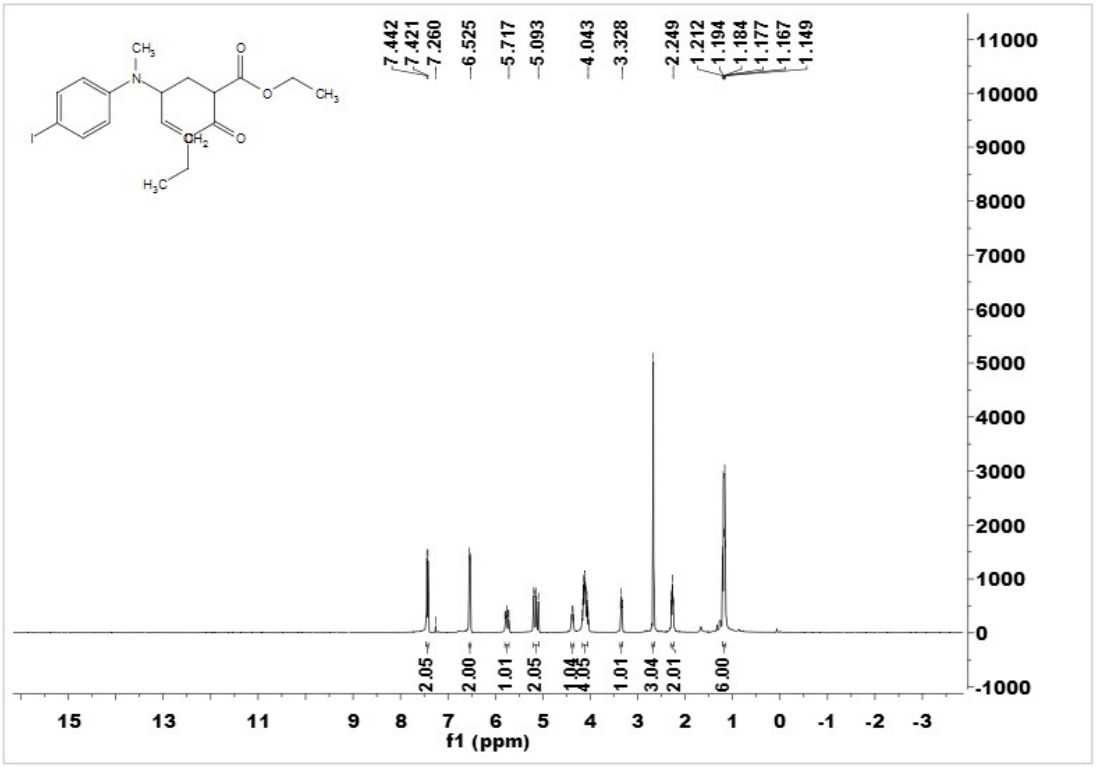


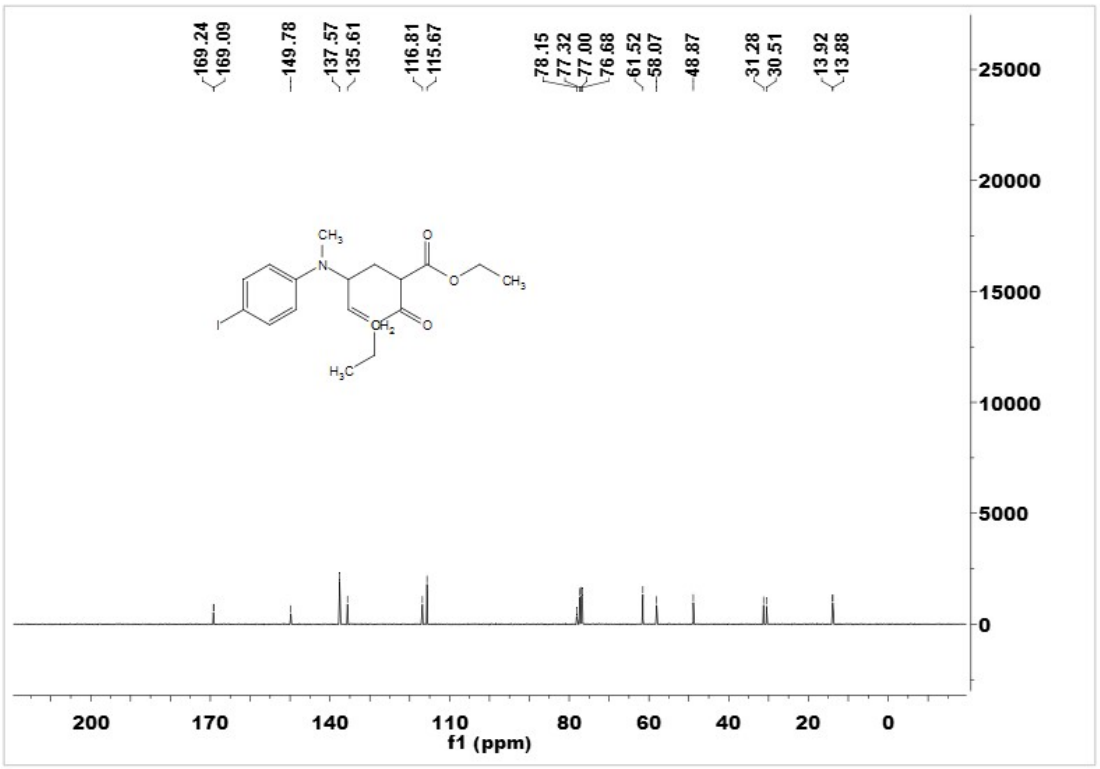
Diethyl 2-(2-((4-chlorophenyl)(methyl)amino)but-3-en-1-yl)malonate (4c)



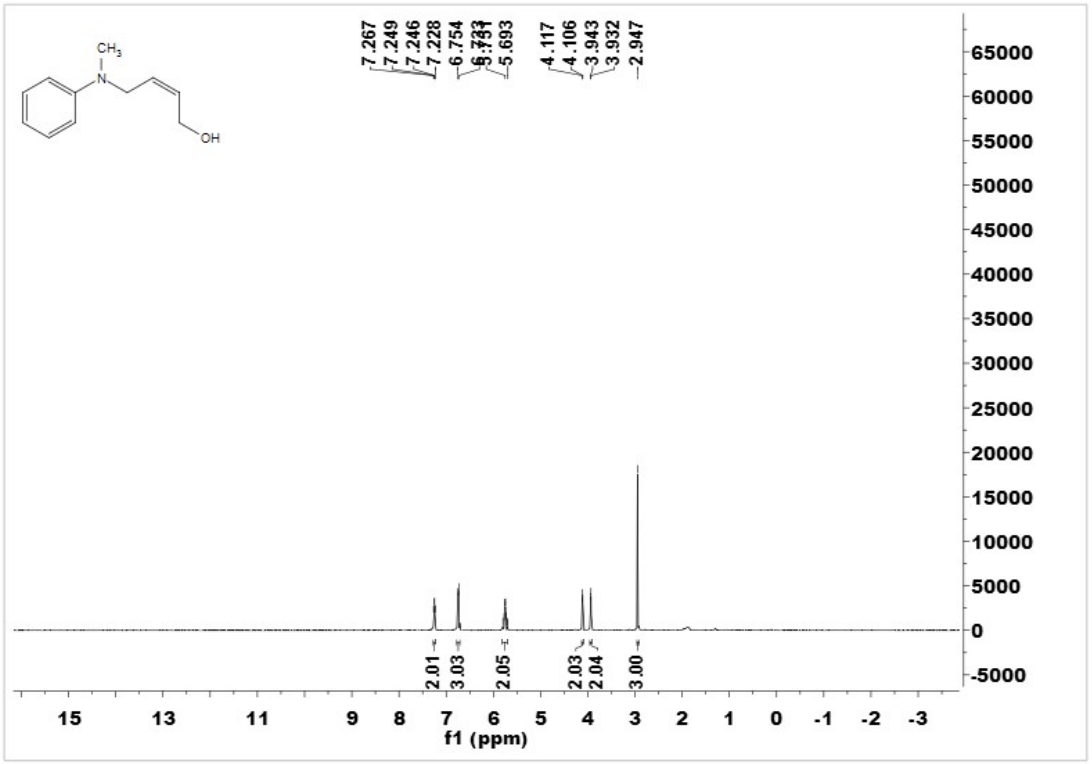


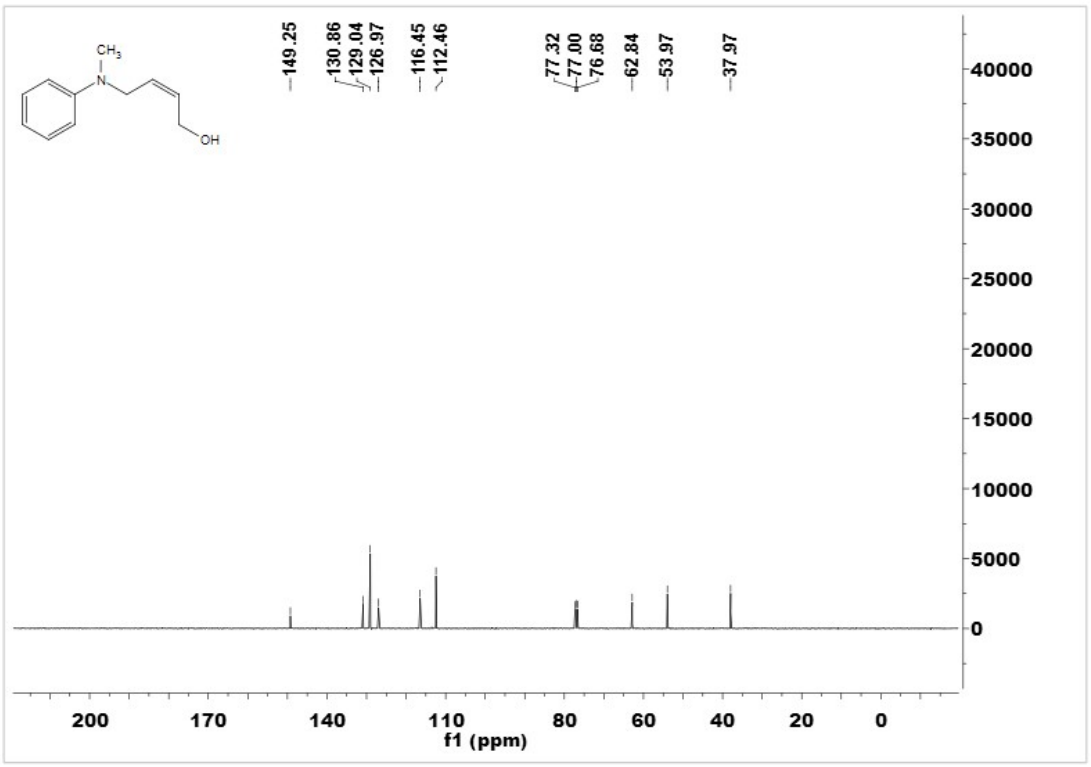
Diethyl 2-(2-((4-iodophenyl)(methyl)amino)but-3-en-1-yl)malonate (4d)



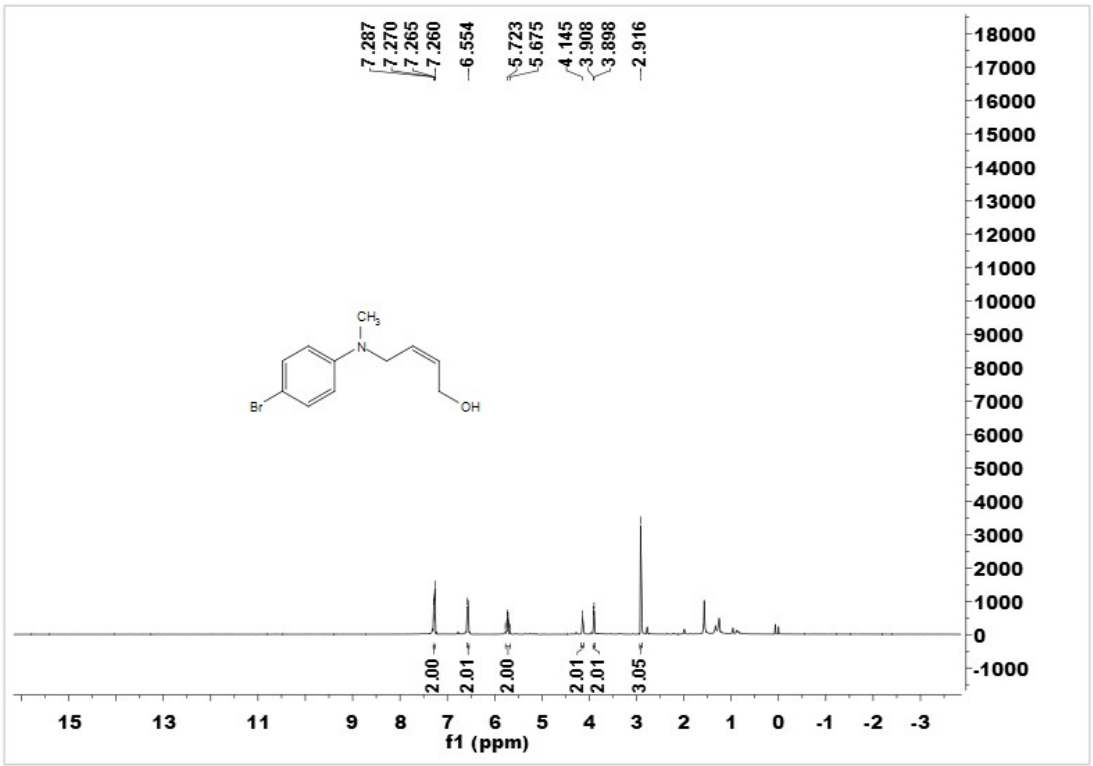


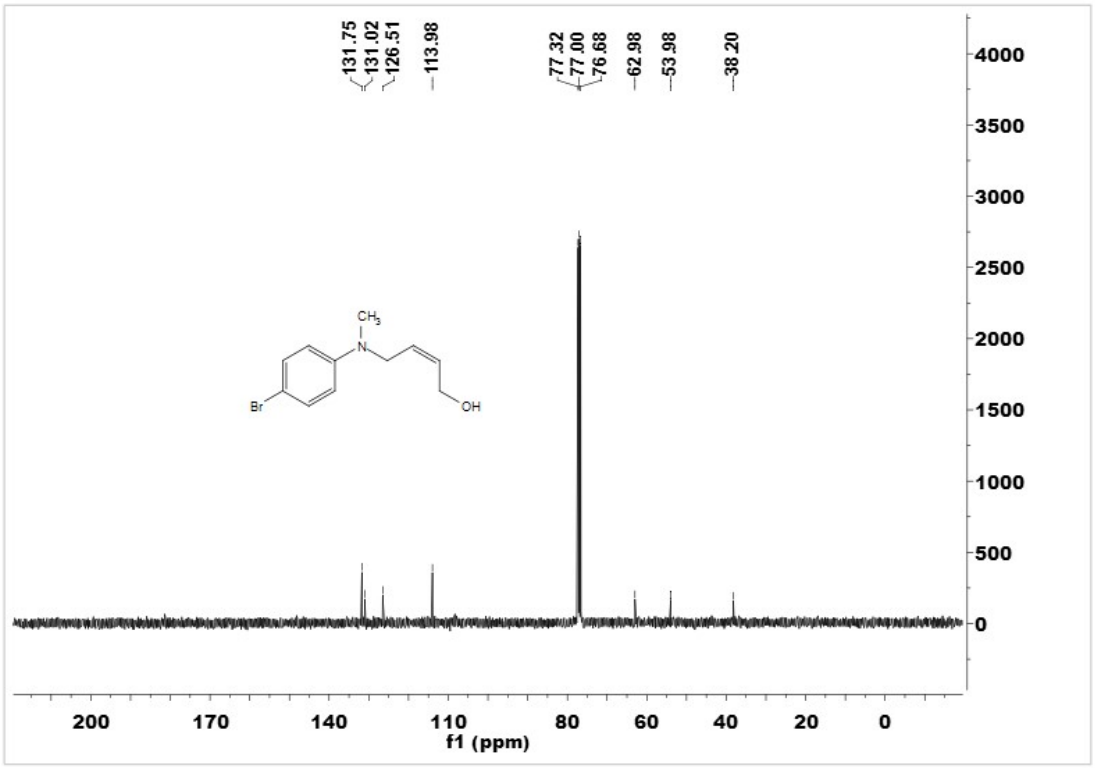
(*Z*)-4-(Methyl(phenyl)amino)but-2-en-1-ol (8a)



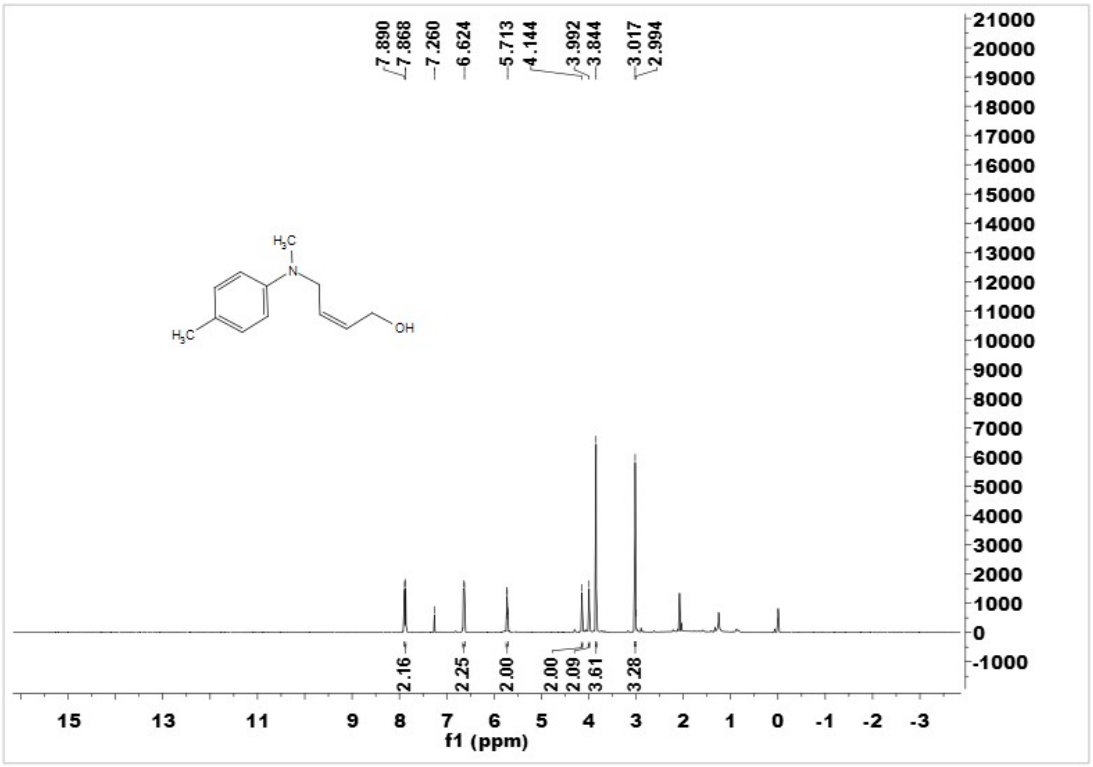


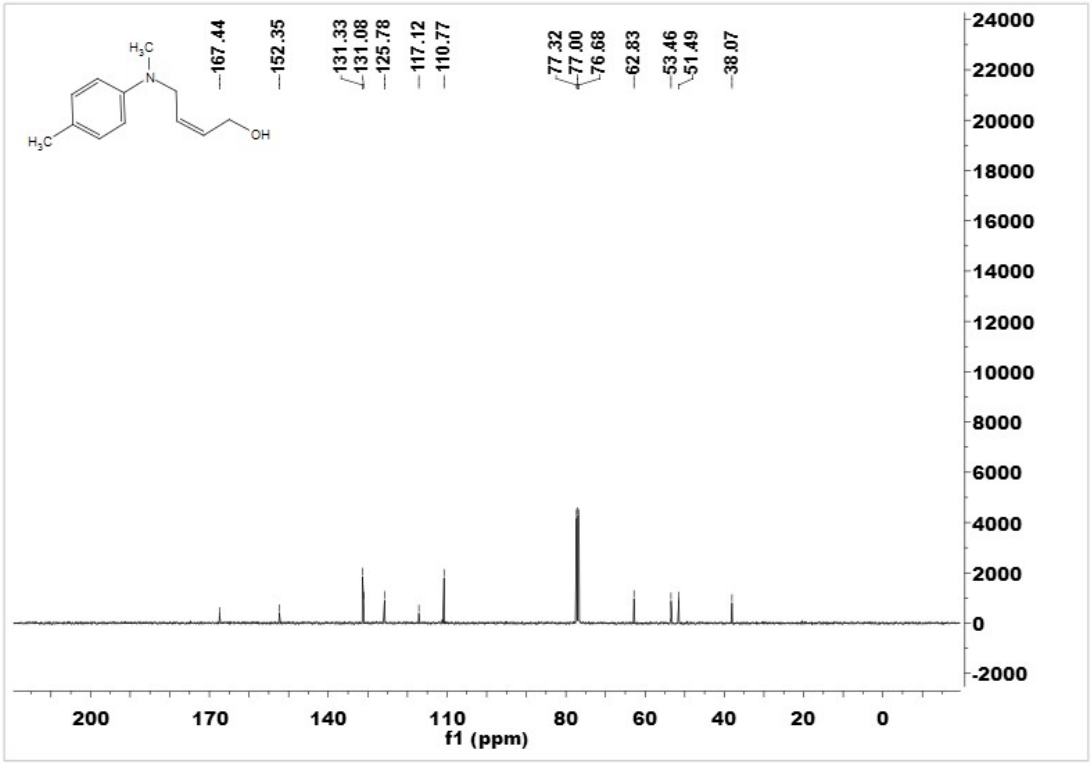
(*Z*)-4-((4-Bromophenyl)(methyl)amino)but-2-en-1-ol (8b)



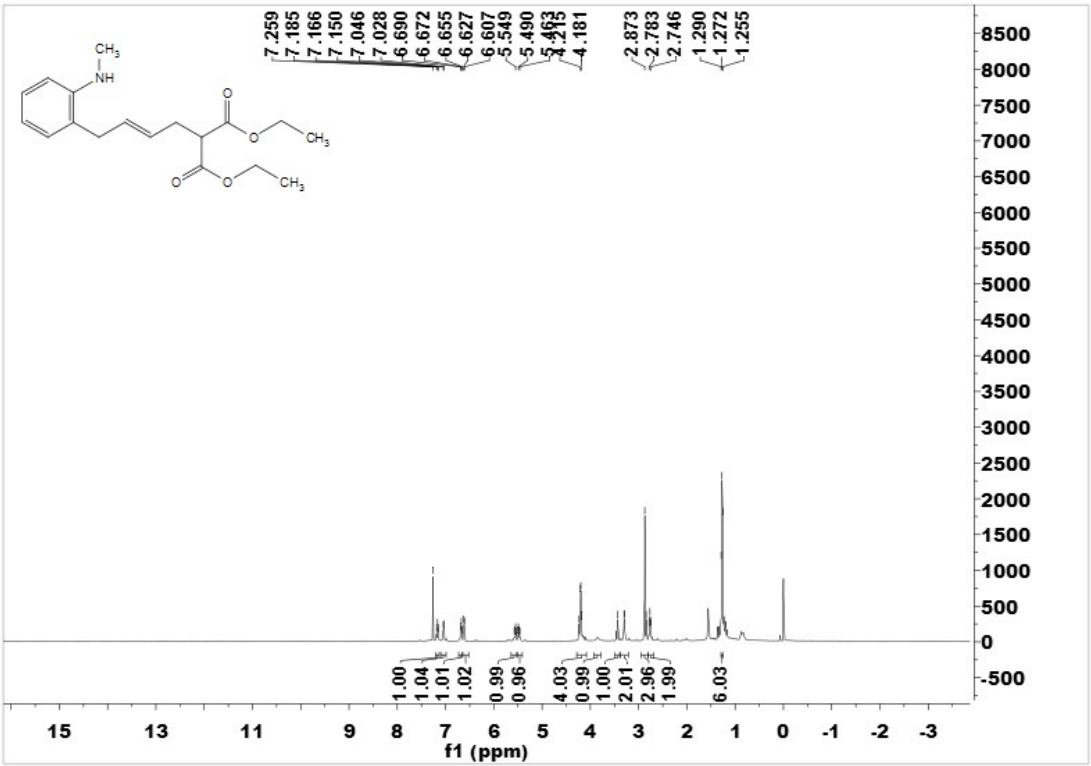


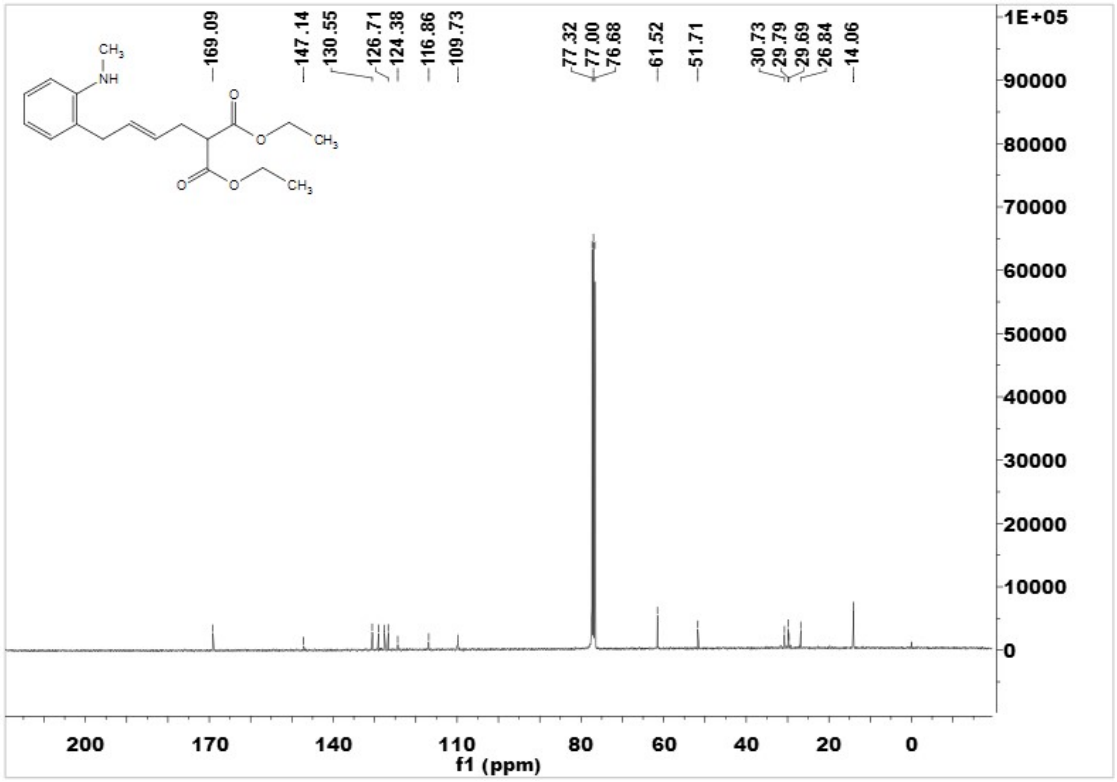
(*Z*)-4-(Methyl(*p*-tolyl)amino)but-2-en-1-ol (8c)



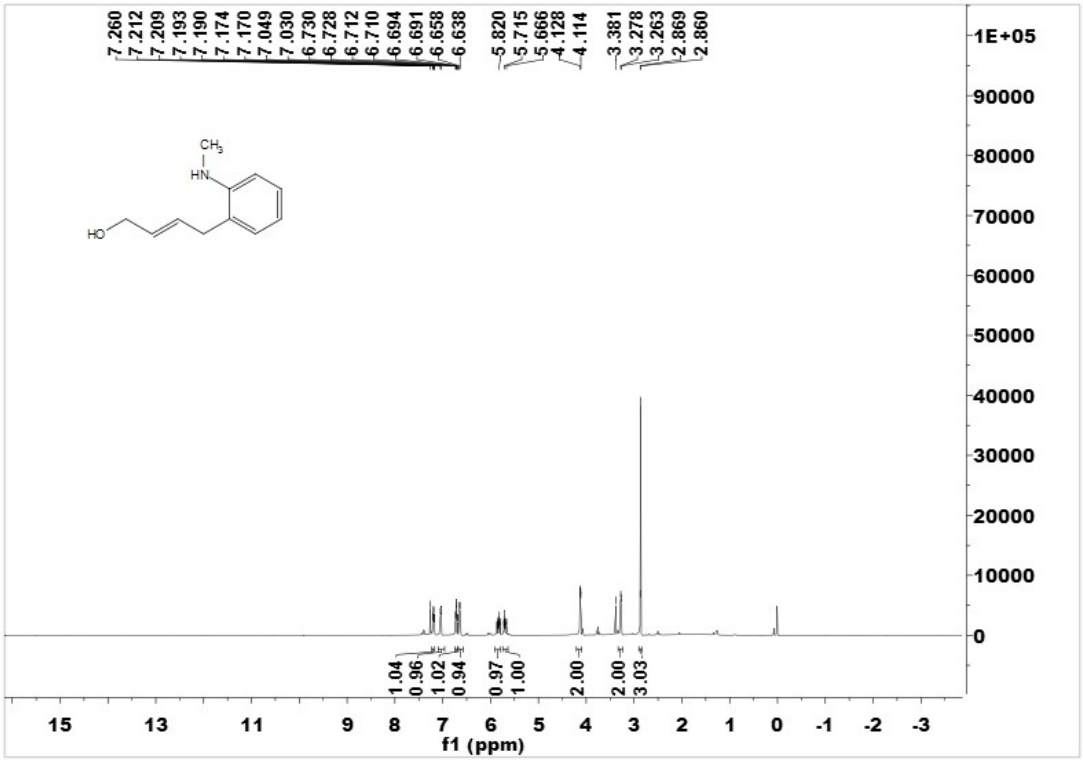


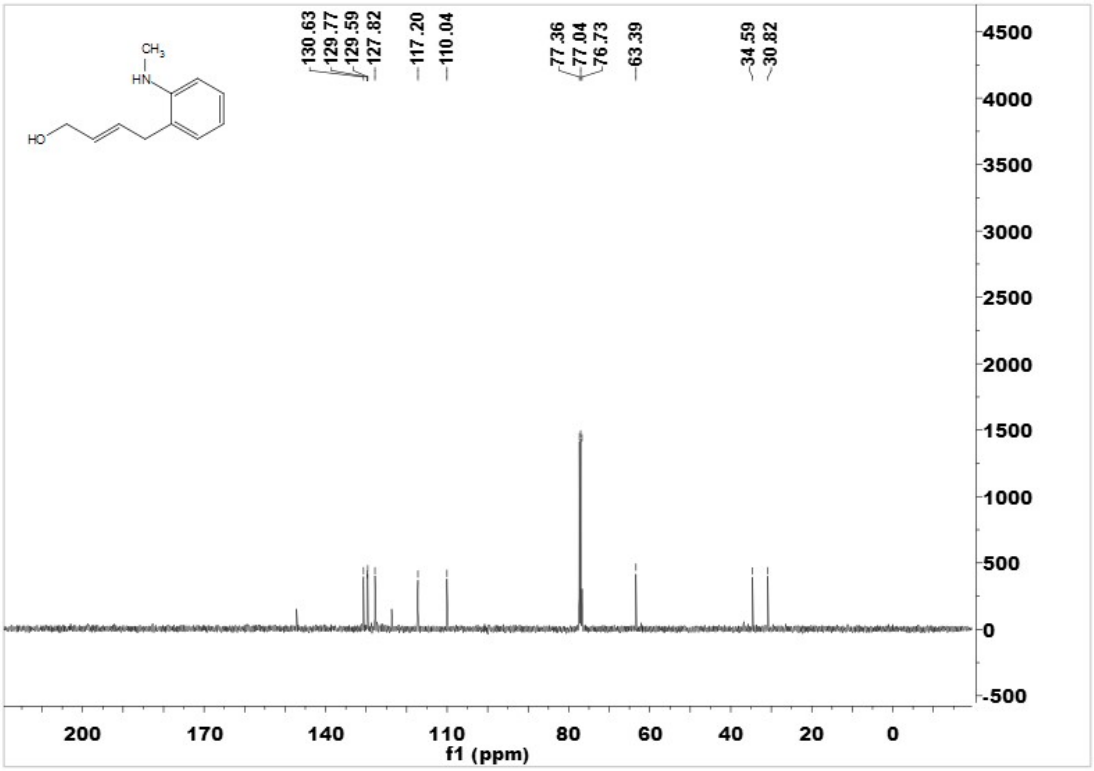
2-(Indolin-1-yl)but-3-en-1-ol (3a-1)



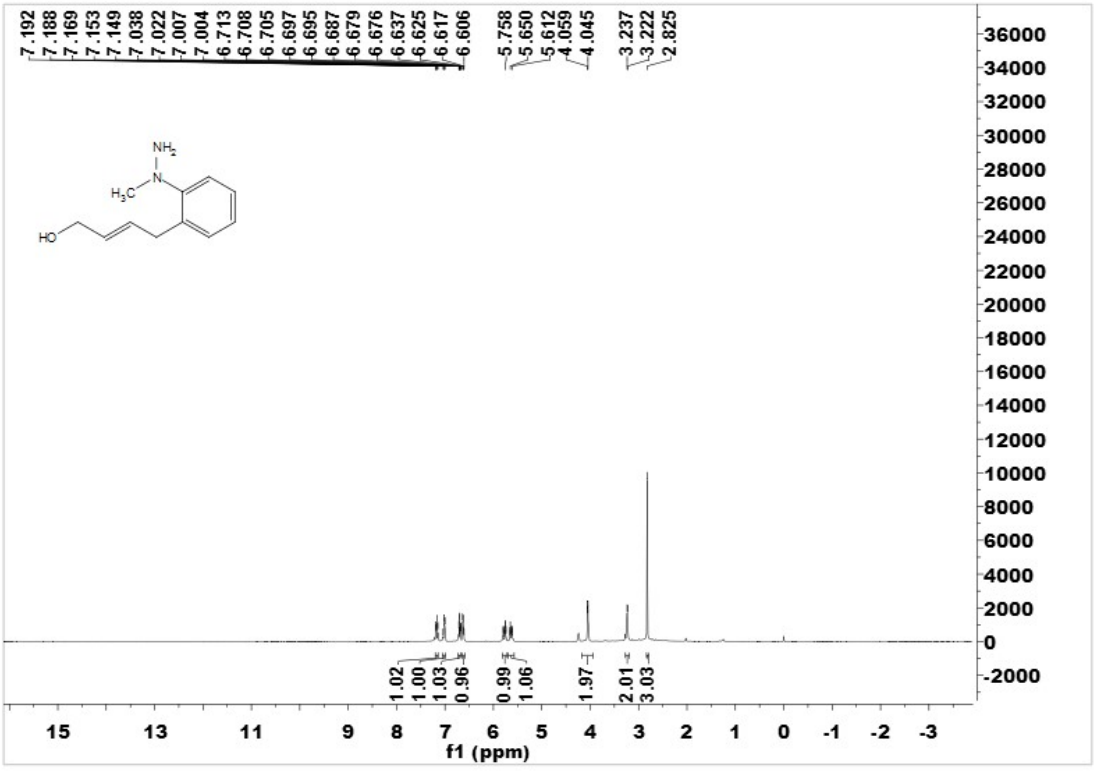


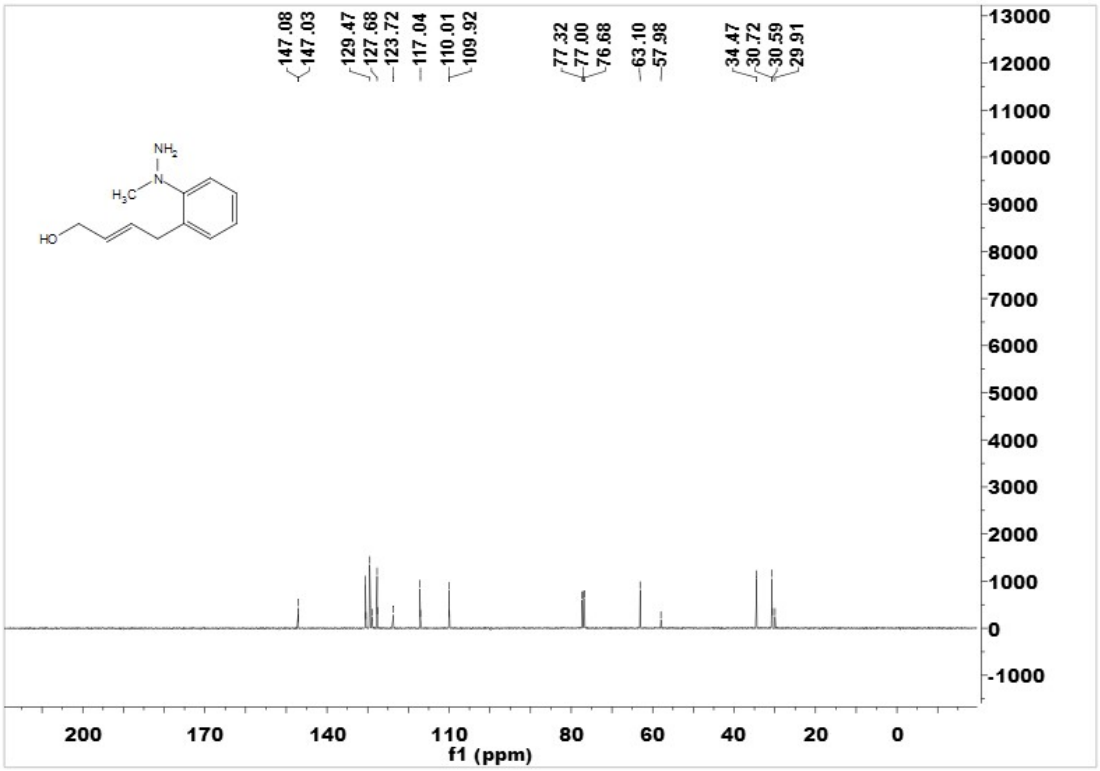
(*E*)-4-(2-(Methylamino)phenyl)but-2-en-1-ol (7a-1)



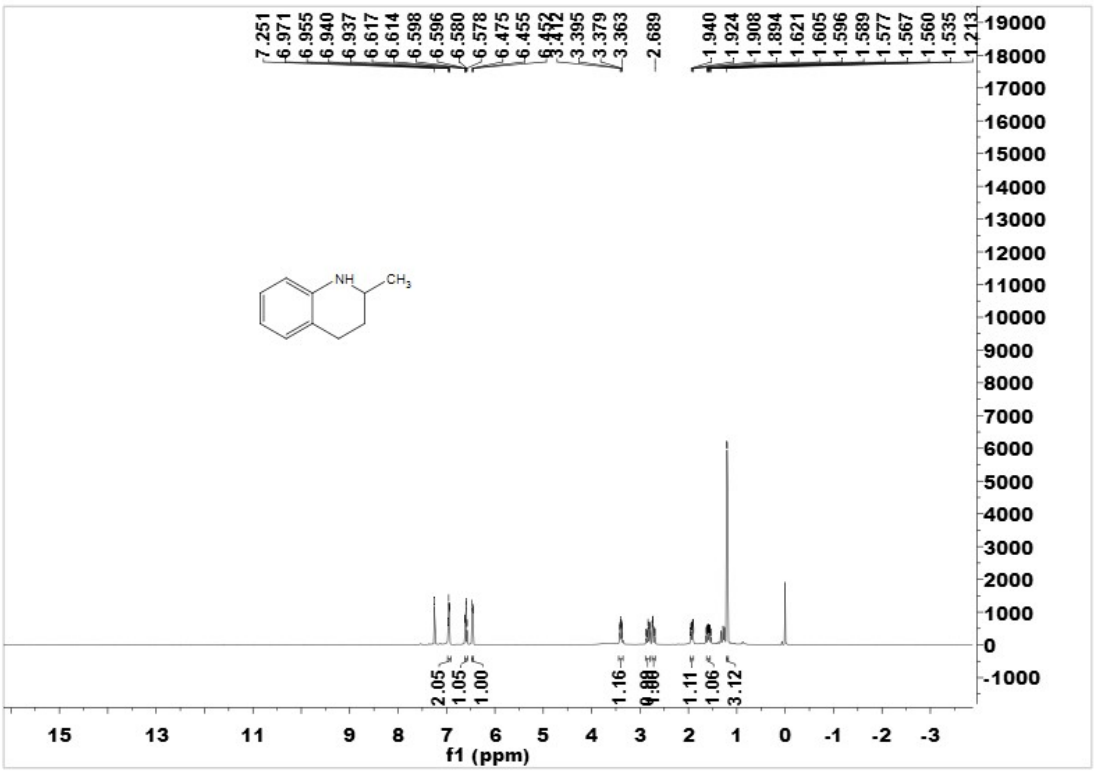


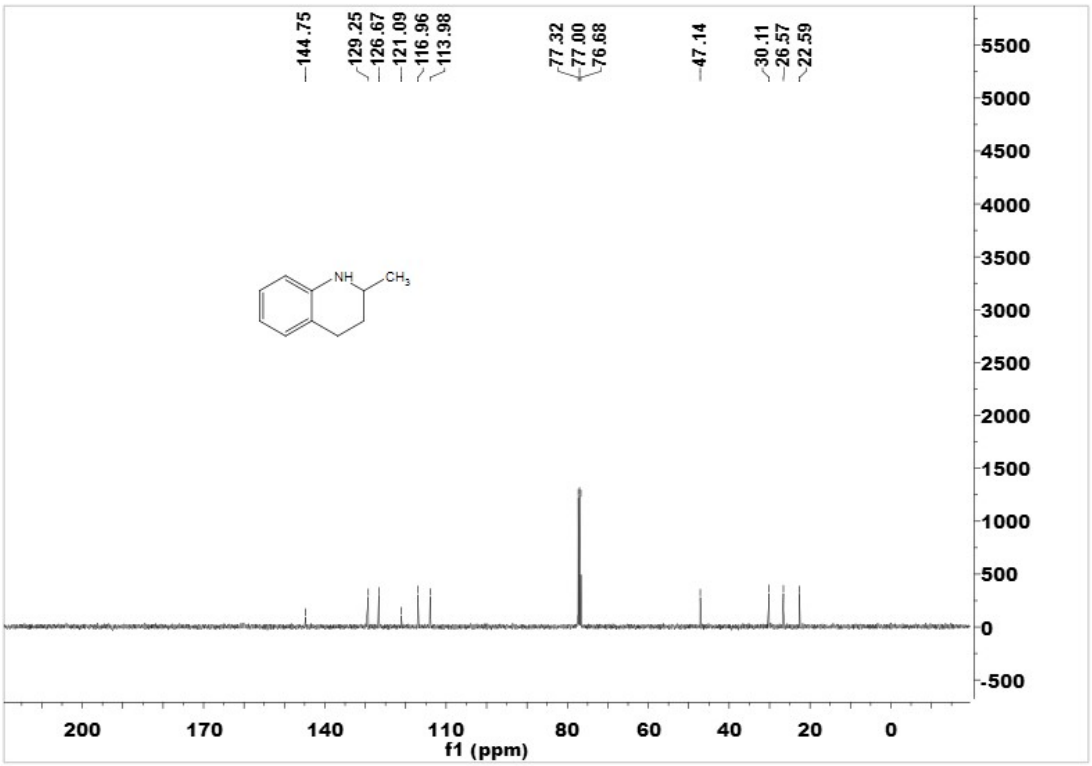
4-(2-(1-Methylhydrazineyl)phenyl)butan-1-ol (7a-2)



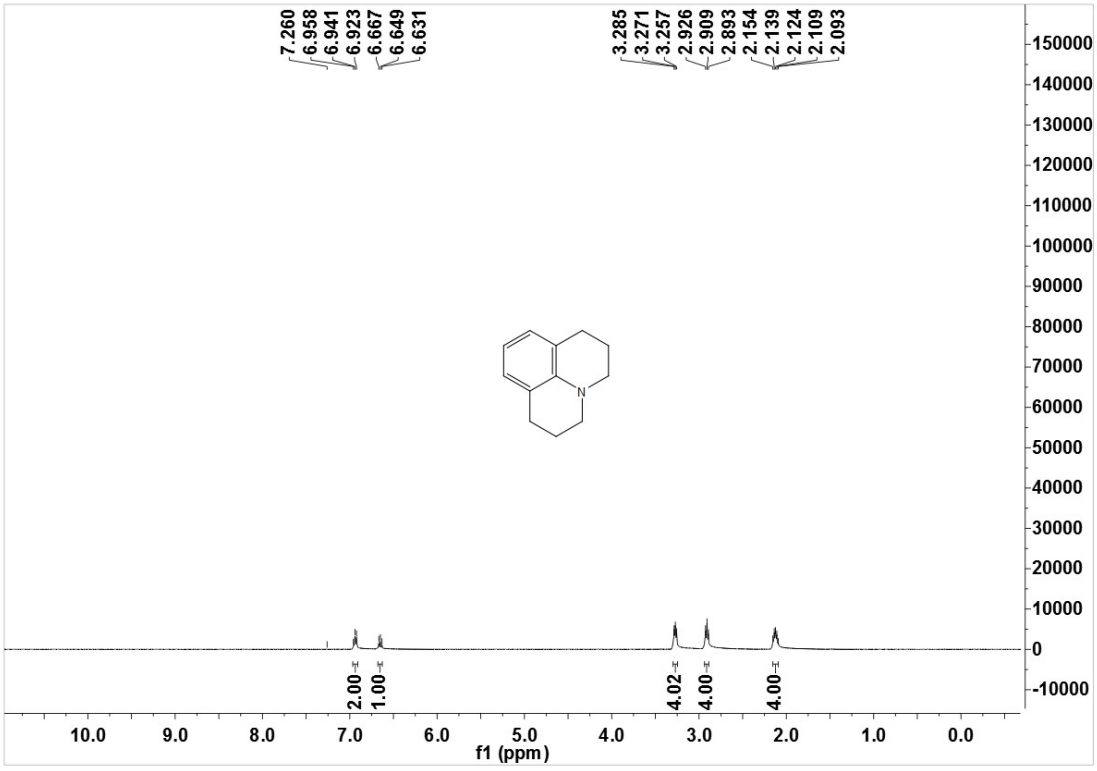


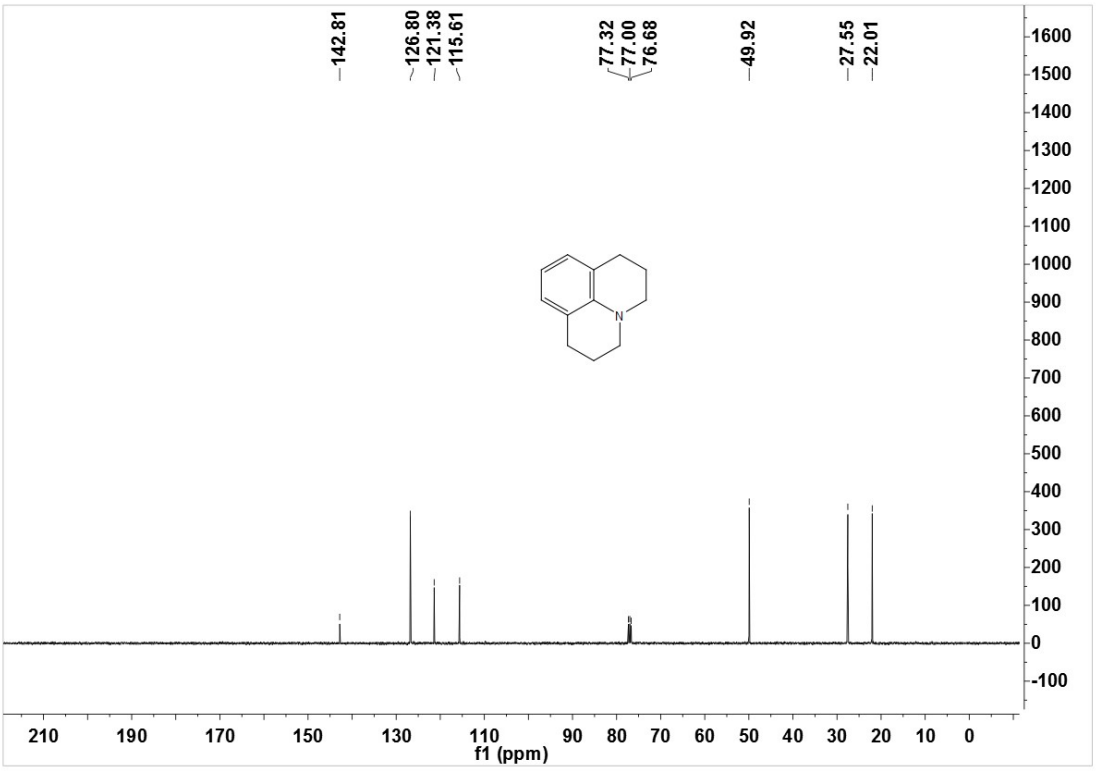
(*S*)-2-Methyl-1,2,3,4-tetrahydroquinoline (9r-1)



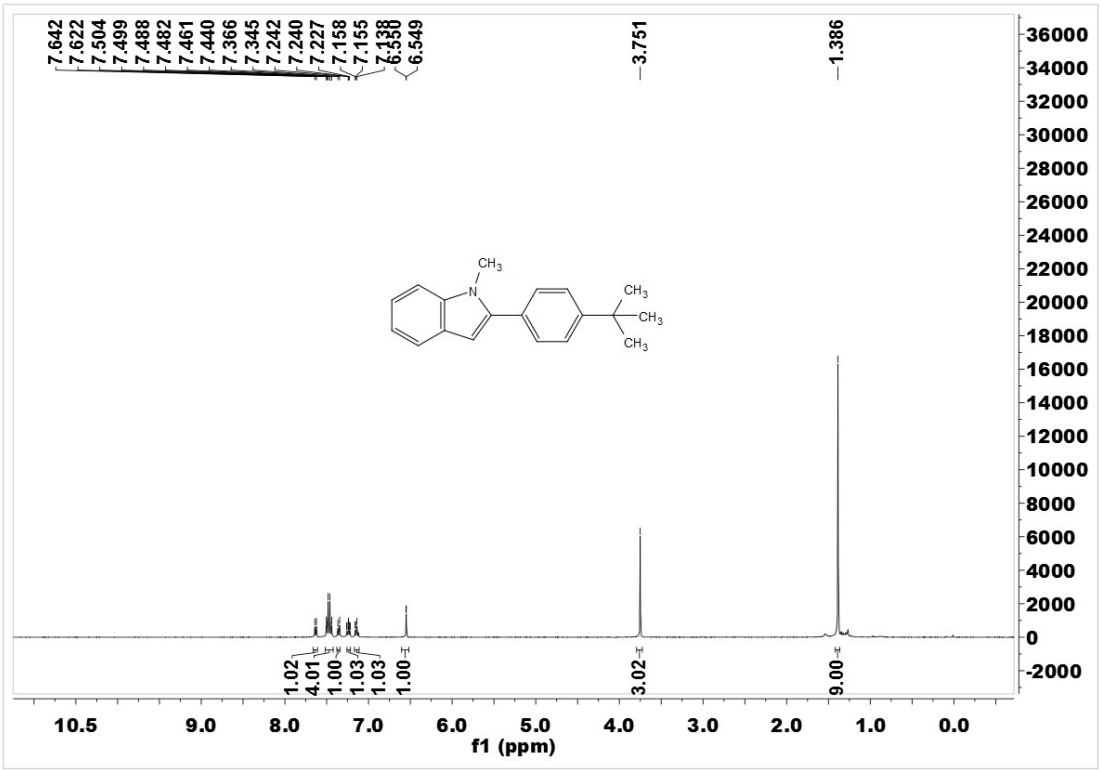


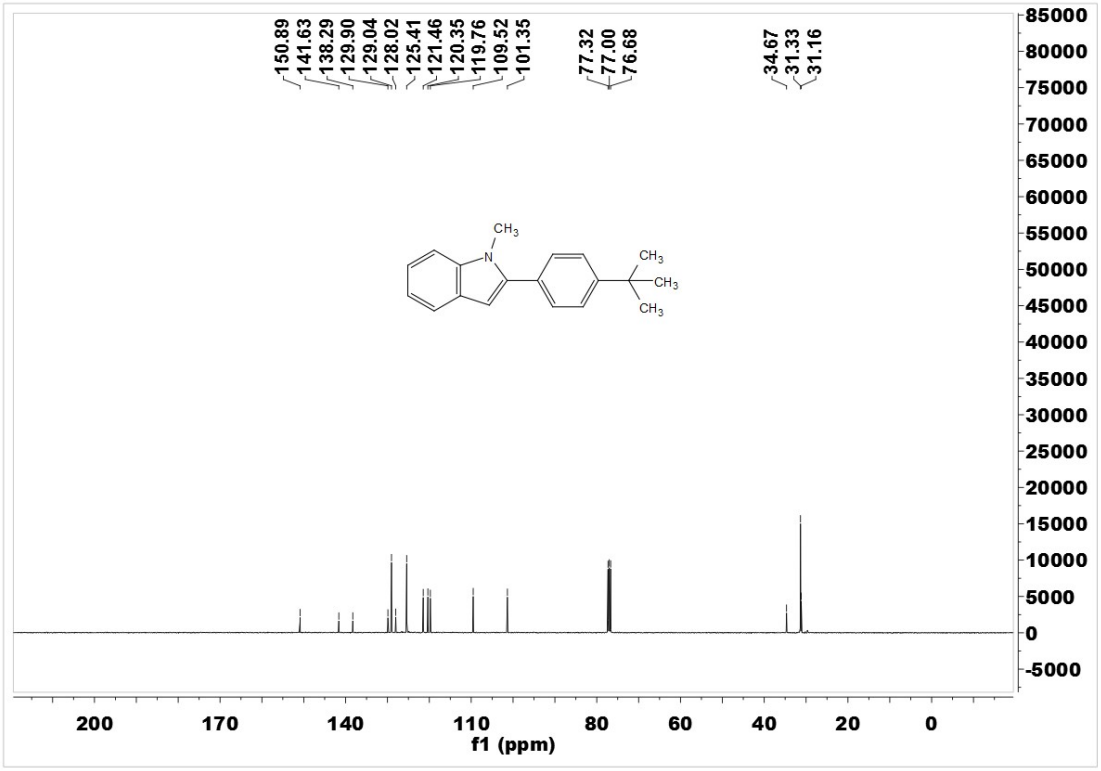
2,3,6,7-Ttrahydro-1*H*,5*H*-pyrido[3,2,1-ij]quinoline (13)



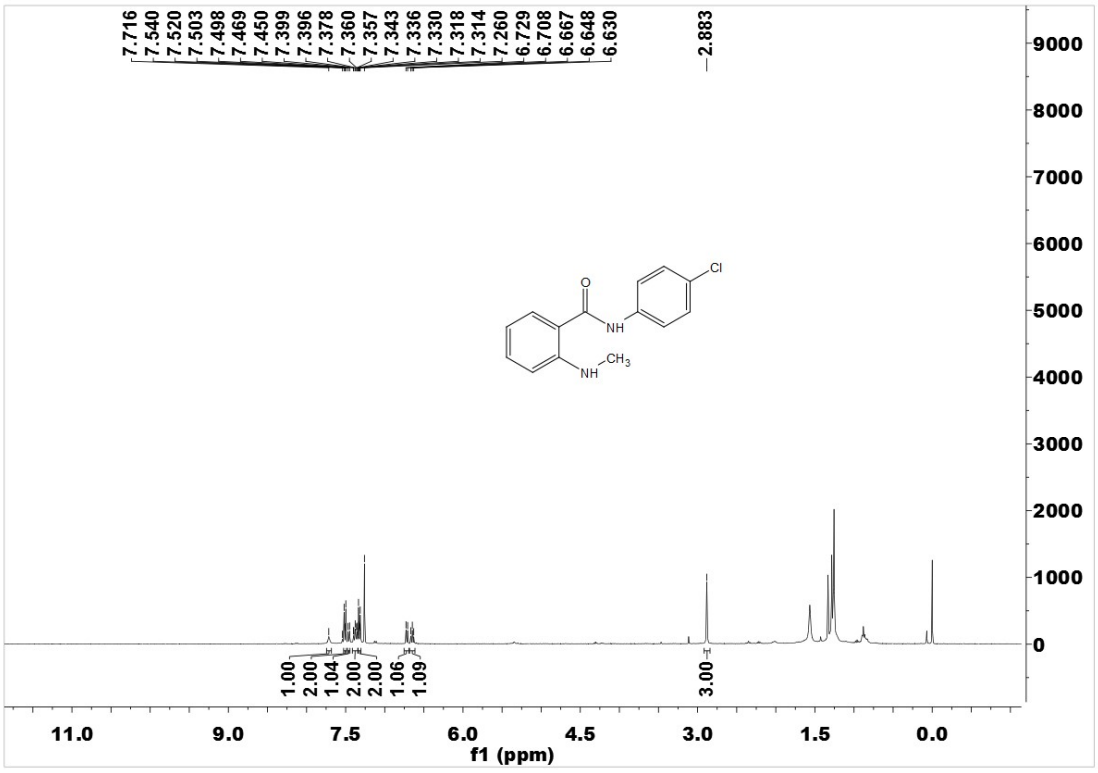


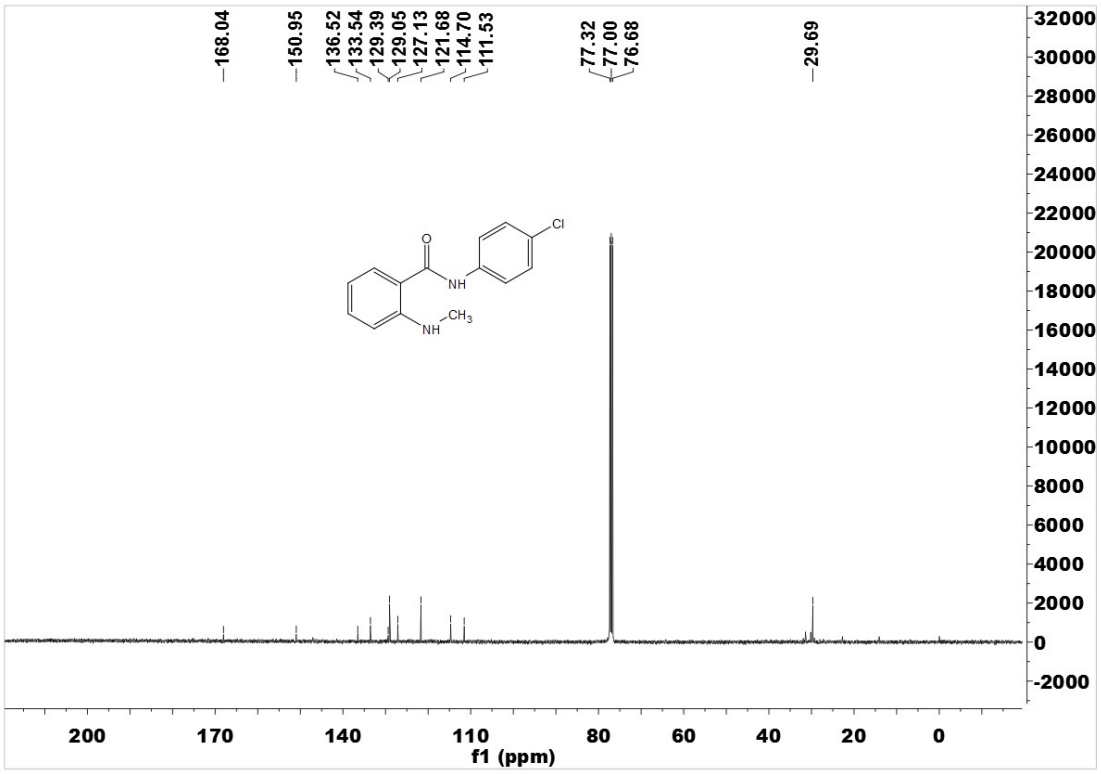
2-(4-(*tert*-Butyl)phenyl)-1-methyl-1*H*-indole (13a)





N-(4-Chlorophenyl)-2-(methylamino)benzamide (15a)

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