Supporting Information

Direct Aziridination of Nitroalkenes Affording N-Alkyl-C-nitroaziridines and the Subsequent Lewis Acid Mediated Isomerization to β-Nitroenamines

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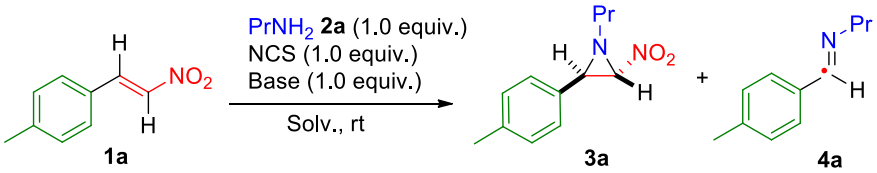
1. Optimization of aziridination conditions

Reaction conditions for aziridination was studied using nitrostyrene **1a** and propylamine **2a** (Table S-1). As depicted, the organic bases did not work enough, giving the aziridinated product **3a** in low yields even though the prolonged reaction time was used (entries 1–9). In some cases, the starting material **1a** was not consumed completely owing to the formation of ammonium nitronate of aza-Micheal adduct with another molecule of amine (entries 1–6). Although a complete conversion of **1a** was observed in the presence of more basic DBU, the imine **4a** was formed as a major product rather than the aziridine **3a** (entry 7). Compared to organic bases, inorganic bases such as carbonate and hydroxide were more suitable for this reaction, and the best result was obtained in the reaction using Cs_2CO_3 as the base (entries 10–14). Indeed, the use of Cs_2CO_3 as a base was proved to be crucial in a variety of aziridinations due to its proper solubility and basicity.[1] Next, different solvents were screened in this transformation. However, replacing THF with other solvents did not improve the yield of **3a** (entries 15–19). In order to examine whether low temperature could suppress the formation of imine **4a** or not, the reaction was conducted at -10 °C, however, both reactions affording **3a** and **4a** were almost suppressed (entry 20). A better result was obtained in the presence of a slightly excess amount of propylamine **2a** and N-chlorosuccinimide (NCS), giving **3a** in 85% yield (entry 21). Although higher loadings of propylamine and NCS were employed to promote the conversion of nitroalkene, the transformation did not proceed thoroughly, which might be caused by the equilibrium process between propylamine and NCS (entry 22).[2] Overall, the reaction conditions utilized in entry 21 were determined to be optimal. Instead of NCS, other halosuccinimides such as N-bromosuccinimide (NBS) and N-iodosuccinimide (NIS) were also examined, however, the aziridine was not formed owing to the higher steric hindrance of bromo and iodo groups than chloro group.

Table S-1. Optimization of reaction conditions for the aziridination of **1a**

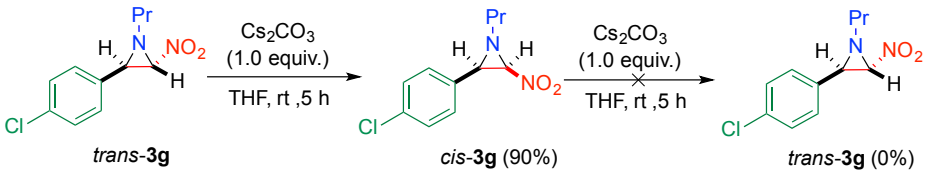


Entry	Base	Time (h)	Solvent	Yield[a] (%)		Recov.[a] (%)
				3a	**4a**	
1	Et_3N	5	THF	23	0	77
2	Et_3N	28	THF	21	39	38
3[b]	Et_3N	28	THF	17	32	51
4	$PrNH_2$	5	THF	17	19	64
5	$PrNH_2$	28	THF	39	20	38
6	Pyridine	28	THF	11	13	60
7	DBU	5	THF	0	74	0
8	*t*-BuOK	5	THF	52	48	0
9	AcONa	5	THF	29	3	37
10	K_2CO_3	5	THF	55	0	45
11	K_2CO_3	28	THF	73	18	5
12	NaOH	5	THF	47	9	33
13	NaOH	28	THF	71	22	0
14	Cs_2CO_3	5	THF	79	11	10
15	Cs_2CO_3	5	MeOH	14	86	0
16	Cs_2CO_3	5	MeCN	77	23	0
17	Cs_2CO_3	5	DMF	52	48	0
18	Cs_2CO_3	5	hexane	18	25	19
19	Cs_2CO_3	5	CH_2Cl_2	70	27	0
20[c]	Cs_2CO_3	5	THF	4	3	93
21[d]	**Cs_2CO_3**	**5**	**THF**	**85**	**6**	**9**
22[e]	Cs_2CO_3	5	THF	73	11	15

[a]Yield and recovery were determined by the integral of ^{1}H NMR of the reaction mixture. [b]2.0 Equiv. of Et_3N was used. [c]The reaction was conducted at -10℃. [d]1.1 Equiv. of propylamine and NCS was used. [e]The reaction involved 1.3 equiv. of propylamine and NCS together with 1.1 equiv. of Cs_2CO_3.

2. Study on interconversion between *trans*- and *cis*-aziridines

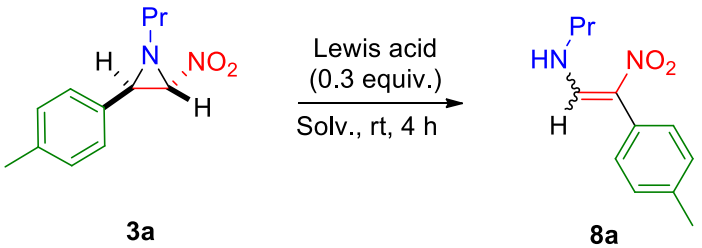
When *trans*-aziridine **3g** was treated in the presence of Cs_2CO_3, *cis*-**3g** was obtained in 90% yield. Similar conversion from *trans*-form to *cis*-form is often observed.[3] Contrary to this, the conversion from *cis*-**3g** to *trans*-**3g** did not occur at all under the same conditions. Thus *trans*-aziridines **3** was not formed *via cis*-aziridines.



3. Optimization of Lewis acid mediated isomerization

In order to identify suitable conditions for isomerization of C-nitroaziridine **3a** into β-aryl-β-nitroenamine **8a**, we commenced the investigation with the scanning of Lewis acids in MeCN (Table S-2, entries 1–10). Several Lewis acids were examined in this transformation, and $SnCl_2 \cdot 2H_2O$ was proved to undergo the reaction most efficiently, giving β-nitroenamine **8a** in 76% isolated yield as a mixture of *Z*/*E* isomers with a 93/7 ratio (entry 9). The replacement of MeCN with other solvents did not afford better results (entries 11-14). Moreover, a low temperature had no impact on the reaction (entry 15).

Table S-2. Screening of the Lewis acids for the rearrangement of the aryl group



3a **8a**

Entry	Lewis acid	Solvent	Yield[a] (%)
1	CuI	MeCN	0
2	$Cu(OAc)_2$	MeCN	0
3	TsOH	MeCN	47
4	$BF_3 \cdot Et_2O$	MeCN	63
5	$ZnCl_2$	MeCN	65
6	$FeCl_3$	MeCN	55
7	$FeCl_2 \cdot 4H_2O$	MeCN	66
8	$AlCl_3$	MeCN	32
9	**$SnCl_2 \cdot 2H_2O$**	**MeCN**	**81 (76[c])**
10	$SnCl_4 \cdot 5H_2O$	MeCN	69
11	$SnCl_2 \cdot 2H_2O$	THF	27
12	$SnCl_2 \cdot 2H_2O$	MeOH	15
13	$SnCl_2 \cdot 2H_2O$	hexane	0
14	$SnCl_2 \cdot 2H_2O$	CH_2Cl_2	62
15[b]	$SnCl_2 \cdot 2H_2O$	MeCN	78

[a]The yield was determined by ^{1}H NMR using dibromomethane as internal standard. [b]The reaction was conducted at -10°C. [c]Isolated yield based on **3a**.

4. Investigation on the instability of aziridines 3

In the present work, the isolated yields of aziridines **3** were considerably diminished upon treatment of the reaction mixture with silica gel column chromatography. In addition, the isolated aziridines also gradually decompose under ambient conditions. Hence, after formation of aziridine was confirmed by ^{1}H NMR, the reaction mixture was subjected to the subsequent conversion to nitroenamines **8** without isolation of the aziridines **3**. Here, the information about the instability of aziridines **3** was mentioned in detail.

4.1. Instability on silica gel

Although the yield of the conversion of β-nitrostyrene **1a** into the aziridine **3a** reached up to 85%, the isolated yield decreased to 31% after purification by silica gel column chromatography. Moreover, other aziridines were also found to decompose on silica gel except for several aziridines containing electron-rich aryls (**3b**, **3c**, **3m**, and **3n**), which were found to isomerize into the corresponding β-nitroenamines completely in the process of silica gel column chromatography due to the high reactivity.

4.2. Effect of temperature

As indicated, the aziridine **3a** in $CDCl_3$ gradually decomposed into *p*-tolualdehyde at room temperature (**Table S-3,** entries 1-4). Furthermore, decomposition of **3a** readily occurs within shorter time under upon heating (entries 5 and 6).

Table S-3. Decomposition of **3a**

Entry	Time (h)	Temp. (°C)	Ratio[a] of **3a**/*p*-tolualdehyde
1	—	rt	90/10
2	12	rt	70/30
3	24	rt	62/38
4	36	rt	50/50
5	1.5	45	75/25
6	2	60	43/57

[a]Ratio was determined by the integral values in the ^{1}H NMR.

The ^{1}H NMR spectra of the isolated aziridine **3a** were shown in Figure S-1, by which formation of *p*-tolualdehyde was observed as a result of decomposition of **3a**.

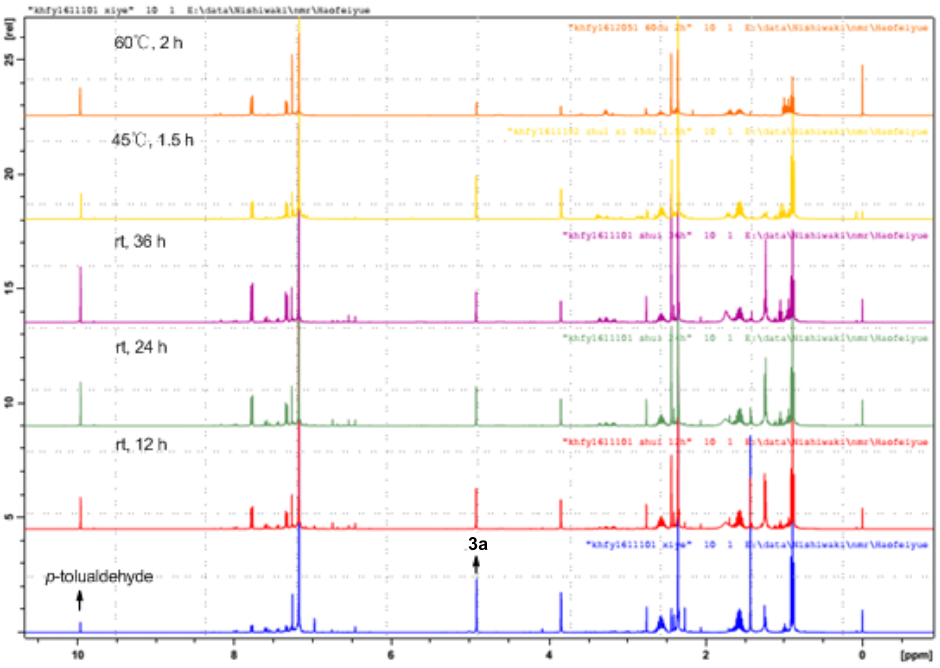


Figure S-1. Confirmation of decomposition of **3a** through ^{1}H NMR

5. Experimental section

5.1. General information

The melting points were determined on SRS-Optimelt Automated Melting Point System, and are uncorrected. All the reagents and solvents were commercially available and used as received. The ^{1}H NMR spectra were measured on a Bruker Ascend-400 at 400 MHz with tetramethylsilane as an internal standard. The ^{13}C NMR spectra were measured on a Bruker Ascend-400 at 100 MHz, and assignments of ^{13}C NMR spectra were performed by DEPT experiments. The high-resolution mass spectra were measured on an AB SCIEX Triple TOF^{TM} 4600. The IR spectra were recorded on a JASCO FT/IR-4200 spectrometer. As observed for aziridine **3a**, the isolated yield was considerably diminished compared with NMR yield because of the instability under ambient conditions and on silica gel. Hence, aziridines **3** were subjected to the subsequent reactions without further purification. The yields of unpurified aziridines were determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as internal standard. Some signals of *E*-isomers of nitroenamines **8** could not be detected in ^{1}H NMR and ^{13}C NMR owing to the low concentration of the compounds in the deuterated solvent. Hence, only spectrum data of *Z*-isomer were shown.

5.2. General procedure for the preparation of nitroalkenes

(*E*)-Aromatic nitrostyrenes **1a**–**k** and **1m**–**o** were successfully synthesized in moderate to good yields upon treatment of aromatic aldehydes with nitromethane or nitroethane in the presence of ammonium acetate.[3]

α-Nitro-β-arylenoate **1l** was prepared through the condensation reaction of *p*-tolualdehyde with ethyl nitroacetate in the presence of dimethylamine hydrochloride.[4]

(*Z*)-nitrostyrene **1e'** was prepared through photoisomerization of the (*E*)-nitrostyrene under the irradiation of a mercury-vapour lamp.[5] It was also confirmed that *Z*-isomer **1e'** did not isomerize to *E*-isomer **1e** under the reaction conditions employed for aziridination.

Aliphatic nitroalkene **1p** was prepared through the condensation reaction of aliphatic aldehyde with nitromethane in the presence of sodium hydroxide followed by MsCl–mediated dehydration.[6]

5.3. General procedure for one-pot synthesis of *trans*-*N*-alkyl-*C*-nitroaziridines 3

***trans*-2-(4-methylphenyl)-3-nitro-1-propylaziridine (3a)**

To a solution of (*E*)-β-nitrostyrenes **1a** (198 mg, 1.22 mmol) and propylamine **2a** (110 μL, 1.34 mmol) in THF (5.0 mL), were added NCS (178 mg, 1.34 mmol) and Cs_2CO_3 (396 mg, 1.22 mmol) successively, and the resultant mixture was stirred at room temperature for 5 h. Then, the solvent was evaporated to afford a reaction mixture as a purple residue, which underwent aqueous workup followed by extraction using CH_2Cl_2. The crude aziridines were obtained as oil after concentration of organic phase, in which aziridine **3a** was included in 72% NMR yield. The mixture was subjected to column chromatography on silica gel to isolate **3a** (eluted with CH_2Cl_2/hexane = 1:2, 82.4 mg, 0.38 mmol, 31% yield) as a yellow oil.

^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.50–1.65 (m, 2H), 2.36 (s, 3H), 2.51–2.64 (m, 2H), 3.85 (d, *J* = 1.2 Hz, 1H), 4.90 (d, *J* = 1.2 Hz, 1H), 7.17 (s, 4H, overlap); ^{13}C NMR ($CDCl_3$) δ 11.6 (CH_3), 21.2 (CH_3), 22.6 (CH_2), 48.3 (CH), 51.9 (CH_2), 75.2 (CH), 128.2 (CH), 128.5 (C), 129.4 (CH), 138.8 (C); IR (ATR/cm^{-1}) ν 1559; HRMS (ESI/TOF) Calcd for $C_{12}H_{16}N_2O_2Na$ [$(M+Na)^+$]: 243.1104, found 243.1100.

When other substrates were used, reactions were conducted in a similar way with 0.61 mmol scale.

***trans*-2-(4-methoxyphenyl)-3-nitro-1-propylaziridine (3b)**

Yellow oil (0.32 mmol, 53%, determined by ^{1}H NMR). ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.49–1.64 (m, 2H), 2.50–2.62 (m, 2H), 3.81 (s, 3H), 3.83 (d, *J* = 1.2 Hz, 1H), 4.88 (d, *J* = 1.2 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 11.6 (CH_3), 22.6 (CH_2), 48.1 (CH), 51.8 (CH_2), 55.3 (CH_3), 75.2 (CH); IR (ATR/cm^{-1}) ν 1554; HRMS (ESI/TOF) Calcd for $C_{12}H_{17}N_2O_3$ [$(M+H)^+$]: 237.1234, found 237.1238.

Note: Compound **3b** was found to completely isomerize into the corresponding β-nitroenamine **8b** in the process of silica gel column chromatography. Therefore, the resultant crude product of **3b** was used for structural characterization. Although the aromatic signals of **3b** in the low field of ^{13}C NMR were ambiguous due to the complexity of the crude product, the featured signals assigned for C2, C3 and *N*-propyl group were definitely detected.

***trans*-2-(2-methoxyphenyl)-3-nitro-1-propylaziridine (3c)**

Yellow oil (0.33 mmol, 54% yield, determined by ^{1}H NMR). ^{1}H NMR ($CDCl_3$) δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.53–1.63 (m, 2H), 2.36–2.42 (m, 1H), 2.58–2.66 (m, 1H), 3.87 (s, 3H), 4.01 (d, *J* = 1.6 Hz, 1H), 4.90 (d, *J* = 1.6 Hz, 1H), 6.89–6.94 (m, 2H), 7.17 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.17 (ddd, *J* = 1.6, 7.6, 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 11.6 (CH_3), 22.5 (CH_2), 45.1 (CH), 52.1 (CH_2), 55.4 (CH_3), 75.2 (CH); IR (ATR/cm^{-1}) ν 1556; HRMS (ESI/TOF) Calcd for $C_{12}H_{17}N_2O_3$ [$(M+H)^+$]: 237.1234, found 237.1241.

Note: Compound **3c** was found to completely isomerize into the corresponding β-nitroenamine **8c** in the process of silica gel column chromatography. Therefore, the resultant crude product of **3c** was used for structural characterization. Although the aromatic signals of **3c** in the low field of ^{13}C NMR were ambiguous due to the complexity of the crude product, the featured signals assigned for C2, C3 and *N*-propyl group were definitely detected.

***trans*-2-(3,5-dimethoxyphenyl)-3-nitro-1-propylaziridine (3d)**

Yellow oil (101.9 mg, 0.38 mol, 63% yield). ^{1}H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.6 Hz, 3H), 1.53–1.67 (m, 2H), 2.58–2.73 (m, 2H), 3.78 (d, *J* = 1.2 Hz, 1H), 3.79 (s, 6H), 4.88 (d, *J* = 1.2 Hz, 1H), 6.43 (s, 3H, overlap); ^{13}C NMR ($CDCl_3$) δ 11.6 (CH_3), 22.6 (CH_2), 48.3 (CH), 52.0 (CH_2), 55.4 (CH_3), 75.2 (CH), 100.5 (CH), 106.1 (CH), 134.5 (C), 161.1 (C); IR (ATR/cm^{-1}) ν 1554; HRMS (ESI/TOF) Calcd for $C_{13}H_{19}N_2O_4$ [$(M+H)^+$]: 267.1339, found 267.1326.

***trans*-3-nitro-2-phenyl-1-propylaziridine (3e)**

Yellow oil (78.3 mg, 0.38 mmol, 63% yield). ^{1}H NMR ($CDCl_3$) δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.52-1.68 (m, 2H), 2.56-2.67 (m, 2H), 3.87 (d, *J* = 1.2 Hz, 1H), 4.93 (d, *J* =

1.2 Hz, 1H), 7.28-7.30 (m, 2H), 7.36-7.39 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 11.6 (CH_3), 22.6 (CH_2), 48.3 (CH), 52.0 (CH_2), 75.2 (CH), 128.2 (CH), 128.7 (CH), 128.8 (CH), 132.0 (C); IR (ATR/cm^{-1}) ν 1558; HRMS (ESI/TOF) Calcd for $C_{11}H_{15}N_2O_2$ [$(M+H)^+$]: 207.1128, found 207.1124.

***trans*-2-(4-bromophenyl)-3-nitro-1-propylaziridine (3f)**

Yellow oil (96.3 mg, 0.34 mmol, 56% yield). ^{1}H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7.2 Hz, 3H), 1.52–1.66 (m, 2H), 2.62–2.73 (m, 2H), 3.78 (d, *J* = 1.2 Hz, 1H), 4.87 (d, *J* = 1.2 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 11.6 (CH_3), 22.6 (CH_2), 47.5 (CH), 52.0 (CH_2), 75.1 (CH), 123.0 (C), 129.5 (CH), 131.6 (C), 131.9 (CH); IR (ATR/cm^{-1}) ν 1559; HRMS (ESI/TOF) Calcd for $C_{11}H_{14}BrN_2O_2$ [$(M+H)^+$]: 285.0233, found 285.0222.

***trans*-2-(4-chlorophenyl)-3-nitro-1-propylaziridine (3g)**

Yellow oil (73.9 mg, 0.31 mmol, 51% yield). ^{1}H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7.2 Hz, 3H), 1.50–1.68 (m, 2H), 2.62–2.73 (m, 2H), 3.79 (d, *J* = 1.2 Hz, 1H), 4.87 (d, *J* = 1.2 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 11.6 (CH_3), 22.6 (CH_2), 47.4 (CH), 52.0 (CH_2), 75.2 (CH), 129.0 (CH), 129.2 (CH), 131.1 (C), 134.9 (C); IR (ATR/cm^{-1}) ν 1559; HRMS (ESI/TOF) Calcd for $C_{11}H_{14}ClN_2O_2$ [$(M+H)^+$]: 241.0738, found 241.0727.

***trans*-2-(4-cyanophenyl)-3-nitro-1-propylaziridine (3h)**

Yellow oil (42.0 mg, 0.18 mmol, 30% yield). ^{1}H NMR ($CDCl_3$) δ 0.95 (t, *J* = 7.2 Hz, 3H), 1.74 (tq, *J* = 7.2, 7.2 Hz, 2H), 2.83 (t, *J* = 7.2 Hz, 2H), 3.80 (d, *J* = 1.2 Hz, 1H), 4.90 (d, *J* = 1.2 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 11.6 (CH_3), 22.7 (CH_2), 47.0 (CH), 52.2 (CH_2), 75.2 (CH), 112.7 (C), 118.2 (C), 128.1 (CH), 132.5 (CH), 139.0 (C); IR (ATR/cm^{-1}) ν 1560; HRMS (ESI/TOF) Calcd for $C_{12}H_{14}N_3O_2$ [$(M+H)^+$]: 232.1081, found 232.1085.

***trans*-3-nitro-2-(4-nitrophenyl)-1-propylaziridine (3i)**

Yellow oil (0.04 mmol, 6%, determined by ^{1}H NMR). ^{1}H NMR ($CDCl_3$) δ 0.96 (t, *J* = 7.2 Hz, 3H), 1.76 (tq, *J* = 7.2, 7.2 Hz, 2H), 2.85 (t, *J* = 7.2 Hz, 2H), 3.86 (d, *J* = 0.4 Hz, 1H), 4.96 (d, *J* = 0.4 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 2H), 8.31 (d, *J* = 8.8 Hz, 2H);

^{13}C NMR ($CDCl_3$) δ 46.8 (CH), 75.3 (CH); IR (ATR/cm^{-1}) ν 1522; Satisfactory HRMS data were not obtained despite several attempts.

Note: Compound **3i** was found to completely decompose in the process of silica gel column chromatography. Therefore, the resultant crude product of **3i** was used for structural characterization. Although the aromatic signals of **3i** in the low field of ^{13}C NMR were ambiguous due to the complexity of the crude product, the featured signals assigned for C2 and C3 were definitely detected.

***trans*-2-(2-naphthyl)-3-nitro-1-propylaziridine (3j)**

Yellow oil (97.6 mg, 0.38 mmol, 63% yield). ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J = 7.2 Hz, 3H), 1.53–1.67 (m, 2H), 2.59–2.70 (m, 2H), 4.01 (d, J = 1.6 Hz, 1H), 5.04 (d, J = 1.6 Hz, 1H), 7.35 (dd, J = 1.6, 8.4 Hz, 1H), 7.49–7.54 (m, 2H), 7.76 (d, J = 1.6 Hz, 1H), 7.83–7.88 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 11.6 (CH_3), 22.7 (CH_2), 48.5 (CH), 52.1 (CH_2), 75.3 (CH), 125.2 (CH), 126.7 (CH), 126.8 (CH), 127.7 (CH), 127.8 (CH), 127.9 (CH), 128.6 (CH), 129.5 (C), 133.0 (C), 133.3 (C); IR (ATR/cm^{-1}) ν 1558; HRMS (ESI/TOF) Calcd for $C_{15}H_{17}N_2O_2$ [$(M+H)^+$]: 257.1285, found 257.1272.

***trans*-3-nitro-1-propyl-2-(2-thienyl)aziridine (3m)**

Yellow oil (0.21 mmol, 34% yield, determined by ^{1}H NMR). ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7.2 Hz, 3H), 1.68–1.76 (m, 2H), 2.60 (t, J = 7.2 Hz, 2H), 4.07 (d, J = 1.2 Hz, 1H), 4.87 (d, J = 1.2 Hz, 1H), 7.03 (dd, J = 4.0, 4.4 Hz, 1H), 7.28 (d, J = 4.0 Hz, 1H), 7.37 (d, J = 4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 11.6 (CH_3), 22.4 (CH_2), 43.5 (CH), 51.8 (CH_2), 76.2 (CH); IR (ATR/cm^{-1}) ν 1559; HRMS (ESI/TOF) Calcd for $C_9H_{13}N_2O_2S$ [$(M+H)^+$]: 213.0692, found 213.0687.

Note: Compound **3m** was found to completely isomerize into the corresponding β-nitroenamine **8m** in the process of silica gel column chromatography. Therefore, the resultant crude product of **3m** was used for structural characterization. Although the aromatic signals of **3m** in the low field of ^{13}C NMR were ambiguous due to the complexity of the crude product, the featured signals assigned for C2, C3 and *N*-propyl group were definitely detected.

***trans*-2-(2-furyl)-1-propyl-3-nitroaziridine (3n)**

Yellow oil (0.24 mmol, 40% yield, determined by ^{1}H NMR). ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.49–1.62 (m, 2H), 2.48–2.54 (m, 1H), 2.61–2.67 (m, 1H), 3.88 (d, *J* = 1.6 Hz, 1H), 5.01 (d, *J* = 1.6 Hz, 1H), 6.41 (dd, *J* = 2.0, 3.6 Hz, 1H), 6.48 (d, *J* = 3.6 Hz, 1H), 7.42 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 11.5 (CH_3), 22.3 (CH_2), 40.7 (CH), 52.2 (CH_2), 74.7 (CH), 111.0 (CH), 112.3 (CH), 143.5 (CH); IR (ATR/cm^{-1}) ν 1559; HRMS (ESI/TOF) Calcd for $C_9H_{13}N_2O_3$ [$(M+H)^+$]: 197.0921, found 197.0914.

Note: Compound **3n** was found to completely isomerize into the corresponding β-nitroenamine **8n** in the process of silica gel column chromatography. Therefore, the resultant crude product of **3n** was used for structural characterization. Although the aromatic signals of **3n** in the low field of ^{13}C NMR were ambiguous due to the complexity of the crude product, the featured signals assigned for C2, C3 and *N*-propyl group were definitely detected.

***trans*-3-nitro-1-propyl-2-(3-pyridyl)aziridine (3o)**

Yellow oil (57.4 mg, 0.28 mmol, 46% yield). ^{1}H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.2 Hz, 3H), 1.60 (tq, *J* = 7.2, 7.2 Hz, 2H), 2.72 (t, *J* = 7.2 Hz, 2H), 3.83 (d, *J* = 1.2 Hz, 1H), 4.95 (d, *J* = 1.2 Hz, 1H), 7.30–7.35 (m, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 8.60 (s, 2H, overlap); ^{13}C NMR ($CDCl_3$) δ 11.5 (CH_3), 22.5 (CH_2), 45.6 (CH), 52.0 (CH_2), 74.7 (CH), 123.4 (CH), 128.6 (C), 135.2 (CH), 149.4 (CH), 150.0 (CH); IR (ATR/cm^{-1}) ν 1559; HRMS (ESI/TOF) Calcd for $C_{10}H_{14}N_3O_2$ [$(M+H)^+$]: 208.1081, found 208.1078.

***trans*-3-nitro-2-(2-phenylethyl)-1-propylaziridine (3p)**

Colorless oil (92.0 mg, 0.39 mmol, 65% yield). ^{1}H NMR ($CDCl_3$) δ 0.94 (t, *J* = 7.2 Hz, 3H), 1.56–1.65 (m, 2H), 1.76–1.85 (m, 1H), 1.92–2.00 (m, 1H), 2.49–2.55 (m, 1H), 2.62–2.68 (m, 1H), 2.72–2.87 (m, 3H), 4.20 (d, *J* = 1.2 Hz, 1H), 7.16 (dd, *J* = 1.2, 8.0 Hz, 2H), 7.22 (tt, *J* = 1.2, 8.0 Hz, 1H), 7.30 (dd, *J* = 8.0, 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 11.6 (CH_3), 22.8 (CH_2), 27.7 (CH_2), 33.6 (CH_2), 46.1 (CH), 51.9 (CH_2), 75.5 (CH), 126.5 (CH), 128.2 (CH), 128.7 (CH), 140.1 (C); IR (ATR/cm^{-1}) ν 1555; HRMS (ESI/TOF) Calcd for $C_{13}H_{19}N_2O_2$ [$(M+H)^+$]: 235.1441, found 235.1430.

***trans*-2-(4-methylphenyl)-1-(2-methylpropyl)-3-nitroaziridine (3q)**

Yellow oil (77.5 mg, 0.33 mmol, 54% yield). ^{1}H NMR ($CDCl_3$) δ 0.90 (d, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 1.76–1.95 (m, 1H), 2.36 (s, 3H), 2.36–2.45 (m, 1H), 2.49-2.54 (m, 1H), 3.80 (d, *J* = 1.6 Hz, 1H), 4.89 (d, *J* = 1.6 Hz, 1H), 7.17 (s, 4H, overlap); ^{13}C NMR ($CDCl_3$) δ 20.5 (CH_3), 20.5 (CH_3), 21.2 (CH_3), 28.9 (CH), 48.1 (CH), 57.9 (CH_2), 75.7 (CH), 128.0 (CH), 129.4 (CH), 129.7 (C), 138.8 (C); IR (ATR/cm^{-1}) ν 1557; HRMS (ESI/TOF) Calcd for $C_{13}H_{19}N_2O_2$ [$(M+H)^+$]: 235.1441, found 235.1446.

***trans*-1-(2-butyl)-2-(4-methylphenyl)-3-nitroaziridine (3r)**

Yellow oil (43.8 mg, 0.19 mmol, 31% yield). ^{1}H NMR ($CDCl_3$) δ 0.74 (t, *J* = 7.2 Hz, 1H), 0.89-0.93 (m, 4H, overlap), 1.20 (d, *J* = 6.0 Hz, 1H), 1.36–1.39 (m, 1H), 1.54-1.66 (m, 1H), 2.35 (s, 3H), 2.56–2.62 (m, 1H), 3.85 (d, *J* = 1.2 Hz, 1H), 4.96 (d, *J* = 1.2 Hz, 1H), 7.17 (s, 4H, overlap); ^{13}C NMR ($CDCl_3$) δ 10.0 (CH_3), 18.6 (CH_3), 21.1 (CH_3), 29.6 (CH_2), 48.2 (CH), 55.9 (CH), 74.6 (CH), 127.9 (CH), 129.3 (CH), 129.4 (C), 138.7 (C); IR (ATR/cm^{-1}) ν 1559; HRMS (ESI/TOF) Calcd for $C_{13}H_{19}N_2O_2$ [$(M+H)^+$]: 235.1441, found 235.1431.

***trans*-2-(4-methylphenyl)-3-nitro-1-(phenylmethyl)aziridine (3t)**

Yellow oil (67.1 mg, 0.25 mmol, 41% yield). ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3H), 3.75 (d, *J* = 14.0 Hz, 1H), 3.83 (d, *J* = 14.0 Hz, 1H), 3.99 (d, *J* = 1.2 Hz, 1H), 5.00 (d, *J* = 1.2 Hz, 1H), 7.16 (s, 4H, overlap), 7.27–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 21.2 (CH_3), 48.9 (CH), 53.5 (CH_2), 74.8 (CH), 127.6 (CH), 128.0 (CH), 128.2 (C), 128.4 (CH), 128.6 (CH), 129.5 (CH), 137.0 (C), 139.1 (C); IR (ATR/cm^{-1}) ν 1559; HRMS (ESI/TOF) Calcd for $C_{16}H_{17}N_2O_2$ [$(M+H)^+$]: 269.1285, found 269.1274.

***trans*-2-(4-methylphenyl)-3-nitro-1-(propene-3-yl)aziridine (3v)**

Yellow oil (88.7 mg, 0.41 mmol, 67% yield). ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3H), 3.18 (dd, *J* = 4.8, 14.0 Hz, 1H), 3.28 (dd, *J* = 4.8, 14.0 Hz, 1H), 3.92 (d, *J* = 1.6 Hz, 1H), 4.94 (d, *J* = 1.6 Hz, 1H), 5.14 (dd, *J* = 1.2, 9.2 Hz, 1H), 5.16 (dd, *J* = 1.2, 17.2 Hz, 1H), 5.83–5.93 (m, 1H), 7.18 (s, 4H, overlap); ^{13}C NMR ($CDCl_3$) δ 21.2 (CH_3), 48.4 (CH), 52.2 (CH_2), 74.6 (CH), 117.7 (CH_2), 128.0 (C), 128.4 (CH), 129.4 (CH), 133.2

(C), 139.0 (C); IR (ATR/cm^{-1}) ν 1558; HRMS (ESI/TOF) Calcd for $C_{12}H_{15}N_2O_2$ [$(M+H)^+$]: 219.1128, found 219.1117.

***trans*-1-(2-hydroxyethyl)-2-(4-methylphenyl)-3-nitroaziridine (3w)**

Yellow oil (39.6 mg, 0.18 mmol, 30% yield). ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3H), 2.72 (br s, 1H), 2.73 (t, *J* = 5.2 Hz, 2H), 3.68–3.86 (m, 2H), 3.87 (d, *J* = 1.6 Hz, 1H), 5.07 (d, *J* = 1.6 Hz, 1H), 7.18 (s, 4H, overlap); ^{13}C NMR ($CDCl_3$) δ 21.1 (CH_3), 47.6 (CH), 51.8 (CH_2), 61.4 (CH_2), 75.0 (CH), 127.7 (C), 128.4 (CH), 129.5 (CH), 139.1 (C); IR (ATR/cm^{-1}) ν 1557; HRMS (ESI/TOF) Calcd for $C_{11}H_{15}N_2O_3$ [$(M+H)^+$]: 223.1077, found 223.1066.

***trans*-1-(3-hydroxypropyl)-2-(4-methylphenyl)-3-nitroaziridine (3x)**

Yellow oil (49.9 mg, 0.21 mmol, 35% yield). ^{1}H NMR ($CDCl_3$) δ 1.73–1.77 (m, 2H), 2.25 (br s, 1H), 2.36 (s, 3H), 2.72 (t, *J* = 6.4 Hz, 2H), 3.74 (t, *J* = 5.6 Hz, 2H), 3.89 (s, 1H), 4.98 (s, 1H), 7.17 (s, 4H, overlap); ^{13}C NMR ($CDCl_3$) δ 21.2 (CH_3), 31.5 (CH_2), 47.8 (CH_2), 48.4 (CH), 61.2 (CH_2), 74.9 (CH), 127.6 (C), 128.4 (CH), 129.5 (CH), 139.1 (C); IR (ATR/cm^{-1}) ν 1558; HRMS (ESI/TOF) Calcd for $C_{12}H_{17}N_2O_3$ [$(M+H)^+$]: 237.1234, found 237.1228.

5.4. Isomerization of *trans*-N-alkyl-*C*-nitroaziridine 3a to β-nitroenamine 8a

(*Z*)-1-(4-methylphenyl)-1-nitro-2-(propylamino)ethene (8a)

To a solution of *trans*-*N*-alkyl-*C*-nitroaziridines **3a** (220 mg, 1.0 mmol) in MeCN (7.5 mL), was added $SnCl_2{\cdot}2H_2O$ (14 mg, 0.06 mmol), and the resultant mixture was stirred at room temperature for 4 h. Then, the solvent was evaporated to afford a mixture as a yellow residue, which was treated by column chromatography on silica gel to afford β-nitroenamines **8a** (eluted with CH_2Cl_2, 165.5 mg, 0.75 mmol, 76% yield) as a yellow solid.

Mp 84−86 °C. ^{1}H NMR ($CDCl_3$) δ 1.01 (t, *J* = 7.2 Hz, 3H), 1.71 (tq, *J* = 7.2, 7.2 Hz, 2H), 2.36 (s, 3H), 3.38 (dt, *J* = 6.8, 7.2 Hz, 2H), 7.08 (d, *J* = 14.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 9.45−9.55 (br, 1H); ^{13}C{^{1}H}NMR ($CDCl_3$) δ 11.0 (CH_3), 21.2 (CH_3), 24.1 (CH_2), 51.6 (CH_2), 122.4 (C), 129.0 (CH), 129.6 (CH),

130.2 (C), 137.7 (C), 148.4 (CH); IR (ATR/cm^{-1}) ν 3288, 1646, 1517; HRMS (ESI/TOF) Calcd for $C_{12}H_{16}N_2O_2Na$ [$(M+Na)^+$]: 243.1104, found 243.1093.

When other aziridines **3** were used, experiments were conducted in a similar way with 0.2 mmol scale.

(*Z*)-1-(4-methoxyphenyl)-1-nitro-2-(propylamino)ethene (8b)

Yellow solid (41.1 mg, 0.17 mmol, 87%). Mp 122−124 °C; ^{1}H NMR ($CDCl_3$,) δ 1.01 (t, *J* = 7.2 Hz, 3H), 1.71 (tq, *J* = 7.2, 7.2 Hz, 2H), 3.37 (dt, *J* = 6.8, 7.2 Hz, 2H), 3.81 (s, 3H), 6.98 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 14.0 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 9.45−9.53 (br, 1H); ^{13}C{^{1}H}NMR ($CDCl_3$) δ 11.0 (CH_3), 24.0 (CH_2), 51.6 (CH_2), 55.3 (CH_3), 113.8 (CH), 122.1 (C), 125.5 (C), 131.1 (CH), 148.3 (CH), 159.2 (C); IR (ATR/cm^{-1}) ν 3291, 1643, 1517; HRMS (ESI/TOF) Calcd for $C_{12}H_{17}N_2O_3$ [$(M+H)^+$]: 237.1234, found 237.1232.

(*Z*)-1-(2-methoxyphenyl)-1-nitro-2-(propylamino)ethene (8c)

Yellow oil (41.9 mg, 0.18 mmol, 89%). ^{1}H NMR ($CDCl_3$) δ 1.00 (t, *J* = 7.2 Hz, 3H), 1.70 (tq, *J* = 7.2, 7.2 Hz, 2H), 3.35 (dt, *J* = 6.8, 7.2 Hz, 2H), 3.80 (s, 3H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.96 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.00 (d, *J* = 14.4 Hz, 1H), 7.20 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.33 (ddd, *J* = 1.6, 8.0, 8.0 Hz, 1H), 9.42−9.50 (br, 1H); ^{13}C{^{1}H}NMR ($CDCl_3$) δ 11.0 (CH_3), 24.0 (CH_2), 51.5 (CH_2), 55.7 (CH_3), 111.2 (CH), 118.5 (C), 120.5 (CH), 122.1 (C), 130.1 (CH), 132.0 (CH), 149.0 (CH), 157.9 (C); IR (ATR/cm^{-1}) ν 3300, 1646, 1560; HRMS (ESI/TOF) Calcd for $C_{12}H_{17}N_2O_3$ [$(M+H)^+$]: 237.1234, found 237.1240.

(*Z*)-1-(3,5-dimethoxyphenyl)-1-nitro-2-(propylamino)ethene (8d)

Yellow oil (23.6 mg, 0.09 mmol, 45%). ^{1}H NMR ($CDCl_3$) δ 1.01 (t, *J* = 7.2 Hz, 3H), 1.71 (tq, *J* = 7.2, 7.2 Hz, 2H), 3.38 (dt, *J* = 6.8, 7.2 Hz, 2H), 6.42 (t, *J* = 2.4 Hz, 1H), 6.53 (d, *J* = 2.4 Hz, 2H), 7.12 (d, *J* = 14.0 Hz, 1H), 9.47−9.53 (br, 1H); ^{13}C{^{1}H}NMR ($CDCl_3$) δ 11.0 (CH_3), 24.0 (CH_2), 51.7 (CH_2), 55.4 (CH_3), 99.9 (CH), 107.9 (CH), 122.3 (C), 134.9 (C), 148.6 (CH), 160.6 (C); IR (ATR/cm^{-1}) ν 3293, 1645, 1559; HRMS (ESI/TOF) Calcd for $C_{13}H_{19}N_2O_4$ [$(M+H)^+$]: 267.1339, found 267.1338.

(*Z*)-1-nitro-1-phenyl-2-(propylamino)ethene (8e)

Yellow oil (16.2 mg, 0.08 mmol, 40%). ^{1}H NMR ($CDCl_3$) δ 1.02 (t, *J* = 7.2 Hz, 3H), 1.72 (tq, *J* = 7.2, 7.2 Hz, 2H), 3.39 (dt, *J* = 6.8, 7.2 Hz, 2H), 7.10 (d, *J* = 13.6 Hz, 1H), 7.28−7.33 (m, 1H), 7.35−7.38 (m, 4H), 9.50−9.56 (br, 1H); ^{13}C{^{1}H}NMR ($CDCl_3$) δ 11.0 (CH_3), 24.0 (CH_2), 51.7 (CH_2), 126.8 (C), 127.7 (CH), 128.3 (CH), 129.6 (CH), 133.1 (C), 148.6 (CH); IR (ATR/cm^{-1}) ν 3277, 1646, 1559; HRMS (ESI/TOF) Calcd for $C_{11}H_{15}N_2O_2$ [$(M+H)^+$]: 207.1128, found 207.1131.

(*Z*)-1-(4-bromophenyl)-1-nitro-2-(propylamino)ethene (8f)

Yellow solid (27.8 mg, 0.10 mmol, 49%). Mp 61−62 °C; ^{1}H NMR ($CDCl_3$) δ 1.02 (t, *J* = 7.2 Hz, 3H), 1.73 (tq, *J* = 7.2, 7.2 Hz, 2H), 3.40 (dt, *J* = 6.8, 7.2 Hz, 2H), 7.08 (d, *J* = 14.0 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 9.47−9.55 (br, 1H); ^{13}C{^{1}H}NMR ($CDCl_3$) δ 11.0 (CH_3), 24.0 (CH_2), 51.7 (CH_2), 121.5 (C), 121.7 (C), 131.1 (CH), 131.5 (CH), 132.0 (C), 148.3 (CH); IR (ATR/cm^{-1}) ν 3268, 1637, 1539; HRMS (ESI/TOF) Calcd for $C_{11}H_{14}BrN_2O_2$ [$(M+H)^+$]: 285.0233, found 285.0235.

(*Z*)-1-(4-chlorophenyl)-1-nitro-2-(propylamino)ethene (8g)

Yellow solid (21.3 mg, 0.09 mmol, 45%). Mp 77−79 °C; ^{1}H NMR ($CDCl_3$) δ 1.02 (t, *J* = 7.2 Hz, 3H), 1.72 (tq, *J* = 7.2, 7.2 Hz, 2H), 3.40 (dt, *J* = 6.8, 7.2 Hz, 2H), 7.08 (d, *J* = 14.0 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 9.48−9.54 (br, 1H); ^{13}C{^{1}H}NMR ($CDCl_3$) δ 11.0 (CH_3), 24.0 (CH_2), 51.7 (CH_2), 121.5 (C), 128.5 (CH), 130.9 (CH), 131.5 (C), 133.6 (C), 148.3 (CH); IR (ATR/cm^{-1}) ν 3280, 1642, 1539; HRMS (ESI/TOF) Calcd for $C_{11}H_{14}ClN_2O_2$ [$(M+H)^+$]: 241.0738, found 241.0749.

(*Z*)-1-(2-naphthyl)-1-nitro-2-(propylamino)ethene (8j)

Yellow solid (42.3 mg, 0.17 mmol, 83%). Mp 82−85 °C; ^{1}H NMR ($CDCl_3$) δ 1.02 (t, *J* = 7.2 Hz, 3H), 1.72 (tq, *J* = 7.2, 7.2 Hz, 2H), 3.40 (dt, *J* = 6.8, 7.2 Hz, 2H), 7.21 (d, *J* = 14.0 Hz, 1H), 7.45−7.49 (m, 2H), 7.56 (dd, *J* = 1.2, 8.4 Hz, 1H), 7.71 (d, *J* = 1.2 Hz, 1H), 7.78−7.83 (m, 3H), 9.54−9.60 (br, 1H); ^{13}C{^{1}H}NMR ($CDCl_3$) δ 11.0 (CH_3), 24.1 (CH_2), 51.7 (CH_2), 122.5 (C), 126.2 (CH), 126.3 (CH), 127.6 (CH), 127.7 (CH), 127.8 (CH), 127.8 (CH), 127.9 (CH), 130.7 (C), 132.7 (C), 133.2 (C), 148.8

(CH); IR (ATR/cm^{-1}) ν 3295, 1643, 1560; HRMS (ESI/TOF) Calcd for $C_{15}H_{17}N_2O_2$ [$(M+H)^+$]: 257.1285, found 257.1283.

(*Z*)-1-nitro-2-propylamino-1-(2-thienyl)ethene (8m)

Yellow oil (42.5 mg, 0.20 mmol, quant.). ^{1}H NMR ($CDCl_3$) δ 1.03 (t, *J* = 7.2 Hz, 3H), 1.74 (tq, *J* = 7.2, 7.2 Hz, 2H), 3.44 (dt, *J* = 6.8, 7.2 Hz, 2H), 6.99 (dd, *J* = 3.6, 5.2 Hz, 1H), 7.03 (d, *J* = 3.6 Hz, 1H), 7.30 (d, *J* = 5.2 Hz, 1H), 7.43 (d, *J* = 14.0 Hz, 1H), 9.74−9.80 (br, 1H); ^{13}C{^{1}H}NMR ($CDCl_3$) δ 11.0 (CH_3), 23.9 (CH_2), 51.9 (CH_2), 117.6 (C), 123.8 (CH), 125.7 (CH), 126.2 (CH), 134.8 (C), 148.3 (CH); IR (ATR/cm^{-1}) ν 3288, 1646, 1559; HRMS (ESI/TOF) Calcd for $C_9H_{13}N_2O_2S$ [$(M+H)^+$]: 213.0692, found 213.0691.

(*Z*)-1-(2-furyl)-1-nitro-2-(propylamino)ethene (8n)

Yellow solid (31.1 mg, 0.16 mmol, 80%). Mp 63−64 °C; ^{1}H NMR ($CDCl_3$) δ 1.03 (t, *J* = 7.2 Hz, 3H), 1.75 (tq, *J* = 7.2, 7.2 Hz, 2H), 3.47 (dt, *J* = 6.8, 7.2 Hz, 2H), 6.44 (dd, *J* = 1.6, 3.6 Hz, 1H), 6.81 (dd, *J* = 0.8, 3.6 Hz, 1H), 7.31 (dd, *J* = 0.8, 1.6 Hz, 1H), 7.68 (d, *J* = 14.4 Hz, 1H), 9.82−9.90 (br, 1H); ^{13}C{^{1}H}NMR ($CDCl_3$) δ 10.9 (CH_3), 23.9 (CH_2), 52.1 (CH_2), 107.6 (CH), 111.6 (CH), 116.4 (C), 140.1 (CH), 145.8 (C), 147.7 (CH); IR (ATR/cm^{-1}) ν 3255, 1653, 1559; HRMS (ESI/TOF) Calcd for $C_9H_{13}N_2O_3$ [$(M+H)^+$]: 197.0921, found 197.0916.

(*Z*)-1-(4-methylphenyl)-2-[(2-methylpropyl)amino]-1-nitroethene (8q)

Yellow oil (34.1 mg, 0.15 mmol, 73%). ^{1}H NMR ($CDCl_3$) δ 1.00 (d, *J* = 6.8 Hz, 6H), 1.91 (triple septet, *J* = 6.4, 6.8 Hz, 1H), 2.36 (s, 3H), 3.22 (dt, *J* = 6.4, 6.4 Hz, 2H), 7.05 (d, *J* = 14.0 Hz, 1H), 7.18 (1H, *J* = 8.0 Hz, 2H), 7.25 (1H, *J* = 8.0 Hz, 2H), 9.50−9.59 (br, 1H); ^{13}C{^{1}H}NMR ($CDCl_3$) δ 19.7 (CH_3), 21.2 (CH_3), 29.7 (CH), 57.6 (CH_2), 122.3 (C), 129.0 (CH), 129.6 (CH), 130.2 (C), 137.6 (C), 148.7 (CH); IR (ATR/cm^{-1}) ν 3281, 1643, 1517; HRMS (ESI/TOF) Calcd for $C_{13}H_{19}N_2O_2$ [$(M+H)^+$]: 235.1441, found 235.1431.

(*Z*)-2-(2-butylamino)-1-(4-methylphenyl)-1-nitroethene (8r)

Yellow solid (37.4 mg, 0.16 mmol, 80%). Mp 68−70 °C; ^{1}H NMR ($CDCl_3$) δ 0.99 (t, *J* = 7.2 Hz, 3H), 1.35 (d, *J* = 6.4 Hz, 3H), 1.61−1.69 (m, 2H), 2.36 (s, 3H), 3.37 (dtq, *J* = 6.4, 6.8, 7.2 Hz, 1H), 7.11 (d, *J* = 14.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H),

7.26 (d, *J* = 8.0 Hz, 2H), 9.40−9.48 (br, 1H); $^{113}C\{^{1}H\}$NMR ($CDCl_3$) δ 10.3 (CH_3), 21.2 (CH_3), 21.3 (CH_3), 30.5 (CH_2), 57.7 (CH), 122.1 (C), 129.0 (CH), 129.6 (CH), 130.3 (C), 137.6 (C), 146.9 (CH); IR (ATR/cm^{-1}) ν 3276, 1638, 1517; HRMS (ESI/TOF) Calcd for $C_{13}H_{19}N_2O_2$ $[(M+H)^+]$: 235.1441, found 235.1442.

(*Z*)-1-(4-methylphenyl)-1-nitro-2-[(phenylmethyl)amino]ethene (8t)

Yellow solid (45.7 mg, 0.17 mmol, 86%). Mp 92−94 °C; ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3H), 4.57 (d, *J* = 6.0 Hz, 2H), 7.12 (d, *J* = 14.0 Hz, 1H), 7.16−7.42 (m, 9H), 9.60−9.68 (br, 1H); $^{13}C\{^{1}H\}$NMR ($CDCl_3$) δ 21.2 (CH_3), 53.3 (CH_2), 123.2 (C), 127.5 (CH), 128.5 (CH), 129.1 (CH), 129.2 (CH), 129.6 (CH), 130.0 (C), 136.1 (C), 137.8 (C), 147.7 (CH); IR (ATR/cm^{-1}) ν 3287, 1640, 1517; HRMS (ESI/TOF) Calcd for $C_{16}H_{17}N_2O_2$ $[(M+H)^+]$: 269.1285, found 269.1284.

(*Z*)-1-(4-methylphenyl)-1-nitro-2-[(propene-3-yl)amino]ethene (8v)

Yellow solid (35.6 mg, 0.16 mmol, 82%). Mp 88−90 °C; ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3H), 4.01 (dd, *J* = 5.6, 5.6 Hz, 2H), 5.30 (dd, *J* = 0.8, 8.8 Hz, 1H), 5.33 (dd, *J* = 0.8, 17.2 Hz, 1H), 5.87-5.97 (m, 1H), 7.05 (d, *J* = 13.6 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 9.38−9.46 (br, 1H); $^{13}C\{^{1}H\}$NMR ($CDCl_3$) δ 21.2 (CH_3), 51.5 (CH_2), 118.7 (CH_2), 123.1 (C), 129.0 (CH), 129.6 (CH), 130.0 (C), 132.8 (CH), 137.8 (C), 147.8 (CH); IR (ATR/cm^{-1}) ν 3292, 1637, 1518; HRMS (ESI/TOF) Calcd for $C_{12}H_{15}N_2O_2$ $[(M+H)^+]$: 219.1128, found 219.1128.

(*Z*)-2-[(2-hydroxyethyl)amino]]-1-(4-methylphenyl)-1-nitroethene (8w)

Yellow solid (28.3 mg, 0.13 mmol, 64%). Mp 96−98 °C; ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 3H), 2.97−3.02 (br, 1H), 3.52 (dt, *J* = 5.6, 5.6 Hz, 2H), 3.83 (dt, *J* = 4.4, 5.6 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 15.2 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 9.58−9.66 (br, 1H); $^{13}C\{^{1}H\}$NMR ($CDCl_3$) δ 21.2 (CH_3), 52.1 (CH_2), 61.5 (CH_2), 122.4 (C), 129.0 (CH), 129.6 (CH), 129.9 (C), 137.7 (C), 149.8 (CH); IR (ATR/cm^{-1}) ν 3296, 1642, 1517; HRMS (ESI/TOF) Calcd for $C_{11}H_{15}N_2O_3$ $[(M+H)^+]$: 223.1077, found 223.1073.

(*Z*)-2-[(3-hydroxypropyl)amino]-1-(4-methylphenyl)-1-nitroethene (8x)

Yellow oil (34.9 mg, 0.15 mmol, 74%). ^{1}H NMR ($CDCl_3$) δ 1.80−1.85 (br, 1H), 1.92 (tt, *J* = 5.6, 5.6 Hz, 2H), 2.36 (s, 3H), 3.59 (dt, *J* = 5.6, 6.4 Hz, 2H), 3.81 (dt, *J* =

4.8, 5.6 Hz, 2H), 7.12 (d, *J* = 14.0 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 9.62−9.70 (br, 1H); $^{13}C\{^{1}H\}$NMR ($CDCl_3$) δ 21.2 (CH_3), 32.7 (CH_2), 47.0 (CH_2), 59.4 (CH_2), 122.4 (C), 129.0 (CH), 129.5 (CH), 130.1 (C), 137.7 (C), 148.8 (CH); IR (ATR/cm^{-1}) ν 3373, 1646, 1517; HRMS (ESI/TOF) Calcd for $C_{12}H_{16}N_2O_3Na$ [$(M+Na)^+$]: 259.1053, found 259.1060.

6. References

(1) (a) Aichhorn, S.; Gururaja, G. N.; Reisinger, M.; Waser, M. *RSC Adv.* **2013**, *3*, 4552. (b) Adamo, M. F. A.; Bruschi, S.; Suresh, S.; Piras, L. *Tetrahedron Lett.* **2008**, *49*, 7406. (c) Crawley, S. L.; Funk, R. L. *Org. Lett.* **2006**, *8*, 3995. (d) Barrosa, M. T.; Maycockb, C. D.; Venturab, M. R. *Tetrahedron Lett.* **2002**, *43*, 4329.

(2) Guillemin, J. C.; Denis, J. *Angew. Chem. Suppl.* **1982**, 1515.

(3) (a) de Ceglie, M. C.; Musio, B. Affortunato, F. Moliterni, A. Altomare, A. Florio, S.; Luis, R. *Chm. Eur. J.* **2011**, *17*, 286. (b) Affortunato, F.; Florio, S.; Luisi, R.; Musio, B. *J. Org. Chem.* **2008**, *73*, 9214.

Liu, J. T.; Yao, C. F. *Tetrahedron Lett.* **2001**, *42*, 6147.

(4) Liu, J.; Gong, L.; Meggers, E. *Tetrahedron Lett.* **2015**, *56*, 4653.

(5) Augustin, M. V.; Alexakis, A. *Eur. J. Org. Chem.* **2007**, 5852.

(6) (a) Kiyokawa, K.; Nagata, T.; Hayakawa, J.; Minakata, S. *Chem. Eur. J.* **2015**, *21*, 1280. (b) Simpson, A. J.; Lam, H. W. *Org. Lett.* **2013**, *15*, 2586.

7. Single crystal X-ray diffraction data for compound 8a

Single crystal of compound **8a** was obtained by recrystallization from chloroform. The structure was shown in Figure S-2. X-ray diffraction data and the refinement was shown in Table S-4. CIF file of **8a** can be obtained from the Cambridge Crystallographic Data Center using deposition number CCDC: 1558941.

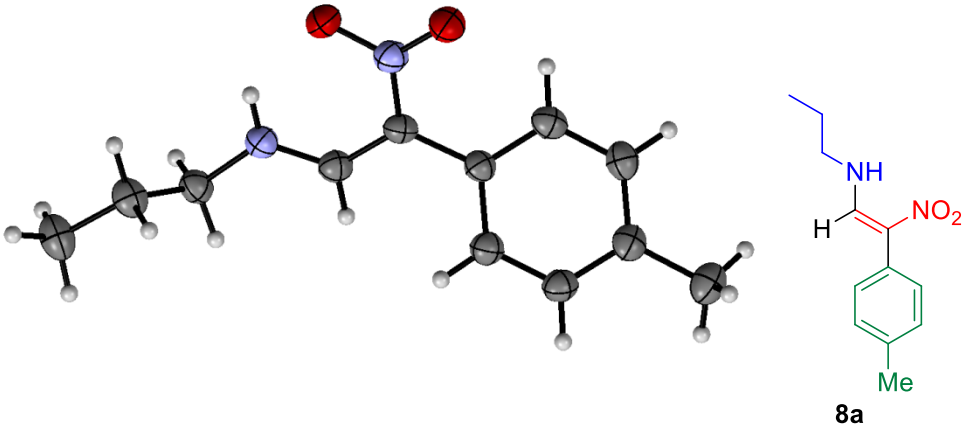


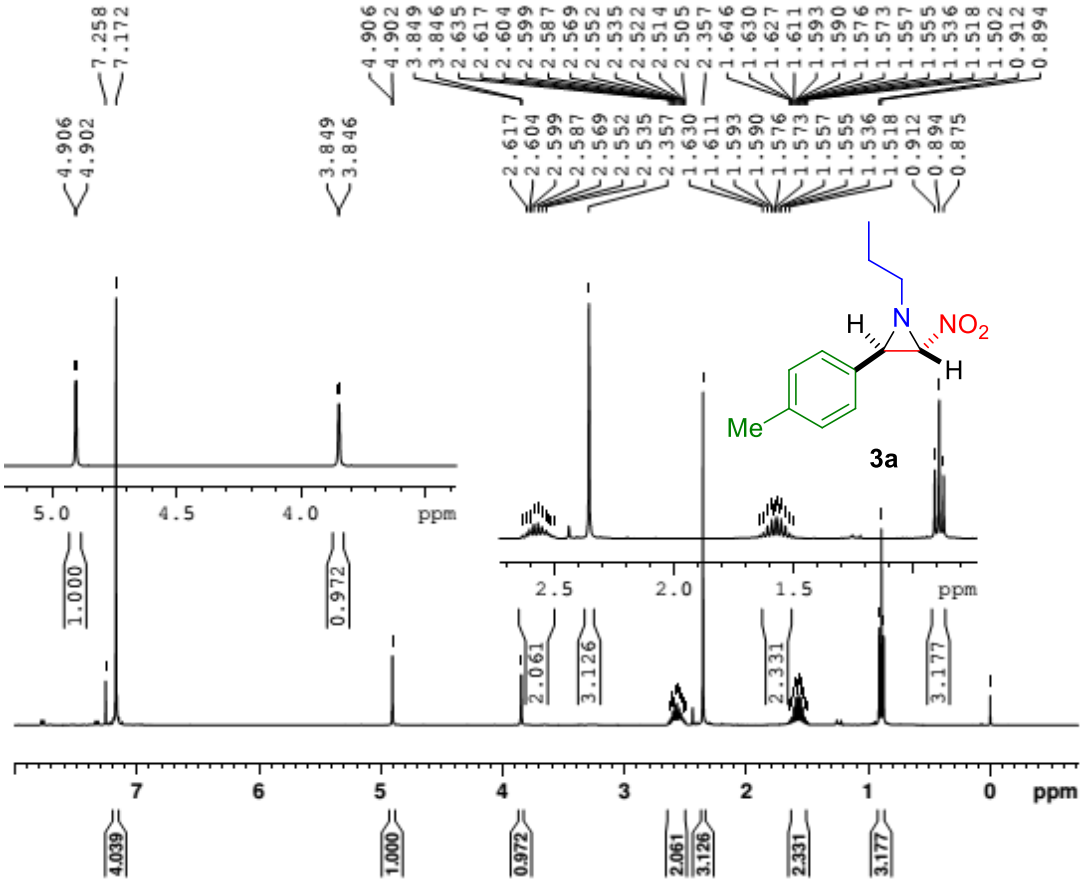
Figure S-2. X-ray single crystal structure of **8a** (50% probability factor for the thermal ellipsoids)

Table S-4. Crystal data and structure refinement for **8a**

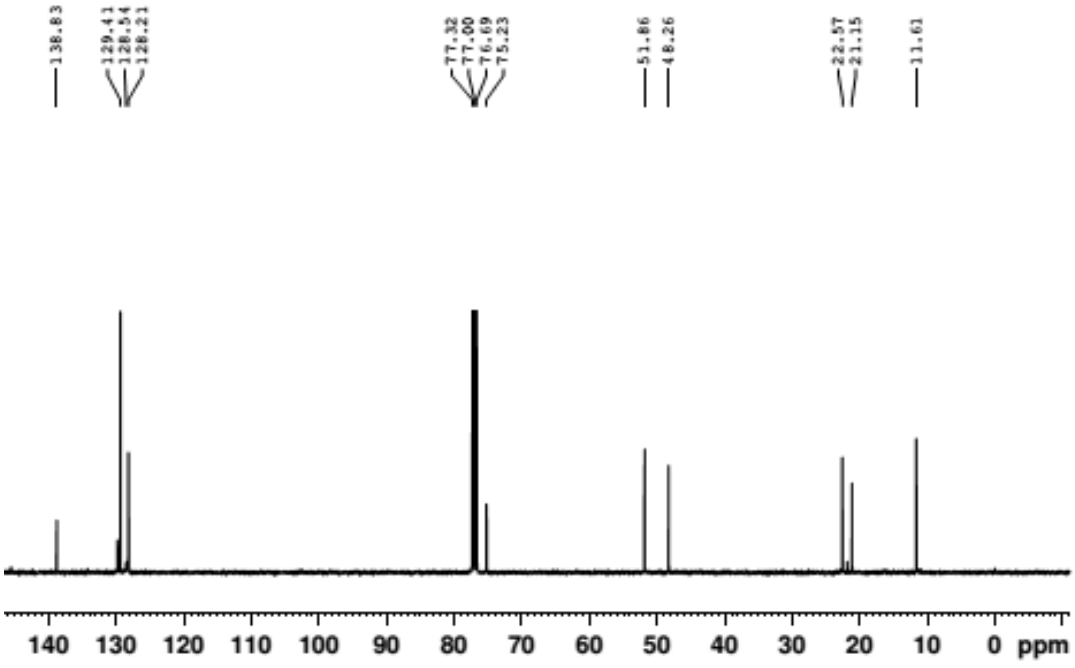
Empirical Formula	$C_{12}H_{16}N_2O_2$
Formula Weight	220.27
Crystal Color, Habit	yellow, block
Crystal Dimensions	0.400×0.200×0.200 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 11.9025(8) Å
	b = 7.4111(6) Å
	c = 13.2657(9) Å
	V = 1170.17(15) $Å^3$
Space Group	$Pna2_1$ (#33)
Z value	4

D_{calc}	1.250 g/cm^3
F_{000}	472.00
μ(MoKa)	0.861 cm^{-1}
Radiation	MoKa (l = 0.71075 Å)
	graphite monochromated
No. Observations (All reflections)	3567
No. Variables	145
Reflection/Parameter Ratio	24.60
Residuals: R1 (I>2.00s(I))	0.0567
Residuals: R (All reflections)	0.1021
Residuals: wR2 (All reflections)	0.1591
Goodness of Fit Indicator	0.910
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.26 e$^-$/Å^3
Minimum peak in Final Diff. Map	-0.25 e$^-$/Å^3
Temperature	-150.0℃
Detector Aperture	460.0×256.0 mm
Data Images	44 exposures
w oscillation Range (c=45.0, f=0.0)	130.0 - 190.0°
Exposure Rate	60.0 sec./°
w oscillation Range (c=45.0, f=180.0)	0.0 - 160.0°
Exposure Rate	60.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2q_{max}$	61.0°

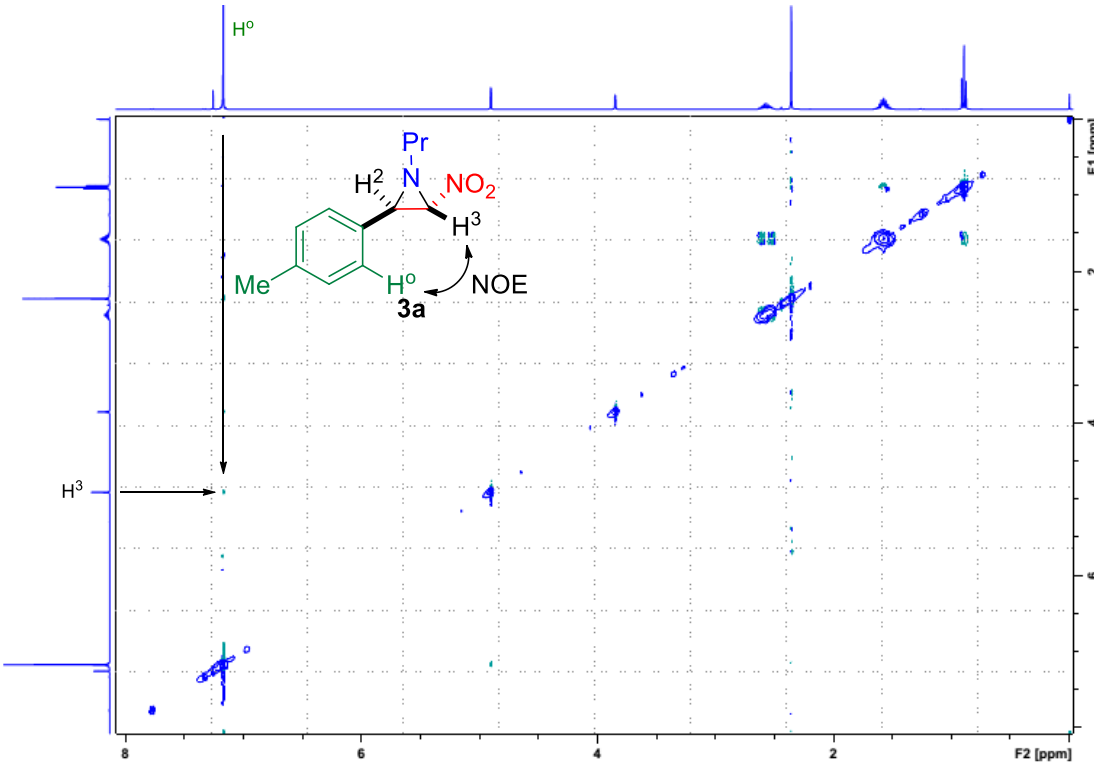
8. Copies of NMR spectra



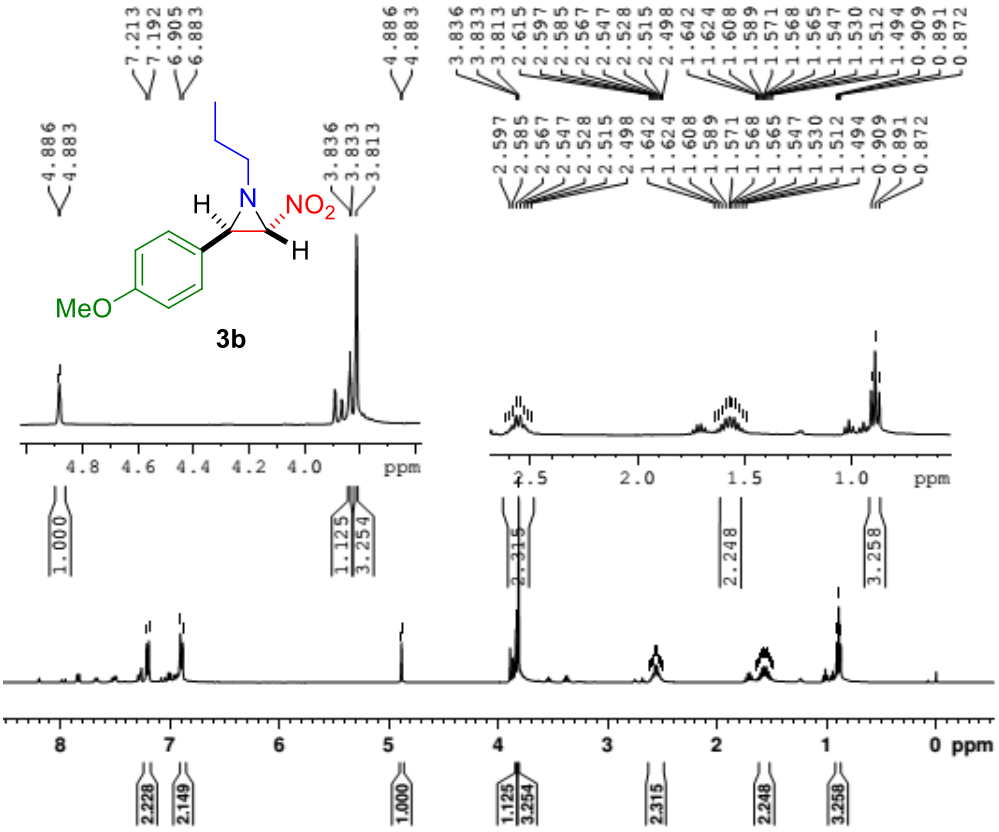
^{1}H NMR (400 MHz) in $CDCl_3$



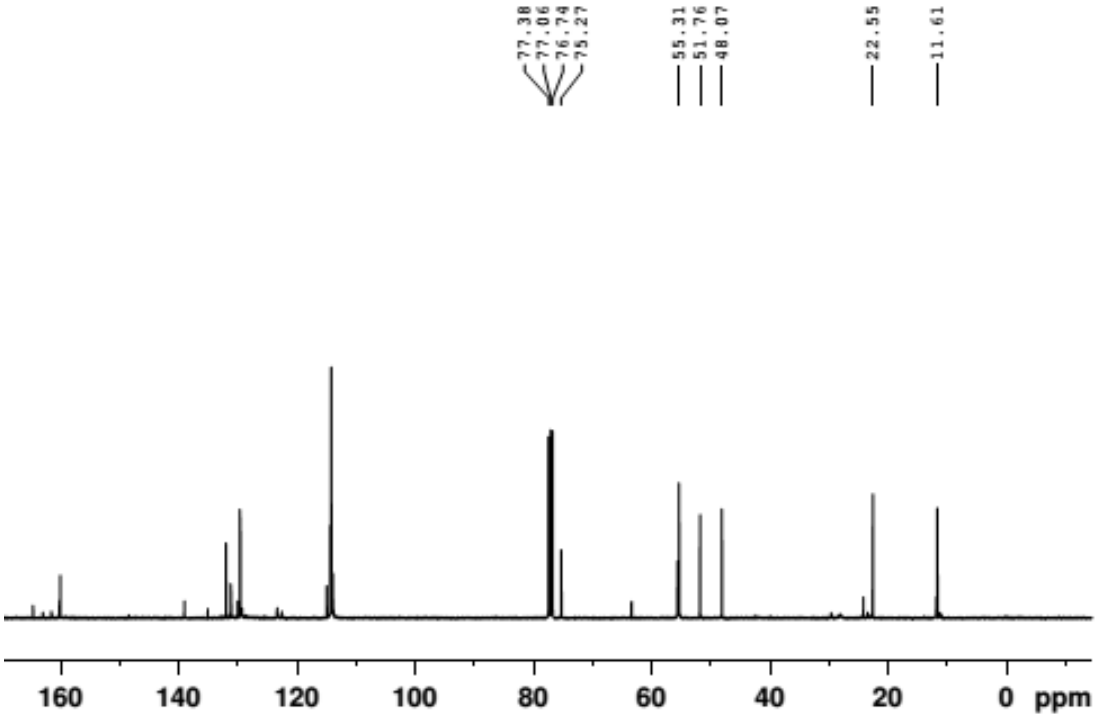
^{13}C NMR (100 MHz) in $CDCl_3$



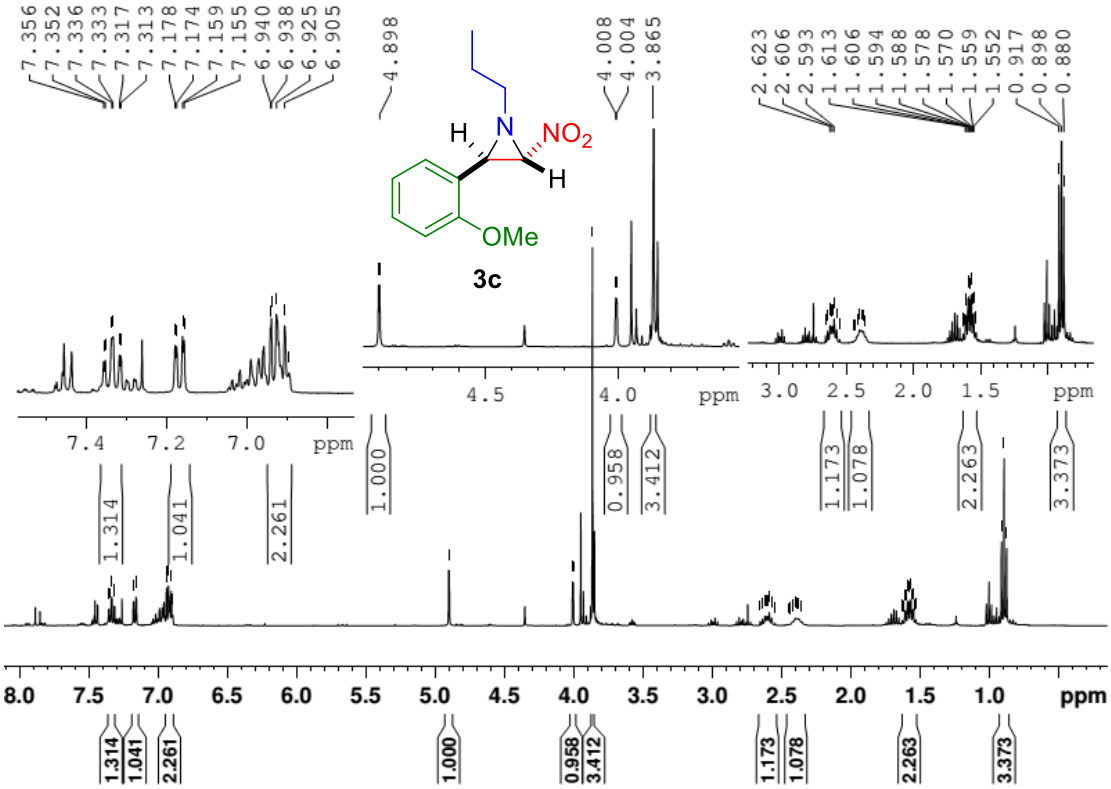
^{1}H-^{1}H NOESY in $CDCl_3$



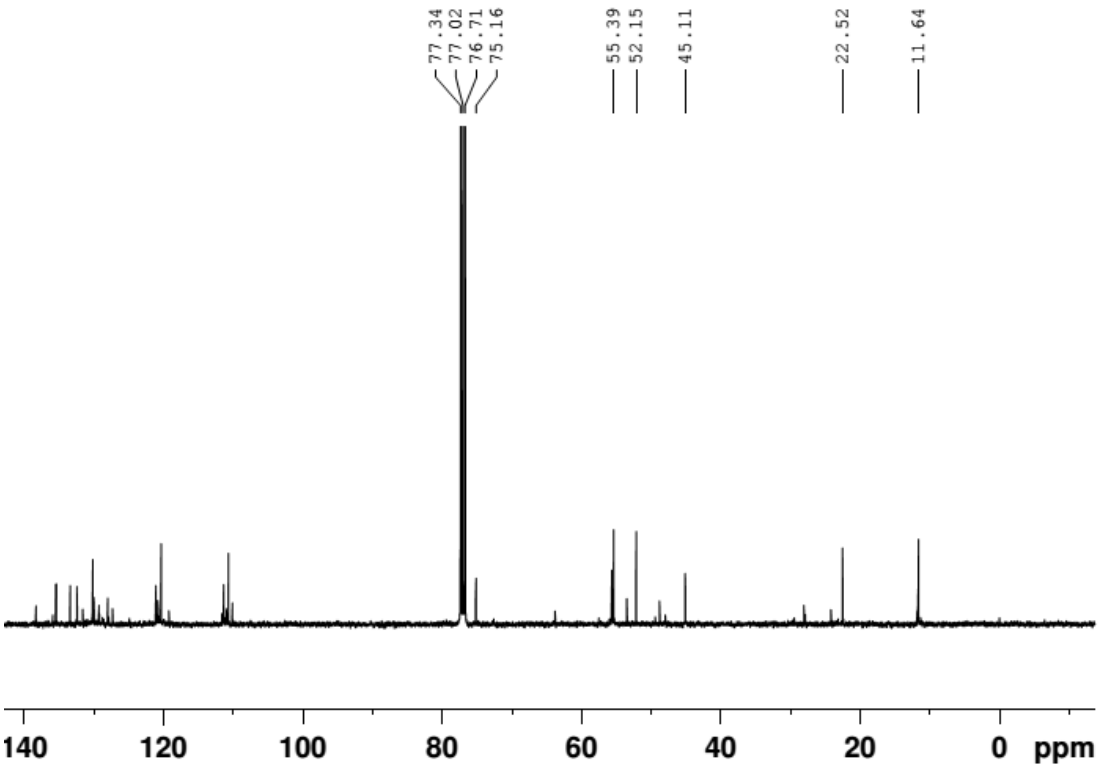
^{1}H NMR (400 MHz) of the reaction mixture in $CDCl_3$



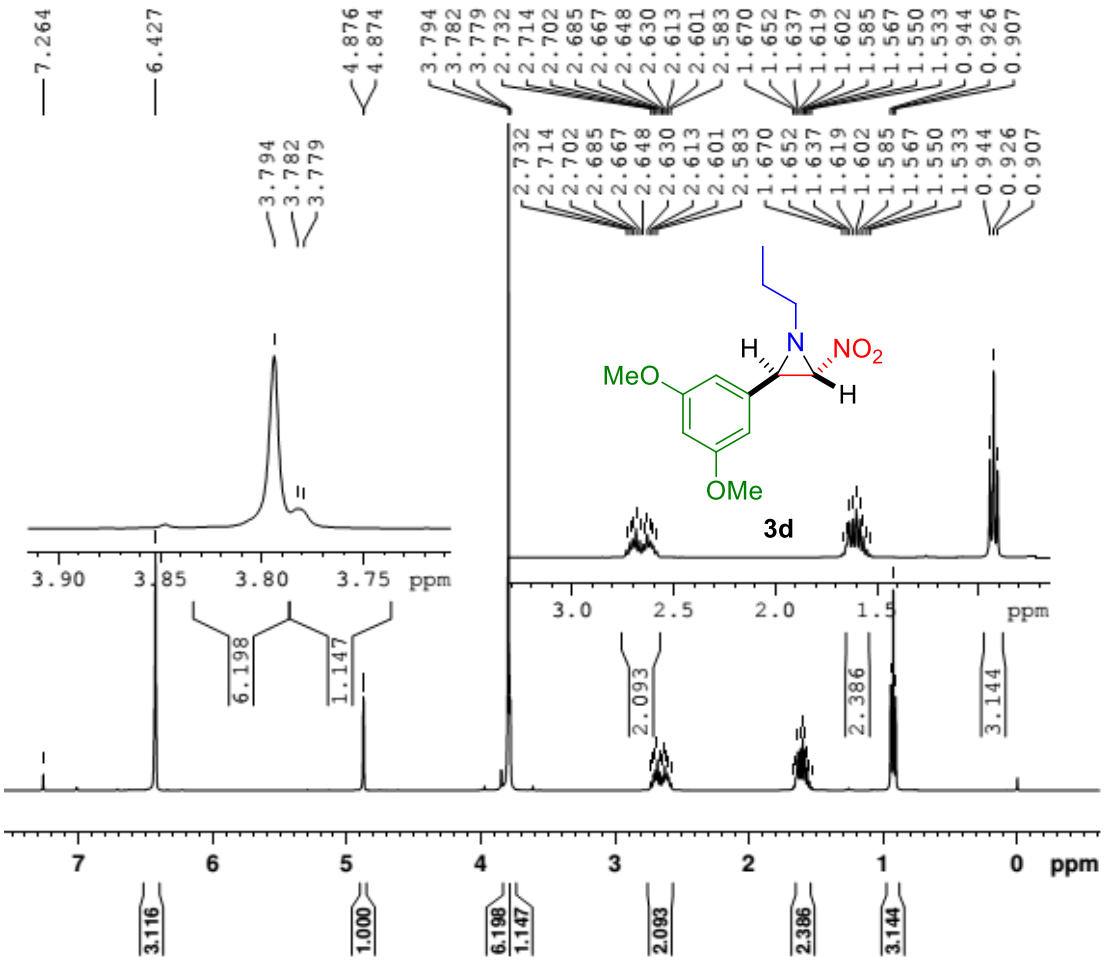
^{13}C NMR (100 MHz) of the reaction mixture in $CDCl_3$



^{1}H NMR (400 MHz) of the reaction mixture in $CDCl_3$



^{13}C NMR (100 MHz) of the reaction mixture in $CDCl_3$



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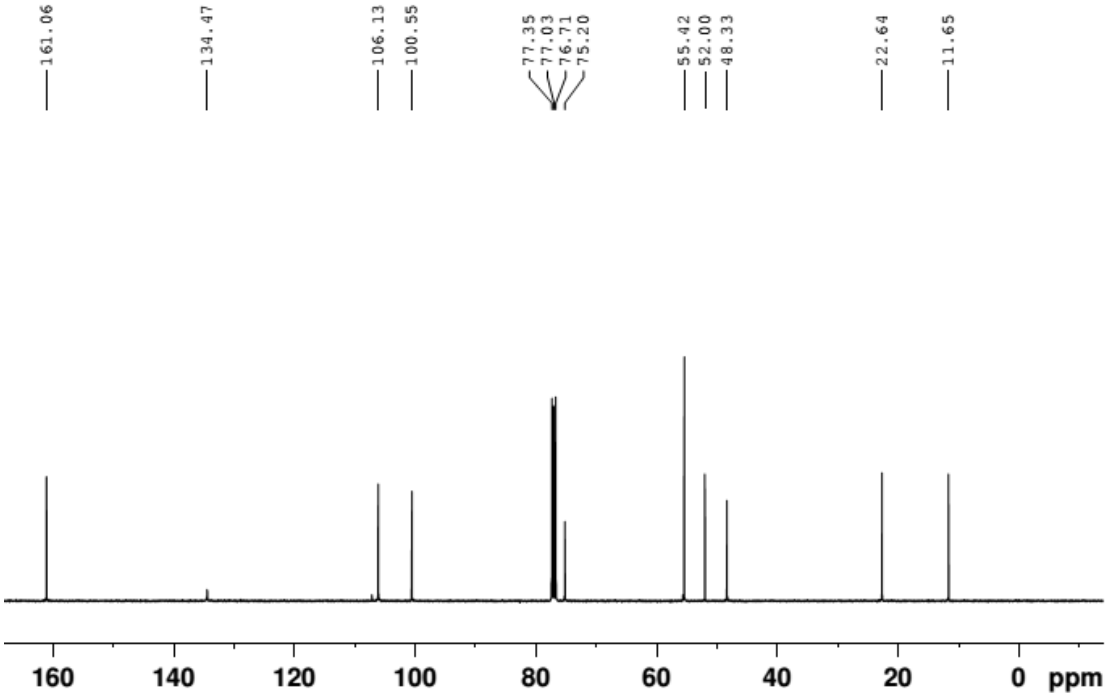

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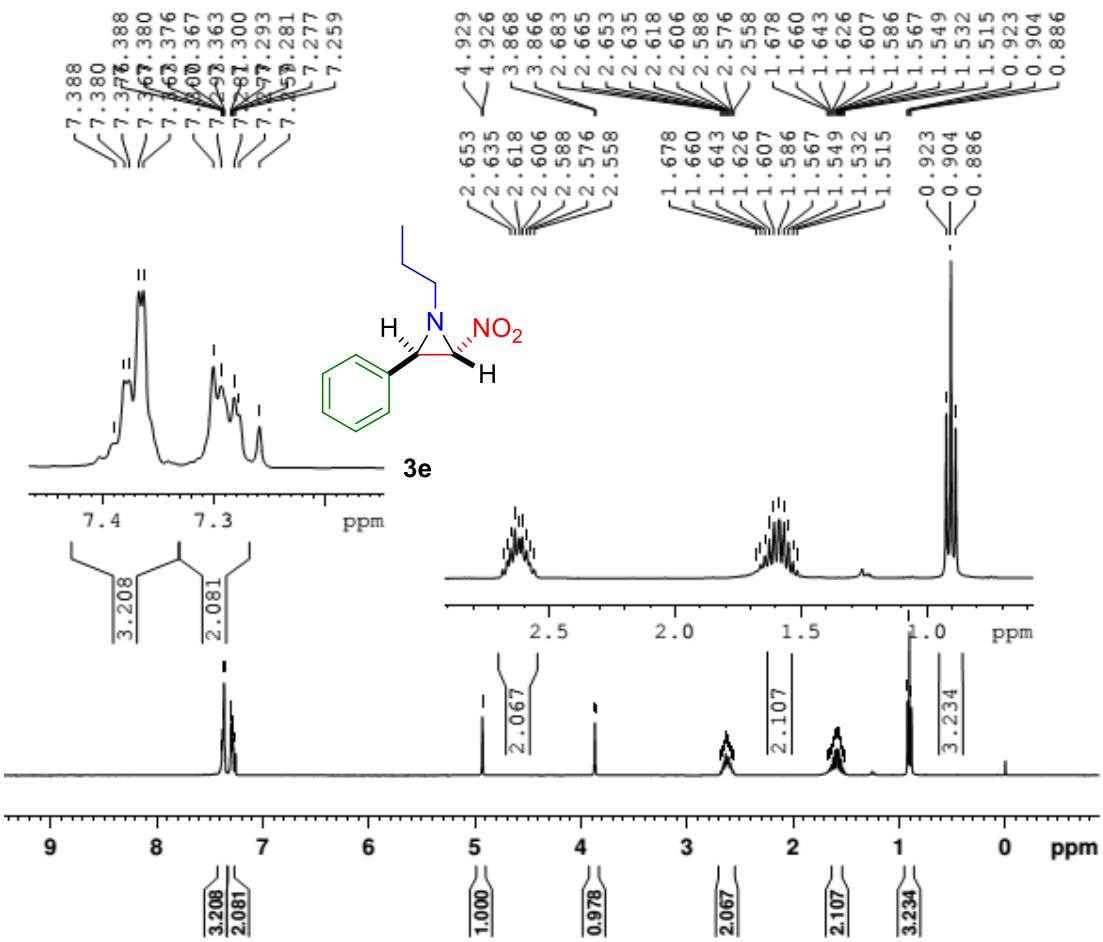

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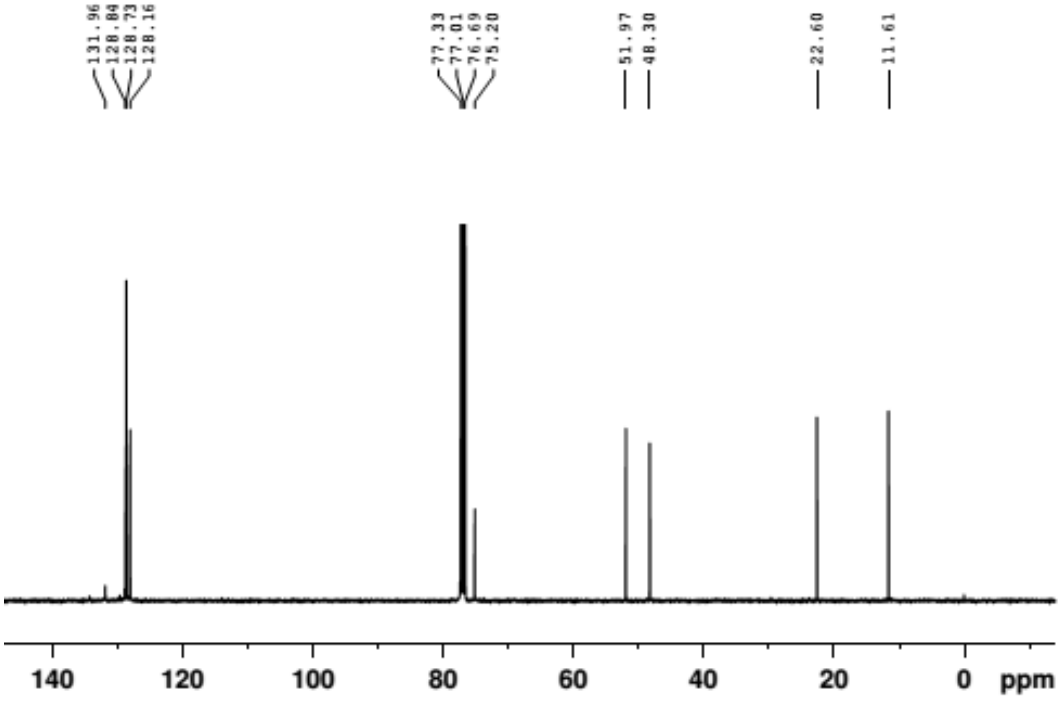
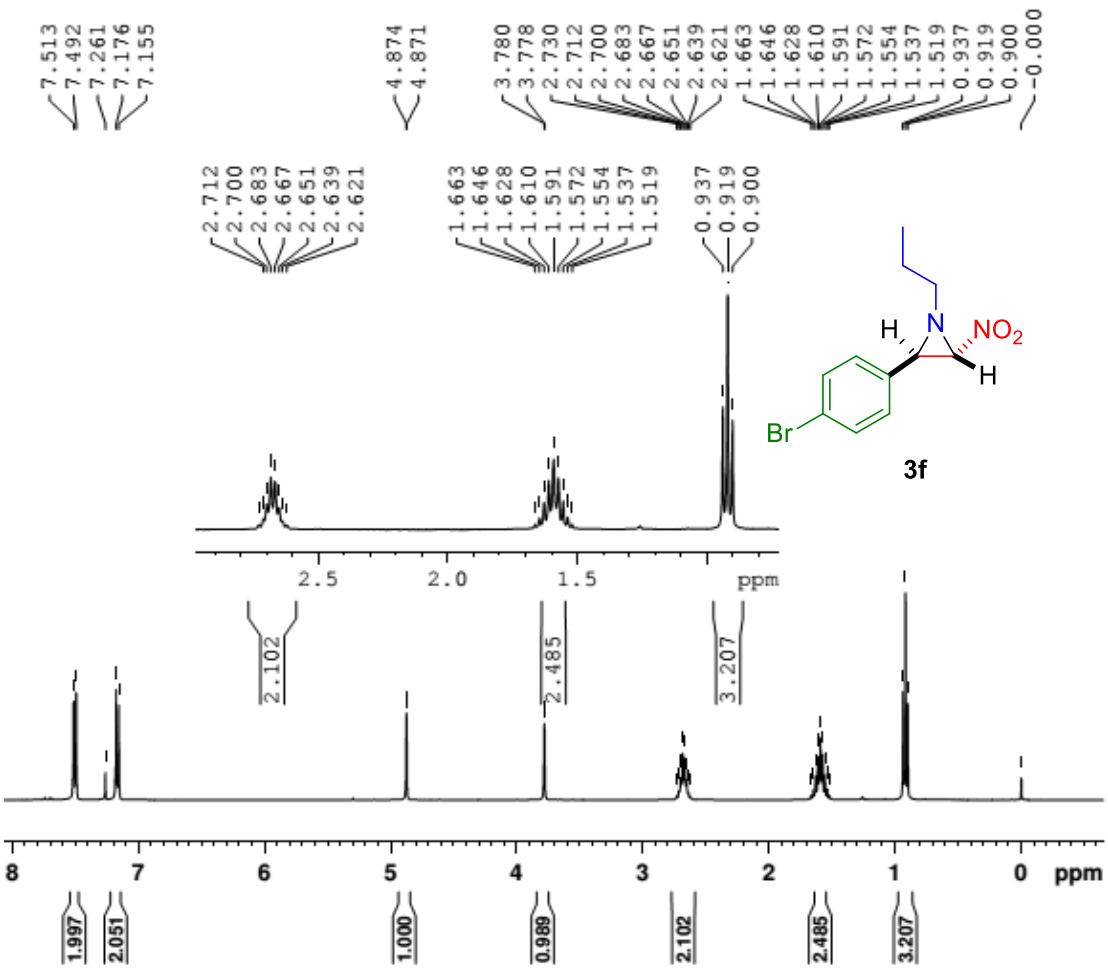
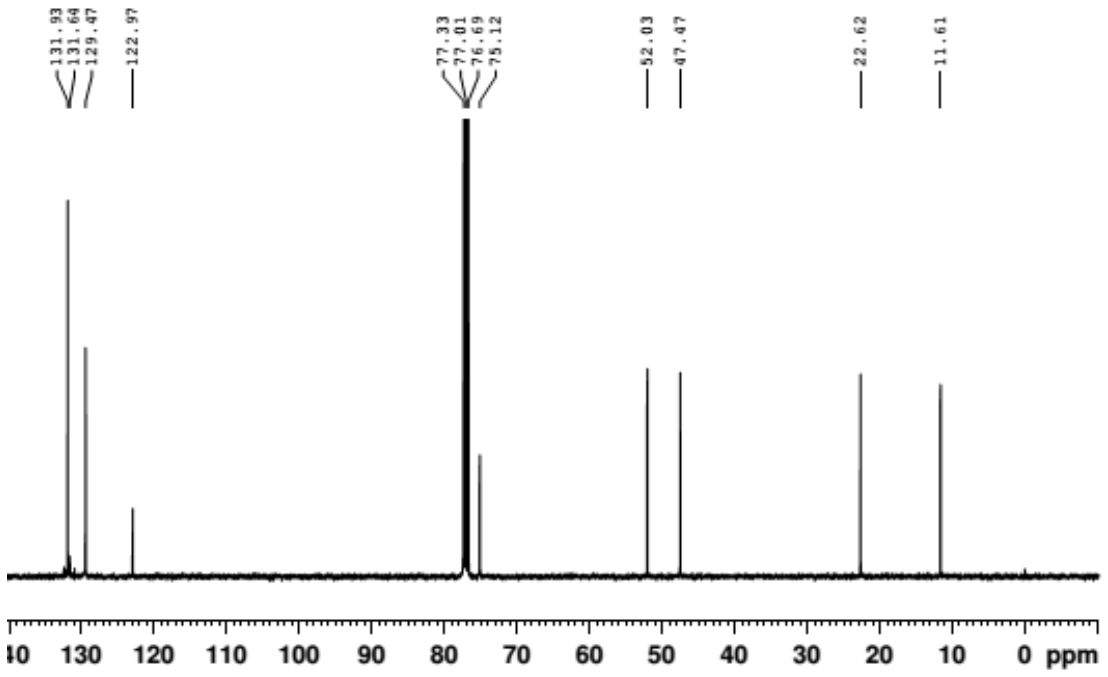


^{13}C NMR (100 MHz) in $CDCl_3$



^{1}H NMR (400 MHz) in $CDCl_3$



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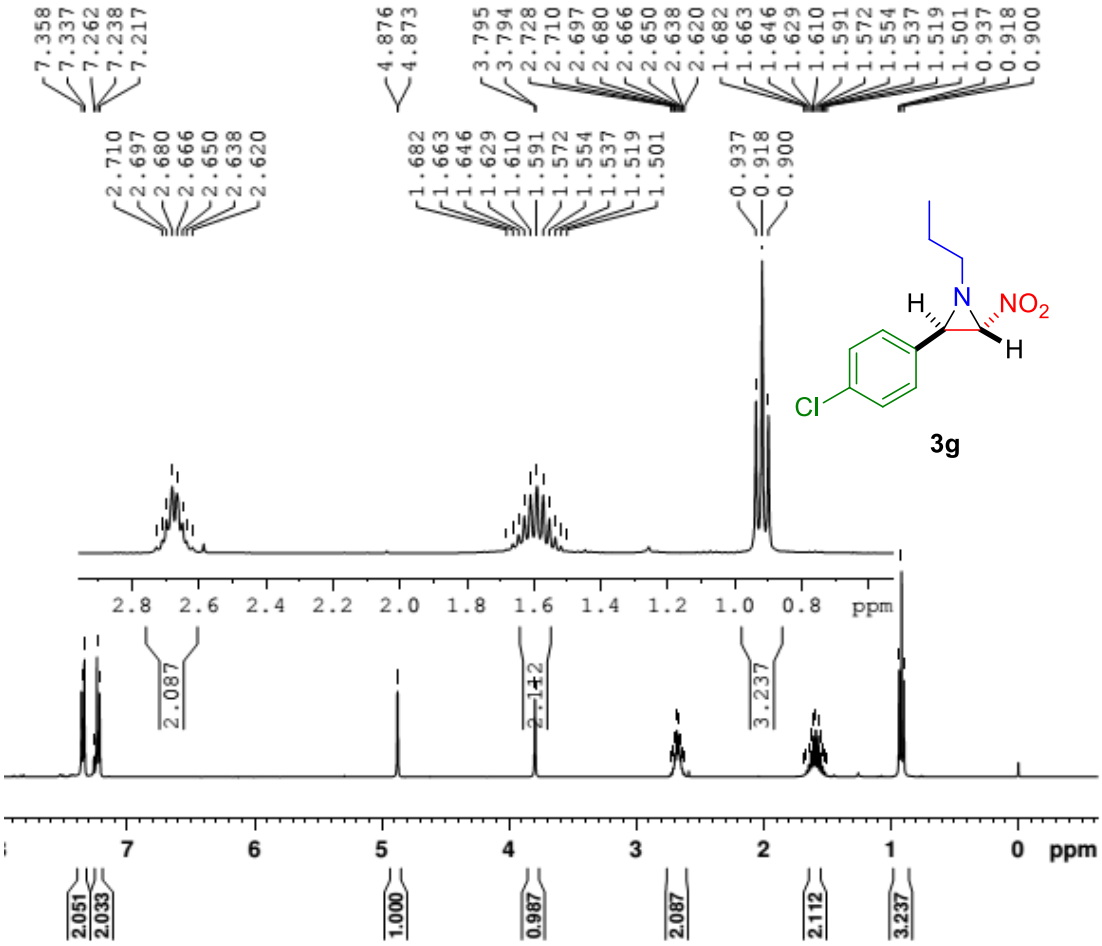

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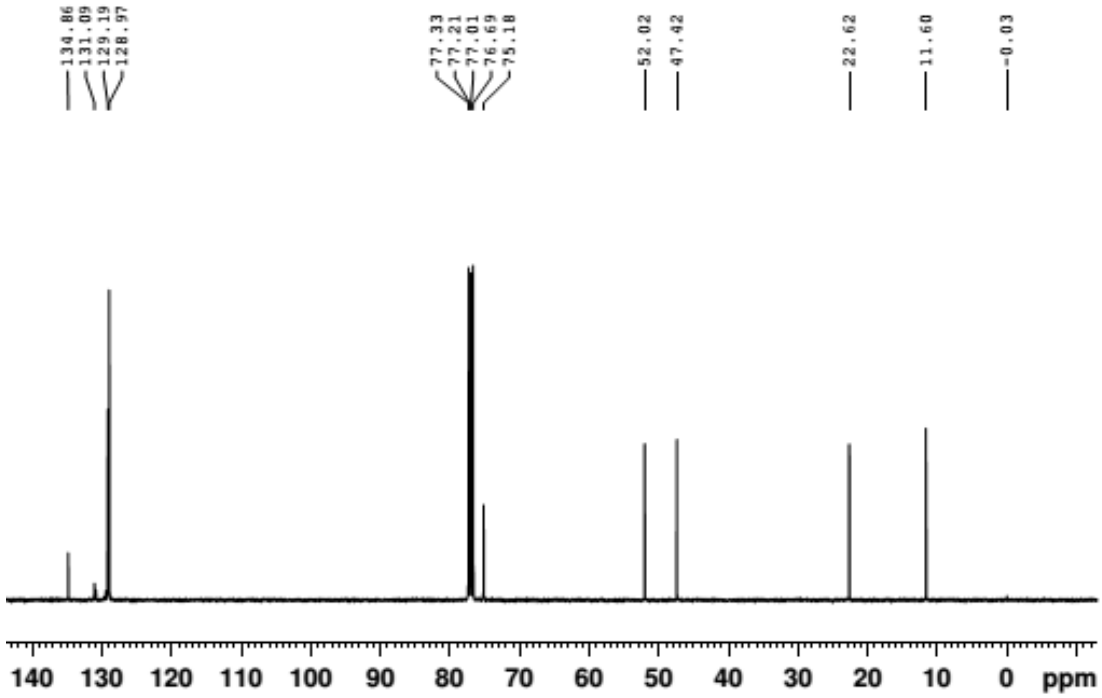

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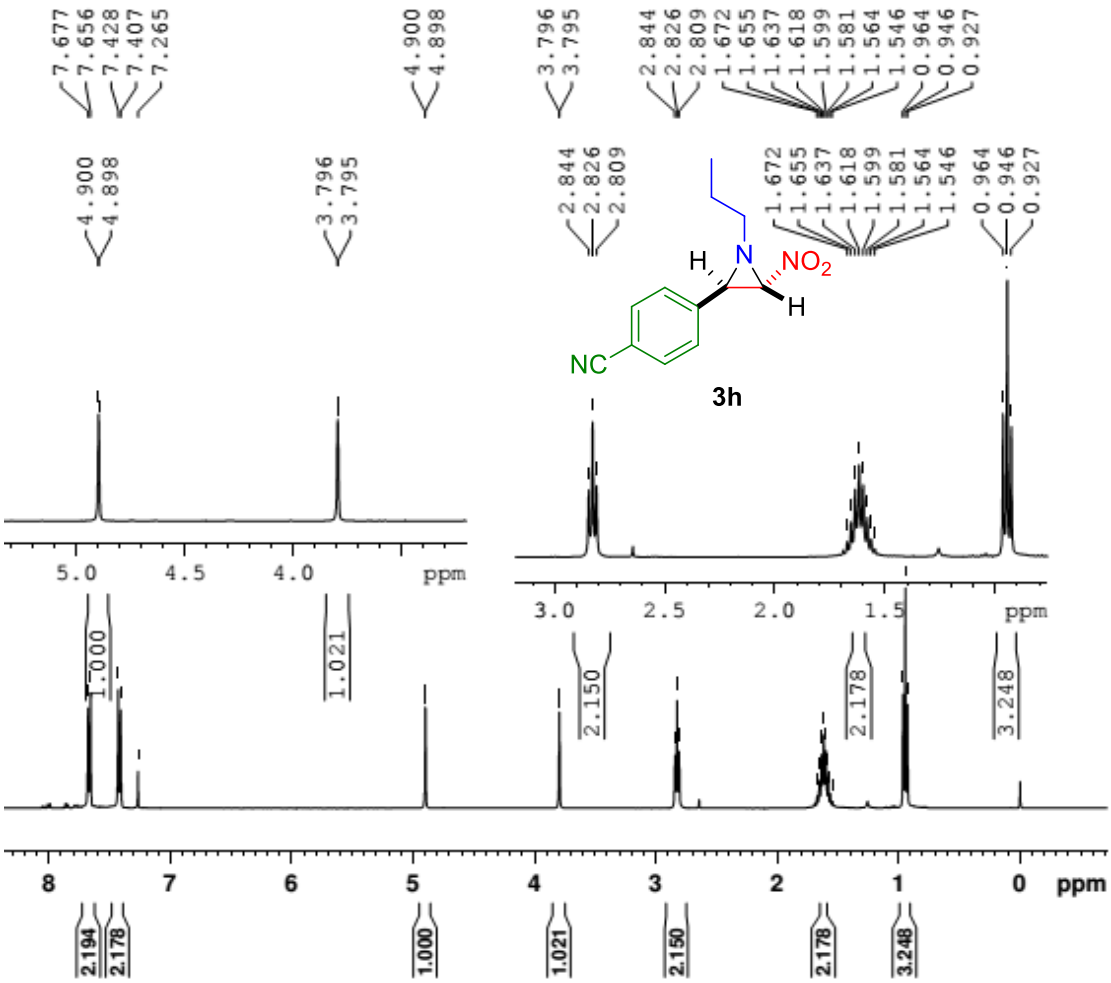

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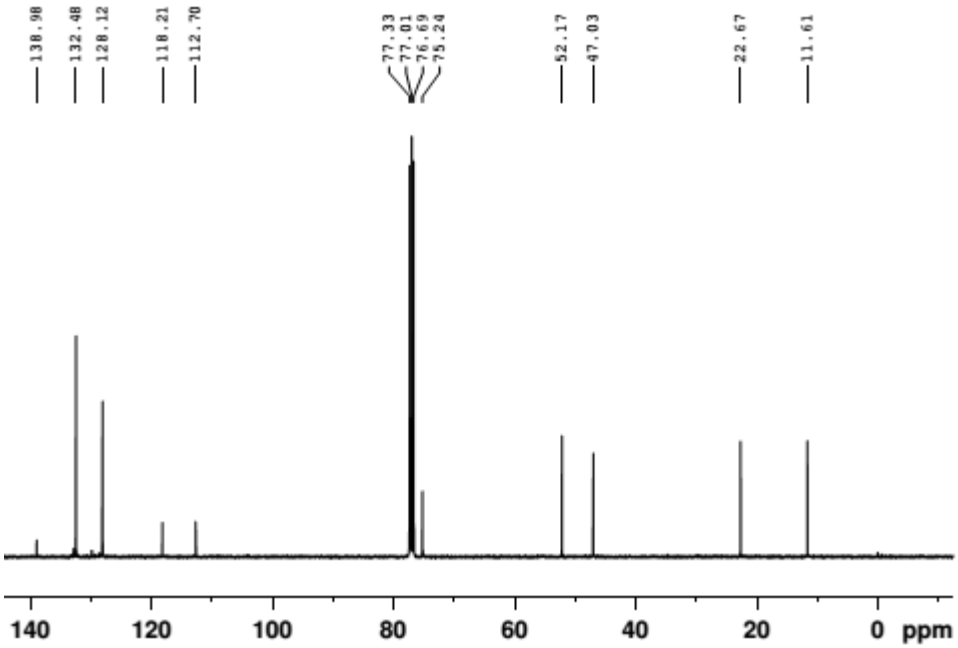

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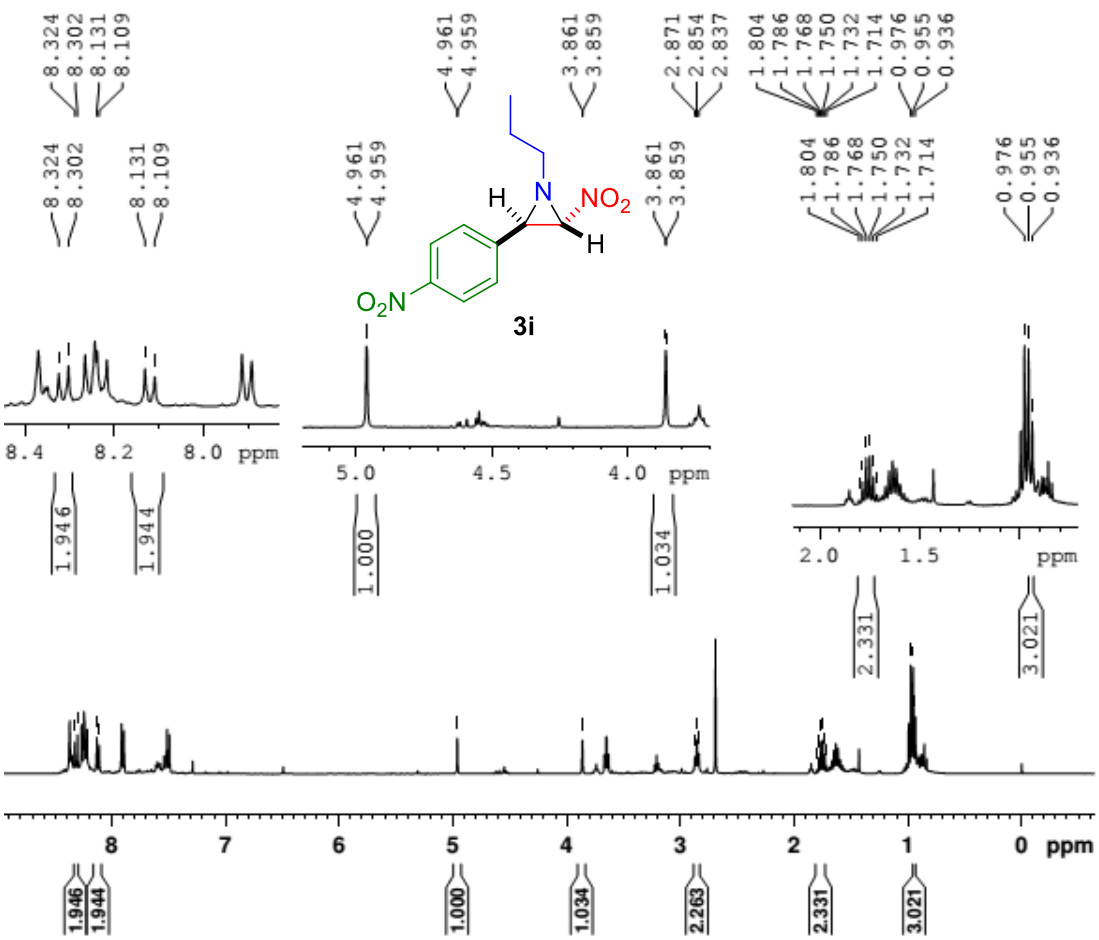
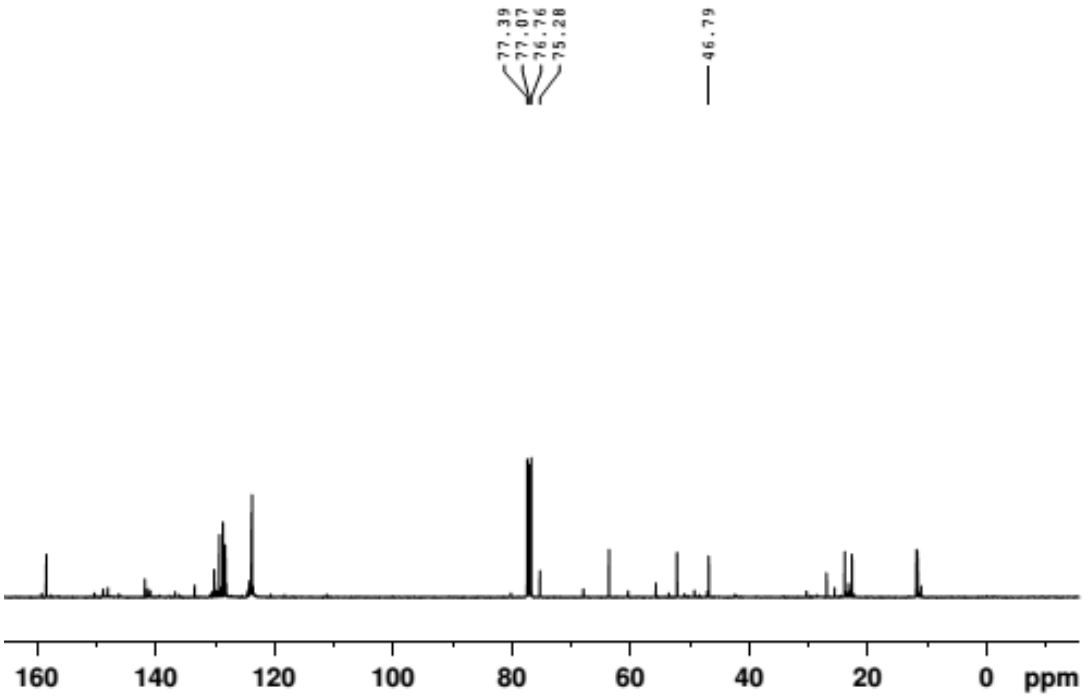


^{1}H NMR (400 MHz) of the reaction mixture in $CDCl_3$



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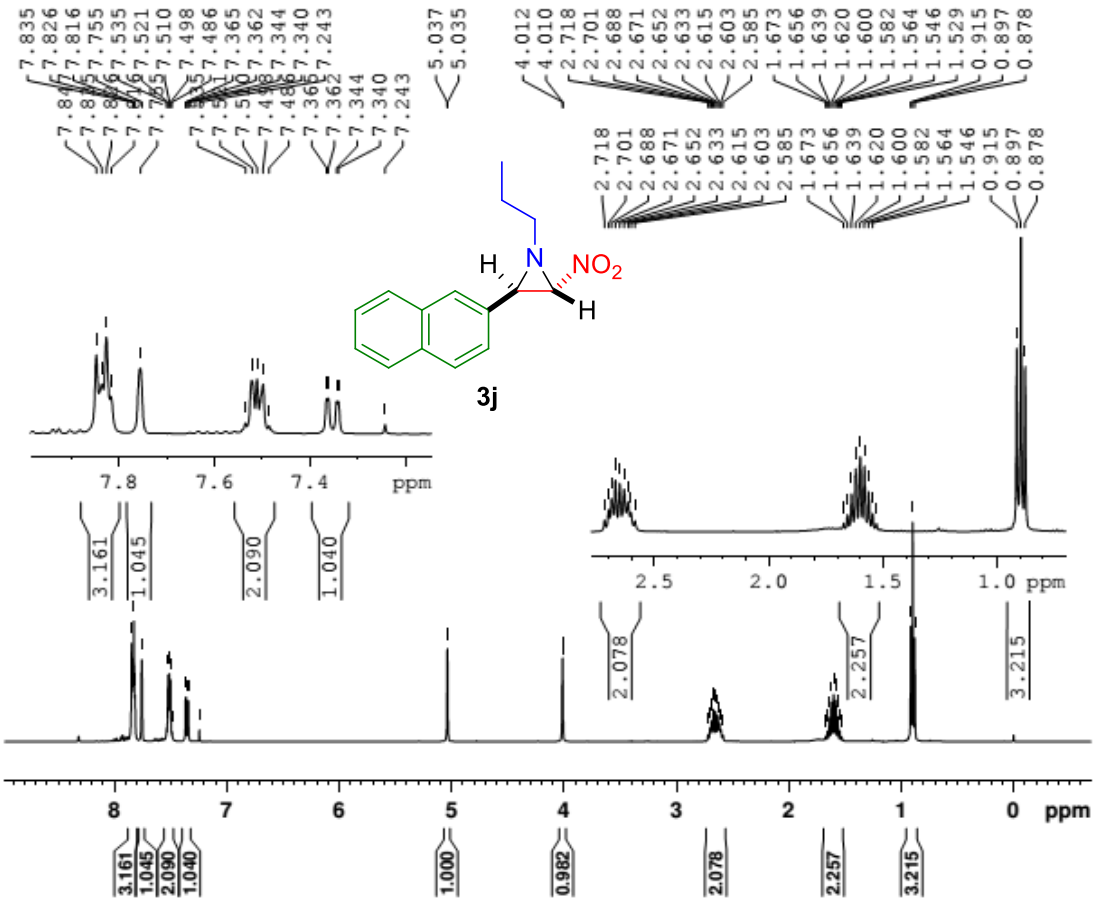

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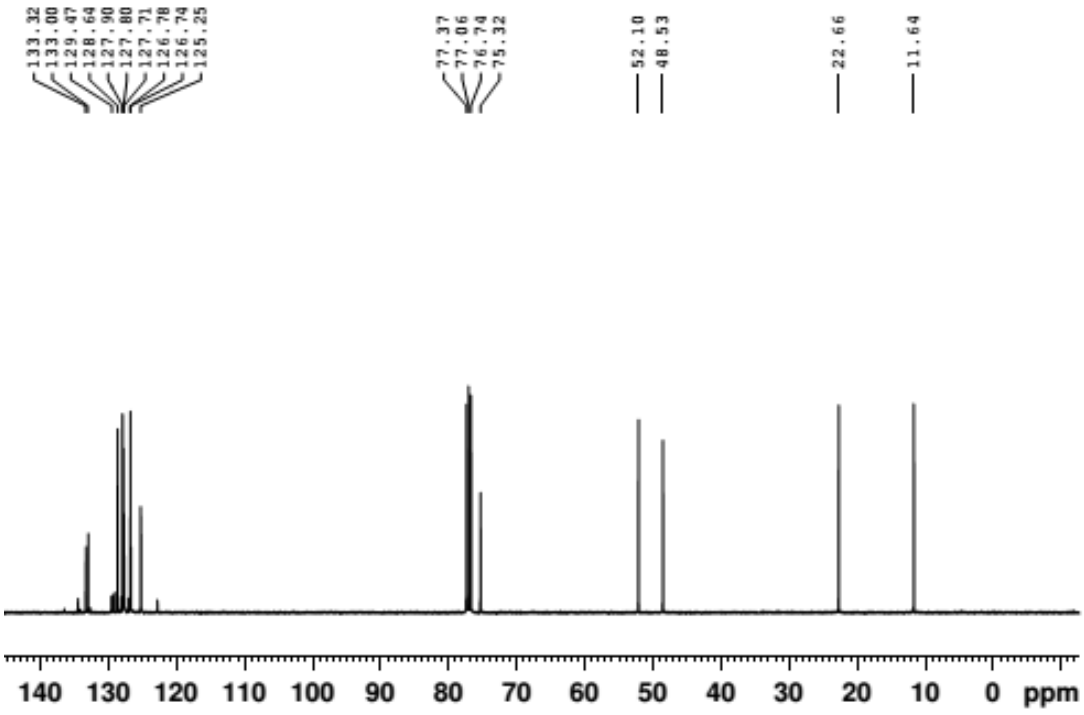

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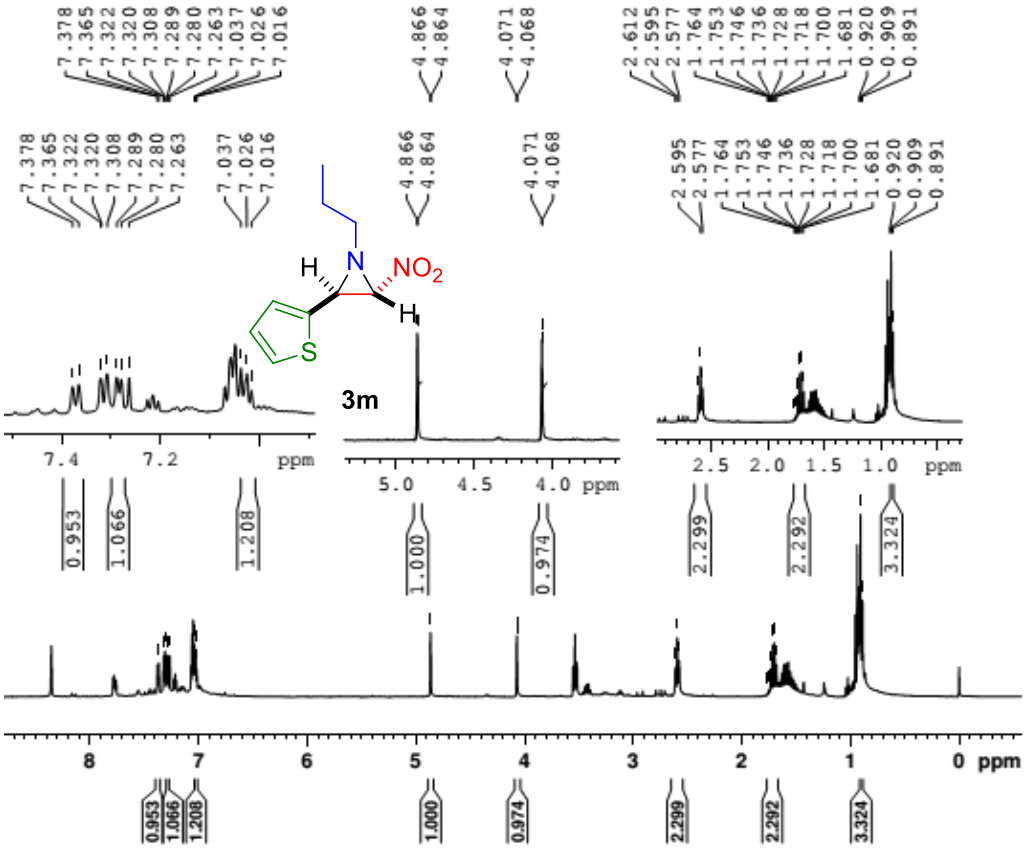
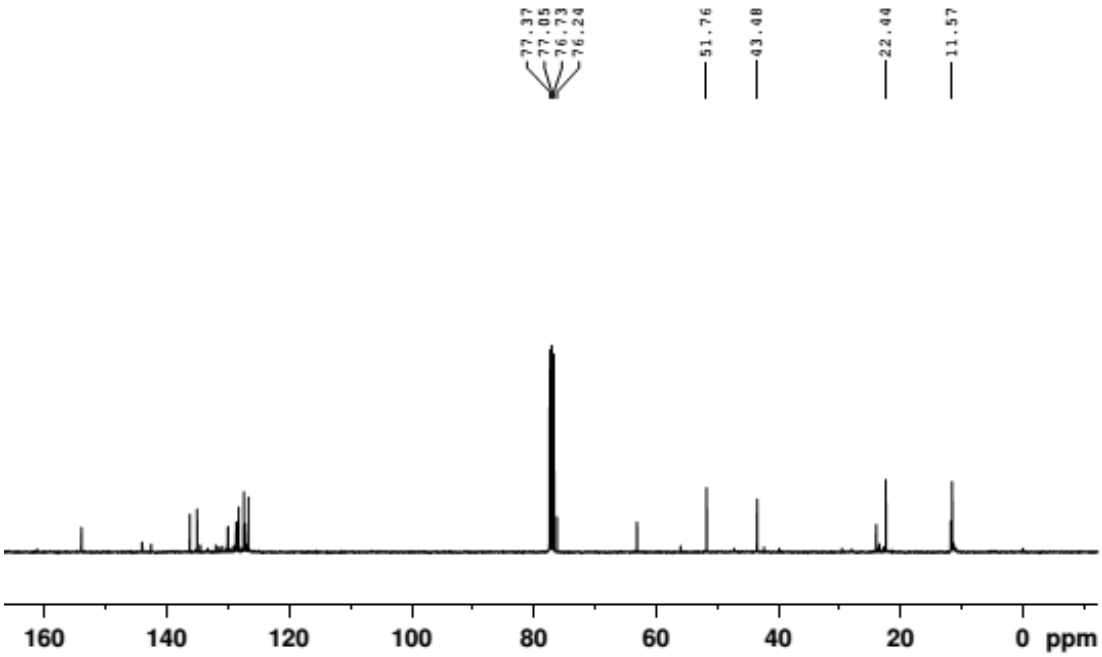


^{1}H NMR (400 MHz) of the reaction mixture in $CDCl_3$



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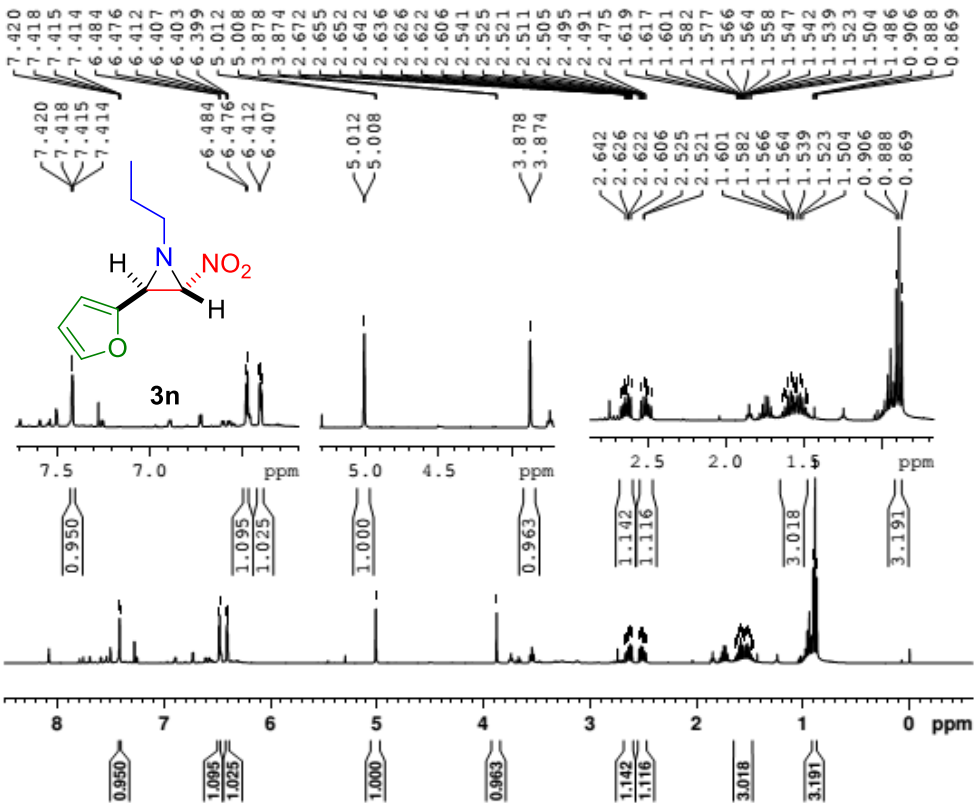

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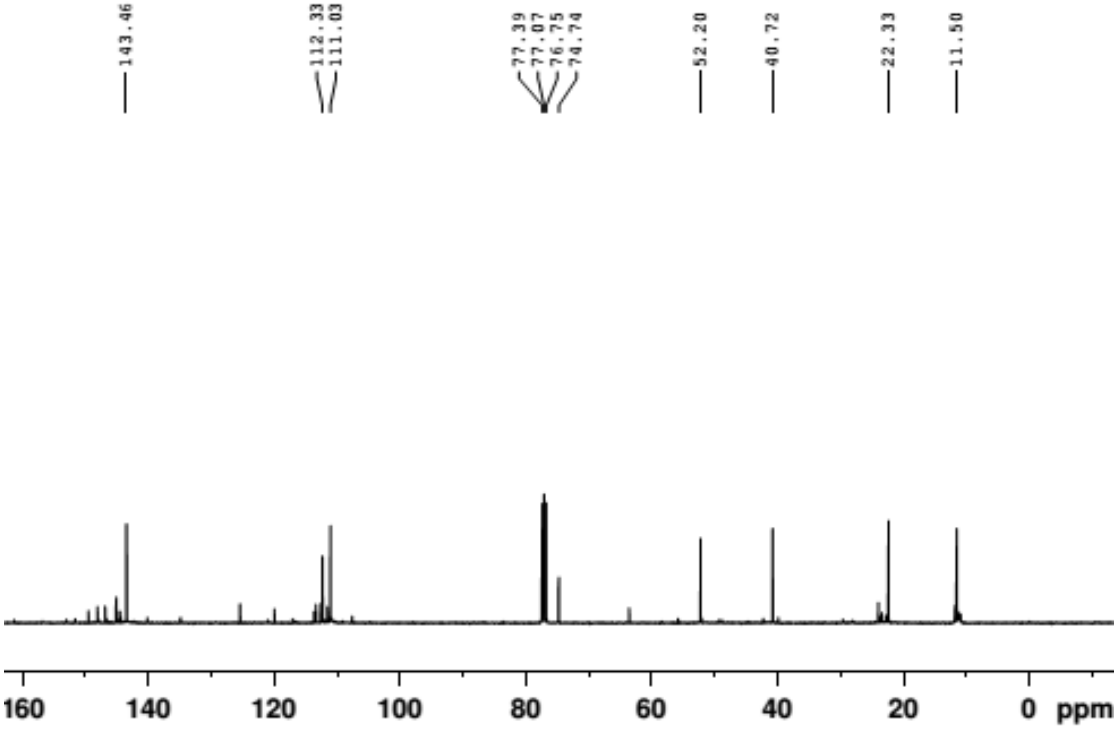

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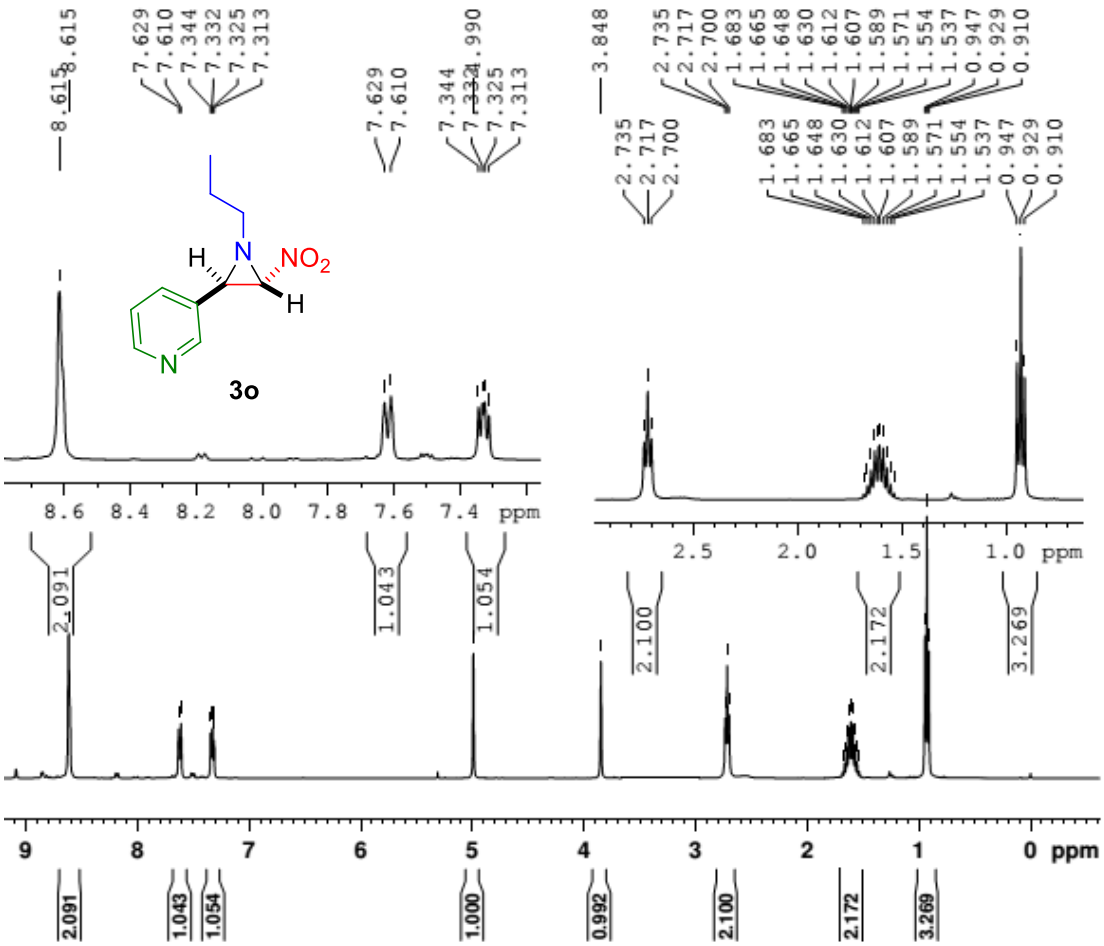

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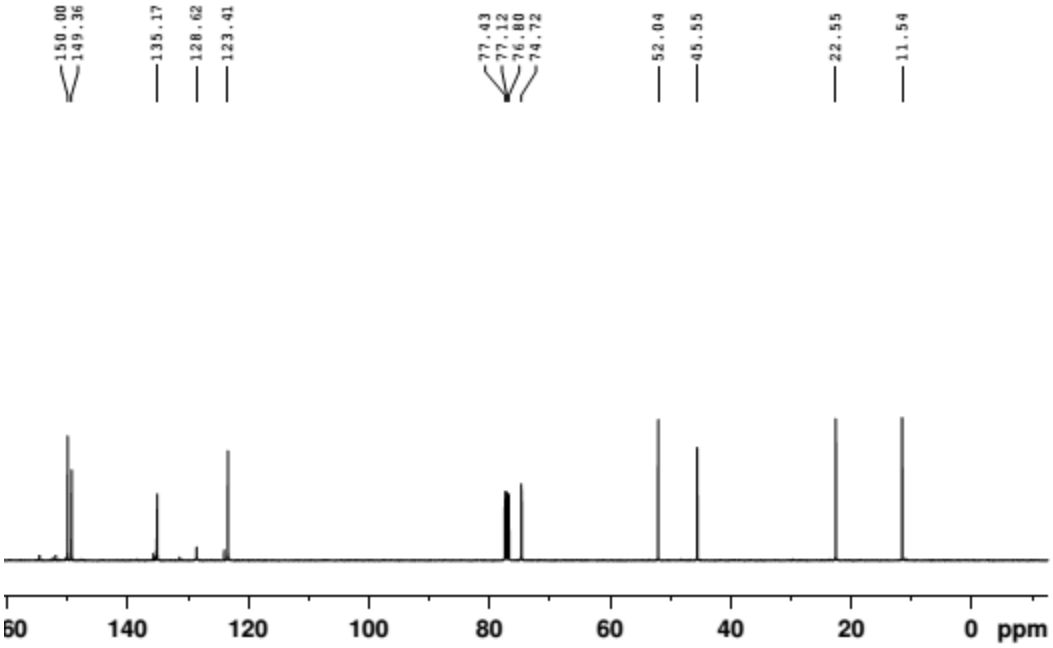

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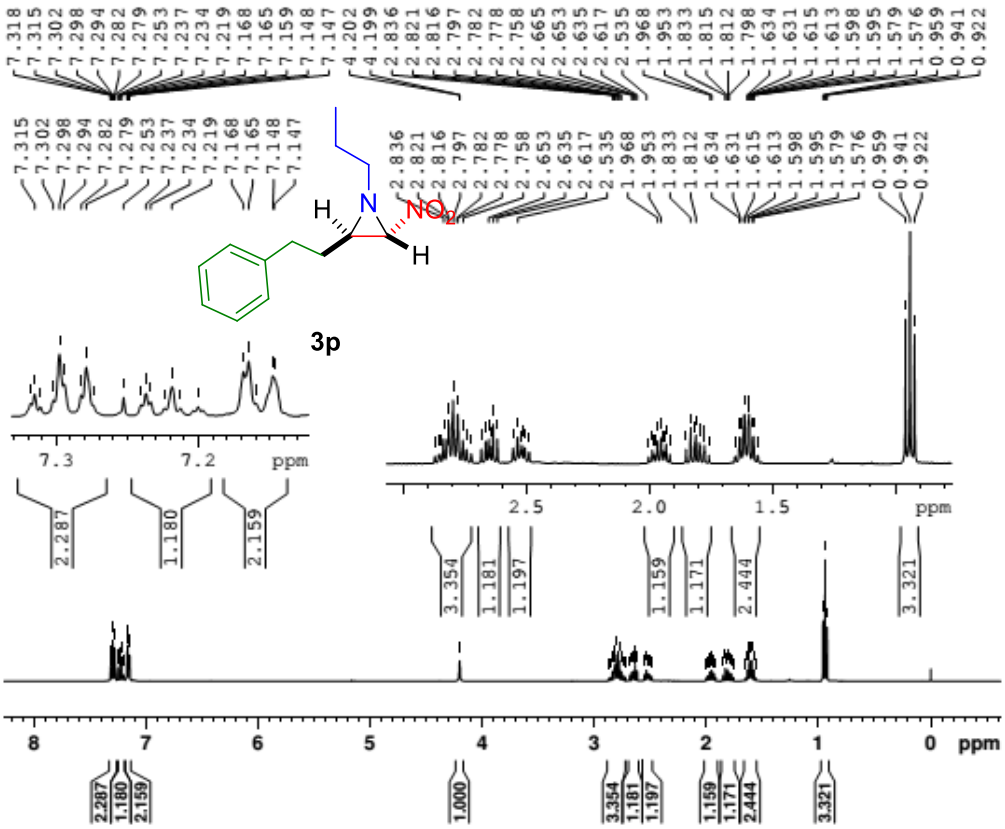

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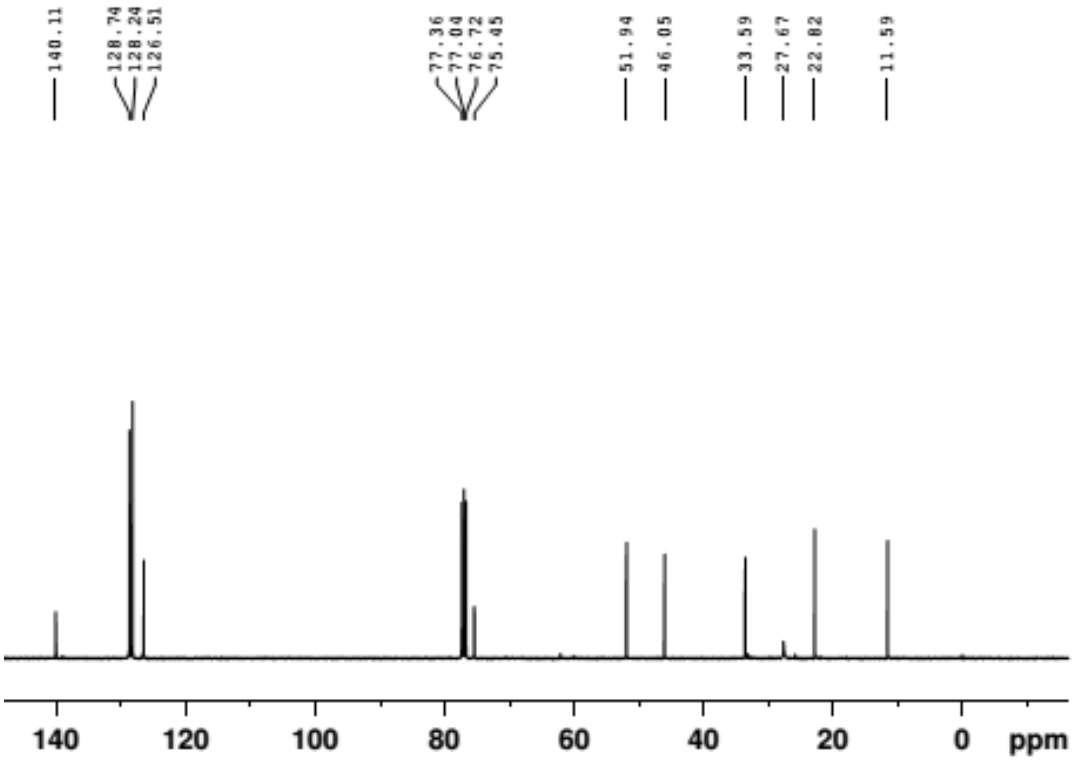
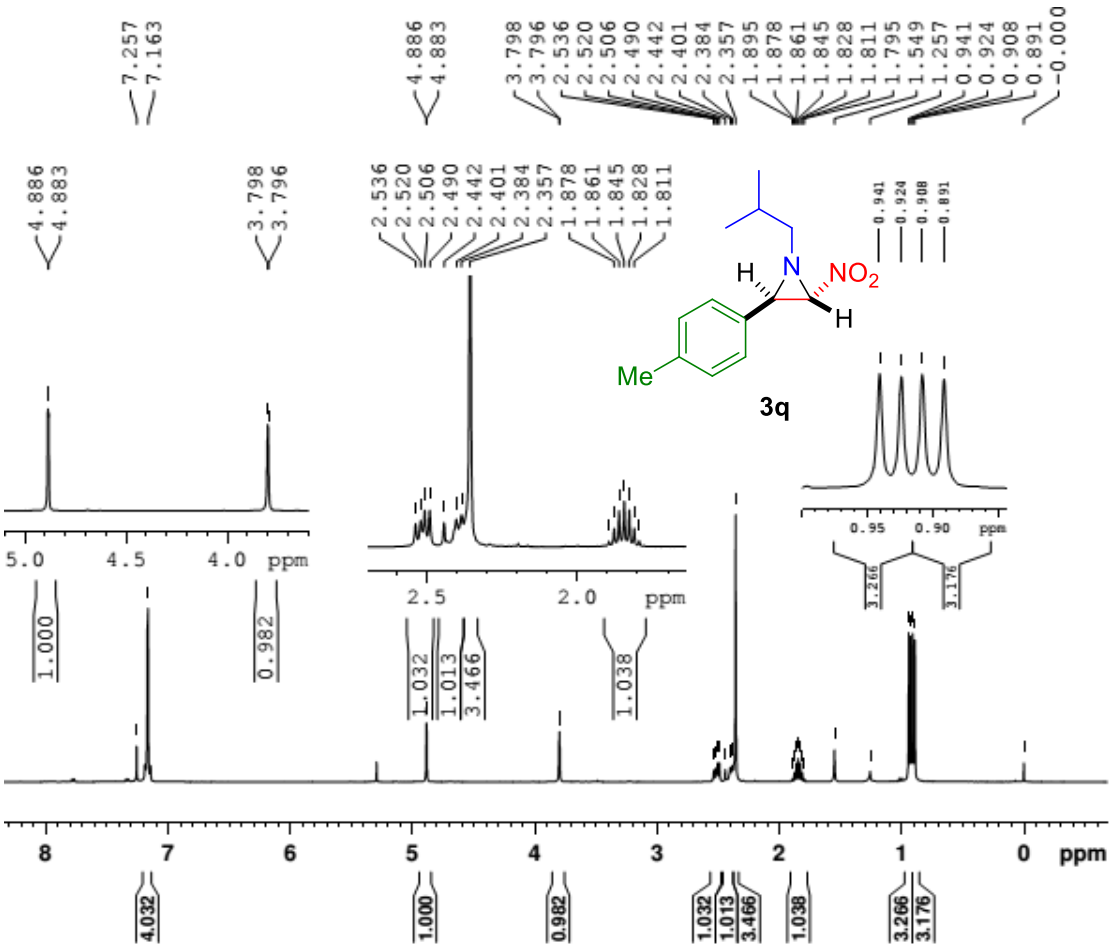


^{13}C NMR (100 MHz) in $CDCl_3$



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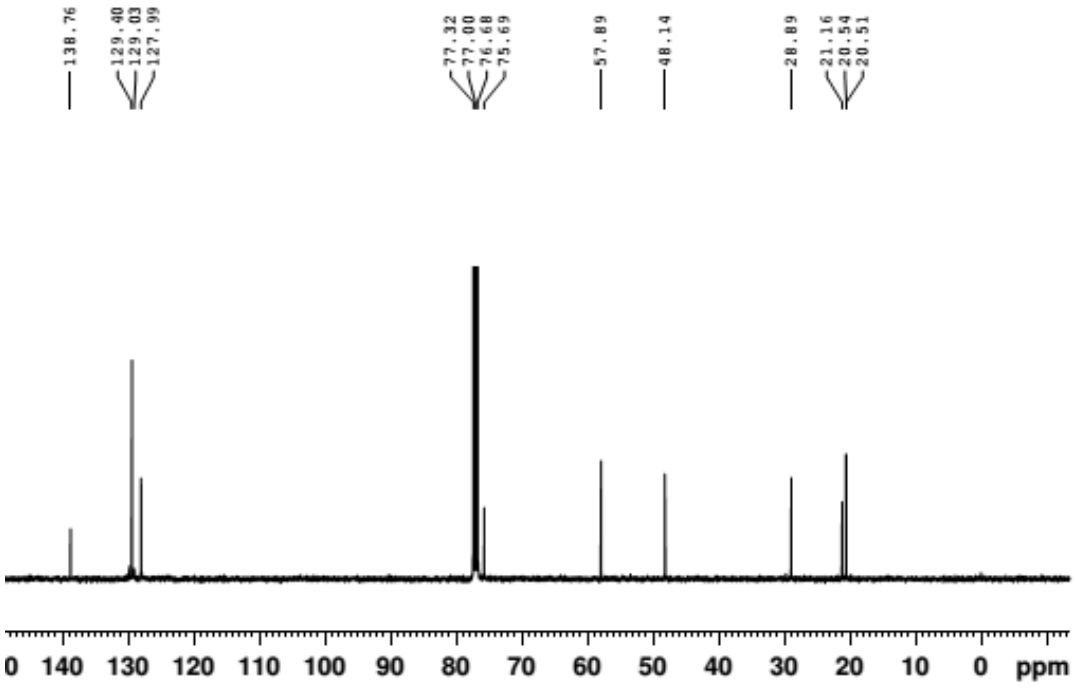

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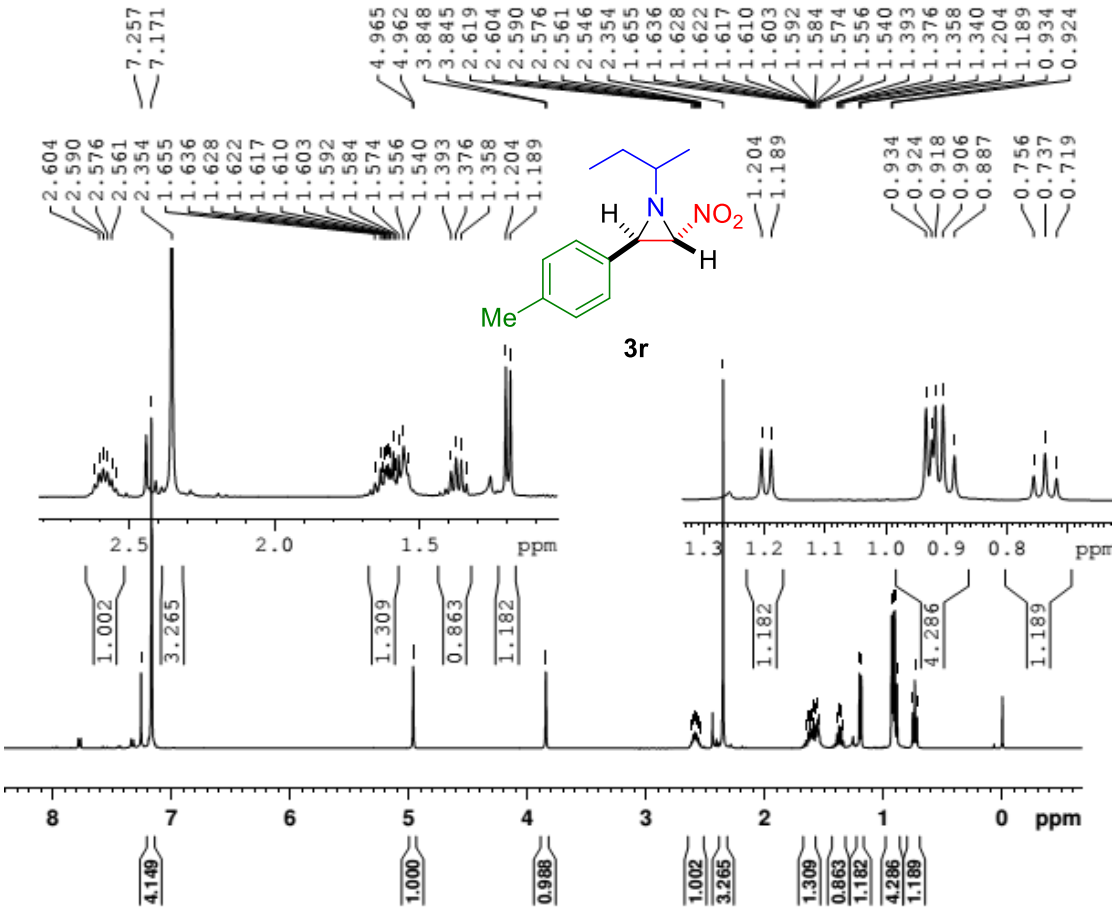

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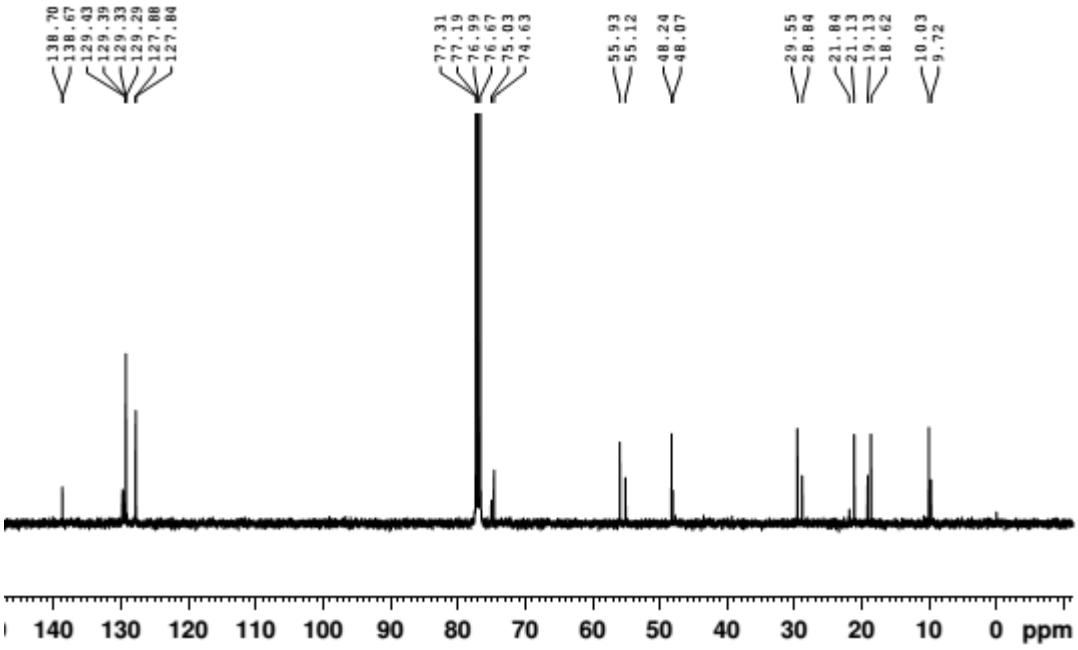
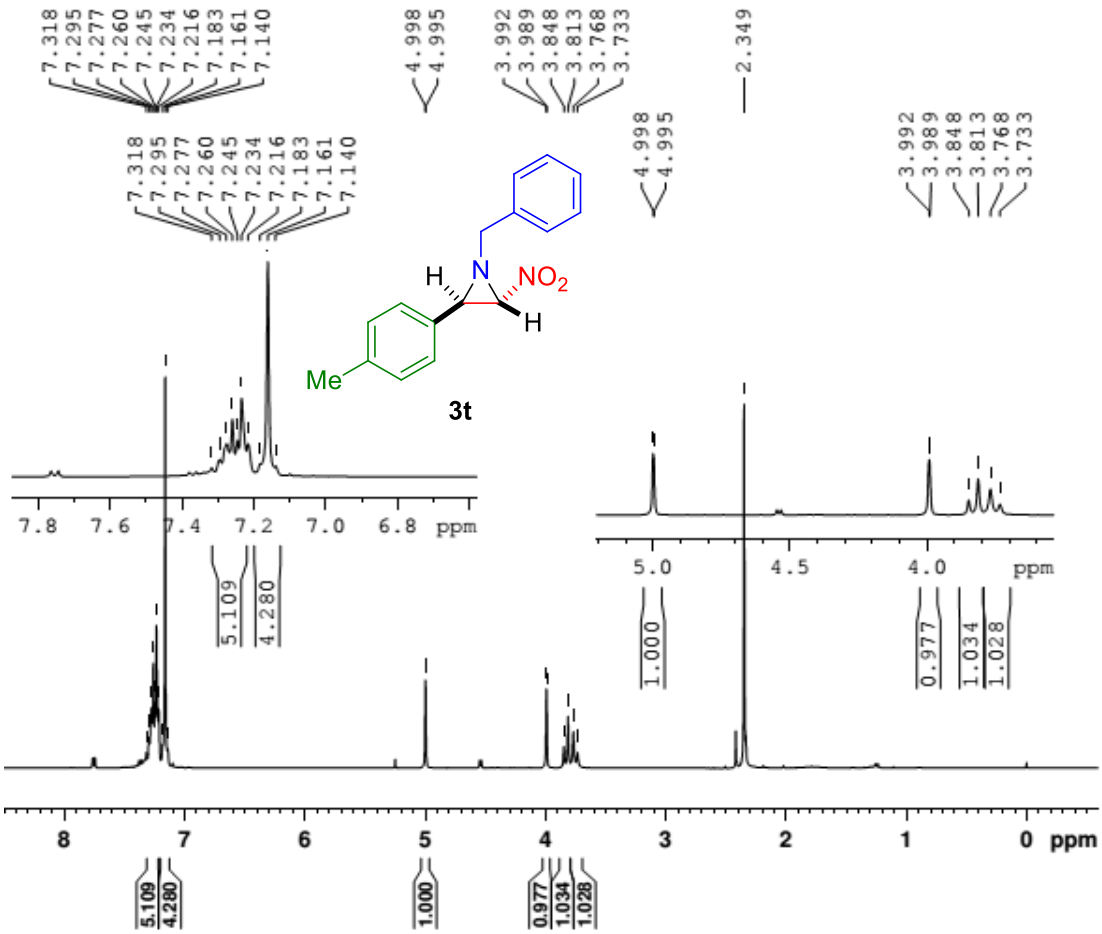
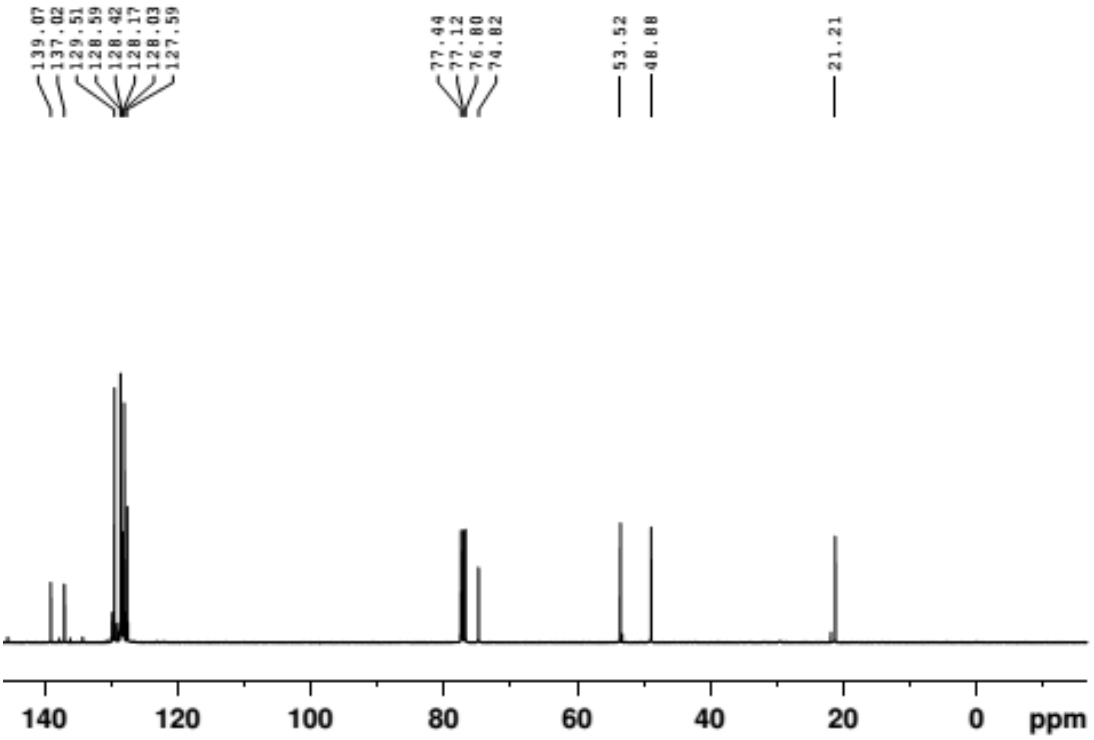


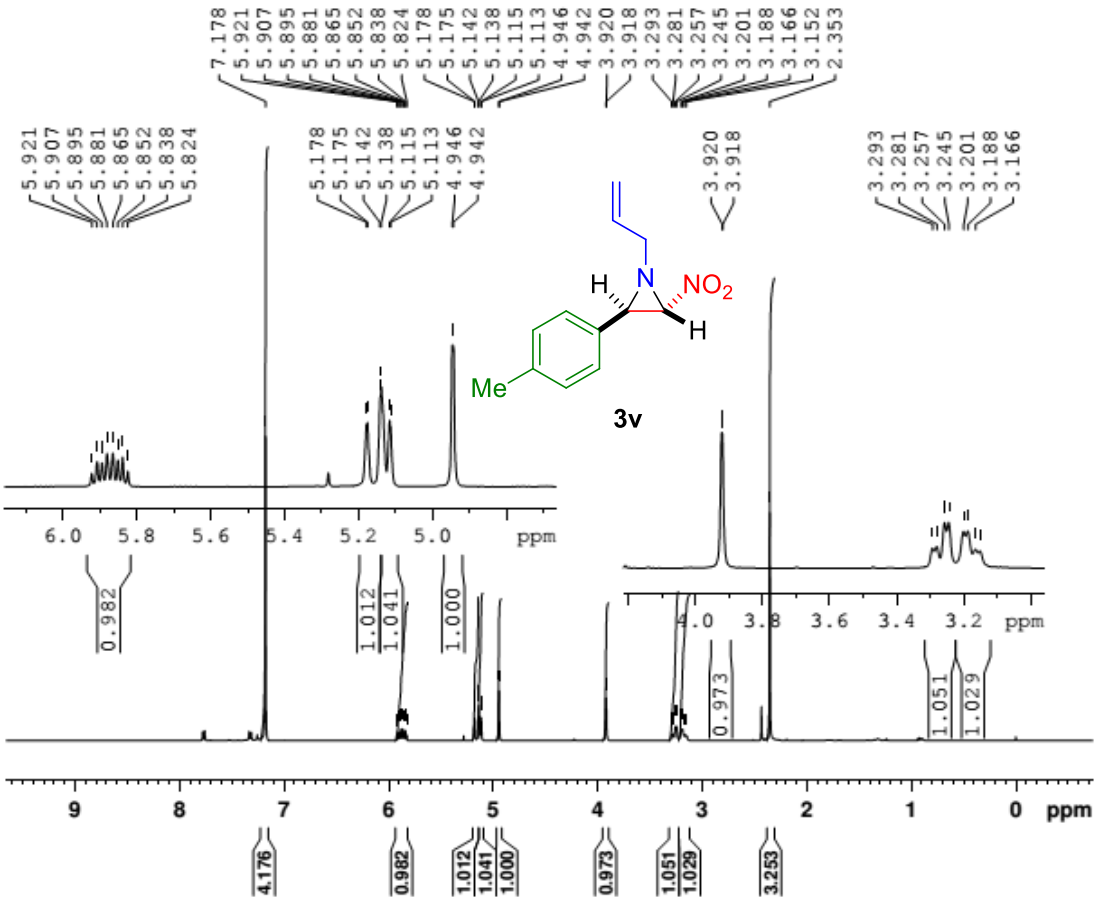
^{13}C NMR (100 MHz) in $CDCl_3$



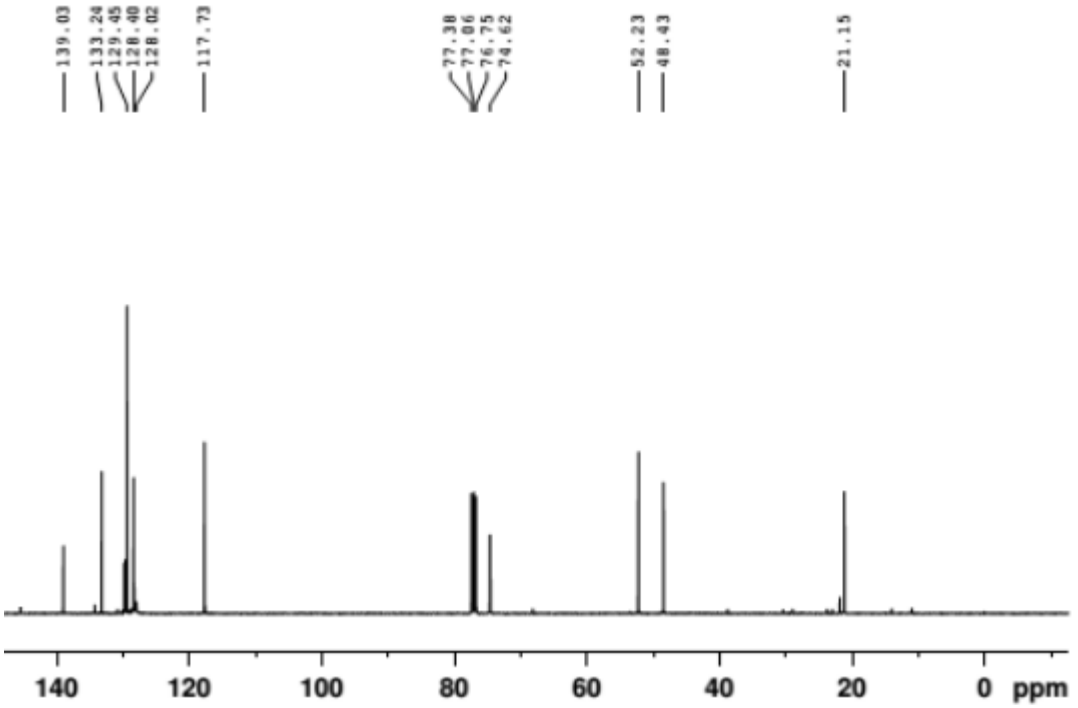
^{1}H NMR (400 MHz) in $CDCl_3$



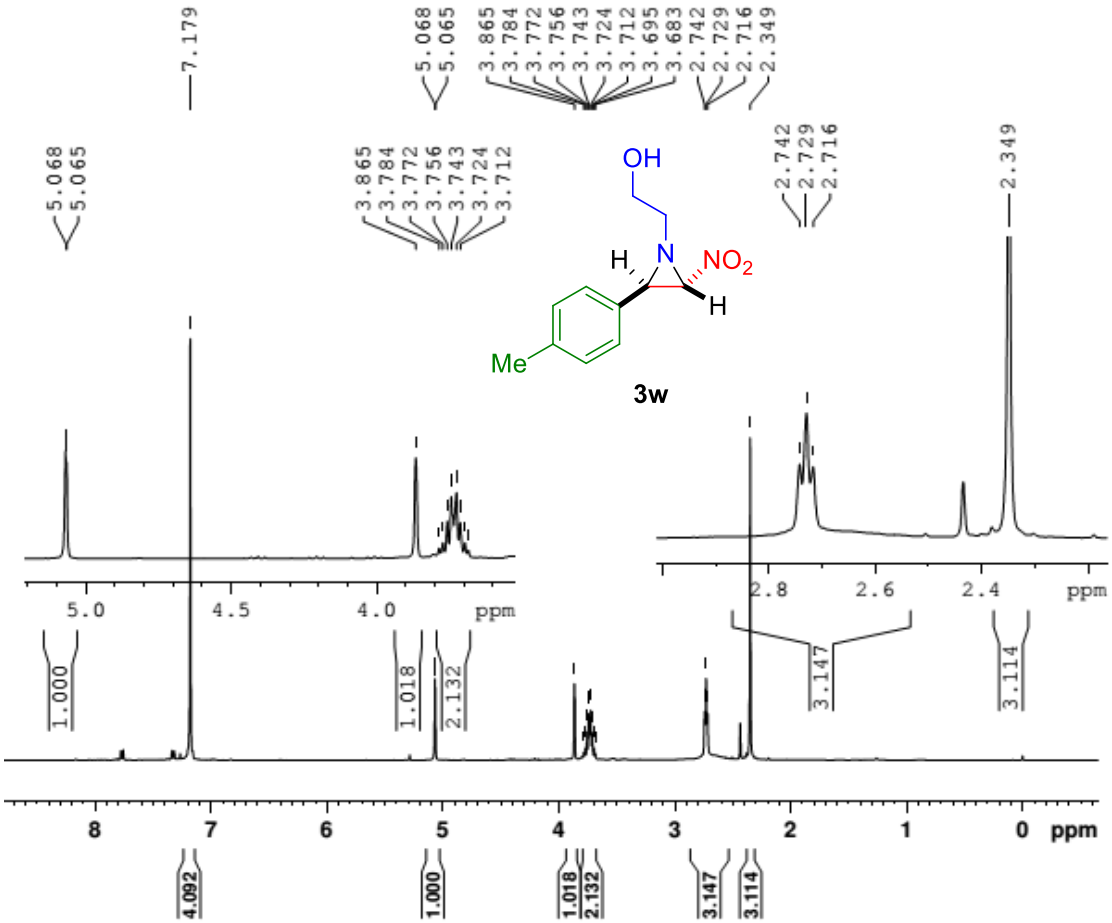
^{13}C NMR (100 MHz) in $CDCl_3$



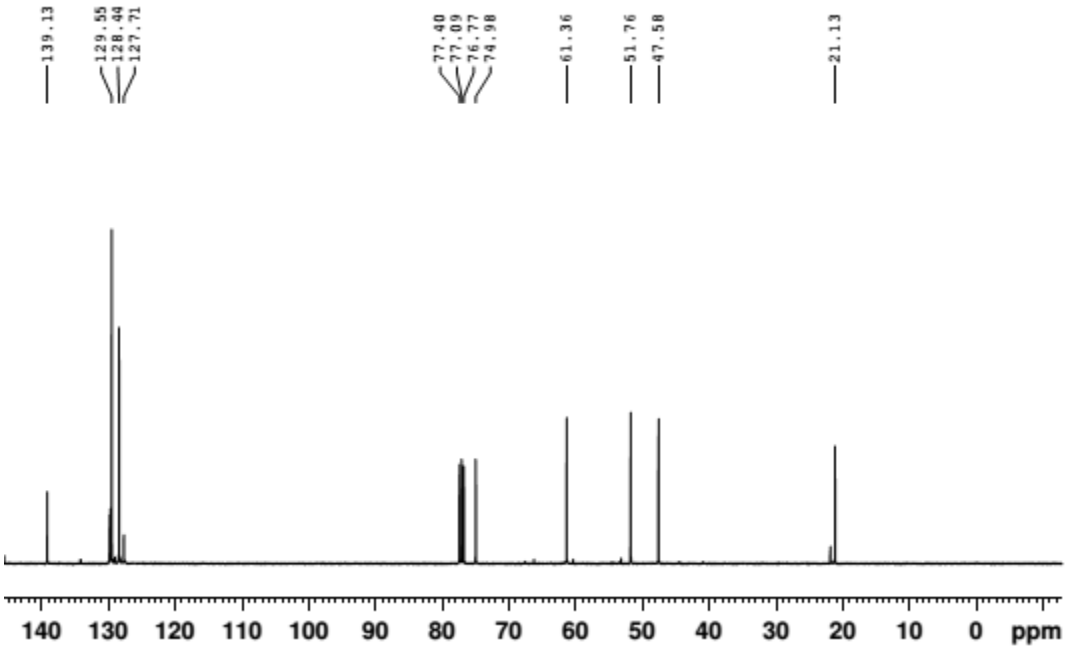
^{1}H NMR (400 MHz) in $CDCl_3$



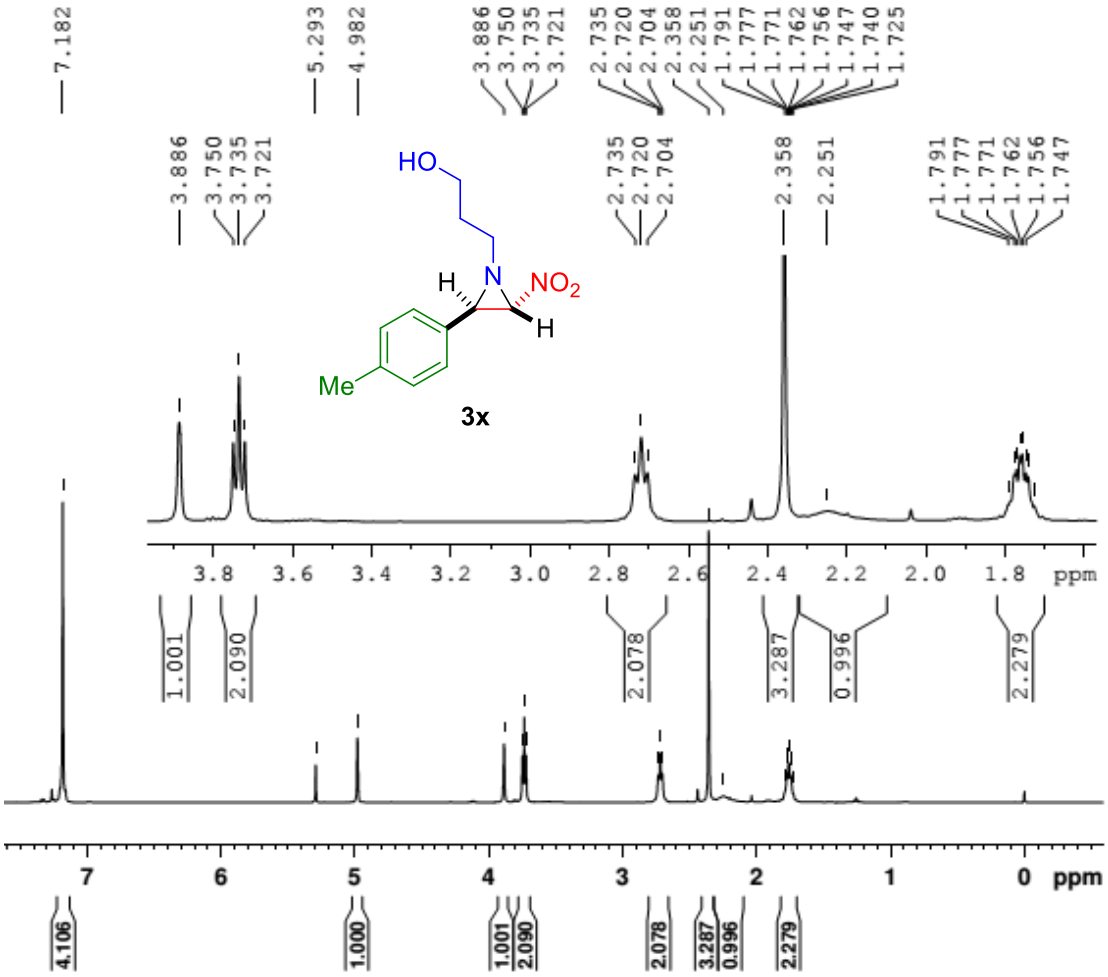
^{13}C NMR (100 MHz) in $CDCl_3$



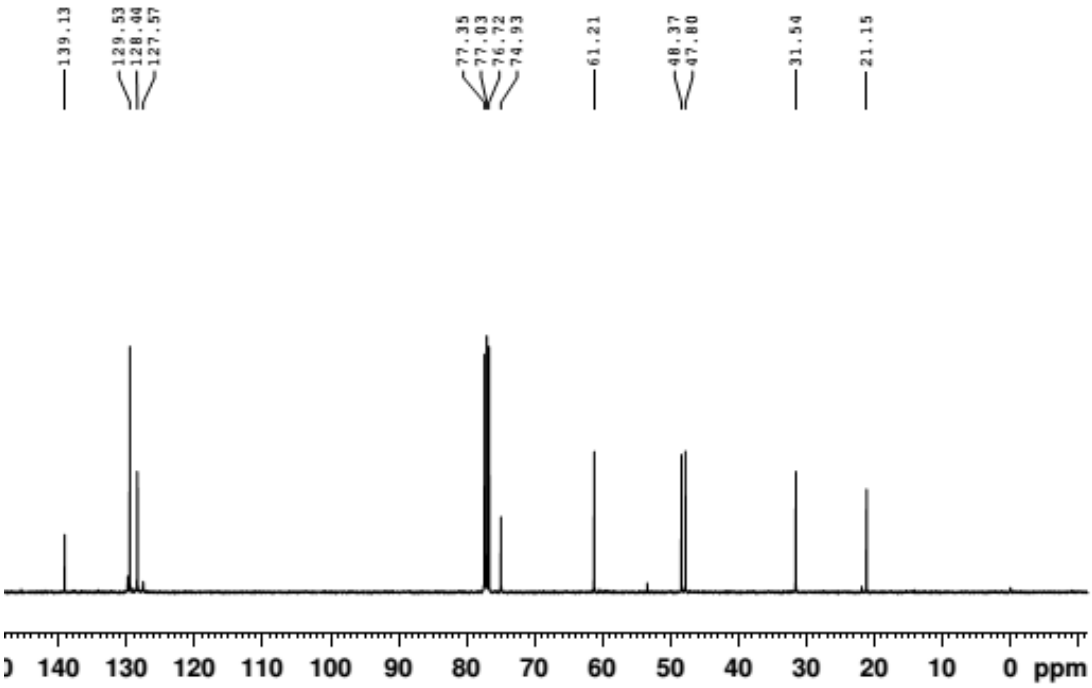
^{1}H NMR (400 MHz) in $CDCl_3$



^{13}C NMR (100 MHz) in $CDCl_3$



^{1}H NMR (400 MHz) in $CDCl_3$



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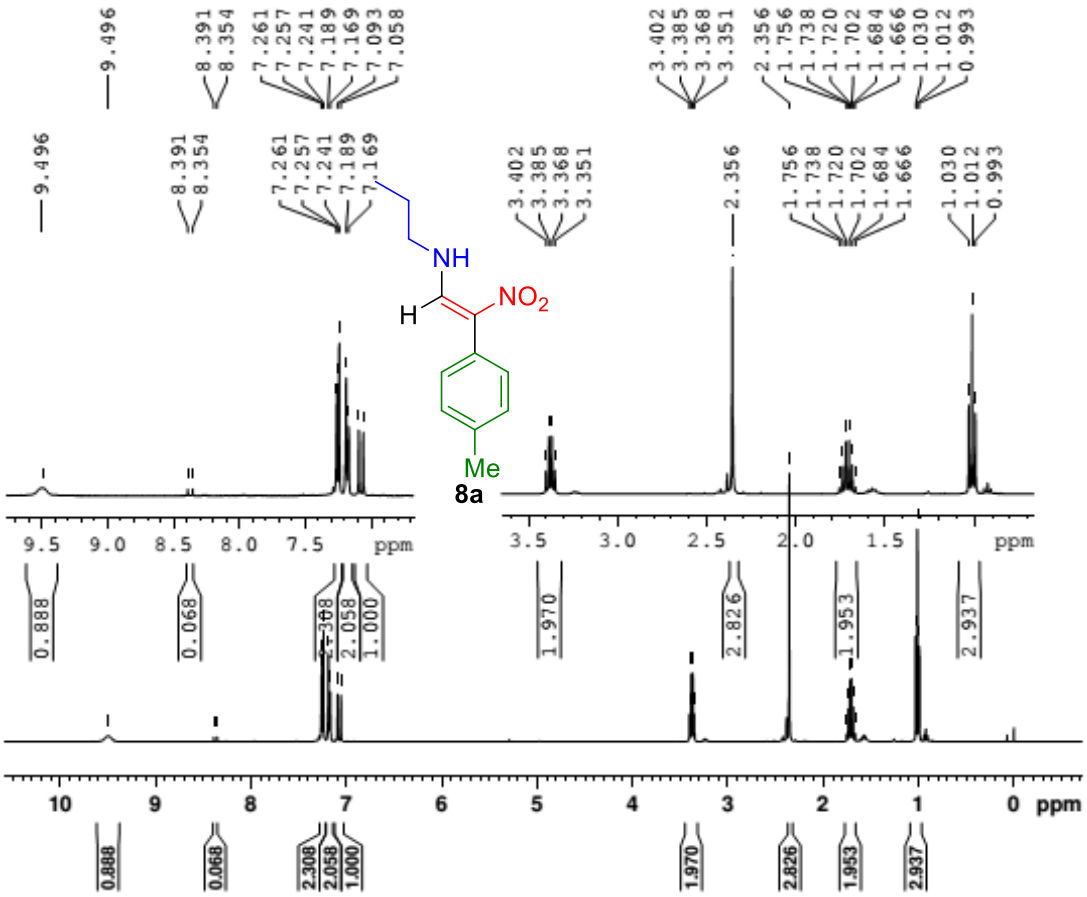

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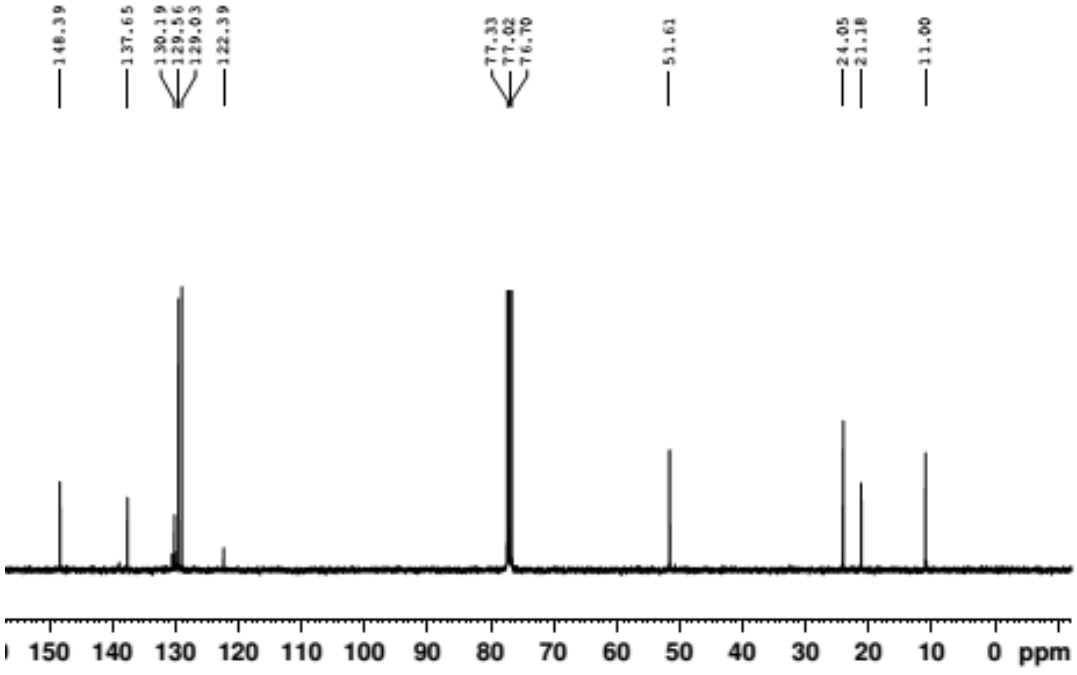

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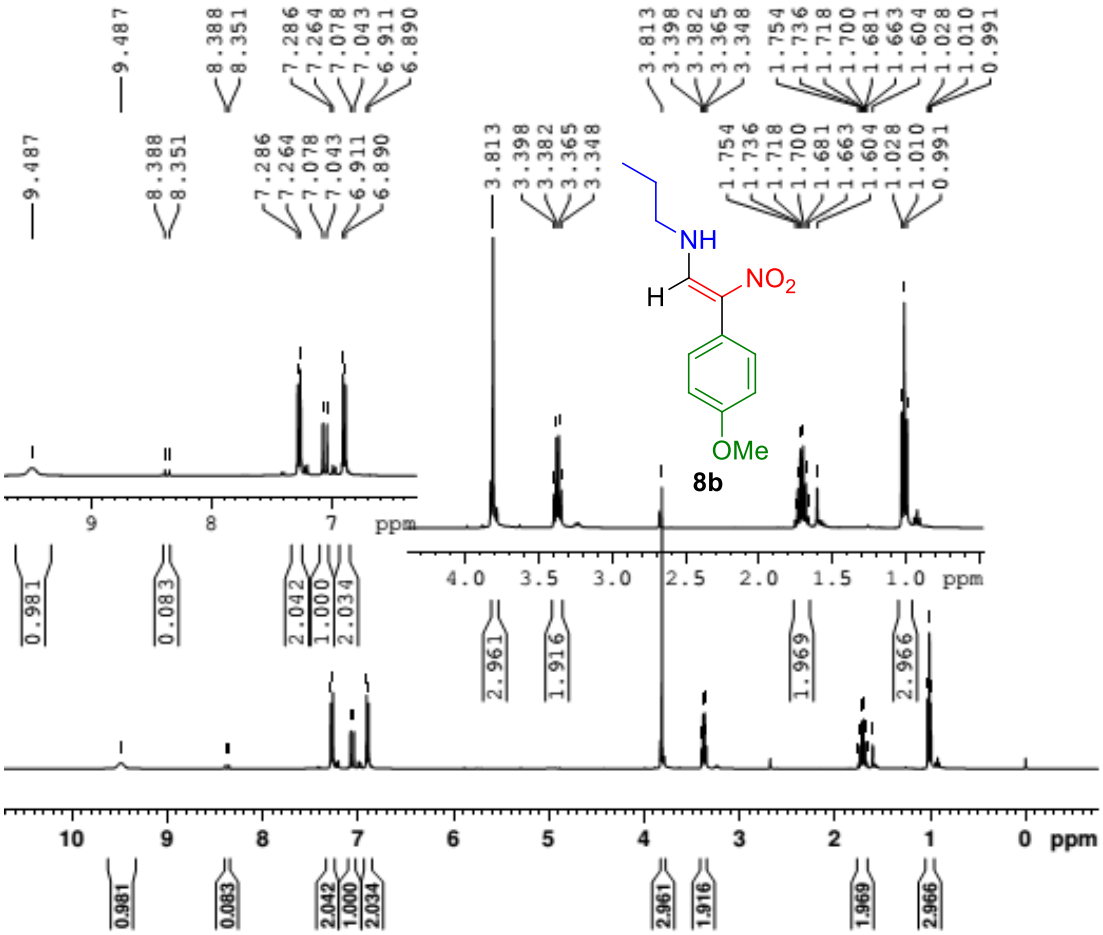

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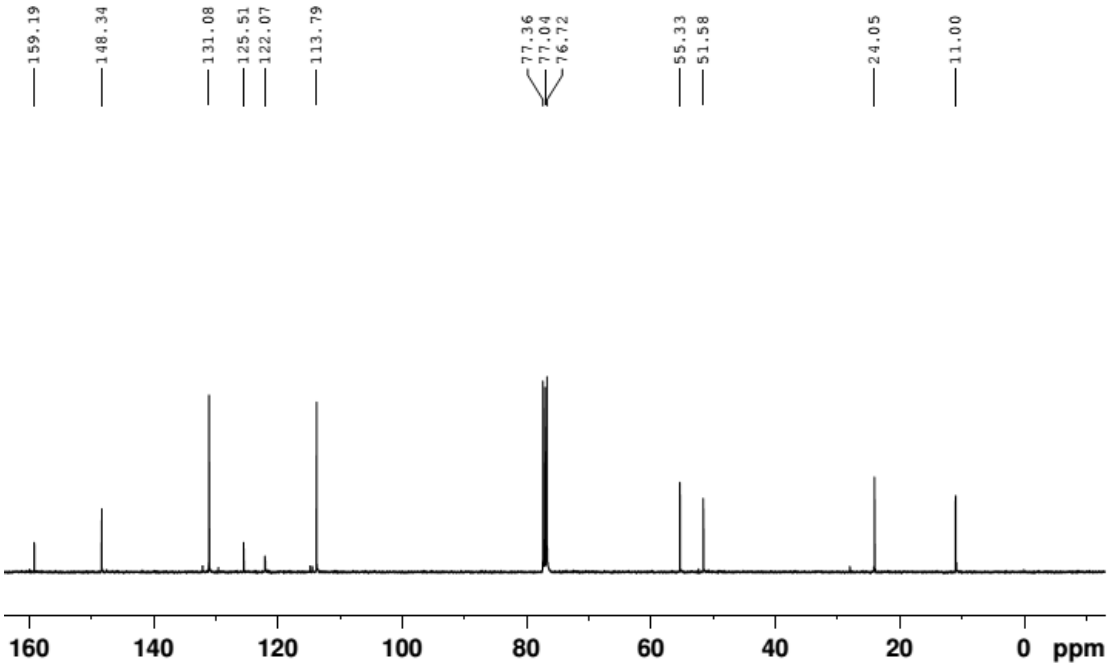

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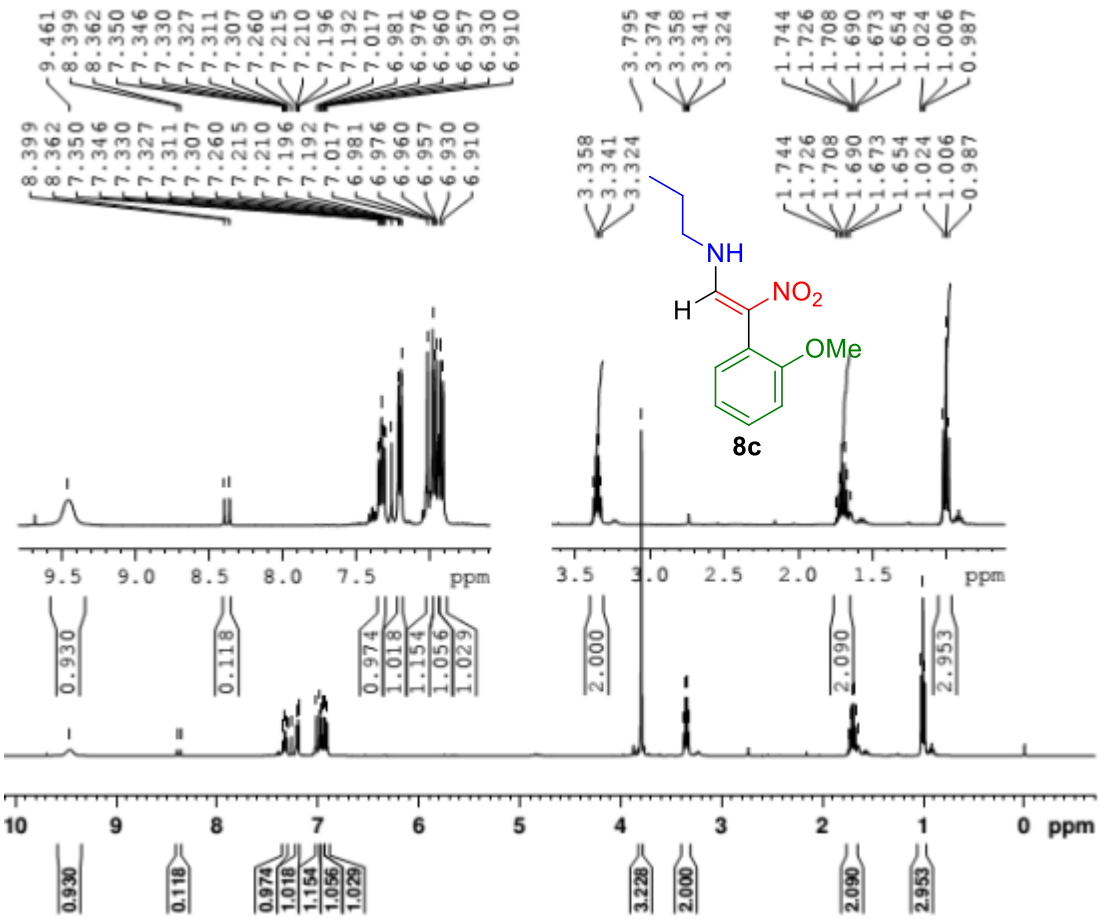

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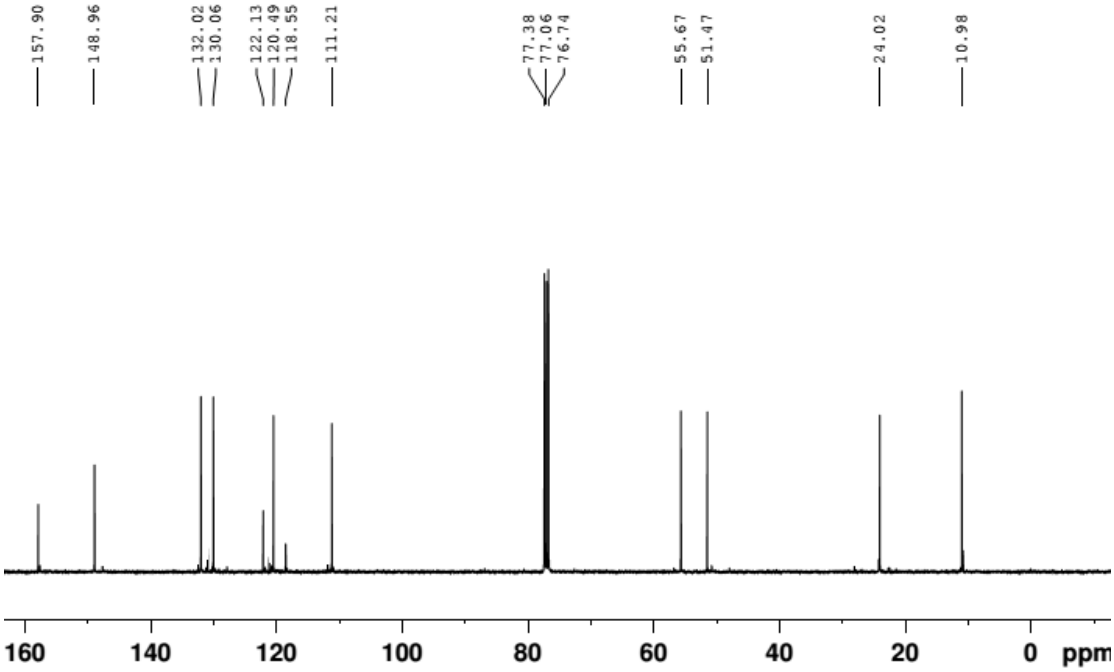

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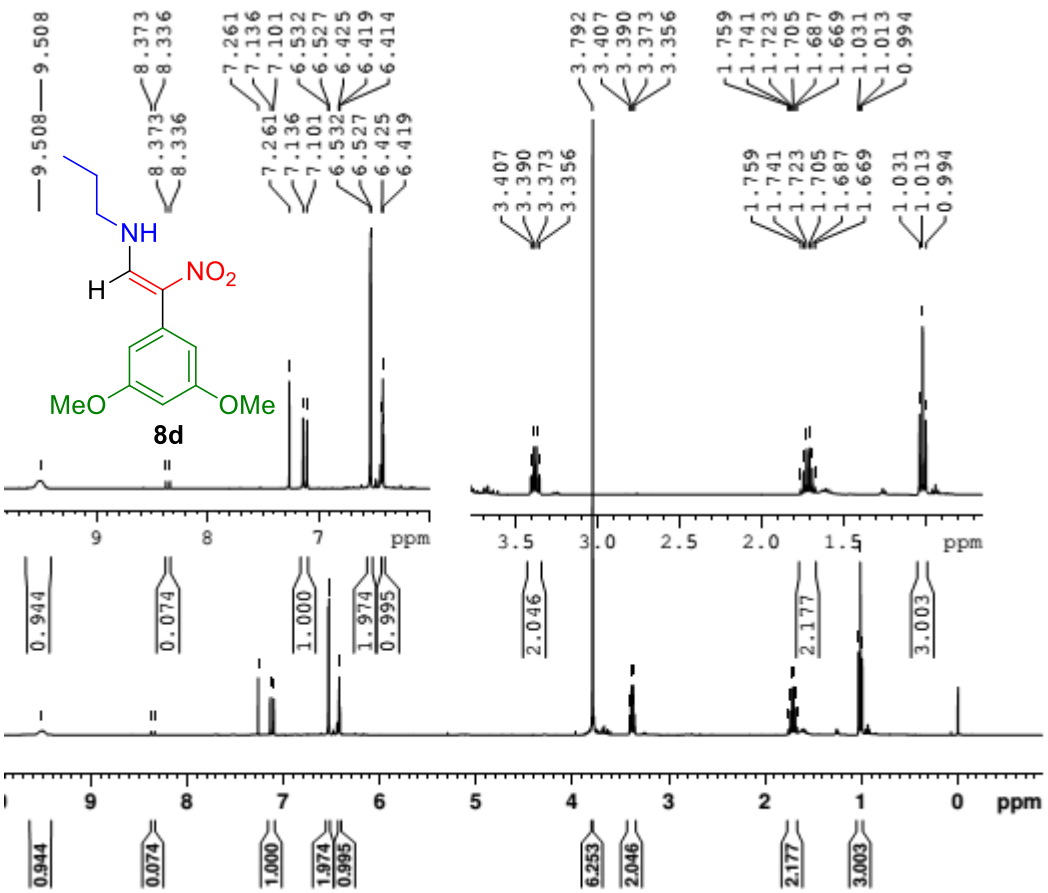

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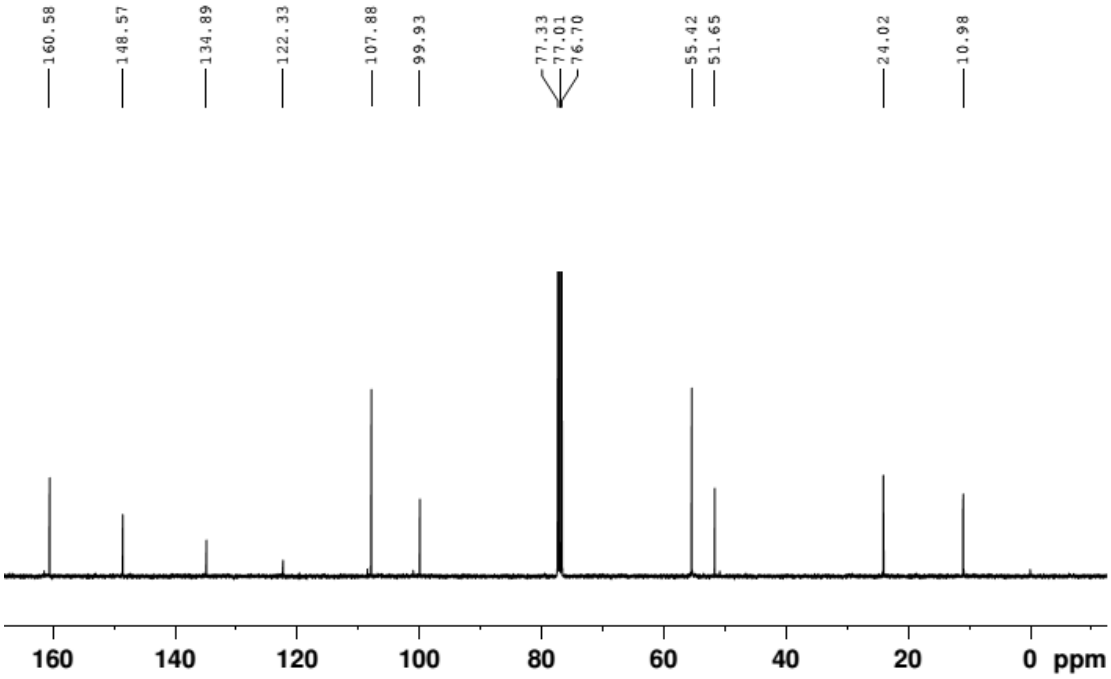

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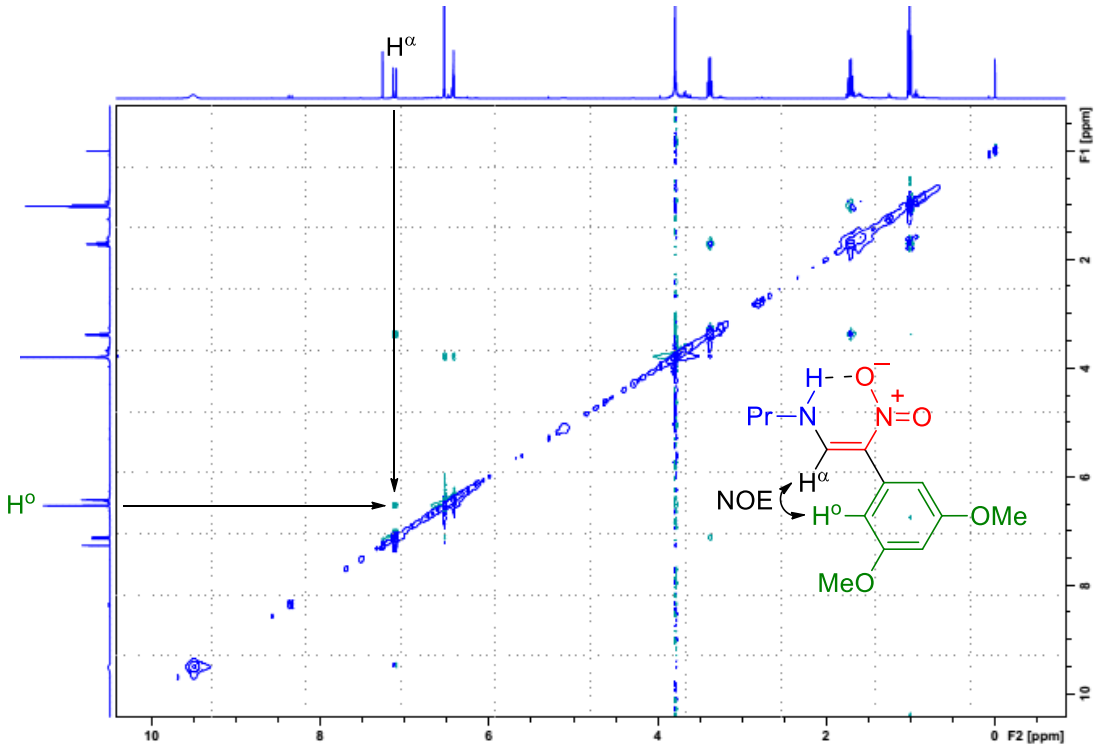
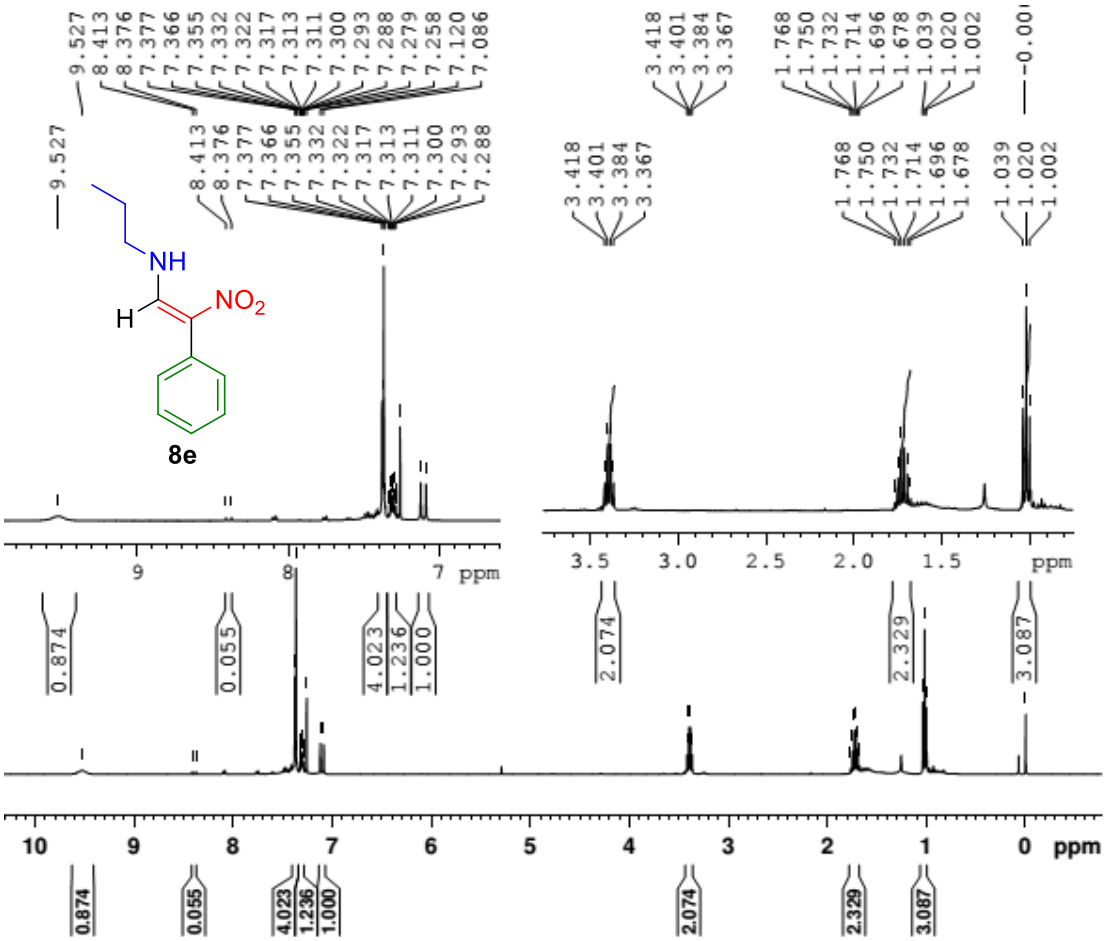


^{1}H-^{1}H NOESY in $CDCl_3$



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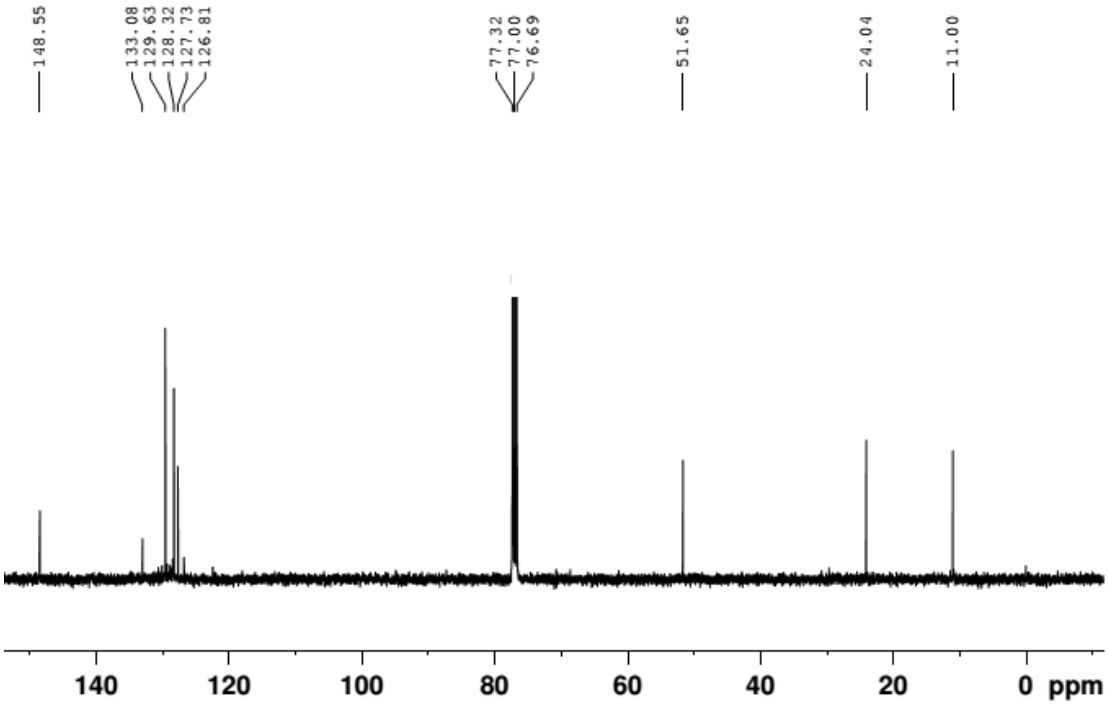

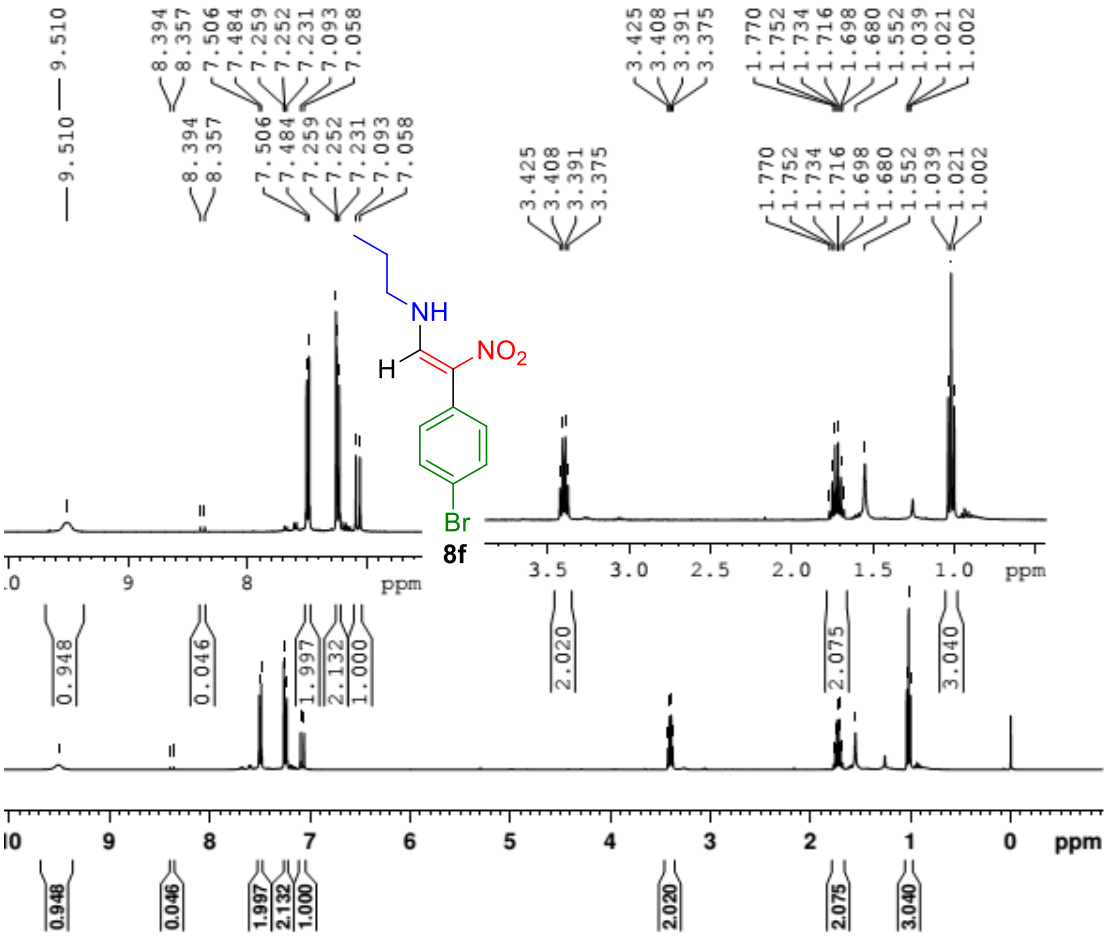

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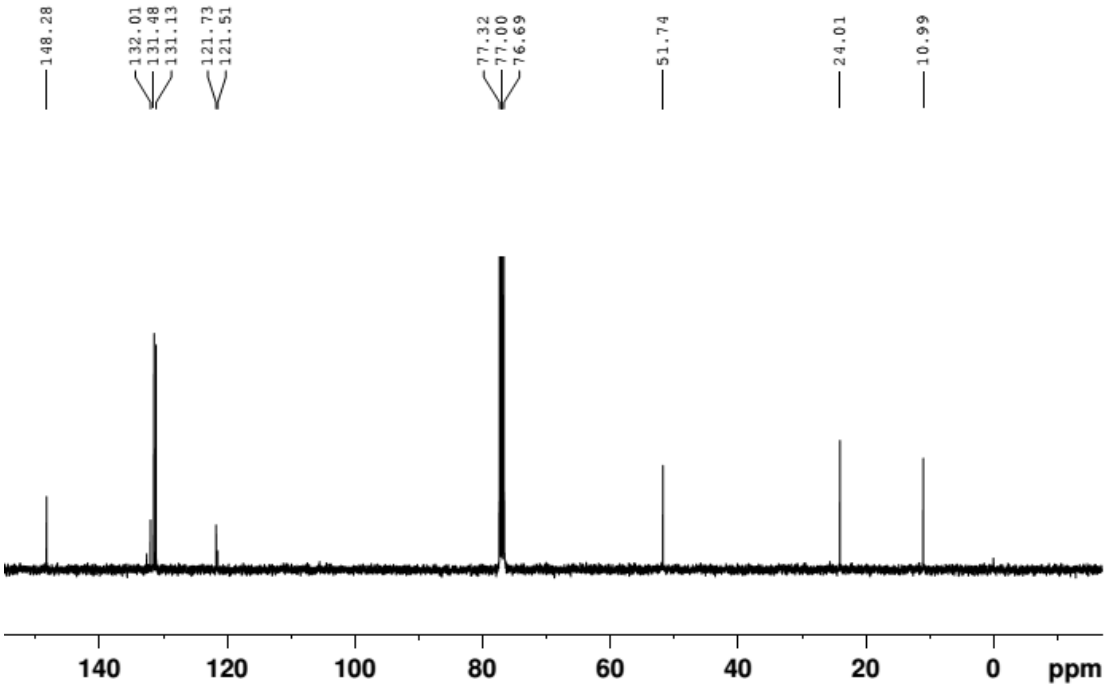

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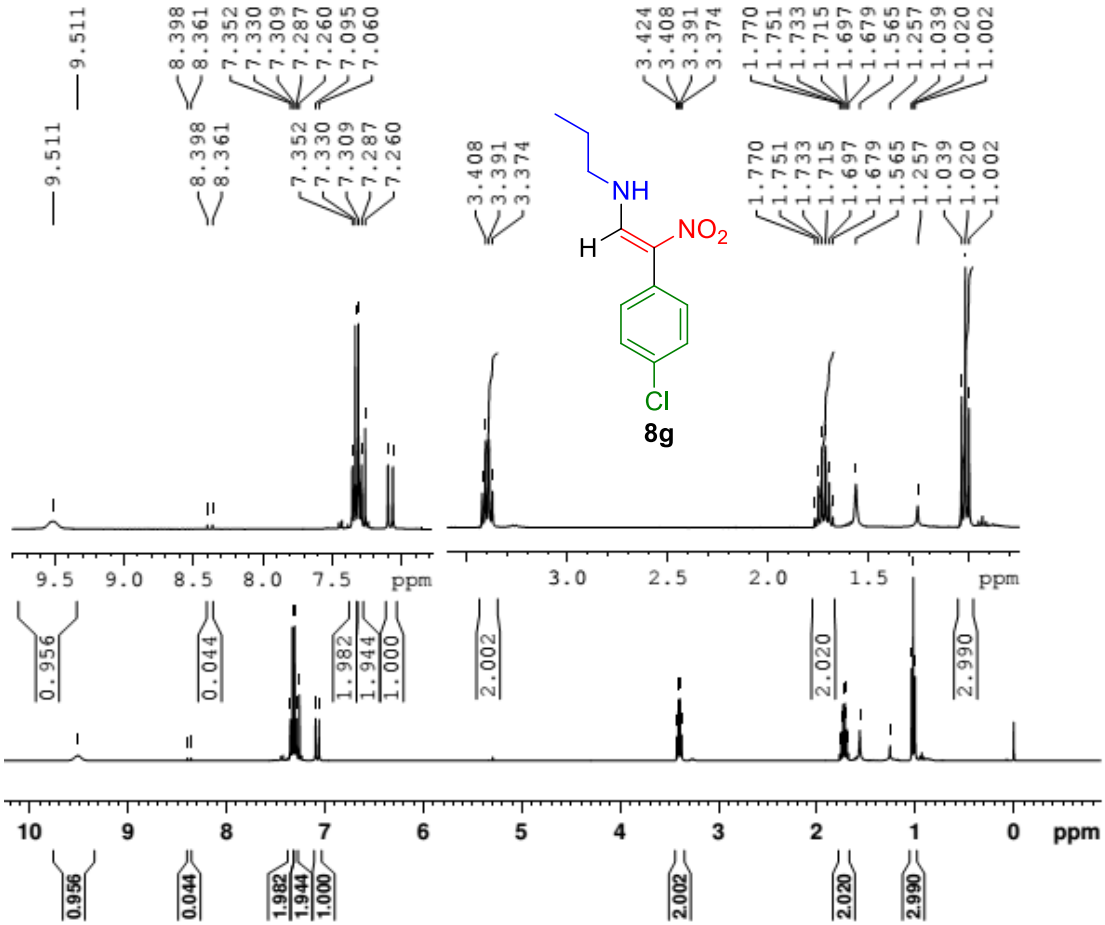

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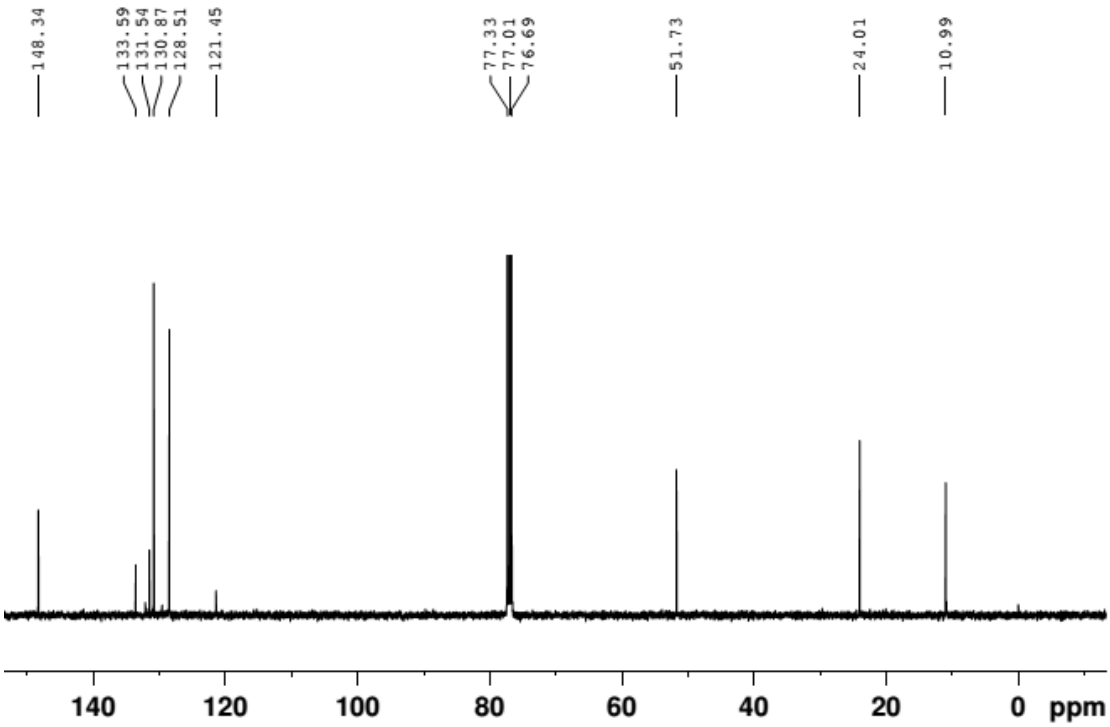

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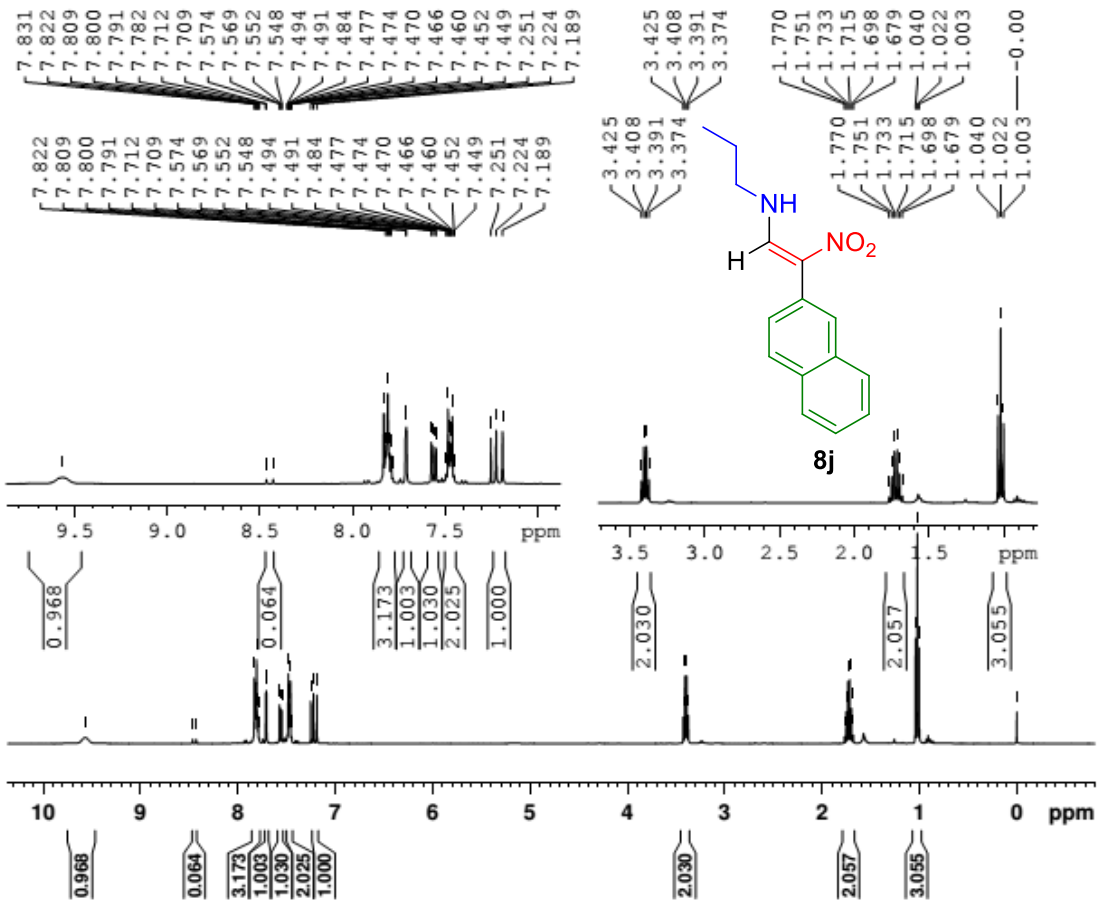

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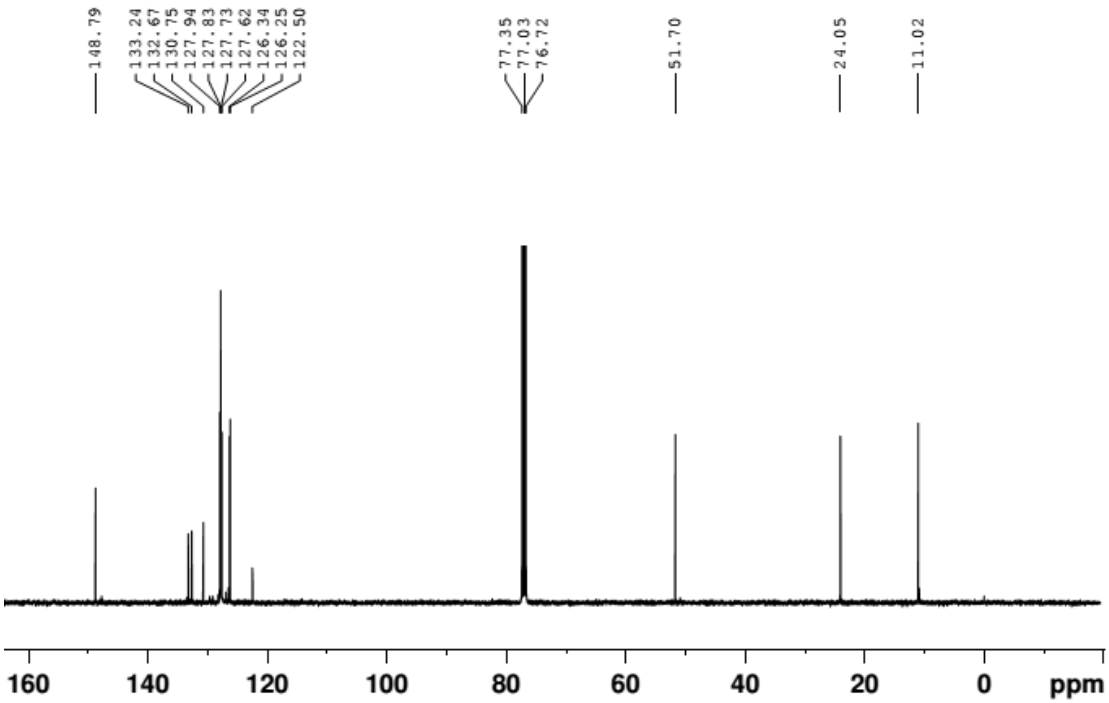

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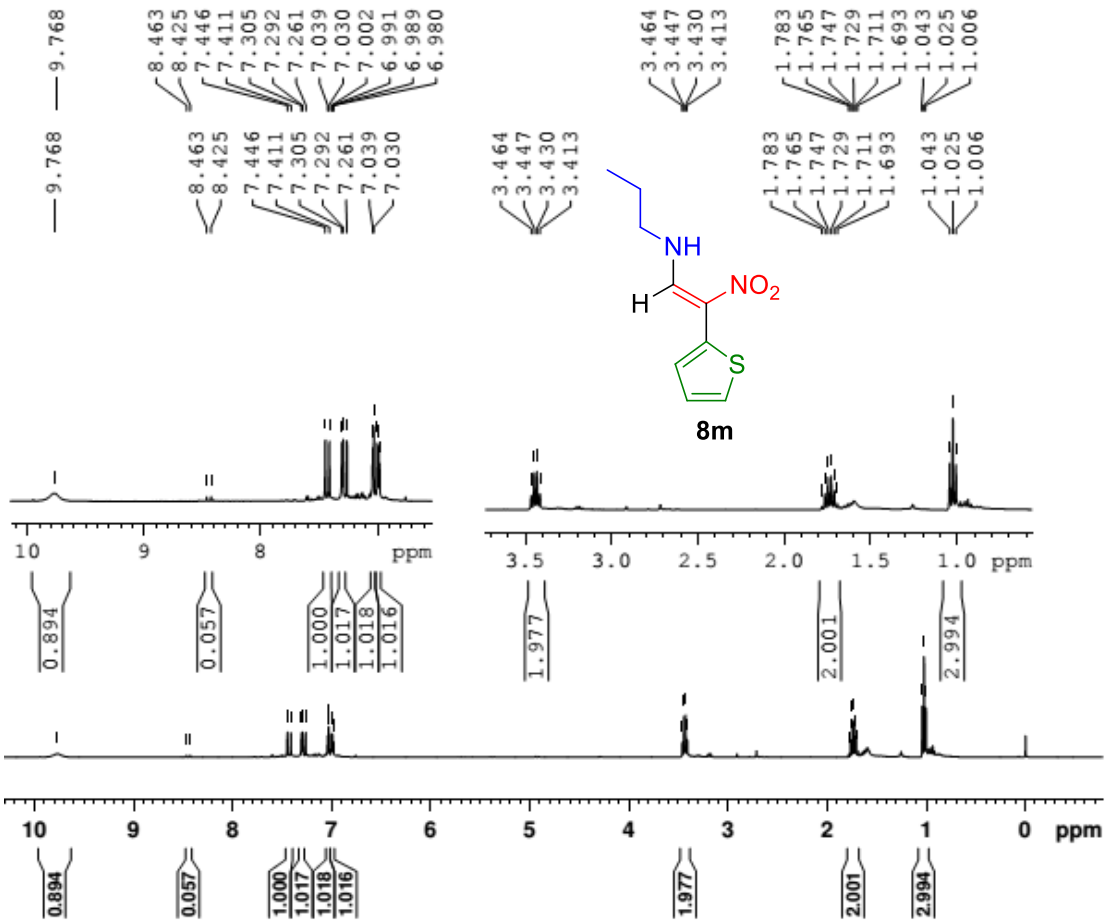

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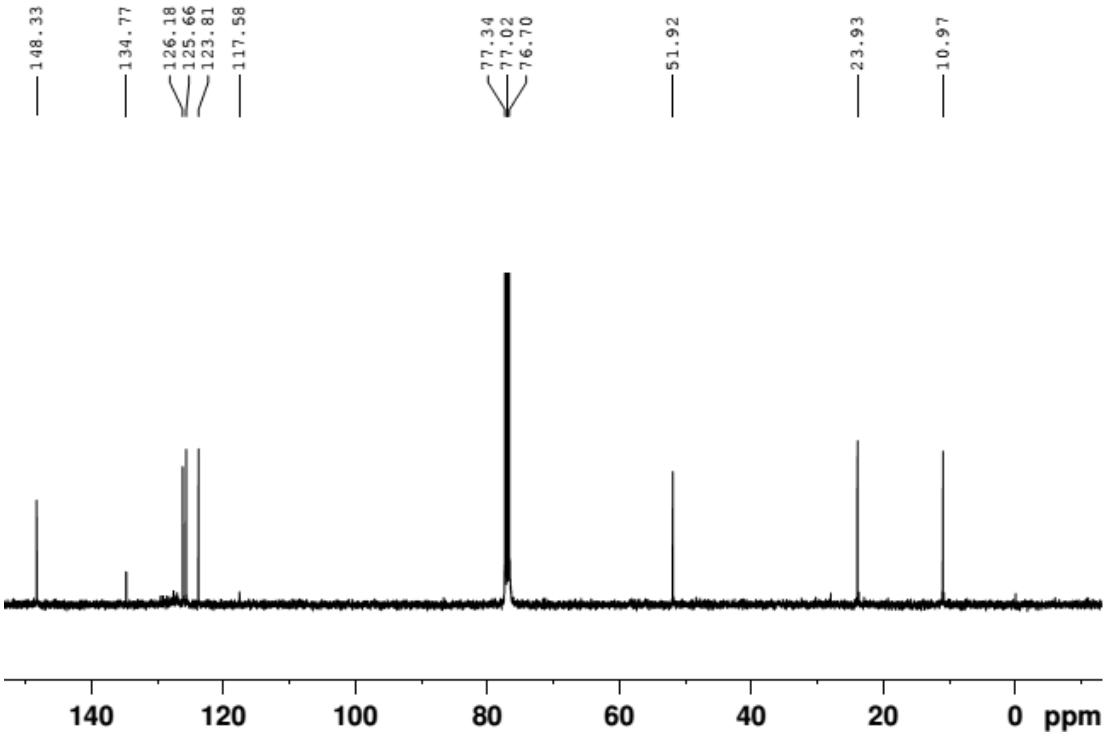

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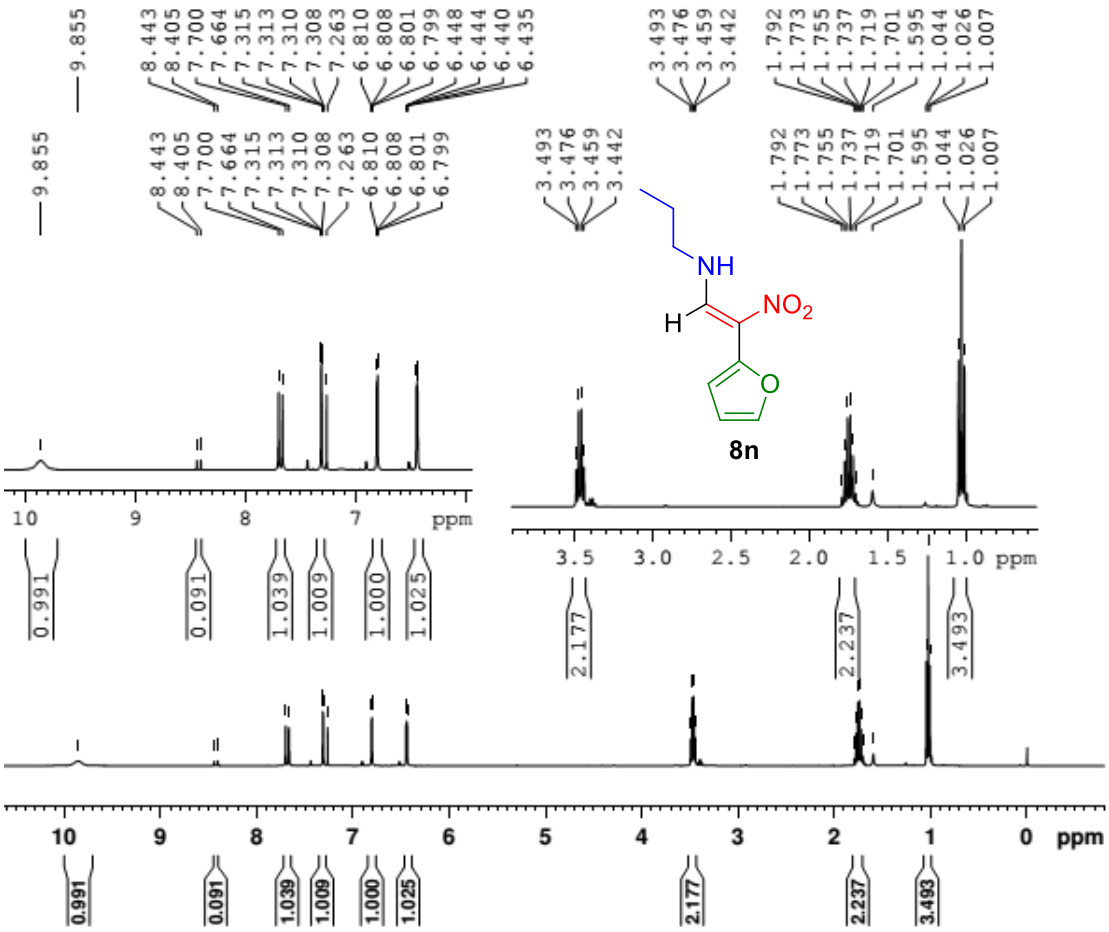

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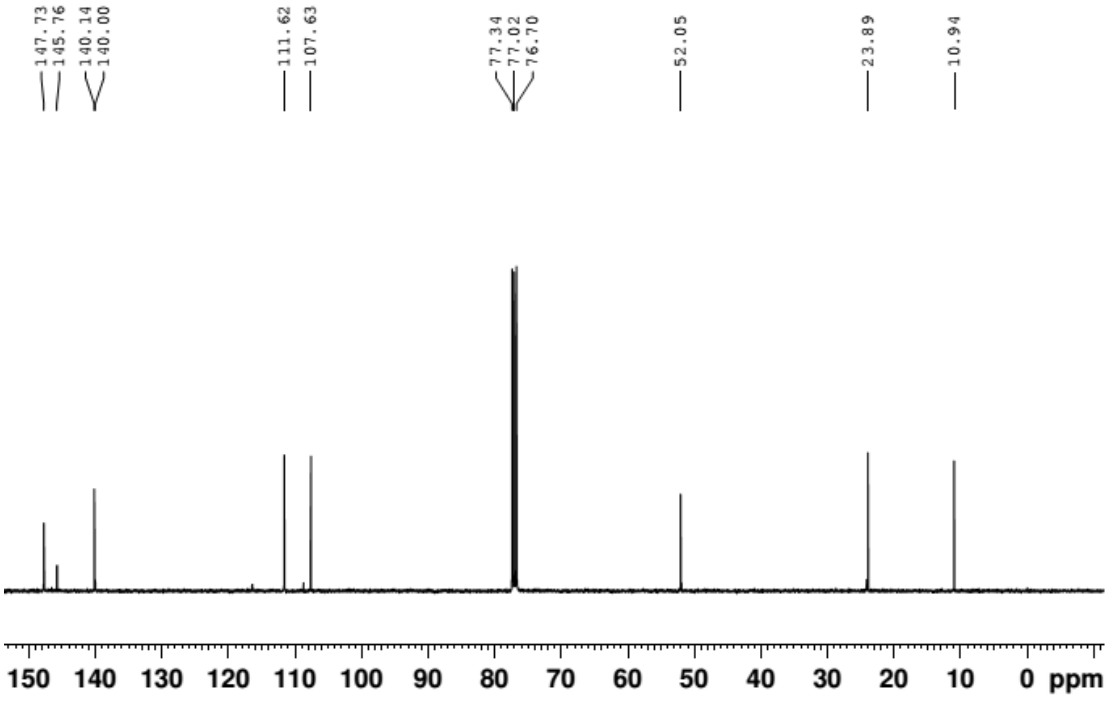

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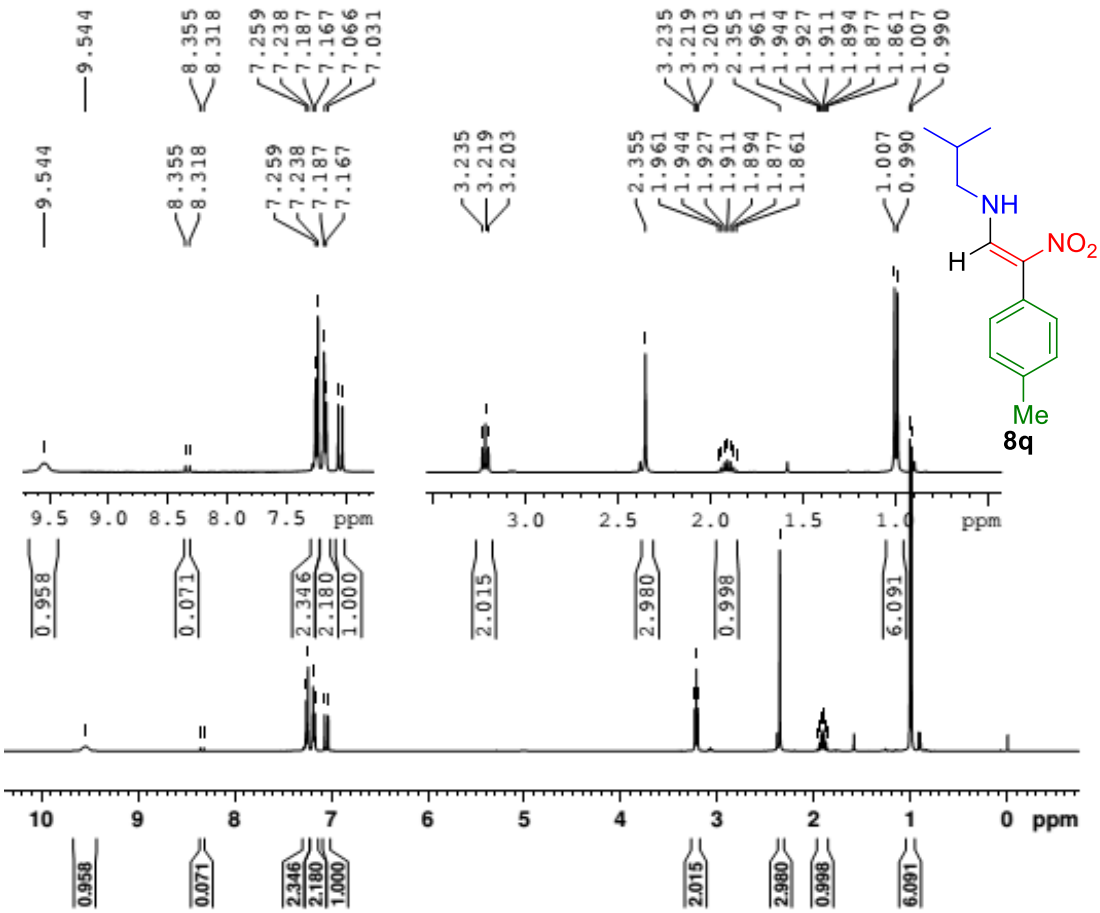

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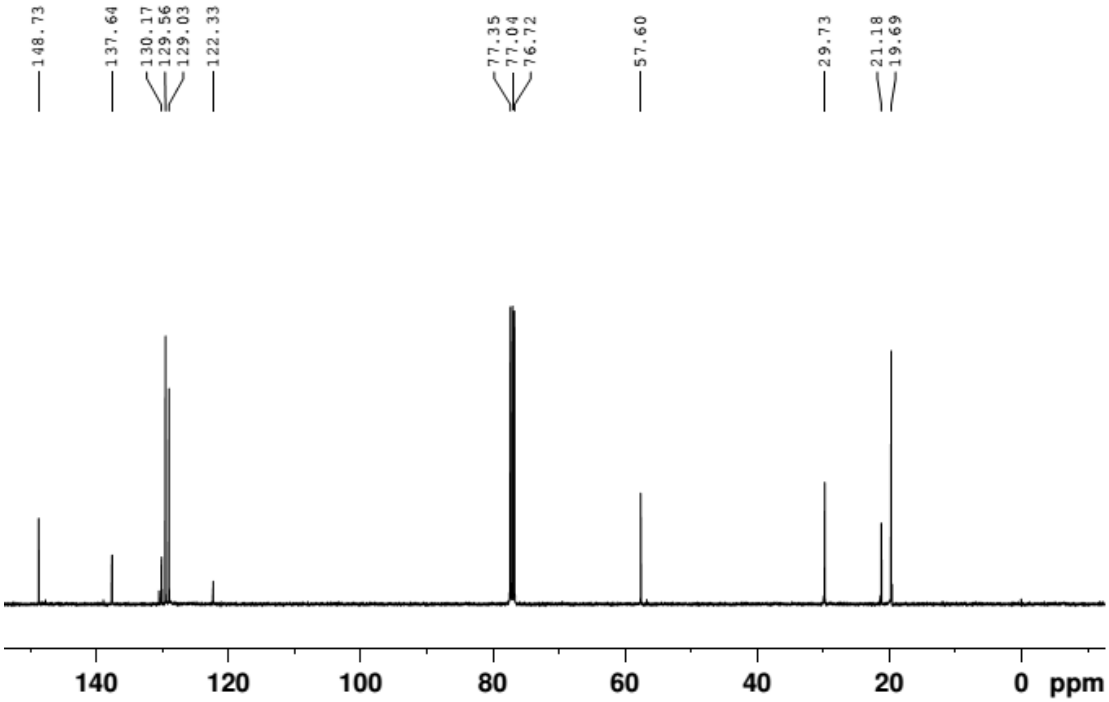

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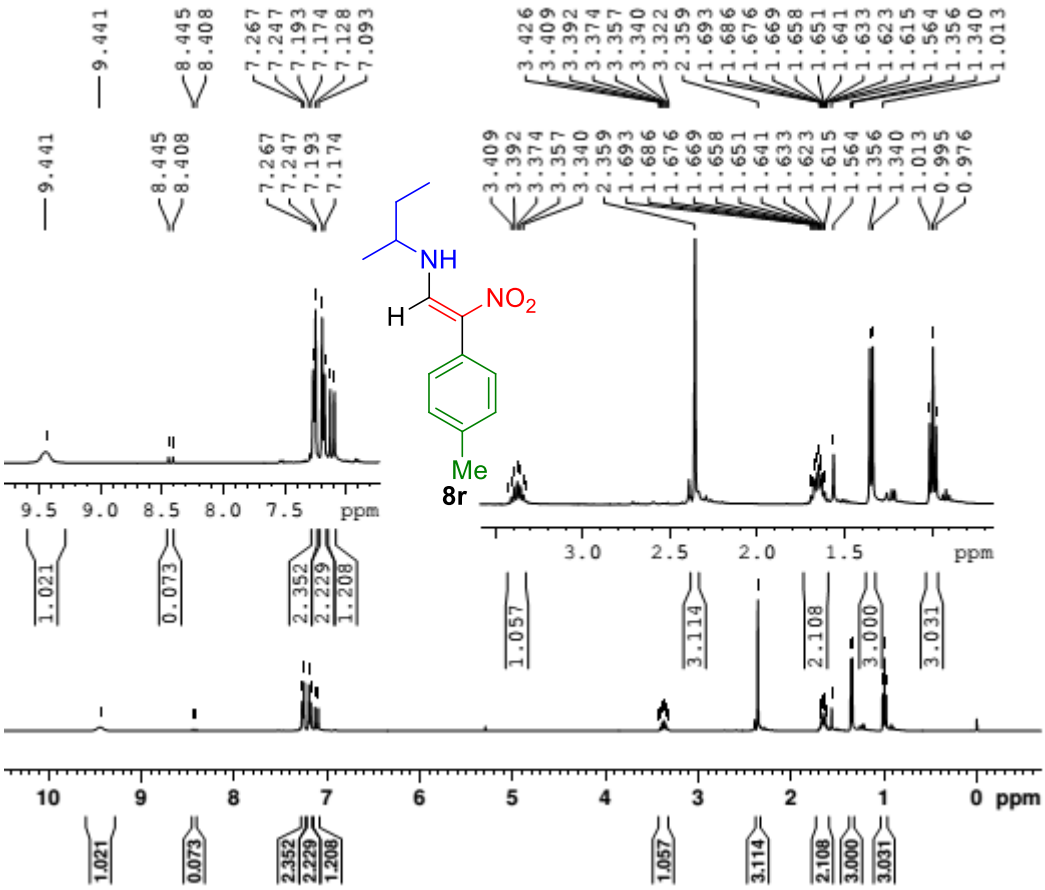

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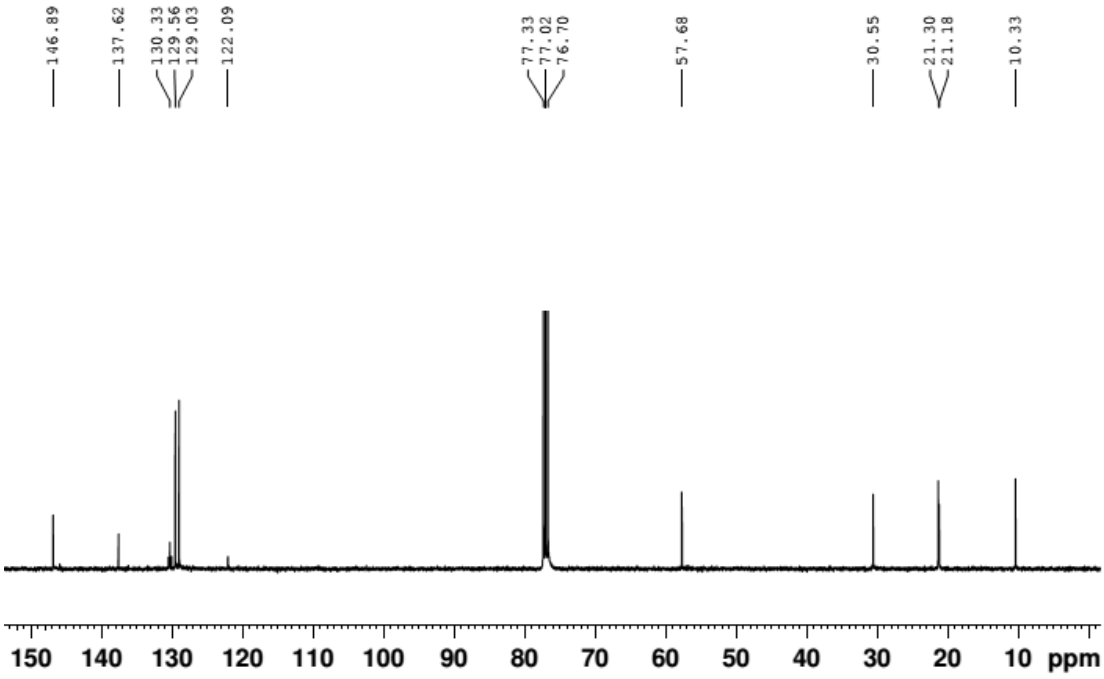

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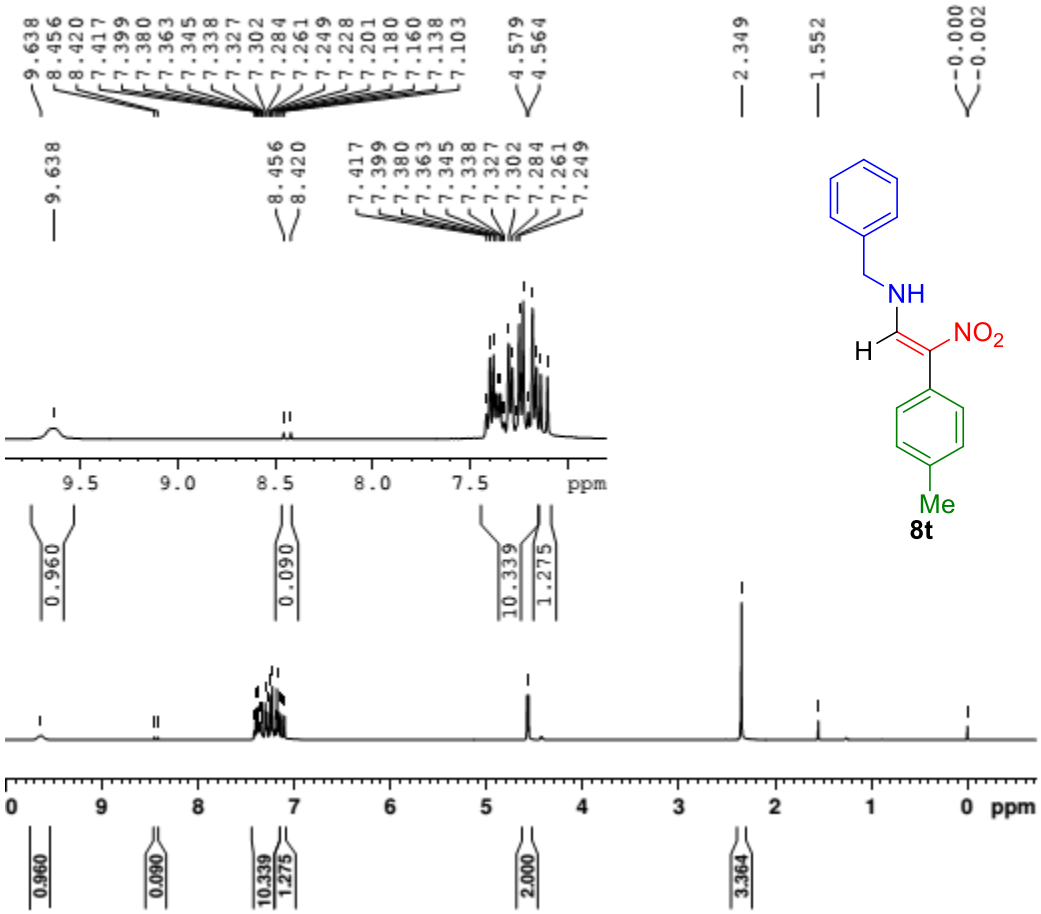

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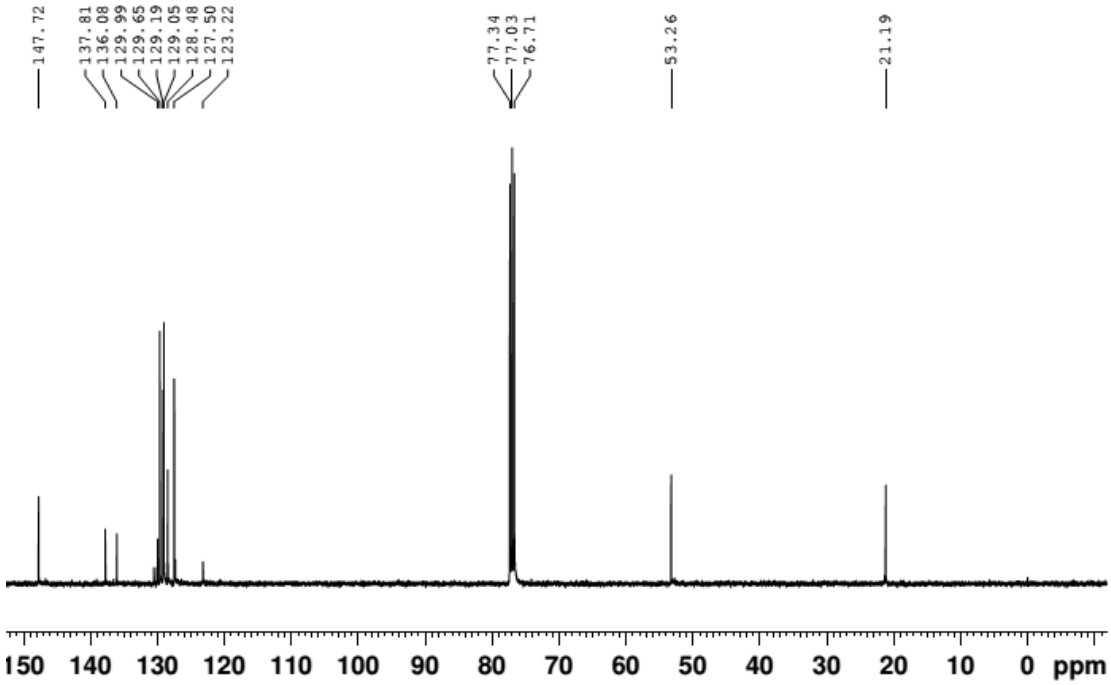

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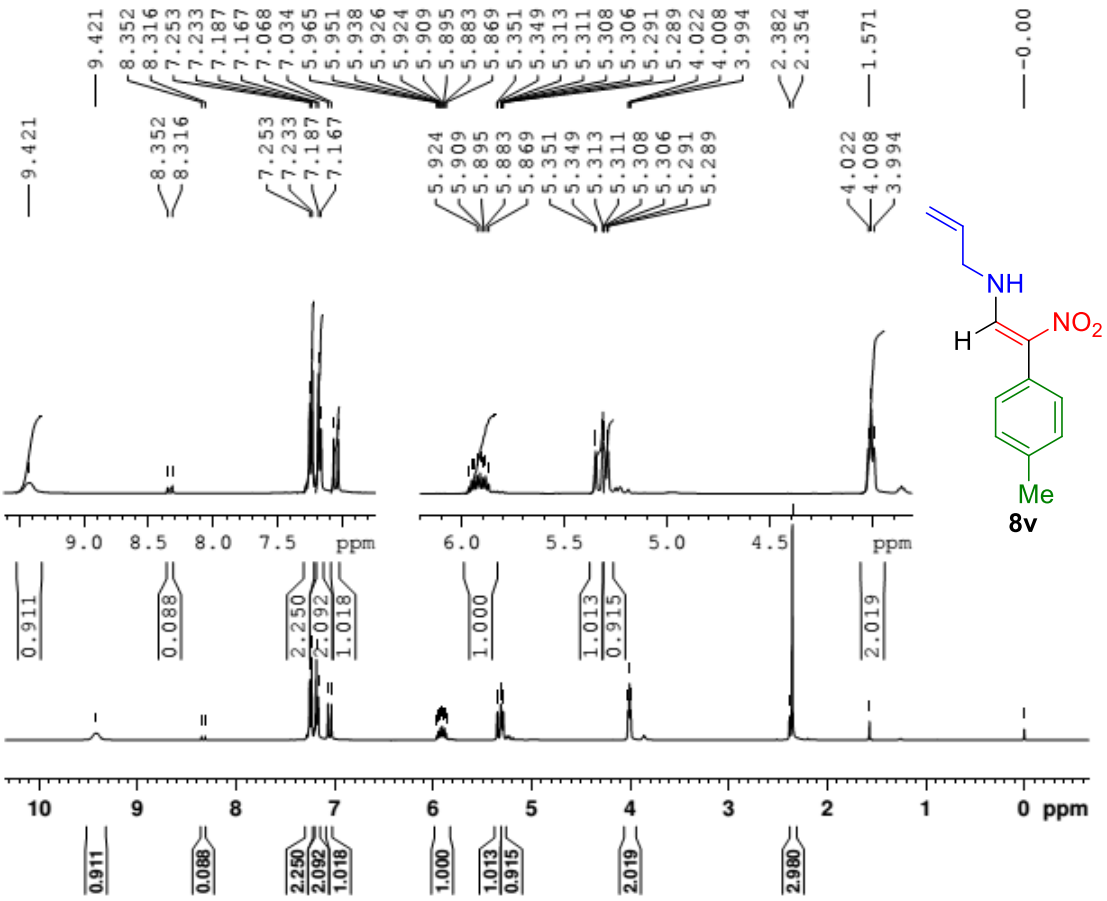

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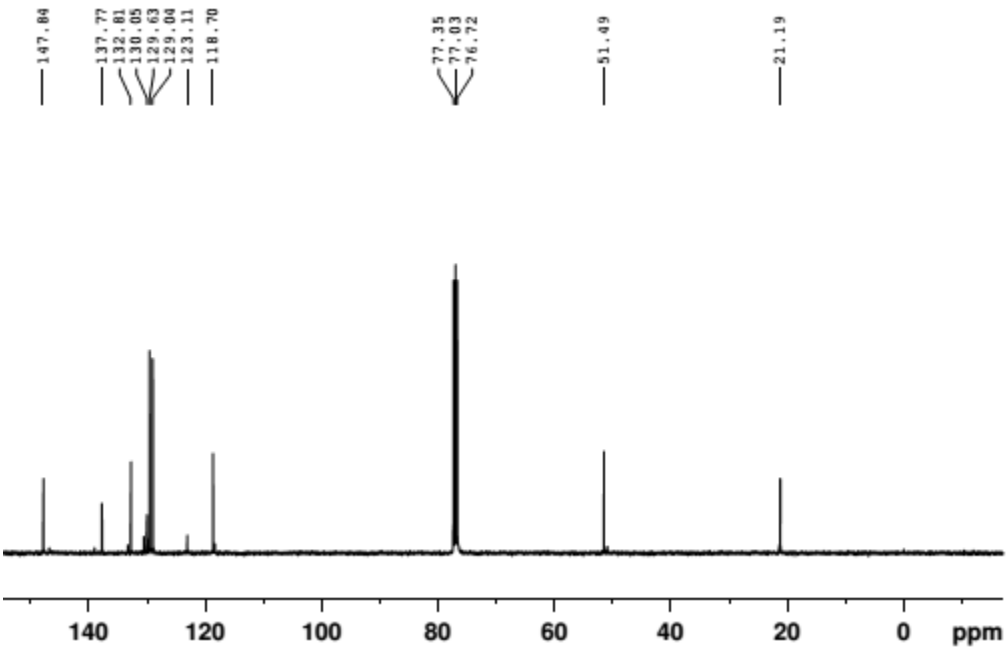

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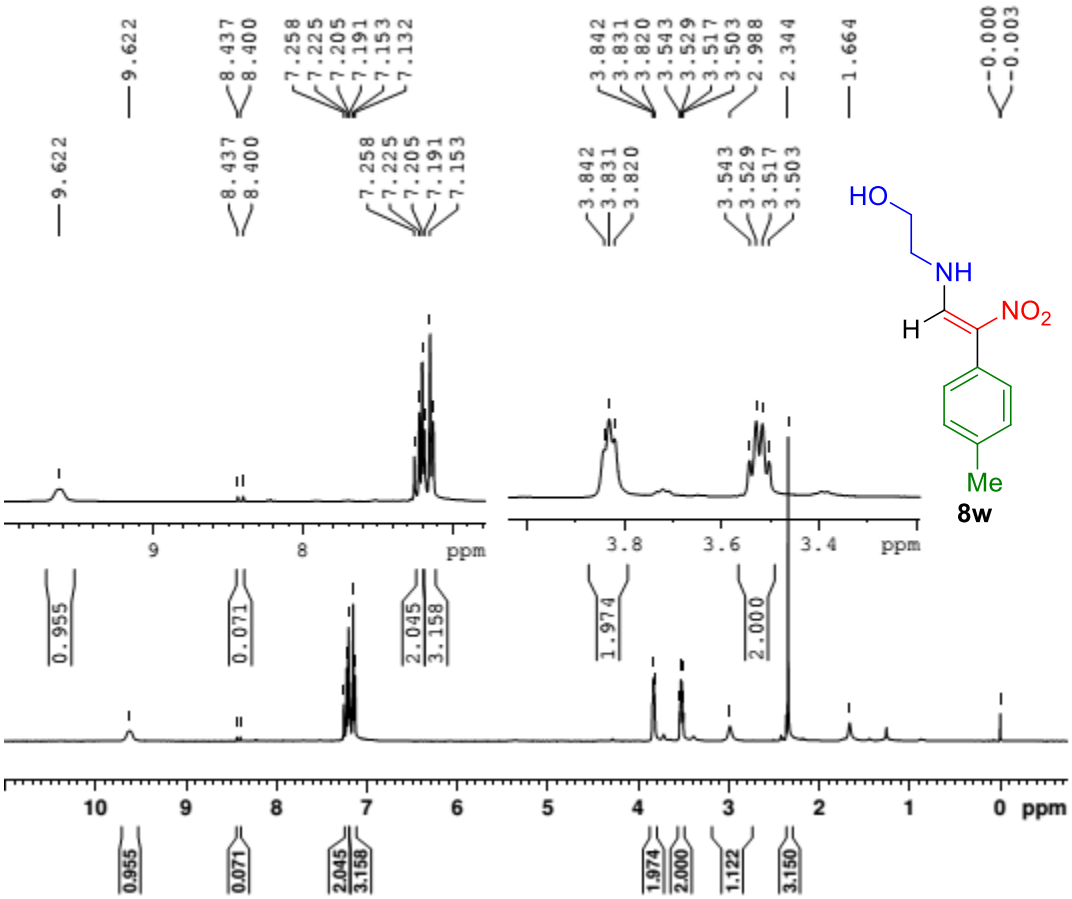

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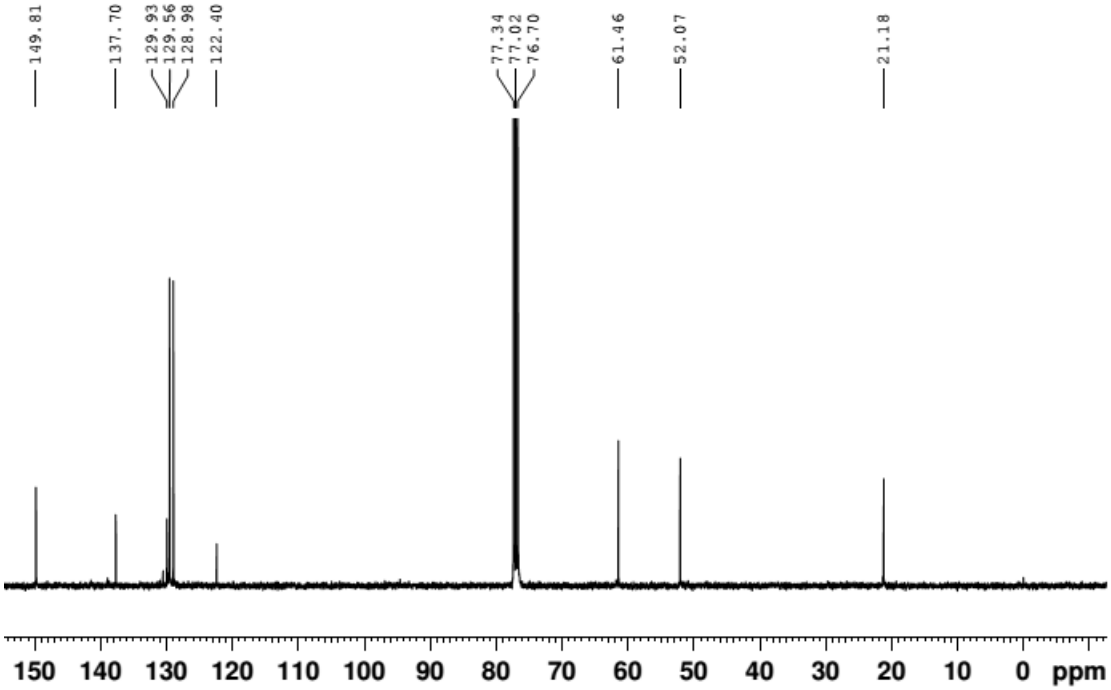

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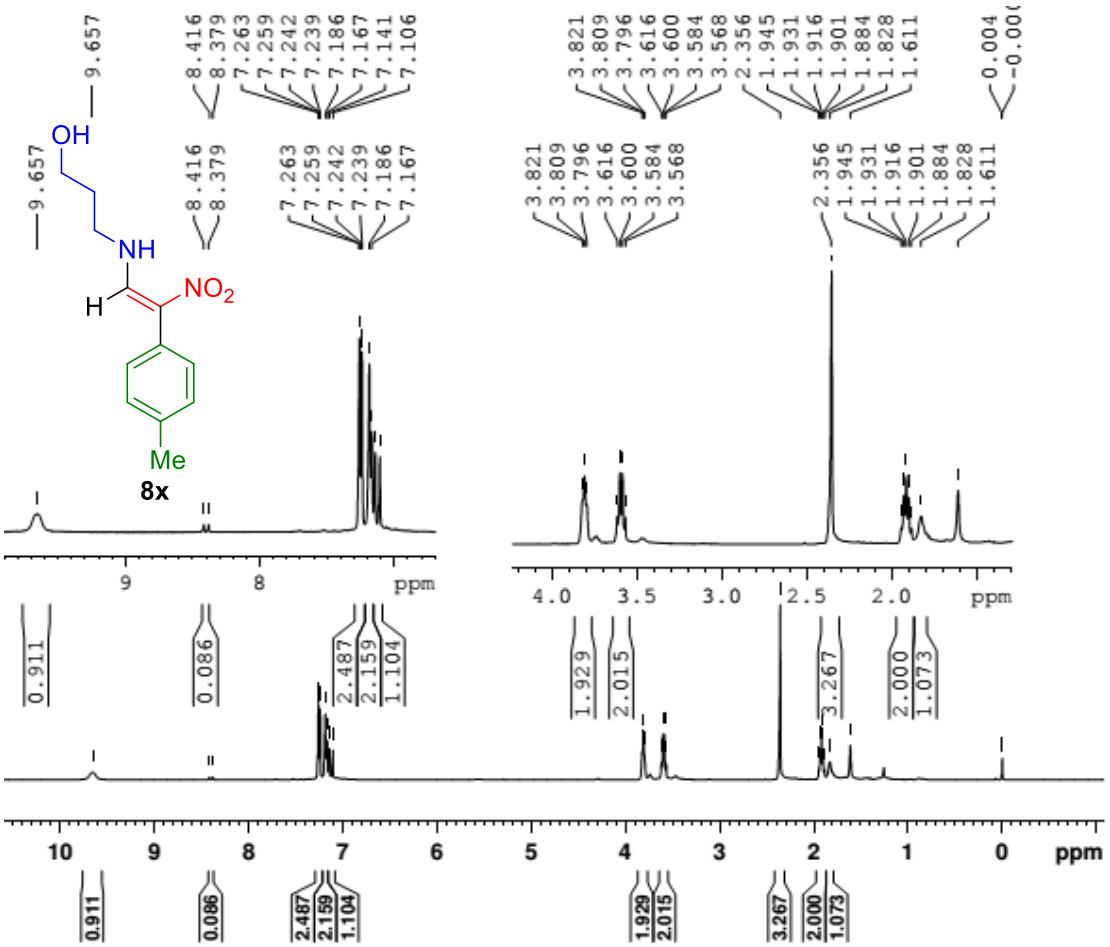

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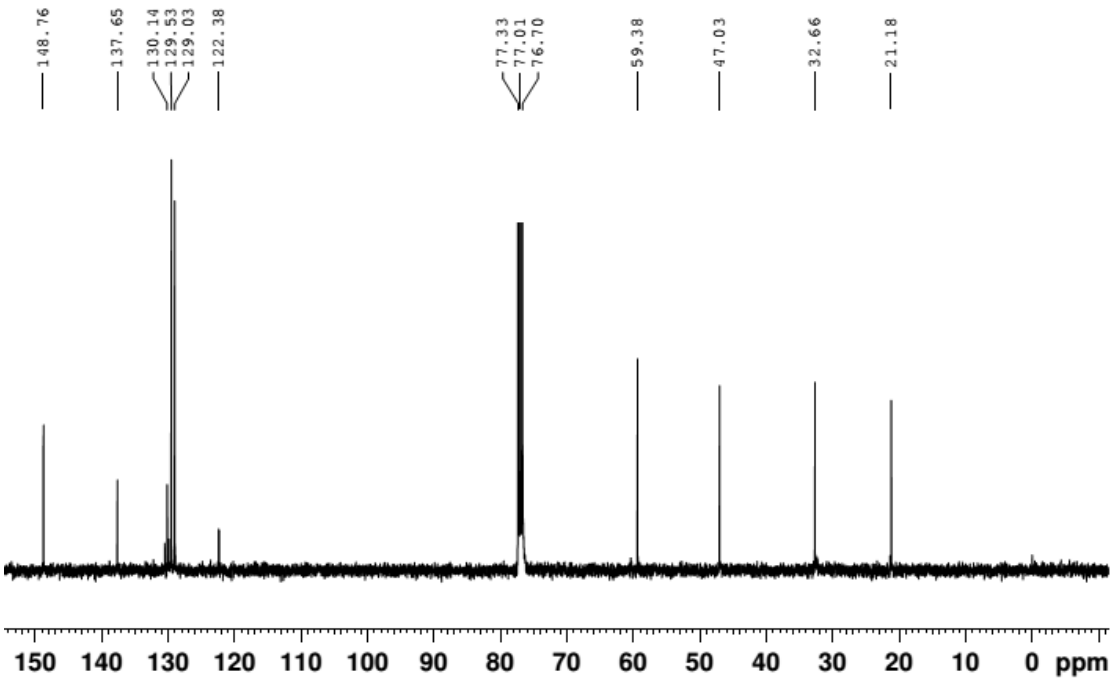

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