Supporting Information

An efficient synthesis of *N*-nitrosamines under solvent, metal and acid free conditions using *tert*-butyl nitrite

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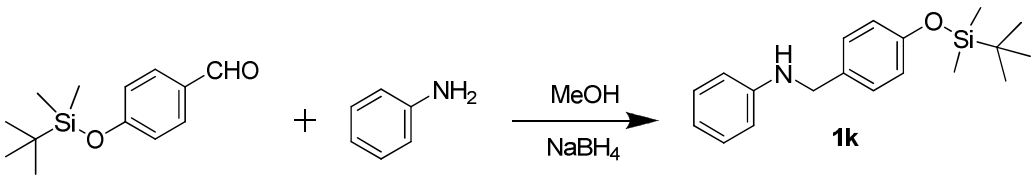
1. GENERAL INFORMATION

Solvents and chemicals were purchased from commercial sources and used without further purifications. The NMR spectra were recorded on Bruker Avance 400 MHz or 500 MHz NMR spectrometer. A short purification of the products were performed on silica gel (60-120 mesh) using a mixture of ethyl acetate and hexane. Thin layer chromatography was performed using pre-coated plates obtained from E. Merck (TLC silica gel 60 F254). The proton and carbon NMR was recorded for all the compounds and compared with the literature reports.

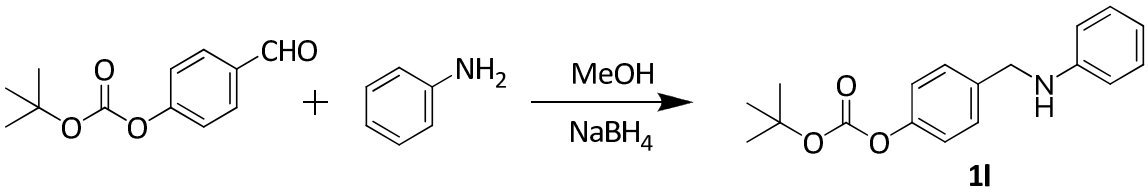
2. PREPARATION OF SECONDARY AMINES 1k and 1l

2.1 ***N*-[4-(tert-butyldimethylsilyloxy)benzyl] aniline**



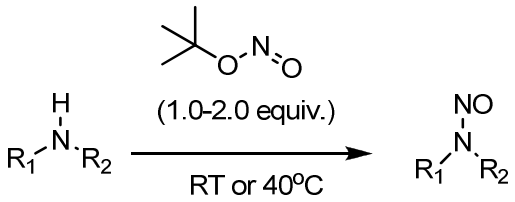
4-(tert-Butyldimethylsilyloxy)benzaldehyde (2.4 mmol, 0.566 g) and aniline (2.40 mmol, 0.223g) was stirred in methanol (15 ml) for 12 hrs at room temperature. Then the reaction mixture was cooled to 0^{o}C to which sodium borohydride (1.2 mmol, 0.444g) was added in a portion wise and allowed to stir for 4 hrs at room temperature. After completion, methanol was evaporated and the residue was diluted with ethyl acetate and washed with water and brine. The organic layer was dried over anhydrous sodium sulphate, concentrated and subjected for column chromatography (SiO_2: ethyl acetate/hexane). The title product was obtained as pale yellow liquid (0.650 g, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (t, *J* =8.0 Hz, 2H), 7.22 (t, *J* =7.7 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 2H), 4.15 (s, 2H), 3.84 (br, 1H), 0.91 (s, 9H), 0.12 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 148.4, 132.2, 129.4, 128.9, 120.3, 117.6, 113.0, 48.1, 25.9, -4.21. HRMS: Calc. for $C_{19}H_{28}NOSi$ $[M+H]^{+}$: 314.1940, Obser. 314.1933.

2.2 ***N*-[4-(tert-Butoxycarbonyloxy)benzyl] aniline**



4-(tert-Butoxycarbonyloxy)benzaldehyde (2.0 mmol, 0.444g) and aniline (2.0 mmol, 0.186g) was stirred in methanol (15 ml) for 12 hrs at RT. Then the reaction mixture was cooled to 0^{o}C to which sodium borohydride (1.0 mmol, 0.037g) was added in a portion wise and allowed to stir for 1hr at room temperature. After completion, methanol was evaporated and the residue was dissolved in water and extracted with ethyl acetate (3 X 20 ml). The organic layer was washed with brine solution and dried over anhydrous sodium sulphate, concentrated and subjected for column chromatography (SiO_2: ethyl acetate/hexane). The title product was obtained as pale yellow crystals (0.510 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 27.4 Hz, 4H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.7 Hz, 2H), 4.30 (s, 2H), 4.03 (br, 1H), 1.54 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2, 150.4, 148.2, 137.1, 129.5, 128.6, 121.6, 117.9, 113.0, 47.9, 29.9. HRMS: Calc. for $C_{18}H_{22}NO_3$ $[M+H]^+$: 300.1600, Obser. 300.1594.

3. Experimental procedures for *N*-nitrosation of secondary amines:



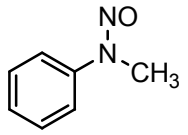
For optimization: To a stirred solution of *N*-methyl aniline (107mg, 1mmol) in an appropriate solvent (2 mL), tert-butyl nitrite (1.0 or 1.5 equiv.) was added at room temperature and the reaction progress was monitored by TLC. After completion, the reaction mixture was diluted with diethyl ether and washed with brine. The organic layer was dried over anhydrous sodium sulphate, concentrated and subjected for column chromatography (SiO_2: ethyl acetate/hexane) to obtain *N*-methyl-*N*-nitrosoaniline (**2a**).

General procedure for Solvent free reaction: Secondary amine (1.0 mmol) and tert-butyl nitrite (1.0 equiv for anilines, 1.5 equiv. for benzyl amines and 2.0 equiv. for alkyl amines)

was mixed carefully at room temperature and allowed to stir in appropriate temperature for appropriate time. After completion (as seen by TLC), the reaction mixture was diluted with diethyl ether and washed with brine. The organic layer was dried over anhydrous sodium sulphate and evaporated to obtain pure products. On the other hand, after completion of the reaction, the crude product was directly subjected for short column chromatography (SiO_2: ethyl acetate/hexane) to obtain pure products.

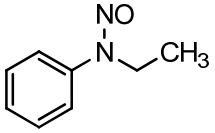
4. **Analytical data for the products:**

4.1 ***N*-Methyl-*N*-nitrosoaniline (2a)**[1] was obtained as yellow oil (131 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.51 (m, 2H), 7.47–7.43 (m, 2H), 7.36–7.32 (m, 1H), 3.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 129.6, 127.5, 119.4, 31.6. HRMS: Calc. for $C_7H_9N_2O_3$ $[M+H]^+$: 137.0715, Obser. 137.0697.



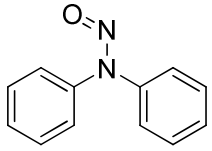
2a

4.2 ***N*-Ethyl-*N*-nitrosoaniline (2b)**[1] was obtained as yellow oil (143 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 1.1 Hz, 2H), 7.48 (t, 2H), 7.39 – 7.34 (t, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 129.7, 127.5, 119.7, 39.4, 11.9. HRMS: Calc. for $C_8H_{11}N_2O$ $[M+H]^+$: 151.0871, Obser. 151.0871.



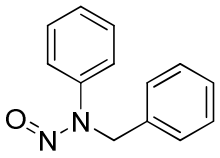
2b

4.3 ***N*-Nitrosodiphenyl amine (2c)**[2] was obtained as yellow solid crystals (194 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.5 –7.43 (m, 3H), 7.43–7.37 (m, 4H), 7.32 (dq, *J* = 8.6, 4.2 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 136.9, 129.9, 129.6, 129.4, 127.5, 127.1, 119.8. HRMS: Calc. for $C_{12}H_{11}N_2O$ $[M+H]^+$: 199.0871, Obser. 199.0867.



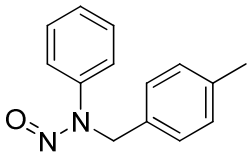
2c

4.4 ***N*-Benzyl-*N*-nitrosoaniline (2d)**[3] was obtained as yellowish orange crystals (201 mg, 96%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.3 Hz, 2H),7.36 (t, *J* = 7.8 Hz, 2H),7.29 – 7.14 (m, 5H), 7.02 (d, *J* = 7.2 Hz, 2H), 5.18 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 134.4, 129.6, 128.9, 127.7, 127.5, 127.1, 119.7, 47.4. HRMS: Calc. for $C_{13}H_{13}N_2O$ $[M+H]^+$: 213.1028, Obser. 213.1019.



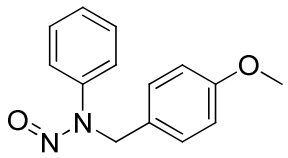
2d

4.5 ***N*-(4-Methylbenzyl) *N*-nitrosoaniline (2e)** was obtained as yellow oil (214 mg, 95%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54–7.51 (m, 2H), 7.43–7.38 (m, 2H), 7.32 (td, *J* = 7.1, 3.4 Hz, 1H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 5.20 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 137.5, 131.4, 129.6, 129.6, 127.5, 127.1, 119.7, 47.2, 21.2. HRMS: Calc. for $C_{14}H_{15}N_2O$ $[M+H]^+$: 227.1184, Obser. 227.1184.



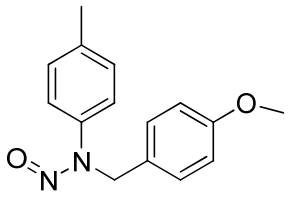
2e

4.6 ***N*-(4-Methoxybenzyl)-*N*-nitrosoaniline** (**2f**) was obtained as yellow orange crystals (227 mg, 94%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.50 (m, 2H), 7.45–7.40 (m, 2H), 7.36–7.31 (m, 1H), 7.03 (d, *J* = 8.8 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 1H),5.19 (s, 2H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 141.9, 129.5, 128.7, 127.5, 126.5, 119.9, 114.3, 55.4, 46.9. HRMS: Calc. for $C_{14}H_{15}N_2O_2$ $[M+Na]^+$: 265.1134, Obser. 265.0957.



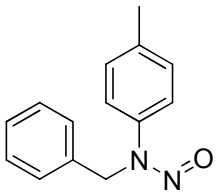
2f

4.7 ***N*-[(4-Methoxy)benzyl]-*N*-nitroso-(4-methyl)aniline** (**2g**) was obtained as yellow powder (240 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.26–7.20 (m, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.82–6.77 (m, 2H), 5.16 (s, 2H), 3.76 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 139.5, 137.6, 130.2, 128.8, 126.7, 120.2, 114.3, 77.2, 55.4, 47.1, 21.1. HRMS: Calc. for $C_{15}H_{17}N_2O_2$ $[M+Na]^+$: 279.1109, Obser. 279.1109.



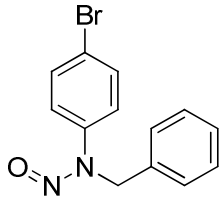
2g

4.8 ***N*-Benzyl-*N*-nitroso-(4-methyl)aniline** (**2h**) was obtained as yellow oil (214 mg, 95%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.37 (m, 2H), 7.29–7.19 (m, 5H), 7.08–7.04 (m, 2H), 5.21 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 137.5, 134.5, 130.1, 128.9, 127.7, 127.2, 119.8, 47.6, 21.0. HRMS: Calc. for $C_{14}H_{15}N_2O$ $[M+H]^+$: 227.1184, Obser. 227.1187.



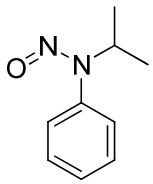
2h

4.9 ***N*-benzyl p-bromo *N*-nitrosoaniline** (**2i**) was obtained as yellow crystals. (276 mg, 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.28 (dd, *J* = 15.1, 7.8 Hz, 4H), 7.05 (d, *J* = 7.2 Hz, 2H), 5.22 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.9, 134.1, 132.7, 129.1, 128.0, 127.1, 120.9, 77.4, 77.2, 76.9, 47.0. HRMS: Calc. for $C_{13}H_{11}BrN_2O$ $[M+H]^+$: 291.0133, Obser. 291.0127.



2i

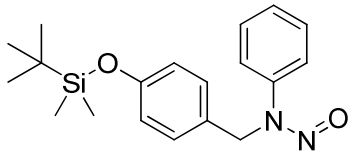
4.10 ***N*-Isopropyl-*N*-nitrosoaniline** (**2j**)[2] was obtained as dark brown oil [149 mg, 91%, mixture of two isomers in ≈6:4 ratio]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.36 (m, 5H), 7.32 (dd, *J* = 5.3, 3.0 Hz, 2H), 5.20 (hept, *J* = 6.9 Hz, 1H), 5.03 (hept, *J* = 6.8 Hz, 1H), 1.43 (d, *J* = 6.8 Hz, 3H), 1.16 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 136.5, 129.4, 129.2, 129.16, 128.8, 127.7, 125.9, 56.1, 46.3, 22.0, 19.7. HRMS: Calc. for $C_9H_{13}N_2O$ $[M+H]^+$: 165.1028, Obser. 165.1021.



2j

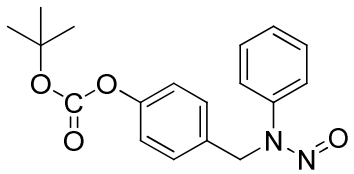
4.11 ***N*-[4-(TBDMS)Benzyl]-*N*-nitrosoaniline** (**2k**) was obtained as yellow oil (310 mg, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.47 (m, 2H), 7.43–7.38 (m, 2H), 7.34–7.29 (m, 1H), 6.94 (t,

J = 5.7 Hz, 2H), 6.74–6.70 (m, 2H), 5.16 (s, 2H), 0.94 (s, 9H), 0.14 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 141.8, 129.4, 128.5, 127.3, 127.0, 120.3, 119.8, 46.9, 25.6, 18.1, -4.4. HRMS: Calc. for $C_{19}H_{27}N_2O_2Si$ $[M+Na]^+$: 365.1842, Obser. 365.1654.



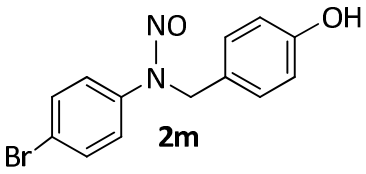
2k

4.12 ***N*- [4-(Boc)Benzyl]-*N*-nitrosoaniline** (**2l**) was obtained as yellow solid crystals (314 mg, 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 5.4, 3.5 Hz, 2H), 7.44–7.39 (m, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.08 (s, 4H), 5.21 (s, 2H), 1.52 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 150.7, 141.8, 131.9, 129.7, 128.4, 127.6, 121.9, 119.8, 83.9, 46.9, 27.8. HRMS: Calc. for $C_{18}H_{21}N_2O_4$ $[M+H]^+$: 329.1501, Obser. 329.1500.



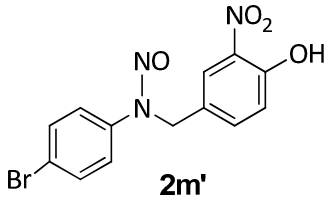
2l

4.13 ***N*-nitroso (4-Hydroxybenzyl)4-bromoaniline (2m)** was obtained as red crystals (279 mg, 91%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.72 (d, *J* = 8.1 Hz, 2H), 5.12 (s, 2H), 4.85 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.9, 132.7, 128.9, 121.2, 115.9, 46.6.HRMS: Calc.for $C_{13}H_{11}BrN_2O_2$ $[M+Na]^+$:328.9902 Obser.328.9896.



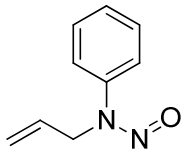
2m

4.14 ***N*-nitroso (4-Hydroxy-3-nitrobenzyl)4-bromoaniline (2m')** was obtained as yellow crystals (296 mg, 84%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.82 (d, *J* = 1.6 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.27 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 1H), 5.14 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.8, 140.3, 136.5, 133.6, 133.0, 126.5, 123.8, 121.5, 121.1, 121.1, 45.9. Calc.for $C_{13}H_{10}BrN_3O_4$ $[M+H]^+$:351.9933 Obser.351.9927.



2m'

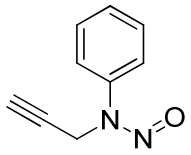
4.15 ***N*-Allyl-*N*-nitrosoaniline** (**2n**) was obtained as dark brown oil (152 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.52 (m, 2H), 7.47-7.42 (m, 2H), 7.36–7.31 (m,1H), 5.74 (ddt, *J* = 17.2, 10.4, 5.2 Hz, 1H), 5.17 (m, *J* = 10.4, 2.5, 1.6 Hz, 1H), 5.10 – 5.04 (m, 1H), 4.62 (dt, *J* = 5.2, 1.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 129.6, 129.5, 127.4, 119.5, 118.1, 46.8. HRMS: Calc. for $C_9H_{11}N_2O$ $[M+H]^+$: 163.0691, Obser.163.0862.



2n

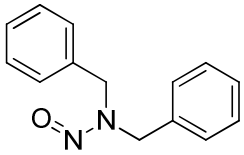
4.16 ***N*-Propargyl *N*-nitrosoaniline** (**2o**) was obtained as dark brown oil (145 mg, 91%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62–7.58 (m, 2H), 7.50–7.45 (m, 2H), 7.39–7.35 (m, 1H), 4.70 (dd, *J* = 2.5, 1.2 Hz, 2H), 2.18 (t, *J* = 2.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.9, 129.6, 127.8,

119.8, 77.4, 77.2, 76.9, 75.8, 72.2, 32.8. HRMS: Calc. for $C_9H_9N_2O$ $[M+H]^+$: 161.0715, Obser. 161.0711.



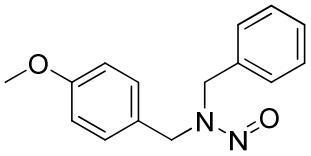
2o

4.17 ***N*-Nitroso dibenzylamine** (**2p**)[3] was obtained as yellow solid crystals (219 mg, 97%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.41–7.34 (m, 3H), 7.33–7.27 (m, 3H), 7.26–7.22 (m, 2H), 7.07–7.02 (m, 2H), 5.20 (s, 2H), 4.66 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 133.8, 129.0, 128.8, 128.5, 128.4, 128.3, 127.8, 77.3, 77.0, 76.7, 54.9, 44.8. HRMS: Calc. for $C_{14}H_{15}N_2O$ $[M+H]^+$: 227.1184, Obser. 227.1163.



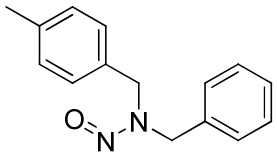
2p

4.18 ***N*-(4-methoxybenzyl)-*N*-nitroso benzylamine** (**2q**) was obtained as dark yellow liquid (244 mg, 95%, mixture of two isomers in ≈1:1 ratio) ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.26 (m, 3H), 7.20 (qdd, *J* = 9.3, 4.8, 2.2 Hz, 6H), 7.11–7.06 (m, 2H), 6.97 (dd, *J* = 7.4, 1.9 Hz, 2H), 6.92–6.87 (m, 2H), 6.85–6.80 (m, 2H), 6.78–6.72 (m, 2H), 5.09 (s, 2H), 5.06 (s, 2H), 4.57 (s,2H), 4.52 (s, 2H), 3.75 (s, 3H), 3.72 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 159.4, 134.7, 134.1, 130.2, 129.9, 129.2, 129.0, 128.6, 128.5, 128.0, 126.4, 126.1, 114.6, 114.3, 55.5, 55.5, 55.0, 54.6, 44.8, 44.6. HRMS: Calc. for $C_{15}H_{17}N_2O_2$ $[M+Na]^+$: 279.1108, Obser. 279.1109.



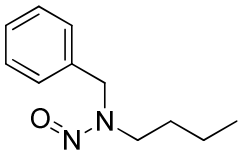
2q

4.19 ***N*-(4-methylbenzyl)-*N*-nitroso benzylamine** (**2r**) was obtained as yellow oil (231 mg, 96%, mixture of two isomers in ≈1:1 ratio). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.37 (m, 3H), 7.35–7.30 (m, 3H), 7.28 (dt, *J* = 7.8, 4.1 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.15 (m, 4H), 7.10–7.06 (m, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 5.20 (s, 2H), 5.18 (s, 2H), 4.68 (s, 2H), 4.65 (s, 2H), 2.40 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 137.8, 134.7, 134.1, 131.5, 131.0, 129.8, 129.6, 129.1, 128.9, 128.7, 128.6, 128.5, 128.0, 54.9, 54.8, 44.8, 44.7, 21.3, 21.3. HRMS: Calc. for $C_{15}H_{17}N_2O$ $[M+H]^+$: 241.1341, Obser. 241.1340.



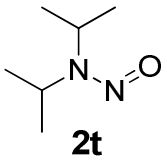
2r

4.20 ***N*-Nitroso *N*-butylbenzylamine** (**2s**) was obtained as yellow oil (174 mg, 91%, mixture of two isomers in ≈1:1 ratio) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–7.26 (m, 1H), 7.26–7.17 (m, 2H), 7.06–7.02 (m, 1H), 5.18 (s, 1H), 4.72 (s, 1H), 3.97 (t, *J* = 7.3 Hz, 1H), 3.38–3.35 (m, 1H), 1.66–1.58 (m, 1H), 1.32–1.10 (m, 4H), 0.89–0.74 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.0, 134.4, 129.1, 128.9, 128.6, 128.3, 128.3, 127.9, 56.2, 51.4, 46.1, 43.0, 30.2, 28.0, 20.4, 19.8, 13.7, 13.6. HRMS: Calc. for $C_{11}H_{17}N_2O$ $[M+H]^+$: 193.1341, Obser. 193.1331.



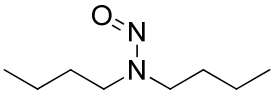
2s

4.21 ***N*-Nitroso diisopropylamine** (**2t**)[3] was obtained as off-white crystals (118 mg, 91%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.04–4.96 (m, 1H), 4.26-4.18 (dh, *J* = 13.0, 6.6 Hz, 1H), 1.48 (dd, *J* = 6.7, 1.4 Hz, 6H), 1.13 (dd, *J* = 6.9, 1.2 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 50.6, 44.6, 23.8, 19.2. HRMS: Calc. for $C_6H_{15}N_2O$ $[M+H]^+$: 131.1184, Obser. 131.1183.



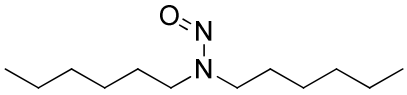
2t

4.22 ***N*-Nitroso dibutylamine** (**2u**)[2] was obtained as pale yellow oil (148 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.97 (t, *J* = 7.3 Hz, 2H), 3.44 (t, *J* = 9.8, 5.5 Hz, 2H), 1.69–1.60 (m, 2H), 1.42–1.34 (m, 2H), 1.33–1.24 (m, 2H), 1.24–1.15 (m, 2H), 0.90–0.85 (t, 3H), 0.84–0.80 (t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 51.9, 43.3, 30.2, 28.0, 20.3, 19.6, 13.5, 13.4. HRMS: Calc. for $C_8H_{19}N_2O$ $[M+H]^+$: 159.1497, Obser. 159.1490.



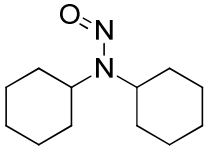
2u

4.23 ***N*-Nitroso dihexylamine** (**2v**)[4] was obtained as yellow oil (171 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.04–4.01 (m, 3H), 3.51–3.47 (m, 3H), 1.72–1.68 (m, 2H), 1.48–1.40 (m, 2H), 1.22–1.22 (m, 12H), 0.88–0.83 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.5, 43.8, 31.5, 31.4, 28.4, 27.0, 26.3, 26.1, 22.6, 14.1. HRMS: Calc. for $C_{12}H_{27}N_2O$ $[M+H]^+$: 215.2123, Obser. 215.2121.



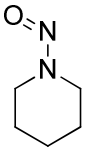
2v

4.24 ***N*-Nitroso dicyclohexylamine** (**2w**)[3] was obtained as off white crystals (189 mg, 90%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.92–4.75 (m, 2H), 3.78–3.61 (m, 2H), 1.94–1.84 (m,6H), 1.69 (m, 4H), 1.56 (dd, *J* = 5.5, 4.2 Hz, 1H), 1.45–1.07 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 58.5, 52.2, 34.3, 29.3, 26.0, 25.4, 25.3, 25.2. HRMS: Calc. for $C_{12}H_{22}N_2O$ $[M+H]^+$: 211.1810, Obser. 211.1790.



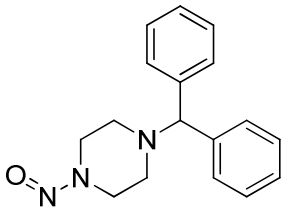
2w

4.25 ***N*-Nitrosopiperidine** (**2x**)[3] was obtained as yellow solid crystals (93 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.16–4.12 (m, 2H), 3.75–3.72 (m, 2H), 1.77–1.72 (m, 4H), 1.53–1.51 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ51.0, 39.9, 26.5, 24.9, 24.33.HRMS: Calc. for $C_5H_{10}N_2O$ $[M+H]^+$: 115.0871, Obser. 115.0859.



2x

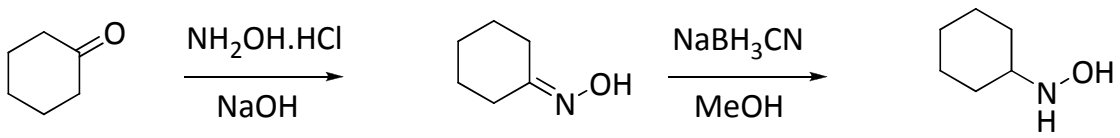
4.26 **1-benzhydryl-4-nitrosopiperazine** (**2y**) was obtained as yellow oil. (230 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.5 Hz, 4H), 7.29 (dd, *J* = 10.4, 4.8 Hz, 4H), 7.20 (ddt, *J* = 6.2, 5.0, 2.5 Hz, 2H), 4.30 (s, 1H), 4.25 – 4.22 (m, 2H), 3.81 (dd, *J* = 12.6, 7.1 Hz, 2H), 2.59 (dd, *J* = 12.5, 7.2 Hz, 2H), 2.40 – 2.27 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 128.9, 127.9, 127.5, 52.0, 50.6, 50.0, 39.9, 29.8. HRMS: Calc. for $C_{17}H_{19}N_3O$ $[M+H]^+$: 282.1606, Obser. 282.1607.



2y

5. SYNTHESIS OF N-NITROSO-N-CYCLOHEXYLHYDROXYLAMINE (G)

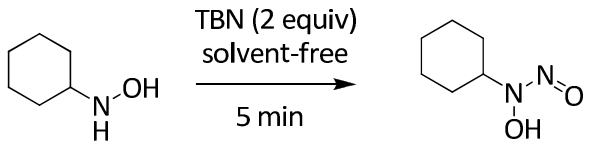
5.1 Procedure for preparation of *n*-cyclohexylhydroxylamine[5]



A round-bottom flask was charged with 1.67g of $NH_2OH.HCl$ (24 mmol, 1.2 equiv) and 0.96 g of NaOH (24 mmol, 1.2equiv.) in 10ml of water at 0^oC to which 2.24 g of cyclohexylhydroxylamine (20 mmol) was added drop wise. Then, the reaction mixture was allowed to stir for approximately for 2 hrs at 0^oC after which 15 ml of methanol was added along with a drop of methyl orange. The solution was acidified to a pink colour with addition of 2M HCl in methanol and then $NaBH_3CN$ (0.73 g, 11.6 mmol, 0.67 equiv) was added portion wise at 0^oC. After 1 hr, the reaction mixture was neutralized with NaOH (2 X 10 ml) and extracted with ethyl acetate (2 X 15 ml). The organic layer was dried over sodium sulphate, evaporated and subjected for column chromatography to obtain the title product as white solid (542 mg, 24%).

^{1}H NMR (500 MHz, $CDCl_3$+CD_3OD)[5] δ 3.79 (s, 2H), 2.67 (tt, *J* = 10.8, 3.6 Hz, 1H), 1.80 (d, *J* = 10.7 Hz, 2H), 1.65 (d, *J* = 13.3 Hz, 2H), 1.54 (d, *J* = 12.7 Hz, 1H), 1.22 – 1.12 (m, 2H), 1.10 – 1.02 (m, 1H), 1.01 – 0.91 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$+ CD_3OD) δ 60.5, 30.1, 26.0, 24.6.

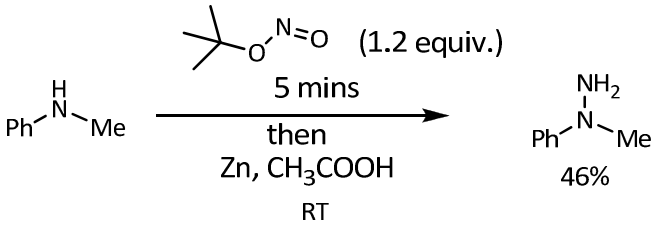
5.1 *N*-nitrosation of *N*-cyclohexylhydroxylamine



G

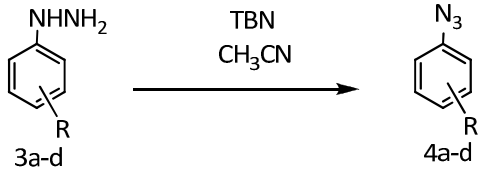
N-cyclohexylhydroxylamine (1.0 mmol) and tert-butyl nitrite (2.0 equiv.) was added at room temperature and allowed to stir for 5 min. After completion (as seen by TLC), the desired product was obtained in high purity through short silica purification as off-white to pale yellow solid. (95 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.04 (tt, *J* = 11.4, 3.7 Hz, 1H), 1.88 (dd, *J* = 44.4, 12.3 Hz, 4H), 1.69–1.56 (m, 3H), 1.42–1.29 (m, 2H), 1.26–1.16 (m, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 65.9, 28.4, 25.2, 24.8.

6. PROCEDURE FOR ONE-POT SYNTHESIS OF 1-METHYL 1- PHENYLHYDRAZINE



N-Methylaniline (2 mmol, 250 mg) and tert-butyl nitrite (1.2 equiv.) was stirred in a round bottom flask at room temperature approximately for 5 mins. Then the reaction mixture was diluted with glacial acetic acid (1 ml) and transferred to the flask containing a mixture of Zn dust (500mg) and water (1ml) while the temperature was maintained at ~15^{o}C. Further the reaction mixture was allowed to stirr for 3 hrs at room temperature and warmed to 80^{o}C on a steam bath.[6] The hot solution was filtered from un-reacted Zn and washed with 5% HCl solution (5 ml). The companied filtrate was treated with 40% NaOH solution and extracted with diethyl ether (3x5 ml). The organic layer was dried over anhydrous sodium sulphate and evaporated to dryness. The yield was calculated based on crude proton NMR. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.29 (m, 2H), 7.80–7.01 (m, 2H), 6.90–6.84 (m, 1H), 3.70 (s, 2H), 3.12 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 129.0, 18.6, 113.6, 44.5.

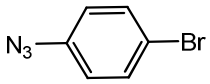
7. PROCEDURE FOR THE SYNTHESIS OF ARYL AZIDES FROM ARYL HYDRAZINES



To a stirred solution of aryl hydrazine (2 mmol) in acetonitrile (3 ml), tert-butyl nitrite (2.0 equiv. for **3a**-**3c** and 5.0 equiv. for **3d**) was added drop-wise at room temperature. Further, the reaction mixture was allowed to stir at room temperature for appropriate time while the reaction progress was monitored by TLC. After completion, the reaction mixture was diluted with ethyl acetate and washed with saturated $NaHCO_3$ (2 X 5ml) and brine (2 X 5ml).

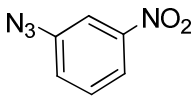
The companied organic layer was dried over sodium sulphate, evaporated and the residue was subjected to column chromatography to obtain the desired products.

7.1 **4-Bromophenyl azide** (**4a**)[7] was obtained as yellow oil (360 mg, 91%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.5 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 133.0, 120.8, 117.9.



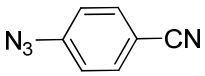
4a

7.2 **3-Nitrophenyl azide** (**4b**)[8] was obtained as dark orange solid (278 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (ddd, *J* = 8.2, 2.1, 0.9 Hz, 1H), 7.87 (t, *J* = 2.1 Hz, 1H), 7.55–7.49 (m, 1H), 7.32 (ddd, *J* = 8.1, 2.2, 0.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3,142.2, 130.8, 125.1, 119.9, 114.3.



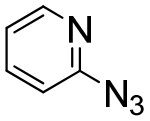
4b

7.3 **4-cyanophenyl azide** (**4c**)[9] was obtained as yellow crystals (256 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.61 (m, 2H), 7.11–7.07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 134.0, 119.9, 118.5, 108.5.



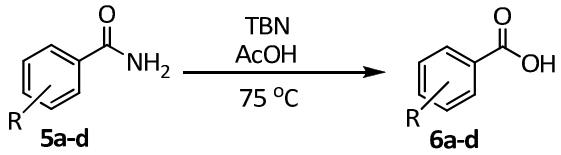
4c

7.4 **2-Azido pyridine** (**4d**)[10] was obtained as yellowish red crystals (224 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 6.9 Hz, 1H), 8.10 (d, *J* = 9.0 Hz, 1H), 7.72 (ddd, *J* = 8.9, 6.8, 0.8 Hz, 1H), 7.30–7.25 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 132.0 125.6, 116.7, 116.2.



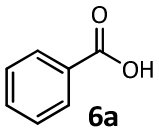
4d

8. PROCEDURE FOR THE SYNTHESIS OF SUBSTITUTED BENZOIC ACIDS FROM CORRESPONDING AMIDES:



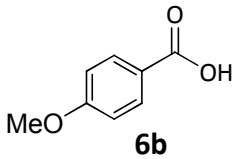
To a stirred solution of primary amide (1mmol) in acetic acid (3 ml), tert-butyl nitrite (3 equiv.) was added slowly under N_2 atmosphere. Then the reaction mixture was allowed to stir for 60 min at 75^{o}C while the progress was monitored by TLC. After completion, the reaction mixture was evaporated to dryness to obtain corresponding benzoic acids in quantitative yield. However, to obtain high purity for NMR analysis, the crude products were subjected to short silica filtration using a mixture of ethyl acetate and hexane.

8.1 **Benzoic acid** (**6a**)[11] was obtained as white crystalline solid {Crude yield, >120 mg (>99%); After purification, 115 mg (95%)}. Melting point: 122^{O}C (observed), Lit. 122 ^{O}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.43 (s, 1H), 8.18 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.7, 133.8, 130.2, 129.3, 128.5.



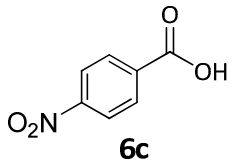
6a

8.2 **4-Methoxy benzoic acid** (**6b**)[12] was obtained as white crystals {(Crude yield, >150mg, (>99%); After purification, 144 mg (95%)}. Melting point: 183^{O}C (observed), Lit. 184 ^{O}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 163.6, 132.1, 122.7, 113.7, 55.5.



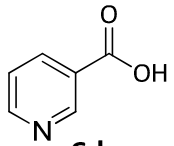
6b

8.3 **4-Nitrobenzoic acid** (**6c**)[13] was obtained as white to yellow crystals {(Crude yield, >165mg, (>99%); After purification, 155 mg (93%)}. Melting point: 237 ^{O}C (Observed), Lit. 240 ^{O}C] ^{1}H NMR (500 MHz, DMSO) δ 13.59 (s, 1H), 8.36 (d, *J* = 8.0 Hz, 2H), 8.21 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, DMSO) δ 165.8, 149.9, 136.6, 130.6, 123.6.



6c

8.4 **Nicotinic acid** (**6d**)[14] was obtained as white crystals (113 mg, 92%). Melting Point: 143 ^{O}C (Observed), Lit. 141 ^{O}C. ^{1}H NMR (500 MHz, DMSO) δ 13.41 (s, 1H), 9.07 (s, 1H), 8.8 –8.76 (m, 1H), 8.26 (d, *J* = 7.8 Hz, 1H), 7.56–7.50 (m, 1H). ^{13}C NMR (125 MHz, DMSO) δ 166.2, 153.2, 150.2, 136.9, 126.5, 123.7.



6d

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14) M. Yoshida, *Org. Biomol. Chem.,* 2009, **7**, 4062-4066

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 2F

```
Bond precision:  C-C = 0.0034 A          Wavelength=0.71073

Cell:            a=7.5292(5)    b=5.7936(3)        c=13.9668(9)
                 alpha=90       beta=93.766(4)     gamma=90
Temperature:     293 K

                Calculated                Reported
Volume          607.93(6)                 607.93(6)
Space group     P 21                      P 21
Hall group      P 2yb                     P 2yb
Moiety formula  C14 H14 N2 O2             ?
Sum formula     C14 H14 N2 O2             C14 H14 N2 O2
Mr              242.27                    242.27
Dx,g cm-3       1.324                     1.324
Z               2                         2
Mu (mm-1)       0.090                     0.090
F000            256.0                     256.0
F000'           256.11
h,k,lmax        8,6,16                    8,6,16
Nref            2145[ 1188]               2141
Tmin,Tmax       0.973,0.982               0.750,0.760
Tmin'           0.973

Correction method= # Reported T Limits: Tmin=0.750 Tmax=0.760
AbsCorr = MULTI-SCAN

Data completeness= 1.80/1.00      Theta(max)= 25.000

R(reflections)= 0.0299( 1888)     wR2(reflections)= 0.0712( 2141)

S = 1.046                 Npar= 164
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT089_ALERT_3_C Poor Data / Parameter Ratio (Zmax < 18) ........       7.24 Note
PLAT480_ALERT_4_C Long H...A H-Bond Reported H8B    ..  N2      ..       2.67 Ang.
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Alert level G

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PLAT032_ALERT_4_G Std. Uncertainty on Flack Parameter Value High .      0.400 Report
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)        293 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)        293 Check
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```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   3 ALERT level G = General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   0 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   2 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

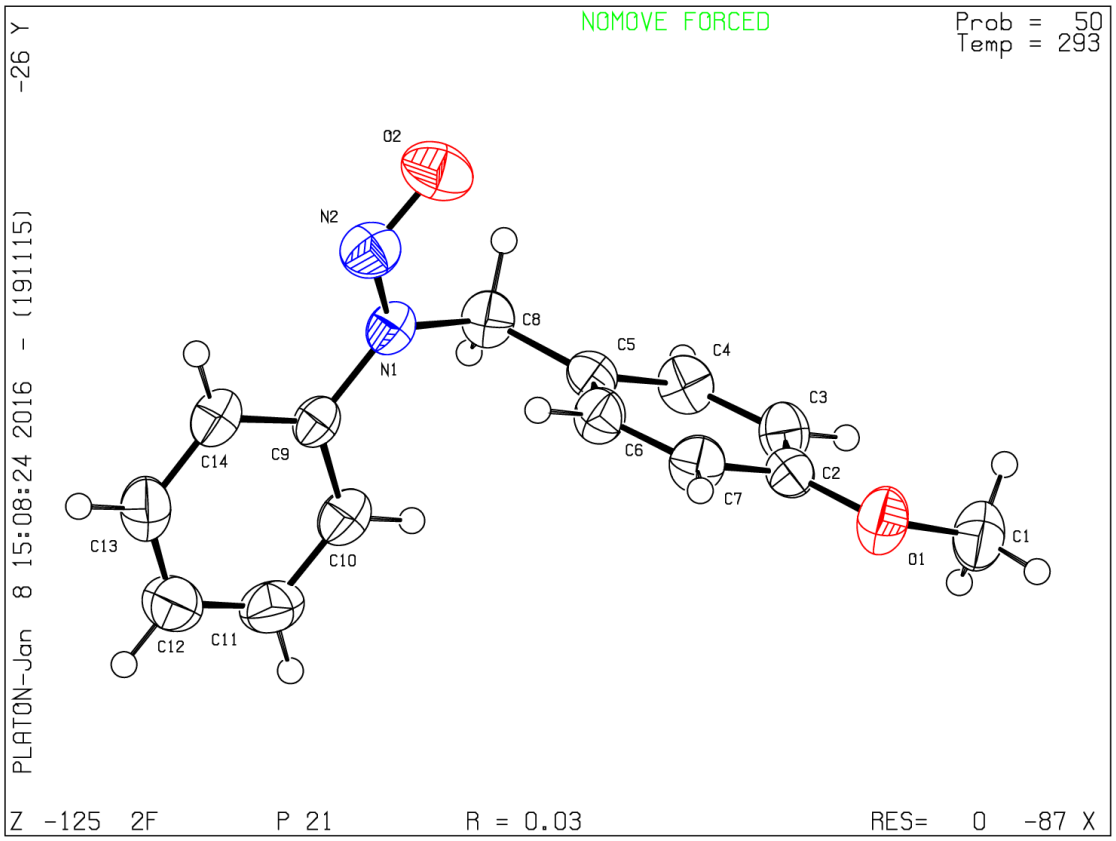
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

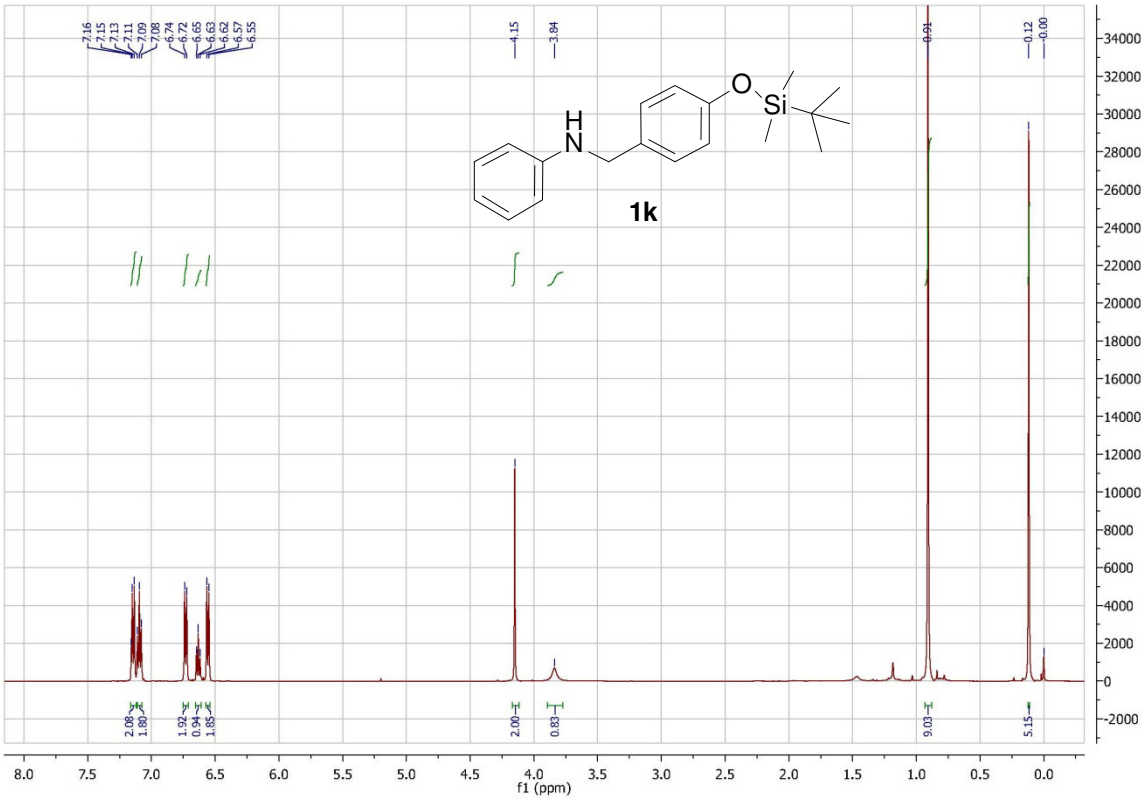
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 19/11/2015; check.def file version of 17/11/2015

Datablock 2F - ellipsoid plot

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0.12
0.00
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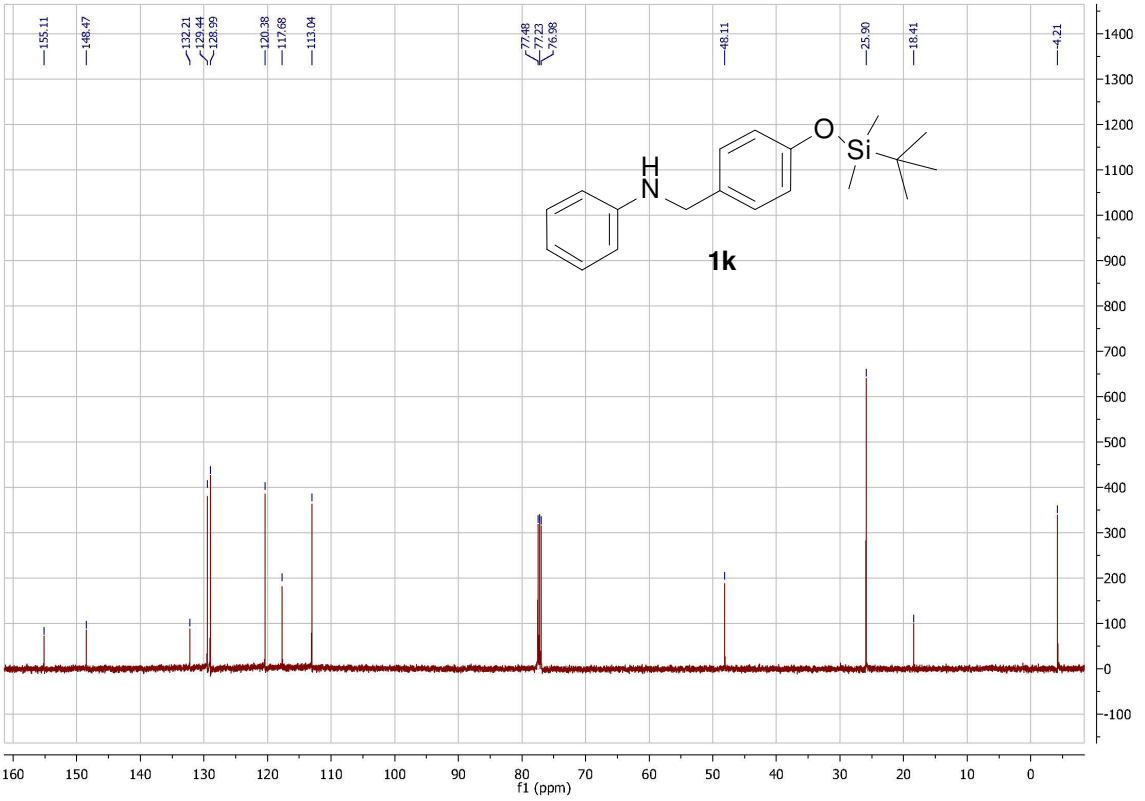
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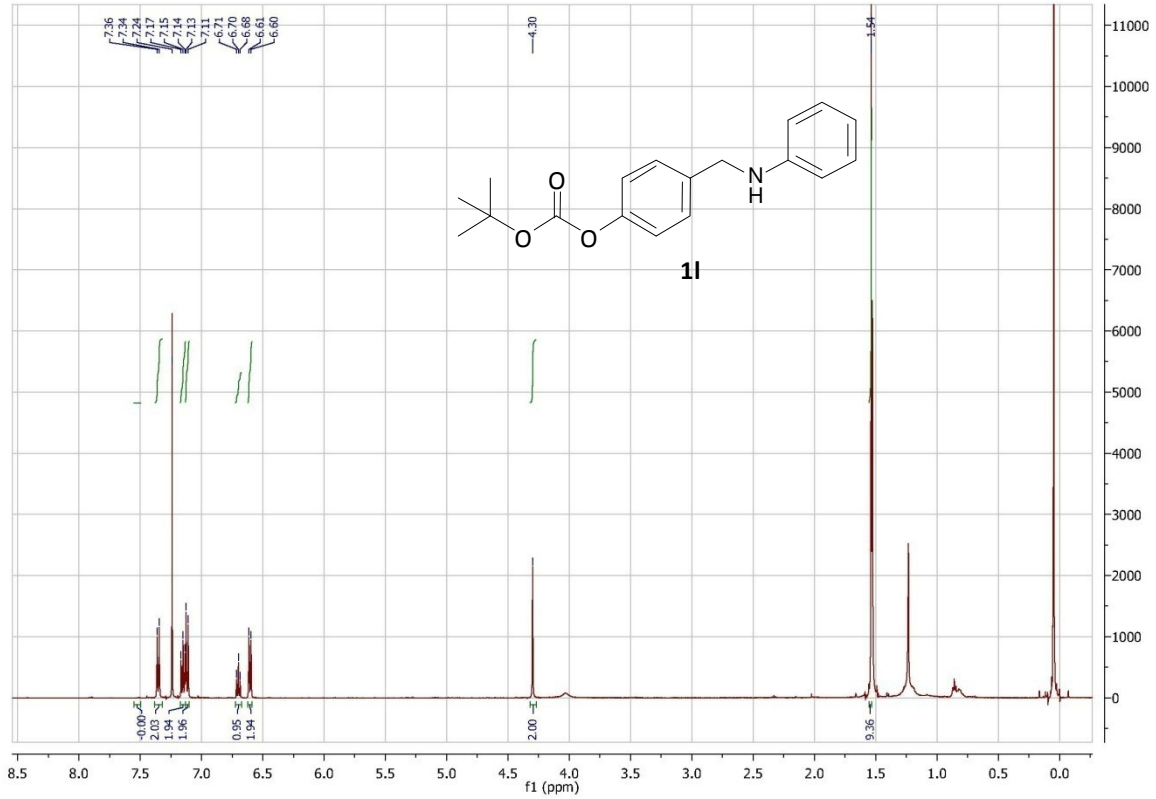
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O
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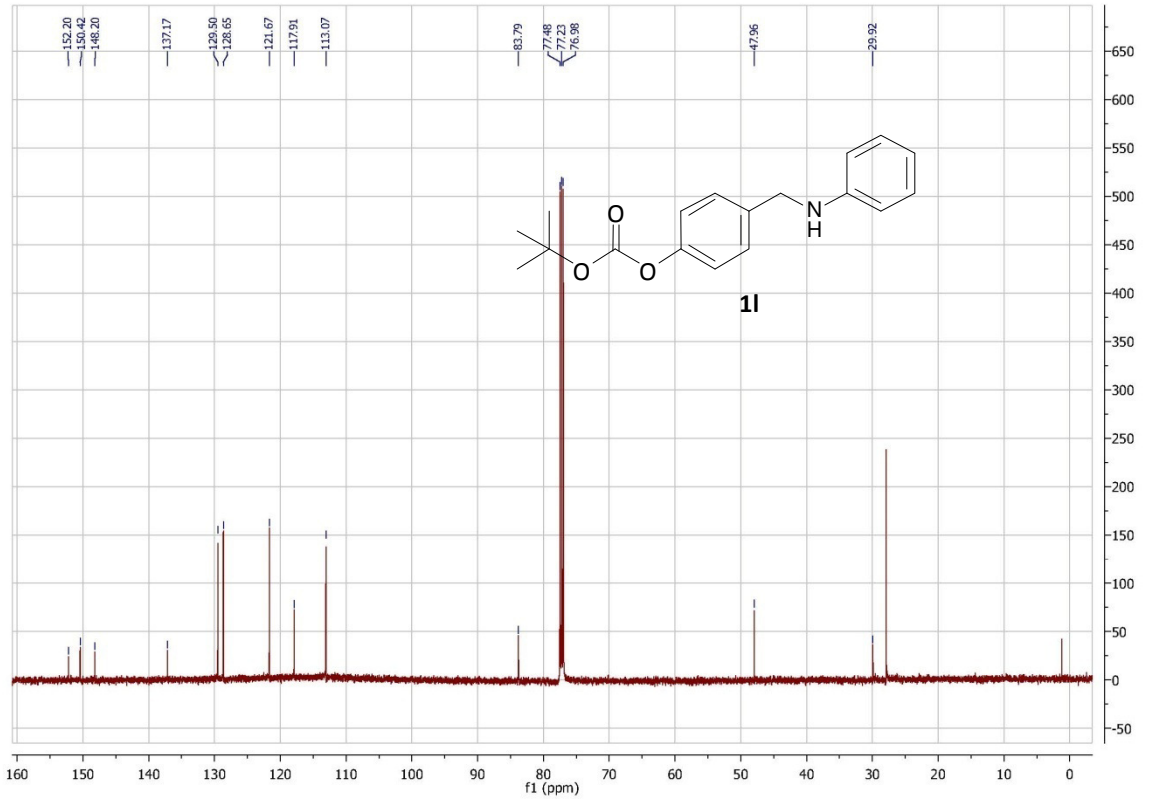
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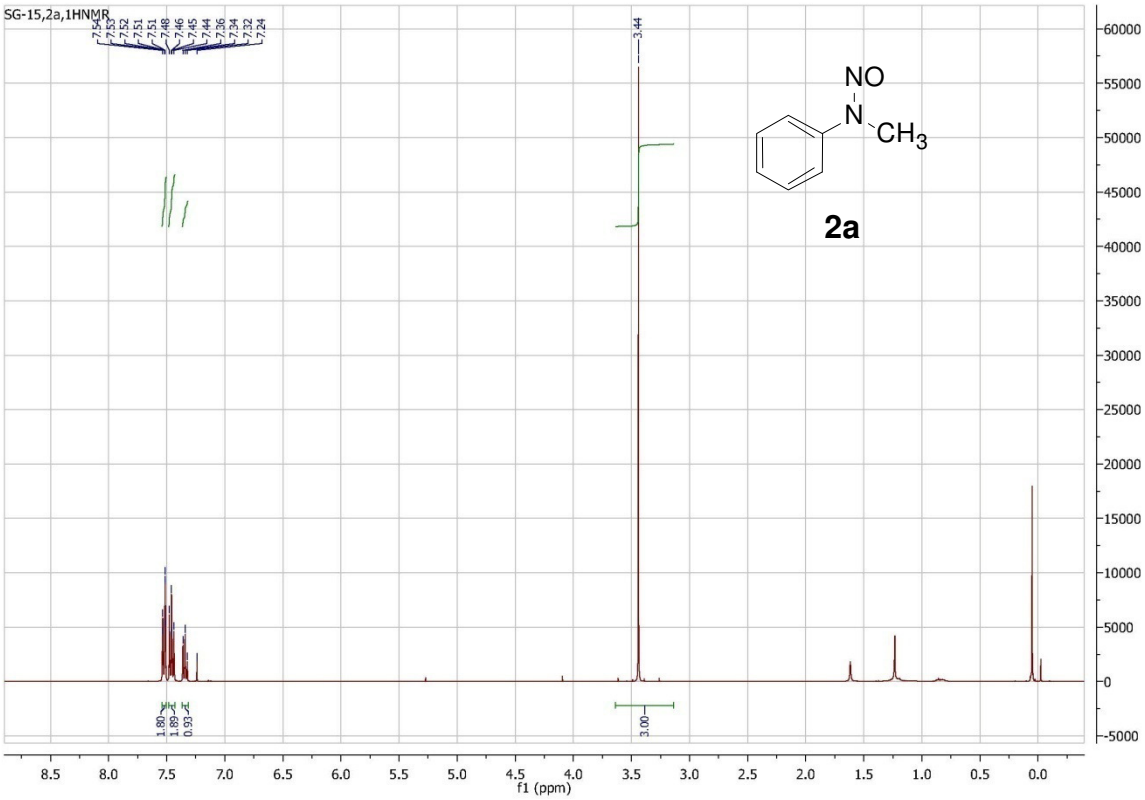
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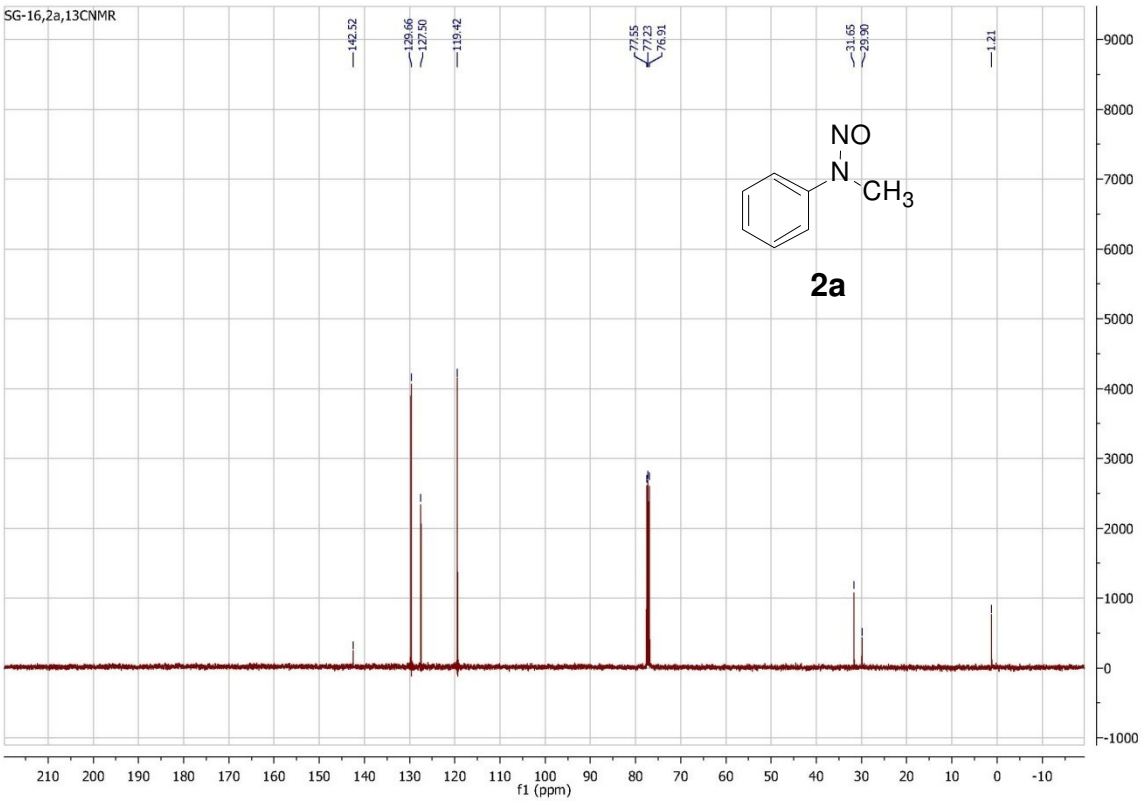
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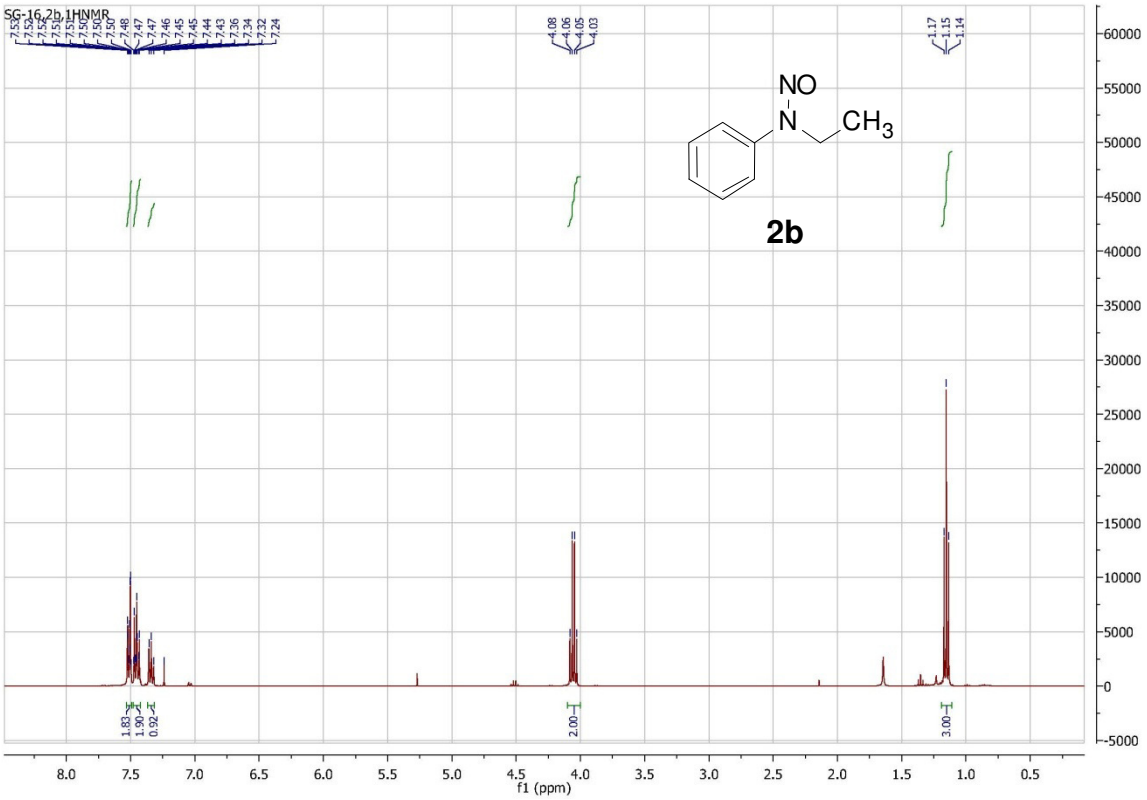
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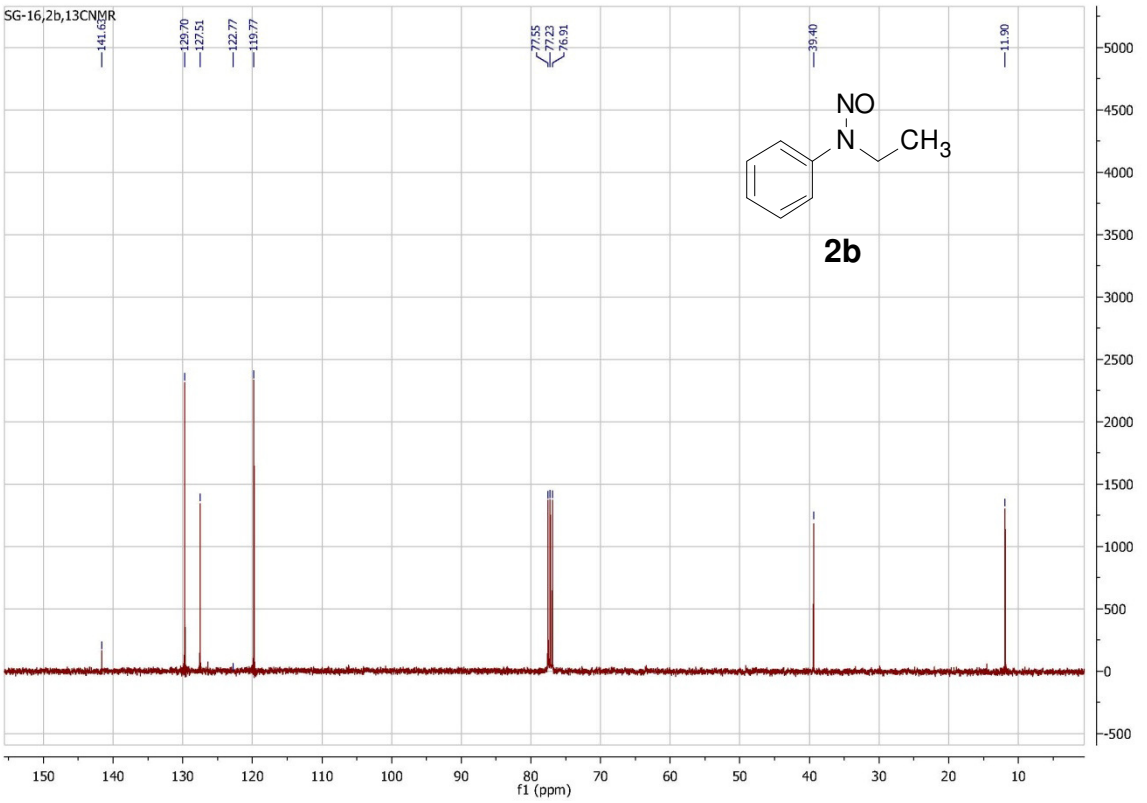
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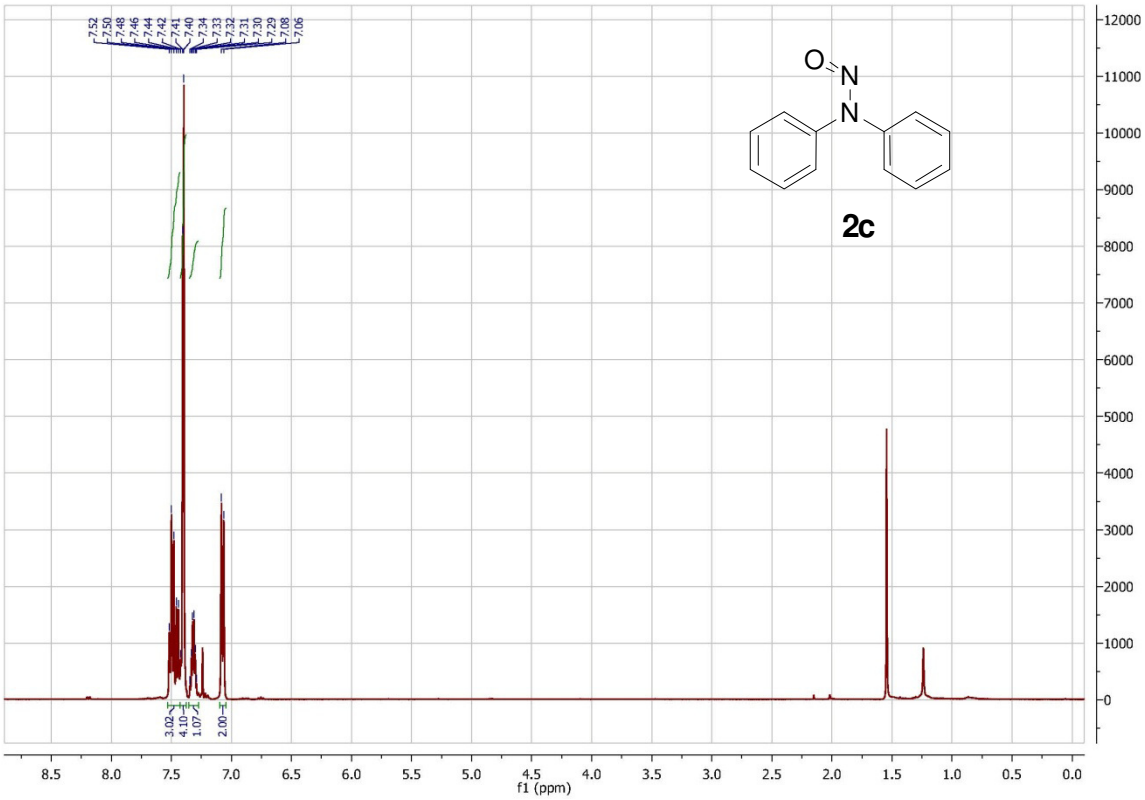
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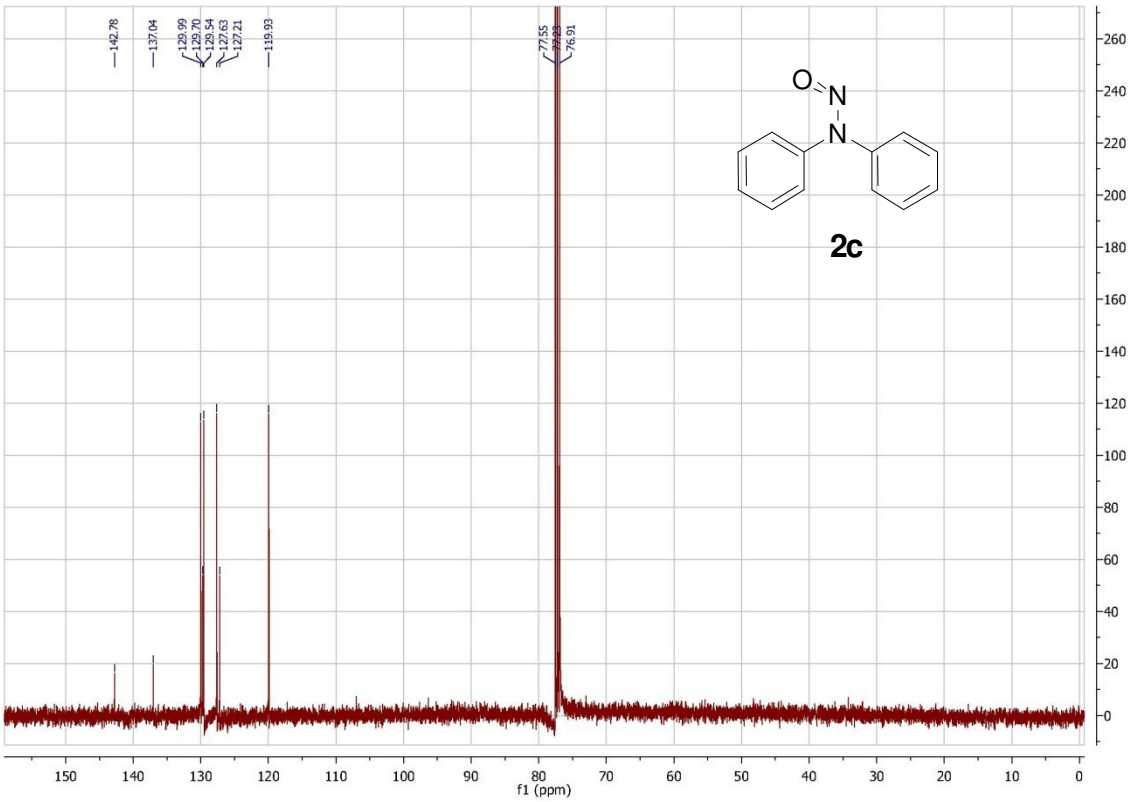
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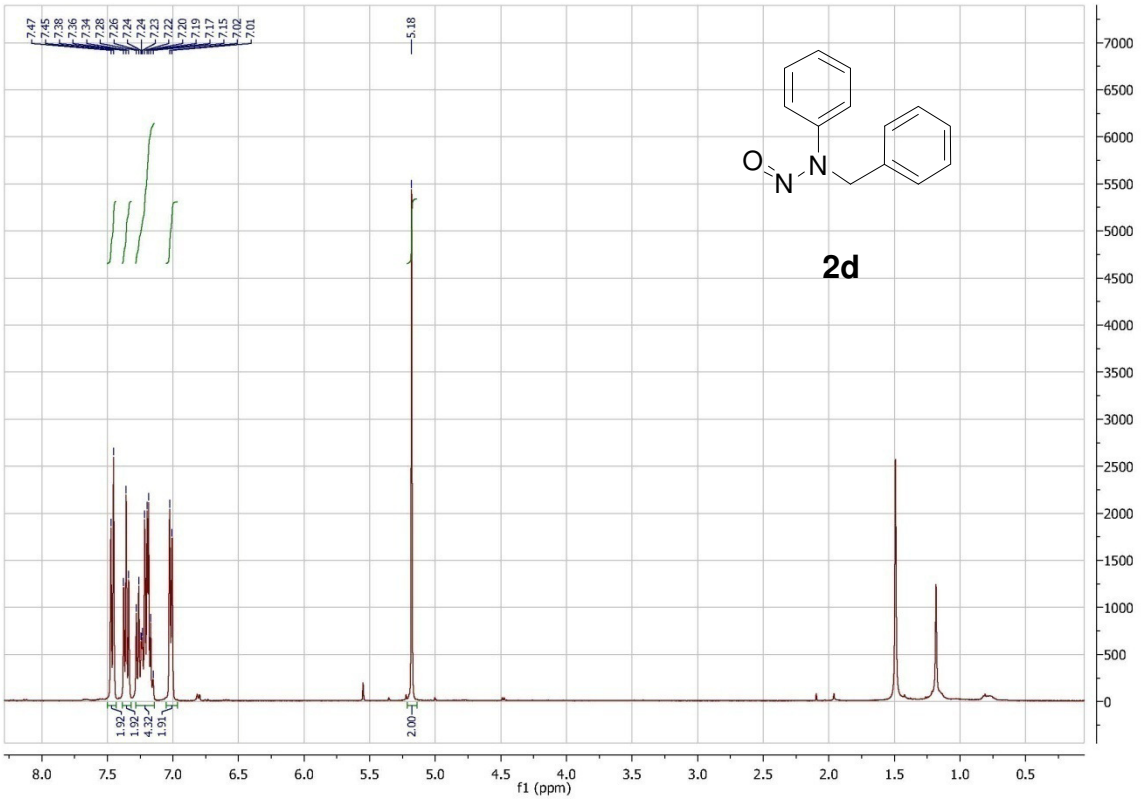
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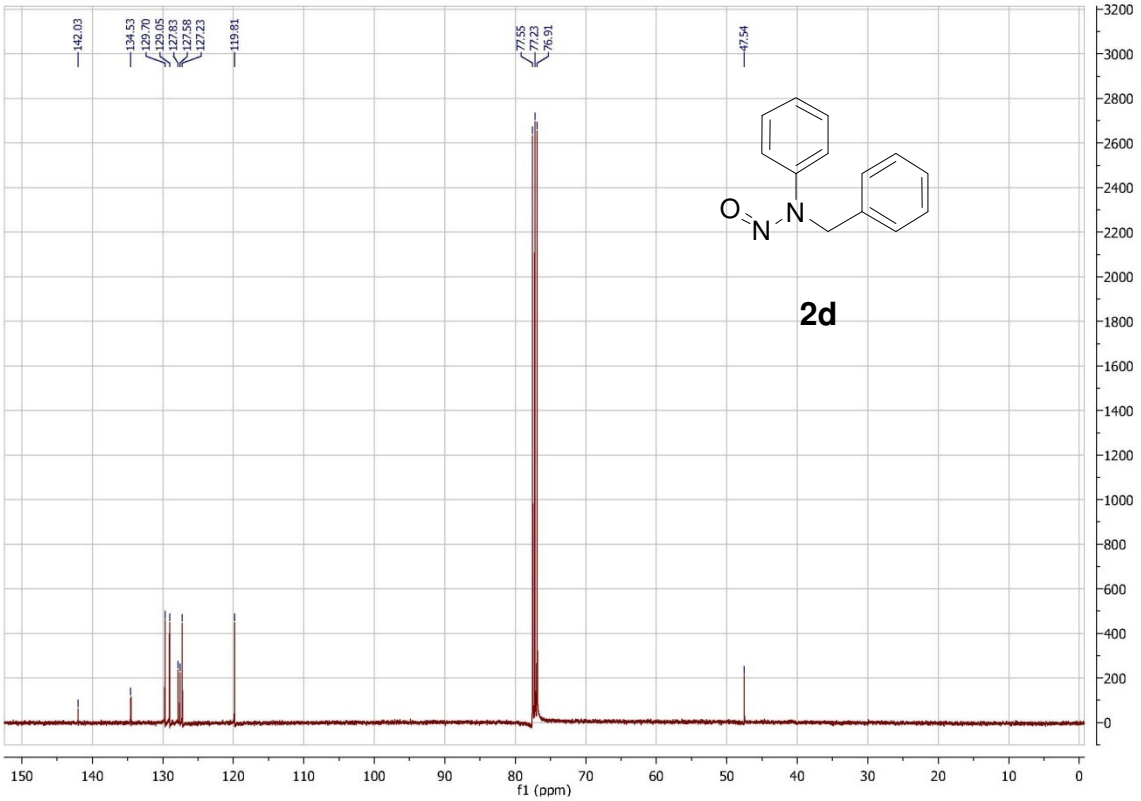
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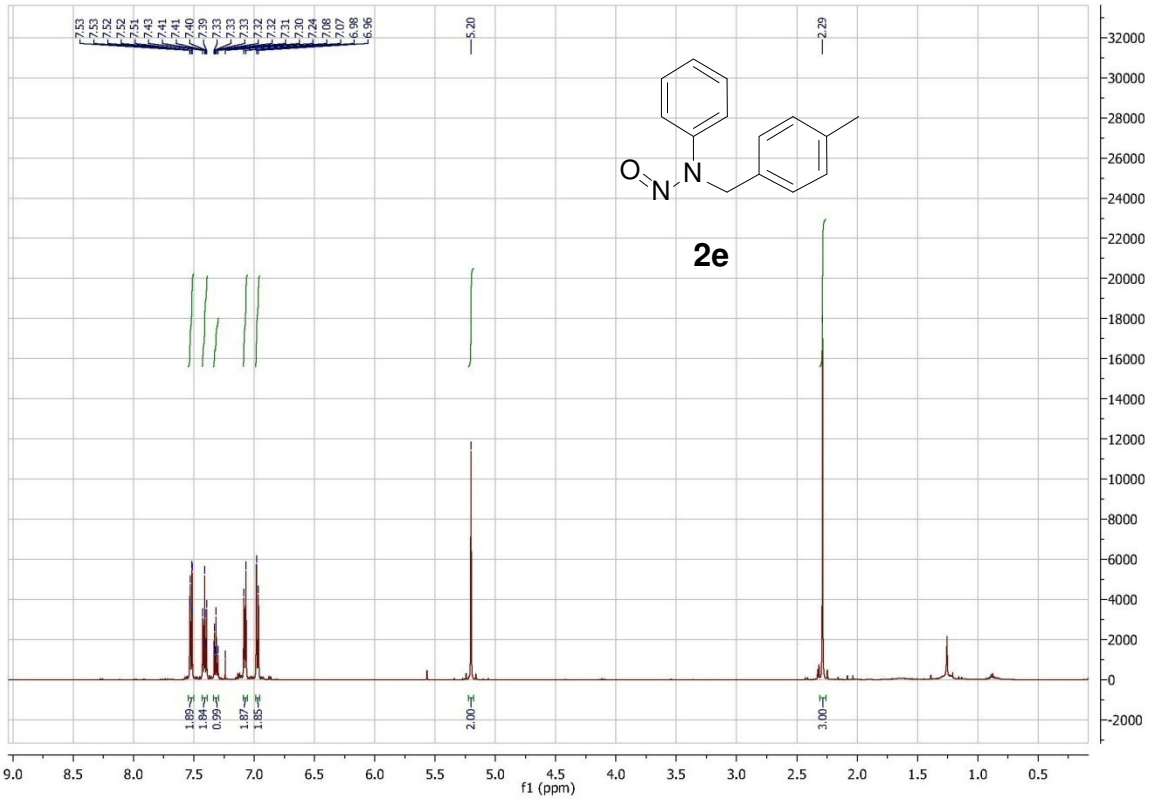
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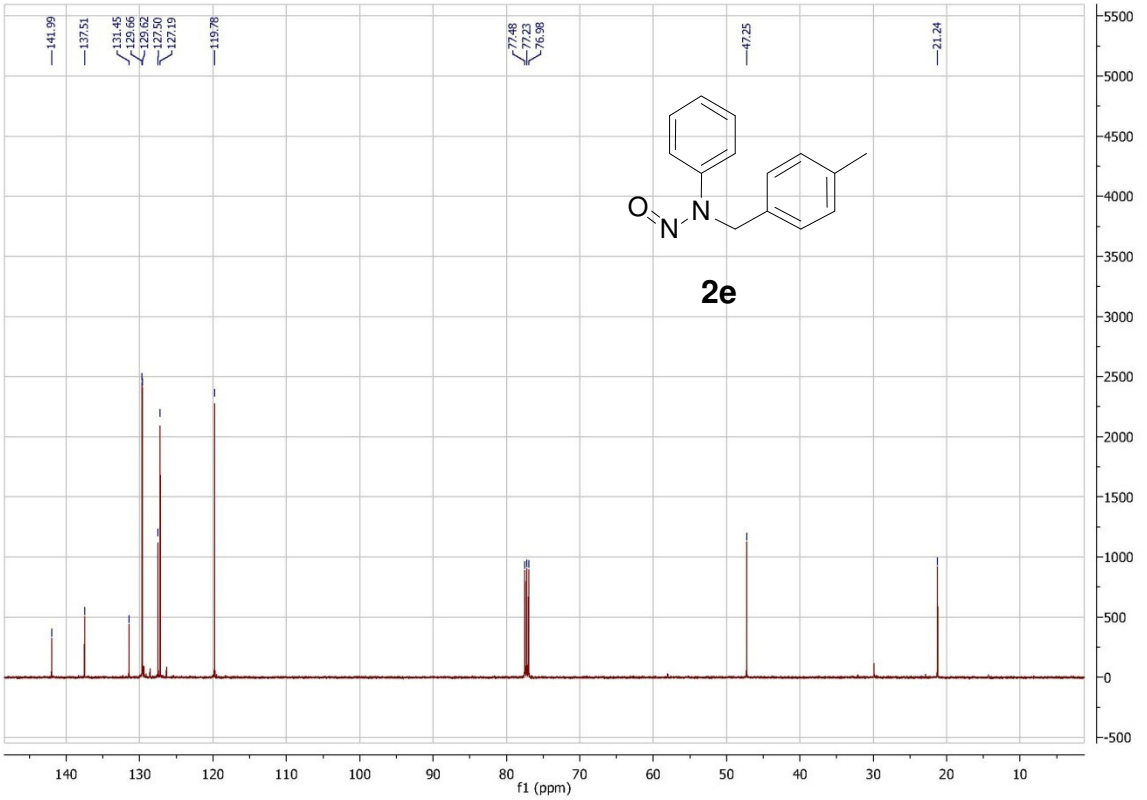
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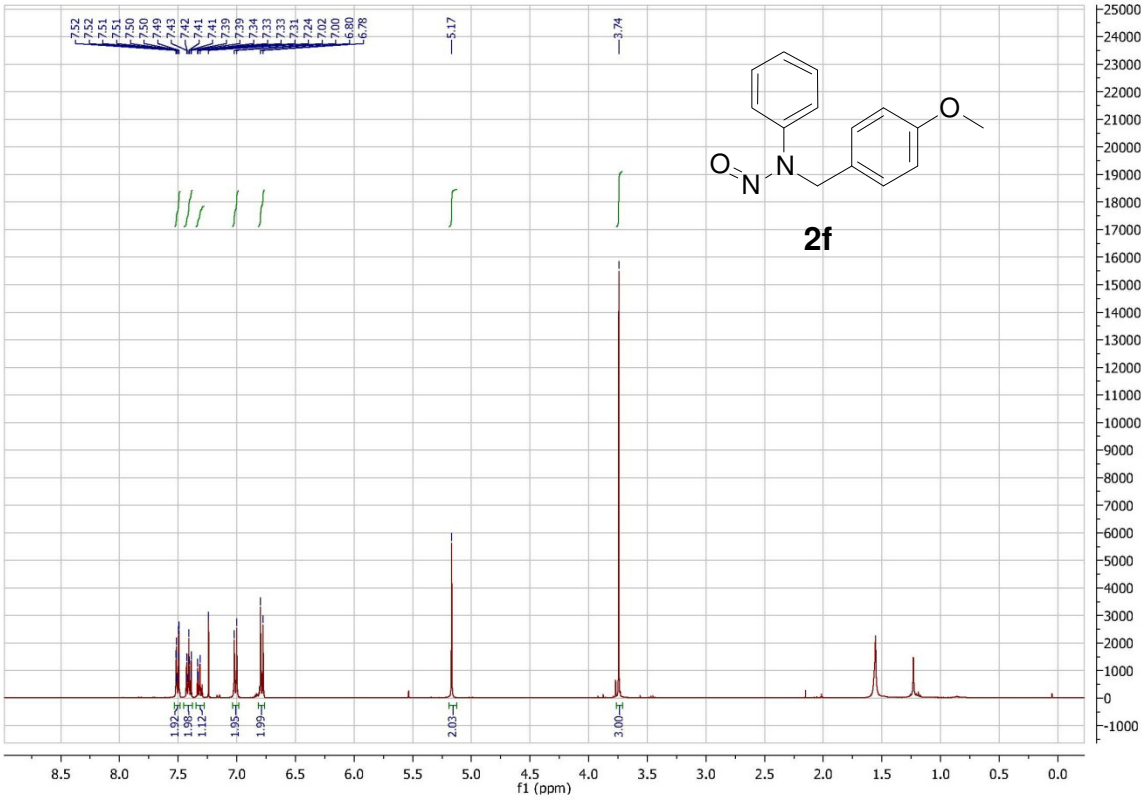
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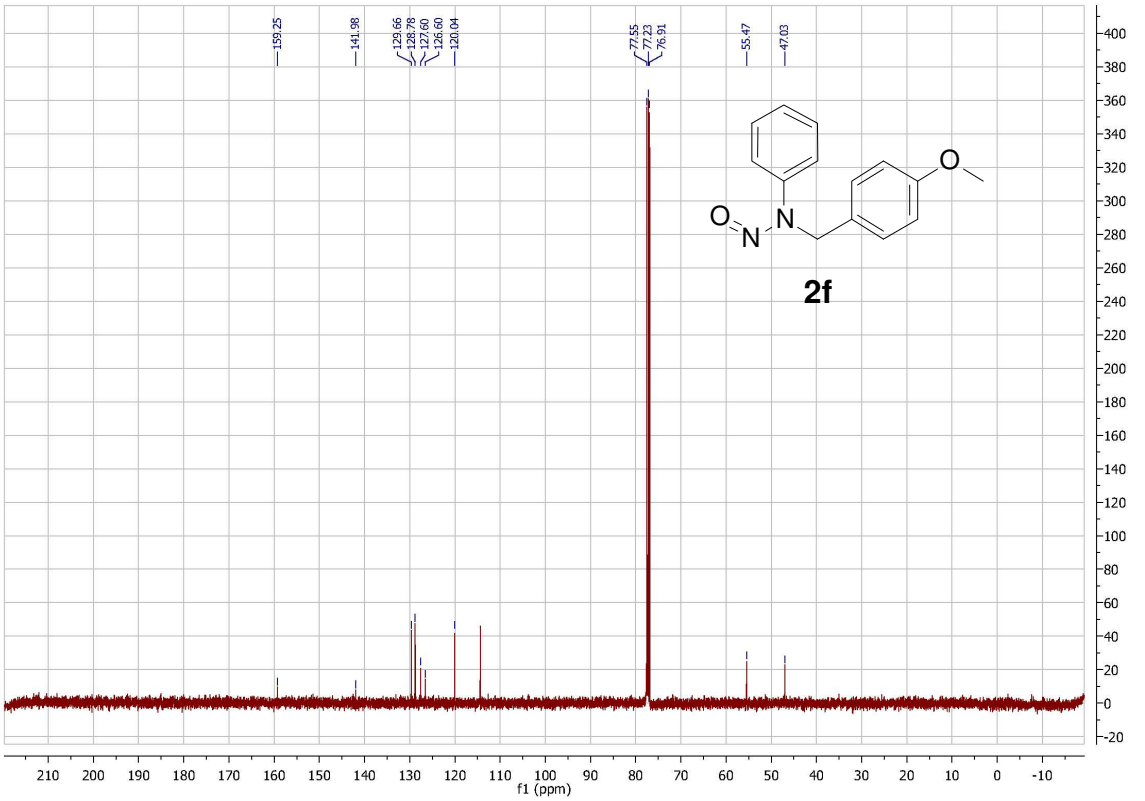
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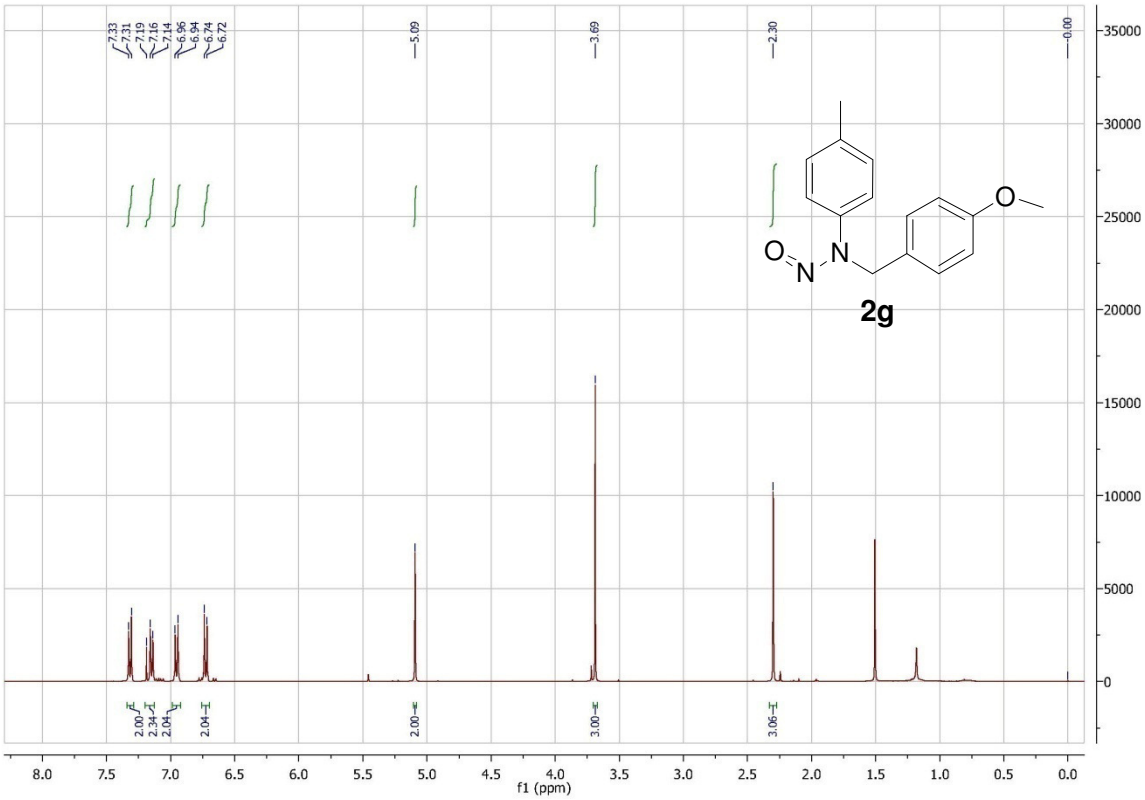
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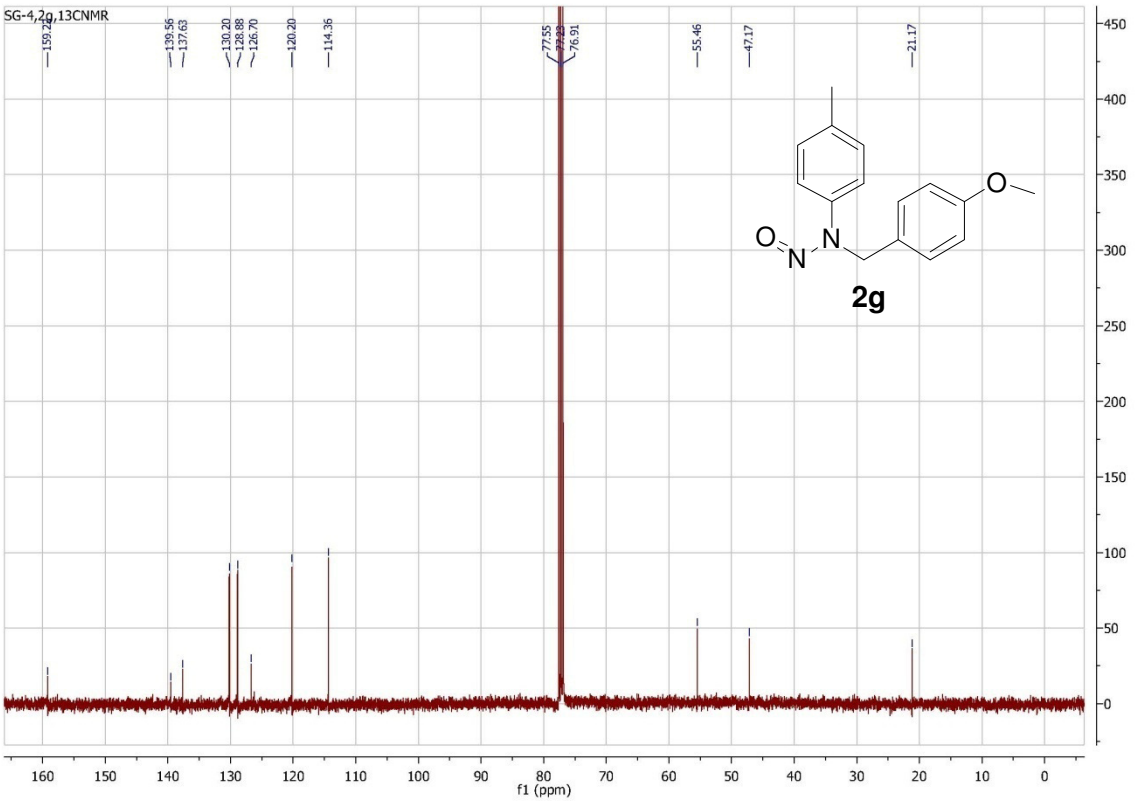
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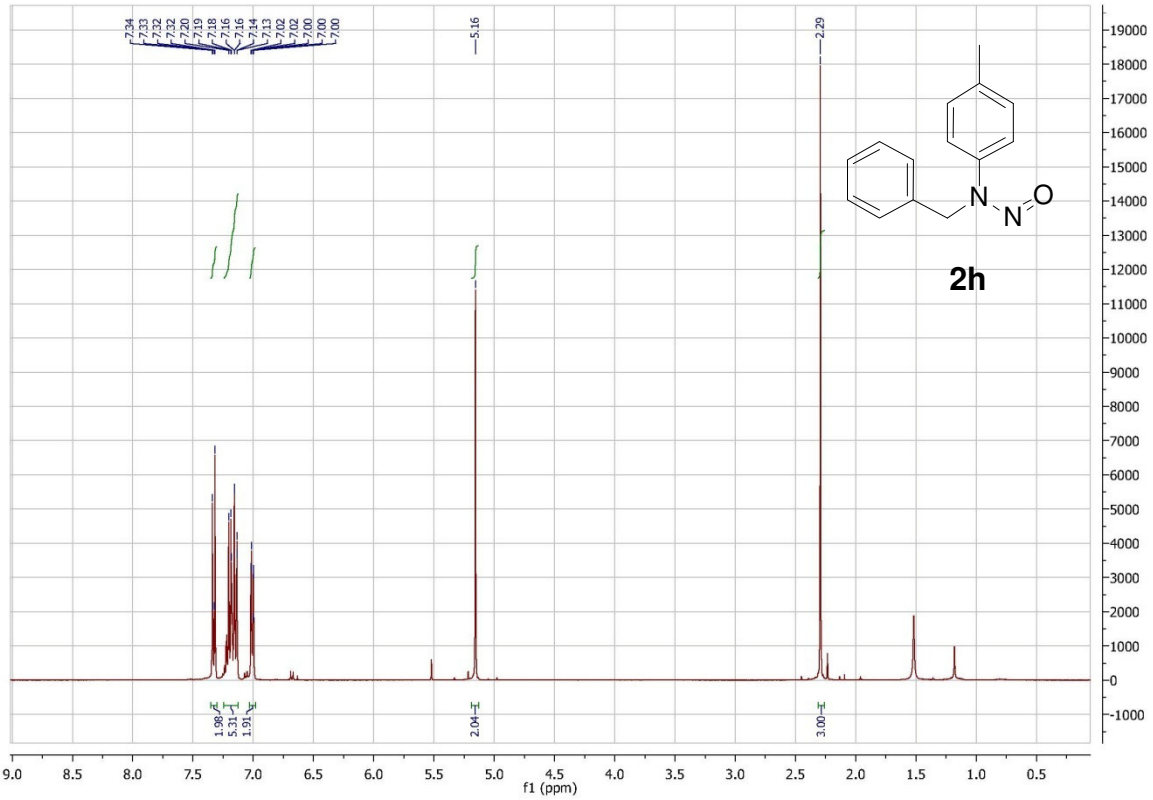
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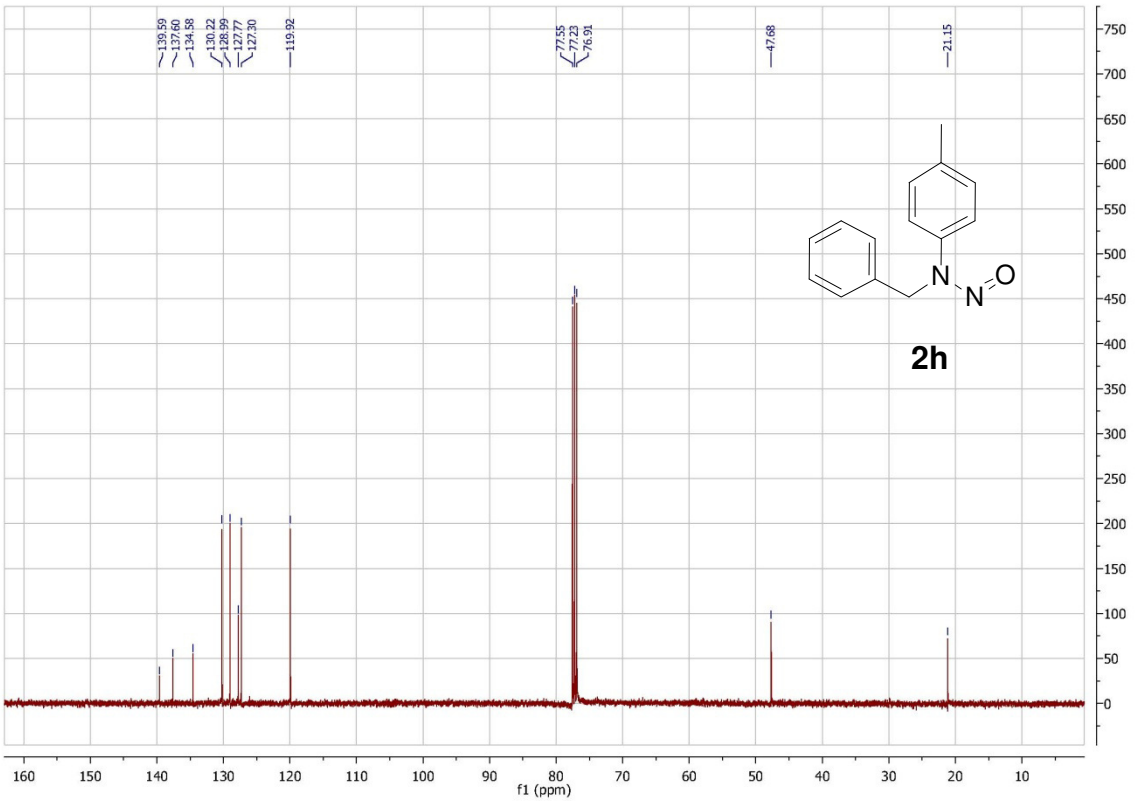
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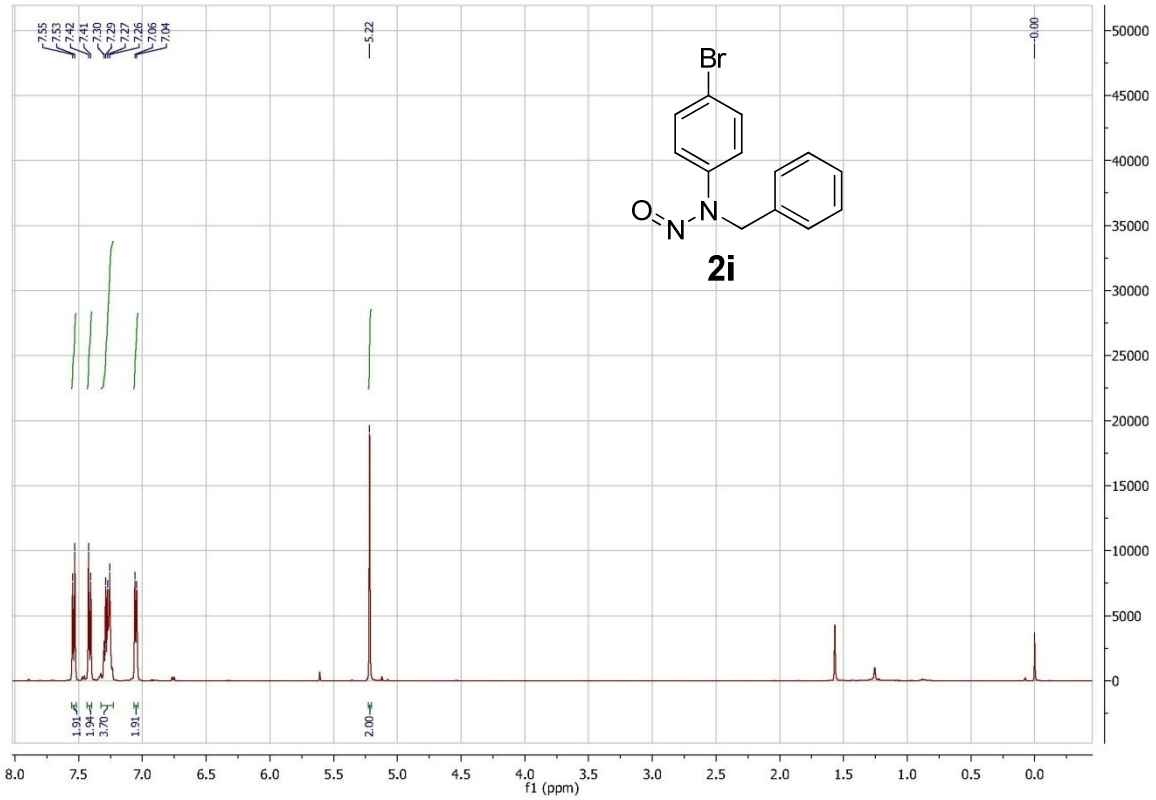
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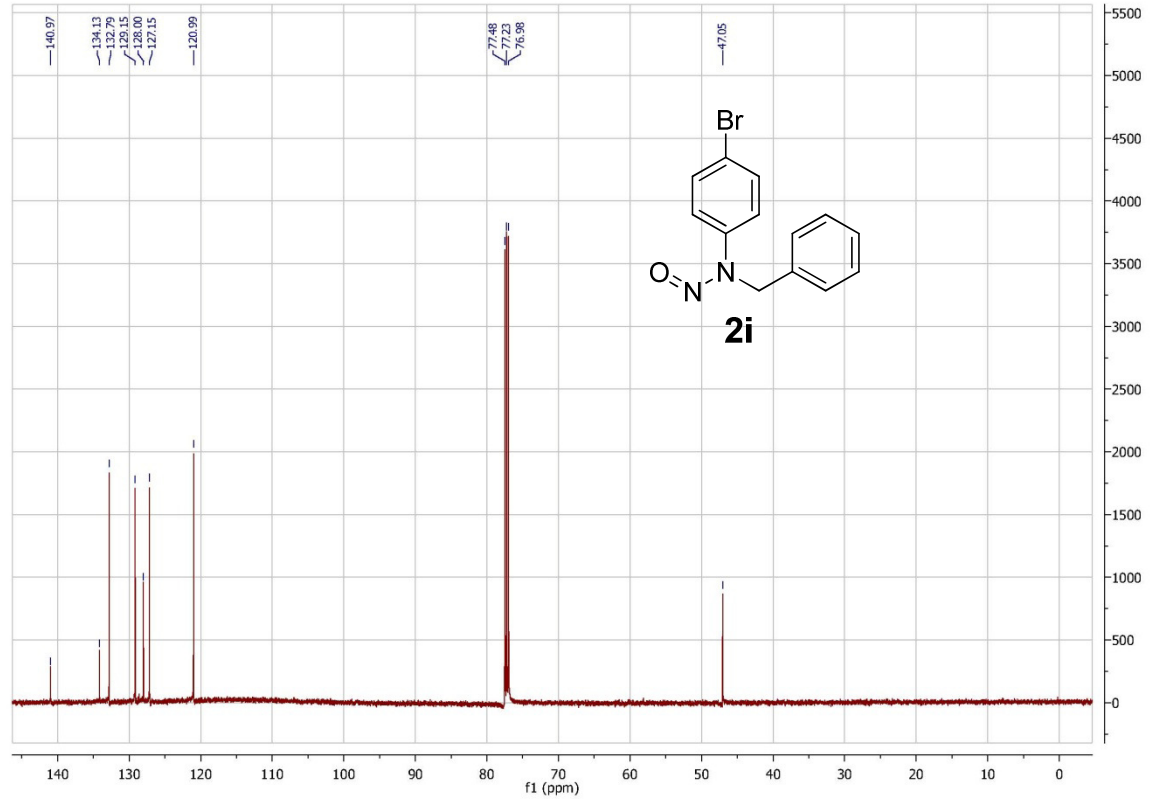
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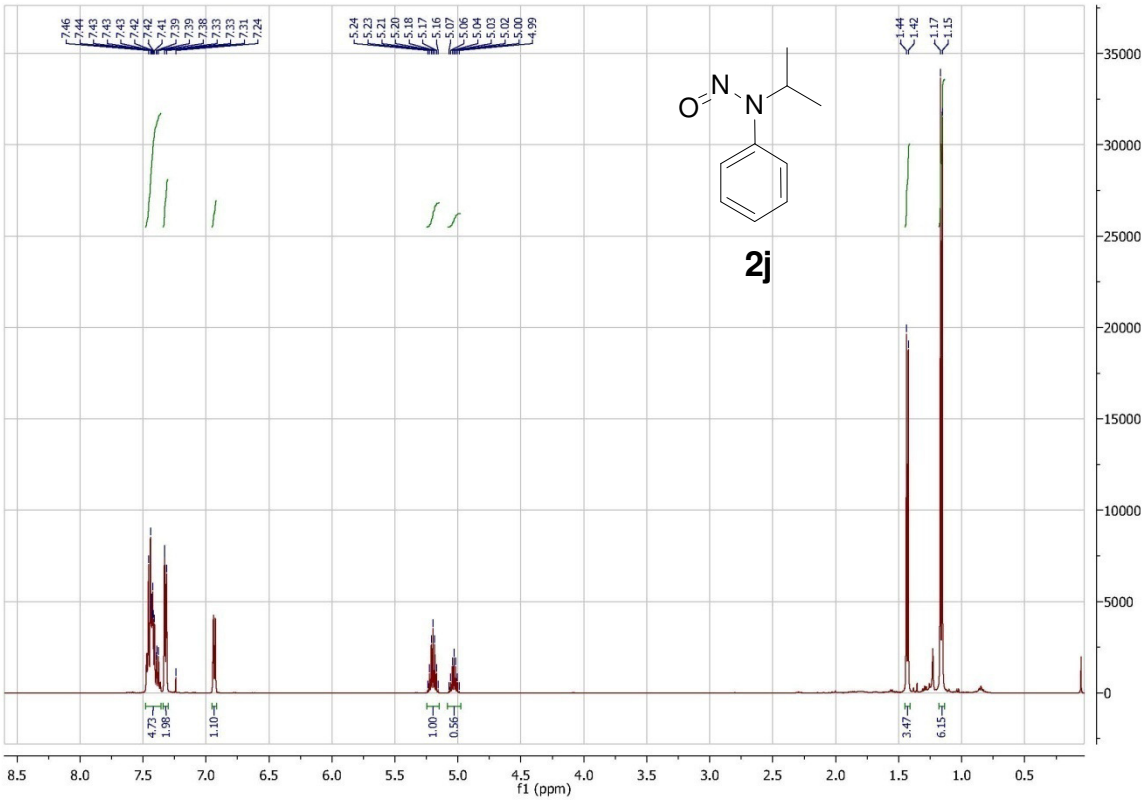
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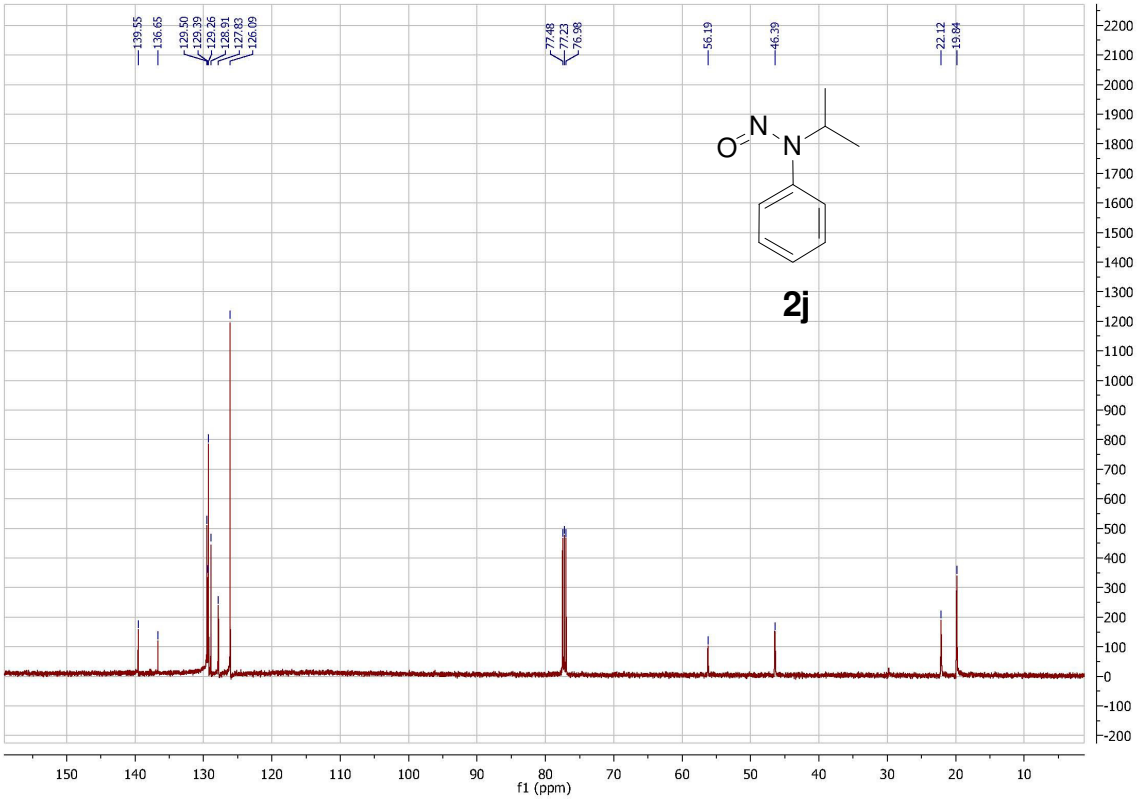
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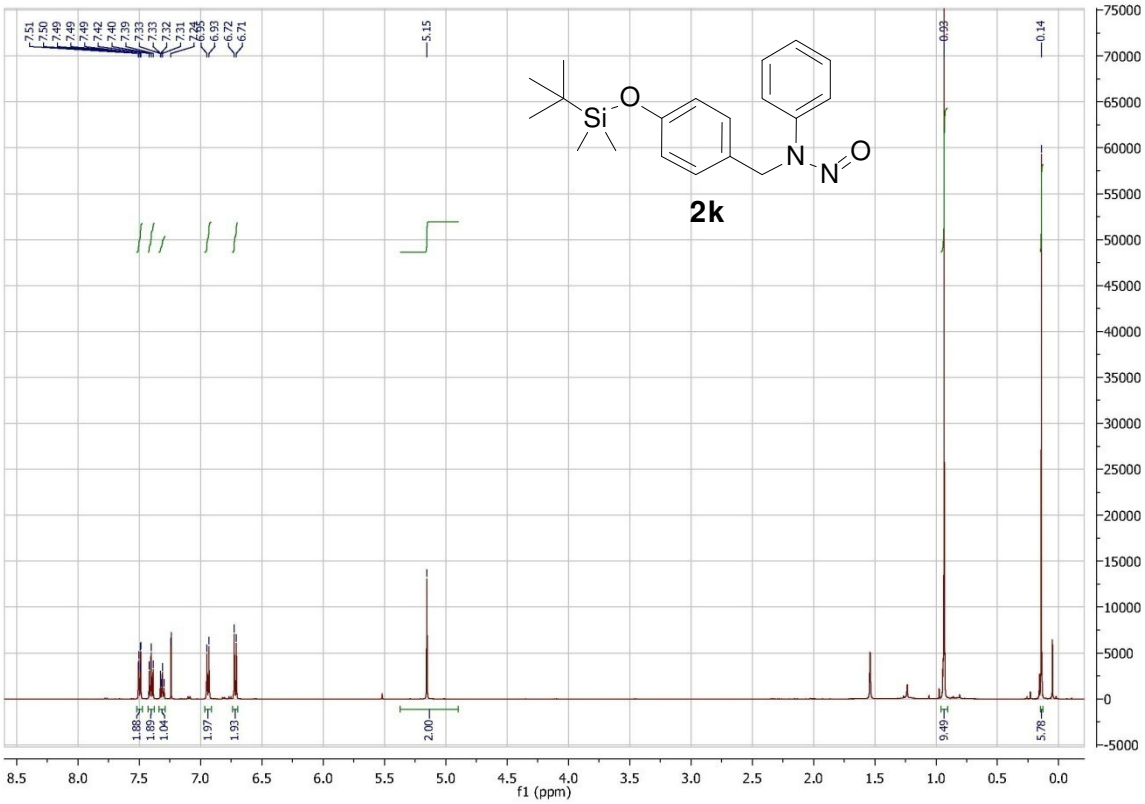
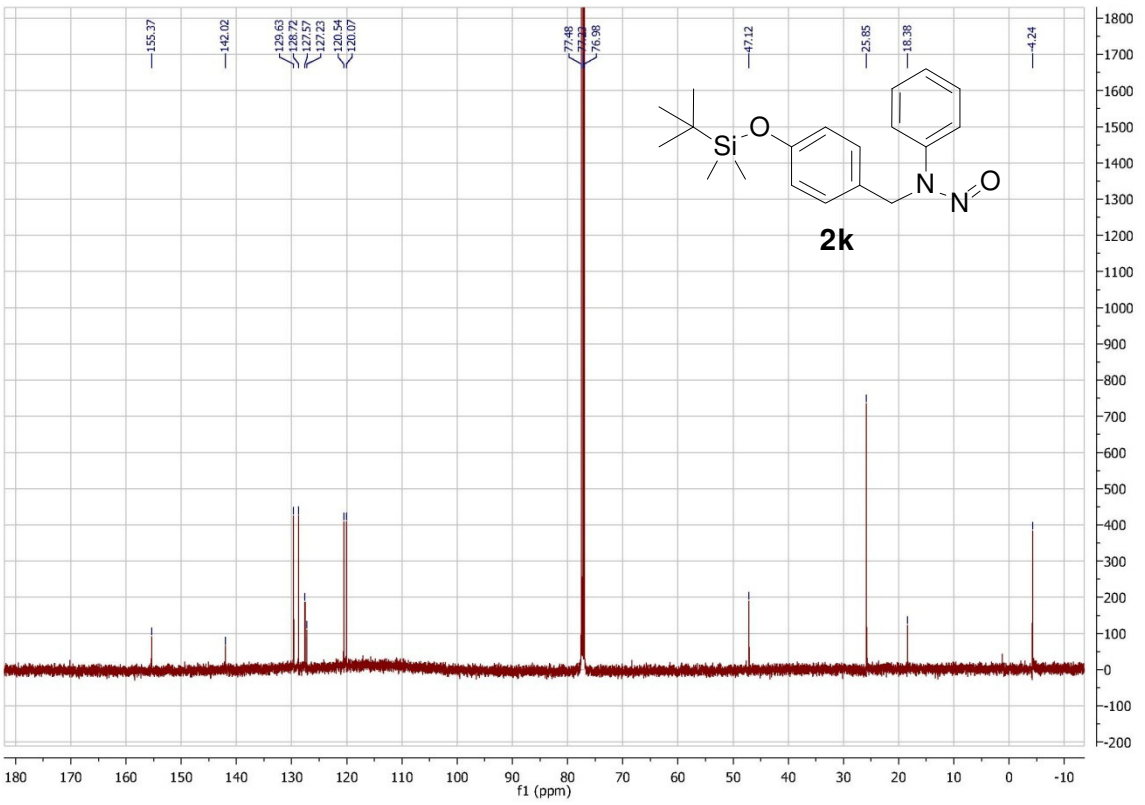
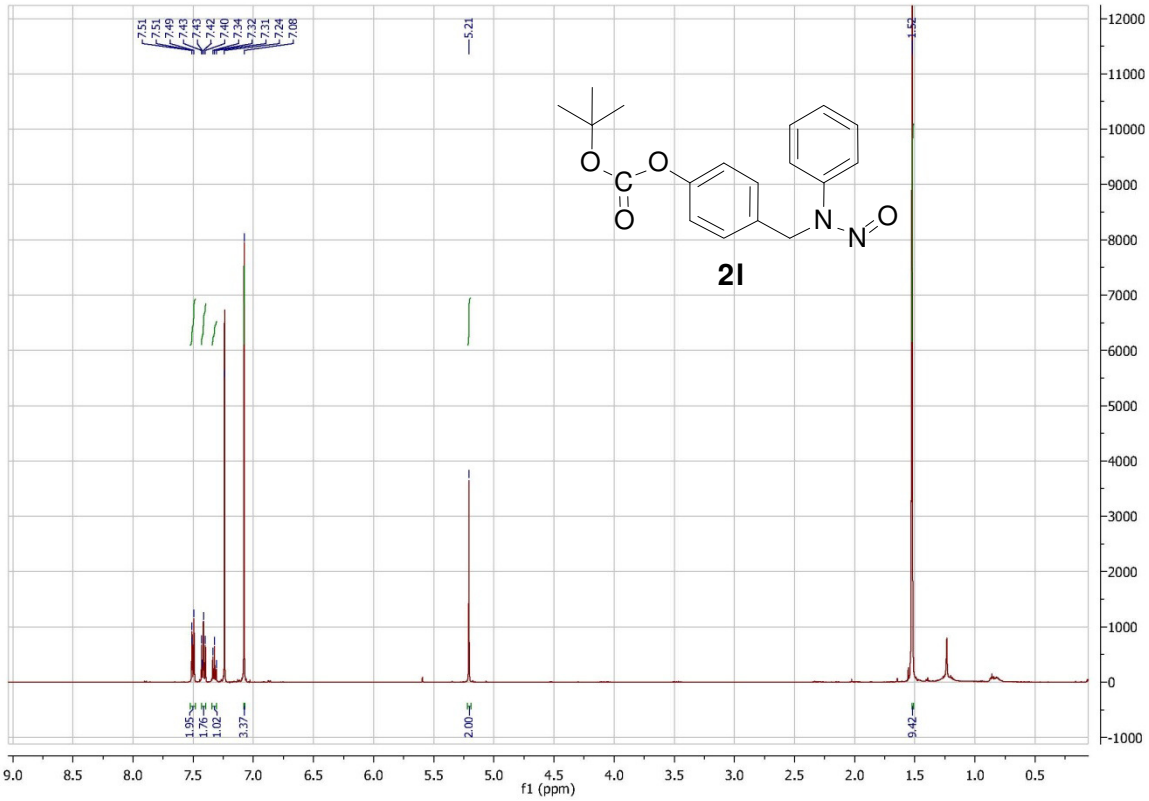
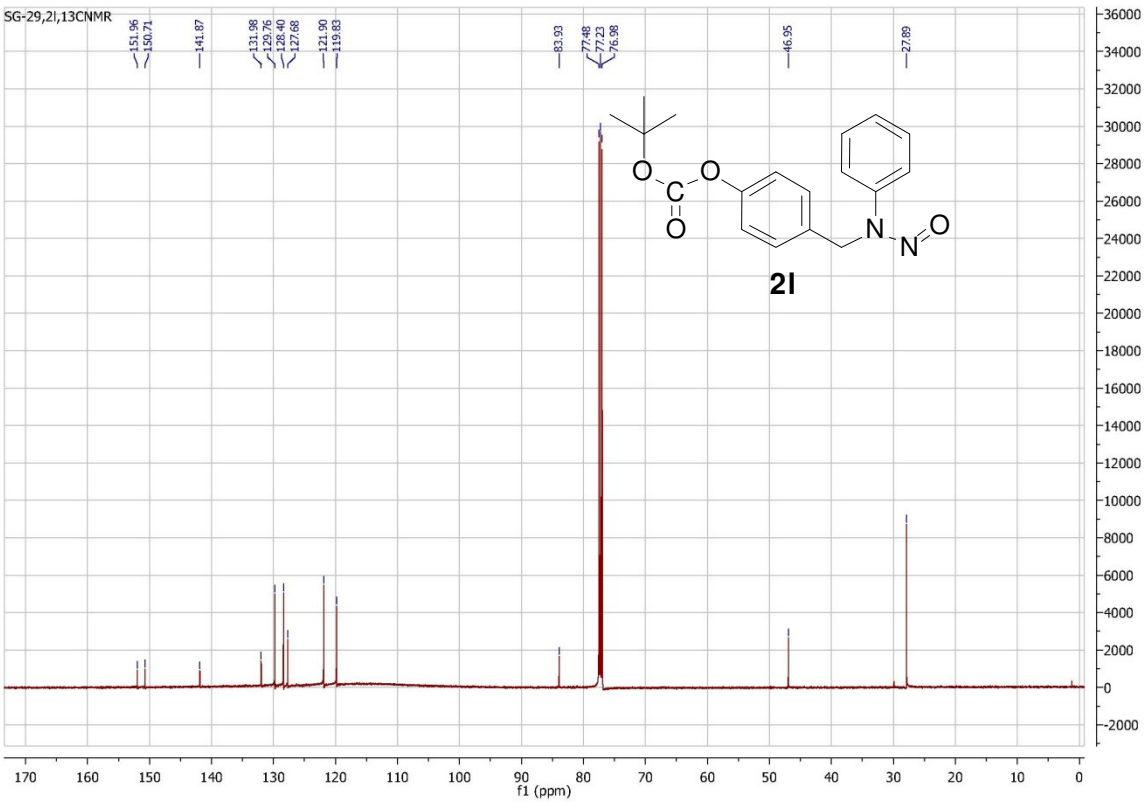
f1 (ppm)

2j


7.51
7.50
7.49
7.49
7.49
7.42
7.40
7.39
7.33
7.33
7.32
7.31
6.93
6.72
6.71
5.15
0.93
0.14
Si
O
N
N
O
2k
1.88
1.89
1.04
1.97
1.93
2.00
9.49
5.78
f1 (ppm)


155.37
142.02
129.63
128.72
127.57
127.23
120.54
120.07
77.48
77.03
76.98
47.12
25.85
18.38
-4.24
Si
O
N
N
O
2k
f1 (ppm)


7.51
7.51
7.49
7.43
7.43
7.42
7.40
7.34
7.32
7.31
7.24
7.08
5.21
1.52
1.95
1.76
1.02
3.37
2.00
9.42
2I
f1 (ppm)


SG-29,2I,13CNMR
151.96
150.71
141.87
131.98
129.76
128.40
127.68
121.90
119.83
83.93
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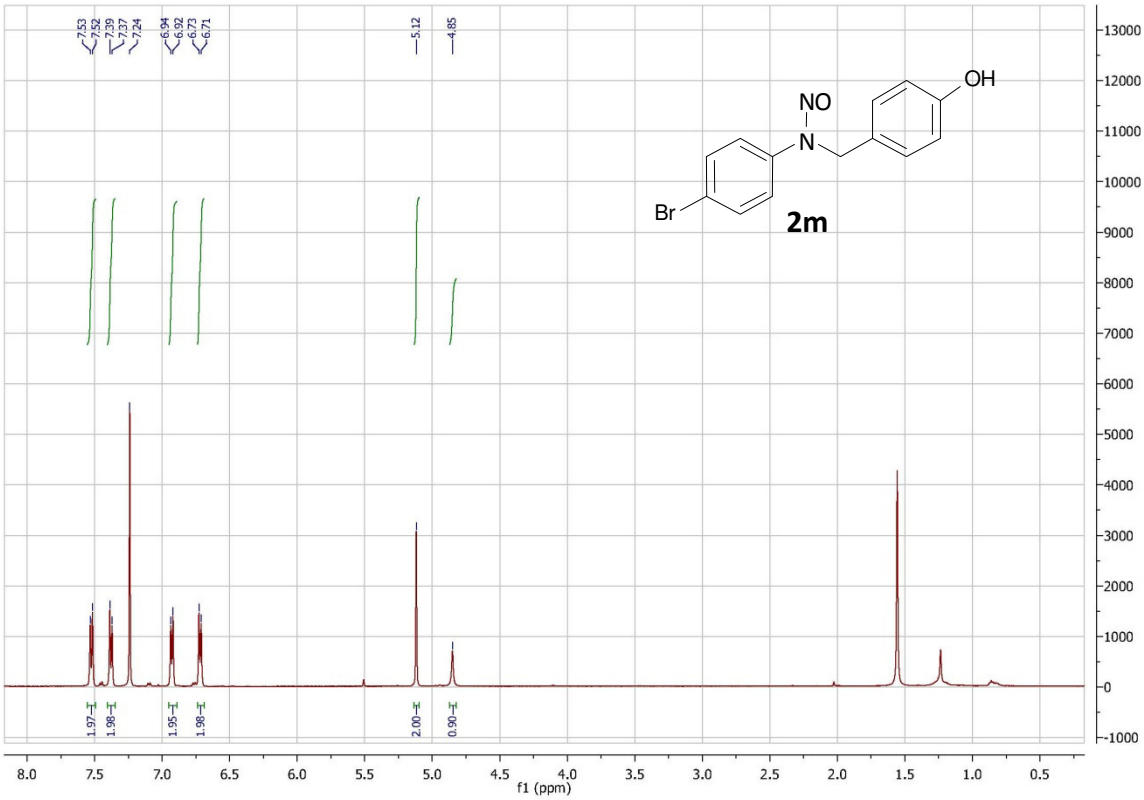
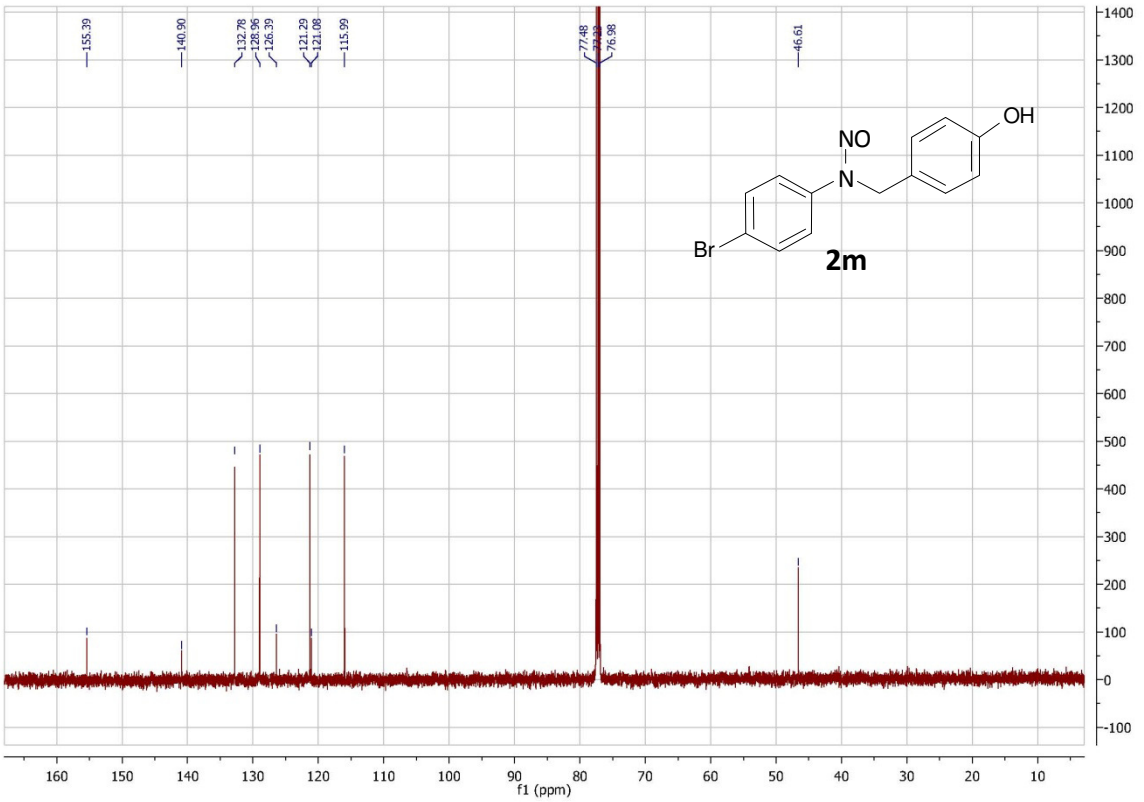
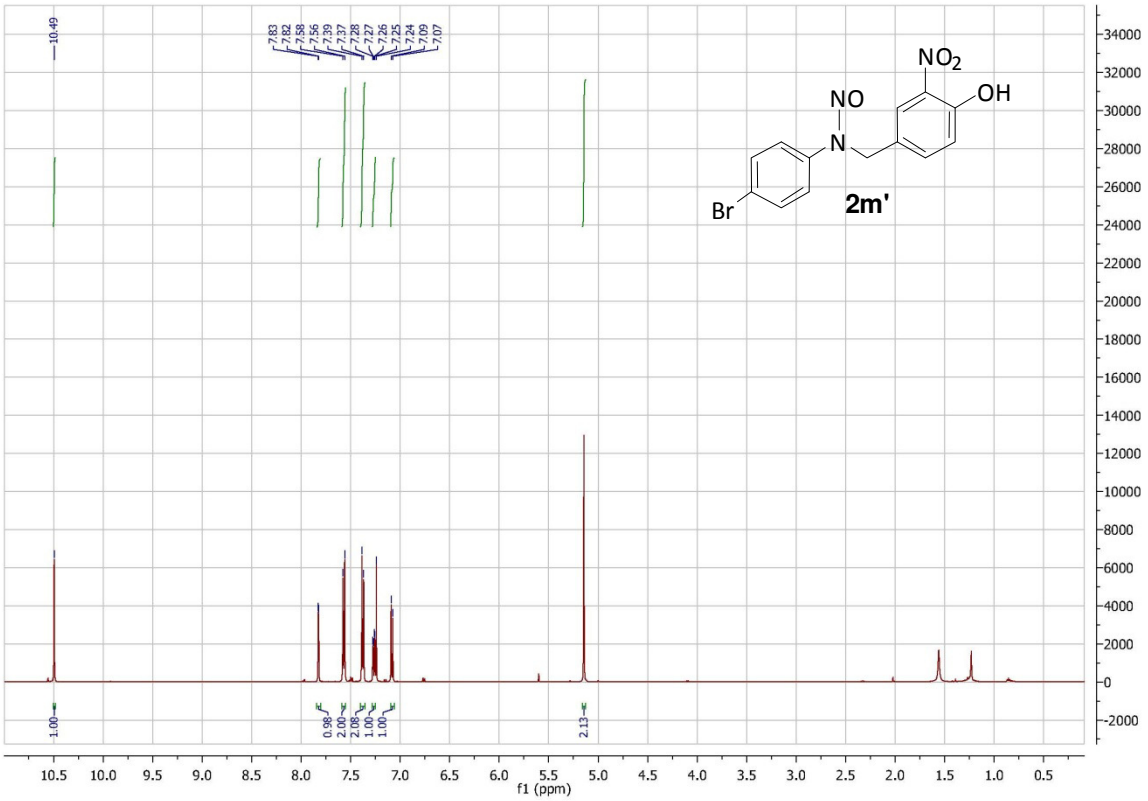
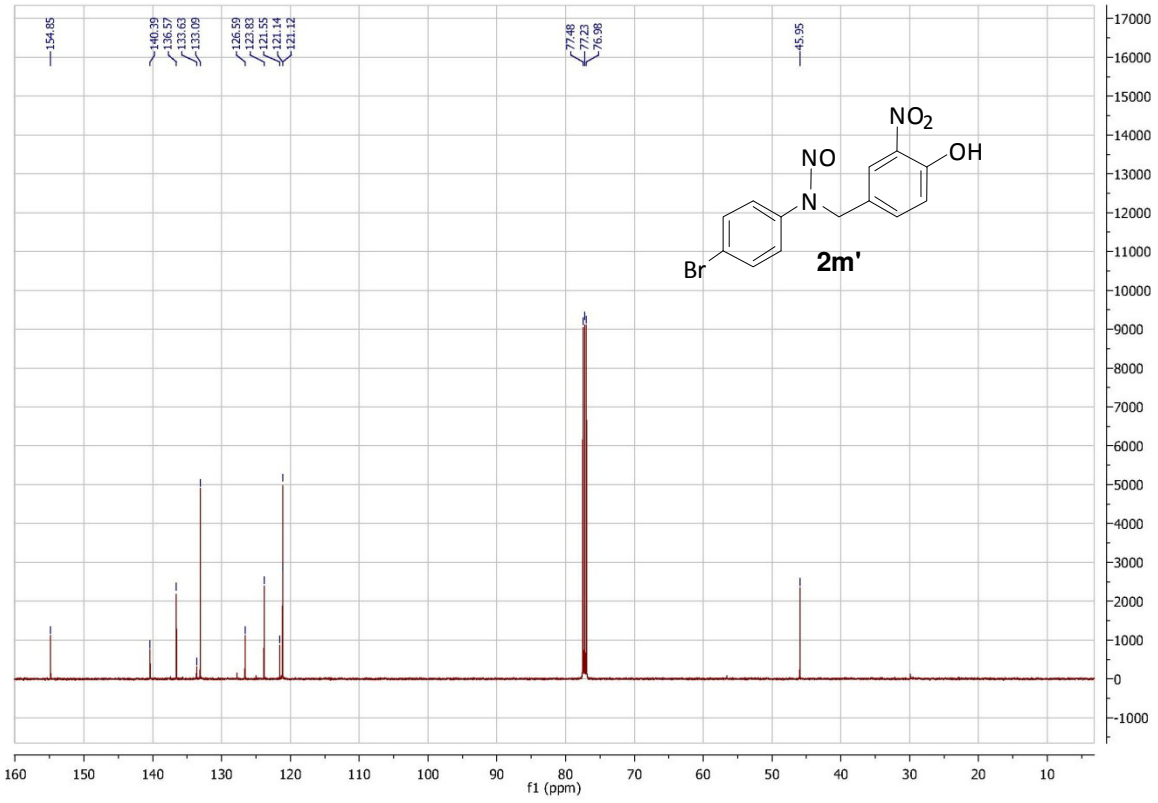
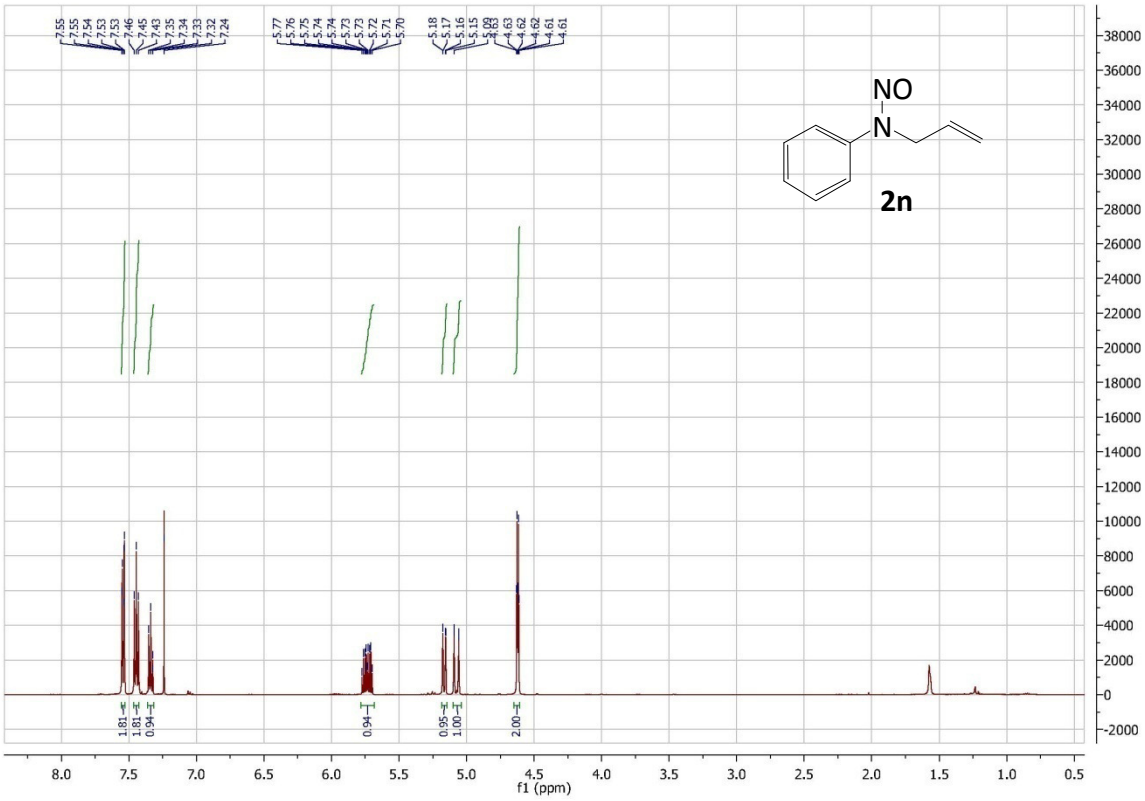
77.23
76.98
46.95
27.89
2I
f1 (ppm)

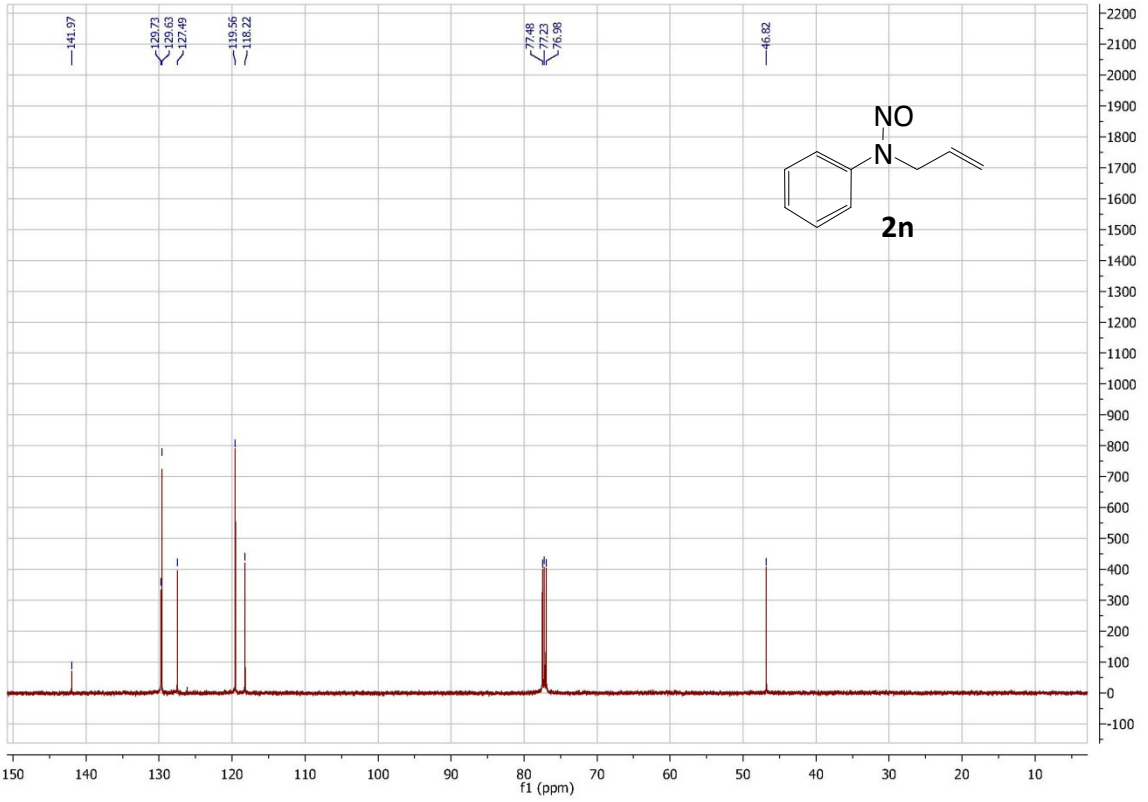

7.53
7.52
7.39
7.37
7.24
6.94
6.92
6.73
6.71
5.12
4.85
1.97
1.98
1.95
1.98
2.00
0.90
NO
N
OH
Br
2m
f1 (ppm)

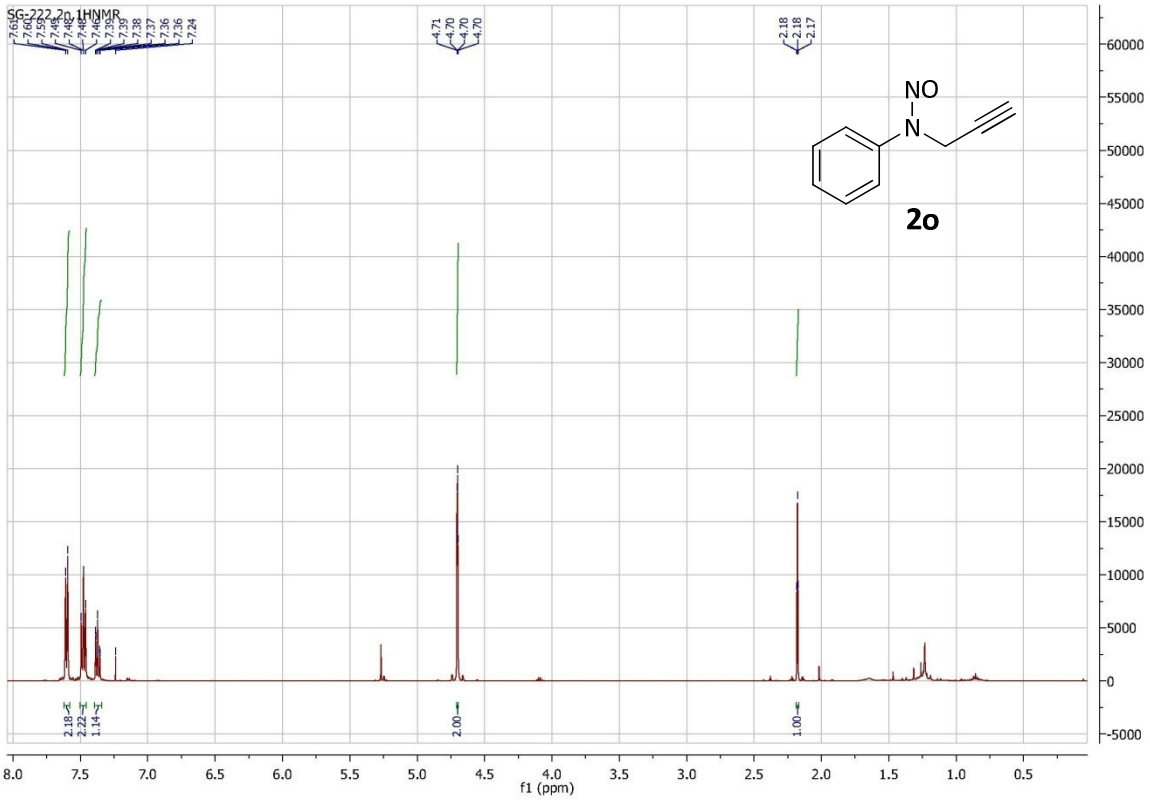

155.39
140.90
132.78
128.96
126.39
121.29
121.08
115.99
77.48
77.23
76.98
46.61
NO
N
OH
Br
2m
f1 (ppm)

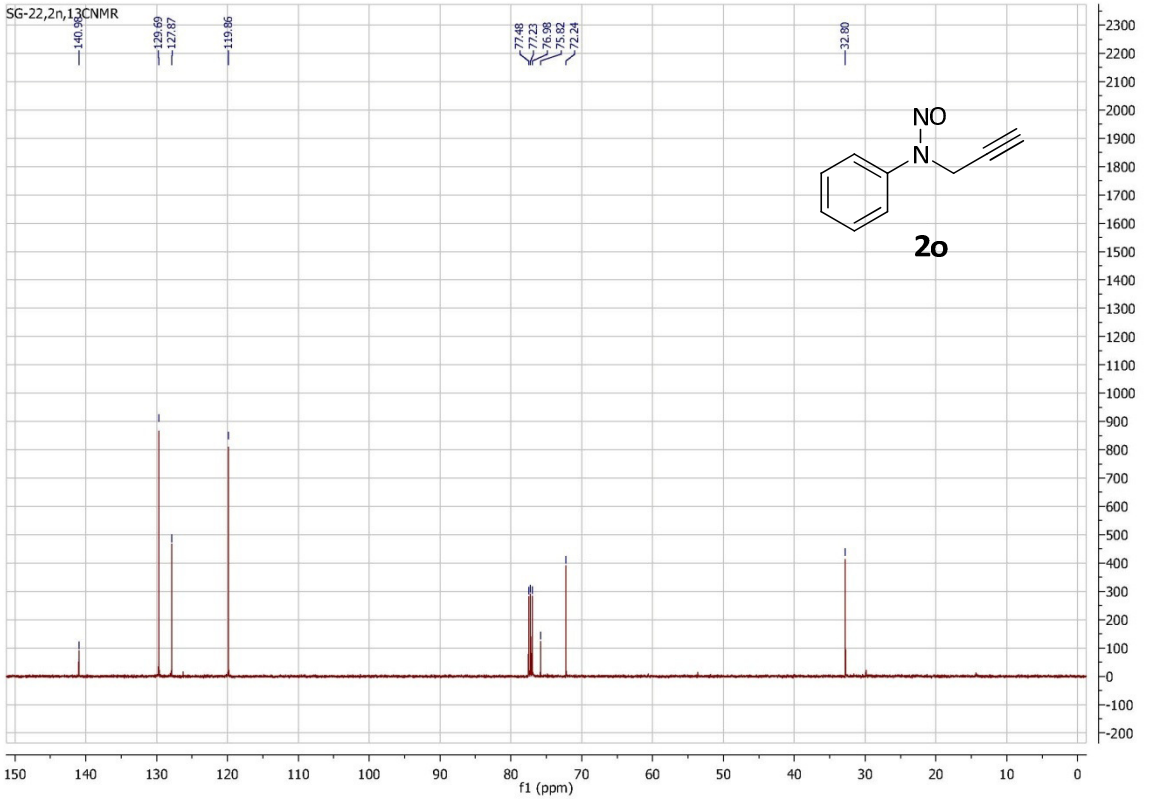

10.49
7.83
7.82
7.58
7.56
7.39
7.37
7.28
7.27
7.26
7.25
7.24
7.09
7.07
NO2
OH
NO
N
Br
2m'
1.00
0.98
2.00
2.08
1.00
1.00
2.13
f1 (ppm)

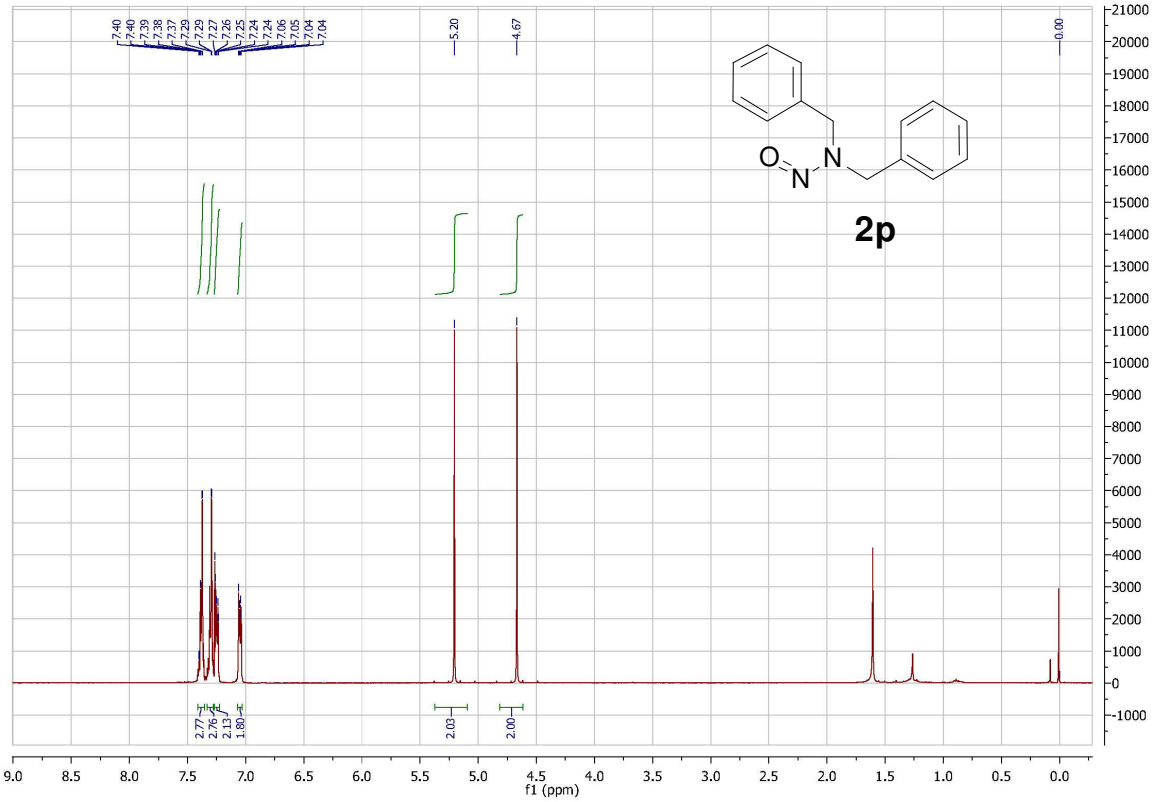

154.85
140.39
136.57
133.63
133.09
126.59
123.83
121.55
121.14
121.12
77.48
77.23
76.98
45.95
NO2
OH
NO
N
Br
2m'
f1 (ppm)


7.55
7.55
7.54
7.53
7.53
7.46
7.45
7.43
7.35
7.34
7.33
7.32
7.24
5.77
5.76
5.75
5.74
5.74
5.73
5.73
5.72
5.71
5.70
5.18
5.17
5.16
5.15
5.09
4.63
4.62
4.62
4.61
4.61
NO
N
2n
1.81
1.81
0.94
0.94
0.95
1.00
2.00
f1 (ppm)


141.97
129.73
129.63
127.49
119.56
118.22
77.48
77.23
76.98
46.82
NO
N
2n
f1 (ppm)


SG-222,2n,1HNMR
NO
N
2o
f1 (ppm)


SG-22,2n,13CNMR
NO
N
2o
f1 (ppm)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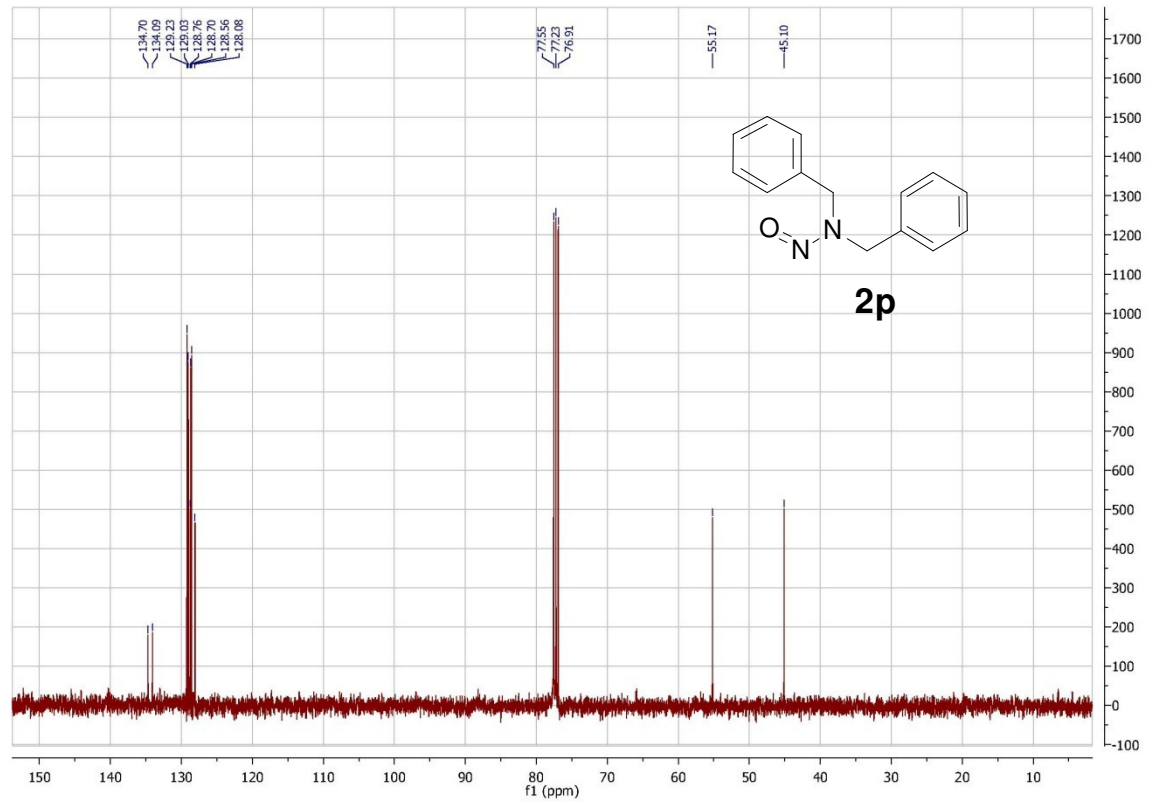
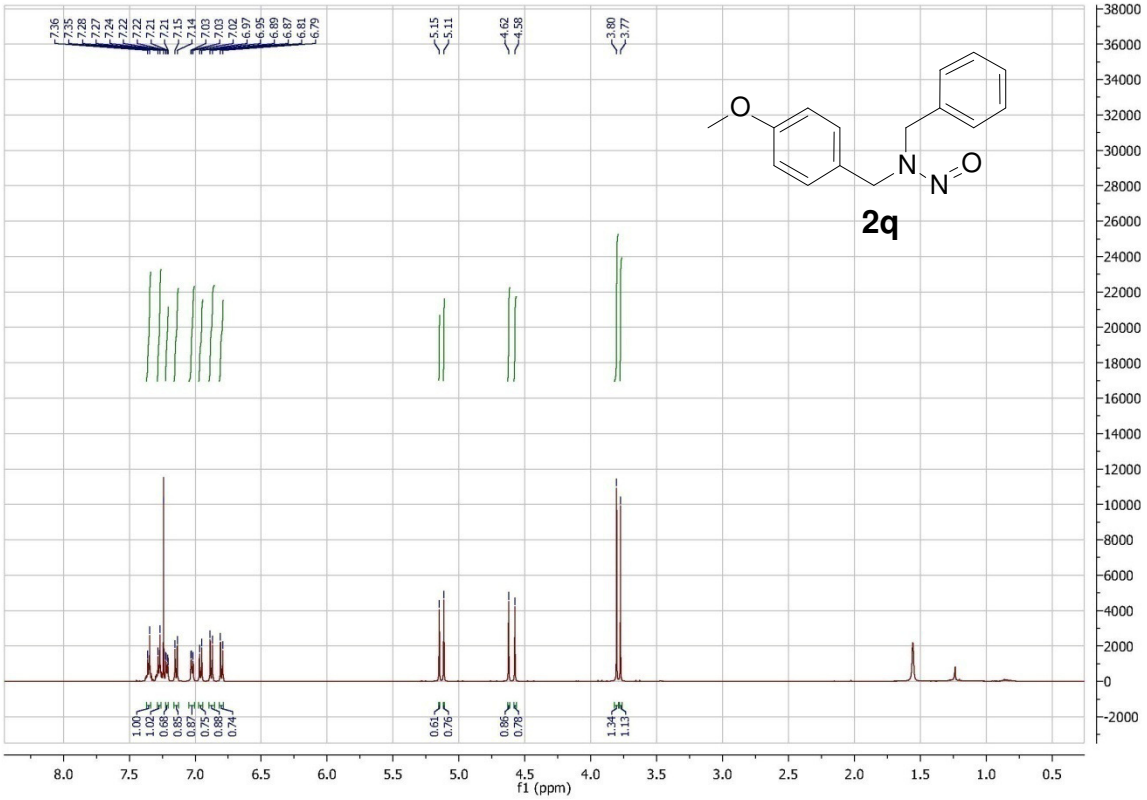
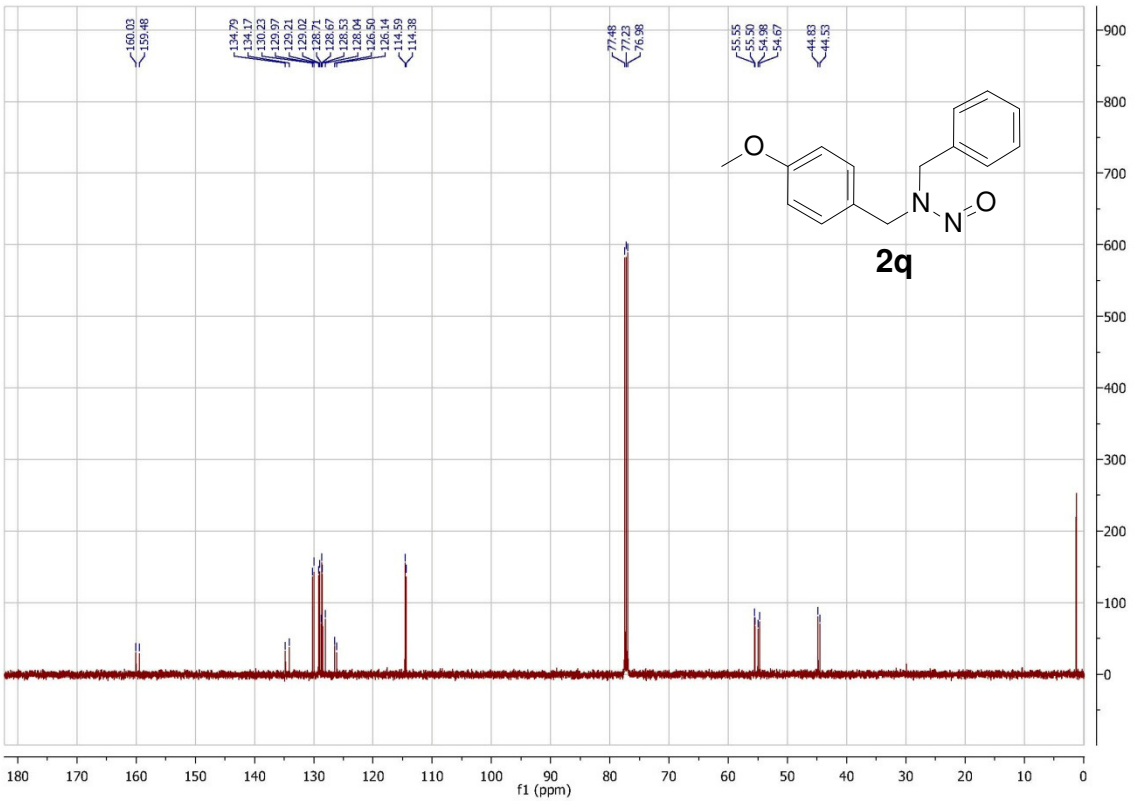
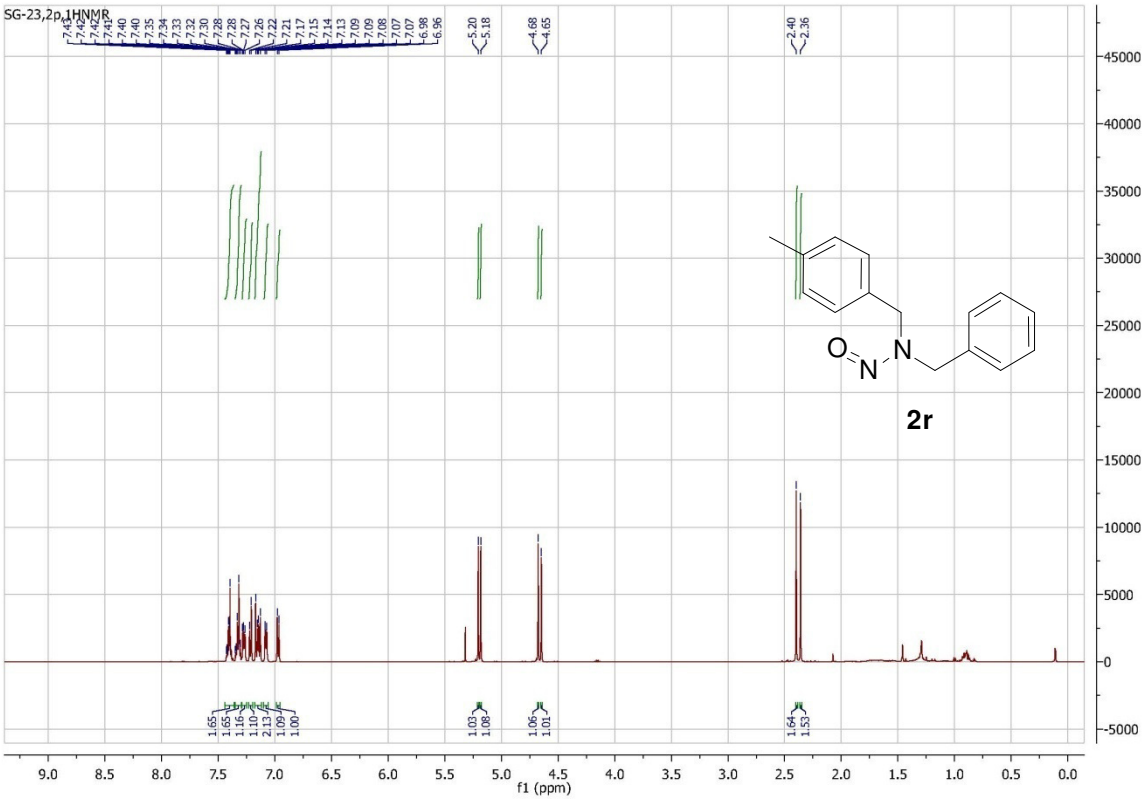
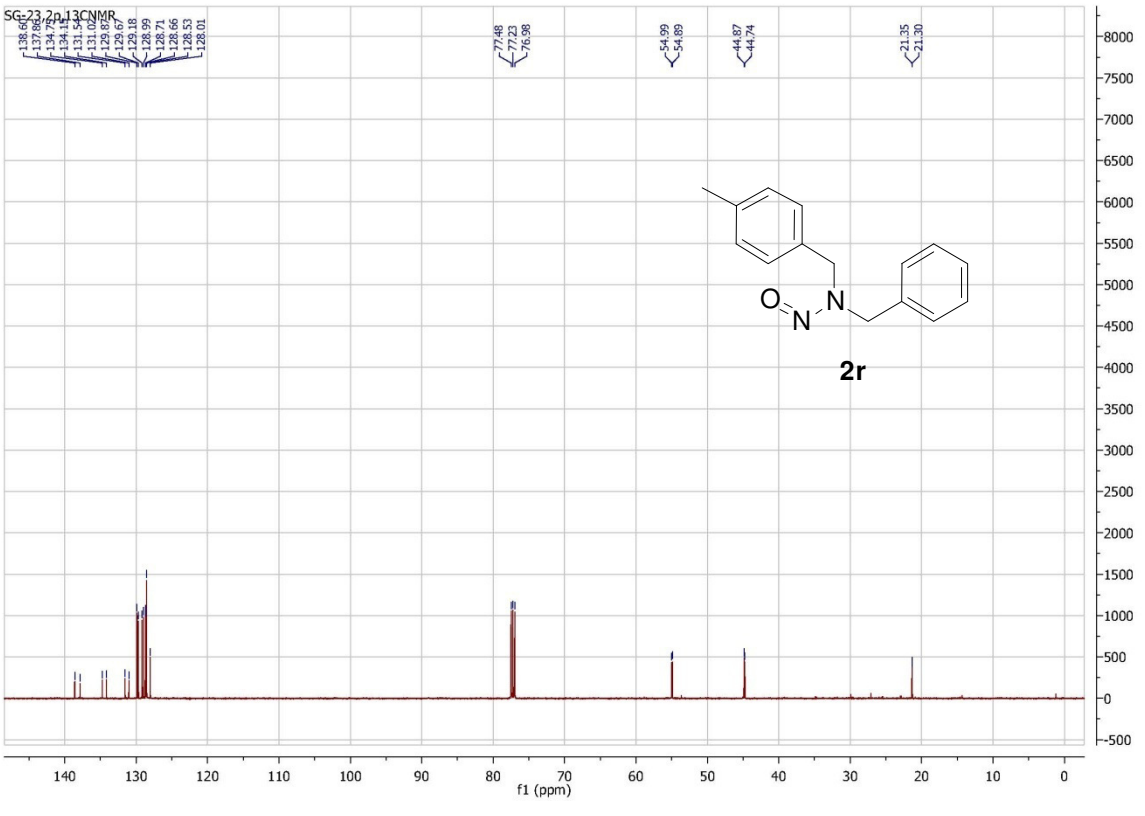
7.40
7.39
7.38
7.37
7.29
7.29
7.27
7.26
7.25
7.24
7.24
7.06
7.05
7.04
7.04
5.20
4.67
0.00
2.77
2.76
2.13
1.80
2.03
2.00
O
N
N
2p
f1 (ppm)

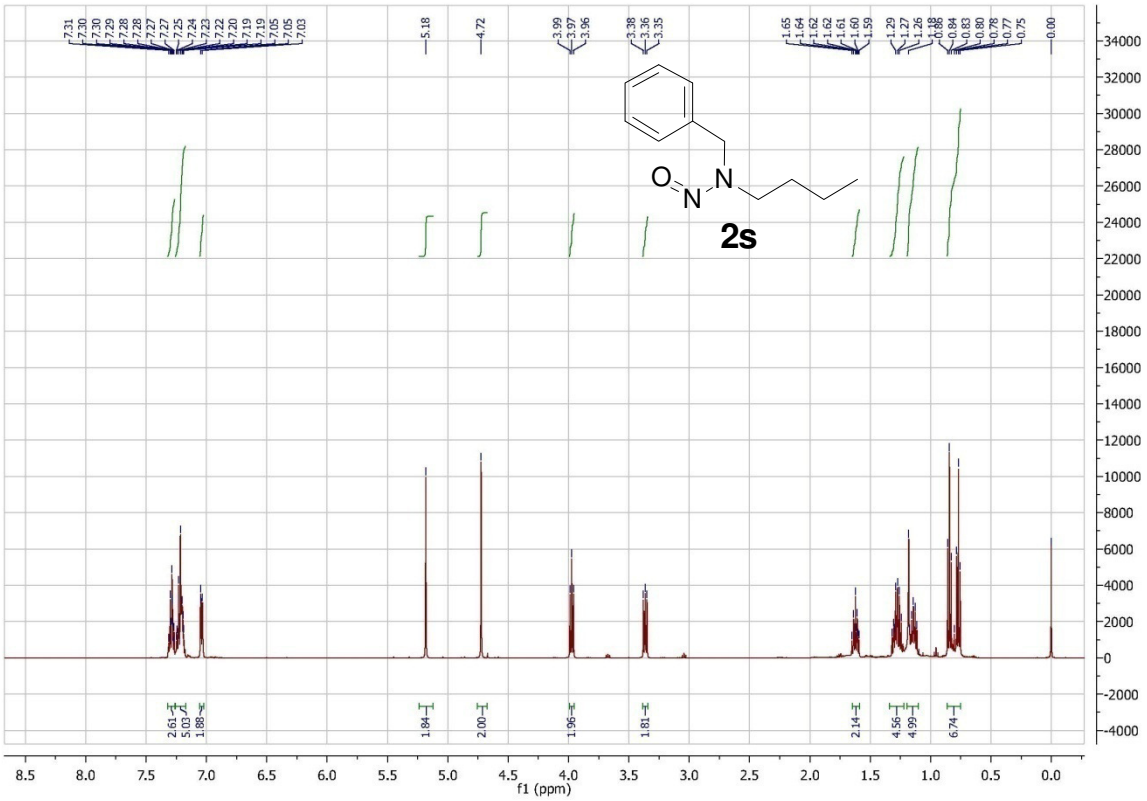

134.70
134.09
129.23
129.03
128.76
128.70
128.56
128.08
77.55
77.23
76.91
55.17
45.10
O
N
N
2p
f1 (ppm)

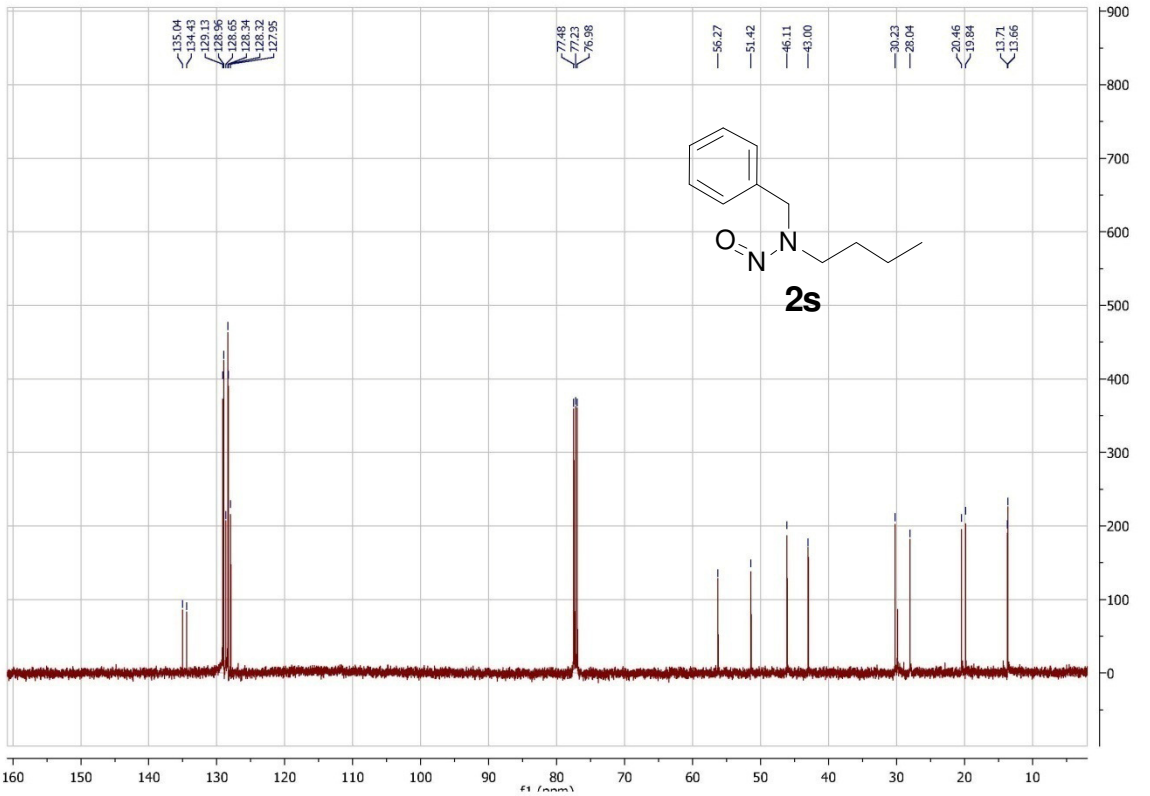

7.36
7.35
7.28
7.27
7.24
7.22
7.22
7.21
7.21
7.15
7.14
7.03
7.03
7.02
6.97
6.95
6.89
6.87
6.81
6.79
5.15
5.11
4.62
4.58
3.80
3.77
O
N
N
O
2q
1.00
1.02
0.68
0.85
0.87
0.75
0.88
0.74
0.61
0.76
0.86
0.78
1.34
1.13
f1 (ppm)

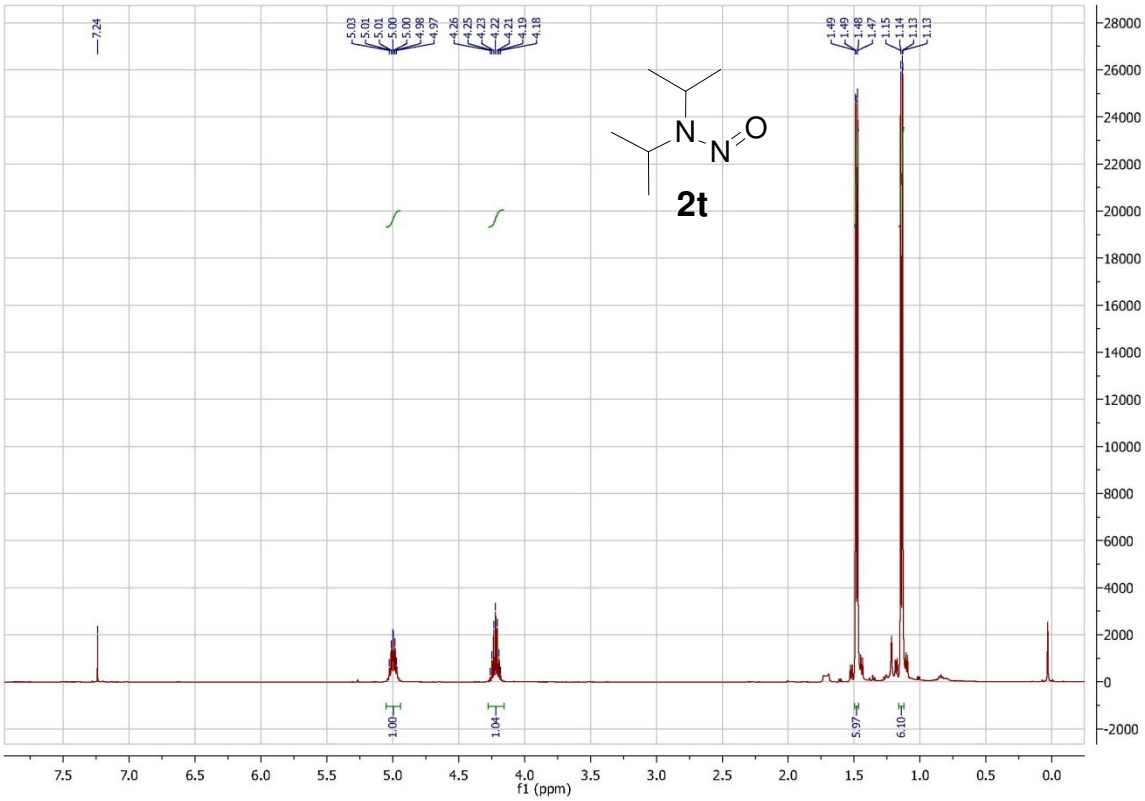

160.03
159.48
134.79
134.17
130.23
129.97
129.21
129.02
128.71
128.67
128.53
128.04
126.50
126.14
114.59
114.38
77.48
77.23
76.98
55.55
55.50
54.98
54.67
44.83
44.53
O
N
N
O
2q
f1 (ppm)

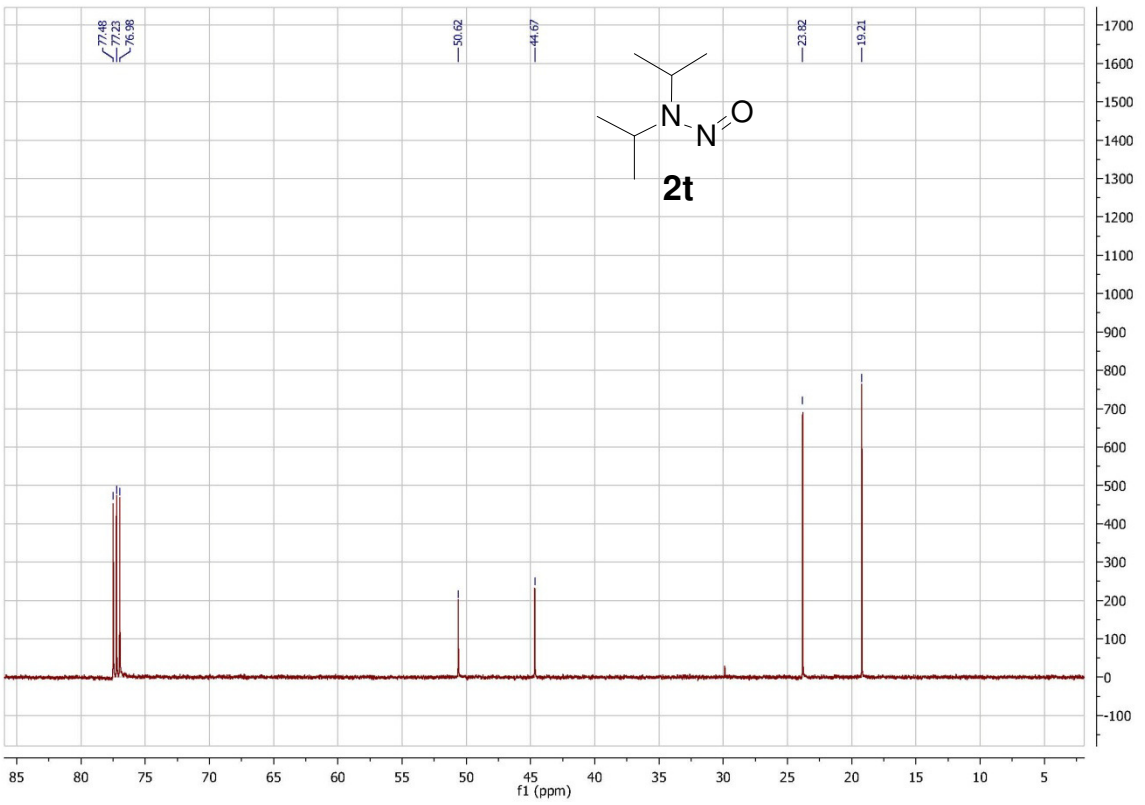

SG-23,2p,1HNMR
2r
f1 (ppm)

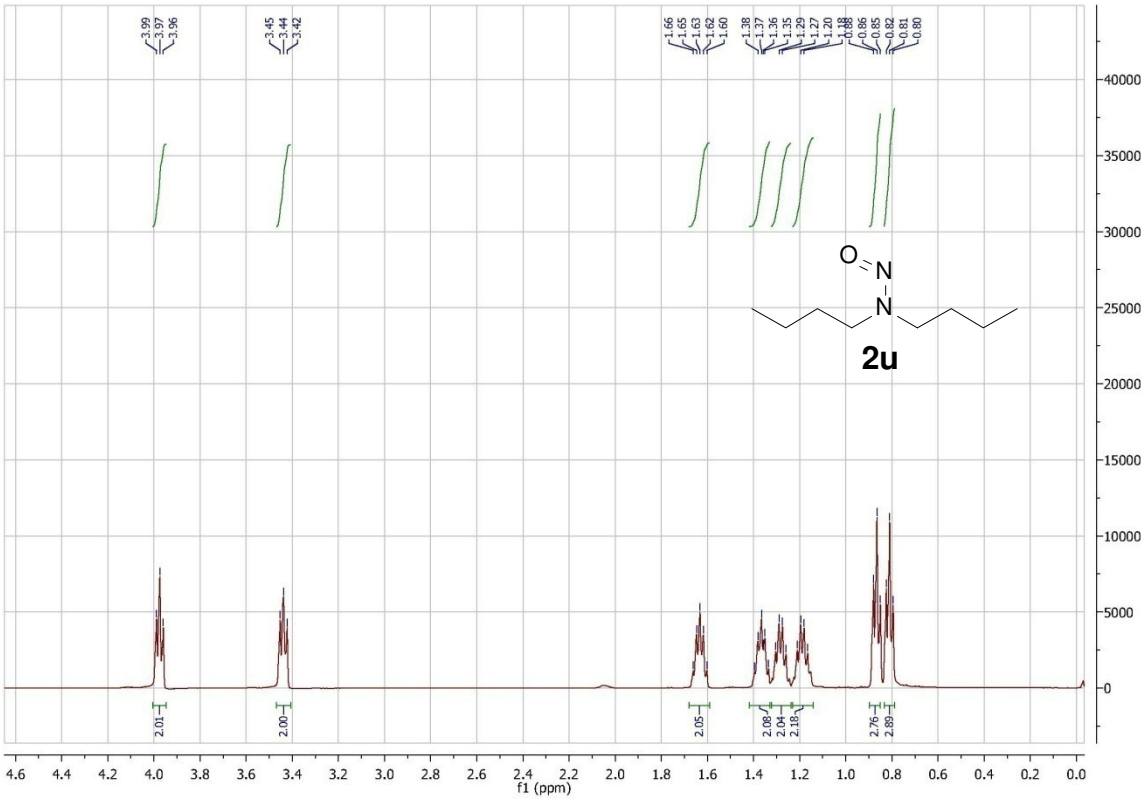

SG-23,2p,13CNMR
2r
f1 (ppm)

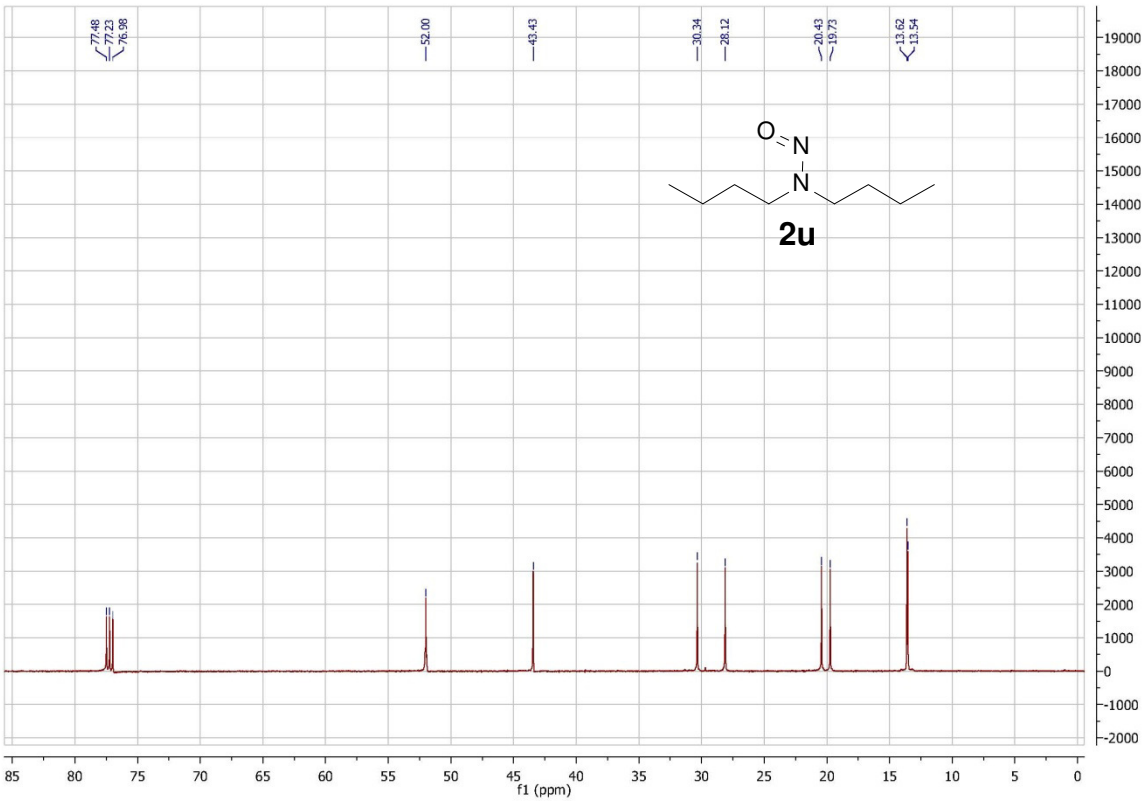

7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.27
7.25
7.24
7.23
7.22
7.20
7.19
7.19
7.05
7.05
7.03
5.18
4.72
3.99
3.97
3.96
3.38
3.36
3.35
1.65
1.64
1.62
1.62
1.61
1.60
1.59
1.29
1.27
1.26
0.94
0.83
0.80
0.78
0.77
0.75
0.00
2s
2.61
5.03
1.88
1.84
2.00
1.96
1.81
2.14
4.56
4.99
6.74
f1 (ppm)

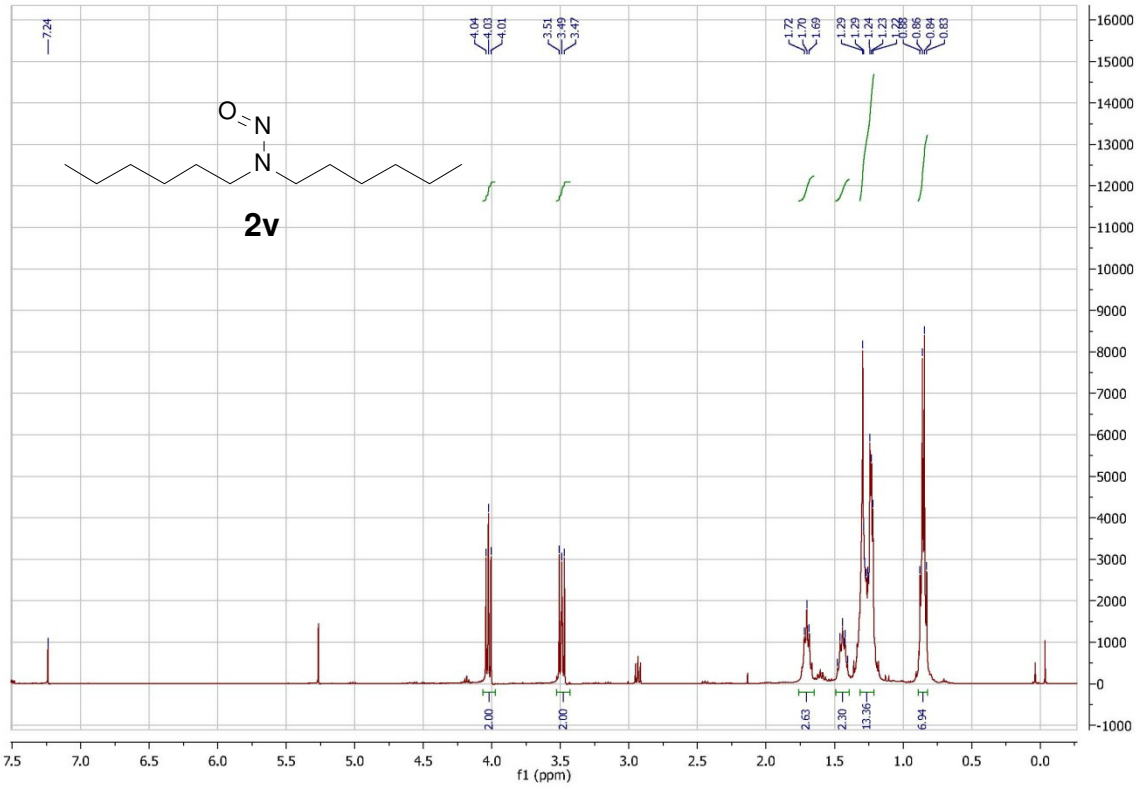

135.04
134.43
129.13
128.96
128.65
128.34
128.32
127.95
77.48
77.23
76.98
56.27
51.42
46.11
43.00
30.23
28.04
20.46
19.84
13.71
13.66
2s

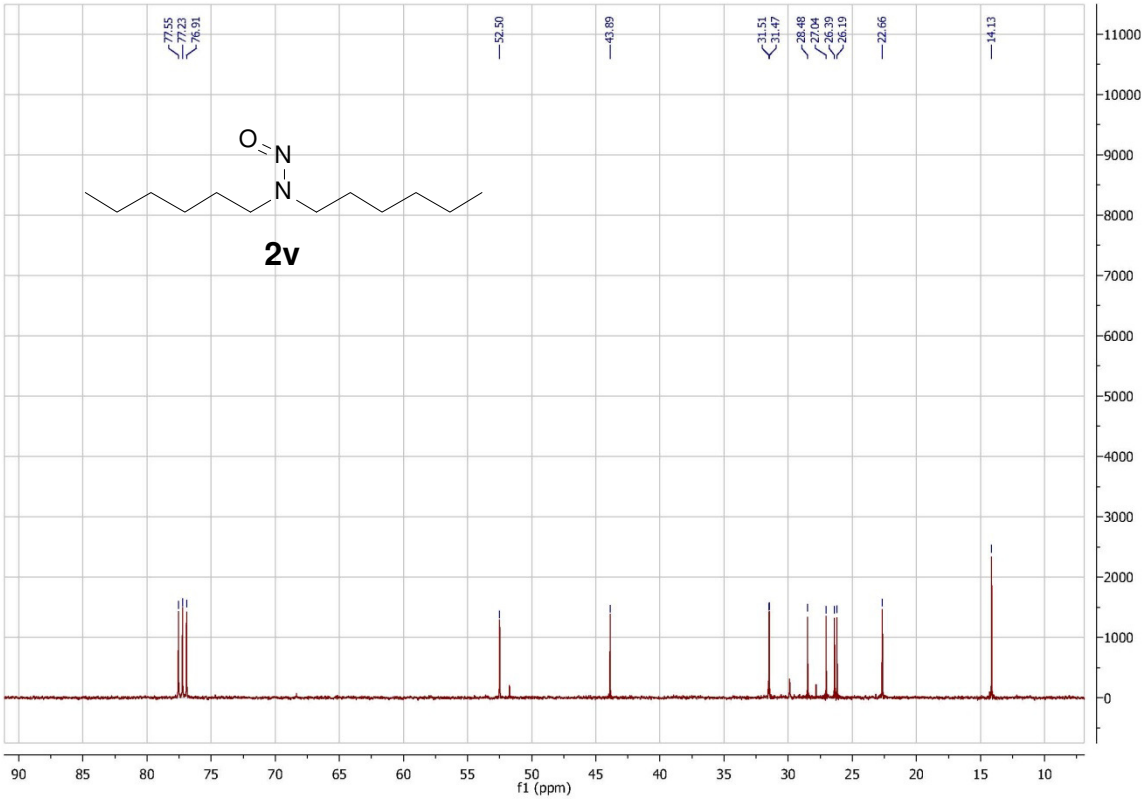

7.24
5.03
5.01
5.01
5.00
5.00
4.98
4.97
4.26
4.25
4.23
4.22
4.21
4.19
4.18
1.49
1.49
1.48
1.47
1.15
1.14
1.13
1.13
N
N
O
2t
1.00
1.04
5.97
6.10
f1 (ppm)

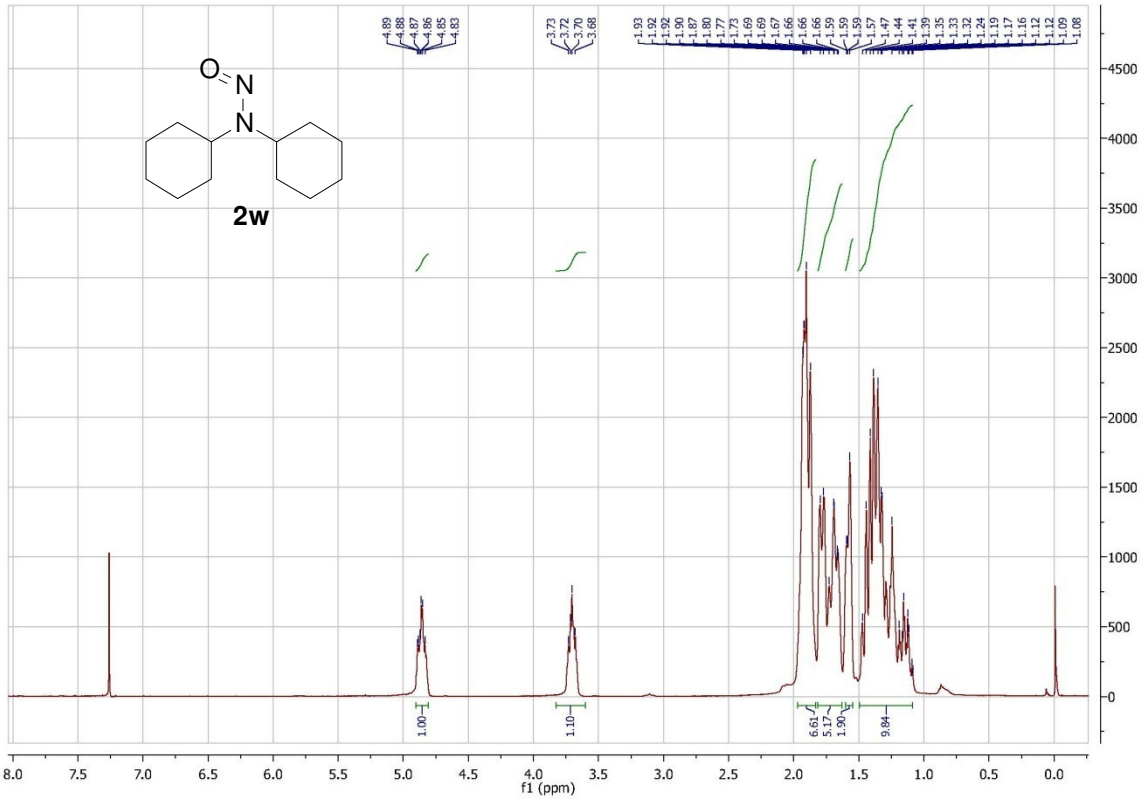

77.48
77.23
76.98
50.62
44.67
23.82
19.21
N
N
O
2t
f1 (ppm)

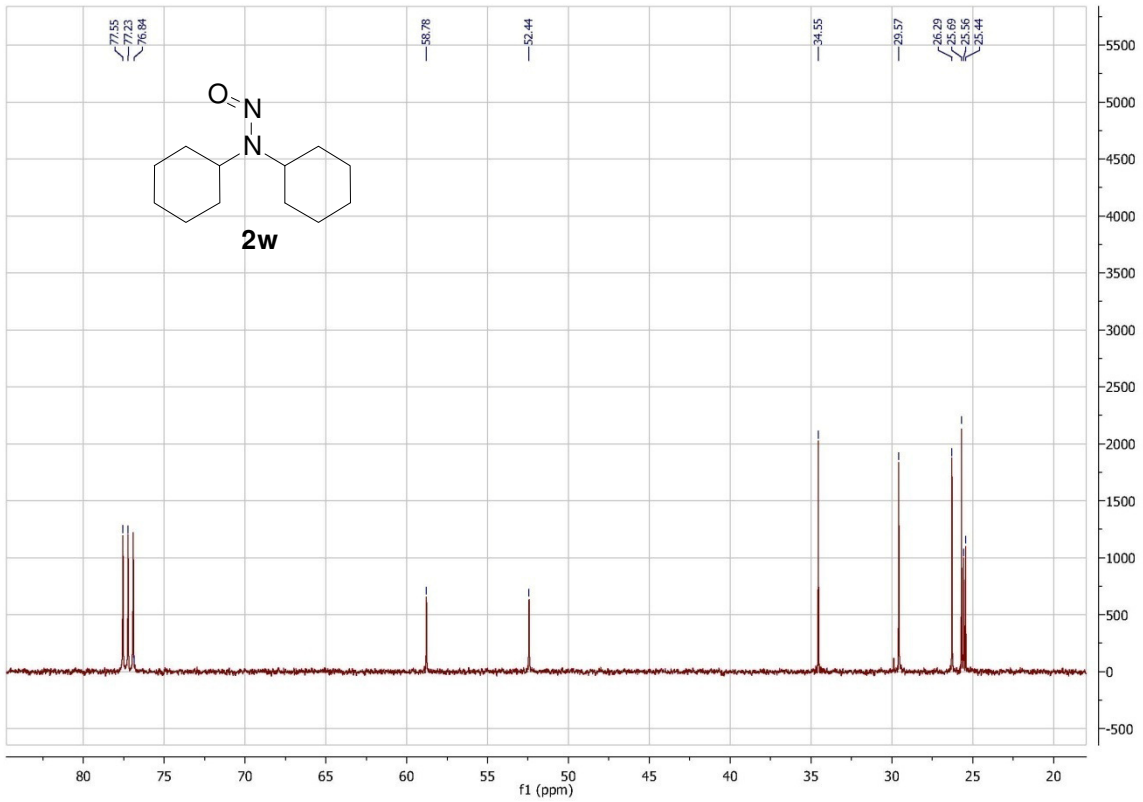

3.99
3.97
3.96
3.45
3.44
3.42
1.66
1.65
1.63
1.62
1.60
1.38
1.37
1.36
1.35
1.29
1.27
1.20
0.88
0.86
0.85
0.82
0.81
0.80
O
N
N
2u
2.01
2.00
2.05
2.08
2.04
2.18
2.76
2.89
f1 (ppm)

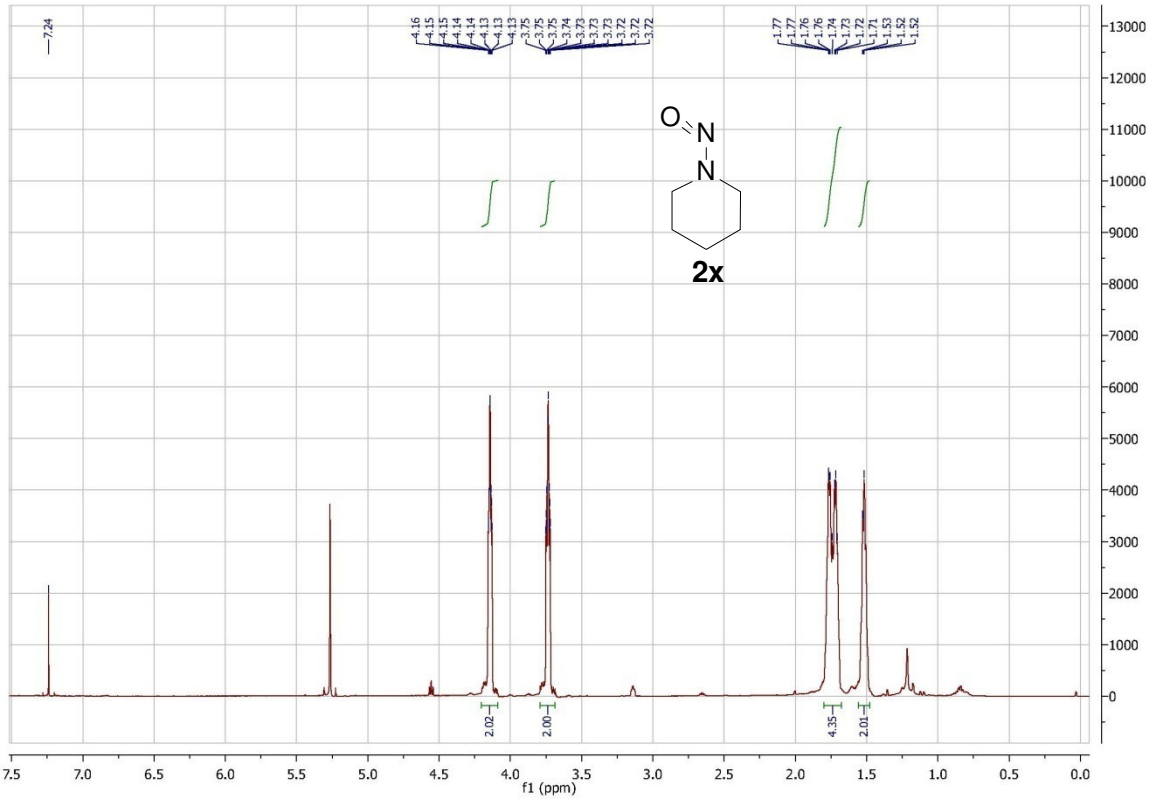

77.48
77.23
76.98
52.00
43.43
30.34
28.12
20.43
19.73
13.62
13.54
O
N
N
2u
f1 (ppm)

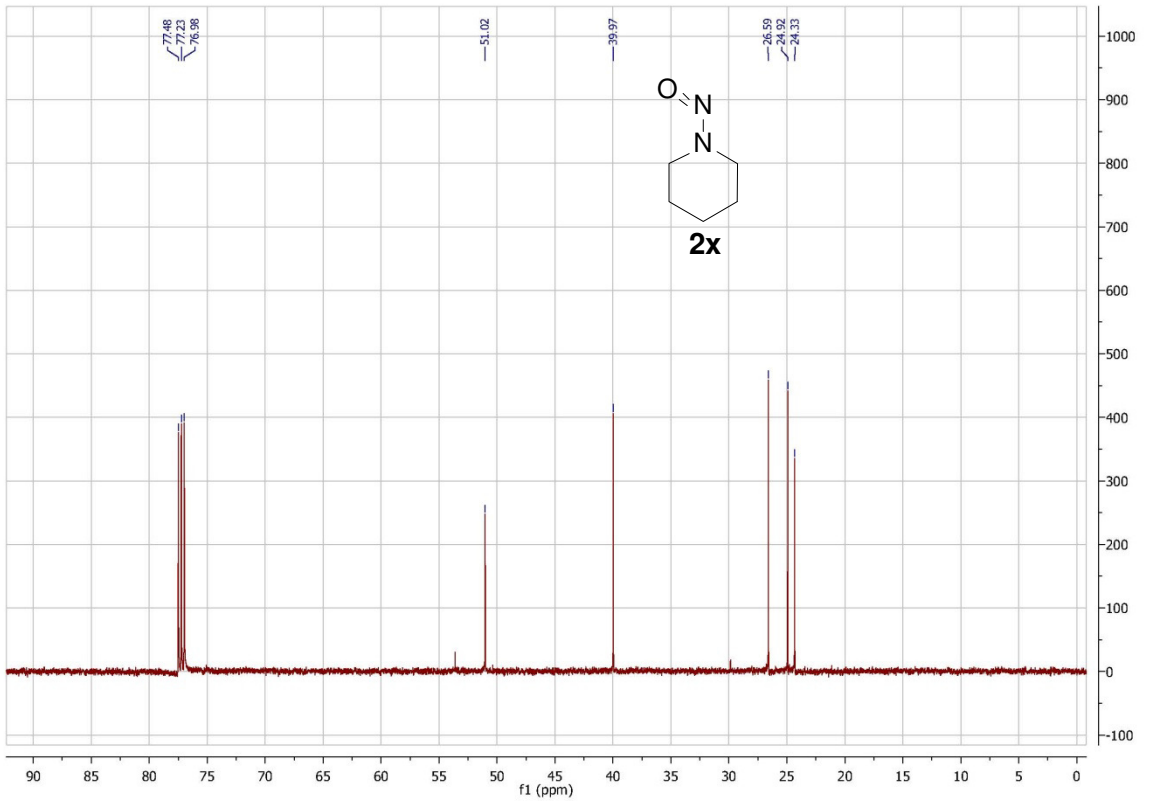

7.24
4.04
4.03
4.01
3.51
3.49
3.47
1.72
1.70
1.69
1.29
1.29
1.24
1.23
1.22
0.88
0.86
0.84
0.83
O
N
N
2v
2.00
2.00
2.63
2.30
13.36
6.94
f1 (ppm)

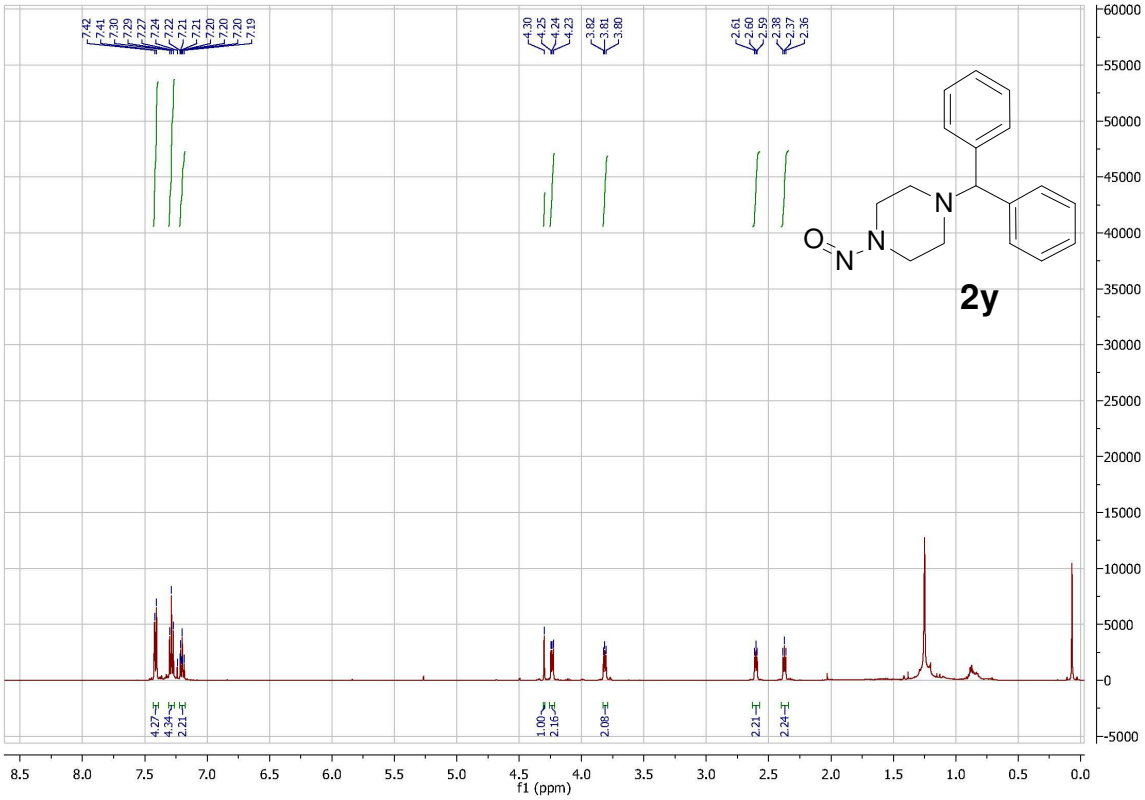

77.55
77.23
76.91
52.50
43.89
31.51
31.47
28.48
27.04
26.39
26.19
22.66
14.13
O
N
N
2v
f1 (ppm)

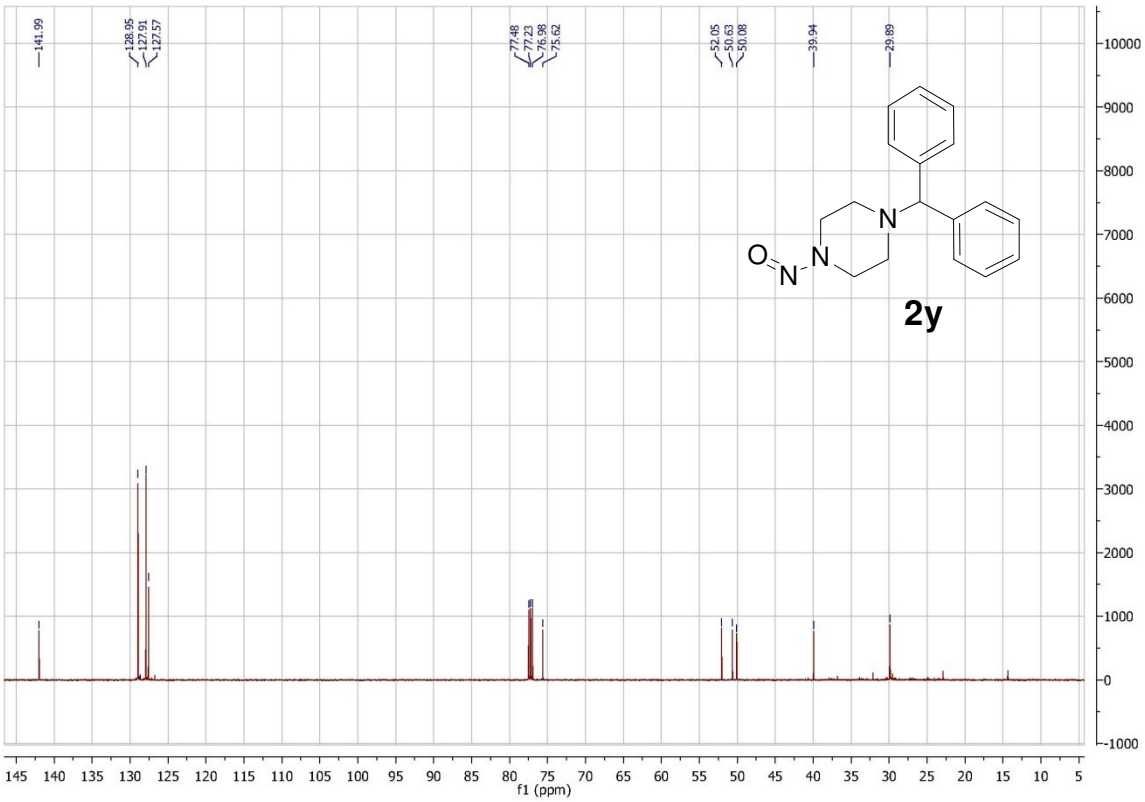

4.89
4.88
4.87
4.86
4.85
4.83
3.73
3.72
3.70
3.68
1.93
1.92
1.92
1.90
1.87
1.80
1.77
1.73
1.69
1.69
1.67
1.66
1.66
1.66
1.59
1.59
1.59
1.57
1.47
1.44
1.41
1.39
1.35
1.33
1.32
1.24
1.19
1.17
1.16
1.12
1.12
1.09
1.08
O
N
N
2w
1.00
1.10
6.61
5.17
1.90
9.84
f1 (ppm)

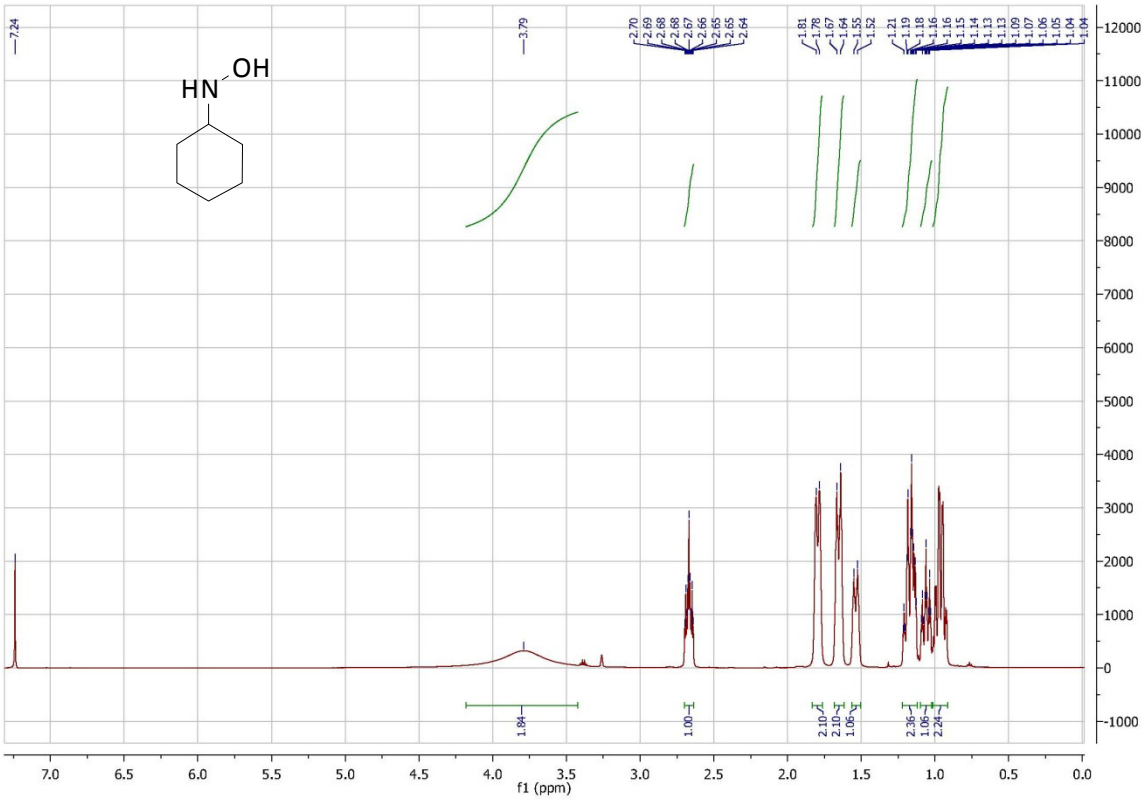

77.55
77.23
76.84
58.78
52.44
34.55
29.57
26.29
25.69
25.56
25.44
O
N
N
2w
f1 (ppm)

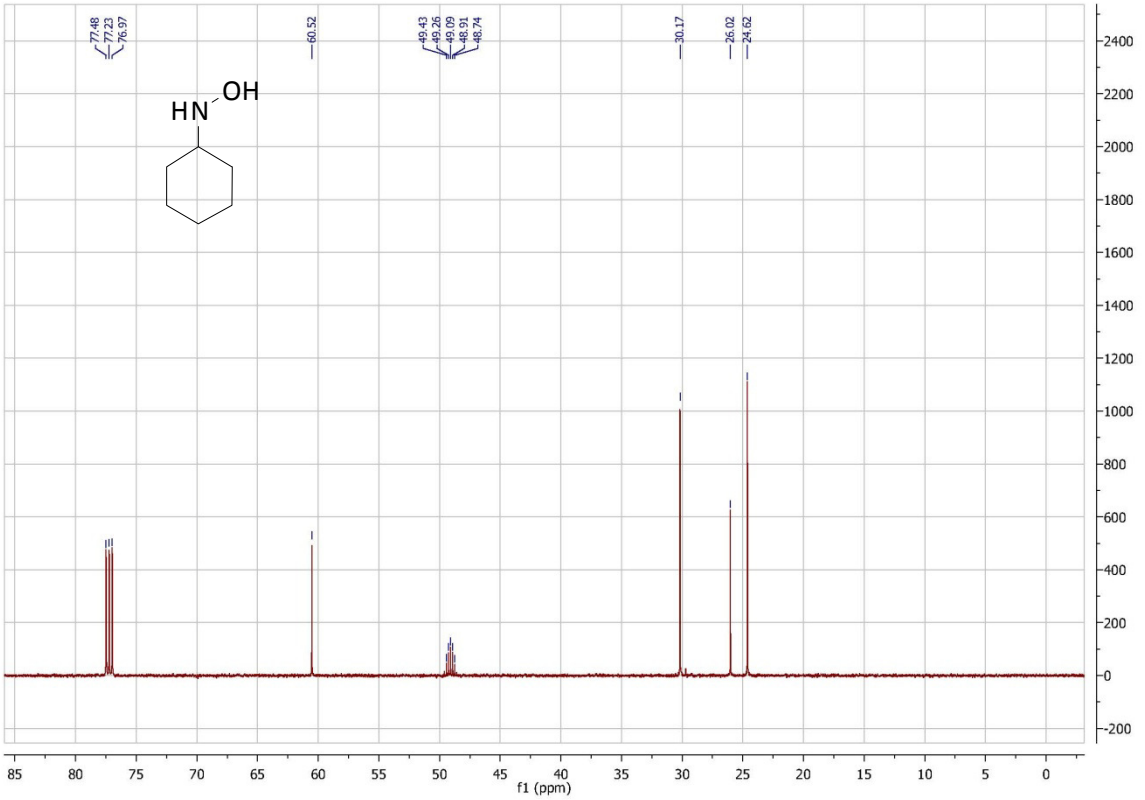

7.24
4.16
4.15
4.15
4.14
4.14
4.13
4.13
3.75
3.75
3.74
3.74
3.73
3.73
3.72
3.72
3.72
1.77
1.77
1.76
1.76
1.74
1.72
1.71
1.53
1.52
1.52
O
N
N
2x
2.02
2.00
4.35
2.01
f1 (ppm)

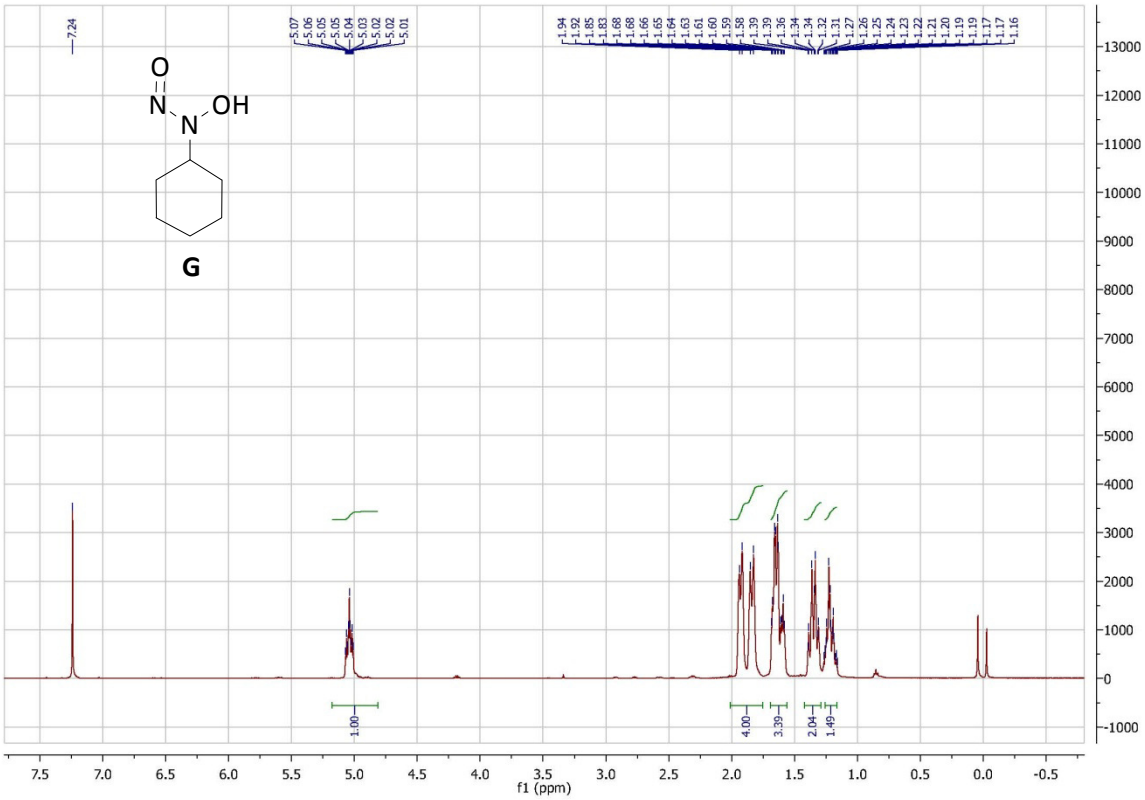

77.48
77.23
76.98
51.02
39.97
26.59
24.92
24.33
O
N
N
2x
f1 (ppm)


7.42
7.41
7.30
7.29
7.23
7.24
7.22
7.21
7.21
7.20
7.20
7.20
7.19
4.30
4.25
4.24
4.23
3.82
3.81
3.80
2.61
2.60
2.59
2.38
2.37
2.36
4.27
4.34
2.21
1.00
2.16
2.08
2.21
2.24
f1 (ppm)
2y

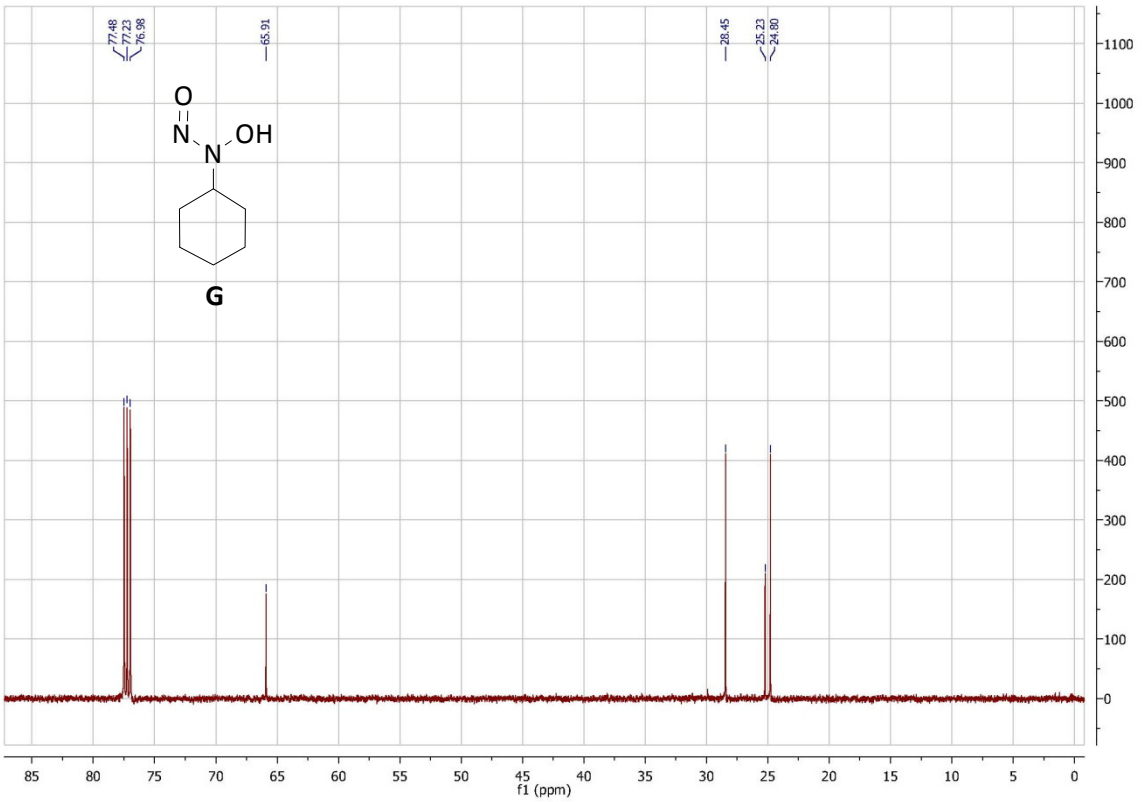

141.99
128.95
127.91
127.71
127.57
77.48
77.23
76.98
75.62
52.05
50.63
50.08
39.94
29.89
f1 (ppm)
2y


HN
OH
7.24
3.79
2.70
2.69
2.68
2.68
2.67
2.66
2.65
2.65
2.64
1.81
1.78
1.67
1.64
1.55
1.52
1.21
1.19
1.18
1.16
1.16
1.15
1.14
1.13
1.13
1.09
1.07
1.06
1.05
1.04
1.04
1.04
1.00
2.10
2.10
1.06
2.36
1.06
2.24
f1 (ppm)

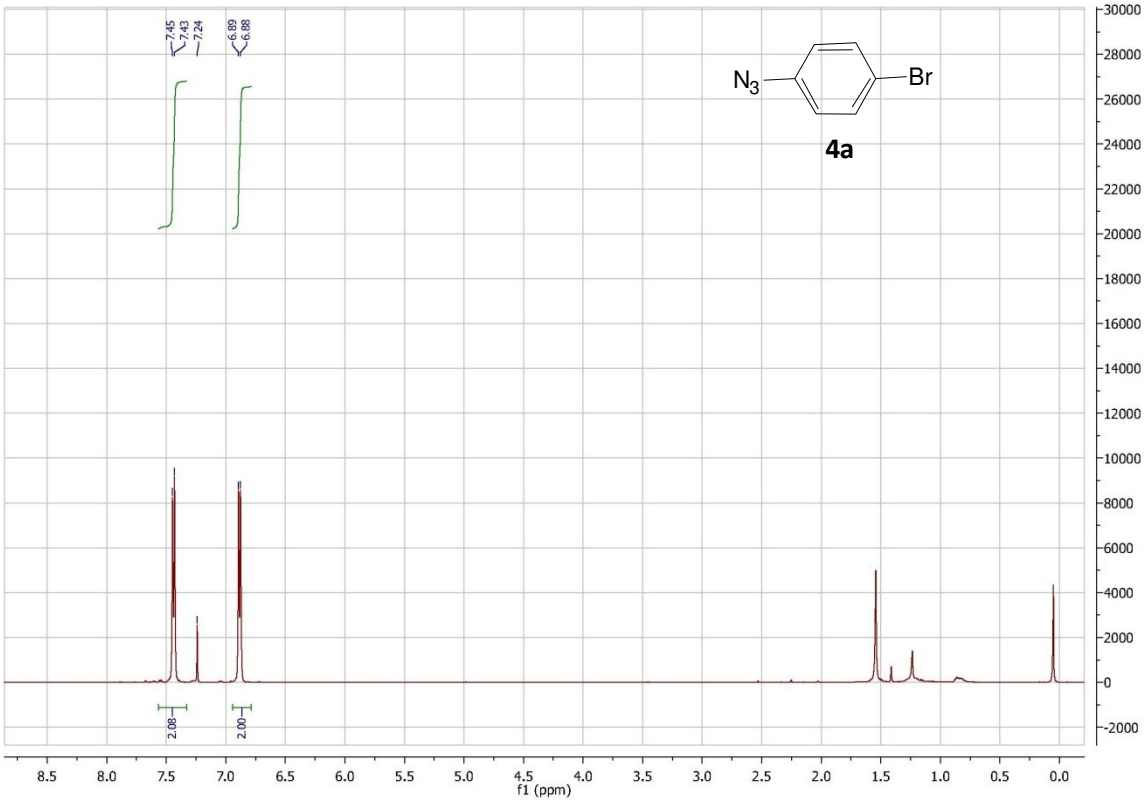

HN
OH
77.48
77.23
76.97
60.52
49.43
49.26
49.09
48.91
48.74
30.17
26.02
24.62
f1 (ppm)

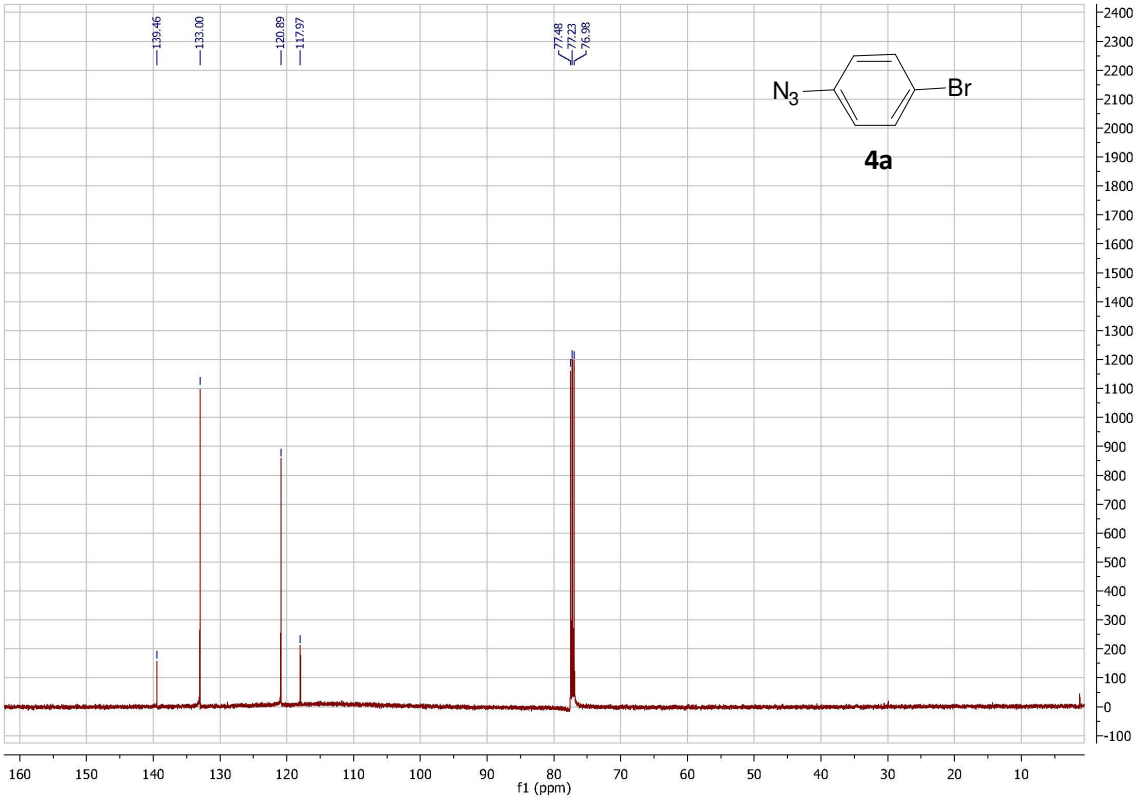

7.24
5.07
5.06
5.05
5.05
5.04
5.03
5.02
5.02
5.01
1.94
1.92
1.85
1.83
1.68
1.68
1.66
1.65
1.64
1.63
1.61
1.60
1.59
1.58
1.39
1.36
1.34
1.34
1.32
1.31
1.27
1.26
1.25
1.24
1.23
1.22
1.21
1.20
1.19
1.19
1.17
1.17
1.16
O
N
N
OH
1.00
4.00
3.39
2.04
1.49
f1 (ppm)

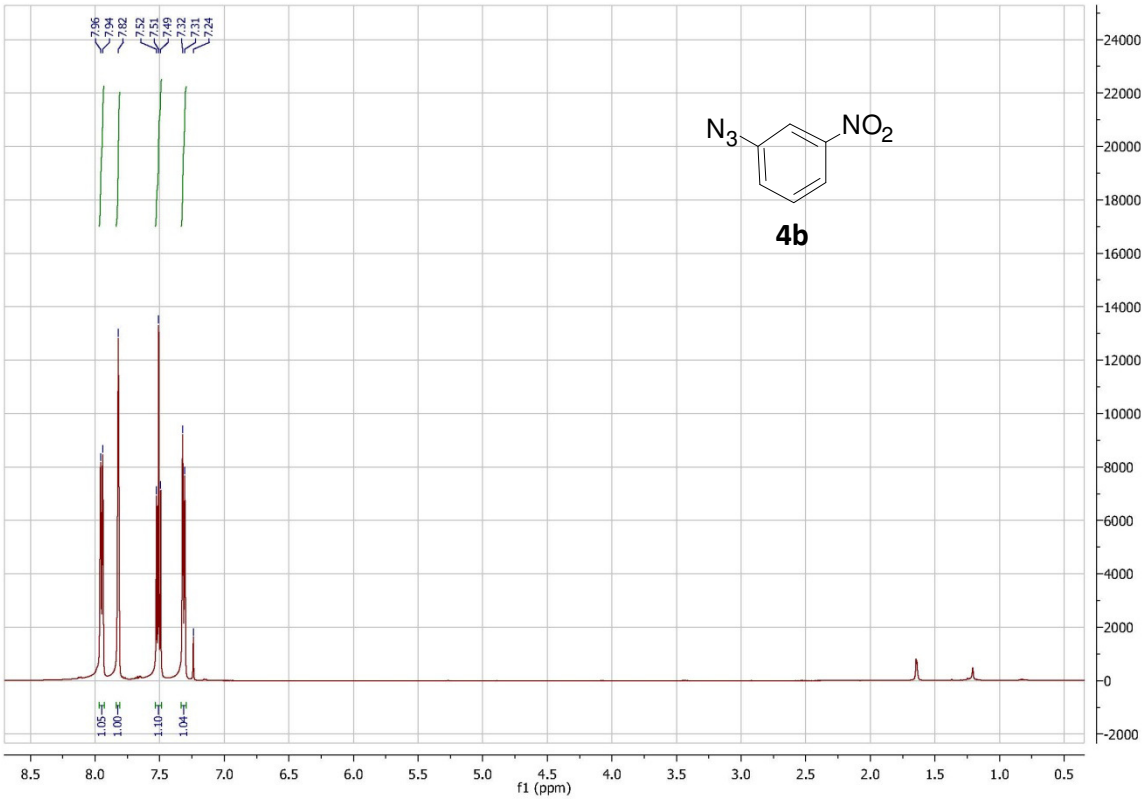
G

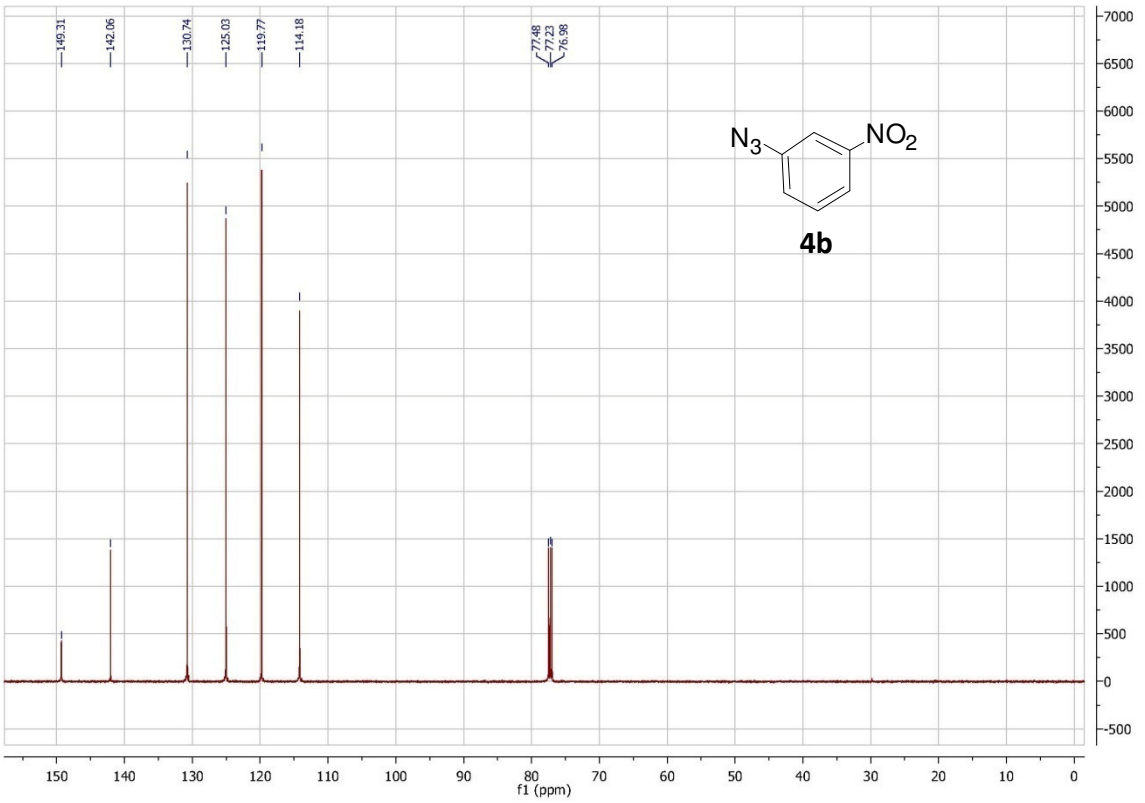

77.48
77.23
76.98
65.91
28.45
25.23
24.80
O
N
N
OH
f1 (ppm)

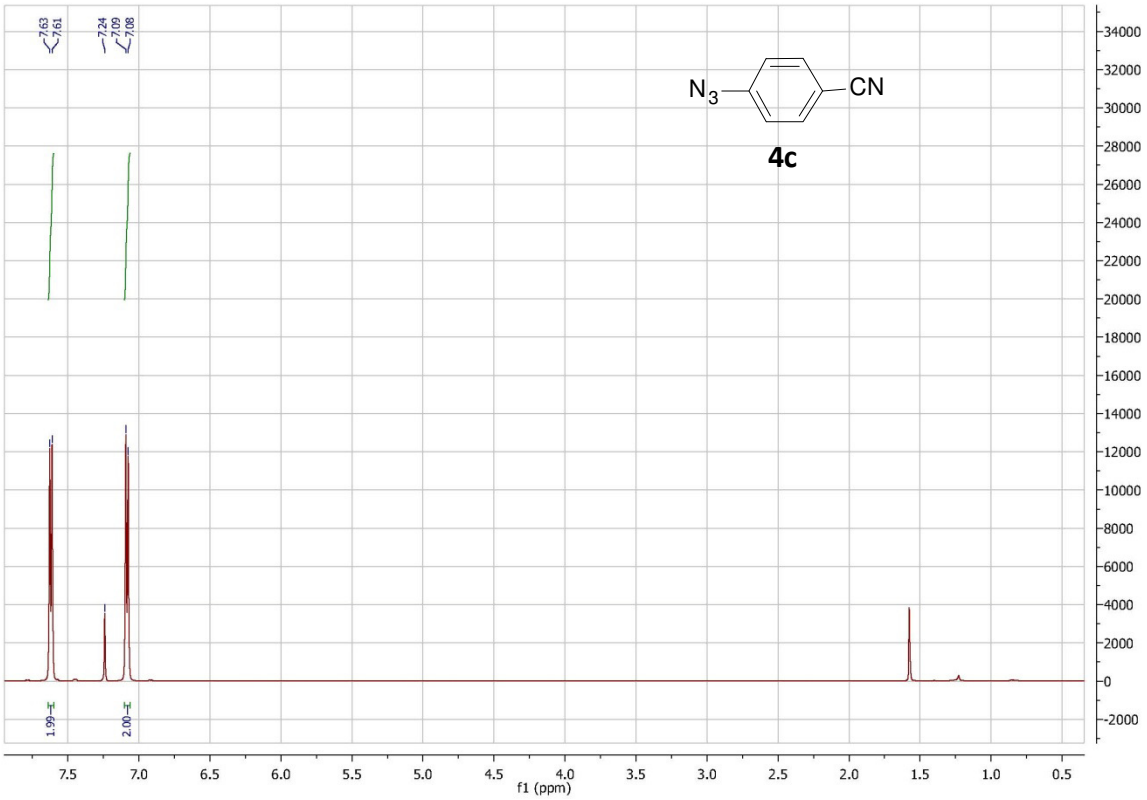
G


7.45
7.43
7.24
6.89
6.88
N3
Br
4a
2.08
2.00
f1 (ppm)


139.46
133.00
120.89
117.97
77.48
77.23
76.98
N3
Br
4a
f1 (ppm)

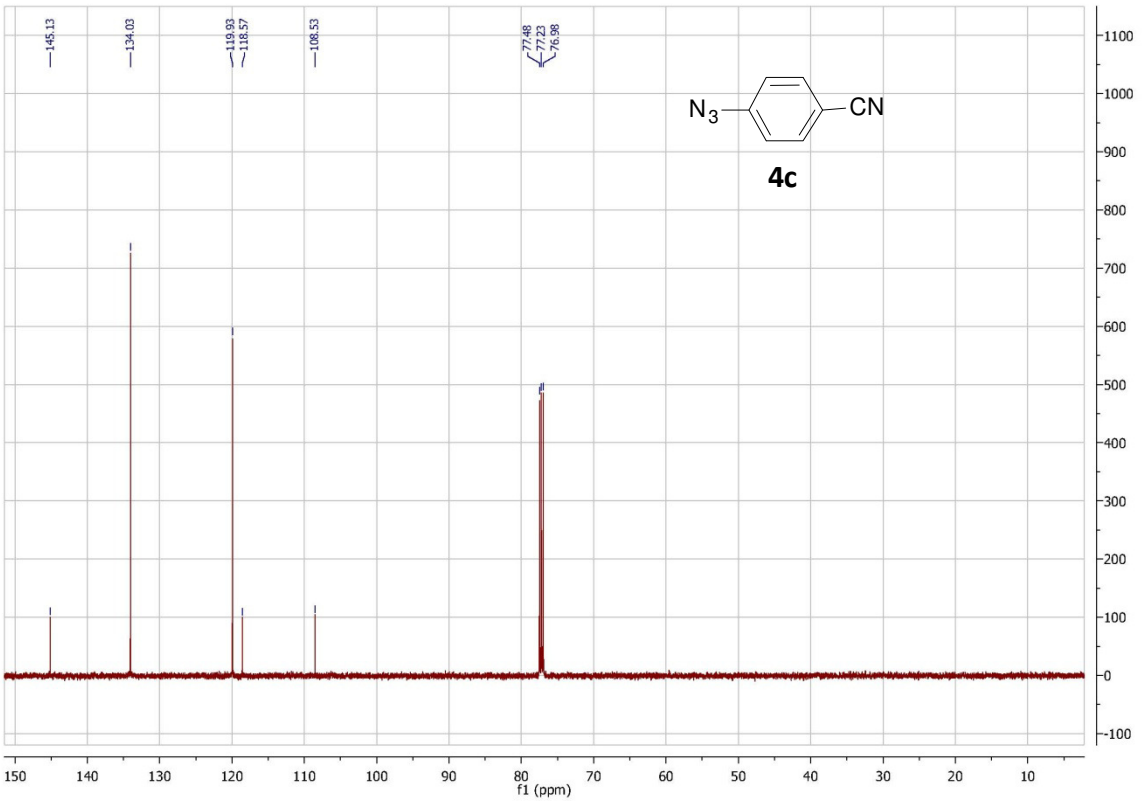

7.96
7.94
7.82
7.52
7.51
7.49
7.32
7.31
7.24
1.05
1.00
1.10
1.04
N3
NO2
4b
f1 (ppm)


149.31
142.06
130.74
125.03
119.77
114.18
77.48
77.23
76.98
N3
NO2
4b
f1 (ppm)


7.63
7.61
7.24
7.09
7.08
1.99
2.00
f1 (ppm)

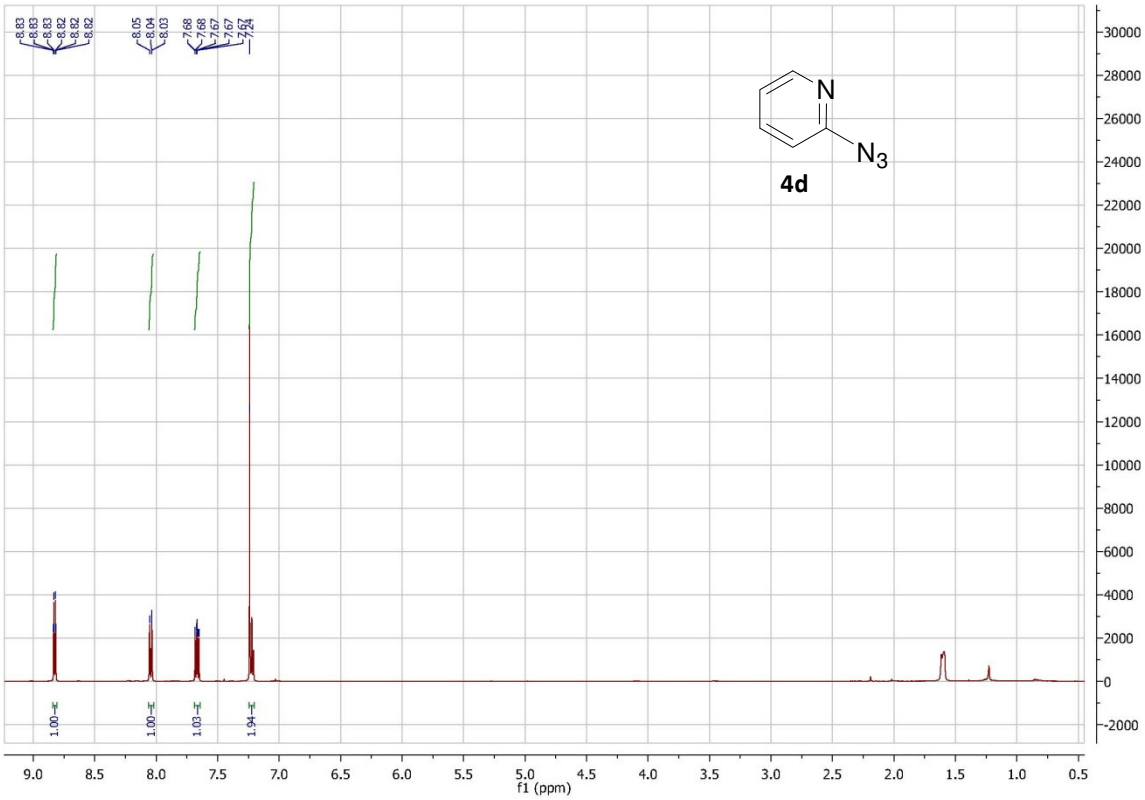
N3
CN

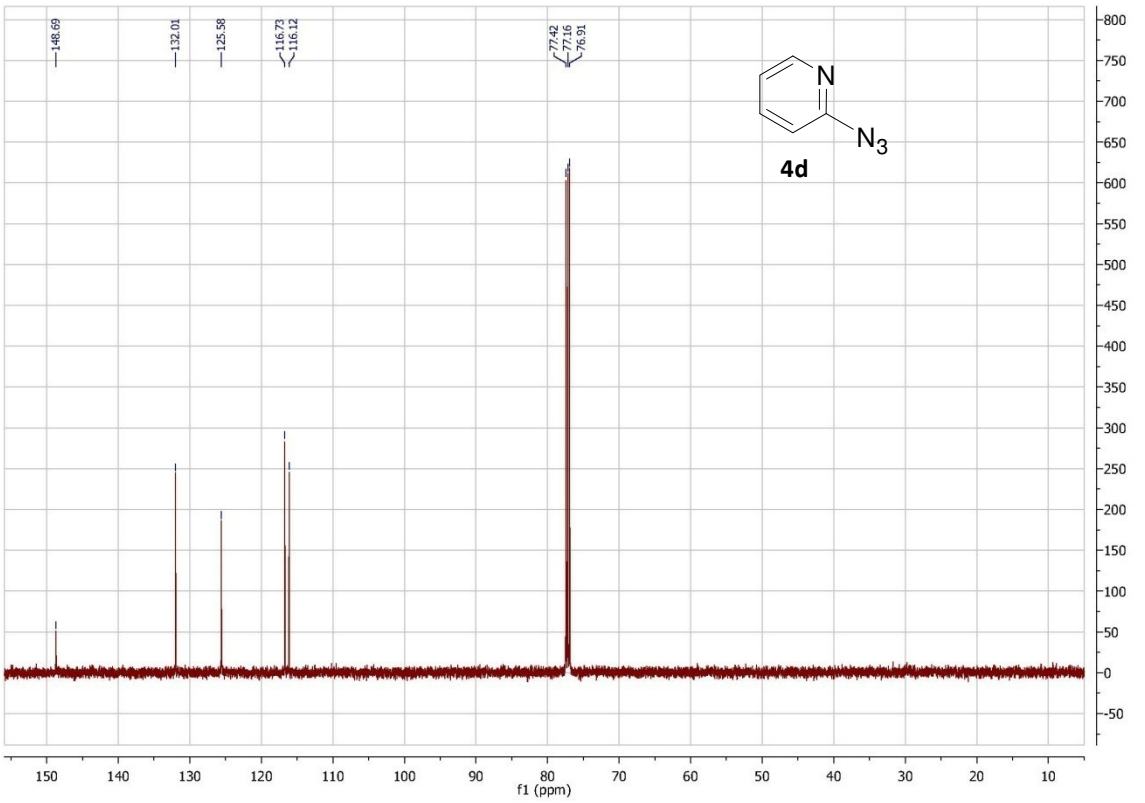
4c

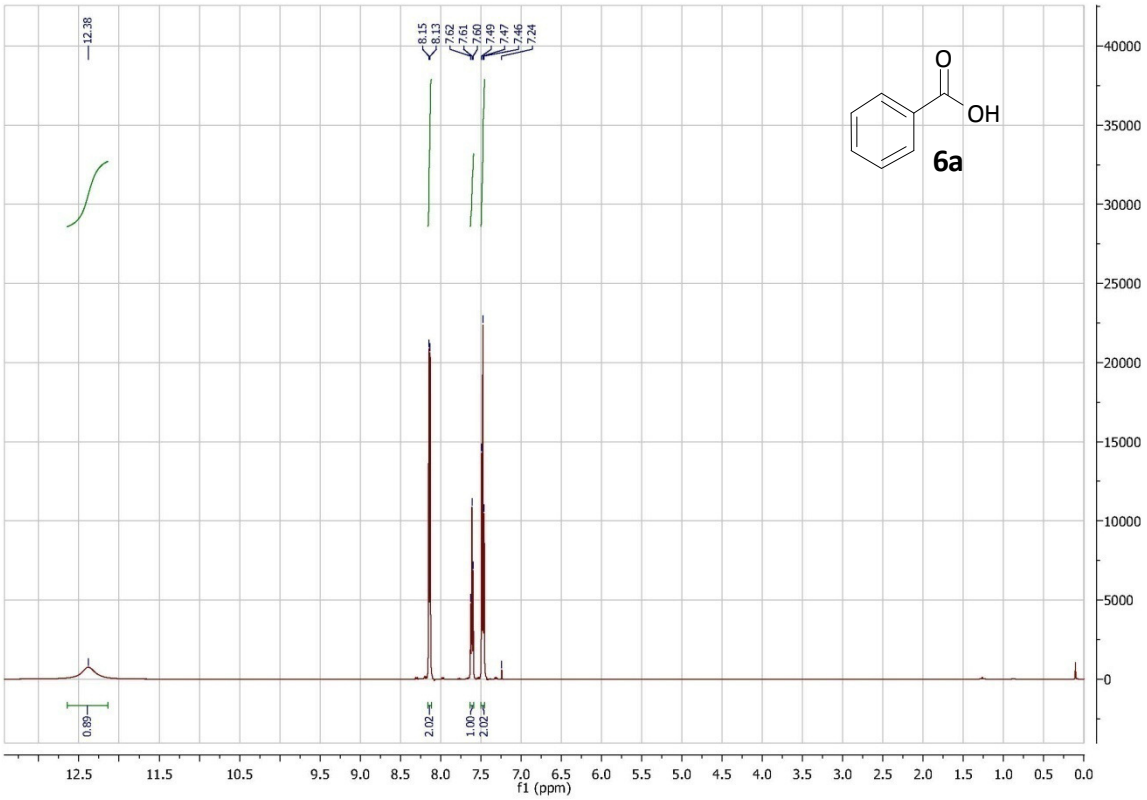

145.13
134.03
119.93
118.57
108.53
77.48
77.23
76.98
f1 (ppm)

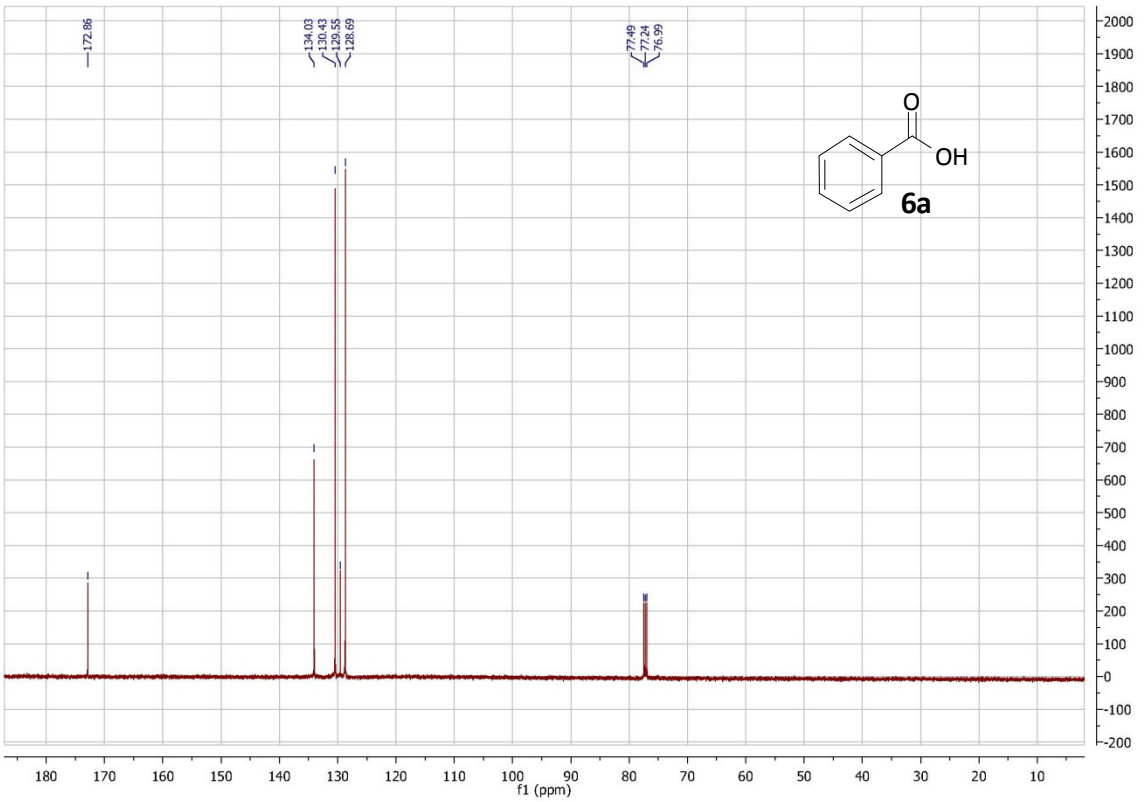
N3
CN

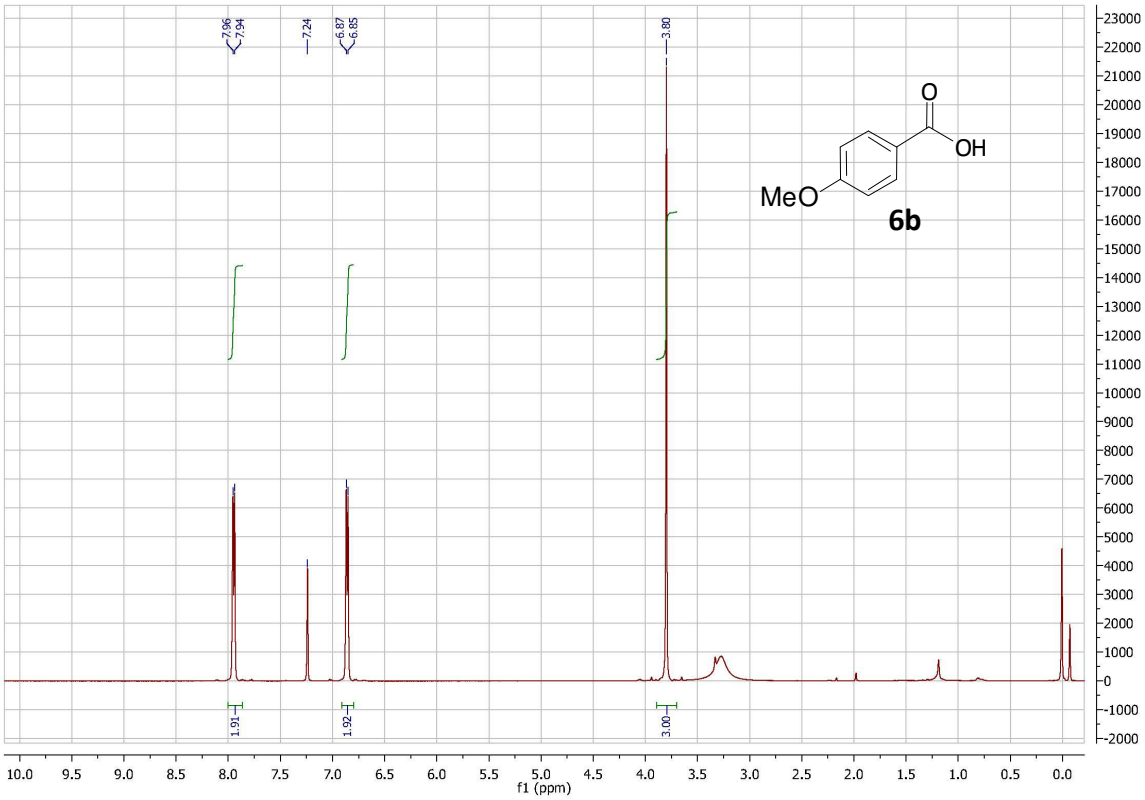
4c

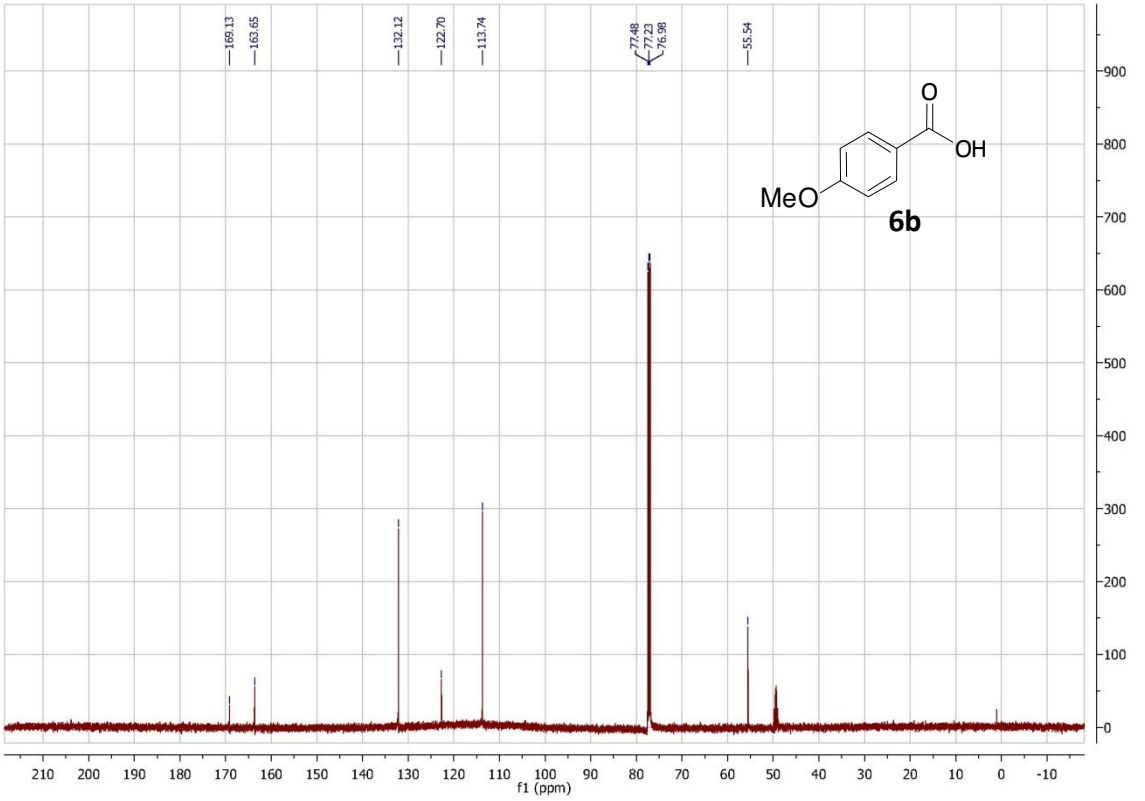

8.83
8.83
8.83
8.82
8.82
8.82
8.05
8.04
8.03
7.68
7.68
7.67
7.67
7.64
7.64
N
N3
4d
1.00
1.00
1.03
1.94
f1 (ppm)

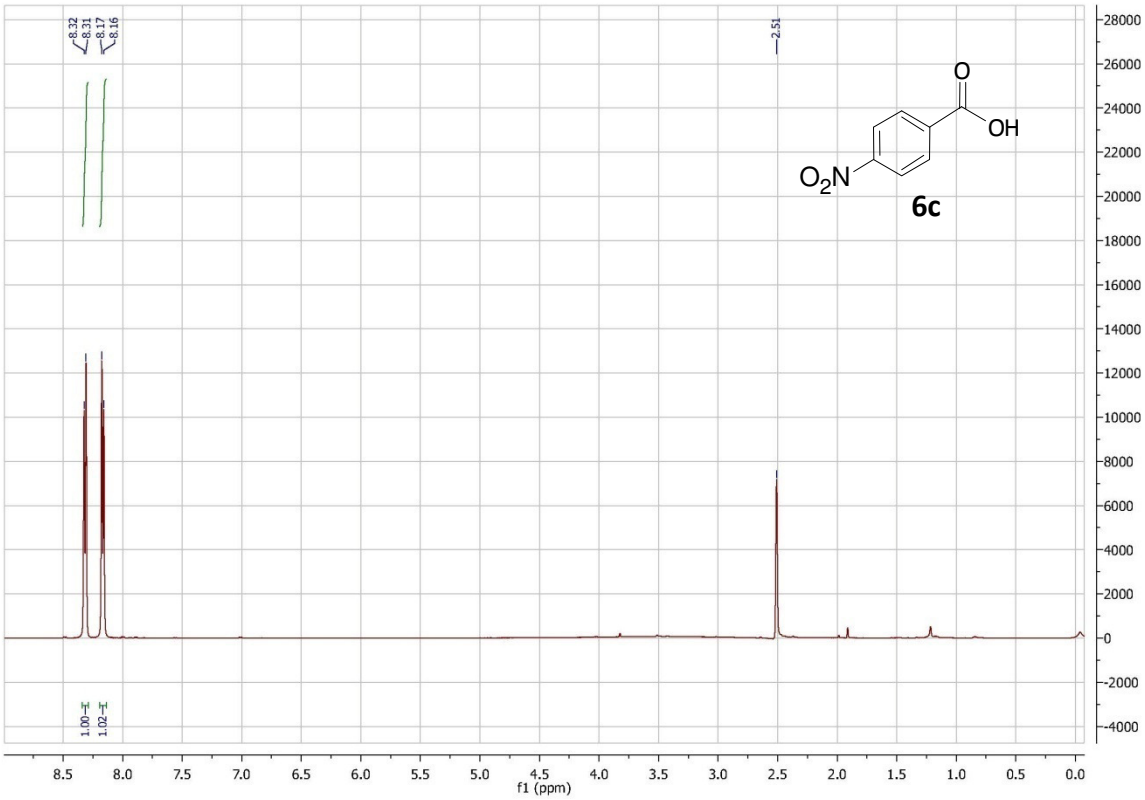

148.69
132.01
125.58
116.73
116.12
77.42
77.16
76.91
N
N3
4d
f1 (ppm)

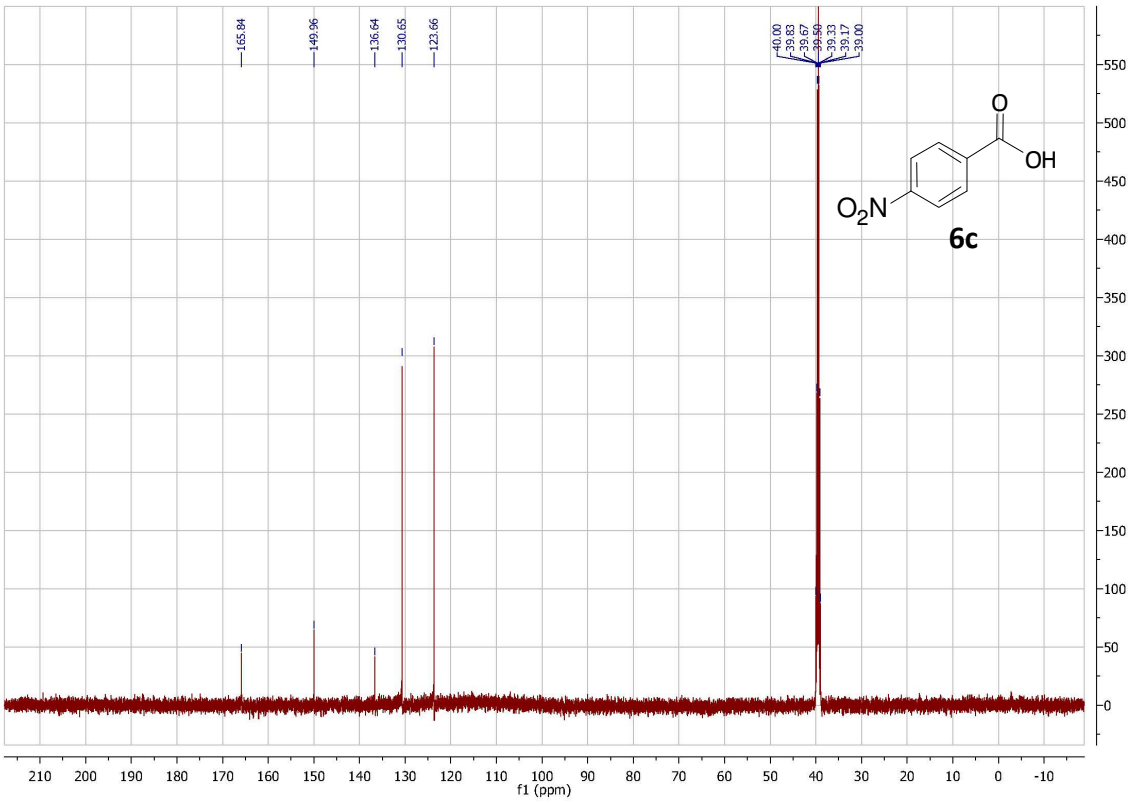

12.38
8.15
8.13
7.62
7.61
7.60
7.49
7.47
7.46
7.24
O
OH
6a
0.89
2.02
1.00
2.02
f1 (ppm)

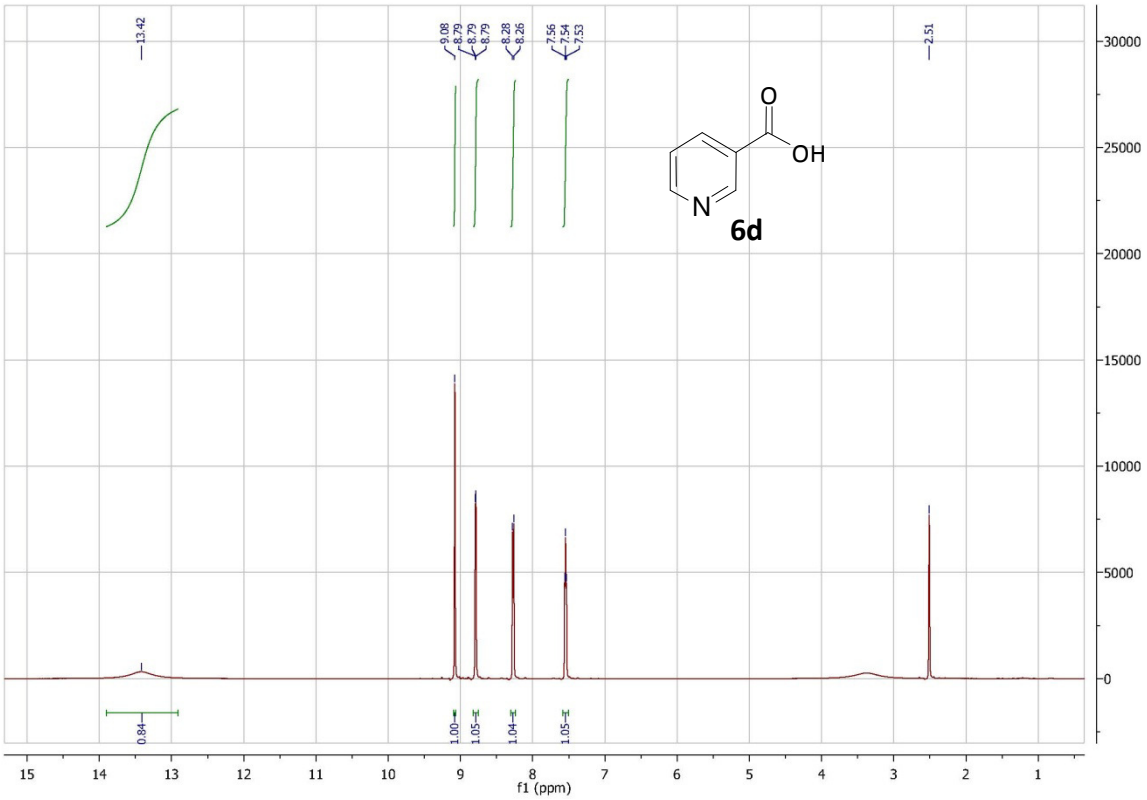

172.86
134.03
130.43
129.55
128.69
77.49
77.24
76.99
O
OH
6a
f1 (ppm)

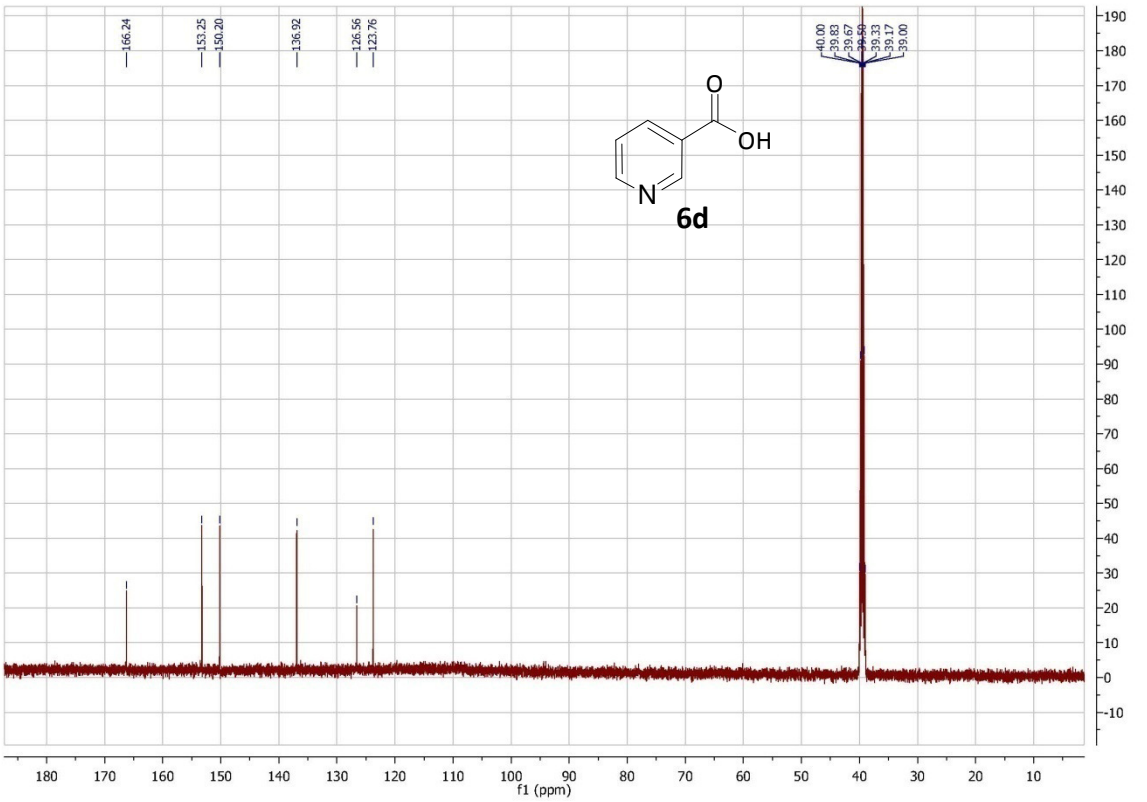

7.96
7.94
7.24
6.87
6.85
3.80
O
OH
MeO
6b
1.91
1.92
3.00
f1 (ppm)


169.13
163.65
132.12
122.70
113.74
77.48
77.23
76.98
55.54
O
OH
MeO
6b
f1 (ppm)


8.32
8.31
8.17
8.16
2.51
1.00
1.02
O
OH
O_2N
6c
f1 (ppm)


165.84
149.96
136.64
130.65
123.66
40.00
39.83
39.67
39.50
39.33
39.17
39.00
O
OH
O_2N
6c
f1 (ppm)


13.42
9.08
8.79
8.79
8.79
8.28
8.26
7.56
7.54
7.53
2.51
O
OH
N
6d
0.84
1.00
1.05
1.04
1.05
f1 (ppm)


166.24
153.25
150.20
136.92
126.56
123.76
40.00
39.83
39.67
39.50
39.33
39.17
39.00
O
OH
N
6d
f1 (ppm)