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Fluorinated β-Nitro Amines by a Selective $ZrCl_4$-Catalyzed aza-Henry Reaction of (*E*)-Trifluoromethyl Aldimines

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General Experimental Methods. All the commercial available reagents were used as received from commercial suppliers. The reactions were monitored by ^{1}H NMR analyses. Flash chromatography were performed on silica gel (60, particle size: 0.040-0.063 mm). FT-IR spectra were recorded on a Perkin-Elmer 1600 spectrophotometer in $CHCl_3$ as the solvent. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ were recorded at 300 and 75 MHz on a VARIAN XL-300 spectrometer using $CHCl_3$ and $CDCl_3$ as the internal standard, respectively. HRMS and ES Q-TOF analyses were performed using a Micromass Q-TOF Micro quadrupole-time of flight (TOF) mass spectrometer equipped with an ESI source and a syringe pump. The experiments were conducted in the positive ion mode.

(*E*)-Trifluoromethyl aldimines **1a-d** were synthesized according to the reported procedure.[1] β-Nitro α-trifluoromethyl amines **3d**,**e**[2] and unfluorinated aldimines **5a**[3] and **5b**[4] are known compounds.

1 L. Carroccia, S. Fioravanti, L. Pellacani, P. A. Tardella, *Synthesis* 2010, 4096.

2 V. Yu. Korotaev, A. Yu. Barkov, M. I. Kodess, I. B. Kutyashev, P. A. Slepukhin, A. Ya. Zapevalov, *Russ. Chem. Bull., Int. Ed.* 2009, **58**, 1886.

3 J. J. Lalonde, D. E. Bergbreiter, M. Newcomb, *J. Org. Chem.* 1986, **51**, 1369.

4 D. C. Braddock, K. K. Hii, J. M. Brown, *Angew. Chem.* 1998, **110**, 1798; *Angew. Chem. Int. Ed.* 1998, **37**, 1720.

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General procedure for the synthesis of β-nitro α-trifluoromethyl amines 3a-j. To a mixture of (*E*)-trifluoromethyl aldimine **1a-d** (1 mmol) and nitro compound **2a-c** (5 mmol), $ZrCl_4$ (0.5 mmol) was added. The reactions were performed under solvent-free conditions and stirred at room temperature (2-24 h). Then, after addition of water (5 mL), the crude mixtures were extracted three-fold times with Et_2O. The collected organic layers were dried over anhydrous Na_2SO_4 and the solvent evaporated under vacuum. The crude mixtures were purified by flash chromatography on silica gel.

Synthesis of diamine 4b. Anhydrous ammonium formate (310 mg, 5 mmol) and Pd/C 10% (95 mg) were added, under inert atmosphere (Ar), to a solution of 3b (248 mg, 1 mmol) in anhydrous MeOH. The reaction mixture was kept at reflux for 1.5 h after which it was filtered off to remove the catalyst. The solvent was evaporated under vacuum and 5 mL of water was added; the mixture was extracted three times with Et_2O. The collected organic layers were dried over anhydrous Na_2SO_4 and the solvent evaporated under vacuum.

General procedure for the synthesis of (*E*)-aldimines 5a,b. Equimolar amounts (5 mmol) of aldehyde and cyclohexylamine were reacted under solvent free conditions. The reaction mixtures were stirred at room temperature for 15 min, then CH_2Cl_2 (3 mL) and anhydrous sodium sulfate were added and the mixtures were filtered off. The organic solvent was evaporated under vacuum to give the expected aldimines which were used without further purification.

General procedure for the synthesis of β-nitro amines 6a-d. (*E*)-Aldimines **5** (1 mmol) were stirred at room temperature (3-18 h) with a five-fold excess of nitro compound, under solvent free conditions. After removal of excess nitro compound under vacuum, the crude mixtures were purified through a plug filled with silica gel using AcOEt as eluent.

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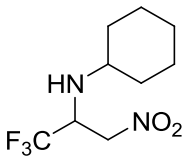
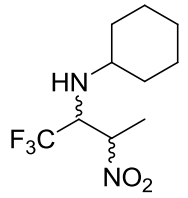


3a

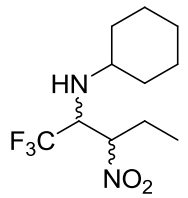
***N*-(1,1,1-Trifluoro-3-nitropropan-2-yl)cyclohexanamine** (**3a**). Yellow-brown oil. Yield 75% (0.180 g). Purified by fast filtration through a plug filled with silica gel using AcOEt as eluent. ν_{max} cm^{-1} 3355, 1567. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 4.61 (dd, *J*=12.6, 4.2 Hz, 1H), 4.35 (dd, *J*=12.6, 9.4 Hz, 1H), 4.14-4.01 (m, 1H), 2.71-2.63 (m, 1H), 1.89-1.48 (m, 5H), 1.35-0.99 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 125.2 (q, *J* = 284.5 Hz), 75.3, 55.7 (q, *J* = 29.1 Hz), 54.8, 34.1, 32.8, 25.9, 24.7, 24.4. HRMS: *m*/*z* $[M + H]^+$ calcd. for $C_9H_{16}F_3N_2O_2$ 241.1164, found 241.1161.



syn/*anti* **3b**

***N*-(1,1,1-Trifluoro-3-nitrobutan-2-yl)cyclohexanamine** (*syn*-**3b**). Pale yellow oil. Yield 24% (0.061 g). Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 98:2). ν_{max} cm^{-1} 3365; 1558. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 4.69-4.60 (m, 1H), 3.74-3.64 (m, 1H), 2.69-2.61 (m, 1H), 1.82-1.54 (m, 6H), 1.63 (dd, *J* = 6.8, 1.4 Hz, 3H), 1.27-1.08 (m, 5H).^{13}C NMR (75 MHz, $CDCl_3$) δ: 125.62 (q, *J* = 285.4 Hz), 83.7, 59.7 (q, *J* = 28.1 Hz), 55.3, 34.2, 32.8, 25.9, 24.8, 24.4, 16.4. HRMS: *m*/*z* $[M + H]^+$ calcd. for $C_{10}H_{18}F_3N_2O_2$ 255.1320, found 255.1326.

***N*-(1,1,1-Trifluoro-3-nitrobutan-2-yl)cyclohexanamine** (*anti*-**3b**). Pale yellow oil. Yield 58% (0.147 g). Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 98:2). ν_{max} cm^{-1} 3365; 1558. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 4.75-4.65(m, 1H), 4.14 (m, *J* = 7.5, 4.3 Hz, 1H), 2.69-2.54 (m, 1H), 1.86-1.63 (m, 6H), 1.55 (dd, *J* = 6.8, 0.7 Hz, 3H), 1.35-1.07 (m, 5H).^{13}C NMR (75 MHz, $CDCl_3$) δ: 125.2 (q, *J* = 285.4 Hz), 81.2, 58.9 (q, *J* = 27.9 Hz), 55.1, 34.1, 32.9, 25.8, 24.7, 24.3, 12.8. HRMS: *m*/*z* $[M + H]^+$ calcd. for $C_{10}H_{18}F_3N_2O_2$ 255.1320, found 255.1322.



syn/*anti* **3c**

***N*-(1,1,1-Trifluoro-3-nitropentan-2-yl)cyclohexanamine** (**3c**). Pale yellow oil. Yield 79% (0.212 g). Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 98:2). ν_{max} cm^{-1} 3373; 1558. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.58-4.42 (m, 2H), 3.92-3.80 (m, 1H, major isomer), 3.66-3.50 (m, 1H, minor isomer), 2.66-2.60 (m, 2H), 2.18-1.95 (m, 4H), 1.88-1.50 (m, 12H), 1.36-1.04 (m, 10H), 0.99 (t, *J* = 7.4 Hz, 6H).^{13}C NMR (75 MHz, $CDCl_3$) δ: 125.2 (q, *J* = 285.1 Hz, 2C), 90.1 (minor isomer), 88.7 (major isomer), 59.2 (q, *J* = 28.1 Hz, major), 58.9 (q, *J* = 28.1 Hz, minor), 55.6 (major), 55.3 (minor), 34.3 (minor), 34.2 (major), 33.2 (major), 32.8 (minor), 25.9 (2C), 24.8

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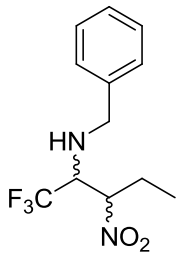
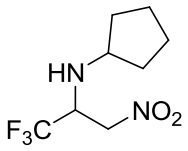
(2C), 24.5 (major), 24.4 (minor), 22.5 (2C), 10.5 (2C). HRMS: *m*/*z* [M + H]$^+$ calcd. for $C_{11}H_{20}F_3N_2O_2$ 269.1477, found 269.1475.



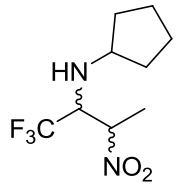
syn/*anti* **3f**

***N*-Benzyl-1,1,1-trifluoro-3-nitropentan-2-amine** (**3f**). Pale yellow oil. Yield 75% (0.207 g). Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 98:2). ν_{max} cm^{-1} 3368; 1560. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.40-7.29 (m, 10H), 4.66-4.60 (m, 1H, minor isomer), 4.59-4.52 (m, 1H, major isomer), 4.15-3.99 (m, 3H), 3.90-3.80 (m, 2H), 3.59-3.49 (m, 1H, minor), 2.19-2.03 (m, 6H), 1.00 (t, *J* = 7.3Hz, 3H, major), 0.96 (t, *J* = 7.4Hz, 3H, minor). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 138.5 (minor isomer), 138.4 (major isomer), 128.6 (2C, major), 128.5 (2C, minor), 128.4 (2C, minor), 128.3 (2C, major), 127.7 (major), 127.6 (minor), 125.4 (q, *J* = 285.9 Hz, 2C), 89.1 (minor), 88.0 (major), 60.8 (q, *J* = 28.0 Hz, major), 60.4 (q, *J* = 28.0 Hz, minor), 52.7 (major), 52.2 (minor), 22.2 (2C), 10.3 (major), 10.2 (minor). HRMS: *m*/*z* [M + H]$^+$ calcd. for $C_{12}H_{16}F_3N_2O_2$ 277.1164, found 277.1172.



3g

***N*-(1,1,1-Trifluoro-3-nitropropan-2-yl)cyclopentanamine** (**3g**). Yellow-brown oil. Yield 86% (0.194 g). Purified by fast filtration through a plug filled with silica gel using AcOEt as eluent. ν_{max} cm^{-1} 3365; 1556. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.60 (dd, *J* = 12.7, 4.2 Hz, 1H), 4.36 (dd, *J* = 12.7, 9.4 Hz, 1H), 4.07-3.94 (m, 1H), 3.39-3.31 (m, 1H), 1.86-1.25 (m, 9H).^{13}C NMR (75 MHz, $CDCl_3$) δ: 125.1 (q, *J* = 284.8 Hz), 74.8, 57.6, 56.9 (q, *J* = 29.0 Hz), 33.8, 32.4, 23.4, 23.3,HRMS: *m*/*z* [M + Na]$^+$ calcd. for $C_8H_{13}F_3N_2NaO_2$ 249.0827, found 249.0828.



syn/*anti* **3h**

***N*-[2-Nitro-1-(trifluoromethyl)propyl]cyclopentanamine** (*syn*-**3h**). Yellow oil. Yield 21% (0.051 g). Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 98:2). ν_{max} cm^{-1} 3370; 1556. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.74-4.67 (m, 1H), 3.66-3.56 (m, 1H), 3.36-3.27 (m, 1H), 1.85-1.59(m, 4H), 1.64 (dd, *J* = 6.8, 1.3 Hz, 3H), 1.58-1.48 (m, 2H), 1.33-1.20 (m, 3H).^{13}C

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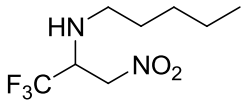
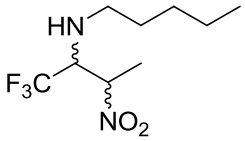
NMR (75 MHz, $CDCl_3$) δ: 125.4 (q, *J* = 185.8 Hz), 83.3, 60.9 (q, *J* = 27.8 Hz), 58.1, 34.0, 32.2, 23.3 (2C), 12.5.HRMS: *m/z* $[M + H]^+$ calcd. for $C_9H_{16}F_3N_2O_2$ 241.1164, found 241.1169.

***N*-[2-Nitro-1-(trifluoromethyl)propyl]cyclopentanamine** (*anti*-**3h**). Yellow oil. Yield 56% (0.135 g). Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 98:2). ν_{max} cm^{-1} 3370; 1556. ^1H NMR (300 MHz, $CDCl_3$) δ: 4.73-4.61 (m, 1H), 4.14-4.05 (m, 1H), 3.36-3.27 (m, 1H), 1.85-1.63(m, 4H), 1.55 (d, *J* = 6.8 Hz, 3H), 1.58-1.46 (m, 2H), 1.36-1.18 (m, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ: 125.4 (q, *J* = 185.8 Hz), 81.0, 60.2 (q, *J* = 27.8 Hz), 58.1, 33.9, 32.4, 23.4, 23.2, 12.5.HRMS: *m/z* $[M + H]^+$ calcd. for $C_9H_{16}F_3N_2O_2$ 241.1164, found 241.1169.



3i

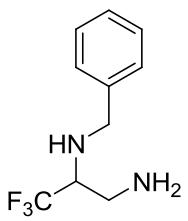
***N*-(1,1,1-Trifluoro-3-nitropropan-2-yl)pentan-1-amine** (**3i**) Yellow-brown oil. Yield 83% (0.190 g). Purified by fast filtration through a plug filled with silica gel using AcOEt as eluent. ν_{max} cm^{-1} 3368; 1569. ^1H NMR (300 MHz, $CDCl_3$) δ: 4.59 (dd, *J* = 13.0, 4.2 Hz, 1H), 4.41 (dd, *J* = 13.0, 9.4 Hz, 1H), 4.01-3.89 (m, 1H), 2.89-2.81 (m, 1H), 2.69-2.60 (m, 1H), 1.50-1.21 (m, 7H), 0.86 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 125.08 (q, *J* = 285.0 Hz), 74.2, 58.4 (q, *J* = 29.2 Hz), 47.8, 29.8, 28.9, 22.3, 13.8. HRMS: *m/z* $[M + H]^+$ calcd. for $C_8H_{16}F_3N_2O_2$ 229.1146, found 229.1148; *m/z* $[M + Na]^+$ calcd. for $C_8H_{15}F_3N_2NaO_2$ 251.0983, found 251.0975.



syn/*anti* **3j**

***N*-(1,1,1-Trifluoro-3-nitrobutan-2-yl)pentan-1-amine** (*syn*-**3j**). Yellow oil. Yield 20% (0.048 g). Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 98:2). ν_{max} cm^{-1} 3368; 1558. ^1H NMR (300 MHz, $CDCl_3$) δ: 4.75-4.66 (m, 1H), 3.62-3.52 (m, 1H), 2.92-2.83 (m, 1H), 2.64-2.55 (m, 1H), 1.65 (dd, *J* = 6.8, 1.3 Hz, 3H), 1.79-1.14 (m, 7H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 125.5 (q, *J* = 285.6 Hz), 83.1, 62.6 (q, *J* = 28.0 Hz), 48.5, 30.0, 28.9, 22.4, 16.4, 12.7. HRMS: *m/z* $[M + H]^+$ calcd. for $C_9H_{18}F_3N_2O_2$ 243.1320, found 243.1324.

***N*-(1,1,1-Trifluoro-3-nitrobutan-2-yl)pentan-1-amine** (*anti*-**3j**). Yellow oil. Yield 58% (0.140 g). Purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 98:2). ν_{max} cm^{-1} 3368; 1558. ^1H NMR (300 MHz, $CDCl_3$) δ: 4.74-4.62 (m, 1H), 4.09-4.00 (m, 1H), 2.94-2.84 (m, 1H), 2.64-2.56 (m, 1H), 1.57 (d, *J* = 6.8 Hz, 3H), 1.78-1.12 (m, 7H), 0.90 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 125.4 (q, *J* = 285.5 Hz), 80.9, 61.8 (q, *J* = 28.0 Hz), 49.1, 30.0, 28.9, 22.4, 16.4, 13.9. HRMS: *m/z* $[M + H]^+$ calcd. for $C_9H_{18}F_3N_2O_2$ 243.1320, found 243.1328.



4b

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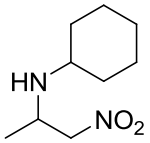
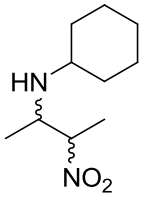
***N*^{2}-benzyl-3,3,3-trifluoropropan-1,2-diamine** (**4b**). Pale yellow oil. Yield 65% (0.142 g) Purified by fast filtration through a plug filled with silica gel using AcOEt as eluent. ν_{max} cm^{-1} 3491; 3393. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.39-7.27 (m, 5H), 3.96 (dd, *J* = 62.6, 13.1 Hz, 2H), 3.11-2.92 (m, 1H), 2.97 (dd, *J* = 13.3, 3.6 Hz, 1H), 2.74 (dd, *J* = 13.0, 8.1 Hz, 1H), 1.83 (br, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.4, 128.4 (2C), 128.1 (2C), 127.2, 126.6 (q, *J* = 284.5 Hz), 60.2 (q, *J* = 26.0 Hz), 51.7, 40.0. HRMS: *m*/*z* [M + H]$^+$ calcd. for $C_{10}H_{14}F_3N_2$ 219.1109, found 219.1105.



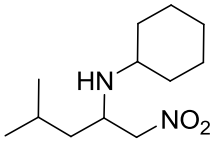
6a

***N*-(1-Nitropropan-2-yl)cyclohexanamine** (**6a**). Yellow-brown oil. Yield 95% (0.177 g). ν_{max} cm^{-1} 3355; 1568. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.38-4.27 (m, 1H), 3.56-3.46 (m, 1H), 2.55-2.46 (m, 1H), 1.86-1.55 (m. 7H), 1.17 (d, *J* = 6.5 Hz, 3H), 1.33-0.99 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 79.8, 53.9, 51.8, 34.2, 33.7, 26.0, 24.8, 24.7, 17.0. HRMS: *m*/*z* [M + H]$^+$ calcd. for $C_9H_{19}N_2O_2$ 187.1447, found 187.1445.



syn/*anti* **6b**

***N*-(3-Nitrobutan-2-yl)cyclohexanamine** (**6b**). Yellow-brown oil. Yield 90% (0.181 g). ν_{max} cm^{-1} 3368; 1555. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.53-4.37 (m, 2H), 3.28-3.14 (m, 2H), 2.38-2.25 (m, 2H), 1.49 (d, *J* = 6.7 Hz, 3H, minor isomer), 1.45 (d, *J* = 6.7 Hz, 3H, major isomer), 1.79-1.43 (m, 12H), 1.07 (d, *J* = 6.5 Hz, 3H, minor), 1.06 (d, *J* = 6.5 Hz, 3H, major), 1.26-0.95 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 87.7 (major isomer), 86.4 (minor isomer), 53.8 (major), 53.7 (minor), 53.0 (2C), 34.0 (major), 33.8 (minor), 33.4 (minor), 33.2 (major), 25.7 (2C), 24.6 (major), 24.5 (2C, minor), 24.3 (major), 17.2 (minor), 16.6 (major), 14.5 (major), 14.4 (minor). HRMS: *m*/*z* [M + H]$^+$ calcd. for $C_{10}H_{21}N_2O_2$ 201.1603, found 201.1609.



6c

***N*-(4-Methyl-1-nitropentan-2-yl)cyclohexanamine** (**6c**). Yellow-brown oil. Yield 90% (0.205 g). ν_{max} cm^{-1} 3363; 1556. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.38-4.26 (m, 2H), 3.39-3.30 (m, 1H), 2.42-2.51 (m, 1H), 1.51-1.88 (m, 7H), 0.98-1.38 (m, 7H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.89 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 79.8, 53.9, 51.8, 42.9, 34.2, 33.7, 25.9, 24.8 (2C), 24.7, 22.8, 22.2. HRMS: *m*/*z* [M + H]$^+$ calcd. for $C_{12}H_{25}N_2O_2$ 229.1916, found 229.1999.

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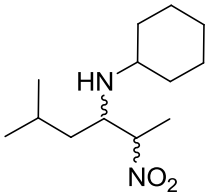

syn/*anti* **6d**

***N*-(5-Methyl-2-nitrohexan-3-yl)cyclohexanamine** (**6d**). Yellow-brown oil. Yield 89% (0.217 g). ν_{max} cm^{-1} 3368; 1555. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.58-4.49 (m, 2H), 3.21-3.11 (m, 2H), 2.96-2.81 (m, 2H), 2.45-2.34 (m, 2H), 2.12-2.05 (m, 4H), 1.79-1.50 (m, 12H), 1.42 (d, *J* = 6.7, 3H, minor isomer), 1.41 (d, *J* = 6.7, 3H, major isomer), 1.27-1.06 (m, 10H), 0.94-0.88 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 85.7 (minor isomer), 84.7 (major isomer), 56.1 (major), 56.0 (minor), 54.4 (minor), 54.1 (major), 41.5 (major), 40.2 (minor), 34.4 (2C, major), 34.2 (2C, minor), 25.9 (2C), 24.8 (2C, major), 24.7 (2C, minor), 24.6 (minor), 24.4 (major), 23.0 (major), 22.7 (minor), 22.3 (major), 22.1 (minor), 13.4 (major), 13.1 (minor). HRMS: *m*/*z* $[M + H]^+$ calcd. for $C_{13}H_{27}N_2O_2$ 243.2073, found 243.2065.

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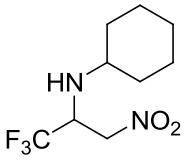
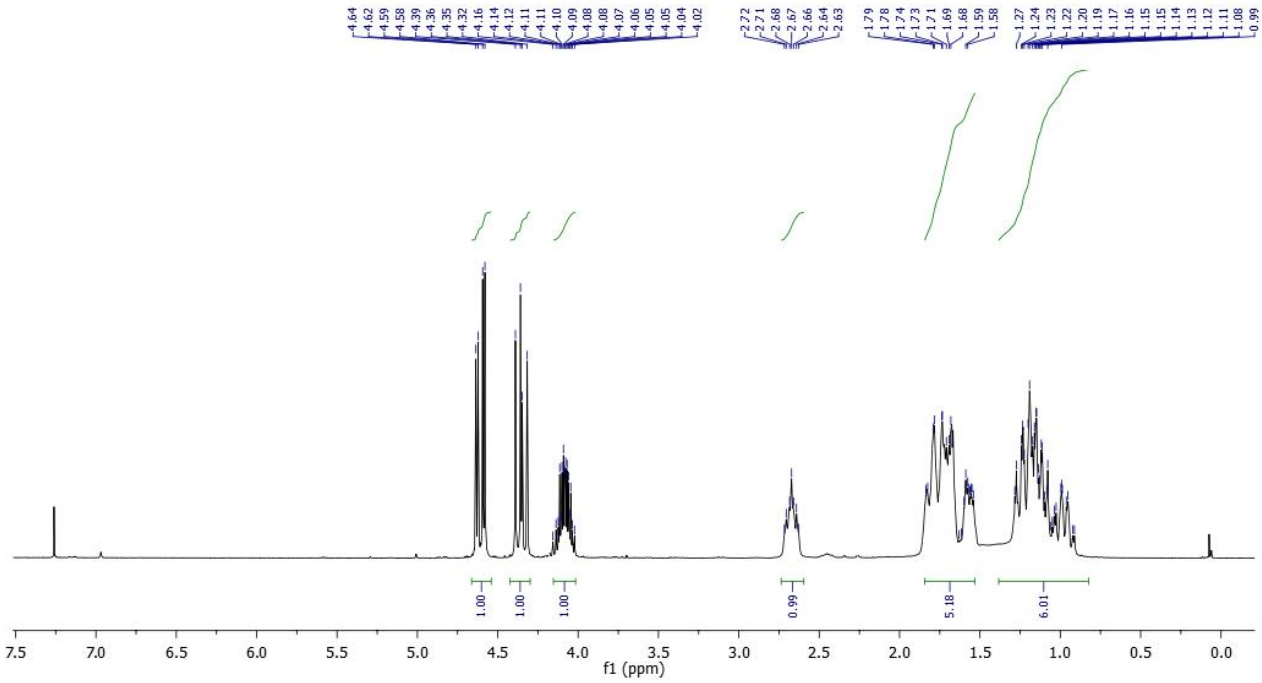
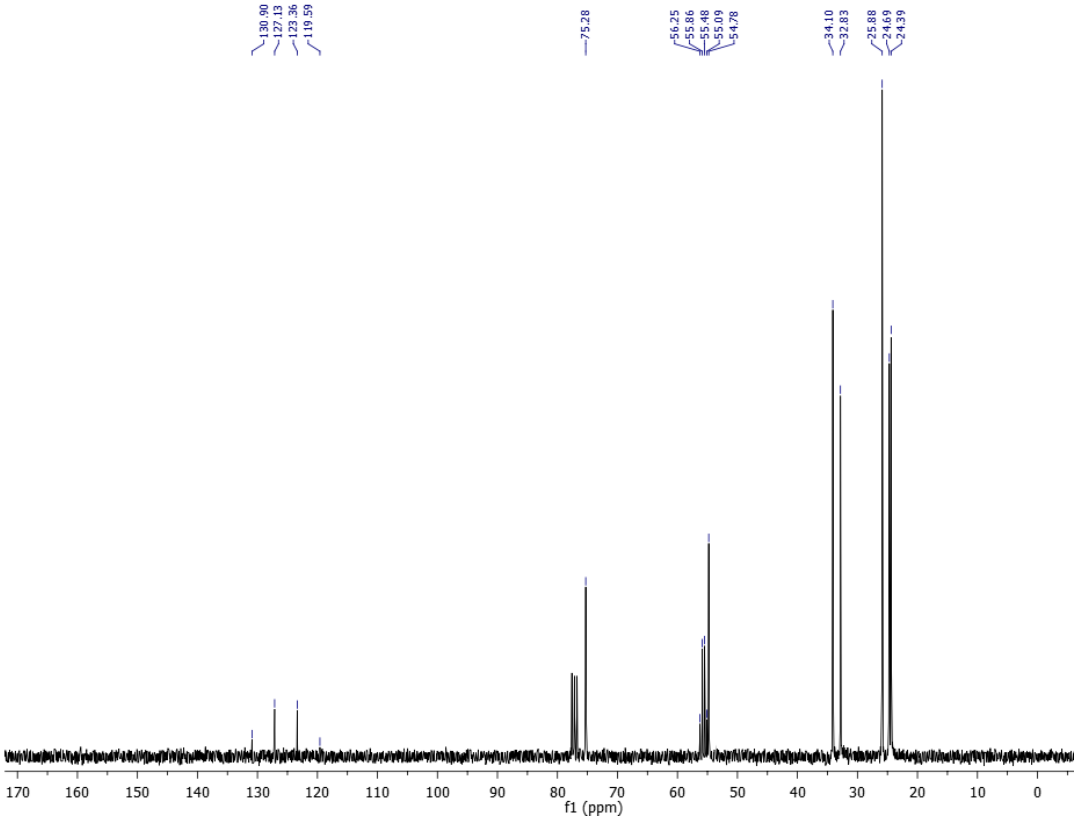


3a





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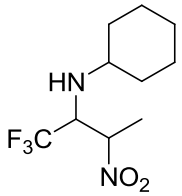
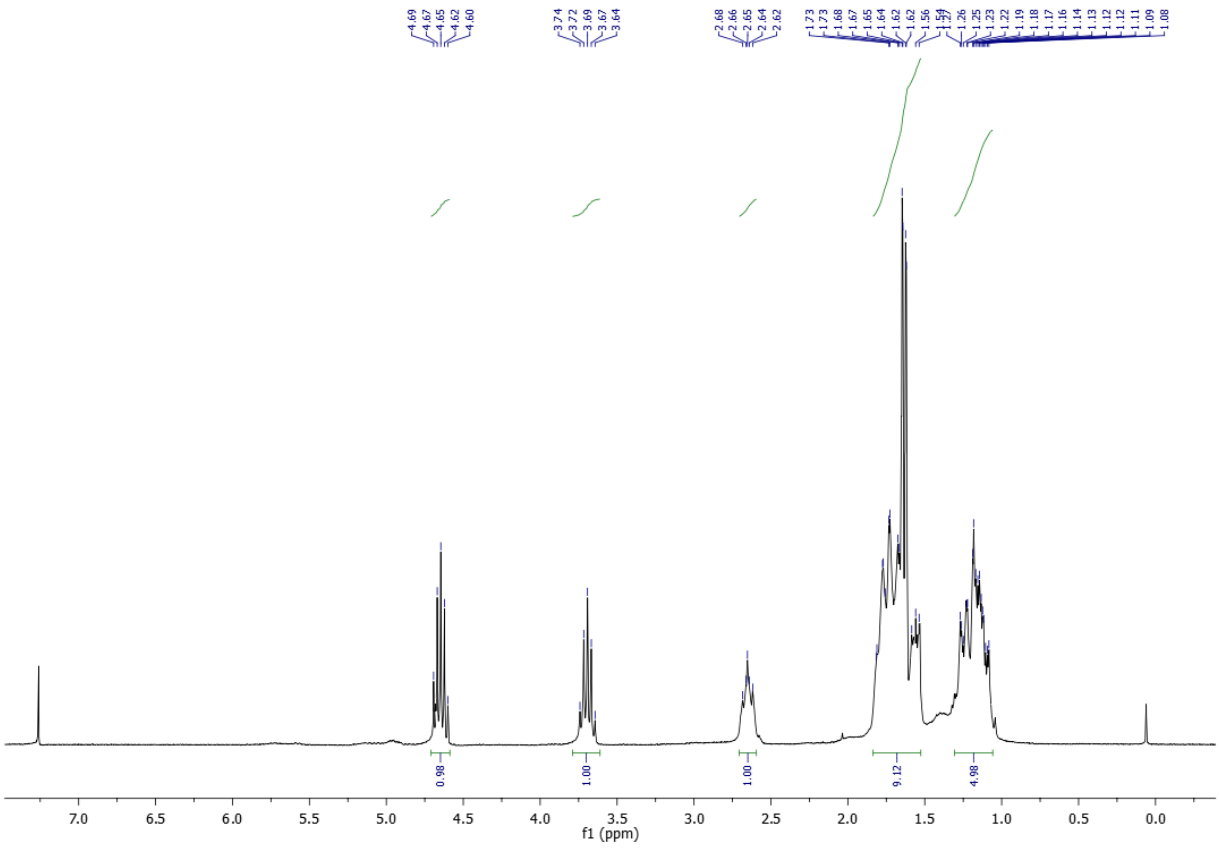
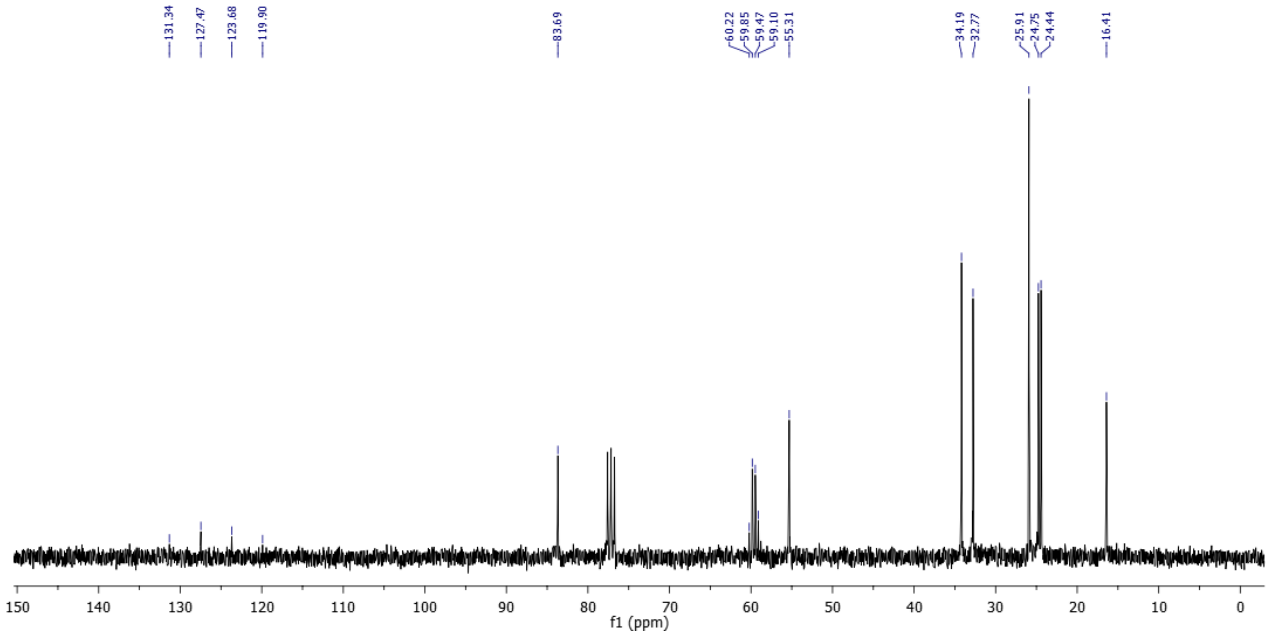


syn **3b**





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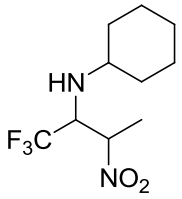

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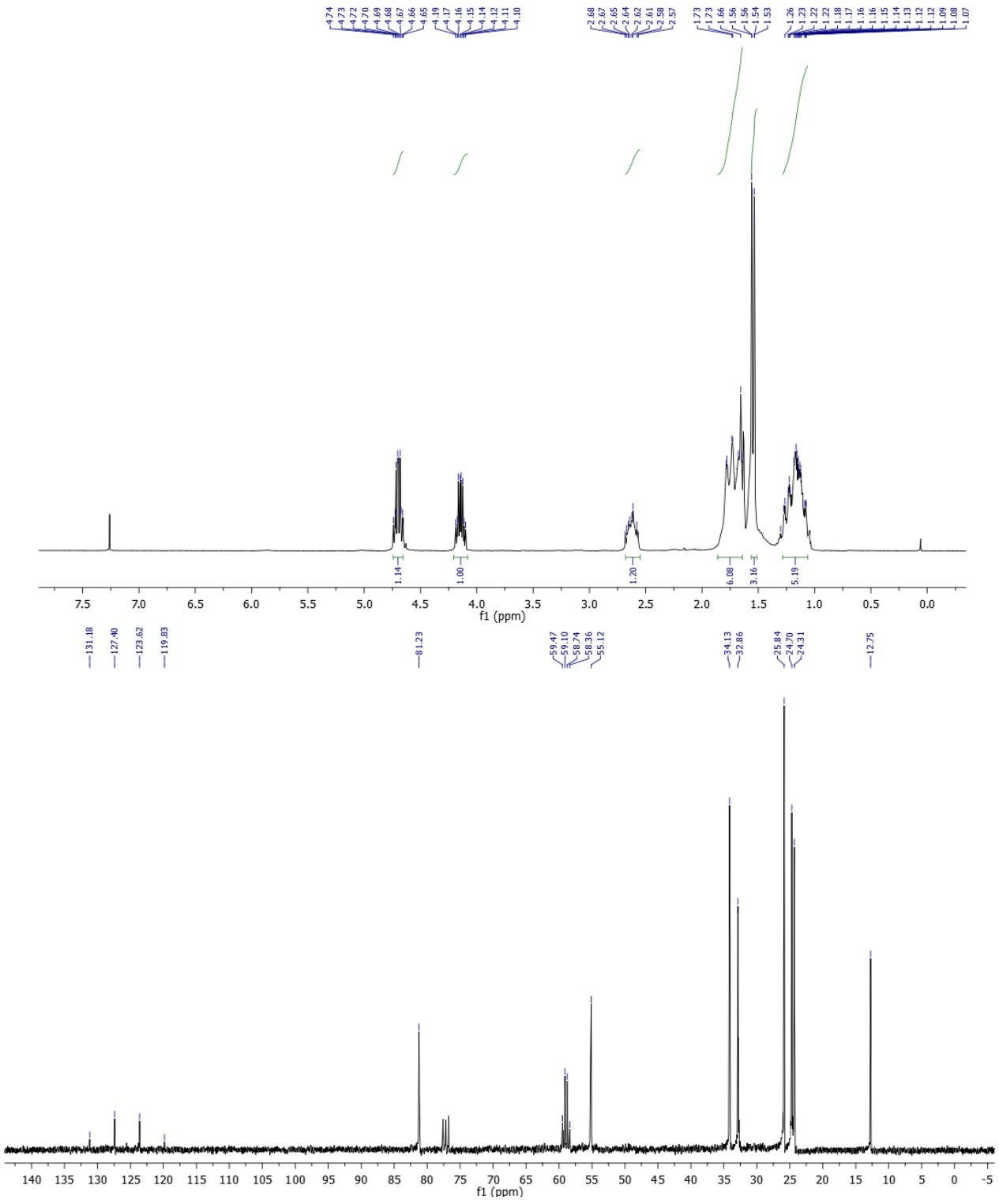

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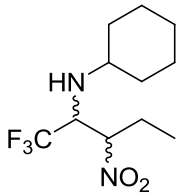

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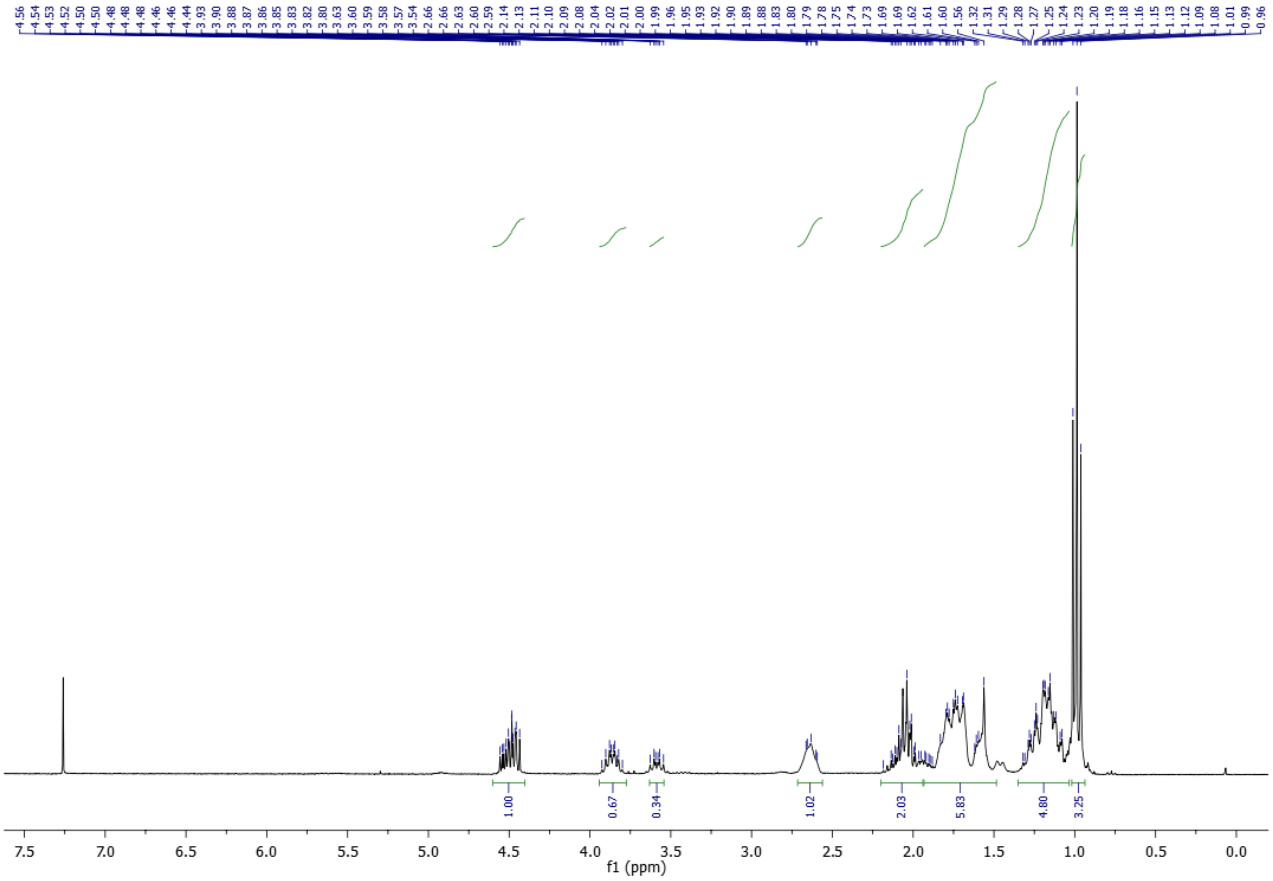

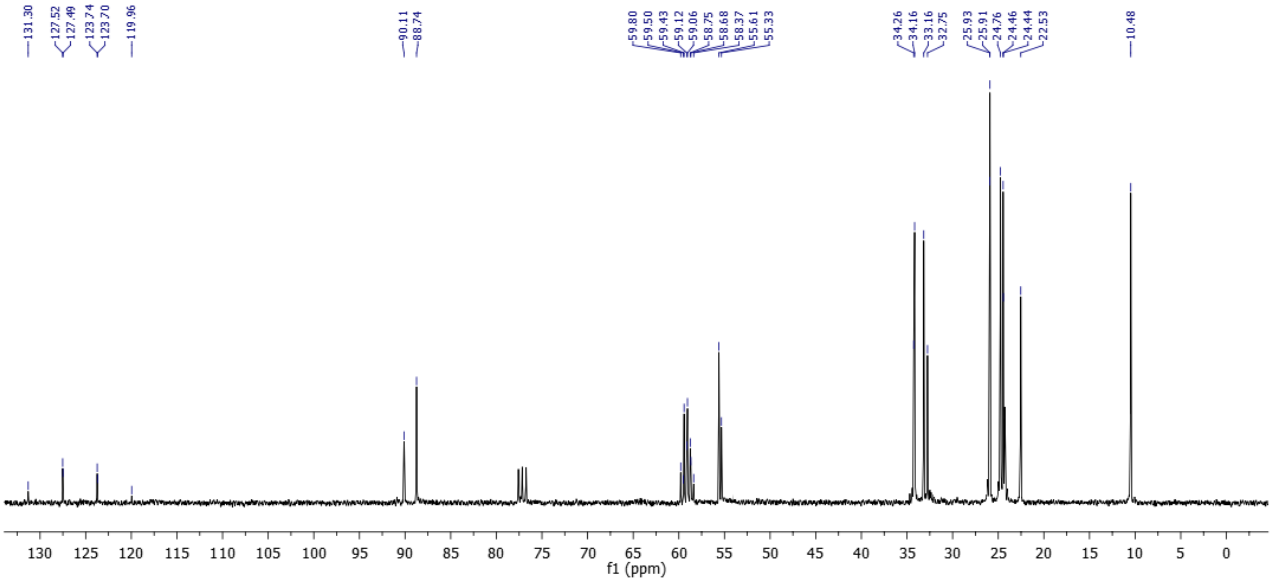

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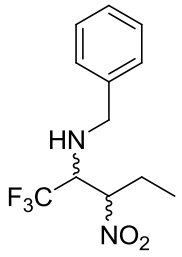
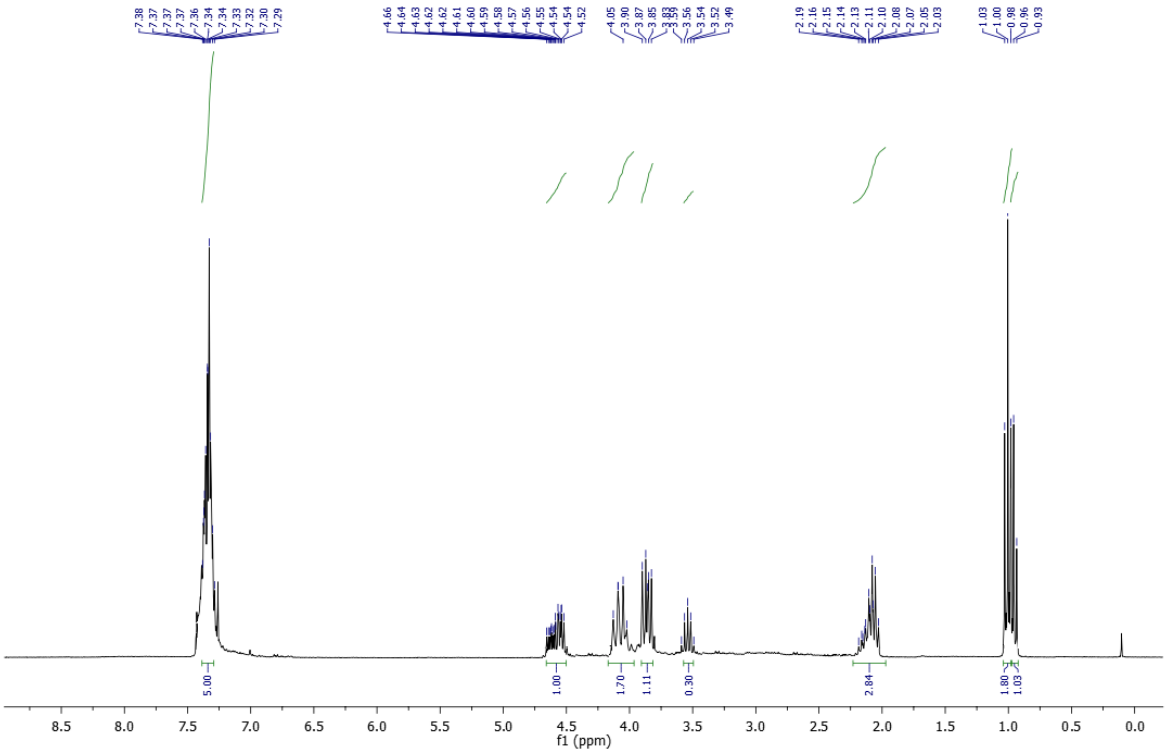
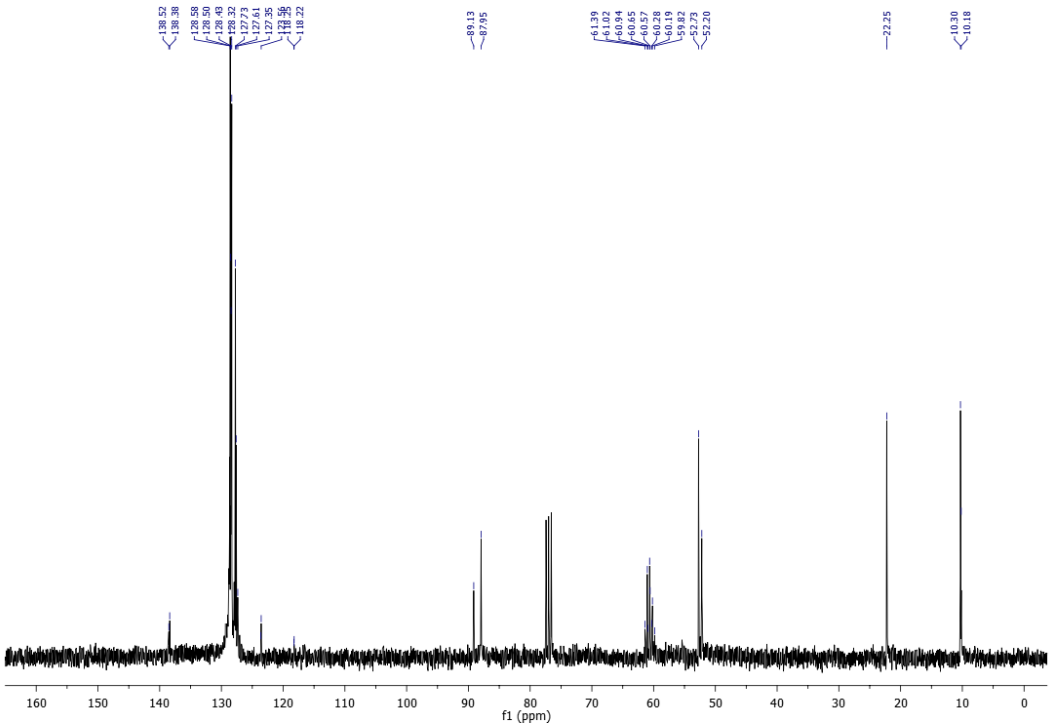


syn/*anti* **3f**





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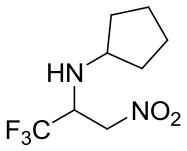
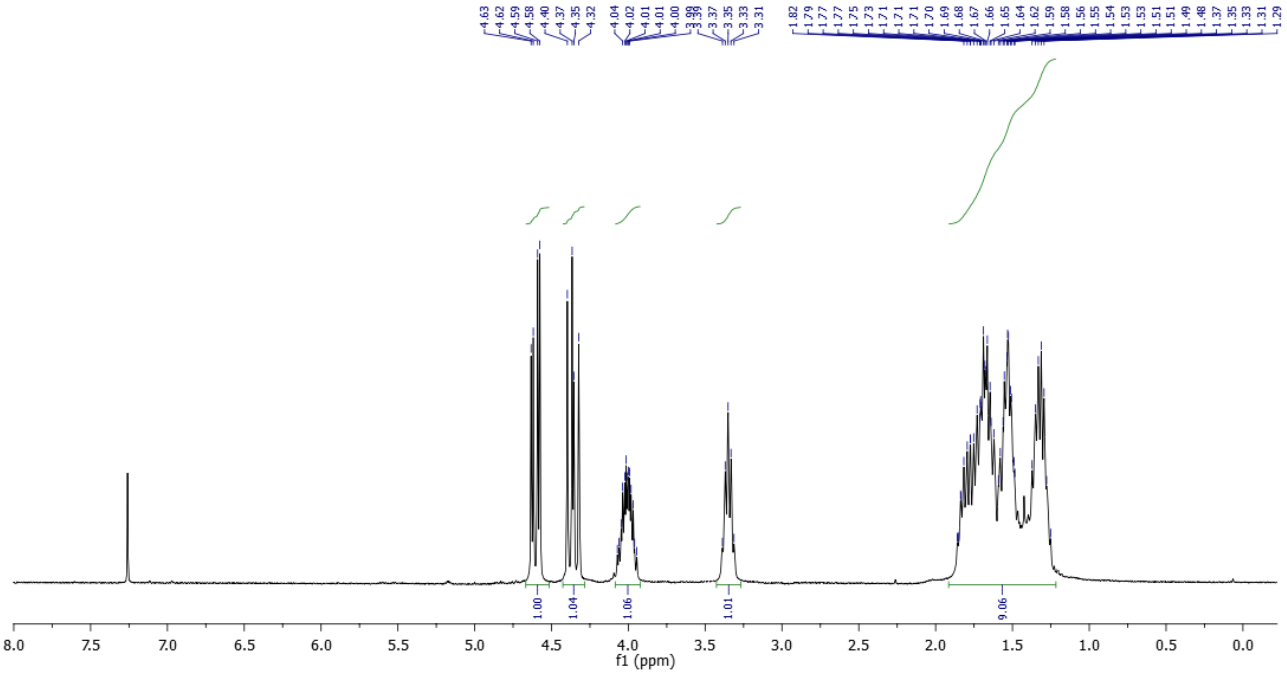
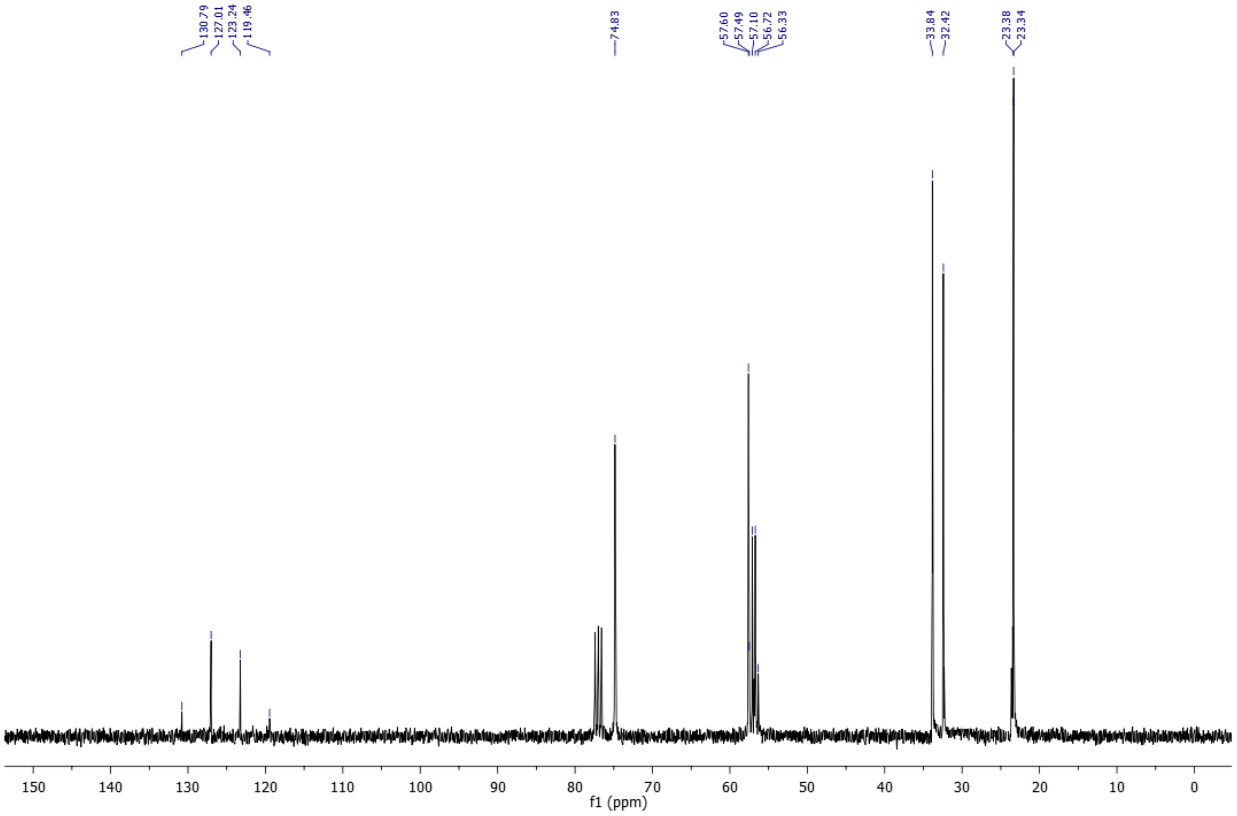


3g





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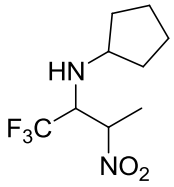
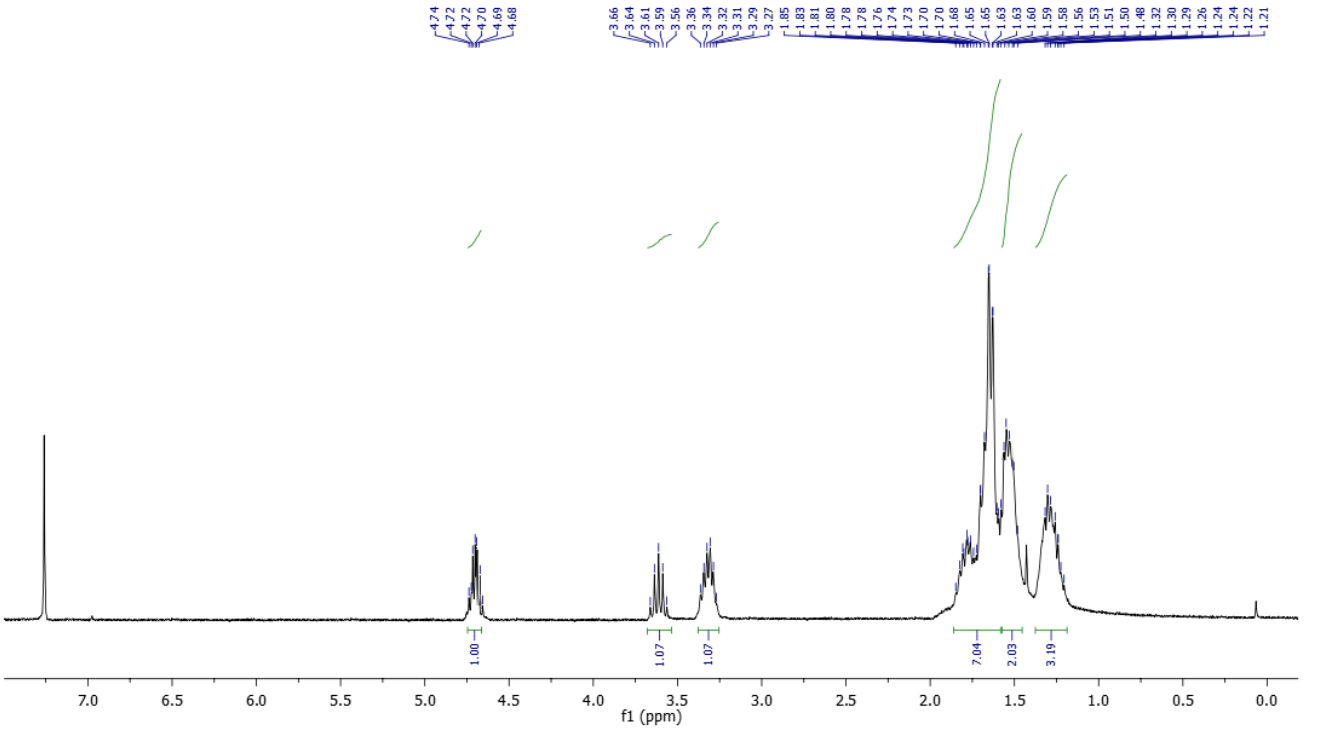
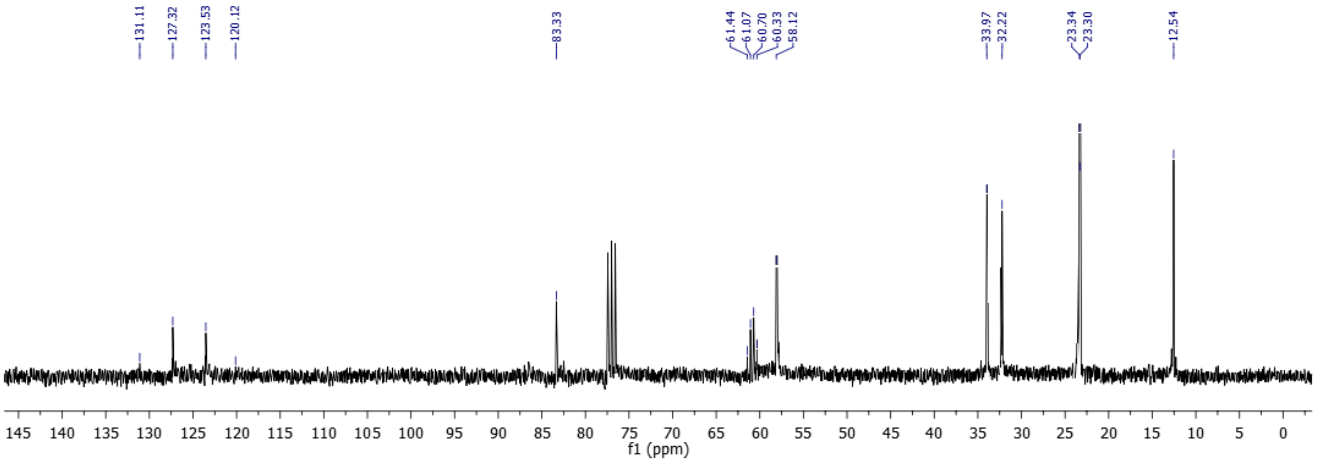


syn **3h**





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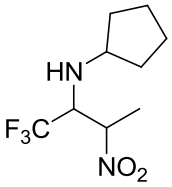

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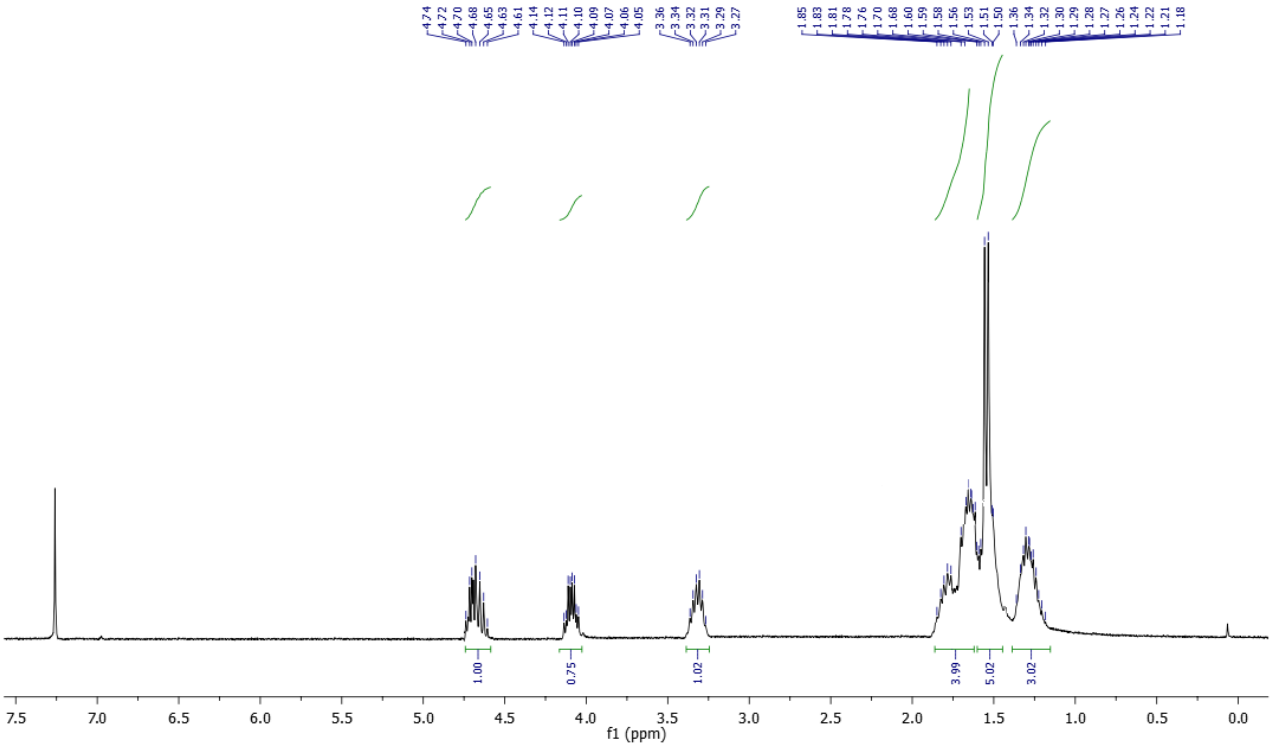

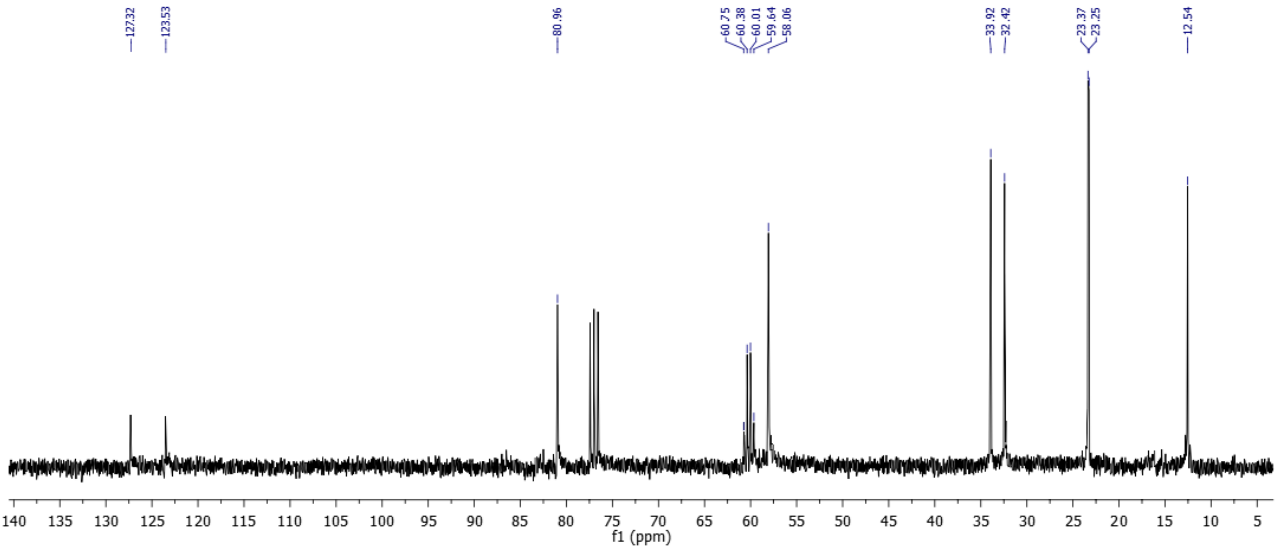

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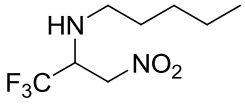

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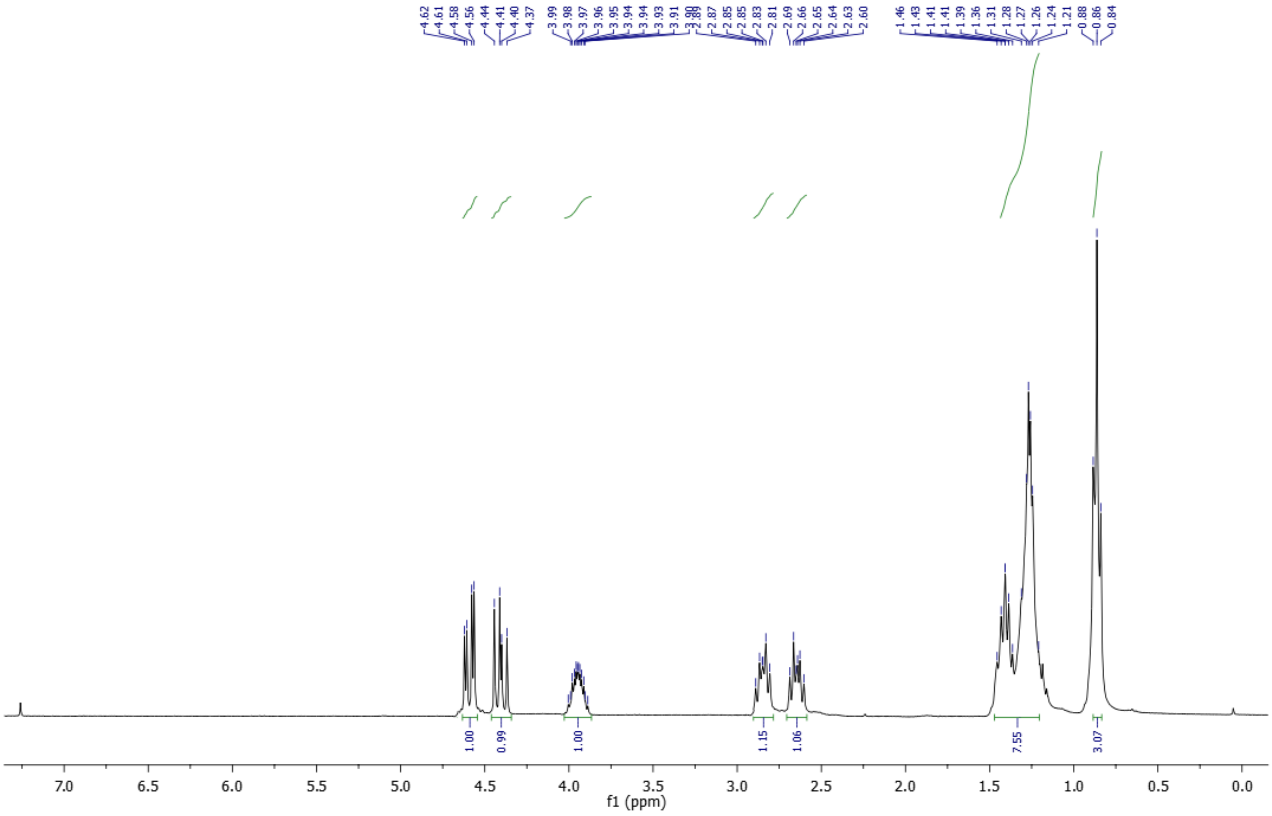

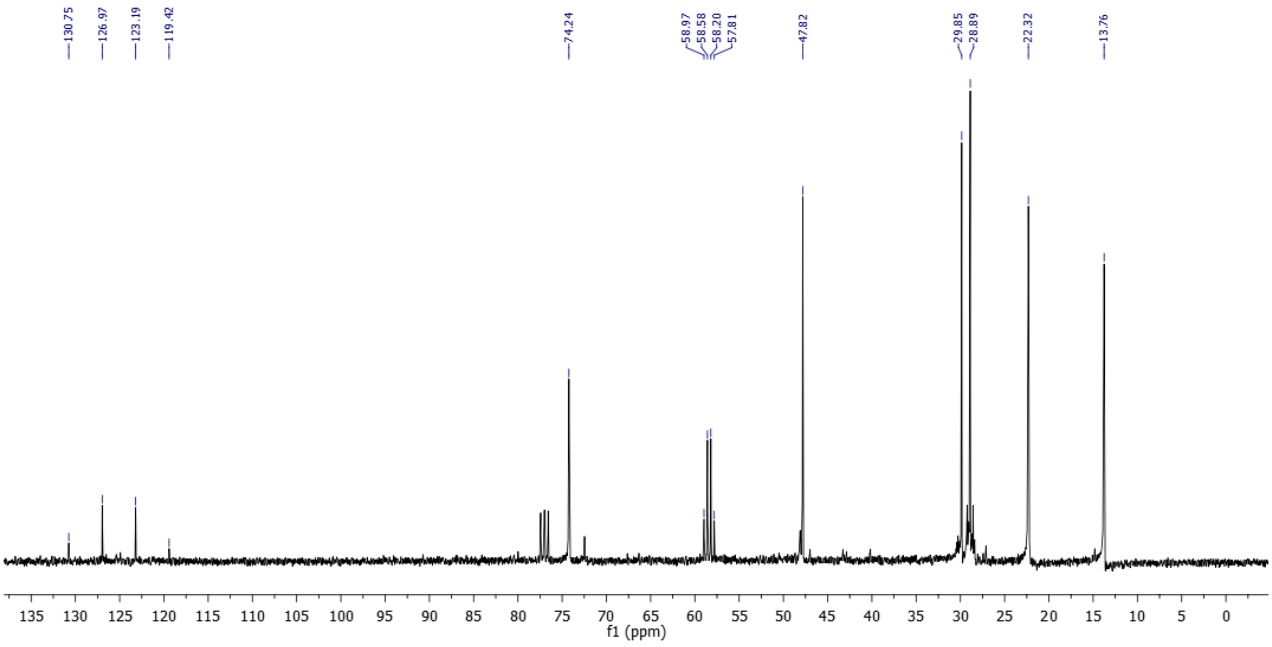

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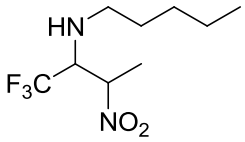
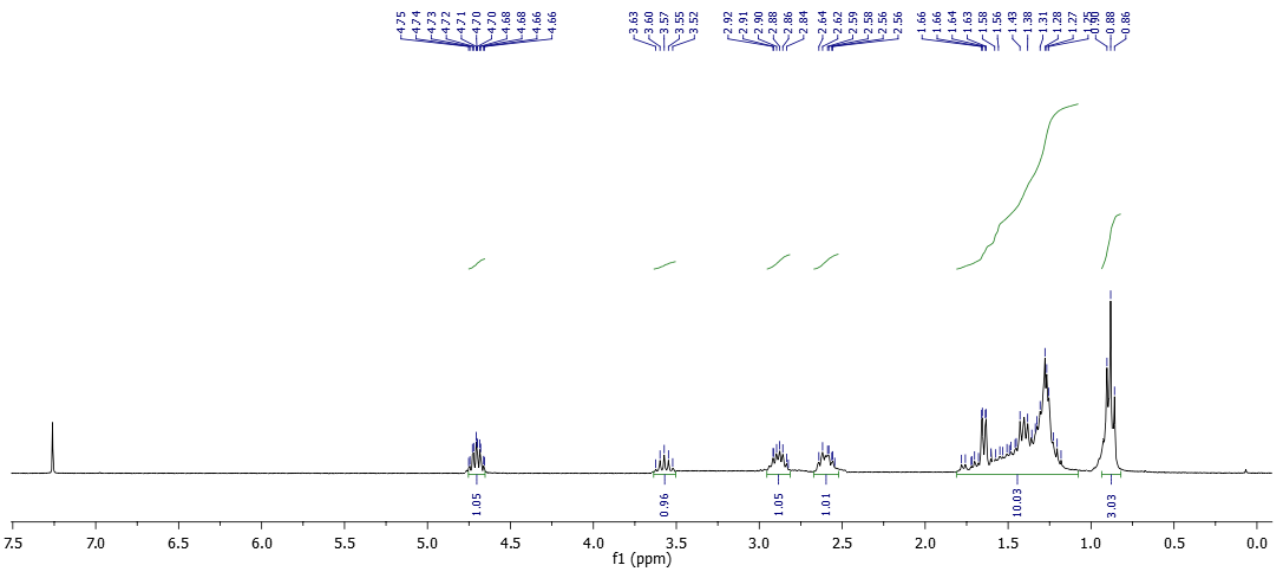
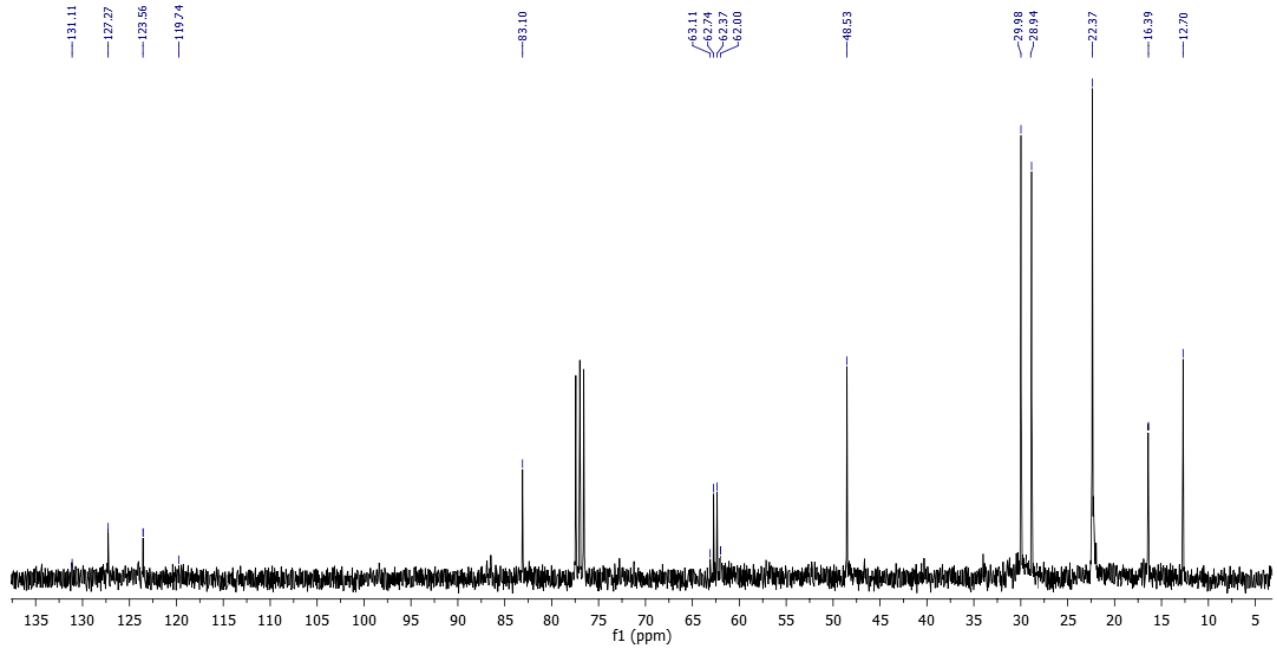


syn **3j**





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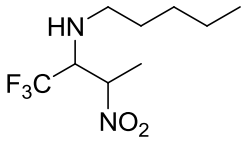

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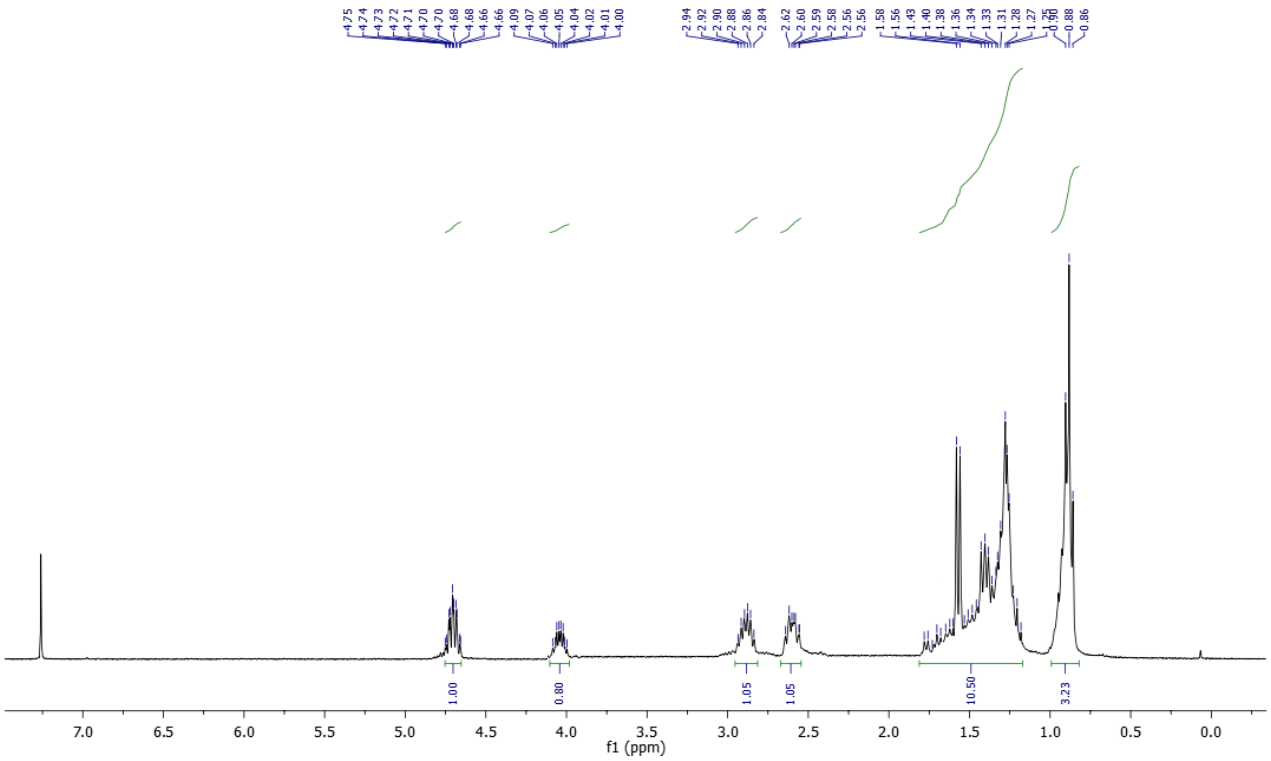

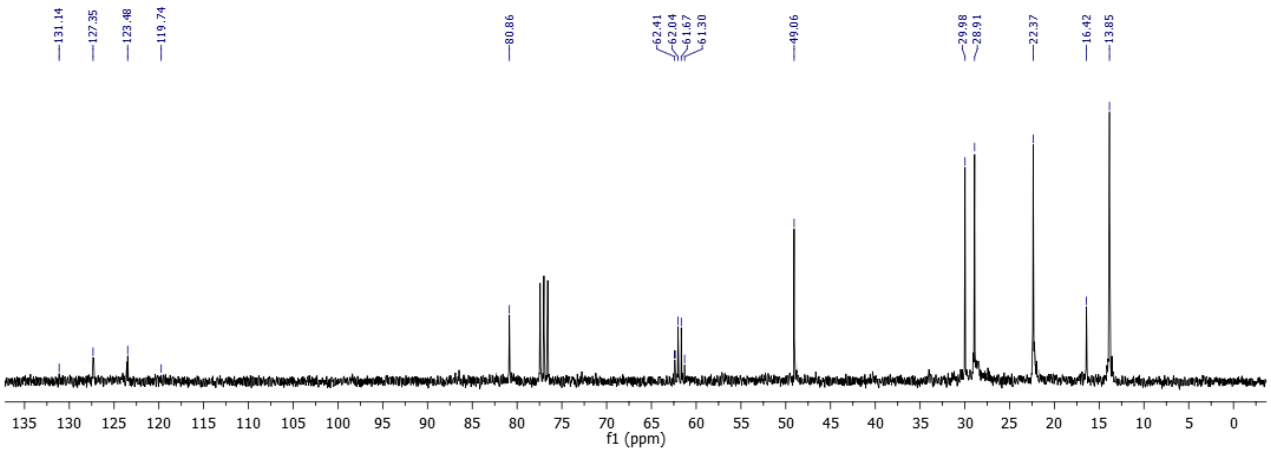

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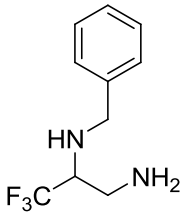

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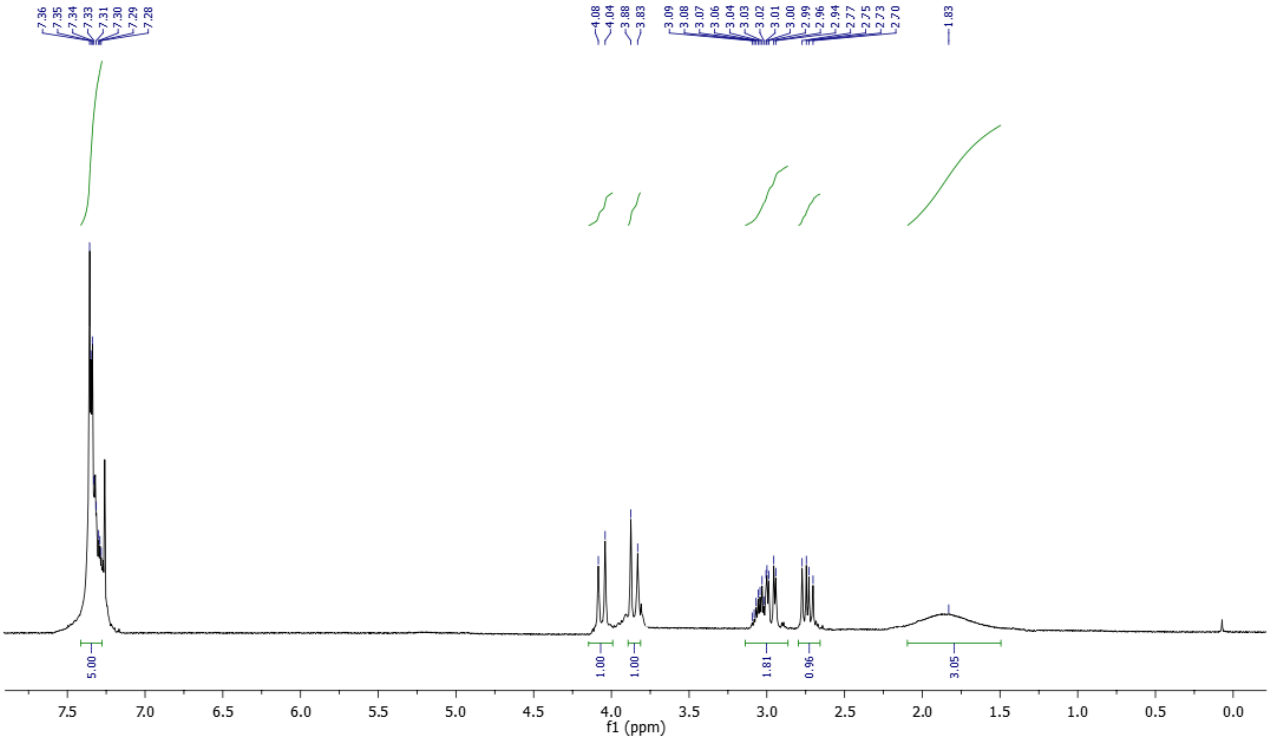

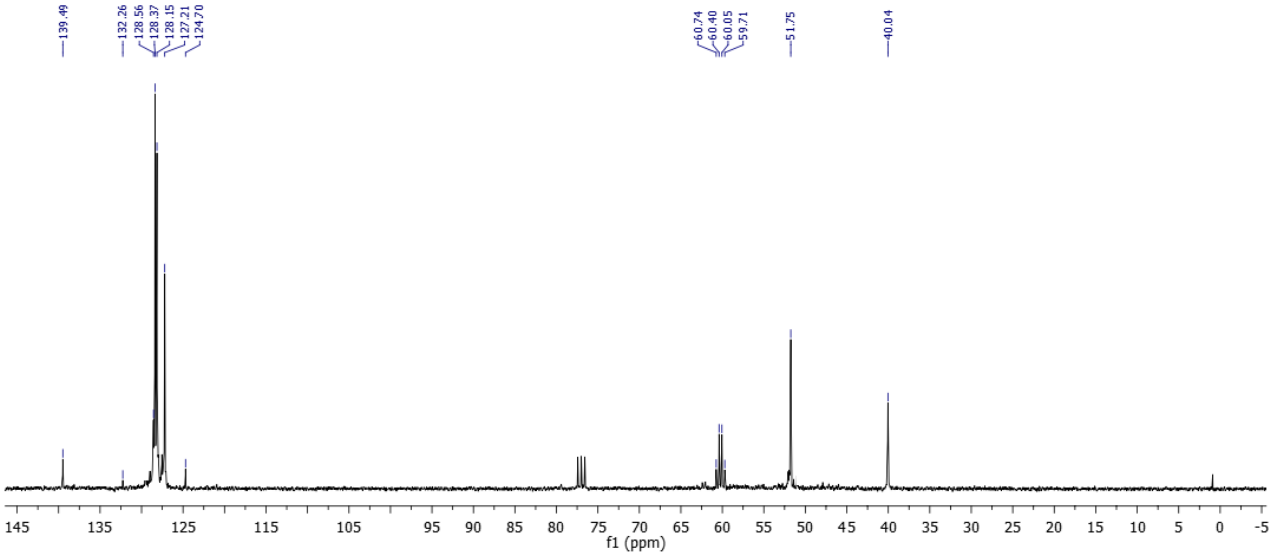

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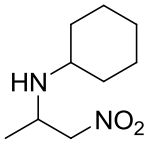
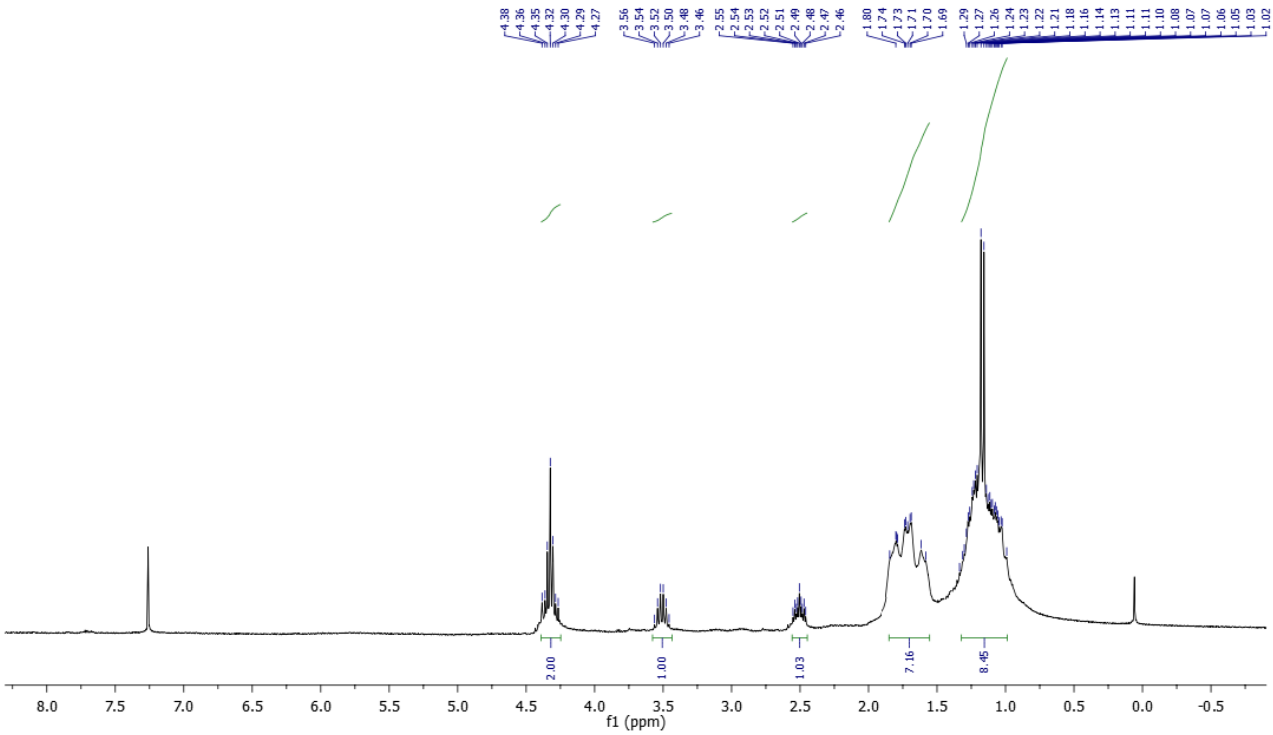
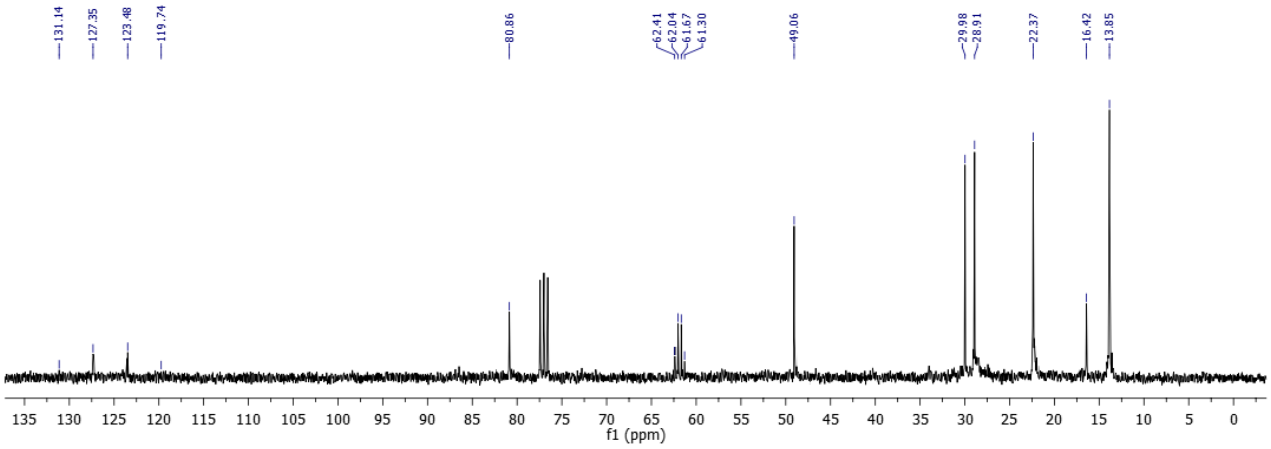


6a





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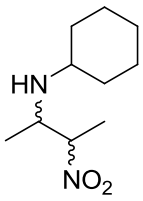
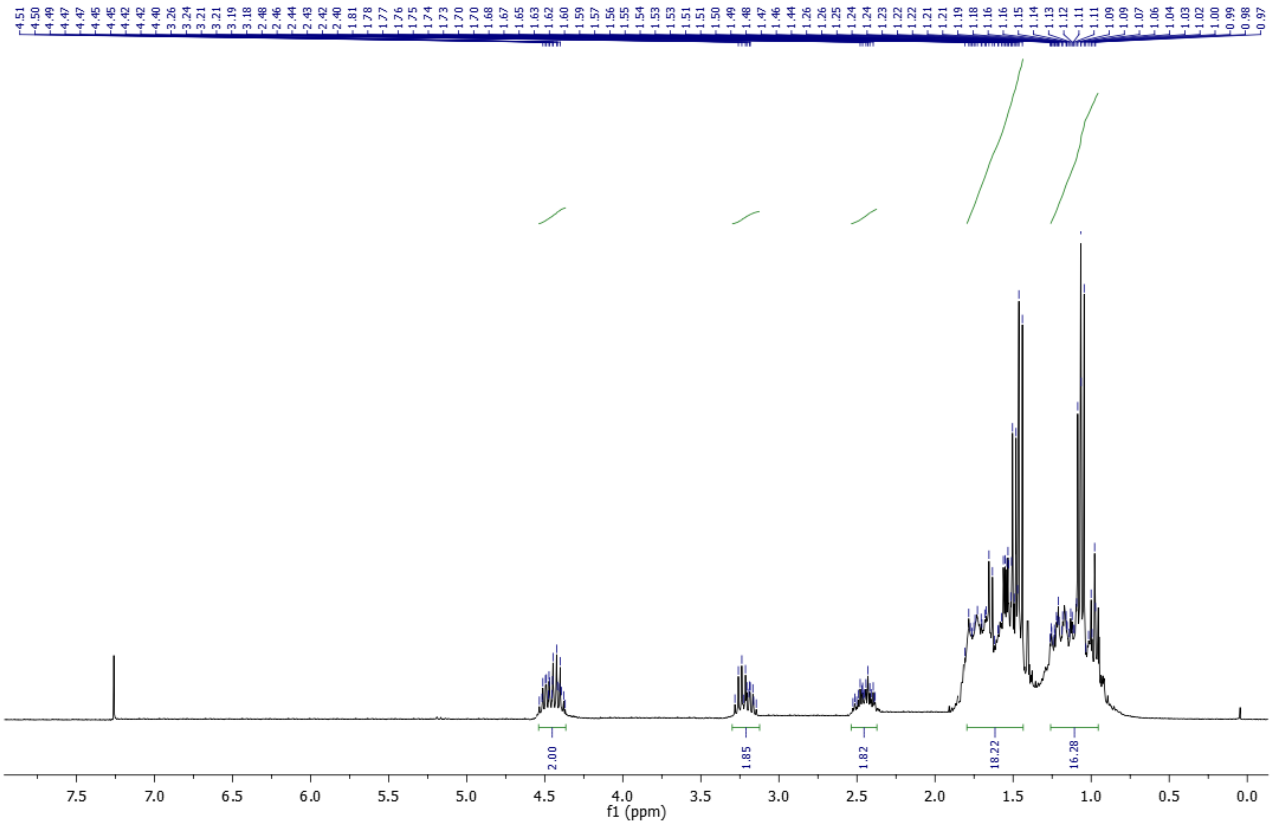
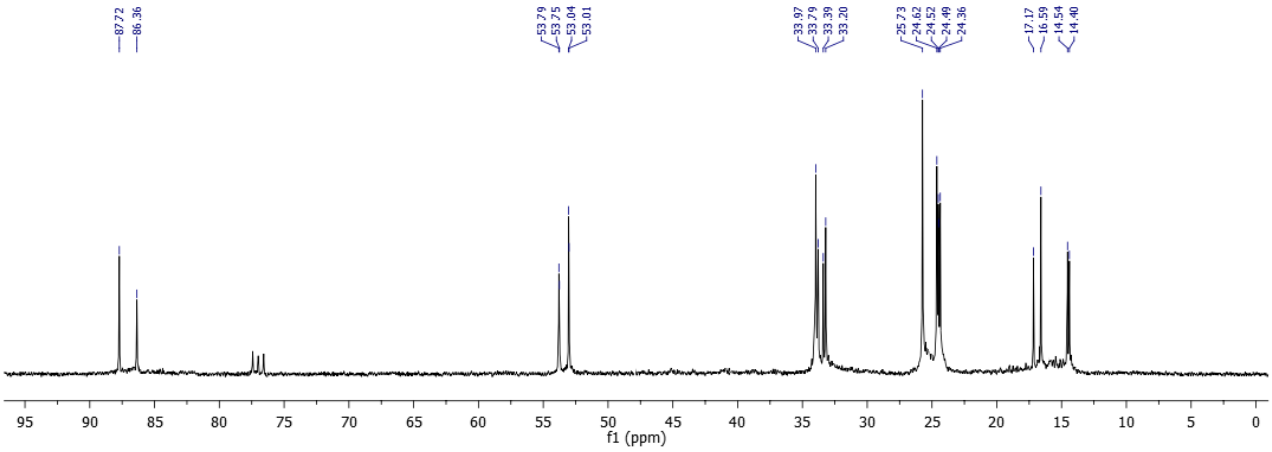


syn/*anti* **6b**





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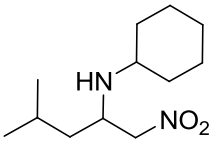

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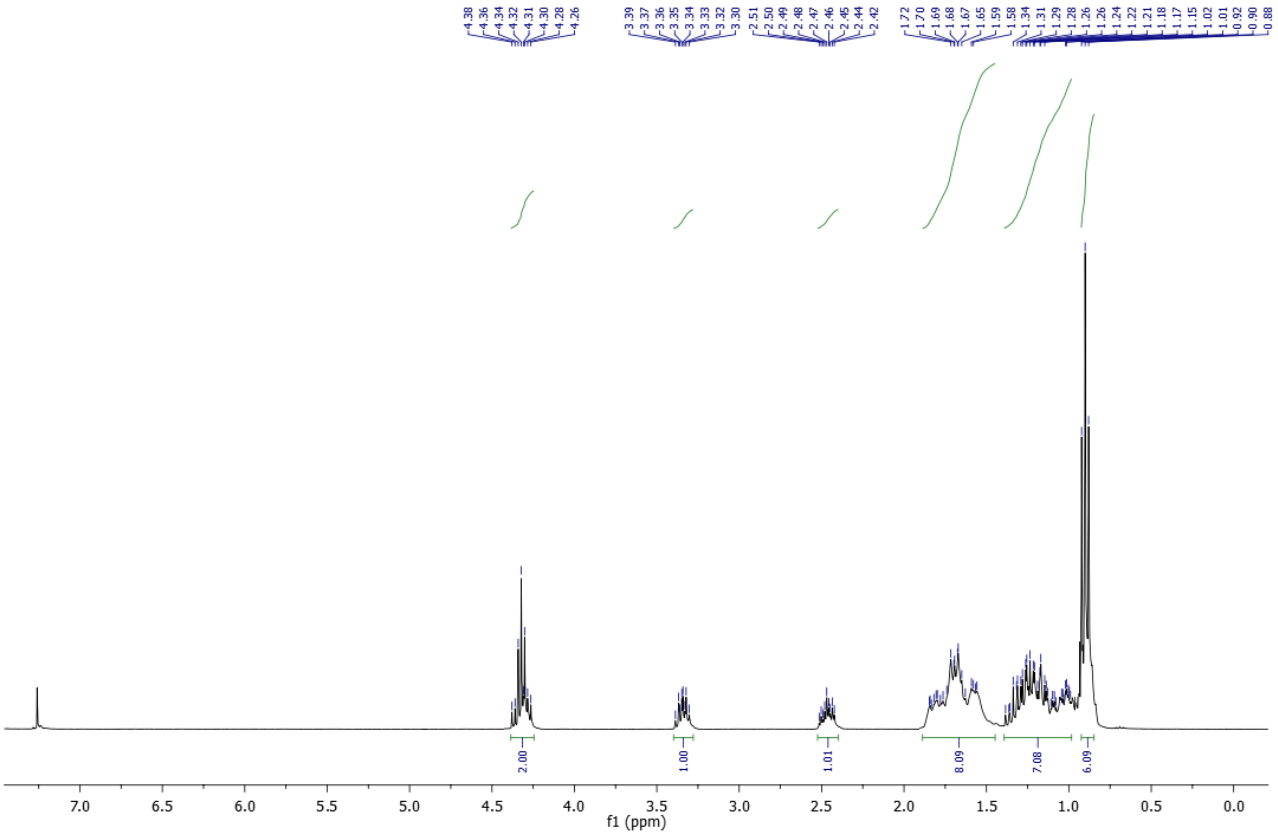

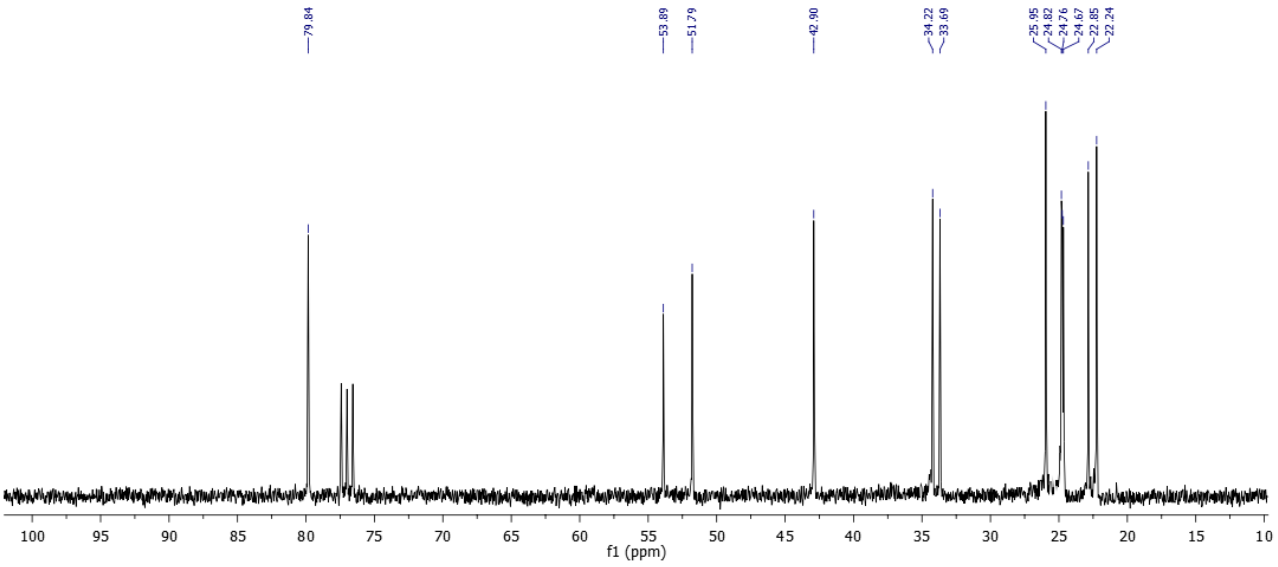

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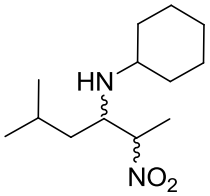

syn/*anti* **6d**