Dipolar HCP materials as alternatives to DMF solvent for azide-based synthesis

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General information

All reagents were purchased from available commercial suppliers and used without purification unless other noted. FT-IR spectra were obtained on Bruker Compass VERTEX 70. Steady state fluorescence spectra were recorded with a RF-5301 PC spectrophotometer. Thermogravimetric analysis (TGA) was performed using Pyris1 TGA in N_2 atmosphere by heating from room temperature to 800 °C. Scanning electron microscope (SEM) was conducted with SU8010. BET surface areas were measured using Micromeritics ASAP 2020 M. Elemental analysis was conducted in Vario Micro cube using CHNS mode. The X-ray photoelectron spectra (XPS) were obtained with the Thermo Scientific K-Alpha paired with a monochromatic Al Kα X-ray source (1486.6 eV). Solid ^{13}C NMR spectra of dipolar HCP materials were recorded on Bruker AV-400. ^{1}H and ^{13}C NMR spectra of organic compounds were recorded on Bruker 400. Chemical shifts are expressed in ppm relative to Me_4Si in $CDCl_3$ or DMSO-*d6*.

Experimental Section

Preparation of HCP materials

Synthesis of **HCP-DMF**: hypercrosslinking of monomer was conducted as described. In a typical procedure, 5 mmol monomer **M1** was added into a 100 mL round-bottom flask equipped with magnetic stirrer and contained 30 mL 1,2-dichloroethane (DCE), formaldehyde dimethyl acetal (FDA, 3.0 equiv.) as linker and anhydrous $FeCl_3$ (3.0 equiv.) as catalyst was subsequently added. The mixture was refluxed for 24 h in N_2 atmosphere to afford resulting precipitate which was then washed and filtrated by HCl (3 N) and EtOH. Resulting material was obtained via Soxhlet extraction for 48 h using EtOH and drying in a vacuum oven at 60 ^{o}C overnight.

Synthesis of **HCP-Ben**: 5 mmol benzene **M2** was used as monomer, target material was obtained according to the typical procedure.

Synthesis of **HCP-DMF-Ben**: 5mmol **M2** and 2 mmol **M1** were used as monomers, target material was obtained according to the typical procedure.

Synthesis of **HCP-DMF-SO_3H**: Sulfonation of the HCP-DMF was performed according to described procedure.[1] 1g **HCP-DMF** was swelled in DCE (40 mL) for 1 hour at 40 °C, followed by dropwise addition of 10 ml fresh DCE solution of “Acetylsulfuric acid” at 65 °C. After 2 h of stirring at 65 °C, the porous solid was filtrated and washed with water and ethanol and dried in in a vacuum oven at 60 °C overnight to give **HCP-DMF-SO_3H** as acid catalyst.

Synthesis of **HCP-Ben-SO_3H** (**HCP-DMF-Ben-SO_3H**): similar sulfonation procedures were carried out to obtained corresponding acidified HCP materials.

SEM images of HCP materials

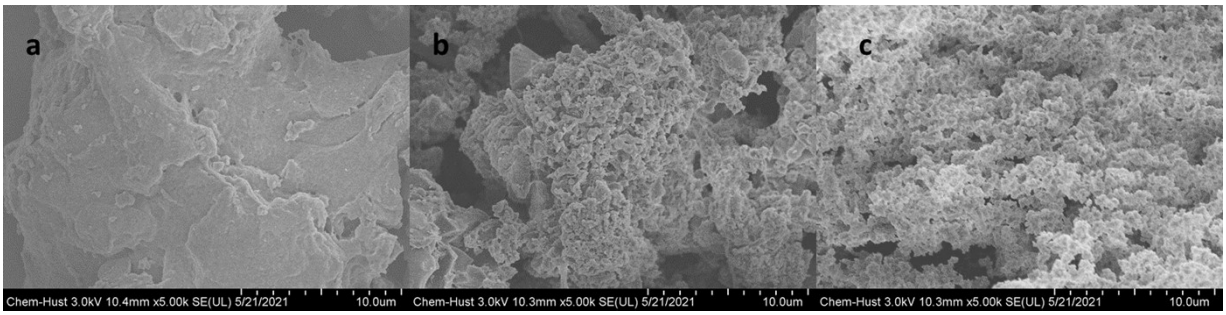


Figure S1. SEM images of (a) HCP-DMF, (b) HCP-DMF-Ben and (c) HCP -Ben

EA of prepared HCP materials

Table S1. Elemental analysis of acidified HCP materials

Material	Weight (mg)	N (%)	C (%)	H (%)	S (%)	-SO_3H (mmol/mg)[a]
HCP-DMF-SO_3H	2.0210	4.76	62.33	5.654	3.714	1.2×10^{-3}
HCP-DMF-Ben-SO_3H	1.9910	2.96	66.29	5.638	3.904	1.2×10^{-3}
HCP-Ben-SO_3H	2.2110	0.01	66.53	5.115	3.149	1.0×10^{-3}

[a]: Concentration of -SO_3H is calculated by the content of S.

Fluorescence spectroscopic measurements

30 mg HCP-Ben, HCP-DMF-Ben and HCP-DMF powder were soaked with 4 mL 3.3×10^{-3} mol/L dichloromethane (DCM) solution of Nile red for 24 hours respectively. DCM was removed by volatilizing in fume cupboard to obtain test samples. Steady state fluorescence spectra were recorded with a RF-5301 PC spectrophotometer.

Measurements of swelling degree *Q* (%)

60 mg (m_1) HCP-Ben, HCP-DMF-Ben and HCP-DMF were soaked with 2 mL EtOH (%) for 12 hours respectively. The swelling HCPs were subjected to suction filtration and weighing, and weight m_2 were recorded. *Q* (%) is calculated according to the following formula：

$$Q = \frac{m_2 - m_1}{m_1} \times 100\%$$

Typical procedure for the synthesis of 2a

To a V-type flask containing solution of *p*-methylbenzyl bromide **1a** (0.3 mmol) and NaN_3 (0.35 mmol) in 1 mL EtOH (95%) was added HCP-DMF (30 mg). The tube reactor equipped with triangular magnetic stirrer was then sealed to react at room temperature for 1.5-2 hours and the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was filtrated and washed with ethyl acetate. Organic filtrate was dried by Na_2SO_4 and concentrated under reduced pressure to afford yellow liquid **2a** (92 % yield) without further purification.

Typical procedure for the synthesis of 4a

To a V-type flask containing solution of *β*-nitrostyrene **3a** (0.3 mmol) and NaN_3 (0.35 mmol) in 1 mL EtOH (95%) was added HCP-DMF-SO_3H (20 mg). The tube reactor equipped with triangular magnetic stirrer was then sealed and heated to 60 ℃ for 4 hours and the reaction was monitored by TLC. After the completion of the reaction, reaction mixture allowed to cool to room temperature and was centrifuged. Organic liquid was then subjected to an isolation with preparative TLC (20 cm × 20 cm) by using eluting

solution (PE/EA = 5/1 (v/v)). Final compound **4a** was obtained in 92% after drying (Na_2SO_4) and removing eluent by reduced pressure distillation.

Typical procedure for the synthesis of 5a

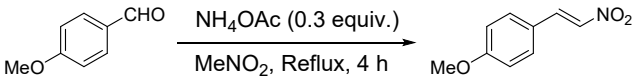
To a tube-type flask containing solution of *p*-methylbenzyl bromide **1a** (0.3 mmol) and NaN_3 (0.33 mmol) in 1 mL EtOH (95%) was added HCP-DMF-SO_3H (20 mg). The tube reactor equipped with triangular magnetic stirrer was then sealed to react at room temperature for 1.5–2 hours and the reaction was monitored by TLC. After the complete conversion of **1a**, *β*-nitrostyrene **3a** (0.33 mmol) was added into tube-type reactor. The reactor was then sealed and heated to 100 °C for 12 hours. After the completion of the reaction, reaction mixture allowed to cool to room temperature and was centrifuged. Organic liquid was then subjected to an isolation with preparative TLC (20 cm × 20 cm) by using eluting solution (PE/EA = 5/1 (v/v)). Final compound **5a** was obtained in 58% after drying (Na_2SO_4) and removing eluent by reduced pressure distillation.

Specific procedure for recycle experiment of HCP-DMF-SO_3H

To a V-type flask containing solution of *β*-nitrostyrene **3a** (0.3 mmol) and NaN_3 (0.35 mmol) in 1 mL EtOH (95%) was added HCP-DMF-SO_3H (20 mg). The tube reactor equipped with triangular magnetic stirrer was then sealed and heated to 60 °C for 4 hours and the reaction was monitored by TLC. After the completion of the reaction, reaction mixture allowed to cool to room temperature. HCP-DMF-SO_3H was centrifuged and washed with EtOH (95%) (2 mL×4), and then directly used for the next run.

Typical procedure for synthesis of nitroolefins (3a-3n)

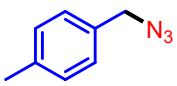
4-methoxybenzaldehyde **S1** (10.0 mmol) and NH_4OAc (3 mmol, 0.3 equiv.) were added into a round bottom flask charged with 20 mL $MeNO_2$. Then the reaction mixture was stirred with reflux for 4 h and monitored by TLC. After reaction completed, nitromethane was removed under reduced pressure. The residue was dissolved in ethyl acetate (5 mL) and washed with brine. Organic layer was extracted and dried over Na_2SO_4, and concentrated under reduced pressure to give the crude product. The obtained crude material passed through flash column chromatography to give pure target product **3a** in high yield. **3b** is commercially available.



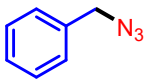
S1 **3a**

Scheme S1. Synthesis of starting materials **3a**.

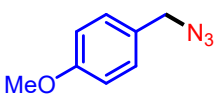
Characterization data of the obtained compounds



1-(azidomethyl)-4-methylbenzene (2a): yellow liquid, 92%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.24 – 7.17 (m, 4H), 4.29 (s, 2H), 2.36 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.3, 132.4, 129.7, 128.4, 54.8, 21.3 ppm.



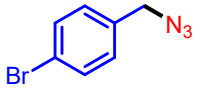
(azidomethyl)benzene (2b): colorless liquid, 89%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 – 7.28 (m, 5H), 4.33 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 135.5, 129.0, 128.4, 128.3, 54.9 ppm.



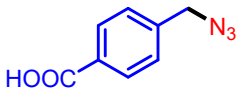
1-(azidomethyl)-4-methoxybenzene (2c): yellow liquid, 95%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 4.25 (s, 2H), 3.80 (s, 3H) ppm. ^{13}C NMR (101

MHz, $CDCl_3$) δ = 159.7, 129.8, 127.5, 114.3, 113.9, 55.4, 54.5 ppm.

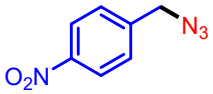
1-(azidomethyl)-4-bromobenzene (2d): colorless liquid, 91%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 4.31 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 134.5, 132.1, 129.9, 122.5, 54.2 ppm.



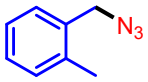
4-(azidomethyl)benzoic acid **(2e):** white solid, 96%, ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.95 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 4.51 (s, 2H) ppm. ^{13}C NMR (400 MHz, DMSO-d_6) δ = 168.5, 138.7, 134.6, 129.6, 123.0, 53.3 ppm.



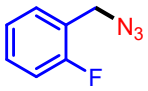
1-(azidomethyl)-4-nitrobenzene (2f): yellow liquid, 94%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.24 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 4.50 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.9, 142.8, 128.7, 124.2, 53.8 ppm.



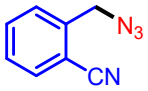
1-(azidomethyl)-2-methylbenzene (2g): colorless liquid, 89%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 – 7.18 (m, 4H), 4.34 (s, 2H), 2.36 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 136.9, 133.5, 130.8, 129.5, 128.8, 126.3, 53.2, 19.1 ppm.



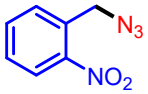
1-(azidomethyl)-2-fluorobenzene (2h): colorless liquid, 88%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 (dd, *J* = 13.6, 6.5 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 9.1 Hz, 1H), 4.41 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 161.0 (d, *J* = 247.7 Hz), 130.6 (d, *J* = 3.8 Hz), 130.4 (d, *J* = 8.1 Hz), 124.6 (d, *J* = 3.7 Hz), 122.8 (d, *J* = 15.4 Hz), 115.8 (d, *J* = 21.3 Hz), 48.6 (d, *J* = 3.3 Hz) ppm. ^{19}F NMR (377 MHz, $CDCl_3$) δ = -117.96 (dd, *J* = 10.9, 5.0 Hz) ppm.



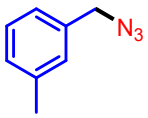
2-(azidomethyl)benzonitrile (2i): colorless liquid, 92%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 4.61 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.5, 133.7, 133.6, 129.5, 129.2, 117.4, 112.5, 53.0 ppm.



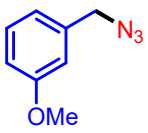
1-(azidomethyl)-2-nitrobenzene (2j): yellow liquid, 93%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11 (d, *J* = 8.3 Hz, 1H), 7.72 – 7.63 (m, 2H), 7.55 – 7.48 (m, 1H), 4.84 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.8, 134.1, 131.7, 130.2, 129.1, 125.4, 52.1 ppm.



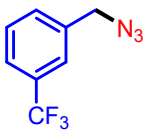
1-(azidomethyl)-3-methylbenzene (2k): yellow liquid, 88%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26 (t, *J* = 7.5 Hz, 1H), 7.13 (dd, *J* = 15.1, 8.6 Hz, 3H), 4.28 (s, 2H), 2.36 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.7, 135.4, 129.2, 129.1, 128.8, 125.4, 54.9, 21.5 ppm.



1-(azidomethyl)-3-methoxybenzene (2l): yellow liquid, 89%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 (t, *J* = 7.8 Hz, 1H), 6.89 (dd, *J* = 14.1, 5.4 Hz, 3H), 4.32 (s, 2H), 3.83 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.1, 137.0, 130.0, 120.5, 114.0, 113.8, 55.4, 54.9 ppm.

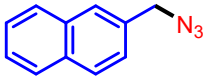


1-(azidomethyl)-3-(trifluoromethyl)benzene (2m): yellow liquid, 94%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 9.2 Hz, 2H), 7.53 (t, *J* = 6.4 Hz, 2H), 4.44 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 136.5, 131.3, 129.4, 125.2, 125.1 (q, *J* = 3.6 Hz), 124.80 (q, *J* = 3.8 Hz), 122.5,



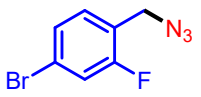
54.2 ppm. ^{19}F NMR (377 MHz, $CDCl_3$) δ = -62.72 ppm.

2-(azidomethyl)naphthalene (2n): yellow liquid, 92%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 (t, *J* = 7.9 Hz, 3H), 7.75 (s, 1H), 7.53 – 7.46 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 4.47 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 133.4, 133.2, 132.9, 128.9, 128.1, 127.9, 127.3, 126.6, 126.5, 126.0, 55.1 ppm.

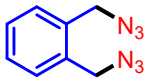


1-(azidomethyl)-3,5-dimethoxybenzene (2o): yellow liquid, 95%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.46 (d, *J* = 1.9 Hz, 2H), 6.43 (d, *J* = 2.0 Hz, 1H), 4.27 (s, 2H), 3.80 (s, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.9, 137.4, 105.8, 99.9, 99.7, 55.1, 54.6 ppm.

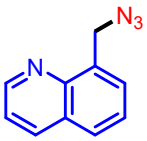
1-(azidomethyl)-4-bromo-2-fluorobenzene (2p): yellow liquid, 92%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 (dd, J = 14.1, 4.9 Hz, 2H), 7.23 (t, J = 7.8 Hz, 1H), 4.37 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.7 (d, J = 252.4 Hz), 131.5 (d, J = 4.5 Hz), 128.0 (d, J = 3.8 Hz), 122.8 (d, J = 9.4 Hz), 122.1 (d, J = 15.3 Hz), 119.5 (d, J = 24.6 Hz), 48.1 (d, J = 3.0 Hz) ppm. ^{19}F NMR (377 MHz, $CDCl_3$) δ = -115.0, -115.0, -115.0 ppm.



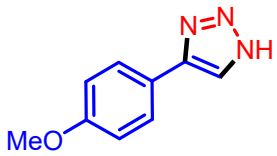
1,2-bis(azidomethyl)benzene (2q): colorless liquid, 93%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 – 7.34 (m, 4H), 4.44 (s, 4H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 134.0, 130.3, 129.1, 52.3 ppm.



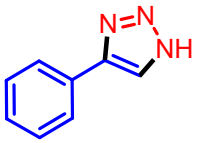
7-(azidomethyl)quinoline (2r): colorless liquid, 95%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.95 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 6.9 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.05 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.1, 146.3, 136.3, 134.1, 129.2, 128.5, 128.4, 126.3, 121.5, 51.1 ppm.



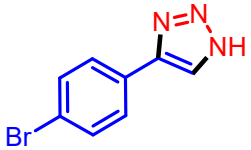
4-(4-methoxyphenyl)-1H-1,2,3-triazole (**4a**)[2]: White solid, 92%, ^{1}H NMR (400 MHz, DMSO-d_6), 1 drop TFA, δ = 8.22 (s, 1H), 7.78 (d, J = 8.5 Hz, 2H), 7.01 (d, J = 8.5 Hz, 2H), 3.78 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6), 1 drop TFA, δ = 144.8, 127.0, 122.8, 116.6, 114.4, 113.7, 55.2 ppm.



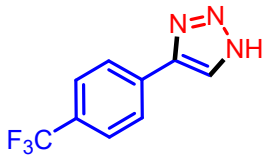
4-phenyl-1H-1,2,3-triazole (**4b**): White solid, 96%, ^{1}H NMR (400 MHz, DMSO-d_6), 1 drop TFA, δ = 8.34 (s, 1H), 7.87 (d, J = 7.4 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6), 1 drop TFA, δ = 145.2, 130.3, 129.0, 128.1, 127.3, 125.6 ppm.



4-(4-Bromophenyl)-1H-1,2,3-triazole (**4c**)[2]: White solid. 93%, ^{1}H NMR (400 MHz, DMSO-d_6), 1 drop TFA, δ = 8.39 (s, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6), 1 drop TFA, δ = 144.5, 132.0, 129.8, 127.6, 121.2 ppm.

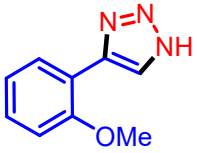


4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**4d**): White solid. 86%, ^{1}H NMR (400 MHz, DMSO-d_6), 1 drop TFA, δ = 8.52 (s, 1H), 8.09 (d, *J* = 8.1 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ= 144.3, 134.6, 128.3 (d, *J* = 31.9 Hz), 126.1, 125.9 (q, *J* = 3.7 Hz), 125.6, 122.9 ppm. ^{19}F NMR (377 MHz, DMSO-d_6) δ= -61.13

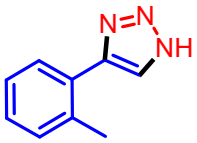


ppm.

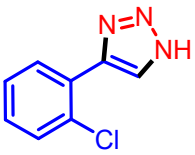
4-(2-Methoxyphenyl)-1H-1,2,3-triazole (**4e**)[2]: White solid, 89%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.17 (s, 1H), 7.93 (s, 1H), 7.33 (t, J = 7.8 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.99 (d, J = 8.3 Hz, 1H), 3.94 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.0, 156.1, 129.9, 128.1, 121.2, 111.3, 55.6 ppm.



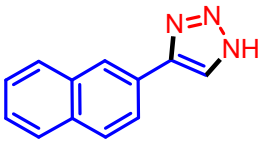
4-(*o*-Tolyl)-1H-1,2,3-triazole (**4f**)[2]: White solid, 82%, ^{1}H (400 MHz, DMSO-d_6) δ = 7.87 (s, 1H), 7.59 (d, J = 7.3 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.25 (t, J = 6.6 Hz, 1H), 2.44 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ = 136.2, 131.0, 129.2, 128.8, 126.2, 21.1 ppm.



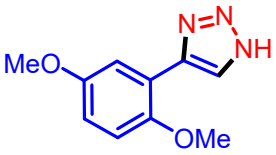
4-(2-Chlorophenyl)-1H-1,2,3-triazole (**4g**)[2]: White solid. 91%, ^{1}H NMR (400 MHz, DMSO-d_6), 1 drop TFA, δ = 8.35 (s, 1H), 7.99 – 7.87 (m, 1H), 7.56 (dd, J = 7.7, 0.9 Hz, 1H), 7.49 – 7.35 (m, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6), 1 drop TFA, δ = 142.3, 131.0, 130.3, 130.3, 129.7, 129.3, 127.6 ppm.



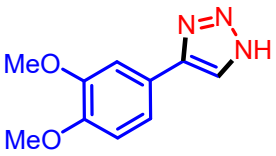
4-(Naphthalen-2-yl)-1H-1,2,3-triazole (**4h**)[2]: White solid, 87%, ^{1}H NMR (400 MHz, DMSO-d_6), 1 drop TFA, δ = 8.46 (d, J = 20.8 Hz, 1H), 8.07 – 7.87 (m, 2H), 7.59 – 7.48 (m, 1H) (dd, J = 8.9, 2.9 Hz, 1H), 3.85 (s, 3H), 3.76 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6), 1 drop TFA, δ = 145.4, 133.2, 132.7, 128.6, 128.0, 127.9, 127.7, 126.7, 126.3, 124.1, 123.9 ppm.



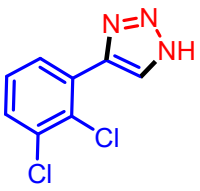
4-(2,5-dimethoxyphenyl)-1H-1,2,3-triazole (**4i**)[2]: White solid, 83%, ^{1}H NMR (400 MHz, DMSO-d_6), 1 drop TFA, δ = 8.21 (s, 1H), 7.56 (d, J = 3.0 Hz, 1H), 7.06 (d, J = 9.0 Hz, 1H), 6.91 (dd, J = 8.9, 2.9 Hz, 1H), 3.85 (s, 3H), 3.76 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6), 1 drop TFA, δ =162.4, 153.3, 150.2, 140.5, 119.2, 114.4, 113.0, 112.4, 56.0, 55.5 ppm.



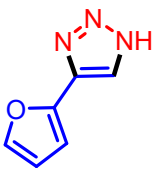
4-(3,4-Dimethoxyphenyl)-1H-1,2,3-triazole (**4j**)[2]: Yellow solid, 94%, ^{1}H NMR (400 MHz, DMSO-d_6), 1 drop TFA, δ = 8.26 (s, 1H), 7.42 (s, 1H), 7.41 – 7.32 (m, 1H), 7.02 (d, J = 8.3 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6), 1 drop TFA, δ =149.2, 149.0, 145.0, 123.0, 118.2, 116.6, 112.2, 109.4, 55.6, 55.6 ppm.



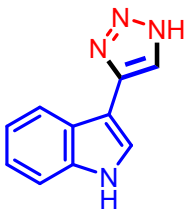
4-(2,3-Dichlorophenyl)-1H-1,2,3-triazole (**4k**)[2]: White solid, 81%, ^{1}H NMR (400 MHz, DMSO-d_6), 1 drop TFA, δ = 8.41 (s, 1H), 7.88 (dd, J = 7.8, 1.2 Hz, 1H), 7.65 (dd, J = 8.0, 1.4 Hz, 1H), 7.45 (t, J = 7.9 Hz, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6), 1 drop TFA, δ =142.3, 132.8, 131.9, 130.1, 129.0, 128.5, 116.6, 113.7 ppm.



4-(Furan-2-yl)-1H-1,2,3-triazole (**4l**)[2]: Yellow solid, 85%, ^{1}H NMR (400 MHz, DMSO-d_6), 1 drop TFA, δ = 8.14 (s, 1H), 7.75 (d, J = 1.0 Hz, 1H), 6.82 (d, J = 2.9 Hz, 1H), 6.59 (dd, J = 3.3, 1.8 Hz, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6), 1 drop TFA, δ =145.8, 143.0, 138.0, 126.8, 111.7, 107.1 ppm.

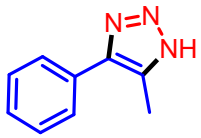


3-(1H-1,2,3-triazol-4-yl)-1H-indole (**4m**)[2]: Yellow solid, 58%, ^{1}H NMR (400 MHz, DMSO-d_6), 1 drop TFA,



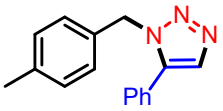
δ = 12.27 (s, 1H), 8.42 (d, J = 13.4 Hz, 1H), 8.25 (d, J = 3.0 Hz, 1H), 8.01 (d, J = 13.4 Hz, 1H), 7.95 (d, J = 7.7 Hz, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.25 (ddd, J = 15.0, 13.8, 7.0 Hz, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6), 1 drop TFA, δ =137.7, 136.4, 134.8, 131.2, 124.7, 123.4, 122.0, 120.6, 112.9, 108.3 ppm.

5-Methyl-4-phenyl-1H-1,2,3-triazole (**4n**)[2]: White solid, 84%, ^{1}H NMR (400 MHz, DMSO-d_6), 1 drop TFA,



δ = 7.70 (d, J = 7.3 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 2.44 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6), 1 drop TFA, δ = 141.7, 131.1, 128.8, 127.6, 126.7, 10.6 ppm.

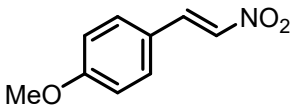
1-(4-methylbenzyl)-4-phenyl-1H-1,2,3-triazole (5a):[3] Yellow oil, 58%, ^{1}H NMR (400 MHz, $CDCl_3$) δ =



7.73 (s, 1H), 7.42 (d, *J* = 6.3 Hz, 3H), 7.30 – 7.23 (m, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 5.50 (s, 2H), 2.31 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.1, 138.0, 133.2, 132.5, 129.5, 128.9, 127.2, 127.0, 51.6, 21.1 ppm. HRMS (TOF, ESI): m/z calcd for $C_{16}H_{16}N_3$, $[M+H]^+$= 250.1336, found 250.1344.

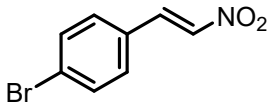
Starting materials

(***E***)**-1-methoxy-4-(2-nitrovinyl)benzene** (**3a**): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.97 (d, J =



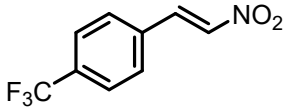
13.6 Hz, 1H), 7.52(d, J = 13.6 Hz, 1H), 7.50(d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ = 163.1, 139.2, 135.2, 131.3, 122.7, 115.1, 55.7 ppm.

(***E***)**-1-bromo-4-(2-nitrovinyl)benzene** (**3c**): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.94 (d, J = 13.7



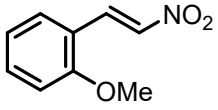
Hz, 1H), 7.59 (dd, J = 11.0, 6.9 Hz, 3H), 7.41 (d, J = 8.4 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ = 137.9, 137.6, 132.9, 130.5, 129.1, 126.9 ppm.

(***E***)**-1-(2-nitrovinyl)-4-(trifluoromethyl)benzene** (**3d**): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.03



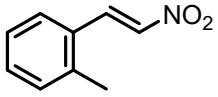
(d, *J* = 13.7 Hz, 1H), 7.71 (dd, *J* = 18.7, 8.3 Hz, 4H), 7.63 (d, *J* = 13.7 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ = 138.99, 137.25, 133.6, 133.6 (d, *J* = 3.3 Hz), 129.40, 126.47 (q, *J* = 3.7 Hz), 123.61 (d, *J* = 272.5 Hz) ppm. ^{19}F NMR (377 MHz, $CDCl_3$) δ = -63.16 ppm.

(***E***)**-1-methoxy-2-(2-nitrovinyl)benzene** (**3e**): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.12 (d, *J* =



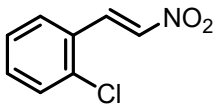
13.6 Hz, 1H), 7.87 (d, *J* = 13.6 Hz, 1H), 7.45 (dd, *J* = 13.4, 7.0 Hz, 2H), 7.05 – 6.93 (m, 2H), 3.94 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ = 159.6, 138.3, 135.6, 133.6, 132.5, 121.2, 119.2, 111.5, 55.7 ppm.

(***E***)**-1-methyl-2-(2-nitrovinyl)benzene** (**3f**): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.30 (d, J = 13.6



Hz, 1H), 7.52 (s, 1H), 7.50 (d, J = 5.1 Hz, 1H), 7.39 (t, J = 7.2 Hz, 1H), 7.26 (dd, J = 12.3, 7.5 Hz, 2H), 2.48 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ = 139.3, 137.7, 136.9, 132.0, 131.5, 129.0, 127.5, 126.9, 20.0 ppm.

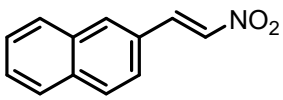
(***E***)**-1-chloro-2-(2-nitrovinyl)benzene** (**3g**): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.40 (d, J = 13.7



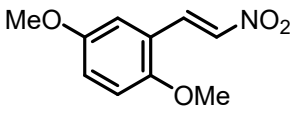
Hz, 1H), 7.63 – 7.55 (m, 2H), 7.49 (dd, J = 8.0, 0.8 Hz, 1H), 7.43 (td, J = 7.8, 1.4 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ = 138.9, 136.2, 135.2,

133.0, 130.9, 128.7, 128.6, 127.6 ppm.

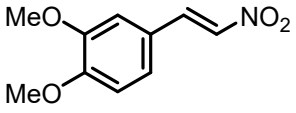
(*E*)-2-(2-nitrovinyl)naphthalene (**3h**): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.14 (d, J = 13.6 Hz, 1H), 7.99 (s, 1H), 7.91 – 7.84 (m, 3H), 7.69 (d, J = 13.6 Hz, 1H), 7.62 – 7.54 (m, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ = 139.3, 137.2, 135.0, 133.2, 132.4, 129.5, 128.9, 128.5, 128.1, 127.6, 127.4, 123.4 ppm.



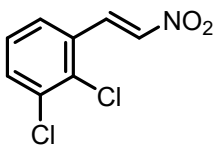
(*E*)-1,4-dimethoxy-2-(2-nitrovinyl)benzene (**3i**): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.11 (d, *J* = 13.6 Hz, 1H), 7.85 (d, *J* = 13.6 Hz, 1H), 7.02 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.96 (d, *J* = 3.0 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 1H), 3.90 (s, 3H), 3.80 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ = 154.0, 153.5, 138.5, 135.3, 119.5, 119.2, 116.3, 112.4, 56.0, 55.9 ppm.



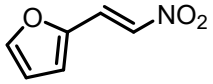
(*E*)-1,2-dimethoxy-4-(2-nitrovinyl)benzene (**3j**): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.96 (d, J = 13.6 Hz, 1H), 7.53 (d, J = 13.6 Hz, 1H), 7.17 (dd, J = 8.3, 1.9 Hz, 1H), 7.01 (d, J = 1.9 Hz, 1H), 6.91 (d, J = 8.3 Hz, 1H), 3.94 (s, 3H), 3.93 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ = 152.9, 149.7, 139.5, 135.3, 124.8, 122.9, 111.5, 110.3, 56.2, 56.2 ppm.



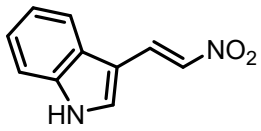
(*E*)-1,2-dichloro-3-(2-nitrovinyl)benzene (**3k**): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.41 (d, J = 13.7 Hz, 1H), 7.60 (dd, J = 8.0, 1.3 Hz, 1H), 7.55 (d, J = 13.7 Hz, 1H), 7.49 (dd, J = 7.8, 1.1 Hz, 1H), 7.29 (t, J = 7.9 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ = 139.8, 135.2, 134.9, 134.2, 133.4, 131.0, 127.9, 126.8 ppm.



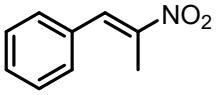
(*E*)-2-(2-nitrovinyl)furan (**3m**): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.77 (d, J = 13.2 Hz, 1H), 7.59 (d, J = 1.0 Hz, 1H), 7.52 (d, J = 13.2 Hz, 1H), 6.89 (d, J = 3.5 Hz, 1H), 6.58 (dd, J = 3.4, 1.8 Hz, 1H). ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ = 147.0, 146.8, 135.1, 125.6, 120.1, 113.5 ppm.



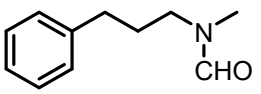
(*E*)-3-(2-nitrovinyl)-1H-indole (**3l**): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.76 (s, 1H), 8.30 (d, J = 13.5 Hz, 1H), 7.84 – 7.77 (m, 2H), 7.69 (d, J = 2.9 Hz, 1H), 7.48 (dd, J = 5.9, 2.9 Hz, 1H), 7.39 – 7.31 (m, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ = 133.6, 133.2, 132.5, 124.5, 122.8, 120.7, 112.4, 109.9, 100.1, 94.8 ppm.



(*E*)-(2-nitroprop-1-en-1-yl)benzene (**3n**): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.10 (s, 1H), 7.53 – 7.36 (m, 5H), 2.46 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ = 147.9, 133.7, 132.6, 130.1, 130.1, 129.0, 14.2 ppm.



***N*-methyl-N-(3-phenylpropyl)formamide(M1)**: Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$, mixtures of rotamers) minor rotamer: δ = 8.06 (s, 1H), major rotamer: 8.02 (s, 1H), 7.37 – 7.28 (m, 4H), 7.22 (dt, *J* = 12.1, 5.6 Hz, 5H), 3.45 – 3.38 (m, 1H), 3.26 (t, *J* = 7.0 Hz, 2H), 2.94 (s, 2H), 2.89 (s, 3H), 2.64 (dd, *J* = 16.6, 9.1 Hz, 4H), 2.45 – 2.36 (m, 1H), 1.92 (dq, *J* = 15.4, 7.6 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ = 162.7, 162.6, 142.3, 141.4, 140.6, 128.6, 128.4, 128.4, 128.3, 126.2, 126.0, 125.7, 57.1, 48.8, 43.9, 42.1, 34.5, 33.7, 33.1, 32.3, 29.3, 29.2, 29.0, 28.4 ppm. IR: 2930, 2858, 1672, 1495,1454, 1396, 1086, 1072, 750, 700 cm^{-1}. HRMS calcd. for $[C_{11}H_{16}NO]^+$: 178.1226; Found: 178.1232.

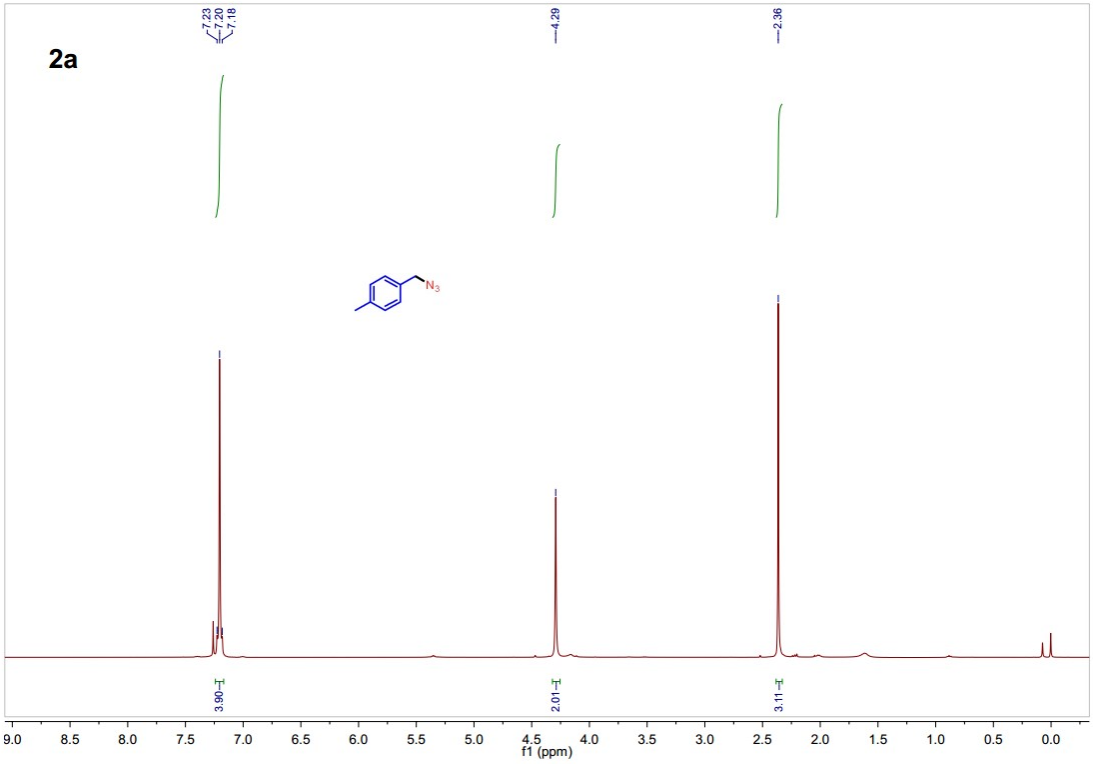


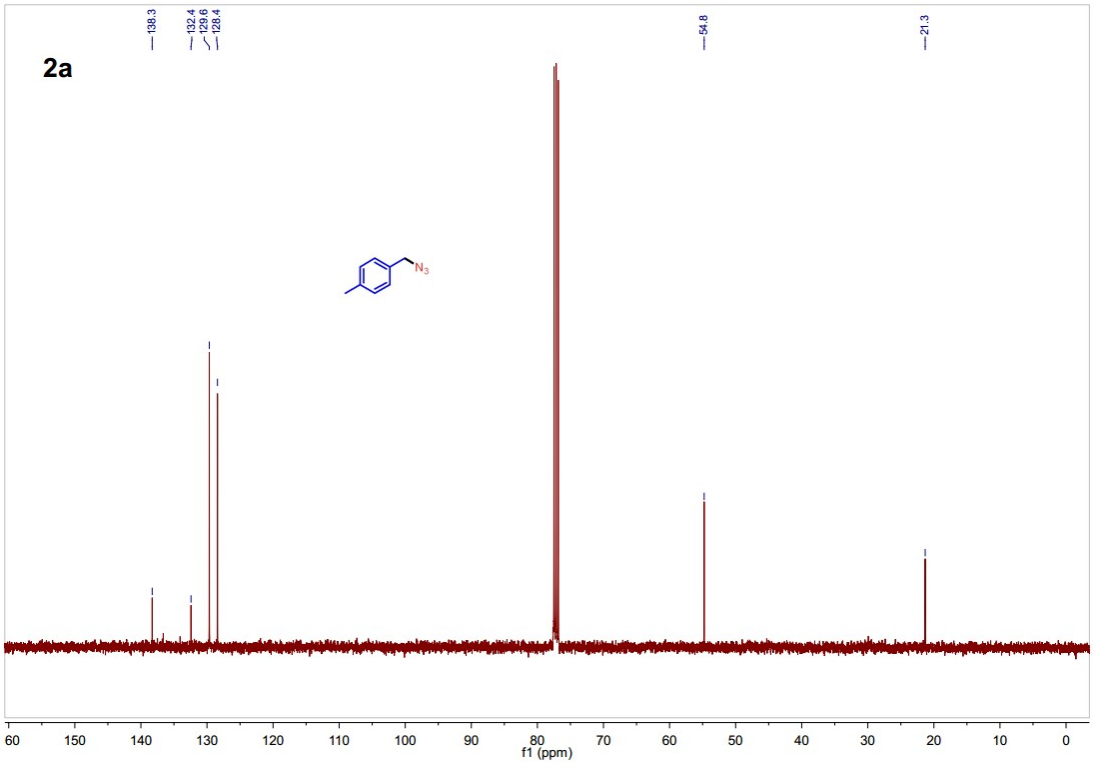
Reference

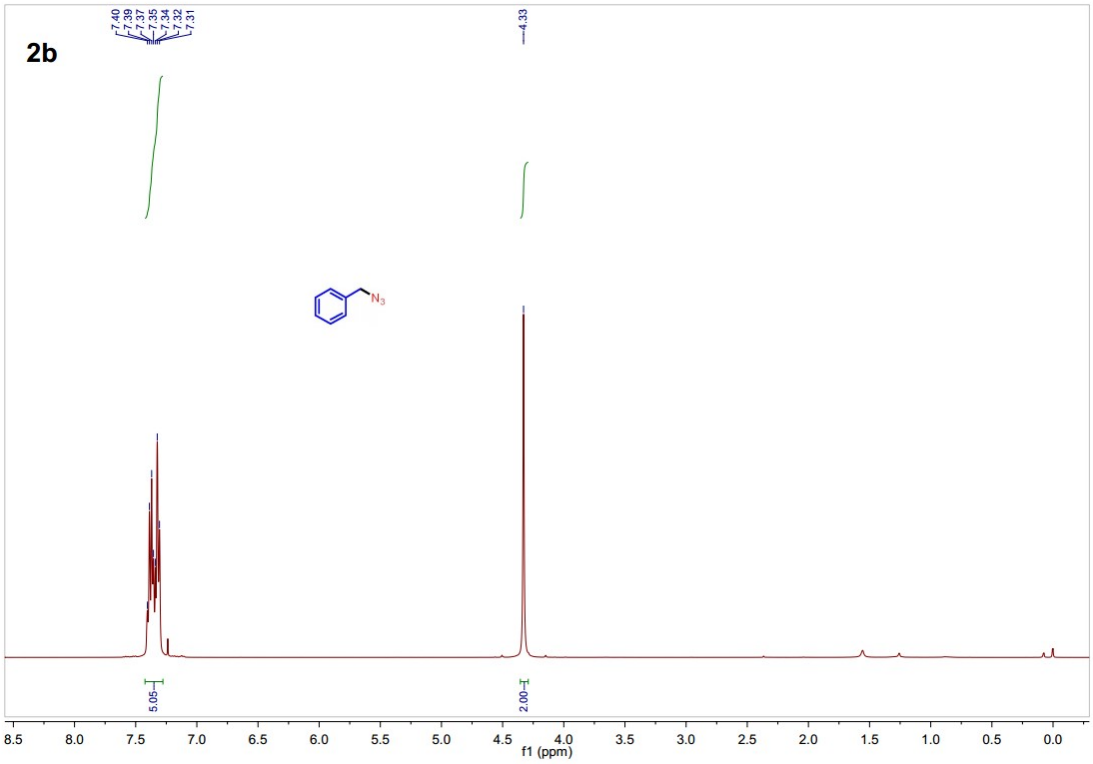
1 B. Li, F. Su, H.-K. Luo, L. Liang and B. Tan, *Microporous and Mesoporous Materials*, 2011, **138**, 207-214.

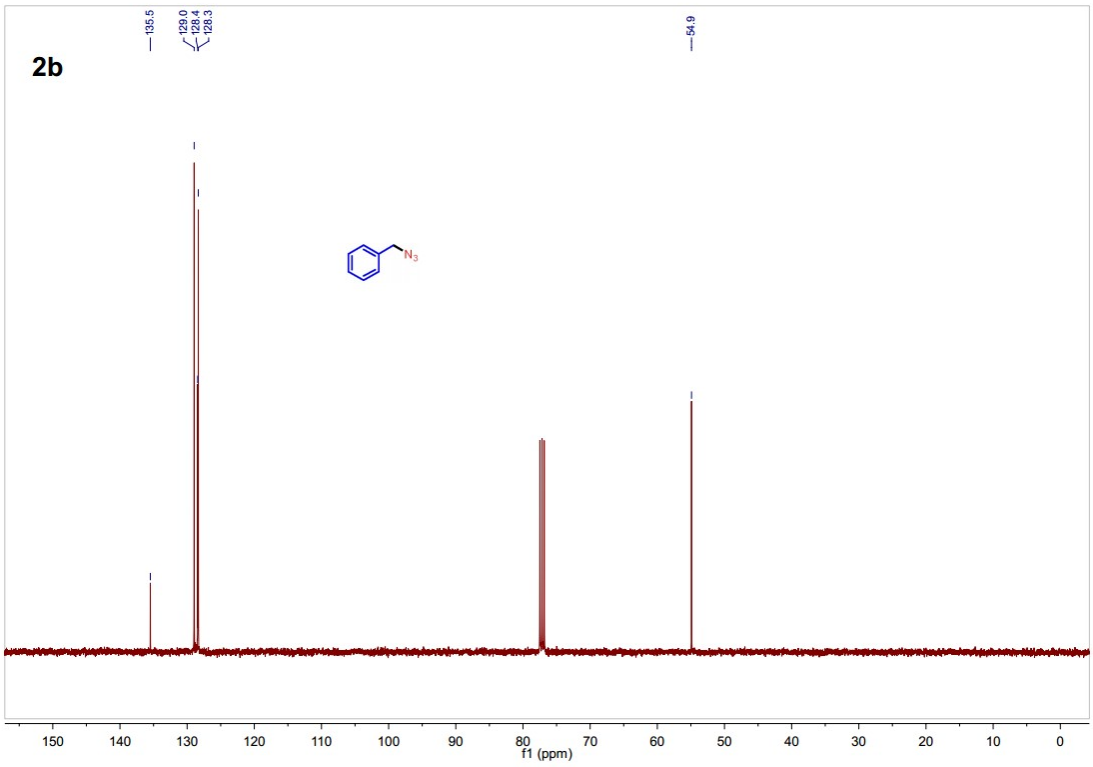
2 K. S. Kumar, S. R. Meesa and P. K. Naikawadi, *Org Lett*, 2018, **20**, 6079-6083.

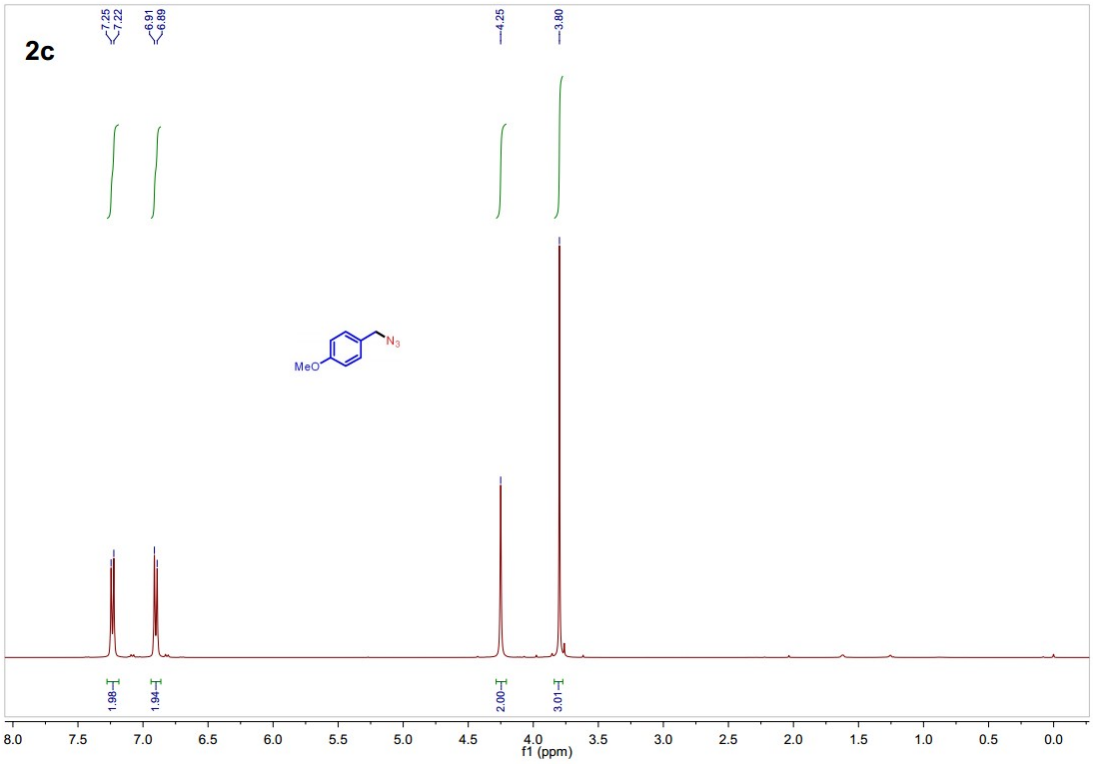
3 D. Gangaprasad, J. Paul Raj, T. Kiranmye, R. Sasikala, K. Karthikeyan, S. Kutti Rani and J. Elangovan, *Tetrahedron Letters*, 2016, **57**, 3105-3108.






2b
7.40
7.39
7.37
7.35
7.34
7.32
7.31
4.33
5.05
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


2b
135.5
129.0
128.4
128.3
54.9
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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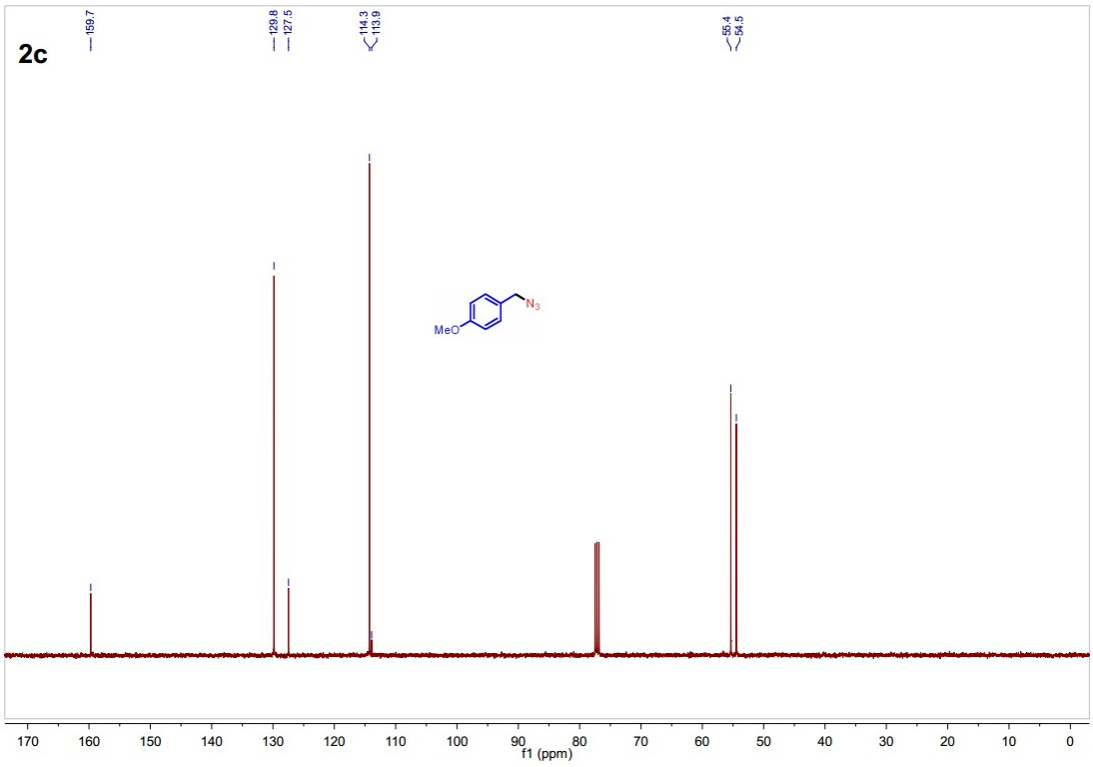
4.25
3.80
MeO
N3
1.98
1.94
2.00
3.01
f1 (ppm)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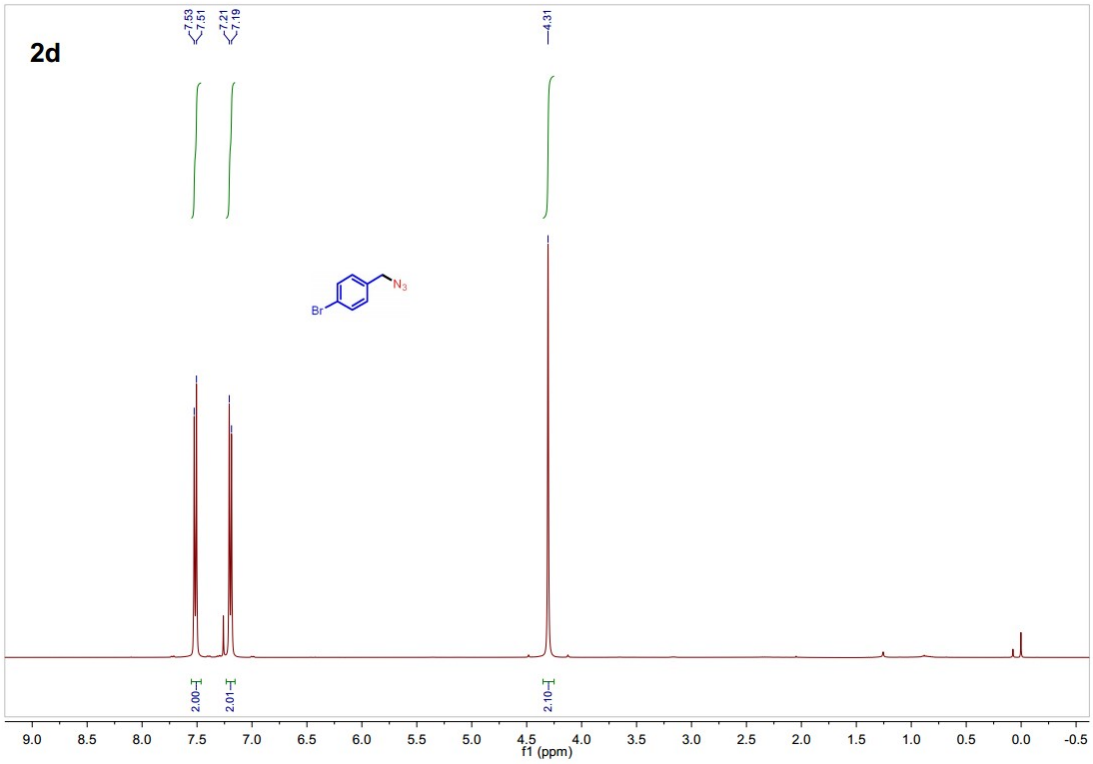
159.7
129.8
127.5
114.3
113.9
55.4
54.5
MeO
N3
f1 (ppm)


2d
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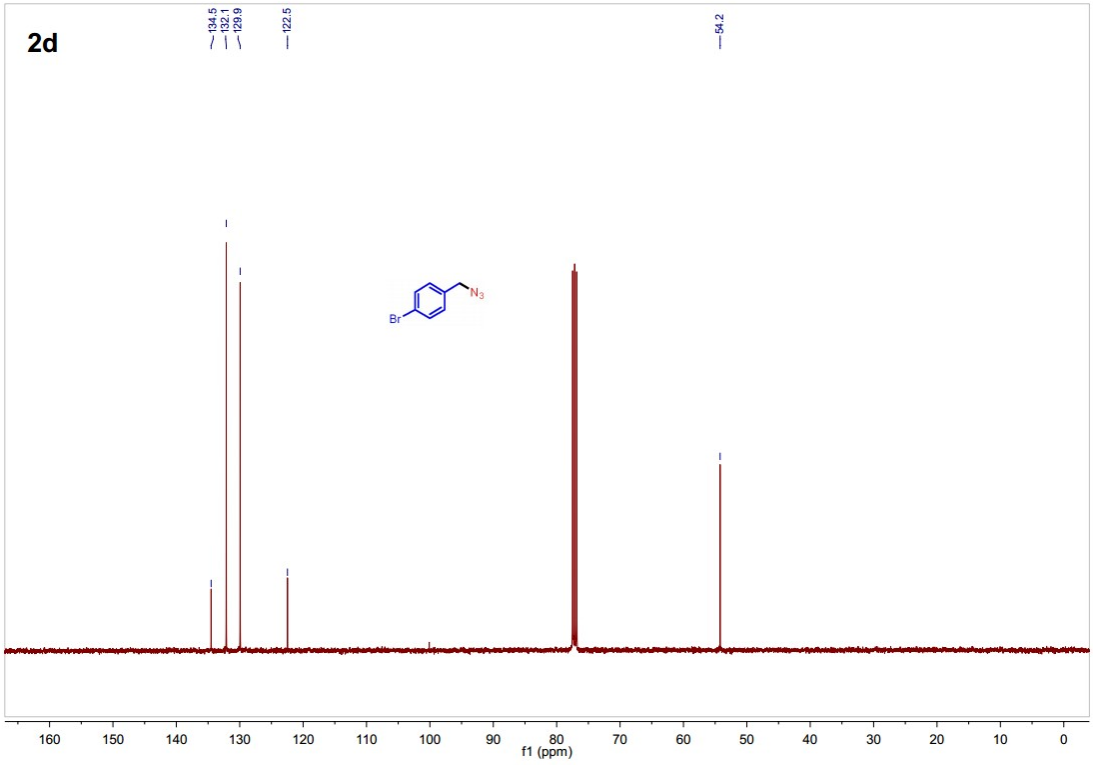
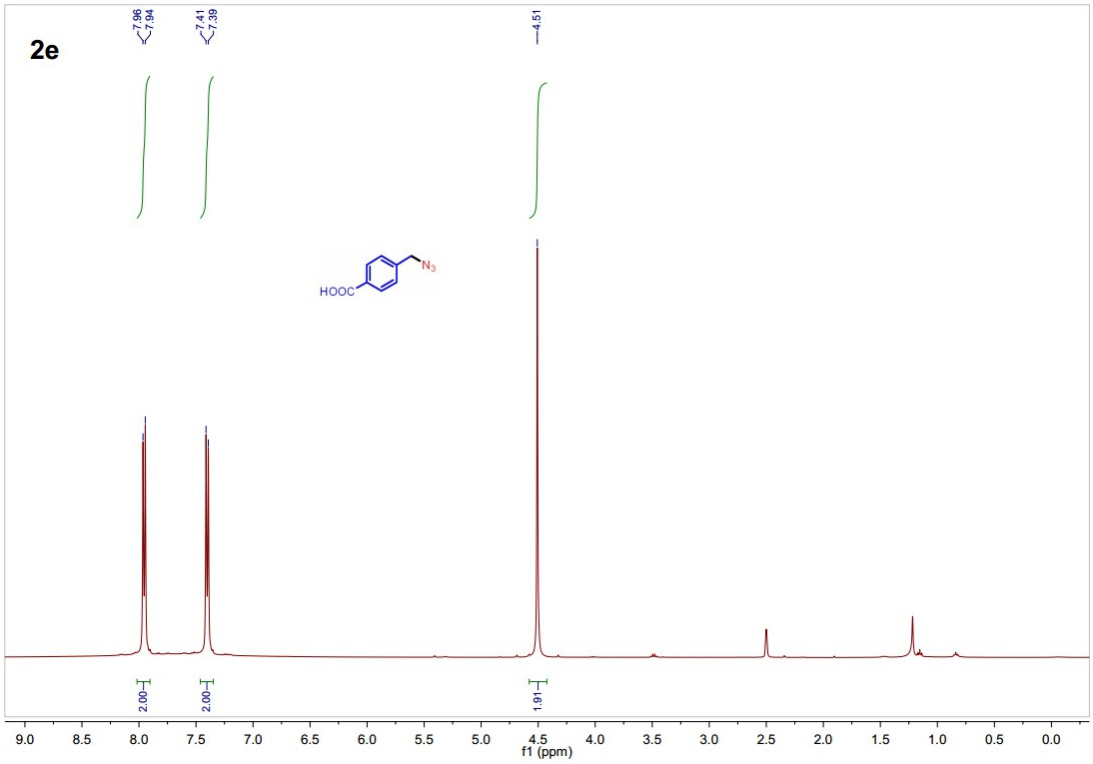
7.51
7.21
7.19
4.31
Br
N3
2.00
2.01
2.10
f1 (ppm)


2d
134.5
132.1
129.9
122.5
54.2
Br
N3
f1 (ppm)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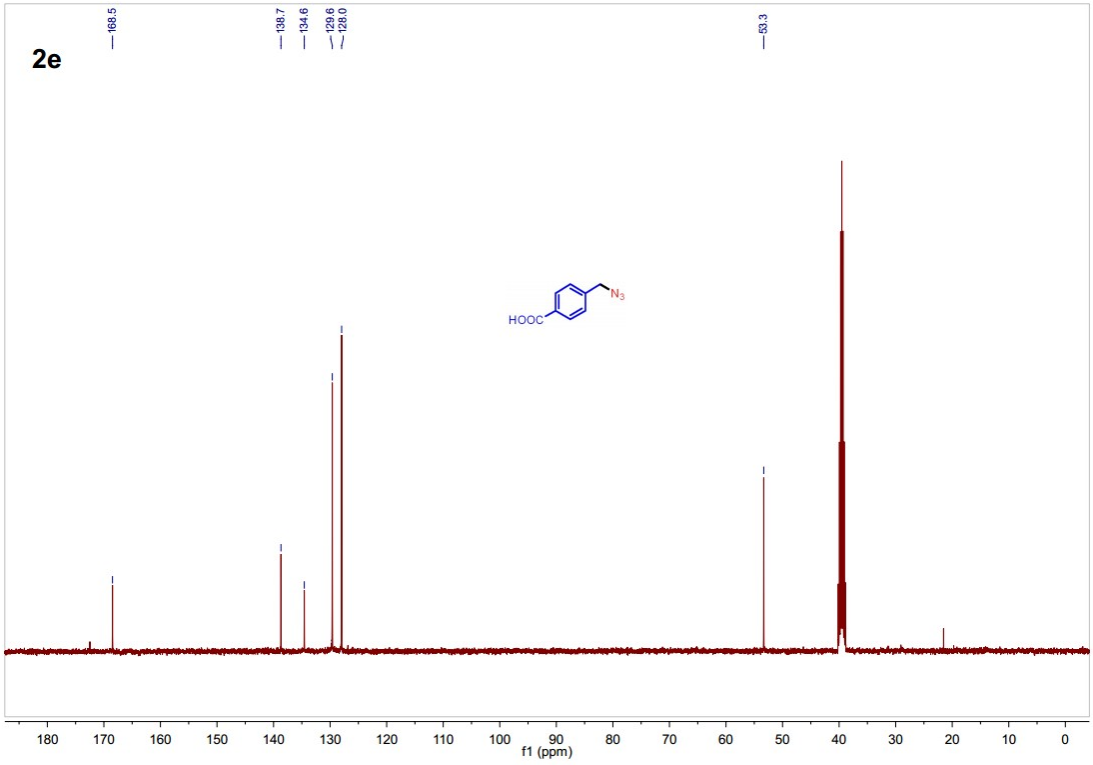
7.39
4.51
HOOC
N3
2.00
2.00
1.91
f1 (ppm)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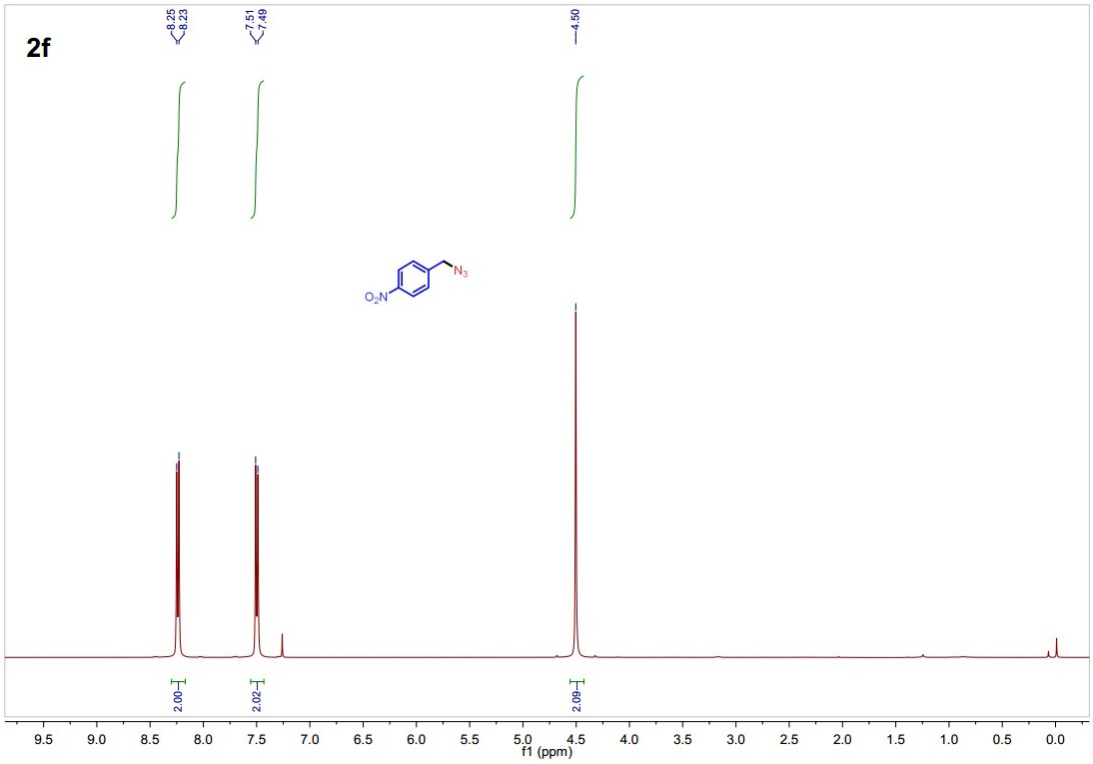
138.7
134.6
129.6
128.0
53.3
HOOC
N3
f1 (ppm)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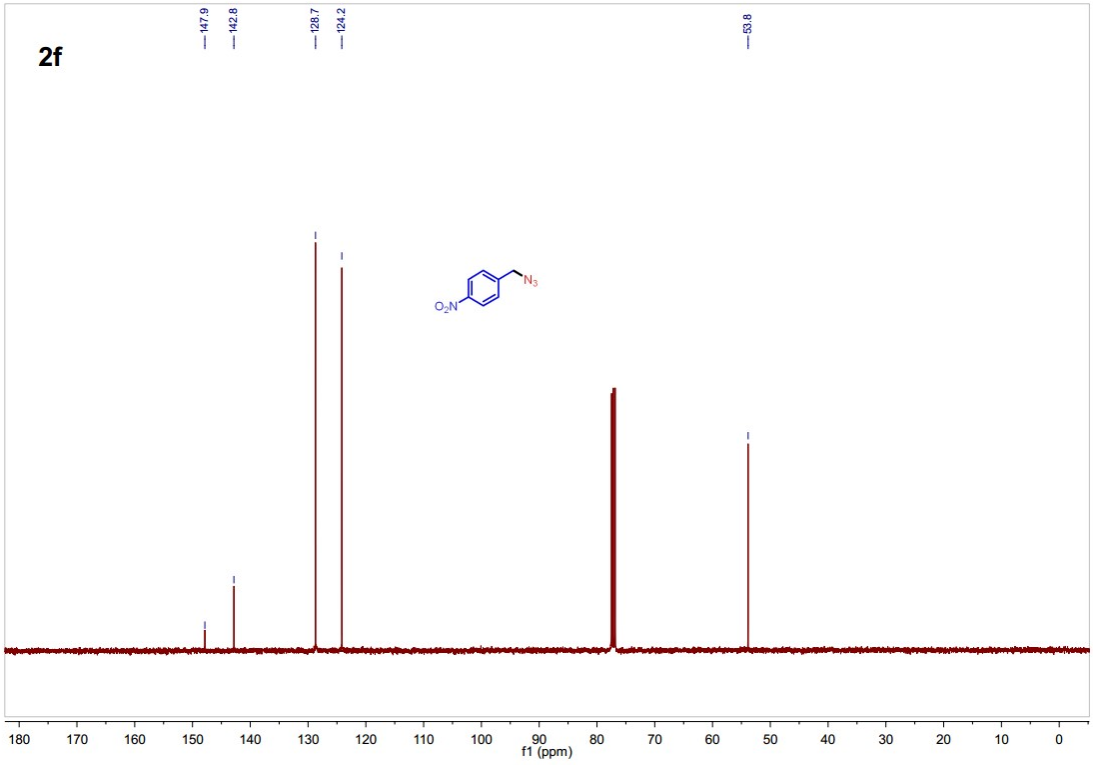
8.23
7.51
7.49
4.50
2.00
2.02
2.09
f1 (ppm)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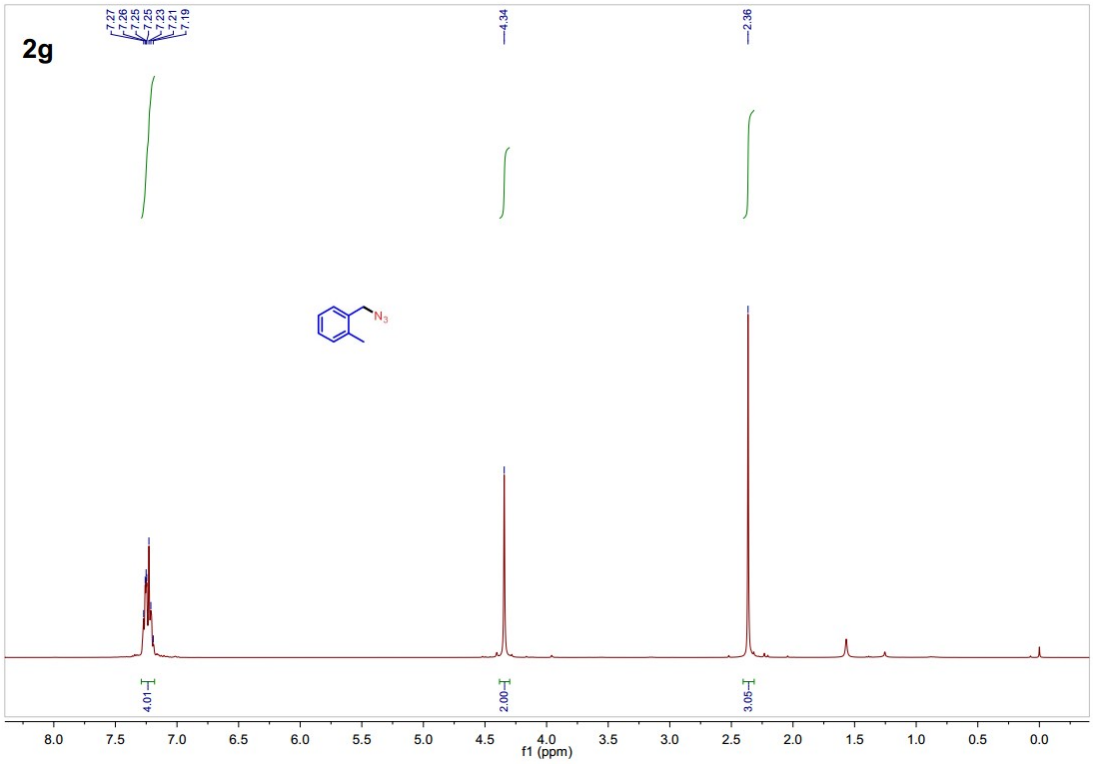
147.9
142.8
128.7
124.2
53.8
f1 (ppm)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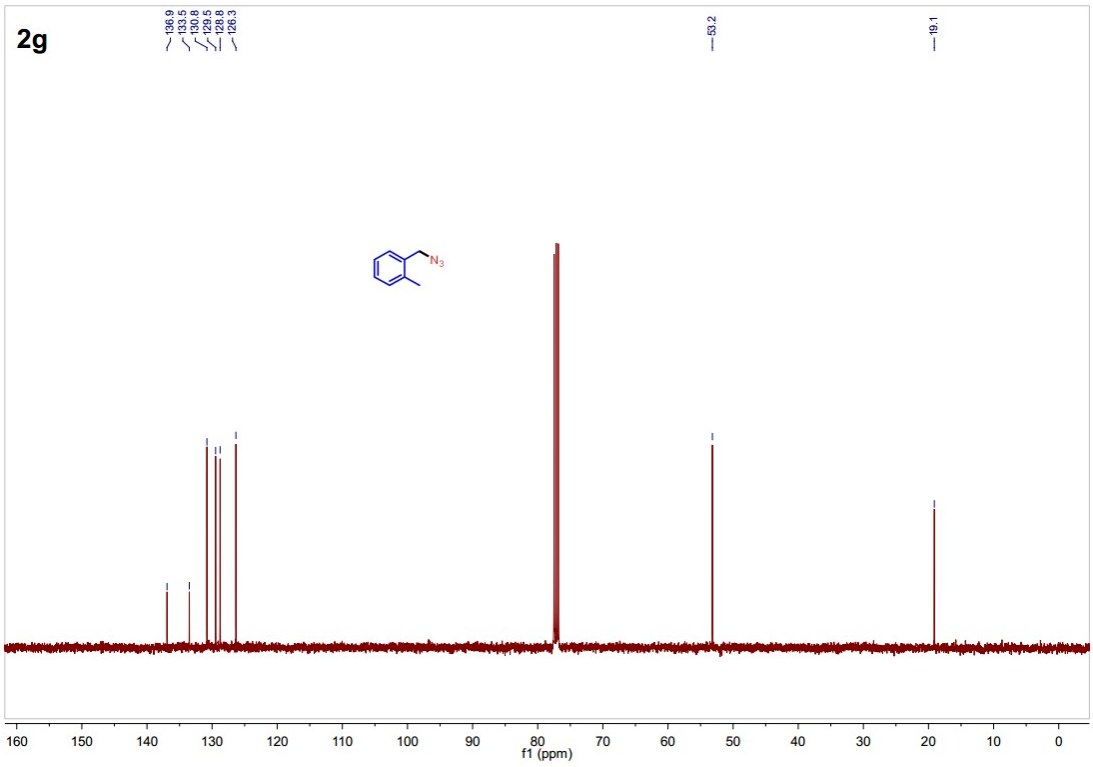
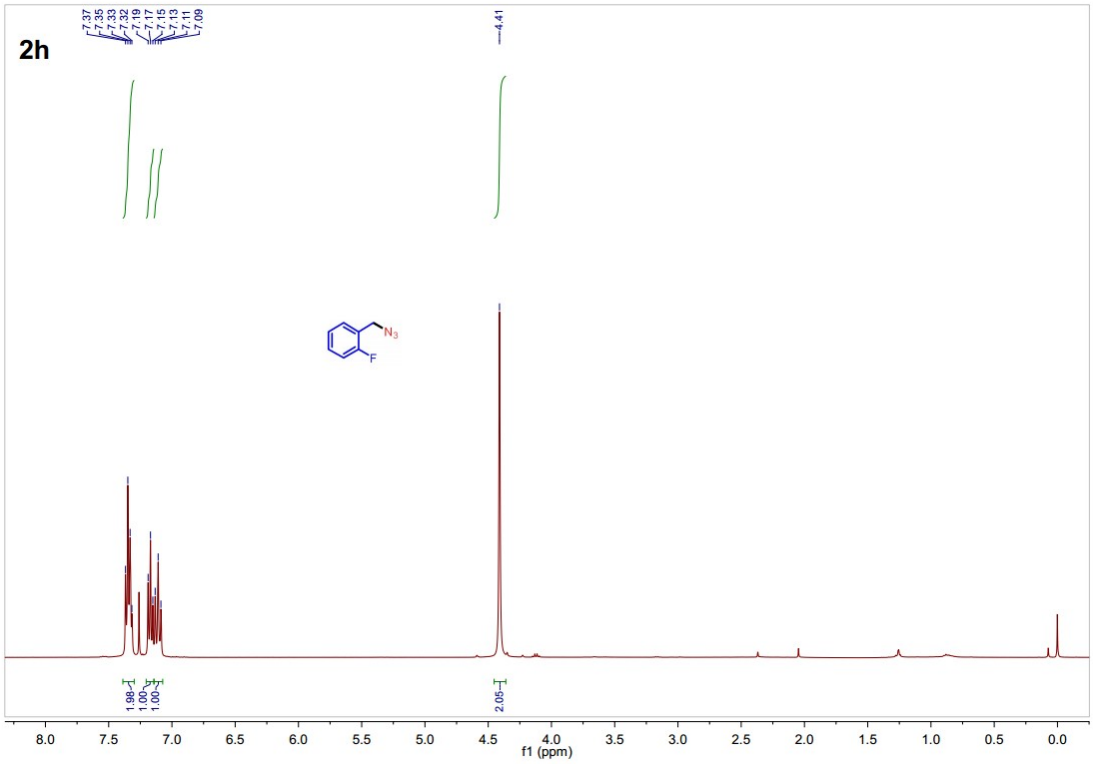
7.26
7.25
7.25
7.23
7.21
7.19
4.34
2.36
N3
4.01
2.00
3.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


2g
136.9
133.5
130.8
129.5
128.8
126.3
53.2
19.1
N3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


2h
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7.33
7.32
7.19
7.17
7.15
7.13
7.11
7.09
4.41
N3
F
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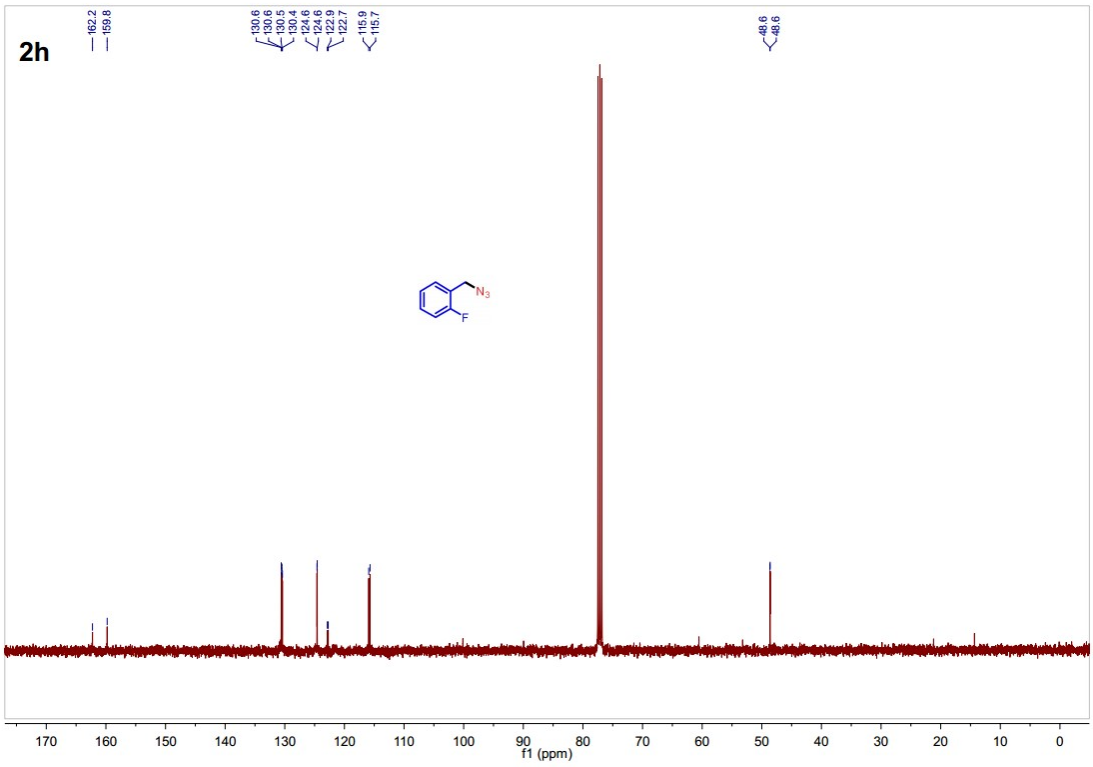
1.00
1.00
2.05
f1 (ppm)


2h
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130.6
130.5
130.4
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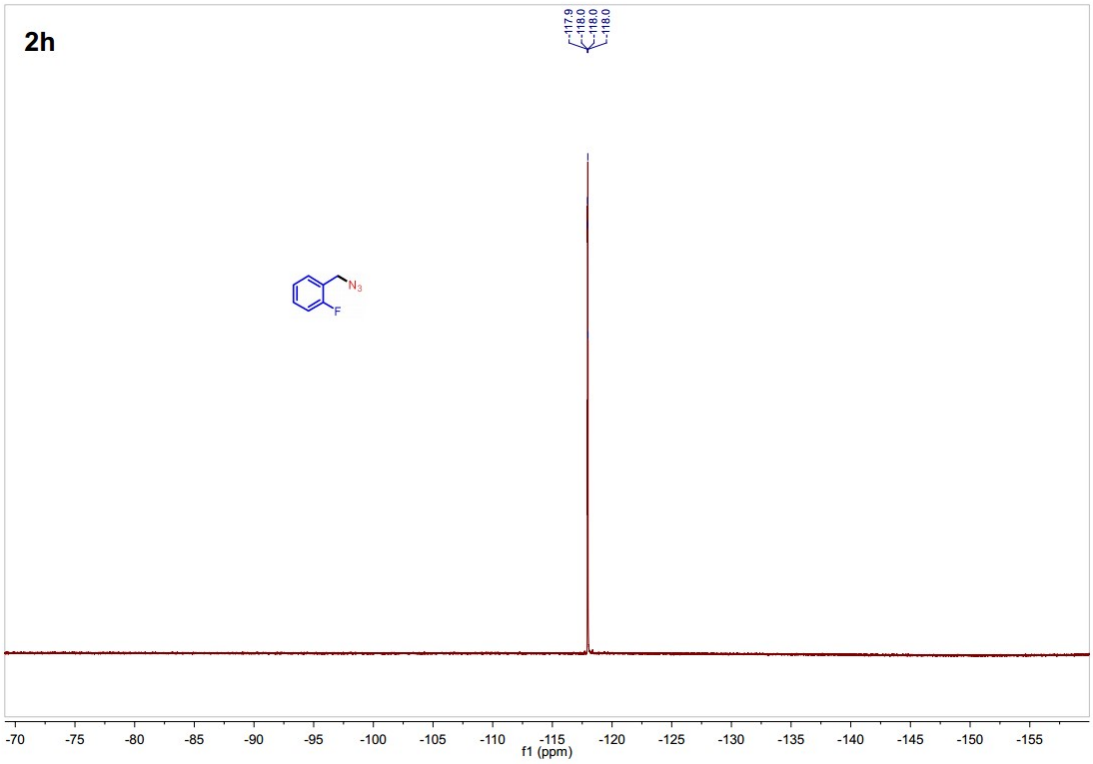
124.6
122.9
122.7
115.9
115.7
48.6
48.6
N3
F
f1 (ppm)


2h
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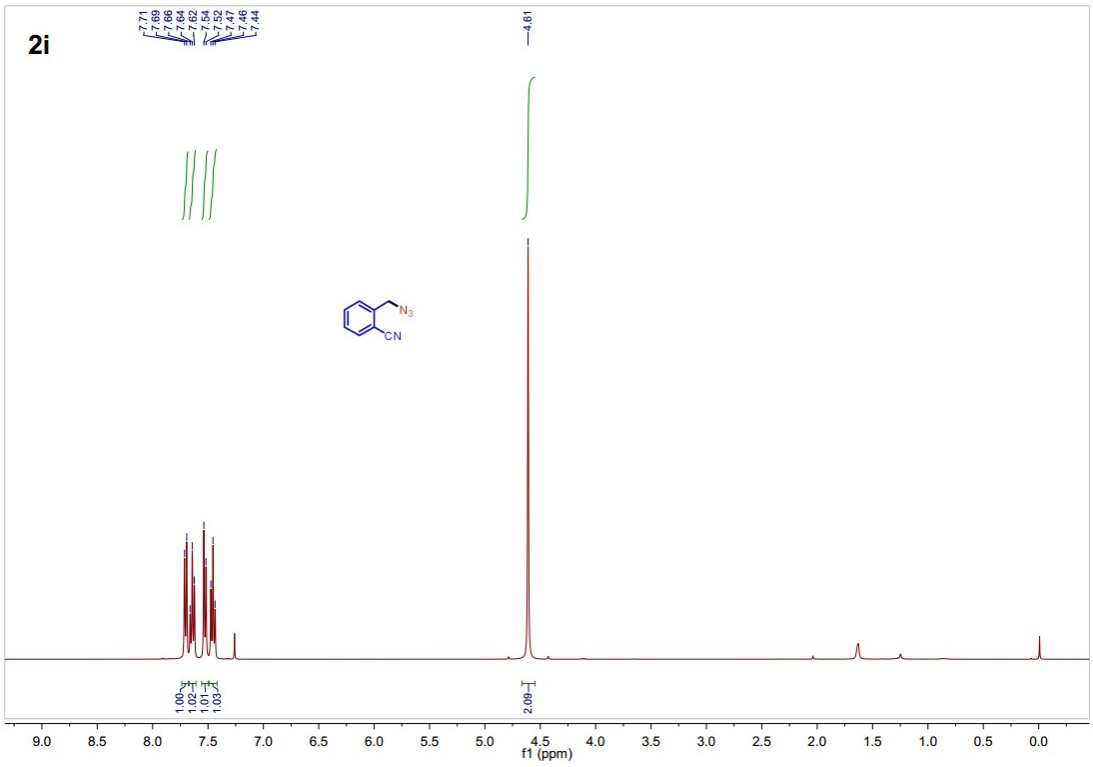
-118.0
-118.0
-118.0
N3
F
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155
f1 (ppm)


2i
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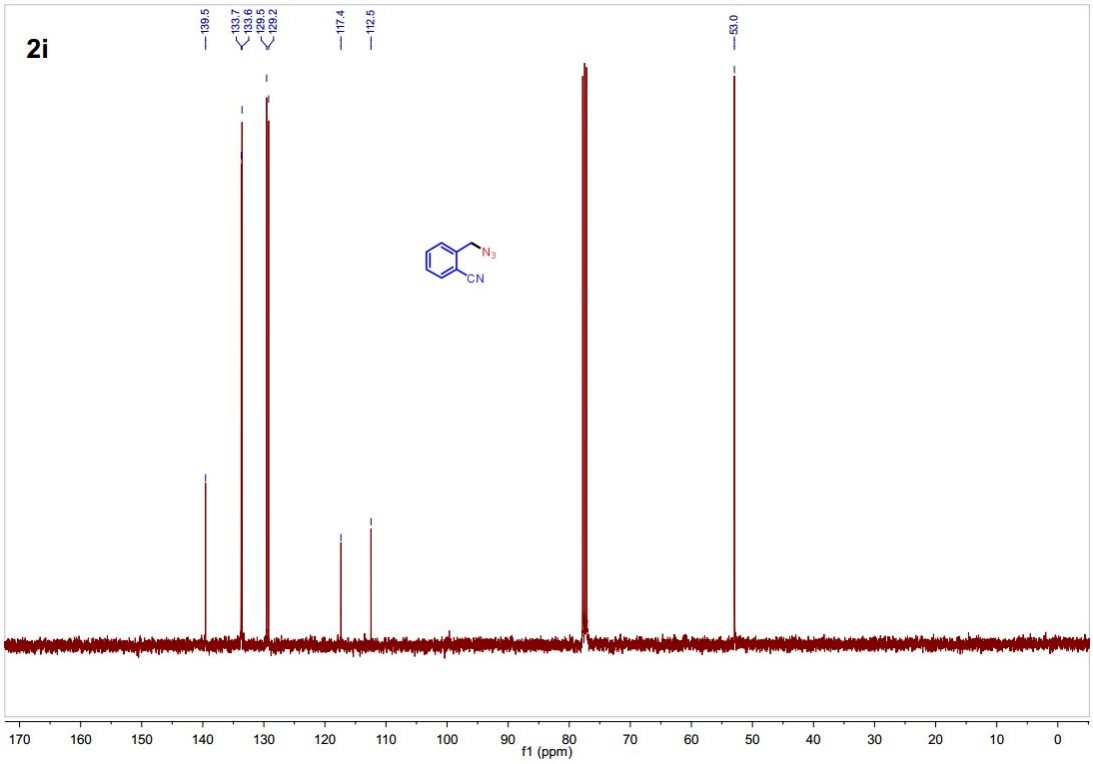
7.66
7.64
7.62
7.54
7.52
7.47
7.46
7.44
4.61
N3
CN
1.00
1.02
1.01
1.03
2.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


2i
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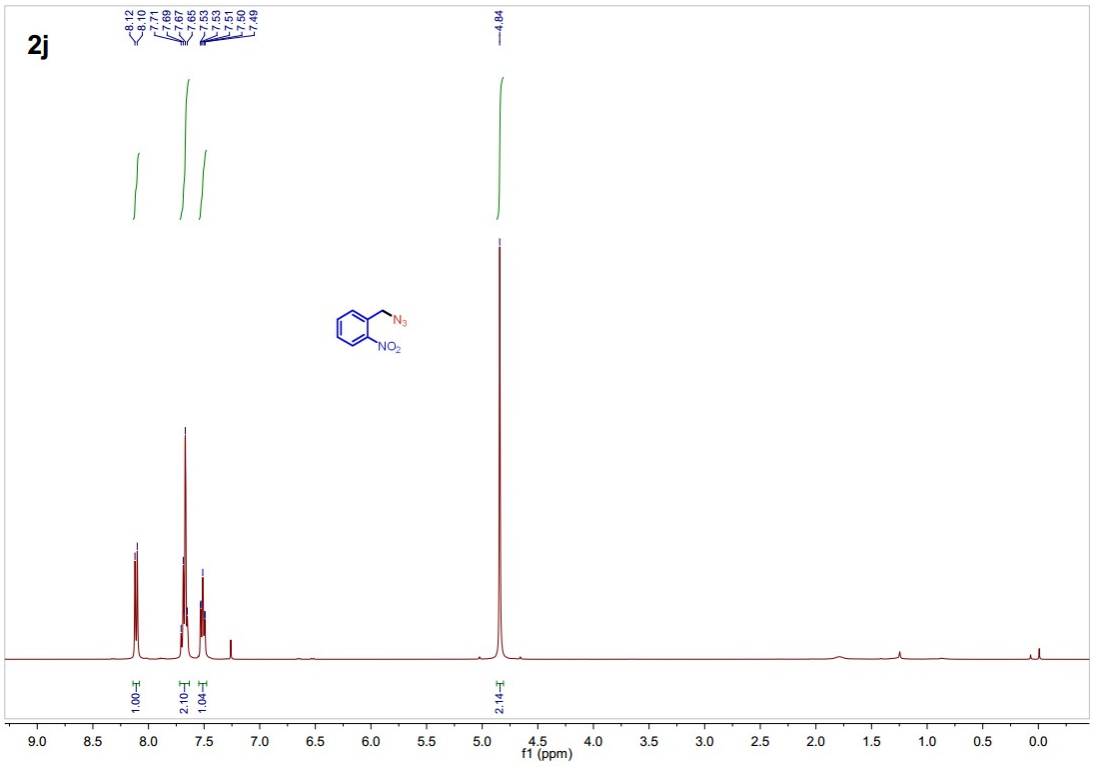
133.7
133.6
129.5
129.2
117.4
112.5
53.0
N3
CN
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.53
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7.51
7.50
7.49
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NO2
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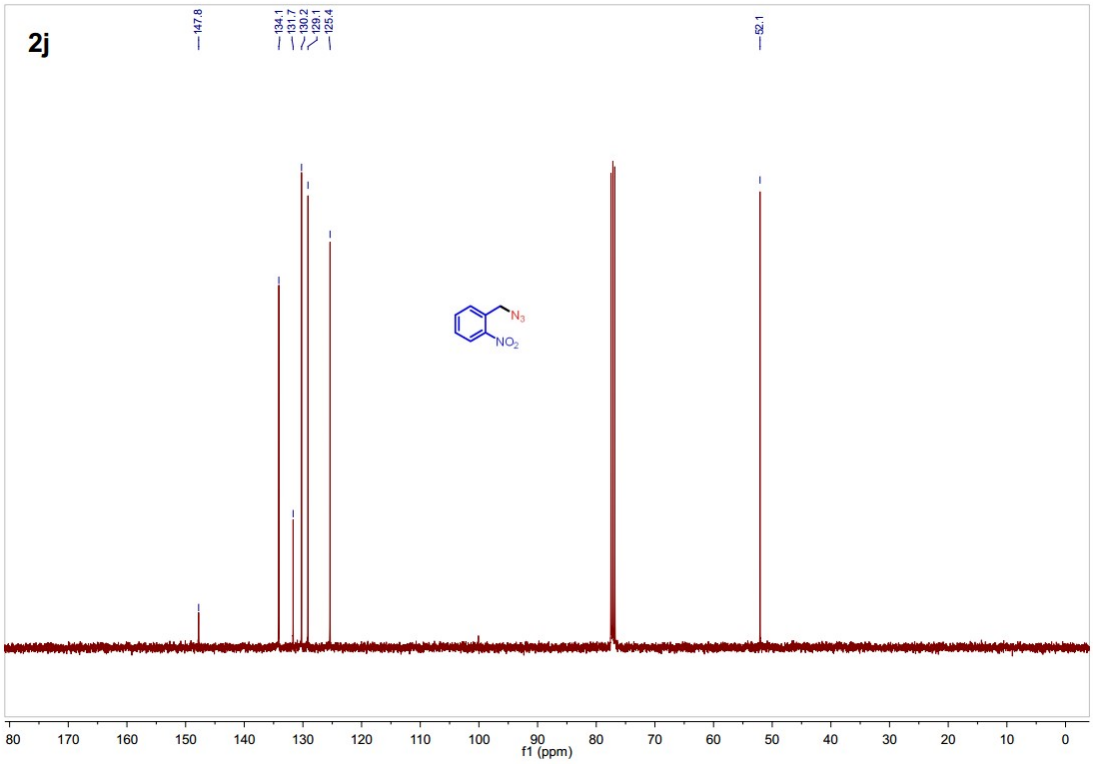
1.04
2.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2j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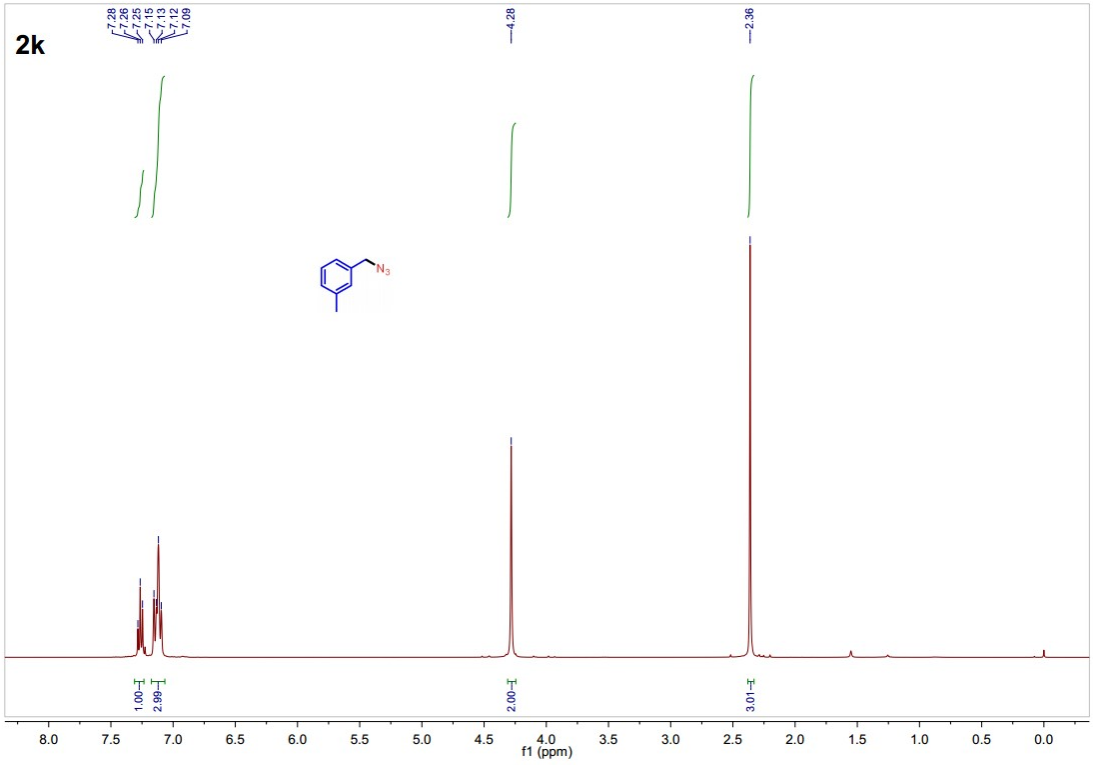
131.7
130.2
129.1
125.4
52.1
N3
NO2
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2k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7.15
7.13
7.12
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N3
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2.00
3.01
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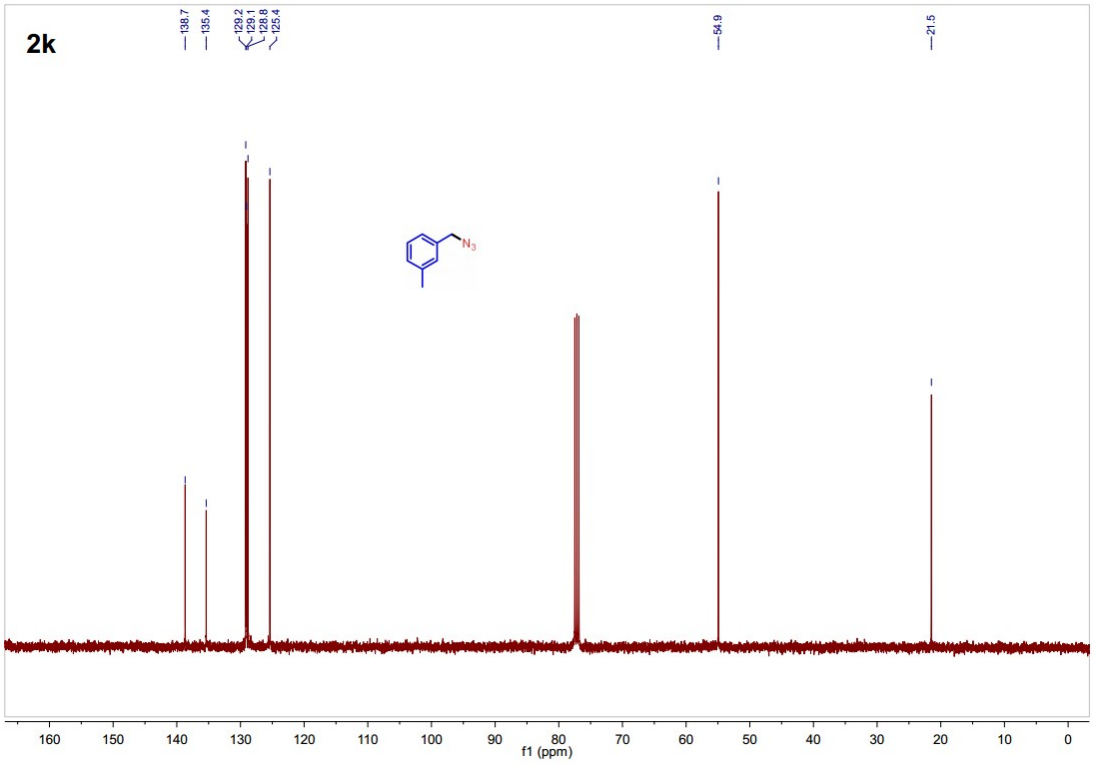
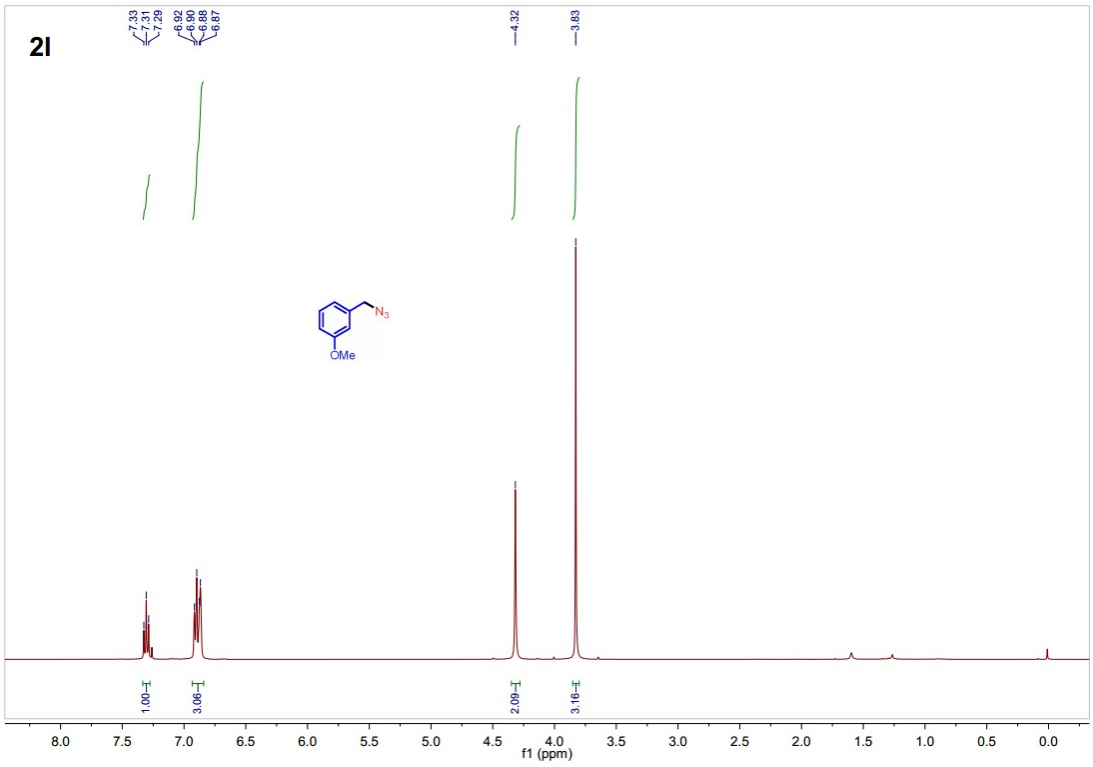
f1 (ppm)


2k
138.7
135.4
129.2
129.1
128.8
125.4
54.9
21.5
N3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


2l
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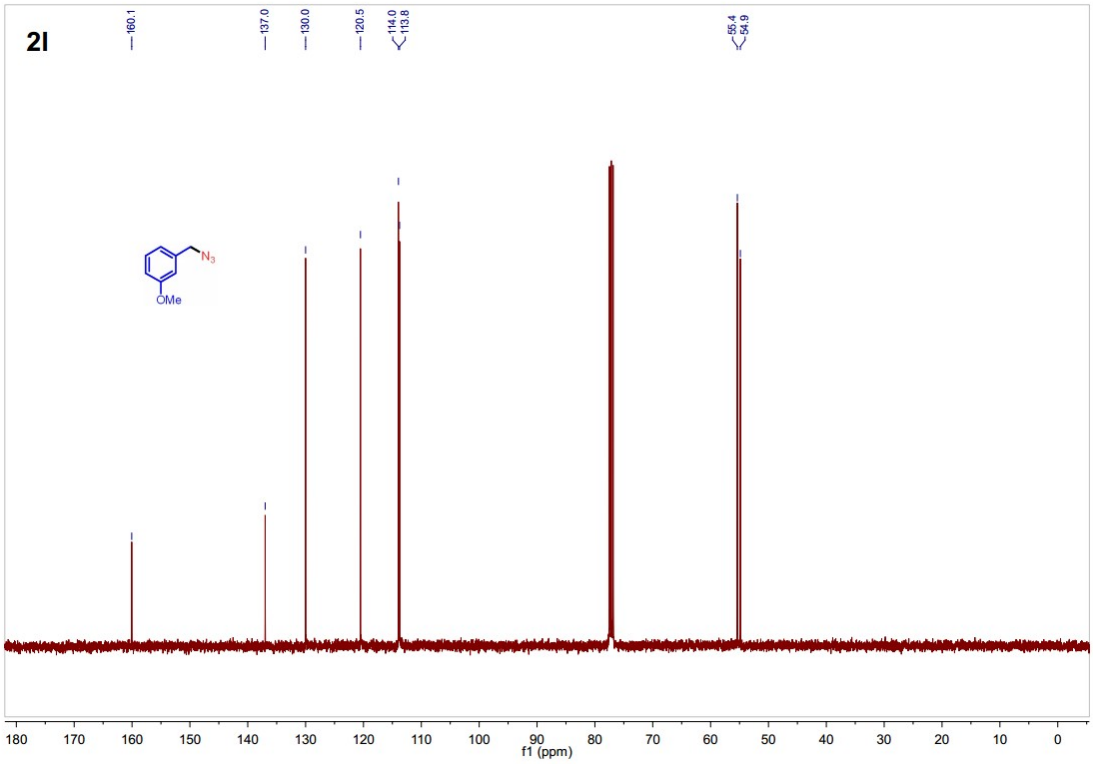
7.29
6.92
6.90
6.88
6.87
4.32
3.83
N3
OMe
1.00
3.06
2.09
3.16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


2l
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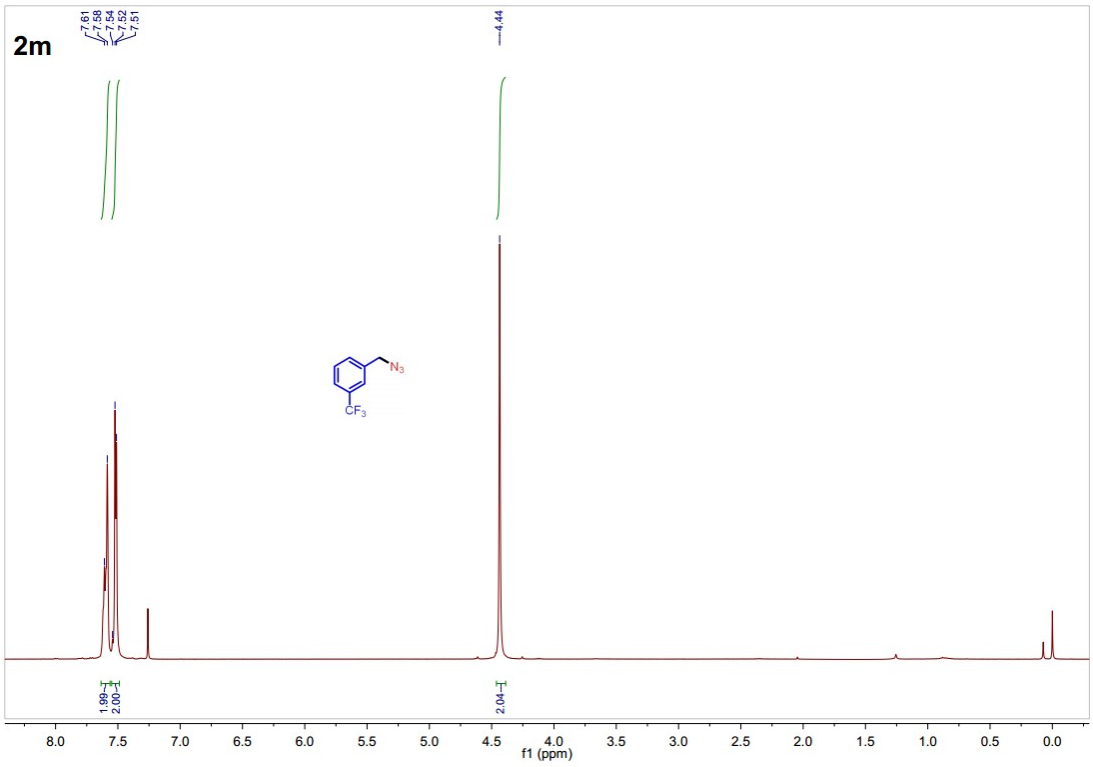
137.0
130.0
120.5
114.0
113.8
55.4
54.9
N3
OMe
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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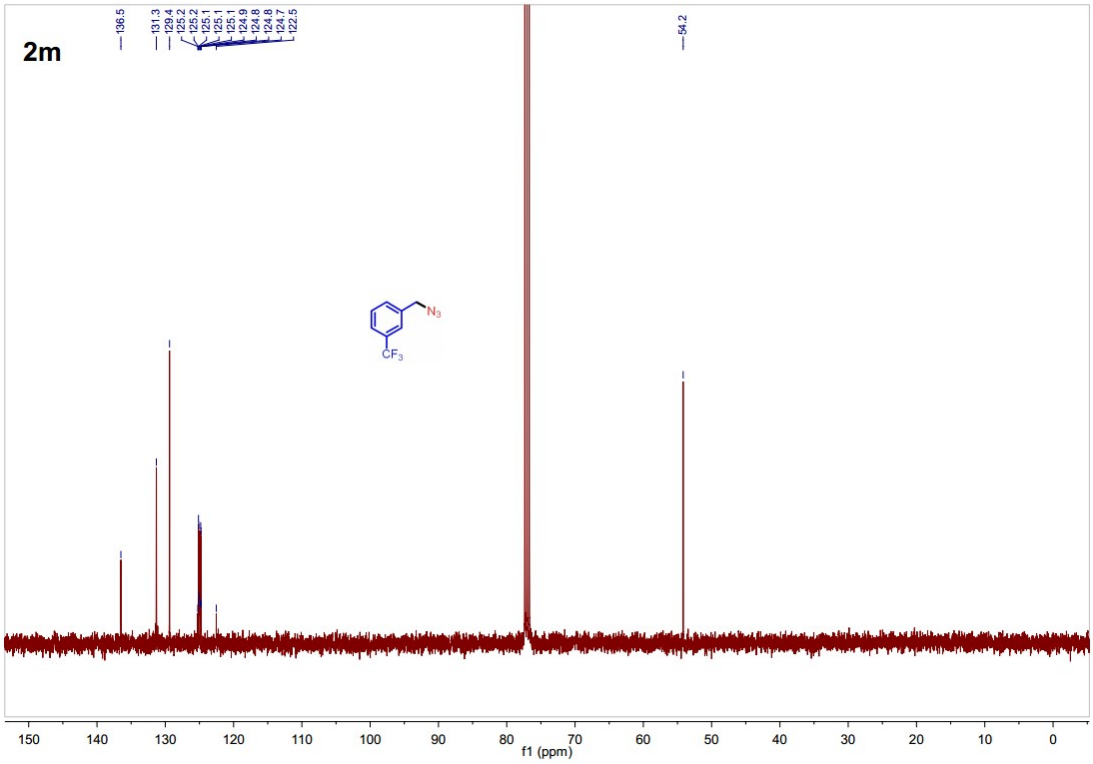
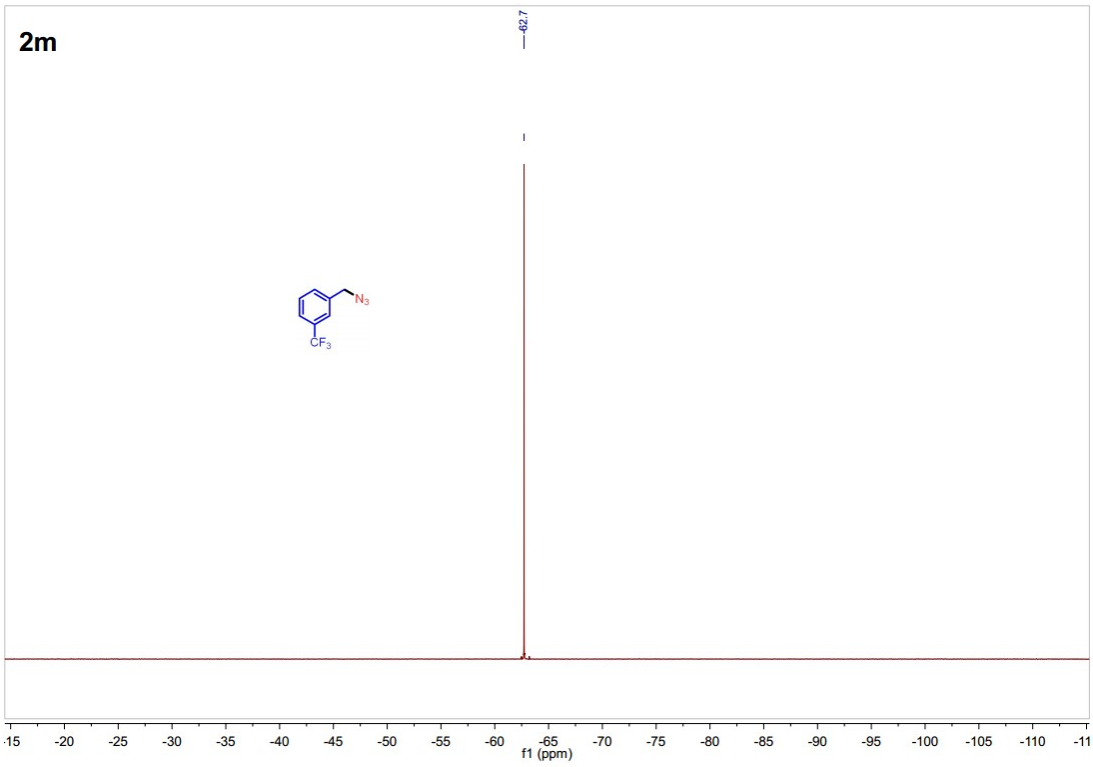
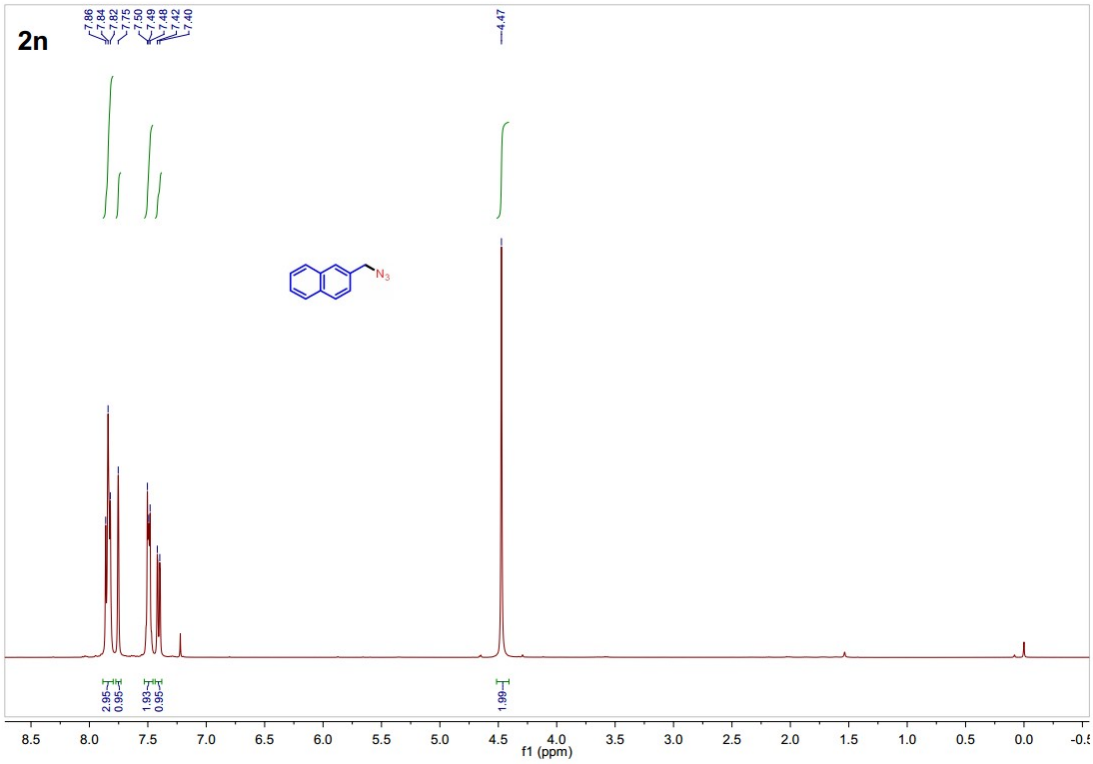
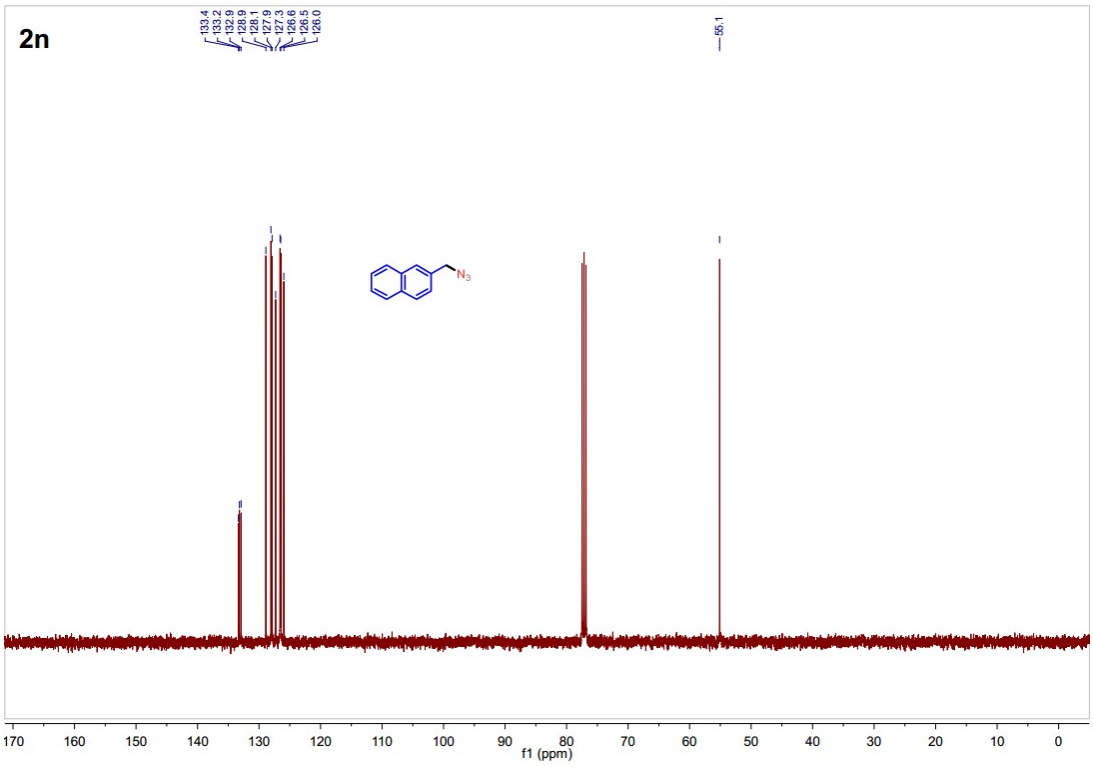
7.54
7.52
7.51
4.44
N3
CF3
1.99
2.00
2.04
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

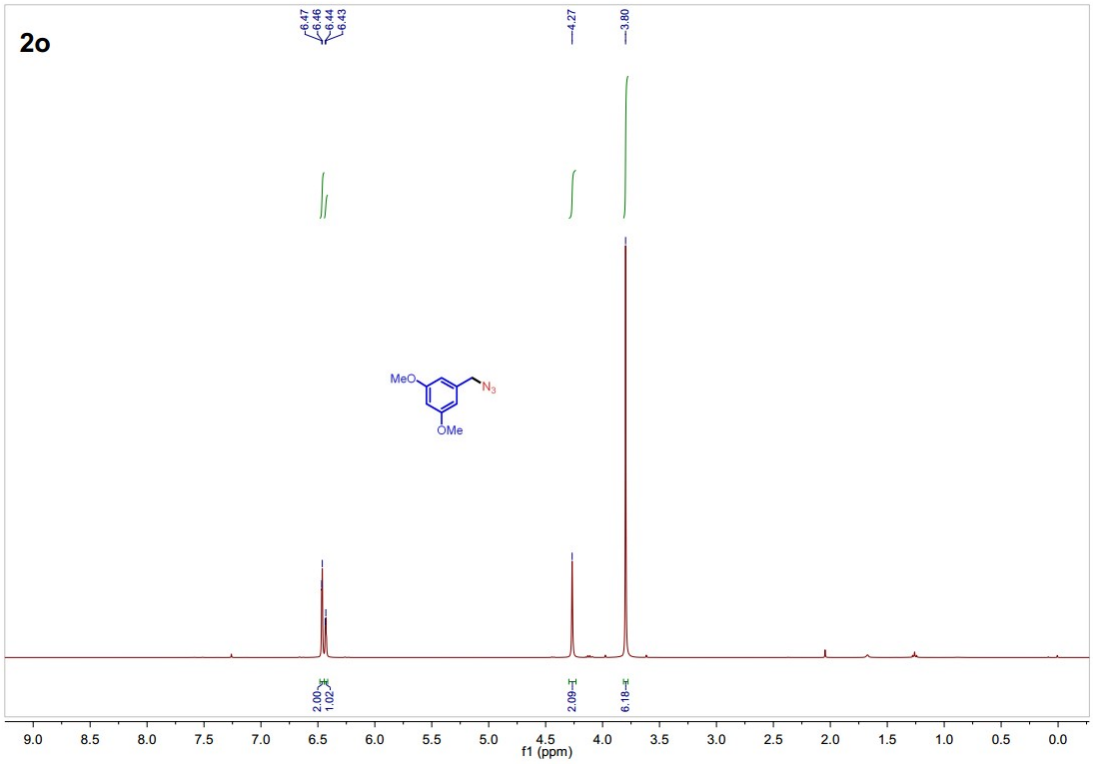

2m
136.5
131.3
129.4
125.2
125.2
125.1
125.1
124.9
124.8
124.8
124.7
122.5
54.2
N3
CF3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


2m
-62.7
N3
CF3
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-11
f1 (ppm)

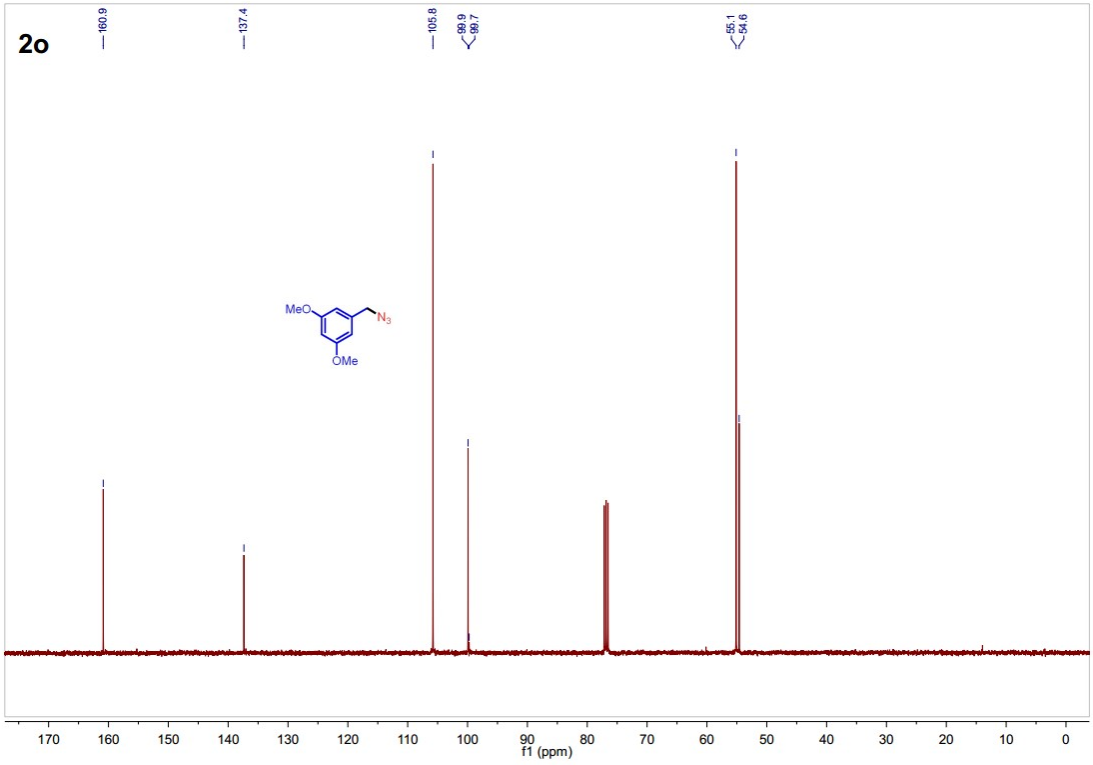

2n
7.86
7.84
7.82
7.75
7.50
7.49
7.48
7.42
7.40
4.47
N3
2.95
0.95
1.93
0.95
1.99
f1 (ppm)

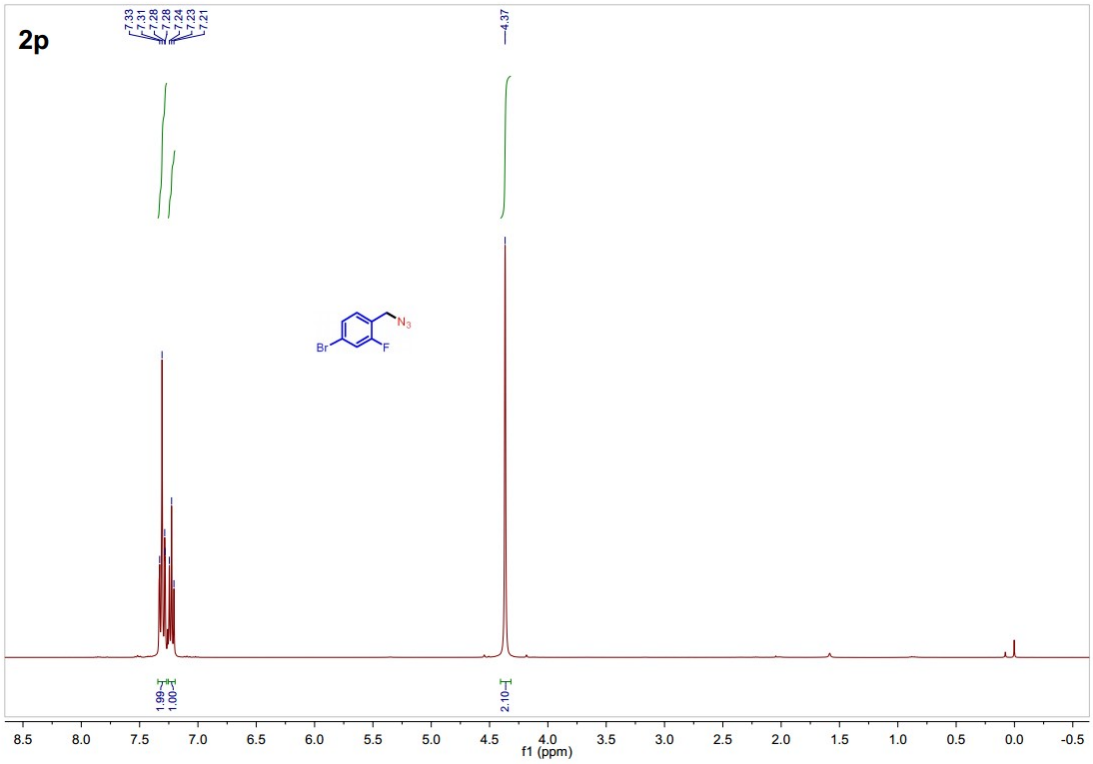

2n
133.4
133.2
132.9
128.9
128.1
127.9
127.3
126.6
126.5
126.0
55.1
N3
f1 (ppm)

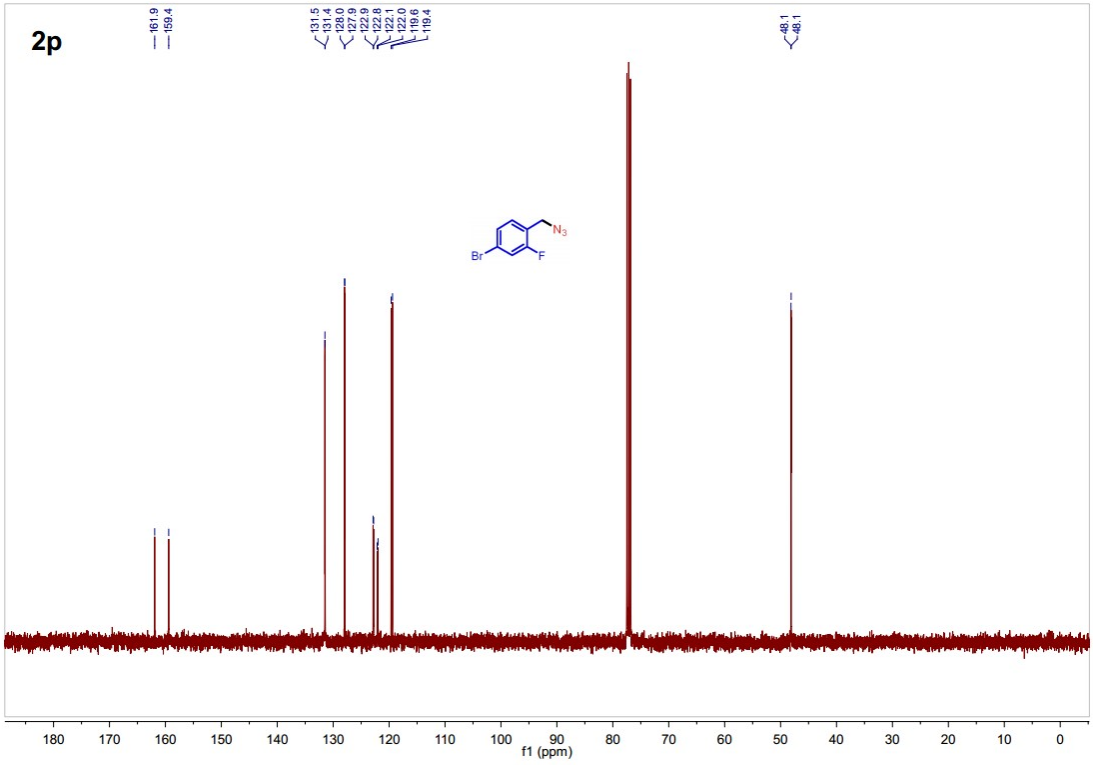
2o


6.47
6.46
6.44
6.43
4.27
3.80
MeO
N3
OMe
2.00
1.02
2.09
6.18
f1 (ppm)

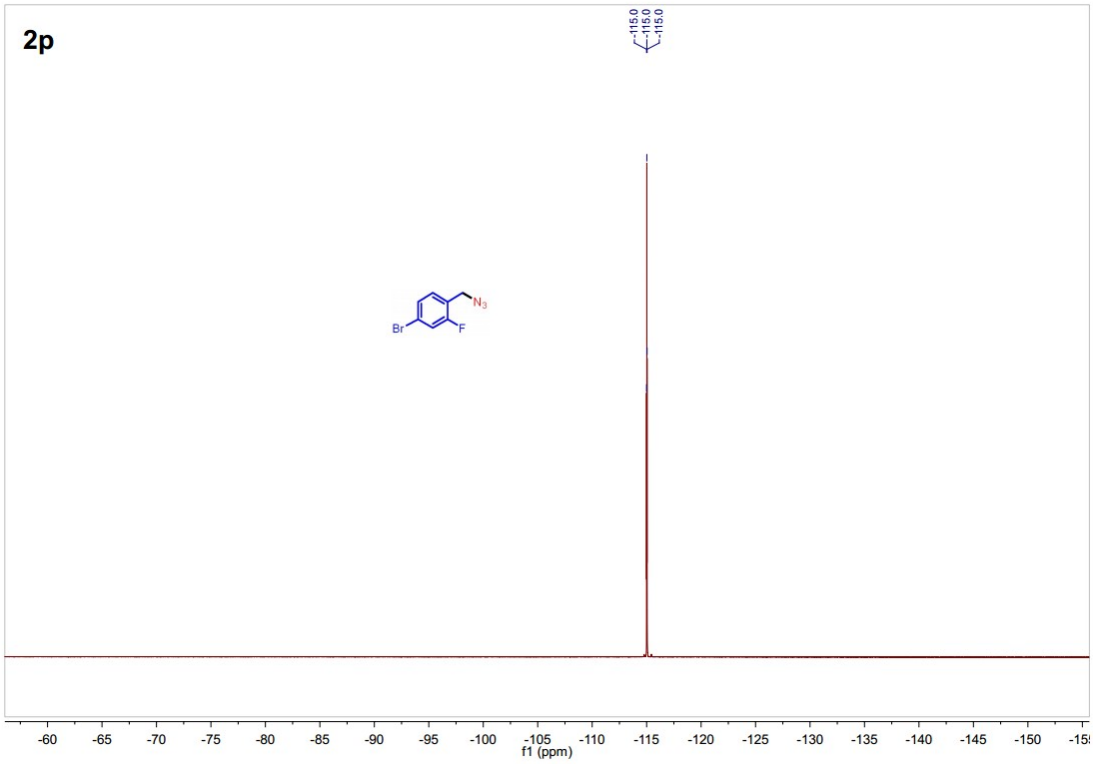
2o


160.9
137.4
105.8
99.9
99.7
55.1
54.6
MeO
N3
OMe
f1 (ppm)

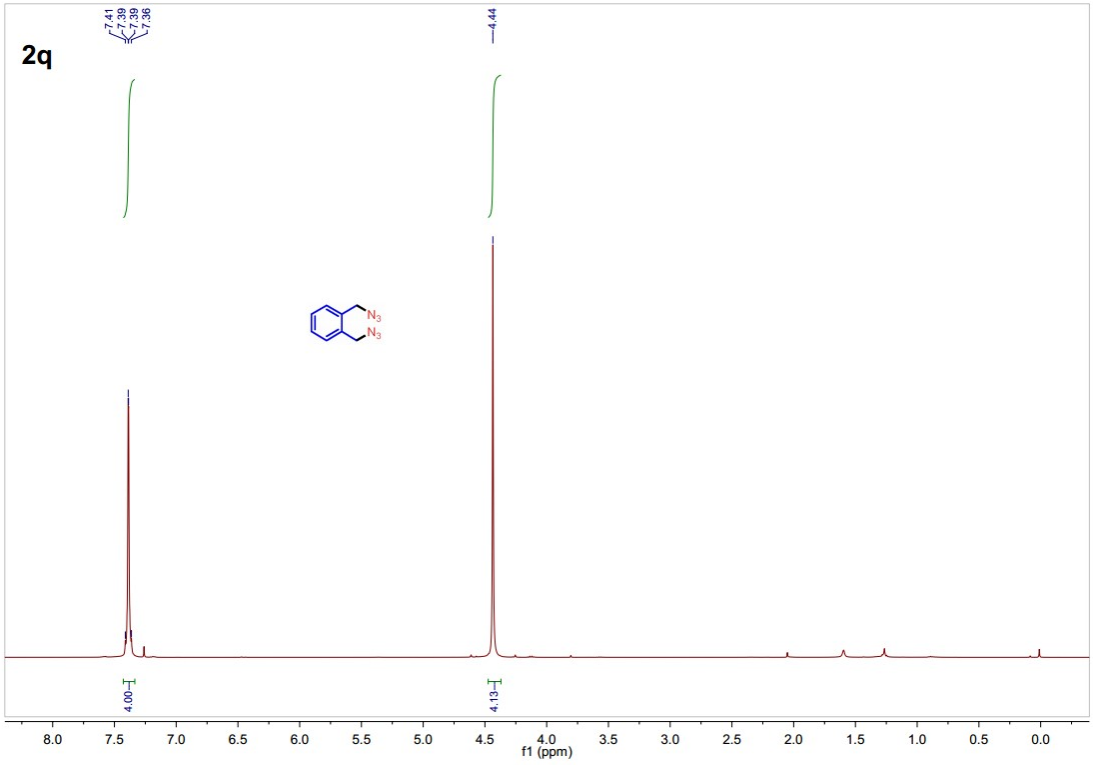

2p
7.33
7.31
7.28
7.28
7.24
7.23
7.21
4.37
Br
F
N3
1.99
1.00
2.10
f1 (ppm)

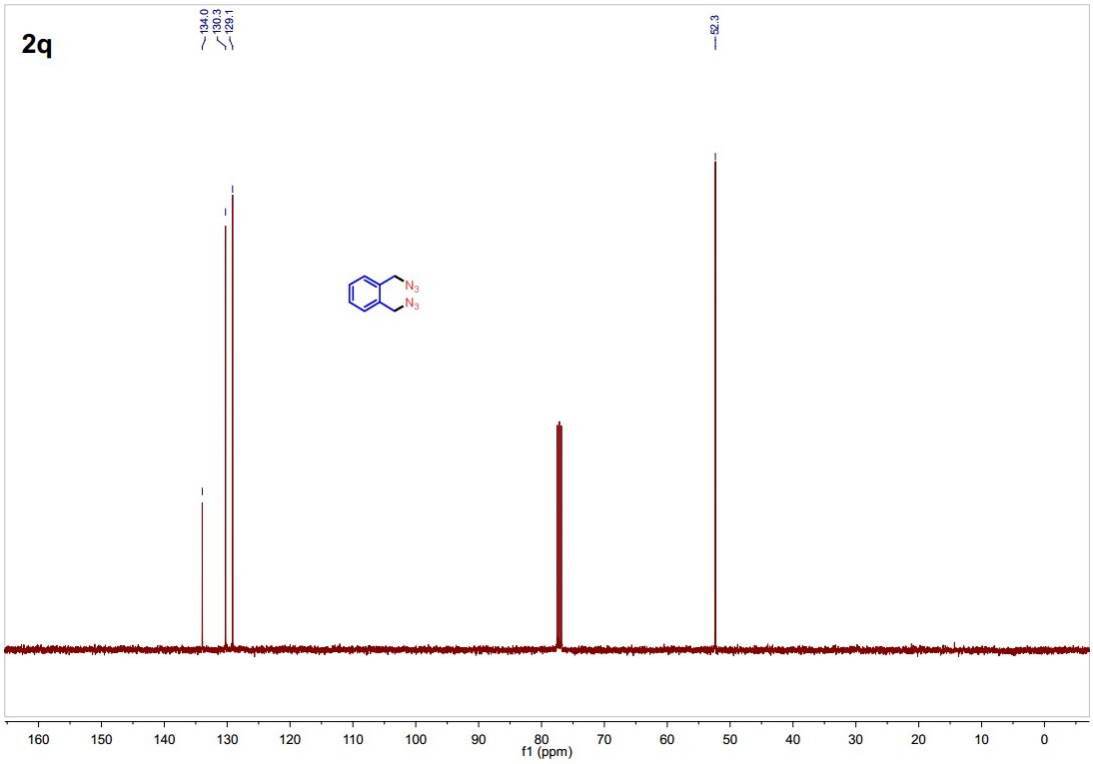

2p
161.9
159.4
131.5
131.4
130.0
127.9
122.9
122.8
122.1
122.0
119.6
119.4
48.1
48.1
Br
F
N3
f1 (ppm)

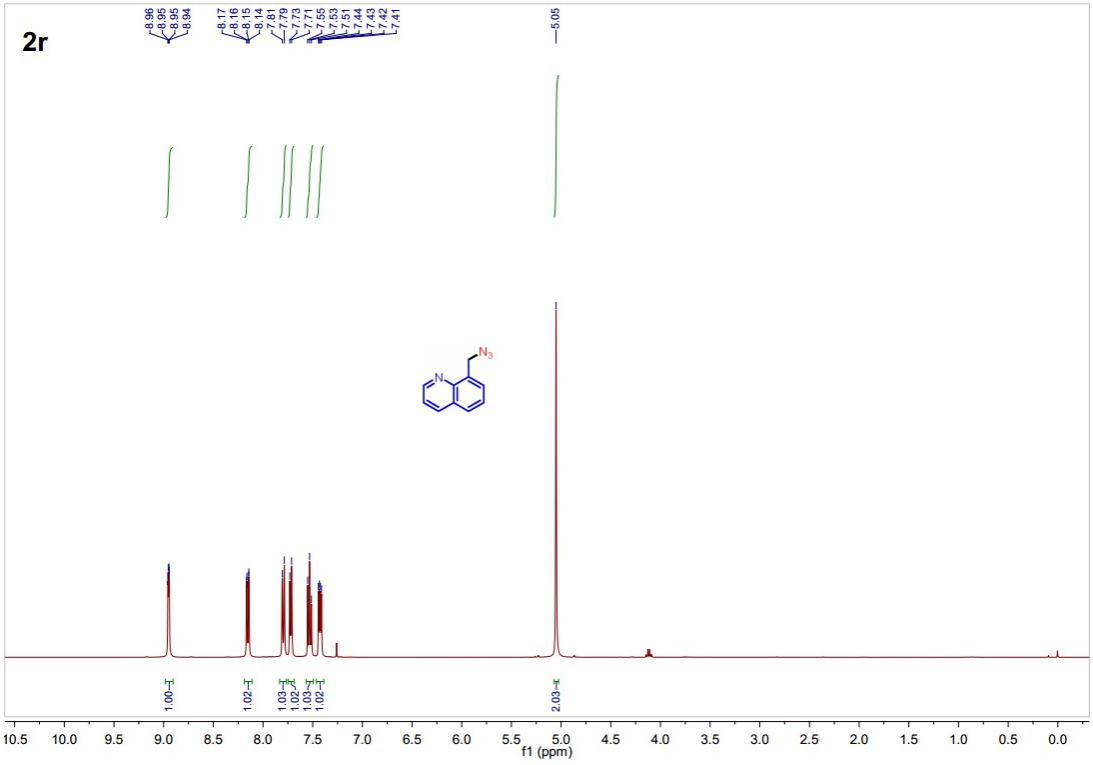
2p

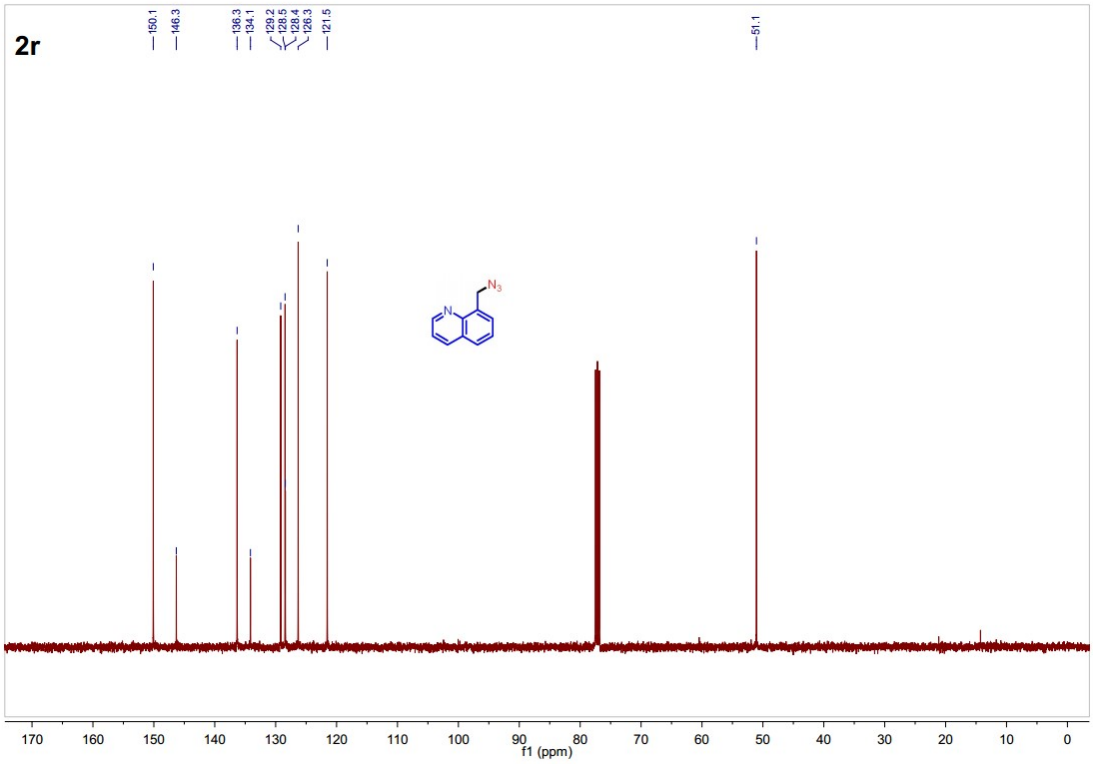

-115.0
-115.0
-115.0
Br
F
N3
-60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)

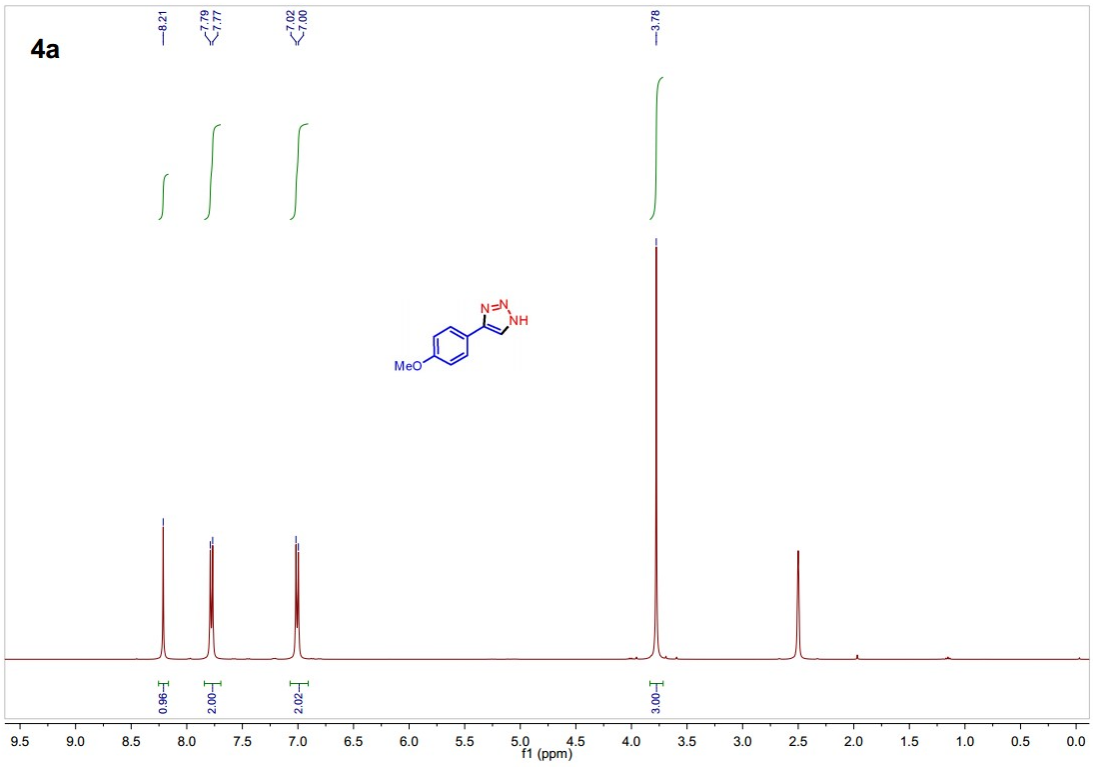
2q

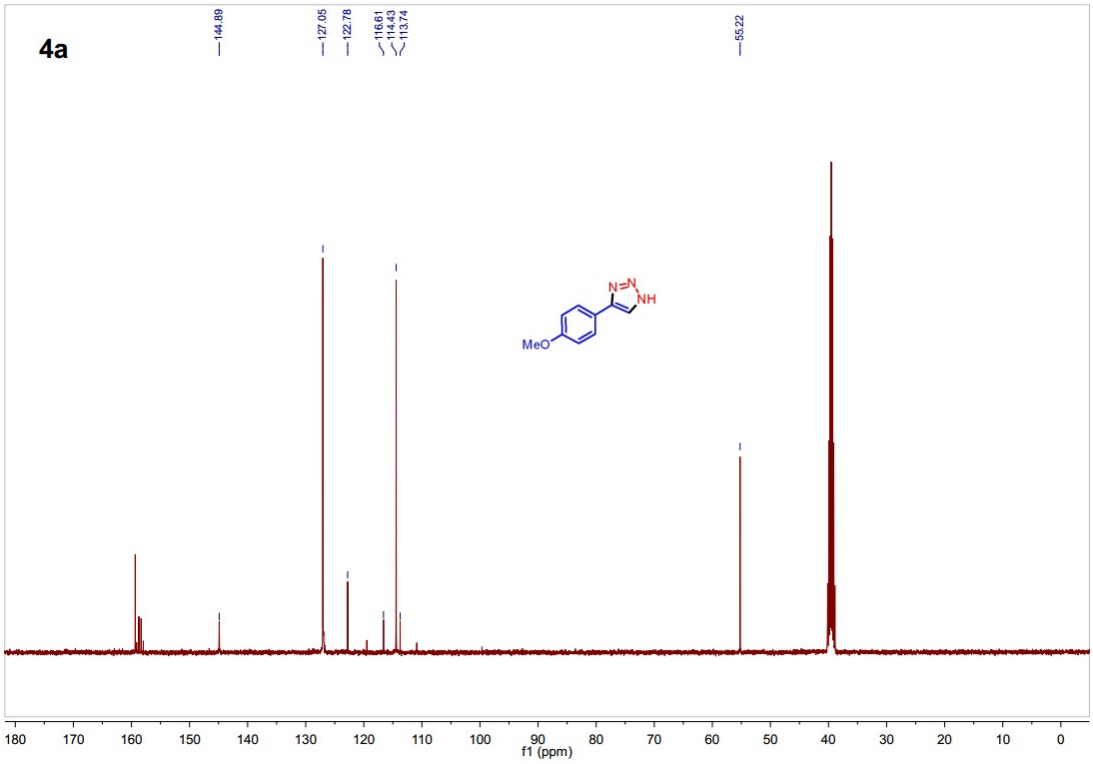

7.41
7.39
7.39
7.36
4.44
N3
N3
4.00
4.13
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

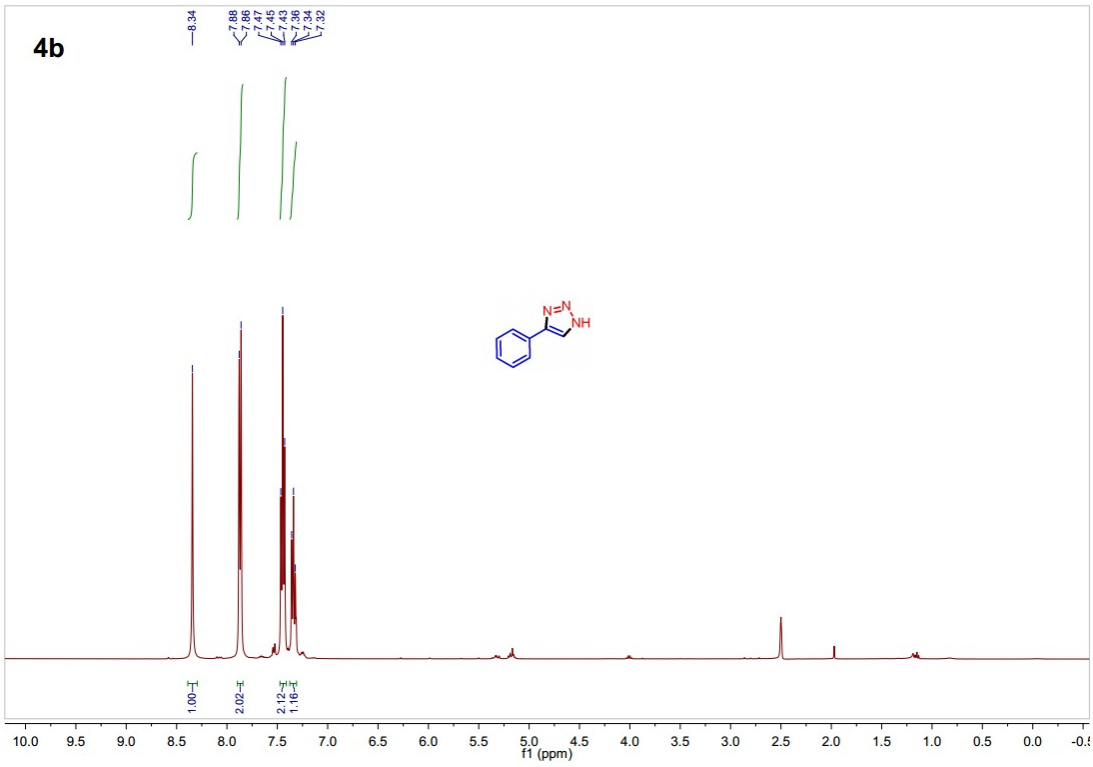

2q
134.0
130.3
129.1
52.3
N3
N3
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

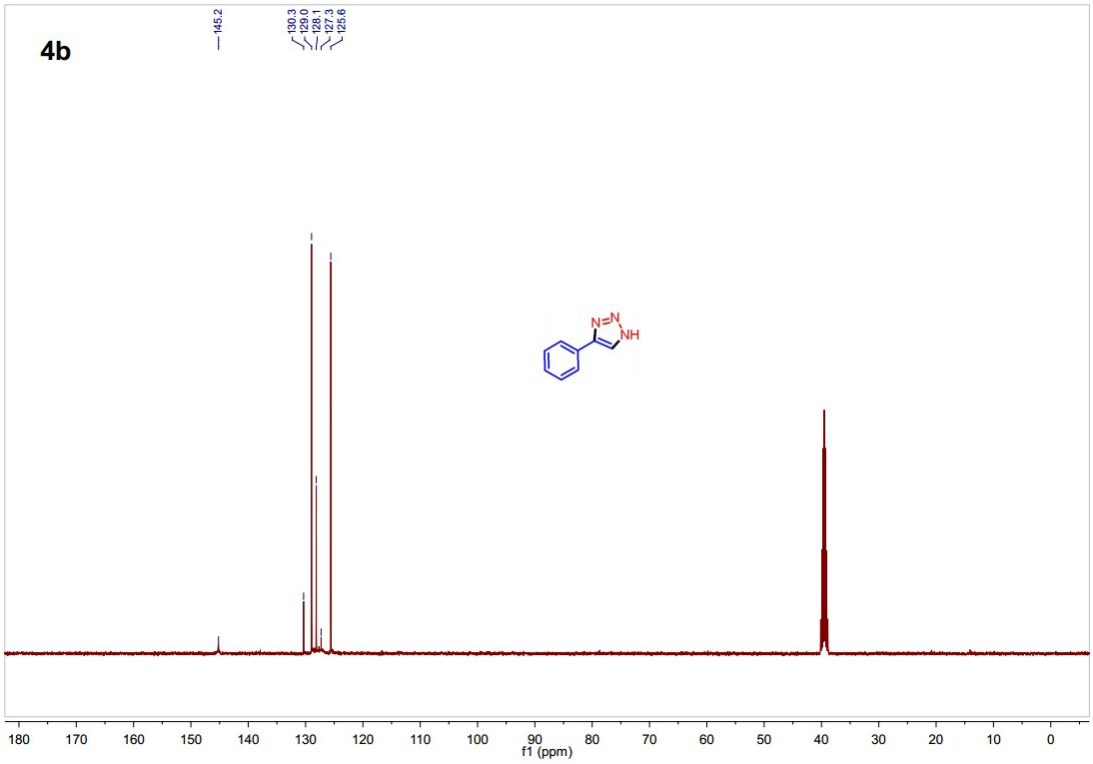

2r
8.96
8.95
8.95
8.94
8.17
8.16
8.15
8.14
7.81
7.79
7.73
7.71
7.55
7.53
7.51
7.44
7.43
7.42
7.41
5.05
N3
N
1.00
1.02
1.03
1.02
1.03
1.02
2.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

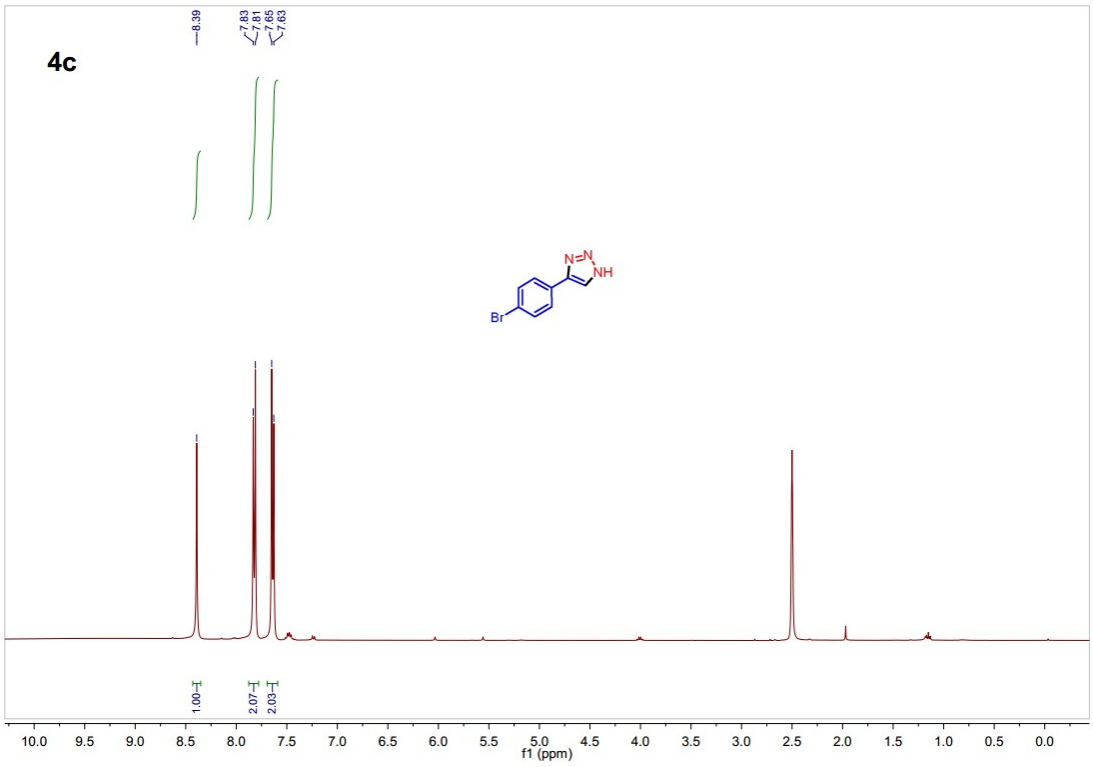

2r
150.1
146.3
136.3
134.1
129.2
128.5
128.4
126.3
121.5
51.1
N3
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

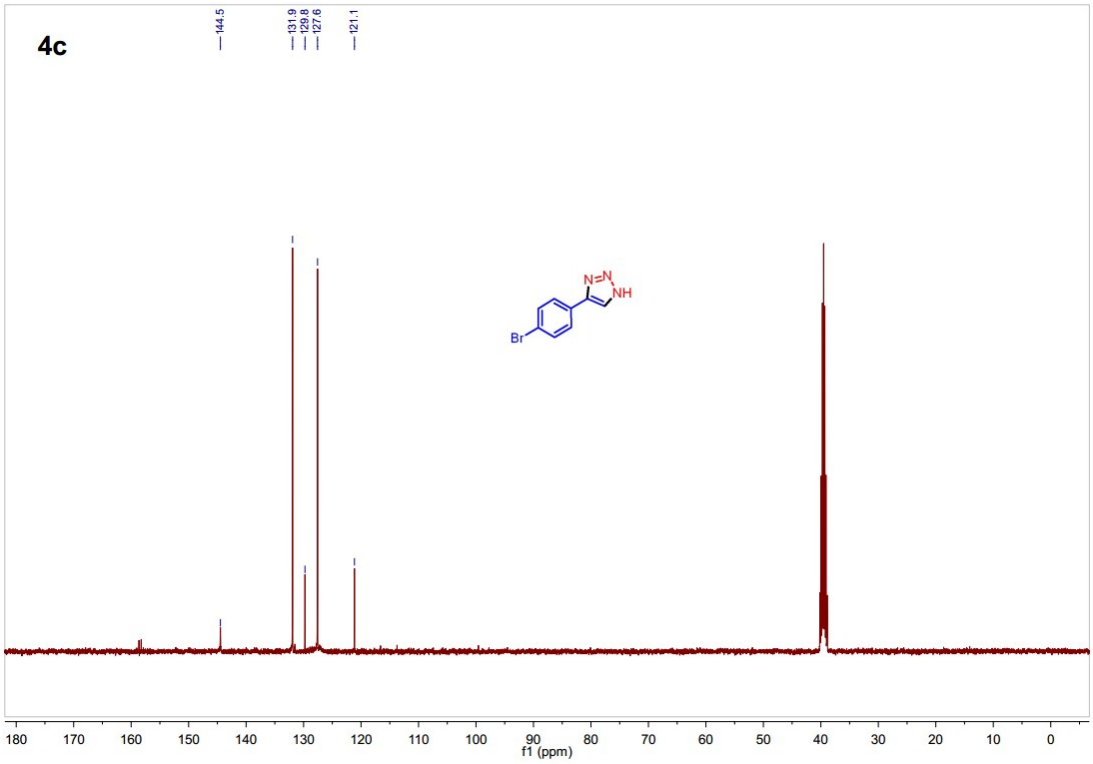

4a
8.21
7.79
7.77
7.02
7.00
3.78
N=N
NH
MeO
0.96
2.00
2.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

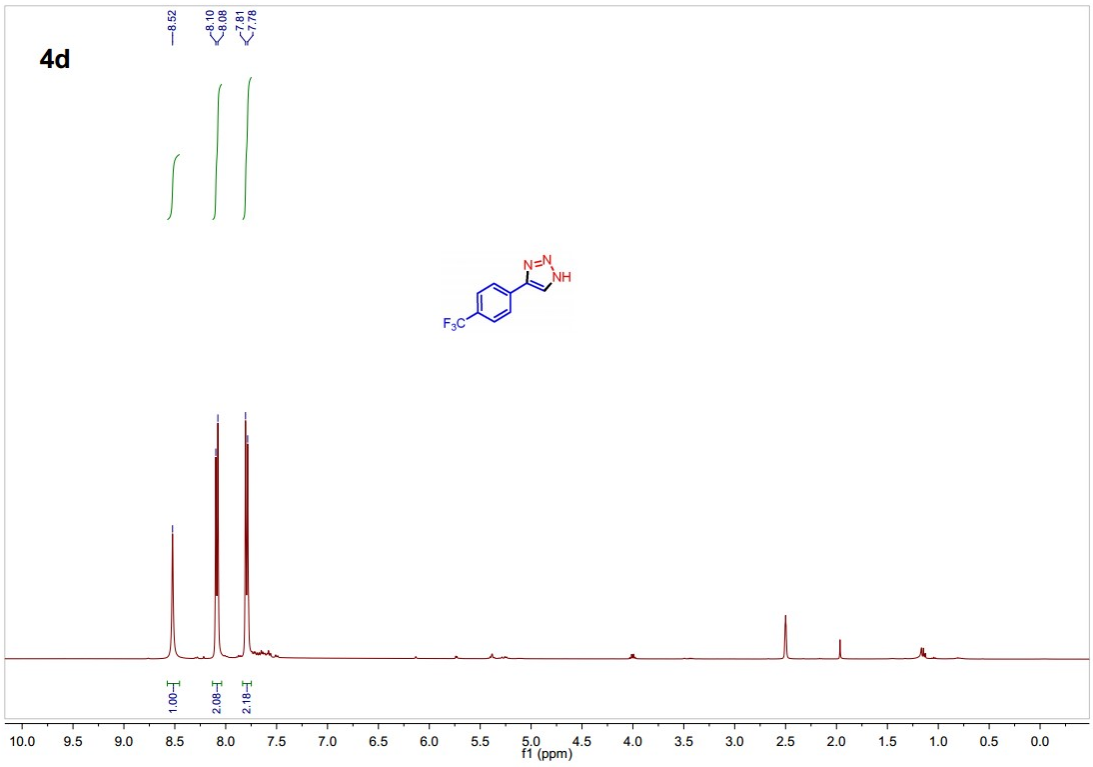

4a
144.89
127.05
122.78
116.61
114.43
113.74
55.22
MeO
NH
N=N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

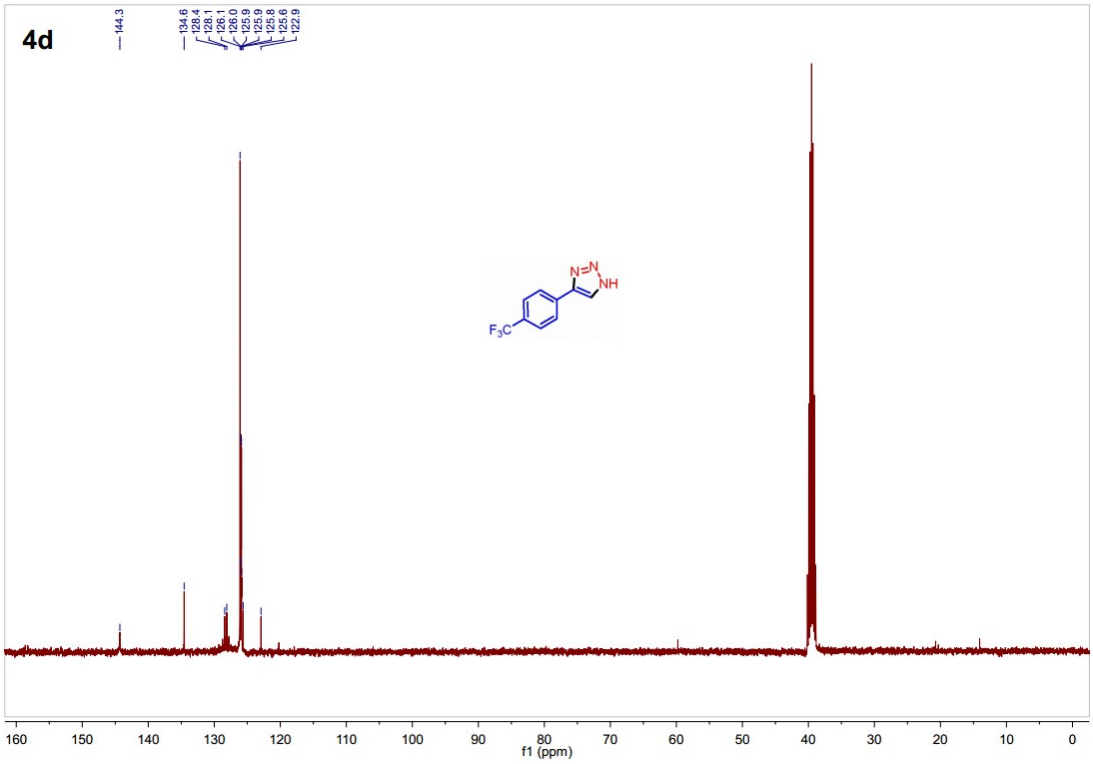

4b
8.34
7.88
7.86
7.47
7.45
7.43
7.36
7.34
7.32
NH
N=N
1.00
2.02
2.12
1.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

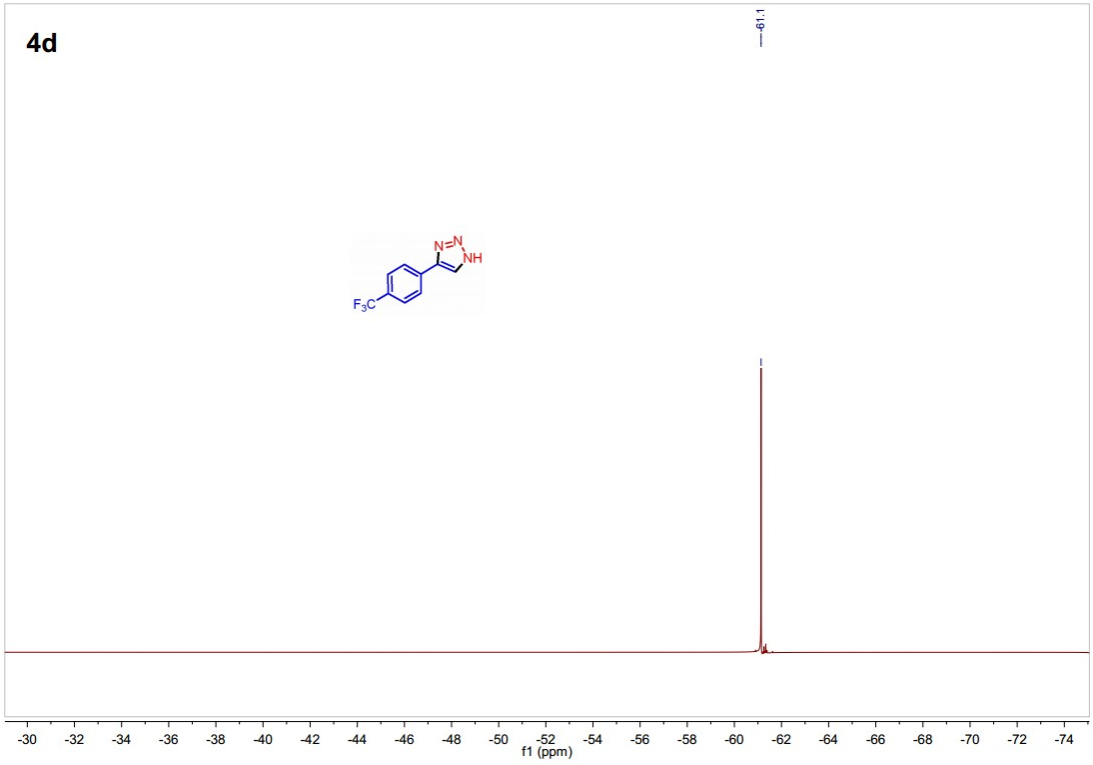

4b
145.2
130.3
129.0
128.1
127.3
125.6
N=N
NH
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

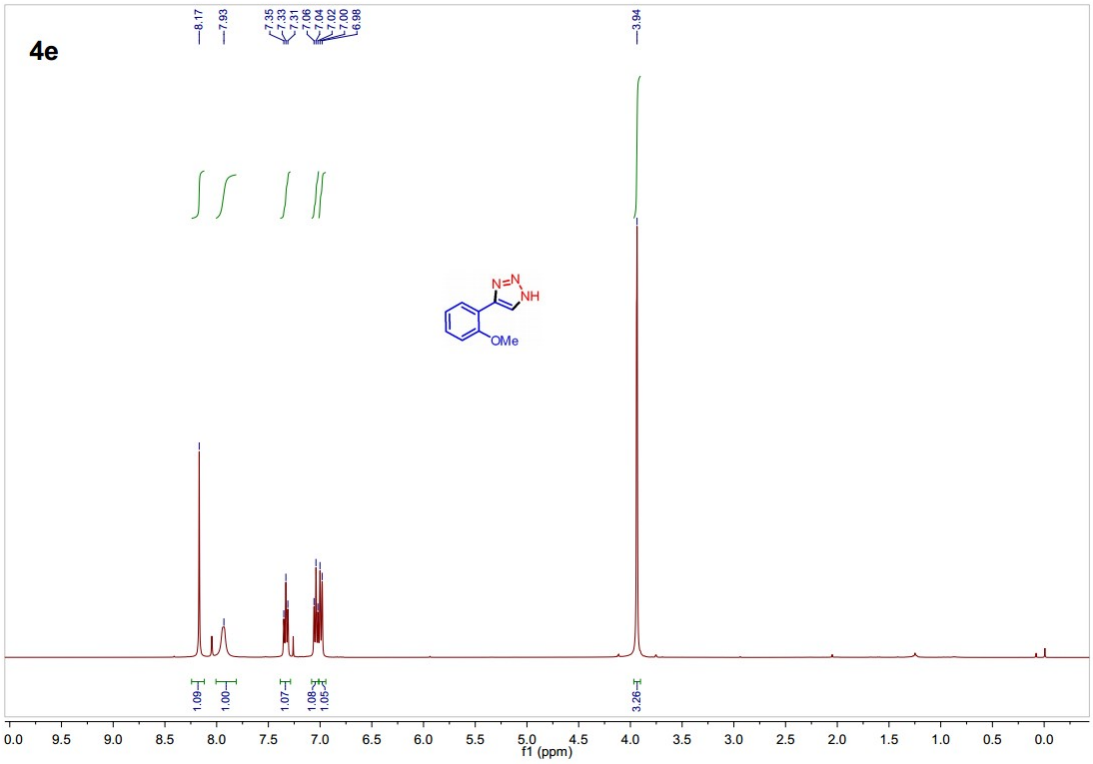

4c
8.39
7.83
7.81
7.65
7.63
N=N
NH
Br
1.00
2.07
2.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

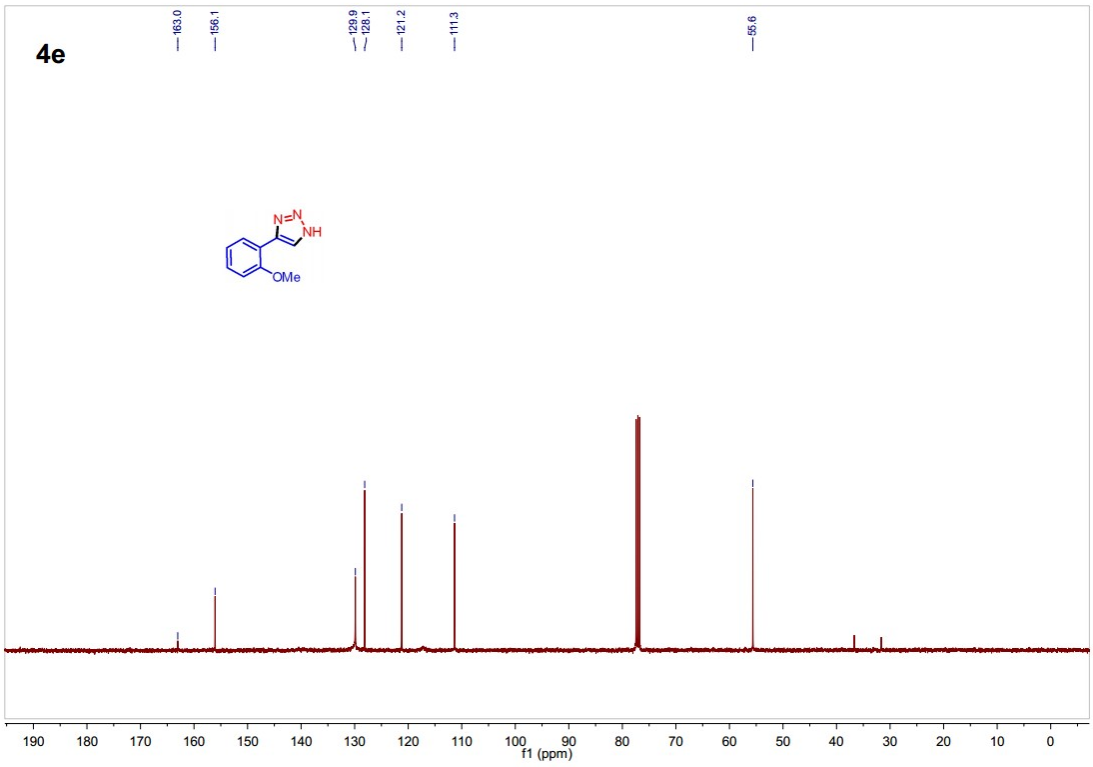

4c
144.5
131.9
129.8
127.6
121.1
N=N
NH
Br
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

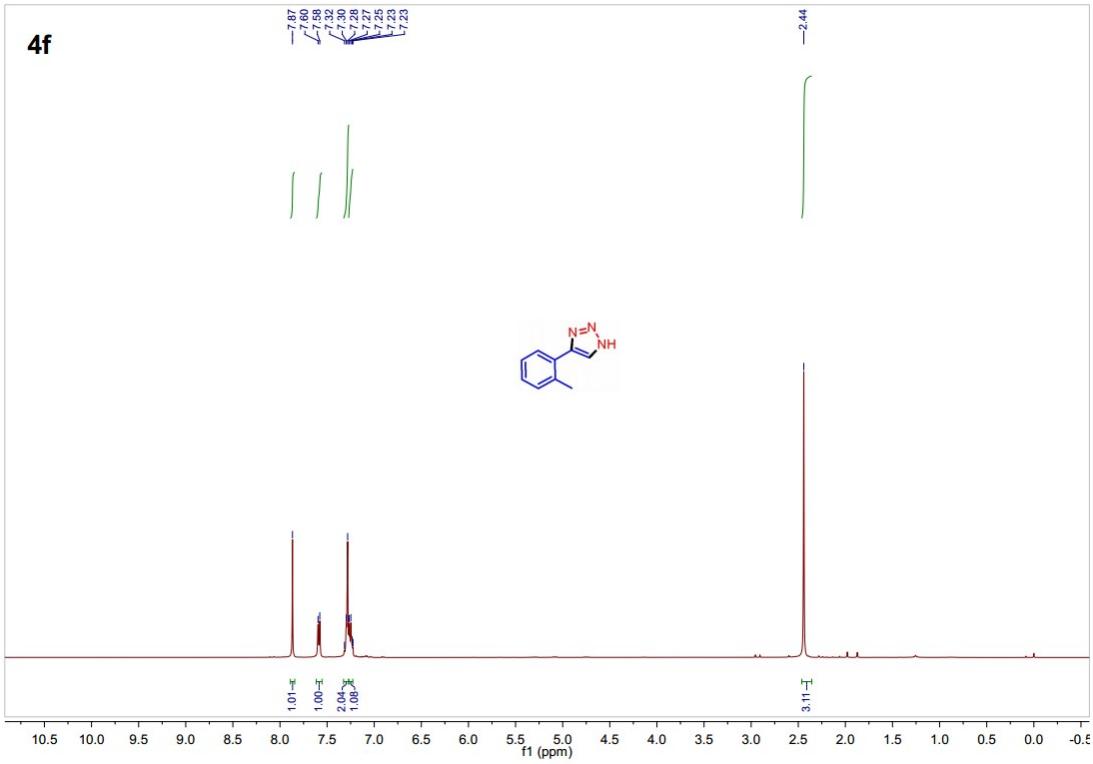

4d
8.52
8.10
8.08
7.81
7.78
N=N
NH
F3C
1.00
2.08
2.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

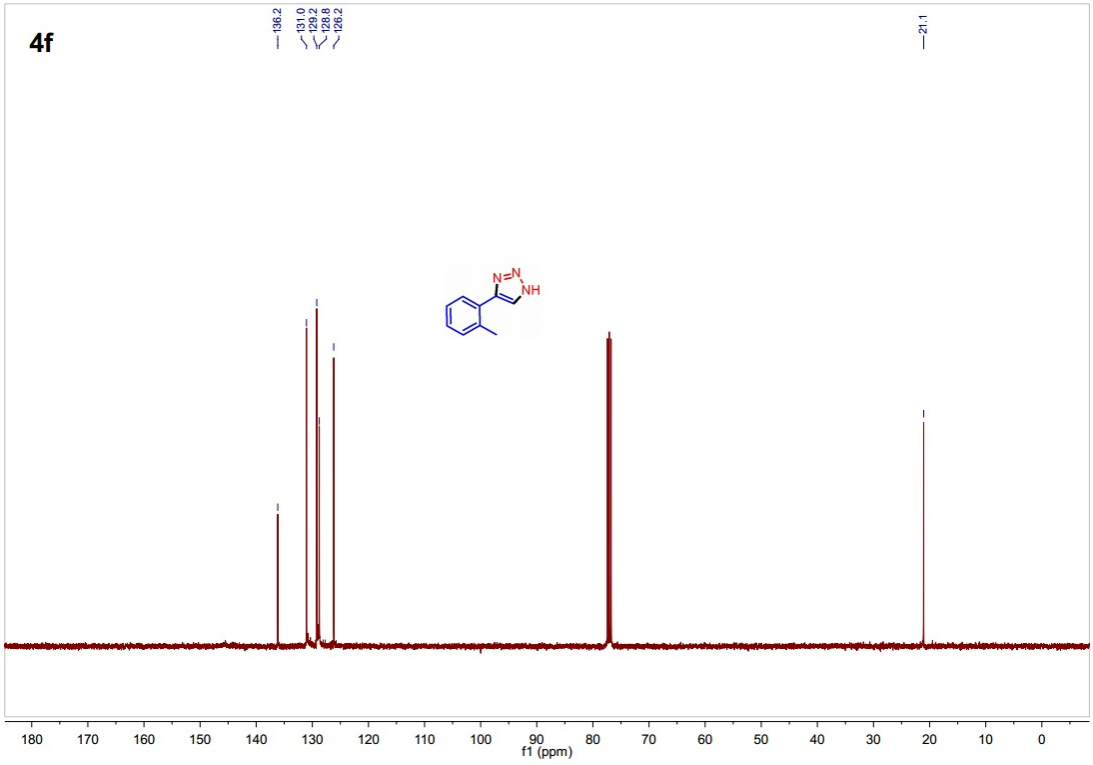

4d
144.3
134.6
128.4
128.1
126.1
126.0
125.9
125.9
125.8
125.6
122.9
N=N
NH
F3C
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

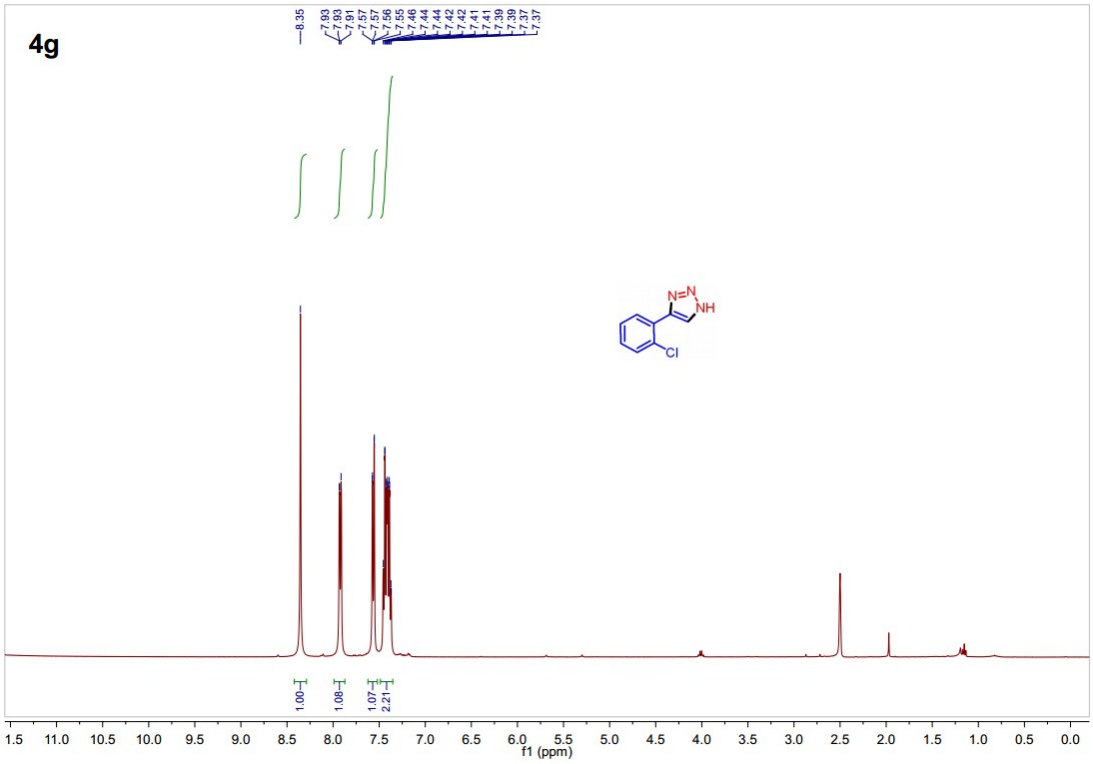

4d
-61.1
N=N
NH
F3C
-30
-32
-34
-36
-38
-40
-42
-44
-46
-48
-50
-52
-54
-56
-58
-60
-62
-64
-66
-68
-70
-72
-74
f1 (ppm)

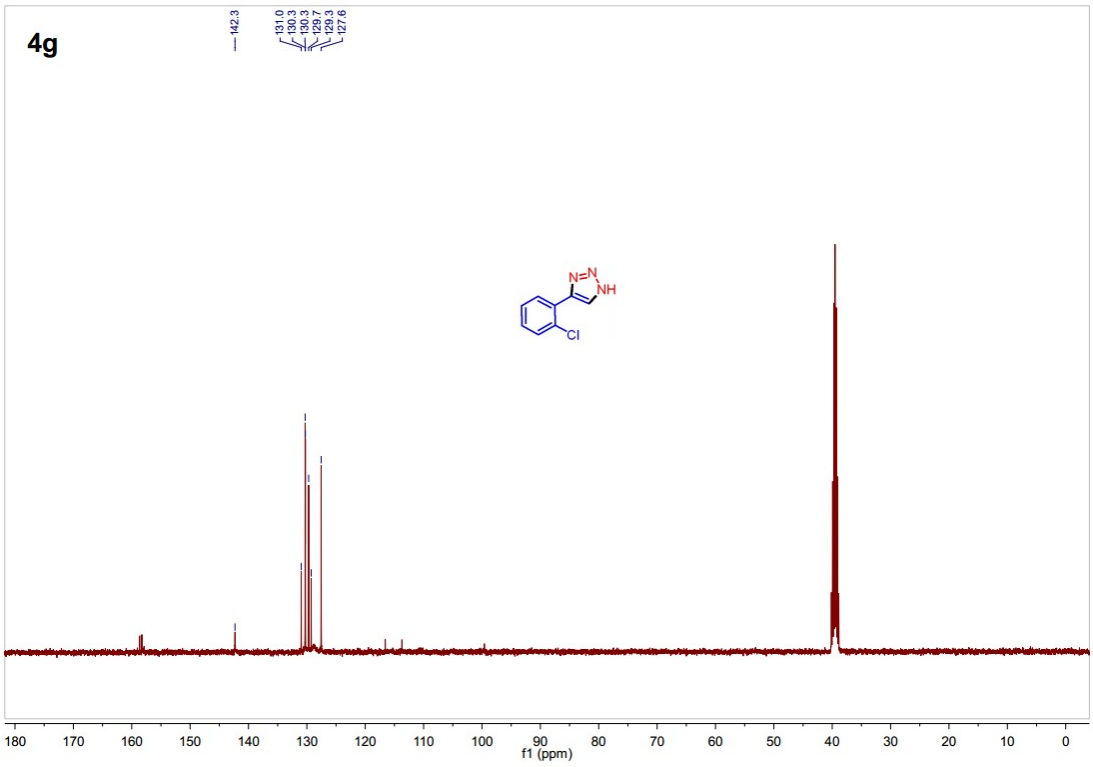

4e
8.17
7.93
7.35
7.33
7.31
7.06
7.04
7.02
7.00
6.98
3.94
N=N
NH
OMe
1.09
1.00
1.07
1.08
1.05
3.26
f1 (ppm)

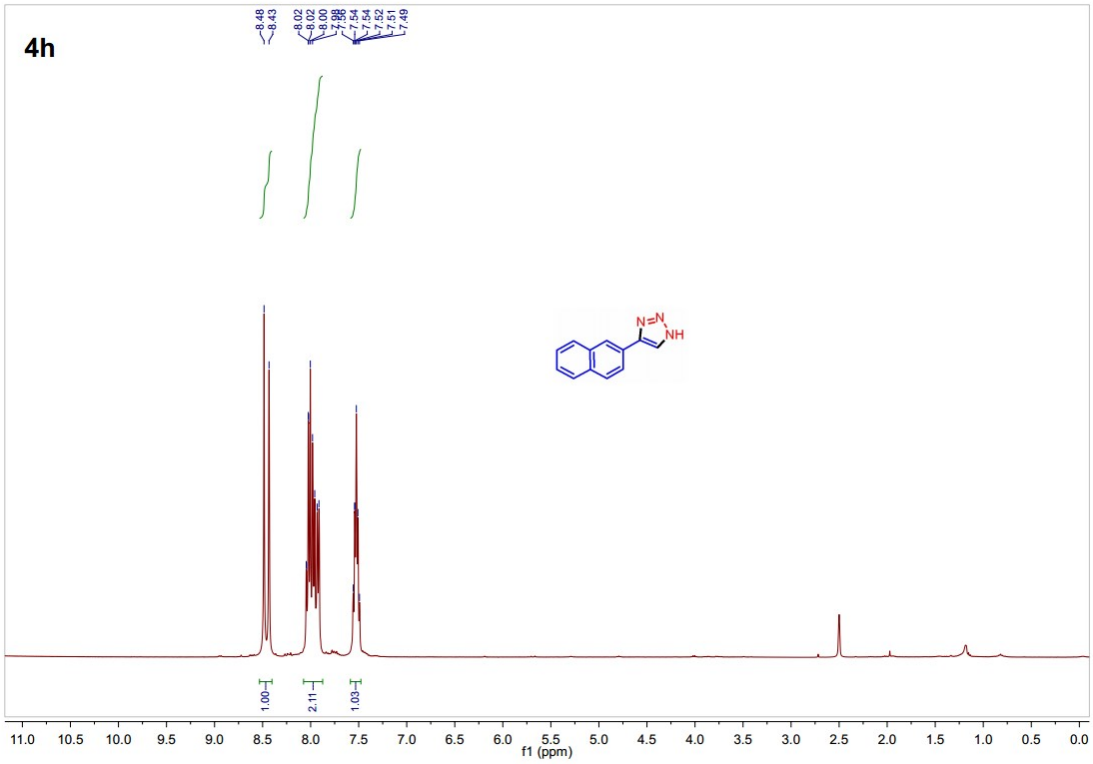

4e
163.0
156.1
129.9
128.1
121.2
111.3
55.6
N=N
NH
OMe
f1 (ppm)

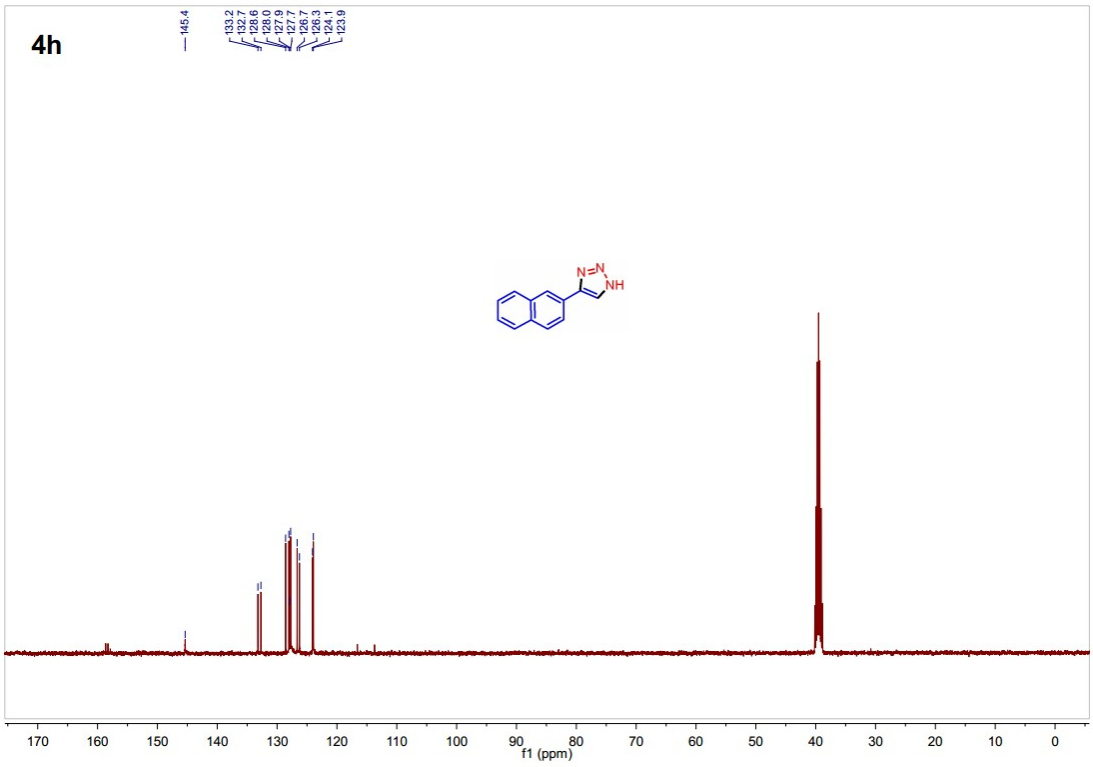

4f
7.87
7.60
7.58
7.32
7.30
7.29
7.27
7.25
7.23
7.23
2.44
1.01
1.00
2.04
1.08
3.11
f1 (ppm)


4f
136.2
131.0
129.2
128.8
126.2
21.1
f1 (ppm)

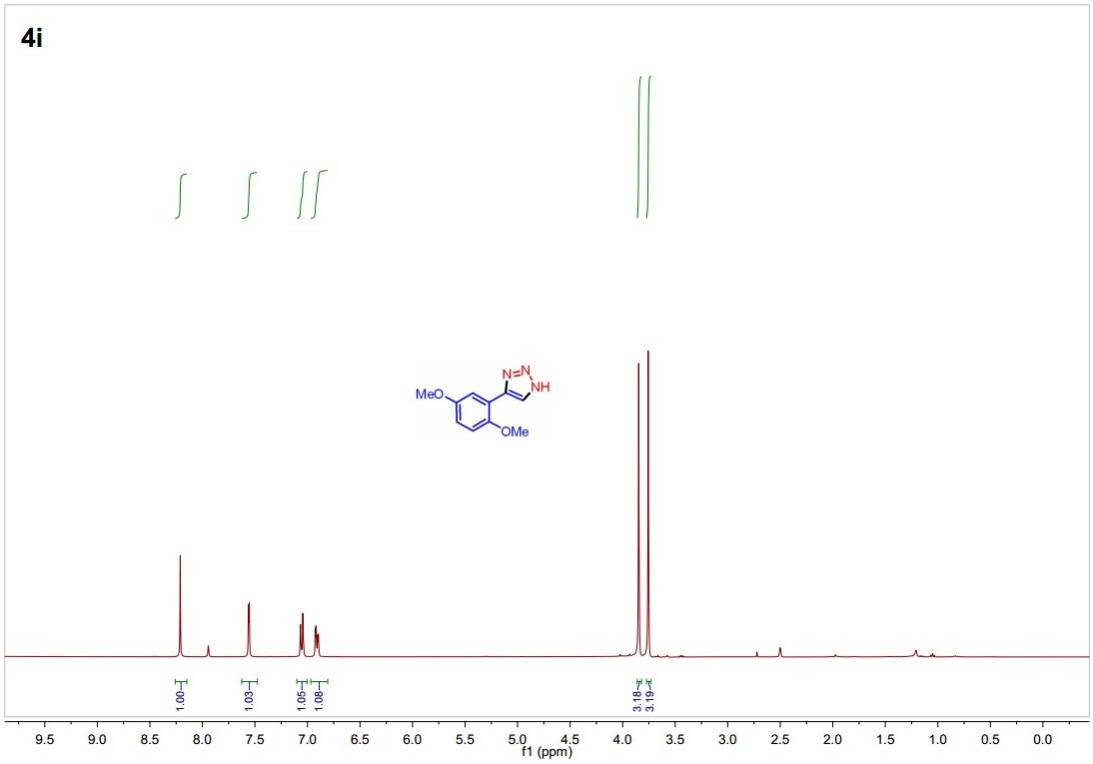

4g
8.35
7.93
7.91
7.57
7.56
7.55
7.46
7.44
7.42
7.41
7.39
7.37
1.00
1.08
1.07
2.21
N=N
NH
Cl
f1 (ppm)


4g
142.3
131.0
130.3
130.3
129.7
129.3
127.6
N=N
NH
Cl
f1 (ppm)

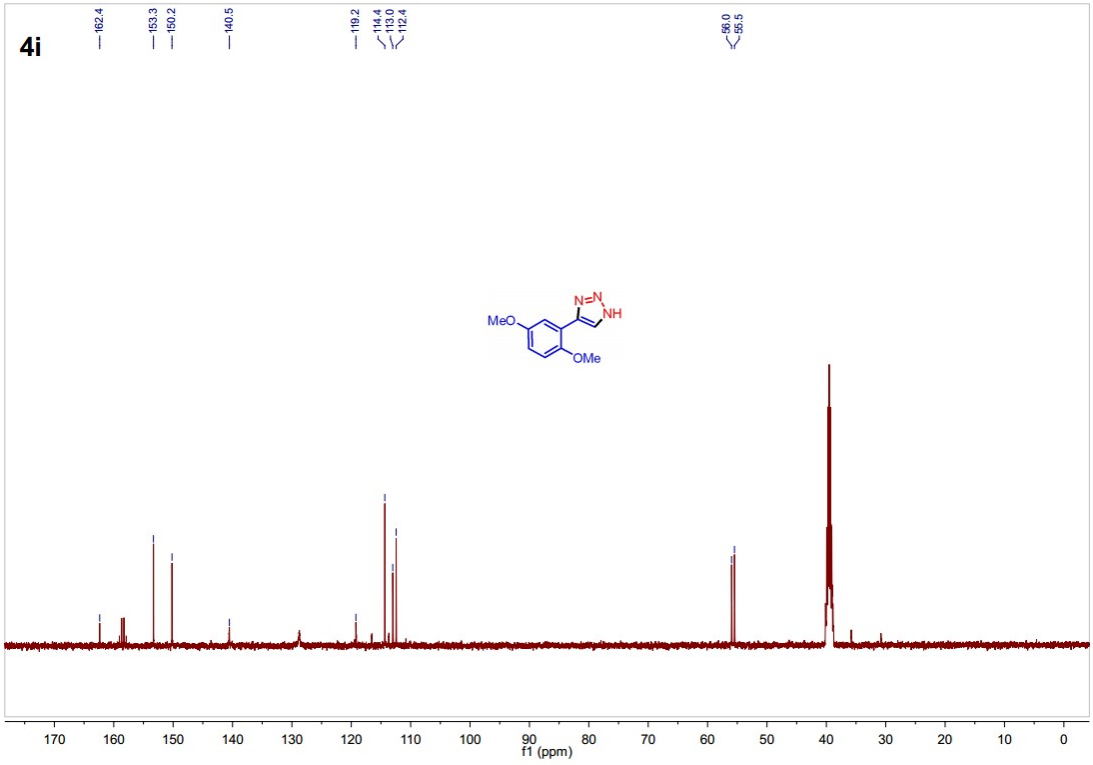

4h
8.48
8.43
8.02
8.02
8.00
7.54
7.54
7.52
7.51
7.49
N=N
NH
1.00
2.11
1.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

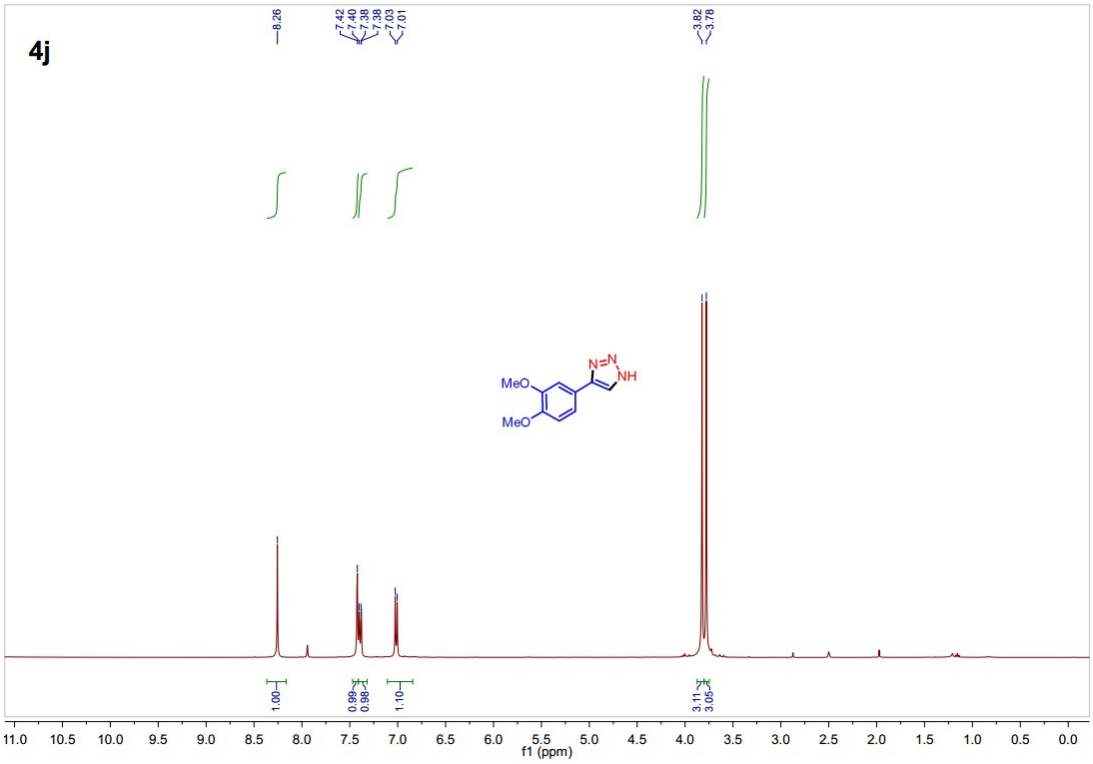

4h
145.4
133.2
132.7
128.6
128.0
127.9
127.7
126.7
126.3
124.1
123.9
N=N
NH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

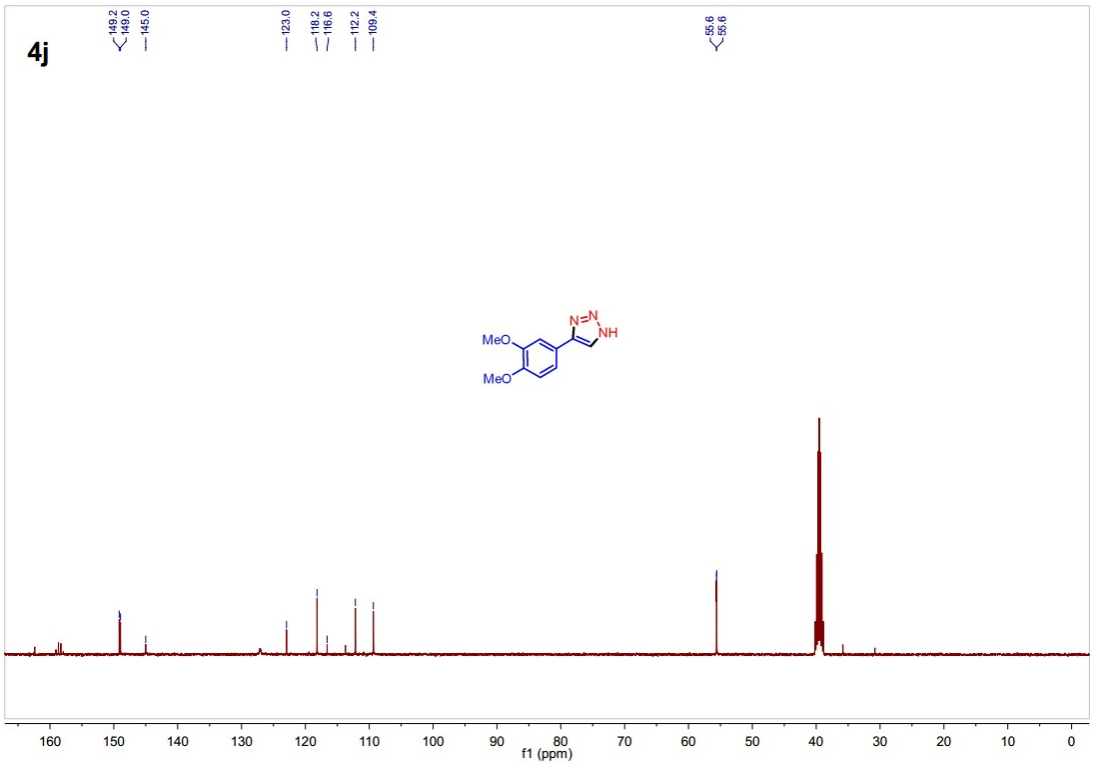
4i

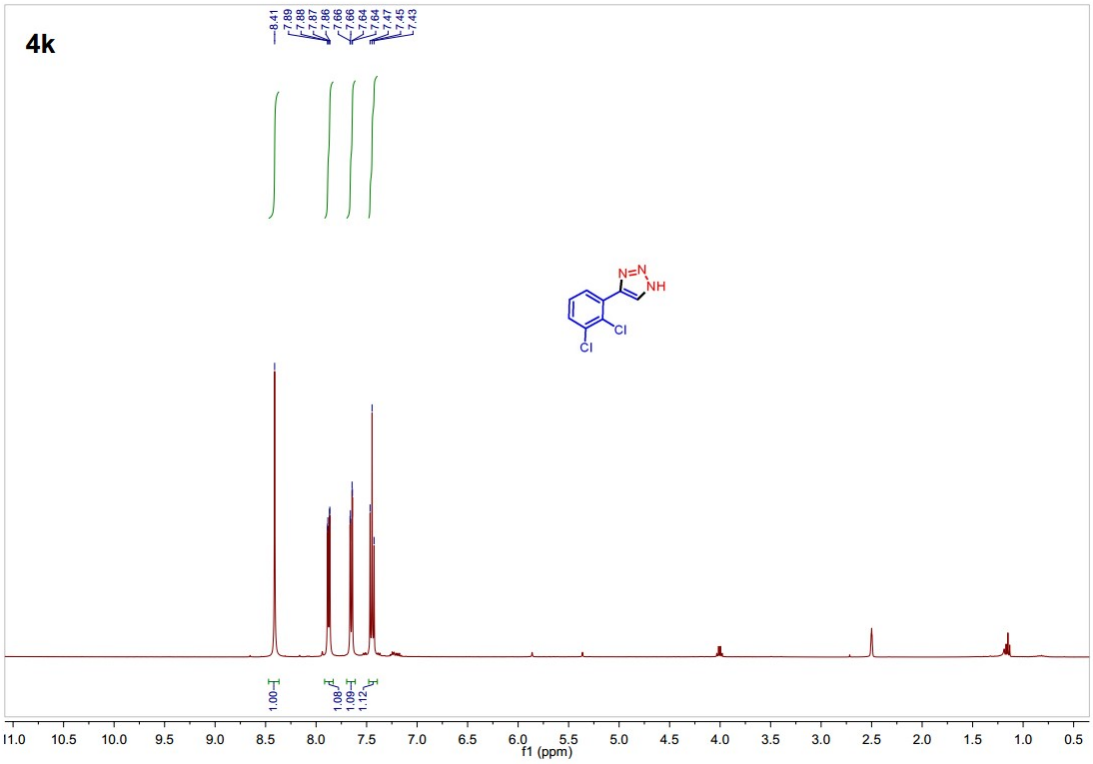

MeO
OMe
NH
1.00
1.03
1.05
1.08
3.18
3.19
f1 (ppm)

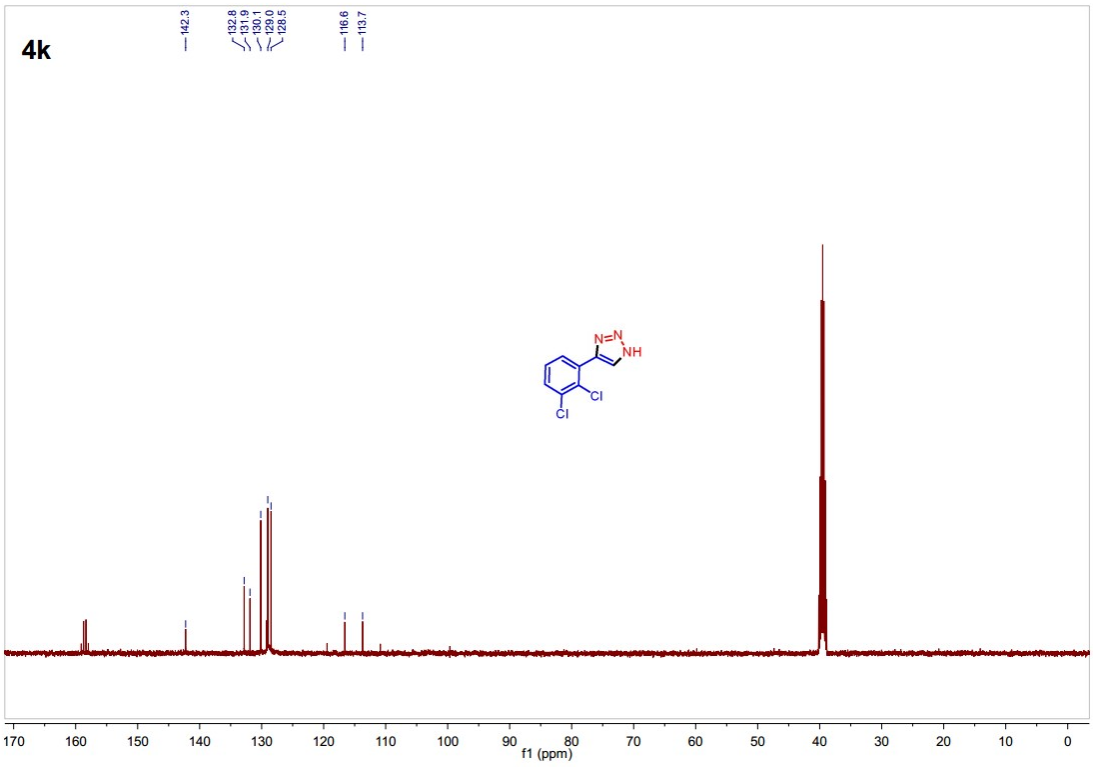
4i

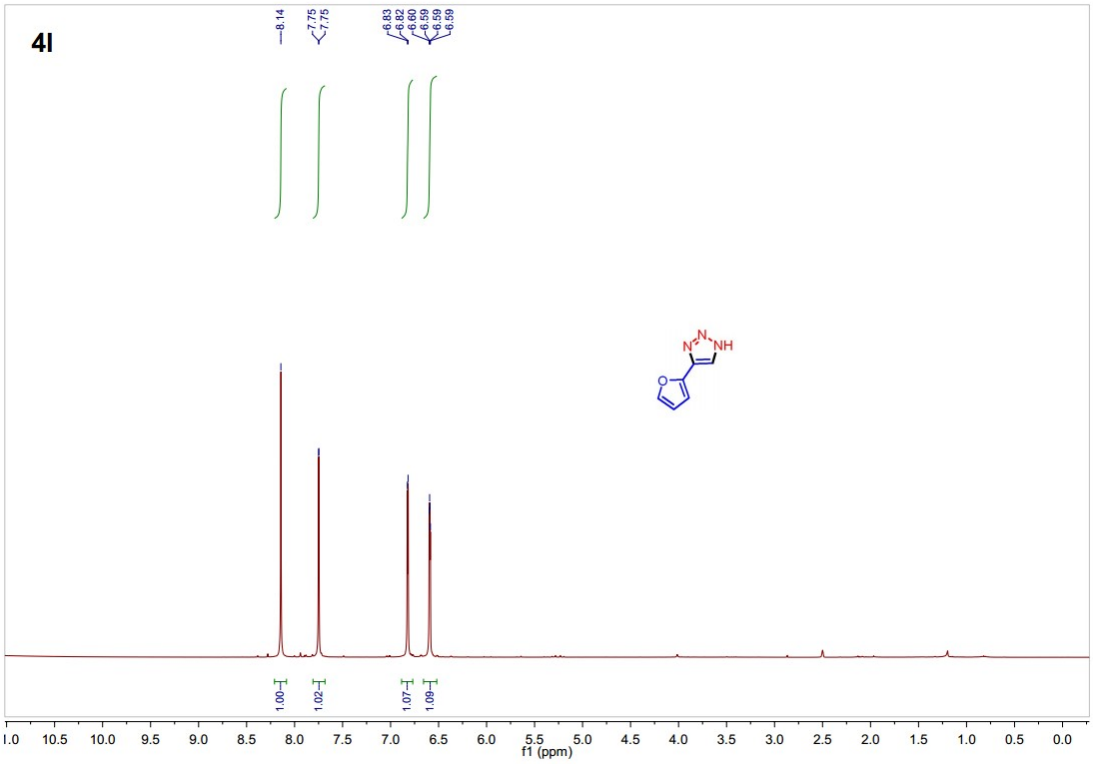

162.4
153.3
150.2
140.5
119.2
114.4
113.0
112.4
56.0
55.5
MeO
OMe
NH
f1 (ppm)

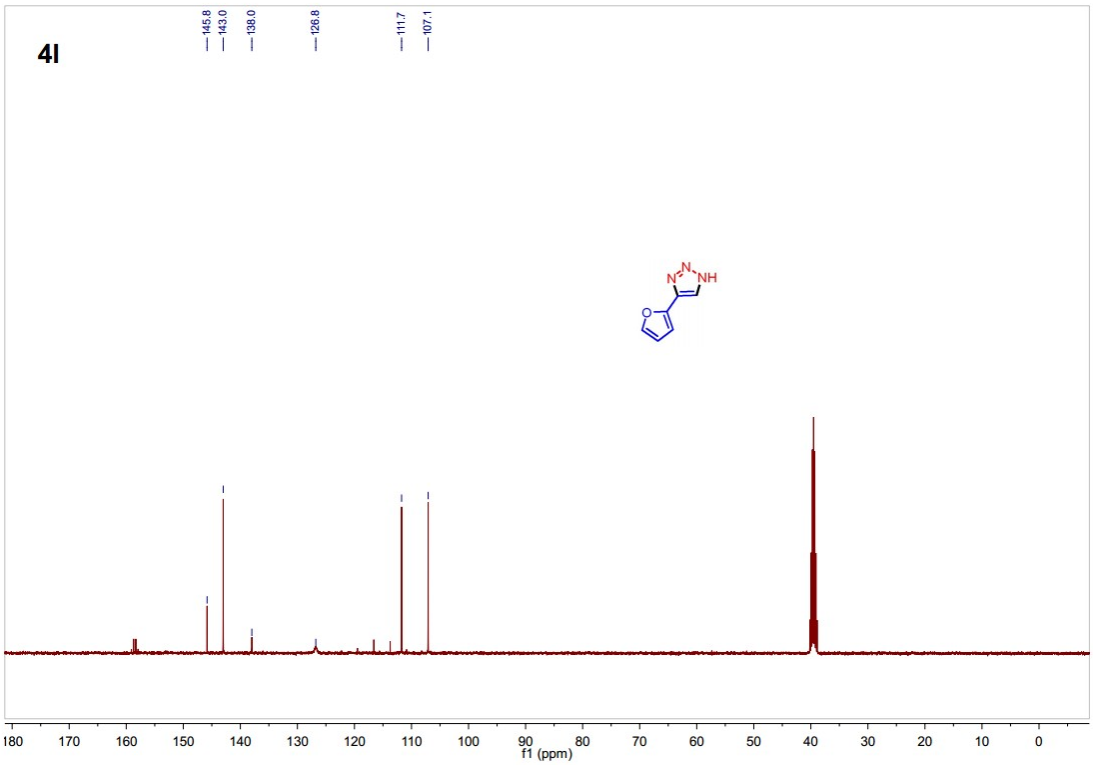

4j
8.26
7.42
7.40
7.38
7.38
7.03
7.01
3.82
3.78
MeO
MeO
N=N
NH
1.00
0.99
0.98
1.10
3.11
3.05
f1 (ppm)

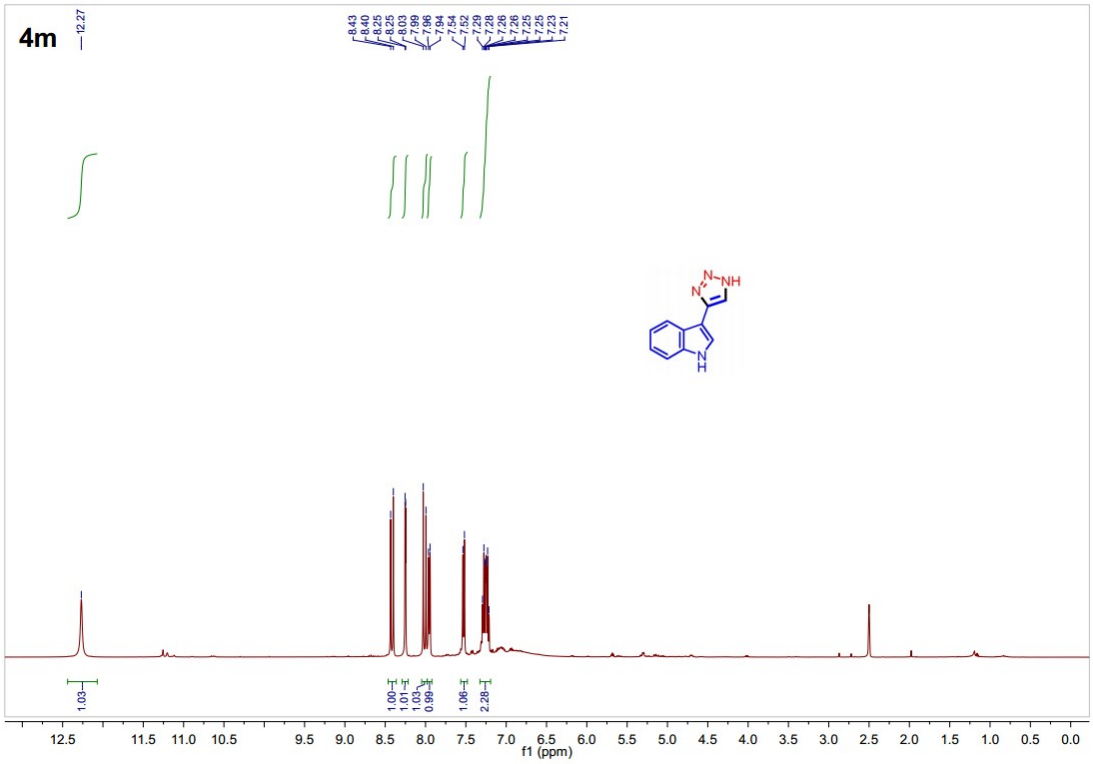

4j
149.2
149.0
145.0
123.0
118.2
116.6
112.2
109.4
55.6
55.6
MeO
MeO
N=N
NH
f1 (ppm)

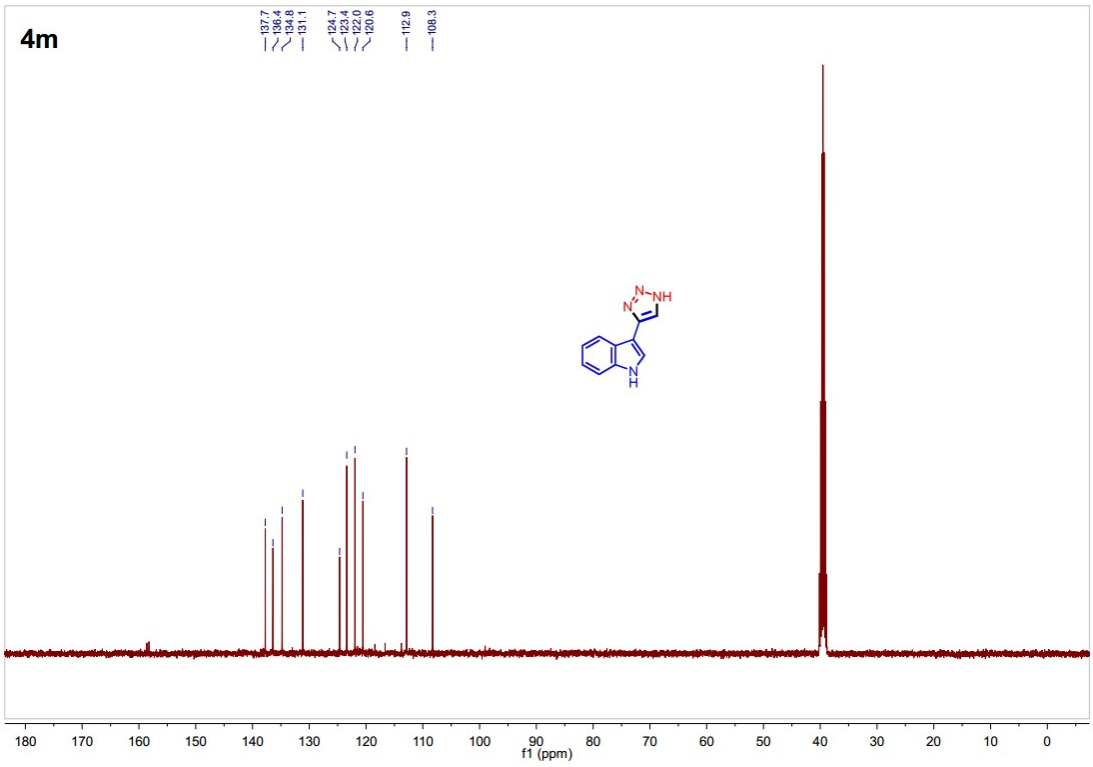

4k
8.41
7.89
7.88
7.87
7.86
7.66
7.64
7.64
7.47
7.45
7.43
N=N
NH
Cl
Cl
1.00
1.08
1.09
1.12
f1 (ppm)

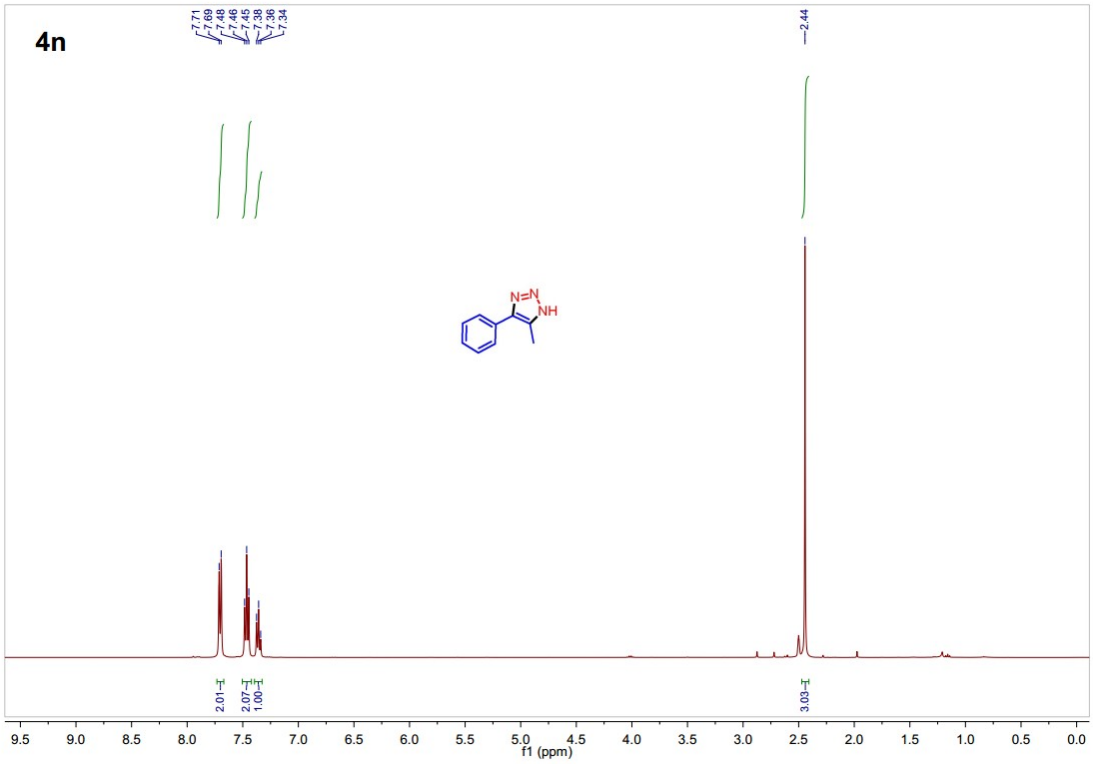

4k
142.3
132.8
131.9
130.1
129.0
128.5
116.6
113.7
N=N
NH
Cl
Cl
f1 (ppm)

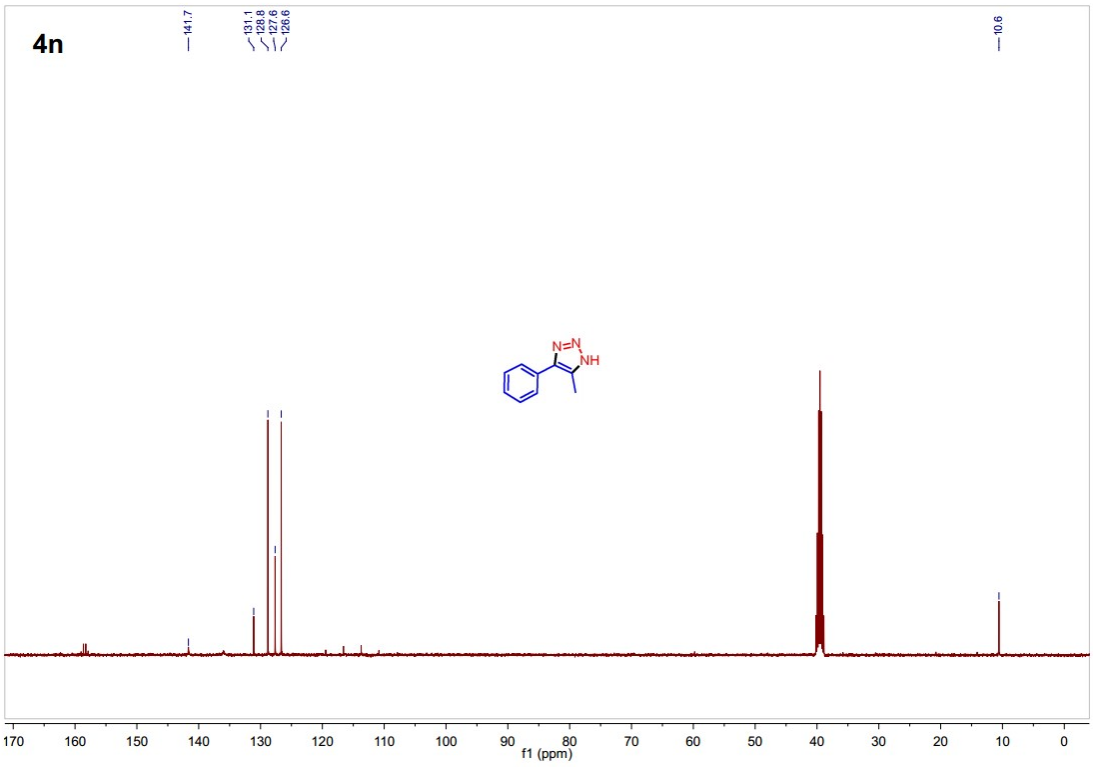

4l
8.14
7.75
7.75
6.83
6.82
6.60
6.59
6.59
6.59
NH
1.00
1.02
1.07
1.09
f1 (ppm)

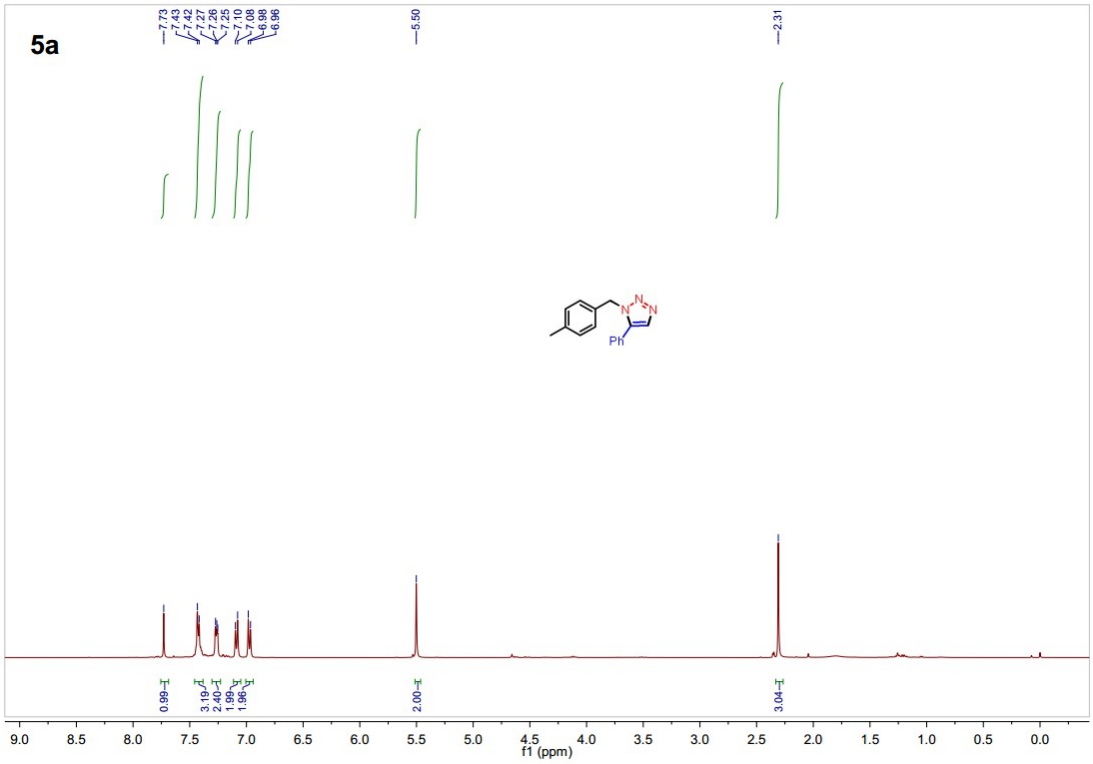

4l
145.8
143.0
138.0
126.8
111.7
107.1
NH
f1 (ppm)

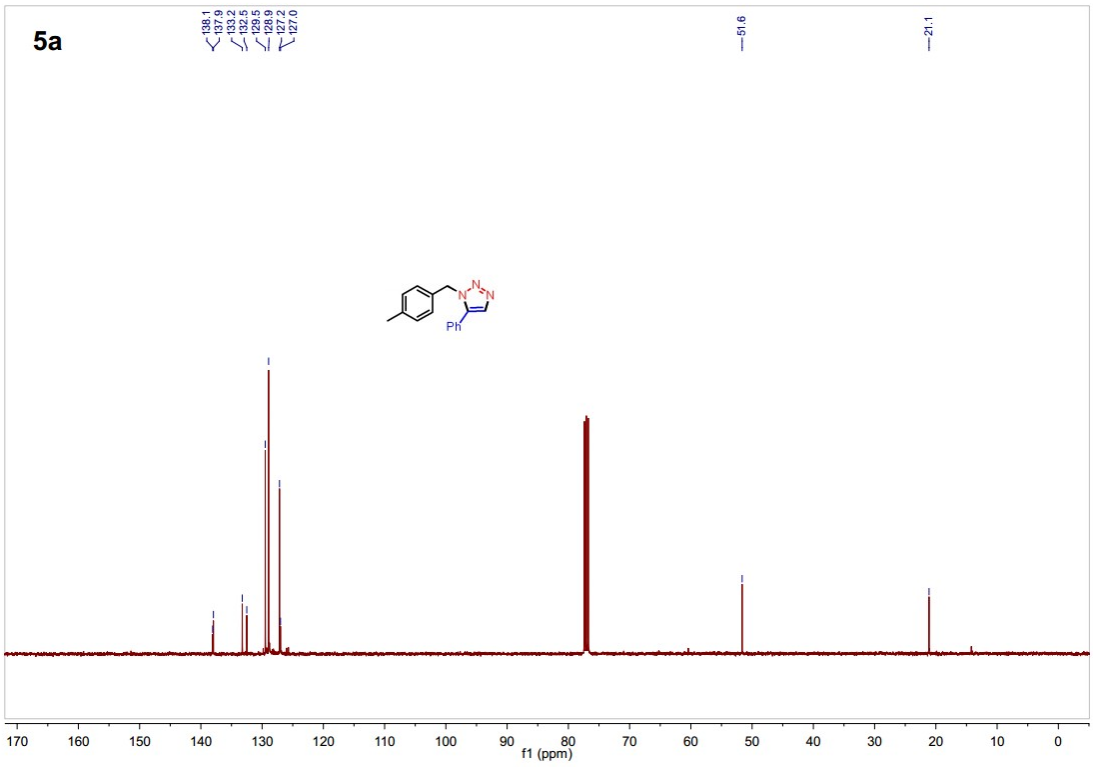

4m
12.27
8.43
8.40
8.25
8.25
8.03
7.99
7.96
7.84
7.84
7.52
7.29
7.28
7.26
7.26
7.25
7.25
7.23
7.21
NH
N
N
H
1.03
1.00
1.01
1.03
0.99
1.06
2.28
f1 (ppm)

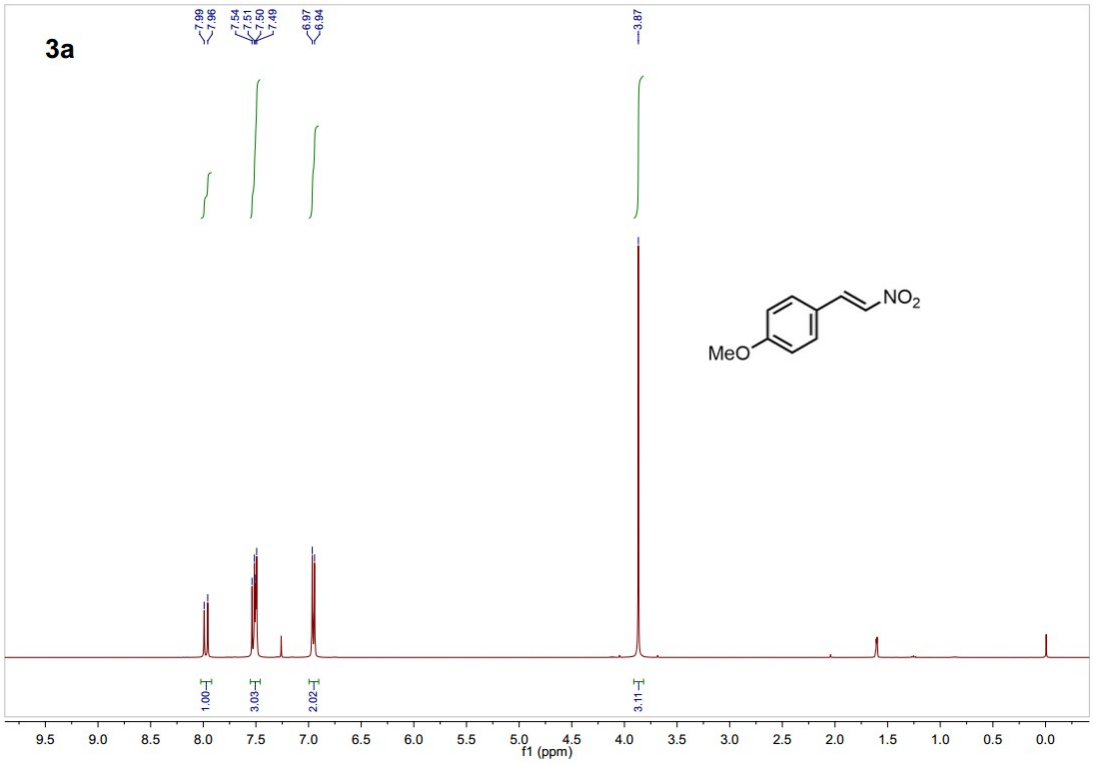

4m
137.7
136.4
134.8
131.1
124.7
123.4
122.0
120.6
112.9
108.3
NH
N
N
H
f1 (ppm)

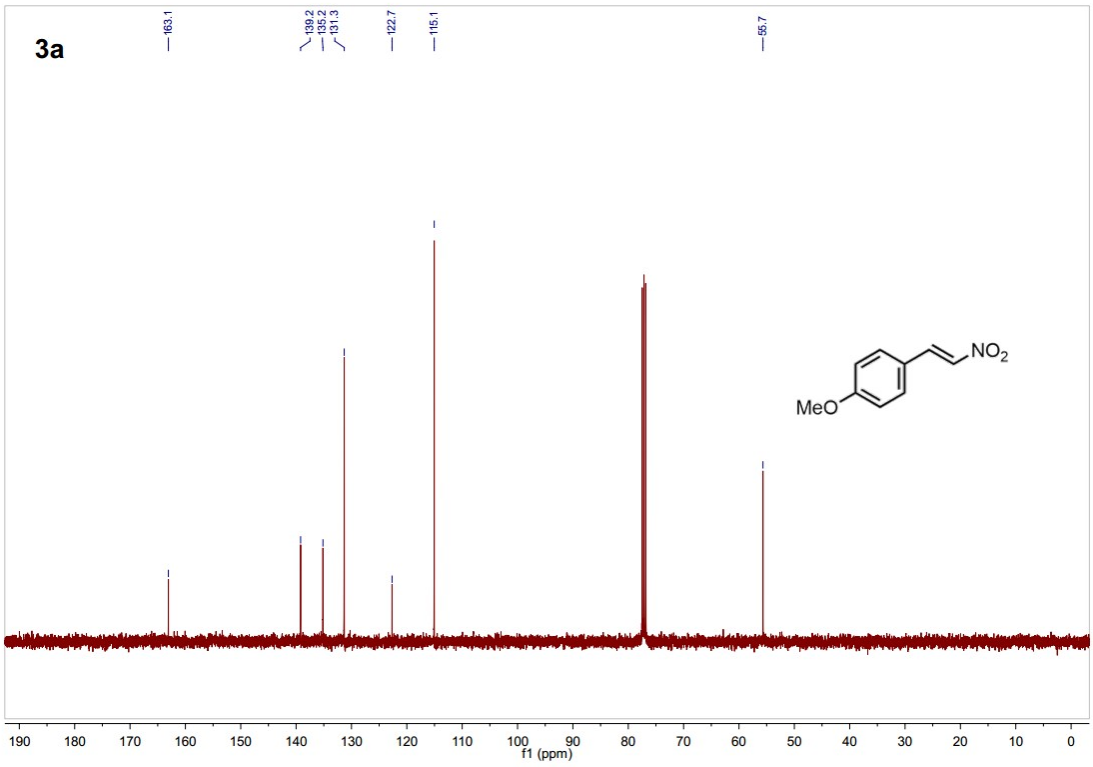

4n
7.71
7.69
7.48
7.46
7.45
7.38
7.36
7.34
2.44
N=N
NH
2.01
2.07
1.00
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

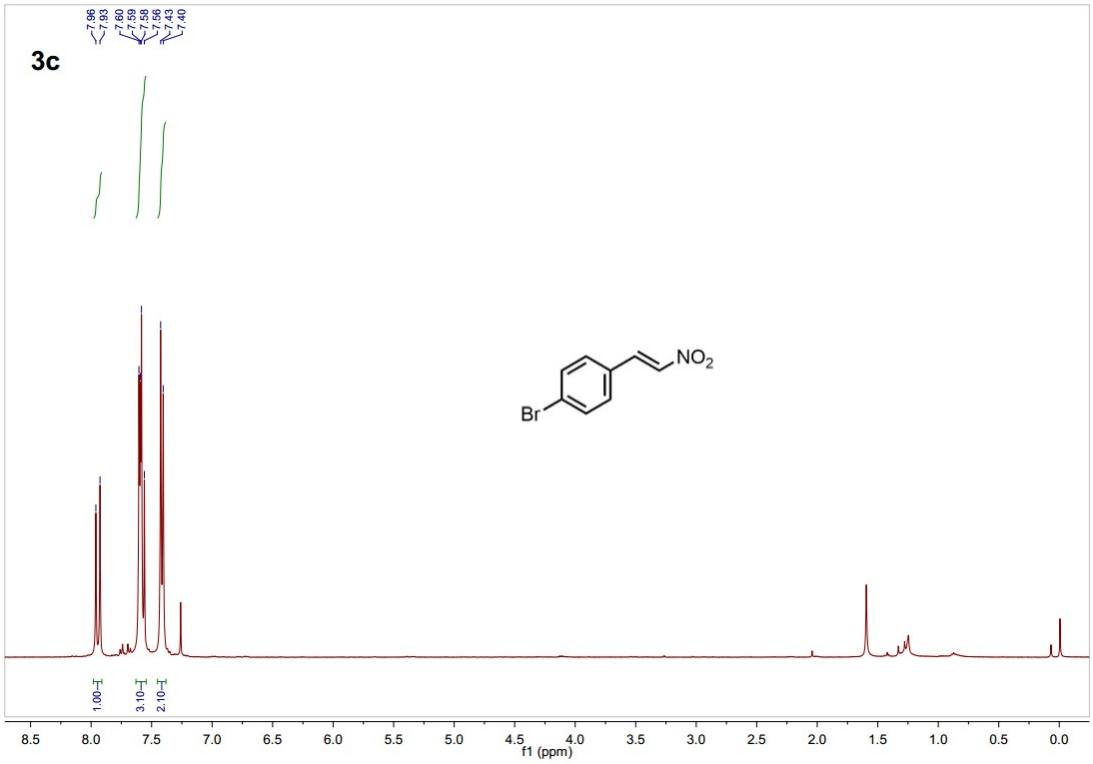

4n
141.7
131.1
128.8
127.6
126.6
10.6
N=N
NH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

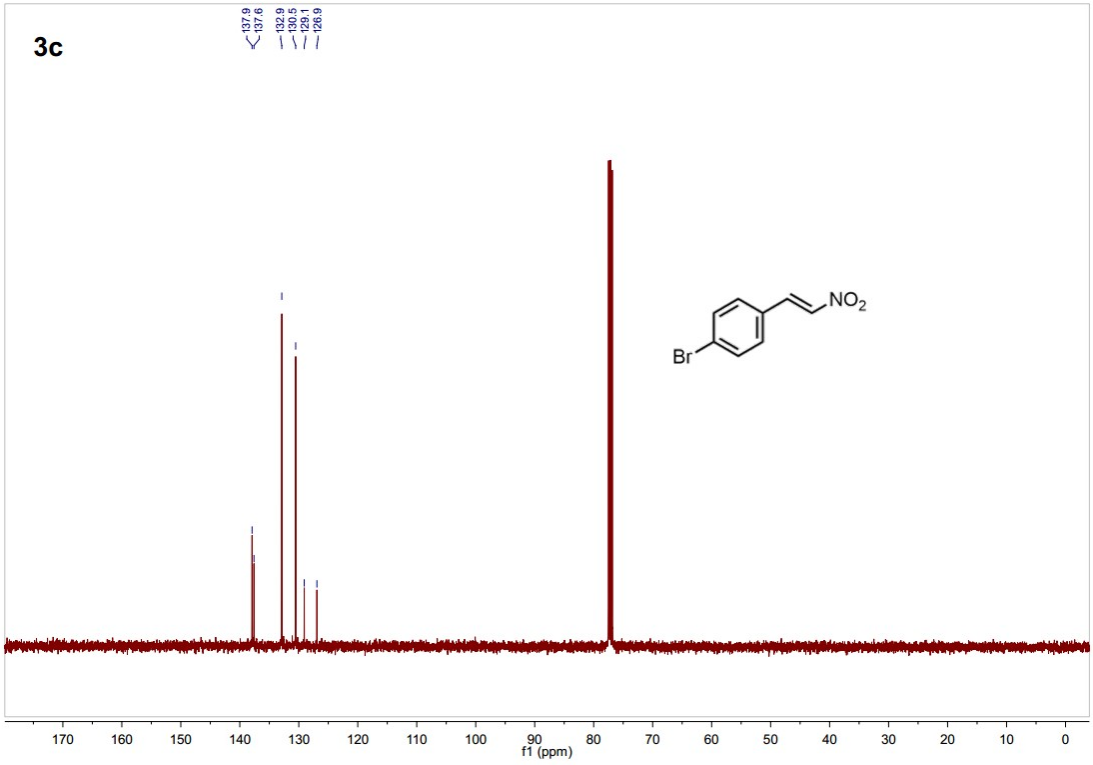

5a
7.73
7.43
7.42
7.27
7.26
7.25
7.10
7.08
6.98
6.96
5.50
2.31
Ph
0.99
3.19
2.40
1.99
1.96
2.00
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

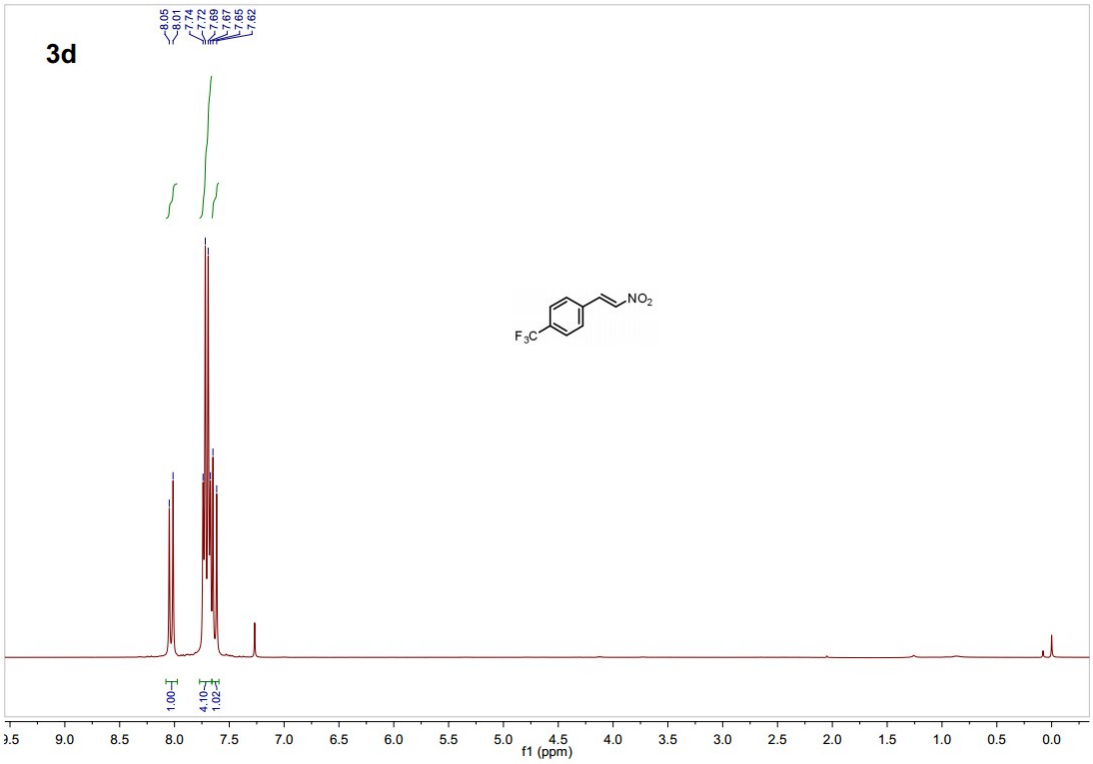

5a
138.1
137.9
133.2
132.5
129.5
128.9
127.2
127.0
51.6
21.1
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

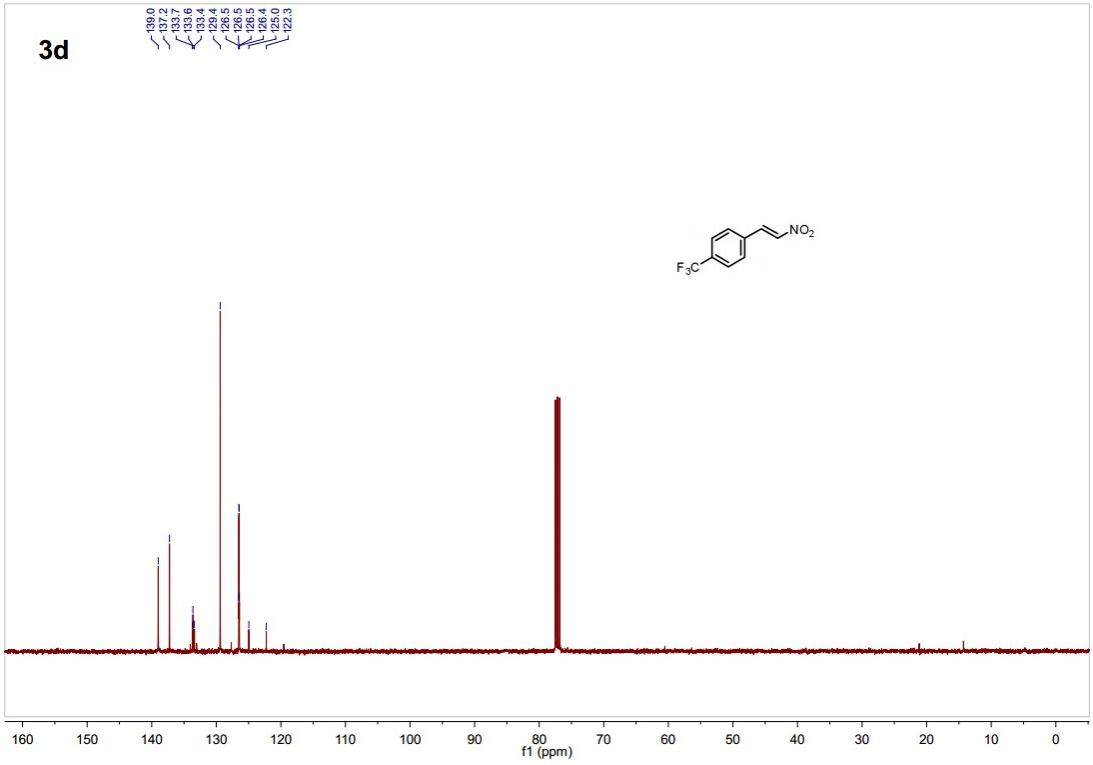

3a
7.99
7.96
7.54
7.51
7.50
7.49
6.97
6.94
3.87
NO2
MeO
1.00
3.03
2.02
3.11
f1 (ppm)


3a
163.1
139.2
135.2
131.3
122.7
115.1
55.7
NO2
MeO
f1 (ppm)

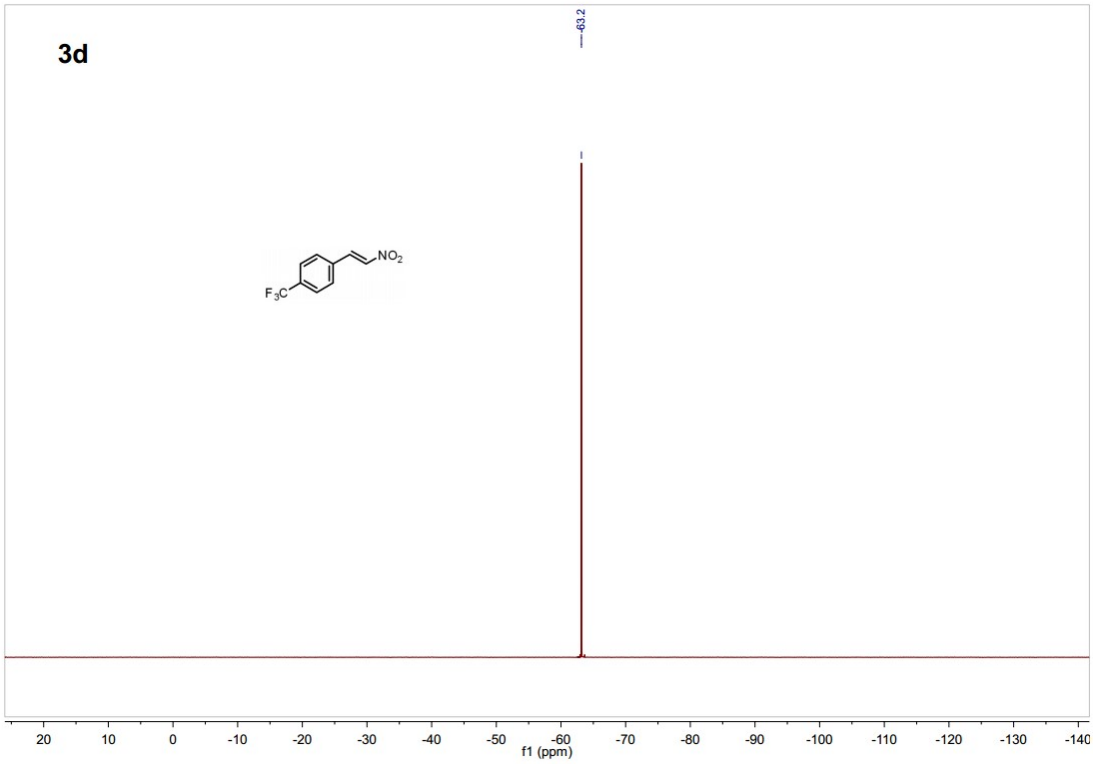

3c
7.96
7.93
7.60
7.59
7.58
7.56
7.43
7.40
NO2
Br
1.00
3.10
2.10
f1 (ppm)


3c
137.9
137.6
132.9
130.5
129.1
126.9
NO2
Br
f1 (ppm)

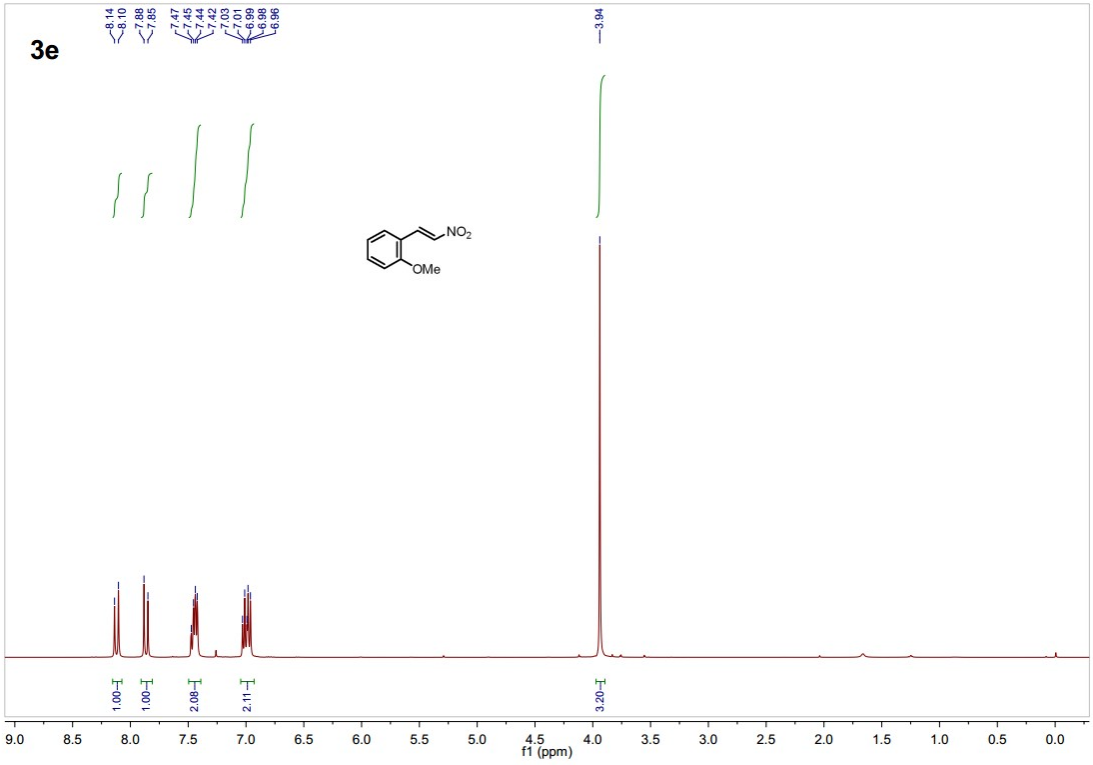

3d
8.05
8.01
7.74
7.72
7.69
7.67
7.65
7.62
NO2
F3C
1.00
4.10
1.02
f1 (ppm)


3d
139.0
137.2
133.7
133.6
133.4
129.4
126.5
126.5
126.5
126.4
125.0
122.3
NO2
F3C
f1 (ppm)

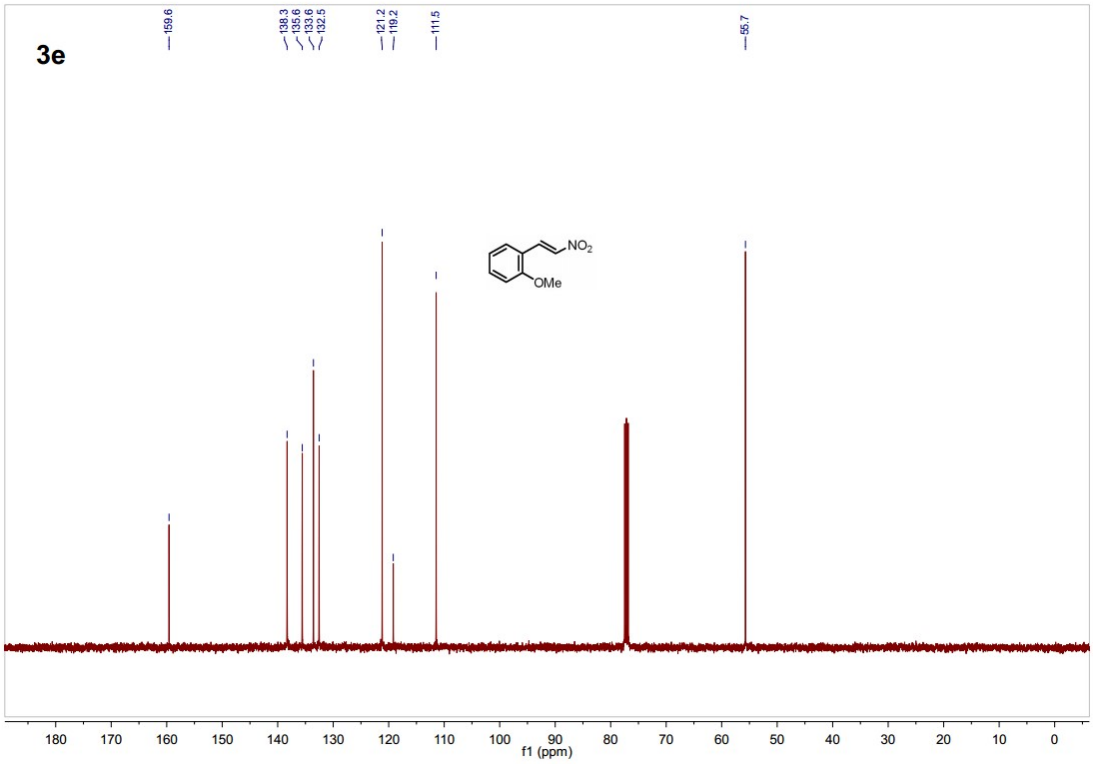
3d


-63.2
NO2
F3C
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)

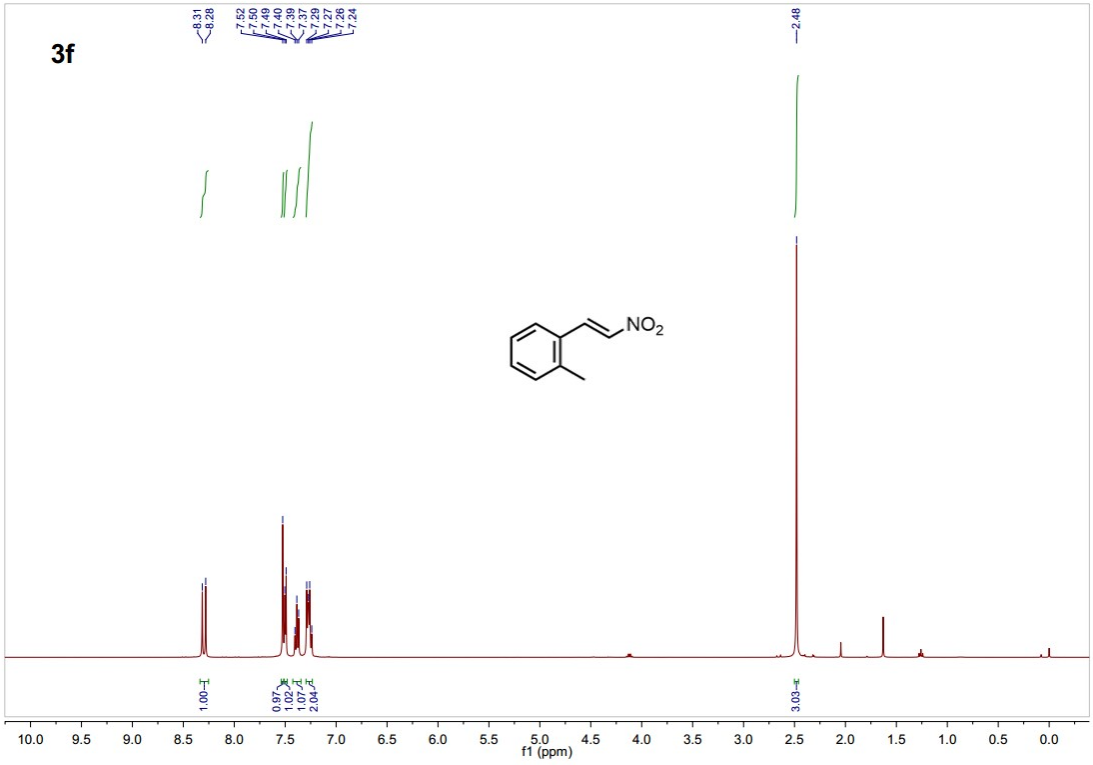
3e


8.14
8.10
7.88
7.85
7.47
7.45
7.44
7.42
7.03
7.01
6.99
6.98
6.96
3.94
NO2
OMe
1.00
1.00
2.08
2.11
3.20
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

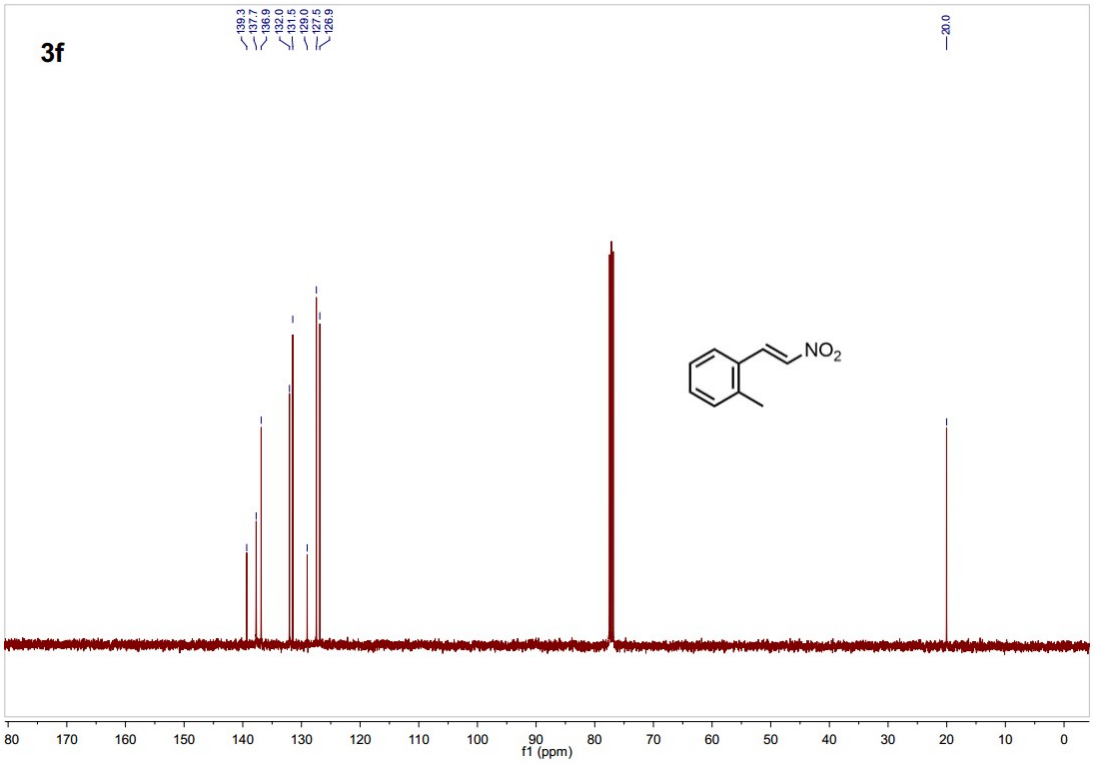
3e


159.6
138.3
135.6
133.6
132.5
121.2
119.2
111.5
55.7
NO2
OMe
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

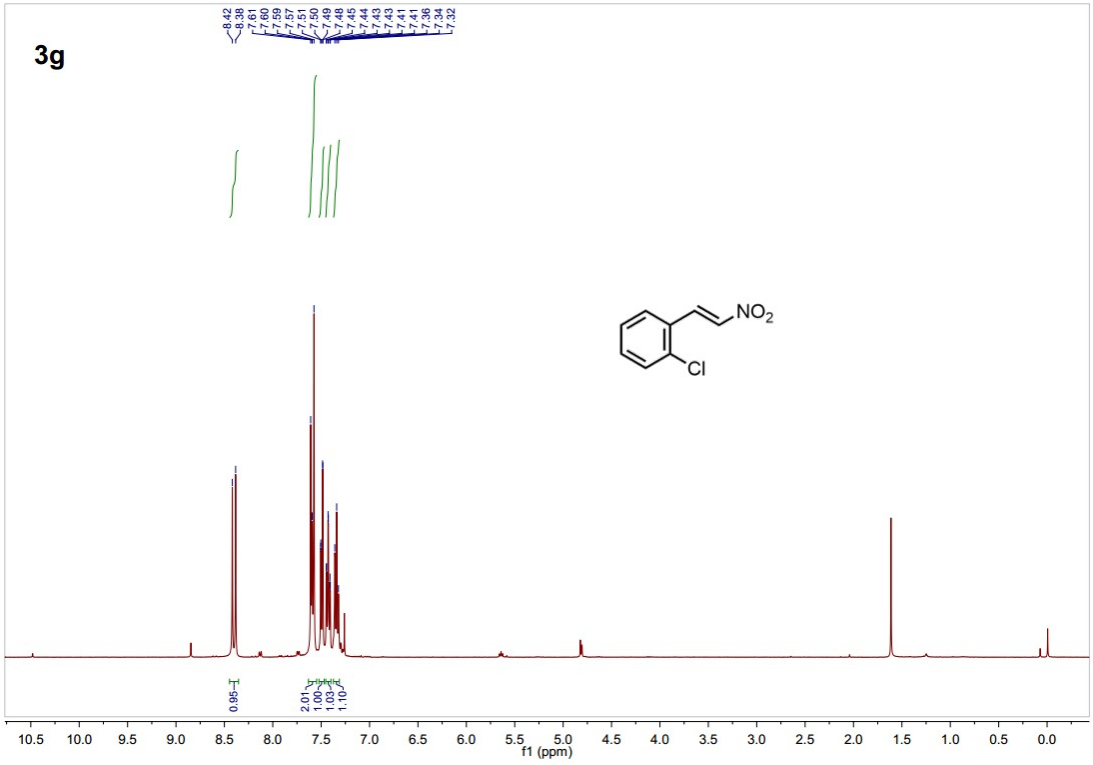
3f

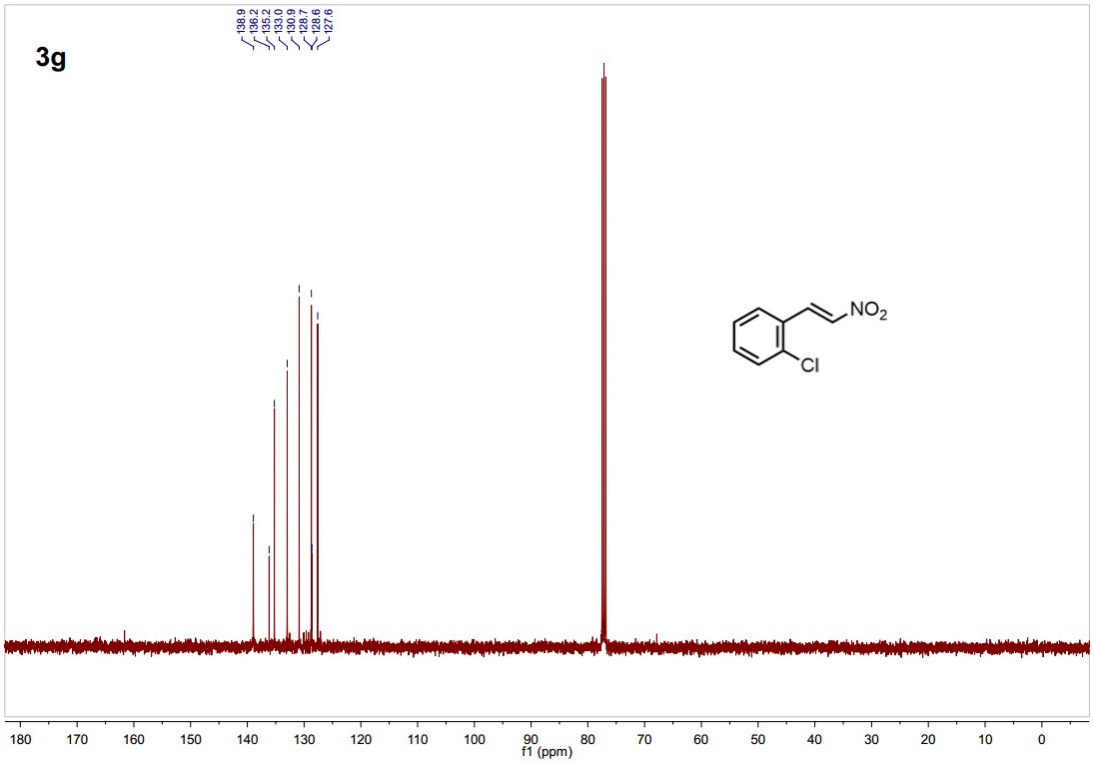

8.31
8.28
7.52
7.50
7.49
7.40
7.39
7.37
7.29
7.27
7.26
7.24
2.48
NO2
1.00
0.97
1.02
1.07
2.04
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

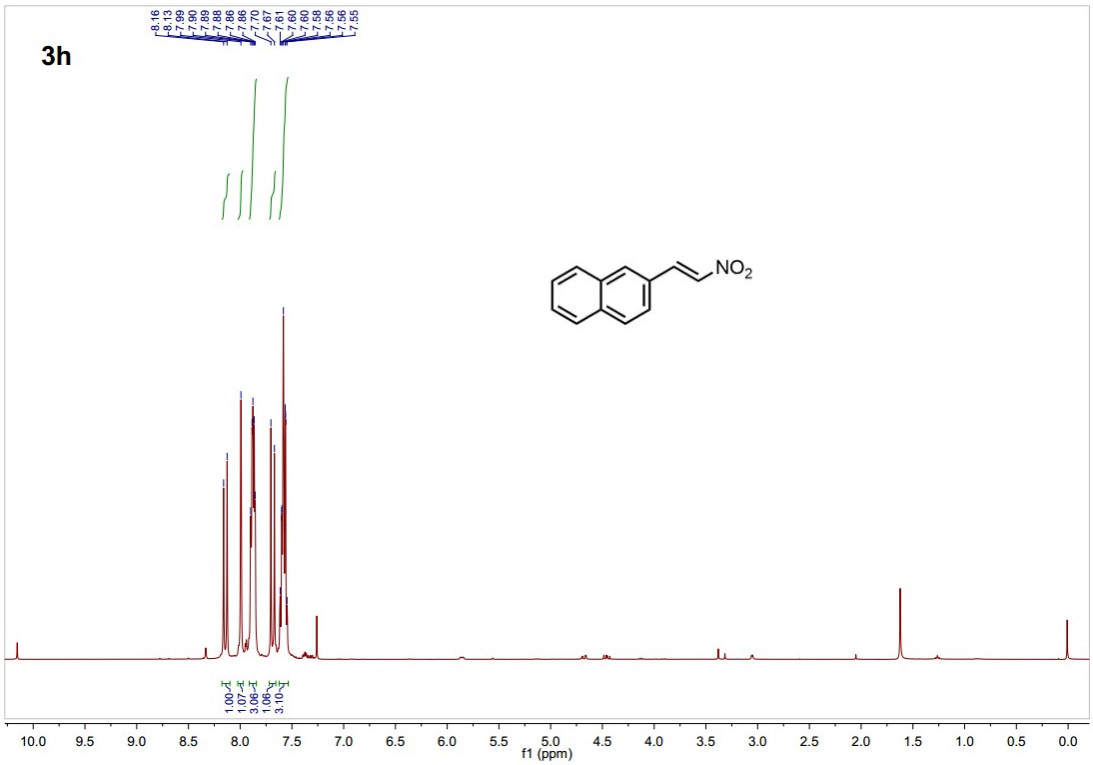
3f

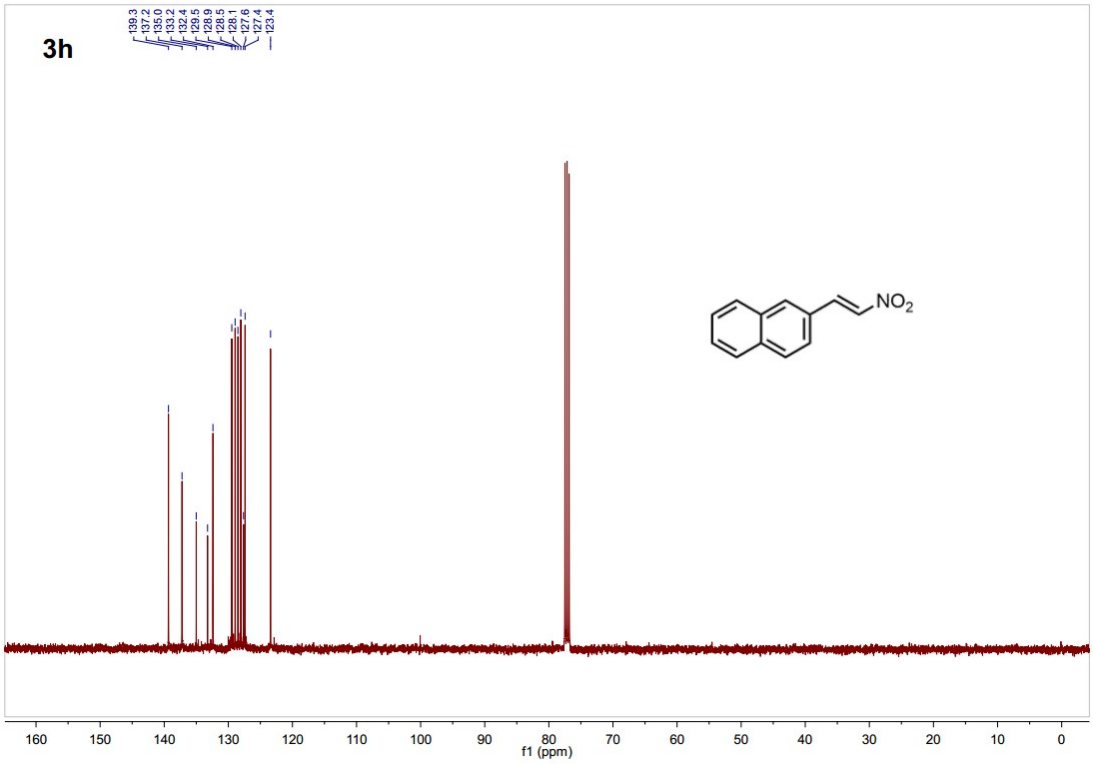

139.3
137.7
136.9
132.0
131.5
129.0
127.5
126.9
20.0
NO2
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

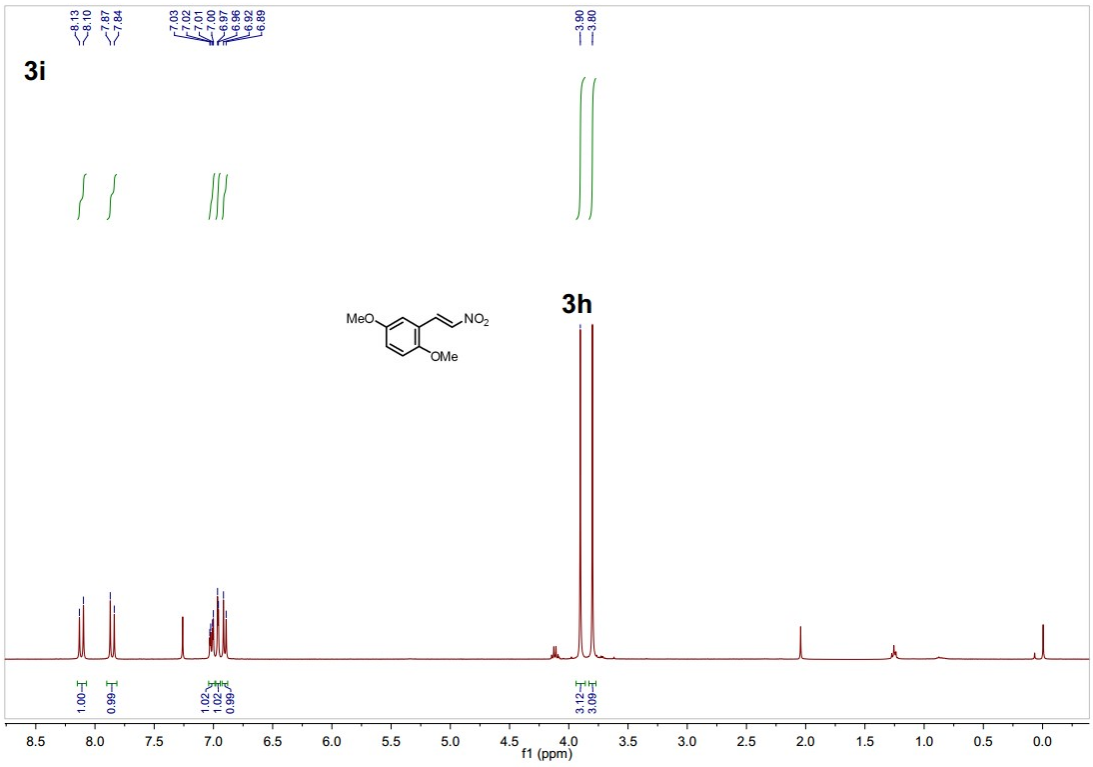
3g

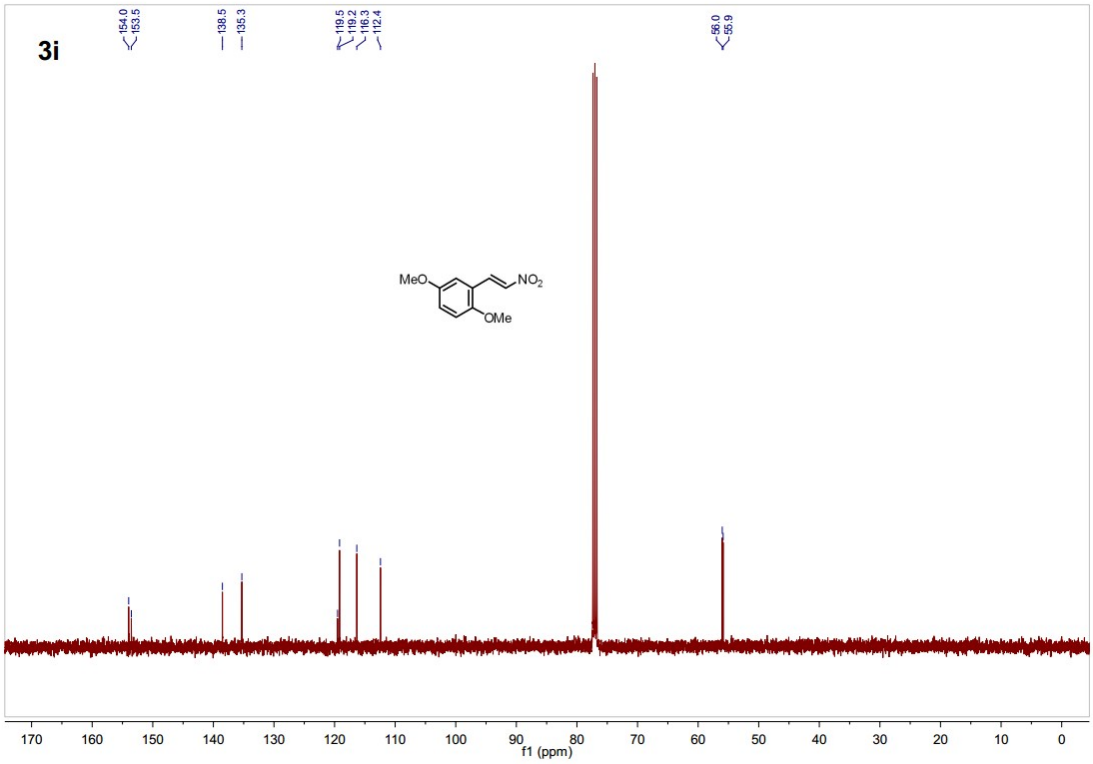

8.42
8.38
7.61
7.60
7.59
7.57
7.51
7.50
7.49
7.48
7.45
7.44
7.43
7.41
7.41
7.36
7.34
7.32
NO2
Cl
0.95
2.01
1.00
1.03
1.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

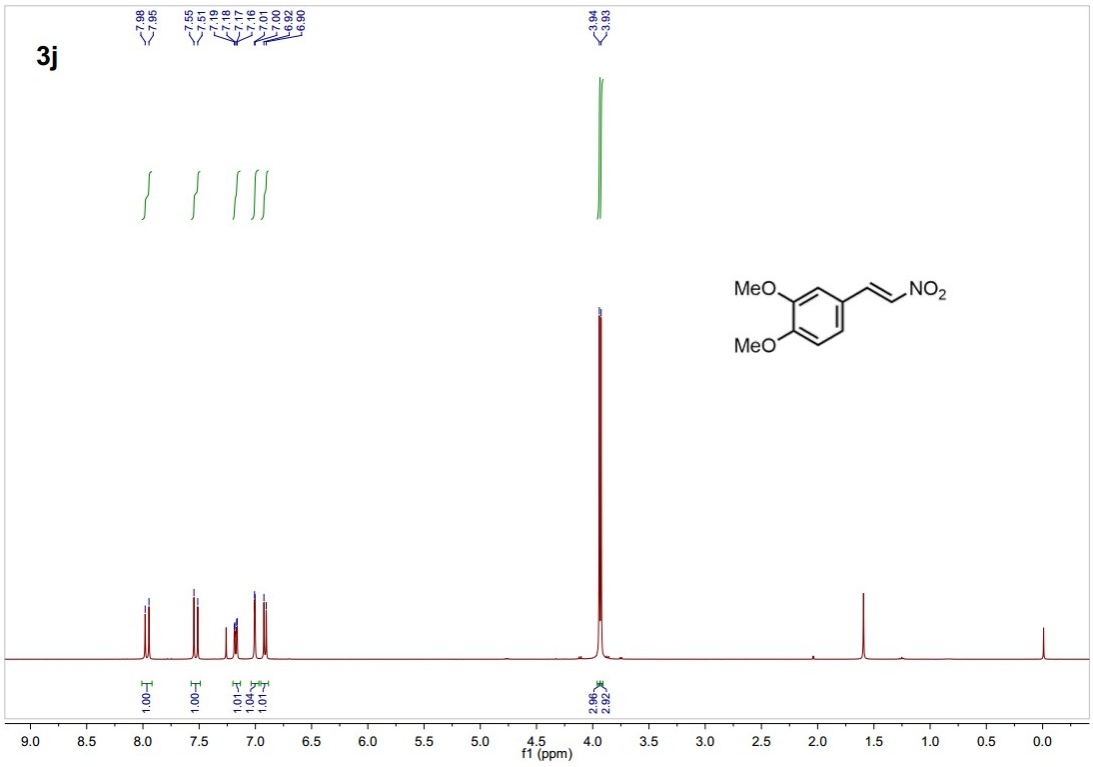

3g
138.9
136.2
135.2
133.0
130.9
128.7
128.6
127.6
NO2
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

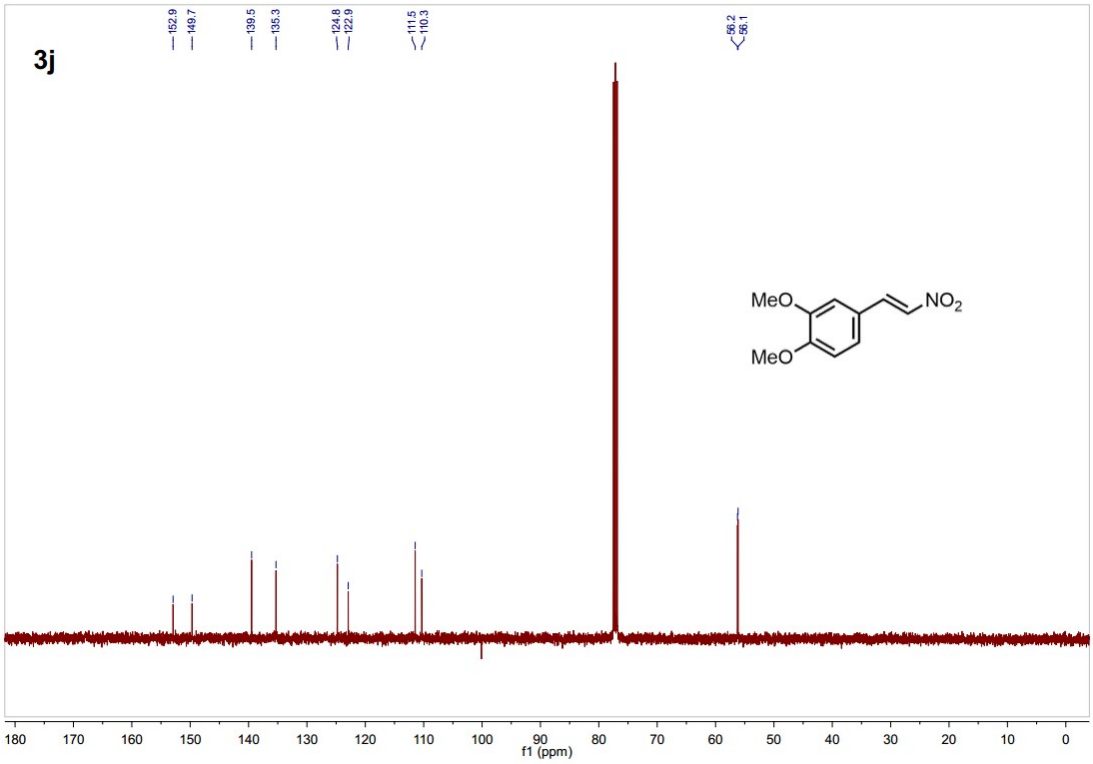

3h
8.16
8.13
7.99
7.90
7.89
7.88
7.86
7.86
7.70
7.67
7.61
7.60
7.60
7.58
7.56
7.56
7.55
NO2
1.00
1.07
3.06
1.06
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

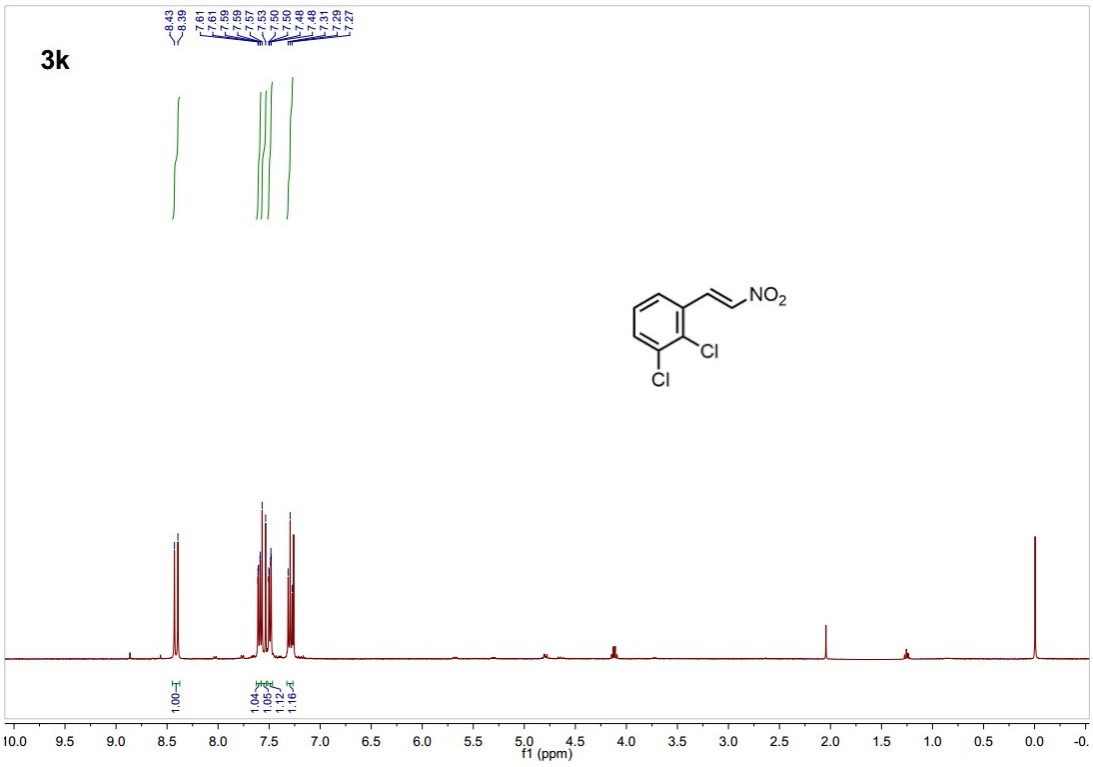

3h
139.3
137.2
135.0
133.2
132.4
129.5
128.9
128.5
128.1
127.6
127.4
123.4
NO2
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

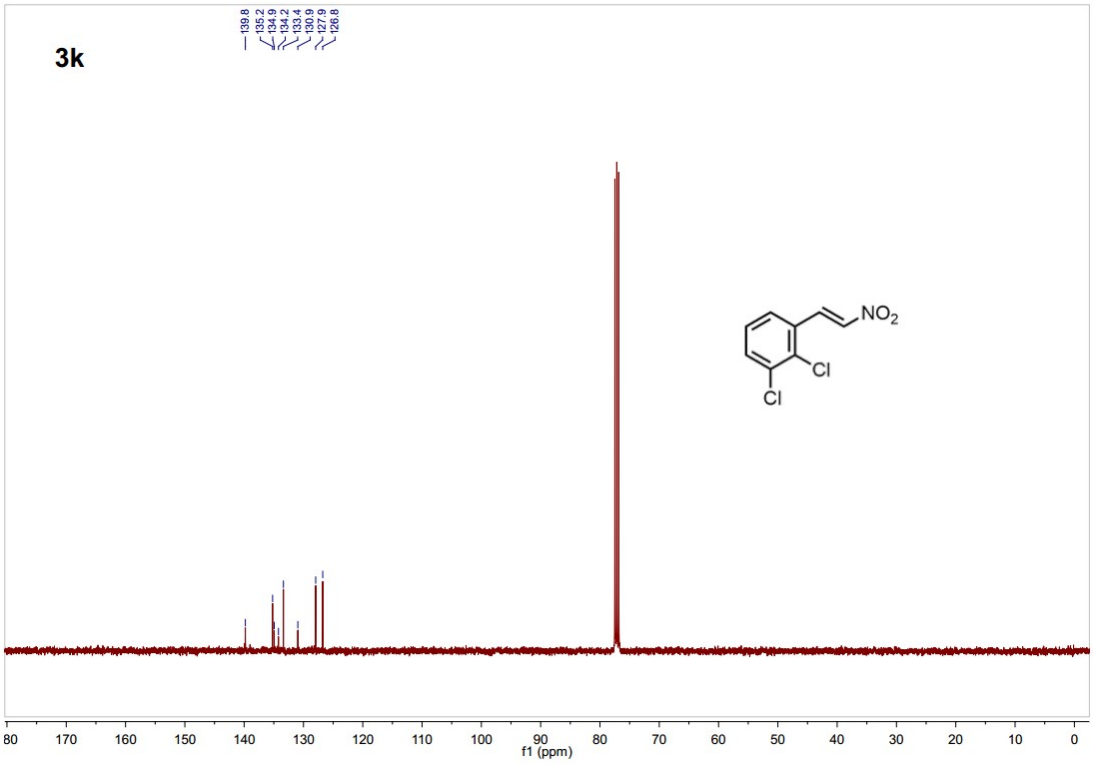

3i
8.13
8.10
7.87
7.84
7.03
7.02
7.01
7.00
6.97
6.96
6.92
6.89
3.90
3.88
3h
MeO
NO2
OMe
1.00
0.99
1.02
1.02
0.99
3.12
3.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

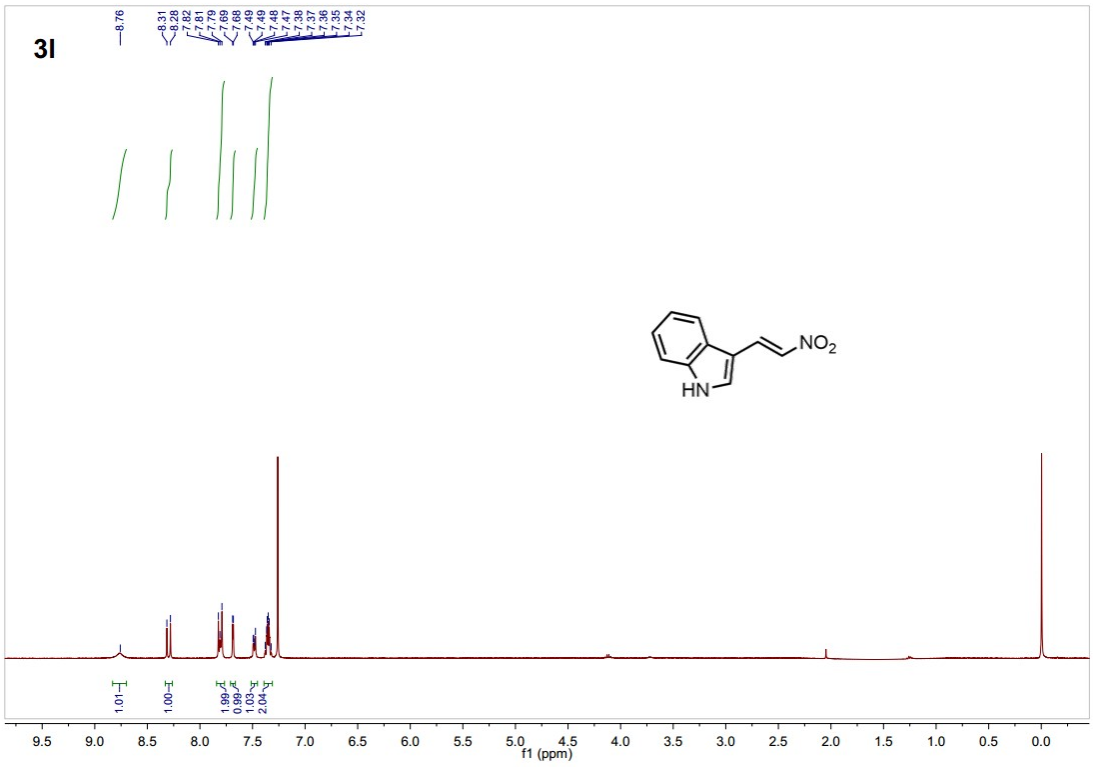

3i
154.0
153.5
138.5
135.3
119.5
119.2
116.3
112.4
56.0
55.9
MeO
NO2
OMe
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

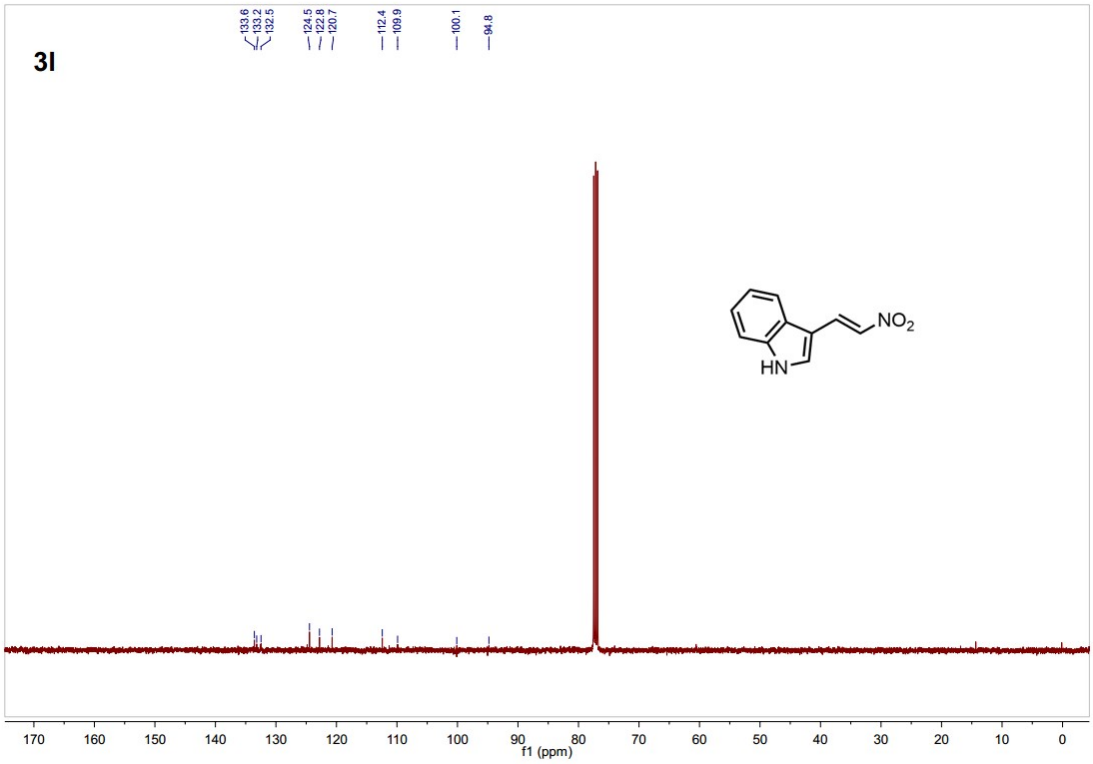

3j
7.98
7.95
7.55
7.51
7.19
7.18
7.17
7.16
7.01
7.00
6.92
6.90
3.94
3.93
MeO
MeO
NO2
1.00
1.00
1.01
1.04
1.01
2.96
2.92
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

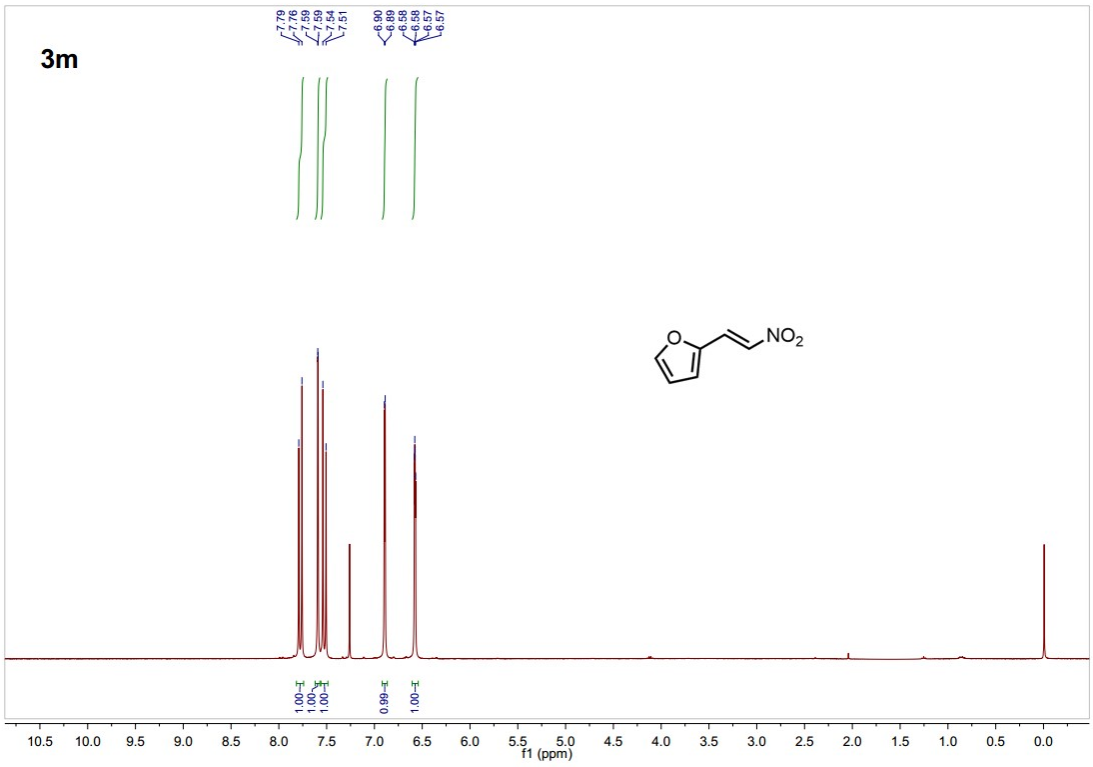

3j
152.9
149.7
139.5
135.3
124.8
122.9
111.5
110.3
56.2
56.1
MeO
MeO
NO2
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

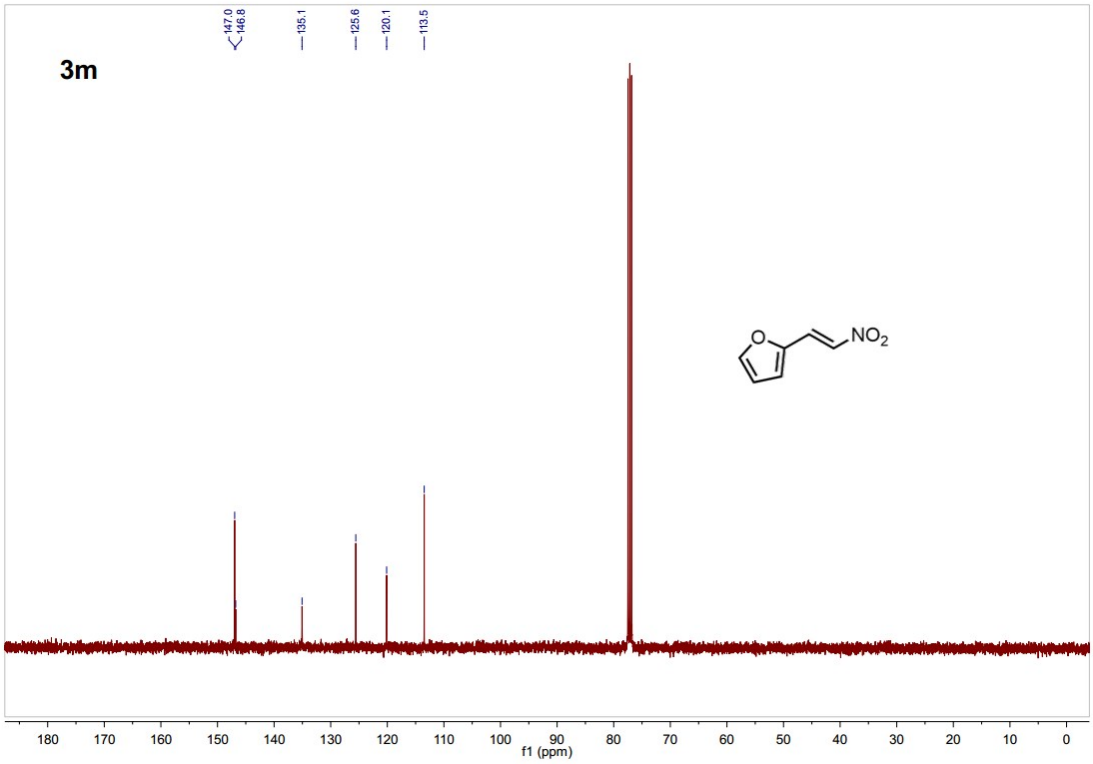

3k
8.43
8.39
7.61
7.59
7.57
7.53
7.50
7.48
7.46
7.31
7.29
7.27
NO2
Cl
Cl
1.00
1.04
1.05
1.12
1.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

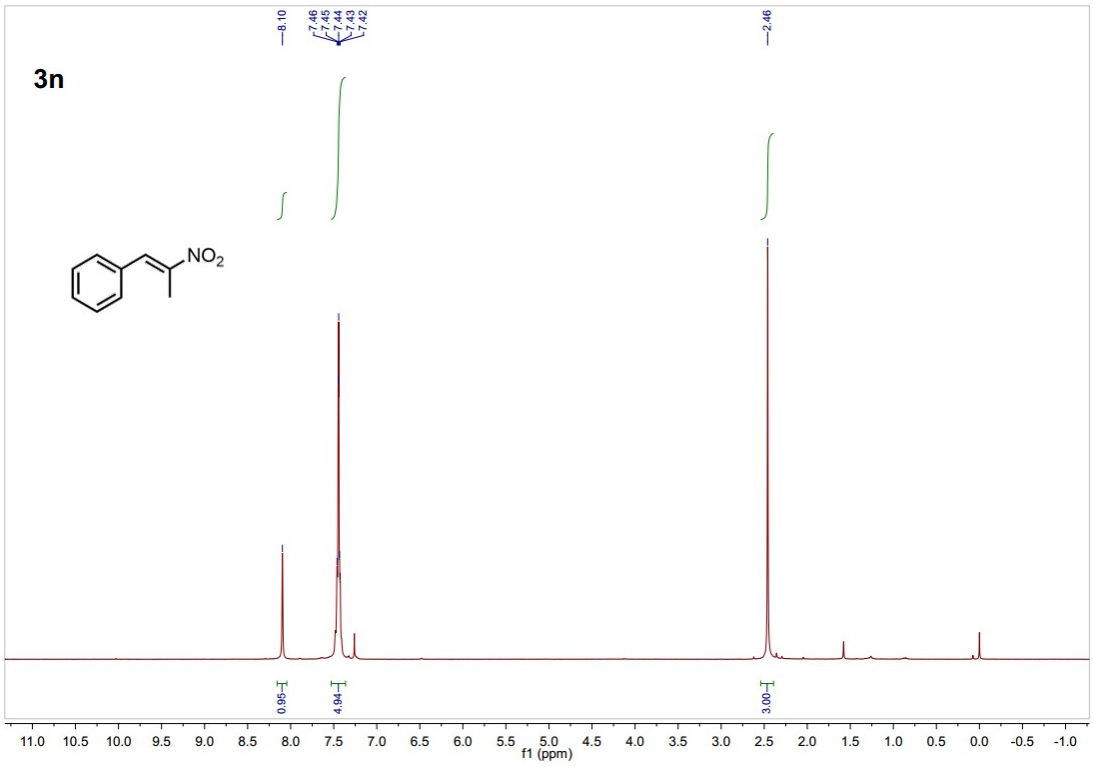

3k
139.8
135.2
134.9
134.2
133.4
130.9
127.9
126.8
NO2
Cl
Cl
f1 (ppm)

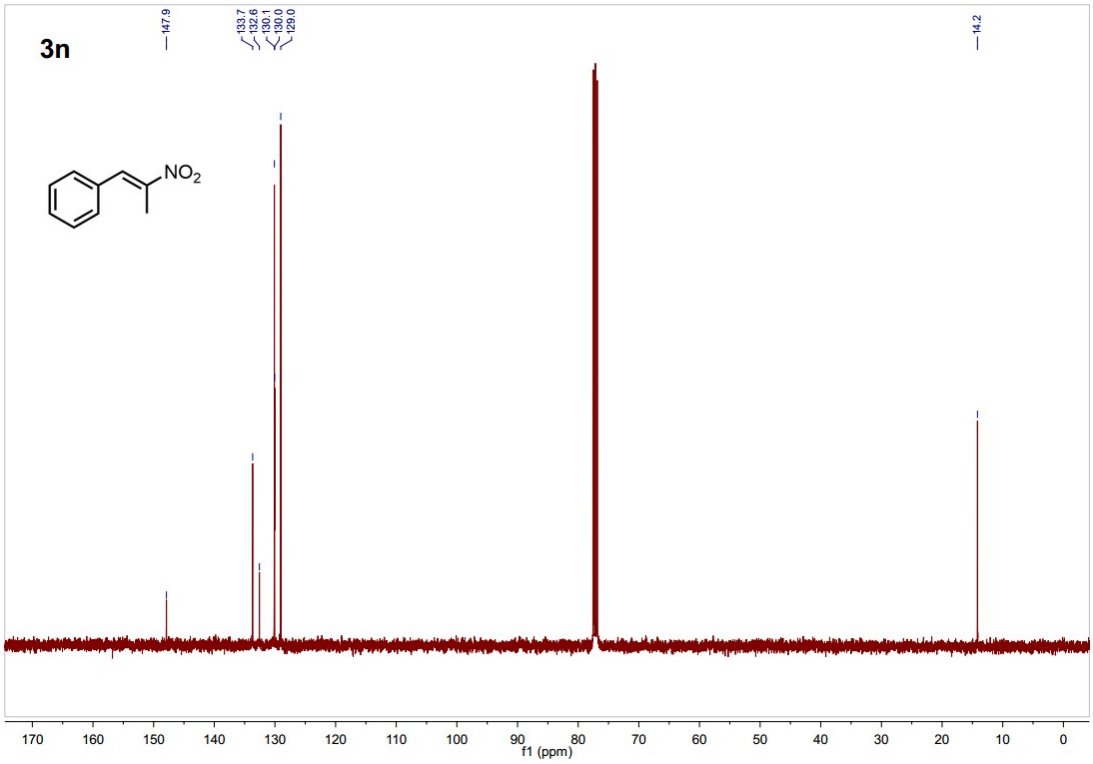

3l
8.76
8.31
8.29
7.82
7.81
7.79
7.69
7.68
7.49
7.48
7.47
7.38
7.37
7.36
7.35
7.34
7.32
NO2
HN
1.01
1.00
1.99
0.99
1.03
2.04
f1 (ppm)


3l
133.6
133.2
132.5
124.5
122.8
120.7
112.4
109.9
100.1
94.8
NO2
HN
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


3m
7.79
7.76
7.59
7.59
7.54
7.51
6.90
6.89
6.58
6.58
6.57
6.57
NO2
O
1.00
1.00
1.00
0.99
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


3m
147.0
146.8
135.1
125.6
120.1
113.5
O
NO2
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


3n
8.10
7.46
7.45
7.44
7.43
7.42
2.46
NO2
0.95
4.94
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


3n
147.9
133.7
132.6
130.1
130.0
129.0
14.2
NO2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)