Supporting Information for

"Electrochemical Azidooxygenation of Alkenes Mediated by a TEMPO–N_3 Charge-Transfer Complex"

Juno C. Siu, Gregory S. Sauer, Ambarneil Saha, Reed L. Macey, Niankai Fu, Timothée Chauviré, Kyle M. Lancaster*, Song Lin*

Table of Contents

General information

All reactions were performed in oven-dried, custom-made two-neck glass tubes unless otherwise noted. The tubes were fitted with a rubber septum and a threaded Teflon cap with airtight, electrical feed-throughs. The reactions were conducted under a nitrogen atmosphere. Flash chromatography was performed using silica gel 60 (230-400 mesh) from SiliCycle. Commercial reagents were purchased from Sigma Aldrich, Alfa Aesar, Acros, TCI, AK Scientific, and Oakwood and used as received with the following exceptions: toluene, dichloromethane, tetrahydrofuran, diethyl ether, and acetonitrile were dried by passing through columns of activated alumina; dimethylformamide was dried by passing through columns of activated molecular sieves. Triethylamine were distilled from CaH_2 at 760 torr.

Instrumentation

Potentiostat

Cyclic voltammetry data were measured with a BASi EC Epsilon potentiostat. The reference electrode consist of a silver wire immersed in a solution of 0.01M $AgNO_3$ and 0.1M $LiClO_4$. The counter electrode is a platinum wire coil of 10 cm length. The working electrode is a glassy carbon electrode with a diameter of 0.3 mm. Before each study, the working electrode was polished to a mirror like finish with 0.3 um alumina on a pad with deionized water. The electrode was then sonicated for 30 seconds in deionized water. The platinum counter electrode was burned with a butane flame for 30 s. The reference electrode solution was made fresh every time and at the end of each experiment, a small amount of ferrocene was added as an internal reference. Analytical solution consist of 6 ml 0.1M $LiClO_4$ in anhydrous acetonitrile. Anhydrous nitrogen gas was purged through the solution for at least 5 minutes and a background scan was taken before any analysis began.

Nuclear magnetic resonance spectroscopy (NMR)

All proton NMR spectra were recorded on either a Varian-mercury 300 (300 MHz), Varian-Mercury 400 (400 MHz), Inova 500 (500 MHz) or Inova 600 (600 MHz) spectrometers at 20°C. Chemical shifts for proton are reported in parts per million downfield from tetramethylsilane and are reference to residual protium in the NMR solvent according to values reported in literature: $\delta(CDCl_3) = 7.26$ppm, δ $(CD_3CN) = 2.33$. Carbon (^{13}C $\{^1H\}$ NMR) was referenced to the carbon resonances of the solvent according to values reported in literature: $\delta(CDCl_3) = 77.16$ppm.

Ultraviolet and visible spectroscopy

All UV Vis spectra were measured on a Agilent Cary-60 spectrophotometer.

Mass spectrometry

All mass spectra were obtained on a ThermoFisher Scientific Exactive series DART Mass Spectrometer.

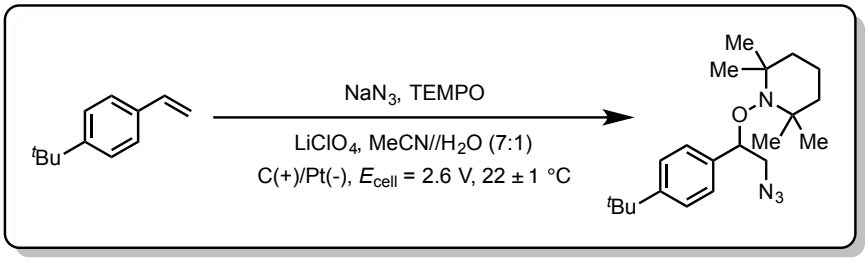
High performance liquid chromatography

All HPLC measurements were measured on a SHIMADZU system using a Roc™ silica 3um column. A 0.5ml/min flow rate with pure hexanes was used in all cases.

Abbreviations

OTMP = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl, ^{t}Bu = *tert*-butyl, MeCN = acetonitrile, TBA = tetrabutylammonium. $TEMPO^+$ = 2,2,6,6-tetramethyl-1-oxopiperidin-1-ium, TEMPO = (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl.

General procedure for electrochemical azidooxygenation



General procedure for azidooxygenation of olefins (GP 1): An oven-dried, 10 mL two-necked glass tube was equipped with a magnetic stir bar, a rubber septum, a threaded Teflon cap fitted with electrical feed-throughs, an carbon felt anode (connected to the electrical feed-through via a graphite rod 9 cm in length and 2 mm in diameter), and a platinum foil cathode (0.5 x 1.0 cm^2). To this vessel was added TEMPO (46.8 mg, 0.3 mmol, 1.5 equiv) and the olefin substrate (0.2mmol, 1.0 equiv). Then the electrolyte solution (0.1 M $LiClO_4$ in MeCN, 3.5 mL) and aqueous NaN_3 (2.0 M in water, 0.3 mL, 0.6 mmol, 3.0 equiv). The flask was then sealed with a septum and the Teflon cap. The reaction solution was then purged with nitrogen gas for another 5 minutes with the aid of an exit needle on the septum. A nitrogen-filled balloon was fitted through the septum to sustain a nitrogen atmosphere. A stirring rate was established at 900 rpm. Electrolysis was initiated at a constant cell potential of 2.6 V at room temperature (22 ± 1 °C). Upon full consumption of olefin starting material as determined by thin-layer chromatography analysis, electrolysis was terminated (usually between 1.5 to 3.0 hours). The entire reaction mixture was then transferred to a short silica gel column (7-10 cm in length, ca. 4 g) and flushed through with 100 mL of a mixture of 10% ethyl acetate and hexanes to eliminate inorganic salts. The resultant solution was concentrated *in vacuo*. The residue was subjected to flash column chromatography on silica gel (eluted with hexanes/ethyl acetate) to yield the purified product.

Carbon felt electrodes (graphite/AvCarb Felt G200) was purchased from Fuel Cell Store. A new piece of carbon felt was used every time.

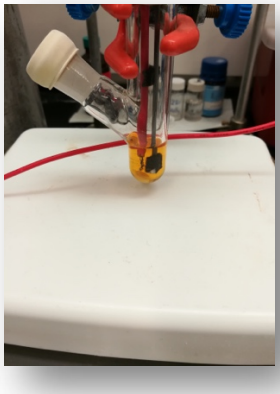
GP 2

All the same with the above procedure except:

0.3ml NaN_3 solution→ 0.2ml NaN_3

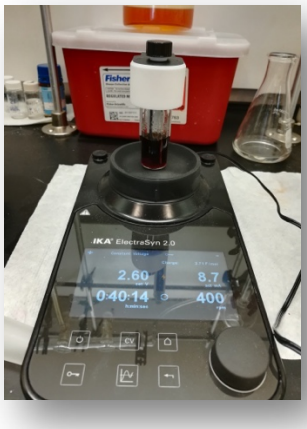
2.60V → 2.20V

Reaction time may extend to 7 hours. In general, GP 2 is slower but more selective than GP 1. Simple aliphatic substrates work better with GP 1 and GP 2 for functional group containing ones.



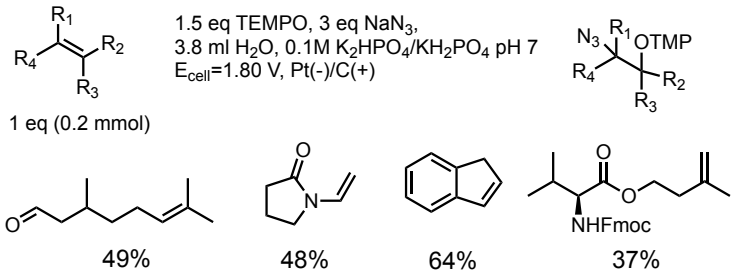
Procedure for Electrosyn

The olefin (0.2 mmol, 1 eq), TEMPO (0.3 mmol, 46.8 mg, 1.5 eq), NaN_3 solution (2 M, 0.3 ml, 3 eq), MeCN (7 ml, 0.1 M $LiClO_4$) and a stir bar was added to the vial. A platinum foil was used to wrap the cathode and held together by conductive tape. The solution was then purged with N_2 for 5 minutes. The cell potential was set to 2.60 V and electrolyzed for 1-8 hours depending on the substrate. A protective atmosphere is usually not required throughout the reaction. More reactive substrates like indene will typically take around 1.5 hour to complete. Whilst less reaction terminal olefins can take as long as 8 hours. Reaction was worked up analogous to previous method. Movement of the azidooxygenated product will typically move slower than the starting material and will stain very nicely with $KMnO_4$.



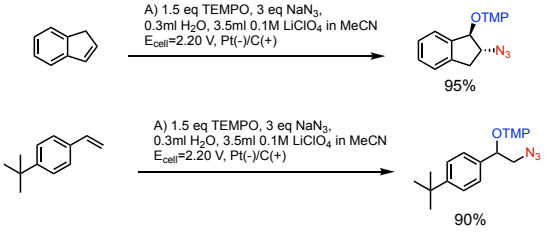
General Procedure for synthesis in water

The substrate (0.2 mmol, 1eq), TEMPO (0.3 mmol, 46.8 mg, 1.5 eq), NaN_3 solution (0.3 ml, 2 M, 3 eq), phosphate buffer solution (KH_2PO_4 and K_2HPO_4, 0.1 M, pH 7, 3.5 ml) was added to the electrochemical cell. The solution was then electrolyzed at a cell potential of 1.80 V for 3.5 hours. Then ether (2x5 ml) was added along with NaCl to the aqueous layer. Organic layers were then combined and dried with Na_2SO_4. Concentrated in vacuo and then purified by flash chromatography.



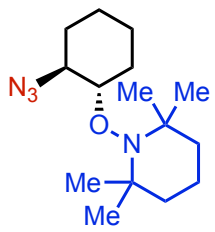
Procedure for the absence of N_2 sparging

An oven-dried, 10 mL two-necked glass tube was equipped with a magnetic stir bar, a rubber septum, a threaded Teflon cap fitted with electrical feed-throughs, an carbon felt anode (connected to the electrical feed-through via a graphite rod 9 cm in length and 2 mm in diameter), and a platinum foil cathode (0.5 x 1.0 cm^2). To this vessel was added TEMPO (46.8 mg, 0.3 mmol, 1.5 equiv) and the olefin substrate (0.2mmol, 1.0 equiv). Then the electrolyte solution (0.1 M $LiClO_4$ in MeCN, 3.5 mL) and aqueous NaN_3 (2.0 M in water, 0.3 mL, 0.6 mmol, 3.0 equiv). A stirring rate was set at 900 rpm. Electrolysis was initiated at a constant cell potential of 2.6 V at room temperature (22 ± 1 °C). Upon full consumption of olefin starting material as determined by thin-layer chromatography analysis, electrolysis was terminated (usually between 1.5 to 3.0 hours). The entire reaction mixture was then transferred to a short silica gel column (7-10 cm in length, ca. 4 g) and flushed through with 100 mL of a mixture of 10% ethyl acetate and hexanes to eliminate inorganic salts. The resultant solution was concentrated *in vacuo*. The residue was subjected to flash column chromatography on silica gel (eluted with hexanes/ethyl acetate) to yield the purified product.



Substrate spectra and methods

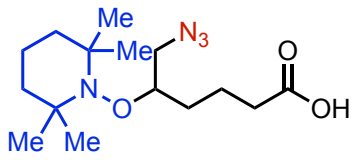
1-(((1S,2S)-2-azidocyclohexyl)oxy)-2,2,6,6-tetramethylpiperidine (2n)



According to **GP 1** with 2,3-dimethylbut-2-ene (17mg, 0.2 mmol, 1eq). After electrolyzing for 3 hours, the reaction mixture was purified via a short column followed by another column chromatography on silica gel (hexanes/ethyl acetate = 19/1) to yield the desired product as a viscous, clear oil (42 mg, 75%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 3.72 (ddd, *J* = 10.3, 8.7, 3.9 Hz, 1H), 3.33 (ddd, *J* = 10.4, 8.6, 4.5 Hz, 1H), 2.40 – 2.29 (m, 1H), 1.99 – 1.88 (m, 1H), 1.76 – 1.00 (m, 24H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 83.975, 65.141, 60.933, 59.123, 40.690, 40.446, 34.705, 34.508, 31.187, 30.867, 24.341, 23.901, 20.707, 17.469. **IR** (film): 2932, 2866, 2096, 1450, 1375, 1360,

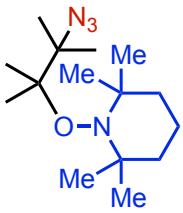
1302, 1259, 1132, 1062 cm^{-1}. **HRMS** (DART) exact mass calculated for $C_{15}H_{29}N_4O$ $[M+H]^+$ m/z = 281.2236, found m/z = 281.2232.

6-azido-5-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)hexanoic acid (2g)



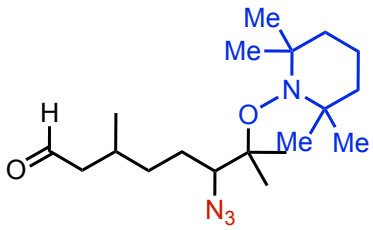
Followed Method from **GP 1** with 1-hexenoic acid (22.8 mg, 0.20 mmol, 1eq). After electrolyzing for 8 hours, the reaction mixture was purified via a short column followed by another column chromatography on silica gel (hexanes/ethyl acetate = 4/1) to yield the desired product as a viscous, clear oil (39.9 mg, 64% yield). **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 3.97-3.91 (m, 1H), 3.64 (dd, *J* = 12.4, 4.2 Hz, 1H), 3.36 (dd, *J* = 12.4, 5.9 Hz, 1H), 2.43 (t, *J* = 7.4 Hz, 2H), 1.87-1.55 (m, 4H), 1.54-1.42 (m, 4H), 1.39-1.24 (m, 2H), 1.20-1.87 (m, 24H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.967, 80.477, 60.427, 59.974, 53.238, 40.457, 34.482, 34.255, 30.991, 21.086, 20.620, 17.342. **IR (film)**: 2933, 2677, 2101, 1713, 1455, 1361, 1259, 1181, 1132, 1082, 1045, 957 cm^{-1}. **HRMS** (DART) exact mass calculated for $C_{15}H_{29}N_4O_3$ $[M+H]^+$ m/z =313.2234, found m/z =313.2229.

1-((3-azido-2,3-dimethylbutan-2-yl)oxy)-2,2,6,6-tetramethylpiperidine (2f)



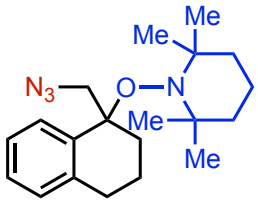
According to **GP 1** with 2,3-dimethylbut-2-ene (17mg, 0.2 mmol, 1 eq). After electrolyzing for 3 hours, the reaction mixture was purified via a short column followed by another column chromatography on silica gel (hexanes/ethyl acetate = 19/1) to yield the desired product as a viscous, clear oil (45.2 mg, 80%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 1.78 – 1.09 (m, 30H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 83.064, 77.414, 77.161, 76.906, 68.745, 60.226, 42.033, 36.207, 24.478, 23.088, 21.329, 17.208. **IR** (film): 2933, 2872, 2106, 1466, 1374, 1269, 1133 cm^{-1}. **HRMS** (DART) exact mass calculated for $C_{15}H_{30}N_4O$ $[M+H]^+$ m/z = 283.24924, found m/z = 283.24937.

6-azido-3,7-dimethyl-7-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)octanal (2i)



According to **GP 2** with citronellal (30.9 mg, 0.2 mmol, 1eq). After electrolyzing for 3 hours, the reaction mixture was purified via a short column followed by another column chromatography on silica gel (hexanes/ethyl acetate = 19/1) to yield the desired product as a viscous, clear oil (44.1 mg, 63%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 9.78 (t, *J* = 2.1 Hz, 1H), 3.46 (ddd, *J* = 11.1, 9.5, 2.0 Hz, 1H), 2.46 (dtd, *J* = 16.4, 5.4, 1.7 Hz, 1H), 2.28 (dddd, *J* = 14.9, 9.4, 7.0, 2.5 Hz, 1H), 2.10 (ddd, *J* = 14.8, 11.3, 6.4 Hz, 1H), 2.00 – 1.81 (m, 1H), 1.68-1.00 (m, 30H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 202.71 , 81.94, 72.40, 59.64, 51.09, 41.06, 35.24 , 28.28, 27.09, 23.63, 22.95 , 21.21, 20.83, 20.13, 17.24. **IR** (film): 2933, 2873, 2822, 2714, 2100, 1727, 1464, 1377, 1363, 1323, 1259, 1181, 1134, 1061, 1043 cm^{-1} **HRMS** (DART) exact mass calculated for $C_{19}H_{36}N_4O_2$ $[M+H]^+$ m/z = 353.29110, found m/z = 353.29133.

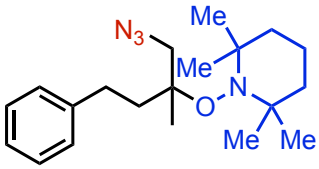
1-((1-(azidomethyl)-1,2,3,4-tetrahydronaphthalen-1-yl)oxy)-2,2,6,6-tetramethylpiperidine (2r)



According to **GP 1** 1-methylene-1,2,3,4-tetrahydronaphthalene (28.8 mg, 0.2 mmol, 1eq). After electrolyzing for 3 hours, the reaction mixture was purified via a short column followed by another column chromatography on silica gel (hexanes/ethyl acetate = 19/1) to yield the desired product as a viscous, clear oil (54 mg, 79%) that decomposes rapidly. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.63 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.23 (td, *J* = 7.6, 1.4 Hz, 1H), 7.17 (td, *J* = 7.4, 1.4 Hz, 1H), 7.03 (dd, *J* = 7.5, 1.3 Hz, 1H), 3.74 (d, *J* = 12.5 Hz, 1H), 3.52 (d, *J* = 12.5 Hz, 1H), 2.89 – 2.77 (m, 1H), 2.71 (dd, *J* = 8.7, 4.0 Hz, 2H), 2.06 – 1.76 (m, 3H), 1.62 – 0.95 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.589, 137.558, 128.235, 128.219, 127.079, 125.764, 80.444, 62.419, 59.870, 59.580, 41.464, 41.091, 34.050, 32.432, 29.642, 28.920, 21.449, 20.729,

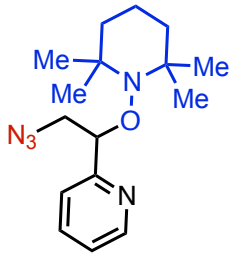
20.656, 17.005. **IR** (film): 2967, 2933, 2871, 2100, 1454, 1376, 1361, 1329, 1302, 1266, 1182, 1132, 919, 905, 763, 735 cm^{-1} **HRMS** (DART) exact mass calculated for $C_{20}H_{30}N_4O$ $[M+H]^+$ m/z = 343.24924, found m/z = 343.24932.
product not stable on the time scale of the ^{13}C NMR

1-((1-azido-2-methyl-4-phenylbutan-2-yl)oxy)-2,2,6,6-tetramethylpiperidine (2l)



According to **GP 2** (3-methylbut-3-en-1-yl)benzene (29.2 mg, 0.2 mmol, 1eq). After electrolyzing for 3 hours, the reaction mixture was purified via a short column followed by another column chromatography on silica gel (hexanes/ethyl acetate = 19/1) to yield the desired product as a viscous, clear oil (66.1mg, 96%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.37 – 7.14 (m, 5H), 3.60 – 3.49 (m, 2H), 2.80 (ddd, *J* = 13.4, 10.7, 6.7 Hz, 1H), 2.68 (ddd, *J* = 13.4, 11.0, 6.7 Hz, 1H), 2.07 – 1.97 (m, 2H), 1.67 – 1.10 (m, 21H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.791, 128.546, 128.508, 125.874, 80.614, 59.833, 59.807, 58.233, 41.108, 41.061, 40.961, 35.096, 34.960, 30.491, 22.714, 21.149, 20.972, 17.203. **IR** (film): 3086, 3063, 2933, 2871, 2100, 1604, 1540, 1497, 1454, 1373, 1359, 1278, 1210, 1181, 1165, 1133, 1098, 1067 cm^{-1}. **HRMS** (DART) exact mass calculated for $C_{20}H_{32}N_4O$ $[M+H]^+$ m/z = 345.26489, found m/z = 345.26497.

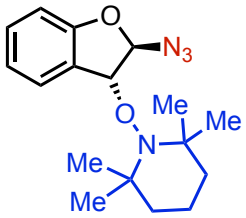
2-(2-azido-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)pyridine (2h)



According to **GP 1** with 2-vinylpyridine (21mg, 0.2 mmol, 1eq). After electrolyzing for 3 hours, the reaction passed through a short column and rinsed with acetone. The mixture was then concentrated *in vacuo* and then purified via column chromatography on silica gel (hexanes/ethyl acetate/triethylamine = 9/1/2.5%) to yield the desired product as a viscous, clear oil (40.4mg, 67%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.58 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.69 (td, *J* = 7.7, 1.8 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.20 (dd, *J* = 7.4, 4.9 Hz, 1H), 4.99 (t, *J* = 4.9 Hz, 1H), 3.92 (dd, *J* = 12.7, 5.4 Hz, 1H), 3.82 (dd, *J* = 12.7, 4.4 Hz, 1H), 1.64 – 0.59 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.809, 149.105, 136.227, 123.533, 122.792, 85.825, 60.181, 53.729, 40.434, 34.394,

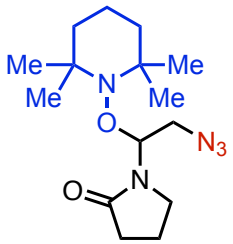
33.468, z.433, 17.137. **IR** (film): 2974, 2933, 2100, 1590, 1572, 1472, 1435, 1435, 1361, 1323, 1293, 1259, 1182, 1132, 1045, 1020 cm^{-1} **HRMS** (DART) exact mass calculated for $C_{16}H_{25}N_5O$ $[M+H]^+$ m/z = 304.21319, found m/z = 304.21303.

1-((2-azido-2,3-dihydrobenzofuran-3-yl)oxy)-2,2,6,6-tetramethylpiperidine (2q)



According to **GP 1** with 2,3-benzofuran (23.6 mg, 0.2 mmol, 1eq). After electrolysis for 3 hours at room temperature, the reaction mixture was passed through a short column and concentrated in vacuo. The crude product was then purified with column chromatography (hexanes/ethyl acetate = 10/1) to yield the desired product as a viscous, clear oil (57.6 mg, 91%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.51 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.31 (td, *J* = 7.8, 1.4 Hz, 1H), 7.03 – 6.92 (m, 2H), 6.15 (d, *J* = 1.0 Hz, 1H), 5.15 (s, 1H), 1.69 – 0.85 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.582, 130.958, 127.840, 124.970, 121.543, 110.826, 96.234, 87.303, 60.454, 60.152, 40.253, 40.159, 34.184, 33.687, 20.495, 17.181. **IR** (film): 2933, 2107, 1600, 1478, 1350, 1235, 1161, 1132, 1015, 955, 751 cm^{-1}; **HRMS** (DART) exact mass calculated for $C_{17}H_{24}N_4O_2$ $[M+H]^+$ m/z = 317.19720, found m/z = 317.19734.

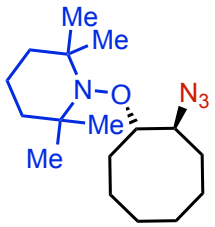
1-(2-azido-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)pyrrolidin-2-one (2k)



According to **GP 1** with 1-vinylpyrrolidin-2-one (22.2 mg, 0.2 mmol, 1eq). After electrolyzing for 1.5 hours, the reaction mixture was purified via a short column followed by another column chromatography on silica gel (hexanes/ethyl acetate = 4/1) to yield the desired product as a crystalline white solid (62mg, 99%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.70 (dd, *J* = 8.3, 4.7 Hz, 1H), 3.64 – 3.51 (m, 3H), 3.44 (dt, *J* = 9.6, 7.7 Hz, 1H), 2.47 – 2.33 (m, 2H), 2.09 – 1.95 (m, 2H), 1.63 – 0.96 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.701, 84.749, 60.912, 59.483, 50.149, 43.105, 40.306, 33.703, 33.015, 31.483, 20.463, 20.101, 17.911, 17.149. **IR** (film): 2934, 2243, 2105, 1705, 1462, 1418, 1376, 1283, 1209, 1184, 1165, 1133, 1107, 1024 cm^{-1} **HRMS**

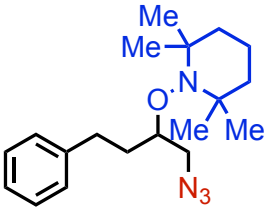
(DART) exact mass calculated for $C_{15}H_{27}N_5O_2$ $[M+H]^+$ m/z = 310.22375, found m/z = 310.22352.

1-((2-azidocyclooctyl)oxy)-2,2,6,6-tetramethylpiperidine (2p)



According to **GP 1** with cyclooctene (22mg, 0.2 mmol, 1eq). After electrolyzing for 3 hours, the reaction mixture was purified via a short column followed by another column chromatography on silica gel (hexanes/ethyl acetate = 19/1) to yield the desired product as a viscous, clear oil (56 mg, 92%) that decomposes rapidly. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 4.11 (t, *J* = 8.8 Hz, 1H), 3.52 (ddd, *J* = 8.8, 6.3, 2.7 Hz, 1H), 2.75 (ddd, *J* = 14.9, 6.1, 3.5 Hz, 1H), 2.00 – 0.90 (m, 29H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 86.235, 67.948, 60.434, 59.273, 40.690, 40.246, 34.671, 33.617, 28.206, 27.605, 27.185, 26.274, 25.302, 22.487, 21.164, 21.106, 17.489. **IR** (film): 2927, 2097, 1466, 1376, 1334, 1294, 1258, 1207, 1182, 1132, 1082, 1060 cm^{-1} **HRMS** (DART) exact mass calculated for $C_{17}H_{32}N_4O$ $[M+H]^+$ m/z = 309.26489, found m/z = 309.26491.

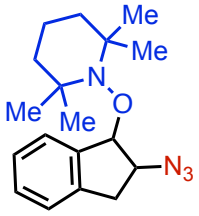
1-((1-azido-4-phenylbutan-2-yl)oxy)-2,2,6,6-tetramethylpiperidine (2s)



According to **GP 2** 4-phenyl-1-butene (27 mg, 0.2 mmol, 1eq). After electrolyzing for 7 hours, the reaction mixture was purified via a short column followed by another column chromatography on silica gel (hexanes/ethyl acetate = 19/1) to yield the desired product as a viscous, clear oil (62.5 mg, 95%).**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.35 – 7.16 (m, 5H), 4.01 – 3.90 (m, 1H), 3.64 (dd, *J* = 12.5, 4.3 Hz, 1H), 3.38 (dd, *J* = 12.5, 5.8 Hz, 1H), 2.69 (dt, *J* = 9.8, 6.2 Hz, 2H), 2.19 – 2.05 (m, 1H), 1.90 (ddt, *J* = 13.6, 9.8, 6.6 Hz, 1H), 1.66 – 1.01 (m, 18H). **^{13}C NMR** (151 MHz, cdcl3) δ 141.998, 128.527, 128.469, 126.020, 80.348, 60.379, 59.918, 53.301, 40.484, 34.451, 34.226, 33.089, 32.124, 20.610, 17.361. **IR** (film): 2980, 2931, 2100, 913, 743 cm^{-1} **HRMS**

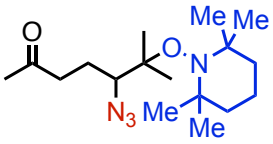
(DART) exact mass calculated for $C_{19}H_{30}N_4O$ $[M+H]^+$ m/z = 331.24924 , found m/z = 331.24928.

1-((2-azido-2,3-dihydro-1*H*-inden-1-yl)oxy)-2,2,6,6-tetramethylpiperidine (2m)



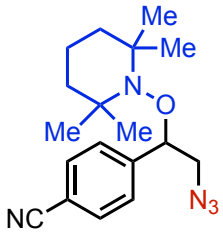
According to **GP 2** with indene (22 mg, 0.2 mmol, 1eq). After electrolyzing for 2 hours, the reaction mixture was purified via a short column followed by another column chromatography on silica gel (hexanes/ethyl acetate = 19/1) to yield the desired product as a viscous, clear oil (62 mg, 99%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.2 Hz, 1H), 7.34 – 7.19 (m, 3H), 5.36 (d, *J* = 4.1 Hz, 1H), 4.42 (dt, *J* = 7.2, 4.7 Hz, 1H), 3.38 (dd, *J* = 16.1, 7.2 Hz, 1H), 2.90 (dd, *J* = 16.2, 5.2 Hz, 1H), 1.72 – 1.01 (m, 18H). **^{13}C NMR** (151 MHz, cdcl$_3$) δ 140.547, 140.203, 128.990, 126.847, 126.698, 124.718, 90.282, 66.727, 60.825, 60.003, 40.379, 36.730, 34.411, 33.870, 20.627, 17.359. **IR** (film): 2975, 2932, 2101, 1463, 1375, 1361, 1258, 1209, 1182, 1132, 1059 cm^{-1} **HRMS** (DART) exact mass calculated for $C_{18}H_{26}N_4O$ $[M+H]^+$ m/z = 315.21794, found m/z = 315.21819.

5-azido-6-methyl-6-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)heptan-2-one (2e)



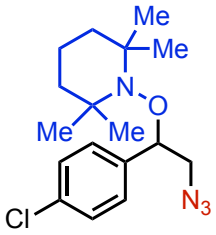
According to **GP 1** with 6-methylhept-5-en-2-one (25 mg, 0.2 mmol, 1eq). After electrolyzing for 3 hours, the reaction mixture was purified via a short column followed by another column chromatography on silica gel (hexanes/ethyl acetate = 9/1) to yield the desired product as a viscous, clear oil (54.4 mg, 84%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 3.58 (dd, *J* = 11.6, 2.4 Hz, 1H), 2.67 (ddd, *J* = 17.6, 8.9, 5.1 Hz, 1H), 2.54 (ddd, *J* = 17.6, 8.6, 6.8 Hz, 1H), 2.18 (s, 3H), 2.15 – 2.06 (m, 1H), 1.62 – 1.02 (m, 25H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 208.148, 82.305, 71.313, 59.741, 59.548, 41.192, 41.116, 41.087, 35.190, 35.111, 30.169, 24.125, 23.791, 22.884, 21.218, 20.936, 17.229. **IR** (film): 2976, 2935, 2096, 1718, 1450, 1376, 1363, 1321, 1259, 1132, 1043, 1010 cm^{-1} **HRMS** (DART) exact mass calculated for $C_{18}H_{26}N_4O$ $[M+H]^+$ m/z =325.25980, found m/z = 325.26023.

4-(2-azido-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)benzonitrile (2d)



According to **GP 1** with 1-cyano-4-vinylbenzene (25.8 mg, 0.2 mmol, 1eq). After electrolysis for 3 hours at 40°C, the reaction solution was passed through a short column, concentrated in vacuo and then purified by column chromatography (hexanes/ethyl acetate = 4/1) to yield the desired product as a viscous, pale yellow oil (54.4 mg, 83%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 4.80 (dd, *J* = 6.9, 4.5 Hz, 1H), 3.71 (dd, *J* = 12.3, 4.5 Hz, 1H), 3.64 (dd, *J* = 12.3, 6.9 Hz, 1H), 1.70 – 0.63 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.394, 133.775, 129.040, 128.569, 84.485, 60.260, 55.234, 40.539, 34.553, 34.276, 20.451, 17.206. **IR** (film): 2932, 2101, 1609, 1462, 1361, 1304, 1258, 1132, 1061, 957, 839 cm^{-1}; **HRMS** (DART) exact mass calculated for $C_{18}H_{25}N_5O$ $[M+H]^+$ m/z = 328.2132, found m/z = 328.2122.

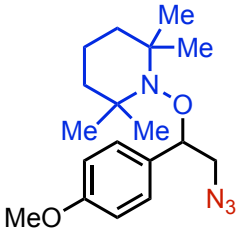
1-(2-azido-1-(4-chlorophenyl)ethoxy)-2,2,6,6-tetramethylpiperidine (2c)



According to **GP 1** with 1-chloro-4-vinylbenzene (27.7 mg, 0.2 mmol, 1eq). After electrolysis for 3 hours at room temperature, the mixture was passed through a short column, concentrated in vacuo and then purified by column chromatography (hexanes/ethyl acetate = 10/1) to yield the desired product as a viscous, pale yellow oil (62.0 mg, 92%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.40 – 7.29 (m, 4H), 4.82 (dd, *J* = 6.9, 4.6 Hz, 1H), 3.74 (dd, *J* = 12.4, 4.5 Hz, 1H), 3.66 (dd, *J* = 12.4, 6.9 Hz, 1H), 1.56 – 0.60 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.398, 133.778, 129.043, 128.573, 84.490, 60.262, 55.237, 40.543, 34.553, 34.291, 20.452, 17.209. **IR** (film):

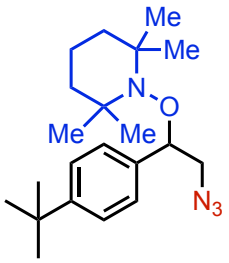
2932, 2100, 1597, 1491, 1349, 1258, 1106, 1014, 974, 922, 816 cm^{-1}; **HRMS** (DART) exact mass calculated for $C_{17}H_{25}ClN_4O$ $[M+H]^+$ m/z = 337.1790, found m/z = 337.1781.

1-(2-azido-1-(4-methoxyphenyl)ethoxy)-2,2,6,6-tetramethylpiperidine (2b)



According to **GP 1** with 1-methoxy-4-vinylbenzene (26.8 mg, 0.2 mmol, 1eq). After electrolysis of 1.5 hours at room temperature, the mixture was passed through a short column, concentrated in vacuo and then purified by column chromatography (hexanes/ethyl acetate = 10/1) to yield the desired product as a viscous, clear oil (59.2 mg, 89%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.30 – 7.23 (m, 2H), 6.93 – 6.86 (m, 2H), 4.78 (dd, *J* = 7.1, 4.8 Hz, 1H), 3.81 (s, 3H), 3.74 (dd, *J* = 12.3, 4.8 Hz, 1H), 3.60 (dd, *J* = 12.2, 7.1 Hz, 1H), 1.62 – 0.59 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.361, 132.929, 128.917, 113.662, 84.451, 60.129, 55.331, 55.292, 40.516, 34.466, 34.226, 20.418, 17.221. **IR** (film): 2931, 2098, 1611, 1513, 1462, 1360, 1245, 1132, 1035, 956, 829 cm^{-1}; **HRMS** (DART) exact mass calculated for $C_{18}H_{28}N_4O_2$ $[M+H]^+$ m/z = 333.2285, found m/z = 333.2277.

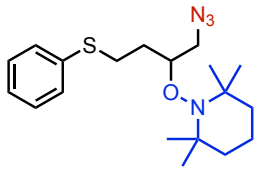
1-(2-azido-1-(4-(*tert*-butyl)phenyl)ethoxy)-2,2,6,6-tetramethylpiperidine (2a)



According to **GP 1** with 1-(*tert*-butyl)-4-vinylbenzene (32.0 mg, 0.2 mmol, 1eq). After electrolysis of 1.5 hours at room temperature, the mixture was passed through a short column, concentrated in vacuo and then purified by column chromatography (hexanes/ethyl acetate = 10/1) to yield the desired product as a viscous, clear oil (67.2 mg, 94%). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 2.7 Hz, 2H), 4.83 (dd, *J* = 6.9, 4.7 Hz, 1H), 3.78 (dd, *J* = 12.2, 4.7 Hz, 1H), 3.64 (dd, *J* = 12.2, 6.9 Hz, 1H), 1.55 – 0.70 (m, 27H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ

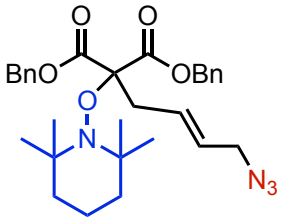
150.889, 137.599, 127.319, 125.172, 84.594, 60.181, 55.347, 40.587, 34.681, 31.516, 20.505, 17.284. **IR** (film): 2932, 2099, 1462, 1375, 1259, 1132, 1015, 956, 924, 833, 820 cm^{-1}; **HRMS** (DART) exact mass calculated for $C_{21}H_{34}N_4O$ $[M+H]^+$ m/z = 359.2805, found m/z = 359.2794.

1-((1-azido-4-(phenylthio)butan-2-yl)oxy)-2,2,6,6-tetramethylpiperidine (2w)



According to **GP 2** with but-3-en-1-yl(phenyl)sulfane (32.0 mg, 0.2 mmol, 1eq). After electrolysis of 8 hours at room temperature, the mixture was passed through a short column, concentrated in vacuo and then purified by column chromatography (hexanes/ethyl acetate = 40/1) to yield the desired product as a viscous, clear oil (49.4 mg, 68%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.38 (m, 2H), 7.31 (m, 2H), 7.21 (m, 1H), 4.10 (qd, *J* = 6.1, 4.2 Hz, 1H), 3.72 (dd, *J* = 12.4, 4.2 Hz, 1H), 3.35 (dd, *J* = 12.4, 6.4 Hz, 1H), 3.04 (qdd, *J* = 12.9, 8.8, 6.3 Hz, 2H), 2.10 (ddt, *J* = 12.6, 8.9, 6.3 Hz, 1H), 1.93 (ddt, *J* = 14.6, 8.8, 6.2 Hz, 1H), 1.67 – 1.03 (m, 18H).**^{13}C NMR (126 MHz, $CDCl_3$)** δ 136.413, 129.266, 129.054, 126.082, 79.270, 60.527, 59.902, 53.211, 40.531, 40.433, 34.530, 34.179, 31.376, 30.041, 20.663, 20.581, 17.332. IR: 3023, 2973, 2931, 2102, 1584, 1480, 1438, 1375, 1360, 1273, 1182, 1132, 1044, 1025, 941, 913, 737, 690. **HRMS** (DART): calculated exact mass of $C_{19}H_{30}N_4OS$ $[M+H]^+$=363.22186 m/z , found: 363.22172 m/z.

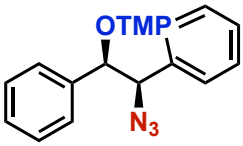
dibenzyl(*E*)-2-(4-azidobut-2-en-1-yl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)malonate (2u)



According to **GP 1** with dibenzyl 2-vinylcyclopropane-1,1-dicarboxylate (66.0 mg, 0.2 mmol, 1eq). After stirring 3 hours at room temperature, a short column chromatography followed by preparatory TLC (hexanes/ethyl acetate = 10/1) yielded the desired product as a viscous, clear oil (13.4 mg, 13%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 (s, 10H), 5.76 (dt, *J* = 14.9, 7.3 Hz, 1H), 5.42 (dt, *J* = 14.7, 6.8 Hz, 1H), 3.51 (d, *J* = 6.7 Hz, 2H), 3.02 (d, *J* = 7.3 Hz, 2H), 1.51 – 0.98 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.751, 135.149, 130.591, 128.857, 128.832, 128.644, 128.617, 128.515, 128.493, 128.434, 128.407, 126.736, 88.754, 67.209, 61.057, 52.521, 41.061, 37.590, 33.311,

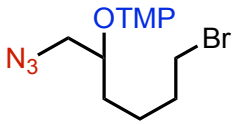
20.899, 16.918. **IR** (film): 2934, 2102, 1736, 1498, 1456, 1377, 1362, 1234, 1131, 1054, 1029 cm^{-1} **HRMS** (ESI): calculated mass for $C_{30}H_{38}N_4O_5$ $(M+H)^+$ m/z=535.29205. Found: m/z=535.29304.

1-(2-azido-1,2-diphenylethoxy)-2,2,6,6-tetramethylpiperidine (1o)



According to **GP 1** with *cis*-stilbene (36mg, 0.2 mmol, 1eq). After electrolysis for 2 hours at room temperature, the crude reaction was passed through a short column and concentrated in vacuo. The crude product was then purified by column chromatography (hexanes/ethyl acetate = 9:1) to yield the desired product as a viscous, clear oil (61.4mg, 81%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.24 – 6.88 (m, 10H), 5.12 (d, *J* = 8.0 Hz, 1H), 5.01 (d, *J* = 8.0 Hz, 1H), 1.94 – -0.07 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.896, 136.833, 129.697, 128.150, 128.101, 127.890, 127.814, 127.385, 89.196, 69.339, 61.131, 59.421, 41.001, 34.825, 34.116, 20.633, 17.222. **IR**: 3063, 3031, 3004, 2970, 2929, 2870, 2100, 1712, 1453, 1375, 1361, 1256, 1207, 1182, 1132, 1074, 1019, 986, 955, 908, 878, 839, 782, 756, 697 cm^{-1}. **HRMS**: Calculated accurate mass of $C_{23}H_{30}N_4O$ $[M+H]^+$ = 379.24924 m/z. Found: 379.24979 m/z.

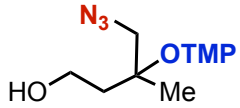
1-((1-azido-6-bromohexan-2-yl)oxy)-2,2,6,6-tetramethylpiperidine (2j)



According to **GP 1** with 6-bromohex-1-ene (32.6 mg, 0.2 mmol, 1eq). After electrolysis for 3 hours at room temperature, the crude reaction was passed through a short column, concentrated in vacuo. The crude product was then purified by column chromatography (hexanes/ethyl acetate = 15/1) to yield the desired product as a viscous, pale oil (70 mg, 97%). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 3.89 (td, *J* = 6.1, 4.3 Hz, 1H), 3.58 (dd, *J* = 12.4, 4.3 Hz, 1H), 3.43 (t, *J* = 6.7 Hz, 2H), 3.34 (dd, *J* = 12.4, 5.8 Hz, 1H), 2.00 – 0.99 (m, 24H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 80.627, 77.414, 60.327, 59.966, 53.302, 40.470, 34.526, 34.255, 33.772, 33.037, 30.635, 24.484, 20.586, 17.341. **IR**: 2934, 2871, 2101, 1540, 1455, 1376, 1360, 1250, 1209, 1182, 1132, 1082, 1060, 1015, 991,

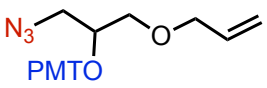
958, 880, 788, 736, 717, 651, 563, 556. **HRMS** (DART): calculated exact mass of $C_{15}H_{29}BrN_4O$ $[M+H]^+$ =361.15975 . Found: m/z= 361.15984.

4-azido-3-methyl-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butan-1-ol (2x)



According to **GP 2** with 3-methylbut-3-en-1-ol (17.2 mg, 0.2 mmol, 1.0 equiv). After electrolysis for 2 hours at room temperature, the crude reaction was passed through a short column, concentrated in vacuo. The crude product was then purified by column chromatography (hexanes/ethyl acetate = 4:1) to yield the desired product as a viscous, pale oil (49.2 mg, 87%). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 3.80 (m, 2H), 3.55 (d, *J* = 12.2 Hz, 1H), 3.45 (d, *J* = 12.2 Hz, 1H), 2.20 – 1.87 (m, 2H), 1.66 – 1.02 (m, 23H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 83.102, 60.490, 60.366, 59.628, 58.377, 40.861, 40.848, 40.075, 34.724, 34.669, 23.926, 21.119, 21.064, 17.068. **IR**: 3340, 2932, 2098, 1452, 1374, 1359, 1257, 1181, 1132, 1054, 1011, 913, 878, 743, 560, 428. **HRMS** (DART): calculated exact mass of $C_{14}H_{28}N_4O_2$ $[M+H]^+$ = 285.22905 found: 285.22903 m/z.

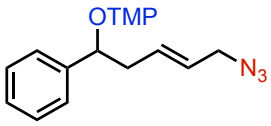
1-((1-(allyloxy)-3-azidopropan-2-yl)oxy)-2,2,6,6-tetramethylpiperidine (2v)



According to **GP 2** with allyl ether (19.6 mg, 0.2 mmol, 1.0 equiv). After electrolysis for 2 hours at room temperature, the crude reaction was passed through a short column, concentrated in vacuo. The crude product was then purified by column chromatography (pure hexanes) to yield the desired product as a viscous, pale oil (25.2 mg, 42%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.90 (ddt, *J* = 17.3, 10.8, 5.6 Hz, 1H), 5.32 – 5.23 (m, 1H), 5.23 – 5.15 (m, 1H), 4.12 – 4.03 (m, 1H), 3.99 (dt, *J* = 5.6, 1.5 Hz, 2H), 3.71 (dd, *J* = 9.7, 4.0 Hz, 1H), 3.62 – 3.42 (m, 4H), 1.80 – 1.04 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 134.816, 117.064, 80.252, 72.361, 68.558, 60.531, 60.040, 51.867, 40.506, 39.818, 34.360, 33.755, 32.529, 20.461, 17.290. **IR**: 3020, 2929, 2871, 2100.6, 1739, 1455, 1376, 1361, 1279, 1132,

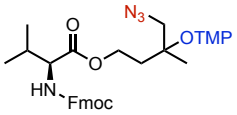
1094, 993, 913, 787, 743 cm^{-1}. **HRMS** (Dart): Calculated exact mass for $C_{15}H_{28}N_4O_2$ $[M+H]^+$= 297.22905 found: 297.22949.

(*E*)-1-((5-azido-1-phenylpent-3-en-1-yl)oxy)-2,2,6,6-tetramethylpiperidine (2t)



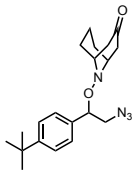
According to **GP 2** with (2-vinylcyclopropyl)benzene (28.8 mg, 0.2 mmol, 1eq). After electrolysis of 2.5 hours at room temperature, the mixture was passed through a short column, concentrated in vacuo and then purified by column chromatography (hexanes/ethyl acetate = 20/1) to yield the desired product as a viscous, clear oil (53.7mg, 78%). The two isomers form an inseparable mixture. **^{1}H NMR** (599 MHz, Chloroform-*d*) δ 7.48 – 7.13 (m, 5H), 5.54 – 5.33 (m, 2H), 4.67 (dd, *J* = 9.3, 4.2 Hz, 1H), 3.57 (d, *J* = 6.1 Hz, 2H), 2.89 (ddd, *J* = 13.9, 7.1, 4.3 Hz, 1H), 2.61 (ddd, *J* = 14.7, 9.3, 6.3 Hz, 1H), 1.69 – 0.49 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.909, 132.684, 128.017, 127.807, 127.277, 125.506, 86.808, 60.091, 59.860, 52.873, 40.574, 39.383, 34.625, 34.211, 20.490, 17.323. **IR**: 3086, 3063, 2972, 2932, 2870, 2099, 1716, 1667, 1493, 1454, 1375,1360, 1258, 1241, 1209, 1183, 1133, 1074, 1044 cm^{-1}. **HRMS** (DART): Calculated exact mass of $C_{20}H_{30}N_4O[M+H]^+$ = 343.24979 m/z, found = 343.24923 m/z. Product is unstable on the time scale of ^{13}C NMR.

3-methylbut-3-en-1-yl (((9*H*-fluoren-9-yl)methoxy)carbonyl)-*L*-valinate



Following GP 2 with (81 mg, 0.2 mmol, 1 eq) of 3-methylbut-3-en-1-yl (((9H-fluoren-9-yl)methoxy)carbonyl)-L-valinate. After electrolysis of 3.5 hours at room temperature, the mixture was passed through a short column, concentrated in vacuo and then purified by column chromatography on the Biotage (hexanes/ethyl acetate = 5-10% over 12 CV) to yield the desired product as a viscous, clear oil (50.2 mg, 42%). The two isomers form an inseparable mixture. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.77 (d, J = 7.5 Hz, 2H), 7.62 (dd, J = 7.6, 3.6 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.33 (t, J = 7.4 Hz, 2H), 5.39 (d, J = 9.2 Hz, 1H), 4.52 – 4.16 (m, 6H), 3.60 – 3.39 (m, 2H), 2.27 – 2.04 (m, 2H), 1.72 – 0.80 (m, 27H). **^{13}C NMR** (126 MHz, CDCl3) δ 172.082,

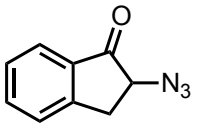
156.223, 143.939, 143.795, 141.298, 127.688, 127.059, 125.101, 119.978, 119.962, 79.639, 79.610, 67.030, 61.882, 59.767, 59.749, 59.727, 59.043, 59.025, 58.599, 47.211, 40.919, 40.903, 40.891, 37.093, 37.061, 34.878, 34.866, 34.740, 34.729, 31.407, 31.396, 22.975, 22.934, 20.930, 20.788, 20.777, 19.018, 17.543, 16.982. **HRMS (ESI+)**: calculated exact mass of $C_{34}H_{47}N_5O_5$ $[M+H]^+$ = 606.36500 m/z. Found = 606.36475 m/z **IR**: 3348, 3007, 2970, 2936, 2872, 2100, 1735, 1727, 1685, 1508, 1466, 1459, 1373, 1364, 1229, 1216, 1206 cm^{-1}.



9-(2-azido-1-(4-(*tert*-butyl)phenyl)ethoxy)-9-azabicyclo[3.3.1]nonan-3-one

Following **GP 1** with 4-tertbutylstyrene (32.6 mg, 0.2 mmol, 1 eq) and 9-Azabicyclo[3,3,1]nonan-3-one-9-oxyl (46mg, 1.5 eq, 0.3 mmol). After electrolysis of 3 hours at room temperature, the mixture was passed through a short column, concentrated in vacuo and then purified by column chromatography on the Biotage (hexanes/ethyl acetate = 10%) to yield the desired product as an inseparable mixture of conformers, viscous, clear oil (30.1mg, 42%). **^{1}H NMR** (599 MHz, Chloroform-*d*) δ 7.41 – 7.35 (m, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 4.90 (dd, *J* = 8.3, 3.7 Hz, 1H), 3.91 (m, 1H), 3.55 (dd, *J* = 13.1, 8.3 Hz, 1H), 3.49 (m, 1H), 3.34 (dd, *J* = 13.1, 3.8 Hz, 1H), 3.15 (dd, *J* = 16.1, 6.8 Hz, 1H), 3.03 (dd, *J* = 16.0, 6.8 Hz, 1H), 2.21 (d, *J* = 16.1 Hz, 1H), 2.10 (d, *J* = 15.9 Hz, 1H), 1.96 – 1.86 (m, 1H), 1.79 – 1.70 (m, 2H), 1.57 (ddt, *J* = 13.7, 4.8, 2.4 Hz, 1H), 1.32 (m, 11H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.859, 151.416, 136.469, 126.528, 125.793, 125.748, 125.515, 83.217, 58.897, 58.718, 55.161, 41.266, 41.184, 34.732, 32.113, 31.800, 31.723, 31.462, 31.437, 22.791, 15.458, 14.260. **HRMS** (DART): calculated exact mass of $C_{20}H_{28}N_4O_2$ $[M+H]^+$ = 357.22850 m/z. found = 357.22881m/z. **IR**: 2951, 2872, 2098, 1711, 1509, 1474, 1466, 1460, 1437, 1400, 1364, 1341, 1314, 1283, 1269, 1224, 1209, 1185, 1105, 1082, 1057, 1033, 1017 cm^{-1}.

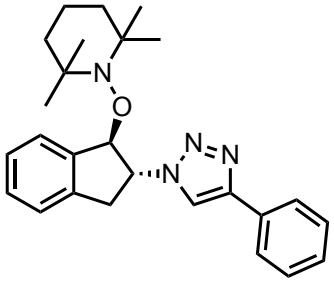
2-azido-2,3-dihydro-1*H*-inden-1-one (4)



A solution of 1-((2-azido-2,3-dihydro-1*H*-inden-1-yl)oxy)-2,2,6,6-tetramethylpiperidine (62mg, 0.2mmol, 1eq) in DCM (2.5ml) was added slowly to a solution of mete-chloroperoxybenzoic acid (96 mg, 0.26 mmol, 1.3eq) in DCM (2.5ml). After stirring at room temperature for 1 hour the reaction solution was quenched with saturated solution of $NaHCO_3$ and DCM (10ml) was added. The organic layer was then dried with Na_2SO_4 and concentrated in vacuo. Crude product was then purified by column chromatography (9/1) to yield a clear liquid (28.8mg. 84.3%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.66 (td, *J* = 7.5, 1.2 Hz, 1H), 7.52 –

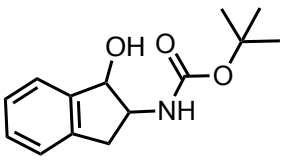
7.37 (m, 2H), 4.32 (dd, *J* = 8.1, 4.7 Hz, 1H), 3.51 (dd, *J* = 17.1, 8.1 Hz, 1H), 2.94 (dd, *J* = 17.1, 4.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 201.753, 151.206, 136.098, 134.266, 128.296, 126.634, 124.734, 77.415, 77.160, 76.906, 62.044, 33.062. **IR** (film): 2900, 2104, 1722, 1609, 1587, 1466, 1432, 1301, 1268, 1224, 1153, 1091, 1033 cm^{-1} **HRMS** (DART) exact mass calculated for $C_9H_{11}N_4O$ $[M+NH_4]^+$ m/z = 191.09274, found m/z = 191.09274.

2,2,6,6-tetramethyl-1-((2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2,3-dihydro-1*H*-inden-1-yl)oxy)piperidine (3)



Copper sulphate (4 mg, 0.016 mmol, 0.1eq) was added to a stirring solution of 1-((2-azido-2,3-dihydro-1*H*-inden-1-yl)oxy)-2,2,6,6-tetramethylpiperidine (50.3 mg, 0.16 mmol, 1eq), phenylacetylene (50 ul, 0.46 mmol, 2.9eq), sodium ascorbate (14 mg, 0.08 mmol, 0.5eq) in ^{t}BuOH(1ml) and water (0.5ml). After stirring at RT for 24h, water (5ml) was added and the reaction extracted with DCM (3x10mL). The combined organic layer was combined and dried with Na_2SO_4 and concentrated in vacuo. The crude product was then purified by column chromatography (9:1) to yield a white crystalline solid (61.2 mg, 92%).**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 6.4 Hz, 3H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.46 – 7.28 (m, 6H), 5.78 (d, *J* = 3.5 Hz, 1H), 5.69 (dt, *J* = 8.0, 4.1 Hz, 1H), 3.81 (dd, *J* = 16.7, 7.9 Hz, 1H), 3.27 (dd, *J* = 16.7, 4.5 Hz, 1H), 1.70 – 0.80 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.527, 140.583, 140.060, 130.906, 129.626, 128.923, 128.148, 127.236, 125.771, 124.893, 118.655, 90.519, 66.128, 60.900, 60.293, 40.453, 40.428, 38.493, 33.934, 33.725, 20.739, 20.663, 17.301. **IR** (film): 2971, 2930, 1458, 1437, 1375, 1362, 1229, 1112, 1045 cm^{-1}. **HRMS** (DART): calculated exact mass of $C_{26}H_{33}N_4O$ $[M+H]^+$= 417.26544 m/z. Found: = 417.26592 m/z.

tert-butyl (1-hydroxy-2,3-dihydro-1H-inden-2-yl)carbamate (5)

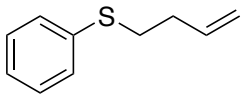


Palladium on carbon (16mg, 0.1eq) was added to a solution of 1-((2-azido-2,3-dihydro-1*H*-inden-1-yl)oxy)-2,2,6,6-tetramethylpiperidine (55 mg, 0.18 mmol, 1eq) in ethanol (1.5ml). The entire reaction mixture was then kept under high pressure of hydrogen gas in a Parr reactor and stirred overnight. Hydrogen pressure was then removed, followed by the addition of Boc_2O (60 mg, 1.25eq). Solution was then stirred for 2 hours. Reaction solution was then filtered through celite and washed with ethyl acetate (10ml). The mixture was then concentrated in vacuo and used in the next step without

purification. Acetic acid (3ml) and water (9ml) was then added to the crude mixture, followed by zinc powder (80 mg, 6.7eq, 1.2mmol). Reaction was then stirred at RT overnight. Reaction was quenched with 1M NaOH, extracted with DCM (3x 10ml), concentrated in vacuo and purified by column chromatography (methanol and DCM, 2%) to yield a clear liquid (40 mg, 89%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.46 – 7.37 (m, 1H), 7.31 – 7.23 (m, 2H), 7.18 (d, *J* = 7.1 Hz, 1H), 5.08 (d, *J* = 6.3 Hz, 1H), 5.00 (br s, 1H), 4.42 (br s, 1H), 4.17 – 4.03 (m, 1H), 3.31 (dd, *J* = 15.2, 8.2 Hz, 1H), 2.70 (dd, *J* = 15.2, 9.1 Hz, 1H), 1.58 (s, 1H), 1.48 (s, 9H). **^{13}C NMR** (126 MHz, DMSO) δ 155.516, 144.175, 138.993, 127.502, 126.531, 124.392, 123.836, 77.947, 77.632, 60.628, 35.840, 28.299. **IR** (film): 3430, 3354, 2127, 1661, 1027, 1008 cm^{-1} **HRMS** (ESI+): Calculated exact mass of $C_{14}H_{19}NO_3$ $[M+Na]^+$=272.126262. Found m/z=272.126452.

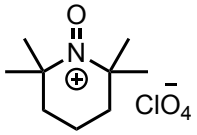
Synthesis of substrates

But-3-en-1-yl(phenyl)sulfane



Following a slightly modified procedure[1]. Thiophenol (310ul, 1 eq, 3mmol), 4-bromobut-1-ene (403 mg, 1 eq, 3mmol) and sodium carbonate (630 mg, 2 eq) was dissolved in methanol (25ml). Nitrogen was then used to purge the solution for 10 minutes. The reaction was then refluxed for 16 hours. **^{1}H NMR** (599 MHz, Chloroform-*d*) δ 7.37 – 7.32 (m, 2H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.21 – 7.14 (m, 1H), 6.00 – 5.59 (m, 1H), 5.22 – 4.86 (m, 2H), 2.98 (t, *J* = 7.5 Hz, 2H), 2.54 – 2.25 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.526, 129.406, 129.021, 126.080, 116.380, 33.495, 33.163. **HRMS**: Calculated accurate mass of $C_{10}H_{12}S$ $[M+H]^+$ = 165.07325 m/z. Found: 165.07334 m/z.

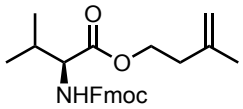
2,2,6,6-tetramethyl-1-oxopiperidin-1-ium perchlorate



Following a modified procedure[2]. Concentrated perchloric acid (0.5ml, 70%, 16 mmol, 1.5eq) was added to a cooled (0°C) solution TEMPO (800 mg, 5.12 mmol, 1 eq) in diethyl ether (7ml). Then aqueous sodium hypochlorite (10 ml, ~5%, ~1.3eq) solution was added dropwise over 5 minutes. The solution was then allowed to react for another 10 minutes. After which the solution was filtered and washed with cold water (0°C, 10

ml) and ether (50 ml). The crude product was recrystallized in boiling water to afford yellow needle crystals (1.08g, 83%). **HRMS**: calculated accurate mass for $C_9H_{18}NO$ $[M]^+$=156.13829 m/z. Found= 156.13870 m/z.

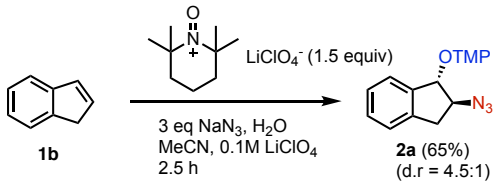
3-methylbut-3-en-1-yl (((9*H*-fluoren-9-yl)methoxy)carbonyl)-*L*-valinate



(((9*H*-fluoren-9-yl)methoxy)carbonyl)-*L*-valine (339 mg, 1 mmol, 1 eq), 3-methylbut-3-en-1-ol (96, 1.1 mmol, 1.1 eq), EDCl (1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide) (228 mg, 1 mmol, 1eq), DMAP (9 mg, 0.07 mmol, 0.07 eq) and DCM (20 ml) was added to a round bottom flask and stirred overnight. The reaction was washed with water and extracted with DCM (2*20ml). The organic layer was combined, dried with Na_2SO_4 and concentrated in vacuo. The crude product was then purified on the biotage (5-10 % 10 CV) to yield a clear sticky oil (327.8 mg, 80%). **^{1}H NMR** (500 MHz,) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.67 – 7.56 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.32 (td, *J* = 7.5, 1.6 Hz, 2H), 4.82 (s, 1H), 4.74 (s, 1H), 4.47 – 4.19 (m, 6H), 2.37 (t, *J* = 6.9 Hz, 2H), 2.24 – 2.11 (sept, 7.0Hz, 1H), 1.76 (s, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.193, 156.366, 144.073, 143.941, 141.451, 141.339, 127.843, 127.204, 125.240, 120.132, 120.116, 112.710, 67.160, 63.517, 59.172, 47.354, 36.765, 31.736, 31.460, 22.803, 22.528, 19.139, 17.663, 14.272.

Mechanistic study

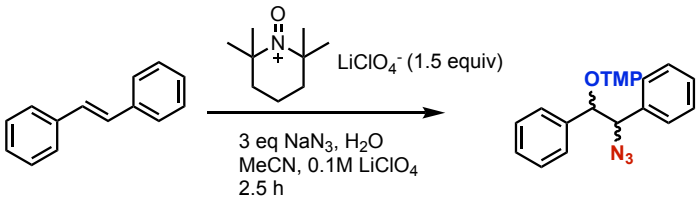
Chemical reaction



Indene (23 mg, 0.2 mmol, 1 eq), MeCN (3.5ml, 0.1M $LiClO_4$) and $TEMPOClO_4$ (77 mg, 0.3 mmol, 1.5eq) was added to a 10 ml round bottom flask under stirring. Then N2 gas was used to purge the entire reaction solution for 10 minutes before the addition of NaN_3 solution (0.3ml, 2M, 3 eq). The reaction was allowed to stir for 2.5 hours after which it was passed through a silica plug. The crude mixture was analysed by NMR.

Entry	Condition	d.r of **2a**
2	1.5 equiv $TEMPOClO_4$	4.5:1

Stilbene Reaction



trans-stilbene (36 mg, 0.2 mmol, 1 eq), MeCN (3.5ml, 0.1M $LiClO_4$) and $TEMPOClO_4$ (77 mg, 0.3 mmol, 1.5eq) was added to a 10 ml round bottom flask under stirring. Then N2 gas was used to purge the entire reaction solution for 10 minutes before the addition of NaN_3 solution (0.3ml, 2M, 3 eq). The reaction was allowed to stir for 2.5 hours after which it was passed through a silica plug. The crude mixture was analysed by NMR.

Entry	Variation from standard condition	d.r of trans:cis
1	none	1:1.36
2	Cis-stilbene instead of trans-stilbene	1:1.37
3	Partial conversion of cis-stilbene, followed by recovery of starting material	100% cis-stilbene.
4	Cis-stilbene with no NaN_3	100% cis-stilbene

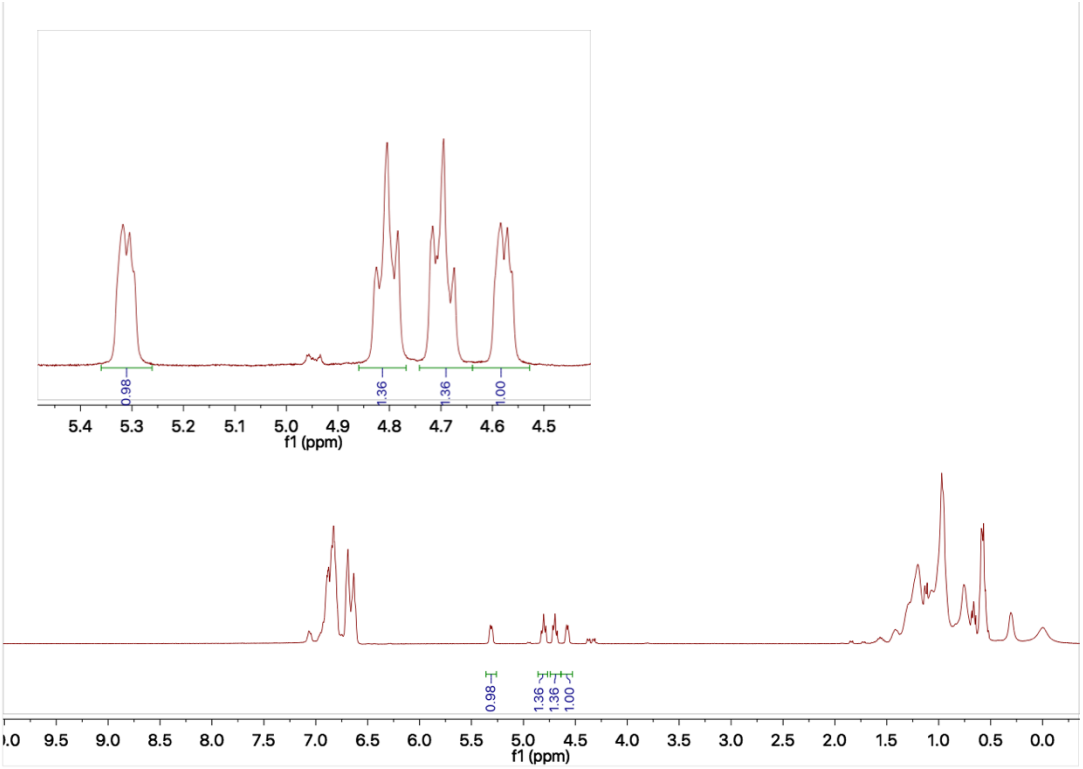
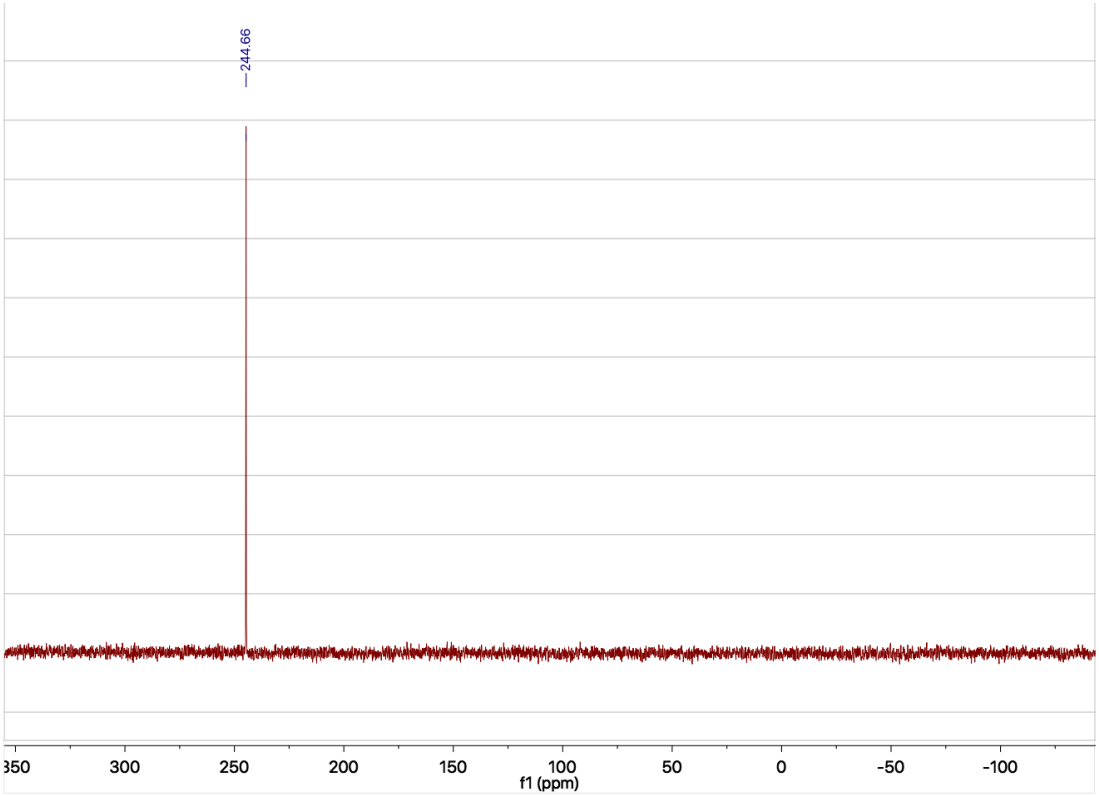


Figure S1. Example spectrum of a crude mixture

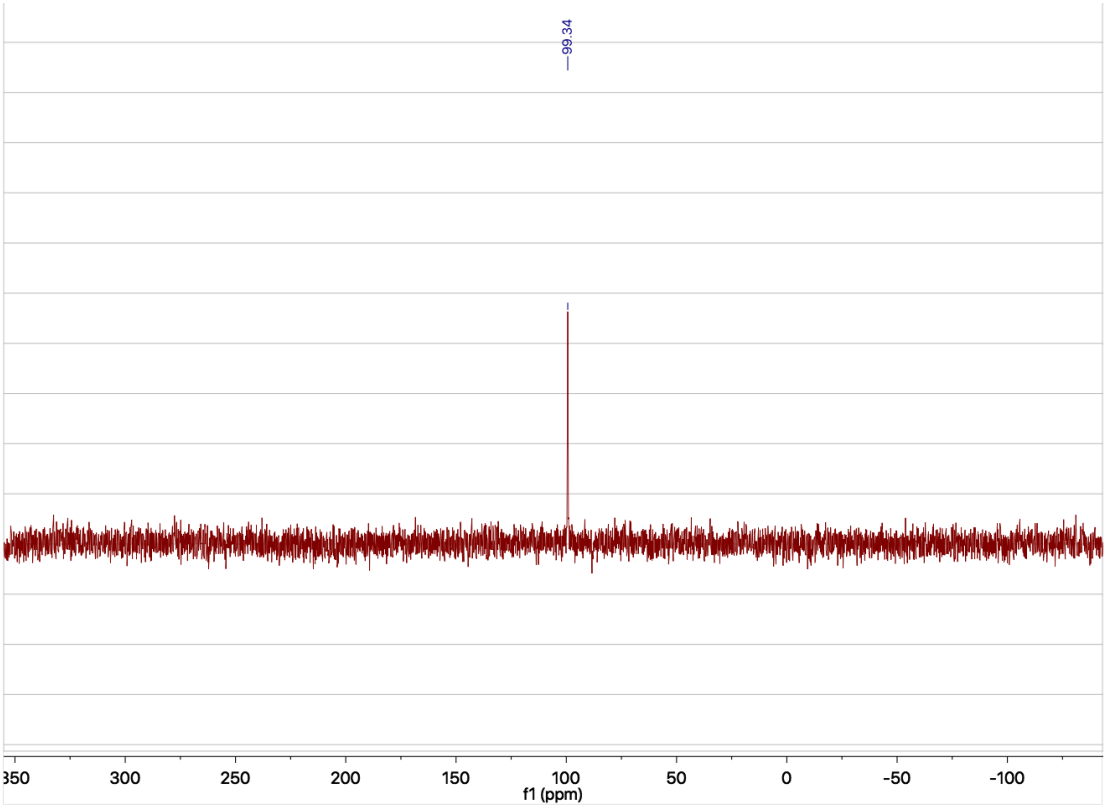
^{15}N NMR of the TEMPO azide complex.

All ^{15}N-NMR was obtained on a Bruker 500 MHz spectrometer. Pulse sequence used: d1 = 30s. nt = 256. At = 3s. T = 300K.

Sample preparation: $TEMPOClO_4$ (14 mg, 55 mmol) and $Na^{15}N_3$ (3.8 mg, 57mmol) was dissolved in MeCN-d_3 (0.6 ml) and shaken vigorously for 5 minutes before transferred in to an NMR tube.



Sample preparation: $Na^{15}N_3$ (3.8 mg, 57 mM) was added to a NMR tube and dissolved in D_2O (0.6 ml).



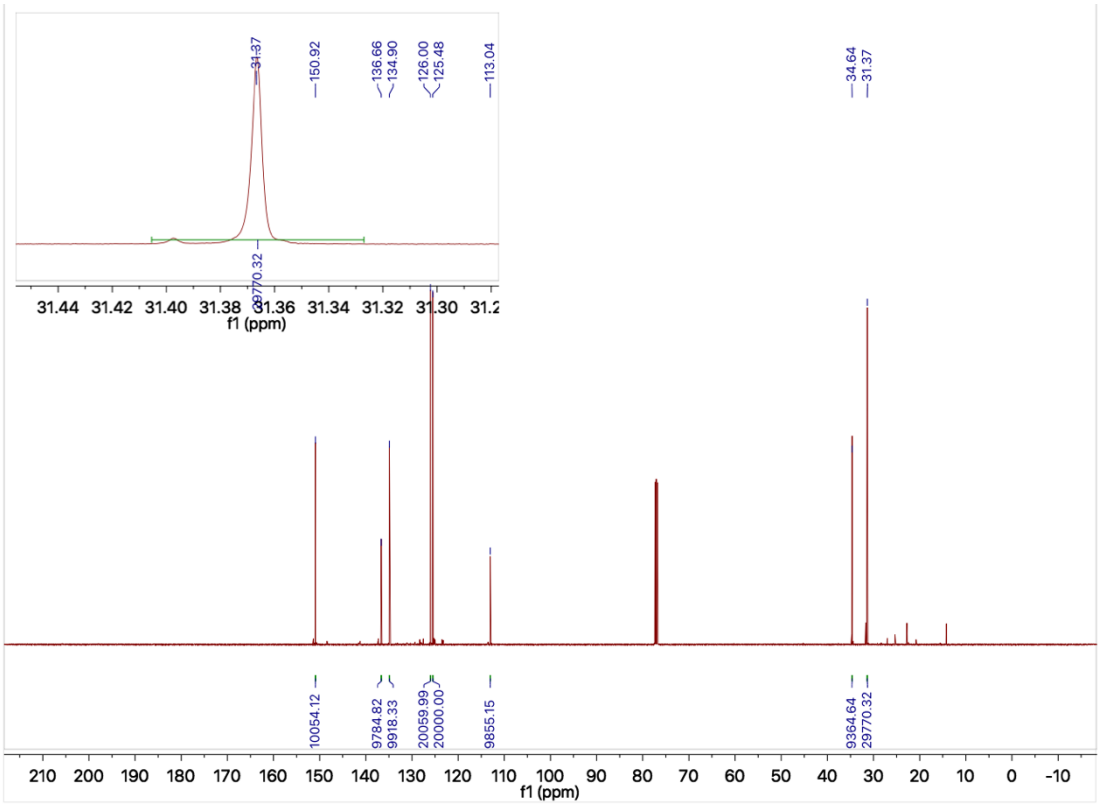
Natural abundance Carbon Kinetic Isotope study

Based on the method outlined in **GP 1**, the reaction was scaled up 5 times. In an oven dried echem cell, 4-tert-butylstyrene (160.3mg, 1mmol, 1eq), TEMPO (234.4mg, 1.5mmol, 1.5eq) and 1,2,4-trichlorobenzene (36mg, 0.2mmol, 0.2eq) was added. Then acetonitrile (10ml) and sodium azide solution (1.5ml, 2M, 3eq) was added. Nitrogen was purged through the solution for 10 minutes. The reaction was initiated by an application of a constant potential of 2.6V. The potentiostat was set to terminate reaction when a fixed amount of charged has passed based on a coulombic efficiency of 59.2%. e.g 137 coulombs of set for a conversion of around 84%. After which the reaction was concentrated in vacuo and then purified with FC with pure hexanes. 25mg of sample was then taken and dissolved in 500ul of $CDCl_3$ and analysed by the quantitative ^{13}C pulse sequence. A 50ul crude reaction mixture was also taken for conversion determination via HPLC.

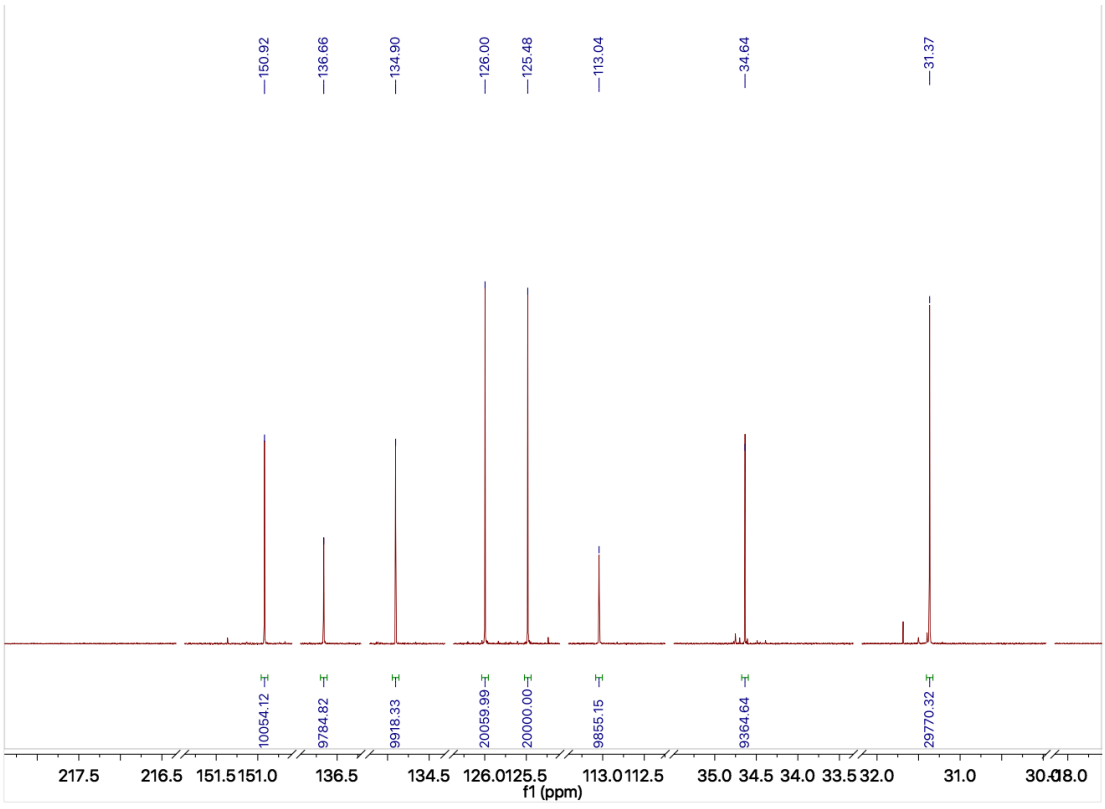
General method for ^{13}C measurements

The spectrums were recorded on a 126MHz Bruker 500 using inverse gated decoupling and calibrated at $\pi/2$ pulses. Following a general method outlined by the Singleton group[3]. A relaxation delay of 70s was used with no noticeable difference in integration when a relaxation delay of 180s was used. Acquisition time was 10s. The spectrums were processed in Mestrenova 11 without the application of any window functions. A manual phase correction and an eighth order polynomial baseline correction was applied. Each peak was integrated between ±5Hz.

Example spectrum

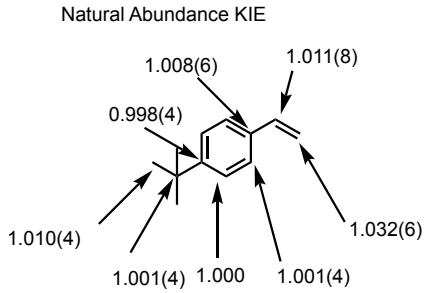


Showing the impurity peak next to 31.37ppm.



	Carbon/ppm								
Trial	31.37	34.70	113.09	125.47	126.08	134.88	136.64	150.91	Conversion
Starting material	29770.32	9364.64	9855.15	20000	20059.99	9918.33	9784.82	10054.12	
1	30007.37	9342.1	10151.53	20000	20099.68	10022.85	9799.3	10074.67	54.1
KIE	1.010282	0.996917	1.039527	1	1.002543	1.013636	1.001901	1.002627	
2	30234.22	9424.95	10224.93	20000	20141.99	9994.78	9887.84	9988.3	64.4
KIE	1.015181	1.006247	1.036939	1	1.003960	1.007481	1.010232	0.993687	
3	29844.73	9372.47	9977.35	20000	20076.06	10031.91	9853.3	10058.34	38.1
KIE	1.005238	1.001747	1.026405	1	1.001674	1.024348	1.014774	1.000876	
4	30152.48	9445.26	10380.98	20000	20112.84	10007.42	9972.29	9994.61	83.9
KIE	1.007023	1.004709	1.029255	1	1.001440	1.004913	1.010486	0.996764	
5	30473.03	9320.19	10378.65	20000	19860.93	9983.51	9804.61	9973.95	83.7
KIE	1.013012	0.997387	1.029332	1	0.994538	1.003619	1.001113	0.995611	
Average	1.0101	1.0014	1.0323	1	1.0008	1.0108	1.0077	0.9979	
Standard deviation	0.0041	0.0042	0.0056	0	0.0037	0.0084	0.0059	0.0037	

Table S- 1. Table containing all the raw integrations of every carbon and their and KIE values with conversion.



UV-vis study

Method: In a 3 ml quartz cell , MeCN (2.45 ml) was added and the blank taken. Then the same cell was washed with MeCN and dried with compressed air before the following contents were added.

Stock solution concentration:

$TEMPOClO_4$ = 2 mM

TBA azide = 24.5 mM

Sample	TBA azide /ul	$TEMPOClO_4$ /ul	MeCN /ul
1	35	430	1985
2	35	343	2072
3	35	257	2158
4	35	171	2244
5	35	86	2329
6	70	430	1950

7	105	430	1915
8	140	430	1880
9	175	430	1845

Proportionality study of the complex.

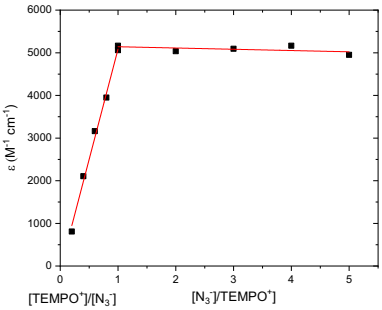


Figure S2. UV vis titration of the complex. The first 5 points was a titration of azide against $TEMPO^+$.

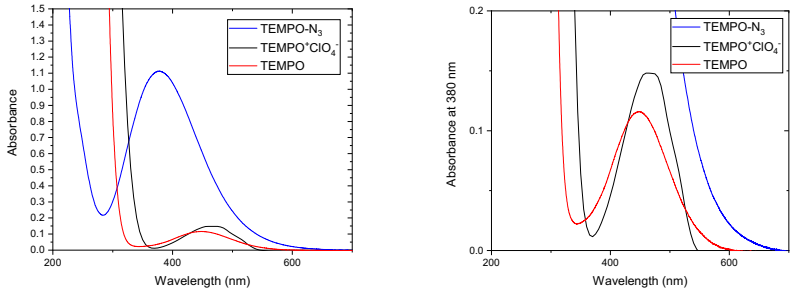


Figure S3. UV vis spectra of TEMPO-N_3 complex (0.2 mM), TEMPO (10 mM) and TEMPOClO_4 (10 mM).

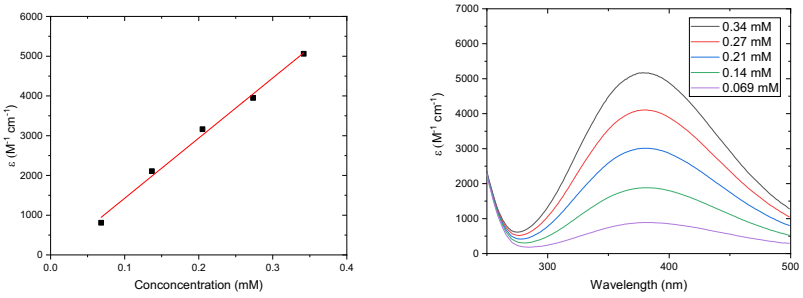


Figure S4. Quantitative titration of the TEMPO-N_3 complex using excess $TBAN_3$. The molar extinct coefficient is determined to be 5174 M^{-1} cm^{-1}.

[TEMPOClO₄]/mM	[TBA azide]/mM	Absorbance
0.34	0.35	1.731
0.27	0.35	1.352
0.21	0.35	1.082
0.14	0.35	0.720
0.069	0.35	0.276

Cyclic voltammetry study

Azide dependence study

The analytic cell was prepared as described before.
Scan rate: 0.1V/s. Supporting electrolyte: 0.1M $LiClO_4$. Working electrode: ∅ 0.3mm glassy carbon. Counter electrode: 10 cm platinum coil. Analytical solution volume: 6 ml MeCN.

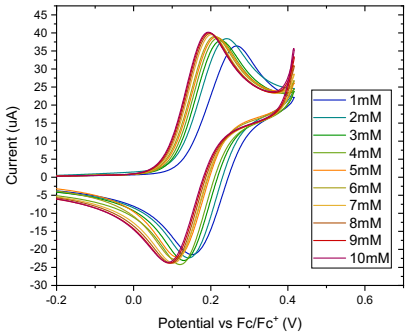


Figure S5.Cyclic voltammogram of the TEMPO redox couple with various concentration of TBA azide.

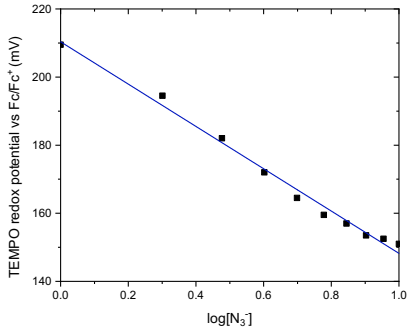


Figure S6. A plot of the redox potential of TEMPO, as determined by the mid-point between the oxidation and reduction peak against Log[N_3^-]. Equation = -62.134x +210.36.

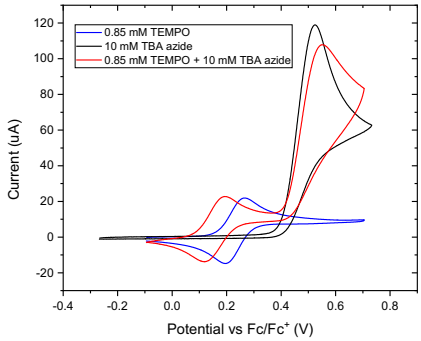


Figure S7. CV traces of TEMPO (0.85mM), TBA azide (10mM), and a combination of TBA azide (10 mM) and TEMPO (0.85mM).

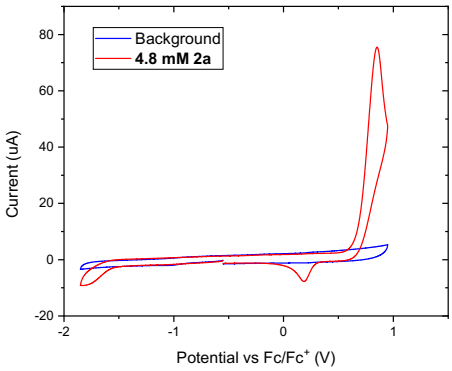


*Figure S8. CV traces of a **2a** (4.8mM) and the background. Showing that the product is stable against further electrochemical oxidation.*

Kinetic studies

TEMPO dependence

Data collection frequency: 100 min^{-1}. Wavelength: 380 nm. Collection duration : 6 min

Stock solution concentration

Compound	Concentration/ mM
(3-methylbut-3-en-1-yl)benzene	24.5
TEMPO	24.5
$TEMPOClO_4$	2.0
TBA azide	24.5

Procedure: In a 3 ml quartz UV-vis cell, $TEMPOClO_4$, MeCN and TEMPO was added. Then TBA azide and alkene was added together and shaken for 2 seconds before acquisition. Reaction concentration = 0.4 mM

Azide/ul	eq	$TEMPO^+$/ul	eq	Alkene /ul	eq	TEMPO	eq	MeCN/ul
40	1	490	1	40	1	0	0	1880
40	1	490	1	40	1	8	0.2	1872
40	1	490	1	40	1	12	0.3	1868
40	1	490	1	40	1	16	0.4	1864
40	1	490	1	40	1	40	1	1840
40	1	490	1	40	1	80	2	1800

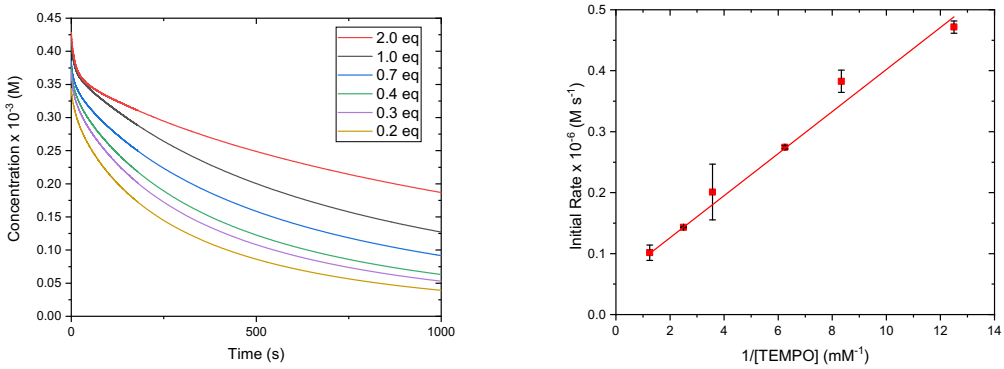


Figure S9. Rate at different conversion and equivalent of exogenous TEMPO.

	30% conversion
1/eq	Rate x 10^{-6} (M s^{-1})
5.0	0.471
3.3	0.382
2.5	0.274
1.4	0.201
1.0	0.143
0.5	0.102

Azide dependence

Stock solution concentration

Compound	Concentration/ mM
(3-methylbut-3-en-1-yl)benzene	24.5
$TEMPOClO_4$	2.0
TBA azide	24.5

Procedure: In a 3 ml quartz UV vis cell, $TEMPOClO_4$, MeCN and TEMPO was added. Then TBA azide and alkene was added together and shaken for 2 seconds before acquisition. Reaction solution concentration: 0.4 mM.

Azide/ul	eq	$TEMPO^+$/ul	eq	Alkene /ul	eq	MeCN/ul
40	1	490	1	40	1	1870
60	1.5	490	1	40	1	1850
80	2	490	1	40	1	1830
120	3	490	1	40	1	1790
160	4	490	1	40	1	1750
200	5	490	1	40	1	1710

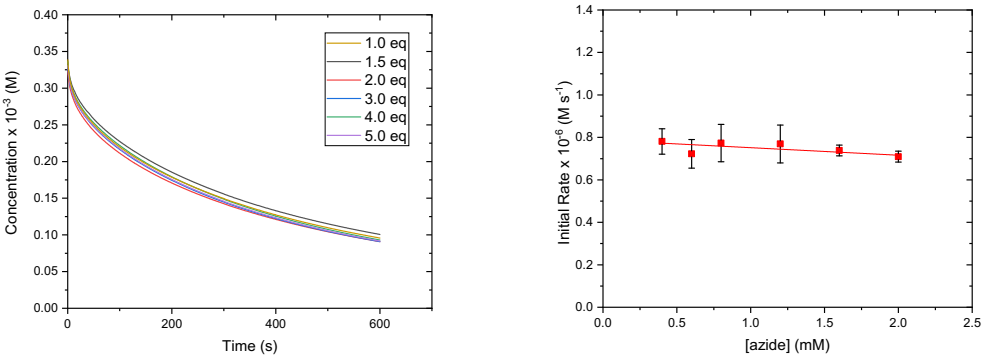


Figure S10. Rate at different conversion and azide equivalence.

	30% conversion
Eq	Rate x 10^{-6} (M s^{-1})
1	0.780
1.5	0.723
2	0.773
3	0.769
4	0.738
5	0.709

Alkene dependence

Stock solution concentration

Compound	Concentration/ mM
(3-methylbut-3-en-1-yl)benzene	24.5
$TEMPOClO_4$	2.0
TBA azide	24.5

Procedure: In a 3 ml quartz UV vis cell, $TEMPOClO_4$, MeCN and TEMPO was added. Then TBA azide and alkene was added together and shaken for 2 seconds before acquisition. Reaction solution concentration: 0.5 mM

Azide/ul	eq	$TEMPO^+$/ul	eq	Alkene /ul	eq	MeCN/ul
40	1	490	1	0	0	1920
40	1	490	1	40	1	1880
40	1	490	1	60	1.5	1860
40	1	490	1	80	2	1840
40	1	490	1	100	2.5	1820
40	1	490	1	120	3	1800
40	1	490	1	140	3.5	1780
40	1	490	1	240	6	1680
40	1	490	1	400	10	1520

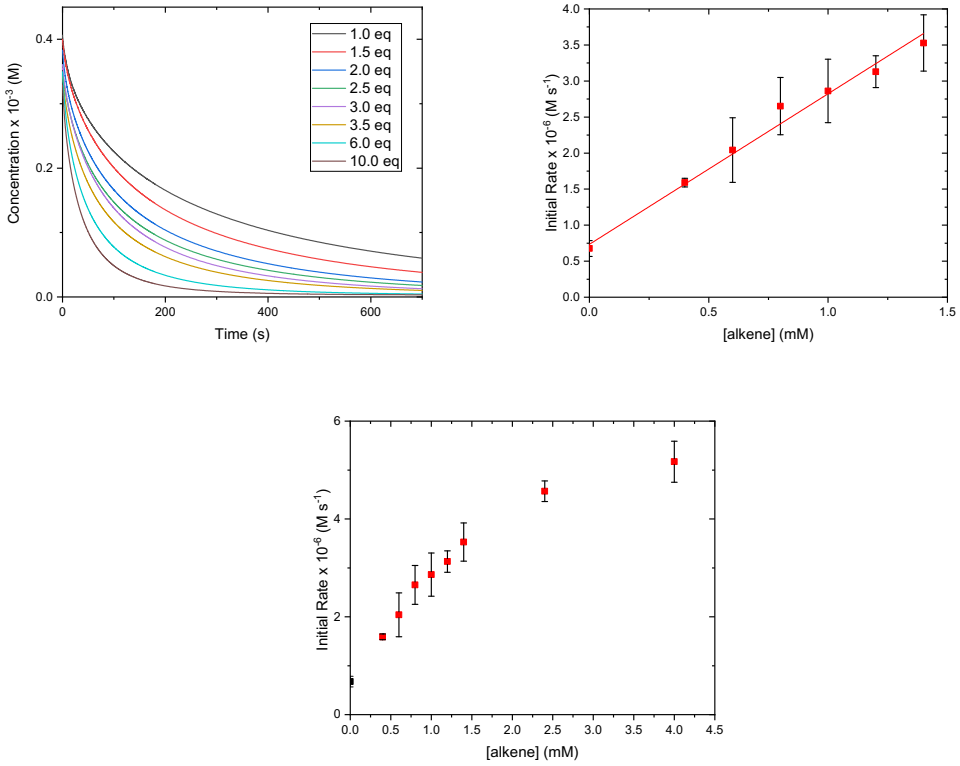


Figure S11. Rate at different conversion and equivalence of alkene. Saturation kinetics was observed beyond 3.5 eq of alkene and is consistent with the rate law predictions.

	30% conversion
eq	Rate x 10^{-6} (M s^{-1})
0	0.676
1	1.59
1.5	2.04
2	2.65
2.5	2.86
3	3.12
3.5	3.52
6	4.56
10	5.17

Rate dependence at high alkene concentration

Stock solution concentration

Compound	Concentration/ mM
$TEMPOClO_4$	2.0
TBA azide	24.5
TEMPO	24.5

Procedure: In a 3 ml quartz UV vis cell, $TEMPOClO_4$, MeCN and TEMPO was added. Then TBA azide and alkene was added together and shaken for 2 seconds before acquisition. Reaction solution concentration: 0.5 mM

Azide/ul	eq	$TEMPO^+$/ul	eq	Alkene /mg	TEMPO	eq	MeCN/ul
40	1	490	1	17.6	0	0	1920
40	1	490	1	17.6	8	0.2	1912
40	1	490	1	17.6	12	0.3	1908
40	1	490	1	17.6	16	0.4	1904
40	1	490	1	17.6	40	1	1880
40	1	490	1	17.6	80	2	1840

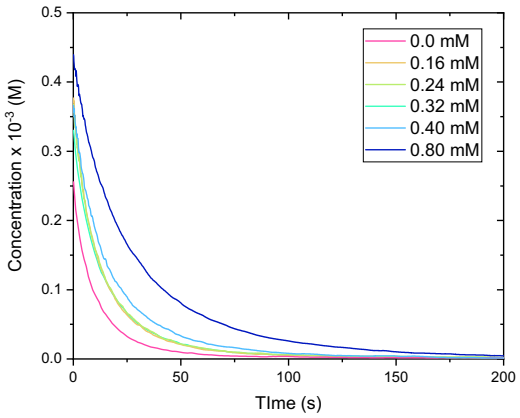


Figure S12. Rate at different concentration of exogenous TEMPO at normal alkene concentration.

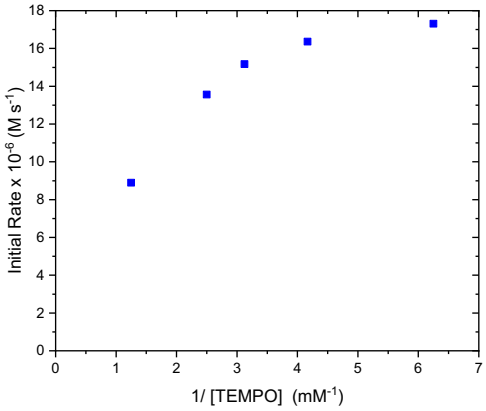


Figure S13. Initial rate at different concentration of exogenous TEMPO.

	30% conversion
eq	Rate x 10^{-6} (M s^{-1})
0	1.731
1	1.636
1.5	1.517
2	1.355
2.5	0.889

TEMPO dependence on decomposition rate study

Procedure: In a 3 ml quartz UV vis cell, $TEMPOClO_4$, MeCN and TEMPO was added. Then TBA azide and alkene was added together and shaken for 2 seconds before acquisition. Reaction solution concentration: 0.5 mM

Stock solution concentration

Compound	Concentration/ mM
TEMPO	24.5
$TEMPOClO_4$	2.0
TBA azide	24.5

$TEMPO^+$/ul	eq	TBA azide /ul	eq	TEMPO /ul	eq	MeCN/ul
490	1	40	1	8	0.2	1912
490	1	40	1	12	0.3	1908
490	1	40	1	16	0.4	1904
490	1	40	1	40	1.0	1880
490	1	40	1	80	2.0	1840

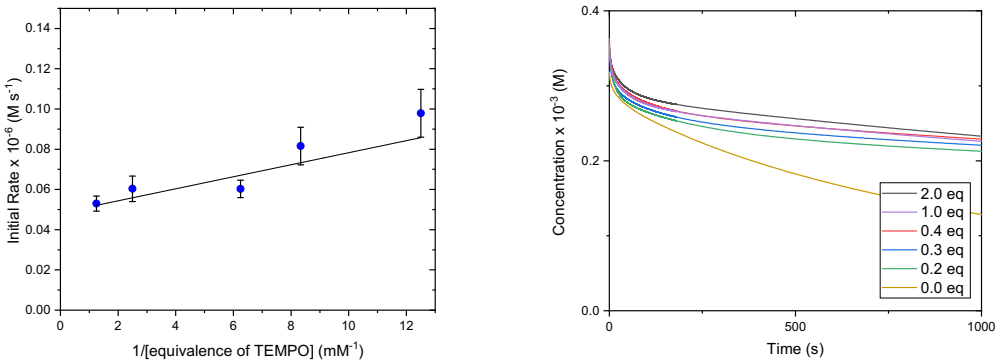


Figure S14. Rate of decomposition with respect to [TEMPO].

	30% conversion
1/eq	Rate x 10^{-6} (M s^{-1})
0.50	0.0530
1.00	0.0603
2.50	0.0603
3.33	0.0816
5.00	0.0979

ESR studies

ESR experiments was carried at X band frequency with a Brüker Elexsys E500 spectrometer. The samples were inserted in 1.6 mm i.d. (2mm o.d.) glass capillary. The spectra were recorded at room temperature in rectangular cavity 4102ST0202 at 2mW microwave power (20dB attenuation) with a 0.1G amplitude modulation. Preparation of sample: a 6.17 mM solution of $TEMPOClO_4$ was measured directly. It is reported in literature that there will always be a trace amount of TEMPO in $TEMPOClO_4$ salts[4]. The complex was formed by adding the same stock solution of $TEMPOClO_4$ to 1 mg of NaN_3 and shaken in a vial for 5 minutes. However, by adding 2 equivalent of DMPO to the complex solution, we were unable to trap the azidyl radical with the addition of DMPO.

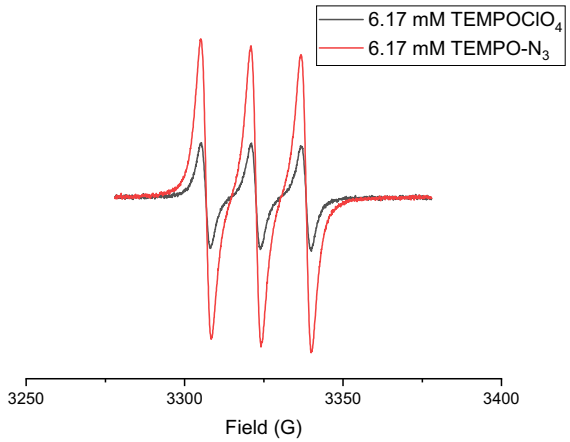


Figure S15 ESR spectrum showing TEMPOClO$_4$ in MeCN (6.17 mM). TEMPOClO4 (6.17 mM) with excess NaN$_3$. The increased in intensity of the TEMPO signal in the complex indicates that decomposition leads to TEMPO free radicals.

X-ray crystallography data

General information: Low-temperature X-ray diffraction data for (CCDC-1843443) were collected on a Rigaku XtaLAB Synergy diffractometer coupled to a RigakuHypix detector with Cu Kα radiation (λ =1.54184 Å), from a PhotonJet micro-focus X-ray source at 100 K. The diffraction images were processed and scaled using the CrysAlisPro software[5]. The structures were solved through intrinsic phasing using SHELXT[6] and refined against F2 on all data by full-matrix least squares with SHELXL[7] following established refinement strategies[8] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bound to carbon were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the Ueq value of the atoms they are linked to (1.5 times for methyl groups). Details of the data quality and a summary of the residual values of the refinements are listed in Tables S1- S2.

Table S- 2. Crystal data and structure refinement for Rjcs2.

Identification code	rjcs2_abs	
Empirical formula	C23 H30 N4 O	
Formula weight	378.51	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 12.88010(10) Å	α= 90°.

	b = 14.63750(10) Å	β= 93.5250(10)°.
	c = 11.22330(10) Å	γ = 90°.
Volume	2111.95(3) Å^3	
Z	4	
Density (calculated)	1.190 Mg/m^3	
Absorption coefficient	0.584 mm^{-1}	
F(000)	816	
Crystal size	0.136 x 0.088 x 0.069 mm^3	
Theta range for data collection	3.438 to 74.486°.	
Index ranges	-16<=h<=16, -18<=k<=17, -14<=l<=14	
Reflections collected	86822	
Independent reflections	4317 [R(int) = 0.0424]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.828	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4317 / 0 / 257	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.1041	
R indices (all data)	R1 = 0.0400, wR2 = 0.1050	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.278 and -0.237 e.Å^{-3}	

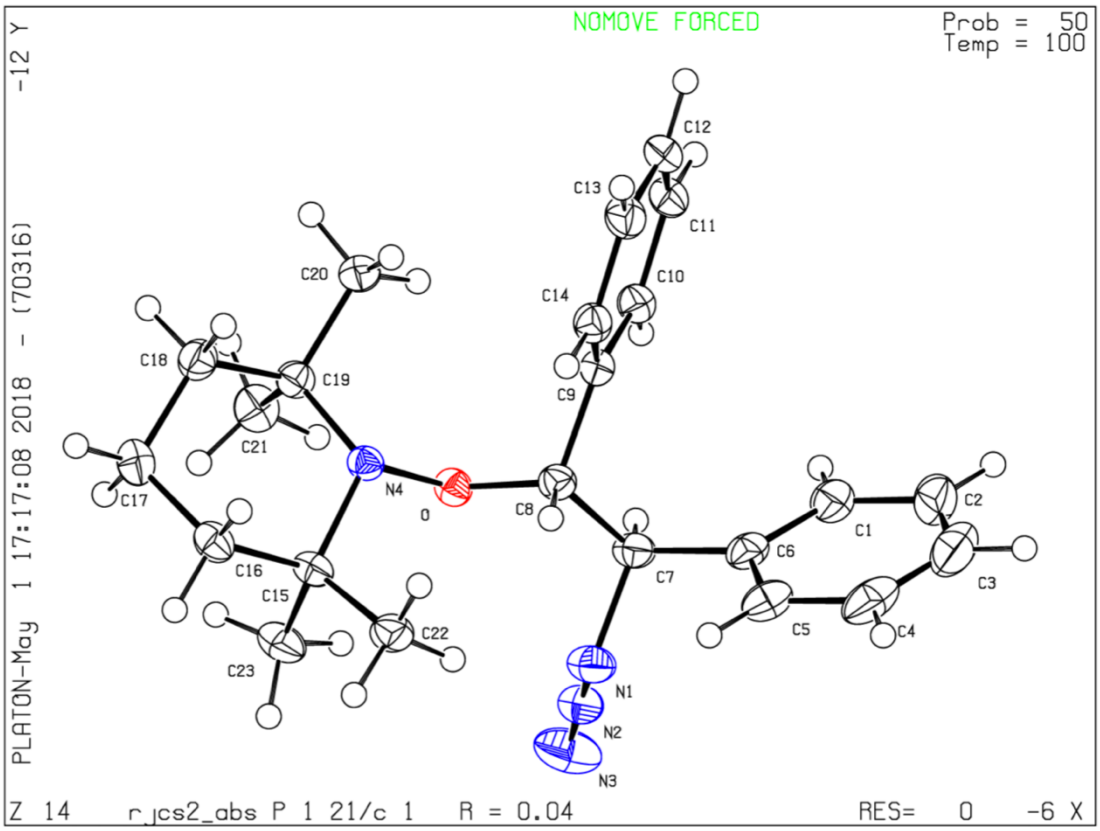


Table S- 3.Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Rjcs2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O	2278(1)	6316(1)	1979(1)	22(1)
N(1)	3994(1)	5173(1)	2347(1)	31(1)
N(2)	4124(1)	4744(1)	1419(1)	31(1)
N(3)	4230(1)	4272(1)	632(1)	49(1)
N(4)	1303(1)	6385(1)	2581(1)	20(1)
C(1)	5833(1)	7021(1)	2491(1)	34(1)
C(2)	6707(1)	7301(1)	3183(2)	46(1)
C(3)	6848(1)	7028(1)	4366(2)	50(1)
C(4)	6119(1)	6478(1)	4860(1)	44(1)
C(5)	5239(1)	6208(1)	4175(1)	33(1)
C(6)	5088(1)	6478(1)	2986(1)	27(1)
C(7)	4115(1)	6189(1)	2256(1)	25(1)
C(8)	3144(1)	6634(1)	2744(1)	22(1)
C(9)	3220(1)	7664(1)	2812(1)	22(1)
C(10)	3554(1)	8192(1)	1873(1)	24(1)

C(11)	3572(1)	9139(1)	1958(1)	28(1)
C(12)	3266(1)	9571(1)	2980(1)	30(1)
C(13)	2941(1)	9053(1)	3920(1)	29(1)
C(14)	2918(1)	8104(1)	3834(1)	25(1)
C(15)	1027(1)	5440(1)	2977(1)	23(1)
C(16)	-52(1)	5502(1)	3483(1)	26(1)
C(17)	-881(1)	5925(1)	2636(1)	29(1)
C(18)	-512(1)	6868(1)	2289(1)	27(1)
C(19)	543(1)	6858(1)	1720(1)	23(1)
C(20)	893(1)	7850(1)	1596(1)	28(1)
C(21)	422(1)	6438(1)	463(1)	31(1)
C(22)	1793(1)	5161(1)	4016(1)	28(1)
C(23)	1051(1)	4692(1)	2019(1)	31(1)

Table S- 4. Bond lengths [Å] and angles [°] for Rjcs2.

O-N(4)	1.4659(11)
O-C(8)	1.4418(12)
N(1)-N(2)	1.2364(14)
N(1)-C(7)	1.4988(13)
N(2)-N(3)	1.1362(15)
N(4)-C(15)	1.5031(12)
N(4)-C(19)	1.5014(13)
C(1)-H(1)	0.9500
C(1)-C(2)	1.3891(19)
C(1)-C(6)	1.3883(16)
C(2)-H(2)	0.9500
C(2)-C(3)	1.388(2)
C(3)-H(3)	0.9500
C(3)-C(4)	1.379(2)
C(4)-H(4)	0.9500
C(4)-C(5)	1.3876(19)
C(5)-H(5)	0.9500
C(5)-C(6)	1.3940(17)
C(6)-C(7)	1.5151(16)
C(7)-H(7)	1.0000
C(7)-C(8)	1.5402(14)
C(8)-H(8)	1.0000
C(8)-C(9)	1.5127(14)
C(9)-C(10)	1.3958(14)
C(9)-C(14)	1.3916(14)
C(10)-H(10)	0.9500
C(10)-C(11)	1.3896(15)
C(11)-H(11)	0.9500
C(11)-C(12)	1.3877(16)
C(12)-H(12)	0.9500
C(12)-C(13)	1.3851(16)
C(13)-H(13)	0.9500
C(13)-C(14)	1.3920(16)
C(14)-H(14)	0.9500
C(15)-C(16)	1.5371(14)
C(15)-C(22)	1.5352(15)

C(15)-C(23)	1.5351(14)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(16)-C(17)	1.5174(16)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(17)-C(18)	1.5182(15)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(18)-C(19)	1.5362(14)
C(19)-C(20)	1.5292(14)
C(19)-C(21)	1.5382(14)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800

C(8)-O-N(4)	110.91(7)
N(2)-N(1)-C(7)	115.27(9)
N(3)-N(2)-N(1)	173.14(12)
O-N(4)-C(15)	107.33(7)
O-N(4)-C(19)	106.21(7)
C(19)-N(4)-C(15)	117.22(8)
C(2)-C(1)-H(1)	120.0
C(6)-C(1)-H(1)	120.0
C(6)-C(1)-C(2)	120.08(13)
C(1)-C(2)-H(2)	119.9
C(3)-C(2)-C(1)	120.25(14)
C(3)-C(2)-H(2)	119.9
C(2)-C(3)-H(3)	120.0

C(4)-C(3)-C(2)	120.01(13)
C(4)-C(3)-H(3)	120.0
C(3)-C(4)-H(4)	120.1
C(3)-C(4)-C(5)	119.85(13)
C(5)-C(4)-H(4)	120.1
C(4)-C(5)-H(5)	119.7
C(4)-C(5)-C(6)	120.66(13)
C(6)-C(5)-H(5)	119.7
C(1)-C(6)-C(5)	119.14(11)
C(1)-C(6)-C(7)	120.83(10)
C(5)-C(6)-C(7)	120.03(10)
N(1)-C(7)-C(6)	109.05(9)
N(1)-C(7)-H(7)	109.8
N(1)-C(7)-C(8)	107.74(8)
C(6)-C(7)-H(7)	109.8
C(6)-C(7)-C(8)	110.59(9)
C(8)-C(7)-H(7)	109.8
O-C(8)-C(7)	105.51(8)
O-C(8)-H(8)	108.3
O-C(8)-C(9)	113.35(8)
C(7)-C(8)-H(8)	108.3
C(9)-C(8)-C(7)	112.84(8)
C(9)-C(8)-H(8)	108.3
C(10)-C(9)-C(8)	122.37(9)
C(14)-C(9)-C(8)	118.91(9)
C(14)-C(9)-C(10)	118.69(10)
C(9)-C(10)-H(10)	119.8
C(11)-C(10)-C(9)	120.34(10)
C(11)-C(10)-H(10)	119.8
C(10)-C(11)-H(11)	119.8
C(12)-C(11)-C(10)	120.47(10)
C(12)-C(11)-H(11)	119.8
C(11)-C(12)-H(12)	120.2
C(13)-C(12)-C(11)	119.64(10)
C(13)-C(12)-H(12)	120.2
C(12)-C(13)-H(13)	120.0
C(12)-C(13)-C(14)	119.93(10)
C(14)-C(13)-H(13)	120.0

C(9)-C(14)-C(13)	120.93(10)
C(9)-C(14)-H(14)	119.5
C(13)-C(14)-H(14)	119.5
N(4)-C(15)-C(16)	106.87(8)
N(4)-C(15)-C(22)	108.42(8)
N(4)-C(15)-C(23)	115.70(8)
C(22)-C(15)-C(16)	106.77(8)
C(23)-C(15)-C(16)	111.04(9)
C(23)-C(15)-C(22)	107.66(9)
C(15)-C(16)-H(16A)	108.7
C(15)-C(16)-H(16B)	108.7
H(16A)-C(16)-H(16B)	107.6
C(17)-C(16)-C(15)	114.19(9)
C(17)-C(16)-H(16A)	108.7
C(17)-C(16)-H(16B)	108.7
C(16)-C(17)-H(17A)	110.1
C(16)-C(17)-H(17B)	110.1
C(16)-C(17)-C(18)	108.22(9)
H(17A)-C(17)-H(17B)	108.4
C(18)-C(17)-H(17A)	110.1
C(18)-C(17)-H(17B)	110.1
C(17)-C(18)-H(18A)	108.9
C(17)-C(18)-H(18B)	108.9
C(17)-C(18)-C(19)	113.31(9)
H(18A)-C(18)-H(18B)	107.7
C(19)-C(18)-H(18A)	108.9
C(19)-C(18)-H(18B)	108.9
N(4)-C(19)-C(18)	107.24(8)
N(4)-C(19)-C(20)	108.15(8)
N(4)-C(19)-C(21)	115.53(9)
C(18)-C(19)-C(21)	110.07(9)
C(20)-C(19)-C(18)	107.54(9)
C(20)-C(19)-C(21)	108.04(9)
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20C)	109.5

H(20B)-C(20)-H(20C)	109.5
C(19)-C(21)-H(21A)	109.5
C(19)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(15)-C(22)-H(22A)	109.5
C(15)-C(22)-H(22B)	109.5
C(15)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(15)-C(23)-H(23A)	109.5
C(15)-C(23)-H(23B)	109.5
C(15)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S- 5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Rjcs2. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O	23(1)	22(1)	22(1)	0(1)	5(1)	-1(1)
N(1)	35(1)	22(1)	36(1)	2(1)	11(1)	3(1)
N(2)	34(1)	24(1)	35(1)	1(1)	1(1)	1(1)
N(3)	79(1)	28(1)	39(1)	-3(1)	2(1)	-1(1)
N(4)	21(1)	19(1)	21(1)	1(1)	4(1)	-1(1)
C(1)	27(1)	31(1)	46(1)	0(1)	8(1)	4(1)
C(2)	27(1)	40(1)	72(1)	-9(1)	5(1)	2(1)
C(3)	34(1)	49(1)	66(1)	-22(1)	-13(1)	13(1)
C(4)	45(1)	44(1)	41(1)	-12(1)	-8(1)	23(1)
C(5)	35(1)	32(1)	34(1)	-2(1)	4(1)	12(1)
C(6)	25(1)	24(1)	33(1)	-2(1)	5(1)	8(1)
C(7)	27(1)	20(1)	28(1)	3(1)	7(1)	2(1)
C(8)	23(1)	21(1)	23(1)	2(1)	3(1)	0(1)
C(9)	18(1)	22(1)	25(1)	1(1)	0(1)	0(1)
C(10)	24(1)	24(1)	26(1)	1(1)	3(1)	-1(1)
C(11)	26(1)	25(1)	33(1)	5(1)	2(1)	-4(1)
C(12)	26(1)	20(1)	43(1)	-2(1)	0(1)	-3(1)
C(13)	27(1)	28(1)	31(1)	-7(1)	2(1)	-1(1)
C(14)	24(1)	26(1)	25(1)	1(1)	1(1)	-1(1)
C(15)	27(1)	18(1)	24(1)	1(1)	4(1)	-2(1)
C(16)	28(1)	25(1)	26(1)	1(1)	6(1)	-5(1)
C(17)	24(1)	32(1)	31(1)	-2(1)	3(1)	-5(1)
C(18)	24(1)	28(1)	28(1)	0(1)	-1(1)	1(1)
C(19)	25(1)	22(1)	21(1)	1(1)	-1(1)	-1(1)
C(20)	28(1)	23(1)	32(1)	6(1)	-3(1)	1(1)
C(21)	35(1)	35(1)	21(1)	0(1)	-1(1)	-3(1)
C(22)	30(1)	25(1)	30(1)	8(1)	5(1)	0(1)
C(23)	40(1)	21(1)	34(1)	-4(1)	9(1)	-4(1)

Table S- 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Rjcs2.

	x	y	z	U(eq)
H(1)	5745	7202	1678	41
H(2)	7211	7680	2844	55
H(3)	7447	7220	4836	60
H(4)	6219	6285	5667	53
H(5)	4734	5834	4520	40
H(7)	4172	6368	1402	30
H(8)	3062	6393	3567	27
H(10)	3769	7902	1172	29
H(11)	3795	9493	1312	33
H(12)	3280	10219	3034	35
H(13)	2733	9345	4623	35
H(14)	2692	7753	4481	30
H(16A)	-279	4880	3697	31
H(16B)	6	5868	4226	31
H(17A)	-1546	5973	3030	35
H(17B)	-996	5539	1915	35
H(18A)	-457	7259	3010	32
H(18B)	-1039	7144	1719	32
H(20A)	1038	8114	2391	42
H(20B)	340	8200	1167	42
H(20C)	1524	7870	1152	42
H(21A)	1111	6300	184	46
H(21B)	63	6872	-84	46
H(21C)	15	5873	490	46
H(22A)	2478	5045	3713	42
H(22B)	1542	4606	4392	42
H(22C)	1848	5656	4605	42
H(23A)	429	4742	1474	47
H(23B)	1065	4091	2402	47
H(23C)	1673	4768	1569	47

Computational Studies

General information: All DFT calculations were run using Gaussian 09[9] using default convergance criteria. Avogadro[10] was used to analyse formatted checkpoint files for predicted UV-Vis spectra to identify and visualize the orbitals involved in predicted transitions. Chimera[11] was used to produce images of these orbitals. Gaussview was used to generate cube files from the associated formatted checkpoint files, and to create images of electrostatic potential surfaces. CYLView[12] was used to create images of structures where no surface is applied. For specific details regarding computational methods associated with each portion of this study, see the associated subsection.

Identification of possible charge transfer complex structures

All calculations consisted of a geometry optimization followed by a frequency calculation. All energies reported are ground state energies corrected for zero point energy (E+ZPE). Initially, a broad structural survey was conducted using an unrestricted B3LYP hybrid functional[13] and the 6-31+G* basis set.[14] The 4 lowest energy structures from this survey (Figure 6 of the main text) were then optimized using the same functional, and a higher order basis set (def2TZVP)[15] as well as a polarizable continuum model (PCM) solvent model[16], using acetonitrile as the solvent. As part of this series, the proton, sodium, and lithium adduct of the minimum energy [3 + 2] charge transfer complex were calculated as well. Results for the 4 lowest energy structures were identical to the lower order basis set in terms of energetic ordering (Table S- 7), and structural changes were observed to be minimal. A further screen of the 4 structures noted above was conducted using a series of functionals, basis sets, and solvent models, [(UB3LYP, 6-311+G**, and a conductor-like polarizable continuum model (CPCM)[13] = acetonitrile), (UB3LYP, cc-pvtz[17], PCM=acetonitrile), (M062X[18], def2TZVP, PCM=acetonitrile), (ωB97X-D,[19] def2TZVP, PCM=acetonitrile)], all of which provided structure I4 as the lowest energy structure, generally with minimal structural deviation observed . The only notable differences observed were in structure I2 using both M062X and ωB97X-D, wherein the azide rotated to associate with the hydrogen on a TEMPO methyl group, resulting in notably higher energy (Table S- 7). All structures were observed to be true local minima (having no imaginary frequencies) except for the sodium adduct calculation, for which a true local minimum could not be found.

Functional / basis set / solvent model	Structure	UB3LYP/ 6-31+G*/ N/A	UB3LYP/ def2TZVP/ pcm	UB3LYP/ 6-311+g**/ cpcm	UB3LYP/ cc-pvtz/ pcm	M06-2X/ def2TZVP/ pcm	ωB97X-D/ def2TZVP/ pcm
E+ZPE (hartree)	**I4**	-647.62278	-647.864462	-647.799207	-647.849676	-647.572106	-647.655007
	I1	-647.608059	-647.854386	-647.789352	-647.838675	-647.56111	-647.645463
	I2	-647.614835	-647.86015	-647.795115	-647.844057	-647.55704	-647.643779
	I3	-647.618235	-647.859516	-647.794259	-647.844692	-647.566037	-647.6499
Erel (hartree)	**I4**	0	0	0	0	0	0
	I1	0.014721	0.010076	0.009855	0.011001	0.010996	0.009544
	I2	0.007945	0.004312	0.004092	0.005619	0.015066	0.011228
	I3	0.004545	0.004946	0.004948	0.004984	0.006069	0.005107
Erel (kcal/mol)	**I4**	0	0	0	0	0	0
	I1	9.237559989	6.322780684	6.184101195	6.903226509	6.900088964	5.988945896
	I2	4.985559005	2.705818808	2.567766828	3.525973071	9.454050594	7.045671052
	I3	2.852028405	3.103659514	3.104914532	3.127504856	3.808352121	3.204688463

Table S- 7. Summary of calculated energies towards study of possible charge complexes.

Prediction of UV-Vis spectra

UV-Vis spectra were predicted for the output structures of the UB3LYP, def2TZVP, pcm=acetonitrile series of adducts described above, including the sodiated and protiated adducts. Each of these structures was subjected to a TD-DFT[20] calculation using the CAM-B3LYP hybrid functional with long range corrections[21], searching for the ten lowest energy excited states, and using the def2TZVP basis set and a PCM solvent model (acetonitrile). Results are presented below in Figure S13. It is noted that calculated extinction coefficients are estimated by Gaussian based on calculated oscillator strengths, but have been used in comparison with experimental UV-vis data.

Species	λ max, true (nm)	λ max, calc (nm)	ε, true (1/M*cm)	ε, calc (1/M*cm)
TEMPO	446	439	2	8.1
TEMPO+	455	466	1	4.1
I1		607		5500
I2		455		15500
I3		331		15300
I4	380	**350**	5174	**13100**
I4 (H+)		305		8.1
I4 (Li+)		318		14800
I4 (Na+)		330		14200
			values from ref. 28	

Table S- 8. Summary or predicted UV-Vis absorbance maxima and estimated molar extinction coefficients.

Prediction of Nitrogen NMR spectra

Nitrogen NMR spectra were predicted using a method similar to that developed by Chapyshev et. al.[22] All structures were optimized using an unrestricted B3LYP hybrid functional using 6-311+G** as the basis set and a CPCM solvent model using the same solvent as the experimental system. Optimized structures were then subjected to a Gauge Independent Atomic Orbitals (GIAO) calculation[23] using a TPSSh hybrid functional[24] and 6-311+G** as the basis. The isotropic nuclear magnetic shielding tensors were recorded. Both ammonia (ppm_{true} = 0ppm) and nitromethane (ppm_{true} = 347.2ppm) have known 15N chemical shifts and were calculated to serve as references associating calculated nuclear magnetic shielding tensors to chemical shifts using water in the CPCM solvent model. Calculated nuclear magnetic shielding tensors of analytes were subtracted from that predicted for ammonia and the difference was multiplied by the ratio ($ppm_{true,MeNO2}$ - $ppm_{true,NH3}$)/-(Shielding $tensor_{MeNO2}$ – Shielding $tensor_{NH3}$) to determine the predicted chemical shift.

Species	Isotropic shielding tensor (calc'd)		calculated δ
NH3 (water)	261.24	0 (known)	N/A
MeNO2 (water)	-140.88	347.2 (known)	N/A
N3- (water)	159.12	99.3 (measured)	88.1728439
adduct, N proximal to N (Acetonitrile)	-34.97	244.6 (measured)	255.75478
adduct, N proximal to O (Acetonitrile)	-9.64	244.6 (measured)	233.884253

Table S- 9. Summary of calculated magnetic shielding tensors and chemical shifts derived therefrom. Ammonia and nitromethane serve as references of known chemical shift.

Prediction of ^{13}C Kinetic Isotope Effects

The carbon-centered radical intermediate derived from azidyl addition to 4-*t*Bu-styrene was optimized using an unrestricted B3LYP hybrid functional, def2TZVP as the basis set, and a PCM solvent model (acetonitrile). This optimized geometry was subjected to an optimization modifying reduntant internal coordinates lengthening the C-N bond (0.1 angstroms per iteration, 20 iterations) using the same functional, basis set, and solvent model. The highest energy iteration was then used as the input geometry for a saddle point calculation again using the same functional, basis set, and solvent model. Output files were analysed to ensure only one imaginary frequency was present, and the vibrational mode reflected was that of a C-N bond forming. Additional saddle point calculations under identical conditions were conducted on C-C-N-N dihedral rotamers of the initially identified transition state structure to identify

the lowest energy transition state. The starting material (4-^{t}Bu-styrene) was optimized using the same functional, basis set, and solvent model.
The lowest energy transition state structure was used in the prediction of ^{13}C KIEs, which were calculated based on the Bigeleisen equation[25] via IsoEFF98.[26]

Reaction Coordinate Diagram

All structures were calculated using an unrestricted B3LYP hybrid functional, def2TZVP as the basis set, and a PCM solvent model (acetonitrile). All calculations consisted of an optimization and frequency calculation. All energies reported in the main text are a summation of the E+ZPE for each reaction coordinate (Table XX). The energy of each treating any non-coordinated species as existing at infinite distance. Structures calculated consist of $TEMPO^+$, TEMPO, N_3^-, $\cdot N_3$, 4-phenyl-2-methylbut-1-ene and the carbon centered radical derived from azidyl addition thereto, The transition state of that azidyl addition, and the final product.

Universal Species	
Species	**E+ZPE (Hartree)**
tempo+	-483.455174
tempo	-483.647628
n3-	-164.388385
n3	-164.19992
I4	-647.864462

4-tbutylstyrene	
substrate	-466.835076
preTS complex	-631.037759
TS	-631.035783
intermediate	-631.05199
product	-1114.721328

4-phenyl-2-methyl-1-butene	
substrate	-427.536201
preTS complex	-591.73718
TS	-591.732726
intermediate	-591.741276
product	-1075.414762

4-tbutylstyrene	E+ZPE (Hartree)	Erel (Hartree), **product**	Erel (kcal/mol), **product**	Erel (kcal/mol), **I4**
TEMPO+ / N3- / alkene	-1114.67864	0.042693	26.79024174	13.11682063
I4 / alkene	-1114.69954	0.02179	13.67342111	0
TEMPO/ N3 / alkene	-1114.68262	0.038704	24.28710834	10.61368723
pre-TS complex / TEMPO	-1114.68539	0.035941	22.55330097	8.879879859
TS / TEMPO	-1114.68341	0.037917	23.79325875	10.11983764
N3 intermediate / TEMPO	-1114.69962	0.02171	13.62322039	-0.05020072
Product	-1114.72133	0	0	-13.67342111

4-phenyl-2-methyl-1-butene	E+ZPE (Hartree)	Erel (Hartree), **Product**	Erel (kcal/mol), **product**	Erel (kcal/mol), **I4**
TEMPO+ / N3- / alkene	-1075.37976	0.035002	21.96407002	13.11682063
I4 / alkene	-1075.40066	0.014099	8.847249391	0
TEMPO/ N3 / alkene	-1075.38375	0.031013	19.46093662	10.61368723
pre-TS complex / TEMPO	-1075.38481	0.029954	18.79640459	9.949155195
TS / TEMPO	-1075.38035	0.034408	21.59132967	12.74408028
N3 intermediate / TEMPO	-1075.3889	0.025858	16.22612772	7.378878331
Product	-1075.41476	0	0	-8.847249391

Table S- 10. Summary of raw data and calculated relative energies towards reaction coordinate diagram. All energies are reported in terms of E+ZPE.

The formation of the charge-transfer complex **I** is predicted to be downhill by 13.1 kcal/mol, although this value is likely exaggerated due to the inherent limitations of the polarizable continuum solvent models in predicting the energy of ionic species.[27] The decomposition of **I** into TEMPO and $N_3\cdot$ is 10.6 kcal/mol uphill. The $N_3\cdot$ addition step has an activation barrier of 1.2 kcal/mol with alkene **1a** and 2.8 kcal/mol with **1l**. The overall reaction is thermodynamically favorable by –26.8 kcal/mol with **1a** and –21.5 kcal/mol with **1l**. Since this reaction is not a unimolecular reaction, in order to obtain meaningful TS energy for the azidyl-alkene addition, we also computed the energy of the pre-TS complex of this step.

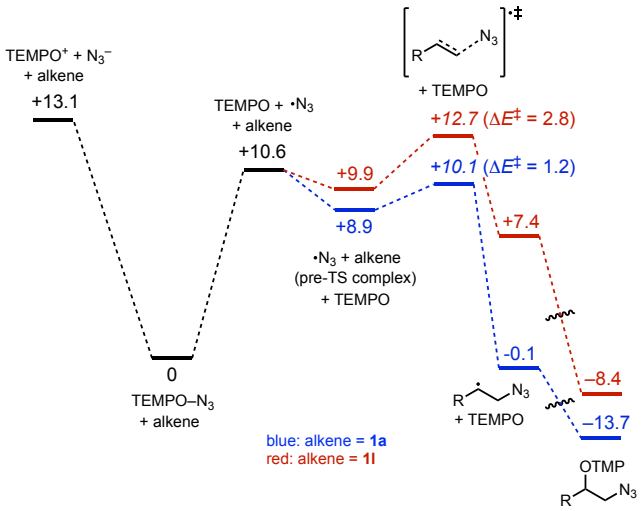
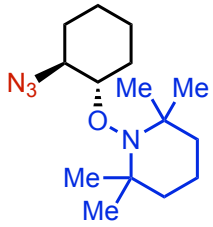
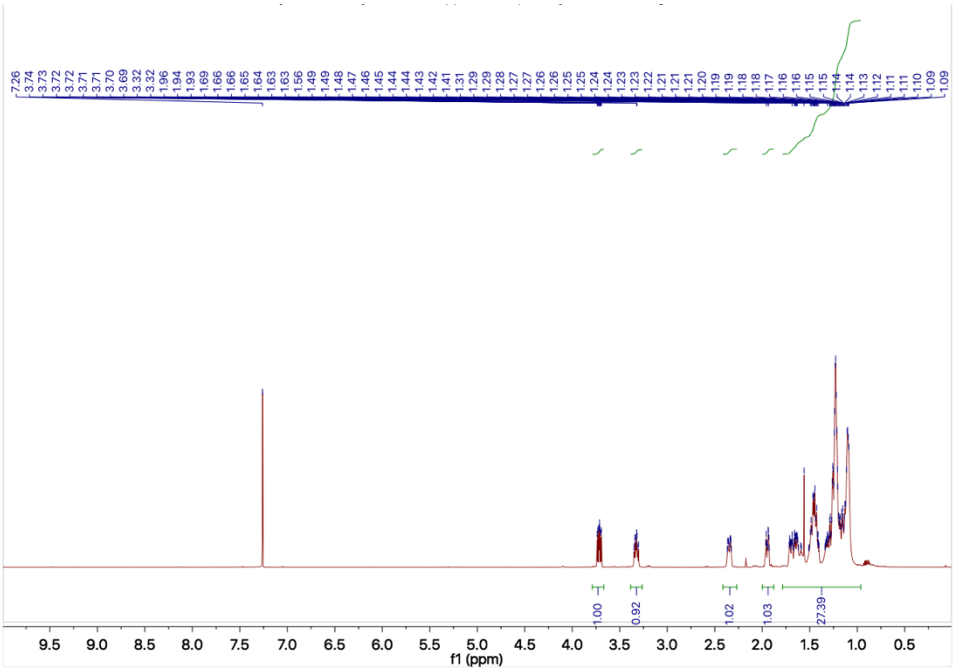


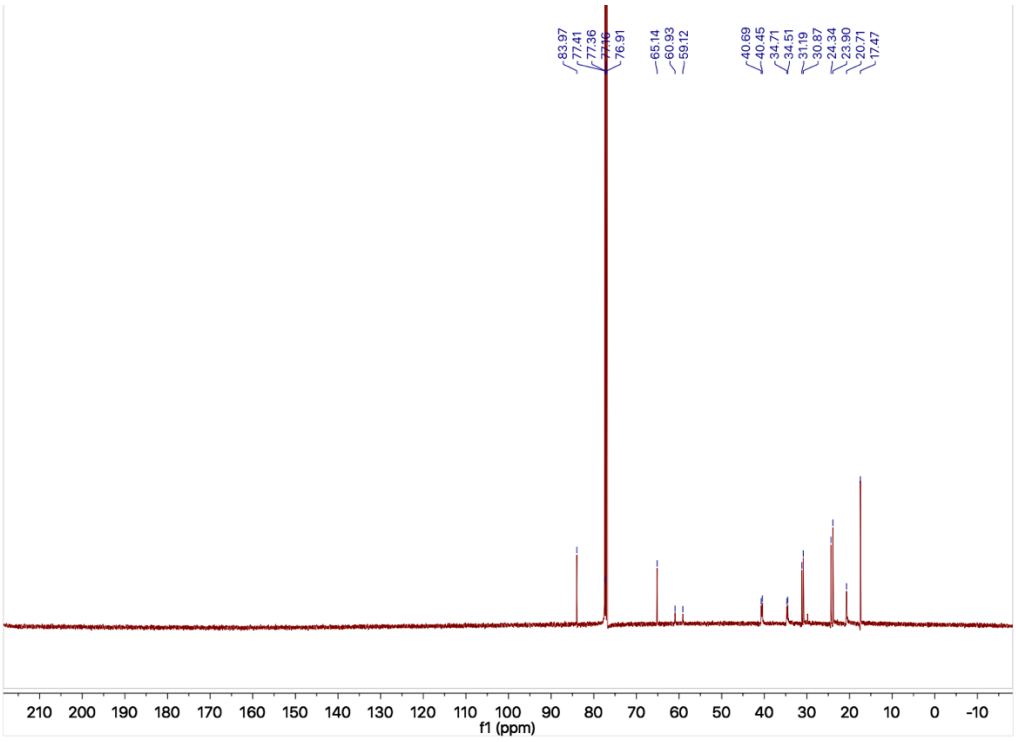
Figure S16. Computed energy diagram. All energies are reported in terms of E+ZPE. Italicized energy values are transition state energies. Owing to the limited capability of the applied DFT method to accurately predict the energies of ions and transition states of open-shell pathways, the computed energy diagram should be used as a qualitative reference.

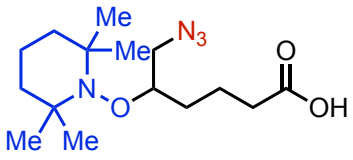
NMR spectra



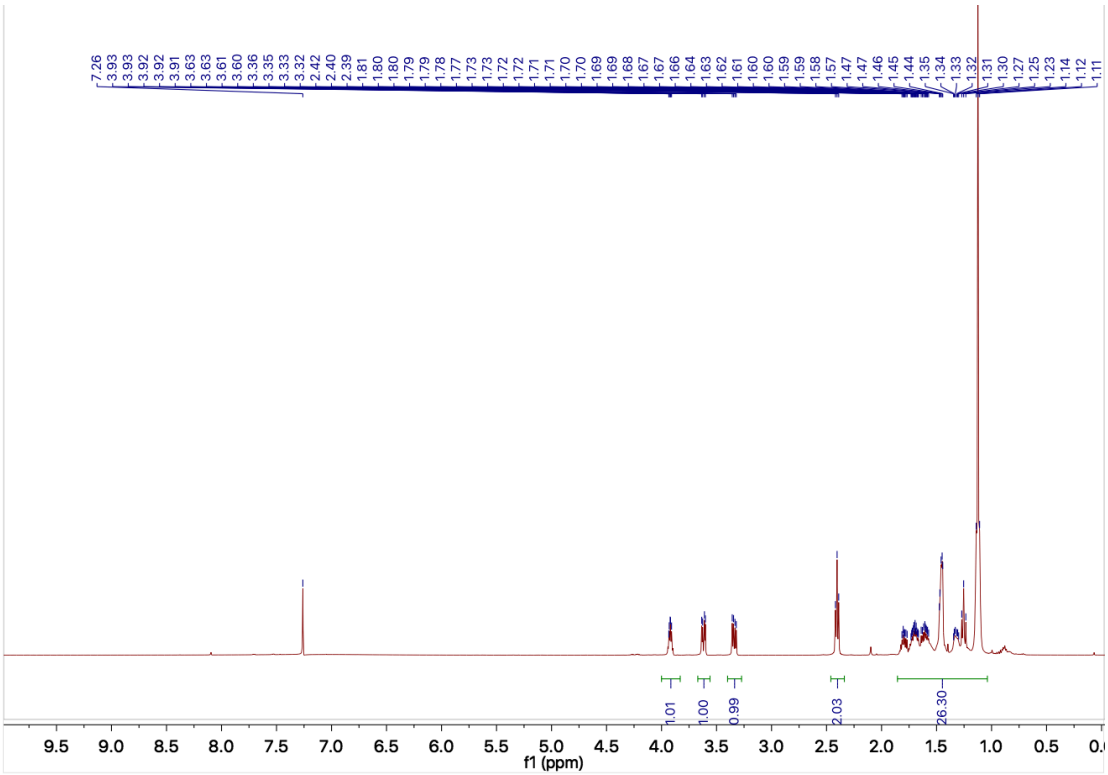
(**2n**)

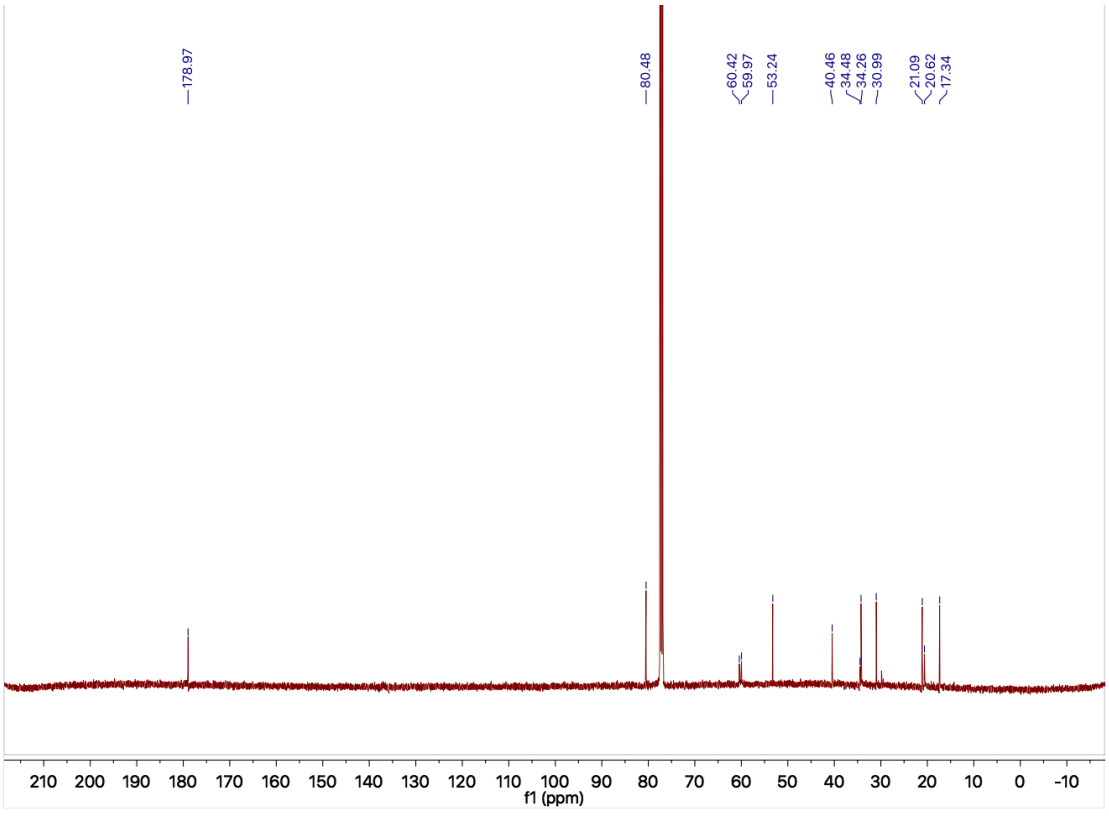


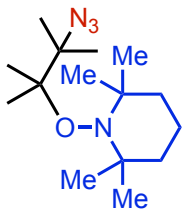



Me
N3
Me
O
N
O
OH
Me
Me

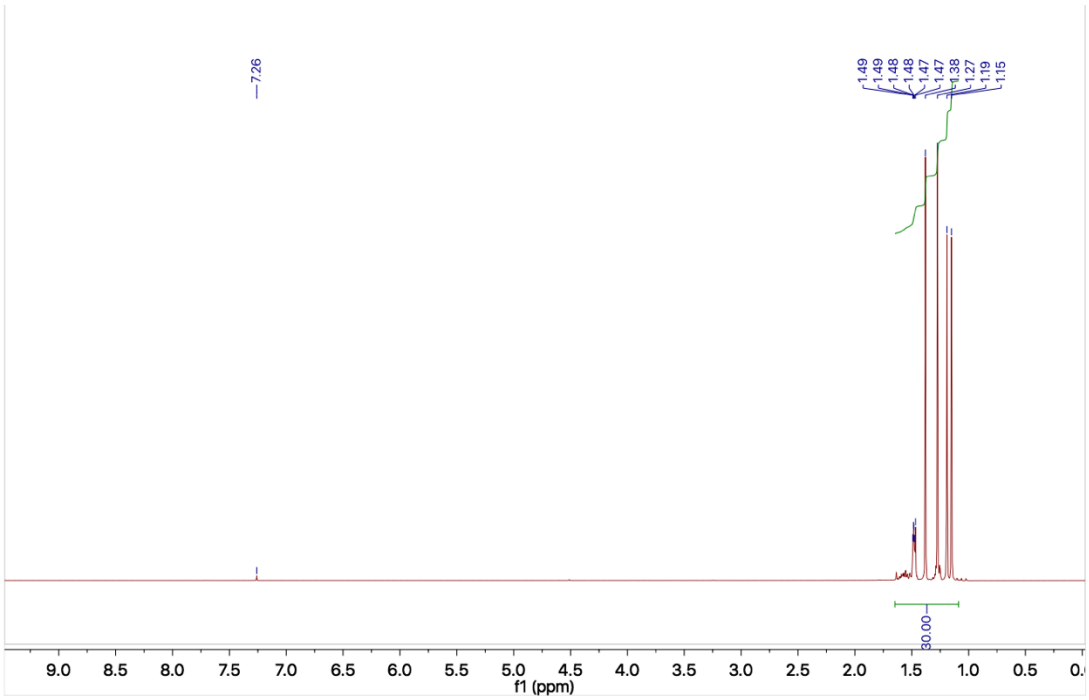
(2g)

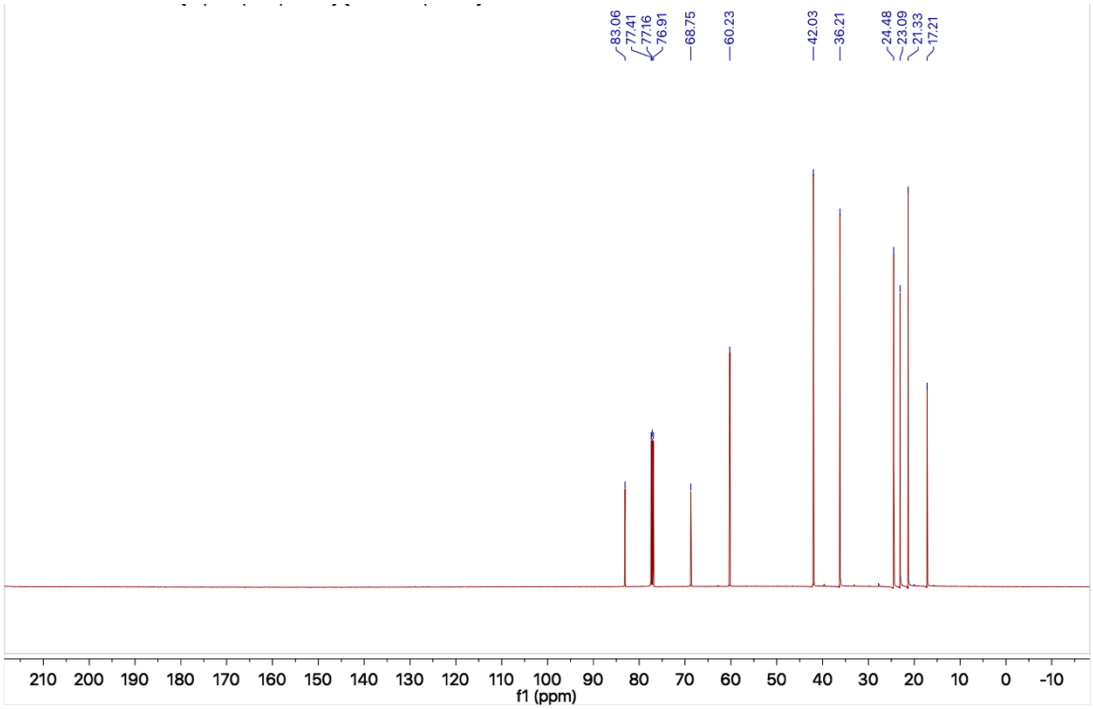

7.26
3.93
3.92
3.91
3.63
3.61
3.60
3.36
3.35
3.33
3.32
2.42
2.40
2.39
1.81
1.80
1.79
1.78
1.77
1.73
1.72
1.71
1.70
1.69
1.68
1.67
1.66
1.64
1.63
1.62
1.61
1.60
1.59
1.58
1.57
1.47
1.46
1.45
1.44
1.35
1.34
1.33
1.32
1.31
1.30
1.27
1.25
1.23
1.14
1.12
1.11
1.01
1.00
0.99
2.03
26.30
9.5
9.0
8.5
8.0
7.5
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
f1 (ppm)

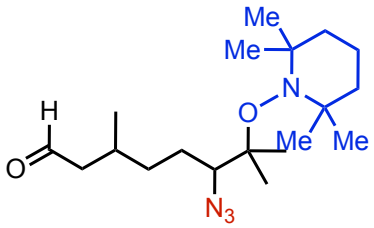

178.97
80.48
60.42
59.97
53.24
40.46
34.48
34.26
30.99
21.09
20.62
17.34
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


N3
Me
Me
O
N
Me
Me

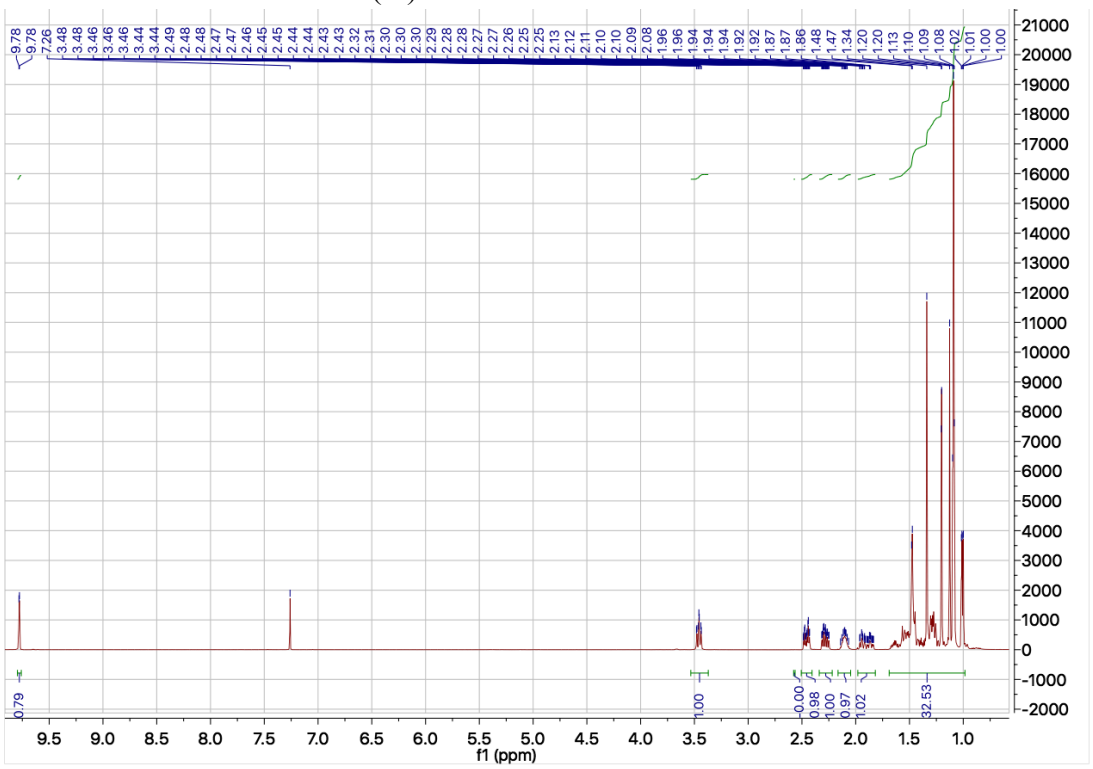
(**2f**)

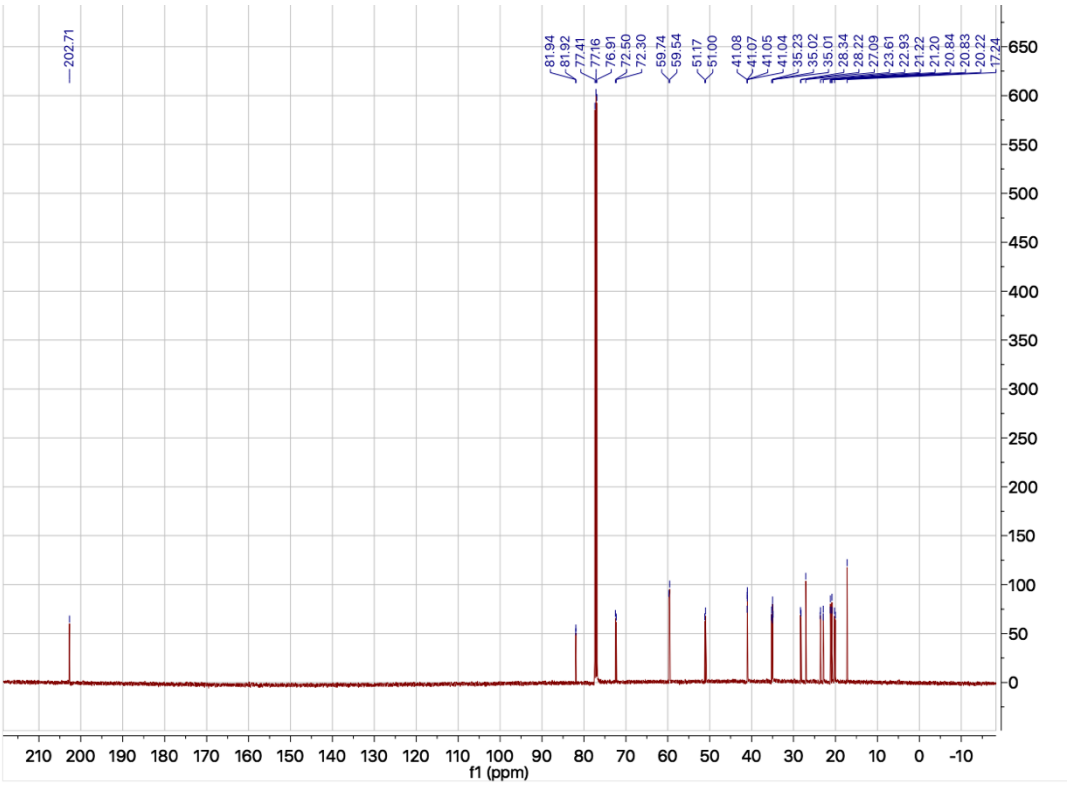

7.26
1.49
1.49
1.48
1.48
1.47
1.47
1.38
1.27
1.19
1.15
30.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

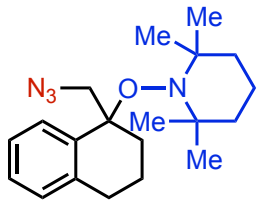

83.06
77.41
77.16
76.91
68.75
60.23
42.03
36.21
24.48
23.09
21.33
17.21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



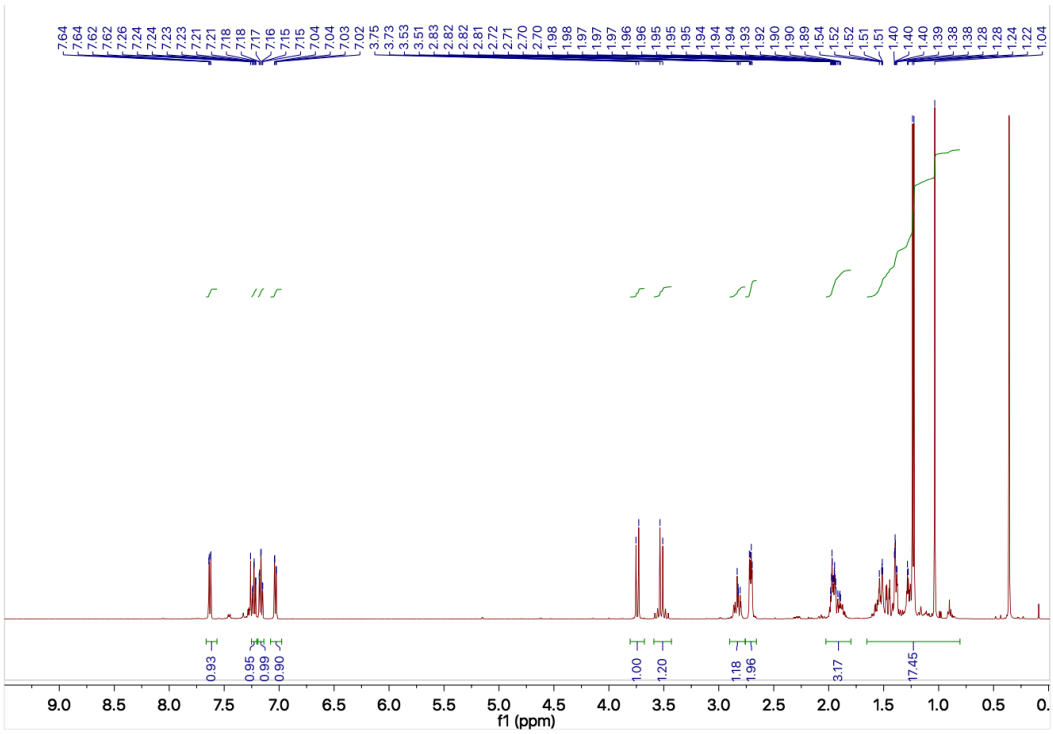
(**2i**)

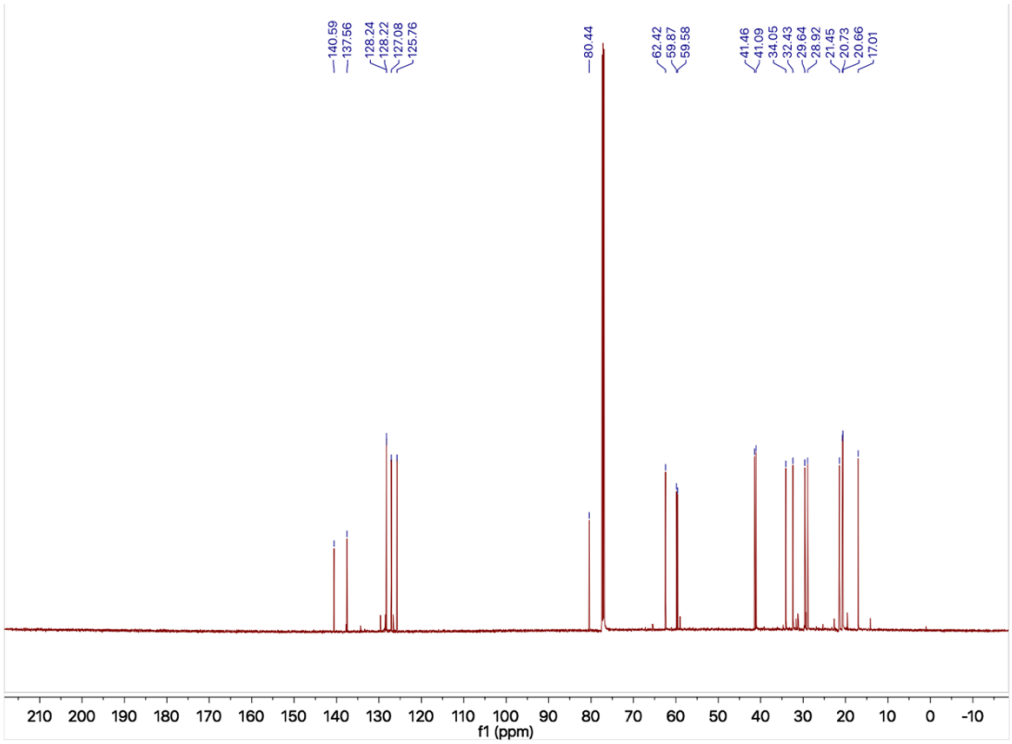


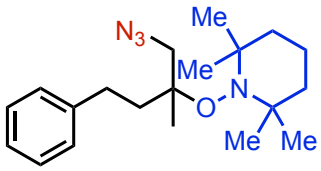



Me
Me
N3
O
N
Me
Me

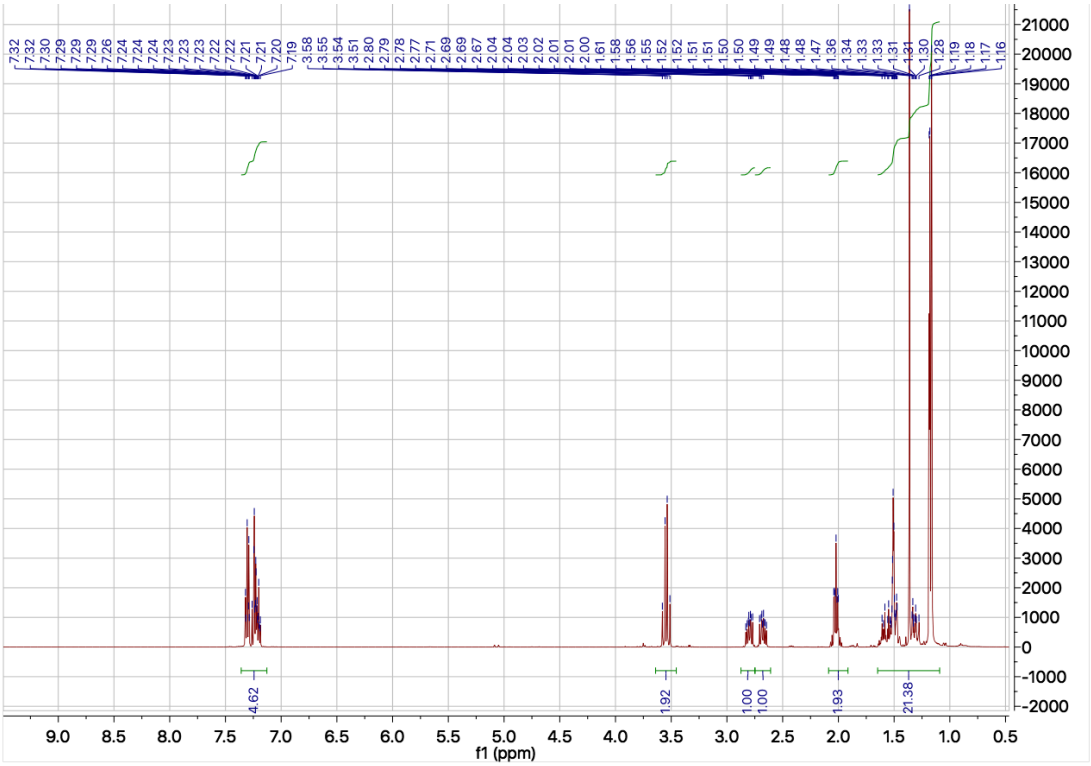
(**2r**)

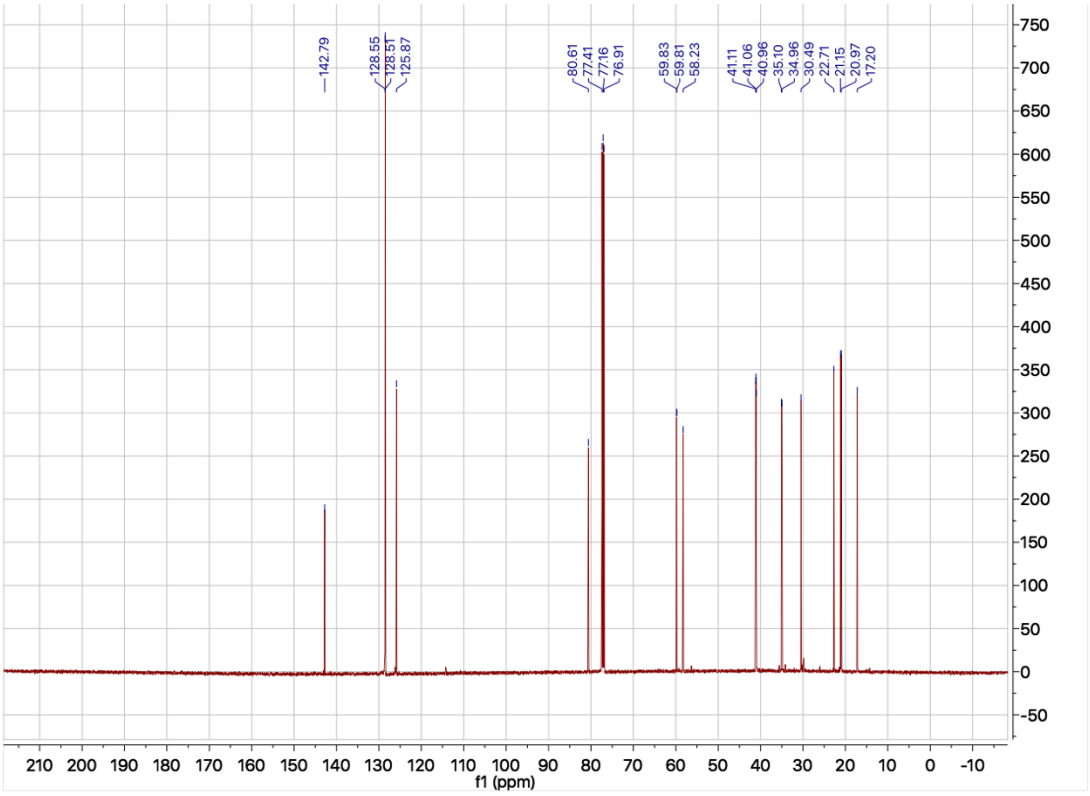

7.64 7.64 7.62 7.62 7.26 7.24 7.24 7.23 7.23 7.21 7.21 7.18 7.18 7.17 7.16 7.15 7.15 7.04 7.04 7.03 7.02
3.75 3.73 3.53 3.51 2.83 2.82 2.82 2.81 2.72 2.71 2.70 2.70 1.98 1.98 1.97 1.97 1.97 1.96 1.96 1.95 1.95 1.95 1.94 1.94 1.94 1.93 1.92 1.90 1.90 1.89 1.54 1.52 1.52 1.51 1.51 1.40 1.40 1.40 1.39 1.38 1.38 1.28 1.28 1.24 1.22 1.04
0.93 0.95 0.99 0.90 1.00 1.20 1.18 1.96 3.17 17.45
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
f1 (ppm)

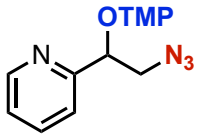

140.59 137.56 128.24 128.22 127.08 125.76
80.44
62.42 59.87 59.58
41.46 41.09 34.05 32.43 29.64 28.92 21.45 20.73 20.66 17.01
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N3
Me
Me
N
O
Me
Me

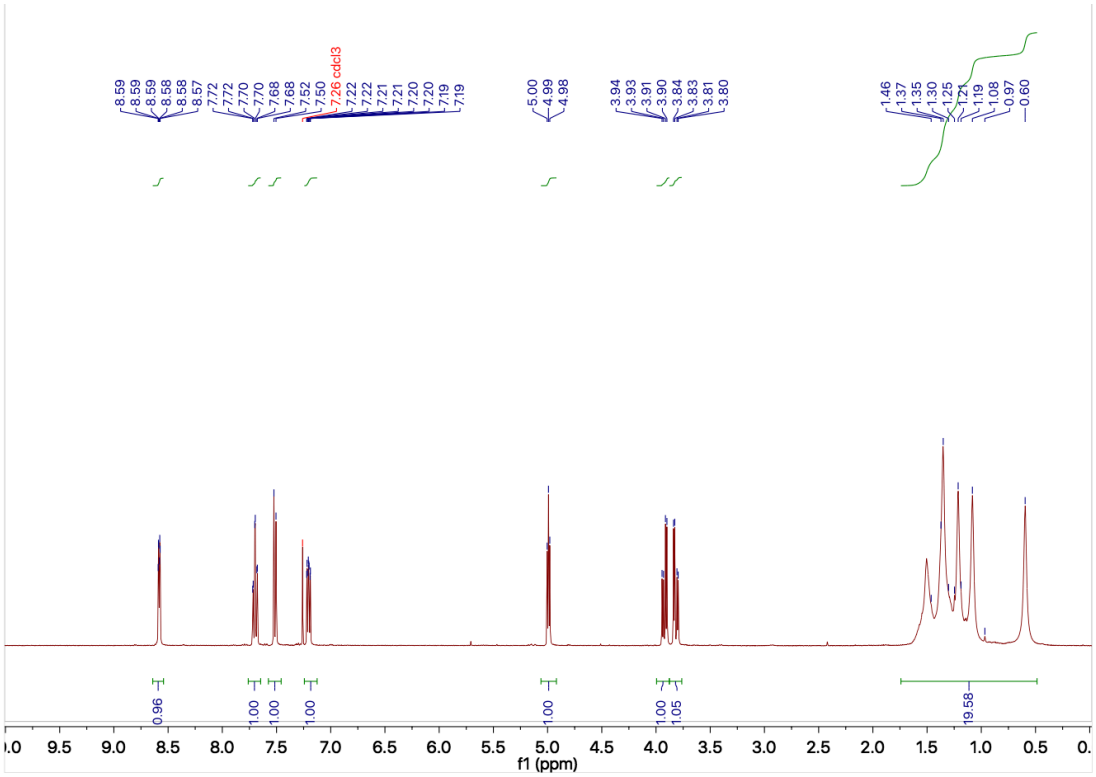
(**2l**)

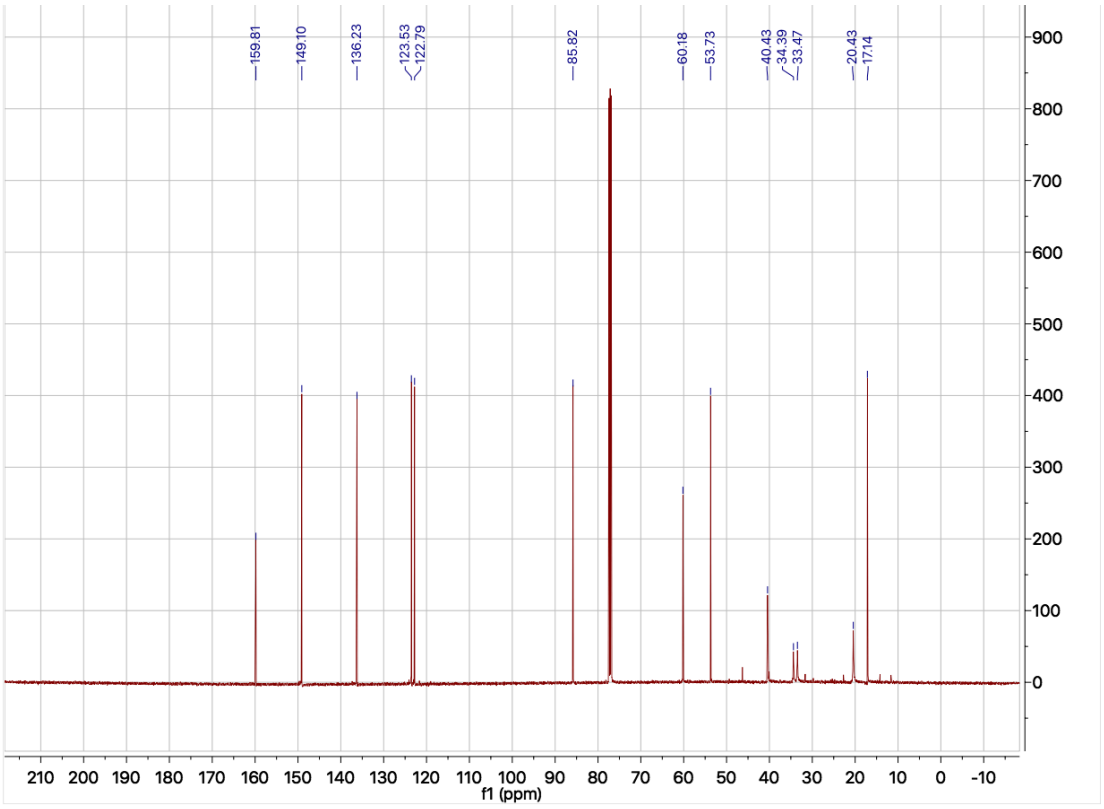

7.32
7.32
7.30
7.29
7.29
7.29
7.26
7.24
7.24
7.24
7.23
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.19
3.58
3.55
3.54
3.51
2.80
2.79
2.78
2.77
2.71
2.69
2.69
2.67
2.04
2.04
2.03
2.02
2.01
2.01
2.00
1.61
1.58
1.56
1.55
1.52
1.52
1.51
1.51
1.50
1.50
1.49
1.49
1.48
1.48
1.47
1.36
1.34
1.33
1.33
1.31
1.31
1.30
1.28
1.19
1.18
1.17
1.16
4.62
1.92
1.00
1.00
1.93
21.38
f1 (ppm)

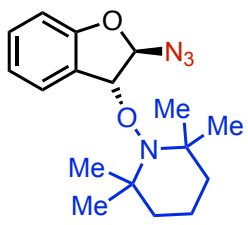

142.79
128.55
128.51
125.87
80.61
77.41
77.16
76.91
59.83
59.81
58.23
41.11
41.06
40.96
35.10
34.96
30.49
22.71
21.15
20.97
17.20
f1 (ppm)


OTMP
N
N3

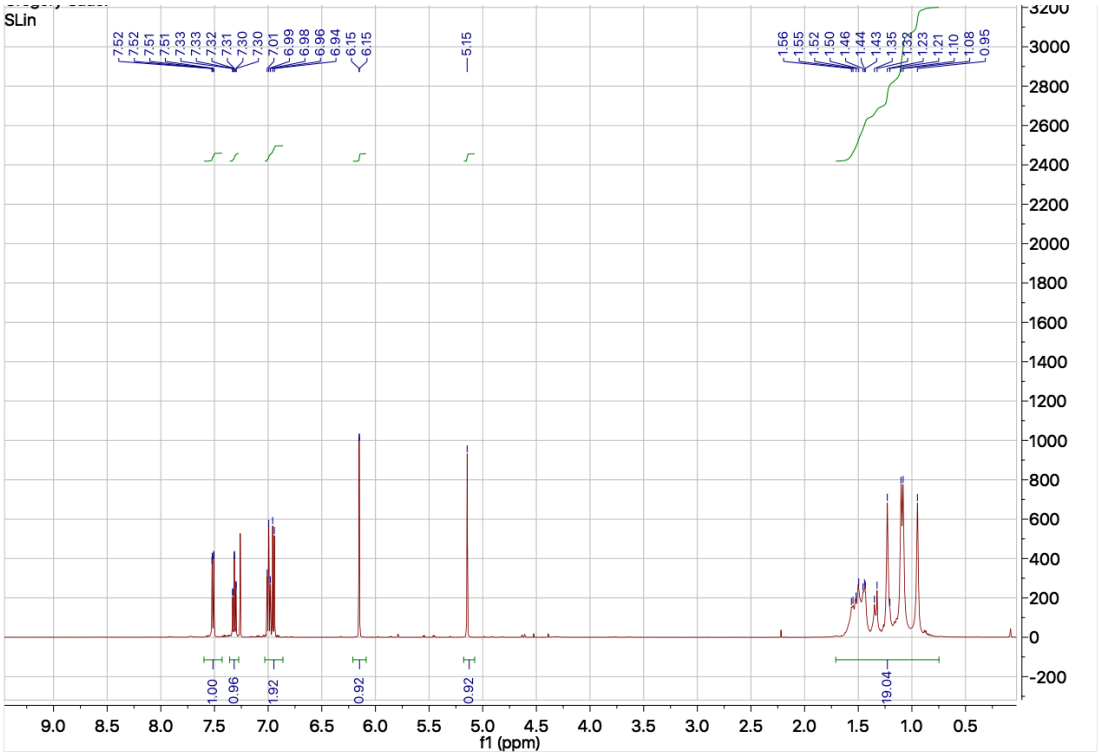
(**2h**)

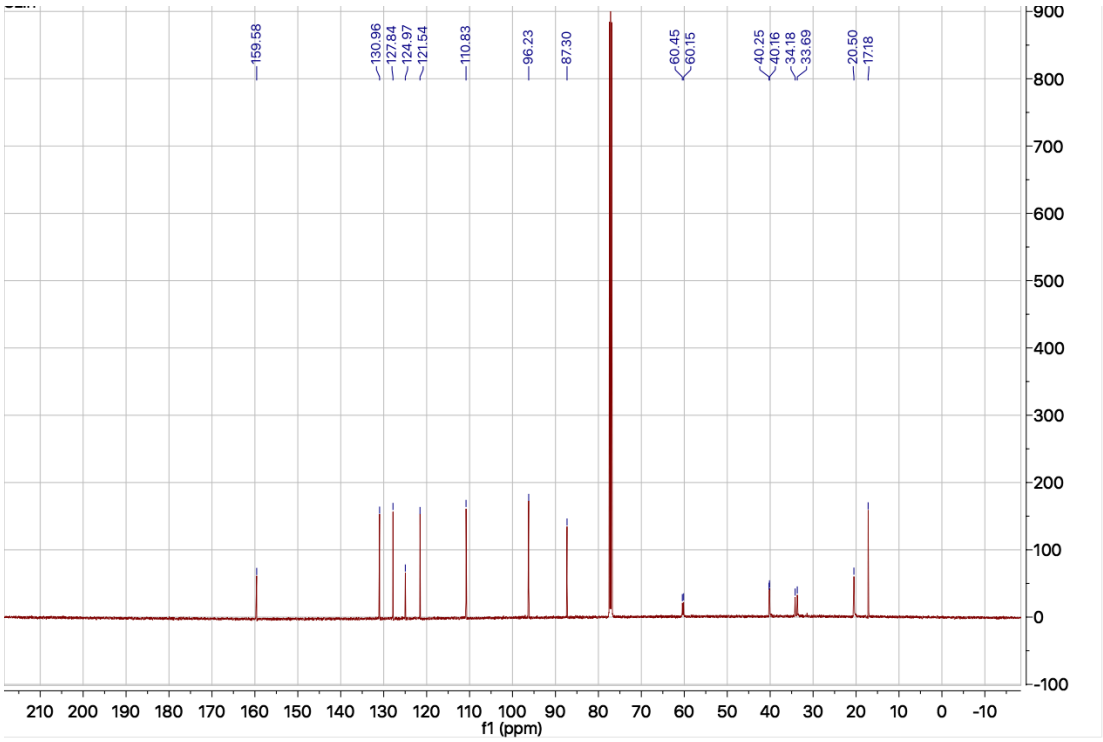

8.59
8.59
8.59
8.58
8.58
8.57
7.72
7.72
7.70
7.70
7.68
7.68
7.52
7.50
7.26 cdcl3
7.22
7.22
7.21
7.21
7.20
7.20
7.19
7.19
5.00
4.99
4.98
3.94
3.93
3.91
3.90
3.84
3.83
3.81
3.80
1.46
1.37
1.35
1.30
1.25
1.21
1.19
1.08
0.97
0.60
0.96
1.00
1.00
1.00
1.00
1.00
1.05
19.58
f1 (ppm)

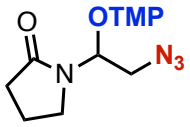

159.81
149.10
136.23
123.53
122.79
85.82
60.18
53.73
40.43
34.39
33.47
20.43
17.14
f1 (ppm)


O
N3
O
N
Me
Me
Me
Me

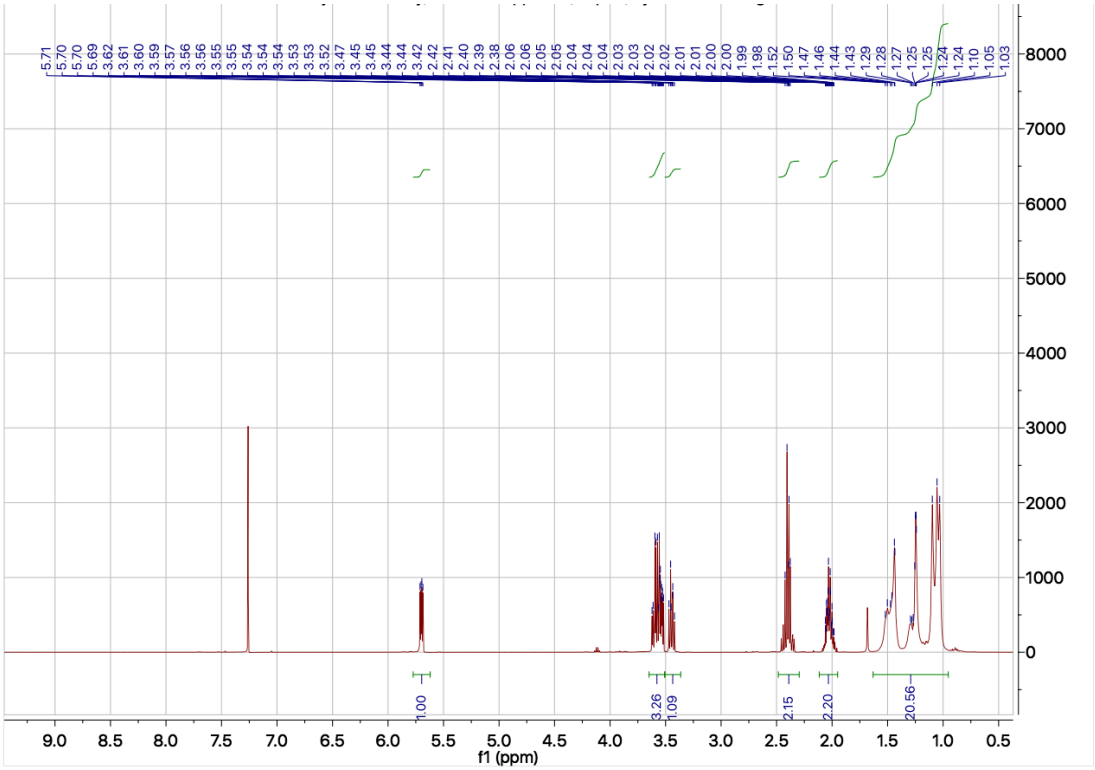
(2q)

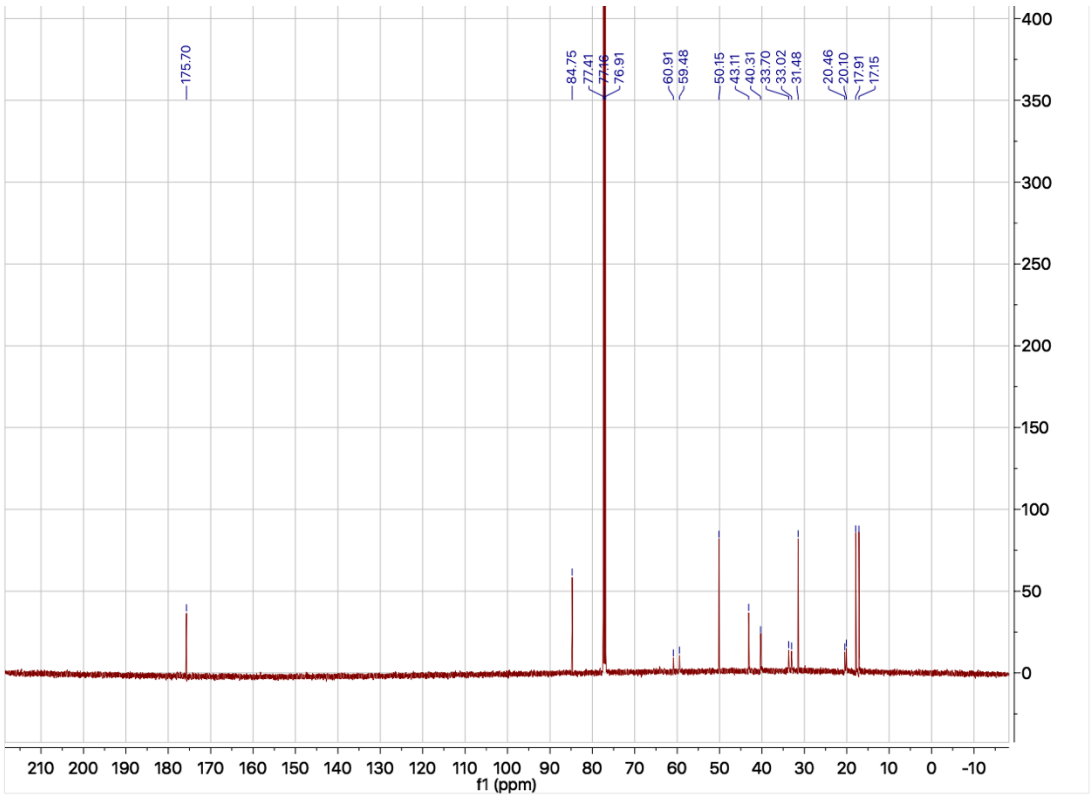

SLin
7.52
7.52
7.51
7.51
7.33
7.33
7.32
7.31
7.30
7.30
7.01
6.99
6.98
6.96
6.94
6.15
6.15
5.15
1.56
1.55
1.52
1.50
1.46
1.44
1.43
1.35
1.32
1.23
1.21
1.10
1.08
0.95
1.00
0.96
1.92
0.92
0.92
19.04
f1 (ppm)

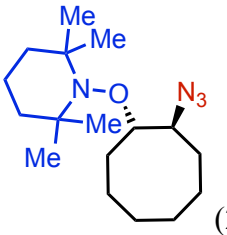

159.58
130.96
127.84
124.97
121.54
110.83
96.23
87.30
60.45
60.15
40.25
40.16
34.18
33.69
20.50
17.18
f1 (ppm)



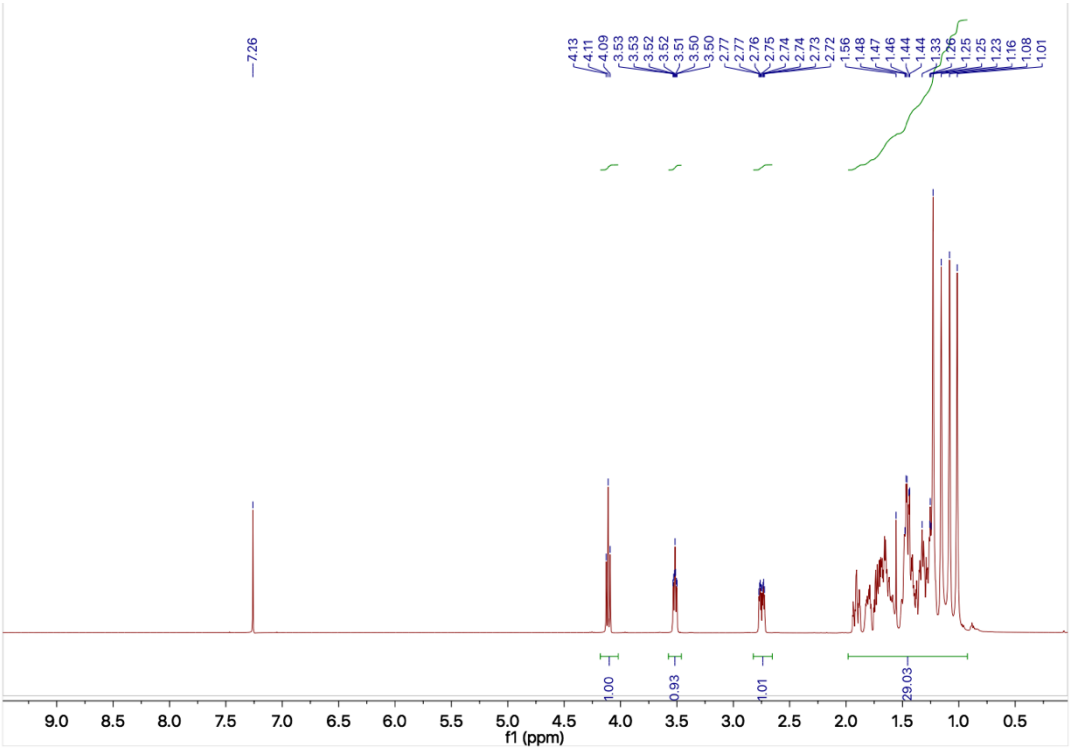
(**2k**)

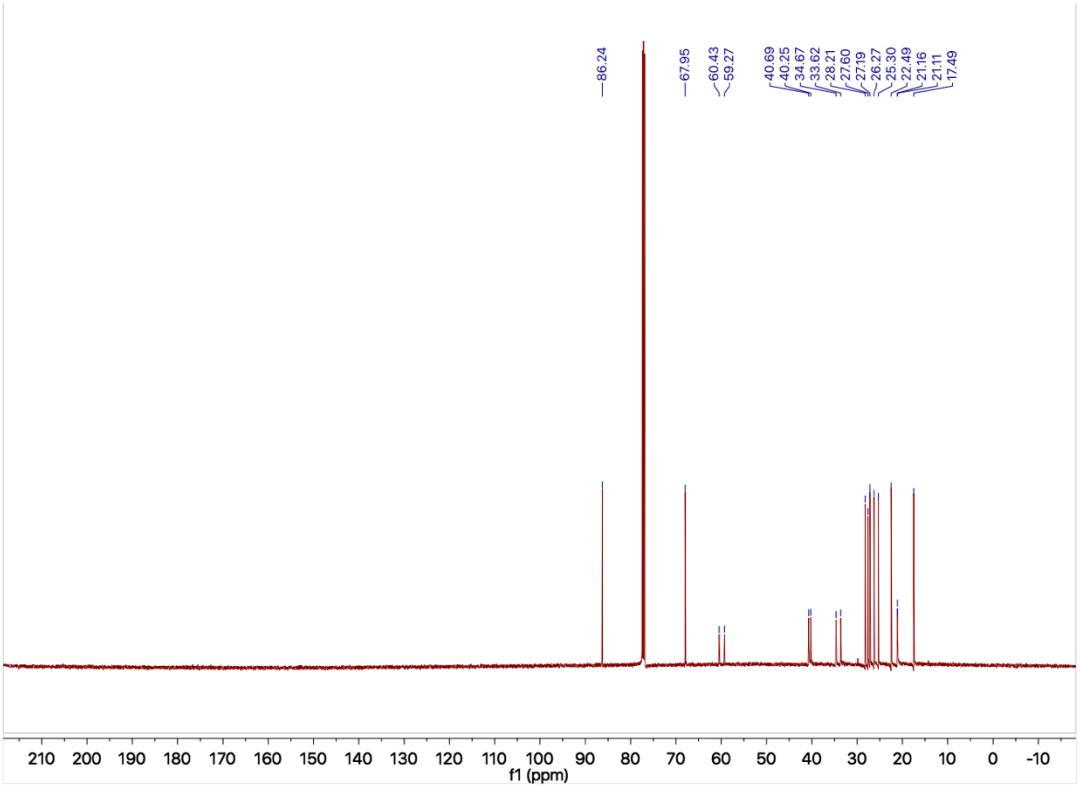


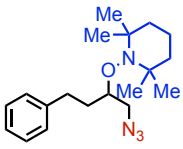



Me
Me
N
O
Me
Me
N3

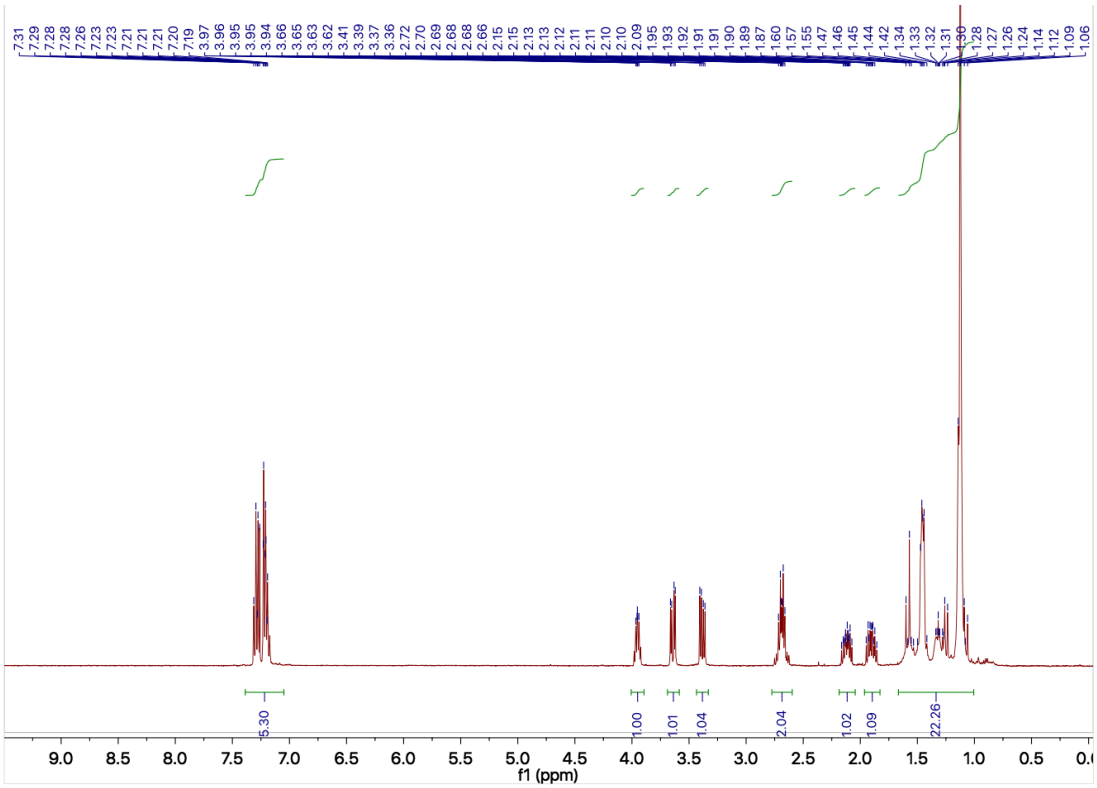
(2p)

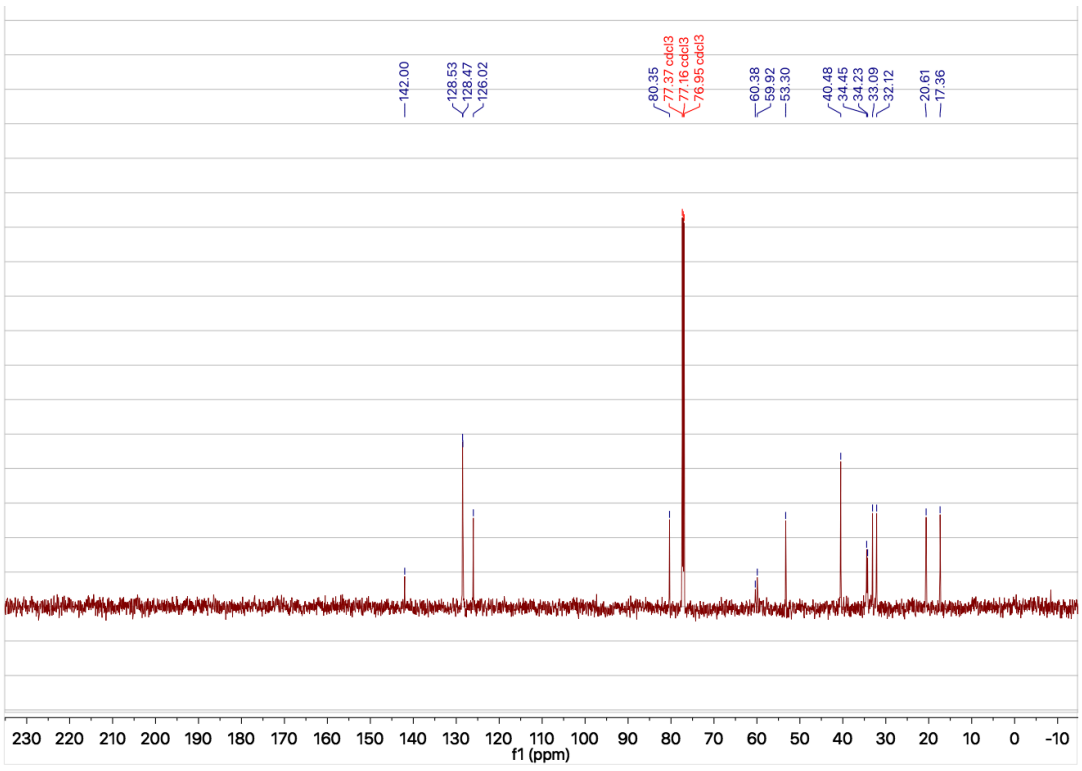

7.26
4.13
4.11
4.09
3.53
3.53
3.52
3.52
3.51
3.50
3.50
2.77
2.77
2.76
2.75
2.74
2.74
2.73
2.72
1.56
1.48
1.47
1.46
1.44
1.44
1.33
1.26
1.25
1.25
1.23
1.16
1.08
1.01
1.00
0.93
1.01
29.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

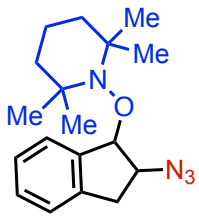

86.24
67.95
60.43
59.27
40.69
40.25
34.67
33.62
28.21
27.60
27.19
26.27
25.30
22.49
21.16
21.11
17.49
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



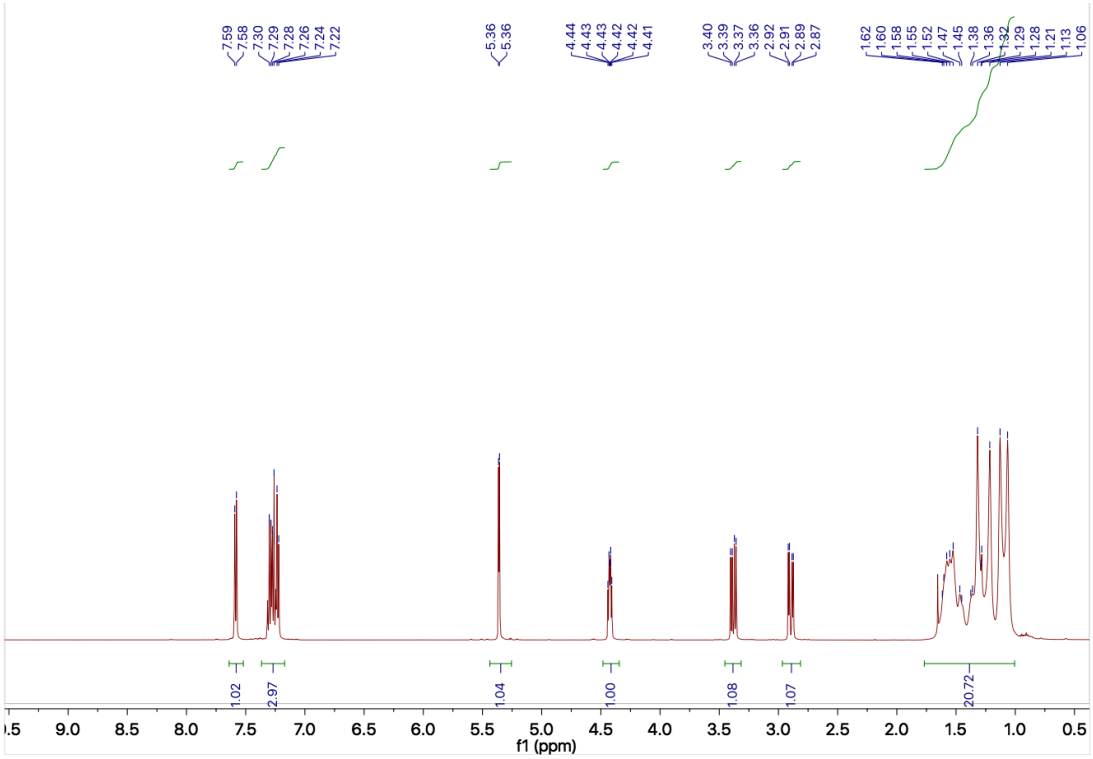
(2s)

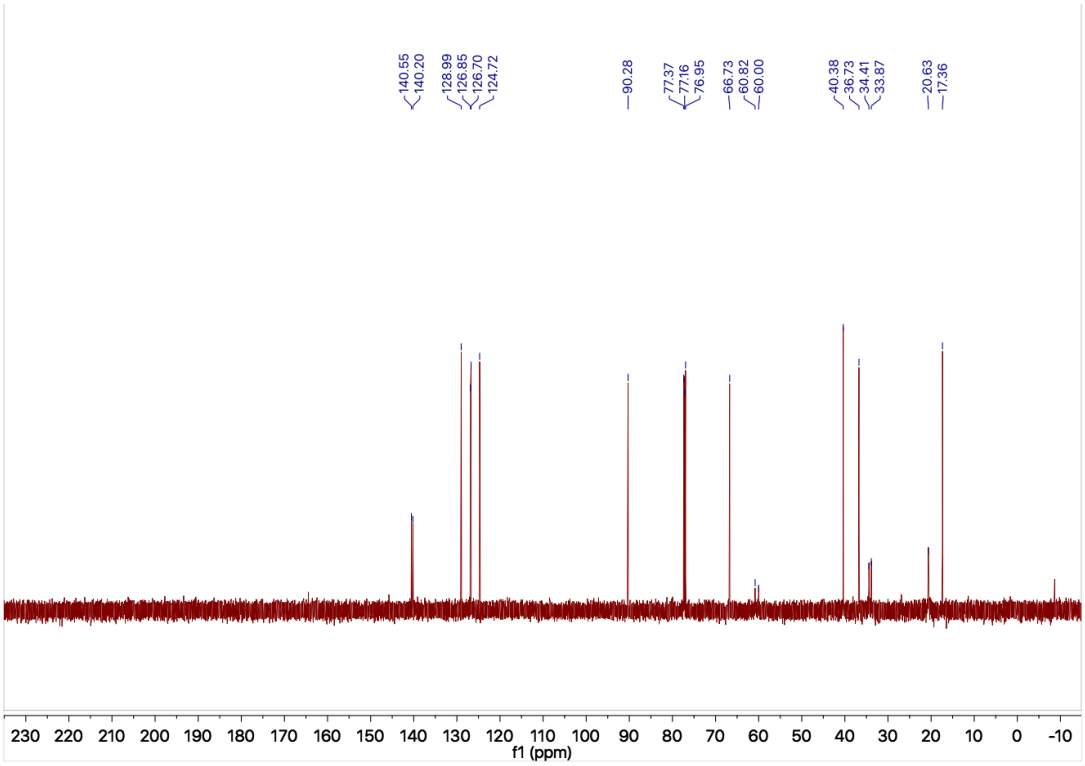


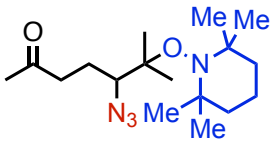



Me
Me
N
O
Me
Me
N3

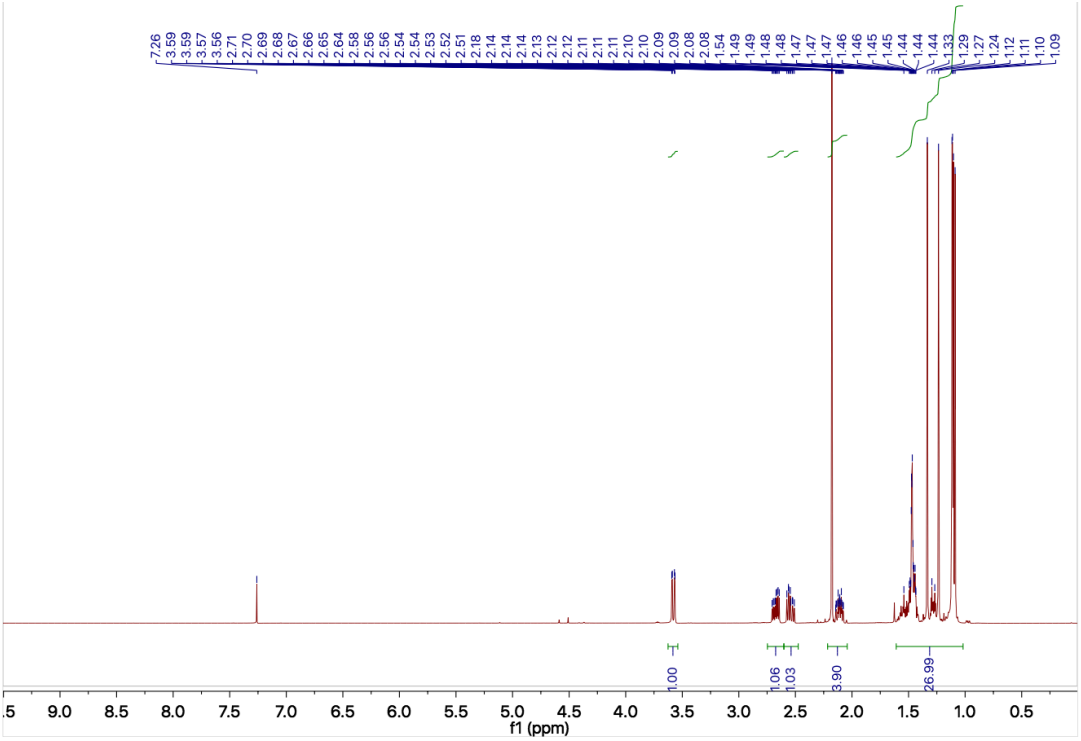
(**2m**)

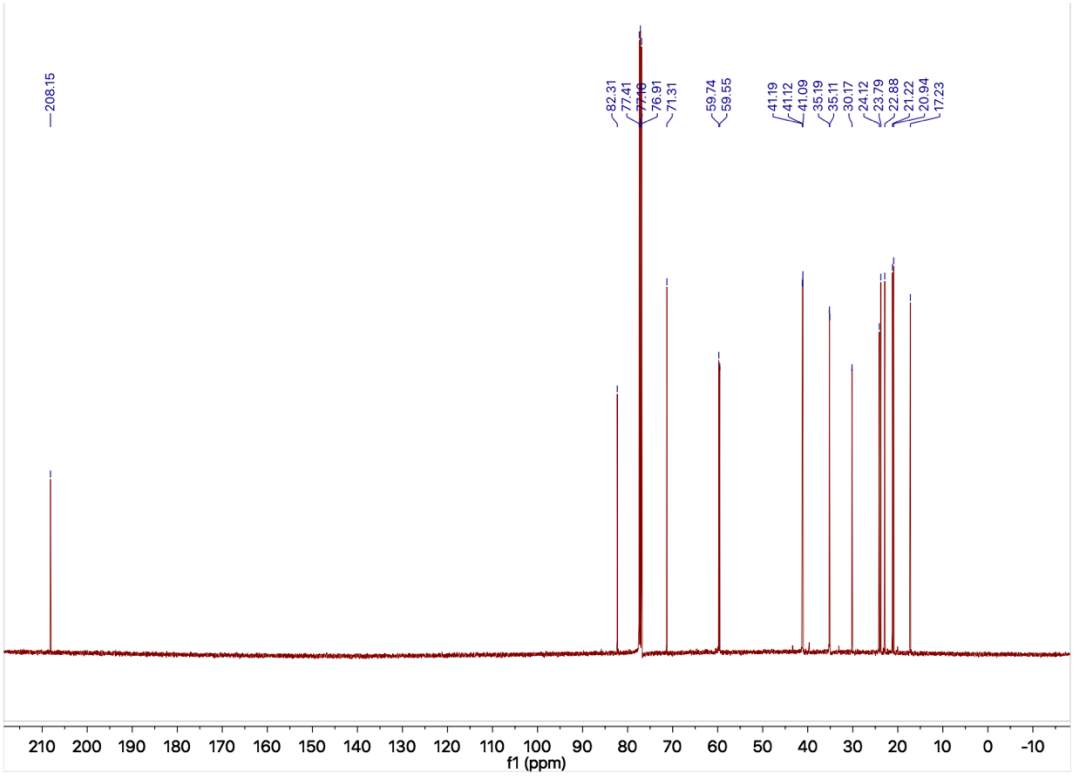

7.59
7.58
7.30
7.29
7.28
7.26
7.24
7.22
5.36
5.36
4.44
4.43
4.43
4.42
4.42
4.41
3.40
3.39
3.37
3.36
2.92
2.91
2.89
2.87
1.62
1.60
1.58
1.55
1.52
1.47
1.45
1.38
1.36
1.32
1.29
1.28
1.21
1.13
1.06
1.02
2.97
1.04
1.00
1.08
1.07
20.72
f1 (ppm)

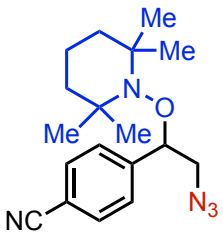

140.55
140.20
128.99
126.85
126.70
124.72
90.28
77.37
77.16
76.95
66.73
60.82
60.00
40.38
36.73
34.41
33.87
20.63
17.36
f1 (ppm)


O
Me Me
O
N
N3 Me
Me

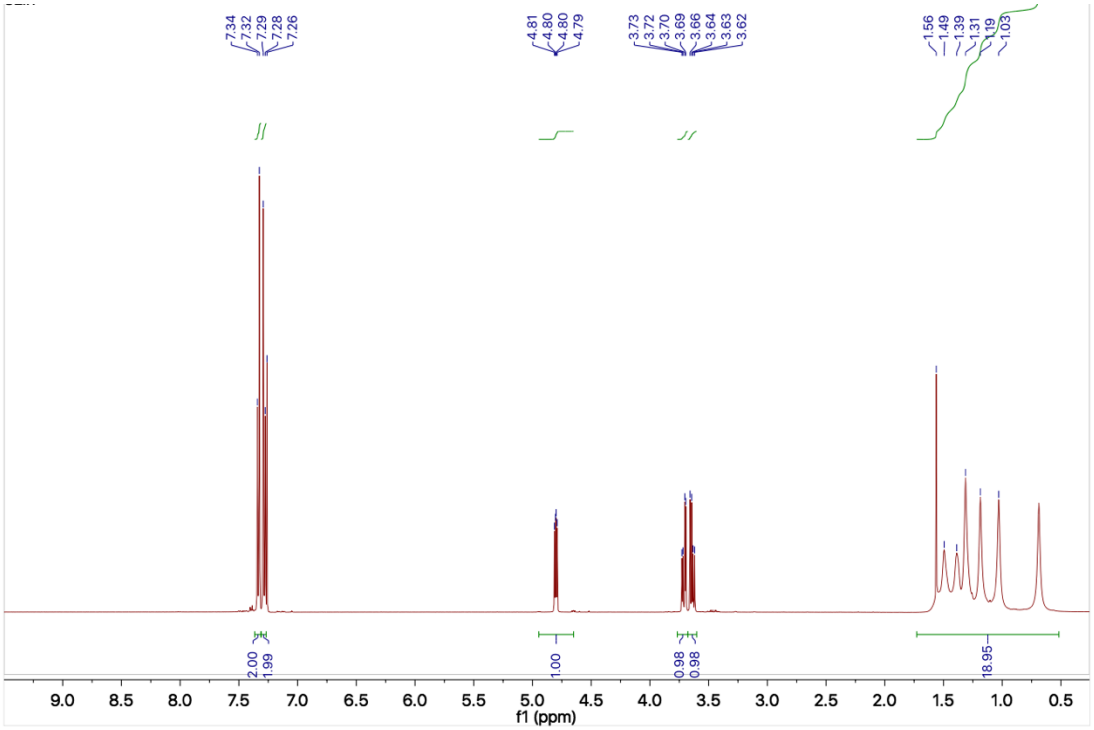
(**2e**)

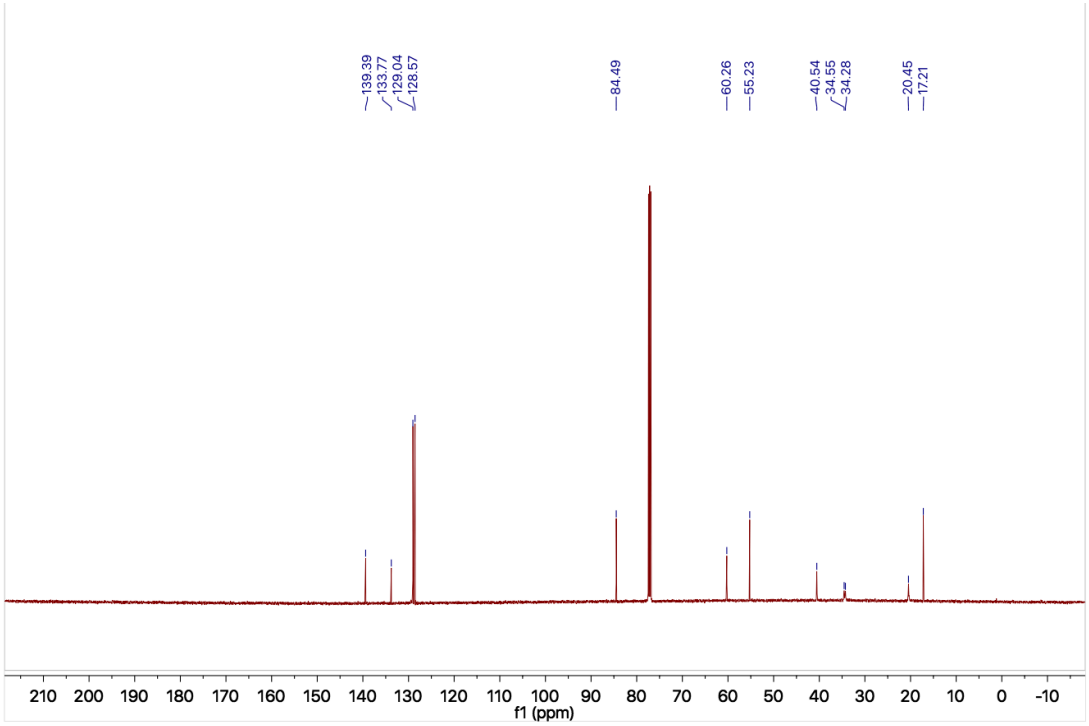

7.26
3.59
3.59
3.57
3.56
2.71
2.70
2.69
2.68
2.67
2.66
2.65
2.64
2.58
2.56
2.56
2.54
2.54
2.53
2.52
2.51
2.18
2.14
2.14
2.13
2.12
2.12
2.11
2.11
2.10
2.10
2.09
2.09
2.08
2.08
1.54
1.49
1.49
1.48
1.48
1.47
1.47
1.47
1.46
1.46
1.45
1.45
1.44
1.44
1.44
1.33
1.29
1.27
1.24
1.12
1.11
1.10
1.09
1.00
1.06
1.03
3.90
26.99
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
f1 (ppm)

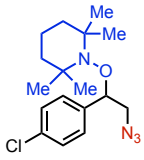

208.15
82.31
77.41
77.16
76.91
71.31
59.74
59.55
41.19
41.12
41.09
35.19
35.11
30.17
24.12
23.79
22.88
21.22
20.94
17.23
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
Me
N
O
Me
Me
N3
NC

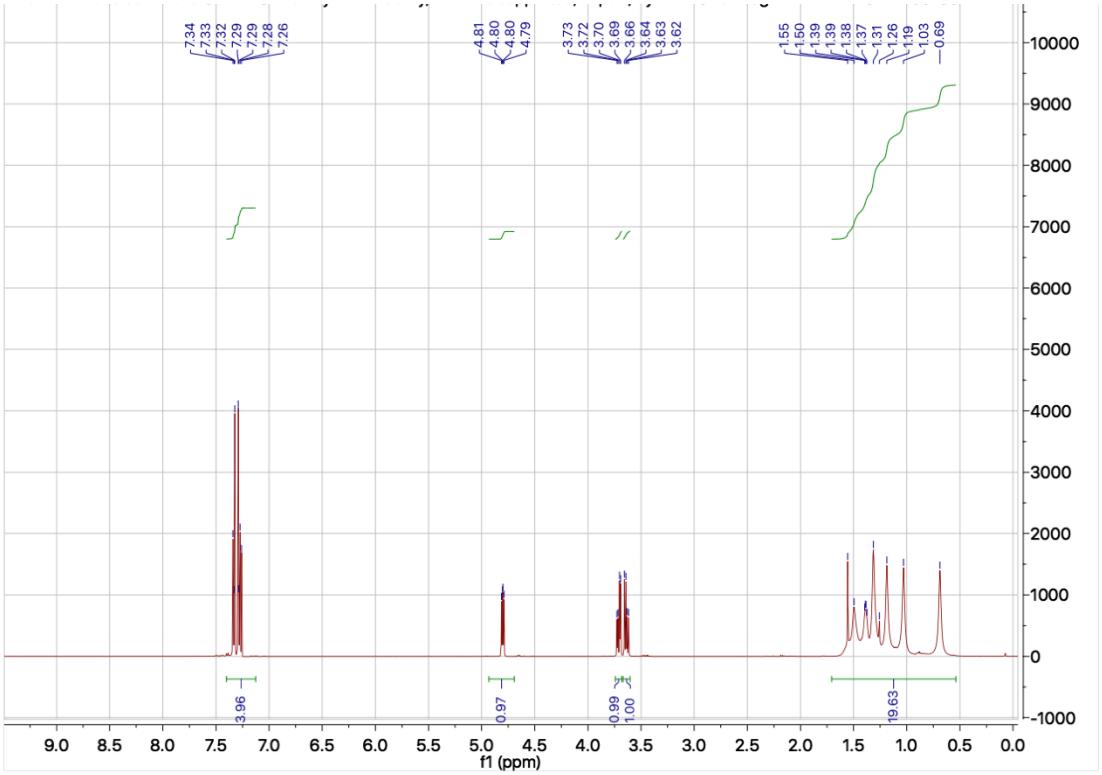
(2d)

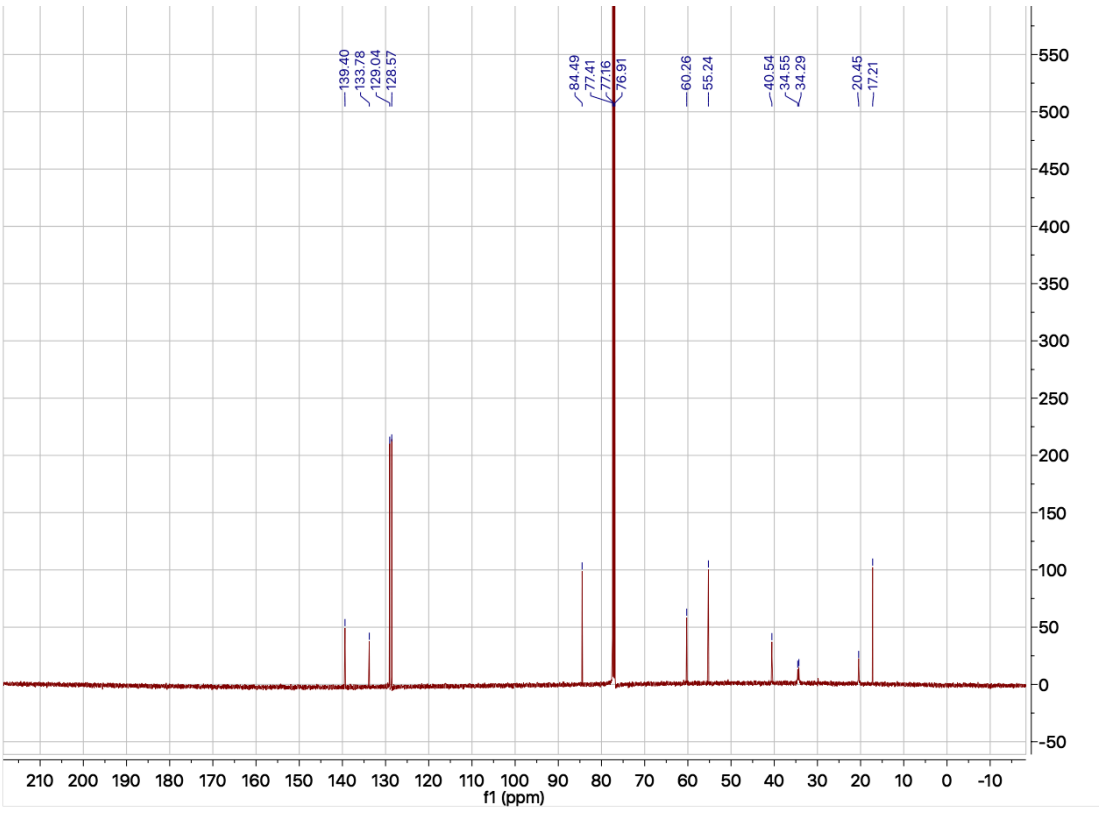

7.34
7.32
7.29
7.28
7.26
4.81
4.80
4.80
4.79
3.73
3.72
3.70
3.69
3.66
3.64
3.63
3.62
1.56
1.49
1.39
1.31
1.19
1.03
2.00
1.99
1.00
0.98
0.98
18.95
f1 (ppm)

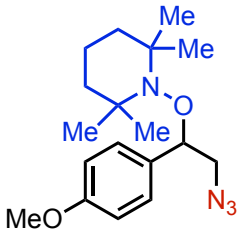

139.39
133.77
129.04
128.57
84.49
60.26
55.23
40.54
34.55
34.28
20.45
17.21
f1 (ppm)


Me
Me
N
O
Me
Me
Cl
N3

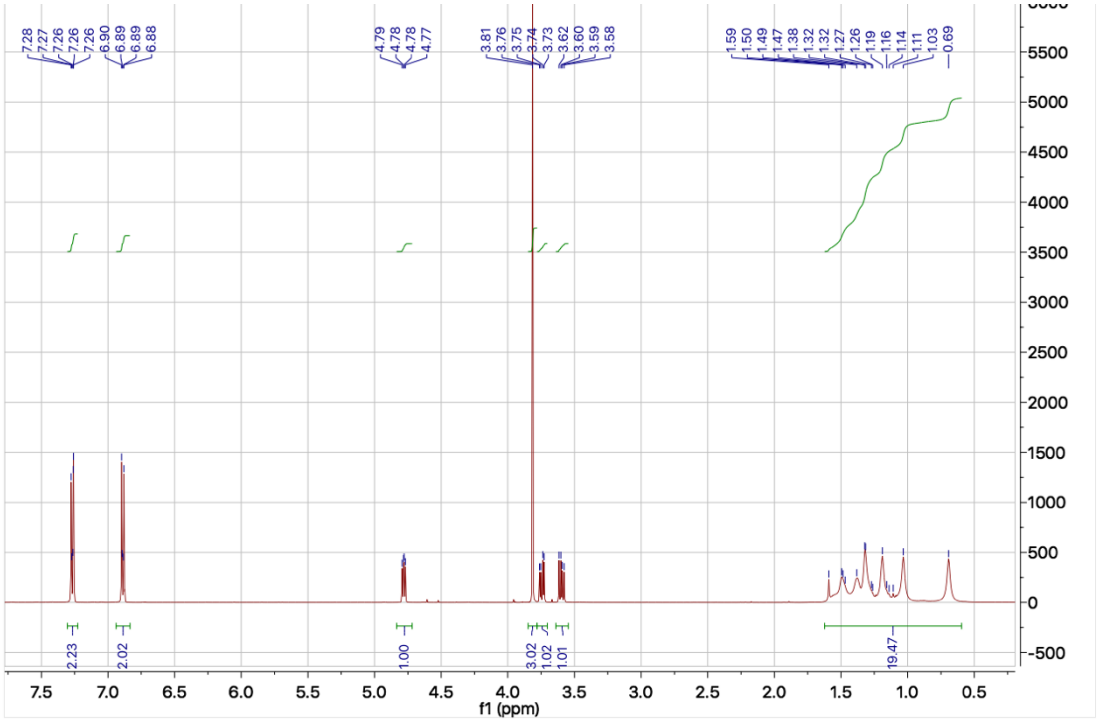
(2c)

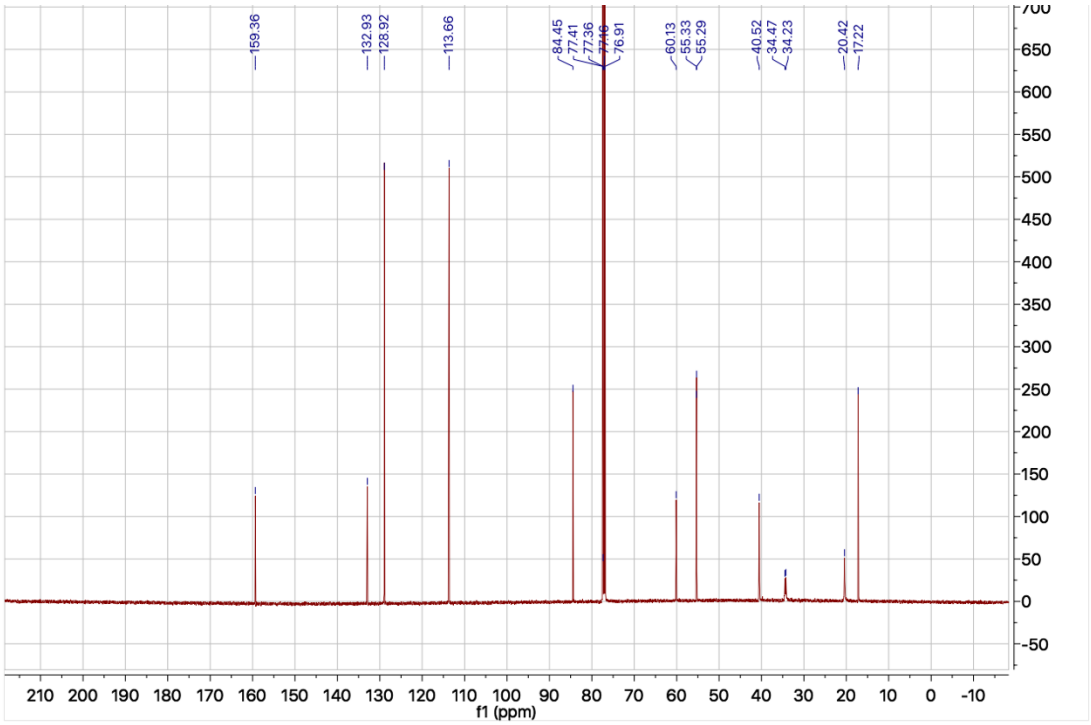

7.34
7.33
7.32
7.29
7.29
7.28
7.26
4.81
4.80
4.80
4.79
3.73
3.72
3.70
3.69
3.66
3.64
3.63
3.62
1.55
1.50
1.39
1.39
1.38
1.37
1.31
1.26
1.19
1.03
0.69
3.96
0.97
0.99
1.00
19.63
f1 (ppm)

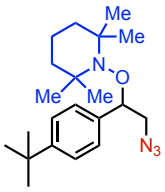

139.40
133.78
129.04
128.57
84.49
77.41
77.16
76.91
60.26
55.24
40.54
34.55
34.29
20.45
17.21
f1 (ppm)


Me
Me
N
O
Me
Me
N3
MeO

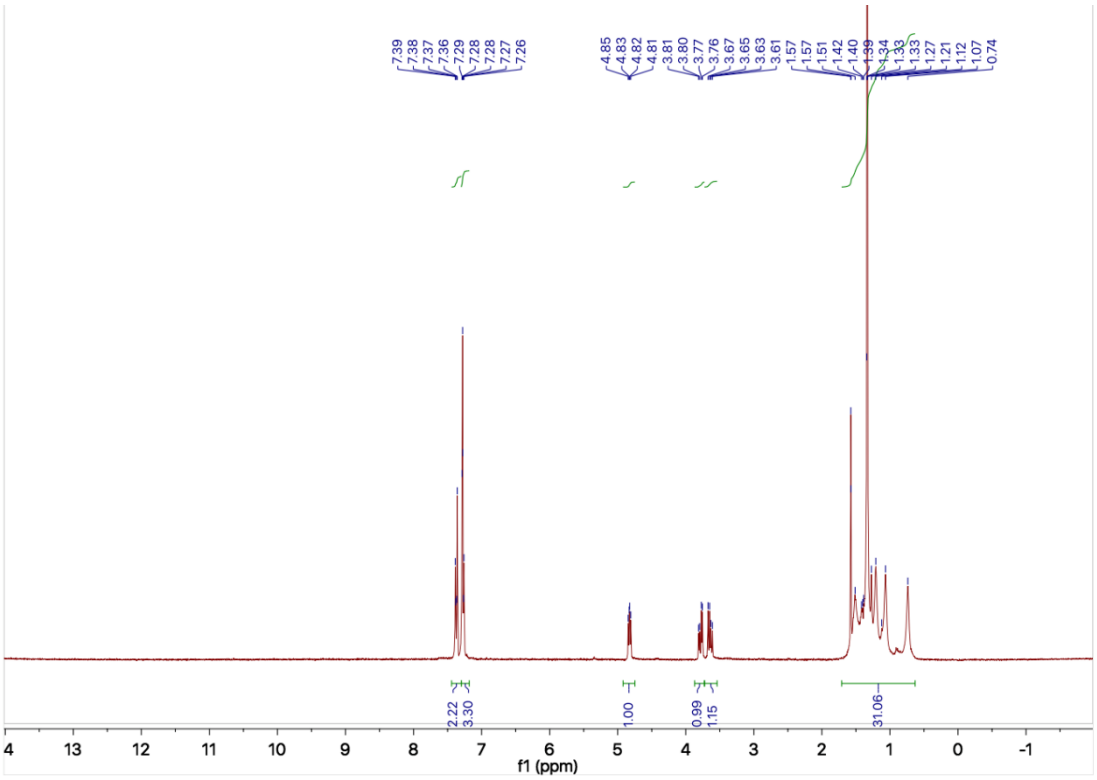
(**2b**)

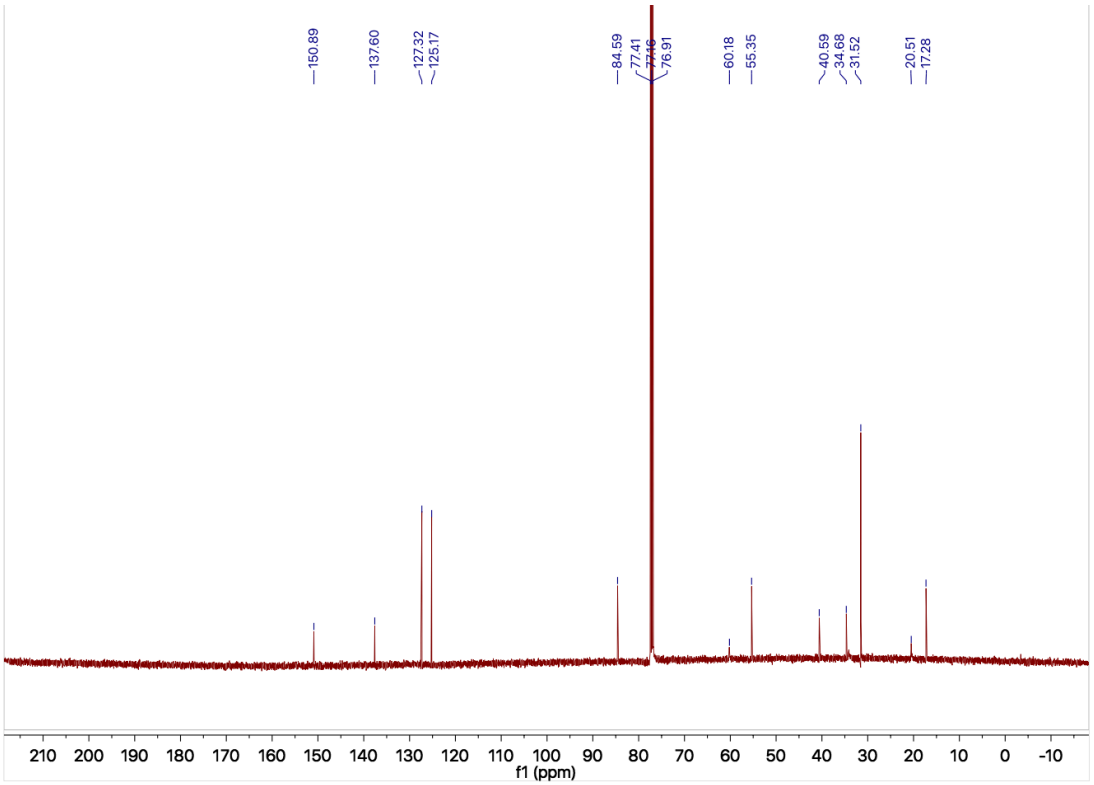

7.28
7.27
7.26
7.26
7.26
6.90
6.89
6.89
6.88
4.79
4.78
4.78
4.77
3.81
3.76
3.75
3.74
3.73
3.62
3.60
3.59
3.58
1.59
1.50
1.49
1.47
1.38
1.32
1.32
1.27
1.26
1.19
1.16
1.14
1.11
1.03
0.69
2.23
2.02
1.00
3.02
1.02
1.01
19.47
f1 (ppm)

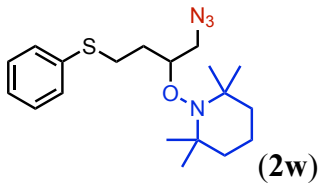

159.36
132.93
128.92
113.66
84.45
77.41
77.36
77.16
76.91
60.13
55.33
55.29
40.52
34.47
34.23
20.42
17.22
f1 (ppm)


Me
Me
N
O
Me
Me
N3

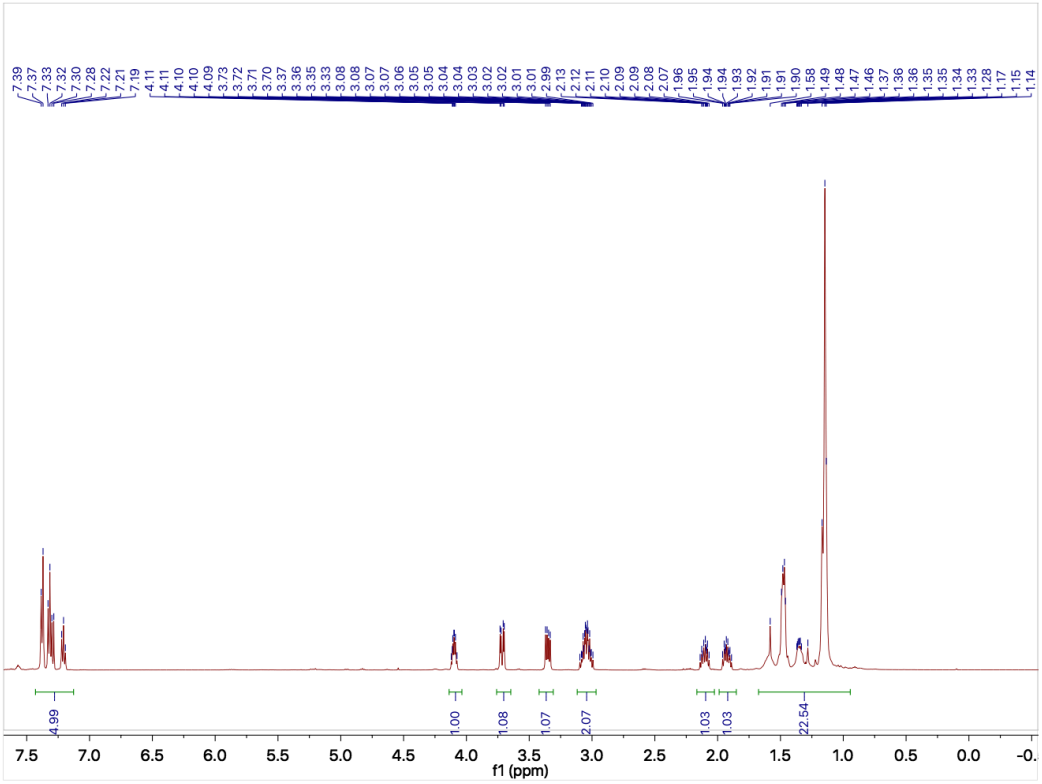
(2a)

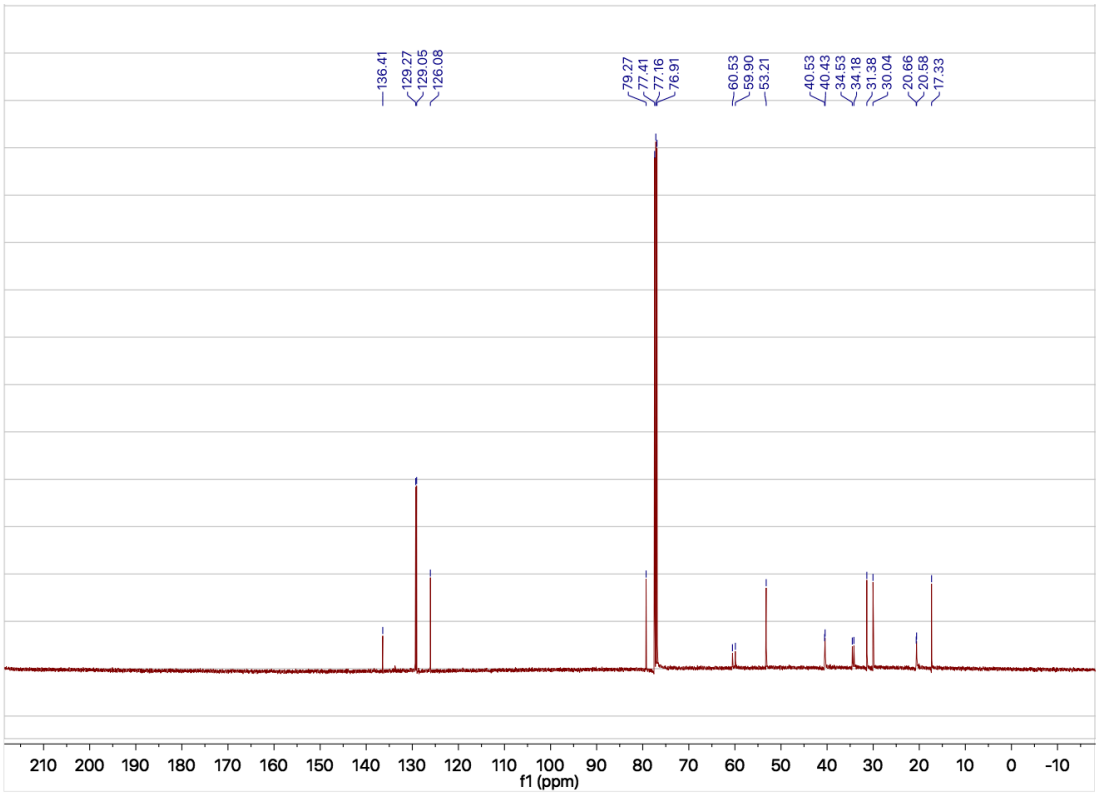

7.39
7.38
7.37
7.36
7.29
7.28
7.28
7.27
7.26
4.85
4.83
4.82
4.81
3.81
3.80
3.77
3.76
3.67
3.65
3.63
3.61
1.57
1.57
1.51
1.42
1.40
1.39
1.34
1.33
1.27
1.21
1.12
1.07
0.74
2.22
3.30
1.00
0.99
1.15
31.06
f1 (ppm)

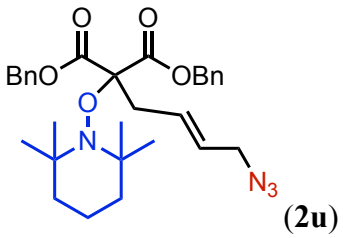

150.89
137.60
127.32
125.17
84.59
77.41
77.16
76.91
60.18
55.35
40.59
34.68
31.52
20.51
17.28
f1 (ppm)



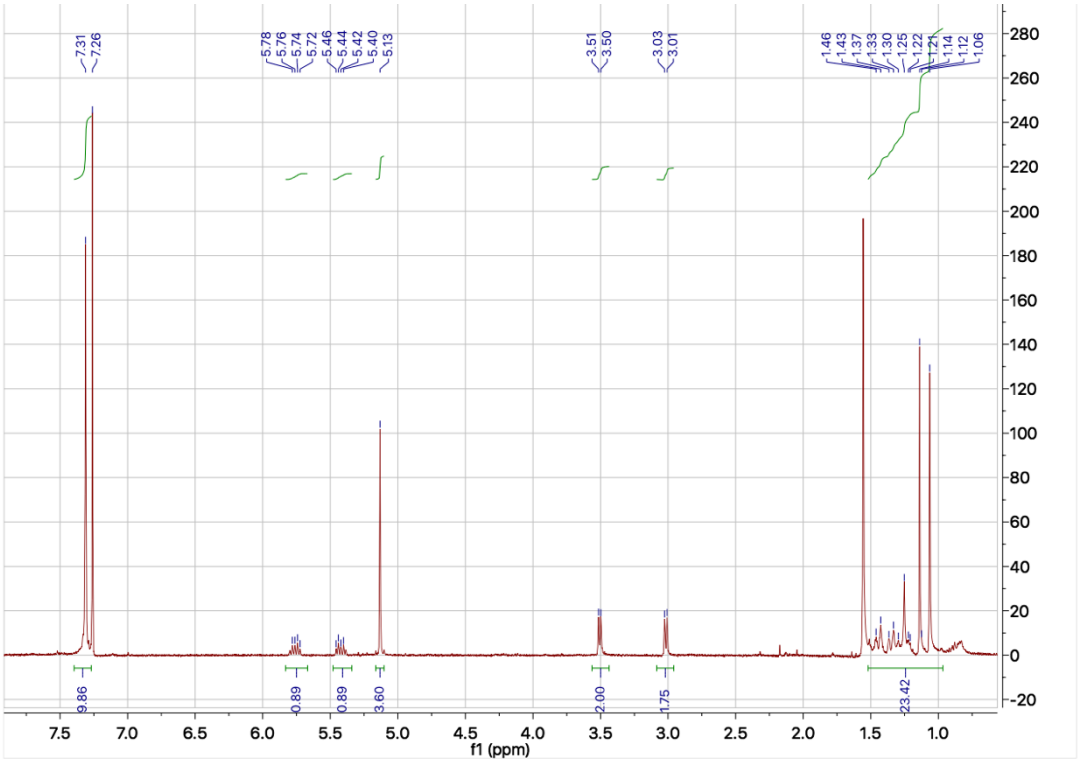
(2w)

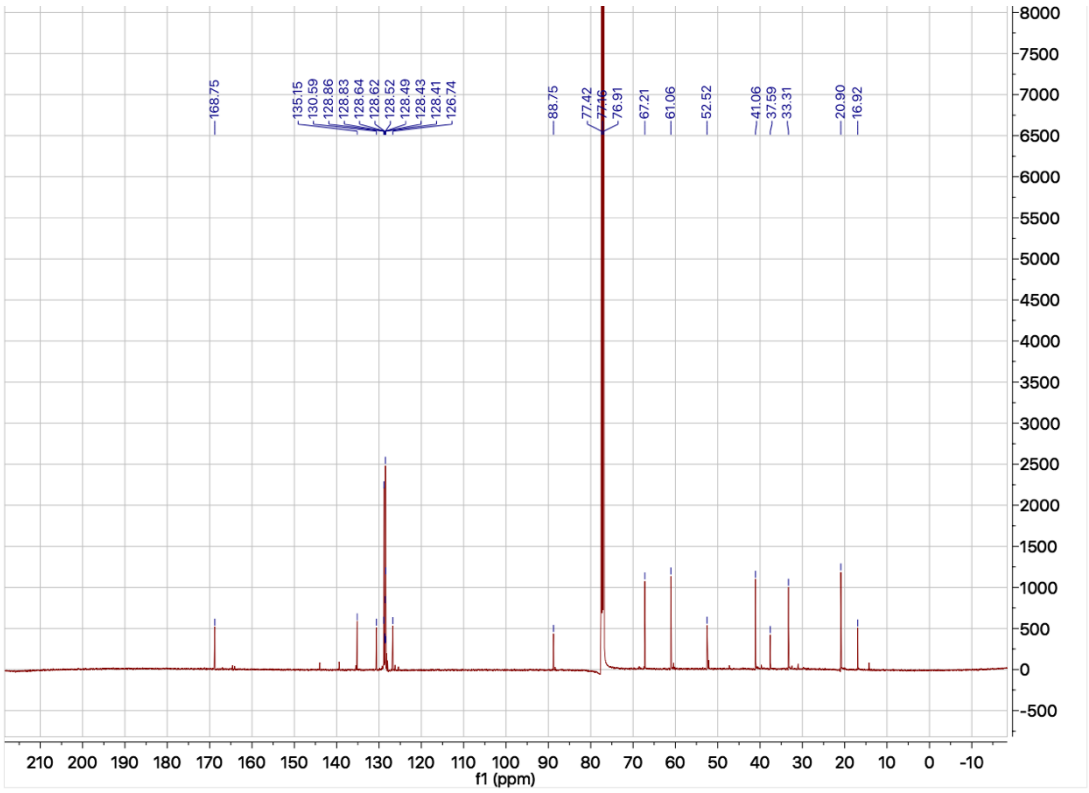

7.39
7.37
7.33
7.32
7.30
7.28
7.22
7.21
7.19
4.11
4.11
4.10
4.10
4.09
3.73
3.72
3.71
3.70
3.37
3.36
3.35
3.33
3.08
3.08
3.07
3.07
3.06
3.05
3.05
3.04
3.04
3.03
3.02
3.02
3.01
3.01
2.99
2.13
2.12
2.11
2.10
2.09
2.09
2.08
2.07
1.96
1.95
1.94
1.94
1.93
1.92
1.91
1.91
1.90
1.58
1.49
1.48
1.47
1.46
1.37
1.36
1.36
1.35
1.35
1.34
1.33
1.28
1.17
1.15
1.14
4.99
1.00
1.08
1.07
2.07
1.03
1.03
22.54
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)

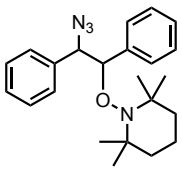

136.41
129.27
129.05
126.08
79.27
77.41
77.16
76.91
60.53
59.90
53.21
40.53
40.43
34.53
34.18
31.38
30.04
20.66
20.58
17.33
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
O
BnO
OBn
O
N
N3

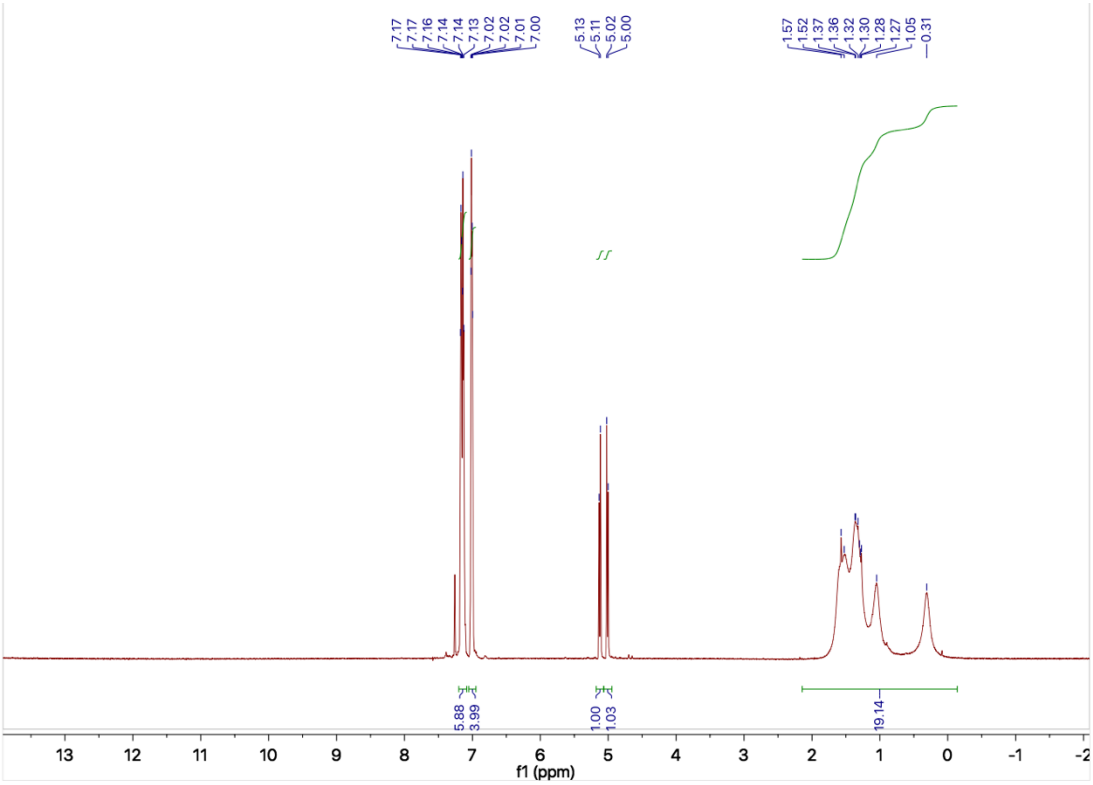
(**2u**)

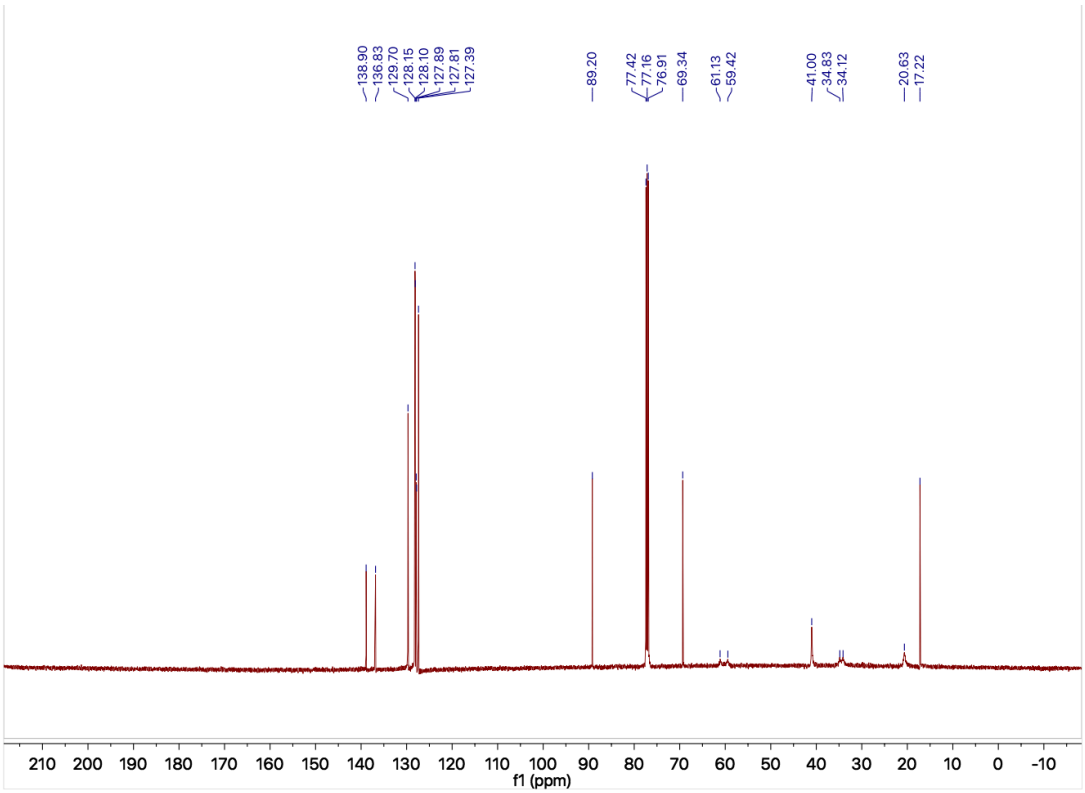

7.31
7.26
5.78
5.76
5.74
5.72
5.46
5.44
5.42
5.40
5.13
3.51
3.50
3.03
3.01
1.46
1.43
1.37
1.33
1.30
1.25
1.22
1.21
1.14
1.12
1.06
9.86
0.89
0.89
3.60
2.00
1.75
23.42
f1 (ppm)

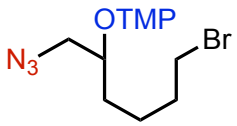

168.75
135.15
130.59
128.86
128.83
128.64
128.62
128.52
128.49
128.43
128.41
126.74
88.75
77.42
77.16
76.91
67.21
61.06
52.52
41.06
37.59
33.31
20.90
16.92
f1 (ppm)



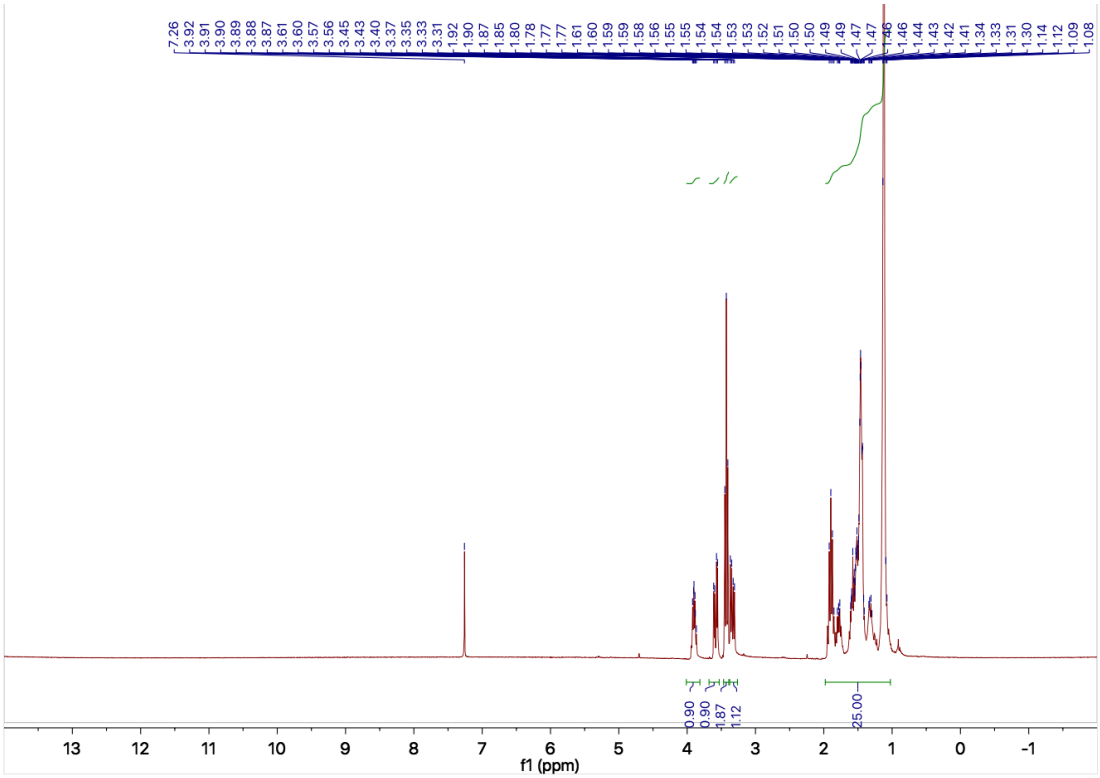
(**2o**)

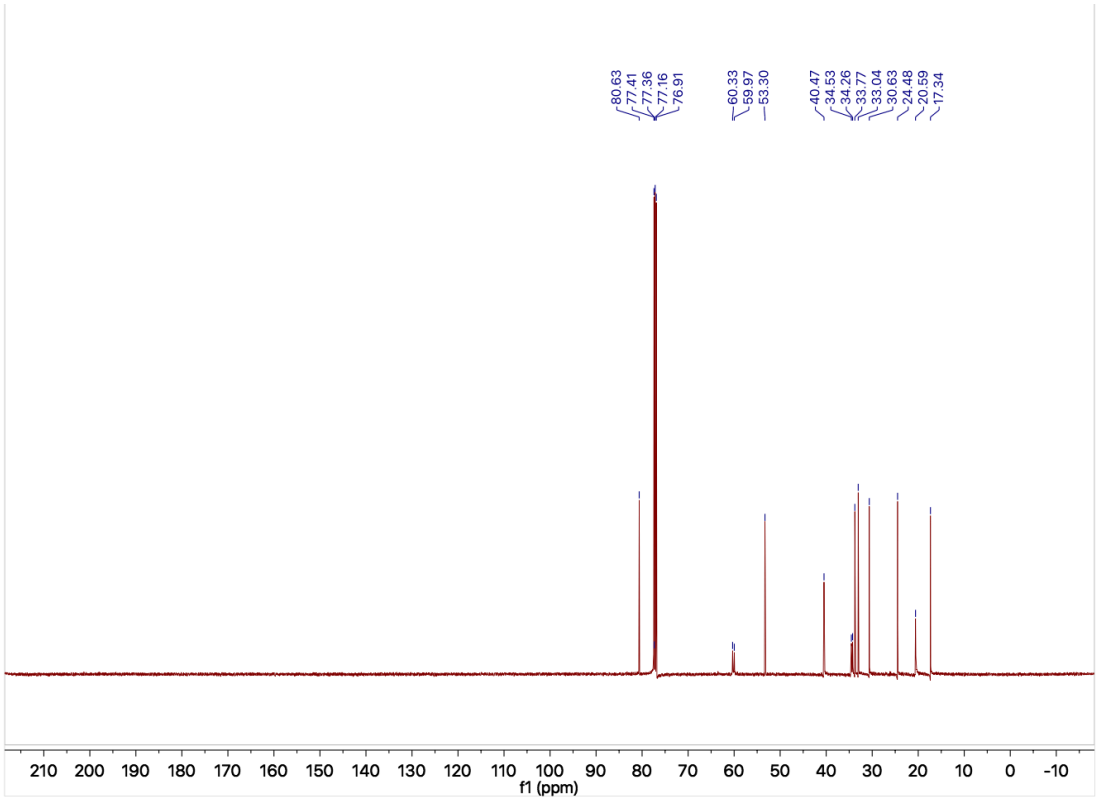

7.17
7.17
7.16
7.14
7.14
7.13
7.02
7.02
7.01
7.00
5.13
5.11
5.02
5.00
1.57
1.52
1.37
1.36
1.32
1.30
1.28
1.27
1.05
0.31
5.88
3.99
1.00
1.03
19.14
f1 (ppm)

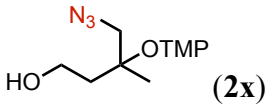

138.90
136.83
129.70
128.15
128.10
127.89
127.81
127.39
89.20
77.42
77.16
76.91
69.34
61.13
59.42
41.00
34.83
34.12
20.63
17.22
f1 (ppm)


OTMP
N3
Br

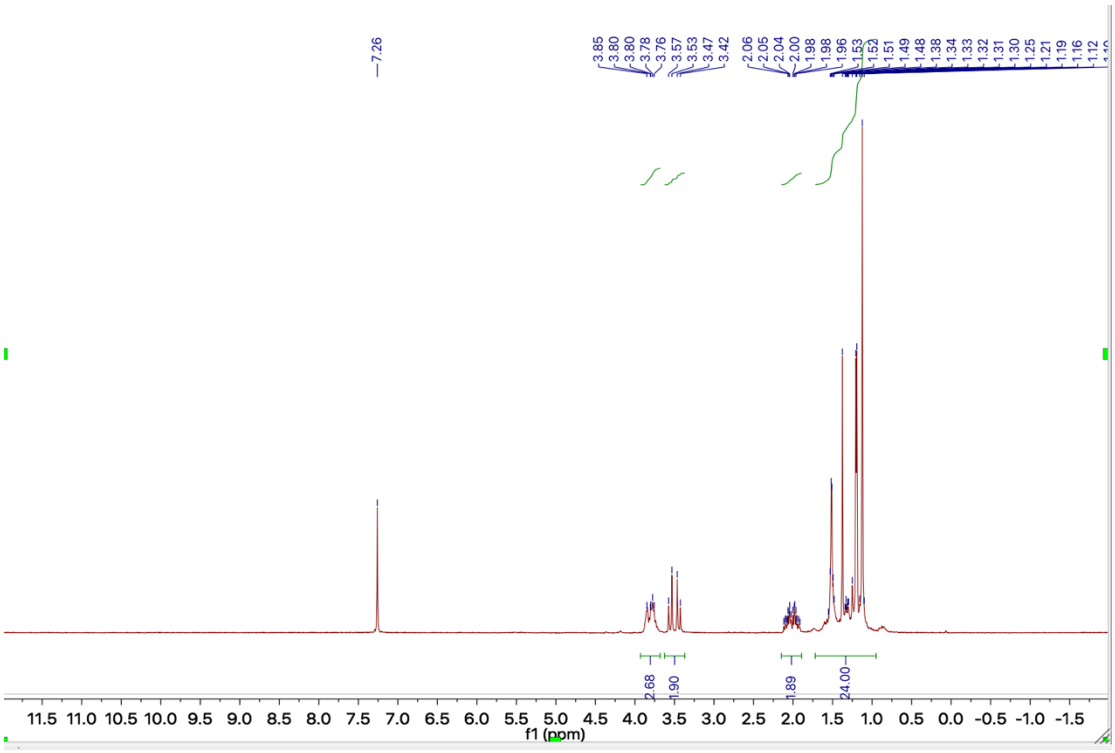
(2j)

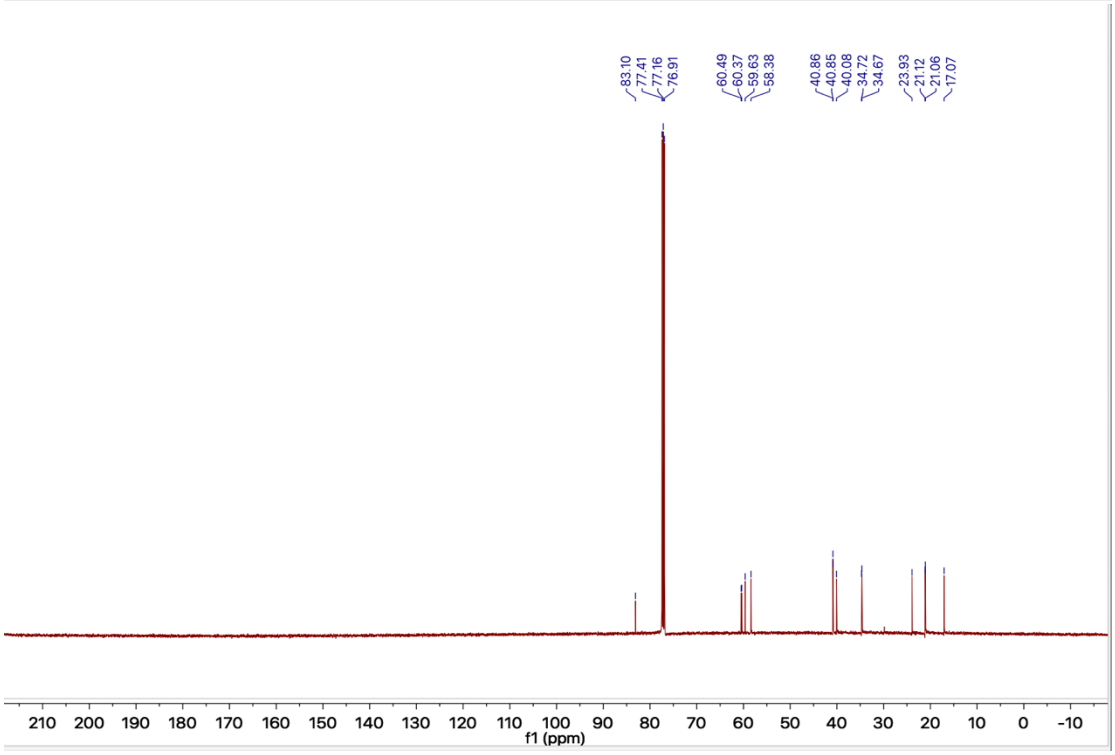

7.26
3.92
3.91
3.90
3.89
3.88
3.87
3.61
3.60
3.57
3.56
3.45
3.43
3.40
3.37
3.35
3.33
3.31
1.92
1.90
1.87
1.85
1.80
1.78
1.77
1.77
1.61
1.60
1.59
1.59
1.58
1.56
1.55
1.55
1.54
1.54
1.53
1.53
1.52
1.51
1.50
1.50
1.49
1.49
1.47
1.47
1.46
1.46
1.44
1.43
1.42
1.41
1.34
1.33
1.31
1.30
1.14
1.12
1.09
1.08
0.90
0.90
1.87
1.12
25.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

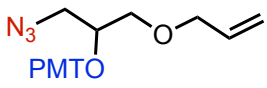

80.63
77.41
77.36
77.16
76.91
60.33
59.97
53.30
40.47
34.53
34.26
33.77
33.04
30.63
24.48
20.59
17.34
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


N3
OTMP
HO

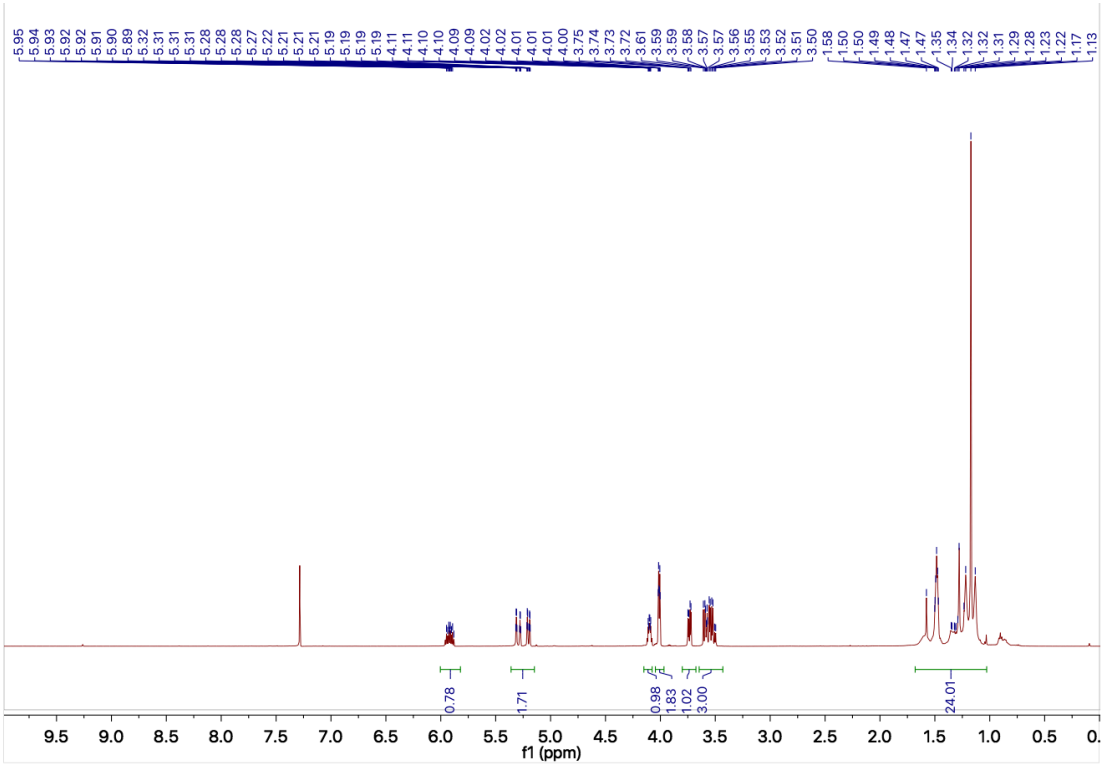
(**2x**)

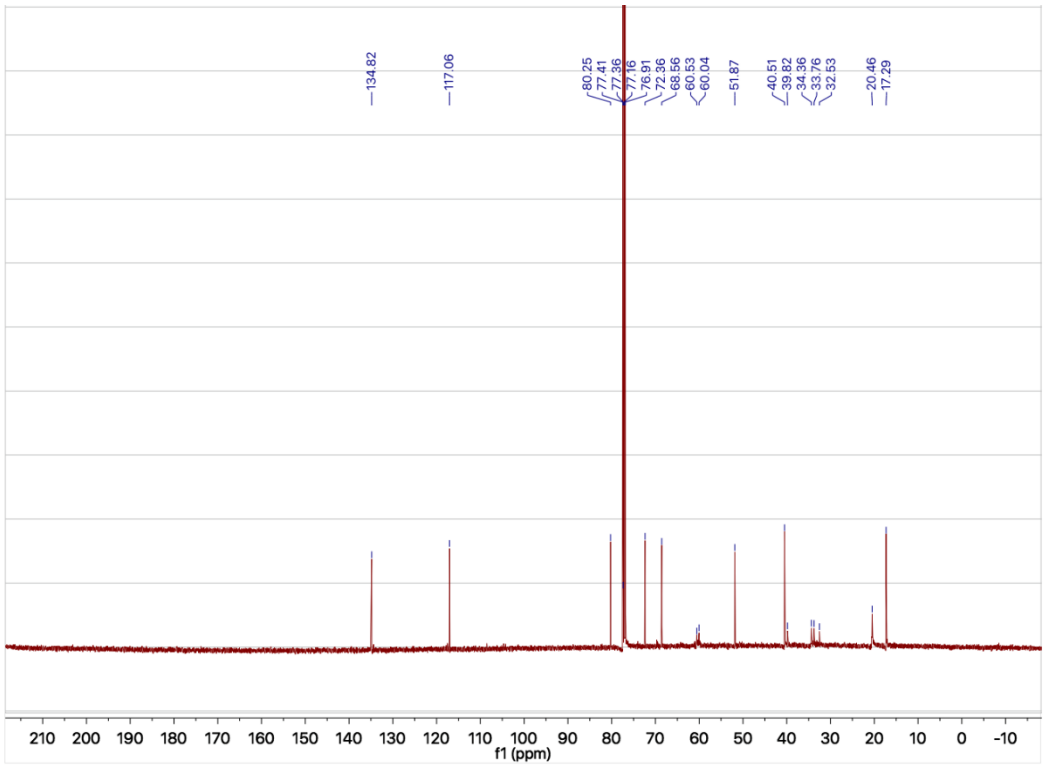

7.26
3.85
3.80
3.80
3.78
3.76
3.57
3.53
3.47
3.42
2.06
2.05
2.04
2.00
1.98
1.98
1.96
1.53
1.52
1.51
1.49
1.48
1.38
1.34
1.33
1.32
1.31
1.30
1.25
1.21
1.19
1.16
1.12
2.68
1.90
1.89
24.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

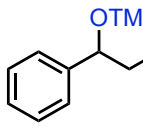

83.10
77.41
77.16
76.91
60.49
60.37
59.63
58.38
40.86
40.85
40.08
34.72
34.67
23.93
21.12
21.06
17.07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N3
PMTO
O

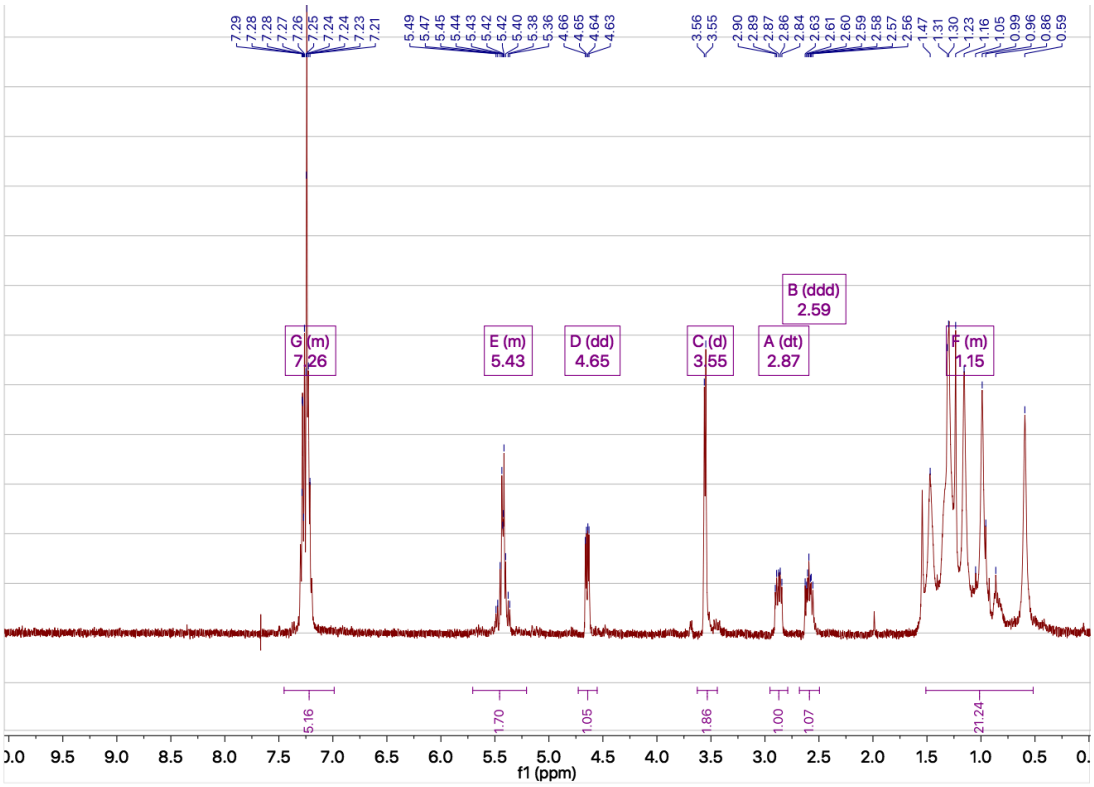
(**2v**)

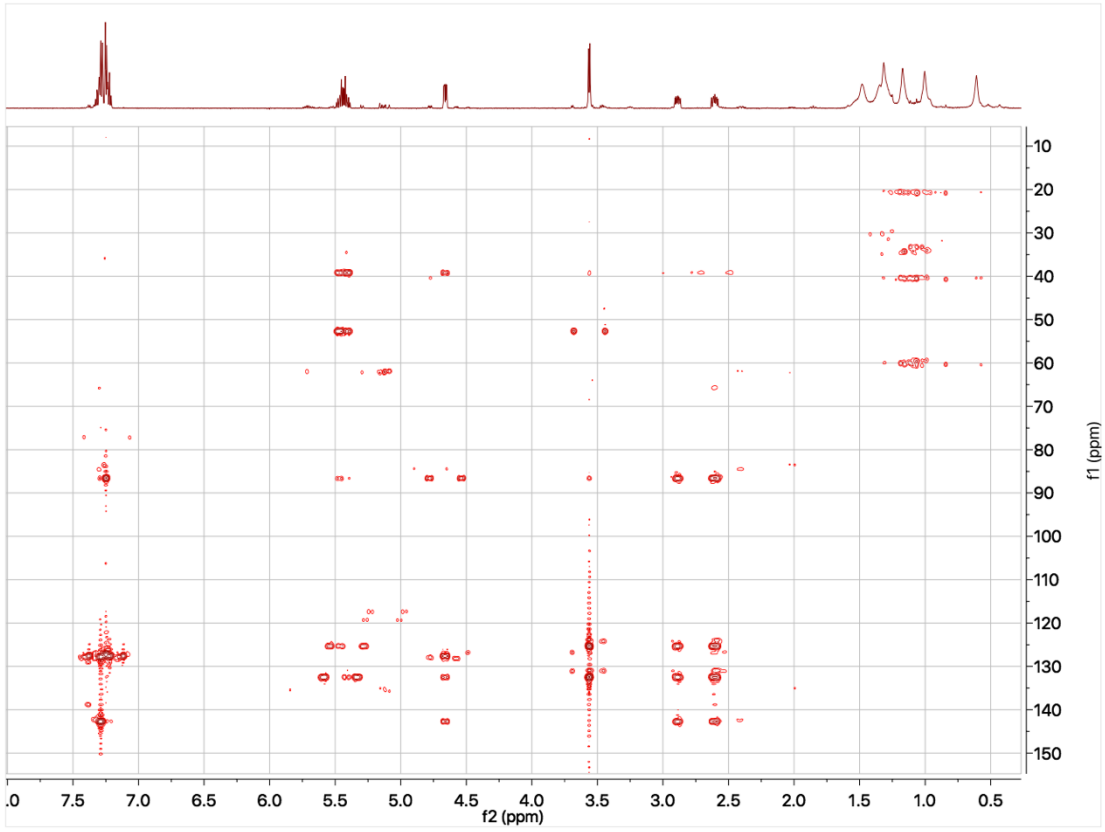

5.95 5.94 5.93 5.92 5.92 5.91 5.90 5.89 5.32 5.31 5.31 5.28 5.28 5.27 5.22 5.21 5.21 5.19 5.19 5.19 4.11 4.10 4.09 4.09 4.02 4.02 4.01 4.01 4.01 4.00 3.75 3.74 3.73 3.72 3.61 3.59 3.59 3.58 3.57 3.56 3.55 3.53 3.52 3.51 3.50 1.58 1.50 1.50 1.49 1.48 1.47 1.47 1.35 1.34 1.32 1.32 1.31 1.29 1.28 1.23 1.22 1.17 1.13
0.78
1.71
0.98
1.83
1.02
3.00
24.01
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.
f1 (ppm)

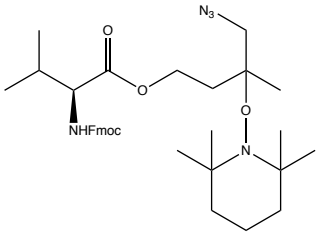

134.82
117.06
80.25
77.41
77.36
77.16
76.91
72.36
68.56
60.53
60.04
51.87
40.51
39.82
34.36
33.76
32.53
20.46
17.29
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

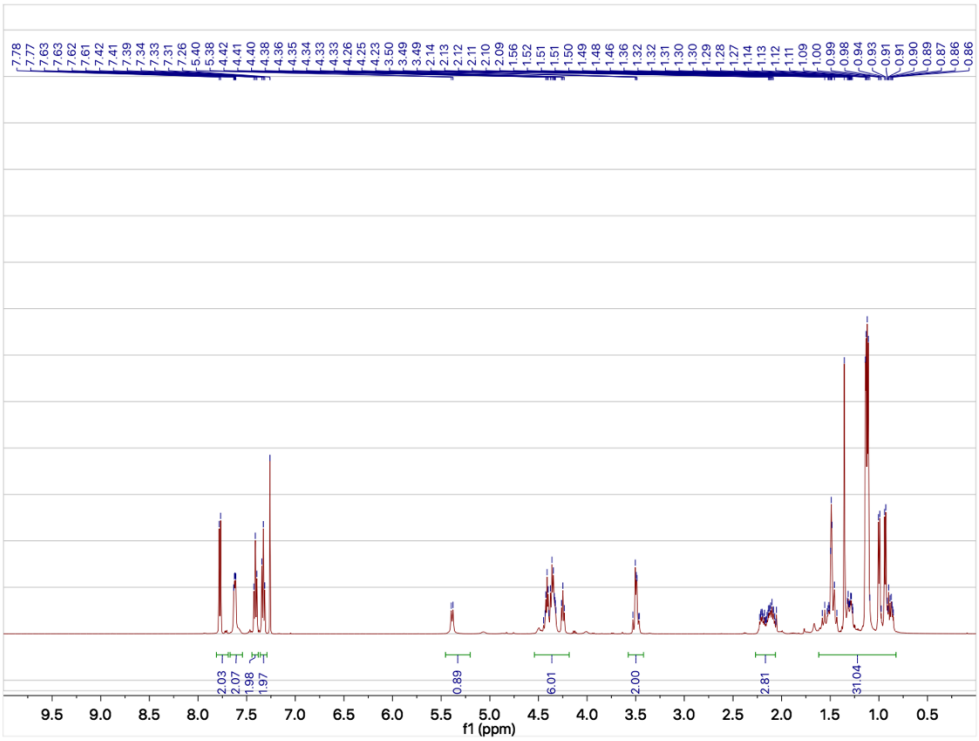

OTMP
N3

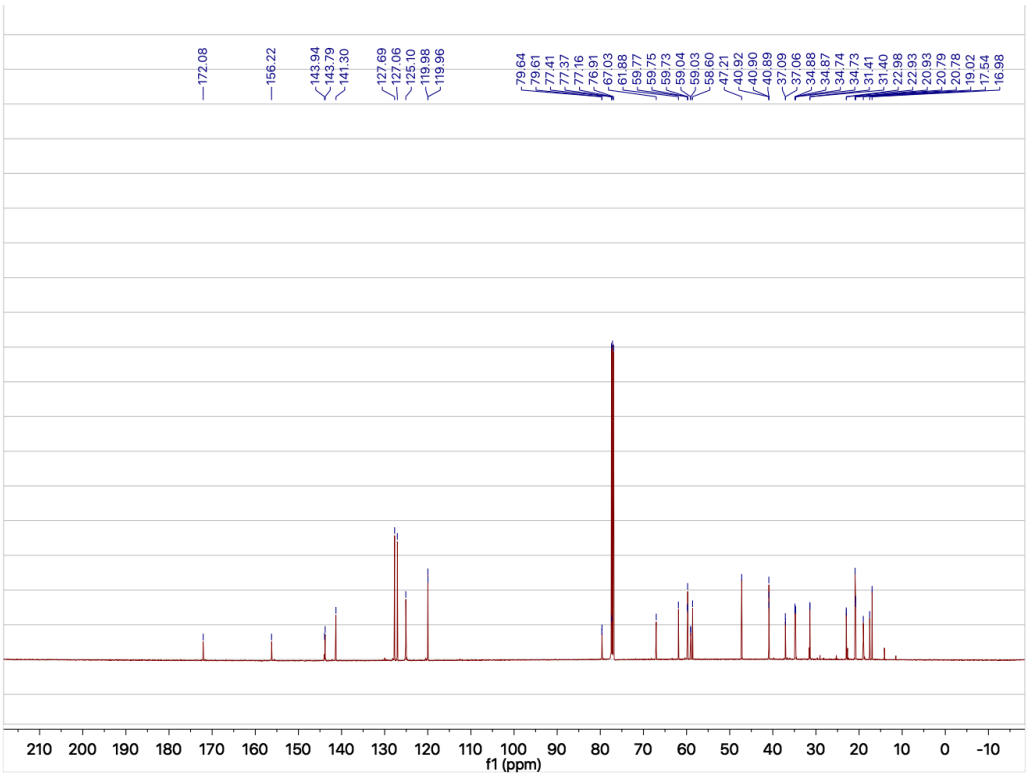
(2t)

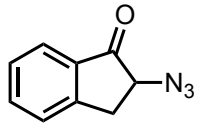

G (m) 7.26
E (m) 5.43
D (dd) 4.65
C (d) 3.55
A (dt) 2.87
B (ddd) 2.59
F (m) 1.15
f1 (ppm)


f2 (ppm)
f1 (ppm)

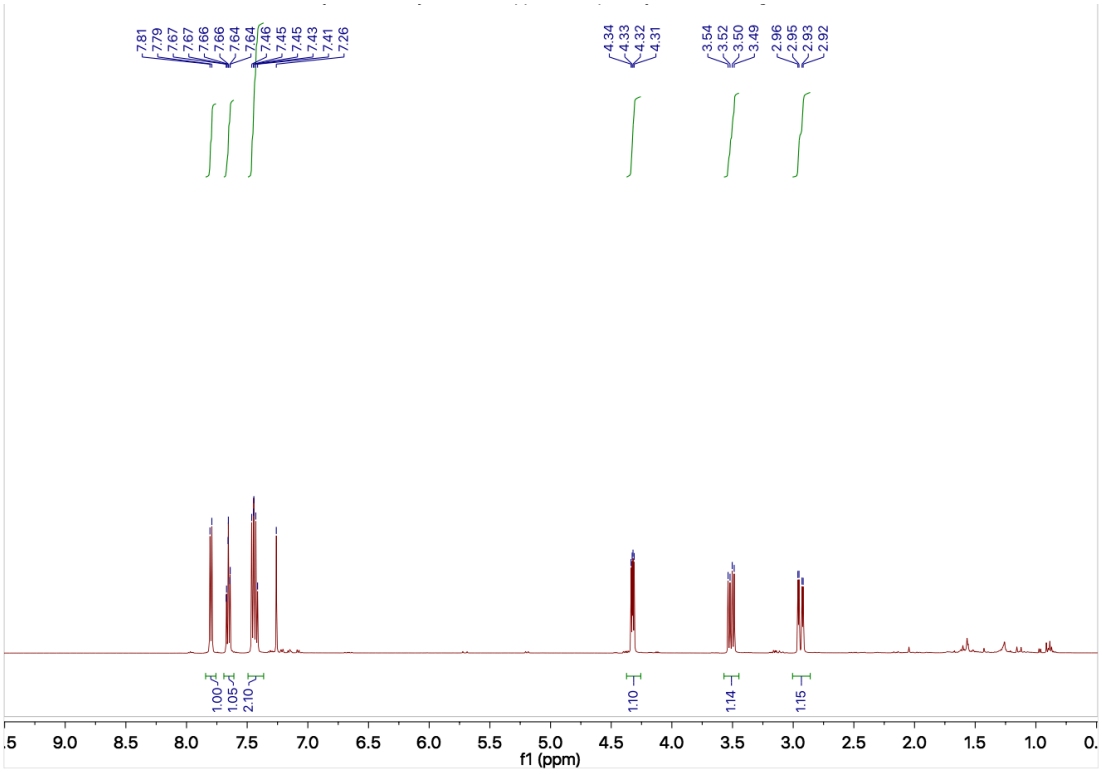

N3
O
O
O
NHFmoc
N

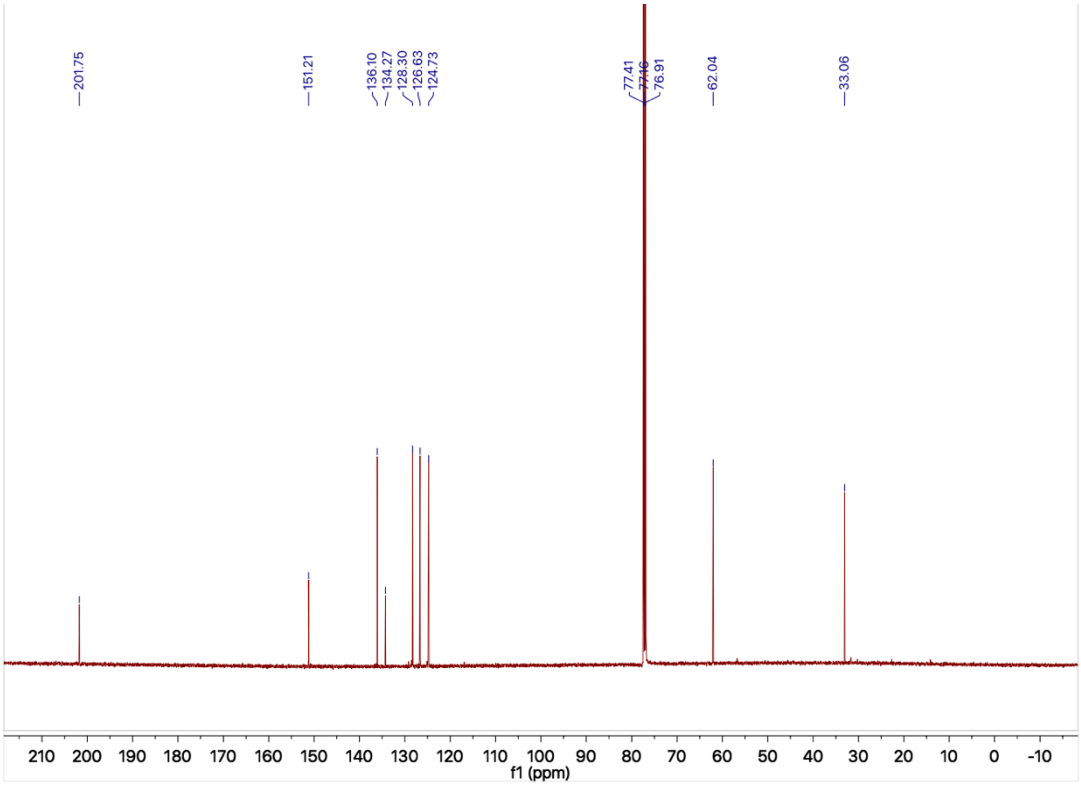

7.78 7.77 7.63 7.63 7.62 7.61 7.42 7.41 7.39 7.34 7.33 7.31 7.26 5.40 5.38 4.42 4.41 4.40 4.38 4.36 4.35 4.34 4.33 4.33 4.26 4.25 4.23 3.50 3.49 3.49 3.14 2.13 2.12 2.11 2.10 2.09 1.56 1.52 1.51 1.51 1.50 1.49 1.48 1.46 1.36 1.32 1.32 1.31 1.30 1.30 1.29 1.28 1.27 1.14 1.13 1.12 1.11 1.09 1.00 0.99 0.98 0.94 0.93 0.91 0.91 0.90 0.89 0.87 0.86 0.86
2.03 2.07 1.98 1.97 0.89 6.01 2.00 2.81 31.04
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
f1 (ppm)

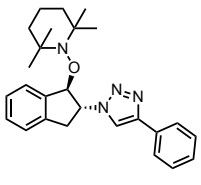

172.08 156.22 143.94 143.79 141.30 127.69 127.06 125.10 119.98 119.96
79.64 79.61 77.41 77.37 77.16 76.91 67.03 61.88 59.77 59.75 59.73 59.04 59.03 58.60 47.21 40.92 40.90 40.89 37.09 37.06 34.88 34.87 34.74 34.73 31.41 31.40 22.98 22.93 20.93 20.79 20.78 19.02 17.54 16.98
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
N3

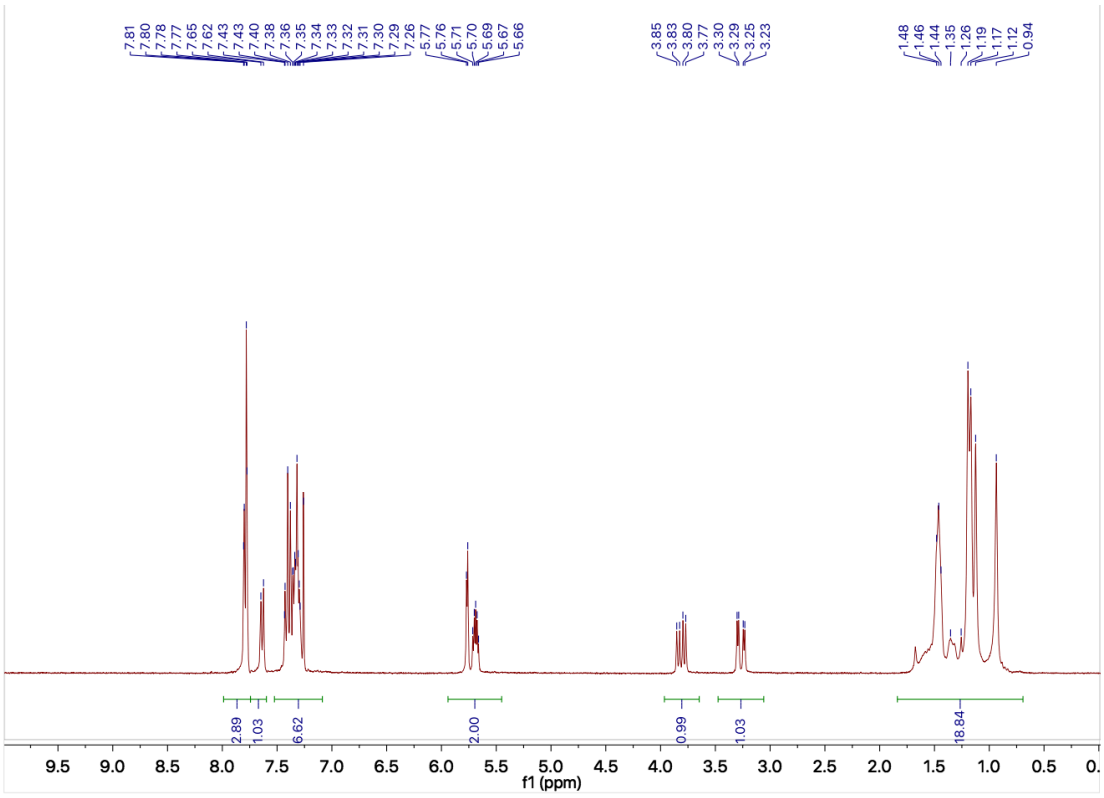
(4)

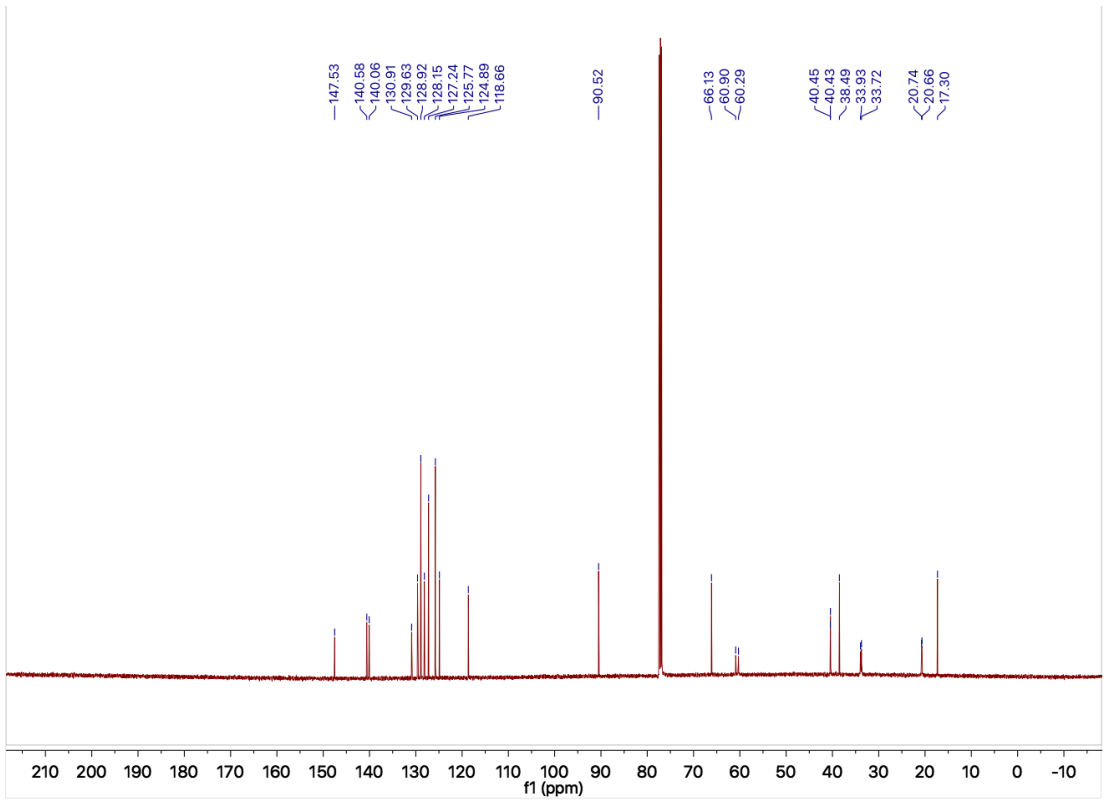

7.81
7.79
7.67
7.67
7.66
7.66
7.64
7.64
7.46
7.45
7.45
7.43
7.41
7.26
4.34
4.33
4.32
4.31
3.54
3.52
3.50
3.49
2.96
2.95
2.93
2.92
1.00
1.05
2.10
1.10
1.14
1.15
f1 (ppm)

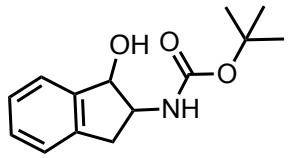

201.75
151.21
136.10
134.27
128.30
126.63
124.73
77.41
77.16
76.91
62.04
33.06
f1 (ppm)



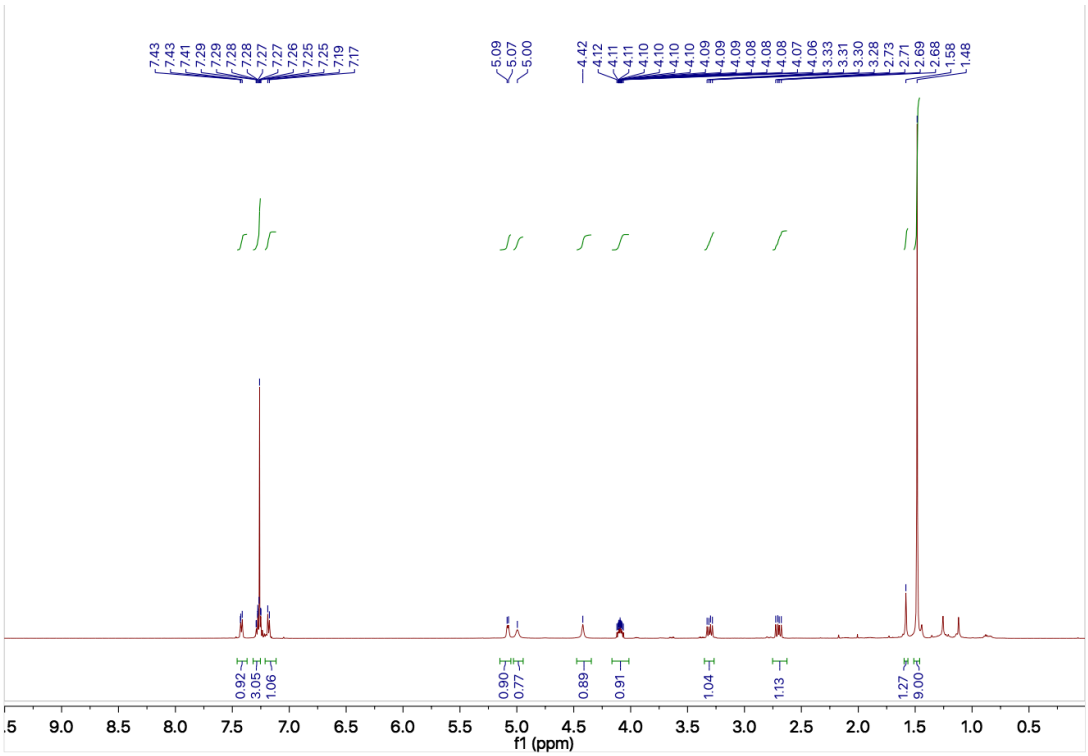
(3)

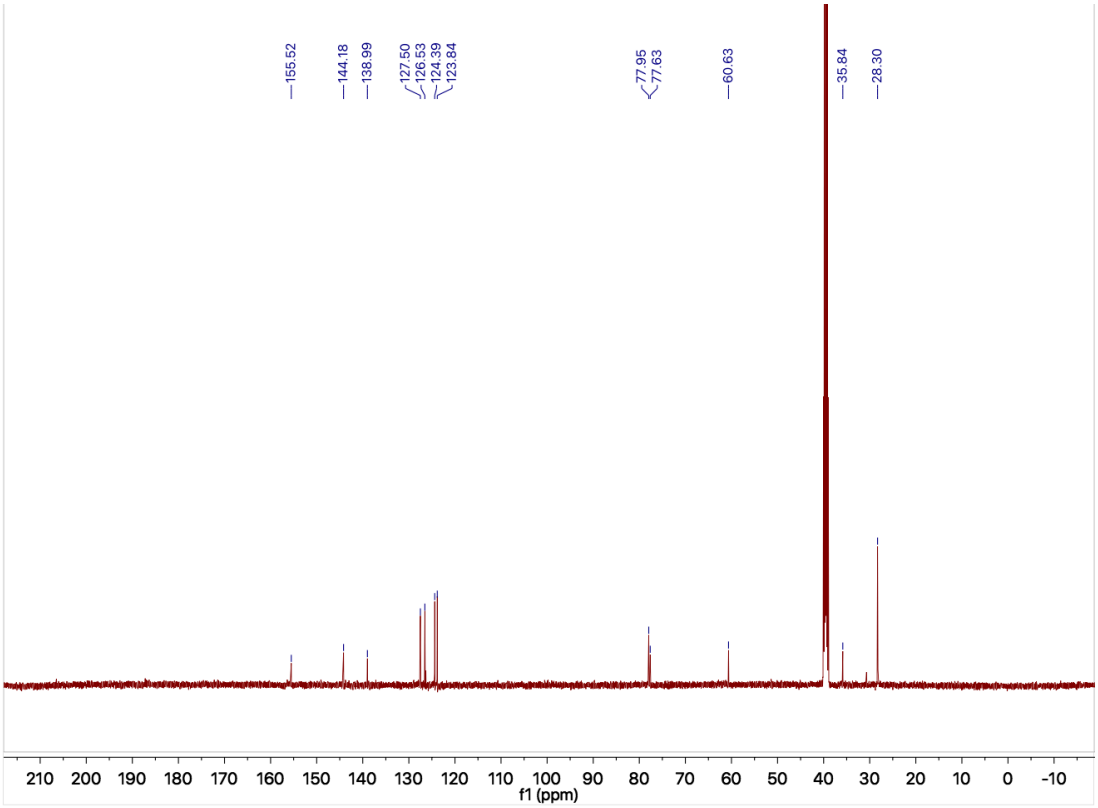

7.81
7.80
7.78
7.77
7.65
7.62
7.43
7.40
7.38
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.29
7.26
5.77
5.76
5.71
5.70
5.69
5.67
5.66
3.85
3.83
3.80
3.77
3.30
3.29
3.25
3.23
1.48
1.46
1.44
1.35
1.26
1.19
1.17
1.12
0.94
2.89
1.03
6.62
2.00
0.99
1.03
18.84
f1 (ppm)


147.53
140.58
140.06
130.91
129.63
128.92
128.15
127.24
125.77
124.89
118.66
90.52
66.13
60.90
60.29
40.45
40.43
38.49
33.93
33.72
20.74
20.66
17.30
f1 (ppm)


OH
O
O
NH

(**5**)


7.43
7.43
7.41
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.25
7.19
7.17
5.09
5.07
5.00
4.42
4.12
4.11
4.11
4.10
4.10
4.10
4.10
4.09
4.09
4.09
4.08
4.08
4.08
4.07
4.06
3.33
3.31
3.30
3.28
2.73
2.71
2.69
2.68
1.58
1.48
0.92
3.05
1.06
0.90
0.77
0.89
0.91
1.04
1.13
1.27
9.00
f1 (ppm)

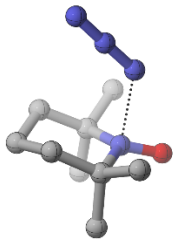

155.52
144.18
138.99
127.50
126.53
124.39
123.84
77.95
77.63
60.63
35.84
28.30
f1 (ppm)

Coordinates From Output Geometries

Identification of possible charge transfer complex structures

UB3LYP/6-31+G*

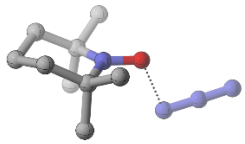
I1



C	0.21330600	0.00000200	2.15710000
C	-0.10915100	1.26694400	1.35618200
C	0.61088900	1.35690700	0.00018600
C	0.61083400	-1.35692500	0.00019600
C	-0.10923000	-1.26691600	1.35617500
H	-1.18906200	1.33357700	1.19718800
H	0.17559200	2.15813000	1.93021300
H	1.26412900	-0.00003200	2.47481300
H	-0.38184000	0.00001800	3.07779200
H	-1.18914400	-1.33347400	1.19715900
H	0.17544300	-2.15812300	1.93020700
C	2.12139700	-1.65530200	0.16934900
H	2.21879000	-2.70000800	0.48324900
H	2.65028900	-1.53696400	-0.78083500
H	2.60599100	-1.03668100	0.92652600
C	2.12146900	1.65521900	0.16930200
H	2.65032400	1.53689000	-0.78090200
H	2.21891800	2.69991000	0.48323500
H	2.60606100	1.03655200	0.92644100
C	0.00461700	2.44315900	-0.89576900
H	0.02294500	3.38785300	-0.34101000
H	0.58318600	2.56988600	-1.81454200
H	-1.02457400	2.19822500	-1.16070200
C	0.00452000	-2.44315100	-0.89576800
H	0.58316400	-2.56999700	-1.81447800
H	0.02265900	-3.38782000	-0.34096200
H	-1.02460400	-2.19805900	-1.16081000
N	0.50013900	-0.00001400	-0.73960400
O	0.83672800	-0.00003300	-1.91555600

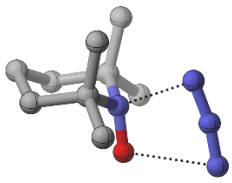
N	-1.79484800	0.00002400	-1.12228400
N	-2.67084200	0.00001600	-0.29477900
N	-3.53073400	0.00008200	0.49811500

I2



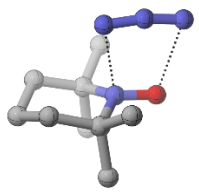
C	2.92426000	0.00010400	0.22256300
C	2.25454300	-1.25227800	-0.34810000
C	0.73905200	-1.33695300	-0.06365700
C	0.73892200	1.33696900	-0.06366000
C	2.25443000	1.25244000	-0.34807100
H	2.40936800	-1.27262600	-1.43603500
H	2.71851200	-2.16172800	0.05311100
H	2.88034400	0.00008800	1.31874000
H	3.98888700	0.00015600	-0.04153600
H	2.40927200	1.27283200	-1.43600300
H	2.71830600	2.16192400	0.05317100
C	0.44842100	1.70485000	1.41004400
H	0.73235400	2.75196900	1.56730400
H	-0.61635900	1.59253800	1.62942200
H	1.01678700	1.09511800	2.11671300
C	0.44863300	-1.70483100	1.41006400
H	-0.61614600	-1.59258600	1.62947900
H	0.73264800	-2.75192700	1.56733100
H	1.01698400	-1.09504500	2.11670100
C	0.09336800	-2.38565700	-0.98251100
H	0.61916300	-3.33738900	-0.84862900
H	-0.96191900	-2.53493000	-0.74409900
H	0.17265100	-2.09260500	-2.03482300
C	0.09316100	2.38559500	-0.98254700
H	-0.96215400	2.53475200	-0.74418000
H	0.61884400	3.33738700	-0.84865000
H	0.17251900	2.09254500	-2.03485400
N	0.11170500	-0.00002300	-0.38599100
O	-1.10125200	-0.00007800	-0.69847600
N	-2.37604900	-0.00011600	0.87628500
N	-3.39727000	0.00009200	0.23048500
N	-4.36821200	-0.00013700	-0.40936600

I3



C	2.62790000	-0.00073300	-0.41836400
C	1.81221600	-1.27118100	-0.69685100
C	0.47623000	-1.34816200	0.09188900
C	0.47707400	1.34801000	0.09185900
C	1.81294600	1.27014100	-0.69700400
H	1.57885300	-1.32643000	-1.76783600
H	2.39742500	-2.16528400	-0.44728700
H	2.99766500	-0.00076600	0.61438200
H	3.52014200	-0.00102400	-1.05705900
H	1.57949800	1.32535400	-1.76797200
H	2.39869100	2.16394500	-0.44763800
C	0.70787900	1.57782000	1.59208800
H	0.98750600	2.62920700	1.72368700
H	-0.20464900	1.39339800	2.16115000
H	1.51715300	0.98030700	2.01154200
C	0.70672000	-1.57799500	1.59214000
H	-0.20592400	-1.39326300	2.16092000
H	0.98602400	-2.62945700	1.72383200
H	1.51605100	-0.98067000	2.01172800
C	-0.40564000	-2.47807100	-0.45112800
H	0.12969700	-3.42392000	-0.31431000
H	-1.34783800	-2.53560000	0.10225200
H	-0.62948800	-2.35261600	-1.51109800
C	-0.40428600	2.47826700	-0.45121800
H	-1.34633400	2.53640200	0.10235400
H	0.13158700	3.42385800	-0.31474200
H	-0.62843800	2.35267300	-1.51111500
N	-0.22889900	0.00014700	-0.24444000
O	-0.79693900	0.00044800	-1.35494700
N	-1.85058200	0.00062400	1.17565200
N	-2.64908400	0.00057900	0.27941000
N	-3.25262800	0.00032500	-0.71829200

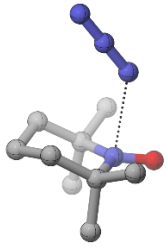
I4



C	2.16086200	0.00042600	-1.27024600
C	1.29777500	-1.26065500	-1.14928000
C	0.50177400	-1.35308400	0.16361100
C	0.50114100	1.35319200	0.16351300
C	1.29709200	1.26104400	-1.14943000
H	0.59123100	-1.29456200	-1.98461400
H	1.92319900	-2.16036900	-1.21549800
H	2.95910300	0.00068900	-0.51680800
H	2.66399800	0.00050900	-2.24484300
H	0.59047400	1.29446300	-1.98472500
H	1.92201700	2.16109000	-1.21577600
C	1.41141500	1.65390900	1.37804200
H	1.76115900	2.68817700	1.29205500
H	0.84969300	1.56165700	2.31244900
H	2.29355100	1.01389700	1.43181400
C	1.41195900	-1.65338700	1.37823000
H	0.85018000	-1.56092300	2.31258400
H	1.76172600	-2.68767700	1.29252700
H	2.29407700	-1.01334500	1.43189100
C	-0.56248700	-2.45534200	0.08562000
H	-0.04801800	-3.41513900	-0.03357400
H	-1.16222100	-2.49661300	0.99810500
H	-1.22150900	-2.30967600	-0.77122400
C	-0.56345700	2.45515800	0.08556600
H	-1.16342300	2.49595500	0.99792000
H	-0.04921200	3.41513600	-0.03314000
H	-1.22227700	2.30980100	-0.77150500
N	-0.20282500	-0.00002600	0.43524300
O	-1.03507300	-0.00020600	1.35515200
N	-1.54116200	-0.00038200	-1.43472800
N	-2.46714300	-0.00046200	-0.67899100
N	-3.22452900	-0.00041400	0.21381600

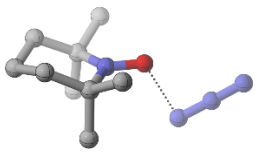
UB3LYP/def2TZVP/PCM

I1



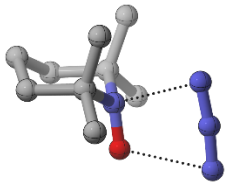
C	-0.35211200	-0.00001400	2.13763500
C	-0.00480900	-1.25739500	1.34758600
C	-0.69557200	-1.35538800	-0.01772400
C	-0.69559500	1.35538200	-0.01770000
C	-0.00479900	1.25736500	1.34759200
H	1.07336100	-1.30570700	1.19315800
H	-0.28724400	-2.15085100	1.90783900
H	-1.40522000	-0.00000900	2.42647900
H	0.21511700	-0.00001900	3.06991400
H	1.07337000	1.30566000	1.19314200
H	-0.28721100	2.15082100	1.90785500
C	-2.20475900	1.66171300	0.11583400
H	-2.28777900	2.70066600	0.43404800
H	-2.71144900	1.55766200	-0.84287200
H	-2.70569600	1.04415100	0.85495600
C	-2.20472800	-1.66176300	0.11578200
H	-2.71140400	-1.55770600	-0.84293000
H	-2.28772700	-2.70072400	0.43397400
H	-2.70569100	-1.04422800	0.85490800
C	-0.05033400	-2.41559000	-0.90571200
H	-0.04225500	-3.35095500	-0.34606800
H	-0.61409400	-2.57240000	-1.82339600
H	0.97119500	-2.13420200	-1.15098200
C	-0.05039300	2.41560700	-0.90568700
H	-0.61416600	2.57241100	-1.82336500
H	-0.04233100	3.35096700	-0.34603500
H	0.97114000	2.13424400	-1.15096900
N	-0.59782400	0.00000700	-0.74531700
O	-0.71073900	0.00003000	-1.93544600
N	2.05127300	0.00004100	-0.98304400
N	2.94891600	0.00002300	-0.21318400
N	3.83515000	-0.00000300	0.54558400

I2



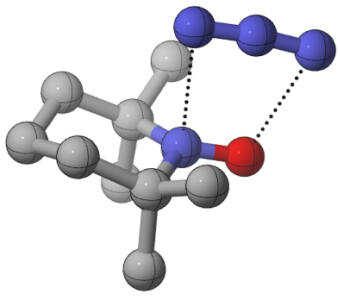
C	2.93959400	-0.06383300	0.19613600
C	2.23731000	-1.29225500	-0.36784400
C	0.73220000	-1.35147300	-0.06028200
C	0.80360000	1.33975500	-0.06594800
C	2.30432600	1.19966900	-0.36929700
H	2.37198200	-1.31262000	-1.45281100
H	2.67951600	-2.21066500	0.02222300
H	2.91217000	-0.06281900	1.28775500
H	3.99452100	-0.09214800	-0.08182000
H	2.44281300	1.21254600	-1.45384300
H	2.79344000	2.09358200	0.02157800
C	0.53647200	1.71011800	1.40581000
H	0.85210900	2.74394900	1.54891300
H	-0.52610700	1.63528300	1.63290800
H	1.09295300	1.08862400	2.10296800
C	0.45008600	-1.69861700	1.41443700
H	-0.60667500	-1.56700100	1.64289800
H	0.71205500	-2.74649300	1.56319900
H	1.03972700	-1.10265700	2.10671200
C	0.04111800	-2.36757900	-0.97002400
H	0.55171700	-3.32354200	-0.85360100
H	-1.00547600	-2.50292800	-0.70660900
H	0.10685200	-2.06883500	-2.01643800
C	0.16945900	2.38598700	-0.98317500
H	-0.86884500	2.57847000	-0.72264600
H	0.73034100	3.31379900	-0.87103600
H	0.22111200	2.07811700	-2.02773500
N	0.10879700	0.01091500	-0.33350700
O	-1.06096500	0.04093400	-0.64955300
N	-2.60867400	0.06813800	1.00982700
N	-3.48990100	0.03185300	0.22060600
N	-4.33757700	-0.00416000	-0.57479500

I3



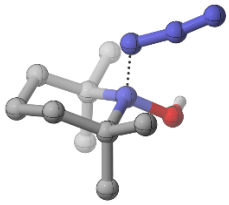
C	2.66565400	0.00133700	-0.30671100
C	1.87410200	-1.26174500	-0.63654900
C	0.49764600	-1.35074000	0.07650400
C	0.49609500	1.35109100	0.07684600
C	1.87282200	1.26375600	-0.63595400
H	1.69969500	-1.31255900	-1.71453800
H	2.43660200	-2.15535100	-0.35891900
H	2.97425400	0.00125100	0.74024500
H	3.58840500	0.00194100	-0.89079800
H	1.69850400	1.31491600	-1.71394200
H	2.43436000	2.15780800	-0.35781800
C	0.64504100	1.58329800	1.57977100
H	0.94433600	2.62290400	1.71619100
H	-0.30057400	1.42770100	2.09173200
H	1.40794500	0.96903600	2.04491100
C	0.64768500	-1.58312100	1.57930800
H	-0.29751300	-1.42818100	2.09221600
H	0.94755000	-2.62263100	1.71526500
H	1.41076200	-0.96866900	2.04394200
C	-0.34472000	-2.47223600	-0.52314100
H	0.16463700	-3.41471900	-0.32331500
H	-1.32864400	-2.51302800	-0.05579600
H	-0.46746500	-2.36876000	-1.59779700
C	-0.34740100	2.47159000	-0.52306900
H	-1.33132600	2.51166500	-0.05567100
H	0.16111700	3.41459900	-0.32362000
H	-0.47014600	2.36761500	-1.59769300
N	-0.17810500	-0.00007600	-0.29250900
O	-0.80161800	-0.00002300	-1.34207900
N	-2.03441500	-0.00135400	1.23176800
N	-2.71288100	-0.00113300	0.26927200
N	-3.26047000	-0.00097000	-0.75710200

I4



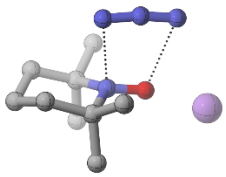
C	2.10247700	-0.00009300	-1.34632800
C	1.25121800	-1.25579100	-1.18310800
C	0.52797200	-1.35454000	0.16370800
C	0.52808900	1.35448600	0.16373900
C	1.25142400	1.25573600	-1.18303100
H	0.50403400	-1.28973900	-1.97672200
H	1.86769100	-2.15182700	-1.28152100
H	2.93620400	-0.00018500	-0.64055200
H	2.55049100	-0.00010000	-2.34172000
H	0.50428500	1.28987100	-1.97667500
H	1.86805100	2.15168000	-1.28135000
C	1.49791800	1.65834100	1.32468900
H	1.84060200	2.68592900	1.20449100
H	0.98847900	1.57928500	2.28458500
H	2.37435500	1.01731800	1.33466300
C	1.49784400	-1.65841900	1.32461800
H	0.98846100	-1.57932600	2.28454300
H	1.84047800	-2.68602100	1.20441400
H	2.37430800	-1.01743000	1.33453700
C	-0.54229900	-2.44353900	0.13670800
H	-0.04241200	-3.39183300	-0.06123300
H	-1.05741600	-2.52589600	1.09163500
H	-1.26620900	-2.26634400	-0.65426800
C	-0.54207400	2.44358700	0.13665000
H	-1.05713500	2.52612400	1.09158600
H	-0.04210900	3.39180800	-0.06145200
H	-1.26603000	2.26633200	-0.65426800
N	-0.14531800	-0.00001400	0.49254100
O	-0.97732200	-0.00005600	1.37901100
N	-1.71624000	0.00004900	-1.46971800
N	-2.53723500	0.00011500	-0.62765700
N	-3.24734500	0.00016300	0.29645700

I4, proton adduct



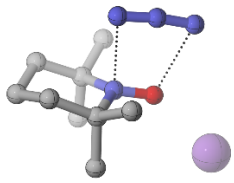
C	2.00945100	-0.78536400	-1.29749300
C	0.75354600	-1.63966200	-1.13746100
C	-0.01719300	-1.41574100	0.16730300
C	1.01086300	1.13791700	0.08920600
C	1.69257500	0.70674700	-1.21386900
H	0.08292100	-1.46760800	-1.98077100
H	1.01277800	-2.69972900	-1.15642800
H	2.76365800	-1.06308600	-0.55935100
H	2.45277500	-0.99393100	-2.27193400
H	1.06985400	1.00247500	-2.05943600
H	2.61051600	1.29340600	-1.28219500
C	1.92829200	1.01526200	1.30703800
H	2.57654000	1.89069900	1.29632000
H	1.38624600	1.02480200	2.25023600
H	2.56840000	0.14188200	1.28023700
C	0.74033200	-1.89617500	1.40479200
H	0.27658400	-1.55454200	2.32674800
H	0.69033400	-2.98445300	1.39262300
H	1.78884800	-1.62509700	1.40815500
C	-1.38058600	-2.10421600	0.12291100
H	-1.19224700	-3.17710400	0.10913000
H	-1.97959800	-1.88865400	1.00619800
H	-1.94423100	-1.86984200	-0.77703300
C	0.49818400	2.57542500	-0.00486600
H	0.04902100	2.93540600	0.92427300
H	1.36849800	3.20663700	-0.18053900
H	-0.19569700	2.72555100	-0.82646600
N	-0.27969700	0.17677800	0.26046300
O	-0.91758300	0.39286400	1.48060000
N	-1.15290500	0.53710100	-0.88007300
N	-2.34493800	0.64342000	-0.55153400
N	-3.44638800	0.79188600	-0.40369800
H	-0.88982400	1.35082000	1.65395800

I4, lithium adduct



C	2.37369900	0.00009300	-1.04214300
C	1.50751200	-1.25578000	-1.04345400
C	0.54970700	-1.35861800	0.14745200
C	0.54953800	1.35867900	0.14738200
C	1.50736100	1.25586000	-1.04351900
H	0.92264000	-1.29041200	-1.96318200
H	2.13226100	-2.15118000	-1.02628500
H	3.05852300	0.00015400	-0.19145200
H	3.00256600	0.00011300	-1.93417000
H	0.92248800	1.29036500	-1.96325400
H	2.13200300	2.15133500	-1.02640500
C	1.29391200	1.65185800	1.46616900
H	1.65811900	2.67752600	1.41309100
H	0.62145000	1.57477500	2.31952300
H	2.15088500	1.00624900	1.62971100
C	1.29412900	-1.65164900	1.46624500
H	0.62172600	-1.57436200	2.31962700
H	1.65823500	-2.67736200	1.41331700
H	2.15117800	-1.00609900	1.62963000
C	-0.48903700	-2.45673900	-0.07030100
H	0.04256700	-3.40640000	-0.12826500
H	-1.19191100	-2.51586700	0.75843400
H	-1.03196700	-2.31222100	-1.00032000
C	-0.48932500	2.45666900	-0.07046200
H	-1.19237800	2.51558800	0.75813700
H	0.04213900	3.40642200	-0.12819800
H	-1.03203800	2.31219000	-1.00061500
N	-0.18216800	-0.00000400	0.33753000
O	-1.11928700	-0.00006600	1.12822000
N	-1.31756200	-0.00008300	-1.69315300
N	-2.31608300	-0.00018100	-1.06655300
N	-3.20358400	-0.00021600	-0.31740000
Li	-2.38779600	0.00028600	2.84257700

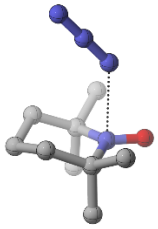
I4, sodium adduct



C	2.78062200	0.38515300	-0.00282300
C	2.07785600	-0.12430400	1.25221400
C	0.60565200	0.28630700	1.35468200
C	0.59919800	0.28965500	-1.35639400
C	2.07443100	-0.11337500	-1.26007600
H	2.13805200	-1.21271500	1.28464700
H	2.57604900	0.25231000	2.14811400
H	2.84216600	1.47565900	0.00180900
H	3.81127500	0.02575400	-0.00616800
H	2.13879600	-1.20142100	-1.30281500
H	2.56863800	0.27277700	-2.15407200
C	0.42404900	1.79287200	-1.65412300
H	0.75083600	1.96343300	-2.67978200
H	-0.62377100	2.08173600	-1.57939200
H	1.01574600	2.43372100	-1.00790100
C	0.44808800	1.79052500	1.65533700
H	-0.59391900	2.09755800	1.57920200
H	0.77435300	1.95260300	2.68259100
H	1.05191400	2.42469500	1.01394300
C	-0.11285600	-0.49800800	2.45028300
H	0.37158700	-0.26105400	3.39765300
H	-1.16082100	-0.21467900	2.52748900
H	-0.03616900	-1.56885500	2.28503000
C	-0.11447100	-0.50028200	-2.45153700
H	-1.16513000	-0.22689300	-2.52764500
H	0.36718200	-0.25827000	-3.39914100
H	-0.02700500	-1.57027500	-2.28665400
N	-0.10302700	0.02157000	-0.00045600
O	-1.32435000	0.08565400	0.00114100
N	0.18617400	-2.36093200	0.00000500
N	-0.99068300	-2.40668400	0.00048300
N	-2.14838400	-2.29539900	0.00232500
Na	-3.40990500	1.84432200	0.00655200

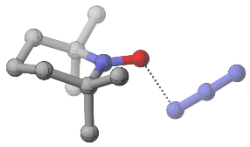
UB3LYP/6-311+G/CPCM**

I1



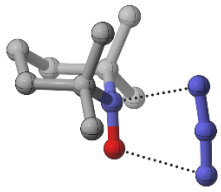
C	0.39693300	0.00000100	2.14412600
C	0.03244900	1.25993500	1.35868700
C	0.70132100	1.36012200	-0.02108300
C	0.70133300	-1.36011800	-0.02108200
C	0.03245700	-1.25993500	1.35868700
H	-1.04977700	1.30568500	1.22119300
H	0.32282300	2.15525800	1.91490100
H	1.45704800	0.00000500	2.41276600
H	-0.15289300	0.00000000	3.08854200
H	-1.04976800	-1.30569000	1.22119000
H	0.32283600	-2.15525600	1.91490200
C	2.21576500	-1.66757900	0.08563100
H	2.30303300	-2.70553200	0.41203700
H	2.70415500	-1.57359500	-0.88544600
H	2.73295500	-1.04351700	0.81052800
C	2.21575100	1.66759500	0.08562800
H	2.70414000	1.57361500	-0.88544900
H	2.30301200	2.70554900	0.41203600
H	2.73294500	1.04353500	0.81052300
C	0.03591900	2.41937700	-0.90122000
H	0.03820700	3.35779200	-0.34328900
H	0.58204600	2.57382000	-1.83186700
H	-0.99141200	2.13467500	-1.12450400
C	0.03594100	-2.41938000	-0.90121900
H	0.58207200	-2.57382000	-1.83186400
H	0.03823500	-3.35779300	-0.34328600
H	-0.99139100	-2.13468400	-1.12450600
N	0.59161700	0.00000100	-0.74741400
O	0.67730300	0.00000100	-1.94302900
N	-2.05128300	-0.00001400	-0.94405200
N	-2.97295800	0.00000300	-0.19702700
N	-3.88364800	-0.00001500	0.54090700

I2



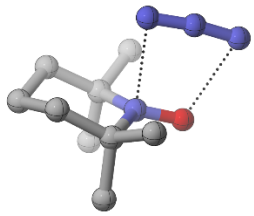
C	-2.94344000	-0.00034800	0.21174200
C	-2.27845800	1.24886400	-0.36180300
C	-0.76990000	1.35091400	-0.06574100
C	-0.76950400	-1.35099400	-0.06568000
C	-2.27809400	-1.24940000	-0.36173200
H	-2.42279000	1.26372500	-1.44716100
H	-2.74264500	2.15691200	0.03150800
H	-2.90497000	-0.00031000	1.30467900
H	-4.00287200	-0.00051000	-0.05634900
H	-2.42243300	-1.26436700	-1.44708800
H	-2.74201300	-2.15755900	0.03163700
C	-0.48260500	-1.70866200	1.40912800
H	-0.77200600	-2.75112500	1.55812300
H	0.58085900	-1.60563500	1.62840500
H	-1.05126100	-1.09761100	2.10843900
C	-0.48313100	1.70872300	1.40906300
H	0.58035600	1.60599300	1.62836500
H	-0.77282400	2.75111100	1.55801200
H	-1.05163100	1.09753800	2.10838400
C	-0.11050800	2.38209200	-0.98788300
H	-0.64189400	3.32809300	-0.86738700
H	0.93723400	2.54120100	-0.73569000
H	-0.18228900	2.07896400	-2.03437900
C	-0.10981400	-2.38199800	-0.98780000
H	0.93797800	-2.54078400	-0.73561400
H	-0.64091400	-3.32815600	-0.86726800
H	-0.18170100	-2.07892500	-2.03430400
N	-0.11015400	0.00005800	-0.33899800
O	1.06338100	0.00022300	-0.65339800
N	2.60432600	0.00051500	1.01313200
N	3.49329900	0.00018900	0.22592700
N	4.34702800	-0.00011700	-0.57161700

I3



C	2.66881100	-0.00015100	-0.31451900
C	1.87314900	-1.26599200	-0.64281100
C	0.49707000	-1.35471400	0.07780000
C	0.49722700	1.35468200	0.07775100
C	1.87330000	1.26577400	-0.64285100
H	1.69369900	-1.31596000	-1.72162400
H	2.43701500	-2.16135000	-0.36724300
H	2.98150300	-0.00015000	0.73292200
H	3.59056200	-0.00021600	-0.90302000
H	1.69385400	1.31572700	-1.72166500
H	2.43727200	2.16107400	-0.36731500
C	0.65086600	1.58270700	1.58420700
H	0.94793700	2.62451300	1.72306900
H	-0.29429800	1.42247700	2.09894800
H	1.41868600	0.96870800	2.04556100
C	0.65071000	-1.58272400	1.58426300
H	-0.29433800	-1.42211800	2.09909700
H	0.94738200	-2.62464000	1.72315500
H	1.41882100	-0.96901400	2.04552600
C	-0.35208400	-2.47778300	-0.51855000
H	0.15978500	-3.42202600	-0.32410600
H	-1.33334800	-2.51958400	-0.04187800
H	-0.48323100	-2.37179600	-1.59370800
C	-0.35177300	2.47785200	-0.51862900
H	-1.33307400	2.51971500	-0.04204400
H	0.16016100	3.42204400	-0.32410100
H	-0.48283100	2.37192000	-1.59380300
N	-0.18103900	0.00002100	-0.29105000
O	-0.80149800	0.00002300	-1.34784300
N	-2.01511200	0.00028800	1.22653300
N	-2.71530200	0.00010900	0.27339100
N	-3.27386600	-0.00004700	-0.75244500

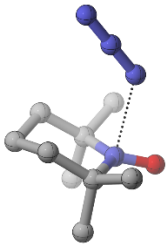
I4



C	2.10272900	-0.00001200	1.35045100
C	1.24973500	1.25920900	1.18633400
C	0.52770800	1.35879800	-0.16486300
C	0.52769200	-1.35880100	-0.16486300
C	1.24972100	-1.25922400	1.18633300
H	0.49994500	1.29335000	1.97939400
H	1.86773900	2.15613100	1.28552600
H	2.93869200	-0.00001700	0.64478600
H	2.54997600	-0.00001500	2.34792000
H	0.49993000	-1.29335700	1.97939200
H	1.86771500	-2.15615300	1.28552400
C	1.50139700	-1.65735200	-1.32814800
H	1.84519100	-2.68673200	-1.21024100
H	0.99284100	-1.57609300	-2.29021700
H	2.37907600	-1.01522700	-1.33430300
C	1.50141500	1.65733500	-1.32815000
H	0.99285700	1.57608400	-2.29021800
H	1.84522600	2.68670900	-1.21024300
H	2.37908400	1.01519600	-1.33430700
C	-0.54463900	2.45076800	-0.14227000
H	-0.04455300	3.40048400	0.05781700
H	-1.05652700	2.53289200	-1.10092400
H	-1.27249700	2.27432400	0.64730600
C	-0.54466400	-2.45076200	-0.14227000
H	-1.05653300	-2.53290100	-1.10093400
H	-0.04459100	-3.40047800	0.05784800
H	-1.27253900	-2.27429700	0.64728600
N	-0.15071900	0.00000400	-0.49018300
O	-0.98368700	0.00001400	-1.38186100
N	-1.68895800	0.00002100	1.45950600
N	-2.53616500	0.00000900	0.63664900
N	-3.26245900	-0.00000100	-0.28052200

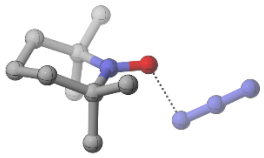
UB3LYP/cc-pvtz/PCM

I1



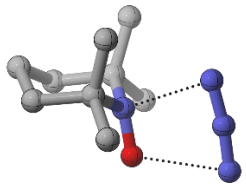
C	0.28641500	0.00000600	2.13668500
C	-0.04508800	1.25876300	1.34056800
C	0.67284900	1.35721500	-0.01017600
C	0.67290400	-1.35719500	-0.01016900
C	-0.04504000	-1.25876600	1.34057300
H	-1.11926300	1.31001200	1.16964400
H	0.22790200	2.15002700	1.90716500
H	1.33309700	0.00002700	2.44464300
H	-0.29756900	-0.00000300	3.05737100
H	-1.11921300	-1.31005600	1.16964500
H	0.22798200	-2.15001700	1.90717300
C	2.17906200	-1.66174000	0.15404200
H	2.25830200	-2.69831200	0.47795100
H	2.70295700	-1.56041100	-0.79451400
H	2.66494600	-1.04101800	0.89928800
C	2.17899500	1.66182200	0.15403200
H	2.70289100	1.56051300	-0.79452600
H	2.25819300	2.69839800	0.47793800
H	2.66490600	1.04112200	0.89927700
C	0.04856800	2.41954100	-0.91075000
H	0.03810700	3.35660800	-0.35574800
H	0.62754200	2.56785700	-1.81921700
H	-0.96915400	2.14346400	-1.17183600
C	0.04866800	-2.41955200	-0.91073900
H	0.62765100	-2.56784900	-1.81920400
H	0.03824500	-3.35661600	-0.35573300
H	-0.96906400	-2.14351900	-1.17183000
N	0.58830000	0.00000700	-0.74256300
O	0.76570500	0.00000800	-1.92785200
N	-1.99546900	-0.00005000	-1.04536200
N	-2.86774700	-0.00005400	-0.24371000
N	-3.72624100	-0.00002400	0.54462600

I2



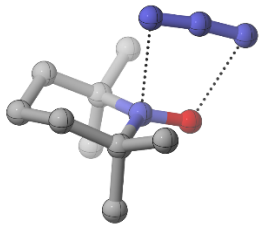
C	-2.92995000	0.11034900	0.23128200
C	-2.21391600	1.32542200	-0.34527200
C	-0.70331300	1.35513800	-0.06206500
C	-0.82685500	-1.33405700	-0.07214600
C	-2.32970100	-1.16419500	-0.34848700
H	-2.36555200	1.34640200	-1.42703100
H	-2.63237900	2.25170800	0.04965000
H	-2.88091400	0.10727500	1.32124500
H	-3.98837700	0.15948300	-0.02574700
H	-2.48737400	-1.16992900	-1.42947400
H	-2.82938800	-2.04885300	0.04731400
C	-0.54160600	-1.71850600	1.39251500
H	-0.87689600	-2.74494600	1.53774800
H	0.52526000	-1.66663500	1.60000400
H	-1.07132800	-1.08811500	2.10126500
C	-0.39081400	1.69784900	1.40757500
H	0.66653800	1.54859800	1.61686100
H	-0.63414400	2.74842700	1.56249900
H	-0.97681200	1.10985300	2.10856600
C	-0.00842500	2.35787200	-0.98437700
H	-0.49326200	3.32472300	-0.85656900
H	1.04560100	2.46735200	-0.74347900
H	-0.10295300	2.06252400	-2.02864700
C	-0.23021800	-2.38787300	-1.00654700
H	0.80951000	-2.59699900	-0.76975200
H	-0.80271700	-3.30645400	-0.88612600
H	-0.29946000	-2.07501700	-2.04770800
N	-0.11128500	-0.01832200	-0.34674900
O	1.06068600	-0.07047200	-0.66690700
N	2.56829900	-0.12428000	0.98874600
N	3.47490800	-0.05632700	0.22745600
N	4.34778500	0.01070000	-0.53662900

I3



C	2.66173200	0.00049600	-0.31210400
C	1.86843900	-1.26283100	-0.63994600
C	0.49527000	-1.35151900	0.07751000
C	0.49473100	1.35163200	0.07762500
C	1.86793600	1.26353700	-0.63983400
H	1.69039100	-1.31179900	-1.71640900
H	2.43209000	-2.15575500	-0.36619500
H	2.97160600	0.00051200	0.73349900
H	3.58244400	0.00070800	-0.89743100
H	1.68987700	1.31252300	-1.71629600
H	2.43123500	2.15666000	-0.36600600
C	0.64754500	1.58475500	1.58014400
H	0.94801900	2.62322900	1.71609400
H	-0.29705600	1.42981800	2.09212700
H	1.40964300	0.96974500	2.04381000
C	0.64822600	-1.58467200	1.58000100
H	-0.29641000	-1.43009200	2.09202800
H	0.94906900	-2.62304900	1.71588400
H	1.41013300	-0.96942300	2.04366900
C	-0.35070100	-2.47209100	-0.51975800
H	0.15890700	-3.41449400	-0.32494900
H	-1.33122400	-2.51307400	-0.04746300
H	-0.47961100	-2.36535300	-1.59239600
C	-0.35172100	2.47184100	-0.51963800
H	-1.33224600	2.51245500	-0.04731500
H	0.15751900	3.41445100	-0.32488100
H	-0.48063100	2.36501000	-1.59227100
N	-0.18369400	-0.00005300	-0.28752700
O	-0.80444900	-0.00006600	-1.34220600
N	-2.02419900	-0.00061700	1.23370100
N	-2.70252100	-0.00037100	0.26990500
N	-3.24200100	-0.00016500	-0.76062800

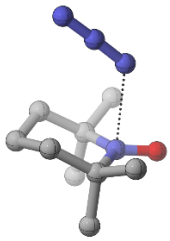
I4



C	2.11768100	-0.00000500	1.32608500
C	1.26339500	1.25578900	1.17540800
C	0.52386100	1.35571500	-0.16229800
C	0.52385200	-1.35572200	-0.16229000
C	1.26337800	-1.25578900	1.17542000
H	0.52661200	1.28699700	1.97738300
H	1.87953000	2.15146500	1.26820000
H	2.93921000	-0.00001400	0.60780600
H	2.58046200	-0.00000300	2.31355500
H	0.52659200	-1.28697800	1.97739300
H	1.87950000	-2.15147200	1.26822300
C	1.47839700	-1.66001900	-1.33537000
H	1.82720000	-2.68487800	-1.21749600
H	0.95491700	-1.58570200	-2.28697200
H	2.35113800	-1.01581800	-1.36066600
C	1.47840600	1.66000900	-1.33537700
H	0.95493200	1.58566800	-2.28698000
H	1.82718700	2.68487800	-1.21751800
H	2.35116100	1.01582600	-1.36065800
C	-0.54649000	2.44444700	-0.12101200
H	-0.04428600	3.39563100	0.05025200
H	-1.08686100	2.51165300	-1.06196000
H	-1.24787100	2.27560100	0.69038400
C	-0.54651200	-2.44444200	-0.12100800
H	-1.08692300	-2.51159700	-1.06193800
H	-0.04431100	-3.39563900	0.05018700
H	-1.24786200	-2.27563500	0.69042400
N	-0.15527700	-0.00000500	-0.48282200
O	-0.98599100	-0.00001700	-1.37433900
N	-1.69442600	0.00000300	1.46802400
N	-2.52482500	0.00002200	0.63352900
N	-3.23807400	0.00001700	-0.28762400

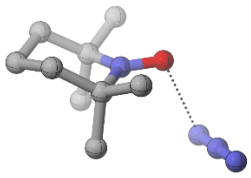
M06-2X/def2TZVP/PCM

I1



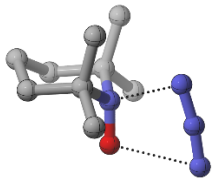
C	0.04710300	-0.00002500	2.08585300
C	-0.19618800	1.25498300	1.26013400
C	0.66909000	1.34275600	0.00402500
C	0.66769600	-1.34323200	0.00399500
C	-0.19777900	-1.25455100	1.25987600
H	-1.24633600	1.31325900	0.97333700
H	0.03165400	2.14754600	1.84586300
H	1.05794700	-0.00071800	2.49823600
H	-0.63109000	0.00032000	2.93928600
H	-1.24794300	-1.31132600	0.97280600
H	0.02872000	-2.14752400	1.84549600
C	2.14375100	-1.62436400	0.34165200
H	2.19828000	-2.67761800	0.61547100
H	2.78281700	-1.46306400	-0.52636300
H	2.50937700	-1.03941800	1.18018900
C	2.14549100	1.62251800	0.34130900
H	2.78418700	1.46061100	-0.52686400
H	2.20106700	2.67572500	0.61510000
H	2.51078700	1.03724700	1.17975900
C	0.16453500	2.39401600	-0.97053500
H	0.06428100	3.32457800	-0.41253900
H	0.86751900	2.55452100	-1.78565200
H	-0.80591300	2.10157300	-1.36667800
C	0.16239900	-2.39405500	-0.97065900
H	0.86538900	-2.55518800	-1.78564600
H	0.06120600	-3.32452900	-0.41268200
H	-0.80770700	-2.10072900	-1.36695900
N	0.66790200	-0.00023300	-0.72191000
O	0.86495200	-0.00032900	-1.88004100
N	-1.95763100	0.00082000	-1.13779500
N	-2.79414600	0.00109600	-0.31502300
N	-3.59904600	0.00104400	0.52105100

I2



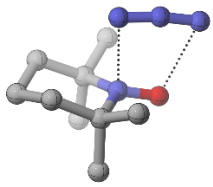
C	-2.57118600	1.05993400	0.49404000
C	-1.49842100	1.89876800	-0.18245900
C	-0.09310400	1.29489900	-0.09112300
C	-1.29773100	-1.08789500	-0.04709100
C	-2.62243400	-0.32373300	-0.13334400
H	-1.75204300	2.03174300	-1.23754900
H	-1.43457700	2.89310500	0.26217800
H	-2.39908400	0.99476300	1.56943900
H	-3.53837100	1.54589200	0.36642800
H	-2.90381700	-0.23517800	-1.18624400
H	-3.37291700	-0.95044100	0.35079500
C	-0.95023800	-1.52598900	1.38383400
H	-1.56299600	-2.40065500	1.60110400
H	0.10207300	-1.80497900	1.45034600
H	-1.17384300	-0.76298600	2.12338900
C	0.47639000	1.33456500	1.33630000
H	1.30288100	0.63186900	1.44455100
H	0.85368100	2.34496100	1.49114000
H	-0.27297900	1.13256700	2.09553600
C	0.87121900	1.97606800	-1.04740500
H	0.83619700	3.04330000	-0.83109400
H	1.89207600	1.62230100	-0.90312800
H	0.57503100	1.82133900	-2.08477600
C	-1.28967300	-2.29271500	-0.97337400
H	-0.38965200	-2.89002700	-0.84147000
H	-2.15604000	-2.90163800	-0.71827200
H	-1.37116400	-1.98899500	-2.01682100
N	-0.17922600	-0.16494400	-0.49404300
O	0.70724900	-0.62786200	-1.11931200
N	2.42431800	-1.45063600	0.48398400
N	3.15939600	-0.56981900	0.23837000
N	3.87531400	0.31290500	-0.00221400

I3



C	2.58082200	0.00010900	-0.47221200
C	1.76476100	-1.26480800	-0.72696000
C	0.46492500	-1.33074500	0.09965000
C	0.46481800	1.33076400	0.09965700
C	1.76464200	1.26494400	-0.72697500
H	1.49614500	-1.32308000	-1.78492200
H	2.34728900	-2.15544600	-0.48397900
H	2.97364700	0.00013600	0.54574300
H	3.44999800	0.00014900	-1.13104000
H	1.49600900	1.32317500	-1.78493500
H	2.34708800	2.15564000	-0.48401100
C	0.74997000	1.52266200	1.58485600
H	0.94718600	2.58467200	1.73176500
H	-0.10718300	1.24897200	2.19371600
H	1.62786200	0.98741600	1.93019800
C	0.75007200	-1.52264500	1.58484900
H	-0.10712200	-1.24907500	2.19370700
H	0.94741400	-2.58463600	1.73173200
H	1.62789200	-0.98730500	1.93022500
C	-0.43797600	-2.45246000	-0.38953600
H	0.08418200	-3.39491200	-0.22791400
H	-1.36560500	-2.47056300	0.18428600
H	-0.66802700	-2.35870200	-1.44691100
C	-0.43818700	2.45240900	-0.38949600
H	-1.36579400	2.47044400	0.18436300
H	0.08390800	3.39489900	-0.22789700
H	-0.66827300	2.35862900	-1.44686100
N	-0.22579100	-0.00001500	-0.25392300
O	-0.76632800	-0.00003200	-1.34823600
N	-1.78231200	-0.00008200	1.12189000
N	-2.59737500	-0.00006000	0.26413300
N	-3.25153200	-0.00006100	-0.67558200

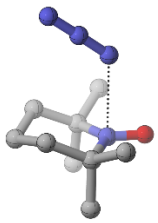
I4



C	2.08943300	-0.00000500	1.31212500
C	1.23727100	1.25463800	1.16851700
C	0.49507900	1.33977400	-0.16125500
C	0.49505800	-1.33978000	-0.16126000
C	1.23729800	-1.25466600	1.16849000
H	0.50782900	1.29686900	1.97753400
H	1.85957400	2.14953200	1.23652700
H	2.90113300	0.00001400	0.58187600
H	2.56351700	-0.00001000	2.29402100
H	0.50788100	-1.29693700	1.97752500
H	1.85962400	-2.14954800	1.23646100
C	1.44820800	-1.61495900	-1.33460000
H	1.75068100	-2.65960000	-1.26741700
H	0.93890100	-1.46682400	-2.28663200
H	2.34839100	-1.00859600	-1.31020100
C	1.44827700	1.61491900	-1.33456500
H	0.93901500	1.46674500	-2.28661500
H	1.75073700	2.65956500	-1.26740800
H	2.34846600	1.00856400	-1.31010000
C	-0.56666100	2.42999900	-0.14571600
H	-0.05830000	3.37525500	0.04377800
H	-1.07454200	2.50173800	-1.10583600
H	-1.29385900	2.26542900	0.64473200
C	-0.56669800	-2.42998800	-0.14568000
H	-1.07463100	-2.50170800	-1.10577300
H	-0.05834400	-3.37525500	0.04377600
H	-1.29385300	-2.26541400	0.64480800
N	-0.18787300	0.00000800	-0.46454600
O	-0.99491200	0.00003600	-1.36043300
N	-1.50621200	0.00001900	1.39548000
N	-2.42532100	0.00001000	0.66281600
N	-3.21866800	0.00000500	-0.17288300

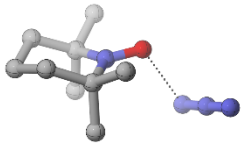
ωB97X-D/def2TZVP/PCM

I1



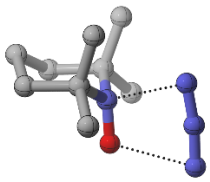
C	0.16593200	0.00000700	2.10534800
C	-0.11782800	1.24943400	1.28872400
C	0.68874400	1.34232800	-0.00657000
C	0.68882300	-1.34229900	-0.00655900
C	-0.11775700	-1.24944200	1.28873200
H	-1.17887400	1.29473700	1.04374900
H	0.11945800	2.14684000	1.86197200
H	1.19303600	0.00003700	2.47568500
H	-0.47493600	-0.00000900	2.98717900
H	-1.17880000	-1.29480700	1.04375600
H	0.11957800	-2.14683100	1.86198700
C	2.17528600	-1.64388300	0.26157400
H	2.22735600	-2.68634300	0.57305600
H	2.76955200	-1.52763600	-0.64400300
H	2.59891500	-1.03468500	1.05436800
C	2.17519000	1.64399900	0.26155900
H	2.76946000	1.52778600	-0.64402000
H	2.22720000	2.68646200	0.57304100
H	2.59885700	1.03482600	1.05435100
C	0.12031800	2.38828800	-0.95268500
H	0.03595300	3.31884000	-0.39216800
H	0.77245400	2.56093100	-1.80664500
H	-0.86715000	2.08369900	-1.29579400
C	0.12046100	-2.38829900	-0.95266800
H	0.77260800	-2.56090900	-1.80662600
H	0.03615000	-3.31885200	-0.39214500
H	-0.86702400	-2.08377100	-1.29578000
N	0.66720100	0.00001100	-0.72911200
O	0.82362900	0.00001100	-1.89665100
N	-2.05496300	-0.00007200	-1.10900600
N	-2.88041100	-0.00007700	-0.27327200
N	-3.68294600	-0.00003200	0.56803500

I2



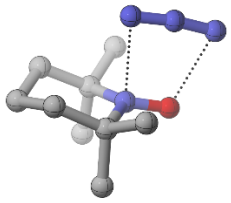
C	-2.67230600	0.95316000	0.36494100
C	-1.59721100	1.84257000	-0.23636800
C	-0.17258100	1.30704600	-0.05189600
C	-1.25237700	-1.12576200	-0.07400300
C	-2.60424100	-0.43038500	-0.25761400
H	-1.78612400	1.96504000	-1.30600400
H	-1.61798400	2.83818100	0.20833100
H	-2.57227600	0.89805600	1.45069700
H	-3.65131100	1.39044400	0.16923500
H	-2.81186300	-0.35271800	-1.32804100
H	-3.35943100	-1.09258300	0.16777200
C	-1.00779900	-1.57363900	1.37523000
H	-1.60386000	-2.47005900	1.54313900
H	0.04326200	-1.81723800	1.52890500
H	-1.31130500	-0.82545300	2.10212400
C	0.30676700	1.41724100	1.40422300
H	1.21527300	0.83545700	1.55668000
H	0.52554200	2.46832400	1.59003200
H	-0.44435000	1.09726900	2.12068000
C	0.80047400	2.03529100	-0.96756300
H	0.69032500	3.10256300	-0.77837800
H	1.83431600	1.75356600	-0.77173200
H	0.57325200	1.84769400	-2.01711000
C	-1.13078700	-2.32161600	-1.00842900
H	-0.21961700	-2.88638400	-0.82301100
H	-1.98570000	-2.97097300	-0.82275400
H	-1.15367200	-2.01259000	-2.05355200
N	-0.14862600	-0.15596900	-0.42337000
O	0.84107200	-0.59344600	-0.92263700
N	2.43726900	-1.24034200	0.65314400
N	3.24349600	-0.50188500	0.21546300
N	4.02319100	0.23470200	-0.22338700

I3



C	2.62900500	-0.00022700	-0.37074900
C	1.82551100	-1.25893400	-0.67249900
C	0.48052200	-1.33229800	0.08425100
C	0.48074800	1.33225200	0.08421700
C	1.82576200	1.25864500	-0.67247200
H	1.61637800	-1.30743800	-1.74440000
H	2.39200400	-2.15390000	-0.41023200
H	2.97061600	-0.00027500	0.66559600
H	3.53060600	-0.00030400	-0.98488200
H	1.61670300	1.30722700	-1.74438000
H	2.39241600	2.15349300	-0.41014500
C	0.68357600	1.54313700	1.57998200
H	0.91259000	2.59843800	1.72664700
H	-0.22282600	1.30801700	2.13090400
H	1.51262300	0.97769900	1.99123200
C	0.68336100	-1.54316700	1.58002500
H	-0.22288500	-1.30757800	2.13100000
H	0.91189600	-2.59855900	1.72676400
H	1.51271000	-0.97808900	1.99116400
C	-0.38886100	-2.45259100	-0.46606600
H	0.12653100	-3.39517500	-0.28511600
H	-1.34869100	-2.48275400	0.05052700
H	-0.56150000	-2.35269500	-1.53403900
C	-0.38839800	2.45271100	-0.46613500
H	-1.34827500	2.48299800	0.05036400
H	0.12712200	3.39520800	-0.28508900
H	-0.56095000	2.35289200	-1.53412700
N	-0.19019800	0.00002500	-0.27959700
O	-0.79461200	0.00003400	-1.33225300
N	-1.95776700	0.00018400	1.20830300
N	-2.65531500	0.00015400	0.26376100
N	-3.19493900	0.00011600	-0.75776600

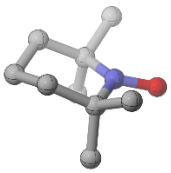
I4

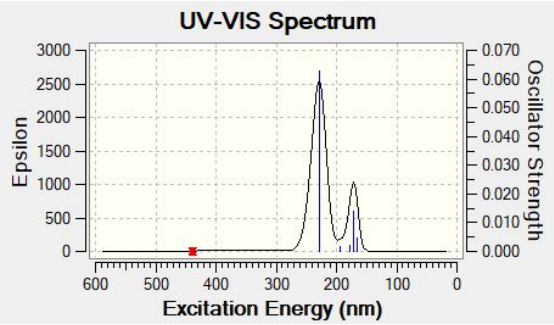


C	2.08815400	0.00001400	1.33215100
C	1.23604400	1.24995300	1.17504000
C	0.51098500	1.33884000	-0.16552500
C	0.51100300	-1.33883500	-0.16552100
C	1.23605800	-1.24993500	1.17504500
H	0.49136200	1.28277100	1.97052900
H	1.84993000	2.14811900	1.26322400
H	2.91245600	0.00001700	0.61583300
H	2.54586200	0.00001900	2.32178500
H	0.49137500	-1.28275900	1.97053300
H	1.84995400	-2.14809400	1.26323300
C	1.47893000	-1.63151200	-1.32326900
H	1.80027500	-2.66785600	-1.22533100
H	0.97983200	-1.51750000	-2.28507500
H	2.36818300	-1.00836700	-1.30787500
C	1.47890500	1.63152200	-1.32327700
H	0.97979700	1.51752500	-2.28508000
H	1.80026100	2.66786200	-1.22533100
H	2.36815200	1.00836800	-1.30789900
C	-0.55252300	2.42783900	-0.14340500
H	-0.04992300	3.37218600	0.06453500
H	-1.05721500	2.51568000	-1.10348500
H	-1.28376900	2.24838000	0.64056300
C	-0.55249500	-2.42784500	-0.14340100
H	-1.05715300	-2.51572400	-1.10349600
H	-0.04989300	-3.37217900	0.06459200
H	-1.28376900	-2.24836000	0.64053300
N	-0.15937700	-0.00000300	-0.48235600
O	-0.98926000	-0.00001200	-1.35865300
N	-1.64789100	-0.00000300	1.46223400
N	-2.48235000	-0.00000900	0.63977100
N	-3.18924000	-0.00001900	-0.27816300

UV-Vis Prediction (Optimization and UV-Vis prediction structures are identical)

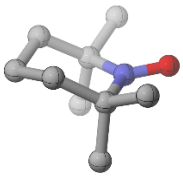
TEMPO

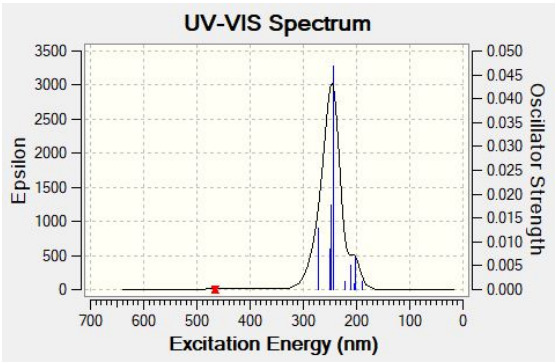




C	0.00000000	2.11819200	0.00303400
C	1.24155500	1.38828100	-0.49316200
C	1.33100700	-0.07387900	-0.02413400
C	-1.33100500	-0.07387900	-0.02413400
C	-1.24155300	1.38828000	-0.49316300
H	1.24125700	1.40590600	-1.58740600
H	2.15263300	1.89770700	-0.17158000
H	-0.00000100	2.19420500	1.09333900
H	0.00000000	3.14285300	-0.37522800
H	-1.24125400	1.40590400	-1.58740800
H	-2.15263200	1.89770600	-0.17158300
C	-1.76657600	-0.16357400	1.44956300
H	-2.79252200	0.19490900	1.54864600
H	-1.72965200	-1.19885400	1.78867400
H	-1.13655300	0.43691600	2.10445000
C	1.76657600	-0.16357600	1.44956200
H	1.72965000	-1.19885600	1.78867300
H	2.79252200	0.19490500	1.54864700
H	1.13655400	0.43691400	2.10445000
C	2.34480000	-0.82136400	-0.89753600
H	3.30296700	-0.30087300	-0.85518500
H	2.48952900	-1.84281900	-0.55215000
H	2.01495700	-0.84844500	-1.93723300
C	-2.34480200	-0.82136300	-0.89753500
H	-2.48953500	-1.84281700	-0.55214500
H	-3.30296700	-0.30086900	-0.85518600
H	-2.01495900	-0.84844900	-1.93723200
N	-0.00000100	-0.75318200	-0.18499100
O	0.00000000	-2.02704700	-0.06682200

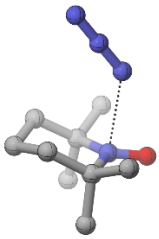
TEMPO$^+$

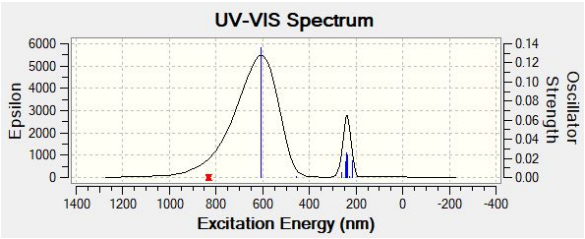




C	-0.00000600	2.09300800	-0.25974500
C	1.24872000	1.31103200	-0.64039500
C	1.35851000	-0.07653700	0.02368400
C	-1.35851800	-0.07653600	0.02368800
C	-1.24873200	1.31102900	-0.64039300
H	1.27765600	1.17634400	-1.72403900
H	2.15397800	1.85268200	-0.36232000
H	-0.00000500	2.34979800	0.80071400
H	-0.00000700	3.04076000	-0.79999900
H	-1.27766900	1.17634100	-1.72403700
H	-2.15398900	1.85268100	-0.36231900
C	-1.66185800	0.01592400	1.53504800
H	-2.70060600	0.33460600	1.61564800
H	-1.56485800	-0.95453900	2.01935600
H	-1.04502800	0.74239500	2.05323000
C	1.66185200	0.01593600	1.53504900
H	1.56487500	-0.95452900	2.01935700
H	2.70059300	0.33464300	1.61564000
H	1.04500500	0.74239200	2.05322900
C	2.40453500	-0.94613700	-0.66391900
H	3.34290700	-0.39316800	-0.64729800
H	2.55638500	-1.89238400	-0.14896700
H	2.14107800	-1.14289900	-1.70266100
C	-2.40452200	-0.94615000	-0.66392700
H	-2.55636300	-1.89240000	-0.14897900
H	-3.34290300	-0.39319400	-0.64731000
H	-2.14105600	-1.14290200	-1.70266800
N	0.00000900	-0.78604500	-0.11778500
O	0.00000700	-1.94296700	-0.35957800

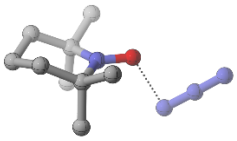
I1

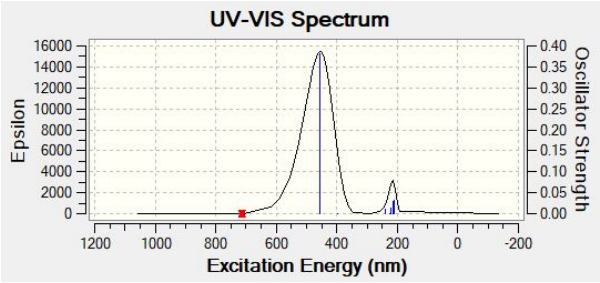




C	-0.35211200	-0.00001400	2.13763500
C	-0.00480900	-1.25739500	1.34758600
C	-0.69557200	-1.35538800	-0.01772400
C	-0.69559500	1.35538200	-0.01770000
C	-0.00479900	1.25736500	1.34759200
H	1.07336100	-1.30570700	1.19315800
H	-0.28724400	-2.15085100	1.90783900
H	-1.40522000	-0.00000900	2.42647900
H	0.21511700	-0.00001900	3.06991400
H	1.07337000	1.30566000	1.19314200
H	-0.28721100	2.15082100	1.90785500
C	-2.20475900	1.66171300	0.11583400
H	-2.28777900	2.70066600	0.43404800
H	-2.71144900	1.55766200	-0.84287200
H	-2.70569600	1.04415100	0.85495600
C	-2.20472800	-1.66176300	0.11578200
H	-2.71140400	-1.55770600	-0.84293000
H	-2.28772700	-2.70072400	0.43397400
H	-2.70569100	-1.04422800	0.85490800
C	-0.05033400	-2.41559000	-0.90571200
H	-0.04225500	-3.35095500	-0.34606800
H	-0.61409400	-2.57240000	-1.82339600
H	0.97119500	-2.13420200	-1.15098200
C	-0.05039300	2.41560700	-0.90568700
H	-0.61416600	2.57241100	-1.82336500
H	-0.04233100	3.35096700	-0.34603500
H	0.97114000	2.13424400	-1.15096900
N	-0.59782400	0.00000700	-0.74531700
O	-0.71073900	0.00003000	-1.93544600
N	2.05127300	0.00004100	-0.98304400
N	2.94891600	0.00002300	-0.21318400
N	3.83515000	-0.00000300	0.54558400

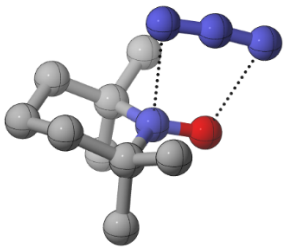
I2

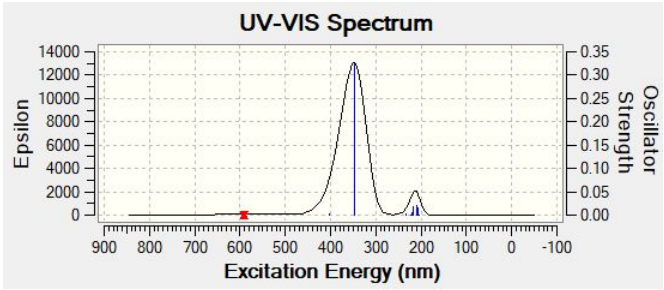




C	2.93959400	-0.06383300	0.19613600
C	2.23731000	-1.29225500	-0.36784400
C	0.73220000	-1.35147300	-0.06028200
C	0.80360000	1.33975500	-0.06594800
C	2.30432600	1.19966900	-0.36929700
H	2.37198200	-1.31262000	-1.45281100
H	2.67951600	-2.21066500	0.02222300
H	2.91217000	-0.06281900	1.28775500
H	3.99452100	-0.09214800	-0.08182000
H	2.44281300	1.21254600	-1.45384300
H	2.79344000	2.09358200	0.02157800
C	0.53647200	1.71011800	1.40581000
H	0.85210900	2.74394900	1.54891300
H	-0.52610700	1.63528300	1.63290800
H	1.09295300	1.08862400	2.10296800
C	0.45008600	-1.69861700	1.41443700
H	-0.60667500	-1.56700100	1.64289800
H	0.71205500	-2.74649300	1.56319900
H	1.03972700	-1.10265700	2.10671200
C	0.04111800	-2.36757900	-0.97002400
H	0.55171700	-3.32354200	-0.85360100
H	-1.00547600	-2.50292800	-0.70660900
H	0.10685200	-2.06883500	-2.01643800
C	0.16945900	2.38598700	-0.98317500
H	-0.86884500	2.57847000	-0.72264600
H	0.73034100	3.31379900	-0.87103600
H	0.22111200	2.07811700	-2.02773500
N	0.10879700	0.01091500	-0.33350700
O	-1.06096500	0.04093400	-0.64955300
N	-2.60867400	0.06813800	1.00982700
N	-3.48990100	0.03185300	0.22060600
N	-4.33757700	-0.00416000	-0.57479500

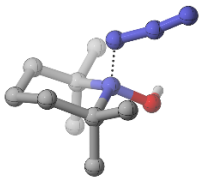
I4

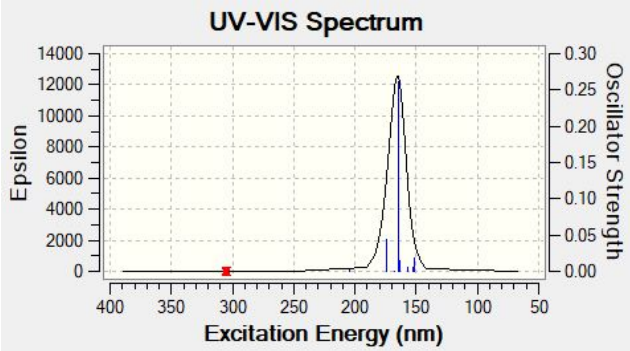




C	2.10247700	-0.00009300	-1.34632800
C	1.25121800	-1.25579100	-1.18310800
C	0.52797200	-1.35454000	0.16370800
C	0.52808900	1.35448600	0.16373900
C	1.25142400	1.25573600	-1.18303100
H	0.50403400	-1.28973900	-1.97672200
H	1.86769100	-2.15182700	-1.28152100
H	2.93620400	-0.00018500	-0.64055200
H	2.55049100	-0.00010000	-2.34172000
H	0.50428500	1.28987100	-1.97667500
H	1.86805100	2.15168000	-1.28135000
C	1.49791800	1.65834100	1.32468900
H	1.84060200	2.68592900	1.20449100
H	0.98847900	1.57928500	2.28458500
H	2.37435500	1.01731800	1.33466300
C	1.49784400	-1.65841900	1.32461800
H	0.98846100	-1.57932600	2.28454300
H	1.84047800	-2.68602100	1.20441400
H	2.37430800	-1.01743000	1.33453700
C	-0.54229900	-2.44353900	0.13670800
H	-0.04241200	-3.39183300	-0.06123300
H	-1.05741600	-2.52589600	1.09163500
H	-1.26620900	-2.26634400	-0.65426800
C	-0.54207400	2.44358700	0.13665000
H	-1.05713500	2.52612400	1.09158600
H	-0.04210900	3.39180800	-0.06145200
H	-1.26603000	2.26633200	-0.65426800
N	-0.14531800	-0.00001400	0.49254100
O	-0.97732200	-0.00005600	1.37901100
N	-1.71624000	0.00004900	-1.46971800
N	-2.53723500	0.00011500	-0.62765700
N	-3.24734500	0.00016300	0.29645700

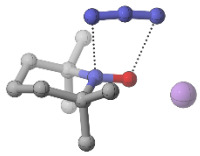
I4, proton adduct

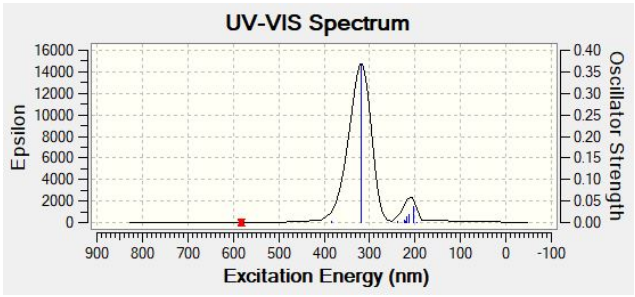




C	2.00945100	-0.78536400	-1.29749300
C	0.75354600	-1.63966200	-1.13746100
C	-0.01719300	-1.41574100	0.16730300
C	1.01086300	1.13791700	0.08920600
C	1.69257500	0.70674700	-1.21386900
H	0.08292100	-1.46760800	-1.98077100
H	1.01277800	-2.69972900	-1.15642800
H	2.76365800	-1.06308600	-0.55935100
H	2.45277500	-0.99393100	-2.27193400
H	1.06985400	1.00247500	-2.05943600
H	2.61051600	1.29340600	-1.28219500
C	1.92829200	1.01526200	1.30703800
H	2.57654000	1.89069900	1.29632000
H	1.38624600	1.02480200	2.25023600
H	2.56840000	0.14188200	1.28023700
C	0.74033200	-1.89617500	1.40479200
H	0.27658400	-1.55454200	2.32674800
H	0.69033400	-2.98445300	1.39262300
H	1.78884800	-1.62509700	1.40815500
C	-1.38058600	-2.10421600	0.12291100
H	-1.19224700	-3.17710400	0.10913000
H	-1.97959800	-1.88865400	1.00619800
H	-1.94423100	-1.86984200	-0.77703300
C	0.49818400	2.57542500	-0.00486600
H	0.04902100	2.93540600	0.92427300
H	1.36849800	3.20663700	-0.18053900
H	-0.19569700	2.72555100	-0.82646600
N	-0.27969700	0.17677800	0.26046300
O	-0.91758300	0.39286400	1.48060000
N	-1.15290500	0.53710100	-0.88007300
N	-2.34493800	0.64342000	-0.55153400
N	-3.44638800	0.79188600	-0.40369800
H	-0.88982400	1.35082000	1.65395800

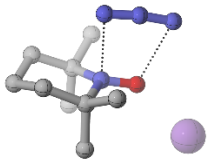
I4, lithium adduct

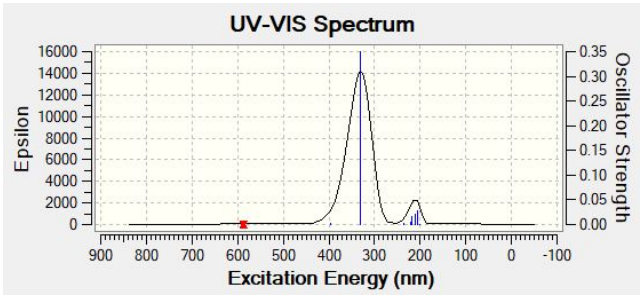




C	2.37369900	0.00009300	-1.04214300
C	1.50751200	-1.25578000	-1.04345400
C	0.54970700	-1.35861800	0.14745200
C	0.54953800	1.35867900	0.14738200
C	1.50736100	1.25586000	-1.04351900
H	0.92264000	-1.29041200	-1.96318200
H	2.13226100	-2.15118000	-1.02628500
H	3.05852300	0.00015400	-0.19145200
H	3.00256600	0.00011300	-1.93417000
H	0.92248800	1.29036500	-1.96325400
H	2.13200300	2.15133500	-1.02640500
C	1.29391200	1.65185800	1.46616900
H	1.65811900	2.67752600	1.41309100
H	0.62145000	1.57477500	2.31952300
H	2.15088500	1.00624900	1.62971100
C	1.29412900	-1.65164900	1.46624500
H	0.62172600	-1.57436200	2.31962700
H	1.65823500	-2.67736200	1.41331700
H	2.15117800	-1.00609900	1.62963000
C	-0.48903700	-2.45673900	-0.07030100
H	0.04256700	-3.40640000	-0.12826500
H	-1.19191100	-2.51586700	0.75843400
H	-1.03196700	-2.31222100	-1.00032000
C	-0.48932500	2.45666900	-0.07046200
H	-1.19237800	2.51558800	0.75813700
H	0.04213900	3.40642200	-0.12819800
H	-1.03203800	2.31219000	-1.00061500
N	-0.18216800	-0.00000400	0.33753000
O	-1.11928700	-0.00006600	1.12822000
N	-1.31756200	-0.00008300	-1.69315300
N	-2.31608300	-0.00018100	-1.06655300
N	-3.20358400	-0.00021600	-0.31740000
Li	-2.38779600	0.00028600	2.84257700

I4, sodium adduct

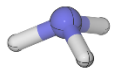




C	2.78062200	0.38515300	-0.00282300
C	2.07785600	-0.12430400	1.25221400
C	0.60565200	0.28630700	1.35468200
C	0.59919800	0.28965500	-1.35639400
C	2.07443100	-0.11337500	-1.26007600
H	2.13805200	-1.21271500	1.28464700
H	2.57604900	0.25231000	2.14811400
H	2.84216600	1.47565900	0.00180900
H	3.81127500	0.02575400	-0.00616800
H	2.13879600	-1.20142100	-1.30281500
H	2.56863800	0.27277700	-2.15407200
C	0.42404900	1.79287200	-1.65412300
H	0.75083600	1.96343300	-2.67978200
H	-0.62377100	2.08173600	-1.57939200
H	1.01574600	2.43372100	-1.00790100
C	0.44808800	1.79052500	1.65533700
H	-0.59391900	2.09755800	1.57920200
H	0.77435300	1.95260300	2.68259100
H	1.05191400	2.42469500	1.01394300
C	-0.11285600	-0.49800800	2.45028300
H	0.37158700	-0.26105400	3.39765300
H	-1.16082100	-0.21467900	2.52748900
H	-0.03616900	-1.56885500	2.28503000
C	-0.11447100	-0.50028200	-2.45153700
H	-1.16513000	-0.22689300	-2.52764500
H	0.36718200	-0.25827000	-3.39914100
H	-0.02700500	-1.57027500	-2.28665400
N	-0.10302700	0.02157000	-0.00045600
O	-1.32435000	0.08565400	0.00114100
N	0.18617400	-2.36093200	0.00000500
N	-0.99068300	-2.40668400	0.00048300
N	-2.14838400	-2.29539900	0.00232500
Na	-3.40990500	1.84432200	0.00655200

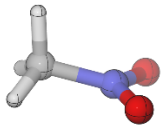
Prediction of Nitrogen NMR Spectra (optimization and NMR prediction structures are identical)

Ammonia



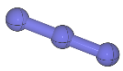
N	0.00000000	0.00000000	0.11438600
H	0.00000000	0.94198700	-0.26690100
H	-0.81578500	-0.47099400	-0.26690100
H	0.81578500	-0.47099400	-0.26690100

Nitromethane



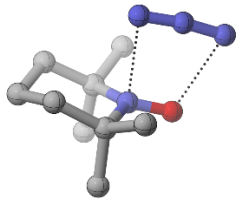
N	0.16599000	0.00000100	-0.00948300
O	0.73763700	1.08221200	0.00240800
O	0.73747300	-1.08229700	0.00240800
C	-1.33163700	0.00008100	-0.00280200
H	-1.63546800	-0.00076000	1.04405100
H	-1.66872700	0.90472800	-0.49898900
H	-1.66879200	-0.90377900	-0.50039200

Azide



N	0.00000000	0.00000000	-1.18054300
N	0.00000000	0.00000000	-0.00004600
N	0.00000000	0.00000000	1.18058900

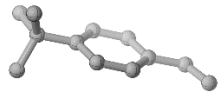
I4



C	2.10272900	-0.00001200	1.35045100
C	1.24973500	1.25920900	1.18633400
C	0.52770800	1.35879800	-0.16486300
C	0.52769200	-1.35880100	-0.16486300
C	1.24972100	-1.25922400	1.18633300
H	0.49994500	1.29335000	1.97939400
H	1.86773900	2.15613100	1.28552600
H	2.93869200	-0.00001700	0.64478600
H	2.54997600	-0.00001500	2.34792000
H	0.49993000	-1.29335700	1.97939200
H	1.86771500	-2.15615300	1.28552400
C	1.50139700	-1.65735200	-1.32814800
H	1.84519100	-2.68673200	-1.21024100
H	0.99284100	-1.57609300	-2.29021700
H	2.37907600	-1.01522700	-1.33430300
C	1.50141500	1.65733500	-1.32815000
H	0.99285700	1.57608400	-2.29021800
H	1.84522600	2.68670900	-1.21024300
H	2.37908400	1.01519600	-1.33430700
C	-0.54463900	2.45076800	-0.14227000
H	-0.04455300	3.40048400	0.05781700
H	-1.05652700	2.53289200	-1.10092400
H	-1.27249700	2.27432400	0.64730600
C	-0.54466400	-2.45076200	-0.14227000
H	-1.05653300	-2.53290100	-1.10093400
H	-0.04459100	-3.40047800	0.05784800
H	-1.27253900	-2.27429700	0.64728600
N	-0.15071900	0.00000400	-0.49018300
O	-0.98368700	0.00001400	-1.38186100
N	-1.68895800	0.00002100	1.45950600
N	-2.53616500	0.00000900	0.63664900
N	-3.26245900	-0.00000100	-0.28052200

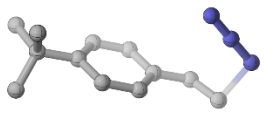
Prediction of ^{13}C kinetic isotope effects

4-^{t}Bustyrene



C	-0.07156500	1.29703600	-0.00004200
C	1.31788100	1.37979000	-0.00005300
C	2.11993300	0.23648800	-0.00007200
C	1.46443300	-1.00377000	-0.00014100
C	0.08314700	-1.08125900	-0.00011700
C	-0.72673700	0.06573300	-0.00005000
H	-0.63826700	2.21717200	-0.00005600
H	1.78865500	2.35635300	-0.00003500
H	2.03890200	-1.92147000	-0.00026400
H	-0.37467900	-2.06230900	-0.00017200
C	3.58094900	0.38248200	-0.00003400
C	4.49591300	-0.58894100	0.00018300
H	3.92955300	1.41169200	-0.00016700
H	5.55198400	-0.35332600	0.00019200
H	4.23578700	-1.64035000	0.00037000
C	-2.25504200	-0.07071400	0.00002100
C	-2.96272900	1.29244600	-0.00004900
H	-4.04372100	1.14081700	-0.00003800
H	-2.71207900	1.88121100	0.88456000
H	-2.71205900	1.88113900	-0.88470200
C	-2.70161100	-0.84513900	-1.25804800
H	-2.26573300	-1.84428200	-1.29502800
H	-3.78854400	-0.95435600	-1.26609600
H	-2.40751900	-0.31502800	-2.16641300
C	-2.70143500	-0.84490000	1.25829800
H	-3.78836200	-0.95420200	1.26651000
H	-2.26547700	-1.84400000	1.29545100
H	-2.40727500	-0.31456600	2.16651400

Transition State

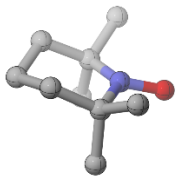


C	2.52400400	-1.40293000	-0.05492900
C	3.52130400	-1.08151800	0.83889400
H	2.79993400	-2.00153900	-0.91653200
H	4.46894700	-1.59281500	0.77597300
H	3.30051800	-0.61236900	1.78618200
N	4.47508800	0.68194800	0.12486200
N	3.66676800	1.38894200	-0.39623800
N	2.88892000	2.07290800	-0.90691500
C	1.15782800	-0.96916800	-0.00712900
C	0.28345000	-1.33740500	-1.04869800
C	0.61607000	-0.19742100	1.04588900
C	-1.04651600	-0.95554400	-1.04486900
H	0.66592800	-1.93181700	-1.86964700
C	-0.70966900	0.17666700	1.03909300
H	1.24161900	0.10634300	1.87441000
C	-1.58196500	-0.18736100	-0.00399400
H	-1.67101900	-1.26448600	-1.86999400
H	-1.08086700	0.76612400	1.86676000
C	-3.04680400	0.25651800	0.03592600
C	-3.11022700	1.79914900	0.07429200
H	-2.64611900	2.23061200	-0.81474100
H	-4.15186000	2.12575700	0.10665300
H	-2.60532500	2.20588500	0.95109000
C	-3.84023900	-0.22857200	-1.18608100
H	-3.85933900	-1.31792400	-1.25295800
H	-4.87276500	0.11529200	-1.10599300
H	-3.43242300	0.16556400	-2.11880400
C	-3.71630500	-0.31212700	1.30619500
H	-3.69144400	-1.40367100	1.30557600
H	-3.22588600	0.03714400	2.21528900
H	-4.76091900	0.00360300	1.34723300

Reaction Coordinate Diagram

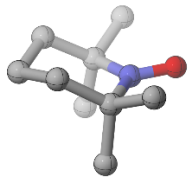
Universal structures

TEMPO



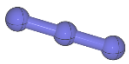
C	0.00000000	2.11819200	0.00303400
C	1.24155500	1.38828100	-0.49316200
C	1.33100700	-0.07387900	-0.02413400
C	-1.33100500	-0.07387900	-0.02413400
C	-1.24155300	1.38828000	-0.49316300
H	1.24125700	1.40590600	-1.58740600
H	2.15263300	1.89770700	-0.17158000
H	-0.00000100	2.19420500	1.09333900
H	0.00000000	3.14285300	-0.37522800
H	-1.24125400	1.40590400	-1.58740800
H	-2.15263200	1.89770600	-0.17158300
C	-1.76657600	-0.16357400	1.44956300
H	-2.79252200	0.19490900	1.54864600
H	-1.72965200	-1.19885400	1.78867400
H	-1.13655300	0.43691600	2.10445000
C	1.76657600	-0.16357600	1.44956200
H	1.72965000	-1.19885600	1.78867300
H	2.79252200	0.19490500	1.54864700
H	1.13655400	0.43691400	2.10445000
C	2.34480000	-0.82136400	-0.89753600
H	3.30296700	-0.30087300	-0.85518500
H	2.48952900	-1.84281900	-0.55215000
H	2.01495700	-0.84844500	-1.93723300
C	-2.34480200	-0.82136300	-0.89753500
H	-2.48953500	-1.84281700	-0.55214500
H	-3.30296700	-0.30086900	-0.85518600
H	-2.01495900	-0.84844900	-1.93723200
N	-0.00000100	-0.75318200	-0.18499100
O	0.00000000	-2.02704700	-0.06682200

TEMPO$^+$



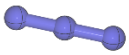
C	-0.00000600	2.09300800	-0.25974500
C	1.24872000	1.31103200	-0.64039500
C	1.35851000	-0.07653700	0.02368400
C	-1.35851800	-0.07653600	0.02368800
C	-1.24873200	1.31102900	-0.64039300
H	1.27765600	1.17634400	-1.72403900
H	2.15397800	1.85268200	-0.36232000
H	-0.00000500	2.34979800	0.80071400
H	-0.00000700	3.04076000	-0.79999900
H	-1.27766900	1.17634100	-1.72403700
H	-2.15398900	1.85268100	-0.36231900
C	-1.66185800	0.01592400	1.53504800
H	-2.70060600	0.33460600	1.61564800
H	-1.56485800	-0.95453900	2.01935600
H	-1.04502800	0.74239500	2.05323000
C	1.66185200	0.01593600	1.53504900
H	1.56487500	-0.95452900	2.01935700
H	2.70059300	0.33464300	1.61564000
H	1.04500500	0.74239200	2.05322900
C	2.40453500	-0.94613700	-0.66391900
H	3.34290700	-0.39316800	-0.64729800
H	2.55638500	-1.89238400	-0.14896700
H	2.14107800	-1.14289900	-1.70266100
C	-2.40452200	-0.94615000	-0.66392700
H	-2.55636300	-1.89240000	-0.14897900
H	-3.34290300	-0.39319400	-0.64731000
H	-2.14105600	-1.14290200	-1.70266800
N	0.00000900	-0.78604500	-0.11778500
O	0.00000700	-1.94296700	-0.35957800

Azide



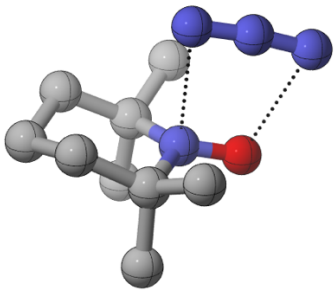
N	0.00000000	0.00000000	-1.17616100
N	0.00000000	0.00000000	-0.00002900
N	0.00000000	0.00000000	1.17619000

Azidyl



N	0.00000000	0.00000000	-1.17160200
N	0.00000000	0.00000000	0.00000000
N	0.00000000	0.00000000	1.17160200

I4

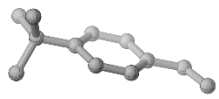


C	2.10247700	-0.00009300	-1.34632800
C	1.25121800	-1.25579100	-1.18310800
C	0.52797200	-1.35454000	0.16370800
C	0.52808900	1.35448600	0.16373900
C	1.25142400	1.25573600	-1.18303100
H	0.50403400	-1.28973900	-1.97672200
H	1.86769100	-2.15182700	-1.28152100
H	2.93620400	-0.00018500	-0.64055200
H	2.55049100	-0.00010000	-2.34172000
H	0.50428500	1.28987100	-1.97667500

H	1.86805100	2.15168000	-1.28135000
C	1.49791800	1.65834100	1.32468900
H	1.84060200	2.68592900	1.20449100
H	0.98847900	1.57928500	2.28458500
H	2.37435500	1.01731800	1.33466300
C	1.49784400	-1.65841900	1.32461800
H	0.98846100	-1.57932600	2.28454300
H	1.84047800	-2.68602100	1.20441400
H	2.37430800	-1.01743000	1.33453700
C	-0.54229900	-2.44353900	0.13670800
H	-0.04241200	-3.39183300	-0.06123300
H	-1.05741600	-2.52589600	1.09163500
H	-1.26620900	-2.26634400	-0.65426800
C	-0.54207400	2.44358700	0.13665000
H	-1.05713500	2.52612400	1.09158600
H	-0.04210900	3.39180800	-0.06145200
H	-1.26603000	2.26633200	-0.65426800
N	-0.14531800	-0.00001400	0.49254100
O	-0.97732200	-0.00005600	1.37901100
N	-1.71624000	0.00004900	-1.46971800
N	-2.53723500	0.00011500	-0.62765700
N	-3.24734500	0.00016300	0.29645700

4-^{t}Bustyrene structures

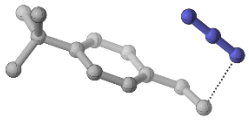
4-^{t}Bustyrene



C	-0.07156500	1.29703600	-0.00004200
C	1.31788100	1.37979000	-0.00005300
C	2.11993300	0.23648800	-0.00007200
C	1.46443300	-1.00377000	-0.00014100
C	0.08314700	-1.08125900	-0.00011700
C	-0.72673700	0.06573300	-0.00005000
H	-0.63826700	2.21717200	-0.00005600
H	1.78865500	2.35635300	-0.00003500
H	2.03890200	-1.92147000	-0.00026400
H	-0.37467900	-2.06230900	-0.00017200
C	3.58094900	0.38248200	-0.00003400

C	4.49591300	-0.58894100	0.00018300
H	3.92955300	1.41169200	-0.00016700
H	5.55198400	-0.35332600	0.00019200
H	4.23578700	-1.64035000	0.00037000
C	-2.25504200	-0.07071400	0.00002100
C	-2.96272900	1.29244600	-0.00004900
H	-4.04372100	1.14081700	-0.00003800
H	-2.71207900	1.88121100	0.88456000
H	-2.71205900	1.88113900	-0.88470200
C	-2.70161100	-0.84513900	-1.25804800
H	-2.26573300	-1.84428200	-1.29502800
H	-3.78854400	-0.95435600	-1.26609600
H	-2.40751900	-0.31502800	-2.16641300
C	-2.70143500	-0.84490000	1.25829800
H	-3.78836200	-0.95420200	1.26651000
H	-2.26547700	-1.84400000	1.29545100
H	-2.40727500	-0.31456600	2.16651400

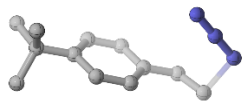
Pre-TS complex



C	2.58326000	-1.49132000	-0.10711000
C	3.54784100	-1.29882900	0.81516200
H	2.85112300	-2.01921700	-1.01707300
H	4.54077200	-1.69528800	0.66084300
H	3.36478200	-0.80568100	1.75975300
N	4.42202800	1.03097900	-0.08319600
N	3.42076800	1.59806100	-0.34087000
N	2.42870300	2.15461800	-0.59614500
C	1.20812100	-1.03639400	-0.04284300
C	0.35602700	-1.28039900	-1.13127000
C	0.65982700	-0.36348200	1.06784200
C	-0.97057800	-0.87980300	-1.11505100
H	0.74645700	-1.79591000	-2.00061500
C	-0.66284200	0.02938500	1.07643800
H	1.27396000	-0.15525500	1.93381400
C	-1.51787400	-0.21610300	-0.01172800
H	-1.58101400	-1.09341900	-1.97996400
H	-1.04117000	0.54023200	1.95184900

C	-2.97943100	0.23945800	0.04553000
C	-3.02807800	1.77195500	0.22918600
H	-2.54564500	2.28071200	-0.60775900
H	-4.06635300	2.10731400	0.27749000
H	-2.53230600	2.08727500	1.14777300
C	-3.75597700	-0.11803500	-1.23003000
H	-3.78467900	-1.19592400	-1.40049100
H	-4.78630500	0.22844700	-1.13478800
H	-3.32799900	0.35812300	-2.11415700
C	-3.67810100	-0.43954400	1.24367000
H	-3.66343900	-1.52627300	1.13865400
H	-3.20152100	-0.18445000	2.19074200
H	-4.72034100	-0.11761000	1.29664600

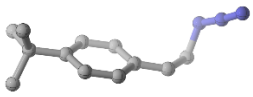
Transition State



C	2.52400400	-1.40293000	-0.05492900
C	3.52130400	-1.08151800	0.83889400
H	2.79993400	-2.00153900	-0.91653200
H	4.46894700	-1.59281500	0.77597300
H	3.30051800	-0.61236900	1.78618200
N	4.47508800	0.68194800	0.12486200
N	3.66676800	1.38894200	-0.39623800
N	2.88892000	2.07290800	-0.90691500
C	1.15782800	-0.96916800	-0.00712900
C	0.28345000	-1.33740500	-1.04869800
C	0.61607000	-0.19742100	1.04588900
C	-1.04651600	-0.95554400	-1.04486900
H	0.66592800	-1.93181700	-1.86964700
C	-0.70966900	0.17666700	1.03909300
H	1.24161900	0.10634300	1.87441000
C	-1.58196500	-0.18736100	-0.00399400
H	-1.67101900	-1.26448600	-1.86999400
H	-1.08086700	0.76612400	1.86676000
C	-3.04680400	0.25651800	0.03592600
C	-3.11022700	1.79914900	0.07429200
H	-2.64611900	2.23061200	-0.81474100
H	-4.15186000	2.12575700	0.10665300

H	-2.60532500	2.20588500	0.95109000
C	-3.84023900	-0.22857200	-1.18608100
H	-3.85933900	-1.31792400	-1.25295800
H	-4.87276500	0.11529200	-1.10599300
H	-3.43242300	0.16556400	-2.11880400
C	-3.71630500	-0.31212700	1.30619500
H	-3.69144400	-1.40367100	1.30557600
H	-3.22588600	0.03714400	2.21528900
H	-4.76091900	0.00360300	1.34723300

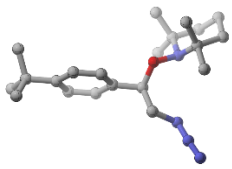
Intermediate



C	1.25749900	1.31394400	-0.10296500
C	-0.08230600	1.50360600	-0.35544500
C	-0.96202200	0.40778500	-0.57172300
C	-0.38281900	-0.88399900	-0.50411500
C	0.96612900	-1.05657500	-0.24718200
C	1.82931200	0.02829400	-0.04181900
H	1.88010400	2.18603400	0.05112600
H	-0.48379000	2.50947100	-0.39425100
H	-1.00080500	-1.76044400	-0.64764700
H	1.34906800	-2.06629800	-0.20615600
C	-2.32685900	0.64344600	-0.83721700
C	-3.35114900	-0.40775500	-1.07423300
H	-2.67095800	1.67112100	-0.81983000
H	-2.93496900	-1.29207700	-1.54917300
H	-4.15518600	-0.02935800	-1.70805200
N	-3.96538300	-0.94131600	0.20255100
N	-4.72504200	-0.18740500	0.79053700
N	-5.44224600	0.43423500	1.40803500
C	3.32655900	-0.13389400	0.24050800
C	4.13635600	0.59957800	-0.85046900
H	3.90204300	1.66425600	-0.88293000
H	5.20620700	0.49898800	-0.65401800
H	3.93142300	0.17816800	-1.83683300
C	3.76431900	-1.60574100	0.25410100
H	4.83552200	-1.66408800	0.45519700
H	3.25135000	-2.17601500	1.03094700

H	3.58112600	-2.09301400	-0.70553100
C	3.65775200	0.48102000	1.61755900
H	4.72532000	0.38041900	1.82653900
H	3.40838200	1.54201400	1.65799400
H	3.10724800	-0.02602200	2.41276200

Product

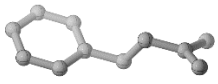


C	-4.74979000	-2.06546500	-0.08074400
C	-4.67372800	-0.72245800	0.63102600
C	-3.24987100	-0.33551100	1.07879400
C	-2.33584800	-1.72948600	-0.88434300
C	-3.79367300	-2.05996600	-1.26406200
H	-5.04461700	0.05570200	-0.04337500
H	-5.31741500	-0.70959000	1.51401300
H	-4.51215100	-2.88211600	0.60534200
H	-5.77048500	-2.24601300	-0.42741200
H	-4.13616500	-1.31734400	-1.99157700
H	-3.79522500	-3.02645800	-1.77402100
C	-1.67719600	-2.91377800	-0.14629000
H	-1.47788200	-3.71377300	-0.86197600
H	-0.72737900	-2.61059200	0.29214000
H	-2.30222800	-3.33004200	0.63923900
C	-2.80913500	-1.18293300	2.29229800
H	-1.74914000	-1.04045300	2.49787400
H	-3.36812100	-0.85698200	3.17166500
H	-2.99518200	-2.24622700	2.16649800
C	-3.29836100	1.12762300	1.53614500
H	-4.07780100	1.24055300	2.29203100
H	-2.35657500	1.43898400	1.98567200
H	-3.52576600	1.78654700	0.70046900
C	-1.56545100	-1.52331200	-2.19820200
H	-0.49254800	-1.42887700	-2.03338500
H	-1.71918800	-2.39291900	-2.83979000
H	-1.92480600	-0.64170700	-2.73048500
N	-2.35816800	-0.42851400	-0.12724000
O	-1.01166300	-0.13803200	0.32471800
C	-0.27895700	0.81118800	-0.47196400

C	1.18536200	0.46330700	-0.29459000
C	-0.50478400	2.27997100	-0.09343100
C	1.73753800	0.26833200	0.97351100
C	2.02937800	0.36228000	-1.39466400
H	-0.61317600	2.38398300	0.98816700
C	3.08646200	-0.01802600	1.12351700
C	3.38474300	0.07750700	-1.23889200
H	1.63217400	0.50734800	-2.39271200
C	3.94769100	-0.11963500	0.02232300
H	3.47087700	-0.16412500	2.12502000
H	3.99639800	0.00820100	-2.12707400
H	-0.55123300	0.70076600	-1.51910600
N	-1.69072900	2.82521500	-0.79623900
N	-2.01418900	3.96497400	-0.50527600
N	-2.40516500	5.00873200	-0.30760400
H	0.37072200	2.85492100	-0.40441400
C	5.43584900	-0.43319200	0.23461700
C	6.20905300	-0.52219100	-1.08921900
H	7.25690400	-0.74745000	-0.88279800
H	5.82141600	-1.31295400	-1.73446800
H	6.17577000	0.41796500	-1.64303900
C	5.57872800	-1.78420400	0.96667900
H	6.63453200	-2.01561200	1.12595000
H	5.08976800	-1.77094000	1.94136000
H	5.13919000	-2.59359900	0.37984700
C	6.07573400	0.67909500	1.09199500
H	6.00051500	1.64738300	0.59255800
H	5.59549600	0.76489300	2.06749300
H	7.13405000	0.46476300	1.25832600
H	1.10785800	0.33229500	1.85171400

4-phenyl-2-methylbut-1-ene structures

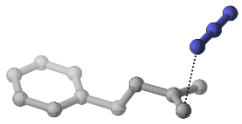
4-phenyl-2-methylbut-1-ene



C	2.93214900	0.12344300	-0.22803200
C	3.67319300	1.22379400	-0.35810300
H	4.73577700	1.22159900	-0.14417800

H	3.24111900	2.16256300	-0.68504900
C	1.45321600	0.13210700	-0.53061600
H	1.18384200	1.07902700	-1.00336100
H	1.22704600	-0.66130100	-1.25168000
C	3.52776900	-1.18592100	0.21354600
H	3.07997600	-1.53514700	1.14784800
H	3.34157500	-1.96548200	-0.53164400
H	4.60399900	-1.10420700	0.36516200
C	0.55810400	-0.07433200	0.71299100
H	0.80001600	-1.02966000	1.18293600
H	0.78613500	0.70817800	1.44090900
C	-0.91248100	-0.04224300	0.37626200
C	-1.58923500	-1.20636000	0.00352900
C	-1.62675300	1.15809000	0.39807200
C	-2.93690000	-1.17327800	-0.34019100
H	-1.05586500	-2.15024500	-0.01289600
C	-2.97466700	1.19707200	0.05567900
H	-1.12233600	2.07198600	0.69115400
C	-3.63505000	0.03019000	-0.31630400
H	-3.44276900	-2.08848200	-0.62255600
H	-3.50990600	2.13831800	0.08313600
H	-4.68467300	0.05747700	-0.58077600

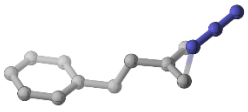
Pre-TS complex



C	-1.77136600	-0.81060900	0.52280200
C	-2.46177000	-1.73144800	-0.17328000
H	-3.40587400	-2.12119000	0.18515900
C	-0.44268700	-0.29957300	0.03480100
H	-0.30066800	-0.58401700	-1.00921900
H	-0.43727200	0.79440500	0.07766800
C	-2.30601400	-0.23270800	1.79640500
H	-1.57947500	-0.31109600	2.60933500
H	-2.50519200	0.83839400	1.66948000
H	-3.22884000	-0.71942700	2.10861300
C	0.75738800	-0.82587300	0.86102600
H	0.63013300	-0.54502400	1.90807200
H	0.75740900	-1.91734700	0.81820000

C	2.07590900	-0.29557200	0.35405300
C	2.61405100	0.89064000	0.85852600
C	2.77492600	-0.96319000	-0.65443000
C	3.81397200	1.39702400	0.36941100
H	2.09090700	1.42115200	1.64614100
C	3.97487700	-0.46097300	-1.14737700
H	2.37700700	-1.88861800	-1.05535700
C	4.49848100	0.72300500	-0.63712400
H	4.21621100	2.31614300	0.77748700
H	4.50256200	-0.99635200	-1.92709400
H	5.43368800	1.11451100	-1.01722800
H	-2.07895000	-2.14214800	-1.09851800
N	-3.79702300	0.15063100	-1.64683400
N	-4.17366300	0.97269700	-0.89063300
N	-4.54906400	1.79042600	-0.14847800

Transition State



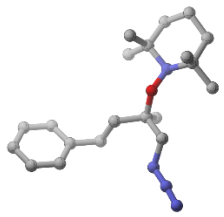
C	-1.73353800	-0.43057900	-0.52895700
C	-2.51875700	0.55818500	-1.10101400
H	-3.39208100	0.28126600	-1.67672500
C	-0.38032200	-0.10185500	0.02154700
H	-0.32118400	0.96210200	0.25875200
H	-0.21280100	-0.65722500	0.94853000
C	-2.23622200	-1.82551400	-0.37214800
H	-1.48376200	-2.55117700	-0.69430900
H	-2.42729500	-2.04051200	0.68637700
H	-3.15421900	-2.00254800	-0.93035300
C	0.76263700	-0.45240600	-0.97131700
H	0.69456300	-1.50921000	-1.23649300
H	0.61564100	0.12072500	-1.88889800
C	2.12696100	-0.16015400	-0.39748000
C	2.83016200	-1.13825800	0.30921500
C	2.70693600	1.10287200	-0.53739800
C	4.07714800	-0.86412300	0.86144500
H	2.39928000	-2.12646800	0.42362700
C	3.95344400	1.38203200	0.01321400
H	2.17950500	1.87388500	-1.08762100

C	4.64308600	0.39864600	0.71581600
H	4.60817800	-1.63798600	1.40191500
H	4.38795900	2.36636200	-0.11039500
H	5.61489200	0.61334300	1.14217600
H	-2.07309200	1.51019500	-1.35145800
N	-3.54297000	1.38835300	0.43237500
N	-4.42971000	0.65129400	0.76377200
N	-5.28800600	-0.04190900	1.09490100

Intermediate

C	-1.65777700	0.99313700	0.20523500
C	-2.74424400	0.06362400	0.58948400
H	-3.42021800	0.51862200	1.31867900
C	-0.32917600	0.45694800	-0.22004300
H	-0.40444400	-0.60926700	-0.44981800
H	0.00006600	0.95781200	-1.13781300
C	-1.96458200	2.44065500	0.03063700
H	-1.06802000	3.05854100	0.11645300
H	-2.38828900	2.63958300	-0.96571100
H	-2.69865300	2.79389900	0.75905500
C	0.78081000	0.65034300	0.85165700
H	0.85362300	1.71349100	1.09183900
H	0.47806500	0.13460600	1.76543700
C	2.12438100	0.13697900	0.39804500
C	2.98429400	0.94353300	-0.35214100
C	2.53007600	-1.16707800	0.69139900
C	4.21181700	0.46331200	-0.79614200
H	2.69168000	1.96116200	-0.58555900
C	3.75719500	-1.65242800	0.25033400
H	1.88003900	-1.80760800	1.27681300
C	4.60293600	-0.83828000	-0.49637100
H	4.86525600	1.10709100	-1.37210600
H	4.05425500	-2.66522300	0.49361300
H	5.55984500	-1.21277800	-0.83765700
H	-2.34610200	-0.86429700	1.00722000
N	-3.58286600	-0.30550600	-0.63202500
N	-4.48313300	-1.09963800	-0.41479700
N	-5.33849800	-1.83344200	-0.29503700

Product



C	0.04231000	2.26573700	0.11946200
C	1.30065600	0.06374600	0.04138500
H	1.59524500	0.43273400	1.02788800
H	1.03545700	-0.98294700	0.18304000
C	-0.24054300	0.79170300	-1.88995300
H	0.49341900	1.43411000	-2.37758300
H	-0.15105900	-0.20496500	-2.31218900
H	-1.23425500	1.17156300	-2.11571100
C	2.51805000	0.12733400	-0.90054500
H	2.25353100	-0.30754900	-1.86627200
H	2.79524400	1.16562300	-1.07842800
C	3.69975900	-0.62063200	-0.32952300
C	3.88979800	-1.97857000	-0.59707400
C	4.61943000	0.02162800	0.50373700
C	4.96218200	-2.67517500	-0.04869900
H	3.19261600	-2.49545500	-1.24698100
C	5.69363500	-0.66950500	1.05484700
H	4.49451600	1.07672800	0.71950200
C	5.86861500	-2.02272900	0.78121700
H	5.09191400	-3.72688700	-0.27313400
H	6.39642300	-0.15001200	1.69477800
H	6.70552700	-2.56215600	1.20666300
C	-4.83590100	-1.65114000	0.04250600
C	-4.72893500	-0.14546300	-0.12740700
C	-3.41661500	0.45233300	0.41923500
C	-2.27348300	-1.79654900	-0.12546400
C	-3.64115600	-2.29996400	-0.63438400
H	-4.80276500	0.09601500	-1.19271100
H	-5.55571600	0.36748600	0.36970400
H	-4.88291100	-1.92256900	1.09999100
H	-5.76303900	-2.01462100	-0.40804300
H	-3.70086900	-2.10309700	-1.70937800
H	-3.65875000	-3.38556000	-0.51214200
C	-1.97062700	-2.37049100	1.27381600
H	-1.79079400	-3.44400000	1.18905400

H	-1.07741500	-1.91146300	1.69436300
H	-2.78877600	-2.23260300	1.97623400
C	-3.43091300	0.45687200	1.96236600
H	-2.44958200	0.71852800	2.35450600
H	-4.14434100	1.20759300	2.30871100
H	-3.72939700	-0.49622600	2.39190200
C	-3.37664300	1.91539300	-0.04454100
H	-4.33915900	2.38453300	0.16823200
H	-2.61915300	2.48729700	0.48472900
H	-3.19565000	1.98548200	-1.11746000
C	-1.22948100	-2.35734200	-1.10120700
H	-0.21170300	-2.11902200	-0.80351600
H	-1.31583300	-3.44522200	-1.12674900
H	-1.39882700	-1.98253400	-2.11018300
N	-2.26309800	-0.28914500	-0.20772000
O	-1.05052600	0.18729000	0.41884600
H	0.01362800	2.25303000	1.21153500
C	0.01053400	0.81165100	-0.39099500
H	-0.82441700	2.80960900	-0.25146100
N	1.27028300	2.96502400	-0.33285000
N	1.35210100	4.14769900	-0.04835000
N	1.52743900	5.24574000	0.16287100

References

(1) Tzur, E.; Ivry, E.; Diesendruck, C.; Vidavsky Y.; Goldberg, I.; Lemcoff, G. N. *J. Organomet. Chem.* **2014**, *769*, 24.

(2) Qiu J Pradhan P Blanck N Bobbitt J Bailey W. *Org. lett.* **2012**, *12*, 350.

(3) Singleton, D. A.; Thomas, A. A. *J. Am. Chem. Soc.*, **1995**, *117* (36), 9357.

(4) Bobbitt J Eddy N Cady C Jin J Gascon J.; Gelpí-Dominguez, S.; Jerzy Zakrzewski, J.; Morton, M. D. *J. Org. Chem.,* **2017**, *82*, 9279.

(5) CrysAlisPro; Rigaku OD, The Woodlands, TX, 2015.

(6) Sheldrick, G. M. *Acta Crystallogr.* **2015**, A71, 3.

(7) Sheldrick, G.M. *Acta Crystallogr.* **2008**, A64, 112.

(8) Müller, P. *Crystallogr. Rev.* **2009**, *15*, 57.

(9) Gaussian 09, Revision C.01, Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross,

J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian, Inc., Wallingford, CT
(10) Hanwell, M. D.; Curtis, D. E.; Lonie, D. C.; Vandermeersch, T.; Zurek, E.; Hutchison, G. R. *Journal of Cheminformatics* **2012**, *4:17*.
(11) Pettersen, E. F.; Goddard, T. D.; Huang, C. C.; Couch, G. S.; Greenblatt, D. M.; Meng, E. C.; Ferrin, T. E. *J. Comput. Chem*. **2004**, *25*, 1605.
(12) CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org)
(13) (a) Becke, A.D. *J. Chem. Phys*. **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200. (d) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
(14) Ditchfield, R.; Hehre, W. J.; Pople, J. A.; *J. Chem. Phys.* **1971**, *54*, 724.
(15) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005***, 7*, 3297.
(16) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999.
(17) Dunning Jr., T. H. *J. Chem. Phys.* **1989**, *90*, 1007.
(18) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.
(19) Chai, J-D.; Head-Gordon, M. *J. Chem. Phys*. **2008**, *128*, 084106.
(20) Bauernschmitt, R.; Ahlrichs, R. *Chem. Phys. Lett.* **1996**, *256*, 454.
(21) T. Yanai, Pew, D. P.; Handy, N. C. *Chemi. Phys. Lett.* **2004**, *393*, 51.
(22) Chapychev, S. V.; Chernyak, A. V. Ushakov, E. N. *Magn. Reson. Chem.* **2017**, *55*, 99.
(23) Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys*. **1996**, *104*, 5497.
(24) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401.
(25) Bigeleisen, J. *J. Chem. Phys.* **1949**, *17*, 675.
(26) Anisimov, V. Paneth, P. *J. Math. Chem.* **1999**, *26*, 75.
(27) da Silva, E. F.; Svendsen, H. F.; Merz, K. M. *J. Phys. Chem. A* **2009**, *113*, 6404.