Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Simple, Catalytic C(sp3)–H Azidation Using the C–H Donor as the Limiting Reagent

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General Information

All reagents were purchased from commercially available sources without further purification. All reactions were carried out in an oven dried vial with a magnetic stirring bar under N_2 atmosphere.

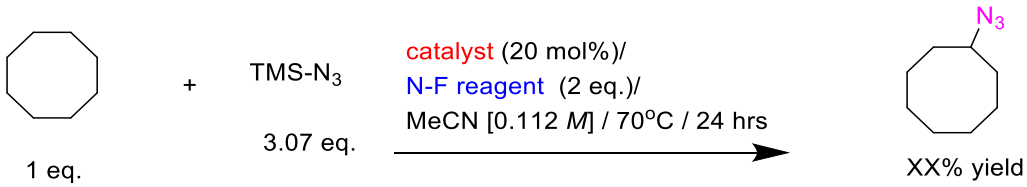
^{1}H-NMR and ^{13}C{^{1}H}-NMR spectra were performed on a Bruker DRX-600 spectrometer operating at 600 MHz for proton nuclei and 151 MHz for carbon were calibrated using residual undeuterated solvent as an internal reference (CDCl3: 7.26 ppm ^{1}H-NMR and 77.20 ppm ^{13}C{^{1}H}-NMR).

For reporting NMR peak multiplicities, the following abbreviations were used: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, hept = heptet, m = multiplet, br = broad.

CAUTION: Azides are potentially explosive compounds; Extreme caution is necessary and proper safety measures should be taken.

Organic azides with (NC + NO)/NN ratio more than 3 are normally stable and can be isolated and stored in pure form. Azides with (NC + NO)/NN less than 3 but more than 1 can be isolated but should be stored in fridge at no more than 1 *M* concentration and at a maximum of 5 grams of material. Azides with (NC + NO)/NN < 1 should never be isolated, as they are very unstable and potentially explosive.

Mn Catalyst Screening for the Azidation of Cyclooctane



N-F reagent	Mn catalyst	Yield of azidocyclooctane
Selectfluor	$Mn(OAc)_3\ 2H_2O$	38%
NFSI	$Mn(OAc)_3\ 2H_2O$	5%
Selectfluor	[Mn(TPP)Cl]	3%
NFSI	[Mn(TPP)Cl]	trace
Selectfluor	(*S*,*S*)-Jacobsen's catalyst	29%
NFSI	(*S*,*S*)-Jacobsen's catalyst	1%
Selectfluor	MnF_3	39%
NFSI	MnF_3	8% (and 2% yield of fluorocyclooctane)
Selectfluor	$Mn(OAc)_2\ 4H_2O$	34%
NFSI	$Mn(OAc)_2\ 4H_2O$	trace (and 2% yield of fluorocyclooctane)
Selectfluor	$MnBr_2$	33% (and 16% yield of bromocyclooctane)
NFSI	$MnBr_2$	none (and 20% yield of bromocyclooctane)
Selectfluor	$Mn(acac)_3$	26%
NFSI	$Mn(acac)_3$	7% (and 17% yield of fluorocyclooctane)
Selectfluor	$Mn(acac)_2$	37%
NFSI	$Mn(acac)_2$	none
Selectfluor	$Mn(OTf)_2$	35%
NFSI	$Mn(OTf)_2$	5% (and 30% yield of fluorocyclooctane)

[Mn(TPP)Cl] is (5,10,15,20-tetraphenylporphyrinato)manganese(III) chloride which is also known as 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine manganese(III) chloride or Mn(III) *meso*-tetraphenylporphine chloride. (*S*,*S*)-Jacobsen's catalyst is (*S*,*S*)-(+)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminomanganese(III) chloride.

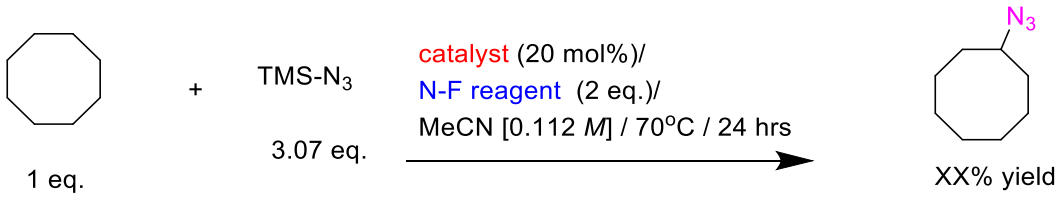
General procedure: Cyclooctane (1 eq., 0.000446 mol = 0.446 mmol, 0.06 mL) was added to a vial with a stir bar followed by 4 mL MeCN. Next the catalyst (20 mol%, 0.0000892 mol = 0.0892 mmol) was added to the vial. Then, the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial and lastly the N-F reagent (2 eq., 0.000892 mol = 0.892 mmol) was added to the vial. The vial was sealed tightly and placed on to a pre-heated 70°C sand bath. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times with DCM, and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

Azidocyclooctane (also known as cyclooctyl azide) has previously been characterized.[1,2] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.55 (tt, *J* = 8.5, 4.0 Hz, 1H), 1.89 – 1.84 (m, 2H), 1.74 – 1.66 (m, 4H), 1.57 – 1.46 (m, 8H).

Fluorocyclooctane has previously been characterized.[3] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 4.69 (dm, *J* = 48 Hz, 1H), 1.93 – 1.86 (m, 4H), 1.74 – 1.69 (m, 2H), 1.59 – 1.44 (m, 8H).

Bromocyclooctane (also known as cyclooctyl bromide) has previously been characterized.[4] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 4.44 – 4.39 (m, 1H), 2.25 – 2.19 (m 2H), 2.16 – 2.10 (m 2H), 1.78 – 1.70 (m, 2H), 1.61 – 1.45 (m, 8H).

Fe Catalyst Screening for the Azidation of Cyclooctane



N-F reagent	Fe catalyst	Yield of azidocyclooctane
Selectfluor	$FeCl_3$ (anhydrous)	58% (and 13% yield of cyclooctyl chloride)
NFSI	$FeCl_3$ (anhydrous)	34% (and 11% yield of cyclooctyl chloride)
Selectfluor	$FeCl_3$ $6H_2O$	52% (and 16% yield of cyclooctyl chloride)
NFSI	$FeCl_3$ $6H_2O$	43% (and 9% yield of cyclooctyl chloride)
Selectfluor	**$Fe(NO_3)_3$ $9H_2O$**	**69%**
NFSI	$Fe(NO_3)_3$ $9H_2O$	37%
Selectfluor	$Fe_2(SO_4)_3$ $5H_2O$	4%
NFSI	$Fe_2(SO_4)_3$ $5H_2O$	none
Selectfluor	Fe(III) oxalate $6H_2O$	15%
NFSI	Fe(III) oxalate $6H_2O$	43%
Selectfluor	**$Fe(OTf)_3$**	**69%**
NFSI	$Fe(OTf)_3$	12%
Selectfluor	FeF_3	43%
NFSI	FeF_3	49%
Selectfluor	$Fe(OAc)_2$	10%
NFSI	$Fe(OAc)_2$	43%
Selectfluor	$Fe(OTf)_2$	33%
NFSI	$Fe(OTf)_2$	trace
Selectfluor	$FeCl_2$	26% (and 5% yield of cyclooctyl chloride)
NFSI	$FeCl_2$	46% (and 10% yield of cyclooctyl chloride)
Selectfluor	$FeBr_3$	26% (and 16% yield of bromocyclooctane)
NFSI	$FeBr_3$	none (and 9% yield of bromocyclooctane)
Selectfluor	FeF_2	20%
NFSI	FeF_2	16%
Selectfluor	Fe_2O_3	3%
NFSI	Fe_2O_3	none
Selectfluor	$Fe(acac)_2$	12%
NFSI	$Fe(acac)_2$	none
Selectfluor	$Fe(acac)_3$	8%
NFSI	$Fe(acac)_3$	none

General procedure:

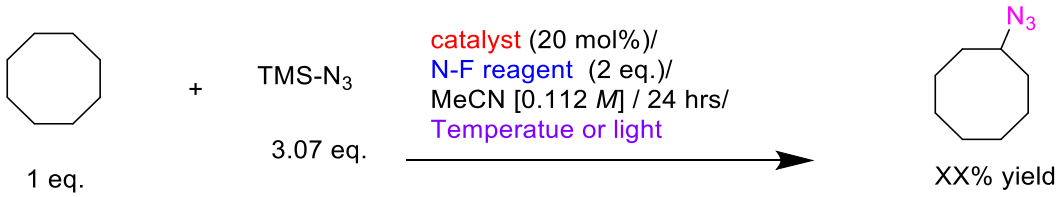
Cyclooctane (1 eq., 0.000446 mol = 0.446 mmol, 0.06 mL) was added to a vial with a stir bar followed by 4 mL MeCN. Next the catalyst (20 mol%, 0.0000892 mol = 0.0892 mmol) was added to the vial. Then, the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial and lastly the N-F reagent (2 eq., 0.000892 mol = 0.892 mmol) was added to the vial. The vial was sealed tightly and placed on to a pre-heated 70^{o}C sand bath. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times with DCM, and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

Azidocyclooctane (also known as cyclooctyl azide) has previously been characterized.[1,2] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.55 (tt, *J* = 8.5, 4.0 Hz, 1H), 1.89 – 1.84 (m, 2H), 1.74 – 1.66 (m, 4H), 1.57 – 1.46 (m, 8H).

Cyclooctyl chloride (also known as chlorocyclooctane) has previously been characterized.[5]
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.27 – 4.20 (m, 1H), 2.15 – 2.08 (m, 2H), 2.02 – 1.95 (m, 2H), 1.80 – 1.71 (m, 2H), 1.64 – 1.45 (m, 8H).

Bromocyclooctane (also known as cyclooctyl bromide) has previously been characterized.[4]
^{1}H-NMR (600 MHz, $CDCl_3$) δ 4.44 – 4.39 (m, 1H), 2.25 – 2.19 (m 2H), 2.16 – 2.10 (m 2H), 1.78 – 1.70 (m, 2H), 1.61 – 1.45 (m, 8H).

Screening $Fe(NO_3)_3$ $9H_2O$ with a Variety of Temperature or Light Conditions for the Azidation of Cyclooctane at 0.112 *M* in MeCN



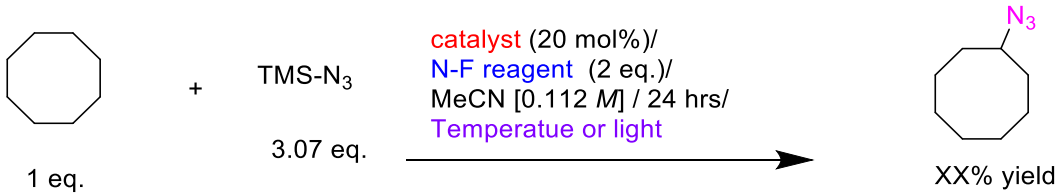
Catalyst	N-F reagent	Temperature or light	Yield of azidocyclooctane
$Fe(NO_3)_3$ $9H_2O$	Selectfluor	RT	40%
$Fe(NO_3)_3$ $9H_2O$	**Selectfluor**	**70°C**	**69%**
$Fe(NO_3)_3$ $9H_2O$	Selectfluor	RT, 40 W blue LEDs (390 nm, 1 cm, 25% intensity)	57%
$Fe(NO_3)_3$ $9H_2O$	NFSI	RT	Trace
$Fe(NO_3)_3$ $9H_2O$	NFSI	70°C	37%

General procedure:

Cyclooctane (1 eq., 0.000446 mol = 0.446 mmol, 0.06 mL) was added to a vial with a stir bar followed by 4 mL MeCN. Next the catalyst (20 mol%, 0.0000892 mol = 0.0892 mmol) was added to the vial. Then, the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial and lastly the N-F reagent (2 eq., 0.000892 mol = 0.892 mmol) was added to the vial. The vial was sealed tightly and placed on/into the correct conditions regarding the temperature or light. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times with DCM, and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

Azidocyclooctane (also known as cyclooctyl azide) has previously been characterized.[1,2] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.55 (tt, *J* = 8.5, 4.0 Hz, 1H), 1.89 – 1.84 (m, 2H), 1.74 – 1.66 (m, 4H), 1.57 – 1.46 (m, 8H).

Screening $Fe(OTf)_3$ with a Variety of Temperature or Light Conditions for the Azidation of Cyclooctane at 0.112 *M* in MeCN



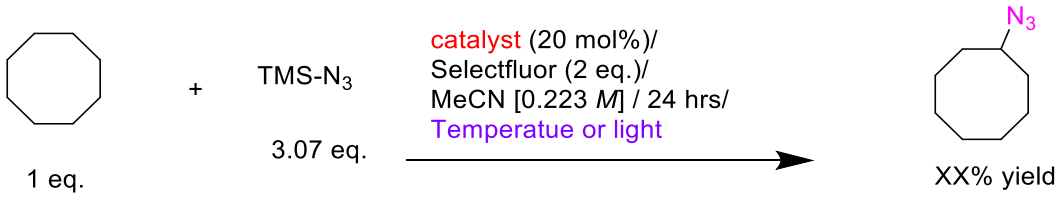
Catalyst	N-F reagent	Temperature or light	Yield of azidocyclooctane
$Fe(OTf)_3$	Selectfluor	RT	54%
$Fe(OTf)_3$	**Selectfluor**	**70°C**	**69%**
$Fe(OTf)_3$	NFSI	RT	4%
$Fe(OTf)_3$	NFSI	70°C	12%

General procedure:

Cyclooctane (1 eq., 0.000446 mol = 0.446 mmol, 0.06 mL) was added to a vial with a stir bar followed by 4 mL MeCN. Next the catalyst (20 mol%, 0.0000892 mol = 0.0892 mmol) was added to the vial. Then, the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial and lastly the N-F reagent (2 eq., 0.000892 mol = 0.892 mmol) was added to the vial. The vial was sealed tightly and placed on/into the correct conditions regarding the temperature or light. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times with DCM, and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

Azidocyclooctane (also known as cyclooctyl azide) has previously been characterized.[1,2] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.55 (tt, *J* = 8.5, 4.0 Hz, 1H), 1.89 – 1.84 (m, 2H), 1.74 – 1.66 (m, 4H), 1.57 – 1.46 (m, 8H).

Screening $Fe(NO_3)_3$ $9H_2O$ with a Variety of Temperature or Light Conditions for the Azidation of Cyclooctane at 0.223 *M* in MeCN



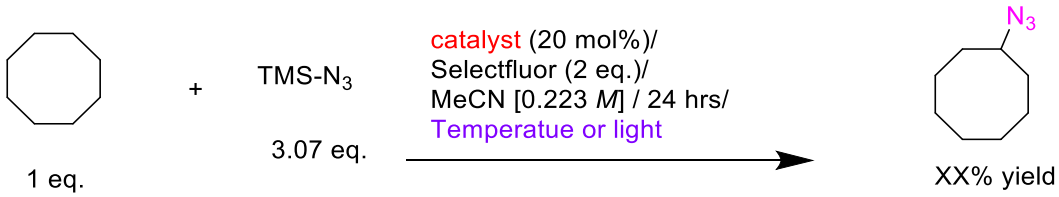
Catalyst	Temperature or light	Yield of azidocyclooctane
$Fe(NO_3)_3$ $9H_2O$	RT	28%
$Fe(NO_3)_3$ $9H_2O$	**RT, 40 W blue LEDs (390 nm, 1 cm, 25% intensity)**	**66%**
$Fe(NO_3)_3$ $9H_2O$	RT, 40 W blue LEDs (427 nm, 1 cm, 25% intensity)	41%
$Fe(NO_3)_3$ $9H_2O$	**70°C**	**71%**

General procedure:

Cyclooctane (1 eq., 0.000446 mol = 0.446 mmol, 0.06 mL) was added to a vial with a stir bar followed by 4 mL MeCN. Next the catalyst (20 mol%, 0.0000892 mol = 0.0892 mmol) was added to the vial. Then, the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial and lastly the Selectfluor (2 eq., 0.000892 mol = 0.892 mmol, 316 mg) was added to the vial. The vial was sealed tightly and placed into the correct conditions regarding the temperature or light. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times with DCM, and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

Azidocyclooctane (also known as cyclooctyl azide) has previously been characterized.[1,2] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.55 (tt, *J* = 8.5, 4.0 Hz, 1H), 1.89 – 1.84 (m, 2H), 1.74 – 1.66 (m, 4H), 1.57 – 1.46 (m, 8H).

Screening $Fe(OTf)_3$ with a Variety of Temperature or Light Conditions for the Azidation of Cyclooctane at 0.223 *M* in MeCN



Catalyst	Temperature or light	Yield of azidocyclooctane
$Fe(OTf)_3$	RT	52%
$Fe(OTf)_3$	RT, 40 W blue LEDs (390 nm, 1 cm, 25% intensity)	51%
$Fe(OTf)_3$	RT, 40 W blue LEDs (427 nm, 1 cm, 25% intensity)	48%
$Fe(OTf)_3$	**70°C**	**69%**

General procedure:

Cyclooctane (1 eq., 0.000446 mol = 0.446 mmol, 0.06 mL) was added to a vial with a stir bar followed by 4 mL MeCN. Next the catalyst (20 mol%, 0.0000892 mol = 0.0892 mmol) was added to the vial. Then, the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial and lastly the Selectfluor (2 eq., 0.000892 mol = 0.892 mmol, 316 mg) was added to the vial. The vial was sealed tightly and placed into the correct conditions regarding the temperature or light. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times with DCM, and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

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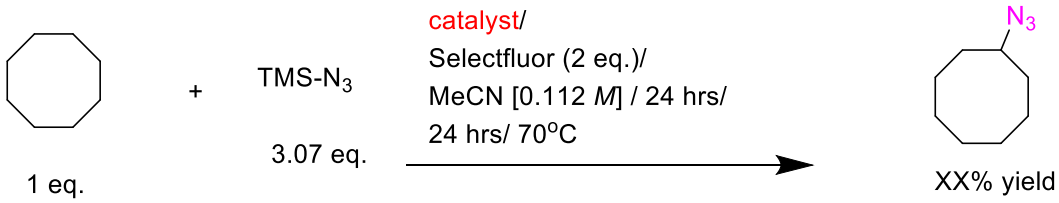
Screening the amount of $Fe(NO_3)_3$ $9H_2O$ for the Azidation of Cyclooctane



Catalyst	Amount of catalyst	Yield of azidocyclooctane
$Fe(NO_3)_3$ $9H_2O$	10 mol%	50%
$Fe(NO_3)_3$ $9H_2O$	**20 mol%**	**69%**
$Fe(NO_3)_3$ $9H_2O$	**30 mol%**	**73%**

General procedure:

Cyclooctane (1 eq., 0.000446 mol = 0.446 mmol, 0.06 mL) was added to a vial with a stir bar followed by 4 mL MeCN. Next the catalyst was added to the vial. Then, the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial and lastly the Selectfluor (2 eq., 0.000892 mol = 0.892 mmol, 316 mg) was added to the vial. The vial was sealed tightly and placed on to a pre-heated 70°C sand-bath. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times with DCM, and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

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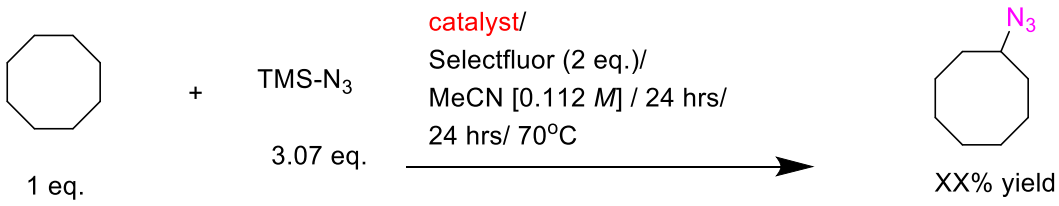
Screening the amount of $Fe(OTf)_3$ for the Azidation of Cyclooctane



Catalyst	Amount of catalyst	Yield of azidocyclooctane
$Fe(OTf)_3$	10 mol%	54%
$Fe(OTf)_3$	**20 mol%**	**69%**
$Fe(OTf)_3$	**30 mol%**	**72%**

General procedure:

Cyclooctane (1 eq., 0.000446 mol = 0.446 mmol, 0.06 mL) was added to a vial with a stir bar followed by 4 mL MeCN. Next the catalyst was added to the vial. Then, the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial and lastly the Selectfluor (2 eq., 0.000892 mol = 0.892 mmol, 316 mg) was added to the vial. The vial was sealed tightly and placed on to a pre-heated 70°C sand-bath. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times with DCM, and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

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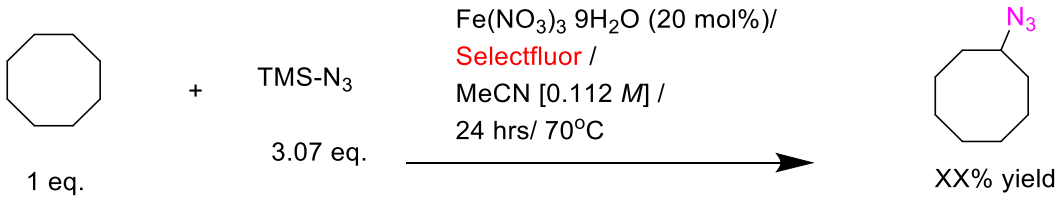
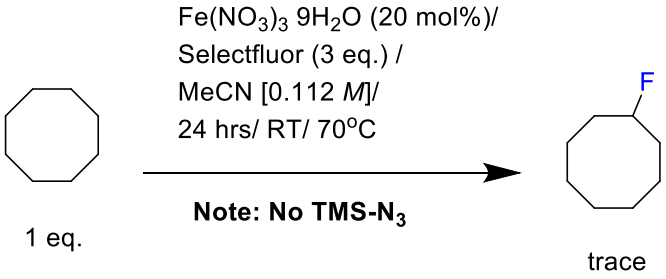
Screening 20 mol% $Fe(NO_3)_3$ $9H_2O$ at 70°C with Selectfluor for the Azidation of Cyclooctane



Amount of Selectfluor	Yield of azidocyclooctane
(none)	17%
1 eq.	42%
2 eq.	69%
3 eq.	**92%**



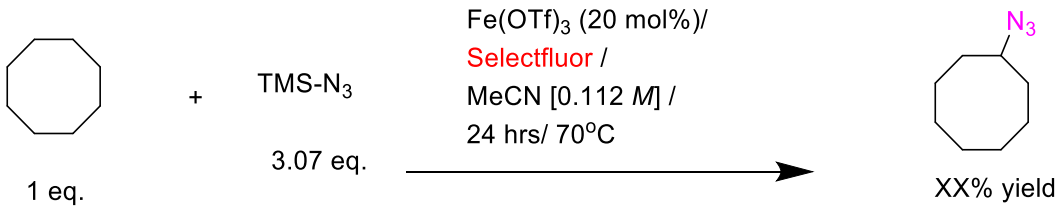
General procedure:

Cyclooctane (1 eq., 0.000446 mol = 0.446 mmol, 0.06 mL) was added to a vial with a stir bar followed by 4 mL MeCN. Next the $Fe(NO_3)_3$ $9H_2O$ (20 mol%, 0.0000892 mol = 0.0892 mmol, 36 mg) was added to the vial. Then, (**if applicable**) the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial and lastly the Selectfluor was added to the vial. The vial was sealed tightly and placed on to a pre-heated 70°C sand-bath. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times with DCM, and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

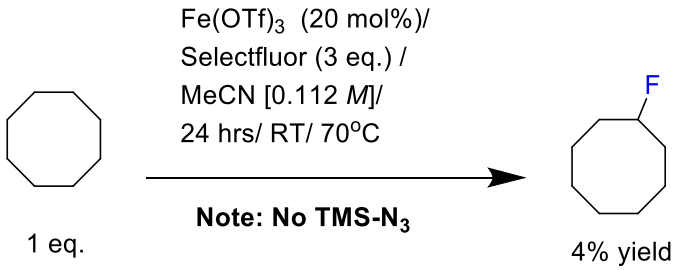
Azidocyclooctane (also known as cyclooctyl azide) has previously been characterized.[1,2] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.55 (tt, *J* = 8.5, 4.0 Hz, 1H), 1.89 – 1.84 (m, 2H), 1.74 – 1.66 (m, 4H), 1.57 – 1.46 (m, 8H).

Fluorocyclooctane has previously been characterized.[3] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 4.69 (dm, *J* = 48 Hz, 1H), 1.93 – 1.86 (m, 4H), 1.74 – 1.69 (m, 2H), 1.59 – 1.44 (m, 8H).

Screening 20 mol% $Fe(OTf)_3$ at 70°C with Selectfluor for the Azidation of Cyclooctane



Amount of Selectfluor	Yield of azidocyclooctane
(none)	6%
1 eq.	45%
2 eq.	69%
3 eq.	**82%**
4 eq.	74% (and 12% cyclooctanone)



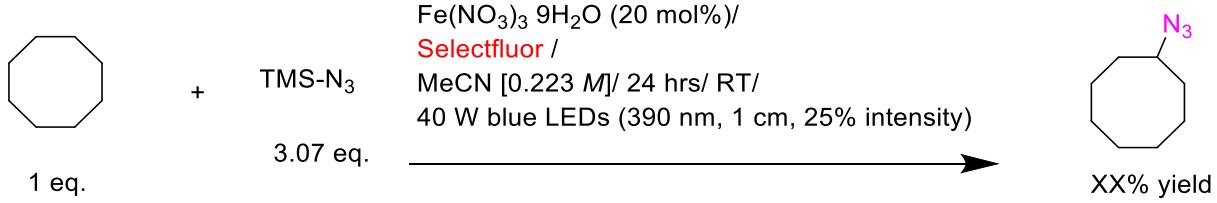
General procedure: Cyclooctane (1 eq., 0.000446 mol = 0.446 mmol, 0.06 mL) was added to a vial with a stir bar followed by 4 mL MeCN. Next the $Fe(OTf)_3$ (20 mol%, 0.0000892 mol = 0.0892 mmol, 44.9 mg) was added to the vial. Then, (**if applicable**) the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial and lastly the Selectfluor was added to the vial. The vial was sealed tightly and placed on to a pre-heated 70°C sand-bath. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times with DCM, and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

Azidocyclooctane (also known as cyclooctyl azide) has previously been characterized.[1,2] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.55 (tt, *J* = 8.5, 4.0 Hz, 1H), 1.89 – 1.84 (m, 2H), 1.74 – 1.66 (m, 4H), 1.57 – 1.46 (m, 8H).

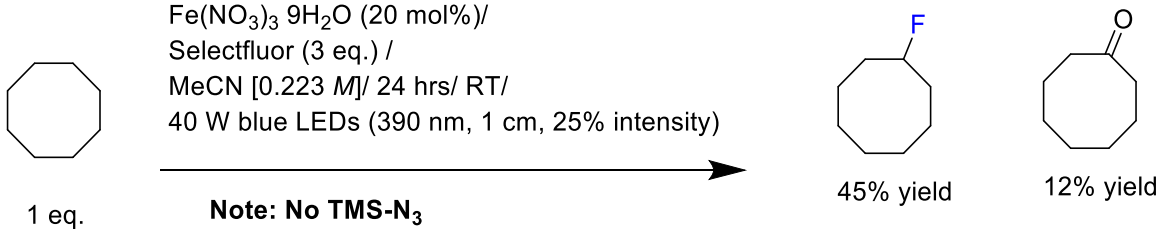
Fluorocyclooctane has previously been characterized.[3] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 4.69 (dm, *J* = 48 Hz, 1H), 1.93 – 1.86 (m, 4H), 1.74 – 1.69 (m, 2H), 1.59 – 1.44 (m, 8H).

Cyclooctanone has previously been characterized.[6] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.43 – 2.40 (m, 1H), 1.90 – 1.86 (m, 1H), 1.57 – 1.53 (m, 1H), 1.40 – 1.35 (m, 1H).

Screening 20 mol% $Fe(NO_3)_3$ $9H_2O$ under 390 nm LEDs with Selectfluor for the Azidation of Cyclooctane



Amount of Selectfluor	Yield of azidocyclooctane
(none)	31%
1 eq.	58%
2 eq.	66%
3 eq.	**68%** (and 18% cyclooctanone)



General procedure:

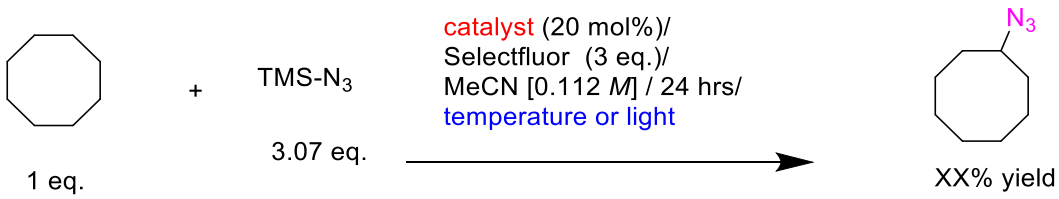
Cyclooctane (1 eq., 0.000446 mol = 0.446 mmol, 0.06 mL) was added to a vial with a stir bar followed by 2 mL MeCN. Next the $Fe(NO_3)_3$ $9H_2O$ (20 mol%, 0.0000892 mol = 0.0892 mmol, 36 mg) was added to the vial. Then, (**if applicable**) the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial and lastly the Selectfluor was added to the vial. The vial was sealed tightly and placed 1 cm from 40 W Blue LEDs (390 nm, 25% intensity). The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times with DCM, and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

Azidocyclooctane (also known as cyclooctyl azide) has previously been characterized.[1,2] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.55 (tt, *J* = 8.5, 4.0 Hz, 1H), 1.89 – 1.84 (m, 2H), 1.74 – 1.66 (m, 4H), 1.57 – 1.46 (m, 8H).

Fluorocyclooctane has previously been characterized.[3] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 4.69 (dm, *J* = 48 Hz, 1H), 1.93 – 1.86 (m, 4H), 1.74 – 1.69 (m, 2H), 1.59 – 1.44 (m, 8H).

Cyclooctanone has previously been characterized.[6] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.43 – 2.40 (m, 1H), 1.90 – 1.86 (m, 1H), 1.57 – 1.53 (m, 1H), 1.40 – 1.35 (m, 1H).

Screening a Variety of Catalysts and 3 eq. Selectfluor for the Azidation of Cyclooctane



Catalyst (20 mol%)	**Temperature or light**	**Yield of azidocyclooctane**
$Fe(NO_3)_3$ $9H_2O$	**70°C**	**92%**
$Fe(NO_3)_3$ $9H_2O$*	**RT, 40 W blue LEDs (390 nm, 1 cm, 25% intensity)***	**68%***
$Fe(OTf)_3$	**70°C**	**82%**
FeF_3	**70°C**	**65%**
$FeBr_3$	70°C	40% (and 20% yield of bromocyclooctane)
FeF_2	70°C	36%
$Fe(acac)_2$	**70°C**	**64%**
$FeCl_2$	**70°C**	**76% (and 12% yield of cyclooctyl chloride)**
$Fe(OAc)_2$	**70°C**	**67%**
$Fe(OTf)_2$	**70°C**	**62%**
$MnBr_2$	70°C	44% (and 16% yield of bromocyclooctane)
$Mn(OAc)_2$ $4H_2O$	**70°C**	**67%**
$Mn(OAc)_3$ $2H_2O$	70°C	53%
MnF_3	**70°C**	**61%**
Mn(OTf)2	70°C	50%
(none)	70°C	28%
(none)*	RT, 40 W blue LEDs (390 nm, 1 cm, 25% intensity)*	22%*
$Mn(OAc)_3$ $4H_2O$ (5 mol%) and BPhen (5 mol%)	70°C	37%
$Mn(OAc)_3$ $4H_2O$ (20 mol%) and 4,4'-dimethyl-bipy (20 mol%)	70°C	56%

*concentration is 0.223 *M* (with 2 mL MeCN) instead of 0.112 *M*

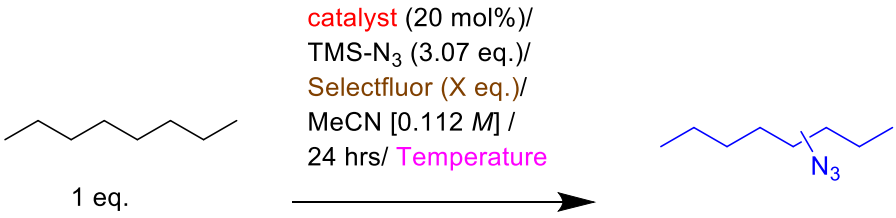
General procedure: Cyclooctane (1 eq., 0.000446 mol = 0.446 mmol, 0.06 mL) was added to a vial with a stir bar followed by 4 mL MeCN (for 0.112 *M*). Next the catalyst (20 mol%, 0.0000892 mol = 0.0892 mmol) was added to the vial. Then, the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial and lastly the Selectfluor (3 eq., 0.001338 mol = 1.338 mmol, 474 mg) was added to the vial. The vial was sealed tightly and placed on to a pre-heated 70°C sand bath. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times with DCM, and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

Azidocyclooctane (also known as cyclooctyl azide) has previously been characterized.[1,2] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.55 (tt, *J* = 8.5, 4.0 Hz, 1H), 1.89 – 1.84 (m, 2H), 1.74 – 1.66 (m, 4H), 1.57 – 1.46 (m, 8H).

Cyclooctyl chloride (also known as chlorocyclooctane) has previously been characterized.[5]
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.27 – 4.20 (m, 1H), 2.15 – 2.08 (m, 2H), 2.02 – 1.95 (m, 2H), 1.80 – 1.71 (m, 2H), 1.64 – 1.45 (m, 8H).

Bromocyclooctane (also known as cyclooctyl bromide) has previously been characterized.[4]
^{1}H-NMR (600 MHz, $CDCl_3$) δ 4.44 – 4.39 (m, 1H), 2.25 – 2.19 (m 2H), 2.16 – 2.10 (m 2H), 1.78 – 1.70 (m, 2H), 1.61 – 1.45 (m, 8H).

Screening Catalysts in the Presence of Selectfluor for the Azidation of *n*-Octane



Temp.	Eq. of Selectfluor	catalyst	Yield of azidation products: 2-azidooctane, 3-azidooctane, and 4-azidooctane
RT	3	$Fe(NO_3)_3\ 9H_2O$	7%
70°C	3	$Fe(NO_3)_3\ 9H_2O$	31%
RT	3	$Fe(OTf)_3$	16%
70°C	**3**	**$Fe(OTf)_3$**	**35%**
RT, 390 nm*	3*	$Fe(NO_3)_3\ 9H_2O$*	22%*
RT, 390 nm*	2*	$Fe(NO_3)_3\ 9H_2O$*	22%*
RT	3	$Fe(OAc)_2$	5%
70°C	3	$Fe(OAc)_2$	20%
RT	3	$Mn(OAc)_2\ 4H_2O$	22%
70°C	**3**	**$Mn(OAc)_2\ 4H_2O$**	**36%**
RT	3	$Mn(OAc)_3\ 2H_2O$	28%
70°C	3	$Mn(OAc)_3\ 2H_2O$	30%
RT	3	$Fe(OTf)_2$	4%
70°C	**3**	**$Fe(OTf)_2$**	**35%**
RT	3	(none)	5%
70°C	3	(none)	28%
RT	3	(*S*,*S*)-Jacobsen's catalyst	19%
70°C	3	(*S*,*S*)-Jacobsen's catalyst	21%
RT	3	MnF_3	14%
70°C	3	MnF_3	27%
RT	3	FeF_3	13%
70°C	3	FeF_3	25%
RT	3	$Mn(OTf)_2$	20%
70°C	3	$Mn(OTf)_2$	30%

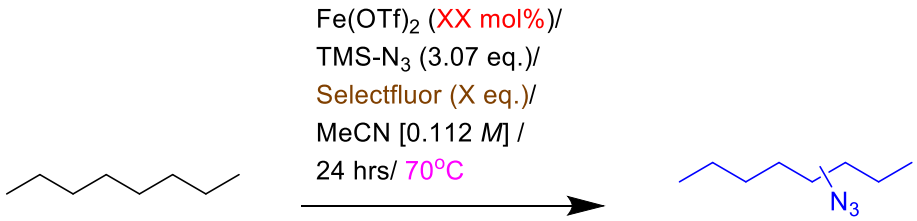
*concentration is 0.223 *M* (with 2 mL MeCN) instead of 0.112 *M*; 390 nm (40 W blue LEDs, 1 cm, 25% intensity)

General procedure:

n-Octane (1 eq., 0.000446 mol = 0.446 mmol, 0.051 g) was added to a vial with a stir bar followed by 4 mL MeCN. Next the catalyst (20 mol%, 0.0000892 mol = 0.0892 mmol) was added to the vial. Then, the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial and lastly Selectfluor (3 eq., 0.001338 mol = 1.338 mmol, 0.474 g) was added to the vial. The vial was sealed tightly and placed on/into the correct conditions regarding the temperature or light. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times with DCM, and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

2-azidooctane, 3-azidooctane, and 4-azidooctane have all previously been characterized.[1,8] They are characterized here as an inseperable mixture. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.47 – 3.36 (m, 0.33H), 3.23 (m, 0.33H), 3.17 (m, 0.33H), 1.61 – 1.42 (m, 5H), 1.34 – 1.25 (m, 5H), 1.00 – 0.86 (m, 6H).

Screening Conditions with $Fe(OTf)_2$ for the Azidation of *n*-Octane

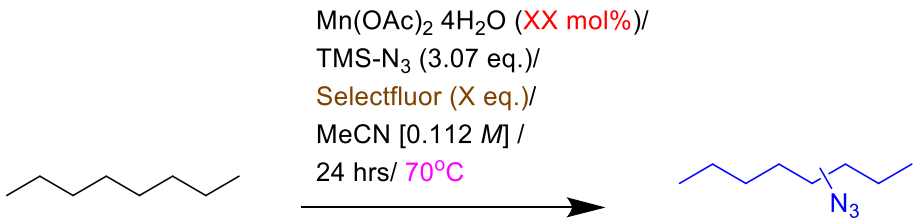


1 eq.

Temp.	Eq. of Selectfluor	Amount of $Fe(OTf)_2$	Yield of azidation products: 2-azidooctane, 3-azidooctane, and 4-azidooctane
70°C	**3**	**5 mol %**	**36%**
70°C	**3**	**10 mol %**	**36%**
70°C	**3**	**20 mol%**	**35%**
70°C	2	20 mol%	19%
70°C*	4*	20 mol%*	33%*
70°C	**3**	**30 mol%**	**35%**

*other changes besides 4 eq. Selectfluor are the concentration is 0.074 *M* (with 6 mL MecN) instead of 0.112 *M* and using 4.26 eq TMS-N_3 (with 0.0019 mol TMS-N_3, 0.25 mL TMS-N_3) instead of 3 eq. TMS-N_3.

Screening Conditions with $Mn(OAc)_2$ $4H_2O$ for the Azidation of *n*-Octane

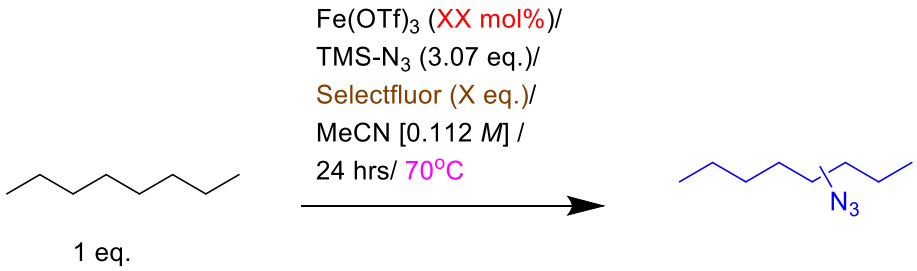


1 eq.

Temp.	Eq. of Selectfluor	Amount of $Mn(OAc)_2$ $4H_2O$	Yield of azidation products: 2-azidooctane, 3-azidooctane, and 4-azidooctane
70°C	3	5 mol %	11%
70°C	3	10 mol %	19%
70°C	**3**	**20 mol%**	**36%**
70°C	2	20 mol%	14%
70°C*	**4***	**20 mol%***	**36%***
70°C	3	30 mol%	30%

*other changes besides 4 eq. Selectfluor are the concentration is 0.074 *M* (with 6 mL MecN) instead of 0.112 *M* and using 4.26 eq TMS-N_3 (with 0.0019 mol TMS-N_3, 0.25 mL TMS-N_3) instead of 3 eq. TMS-N_3.

Screening Conditions with $Fe(OTf)_3$ for the Azidation of *n*-Octane

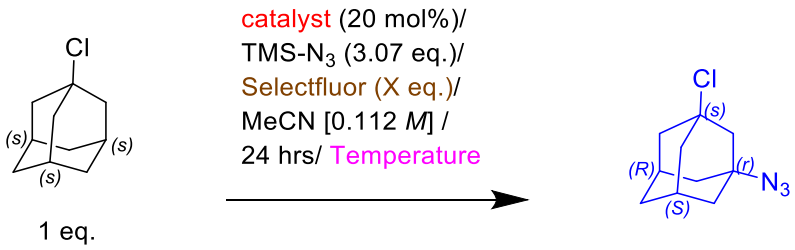


Temp.	Eq. of Selectfluor	Amount of $Fe(OTf)_3$	Yield of azidation products: 2-azidooctane, 3-azidooctane, and 4-azidooctane
70°C	3	5 mol %	35%
70°C	3	10 mol %	38%
70°C	3	20 mol%	35%
70°C	**2**	**20 mol%**	**42%**
70°C*	4*	20 mol%*	32%*
70°C	**3**	**30 mol%**	**43%**

*other changes besides 4 eq. Selectfluor are the concentration is 0.074 *M* (with 6 mL MecN) instead of 0.112 *M* and using 4.26 eq TMS-N_3 (with 0.0019 mol TMS-N_3, 0.25 mL TMS-N_3) instead of 3 eq. TMS-N_3.

2-azidooctane, 3-azidooctane, and 4-azidooctane have all previously been characterized.[1,8] They are characterized here as an inseperable mixture. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.47 – 3.36 (m, 0.33H), 3.23 (m, 0.33H), 3.17 (m, 0.33H), 1.61 – 1.42 (m, 5H), 1.34 – 1.25 (m, 5H), 1.00 – 0.86 (m, 6H).

Screening Catalysts in the Presence of Selectfluor for the Azidation of 1-Chloroadamantane



Temp. or light	Eq. of Selectfluor	catalyst	**Yield** of (1*r*,3*s*,5*R*,7*S*)-1-azido-3-chloroadamantane
RT	3	$Fe(NO_3)_3\ 9H_2O$	32%
70°C	3	$Fe(NO_3)_3\ 9H_2O$	25%
RT	3	$Fe(OTf)_3$	17%
70°C	3	$Fe(OTf)_3$	15%
RT, 390 nm*	3*	$Fe(NO_3)_3\ 9H_2O$*	24%*
RT, 390 nm*	2*	$Fe(NO_3)_3\ 9H_2O$*	24%*
RT	3	$Fe(OAc)_2$	13%
70°C	3	$Fe(OAc)_2$	26%
RT	**3**	**$Mn(OAc)_2\ 4H_2O$**	**50%**
70°C	**3**	**$Mn(OAc)_2\ 4H_2O$**	**50%**
RT	**3**	**$Mn(OAc)_3\ 2H_2O$**	**50%**
70°C	**3**	**$Mn(OAc)_3\ 2H_2O$**	**50%**
RT	3	$Fe(OTf)_2$	8%
70°C	3	$Fe(OTf)_2$	14%
RT	3	(none)	16%
70°C	3	(none)	20%
RT	**3**	**(*S*,*S*)-Jacobsen's catalyst**	**40%**
70°C	3	(*S*,*S*)-Jacobsen's catalyst	28%
RT	3	MnF_3	38%
70°C	**3**	**MnF_3**	**47%**
RT	**3**	**FeF_3**	**40%**
70°C	**3**	**FeF_3**	**42%**
RT	3	$Mn(OTf)_2$	36%
70°C	**3**	**$Mn(OTf)_2$**	**44%**
RT	3 NFSI**	$Fe(OAc)_2$	5%
70°C	3 NFSI**	$Fe(OAc)_2$	22%

*concentration is 0.223 *M* (with 2 mL MeCN) instead of 0.112 *M*; 390 nm (40 W blue LEDs, 1 cm, 25% intensity)

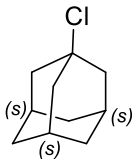
**NFSI instead of Selectfluor

General procedure:

1-chloroadamantane (1 eq., 0.000446 mol = 0.446 mmol, 0.076 g) was added to a vial with a stir bar followed by 4 mL MeCN. Next the catalyst (20 mol%, 0.0000892 mol = 0.0892 mmol) was added to the vial. Then, the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial and lastly Selectfluor (3 eq., 0.001338 mol = 1.338 mmol, 0.474 g) was added to the vial. The vial was sealed tightly and placed on/into the correct conditions regarding the temperature or light. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times with DCM, and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

(1*r*,3*s*,5*R*,7*S*)-1-azido-3-chloroadamantane has previously been characterized.[2] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.27 (s, 2H), 2.09 (s, 2H), 1.99 (q, *J* = 12.3 Hz, 4H), 1.70 (s, 3H), 1.53 (q, *J* = 12.0 Hz, 2H) 1.18 (s, br, 1H). $^{13}C\{^1H\}$-NMR (151 MHz, $CDCl_3$) δ 66.5, 60.4, 51.1, 46.0, 39.8, 34.0, 31.8.

Screening Ligands (20 mol%) with $Mn(OAc)_2$ $4H_2O$ (20 mol%) for the Azidation of 1-Chloroadamantane



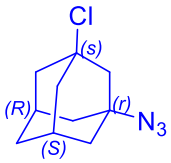
1 eq.

\+

TMS-N_3

(3.07 eq.)

$Mn(OAc)_2$ $4H_2O$ (20 mol%)/
ligand (20 mol%)
Selectfluor (X eq.)/
MeCN [0.112 *M*] /
24 hrs/ Temperature



Temperature	**Equivalents of Selectfluor**	**Ligand (20 mol%) used with $Mn(OAc)_2$ $4H_20$ (20 mol%)**	**Yield** of (1*r*,3*s*,5*R*,7*S*)-1-azido-3-chloroadamantane
RT	3	ethyl-salen	17%
70°C	3	ethyl-salen	21%
RT	3	propyl-salen	12%
70°C	3	propyl-salen	25%
RT	3	salphen	12%
70°C	3	salphen	18%
RT	3	(*S*,*S*)-Jacobsen's ligand	42%
70°C	3	(*S*,*S*)-Jacobsen's ligand	17%
RT	3	2,2'-bipy	21%
70°C	**3**	**2,2'-bipy**	**60%**
RT	3	1,10-phen	13%
70°C	**3**	**1,10-phen**	**57%**
RT	3	Sigman's ligand	44%
70°C	3	Sigman's ligand	48%
RT	3	pybox	41%
70°C	**3**	**pybox**	**55%**
RT	3	4,4'-dimethyl-2,2'-bipy	21%
70°C	**3**	**4,4'-dimethyl-2,2'-bipy**	**52%**
RT	3	4,4'-dimethoxy-2,2'-bipy	28%
70°C	**3**	**4,4'-dimethoxy-2,2'-bipy**	**56%**
RT	3	4,4'-di-*tert*-butyl-2,2'-bipy	20%
70°C	**3**	**4,4'-di-*tert*-butyl-2,2'-bipy**	**57%**
RT	3	5,5'-dimethyl-2,2'-bipy	20%
70°C	**3**	**5,5'-dimethyl-2,2'-bipy**	**58%**
RT	**3**	**6,6'-dimethyl-2,2'-bipy**	**52%**
70°C	3	6,6'-dimethyl-2,2'-bipy	46%
RT	3	BPhen	23%
70°C	**3**	**BPhen**	**55%**
RT	3	neocuproine	44%
70°C	3	neocuproine	47%
RT	**3**	**bathocuproine**	**53%**
70°C	3	bathocuproine	50%
RT	3	2,2':6',2''-terpy	33%
70°C	3	2,2':6',2''-terpy	48%
RT	3	pymox	41%

70°C	**3**	**pymox**	**56%**
RT	3	4,4'',4''-tri-*tert*-butyl-2,2':6',2''-terpy	11%
70°C	3	4,4'',4''-tri-*tert*-butyl-2,2':6',2''-terpy	50%
RT	3	2-ampy	22%
70°C	3	2-ampy	50%
RT	3	di-(2-picolyl)amine	15%
70°C	3	di-(2-picolyl)amine	46%
RT	3	4,4'-bis(CF_3)-2,2'-bipy	35%
70°C	**3**	**4,4'-bis(CF_3)-2,2'-bipy**	**56%**
RT	3	2,2'-bpz	50%
70°C	3	2,2'-bpz	50%
RT	3	2,2'-bpm	23%
70°C	3	2,2'-bpm	50%

Ethyl-salen is *N*,*N*'-bis(salicylidene)ethylenediamine. Propyl-salen is *N*,*N*'-bis(salicylidene)-1,3-propanediamine. Salphen is *N*,*N*'-bis(salicylidene)-*o*-phenylenediamine which is also known as *N*,*N*'-bis(salicylidene)-*ortho*-phenylenediamine or *N*,*N*'-bis(salicylidene)-1,2-phenylenediamine. (*S*,*S*)-Jacobsen's ligand is (*S*,*S*)-(+)-*N*,*N*'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine. 2,2'-bipy is 2,2'-bipyridine. 1,10-phen is 1,10-phenanthroline. Sigman's ligand is 2-(2-quinolinyl)oxazoline which is also known as 2-(4,5-dihydro-2-oxazolyl)quinoline. Pybox is 2,6-bis(4,5-dihydrooxazol-2-yl)pyridine which is also known as 2,6-di(2-oxazolyl)pyridine. 4,4'-dimethyl-2,2'-bipy is 4,4'-dimethyl-2,2'-bipyridine. 4,4'-dimethoxy-2,2'-bipy is 4,4'-dimethoxy-2,2'-bipyridine. 4,4'-di-*tert*-butyl-2,2'-bipy is 4,4'-di-*tert*-butyl-2,2'-bipyridine. 5,5'-dimethyl-2,2'-bipy is 5,5'-dimethyl-2,2'-bipyridine. 6,6'-dimethyl-2,2'-bipy is 6,6'-dimethyl-2,2'-bipyridine. BPhen is bathophenanthroline which is also known as 4,7-diphenyl-1,10-phenanthroline Neocuproine is 2,9-dimethyl-1,10-phenanthroline. Bathocuproine is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline. 2,2':6',2''-terpy is 2,2':6',2''-terpyridine which is also known as either 2,6-bis(2-pyridyl)pyridine or $1^2,2^2:2^6,3^2$-terpyridine. Pymox is 2-pyrid-2-ylmonooxazoline which is also known as 2-(pyridin-2-yl)-4,5-dihydrooxazole or 2-(2-pyridyl)-4,5-dihydrooxazole or 2-pyrid-2-yloxazoline. 4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpy is 4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine which is also known as $1^4,2^4,3^4$-tri-*tert*-butyl-$1^2,2^2:2^6,3^2$-terpyridine. 2-ampy is 2-aminomethylpyridine which is also known as (pyridin-2-yl)methanamine or 2-picolylamine. Di-(2-picolyl)amine is also known as 2-(2-pyridylmethyl)aminomethylpyridine or bis(2-pyridylmethyl)amine or bis(pyridin-2-ylmethyl)amine. 4,4'-bis(CF_3)-2,2'-bipy is 4,4'-bis(trifluoromethyl)-2,2'-bipyridine. 2,2'-bpz is 2,2'-bipyrazine. 2,2'-bpm is 2,2'-bipyrimidine.

General procedure:

The ligand (20 mol%, 0.0000892 mol = 0.0892 mmol) was placed into a vial with a stir bar followed by 4 mL MeCN. Next, $Mn(OAc)_2$ $4H_2O$ (20 mol%, 0.0000892 mol = 0.0892 mmol) was added to the vial and the vial was sealed and allowed to stir vigorously for 5 min at RT. Then, the 1-chloroadamantane (1 eq., 0.000446 mol = 0.446 mmol, 0.076 g) was added to the vial and then the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial. Lastly, the Selectfluor (3 eq., 0.001338 mol = 1.338 mmol, 0.474 g) was added to the vial. The vial was sealed tightly and placed on/into the correct conditions regarding the temperature. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times with DCM, and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

(1*r*,3*s*,5*R*,7*S*)-1-azido-3-chloroadamantane has previously been characterized.[2] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.27 (s, 2H), 2.09 (s, 2H), 1.99 (q, *J* = 12.3 Hz, 4H), 1.70 (s, 3H), 1.53 (q, *J* = 12.0 Hz, 2H) 1.18 (s, br, 1H). ^{13}C{^{1}H}-NMR (151 MHz, $CDCl_3$) δ 66.5, 60.4, 51.1, 46.0, 39.8, 34.0, 31.8.

Screening Ligands (20 mol%) with $Mn(OAc)_3\ 2H_2O$ (20 mol%) for the Azidation of 1-Chloroadamantane

Temperature	Equivalents of Selectfluor	Ligand (20 mol%) used with $Mn(OAc)_3\ 2H_20$ (20 mol%)	**Yield** of (1*r*,3*s*,5*R*,7*S*)-1-azido-3-chloroadamantane
RT	3	ethyl-salen	6%
70°C	3	ethyl-salen	17%
RT	3	propyl-salen	8%
70°C	3	propyl-salen	15%
RT	3	salphen	7%
70°C	3	salphen	14%
RT	3	(*S*,*S*)-Jacobsen's ligand	36%
70°C	3	(*S*,*S*)-Jacobsen's ligand	23%
RT	3	2,2'-bipy	28%
70°C	**3**	**2,2'-bipy**	**59%**
RT	3	1,10-phen	22%
70°C	**3**	**1,10-phen**	**57%**
RT	3	Sigman's ligand	37%
70°C	**3**	**Sigman's ligand**	**54%**
RT	3	pybox	49%
70°C	3	pybox	50%
RT	3	4,4'-dimethyl-2,2'-bipy	22%
70°C	**3**	**4,4'-dimethyl-2,2'-bipy**	**64%**
RT	3	4,4'-dimethoxy-2,2'-bipy	30%
70°C	**3**	**4,4'-dimethoxy-2,2'-bipy**	**53%**
RT	3	4,4'-di-*tert*-butyl-2,2'-bipy	23%
70°C	**3**	**4,4'-di-*tert*-butyl-2,2'-bipy**	**55%**
RT	3	5,5'-dimethyl-2,2'-bipy	13%
70°C	**3**	**5,5'-dimethyl-2,2'-bipy**	**58%**
RT	**3**	**6,6'-dimethyl-2,2'-bipy**	**52%**
70°C	**3**	**6,6'-dimethyl-2,2'-bipy**	**52%**
RT	3	BPhen	29%
70°C	**3**	**BPhen**	**58%**
RT	3	neocuproine	47%
70°C	**3**	**neocuproine**	**56%**
RT	**3**	**bathocuproine**	**56%**
70°C	3	bathocuproine	50%
RT	3	2,2':6',2''-terpy	35%
70°C	3	2,2':6',2''-terpy	50%
RT	3	pymox	45%

70°C	**3**	**pymox**	**56%**
RT	3	4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpy	21%
70°C	3	4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpy	50%
RT	3	2-ampy	30%
70°C	**3**	**2-ampy**	**55%**
RT	3	di-(2-picolyl)amine	25%
70°C	3	di-(2-picolyl)amine	41%
RT	3	4,4'-bis(CF_3)-2,2'-bipy	37%
70°C	**3**	**4,4'-bis(CF_3)-2,2'-bipy**	**56%**
RT	3	2,2'-bpz	50%
70°C	3	2,2'-bpz	50%
RT	3	2,2'-bpm	33%
70°C	3	2,2'-bpm	50%

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Screening Ligands with $Mn(OAc)_2$ $4H_2O$ for the Azidation of 1-Chloroadamantane

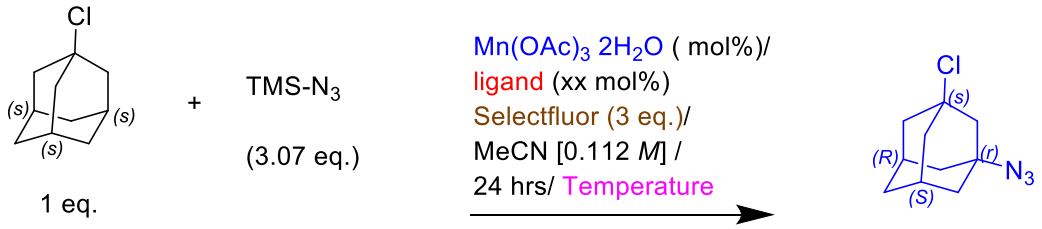
Temperature	$Mn(OAc)_2$ $4H_2O$	Ligand	**Yield** of (1*r*,3*s*,5*R*,7*S*)-1-azido-3-chloroadamantane
RT	5 mol%	(none)	41%
70°C	5 mol%	(none)	38%
RT	10 mol%	(none)	50%
70°C	10 mol%	(none)	50%
RT	30 mol%	(none)	55%
70°C	30 mol%	(none)	60%
70°C	5 mol%	2,2'-bipy (5 mol%)	49%
RT, 390 nm Blue LEDS	5 mol%	2,2'-bipy (5 mol%)	11%
RT, 427 nm Blue LEDS	5 mol%	2,2'-bipy (5 mol%)	14%
70°C	5 mol%	2,2'-bipy (10 mol%)	46%
70°C	**10 mol%**	**2,2'-bipy (10 mol%)**	**57%**
70°C	10 mol%	2,2'-bipy (20 mol%)	50%
70°C	20 mol%	2,2'-bipy (30 mol%)	58%
70°C	20 mol%	2,2'-bipy (40 mol%)	56%
70°C	30 mol%	2,2'-bipy (30 mol%)	60%
70°C	5 mol%	1,10-phen (5 mol%)	44%
70°C	5 mol%	1,10-phen (10 mol%)	41%
70°C	10 mol%	1,10-phen (10 mol%)	54%
70°C	10 mol%	1,10-phen (20 mol%)	56%
70°C	30 mol%	1,10-phen (30 mol%)	57%
70°C	5 mol%	4,4'-di-*tert*-butyl-2,2'-bipy (5 mol%)	48%
70°C	5 mol%	4,4'-di-*tert*-butyl-2,2'-bipy (10 mol%)	52%
70°C	10 mol%	4,4'-di-*tert*-butyl-2,2'-bipy (10 mol%)	56%
70°C	10 mol%	4,4'-di-*tert*-butyl-2,2'-bipy (20 mol%)	54%
70°C	30 mol%	4,4'-di-*tert*-butyl-2,2'-bipy (30 mol%)	56%
70°C	5 mol%	5,5'-dimethyl-2,2'-bipy (5 mol%)	42%
70°C	5 mol%	5,5'-dimethyl-2,2'-bipy (10 mol%)	47%
70°C	10 mol%	5,5'-dimethyl-2,2'-bipy (10 mol%)	51%
70°C	10 mol%	5,5'-dimethyl-2,2'-bipy (20 mol%)	50%
70°C	30 mol%	5,5'-dimethyl-2,2'-bipy (30 mol%)	55%

General procedure:

The ligand was placed into a vial with a stir bar followed by 4 mL MeCN. Next, $Mn(OAc)_2$ $4H_2O$ was added to the vial and the vial was sealed and allowed to stir vigorously for 5 min at RT. Then, the 1-chloroadamantane (1 eq., 0.000446 mol = 0.446 mmol, 0.076 g) was added to the vial and then the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial. Lastly, the Selectfluor (3 eq., 0.001338 mol = 1.338 mmol, 0.474 g) was added to the vial. The vial was sealed tightly and placed on/into the correct conditions regarding the temperature. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times with DCM, and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

(1*r*,3*s*,5*R*,7*S*)-1-azido-3-chloroadamantane has previously been characterized.[2] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.27 (s, 2H), 2.09 (s, 2H), 1.99 (q, *J* = 12.3 Hz, 4H), 1.70 (s, 3H), 1.53 (q, *J* = 12.0 Hz, 2H) 1.18 (s, br, 1H). $^{13}C\{^1H\}$-NMR (151 MHz, $CDCl_3$) δ 66.5, 60.4, 51.1, 46.0, 39.8, 34.0, 31.8.

Screening Ligands with $Mn(OAc)_3\ 2H_2O$ for the Azidation of 1-Chloroadamantane



Temperature	$Mn(OAc)_3\ 2H_2O$	Ligand	**Yield** of (1*r*,3*s*,5*R*,7*S*)-1-azido-3-chloroadamantane
RT	5 mol%	(none)	34%
70°C	5 mol%	(none)	38%
RT	10 mol%	(none)	50%
70°C	10 mol%	(none)	54%
RT	30 mol%	(none)	54%
70°C	30 mol%	(none)	58%
70°C	5 mol%	2,2'-bipy (5 mol%)	45%
RT, 390 nm Blue LEDS	5 mol%	2,2'-bipy (5 mol%)	15%
RT, 427 nm Blue LEDS	5 mol%	2,2'-bipy (5 mol%)	17%
70°C	5 mol%	2,2'-bipy (10 mol%)	51%
70°C	5 mol%	2,2'-bipy (15 mol%)	50%
70°C	**10 mol%**	**2,2'-bipy (10 mol%)**	**58%**
70°C	10 mol%	2,2'-bipy (20 mol%)	54%
70°C	20 mol%	2,2'-bipy (30 mol%)	55%
70°C	20 mol%	2,2'-bipy (40 mol%)	55%
70°C	30 mol%	2,2'-bipy (30 mol%)	56%
70°C	5 mol%	1,10-phen (5 mol%)	49%
70°C	5 mol%	1,10-phen (10 mol%)	49%
70°C	10 mol%	1,10-phen (10 mol%)	56%
70°C	10 mol%	1,10-phen (20 mol%)	50%
70°C	30 mol%	1,10-phen (30 mol%)	60%
70°C	5 mol%	4,4'-dimethyl-2,2'-bipy (5 mol%)	52%
70°C	5 mol%	4,4'-dimethyl-2,2'-bipy (10 mol%)	52%
70°C	10 mol%	4,4'-dimethyl-2,2'-bipy (10 mol%)	55%
70°C	10 mol%	4,4'-dimethyl-2,2'-bipy (20 mol%)	51%
70°C	none	4,4'-dimethyl-2,2'-bipy (20 mol%)	22%
70°C	20 mol%	4,4'-dimethyl-2,2'-bipy (30 mol%)	57%
70°C	20 mol%	4,4'-dimethyl-2,2'-bipy (40 mol%)	59%
70°C	30 mol%	4,4'-dimethyl-2,2'-bipy (30 mol%)	57%
70°C	5 mol%	4,4'-di-*tert*-butyl-2,2'-bipy (5 mol%)	50%
70°C	5 mol%	4,4'-di-*tert*-butyl-2,2'-bipy (10 mol%)	53%
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70°C	10 mol%	4,4'-di-*tert*-butyl-2,2'-bipy (20 mol%)	50%
70°C	30 mol%	4,4'-di-*tert*-butyl-2,2'-bipy (30 mol%)	56%
70°C	5 mol%	5,5'-dimethyl-2,2'-bipy (5 mol%)	48%

70°C	5 mol%	5,5'-dimethyl-2,2'-bipy	(10 mol%)	54%
70°C	5 mol%	5,5'-dimethyl-2,2'-bipy	(15 mol%)	52%
70°C	10 mol%	5,5'-dimethyl-2,2'-bipy	(10 mol%)	57%
70°C	10 mol%	5,5'-dimethyl-2,2'-bipy	(20 mol%)	56%
70°C	30 mol%	5,5'-dimethyl-2,2'-bipy	(30 mol%)	55%
70°C	**5 mol%**	**BPhen**	**(5 mol%)**	**54%**
70°C	none	BPhen	(5 mol%)	18%
RT	5 mol%	BPhen	(5 mol%)	32%
RT, 390 nm Blue LEDS	5 mol%	BPhen	(5 mol%)	33%
RT, 427 nm Blue LEDS	5 mol%	BPhen	(5 mol%)	30%
70°C	5 mol%	BPhen	(10 mol%)	54%
70°C	10 mol%	BPhen	(10 mol%)	50%
70°C	10 mol%	BPhen	(20 mol%)	47%
70°C	30 mol%	BPhen	(30 mol%)	58%

General procedure:

The ligand was placed into a vial with a stir bar followed by 4 mL MeCN. Next, $Mn(OAc)_3$ $2H_2O$ was added to the vial and the vial was sealed and allowed to stir vigorously for 5 min at RT. Then, the 1-chloroadamantane (1 eq., 0.000446 mol = 0.446 mmol, 0.076 g) was added to the vial and then the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial. Lastly, the Selectfluor (3 eq., 0.001338 mol = 1.338 mmol, 0.474 g) was added to the vial. The vial was sealed tightly and placed on/into the correct conditions regarding the temperature. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times with DCM, and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

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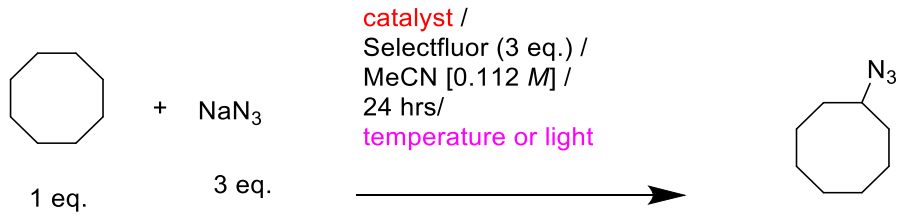
Screening NaN_3 instead of TMS-N_3 for the Azidation of Cyclooctane



Temp. or light	Catalyst	Yield of azidocyclooctane
70°C	$Fe(NO_3)_3$ $9H_2O$ (20 mol%)	21% (and 5% yield of fluorocyclooctane)
70°C	$Fe(OTf)_3$ (20 mol%)	8% (and 9% yield of fluorocyclooctane) (and 4% yield of cyclooctanone)
RT, 390 nm* 40 W, Blue LEDs	$Fe(NO_3)_3$ $9H_2O$* (20 mol%)	22%* (and 13% yield of fluorocyclooctane)* (and 4% yield of cyclooctanone)*
70°C	$Mn(OAc)_3$ $2H_2O$ (5 mol%) and BPhen (5 mol%)	8% (and 4% yield of fluorocyclooctane) (and 1% yield of cyclooctanone)
70°C	$Mn(OAc)_3$ $2H_2O$ (20 mol%) and 1,4-dimethyl-bipy (20 mol%)	12% (and 4% yield of fluorocyclooctane) (and 2% yield of cyclooctanone)

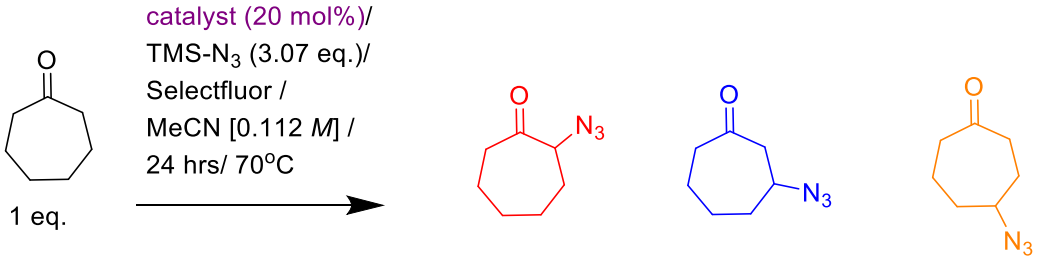
*2 eq. Selectfluor and the concentration is 0.223 *M* (with 2 mL MeCN) instead of 0.112 *M*; 390 nm (40 W blue LEDs, 1 cm, 25% intensity)

Azidocyclooctane (also known as cyclooctyl azide) has previously been characterized.[1,2] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.55 (tt, *J* = 8.5, 4.0 Hz, 1H), 1.89 – 1.84 (m, 2H), 1.74 – 1.66 (m, 4H), 1.57 – 1.46 (m, 8H).

Fluorocyclooctane has previously been characterized.[3] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 4.69 (dm, *J* = 48 Hz, 1H), 1.93 – 1.86 (m, 4H), 1.74 – 1.69 (m, 2H), 1.59 – 1.44 (m, 8H).

Cyclooctanone has previously been characterized.[6] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.43 – 2.40 (m, 1H), 1.90 – 1.86 (m, 1H), 1.57 – 1.53 (m, 1H), 1.40 – 1.35 (m, 1H).

Screening Conditions for the Azidation of Cycloheptanone with Selectfluor



Catalyst (20 mol%)	**Selectfluor**	2-azidocycloheptanone	3-azidocycloheptanone	4-azidocycloheptanone
$Fe(NO_3)_3\ 9H_2O$	2 eq.	17%	trace	trace
$Fe(NO_3)_3\ 9H_2O$	3 eq.	**53%**	**16%**	16%
$Fe(NO_3)_3\ 9H_2O$ with 1 eq. Na_2CO_3	3 eq.	16%	8%	10%
$Fe(OTf)_3$	3 eq.	2%	4%	**20%**
(none)	3 eq.	27%	2%	2%
(none) with 1 eq. Na_2CO_3	3 eq.	10%	1%	1%
$Fe(OAc)_2$	3 eq.	29%	trace	trace
$Fe(OTf)_2$	3 eq.	7%	trace	trace
Fe(III) oxalate $6H_2O$	3 eq.	27%	trace	trace
$Mn(OAc)_2\ 4H_2O$	3 eq.	5%	trace	trace
MnF_3	3 eq.	18%	4%	4%
$Mn(OAc)_3\ 2H_2O$	3 eq.	16%	3%	3%
$Mn(OTf)_2$	3 eq.	18%	5%	7%
$Mn(OAc)_3\ 2H_2O$ (5 mol%), BPhen (5 mol%)	3 eq.	21%	4%	4%
$Mn(OAc)_3\ 2H_2O$ (20 mol%), 4,4'-dimethyl-bipy (20 mol%)	3 eq.	24%	4%	4%
$Fe(NO_3)_3\ 9H_2O$ with 1 eq. NaN_3 (as well as the TMS-N_3)	3 eq.	14%	3%	3%
$Fe(NO_3)_3\ 9H_2O$ (1 eq.)	0 eq.	14%	none	none

General procedure:

Cycloheptanone (1 eq., 0.000446 mol = 0.446 mmol, 0.053 mL) was added to a vial with a stir bar followed by 4 mL MeCN (for 0.112 *M*). Next the catalyst (20 mol%, 0.0000892 mol = 0.0892 mmol) was added to the vial. Then, the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial and lastly the Selectfluor (3 eq., 0.001338 mol = 1.338 mmol, 474 mg) was added to the vial. The vial was sealed tightly and placed on to a pre-heated 70^{o}C sand bath. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times (with a mixture of ethyl acetate and hexanes in a 1:1 ratio), and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

2-azidocycloheptan-1-one (also known as 2-azidocycloheptanone or α-azidocycloheptanone) has previously been characterized.[9]
^{1}H-NMR (600 MHz, $CDCl_3$) δ 4.08 (dd, *J* = 9.2, 3.7 Hz, 1H), 2.64 – 2.59 (m, 1H), 2.53 (ddd, *J* = 15.9, 10.1, 4.0 Hz, 1H), 1.86 – 1.60 (m, 6H), 1.48 – 1.43 (m, 1H).
^{13}C{^{1}H}-NMR (151 MHz, $CDCl_3$) δ 208.6, 67.8, 41.4, 30.8, 28.9, 26.6, 23.6.

3-azidocycloheptan-1-one (also known as 3-azidocycloheptanone or β-azidocycloheptanone) has previously been characterized.[10]

4-azidocycloheptan-1-one (also known as 4-azidocycloheptanone or γ-azidocycloheptanone) has previously been characterized.[1]

General procedure for Method A ([Fe] Conditions)

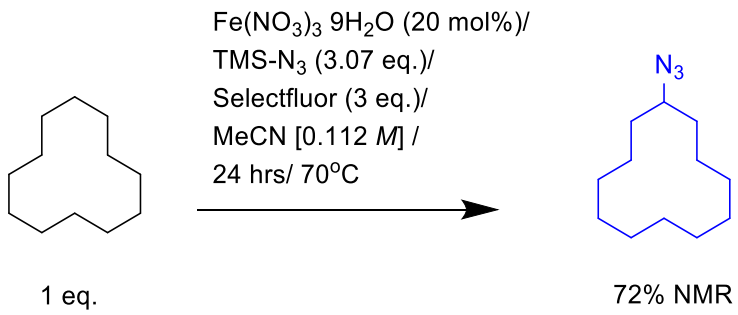
The substrate (1 eq., 0.000446 mol = 0.446 mmol) was added to a vial with a stir bar followed by 4 mL MeCN (for 0.112 *M*). Next the $Fe(NO_3)_3$ $9H_2O$ (20 mol%, 0.0000892 mol = 0.0892 mmol, 36 mg) was added to the vial. Then, the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial and lastly the Selectfluor (3 eq., 0.001338 mol = 1.338 mmol, 474 mg) was added to the vial. The vial was sealed tightly and placed on to a pre-heated 70°C sand bath. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

General procedure for Method B (alternative [Mn] Conditions not presented in main text)

BPhen (5 mol%, 0.0000223 mol = 0.0223 mmol, 7.4 mg) was placed into a vial with a stir bar followed by 4 mL MeCN. Next, $Mn(OAc)_3$ $2H_2O$ (5 mol%, 0.0000223 mol = 0.0223 mmol, 5.98 mg) was added to the vial and the vial was sealed and allowed to stir vigorously for 5 min at RT. Next, the substrate (1 eq., 0.000446 mol = 0.446 mmol) was added to a vial. Then, the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial and lastly the Selectfluor (3 eq., 0.001338 mol = 1.338 mmol, 474 mg) was added to the vial. The vial was sealed tightly and placed on to a pre-heated 70°C sand bath. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

General procedure for Method C ([Mn] conditions)

4,4'-dimethyl-2,2'-bipy (20 mol%, 0.0000892 mol = 0.0892 mmol, 16 mg) was placed into a vial with a stir bar followed by 4 mL MeCN. Next, $Mn(OAc)_3$ $2H_2O$ (20 mol%, 0.0000892 mol = 0.0892 mmol, 23.9 mg) was added to the vial and the vial was sealed and allowed to stir vigorously for 5 min at RT. Next, the substrate (1 eq., 0.000446 mol = 0.446 mmol) was added to a vial. Then, the TMS-N_3 (3.07 eq., 0.00137 mol = 1.37 mmol, 0.18 mL) was added to the vial and lastly the Selectfluor (3 eq., 0.001338 mol = 1.338 mmol, 474 mg) was added to the vial. The vial was sealed tightly and placed on to a pre-heated 70°C sand bath. The reaction was stirred vigorously for 24 hours. Then, the reaction was diluted with DCM and ran over a short silica pad, which was washed multiple times and then concentrated on the rotary evaporator. The NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

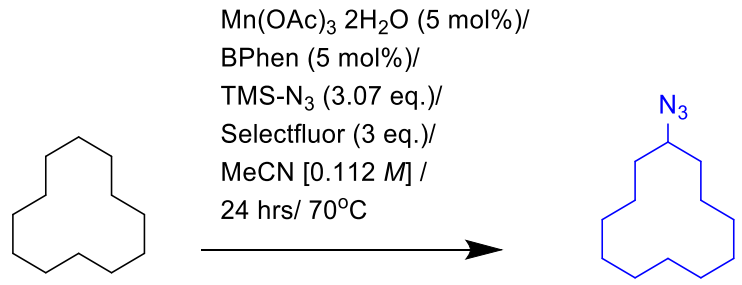


66% isolated yield

(62.1 mg)

1 eq.

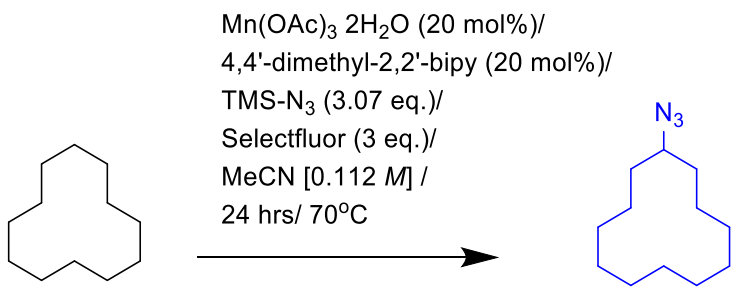
72% NMR yield



Chemical Formula: $C_{12}H_{23}N_3$
Exact Mass: 209.1892
Molecular Weight: 209.3370

1 eq.

40% NMR yield



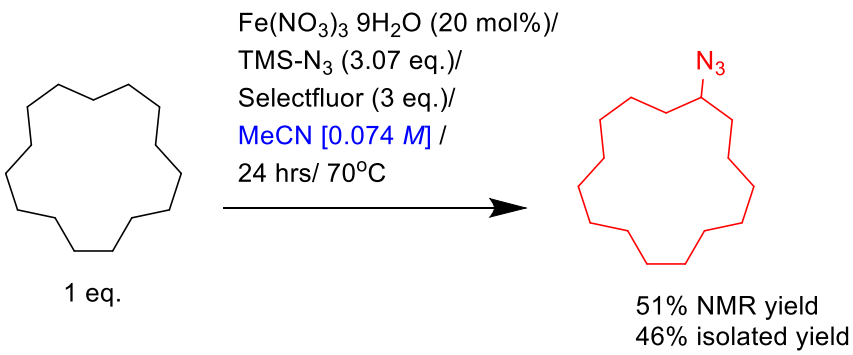
39% isolated yield

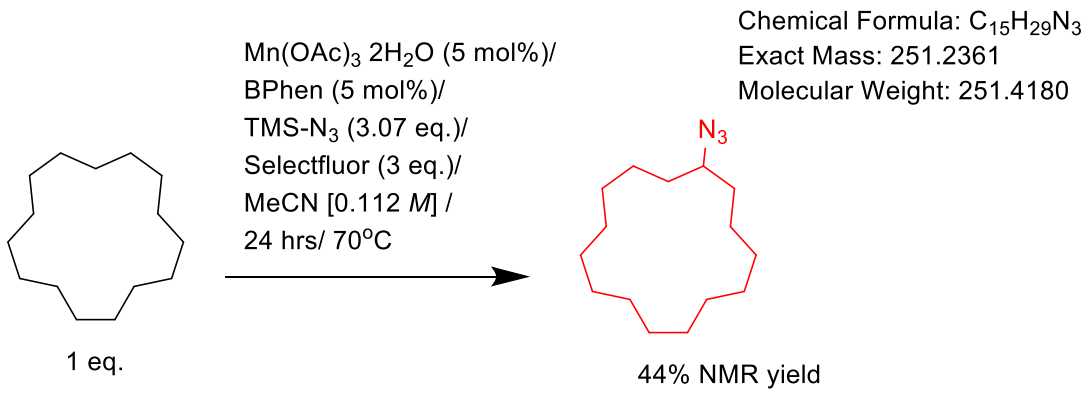
(36.2 mg)

1 eq.

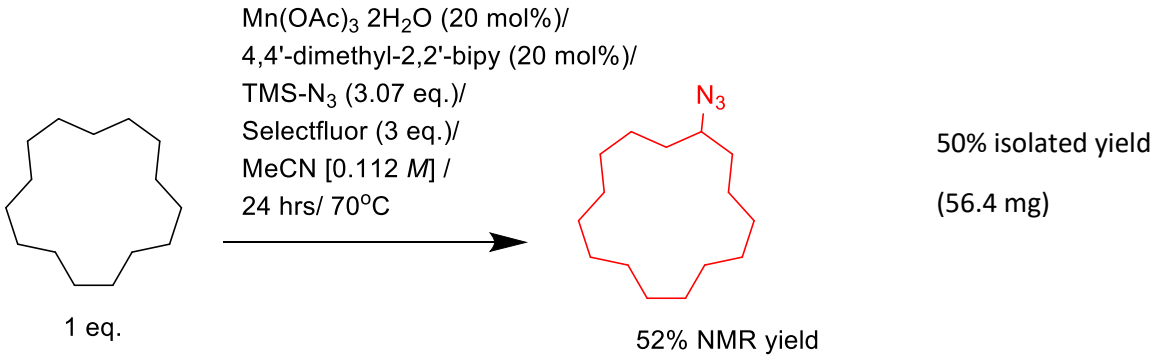
43% NMR yield

Azidocyclododecane (also known as cyclododecyl azide) has previously been characterized.[2,7] ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.53 – 3.43 (m, 1H), 1.73 – 1.60 (m, 2H), 1.53 – 1.44 (m, 4H), 1.42 – 1.32 (m, 16H).



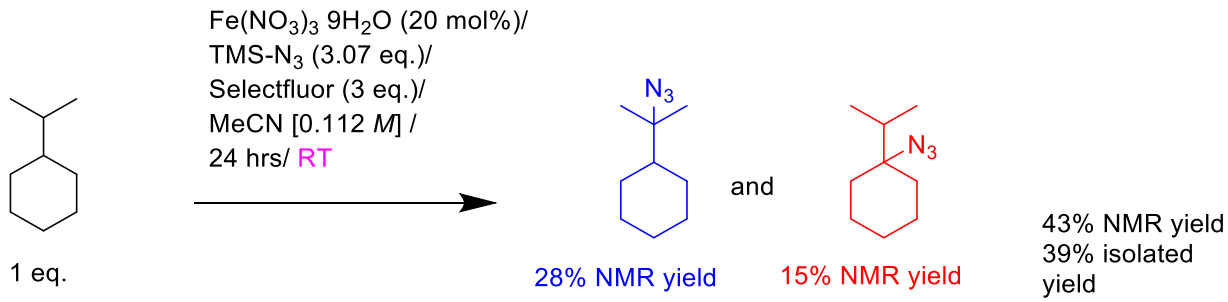


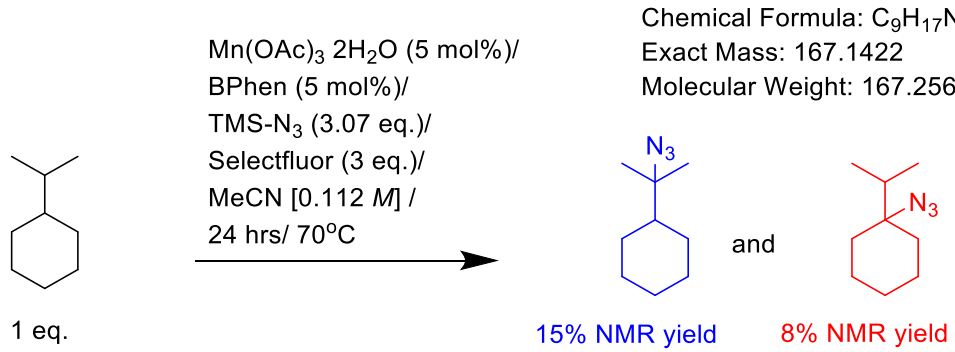
Chemical Formula: $C_{15}H_{29}N_3$
Exact Mass: 251.2361
Molecular Weight: 251.4180

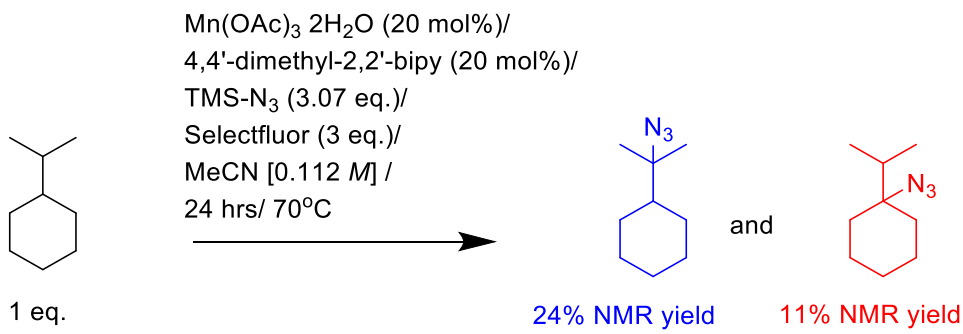


After purification with flash column chromatography on silica gel, the reaction produced a 46% isolated yield (51mg) of azidocyclopentadecane (also known as cyclopentadecyl azide) as a clear solid using conditions A and 50% isolated yield (56.4mg) using conditions C.

^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.35-3.29 (p, *J* = 6.15 Hz, 1H), 1.55-1.46 (m, 5H), 1.35-1.31 (s, br, 7H), 1.30-1.22 (s, br, 16H). $^{13}C\{^{1}H\}$-NMR (151 MHz, $CDCl_3$) δ 61.0, 31.7, 26.84, 26.77, 26.73, 26.68, 26.63, 23.6. HRAPCIMS m/z 224.2368 $[M\text{-}N_2\text{+}H]^+$ (calcd for $C_{15}H_{29}N_1\text{+}H^+$, 224.2378).

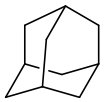






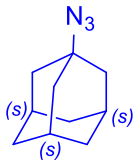
After purification with flash column chromatography on silica gel, the reaction produced a 39% isolated yield (29mg) of (2-azidopropan-2-yl)cyclohexane and 1-azido-1-isopropylcyclohexane as a clear liquid. Both (2-azidopropan-2-yl)cyclohexane and 1-azido-1-isopropylcyclohexane have previously been characterized together as a mixture of the two isomers.[2]

^{1}H-NMR (600 MHz, $CDCl_3$) δ 1.82 – 1.76 (m, 3H), 1.70 – 1.64 (m, 2H), 1.61 – 1.53 (m, 1H), 1.42 – 1.27 (m, 2H), 1.22 (s, 4H), 1.15 – 1.09 (m, 1H), 1.04 – 0.91 (m, 2H), 0.96 (d, *J* = 6.8 Hz, 2H).
^{13}C{^{1}H}-NMR (151 MHz, $CDCl_3$) δ 67.1, 64.7, 47.5, 37.2 (broad), 31.5, 27.7, 26.6, 26.4, 25.5, 23.5, 22.2, 17.2.



1 eq.

$Fe(NO_3)_3$ $9H_2O$ (20 mol%)/
$TMS\text{-}N_3$ (3.07 eq.)/
Selectfluor (3 eq.)/
MeCN [0.112 *M*] /
24 hrs/ RT

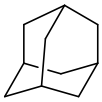


33% NMR yield

35% isolated yield

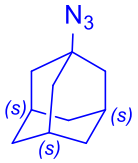
(27.9 mg)

Chemical Formula: $C_{10}H_{15}N_3$
Exact Mass: 177.1266
Molecular Weight: 177.2510

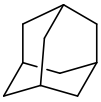


1 eq.

$Mn(OAc)_3$ $2H_2O$ (5 mol%)/
BPhen (5 mol%)/
$TMS\text{-}N_3$ (3.07 eq.)/
Selectfluor (3 eq.)/
MeCN [0.112 *M*] /
24 hrs/ 70°C

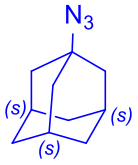


22% NMR yield



1 eq.

$Mn(OAc)_3$ $2H_2O$ (20 mol%)/
4,4'-dimethyl-bipy (20 mol%)/
$TMS\text{-}N_3$ (3.07 eq.)/
Selectfluor (3 eq.)/
MeCN [0.112 *M*] /
48 hrs/ RT



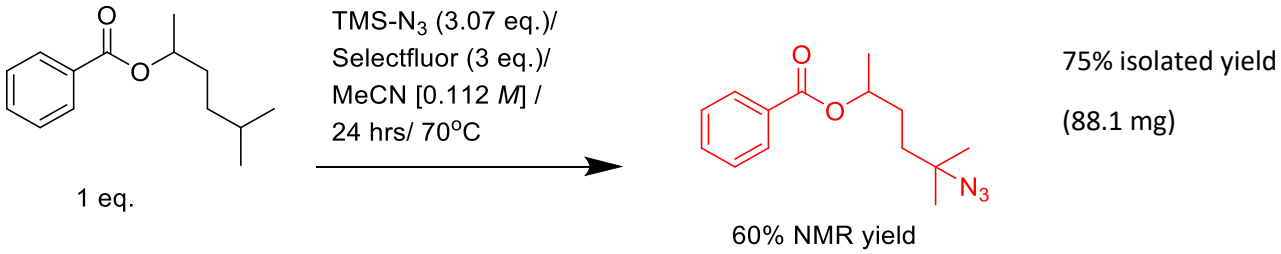
45% NMR yield

40% isolated yield

(31.9 mg)

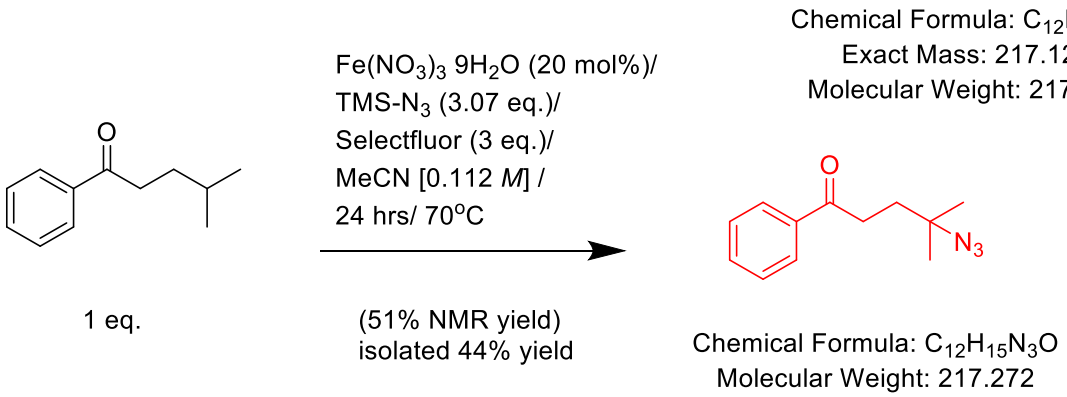
(3*s*,5*s*,7*s*)-1-azidoadamantane (also known as (3*s*,5*s*,7*s*)-1-adamantyl azide) has previously been characterized.[1, 16] The product was isolated as a white solid in 35% yield (27.9 mg) using conditions A [Fe] and 40% yield (31.9 mg) using conditions C [Mn]

^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.15 (s, 3H), 1.80 (d, *J* = 2.8 Hz, 6H), 1.71 – 1.61 (m, 6H).
$^{13}C\{^1H\}$-NMR (151 MHz, $CDCl_3$) δ 59.0, 41.5, 35.9, 29.8.



5-azido-5-methylhexan-2-yl benzoate (also known as 4-azido-1,4-dimethylpentyl benzoate) has previously been characterized.[1, 18] It was isolated as a colorless oil in 75% yield (88.1 mg) using conditions A [Fe] and 70% yield (82.2 mg) using conditions C [Mn].

^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 1.3 Hz, 2H), 7.54 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 5.18 – 5.10 (m, 1H), 1.82 – 1.77 (m, 1H), 1.71 (m, 1H), 1.62 (ddd, *J* = 13.6, 12.1, 4.5 Hz, 1H), 1.58 – 1.49 (m, 1H), 1.36 (d, *J* = 6.3 Hz, 3H), 1.27 (s, 6H).

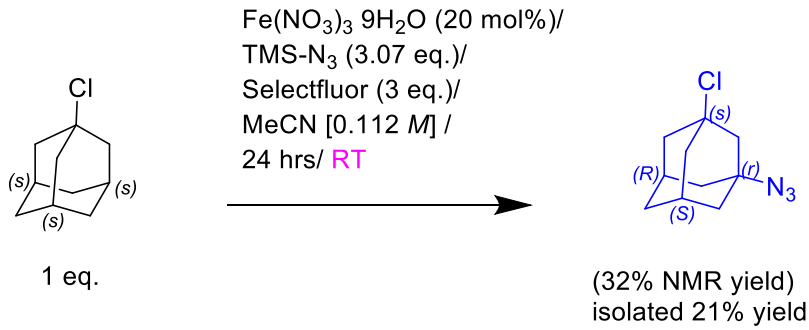


4-azido-4-methyl-1-phenylpentan-1-one (also known as 4-azido-4-methyl-1-phenyl-1-pentanone or 4-azido-4-methylvalerophenone) has previously been characterized.[18]

After purification with flash column chromatography on silica gel, the reaction produced a 44% isolated yield (42.6mg) of 4-azido-4-methyl-1-phenylpentan-1-one as a clear liquid. The reaction was also isolable in 41% yield (40.0 mg) using conditions C [Mn].

^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.89 (d, *J* = 8.4 Hz, 2H), 7.52 – 7.48 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 3.02 – 2.98 (m, 2H), 1.90 – 1.86 (m, 2H), 1.27 (s, 6H).

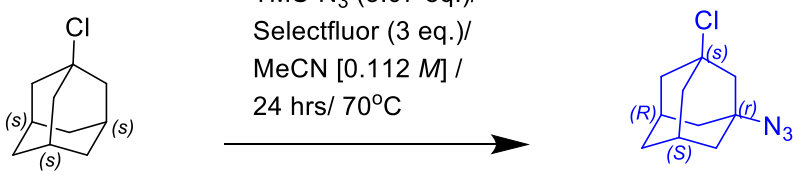
$^{13}C\{^{1}H\}$-NMR (151 MHz, $CDCl_3$) δ 199.5, 136.8, 133.2, 128.7, 128.1, 61.1, 35.4, 33.6, 26.1.



1 eq.

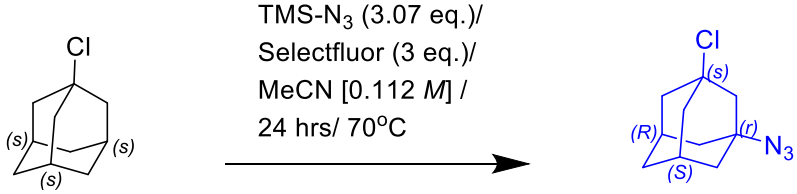
(32% NMR yield)
isolated 21% yield

Chemical Formula: $C_{10}H_{14}ClN_3$
Exact Mass: 211.0876
Molecular Weight: 211.6930



1 eq.

54% NMR yield



1 eq.

64% NMR yield

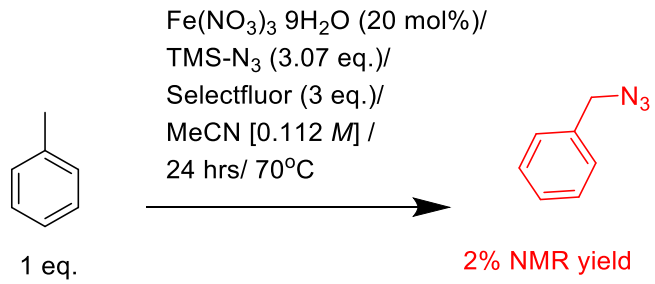
51% isolated yield

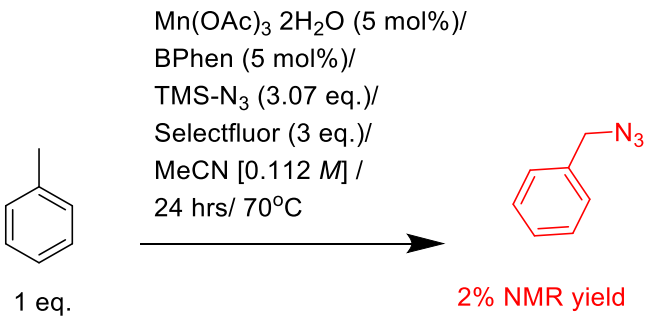
(48.5 mg)

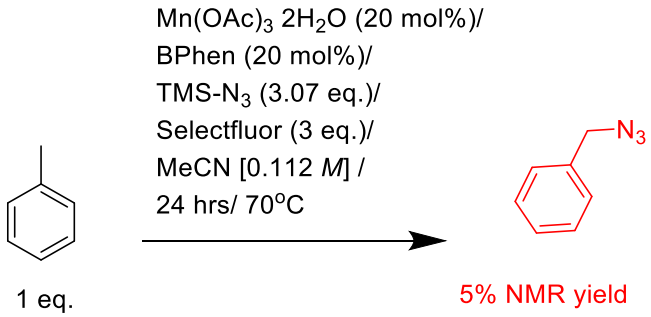
(1*r*,3*s*,5*R*,7*S*)-1-azido-3-chloroadamantane has previously been characterized.[2]

After purification with flash column chromatography on silica gel, the reaction produced a 21% isolated yield (19.8mg) of (1*r*,3*s*,5*R*,7*S*)-1-azido-3-chloroadamantane as a clear compound using Conditions A [Fe] and 51% yield (48.5 mg) using Conditions C [Mn].

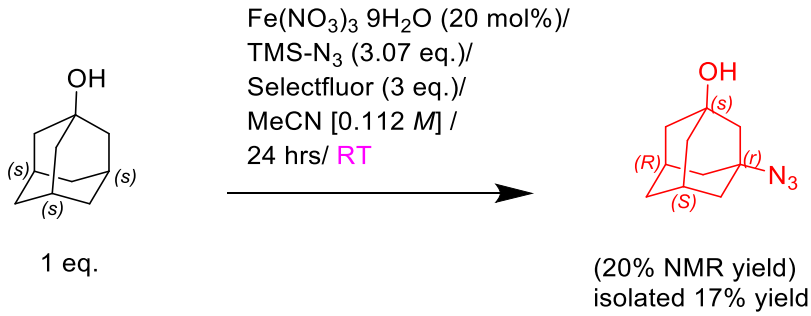
^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.27 (s, 2H), 2.09 (s, 2H), 1.99 (q, *J* = 12.3 Hz, 4H), 1.70 (s, 3H), 1.53 (q, *J* = 12.0 Hz, 2H) 1.18 (s, br, 1H). $^{13}C\{^{1}H\}$-NMR (151 MHz, $CDCl_3$) δ 66.5, 60.4, 51.1, 46.0, 39.8, 34.0, 31.8.



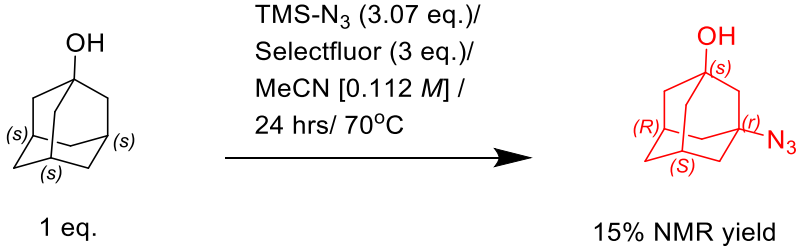


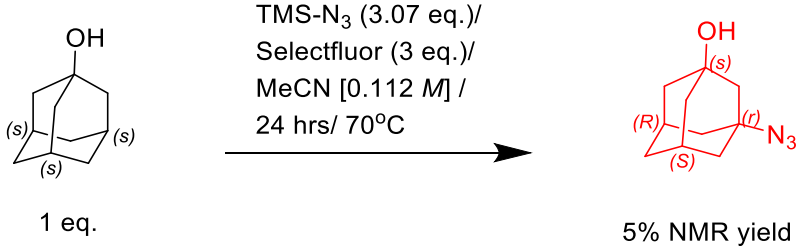


Benzyl azide (also known as either (azidomethyl)benzene or 1-(azidomethyl)benzene) has previously been characterized.[15, 17]



Chemical Formula: $C_{10}H_{15}N_3O$
Exact Mass: 193.1215
Molecular Weight: 193.2500

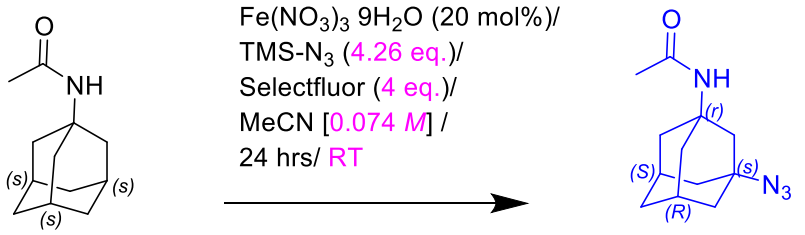




(1*s*,3*r*,5*R*,7*S*)-3-azidoadamantan-1-ol (also known as (1*r*,3*s*,5*R*,7*S*)-1-azidoadamantan-3-ol) has previously been characterized.[19]

After purification with flash column chromatography on silica gel, the reaction produced a 17% isolated yield (14.6mg) of (1*s*,3*r*,5*R*,7*S*)-3-azidoadamantan-1-ol as a white solid.

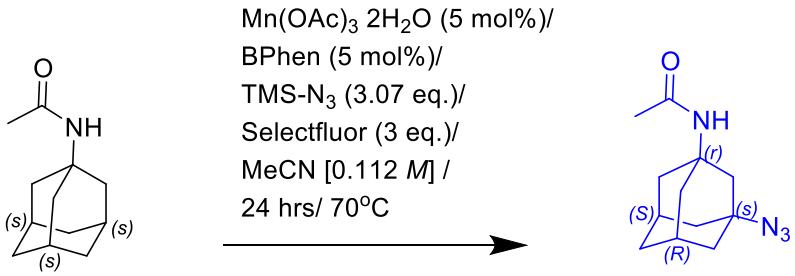
^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.27 (s, br, 2H), 1.70 (s, 2H), 1.65 (s, br, 4H), 1.62 (s, br, 4H), 1.49 – 1.46 (s, br, 2H). $^{13}C\{^{1}H\}$-NMR (151 MHz, $CDCl_3$) δ 69.6, 60.7, 49.1, 43.8, 40.2, 34.5, 30.3.



1 eq.

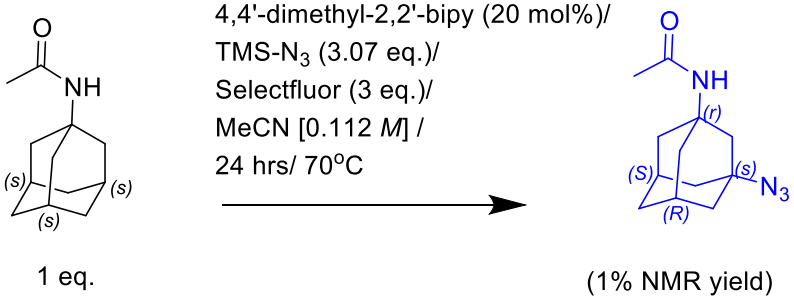
Chemical Formula: $C_{12}H_{18}N_4O$
Exact Mass: 234.1481
Molecular Weight: 234.3030

(30% NMR yield)
isolated 22% yield



1 eq.

trace

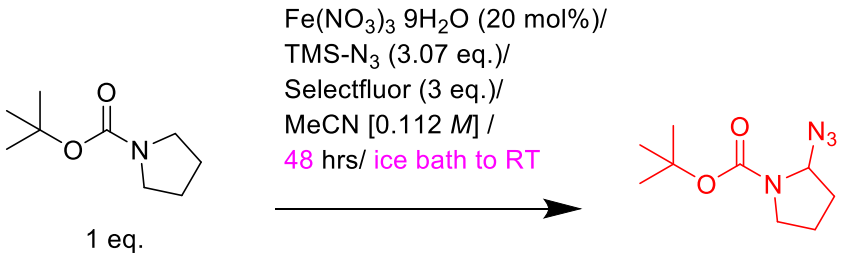


1 eq.

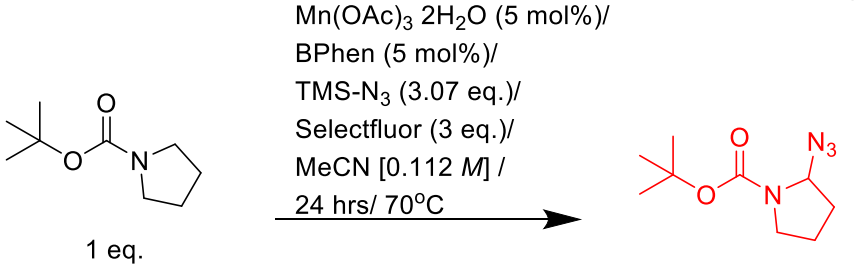
(1% NMR yield)

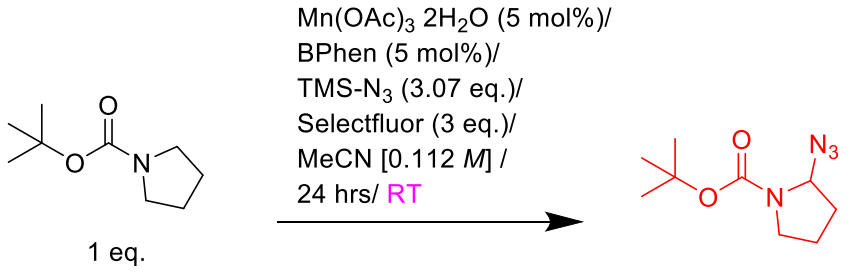
After purification with flash column chromatography on silica gel, the reaction produced a 22% isolated yield (23mg) of *N*-((1*r*,3*s*,5*R*,7*S*)-3-azidoadamantan-1-yl)acetamide as a white solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.22 (s, 2H), 2.01 (s, 2H), 1.91 (s, 3H), 1.86-1.81 (m, 4H), 1.71 (d, *J* = 11.9 Hz, 2H), 1.67 (d, *J* = 12.2 Hz, 2H), 1.56 (d, *J* = 13.2 Hz, 1H), 1.50 (d, *J* = 13.2 Hz, 1H).
^{13}C{^{1}H}-NMR (151 MHz, $CDCl_3$) δ 169.5, 59.6, 53.4, 45.1, 41.6, 40.5, 40.2, 36.3, 34.8, 30.0, 29.4, 24.6.
HRAPCIMS m/z 207.1492 $[M-N_2+H]^+$ (calcd for $C_{12}H_{18}N_2O_1+H^+$, 207.1497).

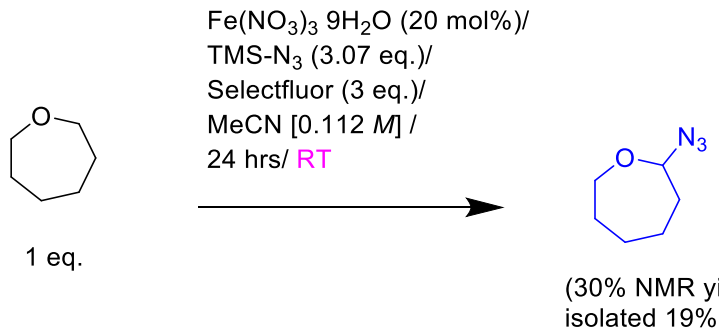


Chemical Formula: $C_9H_{16}N_4O_2$
Exact Mass: 212.1273
Molecular Weight: 212.2530

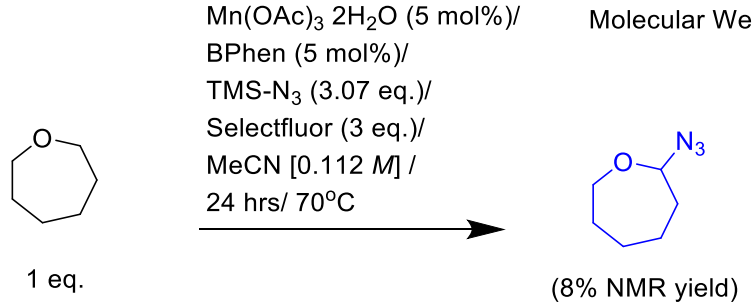


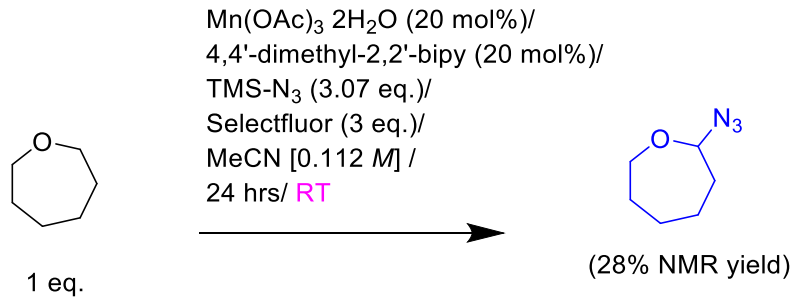


Tert-butyl 2-azidopyrrolidine-1-carboxylate (also known as 1-Boc-2-azidopyrrolidine, 1-Boc-α-azidopyrrolidine, or 1-Boc-pyrrolidin-2-yl azide) has previously been characterized.[11]
^{1}H-NMR (600 MHz, $CDCl_3$) δ 5.53 – 5.38 (m, 1H), 3.60 – 3.46 (m, 1H), 3.34 – 3.25 (m, 1H), 2.25 – 2.11 (m, 1H), 1.95 – 1.80 (m, 3H), 1.52 – 1.48* (m, 9H). *multiple rotamers present at RT in $CDCl_3$



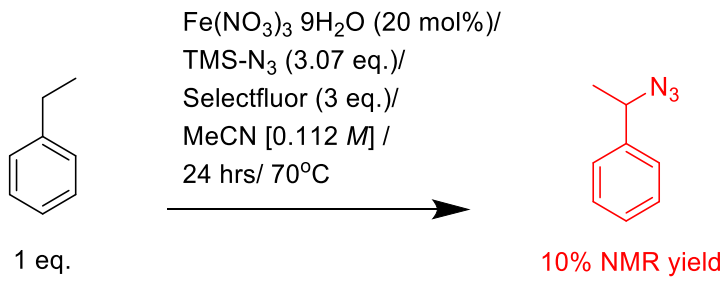
Chemical Formula: $C_6H_{11}N_3O$
Exact Mass: 141.0902
Molecular Weight: 141.1740





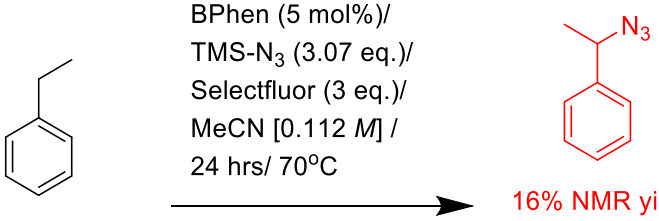
After purification with flash column chromatography on silica gel, the reaction produced a 19% isolated yield (12mg) of 2-azidooxepane (also known as 2-oxepanyl azide, 2-azidohexamethylene oxide, α-azidooxepane, or α-azidohexamethylene oxide).

^{1}H-NMR (600 MHz, $CDCl_3$) δ 5.17 (apparent dd, *J* = 9.6, 5.2 Hz, 1H), 3.85 (ddd, *J* = 12.6, 10.6, 1.9 Hz, 1H), 3.73 (dddd, *J* = 12.7, 4.5, 3.3, 1.3 Hz, 1H), 2.02 (dddq, *J* = 14.6, 7.9, 5.2, 1.5 Hz, 1H), 1.84 – 1.80 (m, 1H), 1.77 – 1.69 (m, 2H), 1.67 – 1.57 (m, 2H), 1.45 (dtt, *J* = 13.1, 11.0, 1.7 Hz, 1H), 1.36 (dtdd, *J* = 14.2, 11.7, 4.5, 2.6 Hz, 1H). ^{13}C{^{1}H}-NMR (151 MHz, $CDCl_3$) δ 91.7, 64.2, 34.7, 30.6, 28.9, 23.0.
HRAPCIMS m/z 114.0916 $[M\text{-}N_2+H]^+$ (calcd for $C_6H_{11}N_1O_1+H^+$, 114.0919).



1 eq.

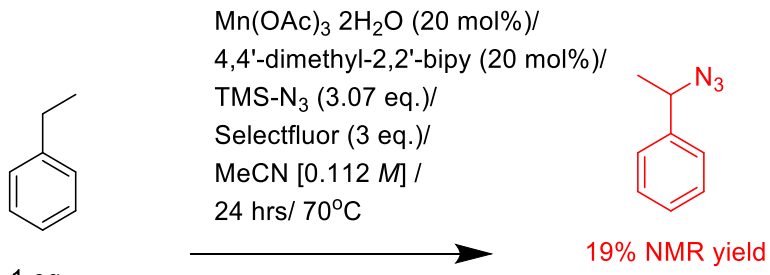
10% NMR yield



1 eq.

16% NMR yield

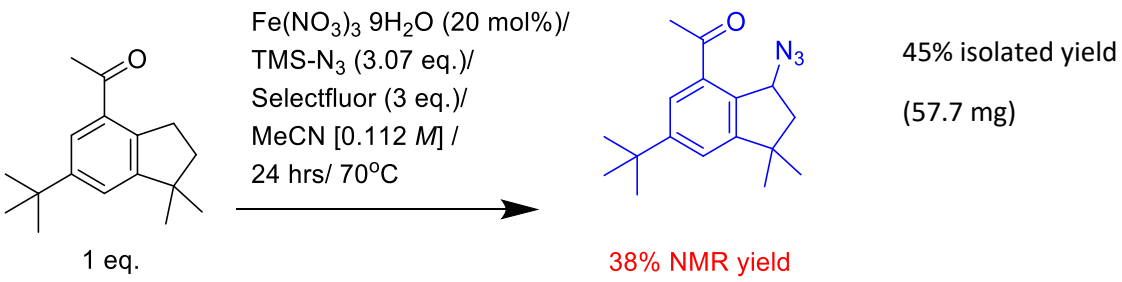
Chemical Formula: $C_8H_9N_3$
Exact Mass: 147.0796
Molecular Weight: 147.1810



1 eq.

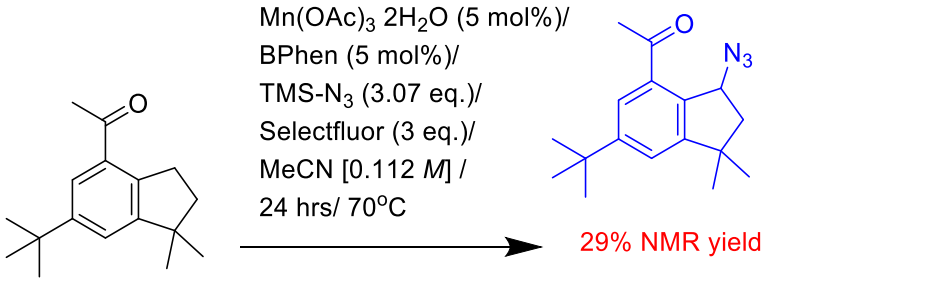
19% NMR yield

1-azidoethylbenzene (also known as 1-phenylethyl azide, α-methylbenzyl azide, or 1-azido-1-phenylethane) has previously been characterized.[12]
^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.30 (m, 2H), 7.25 (m, 3H), 4.58 (q, *J* = 6.8 Hz, 1H) 1.45 (d, *J* = 6.8 Hz, 3H).
$^{13}C\{^1H\}$-NMR (151 MHz, $CDCl_3$) δ 140.8, 128.8, 128.1, 126.4, 61.1, 21.6.

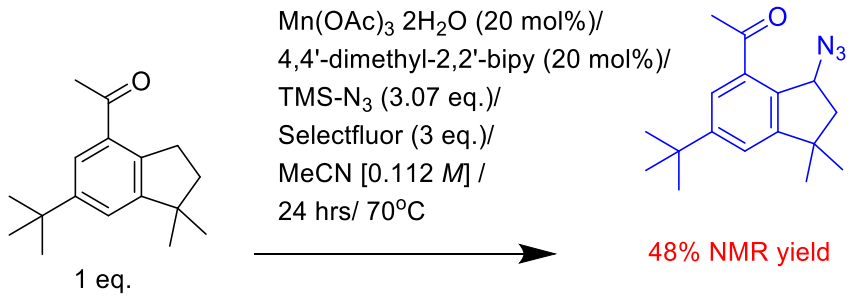


45% isolated yield

(57.7 mg)



Chemical Formula: $C_{17}H_{23}N_3O$
Exact Mass: 285.1841
Molecular Weight: 285.3910

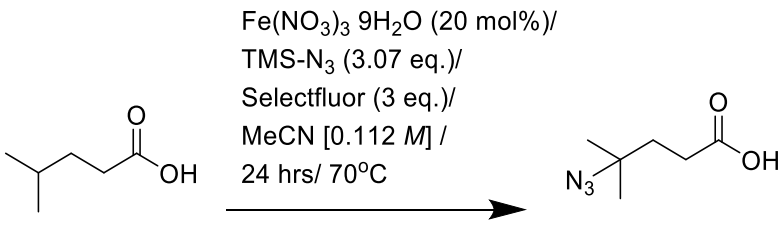


54% isolated yield

(69.3 mg)

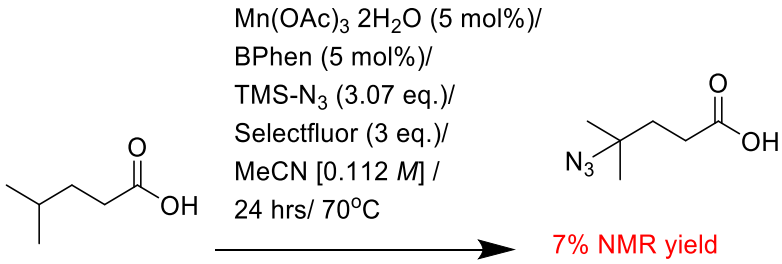
3-azido-celestolide (also known as 1-(3-azido-6-(*tert*-butyl)-1,1-dimethyl-2,3-dihydro-1*H*-inden-4-yl)ethan-1-one or 4-acetyl-3-azido-6-*tert*-butyl-1,1-dimethylindan) has previously been characterized.[13] It was isolated as a colorless oil in 45% yield (57.7 mg) using Conditions A [Fe] and 54% yield (69.3 mg) using conditions C [Mn]

^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 1.7 Hz, 1H), 7.31 (d, *J* = 1.7 Hz, 1H), 5.46 (dd, *J* = 7.4, 1.7 Hz, 1H), 2.53 (s, 3H), 2.05 (dd, *J* = 13.7, 7.4 Hz, 1H), 1.95 (dd, *J* = 13.6, 1.7 Hz, 1H) 1.36 (s, 9H), 1.31 (d, *J* = 9.0 Hz, 6H)



1 eq.

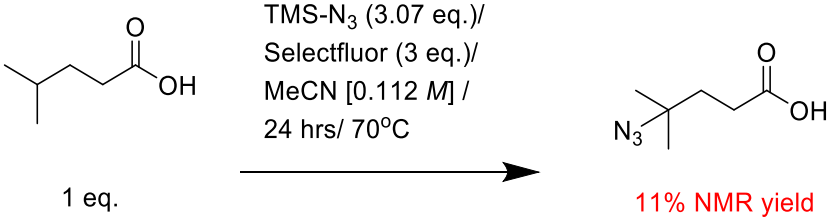
43% NMR yield



1 eq.

7% NMR yield

Chemical Formula: $C_6H_{11}N_3O_2$
Exact Mass: 157.0851
Molecular Weight: 157.1730

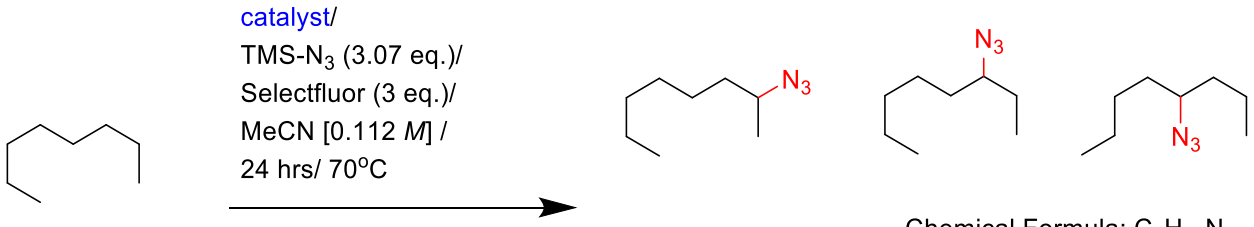


1 eq.

11% NMR yield

4-azido-4-methylpentanoic acid (also known as 4-azido-4-methylvaleric acid or 4-azidoisocaproic acid) has previously been characterized.[18, 20]

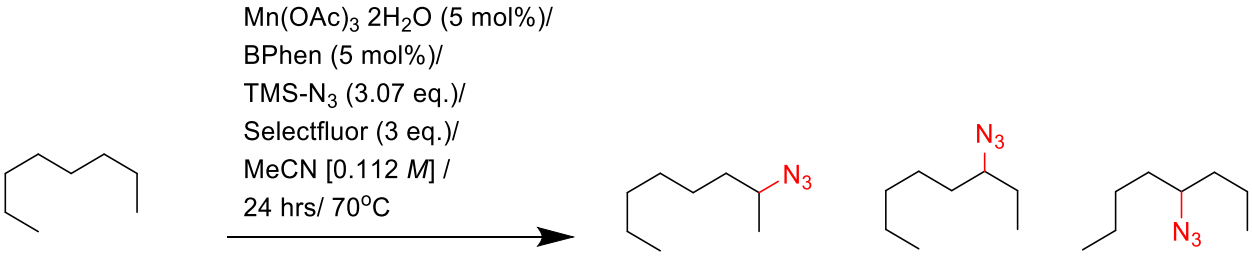
^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.55 (t, *J* = 8.1 Hz, 2H), 1.98 (t, *J* = 8.0 Hz, 2H), 1.36 (s, 6H).



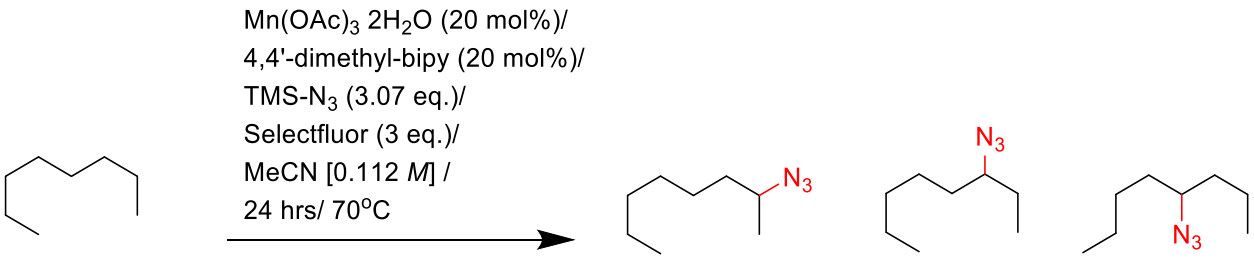
Chemical Formula: $C_8H_{17}N_3$
Exact Mass: 155.1422
Molecular Weight: 155.2450

$Fe(NO_3)_3$ $9H_2O$ (20 mol%) gave a 31% NMR yield, mixture of isomers

$Fe(OTf)_3$ (30 mol%) gave a 43% NMR yield, mixture of isomers

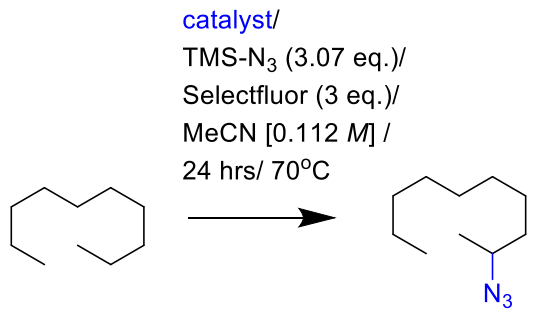


34% NMR yield, mixture of isomers

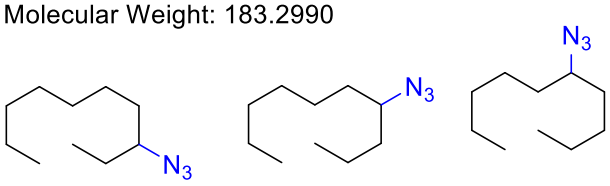


37% NMR yield, mixture of isomers

After purification with flash column chromatography on silica gel, the reaction produced a mixture of the following isomers: 2-azidooctane, 3-azidooctane, and 4-azidooctane. 2-azidooctane, 3-azidooctane, and 4-azidooctane have all previously been characterized.[1,8] They are characterized here as an inseperable mixture. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.47 – 3.36 (m, 0.33H), 3.23 (m, 0.33H), 3.17 (m, 0.33H), 1.61 – 1.42 (m, 5H), 1.34 – 1.25 (m, 5H), 1.00 – 0.86 (m, 6H).



Chemical Formula: $C_{10}H_{21}N_3$
Exact Mass: 183.1735
Molecular Weight: 183.2990

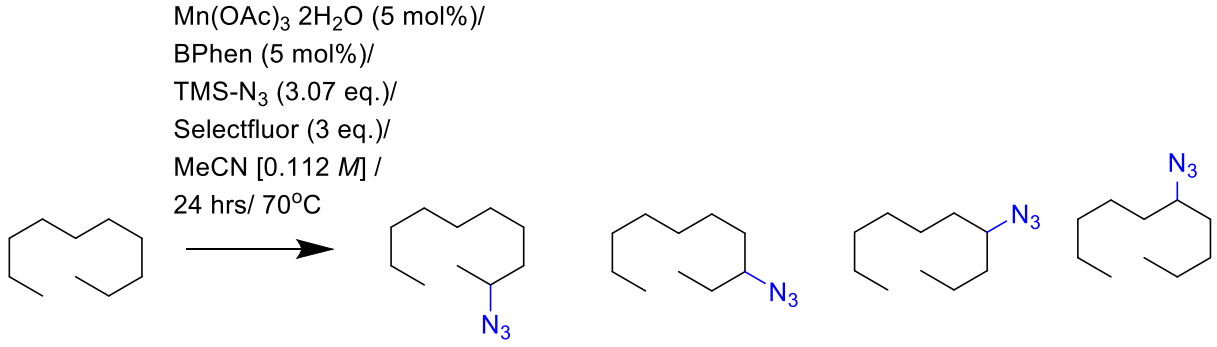


$Fe(NO_3)_3\ 9H_2O$ (20 mol%) gave a 43% yield

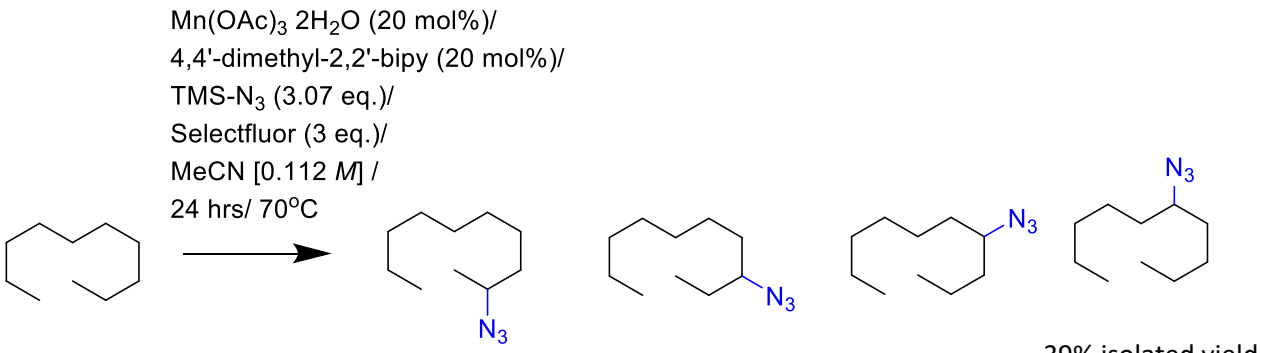
$Fe(OTf)_3$ (30 mol%) gave a 62% yield

50% isolated yield

(41.2 mg)



(34% NMR yield, mixture of isomers)

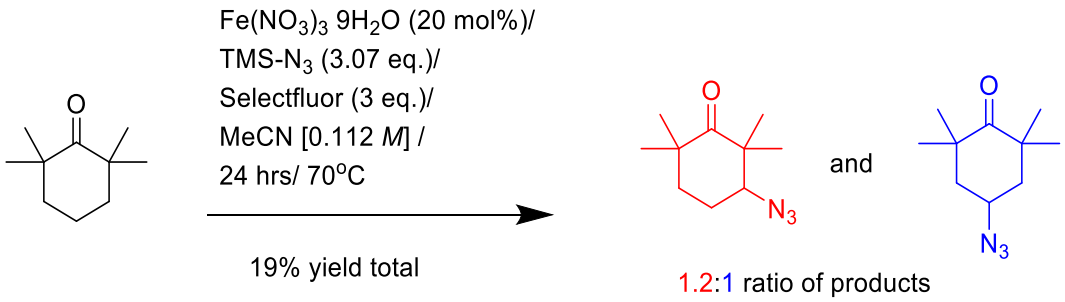


39% isolated yield

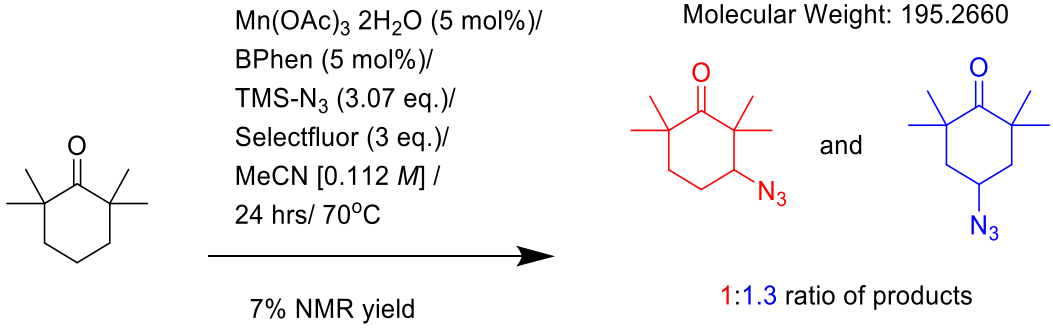
(51% NMR yield, mixture of isomers) (32.1 mg)

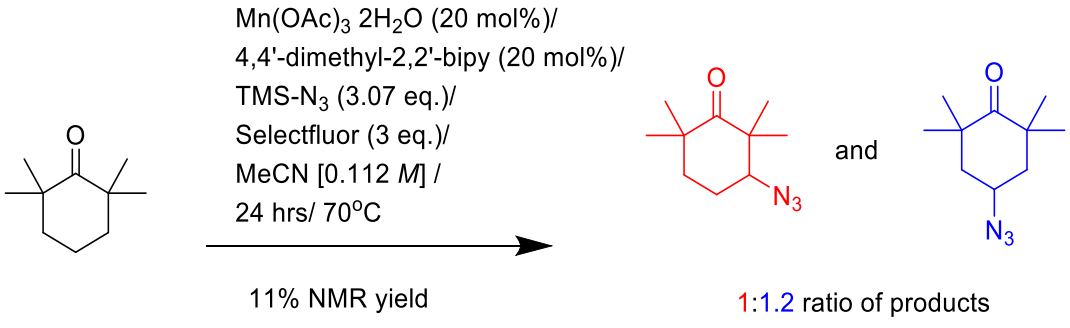
After purification with flash column chromatography on silica gel, the reaction produced the following isomers: 2-azidodecane, 3-azidodecane, 4-azidodecane, and 5-azidodecane. The HRAPCIMS for the mixture of 2-azidodecane, 3-azidodecane, 4-azidodecane, and 5-azidodecane has previously been reported.[1] They are characterized here as an inseperable mixture and were isolated as a colorless oil in 50% yield (41.2 mg) using conditions A [Fe] replacing 20% $Fe(NO)_3 \bullet 9H_2O$ with 30% $Fe(OTf)_3$ and 40% yield (31.9 mg) using Conditions C [Mn]. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.41 (h, J = 6.6 Hz, 0.1H), 3.29 – 3.15 (m, 0.9H), 1.68 – 1.22 (m, 14.5H), 1.04 – 0.85 (m, 5.5H). $^{13}C\{^1H\}$-NMR (151 MHz, $CDCl_3$) δ 64.6, 63.2, 62.9, 58.1, 36.6, 36.20 34.42, 34.38, 34.1, 34.0, 31.9, 31.8, 31.74, 31.65, 29.5, 29.43, 29.40, 29.24,

29.20, 29.1, 28.3, 27.4, 26.2, 26.1, 25.8, 22.67, 22.65, 22.59, 22.56, 22.55, 19.5, 19.4, 14.10, 14.09, 14.06, 14.01, 13.99, 13.89, 10.5.

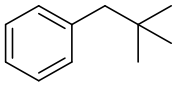


Chemical Formula: $C_{10}H_{17}N_3O$
Exact Mass: 195.1372
Molecular Weight: 195.2660





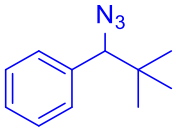
After purification with flash column chromatography on silica gel, the reaction produced a mixture of 3-azido-2,2,6,6-tetramethylcyclohexan-1-one (also known as 3-azido-2,2,6,6-tetramethylcyclohexanone) and 4-azido-2,2,6,6-tetramethylcyclohexan-1-one (also known as 4-azido-2,2,6,6-tetramethylcyclohexanone). ^{1}H-NMR (600 MHz, C_6D_6) δ 3.37 (tt, *J* = 11.7, 4.1 Hz, 0.45H), 2.83 (dd, *J* = 8.9, 4.6 Hz, 0.55H), 1.58 – 1.53 (m, 1H), 1.47 – 1.41 (m, 1H), 1.39 – 1.25 (m, 5H), 1.04 (s, 1.5H), 0.97 (s, 1.5H), 0.95 (s, 1.5H), 0.92 (s, 1.5H), 0.86 (s, 1.5H), 0.77 (s, 1.5H). ^{13}C{^{1}H}-NMR (151 MHz, C_6D_6) δ 215.4, 215.0, 68.5, 52.6, 49.3, 44.1, 43.3, 43.0, 34.6, 29.9, 27.5, 27.4, 27.3, 26.9, 24.7, 22.6, 21.8. HRAPCIMS m/z 168.138 $[M-N_2+H]^+$ (calcd for $C_{10}H_{18}N_1O_1$, 168.1388).



1 eq.

$Fe(NO_3)_3$ $9H_2O$ (20 mol%)/
$TMS\text{-}N_3$ (3.07 eq.)/
Selectfluor (3 eq.) /
MeCN [0.112 *M*] /
24 hrs/ 70°C

6% NMR yield
4% isolated yield



Chemical Formula: $C_{11}H_{15}N_3$
Exact Mass: 189.1266
Molecular Weight: 189.2620

Conditions C [Mn]

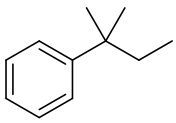
8% NMR yield

6% isolated yield

(5.1 mg)

After purification with flash column chromatography on silica gel, the reaction produced a 4% isolated yield (3.4 mg) of (1-azido-2,2-dimethylpropyl)benzene (which is also known as 1-azido-1-phenyl-2,2-dimethylpropane) using conditions A [Fe] and 6% isolated yield (5.1 mg) using Conditions C [Mn]. This compound has previously been characterized.[14]

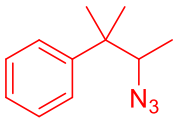
^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 2H), 7.32 – 7.30 (m, 1H), 7.27 – 7.24 (m, 2H), 4.28 (s, 1H), 0.91 (s, 9H). $^{13}C\{^1H\}$-NMR (151 MHz, $CDCl_3$) δ 137.6, 128.5, 127.9, 127.8, 74.4, 35.8, 26.4.



1 eq.

$Fe(NO_3)_3$ $9H_2O$ (20 mol%)/
$TMS\text{-}N_3$ (3.07 eq.)/
Selectfluor (3 eq.) /
MeCN [0.112 *M*] /
24 hrs/ 70°C

7% NMR yield
6% isolated yield



Chemical Formula: $C_{11}H_{15}N_3$
Exact Mass: 189.1266
Molecular Weight: 189.2620

Conditions C [Mn]

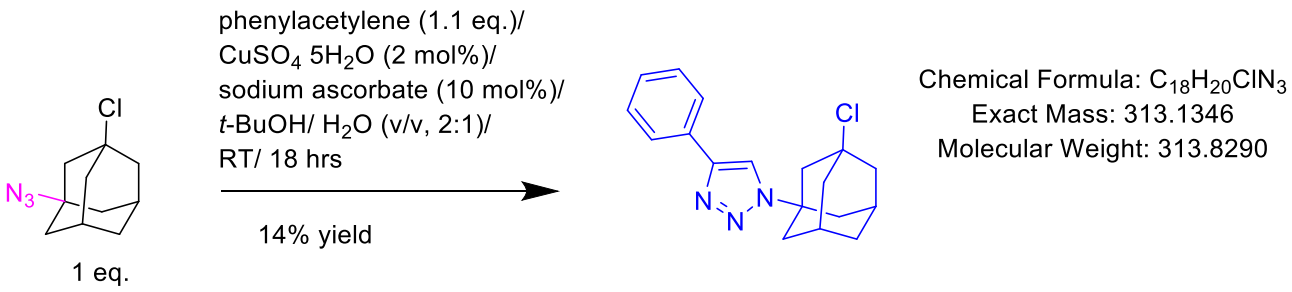
12% NMR yield

8% isolated yield

(6.8 mg)

After purification with flash column chromatography on silica gel, the reaction produced a 6% isolated yield (5mg) of (3-azido-2-methylbutan-2-yl)benzene (also known as either (2-methyl-2-phenyl-butan-3-yl)azide or 3-azido-2-phenyl-2-methylbutane) using Conditions A [Fe] and 8% isolated yield (6.8 mg) using conditions C [Mn].

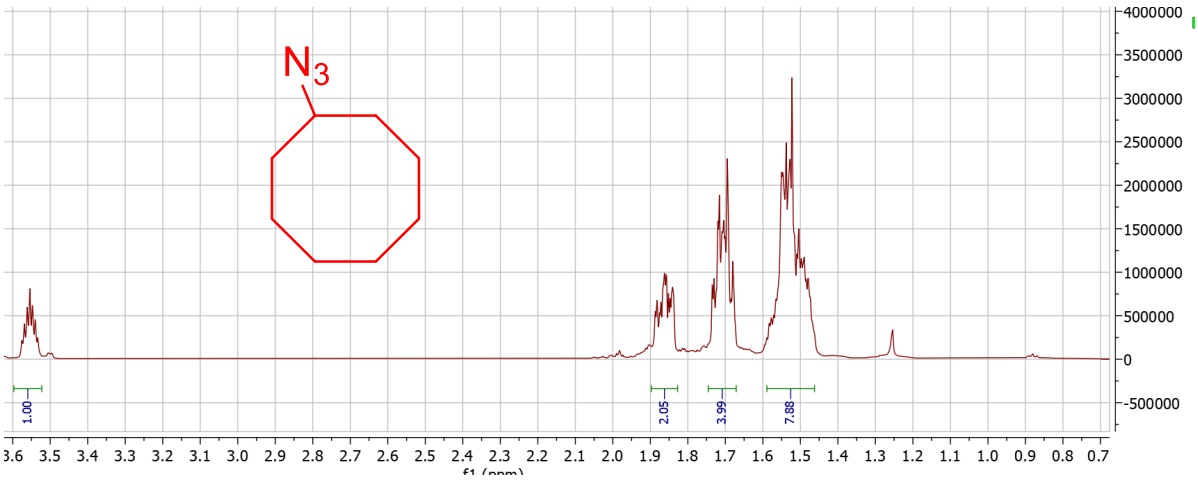
^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 4H), 7.18 – 7.14 (m, 1H), 3.61 (q, *J* = 6.7 Hz, 1H), 1.29 (s, 3H), 1.26 (s, 3H), 1.00 (d, *J* = 6.7 Hz, 3H).
$^{13}C\{^1H\}$-NMR (151 MHz, $CDCl_3$) δ 146.3, 128.2, 126.4, 126.3, 67.2, 42.3, 25.9, 23.1, 14.7.
HRAPCIMS m/z 162.1277 $[M\text{-}N_2+H]^+$ (calcd for $C_{11}H_{15}N_1+H^+$, 162.1283).



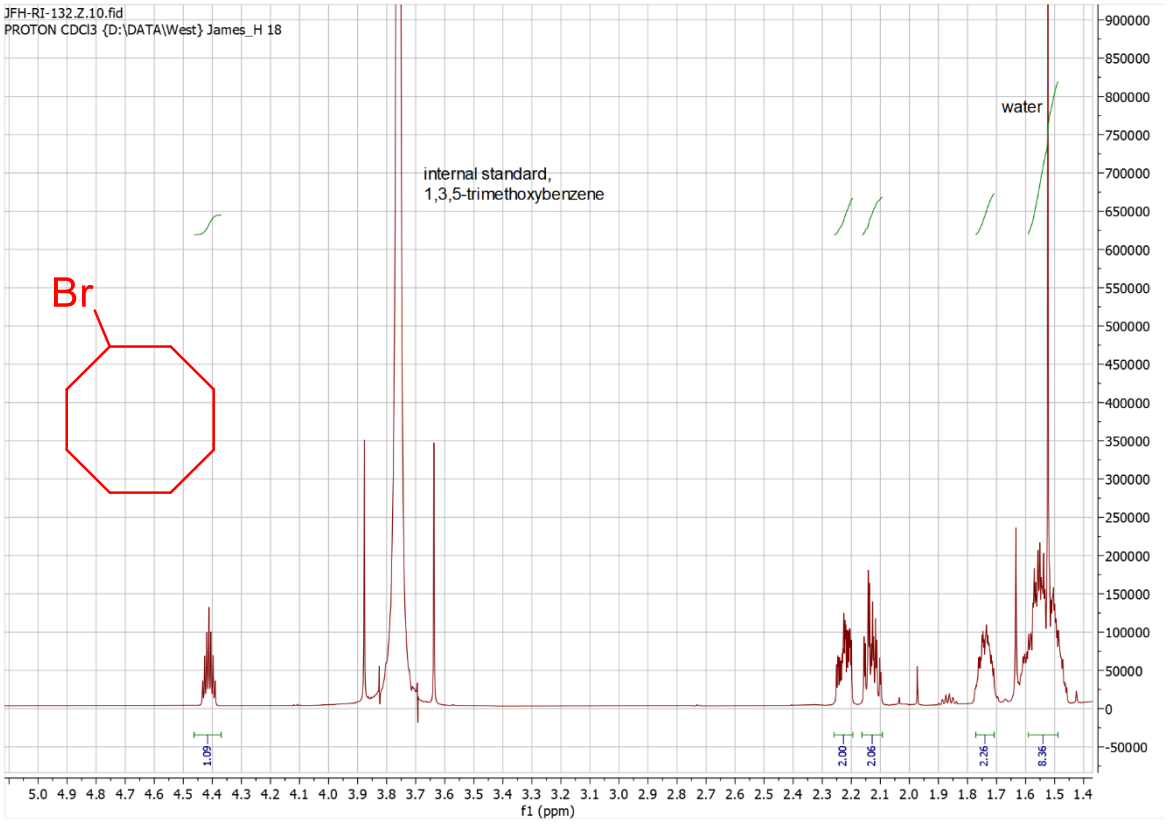
Applying the previously published literature,[21] 1 eq. of (1*r*,3*s*,5*R*,7*S*)-1-azido-3-chloroadamantane (95 mg, 0.000449 mol = 0.449 mmol) was dissolved in 1.33 mL *tert*-butanol and 0.66mL water. Then, 1.1 eq of phenylacetylene (0.000494 mol = 0.494 mmol, 0.054 mL) was added to the vial. Next 10 mol% sodium ascorbate (0.0000449 mol = 0.0449 mol, 8.89 mg) was added to the vial. Finally, 2 mol% $CuSO_4$ $5H_2O$ (0.0000089 mol = 0.0089mmol, 2.2mg) was added to the vial. The vial was stirred vigorously for 18 hours at RT. Then the mixture was extracted with DCM and water three times. The DCM layers were combined and dried over anhydrous Na_2SO_4. Then the Na_2SO_4 was filtered off, and the organic layer was concentrated on the Rotary Evaporator. Finally, the crude compound was purified by flash column chromatography on silica gel to give a 14% yield (20 mg) of 1-((1*r*,3*s*,5*R*,7*S*)-3-chloroadamantan-1-yl)-4-phenyl-1*H*-1,2,3-triazole as a white solid.

^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.84 – 7.83 (m, 1H), 7.83 – 7.82 (m, 1H), 7.82 (s, 1H), 7.44 – 7.40 (m, 2H), 7.34 – 7.31 (m, 1H), 2.65 (s, 2H), 2.50-2.46 (m, 2H), 2.27 (s, br, 4H), 2.21 (d, *J* = 3.1 Hz, 4H), 1.75 (d, br, *J* = 3.2 Hz, 2H). ^{13}C{^{1}H}-NMR (151 MHz, $CDCl_3$) δ 147.1, 130.8, 128.8, 128.1, 125.7, 116.0, 65.8, 61.3, 52.1, 46.1, 41.3, 34.0, 31.5.

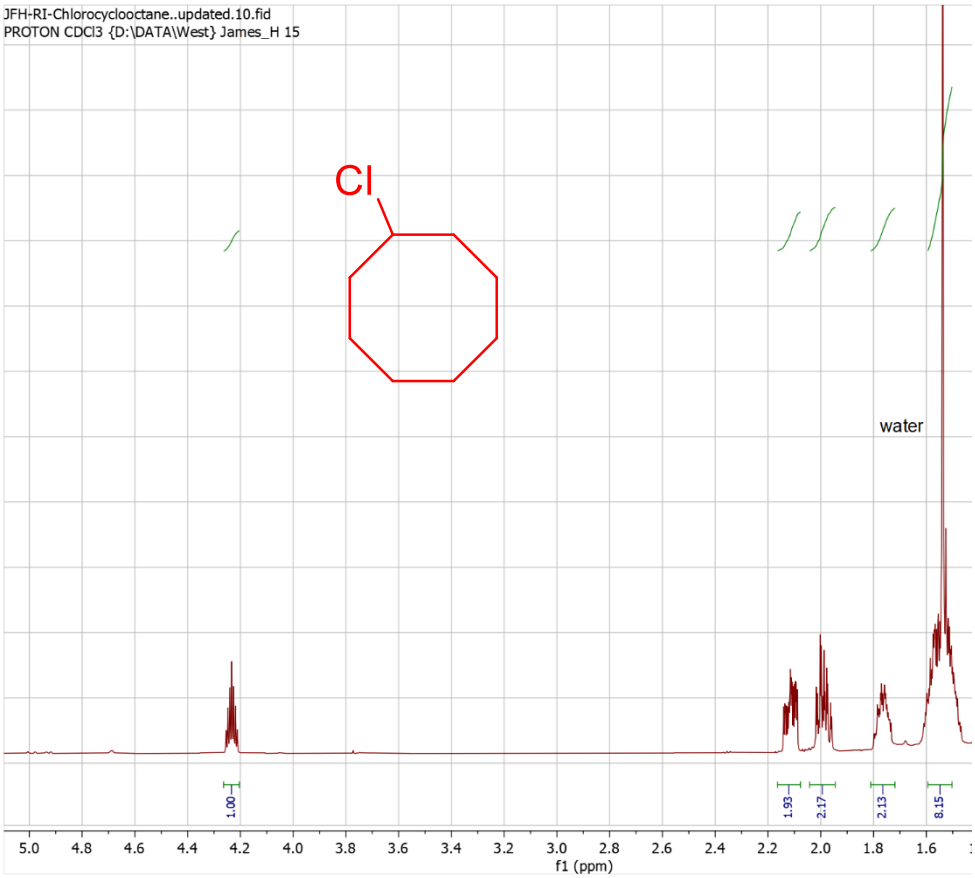
Crude ^{1}H-NMR of azidocyclooctane



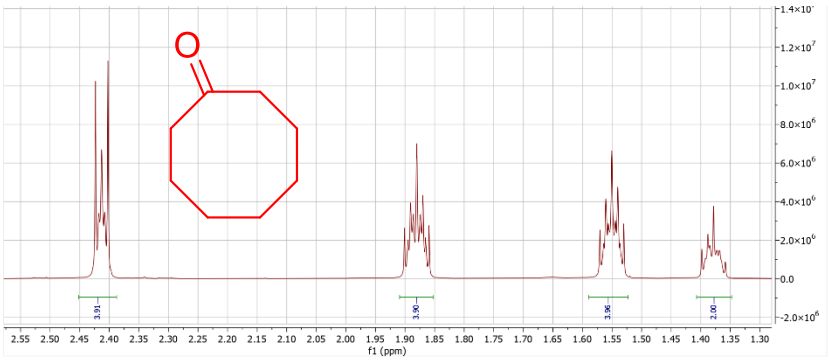
Crude ^{1}H-NMR of bromocyclooctane



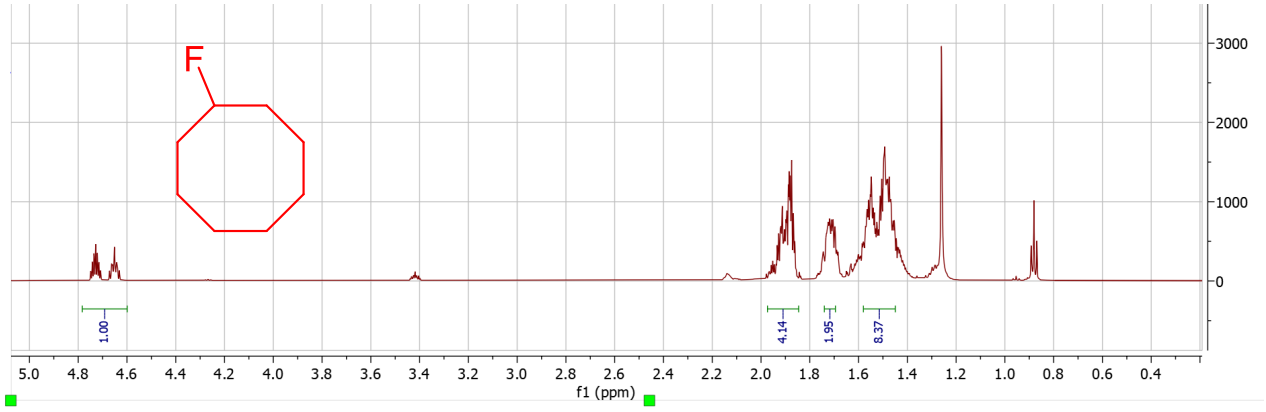
Crude ^{1}H-NMR of chlorocyclooctane



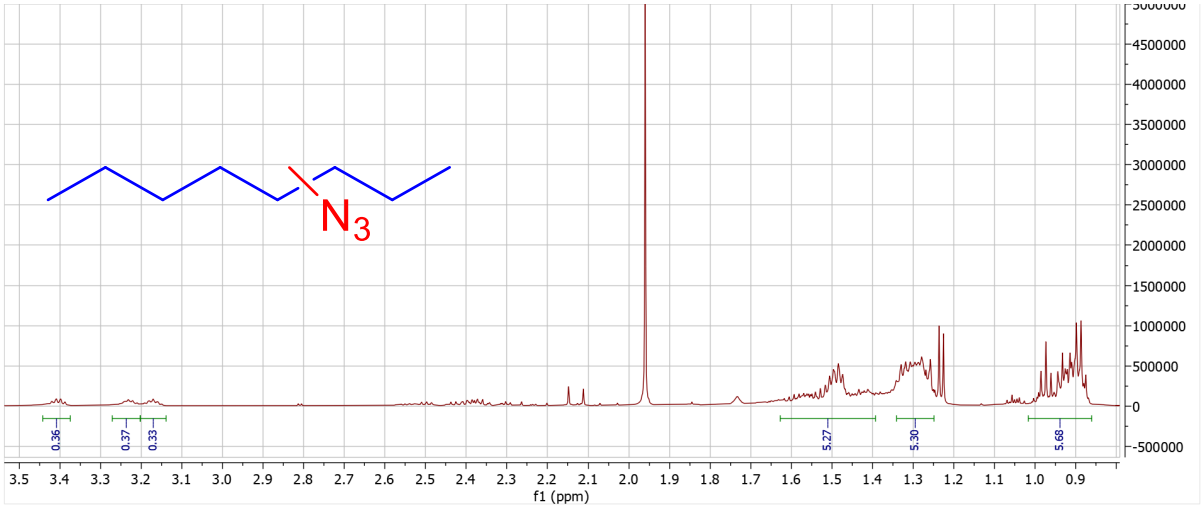
Crude ^{1}H-NMR of cyclooctanone



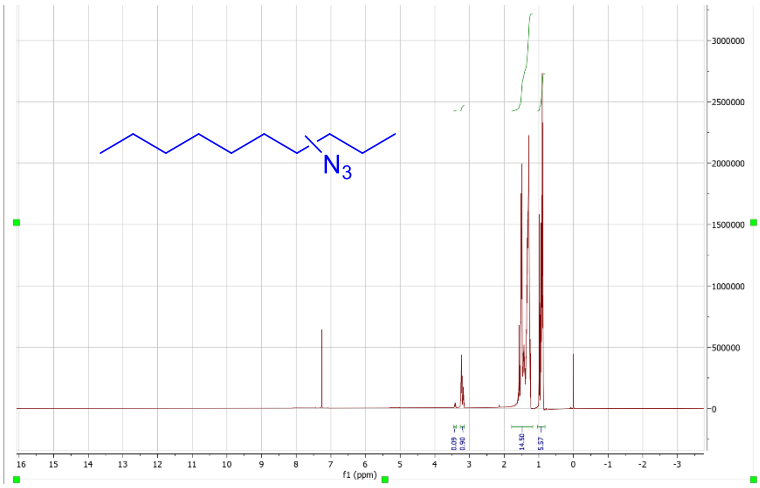
Crude^{1}H-NMR of fluorocyclooctane



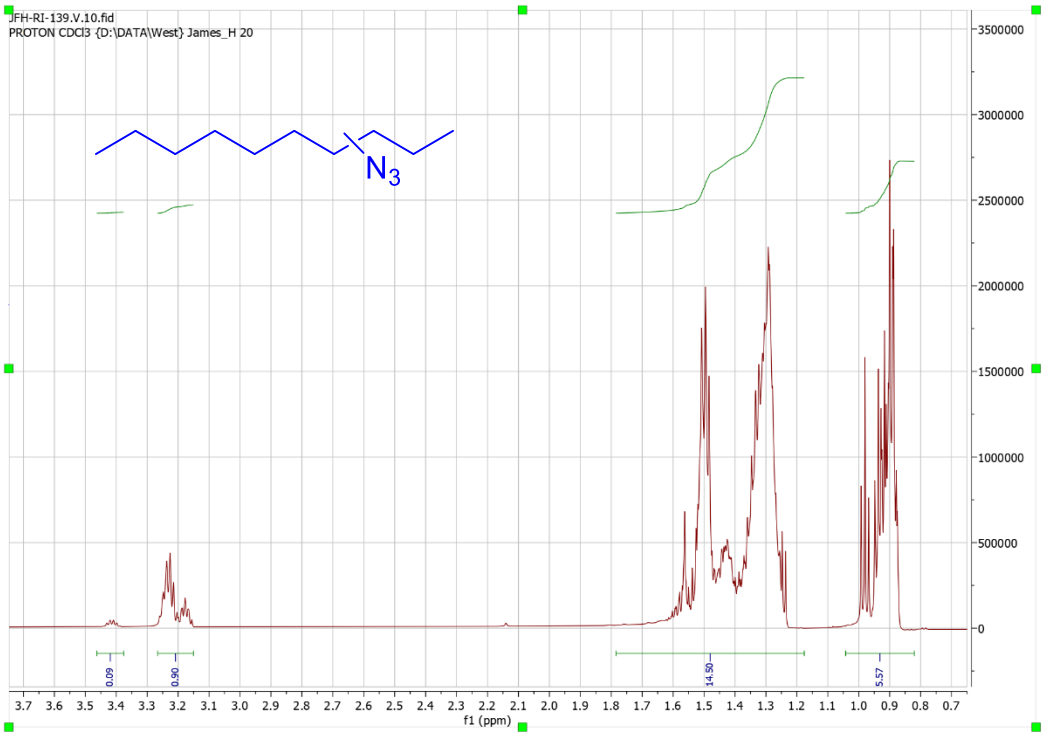
Crude^{1}H-NMR of 2-azidooctane, 3-azidooctane, and 4-azidooctane



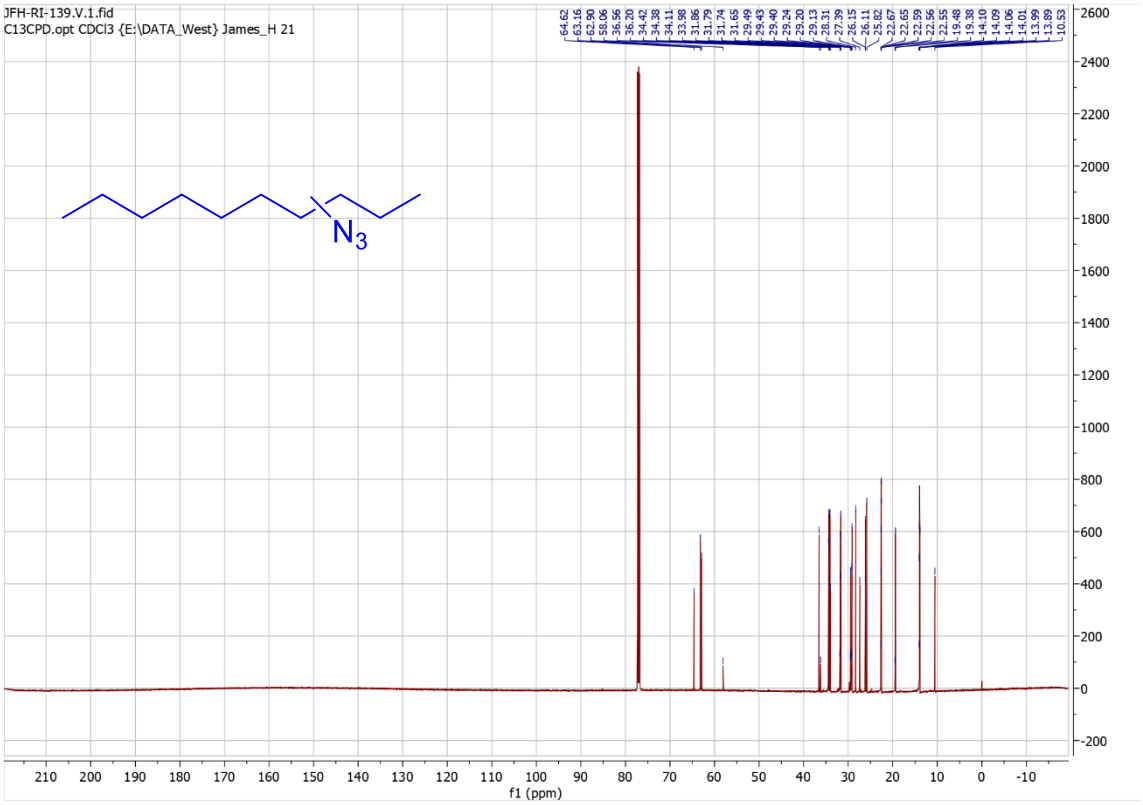
^{1}H-NMR of 2-azidodecane, 3-azidodecane, 4-azidodecane, and 5-azidodecane, full spectrum



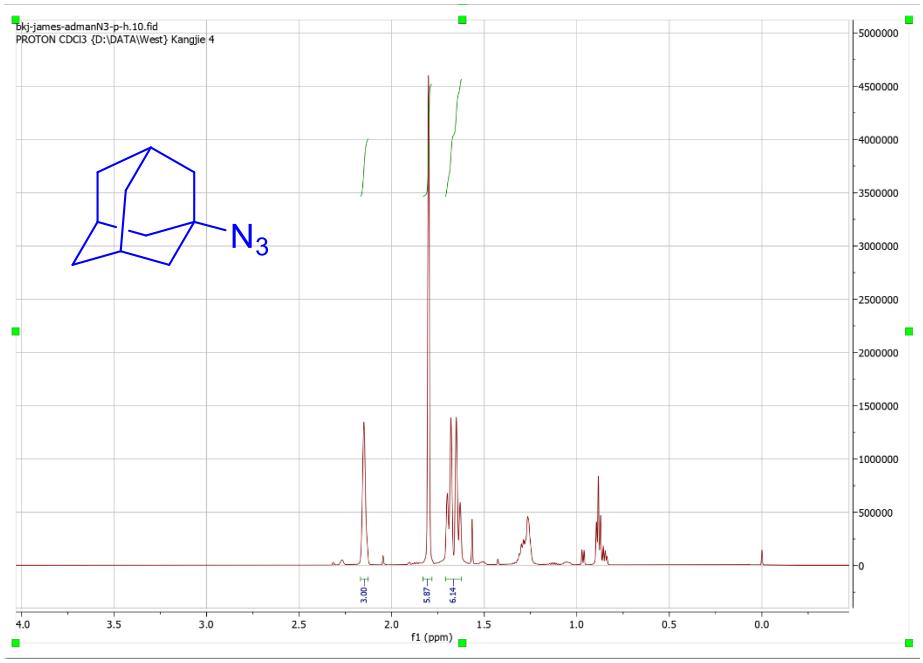
^{1}H-NMR of 2-azidodecane, 3-azidodecane, 4-azidodecane, and 5-azidodecane, magnified spectrum



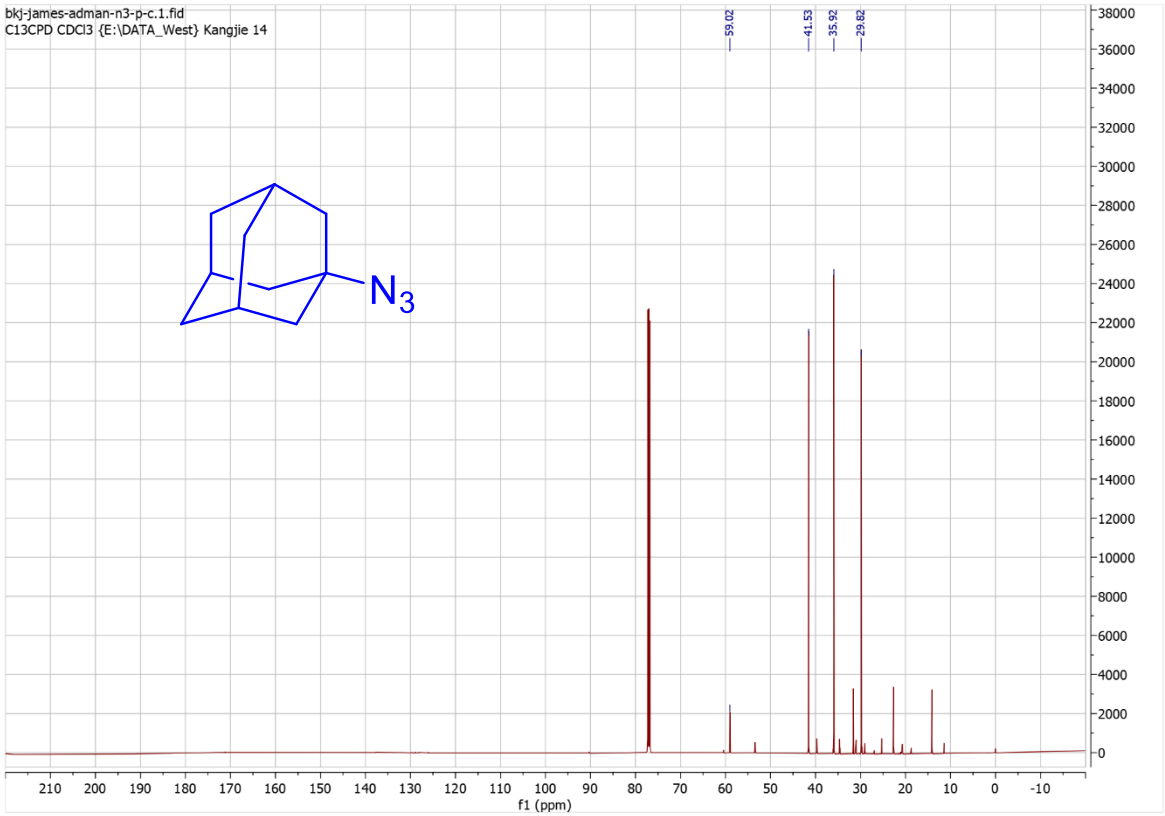
$^{13}C\{^{1}H\}$-NMR of 2-azidodecane, 3-azidodecane, 4-azidodecane, and 5-azidodecane



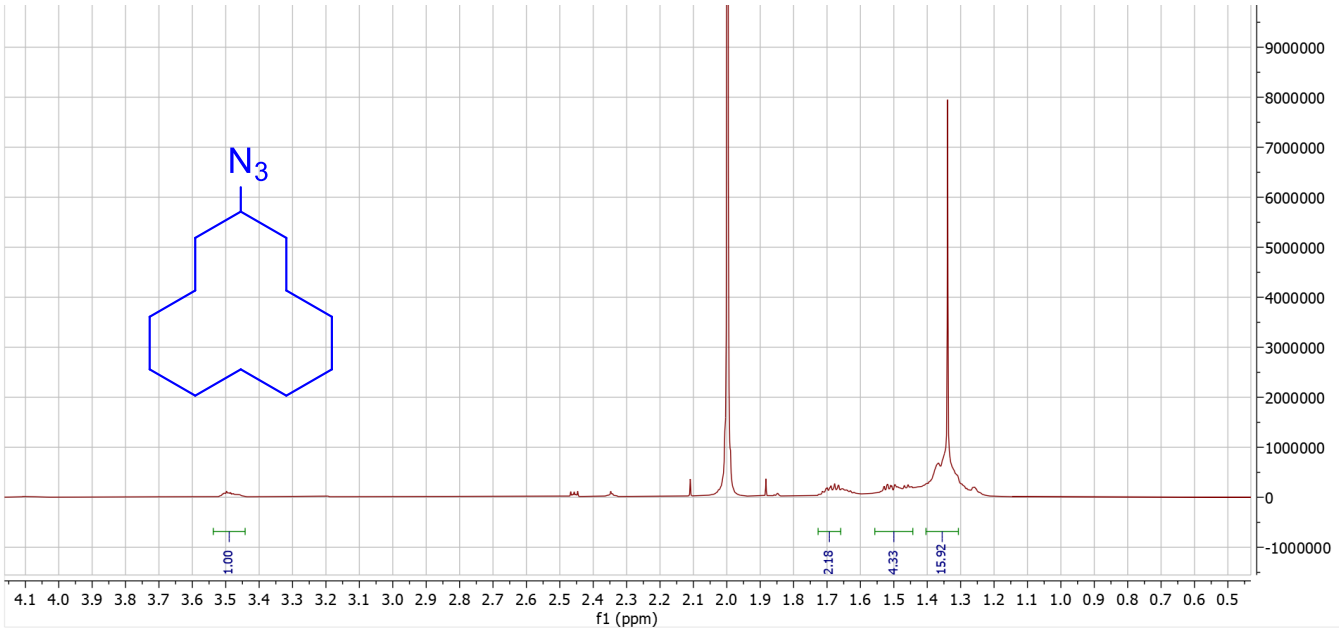
^{1}H-NMR of (3*s*,5*s*,7*s*)-1-azidoadamantane



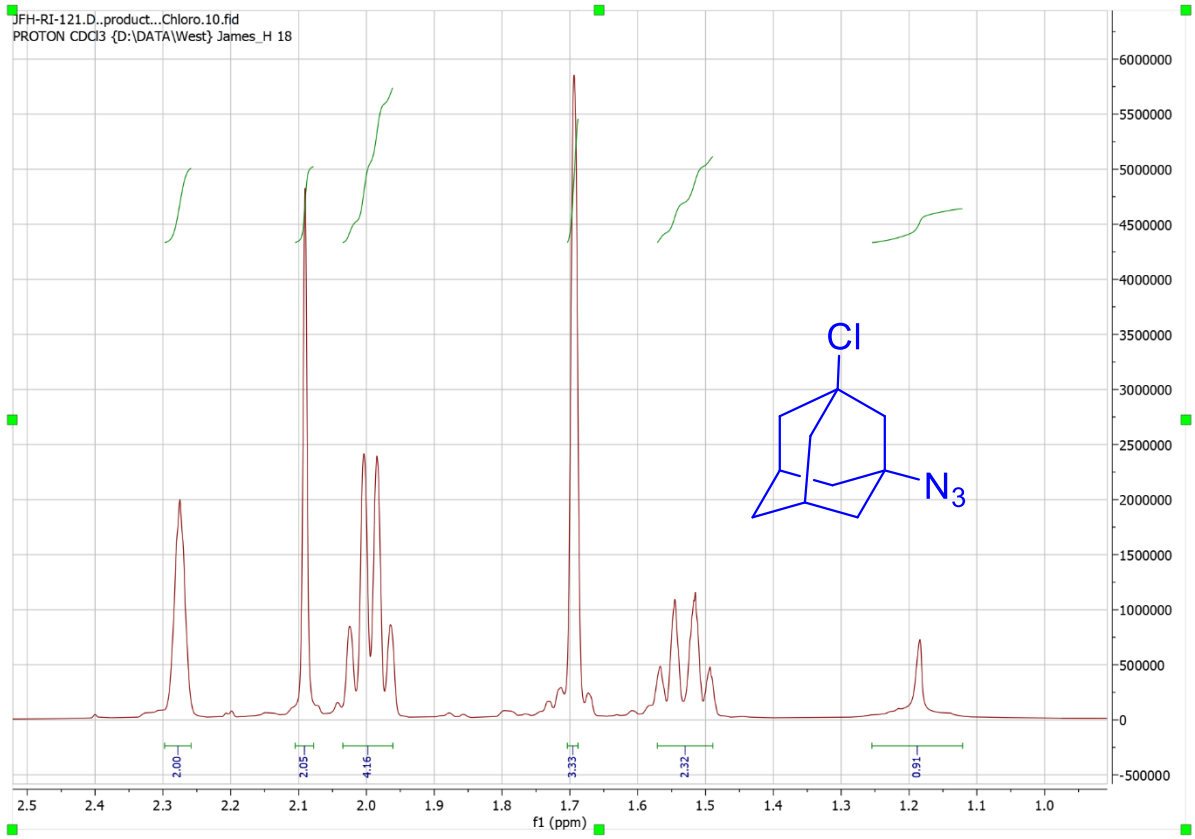
^{13}C{^{1}H}-NMR of (3*s*,5*s*,7*s*)-1-azidoadamantane



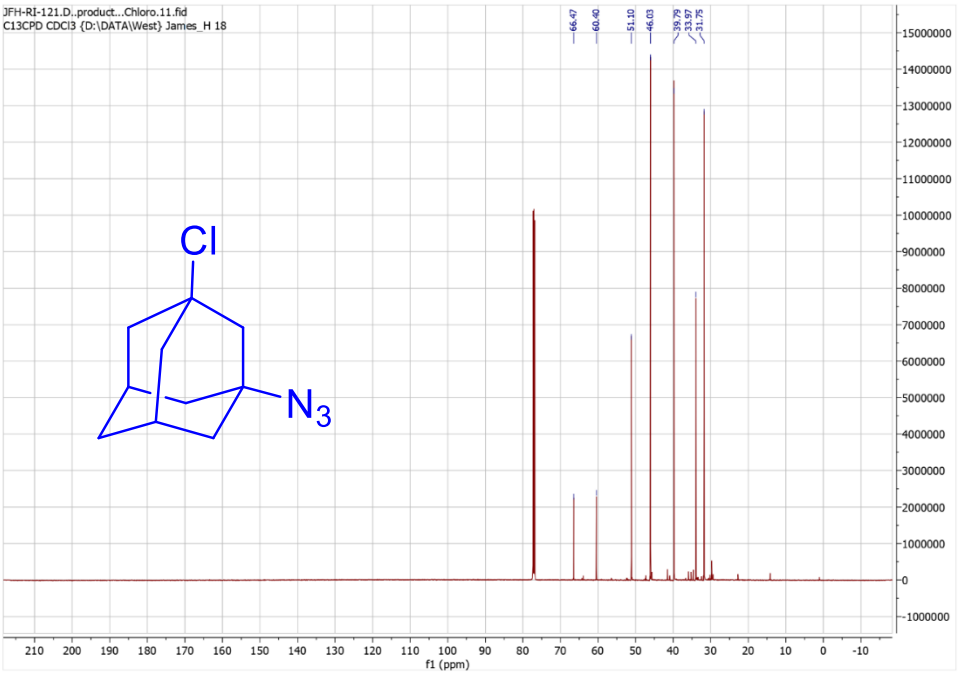
Crude ^{1}H-NMR of azidocyclododecane



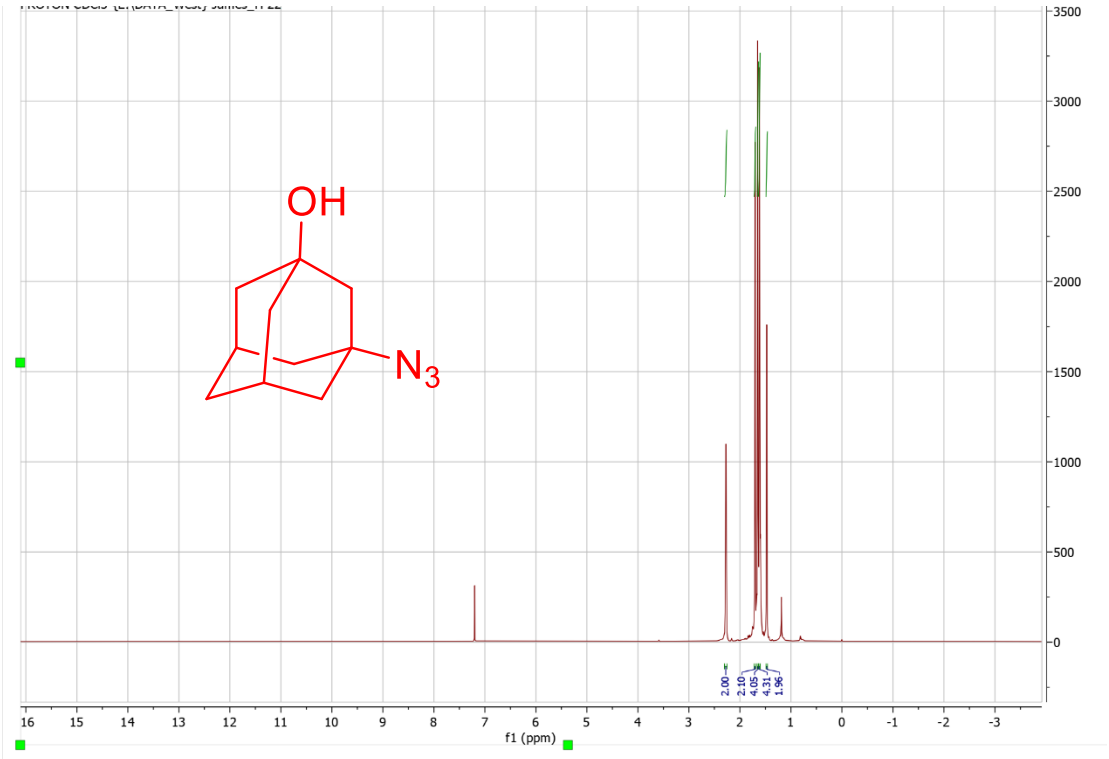
^{1}H-NMR of (1*r*,3*s*,5*R*,7*S*)-1-azido-3-chloroadamantane



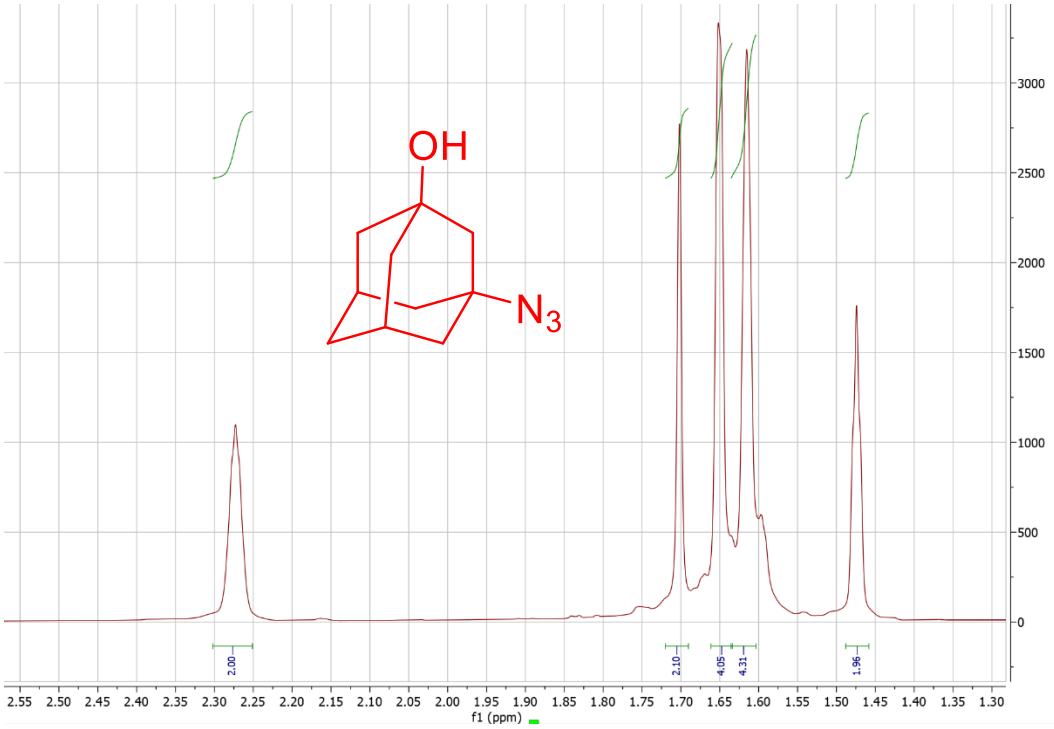
$^{13}C\{^{1}H\}$-NMR of (1*r*,3*s*,5*R*,7*S*)-1-azido-3-chloroadamantane



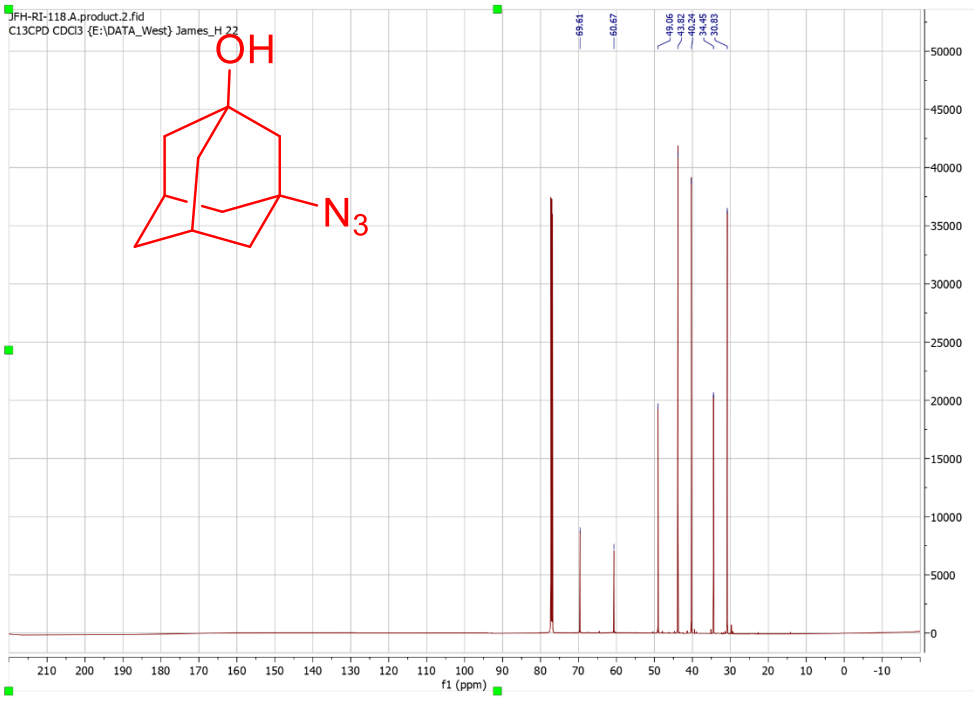
^{1}H-NMR of (1*s*,3*r*,5*R*,7*S*)-3-azidoadamantan-1-ol, full spectrum



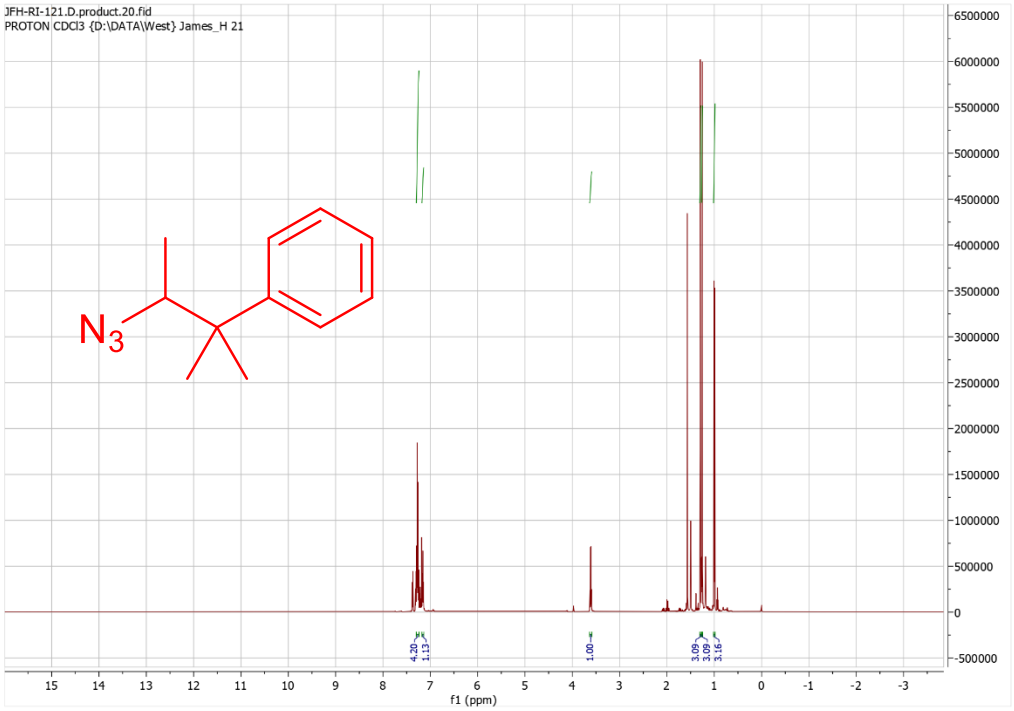
^{1}H-NMR of (1*s*,3*r*,5*R*,7*S*)-3-azidoadamantan-1-ol, magnified spectrum



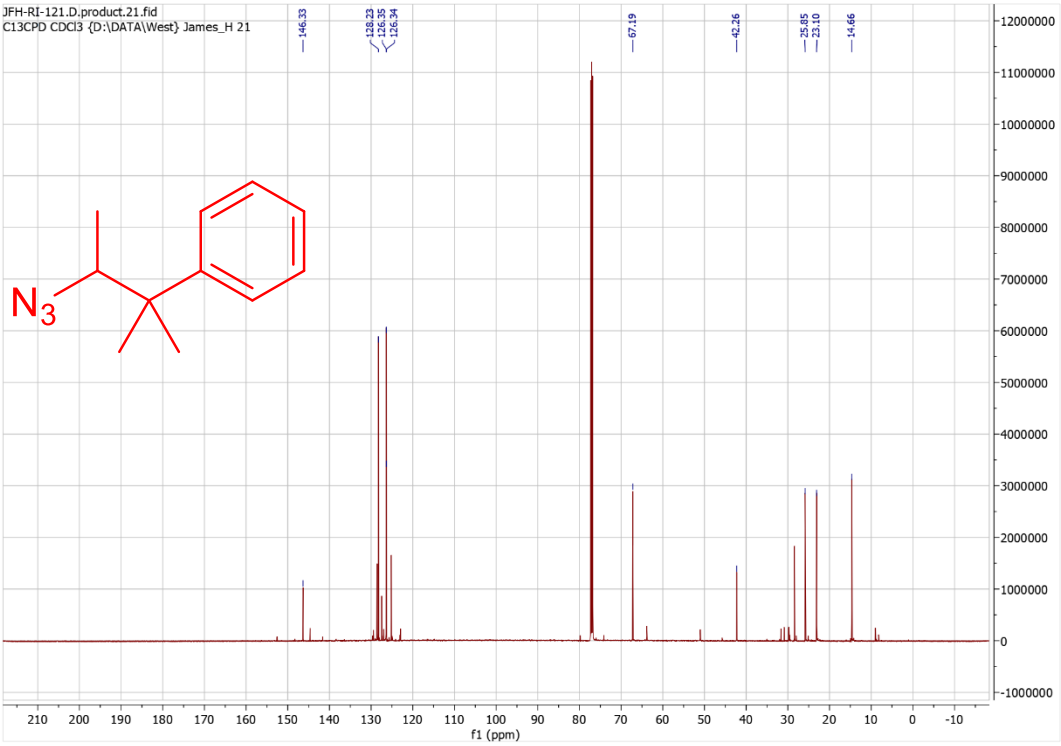
^{13}C{^{1}H}-NMR of (1*s*,3*r*,5*R*,7*S*)-3-azidoadamantan-1-ol



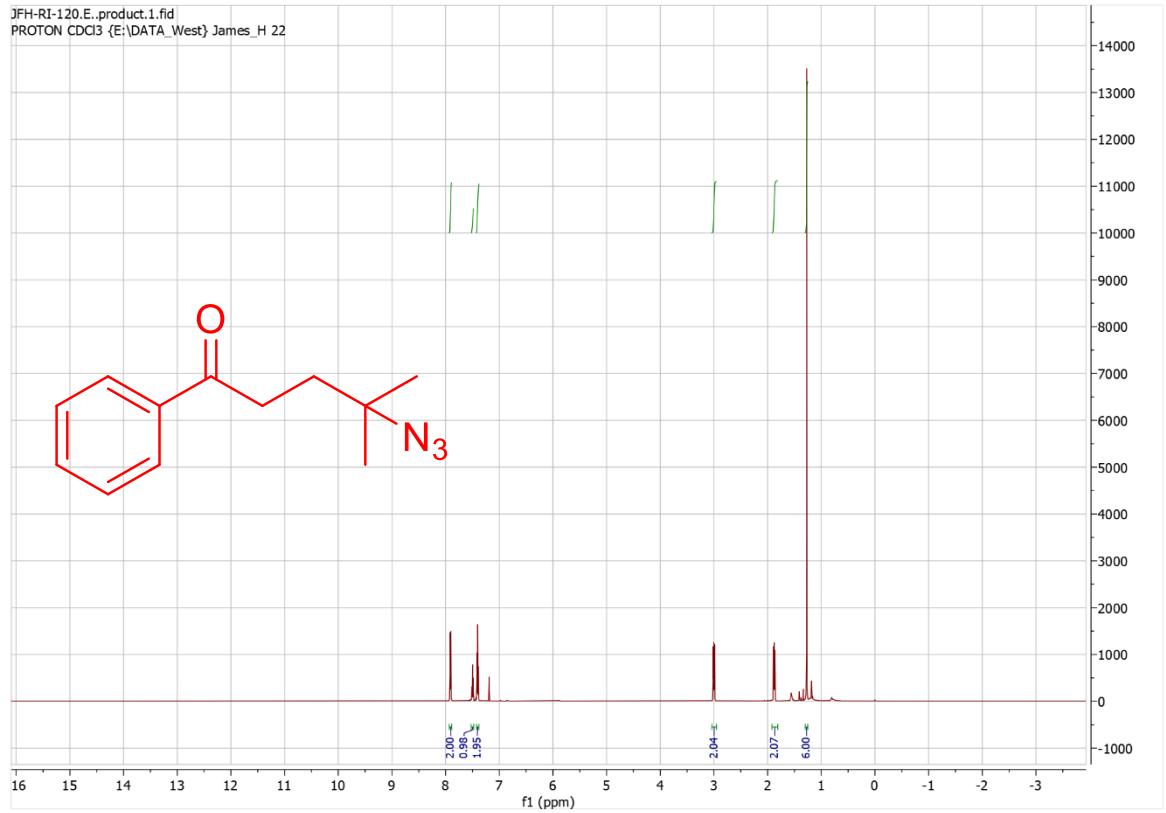
^{1}H-NMR of (3-azido-2-methylbutan-2-yl)benzene



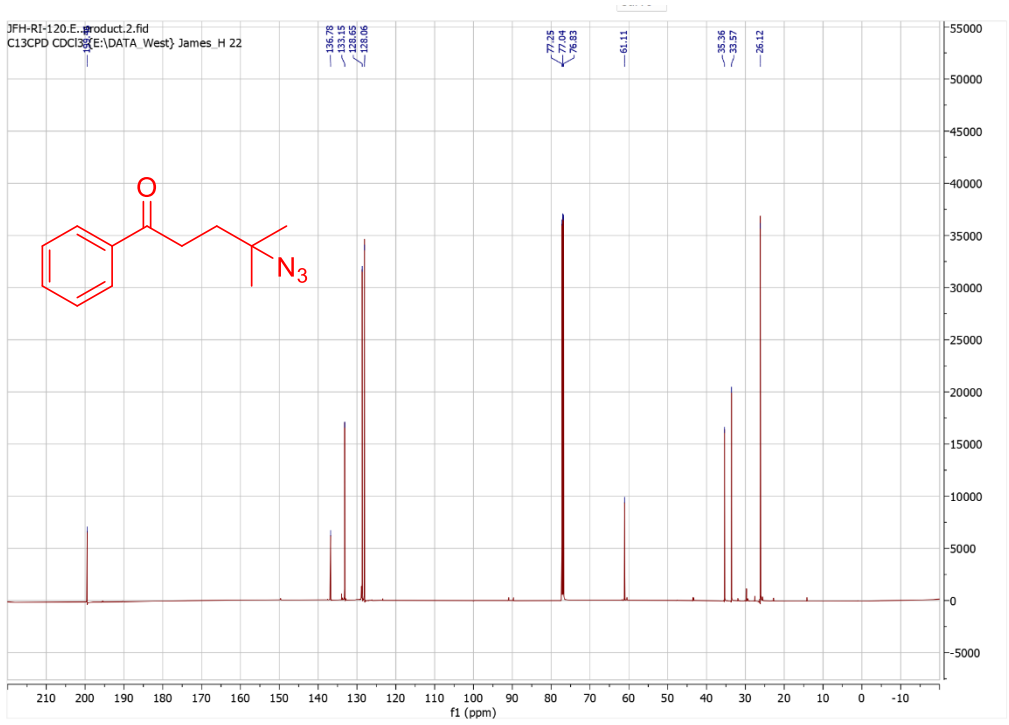
^{13}C{^{1}H}-NMR of (3-azido-2-methylbutan-2-yl)benzene



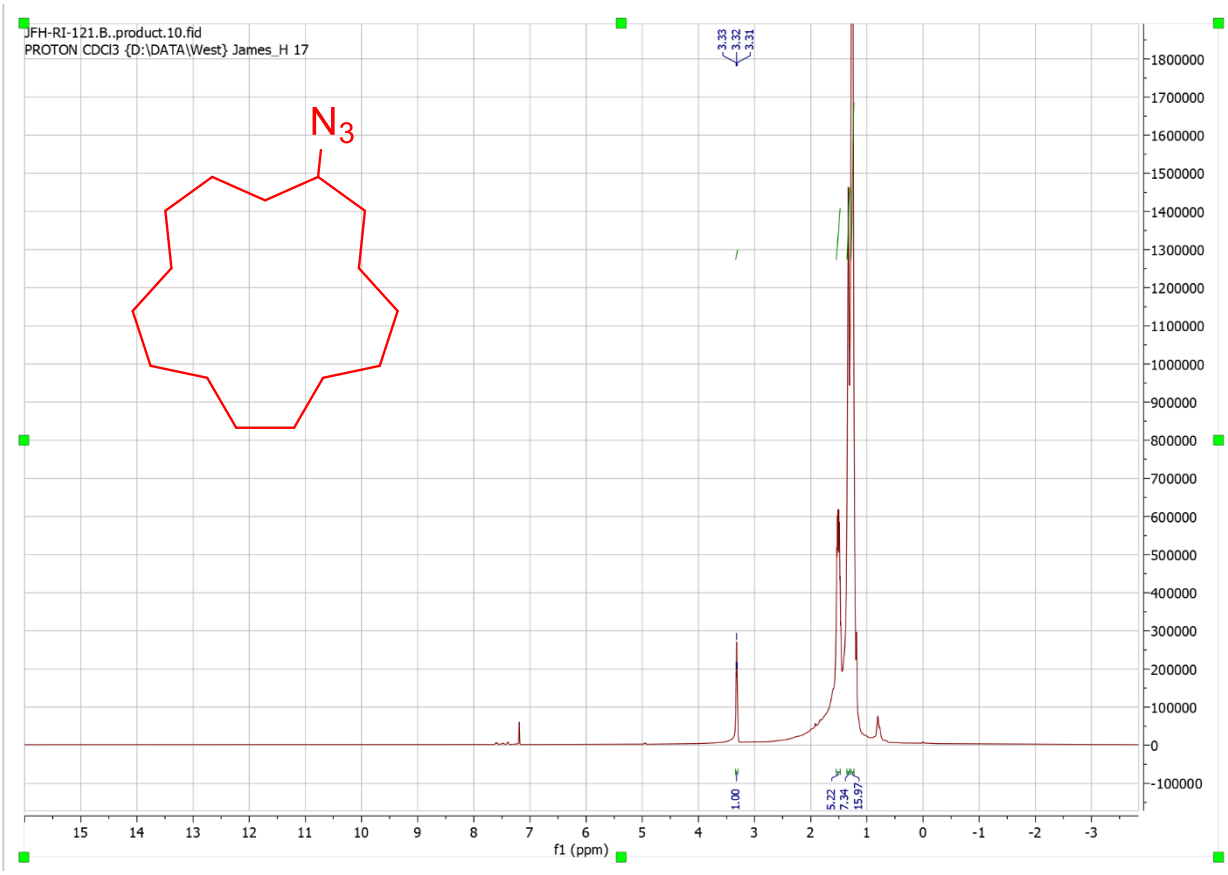
^{1}H-NMR of 4-azido-4-methyl-1-phenylpentan-1-one



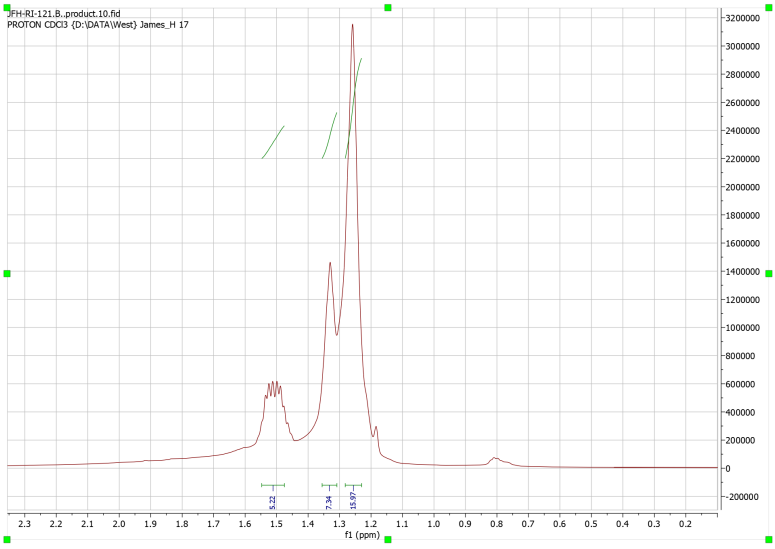
^{13}C{^{1}H}-NMR of 4-azido-4-methyl-1-phenylpentan-1-one

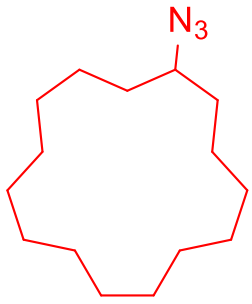


^{1}H-NMR of azidocyclopentadecane, full spectrum

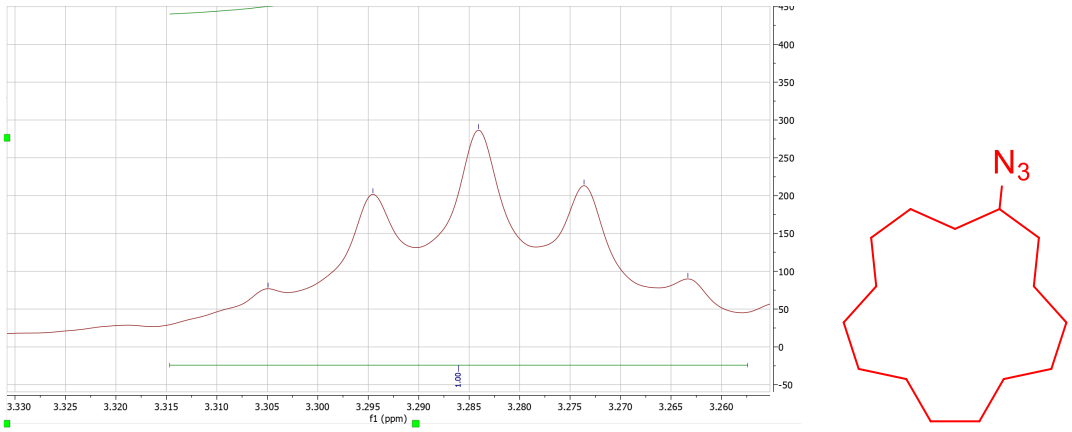


^{1}H-NMR of azidocyclopentadecane, magnified spectrum 0.2ppm to 2.3 ppm

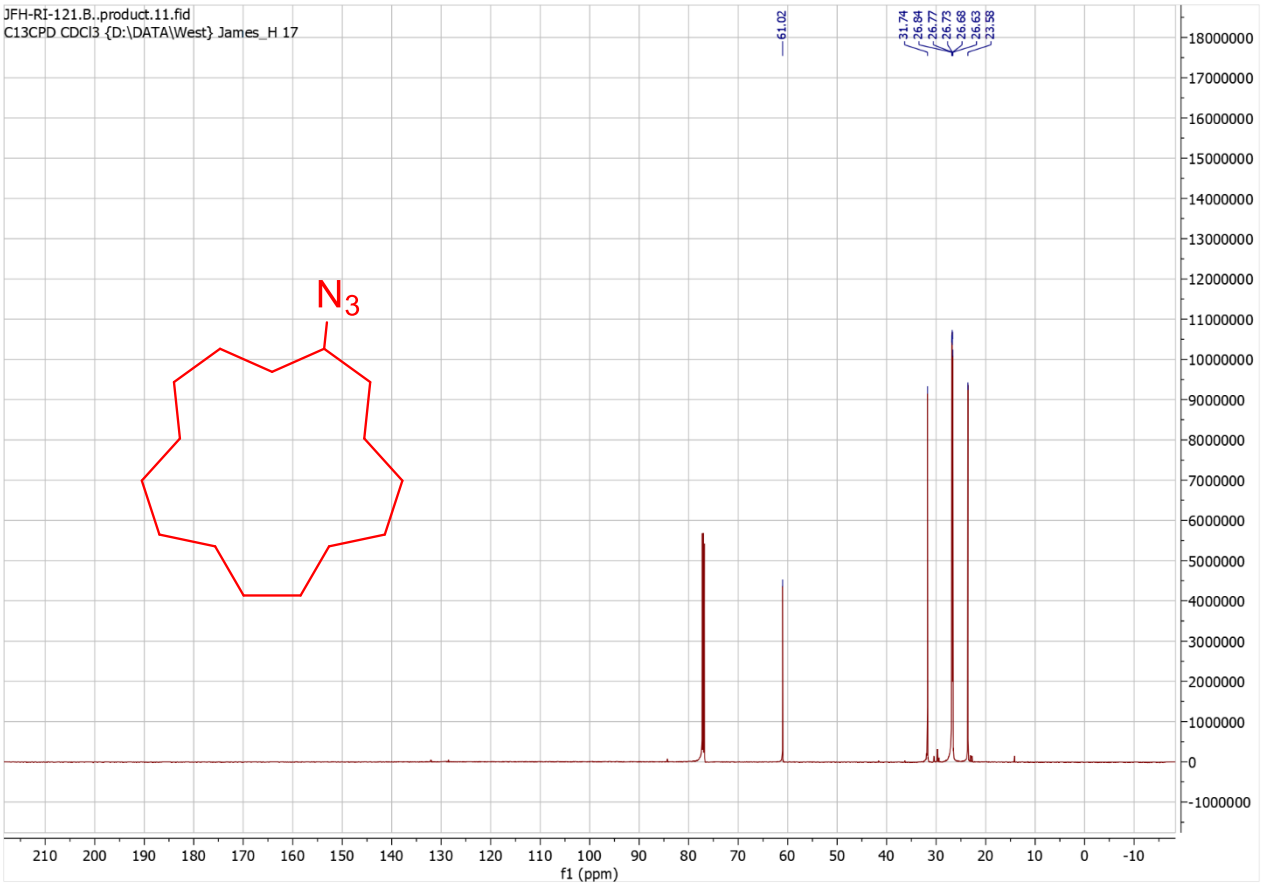




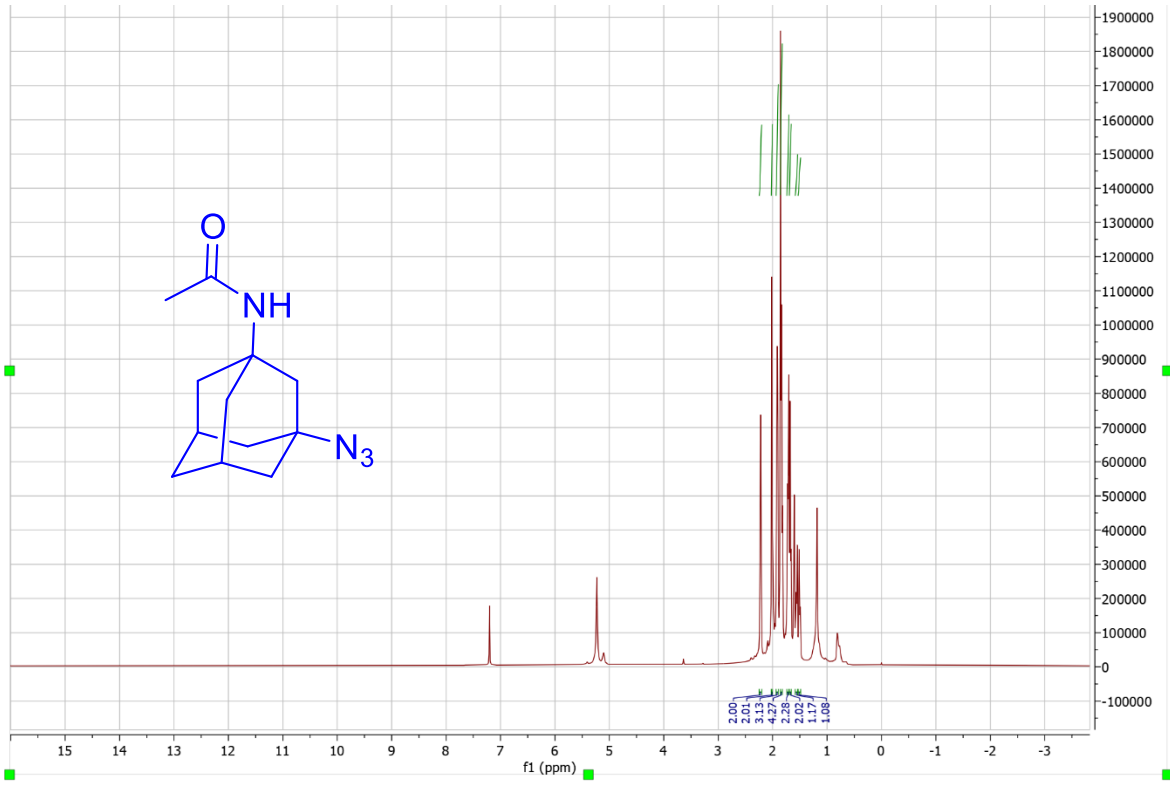
^{1}H-NMR of azidocyclopentadecane, magnified spectrum 3.26ppm to 3.33 ppm



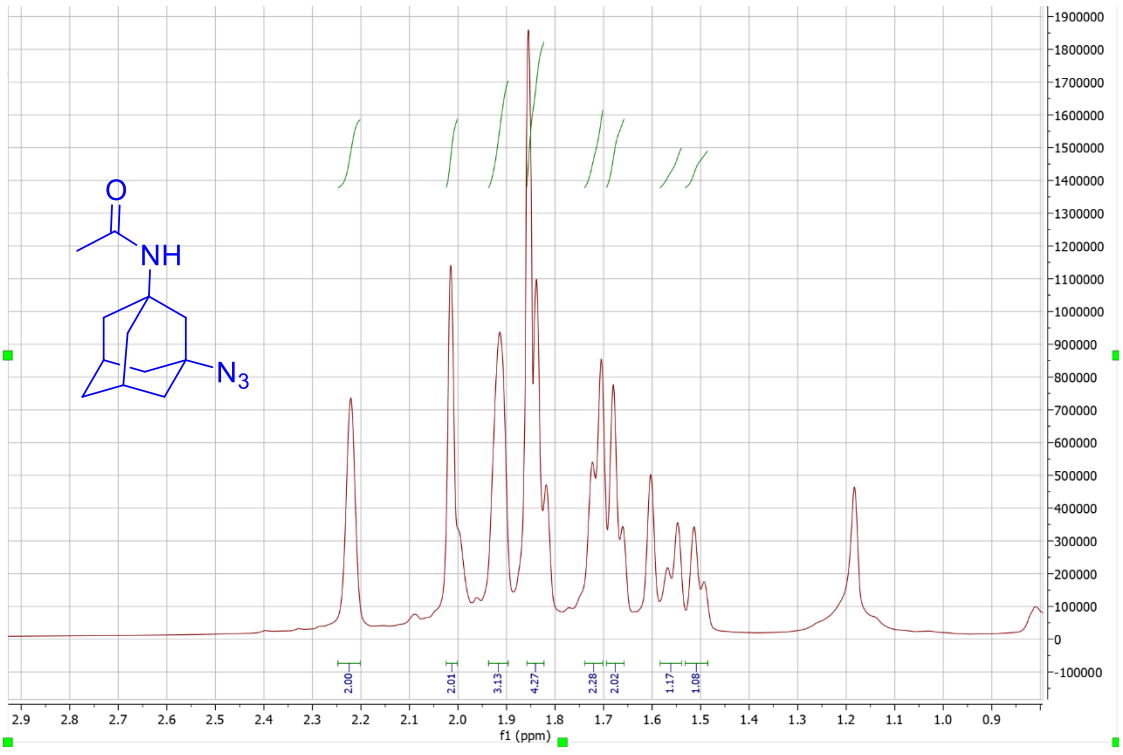
^{13}C{^{1}H}-NMR of azidocyclopentadecane



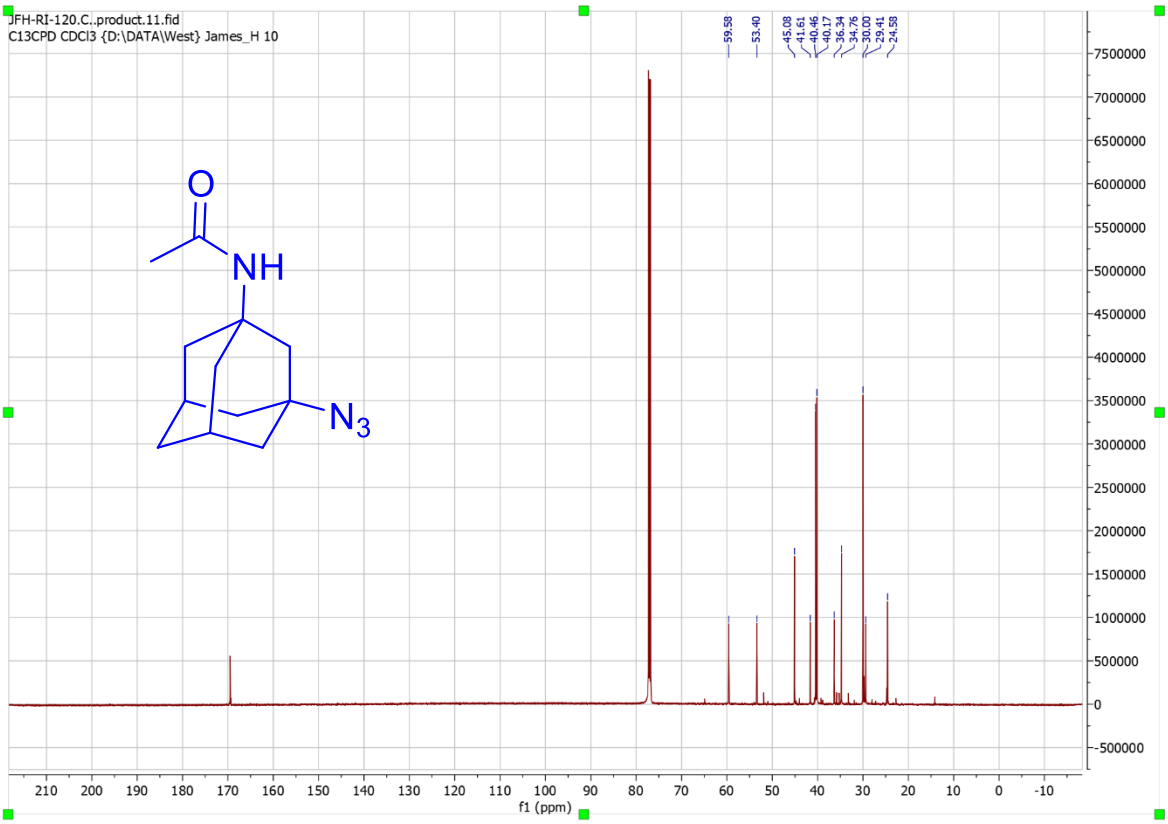
^{1}H-NMR of *N*-((1*r*,3*s*,5*R*,7*S*)-3-azidoadamantan-1-yl)acetamide, full spectrum



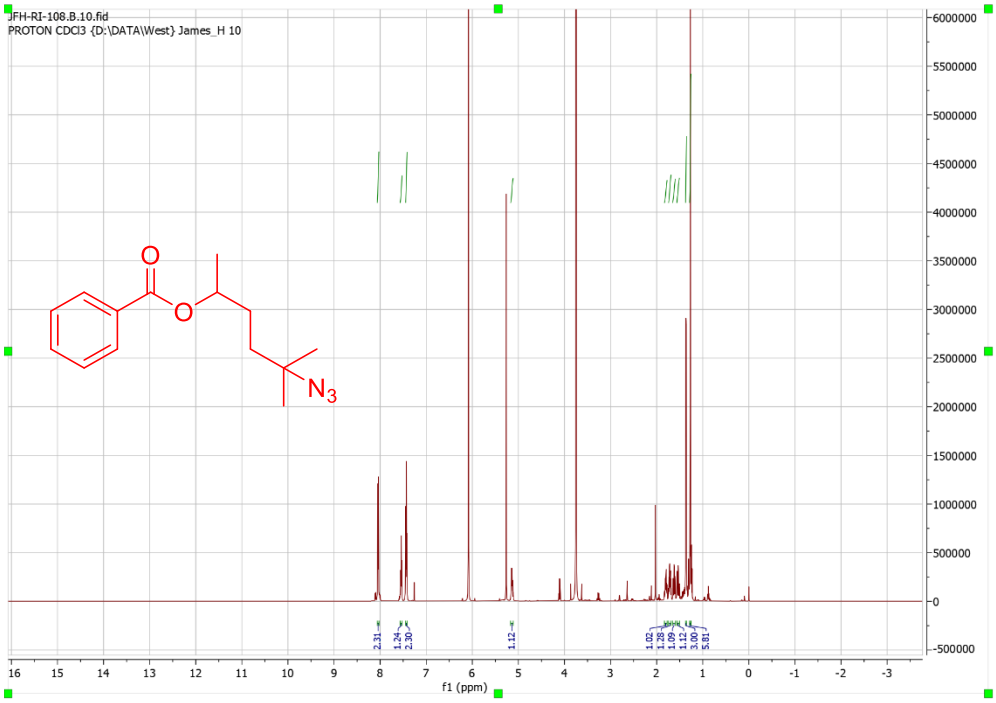
^{1}H-NMR of *N*-((1*r*,3*s*,5*R*,7*S*)-3-azidoadamantan-1-yl)acetamide, magnified spectrum



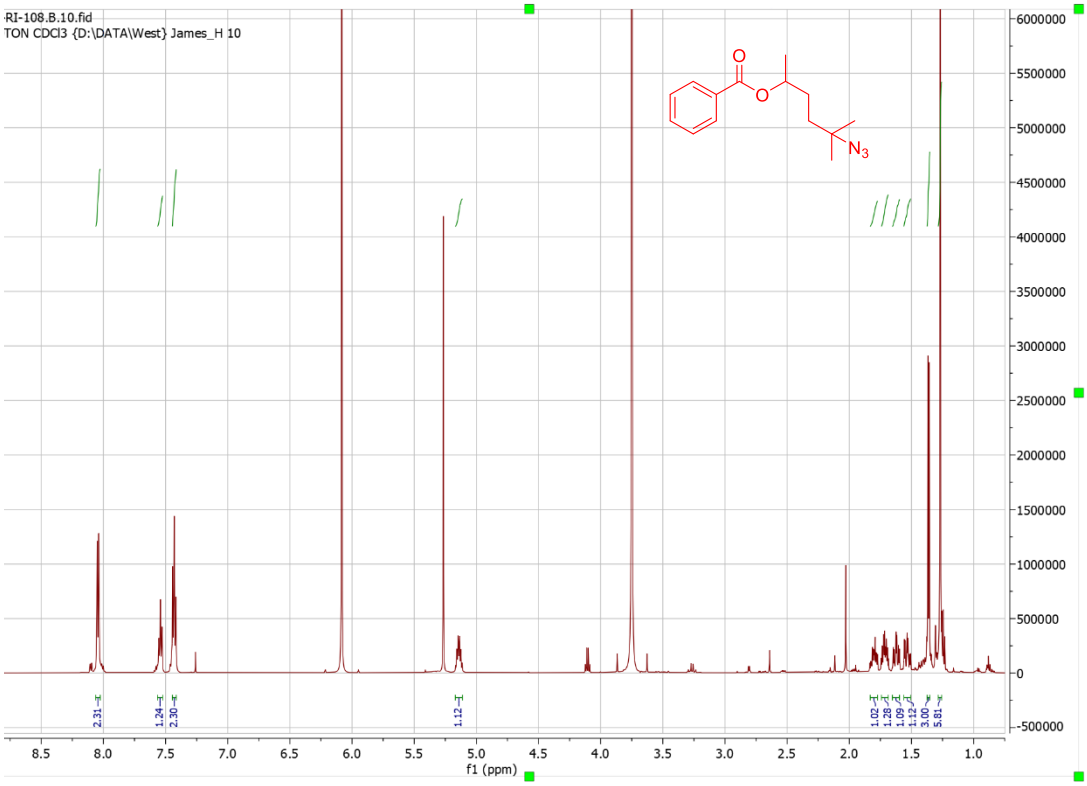
$^{13}C\{^{1}H\}$-NMR of *N*-((1*r*,3*s*,5*R*,7*S*)-3-azidoadamantan-1-yl)acetamide



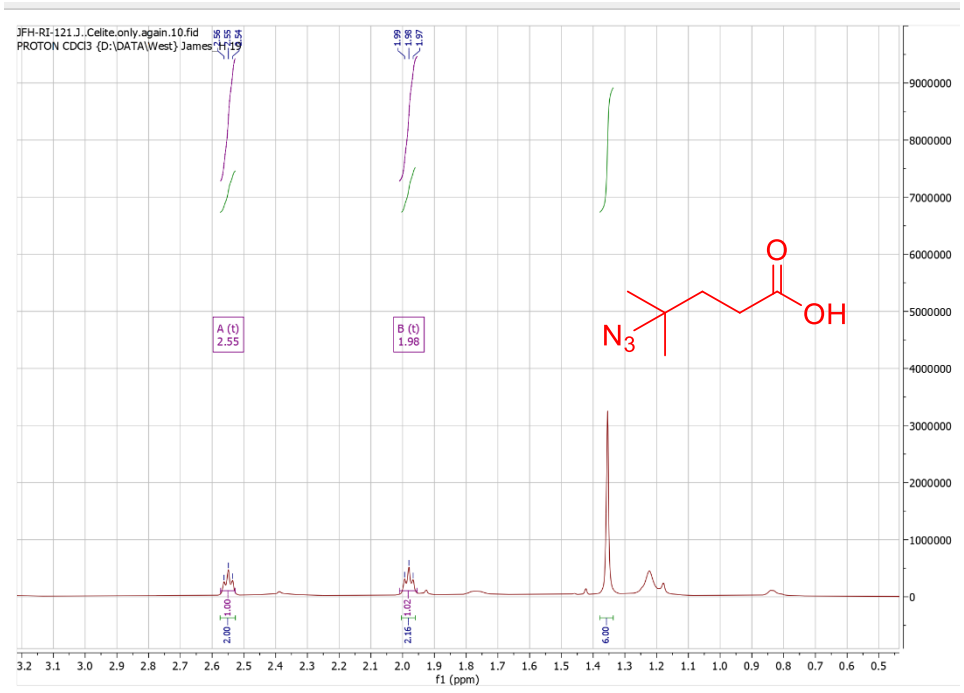
^{1}H-NMR of 5-azido-5-methylhexan-2-yl benzoate, full spectrum



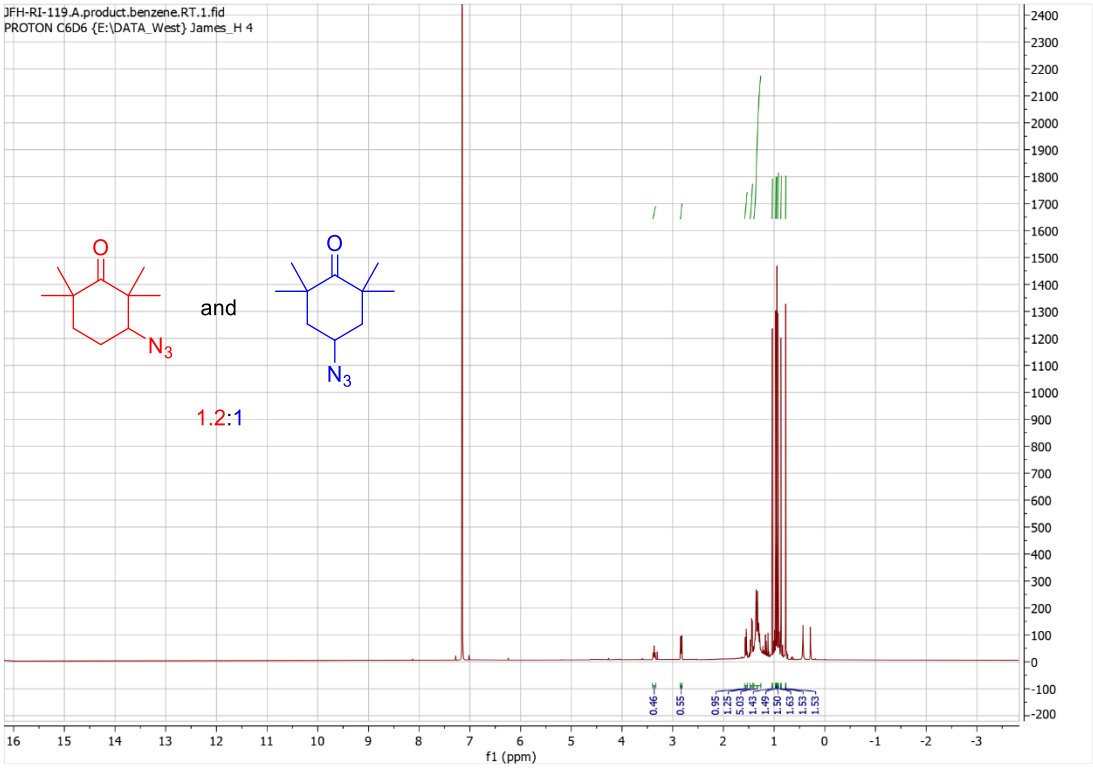
^{1}H-NMR of 5-azido-5-methylhexan-2-yl benzoate, magnified spectrum



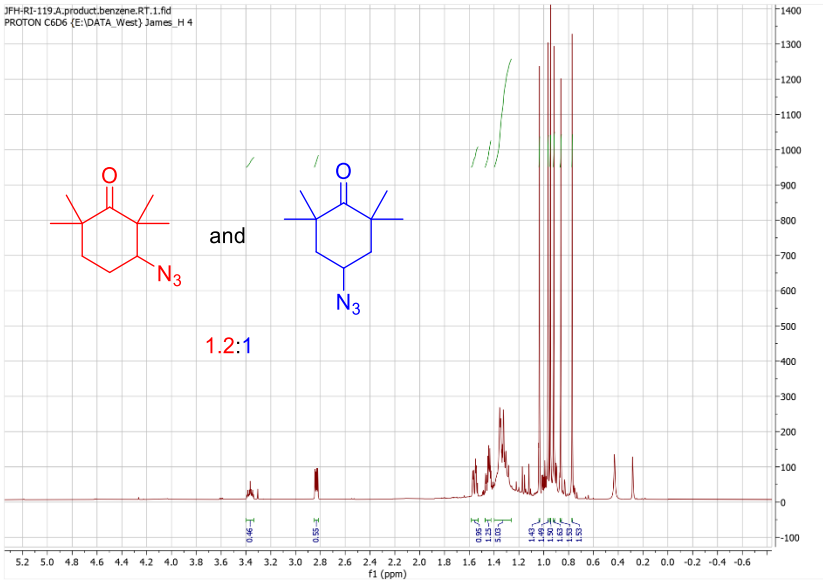
Crude ^{1}H-NMR of 4-azido-4-methylpentanoic acid



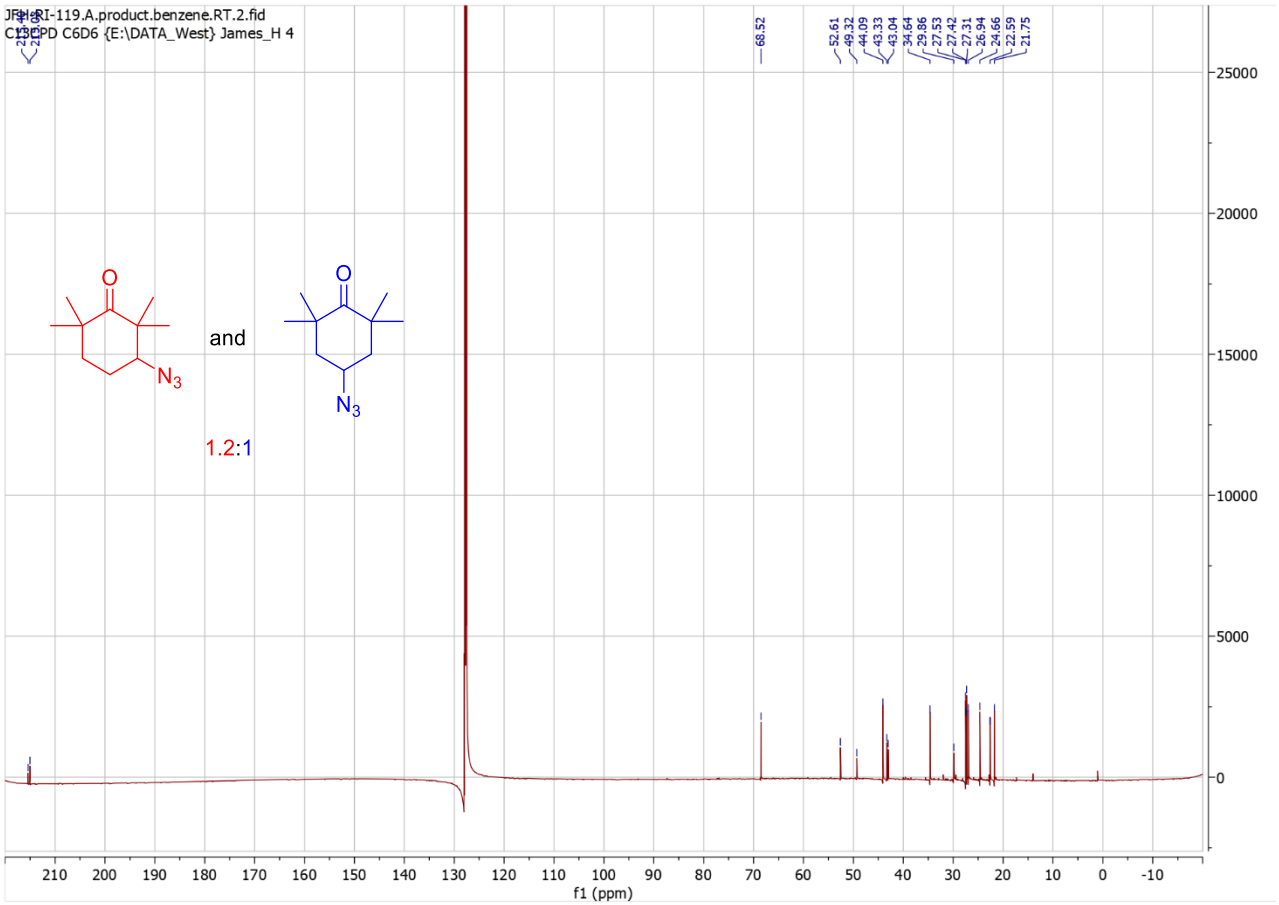
^{1}H-NMR of 4-azido-2,2,6,6-tetramethylcyclohexan-1-one and 3-azido-2,2,6,6-tetramethylcyclohexanone, full spectrum



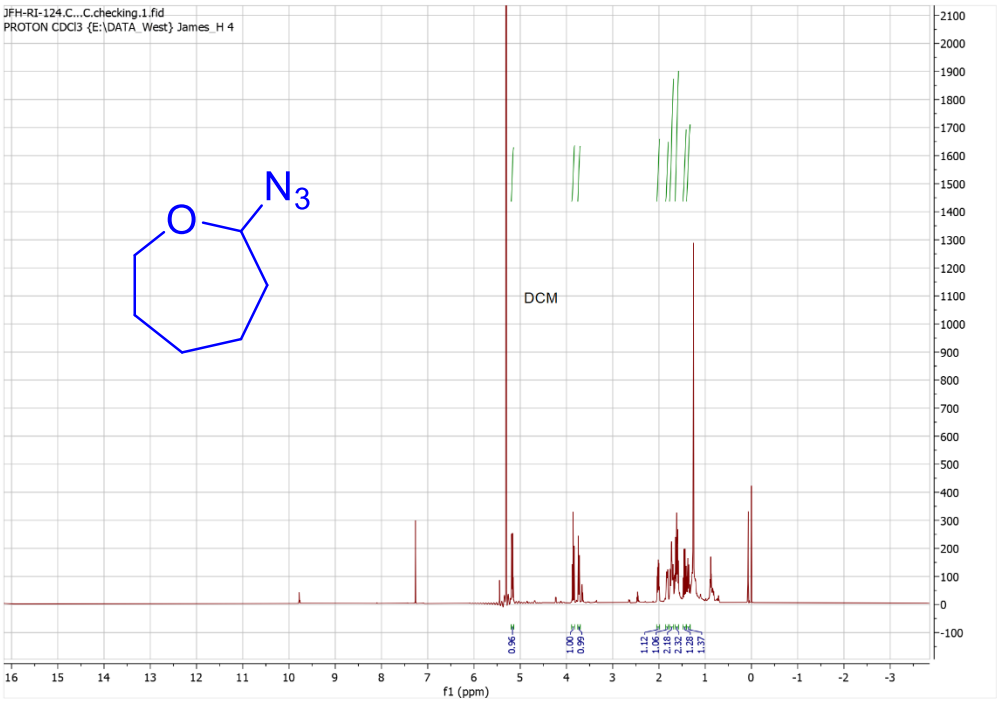
^{1}H-NMR of 4-azido-2,2,6,6-tetramethylcyclohexan-1-one and 3-azido-2,2,6,6-tetramethylcyclohexanone, magnified spectrum



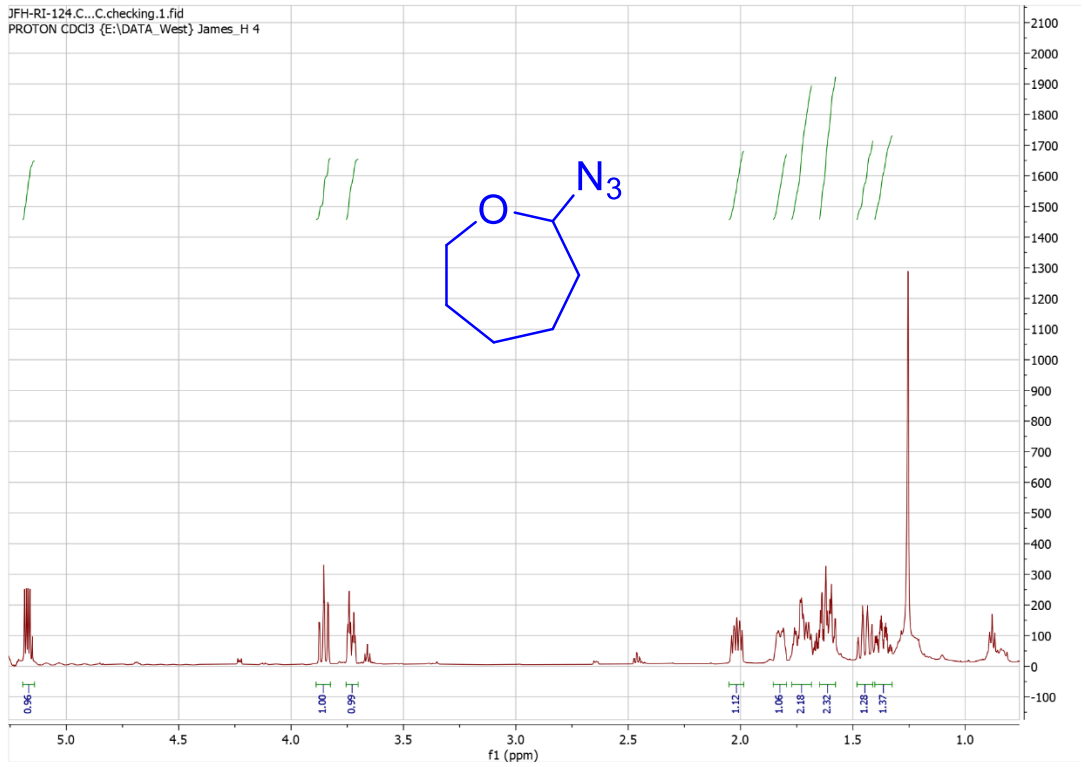
$^{13}C\{^{1}H\}$-NMR of 4-azido-2,2,6,6-tetramethylcyclohexan-1-one and 3-azido-2,2,6,6-tetramethylcyclohexanone



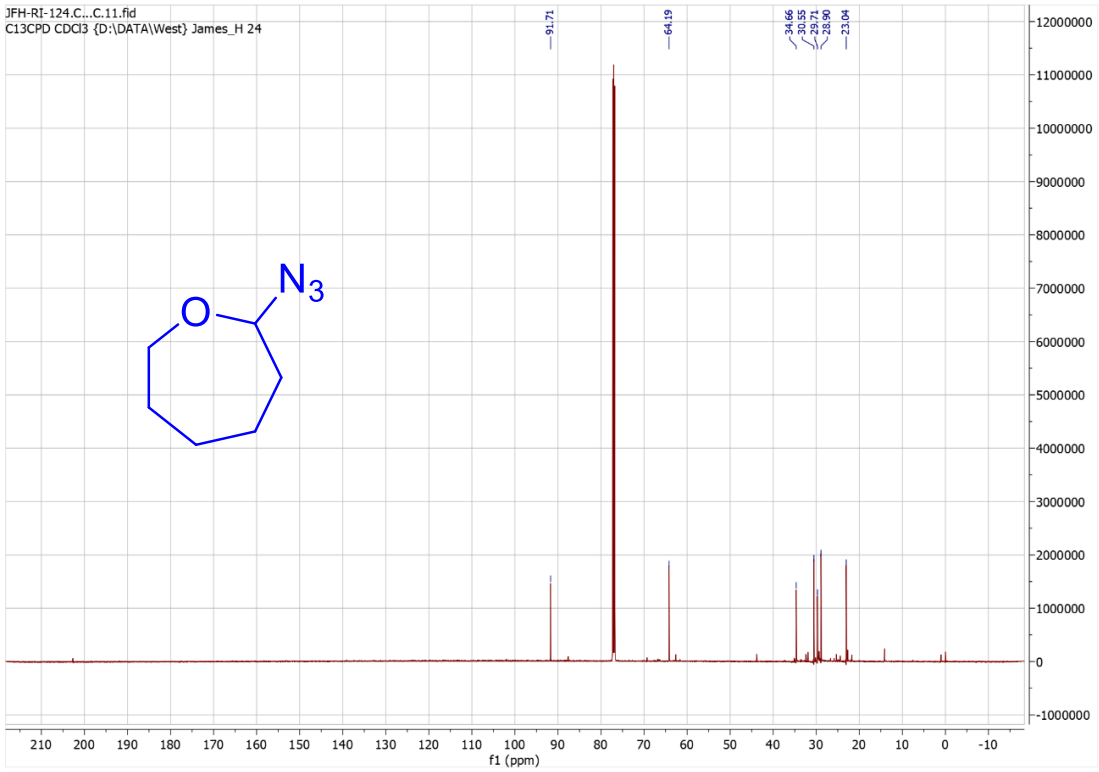
^{1}H-NMR of 2-azidooxepane, full spectrum



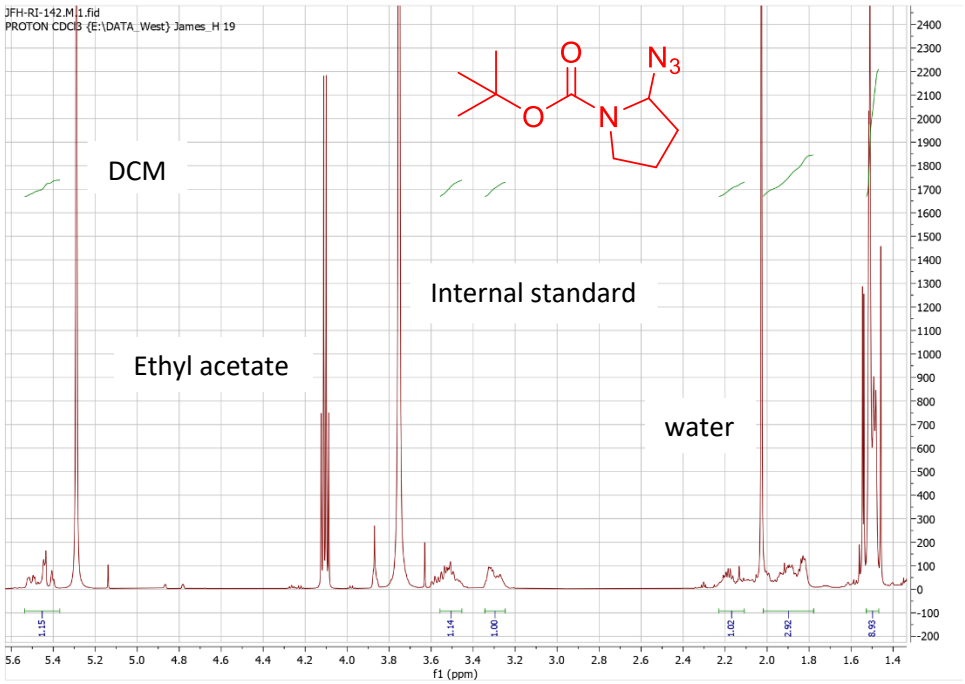
^{1}H-NMR of 2-azidooxepane, magnified spectrum



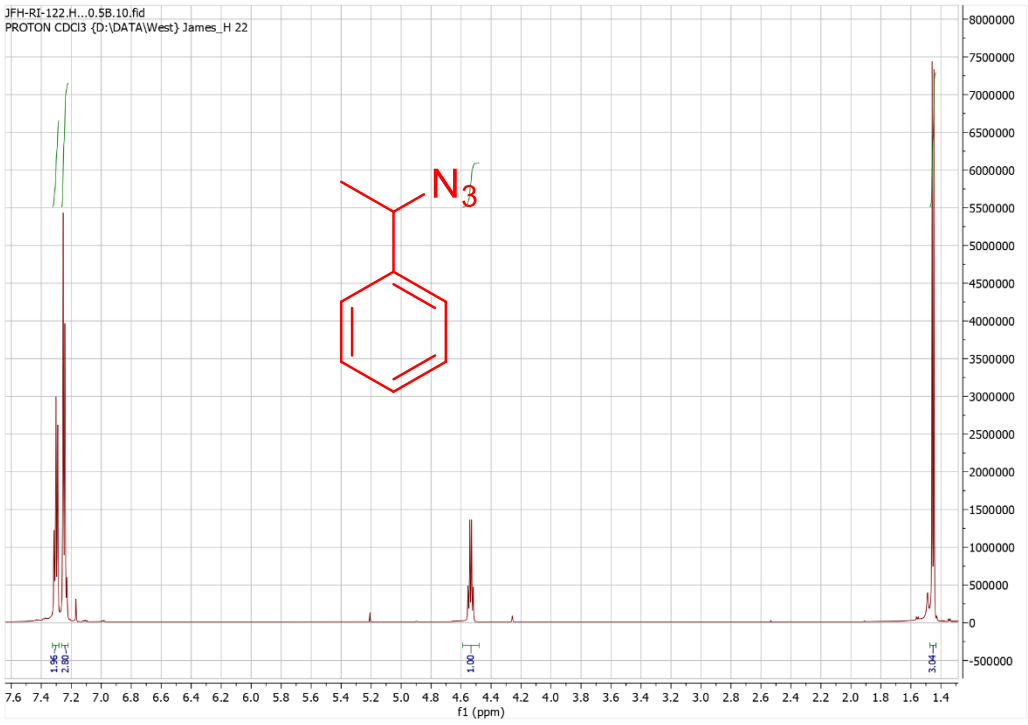
$^{13}C\{^{1}H\}$-NMR of 2-azidooxepane



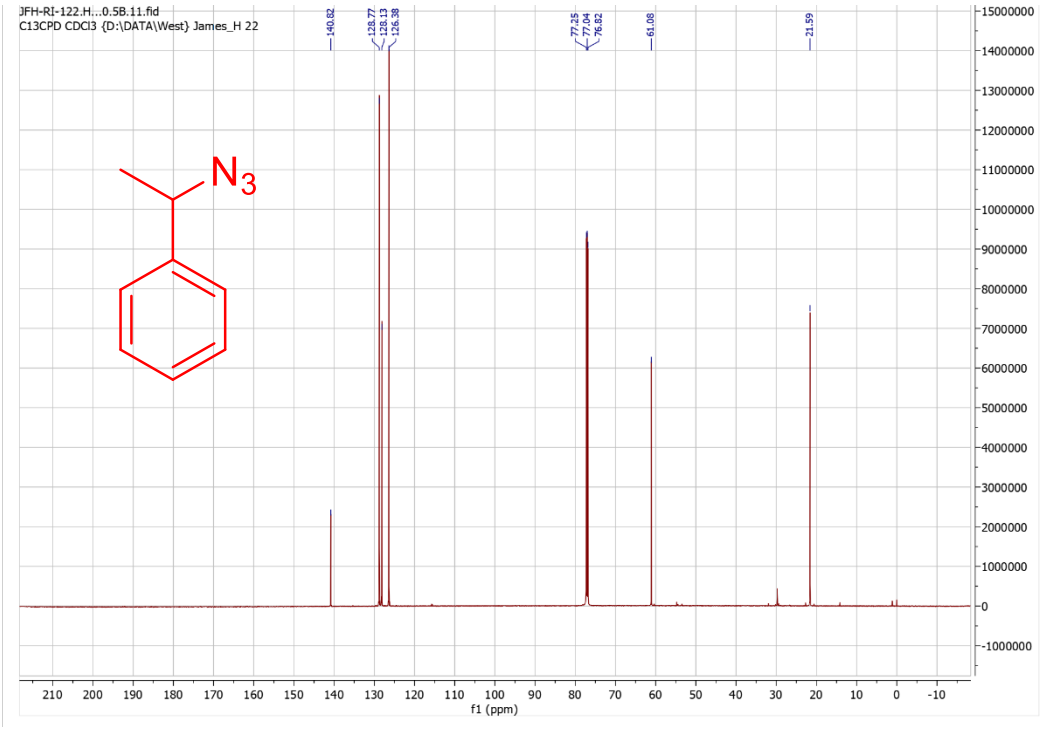
Crude ^{1}H-NMR of *tert*-butyl 2-azidopyrrolidine-1-carboxylate



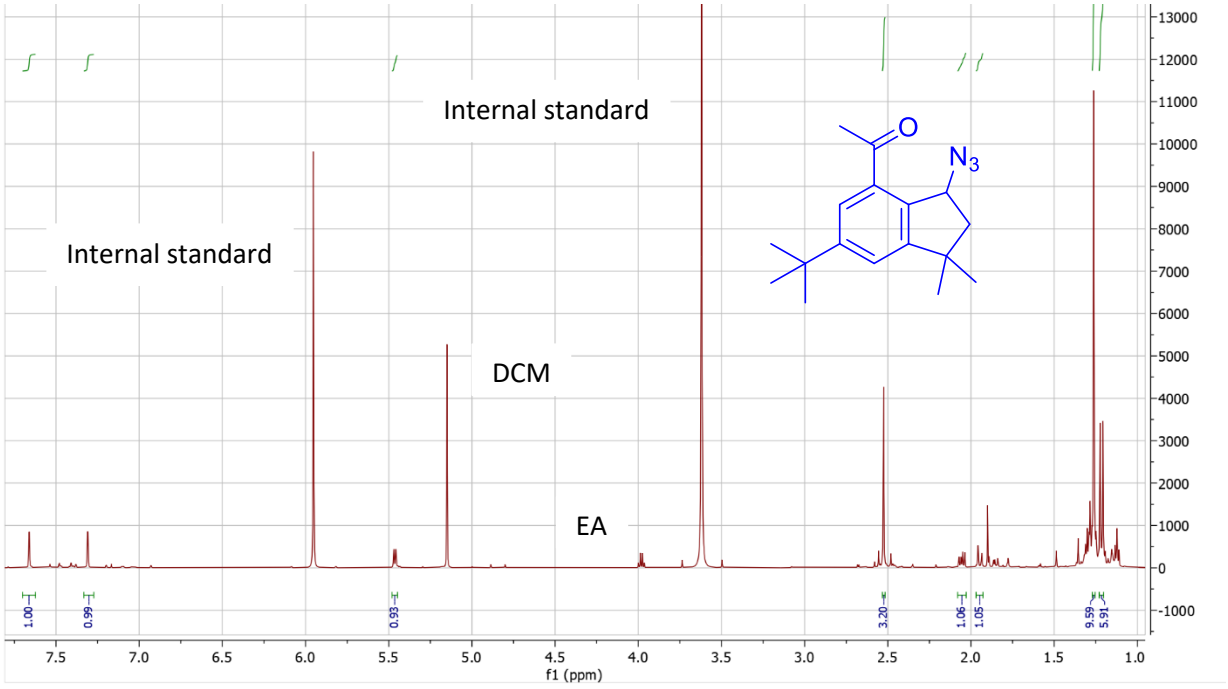
^{1}H-NMR of 1-azidoethylbenzene



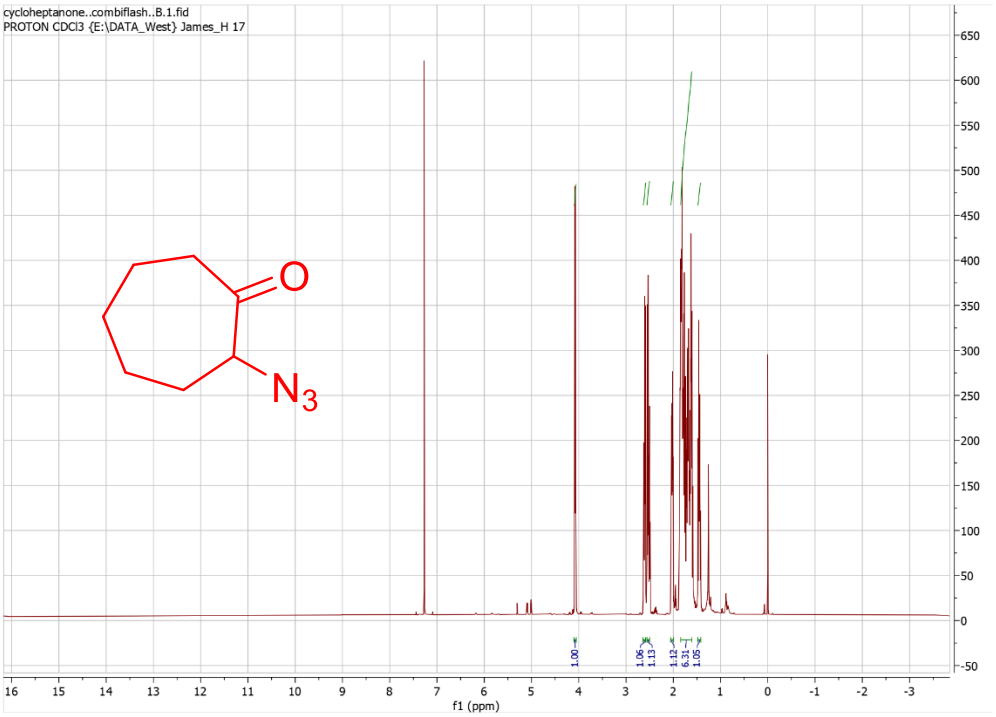
$^{13}C\{^{1}H\}$-NMR of 1-azidoethylbenzene



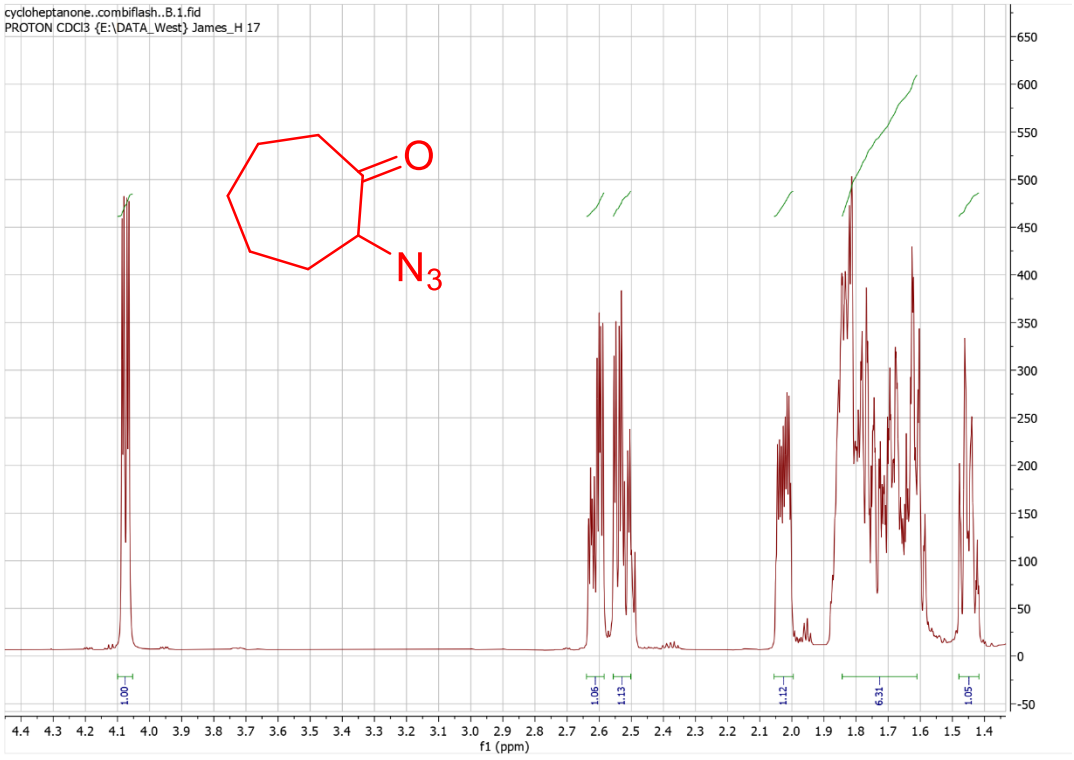
Crude ^{1}H-NMR of benzylic-azido-celestolide



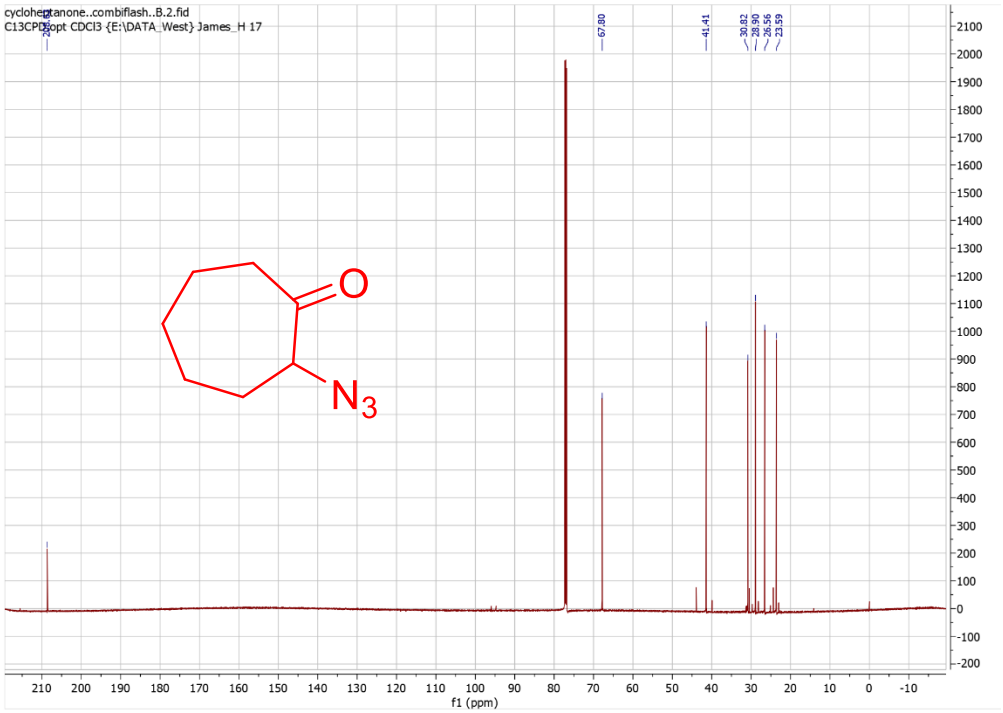
^{1}H-NMR of 2-azidocycloheptan-1-one, full spectrum



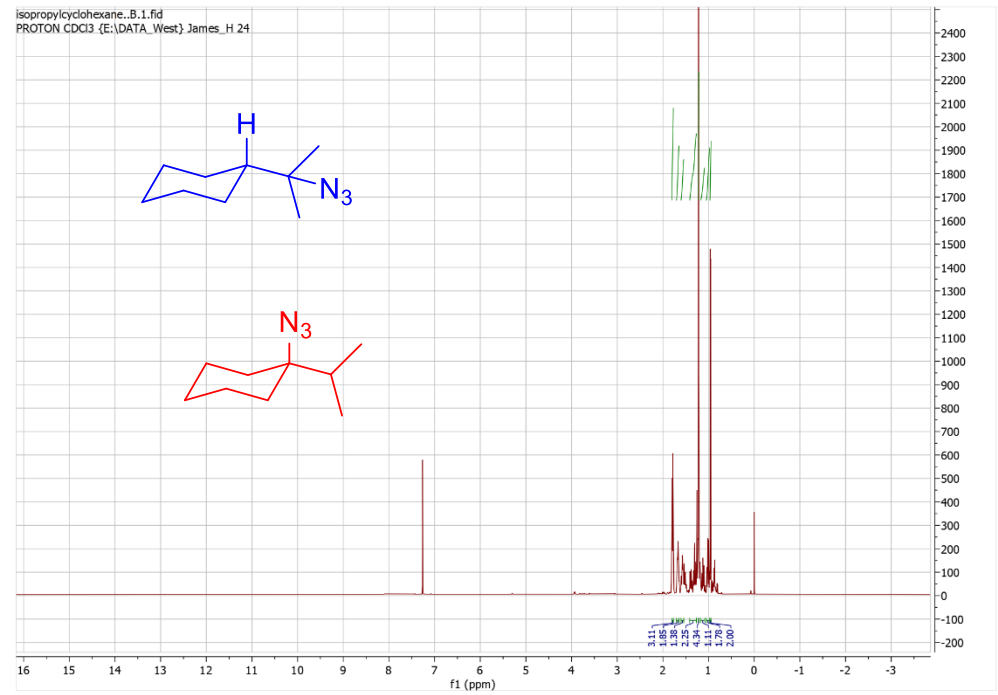
^{1}H-NMR of 2-azidocycloheptan-1-one, magnified spectrum



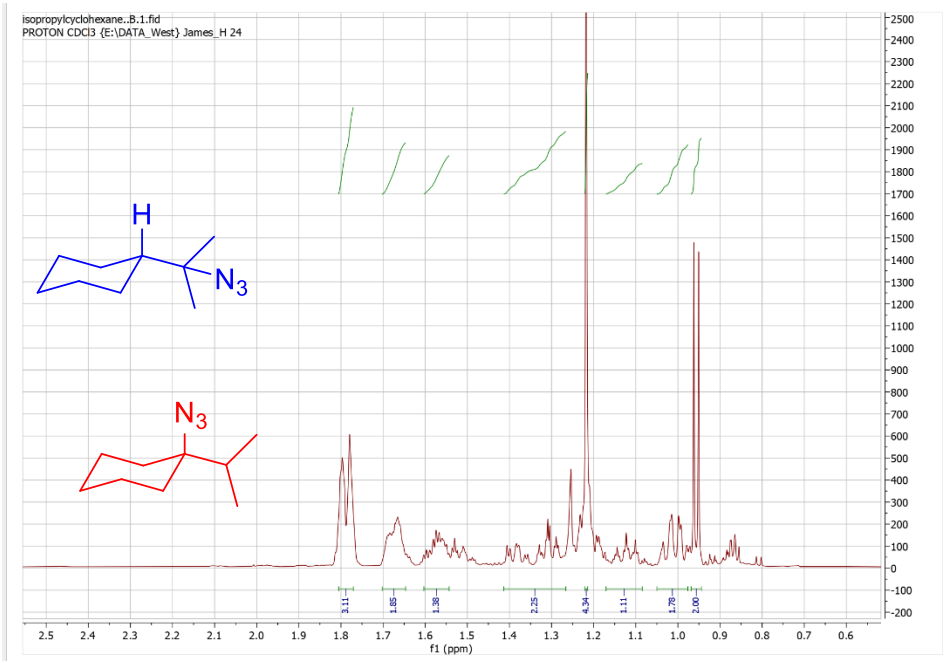
$^{13}C\{^{1}H\}$-NMR of 2-azidocycloheptan-1-one



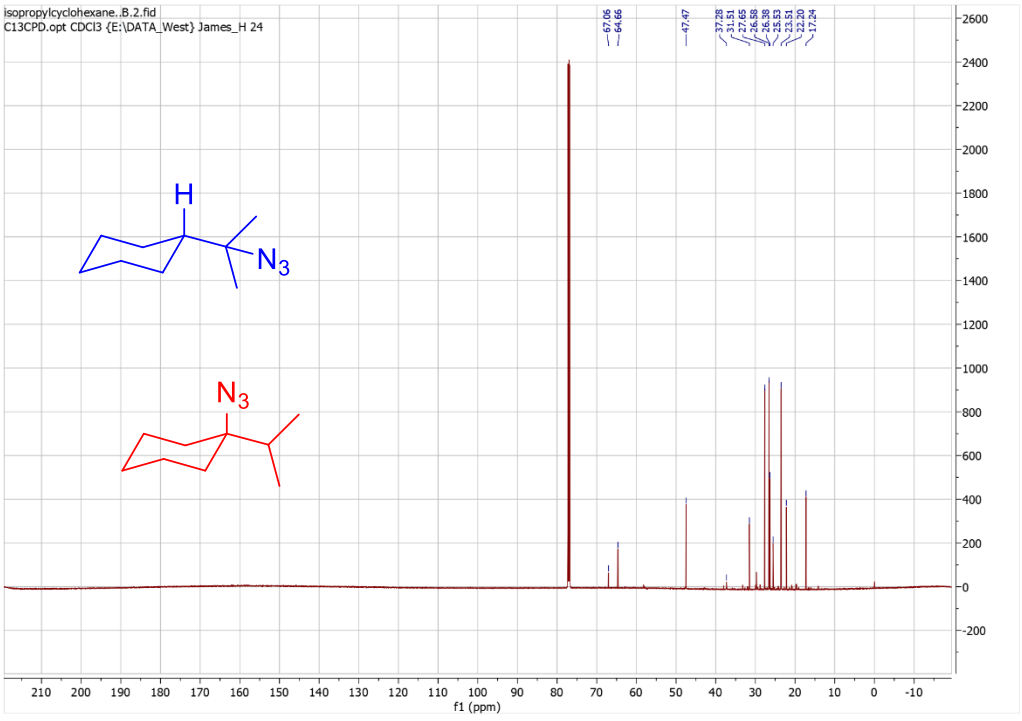
^{1}H-NMR of 1-azido-1-isopropylcyclohexane and (2-azidopropan-2-yl)cyclohexane, full spectrum



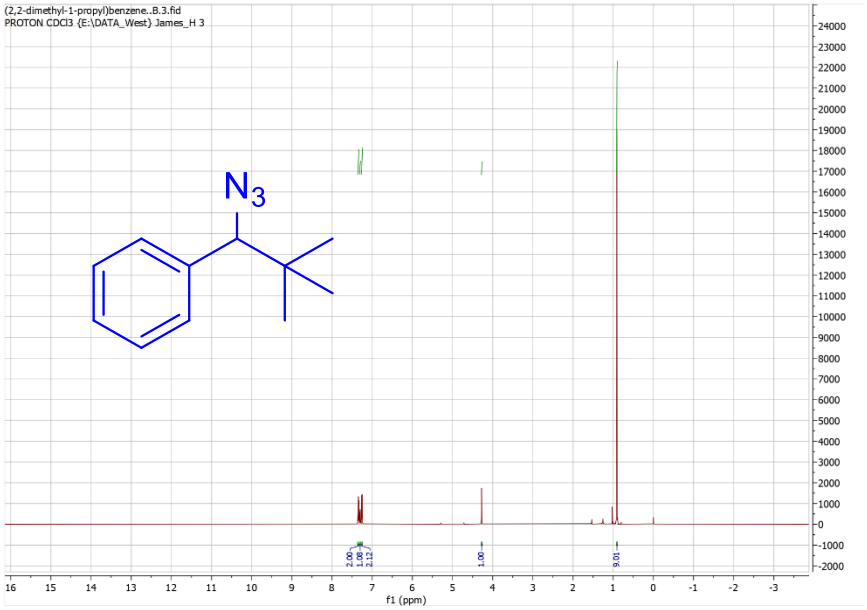
^{1}H-NMR of 1-azido-1-isopropylcyclohexane and (2-azidopropan-2-yl)cyclohexane, magnified spectrum



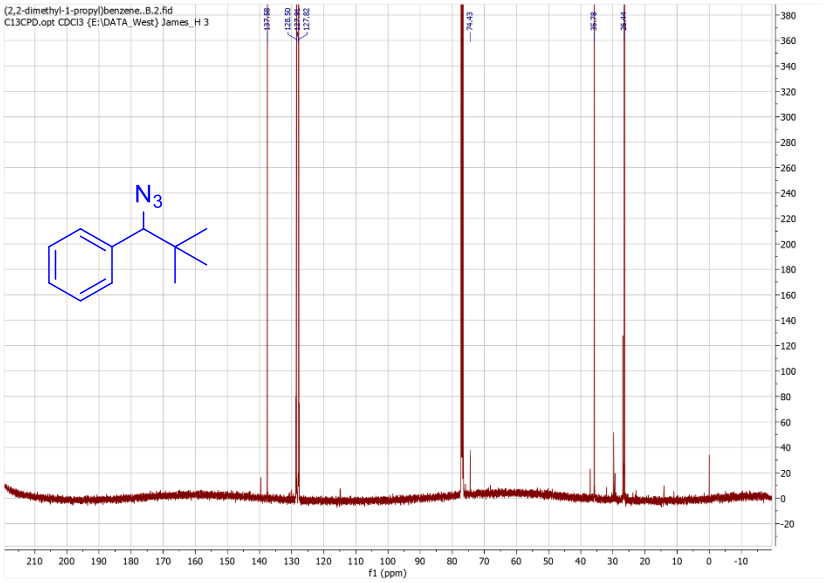
^{13}C{^{1}H}-NMR of 1-azido-1-isopropylcyclohexane and (2-azidopropan-2-yl)cyclohexane



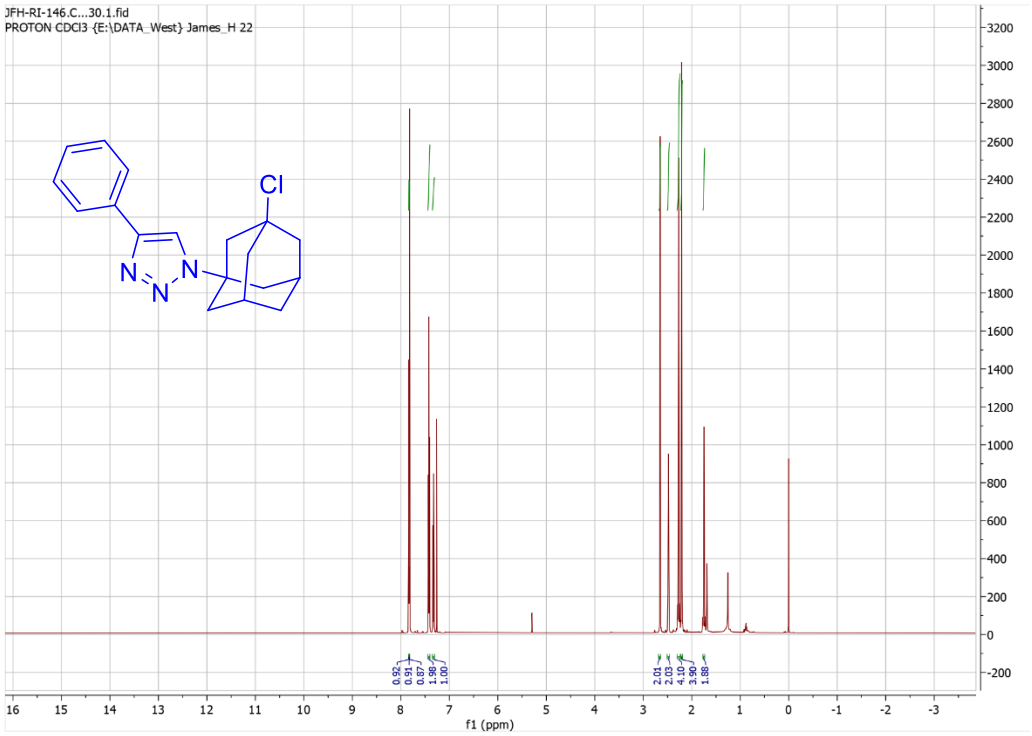
^{1}H-NMR of (1-azido-2,2-dimethylpropyl)benzene



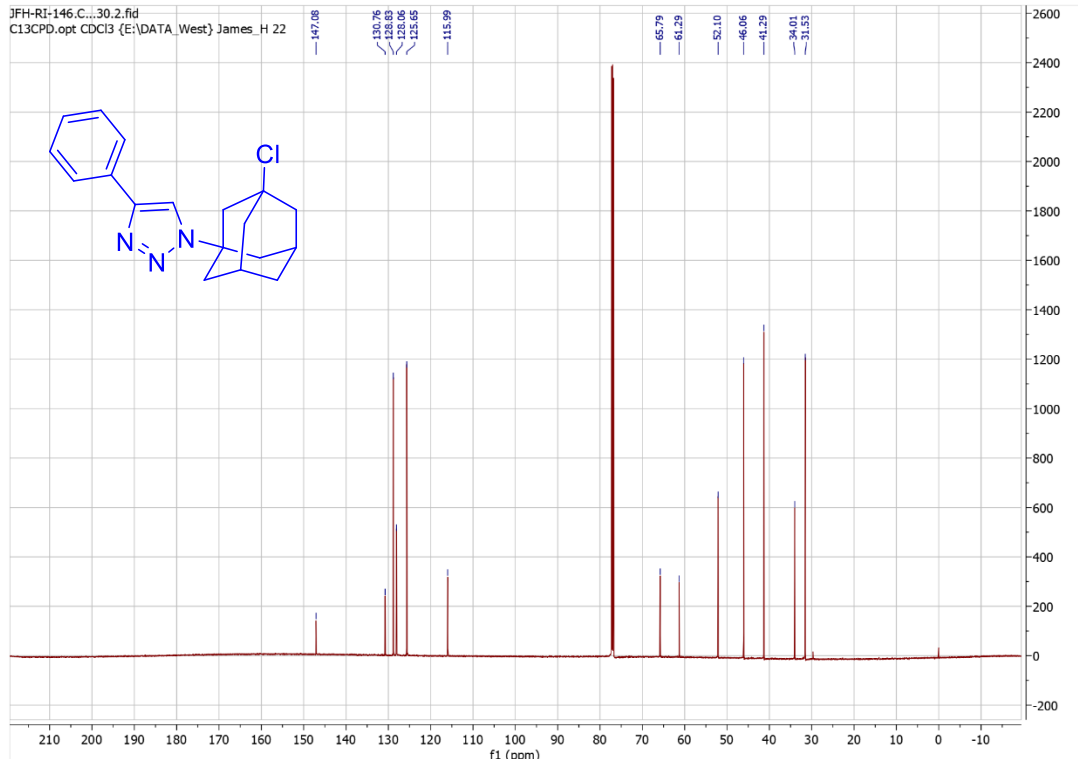
^{13}C{^{1}H}-NMR of (1-azido-2,2-dimethylpropyl)benzene



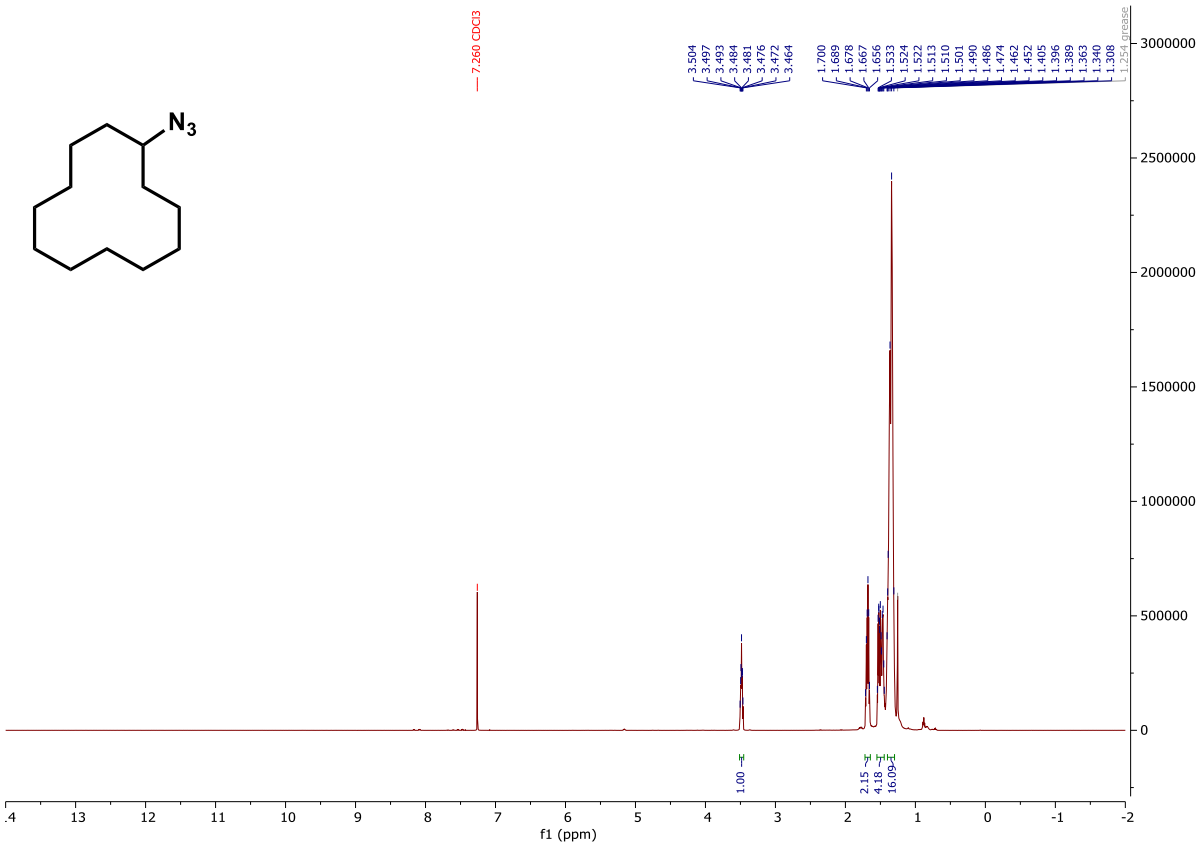
^{1}H-NMR of 1-((1*r*,3*s*,5*R*,7*S*)-3-chloroadamantan-1-yl)-4-phenyl-1*H*-1,2,3-triazole

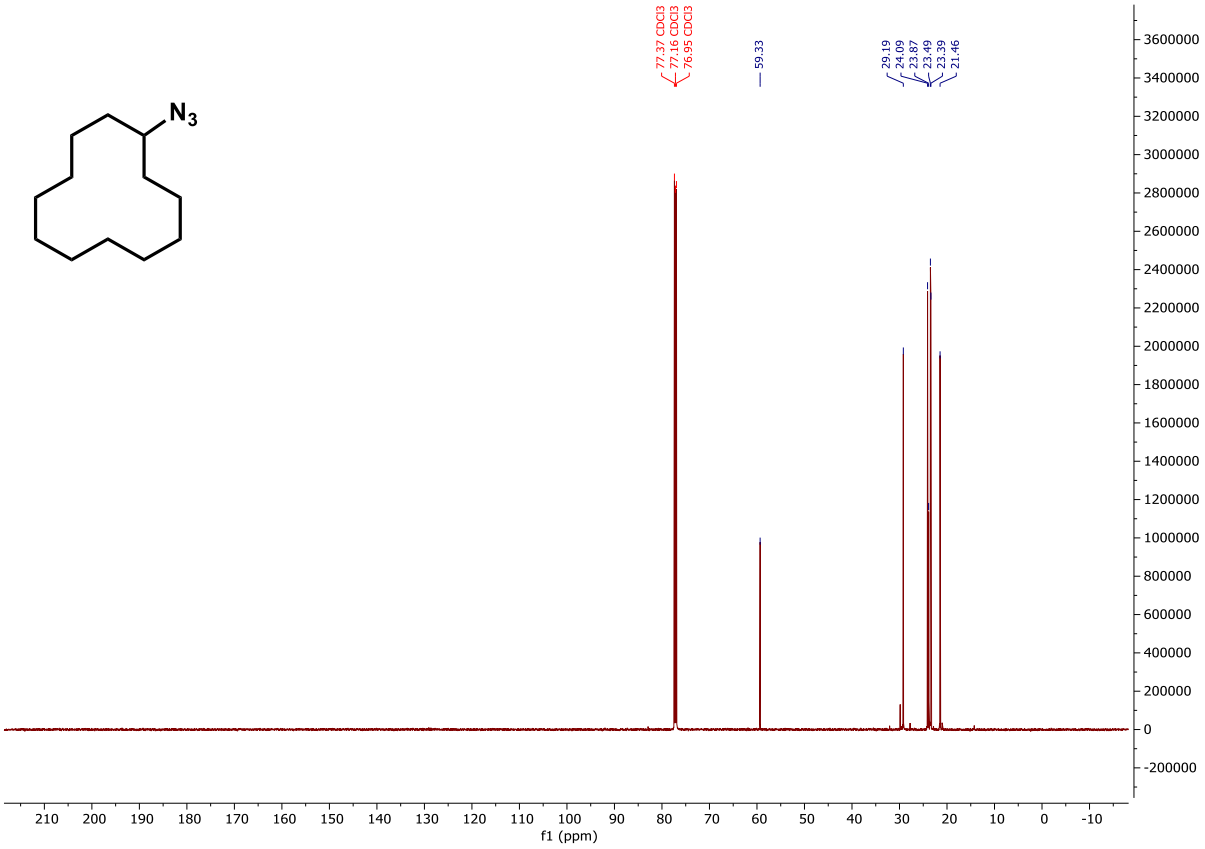


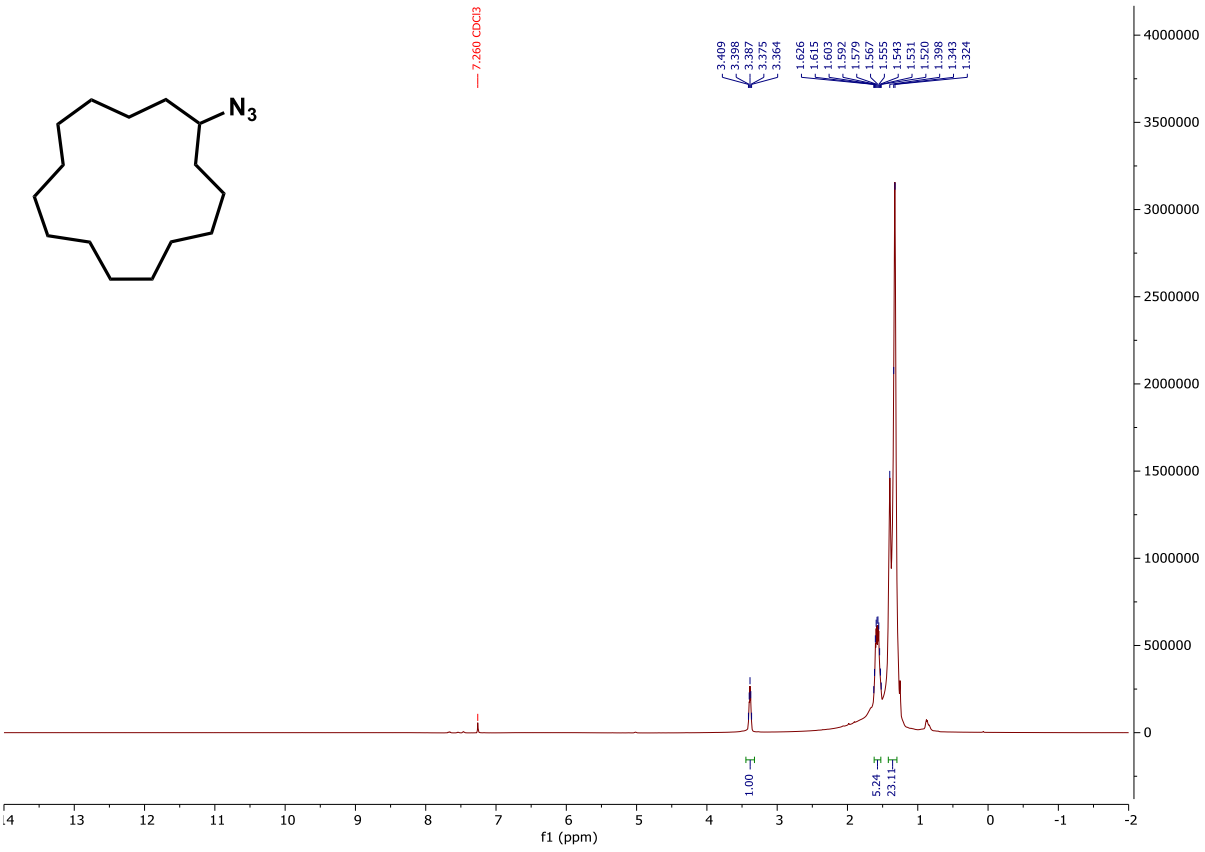
^{13}C{^{1}H}-NMR of 1-((1*r*,3*s*,5*R*,7*S*)-3-chloroadamantan-1-yl)-4-phenyl-1*H*-1,2,3-triazole

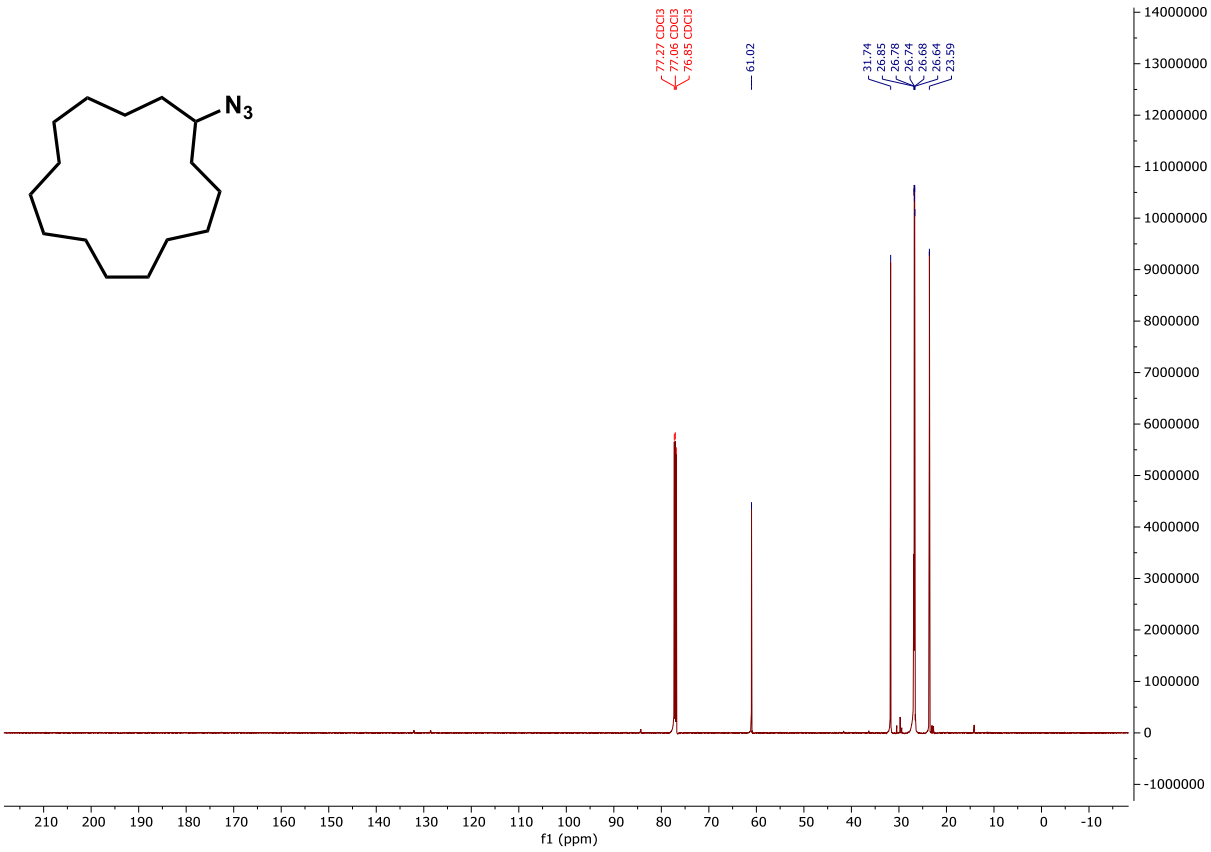


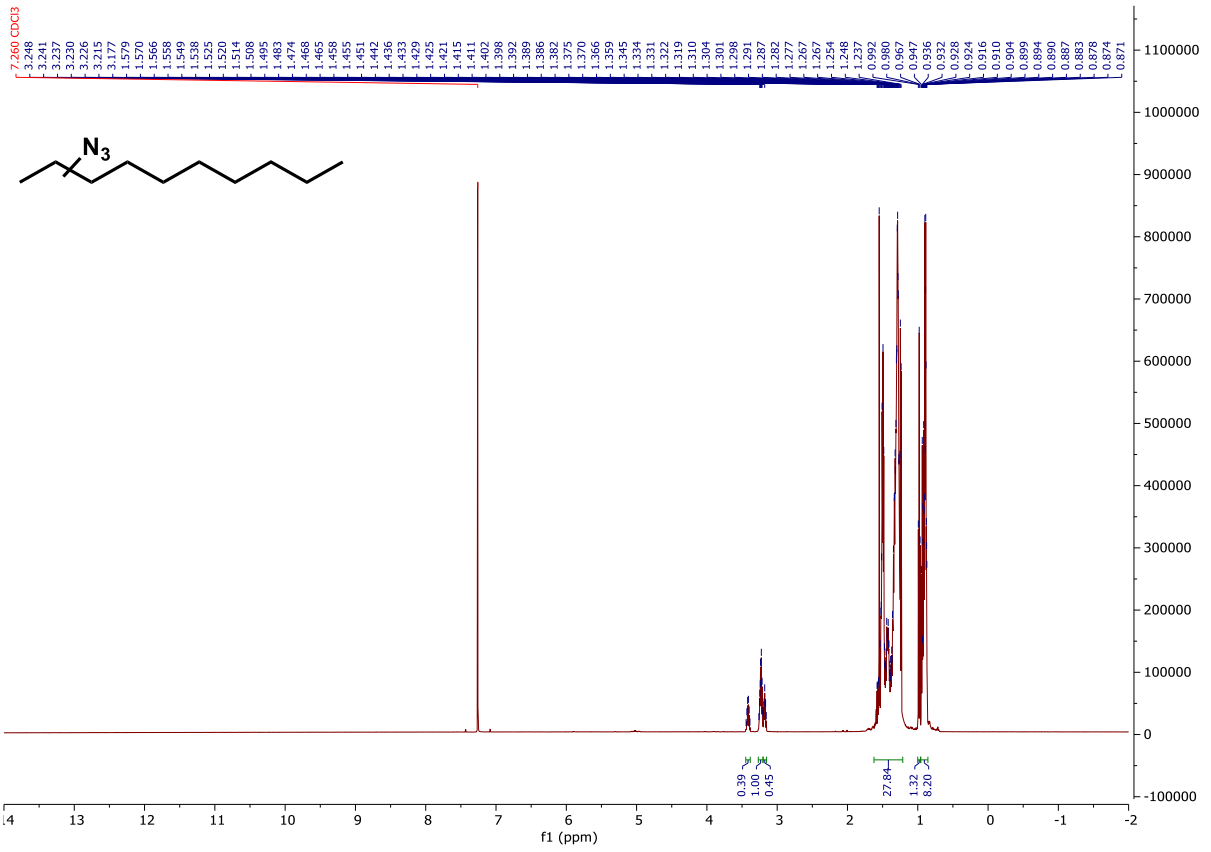
Additional Isolated Product Spectra

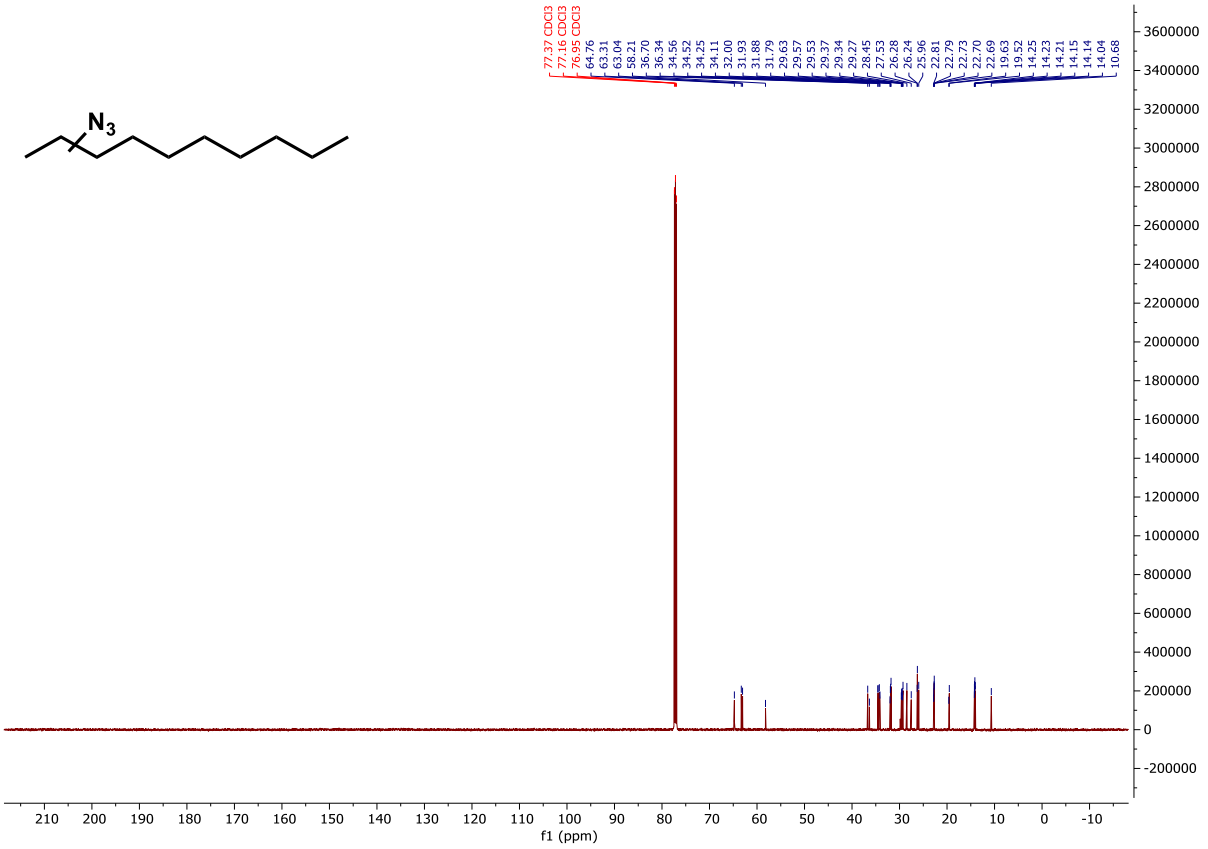


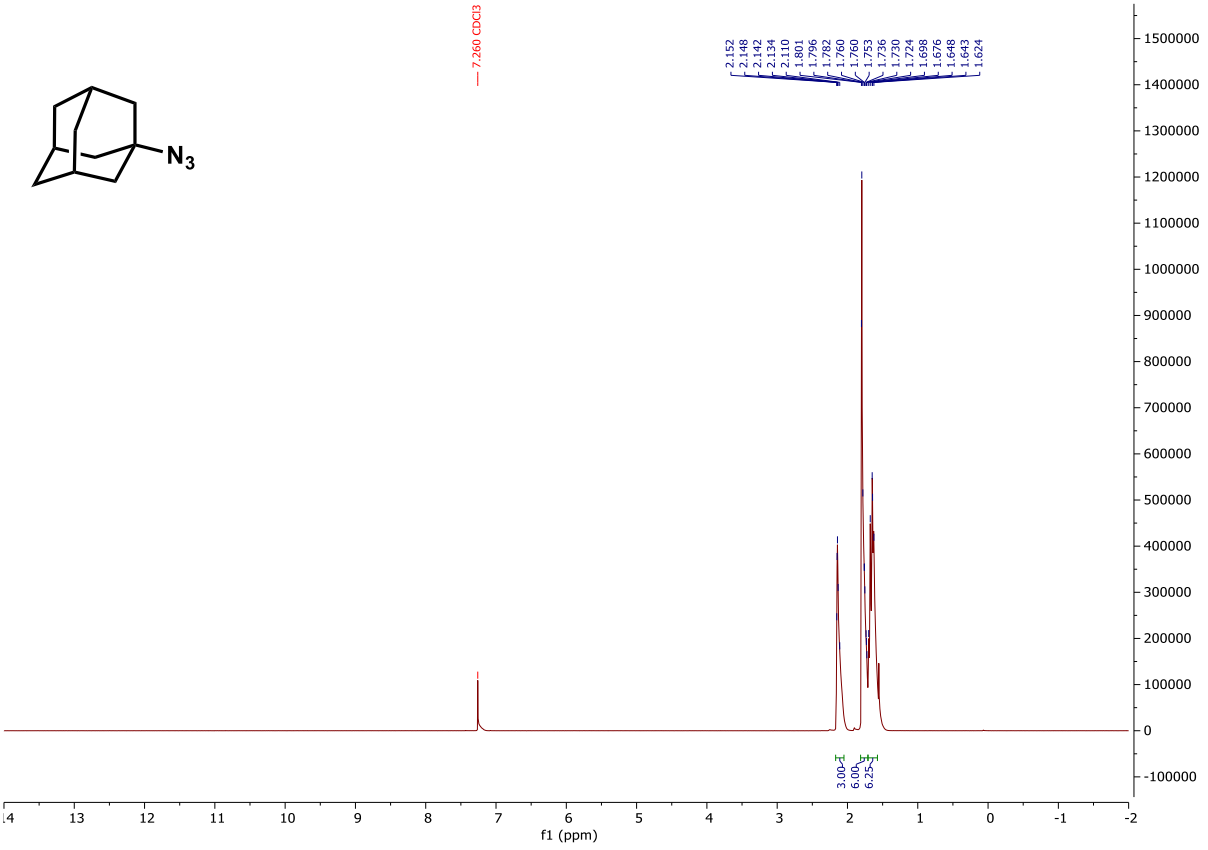

N3
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
59.33
29.19
24.09
23.87
23.49
23.39
21.46
f1 (ppm)

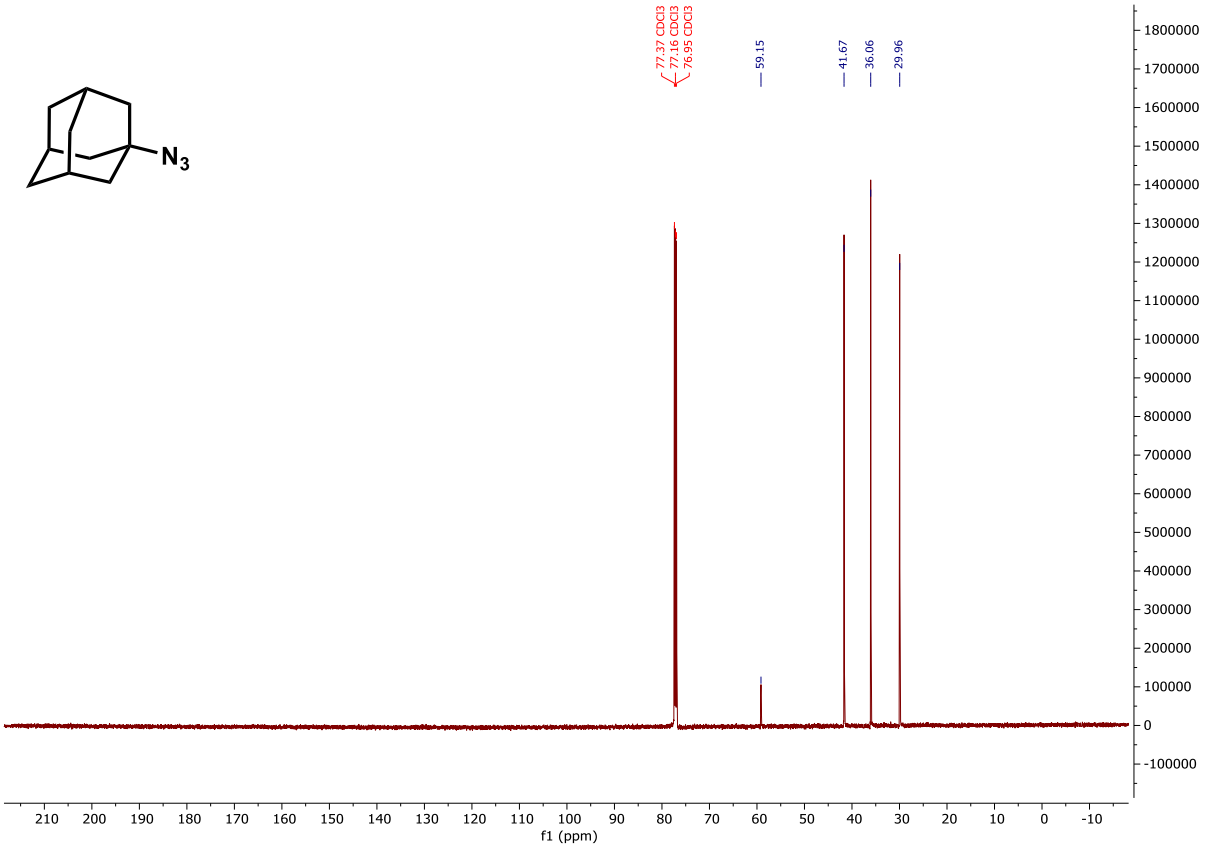

N3
7.260 CDCl3
3.409
3.398
3.387
3.375
3.364
1.626
1.615
1.603
1.592
1.579
1.567
1.555
1.543
1.531
1.520
1.398
1.343
1.324
1.00
5.24
23.11
f1 (ppm)

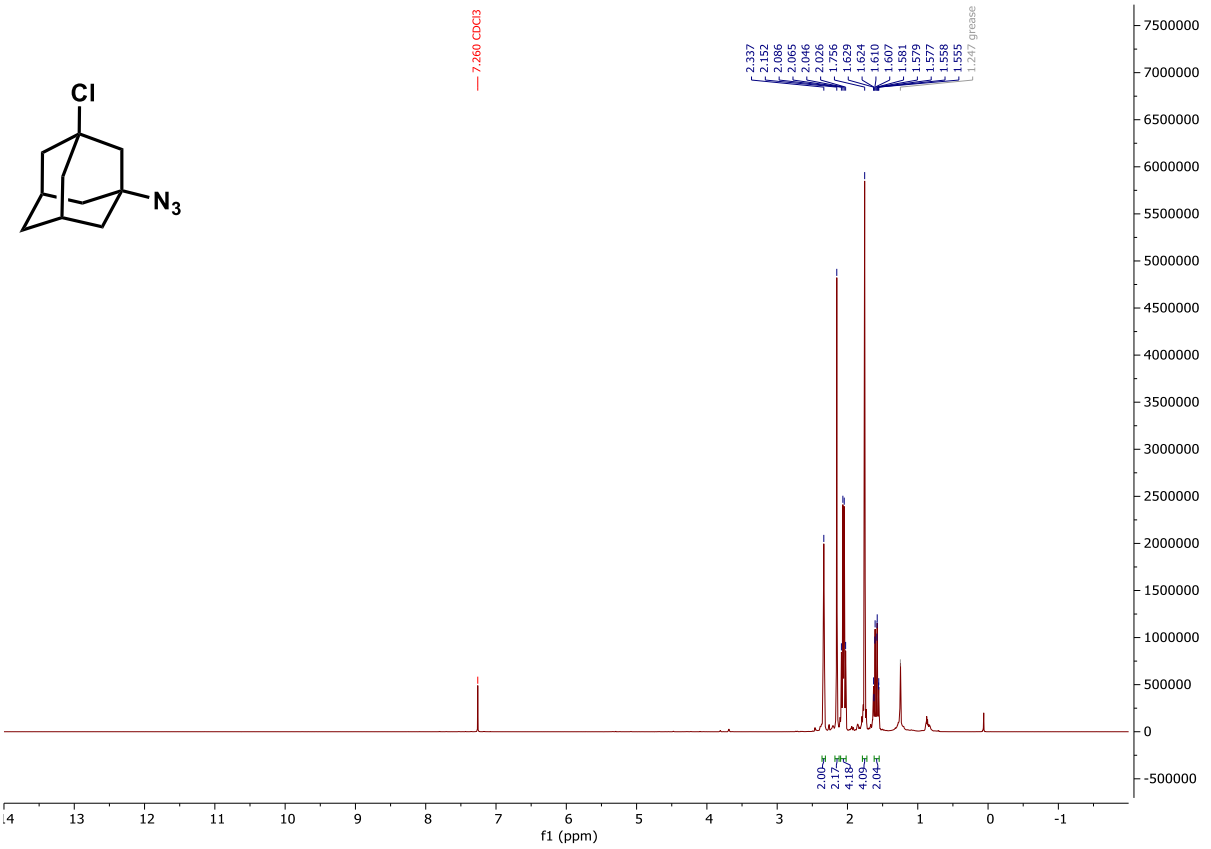

N3
77.27 CDCl3
77.06 CDCl3
76.85 CDCl3
61.02
31.74
26.85
26.78
26.74
26.68
26.64
25.59
f1 (ppm)

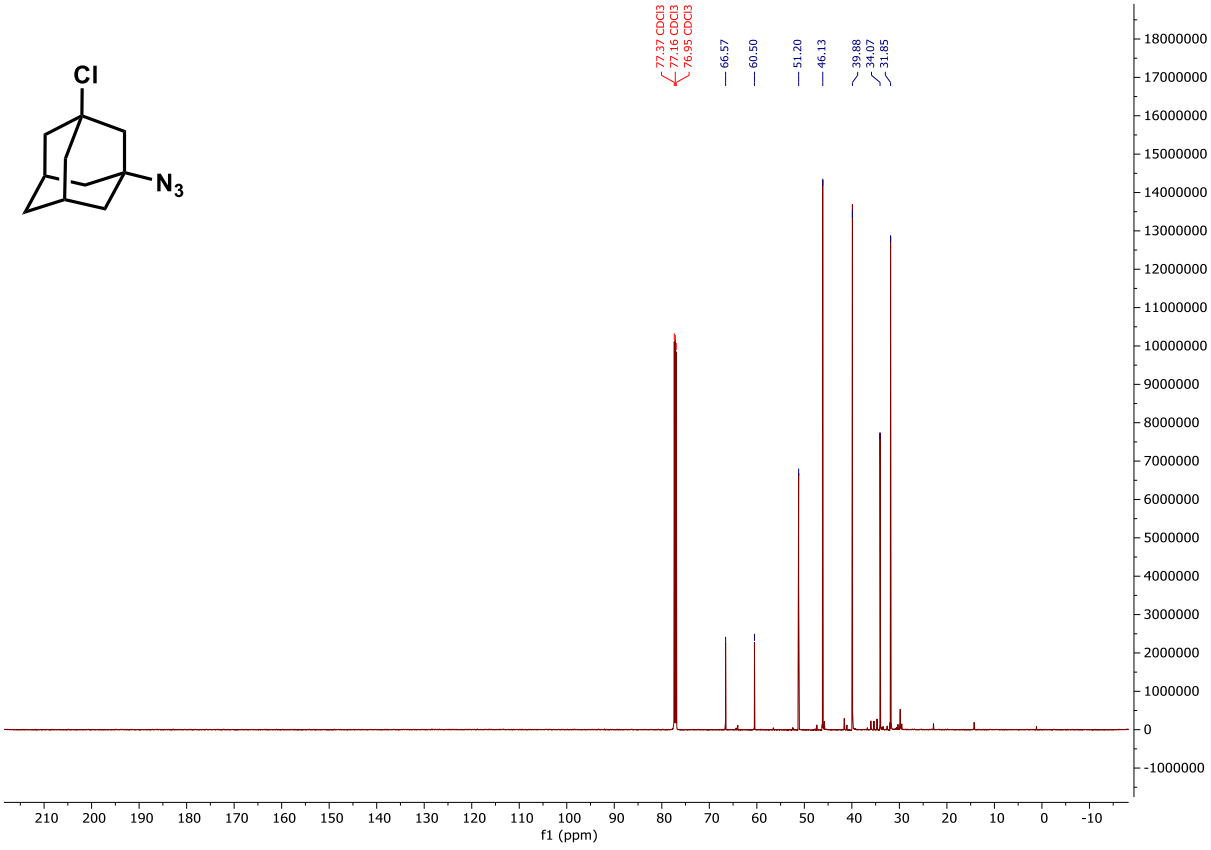

N3
7.260 CDCl3
0.39
1.00
0.45
27.84
1.32
8.20
f1 (ppm)

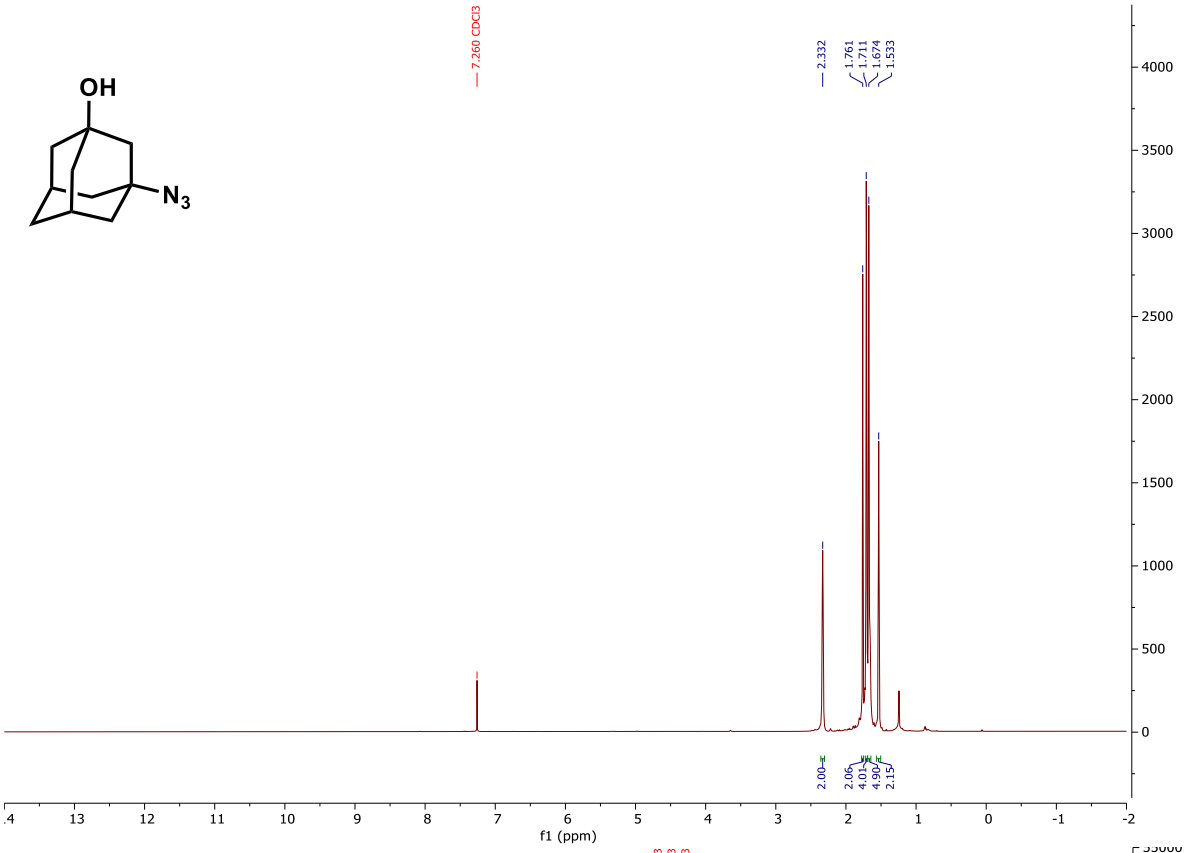

N3
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
64.76
63.31
63.04
58.21
36.70
36.34
34.56
34.52
34.25
34.11
32.00
31.93
31.88
31.79
29.63
29.57
29.53
29.37
29.34
29.27
28.45
27.53
26.28
25.44
25.46
22.81
22.79
22.73
22.70
22.69
19.63
19.52
14.25
14.23
14.21
14.15
14.14
14.04
10.68
f1 (ppm)

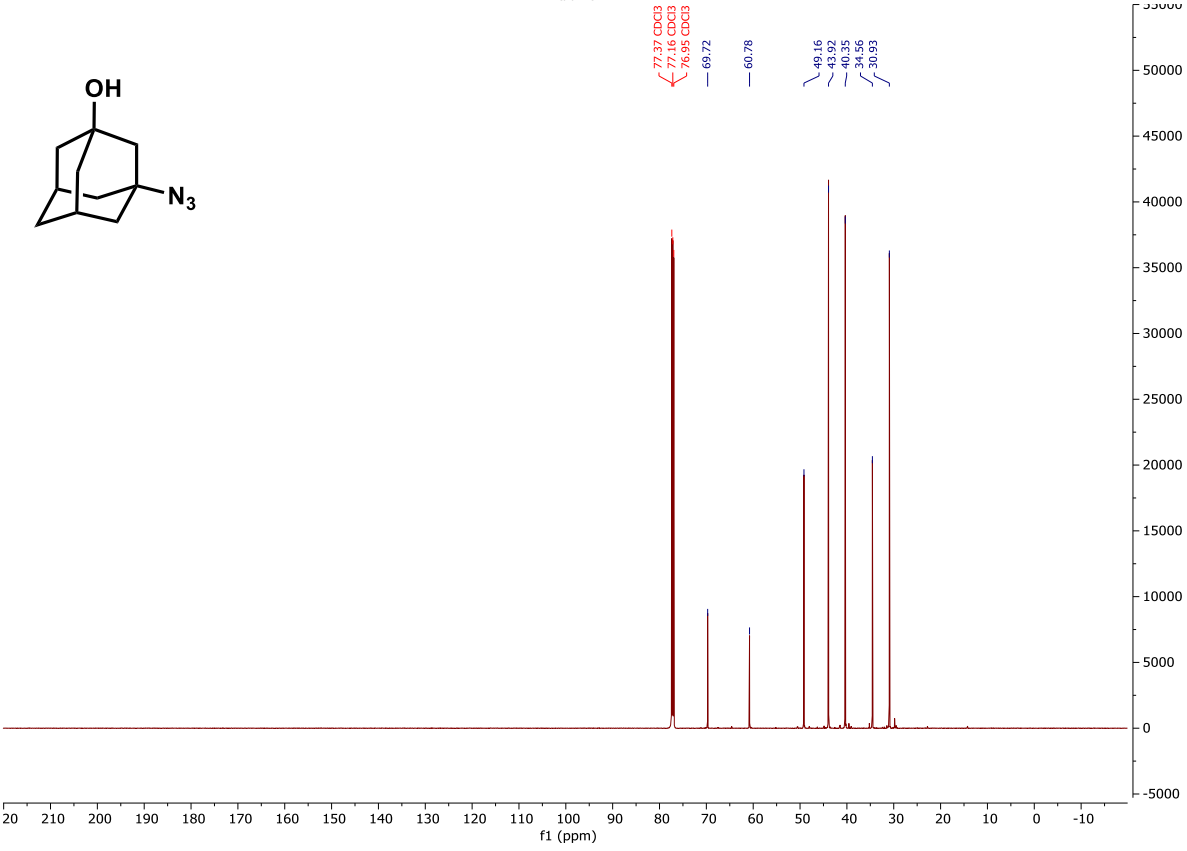

N3
7.260 CDCl3
2.152
2.148
2.142
2.134
2.110
1.801
1.796
1.782
1.760
1.760
1.753
1.736
1.730
1.724
1.698
1.676
1.648
1.643
1.624
3.00
6.00
6.25
f1 (ppm)

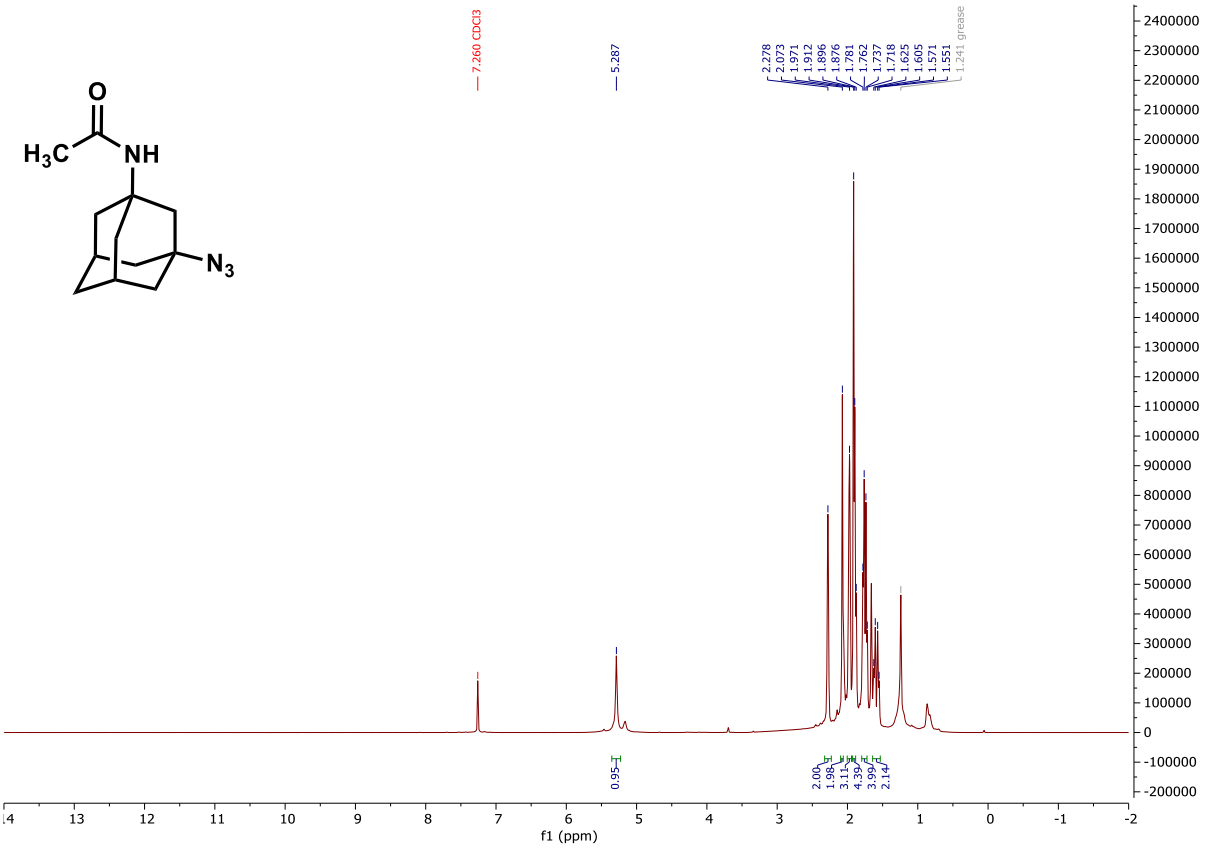

77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
59.15
41.67
36.06
29.96
N3
f1 (ppm)

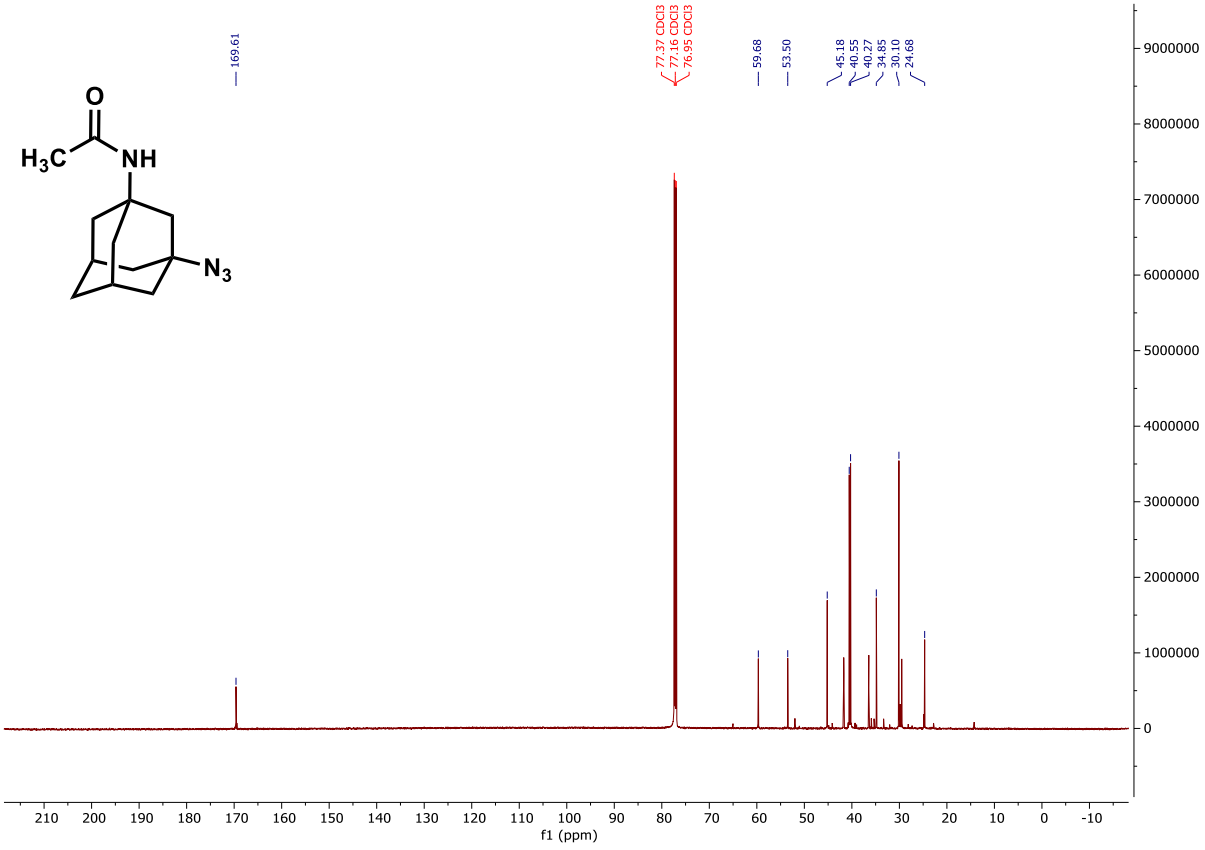

Cl
N3
7.260 CDCl3
2.337
2.152
2.086
2.065
2.046
2.026
1.756
1.629
1.624
1.610
1.607
1.581
1.579
1.577
1.558
1.555
1.247 grease
2.00
2.17
4.18
4.09
2.04
f1 (ppm)

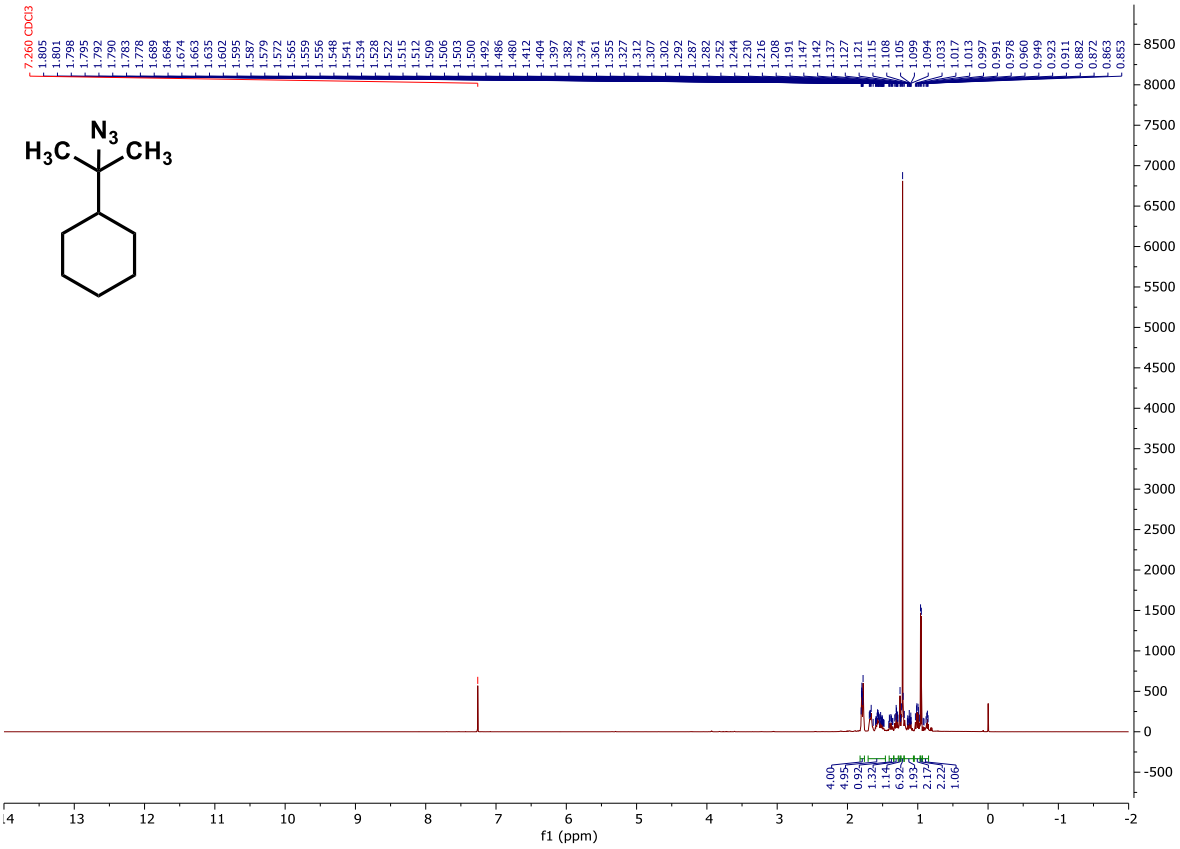

Cl
N3
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
66.57
60.50
51.20
46.13
39.88
34.07
31.85
f1 (ppm)

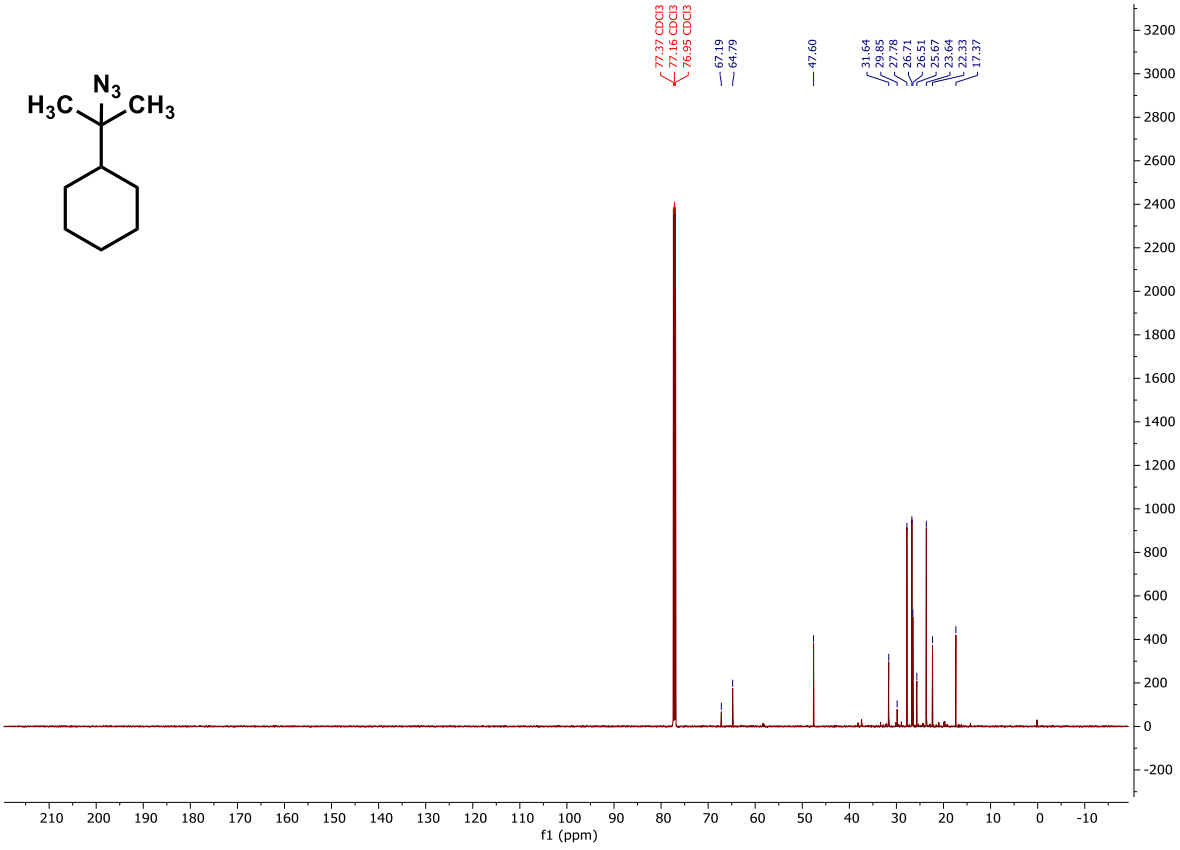

OH
N3
7.260 CDCl3
2.332
1.761
1.711
1.674
1.533
2.00
2.06
4.01
4.90
2.15
f1 (ppm)

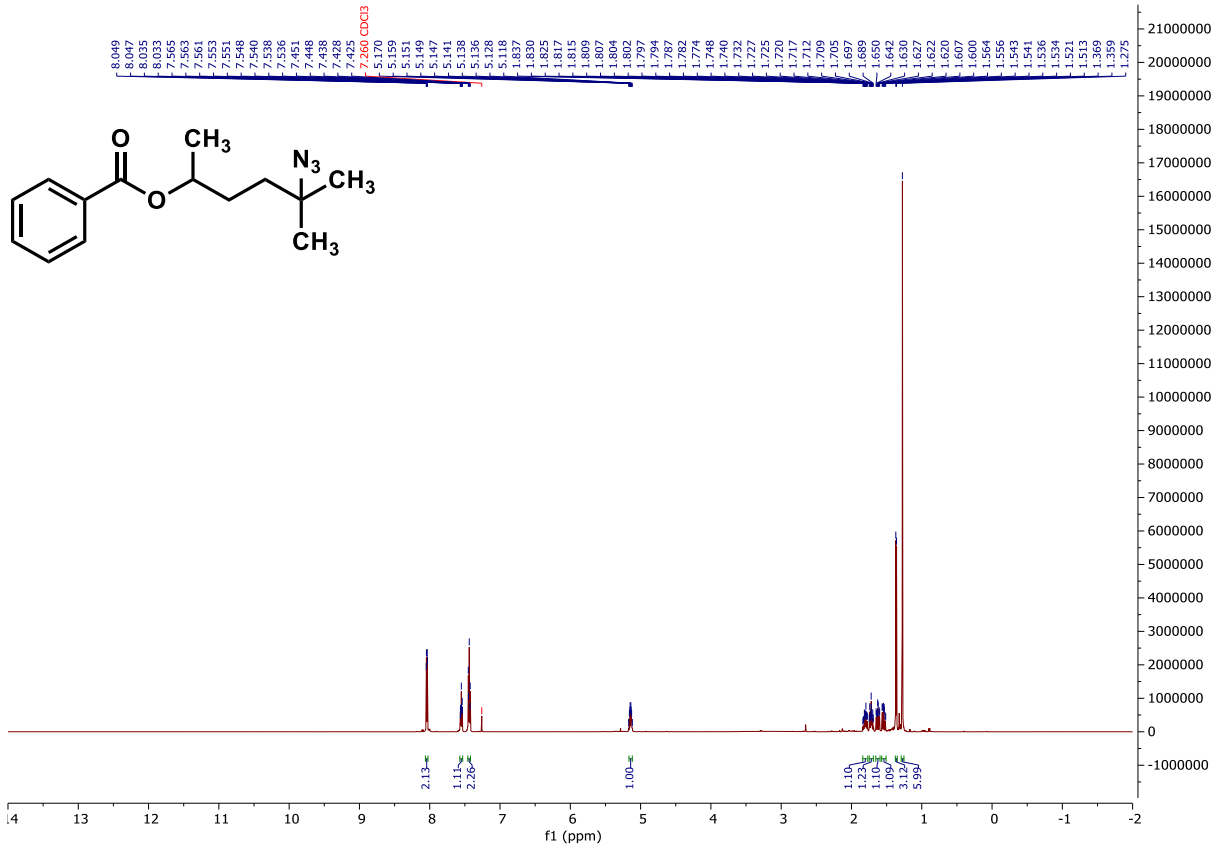

OH
N3
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
69.72
60.78
49.16
43.92
40.35
34.56
30.93
f1 (ppm)

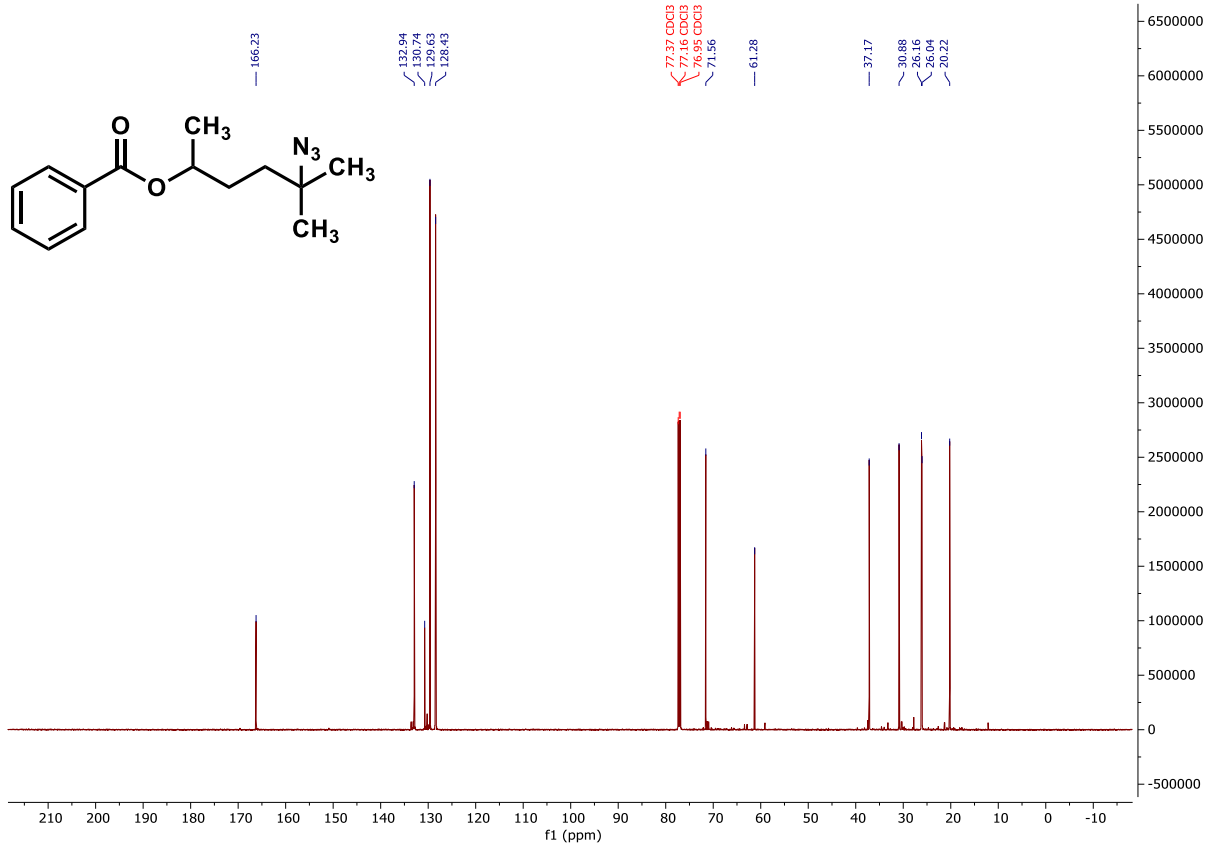

7.260 CDCl3
5.287
2.278
2.073
1.971
1.912
1.896
1.876
1.781
1.762
1.737
1.718
1.625
1.605
1.571
1.551
1.241 grease
0.95
2.00
1.98
3.11
4.39
3.99
2.14
f1 (ppm)

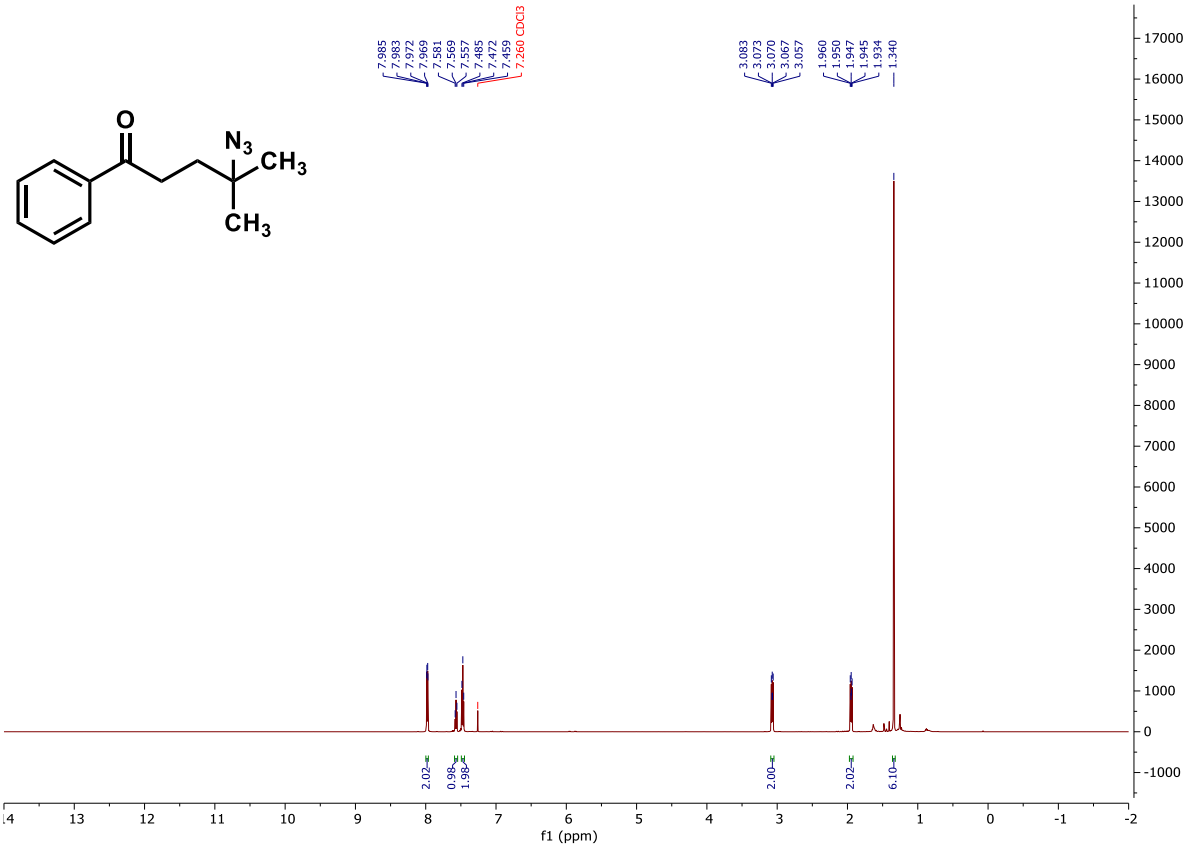

169.61
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
59.68
53.50
45.18
40.55
40.27
34.85
30.10
24.68
f1 (ppm)

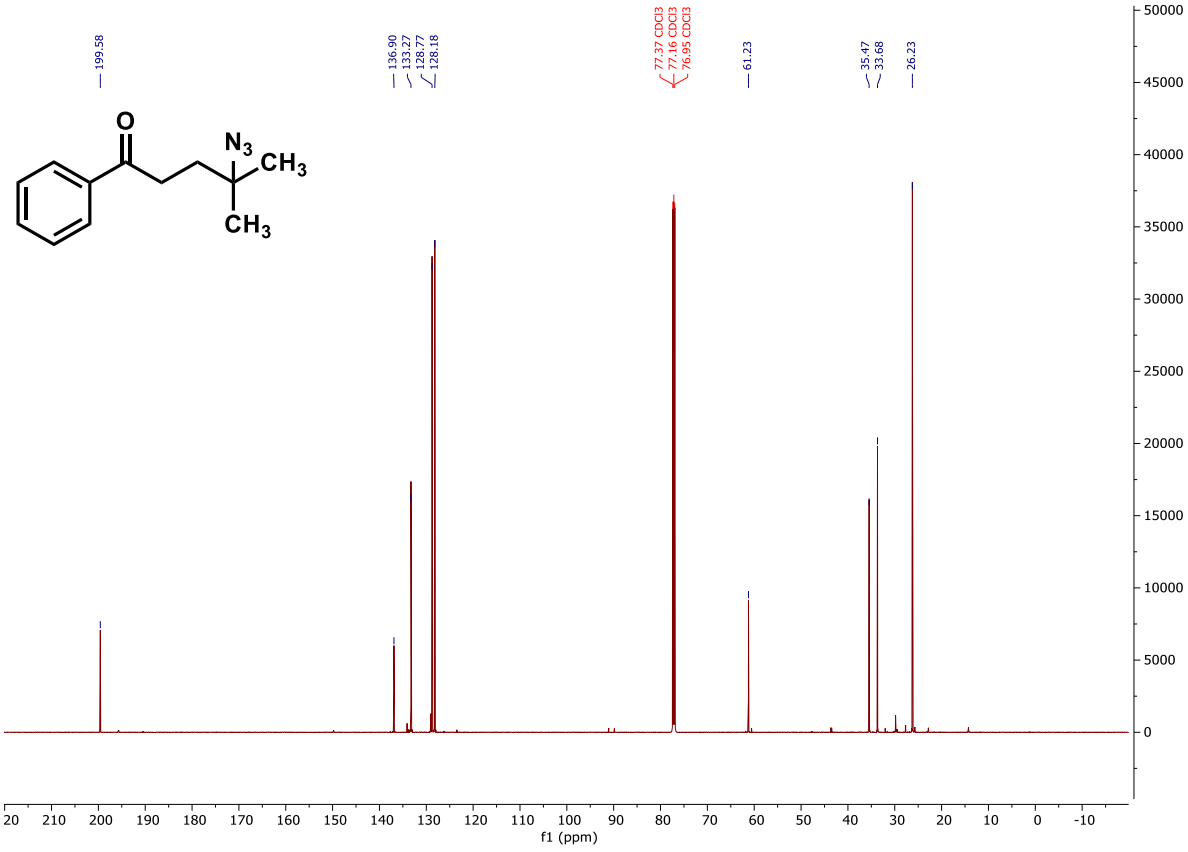

7.260 CDCl3
f1 (ppm)

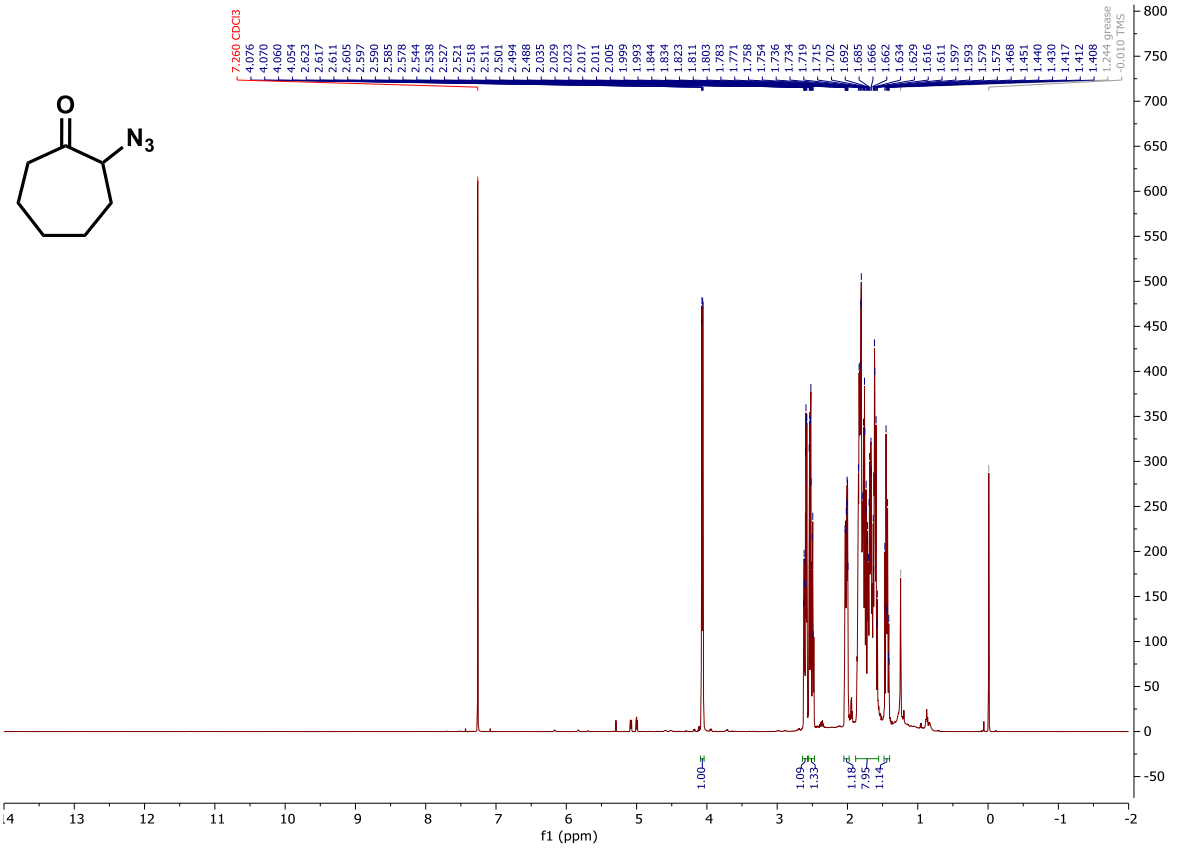

77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
f1 (ppm)

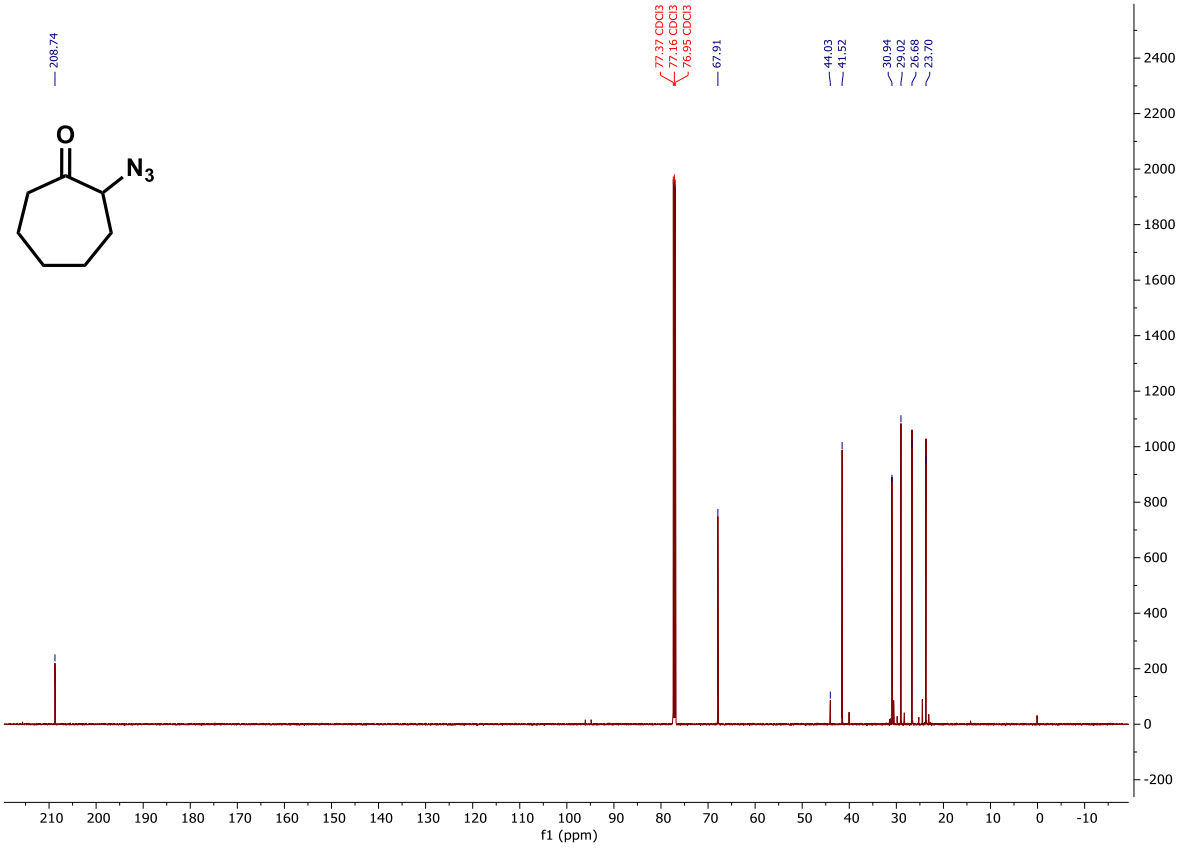

8.049
8.047
8.035
8.033
7.565
7.563
7.561
7.553
7.551
7.548
7.540
7.538
7.536
7.451
7.448
7.438
7.428
7.425
7.260 CDCl3
5.170
5.159
5.151
5.149
5.147
5.141
5.138
5.136
5.128
5.118
1.837
1.830
1.825
1.817
1.815
1.809
1.807
1.804
1.802
1.797
1.794
1.787
1.782
1.774
1.748
1.740
1.732
1.727
1.725
1.720
1.717
1.712
1.709
1.705
1.697
1.689
1.650
1.642
1.630
1.627
1.622
1.620
1.607
1.600
1.564
1.556
1.543
1.541
1.536
1.534
1.521
1.513
1.369
1.359
1.275
O
CH3
N3
CH3
O
CH3
2.13
1.11
2.26
1.00
1.10
1.23
1.10
1.09
3.12
5.99
f1 (ppm)

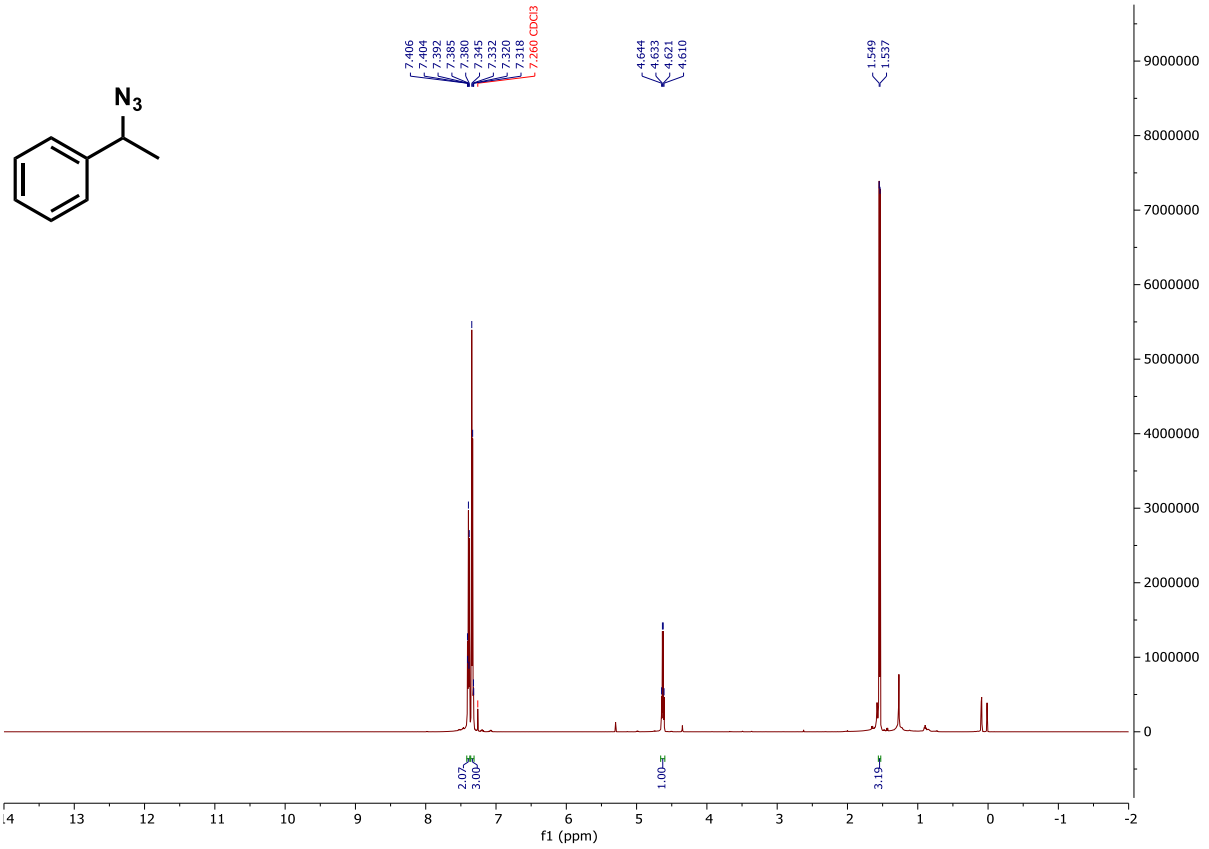

166.23
132.94
130.74
129.63
128.43
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
71.56
61.28
37.17
30.88
26.16
26.04
20.22
O
CH3
N3
CH3
O
CH3
f1 (ppm)

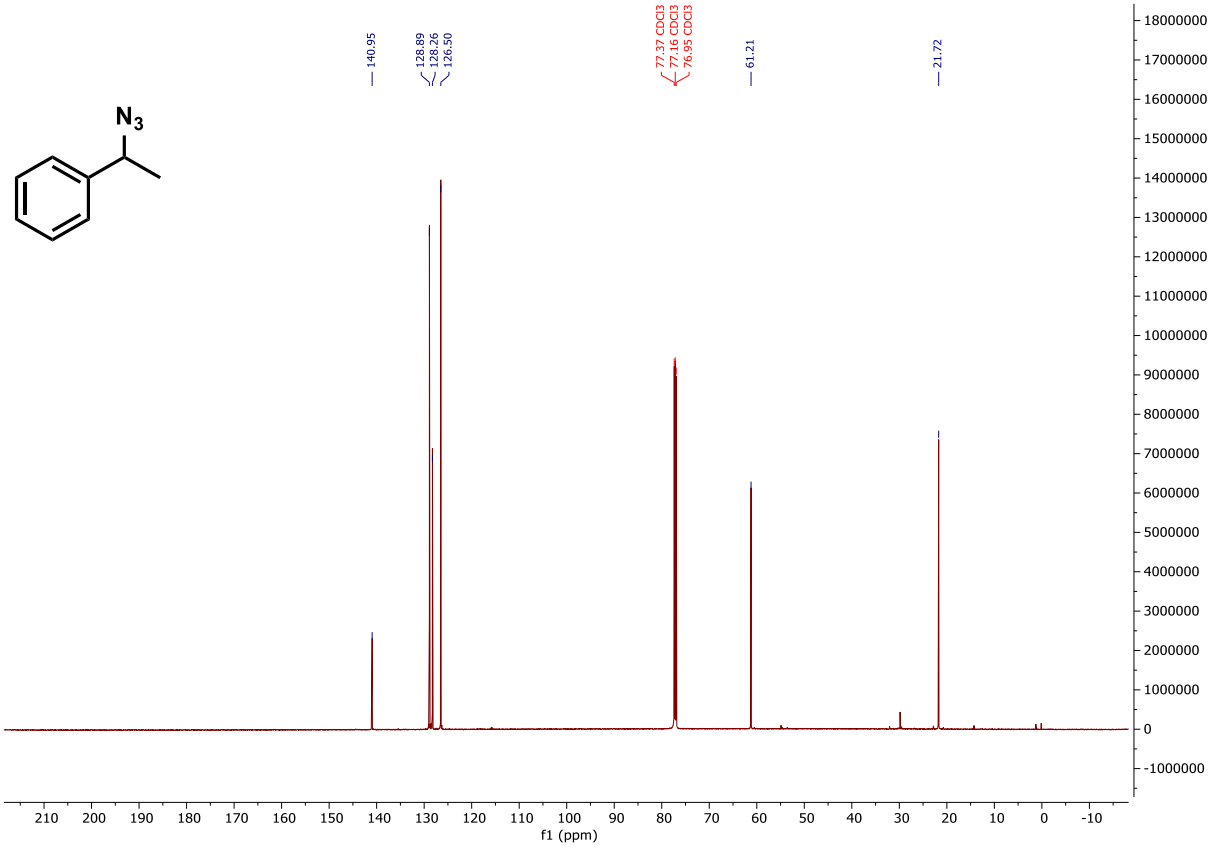

7.985
7.983
7.972
7.969
7.581
7.569
7.557
7.485
7.472
7.459
7.260 CDCl3
3.083
3.073
3.070
3.067
3.057
1.960
1.950
1.947
1.945
1.934
1.340
O
N3
CH3
CH3
2.02
0.98
1.98
2.00
2.02
6.10
f1 (ppm)

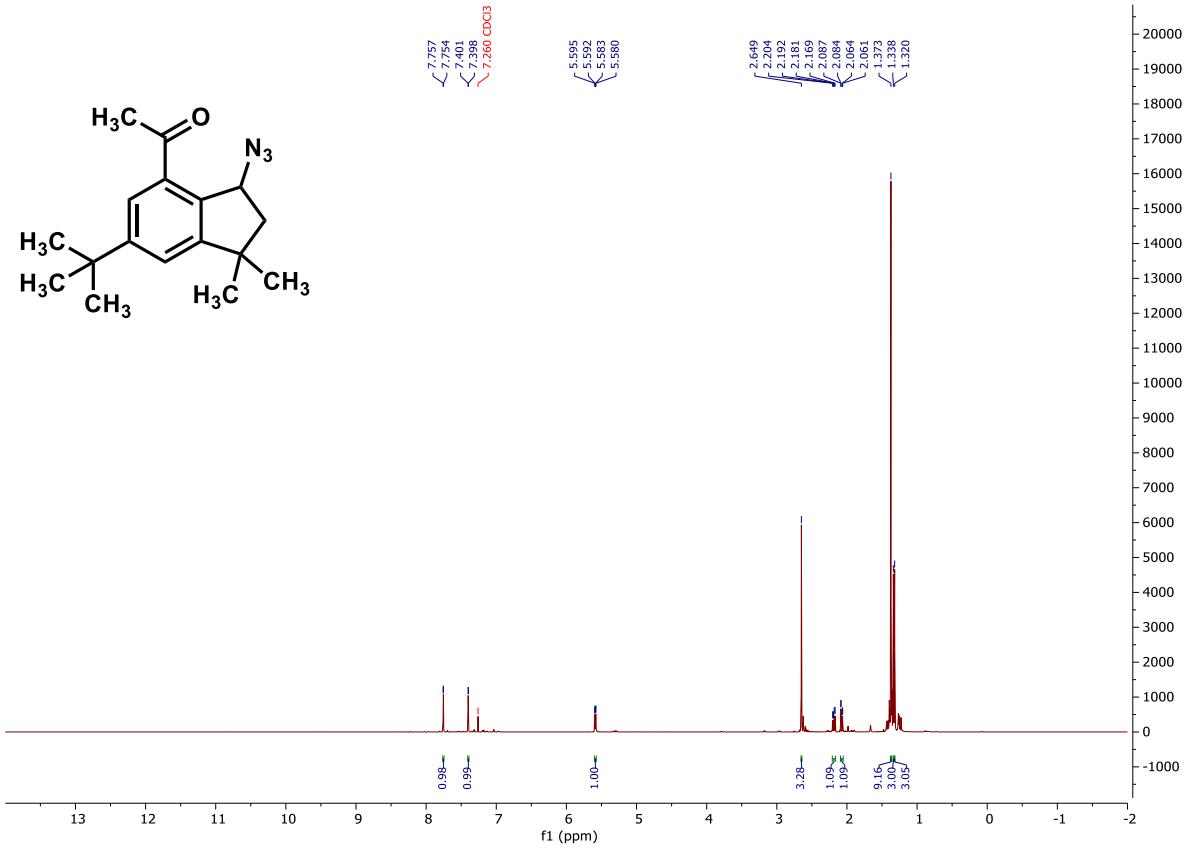

199.58
136.90
133.27
128.77
128.18
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
61.23
35.47
33.68
26.23
O
N3
CH3
CH3
f1 (ppm)

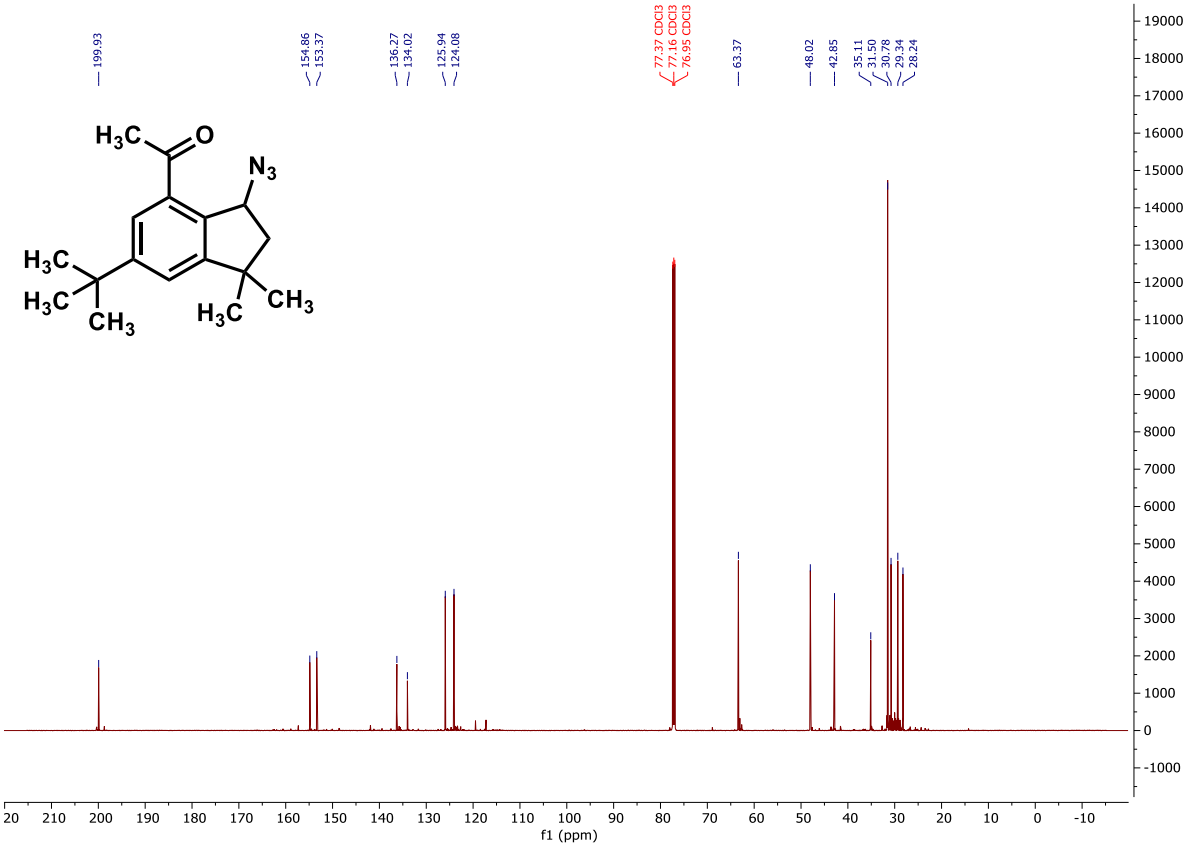

O
N3
7.260 CDCl3
1.244 grease
0.010 TMS
1.00
1.09
1.33
1.18
7.95
1.14
f1 (ppm)

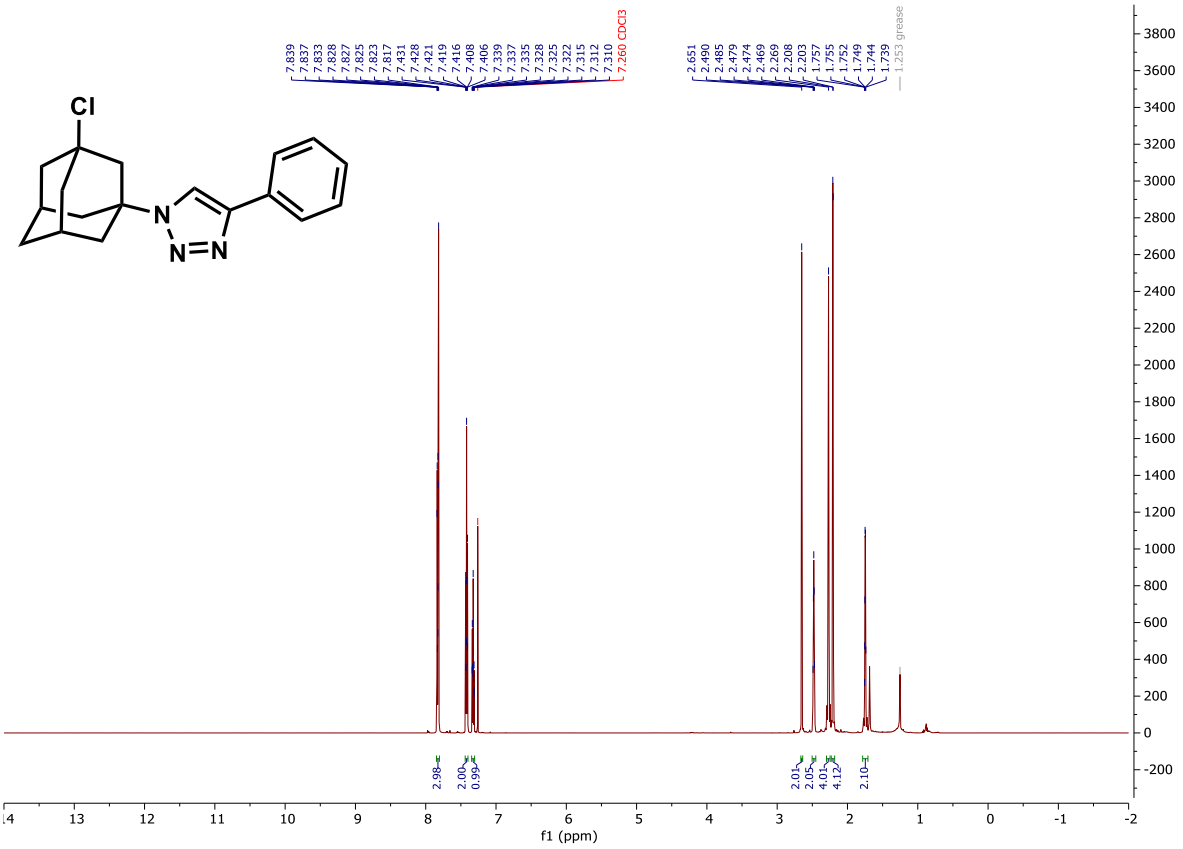

O
N3
208.74
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
67.91
44.03
41.52
30.94
29.02
26.68
23.70
f1 (ppm)


N3
7.406
7.404
7.392
7.385
7.380
7.345
7.332
7.320
7.318
7.260 CDCl3
4.644
4.633
4.621
4.610
1.549
1.537
2.07
3.00
1.00
3.19
f1 (ppm)


N3
140.95
128.89
128.26
126.50
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
61.21
21.72
f1 (ppm)


7.757
7.754
7.401
7.398
7.260 CDCl3
5.595
5.592
5.583
5.580
2.649
2.204
2.192
2.181
2.169
2.087
2.084
2.064
2.061
1.373
1.338
1.320
0.98
0.99
1.00
3.28
1.09
1.09
9.16
3.00
3.05
f1 (ppm)


199.93
154.86
153.37
136.27
134.02
125.94
124.08
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
63.37
48.02
42.85
35.11
31.50
30.78
29.34
28.24
f1 (ppm)


Cl
N
N=N
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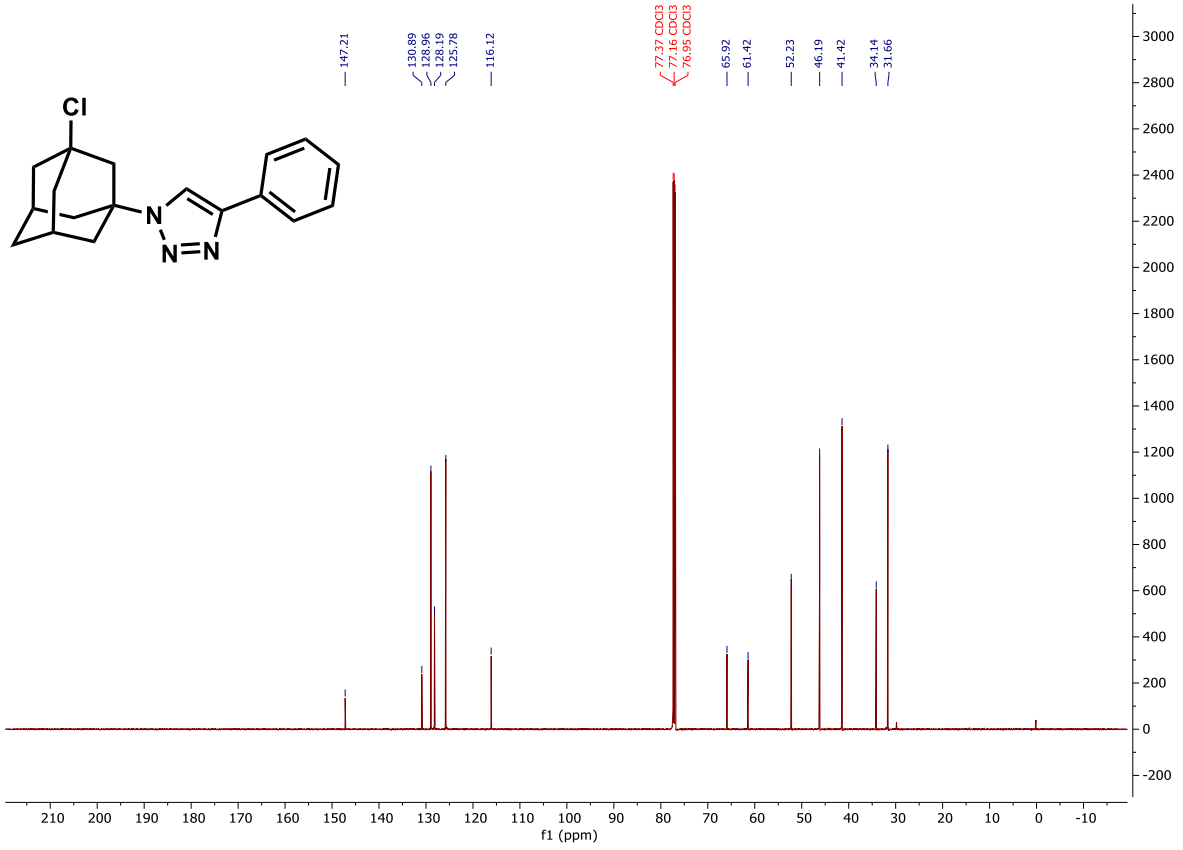
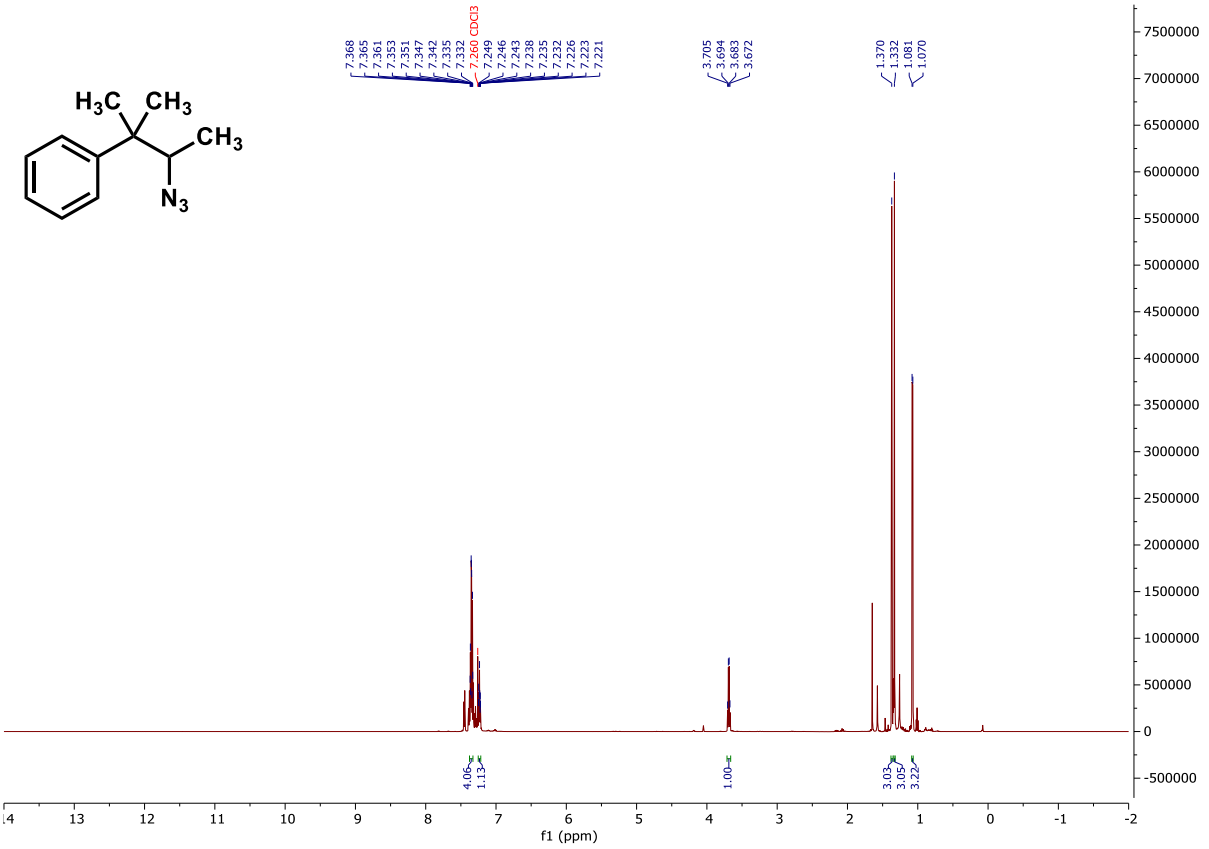
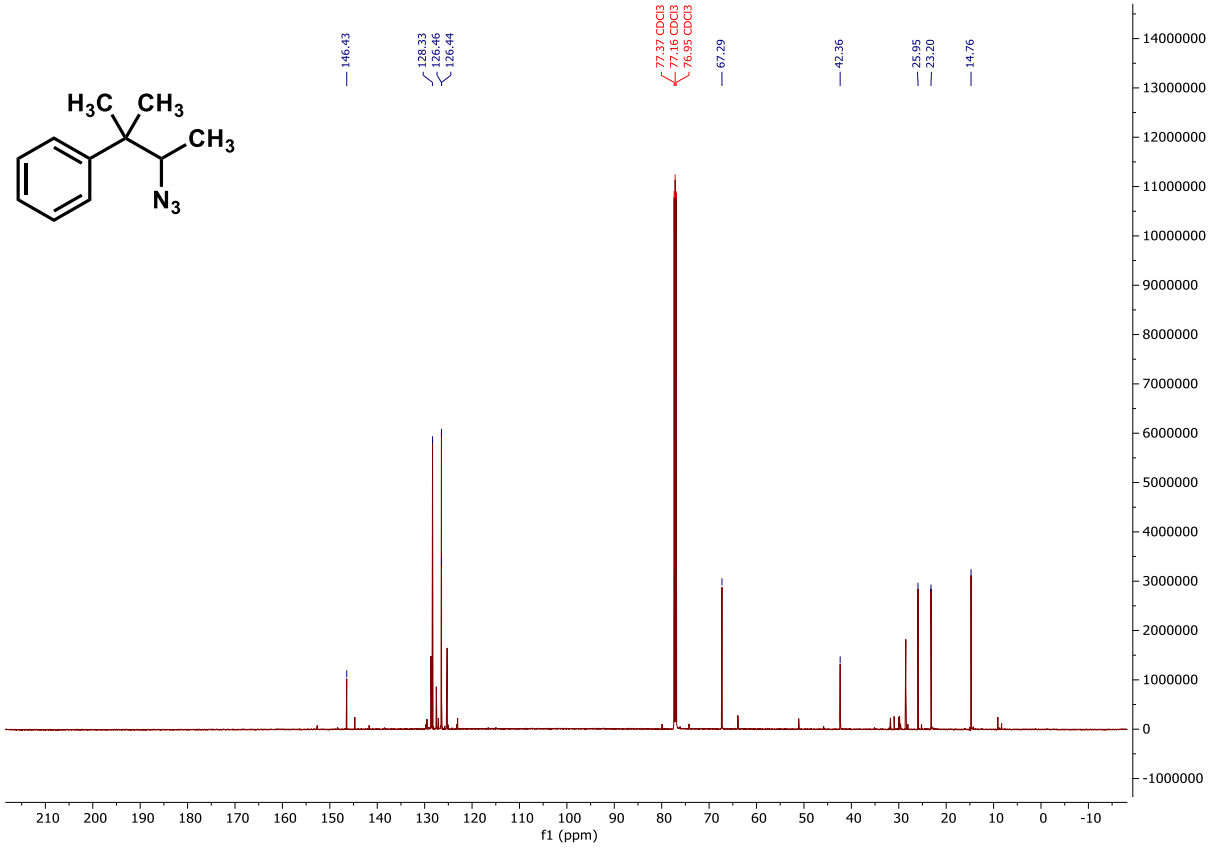
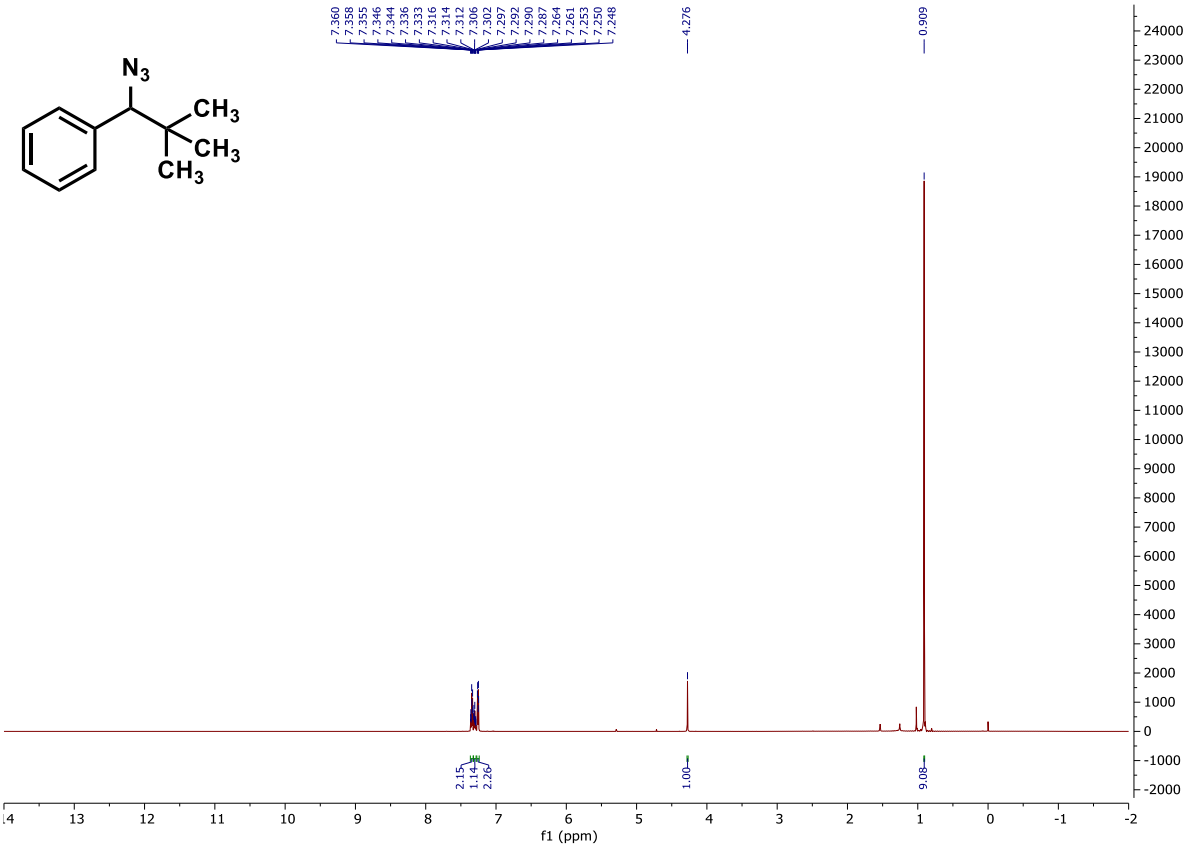
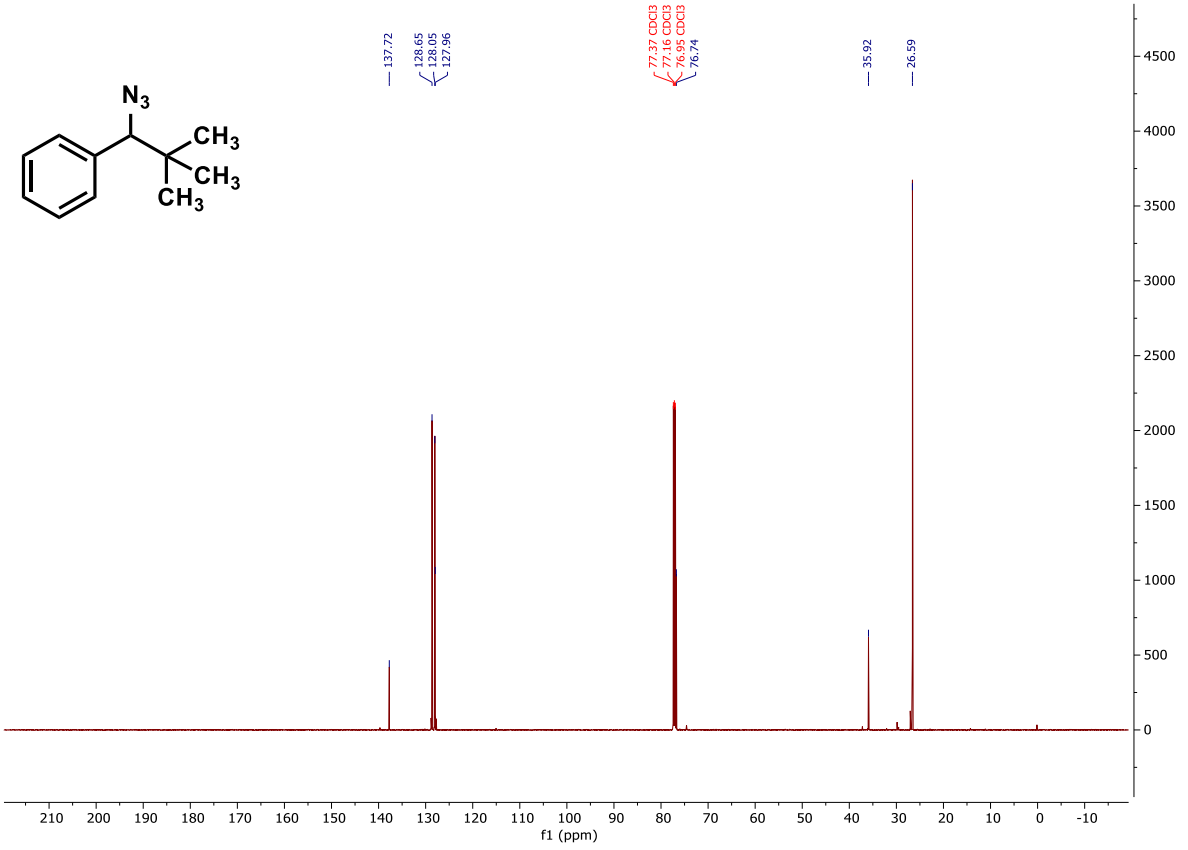
7.837
7.833
7.828
7.827
7.825
7.823
7.817
7.431
7.428
7.421
7.419
7.416
7.408
7.406
7.339
7.337
7.335
7.328
7.325
7.322
7.315
7.312
7.310
7.260 CDCl3
2.651
2.490
2.485
2.479
2.474
2.469
2.269
2.208
2.203
1.757
1.755
1.752
1.749
1.744
1.739
1.253 grease
2.98
2.00
0.99
2.01
2.05
4.01
4.12
2.10
f1 (ppm)


Cl
N
N=N
147.21
130.89
128.96
128.19
125.78
116.12
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
65.92
61.42
52.23
46.19
41.42
34.14
31.66
f1 (ppm)


7.368
7.365
7.361
7.353
7.351
7.347
7.342
7.335
7.332
7.260 CDCl3
7.249
7.246
7.243
7.238
7.235
7.232
7.226
7.223
7.221
3.705
3.694
3.683
3.672
1.370
1.332
1.091
1.070
4.06
1.13
1.00
3.03
3.05
3.22
f1 (ppm)


146.43
128.33
126.46
126.44
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
67.29
42.36
25.95
23.20
14.76
f1 (ppm)


N3
CH3
CH3
CH3
7.360
7.358
7.355
7.346
7.344
7.336
7.333
7.316
7.314
7.312
7.306
7.302
7.297
7.292
7.290
7.287
7.264
7.261
7.253
7.250
7.248
4.276
0.909
2.15
1.14
2.26
1.00
9.08
f1 (ppm)


N3
CH3
CH3
CH3
137.72
128.65
128.05
127.96
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
76.74
35.92
26.59
f1 (ppm)

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