

## *Supporting Information*

# **Mangana(III/IV)electro-Catalyzed C(sp<sup>3</sup>)–H Azidation**

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## General Remarks

Electrocatalytic reactions were carried out under an atmosphere of nitrogen, in undivided electrochemical cells (10 mL) using pre-dried glassware, unless stated otherwise. Acetonitrile was dried and distilled over activated 3 Å molecular sieve. Glacial acetic acid was used without further purification. All solvents were degassed using freeze-pump-thaw method. For flash chromatography technical grade solvents were used, which were distilled prior to use. Substrates **1d**,<sup>[1]</sup> **1e**,<sup>[2]</sup> **1f**,<sup>[3]</sup> **1g**,<sup>[4]</sup> **1n**,<sup>[5]</sup> **1p**,<sup>[6]</sup> **1r**,<sup>[7]</sup> **1s**,<sup>[8]</sup> Methyl 4'-hexyl-[1,1'-biphenyl]-4-carboxylate **5a**,<sup>[9]</sup> ibuprofen methyl ester **5b**,<sup>[10]</sup> menthol acetate **5d**,<sup>[11]</sup> estrone acetate **5e**,<sup>[9]</sup> salen<sup>[12]</sup> and porphyrin ligands,<sup>[13]</sup> as well as the corresponding manganese complexes<sup>[13a, 12c]</sup> were synthesized according to previously described methods. Other substrates were obtained from commercial sources and used without further purification. Platinum electrodes (10 mm × 15 mm × 0.125 mm, 99.9%, obtained from ChemPur® Karlsruhe, Germany) and graphite felt electrodes (10 mm × 15 mm × 6 mm, SIGRACELL®GFA 6 EA, obtained from SGL Carbon) were connected using stainless steel adapters, following the recently published protocol.<sup>[14]</sup> Electrocatalysis was conducted using an AXIOMET AX-3003P potentiostat in constant current (CCE) mode; CV studies were performed using a Metrohm Autolab PGSTAT204 workstation and Nova 2.1 software. Yields refer to isolated compounds, estimated to be >95% pure as determined by <sup>1</sup>H-NMR spectroscopy and GC-MS. Chromatography: Preparative chromatographic separations were carried out on Merck Geduran SI 60 (40–63 µm, 70–230 mesh ASTM) silica gel. The silica gel was neutralized with Et<sub>3</sub>N prior to use. The solvents were used as indicated as eluent with 0.3–0.5 bar pressure. TLC: Analytical thin layer chromatography (TLC) was performed on TLC Silica gel 60 F<sub>254</sub> from Merck with visualization under UV light at 254 nm or permanganate stain. GC: Gas chromatographic analysis (GC) was performed on an Agilent 7890A GC System or Agilent 7890B GC System equipped with a flame-ionization detector (FID) using hydrogen as the carrier gas. Gas-chromatography coupled with mass-spectrometry (GC-MS) was performed on the same instrument coupled with Agilent 5875C Triple-Axis-Detector or Agilent 5977B MSD. Mass spectra were obtained with electron-ionization (EI) at 70 eV in positive ion mode. NMR: Spectra were recorded on a Bruker *Avance III 300*, Bruker *Avance III HD 400* and Bruker *Avance III HD 500* in the solvent indicated; chemical shifts ( $\delta$ ) are given in ppm relative to the residual solvent peak. All IR spectra were recorded on a Bruker *FT-IR Alpha* device. MS: EI-MS were recorded with Finnigan *MAT 95*, 70 eV and Finnigan *LCQ*; High resolution mass spectrometry (HR-MS) with *APEX IV 7T FTICR*; ESI-MS were recorded with Bruker

*Daltonics maXis* (ESI-QTOF-MS), Bruker Daltonics *micrOTOF* (ESI-TOF-MS) or Thermo Scientific *LTQ Orbitrap XL* (ESI-Orbitrap-MS). M. p.: Stuart melting point apparatus *SMP3*, Barloworld Scientific, values are uncorrected. UV–vis: Ultraviolet–visible spectroscopy was performed on a Jasco *V-770* UV–vis/NIR spectrophotometer. Elemental analysis: Elemental analyses were performed on a *4.1 vario EL 3* from Elementar.

**Caution: Experimentation with Organic Azides<sup>[15]</sup>**

Special safety consideration should be taken for any experimentation with organic azide compounds as they can be considered as often toxic and potentially explosive chemicals that can decompose under external impact such as heat, pressure, shock. For safety, thus all reactions and processing steps involving azides were carried out behind a blast shield. Recommended storage of organic azides is below room temperature and away from light sources. As a recommended rule of thumb, azide compounds fulfilling equation (1) are generally stable.

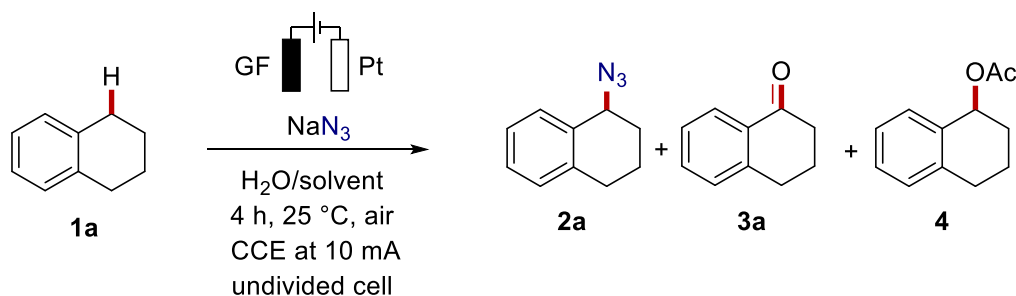
$$(1) \quad \frac{(N_{\text{Carbon}} + N_{\text{Oxygen}})}{N_{\text{Nitrogen}}} \geq 3$$

Azide compounds with a ratio of 1–3 can be isolated but should be stored in small amounts of less than 5 grams and in diluted concentrations. Special care should be taken for the mixture of azides with strong acids as highly toxic and explosive hydrazoic acid can be generated. Solutions of sodium azide can react with halogenated solvents and extremely explosive organic azides with a ratio <1 can be generated such as diazidomethane.<sup>[16]</sup> The azide waste formed during the following procedures was separated, collected and diluted to aqueous solutions of less than 5% sodium azide and treated with freshly prepared nitrous acid.<sup>[17]</sup>

## General Procedure for Metal-Free Electro C(sp<sup>3</sup>)-H Azidations

The electrocatalysis was carried out in an undivided cell, with a graphite felt anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.125 mm). An aqueous solution of sodium azide (2.0 mL, 2.0 M), AcOH (2.0 mL), and 1,2,3,4-tetrahydronaphthalene **1a** (66.1 mg, 0.50 mmol) were placed in a 10 mL cell. The reaction mixture was stirred at 400 rpm. The electrodes were connected and electrolysis was performed at 25 °C with a constant current of 10 mA maintained for 4 h (2.98 F/mol). At ambient temperature, the reaction mixture was quenched with sat. aq. NaHCO<sub>3</sub> (20 mL) and EtOAc (10 mL) was added, and the graphite felt anode was washed with EtOAc (3 × 5 mL) in an ultrasonic bath. The separated aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvents were removed *in vacuo*. The crude product mixture was purified by column chromatography.

**Table S-1:** Optimization of the Reaction Conditions for Metal-Free Electro C(sp<sup>3</sup>)-H Azidations.<sup>[a]</sup>

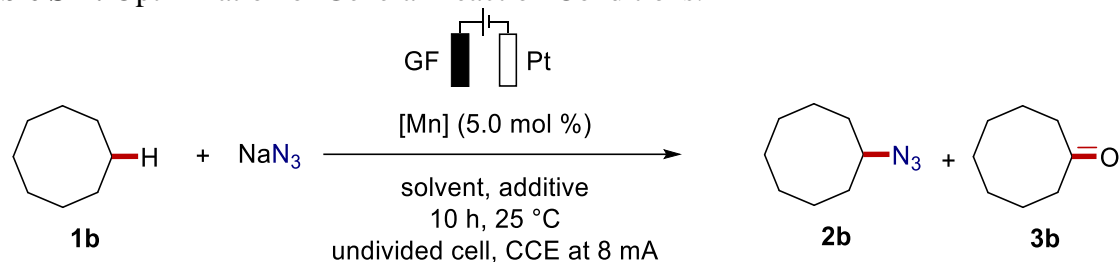


Entry	Solvent	Yield [%] <b>2a/3a/4</b>	Yield <b>1a</b> [%]
1	AcOH	15/48/25	13
2	EtOAc	1/1/0	92
3	MeOH	0/4/0	69
4	MeCN	6/32/0	33
5	CF <sub>3</sub> CH <sub>2</sub> OH	5/4/0	62
6 <sup>[b]</sup>	AcOH	20/28/3	30

[a] Reaction conditions: **1a** (0.50 mmol), aq. NaN<sub>3</sub> (2.0 mL, 2.0 M), additive (1.00 equiv.), solvent (2 mL), 4 h, CCE = 10 mA, 25 °C. Undivided cell, graphite felt (GF) anode and platinum plate cathode. Yields and ratios were determined by gas chromatography (GC-FID) with *n*-dodecane as internal standard. Calibrations were conducted with authentic samples and compared with <sup>1</sup>H-NMR spectroscopy, using 1,3,5-trimethoxybenzene as internal standard, and isolated yields, respectively. [b] Reticulated vitreous carbon (RVC) instead of GF.

## Optimization of the Reaction Conditions

**Table S-2:** Optimization of General Reaction Conditions.<sup>[a]</sup>



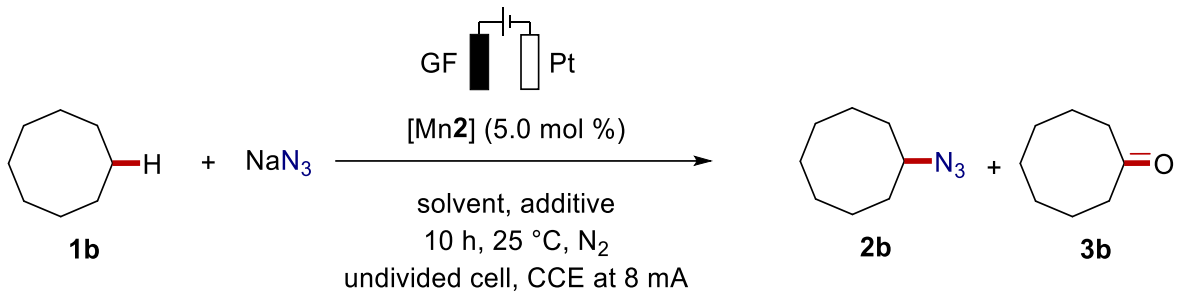
**[Mn1]**

$\text{R}^1 = \text{H}; \text{R}^2 = \text{Ph}: [\text{Mn2}]$   
 $\text{R}^1 = \text{R}^2 = \text{H}: [\text{Mn3}]$   
 $\text{R}^1 = t\text{-Bu}; \text{R}^2 = \text{H}: [\text{Mn4}]$   
 $\text{R}^1 = t\text{-Bu}; \text{R}^2 = \text{Ph}: [\text{Mn5}]$

Entry	[Mn]	Solvent	Additive (equiv.)	Yield [%]	
				Ratio <b>2b/3b</b>	<b>1b</b>
1 <sup>[b]</sup>	[Mn1]	AcOH/H <sub>2</sub> O	PhI (0.2)	25 (2.6:1.0)	63
2 <sup>[b]</sup>	[Mn2]	AcOH/H <sub>2</sub> O	PhI (0.2)	33 (2.0:1.0)	55
3 <sup>[b]</sup>	[Mn2]	AcOH/H <sub>2</sub> O	---	30 (2.8:1.0)	59
4 <sup>[b]</sup>	[Mn2]	AcOH/MeCN	LiClO <sub>4</sub> (1.0)	31 (5.2:1.0)	57
5 <sup>[c]</sup>	[Mn2]	AcOH/MeCN	LiClO <sub>4</sub> (1.0)	43 (3.3:1.0)	28
6 <sup>[c,d]</sup>	[Mn2]	AcOH/MeCN	LiClO <sub>4</sub> (1.0)	40 (12.3:1.0)	44
7 <sup>[d]</sup>	[Mn2]	AcOH/MeCN	LiClO <sub>4</sub> (1.0)	45 (10.0:1.0)	30
8 <sup>[d,e]</sup>	[Mn2]	AcOH/MeCN	LiClO <sub>4</sub> (1.0)	30 (1.0:1.0)	4
9 <sup>[d,f]</sup>	[Mn2]	AcOH/MeCN	LiClO <sub>4</sub> (1.0)	42 (9.5:1.0)	35
10 <sup>[d,g]</sup>	[Mn2]	AcOH/MeCN	LiClO <sub>4</sub> (1.0)	42 (10.0:1.0)	32
11 <sup>[d,h]</sup>	[Mn2]	AcOH/MeCN	LiClO <sub>4</sub> (1.0)	46 (5.6:1.0)	36
12 <sup>[d]</sup>	[Mn1]	AcOH/MeCN	LiClO <sub>4</sub> (1.0)	44 (1.6:1.0)	14
13 <sup>[d]</sup>	[Mn3]	AcOH/MeCN	LiClO <sub>4</sub> (1.0)	10 (4.0:1.0)	90
14 <sup>[d]</sup>	[Mn4]	AcOH/MeCN	LiClO <sub>4</sub> (1.0)	39 (12.0:1.0)	53
15 <sup>[d]</sup>	[Mn5]	AcOH/MeCN	LiClO <sub>4</sub> (1.0)	47 (8.4:1.0)	38
16 <sup>[d,i]</sup>	[Mn6]	AcOH/MeCN	LiClO <sub>4</sub> (1.0)	32 (9.7:1.0)	62
17 <sup>[d]</sup>	---	AcOH/MeCN	LiClO <sub>4</sub> (1.0)	10 (2.0:1.0)	51

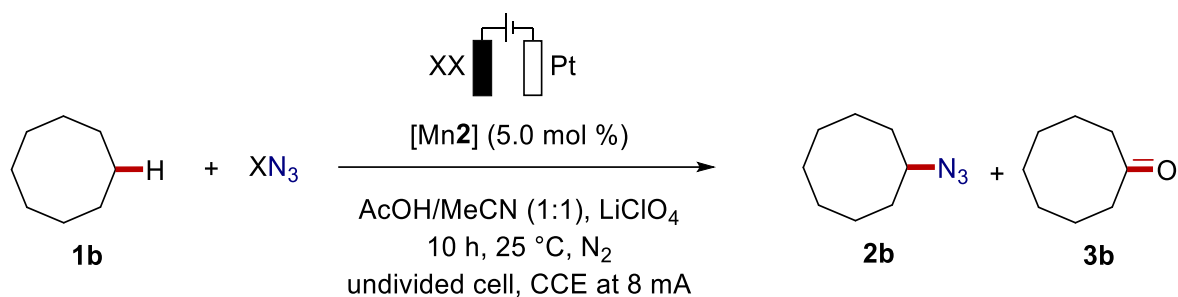
[a] Reaction conditions: **1b** (0.50 mmol), NaN<sub>3</sub> (4.00 mmol, 8.00 equiv.), [Mn] (5.0 mol %), additive (xx equiv.), solvent (1:1, 5.0 mL), 10 h, CCE = 8 mA, 25 °C. Undivided cell, graphite felt (GF) anode and platinum plate cathode. Yields and ratios were determined by gas chromatography (GC-FID) with *n*-dodecane as internal standard. Calibrations were conducted with authentic samples and compared with <sup>1</sup>H-NMR spectroscopy, using 1,3,5-trimethoxybenzene as internal standard, and isolated yields, respectively. [b] 5 h, 6 mA. [c] 10 h, 6 mA. [d] under nitrogen atmosphere. [e] Light irradiation with blue LEDs. [f] 50 °C. [g] reaction was performed in dark. [h] [Mn2] (2.5 mol %). [i] [Mn6] = (*S,S*)-Jacobsen's catalyst.

**Table S-3:** Optimization of Solvents.<sup>[a]</sup>



Entry	Solvent	Additive (equiv.)	Yield [%]	
			Ratio <b>2b/3b</b>	<b>1b</b>
1	AcOH/MeCN	LiClO <sub>4</sub> (1.0)	45 (10.0:1.0)	30
2 <sup>[b]</sup>	AcOH/MeCN	LiClO <sub>4</sub> (1.0)	31 (30.0:1.0)	60
3	AcOH/H <sub>2</sub> O	---	25 (2.1:1.0)	57
4	MeCN/H <sub>2</sub> O	---	17 (7.5:1.0)	72
5	MeOH/H <sub>2</sub> O	---	4 (1.0:1.0)	96
6 <sup>[c]</sup>	AcOH/Acetone	LiClO <sub>4</sub> (1.0)	24 (12.0:1.0)	74
7 <sup>[c]</sup>	AcOH/EtOAc	LiClO <sub>4</sub> (1.0)	4 (3.0:1.0)	94
8 <sup>[c]</sup>	AcOH/MeNO <sub>2</sub>	LiClO <sub>4</sub> (1.0)	21 (9.0:1.0)	71
9 <sup>[d]</sup>	EtOAc/H <sub>2</sub> O	---	1 (0:1.0)	99

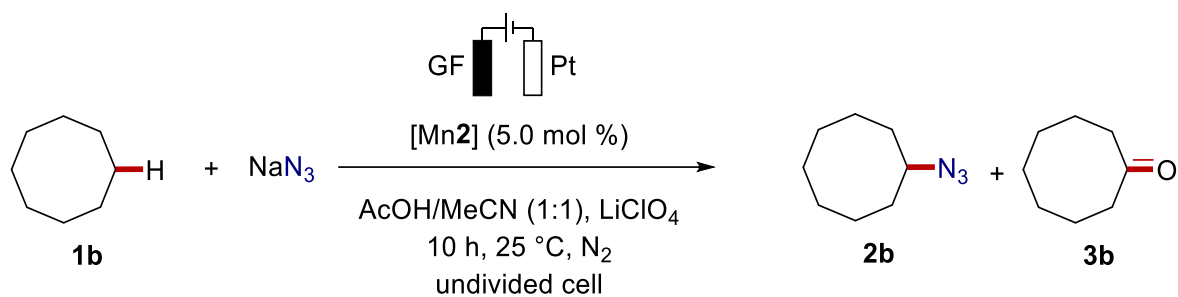
[a] Reaction conditions: **1b** (0.50 mmol), NaN<sub>3</sub> (4.00 mmol, 8.00 equiv.), [Mn2] (5.0 mol %), additive (xx equiv.), solvent (1:1, 5.0 mL), 10 h, CCE = 8 mA, 25 °C. Undivided cell, graphite felt (GF) anode and platinum plate cathode. Yields and ratios were determined by gas chromatography (GC-FID) with *n*-dodecane as internal standard. Calibrations were conducted with authentic samples and compared with <sup>1</sup>H-NMR spectroscopy, using 1,3,5-trimethoxybenzene as internal standard, and isolated yields, respectively. [b] MeCN/AcOH (3:1). [c] 10 h, CPE = 2.0 V. [d] [Mn1] instead of [Mn2].

**Table S-4:** Optimization of Electrode Material and Azide Source.<sup>[a]</sup>

Entry	XN <sub>3</sub> (equiv.)	Anode XX	Yield [%]	
			Ratio <b>2b/3b</b>	<b>1b</b>
1	NaN <sub>3</sub> (8.0)	GF	45 (10.0:1.0)	30
2	NaN <sub>3</sub> (4.0)	GF	35 (4.8:1.0)	33
3	KN <sub>3</sub> (8.0)	GF	44 (5.3:1.0)	31
4	TMSN <sub>3</sub> (4.0)	GF	30 (8.0:1.0)	13
5	4-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> N <sub>3</sub> (2.0)	GF	0	96
6	TsN <sub>3</sub> (4.0)	GF	0	75
7	NaN <sub>3</sub> (8.0)	GC	6 (1.0:0.0)	89
8	NaN <sub>3</sub> (8.0)	RVC	15 (6.5:1.0)	77
9	NaN <sub>3</sub> (8.0)	graphite	19 (1.0:0.0)	71
10	NaN <sub>3</sub> (8.0)	Pt	0	99

[a] Reaction conditions: **1b** (0.50 mmol), XN<sub>3</sub> (xx equiv.), [Mn2] (5.0 mol %), LiClO<sub>4</sub> (1.0 equiv.), AcOH/MeCN (1:1, 5.0 mL), 10 h, CCE = 8 mA, 25 °C. Undivided cell, anode XX and platinum plate cathode. Glassy carbon (GC). Reticulated vitreous carbon (RVC). Yields and ratios were determined by gas chromatography (GC-FID) with *n*-dodecane as internal standard. Calibrations were conducted with authentic samples and compared with <sup>1</sup>H-NMR spectroscopy, using 1,3,5-trimethoxybenzene as internal standard, and isolated yields, respectively.



**Table S-5:** Optimization of Current or Potential.<sup>[a]</sup>

Entry	Mode of Electrolysis	Yield [%]	
		Ratio <b>2b/3b</b>	<b>1b</b>
1	CCE at 8.0 mA	45 (10.0:1.0)	30
2	No current	0	91
3	No current, under air	0	90
4 <sup>[b]</sup>	CCE at 4.0 mA	44 (6.3:1.0)	27
5	CCE at 6.0 mA	43 (3.3:1.0)	20
6	CCE at 10.0 mA	26 (2.6:1.0)	6
7	CPE at 1.0 V	0	99
8	CPE at 1.5 V	11 (10.0:1.0)	85
9	CPE at 2.0 V	37 (6.4:1.0)	49
10 <sup>[c]</sup>	CPE at 2.0 V	23 (1.0:1.0)	55
11	CPE at 2.5 V	44 (5.3:1.0)	26

[a] Reaction conditions: **1b** (0.50 mmol),  $\text{NaN}_3$  (8.0 equiv.),  $[\text{Mn}2]$  (5.0 mol %),  $\text{LiClO}_4$  (1.0 equiv.),  $\text{AcOH/MeCN}$  (1:1, 5.0 mL), 10 h, 25 °C. Undivided cell, GF anode and Pt plate cathode. Yields and ratios were determined by gas chromatography (GC-FID) with *n*-dodecane as internal standard. Calibrations were conducted with authentic samples and compared with  $^1\text{H-NMR}$  spectroscopy, using 1,3,5-trimethoxybenzene as internal standard, and isolated yields, respectively. [b] 15 h. [c] 20 h.

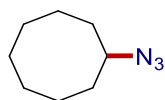
### General Procedure A for Manganaelectro-Catalyzed C(sp<sup>3</sup>)-H Azidations

The electrocatalysis was carried out in an undivided cell, with a graphite felt anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.125 mm). The manganese catalyst [Mn<sup>2+</sup>] (12.7 mg, 25.0 μmol, 5.0 mol %), sodium azide (260 mg, 4.00 mmol, 8.00 equiv.), substrate **1** or **5** (0.50 mmol, 1.00 equiv.) and LiClO<sub>4</sub> (53.2 mg, 0.50 mmol, 1.00 equiv.) were placed in a 10 mL cell under nitrogen atmosphere. The reaction components were dissolved in MeCN (2.5 mL), followed by AcOH (2.5 mL) and the reaction mixture was stirred at 400 rpm. The electrodes were connected under vigorous nitrogen-flow. Electrolysis was performed at 25 °C with a constant current of 8 mA maintained for 10 h (5.97 F/mol). At ambient temperature, the reaction mixture was quenched with sat. aq. NaHCO<sub>3</sub> (20 mL) and EtOAc (10 mL) was added, and the graphite felt anode was washed with EtOAc (3 × 5 mL) in an ultrasonic bath. The combined mixture was washed with H<sub>2</sub>O (3 × 10 mL), and then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvents were removed *in vacuo*. The crude product mixture was purified by column chromatography.

### General Procedure B for Manganaelectro-Catalyzed C(sp<sup>3</sup>)-H Azidations

The electrocatalysis was carried out in an undivided cell, with a graphite felt anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.125 mm). The manganese catalyst [Mn<sup>2+</sup>] (6.4 mg, 12.5 μmol, 2.5 mol %), sodium azide (260 mg, 4.00 mmol, 8.00 equiv.), substrate **1** or **5** (0.50 mmol, 1.00 equiv.) and LiClO<sub>4</sub> (53.2 mg, 0.50 mmol, 1.00 equiv.) were placed in a 10 mL cell under nitrogen atmosphere. The reaction components were dissolved in MeCN (2.5 mL), followed by AcOH (2.5 mL) and the reaction mixture was stirred at 400 rpm. The electrodes were connected under vigorous nitrogen-flow. Electrolysis was performed at 25 °C with a constant current of 8 mA maintained for 10 h (5.97 F/mol). At ambient temperature, the reaction mixture was quenched with sat. aq. NaHCO<sub>3</sub> (20 mL) and EtOAc (10 mL) was added, and the graphite felt anode was washed with EtOAc (3 × 5 mL) in an ultrasonic bath. The combined mixture was washed with H<sub>2</sub>O (3 × 10 mL), and then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvents were removed *in vacuo*. The crude product mixture was purified by column chromatography.

## Characterization Data



### Azidocyclooctane (2b)

The general procedure **A** was followed using cyclooctane **1b** (56.1 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 99:1) yielded **2b** (30.8 mg, 201  $\mu$ mol, 40%) as a colorless liquid.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.64–3.51 (m, 1H), 1.94–1.84 (m, 2H), 1.79–1.67 (m, 4H), 1.61–1.48 (m, 8H).

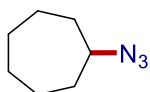
**<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 62.4 (CH), 31.0 (CH<sub>2</sub>), 27.4 (CH<sub>2</sub>), 25.3 (CH<sub>2</sub>), 23.3 (CH<sub>2</sub>).

**IR** (ATR):  $\tilde{\nu}$  = 2927, 2854, 2091, 1474, 1259, 1095, 940, 668 cm<sup>-1</sup>.

**MS** (EI) *m/z* (relative intensity): 125 (5) [M–N<sub>2</sub>]<sup>+</sup>, 110 (10), 96 (50), 82 (100), 67 (70), 55 (15).

**HR-MS** (EI) *m/z* calcd for C<sub>8</sub>H<sub>15</sub>N<sub>1</sub> [M–N<sub>2</sub>]<sup>+</sup>: 125.1204, found: 125.1200.

The analytical data corresponds with those reported in the literature.<sup>[18]</sup>



### Azidocycloheptane (2c)

The general procedure **A** was followed using cycloheptane **1c** (49.1 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 99:1) yielded **2c** (23.1 mg, 165  $\mu$ mol, 33%) as a colorless liquid.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.57–3.48 (m, 1H), 1.99–1.88 (m, 2H), 1.74–1.51 (m, 8H), 1.49–1.36 (m, 2H).

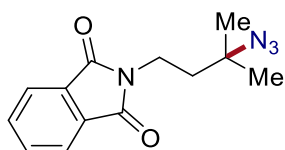
**<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 62.8 (CH), 33.9 (CH<sub>2</sub>), 28.0 (CH<sub>2</sub>), 23.6 (CH<sub>2</sub>).

**IR** (ATR):  $\tilde{\nu}$  = 2927, 2858, 2083, 1459, 1249, 958, 830, 560 cm<sup>-1</sup>.

**MS** (EI) *m/z* (relative intensity): 110 (15) [M–N<sub>2</sub>]<sup>+</sup>, 96 (25), 91 (5), 82 (100), 68 (40), 55 (55).

**HR-MS** (EI) *m/z* calcd for C<sub>7</sub>H<sub>13</sub>N<sub>1</sub> [M–N<sub>2</sub>]<sup>+</sup>: 111.1048, found: 111.1044.

The analytical data corresponds with those reported in the literature.<sup>[19]</sup>



### 2-(3-Azido-3-methylbutyl)isoindoline-1,3-dione (2d)

The general procedure **B** was followed using 2-isopentylisoindoline-1,3-dione **1d** (109 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 10:1) yielded **2d** (74.9 mg, 290  $\mu$ mol, 58%) as a colorless liquid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.83 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.1 Hz, 2H), 3.85–3.72 (m, 2H), 1.93–1.80 (m, 2H), 1.36 (s, 6H).

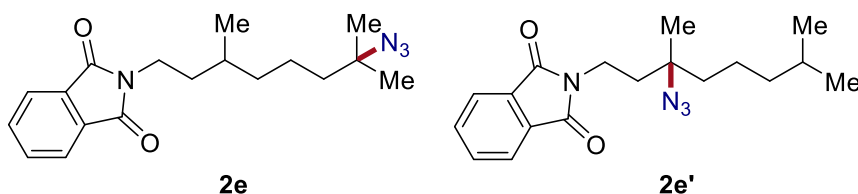
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 168.3 (C<sub>q</sub>), 134.1 (CH), 132.2 (C<sub>q</sub>), 123.4 (CH), 60.3 (C<sub>q</sub>), 39.3 (CH<sub>2</sub>), 33.9 (CH<sub>2</sub>), 26.1 (CH<sub>3</sub>).

IR (ATR):  $\tilde{\nu}$  = 2973, 2094, 1704, 1399, 1370, 1084, 1020, 716, 607, 530 cm<sup>-1</sup>.

MS (ESI) *m/z* (relative intensity): 539 (5) [2M+Na]<sup>+</sup>, 281 (100) [M+Na]<sup>+</sup>, 259 (2) [M+H]<sup>+</sup>, 216 (10) [M-N<sub>3</sub>]<sup>+</sup>.

HR-MS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>15</sub>N<sub>4</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 259.1190, found: 259.1189.

The analytical data corresponds with those reported in the literature.<sup>[20]</sup>



### 2-(7-Azido-3,7-dimethyloctyl)isoindoline-1,3-dione (**2e**)

The general procedure **B** was followed using 2-(3,7-dimethyloctyl)isoindoline-1,3-dione **1e** (144 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). The ratio of **2e/2e'** (3:1) was determined by <sup>1</sup>H-NMR spectroscopy of the crude reaction mixture. Purification by column chromatography on silica gel (*n*-hexane/EtOAc 10:1) yielded **2e/2e'** (65.7 mg, 200  $\mu$ mol, 40%) as a colorless liquid.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.83 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H), 3.70 (t, *J* = 7.4 Hz, 2H), 1.77–1.64 (m, 1H), 1.54–1.40 (m, 4H), 1.38–1.29 (m, 3H), 1.23 (s, 6H), 1.20–1.16 (m, 1H), 0.97 (d, *J* = 6.4 Hz, 3H).

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 168.5 (C<sub>q</sub>), 134.0 (CH), 132.3 (C<sub>q</sub>), 123.3 (CH), 61.8 (C<sub>q</sub>), 41.7 (CH<sub>2</sub>), 37.1 (CH<sub>2</sub>), 36.4 (CH<sub>2</sub>), 35.6 (CH<sub>2</sub>), 30.7 (CH), 26.1 (CH<sub>3</sub>), 26.1 (CH<sub>3</sub>), 21.6 (CH<sub>2</sub>), 19.4 (CH<sub>3</sub>).

IR (ATR):  $\tilde{\nu}$  = 2940, 2096, 1773, 1710, 1396, 1369, 1261, 1062, 719, 530 cm<sup>-1</sup>.

MS (ESI) *m/z* (relative intensity): 679 (30) [2M+Na]<sup>+</sup>, 351 (100) [M+Na]<sup>+</sup>, 329 (15) [M+H]<sup>+</sup>, 301 (75), 286 (70) [M-N<sub>3</sub>]<sup>+</sup>.

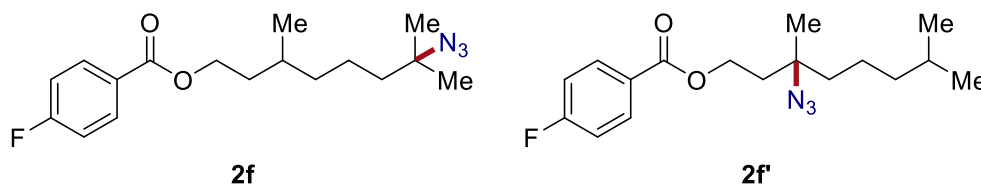
HR-MS (ESI) *m/z* calcd for C<sub>18</sub>H<sub>25</sub>N<sub>4</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 329.1972, found: 329.1969.

Minor isomer: 2-(3-Azido-3,7-dimethyloctyl)isoindoline-1,3-dione (**2e'**)

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.84 (dd,  $J$  = 5.4, 3.0 Hz, 2H), 7.71 (dd,  $J$  = 5.4, 3.0 Hz, 2H), 3.76 (d,  $J$  = 8.0 Hz, 2H), 1.96–1.74 (m, 2H), 1.60–1.48 (m, 3H), 1.43–1.35 (m, 2H), 1.35 (s, 3H), 1.23–1.16 (m, 2H), 0.88 (d,  $J$  = 6.6 Hz, 6H).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 168.3 (C<sub>q</sub>), 134.1 (CH), 132.3 (C<sub>q</sub>), 123.4 (CH), 63.0 (C<sub>q</sub>), 39.8 (CH<sub>2</sub>), 39.3 (CH<sub>2</sub>), 37.3 (CH<sub>2</sub>), 33.8 (CH<sub>2</sub>), 28.0 (CH), 23.4 (CH<sub>3</sub>), 22.7 (CH<sub>3</sub>), 22.7 (CH<sub>3</sub>), 21.8 (CH<sub>2</sub>).

The analytical data corresponds with those reported in the literature.<sup>[21]</sup>



### 7-azido-3,7-dimethyloctyl 4-fluorobenzoate (**2f**)

The general procedure **B** was followed using 3,7-dimethyloctyl 4-fluorobenzoate **1f** (140 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). The ratio of **2f/2f'** (5.5:1) was determined by <sup>1</sup>H-NMR spectroscopy of the crude reaction mixture. Purification by column chromatography on silica gel (*n*-hexane/EtOAc 25:1) yielded **2f/2f'** (57.9 mg, 180  $\mu$ mol, 36%) as a colorless liquid.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.05 (dd,  $J$  = 8.8, 5.4 Hz, 2H), 7.10 (dd,  $J$  = 8.8, 8.6 Hz, 2H), 4.43–4.25 (m, 2H), 1.83–1.77 (m, 1H), 1.68–1.53 (m, 2H), 1.49–1.30 (m, 5H), 1.25 (s, 6H), 1.23–1.14 (m, 1H), 0.97 (d,  $J$  = 6.4 Hz, 3H).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 165.9 (d, <sup>1</sup> $J_{C-F}$  = 253.6 Hz, C<sub>q</sub>), 165.8 (C<sub>q</sub>), 132.2 (d, <sup>3</sup> $J_{C-F}$  = 9.3 Hz, CH), 126.8 (d, <sup>4</sup> $J_{C-F}$  = 2.9 Hz, C<sub>q</sub>), 115.6 (d, <sup>2</sup> $J_{C-F}$  = 22.0 Hz, CH), 63.7 (CH<sub>2</sub>), 61.8 (C<sub>q</sub>), 41.8 (CH<sub>2</sub>), 37.2 (CH<sub>2</sub>), 35.7 (CH<sub>2</sub>), 30.1 (CH), 26.2 (CH<sub>3</sub>), 26.1 (CH<sub>3</sub>), 21.7 (CH<sub>2</sub>), 19.6 (CH<sub>3</sub>).

**<sup>19</sup>F-NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  = –105.9 to –106.0 (m).

**IR** (ATR):  $\tilde{\nu}$  = 2958, 2095, 1718, 1603, 1508, 1153, 1111, 854, 767, 609 cm<sup>-1</sup>.

**MS** (ESI)  $m/z$  (relative intensity): 665 (5) [2M+Na]<sup>+</sup>, 381 (30), 344 (100) [M+Na]<sup>+</sup>.

**HR-MS** (ESI)  $m/z$  calcd for C<sub>17</sub>H<sub>24</sub>FN<sub>3</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>: 344.1745, found: 344.1745.

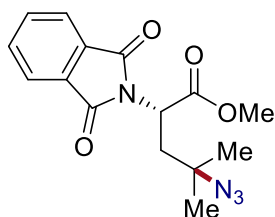
### Minor isomer: 3-Azido-3,7-dimethyloctyl 4-fluorobenzoate (**2f'**)

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.05 (dd,  $J$  = 8.9, 5.4 Hz, 2H), 7.11 (dd,  $J$  = 8.9, 8.7 Hz, 2H), 4.42 (t,  $J$  = 6.9 Hz, 2H), 1.98 (td,  $J$  = 6.9, 4.4 Hz, 2H), 1.61–1.49 (m, 3H), 1.44–1.36 (m, 2H), 1.35 (s, 3H), 1.24–1.09 (m, 2H), 0.88 (d,  $J$  = 6.6 Hz, 6H).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 166.0 (d, <sup>1</sup> $J_{C-F}$  = 254.2 Hz, C<sub>q</sub>), 165.7 (C<sub>q</sub>), 132.3 (d, <sup>3</sup> $J_{C-F}$  = 9.4 Hz, CH), 126.5 (d, <sup>4</sup> $J_{C-F}$  = 3.0 Hz, C<sub>q</sub>), 115.7 (d, <sup>2</sup> $J_{C-F}$  = 21.8 Hz, CH), 63.0 (C<sub>q</sub>), 61.5

(CH<sub>2</sub>), 40.2 (CH<sub>2</sub>), 39.3 (CH<sub>2</sub>), 37.8 (CH<sub>2</sub>), 28.0 (CH), 23.8 (CH<sub>3</sub>), 22.7 (CH<sub>3</sub>), 22.7 (CH<sub>3</sub>), 21.9 (CH<sub>2</sub>).

<sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -105.5 to -105.6 (m).



### Methyl (*S*)-4-azido-2-(1,3-dioxoisindolin-2-yl)-4-methylpentanoate (**2g**)

The general procedure **B** was followed using methyl methyl (*S*)-2-(1,3-dioxoisindolin-2-yl)-4-methylpentanoate **1g** (138 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 10:1) yielded **2g** (82.3 mg, 260  $\mu$ mol, 52%) as a colorless liquid.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.87 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), 5.05 (dd, *J* = 10.0, 2.9 Hz, 1H), 3.72 (s, 3H), 2.52 (dd, *J* = 15.2, 10.0 Hz, 1H), 2.42 (dd, *J* = 15.2, 2.9 Hz, 1H), 1.37 (s, 3H), 1.30 (s, 3H).

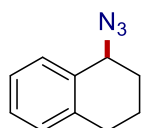
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 169.8 (C<sub>q</sub>), 167.7 (C<sub>q</sub>), 134.4 (CH), 132.0 (C<sub>q</sub>), 123.7 (CH), 60.3 (C<sub>q</sub>), 53.2 (CH<sub>3</sub>), 48.6 (CH), 39.1 (CH<sub>2</sub>), 26.9 (CH<sub>3</sub>), 25.4 (CH<sub>3</sub>).

IR (ATR):  $\tilde{\nu}$  = 2956, 2094, 1745, 1710, 1385, 1236, 1152, 914, 717, 530 cm<sup>-1</sup>.

MS (ESI) *m/z* (relative intensity): 655 (80) [2M+Na]<sup>+</sup>, 339 (100) [M+Na]<sup>+</sup>, 317 (60) [M+H]<sup>+</sup>, 274 (75) [M-N<sub>3</sub>]<sup>+</sup>.

HR-MS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>17</sub>N<sub>4</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 317.1244, found: 317.1246.

The analytical data corresponds with those reported in the literature.<sup>[20]</sup>



### 1-Azido-1,2,3,4-tetrahydronaphthalene (**2a**)

The general procedure **A** was followed using 1,2,3,4-tetrahydronaphthalene **1a** (66.1 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 99:1) yielded **2a** (48.6 mg, 281  $\mu$ mol, 56%) as a colorless liquid.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.33–7.27 (m, 1H), 7.26–7.19 (m, 2H), 7.17–7.10 (m, 1H), 4.57 (t, *J* = 4.9 Hz, 1H), 2.90–2.81 (m, 1H), 2.81–2.68 (m, 1H), 2.08–1.91 (m, 3H), 1.89–1.72 (m, 1H).

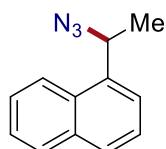
$^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 137.5$  ( $\text{C}_q$ ), 133.9 ( $\text{C}_q$ ), 129.6 (CH), 129.3 (CH), 127.8 (CH), 126.3 (CH), 59.6 (CH), 29.3 ( $\text{CH}_2$ ), 28.9 ( $\text{CH}_2$ ), 19.1 ( $\text{CH}_2$ ).

**IR** (ATR):  $\tilde{\nu} = 2937, 2870, 2093, 1454, 1233, 943, 766, 741 \text{ cm}^{-1}$ .

**MS** (EI)  $m/z$  (relative intensity): 155 (10), 145 (20) [ $\text{M-N}_2$ ] $^+$ , 131 (100), 115 (45), 102 (5), 91 (20), 77 (5).

**HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{10}\text{H}_{13}\text{N}_3\text{Na}$  [ $\text{M+Na}$ ] $^+$ : 196.0845, found: 196.0845.

The analytical data corresponds with those reported in the literature.<sup>[22]</sup>



### 1-(1-Azidoethyl)naphthalene (**2h**)

The general procedure **B** was followed using 1-ethylnaphthalene **1h** (78.1 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-hexane/ $\text{Et}_2\text{O}$  25:1) yielded **2h** (51.3 mg, 260  $\mu\text{mol}$ , 52%) as a colorless liquid.

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.12$  (d,  $J = 8.2$  Hz, 1H), 7.93 (dd,  $J = 8.2, 1.4$  Hz, 1H), 7.86 (d,  $J = 8.2$  Hz, 1H), 7.64–7.48 (m, 4H), 5.38 (q,  $J = 6.8$  Hz, 1H), 1.75 (d,  $J = 6.8$  Hz, 3H).

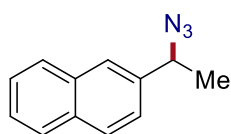
$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = 136.2$  ( $\text{C}_q$ ), 134.1 ( $\text{C}_q$ ), 130.7 ( $\text{C}_q$ ), 129.1 (CH), 128.9 (CH), 126.6 (CH), 125.9 (CH), 125.4 (CH), 123.7 (CH), 123.1 (CH), 57.6 (CH), 20.8 ( $\text{CH}_3$ ).

**IR** (ATR):  $\tilde{\nu} = 2979, 2094, 1598, 1510, 1377, 1240, 798, 774, 737, 557 \text{ cm}^{-1}$ .

**MS** (EI)  $m/z$  (relative intensity): 197 (5) [ $\text{M}$ ] $^+$ , 168 (50), 155 (100) [ $\text{M-N}_3$ ] $^+$ , 127 (30).

**HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{12}\text{H}_{11}\text{N}_3$  [ $\text{M}$ ] $^+$ : 197.0947, found: 197.0943.

The analytical data corresponds with those reported in the literature.<sup>[23]</sup>



### 2-(1-Azidoethyl)naphthalene (**2i**)

The general procedure **B** was followed using 2-ethylnaphthalene **1i** (78.1 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-hexane/ $\text{Et}_2\text{O}$  25:1) yielded **2i** (37.5 mg, 190  $\mu\text{mol}$ , 38%) as a colorless liquid.

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.93$ –7.82 (m, 3H), 7.79 (s, 1H), 7.57–7.44 (m, 3H), 4.80 (q,  $J = 6.8$  Hz, 1H), 1.63 (d,  $J = 6.8$  Hz, 3H).

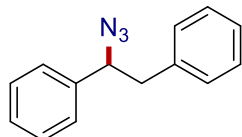
$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = 138.4$  ( $\text{C}_q$ ), 133.3 ( $\text{C}_q$ ), 133.2 ( $\text{C}_q$ ), 128.9 (CH), 128.1 (CH), 127.8 (CH), 126.5 (CH), 126.4 (CH), 125.4 (CH), 124.4 (CH), 61.4 (CH), 21.7 ( $\text{CH}_3$ ).

**IR** (ATR):  $\tilde{\nu} = 2978, 2098, 1602, 1508, 1244, 1059, 858, 817, 748, 560 \text{ cm}^{-1}$ .

**MS** (EI)  $m/z$  (relative intensity): 197 (7)  $[M]^+$ , 169 (5)  $[M-N_2]$ , 155 (100)  $[M-N_3]^+$ , 143 (15), 127 (35), 116 (15), 103 (40), 89 (15), 76 (30).

**HR-MS** (EI)  $m/z$  calcd for  $C_{12}H_{11}N_3$   $[M]^+$ : 197.0947, found: 197.0948.

The analytical data corresponds with those reported in the literature.<sup>[24]</sup>



### (1-Azidoethane-1,2-diyl)dibenzene (**2j**)

The general procedure **A** was followed using 1,2-diphenylethane **1j** (91.2 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc 99:1) yielded **2j** (72.1 mg, 309  $\mu$ mol, 62%) as a colorless liquid.

**<sup>1</sup>H-NMR** (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.40–7.32 (m, 3H), 7.31–7.23 (m, 5H), 7.17–7.13 (m, 2H), 4.68 (td,  $J$  = 8.4, 6.2 Hz, 1H), 3.13–3.00 (m, 2H).

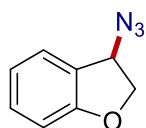
**<sup>13</sup>C-NMR** (101 MHz,  $CDCl_3$ ):  $\delta$  = 139.5 ( $C_q$ ), 137.6 ( $C_q$ ), 129.5 (CH), 128.9 (CH), 128.6 (CH), 128.5 (CH), 127.1 (CH), 126.9 (CH), 67.8 (CH), 43.2 ( $CH_2$ ).

**IR** (ATR):  $\tilde{\nu}$  = 3030, 2921, 2094, 1495, 1453, 1247, 757, 696  $cm^{-1}$ .

**MS** (ESI)  $m/z$  (relative intensity): 381 (90)  $[2M-2N_3]^+$ , 246 (2)  $[M+Na]^+$ , 181 (100)  $[M-N_3]^+$ , 117 (60).

**HR-MS** (ESI)  $m/z$  calcd for  $C_{14}H_{13}N_3Na$   $[M+Na]^+$ : 246.1002, found: 246.1002.

The analytical data corresponds with those reported in the literature.<sup>[22]</sup>



### 3-Azido-2,3-dihydrobenzofuran (**2k**)

The general procedure **A** was followed using 2,3-dihydrobenzofuran **1k** (60.0 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc = 99:1) yielded **2k** (47.7 mg, 296  $\mu$ mol, 59%) as a colorless liquid.

**<sup>1</sup>H-NMR** (400 MHz,  $CDCl_3$ )  $\delta$  = 7.41 (d,  $J$  = 7.5 Hz, 1H), 7.31 (dd,  $J$  = 7.5, 1.5 Hz, 1H), 6.99 (dd,  $J$  = 7.5, 1.5 Hz, 1H), 6.92 (d,  $J$  = 7.5 Hz, 1H), 5.03 (dd,  $J$  = 7.1, 2.8 Hz, 1H), 4.56 (dd,  $J$  = 10.5, 7.1 Hz, 1H), 4.50 (dd,  $J$  = 10.5, 2.8 Hz, 1H).

**<sup>13</sup>C-NMR** (101 MHz,  $CDCl_3$ )  $\delta$  = 160.4 ( $C_q$ ), 131.3 (CH), 125.5 (CH), 124.0 ( $C_q$ ), 121.4 (CH), 110.9 (CH), 76.4 ( $CH_2$ ), 62.1 (CH).

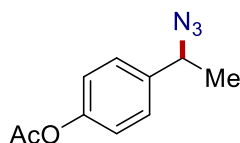
**IR** (ATR):  $\tilde{\nu}$  = 2093, 1596, 1478, 1465, 1235, 1150, 905, 752, 730, 648, 570  $cm^{-1}$ .

**MS** (ESI)  $m/z$  (relative intensity): 119 (10)  $[M-N_3]$ , 118 (10)  $[M-HN_3]$ .



**HR-MS** (EI)  $m/z$  calcd for  $C_8H_8N_3O$   $[M+H]^+$ : 162.0617, found: 162.0618.

The analytical data corresponds with those reported in the literature.<sup>[25]</sup>



#### 4-(1-Azidoethyl)phenyl acetate (**2l**)

The general procedure **A** was followed using 4-ethylphenyl acetate **1l** (82.1 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc = 99:1) yielded **2l** (40.6 mg, 198  $\mu$ mol, 40%) as a colorless liquid.

**<sup>1</sup>H-NMR** (400 MHz,  $CDCl_3$ )  $\delta$  = 7.34 (d,  $J$  = 9.1, 2H), 7.10 (d,  $J$  = 9.1 Hz, 2H), 4.62 (q,  $J$  = 7.2 Hz, 1H), 2.30 (s, 3H), 1.52 (d,  $J$  = 7.2 Hz, 3H).

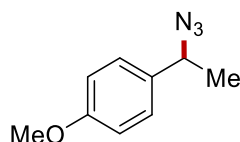
**<sup>13</sup>C-NMR** (101 MHz,  $CDCl_3$ )  $\delta$  169.5 ( $C_q$ ), 150.5 ( $C_q$ ), 138.6 ( $C_q$ ), 127.6 (CH), 122.0 (CH), 60.6 (CH), 21.8 ( $CH_3$ ), 21.3 ( $CH_3$ ).

**IR** (ATR):  $\tilde{\nu}$  = 2100, 1753, 1508, 1189, 1165, 1015, 910, 798  $cm^{-1}$ .

**MS** (ESI)  $m/z$  (relative intensity): 228 (50)  $[M+Na]^+$ , 163 (50)  $[M-N_3]^+$ , 121 (100)  $[M-C_2N_3O]^+$ .

**HR-MS** (ESI)  $m/z$  calcd for  $C_{10}H_{11}N_3O_2Na$   $[M+Na]^+$ : 228.0743, found: 228.0744.

The analytical data corresponds with those reported in the literature.<sup>[23]</sup>



#### 1-(1-Azidoethyl)-4-methoxybenzene (**2m**)

The general procedure **A** was followed using 1-ethyl-4-methoxybenzene **1m** (68.1 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc = 99:1) yielded **2m** (33.9 mg, 191  $\mu$ mol, 38%) as a colorless liquid.

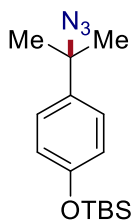
**<sup>1</sup>H-NMR** (400 MHz,  $CDCl_3$ )  $\delta$  = 7.26 (dd,  $J$  = 6.5, 1.7 Hz, 2H), 6.91 (dd,  $J$  = 6.5, 1.7 Hz, 2H), 4.57 (q,  $J$  = 6.9 Hz, 1H), 3.81 (s, 3H), 1.51 (d,  $J$  = 6.9, 3H).

**<sup>13</sup>C-NMR** (101 MHz,  $CDCl_3$ )  $\delta$  = 159.5 ( $C_q$ ), 133.0 ( $C_q$ ), 127.1 (CH), 114.2 (CH), 60.8 (CH), 55.4 ( $CH_3$ ), 21.6 ( $CH_3$ ).

**IR** (ATR):  $\tilde{\nu}$  = 2837, 2100, 1612, 1512, 1245, 1176, 1032, 830, 731, 542  $cm^{-1}$ .

**MS** (ESI)  $m/z$  (relative intensity): 243 (100), 163 (5)  $[M-N]^+$ , 135 (5)  $[M-N_3]^+$ .

The analytical data corresponds with those reported in the literature.<sup>[23]</sup>



### [4-(2-Azidopropan-2-yl)phenoxy](*tert*-butyl)dimethylsilane (**2n**)

The general procedure **B** was followed using *tert*-butyl(4-isopropylphenoxy)dimethylsilane **1n** (125 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-hexane/Et<sub>2</sub>O 50:1) yielded **2n** (139 mg, 475 μmol, 95%) as a colorless liquid.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) δ = 7.31 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 1.63 (s, 6H), 1.01 (s, 9H), 0.23 (s, 6H).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>) δ = 155.0 (C<sub>q</sub>), 137.4 (C<sub>q</sub>), 126.5 (CH), 120.0 (CH), 63.6 (C<sub>q</sub>), 28.5 (CH<sub>3</sub>), 25.8 (CH<sub>3</sub>), 18.3 (C<sub>q</sub>), -4.3 (CH<sub>3</sub>).

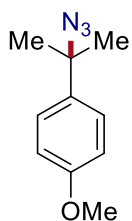
**<sup>29</sup>Si-NMR** (79 MHz, CDCl<sub>3</sub>) δ = 20.86.

**IR** (ATR):  $\tilde{\nu}$  = 2931, 2859, 2101, 1510, 1251, 1177, 912, 835, 779, 561 cm<sup>-1</sup>.

**MS** (ESI) *m/z* (relative intensity): 249 (100) [M-N<sub>3</sub>]<sup>+</sup>.

**HR-MS** (ESI) *m/z* calcd for C<sub>15</sub>H<sub>25</sub>O<sup>28</sup>Si [M-N<sub>3</sub>]<sup>+</sup>: 249.1669, found: 249.1671.

The analytical data corresponds with those reported in the literature.<sup>[26]</sup>



### 1-(2-Azidopropan-2-yl)-4-methoxybenzene (**2o**)

The general procedure **B** was followed using 1-isopropyl-4-methoxybenzene **1o** (75.1 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-hexane/Et<sub>2</sub>O 50:1) yielded **2o** (80.3 mg, 420 μmol, 84%) as a colorless liquid.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) δ = 7.39 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 1.64 (s, 6H).

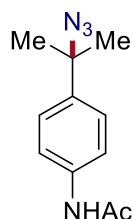
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>) δ = 158.9 (C<sub>q</sub>), 136.8 (C<sub>q</sub>), 126.5 (CH), 113.8 (CH), 63.6 (C<sub>q</sub>), 55.3 (CH<sub>3</sub>), 28.5 (CH<sub>3</sub>).

**IR** (ATR):  $\tilde{\nu}$  = 2976, 2837, 2098, 1512, 1243, 1181, 1143, 1033, 829, 615 cm<sup>-1</sup>.

**MS** (ESI) *m/z* (relative intensity): 214 (2) [M+Na]<sup>+</sup>, 149 (100) [M-N<sub>3</sub>]<sup>+</sup>.

**HR-MS** (ESI) *m/z* calcd for C<sub>10</sub>H<sub>13</sub>N<sub>3</sub>NaO [M+Na]<sup>+</sup>: 214.0951, found: 214.0947.

The analytical data corresponds with those reported in the literature.<sup>[26]</sup>



#### ***N*-[4-(2-Azidopropan-2-yl)phenyl]acetamide (**2p**)**

The general procedure **B** was followed using *N*-(4-isopropylphenyl)acetamide **1p** (88.6 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **2p** (105 mg, 480  $\mu$ mol, 96%) as a white solid.

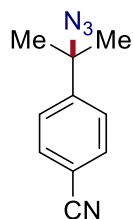
**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.83 (bs, 1H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 2.15 (s, 3H), 1.60 (s, 6H).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 168.9 (C<sub>q</sub>), 140.6 (C<sub>q</sub>), 137.3 (C<sub>q</sub>), 125.9 (CH), 120.1 (CH), 63.6 (C<sub>q</sub>), 28.4 (CH<sub>3</sub>), 24.6 (CH<sub>3</sub>).

**IR** (ATR):  $\tilde{\nu}$  = 3295, 2974, 2096, 1668, 1550, 1239, 1141, 835, 734, 601 cm<sup>-1</sup>.

**MS** (ESI) *m/z* (relative intensity): 459 (15) [2M+Na]<sup>+</sup>, 437 (5) [2M+H]<sup>+</sup>, 241 (60) [M+Na]<sup>+</sup>, 219 (70) [M+H]<sup>+</sup>, 176 (100) [M-N<sub>3</sub>]<sup>+</sup>.

**HR-MS** (ESI) *m/z* calcd for C<sub>11</sub>H<sub>15</sub>N<sub>4</sub>O [M+H]<sup>+</sup>: 219.1240, found: 219.1241.



#### **4-(2-Azidopropan-2-yl)benzotrile (**2q**)**

The general procedure **A** was followed using 4-isopropylbenzotrile **1q** (72.6 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-hexane/Et<sub>2</sub>O 10:1) yielded **2q** (69.0 mg, 371  $\mu$ mol, 74%) as a colorless liquid.

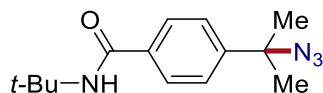
**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.65 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 1.64 (s, 6H).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 150.1 (C<sub>q</sub>), 132.5 (CH), 126.1 (CH), 118.6 (C<sub>q</sub>), 111.4 (C<sub>q</sub>), 63.4 (C<sub>q</sub>), 28.2 (CH<sub>3</sub>).

**IR** (ATR):  $\tilde{\nu}$  = 2980, 2230, 2101, 1608, 1504, 1369, 1250, 1095, 837, 566 cm<sup>-1</sup>.

**MS** (ESI) *m/z* (relative intensity): 241 (100), 209 (90) [M+Na]<sup>+</sup>, 187 (5) [M+H]<sup>+</sup>.

**HR-MS** (ESI) *m/z* calcd for C<sub>10</sub>H<sub>11</sub>N<sub>4</sub> [M+H]<sup>+</sup>: 187.0978, found: 187.0978.



#### 4-(2-Azidopropan-2-yl)-*N*-(*tert*-butyl)benzamide (**2r**)

The general procedure **A** was followed using *N*-(*tert*-butyl)-4-isopropylbenzamide **1r** (110 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 10:1) yielded **2r** (67.7 mg, 260  $\mu$ mol, 52%) as a white solid.

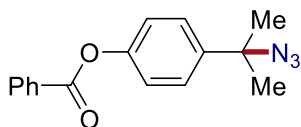
**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.69 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.03 (bs, 1H), 1.60 (s, 6H), 1.44 (s, 9H).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 166.5 (C<sub>q</sub>), 147.7 (C<sub>q</sub>), 135.1 (C<sub>q</sub>), 127.1 (CH), 125.3 (CH), 63.6 (C<sub>q</sub>), 51.7 (C<sub>q</sub>), 28.9 (CH<sub>3</sub>), 28.3 (CH<sub>3</sub>).

**IR** (ATR):  $\tilde{\nu}$  = 3375, 2974, 2101, 1637, 1536, 1452, 1365, 1149, 855, 708 cm<sup>-1</sup>.

**MS** (ESI) *m/z* (relative intensity): 543 (15) [2M+Na]<sup>+</sup>, 521 (10) [2M+H]<sup>+</sup>, 283 (30) [M+Na]<sup>+</sup>, 261 (100) [M+H]<sup>+</sup>.

**HR-MS** (ESI) *m/z* calcd for C<sub>14</sub>H<sub>21</sub>N<sub>3</sub>O [M+H]<sup>+</sup>: 261.1710, found: 261.1713.



#### 4-(2-Azidopropan-2-yl)phenyl benzoate (**2s**)

The general procedure **A** was followed using 4-isopropylphenyl benzoate **1s** (120 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 25:1) yielded **2s** (101 mg, 360  $\mu$ mol, 72%) as a colorless liquid.

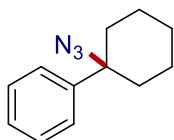
**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.24 (d, *J* = 8.6 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.57–7.53 (m, 4H), 7.26 (d, *J* = 8.6 Hz, 2H), 1.69 (s, 6H).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 165.2 (C<sub>q</sub>), 150.2 (C<sub>q</sub>), 142.4 (C<sub>q</sub>), 133.8 (CH), 130.3 (CH), 129.5 (C<sub>q</sub>), 128.7 (CH), 126.5 (CH), 121.8 (CH), 63.6 (C<sub>q</sub>), 28.6 (CH<sub>3</sub>).

**IR** (ATR):  $\tilde{\nu}$  = 2978, 2102, 1737, 1509, 1261, 1206, 1172, 1024, 878, 707 cm<sup>-1</sup>.

**MS** (ESI) *m/z* (relative intensity): 304 (100) [M+Na]<sup>+</sup>, 299 (20) [M+NH<sub>4</sub>]<sup>+</sup>, 239 (80) [M-N<sub>3</sub>]<sup>+</sup>, 169 (20), 105 (30).

**HR-MS** (ESI) *m/z* calcd for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>: 304.1056, found: 304.1056.



### (1-Azidocyclohexyl)benzene (2t)

The general procedure **A** was followed using cyclohexylbenzene **1t** (60.0 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc = 99:1) yielded **2t** (34.0 mg, 169  $\mu$ mol, 34%) as a colorless liquid.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.50–7.45 (m, 2H), 7.43–7.37 (m, 2H), 7.34–7.28 (m, 1H), 2.06–2.00 (m, 2H), 1.91–1.82 (m, 2H), 1.78–1.63 (m, 5H), 1.34–1.29 (m, 1H).

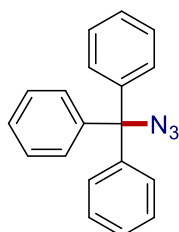
**<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 144.5 (C<sub>q</sub>), 128.8 (CH), 127.7 (CH), 125.6 (CH), 66.8 (C<sub>q</sub>), 36.1 (CH<sub>2</sub>), 25.4 (CH<sub>2</sub>), 22.6 (CH<sub>2</sub>).

**IR** (ATR):  $\tilde{\nu}$  = 2937, 2101, 1254, 905, 729, 696, 649 cm<sup>-1</sup>.

**MS** (ESI) *m/z* (relative intensity): 174 (80) [M+H-N<sub>2</sub>]<sup>+</sup>, 118 (100).

**HR-MS** (EI) *m/z* calcd for C<sub>12</sub>H<sub>16</sub>N [M+H-N<sub>2</sub>]<sup>+</sup>: 174.1233, found: 174.1232.

The analytical data corresponds with those reported in the literature.<sup>[27]</sup>



### (Azidomethanetriyl)tribenzene (2u)

The general procedure **A** was followed using triphenylmethane **1u** (122 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc = 99:1) yielded **2u** (135 mg, 474  $\mu$ mol, 95%) as a colorless liquid.

**<sup>1</sup>H-NMR** (400 MHz, Chloroform-*d*)  $\delta$  = 7.38–7.31 (m, 8H), 7.32–7.26 (m, 7H).

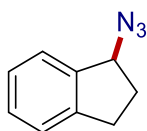
**<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 143.1 (C<sub>q</sub>), 128.5 (CH), 128.2 (CH), 127.7 (CH), 77.1 (C<sub>q</sub>).

**IR** (ATR):  $\tilde{\nu}$  = 2097, 1490, 1446, 1258, 717, 697 cm<sup>-1</sup>.

**MS** (ESI) *m/z* (relative intensity): 244 (100) [M-N<sub>3</sub>]<sup>+</sup>, 165 (73).

**HR-MS** (ESI) *m/z* calcd for C<sub>19</sub>H<sub>15</sub>N<sub>3</sub>Na [M+Na]<sup>+</sup>: 308.1158; found: 308.1148.

The analytical data corresponds with those reported in the literature.<sup>[23]</sup>



### 1-Azido-2,3-dihydro-1H-indene (2v)

The general procedure **A** was followed using 2,3-dihydro-1*H*-indene **1v** (59.1 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-pentane/EtOAc = 99:1) yielded **2v** (45.0 mg, 283  $\mu$ mol, 57%) as a colorless liquid.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.41–7.39 (m, 1H), 7.33–7.21 (m, 3H), 4.87 (dd,  $J$  = 4.9, 2.1 Hz, 1H), 3.09 (ddd,  $J$  = 16.3, 8.4, 6.1 Hz, 1H), 2.88 (dddd,  $J$  = 15.7, 8.4, 5.3, 2.1 Hz, 1H), 2.45 (dddd,  $J$  = 15.7, 13.1, 8.4, 2.1 Hz, 1H), 2.13 (ddd,  $J$  = 16.3, 8.4, 6.1 Hz, 1H).

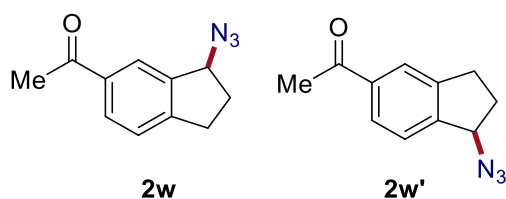
**<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 143.8 (C<sub>q</sub>), 140.8 (C<sub>q</sub>), 129.0 (CH), 126.0 (CH), 125.2 (CH), 124.7 (CH), 66.0 (CH), 32.6 (CH<sub>2</sub>), 30.6 (CH<sub>2</sub>).

**IR** (ATR):  $\tilde{\nu}$  = 2082, 1478, 1460, 1325, 1460, 754, 729, 634, 558 cm<sup>-1</sup>.

**MS** (ESI)  $m/z$  (relative intensity): 210 (100), 146 (5) [M+H-N]<sup>+</sup>, 132 (10) [M+H-N<sub>2</sub>]<sup>+</sup>.

**HR-MS** (EI)  $m/z$  calcd for C<sub>9</sub>H<sub>10</sub>N [M+H-N<sub>2</sub>]<sup>+</sup>: 132.0763, found: 132.0764.

The analytical data correspond with those reported in the literature.<sup>[24]</sup>



### 1-(3-Azido-2,3-dihydro-1H-inden-5-yl)ethan-1-one (2w)

The general procedure A was followed using 1-(2,3-dihydro-1H-inden-5-yl)ethan-1-one **1w** (80.0 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). The ratio of **2w/2w'** (1:1) was determined by <sup>1</sup>H-NMR spectroscopy of the crude reaction mixture. Purification by column chromatography on silica gel (*n*-hexane/EtOAc 10:1) yielded **2w/2w'** (42.3 mg, 210  $\mu$ mol, 42%) as a colorless liquid. Analytical data is reported for **2w/2w'** as a 1:1 of both regioisomers.

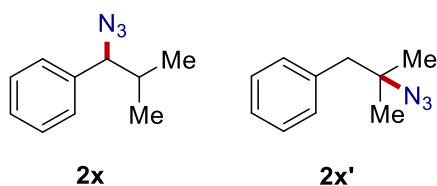
**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.96 (s, 1H), 7.90 (d,  $J$  = 7.9 Hz, 1H), 7.86–7.85 (m, 2H), 7.46 (d,  $J$  = 8.2 Hz, 1H), 7.35 (d,  $J$  = 7.9 Hz, 1H), 4.89 (m, 2H), 3.18–3.02 (m, 2H), 2.96–2.88 (m, 2H), 2.60 (s, 3H), 2.60 (s, 3H), 2.54–2.42 (m, 2H), 2.25–2.10 (m, 2H).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 198.0 (C<sub>q</sub>), 197.6 (C<sub>q</sub>), 149.4 (C<sub>q</sub>), 145.9 (C<sub>q</sub>), 144.2 (C<sub>q</sub>), 141.5 (C<sub>q</sub>), 137.9 (C<sub>q</sub>), 136.5 (C<sub>q</sub>), 129.4 (CH), 127.6 (CH), 125.3 (CH), 125.0 (CH), 124.6 (CH), 124.6 (CH), 65.4 (CH), 65.4 (CH), 32.7 (CH<sub>2</sub>), 32.7 (CH<sub>2</sub>), 30.7 (CH<sub>2</sub>), 30.3 (CH<sub>2</sub>), 26.9 (CH<sub>3</sub>), 26.8 (CH<sub>3</sub>).

**IR** (ATR):  $\tilde{\nu}$  = 2947, 2088, 1679, 1610, 1423, 1357, 1250, 824, 704, 584 cm<sup>-1</sup>.

**MS** (ESI)  $m/z$  (relative intensity): 224 (100) [M+Na]<sup>+</sup>, 202 (45) [M+H]<sup>+</sup>, 159 (70) [M-N<sub>3</sub>]<sup>+</sup>.

**HR-MS** (ESI)  $m/z$  calcd for C<sub>11</sub>H<sub>12</sub>N<sub>3</sub>O [M+H]<sup>+</sup>: 202.0975, found: 202.0975.



### (1-Azido-2-methylpropyl)benzene (2x)

The general procedure **A** was followed using isobutylbenzene **1x** (67.1 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). The ratio of **2x/2x'** (2.7:1) was determined by <sup>1</sup>H-NMR spectroscopy of the crude reaction mixture.<sup>[28]</sup> Purification by column chromatography on silica gel (*n*-pentane/EtOAc 99:1) yielded **2x/2x'** (49.2 mg, 281 μmol, 56%) as a colorless liquid. Analytical data is reported for **2x**.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.41–7.34 (m, 2H), 7.34–7.29 (m, 1H), 7.28–7.24 (m, 2H), 4.13 (d, *J* = 8.0 Hz, 1H), 2.00 (dh, *J* = 8.0, 6.7 Hz, 1H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.80 (d, *J* = 6.7 Hz, 3H).

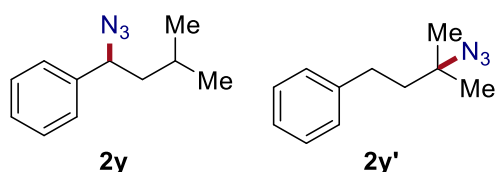
**<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>): δ = 139.1 (C<sub>q</sub>), 128.7 (CH), 128.2 (CH), 127.6 (CH), 73.4 (CH), 34.2 (CH), 19.7 (CH<sub>3</sub>), 19.4 (CH<sub>3</sub>).

**IR** (ATR):  $\tilde{\nu}$  = 2963, 2928, 2096, 1468, 1249, 1153, 747, 701 cm<sup>-1</sup>.

**MS** (EI) *m/z* (relative intensity): 146 (20) [M–N<sub>2</sub>]<sup>+</sup>, 132 (30), 117 (60), 104 (100), 91 (55), 77 (55).

**HR-MS** (EI) *m/z* calcd for C<sub>10</sub>H<sub>12</sub>N<sub>1</sub> [M–N<sub>2</sub>]<sup>+</sup>: 146.0964, found: 146.0966.

The analytical data corresponds with those reported in the literature.<sup>[23]</sup>



#### (1-Azido-3-methylbutyl)benzene (**2y**)

The general procedure **A** was followed using isopentylbenzene **2y** (74.1 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). The ratio of **2y/2y'** (3:1) was determined by <sup>1</sup>H-NMR spectroscopy of the crude reaction mixture. Purification by column chromatography on silica gel (*n*-pentane/Et<sub>2</sub>O 50:1) yielded **2y** (34.1 mg, 180 μmol, 36%) and **2y'** (10.4 mg, 55 μmol, 11%) as colorless liquids.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>) δ = 7.41–7.38 (m, 2H), 7.35–7.31 (m, 3H), 4.48 (t, *J* = 7.5 Hz, 1H), 1.81–1.74 (m, 1H), 1.70–1.64 (m, 1H), 1.63–1.54 (m, 1H), 0.95 (d, *J* = 6.5 Hz, 6H).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>) δ = 140.2 (C<sub>q</sub>), 128.9 (CH), 128.3 (CH), 127.0 (CH), 64.7 (CH), 45.2 (CH<sub>2</sub>), 25.1 (CH), 22.8 (CH<sub>3</sub>), 22.3 (CH<sub>3</sub>).

**IR** (ATR):  $\tilde{\nu}$  = 2958, 2091, 1454, 1368, 1243, 908, 756, 698, 669, 539 cm<sup>-1</sup>.

The analytical data corresponds with those reported in the literature.<sup>[4]</sup>

**MS** (EI) *m/z* (relative intensity): 160 (25) [M–N<sub>2</sub>]<sup>+</sup>, 146 (15) [M–N<sub>2</sub>–H]<sup>+</sup>, 131 (25), 105 (30), 91 (100), 77 (40).

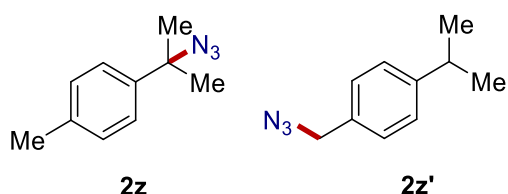
**HR-MS** (EI) *m/z* calcd for C<sub>11</sub>H<sub>14</sub>N [M–N<sub>2</sub>–H]<sup>+</sup>: 160.1121, found: 160.1120.

Minor isomer: **(3-Azido-3-methylbutyl)benzene (2y')**

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.37–7.25 (m, 2H), 7.24–7.14 (m, 3H), 2.74–2.62 (m, 2H), 1.80 (m, 2H), 1.34 (s, 6H).

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 142.0 (C<sub>q</sub>), 128.6 (CH), 128.5 (CH), 126.1 (CH), 61.6 (C<sub>q</sub>), 43.7 (CH<sub>2</sub>), 30.9 (CH<sub>2</sub>), 26.2 (CH<sub>3</sub>).

The analytical data corresponds with those reported in the literature.<sup>[28]</sup>



### 1-(2-Azidopropan-2-yl)-4-methylbenzene (**2z**)

The general procedure **A** was followed using *p*-cymene **1z** (67.1 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). The ratio of **2z/2z'** (33:1) was determined by <sup>1</sup>H-NMR spectroscopy of the crude reaction mixture. Purification by column chromatography on silica gel (*n*-pentane/EtOAc 99:1) yielded **2z/2z'** (59.4 mg, 339  $\mu$ mol, 66%) as a colorless liquid. Analytical data is reported for **2z**.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.36 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 2.37 (s, 3H), 1.65 (s, 6H).

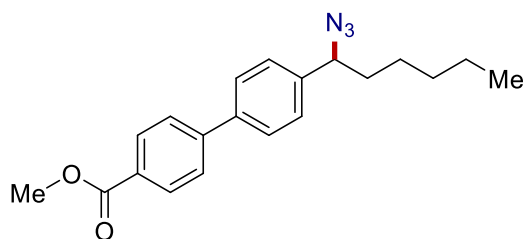
**<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 141.8 (C<sub>q</sub>), 137.2 (C<sub>q</sub>), 129.3 (CH), 125.2 (CH), 63.8 (C<sub>q</sub>), 28.6 (CH<sub>3</sub>), 21.1 (CH<sub>3</sub>).

**IR** (ATR):  $\tilde{\nu}$  = 2978, 2925, 2103, 1515, 1460, 1256, 1099, 816 cm<sup>-1</sup>.

**MS** (EI) *m/z* (relative intensity): 133 (20) [M-N<sub>3</sub>]<sup>+</sup>, 132 (98), 117 (100), 105 (10), 91 (40), 77 (5).

**HR-MS** (EI) *m/z* calcd for C<sub>10</sub>H<sub>13</sub> [M-N<sub>3</sub>]<sup>+</sup>: 133.1012, found: 133.1012.

The analytical data corresponds with those reported in the literature.<sup>[29]</sup>



### Methyl 4'-(1-azidohexyl)-[1,1'-biphenyl]-4-carboxylate (**6a**)

The general procedure **A** was followed using methyl 4'-hexyl-[1,1'-biphenyl]-4-carboxylate **5a** (148 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column



chromatography on silica gel (*n*-hexane/EtOAc 10:1) yielded **6a** (65.7 mg, 195  $\mu$ mol, 39%) as a colorless liquid.

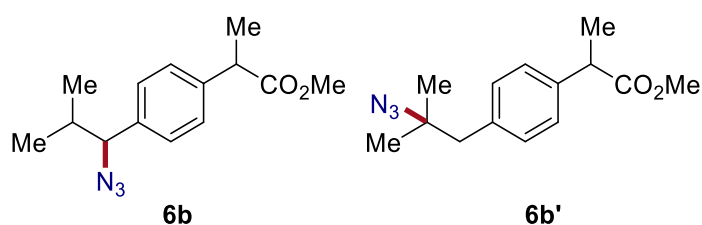
**<sup>1</sup>H-NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.13–8.10 (m, 2H), 7.68–7.65 (m, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.41–7.38 (m, 2H), 4.46 (dd, *J* = 7.8, 6.6 Hz, 1H), 3.95 (s, 3H), 1.92–1.82 (m, 1H), 1.81–1.73 (m, 1H), 1.47–1.36 (m, 1H), 1.36–1.25 (m, 5H), 0.91–0.86 (m, 3H).

**<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 167.1 (C<sub>q</sub>), 145.1 (C<sub>q</sub>), 140.1 (C<sub>q</sub>), 139.9 (C<sub>q</sub>), 130.3 (CH), 129.2 (C<sub>q</sub>), 127.8 (CH), 127.6 (CH), 127.1 (CH), 66.2 (CH), 52.3 (CH<sub>3</sub>), 36.3 (CH<sub>2</sub>), 31.6 (CH<sub>2</sub>), 26.1 (CH<sub>2</sub>), 22.6 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>).

**IR** (ATR):  $\tilde{\nu}$  = 2932, 2859, 2093, 1719, 1608, 1435, 1275, 1110, 773 cm<sup>-1</sup>.

**MS** (ESI) *m/z* (relative intensity): 697 (100) [2M+Na]<sup>+</sup>, 360 (70) [M+Na]<sup>+</sup>, 295 (10) [M-N<sub>3</sub>]<sup>+</sup>.

**HR-MS** (ESI) *m/z* calcd for C<sub>20</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup>: 360.1682, found: 360.1681.



### Methyl 2-[4-(1-azido-2-methylpropyl)phenyl]propanoate (**6b**)

The general procedure **B** was followed using methyl 2-(4-isobutylphenyl)propanoate **5b** (110 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). The ratio of **6b/6b'** (2.3:1) was determined by <sup>1</sup>H-NMR spectroscopy of the crude reaction mixture. Purification by column chromatography on silica gel (*n*-hexane/Et<sub>2</sub>O 50:1) yielded **6b/6b'** (54.9 mg, 210  $\mu$ mol, 42%) as a colorless liquid. Analytical data is reported for **6b**.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.29–7.28 (m, 1H), 7.23–7.20 (m, 2H), 7.18–7.12 (m, 1H), 4.12 (d, *J* = 7.7 Hz, 1H), 3.72 (q, *J* = 7.2 Hz, 1H), 3.66 (s, 3H), 1.97 (hept, *J* = 6.8 Hz, 1H), 1.51–1.48 (m, 3H), 1.01 (d, *J* = 6.6 Hz, 3H), 0.80 (d, *J* = 6.6 Hz, 3H).

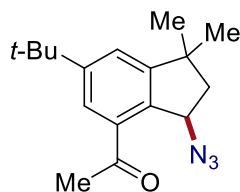
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 175.0 (C<sub>q</sub>), 140.3 (C<sub>q</sub>), 138.0 (C<sub>q</sub>), 127.8 (CH), 127.7 (CH), 73.0 (CH), 52.2 (CH<sub>3</sub>), 45.2 (CH), 34.1 (CH), 19.6 (CH<sub>3</sub>), 19.2 (CH<sub>3</sub>), 18.7 (CH<sub>3</sub>).

**IR** (ATR):  $\tilde{\nu}$  = 2974, 2094, 1735, 1456, 1249, 1205, 1161, 965, 860, 559 cm<sup>-1</sup>.

**MS** (ESI) *m/z* (relative intensity): 284 (100) [M+Na]<sup>+</sup>, 262 (2) [M+H]<sup>+</sup>, 219 (90) [M-N<sub>3</sub>]<sup>+</sup>.

**HR-MS** (ESI) *m/z* calcd for C<sub>14</sub>H<sub>20</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 262.1550, found: 262.1550.

The analytical data corresponds with those reported in the literature.<sup>[22]</sup>



### 1-[3-Azido-6-(*tert*-butyl)-1,1-dimethyl-2,3-dihydro-1*H*-inden-4-yl]ethan-1-one (**6c**)

The general procedure **A** was followed using 1-(6-(*tert*-butyl)-1,1-dimethyl-2,3-dihydro-1*H*-inden-4-yl)ethan-1-one **5c** (122 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 50:1) yielded **6c** (92.8 mg, 325  $\mu$ mol, 65%) as a colorless liquid.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.76 (d, *J* = 1.8 Hz, 1H), 7.40 (d, *J* = 1.8 Hz, 1H), 5.59 (dd, *J* = 7.3, 1.8 Hz, 1H), 2.65 (s, 3H), 2.19 (dd, *J* = 13.8, 7.3 Hz, 1H), 2.07 (dd, *J* = 13.8, 1.8 Hz, 1H), 1.38 (s, 9H), 1.34 (s, 3H), 1.32 (s, 3H).

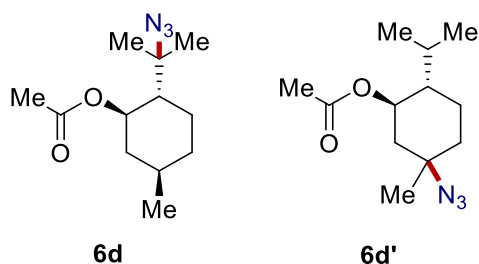
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 199.9 (C<sub>q</sub>), 154.9 (C<sub>q</sub>), 153.4 (C<sub>q</sub>), 136.3 (C<sub>q</sub>), 134.0 (C<sub>q</sub>), 125.9 (CH), 124.1 (CH), 63.4 (CH), 48.0 (CH<sub>2</sub>), 42.9 (C<sub>q</sub>), 35.1 (C<sub>q</sub>), 31.5 (CH<sub>3</sub>), 30.8 (CH<sub>3</sub>), 29.3 (CH<sub>3</sub>), 28.2 (CH<sub>3</sub>).

**IR** (ATR):  $\tilde{\nu}$  = 2958, 2099, 1682, 1464, 1318, 1255, 1234, 882, 662, 578 cm<sup>-1</sup>.

**MS** (ESI) *m/z* (relative intensity): 593 (35) [2M+Na]<sup>+</sup>, 308 (75) [M+Na]<sup>+</sup>, 286 (5) [M+H]<sup>+</sup>, 258 (20), 243 (100) [M-N<sub>3</sub>]<sup>+</sup>.

**HR-MS** (ESI) *m/z* calcd for C<sub>17</sub>H<sub>24</sub>N<sub>3</sub>O [M+H]<sup>+</sup>: 286.1914, found: 286.1910.

The analytical data corresponds with those reported in the literature.<sup>[22]</sup>



### (1*R*,2*S*,5*R*)-2-(2-Azidopropan-2-yl)-5-methylcyclohexyl acetate (**6d**)

The general procedure **A** was followed using (–)-menthol acetate **5d** (99.2 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). The ratio of **6d/6d'** (3:1) was determined by <sup>1</sup>H-NMR of the crude reaction mixture. Purification by column chromatography on silica gel (*n*-pentane/EtOAc 95:5) yielded **6d/6d'** (57.6 mg, 241  $\mu$ mol, 48%) as a colorless liquid. Analytical data is reported for **6d**.

**<sup>1</sup>H-NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.81 (td, *J* = 10.7, 4.5 Hz, 1H), 2.05 (s, 3H), 1.99–1.94 (m, 1H), 1.92 (dq, *J* = 13.4, 3.5 Hz, 1H), 1.71 (ddq, *J* = 11.9, 3.6, 2.3 Hz, 1H), 1.68–1.63 (m, 1H),

1.53–1.45 (m, 1H), 1.26 (s, 3H), 1.24 (s, 3H), 1.11 (tdd,  $J = 13.3, 12.3, 3.6$  Hz, 1H), 1.01 (td,  $J = 12.3, 10.9$  Hz, 1H), 0.93–0.90 (m, 1H), 0.90 (d,  $J = 6.5$  Hz, 3H).

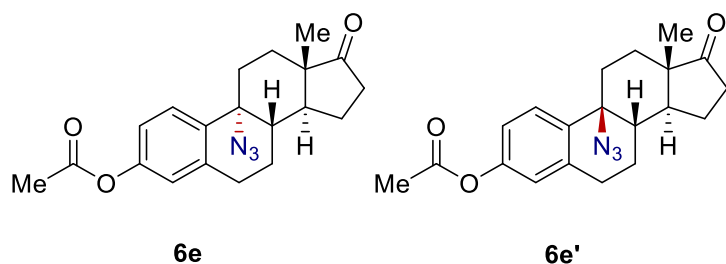
$^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 170.5$  ( $\text{C}_q$ ), 73.4 (CH), 63.6 ( $\text{C}_q$ ), 49.1 (CH), 41.4 ( $\text{CH}_2$ ), 34.2 ( $\text{CH}_2$ ), 31.3 (CH), 26.6 ( $\text{CH}_2$ ), 25.1 ( $\text{CH}_3$ ), 24.7 ( $\text{CH}_3$ ), 21.8 ( $\text{CH}_3$ ), 21.8 ( $\text{CH}_3$ ).

**IR** (ATR):  $\tilde{\nu} = 2955, 2872, 2099, 1734, 1457, 1371, 1239, 1027$   $\text{cm}^{-1}$ .

**MS** (ESI)  $m/z$  (relative intensity): 379 (10), 262 (100)  $[\text{M}+\text{Na}]^+$ , 197 (10)  $[\text{M}-\text{N}_3]^+$ , 152 (10).

**HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{12}\text{H}_{21}\text{N}_3\text{O}_2\text{Na}$   $[\text{M}+\text{Na}]^+$ : 262.1526, found: 262.1528.

The analytical data corresponds with those reported in the literature.<sup>[11]</sup>



**(8*S*,9*R*,13*S*,14*S*)-9-Azido-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl acetate (6e)**

The general procedure **A** was followed using estrone acetate **5e** (156 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 99:1  $\rightarrow$  80:20) yielded **6e** (66.3 mg, 188  $\mu\text{mol}$ , 38%) and **6e'** (65.3 mg, 185  $\mu\text{mol}$ , 37%) as a mixture of diastereomers as colorless liquids.

$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.43$  (d,  $J = 8.5$  Hz, 1H), 6.96 (dd,  $J = 8.3, 2.5$  Hz, 1H), 6.93 (d,  $J = 2.5$  Hz, 1H), 3.00–2.88 (m, 3H), 2.66–2.59 (m, 1H), 2.49 (ddd,  $J = 19.2, 8.9, 1.1$  Hz, 1H), 2.30 (s, 3H), 2.17 (dt,  $J = 19.2, 8.9$  Hz, 1H), 2.05–1.95 (m, 2H), 1.89 (td,  $J = 11.4, 10.7, 2.9$  Hz, 1H), 1.84–1.74 (m, 4H), 1.61–1.56 (m, 1H), 0.89 (s, 3H).

$^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 219.7$  ( $\text{C}_q$ ), 169.6 ( $\text{C}_q$ ), 150.5 ( $\text{C}_q$ ), 138.5 ( $\text{C}_q$ ), 134.3 ( $\text{C}_q$ ), 126.2 (CH), 122.9 (CH), 119.2 (CH), 65.3 ( $\text{C}_q$ ), 47.6 ( $\text{C}_q$ ), 43.6 (CH), 40.8 (CH), 35.9 ( $\text{CH}_2$ ), 29.5 ( $\text{CH}_2$ ), 28.9 ( $\text{CH}_2$ ), 28.0 ( $\text{CH}_2$ ), 21.4 ( $\text{CH}_2$ ), 21.3 ( $\text{CH}_3$ ), 20.5 ( $\text{CH}_2$ ), 13.4 ( $\text{CH}_3$ ).

**IR** (ATR):  $\tilde{\nu} = 2937, 2856, 2093, 1763, 1738, 1494, 1262, 1200, 756$   $\text{cm}^{-1}$ .

**MS** (ESI)  $m/z$  (relative intensity): 729 (10)  $[2\text{M}+\text{Na}]^+$ , 376 (100)  $[\text{M}+\text{Na}]^+$ , 311 (50)  $[\text{M}-\text{N}_3]^+$ .

**HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{23}\text{N}_3\text{O}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ : 376.1632, found: 376.1629.

The analytical data corresponds with those reported in the literature.<sup>[22]</sup>

**(8*S*,9*S*,13*S*,14*S*)-9-Azido-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl acetate (6e')**

**<sup>1</sup>H-NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.44 (d,  $J$  = 8.6 Hz, 1H), 6.99 (dd,  $J$  = 8.6, 2.6 Hz, 1H), 6.95 (d,  $J$  = 2.5 Hz, 1H), 2.84–2.79 (m, 3H), 2.71 (dt,  $J$  = 14.4, 3.3 Hz, 1H), 2.47 (ddd,  $J$  = 19.4, 8.9, 1.1 Hz, 2H), 2.29 (s, 4H), 2.11–2.02 (m, 4H), 1.96–1.91 (m, 1H), 1.81–1.75 (m, 2H), 1.71 (dt,  $J$  = 13.6, 3.4 Hz, 2H), 1.66 (ddd,  $J$  = 12.5, 9.0, 3.5 Hz, 1H), 1.61–1.53 (m, 3H), 1.14 (td,  $J$  = 13.8, 3.5 Hz, 2H), 1.02 (s, 4H).

**<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 218.8 (C<sub>q</sub>), 169.4 (C<sub>q</sub>), 150.4 (C<sub>q</sub>), 138.9 (C<sub>q</sub>), 130.5 (C<sub>q</sub>), 127.1 (CH), 123.0 (CH), 119.8 (CH), 65.9 (C<sub>q</sub>), 47.5 (C<sub>q</sub>), 43.2 (CH), 39.4 (CH), 35.8 (CH<sub>2</sub>), 30.6 (CH<sub>2</sub>), 28.4 (CH<sub>2</sub>), 25.2 (CH<sub>2</sub>), 21.9 (CH<sub>2</sub>), 21.3 (CH<sub>3</sub>), 19.6 (CH<sub>2</sub>), 13.6 (CH<sub>3</sub>).

**IR** (ATR):  $\tilde{\nu}$  = 2948, 2864, 2093, 1763, 1740, 1495, 1204, 1013, 755 cm<sup>-1</sup>.

**MS** (ESI)  $m/z$  (relative intensity): 729.4 (10) [2M+Na]<sup>+</sup>, 376.2 (100) [M+Na]<sup>+</sup>, 311.2 (30) [M-N<sub>3</sub>]<sup>+</sup>.

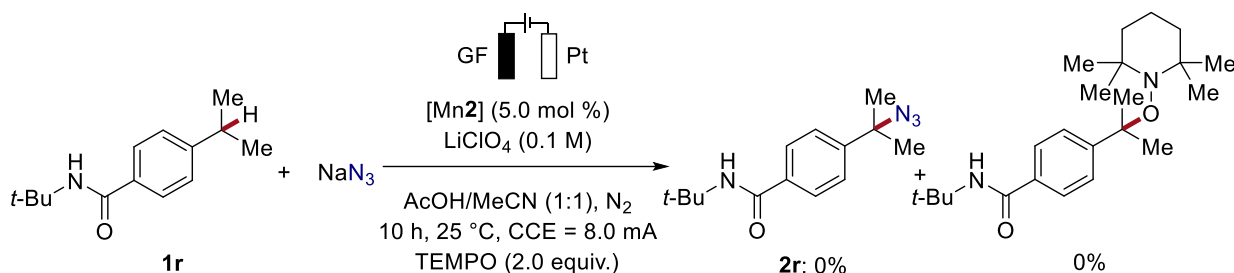
**HR-MS** (ESI)  $m/z$  calcd for C<sub>20</sub>H<sub>23</sub>N<sub>3</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup>: 376.1632, found: 360.1634.

### Gram-Scale Reaction for Manganese-Catalyzed C(sp<sup>3</sup>)-H Azidation

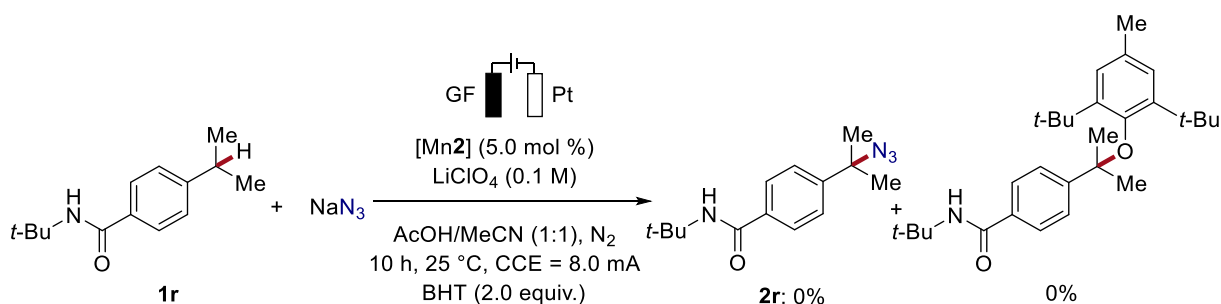
The electrocatalysis was carried out in an undivided cell, with a graphite felt anode (25 mm × 50 mm × 6 mm) and a platinum cathode (25 mm × 50 mm × 0.125 mm). The manganese catalyst [Mn2] (63.6 mg, 125  $\mu$ mol, 2.50 mol %), sodium azide (2.60 g, 40.0 mmol, 8.00 equiv.), substrate **1n** (1.25 g, 5.00 mmol, 1.00 equiv.) and LiClO<sub>4</sub> (532 mg, 5.00 mmol, 1.00 equiv.) were placed in a 100 mL cell under nitrogen atmosphere. The reaction components were dissolved in MeCN (22 mL), followed by AcOH (22 mL) and the reaction mixture was stirred at 750 rpm. The electrodes were connected under vigorous nitrogen-flow. Electrolysis was performed at 25 °C with a constant current of 24 mA maintained for 24 h (4.30 F). At ambient temperature, the reaction mixture was quenched with sat. aq. NaHCO<sub>3</sub> (200 mL) and EtOAc (100 mL) was added, and the graphite felt anode was washed with EtOAc (4 × 25 mL) in an ultrasonic bath. The organic layer was separated, and the aqueous layer was extracted with EtOAc (4 × 50 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvents were removed *in vacuo*. Purification by column chromatography on silica gel (*n*-hexane/Et<sub>2</sub>O 50:1) yielded **2n** (1.22 g, 4.19 mmol, 84%) as a colorless liquid.

## Mechanistic Studies

### Radical Trap Experiments



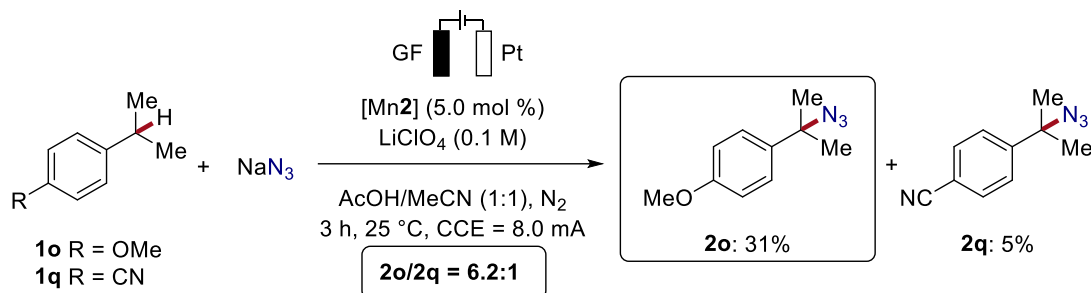
$[\text{Mn}2]$  (12.7 mg, 25.0  $\mu\text{mol}$ , 5.0 mol %), sodium azide (260 mg, 4.00 mmol, 8.00 equiv.), *N*-(*tert*-butyl)-4-isopropylbenzamide **1r** (110 mg, 0.50 mmol, 1.00 equiv.),  $\text{LiClO}_4$  (53.2 mg, 0.50 mmol, 1.00 equiv.) and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (156 mg, 1.00 mmol, 2.0 equiv.) were placed in an undivided cell under nitrogen atmosphere. The reaction components were dissolved in MeCN (2.5 mL), followed by AcOH (2.5 mL) and the reaction mixture was stirred at 400 rpm. The electrodes were connected under vigorous nitrogen-flow. Electrolysis was performed at 25 °C with a constant current of 8 mA maintained for 10 h (5.97 F/mol). The reaction was monitored with ESI mass spectrometry to detect putative reaction intermediates. At ambient temperature, the reaction mixture was quenched with  $\text{H}_2\text{O}$  (20 mL) and EtOAc (10 mL) was added, and the graphite felt anode was washed with EtOAc ( $3 \times 5$  mL) in an ultrasonic bath. The combined mixture was washed with  $\text{H}_2\text{O}$  ( $3 \times 10$  mL), and then dried over  $\text{Na}_2\text{SO}_4$ , filtered and the solvents were removed *in vacuo*. The crude mixture was analyzed by  $^1\text{H-NMR}$  spectroscopy, but no desired product was detected. Column chromatography of the crude reaction mixture afforded substrate **1r** (98.1 mg, 446  $\mu\text{mol}$ , 89%) as the sole product.



$[\text{Mn}2]$  (12.7 mg, 25.0  $\mu\text{mol}$ , 5.0 mol %), sodium azide (260 mg, 4.00 mmol, 8.00 equiv.), *N*-(*tert*-butyl)-4-isopropylbenzamide **1r** (110 mg, 0.50 mmol, 1.00 equiv.),  $\text{LiClO}_4$  (53.2 mg, 0.50 mmol, 1.00 equiv.) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) (220 mg, 1.00 mmol, 2.0 equiv.) were placed in an undivided cell under nitrogen atmosphere. The reaction components were dissolved in MeCN (2.5 mL), followed by AcOH (2.5 mL) and the reaction mixture was

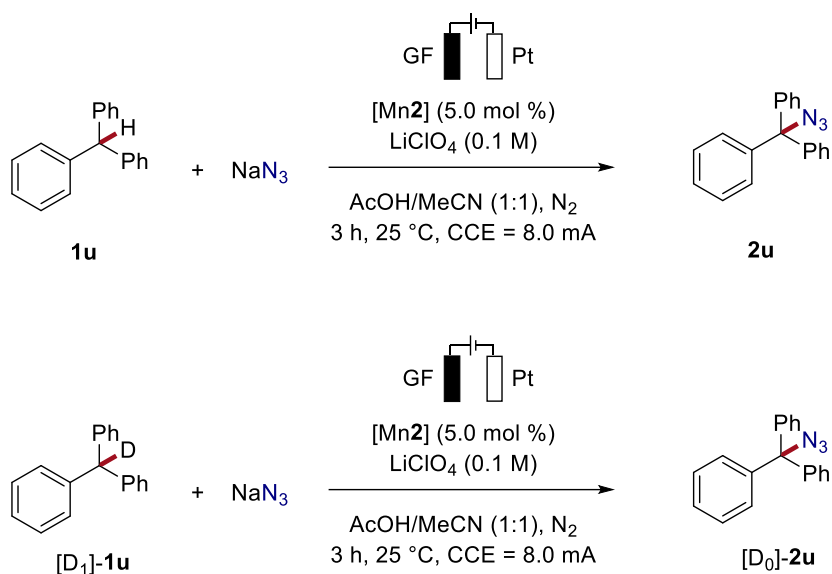
stirred at 400 rpm. The electrodes were connected under vigorous nitrogen-flow. Electrolysis was performed at 25 °C with a constant current of 8 mA maintained for 10 h (5.97 F/mol). At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (20 mL) and EtOAc (10 mL) was added, and the graphite felt anode was washed with EtOAc (3 × 5 mL) in an ultrasonic bath. The combined mixture was washed with H<sub>2</sub>O (3 × 10 mL), and then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvents were removed *in vacuo*. The crude mixture was analyzed by <sup>1</sup>H-NMR spectroscopy, but no desired product was detected.

### Intermolecular Competition Experiment



[Mn2] (12.7 mg, 25.0 μmol, 5.0 mol %), sodium azide (260 mg, 4.00 mmol, 8.00 equiv.), 1-isopropyl-4-methoxybenzene **1o** (75.1 mg, 0.50 mmol, 1.00 equiv.), 4-isopropylbenzonitrile **1q** (72.6 mg, 0.50 mmol, 1.00 equiv.) and LiClO<sub>4</sub> (53.2 mg, 0.50 mmol, 1.00 equiv.) were placed in an undivided cell under nitrogen atmosphere. The reaction components were dissolved in MeCN (2.5 mL), followed by AcOH (2.5 mL) and the reaction mixture was stirred at 400 rpm. The electrodes were connected under vigorous nitrogen-flow. Electrolysis was performed at 25 °C with a constant current of 8 mA maintained for 3 h. At ambient temperature, the reaction mixture was quenched with H<sub>2</sub>O (20 mL) and EtOAc (10 mL) was added, and the graphite felt anode was washed with EtOAc (3 × 5 mL) in an ultrasonic bath. The combined mixture was washed with H<sub>2</sub>O (3 × 10 mL), and then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvents were removed *in vacuo*. Column chromatography (*n*-pentane/EtOAc 99:1 → 10:1) of the crude reaction mixture afforded product **2o** (29.6 mg, 155 μmol, 31%) and product **2q** (4.2 mg, 24.9 μmol, 5%) in a distribution of 6.2:1 in favor of **2o**.

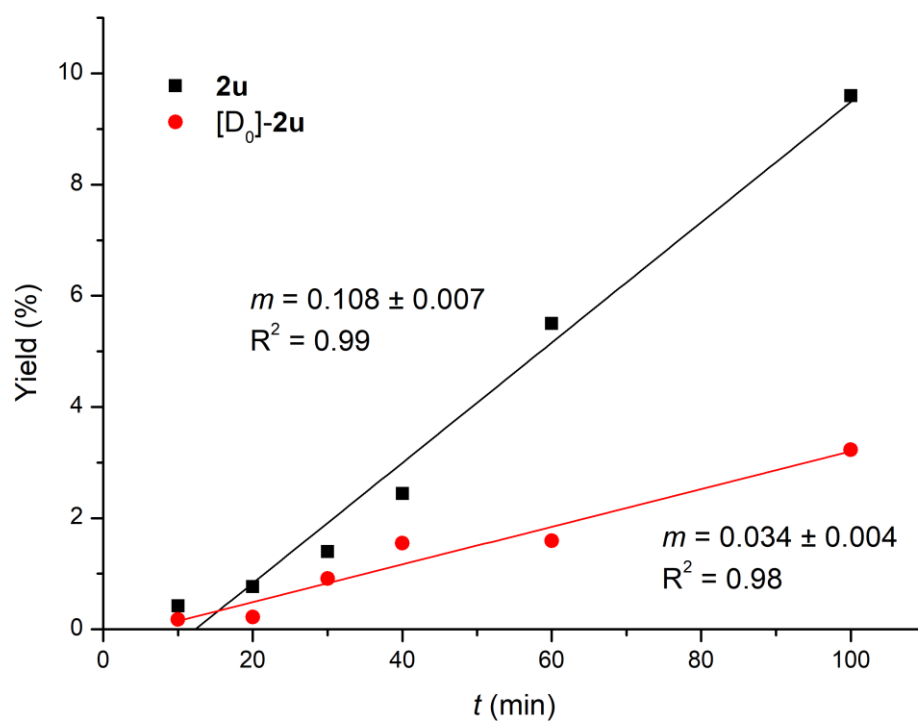
## KIE Studies



Two parallel reactions were run following the procedure **A**, using triphenylmethane **1u** (122.2 mg, 0.50 mmol) or  $[D_1]$ -triphenylmethane **[D<sub>1</sub>]-1u** (122.7 mg, 0.50 mmol), respectively, **[Mn2]** catalyst (12.7 mg, 0.025 mmol),  $\text{LiClO}_4$  (53.2 mg, 0.50 mmol) and sodium azide (260 mg, 4.00 mmol) under  $\text{N}_2$  atmosphere. The suspension was stirred until complete solubilization of all the components, then electricity was applied at a constant current of 8.0 mA. Aliquots of 0.1 mL were prelevated from the cell each fixed interval, quenched with sat. aq.  $\text{NaHCO}_3$  and extracted with a stock solution of *n*-dodecane in EtOAc (0.1 M). The solution was filtered *via* short silica column prior injection to the GC. The yields of the corresponding product were determined by GC-FID in presence of *n*-dodecane as internal standard. The KIE was determined by the analysis of the initial rates (KIE = 3.0).

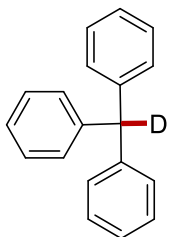
**Table S-6:** GC-Conversion for **1u** and **[D<sub>1</sub>]-1u** during 100 min reaction time.

Time [min]	10	20	30	40	60	100
<b>2u</b> [%]	0.42	0.77	1.4	2.4	5.5	9.6
<b>[D<sub>0</sub>]-2u</b> [%]	0.18	0.22	0.91	1.5	1.6	3.2



**Figure S-1:** Initial rates analysis of **2u** and **[D<sub>0</sub>]-2u**.





### (Methanetriyl-*d*)tribenzene [**D**<sub>1</sub>]-**1u**

[**D**<sub>1</sub>]-**1u** was synthesized according to a modified described procedure.<sup>[30]</sup> AlCl<sub>3</sub> (1.33 g, 10.0 mmol) and the ionic liquid BMIC (0.873 mg, 5.00 mmol) were added into a two neck 100 mL round-bottom flask and kept under *vacuum* at 100 °C for 5 h to remove trace amounts of water. Benzene (27.0 mL, 300 mmol) was then added to the colorless mixture at 0 °C and stirred for 30 minutes before the dropwise addition of CDCl<sub>3</sub> (1.6 mL, 20.0 mmol) at the same temperature. The resulting red suspension was stirred for 14 h at 25 °C. The upper benzene layer, containing the alkylated products, was separated from the rest of the mixture by decantation and the remaining solvent was removed *in vacuo*. Purification by column chromatography on silica gel (*n*-pentane/Et<sub>2</sub>O 95:5) yielded [**D**<sub>1</sub>]-**1u** (670 mg, 2.73 mmol, 14%) as white solid. Deuterium incorporation was >99% based on <sup>1</sup>H-NMR spectroscopy.

**Mp**: 96.5–97.0 °C.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.33–7.26 (m, 6H), 7.25–7.19 (m, 3H), 7.18–7.07 (m, 6H).

**<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 144.0 (C<sub>q</sub>), 129.6 (CH), 128.4 (CH), 126.4 (CH).

**IR**: 1492, 1444, 752, 729, 697, 653, 596, 489, 465 cm<sup>-1</sup>.

**MS** (ESI) *m/z* (relative intensity): 244 (25) [M–D]<sup>+</sup>.

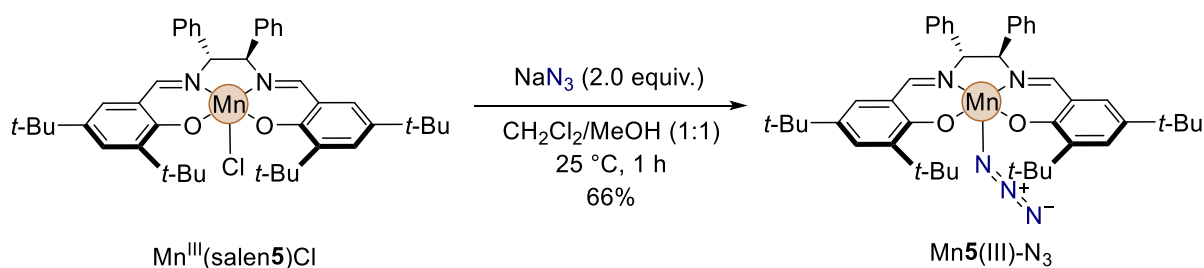
**HR-MS** (EI) *m/z* calcd for C<sub>19</sub>H<sub>15</sub>D<sub>1</sub> [M]<sup>+</sup>: 246.1343, found: 246.1344.

## Synthesis of Manganese Salen Azide Complexes Mn<sup>5</sup>(III)-N<sub>3</sub> and Mn<sup>5</sup>(IV)-(N<sub>3</sub>)<sub>2</sub>

For the synthesis of manganese salen complex Mn<sup>5</sup>(III)-N<sub>3</sub> and Mn<sup>5</sup>(IV)-(N<sub>3</sub>)<sub>2</sub>, procedures by Fuji on related Jacobsen-azide complexes were followed, respectively.<sup>[31]</sup>

### Caution

Special care should be taken for the preparation of the following metal-azide complexes (*vide supra*). The azide complexes are potentially toxic and explosive and should be handled only in small amounts. Due to high solubility of the complexes in chlorinated solvents, synthesis and purification was performed in CH<sub>2</sub>Cl<sub>2</sub>. To prevent unwanted generation of diazidomethane,<sup>[16]</sup> solutions should always be kept at low temperatures and residues should be neutralized immediately after the procedure was completed.



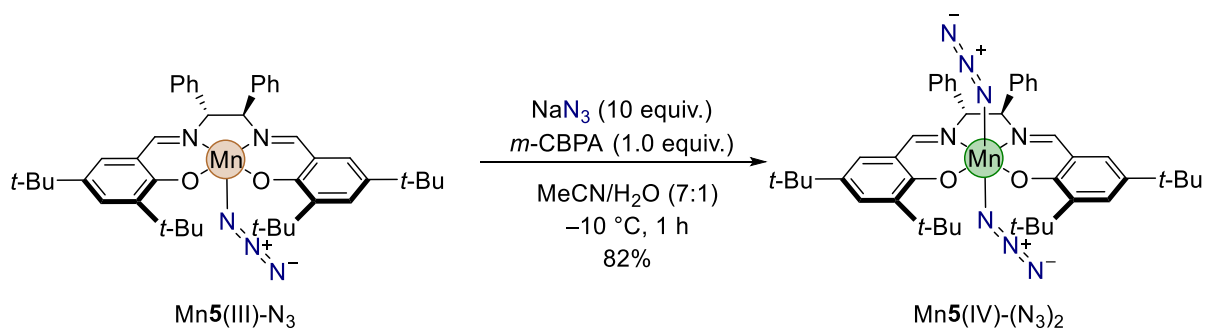
A Schlenk tube was charged with Mn<sup>III</sup>(salen<sup>5</sup>)Cl (366 mg, 0.50 mmol, 1.00 equiv.), CH<sub>2</sub>Cl<sub>2</sub> (5.0 mL) and MeOH (5.0 mL). NaN<sub>3</sub> (65.0 mg, 1.00 mmol, 2.00 equiv.) was dissolved in distilled water (1.0 mL) and added to the mixture. The reaction mixture was stirred at 25 °C for 1 h. Subsequently, the solvent was removed under reduced pressure, at ambient temperature. To the crude solids, CH<sub>2</sub>Cl<sub>2</sub> (5.0 mL) was added and the dark brown solution was filtered over a pad of celite, followed by a second filtration through a membrane syringe filter. Then, the CH<sub>2</sub>Cl<sub>2</sub> was removed *in vacuo* at ambient temperature and the remaining solid was recrystallized from hot MeCN to yield Mn<sup>5</sup>(III)-N<sub>3</sub> (256 mg, 332 μmol, 66%) as dark brown crystallin needles. The azide complex was subsequently stored in a freezer at -32 °C.

**IR** (ATR):  $\tilde{\nu} = 2955, 2905, 2869, 2044, 2026, 1608, 1532, 1429, 1313, 1251, 699 \text{ cm}^{-1}$ .

**MS** (ESI)  $m/z$  (relative intensity): 697 (100) [M-N<sub>3</sub>]<sup>+</sup>.

**HR-MS** (ESI)  $m/z$  calcd for C<sub>44</sub>H<sub>54</sub>MnN<sub>2</sub>O<sub>2</sub> [M-N<sub>3</sub>]<sup>+</sup>: 697.3560, found: 697.3560.

**Anal.** calcd for C<sub>44</sub>H<sub>54</sub>MnN<sub>5</sub>O<sub>2</sub>: C, 71.43; H, 7.36; N, 9.47. Found: C, 69.19; H, 7.28; N, 9.11.



A Schlenk tube was charged with Mn5(III)-N<sub>3</sub> (74.0 mg, 0.10 mmol, 1.00 equiv.) and MeCN (5.0 mL). NaN<sub>3</sub> (65.0 mg, 1.00 mmol, 10.0 equiv.) and *meta*-chloroperoxybenzoic acid (24.7 mg, 0.1 mmol, 1.00 equiv.) were dissolved in distilled water (1.0 mL) and slowly added to the mixture at -10 °C. The reaction mixture was stirred at -10 °C for 1 h. Subsequently, the solvent was removed under reduced pressure, at -10 °C. To the crude solids, CH<sub>2</sub>Cl<sub>2</sub> (5.0 mL) was added and the dark green solution was filtered over a pad of celite, followed by a second filtration through a membrane syringe filter. Recrystallisation from CH<sub>2</sub>Cl<sub>2</sub> and pentane at -32 °C afforded Mn5(IV)-(N<sub>3</sub>)<sub>2</sub> (64.1 mg, 82.0 μmol, 82%) as dark green crystallin solid. The azide complex was subsequently stored in a freezer at -32 °C.

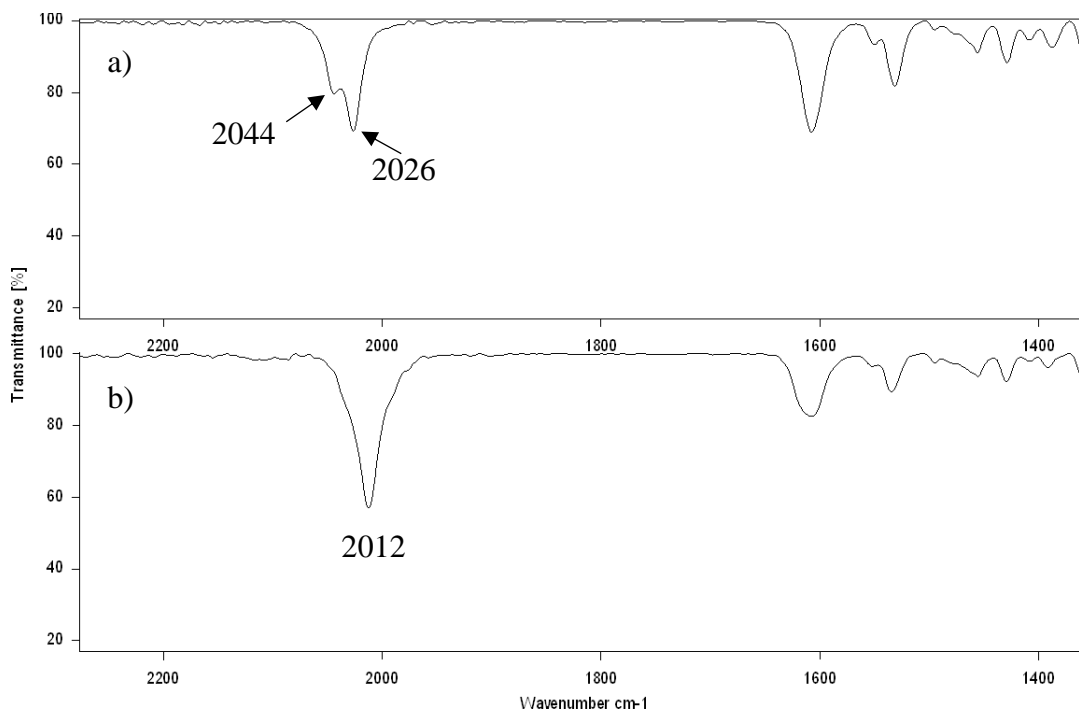
**IR** (ATR):  $\tilde{\nu} = 2956, 2906, 2869, 2012, 1608, 1534, 1430, 1309, 1249, 699 \text{ cm}^{-1}$ .

**MS** (ESI)  $m/z$  (relative intensity): 1438 (15) [2M-3N<sub>3</sub>]<sup>+</sup>, 781 (5) [M]<sup>+</sup>, 762 (5) [M-N<sub>3</sub>+Na]<sup>+</sup>, 739 (5) [M-N<sub>3</sub>]<sup>+</sup>, 697 (100) [M-2N<sub>3</sub>]<sup>+</sup>.

**HR-MS** (ESI)  $m/z$  calcd for C<sub>44</sub>H<sub>54</sub>MnN<sub>5</sub>O<sub>2</sub>Na [M-N<sub>3</sub>+Na]<sup>+</sup>: 762.3550, found: 762.3535.

**Anal.** calcd for C<sub>44</sub>H<sub>54</sub>MnN<sub>8</sub>O<sub>2</sub>: C, 67.59; H, 6.96; N, 14.33. Found: C, 67.01; H, 6.91; N, 13.94.

Previous studies have investigated and unambiguously characterized similar manganese(III)/(IV) Schiff base complexes.<sup>31</sup> The authors had shown analogous issues with the mass-spectrometric detection of manganese(IV) azide complexes and commonly no MS-data was reported. In fact, the signal intensity in the LR-MS(ESI) for the Mn5(IV)-(N<sub>3</sub>)<sub>2</sub> (with matching isotopic pattern) is very low and the corresponding HR-MS(ESI) did not match. However, elemental analysis, CV and IR-spectroscopy provide strong support for the formation of the manganese(IV) complex Mn5(IV)-(N<sub>3</sub>)<sub>2</sub>. Furthermore, the ESI source can be described as a small electrolytic cell and redox reactions are forced to occur. Although oxidation reactions are reported to occur more frequently in positive ESI-MS, reduction of substrates in positive electrospray ionization mass spectrometry has likewise been reported, such as for quinone derivates (*J. Am. Soc. Mass Spectrom.* **2017**, *28*, 2454–2461) or copper(II) complexes (*Rapid Commun Mass Spectrom* **2001**, *15*, 2347–2353).



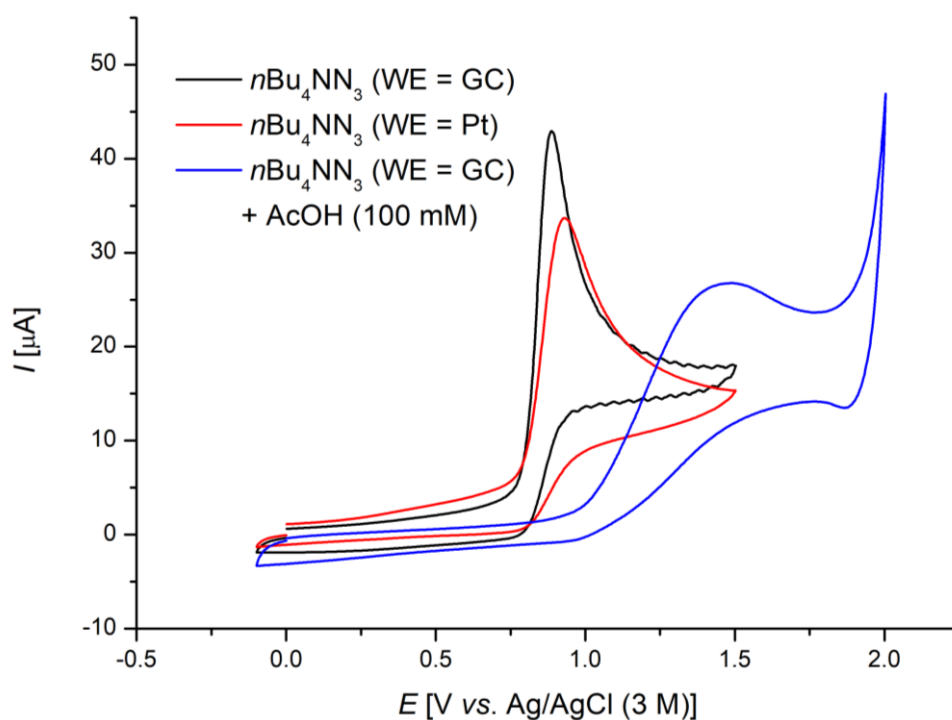
**Figure S-2:** IR spectra comparison of the asymmetric stretching vibrations ( $\nu_{as}$ ) of NNN at a) Mn5(III)-N<sub>3</sub> and b) Mn5(IV)-(N<sub>3</sub>)<sub>2</sub>.

Figure S-2 shows IR bands at 2044 and 2026  $\text{cm}^{-1}$  for complex Mn5(III)-N<sub>3</sub>. The appearance of two distinct asymmetric stretching vibrations ( $\nu_{as}$ ) for the manganese(III) azide complex is in agreement to previous studies of Fuji<sup>[31b]</sup> and can be explained due to the presence of differently azide-bridged, polymeric complexes in solution<sup>[32]</sup> or the presence of different complexes in asymmetric cells, resulting in different N–N–N angles and different azide bond lengths, which was supported by previously published crystal structures of similar complexes.<sup>[31b]</sup> The asymmetric azide stretching vibration is significantly shifted to lower wavelength of  $\nu_{as} = 2012 \text{ cm}^{-1}$  (Mn5(IV)-(N<sub>3</sub>)<sub>2</sub>) upon oxidation of the manganese(III) complex to manganese(IV). This result is giving strong support that the azide bond is significantly weakened upon oxidation of the complex.

The IR bands at 1608  $\text{cm}^{-1}$  for Mn5(III)-N<sub>3</sub> and 1608  $\text{cm}^{-1}$  Mn5(IV)-(N<sub>3</sub>)<sub>2</sub> can be assigned to the C=N stretching mode of the salen ligand, respectively. Thus, revealing only minor or no changes in the salen ligand bond length due to oxidation of the manganese central atom.

## Cyclic Voltammetry

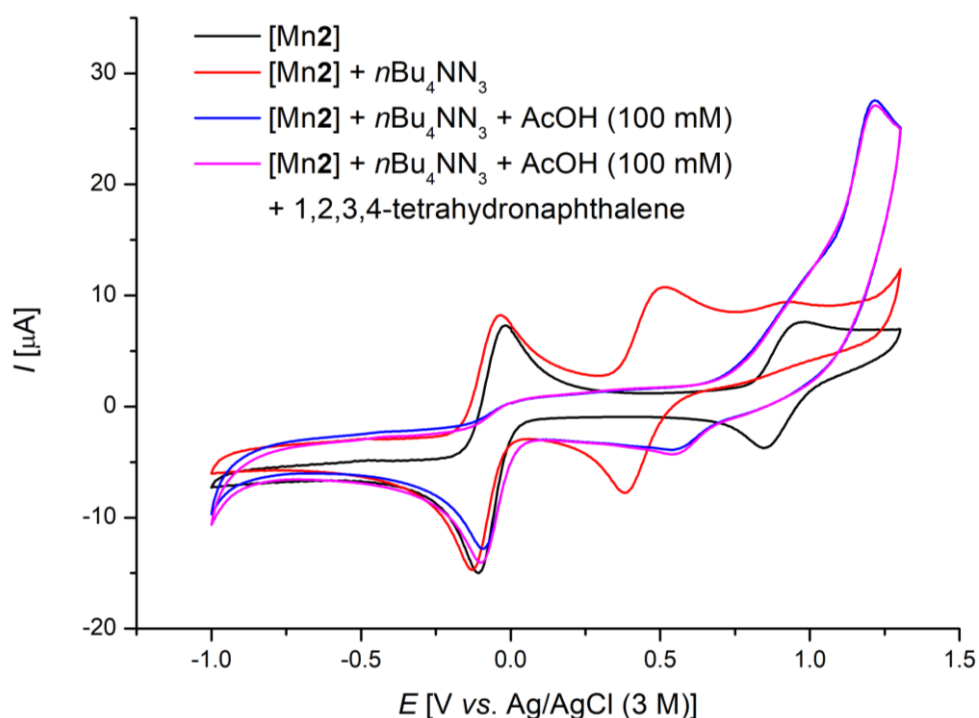
The cyclic voltammetry measurements were carried out using a Metrohm Autolab PGSTAT204 workstation, and the following analysis was performed with Nova 2.1 software. For all experiments a glassy-carbon (GC) electrode (3 mm-diameter, disc-electrode) was used as the working electrode (WE) and a Ag/AgCl (3 M KCl) was used as the reference electrode (RE), if not stated otherwise. The counter electrode (CE) was a coiled platinum wire ( $d = 1$  mm). Measurements were recorded at a scan rate of  $100 \text{ mVs}^{-1}$ , if not indicated otherwise. The working temperature was 298 K. All solutions were degassed via freeze-pump-thaw method prior to use and nitrogen was bubbled through the solutions for at least 5 min before the experiment was performed. The experiments were performed under a constant flow of dry nitrogen. Acetonitrile (MeCN) with 0.1 mol/L  $\text{LiClO}_4$  as conducting salt served as electrolyte for the measurements. The concentration of the analyte was 0.3 mmol/L or not stated otherwise.



**Figure S-3.** Cyclic voltammetry of tetra-*n*-butylammonium azide (0.3 mM) at GC (black) or Pt (red, 3 mm-diameter, disc-electrode) in absence of or and in presence of an excess of AcOH (blue, 100 mM).

The electroanalytic investigation of tetra-*n*-butylammonium azide revealed an anodic onset potential of  $+0.75 \text{ V vs. Ag/AgCl (3 M KCl)}$ , with a irreversible peak potential of  $E_{p,a} = 0.88 \text{ V}$  and  $E_{p,a} = 0.94 \text{ V}$  for GC and Pt as the WE, respectively. This result is indicative, that the anodic working electrode should not have a large influence on the anodic oxidation of azide

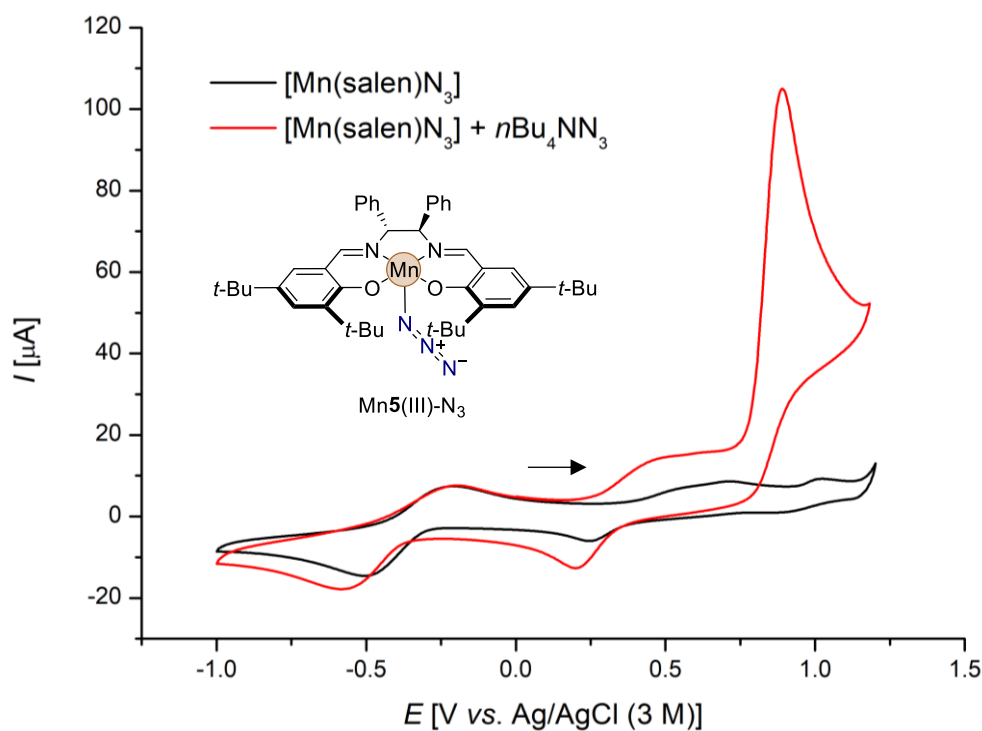
anions. However, it was found that Pt-WE showed no product formation under the reaction conditions (see Table-S4, entry 10). Upon addition of glacial acetic acid (100 mM) the irreversible anodic oxidation event was shifted to an onset potential of 1.0 V vs. Ag/AgCl (3 M KCl) and peak potential of  $E_{p,a} = 1.45$  V. The difference for the oxidation potential is illustrative for a pH dependent oxidation event, following the Nernst equation.



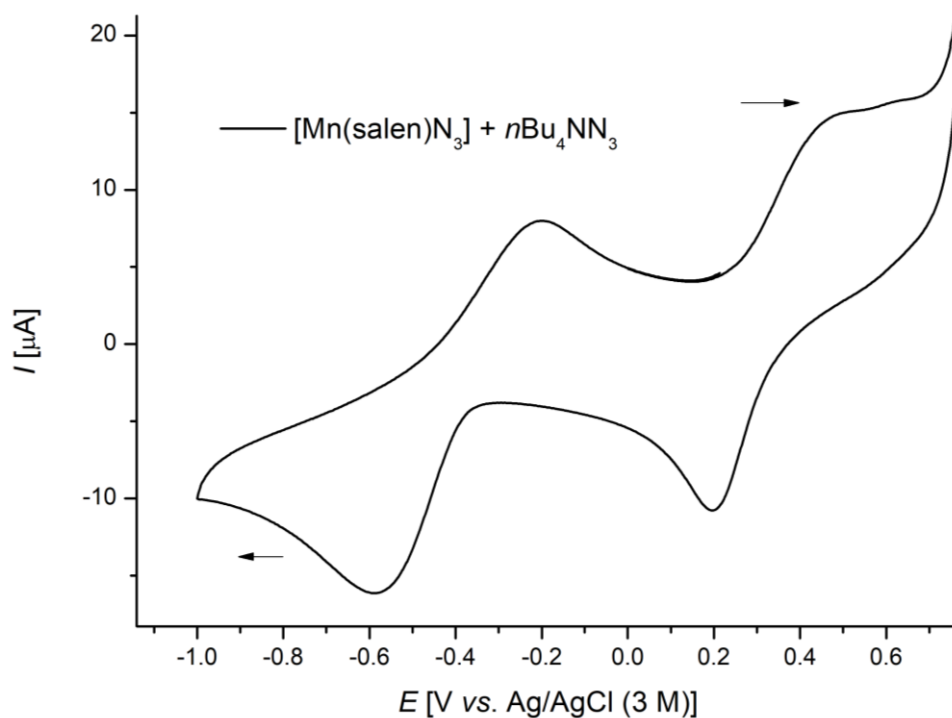
**Figure S-4.** Cyclic voltammetry of a)  $\text{Mn}^{\text{III}}(\text{salen}2)\text{Cl}$  (black); b) in the presence of tetra-*n*-butylammonium azide (red); c) as b) but with the addition of acetic acid (100 mM); d) as c) but in the presence of 1,2,3,4-tetrahydronaphthalene **1a**.

The manganese(III) chloride complex  $[\text{Mn}2]$  showed two redox potentials in acetonitrile. The first, reversible redox event ( $\Delta E_p = 0.091$  V) at  $E_{1/2} = -0.062$  V vs. Ag/AgCl (3 M KCl) was attributed to the Mn(II)/Mn(III) redox couple. The second, quasi-reversible redox-event ( $\Delta E_p = 0.112$  V) at  $E_{1/2} = 0.906$  V vs. Ag/AgCl (3 M KCl) was attributed to the Mn(III)/Mn(IV) redox couple.<sup>[33]</sup> However, reports by Fuji on similar complexes gave strong support for a ligand-centered electron transfer.<sup>[34]</sup> Upon addition of the azide salt, the first, reversible redox event ( $\Delta E_p = 0.091$  V) at  $E_{1/2} = -0.086$  V vs. Ag/AgCl (3 M KCl) was only slightly shifted ( $\Delta E_{1/2} = 0.026$  V). However, a significant change of the second, quasi-reversible redox event ( $\Delta E_p = 0.132$  V) was detected ( $E_{1/2} = 0.448$  V vs. Ag/AgCl (3 M KCl)). The difference ( $\Delta E_{1/2} = 0.458$  V) can be explained by stabilization of the oxidized products by addition of  $\text{N}_3^-$  resulting

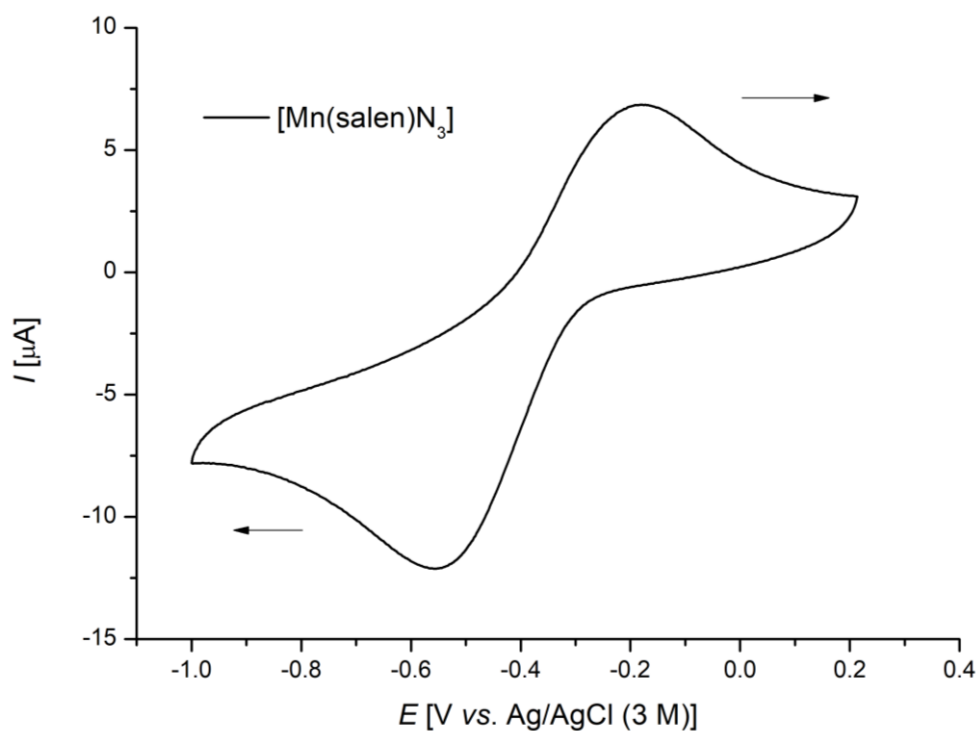
in Mn2(IV)-(N<sub>3</sub>)<sub>2</sub> complexes (*vide infra*). The result is in accordance with similar studies reported earlier, albeit with chloride or cyanide anions.<sup>[35, 33a]</sup> The small irreversible anodic event at  $E_{p,a} = 0.93$  V represents most-likely non-coordinating azide anions, decoordinated chloride anions or free manganese(III) chloride complex [Mn2]. In the presence of an excess of acetic acid, the redox events are diminished, supportive for chemical follow-up reactions.



**Figure S-5.** Cyclic voltammograms of Mn5(III)-N<sub>3</sub> (0.3 mM) in the presence (red) and absence (black) of additional tetra-*n*-butylammonium azide.



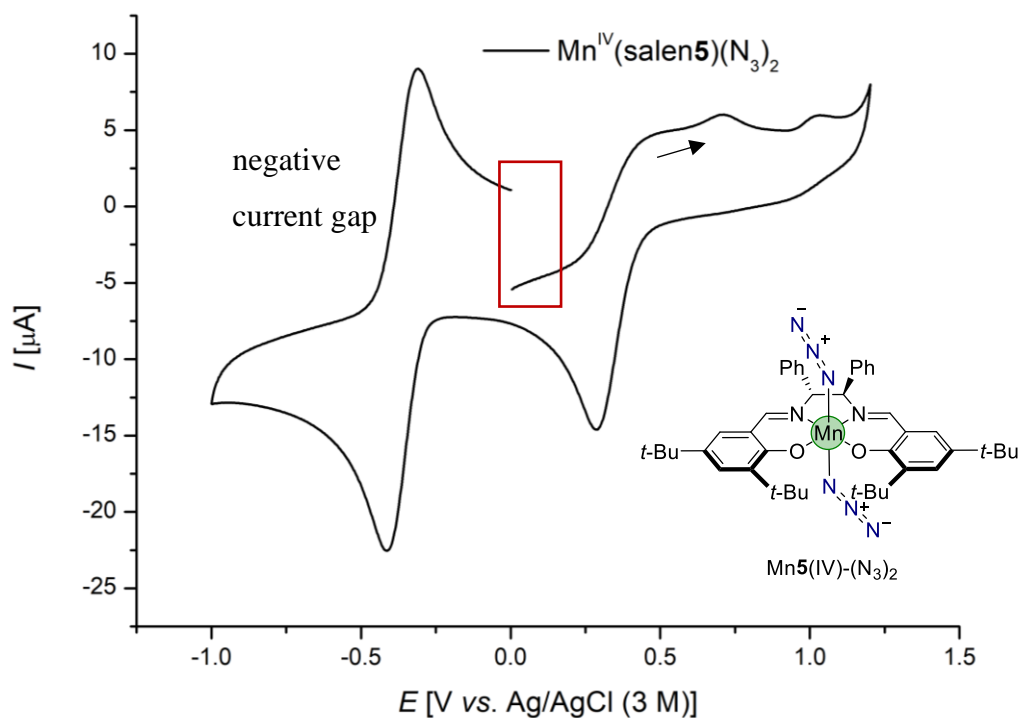
**Figure S-6.** Cyclic voltammograms of Mn5(III)-N<sub>3</sub> (0.3 mM) in the presence of tetra-*n*-butylammonium azide.



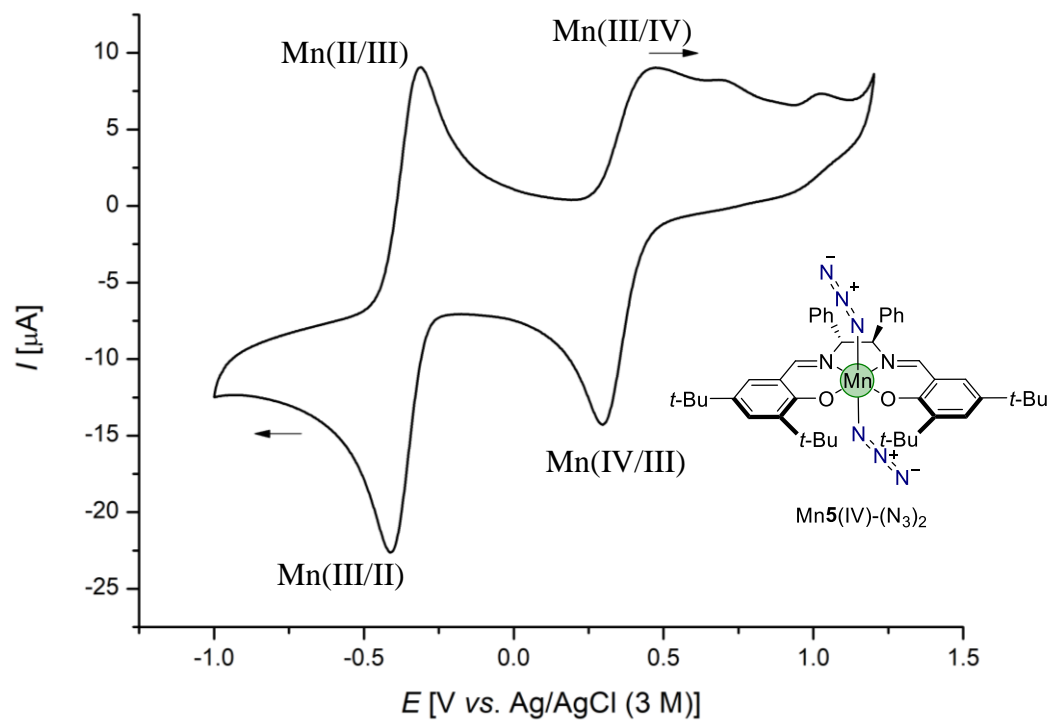
**Figure S-7.** Cyclic voltammograms of Mn5(III)-N<sub>3</sub> (0.3 mM). Two voltammograms were recorded, and the second voltammogram is presented.



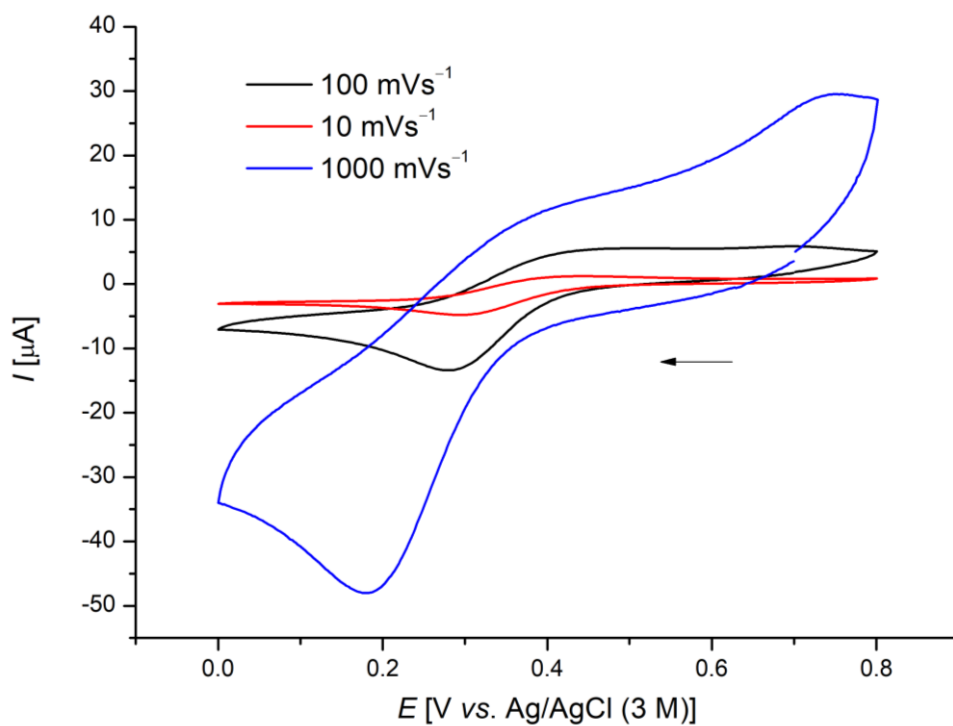
The well-defined manganese(III) azide complex **Mn5(III)-N<sub>3</sub>** showed sluggish redox behavior. The first, quasi-reversible redox event ( $\Delta E_p = 0.372$  V) at  $E_{1/2} = -0.368$  V vs. Ag/AgCl (3 M KCl) was attributed to the Mn(II)/Mn(III) redox couple, thus revealing a more difficult reduction compared to the manganese(III) chloride complex [**Mn2**]. The second, quasi-reversible redox-event ( $\Delta E_p = 0.264$  V) at  $E_{1/2} = 0.328$  V vs. Ag/AgCl (3 M KCl) was attributed to the Mn(III)/Mn(IV) redox couple. Addition of tetra-*n*-butylammonium azide led to increased current response for the second redox event, which is supportive for the anodic formation of the **Mn5(IV)-(N<sub>3</sub>)<sub>2</sub>** complex.



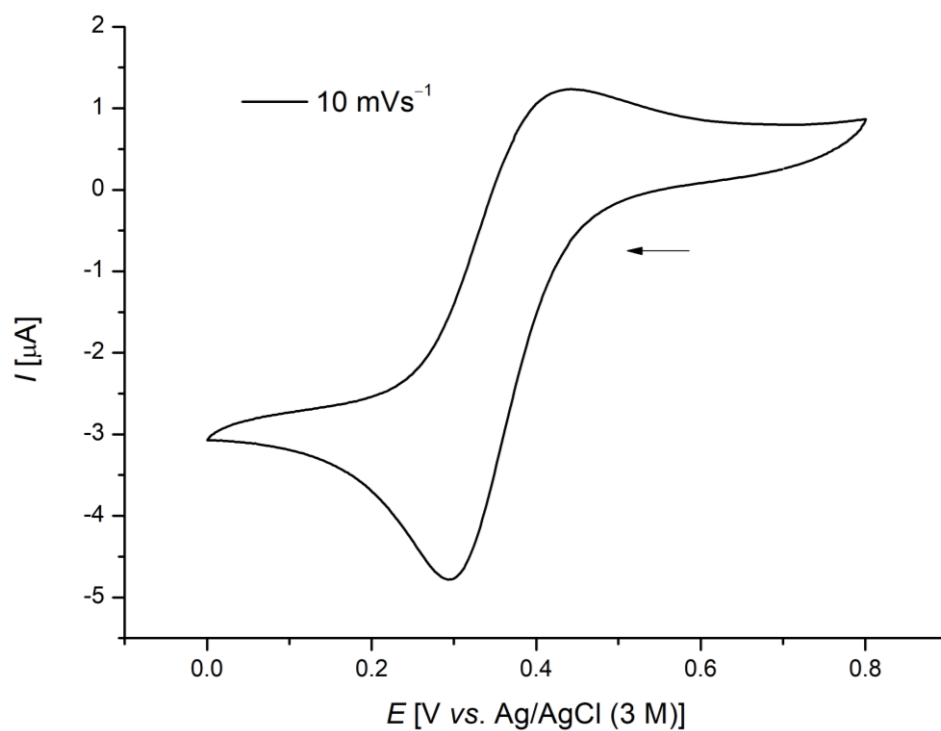
**Figure S-8.** Cyclic voltammograms of  $\text{Mn5(IV)-(N}_3)_2$  (0.3 mM). Two voltammograms were recorded, and the first voltammogram is presented. Starting potential was  $E = 0$  V, with a positive sweep direction.



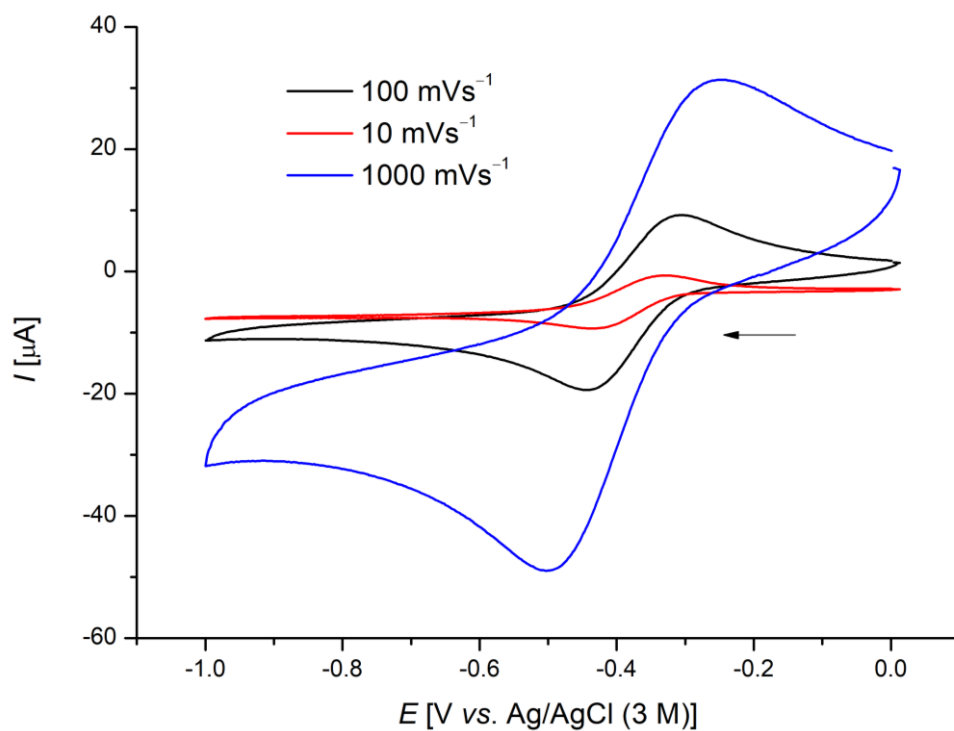
**Figure S-9.** Cyclic voltammograms of  $\text{Mn5(IV)-(N}_3)_2$  (0.3 mM). Two voltammograms were recorded, and the second voltammogram is presented.



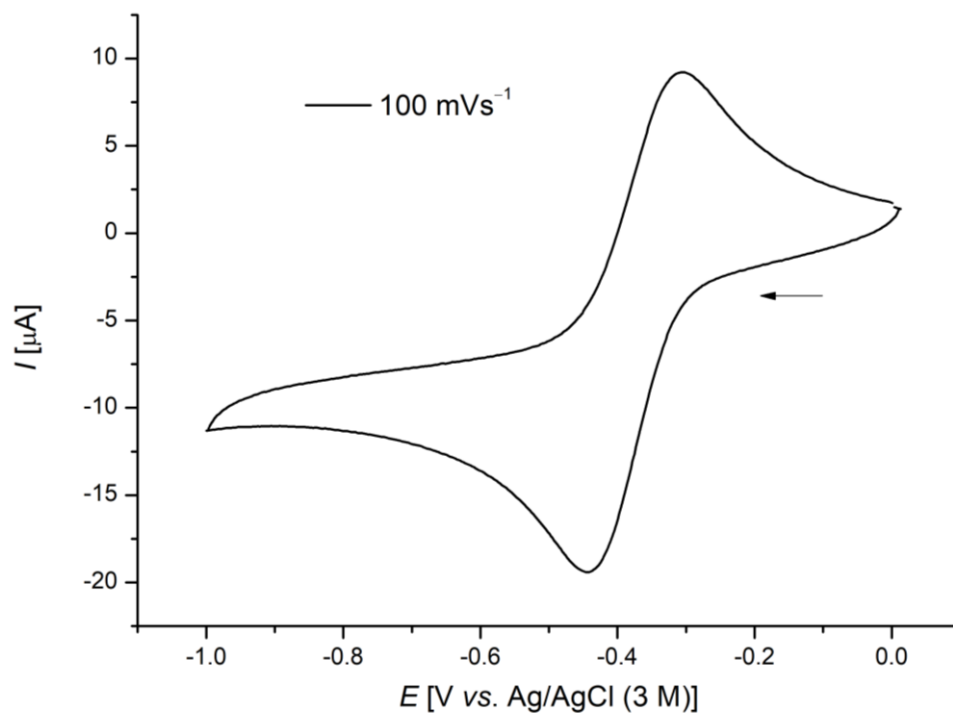
**Figure S-10.** CVs of complex  $\text{Mn5(IV)-(N}_3)_2$  (0.3 mM) at different scan rates. Sweep direction was negative, with a starting potential of 0.8 V on the WE.



**Figure S-11.** CV of complex  $\text{Mn5(IV)-(N}_3)_2$  (0.3 mM) at 10  $\text{mVs}^{-1}$ . Sweep direction was negative, with a starting potential of 0.8 V on the WE.



**Figure S-12.** CVs of complex  $\text{Mn5(IV)-(N}_3)_2$  (0.3 mM) at different scan rates. Sweep direction was negative, with a starting potential of 0.0 V on the WE.



**Figure S-13.** CV of complex  $\text{Mn5(IV)-(N}_3)_2$  (0.3 mM) at 100  $\text{mVs}^{-1}$ . Sweep direction was negative, with a starting potential of 0.0 V on the WE.

The well-defined manganese(IV) azide complex  $\text{Mn}^{\text{IV}}(\text{N}_3)_2$  showed two quasi-reversible redox events (Figure S-8 and S-9). When the first voltammogram was recorded with a starting potential of  $E = 0 \text{ V}$ , a negative current was detected, indicating that the manganese(IV) complex already got reduced at that potential (Figure S-8). Previous reports by Fuji on similar complexes assigned the manganese(III/IV) redox couple to potentials at  $E_{1/2} = -0.17 \text{ V vs. Fc/Fc}^+$ .<sup>[31b]</sup> The second voltammogram of the same mixture revealed both quasi-reversible redox events (Figure S-9). The first quasi-reversible redox event ( $\Delta E_p = 0.136 \text{ V}$ ) at  $E_{1/2} = -0.370 \text{ V vs. Ag/AgCl (3 M KCl)}$  was attributed to the Mn(II)/Mn(III) redox couple with a concomitant loss of both  $\text{N}_3$  ligands, which was reflected in a EC mechanism. The second, quasi-reversible redox-event ( $\Delta E_p = 0.174 \text{ V}$ ) at  $E_{1/2} = 0.366 \text{ V vs. Ag/AgCl (3 M KCl)}$  or  $E_{1/2} = 0.071 \text{ V vs. Fc/Fc}^+$  was attributed to the Mn(III)/Mn(IV) redox couple. Cyclic voltammograms at different scanning rate revealed a fast chemical follow-up reaction upon reduction of the manganese(IV) complex (Figure S-10).

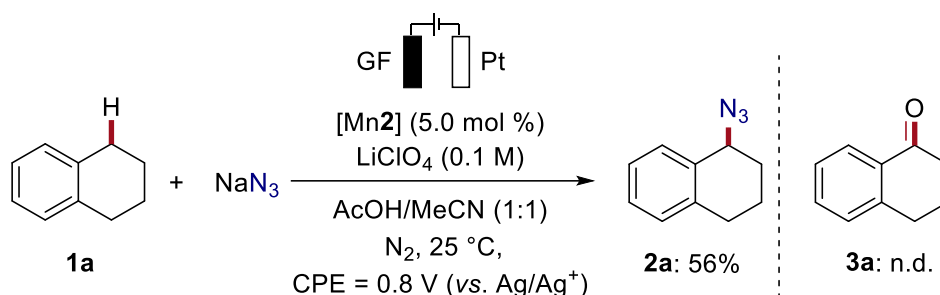
## Constant Potential Electrolysis

For chronoamperometric experiments, a silver-wire ( $d = 1$  mm) was used as the pseudo-reference electrode in close proximity to the graphite felt working electrode. To ensure comparable constant potential conditions with the results gained by cyclic voltammetry, calibration of the silver-wire reference electrode *versus* ferrocene was performed.

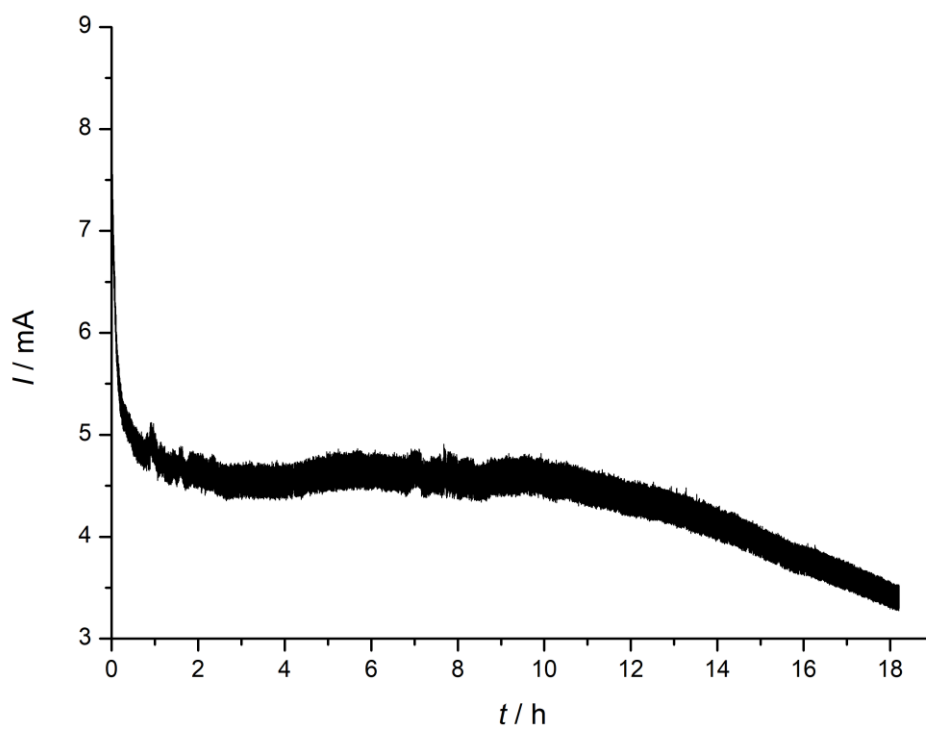
$$E_{\frac{1}{2}}(\text{Fc}|\text{Fc}^+) = 0.36 \text{ V (vs. Ag|AgCl)}$$

$$E_{\frac{1}{2}}(\text{Fc}|\text{Fc}^+) = 0.29 \text{ V (vs. Ag|Ag}^+)$$

Based on previous CV studies, no direct azide oxidation should occur in MeCN/AcOH solvent mixtures at potentials below 1.0 V *vs.* Ag/Ag<sup>+</sup>.



The constant potential electrolysis was carried out in an undivided cell, with a graphite felt anode (10 mm × 15 mm × 6 mm), a platinum cathode (10 mm × 15 mm × 0.125 mm) and a silver wire as the reference electrode. The manganese catalyst [Mn2] (12.7 mg, 25.0 μmol, 5.0 mol %), sodium azide (260 mg, 4.00 mmol, 8.00 equiv.), 1,2,3,4-tetrahydronaphthalene **1a** (66.1 mg, 0.50 mmol, 1.00 equiv.) and  $\text{LiClO}_4$  (53.2 mg, 0.50 mmol, 1.00 equiv.) were placed in a 10 mL cell under nitrogen atmosphere. The reaction components were dissolved in MeCN (2.5 mL), followed by AcOH (2.5 mL) and the reaction mixture was stirred at 400 rpm. The electrodes were connected under vigorous nitrogen-flow. Electrolysis was performed at 25 °C with a constant potential of 0.8 V (vs. Ag/Ag<sup>+</sup>) maintained for 20 h. At ambient temperature, the reaction mixture was quenched with sat. aq.  $\text{NaHCO}_3$  (20 mL) and EtOAc (10 mL) was added, and the graphite felt anode was washed with EtOAc (3 × 5 mL) in an ultrasonic bath. The combined mixture was washed with  $\text{H}_2\text{O}$  (3 × 10 mL), and then dried over  $\text{Na}_2\text{SO}_4$ , filtered and the solvents were removed *in vacuo*. Purification by column chromatography on silica gel (*n*-pentane/EtOAc 99:1) yielded **2a** (48.8 mg, 282 μmol, 56%) as a colorless liquid.

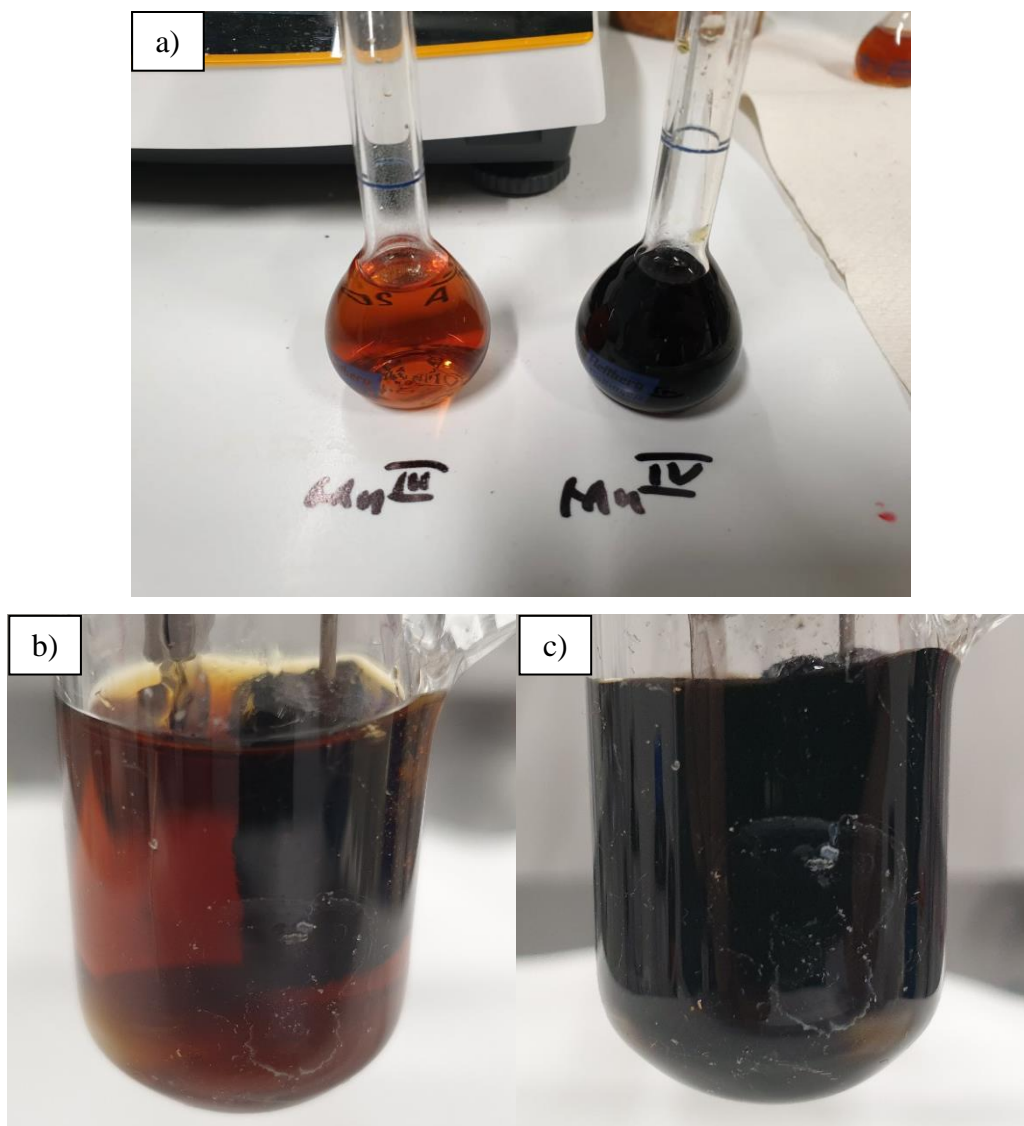


**Figure S-14.** Chronoamperometry at 0.8 V vs. Ag/Ag<sup>+</sup>; resulting current-time response.

The strong interferences in current response during the recording are most likely caused by the stirring plate below the electrolysis cell.

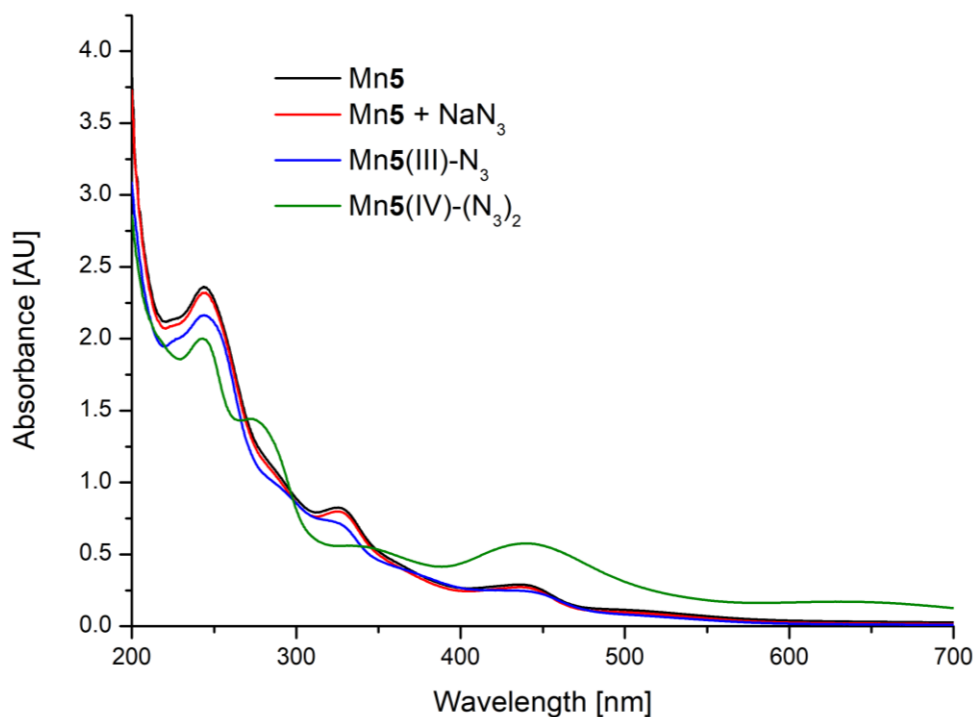
## UV–Vis Spectroscopy

The UV–vis absorption spectroscopy was carried out using a Jasco V-770 UV-vis/NIR spectrophotometer. The working temperature was 298 K and a quartz cell ( $l = 1$  cm) was used. The experiments were performed under a  $N_2$  atmosphere if not stated otherwise. The concentration of the analyte was  $4 \cdot 10^{-5}$  mol/L and  $5 \cdot 10^{-5}$  mol/L for the reaction mixtures, respectively. Acetonitrile (HPLC-grade) was used as the solvent.

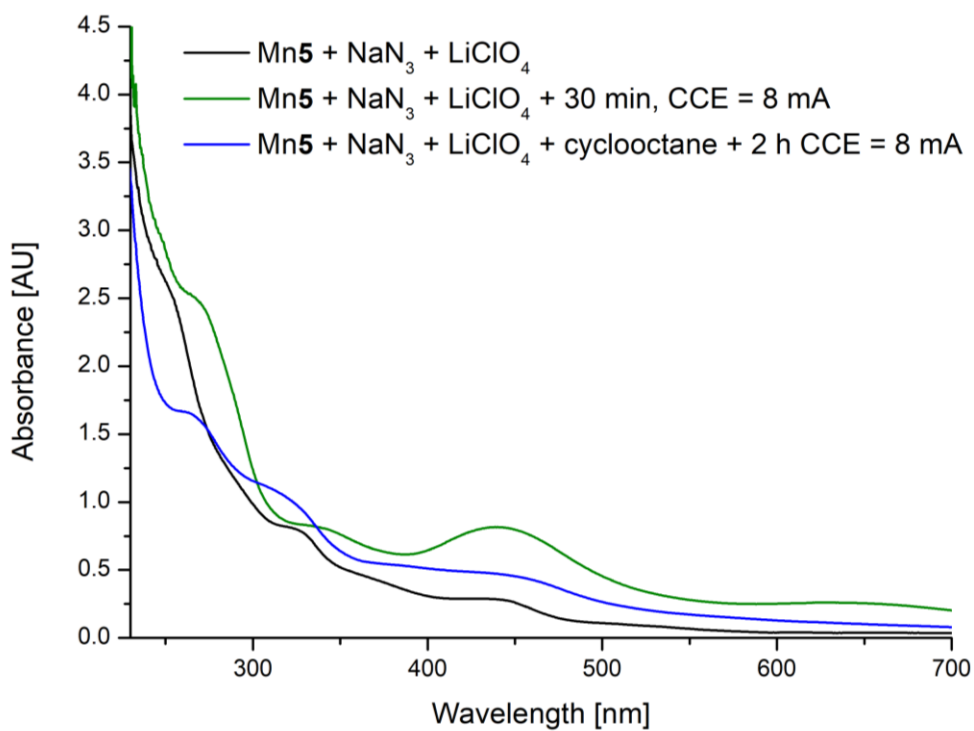


**Figure S-15.** a) Solutions of Mn5(III)-N<sub>3</sub> (brown) and Mn5(IV)-(N<sub>3</sub>)<sub>2</sub> (dark green) in MeCN ( $4 \cdot 10^{-5}$  mol/L). b) Reaction mixture **B** before electrolysis. c) Reaction mixture **B** after 30 min electrolysis with a constant current of 8 mA.





**Figure S-16.** UV-vis studies in MeCN. a) Mn5(III)-Cl [Mn5] (black). b) [Mn5] and NaN<sub>3</sub> (red). c) Mn5(III)-N<sub>3</sub> (blue). d) Mn5(IV)-(N<sub>3</sub>)<sub>2</sub> (green).



**Figure S-17.** UV-vis studies in MeCN. a) A mixture of [Mn5], NaN<sub>3</sub> and LiClO<sub>4</sub> (black). b) Reaction mixture A (green). c) Reaction mixture B (blue).

Due to the absorption of the acetic acid at wavelength lower than 230 nm, the spectra in Figure S-17 was reduced to that minimum.

#### **Preparation of Reaction mixture A**

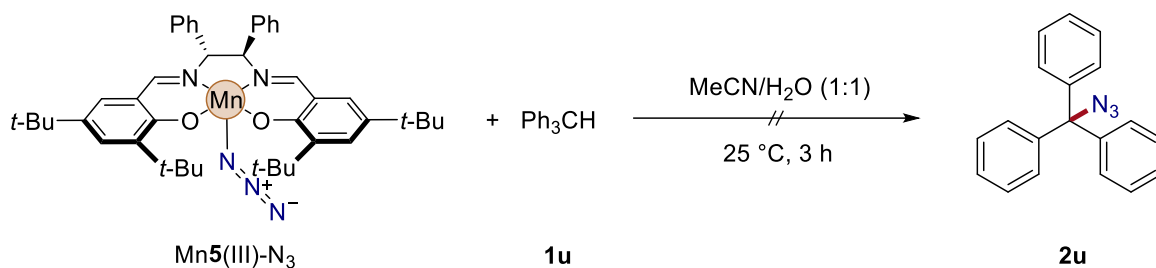
The constant current electrolysis was carried out using standard conditions (*vide supra*). The manganese catalyst [Mn5] (18.3 mg, 25.0  $\mu\text{mol}$ , 5.0 mol %), sodium azide (260 mg, 4.00 mmol, 8.00 equiv.) and  $\text{LiClO}_4$  (53.2 mg, 0.50 mmol, 1.00 equiv.) were placed in a 10 mL cell under nitrogen atmosphere. The reaction components were dissolved in MeCN (2.5 mL), followed by AcOH (2.5 mL) and the reaction mixture was stirred at 400 rpm. The electrodes were connected under vigorous nitrogen-flow. Electrolysis was performed at 25 °C with a constant potential of 8 mA maintained for 30 min. Within few seconds, the dark brown solution turned dark green/black (see Figure S-15). At ambient temperature, 1.0 mL of the crude mixture was removed and diluted to  $5 \cdot 10^{-5}$  mol/L. The diluted mixture was transferred into the cuvette and a UV-vis spectrum was recorded immediately.

#### **Preparation of Reaction mixture B**

The constant current electrolysis was carried out using standard conditions (*vide supra*). The manganese catalyst [Mn5] (18.3 mg, 25.0  $\mu\text{mol}$ , 5.0 mol %), sodium azide (260 mg, 4.00 mmol, 8.00 equiv.),  $\text{LiClO}_4$  (53.2 mg, 0.50 mmol, 1.00 equiv.) and cyclooctane **1b** (56.1 mg, 0.50 mmol) were placed in a 10 mL cell under nitrogen atmosphere. The reaction components were dissolved in MeCN (2.5 mL), followed by AcOH (2.5 mL) and the reaction mixture was stirred at 400 rpm. The electrodes were connected under vigorous nitrogen-flow. Electrolysis was performed at 25 °C with a constant potential of 8 mA maintained for 120 min. Similar to reaction mixture A, the dark brown solution turned dark green/black within few seconds (see Figure S-15). At ambient temperature, 1.0 mL of the crude mixture was removed and diluted to  $5 \cdot 10^{-5}$  mol/L. The diluted mixture was transferred into the cuvette and a UV-vis spectrum was recorded immediately.

### Stoichiometric C–H Azidation using Mn5(III)-N<sub>3</sub>

A mixture of Mn5(III)-N<sub>3</sub> (74.0 mg, 0.10 mmol, 2.00 equiv.) and triphenylmethane (12.2 mg, 50 μmol, 1.00 equiv.) in MeCN (0.50 mL) and AcOH (0.50 mL) was stirred for 3 h at 25 °C. Then, the solvent was evaporated, and the crude reaction mixture was purified by column chromatography on silica gel (*n*-hexane to *n*-hexane/Et<sub>2</sub>O 20:1). No azidation product **2u** was obtained and only unreacted triphenylmethane **1u** (11.0 mg, 45 μmol, 90%) was recovered as a white solid.

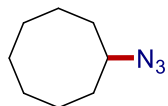


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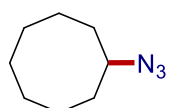
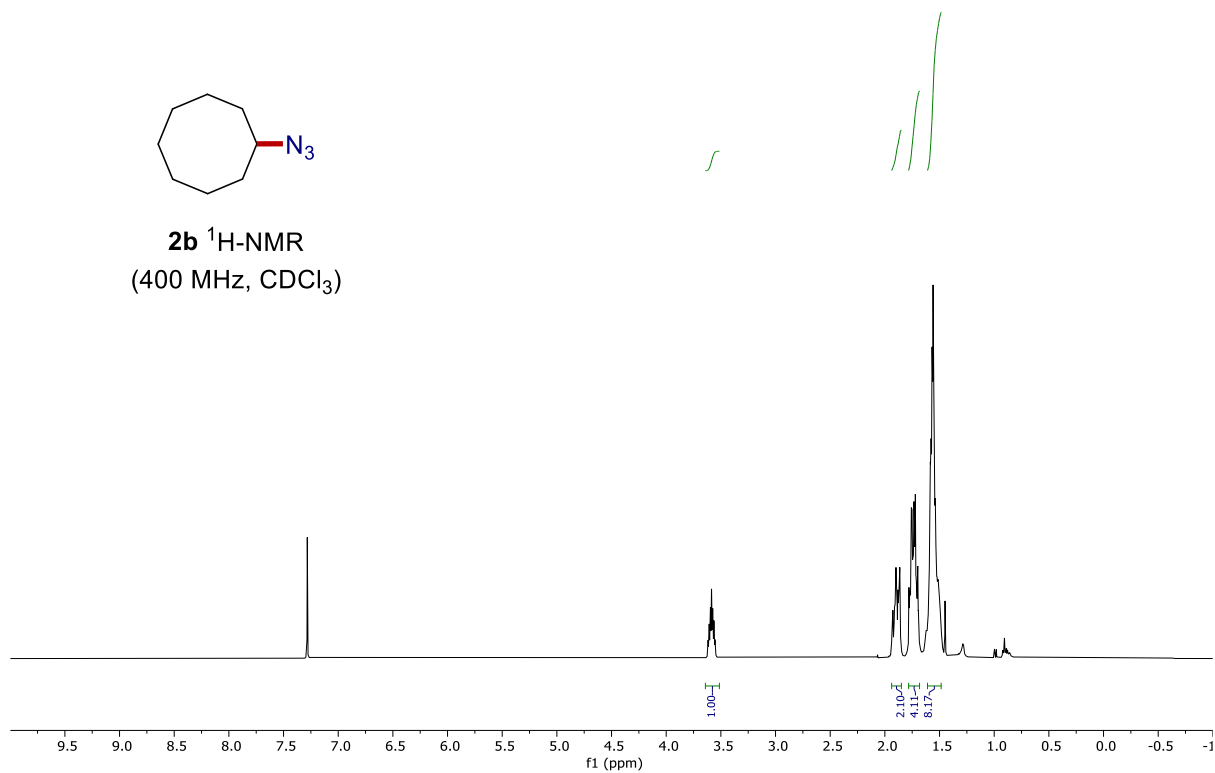
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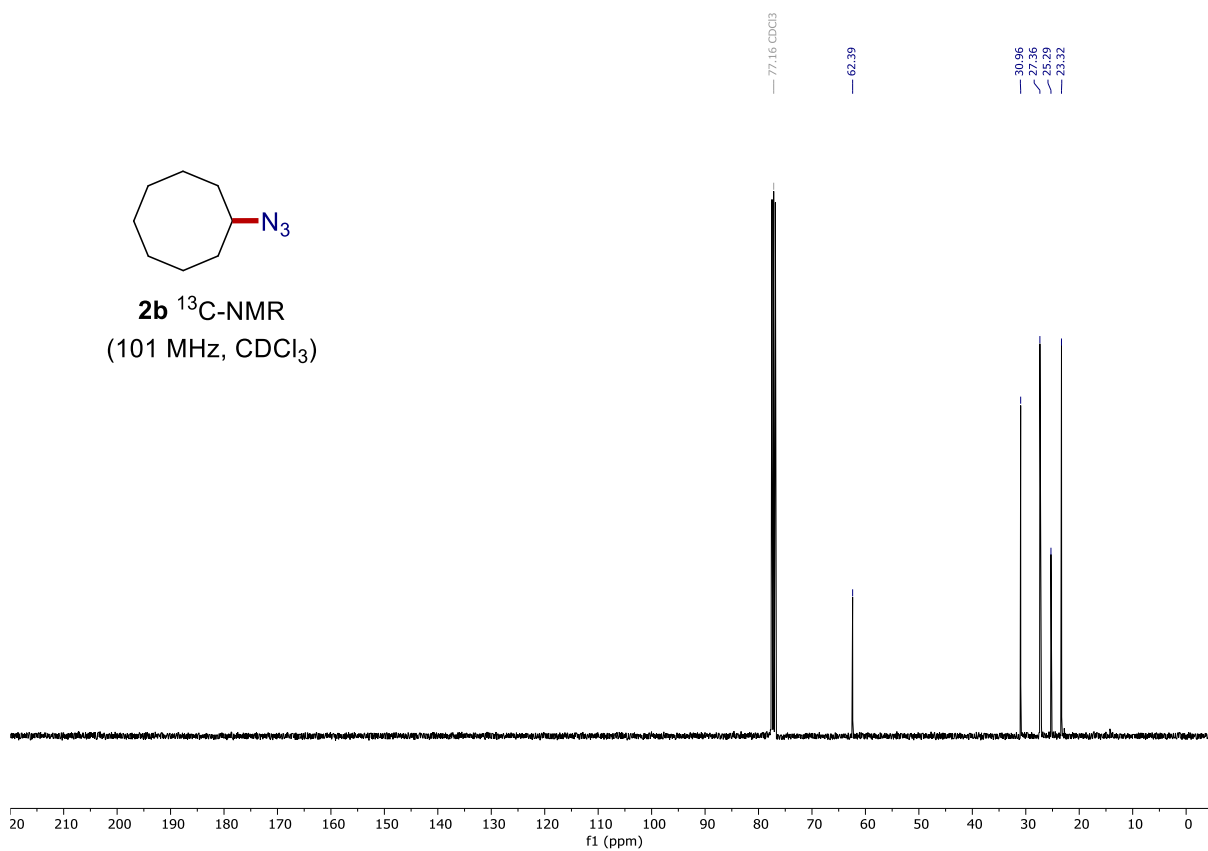
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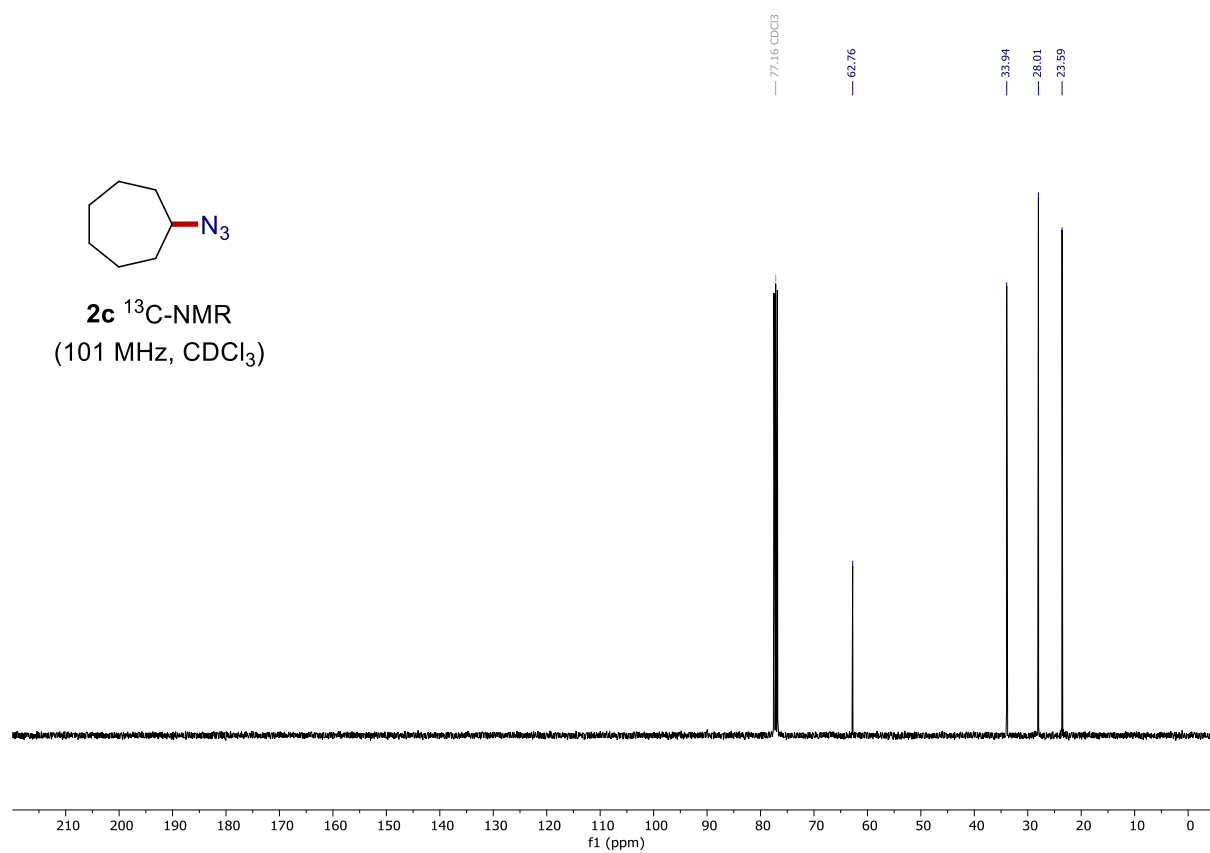
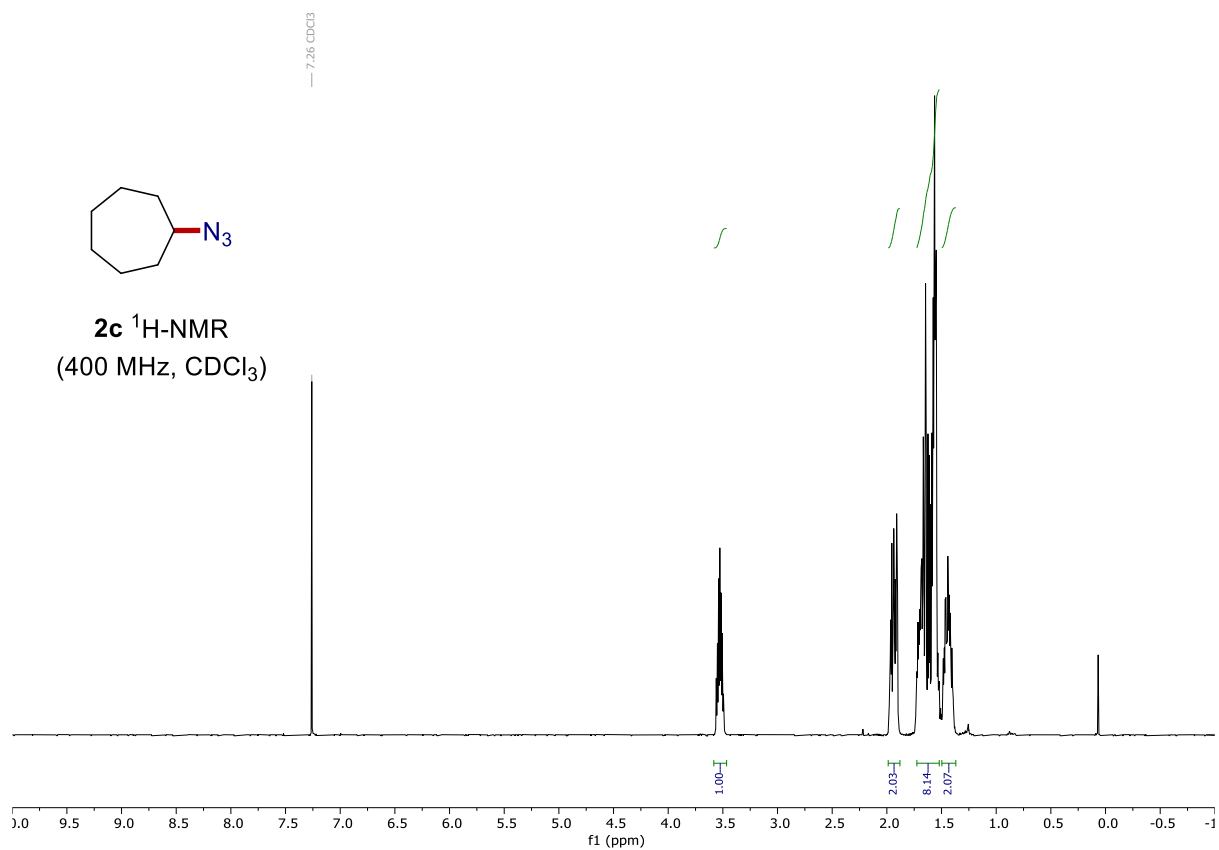


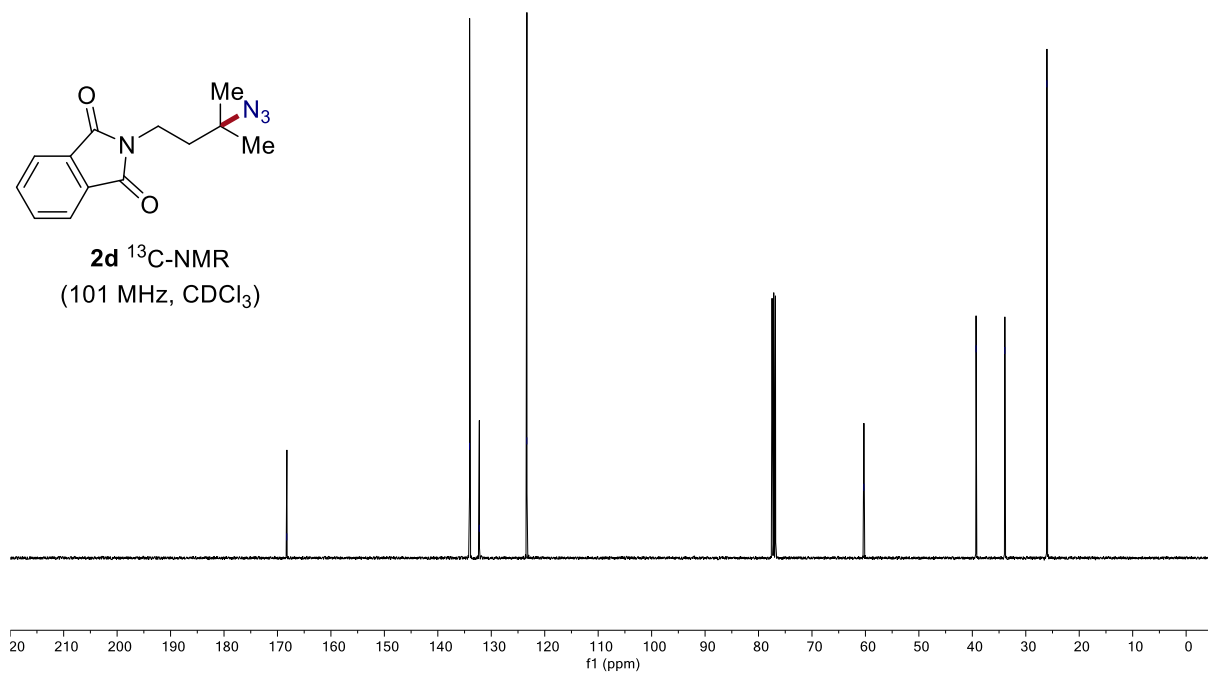
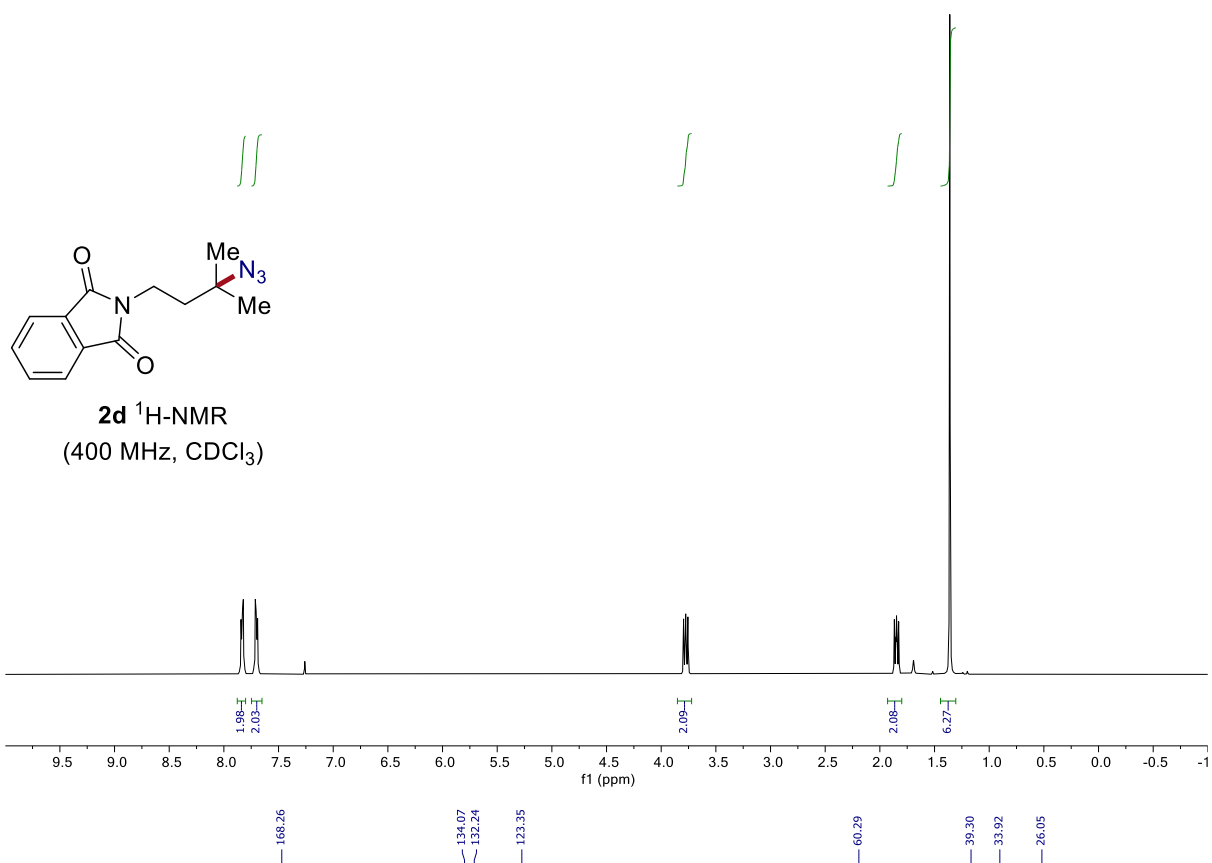
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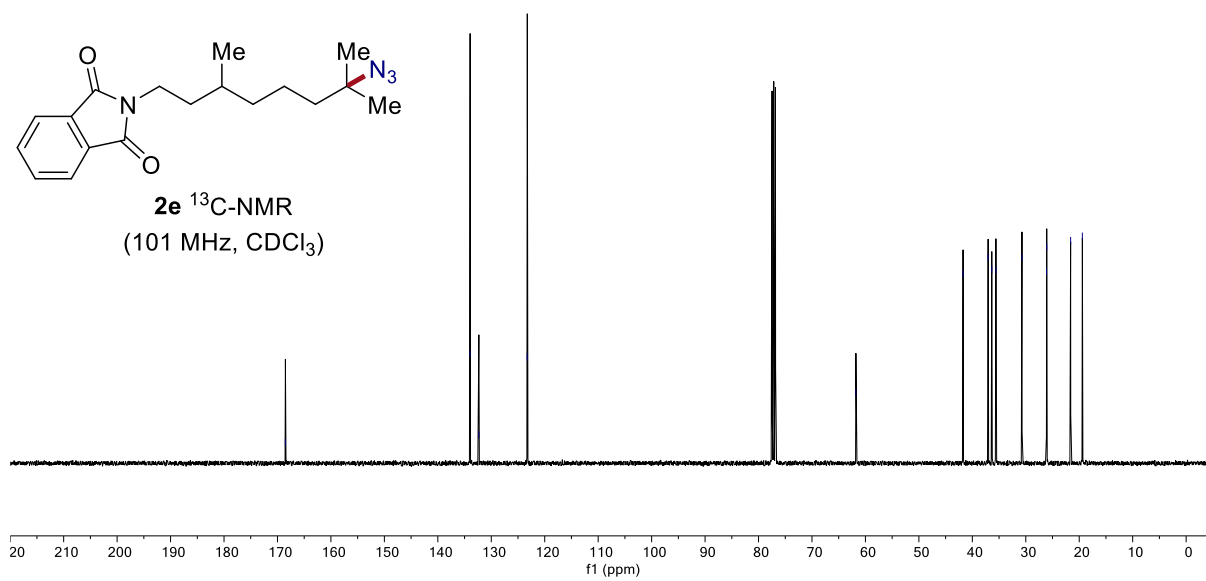
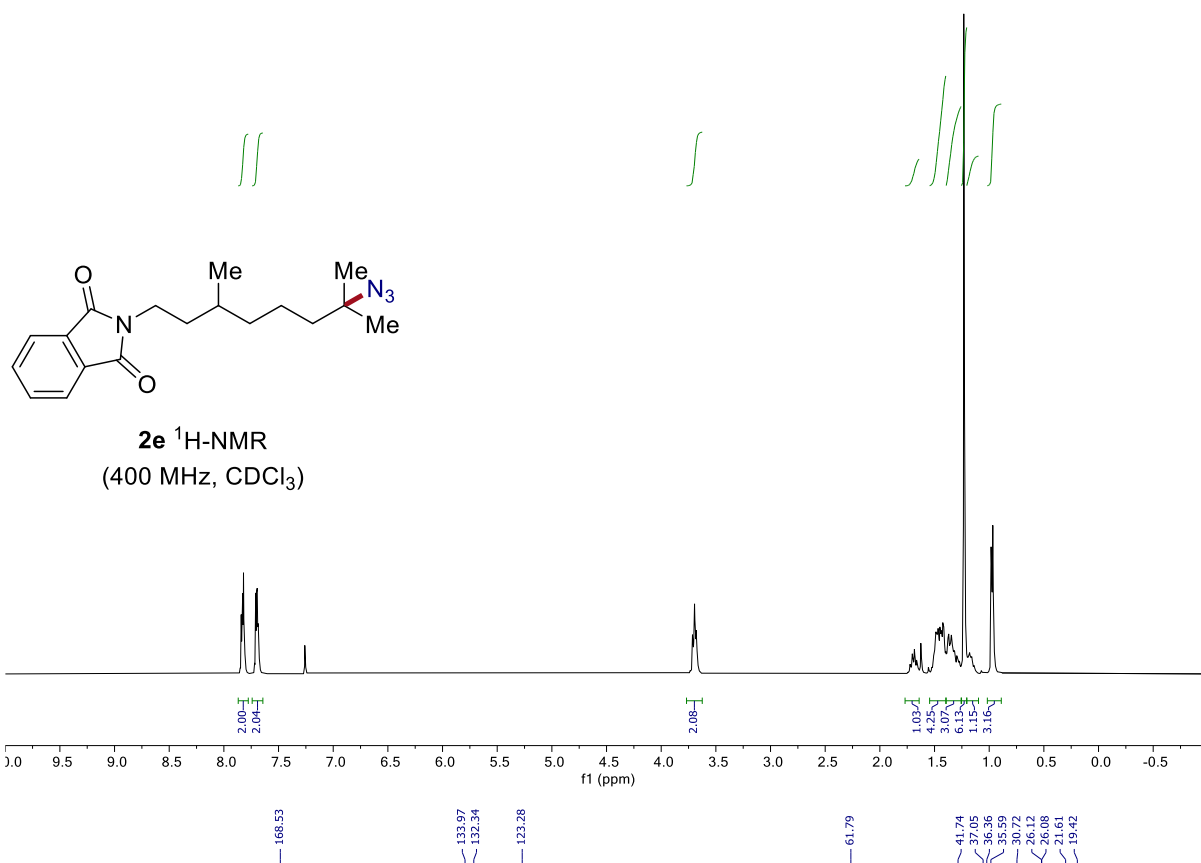
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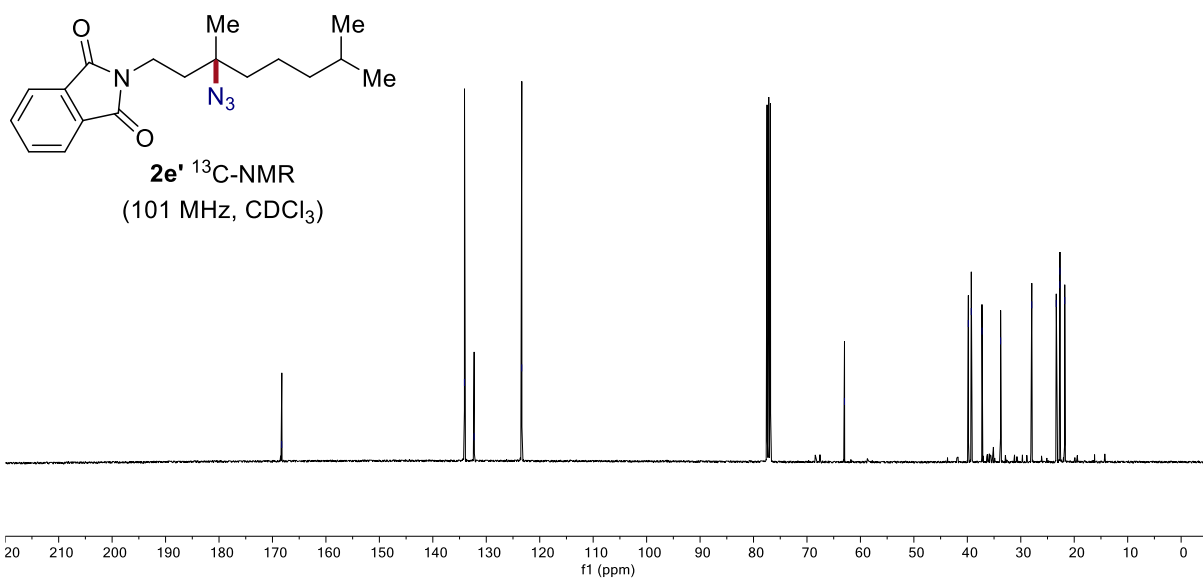
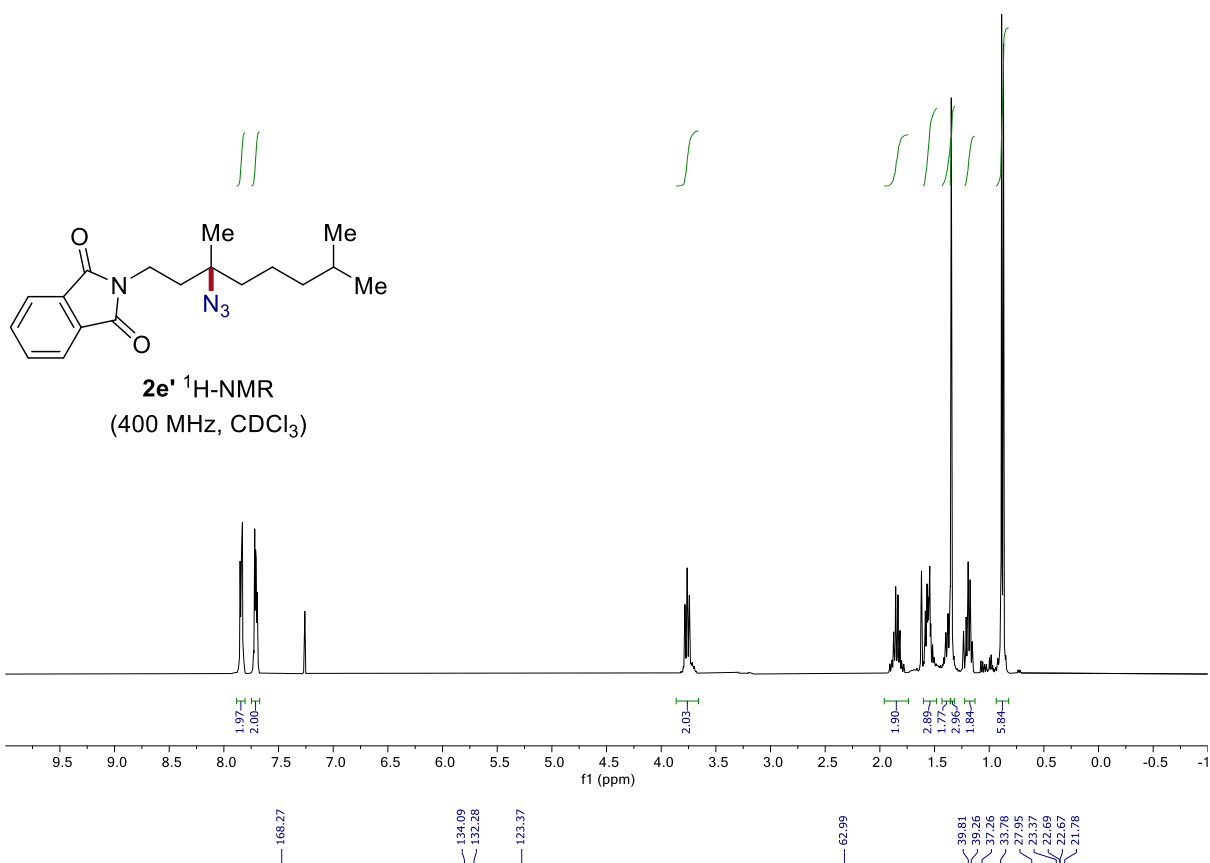


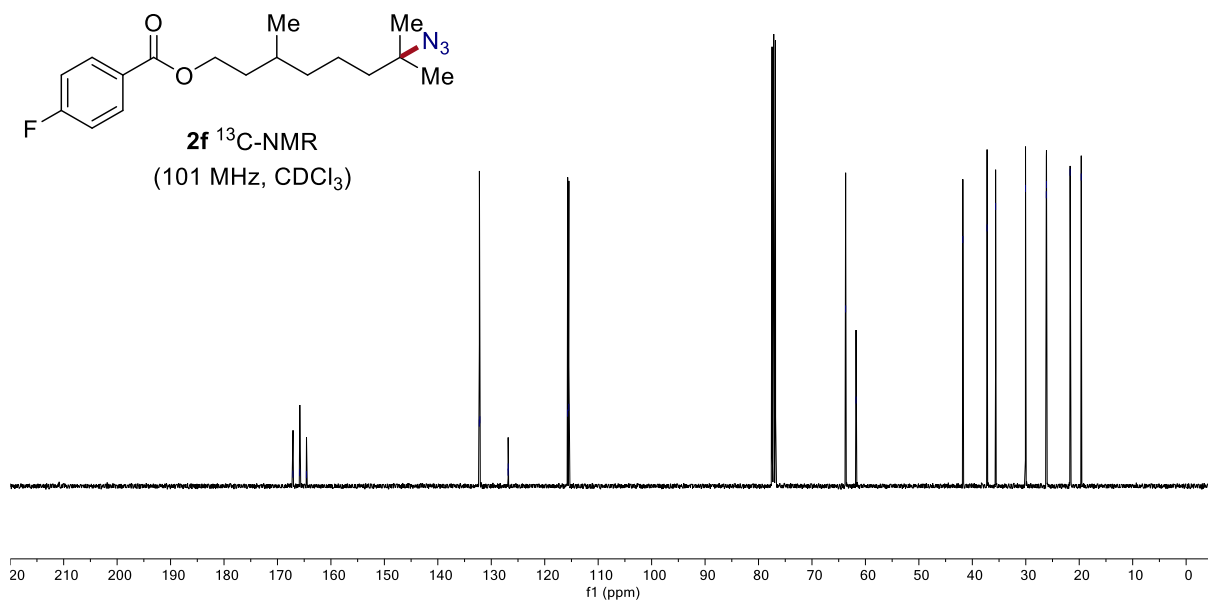
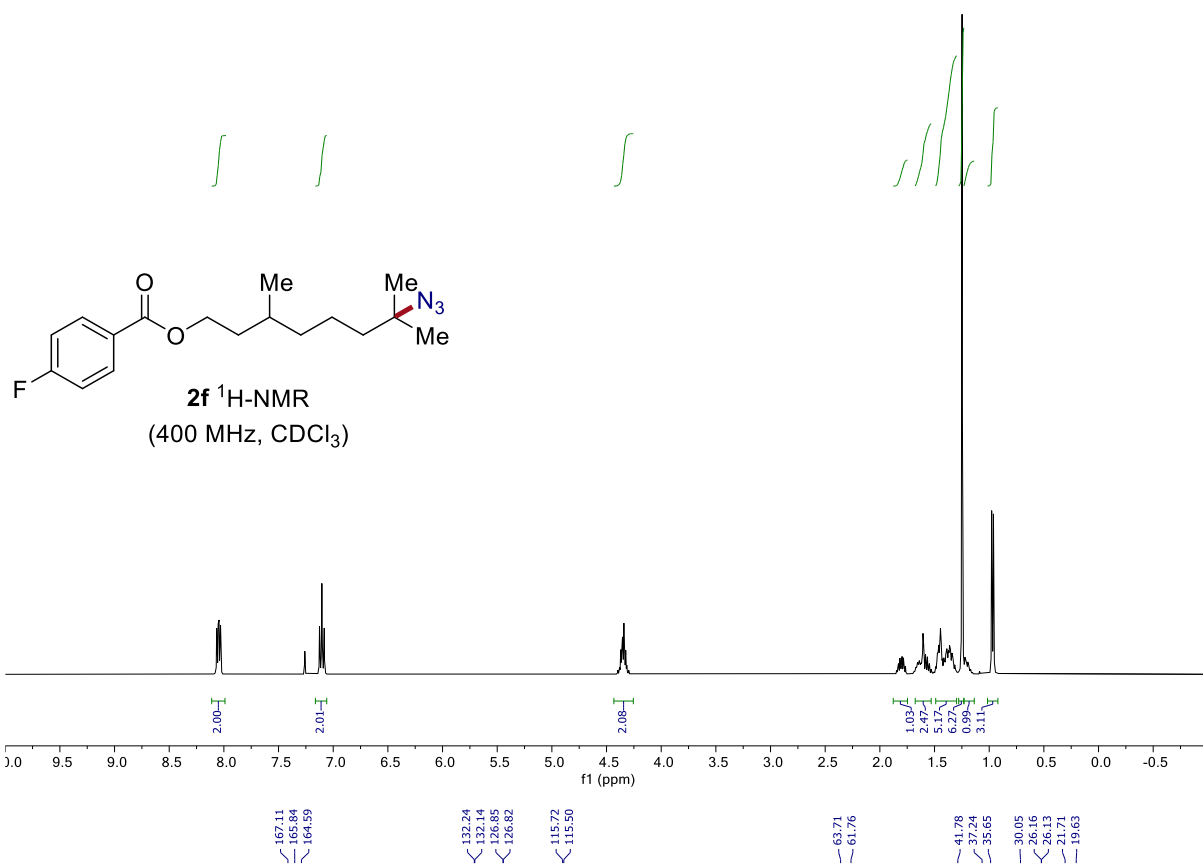


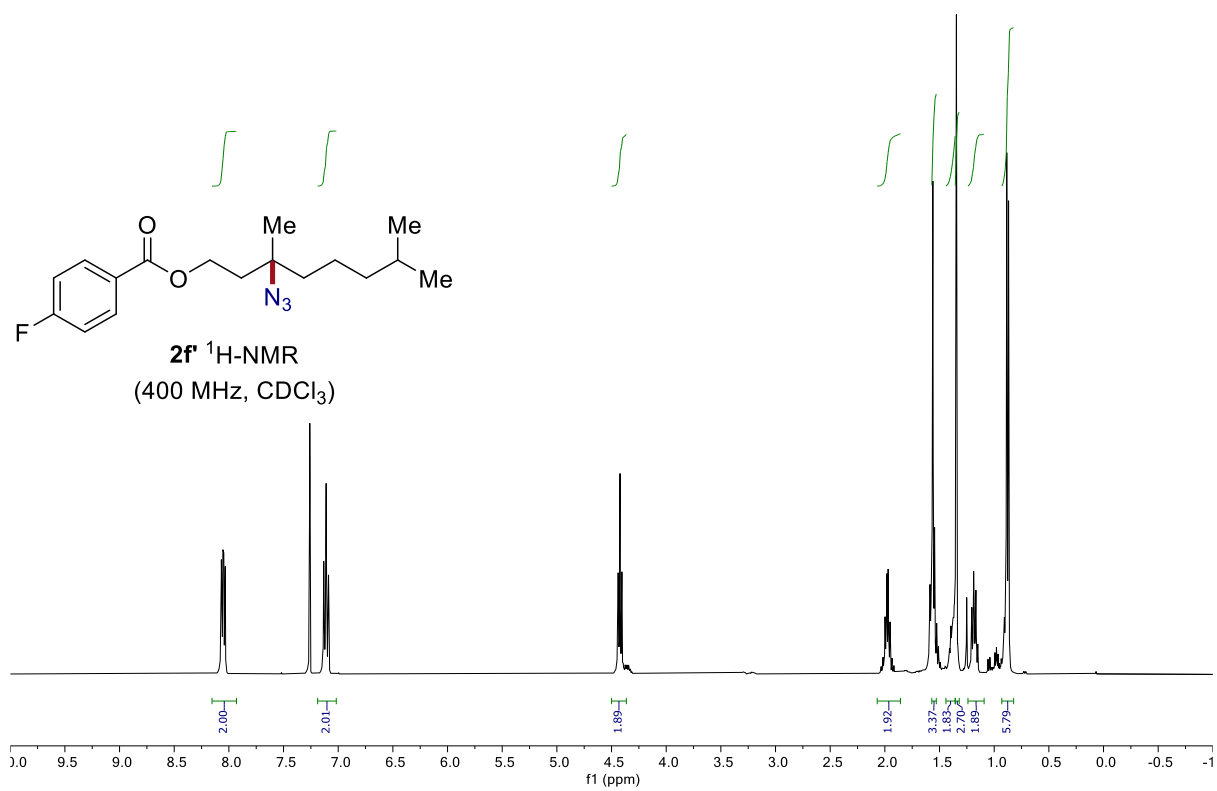
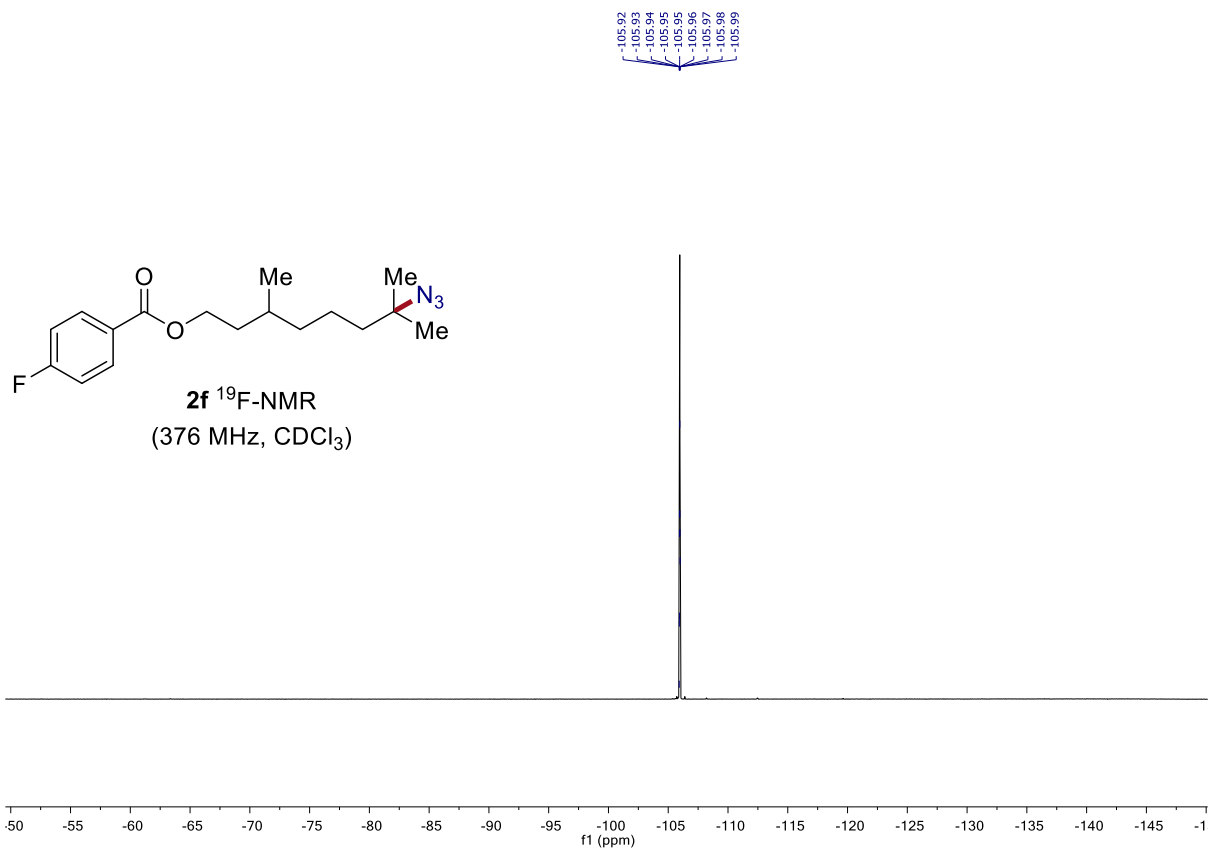


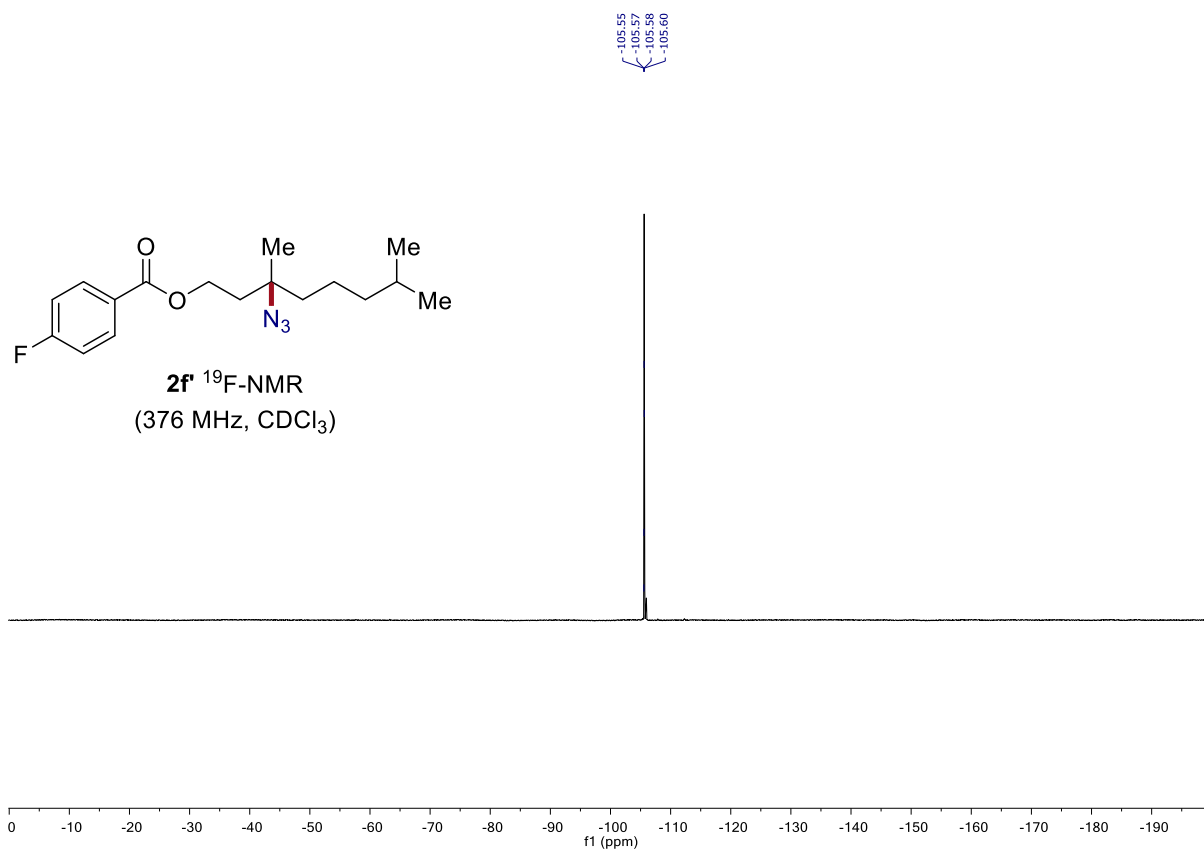
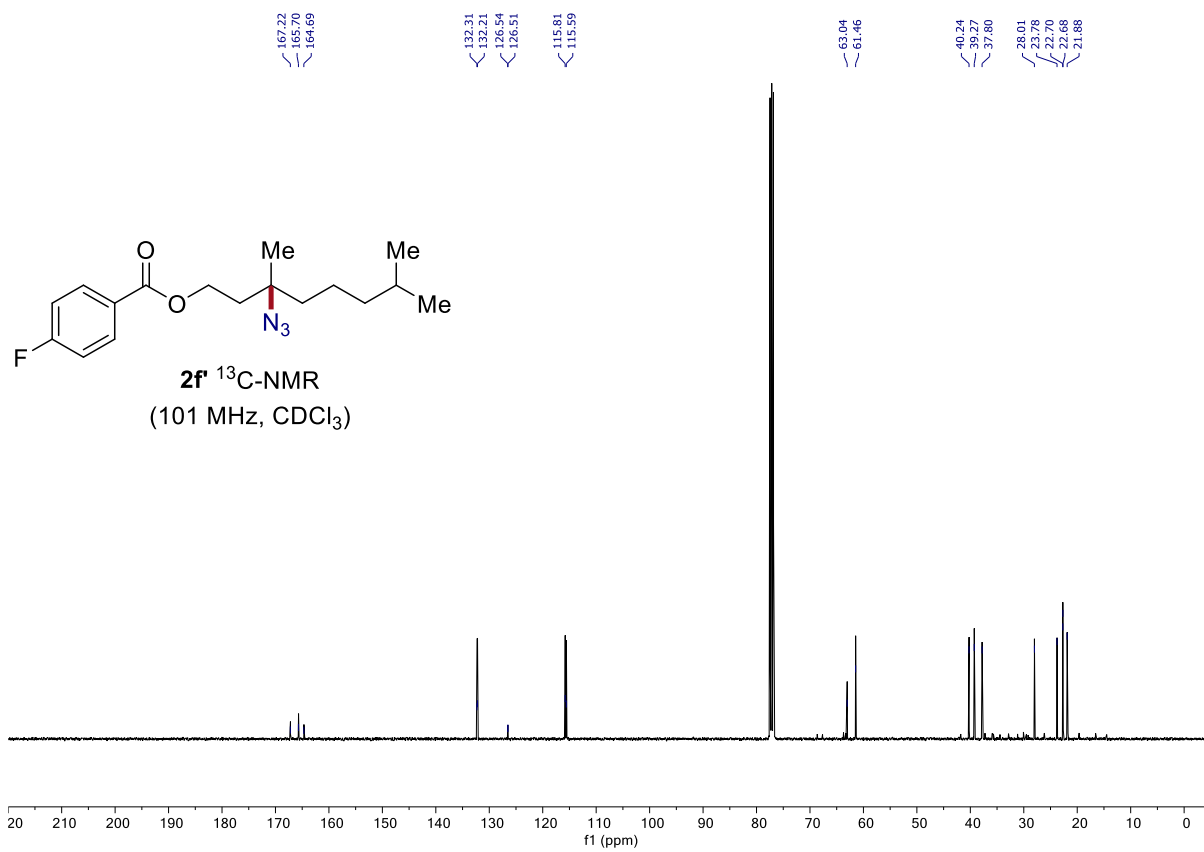


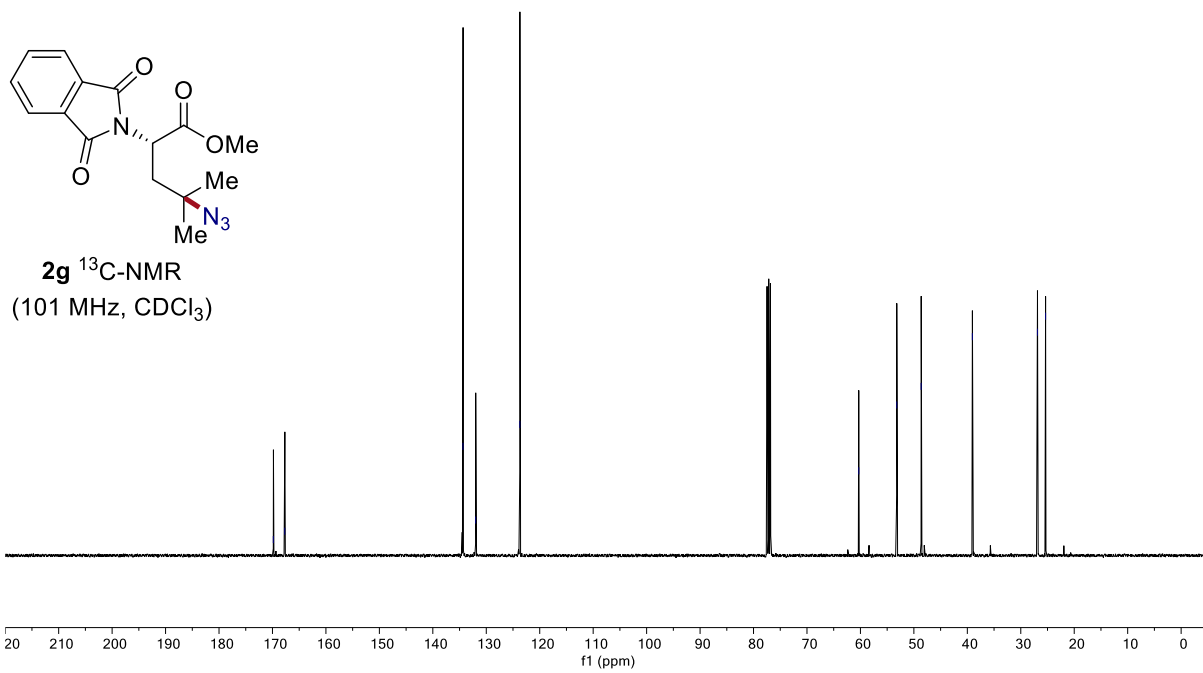
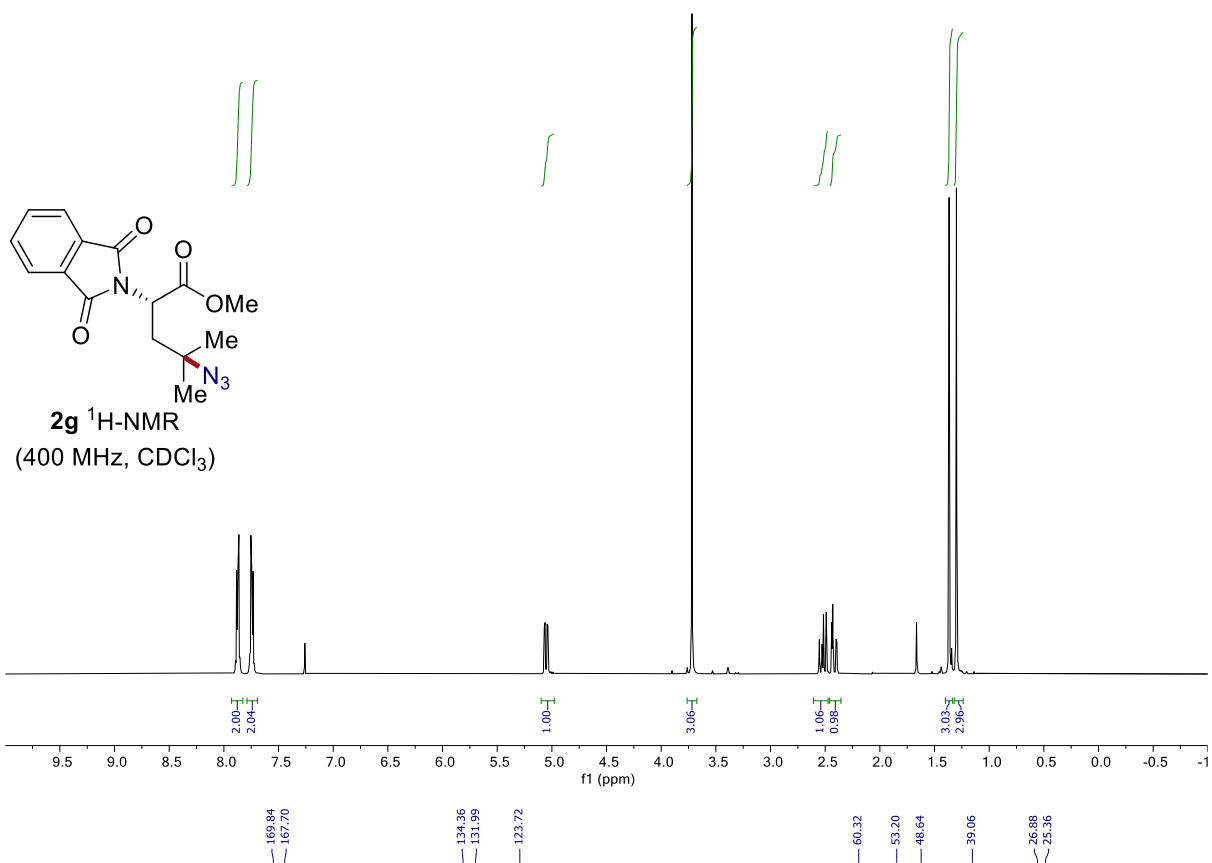


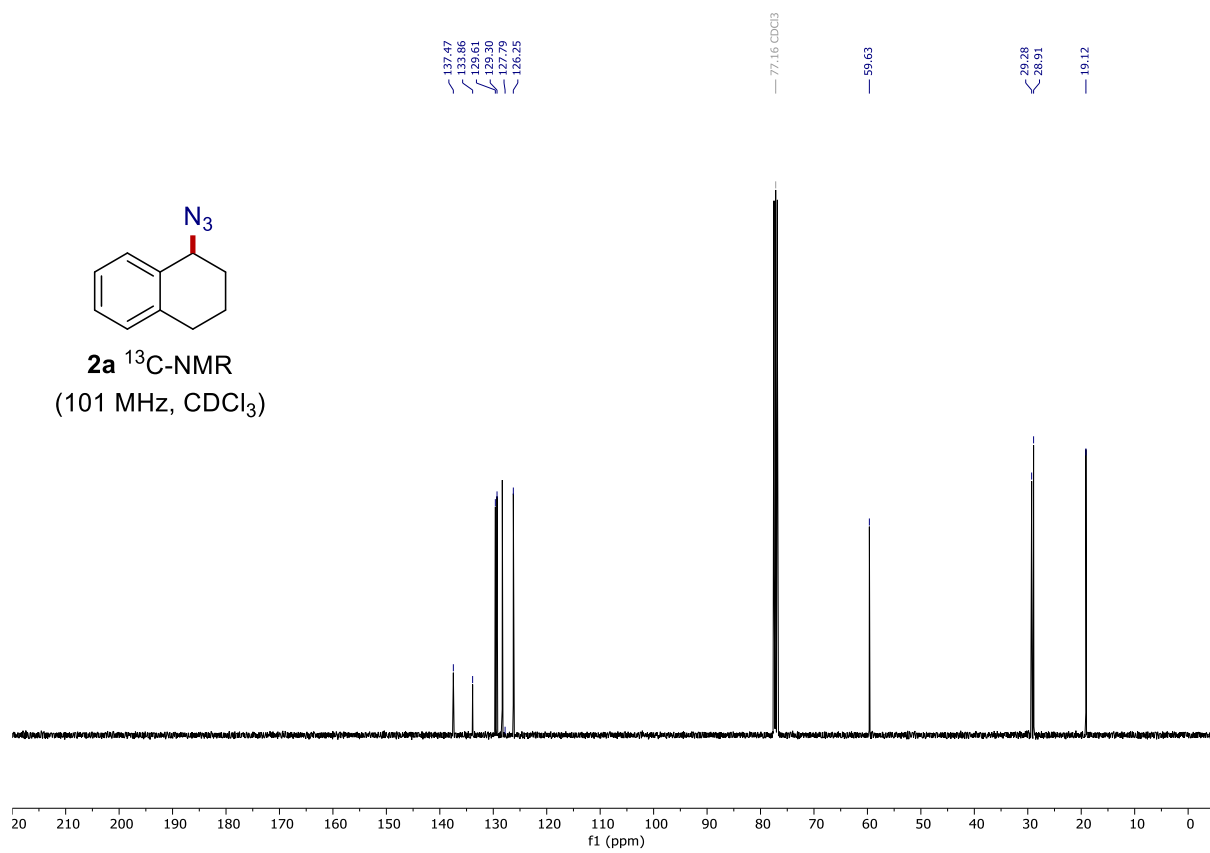
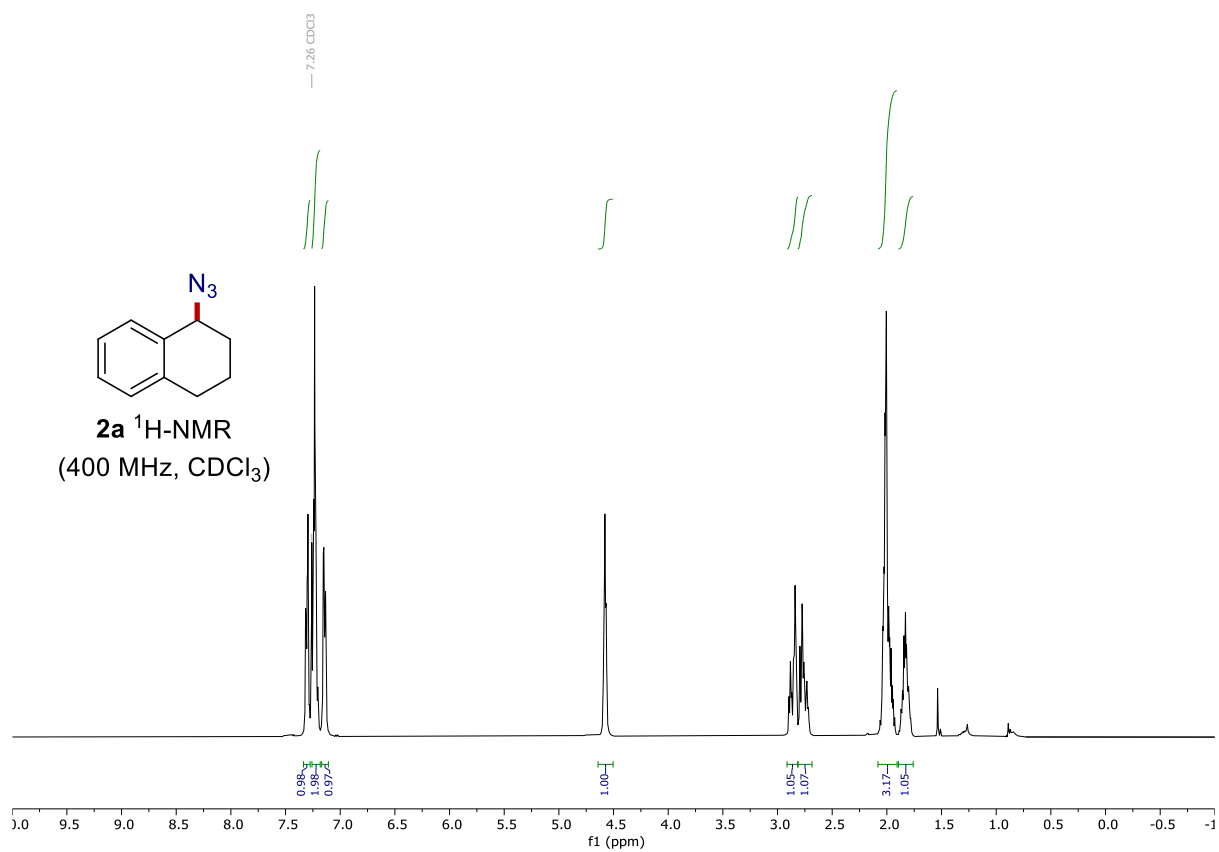


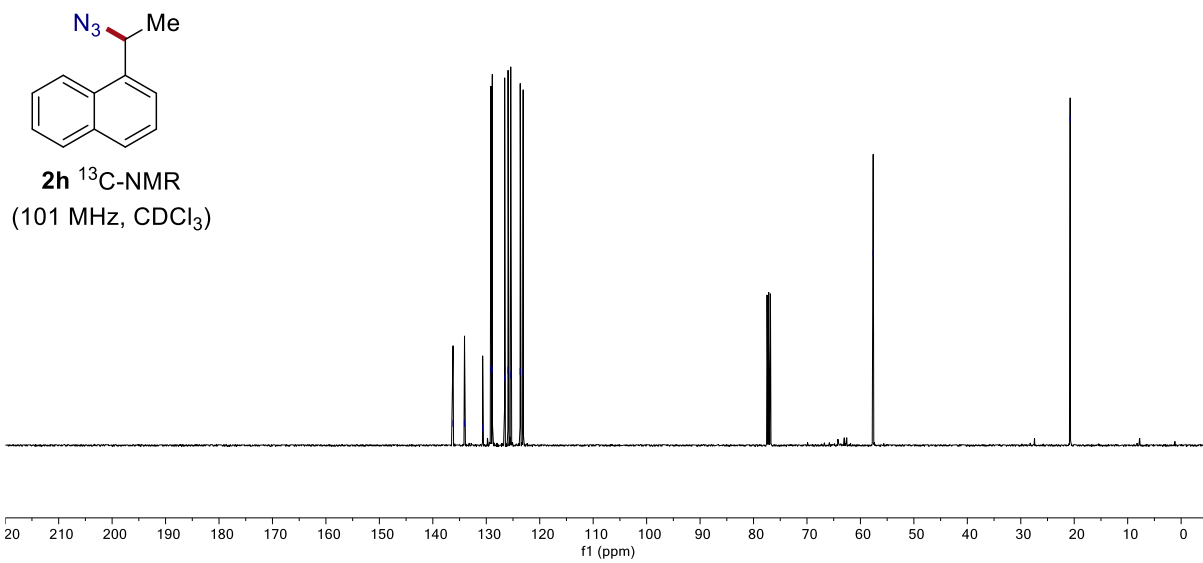
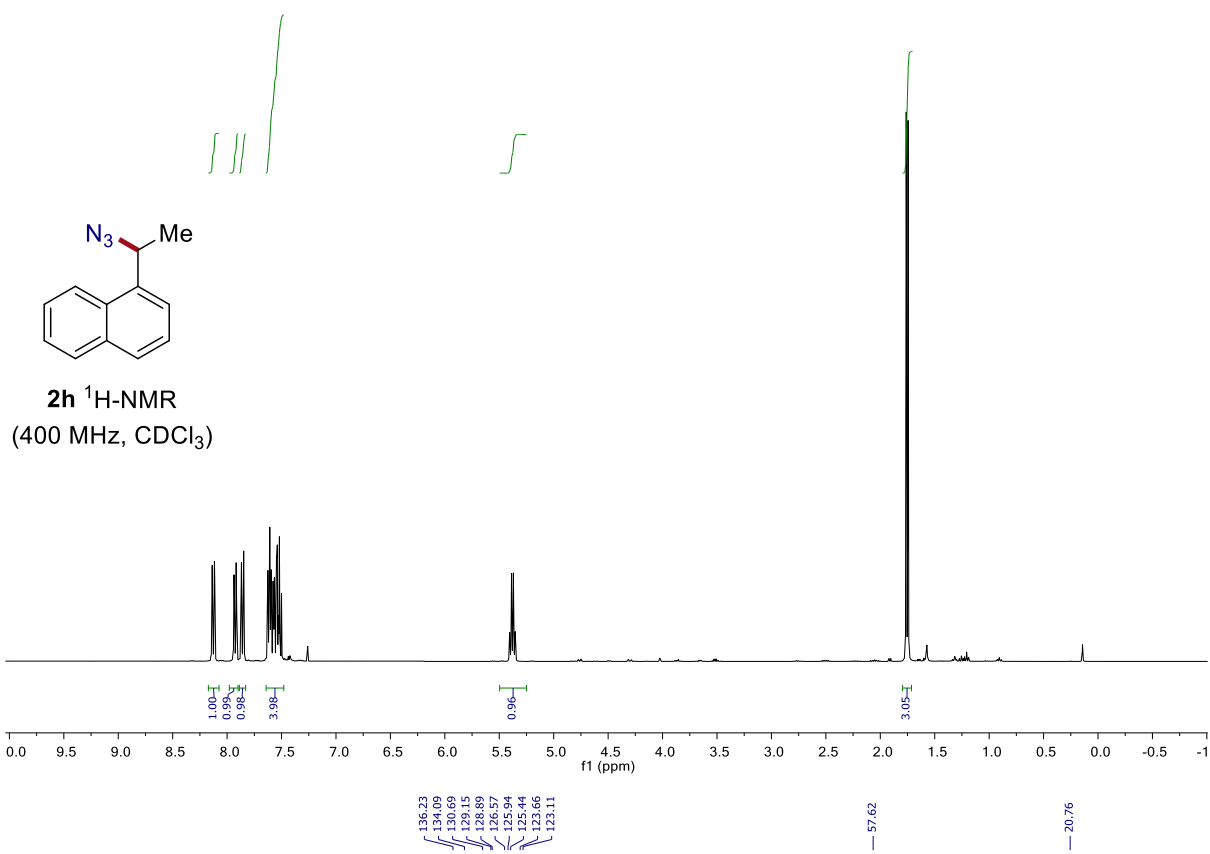




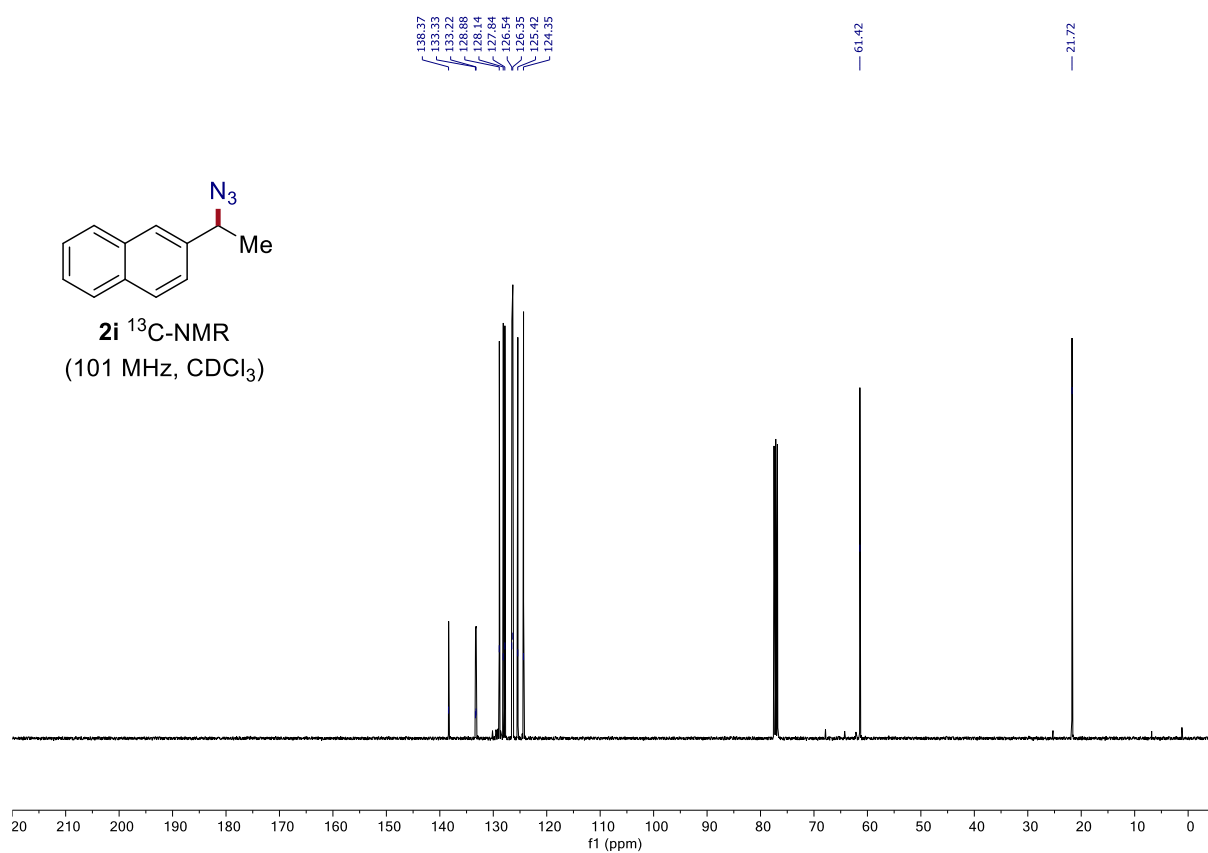
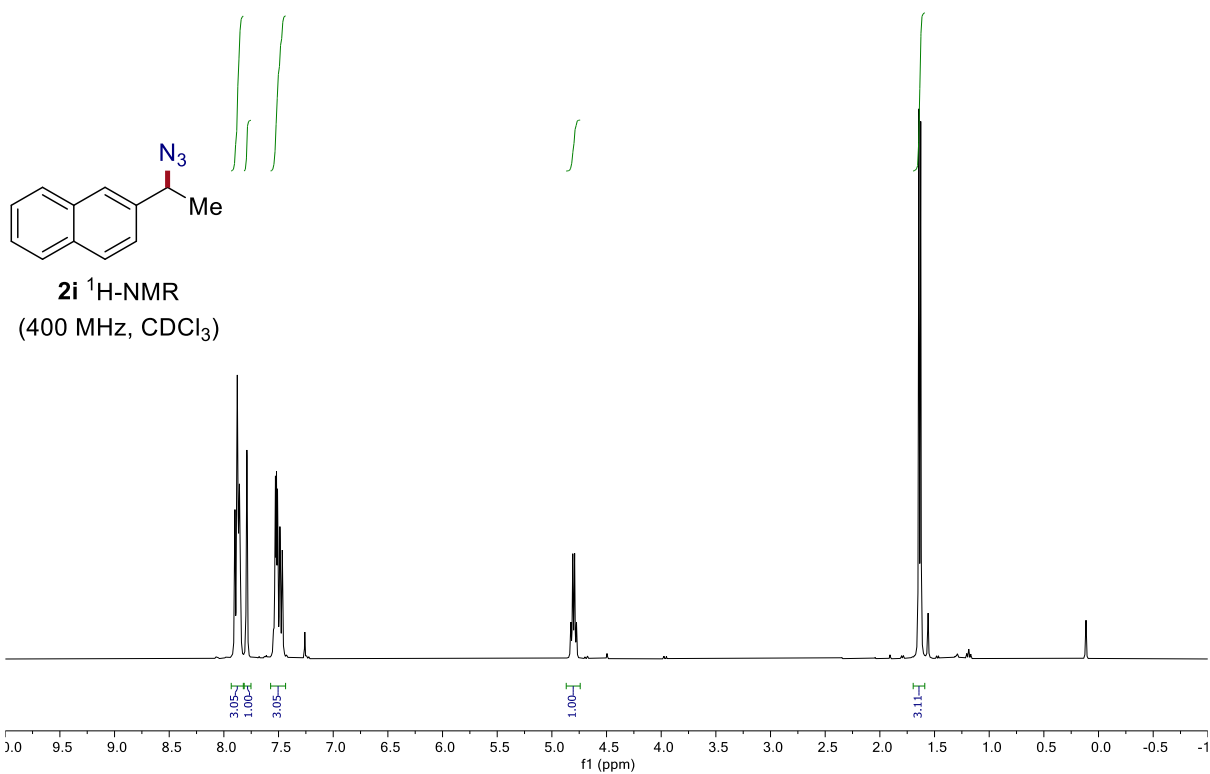




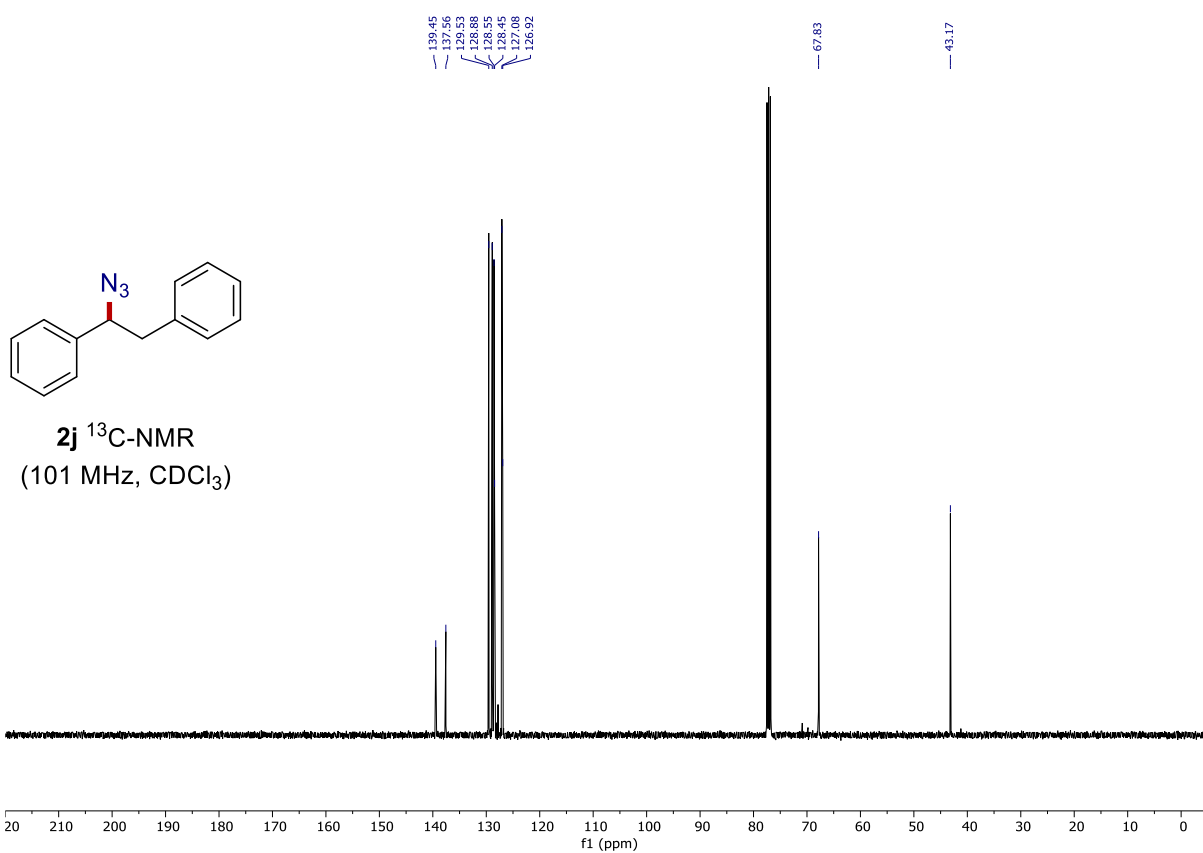
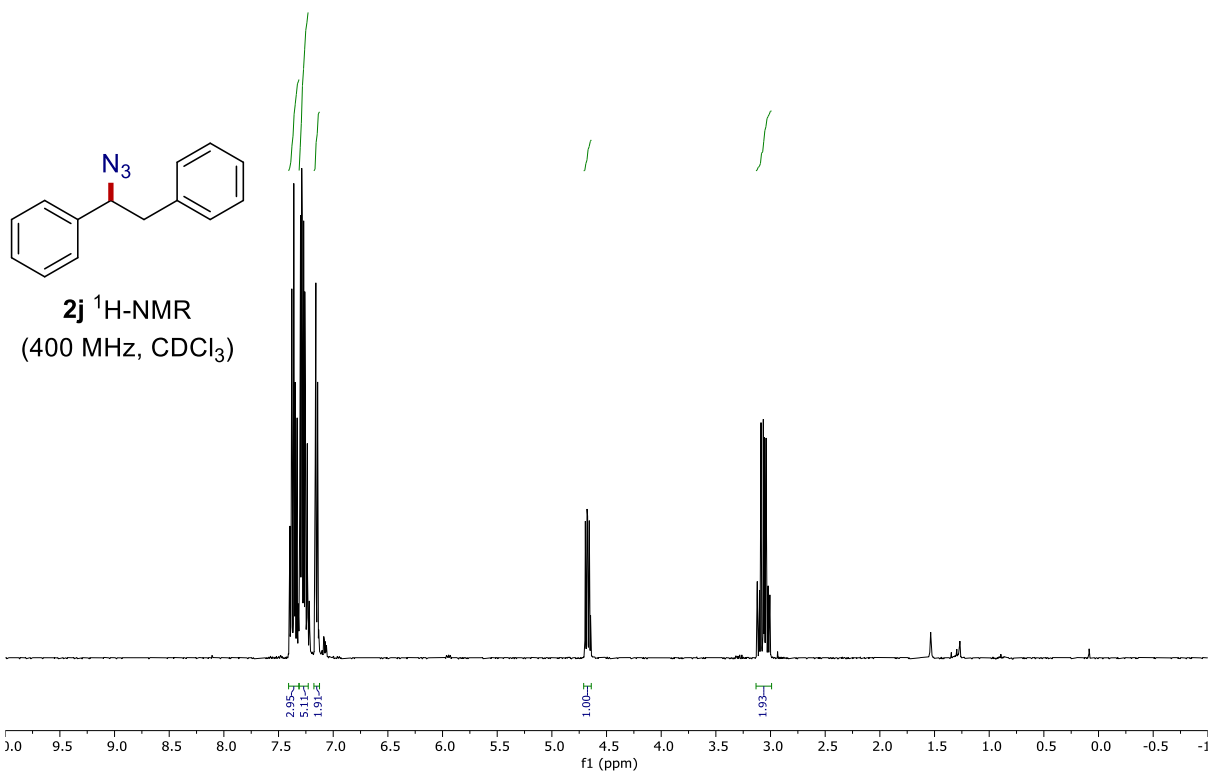


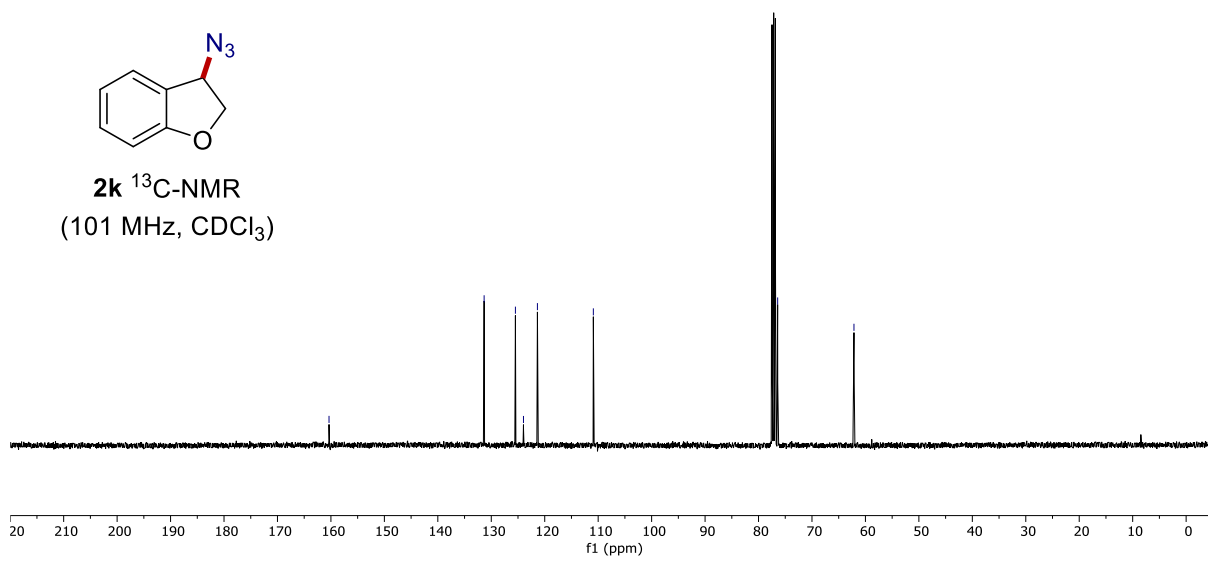
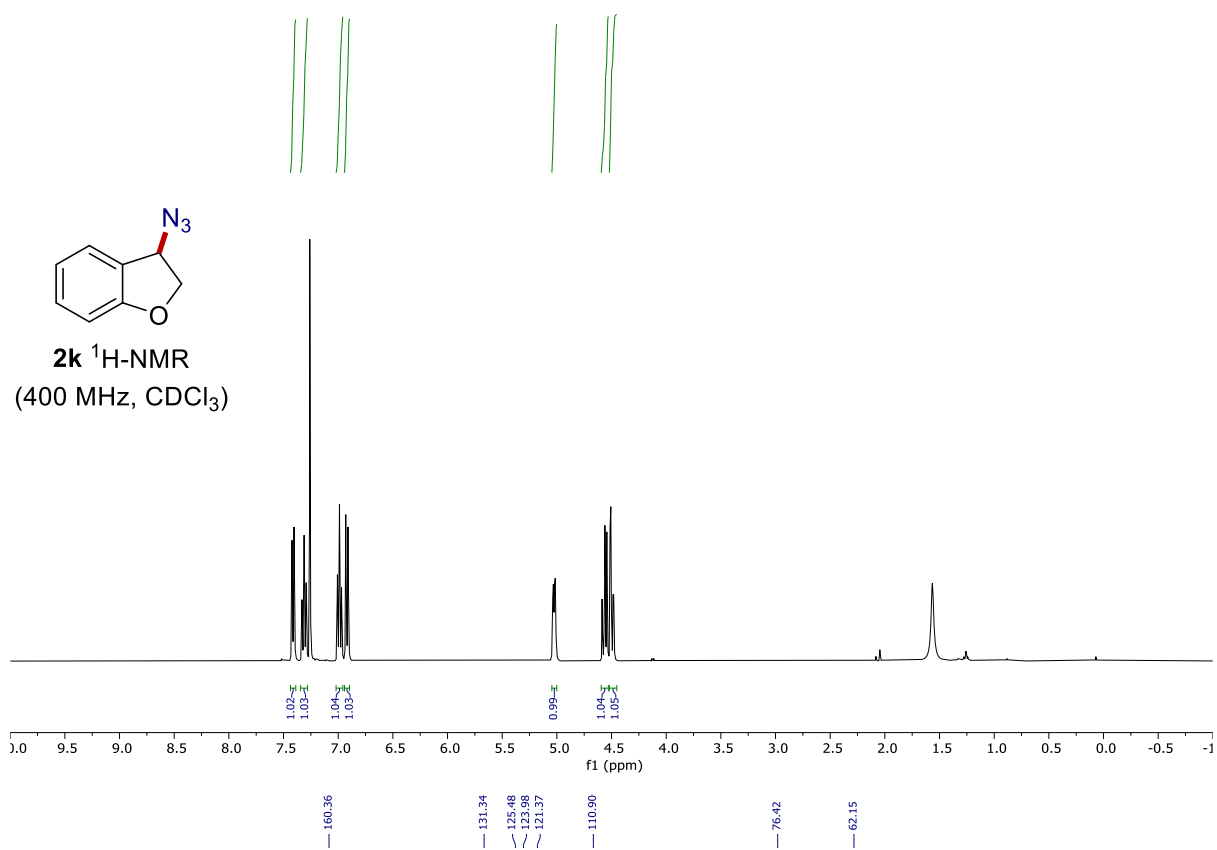


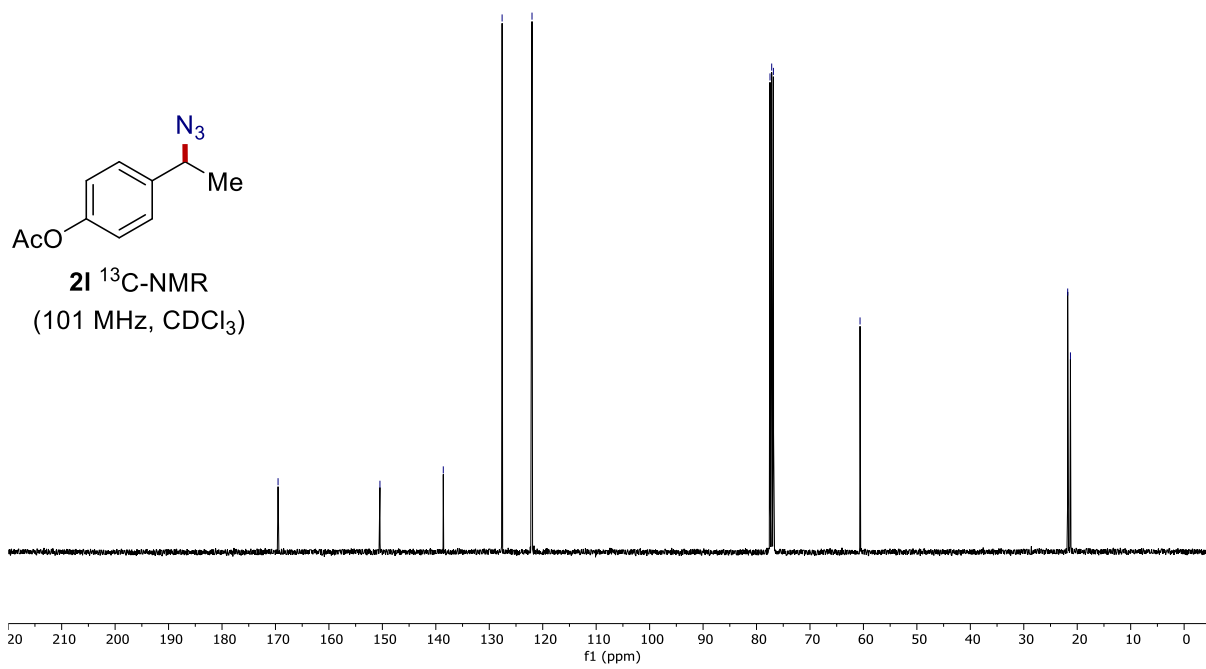
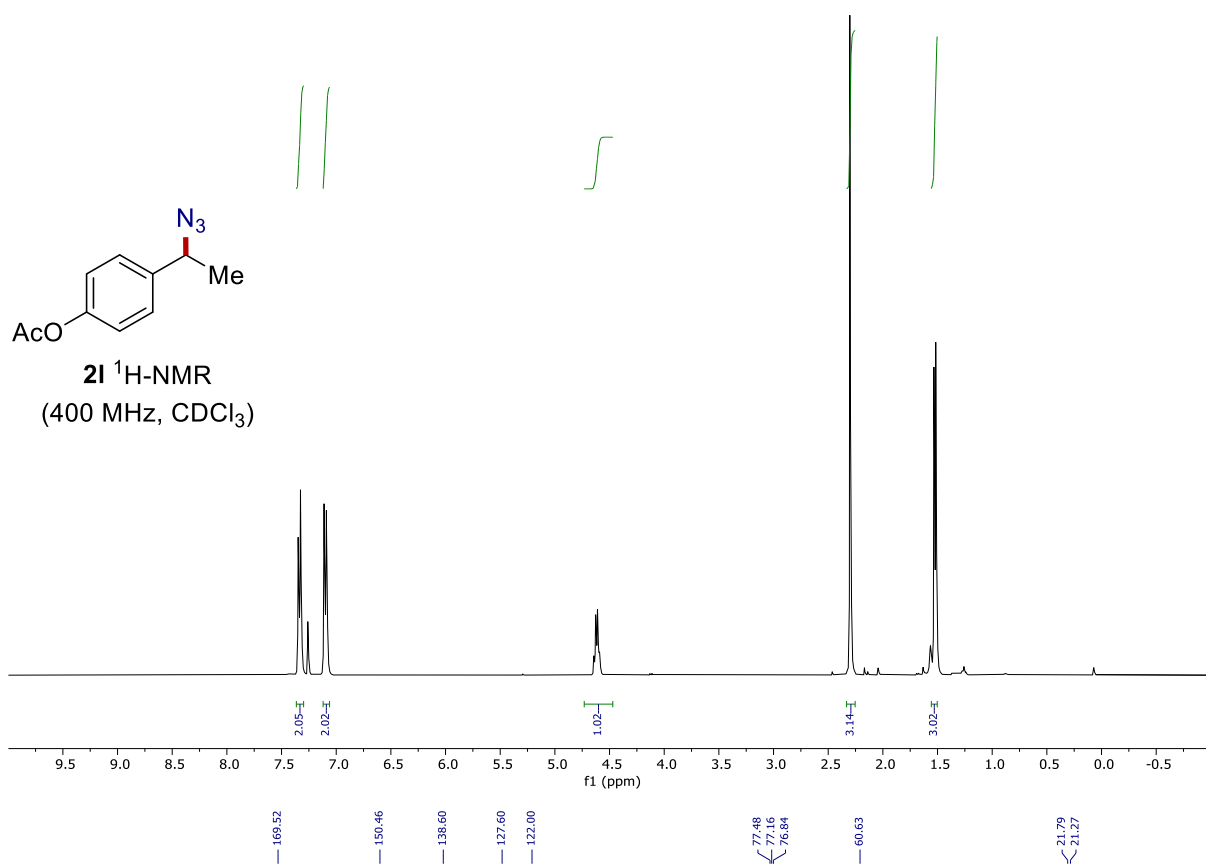


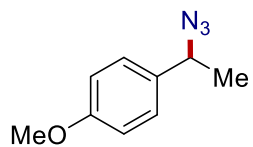


N<sub>3</sub>

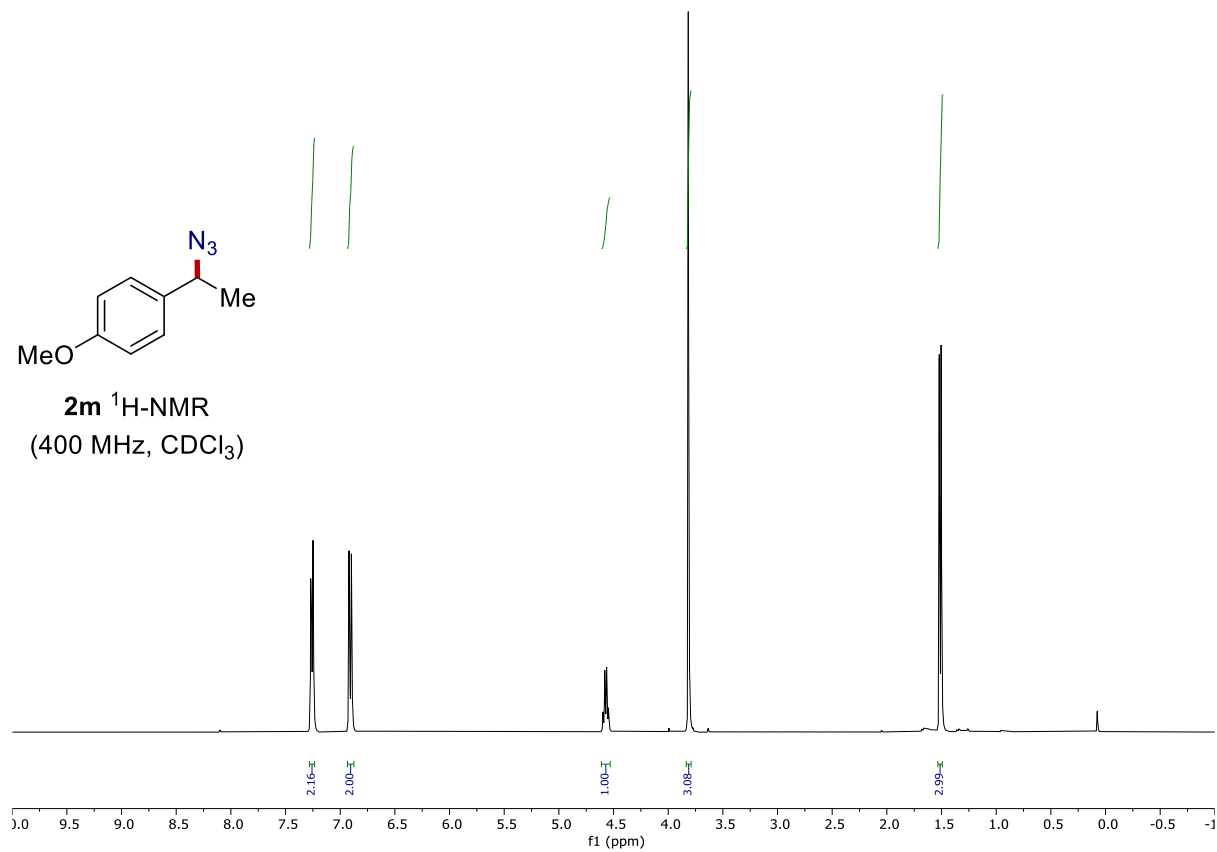








**2m**  $^1\text{H-NMR}$   
(400 MHz,  $\text{CDCl}_3$ )



159.54

133.00

127.81

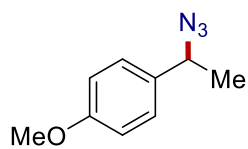
114.22

77.48  $\text{CDCl}_3$   
77.16  $\text{CDCl}_3$   
76.84  $\text{CDCl}_3$

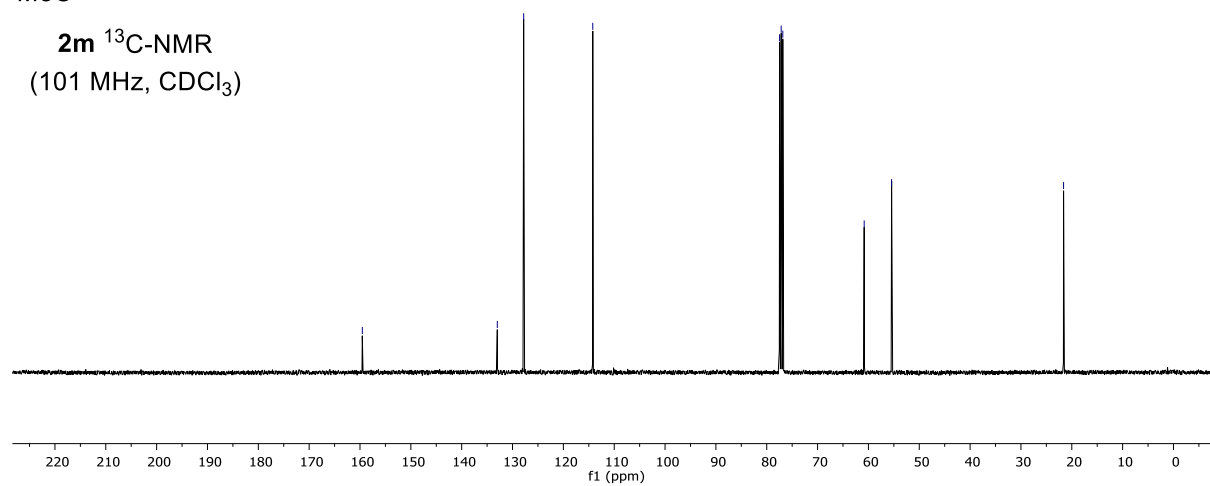
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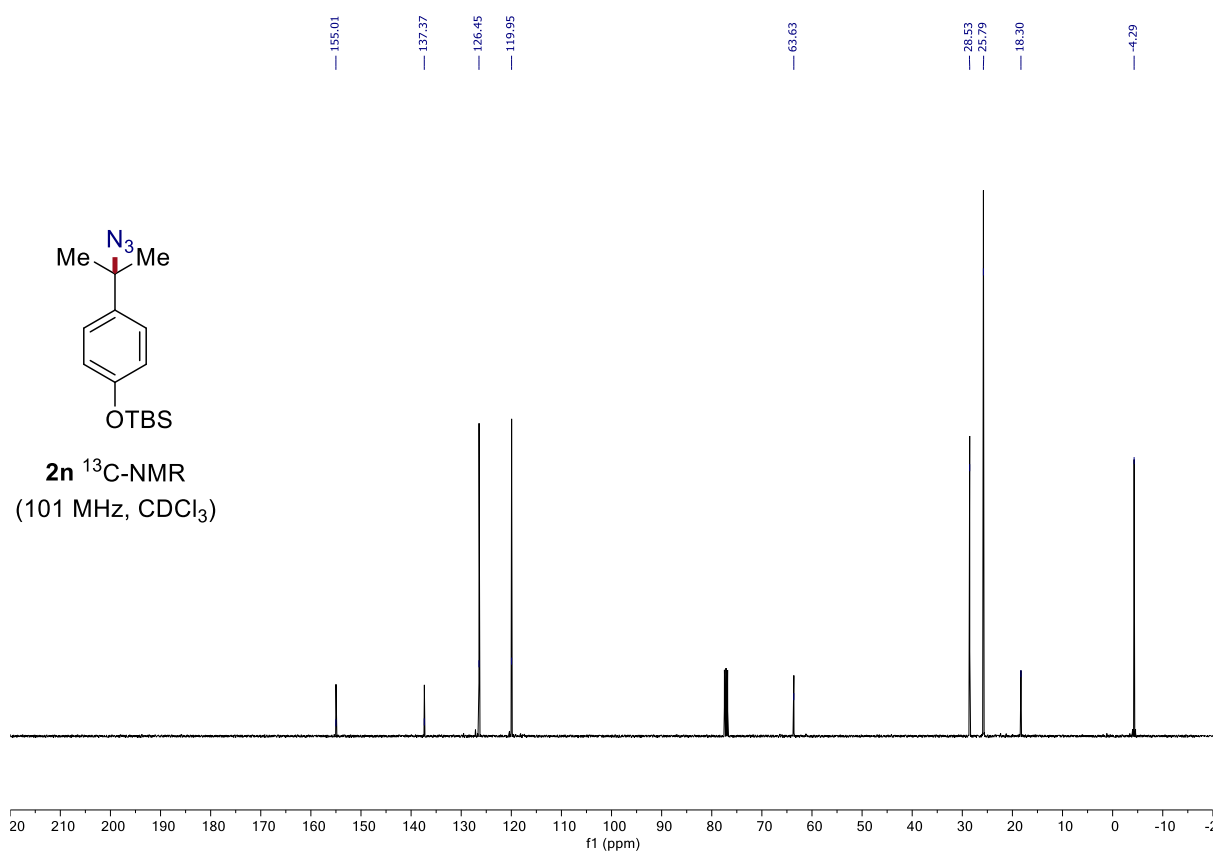
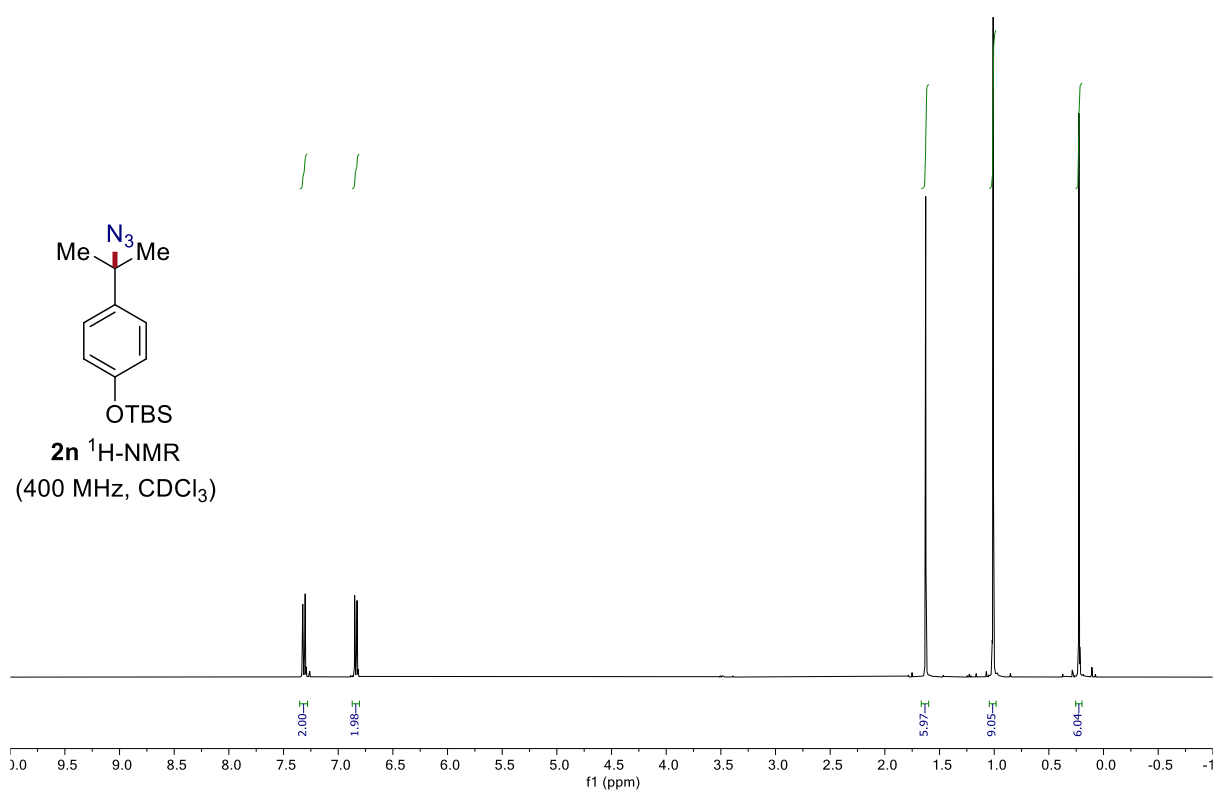
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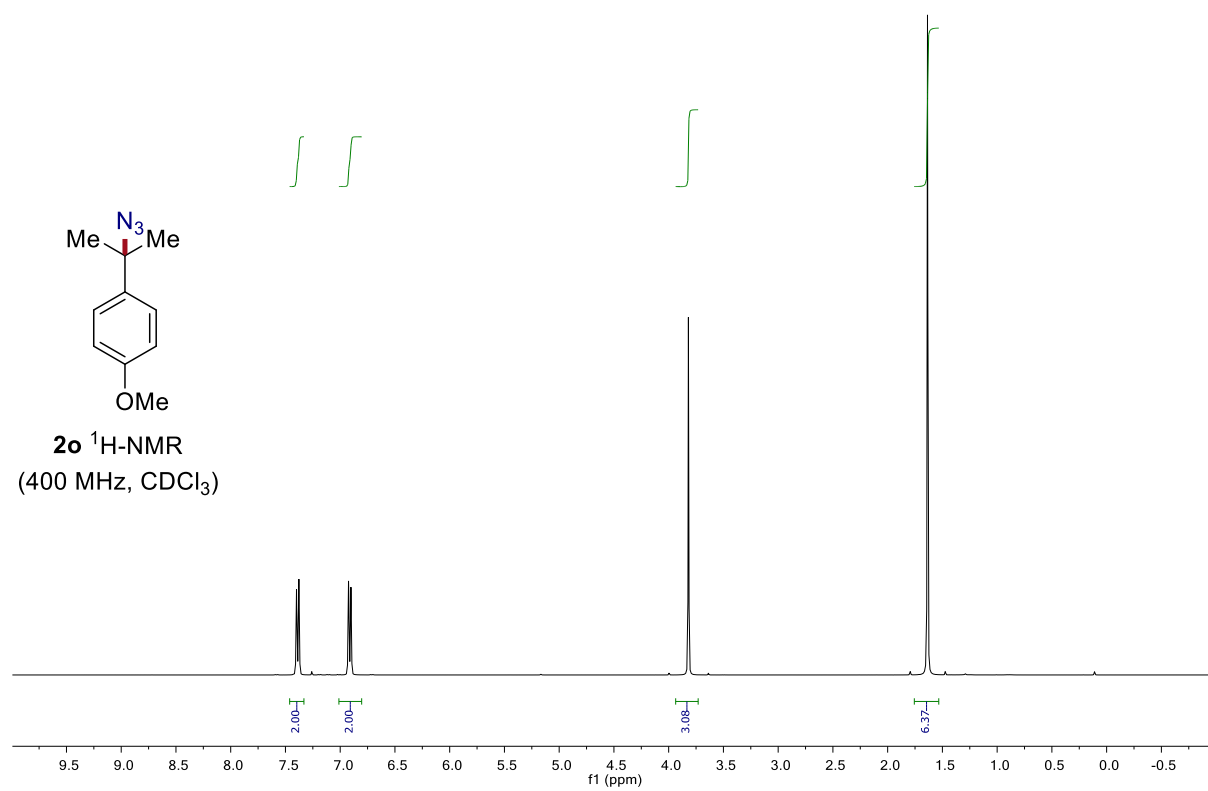
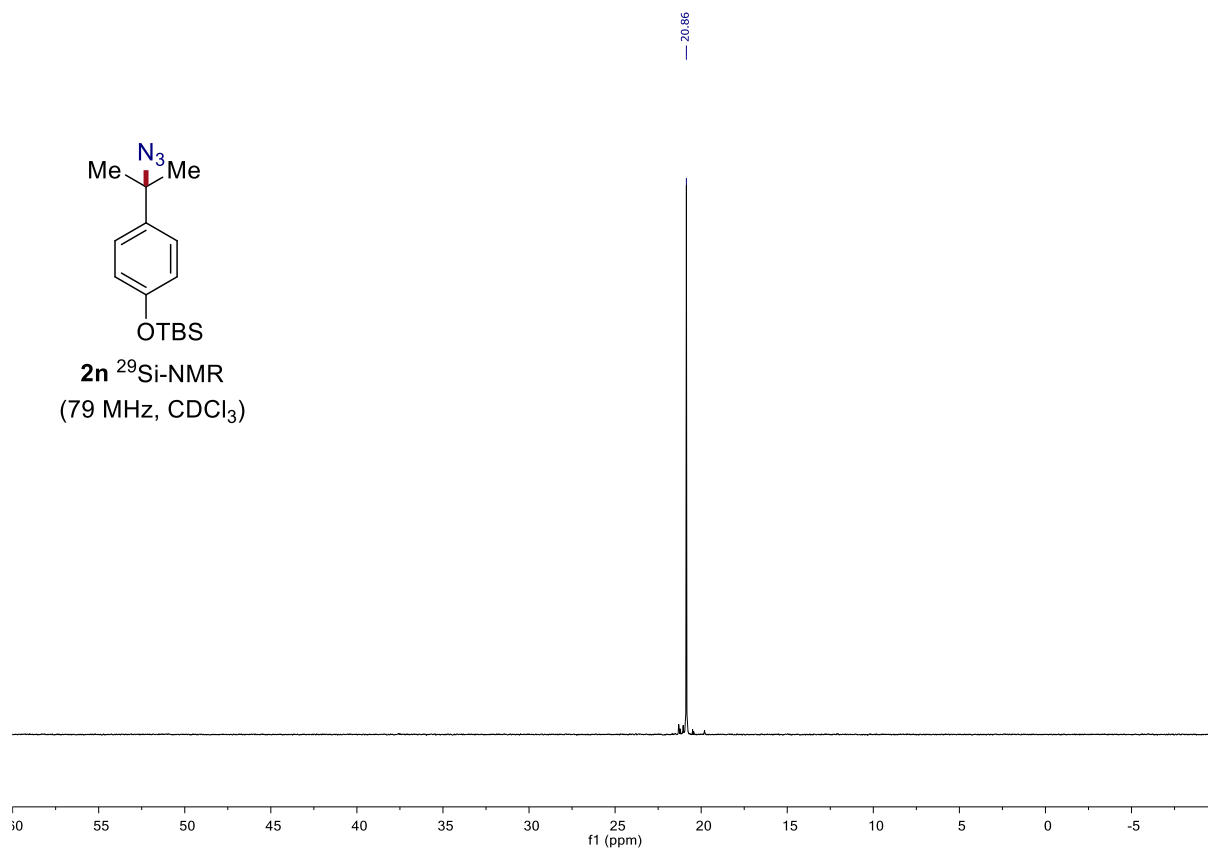
21.62



**2m**  $^{13}\text{C-NMR}$   
(101 MHz,  $\text{CDCl}_3$ )

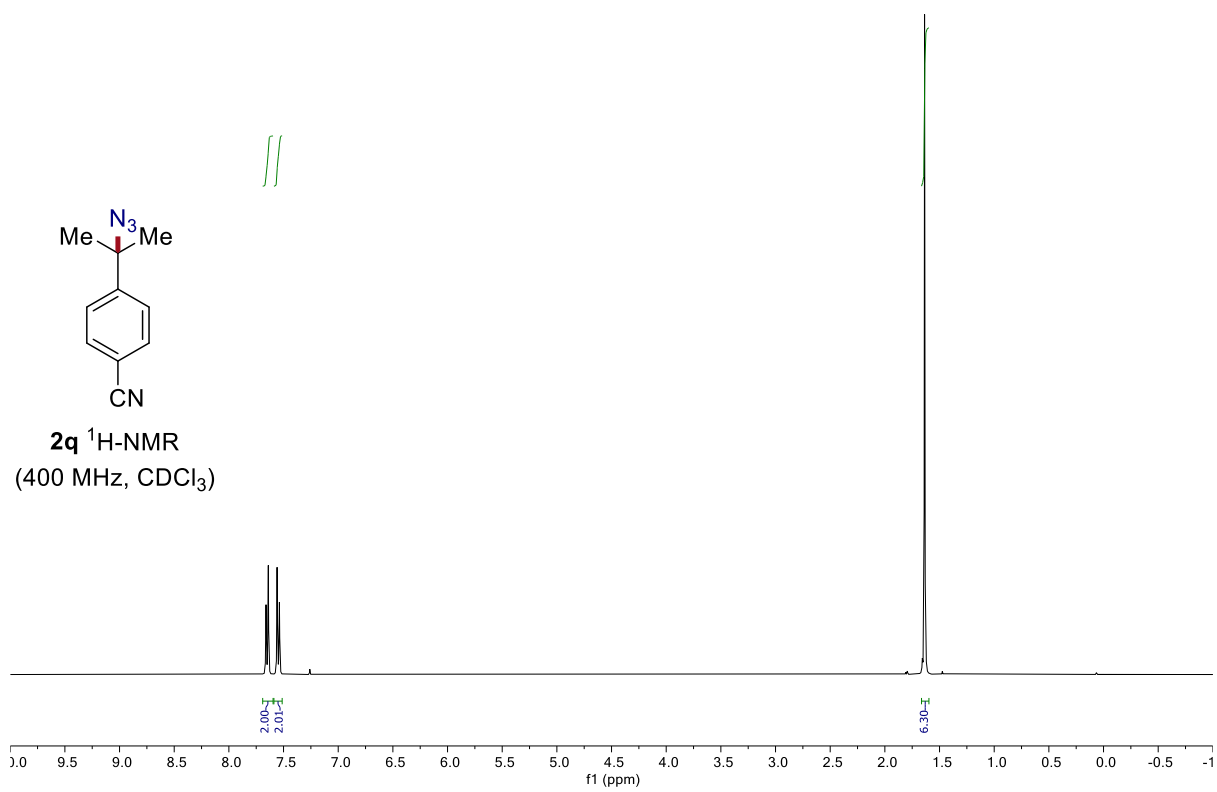
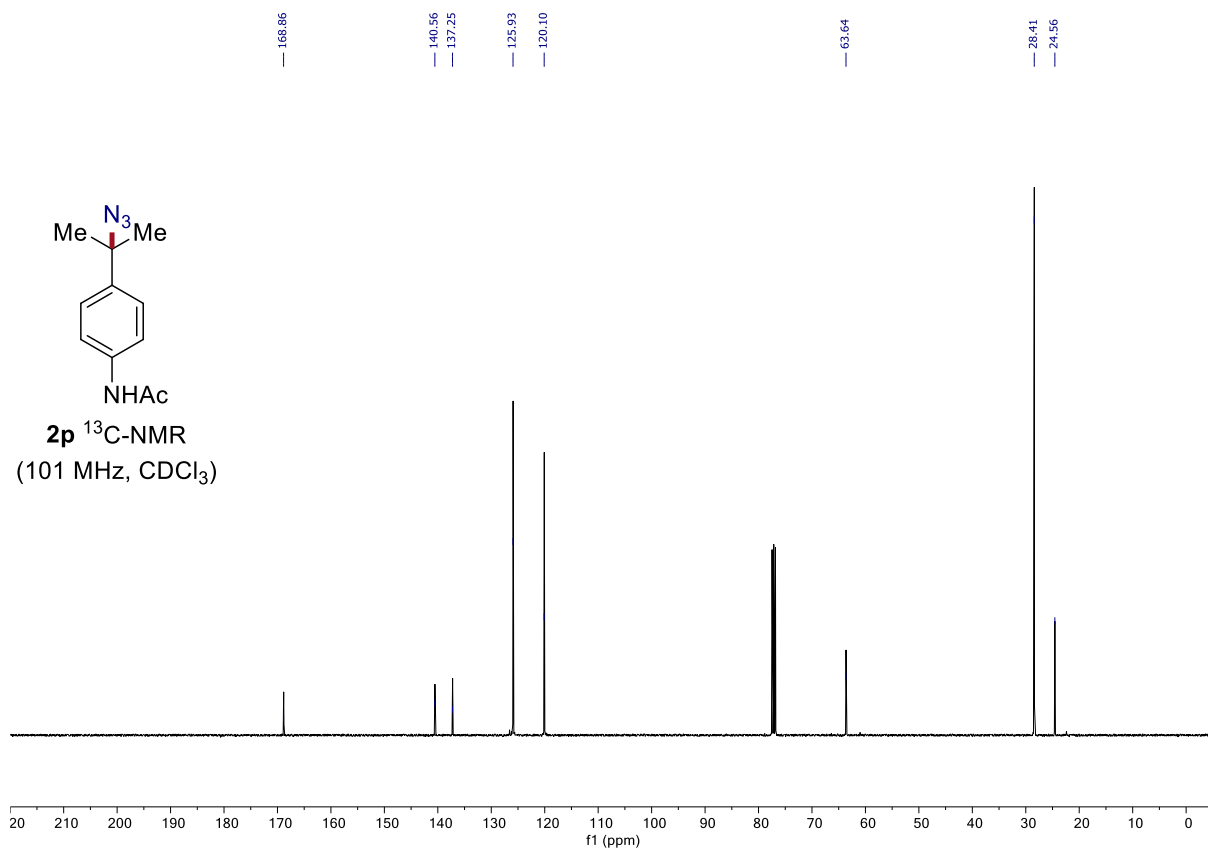


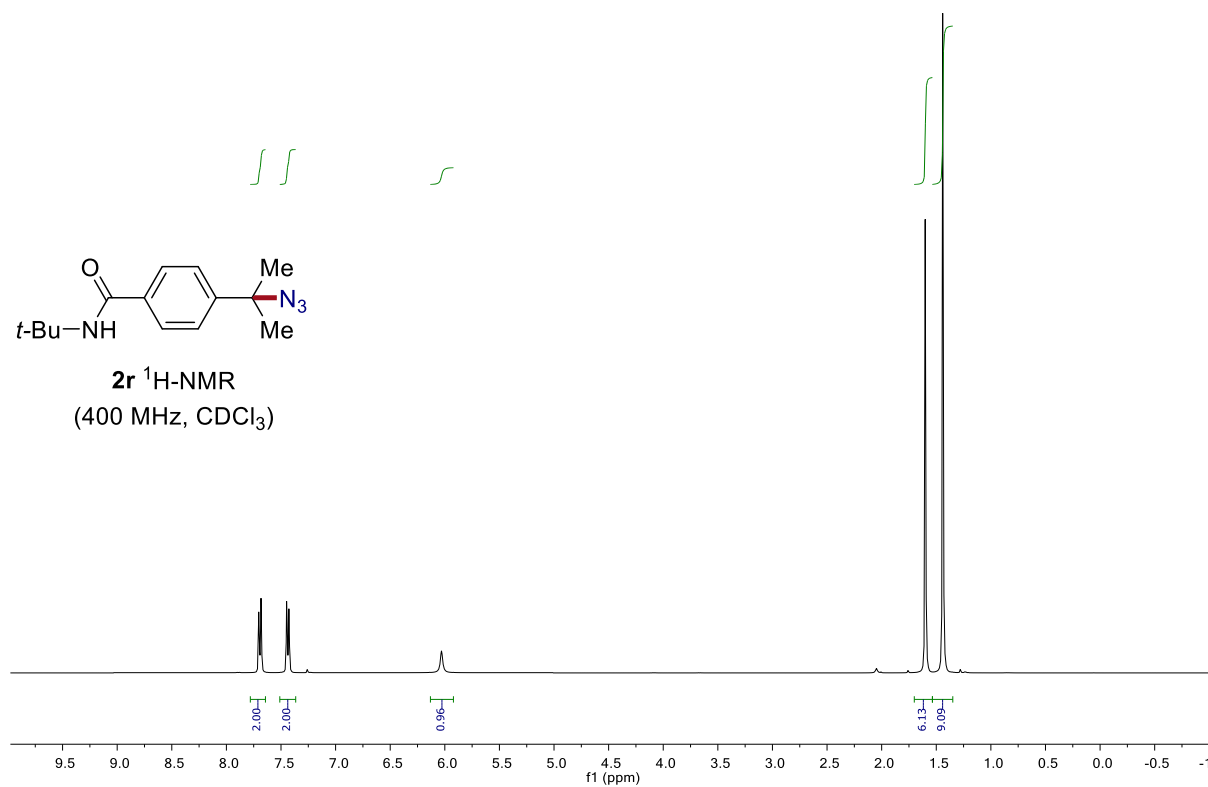
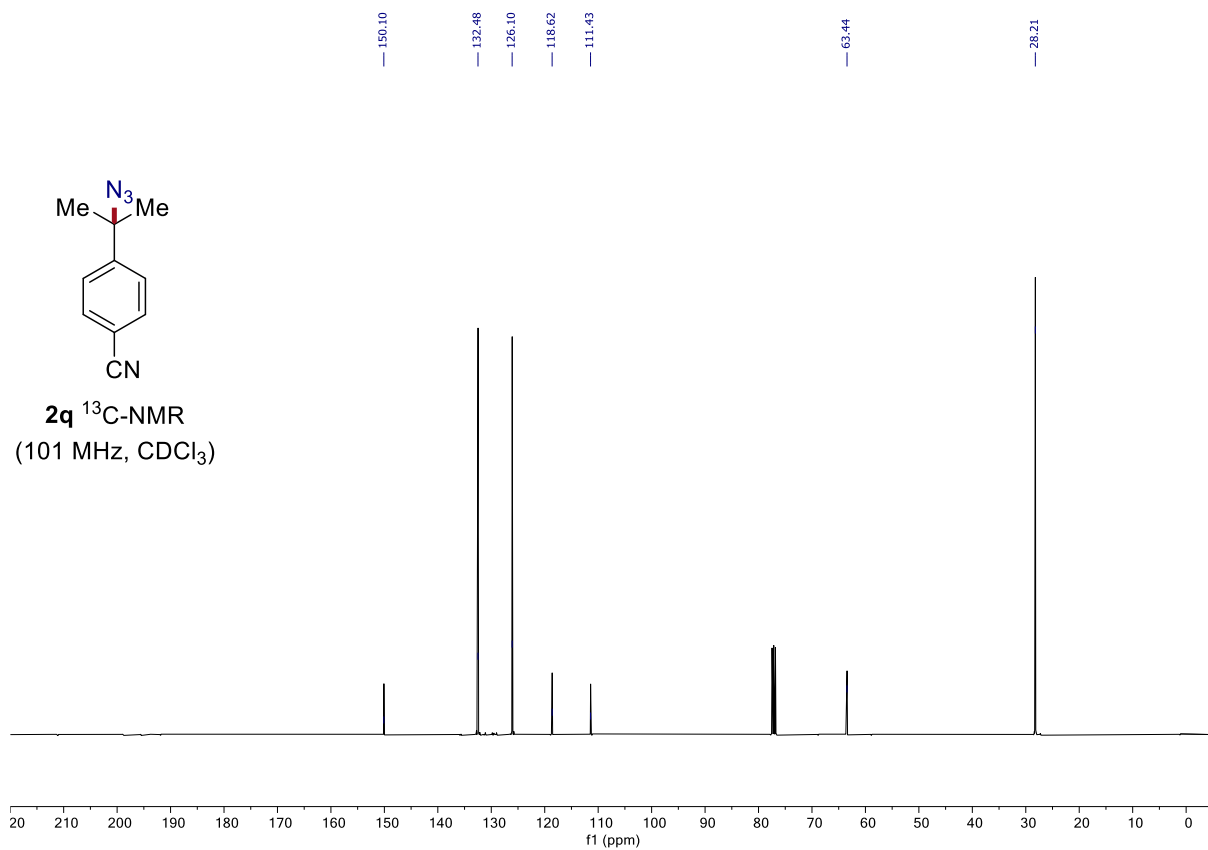


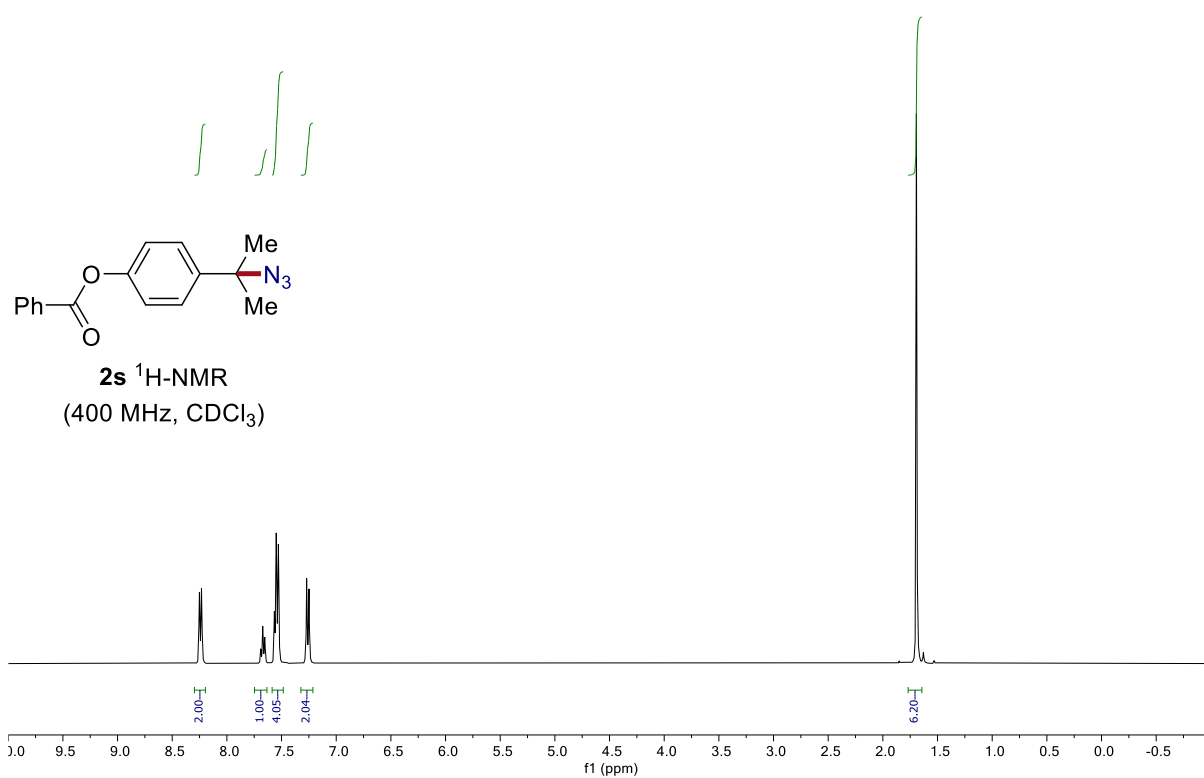
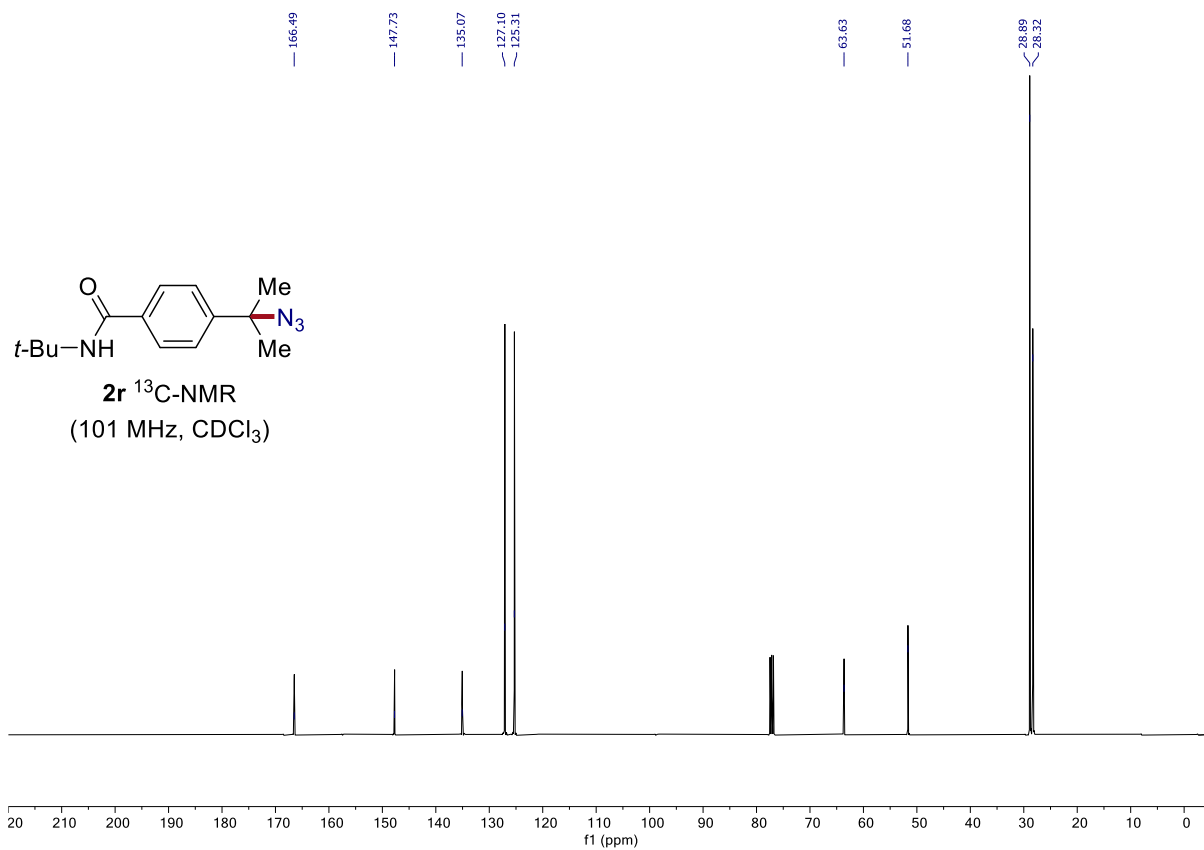


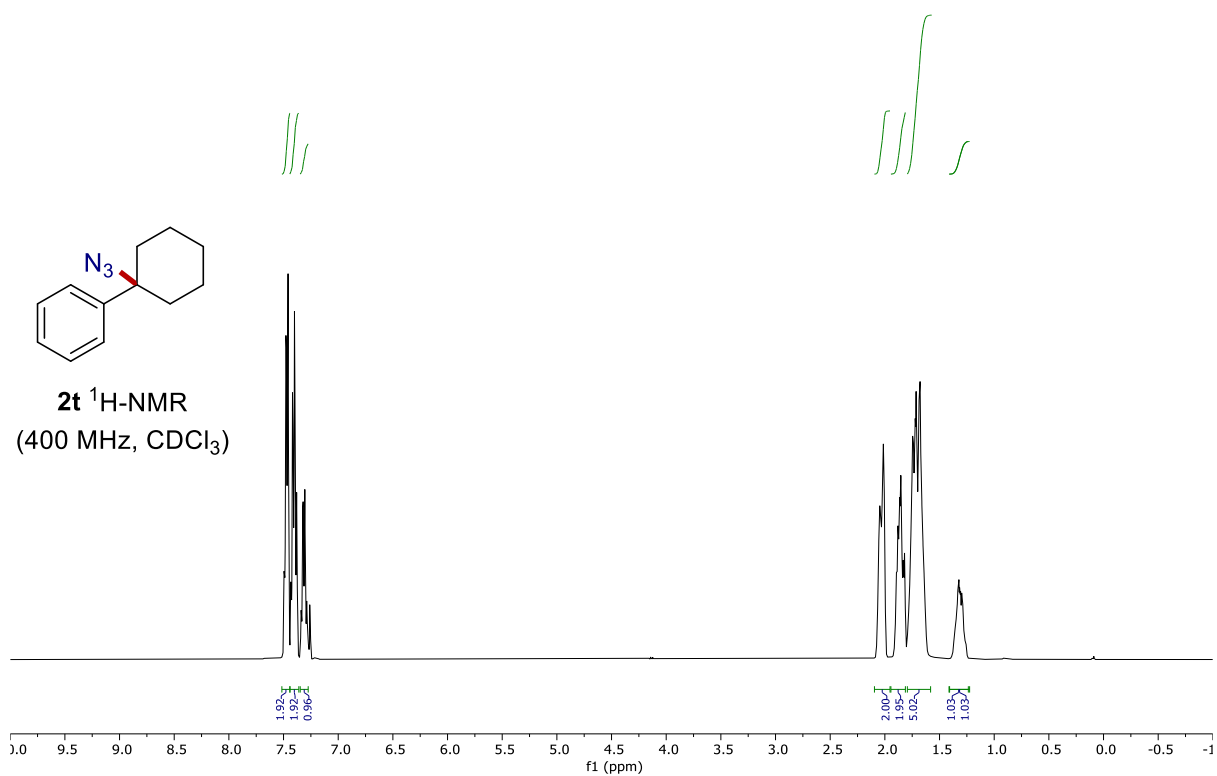
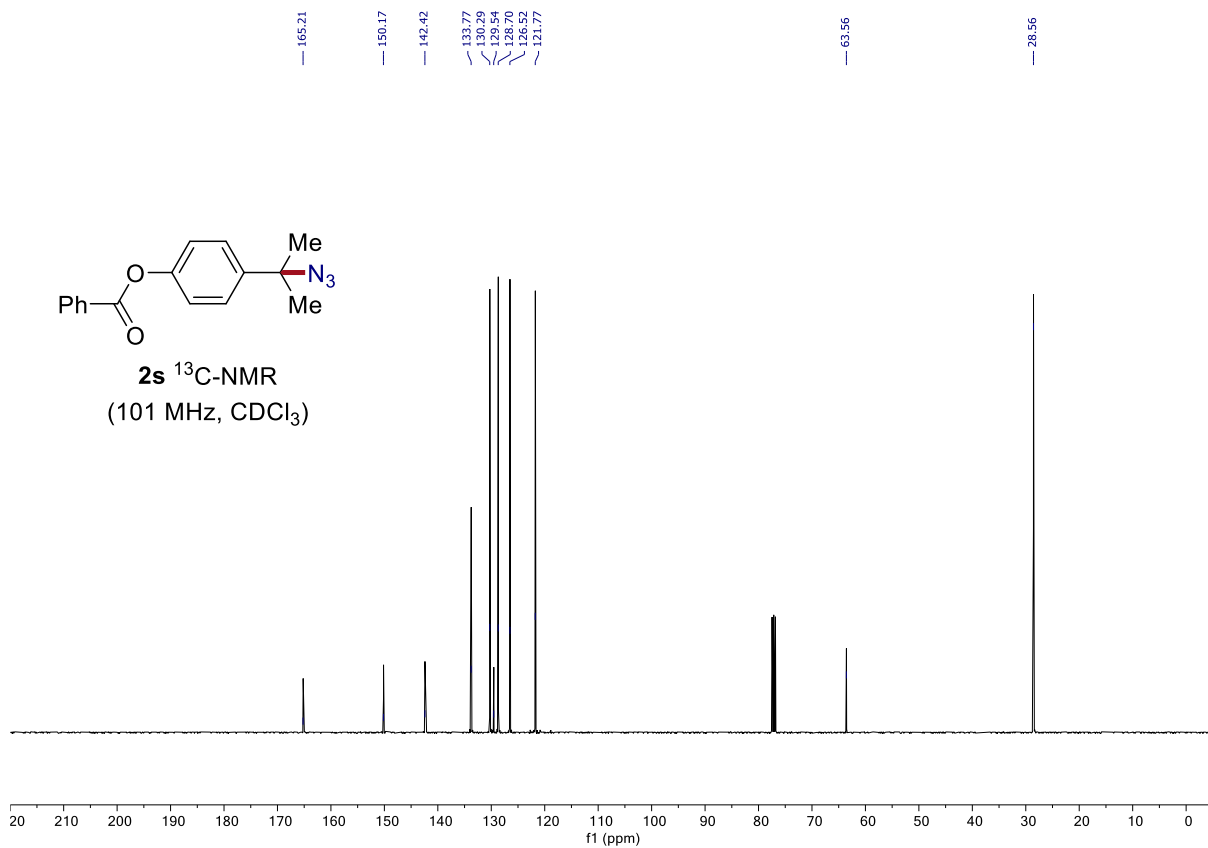


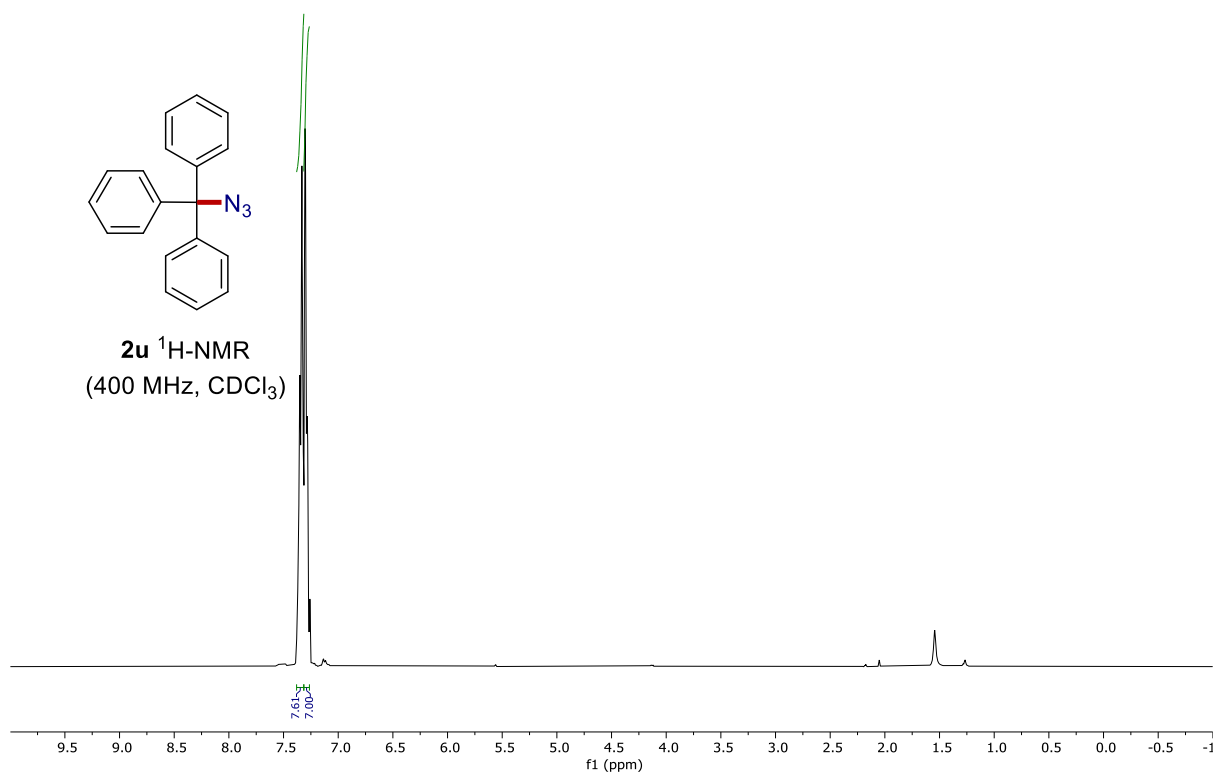
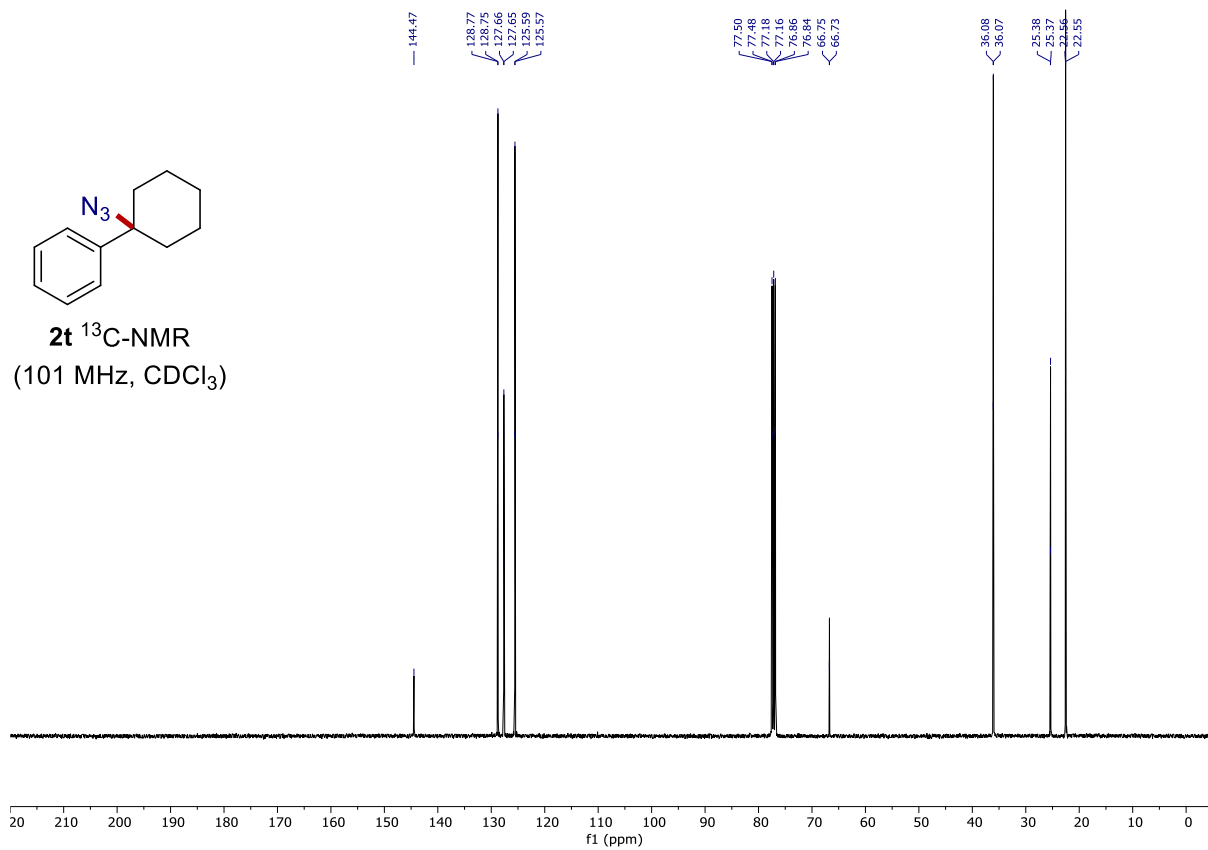


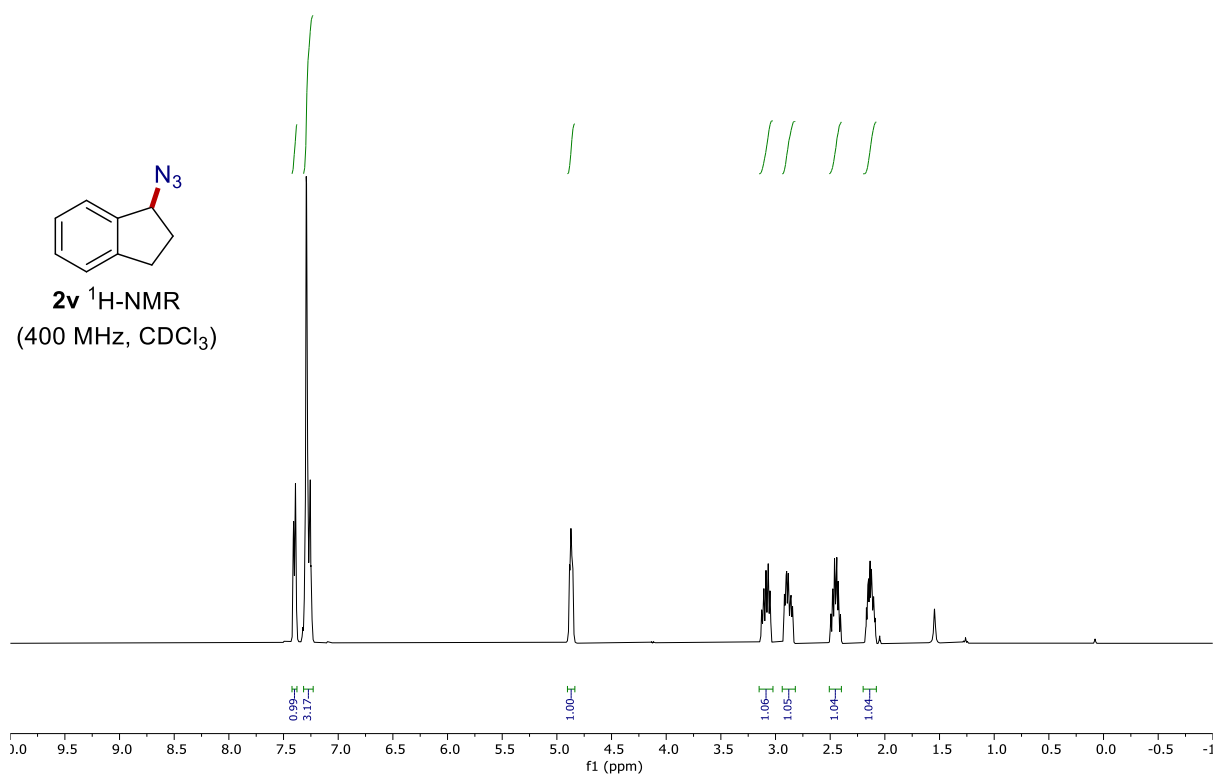
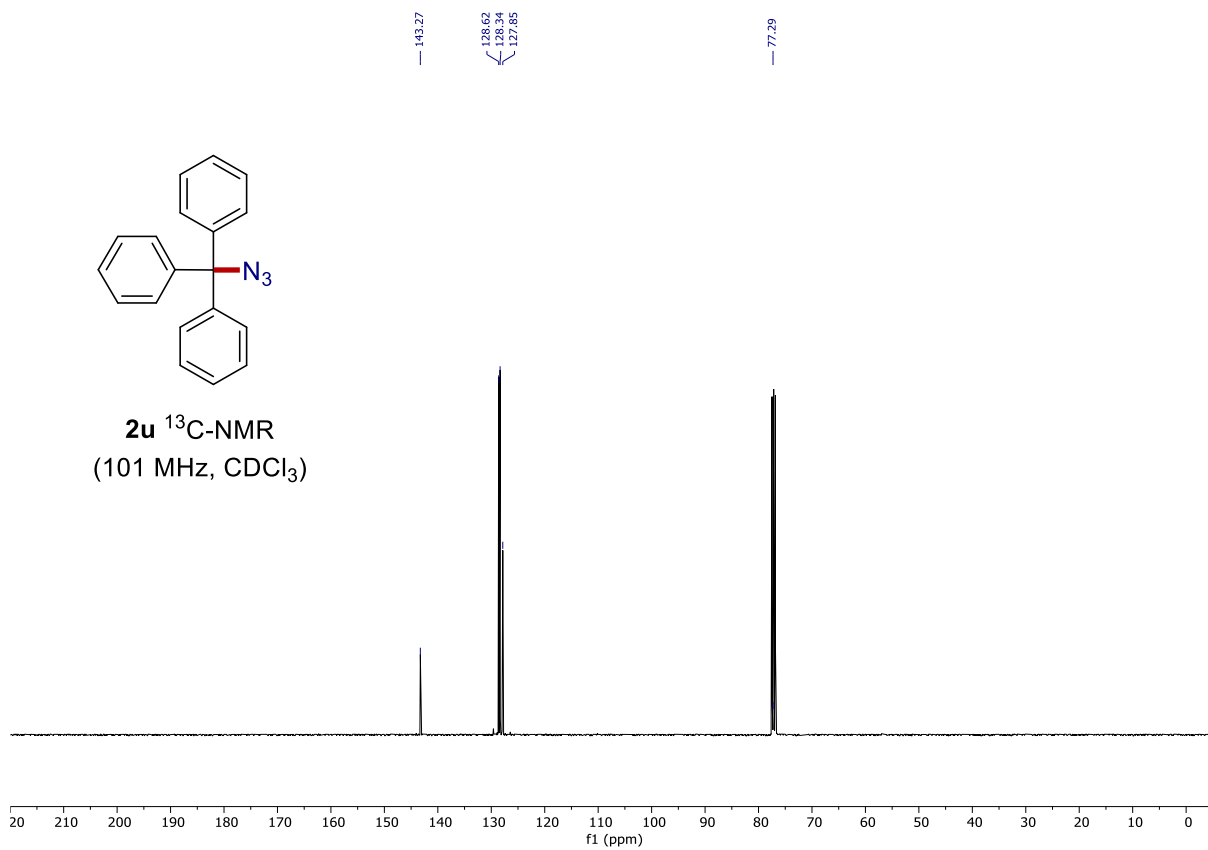


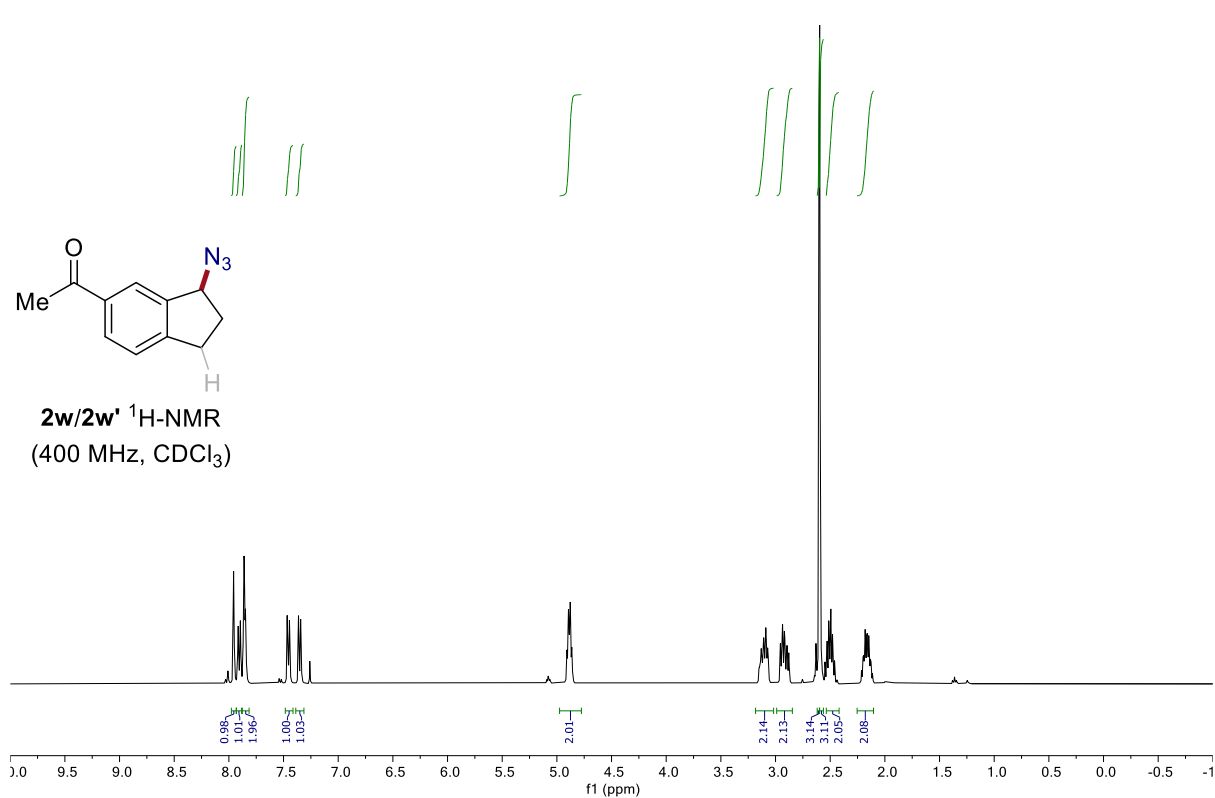
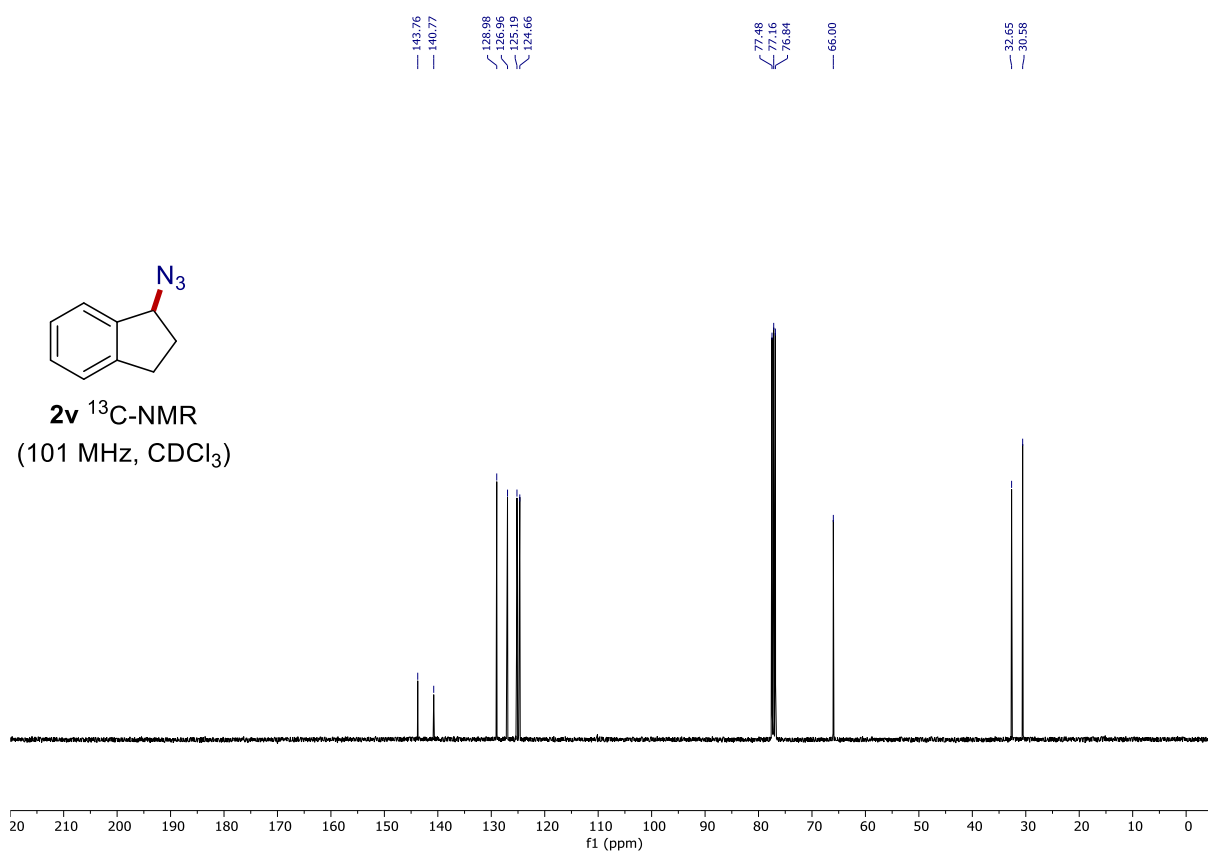


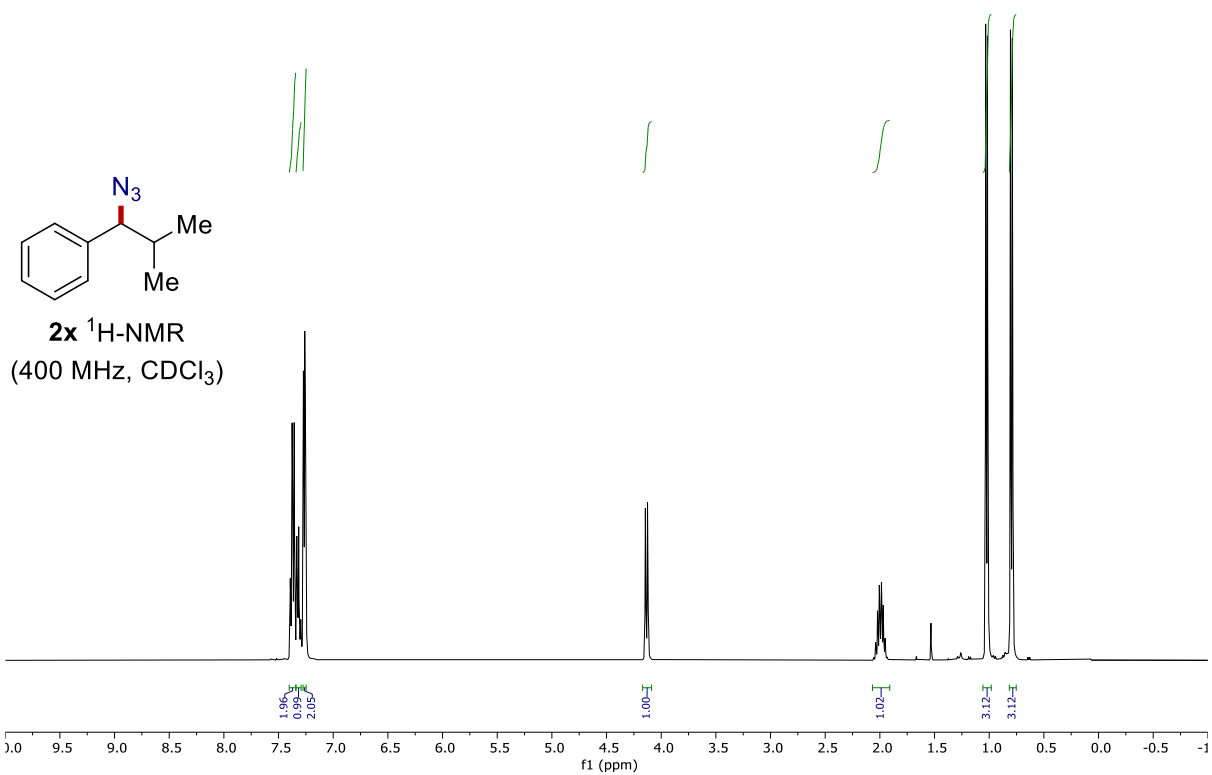
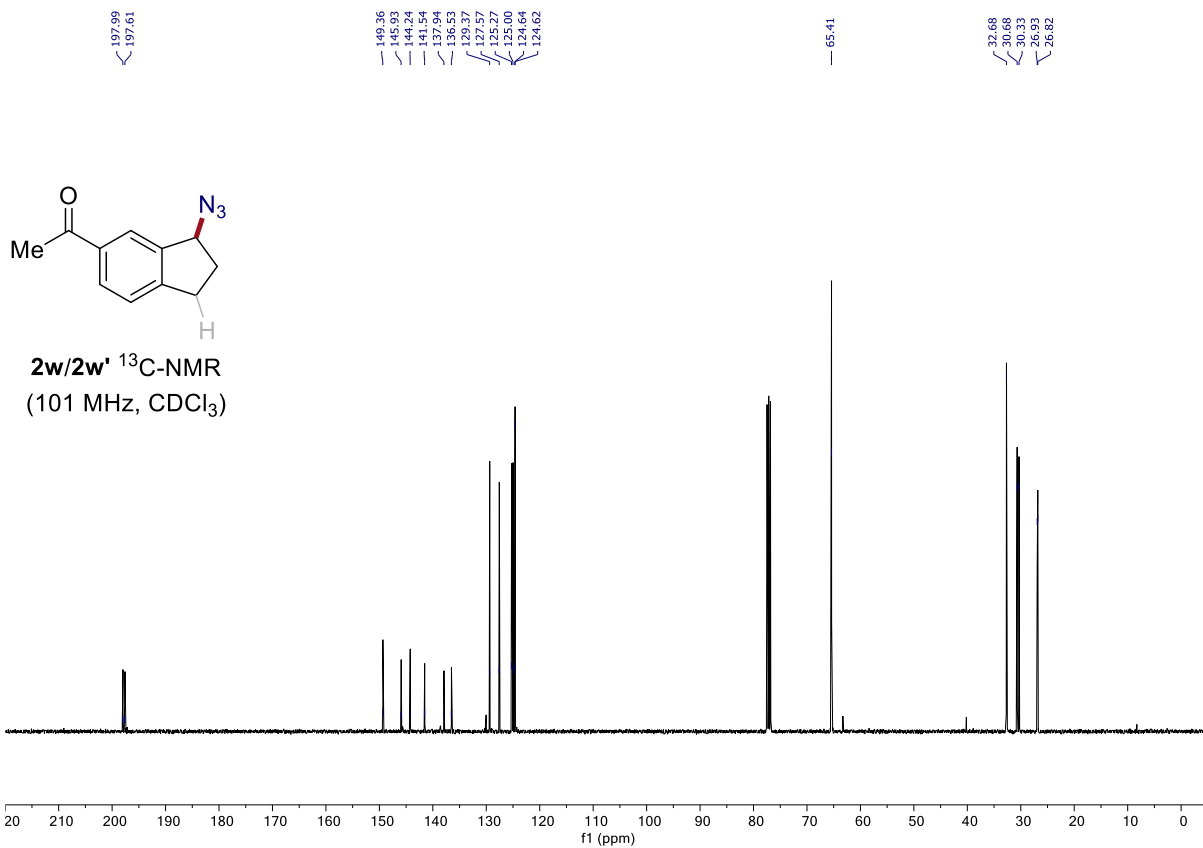




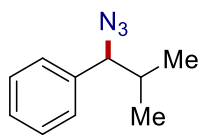




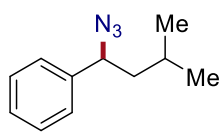
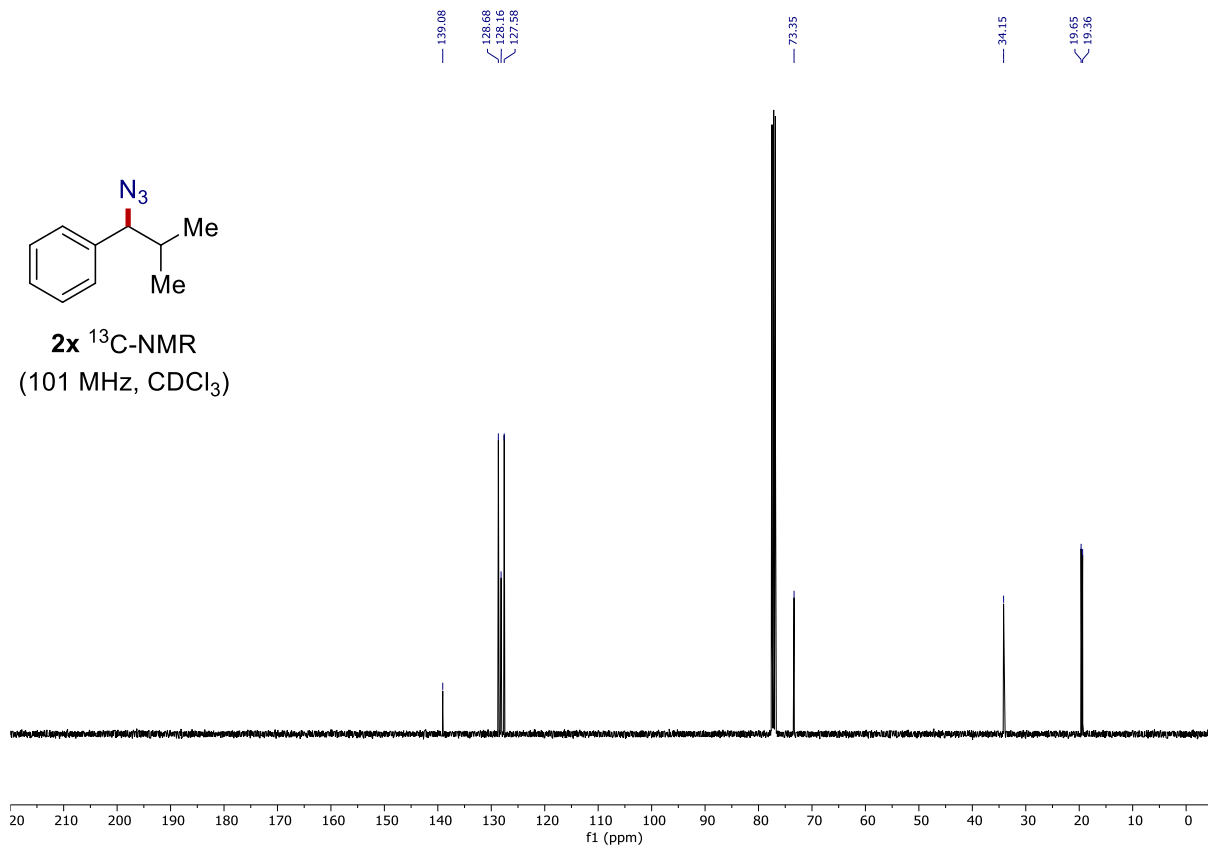








**2x**  $^{13}\text{C}$ -NMR  
(101 MHz,  $\text{CDCl}_3$ )



**2y**  $^1\text{H}$ -NMR  
(400 MHz,  $\text{CDCl}_3$ )

