

# Supporting Information

## Manganese-Catalyzed Oxidative Azidation of C(sp<sup>3</sup>)-H

### Bonds under Electrophotocatalytic Conditions

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## 1. General Information

All manipulations were carried out by standard Schlenk techniques. Unless otherwise stated, analytical grade solvents and commercially available reagents were used to conduct the reactions. LED irradiation was accomplished using the photochemical reactors. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in dichloromethane (bp. 39.8 °C). Gradient flash chromatography was conducted and eluted with a continuous gradient from dichloromethane to the methanol. All the new compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and HRMS or GCMS. The known compounds were characterized by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. The chemical shifts ( $\delta$ ) were given in part per million relative to internal tetramethyl silane (TMS, 0 ppm for  $^1\text{H}$  NMR),  $\text{CDCl}_3$  (77.30 ppm for  $^{13}\text{C}$  NMR). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT Premier or JEOL AccuTOF-MS. GCMS spectra were measured with a GCMS-QP2010SE. Hydrogen gas content was analyzed by gas chromatography (7890-II, Tianmei, China, TCD, nitrogen as a carrier gas and 5 Å molecular sieve column, a thermal conductivity detector).

Electrolysis experiments were performed using a dual display potentiostat (DJS-292B) or galvanostat (made in China). The carbon cloth or felt (made in China) was cut into 15 mm×15 mm pieces before use as anode electrode. The platinum plate (15 mm×15 mm×0.3 mm) (made in China) was purchased as the cathode electrode. Cyclic voltammograms were obtained on a CHI 605E potentiostat.

*CAUTION:* Organic azides are known to be potentially explosive compounds and should be stored below room temperature and away from sources of heat, pressure and shock. While we did not encounter any issues during their synthesis, proper precautions were taken. All azidation reactions and subsequent workups should be performed behind a blast shield.

## 2. Experiment Procedure

**Procedure A1:** In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar. The bottle was equipped with carbon cloth (15 mm×15 mm) and platinum electrode (15 mm×15 mm×0.3 mm). A solution of cyclohexylbenzene (0.5 mmol, 80.2 mg), sodium azide (2.5 mmol, 5 equiv., 162.5 mg), 9H-fluoren-9-one (0.055 mmol, 11.0 mol%, 9.9 mg),  $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$  (0.05 mmol,

10 mol%, 14.3 mg), 1,10-Phen (0.1 mmol, 20 mol%, 18.6 mg), KBr (0.2 mmol, 40 mol%, 23.8 mg), TFA (2.0 mmol, 4 equiv., 228.0 mg) and LiClO<sub>4</sub> (1.0 mmol, 2 equiv., 106.4 mg) in CH<sub>3</sub>CN (9.5 mL) and CH<sub>3</sub>COOH (0.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 4.5 mA and irradiated by blue LEDs at 35 °C for 15 h. After completion of the reaction, H<sub>2</sub> was detected by GC-TCD. Then the reaction system was quenched by water. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and the combined extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product **8** was obtained by flash column chromatography on silica gel (eluent: dichloromethane/ petroleum ether = 1:15). The substrates **4**, **5**, **6**, **8**, **9**, **10**, **14**, **16** and **19** were subjected to **Procedure A1** condition.

**Procedure A2:** In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar. The bottle was equipped with carbon cloth (15 mm×15 mm) and platinum electrode (15 mm×15 mm×0.3 mm). A solution of *p*-cymene (0.5 mmol, 67.1 mg), sodium azide (2.5 mmol, 5 equiv., 162.5 mg), 9H-fluoren-9-one (0.0275 mmol, 5.5 mol%, 5.0 mg), MnBr<sub>2</sub> • 4H<sub>2</sub>O (0.05 mmol, 10 mol%, 14.3 mg), 1,10-Phen (0.1 mmol, 20 mol%, 18.6 mg), KBr (0.2 mmol, 40 mol%, 23.8 mg), TFA (2.0 mmol, 4 equiv., 228.0 mg) and LiClO<sub>4</sub> (1.0 mmol, 2 equiv., 106.4 mg) in CH<sub>3</sub>CN (9.5 mL) and CH<sub>3</sub>COOH (0.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 4.5 mA and irradiated by blue LEDs at 35 °C for 15 h. After completion of the reaction, H<sub>2</sub> was detected by GC-TCD. Then the reaction system was quenched by water. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and the combined extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product **7** was obtained by flash column chromatography on silica gel (eluent: dichloromethane/ petroleum ether = 1:10). The substrates **7**, **23** and **24** were subjected to **Procedure A2** condition.

**Procedure A3:** In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar. The bottle was equipped with carbon cloth (15 mm×15 mm) and platinum electrode (15 mm×15 mm×0.3 mm). A solution of 2-isopropyl-9H-thioxanthen-9-one (0.5 mmol, 127.2 mg), sodium azide (2.5 mmol, 5 equiv., 162.5 mg), DDQ (0.0275 mmol, 5.5 mol%, 6.3 mg), MnBr<sub>2</sub> • 4H<sub>2</sub>O (0.05 mmol, 10 mol%, 14.3 mg), 1,10-Phen (0.1 mmol, 20 mol%, 18.6 mg), KBr (0.2 mmol, 40 mol%, 23.8 mg), TFA (2.0 mmol, 4 equiv., 228.0 mg) and LiClO<sub>4</sub> (1.0 mmol, 2 equiv., 106.4 mg) in CH<sub>3</sub>CN (9.5 mL) and CH<sub>3</sub>COOH (0.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current

of 4.5 mA and irradiated by blue LEDs at 35 °C for 15 h. After completion of the reaction, H<sub>2</sub> was detected by GC-TCD. Then the reaction system was quenched by water. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and the combined extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product **11** was obtained by flash column chromatography on silica gel (eluent: dichloromethane/ petroleum ether = 1:5). The substrates **11** and **25** were subjected to **Procedure A3** condition.

**Procedure A4:** In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar. The bottle was equipped with carbon cloth (15 mm×15 mm) and platinum electrode (15 mm×15 mm×0.3 mm). A solution of 1-ethyl-2-methylbenzene (0.5 mmol, 60.1 mg), sodium azide (2.5 mmol, 5 equiv., 162.5 mg), 9H-fluoren-9-one (0.0275 mmol, 5.5 mol%, 5.0 mg), MnF<sub>2</sub> (0.05 mmol, 10 mol%, 4.6 mg), 1,10-Phen (0.1 mmol, 20 mol%, 18.6 mg), KBr (0.2 mmol, 40 mol%, 23.8 mg), TFA (2.0 mmol, 4 equiv., 228.0 mg) and LiClO<sub>4</sub> (1.0 mmol, 2 equiv., 106.4 mg) in CH<sub>3</sub>CN (9.5 mL) and CH<sub>3</sub>COOH (0.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 4.5 mA and irradiated by blue LEDs at 35 °C for 15 h. After completion of the reaction, H<sub>2</sub> was detected by GC-TCD. Then the reaction system was quenched by water. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and the combined extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product **15** was obtained by flash column chromatography on silica gel (eluent: dichloromethane/ petroleum ether = 1:10). The substrates **15**, **20** and **22** were subjected to **Procedure A4** condition.

**Procedure A5:** In an oven-dried undivided three-necked bottle (10 mL) equipped with a stir bar. The bottle was equipped with carbon felt (15 mm×15 mm) and platinum electrode (15 mm×15 mm×0.3 mm). A solution of 1,2-diphenylethane (1.0 mmol, 182.3 mg), sodium azide (4.0 mmol, 4 equiv., 260.0 mg), DDQ (0.055 mmol, 5.5 mol%, 12.5 mg), MnF<sub>2</sub> (0.025 mmol, 2.5 mol%, 2.3 mg), 1,10-Phen (0.1 mmol, 10 mol%, 18.6 mg), TFA (2.0 mmol, 2 equiv., 228.0 mg) and LiClO<sub>4</sub> (1.0 mmol, 1 equiv., 106.4 mg) in CH<sub>3</sub>CN (3.0 mL), DCE (2.5 mL) and CH<sub>3</sub>COOH (0.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 4.5 mA and irradiated by blue LEDs at 35 °C for 24 h. After completion of the reaction, H<sub>2</sub> was detected by GC-TCD. Then the reaction system was quenched by water. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and the combined extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product **18** was obtained by flash column

chromatography on silica gel (eluent: dichloromethane/ petroleum ether = 1:10). The substrates **18** and **21** were subjected to **Procedure A5** condition.

**Procedure for A6:** In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar. The bottle was equipped with carbon cloth (15 mm×15 mm) and platinum electrode (15 mm×15 mm×0.3 mm). A solution of *sec*-butylbenzene (0.5 mmol, 67.1 mg), sodium azide (2.5 mmol, 5 equiv., 162.5 mg), bis(4-methoxyphenyl)methanone (0.0275 mmol, 5.5 mol%, 6.7 mg), MnF<sub>2</sub> (0.05 mmol, 10 mol%, 4.7 mg), 1,10-Phen (0.1 mmol, 20 mol%, 18.6 mg), KBr (0.2 mmol, 40 mol%, 23.8 mg), TFA (2.0 mmol, 4 equiv., 228.0 mg) and LiClO<sub>4</sub> (1.0 mmol, 2 equiv., 106.4 mg) in CH<sub>3</sub>CN (9.5 mL) and CH<sub>3</sub>COOH (0.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 4.5 mA and irradiated by blue LEDs at 35 °C for 15 h. After completion of the reaction, H<sub>2</sub> was detected by GC-TCD. Then the reaction system was quenched by water. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and the combined extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product **13** was obtained by flash column chromatography on silica gel (eluent: dichloromethane/ petroleum ether = 1:10). The substrates **13** and **17** were subjected to **Procedure A6** condition.

**Procedure B1:** In an oven-dried undivided three-necked bottle (10 mL) equipped with a stir bar. The bottle was equipped with carbon felt (15 mm×15 mm) and platinum electrode (15 mm×15 mm×0.3 mm). A solution of 1,1'-bi(cyclohexane) (1.0 mmol, 166.3 mg), sodium azide (4.0 mmol, 4 equiv., 260.0 mg), DDQ (0.055 mmol, 5.5 mol%, 12.5 mg), MnF<sub>2</sub> (0.05 mmol, 5 mol%, 4.6 mg), 1,10-Phen (0.1 mmol, 10 mol%, 18.6 mg), TFA (2.0 mmol, 2 equiv., 228.0 mg) and LiClO<sub>4</sub> (1.0 mmol, 1 equiv., 106.4 mg) in CH<sub>3</sub>CN (3.0 mL), DCE (2.5 mL) and CH<sub>3</sub>COOH (0.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 8.0 mA and irradiated by blue LEDs at 35 °C for 21 h. After completion of the reaction, H<sub>2</sub> was detected by GC-TCD. Then the reaction system was quenched by water. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and the combined extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product **30** was obtained by flash column chromatography on silica gel (eluent: dichloromethane/ petroleum ether). The substrates **12**, **27**, **29**, **30**, **31**, **32**, **33**, **34**, **39** and **40** were subjected to **Procedure B1** condition.

**Procedure B2:** In an oven-dried undivided three-necked bottle (10 mL) equipped with a stir bar.

The bottle was equipped with carbon felt (15 mm×15 mm) and platinum electrode (15 mm×15 mm×0.3 mm). A solution of celestolide (1.0 mmol, 244.4 mg), sodium azide (4.0 mmol, 4 equiv., 260.0 mg), DDQ (0.055 mmol, 5.5 mol%, 12.5 mg), MnF<sub>2</sub> (0.025 mmol, 2.5 mol%, 2.3 mg), 1,10-Phen (0.1 mmol, 10 mol%, 18.6 mg), TFA (2.0 mmol, 2 equiv., 228.0 mg) and LiClO<sub>4</sub> (1.0 mmol, 1 equiv., 106.4 mg) in CH<sub>3</sub>CN (3.0 mL), DCE (2.5 mL) and CH<sub>3</sub>COOH (0.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 8.0 mA and irradiated by blue LEDs at 35 °C for 21 h. After completion of the reaction, H<sub>2</sub> was detected by GC-TCD. Then the reaction system was quenched by water. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and the combined extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product **38** was obtained by flash column chromatography on silica gel (eluent: dichloromethane/ petroleum ether = 1:5). The substrates **36** and **38** were subjected to **Procedure B2** condition.

**Procedure for 26 and 28:** In an oven-dried undivided three-necked bottle (10 mL) equipped with a stir bar. The bottle was equipped with carbon felt (15 mm×15 mm) and platinum electrode (15 mm×15 mm×0.3 mm). A solution of cyclooctane (0.5 mmol, 56.1 mg), sodium azide (2.5 mmol, 5 equiv., 162.5 mg), DDQ (0.05 mmol, 5.5 mol%, 6.2 mg), MnF<sub>2</sub> (0.05 mmol, 10.0 mol%, 4.6 mg), 1,10-Phen (0.1 mmol, 20.0 mol%, 18.6 mg), TFA (2.0 mmol, 4 equiv., 228.0 mg) and LiClO<sub>4</sub> (1.0 mmol, 2 equiv., 106.4 mg) in CH<sub>3</sub>CN (3.0 mL), DCE (2.5 mL) and CH<sub>3</sub>COOH (0.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 6.0 mA and irradiated by blue LEDs at 35 °C for 15 h. After completion of the reaction, H<sub>2</sub> was detected by GC-TCD. Then the reaction system was quenched by water. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and the combined extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product **26** and **28** were obtained by flash column chromatography on silica gel (eluent: dichloromethane/ petroleum ether = 1:20), while the yield was determined by GC with biphenyl as internal.

**Procedure for 35:** In an oven-dried undivided three-necked bottle (10 mL) equipped with a stir bar. The bottle was equipped with carbon felt (15 mm×15 mm) and platinum electrode (15 mm×15 mm×0.3 mm). A solution of 2-isopentylisoindoline-1,3-dione (0.5 mmol, 108.5 mg), sodium azide (4.0 mmol, 8 equiv., 260.0 mg), DDQ (0.055 mmol, 11.0 mol%, 12.6 mg), MnF<sub>2</sub> (0.0375 mmol, 7.5 mol%, 3.5 mg), 1,10-Phen (0.1 mmol, 20.0 mol%, 18.6 mg), TFA (2.0 mmol, 4 equiv., 228.0 mg)

and LiClO<sub>4</sub> (1.0 mmol, 2 equiv., 106.4 mg) in CH<sub>3</sub>CN (3.0 mL), DCE (2.5 mL) and CH<sub>3</sub>COOH (0.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 8.0 mA and irradiated by blue LEDs at 35 °C for 21 h. After completion of the reaction, H<sub>2</sub> was detected by GC-TCD. Then the reaction system was quenched by water. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and the combined extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product **35** was obtained by flash column chromatography on silica gel (eluent: dichloromethane/ petroleum ether = 1:5).

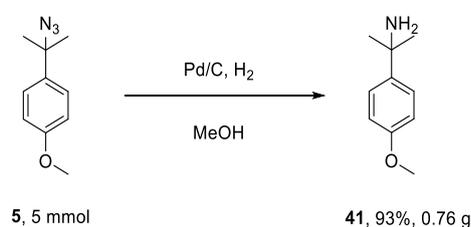
**Procedure for 37:** In an oven-dried undivided three-necked bottle (10 mL) equipped with a stir bar. The bottle was equipped with carbon felt (15 mm×15 mm) and platinum electrode (15 mm×15 mm×0.3 mm). A solution of adapalene precursor (0.5 mmol, 160.5 mg), sodium azide (2.5 mmol, 5 equiv., 162.5 mg), DDQ (0.0275 mmol, 5.5 mol%, 6.3 mg), MnF<sub>2</sub> (0.050 mmol, 10.0 mol%, 4.6 mg), 1,10-Phen (0.1 mmol, 20.0 mol%, 18.6 mg), TFA (2.0 mmol, 4 equiv., 228.0 mg) and LiClO<sub>4</sub> (1.0 mmol, 2 equiv., 106.4 mg) in CH<sub>3</sub>CN (3.0 mL), DCE (2.5 mL) and CH<sub>3</sub>COOH (0.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 4.5 mA and irradiated by blue LEDs at 35 °C for 15 h. After completion of the reaction, H<sub>2</sub> was detected by GC-TCD. Then the reaction system was quenched by water. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL) and the combined extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product **37** was obtained by flash column chromatography on silica gel (eluent: dichloromethane/ petroleum ether = 1:10).

**General procedure for the study of accelerating effect of visible light irradiation in the initial stage of the reaction:** In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar. The bottle was equipped with carbon cloth (15 mm×15 mm) and platinum electrode (15 mm×15 mm×0.3 mm). A solution of 1-isopropyl-4-methoxybenzene (0.5 mmol, 75.1 mg), sodium azide (2.5 mmol, 5.0 equiv., 162.5 mg), bis(4-methoxyphenyl)methanone (0.0275 mmol, 5.5 mol%, 6.7 mg), MnF<sub>2</sub> (0.05 mmol, 10.0 mol%, 4.6 mg), 1,10-Phen (0.1 mmol, 20.0 mol%, 18.6 mg), KBr (0.2 mmol, 40.0 mol%, 23.8 mg), TFA (2.0 mmol, 4.0 equiv., 228.0 mg) and LiClO<sub>4</sub> (1.0 mmol, 2.0 equiv., 106.4 mg) in CH<sub>3</sub>CN (9.5 mL) and CH<sub>3</sub>COOH (0.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 4.5 mA and irradiated by blue LEDs at 35 °C for different times (1.0 h, 1.5 h, 2.0 h, 2.5 h). After completion of the reaction, the reaction system was quenched by water. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and the combined extracts were

dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The yields of products **5** could be determined by <sup>1</sup>H NMR with diphenylmethane as the internal standard. Using the above mentioned procedure, the reaction at different times (1.0 h, 1.5 h, 2.0 h, 2.5 h) under darkness were conducted.

**Procedure for gram scale synthesis:** In an oven-dried undivided three-necked bottle (100 mL) equipped with a stir bar. The bottle was equipped with carbon cloth (30 mm×30 mm) and platinum electrode (15 mm×15 mm×0.3 mm). A solution of 1-isopropyl-4-methoxybenzene (10.0 mmol, 1.5 g), sodium azide (40.0 mmol, 4.0 equiv., 2.6 g), bis(4-methoxyphenyl)methanone (0.55 mmol, 5.5 mol%, 134 mg), MnF<sub>2</sub> (1.0 mmol, 10 mol%, 92 mg), 1,10-Phen (2.0 mmol, 20 mol%, 372 mg), KBr (4.0 mmol, 40 mol%, 476 mg), TFA (40.0 mmol, 4 equiv., 4.6 g) and LiClO<sub>4</sub> (10.0 mmol, 1.0 equiv., 1.06 g) in CH<sub>3</sub>CN (80.0 mL) and CH<sub>3</sub>COOH (7.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 8.0 mA and irradiated by blue LEDs at 35 °C for 72 h. After completion of the reaction, H<sub>2</sub> was detected by GC-TCD. Then the reaction system was quenched by water. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 100 mL) and the combined extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The conversion of reactants and the yield of product could be determined by GC with naphthalene as the internal standard. The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product **5** was obtained by flash column chromatography on silica gel (eluent: dichloromethane/ petroleum ether = 1:5).

**Procedure for azidation reduction experiments:** In an oven-dried undivided three-necked bottle (100 mL) equipped with a stir bar. A solution of 1-(2-azidopropan-2-yl)-4-methoxybenzene **5** (5.0 mmol, 955.5 mg), Pd/C (10 % Pd, 57.3 % H<sub>2</sub>O) (5 mmol, 125.0 mg) in MeOH (25.0 mL) stirring under H<sub>2</sub> (1 atm, hydrogen-filled balloon) was stirred at r.t. for 38 h. After completion of the reaction, Then, the pure product **41** was obtained by flash column chromatography on silica gel.



**Figure S1.** The azide reduction experiment.

**Procedure for radical inhibition experiment:** In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar. The bottle was equipped with carbon cloth (15 mm×15 mm) and

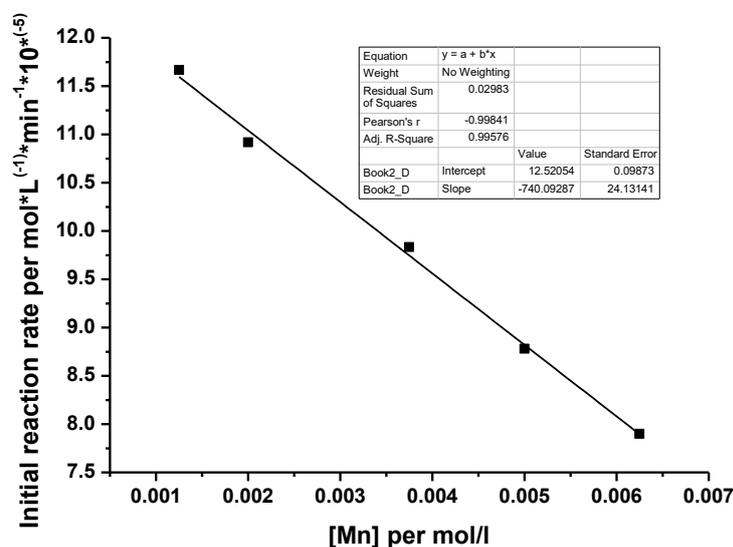
platinum electrode (15 mm×15 mm×0.3 mm). A solution of 1-ethylnaphthalene (0.50 mmol, 78.1 mg), sodium azide (2.5 mmol, 5.0 equiv., 162.5 mg), TEMPO (1.0 mmol, 2.0 equiv., 156.3 mg), 9H-fluoren-9-one (0.0275 mmol, 5.5 mol%, 5.0 mg), MnBr<sub>2</sub> · 4H<sub>2</sub>O (0.05 mmol, 10.0 mol%, 14.3 mg), 1,10-Phen (0.10 mmol, 20.0 mol%, 18.6 mg), KBr (0.20 mmol, 40.0 mol%, 23.8 mg), TFA (2.0 mmol, 4.0 equiv., 228.0 mg) and LiClO<sub>4</sub> (1.0 mmol, 2.0 equiv., 106.4 mg) in CH<sub>3</sub>CN (9.5 mL) and CH<sub>3</sub>COOH (0.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 4.5 mA and irradiated by blue LEDs at 35 °C for 15 h. After completion of the reaction, the reaction results were monitored by TLC and GC-MS.

**Procedure for kinetic of isotopic effect experiments:** In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar. The bottle was equipped with carbon cloth (15 mm×15 mm) and platinum electrode (15 mm×15 mm×0.3 mm). A solution of cyclohexylbenzene (0.50 mmol, 80.1 mg), sodium azide (2.50 mmol, 5.0 equiv., 162.5 mg), bis(4-methoxyphenyl)methanone (0.0275 mmol, 5.5 mol%, 6.7 mg), MnF<sub>2</sub> (0.05 mmol, 10.0 mol%, 4.6 mg), 1,10-Phen (0.10 mmol, 20.0 mol%, 18.6 mg), KBr (0.20 mmol, 40.0 mol%, 23.8 mg), TFA (2.0 mmol, 4.0 equiv., 228.0 mg) and LiClO<sub>4</sub> (1.0 mmol, 2.0 equiv., 106.4 mg) in CH<sub>3</sub>CN (9.5 mL) and CH<sub>3</sub>COOH (0.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 4.5 mA and irradiated by blue LEDs at 35 °C for 2 h. After completion of the reaction, the aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and the combined extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure by rotary evaporation. The yield of product **8** could be determined by GC with naphthalene as the internal standard.

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar. The bottle was equipped with carbon cloth (15 mm×15 mm) and platinum electrode (15 mm×15 mm×0.3 mm). A solution of (cyclohexyl-1-d)benzene (0.50 mmol, 80.1 mg), sodium azide (2.5 mmol, 5.0 equiv., 162.5 mg), bis(4-methoxyphenyl)methanone (0.0275 mmol, 5.5 mol%, 6.7 mg), MnF<sub>2</sub> (0.050 mmol, 10.0 mol%, 4.6 mg), 1,10-Phen (0.10 mmol, 20.0 mol%, 18.6 mg), KBr (0.20 mmol, 40.0 mol%, 23.8 mg), TFA (2.0 mmol, 4 equiv., 228.0 mg) and LiClO<sub>4</sub> (1.0 mmol, 2.0 equiv., 106.4 mg) in CH<sub>3</sub>CN (9.5 mL) and CH<sub>3</sub>COOH (0.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 4.5 mA and irradiated by blue LEDs at 35 °C for 2 h. After completion of the reaction, the aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and the combined extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure by rotary

evaporation. The yield of product **8** could be determined by GC with naphthalene as the internal standard.

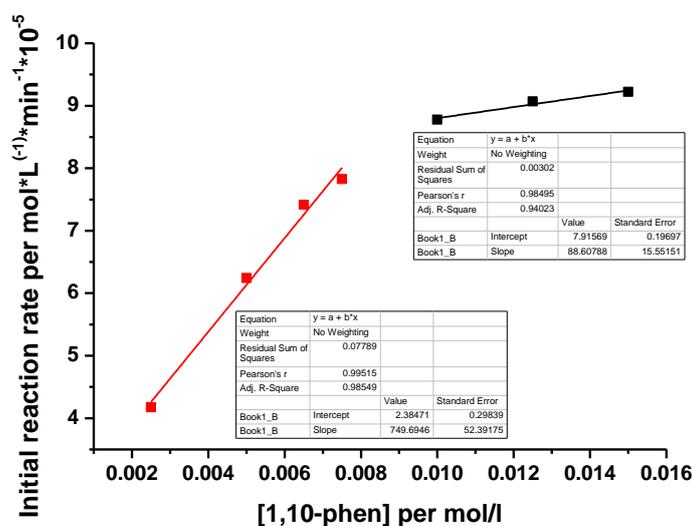
**General procedure for kinetic plots of [Mn]:** The order in catalyst MnF<sub>2</sub> was determined by studying the initial rate of reaction with different concentrations of MnF<sub>2</sub>. Using the above mentioned general procedure, 1-isopropyl-4-methoxybenzene (0.50 mmol, 75.1 mg), sodium azide (2.5 mmol, 5.0 equiv., 162.5 mg), bis(4-methoxyphenyl)methanone (0.0275 mmol, 5.5 mol%, 6.7 mg), MnF<sub>2</sub> (0.0125 mmol, 0.020 mmol, 0.0375 mmol, 0.050 mmol, 0.0625 mmol), 1,10-Phen (0.10 mmol, 20.0 mol%, 18.6 mg), KBr (0.20 mmol, 40.0 mol%, 23.8 mg), TFA (2.0 mmol, 4.0 equiv., 228.0 mg) and LiClO<sub>4</sub> (1.0 mmol, 2.0 equiv., 106.4 mg) in CH<sub>3</sub>CN (9.5 mL) and CH<sub>3</sub>COOH (0.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 4.5 mA and irradiated by blue LEDs at 35 °C for 2 h. The yields of product could be determined by <sup>1</sup>H NMR with diphenylmethane as the internal standard. These experiments were operated two times and the initial rates were determined by the average yields. Finally, the initial rate for different concentration of [Mn] vs relative concentrations could be obtained.



**Figure S2. The kinetic study of [Mn].**

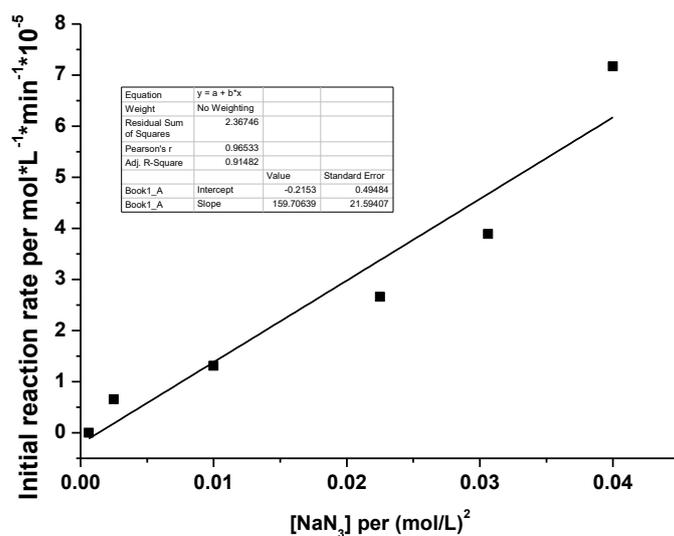
**General procedure for kinetic plots of 1,10-Phen:** The order in ligand 1,10-Phen was determined by studying the initial rate of reaction with different concentrations of 1,10-Phen. Using the above mentioned general procedure, 1-isopropyl-4-methoxybenzene (0.50 mmol, 75.1 mg), sodium azide (2.50 mmol, 5.0 equiv., 162.5 mg), bis(4-methoxyphenyl)methanone (0.0275 mmol, 5.50 mol%, 6.7 mg), MnF<sub>2</sub> (0.050 mmol, 10.0 mol%, 4.6 mg), 1,10-Phen (0.025 mmol, 0.050 mmol, 0.065 mmol,

0.075 mmol, 0.10 mmol, 0.125 mmol, 0.15 mmol), KBr (0.20 mmol, 40.0 mol%, 23.8 mg), TFA (2.0 mmol, 4.0 equiv., 228.0 mg) and LiClO<sub>4</sub> (1.0 mmol, 2.0 equiv., 106.4 mg) in CH<sub>3</sub>CN (9.5 mL) and CH<sub>3</sub>COOH (0.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 4.5 mA and irradiated by blue LEDs at 35 °C for 2 h. The yields of product could be determined by <sup>1</sup>H NMR with diphenylmethane as the internal standard. These experiments were operated two times and the initial rates were determined by the average yields. Finally, the initial rate for different concentration of 1,10-Phen vs relative concentrations could be obtained.



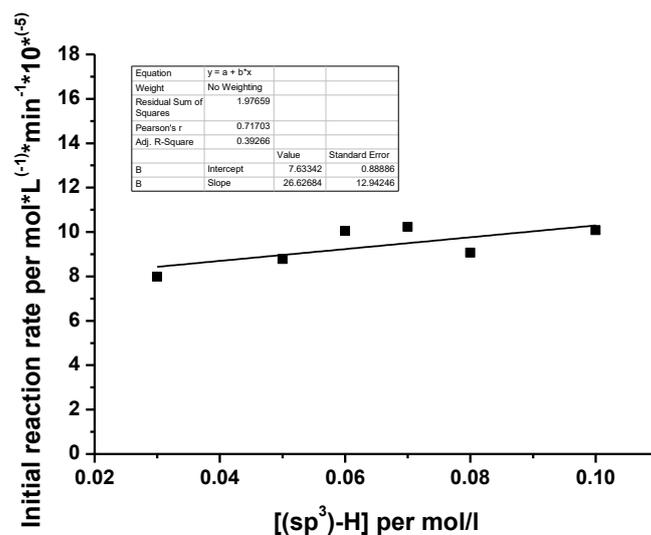
**Figure S3. The kinetic study of [1,10-Phen].**

**General procedure for kinetic plots of NaN<sub>3</sub>:** The order in sodium azide was determined by studying the initial rate of reaction with different concentrations of sodium azide. Using the above mentioned general procedure, 1-isopropyl-4-methoxybenzene (0.50 mmol, 75.1 mg), sodium azide (0.25 mmol, 0.50 mmol, 1.00 mmol, 1.50 mmol, 1.75 mmol, 2.00 mmol), bis(4-methoxyphenyl)methanone (0.0275 mmol, 5.5 mol%, 6.7 mg), MnF<sub>2</sub> (0.05 mmol, 10.0 mol%, 4.6 mg), 1,10-Phen (0.10 mmol, 20.0 mol%, 18.6 mg), KBr (0.20 mmol, 40.0 mol%, 23.8 mg), TFA (2.0 mmol, 4.0 equiv., 228.0 mg) and LiClO<sub>4</sub> (1.0 mmol, 2.0 equiv., 106.4 mg) in CH<sub>3</sub>CN (9.5 mL) and CH<sub>3</sub>COOH (0.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 4.5 mA and irradiated by blue LEDs at 35 °C for 2 h. The yields of product could be determined by <sup>1</sup>H NMR with diphenylmethane as the internal standard. These experiments were operated two times and the initial rates were determined by the average yields. Finally, the initial rate for different concentration of sodium azide vs relative square of concentrations could be obtained.



**Figure S4.** The kinetic study of  $[\text{NaN}_3]$ .

**General procedure for kinetic plots of 1-isopropyl-4-methoxybenzene:** The order in substrate 1-isopropyl-4-methoxybenzene was determined by studying the initial rate of reaction with different concentrations of 1-isopropyl-4-methoxybenzene. Using the above mentioned general procedure, 1-isopropyl-4-methoxybenzene (0.30 mmol, 0.50 mmol, 0.60 mmol, 0.70 mmol, 0.80 mmol, 1.00 mmol), sodium azide (2.5 mmol, 162.5 mg), bis(4-methoxyphenyl)methanone (0.0275 mmol, 6.7 mg),  $\text{MnF}_2$  (0.050 mmol, 4.6 mg), 1,10-Phen (0.10 mmol, 18.6 mg),  $\text{KBr}$  (0.20 mmol, 23.8 mg), TFA (2.0 mmol, 228.0 mg) and  $\text{LiClO}_4$  (1.0 mmol, 106.4 mg) in  $\text{CH}_3\text{CN}$  (9.5 mL) and  $\text{CH}_3\text{COOH}$  (0.5 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 4.5 mA and irradiated by blue LEDs at 35 °C for 2 h. The yields of product could be determined by  $^1\text{H}$  NMR with diphenylmethane as the internal standard. These experiments were operated two times and the initial rates were determined by the average yields. Finally, the initial rate for different concentration of  $\text{C}(\text{sp}^3)\text{-H}$  vs relative concentrations could be obtained.



**Figure S5. The kinetic study of [1-isopropyl-4-methoxybenzene].**

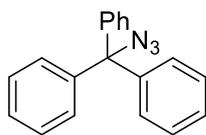
**Procedure for EPR experiments (electrophotocatalytic condition):** In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar. The bottle was equipped with carbon cloth (15 mm×15 mm) and platinum electrode (15 mm×15 mm×0.3 mm). A solution of 1-ethylnaphthalene (0.25 mmol, 39.0 mg), sodium azide (1.25 mmol, 5 equiv., 81.3 mg), bis(4-methoxyphenyl)methanone (0.01375 mmol, 5.5 mol%, 3.4 mg), MnF<sub>2</sub> (0.025 mmol, 10 mol%, 2.4 mg), 1,10-Phen (0.05 mmol, 20 mol%, 9.8 mg), KBr (0.1 mmol, 40 mol%, 11.9 mg), TFA (1.0 mmol, 4 equiv., 114.0 mg) and LiClO<sub>4</sub> (0.5 mmol, 2 equiv., 53.2 mg) in dry CH<sub>3</sub>CN (4.7 mL) and CH<sub>3</sub>COOH (0.25 mL) stirring under nitrogen atmosphere was electrolyzed at a constant current of 4.5 mA and irradiated by blue LEDs at 35 °C for 2.5 h. Then, DMPO (40 μL) was added into the reaction system, which was further electrolyzed at a constant current of 4.5 mA and irradiated by blue LEDs at 35 °C for 5 mins. The solution sample was taken out into a small tube and analyzed by EPR. EPR spectra was recorded at 298 K on EPR spectrometer operated at 9.824 GHz. Typical spectrometer parameters are shown as follows, scan range: 100 G; center field set: 3505 G; time constant: 163.84 ms; S21 scan time: 30.72 s; modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 1.00×10<sup>4</sup>; microwave power: 22.00 mW.

**Procedure for EPR experiments (photocatalytic condition):** A solution of 1-ethylnaphthalene (0.5 mmol, 78.0 mg) and bis(4-methoxyphenyl)methanone (0.12 mol, 30.0 mg) in degassed dry CH<sub>3</sub>CN (1.0 mL) were stirred under nitrogen atmosphere, which was irradiated by blue LEDs or under darkness at 25 °C for 3 h. Then, DMPO (20 μL) was added into the reaction system, which

was further irradiated by blue LEDs or under darkness at 25 °C for 30 mins. The solution sample was taken out into a small tube and analyzed by EPR. EPR spectra was recorded at 298 K on EPR spectrometer operated at 9.818 GHz. Typical spectrometer parameters are shown as follows, scan range: 100 G; center field set: 3503 G; time constant: 163.84 ms; S21 scan time: 30.72 s; modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain:  $1.00 \times 10^5$ ; microwave power: 21.78 mW.

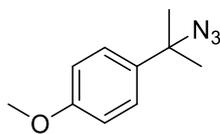
**General procedure for cyclic voltammetry (CV) experiments:** Cyclic voltammetry experiments were performed in a three-electrode cell connected to a Schlenk line at room temperature. The working electrode was a steady glassy carbon disk electrode, the counter electrode a platinum wire. The reference was a Ag/AgCl electrode submerged in saturated aqueous KCl solution, and separated from reaction by a salt bridge. CH<sub>3</sub>CN (10 ml) containing LiClO<sub>4</sub> (1.0 mmol) were poured into the electrochemical cell in all experiments. For some certain experiments, 0.5 mL CH<sub>3</sub>COOH were added. The scan rate is 0.1 V/s, ranging from 0 V to 2.5 or 3.0 V.

### 3. Characterization of Products



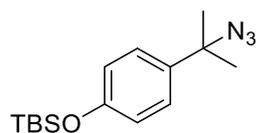
4

**(Azidomethanetriyl)tribenzene (4)<sup>1</sup>:** 141.1 mg colorless liquid was isolated, yield 99%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.34 – 7.22 (m, 15H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  143.20, 128.55, 128.30, 127.80, 77.22.



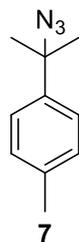
5

**1-(2-Azidopropan-2-yl)-4-methoxybenzene (5):** 91.7 mg colorless liquid was isolated, yield: 96%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.41 – 7.33 (m, 2H), 6.94 – 6.85 (m, 2H), 3.81 (s, 3H), 1.62 (s, 6H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  158.86, 136.76, 126.54, 113.85, 63.65, 55.40, 28.56. HRMS (EI) exact mass calculated for [C<sub>10</sub>H<sub>13</sub>N<sub>3</sub>O], 191.1059, found 191.1066.



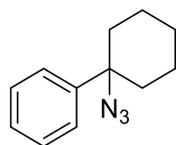
6

**(4-(2-Azidopropan-2-yl)phenoxy)(tert-butyl)dimethylsilane (6):** 116.4 mg colorless liquid was isolated, yield: 80%.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.33 – 7.25 (m, 2H), 6.89 – 6.75 (m, 2H), 1.61 (s, 6H), 0.98 (s, 9H), 0.20 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  154.98, 137.32, 126.46, 119.95, 63.67, 28.54, 25.79, 18.31, -4.27. **HRMS** (EI) exact mass calculated for  $[\text{C}_{15}\text{H}_{23}\text{N}_3\text{OSi}]$ , 291.1767, found 291.1774.



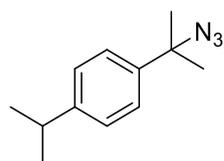
7

**1-(2-Azidopropan-2-yl)-4-methylbenzene (7):** 56.9 mg colorless liquid was isolated, yield: 65%.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.33 (d,  $J = 8.2$  Hz, 2H), 7.17 (d,  $J = 8.2$  Hz, 2H), 2.34 (s, 3H), 1.61 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  141.73, 137.21, 129.30, 125.18, 63.82, 28.51, 21.09. **HRMS** (EI) exact mass calculated for  $[\text{C}_{10}\text{H}_{13}\text{N}_3]$ , 175.1109, found 175.1110.



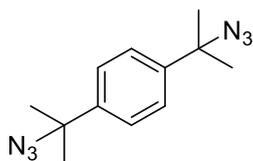
8

**(1-Azidocyclohexyl)benzene (8)<sup>1</sup>:** 70.0 mg colorless liquid was isolated, yield: 69%.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.48 – 7.43 (m, 2H), 7.39 (td,  $J = 6.9, 6.4, 1.9$  Hz, 2H), 7.33 – 7.26 (m, 1H), 2.09 – 1.95 (m, 2H), 1.84 (td,  $J = 13.6, 12.3, 4.4$  Hz, 2H), 1.78 – 1.59 (m, 5H), 1.38 – 1.23 (m, 1H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  144.46, 128.75, 127.65, 125.57, 66.74, 36.05, 25.35, 22.54.



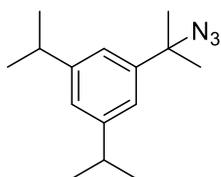
9

**1-(2-Azidopropan-2-yl)-4-isopropylbenzene (9):** 50.5 mg colorless liquid was isolated, yield: 57%.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.40 – 7.31 (m, 2H), 7.26 – 7.16 (m, 2H), 2.90 (hept,  $J = 6.9$  Hz, 1H), 1.62 (s, 6H), 1.25 (d,  $J = 6.9$  Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  148.07, 142.07, 126.64, 125.20, 63.80, 33.78, 28.51, 24.05. **HRMS** (EI) exact mass calculated for  $[\text{C}_{12}\text{H}_{17}\text{N}_3]$ , 203.1422, found 203.1422.



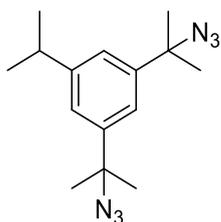
**9'**, diazidation

**1,4-Bis(2-azidopropan-2-yl)benzene (9', diazidation):** 42.7 mg colorless liquid was isolated, yield: 35%.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.43 (s, 4H), 1.64 (s, 12H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  143.89, 125.41, 63.62, 28.42. **GCMS** (EI) exact mass calculated for  $[\text{C}_{12}\text{H}_{16}\text{N}_6\text{-N}_2]$ , 216.14, found 216.05.



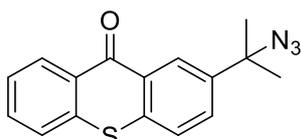
**10**

**1-(2-Azidopropan-2-yl)-3,5-diisopropylbenzene (10):** 77.2 mg colorless liquid was isolated, yield: 63%.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.10 (d,  $J = 1.4$  Hz, 2H), 7.01 (s, 1H), 2.91 (hept,  $J = 6.9$  Hz, 2H), 1.64 (s, 6H), 1.26 (d,  $J = 6.9$  Hz, 12H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  149.14, 144.60, 123.71, 120.85, 64.22, 34.49, 28.67, 24.23. **HRMS** (EI) exact mass calculated for  $[\text{C}_{15}\text{H}_{23}\text{N}_3]$ , 245.1892, found 245.1888.



**10'**, diazidation

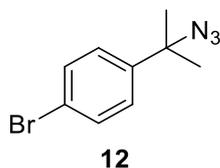
**1,3-Bis(2-azidopropan-2-yl)-5-isopropylbenzene (10', diazidation):** 31.5 mg colorless liquid was isolated, yield: 22%.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.31 (t,  $J = 1.5$  Hz, 1H), 7.20 (d,  $J = 1.3$  Hz, 2H), 3.02 – 2.88 (m, 1H), 1.65 (s, 12H), 1.27 (d,  $J = 6.9$  Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  149.52, 145.05, 122.38, 119.50, 64.11, 34.58, 28.64, 24.17. **HRMS** (EI) exact mass calculated for  $[\text{C}_{15}\text{H}_{22}\text{N}_6]$ , 286.1906, found 286.1912.



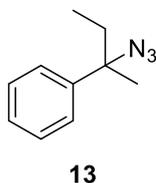
**11**

**2-(2-Azidopropan-2-yl)-9H-thioxanthen-9-one (11):** 73.7 mg yellow liquid was isolated, yield: 50%.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.70 – 8.58 (m, 2H), 7.78 (dd,  $J = 8.5, 2.3$  Hz, 1H), 7.68 – 7.56

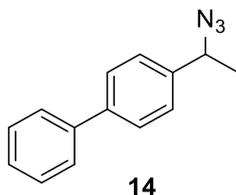
(m, 3H),  $\delta$  7.54 – 7.46 (m, 1H), 1.73 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  179.98, 143.39, 137.22, 136.60, 132.52, 130.06, 129.99, 129.23, 129.05, 126.67, 126.58, 126.19, 126.12, 63.70, 28.40. HRMS (EI) exact mass calculated for  $[\text{C}_{16}\text{H}_{13}\text{N}_3\text{OS}]$ , 295.0779, found 295.0783.



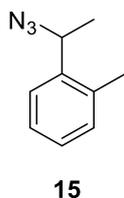
**1-(2-Azidopropan-2-yl)-4-bromobenzene (12):** 151.2 mg colorless liquid was isolated, yield: 63%.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.51 – 7.42 (m, 2H), 7.33 – 7.26 (m, 2H), 1.59 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  143.82, 131.65, 127.05, 121.44, 63.39, 28.30. GCMS (EI) exact mass calculated for  $[\text{C}_9\text{H}_{10}\text{BrN}_3]$ , 239.0, found 239.9.



**(2-Azidobutan-2-yl)benzene (13):** 40.3 mg colorless liquid was isolated, yield: 46%.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.42 – 7.32 (m, 4H), 7.30 – 7.23 (m, 1H), 1.96 – 1.78 (m,  $J = 7.0$  Hz, 2H), 1.66 (s, 3H), 0.79 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  143.41, 128.53, 127.30, 125.75, 67.46, 35.13, 25.23, 8.83. HRMS (EI) exact mass calculated for  $[\text{C}_{10}\text{H}_{13}\text{N}_3]$ , 175.1109, found 175.1110.

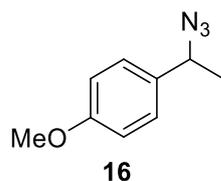


**4-(1-Azidoethyl)-1,1'-biphenyl (14):** 48 mg colorless liquid was isolated, yield: 43%.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.64 – 7.55 (m, 4H), 7.49 – 7.31 (m, 5H), 4.66 (q,  $J = 6.8$  Hz, 1H), 1.57 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  141.19, 140.69, 139.96, 128.94, 127.63, 127.58, 127.24, 126.96, 60.96, 21.72. HRMS (EI) exact mass calculated for  $[\text{C}_{14}\text{H}_{13}\text{N}_3]$ , 223.1109, found 223.1115.

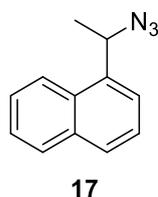


**1-(1-Azidoethyl)-2-methylbenzene (15):** 41.1 mg colorless liquid was isolated, yield: 51%.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.41 – 7.35 (m, 1H), 7.30 – 7.14 (m, 3H), 4.84 (q,  $J = 6.8$  Hz, 1H), 2.37 (s, 3H), 1.53 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  138.86, 135.32, 130.85, 128.01, 126.62, 125.71, 57.51, 20.61, 19.27. HRMS (EI) exact mass calculated for  $[\text{C}_9\text{H}_{11}\text{N}_3]$ , 161.0953, found

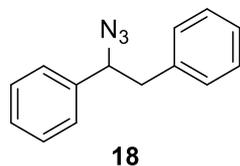
161.0955.



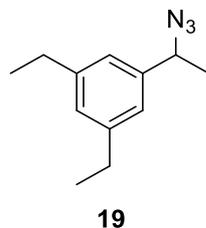
**1-(1-Azidoethyl)-4-methoxybenzene (16)<sup>2</sup>:** 39.8 mg colorless liquid was isolated, yield: 45%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.10 (m, 2H), 7.03 – 6.77 (m, 2H), 4.57 (q, *J* = 6.8 Hz, 1H), 3.81 (s, 3H), 1.51 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 159.48, 132.93, 127.80, 114.17, 60.80, 55.43, 21.62.



**1-(1-Azidoethyl)naphthalene (17):** 60.0 mg colorless liquid was isolated, yield: 61%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.95 – 7.74 (m, 2H), 7.66 – 7.35 (m, 4H), 5.32 (q, *J* = 6.8 Hz, 1H), 1.70 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 136.18, 134.05, 130.66, 129.16, 128.91, 126.60, 125.96, 125.46, 123.67, 123.12, 57.61, 20.79. **HRMS** (EI) exact mass calculated for [C<sub>12</sub>H<sub>11</sub>N<sub>3</sub>], 197.0953, found 197.0952.

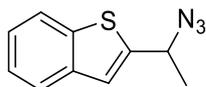


**(1-Azidoethane-1,2-diyl)dibenzene (18):** 122.7 mg colorless liquid was isolated, yield: 55%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.17 (m, 8H), 7.17 – 7.09 (m, 2H), 4.65 (dd, *J* = 8.3, 6.2 Hz, 1H), 3.04 (qd, *J* = 13.8, 7.2 Hz, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 139.38, 137.51, 129.49, 128.83, 128.51, 128.41, 127.03, 126.88, 67.76, 43.10. **HRMS** (EI) exact mass calculated for [C<sub>14</sub>H<sub>13</sub>N<sub>3</sub>-N<sub>2</sub>], 195.1048, found 195.1043.



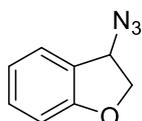
**1-(1-Azidoethyl)-3,5-diethylbenzene (19):** 41.6 mg colorless liquid was isolated, yield: 41%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.00 (s, 1H), 6.97 (s, 2H), 4.57 (q, *J* = 6.8 Hz, 1H), 2.64 (q, *J* = 7.6 Hz, 4H), 1.53 (d, *J* = 6.8 Hz, 3H), 1.24 (t, *J* = 7.6 Hz, 6H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 144.92, 140.96, 127.46, 123.33, 61.42, 28.97, 21.74, 15.71. **HRMS** (EI) exact mass calculated for [C<sub>12</sub>H<sub>17</sub>N<sub>3</sub>], 203.1422,

found 203.1429.



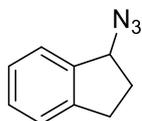
**20**

**2-(1-Azidoethyl)benzo[b]thiophene (20):** 32.5 mg colorless liquid was isolated, yield: 32%. **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.78 (dd,  $J = 29.0, 7.9$  Hz, 2H), 7.34 (p,  $J = 7.1$  Hz, 2H), 7.23 (s, 1H), 4.88 (q,  $J = 6.8$  Hz, 1H), 1.67 (d,  $J = 7.1$  Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  144.82, 139.58, 139.27, 124.79, 124.65, 123.87, 122.60, 121.56, 57.24, 21.77. **HRMS** (EI) exact mass calculated for [C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>S], 203.0517, found 203.0514.



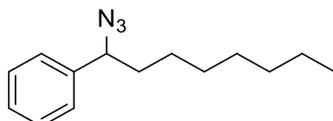
**21**

**3-Azido-2,3-dihydrobenzofuran (21):** 62.8 mg colorless liquid was isolated, yield: 39%. **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.43 – 7.37 (m, 1H), 7.30 (td,  $J = 8.2, 1.3$  Hz, 1H), 6.98 (td,  $J = 7.5, 0.9$  Hz, 1H), 6.91 (d,  $J = 8.1$  Hz, 1H), 5.00 (dd,  $J = 6.9, 2.8$  Hz, 1H), 4.61 – 4.38 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  160.28, 131.27, 125.43, 123.92, 121.29, 110.82, 76.35, 62.06. **HRMS** (EI) exact mass calculated for [C<sub>8</sub>H<sub>7</sub>N<sub>3</sub>O], 161.0589, found 161.0593.



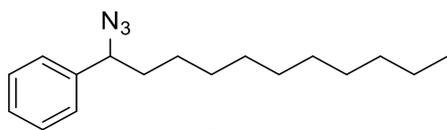
**22**

**1-Azido-2,3-dihydro-1H-indene (22):** 39.8 mg colorless liquid was isolated, yield: 50%. **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.40 (d,  $J = 7.0$  Hz, 1H), 7.32 – 7.21 (m, 3H), 4.87 (dd,  $J = 7.1, 4.7$  Hz, 1H), 3.18 – 3.01 (m, 1H), 2.95 – 2.79 (m, 1H), 2.56 – 2.32 (m, 1H), 2.22 – 1.97 (m, 1H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  143.75, 140.74, 128.97, 126.95, 125.19, 124.65, 65.97, 32.64, 30.57. **HRMS** (EI) exact mass calculated for [C<sub>9</sub>H<sub>9</sub>N<sub>3</sub>], 159.0796, found 159.0801.



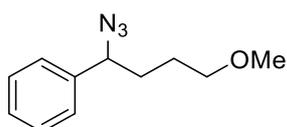
**23**

**(1-Azido-octyl)benzene (23):** 58.9 mg colorless liquid was isolated, yield: 51%. **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.42 – 7.24 (m, 5H), 4.40 (t,  $J = 7.2$  Hz, 1H), 1.90 – 1.68 (m, 2H), 1.40 (dd,  $J = 18.1, 9.1$  Hz, 1H), 1.34 – 1.18 (m, 9H), 0.87 (t,  $J = 6.7$  Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  140.06, 128.86, 128.26, 127.01, 66.56, 36.31, 31.89, 29.35, 29.26, 26.40, 22.76, 14.23. **GCMS** (EI) exact mass calculated for [C<sub>14</sub>H<sub>21</sub>N<sub>3</sub>-N<sub>2</sub>], 203.17, found 203.10.



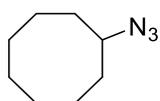
**24**

**(1-Azidoundecyl)benzene (24):** 71.0 mg colorless liquid was isolated, yield: 52%.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.43 – 7.35 (m, 2H), 7.34 – 7.26 (m, 3H), 4.49 – 4.30 (m, 1H), 1.91 – 1.67 (m, 2H),  $\delta$  1.44 – 1.34 (m, 1H), 1.33 – 1.20 (m, 15H), 0.88 (t,  $J = 6.9$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  140.07, 128.86, 128.26, 127.01, 66.56, 36.31, 32.04, 29.71, 29.68, 29.58, 29.45, 29.39, 26.40, 22.83, 14.27. **HRMS** (EI) exact mass calculated for  $[\text{C}_{17}\text{H}_{27}\text{N}_3]$ , 245.2143, found 245.2141.



**25**

**(1-Azido-4-methoxybutyl)benzene (25):** 56.4 mg colorless liquid was isolated, yield: 55%.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.41 – 7.33 (m, 2H), 7.29 – 7.22 (m, 3H), 4.40 – 4.29 (m, 1H), 3.52 (s, 3H), 2.84 – 2.62 (m, 2H), 1.89 – 1.75 (m, 4H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  141.82, 128.52, 128.50, 126.06, 94.21, 56.71, 35.50, 34.14, 26.57. **HRMS** (EI) exact mass calculated for  $[\text{C}_{11}\text{H}_{15}\text{N}_3\text{O}]$ , 177.1154, found 177.1162.



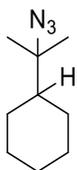
**26**

**Azidocyclooctane (26)**<sup>3</sup>: Colorless liquid was obtained, while GC yield was determined with biphenyl as internal standard: 41%.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  3.57 (tt,  $J = 8.4, 4.0$  Hz, 1H), 1.92 – 1.82 (m, 2H), 1.77 – 1.66 (m, 4H), 1.60 – 1.43 (m, 8H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  62.36, 30.91, 27.34, 25.25, 23.29.



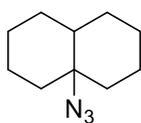
**27**

**Azidocyclododecane (27):** 64.8 mg colorless liquid was isolated, yield: 31%.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  3.91 – 3.14 (m, 1H), 1.75 – 1.63 (m, 2H), 1.50 (ddd,  $J = 14.3, 11.9, 6.0$  Hz, 4H), 1.35 (d,  $J = 11.6$  Hz, 16H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  59.28, 29.15, 24.05, 23.83, 23.45, 23.35, 21.42. **HRMS** (EI) exact mass calculated for  $[\text{C}_{12}\text{H}_{23}\text{N}_3]$ , 209.1892, found 209.1896.



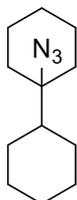
**28**

**(2-Azidopropan-2-yl)cyclohexane (28)<sup>3</sup>:** Colorless liquid was obtained, 2.4:1 site selectivity was determined by <sup>1</sup>H NMR, while GC yield was determined with biphenyl as internal standard: 51%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 1.85 – 1.74 (m, 3H), 1.71 – 1.62 (m, 2H), 1.60 – 1.48 (m, 1H), 1.43 – 1.26 (m, 2H), 1.22 (s, 4.29H), 1.19 – 1.11 (m, 1H), 1.11 – 0.97 (m, 2H), 0.96 (d, *J* = 6.8 Hz, 1.72H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 67.17, 64.78, 47.53, 37.39, 31.58, 27.74, 26.68, 26.48, 25.63, 23.61, 22.30, 17.35.



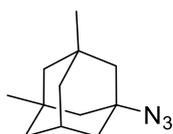
**29**

**4a-Azidodecahydronaphthalene (29):** 68.0 mg colorless liquid was isolated, yield: 38%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 1.82 (m, 1H), 1.77 – 1.65 (m, 2H), 1.55 (m, 3H), 1.26 (m, 8H), 1.03 – 0.74 (m, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 65.29, 44.46, 36.37, 28.82, 26.17, 22.13. **HRMS** (EI) exact mass calculated for [C<sub>10</sub>H<sub>17</sub>N<sub>3</sub>], 179.1422, found 179.1420.



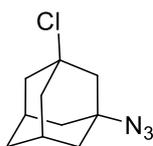
**30**

**1-Azido-1,1'-bi(cyclohexane) (30):** 103.7 mg colorless liquid was isolated, yield: 50%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 1.87 – 1.76 (m, 4H), 1.71 – 1.62 (m, 4H), 1.61 – 1.48 (m, 4H), 1.47 – 1.33 (m, 3H), 1.25 – 1.05 (m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 67.21, 47.72, 31.78, 27.26, 26.87, 26.57, 25.73, 22.34. **HRMS** (EI) exact mass calculated for [C<sub>12</sub>H<sub>21</sub>N<sub>3</sub>], 207.1735, found 207.1745.



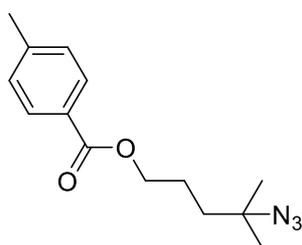
**31**

**(1r,3R,5S,7r)-1-Azido-3,5-dimethyladamantane (31)<sup>3</sup>:** 94.3 mg colorless liquid was isolated, yield: 46%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 2.21 (hept, *J* = 3.1 Hz, 1H), 1.64 (d, *J* = 2.5 Hz, 2H), 1.44 (q, *J* = 12.1 Hz, 4H), 1.38 – 1.27 (m, 4H), 1.15 (s, 2H), 0.88 (s, 6H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 60.52, 50.36, 47.60, 42.38, 40.19, 33.16, 30.51, 30.00.



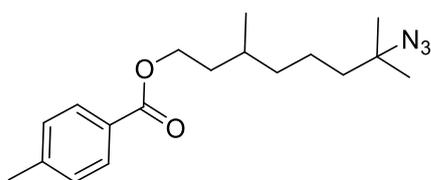
**32**

**(1r,3s,5R,7S)-1-Azido-3-chloroadamantane (32):** 113.9 mg colorless liquid was isolated, yield: 54%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 2.34 (s, 2H), 2.16 (s, 2H), 2.09 – 2.04 (m, 3H), 1.79 – 1.73 (m, 4H), 1.60 (q, *J* = 13.0 Hz, 2H), 1.25 (s, 1H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 66.54, 60.47, 51.17, 46.10, 39.86, 34.04, 31.83. HRMS (EI) exact mass calculated for [C<sub>10</sub>H<sub>14</sub>ClN<sub>3</sub>], 211.0876, found 211.0877.



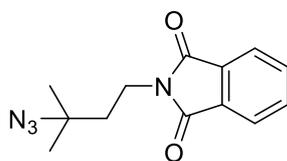
**33**

**4-Azido-4-methylpentyl 4-methylbenzoate (33):** 91.3 mg colorless liquid was isolated, yield: 35%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.31 (t, *J* = 6.5 Hz, 2H), 2.40 (s, 3H), 1.90 – 1.79 (m, 2H), 1.66 – 1.58 (m, 2H), 1.30 (s, 6H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 166.67, 143.64, 129.63, 129.13, 127.56, 64.70, 61.25, 37.86, 26.03, 23.89, 21.70. GCMS (EI) exact mass calculated for [C<sub>14</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>-N<sub>2</sub>], 233.14, found 233.10.



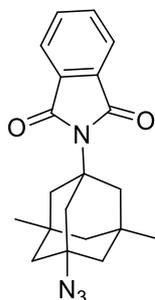
**34**

**7-Azido-3,7-dimethyloctyl 4-methylbenzoate (34):** 120.5 mg colorless liquid was isolated, yield: 38%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.41 – 4.27 (m, 2H), 2.40 (s, 3H), 1.86 – 1.75 (m, 1H), 1.71 – 1.51 (m, 3H), 1.50 – 1.32 (m, 5H), 1.25 (s, 6H), 0.97 (d, *J* = 6.5 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 166.85, 143.57, 129.66, 129.15, 127.82, 63.34, 61.76, 41.74, 37.21, 35.64, 30.02, 26.12, 26.08, 21.76, 21.69, 19.62. HRMS (DART Positive Ion Mode) exact mass calculated for [C<sub>18</sub>H<sub>28</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup>-N<sub>2</sub>], 290.2115, found 290.2113.



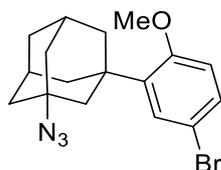
**35**

**2-(3-Azido-3-methylbutyl)isoindoline-1,3-dione (35)**<sup>4</sup>: 45.2 mg pale yellow liquid was isolated, yield: 35%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.84 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.71 (dd, *J* = 5.4, 3.1 Hz, 2H), 3.84 – 3.72 (m, 2H), 1.91 – 1.77 (m, 2H), 1.37 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.31, 134.10, 132.22, 123.38, 60.32, 39.30, 33.92, 26.07.



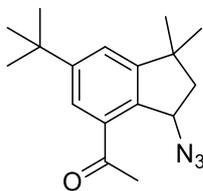
**36**

**2-((1*r*,3*s*,5*R*,7*S*)-3-Azido-5,7-dimethyladamantan-1-yl)isoindoline-1,3-dione (36)**<sup>5</sup>: 106.8 mg white solid was isolated, yield: 35%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.73 (m, 2H), 7.72 – 7.66 (m, 2H), 2.45 (s, 2H), 2.14 (s, 4H), 1.56 (d, *J* = 11.8 Hz, 2H), 1.44 (d, *J* = 11.7 Hz, 2H), 1.25 (s, 1H), 1.17 (d, *J* = 12.9 Hz, 1H), 1.00 (s, 6H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 169.48, 133.97, 131.74, 122.77, 61.76, 60.70, 49.05, 46.44, 44.85, 42.65, 33.91, 29.47.



**37**

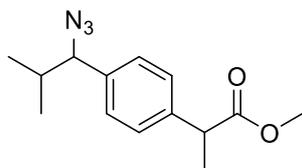
**(1*s*,3*r*,5*R*,7*S*)-1-Azido-3-(5-bromo-2-methoxyphenyl)adamantane (37)**<sup>5</sup>: 77.8 mg colorless liquid was isolated, yield: 43%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.24 (m, 2H), 6.75 (d, *J* = 8.6 Hz, 1H), 3.81 (s, 3H), 2.35 – 2.27 (m, 2H), 2.10 (s, 2H), 2.07 – 2.00 (m, 2H), 1.97 – 1.91 (m, 2H), 1.83 (d, *J* = 2.8 Hz, 4H), 1.69 – 1.64 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 157.67, 138.38, 130.02, 129.66, 113.39, 113.33, 59.90, 55.34, 43.93, 40.93, 39.65, 39.02, 35.41, 30.23.



**38**

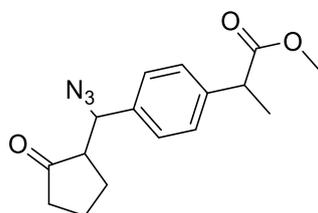
**1-(3-Azido-6-(*tert*-butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)ethan-1-one (38)**<sup>3</sup>: 145.4 mg colorless liquid was isolated, yield: 51%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 1.7 Hz, 1H), 7.41 (d, *J* = 1.7 Hz, 1H), 5.59 (dd, *J* = 7.3, 1.7 Hz, 1H), 2.66 (s, 3H), 2.19 (dd, *J* = 13.7, 7.3 Hz, 1H), 2.08 (dd, *J* = 13.7, 1.8 Hz, 1H), 1.38 (s, 9H), 1.34 (s, 3H), 1.32 (s, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 199.94, 154.83, 153.34, 136.24, 133.94, 125.95, 124.09, 63.35, 47.98, 42.84, 35.10, 31.49, 30.77, 29.31,

28.24.



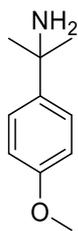
**39**

**Methyl 2-(4-(1-azido-2-methylpropyl)phenyl)propanoate (39)<sup>3</sup>:** 104.4 mg colorless liquid was isolated, yield: 40%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 4.12 (d, *J* = 7.9 Hz, 1H), 3.74 (q, *J* = 7.2 Hz, 1H), 3.67 (s, 3H), 1.97 (dh, *J* = 13.4, 6.7 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H), 1.01 (d, *J* = 6.6 Hz, 3H), 0.80 (d, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 175.03, 140.30, 138.01, 127.78, 127.74, 72.98, 52.22, 45.21, 34.13, 19.66, 19.25, 18.69.



**40**

**Methyl 2-(4-(azido(2-oxocyclopentyl)methyl)phenyl)propanoate (40):** 100.0 mg colorless liquid was isolated, yield: 33%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 3.70 (d, *J* = 7.1 Hz, 1H), 3.65 (s, 3H), 3.13 (dd, *J* = 13.9, 4.0 Hz, 1H), 2.57 – 2.42 (m, 1H), 2.39 – 2.28 (m, 2H), 2.18 – 2.05 (m, 2H), 2.01 – 1.91 (m, 1H), 1.78 – 1.68 (m, 1H), 1.48 (d, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 175.17, 138.93, 138.38, 130.41, 129.19, 127.55, 69.19, 52.09, 51.06, 45.04, 38.24, 35.23, 29.28, 20.59, 18.64. **HRMS (DART Positive Ion Mode)** exact mass calculated for [C<sub>16</sub>H<sub>20</sub>N<sub>3</sub>O<sub>3</sub><sup>+</sup>-N<sub>2</sub>], 274.1438, found 274.1438.



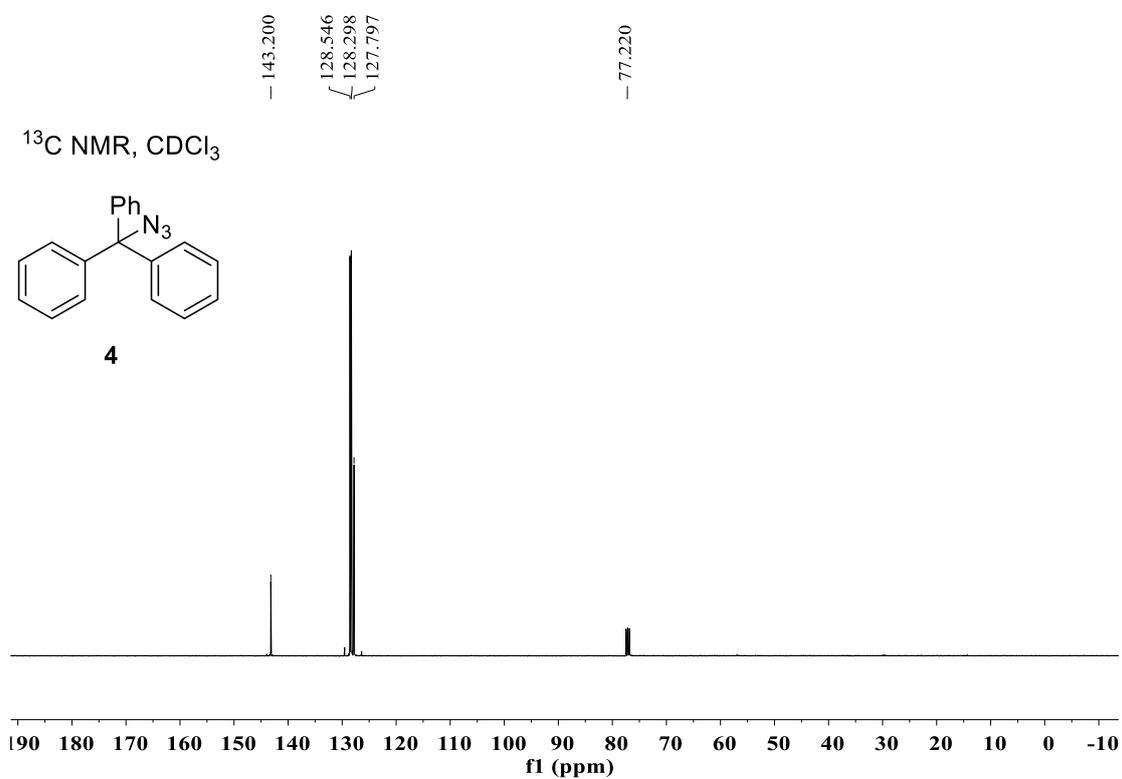
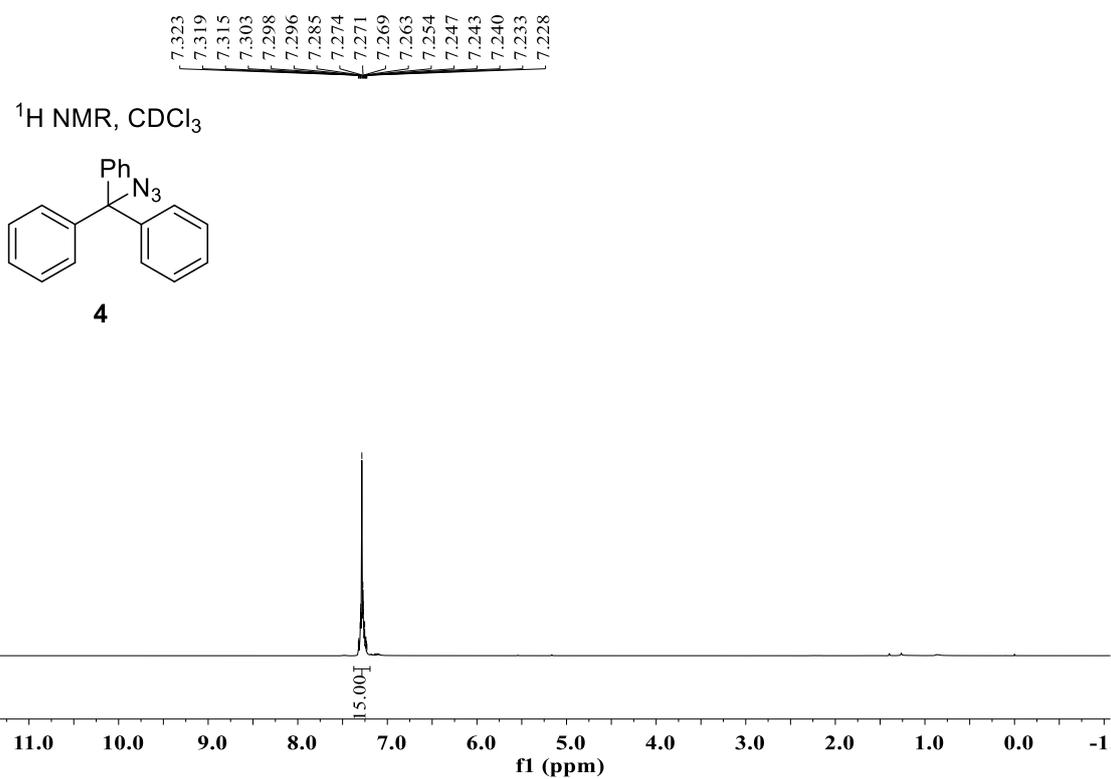
**41**

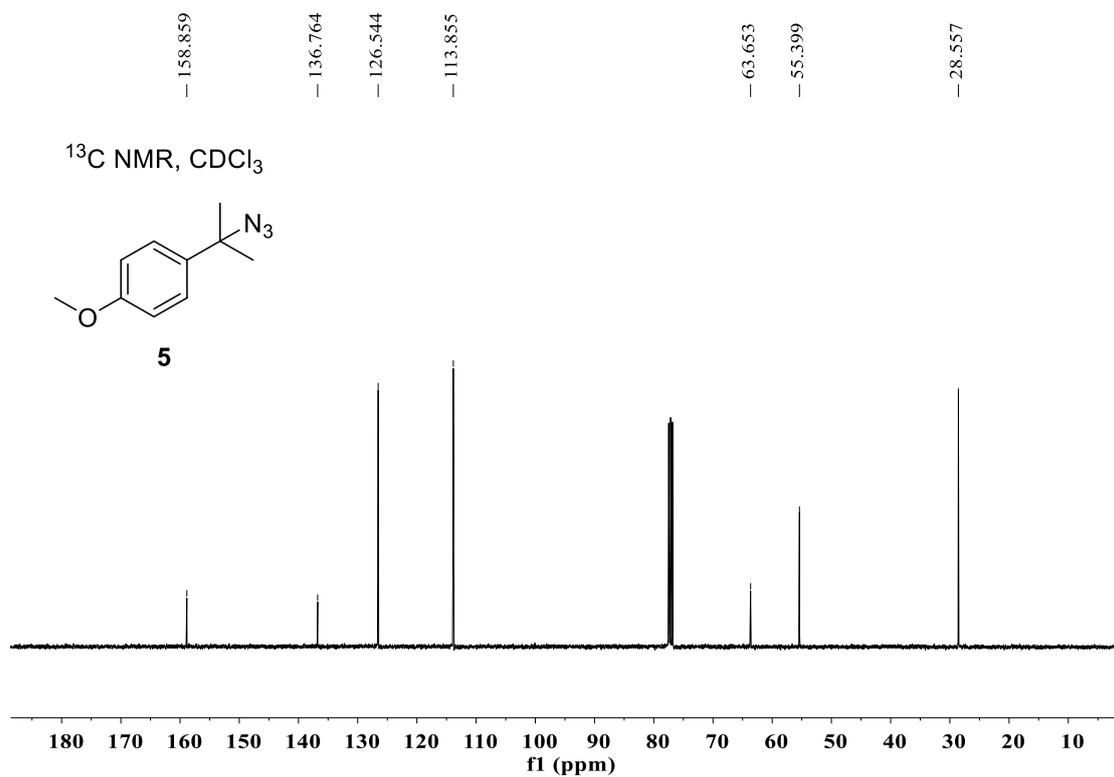
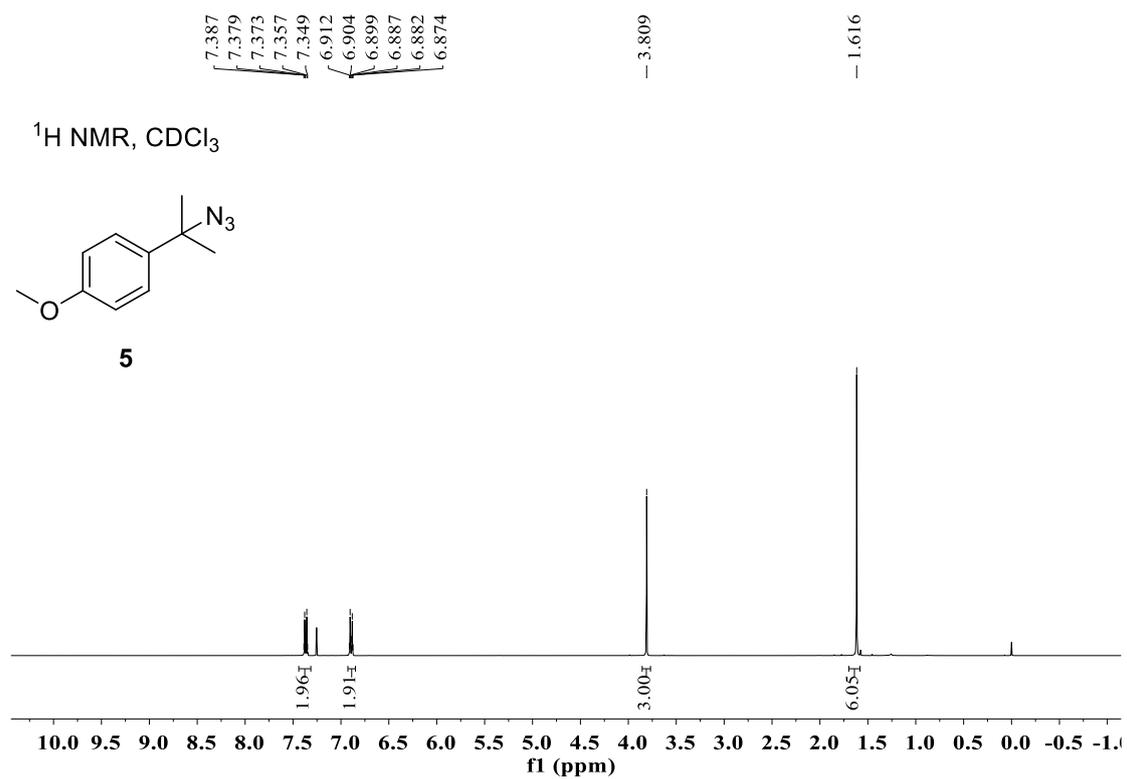
**2-(4-Methoxyphenyl)propan-2-amine (41)<sup>6</sup>:** 764.0 mg pale yellow liquid was isolated, yield: 93%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.39 (m, 2H), 6.90 – 6.83 (m, 2H), 3.79 (s, 3H), 1.64 (s, 2H), 1.47 (s, 6H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 157.92, 142.57, 125.86, 113.47, 55.31, 52.01, 33.03.

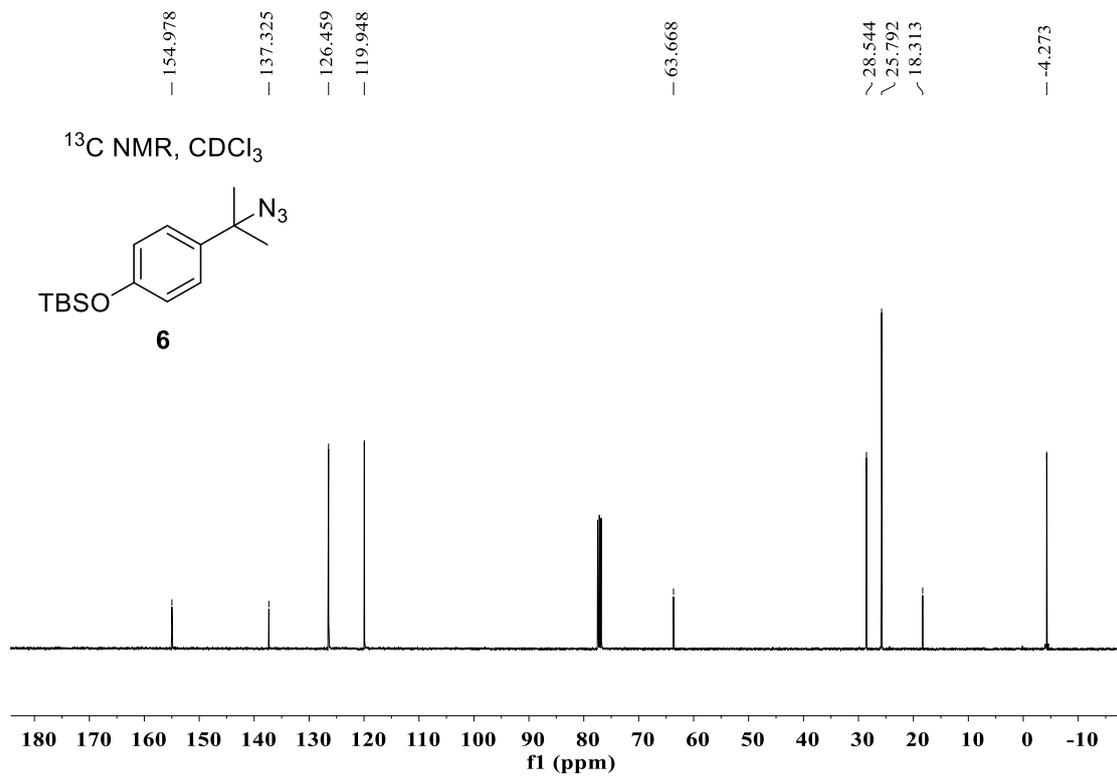
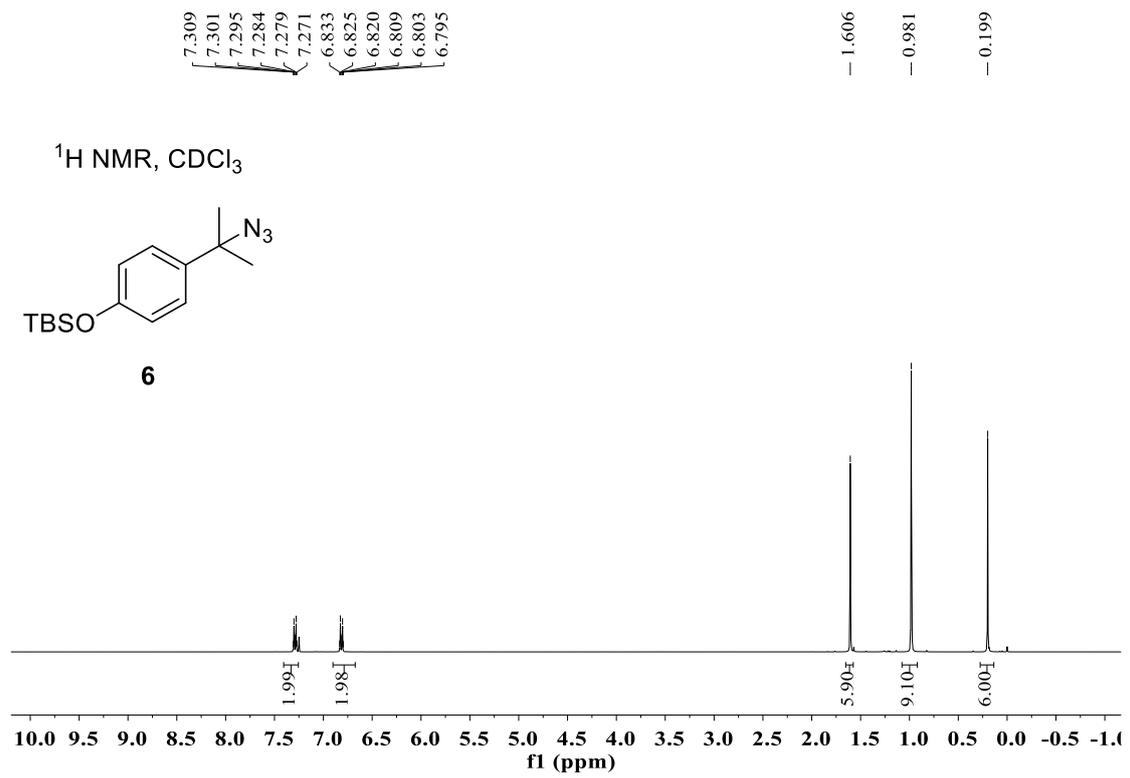
## 4. References

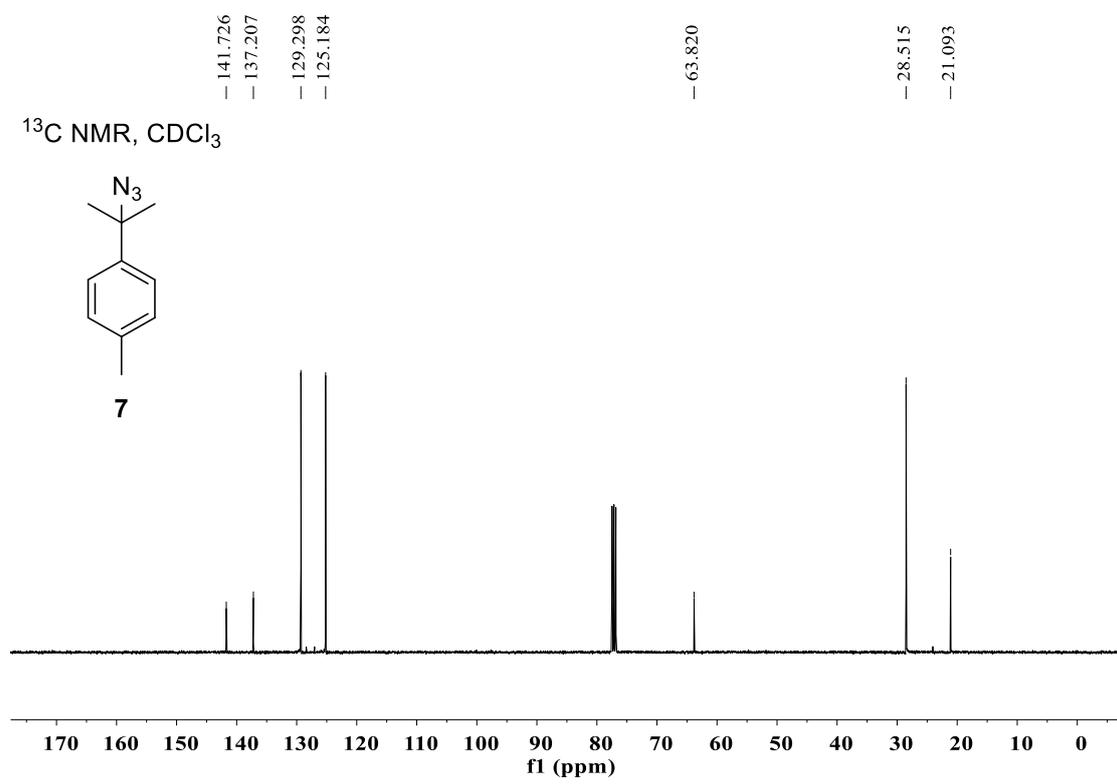
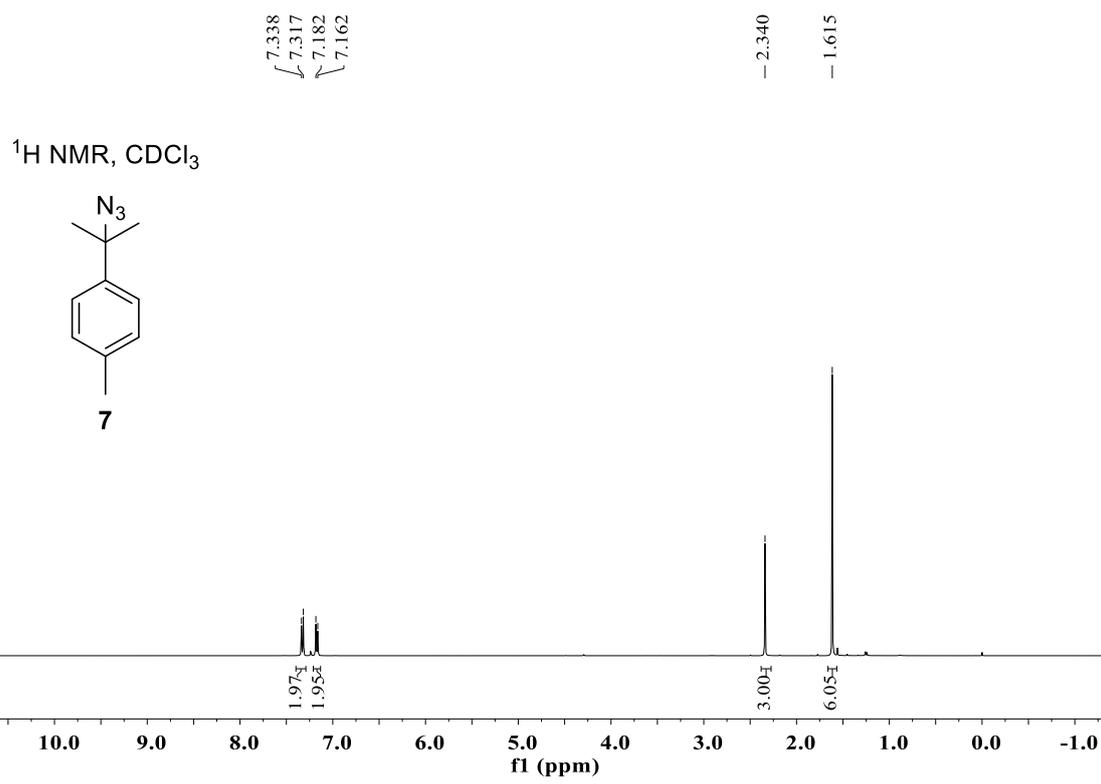
1. Kitamura, M.; Yano, M.; Tashiro, N.; Miyagawa, S.; Sando, M.; Okauchi, T. Direct synthesis of organic azides from primary amines with 2-azido-1, 3-dimethylimidazolium hexafluorophosphate. *Eur. J. Org. Chem.* **2011**, 2011, 458-462.
2. Kapat, A.; König, A.; Montermini, F.; Renaud, P. A radical procedure for the anti-markovnikov hydroazidation of alkenes. *J. Am. Chem. Soc.* **2011**, 133, 13890-13893.
3. Huang, X.; Bergsten, T. M.; Groves, J. T. Manganese-catalyzed late-stage aliphatic C–H azidation. *J. Am. Chem. Soc.* **2015**, 137, 5300-5303.
4. Li, X.; Shi, Z. J. Aliphatic C–H azidation through a peroxydisulfate induced radical pathway. *Org. Chem. Front.* **2016**, 3, 1326-1330.
5. Margrey, K. A.; Czaplyski, W. L.; Nicewicz, D. A.; Alexanian, E. J. A general strategy for aliphatic C–H functionalization enabled by organic photoredox catalysis. *J. Am. Chem. Soc.* **2018**, 140, 4213-4217.
6. Yamashita, Y.; Suzuki, H.; Sato, I.; Hirata, T.; Kobayashi, S. Catalytic direct-type addition reactions of alkylarenes with imines and alkenes. *Angew. Chem. Int. Ed.* **2018**, 57, 6896-6900.

## 5. NMR Spectra of Products



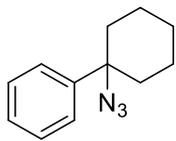




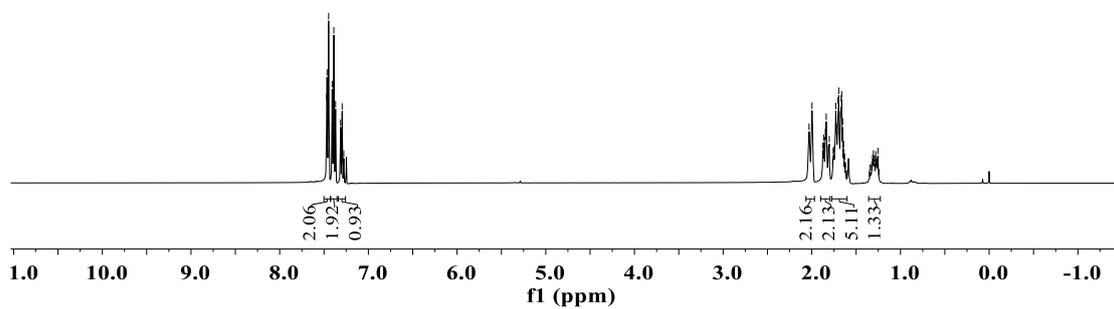


7.470  
7.466  
7.461  
7.448  
7.408  
7.403  
7.390  
7.370  
7.317  
7.314  
7.310  
7.300  
7.296  
7.291  
7.280  
7.277  
2.031  
1.998  
1.875  
1.864  
1.847  
1.837  
1.814  
1.803  
1.765  
1.758  
1.750  
1.729  
1.721  
1.705  
1.696  
1.688  
1.677  
1.669  
1.663  
1.652  
1.641  
1.629  
1.619  
1.316  
1.322  
1.305  
1.299  
1.291  
1.279  
1.272  
1.266  
1.254

<sup>1</sup>H NMR, CDCl<sub>3</sub>

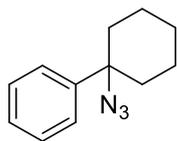


8

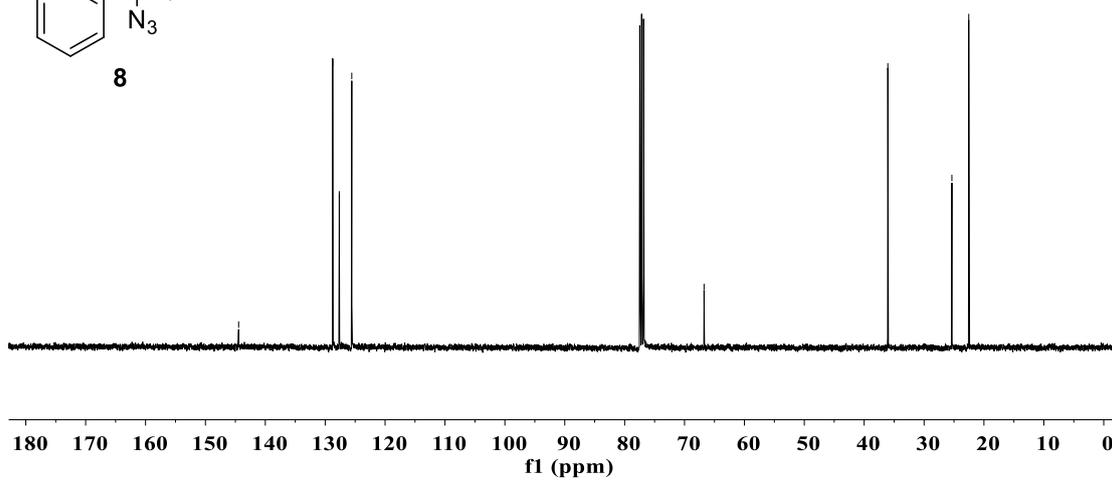


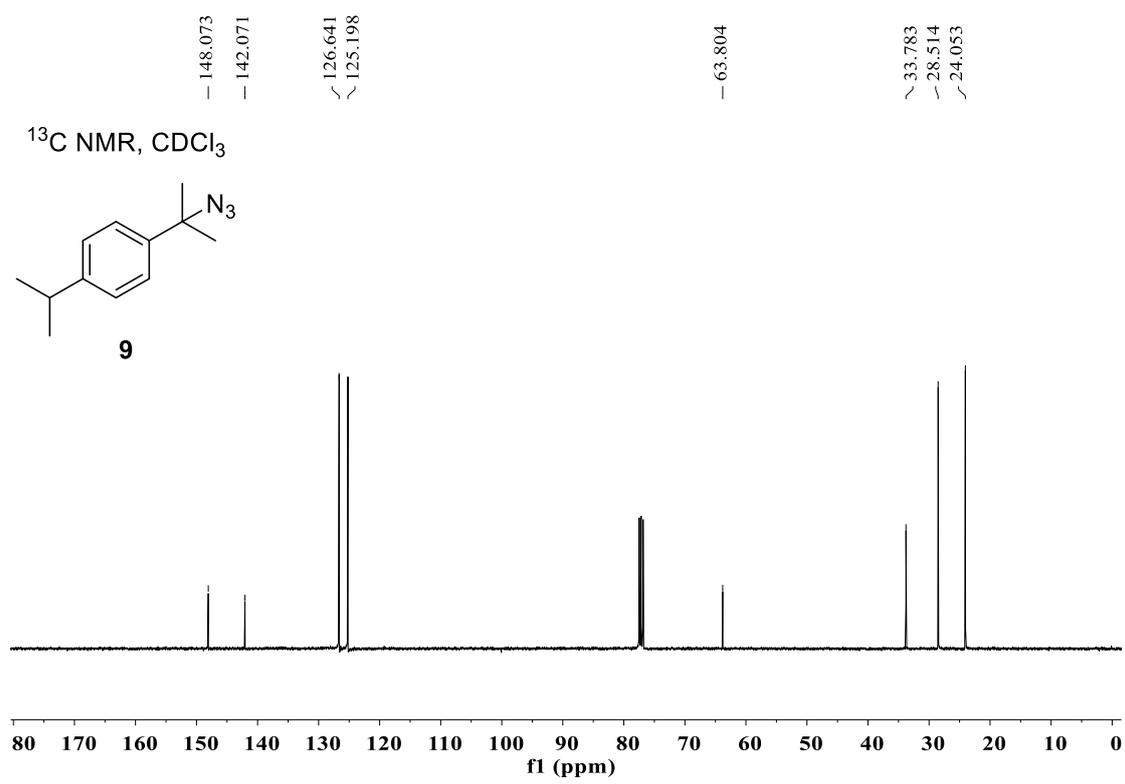
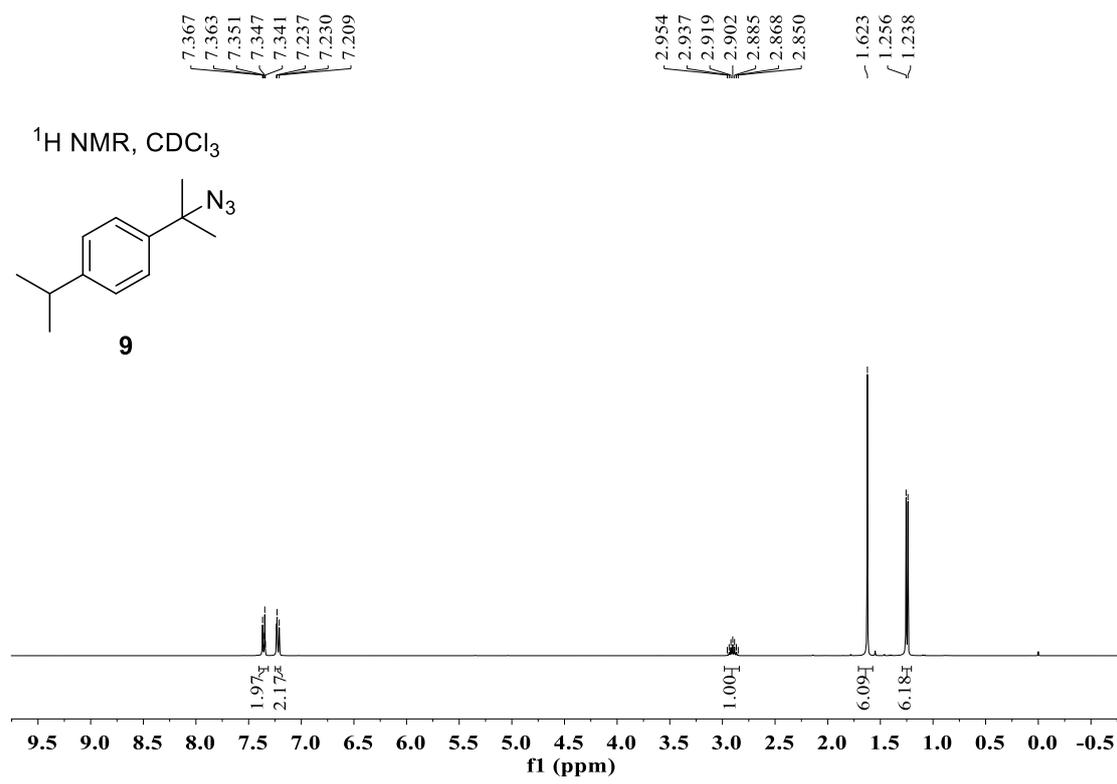
- 144.458  
- 128.754  
- 127.647  
- 125.567  
- 66.739  
- 36.051  
- 25.354  
- 22.537

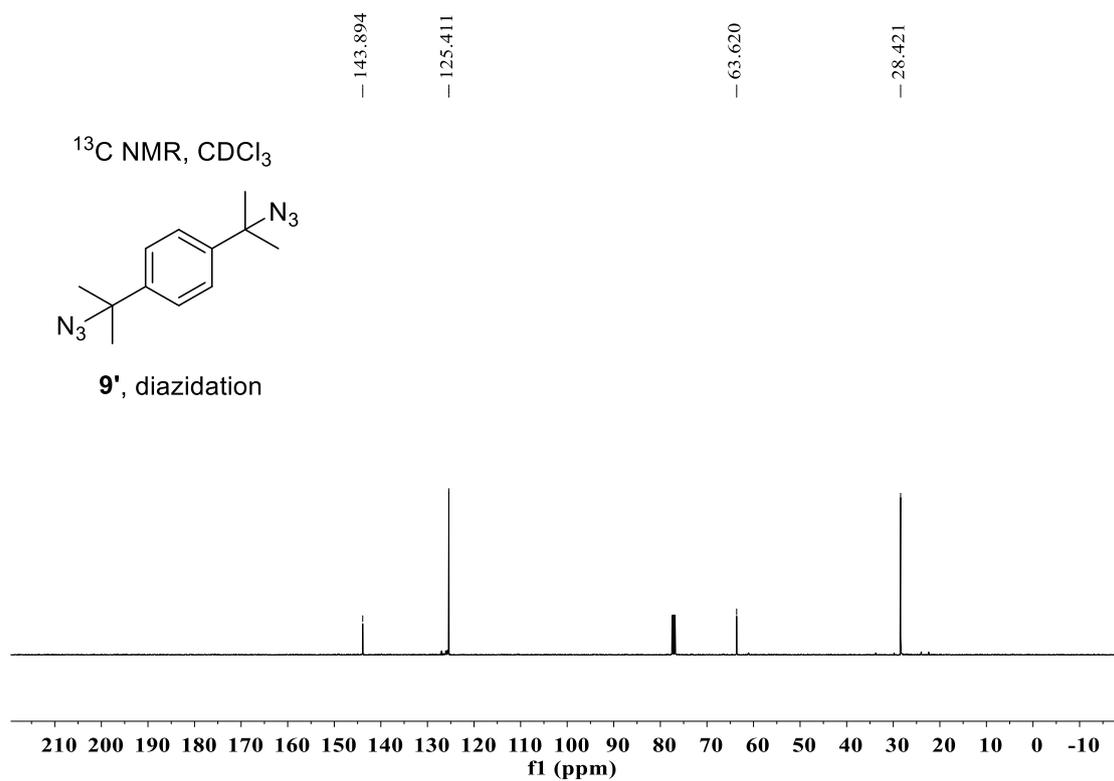
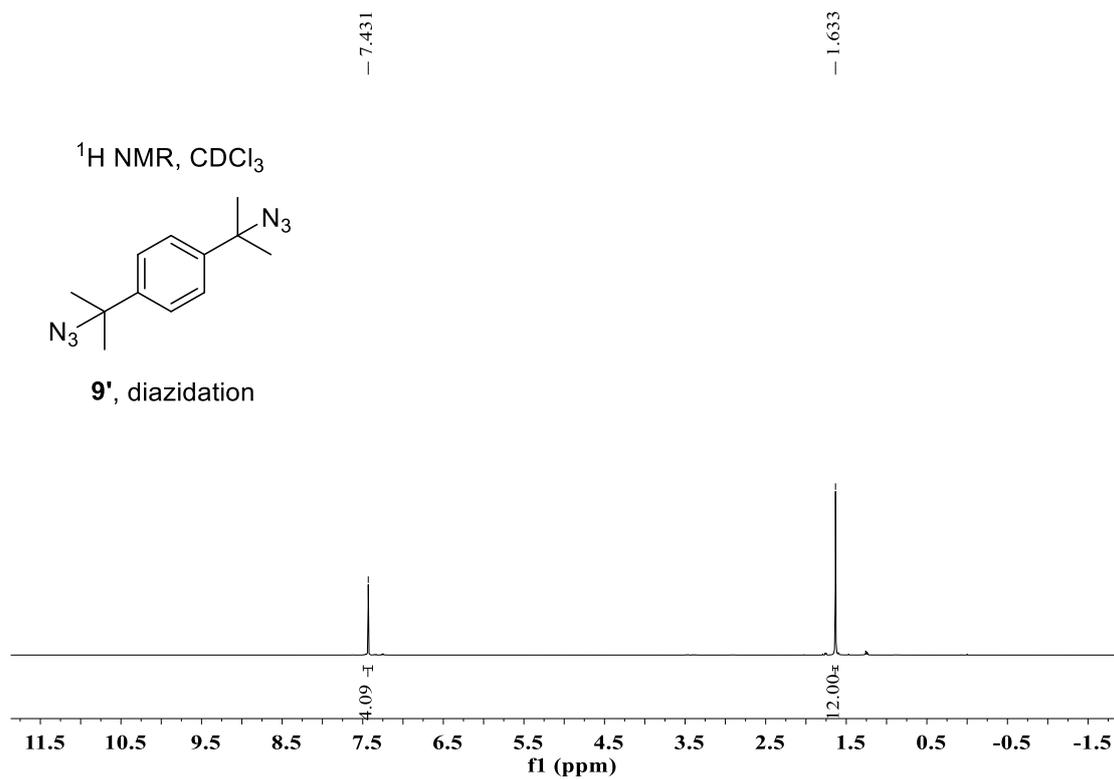
<sup>13</sup>C NMR, CDCl<sub>3</sub>

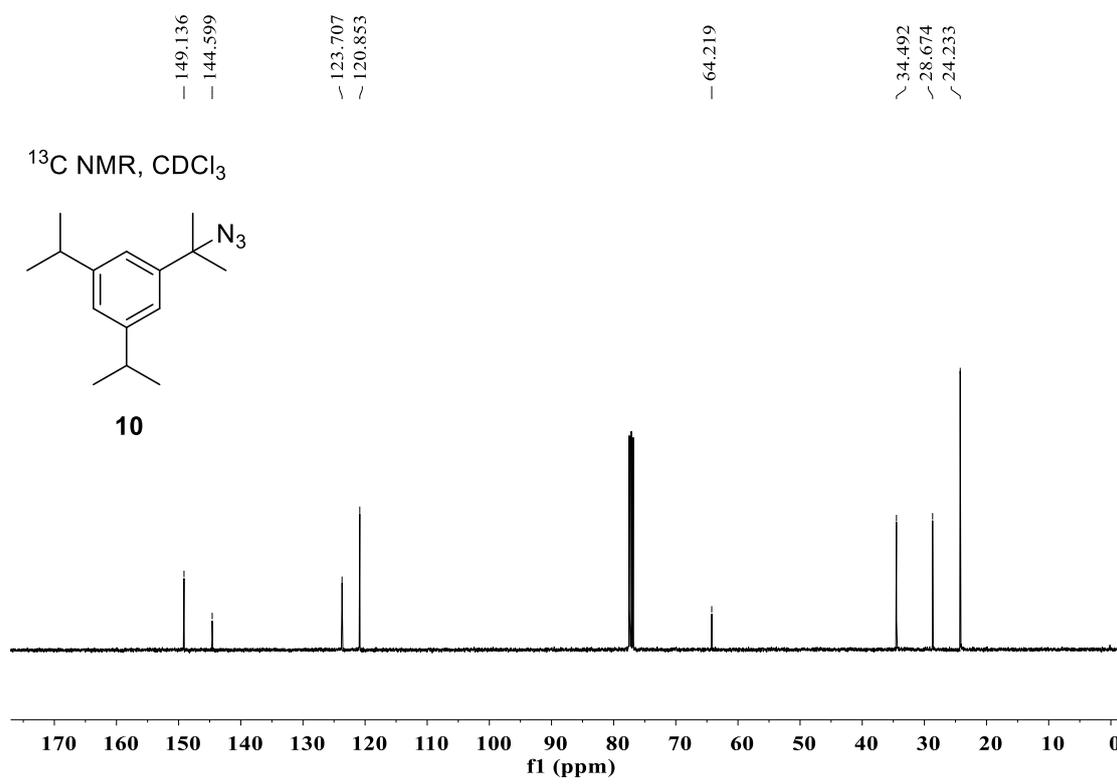
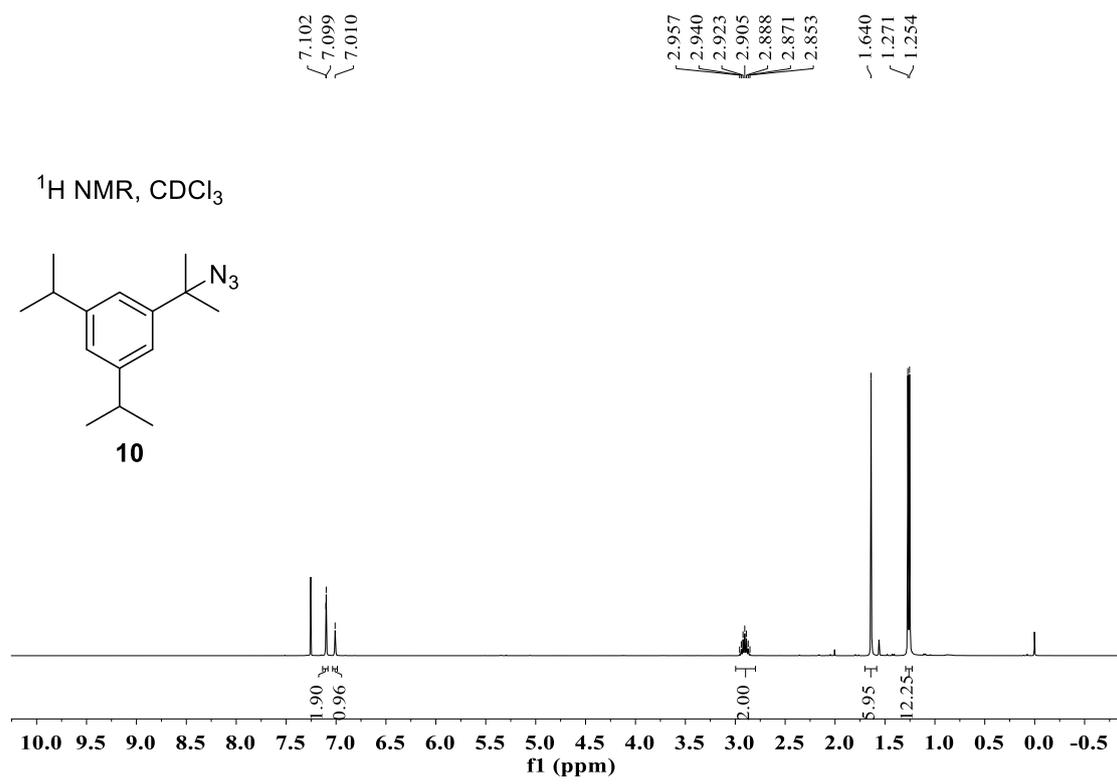


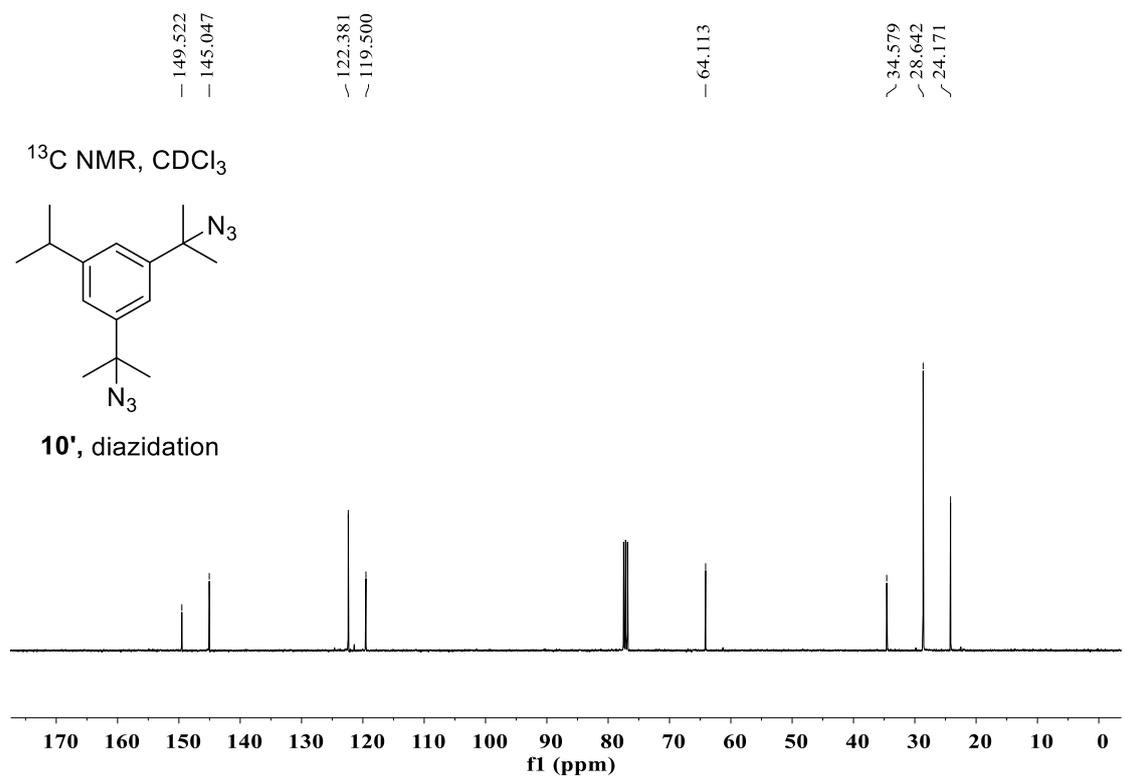
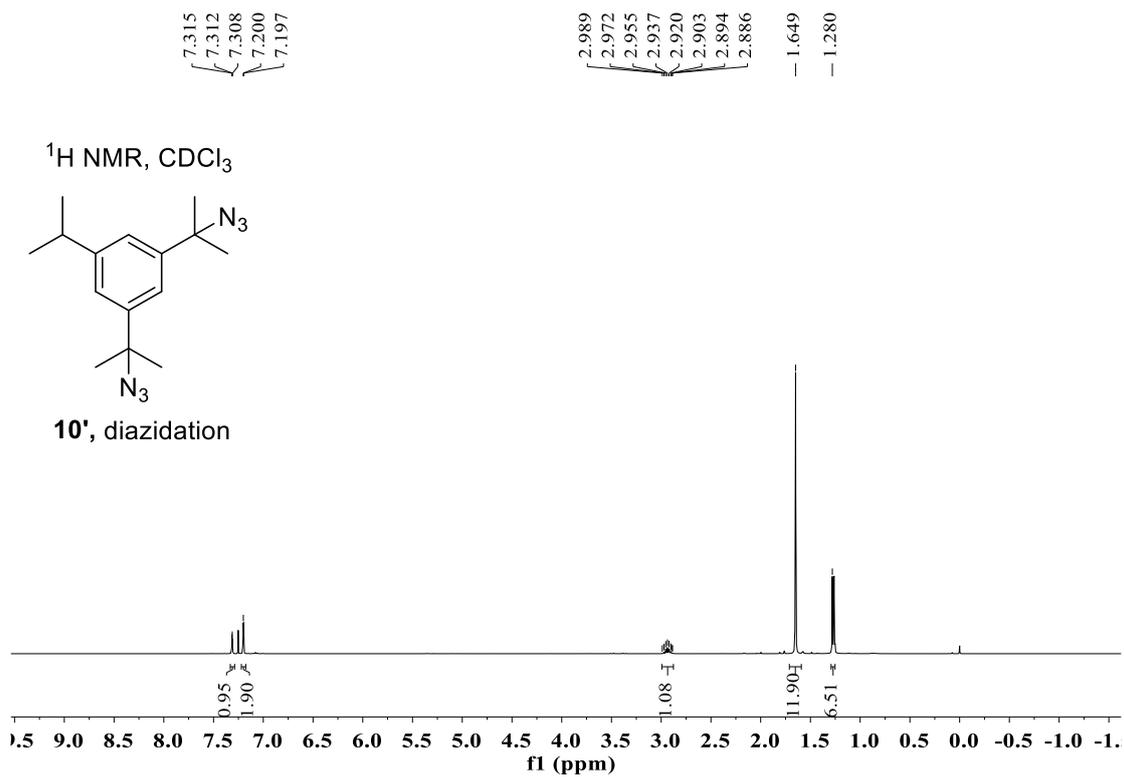
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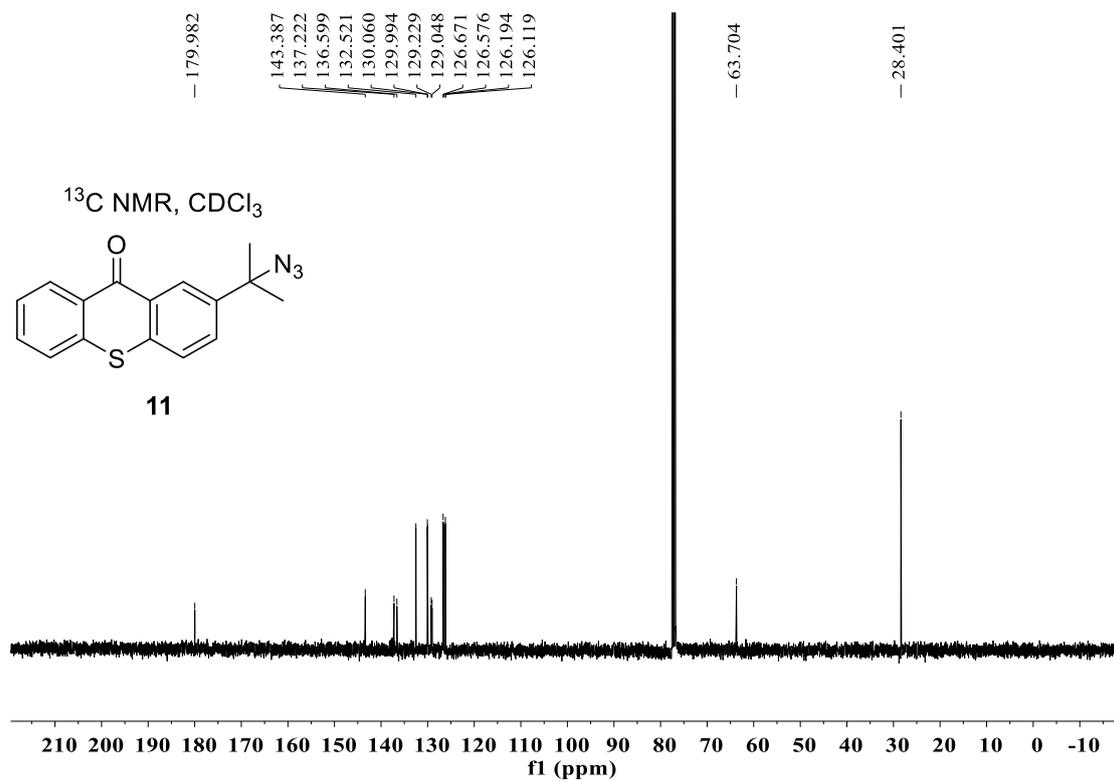
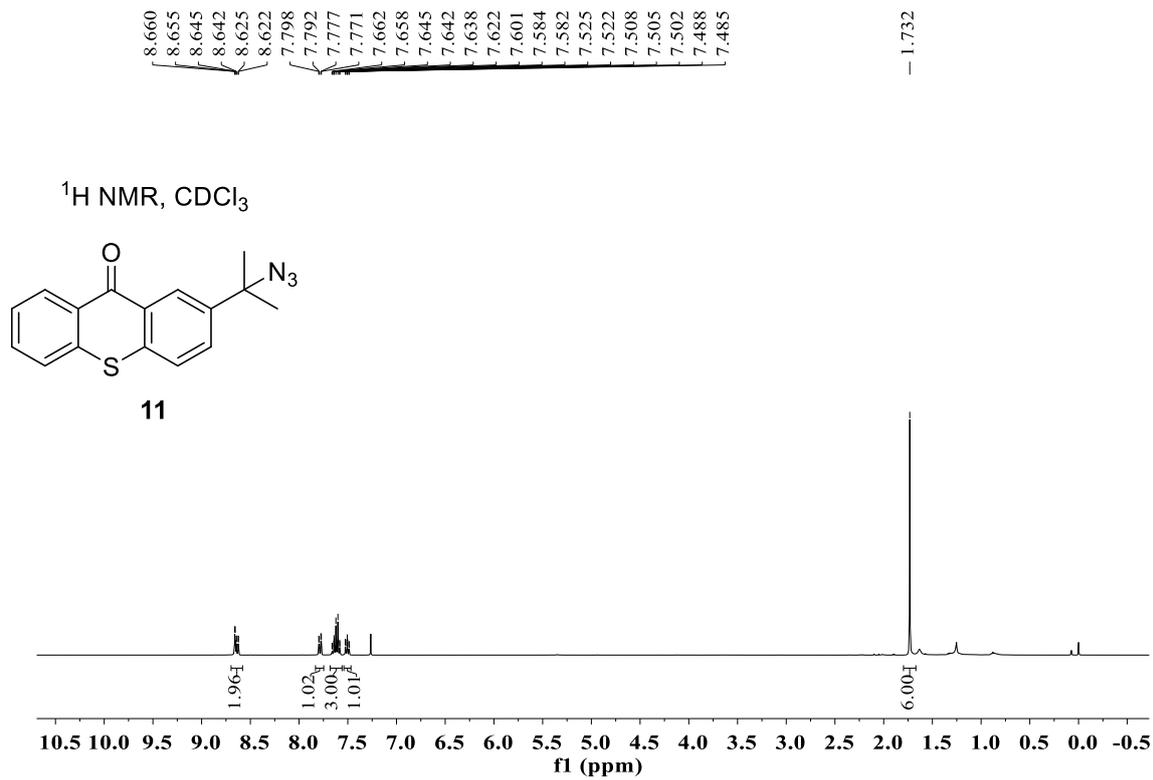


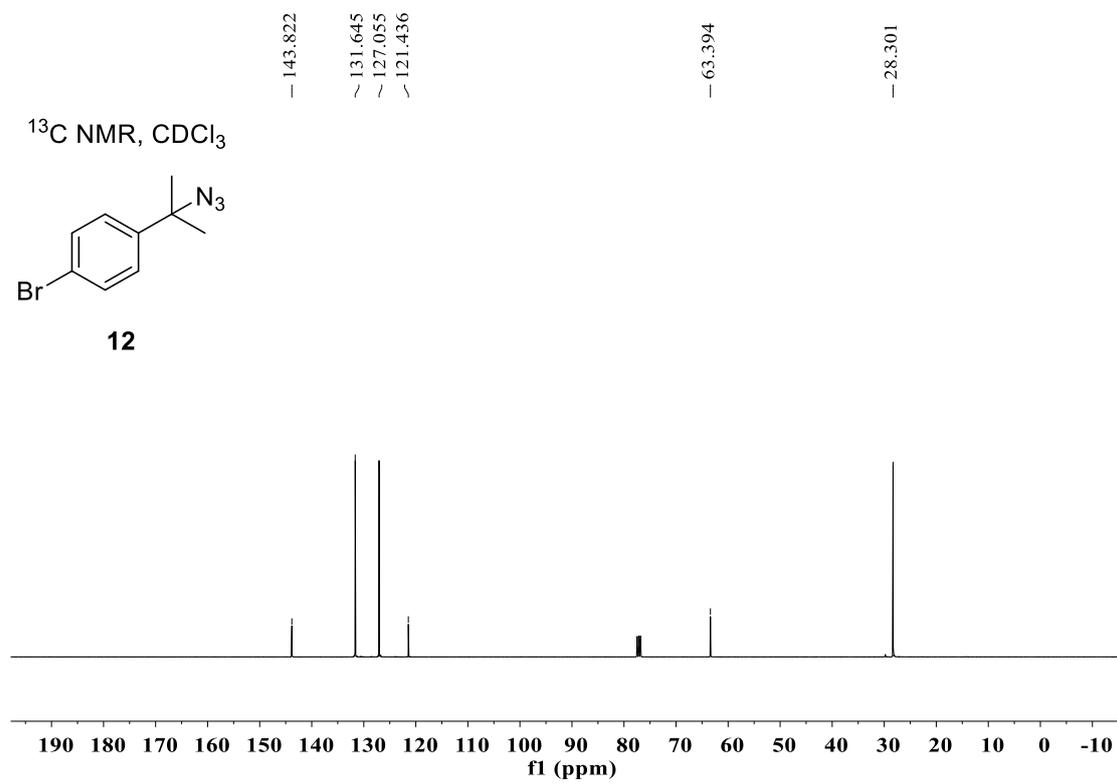
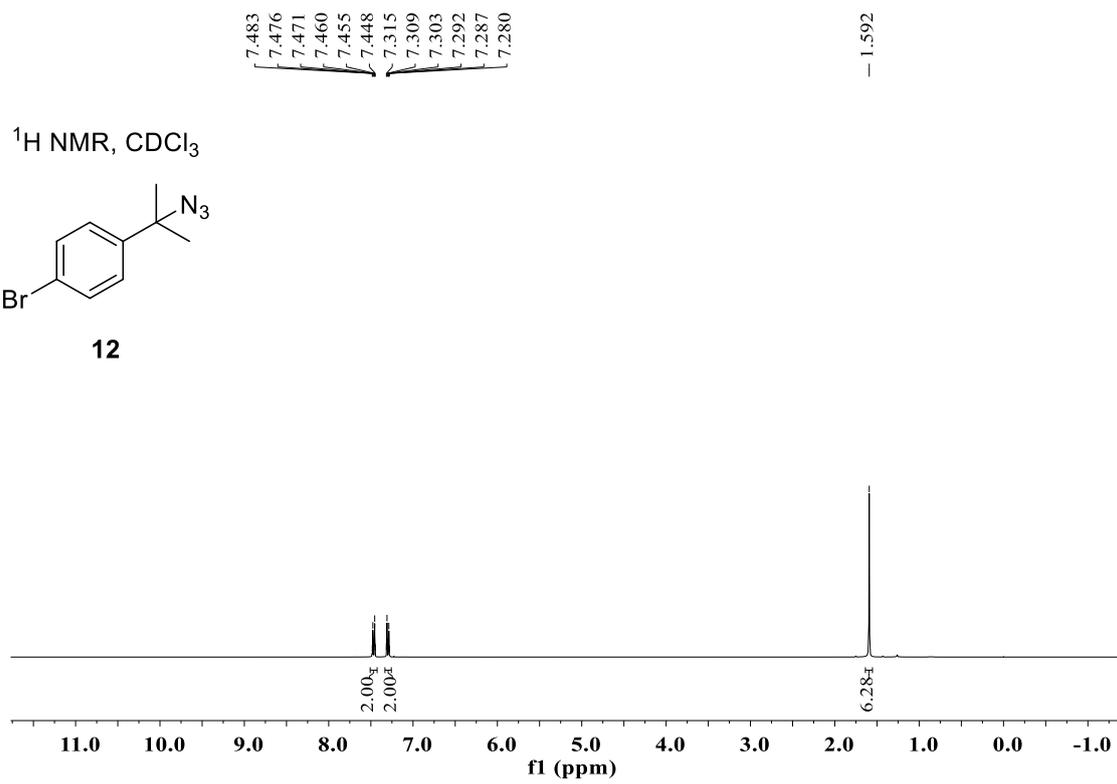








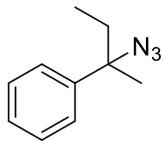




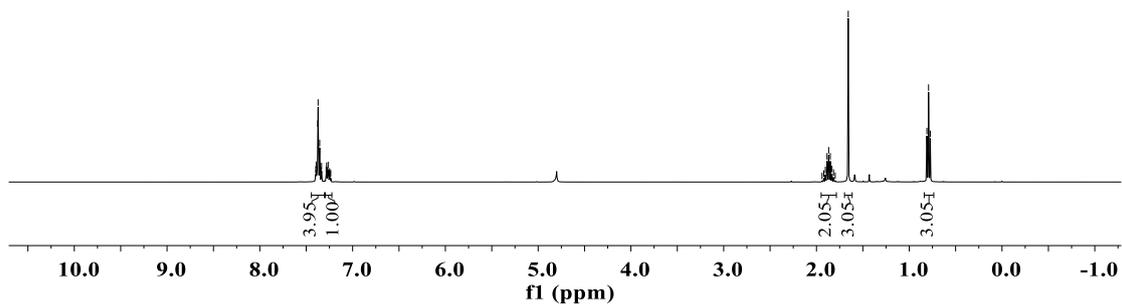
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7.393  
7.387  
7.376  
7.372  
7.355  
7.350  
7.339  
7.335  
7.285  
7.281  
7.275  
7.270  
7.264  
7.258  
7.252  
7.248  
7.243  
7.236

1.940  
1.921  
1.904  
1.886  
1.868  
1.851  
1.833  
1.816  
1.798  
1.657  
0.810  
0.792  
0.773

<sup>1</sup>H NMR, CDCl<sub>3</sub>



**13**



— 143.415

128.532  
127.303  
125.747

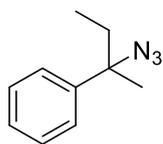
— 67.456

— 35.127

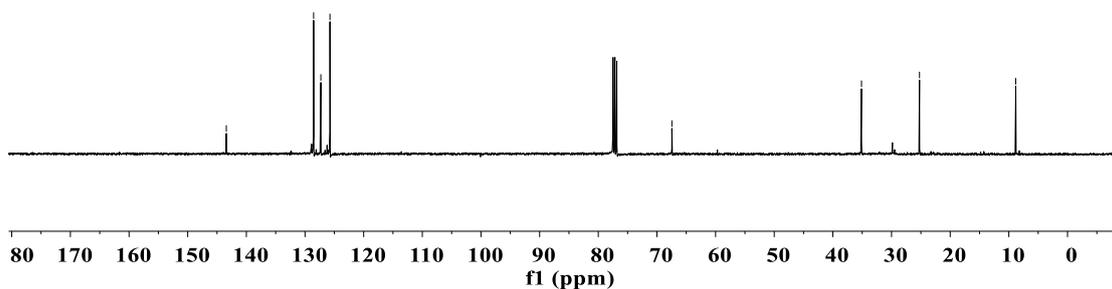
— 25.232

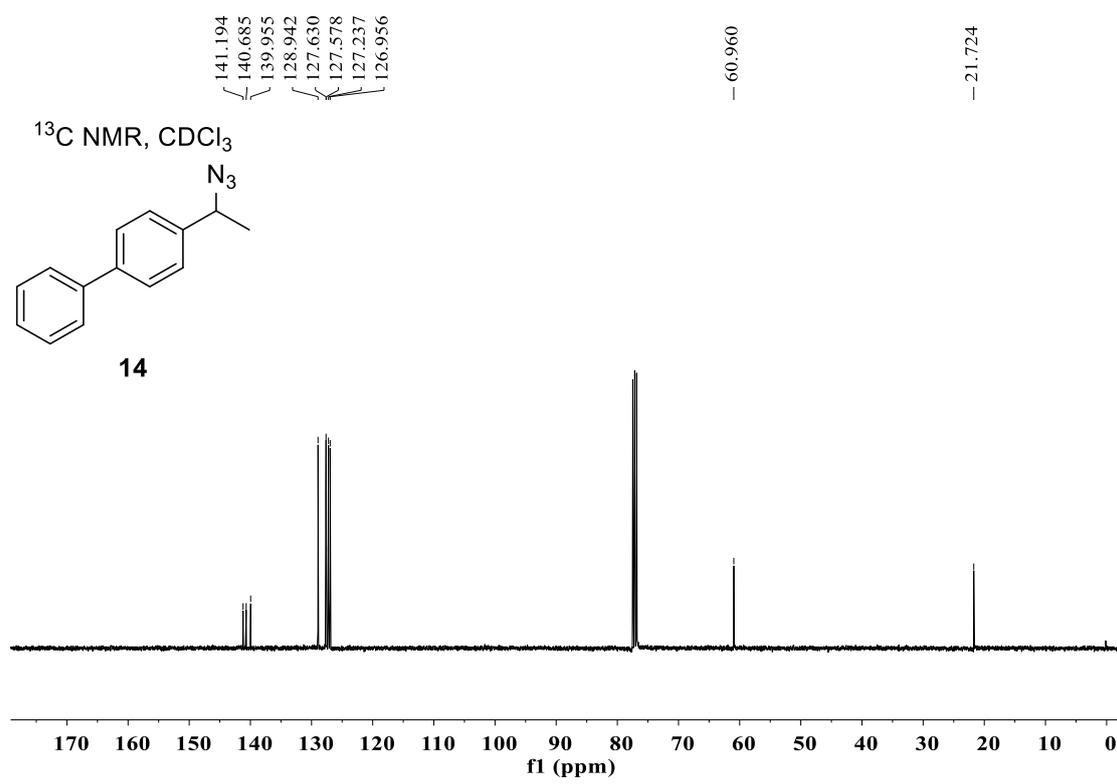
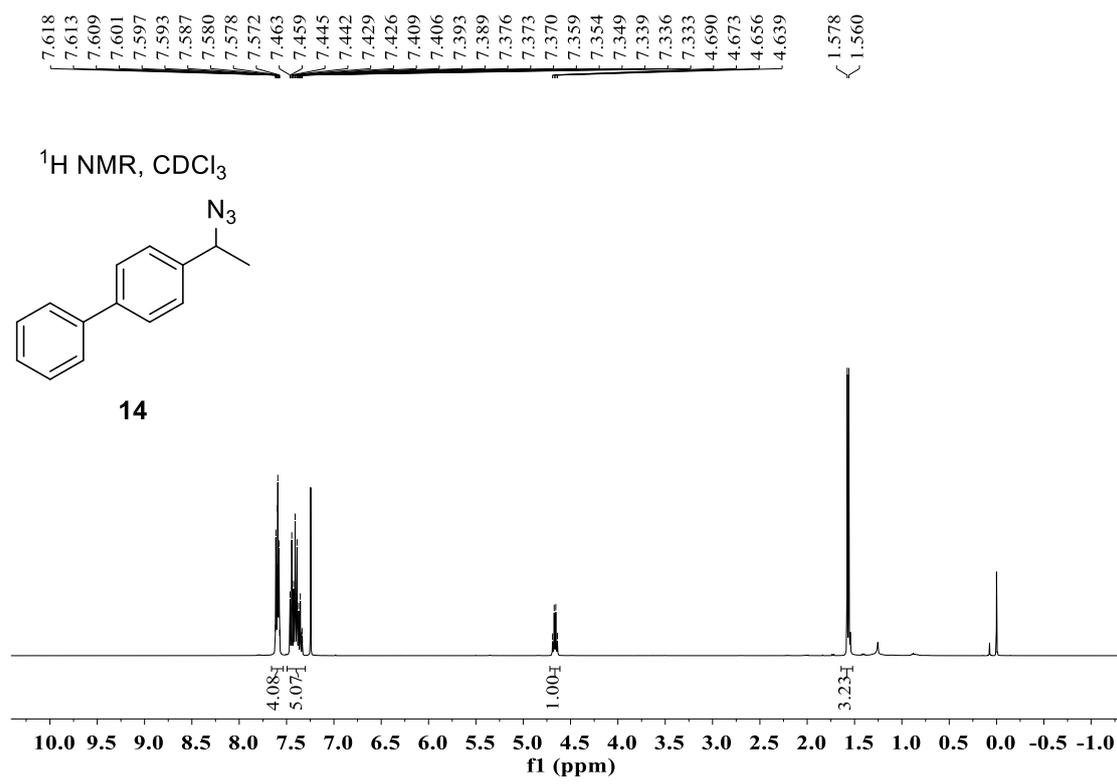
— 8.828

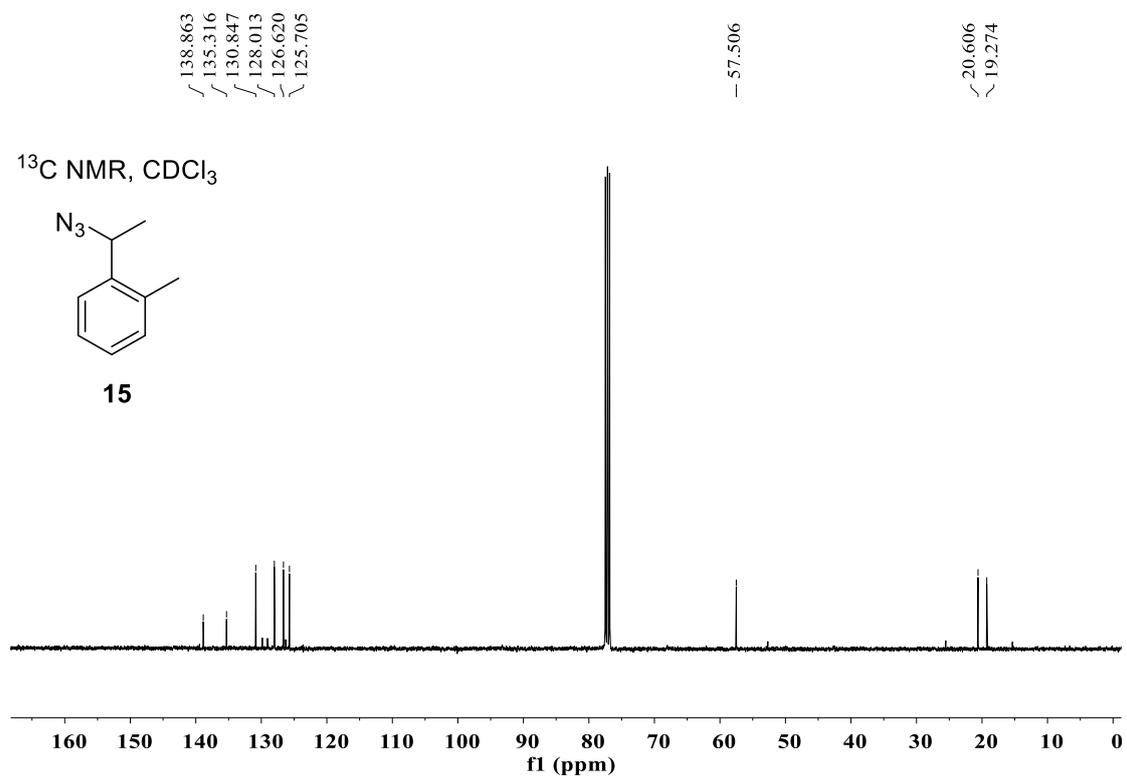
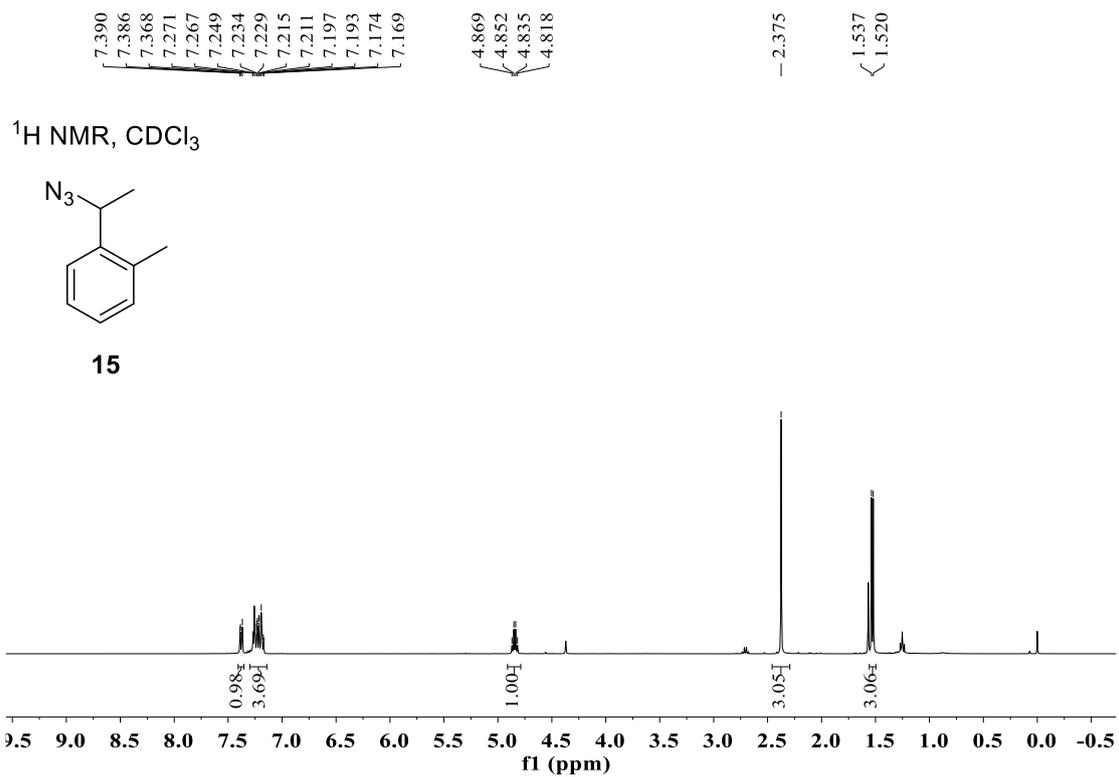
<sup>13</sup>C NMR, CDCl<sub>3</sub>

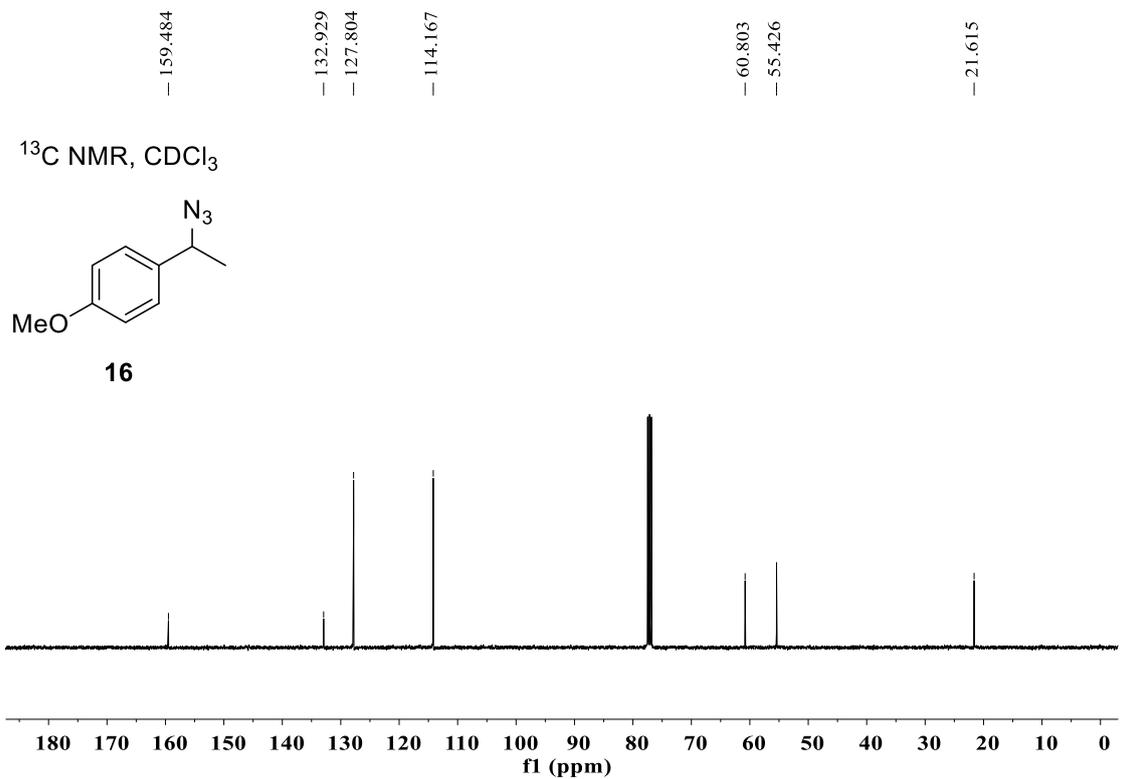
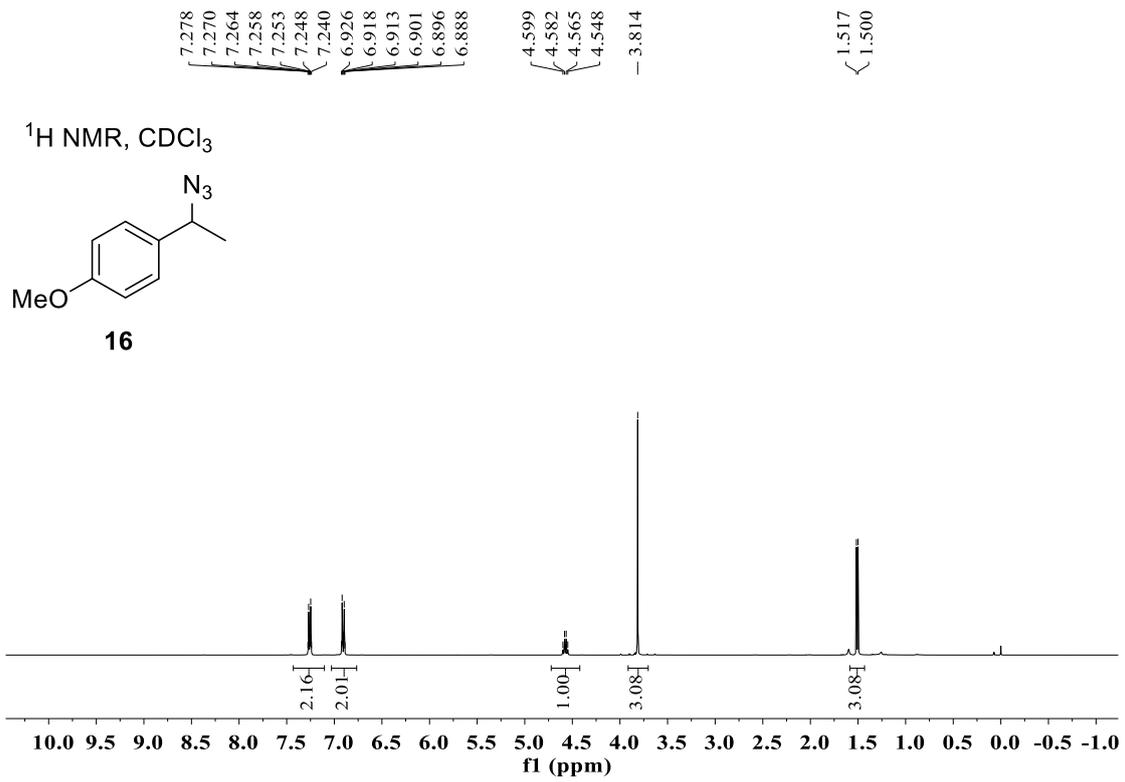


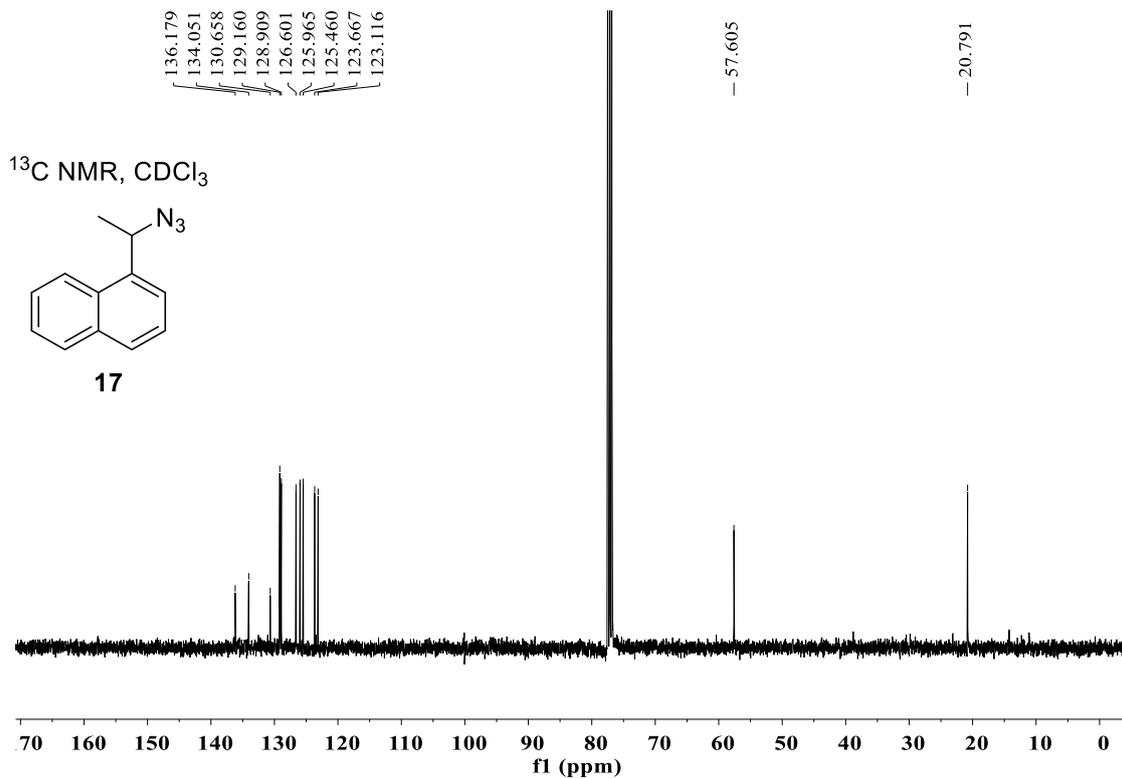
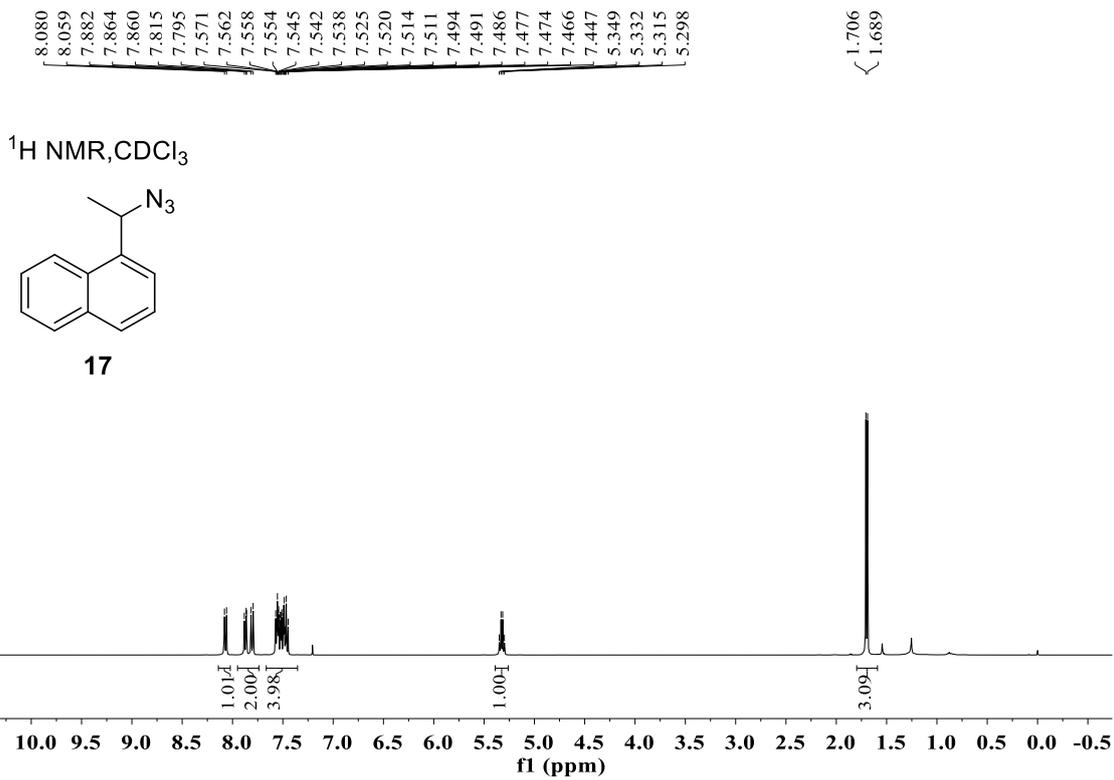
**13**





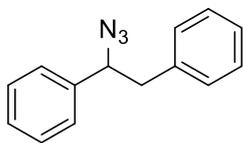




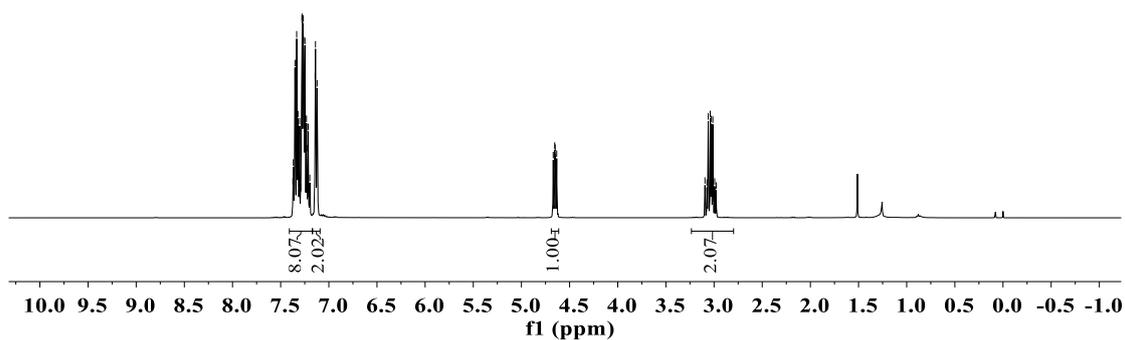


7.352  
7.348  
7.337  
7.334  
7.324  
7.320  
7.316  
7.303  
7.287  
7.280  
7.276  
7.266  
7.261  
7.257  
7.251  
7.248  
7.232  
7.228  
7.214  
7.142  
7.138  
7.122  
4.670  
4.655  
4.649  
4.634  
3.095  
3.074  
3.060  
3.040  
3.028  
3.013  
2.994  
2.990  
2.978

<sup>1</sup>H NMR, CDCl<sub>3</sub>

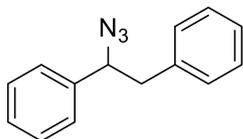


**18**

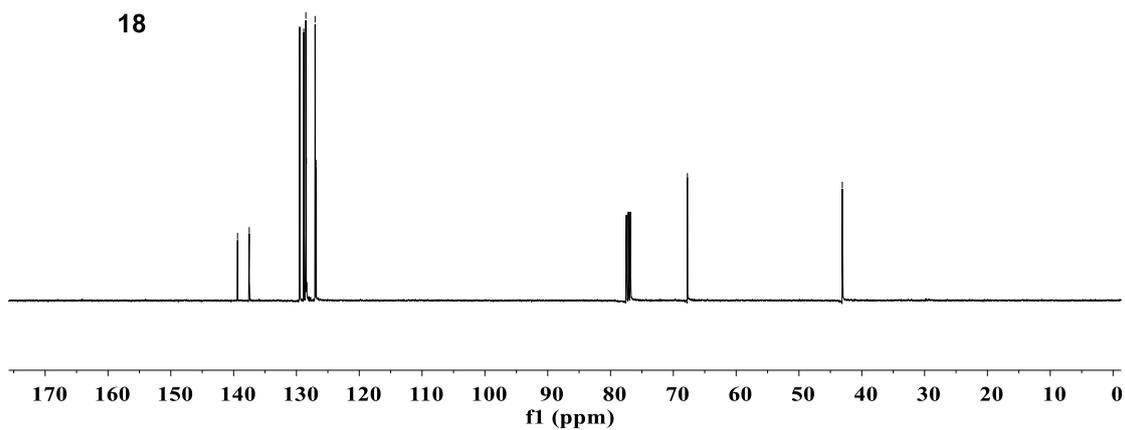


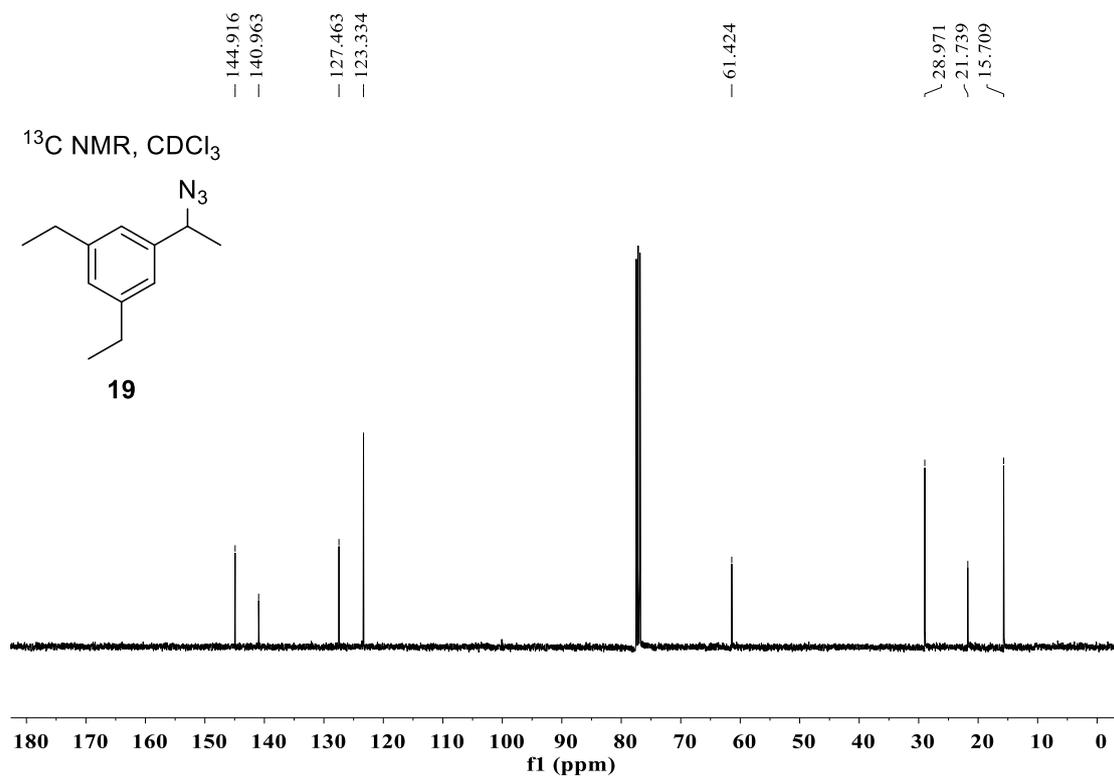
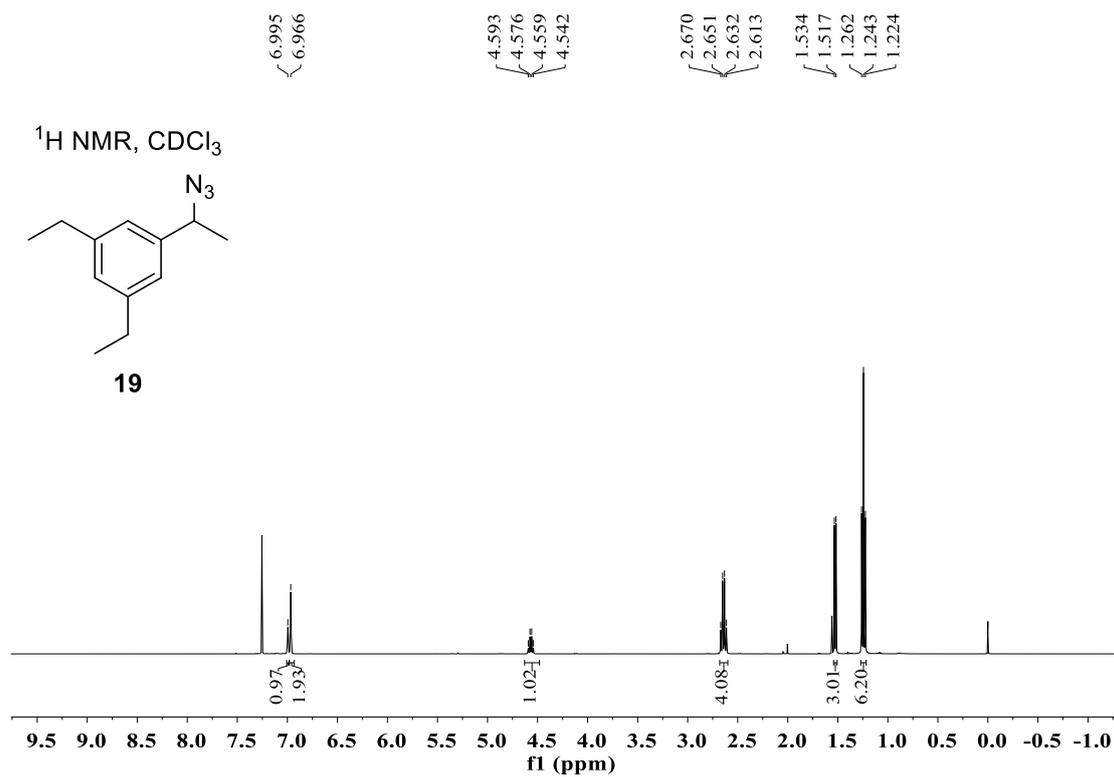
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128.509  
128.406  
127.033  
126.878  
67.760  
43.101

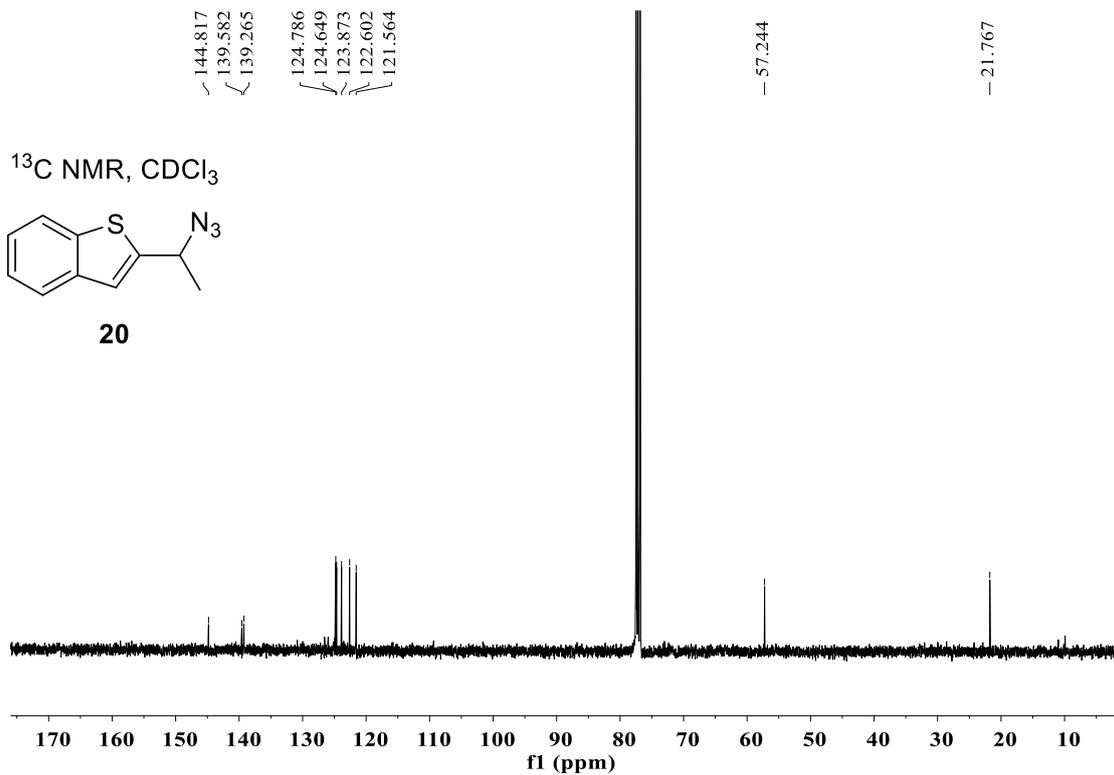
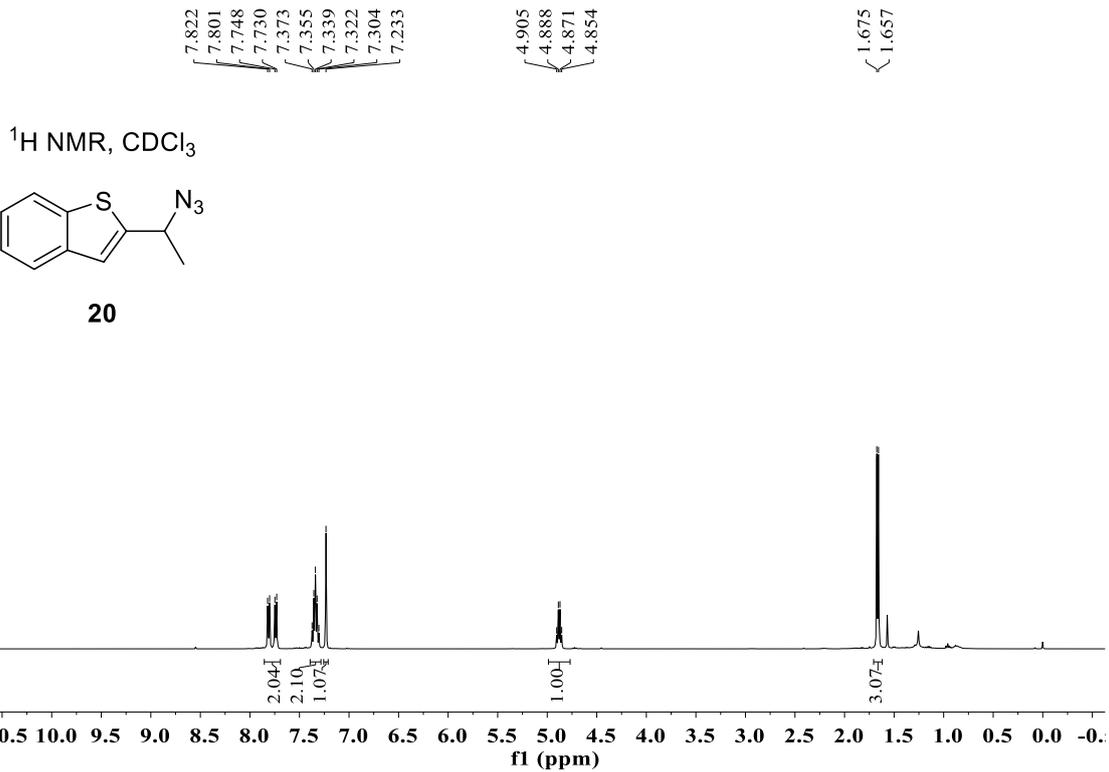
<sup>13</sup>C NMR, CDCl<sub>3</sub>



**18**

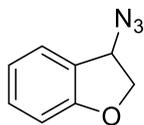




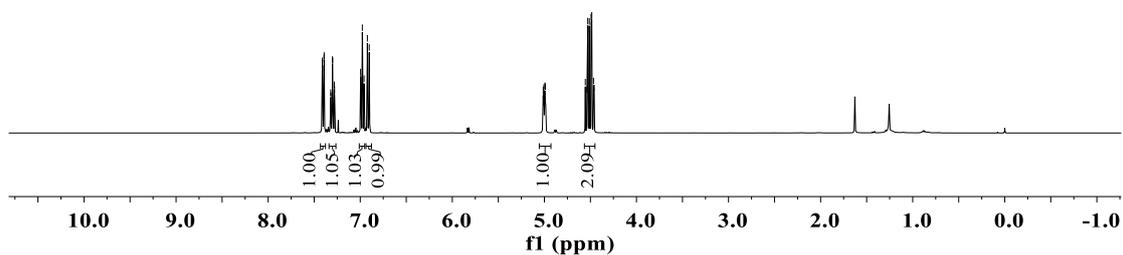


7.412  
7.411  
7.409  
7.393  
7.392  
7.390  
7.321  
7.301  
7.300  
7.282  
7.279  
6.996  
6.994  
6.977  
6.975  
6.959  
6.956  
6.922  
5.006  
5.003  
5.006  
4.995  
4.988  
4.555  
4.538  
4.529  
4.512  
4.492  
4.485  
4.466  
4.459

<sup>1</sup>H NMR, CDCl<sub>3</sub>

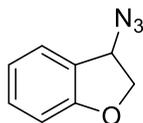


**21**

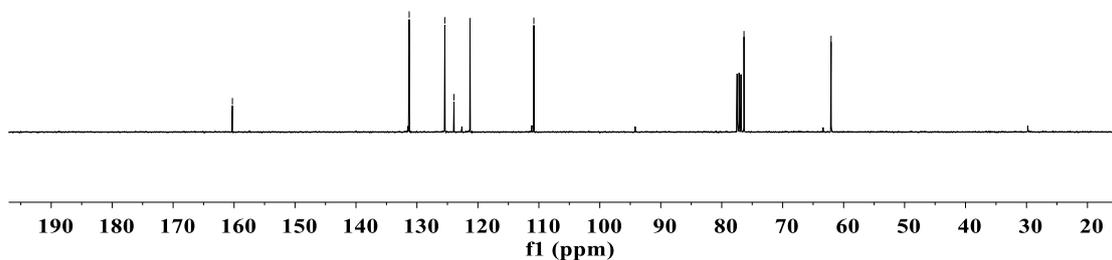


— 160.275  
~ 131.272  
/ 125.426  
~ 123.921  
~ 121.294  
— 110.823  
— 76.348  
— 62.055

<sup>13</sup>C NMR, CDCl<sub>3</sub>

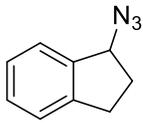


**21**

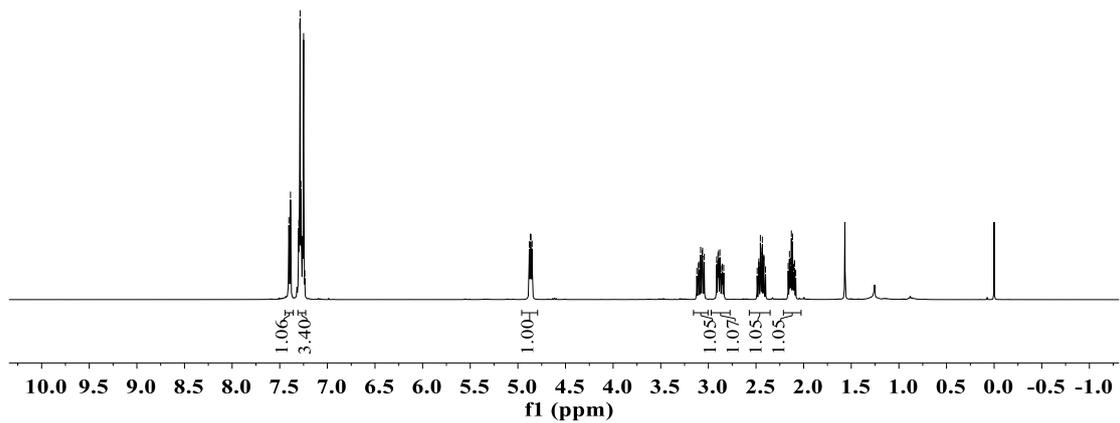


7.404  
7.387  
7.304  
7.300  
7.289  
7.286  
7.277  
7.270  
7.249  
7.249  
4.880  
4.869  
4.862  
4.851  
3.105  
3.101  
3.082  
3.065  
3.061  
3.045  
2.913  
2.900  
2.893  
2.879  
2.874  
2.852  
2.839  
2.839  
2.472  
2.470  
2.467  
2.454  
2.452  
2.449  
2.439  
2.436  
2.434  
2.421  
2.418  
2.416  
2.162  
2.149  
2.141  
2.137  
2.129  
2.117  
2.108  
2.104  
2.096  
2.095

<sup>1</sup>H NMR, CDCl<sub>3</sub>



**22**

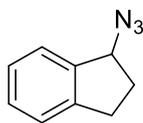


~ 143.753  
~ 140.738  
~ 128.967  
~ 126.948  
~ 125.187  
~ 124.649

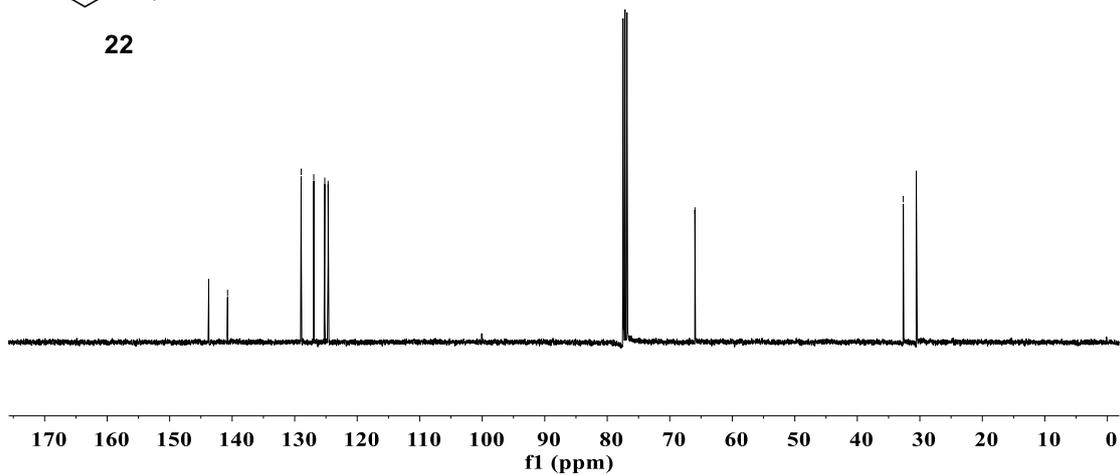
~ 65.973

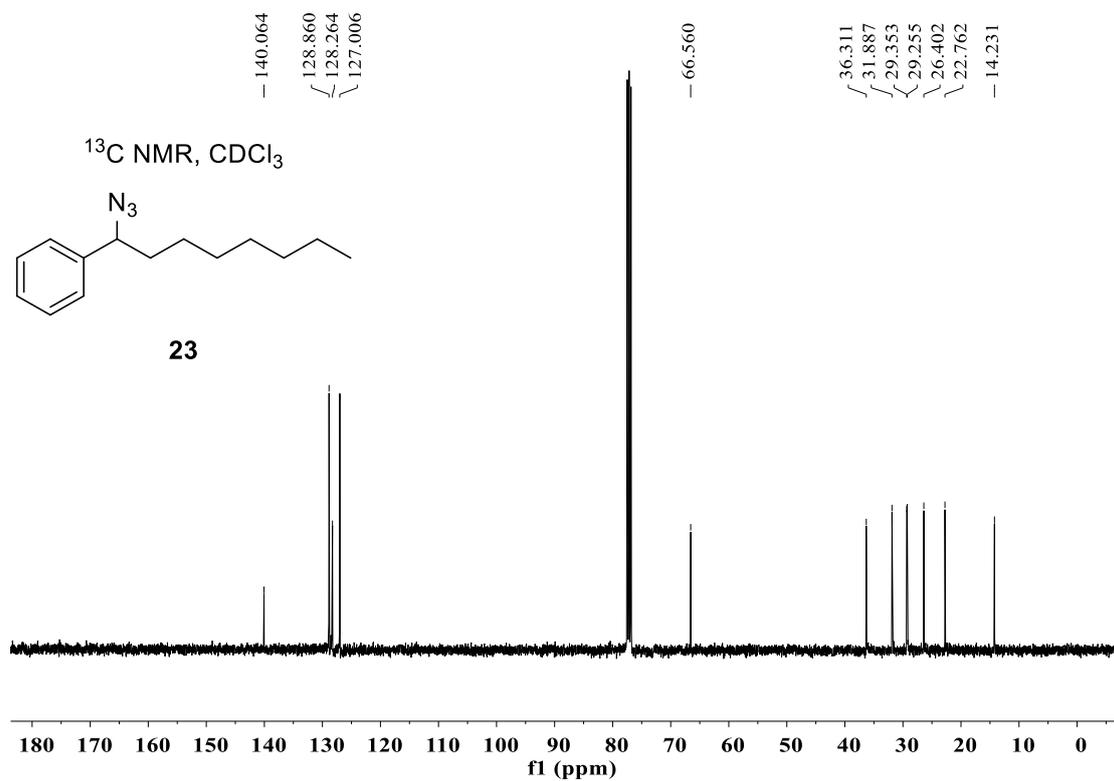
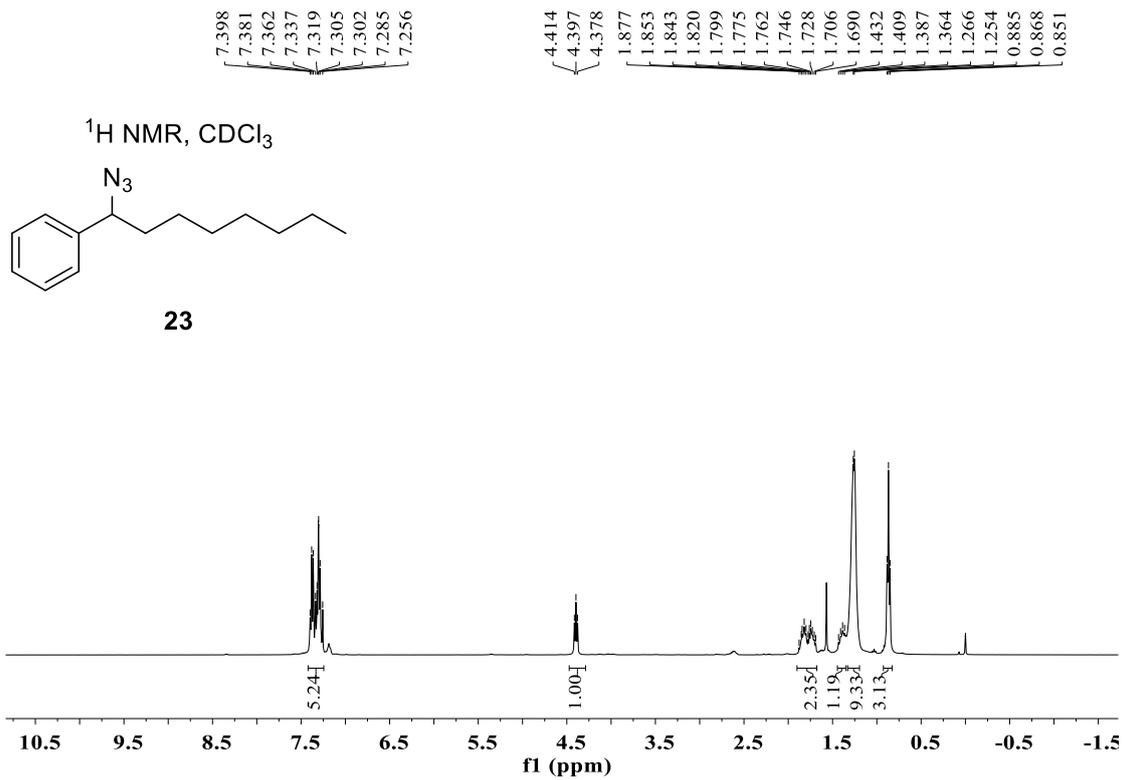
~ 32.642  
~ 30.568

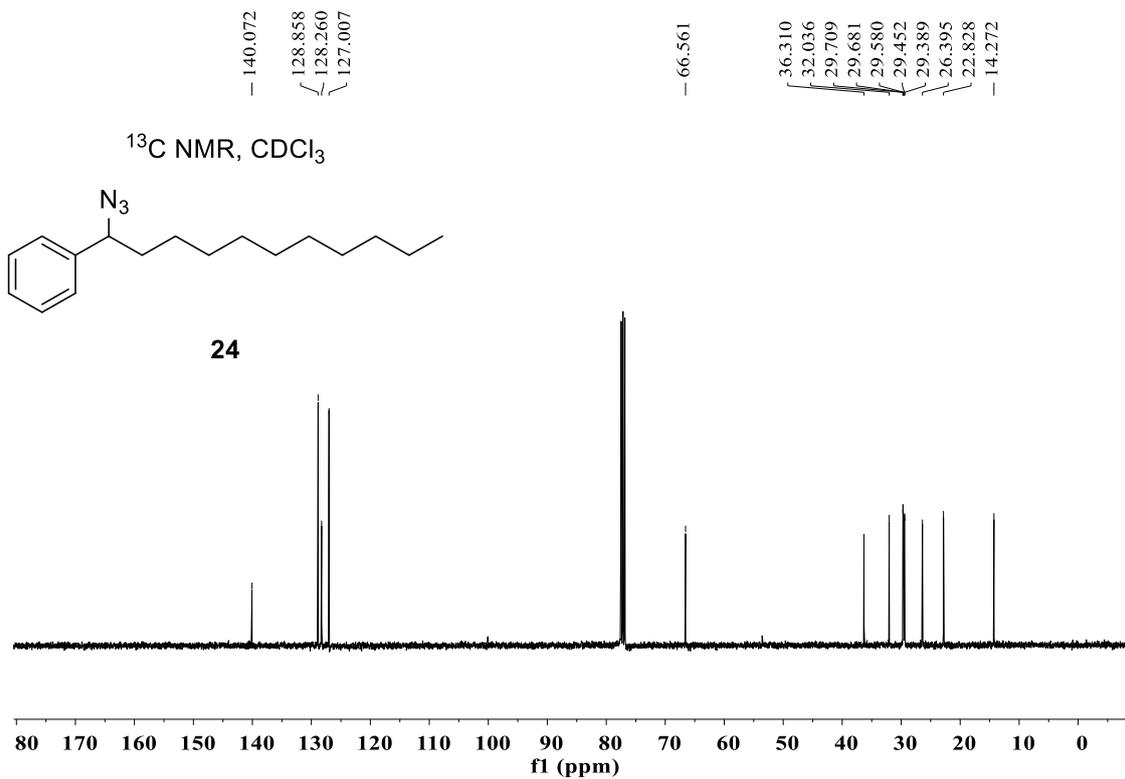
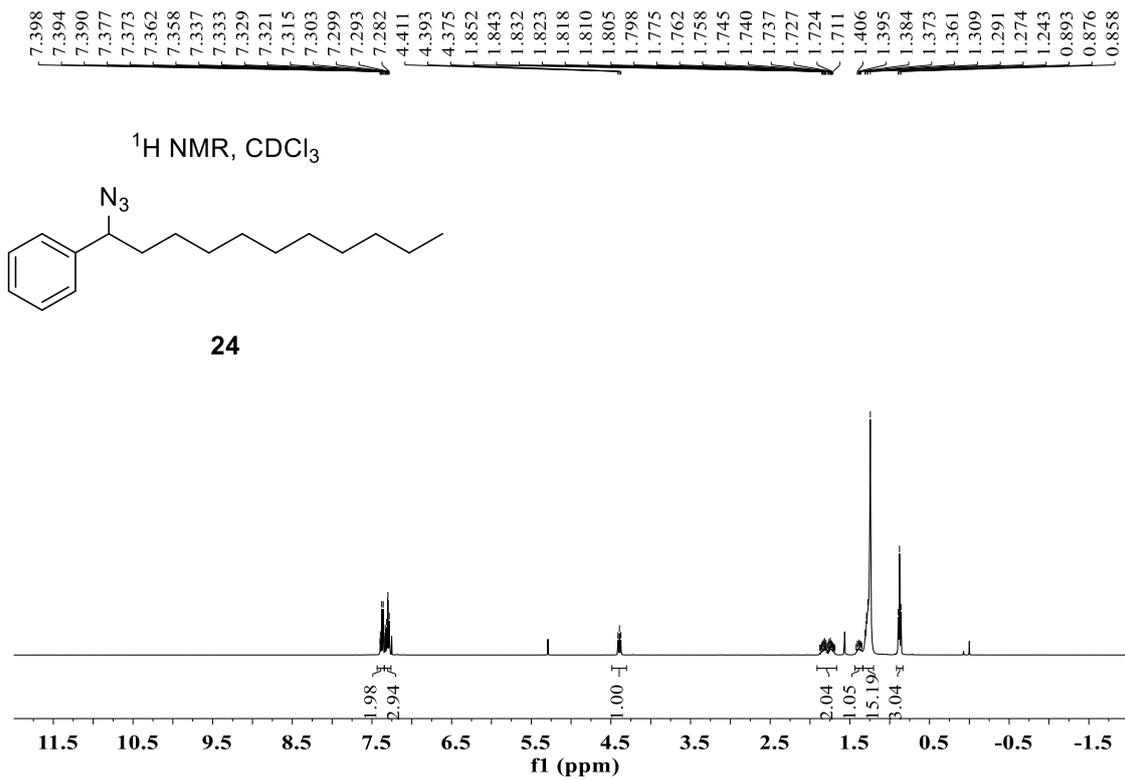
<sup>13</sup>C NMR, CDCl<sub>3</sub>

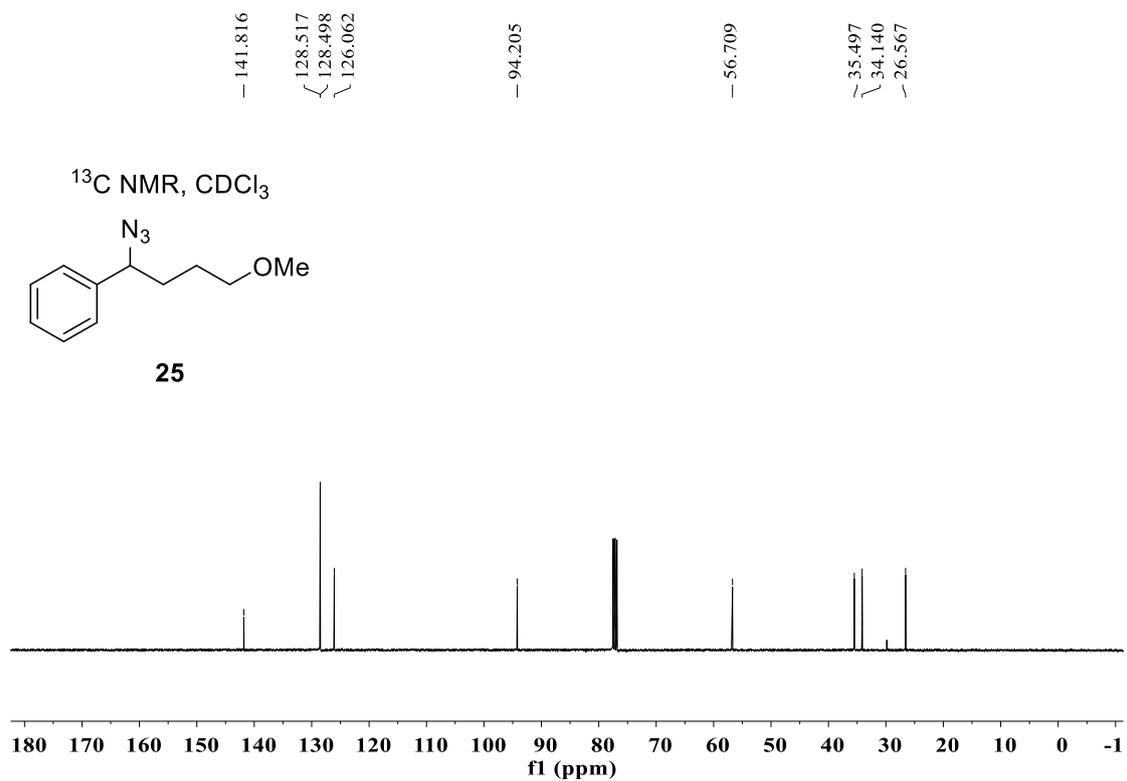
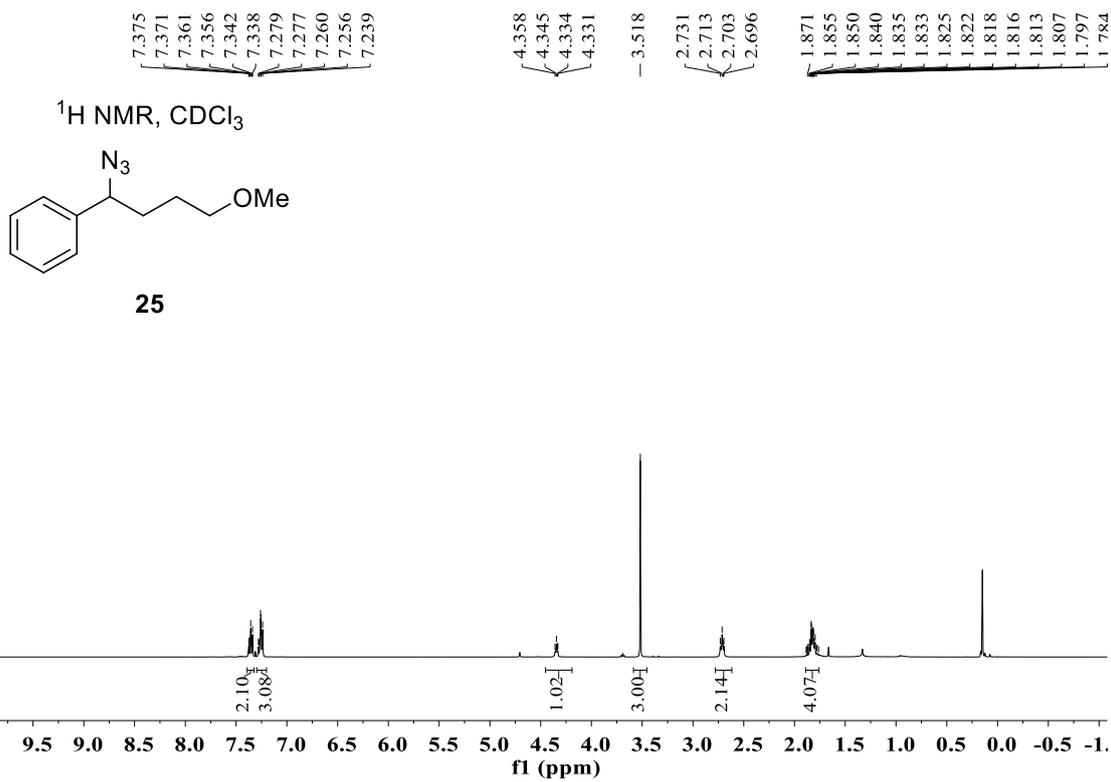


**22**

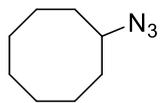




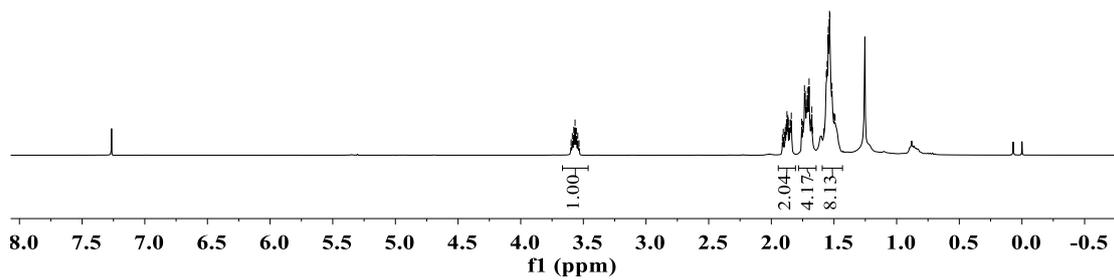




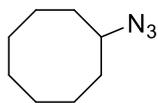
<sup>1</sup>H NMR, CDCl<sub>3</sub>



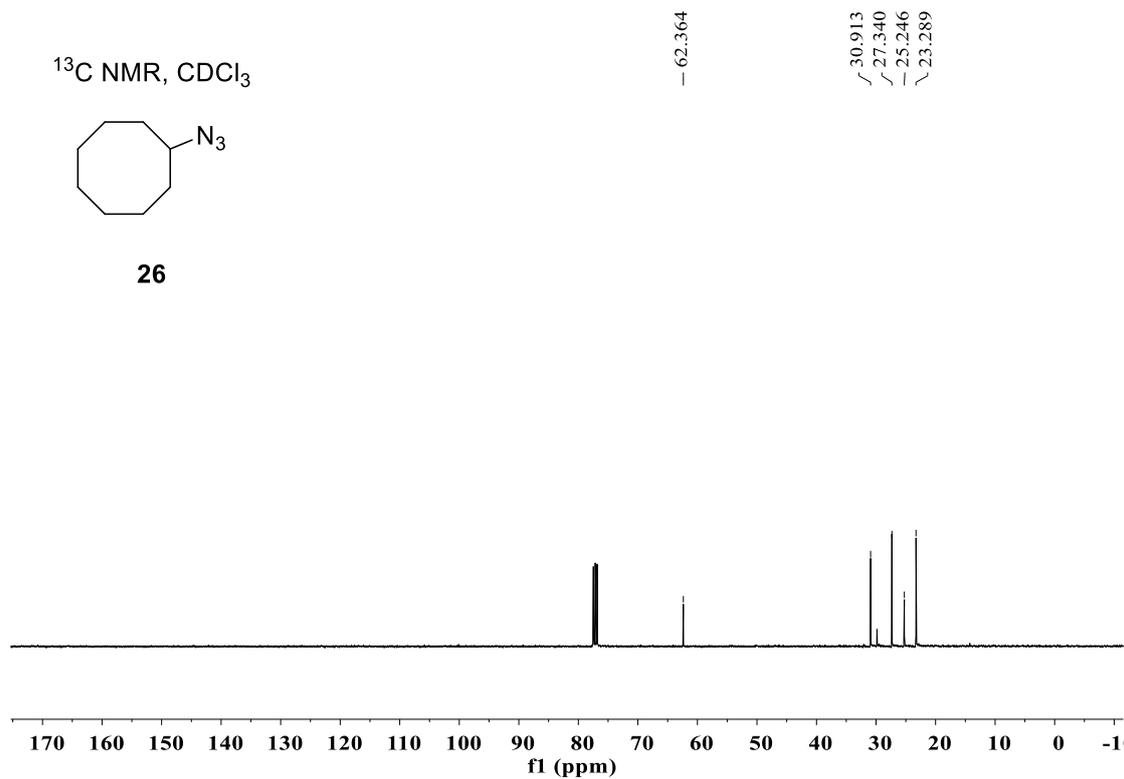
26



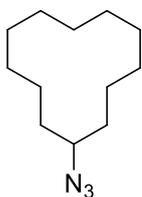
<sup>13</sup>C NMR, CDCl<sub>3</sub>



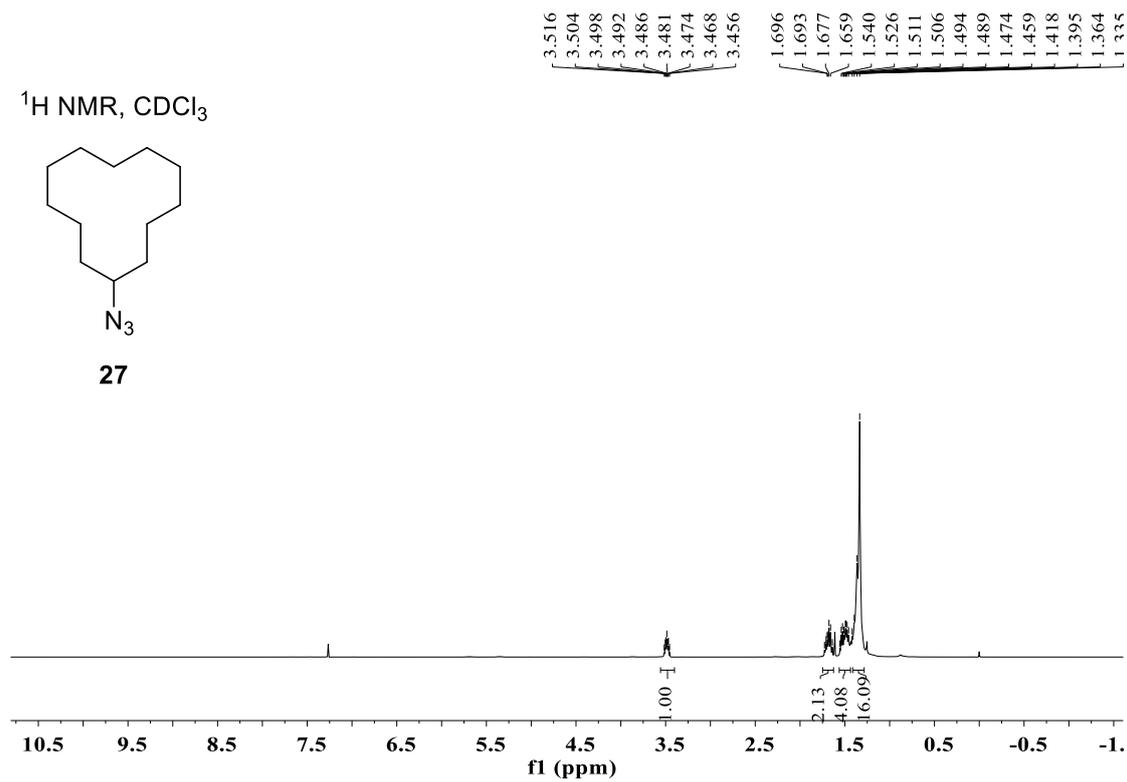
26



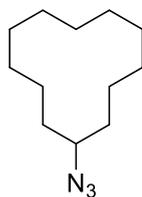
<sup>1</sup>H NMR, CDCl<sub>3</sub>



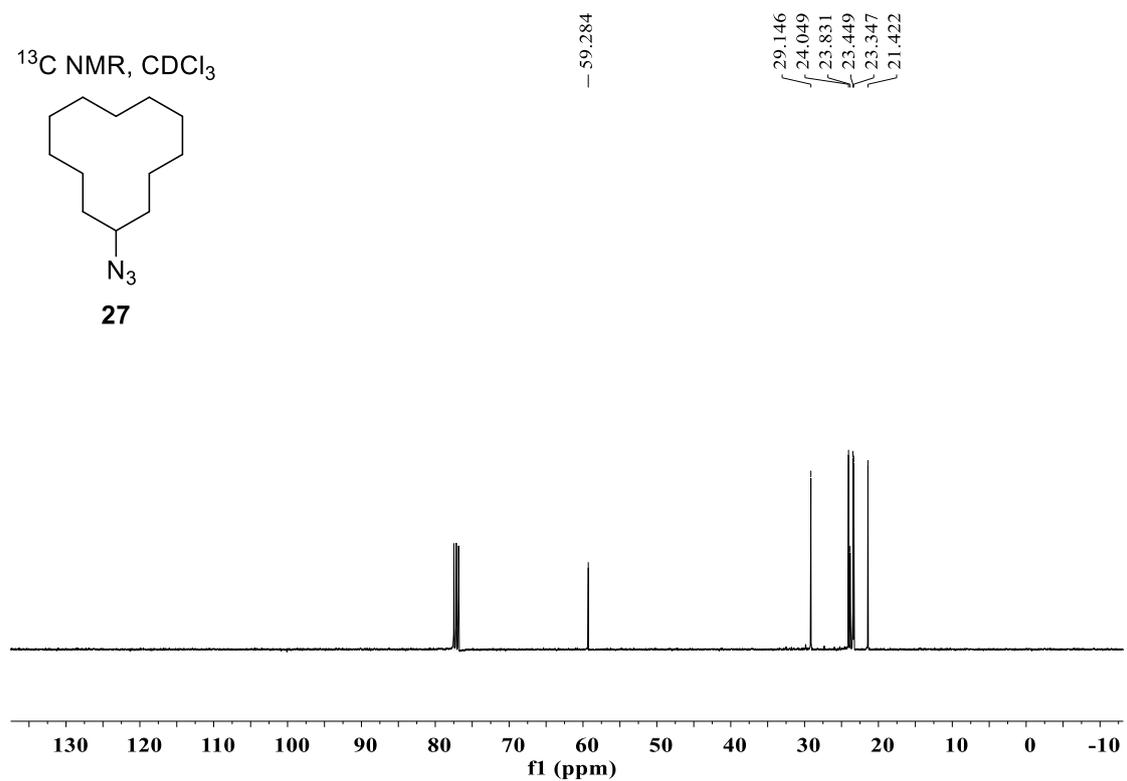
27



<sup>13</sup>C NMR, CDCl<sub>3</sub>

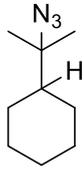


27

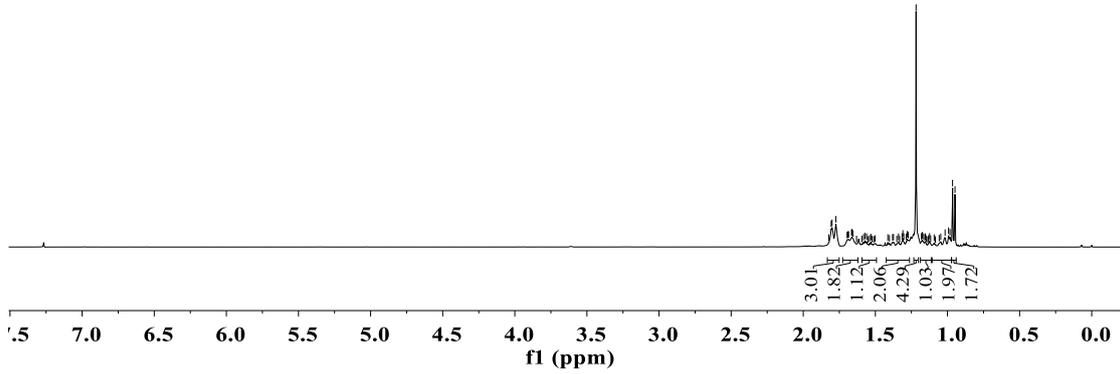


1.824  
1.806  
1.800  
1.774  
1.696  
1.691  
1.685  
1.666  
1.662  
1.656  
1.593  
1.582  
1.571  
1.560  
1.540  
1.531  
1.502  
1.414  
1.403  
1.381  
1.374  
1.351  
1.340  
1.332  
1.315  
1.309  
1.303  
1.286  
1.279  
1.272  
1.218  
1.180  
1.175  
1.170  
1.170  
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1.117  
1.092  
1.058  
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0.948

<sup>1</sup>H NMR, CDCl<sub>3</sub>

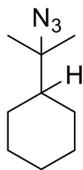


**28**

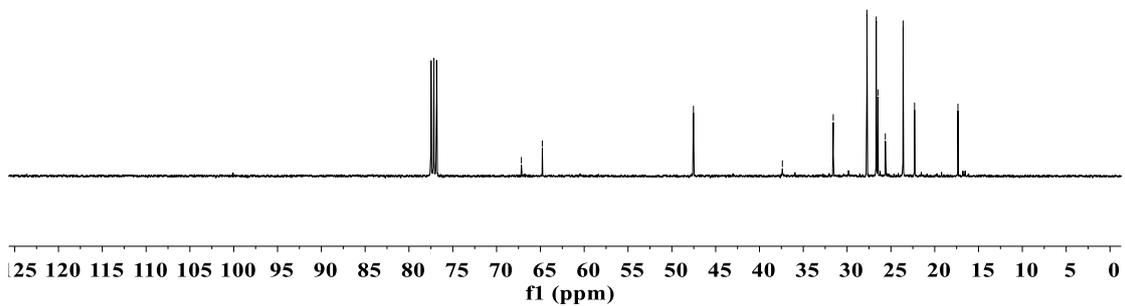


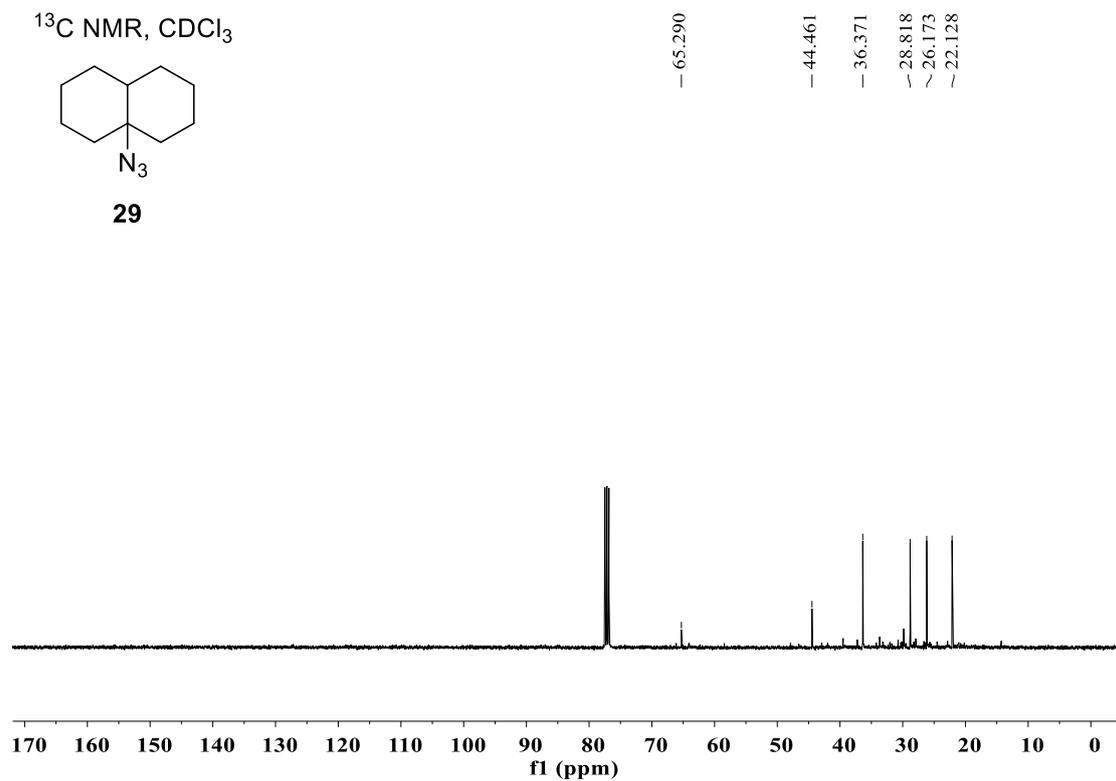
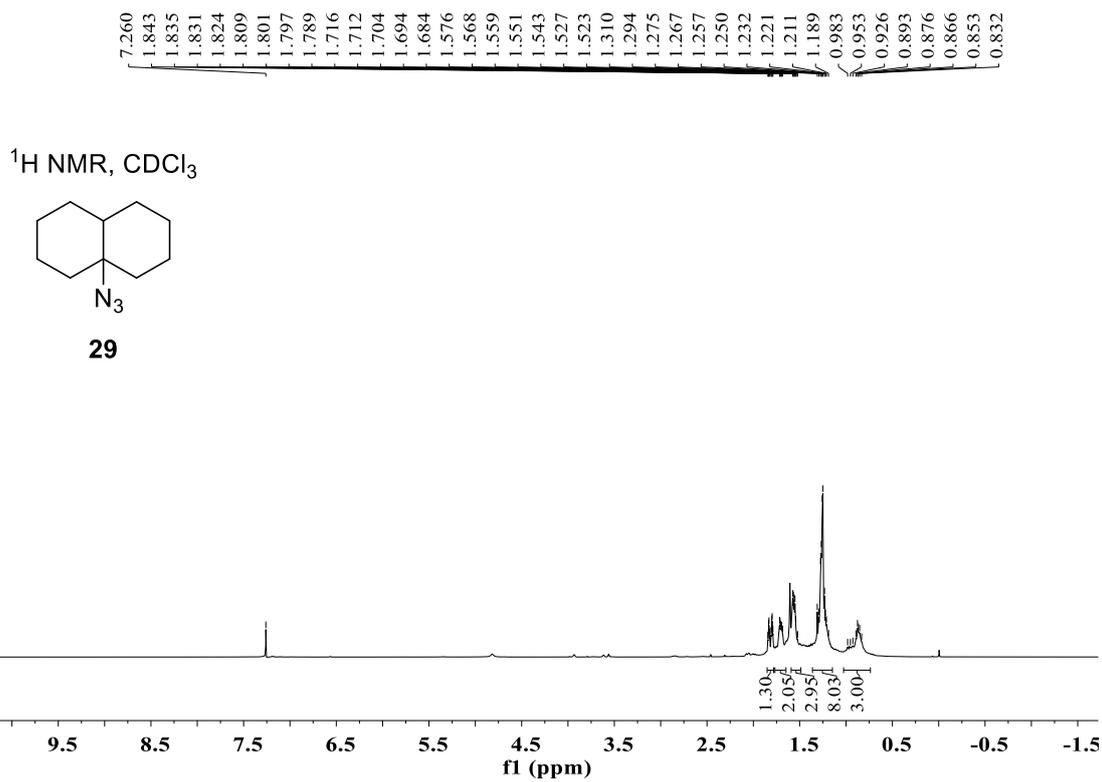
— 67.171  
— 64.785  
  
— 47.535  
  
— 37.386  
/ 31.582  
/ 27.738  
/ 26.679  
/ 26.480  
/ 25.635  
/ 23.609  
/ 22.299  
/ 17.351

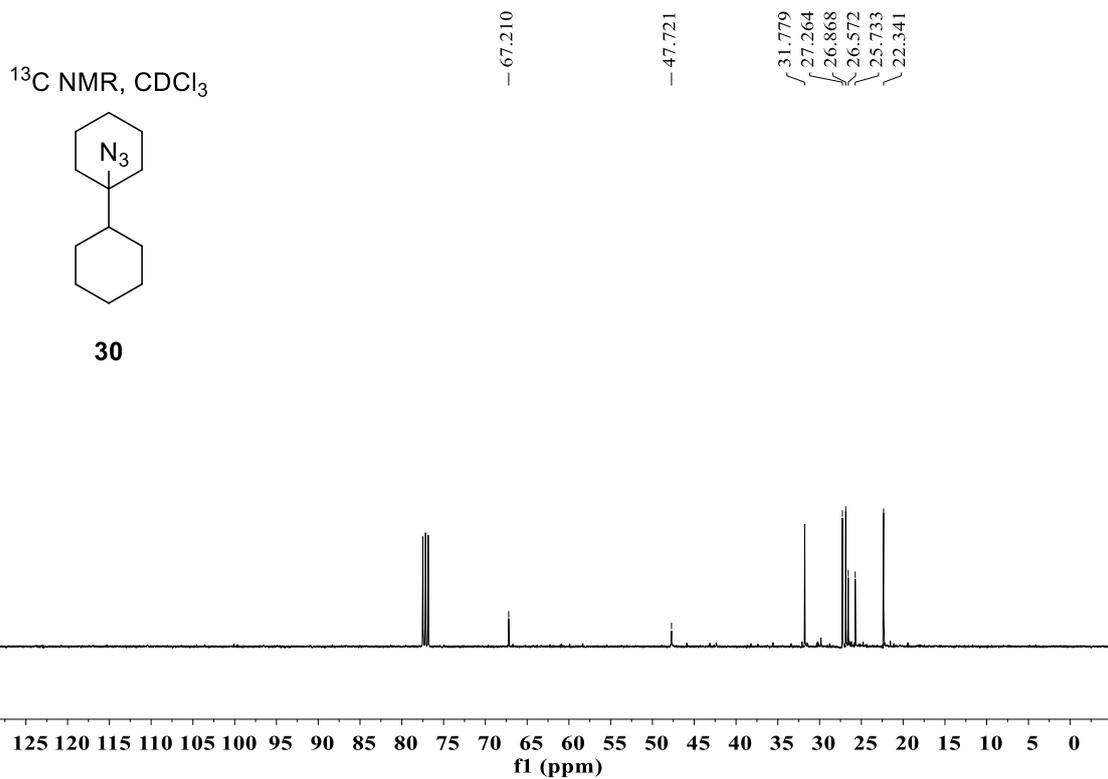
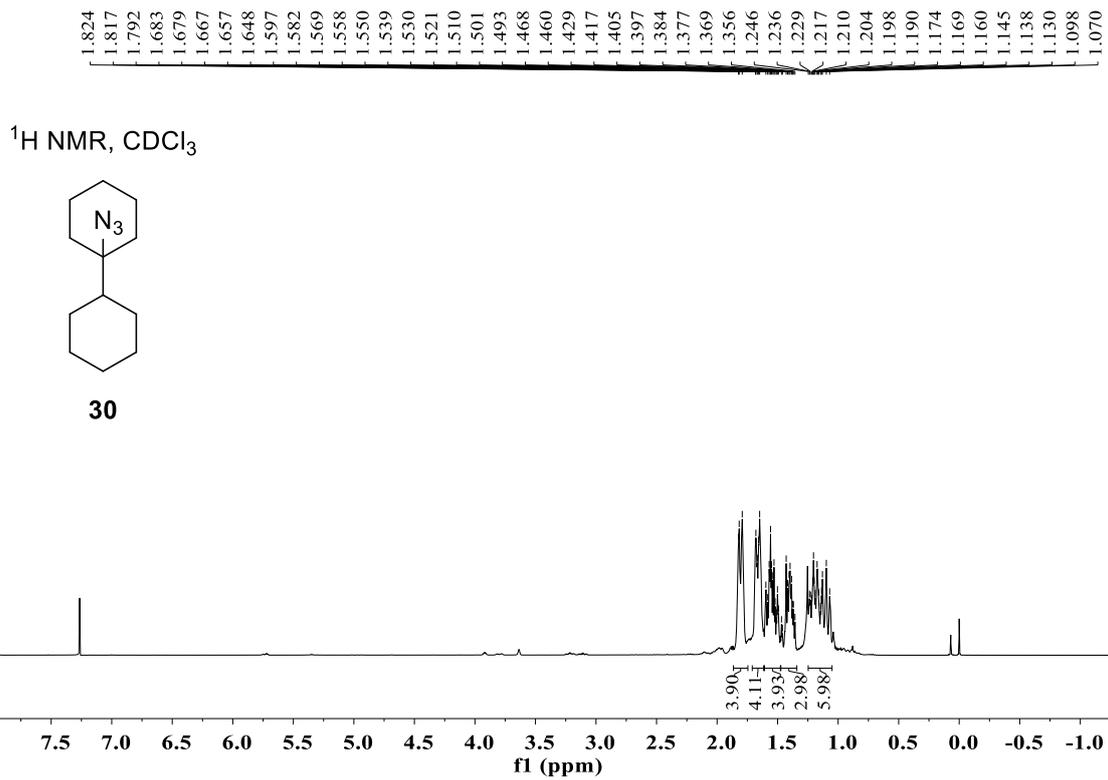
<sup>13</sup>C NMR, CDCl<sub>3</sub>



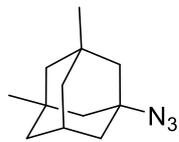
**28**



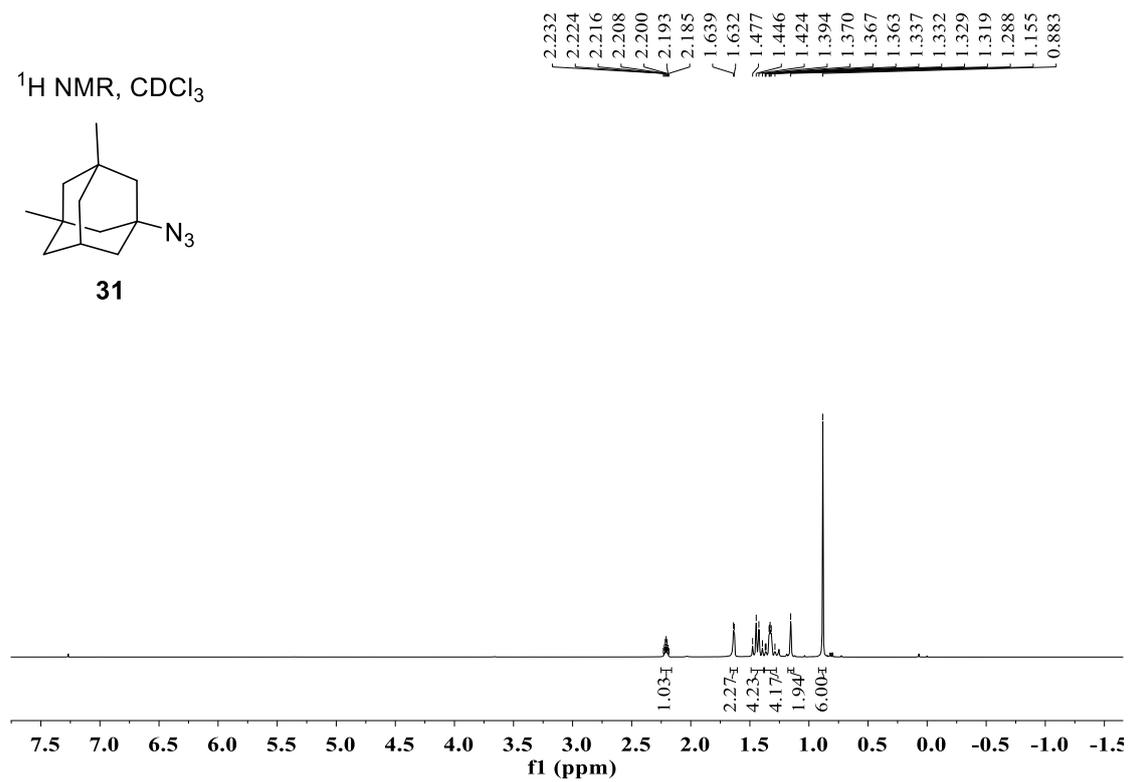




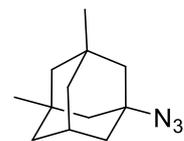
<sup>1</sup>H NMR, CDCl<sub>3</sub>



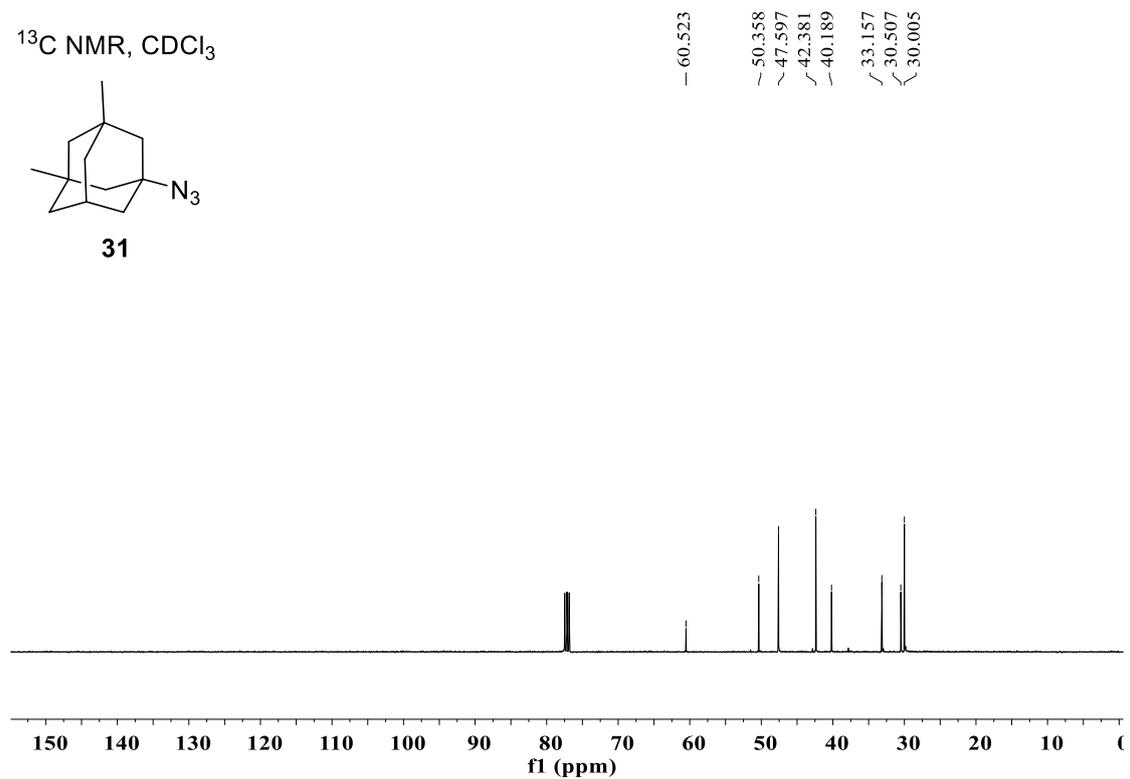
**31**



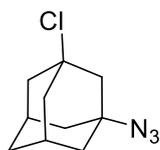
<sup>13</sup>C NMR, CDCl<sub>3</sub>



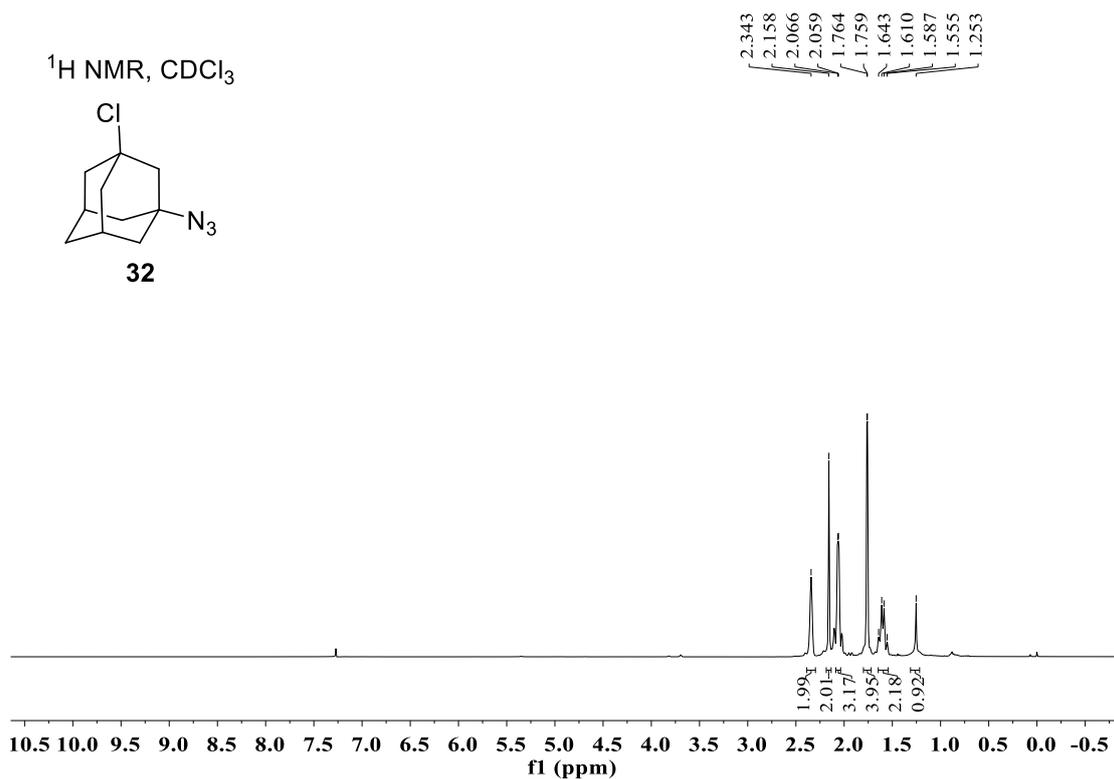
**31**



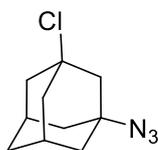
<sup>1</sup>H NMR, CDCl<sub>3</sub>



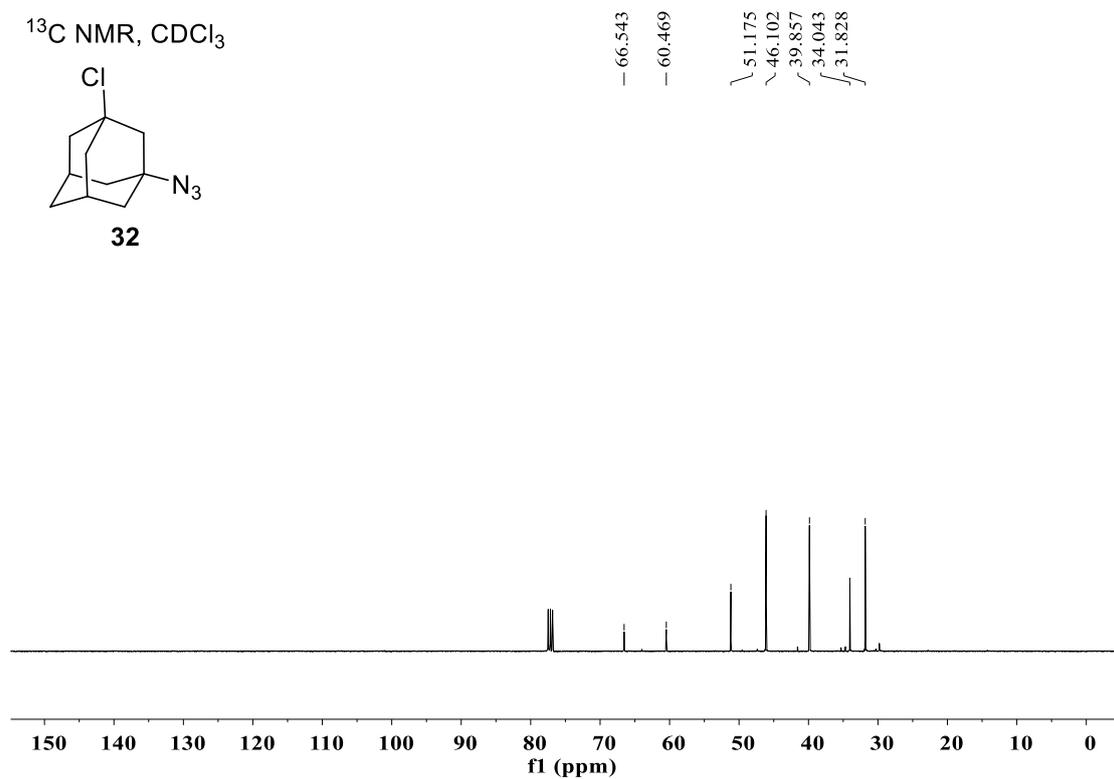
**32**

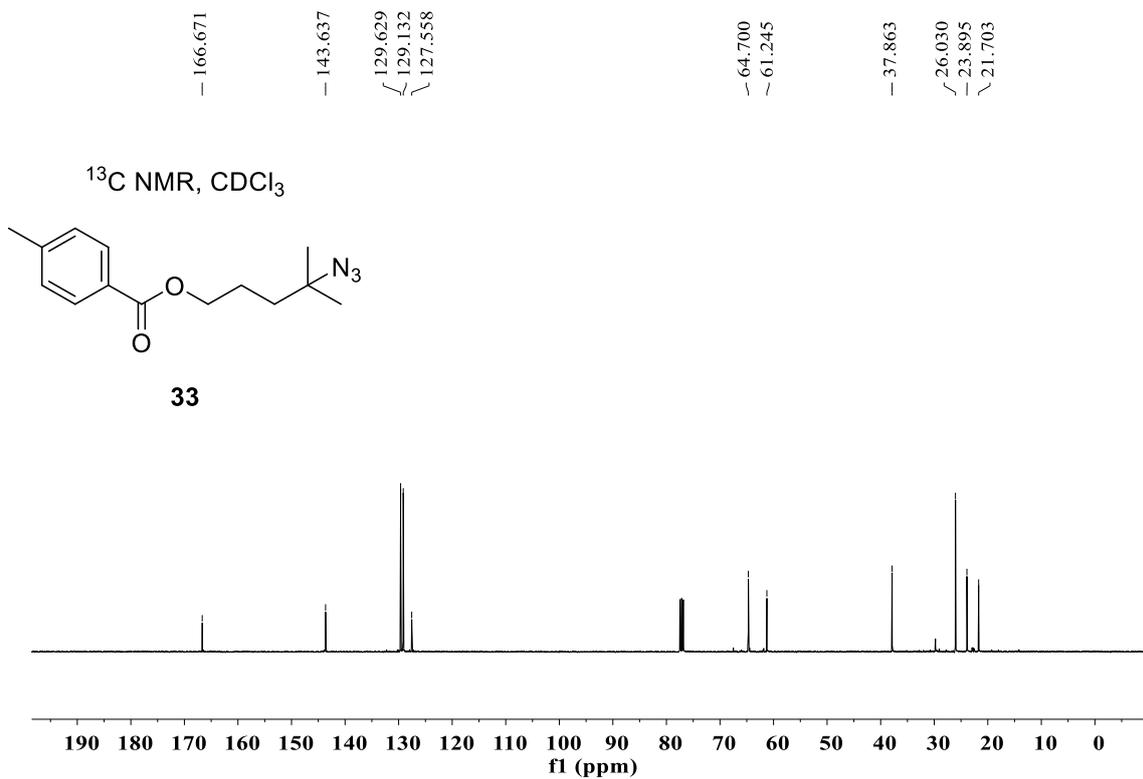
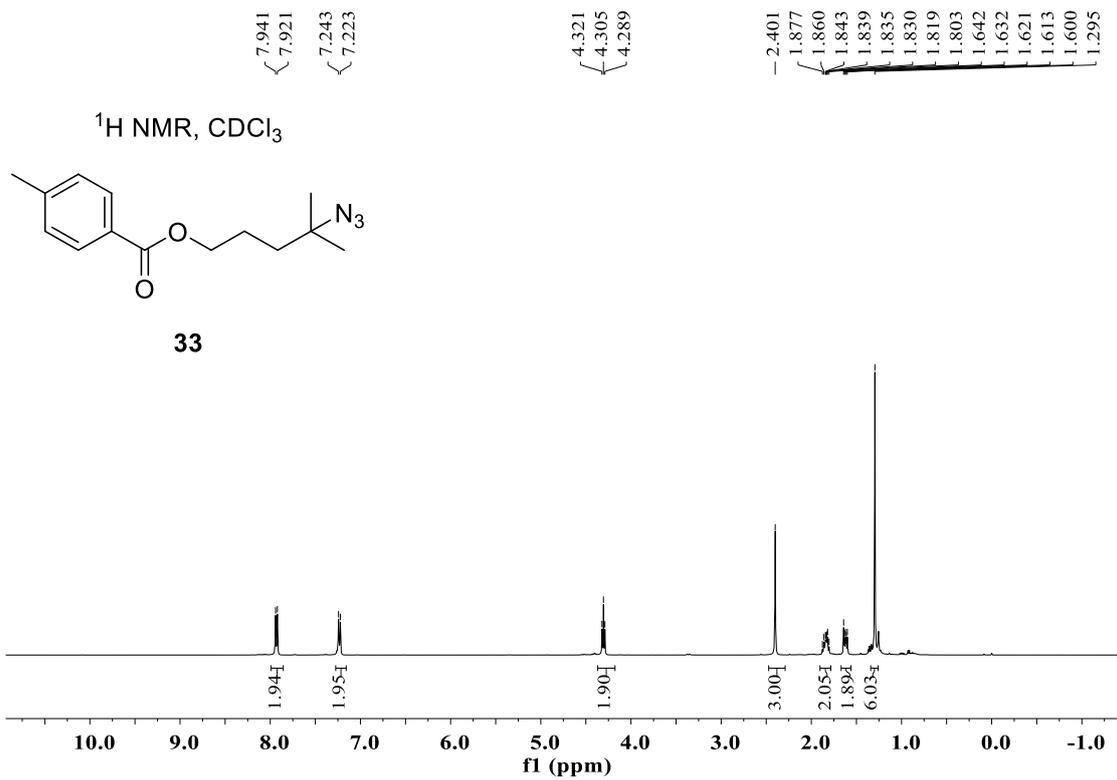


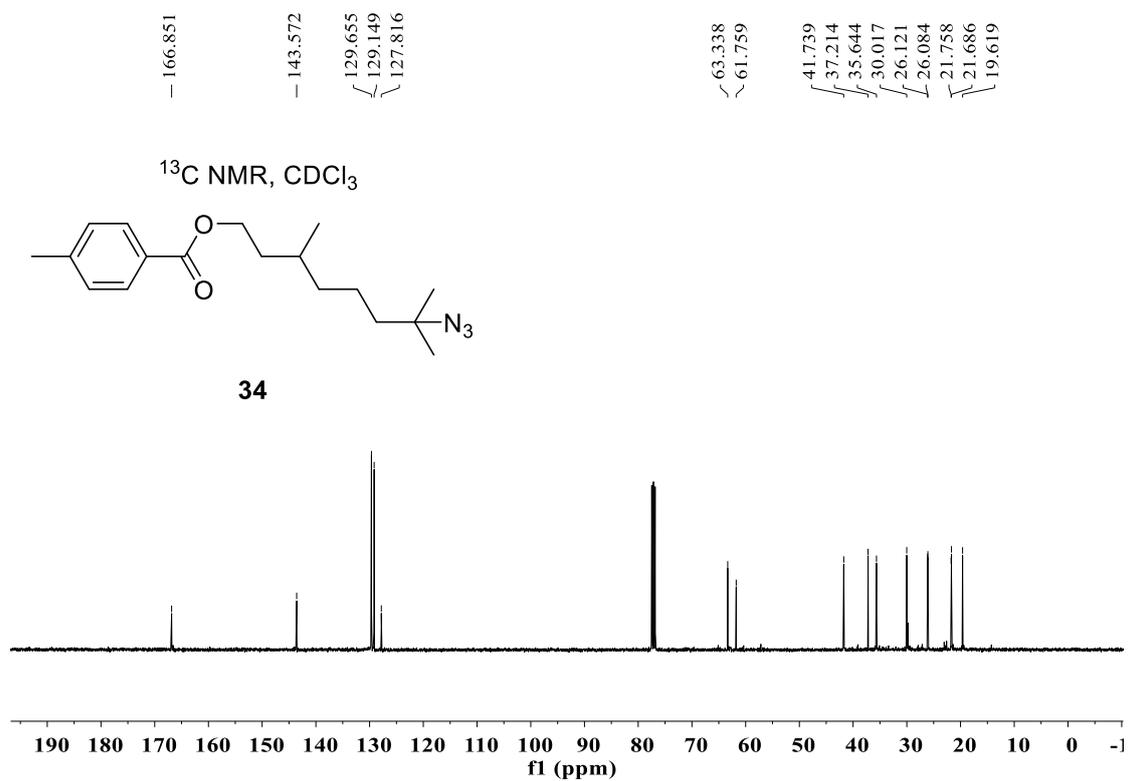
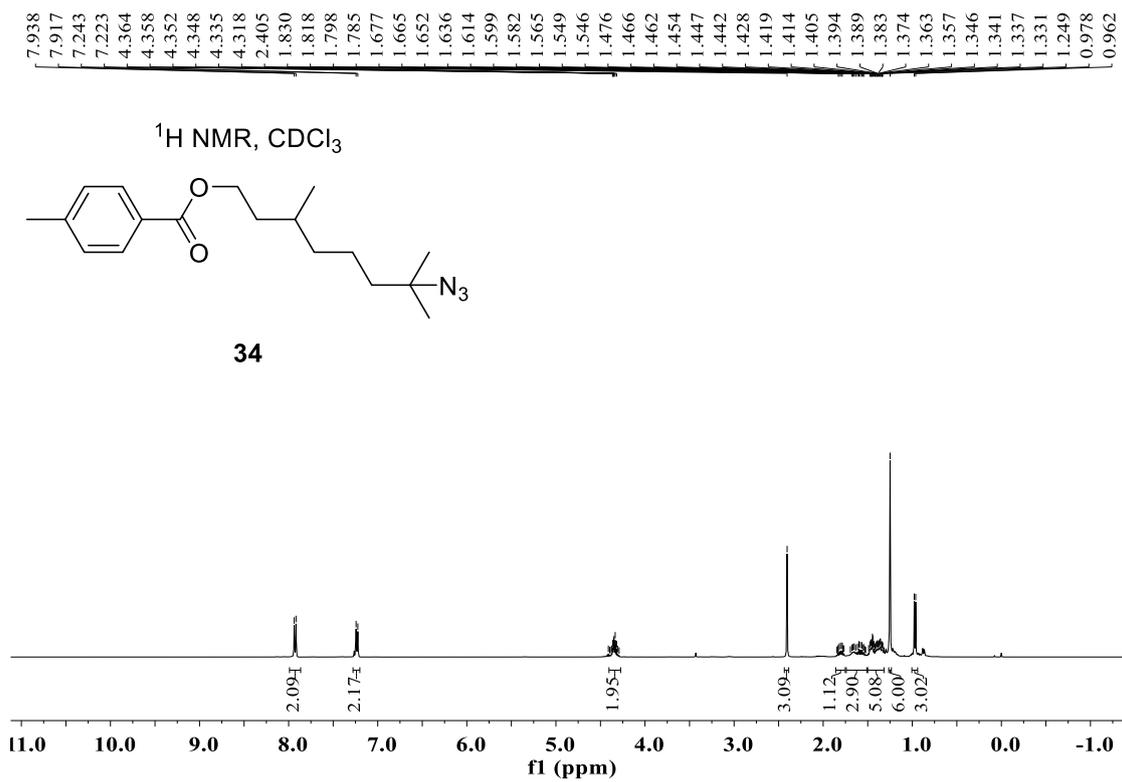
<sup>13</sup>C NMR, CDCl<sub>3</sub>

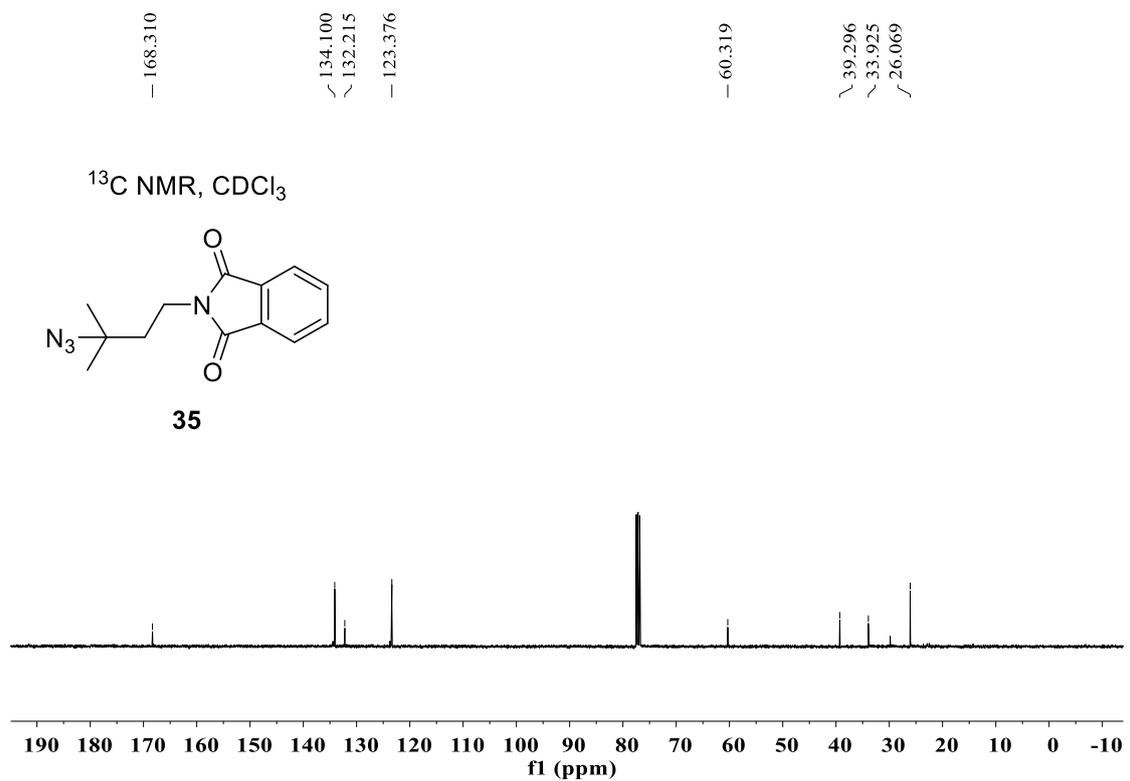
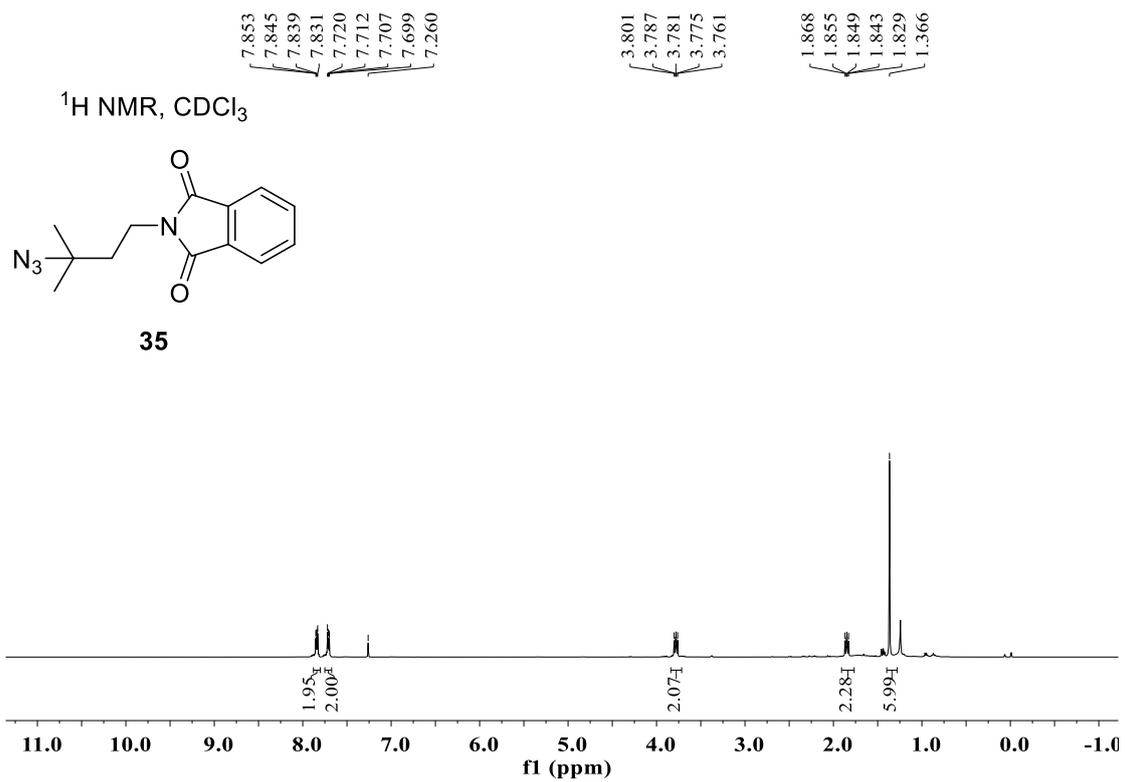


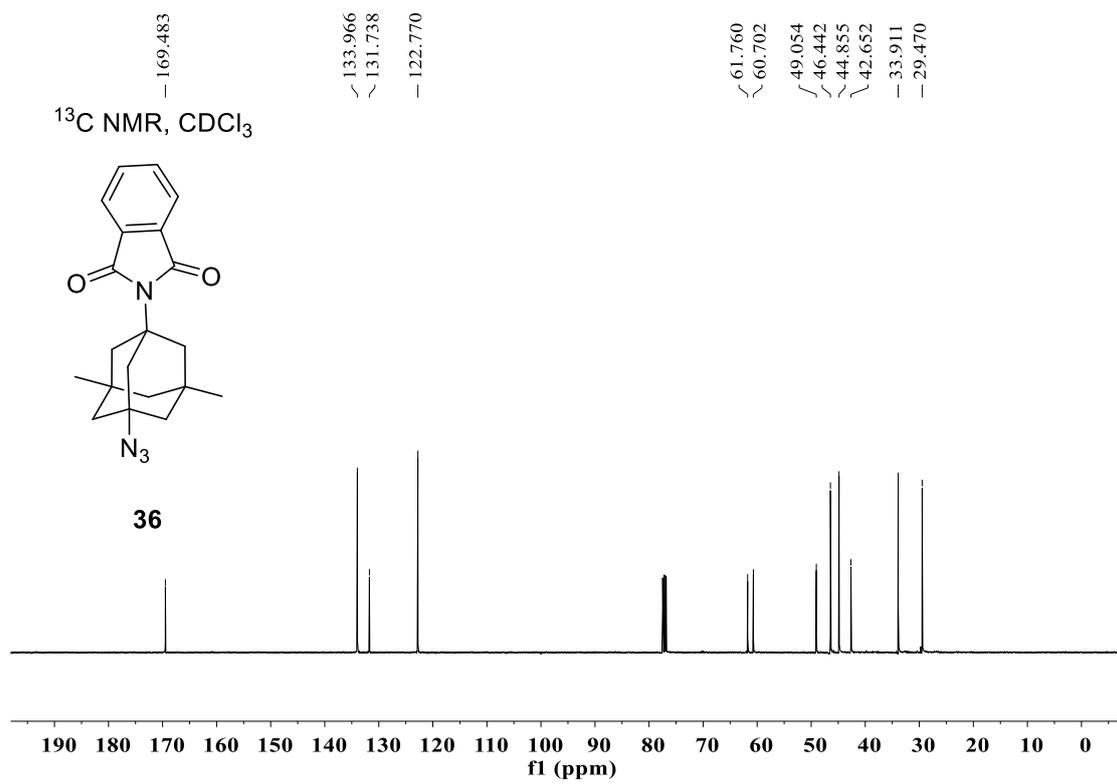
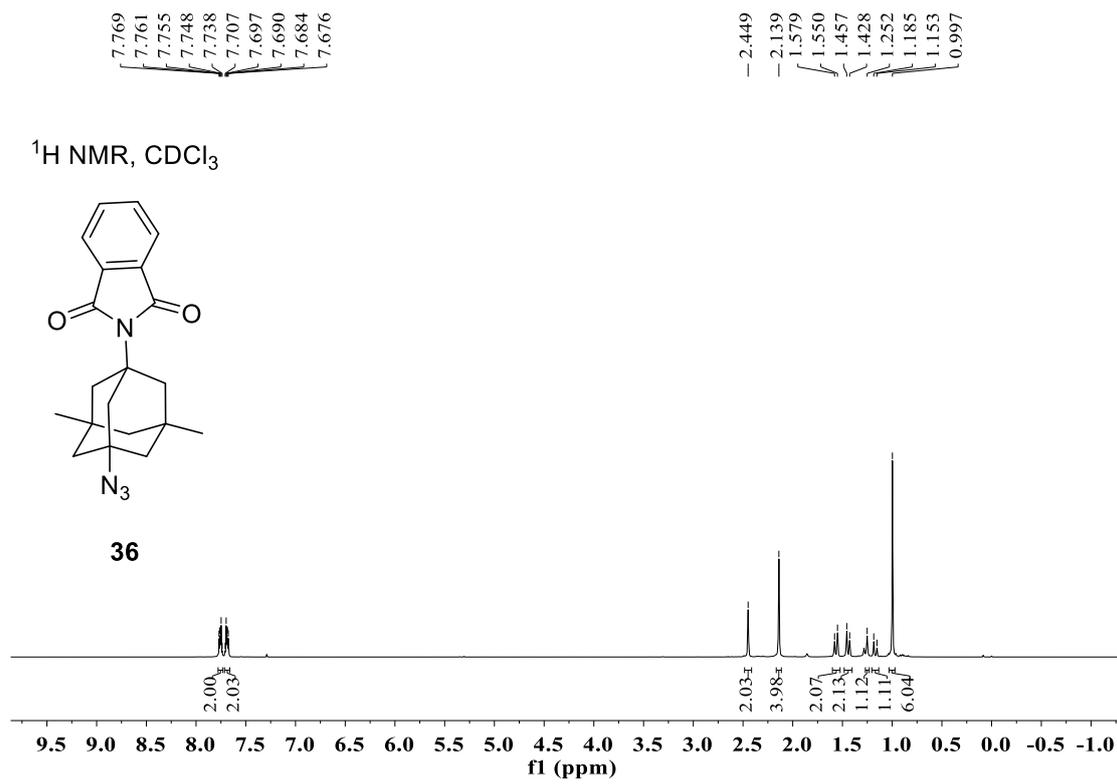
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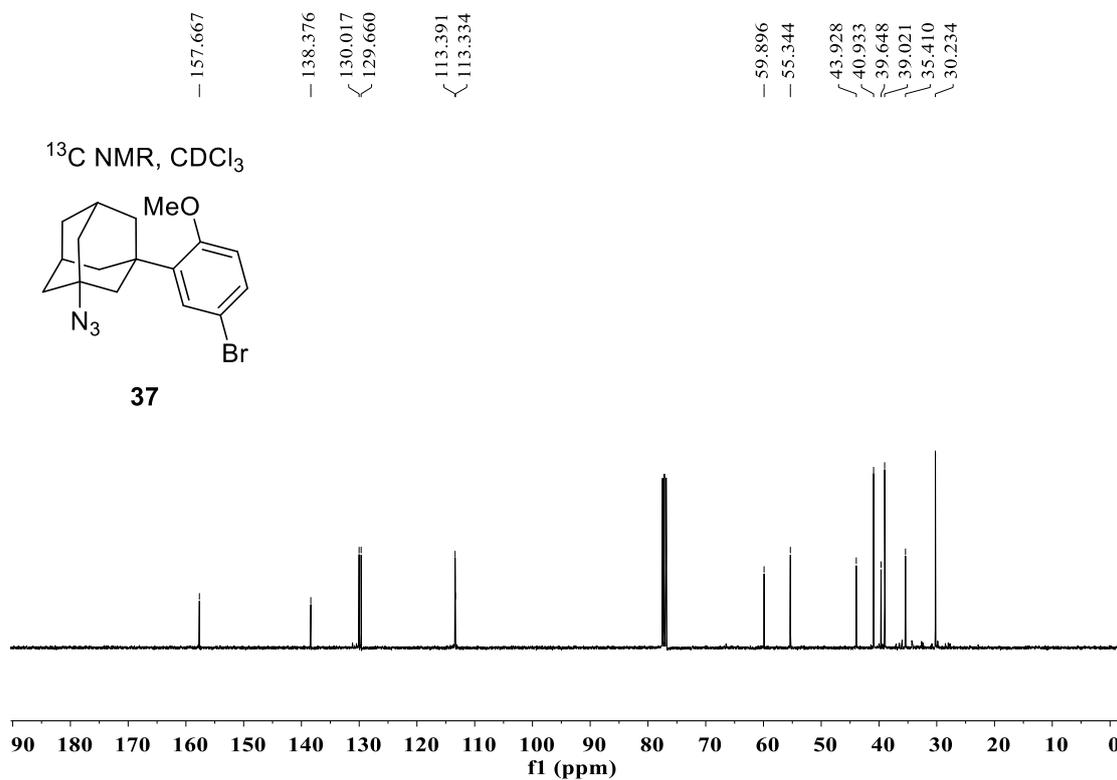
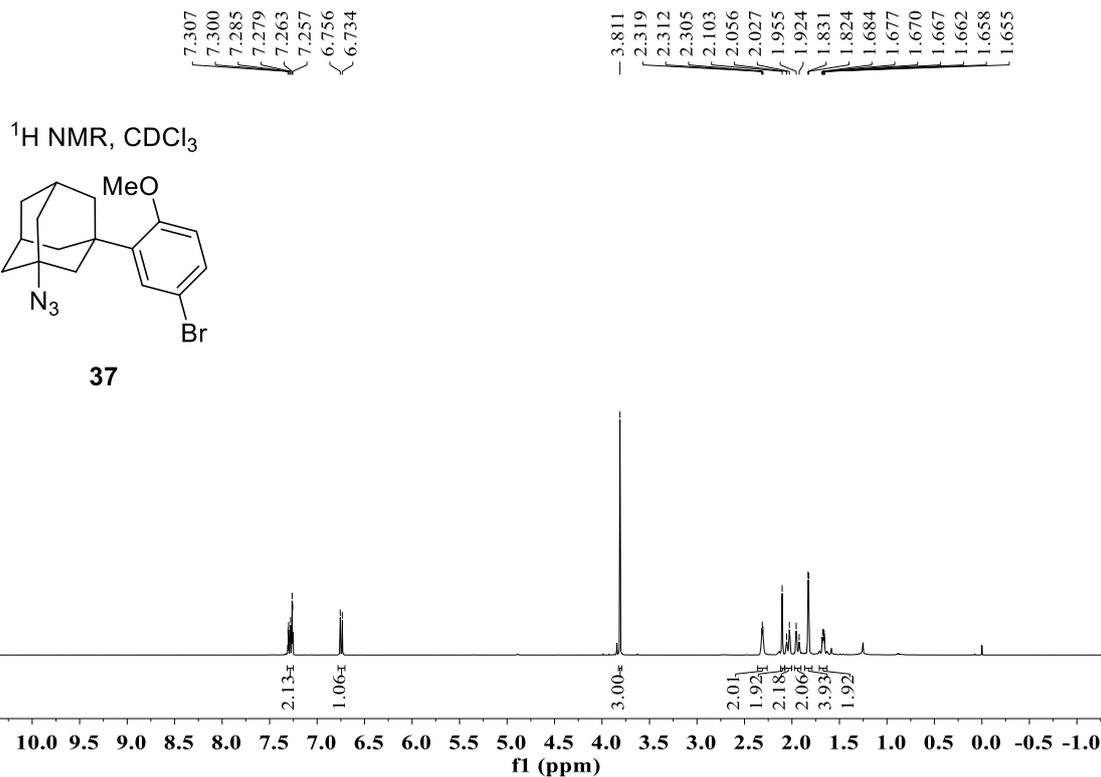




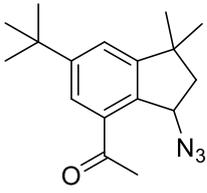




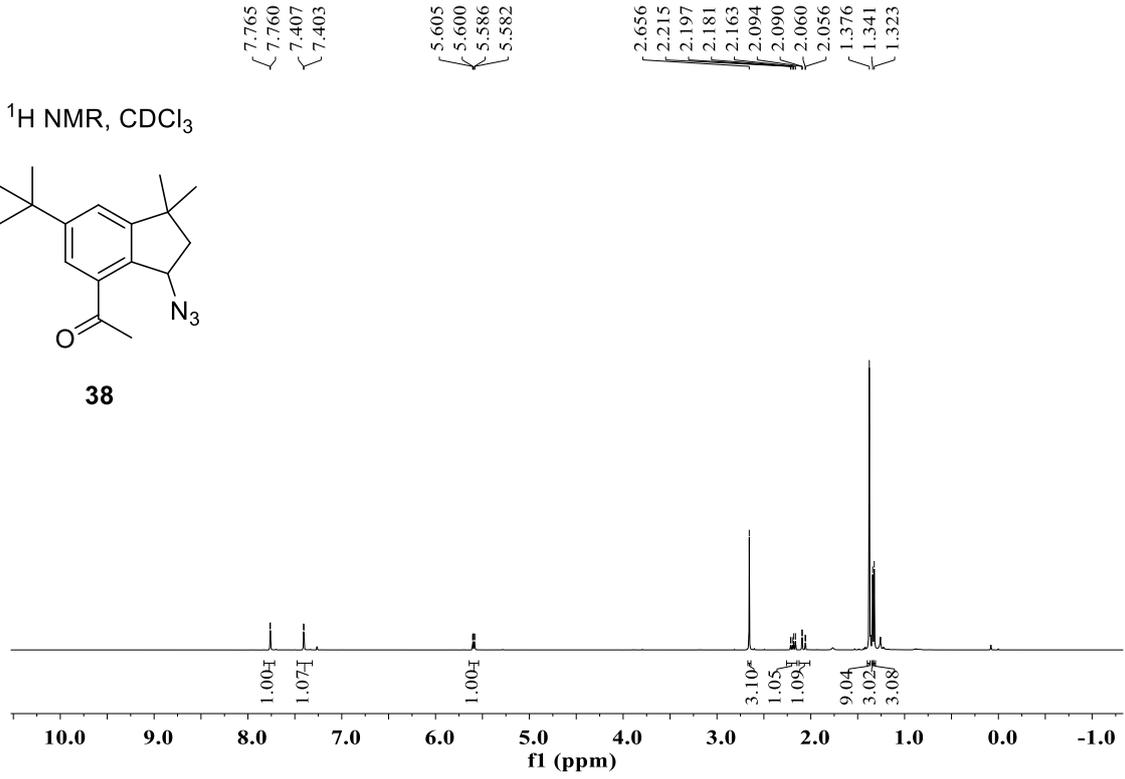




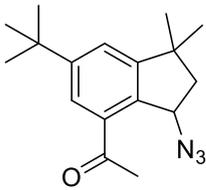
<sup>1</sup>H NMR, CDCl<sub>3</sub>



**38**



<sup>13</sup>C NMR, CDCl<sub>3</sub>



**38**

