

Supporting Information

A Combination of Trimethylsilyl chloride and hydrous natural montmorillonite clay: An efficient solid acid catalyst for the azidation of benzylic and allylic alcohols with trimethylsilyl azide

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I. General remark

All solvents and triethylamine were obtained from Kanto Chemical and used without further purification. Alcohols **1a**, **1b**, **1c**, **1d**, **1e**, **1i**, **1j**, **1k**, **1l**, **1m**, **1n**, **1o**, Me₃SiCl, Me₃SiN₃ and propionic acid were obtained from Tokyo Chemical Industry (TCI), Japan. Alcohols **1f** and **1g** were prepared by reduction of the corresponding carbonyl compounds (ketones or aldehydes) with LiAlH₄ in anhydrous diethyl ether. Alcohol **1h** was prepared by reduction of the corresponding carbonyl compounds (conjugated ketones) with NaBH₄ in methanol. Kunipia-F (Na, 2.69; Al, 11.8; Fe, 1.46; Mg, 1.97%. Cation-exchange capacity = 1.19 mequiv g⁻¹) was obtained from Kunimine Industry, Japan, and used as hydrous Na-Mont containing 14wt% of water. CuI was obtained from Wako Pure Chemical Industries. Phenyl acetylene was obtained from Sigma-Aldrich. Commercially available CH₂Cl₂ (Kanto Chemical Inc.) was used without drying treatment: water content = <0.2% according to the supplier's specification data: https://cica-web.kanto.co.jp/CicaWeb/spec/E_EPDCM11.pdf. Analytical TLC was done on pre-coated silica gel plates. ¹H and ¹³C NMR spectra were recorded on a Bruker AvanceIII500USPlus spectrometer (500 MHz): Chemical shifts of ¹H NMR spectra were reported in parts per million relative to tetramethylsilane ($\delta = 0.00$). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants, *J*, were reported in hertz unit (Hz). Chemical shifts of ¹³C NMR spectra were reported in parts per million relative to residual solvent peak of CDCl₃ ($\delta = 77.16$).

II. The azidation of benzylic and allylic alcohols with a combination of Me₃SiN₃, hydrous Na-Mont and a catalytic amount of Me₃SiCl

A general method for the data in Table 1 and Figure 1:

In a 30 mL-round flask was placed 50 mg of Na-Mont, 1 mmol (0.18 g) of **1a**, 0.06 mmol (7 mg) of Me₃SiCl, 2 mmol (0.23 g) of Me₃SiN₃ and 5 mL of CH₂Cl₂. The mixture was stirred at room temperature (RT) for 40 min. After 40 min, solids were filtered off, and the filtrate was concentrated with a rotary evaporator and analyzed with NMR. The azide product was purified and isolated by column chromatography using hexane/ethyl acetate as an eluent.

Repeated azidation in the one-pot manner:

In a 30 mL-round flask was placed 50 mg of Na-Mont, 1 mmol (0.18 g) of **1a**, 0.06 mmol (7 mg) of trimethylchlorosilane, 2 mmol (0.23 g) of Me₃SiN₃ and 5 mL of CH₂Cl₂. The mixture was stirred at RT for 1 h. Then, into the mixture was added another 1 mmol (0.18 g) of **1a** and 2 mmol (0.23 g) of Me₃SiN₃. The mixture was further stirred at RT for 1 h. The analysis of the reaction mixture revealed that all the additional **1a** was completely consumed, and that 2.0 mmol of the corresponding azide **4a** was present in the mixture. Into the mixture was added another 1 mmol (0.18 g) of **1a** and 2 mmol (0.23 g) of Me₃SiN₃. The mixture was further stirred at RT for 1 h. The analysis of the reaction mixture showed that all the additional **1a** was completely consumed and 2.9 mmol of the corresponding azide **4a** was included in the mixture.

Azidation of (*R*)-1-phenylethanol (1o)

In a 30 mL-flask was placed 50 mg of Na-Mont, 1 mmol (0.12 g) of **1o** (98%ee), 0.06 mmol (7 mg) of Me₃SiCl, 2 mmol (0.23 g) of Me₃SiN₃ and 5 mL of CH₂Cl₂. The mixture was stirred at RT for 40 min. The solid was filtered off, and the filtrate was concentrated with a rotary evaporator. The azide product was isolated in 37% yield by column chromatography using hexane/ethyl acetate as an eluent. Analysis using chiral HPLC (Daicel Chiralpak IB (0.46 cm ϕ x 25cm); MTBE/Hexane = 0.01/99.99) indicated that the azide products were almost racemic (9 %ee).

One-pot synthesis of 1,2,3-triazoles

In a 30 mL-flask was placed 50 mg of Na-Mont, 1 mmol (0.18 g) of **1a**, 0.06 mmol (7 mg) of Me₃SiCl, 1.5 mmol (0.17 g) of Me₃SiN₃ and 2 mL of CH₂Cl₂. The mixture was stirred at RT for 1 h. 1.1 mmol (0.11 g, 0.12 mL) of phenylacetylene, 4.0 mmol (0.40 g, 0.56 mL) of triethylamine, 4.0 mmol (0.30 g, 0.30 mL) of propionic acid, and 0.5 mmol (95 mg) of CuI were added to the reaction mixture, which was stirred further at RT for 1 h. The solid was filtered off, and the filtrate was concentrated with a rotary evaporator. The azide product was isolated by column chromatography using hexane/ethyl acetate as an eluent.

III. Synthesis of starting materials

Synthesis of 5a:

In a 30 mL-flask was placed 80 mg of Sn-Mont, 5 mmol (0.92 g) of **1a** and 5 mL of CH₂Cl₂. The mixture was stirred at RT for 14 h. Then, the solid materials were filtered off, and the filtrate was concentrated with a rotary evaporator. **5a** was purified by column chromatography with 5:1/hexane:ethyl acetate as eluent, and isolated as a white solid in 61% yield.

Synthesis of 5b:

In a 30 mL-flask was placed 4 mmol (0.74 g) of **1a**, 6 mmol of trimethylsilyl cyanide (0.60 g, 0.75 mL), and 10 mL of CH₂Cl₂. The mixture was stirred at RT for 12 h. Then, the mixture was concentrated with a rotary evaporator. **5b** was purified by column chromatography, and isolated as colorless oil in 67% yield.

Synthesis of alcohols by the reduction of the corresponding ketones with LiAlH₄:

In a 50 mL-flask was placed 0.59 g (15 mmol) of LiAlH₄. The flask was evacuated into a vacuum, and then filled with N₂. Fifty mL of anhydrous diethyl ether was introduced into the flask and the mixture was cooled in an ice-water bath. A solution of 4'-methylacetophenone (30 mmol, 4.0 g) in 30 mL of anhydrous diethyl ether was slowly added into the mixture, and the mixture was further stirred for another 2 h. Then, the ice-water bath was removed and the mixture was stirred at RT for another 2 h. Unreacted LiAlH₄ was destroyed with wet diethyl ether. After the work up with an

aqueous acid solution, the product was extracted from the mixture with diethyl ether. The alcohol product was isolated further by Kugelrohr distillation to give 3.4 g of **1f** (83% yield).

Synthesis of alcohol 1h by the reduction with NaBH₄:

Alcohol **1h** was synthesized according to the previously developed methods by Aramini.¹

Preparation of hydrous Na₂SO₄:

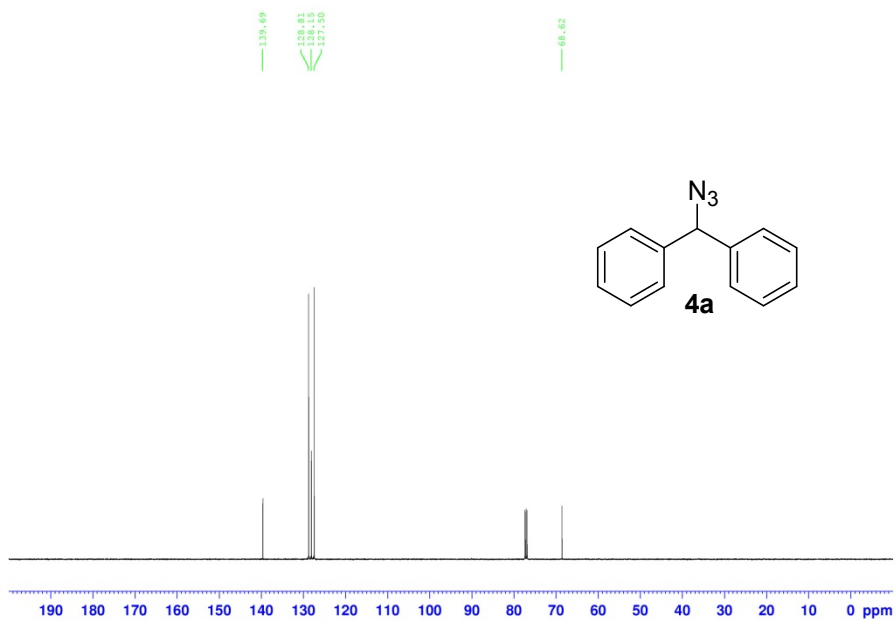
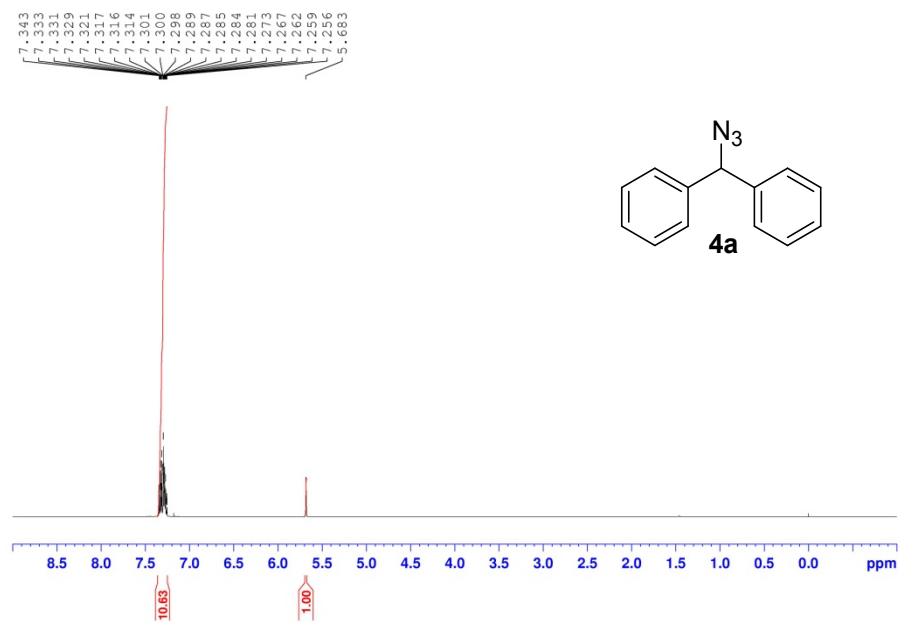
Into a mixture of 4 mL H₂O and 40 mL of acetone was added 4.5 g (32 mmol) of anhydrous Na₂SO₄. The mixture was well stirred for several minutes and was allowed to stand at RT for 12 h. Then, the simple filtration on filter paper gave the wet Na₂SO₄.

IV. Copies of NMR Spectra

4a²

¹H NMR (500 MHz, CDCl₃) δ: 7.37-7.24 (m, 10H), 5.68 (s, 1H).

¹³C NMR (125 MHz, CDCl₃) δ: 139.7, 128.8, 128.2, 127.5, 68.6.



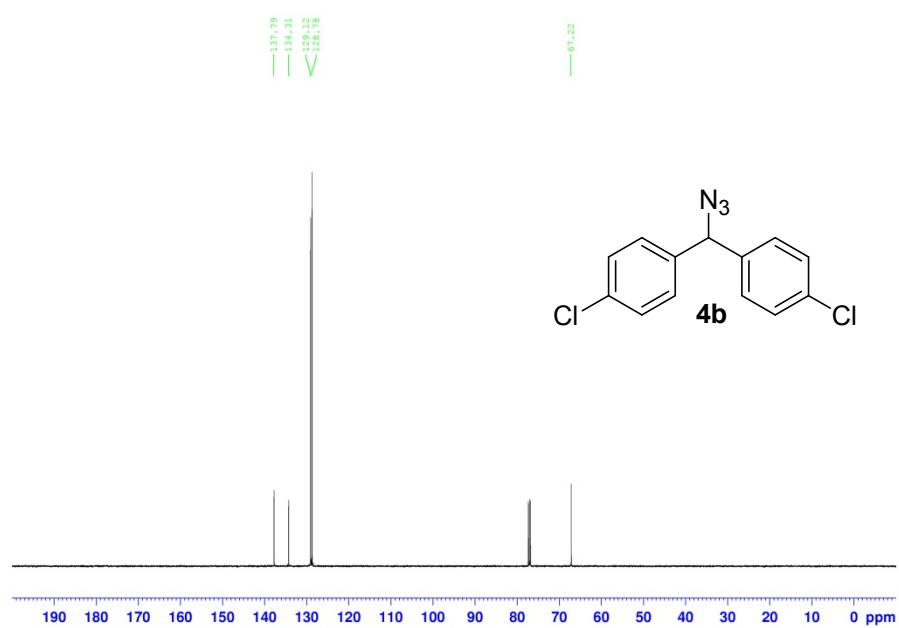
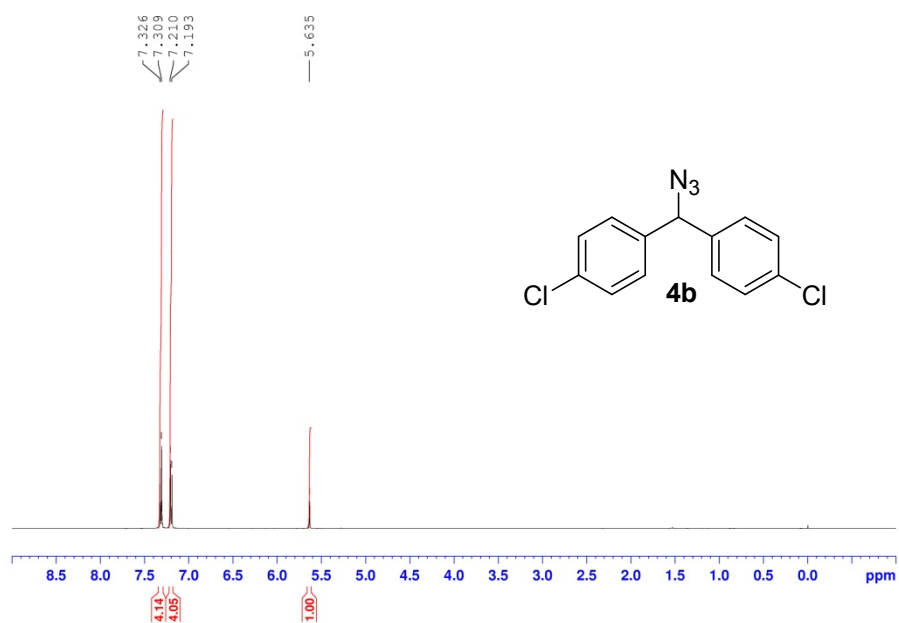
4b

^1H NMR (500 MHz, CDCl_3) δ : 7.35-7.29 (m, 4H), 7.23-7.18 (m, 4H), 5.64 (s, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ : 137.8, 134.3, 129.1, 128.8, 67.2.

IR (neat): 2102 cm^{-1} (N_3).

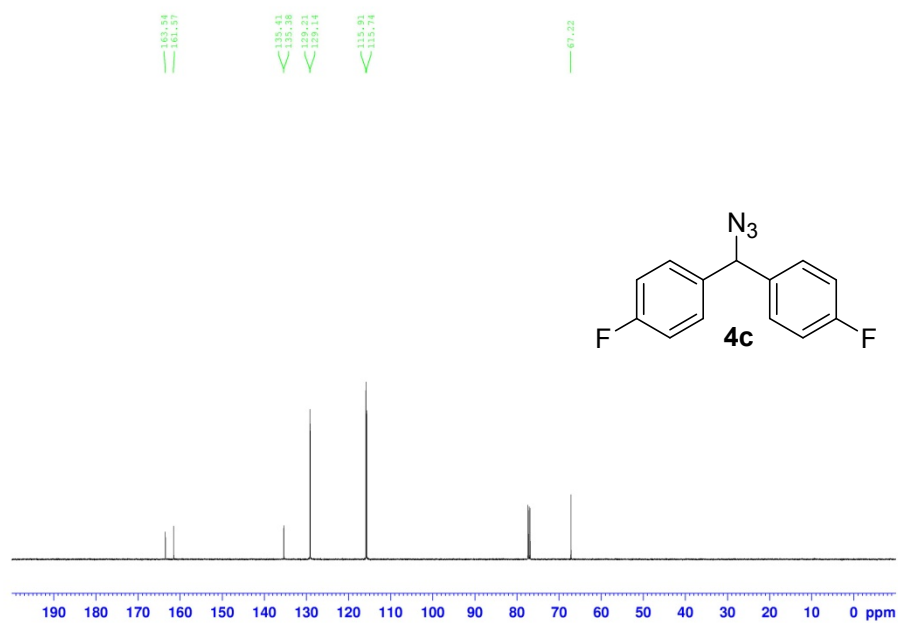
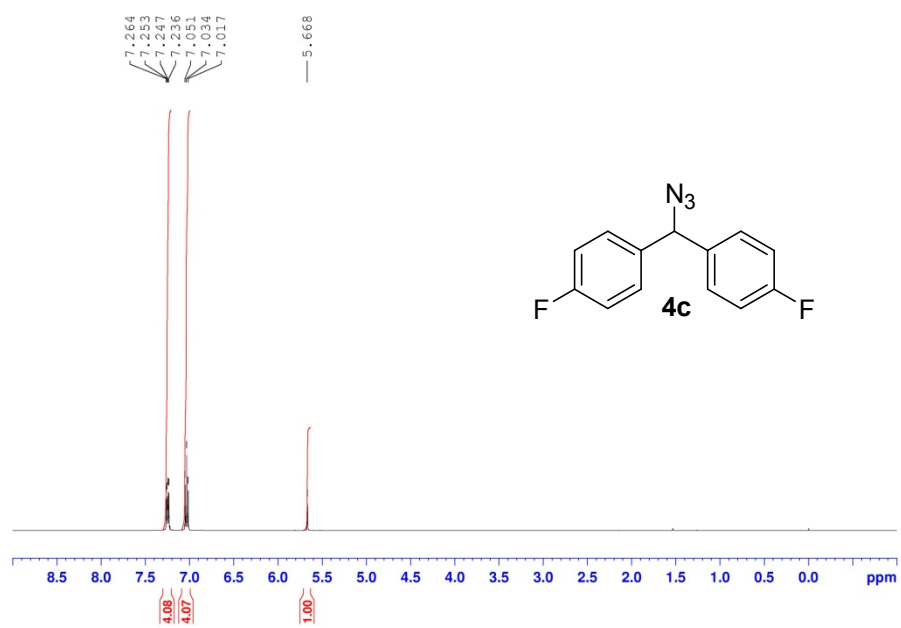
HRMS: Found: m/z 250.0171. Calcd for $\text{C}_{13}\text{H}_9\text{Cl}_2\text{NH}$: ($\text{M}+1-\text{N}_2$), 250.0190.



4c²

¹H NMR (500 MHz, CDCl₃) δ: 7.30-7.21 (m, 4H), 7.09-7.00 (m, 4H), 5.67 (s, 1H).

¹³C NMR (125 MHz, CDCl₃) δ: 163.5, 161.6, 135.41, 135.38, 129.2, 129.1, 115.9, 115.7, 67.2.



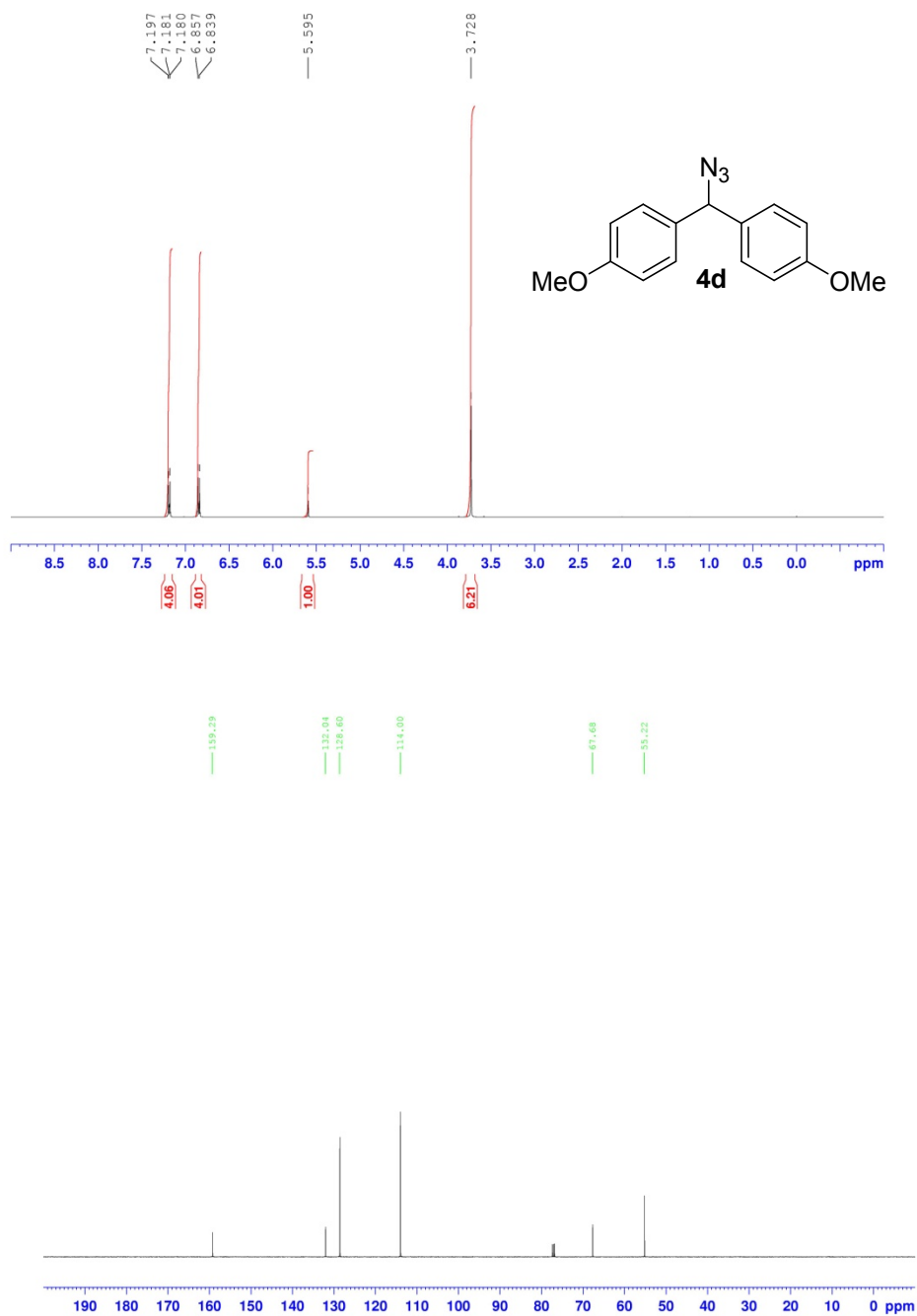
4d

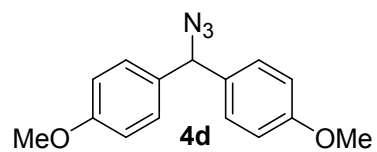
^1H NMR (500 MHz, CDCl_3) δ : 7.23-7.16 (m, 4H), 6.89-6.82 (m, 4H), 5.59 (s, 1H), 3.73 (s, 6H).

^{13}C NMR (125 MHz, CDCl_3) δ : 159.3, 132.0, 128.6, 114.0, 67.7, 55.2.

IR (neat): 2097 cm^{-1} (N_3).

HRMS: Found: m/z 242.1159. Calcd for $\text{C}_{15}\text{H}_{15}\text{O}_2\text{NH}$: ($\text{M}+1-\text{N}_2$), 242.1181.

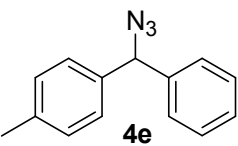
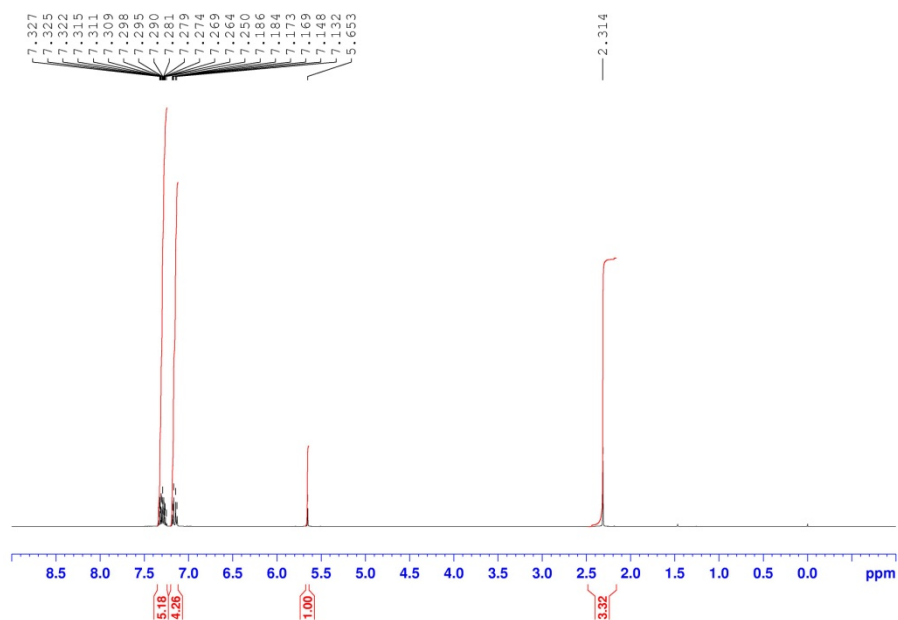


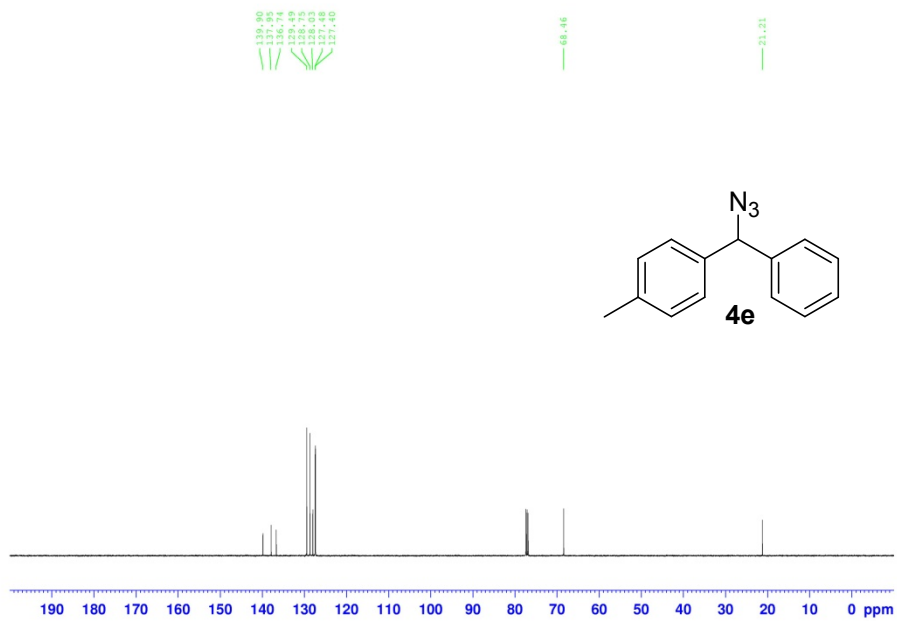


4e²

¹H NMR (500 MHz, CDCl₃) δ: 7.35-7.24 (m, 5H), 7.20-7.11 (m, 4H), 5.65 (s, 1H), 2.31 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ: 139.9, 138.0, 136.7, 129.5, 128.8, 128.0, 127.5, 127.4, 68.5, 21.2.



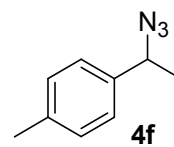


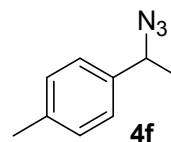
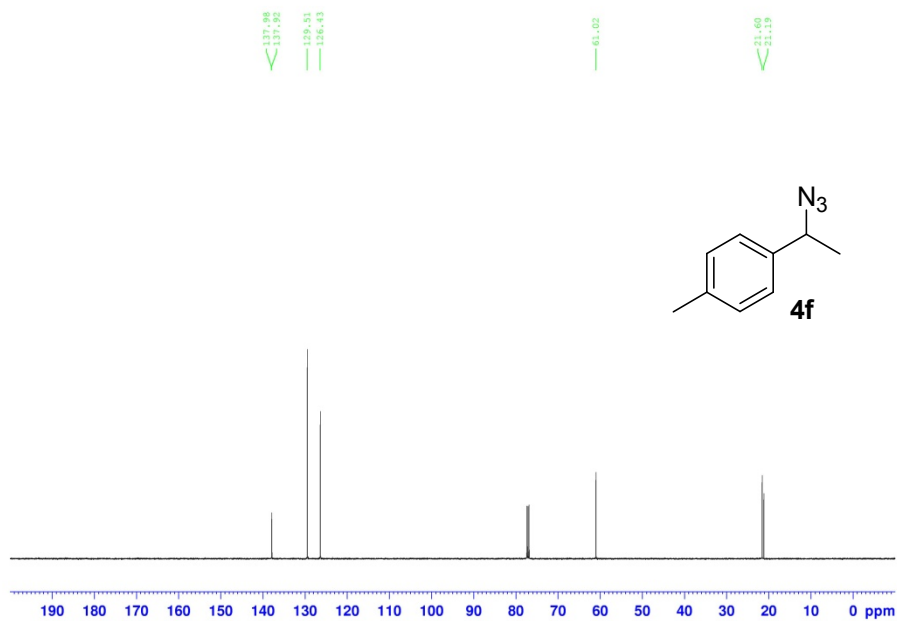
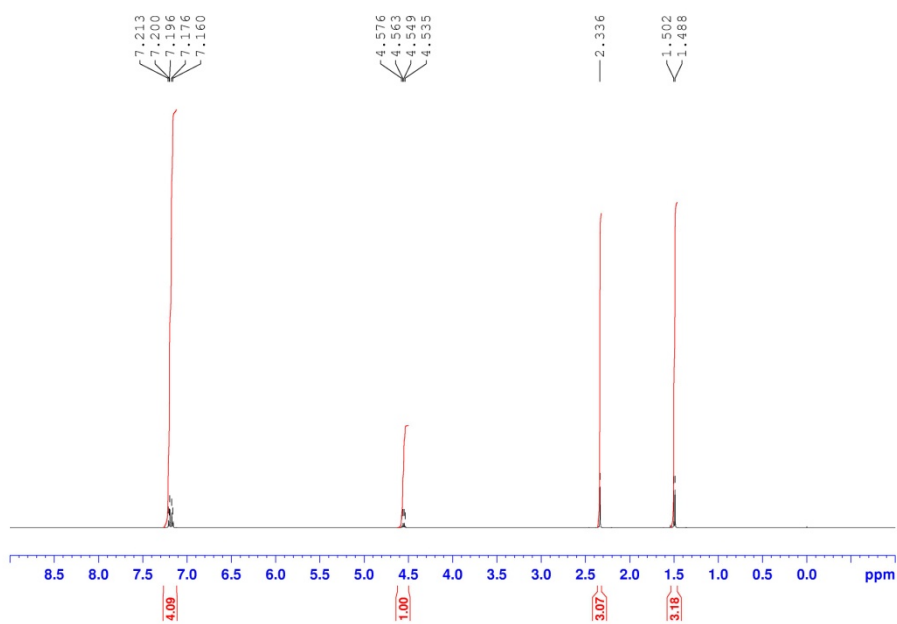
4f³

^1H NMR (500 MHz, CDCl_3) δ : 7.27-7.11 (m, 4H), 4.56 (q, $J = 6.8$ Hz, 1H), 2.34 (s, 3H),

1.49 (d, $J = 6.8$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ : 138.0, 137.9, 129.5, 126.4, 61.0, 21.6, 21.2.

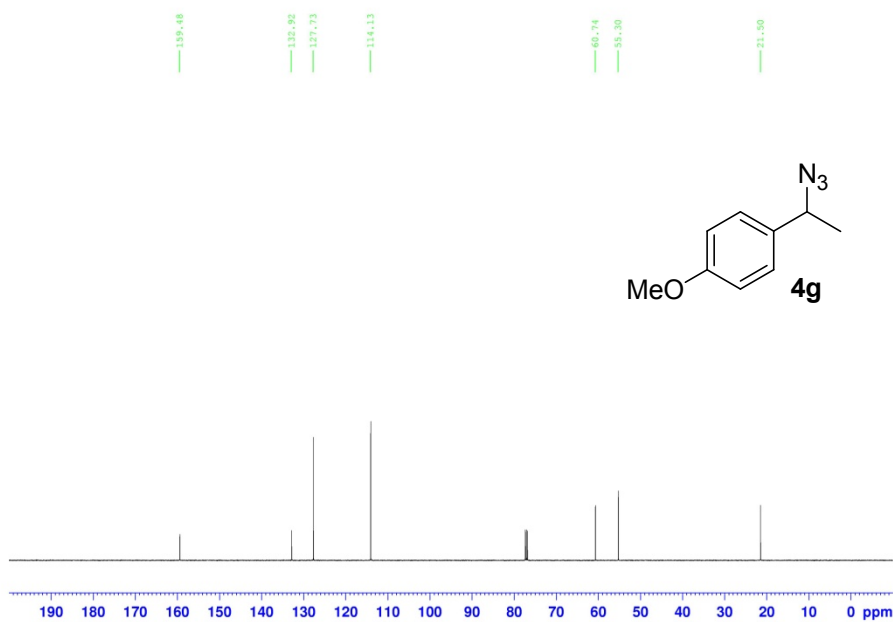
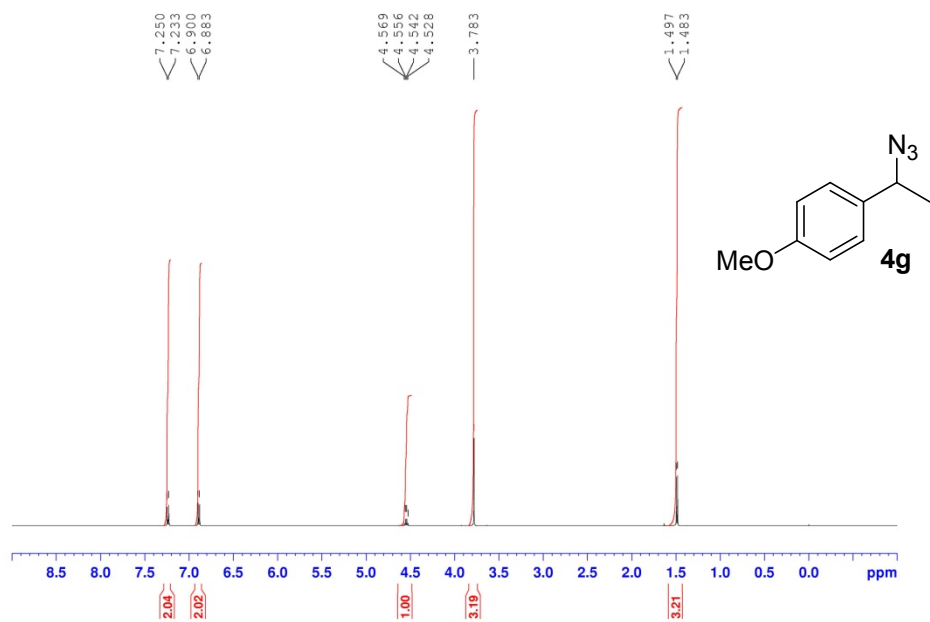




4g³

¹H NMR (500 MHz, CDCl₃) δ: 7.24 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 8.5 Hz, 2H), 4.55 (q, J = 7.0 Hz, 1H), 3.78 (s, 3H), 1.49 (d, J = 7.0 Hz, 3H).

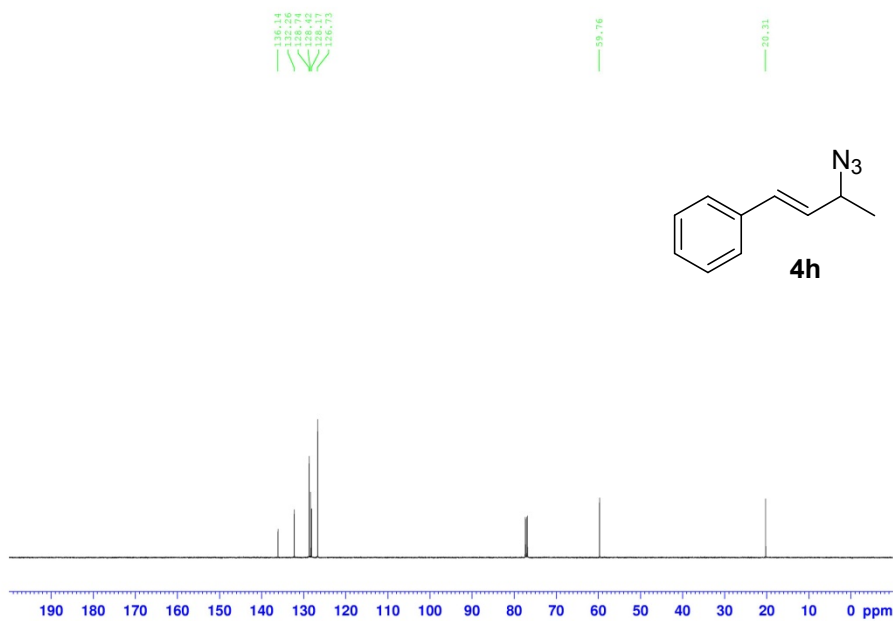
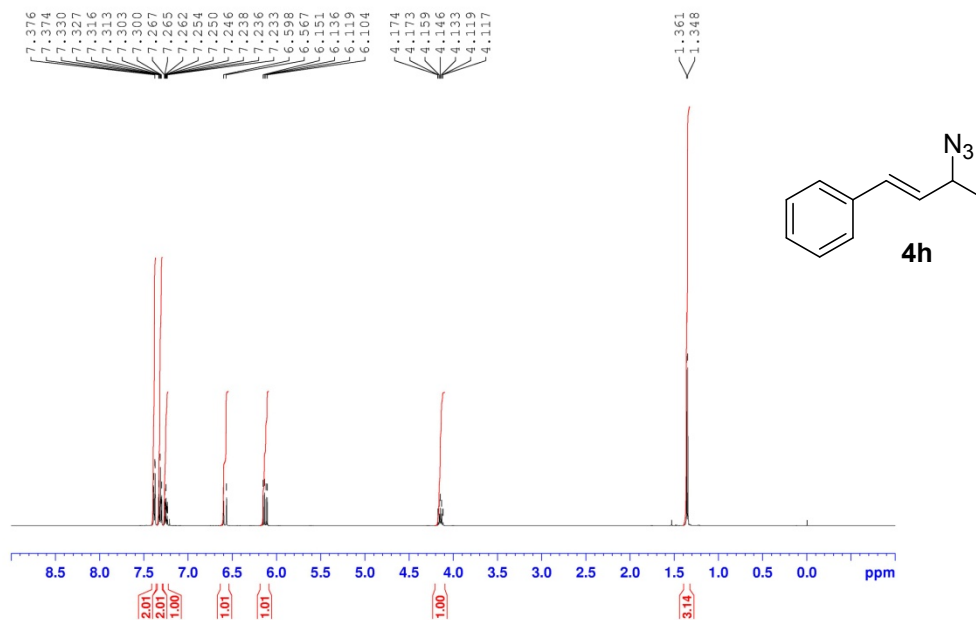
¹³C NMR (125 MHz, CDCl₃) δ: 159.5, 132.9, 127.7, 114.1, 60.7, 55.3, 21.5.



4h⁴

¹H NMR (500 MHz, CDCl₃) δ: 7.41-7.36 (m, 2H), 7.35-7.29 (m, 2H), 7.28-7.22 (m, 1H), 6.58 (d, J = 15.8 Hz, 1H), 6.13 (m, 1H), 4.15 (m, 1H), 1.35 (d, J = 6.7 Hz, 3H).

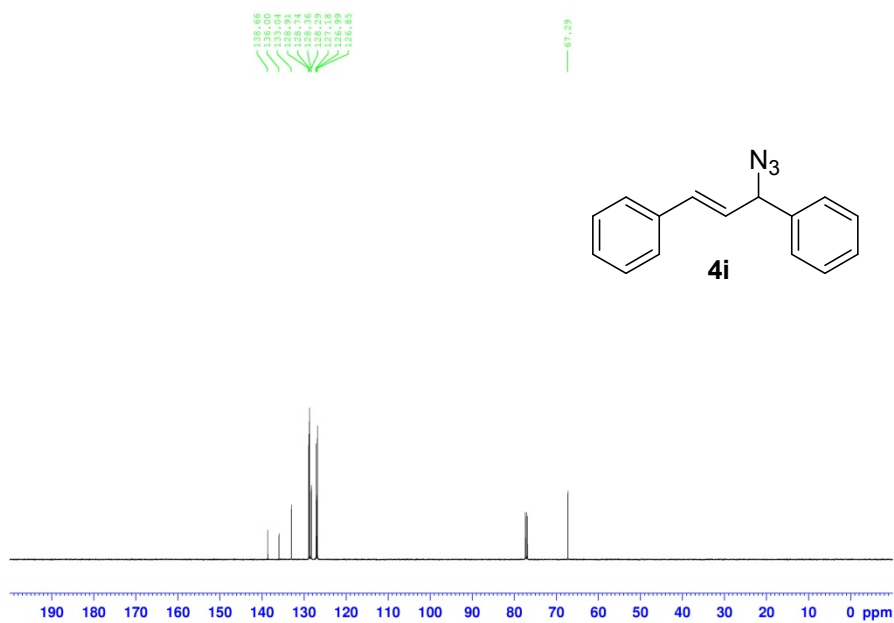
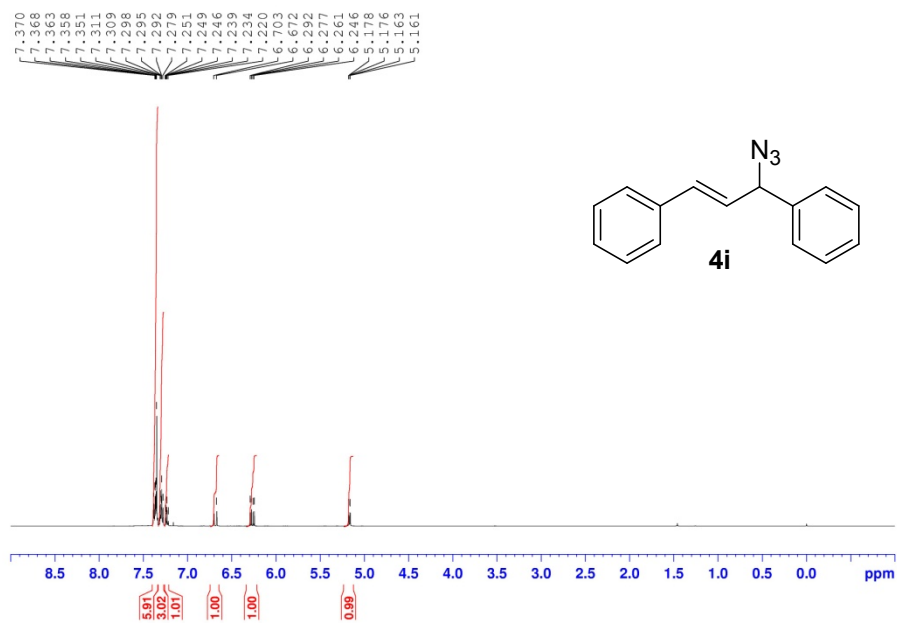
^{13}C NMR (125 MHz, CDCl_3) δ : 136.1, 132.3, 128.7, 128.4, 128.2, 126.7, 59.8, 20.3.



4i⁵

^1H NMR (500 MHz, CDCl_3) δ : 7.40-7.33 (m, 6H), 7.33-7.27 (m, 3H), 7.26-7.21 (m, 1H), 6.69 (d, $J = 15.6$ Hz, 1H), 6.27 (m, 1H), 5.17 (d, $J = 7.2$ Hz, 1H).

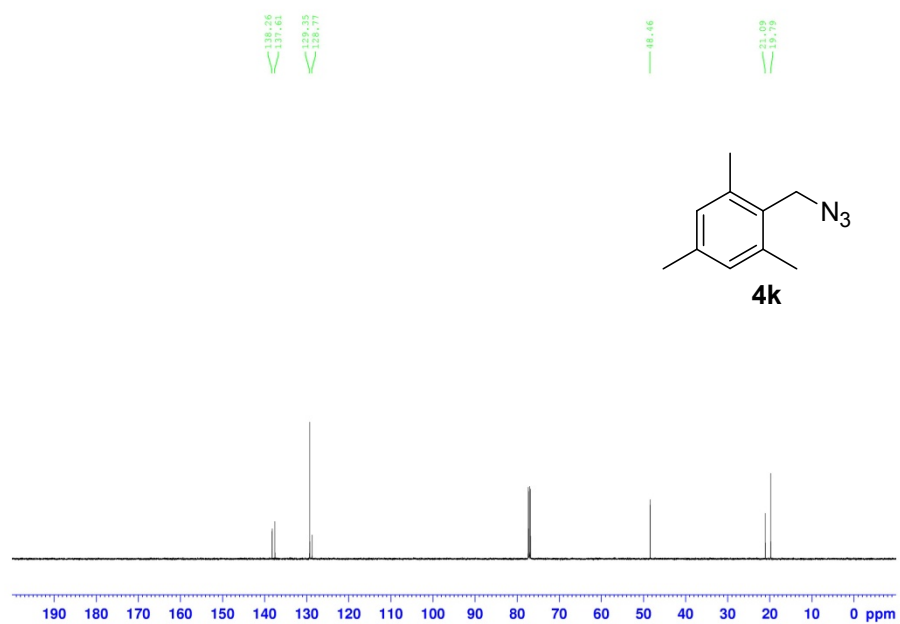
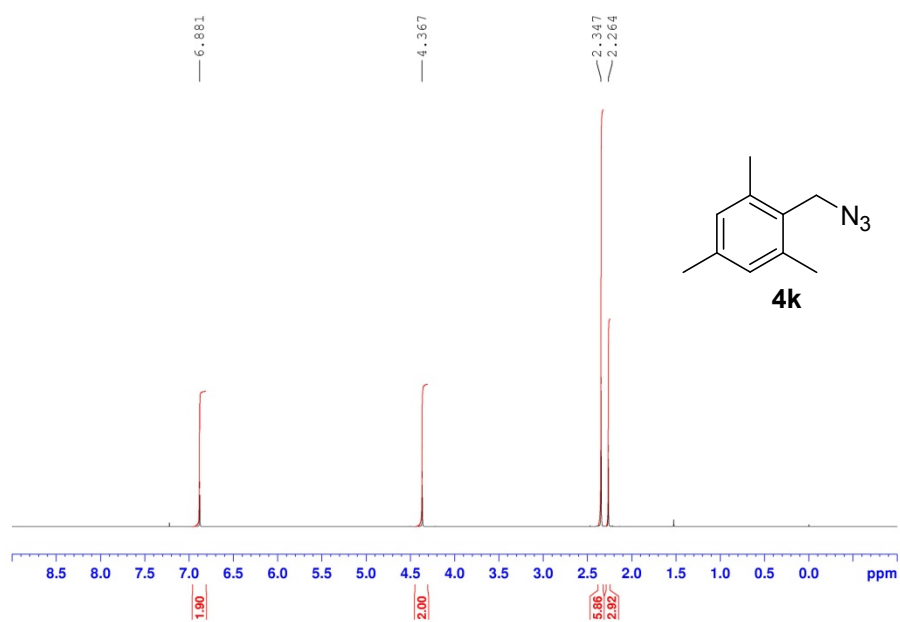
^{13}C NMR (125 MHz, CDCl_3) δ : 138.7, 136.0, 133.0, 128.9, 128.7, 128.4, 128.3, 127.2, 127.0, 126.8, 67.3.



4k⁶

^1H NMR (500 MHz, CDCl_3) δ : 6.88 (s, 2H), 4.37 (s, 2H), 2.35 (s, 6H), 2.26 (s, 3H).

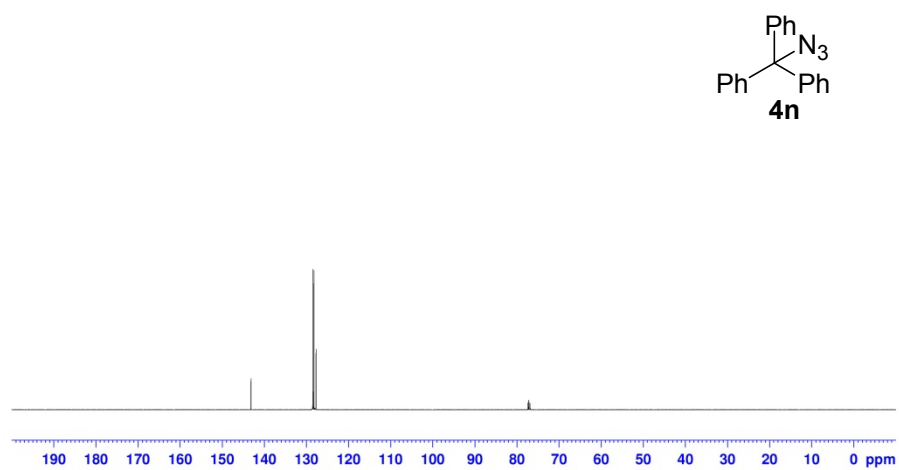
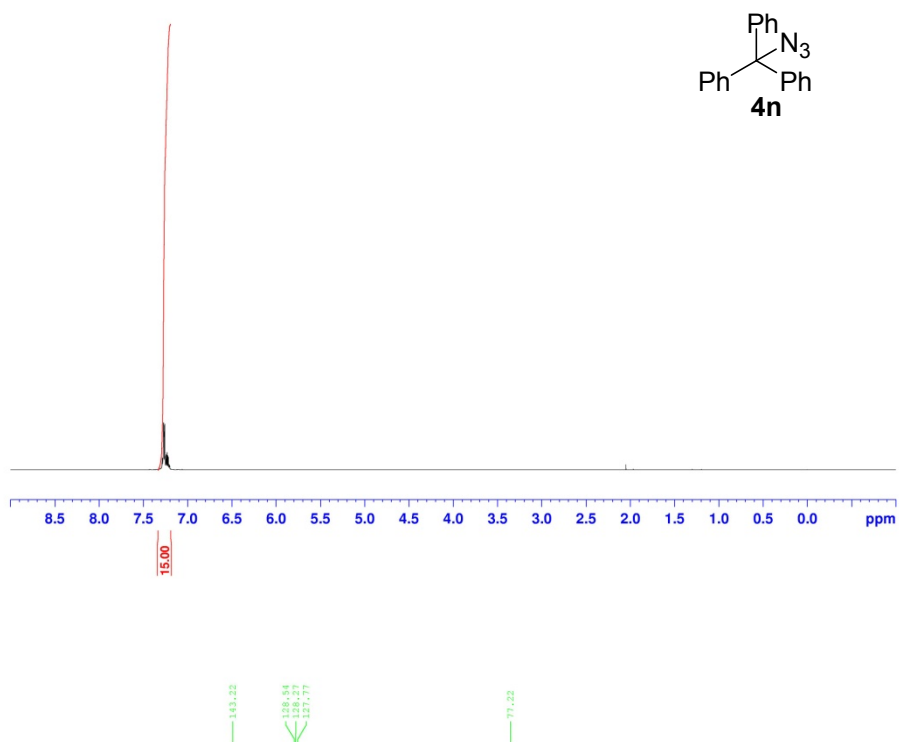
^{13}C NMR (125 MHz, CDCl_3) δ : 138.3, 137.6, 129.4, 128.8, 48.4, 21.1, 19.8.



4n⁷

^1H NMR (500 MHz, CDCl_3) δ : 7.33-7.19 (m, 15H).

^{13}C NMR (125 MHz, CDCl_3) δ : 143.2, 128.5, 128.3, 127.8, 77.2.

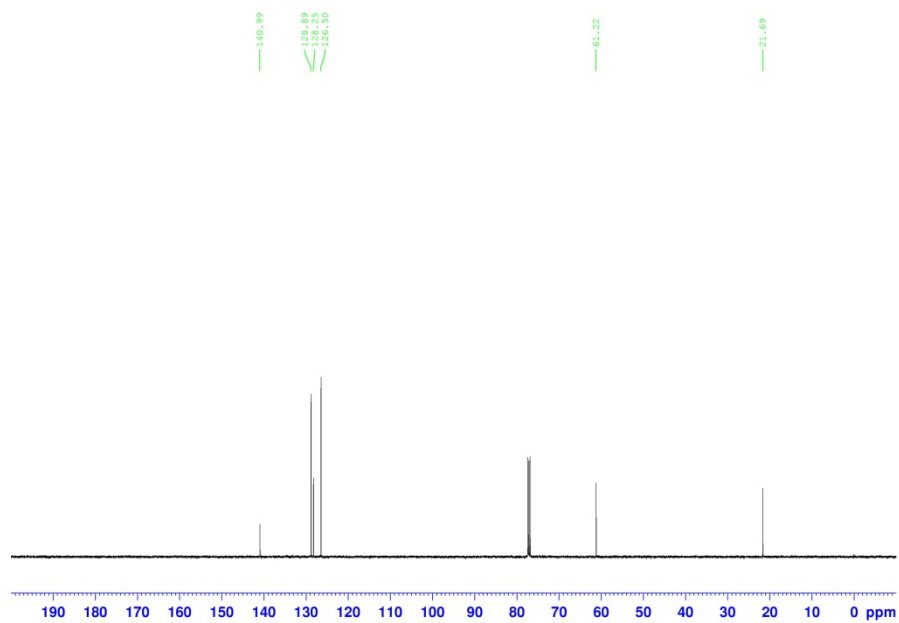
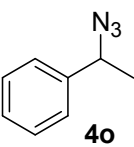
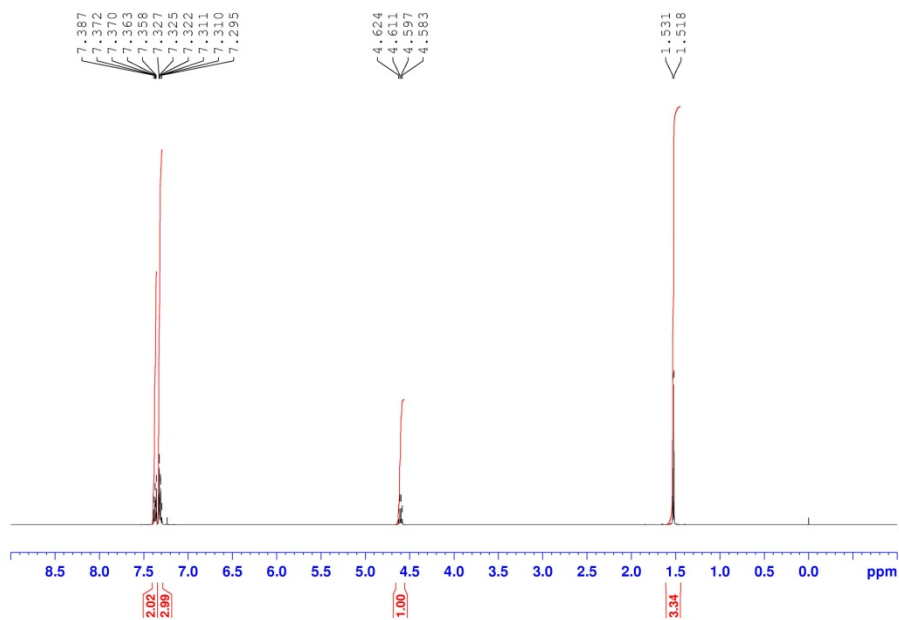


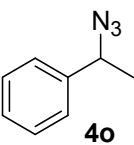
4o⁷

^1H NMR (500 MHz, CDCl_3) δ : 7.40-7.35 (m, 2H), 7.34-7.28 (m, 3H), 4.60 (q, $J = 6.8$ Hz, 1H)

1.52 (d, J = 6.8 Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ : 141.0, 128.9, 128.3, 126.5, 61.2, 21.7.

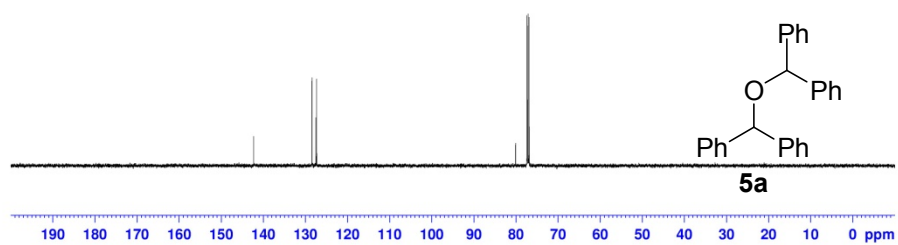
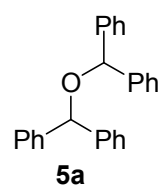
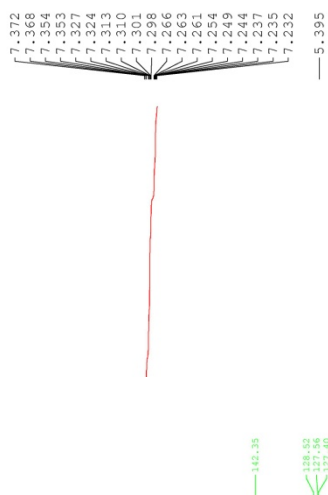




5a⁸

¹H NMR (500 MHz, CDCl₃) δ: 7.38-7.22 (m, 20H), 5.40(s, 2H).

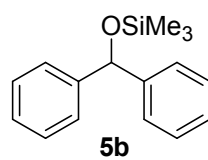
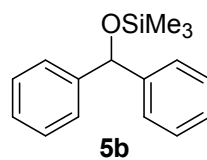
¹³C NMR (125 MHz, CDCl₃) δ: 142.4, 128.5, 127.6, 127.4, 80.1.

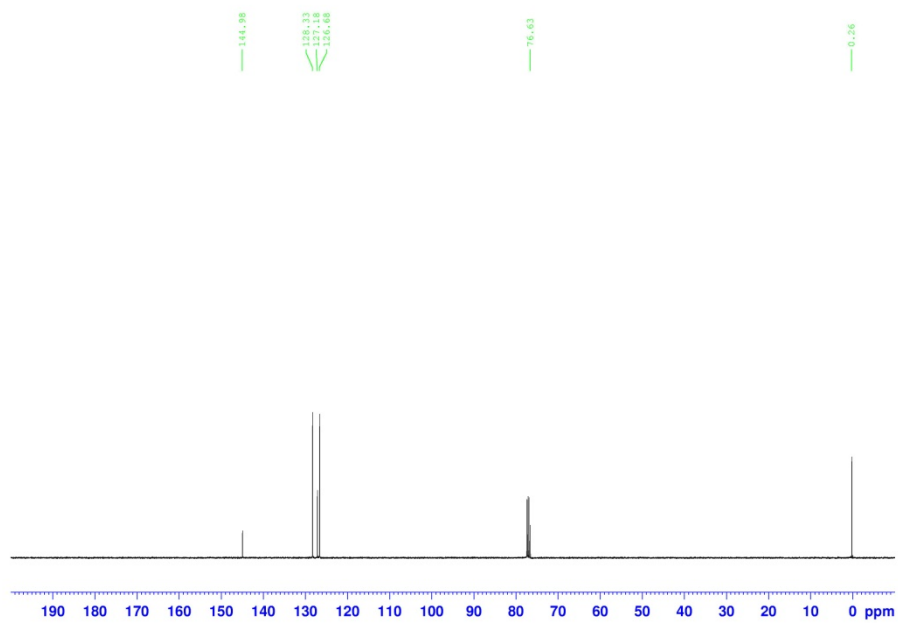
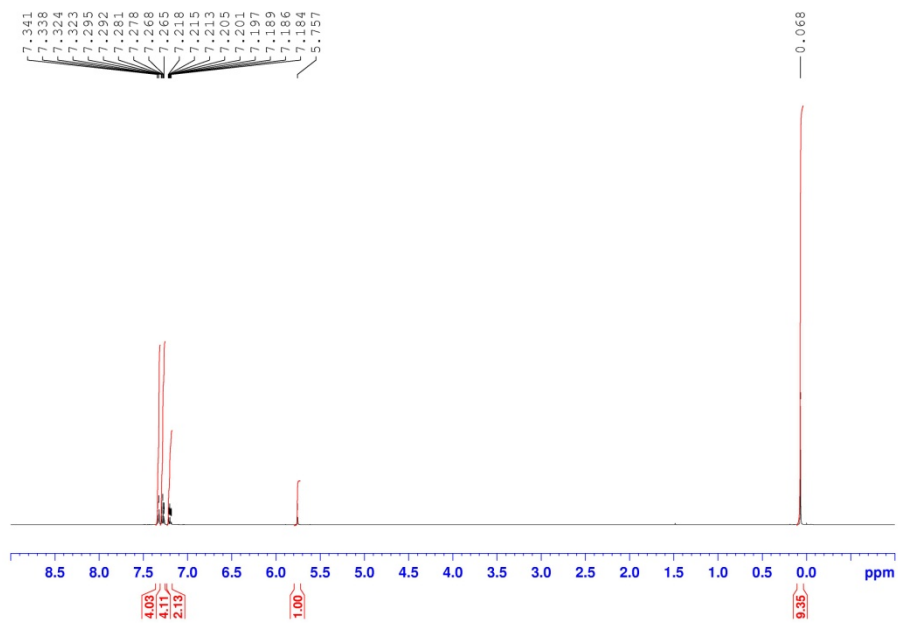


5b⁹

¹H NMR (500 MHz, CDCl₃) δ: 7.37-7.17 (m, 10H), 5.76 (s, 1H), 0.07 (s, 9H).

¹³C NMR (125 MHz, CDCl₃) δ: 145.0, 128.3, 127.2, 126.7, 76.6, 0.3.

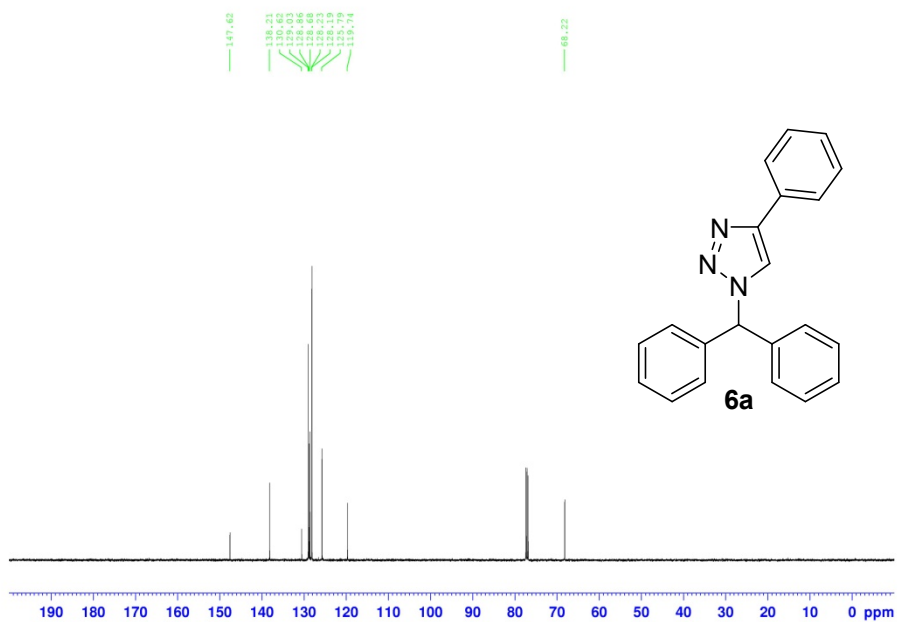
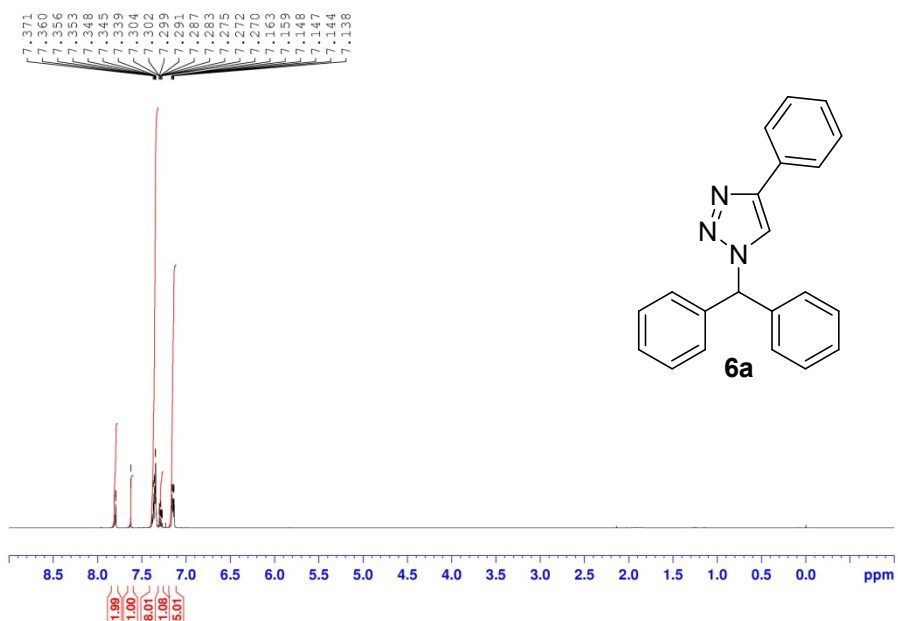




6a¹⁰

¹H NMR (500 MHz, CDCl₃) δ: 7.84-7.77 (m, 2H), 7.62 (s, 1H), 7.41-7.31 (m, 8H), 7.31-7.26 (m, 1H), 7.19-7.12 (m, 5H).

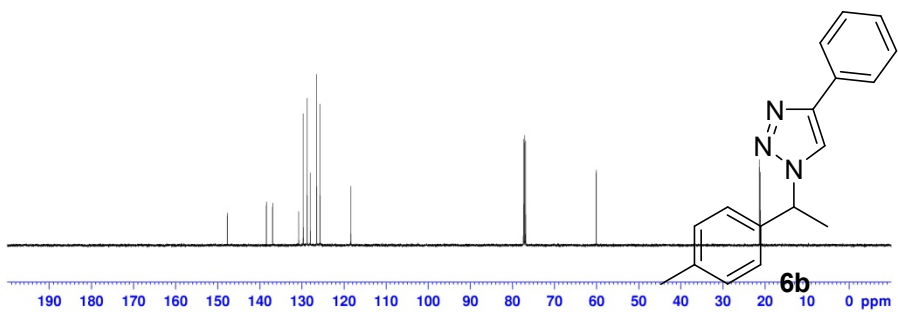
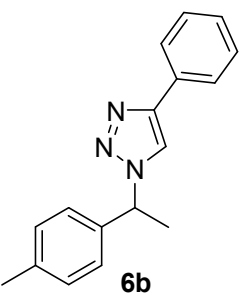
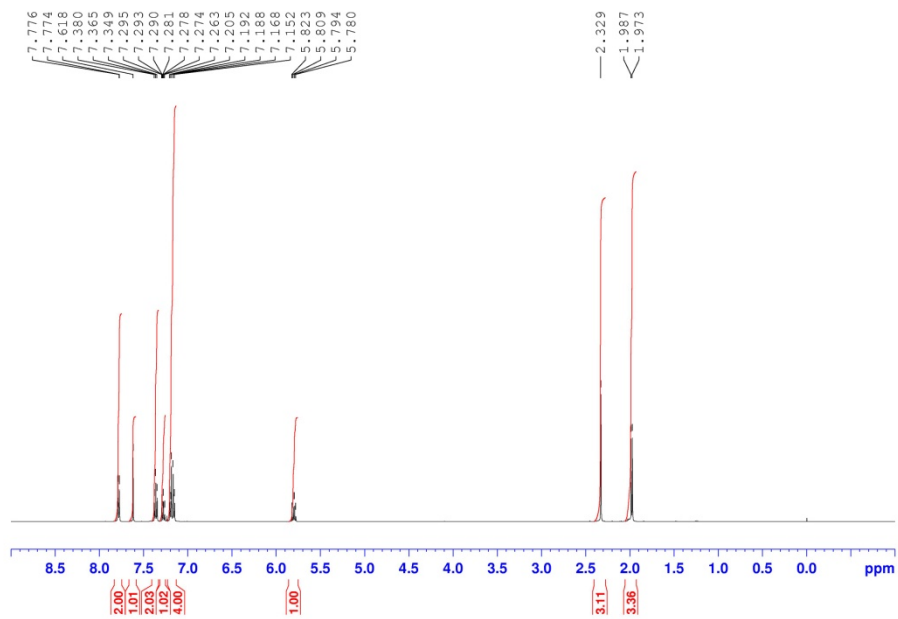
¹³C NMR (125 MHz, CDCl₃) δ: 147.6, 138.2, 130.6, 129.0, 128.9, 128.7, 128.23, 128.19, 125.8, 119.7, 68.2.



6b¹⁰

¹H NMR (500 MHz, CDCl₃) δ: 7.83-7.75 (m, 2H), 7.62 (s, 1H), 7.41-7.33 (m, 2H), 7.31-7.25 (m, 1H), 7.23-7.13 (m, 4H), 5.80 (q, J = 7.1 Hz, 1H), 2.33 (s, 3H), 1.98 (d, J = 7.1 Hz, 3H).

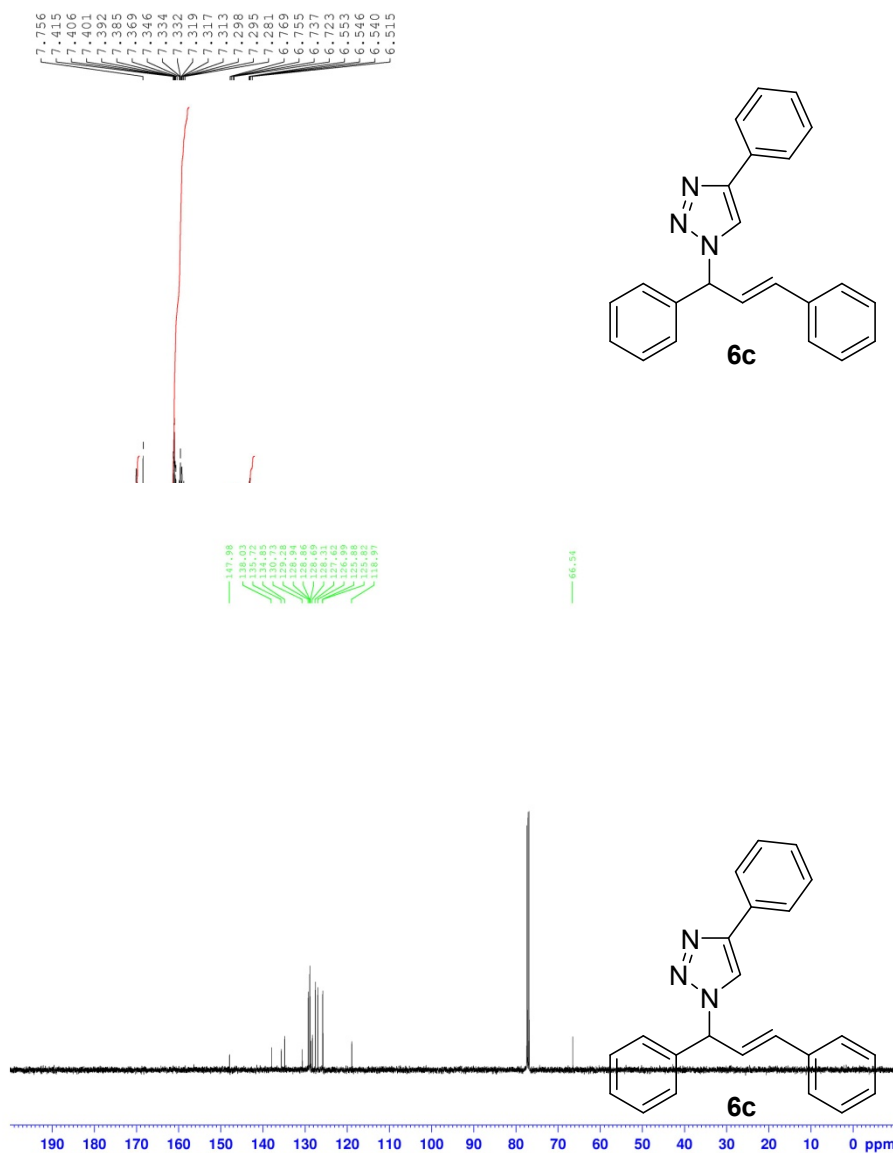
¹³C NMR (125 MHz, CDCl₃) δ: 148.0, 138.0, 135.7, 134.8, 130.7, 129.3, 128.94, 128.86, 128.7, 128.3, 127.6, 127.0, 125.9, 125.8, 119.0, 66.5.



6c¹¹

¹H NMR (500 MHz, CDCl₃) δ: 7.87-7.80 (m, 2H), 7.76 (s, 1H), 7.45-7.23 (m, 14H), 6.79-6.71 (m, 1H), 6.58-6.49 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ: 147.7, 138.5, 137.0, 130.8, 129.7, 128.8, 128.1, 126.6, 125.7, 118.4, 60.1, 21.4, 21.2.



V. Preparation of Sn-Mont and H-Mont

Preparation of Sn-Mont

Sn-Mont was prepared according to our previously reported protocol.¹² Na-Mont (8 g) was ion-exchanged with aqueous $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (0.3 M, 80 mL) at room temperature for 2 h, and this exchange process was then repeated. The collected clay was washed twice with water (80 mL), 6 times with a mixture of water (40 mL) and methanol (40 mL), and once with absolute methanol (80 mL). Finally, Sn-Mont was dried in a vacuum (0.5 mmHg) at room temperature for 6 h, followed by being ground in a mortar with a pestle, passed through a 60-mesh screen and stored in a general glass bottle under ambient conditions.

According to the nitrogen sorption analysis, Sn-Mont has a specific surface area of 370 m²/g. XRD patterns and nitrogen sorption isotherms of Sn-Mont are shown in **Figure S1** and **Figure S2**.

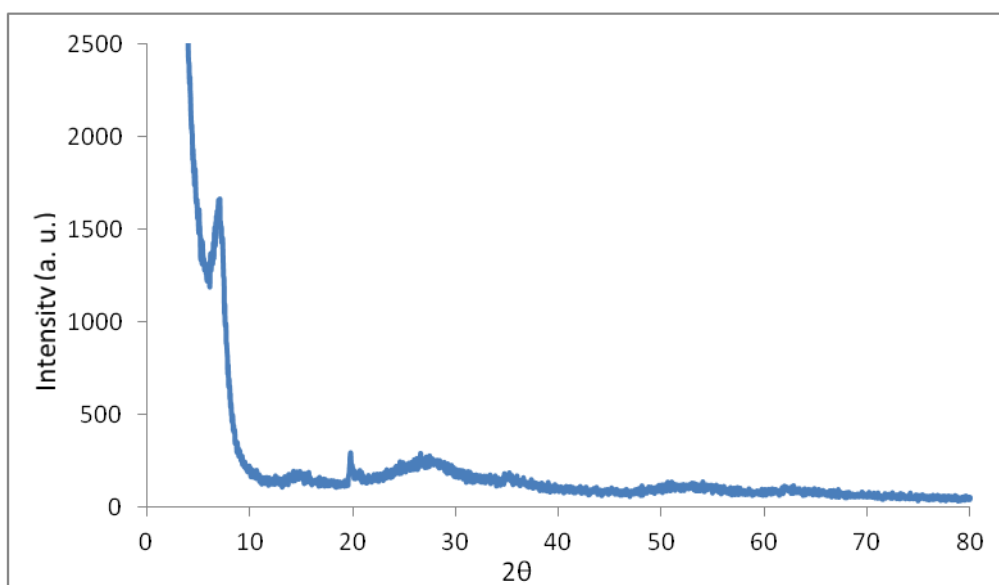


Figure S1. XRD pattern of Sn-Mont

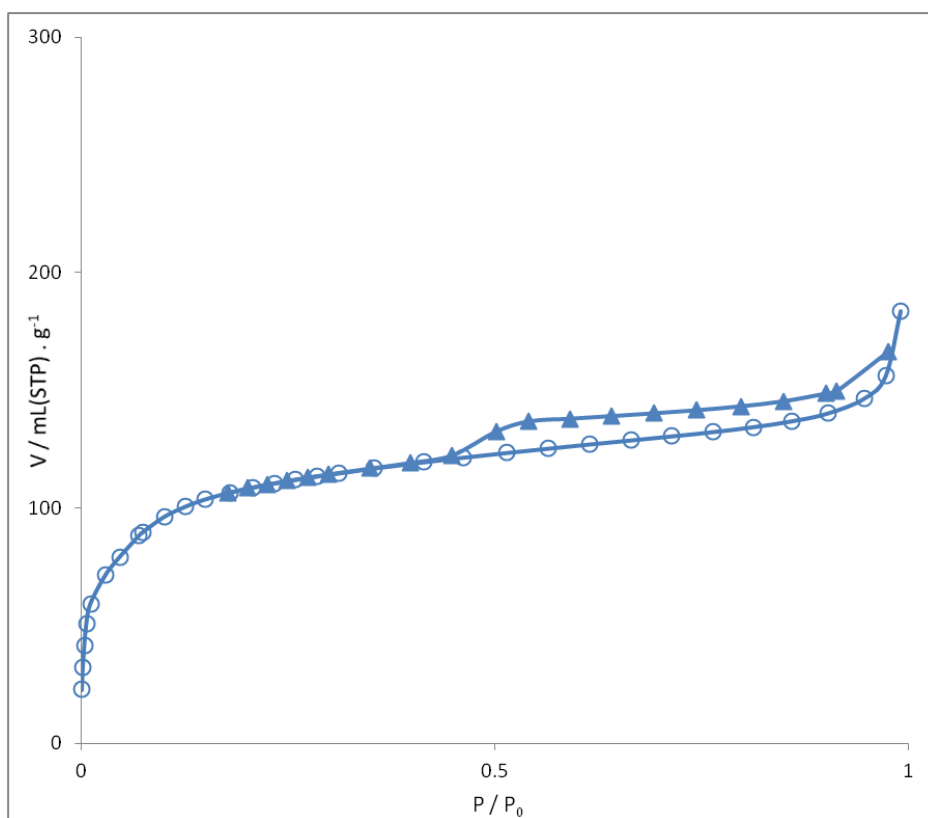


Figure S2. Nitrogen sorption isotherms of Sn-Mont

Preparation of H-Mont

Proton exchanged montmorillonite (H-Mont) was prepared according to the previously reported method.¹³

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