

## Supporting Information

### **C–H Amination Chemistry Mediated by Trinuclear Cu(I) Sites Supported by a Ligand Scaffold Featuring an Arene Platform and Tetramethylguanidinyll Residues<sup>†</sup>**

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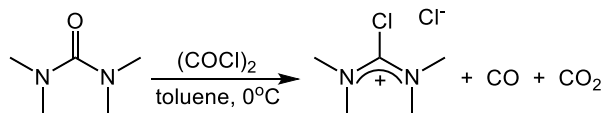
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## EXPERIMENTAL SECTION

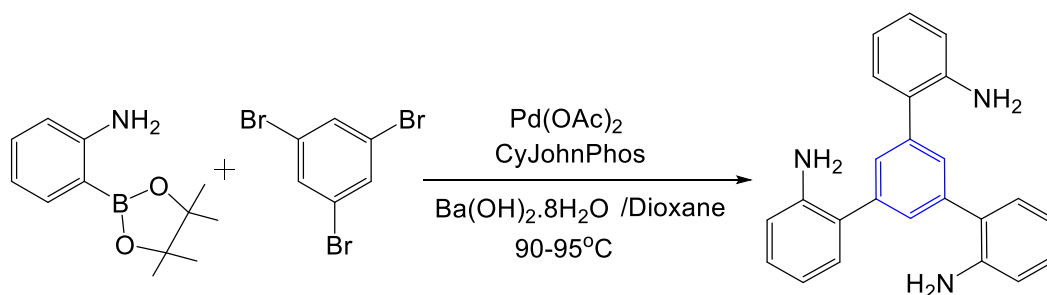
**General Considerations.** All operations were performed under anaerobic conditions under a pure dinitrogen or argon atmosphere, using Schlenk techniques on an inert gas/vacuum manifold or in a dry box ( $O_2$ ,  $H_2O$  < 1 ppm). Anhydrous diethyl ether, methylene chloride, acetonitrile, tetrahydrofuran, hexane, pentane, benzene, toluene, dimethylformamide, dimethylacetamide, and dimethyl sulfoxide were purchased from Sigma-Aldrich (Millipore). Solvents were degassed by three freeze-pump-thaw cycles. Unless otherwise noted, all other reagents were purchased at the highest purity available or synthesized according to the literature procedures noted in the text.

$^1H$  and  $^{13}C$  NMR spectra were recorded on Varian XL-400, Varian INOVA/ UNITY 400 MHz Unity Plus, and a Bruker Avance III 800 MHz NMR spectrometers. IR spectra were obtained on a Perkin-Elmer 883 IR spectrometer and FT-IR spectra on Nicolet Nexus 470 and 670, Magna 750 FT-IR ESP, and Shimadzu IR-Affinity-1 spectrometers. UV-vis spectra were obtained on a Hewlett-Packard 8452A diode array, Varian Cary 50, and Varian Cary 300 spectrophotometers. HRMS data were collected on a Thermo Fisher Scientific LTQ-Orbitrap XL hybrid mass spectrometer, using the Orbitrap analyzer for the acquisition of high-resolution accurate mass data. Samples were infused using the integrated syringe pump at 3  $\mu L/min$  and ionization was *via* the electrospray source with source settings at their defaults. In general, settings for the ion optics were determined automatically during the regular tuning and calibration of the instrument. For high-resolution data, the Orbitrap analyzer is set to a resolution of 100000. Microanalyses were done on an in-house Perkin-Elmer 2400 CHN analyzer. Other physical measurements are noted below.

## Synthesis and Characterization of Ligands and Metal Compounds

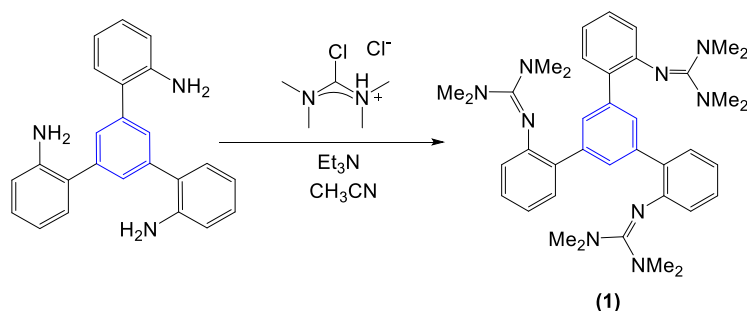


**Chlorotetramethylformamidinium chloride.** To a cooled solution of 1,1,3,3-tetramethyl urea (6.96 g, 59.9 mmol) in toluene (15 mL) at 0 °C, oxalyl chloride (7.68 ml, 89.9 mmol) was slowly added. The temperature of the reaction mixture was kept at 0 °C throughout the addition of oxalyl chloride. After the addition was complete, the reaction mixture was allowed to warm up to room temperature and stirred overnight. The white solid was collected by filtration and washed with diethyl ether (20 mL). The product was dried under vacuum (yield = 8.5 g, 83%).



**5'-(2-aminophenyl)-[1,1':3',1''-terphenyl]-2,2''-diamine.**<sup>1</sup> 2-Aminophenyl boronic acid pinacol ester (500 mg, 1 mmol), 1,3,5-tribromobenzene (215 mg, 0.3 mmol), CyJohnPhos (72 mg, 9 mol%), Pd(OAc)<sub>2</sub> (15 mg, 3 mol%), and Ba(OH)<sub>2</sub>·8H<sub>2</sub>O were charged in an oven-dried resealable Schlenk flask containing a magnetic stir bar. The Schlenk flask was tightly capped with a rubber septum and then evacuated and backfilled with nitrogen. Dry dioxane (25 mL) was added and the suspension was stirred and heated at 90 – 95 °C for 24 hours. The reaction was monitored by TLC for completion, and after completion of the reaction, the reaction mixture was allowed to cool to room temperature and filtered through a thin bed of Celite. The filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica

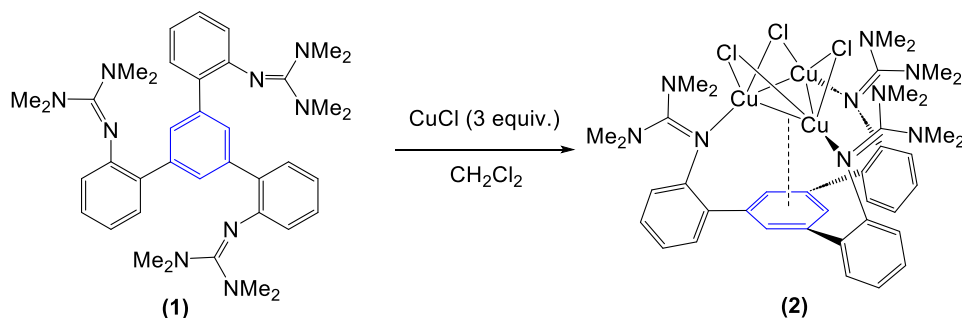
(MeOH-CH<sub>2</sub>Cl<sub>2</sub>, 2:98) to afford 5'-(2-aminophenyl)-[1,1':3',1''-terphenyl]-2,2''-diamine as a light brown solid (110 mg, 41%). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 1.94 ppm): δ 7.44 (s, 3H, aryl), 7.18-7.15 (d, 3H, aryl), 7.11-7.09 (t, 3H, aryl), 6.79-6.73 (m, 6H, aryl), 4.19 (br, 6H, NH<sub>2</sub>). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 118.26, 1.32 ppm): δ 145.6, 141.7, 131.1, 129.4, 128.8, 127.5, 118.6, 116.3. IR (KBr, cm<sup>-1</sup>): ν 3434, 3351, 3028, 1612, 1495, 1450, 1409, 1296, 1059, 895, 801, 750, 621, 454. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (ε (M<sup>-1</sup> cm<sup>-1</sup>)) 225 (10750).



**(TMG<sub>3</sub>trphen-Arene)•1.5CH<sub>2</sub>Cl<sub>2</sub> (1).** 5'-(2-aminophenyl)-[1,1':3',1''-terphenyl]-2,2''-

diamine (300 mg, 0.855 mmol) was dissolved in acetonitrile (15 mL) at room temperature. A solution of chlorotetramethylformamidinium chloride (465 mg, 3 mmol) in acetonitrile (10 mL) was slowly added at 0 – 5 °C. Triethylamine (268 mg, 3 mmol) was added, and the mixture was allowed to warm up to room temperature and was further stirred overnight. The solvent was evacuated to dryness and the resulting residue was stirred with water (20 mL). The reaction mixture was basified with NH<sub>4</sub>OH solution (15 mL) and extracted with EtOAc (20 mL). The organic layer was concentrated to give an oily mass of **1** which solidified on cooling (yield = 347 mg, 63%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 5.32 ppm): δ 7.50 (s, 3H, aryl), 7.28 (dd, 3H, *J* = 7.6, 1.6 Hz, aryl), 7.14 (dt, 3H, *J* = 7.6, 1.6 Hz, aryl), 6.89 (dt, 3H, *J* = 7.4, 1.2 Hz, aryl), 6.69 (d, 3H, *J* = 7.9, aryl), 2.47 (s, 36H, CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 53.84 ppm): δ 158.3, 149.8, 140.7, 133.5, 130.8, 128.0, 127.8, 123.4, 120.4, 39.4. IR (KBr, cm<sup>-1</sup>): ν 3063, 2997, 2916, 2883, 2796, 2160, 2045, 1575, 1553, 1498, 1479,

1375, 1233, 1135, 1016, 886, 749, 443. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  ( $\epsilon$  (M<sup>-1</sup> cm<sup>-1</sup>)) 225 (20310). Elem. Anal. calcd. for C<sub>39</sub>H<sub>51</sub>N<sub>9</sub> (**1** – 1.5 DCM): C, 72.52; H, 7.96, N, 19.52. Found: C, 72.49; H, 7.93, N, 19.58.



**[(TMG<sub>3</sub>trphen-Arene)Cu<sub>3</sub>( $\mu$ -Cl)<sub>3</sub>]•2.56CH<sub>2</sub>Cl<sub>2</sub> (**2**).** To a suspension of CuCl (115.03 mg, 1.16 mmol) in THF (5 mL) was added a solution of **1** (250 mg, 0.387 mmol) in THF (5 mL) at room temperature. The solution was stirred for 24 hours. The volatiles were removed under vacuum and the residue was redissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and stirred for 6 hours. The solution was filtered and concentrated to give a brown-colored powder **2** (yield = 265 g, 73%). The compound was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> to obtain X-ray-quality crystals. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 5.32 ppm):  $\delta$  7.50 (s, 3H, aryl), 7.35 (d, 3H,  $J$  = 7.4 Hz, aryl), 7.26 (t, 3H,  $J$  = 7.7 Hz, aryl), 7.06 (t, 3H,  $J$  = 7.4 Hz, aryl), 6.48 (d, 3H,  $J$  = 7.7 Hz, aryl), 2.78 (s, 36H, CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 53.84 ppm): 166.6, 148.6, 140.4, 133.4, 130.6, 129.4 (intense), 122.3, 121.9, 40.5. IR (KBr, cm<sup>-1</sup>):  $\nu$  2926, 2792, 2114, 1518, 1455, 1392, 1329, 1283, 1202, 1155, 1029, 925, 854, 754, 619, 496, 450. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  ( $\epsilon$  (M<sup>-1</sup> cm<sup>-1</sup>)) 225 (39270). Elem. Anal. calcd. for C<sub>39</sub>H<sub>51</sub>Cl<sub>3</sub>Cu<sub>3</sub>N<sub>9</sub> (**2** – 2.56 DCM): C, 49.68; H, 5.45, N, 13.37. Found: C, 49.62; H, 5.42, N, 13.40.

## Other Physical Measurements

**X-ray crystallography.** Intensity data sets for all the compounds were collected on a Bruker Smart Apex, a Bruker Apex II or a Rigaku 4-circle diffractometer using graphite monochromated Mo ( $\lambda = 0.71073 \text{ \AA}$ ) or Cu ( $\lambda = 1.54178 \text{ \AA}$ )  $K\alpha$  radiation from a fine focus sealed tube X-ray source. Suitable crystals were selected and mounted on a glass fiber using super glue. The datasets were collected at low temperatures (100 - 220 K) and room temperature for metal complexes and purely organic compounds, respectively, employing a scan of  $0.3^\circ$  in  $\omega$  with an exposure time of 20 s/frame using Apex III or SMART software.<sup>2,3</sup> The cell refinement and data reduction were carried out with SAINT, while the program SADABS was used for the absorption correction.<sup>4</sup> The structures were solved by direct methods using SHELXS-97 and difference Fourier syntheses.<sup>5</sup> Full-matrix least-squares refinement against  $|F^2|$  was carried out using the SHELXTL-PLUS<sup>4</sup> suite of programs. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and held in the riding mode during the final refinement. Note that for the crystal structure solution of compounds **1** and **2**, SQUEEZE has been used to treat the scattered e-density from the disordered solvent molecules. From the residual electron density and electron count from the solvent-accessible volume, the number of additional disordered molecules were calculated and added to the final formula.<sup>6</sup> All structures were finally refined with SHELX-2014 using SHELXle.<sup>7</sup> Crystallographic data are collected in Table S1 and S2. ORTEP diagrams are shown in Figures 2, 3 and S1.

**Table S1.** Summary of Crystallographic Data for Compounds **1** and **2**

	(TMG <sub>3</sub> trphen-Arene)•1.5CH <sub>2</sub> Cl <sub>2</sub> ( <b>1</b> )	[(TMG <sub>3</sub> trphen-Arene)- Cu <sub>3</sub> (μ-Cl) <sub>3</sub> ]•2.56CH <sub>2</sub> Cl <sub>2</sub> ( <b>2</b> )
formula	C <sub>40.50</sub> H <sub>54</sub> Cl <sub>3</sub> N <sub>9</sub>	[C <sub>39</sub> H <sub>51</sub> Cl <sub>3</sub> Cu <sub>3</sub> N <sub>9</sub> ,2.56(CH <sub>2</sub> Cl <sub>2</sub> )] <sub>2</sub>
<i>M<sub>r</sub></i>	773.27	2320.53
crystal system	Monoclinic	Triclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.0570(15)	18.1859(16)
<i>b</i> (Å)	24.826(4)	18.3235(16)
<i>c</i> (Å)	17.435(3)	20.8638(18)
<i>α</i> (deg)	90	84.278
<i>β</i> (deg)	105.177	65.979
<i>γ</i> (deg)	90	60.494
<i>V</i> (Å <sup>3</sup> )	4201.2(11)	5482.1(8)
<i>Z</i>	4	2
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.223	1.406
<i>T</i> (K)	173(2)	173(2)
<i>λ</i> (Å)	0.71073	0.71073
<i>μ</i> (mm <sup>-1</sup> )	0.258	1.586
<i>R</i> <sub>1</sub> <sup><i>a</i></sup> (I>2sigma(I))	0.0904	0.0565
<i>wR</i> <sub>2</sub> <sup><i>b</i></sup> (I>2sigma(I))	0.1241	0.0887

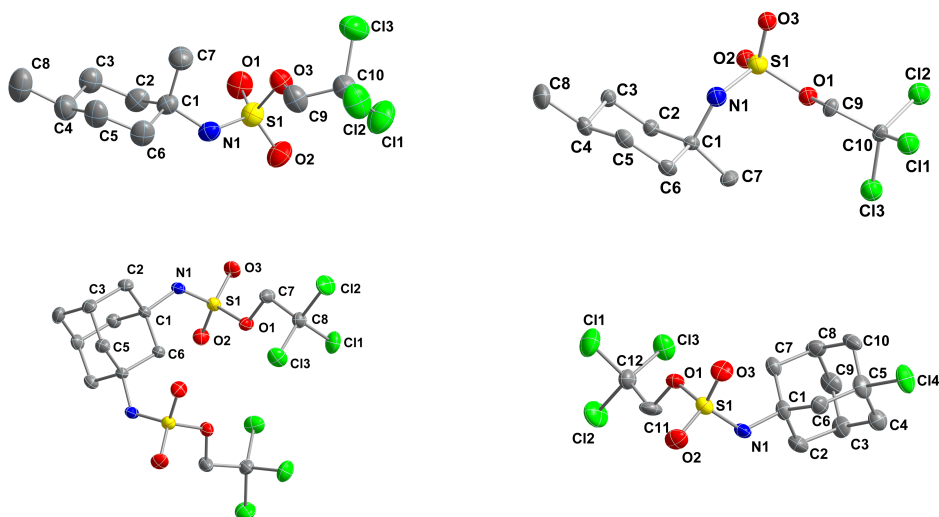
<sup>*a*</sup>  $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ . <sup>*b*</sup>  $wR_2 = [\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}]^{1/2}$



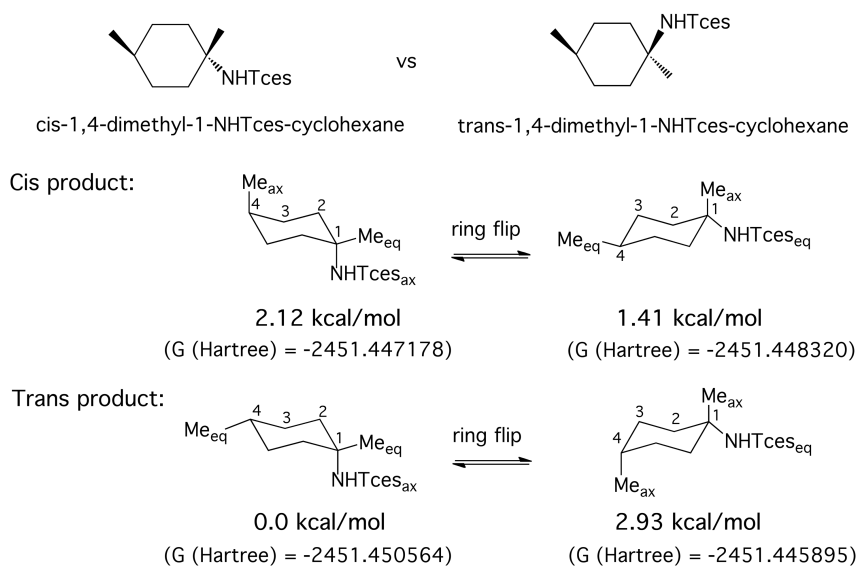
**Table S2.** Summary of Crystallographic Data for Amination Products *cis*-1,4-Me<sub>2</sub>-1-NHTces-Cyclohexane, *trans*-1,4-Me<sub>2</sub>-1-NHTces-Cyclohexane, 1,3-(NHTces)<sub>2</sub>-Adamantane and 1-NHTces-3-Cl-Adamantane

	<i>cis</i> -1,4-Me <sub>2</sub> -1-NHTces-Cyclohexane	<i>trans</i> -1,4-Me <sub>2</sub> -1-NHTces-Cyclohexane	1,3-(NHTces) <sub>2</sub> -Adamantane	1-NHTces-3-Cl-Adamantane
formula	C <sub>10</sub> H <sub>18</sub> Cl <sub>3</sub> NO <sub>3</sub> S	C <sub>10</sub> H <sub>18</sub> Cl <sub>3</sub> NO <sub>3</sub> S	C <sub>14</sub> H <sub>20</sub> Cl <sub>6</sub> N <sub>2</sub> O <sub>6</sub> S <sub>2</sub>	C <sub>12</sub> H <sub>17</sub> Cl <sub>4</sub> NO <sub>3</sub> S
<i>M<sub>r</sub></i>	338.66	338.66	589.14	397.12
crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
space group	<i>P21/c</i>	<i>P21/n</i>	<i>Pbcn</i>	<i>P21</i>
<i>a</i> (Å)	10.639(4)	6.0757(2)	6.2671(3)	10.3350(19)
<i>b</i> (Å)	6.217(2)	10.6419(3)	21.0667(10)	6.6003(11)
<i>c</i> (Å)	22.819(8)	22.7905(7)	17.0969(8)	11.873(2)
<i>α</i> (deg)	90	90	90	90
<i>β</i> (deg)	93.285(5)	93.3490(10)	90	92.336(6)
<i>γ</i> (deg)	90	90	90	90
<i>V</i> (Å <sup>3</sup> )	1506.8(9)	1469.32(8)	2257.25(19)	809.2(2)
<i>Z</i>	4	4	4	2
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.493	1.531	1.734	1.630
<i>T</i> (K)	298(2)	173(2)	173(2)	173(2)
<i>λ</i> (Å)	0.71073	0.71073	0.71073	0.71073
<i>μ</i> (mm <sup>-1</sup> )	0.746	0.765	0.982	0.867
<i>R</i> <sub>1</sub> <sup>a</sup>	0.0626	0.0278	0.0336	0.0913
( <i>I</i> >2σ( <i>I</i> ))				
<i>wR</i> <sub>2</sub> <sup>b</sup>	0.1283	0.0674	0.0818	0.2357
( <i>I</i> >2σ( <i>I</i> ))				

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$



**Figure S1.** ORTEP diagram of *cis*-1,4-Me<sub>2</sub>-1-NHTces-Cyclohexane, *trans*-1,4-Me<sub>2</sub>-1-NHTces-Cyclohexane, 1,3-(NHTces)<sub>2</sub>-Adamantane and 1-NHTces-3-Cl-Adamantane drawn with 40% thermal ellipsoids. Selective interatomic distances [Å] and angles [°] for ***cis*-1,4-Me<sub>2</sub>-1-NHTces-Cyclohexane**: C(1)–N(1) = 1.500(4), C(1)–C(7) = 1.522(5), C(4)–C(8) = 1.530(5), N(1)–S(1) = 1.581(3), S(1)–O(2) = 1.427(3), C(1)–N(1)–S(1) = 127.4(2). For ***trans*-1,4-Me<sub>2</sub>-1-NHTces-Cyclohexane**: C(1)–N(1) = 1.5051(14), C(1)–C(7) = 1.5278(16), C(4)–C(8) = 1.5220(19), N(1)–S(1) = 1.5940(10), S(1)–O(2) = 1.4198(9), C(1)–N(1)–S(1) = 125.98(7). For **1,3-(NHTces)<sub>2</sub>-Adamantane**: C(1)–N(1) = 1.486(2), N(1)–S(1) = 1.5904(15), S(1)–O(2) = 1.4135(14), C(1)–N(1)–S(1) = 127.42(12). For **1-NHTces-3-Cl-Adamantane**: C(1)–N(1) = 1.521(16), C(5)–Cl(4) = 1.815(14), N(1)–S(1) = 1.561(11), S(1)–O(2) = 1.426(10), C(1)–N(1)–S(1) = 127.2(9).



**Figure S2.** Computed Relative Free Energies (BP86-D3BJ/def2-TZVP/gas) of *cis*- and *trans*-1,4-Me<sub>2</sub>-1-NHTces-Cyclohexane Conformers

## Catalytic and Mechanistic Studies

**(a) Catalytic Styrene Aziridination Procedure.** A 20 mL screw-cap vial containing a small magnetic bar was charged in sequence with catalyst **2** (11.8 mg, 0.0125 mmol), N-(p-tolylsulfonyl)imido]phenyliodinane (93.3 mg, 0.25 mmol), molecular sieves (5Å) (20 mg), styrene (208.3 mg, 2.0 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (0.300 g). The reaction mixture was stirred vigorously at 30 °C for 2.0 hours. After completion of the reaction, the aziridination product (yield: 82%) was purified by column chromatography (silica gel) and quantified by <sup>1</sup>H NMR (in CDCl<sub>3</sub>) versus an internal standard (4'-methoxyacetophenone).

**(b) General Catalytic Amination Procedure.** In a standard method for copper-catalyzed amination, a tiny magnetic stirrer was placed in a flame-dried 20 mL screw cap vial. To this vial, catalyst [(TMG<sub>3</sub>trphen-Arene)Cu<sub>3</sub>(μ-Cl)<sub>3</sub>] (**2**) (11.8 mg, 0.0125 mmol), 2,2,2-trichloroethyl(phenyl-λ<sub>3</sub>-iodanylidene)sulfamate (PhINTces) (214.4 mg, 0.500 mmol) and molecular sieves (5Å) (20 mg) were added sequentially. A solution of the substrate (0.250 mmol) in a mixture of α,α,α-trifluorotoluene and HFIP (10:1 v/v, 300 mg) was added to the vial that contained the solids. The reaction was stirred at 30 °C for 24 hours. After completion of the reaction, the products were purified by column chromatography (silica gel) to remove excess substrate and catalyst components using a mixture of hexane and ethyl acetate, and were quantified by <sup>1</sup>H NMR (in CDCl<sub>3</sub>) versus an internal standard (4'-methoxyacetophenone). All products are known compounds,<sup>8</sup> with the exception of the following products:

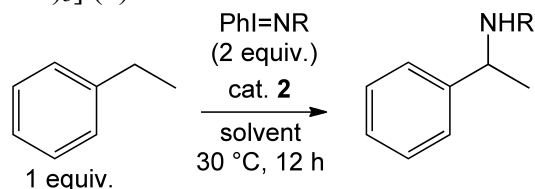
**Trans-1,4-Me<sub>2</sub>-1-NHTces-cyclohexane:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 7.26 ppm): δ 4.64 (s, 2H, Tces), 4.48 (br, 1H, NH), 2.06-1.99 (m, 2H, CH<sub>2</sub>), 1.63-1.55 (m, 2H, CH<sub>2</sub>), 1.46 (s, 3H, Me), 1.41-1.31 (m, 3H, CH<sub>2</sub>, CH), 1.24-1.16 (m, 2H, CH<sub>2</sub>), 0.93 (d, 3H, *J* = 6.4 Hz, Me). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 77.16,

ppm): 93.8, 78.1, 57.4, 37.7, 31.7, 30.2, 28.6, 22.2. Elem. Anal. calcd. for C<sub>10</sub>H<sub>18</sub>Cl<sub>3</sub>NSO<sub>3</sub>: C, 35.46; H, 5.36, N, 4.14. Found: C, 35.49; H, 5.39, N, 4.11.

**1,3-(NHTces)<sub>2</sub>-adamantane:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 7.26 ppm): δ4.63 (s, 4H, Tces), 4.60 (br, 2H, NH), 2.35 (m, 2H, CH), 2.26 (br, 2H, CH<sub>2</sub>), 1.97 (d, 8H, *J* = 3.0 Hz, CH<sub>2</sub>), 1.62 (t, 2H, *J* = 3.3 Hz, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 77.16, ppm): 93.5, 78.4, 56.9, 47.4, 41.1, 34.3, 29.9. Elem. Anal. calcd. for C<sub>14</sub>H<sub>20</sub>Cl<sub>6</sub>N<sub>2</sub>S<sub>2</sub>O<sub>6</sub>: C, 28.54; H, 3.42, N, 4.75. Found: C, 28.49; H, 3.40, N, 4.78.

**1-NHTces-3-Cl-adamantane:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 7.26 ppm): δ4.66 (br, 1H, NH), 4.63 (s, 2H, Tces), 2.37 (br, 2H, CH<sub>2</sub>), 2.33 (m, 2H, CH), 2.07 (br, 4H, CH<sub>2</sub>), 1.97 (br, 4H, CH<sub>2</sub>) 1.61 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 77.16, ppm): 93.5, 78.4, 66.1, 57.8, 52.1, 46.1, 40.8, 34.0, 31.7. Elem. Anal. calcd. for C<sub>12</sub>H<sub>17</sub>Cl<sub>4</sub>NSO<sub>3</sub>: C, 36.29; H, 4.31, N, 3.53. Found: C, 36.27; H, 4.29, N, 3.56.

**Table S3.** Optimization of Catalytic Amination Reaction of Ethylbenzene Mediated by [(TMG<sub>3</sub>trphen-Arene)Cu<sub>3</sub>(μ-Cl)<sub>3</sub>] (**2**)



R	Solvent	Catalyst 2 (mol %)	Yield (%)
Ts	CH <sub>2</sub> Cl <sub>2</sub>	5	7
Ts	PhCl	5	9
Ts	PhCF <sub>3</sub>	5	10
Tces	PhCF <sub>3</sub>	5	18
Tces	PhCF <sub>3</sub> /HFIP (10:1 v/v)	5	42
Tces	PhCl/HFIP (10:1 v/v)	5	43
Tces	1,2-Difluorobenzene/HFIP (10:1 v/v)	5	39
Tces	PhCF <sub>3</sub> /HFIP (10:1 v/v)	2.5	37
Tces	PhCF <sub>3</sub> /HFIP (10:1 v/v)	10	33

Reaction conditions: **2**, 0.0125 mmol (5 mol% or as stated above); ethylbenzene, 0.25 mmol; PhI=NR, 0.50 mmol (R = Ts, Tces); solvent as noted above (300 mg); MS 5 Å, 20 mg; t = 12 h.

**(c) Hammett Plots.** The general procedure for the amination of benzylic substrates was conducted with the assistance of catalyst [(TMG<sub>3</sub>trphen-Bz)Cu<sub>3</sub>(μ-Cl)<sub>3</sub>] (**2**) (11.8 mg, 0.0125 mmol). The reaction mixture was composed of 1.0 mmol of ethylbenzene, 1.0 mmol of *p*-X-ethylbenzene (X = Me, MeO, F, Cl, Br, CF<sub>3</sub>, NO<sub>2</sub>) and PhINTces (2 mmol) in a PhCF<sub>3</sub>/HFIP mixture (10:1 v/v). The reaction vial was sealed tightly and wrapped with aluminum foil to protect the reaction mixture from light. The reactions were stirred for 6 hours. At the end of the reaction, the mixture was flash chromatographed on silica gel (CH<sub>2</sub>Cl<sub>2</sub>) in order to recover the benzylic aminated products and evaluate their ratio (Table S4) by quantitative <sup>1</sup>H-NMR analysis in CDCl<sub>3</sub>.

**Table S4.** Competitive Amination Reactions of para-substituted Ethylbenzenes vs. Ethylbenzene by PhI=NTces in the presence of [(TMG<sub>3</sub>trphen-Arene)Cu<sub>3</sub>(μ-Cl)<sub>3</sub>] (**2**)

<b>X</b>	$\sigma_p$	$\sigma^+$	$k_X/k_H$	$\log(k_X/k_H)$
MeO	-0.27	-0.78	3.2834	0.516
Me	-0.17	-0.31	0.8139	0.089
F	0.06	-0.07	0.8576	-0.067
H	0	0	0	0
Cl	0.23	0.11	0.6675	-0.175
I	0.18	0.11	0.8268	-0.082
Br	0.23	0.15	0.6360	-0.197
CF <sub>3</sub>	0.54	0.61	0.1719	-0.76
NO <sub>2</sub>	0.78	0.79	0.1464	-0.83

Reaction conditions: **2**, 0.0125 mmol; ethylbenzene, 1.0 mmol; *p*-X-ethylbenzene, 1.0 mmol; PhI=NTces, 2 mmol; PhCF<sub>3</sub>/HFIP (10:1 v/v, 300 mg); MS 5 Å, 20 mg; t = 6 h.

**(d) Kinetic Isotope Effects.** The amination of (*S*)-(+)-1-Phenylethane-*d* (99.8 atom % D, 40.15 mg, 0.375 mmol) (synthesized by following a literature report)<sup>9</sup> by PhINTces (107.2 mg, 0.25 mmol), mediated by [(TMG<sub>3</sub>trphen-Arene)Cu<sub>3</sub>(μ-Cl)<sub>3</sub>] (**2**) (11.8 mg, 0.0125 mmol), was conducted according to the general procedure for the amination of ethylbenzene by PhINTces, in a PhCF<sub>3</sub>/HFIP (10:1 v/v, 0.500g) solvent mixture. The reaction was quenched after 24 hours, and the reaction mixture was flash chromatographed on silica gel with hexane/ethyl acetate (95:5 v/v) to recover the aminated product. The ratio of d<sub>0</sub>/d<sub>1</sub> amines is evaluated by <sup>1</sup>H NMR (CD<sub>3</sub>Cl<sub>3</sub>, 120 s relaxation delay) by integrating the CH(D) multiplet against the CH<sub>2</sub> (NTces) and CH<sub>3</sub> peak clusters of the products. An internal integration of the CH<sub>3</sub> peak cluster also permits an independent evaluation of the d<sub>0</sub>/d<sub>1</sub> ratio.

## Computational Methods

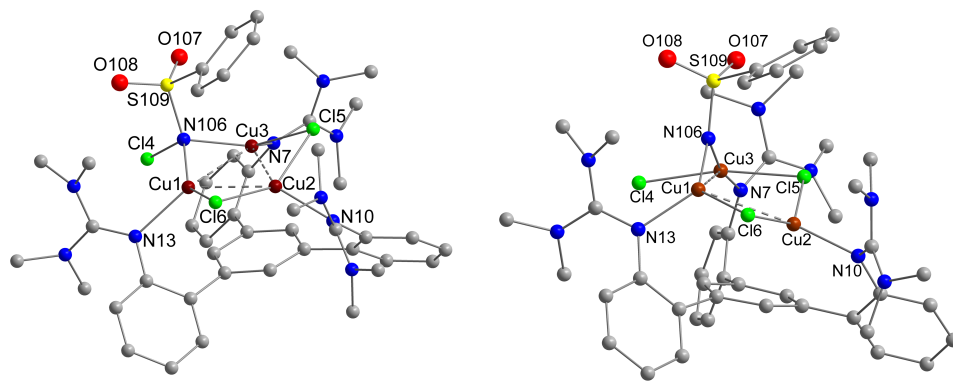
The structures were optimized with ORCA<sup>10,11</sup> with the M06<sup>12</sup> functional in conjunction with the def2-TZVPP basis set.<sup>13</sup> Optimized structures were minima, as no imaginary vibrational frequencies were found. ADF 2022<sup>14,15</sup> was used to calculate the energy decomposition analysis (EDA)<sup>16</sup> with the level of theory PBE exchange-correlation functional (XC) and D3(BJ) dispersion correction<sup>17</sup> with TZ2P basis set. In contrast, Multiwfn<sup>18</sup> with the M06-D4<sup>12,17,19</sup> functional was used to calculate the natural orbitals for chemical valence (NOCV)<sup>13</sup> and Independent Gradient Model Based on Hirshfeld Partition (IGMH).<sup>16,20</sup> EDA provides a qualitative and quantitative chemical bond analysis by breaking the overall bond energy ( $\Delta E$ ) into two major segments, the preparation energy ( $\Delta E_{\text{prep}}$ ) and the interaction energy ( $\Delta E_{\text{int}}$ ).<sup>16,20</sup> The  $\Delta E_{\text{prep}}$  (preparation energy) refers to the energy required to deform the original geometry of the two fragments to the equilibrium geometry and activate their valence electronic configuration.<sup>16</sup> The interaction energy

( $\Delta E_{\text{int}}$ ) is the addition of energy of the attractive classical electrostatic interaction, the repulsive Pauli interaction energy, the dispersion interaction, and the orbital interaction energy.<sup>16</sup> The orbital interaction energy describes the charge transfer and the polarization effect. Independent Gradient Model Based on Hirshfeld Partition (IGMH) was defined using the actual electron density of the fragments. The electron density based on Hirschfeld  $\rho_i^{\text{hirsh}}(r)$  is expressed as  $\rho_i^{\text{hirsh}}(r) = \rho(r)w_i(r)$  where  $\rho$  is the actual electron density and  $w_i(r)$  the Hirshfeld weighting function of the atom  $i$ .<sup>19</sup>

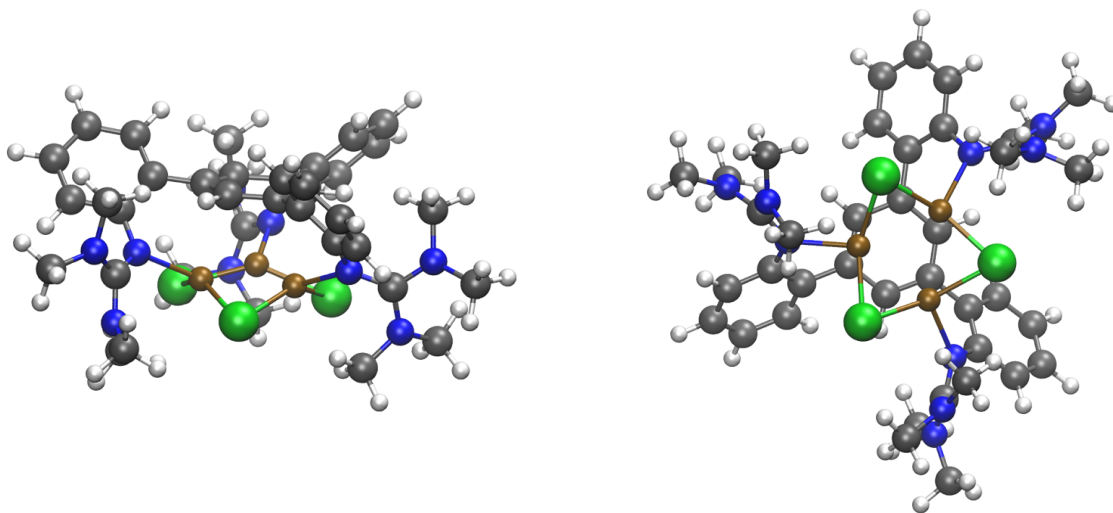
$$w_i(\mathbf{r}) = \frac{\rho_i^{\text{free}}(\mathbf{r})}{\rho^{\text{promolecular}}(\mathbf{r})}$$

The complexes were divided into two neutral fragments: the first is  $\text{Cu}_3(\mu_2\text{-Cl}_3)$  while the other is phenyl moieties. All fragments have a singlet multiplicity. The direction of the charge flow between fragments is encoded from white to red. Only significant orbital interactions are shown.

Copper nitrenes were optimized with the ORCA program,<sup>10,11</sup> using the TPSSh functional<sup>21</sup> with the def2-TZVP basis set with auxiliary basis def2/J and a dispersion correction that included Becke-Johnson damping.<sup>13,22</sup> Non-orthogonal magnetic orbitals of the broken symmetry solution show that a broken symmetry singlet solution exists. No imaginary frequencies were observed. Spin densities were calculated at the optimized structures. Relative energies for the *cis* and *trans* conformers of 1,4-Me<sub>2</sub>-1-NHTces-cyclohexane were calculated at the BP86-D3BJ/def2-TZVP.<sup>17,23</sup>

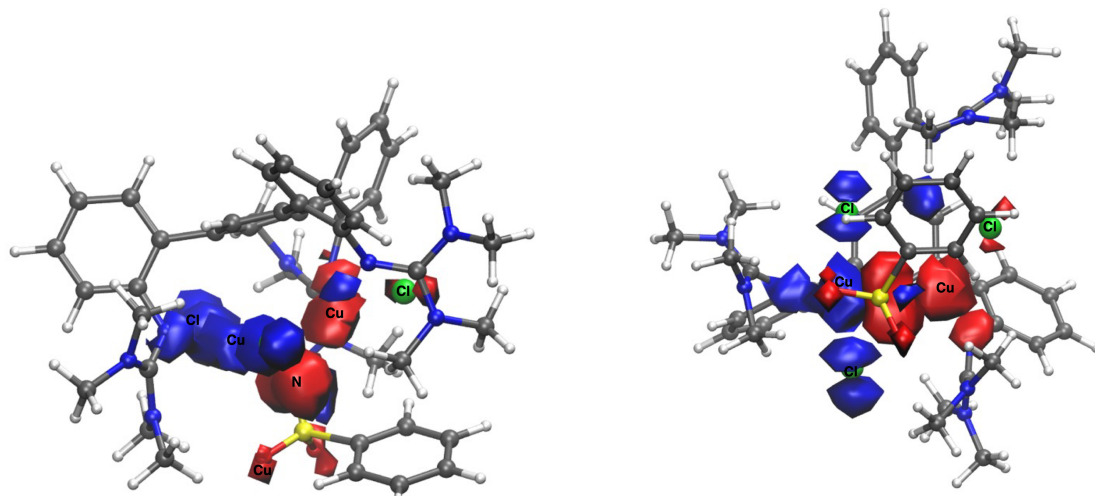


**Figure S3.** Optimized  $[(\text{TMG}_3\text{trphen-Arene})\text{Cu}_3(\mu\text{-Cl})_3]$  with nitrene docked, optimized in a closed-shell singlet  $^1[\text{Cu}]\text{NR}$  (left), and a broken-symmetry singlet  $^{\text{BS}}[\text{Cu}]\text{NR}$  (right). Hydrogens are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for  $^1[\text{Cu}]\text{NR}$ : Cu(1)–N(106) = 1.990, Cu(3)–N(106) = 2.012, Cu(1)–Cu(3) = 2.751, Cu(3)–Cl(4) = 3.271, Cl(4)–N(106) = 1.810, Cu(1)–N(106)–Cu(3) = 86.85, Cu(3)–N(106)–S(109) = 113.21, Cu(1)–N(106)–S(109) = 126.59. For  $^{\text{BS}}[\text{Cu}]\text{NR}$ : Cu(1)–N(106) = 1.826, Cu(3)–N(106) = 1.941, Cu(1)–Cu(3) = 2.962, Cu(3)–Cl(4) = 2.297, Cu(1)–N(106)–Cu(3) = 103.64, Cu(3)–N(106)–S(109) = 119.26, Cu(1)–N(106)–S(109) = 136.78, Cl(4)–Cu(3)–N(106) = 93.55.



**Figure S4.** Optimized structure of  $[(\text{TMG}_3\text{trphen-Arene})\text{Cu}_3(\mu\text{-Cl})_3]$  (**2**) with side and front view (TPSSh/def2-TZVP/gas) (color code: Cu, gold; Cl, green, N, blue; C, dark grey; H, light grey)

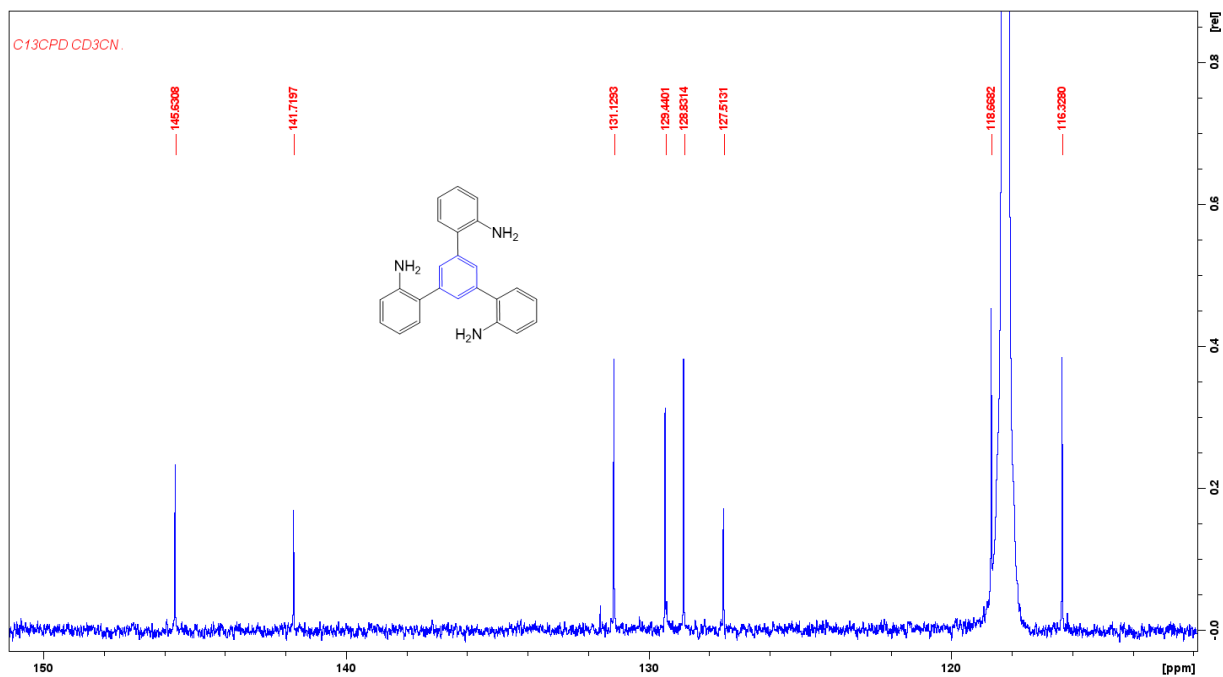
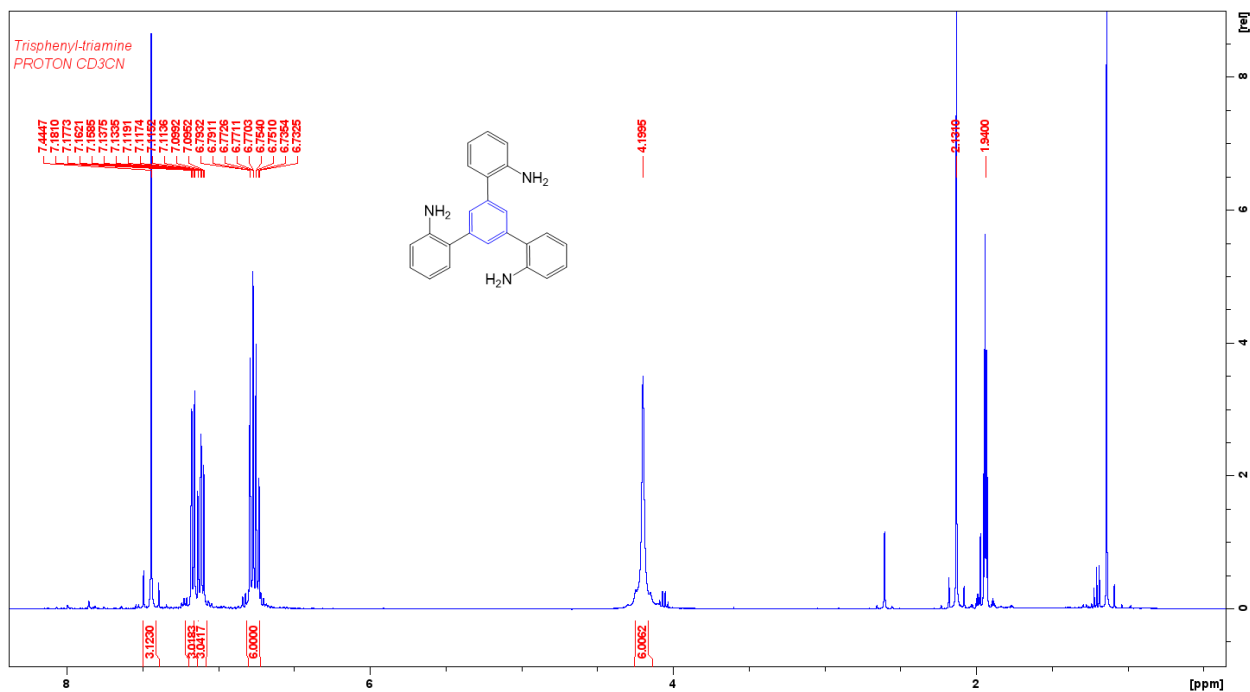




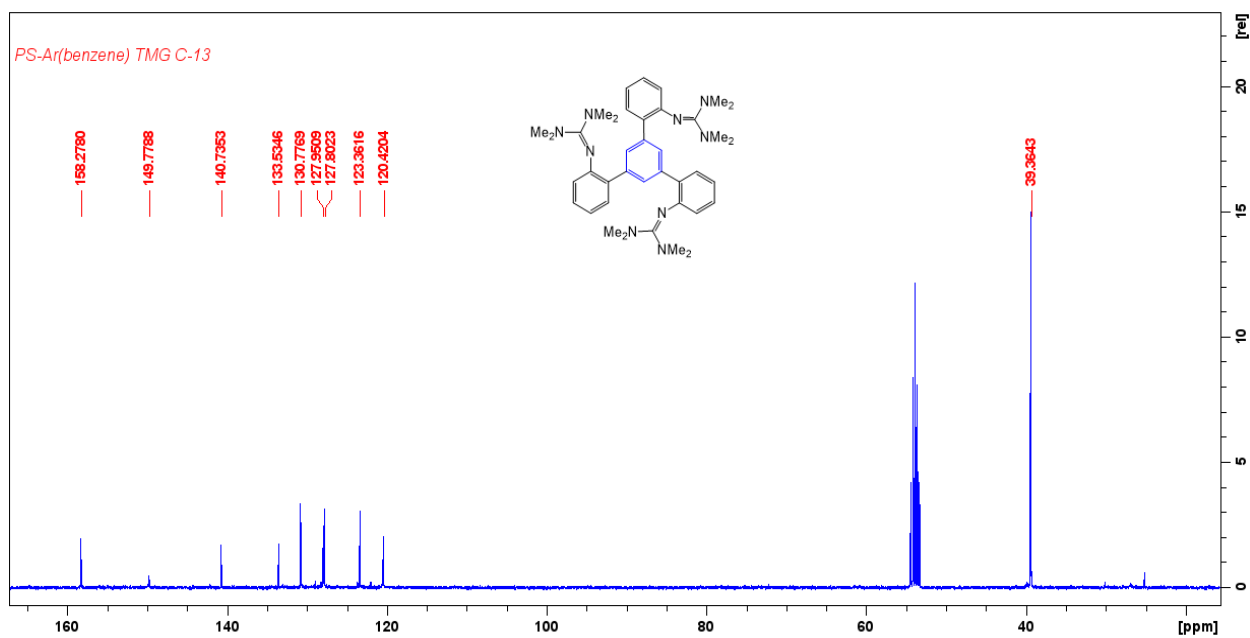
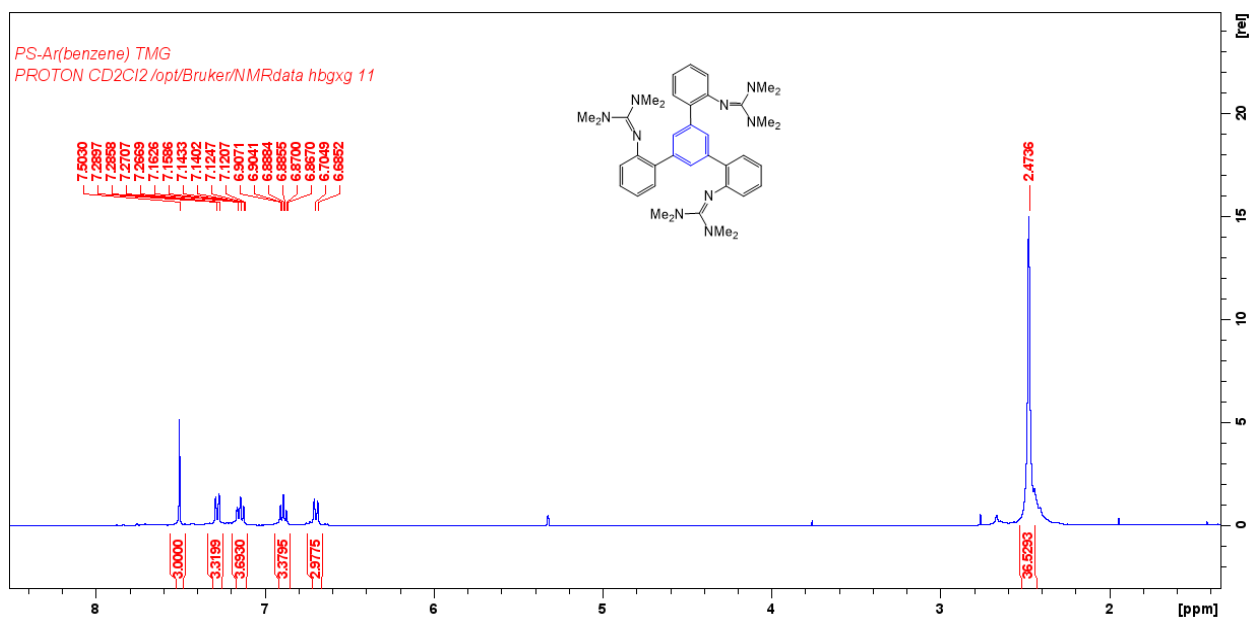
**Figure S5.** (a) Front and (b) side view of spin density profile for broken-symmetry state  $^{BS}[\text{Cu}]_{\text{NR}}$  (TPSSh/def2-TZVP/gas; Isovalue = 0.002 a.u.). The blue surface indicates excess  $\alpha$ -electron density and the red region indicates excess  $\beta$ -electron density.

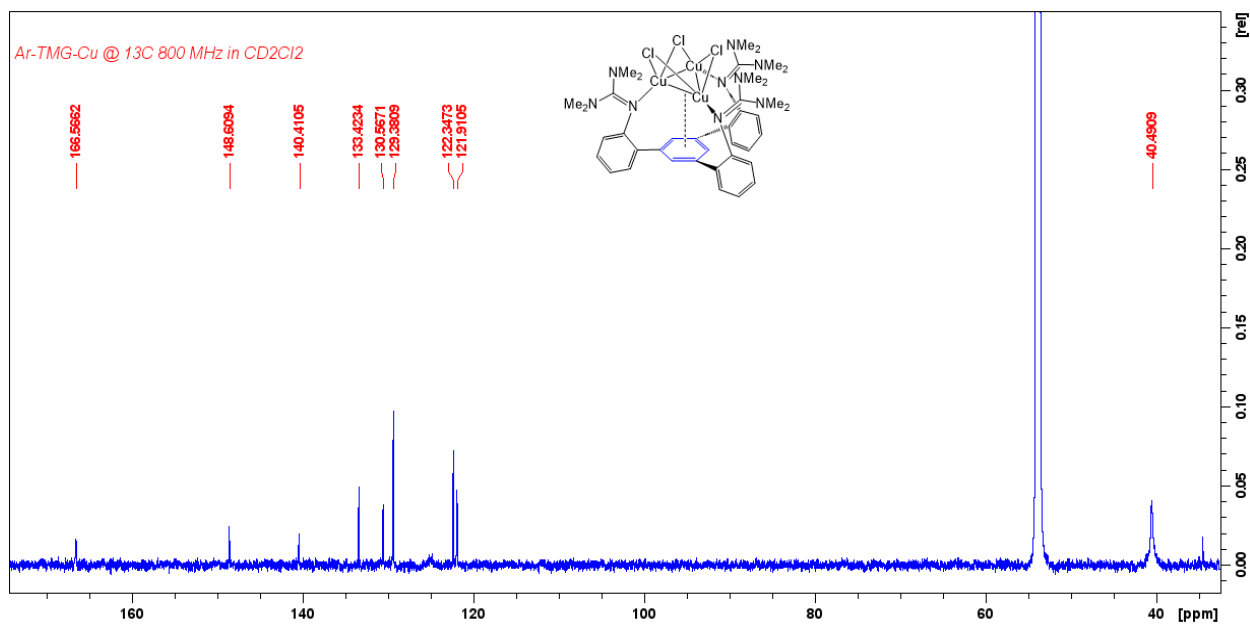
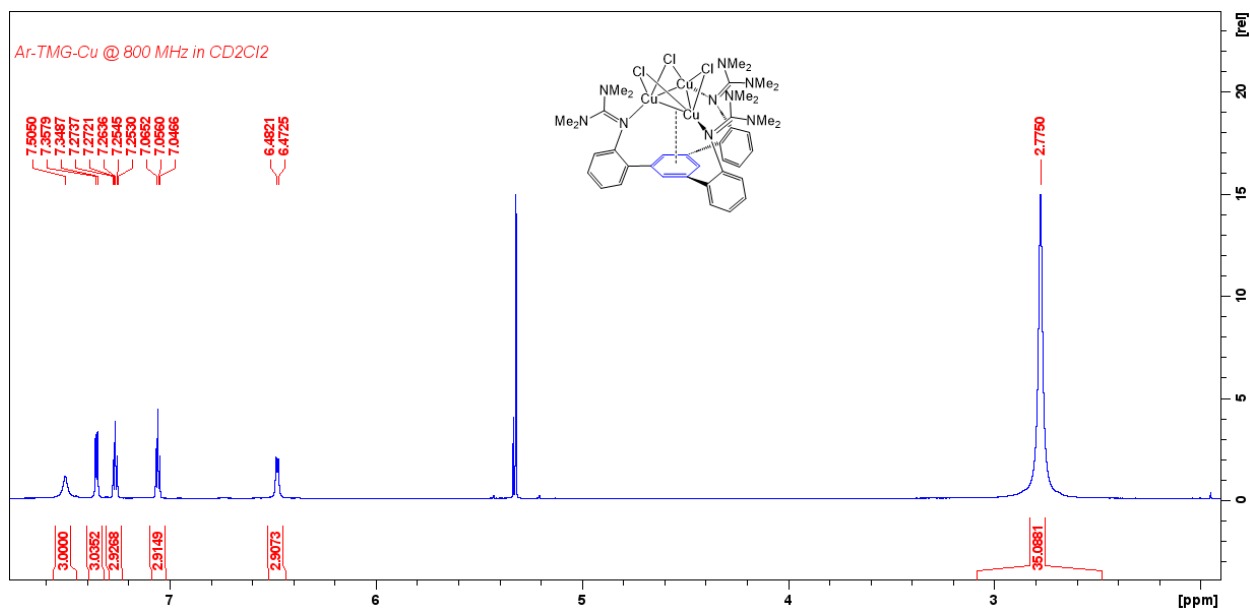
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra

## 5'-(2-aminophenyl)-[1,1':3',1''-terphenyl]-2,2''-diamine

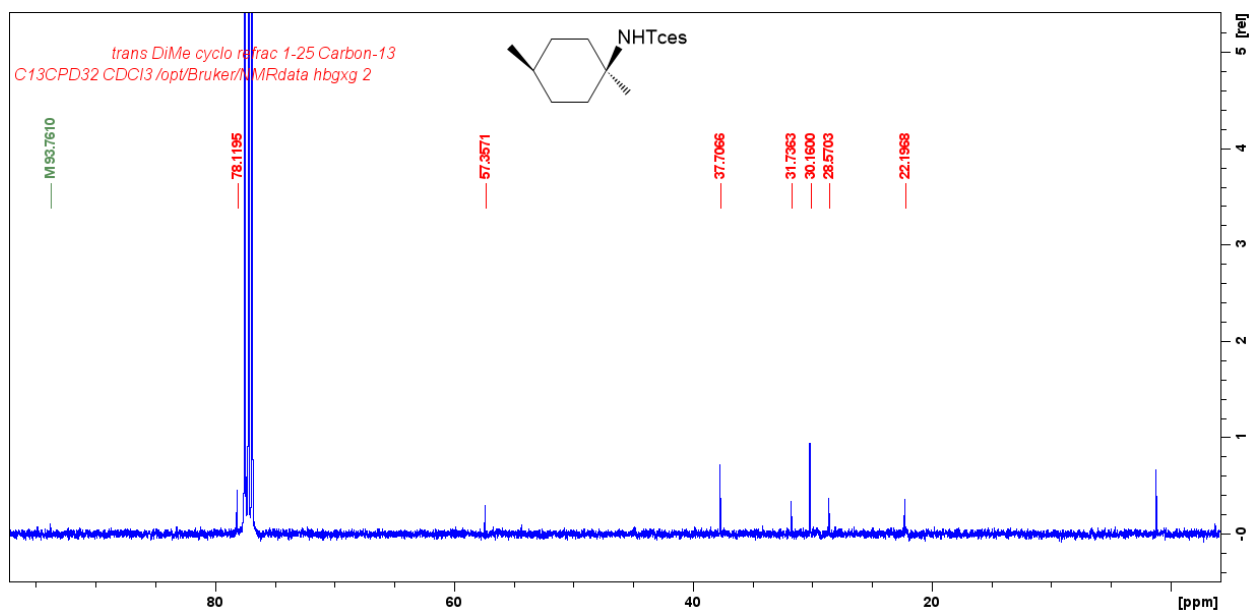
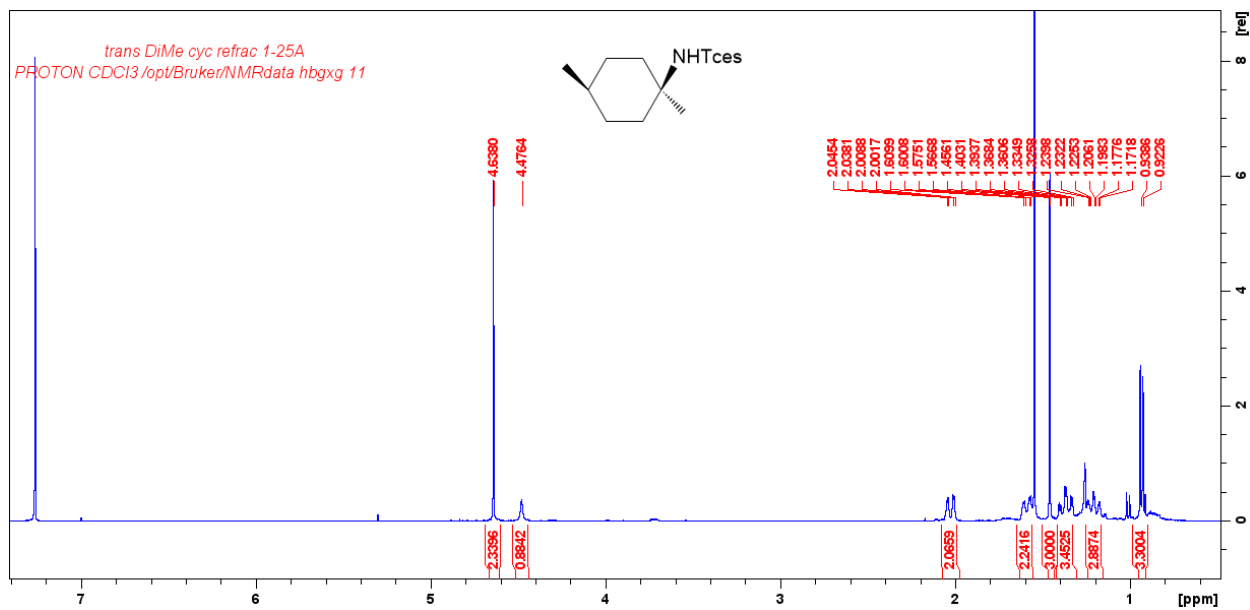


(TMG<sub>3</sub>trphen-Arene)•1.5CH<sub>2</sub>Cl<sub>2</sub>

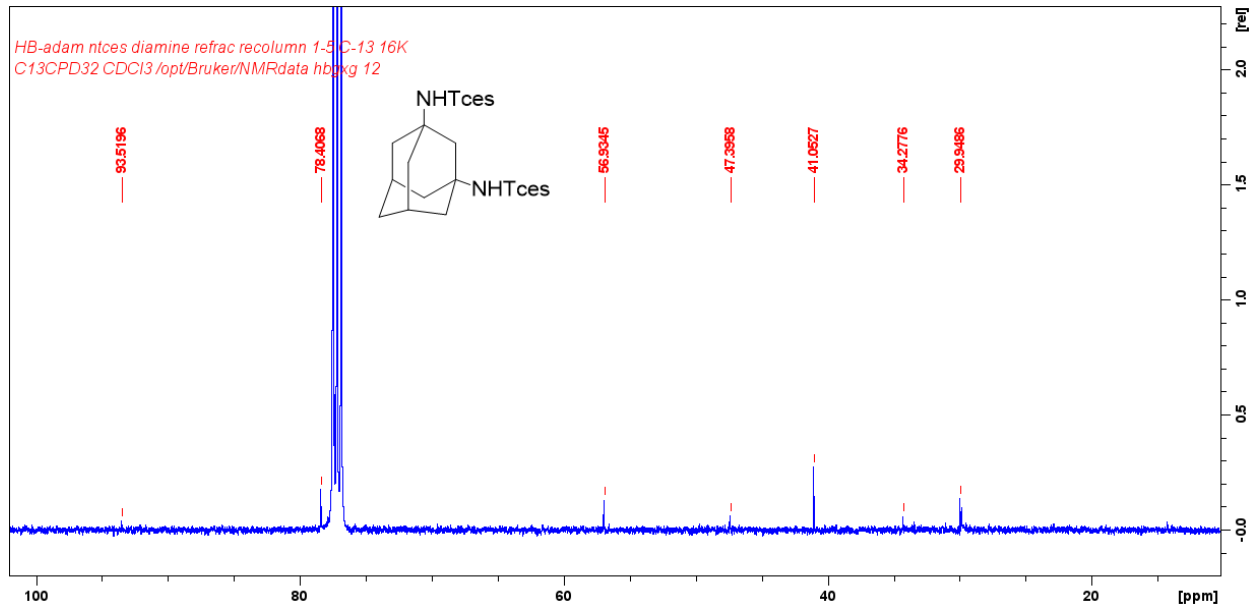
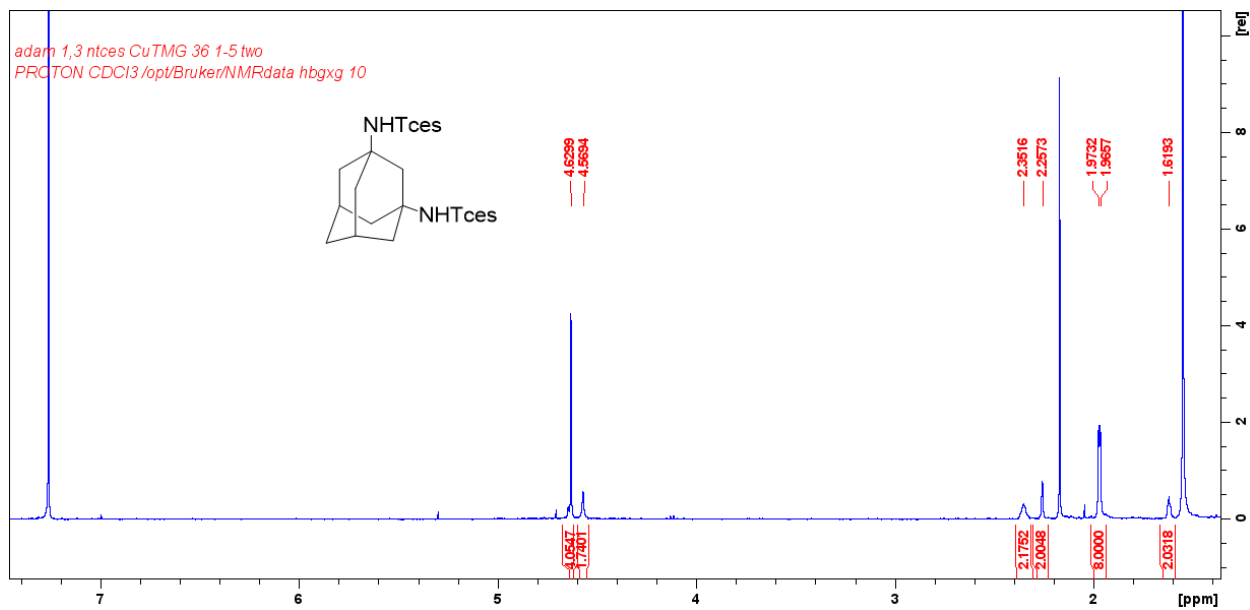




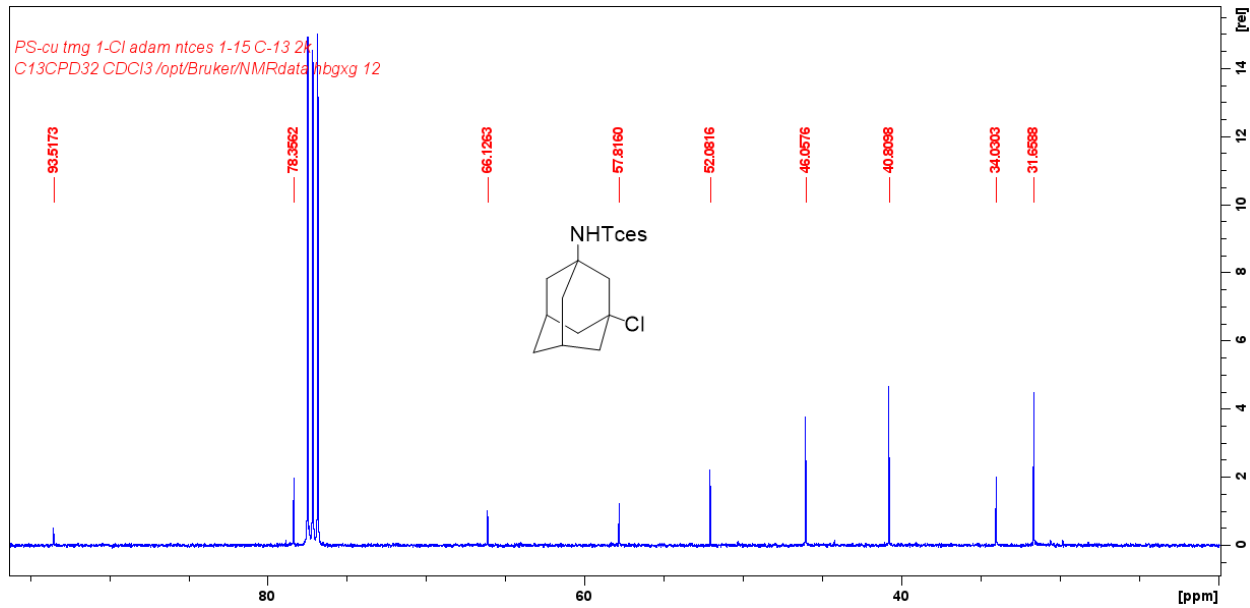
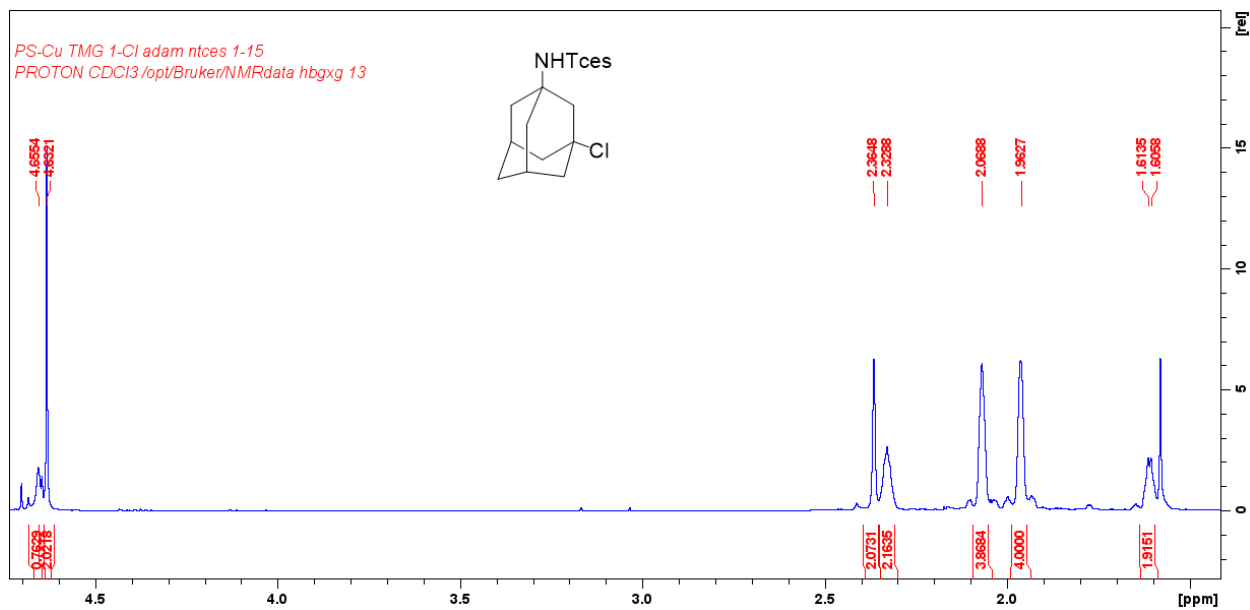
*Trans*-1,4-Me<sub>2</sub>-1-NHTces-cyclohexane



# 1,3-(NHTces)<sub>2</sub>-adamantane



# 1-NHTces-3-Cl-adamantane



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