Electronic Supplementary Material (ESI) for Chemical Communications
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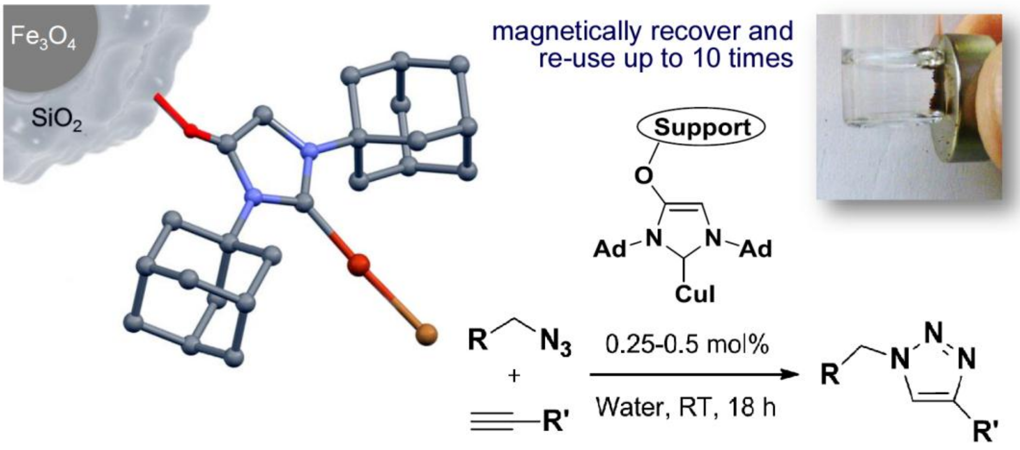
Chemical Communications

Reusable and highly active supported copper(I)-NHC catalysts for Click chemistry



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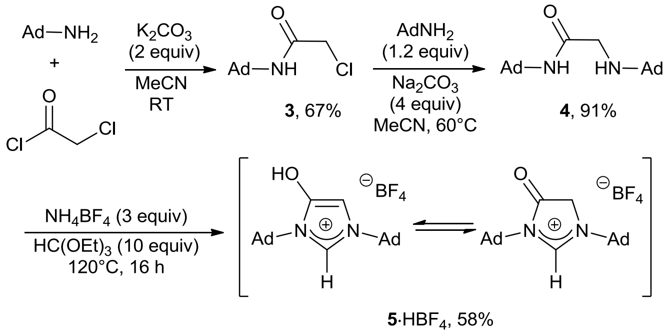
Supporting Information

1. GENERAL CONSIDERATIONS

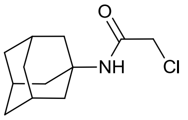
All reagents were used as received. Unless otherwise stated, all reactions were carried out in air and using technical solvents without any particular precautions to exclude moisture or oxygen. Anhydrous THF was obtained by passing the solvent through columns of molecular sieves in a solvent purification system. The silica flakes used were Geduran Si 60 (40-63 μm). ^1H NMR and ^{13}C NMR spectra were recorded on 400 MHz spectrometers at room temperature. Chemical shifts (δ) are reported in ppm with respect to tetramethylsilane (^1H NMR), or $CDCl_3$ (^{13}C NMR) as internal standards. Attribution of some NMR signals was made using quantitative carbon NMR, HMBC and HMQC experiments. All reported yields are isolated yields and in the catalytic studies are the average of at least two independent runs. Mass spectra (MS) were recorded on a Micromass Autospec Premier, Micromass LCT Premier or a VG Platform II spectrometer using EI or ESI techniques at the Mass Spectroscopy Service of Imperial College London. Elemental analysis was performed at the London Metropolitan University (UK). TEM images and EDS data were obtained using a JEOL 2010 high-resolution TEM (80-200 kV) equipped with an Oxford Instruments INCA EDS 80mm X-Max detector system. The grids used were 300 mesh gold with carbon films. ICP analyses were performed using a Perkin-Elmer 2000 DV ICP-OE spectrometer.

2. PREPARATION OF SUPPORTED CATALYSTS

2.1. SYNTHESIS OF THE LIGAND



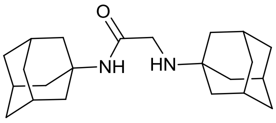
N-Chloroacetyl-1-aminoadamantane (3)



To a suspension of K_2CO_3 (3.70 g, 26.5 mmol) in acetonitrile (50 mL), 1-adamantylamine (2.0 g, 13.2 mmol) was added portion-wise. Then, chloroacetyl chloride (1.1 mL, 13.2 mmol) was introduced and the reaction mixture was stirred at room temperature overnight. The resulting precipitate was filtered off and washed with MeCN. The filtrate was concentrated under reduced pressure and the resulting residue triturated with *n*-hexane and was dried under vacuum to give the title compound as a white solid (2.01 g, 67%).

Spectroscopic data were consistent with previously reported data for this compound.[1]

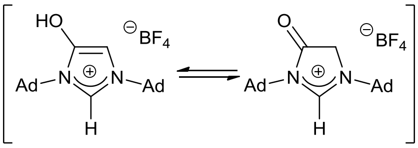
N-Adamantylacetyl-1-aminoadamantane (4)



To 1-aminoadamantane **3** (100 mg, 0.44 mmol), 1-adamantylamine (80 mg, 0.52 mmol), sodium bicarbonate (150 mg, 1.76 mmol, 4 equiv) and MeCN (2 mL) were mixed and stirred at 80°C for 18 h. Once at room temperature, the solvent was evaporated under reduced pressure and the resulting residue was dissolved in dichloromethane, washed with water and brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the title compound as a white solid (137 mg, 91%).

^1H NMR (400 MHz, $CDCl_3$): δ 7.43 (br s, 1H, NH), 3.24 (s, 2H, CH_2), 2.10 (br s, 6H, H^{Ad}), 2.03 (br s, 6H, H^{Ad}), 1.71–1.60 (m, 18H, H^{Ad}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9 (C=O), 51.0 (C(O)CH_2), 44.6 (C^{Ad}), 42.7 (CH_2^{Ad}), 41.6 (CH_2^{Ad}), 36.4 (CH_2, CH_2^{Ad}), 29.4 (CH, CH^{Ad}); HRMS (ESI) calculated for $C_{22}H_{35}N_2O$: 343.2749; found 343.2736 [$(M+H)^+$].

4-Hydroxy-1,3-di(adamantyl)imidazolinium tetrafluoroborate ($5{\cdot}HBF_4$)



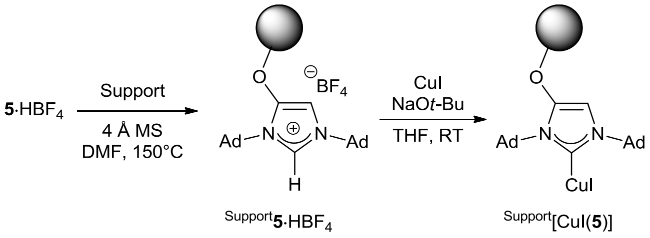
To *N*-adamantylacetyl-1-adamantane **4** (1.00 g, 2.9 mmol), ammonium tetrafluoroborate (1.88 g, 17.5 mmol) and triethylorthoformate (10 mL) were added. The mixture was stirred at 120°C for 18 h, during which the initial white suspension became orange. The resulting mixture was concentrated under reduced pressure and the obtained residue was precipitated with MeCN. The precipitate was redissolved in dichloromethane to remove any remaining ammonium tetrafluoroborate and the resulting filtrate was evaporated to give the title compound as a white solid (0.74 g, 58%).

^1H NMR (400 MHz, $CDCl_3$): δ 8.69 (br s, 1H, NCHN), 6.20 (s, 1H, C(OH)=C*H*), 4.14 (s, 2H, C(O)CH_2), 2.26 (s, 3H, H^{Ad}), 2.03 (s, 15H, H^{Ad}), 1.72–1.67 (m, 12H, H^{Ad}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3 (C=O), 164.6 (NCHN), 61.9 (C^{Ad}), 52.9 (C^{Ad}), 48.7 (CH_2^{Im}), 41.1 (CH_2^{Ad}), 40.3 (CH_2^{Ad}), 36.3 (CH_2^{Ad}), 35.5 (CH_2^{Ad}), 29.4 (CH^{Ad}), 29.3 (CH^{Ad}); HRMS (ESI) calculated for $C_{23}H_{33}N_2OBF_4$: 353.2593; found 353.9654 [$(M+H)^+$].

2.2. SUPPORT PREPARATION

Silica nanoparticles,[2] and the silica coated magnetic nanoparticles[3] were prepared following procedures reported in the literature.

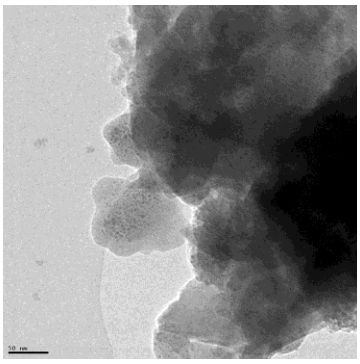
2.3. IMMOBILISATION OF NHC LIGAND AND COMPLEX PREPARATION

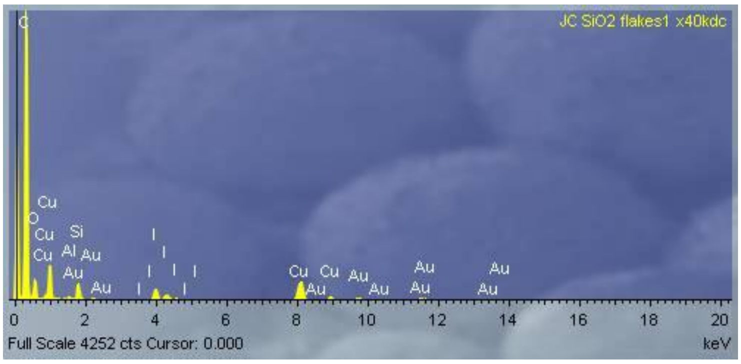


2.3.a. Silica Flakes as Support

$^{\text{Si-FK}}$5·HBF$_4$: Silica flakes (35 mg), **5**·HBF$_4$ (20 mg, 0.045 mmol), 4 Å molecular sieves and DMF (1 mL) were placed in a round bottomed flask and the suspension was stirred at 150°C overnight. The resulting mixture was allowed to cool before the molecular sieves were removed and the flakes then washed with DCM. The flakes were washed with more DCM and dried under vacuum to give a light brown solid (52 mg, 95% mass balance).

$^{\text{Si-FK}}$[CuI(5)]: $^{\text{Si-FK}}$**5**·HBF$_4$ (50 mg), CuI (8 mg, 0.045 mmol) and NaO*t*-Bu (4 mg, 0.045 mmol) were placed in a round bottomed flask, flushed with N_2, then suspended in dry THF (2 mL) and stirred for 18 h at room temperature. The resulting mixture was centrifuged (2500 rpm, 30 min), DCM added (20 mL), centrifuged again and the liquors removed. This process was repeated three times before drying the particles overnight under vacuum (55 mg, 95% mass balance).



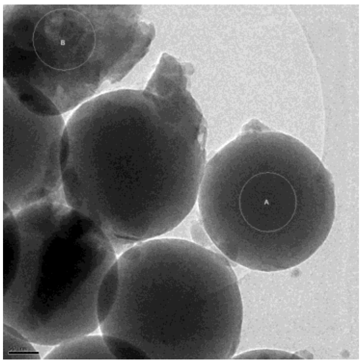


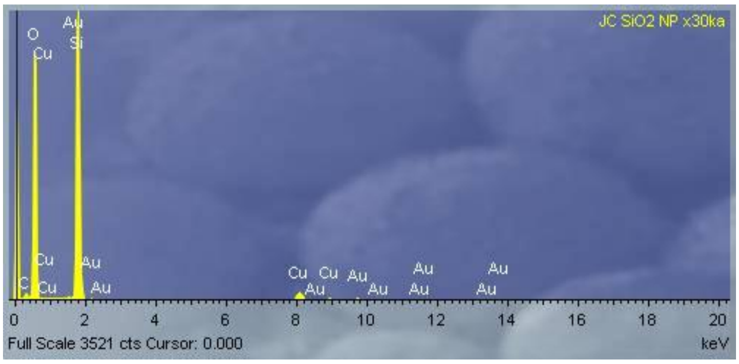
TEM (above left) showed that the silica flakes were >100 nm in size. EDS analysis (above right) revealed the presence of copper, iodine, silica and oxygen (carbon films on 300 mesh gold grids). Infrared data were not diagnostic due to the dominant features of silica. Insolubility prevented analysis by NMR.

2.3.b. Silica Nanoparticles as Support

$^{\text{Si-NP}}$5·HBF$_4$: Silica nanoparticles (100 mg), **5**·HBF$_4$ (20 mg, 0.045 mmol), 4 Å molecular sieves and DMF (1 mL) were placed in a round bottomed flask and the suspension was stirred at 150°C overnight. The reaction mixture was allowed to cool before the molecular sieves were removed. The resultant material was suspended in DCM, centrifuged (2500 rpm, 30 min) and the DCM then decanted (process repeated twice). The solid was then suspended in ethanol (25 mL), centrifuged (2500 rpm, 30 min) and the EtOH decanted. The resulting off-white product was dried under vacuum overnight (119 mg, 99% mass balance).

$^{\text{Si-NP}}$[CuI(5)]: $^{\text{Si-NP}}$**5**·HBF_4 (125 mg), CuI (8 mg, 0.045 mmol) and NaO*t*-Bu (4 mg, 0.045 mmol), were placed in a round bottomed flask, flushed with N_2, then suspended in dry THF (2 mL) and stirred for 18 h at room temperature. The resulting mixture was centrifuged (2500 rpm, 30 min), DCM added (20 mL), centrifuged and the liquors removed. This process was repeated three times before drying the particles overnight under vacuum (134 mg, 98% mass balance).



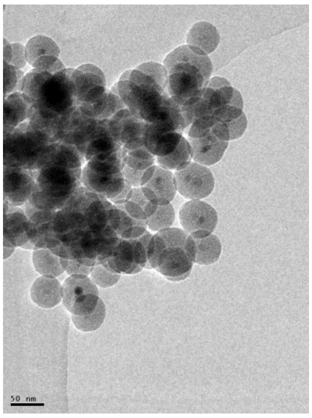


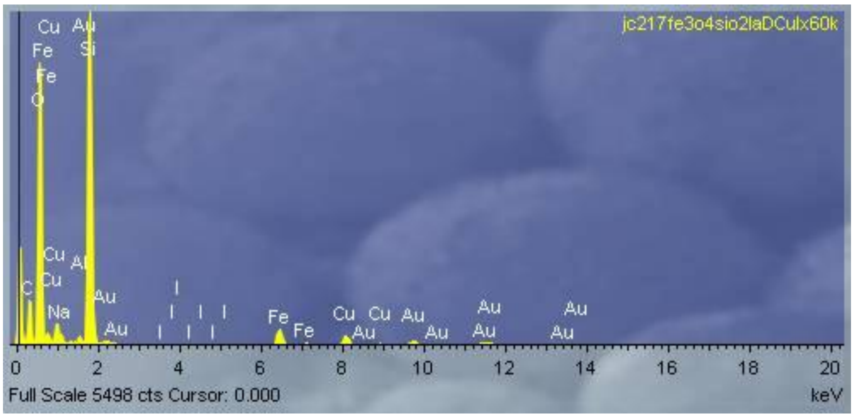
TEM (above left) showed that the silica nanoparticles were 150.4 (±5.3) nm in diameter. EDS analysis (above right) revealed the presence of copper, silica and oxygen (carbon films on 300 mesh gold grids). The presence of iodine could not be determined unequivocally. Infrared data were not diagnostic due to the dominant features of silica. Insolubility prevented analysis by NMR. ICP (dispersed in 50 mL acid solution) showed copper content of 2.025 ppm for 10 mg of sample, which equates to 1.595 x 10^{-4} mmol^{Cu}/mg of material.

2.3.c. Silica-Coated Magnetite Nanoparticles as Support

$^{\text{Fe3O4/Si}}$5·HBF_4: A suspension of magnetite-silica nanoparticles (200 mg), **5**·HBF_4 (100 mg, 0.23 mmol), 4 Å molecular sieves and DMF (1 mL) was stirred on an orbital stirrer under reflux for 16 h. The resulting mixture was allowed to cool and the molecular sieves were removed. DCM was then added and the suspension centrifuged (2500 rpm, 30 min) before decanting the solvents (process repeated twice). The resulting solid was then washed with EtOH (25 mL), centrifuged (2500 rpm, 30 min) and the EtOH then decanted. The resulting brown solid was dried under vacuum overnight (232 mg, 77% mass balance).

$^{\text{Fe3O4/Si}}$[CuI(5)]: $^{\text{Fe3O4/Si}}$**5**·HBF_4 (230 mg), CuI (20 mg, 0.11 mmol) and NaO*t*-Bu (11 mg, 0.11 mmol), were placed in a round bottomed flask, flushed with N_2, then suspended in dry THF (10 mL) and stirred for 18 h at room temperature. The resulting mixture was centrifuged (2500 rpm, 30 min) and the solvent decanted. After addition of DCM (20 mL), the suspension was centrifuged (2500 rpm, 15 min) and then decanted. This process was repeated three times before drying the particles overnight under vacuum (240 mg, 96 % mass balance).





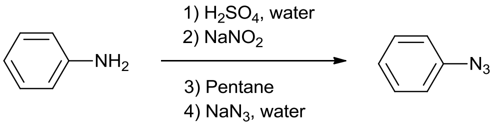
TEM (above left) showed that the Cu-functionalised silica-magnetite nanoparticles were 47.7 (±3.8) nm in diameter. EDS analysis (above right) revealed the presence of copper, iodine, iron, silica and oxygen (carbon films on 300 mesh gold grids). Infrared data were not diagnostic due to the dominant features of silica. Insolubility prevented analysis by NMR. ICP (dispersed in 50 mL acid solution) showed copper content of 5.107 ppm for 12.4 mg of sample, which equates to 3.240 x 10^{-4} mmol^{Cu}/mg of material.

3. SYNTHESIS OF AZIDES (6)

Benzyl and alkyl azides were synthesised from the corresponding bromides by nucleophilic substitution with sodium azide in DMSO (eq. 1).[4]

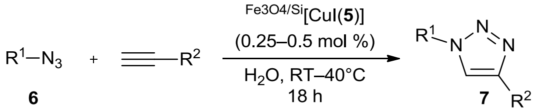
$$R^1\text{—Br} \xrightarrow[\text{DMSO, RT}]{\text{NaN}_3} R^1\text{—N}_3 \qquad (1)$$

Benzyl azide **6a**,[4] 1-(azidomethyl)-3,5-bis(trifluoromethyl)benzene **6b**,[5] 1-(azidomethyl)-4-nitrobenzene **6c**,[6] 1-(azidomethyl)-4-methoxybenzene **6d**,[7] (1-azidoethyl)benzene **6e**,[4] 3-(azidoprop-1-en-yl)benzene **6f**,[8] 1-azidohexane **6h**,[9] 2-(2-azidoethyl)-1,3-dioxolane **6i**,[10] and 2-diisopropylazidoethyl **6j**[11] are known in the literature and the spectroscopic data for all these compounds were in good agreement with the reported data. Phenyl azide **6g** was prepared following a previously reported combination[12] of the methods described by Nölting[13] and Lindsay[14] (eq. 2).

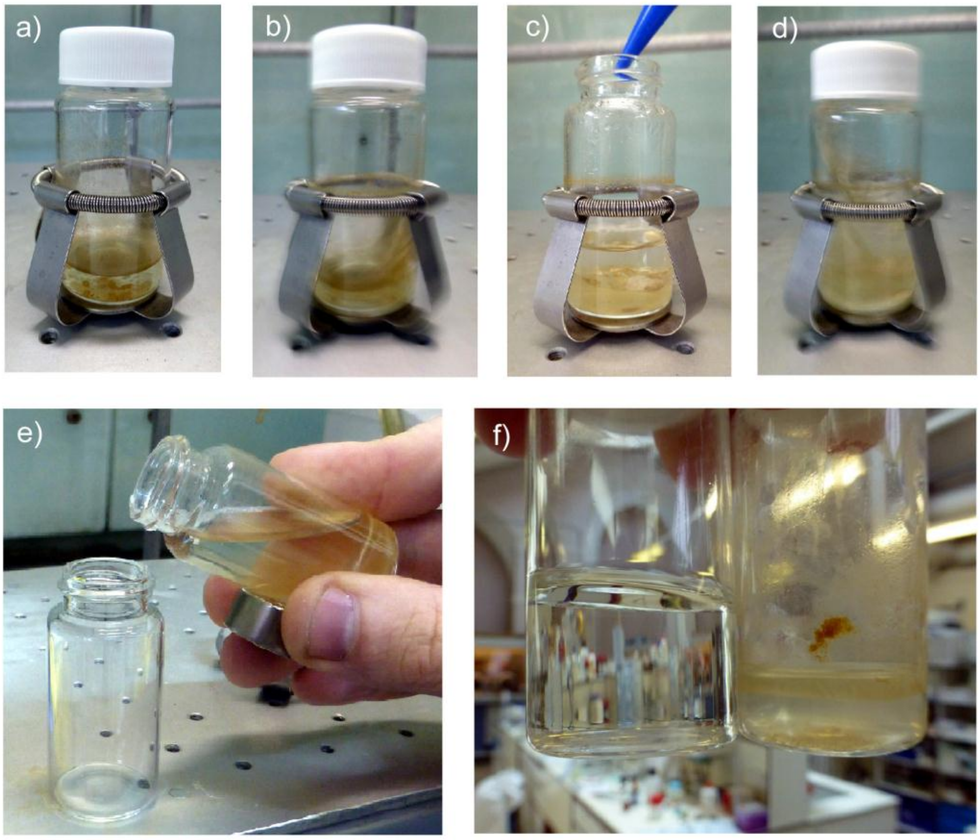


(2)

4. SYNTHESIS OF 1,2,3-TRIAZOLES (7)

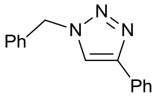


General Procedure: A vial fitted with a screw cap was charged with $^{Fe3O4/Si}$[CuI(**5**)] (8 mg, 0.25 mol % or 16 mg, 0.5 mol %), water (1 mL), azide (1 mmol) and alkyne (1 mmol). The reaction was stirred or shaken vigorously at room temperature or 40°C for 18 h, EtOAc was added and the organic layer was decanted using a magnet to separate the catalyst. More EtOAc was added and the organic washings were combined and washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the expected triazoles. The reaction products were found to be at least 95% pure by ^{1}H NMR. Reported yields are isolated yields and are the average of at least two independent runs. Some representative images of the process are shown below.



a) Catalyst $^{Fe3O4/Si}$[CuI(**5**)] in water with azide and alkyne; b) reaction shaken overnight; c) ethyl acetate added to dissolve triazole formed; d) vial shaken for a few minutes; e) organic layer decanted using hand-held magnet; f) organic and aqueous components.

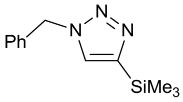
1-Benzyl-4-phenyl-1*H*-[1,2,3]triazole (7a)



Using the general procedure from 62 μL (0.5 mmol) of benzyl azide **6a** and 55 μL (0.5 mmol) of phenylacetylene with 0.25 mol % [Cu] at room temperature, 0.108 g of the title compound was isolated as an off-white solid (92%).

Spectroscopic data for the title compound were consistent with those reported previously.[15]

1-Benzyl-4-(trimethylsilyl)-1*H*-[1,2,3]triazole (7b)

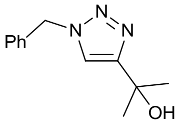


A) Using the general procedure from 124 μL of benzyl azide **6a** and 128 μL of trimethylsilylacetylene with 0.5 mol % [Cu] at room temperature, 0.185 g of the title compound was isolated as an off white solid after washing with pentane (80%).

B) Using the general procedure from 124 μL of benzyl azide **6a** and 128 μL of trimethylsilylacetylene with 0.25 mol % [Cu] at 40°C, 0.191 g of the title compound was isolated as an off white solid after washing with pentane (83%).

Spectroscopic data for the title compound were consistent with those reported previously.[12]

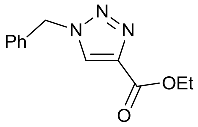
2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-ol (7c)



Using the general procedure from 124 μL of benzyl azide **6a** and 98 μL of 2-methylbut-3-yne-2-ol with 0.25 mol % [Cu] at 40°C, 0.193 g of the title compound was isolated as an off-white solid after washing with pentane (89%).

Spectroscopic data for the title compound were consistent with those reported previously. [12]

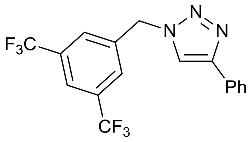
Ethyl 1-(benzyl)-1*H*-1,2,3-triazole-4-carboxylate (7d)



Using the general procedure from 124 μL of benzyl azide **6a** and 100 μL of ethyl propiolate with 0.25 mol % [Cu] at 40°C, 0.221 g of the title compound was isolated as a off-white solid (97% yield).

Spectroscopic data for the title compound were consistent with those reported previously.[16]

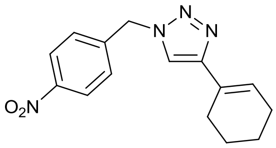
1-[3,5-Bis(trifluoromethyl)benzyl]-4-phenyl-1H-[1,2,3]triazole (7e)



Using the general procedure from 269 mg of azide **6b** and 110 μL of phenylacetylene with 0.25 mol % [Cu] at 40°C, 0.165 g of the title compound was isolated as a white solid (89%).

Spectroscopic data for the title compound were consistent with those reported previously.[5]

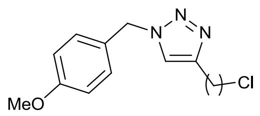
4-Cyclohexenyl-1-(4-nitrobenzyl)-1H-1,2,3-triazole (7f)



Using the general procedure from 0.178 g of azide **6c** and 118 μL of 1-ethynylcyclohexene with 0.25 mol % [Cu] at 40°C, 0.185 g of the title compound was isolated as an off white solid (65%).

Spectroscopic data for the title compound were consistent with those reported previously.[6]

4-(3-Chloropropyl)-1-(4-methoxybenzyl)-1H-[1,2,3]triazole (7g)

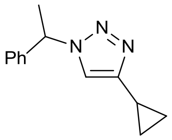


A) Using the general procedure from 0.163 g of azide **6d** and 106 μL of 1-chloropent-4-yne with 0.5 mol % [Cu] at room temperature, 0.255 g of the title compound was isolated as an off-white solid after washing with pentane (96%).

B) Using the general procedure from 0.0815 g of azide **6d** and 53 μL of 1-chloropent-4-yne with 0.25 mol % [Cu] at 40°C, 0.107 g of the title compound was isolated as an off-white solid (81%).

Spectroscopic data for the title compound were consistent with those reported previously.[16]

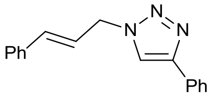
4-Cyclopropyl-1-(1-phenylethyl)-1H-[1,2,3]triazole (7h)



Using the general procedure from 0.147 g of azide **6e** and 84 μL of ethynylcyclopropane with 0.25 mol % [Cu] at 40°C, 0.180 g of the title compound was isolated as a white solid (84%).

Spectroscopic data for the title compound were consistent with those reported previously.[16]

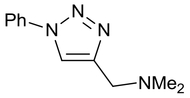
4-Phenyl-1-(3-phenyl-2-propenyl)-1*H*-[1,2,3]triazole (7i)



Using the general procedure from 0.080 g (0.5 mmol) of cinnamyl azide **6f** and 55 μL (0.5 mmol) of phenylacetylene with 0.25 mol % [Cu] at 40°C, 0.116 g of the title compound was isolated as an off-white solid (89%).

Spectroscopic data for the title compound were consistent with those reported previously.[17]

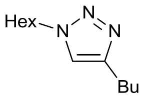
(1-Phenyl-1H-[1,2,3]triazol-4-ylmethyl)dimethylamine (7j)



Using the general procedure from 60 mg (0.5 mmol) of phenyl azide **6g** and 84 μL (0.5 mmol) of 1-dimethylamino-2-propyne with 0.25 mol % [Cu] at room temperature, 0.088 g of the title compound was isolated as an off-white solid (87%).

Spectroscopic data for the title compound were consistent with those reported previously.[18]

1-Hexyl-4-butyl-1*H*-[1,2,3]triazole (7k)

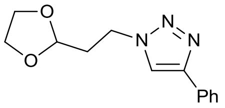


Using the general procedure from 127 mg of 1-azidohexane **6h** and 118 μL of 1-hexyne with 0.25 mol % [Cu] at room temperature, 0.195 g of the title compound was isolated as a light yellow oil (93%).

Spectroscopic data for the title compound were consistent with those reported previously.[19]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (s, 1H, H^{Ar}), 4.34 (s br, 2H, CH_2N), 2.73 (s br, 2H, $=CCH_2$), 1.90 (s br, 2H, CH_2), 1.69 (s br, 2H, CH_2), 1.43–1.32 (m, 8H, CH_2), 0.95 (t, *J* = 5.8 Hz, 3H, CH_3), 0.89 (t, *J* = 5.8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9 (N*C*=), 120.7 (N*C*H=), 50.1 (*C*H_2N), 31.5 (*C*H_2C=), 31.1 (CH_2), 30.2 (CH_2), 26.1 (CH_2), 25.3 (CH_2), 22.3 (CH_2), 13.9 (CH_3), 13.8 (CH_3); HRMS (ESI) calculated for $C_{12}H_{24}N_3$ 209.1892, found 209.1887 [$(M+H)^+$].

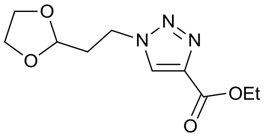
1-(2-(1,3-Dioxolan-2-yl)ethyl)-4-phenyl-1*H*-[1,2,3]triazole (7l)



Using the general procedure from 0.143 g of azide **6i** and 110 µL of phenylacetylene with 0.25 mol % [Cu] at 40 °C, 0.215 g of the title compound was isolated as off-white solid (88%).

Spectroscopic data for the title compound were consistent with those reported previously.[6]

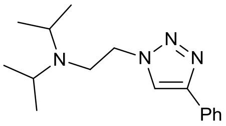
Ethyl 1-(2-(1,3-dioxolan-2-yl)ethyl)-1*H*-1,2,3-triazole-4-carboxylate (7m)



Using the general procedure from 0.072 g (0.5 mmol) of 2 azide **6i** and 50 µL (0.5 mmol) of ethyl propiolate with 0.25 mol % [Cu] at 40°C, 0.117 g of the title compound was isolated as a light yellow oil (98% yield).

Spectroscopic data for the title compound were consistent with those reported previously.[5]

1-(2-Diisopropylaminoethyl)-4-phenyl-1*H*-[1,2,3]triazole (7n)

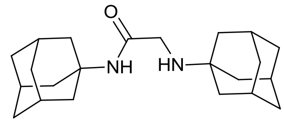


Using the general procedure from 0.060 g (0.5 mmol) of azide **6j** and 55 µL (0.5 mmol) of phenylacetylene with 0.25 mol % [Cu] at room temperature, 0.116 g of the title compound was isolated as an yellow oil (87%).

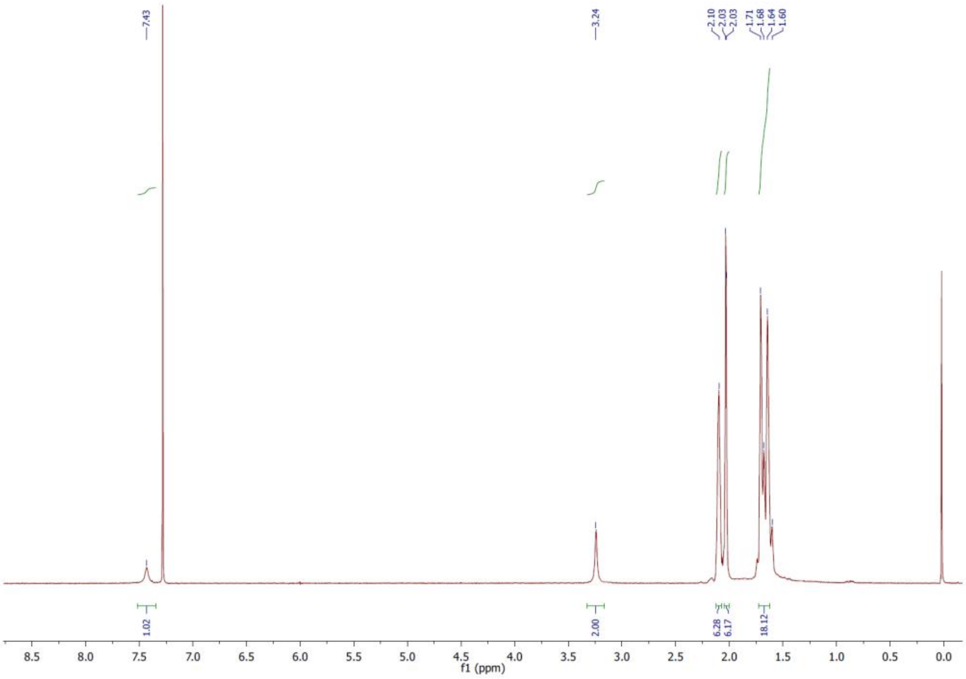
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.81 (m, 3H, H^{Ar}), 7.45 (t, *J* = 6.4 Hz, 2H, H^{Ar}), 7.35 (t, *J* = 6.4 Hz, 1H, H^{Ar}), 4.38 (t, *J* = 6.5 Hz, 2H, CH_2), 3.04 (septet, *J* = 6.5 Hz, 2H, $C\mathit{H}(CH_3)_2$), 2.95 (t, *J* = 6.5 Hz, 2H, CH_2), 0.99 (d, *J* = 6.5 Hz, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1 (NCH=*C*), 130.9 (C^{Ar}), 128.8 (CH^{Ar}), 127.9 (CH^{Ar}), 125.7 (CH^{Ar}), 120.8 (N*C*H=), 51.2 (*C*H_2N), 48.7 (*C*HN), 45.7 (*C*H_2N), 20.8 (CH_3). HRMS calculated for $C_{16}H_{25}N_4$: 273.2079; found 273.2086 [$(M+H)^+$].

5. NMR SPECTRA OF NEW COMPOUNDS

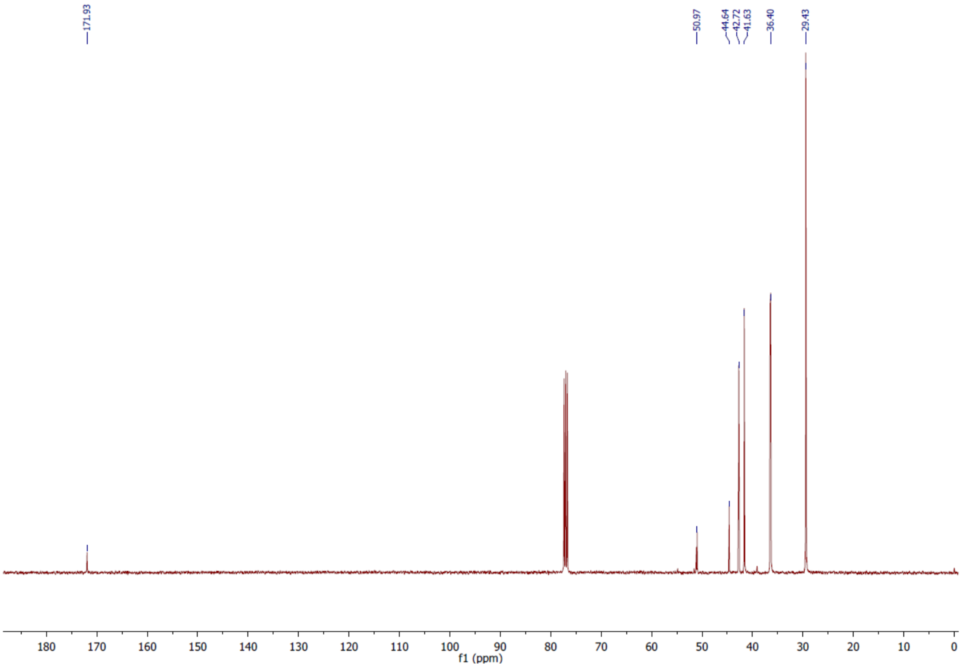
N-Adamantylacetyl-1-aminoadamantane (4)



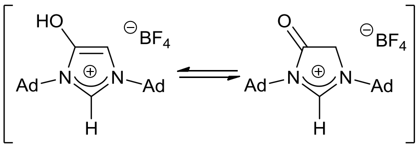
^{1}H NMR of **4** ($CDCl_3$):



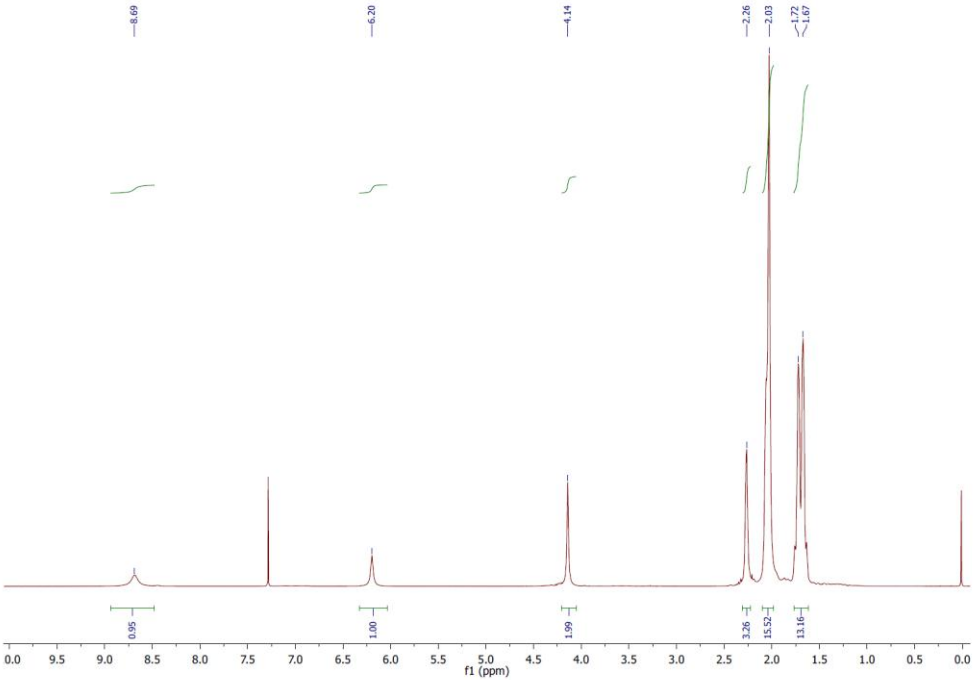
^{13}C NMR of **4** ($CDCl_3$):



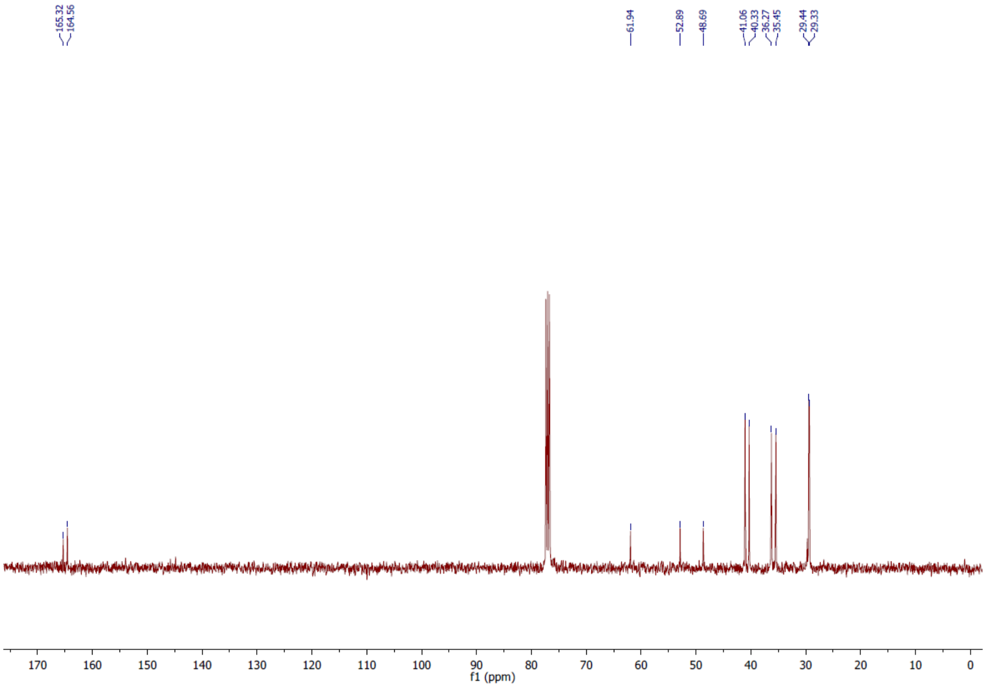
4-Hydroxy-1,3-di(adamantyl)imidazolinium tetrafluoroborate (5·HBF_4)



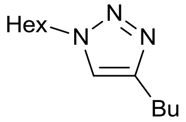
^{1}H NMR of **5**·HBF_4 ($CDCl_3$):



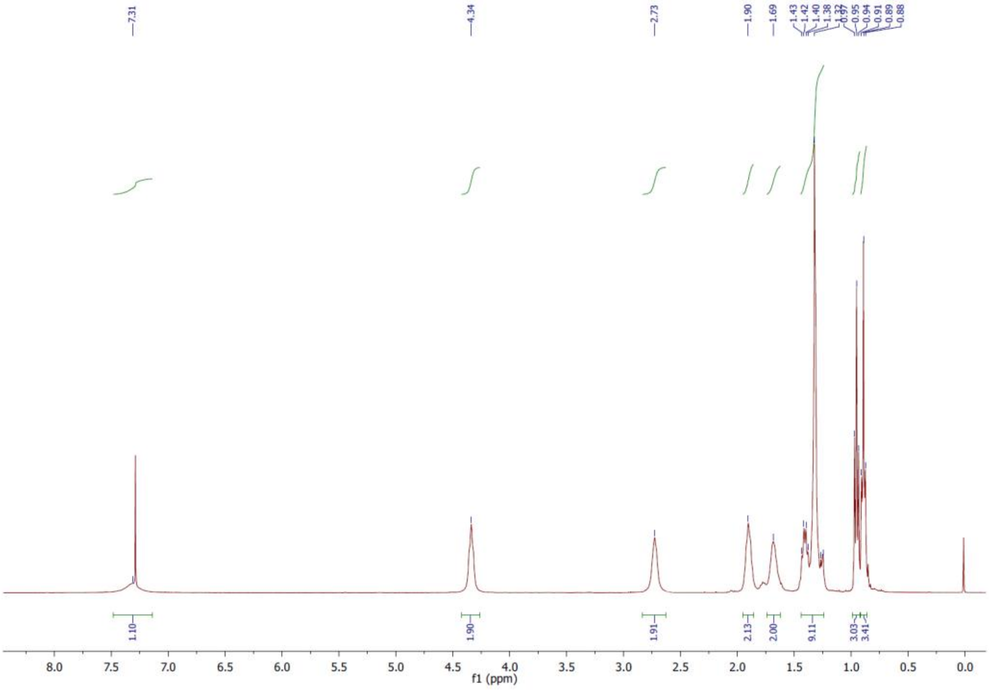
^{13}C NMR of **5**·HBF_4 ($CDCl_3$):



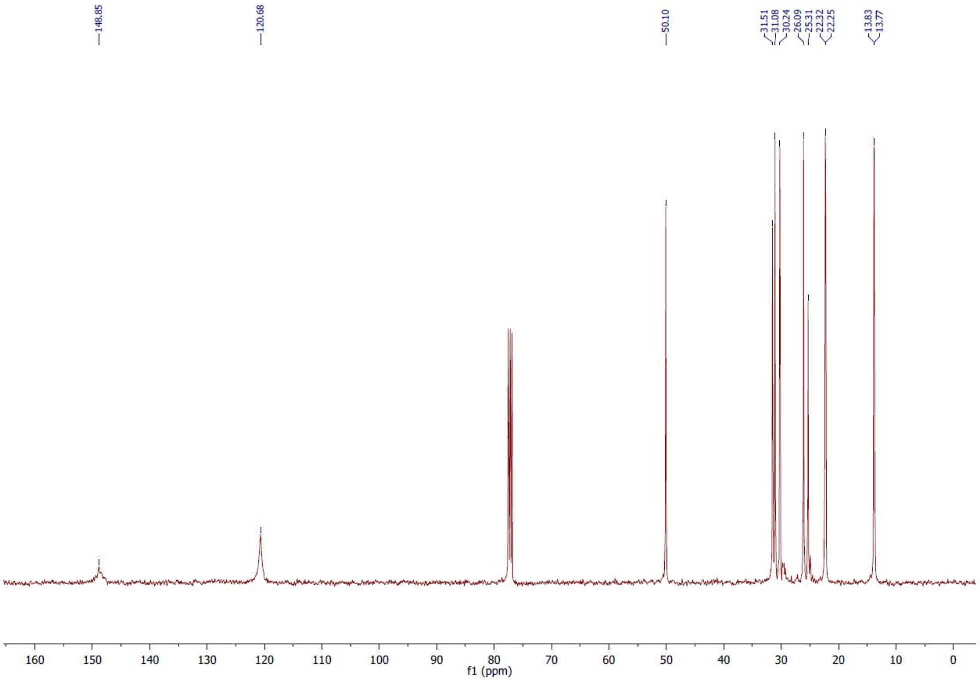
1-Hexyl-4-butyl-1*H*-[1,2,3]triazole (7k)



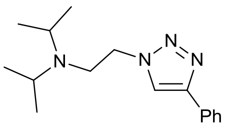
^{1}H NMR of **7k** ($CDCl_3$):



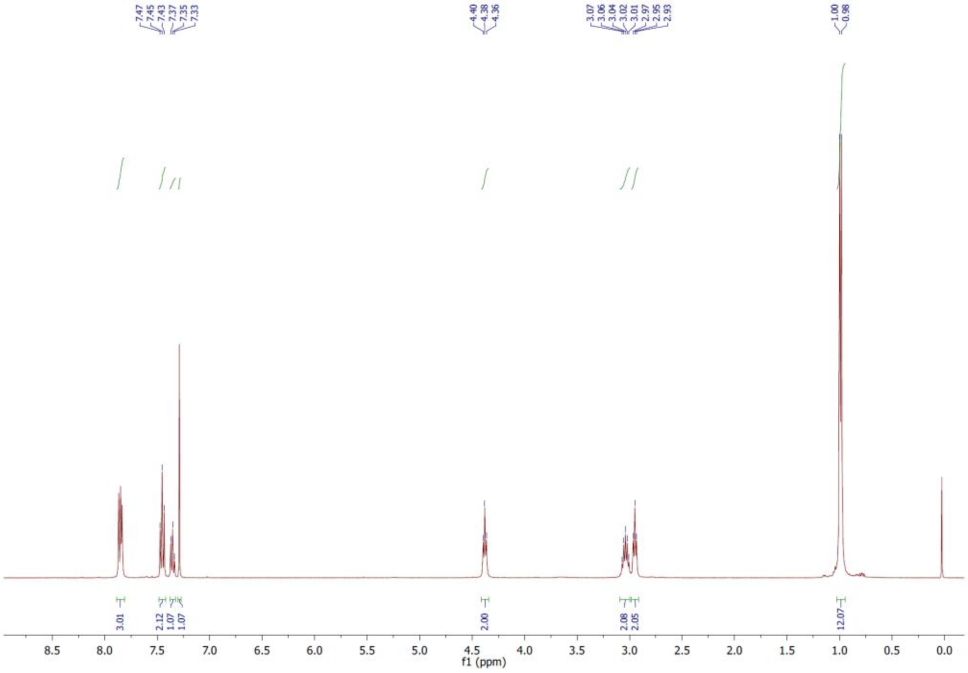
^{13}C NMR of **7k** ($CDCl_3$):



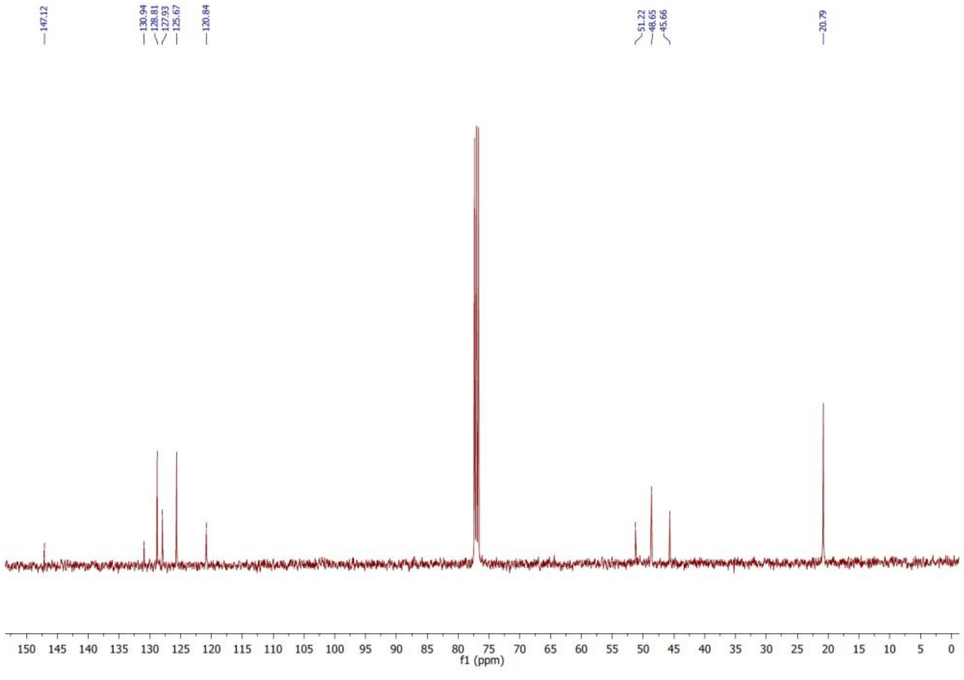
1-(2-Diisopropylaminoethyl)-4-phenyl-1*H*-[1,2,3]triazole (7n)



^{1}H NMR of **7n** (CDCl$_3$):



^{1}H NMR of **7n** (CDCl$_3$):



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