Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

N-heterocyclic silylene stabilized monocordinated copper(I)-arene cationic complexes and their application in Click chemistry

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Contents

S1. Experimental Details:

All experiments were carried out under an atmosphere of dry argon or in vaccuo using standard Schlenk technique and in a dinitrogen filled MBRAUN MB 150-G1 glovebox. The solvents used were purified by MBRAUN solvent purification system MB SPS-800. All the chemicals purchased from Aldrich were used without further purification. ^{1}H, ^{13}C,^{29}Si and ^{19}F NMR spectra were recorded with Bruker 400 MHz spectrometer, using $CDCl_3$ as solvent with an external standard ($SiMe_4$ for ^{1}H, ^{13}C, ^{29}Si and CHF_3 for ^{19}F). Concentrated solution of the samples in $CDCl_3$ were sealed off in a NMR tube for measurement. Mass spectra were recorded using AB Sciex, 4800 plus MALDI TOF/TOF.

Synthesis of 2:

$AgSbF_6$ (0.171g, 0.5 mmol) was dissolved in DCM and added to the solution of **1** (0.295g, 0.25 mmol) in toluene. It was stirred for overnight at room temperature. AgBr was precipitated out from the reaction mixture was filtered off and the volume was reduced to 15 mL and kept it at 0^{o}C. The colorless, block shaped crystals suitable for x-ray analysis was observed after one day. Yield: 0.252g (61%). Mp: 134-139 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 0.29 (*s*, 9H, Si*Me*$_3$), 0.41 (*s*, 9H, Si*Me*$_3$), 1.19 (*s*, 18H, C*Me*$_3$), 2.51 (*s*, 3H, C*H*$_{3,\text{toluene}}$), 7.32-7.38 (*m*, 2H, Ph), 7.46-7.53 (*m*, 4H, Ph), 7.55-7.60 (*m*, 3H, Ph), 7.66-7.70 (*m*, 1H, Ph) ppm. $^{13}C\{^{1}H\}$ NMR (100.613 MHz, $CDCl_3$, 298 K): δ 4.56 (Si*Me*$_3$), 5.93 (Si*Me*$_3$), 21.62 (*C*H$_{3,\text{toluene}}$), 31.70 (C*Me*$_3$), 54.93 (*C*Me$_3$), 121.33, 121.62, 125.20, 125.41, 127.30, 127.48, 128.05, 128.12, 128.18, 129.16, 129.76, 131.21 (Ph-*C*), 170.01 (N*C*N) ppm. $^{29}Si\{^{1}H\}$ NMR (79.495 MHz, $CDCl_3$, 298 K): δ 7.52 (*Si*Me$_3$), 6.72 (*Si*Me$_3$), 2.28 (*Si*N(SiMe$_3$)$_2$) ppm. $^{19}F\{^{1}H\}$ NMR (376.49 MHz, $CDCl_3$, 298): δ -162.88 ppm. MALDI: *m/z* $[C_{29}H_{52}CuN_3Si_3]^{+}$: 482.20 [M-Me$C_6H_5$]. Anal Calcd: C, 42.15; H, 6.34; N, 5.09. Found: C, 42.24; H, 6.44; N, 5.27.

Synthesis of 3:

$AgSbF_6$ (0.171g, 0.5 mmol) was dissolved in DCM and added to the solution of **1** (0.295g, 0.25 mmol) in *m*-xylene. It was stirred overnight at room temperature. The solution was filtered to separate AgBr, concentrated to 10 mL and kept it at 0°C overnight to afford colorless crystals of 3. Yield: 0.280g (67%). Mp: 108-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 0.29 (*s*, 9H, Si*Me*$_3$), 0.47 (*s*, 9H, Si*Me*$_3$), 1.25 (*s*, 18H, C*Me*$_3$), 2.28 (*s*, 6H, C$H_{3,m\text{-xylene}}$), 6.94-7.02 (*m*, 2H, Ph), 7.37-7.53 (m, 7H, Ph) ppm. ^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$, 298 K): δ 3.83 (Si*Me*$_3$), 5.22 (Si*Me*$_3$), 20.33 (*Me*$_2$C$_6$H$_4$), 30.86 (C*Me*$_3$), 53.80 (*C*Me$_3$), 125.58, 126.55, 127.23, 127.51, 127.71, 127.89, 128.16, 128.95, 129.23, 129.99, 130.35 (Ph-*C*), 167.68 (N*C*N) ppm. ^{29}Si{^{1}H} NMR (79.495 MHz, $CDCl_3$, 298 K): δ 7.49 (*Si*Me$_3$) (marched two SiMe$_3$ peak to give a broad peak), 2.80 (*Si*N(SiMe$_3$)$_2$) ppm. ^{19}F{^{1}H} NMR (376.49 MHz, $CDCl_3$, 298): δ -178.35 (br) ppm. MALDI: *m/z* $[C_{30}H_{54}CuN_3Si_3]^+$: 482.25 [M-Me$_2C_6H_4$]. Anal Calcd: C, 42.88; H, 6.48; N, 5.00. Found: C, 42.92; H, 6.62; N, 4.93.

Synthesis of 5:

$AgSbF_6$ (0.171g, 0.5 mmol) was dissolved in DCM and added to the solution of **4** (0.266g, 0.5 mmol) in toluene. Immediately AgBr was precipitaed out. After overnight stirring, AgBr was separated out from the reaction mixture by filtration and reduced the volume to 15 mL and kept it at 0°C. Colorless block shaped crystals suitable for X-ray analysis was observed after one day. Yield: 0.295g (74%). Mp: more than 200°C. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 1.23-1.26 (*m*, 24H, CH(CH_3)$_2$), 2.05 (*s*, 3H, C$H_{3,\text{toluene}}$), 2.40-2.50 (*m*, 4H, C*H*(CH$_3$)$_2$), 6.74-6.81 (*m*, 1H, Ph), 6.87-7.01 (*m*, 1H, Ph), 7.08-7.18 (*m*, 1H, Ph), 7.27 (*s*, 1H, Ph), 7.35-7.37 (*s*, 5H, Ph) 7.55-7.59 (*m*, 2H, Ph) ppm. ^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$, 298 K): δ 21.07, 23.99, 24.59, 28.72, 124.20, 124.45, 131.12, 133.83, 137.91, 145.40 ppm. ^{19}F{^{1}H} NMR (376.49 MHz, $CDCl_3$, 298): δ -183.43

(br) ppm. MALDI: *m/z* $[C_{35}H_{47}CuN_2]^+$: 451.02 [M-MeC_6H_5]. Anal Calcd: C, 52.87; H, 5.96; N, 3.52. Found: C, 52.72; H, 5.80; N, 3.57.

Synthesis of 6:

$AgSbF_6$ (0.171g, 0.5 mmol) was dissolved in DCM and added to the solution of **4** (0.266g, 0.5 mmol) in *m*-xylene. Immediately AgBr was precipitaed out. After overnight stirring, AgBr was separated out from the reaction mixture by filtration and reduced the volume to 10 mL and kept it at 0^{o}C. Colorless block shaped crystals suitable for X-ray analysis was observed after one day. Yield: 0.315g (78%). Mp: 170°C (decomposed). ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 1.20-1.22 (*m*, 24H, CH(CH_3)$_2$), 2.02 (*s*, 6H, C$H_{3,m\text{-xylene}}$), 2.25-2.41 (*m*, 4H, CH(CH_3)$_2$), 6.74-6.76 (*m*, 2H, Ph), 6.86-6.90 (*m*, 1H, Ph), 6.94 (*s*, 1H, Ph), 7.37 (*s*, 4H, *J*= 7.8Hz, Ph) 7.60 (*t*, 2H, *J*= 7.8Hz, Ph) ppm. ^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$, 298 K): δ 21.04, 24.07, 24.38, 28.65, 124.37, 124.44, 131.13, 134.03, 137.93, 145.43 ppm. ^{19}F{^{1}H} NMR (376.49 MHz, $CDCl_3$, 298): δ -160.86 (br) ppm.MALDI: *m/z* $[C_{36}H_{49}CuN_2]^+$: 451.35 [M-$Me_2C_6H_4$]. Anal Calcd: C, 53.44; H, 6.10; N, 3.46. Found: C, 53.42; H, 6.14; N, 3.57.

Synthesis of 7:

Acetonitrile (0.05 mL)was added into the solution of **2** (0.413g, 0.5 mmol) in 20 mL DCM. After overnight stirring, the reaction mixture was dried completely and crystallized in DCM/pentane mixture and kept it at 0^{o}C. Cololess block shaped crystals suitable for X-ray analysis was observed after one day. Yield: 0.270g (47%). MP: 110^{o}C.^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 0.32 (*s*, 6H, Si*Me$_3$*), 0.34 (*s*, 6H, Si*Me$_3$*), 0.37 (*s*, 6H, Si*Me$_3$*),0.45 (*s*, 6H, Si*Me$_3$*),0.47 (*s*, 6H, Si*Me$_3$*),0.55 (*s*, 6H, Si*Me$_3$*),1.24 (*s*, 12H, C*Me$_3$*), 1.26 (*s*, 12H, C*Me$_3$*), 1.30 (*s*, 12H, C*Me$_3$*), 2.21 (acetonitrile), 7.17-7.19 (*m*, 1H, Ph), 7.36-7.39 (*m*, 1H, Ph), 7.44-7.47 (*m*, 1H, Ph), 7.52-7.63 (*m*, 7H, Ph) ppm. ^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$, 298 K): δ 4.54, 4.69, 4.85, 5.69, 5.87, 5.92, 6.25, 31.66,

31.84, 31.88, 54.74, 54.81, 55.10, 116.88, 116.93, 125.28, 126.57, 127.64, 127.70, 127.83, 127.97, 128.21, 128.28, 128.48, 128.77, 129.03, 130.26, 130.53, 130.81, 131.02, 131.37 ppm. $^{29}Si\{^{1}H\}$ NMR (79.495 MHz, $CDCl_3$, 298 K): δ 10.22 (SiMe$_3$) (br), 7.09 (SiMe$_3$) (br), 5.53 (SiN(SiMe$_3$)$_2$),4.11 (SiN(SiMe$_3$)$_2$) ppm. Anal Calcd: C, 44.29; H, 7.26; N, 7.38. Found: C, 44.32; H, 7.21; N, 7.46.

Synthesis of 8:

IPr carbene (0.194g, 0.5 mmol) was dissolved in toluene and added to the solution of **2** (0.413g, 0.5 mmol) in toluene. After overnight stirring, the reaction mixture was filtered and dried completely. Futher the reaction mixture was crystallized in DCM/pentane mixture and kept it at 0^{o}C. Cololess block shaped crystals suitable for X-ray analysis was observed after one day. Yield: 0.320g (58%). Mp: 185^{o}C (decomposed). ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ0.03 (*s*, 9H, Si*Me$_3$*), 0.21 (*s*, 9H, Si*Me$_3$*), 0.90 (*s*, 18H, C*Me$_3$*), 1.22 (*d*, *J*= 6.8, 12H, CH(C*H*$_3$)$_2$), 1.35 (*d*, *J*= 6.8, 12H, CH(C*H*$_3$)$_2$), 2.65-2.76 (*m*, 4H, C*H*(CH$_3$)$_2$), 6.90-6.97 (*m*, 1H, Ph), 7.25-7.26 (*m*, 1H, Ph), 7.32-7,35 (*m*, 5H, Ph), 7.43-7.59 (*m*, 6H, Ph) ppm. $^{13}C\{^{1}H\}$ NMR (100.613 MHz, $CDCl_3$, 298 K): δ 4.81, 5.41, 24.53, 24.64, 28.82, 31.52, 54.19, 124.48, 124.94, 127.90, 128.29, 128.62, 129.99, 131.03, 131.30, 134.98, 145.38, 169.88 ppm. $^{29}Si\{^{1}H\}$ NMR (79.495 MHz, $CDCl_3$, 298 K): δ 4.24 (SiMe$_3$), 3.97 (SiMe$_3$), 3.60 (SiN(SiMe$_3$)$_2$) ppm. $^{19}F\{^{1}H\}$ NMR (376.49 MHz, $CDCl_3$, 298): δ -179.02 (br) ppm. MALDI: *m/z* $[C_{48}H_{77}CuN_5Si_3]^+$: 871.60 $[M]^+$. Anal Calcd: C, 52.05; H, 7.01; N, 6.32. Found: C, 52.24; H, 7.17; N, 6.39.

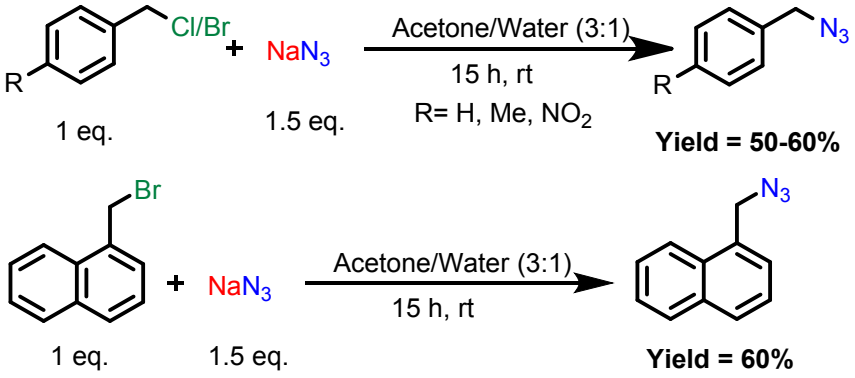
Synthesis of 9:

Acetonitrile (0.05 mL)was added into the solution of **5** (0.397g, 0.5 mmol) in 20 mL DCM. After overnight stirring, the reaction mixture was dried completely and crystallized in DCM/pentane mixture and kept it at 0^{o}C. Cololess triangle shaped crystals suitable for X-ray analysis was

observed after one day. Yield: 0.260g (67%). Mp: 121°C. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 1.26 (dd, *J*= 6.8, 3.6, 24H, CH(CH_3)$_2$), 2.07 (*s*, 6H, $CH_{3,acetonitrile}$), 2.46-2.57 (*m*, 4H, $CH(CH_3)_2$), 7.16-7.21 (*m*, 2H, $CH_{Imidazole}$), 7.36 (*d*, 4H, *J*= 7.8 Hz, Ph), 7.57 (*t*, *J*= 7.8Hz, 2H, Ph) ppm. ^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$, 298 K): δ 21.46, 23.91, 24.69, 28.72, 123.78, 124.31, 125.29, 128.22, 129.03, 130.83, 137.87, 145.60 ppm. ^{19}F{^{1}H} NMR (376.49 MHz, $CDCl_3$, 298): δ 179.39 (br) ppm. MALDI: *m/z* $[C_{31}H_{42}CuN_4]^+$: 533.29 $[M]^+$. Anal Calcd: C, 48.36; H, 5.50; N, 7.28. Found: C, 48.42; H, 5.34; N, 7.19.

Catalytic Reactions:

Synthesis of Azides:



Scheme S1. Schematic representation of the azides synthesis.

General reaction procedure for triazole synthesis: Catalyst (0.5 mol%) was taken in a catalysis tube inside the glove box and 2 mL dry toluene was added into this. Azide (0.2 mmol) and terminal acetylene substituted compound (0.2 mmol) were added into the catalysis tube and the reaction mixture was stirred at 25°C for 5 hours. After 5 hours, the solvent was evaporated by using rota and solid product was obtained.

Table S1. Optimization of reaction conditions for CuAAC reaction using catalyst **2**.[a]

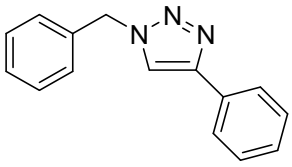
	Catalyst (mol %)	Solvent	Temp.	Time	Conversion Yield (%)[b]
1.	1	THF	25	10	93
2.	0.5	THF	25	10	92
3.	1	Toluene	25	10	>98
4.	0.5	Toluene	25	10	98
5.	**0.5**	**Toluene**	**25**	**5**	**98**
6.	0.5	Toluene	25	3	82
7.	0.5	Toluene	25	1	60
8.	0.5	Toluene	50	3	>99
9.	o.5	Toluene	50	1	80

[a]Reaction conditions for CuAAC reaction: benzyl azide (0.2 mmol), phenyl acetylene (0.2 mmol), solvent (2 mL), catalyst**2**, [b]^{1}H NMR spectroscopy was used to determine the conversion yield of the products.

NMR spectroscopic data of the catalysis products:

I[2]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.58 (*s*, 2H),7.33-7.29 (*m*, 3H), 7.42-7.36 (*m*, 5H), 7.66 (*s*, 1H), 7.81-7.78 (*m*, 2H).

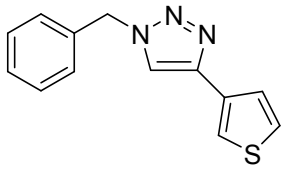
I[5]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.55 (*s*, 2H), 7.33-7.30 (*m*, 5H), 7.39-7.35 (*m*, 3H), 7.67-7.65 (*m*, 2H), 7.75 (*s*, 1H).



1-benzyl-4-phenyl-1H-1,2,3-triazole

II[2]. ^{1}H NMR (400 MHz, $CDCl_3$): δ5.55 (s, 2H), 7.30-7.28 (m, 2H), 7.42-7.34 (m, 5H), 7.56 (s, 1H), 7.65-7.64 (m, 1H).

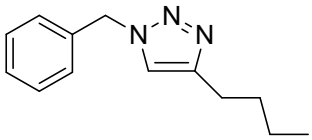
II[5]. ^{1}H NMR (400 MHz, $CDCl_3$): δ5.54 (*s*, 2H), 7.31-7.28 (*m*, 2H), 7.35-7.33 (*m*, 1H), 7.39-7.36 (*m*, 4H), 7.59-7.58 (*m*, 2H).



1-benzyl-4-(thiophen-3-yl)-1H-1,2,3-triazole

III[2]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93-0.89 (*t*, 3H), 1.40-1.31 (*m*, 2H), 1.66-1.58 (*m*, 2H), 2.68 (*t*, 2H), 5.49 (*s*, 2H), 7.18 (*s*, 1H), 7.26-7.24 (*m*, 2H), 7.38-7.34 (*m*, 3H).

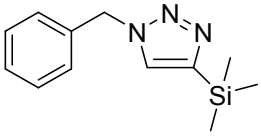
III[5]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (*t*, 3H), 1.39-1.30 (*m*, 2H), 1.65-1.57 (*m*, 2H), 2.67 (*t*, 2H), 5.48 (*s*, 2H), 7.18 (*s*, 1H), 7.25-7.21 (*m*, 2H), 7.38-7.31 (*m*, 3H).



1-benzyl-4-butyl-1H-1,2,3-triazole

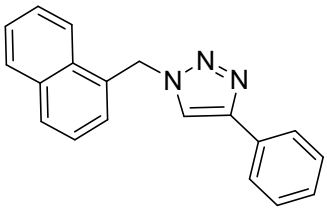
IV[2]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.29 (*s*, 9H), 5.55 (*s*, 2H), 7.33-7.33 (*m*, 1H), 7.39-7.36 (*m*, 4H), 7.42 (*s*, 1H).

IV[5]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.21 (*s*, 9H), 5.53 (*s*, 2H), 7.39-7.33 (*m*, 5H), 7.59 (*s*, 1H).



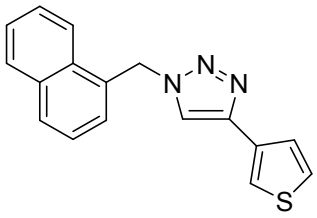
1-benzyl-4-(trimethylsilyl)-1H-1,2,3-triazole

V[2]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.01 (*s*, 2H), 7.31-7.28 (*m*, 1H), 7.39-7.35 (*m*, 2H), 7.56-7.47 (*m*, 5H), 7.77-7.75 (*m*, 2H), 7.94-7.91 (*m*, 2H), 8.04-8.02 (*m*, 1H).



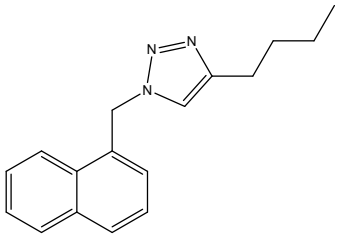
1-(naphthalen-1-ylmethyl)-4-phenyl-1H-1,2,3-triazole

VI[2]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.97 (*s*, 2H), 7.30-7.28 (*m*, 1H), 7.35-7.33 (*m*, 1H), 7.53-7.42 (*m*, 5H), 7.58-7.57 (*m*, 1H), 7.92-7.88 (*m*, 2H), 8.00-7.98 (*m*, 1H).



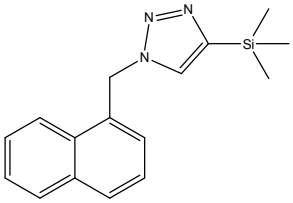
1-(naphthalen-1-ylmethyl)-4-(thiophen-3-yl)-1H-1,2,3-triazole

VII[2]. ^{1}H NMR (400 MHz, CDCl3): δ 5.94 (*s*, 2H), 7.39-7.61 (*m*, 5H), 7.87-7.92 (*m*, 2H), 8.03-8.06 (*d*, 1H).



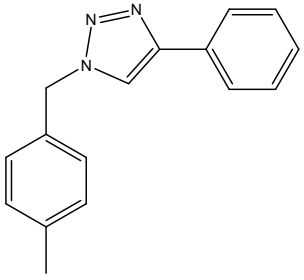
4-butyl-1-(naphthalen-1-ylmethyl)-1H-1,2,3-triazole

VIII[2].^{1}H NMR (400 MHz, CDCl3): δ 6.01 (*s*, 2H), 7.40-7.51 (*m*, 3H), 7.53-7.61 (*m*, 2H), 7.86-7.92 (*m*, 2H), 8.03-8.06 (*d*, 1H).



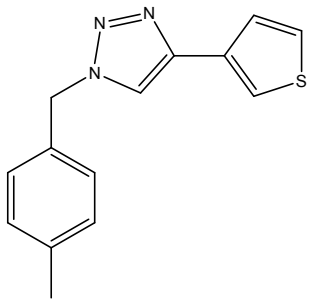
1-(naphthalen-1-ylmethyl)-4-(trimethylsilyl)-1H-1,2,3-triazole

IX[2].^{1}H NMR (400 MHz, CDCl3): δ2.36 (s, 3H), 5.52 (*s*, 2H), 7.18-7.22 (*m*, 4H), 7.29-7.32 (*m*, 1H), 7.37-7.41 (*m*, 2H), 7.64 (*s*, 1H), 7.78-7.80 (*d*, 2H).



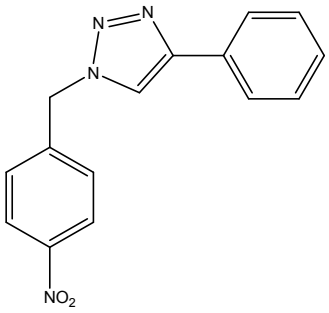
1-(4-methylbenzyl)-4-phenyl-1H-1,2,3-triazole

X². ^{1}H NMR (400 MHz, CDCl3): δ2.35 (*s*, 3H), 5.51 (*s*, 2H), 7.17-7.21 (*m*, 4H), 7.33-7.35 (*m*, 1H), 7.40-7.41 (*m*, 1H), 7.54 (*s*, 1H), 7.63-7.64 (*d*, 1H).



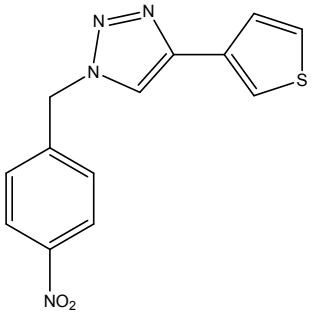
1-**(4-methylbenzyl)-4-(thiophen-3-yl)-1H-1,2,3-triazole**

XI².^{1}H NMR (400 MHz, CDCl3): δ5.69 (*s*, 2H), 7.38-7.44 (m, 2H), 7.47-7.49 (d, 1H), 7.54-7.56 (*d*, 1H), 7.79-7.81 (*d*, 2H), 8.19-8.23 (*m*, 4H).

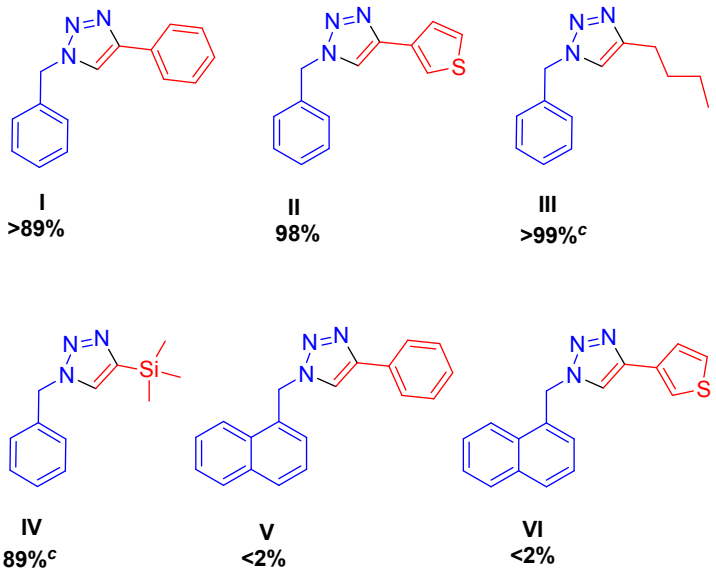


1-(4-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole

XII².^{1}H NMR (400 MHz, CDCl3): δ5.68 (*s*, 2H), 7.22-7.44 (*m*, 1H), 7.48-7.50 (*d*, 1H), 7.55-7.57 (d, 1H), 7.67-7.69 (*m*, 1H), 8.19-8.24 (*m*, 4H),



1-(4-nitrobenzyl)-4-(thiophen-3-yl)-1H-1,2,3-triazole



Scheme S2. Substrate scope for triazole synthesis using catalyst **5.**[a]

[a]Reaction condition:azide (0.2 mmol), alkyne (0.2 mmol), toluene(2 mL) as solvent at room temperature ^{1}H NMR spectroscopy was used to determine the conversion yield of the producst; [c]heat the reaction at 50°C.

S2. Crystal Data and Structure Refinements for 2, 3, 5, 6, 8 and 9:

Crystal data for **3**, **4**, **5, 6, 8** and **9** were collected on a Bruker Smart Apex Duo diffractometer at 100 K using Mo K_α radiation (λ = 0.71073 Å). The absorption correction was done using multi-scan method (SADABS). The structures were solved by direct methods and refined by full-matrix least-squares methods against F^2 (SHELXL-2014/6). Crystallographic data file (including structure factors) for the **2**, **3, 5, 6, 8** and **9** have been deposited with the Cambridge Crystallographic Data Centre. 1896663 (**2**), 1896664 (**3**), 1896665(**5**), 1886948(**6**), 1896666(**8**), 1896670(**9**)

Table S2.

	2	3	5

Chemical formula	$C_{28}H_{49}CuF_6N_3SbSi_3$	$C_{29}H_{51}CuF_6N_3SbSi_3$	$C_{34}H_{44}CuF_6N_2Sb$
Formula weight	811.26	825.29	780.00
Temperature	100(2)	100(2)	100(2)
Wavelength	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	*P*n	*Cc*
Unit cell dimentions	a=11.762(6) Å	a=9.226(7) Å	a=24.087(2) Å
	b=14.725(7) Å	b=11.541(9) Å	b=9.1915(9) Å
	c=21.300(9)Å	c=18.052(14) Å	c=19.165(3) Å
	α=90°	α=90°	α=90°
	β=90°	β=98.414(18)°	β=124.966(2)°
	γ=90°	γ=90°	γ=90°
Volume	3689(3) $Å^3$	1901(2) $Å^3$	3477.2(7) $Å^3$
Z	4	2	4
Density (calculated)	1.461 g/cm^3	1.442 g/cm^3	1.490 g/cm^3
Absorption coefficient	1.458 mm^{-1}	1.416 mm^{-1}	1.446 mm^{-1}
F(000)	1656	844	1584
Theta range for data collection	2.22 to 25.25°	2.23 to 24.00°	2.20 to 25.25°
Reflections collected	81475	39863	43896
Independent reflections	6657[R(int)=0.0983]	5967[R(int)=0.2784]	6285[R(int)=0.1028]
Coverage of independent reflections	99.9%	99.9%	100%

Data/ restraints/ parameters	6657/ 24/ 392	5967/ 98/ 403	6285/ 8/ 406
Goodness-of-fit on F2	1.049	1.012	1.003
Δ/ σ max	0.001	0.023	0.004
Final R indices	5034 data; [I>2σ(I)] R1= 0.0442, wR2= 0.0931	2797 data; [I>2σ(I)] R1= 0.0841, wR2= 0.1605	4635 data; [I>2σ(I)] R1= 0.0449, wR2= 0.0735
	all data, R1= 0.0748, wR2= 0.1065	all data, R1= 0.2138, wR2= 0.2103	all data, R1= 0.0840, wR2= 0.0860
Largest diff. peak and hole	0.567 and -0.420 eÅ^{-3}	0.959 and -0.528 eÅ^{-3}	0.724 and -0.446 eÅ^{-3}
R. M. S deviation from mean	0.073 eÅ^{-3}	0.111 eÅ^{-3}	0.085 eÅ^{-3}

	6	**8**	**9**
Chemical formula	$C_{35}H_{46}CuF_6N_2Sb$	$C_{49}H_{79}Cl_2CuF_6N_5SbSi_3$	$C_{38}H_{50}CuF_6N_4Sb$
Formula weight	794.03	1192.63	862.11
Temperature	100(2)	100(2)	100(2)
Wavelength	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	*Pbca*	*$P2_1/n$*	*Pnma*
Unit cell dimentions	a=18.355(3) Å	a= 21.510(7) Å	a=13.623(5) Å
	b=18.334(3) Å	b= 12.624(4) Å	b=14.768(5) Å
	c=42.496(6) Å	c= 21.590(7) Å	c=20.118(7) Å
	α= 90°	α=90°	α=90°
	β=90°	β= 96.299(9)°	β=90°
	γ=90°	γ=90°	γ=90°

Volume	14301(4) $Å^3$	5827(3) $Å^3$	4047(2) $Å^3$
Z	18	4	4
Density (calculated)	1.660 g/cm^3	1.359 g/cm^3	1.415 g/cm^3
Absorption coefficient	1.583 mm^{-1}	1.037 mm^{-1}	1.251 mm^{-1}
F(000)	7272	2472	1760
Theta range for data collection	2.22 to 25.25	2.15 to 25.25°	2.27 to 25.24°
Reflections collected	177708	109049	139751
Independent reflections	12935 [R(int)= 0.1740]	10536 [R(int)= 0.0648]	3812 [R(int)= 0.1906]
Coverage of independent reflections	99.9%	99.9%	99.9%
Data/ restraints/ parameters	12935/ 0/ 831	10536/ 0/ 624	3812/ 0/ 250
Goodness-of-fit on F2	1.039	1.047	1.001
Δ/ σ max	0.002	0.058	0.001
Final R indices	7894 data; [I>2σ(I)] R1= 0.0479, wR2= 0.0681	8198 data; [I>2σ(I)] R1= 0.0531, wR2= 0.1267	2659 data; [I>2σ(I)] R1= 0.0394, wR2= 0.0588
	all data, R1= 0.1107, wR2= 0.0848	all data, R1= 0.0745, wR2= 0.1449	all data, R1= 0.0787, wR2= 0.0712
Largest diff. peak and hole	0.941 and -0.950 $eÅ^{-3}$	1.180 and -1.616 $eÅ^{-3}$	0.751 and -0.651 $eÅ^{-3}$
R. M. S deviation from mean	0.100 $eÅ^{-3}$	0.138 $eÅ^{-3}$	0.092 $eÅ^{-3}$

S3. Hapticity Deduction of hapticities in 2, 3, 5 and 6.

The assignment of hapticity number for the complexes having low hapticities (η^1- η^3), has always been a complicated task as the difference between M-C bond distances are very less. Therefore,

we used a method proposed by alvarez and coworkers to deduce the hapticity of the metal-arene complexes given in *Organometallics*, 2014, **33**, 6660-6668.

Table S3. Deduction of hapticities in **2, 3, 5** and **6.**

	M-C[a] d_1 d_2 d_3	ρ_1[b]	ρ_2[c]	η[d]
2	2.23, 2.33, 2.43	1.044	1.089	3
3	2.16, 2.19, 2.57	1.013	1.189	2
5	2.06, 2.31, 2.32	1.121	1.126	3
6	2.19, 2.22, 2.42	1.013	1.105	2

[a] M (=Cu), $d_1<d_2<d_3$, [b]$\rho 1 = d_2/d_1$, [c]$\rho 2 = d_3/d_1$, if $\rho_1 \approx \rho_2 \gg 1$ then η^1 , if $\rho_2 > \rho_1 \approx 1$ then η^2, and if $\rho_1 \approx \rho_2 \approx 1$ then η^3

S4. Computational Methodology

All the geometry optimizations were performed with Gaussian 09 program[1] using BP86[2] /def2-SVP basis set.[3] Meta-GGA exchange correlation functional M06[4] with def2-TZVPP basis set[3] was used for the single point calculations on the optimized geometries and the energies were corrected by adding the zero point energies from the BP86/def2-SVP level of theory. The optimization of **2**, **3,** and **5** using metaGGA functional M06[4] and GGA functional with D3BJ dispersion correction by Grimme (BP86-D3-BJ)[5] also leads to the η^2-coordination of the arene ring.The optimization of **6** using metaGGA functional M06[4] leads to η^3-coordination and GGA functional with D3BJ dispersion correction by Grimme (BP86-D3-BJ)[5]leads to the η^2-coordination of the arene ring.Natural Bond Order (NBO)[6] analysis was done at the same level of theory. The nature of Si/C–Cu as well as Cu–arene bonds were studied using EDA-NOCV method at the BP86/TZ2P level of theory using ADF 2014.01 program.[7] Scalar relativistic effects were incorporated using Zeroth Order Regular Approximation (ZORA).[8] The core electrons were treated by the frozencore approximations. Energy Decomposition Analysis (EDA)[9] gives the

instantaneous interaction energy (ΔE_{int}) between two fragents in the frozen geometry of the compound. The interaction energy can be divided into three parts:

$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb}$

ΔE_{elstat} gives the electrostatic interaction energy between the frozen charge densities of the two fragents. ΔE_{Pauli} is the result of repulsive interaction between two fragents, which are caused by the electrons of same spin. ΔE_{orb} is the lowering in energy due to the overlap of orbitals of the two fragents. Sum of ΔE_{int} and ΔE_{prep} (energy necessary to promote the fragents from their ground state geometry to the geometry in the compound) gives $-D_e$ (dissociation energy).

$-D_e = \Delta E_{int} + \Delta E_{prep}$

In the EDA-NOCV analysis method, ΔE_{orb} term is decomposed into the contributions from different natural orbitals of chemical valence (NOCV).[10] It provides the energy contributions for each specific orbital interaction between the fragents to the total bond energy.

Table S4. Charges by natural population analysis (M06/def2-TZVPP//BP86/def2-SVP) on atoms and groups of atoms in the optimized geometry of complexes **2** and **3** ($L^1L^2SiCu(L)^+$)as well as **5** and **6** ($NHCCu(L)^+$), where $L^1 = N(SiMe_3)_2$, $L^2 = (Ph)C(N\textit{t}\text{-}Bu)_2$, NHC = *N*-heterocyclic carbene with $(i\text{-}Pr)_2$Phsubstituent on each N and L = Tol ($C_6H_5(CH_3)$) and m-Xyl (1,3 $C_6H_4(CH_3)_2$).

$L^1L^2SiCu(L)^+$	L^1	L^2	Si	Cu	L
2	-0.53	-0.36	1.43	0.27	0.18
3	-0.53	-0.35	1.43	0.29	0.16
$NHCCu(L)^+$	NHC	C7	Cu	L	--
5	0.33	0.10	0.52	0.16	--
6	0.32	0.10	0.51	0.17	--

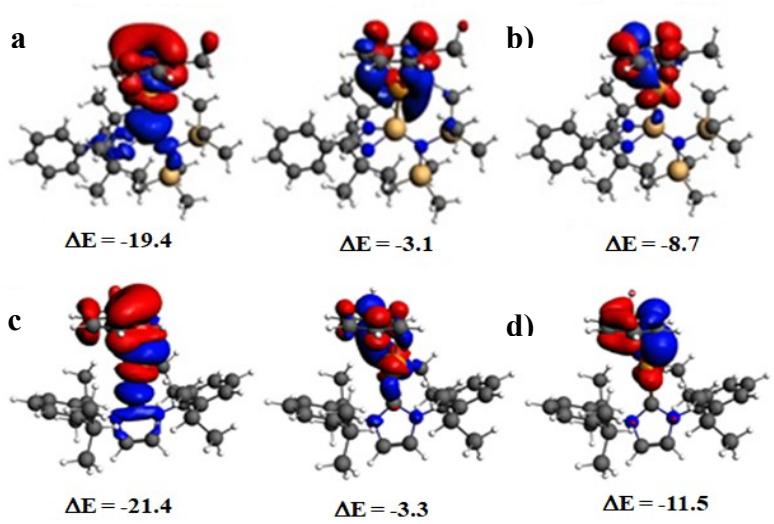


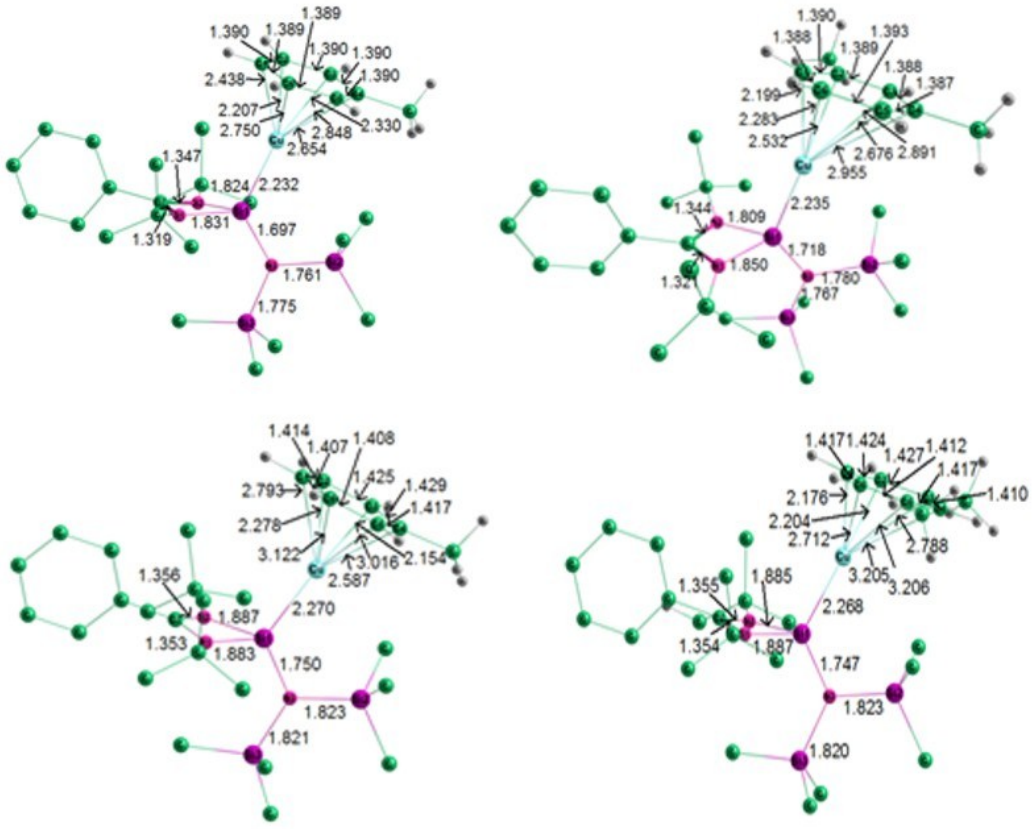
Figure S1: Plot of deformation density (BP86/TZ2P) for a) the donation of π-electrons from toluene to the vacant sp-hybrid orbital on Cu (Toluene→Cu) in complex **2**, b) the donation from the filled d-orbital of Cu to π**-MO of toluene in complex **2,** c) the donation of π-electrons from toluene to the vacant sp-hybrid orbital on Cu (Toluene→Cu) incomplex **5** and d) the donation from the d-orbital of Cu to π**-MO of toluene in complex **5**. The direction of charge flow is from red to blue. The isosurface value for the plot is 0.0003. The associated energy (ΔE) is given in kcal/mol.

Table S5. EDA-NOCV results (BP86/TZ2P) for the interaction of (a) **L^1L^2Si** fragment with **$Cu(Xyl)^+$** in **3** (**$L^1L^2SiCu(Xyl)^+$**) and (b) **$L^1L^2SiCu^+$** fragment with **Xyl**in **3** (**$L^1L^2SiCu(Xyl)^+$**)and (c) **NHC** fragment with **$Cu(Xyl)^+$**in**6** (**$NHCCu(m\text{-}Xyl)^+$**)and (d) **$NHCCu^+$** fragment with **Tol** in **6** (**$NHCCu(m\text{-}Xyl)^+$**), where **L^1** = $N(SiMe_3)_2$ and **L^2** = (Ph)C(N*t*-Bu)$_2$, **m-Xyl** = 1,3 $C_6H_4(CH_3)_2$ and **NHC** = N-heterocyclic carbene with $(i\text{-}Pr)_2Ph$ substituent on each N. Energies are in kcal/mol.

	(a) **$L^1L^2Si\&Cu(Xyl)^+$**	**(b)** **$L^1L^2SiCu^+\&(Xyl)$**	**(c)** **$NHC\&Cu(Xyl)^+$**	**(d)** **$NHCCu^+\&(Xyl)$**
ΔE_{int}	-92.9	-29.1	-93.0	-37.6
ΔE_{Pauli}	103.2	77.0	110.3	73.3
ΔE_{elstat}[a]	-127.5 (65.0%)	-59.9 (56.5%)	-141.1 (69.4%)	-60.5 (54.6%)
ΔE_{orb}[a]	-68.6 (35.0%)	-46.2 (43.5%)	-62.2 (30.6%)	-50.4 (45.4%)
$\Delta E_{m\text{-}Xyl\rightarrow Cu}$[b]	--	-22.7 (49.1%)	--	-25.2 (50.0%)
$\Delta E_{Cu\rightarrow m\text{-}Xyl}$[b]	--	-10.4 (32.3%)	--	-9.2 (27.6%)

$\Delta E_{Si/NHC\rightarrow Cu}$[b]	-44.4 (64.7%)	--	-28.5 (45.8%)	--
$\Delta E_{Cu\rightarrow Si/NHC}$[b]	-4.6 (6.7%)	--	-9.5 (15.3%)	--
ΔE_{rest}[b,c]	-19.6	-13.1	-24.2	-16.0
ΔE_{prep}[d]	7.6	3.5	4.8	4.7
$-D_e$[d]	85.3	25.6	-88.2	-32.9

[a]Values in parentheses give the percentage contribution to the total attractive interactions, $\Delta E_{orb} + \Delta E_{elstat}$. [b]Values in parentheses give the percentage contribution to the orbital interactions, ΔE_{orb}. [c]$\Delta E_{rest} = \Delta E_{orb} - (\Delta E_{M\rightarrow L} + \Delta E_{L\rightarrow M})$. [d]$\Delta E_{prep}$ and De represent the preparatory and dissociation energy respectively.



(A) (B)

Figure S2. a) Experimental and b) optimized (BP86/def2-SVP) geometry of **2**($\mathbf{L^1L^2SiCu(Tol)^+}$) and **3** ($\mathbf{L^1L^2SiCu(m\text{-}Xyl)^+}$), where $L^1 = N(SiMe_3)_2$, $L^2 = (Ph)C(N\textit{t}\text{-}Bu)_2$, Tol = $C_6H_5(CH_3)$, m-Xyl = 1,3 $C_6H_4(CH_3)_2$.

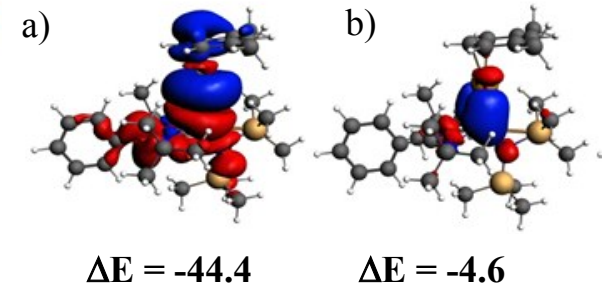


Figure S3. Plot of deformation density (BP86/TZ2P) for the interaction of a) donation of lone pair on silylene to Cu (Si→Cu) in **3**andd) back donation from Cu to silylene in**3**.The direction of charge flow is from red to blue. The isosurface value for the plot is 0.0003. The associated energy (ΔE) is given in kcal/mol.

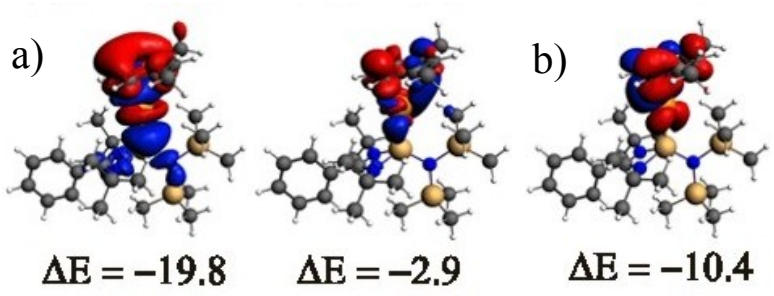


Figure S4. Plots of deformation density (BP86/TZ2P) for a)donation from xylene ring to Cu (Xyl→Cu) in **3** and b) donation from Cu to xylene in **3**. The direction of charge flow is from red to blue. The isosurface value for the plot is 0.0003. The associated energy (ΔE) is given in kcal/mol.

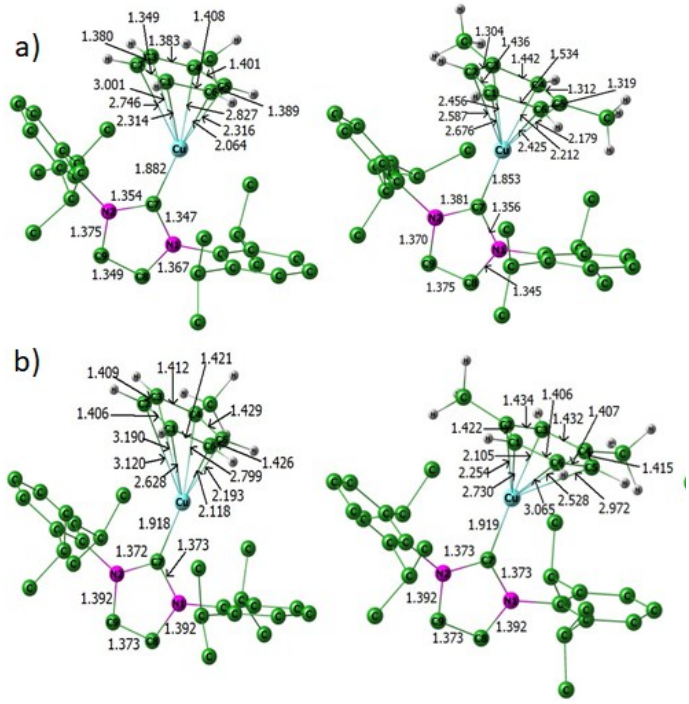


Figure S5. a) Experimental geometry as well asb) optimized (BP86/Def2-SVP) geometry of 5 (**NHCCu(Tol)$^+$**), **6** (**NHCCu(m-Xyl)$^+$**), whereNHC= N-heterocyclic carbene with (i-Pr)$_2$Phsubstituent on each N, Tol = $C_6H_5(CH_3)$, m-Xyl = 1,3 $C_6H_4(CH_3)_2$. H atoms on NHC are hided for clarity.

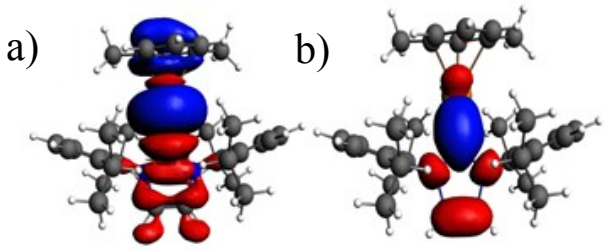


Figure S6. Plots of deformation density (BP86/TZ2P) for the interaction of a) donation of lone pair on NHC to Cu (NHC→Cu) in **6** andb) back donation from Cu to NHC in **6**. The direction of charge flow is from red to blue. The isosurface value for the plot is 0.0003. The associated energy (ΔE) is given in kcal/mol.

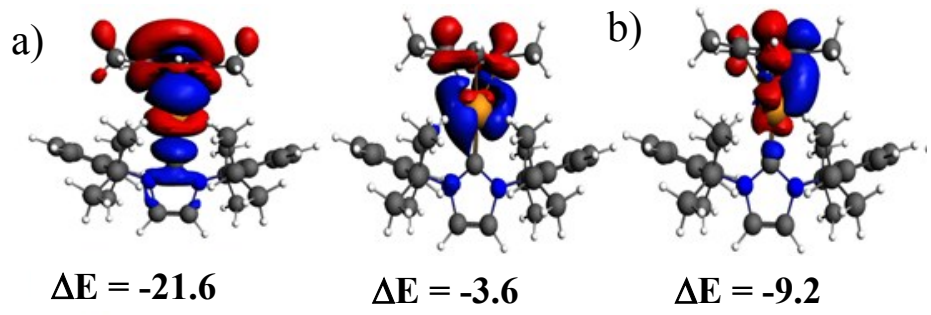
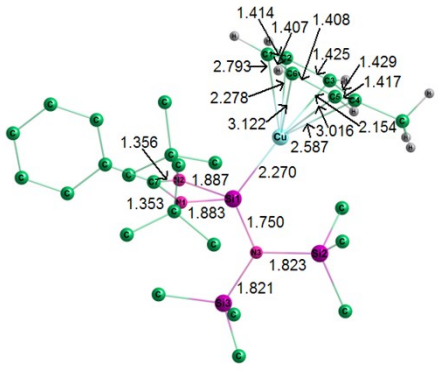


Figure S7. Plots of deformation density (BP86/TZ2P) for the interactiona) donation of xylene ring to Cu (Xylene→Cu) in**6** and b) donation from Cu to Xylene in **6**. The direction of charge flow is from red to blue. The isosurface value for the plot is 0.0003. The associated energy (ΔE) is given in kcal/mol.

Table S6. Optimized geometry (BP86/def2-SVP), Cartesian coordinates, electronic energy E^{el}_{M06} (M06/def2-TZVPP//BP86/def2-SVP), zero-point energy ZPE_{BP86} (BP86/def2-SVP) and total energy E (E^{el}_{M06} + ZPE_{BP86}) of **2** (**$L^1L^2SiCu(Tol)^+$**), **3**(**$L^1L^2SiCu(m\text{-}Xyl)^+$**), **5** (**$NHCCu(Tol)^+$**)and**6**(**$NHCCu(m\text{-}Xyl)^+$**)where L^1 = $N(SiMe_3)_2$, L^2 = $(Ph)C(N\textit{t}\text{-}Bu)_2$, Tol = $C_6H_5(CH_3)$, m-Xyl = 1,3 $C_6H_4(CH_3)_2$ using Gaussian09 program package. The energies are given in a.u.



$L^1L^2SiCu(Tol)^+$

E^{el}_{M06} = -3769.271366
ZPE_{BP86} = 0.692187
E (E^{el}_{M06} + ZPE_{BP86}) = -3768.579179

C	-2.974274000	-2.903213000	-1.182685000
H	-3.416854000	-2.536777000	-2.123827000
C	-1.713264000	-3.565917000	-1.207536000
H	-1.174750000	-3.675988000	-2.161930000
C	-1.202192000	-4.161003000	-0.030694000
H	-0.240554000	-4.695360000	-0.058013000
C	-1.942605000	-4.084552000	1.162818000
H	-1.556809000	-4.555375000	2.080247000
C	-3.177530000	-3.408639000	1.193963000
H	-3.745196000	-3.357920000	2.136813000
C	-3.726378000	-2.817893000	0.028932000
Cu	-1.595921000	-1.425820000	-0.437121000
Si	-0.264071000	0.370462000	-0.046010000
Si	-0.032063000	3.533563000	0.191681000
Si	-2.781685000	1.979445000	0.040044000
N	1.312285000	0.255161000	-1.075944000
N	1.206186000	0.038330000	1.082464000
C	1.363574000	-0.293684000	2.525458000
C	1.586104000	0.096722000	-2.533550000

C	3.422944000	-0.645948000	0.034599000
C	2.811010000	0.933488000	-2.962138000
H	2.668773000	2.005212000	-2.715750000
H	2.951648000	0.854440000	-4.059242000
H	3.742025000	0.579688000	-2.478452000
N	-0.959458000	1.970509000	0.084527000
C	5.014845000	-2.498000000	0.073999000
H	5.213446000	-3.581042000	0.076224000
C	2.020652000	-0.127944000	0.015147000
C	3.688988000	-2.033785000	0.042266000
H	2.856280000	-2.753390000	0.014971000
C	6.083378000	-1.584776000	0.102872000
H	7.121334000	-1.951047000	0.130263000
C	5.823594000	-0.202928000	0.096468000
H	6.656651000	0.516582000	0.121399000
C	4.500929000	0.268163000	0.060440000
H	4.299882000	1.350271000	0.065690000
C	2.701284000	0.226160000	3.092250000
H	2.816768000	1.314979000	2.915985000
H	3.574330000	-0.295396000	2.656283000
H	2.723797000	0.057423000	4.187907000
C	1.252582000	-1.822010000	2.730704000
H	2.100987000	-2.355074000	2.257665000
H	0.305663000	-2.203547000	2.295728000
H	1.262401000	-2.067193000	3.812663000
C	0.331744000	0.621114000	-3.261888000
H	0.139078000	1.685311000	-3.018874000
H	-0.566726000	0.032824000	-2.976536000
H	0.460477000	0.535144000	-4.358993000
C	1.799908000	-1.390104000	-2.897490000
H	1.887471000	-1.504912000	-3.997240000
H	0.939246000	-2.002150000	-2.554717000
H	2.724581000	-1.796239000	-2.443047000
C	1.832354000	3.241075000	0.340514000
H	2.250069000	2.715970000	-0.540032000
H	2.104750000	2.677159000	1.254138000
H	2.319352000	4.237656000	0.402465000
C	0.196667000	0.403437000	3.254213000
H	-0.783478000	0.048885000	2.871939000
H	0.241321000	1.503294000	3.125946000
H	0.236158000	0.179837000	4.338720000
C	-0.535097000	4.513215000	1.732371000
H	-0.446516000	3.897648000	2.652092000
H	-1.563683000	4.919615000	1.690280000
H	0.154017000	5.377629000	1.846371000
C	-3.456536000	0.966698000	1.495666000
H	-3.126165000	1.404741000	2.460950000
H	-3.117229000	-0.090804000	1.469929000
H	-4.567464000	0.970341000	1.487323000
C	-0.304574000	4.551606000	-1.383018000
H	0.095934000	4.024633000	-2.274621000
H	0.234900000	5.519463000	-1.300567000
H	-1.369736000	4.784315000	-1.581153000
C	-5.105581000	-2.206699000	0.038758000
H	-5.861643000	-2.979601000	-0.221249000
H	-5.203425000	-1.390775000	-0.703893000
H	-5.371718000	-1.809462000	1.037496000
C	-3.373214000	1.243908000	-1.608292000
H	-3.004068000	0.202517000	-1.744411000
H	-3.008608000	1.840414000	-2.470668000
H	-4.482993000	1.222425000	-1.654801000
C	-3.547001000	3.702334000	0.185987000
H	-3.177305000	4.437580000	-0.555257000
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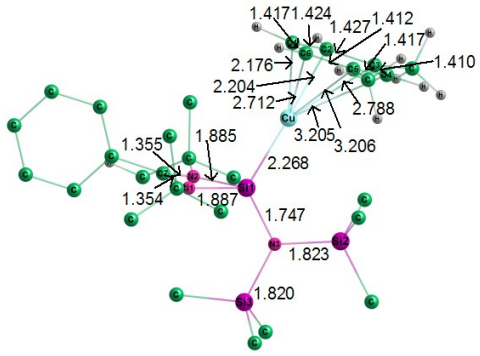

$L^1L^2SiCu(m\text{-}Xyl)^+$

E^{el}_{M06} = -3808.5719326

ZPE_{BP86} = 0.718221

E (E^{el}_{M06} + ZPE_{BP86}) = -3807.8537116

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C	3.457667000	-2.601640000	-0.151221000
H	2.511549000	-3.155080000	-0.253489000
C	4.678587000	-3.297569000	-0.152380000
H	4.681164000	-4.393616000	-0.257628000
C	5.890893000	-2.598657000	-0.019184000
H	6.846032000	-3.146358000	-0.019898000
C	5.881248000	-1.198893000	0.115070000
H	6.828113000	-0.646759000	0.219378000
C	4.664995000	-0.496632000	0.115214000
H	4.659857000	0.599472000	0.215732000
C	2.156397000	-0.432044000	-0.018737000
C	-4.598274000	-1.982517000	0.182983000
H	-5.565009000	-1.496445000	0.395812000
C	-3.893545000	-2.593547000	1.250303000
C	-2.663547000	-3.225582000	0.964044000
H	-2.107872000	-3.729425000	1.770340000
C	-2.159015000	-3.262001000	-0.359485000
H	-1.254065000	-3.849081000	-0.585035000
C	-2.876638000	-2.628606000	-1.413178000
H	-2.531332000	-2.731635000	-2.455033000
C	-4.121448000	-1.984044000	-1.143982000
C	1.767686000	-0.068882000	-2.558557000
C	1.441900000	-1.519838000	-2.983184000

H	1.494084000	-1.623776000	-4.086316000
H	0.415789000	-1.792618000	-2.655692000
H	2.157347000	-2.241669000	-2.541578000
C	1.471153000	-0.565693000	2.483221000
C	2.529987000	2.933120000	0.336056000
H	2.831132000	2.521059000	-0.647032000
H	2.749612000	2.181585000	1.118862000
H	3.163839000	3.823359000	0.536672000
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H	-0.260574000	0.654087000	-3.018643000
H	0.911136000	0.823630000	-4.362320000
C	-4.940908000	-1.400911000	-2.268711000
H	-5.588877000	-2.187322000	-2.714313000
H	-4.305019000	-1.003190000	-3.084033000
H	-5.606656000	-0.589474000	-1.915678000
C	2.807498000	-0.118866000	3.113871000
H	2.941669000	0.979047000	3.033844000
H	3.676640000	-0.615691000	2.641664000
H	2.814756000	-0.381833000	4.191119000
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H	-0.609913000	4.617475000	2.235837000
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H	0.665916000	4.354217000	-2.004929000
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H	-0.672302000	-0.175960000	2.784242000
H	0.383589000	1.240082000	3.117136000
H	0.309904000	-0.122919000	4.283110000
C	1.300777000	-2.096018000	2.617931000
H	2.145604000	-2.643641000	2.156691000
H	0.356820000	-2.424001000	2.135227000
H	1.259031000	-2.383289000	3.688583000
C	-2.888176000	1.846919000	-1.679646000
H	-2.403593000	2.394312000	-2.515150000
H	-3.982929000	2.022017000	-1.750154000
H	-2.706113000	0.761369000	-1.834537000
C	-3.099107000	1.529208000	1.410962000
H	-2.727648000	1.876742000	2.397701000
H	-2.935901000	0.431796000	1.351409000
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C	-2.701059000	4.271816000	0.134353000
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H	-2.317972000	4.783718000	1.038875000
H	-3.810997000	4.302741000	0.190536000
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H	-4.512351000	-1.525054000	3.034997000
H	-3.841462000	-3.157988000	3.354854000
H	-5.489607000	-2.970511000	2.671165000
N	1.380510000	-0.150627000	1.055074000
N	1.531450000	0.098293000	-1.097292000
N	-0.434253000	2.137987000	0.089532000
Cu	-1.555391000	-1.171978000	-0.417539000
Si	-0.009469000	0.450748000	-0.069888000
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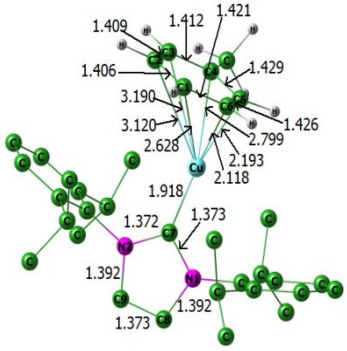

NHCCu(Tol)$^{+}$

E^{el}_{M06} = -3071.379097

ZPE_{BP86} =0.678888

E (E^{el}_{M06} + ZPE_{BP86}) = -3070.700209

29	-0.141282000	-0.384437000	1.233596000
7	-1.342328000	0.526170000	-1.268285000
7	0.819408000	0.654353000	-1.416002000
6	2.944334000	-0.598525000	-1.454030000
6	-0.189535000	0.284966000	-0.563519000
6	-1.060824000	1.032520000	-2.533600000
1	-1.849479000	1.288284000	-3.248556000
6	2.856592000	1.708378000	-0.502967000
6	-3.273404000	-0.975950000	-0.938824000
6	2.103166000	3.005807000	-0.205163000
1	1.017499000	2.799693000	-0.316419000
6	0.306866000	1.113494000	-2.626452000
1	0.955295000	1.451387000	-3.440962000
6	4.321601000	-0.636074000	-1.150466000
1	4.905876000	-1.534512000	-1.404246000
6	4.236510000	1.611245000	-0.227654000
1	4.755695000	2.464493000	0.235858000
6	4.961263000	0.452830000	-0.542506000
1	6.038964000	0.402792000	-0.321040000
6	-4.557066000	-1.175029000	-0.389657000
1	-5.054536000	-2.148844000	-0.517660000
6	-2.674788000	0.297167000	-0.741933000
6	2.072488000	-0.426104000	3.431390000
1	3.019218000	0.097641000	3.633876000
6	-5.216130000	-0.151122000	0.305473000

1	-6.220155000	-0.329337000	0.721456000
6	2.095373000	-1.777392000	3.031659000
1	3.062146000	-2.296230000	2.934750000
6	2.322551000	3.498547000	1.239318000
1	2.046743000	2.719021000	1.978786000
1	1.702567000	4.396666000	1.439587000
1	3.378481000	3.784822000	1.426195000
6	-0.367922000	-0.435001000	3.339129000
1	-1.332943000	0.047246000	3.564751000
6	-2.565607000	-2.108509000	-1.684575000
1	-1.708387000	-1.665782000	-2.235021000
6	2.235456000	0.582166000	-1.107432000
6	0.851388000	0.253398000	3.582337000
1	0.830700000	1.299233000	3.924243000
6	0.904363000	-2.485835000	2.759046000
6	-3.326182000	1.363349000	-0.065203000
6	-2.672429000	2.732829000	0.128271000
1	-1.811471000	2.797391000	-0.570950000
6	2.282994000	-1.791065000	-2.146440000
1	1.208248000	-1.550707000	-2.287223000
6	-4.609083000	1.103469000	0.460002000
1	-5.146877000	1.901908000	0.994046000
6	-0.336195000	-1.792277000	2.903240000
1	-1.282209000	-2.346405000	2.787449000
6	-3.471185000	-2.791009000	-2.729477000
1	-4.316342000	-3.334879000	-2.258434000
1	-2.891130000	-3.535418000	-3.312974000
1	-3.898333000	-2.056926000	-3.442673000
6	2.475554000	4.101540000	-1.230010000
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1	2.276587000	3.776232000	-2.271682000
1	3.552281000	4.363866000	-1.163468000
6	-3.619330000	3.900629000	-0.212958000
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1	0.657351000	-4.560189000	3.303744000
6	2.886123000	-2.036209000	-3.546850000
1	3.958107000	-2.318253000	-3.486544000
1	2.814059000	-1.134074000	-4.188279000
1	2.353552000	-2.863526000	-4.060174000
6	-1.982469000	-3.134786000	-0.687992000
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1	-2.784896000	-3.613467000	-0.087585000
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6	2.350057000	-3.061728000	-1.273882000
1	1.829795000	-3.905557000	-1.772848000
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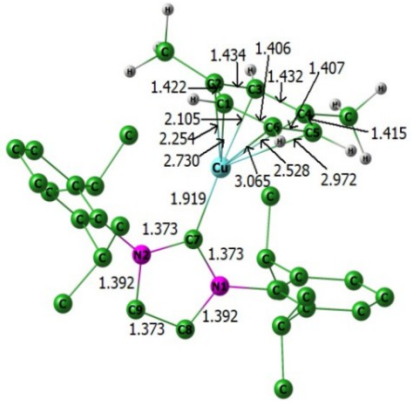
1	3.398057000	-3.379709000	-1.091762000



NHCCu(Xyl)$^{+}$

E^{el}_{M06} = -3110.68268

ZPE_{BP86} =0.705869

E (E^{el}_{M06} + ZPE_{BP86}) = -3109.976811

29	0.031193000	-0.259362000	1.218286000
7	-0.995077000	0.055431000	-1.560790000
7	1.173449000	0.024486000	-1.489214000
6	0.821202000	0.143137000	-2.830568000
1	1.569944000	0.197881000	-3.627096000
6	3.206842000	1.218250000	-0.763927000
6	2.538930000	-0.013329000	-1.000702000
6	0.060302000	-0.033390000	-0.687237000
6	4.478992000	-1.280483000	-0.314137000
1	4.990732000	-2.240742000	-0.146070000
6	-2.392551000	0.043228000	-1.171959000
6	-0.550472000	0.162690000	-2.875863000
1	-1.243028000	0.236405000	-3.720194000
6	4.530593000	1.150295000	-0.281104000
1	5.083870000	2.083203000	-0.090601000
6	-3.055840000	-1.208716000	-1.067046000
6	-2.352083000	-2.538764000	-1.344462000
1	-1.389839000	-2.311397000	-1.850577000
6	0.994261000	-0.102940000	3.250531000
6	2.567228000	2.576775000	-1.057147000
1	1.494957000	2.403757000	-1.289024000
6	-4.410986000	-1.189451000	-0.675869000

1	-4.959554000	-2.139382000	-0.582666000
6	-1.590661000	1.102805000	3.303304000
1	-2.583812000	1.577346000	3.341220000
6	-3.159570000	-3.447922000	-2.293247000
1	-4.107883000	-3.793682000	-1.831775000
1	-2.572760000	-4.354310000	-2.548497000
1	-3.414758000	-2.929075000	-3.239638000
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6	-3.043156000	1.285085000	-0.941863000
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6	2.436710000	-2.598110000	-1.086502000
1	1.524029000	-2.365871000	-1.675497000
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6	3.287592000	-3.568770000	-1.930510000
1	4.184914000	-3.921442000	-1.380857000
1	3.632480000	-3.097512000	-2.873275000
1	2.694615000	-4.468291000	-2.195559000
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1	-1.368245000	-2.627120000	0.620076000
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1	1.296525000	-2.573549000	0.791556000
6	-2.742812000	-1.163199000	3.260517000
1	-3.239669000	-1.077047000	4.250528000
1	-2.513891000	-2.232513000	3.090904000
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1	-1.262463000	2.435723000	-1.279004000
6	-0.197007000	-0.900398000	3.209842000
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6	-2.492294000	3.564770000	0.071218000
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1	-2.112166000	3.082353000	0.994685000
1	-3.547925000	3.858418000	0.248819000
6	-0.430969000	1.898566000	3.344580000
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6	2.617428000	3.525465000	0.157507000
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1	2.123727000	3.073871000	1.042175000
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1	2.693113000	-0.692269000	4.440699000
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1	-2.314888000	4.268047000	-2.615940000

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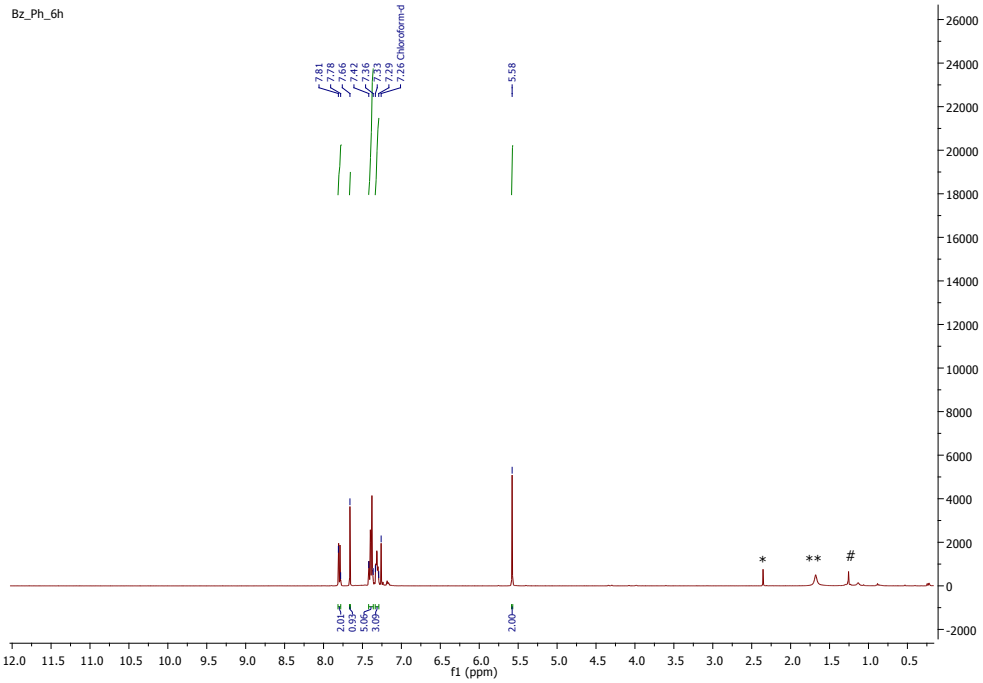
S5. ^{1}H NMR spectrum of the catalysis products:

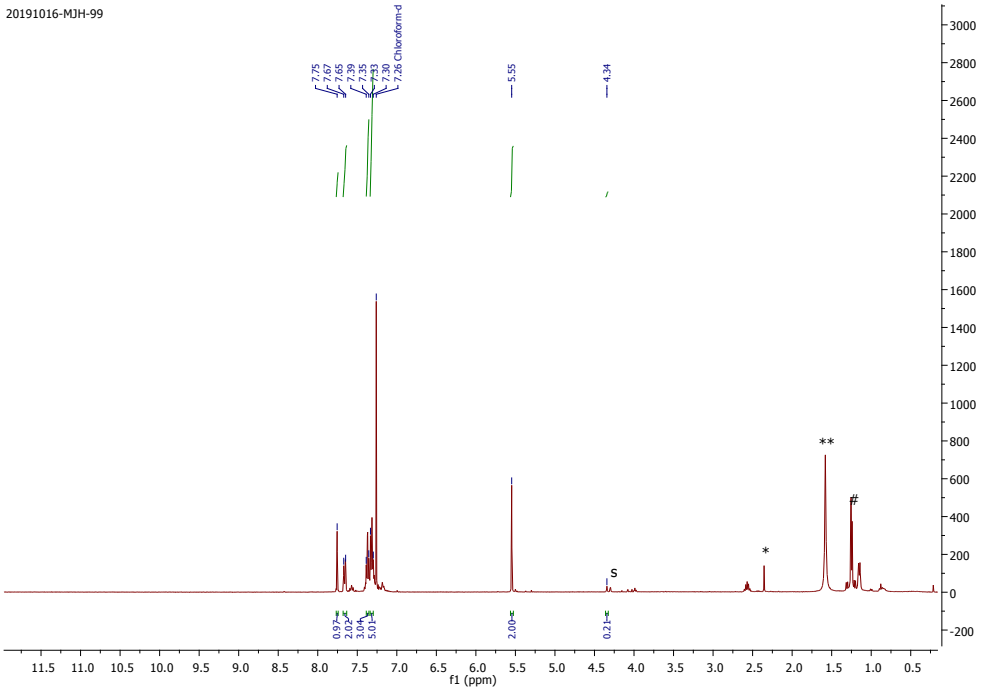
^{1}H NMR (400.31 MHz, $CDCl_3$) of compound I[2].

* = Toluene peak, ** = H_2O peak, # = Grease peak.



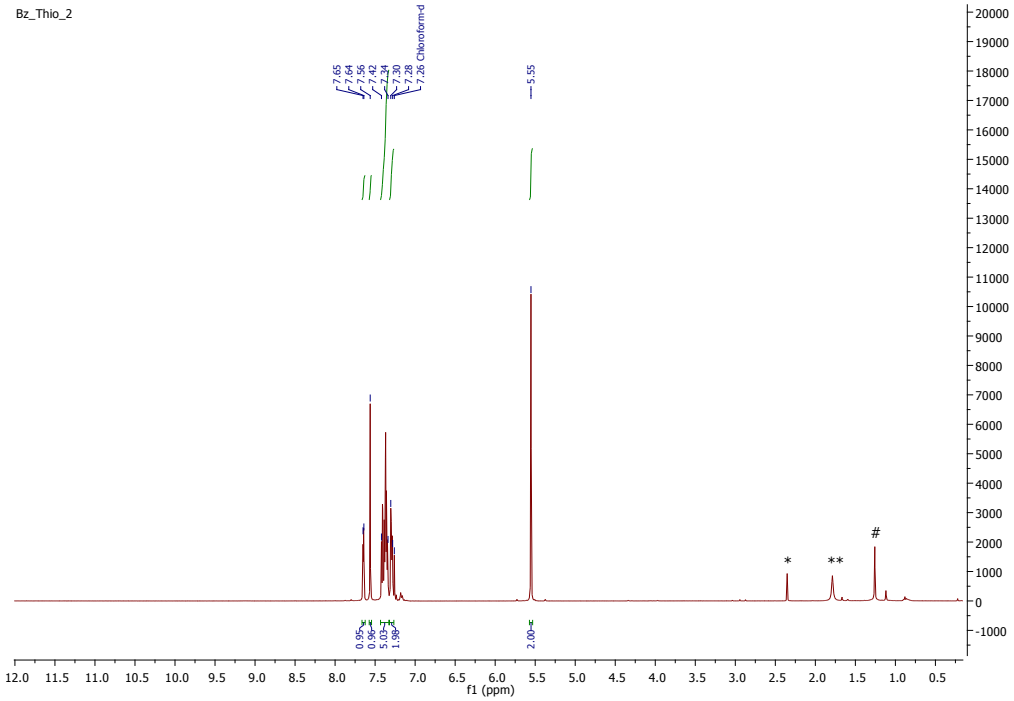
^{1}H NMR (400.31 MHz, $CDCl_3$)of compound I[5].

* = Toluene peak, ** = H_2O peak, # = Grease peak, s = Starting material peak.



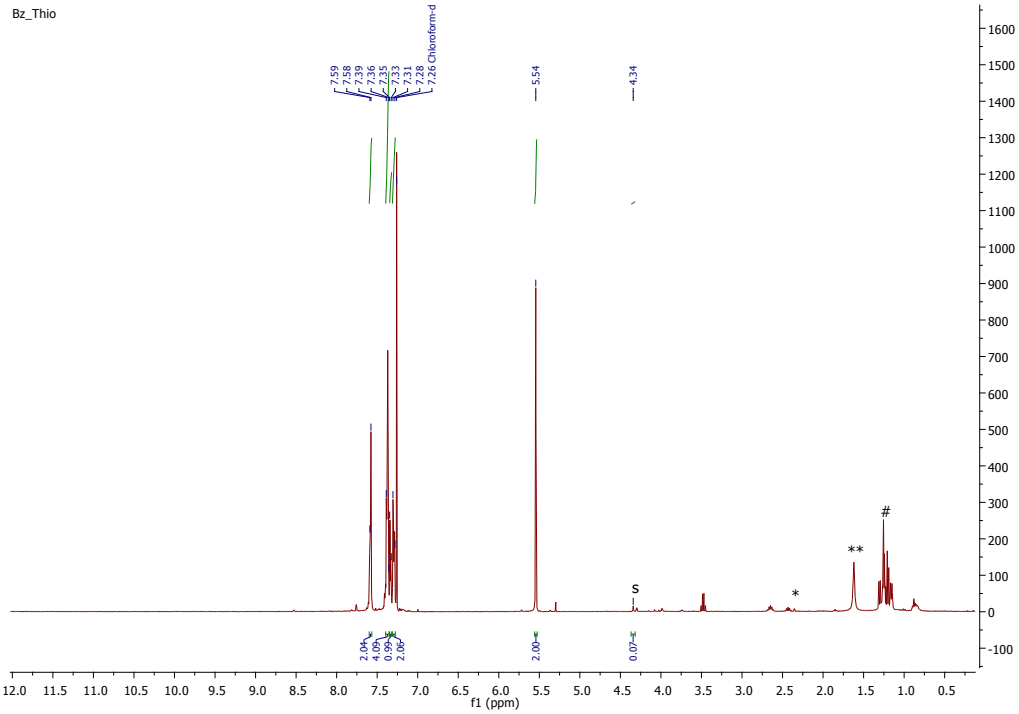
^{1}H NMR (400.31 MHz, $CDCl_3$)of compound II[2].

* = Toluene peak, ** = H_2O peak, # = Grease peak.



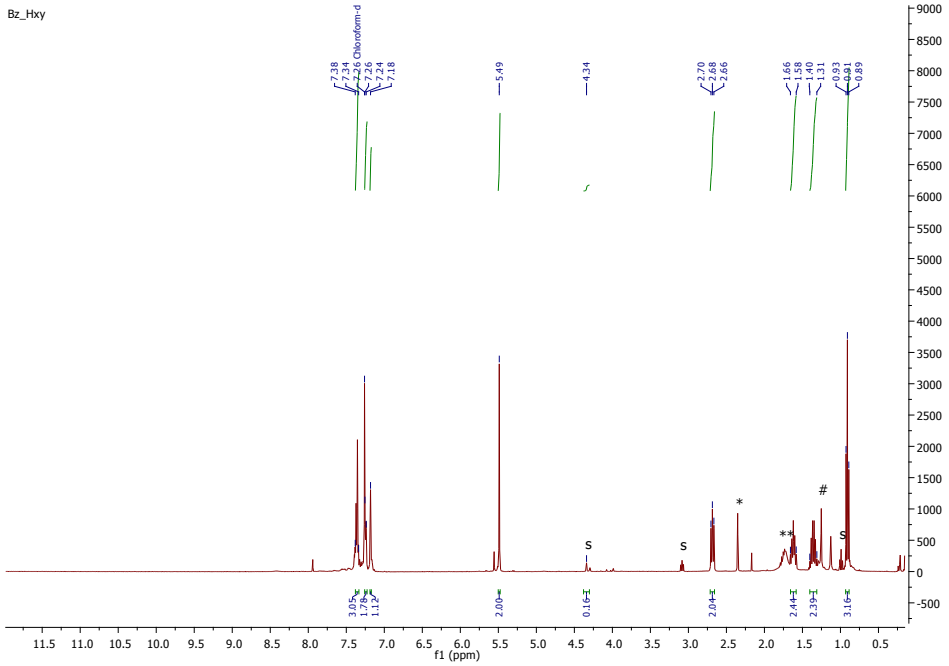
^{1}H NMR of(400.31 MHz, $CDCl_3$) compound II[5].

* = Toluene peak, ** = H_2O peak, # = Grease peak, s = Starting material peak.



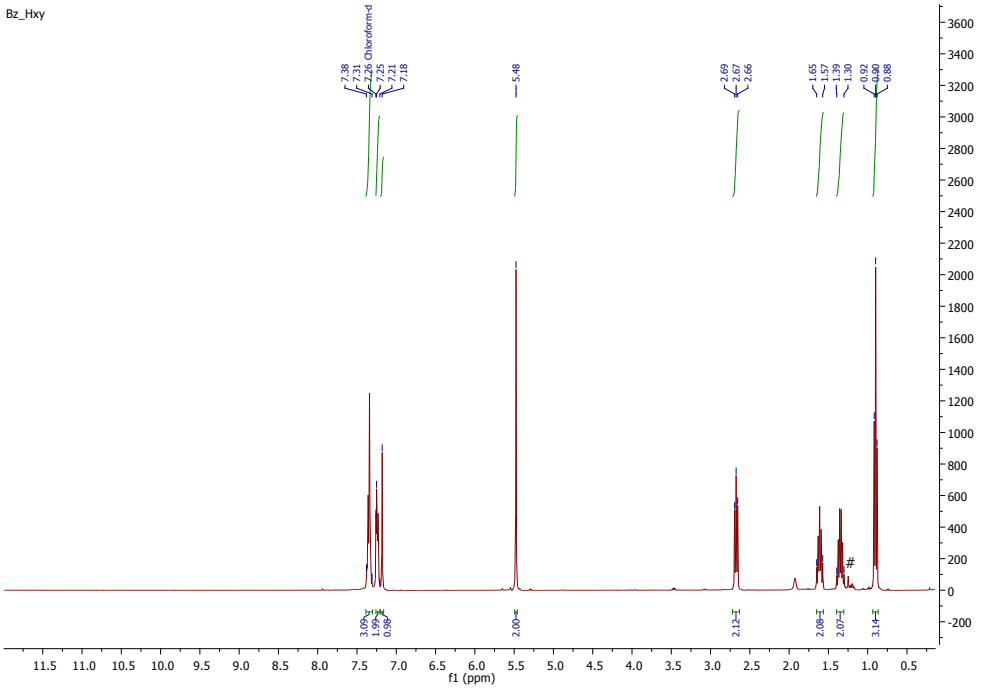
^{1}H NMR (400.31 MHz, $CDCl_3$)of compound III[2].

* = Toluene peak, ** = H_2O peak, # = Grease peak, s = Starting material peak.



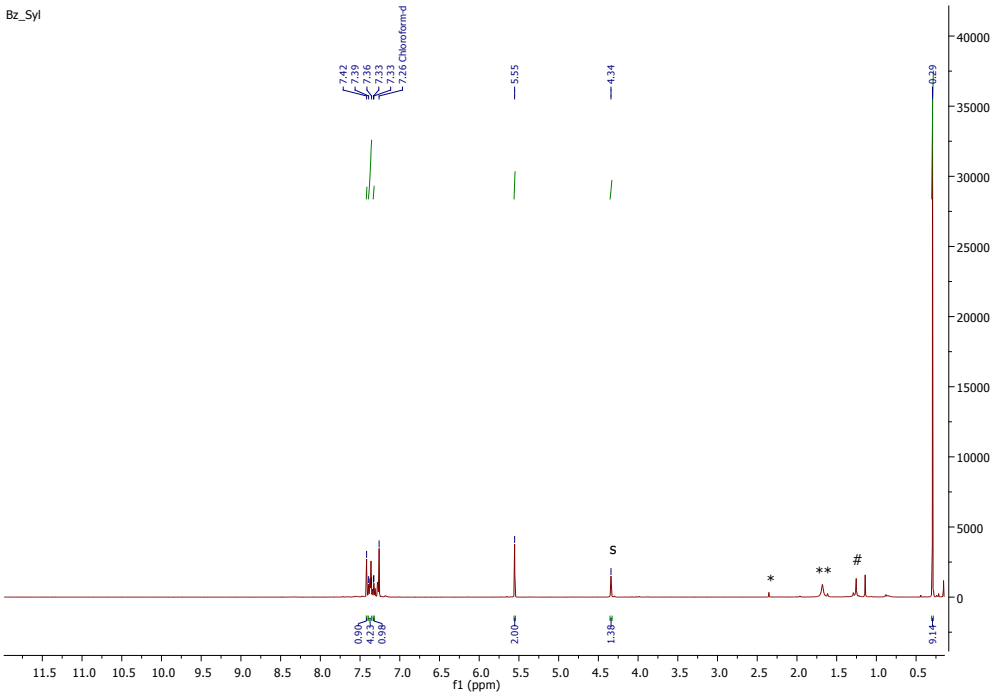
^{1}H NMR (400.31 MHz, $CDCl_3$)of compound III[5].

= Grease peak.



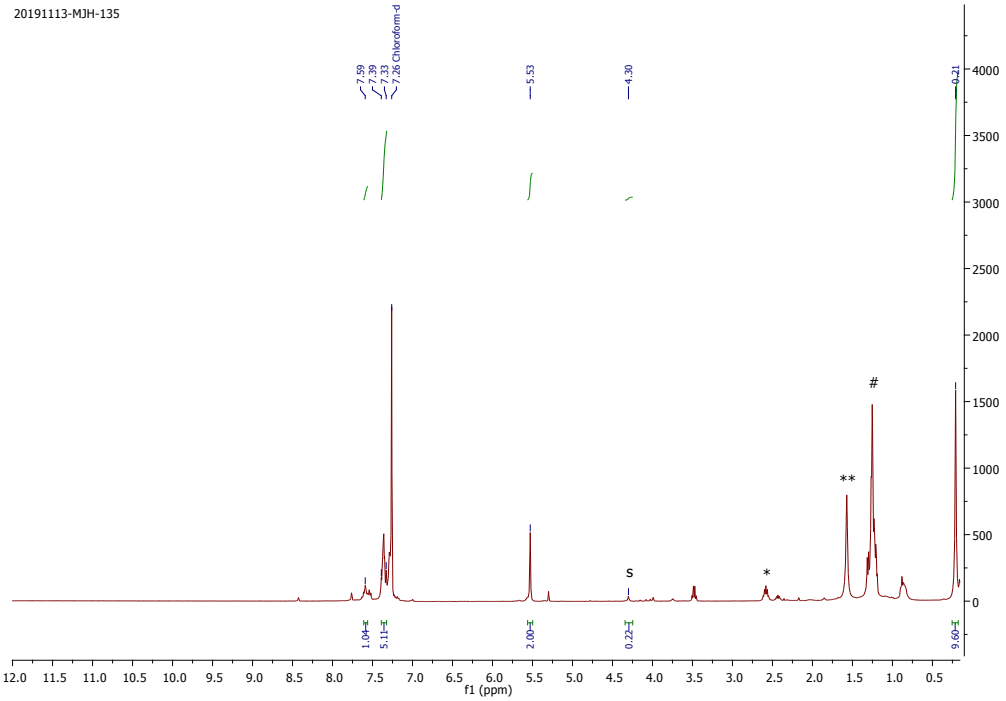
^{1}H NMR(400.31 MHz, $CDCl_3$) of compound IV[2].

* = Toluene peak, ** = H_2O peak, # = Grease peak, s = Starting material peak.



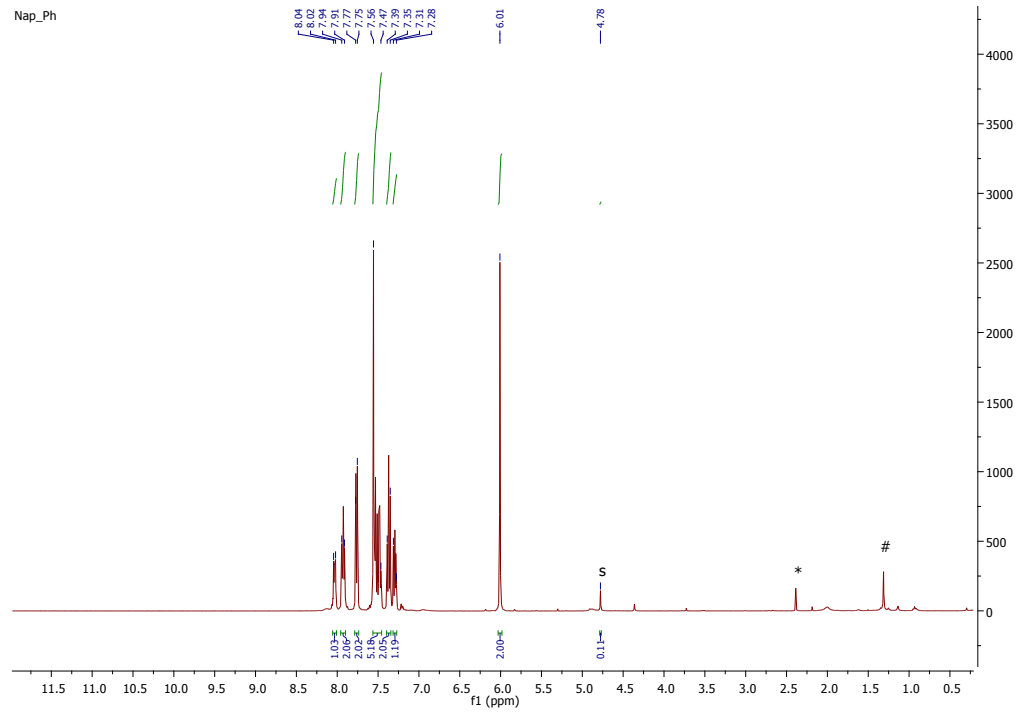
^{1}H NMR (400.31 MHz, $CDCl_3$)of compound IV[5].

* = Toluene peak, ** = H_2O peak, # = Grease peak, s = Starting material peak.



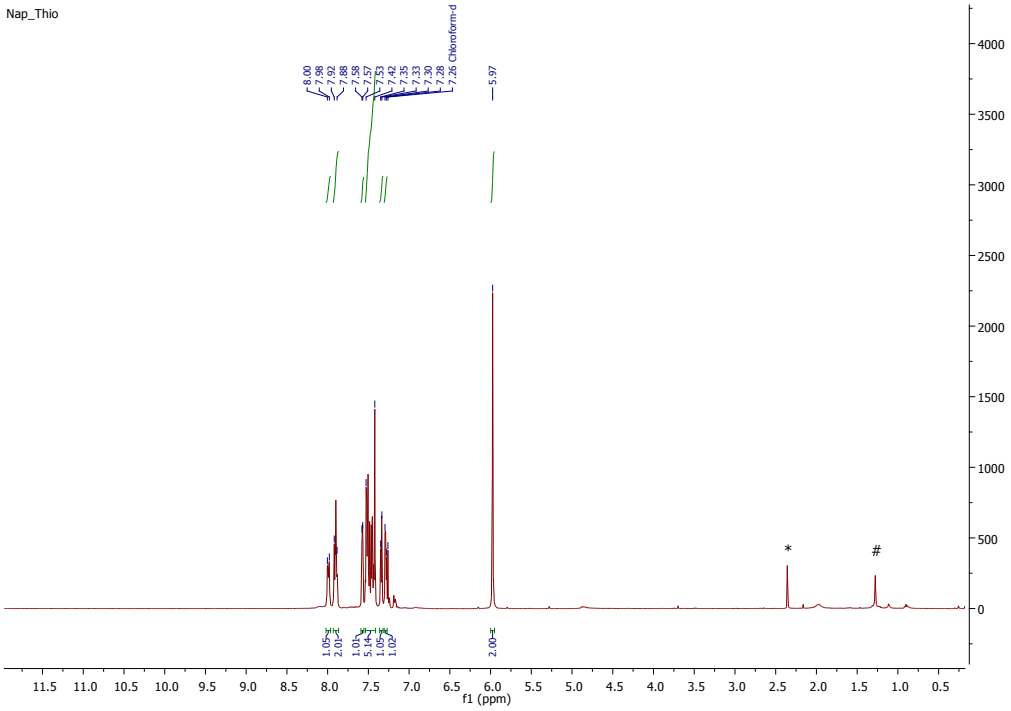
^{1}H NMR (400.31 MHz, $CDCl_3$)of compound V[2].

* = Toluene peak, # = Grease peak, s = Starting material peak.



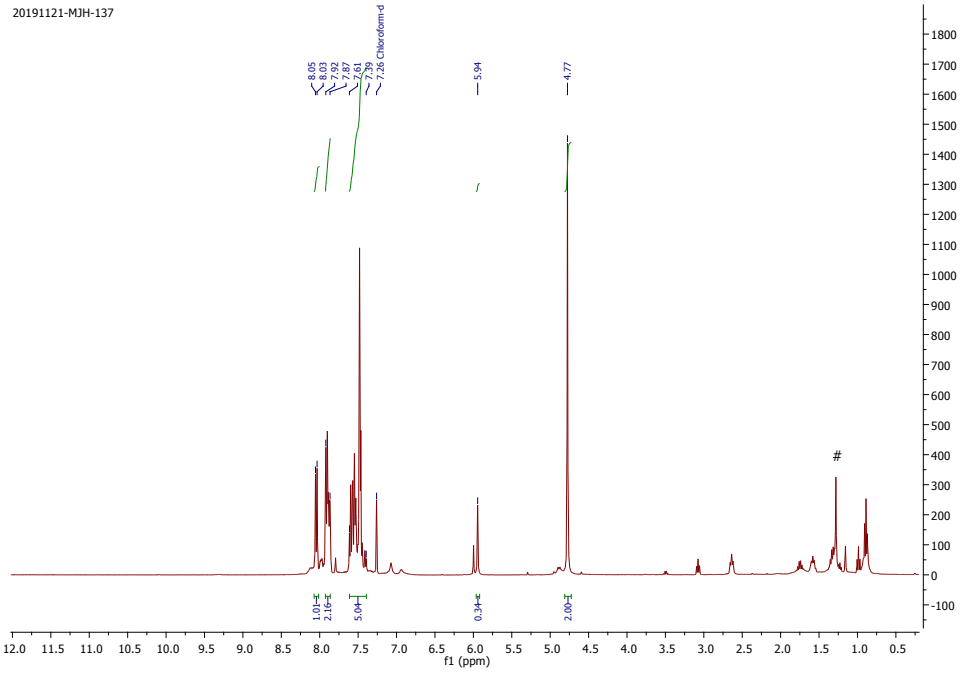
^{1}H NMR (400.31 MHz, $CDCl_3$)of compound VI[2].

* = Toluene peak, # = Grease peak, s = Starting material peak.



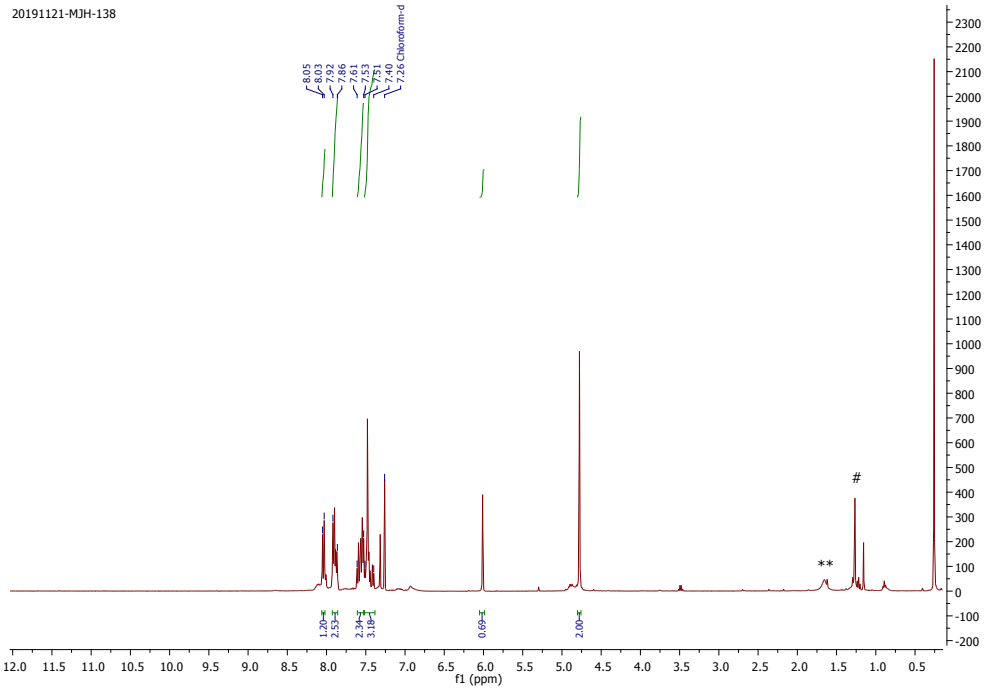
^{1}H NMR (400.31 MHz, $CDCl_3$)of compound VII[2].

= Grease peak



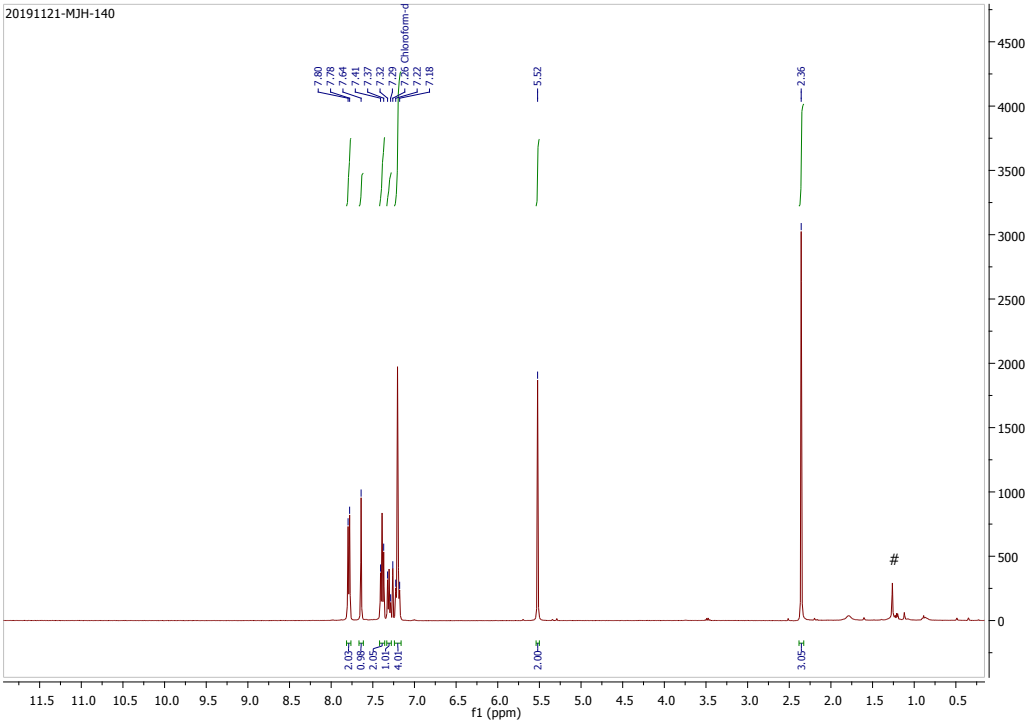
^{1}H NMR (400.31 MHz, $CDCl_3$) of compound VIII[2].

** = H_2O, # = Grease peak



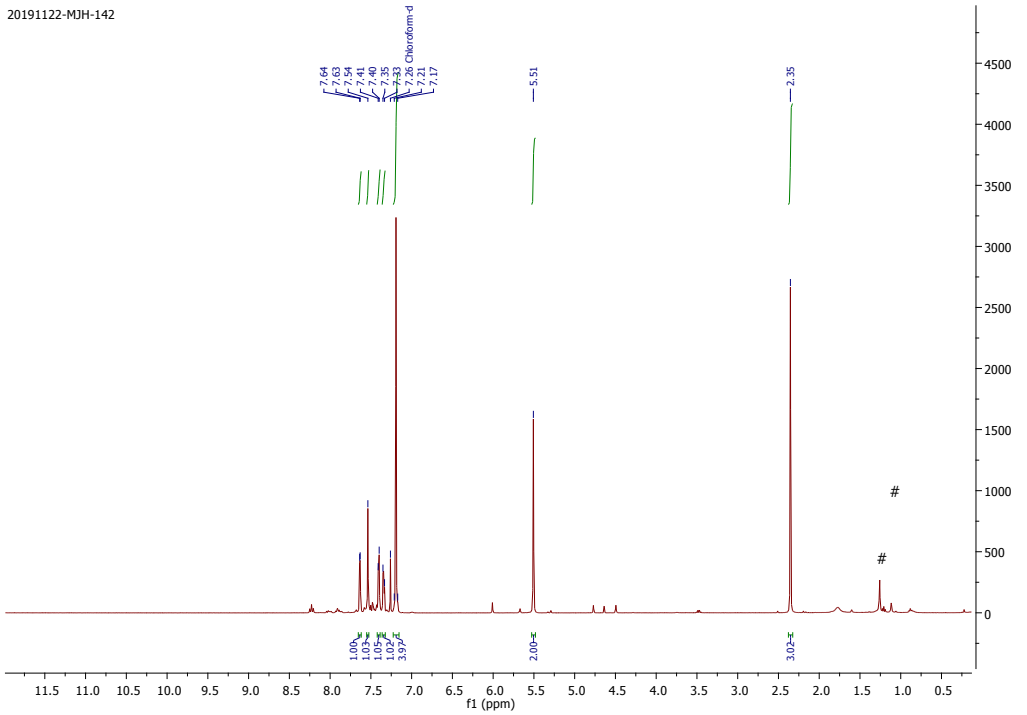
^{1}H NMR (400.31 MHz, $CDCl_3$) of compound IX[2].

= Grease peak



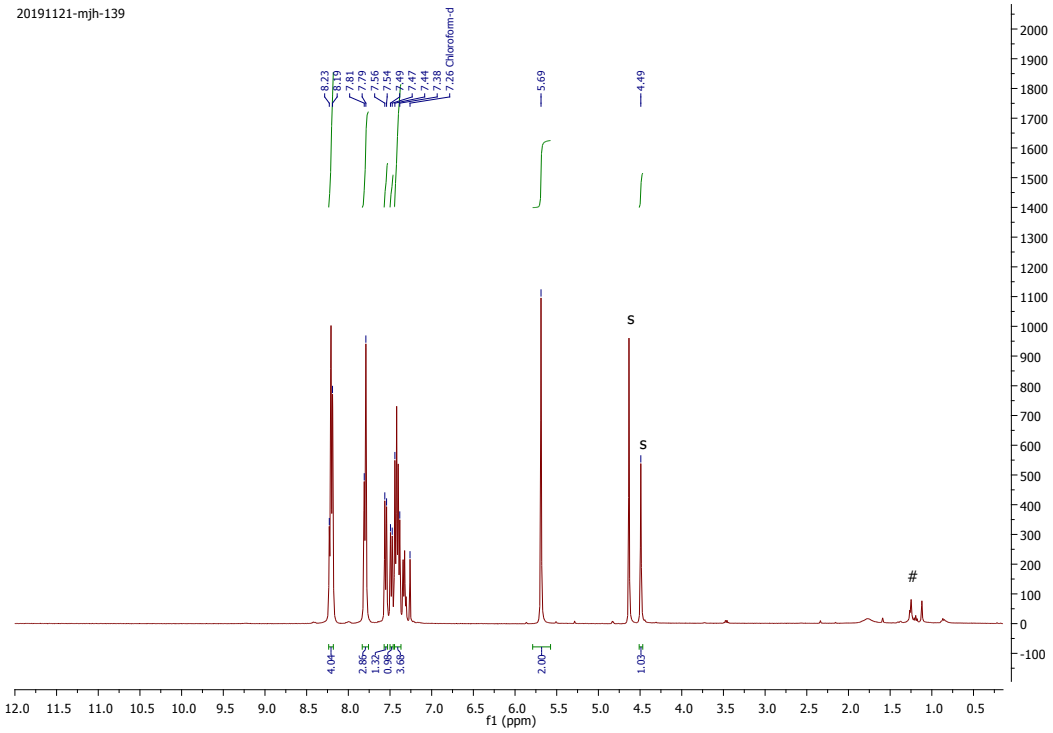
^{1}H NMR (400.31 MHz, $CDCl_3$) of compound X[2].

= Grease peak



^{1}H NMR (400.31 MHz, $CDCl_3$)of compound XI[2].

= Grease peak, s = Starting material peak.



^{1}H NMR (400.31 MHz, $CDCl_3$)of compound XII[2].

** = H_2O peak, # = Grease peak