Electronic Supplementary Material (ESI) for ChemComm.

A Bio-Inspired Imidazole-Functionalised Copper Cage Complex

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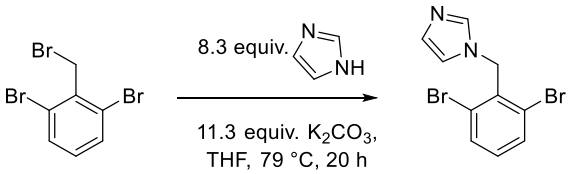
1. General Information

All reactions involving air- or moisture sensitive compounds were carried out under nitrogen using either standard Schlenk and vacuum line techniques or in UNILAB Glovebox from MBraun. All reagents were purchased from commercial sources and used as received unless otherwise stated. Methanol (MeOH) was degassed by sparging with argon and stored over molecular sieves under argon. Tetrahydrofuran (THF), dichloromethane (DCM) and Benzene were taken from a MBRAUN MB SPS-800 solvent purification system. Deuterated DCM was degassed using the freeze -pump-thaw cycles according to the procedure found in literature[1] and subsequently stored over molecular sieves.
^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300, Avance 400 or Avance 500 spectrometer at 25 °C. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to TMS using the residual solvent resonance as internal standard. Infrared spectra were recorded using an ALPHA Platinum-ATR FTIR spectrometer from Bruker. MS measurements were performed at the analytic laboratory of the chemistry department.

2. Experimental Procedures

Compounds **2**[2] and **5**[3] were synthesised as described in literature.

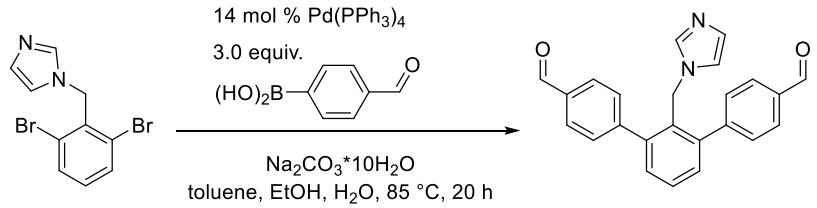
2.1. Synthesis of 3



2 54% **3**

2 (7.36 g, 22.4 mmol), imidazole (12.7 g, 186 mmol) and K_2CO_3 (35 g, 253 mmol) were added to a Schlenk flask with attached reflux condenser under argon containing dry and degassed THF (500 mL). The mixture was stirred for 20 h under reflux and cooled to room temperature afterwards. The resulting mixture was filtered and the filtrates solvent was removed under reduced pressure. The obtained mixture was solved in dichloromethane (50 mL) and washed with saturated aqueous Na_2CO_3 (3 x 30 mL). The organic phase was dried over $MgSO_4$ and filtered. Removal of solvents under reduced pressure gave the crude product that was further purified by recrystallisation from dichloromethane. The product was obtained as colourless crystals (3.79 g, 12.0 mmol, 54%). ^{1}H NMR (300 MHz, CD_2Cl_2): 7.63 (d, *J* = 8.4 Hz, 2H), 7.61 (s, br, 1H) 7.12 (t, *J* = 8.4 Hz, 1H), 7.06 (t, *J* = 1.3 Hz, 1H), 6.95 (t, *J* = 1.1 Hz, 1H), 5.47 (s, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2): 138.16, 134.98, 133.58, 131.97, 129.41, 126.79, 119.52, 51.51. IR (neat): 3075, 2960, 2850, 1430, 1235, 1075, 905, 810, 780, 745, 715, 680, 745, 715, 680, 660, 620. Exact mass ESI MS: $C_{10}H_8N_2Br_2H$ calculated: 314.9127 found: 314.9127.

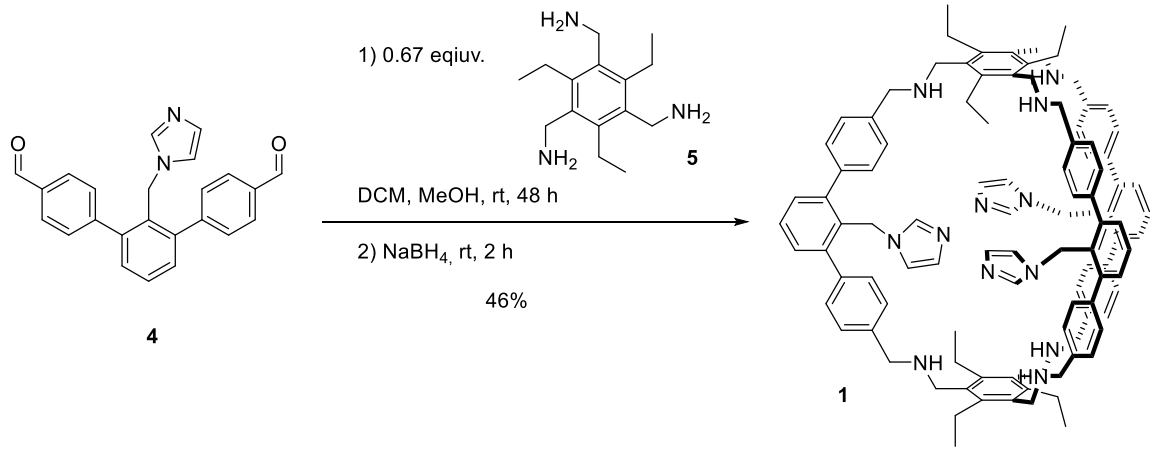
2.2. Synthesis of 4



3 52% **4**

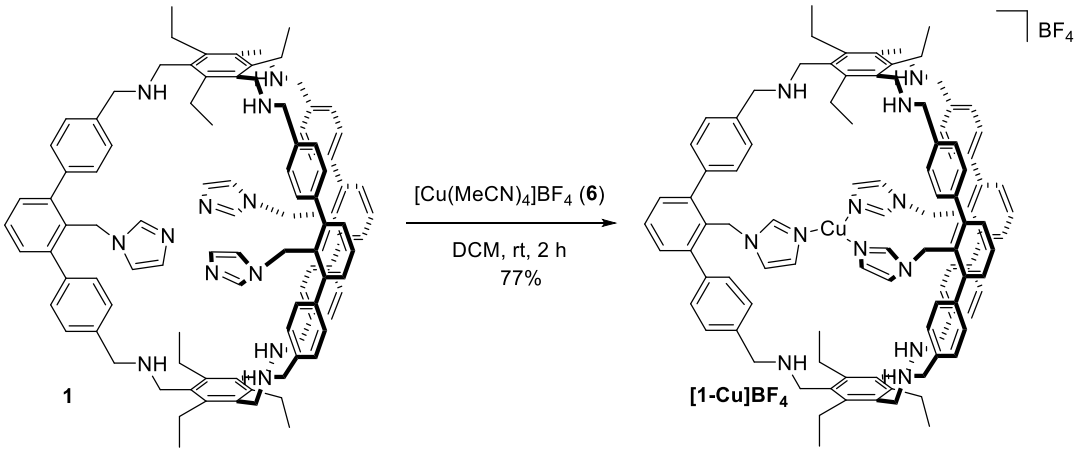
Toluene (60 mL), ethanol (30 mL) and water (30 mL) were added to a Schlenk flask under argon. While stirring, argon was bubbled through the solution for 20 minutes. **3** (1.20 g, 3.80 mmol), 4-formylphenylboronic acid (1.70g, 11.3 mmol), $Na_2CO_3*10H_2O$ (12.0 g, 41.9 mmol) and $Pd(PPh_3)_4$ (0.600 g, 0.519mmol) were added and the mixture was stirred under argon for 20 h at 85 °C (oil bath temperature). Afterwards, the mixture was allowed to cool to room temperature. Water (100 mL) and ethyl acetate (50 mL) were added, the phases were separated and the aqueous phase was extracted with ethyl acetate (2 x 50 mL). The combined organic phases were washed with water (3 x 50 mL), dried over $MgSO_4$ and filtered. The solvents were removed under reduced pressure, the precipitate was solved in DCM (200 ml) and filtered twice through activated charcoal. The solvent was removed under reduced pressure to give the crude product that was further purified upon slow diffusion of pentane into a dichloromethane solution. The product was obtained as colourless crystals (0.722 g, 1.97 mmol, 52%). ^{1}H NMR (300 MHz, $CDCl_3$): 10.06 (s, 2H), 7.92 (d, *J* = 8.3 Hz, 4H), 7.54 (dd, *J* = 8.1 Hz, 7.2 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 4H), 7.35 (d, *J* = 7.7 Hz, 2H), 6.80 (t, *J* = 1.0 Hz, 1H), 6.69 (br, 1H), 6.26 (t, *J* = 1.2 Hz, 1H), 4.98 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 192.01, 146.41, 142.76, 136.46, 135.61, 130.39, 129.29, 129.63, 129.02, 128.40, 118.67, 76.74, 45.51. IR (neat): 2845, 2745, 1700, 1205, 1080, 825, 815, 785, 770, 740, 730, 705, 660, 625, 535. Exact mass ESI MS: $C_{24}H_{18}N_2O_2H$ calculated: 367.1141 found: 367.1142.

2.3. Synthesis of 1



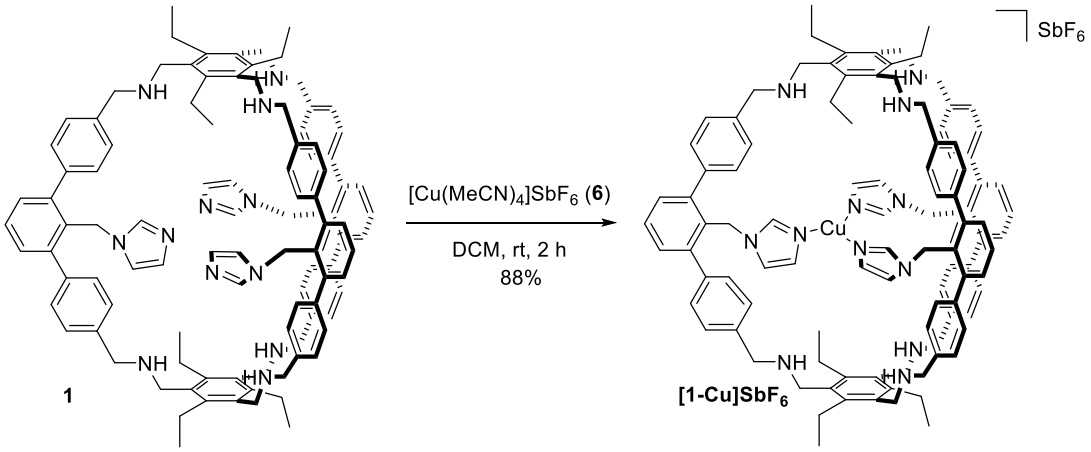
4 (466 mg, 1.27 mmol) and **5** (205 mg, 0.82 mmol) were placed in a dry Schlenk flask under argon. Dry dichloromethane (20 mL) and dry methanol (6 mL) were added and the reaction mixture was stirred for 48 h at room temperature. $NaBH_4$ (106 mg, 2.08 mmol) was added in portions and the resulting mixture was stirred for 3 h at room temperature. The mixture was diluted with dichloromethane (20 mL) and washed with water (4 x 20 mL). After filtration, removal of solvents under reduced pressure gave the crude product that was further purified by column chromatography (DCM:MeOH:7N NH_3 in MeOH = 50:5:1, R_F = 0.73 as eluent). **1** was obtained as a white solid (190 mg, 0.13 mmol, 46%). ^{1}H NMR (500 MHz, $CDCl_3$): 7.39 (t, *J* = 7.9 Hz, 3H) 7.37 (d, *J* = 7.9 Hz, 12H), 7.22 (d, *J* = 7.6 Hz, 6H), 7.06 (d, *J* = 8.1 Hz, 12H), 6.64 (s, 3H), 6.54 (s, 3H), 6.18 (s, 3H), 4.79 (s, 6H), 3.90 (s, 12H), 3.88 (s, 12H), 2.92 (q, *J* = 7.2 Hz, 12H), 1.33 (t, *J* = 7.5 Hz, 18H). ^{1}H DOSY NMR (500 MHz, $CDCl_3$): $D = 4.1*10^{-10}$ m^2 s^{-1}. ^{13}C NMR (75 MHz, CD_2Cl_2): 144.19, 142.92, 140.39, 139.91, 137.14, 134.36, 131.08, 130.57, 129.33, 128.90, 128.58, 118.96, 55.70, 49.00, 45.54, 23.20, 17.37. IR (neat): 2960, 2925, 2865, 1500, 1445, 1180, 1070, 1020, 800, 730, 660, 530. Exact mass ESI MS: $C_{102}H_{108}N_{12}H$ calculated: 1501.8893 found: 1501.8883. Resonances for small amounts of a similar species are found in the ^{1}H NMR spectrum. Further purification can be reached after complexation of Cu(I) (see 2.4. and 2.5.).

2.4. Synthesis of [1-Cu]BF_4



In a glove box **6** (15.0 mg, 48.0 µmol) was placed in a vial. **1** (90.0 mg, 60.0 µmol) was solved in dry and degassed dichloromethane (10 mL) and added to the vial. The vial was closed and the mixture was stirred for 2 h at room temperature. Afterwards, the solvent was removed under reduced pressure and the remaining solid was washed with benzene and extracted with ether. After removal of solvents under reduced pressure **[1-Cu]BF_4** was obtained as a white solid (58.0 mg, 37.1 µmol, 77% (with respect to used copper salt)). ^{1}H NMR (500 MHz, $CDCl_3$): 7.48 (t, *J* = 7.6 Hz, 3H), 7.34 (d, *J* = 7.6 Hz, 12H), 7.30 (d, *J* = 7.7 Hz, 6H), 7.02 (d, *J* = 7.8 Hz, 12H), 7.00 (s, 3H), 6.42 (s, 3H), 6.37 (s, 3H), 4.87 (s, 6H), 3.92 (s, 12H), 3.87 (s, 12H), 2.89 (q, *J* = 7.4 Hz, 12H), 1.34 (t, *J* = 7.5 Hz, 18H). ^{1}H NMR (300 MHz, CD_2Cl_2): 7.48 (t, *J* = 7.7 Hz, 3H), 7.39 (d, *J* = 7.6 Hz, 12H), 7.29 (d, *J* = 7.6 Hz, 6H), 7.08 (d, *J* = 7.7 Hz, 12H), 6.76 (s, 3H), 6.27 (s, 3H) 6.24 (s, 3H), 4.93 (s, 6H), 3.94 (s, 12H), 3.91 (s, 12H), 2.91 (q, *J* = 8.1 Hz, 12H), 1.30 (t, *J* = 7.4 Hz, 18H). ^{1}H DOSY NMR (500 MHz, $CDCl_3$): $D = 4.1*10^{-10}$ m^2 s^{-1}. ^{13}C NMR (125 MHz, $CDCl_3$): 144.52, 142.64, 139.82, 139.09, 136.50, 134.19, 130.25, 129.12, 129.02, 128.94, 128.48, 128.38, 118.62, 55.33, 48.82, 45.16, 23.06, 17.07. ^{19}F NMR (471 MHz, $CDCl_3$): 153.1 (s). IR (neat): 2965, 2930, 2870, 1510, 1445, 1105,1050, 845, 800, 775, 735, 705, 655, 615, 535, 520. Exact mass ESI-MS: $C_{102}H_{108}N_{12}Cu$ calculated: 1563.8110 found: 1563.8112.

2.5. Synthesis of [1-Cu]SbF_6



In a glove box **7** (8.2 mg, 18 µmol) was placed in a vial. **1** (31.0 mg, 20.7 µmol) was solved in dry and degassed dichloromethane (10 mL) and added to the vial. The vial was closed and the mixture was stirred for 2 h at room temperature. Afterwards, the solvent was removed under reduced pressure and the remaining solid was washed with benzene and extracted with tetrahydrofuran. After removal of solvents under reduced pressure, **[1-Cu]SbF_6*3THF** was obtained as a white solid (31.5 mg, 15.6 µmol, 88% (with respect to used copper salt)). ^{1}H NMR (300 MHz, CD_2Cl_2): 7.55 (dd, *J* = 8,1 Hz, 7,2 Hz, 3H), 7.41 (d, *J* = 8.1 Hz, 12H), 7.36 (d, *J* = 7.6 Hz, 6H), 7.13 (d, *J* = 8.1 Hz, 12H), 6.90 (s br, 3H), 6.33 (s, 3H), 6.29 (s, 3H), 5.00 (s, 6H), 3.97 (s, 12H), 3.92 (s, 12H), 3.72 (m, 6H) 2.94 (q, *J* = 7.3 Hz, 12H), 1.86 (m, 6H), 1.35 (t, *J* = 7.3 Hz, 18H). Resonances for small amounts of a similar species are found in the ^{1}H NMR spectrum. Further purification can be reached via extraction with large amounts of diethyl ether (see Figure S23).
^{1}H DOSY NMR (500 MHz, CD_2Cl_2): $D = 5.6*10^{-10}$ m^2 s^{-1}. ^{13}C NMR (125 MHz, CD_2Cl_2): 144.87, 142.80, 140.87, 139.39, 137.15, 134.58, 130.64, 129.52, 129.28, 128.62, 128.55, 128.45, 119.24, 66.22, 55.36, 48.99, 45.62, 23.08, 17.33, 15,67. ^{19}F NMR (471 MHz, CD_2Cl_2): -114.2-(-135.1) (m). IR (neat): 2970, 2930, 2870, 1515, 1450, 1400, 1380, 1110, 1080, 1020, 805, 780, 740, 705, 655, 535. Exact mass ESI-MS: $C_{102}H_{108}N_{12}Cu$ calculated: 1563.8110 found: 1563.8091.

2.6. Oxidation of 8 to 9

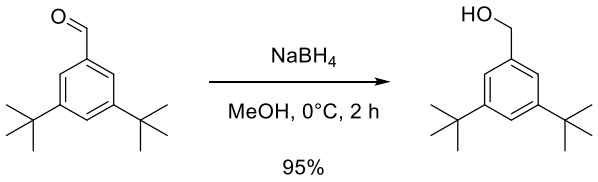
General procedure (Table 1, entries 1 and 2): In a glove box **[1-Cu]BF_4** (16.5 mg, 10.0 µmol, 1 mol%) was placed in a vial. The vial was taken out of the glove box and dichloromethane (9 mL), **8** (136 mg, 1.00 mmol), water (0.2 mL) and TEMPO (11.2 mg, 71.7 µmol) were added. The mixture was stirred for the indicated time at room temperature and was diluted afterwards with dichloromethane (5 mL). The phases were separated and the solvent of the organic phase was removed under reduced pressure. The crude product was subjected to ^{1}H NMR spectroscopy to determine the yield of **9** in the presence of 4-nitrobenzylic alcohol as an internal standard.

Table 1, entry 3: [1-Cu]BF_4 (1.30 mg, 0.787 µmol, 10.3 mol%) was solved in CD_2Cl_2 (0.7 mL) and **8** (10.6 mg, 76.6 µmol), D_2O (0.02 mL) and TEMPO (0.84 mg, 5.36 µmol) were added. The mixture was stirred for 16 h at room temperature. The phases were separated and the organic phase was subjected to ^{1}H NMR spectroscopy to determine the yield of **9** (67.4 µmol, 88%) in the presence of 4-bromobenzaldehyde as an internal standard.

Table 1, entry 9: 8 In a glove box $Cu(MeCN)_4BF_4$ (3.1 mg, 1.0 µmol, 1 mol%) was placed in a vial. The vial was taken out of the glove box and **8** (136 mg, 1.00 mmol), *N*-methylimidazole (2.5 mg, 3.0 µmol, 3 mol%), TEMPO (11.2 mg, 71.7 µmol), DCM (1.5 mL) and H_2O (0.2 mL) and were added. The mixture was stirred for 14 h at room temperature. The phases were separated and the organic phase was subjected to ^{1}H NMR spectroscopy to determine the yield of **9** (0.375 mmol, 37%) in the presence of 4-bromobenzaldehyde as an internal standard.

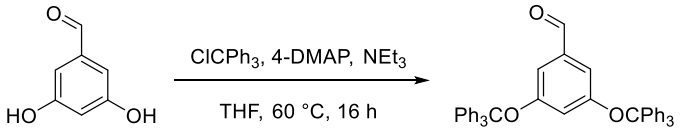
Table 1, entry 9: 8 In a glove box $Cu(MeCN)_4OTf$ (4.7 mg, 1.2 µmol, 1 mol%) was placed in a vial. The vial was taken out of the glove box and **8** (136 mg, 1.00 mmol), *N*-methylimidazole (2.0 mg, 2.4 µmol, 2 mol%), 2-2'-bipyridine (2.0 mg, 1.2 µmol, 1 mol%), TEMPO (11.2 mg, 71.7 µmol), DCM (1.5 mL) and H_2O (0.2 mL) and were added. The mixture was stirred for 14 h at room temperature. The phases were separated and the organic phase was subjected to ^{1}H NMR spectroscopy to determine the yield of **9** (0.385 mmol, 39%) in the presence of 4-bromobenzaldehyde as an internal standard.

2.7. Synthesis of 3,5-di-tert-butyl-benzyl alcohol



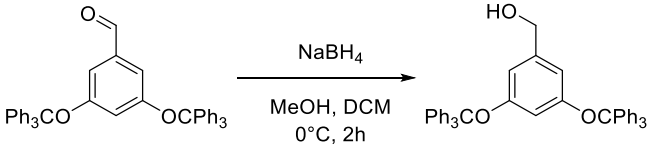
3,5-di-tert-butyl-benzaldehyde (1.05 g, 4.81 mmol) was placed in a round-bottom flask under air. Dry methanol (30 mL) was added and the mixture was cooled to 0 °C. $NaBH_4$ (278 mg, 7.35 mmol) was added in portions and the resulting mixture was stirred for 2 hours at 0 °C. The reaction was quenched upon addition of saturated aqueous NH_4Cl solution (25 mL). The mixture was diluted with ethyl acetate (20 mL) and phases were separated. The aqueous phase was extracted with ethyl acetate (2 x 20 mL) and dichloromethane (2 x 20 mL). The combined organics were washed with water (50 mL) and brine (50 mL), dried over $MgSO_4$ and filtered afterwards. The solvents were removed under reduced pressure to give 3,5-di-tert-benzyl alcohol as a colourless oil (1.00 g, 4.55 mmol, 95%) that crystalises upon storing at 4 °C. The analytical data matched with those reported in literature.[4]

2.8. Synthesis of 3,5-dirityloxybenzaldehyde



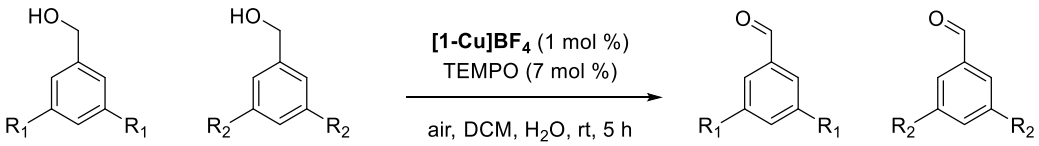
In a Schlenk flask with an attached reflux condenser 3,5-dihydroxybenzaldehyde (1.00 g, 8.04 mmol) was solved in dry THF (60 mL). Trityl chloride (5.33 g, 19.13 mmol), trimethylamine (8.0 mL) and 4-DMAP (220 mg, 1.80 mmol) were added to the mixture. The mixture was stirred at 60 °C for 16 h. The mixture was cooled to room temperature and diluted with dichloromethane (100 mL). The mixture was washed with water (3 x 50 mL), dried over $MgSO_4$ and filtered afterwards. Removal of the solvents under reduced pressure gave the crude product that was further purified by flash column chromatography (DCM:hexane:EtOAc = 2.5:9:1, R_F = 0.54 in hexane:EtOAc = 9:1). 3,5-dirityloxybenzaldehyde was obtained as a white solid (2.36 g, 3.80 mmol, 47%). ^{1}H NMR (300 MHz, $CDCl_3$): 9.42 (s, 1H), 7.23 – 7.16 (m, 30H), 6.59 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 191.66, 156.92, 143.67, 136.50, 128.90, 127.87, 127.34, 121.56, 117.31, 91.50. IR (neat): 3090, 3055, 3030, 2745, 1695, 1585, 1490, 1450, 1295, 1145, 1015, 1000, 950, 770, 705, 640, 610. Exact mass ESI MS: $C_{45}H_{34}O_3Na$ calculated: 645.2400 found: 645.2383.

2.9. Synthesis of 3,5-dirityloxybenzyl alcohol



3,5-dirityloxybenzaldehyde (1.69 g, 2.70 mmol) was placed in a round-bottom flask under air. Dry methanol (20 mL) and dry DCM (20 mL) were added and the mixture was cooled to 0 °C. $NaBH_4$ (156 mg, 4.12 mmol) was added in portions and the resulting mixture was stirred for 2 hours at 0 °C. The reaction was quenched upon addition of saturated aq. NH_4Cl solution (25 mL). The mixture was diluted with DCM (20 mL) and phases were separated. The aqueous phase was extracted with ethyl acetate (2 x 20 mL) and dichloromethane (2 x 20 mL). The combined organics were washed with water (2 x 50 mL), dried over $MgSO_4$ and filtered afterwards. The solvents were removed under reduced pressure to give 3,5-dirityloxybenzyl alcohol as a white solid (1.49 g, 2.39 mmol, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.21 – 7.14 (m, 30H), 6.25 (t, *J* = 2.2 Hz, 1H), 6.07 (d, *J* = 2.2 Hz, 2H), 4.13, (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 156.37, 144.09, 141.14, 128.99, 127.21, 127.07, 115.08, 90.95, 65.04. IR (neat): 3040, 2925, 1580, 1490, 1140, 1025, 1000, 990, 760, 745, 695, 635. Exact mass ESI MS: $C_{45}H_{36}O_3$ calculated: 625.2737 found: 625.2742.

2.10. General procedure for competition experiments with [1-Cu]BF_4 as catalyst (table S2, entry 1,4,7,10)

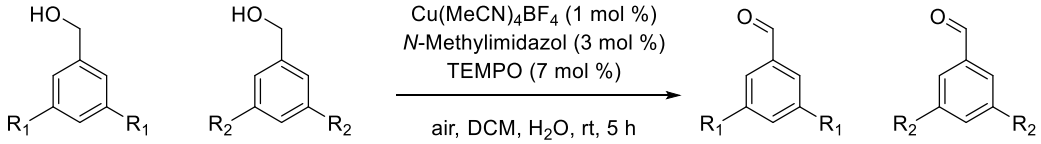


0.5 equiv. 0.5 equiv.

In a glove box **[1-Cu]BF_4** (16.5 mg, 10.0 µmol, 1 mol%) was placed in a vial. The vial was taken out of the glove box and dichloromethane (9 mL), $Ar_{R1}CH_2OH$ (0.50 mmol), $Ar_{R2}CH_2OH$ (0.50 mmol), water (0.2 mL) and TEMPO (11.2 mg, 71.7 µmol) were added. The mixture was stirred for 5 h at room temperature and was diluted afterwards with dichloromethane (5 mL). The phases were separated and most of the solvent of the organic

phase was removed under reduced pressure. The crude product was subjected to ^{1}H NMR spectroscopy in the presence of 4-nitrobenzylic alcohol as an internal standard.

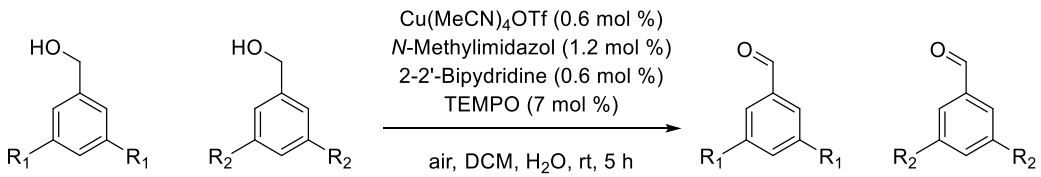
2.11. General procedure for competition experiments with **6**·3(NMI) as catalyst (table S2, entry 2,5,8,11)



0.5 equiv. 0.5 equiv.

In a glove box $Cu(MeCN)_4BF_4$ (3.1 mg, 10 µmol, 1 mol%) was placed in a vial. The vial was taken out of the glove box and dichloromethane (9 mL), $Ar_{R1}CH_2OH$ (0.50 mmol), $Ar_{R2}CH_2OH$ (0.50 mmol), *N*-Methylimidazol (2.5 mg, 30 µmol 3 mol %), water (0.07 mL), and TEMPO (11.2 mg, 71.7 µmol, 7 mol %) were added. The mixture was stirred for 5 h at room temperature. The resulting volume of the mixture was determined and the solvent of a defined sample was removed under reduced pressure. The sample was subjected to ^{1}H NMR spectroscopy in the presence of 4-bromo benzaldehyde as an internal standard.

2.12. General procedure for competition experiments with **10**·(bipy)·2(NMI) as catalyst (table S2, entry 3,6,9,12)



0.5 equiv. 0.5 equiv.

In a glove box $Cu(MeCN)_4OTf$ (2.3 mg, 6.1 µmol, 0.6 mol%) was placed in a vial. The vial was taken out of the glove box and dichloromethane (9 mL), $Ar_{R1}CH_2OH$ (0.5 mmol), $Ar_{R2}CH_2OH$ (0.5 mmol), *N*-Methylimidazol (1.0 mg, 12 µmol, 1.2 mol %) 2-,2'-bipyridine (1.0 mg, 6.1 µmol, 0.6 mol%), water (0.07 mL), and TEMPO (11.2 mg, 70 µmol, 7 mol %) were added. The mixture was stirred for 5 h at room temperature. The resulting volume of the mixture was determined and the solvent of a defined sample was removed under reduced pressure. The sample was subjected to ^{1}H NMR spectroscopy in the presence of 4-bromo benzaldehyde as an internal standard.

2.13. Selectivities and yields of all competition experiments

Table S1. Selectivities and yields of all competition experiments .[a]

entry	[Cu] ([mol%])	R1	R2	PR1:PR2	Yield [%]
1	**[1-Cu]BF$_4$** (1)			59:41	6
2	**6**·3(NMI) (1)	Me	*t*-Bu	42:58	22
3	**10**·(bipy)·2(NMI) (0.6)			52:48	21
4	**[1-Cu]BF$_4$** (1)			67:33	7
5	**6**·3(NMI) (1)	H	*t*-Bu	54:45	4
6	**10**·(bipy)·2(NMI) (0.6)			52:48	3
7	**[1-Cu]BF$_4$** (1)			64:36	9
8	**6**·3(NMI) (1)	OMe	OTr	60:40	7
9	**10**·(bipy)·2(NMI) (0.6)			58:42	10
10	**[1-Cu]BF$_4$** (1)			49:51	16
11	**6**·3(NMI) (1)	OMe	OBn	44:56	11
12	**10**·(bipy)·2(NMI) (0.6)			47:53	12

[a] Substrate concentration = 0.11 M; reactions under air; 1 mol% **[1-Cu]BF$_4$**; 7 mol% TEMPO; 11.1 equiv. H_2O; rt; 5.0 h. All yields were determined by ^{1}H NMR spectroscopy of the crude product mixtures in presence of internal standards.

3. Spectra

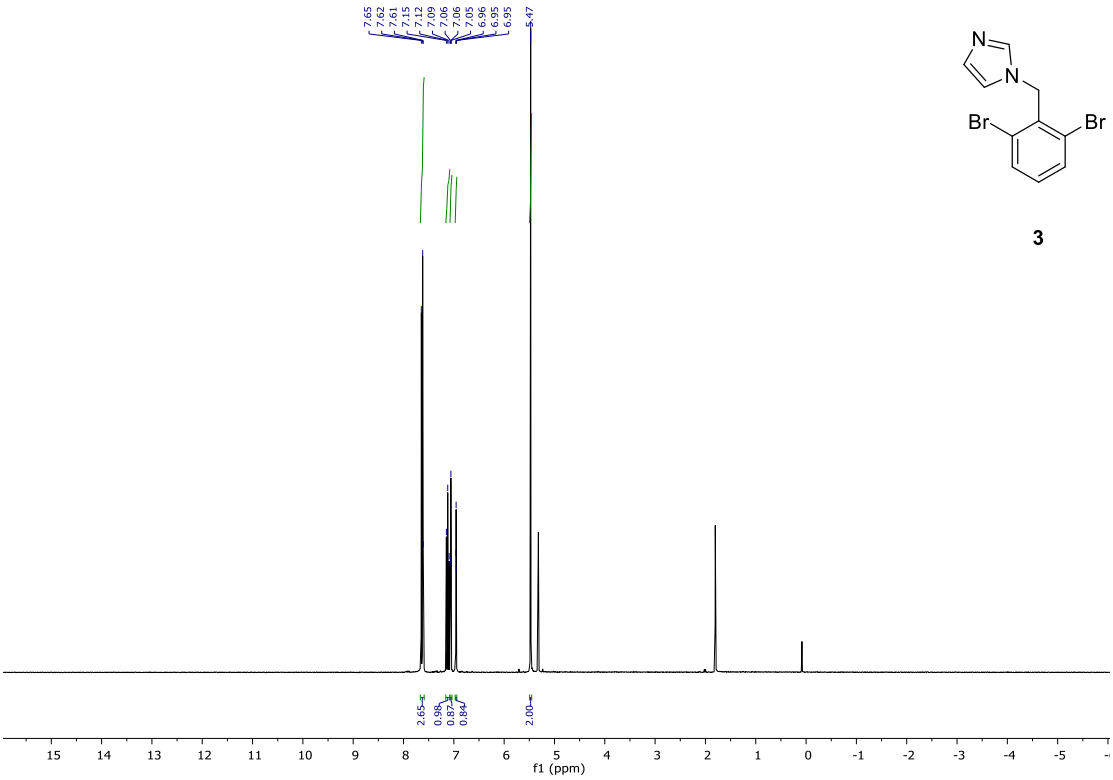


Figure S1. ^{1}H NMR spectrum of **3** in CD_2Cl_2 at rt.

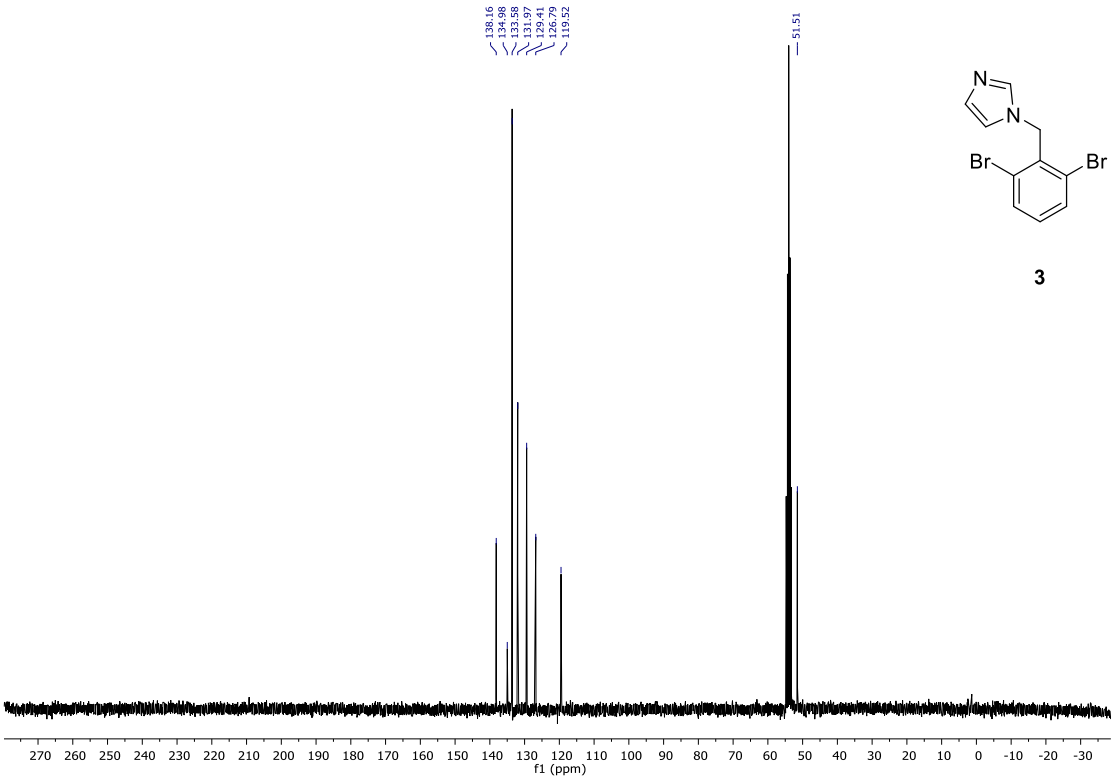


Figure S2. ^{13}C NMR spectrum of **3** in CD_2Cl_2 at rt.

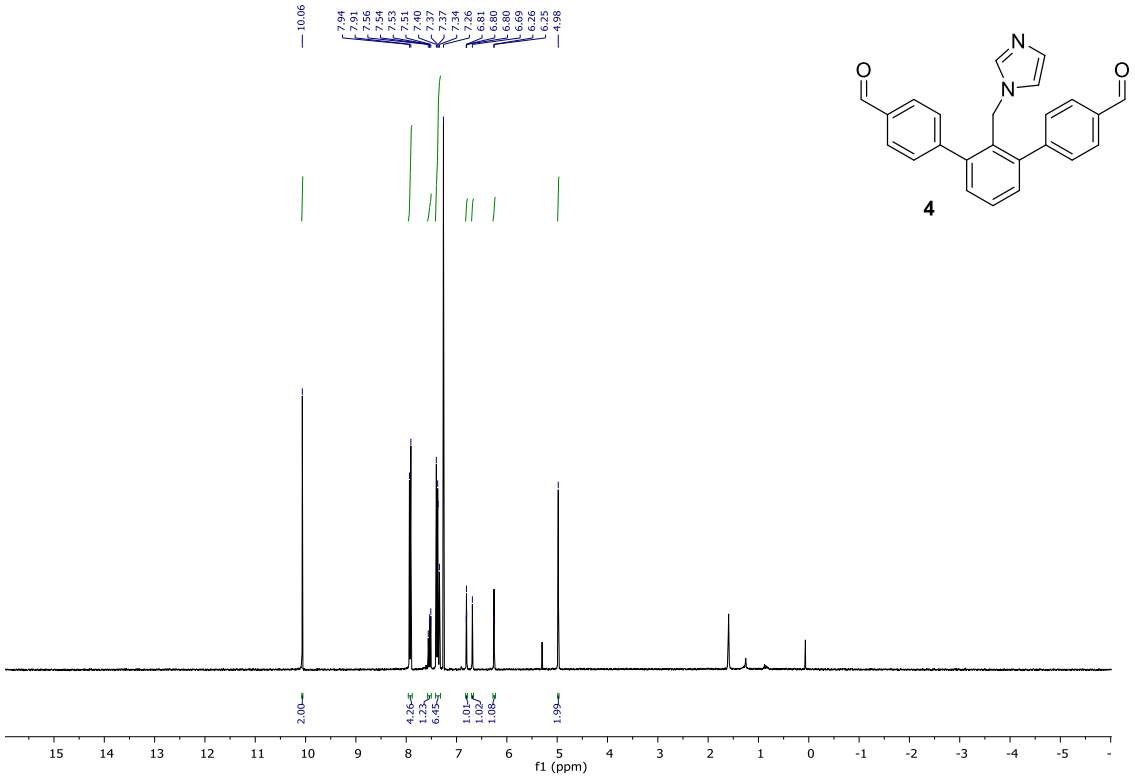


Figure S3. ^{1}H NMR spectrum of **4** in $CDCl_3$ at rt.

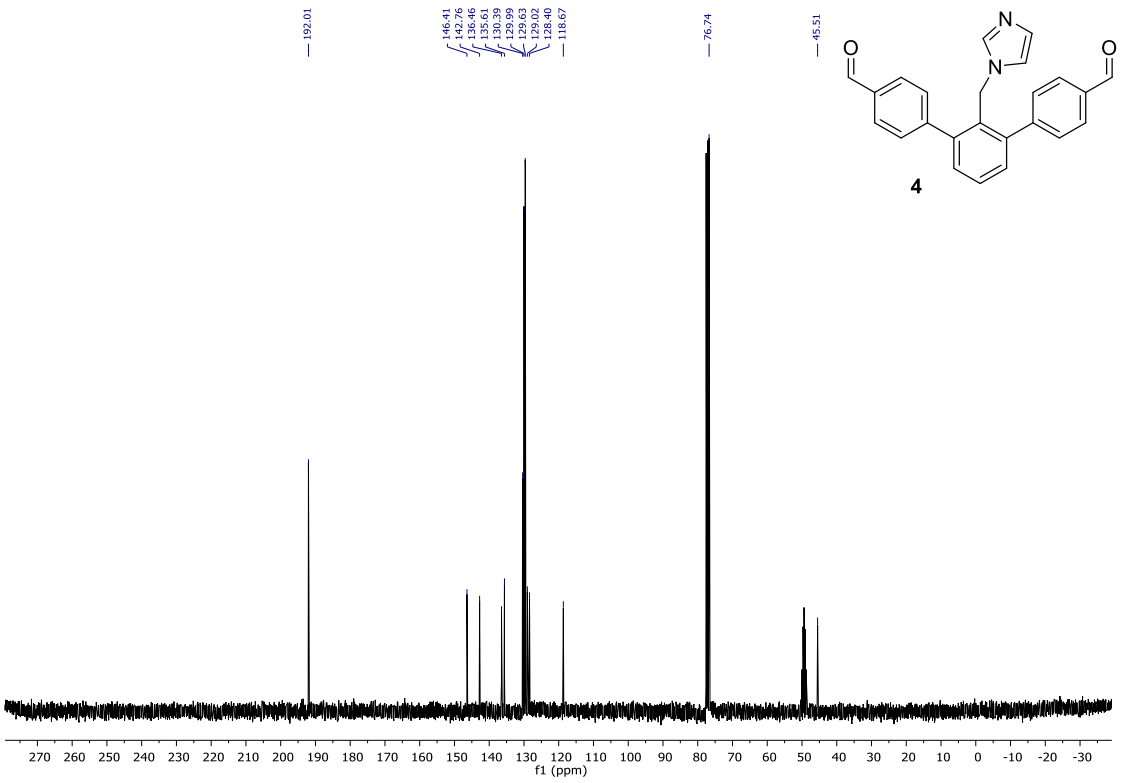


Figure S4. ^{13}C NMR spectrum of **4** in $CDCl_3$ at rt.

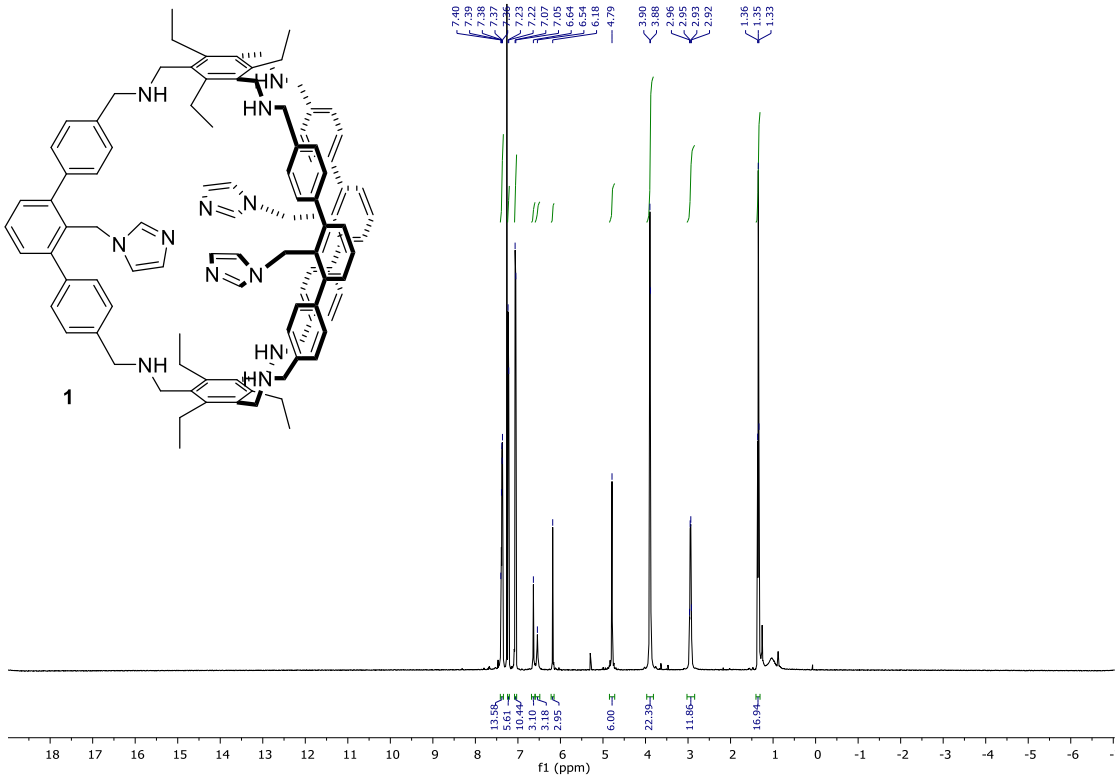


Figure S5. ^{1}H NMR spectrum of **1** in $CDCl_3$ at rt.

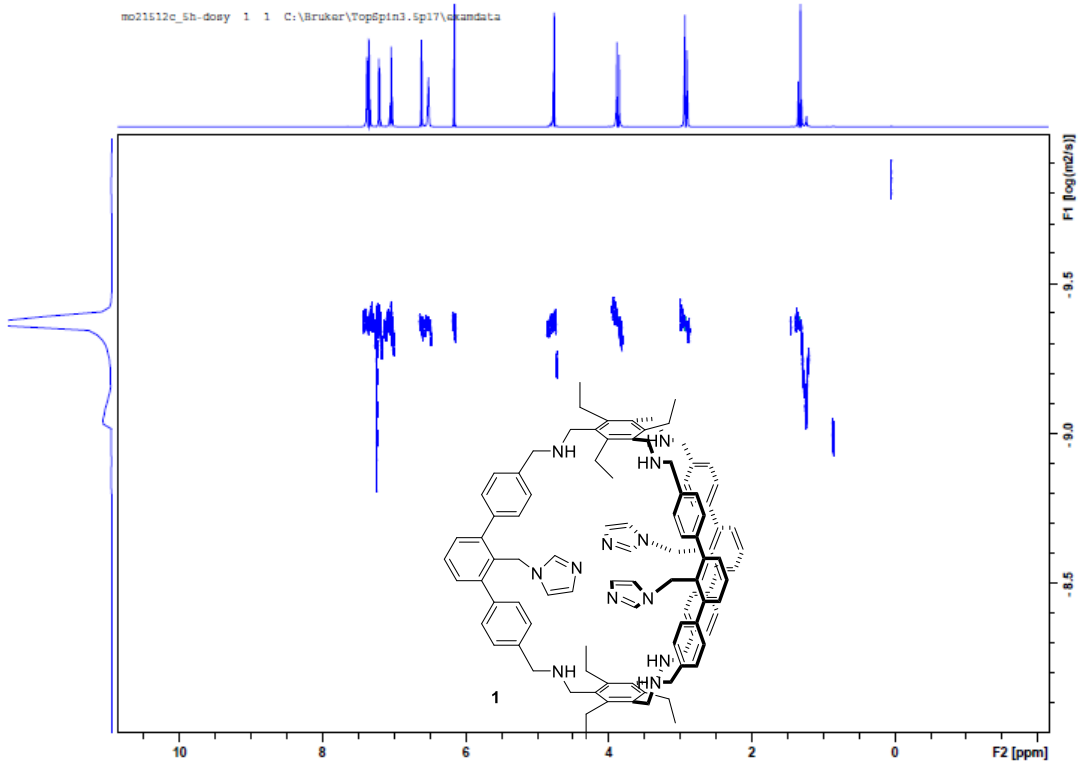


Figure S6. ^{1}H DOSY NMR spectrum of **1** in $CDCl_3$ at rt.

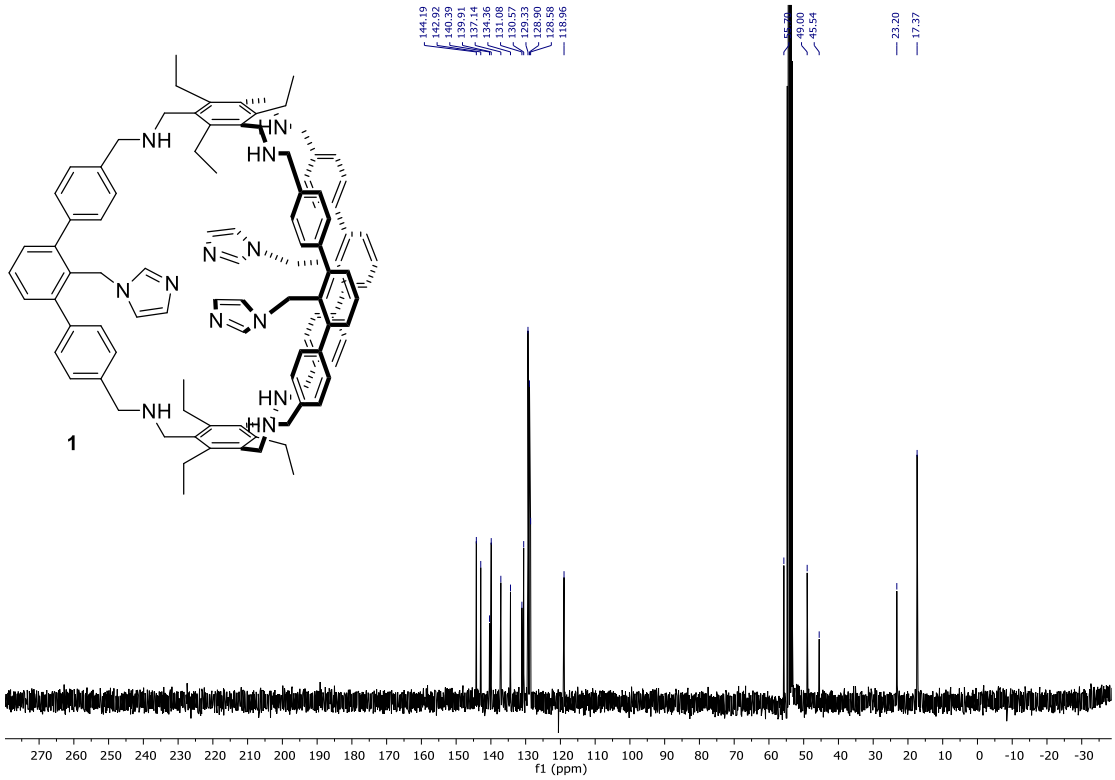


Figure S7. ^{13}C NMR spectrum of **1** in CD_2Cl_2 at rt.

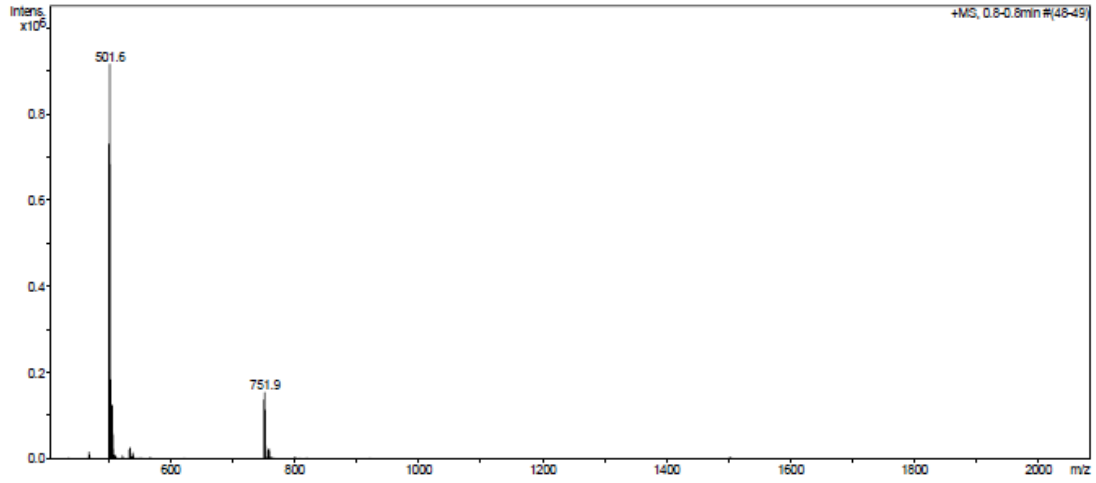


Figure S8. ESI MS of **1**.

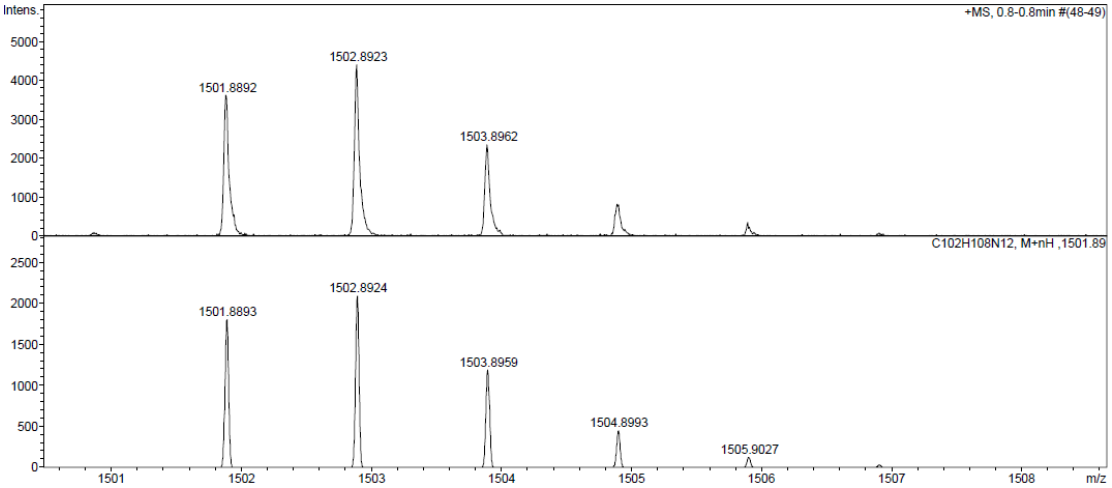


Figure S9. Measured and calculated ESI-MS of **1** for $[M+H]^+$.

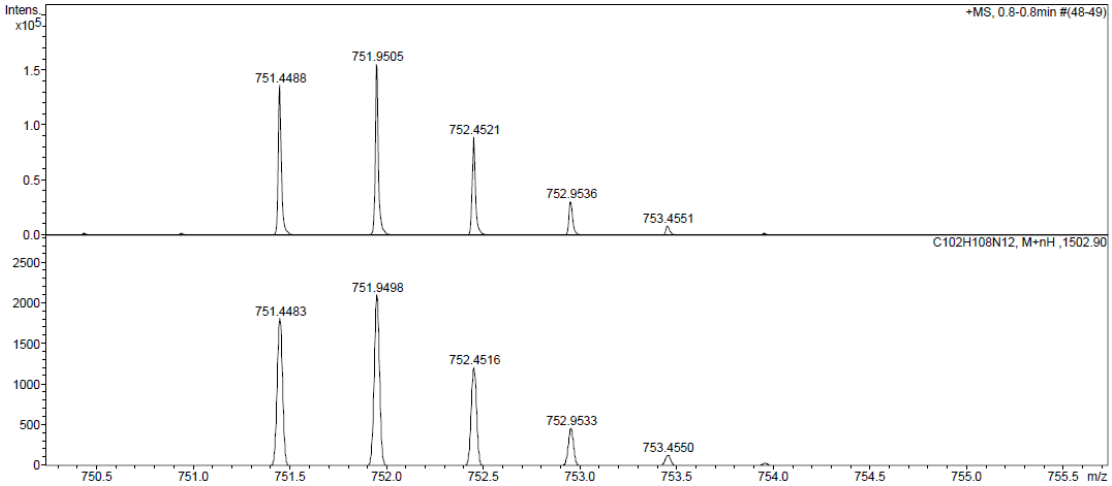


Figure S10. Measured and calculated ESI MS of **1** for $[M+2H]^{2+}$.

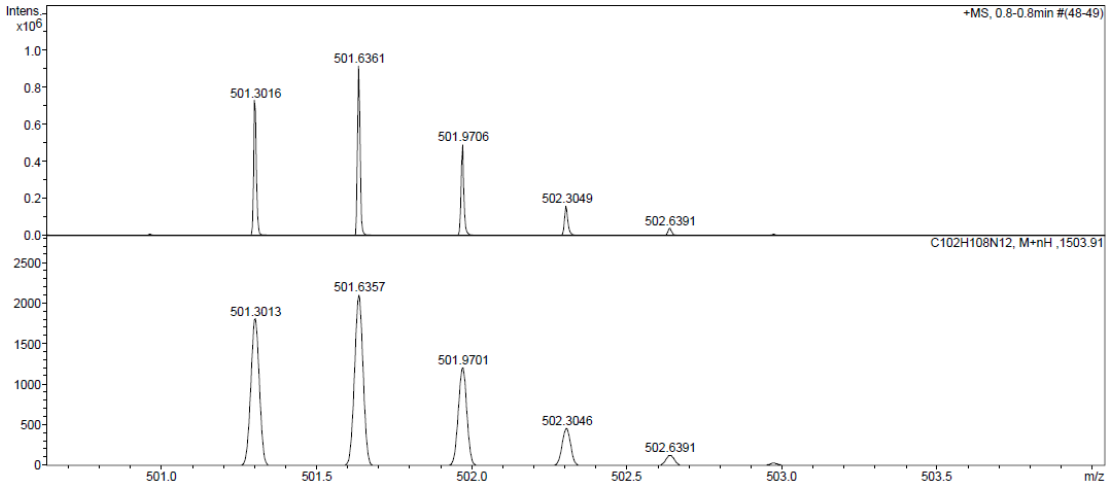


Figure S11: Measured and calculated ESI MS of **1** for $[M+3H]^{3+}$.

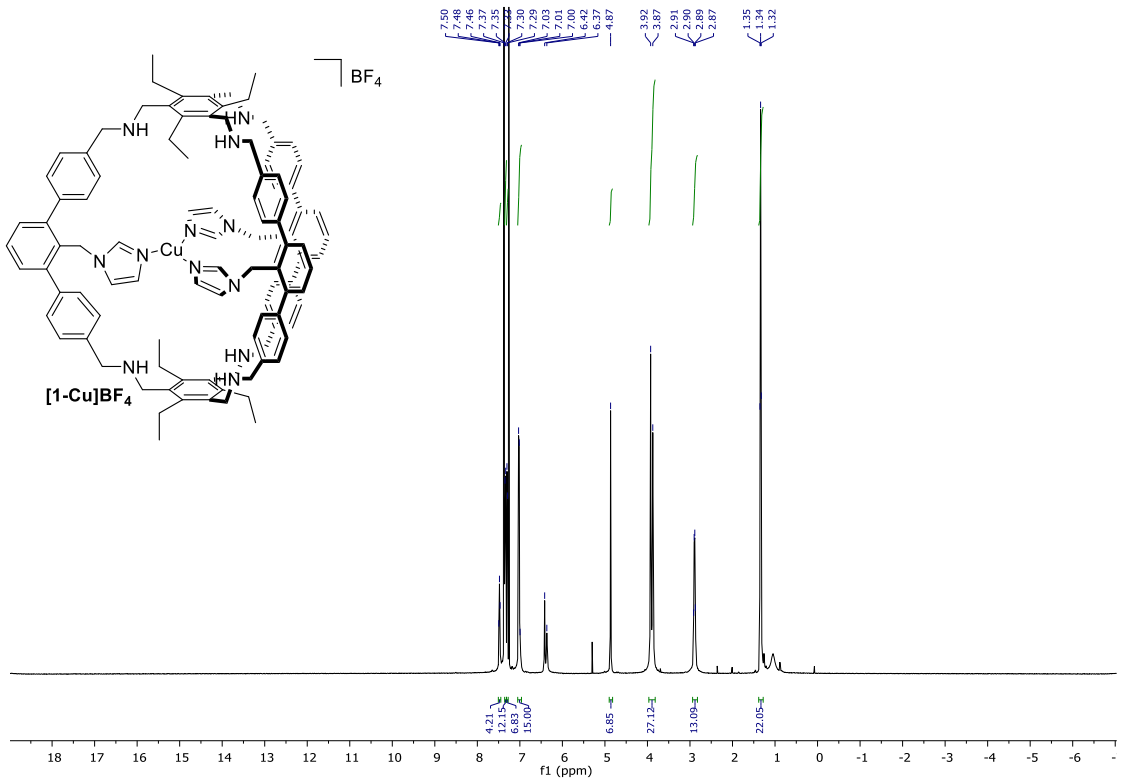


Figure S12. ^{1}H NMR spectrum of **[1-Cu]BF_4** in $CDCl_3$ at rt.

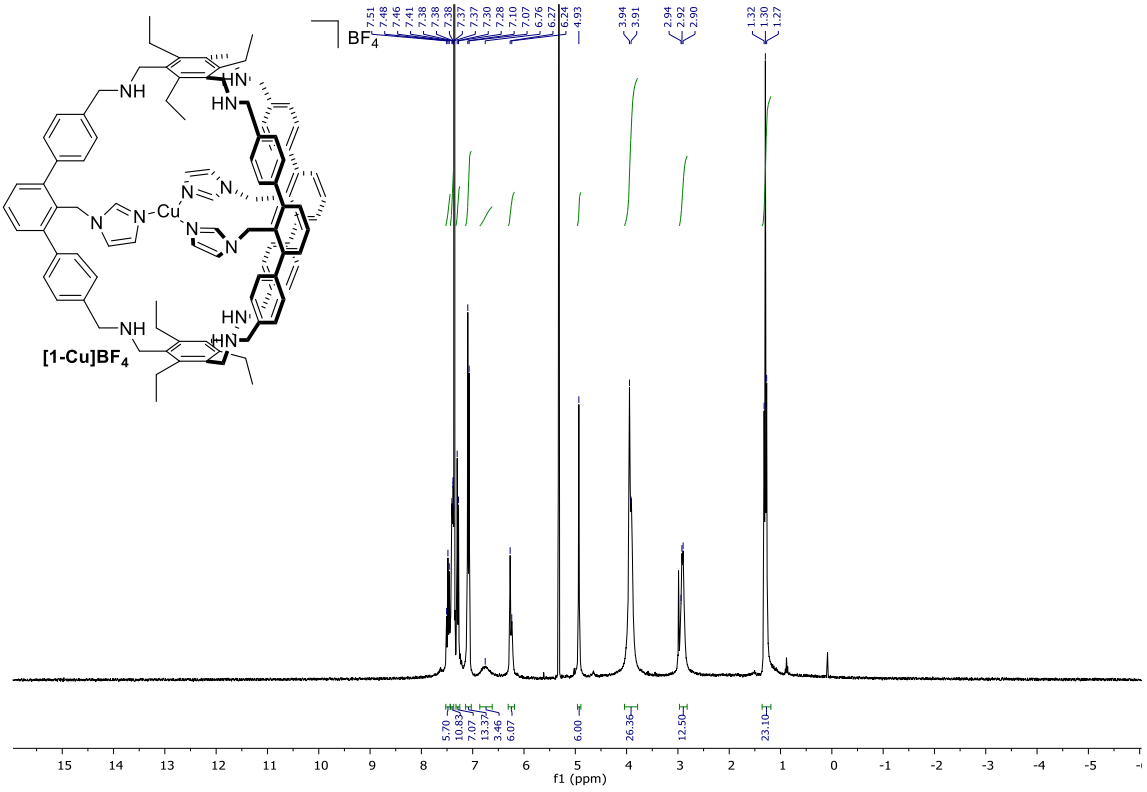


Figure S13. ^{1}H NMR spectrum of **[1-Cu]BF_4** in CD_2Cl_2 at rt.

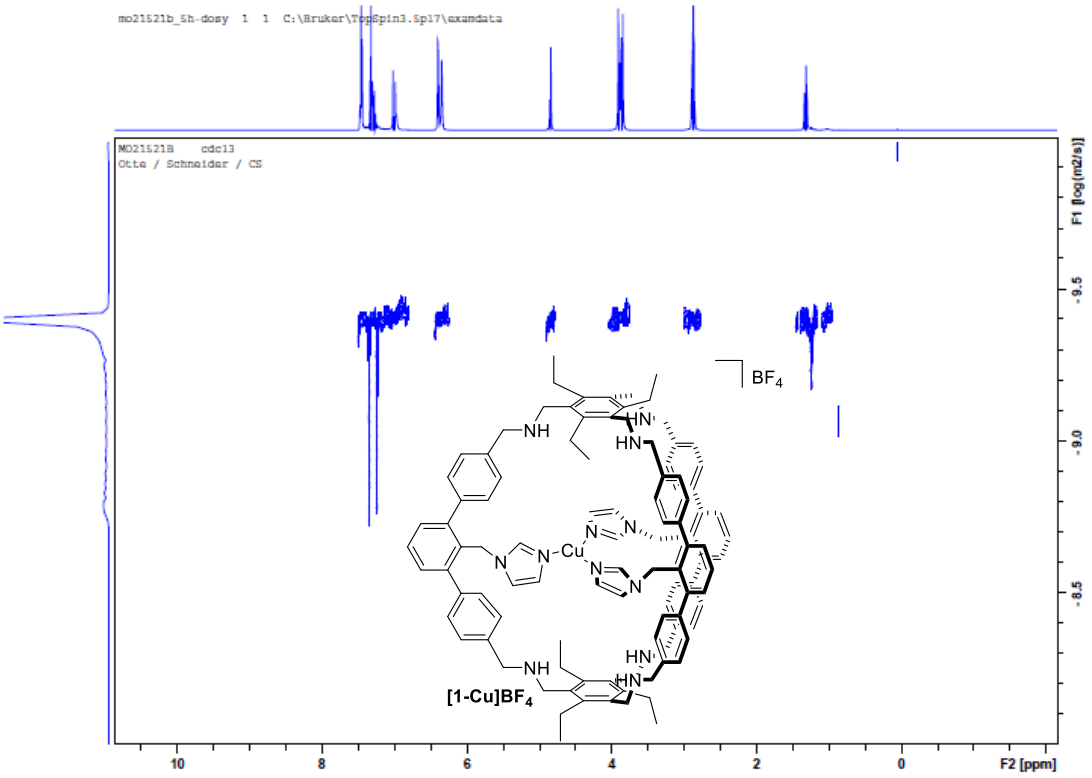


Figure S14. DOSY NMR spectrum of **[1-Cu]BF$_4$** in $CDCl_3$ at rt.

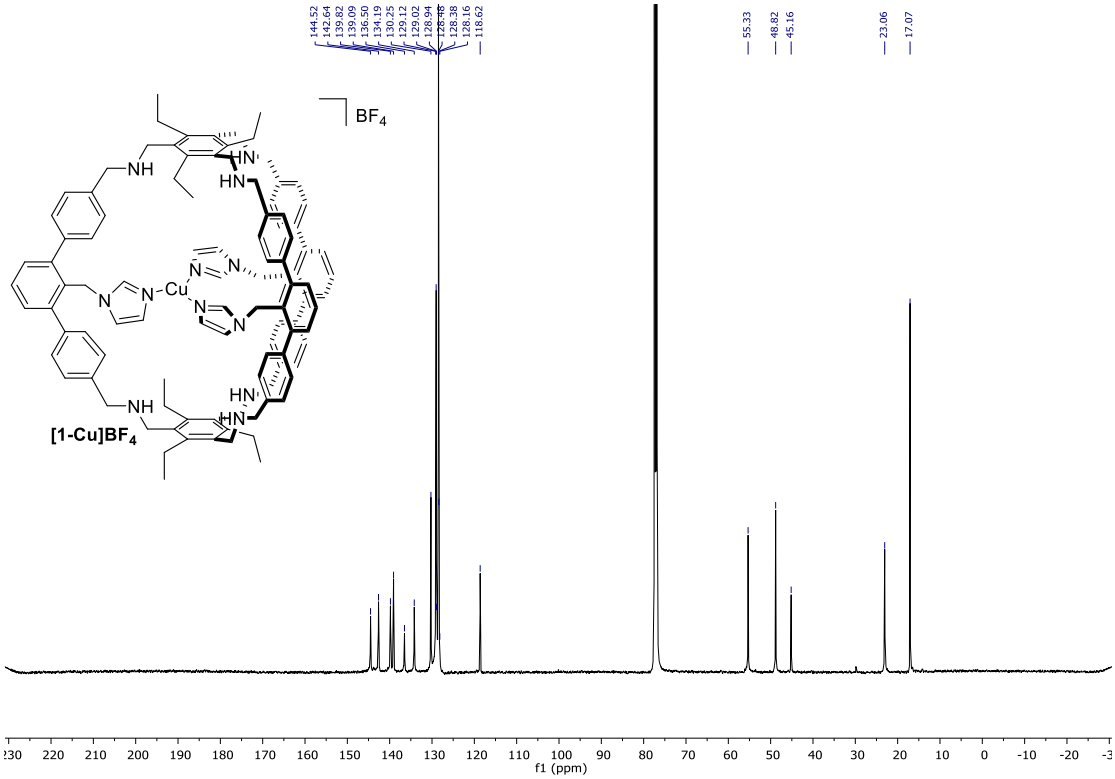


Figure S15. ^{13}C NMR spectrum of **[1-Cu]BF$_4$** in $CDCl_3$ at rt.

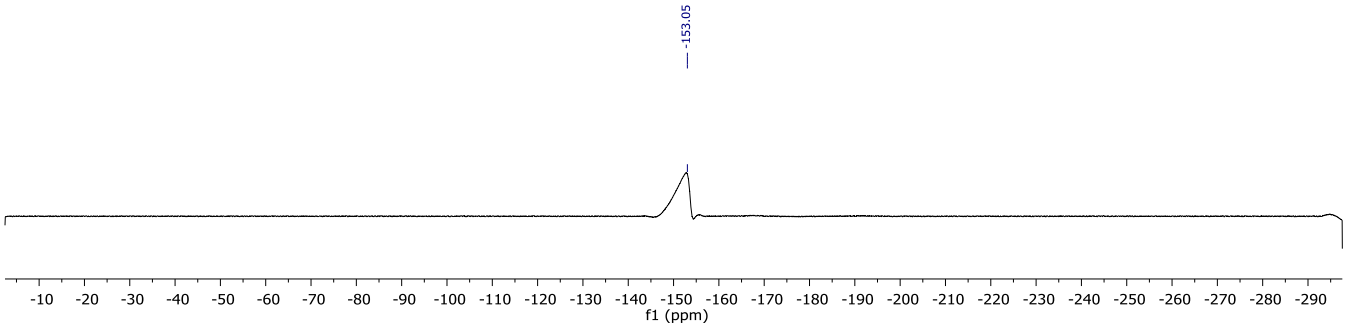


Figure S16. ^{19}F NMR spectrum of **[1-Cu]BF_4** in $CDCl_3$ at rt.

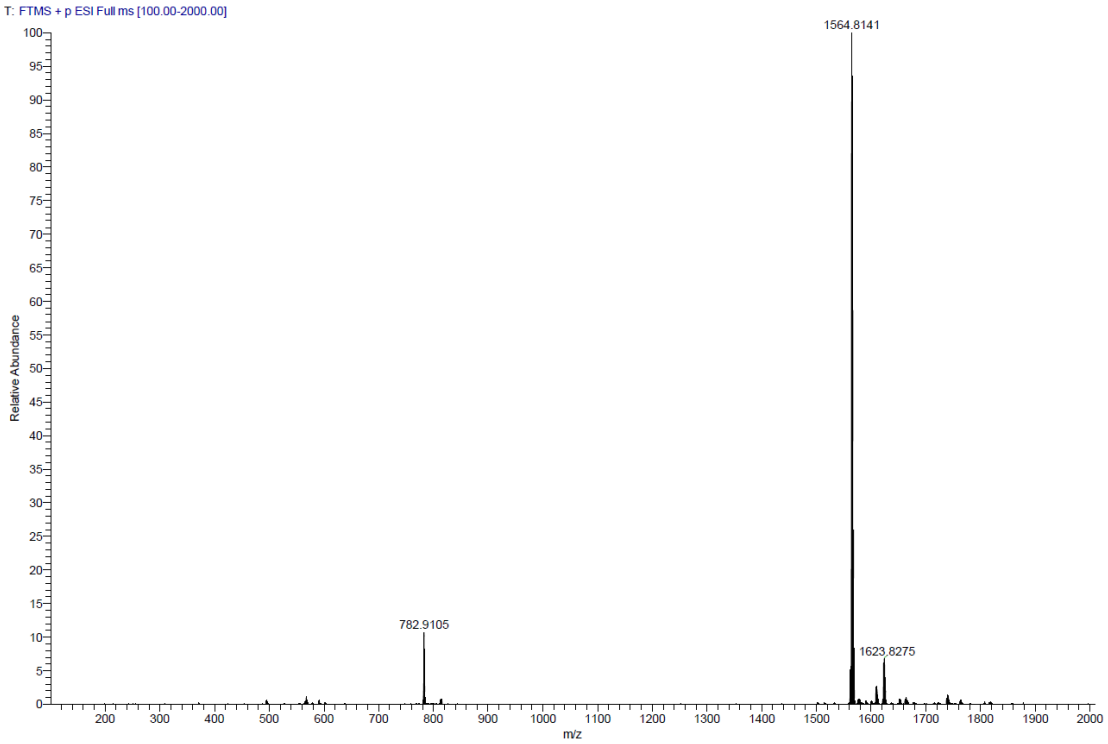


Figure S17. ESI MS spectrum of **[1-Cu]BF_4.**

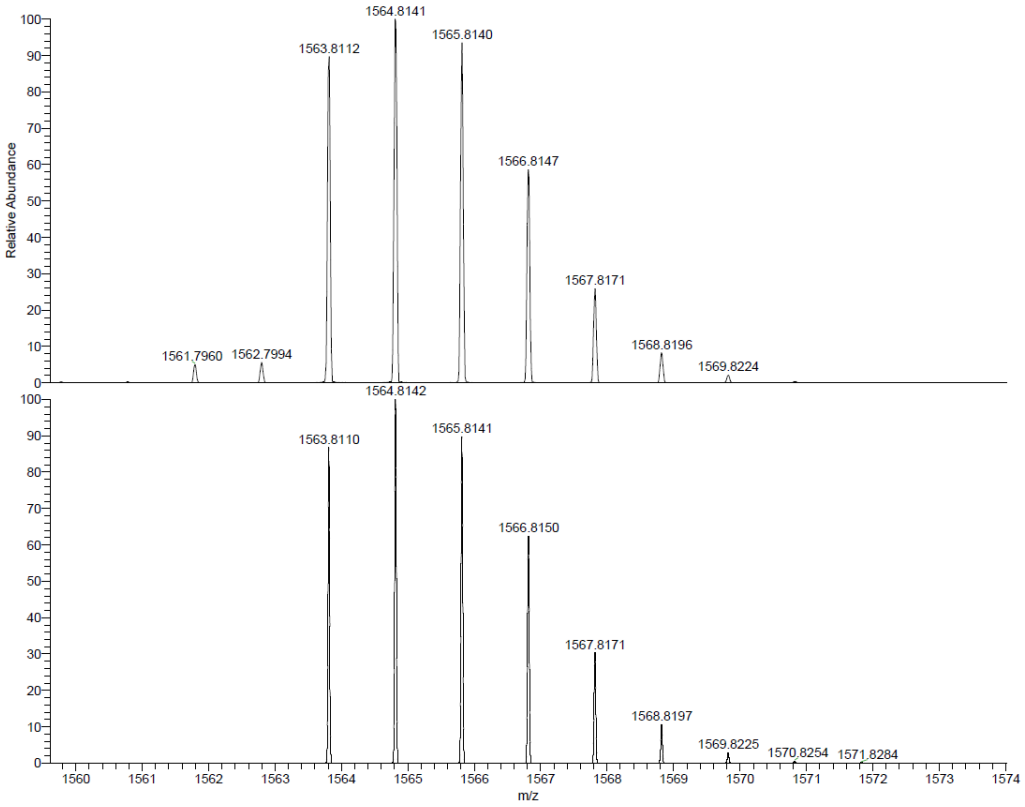


Figure S18. Measured and calculated ESI MS of **[1-Cu]BF_4** for **[1-Cu]$^+$**.

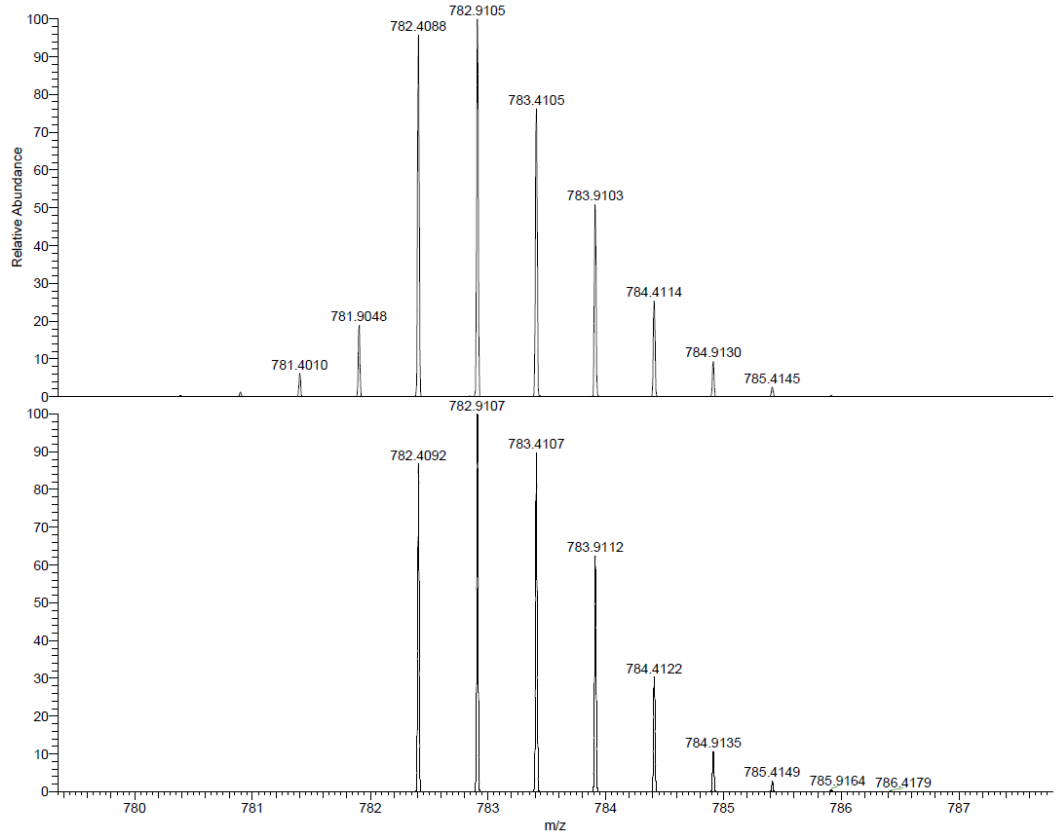


Figure S19. Measured and calculated ESI MS of **[1-Cu]BF_4** for **[1-Cu+1H]$^{2+}$.**

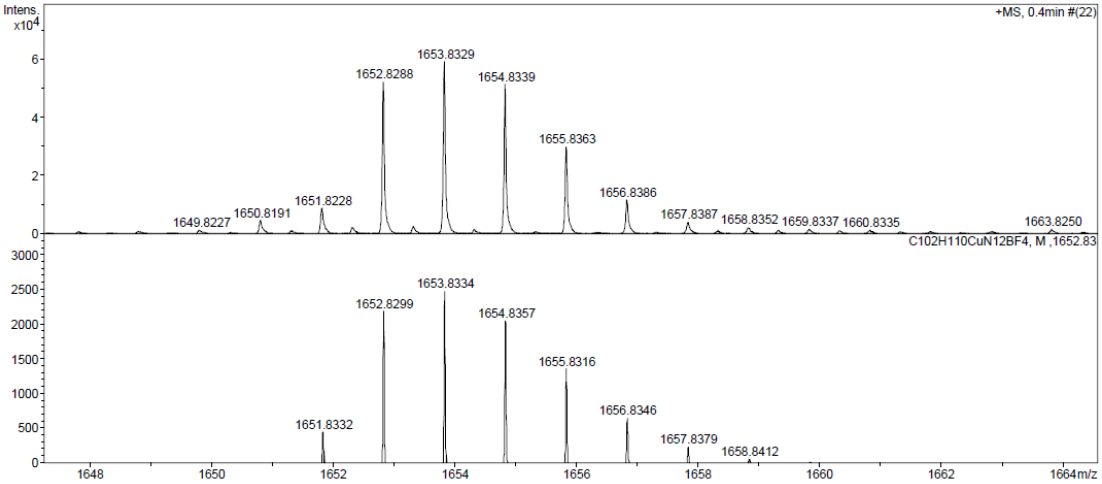


Figure S20: Measured and calculated ESI MS of **[1-Cu]BF_4** for **[1-Cu+1H]BF_4^+.**

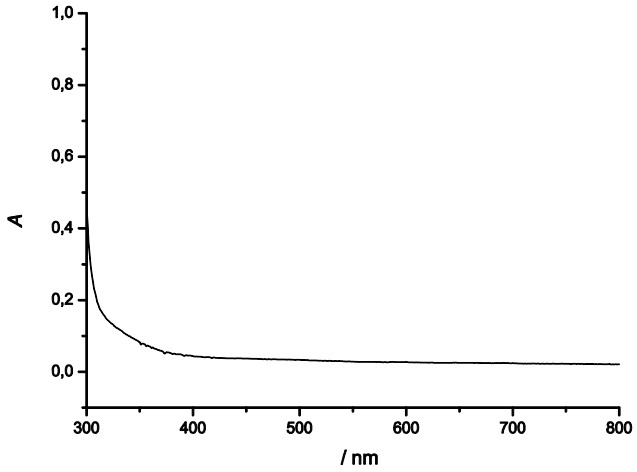


Figure S21: UV/Vis spectrum of **[1-Cu]BF_4** in DCM at rt, $0.8 \cdot 10^{-3}$ M.

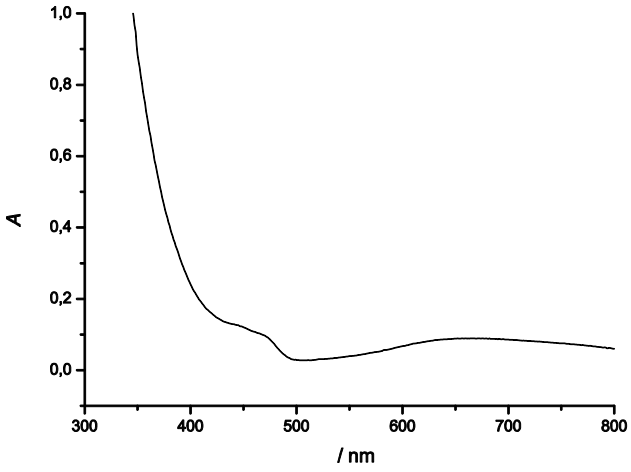


Figure S22: UV/Vis spectrum of **[1-Cu]BF_4** under air in $CHCl_3$ at rt, $0.8 \cdot 10^{-3}$ M.

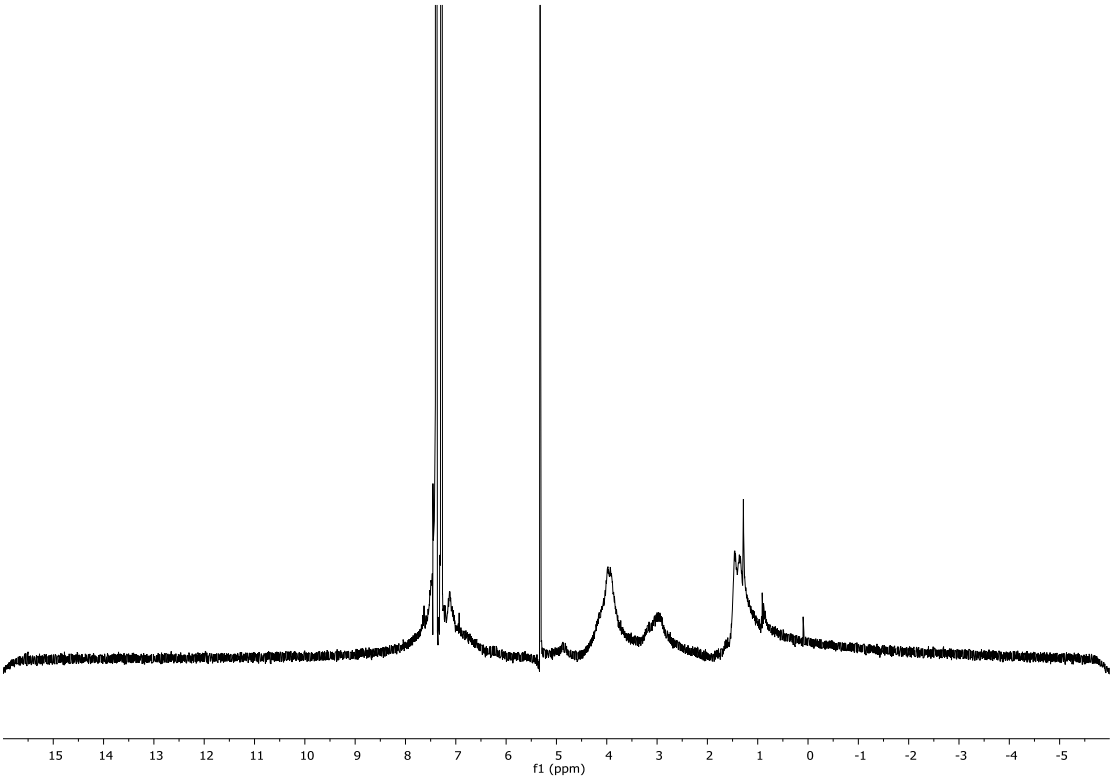


Figure S23. ^{1}H NMR spectrum of **[1-Cu]BF_4** under air in $CDCl_3$ at rt.

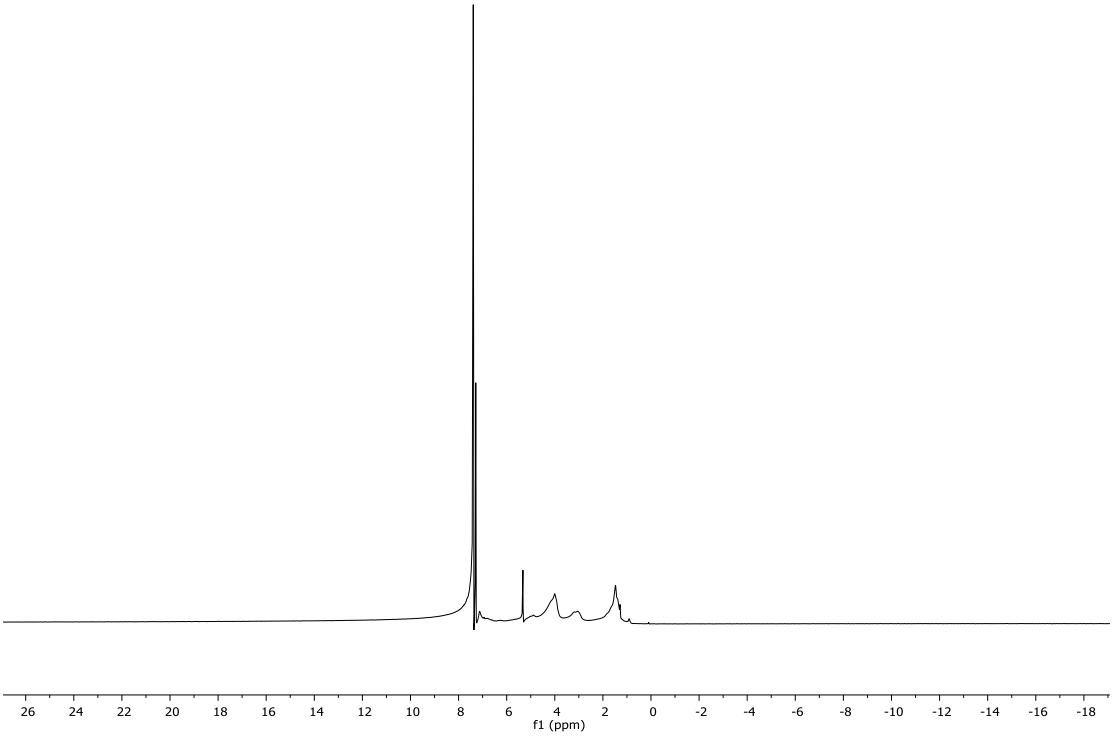


Figure S24. ^{1}H NMR spectrum between 27.00 and -19.00 ppm of **[1-Cu]BF_4** under air in $CDCl_3$ at rt.

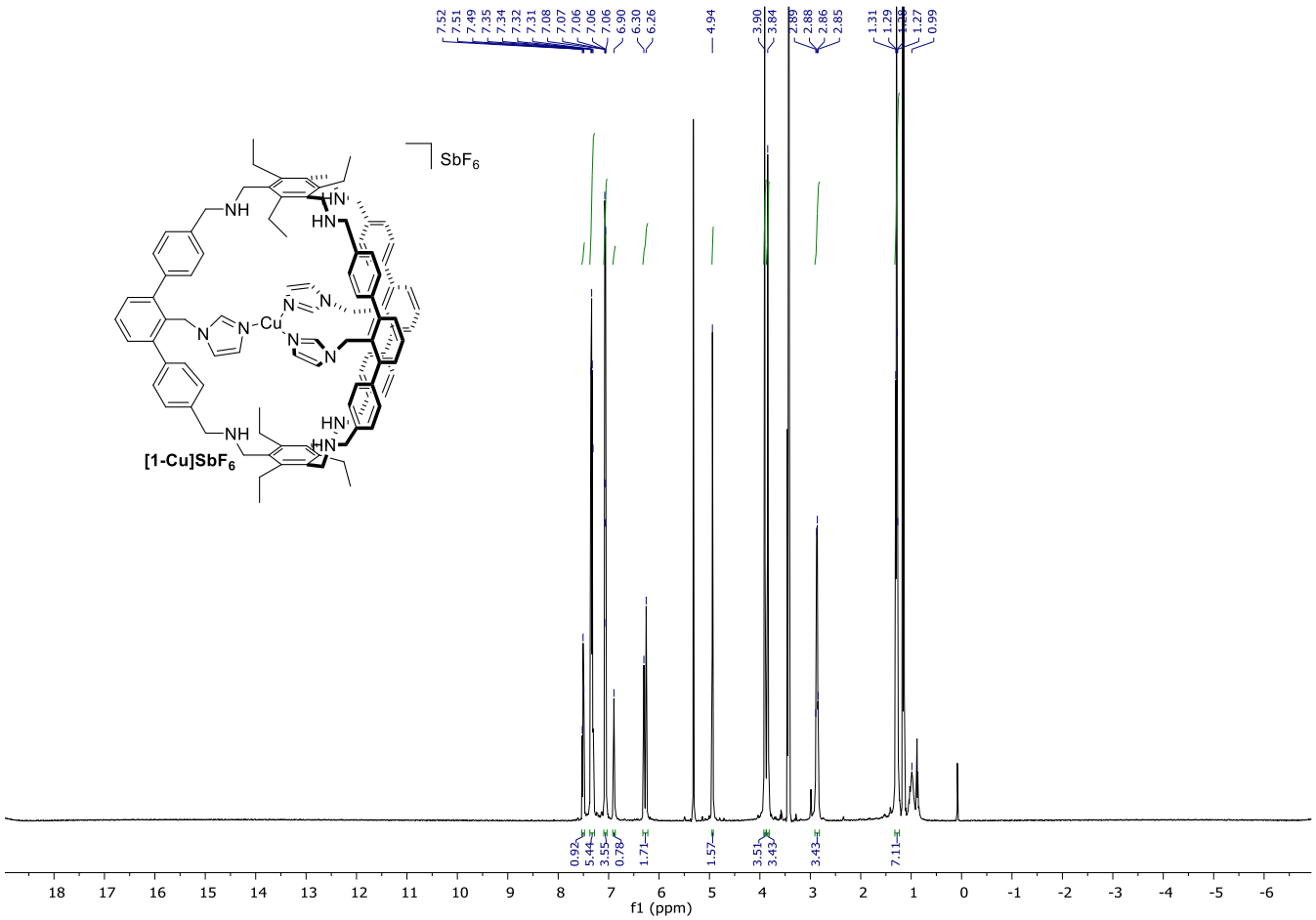


Figure S25. ^{1}H NMR spectrum of **[1-Cu]SbF$_6$** after extraction with Et_2O in CD_2Cl_2 at rt.

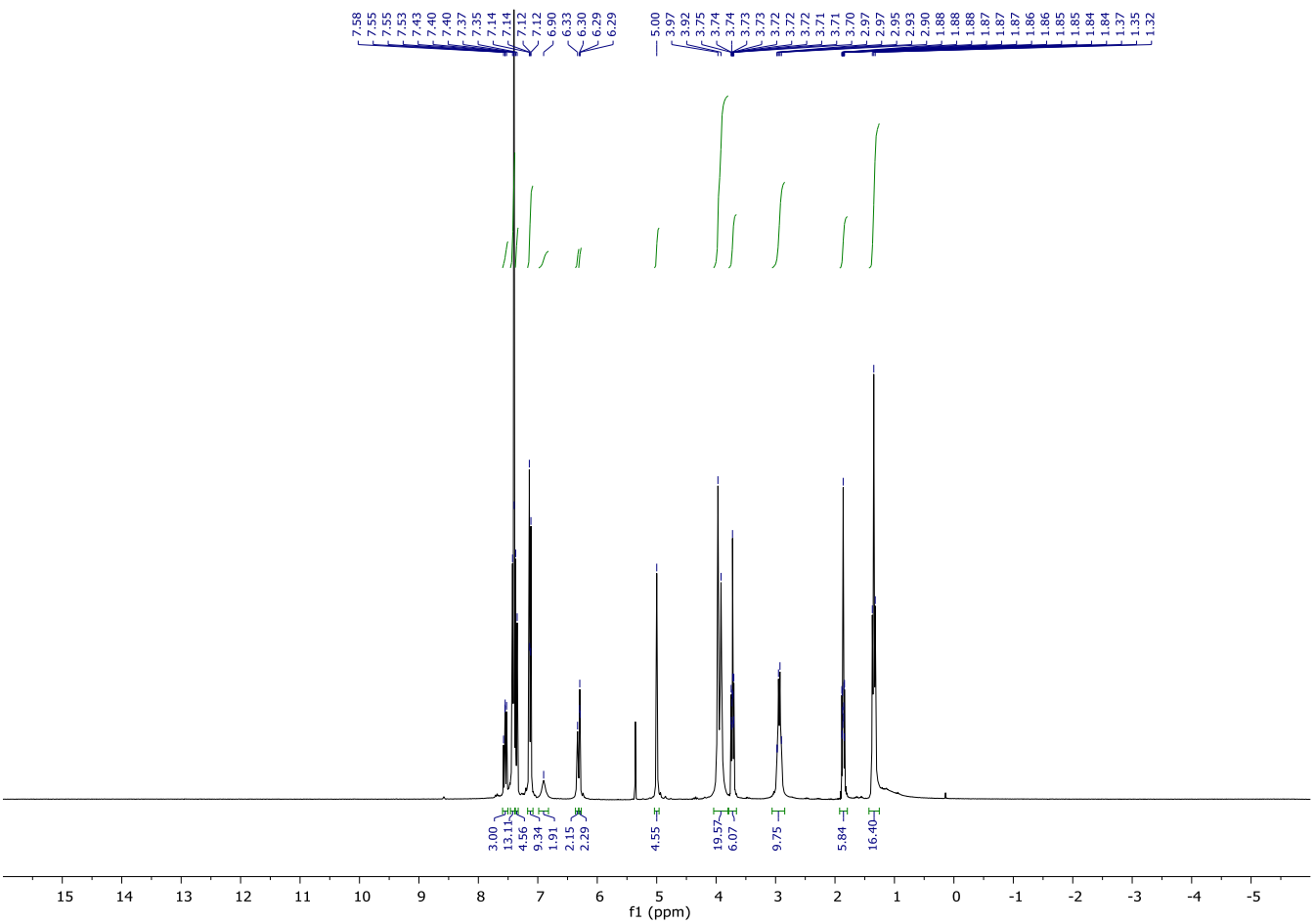


Figure S26. ^{1}H NMR spectrum of **[1-Cu]SbF$_6$** after extraction with THF in CD_2Cl_2 at rt.

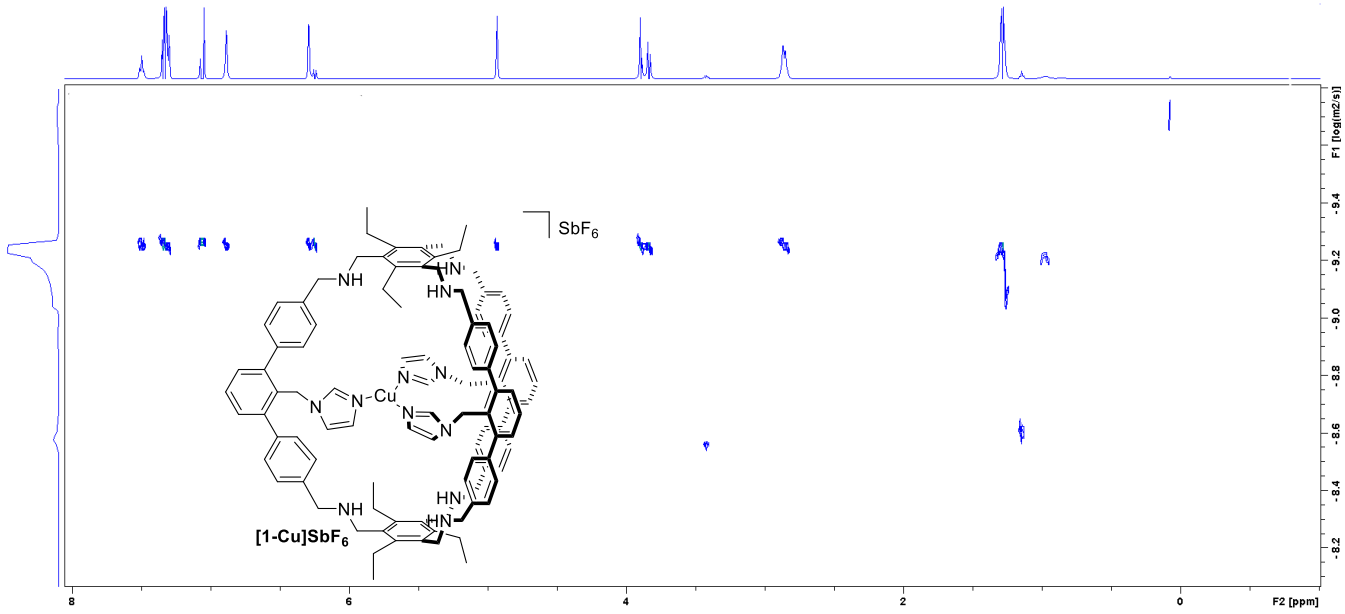


Figure S27. DOSY NMR spectrum of **[1-Cu]SbF$_6$** in CD_2Cl_2 at rt.

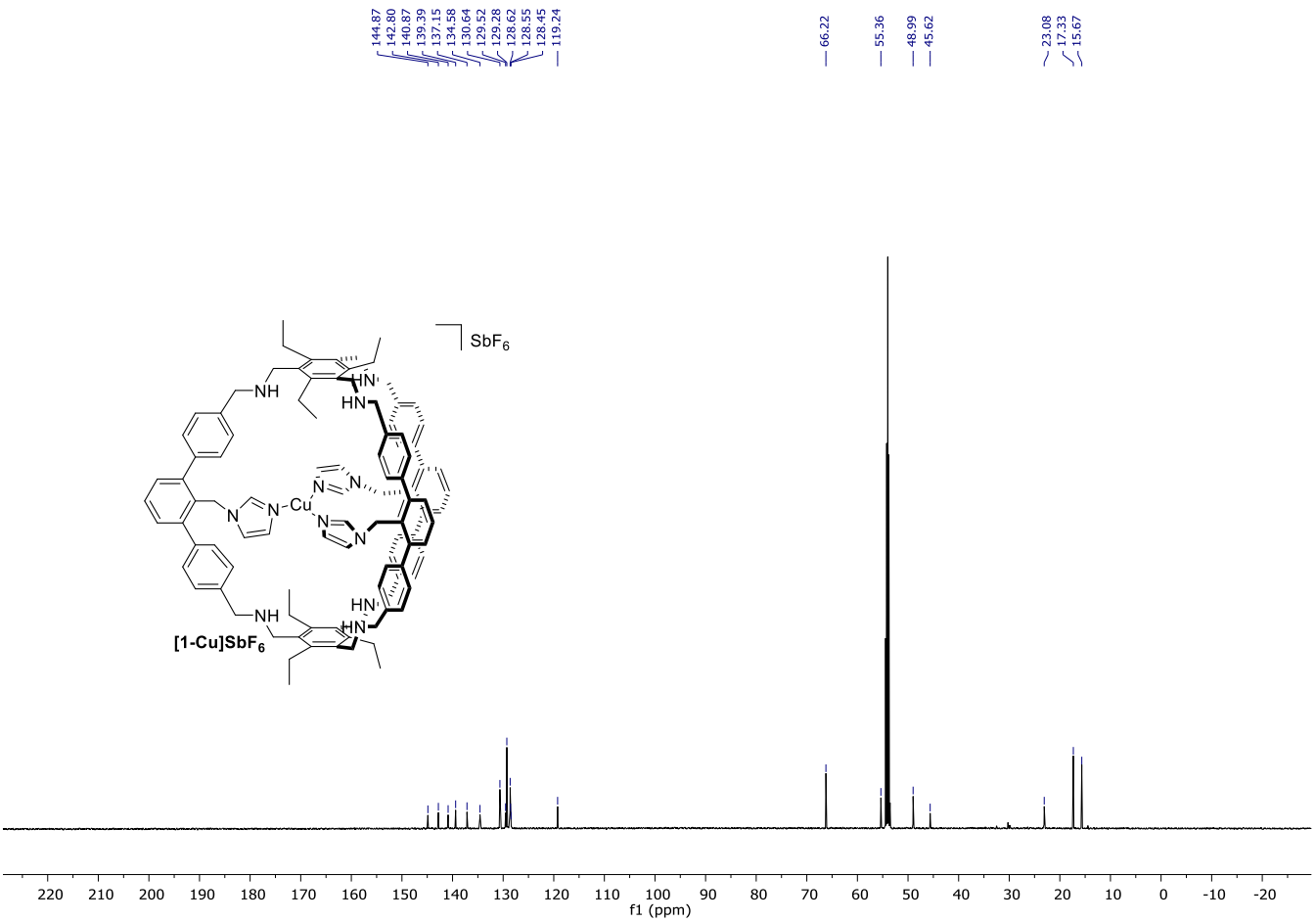


Figure S28. ^{13}C NMR spectrum of **[1-Cu]SbF$_6$** in CD_2Cl_2 at rt.

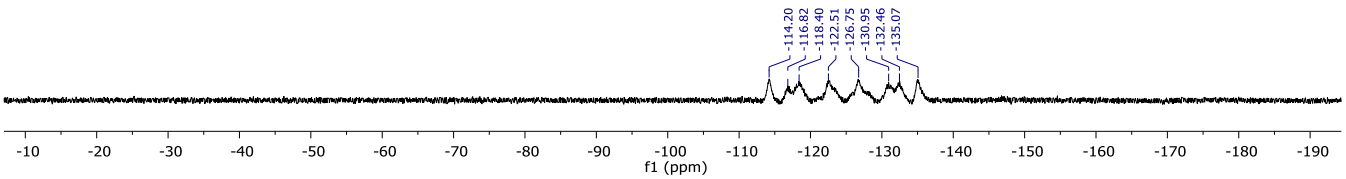


Figure S29. ^{19}F NMR spectrum of **[1-Cu]SbF$_6$** in CD_2Cl_2 at rt.

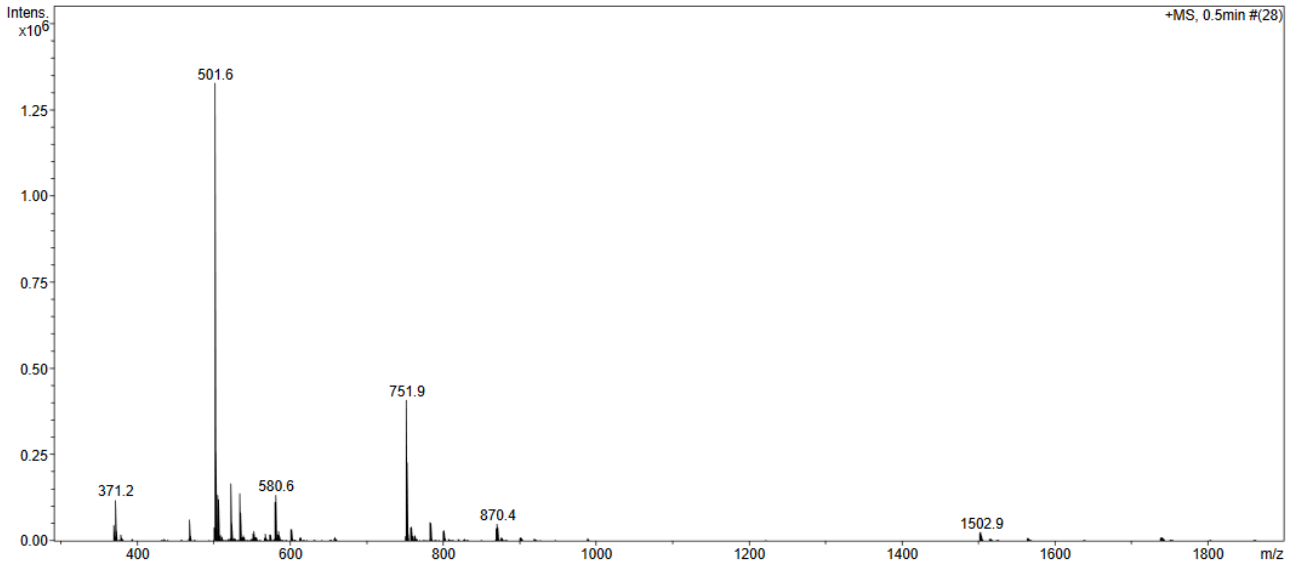


Figure S30. ESI MS Spektrum of **[1-Cu]SbF$_6$.**

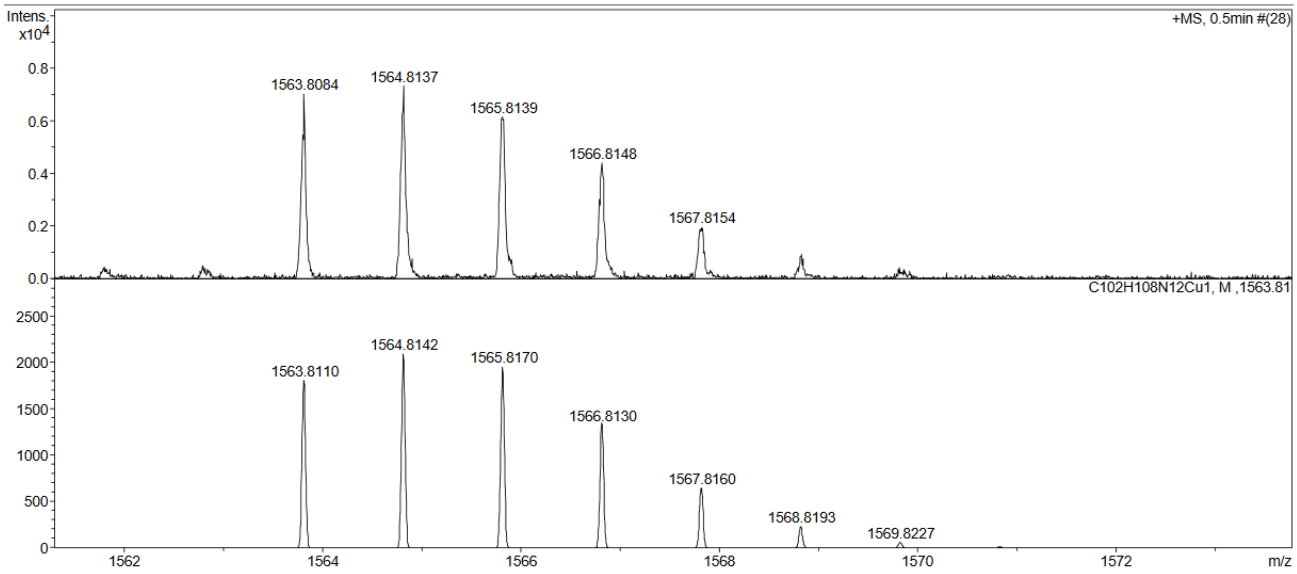


Figure S31. Measured and calculated ESI MS of **[1-Cu]SbF$_6$** for **[1-Cu]$^+$.**

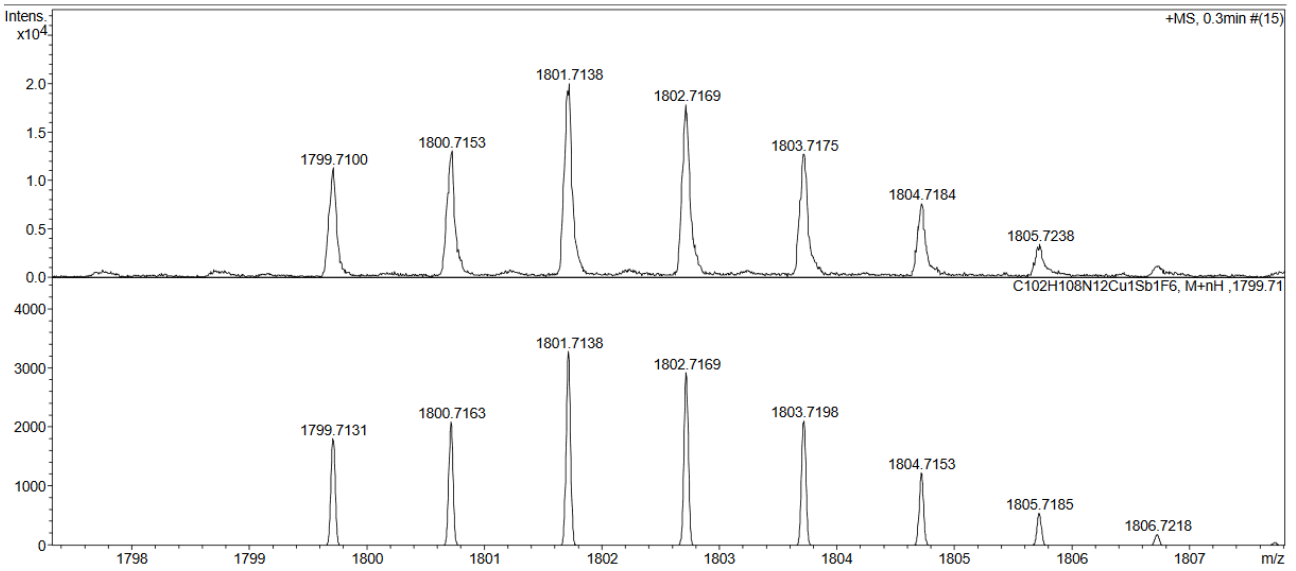


Figure S32. Measured and calculated ESI MS of **[1-Cu]SbF$_6$** for **[1-CuBF$_4$+H]$^+$.**

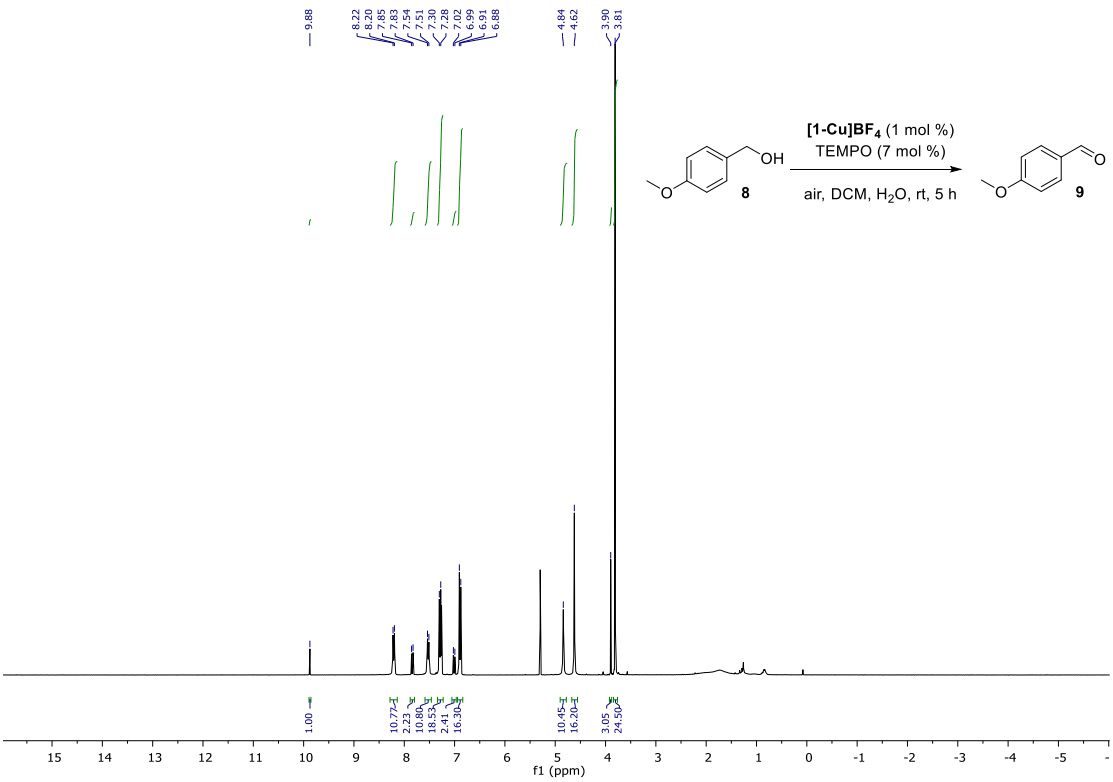


Figure S33. ^{1}H NMR of table 1, entry 1 with 4-nitrobenzylic alcohol as internal standard in $CDCl_3$ at rt.

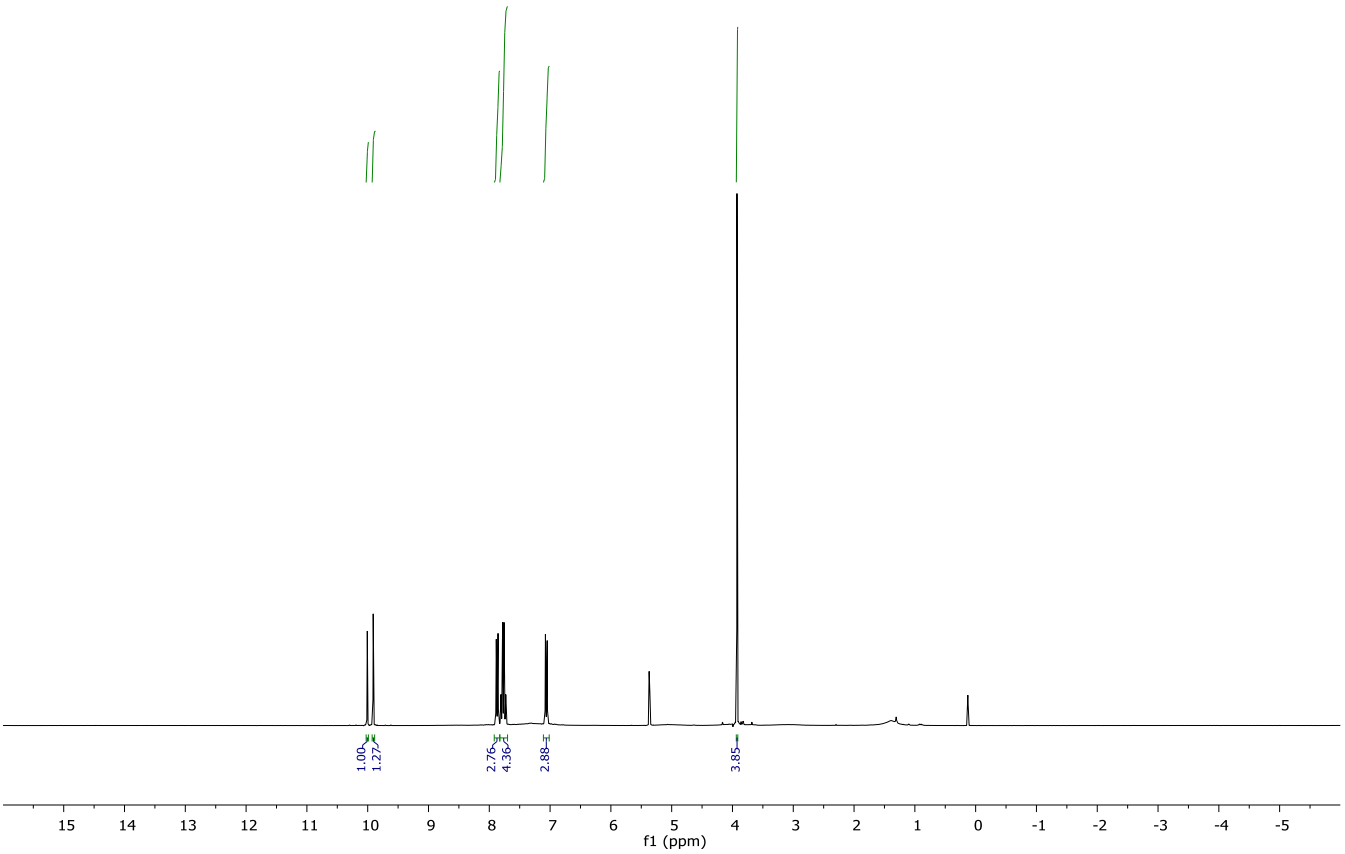


Figure S34. ^{1}H NMR of table 1, entry 3 with 4-bromobenzaldehyde as internal standard in CD_2Cl_2 at rt.

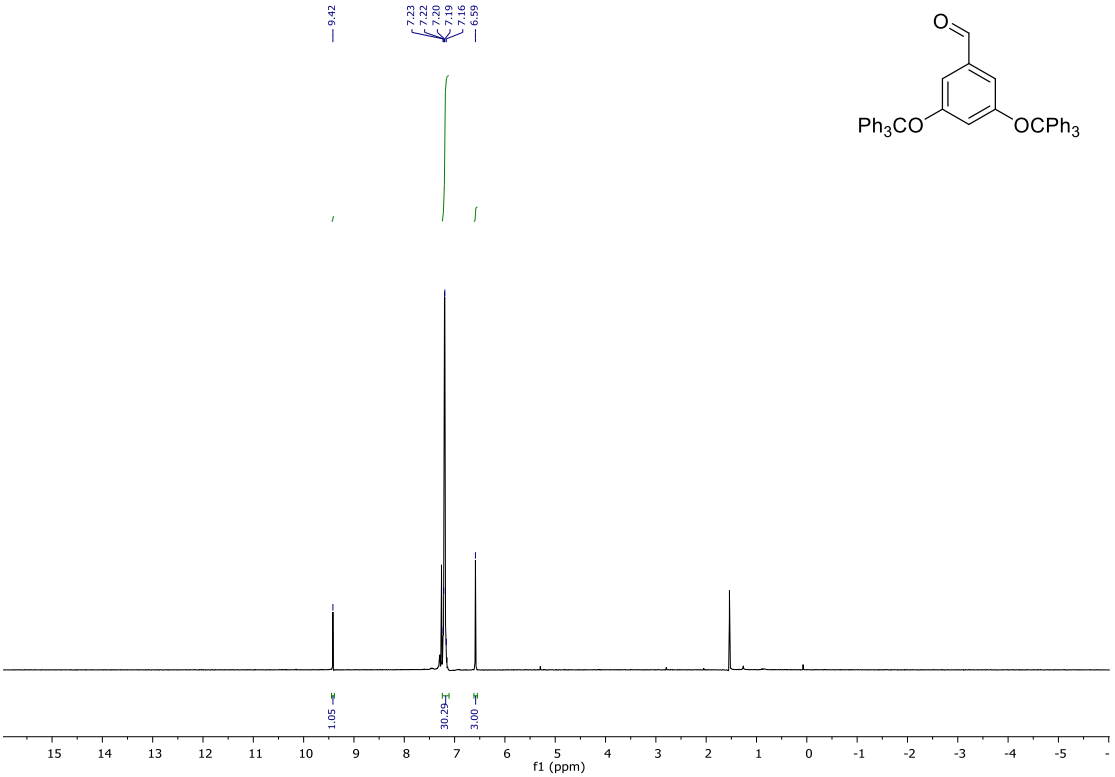


Figure S35. ^{1}H NMR of 3,5-dirityloxybenzaldehyde in $CDCl_3$ at rt.

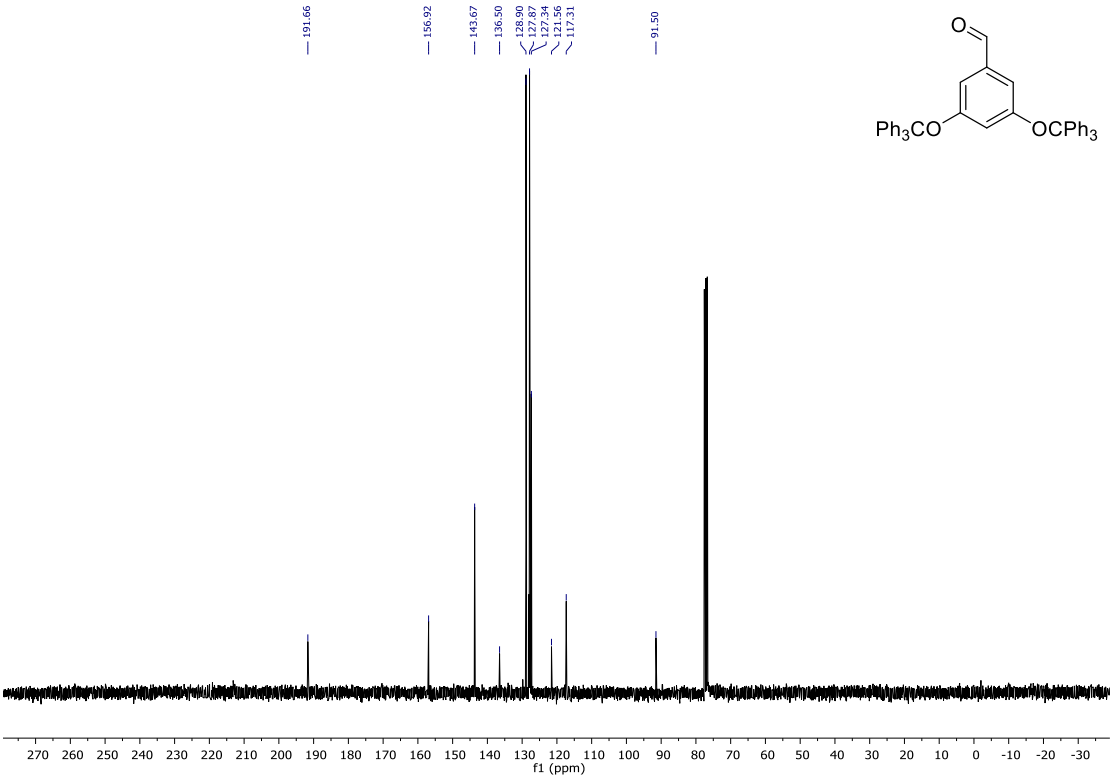


Figure S36. ^{13}C NMR of 3,5-dirityloxybenzaldehyde in $CDCl_3$ at rt.

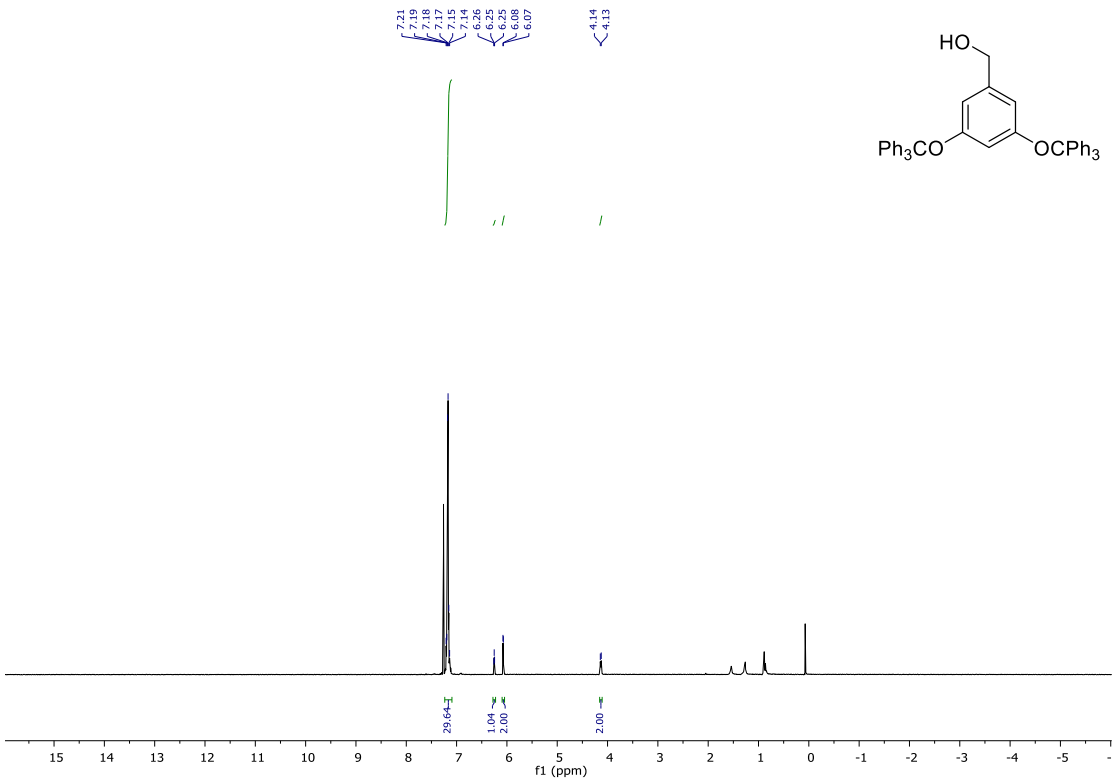


Figure S37. ^{1}H NMR of 3,5-dirityloxybenzyl alcohol in $CDCl_3$ at rt.

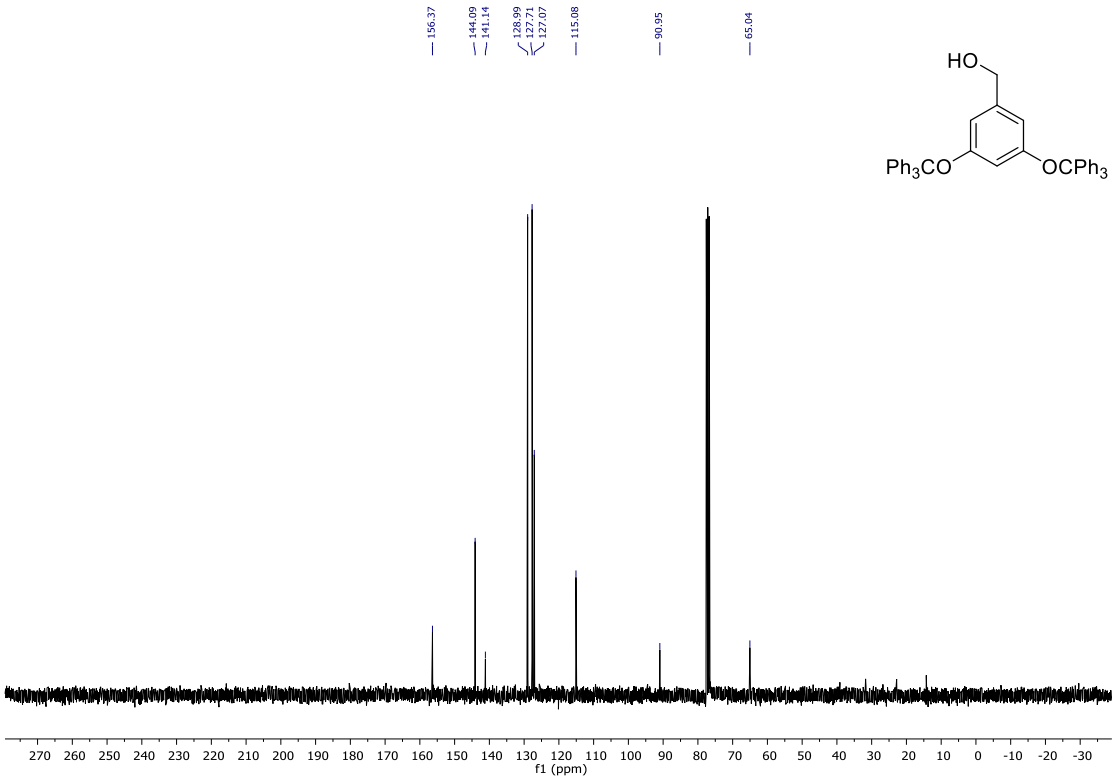


Figure S38. ^{13}C NMR of 3,5-dirityloxybenzyl alcohol in $CDCl_3$ at rt.

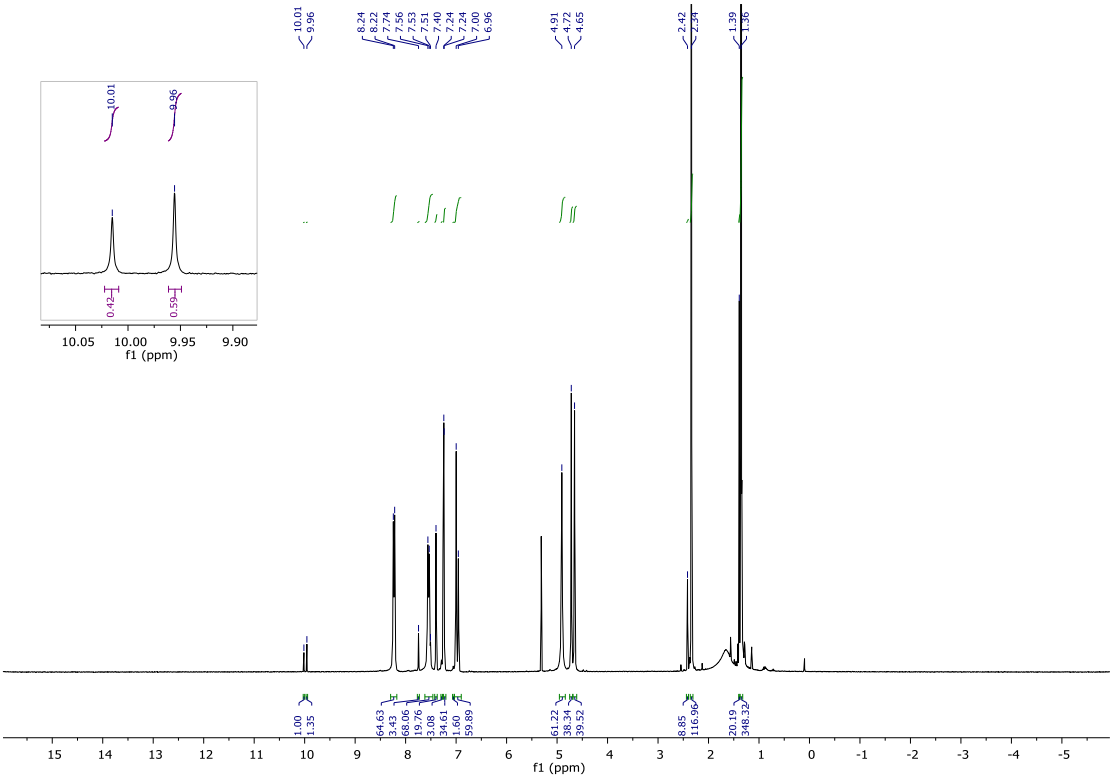


Figure S39. ^{1}H NMR of the competition experiment between 3,5-di-methylbenzyl alcohol and 3,5-di-tert-benzyl alcohol with **[1-Cu]BF$_4$** as catalyst in $CDCl_3$ at rt (table 2, entry 1).

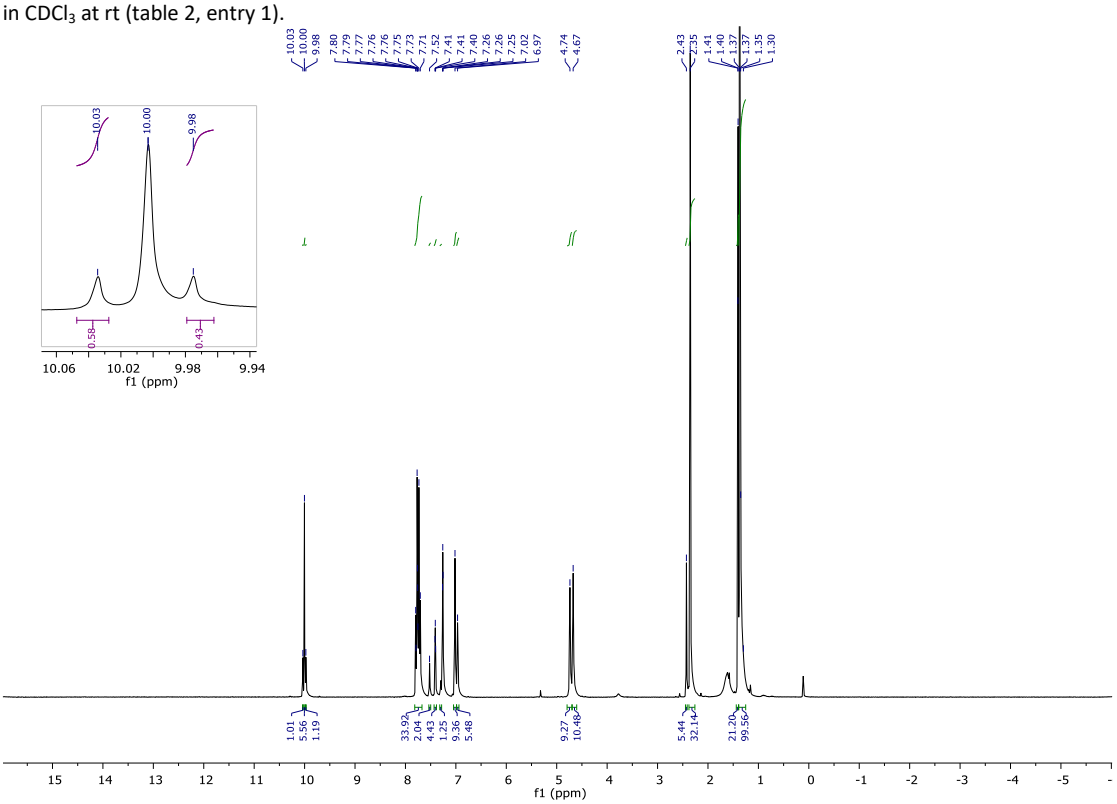


Figure S40. ^{1}H NMR of the competition experiment between 3,5-di-methylbenzyl alcohol and 3,5-di-tert-benzyl alcohol with **6**·3(NMI) as catalyst in $CDCl_3$ at rt (table 2, entry 2).

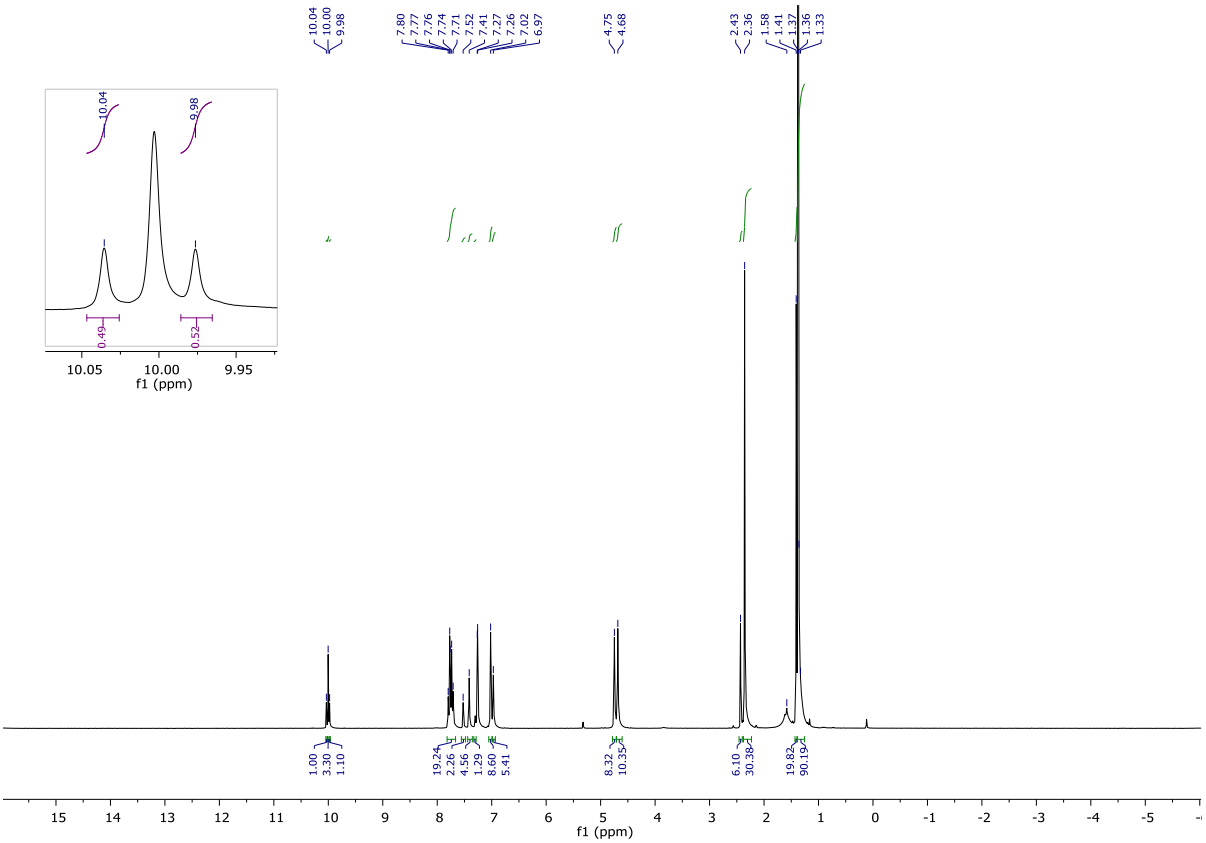


Figure S41. ^{1}H NMR of the competition experiment between 3,5-di-methylbenzyl alcohol and 3,5-di-tert-benzyl alcohol with **10**·(bipy)·2(NMI) as catalyst in $CDCl_3$ at rt (table 2, entry 3).

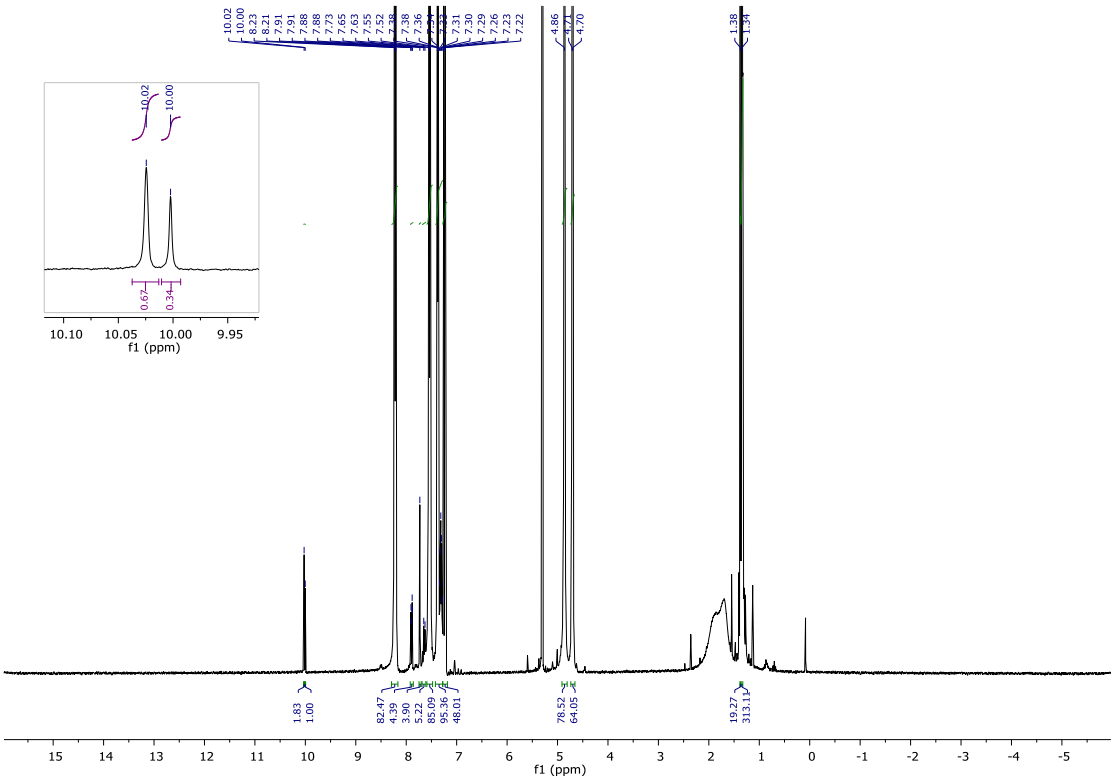


Figure S42. ^{1}H NMR of the competition experiment between benzyl alcohol and 3,5-di-tert-benzyl alcohol with **[1-Cu]BF_4** as catalyst in $CDCl_3$ at rt (table 2, entry 4).

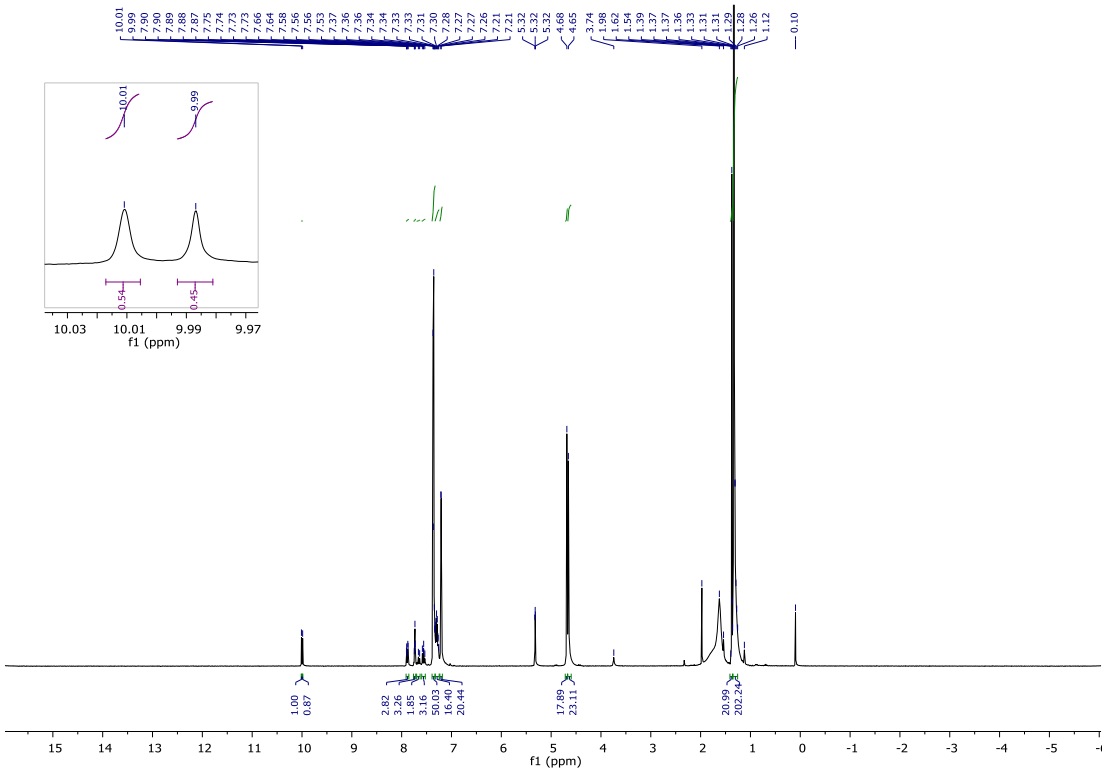


Figure S43. ^{1}H NMR of the competition experiment between benzyl alcohol and 3,5-di-tert-benzyl alcohol with **6**·3(NMI) as catalyst in CD_2Cl_2 at rt (table 2, entry 5).

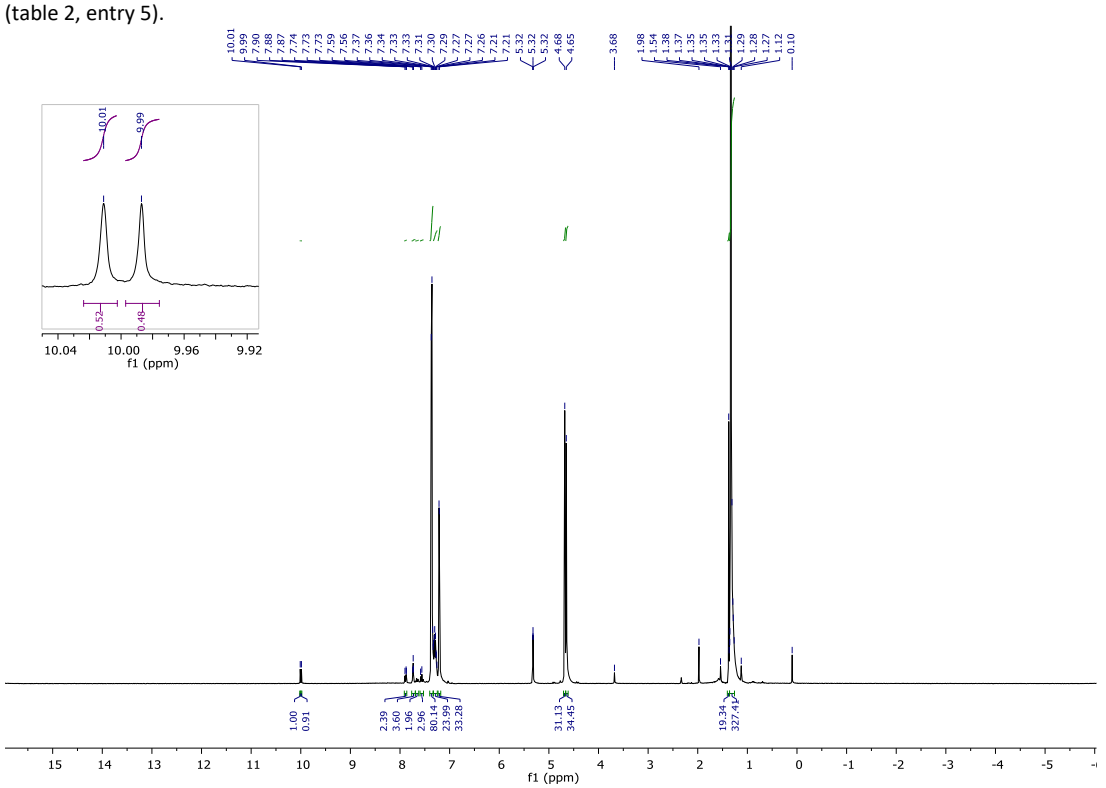


Figure S44. ^{1}H NMR of the competition experiment between benzyl alcohol and 3,5-di-tert-benzyl alcohol with **10**·(bipy)·2(NMI) as catalyst in CD_2Cl_2 at rt (table 2, entry 6).

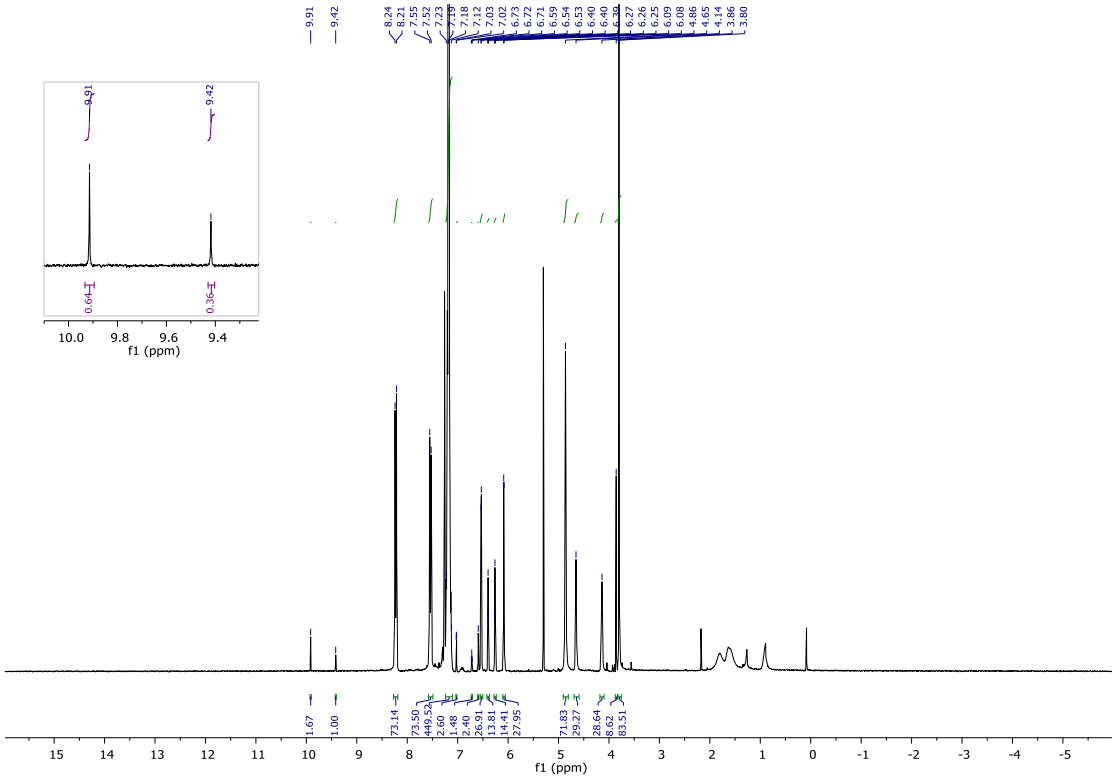


Figure S45. ^{1}H NMR of the competition experiment between 3,5-dimethoxybenzyl alcohol and 3,5-dirityloxybenzyl alcohol with **[1-Cu]BF$_4$** as catalyst in $CDCl_3$ at rt (table S1, entry 7).

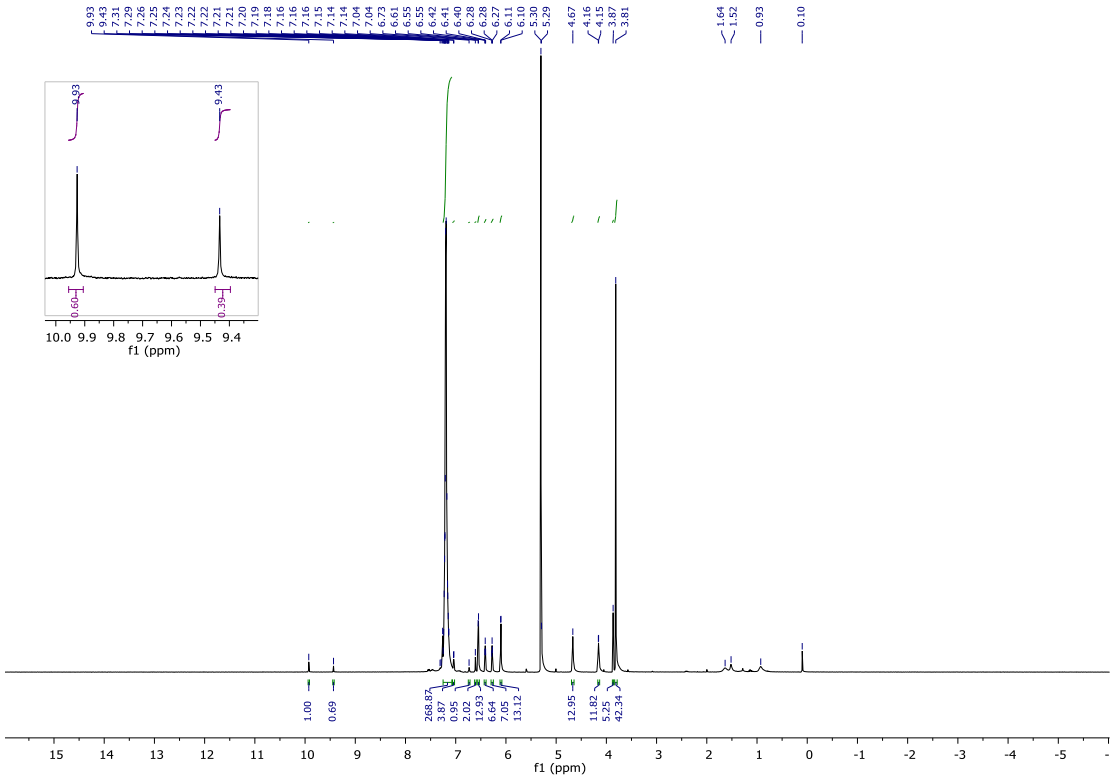


Figure S46. ^{1}H NMR of the competition experiment between 3,5-dimethoxybenzyl alcohol and 3,5-dirityloxybenzyl alcohol with **6**·3(NMI) as catalyst in $CDCl_3$ at rt (table S1, entry 8).

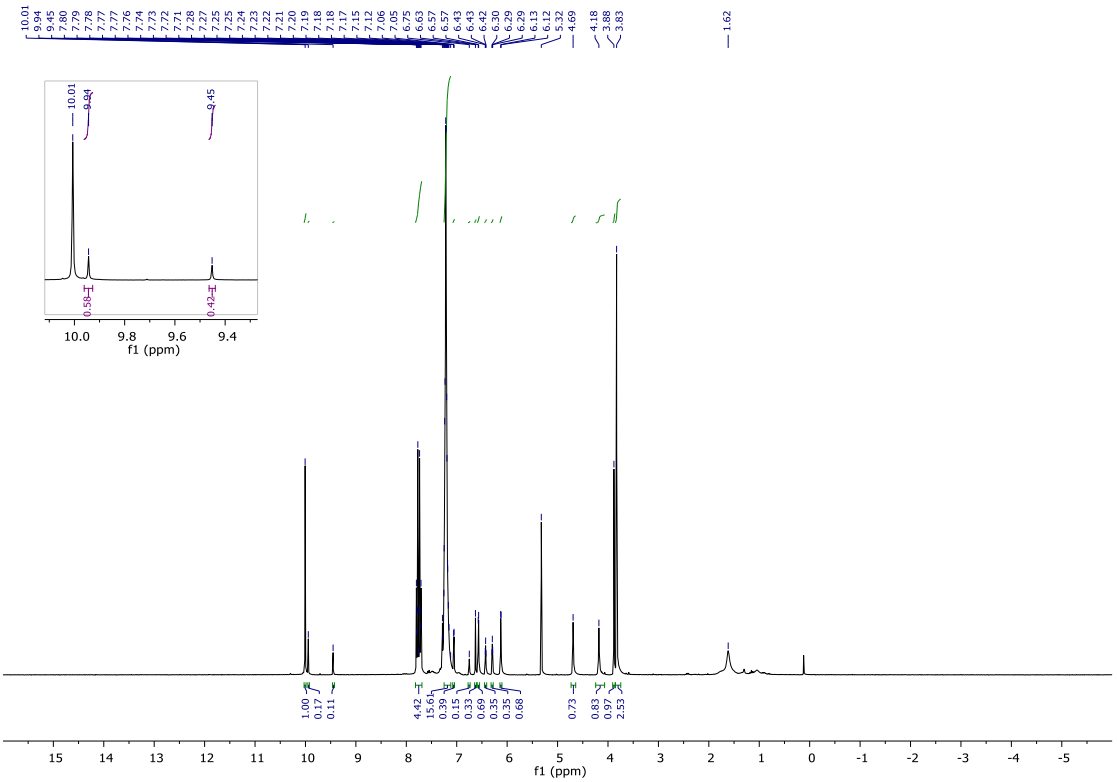


Figure S47. ^{1}H NMR of the competition experiment between 3,5-dimethoxybenzyl alcohol and 3,5-dirityloxybenzyl alcohol with **10**·(bipy)·2(NMI) as catalyst in $CDCl_3$ at rt (table S1, entry 9).

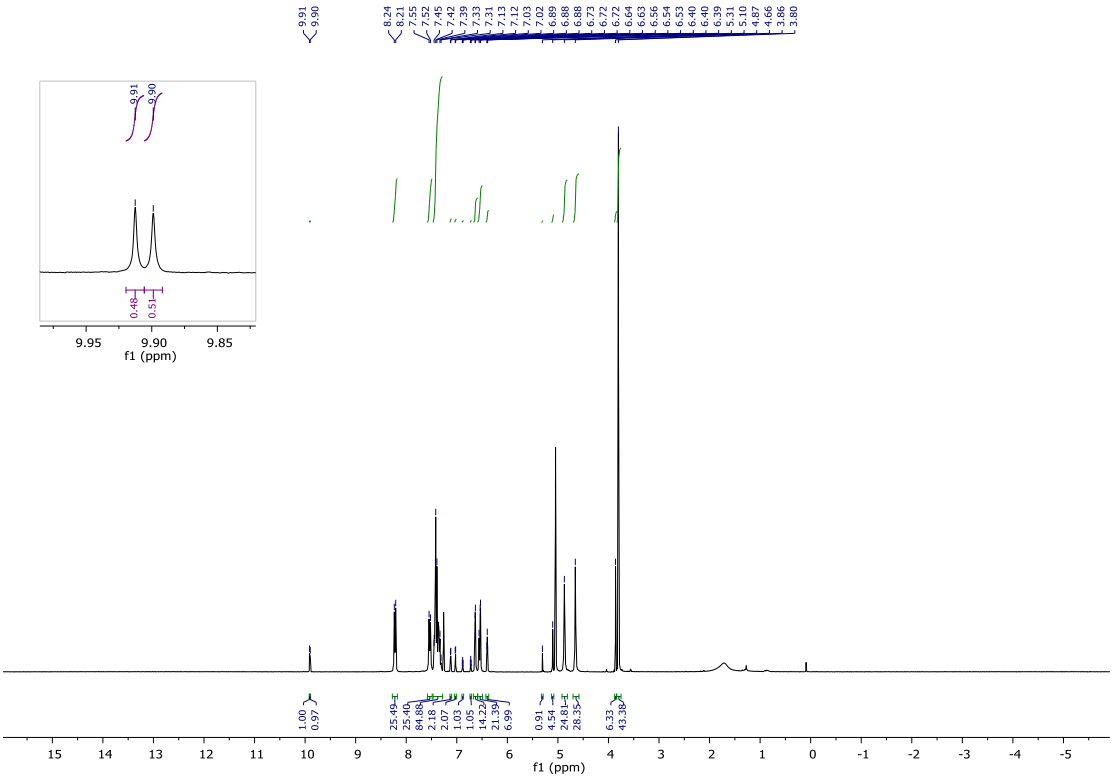


Figure S48. ^{1}H NMR of the competition experiment between 3,5-dimethoxybenzyl alcohol and 3,5-dibenzyloxybenzyl alcohol with **[1-Cu]BF_4** as catalyst in $CDCl_3$ at rt (table S1, entry 10).

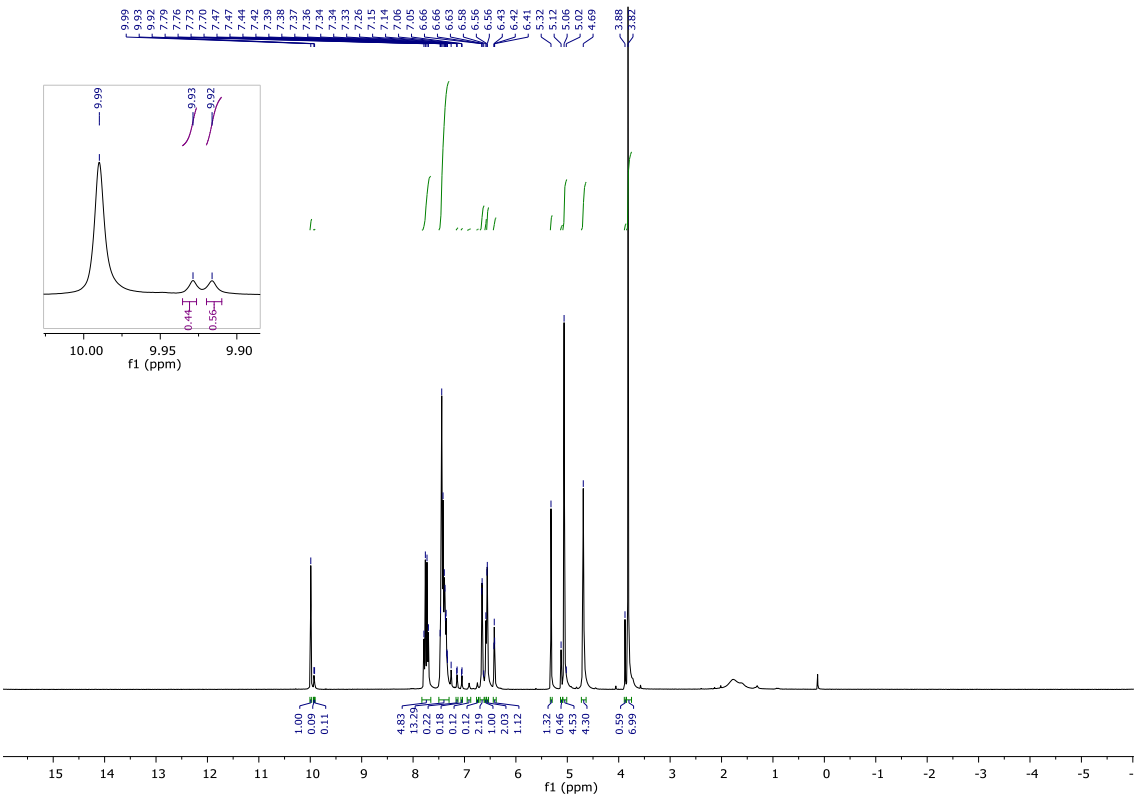


Figure S49. ^{1}H NMR of the competition experiment between 3,5-dimethoxybenzyl alcohol and 3,5-dibenzyloxybenzyl alcohol with **6**·3(NMI) as catalyst in $CDCl_3$ at rt (table S1, entry 11).

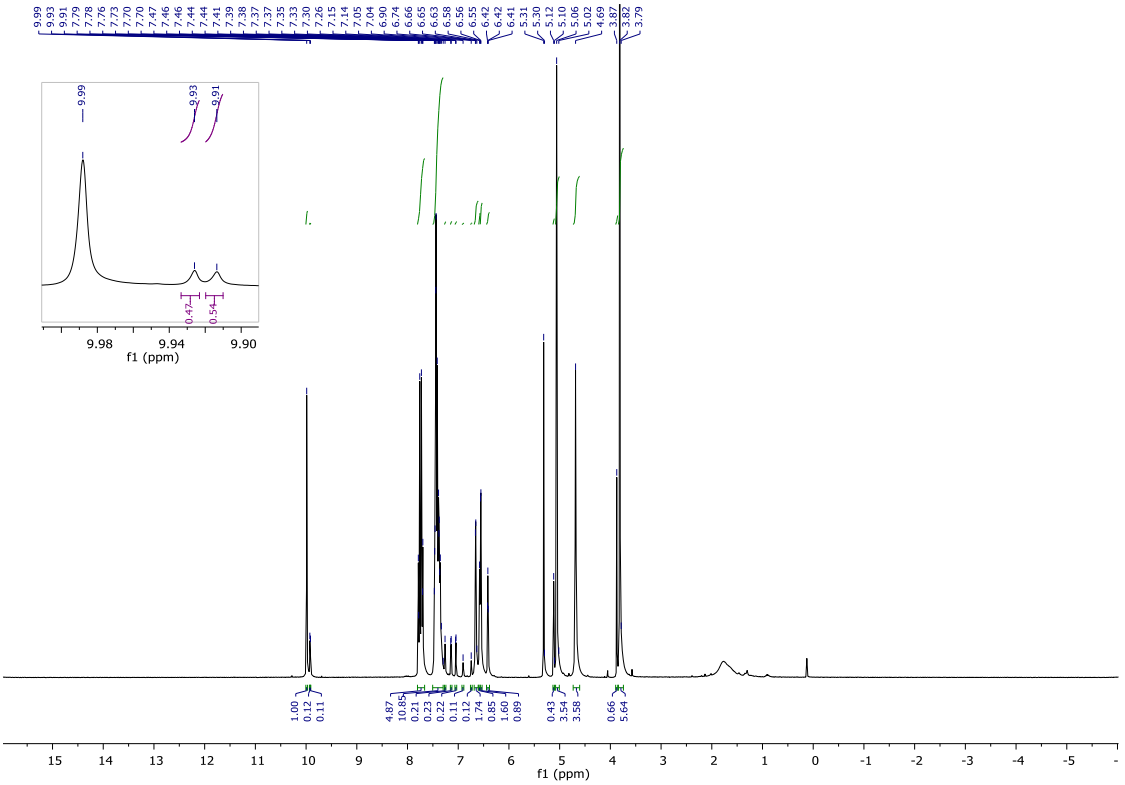


Figure S50. ^{1}H NMR of the competition experiment between 3,5-dimethoxybenzyl alcohol and 3,5-dibenzyloxybenzyl alcohol with **10**·(bipy)·2(NMI) as catalyst in $CDCl_3$ at rt (table S1, entry 12).

4. X-ray Single-Crystal Structure Analysis

CCDC-1868264 **(4)** and CCDC-1876236 **([1-Cu]SbF_6)** contain the supplementary crystallographic data for this paper. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/ products/csd/request/ (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44-1223- 336-033; e-mail: deposit@ccdc.cam.ac.uk).

4.1. Crystallographic Details

Suitable single crystals for X-ray structure determination were selected from the mother liquor under an inert gas atmosphere and transferred in protective perfluoro polyether oil on a microscope slide. The selected and mounted crystals were transferred to the cold gas stream on the diffractometer. The diffraction data were obtained at 100 K on a Bruker D8 three-circle diffractometer, equipped with a PHOTON 100 CMOS detector and an INCOATEC microfocus source with Quazar mirror optics (Mo-Kα radiation, λ= 0.71073 Å).

The data obtained were integrated with SAINT and a semi-empirical absorption correction from equivalents with SADABS was applied. The structures were solved and refined using the Bruker SHELX 2014 software package.[5] All non-hydrogen atoms were refined with anisotropic displacement parameters. All C-H hydrogen atoms were refined isotropically on calculated positions by using a riding model with their U_{iso} values constrained to 1.5 U_{eq} of their pivot atoms for terminal sp3 carbon atoms and 1.2 times for all other atoms.

4.2. X-ray Single-Crystal Structure Analysis of 4

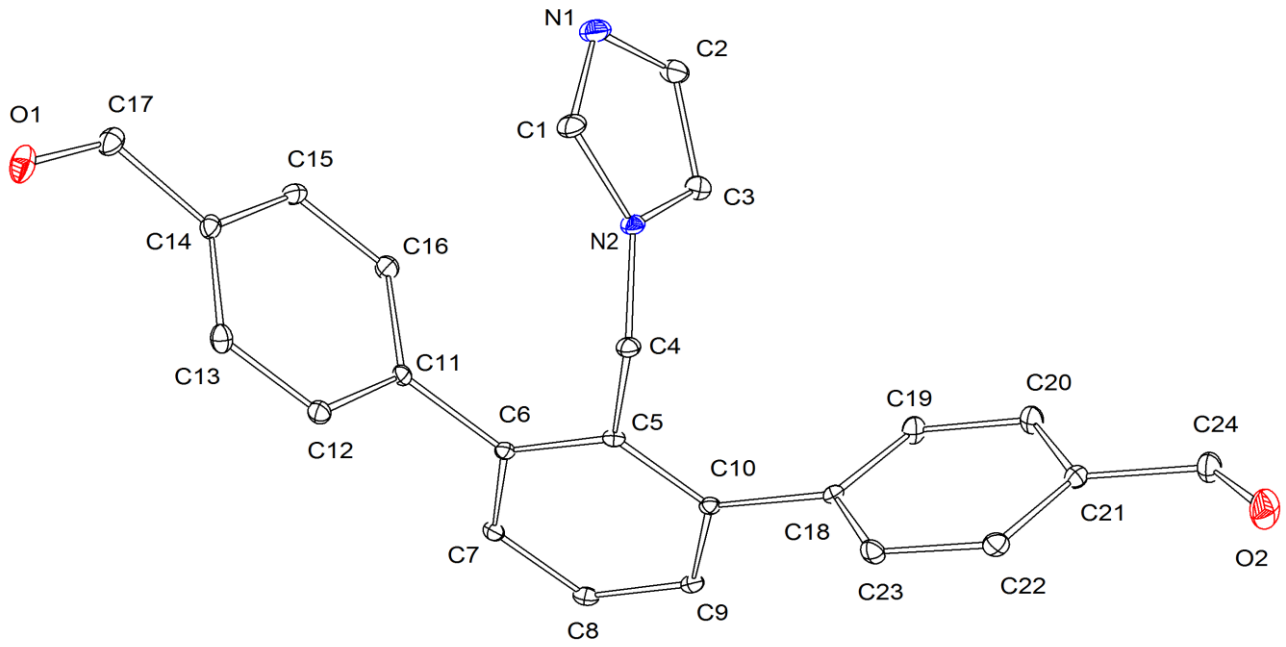


Figure S41. Thermal ellipsoid plot of **4** with the anisotropic displacement parameters drawn at the 50% probability level. The asymmetric unit contains one molecule.

Table S2. Crystal data and structure refinement for **4**.

Identification code	mo_CW_SB_MO_080618_0m_a (Sb2-20)	
Empirical formula	$C_{24}H_{18}N_2O_2$	
Formula weight	366.40	
Temperature	102(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 7.6952(5) Å	α = 90°
	b = 12.1964(8) Å	β = 97.259(3)°
	c = 19.5655(12) Å	γ = 90°
Volume	1821.6(2) $Å^3$	
Z	4	
Density (calculated)	1.336 Mg/m^3	
Absorption coefficient	0.086 mm^{-1}	
F(000)	768	
Crystal size	1.305 x 0.925 x 0.712 m^3	
Crystal shape and color	Block,	clear colourless
Theta range for data collection	2.668 to 28.280°	
Index ranges	-10<=h<=10, -16<=k<=16, -26<=l<=26	
Reflections collected	58448	
Independent reflections	4518 [R(int) = 0.0919]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4518 / 0 / 253	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0494,	wR2 = 0.1078
R indices (all data)	R1 = 0.0687,	wR2 = 0.1173
Largest diff. peak and hole	0.312 and -0.317 $eÅ^{-3}$	

Table S3. Bond lengths [Å] and angles [°] for **4**.

O(1)-C(17)	1.208(2)
O(2)-C(24)	1.2054(19)
N(1)-C(1)	1.312(2)
N(1)-C(2)	1.375(2)
N(2)-C(1)	1.3550(19)
N(2)-C(3)	1.372(2)
N(2)-C(4)	1.4644(18)
C(2)-C(3)	1.362(2)
C(4)-C(5)	1.5125(19)
C(5)-C(10)	1.4053(19)
C(5)-C(6)	1.405(2)
C(6)-C(7)	1.393(2)
C(6)-C(11)	1.4970(19)
C(7)-C(8)	1.388(2)
C(8)-C(9)	1.384(2)
C(9)-C(10)	1.397(2)
C(10)-C(18)	1.500(2)
C(11)-C(16)	1.392(2)
C(11)-C(12)	1.394(2)
C(12)-C(13)	1.385(2)
C(13)-C(14)	1.394(2)
C(14)-C(15)	1.391(2)
C(14)-C(17)	1.476(2)
C(15)-C(16)	1.389(2)
C(18)-C(19)	1.393(2)
C(18)-C(23)	1.397(2)
C(19)-C(20)	1.388(2)
C(20)-C(21)	1.385(2)
C(21)-C(22)	1.397(2)
C(21)-C(24)	1.476(2)
C(22)-C(23)	1.386(2)

C(1)-N(1)-C(2)	104.49(13)
C(1)-N(2)-C(3)	106.62(13)
C(1)-N(2)-C(4)	126.52(13)
C(3)-N(2)-C(4)	126.86(12)
N(1)-C(1)-N(2)	112.54(14)
C(3)-C(2)-N(1)	110.81(15)
C(2)-C(3)-N(2)	105.54(14)

N(2)-C(4)-C(5)	112.13(12)
C(10)-C(5)-C(6)	119.63(13)
C(10)-C(5)-C(4)	120.52(12)
C(6)-C(5)-C(4)	119.85(12)
C(7)-C(6)-C(5)	119.97(13)
C(7)-C(6)-C(11)	119.77(12)
C(5)-C(6)-C(11)	120.26(12)
C(8)-C(7)-C(6)	120.20(13)
C(9)-C(8)-C(7)	120.08(13)
C(8)-C(9)-C(10)	120.85(13)
C(9)-C(10)-C(5)	119.21(13)
C(9)-C(10)-C(18)	117.84(12)
C(5)-C(10)-C(18)	122.93(12)
C(16)-C(11)-C(12)	119.23(13)
C(16)-C(11)-C(6)	120.87(13)
C(12)-C(11)-C(6)	119.87(13)
C(13)-C(12)-C(11)	120.82(14)
C(12)-C(13)-C(14)	119.67(13)
C(15)-C(14)-C(13)	119.86(13)
C(15)-C(14)-C(17)	119.48(14)
C(13)-C(14)-C(17)	120.60(14)
C(16)-C(15)-C(14)	120.19(14)
C(15)-C(16)-C(11)	120.21(14)
O(1)-C(17)-C(14)	124.89(15)
C(19)-C(18)-C(23)	118.96(13)
C(19)-C(18)-C(10)	118.90(13)
C(23)-C(18)-C(10)	122.09(13)
C(20)-C(19)-C(18)	120.44(13)
C(21)-C(20)-C(19)	120.30(14)
C(20)-C(21)-C(22)	119.80(14)
C(20)-C(21)-C(24)	118.44(13)
C(22)-C(21)-C(24)	121.75(13)
C(23)-C(22)-C(21)	119.76(13)
C(22)-C(23)-C(18)	120.71(13)
O(2)-C(24)-C(21)	125.31(15)

Table S4. Torsion angles [°] for **4**.

C(2)-N(1)-C(1)-N(2)	-0.40(18)
C(3)-N(2)-C(1)-N(1)	0.17(18)
C(4)-N(2)-C(1)-N(1)	179.49(13)
C(1)-N(1)-C(2)-C(3)	0.49(18)
N(1)-C(2)-C(3)-N(2)	-0.39(18)
C(1)-N(2)-C(3)-C(2)	0.14(17)
C(4)-N(2)-C(3)-C(2)	-179.18(14)
C(1)-N(2)-C(4)-C(5)	134.02(15)
C(3)-N(2)-C(4)-C(5)	-46.79(19)
N(2)-C(4)-C(5)-C(10)	104.25(15)
N(2)-C(4)-C(5)-C(6)	-74.77(16)
C(10)-C(5)-C(6)-C(7)	2.5(2)
C(4)-C(5)-C(6)-C(7)	-178.47(13)
C(10)-C(5)-C(6)-C(11)	-177.13(12)
C(4)-C(5)-C(6)-C(11)	1.89(19)
C(5)-C(6)-C(7)-C(8)	-1.5(2)
C(11)-C(6)-C(7)-C(8)	178.11(13)
C(6)-C(7)-C(8)-C(9)	-0.5(2)
C(7)-C(8)-C(9)-C(10)	1.5(2)
C(8)-C(9)-C(10)-C(5)	-0.6(2)
C(8)-C(9)-C(10)-C(18)	-179.15(13)
C(6)-C(5)-C(10)-C(9)	-1.5(2)
C(4)-C(5)-C(10)-C(9)	179.52(13)
C(6)-C(5)-C(10)-C(18)	177.06(13)
C(4)-C(5)-C(10)-C(18)	-2.0(2)
C(7)-C(6)-C(11)-C(16)	-91.84(17)
C(5)-C(6)-C(11)-C(16)	87.80(17)
C(7)-C(6)-C(11)-C(12)	90.21(17)
C(5)-C(6)-C(11)-C(12)	-90.15(17)
C(16)-C(11)-C(12)-C(13)	-0.8(2)
C(6)-C(11)-C(12)-C(13)	177.17(13)
C(11)-C(12)-C(13)-C(14)	-0.7(2)
C(12)-C(13)-C(14)-C(15)	1.4(2)
C(12)-C(13)-C(14)-C(17)	-175.82(14)
C(13)-C(14)-C(15)-C(16)	-0.7(2)
C(17)-C(14)-C(15)-C(16)	176.59(14)
C(14)-C(15)-C(16)-C(11)	-0.8(2)
C(12)-C(11)-C(16)-C(15)	1.6(2)
C(6)-C(11)-C(16)-C(15)	-176.40(13)

C(15)-C(14)-C(17)-O(1)	173.83(15)
C(13)-C(14)-C(17)-O(1)	-8.9(2)
C(9)-C(10)-C(18)-C(19)	77.15(17)
C(5)-C(10)-C(18)-C(19)	-101.39(17)
C(9)-C(10)-C(18)-C(23)	-100.27(16)
C(5)-C(10)-C(18)-C(23)	81.19(18)
C(23)-C(18)-C(19)-C(20)	-0.4(2)
C(10)-C(18)-C(19)-C(20)	-177.86(13)
C(18)-C(19)-C(20)-C(21)	1.5(2)
C(19)-C(20)-C(21)-C(22)	-1.6(2)
C(19)-C(20)-C(21)-C(24)	177.86(14)
C(20)-C(21)-C(22)-C(23)	0.4(2)
C(24)-C(21)-C(22)-C(23)	-179.01(14)
C(21)-C(22)-C(23)-C(18)	0.8(2)
C(19)-C(18)-C(23)-C(22)	-0.8(2)
C(10)-C(18)-C(23)-C(22)	176.61(13)
C(20)-C(21)-C(24)-O(2)	175.89(15)
C(22)-C(21)-C(24)-O(2)	-4.7(2)

4.3. X-ray Single-Crystal Structure Analysis of [1-Cu]BF_4

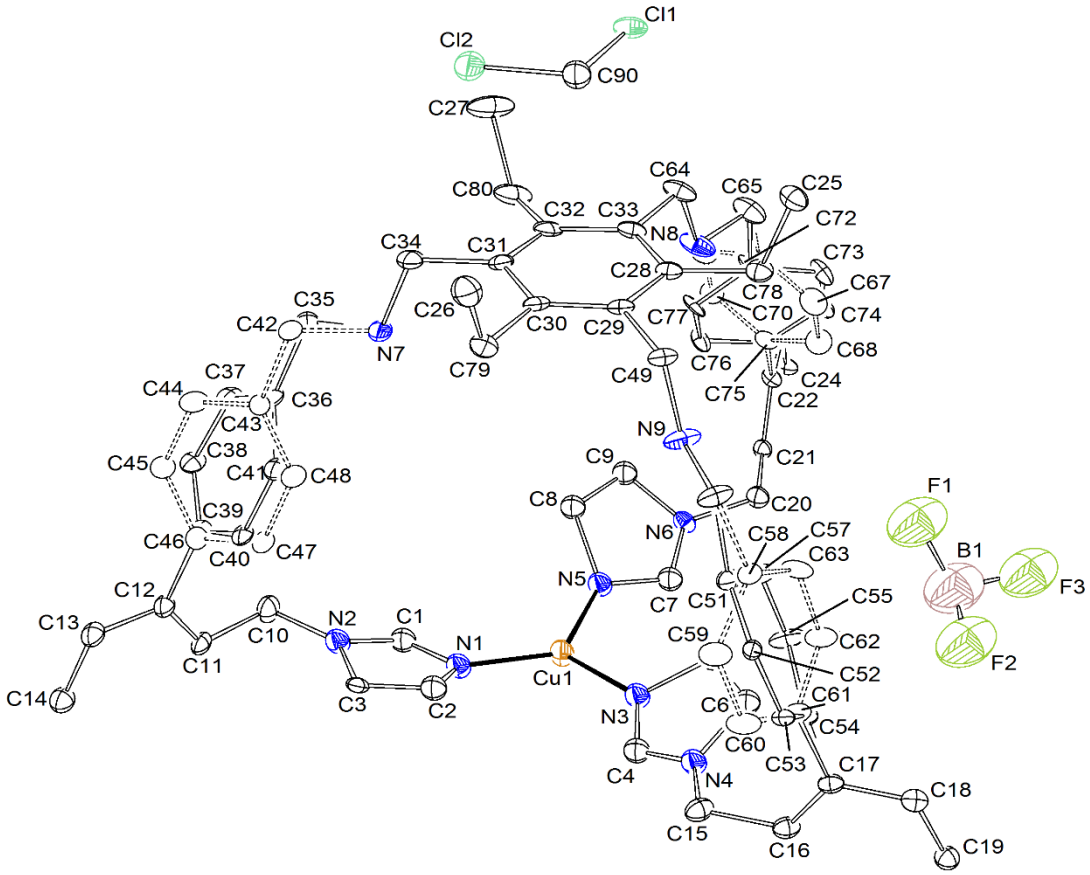


Figure S42. Thermal ellipsoid plot of the asymmetric unit of **[1-Cu]BF_4** with the anisotropic displacement parameters drawn at the 25% probability level. The asymmetric unit contains a half disordered complex molecule a half BF_4^- anion and a half dichlormethane solvent molecule. The disordered complex molecule was refined with population of 0.84(2), 0.66(2) and 0.72(3) on their main domains using some restraints and constraints (RIGU, EADP). The BF_4^- anion was refined using restraints and constraints (SADI, RIGU, DFIX, EADP). 67 reflections were removed from the refinement using OMIT commands. The SQUEEZE algorithm[6] was used to omit several disordered solvent molecules. **The structure was not deposited in the CSD.**

Table S5. Crystal data and structure refinement for **[1-Cu]BF_4**.

Identification code	mo_cw_sb_mo_250618_2_0m_a_sq (Sb2-19)	
Empirical formula	$C_{103}H_{107}BCl_2CuF_4N_{12}$	
Formula weight	1734.25	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/m	
Unit cell dimensions	a = 25.886(2) Å	α = 90°
	b = 22.8920(18) Å	β = 101.789(3)°
	c = 18.3695(14) Å	γ = 90°
Volume	10655.7(15) $Å^3$	
Z	4	
Density (calculated)	1.081 Mg/m^3	
Absorption coefficient	0.309 mm^{-1}	
F(000)	3652	
Crystal size	0.428 x 0.310 x 0.206 mm^3	
Crystal shape and colour	Block,	colourless
Theta range for data collection	2.265 to 25.350°	
Index ranges	-31<=h<=31, -27<=k<=27, -22<=l<=22	
Reflections collected	67699	
Independent reflections	9948 [R(int) = 0.0711]	
Completeness to theta = 25.242°	99.2 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9948 / 799 / 730	
Goodness-of-fit on F^2	2.326	
Final R indices [I>2sigma(I)]	R1 = 0.1712,	wR2 = 0.4887
R indices (all data)	R1 = 0.1953,	wR2 = 0.5122
Largest diff. peak and hole	4.689 and -2.776 $eÅ^{-3}$	

Table S6. Bond lengths [Å] and angles [°] for **[1-Cu]BF_4**.

Cu(1)-N(5)	1.918(12)
Cu(1)-N(1)	1.971(13)
Cu(1)-N(3)	2.001(11)
N(1)-C(1)	1.27(2)
N(1)-C(2)	1.36(2)
N(2)-C(3)	1.312(15)
N(2)-C(1)	1.403(19)
N(2)-C(10)	1.439(14)
N(3)-C(4)	1.262(18)
N(3)-C(5)	1.512(17)
N(4)-C(4)	1.237(18)
N(4)-C(6)	1.450(17)
N(4)-C(15)	1.546(14)
N(5)-C(7)	1.36(2)
N(5)-C(8)	1.543(18)
N(6)-C(7)	1.280(18)
N(6)-C(9)	1.460(18)
N(6)-C(20)	1.490(13)
C(2)-C(3)	1.352(16)
C(5)-C(6)	1.342(18)
C(8)-C(9)	1.36(2)
Cl(1)-C(90)	1.761(11)
Cl(2)-C(90)	1.743(11)
F(1)-B(1)	1.477(11)
F(2)-B(1)	1.519(17)
F(3)-B(1)	1.507(17)
N(7)-C(35)	1.41(2)
N(7)-C(34)	1.457(8)
N(7)-C(42)	1.518(14)
N(8)-C(65)	1.462(10)
N(8)-C(64)	1.491(8)
N(9)-C(50)	1.448(9)
N(9)-C(49)	1.482(8)
C(78)-C(28)	1.512(10)
C(78)-C(25)	1.537(9)
C(79)-C(30)	1.516(10)
C(79)-C(26)	1.520(12)
C(80)-C(32)	1.511(10)
C(80)-C(27)	1.562(11)

C(10)-C(11)	1.503(15)
C(11)-C(12)#1	1.391(8)
C(11)-C(12)	1.391(8)
C(12)-C(13)	1.413(10)
C(12)-C(39)	1.51(4)
C(12)-C(46)	1.509(19)
C(13)-C(14)	1.370(9)
C(14)-C(13)#1	1.370(9)
C(15)-C(16)	1.523(14)
C(16)-C(17)	1.386(8)
C(16)-C(17)#1	1.386(8)
C(17)-C(54)	1.40(6)
C(17)-C(18)	1.420(9)
C(17)-C(61)	1.53(2)
C(18)-C(19)	1.349(8)
C(19)-C(18)#1	1.349(8)
C(20)-C(21)	1.508(12)
C(21)-C(22)#1	1.393(7)
C(21)-C(22)	1.393(7)
C(22)-C(75)	1.35(4)
C(22)-C(23)	1.404(9)
C(22)-C(69)	1.535(17)
C(23)-C(24)	1.381(7)
C(24)-C(23)#1	1.381(7)
C(28)-C(29)	1.399(9)
C(28)-C(33)	1.409(9)
C(29)-C(30)	1.392(10)
C(29)-C(49)	1.520(9)
C(30)-C(31)	1.410(9)
C(31)-C(32)	1.374(10)
C(31)-C(34)	1.520(10)
C(32)-C(33)	1.425(10)
C(33)-C(64)	1.499(10)
C(50)-C(58)	1.531(17)
C(50)-C(51)	1.54(4)
C(65)-C(66)	1.51(2)
C(65)-C(72)	1.52(4)
B(1)-F(1)#1	1.477(11)
C(39)-C(38)	1.40(4)
C(39)-C(40)	1.40(4)

C(35)-C(36)	1.54(3)
C(36)-C(37)	1.32(3)
C(36)-C(41)	1.50(5)
C(37)-C(38)	1.38(3)
C(40)-C(41)	1.36(5)
C(42)-C(43)	1.511(14)
C(43)-C(44)	1.348(16)
C(43)-C(48)	1.37(2)
C(44)-C(45)	1.395(16)
C(45)-C(46)	1.38(2)
C(46)-C(47)	1.42(2)
C(47)-C(48)	1.37(2)
C(66)-C(67)	1.31(3)
C(66)-C(71)	1.46(3)
C(67)-C(68)	1.405(16)
C(68)-C(69)	1.33(3)
C(69)-C(70)	1.36(3)
C(70)-C(71)	1.377(15)
C(72)-C(77)	1.35(5)
C(72)-C(73)	1.51(5)
C(73)-C(74)	1.34(3)
C(74)-C(75)	1.43(5)
C(75)-C(76)	1.51(5)
C(76)-C(77)	1.35(2)
C(58)-C(63)	1.34(2)
C(58)-C(59)	1.46(2)
C(59)-C(60)	1.390(16)
C(60)-C(61)	1.38(3)
C(61)-C(62)	1.38(3)
C(62)-C(63)	1.365(15)
C(55)-C(57)	1.37(4)
C(55)-C(54)	1.49(8)
C(51)-C(52)	1.33(6)
C(51)-C(57)	1.51(5)
C(52)-C(53)	1.36(3)
C(53)-C(54)	1.40(6)

N(5)-Cu(1)-N(1)	128.5(5)
N(5)-Cu(1)-N(3)	114.5(5)
N(1)-Cu(1)-N(3)	113.9(5)

C(1)-N(1)-C(2)	106.7(12)
C(1)-N(1)-Cu(1)	125.6(10)
C(2)-N(1)-Cu(1)	126.0(9)
C(3)-N(2)-C(1)	100.8(13)
C(3)-N(2)-C(10)	133.0(12)
C(1)-N(2)-C(10)	125.9(10)
C(4)-N(3)-C(5)	104.3(11)
C(4)-N(3)-Cu(1)	133.2(11)
C(5)-N(3)-Cu(1)	122.1(8)
C(4)-N(4)-C(6)	105.6(11)
C(4)-N(4)-C(15)	127.4(11)
C(6)-N(4)-C(15)	123.5(10)
C(7)-N(5)-C(8)	102.2(11)
C(7)-N(5)-Cu(1)	124.7(10)
C(8)-N(5)-Cu(1)	125.9(9)
C(7)-N(6)-C(9)	109.4(11)
C(7)-N(6)-C(20)	123.7(11)
C(9)-N(6)-C(20)	122.0(10)
N(1)-C(1)-N(2)	112.3(13)
C(3)-C(2)-N(1)	105.1(15)
N(2)-C(3)-C(2)	111.0(10)
N(4)-C(4)-N(3)	118.4(14)
C(6)-C(5)-N(3)	103.6(11)
C(5)-C(6)-N(4)	107.9(11)
N(6)-C(7)-N(5)	113.8(13)
C(9)-C(8)-N(5)	106.8(12)
C(8)-C(9)-N(6)	106.0(11)
C(35)-N(7)-C(34)	114.9(10)
C(34)-N(7)-C(42)	109.7(6)
C(65)-N(8)-C(64)	111.4(5)
C(50)-N(9)-C(49)	111.5(5)
C(28)-C(78)-C(25)	112.7(5)
C(30)-C(79)-C(26)	113.0(6)
C(32)-C(80)-C(27)	112.8(6)
N(2)-C(10)-C(11)	112.7(8)
C(12)#1-C(11)-C(12)	119.2(9)
C(12)#1-C(11)-C(10)	120.2(5)
C(12)-C(11)-C(10)	120.2(5)
C(11)-C(12)-C(13)	120.0(6)
C(11)-C(12)-C(39)	116.0(19)

C(13)-C(12)-C(39)	123.8(19)
C(11)-C(12)-C(46)	125.2(10)
C(13)-C(12)-C(46)	114.5(10)
C(14)-C(13)-C(12)	120.1(7)
C(13)-C(14)-C(13)#1	120.6(10)
C(16)-C(15)-N(4)	106.0(8)
C(17)-C(16)-C(17)#1	121.4(9)
C(17)-C(16)-C(15)	119.3(4)
C(17)#1-C(16)-C(15)	119.3(4)
C(16)-C(17)-C(54)	127(3)
C(16)-C(17)-C(18)	118.0(6)
C(54)-C(17)-C(18)	114(3)
C(16)-C(17)-C(61)	123.5(14)
C(18)-C(17)-C(61)	118.3(14)
C(19)-C(18)-C(17)	120.4(6)
C(18)#1-C(19)-C(18)	121.7(9)
N(6)-C(20)-C(21)	114.5(8)
C(22)#1-C(21)-C(22)	121.3(8)
C(22)#1-C(21)-C(20)	119.2(4)
C(22)-C(21)-C(20)	119.2(4)
C(75)-C(22)-C(21)	126(3)
C(75)-C(22)-C(23)	116(3)
C(21)-C(22)-C(23)	118.1(6)
C(21)-C(22)-C(69)	124.0(12)
C(23)-C(22)-C(69)	117.8(12)
C(24)-C(23)-C(22)	122.0(6)
C(23)#1-C(24)-C(23)	118.3(7)
C(29)-C(28)-C(33)	119.0(6)
C(29)-C(28)-C(78)	120.7(6)
C(33)-C(28)-C(78)	120.1(6)
C(30)-C(29)-C(28)	120.3(6)
C(30)-C(29)-C(49)	121.0(6)
C(28)-C(29)-C(49)	118.5(6)
C(29)-C(30)-C(31)	120.7(6)
C(29)-C(30)-C(79)	118.2(6)
C(31)-C(30)-C(79)	121.0(6)
C(32)-C(31)-C(30)	119.8(6)
C(32)-C(31)-C(34)	121.5(7)
C(30)-C(31)-C(34)	118.7(7)
C(31)-C(32)-C(33)	119.8(6)

C(31)-C(32)-C(80)	120.8(7)
C(33)-C(32)-C(80)	119.4(7)
C(28)-C(33)-C(32)	120.2(6)
C(28)-C(33)-C(64)	120.5(6)
C(32)-C(33)-C(64)	119.3(6)
N(7)-C(34)-C(31)	111.5(6)
N(9)-C(49)-C(29)	108.5(5)
N(9)-C(50)-C(58)	111.6(9)
N(9)-C(50)-C(51)	108(2)
N(8)-C(64)-C(33)	111.7(5)
N(8)-C(65)-C(66)	114.1(9)
N(8)-C(65)-C(72)	103.1(19)
Cl(2)-C(90)-Cl(1)	114.4(6)
F(1)-B(1)-F(1)#1	107.8(11)
F(1)-B(1)-F(3)	112.8(8)
F(1)#1-B(1)-F(3)	112.8(8)
F(1)-B(1)-F(2)	108.7(8)
F(1)#1-B(1)-F(2)	108.7(8)
F(3)-B(1)-F(2)	105.8(11)
C(38)-C(39)-C(40)	120(3)
C(38)-C(39)-C(12)	127(3)
C(40)-C(39)-C(12)	113(3)
N(7)-C(35)-C(36)	114.6(17)
C(37)-C(36)-C(41)	117(2)
C(37)-C(36)-C(35)	124(2)
C(41)-C(36)-C(35)	117(2)
C(36)-C(37)-C(38)	124(2)
C(37)-C(38)-C(39)	119(2)
C(41)-C(40)-C(39)	121(3)
C(40)-C(41)-C(36)	119(3)
C(43)-C(42)-N(7)	110.5(8)
C(44)-C(43)-C(48)	119.3(12)
C(44)-C(43)-C(42)	119.3(10)
C(48)-C(43)-C(42)	121.1(12)
C(43)-C(44)-C(45)	121.9(11)
C(46)-C(45)-C(44)	120.0(12)
C(45)-C(46)-C(47)	117.0(15)
C(45)-C(46)-C(12)	119.4(15)
C(47)-C(46)-C(12)	123.5(15)
C(48)-C(47)-C(46)	121.4(15)

C(43)-C(48)-C(47)	120.2(14)
C(67)-C(66)-C(71)	118.0(16)
C(67)-C(66)-C(65)	123(2)
C(71)-C(66)-C(65)	119(2)
C(66)-C(67)-C(68)	121.6(14)
C(69)-C(68)-C(67)	120.5(15)
C(68)-C(69)-C(70)	119.9(15)
C(68)-C(69)-C(22)	122(2)
C(70)-C(69)-C(22)	116.5(16)
C(69)-C(70)-C(71)	120.8(12)
C(70)-C(71)-C(66)	118.5(14)
C(77)-C(72)-C(73)	116(3)
C(77)-C(72)-C(65)	129(3)
C(73)-C(72)-C(65)	115(3)
C(74)-C(73)-C(72)	119(2)
C(73)-C(74)-C(75)	128(3)
C(22)-C(75)-C(74)	125(4)
C(22)-C(75)-C(76)	126(4)
C(74)-C(75)-C(76)	108(3)
C(77)-C(76)-C(75)	126(2)
C(76)-C(77)-C(72)	122(2)
C(63)-C(58)-C(59)	119.3(13)
C(63)-C(58)-C(50)	122.5(13)
C(59)-C(58)-C(50)	117.1(13)
C(60)-C(59)-C(58)	118.3(13)
C(61)-C(60)-C(59)	119.4(15)
C(62)-C(61)-C(60)	120.4(17)
C(62)-C(61)-C(17)	116.7(17)
C(60)-C(61)-C(17)	123(2)
C(63)-C(62)-C(61)	121.1(13)
C(58)-C(63)-C(62)	120.8(11)
C(57)-C(55)-C(54)	119(3)
C(52)-C(51)-C(57)	112(3)
C(52)-C(51)-C(50)	124(4)
C(57)-C(51)-C(50)	116(3)
C(51)-C(52)-C(53)	126(3)
C(52)-C(53)-C(54)	123(3)
C(53)-C(54)-C(17)	123(5)
C(53)-C(54)-C(55)	114(4)
C(17)-C(54)-C(55)	122(5)

C(55)-C(57)-C(51)	123(3)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1,z

Table S7. Torsion angles [°] for **[1-Cu]BF_4**.

C(2)-N(1)-C(1)-N(2)	1(2)
Cu(1)-N(1)-C(1)-N(2)	-164.7(10)
C(3)-N(2)-C(1)-N(1)	-13(3)
C(10)-N(2)-C(1)-N(1)	172.8(12)
C(1)-N(1)-C(2)-C(3)	11(3)
Cu(1)-N(1)-C(2)-C(3)	177(2)
C(1)-N(2)-C(3)-C(2)	20(4)
C(10)-N(2)-C(3)-C(2)	-166(2)
N(1)-C(2)-C(3)-N(2)	-21(4)
C(6)-N(4)-C(4)-N(3)	-0.2(19)
C(15)-N(4)-C(4)-N(3)	159.0(12)
C(5)-N(3)-C(4)-N(4)	-2.1(19)
Cu(1)-N(3)-C(4)-N(4)	-174.6(11)
C(4)-N(3)-C(5)-C(6)	3.6(15)
Cu(1)-N(3)-C(5)-C(6)	177.1(9)
N(3)-C(5)-C(6)-N(4)	-3.7(14)
C(4)-N(4)-C(6)-C(5)	2.7(16)
C(15)-N(4)-C(6)-C(5)	-157.5(11)
C(9)-N(6)-C(7)-N(5)	10.9(17)
C(20)-N(6)-C(7)-N(5)	166.5(11)
C(8)-N(5)-C(7)-N(6)	-13.7(16)
Cu(1)-N(5)-C(7)-N(6)	-165.3(10)
C(7)-N(5)-C(8)-C(9)	11.5(14)
Cu(1)-N(5)-C(8)-C(9)	162.6(10)
N(5)-C(8)-C(9)-N(6)	-5.8(14)
C(7)-N(6)-C(9)-C(8)	-2.3(16)
C(20)-N(6)-C(9)-C(8)	-158.3(10)
C(3)-N(2)-C(10)-C(11)	-15(3)
C(1)-N(2)-C(10)-C(11)	157.7(12)
N(2)-C(10)-C(11)-C(12)#1	-84.9(10)
N(2)-C(10)-C(11)-C(12)	102.3(9)
C(12)#1-C(11)-C(12)-C(13)	-1.0(13)
C(10)-C(11)-C(12)-C(13)	171.9(8)
C(12)#1-C(11)-C(12)-C(39)	-175.4(17)
C(10)-C(11)-C(12)-C(39)	-2.4(19)
C(12)#1-C(11)-C(12)-C(46)	172.7(9)
C(10)-C(11)-C(12)-C(46)	-14.3(15)
C(11)-C(12)-C(13)-C(14)	1.0(12)
C(39)-C(12)-C(13)-C(14)	174.9(18)

C(46)-C(12)-C(13)-C(14)	-173.4(10)
C(12)-C(13)-C(14)-C(13)#1	-1.0(15)
C(4)-N(4)-C(15)-C(16)	162.9(13)
C(6)-N(4)-C(15)-C(16)	-41.3(11)
N(4)-C(15)-C(16)-C(17)	101.8(8)
N(4)-C(15)-C(16)-C(17)#1	-78.9(9)
C(17)#1-C(16)-C(17)-C(54)	175(3)
C(15)-C(16)-C(17)-C(54)	-6(4)
C(17)#1-C(16)-C(17)-C(18)	2.2(13)
C(15)-C(16)-C(17)-C(18)	-178.4(7)
C(17)#1-C(16)-C(17)-C(61)	178.6(14)
C(15)-C(16)-C(17)-C(61)	-2.1(18)
C(16)-C(17)-C(18)-C(19)	0.0(10)
C(54)-C(17)-C(18)-C(19)	-173(3)
C(61)-C(17)-C(18)-C(19)	-176.6(14)
C(17)-C(18)-C(19)-C(18)#1	-2.2(14)
C(7)-N(6)-C(20)-C(21)	158.0(11)
C(9)-N(6)-C(20)-C(21)	-49.4(11)
N(6)-C(20)-C(21)-C(22)#1	-81.2(9)
N(6)-C(20)-C(21)-C(22)	103.8(8)
C(22)#1-C(21)-C(22)-C(75)	174(3)
C(20)-C(21)-C(22)-C(75)	-11(3)
C(22)#1-C(21)-C(22)-C(23)	-0.8(12)
C(20)-C(21)-C(22)-C(23)	174.1(7)
C(22)#1-C(21)-C(22)-C(69)	175.6(13)
C(20)-C(21)-C(22)-C(69)	-9.6(17)
C(75)-C(22)-C(23)-C(24)	-177(3)
C(21)-C(22)-C(23)-C(24)	-1.8(11)
C(69)-C(22)-C(23)-C(24)	-178.4(13)
C(22)-C(23)-C(24)-C(23)#1	4.3(14)
C(25)-C(78)-C(28)-C(29)	-86.6(7)
C(25)-C(78)-C(28)-C(33)	88.6(7)
C(33)-C(28)-C(29)-C(30)	2.1(8)
C(78)-C(28)-C(29)-C(30)	177.4(5)
C(33)-C(28)-C(29)-C(49)	177.2(5)
C(78)-C(28)-C(29)-C(49)	-7.6(8)
C(28)-C(29)-C(30)-C(31)	-1.6(9)
C(49)-C(29)-C(30)-C(31)	-176.5(6)
C(28)-C(29)-C(30)-C(79)	179.5(6)
C(49)-C(29)-C(30)-C(79)	4.5(8)

C(26)-C(79)-C(30)-C(29)	84.7(8)
C(26)-C(79)-C(30)-C(31)	-94.2(8)
C(29)-C(30)-C(31)-C(32)	2.7(9)
C(79)-C(30)-C(31)-C(32)	-178.4(6)
C(29)-C(30)-C(31)-C(34)	-179.1(5)
C(79)-C(30)-C(31)-C(34)	-0.2(9)
C(30)-C(31)-C(32)-C(33)	-4.3(9)
C(34)-C(31)-C(32)-C(33)	177.6(5)
C(30)-C(31)-C(32)-C(80)	173.6(6)
C(34)-C(31)-C(32)-C(80)	-4.5(9)
C(27)-C(80)-C(32)-C(31)	88.3(10)
C(27)-C(80)-C(32)-C(33)	-93.9(10)
C(29)-C(28)-C(33)-C(32)	-3.7(8)
C(78)-C(28)-C(33)-C(32)	-179.0(5)
C(29)-C(28)-C(33)-C(64)	178.3(5)
C(78)-C(28)-C(33)-C(64)	3.1(8)
C(31)-C(32)-C(33)-C(28)	4.9(9)
C(80)-C(32)-C(33)-C(28)	-173.0(6)
C(31)-C(32)-C(33)-C(64)	-177.2(5)
C(80)-C(32)-C(33)-C(64)	4.9(8)
C(35)-N(7)-C(34)-C(31)	-156.2(16)
C(42)-N(7)-C(34)-C(31)	173.1(9)
C(32)-C(31)-C(34)-N(7)	94.8(8)
C(30)-C(31)-C(34)-N(7)	-83.3(9)
C(50)-N(9)-C(49)-C(29)	-173.6(6)
C(30)-C(29)-C(49)-N(9)	94.5(7)
C(28)-C(29)-C(49)-N(9)	-80.5(7)
C(49)-N(9)-C(50)-C(58)	-169.4(9)
C(49)-N(9)-C(50)-C(51)	177.0(19)
C(65)-N(8)-C(64)-C(33)	-172.7(7)
C(28)-C(33)-C(64)-N(8)	88.7(8)
C(32)-C(33)-C(64)-N(8)	-89.3(8)
C(64)-N(8)-C(65)-C(66)	-171.4(15)
C(64)-N(8)-C(65)-C(72)	-173(3)
C(11)-C(12)-C(39)-C(38)	79(4)
C(13)-C(12)-C(39)-C(38)	-95(4)
C(11)-C(12)-C(39)-C(40)	-103(3)
C(13)-C(12)-C(39)-C(40)	83(4)
C(34)-N(7)-C(35)-C(36)	-174.6(17)
N(7)-C(35)-C(36)-C(37)	-152(3)

N(7)-C(35)-C(36)-C(41)	44(4)
C(41)-C(36)-C(37)-C(38)	-7(4)
C(35)-C(36)-C(37)-C(38)	-171(2)
C(36)-C(37)-C(38)-C(39)	1(4)
C(40)-C(39)-C(38)-C(37)	2(5)
C(12)-C(39)-C(38)-C(37)	180(3)
C(38)-C(39)-C(40)-C(41)	2(7)
C(12)-C(39)-C(40)-C(41)	-177(4)
C(39)-C(40)-C(41)-C(36)	-7(6)
C(37)-C(36)-C(41)-C(40)	10(5)
C(35)-C(36)-C(41)-C(40)	175(3)
C(34)-N(7)-C(42)-C(43)	-176.3(10)
N(7)-C(42)-C(43)-C(44)	-146.0(14)
N(7)-C(42)-C(43)-C(48)	41(2)
C(48)-C(43)-C(44)-C(45)	-5(3)
C(42)-C(43)-C(44)-C(45)	-178.1(15)
C(43)-C(44)-C(45)-C(46)	2(3)
C(44)-C(45)-C(46)-C(47)	1(3)
C(44)-C(45)-C(46)-C(12)	-177.8(15)
C(11)-C(12)-C(46)-C(45)	112.5(18)
C(13)-C(12)-C(46)-C(45)	-73.4(17)
C(11)-C(12)-C(46)-C(47)	-66(2)
C(13)-C(12)-C(46)-C(47)	108(2)
C(45)-C(46)-C(47)-C(48)	-1(4)
C(12)-C(46)-C(47)-C(48)	178(2)
C(44)-C(43)-C(48)-C(47)	5(3)
C(42)-C(43)-C(48)-C(47)	178(2)
C(46)-C(47)-C(48)-C(43)	-2(4)
N(8)-C(65)-C(66)-C(67)	-95.3(19)
N(8)-C(65)-C(66)-C(71)	80(2)
C(71)-C(66)-C(67)-C(68)	3(3)
C(65)-C(66)-C(67)-C(68)	178.4(14)
C(66)-C(67)-C(68)-C(69)	-8(3)
C(67)-C(68)-C(69)-C(70)	10(3)
C(67)-C(68)-C(69)-C(22)	177.5(17)
C(21)-C(22)-C(69)-C(68)	77(3)
C(23)-C(22)-C(69)-C(68)	-106(2)
C(21)-C(22)-C(69)-C(70)	-114.9(19)
C(23)-C(22)-C(69)-C(70)	61(2)
C(68)-C(69)-C(70)-C(71)	-8(3)

C(22)-C(69)-C(70)-C(71)	-176.4(14)
C(69)-C(70)-C(71)-C(66)	4(2)
C(67)-C(66)-C(71)-C(70)	-1(3)
C(65)-C(66)-C(71)-C(70)	-176.7(13)
N(8)-C(65)-C(72)-C(77)	40(6)
N(8)-C(65)-C(72)-C(73)	-147(4)
C(77)-C(72)-C(73)-C(74)	7(6)
C(65)-C(72)-C(73)-C(74)	-167(3)
C(72)-C(73)-C(74)-C(75)	-2(6)
C(21)-C(22)-C(75)-C(74)	114(5)
C(23)-C(22)-C(75)-C(74)	-72(5)
C(21)-C(22)-C(75)-C(76)	-57(6)
C(23)-C(22)-C(75)-C(76)	117(5)
C(73)-C(74)-C(75)-C(22)	-176(4)
C(73)-C(74)-C(75)-C(76)	-3(6)
C(22)-C(75)-C(76)-C(77)	177(4)
C(74)-C(75)-C(76)-C(77)	4(6)
C(75)-C(76)-C(77)-C(72)	0(5)
C(73)-C(72)-C(77)-C(76)	-6(7)
C(65)-C(72)-C(77)-C(76)	167(4)
N(9)-C(50)-C(58)-C(63)	45.8(15)
N(9)-C(50)-C(58)-C(59)	-122.7(16)
C(63)-C(58)-C(59)-C(60)	9(2)
C(50)-C(58)-C(59)-C(60)	177.9(12)
C(58)-C(59)-C(60)-C(61)	-5(3)
C(59)-C(60)-C(61)-C(62)	0(4)
C(59)-C(60)-C(61)-C(17)	177.8(19)
C(16)-C(17)-C(61)-C(62)	-109(2)
C(18)-C(17)-C(61)-C(62)	67(3)
C(16)-C(17)-C(61)-C(60)	73(3)
C(18)-C(17)-C(61)-C(60)	-111(3)
C(60)-C(61)-C(62)-C(63)	2(4)
C(17)-C(61)-C(62)-C(63)	-176.2(17)
C(59)-C(58)-C(63)-C(62)	-8(2)
C(50)-C(58)-C(63)-C(62)	-175.8(13)
C(61)-C(62)-C(63)-C(58)	2(3)
N(9)-C(50)-C(51)-C(52)	-174(4)
N(9)-C(50)-C(51)-C(57)	39(4)
C(57)-C(51)-C(52)-C(53)	-16(5)
C(50)-C(51)-C(52)-C(53)	-163(3)

C(51)-C(52)-C(53)-C(54)	10(6)
C(52)-C(53)-C(54)-C(17)	-176(4)
C(52)-C(53)-C(54)-C(55)	-4(8)
C(16)-C(17)-C(54)-C(53)	102(7)
C(18)-C(17)-C(54)-C(53)	-86(6)
C(16)-C(17)-C(54)-C(55)	-69(7)
C(18)-C(17)-C(54)-C(55)	103(6)
C(57)-C(55)-C(54)-C(53)	7(8)
C(57)-C(55)-C(54)-C(17)	178(5)
C(54)-C(55)-C(57)-C(51)	-14(7)
C(52)-C(51)-C(57)-C(55)	18(6)
C(50)-C(51)-C(57)-C(55)	168(3)

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Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1,z

4.4. X-ray Single-Crystal Structure Analysis of [1-Cu]SbF_6

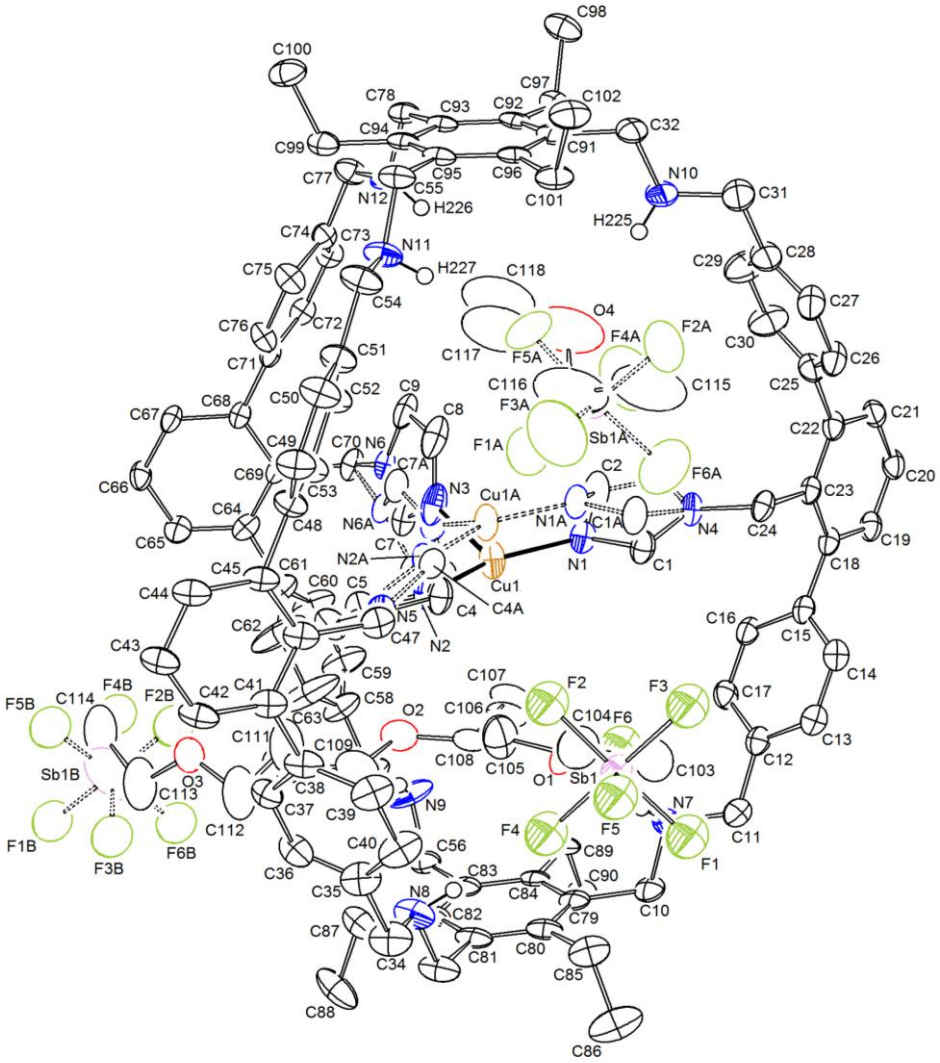

Figure 43. Thermal ellipsoid plot of **[1-Cu]SbF_6** with with the anisotropic displacement parameters drawn at the 50% probability level. The asymmetric unit contains one disordered complex molecule, one disordered SbF_6^- anion and two disordered diethyl ether solvent molecules. The disordered complex molecule was refined with population of 0.744(5) on the main domain using some restraints and constraints (RIGU, EADP). The SbF_6^- anion was refined at three different positions with population of 0.48, 0.37 and 0.15 using PART commands and some restraints and constraints (SADI, RIGU, DFIX, EADP). Both diethyl ether solvent molecules were refined at four different positions with population of 0.62, 0.55, 0.45 and 0.38 using PART commands and some restraints and constraints (SADI, RIGU, DFIX, EADP). The N-H hydrogen atoms were found from the residual density map and isotropically refined using DFIX commands. The reflections -1 0 3 and 0 1 3 were removed from the refinement using OMIT commands.

Table S8. Crystal data and structure refinement for **[1-Cu]SbF_6**.

Identification code	mo_CW_SB_MO_181018_0m_a (sbe1-01-05)	
Empirical formula	$C_{110}H_{128}CuF_6N_{12}O_2Sb$	
Formula weight	1949.53	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 15.9483(12) Å	α = 93.485(2)°
	b = 18.9098(17) Å	β = 110.627(3)°
	c = 20.1274(15) Å	γ = 109.075(2)°
Volume	5261.7(7) $Å^3$	
Z	2	
Density (calculated)	1.231 Mg/m^3	
Absorption coefficient	0.523 mm^{-1}	
F(000)	2044	
Crystal size	0.285 x 0.227 x 0.116 mm^3	
Crystal shape and colour	Block,	clear colourless
Theta range for data collection	2.188 to 25.390°	
Index ranges	-19<=h<=19, -21<=k<=22, -24<=l<=24	
Reflections collected	134868	
Independent reflections	19273 [R(int) = 0.0604]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19273 / 1462 / 1400	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0860,	wR2 = 0.2108
R indices (all data)	R1 = 0.1120,	wR2 = 0.2336
Largest diff. peak and hole	1.915 and -0.804 $eÅ^{-3}$	

Table S9. Bond lengths [Å] and angles [°] for **[1-Cu]SbF_6**.

N(4)-C(1)	1.349(8)
N(4)-C(3)	1.366(6)
N(4)-C(1A)	1.39(2)
N(4)-C(24)	1.471(5)
N(5)-C(4)	1.340(8)
N(5)-C(6)	1.369(6)
N(5)-C(4A)	1.42(2)
N(5)-C(47)	1.477(6)
N(7)-C(11)	1.447(6)
N(7)-C(10)	1.462(6)
N(7)-H(222)	0.891(19)
N(8)-C(34)	1.457(6)
N(8)-C(33)	1.470(6)
N(8)-H(223)	0.89(2)
N(9)-C(57)	1.452(7)
N(9)-C(56)	1.469(6)
N(9)-H(224)	0.89(2)
N(10)-C(31)	1.460(7)
N(10)-C(32)	1.468(6)
N(10)-H(225)	0.90(2)
N(11)-C(54)	1.464(6)
N(11)-C(55)	1.472(6)
N(11)-H(227)	0.90(2)
N(12)-C(77)	1.443(6)
N(12)-C(78)	1.469(5)
N(12)-H(226)	0.89(2)
C(2)-C(3)	1.344(7)
C(2)-N(1A)	1.375(17)
C(2)-N(1)	1.413(8)
C(5)-N(2)	1.331(8)
C(5)-C(6)	1.347(7)
C(5)-N(2A)	1.578(19)
C(10)-C(79)	1.522(7)
C(11)-C(12)	1.513(7)
C(12)-C(17)	1.390(7)
C(12)-C(13)	1.401(6)
C(13)-C(14)	1.376(7)
C(14)-C(15)	1.395(6)
C(15)-C(16)	1.396(6)

C(15)-C(18)	1.486(6)
C(16)-C(17)	1.382(7)
C(18)-C(19)	1.394(6)
C(18)-C(23)	1.414(6)
C(19)-C(20)	1.377(7)
C(20)-C(21)	1.395(6)
C(21)-C(22)	1.388(7)
C(22)-C(23)	1.403(7)
C(22)-C(25)	1.500(6)
C(23)-C(24)	1.505(6)
C(25)-C(30)	1.381(8)
C(25)-C(26)	1.392(7)
C(26)-C(27)	1.394(7)
C(27)-C(28)	1.372(8)
C(28)-C(29)	1.393(8)
C(28)-C(31)	1.515(7)
C(29)-C(30)	1.392(7)
C(32)-C(91)	1.511(7)
C(33)-C(81)	1.525(6)
C(34)-C(35)	1.520(7)
C(35)-C(36)	1.377(8)
C(35)-C(40)	1.399(8)
C(36)-C(37)	1.396(7)
C(37)-C(38)	1.394(7)
C(38)-C(39)	1.410(8)
C(38)-C(41)	1.493(6)
C(39)-C(40)	1.385(7)
C(41)-C(42)	1.392(7)
C(41)-C(46)	1.405(6)
C(42)-C(43)	1.386(7)
C(43)-C(44)	1.377(7)
C(44)-C(45)	1.392(7)
C(45)-C(46)	1.418(6)
C(45)-C(48)	1.491(6)
C(46)-C(47)	1.509(7)
C(48)-C(49)	1.396(6)
C(48)-C(53)	1.402(6)
C(49)-C(50)	1.378(7)
C(50)-C(51)	1.394(6)
C(51)-C(52)	1.390(7)

C(51)-C(54)	1.514(6)
C(52)-C(53)	1.377(7)
C(55)-C(95)	1.519(6)
C(56)-C(83)	1.512(7)
C(57)-C(58)	1.523(7)
C(58)-C(63)	1.363(8)
C(58)-C(59)	1.374(8)
C(59)-C(60)	1.391(7)
C(60)-C(61)	1.374(7)
C(61)-C(62)	1.368(8)
C(61)-C(64)	1.499(6)
C(62)-C(63)	1.390(8)
C(64)-C(65)	1.397(7)
C(64)-C(69)	1.400(7)
C(65)-C(66)	1.381(7)
C(66)-C(67)	1.384(6)
C(67)-C(68)	1.403(6)
C(68)-C(69)	1.408(6)
C(68)-C(71)	1.489(6)
C(69)-C(70)	1.528(6)
C(70)-N(6A)	1.488(15)
C(70)-N(6)	1.496(6)
C(71)-C(72)	1.392(6)
C(71)-C(76)	1.400(6)
C(72)-C(73)	1.396(6)
C(73)-C(74)	1.394(6)
C(74)-C(75)	1.402(6)
C(74)-C(77)	1.502(6)
C(75)-C(76)	1.388(6)
C(78)-C(93)	1.519(6)
C(79)-C(84)	1.397(7)
C(79)-C(80)	1.417(6)
C(80)-C(81)	1.402(7)
C(80)-C(85)	1.525(7)
C(81)-C(82)	1.393(7)
C(82)-C(83)	1.412(6)
C(82)-C(87)	1.515(7)
C(83)-C(84)	1.398(6)
C(84)-C(89)	1.526(6)
C(85)-C(86)	1.532(8)

C(87)-C(88)	1.533(7)
C(89)-C(90)	1.535(6)
C(91)-C(92)	1.405(6)
C(91)-C(96)	1.415(6)
C(92)-C(93)	1.404(6)
C(92)-C(97)	1.516(6)
C(93)-C(94)	1.411(6)
C(94)-C(95)	1.411(6)
C(94)-C(99)	1.509(7)
C(95)-C(96)	1.397(7)
C(96)-C(101)	1.512(6)
C(97)-C(98)	1.528(6)
C(99)-C(100)	1.537(6)
C(101)-C(102)	1.545(6)
O(2)-C(109)	1.418(10)
O(2)-C(108)	1.427(10)
C(107)-C(108)	1.504(12)
C(109)-C(110)	1.499(14)
O(1)-C(104)	1.394(13)
O(1)-C(105)	1.428(13)
C(103)-C(104)	1.487(12)
C(105)-C(106)	1.499(15)
O(3)-C(112)	1.403(13)
O(3)-C(113)	1.426(13)
C(111)-C(112)	1.505(15)
C(113)-C(114)	1.537(12)
Cu(1)-N(2)	1.911(6)
Cu(1)-N(1)	1.916(6)
Cu(1)-N(3)	2.117(10)
N(1)-C(1)	1.330(9)
N(2)-C(4)	1.323(9)
N(3)-C(7)	1.327(11)
N(3)-C(8)	1.357(13)
N(6)-C(7)	1.358(10)
N(6)-C(9)	1.387(9)
C(8)-C(9)	1.346(10)
Cu(1A)-N(1A)	1.888(17)
Cu(1A)-N(2A)	1.894(18)
Cu(1A)-N(3A)	2.12(3)
N(1A)-C(1A)	1.30(3)

N(2A)-C(4A)	1.30(3)
N(3A)-C(7A)	1.31(4)
N(3A)-C(8A)	1.35(3)
N(6A)-C(7A)	1.30(3)
N(6A)-C(9A)	1.39(2)
C(8A)-C(9A)	1.31(3)
F(1B)-Sb(1B)	1.830(12)
Sb(1B)-F(4B)	1.806(12)
Sb(1B)-F(6B)	1.809(12)
Sb(1B)-F(5B)	1.818(12)
Sb(1B)-F(2B)	1.837(12)
Sb(1B)-F(3B)	1.841(12)
Sb(1A)-F(4A)	1.779(16)
Sb(1A)-F(6A)	1.820(14)
Sb(1A)-F(1A)	1.846(11)
Sb(1A)-F(3A)	1.862(15)
Sb(1A)-F(2A)	1.873(10)
Sb(1A)-F(5A)	1.874(10)
F(5)-Sb(1)	1.869(8)
F(6)-Sb(1)	1.863(9)
Sb(1)-F(2)	1.856(8)
Sb(1)-F(4)	1.858(8)
Sb(1)-F(3)	1.863(8)
Sb(1)-F(1)	1.883(8)
C(118)-C(117)	1.459(14)
C(117)-O(4)	1.455(14)
C(116)-O(4)	1.410(14)
C(116)-C(115)	1.501(15)

Table S10. Torsion angles [°] for **[1-Cu]SbF_6**.

C(1)-N(4)-C(3)	108.5(4)
C(3)-N(4)-C(1A)	100.8(9)
C(1)-N(4)-C(24)	123.5(4)
C(3)-N(4)-C(24)	128.1(4)
C(1A)-N(4)-C(24)	124.7(9)
C(4)-N(5)-C(6)	104.7(5)
C(6)-N(5)-C(4A)	110.4(9)
C(4)-N(5)-C(47)	124.6(5)
C(6)-N(5)-C(47)	130.1(4)

C(4A)-N(5)-C(47)	116.6(10)
C(11)-N(7)-C(10)	112.4(4)
C(11)-N(7)-H(222)	111(3)
C(10)-N(7)-H(222)	110(3)
C(34)-N(8)-C(33)	113.0(4)
C(34)-N(8)-H(223)	108(4)
C(33)-N(8)-H(223)	101(4)
C(57)-N(9)-C(56)	111.5(4)
C(57)-N(9)-H(224)	121(6)
C(56)-N(9)-H(224)	109(6)
C(31)-N(10)-C(32)	112.7(4)
C(31)-N(10)-H(225)	116(5)
C(32)-N(10)-H(225)	111(5)
C(54)-N(11)-C(55)	110.8(4)
C(54)-N(11)-H(227)	109(4)
C(55)-N(11)-H(227)	107(4)
C(77)-N(12)-C(78)	113.7(4)
C(77)-N(12)-H(226)	118(4)
C(78)-N(12)-H(226)	114(4)
C(3)-C(2)-N(1A)	109.0(8)
C(3)-C(2)-N(1)	109.0(4)
C(2)-C(3)-N(4)	106.5(4)
N(2)-C(5)-C(6)	110.4(5)
C(6)-C(5)-N(2A)	104.3(7)
C(5)-C(6)-N(5)	106.9(4)
N(7)-C(10)-C(79)	110.6(4)
N(7)-C(11)-C(12)	112.9(4)
C(17)-C(12)-C(13)	118.2(4)
C(17)-C(12)-C(11)	121.7(4)
C(13)-C(12)-C(11)	120.0(4)
C(14)-C(13)-C(12)	120.7(4)
C(13)-C(14)-C(15)	121.3(4)
C(14)-C(15)-C(16)	118.0(4)
C(14)-C(15)-C(18)	121.0(4)
C(16)-C(15)-C(18)	121.0(4)
C(17)-C(16)-C(15)	120.9(4)
C(16)-C(17)-C(12)	121.0(4)
C(19)-C(18)-C(23)	119.2(4)
C(19)-C(18)-C(15)	119.7(4)
C(23)-C(18)-C(15)	121.1(4)

C(20)-C(19)-C(18)	121.0(4)
C(19)-C(20)-C(21)	119.8(4)
C(22)-C(21)-C(20)	120.6(4)
C(21)-C(22)-C(23)	119.8(4)
C(21)-C(22)-C(25)	118.9(4)
C(23)-C(22)-C(25)	121.3(4)
C(22)-C(23)-C(18)	119.5(4)
C(22)-C(23)-C(24)	121.1(4)
C(18)-C(23)-C(24)	119.3(4)
N(4)-C(24)-C(23)	112.1(3)
C(30)-C(25)-C(26)	118.2(4)
C(30)-C(25)-C(22)	119.6(4)
C(26)-C(25)-C(22)	122.2(4)
C(25)-C(26)-C(27)	120.8(5)
C(28)-C(27)-C(26)	120.8(5)
C(27)-C(28)-C(29)	118.7(5)
C(27)-C(28)-C(31)	121.4(5)
C(29)-C(28)-C(31)	119.9(5)
C(30)-C(29)-C(28)	120.6(6)
C(25)-C(30)-C(29)	120.9(5)
N(10)-C(31)-C(28)	110.8(4)
N(10)-C(32)-C(91)	110.8(4)
N(8)-C(33)-C(81)	109.6(4)
N(8)-C(34)-C(35)	110.4(4)
C(36)-C(35)-C(40)	119.3(5)
C(36)-C(35)-C(34)	120.2(5)
C(40)-C(35)-C(34)	120.4(5)
C(35)-C(36)-C(37)	121.1(5)
C(38)-C(37)-C(36)	120.2(5)
C(37)-C(38)-C(39)	118.4(4)
C(37)-C(38)-C(41)	118.4(5)
C(39)-C(38)-C(41)	123.2(4)
C(40)-C(39)-C(38)	120.9(5)
C(39)-C(40)-C(35)	120.1(5)
C(42)-C(41)-C(46)	119.2(4)
C(42)-C(41)-C(38)	117.8(4)
C(46)-C(41)-C(38)	123.0(4)
C(43)-C(42)-C(41)	121.6(4)
C(44)-C(43)-C(42)	119.5(5)
C(43)-C(44)-C(45)	120.9(4)

C(44)-C(45)-C(46)	119.7(4)
C(44)-C(45)-C(48)	118.4(4)
C(46)-C(45)-C(48)	121.9(4)
C(41)-C(46)-C(45)	119.1(4)
C(41)-C(46)-C(47)	121.2(4)
C(45)-C(46)-C(47)	119.7(4)
N(5)-C(47)-C(46)	113.4(4)
C(49)-C(48)-C(53)	117.5(4)
C(49)-C(48)-C(45)	120.8(4)
C(53)-C(48)-C(45)	121.6(4)
C(50)-C(49)-C(48)	121.1(4)
C(49)-C(50)-C(51)	120.9(4)
C(52)-C(51)-C(50)	118.5(4)
C(52)-C(51)-C(54)	122.3(4)
C(50)-C(51)-C(54)	119.1(4)
C(53)-C(52)-C(51)	120.5(4)
C(52)-C(53)-C(48)	121.6(4)
N(11)-C(54)-C(51)	113.8(4)
N(11)-C(55)-C(95)	110.9(4)
N(9)-C(56)-C(83)	111.6(4)
N(9)-C(57)-C(58)	111.9(5)
C(63)-C(58)-C(59)	117.4(5)
C(63)-C(58)-C(57)	120.2(5)
C(59)-C(58)-C(57)	122.3(5)
C(58)-C(59)-C(60)	121.1(5)
C(61)-C(60)-C(59)	121.4(5)
C(62)-C(61)-C(60)	117.1(5)
C(62)-C(61)-C(64)	118.3(4)
C(60)-C(61)-C(64)	124.5(4)
C(61)-C(62)-C(63)	121.5(5)
C(58)-C(63)-C(62)	121.5(6)
C(65)-C(64)-C(69)	119.8(4)
C(65)-C(64)-C(61)	117.3(4)
C(69)-C(64)-C(61)	122.7(4)
C(66)-C(65)-C(64)	121.0(4)
C(65)-C(66)-C(67)	119.5(4)
C(66)-C(67)-C(68)	120.9(4)
C(67)-C(68)-C(69)	119.4(4)
C(67)-C(68)-C(71)	118.2(4)
C(69)-C(68)-C(71)	122.2(4)

C(64)-C(69)-C(68)	119.3(4)
C(64)-C(69)-C(70)	121.3(4)
C(68)-C(69)-C(70)	119.4(4)
N(6A)-C(70)-C(69)	110.4(6)
N(6)-C(70)-C(69)	114.5(4)
C(72)-C(71)-C(76)	118.1(4)
C(72)-C(71)-C(68)	124.2(4)
C(76)-C(71)-C(68)	117.6(4)
C(71)-C(72)-C(73)	120.6(4)
C(74)-C(73)-C(72)	121.4(4)
C(73)-C(74)-C(75)	118.0(4)
C(73)-C(74)-C(77)	122.4(4)
C(75)-C(74)-C(77)	119.5(4)
C(76)-C(75)-C(74)	120.5(4)
C(75)-C(76)-C(71)	121.4(4)
N(12)-C(77)-C(74)	112.4(4)
N(12)-C(78)-C(93)	110.2(3)
C(84)-C(79)-C(80)	120.2(4)
C(84)-C(79)-C(10)	119.9(4)
C(80)-C(79)-C(10)	119.7(4)
C(81)-C(80)-C(79)	118.9(4)
C(81)-C(80)-C(85)	121.2(4)
C(79)-C(80)-C(85)	119.9(5)
C(82)-C(81)-C(80)	121.0(4)
C(82)-C(81)-C(33)	119.8(5)
C(80)-C(81)-C(33)	119.0(5)
C(81)-C(82)-C(83)	119.6(4)
C(81)-C(82)-C(87)	120.4(4)
C(83)-C(82)-C(87)	120.0(4)
C(84)-C(83)-C(82)	119.9(4)
C(84)-C(83)-C(56)	119.9(4)
C(82)-C(83)-C(56)	120.1(4)
C(79)-C(84)-C(83)	120.2(4)
C(79)-C(84)-C(89)	120.2(4)
C(83)-C(84)-C(89)	119.6(4)
C(80)-C(85)-C(86)	113.4(4)
C(82)-C(87)-C(88)	112.2(5)
C(84)-C(89)-C(90)	113.6(3)
C(92)-C(91)-C(96)	120.3(4)
C(92)-C(91)-C(32)	119.5(4)

C(96)-C(91)-C(32)	120.2(4)
C(93)-C(92)-C(91)	119.5(4)
C(93)-C(92)-C(97)	120.3(4)
C(91)-C(92)-C(97)	120.2(4)
C(92)-C(93)-C(94)	120.8(4)
C(92)-C(93)-C(78)	120.7(4)
C(94)-C(93)-C(78)	118.4(4)
C(93)-C(94)-C(95)	119.0(4)
C(93)-C(94)-C(99)	120.6(4)
C(95)-C(94)-C(99)	120.5(4)
C(96)-C(95)-C(94)	120.8(4)
C(96)-C(95)-C(55)	119.1(4)
C(94)-C(95)-C(55)	120.1(4)
C(95)-C(96)-C(91)	119.6(4)
C(95)-C(96)-C(101)	120.0(4)
C(91)-C(96)-C(101)	120.4(4)
C(92)-C(97)-C(98)	113.1(4)
C(94)-C(99)-C(100)	113.1(4)
C(96)-C(101)-C(102)	114.0(4)
C(109)-O(2)-C(108)	114.9(8)
O(2)-C(108)-C(107)	112.7(11)
O(2)-C(109)-C(110)	110.8(10)
C(104)-O(1)-C(105)	116.5(13)
O(1)-C(104)-C(103)	107.8(12)
O(1)-C(105)-C(106)	108.5(19)
C(112)-O(3)-C(113)	122.1(12)
O(3)-C(112)-C(111)	108.0(15)
O(3)-C(113)-C(114)	110.9(13)
N(2)-Cu(1)-N(1)	150.7(3)
N(2)-Cu(1)-N(3)	106.2(4)
N(1)-Cu(1)-N(3)	101.4(4)
C(1)-N(1)-C(2)	105.3(5)
C(1)-N(1)-Cu(1)	129.6(5)
C(2)-N(1)-Cu(1)	123.5(4)
C(4)-N(2)-C(5)	105.1(6)
C(4)-N(2)-Cu(1)	124.5(5)
C(5)-N(2)-Cu(1)	129.5(4)
C(7)-N(3)-C(8)	105.7(8)
C(7)-N(3)-Cu(1)	134.4(8)
C(8)-N(3)-Cu(1)	119.0(6)

C(7)-N(6)-C(9)	107.5(6)
C(7)-N(6)-C(70)	123.8(6)
C(9)-N(6)-C(70)	128.7(5)
N(1)-C(1)-N(4)	110.3(6)
N(2)-C(4)-N(5)	112.4(6)
N(3)-C(7)-N(6)	110.3(8)
C(9)-C(8)-N(3)	111.7(7)
C(8)-C(9)-N(6)	104.8(7)
N(1A)-Cu(1A)-N(2A)	149.2(8)
N(1A)-Cu(1A)-N(3A)	103.4(11)
N(2A)-Cu(1A)-N(3A)	105.2(11)
C(1A)-N(1A)-C(2)	101.7(15)
C(1A)-N(1A)-Cu(1A)	129.0(15)
C(2)-N(1A)-Cu(1A)	125.7(11)
C(4A)-N(2A)-C(5)	106.3(15)
C(4A)-N(2A)-Cu(1A)	127.2(15)
C(5)-N(2A)-Cu(1A)	125.2(11)
C(8A)-N(3A)-Cu(1A)	118.2(19)
C(7A)-N(6A)-C(9A)	103.6(17)
C(7A)-N(6A)-C(70)	119.3(17)
C(9A)-N(6A)-C(70)	135.8(14)
N(1A)-C(1A)-N(4)	115.0(17)
N(2A)-C(4A)-N(5)	107.6(18)
C(8A)-C(9A)-N(6A)	107.0(17)
F(4B)-Sb(1B)-F(6B)	93.3(7)
F(4B)-Sb(1B)-F(5B)	92.4(7)
F(6B)-Sb(1B)-F(5B)	173.6(10)
F(4B)-Sb(1B)-F(1B)	91.1(6)
F(6B)-Sb(1B)-F(1B)	87.9(12)
F(5B)-Sb(1B)-F(1B)	94.8(12)
F(4B)-Sb(1B)-F(2B)	89.6(6)
F(6B)-Sb(1B)-F(2B)	92.7(12)
F(5B)-Sb(1B)-F(2B)	84.6(12)
F(1B)-Sb(1B)-F(2B)	179.1(10)
F(4B)-Sb(1B)-F(3B)	178.0(10)
F(6B)-Sb(1B)-F(3B)	85.1(12)
F(5B)-Sb(1B)-F(3B)	89.1(11)
F(1B)-Sb(1B)-F(3B)	90.1(6)
F(2B)-Sb(1B)-F(3B)	89.3(6)
F(4A)-Sb(1A)-F(6A)	76.5(10)

F(4A)-Sb(1A)-F(1A)	85.2(7)
F(6A)-Sb(1A)-F(1A)	93.8(6)
F(4A)-Sb(1A)-F(3A)	177.4(8)
F(6A)-Sb(1A)-F(3A)	102.8(9)
F(1A)-Sb(1A)-F(3A)	92.3(7)
F(4A)-Sb(1A)-F(2A)	90.9(6)
F(6A)-Sb(1A)-F(2A)	88.8(6)
F(1A)-Sb(1A)-F(2A)	174.7(6)
F(3A)-Sb(1A)-F(2A)	91.7(6)
F(4A)-Sb(1A)-F(5A)	93.9(8)
F(6A)-Sb(1A)-F(5A)	170.4(9)
F(1A)-Sb(1A)-F(5A)	86.2(5)
F(3A)-Sb(1A)-F(5A)	86.7(8)
F(2A)-Sb(1A)-F(5A)	90.5(5)
F(2)-Sb(1)-F(4)	89.2(4)
F(2)-Sb(1)-F(3)	90.6(4)
F(4)-Sb(1)-F(3)	179.7(4)
F(2)-Sb(1)-F(6)	91.3(4)
F(4)-Sb(1)-F(6)	89.0(4)
F(3)-Sb(1)-F(6)	90.8(4)
F(2)-Sb(1)-F(5)	91.1(4)
F(4)-Sb(1)-F(5)	91.0(4)
F(3)-Sb(1)-F(5)	89.2(4)
F(6)-Sb(1)-F(5)	177.6(4)
F(2)-Sb(1)-F(1)	179.2(4)
F(4)-Sb(1)-F(1)	91.6(4)
F(3)-Sb(1)-F(1)	88.6(4)
F(6)-Sb(1)-F(1)	88.6(4)
F(5)-Sb(1)-F(1)	89.0(4)
O(4)-C(117)-C(118)	115.4(16)
O(4)-C(116)-C(115)	97.6(15)
C(116)-O(4)-C(117)	107.9(14)

Table S11. Torsion angles [°] for **[1-Cu]SbF$_6$**.

N(1A)-C(2)-C(3)-N(4)	27.7(11)
N(1)-C(2)-C(3)-N(4)	-5.9(6)
C(1)-N(4)-C(3)-C(2)	6.7(6)
C(1A)-N(4)-C(3)-C(2)	-22.6(12)
C(24)-N(4)-C(3)-C(2)	-174.9(5)
N(2)-C(5)-C(6)-N(5)	6.6(7)
N(2A)-C(5)-C(6)-N(5)	-19.6(9)
C(4)-N(5)-C(6)-C(5)	-6.5(6)
C(4A)-N(5)-C(6)-C(5)	22.3(11)
C(47)-N(5)-C(6)-C(5)	-177.8(5)
C(11)-N(7)-C(10)-C(79)	165.6(4)
C(10)-N(7)-C(11)-C(12)	166.5(4)
N(7)-C(11)-C(12)-C(17)	-32.2(6)
N(7)-C(11)-C(12)-C(13)	150.8(4)
C(17)-C(12)-C(13)-C(14)	-1.2(7)
C(11)-C(12)-C(13)-C(14)	175.9(4)
C(12)-C(13)-C(14)-C(15)	-0.4(7)
C(13)-C(14)-C(15)-C(16)	1.6(6)
C(13)-C(14)-C(15)-C(18)	-177.8(4)
C(14)-C(15)-C(16)-C(17)	-1.3(6)
C(18)-C(15)-C(16)-C(17)	178.1(4)
C(15)-C(16)-C(17)-C(12)	-0.3(7)
C(13)-C(12)-C(17)-C(16)	1.5(7)
C(11)-C(12)-C(17)-C(16)	-175.5(4)
C(14)-C(15)-C(18)-C(19)	96.5(5)
C(16)-C(15)-C(18)-C(19)	-82.9(5)
C(14)-C(15)-C(18)-C(23)	-84.3(5)
C(16)-C(15)-C(18)-C(23)	96.3(5)
C(23)-C(18)-C(19)-C(20)	-0.5(7)
C(15)-C(18)-C(19)-C(20)	178.6(4)
C(18)-C(19)-C(20)-C(21)	-1.2(7)
C(19)-C(20)-C(21)-C(22)	2.1(7)
C(20)-C(21)-C(22)-C(23)	-1.0(7)
C(20)-C(21)-C(22)-C(25)	-178.1(4)
C(21)-C(22)-C(23)-C(18)	-0.8(6)
C(25)-C(22)-C(23)-C(18)	176.2(4)
C(21)-C(22)-C(23)-C(24)	-178.4(4)
C(25)-C(22)-C(23)-C(24)	-1.4(6)
C(19)-C(18)-C(23)-C(22)	1.5(6)

C(15)-C(18)-C(23)-C(22)	-177.6(4)
C(19)-C(18)-C(23)-C(24)	179.2(4)
C(15)-C(18)-C(23)-C(24)	0.1(6)
C(1)-N(4)-C(24)-C(23)	152.2(5)
C(3)-N(4)-C(24)-C(23)	-25.9(6)
C(1A)-N(4)-C(24)-C(23)	-172.2(14)
C(22)-C(23)-C(24)-N(4)	97.9(5)
C(18)-C(23)-C(24)-N(4)	-79.8(5)
C(21)-C(22)-C(25)-C(30)	66.9(6)
C(23)-C(22)-C(25)-C(30)	-110.1(6)
C(21)-C(22)-C(25)-C(26)	-112.4(6)
C(23)-C(22)-C(25)-C(26)	70.6(6)
C(30)-C(25)-C(26)-C(27)	1.5(8)
C(22)-C(25)-C(26)-C(27)	-179.2(5)
C(25)-C(26)-C(27)-C(28)	0.1(8)
C(26)-C(27)-C(28)-C(29)	-0.5(8)
C(26)-C(27)-C(28)-C(31)	178.2(5)
C(27)-C(28)-C(29)-C(30)	-0.6(9)
C(31)-C(28)-C(29)-C(30)	-179.4(6)
C(26)-C(25)-C(30)-C(29)	-2.6(9)
C(22)-C(25)-C(30)-C(29)	178.1(5)
C(28)-C(29)-C(30)-C(25)	2.1(10)
C(32)-N(10)-C(31)-C(28)	-173.9(5)
C(27)-C(28)-C(31)-N(10)	-125.7(6)
C(29)-C(28)-C(31)-N(10)	53.0(7)
C(31)-N(10)-C(32)-C(91)	-175.0(4)
C(34)-N(8)-C(33)-C(81)	-169.2(5)
C(33)-N(8)-C(34)-C(35)	-176.8(5)
N(8)-C(34)-C(35)-C(36)	72.6(7)
N(8)-C(34)-C(35)-C(40)	-104.5(6)
C(40)-C(35)-C(36)-C(37)	-2.0(8)
C(34)-C(35)-C(36)-C(37)	-179.1(4)
C(35)-C(36)-C(37)-C(38)	0.0(7)
C(36)-C(37)-C(38)-C(39)	1.6(7)
C(36)-C(37)-C(38)-C(41)	-177.0(4)
C(37)-C(38)-C(39)-C(40)	-1.1(8)
C(41)-C(38)-C(39)-C(40)	177.4(5)
C(38)-C(39)-C(40)-C(35)	-0.9(8)
C(36)-C(35)-C(40)-C(39)	2.5(8)
C(34)-C(35)-C(40)-C(39)	179.6(5)

C(37)-C(38)-C(41)-C(42)	56.4(6)
C(39)-C(38)-C(41)-C(42)	-122.1(5)
C(37)-C(38)-C(41)-C(46)	-122.1(5)
C(39)-C(38)-C(41)-C(46)	59.4(6)
C(46)-C(41)-C(42)-C(43)	-0.4(7)
C(38)-C(41)-C(42)-C(43)	-179.0(4)
C(41)-C(42)-C(43)-C(44)	1.2(7)
C(42)-C(43)-C(44)-C(45)	0.7(7)
C(43)-C(44)-C(45)-C(46)	-3.3(7)
C(43)-C(44)-C(45)-C(48)	176.4(4)
C(42)-C(41)-C(46)-C(45)	-2.2(6)
C(38)-C(41)-C(46)-C(45)	176.3(4)
C(42)-C(41)-C(46)-C(47)	175.4(4)
C(38)-C(41)-C(46)-C(47)	-6.1(6)
C(44)-C(45)-C(46)-C(41)	4.0(6)
C(48)-C(45)-C(46)-C(41)	-175.7(4)
C(44)-C(45)-C(46)-C(47)	-173.6(4)
C(48)-C(45)-C(46)-C(47)	6.6(6)
C(4)-N(5)-C(47)-C(46)	176.3(6)
C(6)-N(5)-C(47)-C(46)	-13.9(7)
C(4A)-N(5)-C(47)-C(46)	144.9(10)
C(41)-C(46)-C(47)-N(5)	81.0(5)
C(45)-C(46)-C(47)-N(5)	-101.4(5)
C(44)-C(45)-C(48)-C(49)	53.7(6)
C(46)-C(45)-C(48)-C(49)	-126.6(5)
C(44)-C(45)-C(48)-C(53)	-122.8(5)
C(46)-C(45)-C(48)-C(53)	56.9(7)
C(53)-C(48)-C(49)-C(50)	-0.2(8)
C(45)-C(48)-C(49)-C(50)	-176.8(5)
C(48)-C(49)-C(50)-C(51)	0.6(8)
C(49)-C(50)-C(51)-C(52)	-0.3(8)
C(49)-C(50)-C(51)-C(54)	177.6(5)
C(50)-C(51)-C(52)-C(53)	-0.4(8)
C(54)-C(51)-C(52)-C(53)	-178.3(5)
C(51)-C(52)-C(53)-C(48)	0.8(8)
C(49)-C(48)-C(53)-C(52)	-0.5(8)
C(45)-C(48)-C(53)-C(52)	176.1(5)
C(55)-N(11)-C(54)-C(51)	174.1(5)
C(52)-C(51)-C(54)-N(11)	-6.1(8)
C(50)-C(51)-C(54)-N(11)	176.1(5)

C(54)-N(11)-C(55)-C(95)	163.0(4)
C(57)-N(9)-C(56)-C(83)	-177.8(5)
C(56)-N(9)-C(57)-C(58)	167.4(5)
N(9)-C(57)-C(58)-C(63)	-51.2(10)
N(9)-C(57)-C(58)-C(59)	132.8(7)
C(63)-C(58)-C(59)-C(60)	-1.0(11)
C(57)-C(58)-C(59)-C(60)	175.1(6)
C(58)-C(59)-C(60)-C(61)	2.6(11)
C(59)-C(60)-C(61)-C(62)	-2.7(10)
C(59)-C(60)-C(61)-C(64)	-178.4(6)
C(60)-C(61)-C(62)-C(63)	1.4(13)
C(64)-C(61)-C(62)-C(63)	177.4(8)
C(59)-C(58)-C(63)-C(62)	-0.4(14)
C(57)-C(58)-C(63)-C(62)	-176.6(9)
C(61)-C(62)-C(63)-C(58)	0.2(16)
C(62)-C(61)-C(64)-C(65)	-69.1(7)
C(60)-C(61)-C(64)-C(65)	106.5(6)
C(62)-C(61)-C(64)-C(69)	105.7(7)
C(60)-C(61)-C(64)-C(69)	-78.6(7)
C(69)-C(64)-C(65)-C(66)	-0.3(7)
C(61)-C(64)-C(65)-C(66)	174.7(4)
C(64)-C(65)-C(66)-C(67)	-2.5(7)
C(65)-C(66)-C(67)-C(68)	2.2(7)
C(66)-C(67)-C(68)-C(69)	0.8(6)
C(66)-C(67)-C(68)-C(71)	-174.6(4)
C(65)-C(64)-C(69)-C(68)	3.3(6)
C(61)-C(64)-C(69)-C(68)	-171.4(4)
C(65)-C(64)-C(69)-C(70)	-177.7(4)
C(61)-C(64)-C(69)-C(70)	7.6(6)
C(67)-C(68)-C(69)-C(64)	-3.6(6)
C(71)-C(68)-C(69)-C(64)	171.7(4)
C(67)-C(68)-C(69)-C(70)	177.4(4)
C(71)-C(68)-C(69)-C(70)	-7.3(6)
C(64)-C(69)-C(70)-N(6A)	-61.9(8)
C(68)-C(69)-C(70)-N(6A)	117.1(8)
C(64)-C(69)-C(70)-N(6)	-102.5(5)
C(68)-C(69)-C(70)-N(6)	76.4(5)
C(67)-C(68)-C(71)-C(72)	-108.7(5)
C(69)-C(68)-C(71)-C(72)	76.0(6)
C(67)-C(68)-C(71)-C(76)	68.9(5)

C(69)-C(68)-C(71)-C(76)	-106.4(5)
C(76)-C(71)-C(72)-C(73)	2.1(6)
C(68)-C(71)-C(72)-C(73)	179.6(4)
C(71)-C(72)-C(73)-C(74)	-1.9(7)
C(72)-C(73)-C(74)-C(75)	0.7(7)
C(72)-C(73)-C(74)-C(77)	-176.6(4)
C(73)-C(74)-C(75)-C(76)	0.4(7)
C(77)-C(74)-C(75)-C(76)	177.7(4)
C(74)-C(75)-C(76)-C(71)	-0.2(7)
C(72)-C(71)-C(76)-C(75)	-1.0(7)
C(68)-C(71)-C(76)-C(75)	-178.8(4)
C(78)-N(12)-C(77)-C(74)	-169.3(4)
C(73)-C(74)-C(77)-N(12)	-134.9(5)
C(75)-C(74)-C(77)-N(12)	47.8(6)
C(77)-N(12)-C(78)-C(93)	177.7(4)
N(7)-C(10)-C(79)-C(84)	78.8(5)
N(7)-C(10)-C(79)-C(80)	-96.8(5)
C(84)-C(79)-C(80)-C(81)	3.1(6)
C(10)-C(79)-C(80)-C(81)	178.7(4)
C(84)-C(79)-C(80)-C(85)	-177.2(4)
C(10)-C(79)-C(80)-C(85)	-1.6(6)
C(79)-C(80)-C(81)-C(82)	-2.8(6)
C(85)-C(80)-C(81)-C(82)	177.5(4)
C(79)-C(80)-C(81)-C(33)	-178.8(4)
C(85)-C(80)-C(81)-C(33)	1.5(6)
N(8)-C(33)-C(81)-C(82)	-81.3(6)
N(8)-C(33)-C(81)-C(80)	94.7(6)
C(80)-C(81)-C(82)-C(83)	2.0(6)
C(33)-C(81)-C(82)-C(83)	177.9(4)
C(80)-C(81)-C(82)-C(87)	-177.8(4)
C(33)-C(81)-C(82)-C(87)	-1.9(6)
C(81)-C(82)-C(83)-C(84)	-1.3(6)
C(87)-C(82)-C(83)-C(84)	178.5(4)
C(81)-C(82)-C(83)-C(56)	-178.7(4)
C(87)-C(82)-C(83)-C(56)	1.1(6)
N(9)-C(56)-C(83)-C(84)	-84.0(5)
N(9)-C(56)-C(83)-C(82)	93.4(5)
C(80)-C(79)-C(84)-C(83)	-2.5(6)
C(10)-C(79)-C(84)-C(83)	-178.1(4)
C(80)-C(79)-C(84)-C(89)	177.0(4)

C(10)-C(79)-C(84)-C(89)	1.4(6)
C(82)-C(83)-C(84)-C(79)	1.6(6)
C(56)-C(83)-C(84)-C(79)	179.0(4)
C(82)-C(83)-C(84)-C(89)	-177.9(4)
C(56)-C(83)-C(84)-C(89)	-0.5(6)
C(81)-C(80)-C(85)-C(86)	90.8(6)
C(79)-C(80)-C(85)-C(86)	-88.9(6)
C(81)-C(82)-C(87)-C(88)	-88.9(5)
C(83)-C(82)-C(87)-C(88)	91.3(6)
C(79)-C(84)-C(89)-C(90)	92.9(5)
C(83)-C(84)-C(89)-C(90)	-87.6(5)
N(10)-C(32)-C(91)-C(92)	-80.0(5)
N(10)-C(32)-C(91)-C(96)	97.7(5)
C(96)-C(91)-C(92)-C(93)	2.7(6)
C(32)-C(91)-C(92)-C(93)	-179.6(4)
C(96)-C(91)-C(92)-C(97)	-176.4(4)
C(32)-C(91)-C(92)-C(97)	1.3(6)
C(91)-C(92)-C(93)-C(94)	-0.4(6)
C(97)-C(92)-C(93)-C(94)	178.7(4)
C(91)-C(92)-C(93)-C(78)	-176.8(4)
C(97)-C(92)-C(93)-C(78)	2.2(6)
N(12)-C(78)-C(93)-C(92)	97.0(5)
N(12)-C(78)-C(93)-C(94)	-79.6(5)
C(92)-C(93)-C(94)-C(95)	-0.5(6)
C(78)-C(93)-C(94)-C(95)	176.1(4)
C(92)-C(93)-C(94)-C(99)	179.4(4)
C(78)-C(93)-C(94)-C(99)	-4.1(5)
C(93)-C(94)-C(95)-C(96)	-1.0(6)
C(99)-C(94)-C(95)-C(96)	179.1(4)
C(93)-C(94)-C(95)-C(55)	-179.2(4)
C(99)-C(94)-C(95)-C(55)	0.9(6)
N(11)-C(55)-C(95)-C(96)	-91.4(5)
N(11)-C(55)-C(95)-C(94)	86.9(5)
C(94)-C(95)-C(96)-C(91)	3.3(6)
C(55)-C(95)-C(96)-C(91)	-178.5(4)
C(94)-C(95)-C(96)-C(101)	-175.3(4)
C(55)-C(95)-C(96)-C(101)	3.0(6)
C(92)-C(91)-C(96)-C(95)	-4.1(6)
C(32)-C(91)-C(96)-C(95)	178.2(4)
C(92)-C(91)-C(96)-C(101)	174.4(4)

C(32)-C(91)-C(96)-C(101)	-3.3(6)
C(93)-C(92)-C(97)-C(98)	86.1(5)
C(91)-C(92)-C(97)-C(98)	-94.8(5)
C(93)-C(94)-C(99)-C(100)	-88.8(5)
C(95)-C(94)-C(99)-C(100)	91.0(5)
C(95)-C(96)-C(101)-C(102)	-89.7(5)
C(91)-C(96)-C(101)-C(102)	91.8(5)
C(109)-O(2)-C(108)-C(107)	-171.0(11)
C(108)-O(2)-C(109)-C(110)	-175.8(9)
C(105)-O(1)-C(104)-C(103)	-174.0(15)
C(104)-O(1)-C(105)-C(106)	153(2)
C(113)-O(3)-C(112)-C(111)	176.3(17)
C(112)-O(3)-C(113)-C(114)	-171.2(13)
C(3)-C(2)-N(1)-C(1)	2.9(7)
C(3)-C(2)-N(1)-Cu(1)	169.6(4)
C(6)-C(5)-N(2)-C(4)	-3.8(8)
C(6)-C(5)-N(2)-Cu(1)	-173.3(5)
C(69)-C(70)-N(6)-C(7)	87.9(6)
C(69)-C(70)-N(6)-C(9)	-95.5(7)
C(2)-N(1)-C(1)-N(4)	1.4(8)
Cu(1)-N(1)-C(1)-N(4)	-164.2(5)
C(3)-N(4)-C(1)-N(1)	-5.1(8)
C(24)-N(4)-C(1)-N(1)	176.5(5)
C(5)-N(2)-C(4)-N(5)	-0.5(9)
Cu(1)-N(2)-C(4)-N(5)	169.6(5)
C(6)-N(5)-C(4)-N(2)	4.4(8)
C(47)-N(5)-C(4)-N(2)	176.4(6)
C(8)-N(3)-C(7)-N(6)	-1.0(10)
Cu(1)-N(3)-C(7)-N(6)	-169.1(8)
C(9)-N(6)-C(7)-N(3)	1.5(8)
C(70)-N(6)-C(7)-N(3)	178.7(7)
C(7)-N(3)-C(8)-C(9)	0.1(11)
Cu(1)-N(3)-C(8)-C(9)	170.4(6)
N(3)-C(8)-C(9)-N(6)	0.8(9)
C(7)-N(6)-C(9)-C(8)	-1.3(7)
C(70)-N(6)-C(9)-C(8)	-178.4(5)
C(3)-C(2)-N(1A)-C(1A)	-19.7(19)
C(3)-C(2)-N(1A)-Cu(1A)	-179.9(11)
N(2A)-Cu(1A)-N(1A)-C(1A)	4(3)
N(3A)-Cu(1A)-N(1A)-C(1A)	-154(2)

N(2A)-Cu(1A)-N(1A)-C(2)	158.4(14)
N(3A)-Cu(1A)-N(1A)-C(2)	0.4(18)
C(6)-C(5)-N(2A)-C(4A)	11.2(17)
C(6)-C(5)-N(2A)-Cu(1A)	178.8(11)
N(1A)-Cu(1A)-N(2A)-C(4A)	29(3)
N(3A)-Cu(1A)-N(2A)-C(4A)	-173(2)
N(1A)-Cu(1A)-N(2A)-C(5)	-135.9(15)
N(3A)-Cu(1A)-N(2A)-C(5)	21.8(16)
C(69)-C(70)-N(6A)-C(7A)	-92.6(15)
C(69)-C(70)-N(6A)-C(9A)	102.6(18)
C(2)-N(1A)-C(1A)-N(4)	5(2)
Cu(1A)-N(1A)-C(1A)-N(4)	164.1(14)
C(3)-N(4)-C(1A)-N(1A)	11(2)
C(24)-N(4)-C(1A)-N(1A)	164.7(15)
C(5)-N(2A)-C(4A)-N(5)	2(2)
Cu(1A)-N(2A)-C(4A)-N(5)	-165.4(13)
C(6)-N(5)-C(4A)-N(2A)	-14.6(19)
C(47)-N(5)-C(4A)-N(2A)	-177.5(12)
C(9A)-N(6A)-C(7A)-N(3A)	-1(3)
C(70)-N(6A)-C(7A)-N(3A)	-170(2)
C(8A)-N(3A)-C(7A)-N(6A)	2(3)
Cu(1A)-N(3A)-C(7A)-N(6A)	172(2)
C(7A)-N(3A)-C(8A)-C(9A)	-2(3)
Cu(1A)-N(3A)-C(8A)-C(9A)	-174.6(17)
N(3A)-C(8A)-C(9A)-N(6A)	1(3)
C(7A)-N(6A)-C(9A)-C(8A)	0(2)
C(70)-N(6A)-C(9A)-C(8A)	166.1(16)
C(115)-C(116)-O(4)-C(117)	169.7(17)
C(118)-C(117)-O(4)-C(116)	-146(2)

Table S12. Hydrogen bonds for **[1-Cu]SbF_6**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(7)-H(222)...F(6)	0.891(19)	2.39(3)	3.218(9)	155(4)
N(7)-H(222)...O(1)	0.891(19)	2.34(2)	3.218(10)	168(4)
N(8)-H(223)...F(4)	0.89(2)	2.32(3)	3.178(10)	161(5)
N(10)-H(225)...O(4)	0.90(2)	2.37(3)	3.255(14)	169(7)
N(9)-H(224)...O(2)	0.89(2)	2.56(4)	3.420(7)	162(8)

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