

Supporting Information

**Distinct Mechanism of Oxidative Trifluoromethylation with a Well-Defined Cu(II)
Fluoride Promoter: Hidden Catalysis**

Noel Nebra and Vladimir V. Grushin*

Institute of Chemical Research of Catalonia (ICIQ), Tarragona 43007, Spain

Contents

I. General Information	S2
II. Optimization Experiments.....	S2
III. Reaction of 1 with TMSCF₃ under Argon.....	S4
IV. Reaction of 1 with TMSCF₃ in Air.....	S7
V. Reaction of 1 with CF₃SiMe₃ and PhB(OH)₂ in Air.....	S11
VI. References	S12

I. General Information

All chemicals, solvents, and deuterated solvents were purchased from Aldrich, Alfa Aesar, Apollo Scientific, TCI, Acros, and Deutero companies. Anhydrous DMF (Alfa Aesar or from an MBraun SPS) was stored over freshly calcined 4 Å molecular sieves in a glove-box. Complexes [(bpy)CuF₂(H₂O)]·2H₂O (**1**) and [(phen)CuF₂(H₂O)]·2H₂O (**2**) were prepared following the literature procedures.¹⁻³ ¹H and ¹⁹F NMR spectra were recorded on a Bruker Avance 400 Ultrashield spectrometer. Quantitative ¹⁹F NMR analysis was carried out with D1 = 5 s.

II. Optimization Experiments

Trifluoromethylation of PhB(OH)₂ with TMSCF₃ in the presence of [(bpy)CuF₂(H₂O)]·2H₂O (1**) or [(phen)CuF₂(H₂O)]·2H₂O (**2**) (Table S1).** In air, to a stirring mixture of **1** or **2** (0.125 mmol) and dry DMF (see Table 1 for specifics) was added TMSCF₃ (2-10 equiv). After 1 min of agitation, to the resultant dark-orange solution was added dropwise a solution of PhB(OH)₂ (0.125 mmol) in DMF (1 mL) over a period of 2 min. After 5-14 h (see Table S1), 1,3-bis(trifluoromethyl)benzene (internal standard; 0,063 mmol; 9.7 μL), water (5 mL), and ether (2 mL) were added at agitation. The organic layer was filtered through a short silica gel plug and the filtrate was analyzed by ¹⁹F NMR.

The purity of **1** for these and other experiments was confirmed by microanalysis data. Calcd for C₁₀H₁₄CuF₂N₂O₃, %: C, 38.5; H, 4.5; N, 9.0. Found: C, 38.7; H, 4.3; N, 9.1.

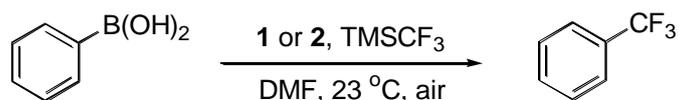
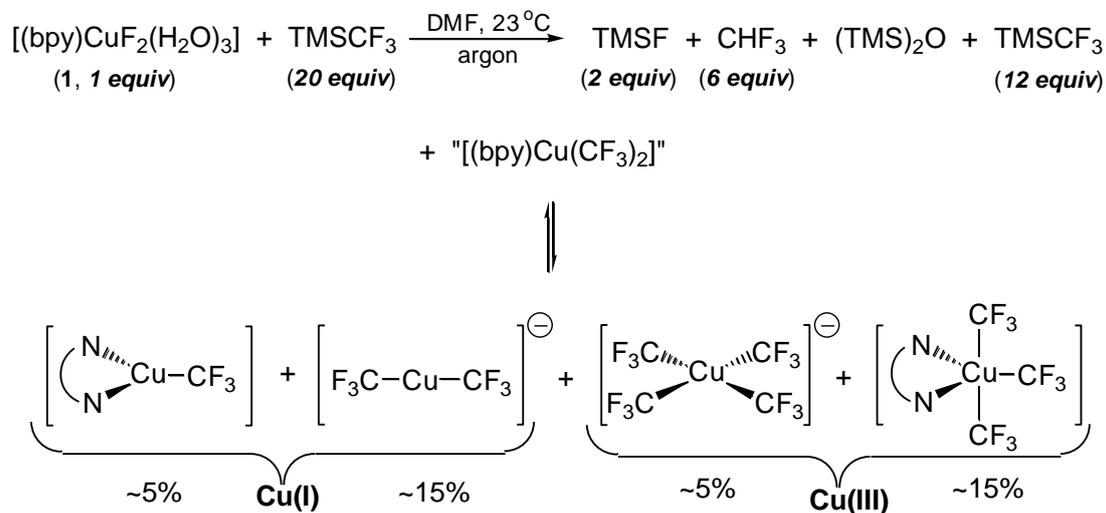


Table S1. Optimization of reaction conditions for trifluoromethylation of PhB(OH)₂.

Entry	Cu complex	DMF, mL	TMSCF ₃ , equiv	Time, h	Yield of PhCF ₃ , % ^a
1	1	1.5	10	5	75
2	2	1.5	10	5	25
3	1	1.5	10	14	83
4	1	1.0	10	14	90
5	1	0.5	10	14	85
6	1	0.2	10	14	83
7 ^b	1	2.0	10	14	89
8 ^b	1	3.0	10	14	92
9 ^c	1	1.0	10	14	75
10 ^d	1	1.0	10	14	91
11 ^e	1	1.0	10	14	97
12 ^{e,f}	1	1.0	10	14	0
13 ^e	1	1.0	5	14	65
14 ^e	1	1.0	2	14	27

^a Determined by ¹⁹F NMR using 1,3-bis(trifluoromethyl)benzene as an internal standard (0.063 mmol). ^b PhB(OH)₂ was added in one portion. ^c PhB(OH)₂ was added 0.5 min after mixing **1** and TMSCF₃ in DMF. ^d PhB(OH)₂ was added 2 min after mixing **1** and TMSCF₃ in DMF. ^e In the presence of bpy (0.125 mmol; 1 equiv). ^f Under argon (glove-box).

III. Reaction of **1** with TMSCF₃ under Argon



In an argon-filled glove-box, a 5-mm NMR-tube was charged with **1** (20 mg; 0.063 mmol), 4,4'-difluorobiphenyl (internal standard; 12 mg; 0.063 mmol), and DMF-d₇ (1 mL). TMSCF₃ (195 μL; 0.125 mmol) was added, the tube was sealed with a rubber septum, and brought out. The poorly soluble pale-blue copper complex quickly dissolved upon shaking the tube to produce a solid-free dark-orange solution. The solution was analyzed by ¹⁹F NMR ca. 10 min after **1** had dissolved. The full ¹⁹F NMR spectrum and its “CuCF₃” region are shown in Figures S1 and S2, respectively. No evolution of the spectral pattern was observed in the next 4 h. Adding PhB(OH)₂ (8 mg; 0.063 mmol) to this solution under argon did not produce PhCF₃ in ¹⁹F NMR-detectable amounts after 30 min, 3 h, or 1 day.

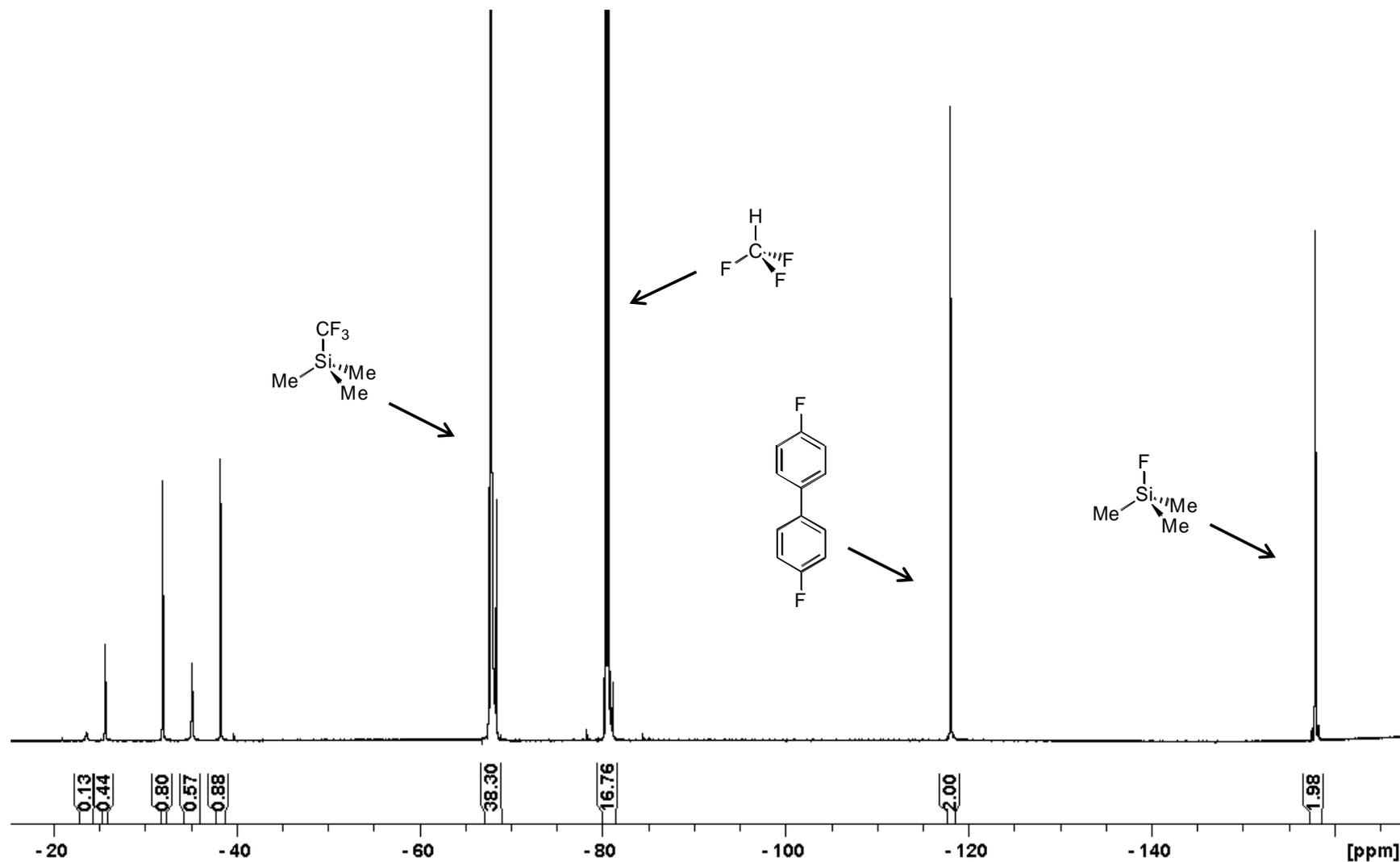


Figure S1. ^{19}F NMR spectrum of the reaction mixture obtained upon treatment of **1** with 20 equiv of TMSCF_3 in DMF with 4,4'-difluorobiphenyl as an internal standard under argon.

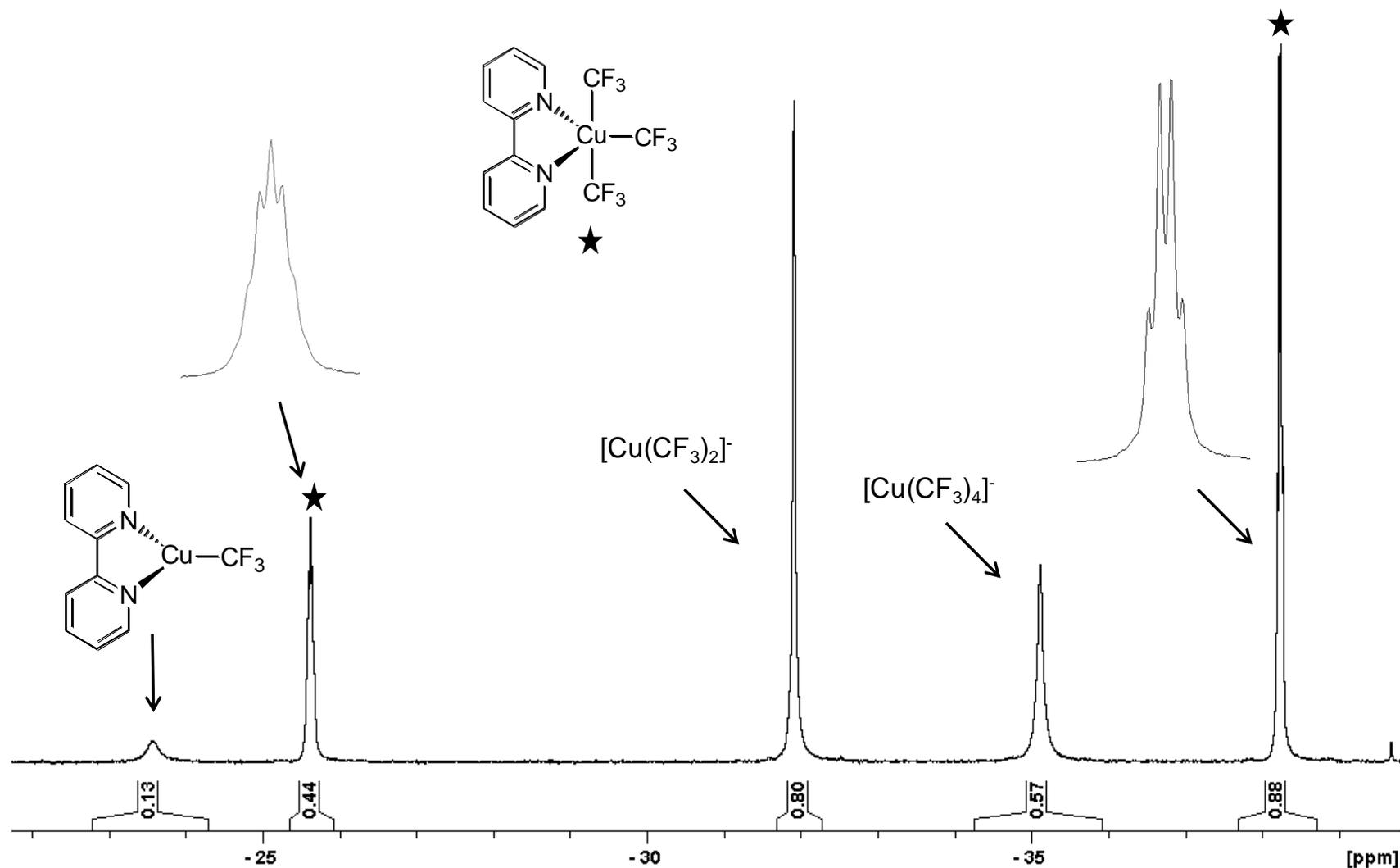


Figure S2. The CuCF_3 region of the ^{19}F NMR spectrum of the reaction mixture obtained upon treatment of **1** with 20 equiv of TMSCF_3 in DMF with 4,4'-difluorobiphenyl as an internal standard under argon.

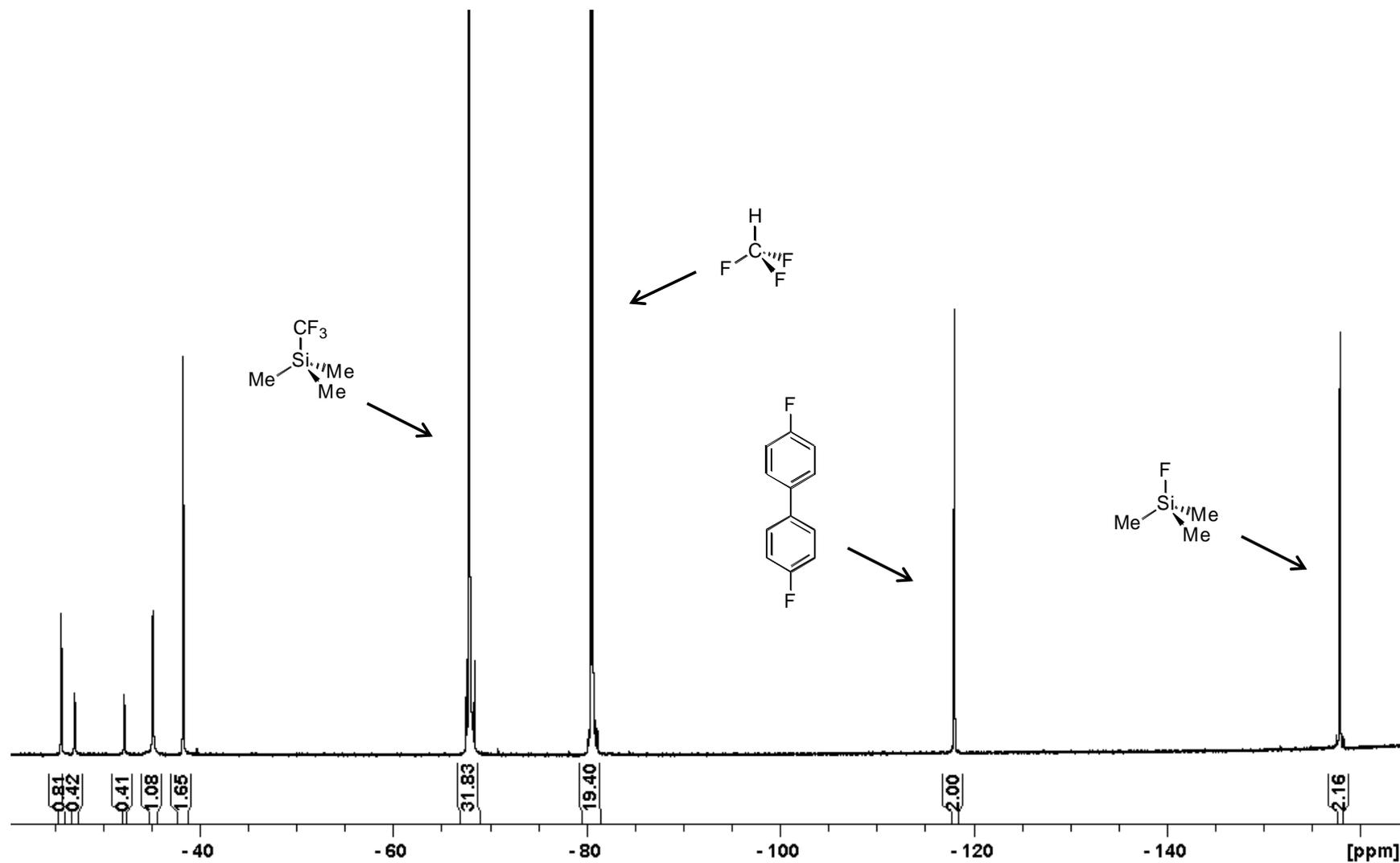


Figure S3. ^{19}F NMR spectrum of the reaction mixture obtained upon treatment of **1** with 20 equiv of TMSCF_3 in DMF with 4,4'-difluorobiphenyl as an internal standard in air.

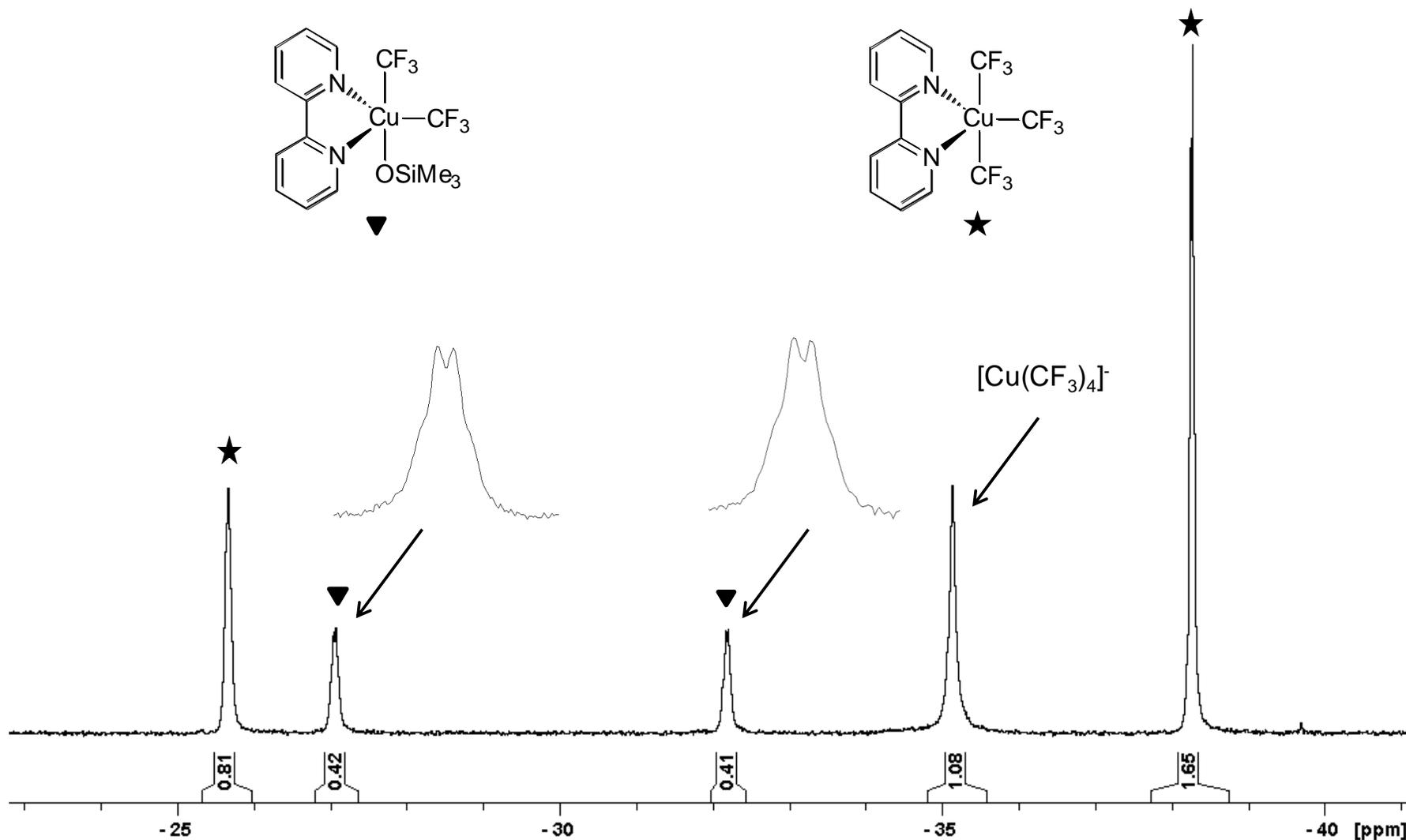


Figure S4. The CuCF_3 region of the ^{19}F NMR spectrum of the reaction mixture obtained upon treatment of **1** with 20 equiv of TMSCF_3 in DMF with 4,4'-difluorobiphenyl as an internal standard in air.

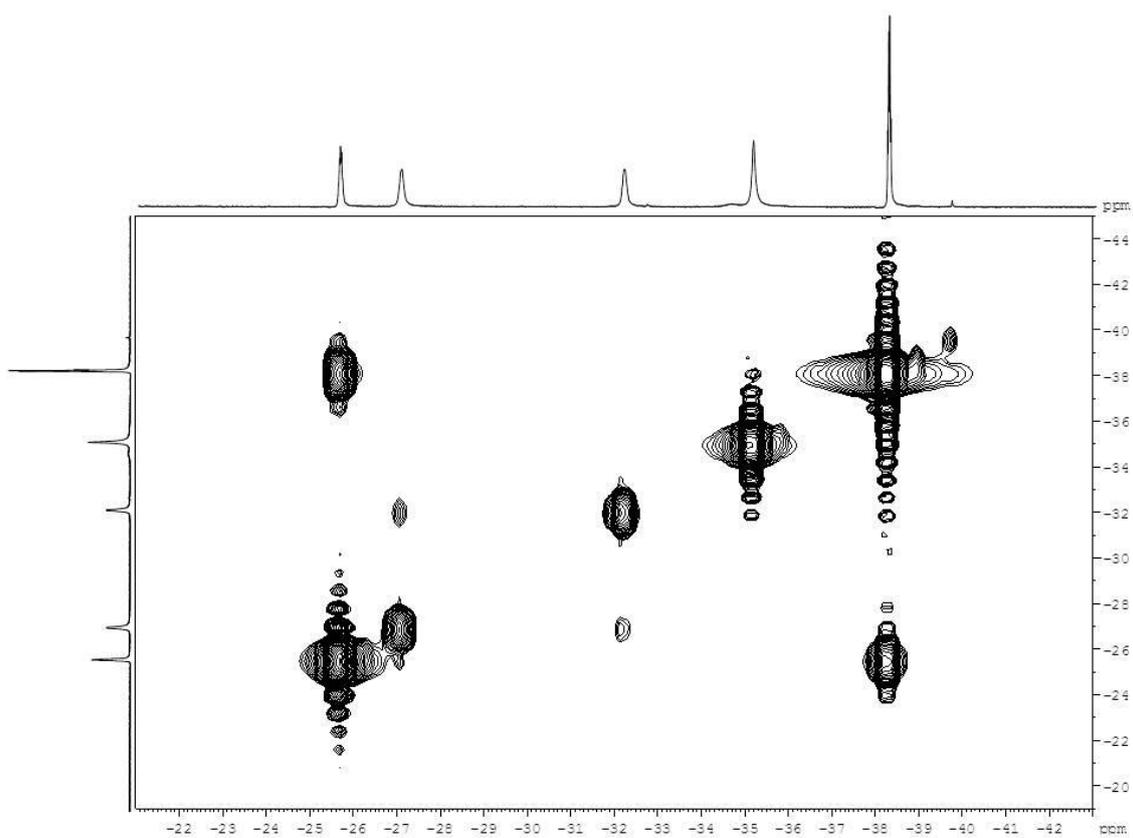
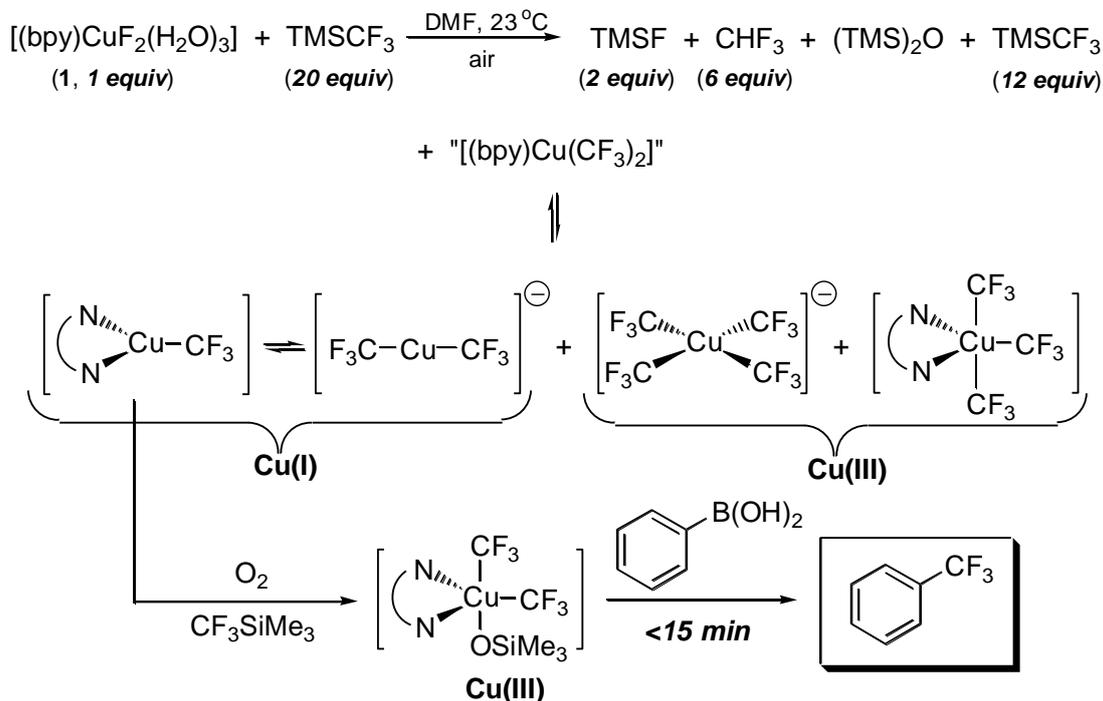


Figure S5. ^{19}F - ^{19}F COSY of the CuCF_3 region for the reaction mixture obtained upon treatment of **1** with 20 equiv of TMSCF_3 in DMF with 4,4'-difluorobiphenyl as an internal standard in air.

V. Reaction of **1** with CF_3SiMe_3 and $\text{PhB}(\text{OH})_2$ in Air



In air, a 5-mm NMR-tube was charged with **1** (20 mg; 0.063 mmol), 4,4'-difluorobiphenyl (internal standard; 12 mg; 0.063 mmol), and DMF (1 mL). On addition of TMSCF_3 (195 μL ; 0.125 mmol) and shaking for 2 min, the poorly soluble pale-blue copper complex quickly dissolved. ^{19}F NMR analysis performed without delay indicated the formation of $[(\text{bpy})\text{Cu}(\text{CF}_3)_2(\text{OTMS})]$, as in the previous experiment. Immediately after the ^{19}F NMR spectrum was recorded, $\text{PhB}(\text{OH})_2$ (8 mg; 0.063 mmol) was added and the tube was sealed in air. After shaking for 15 min, PhCF_3 (-63.7 ppm, s) was produced in 80% yield. After the tube was reopened to air, the yield of PhCF_3 raised to nearly quantitative.

VI. References

- (1) Gibbs, P. R.; Graves, P. R.; Gulliver, D. J.; Levason, W. *Inorg. Chim. Acta* **1980**, *45*, L207.
- (2) Emsley, J.; Arif, M.; Bates, P. A.; Hursthouse, M. B. *J. Crystallogr. Spectrosc. Res.* **1987**, *17*, 605.
- (3) Emsley, J.; Arif, M.; Bates, P. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 2397.