Supporting Information

Unexpected Facile $C_{carbene}$–X (X: I, Br, Cl) Reductive Elimination From N-Heterocyclic Carbene Copper Halides Under Oxidative Conditions

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General Information: All air and/or moisture sensitive compounds were manipulated in a glove box under a N_2 atmosphere. Dry acetonitrile was obtained by elution through a Innovative Technology solvent purification system. IPrCuCl, $Cu(CF_3SO_3)_2$, $[Cp_2Fe]^+PF_6^-$, $[Ph_2I]^+PF_6^-$, $NO^+SbF_6^-$, and Selectfluor® were purchased from Sigma-Aldrich. IPrCuF, IPrCuBr, and IPrCuI were synthesized according to literature procedures.[s1] A modified literature procedure was used to prepare $[(1, 10\text{-phenanthroline})_3Fe^{III}]^{3+}$.[s2] ^1H, ^{13}C, and ^{19}F NMR spectra were recorded at room temperature (RT) using a Varian Mercury 400 (^1H, 400 MHz, ^{13}C, 125.9 MHz, and ^{19}F, 376.4 MHz) spectrometer. ^1H and ^{13}C NMR spectra were referenced to TMS using the residual proto- signal of the solvent. ^{19}F NMR spectra were referenced to $CFCl_3$. Chemical shifts are reported using the standard δ notation in parts per million, and coupling constant are reported in Hz. Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), heptet (h). Cyclic voltammetry was performed using a BAS CV-50W voltammetric analyzer, a Ag wire reference electrode, a platinum disk working electrode, and a platinum wire counter electrode with 0.1 M Bu_4NPF_6 solutions in acetonitrile (room temperature and *ca.* -40 °C) or propionitrile (room temperature and *ca.* -78 °C) with variable scan rates (50 to 1V/s). Ferrocene was used as an internal standard. Low-temperature UV-vis spectroscopy was performed using a Cary 50 spectrometer with a custom-designed immersible fiber-optic quartz probe with a variable path length (1 and 10 mm; Hellma, Inc.). Constant low temperatures were maintained by a dry ice/acetonitrile or dry ice/acetone bath. Solution temperatures were monitored directly by insertion of an Omega temperature probe in the solutions. The Notre Dame X-ray Crystallography Laboratory provided the X-ray analysis. Stanford University Mass Spectroscopy Laboratory provided the high-resolution mass spectroscopic analysis.

Synthesis of $\mathbf{2_{Cl}}\cdot SbF_6$: $NO^+SbF_6^-$ (18 mg, 0.68 mmol) and $[Cu(CH_3CN)_4]^+SbF_6^-$ (36 mg, 0.078 mmol) were dissolved in MeCN (1 ml) and fully mixed at RT under N_2. To the resultant blue solution was added IPrCuCl (15 mg, 0.031 mmol). The solution turns light blue immediately upon mixing. The solvent was removed under vacuum to give a solid residue, to which was added 5 ml deionized water and several drops of 1N aqueous ammonia. The mixture was extracted with 5 ml CH_2Cl_2 (3x), and the solvent of the combined organic fractions was removed to give a white power, $\mathbf{2_{Cl}}\cdot SbF_6$ (20 mg, 99% yield). ^1H NMR (CD_2Cl_2): 1.25 (d, 6H, $^3J_{HH}$ 6.8), 1.31 (d, 6H, $^3J_{HH}$ 6.8), 2.34 (h, 2H, $^3J_{HH}$ 6.8), 7.48 (d, 4H, $^3J_{HH}$ 8.0), 7.72 (t, 2H, $^3J_{HH}$ 8.0), 7.86 (s, 2H); ^{13}C NMR (CD_2Cl_2): 23.46 24.07, 29.69, 125.70, 126.58, 128.42, 133.34, 134.80, 145.36; ^{19}F NMR (CD_2Cl_2): -153.7. HRMS $[\mathbf{2_{Cl}}]^+$ found 423.2559, calculated 423.2567. Crystals suitable for X-ray structural analysis ($\mathbf{2_{Cl}}\cdot SbF_6\cdot CH_2Cl_2$) were obtained by thermal diffusion of pentane into a $\mathbf{2_{Cl}}\cdot SbF_6/CH_2Cl_2$ solution at RT.[s3]

Synthesis of $\mathbf{2_{Br}}\cdot CF_3SO_3$: $Cu(CF_3SO_3)_2$ (29 mg, 0.08 mmol) and IPrCuBr (21 mg, 0.039 mmol) was dissolved in MeCN (1 ml) and fully mixed at RT under N_2. A colorless solution was obtained immediately. The solvent was removed under vacuum to give a solid residue to which was added 5 ml deionized water and several drops of 1N aqueous ammonia. The mixture was extracted with 5 ml CH_2Cl_2 (3x), and the solvent of the combined organic fractions were removed to give a white power, $\mathbf{2_{Br}}\cdot CF_3SO_3$ (24 mg,

98% yield). ^{1}H NMR (CD_2Cl_2): 1.26 (d, 6H, $^3J_{HH}$ 6.8), 1.29 (d, 6H, $^3J_{HH}$ 6.8), 2.30 (h, 2H, $^3J_{HH}$ 6.8), 7.46 (d, 4H, $^3J_{HH}$ 8.0), 7.70 (t, 2H, $^3J_{HH}$ 8.0), 8.13 (s, 2H); ^{13}C NMR (CD_2Cl_2): 23.31, 24.27, 29.65, 125.28, 125.60, 128.45, 129.80, 133.11, 144.75, 145.24; ^{19}F NMR (CD_2Cl_2): -80.3. HRMS [$\mathbf{2_{Br}}$]$^+$ found 467.2046, calculated 467.2062. Crystals suitable for X-ray structural analysis ($\mathbf{2_{Br}}\cdot CF_3SO_3\cdot CH_2Cl_2$) were obtained by thermal diffusion of pentane into a $\mathbf{2_{Cl}}\cdot SbF_6/CH_2Cl_2$ solution at RT.[s3]

Synthesis of $\mathbf{2_I}\cdot I_3$: I_2 (104 mg, 0.409 mmol) and IPrCuCl (59 mg, 0.121 mmol) was dissolved in MeCN (1 ml) and fully mixed at RT in air. A brown solution was obtained immediately. Solvent removal under vacuum gave a solid residue to which were added 5 ml deionized water and several drops of 1N aqueous ammonia. The mixture was extracted with 5 ml CH_2Cl_2 (3x), and the solvent of the combined organic fractions was removed to give a brown powder, $\mathbf{2_I}\cdot I_3$ (108 mg, 99% yield). ^{1}H NMR (CD_2Cl_2): 1.26 (d, 6H, $^3J_{HH}$ 6.8), 1.32 (d, 6H, $^3J_{HH}$ 6.8), 2.27 (h, 2H, $^3J_{HH}$ 6.8), 7.46 (d, 4H, $^3J_{HH}$ 8.0), 7.71 (t, 2H, $^3J_{HH}$ 8.0), 7.79 (s, 2H); ^{13}C NMR (CD_2Cl_2): 23.33, 24.79, 29.68, 113.07, 125.59, 127.71, 131.79, 132.93, 145.16. HRMS [$\mathbf{2_I}$]$^+$ found 515.1924, calculated 515.1923. Crystals suitable for X-ray structural analysis ($\mathbf{2_I}\cdot I_3$) were obtained by slow evaporation of a $\mathbf{2_I}\cdot I_3/CH_2Cl_2$ solution at RT.

General Procedure for Oxidations of IPrCuX (F, Cl, Br, and I) with Selectfluor® or $Cu(CF_3SO_3)_2$:
IPrCuX (X = Cl, Br, and I) and an appropriate amount of oxidant were dissolved in CD_3CN (0.75 ml) and fully mixed at RT under N_2. ^{1}H NMR of the resulting $\mathbf{2_X}$ (X = Cl, Br, and I) indicated a quantitative formation if a sufficient amount of oxidant was used. Reactions run in air led to same yields of $\mathbf{2_X}$.

IPrCu(CF_3SO_3) was quantitatively formed in reaction of IPrCuF with *ca*. 2 eq. $Cu(CF_3SO_3)_2$. The ^{1}H NMR spectrum of IPrCu(CF_3SO_3) is consistent with literature data.[s3] Crystals suitable for X-ray structural analysis were obtained by thermal diffusion of pentane into a IPrCu(CF_3SO_3)/CH_2Cl_2 solution at RT. It should be noted that an X-ray crystal structure of IPrCu(CF_3SO_3) has been reported.[s3]

Reference:

s1. (a) IPrCuF: Herron, J. R.; Ball, Z. T. *J. Am. Chem. Soc.* **2008**, *130*, 16486-16487. (b) IPrCuBr and IPrCuI: Liu, J. M.; Zhang, R. Z.; Wang, S. F.; Sun, W.; Xia, C. G. *Org. Lett.* **2009**, *11*, 1321-1324.
s2. [(1, 10-phenanthroline)$_3$Fe^{III}]$^{3+}$ was obtained by oxidation of [(1, 10-phenanthroline)$_3$ Fe^{II}](OTf)$_2$ with NO^+SbF_6 in MeCN. (Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1977**, *101*, 5593-5603.)
s3. During the preparation of this manuscript, a free carbene route for the synthesis of $\mathbf{2_{Cl}}$ and $\mathbf{2_{Br}}$ was reported: Mendoza-Espinosa, D.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc.* **2010**, *132*, 7264-7265.
s4. Goj, L. A.; Blue, E. D.; Delp, S. A.; Gunnoe, T. B.; Cundari, T. R.; Petersen, J. L. *Organometallics* **2006**, *25*, 4097-4104.

Figure S1. Crystal structure for $\mathbf{2}_{Cl}\cdot SbF_6\cdot CH_2Cl_2$.

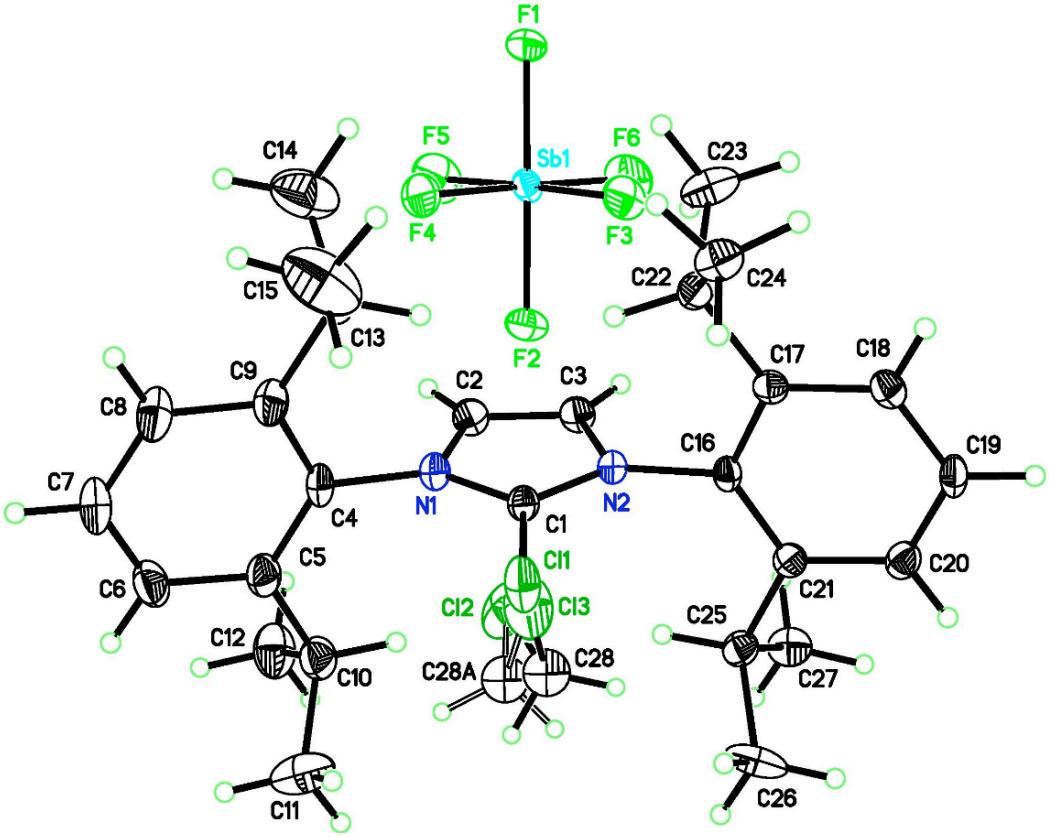

Table S1. Crystal data and structure refinement for $\mathbf{2}_{\mathbf{Cl}}\cdot SbF_6\cdot CH_2Cl_2$.

Empirical formula	$C_{28}H_{38}Cl_3F_6N_2Sb$
Formula weight	744.70
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 10.37220(10) Å α = 77.6800(10)°
	b = 11.18180(10) Å β = 75.8820(10)°
	c = 16.0498(2) Å γ = 66.3380(10)°
Volume	1639.43(3) $Å^3$
Z	2
Density (calculated)	1.509 $g.cm^{-3}$
Absorption coefficient (μ)	9.405 mm^{-1}
F(000)	752
Crystal size	0.44 × 0.12 × 0.07 mm^3
θ range for data collection	2.86 to 69.73°
Index ranges	$-12 \le h \le 12$, $-13 \le k \le 13$, $-19 \le l \le 19$
Reflections collected	16090
Independent reflections	5778 [R_{int} = 0.0200]
Completeness to θ = 69.73°	93.3 %
Absorption correction	Numerical
Max. and min. transmission	0.6520 and 0.2308
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5778 / 0 / 368
Goodness-of-fit on F^2	1.032
Final R indices [I>2σ(I)]	R_1 = 0.0290, wR_2 = 0.0720
R indices (all data)	R_1 = 0.0308, wR_2 = 0.0733
Largest diff. peak and hole	0.951 and -0.630 $e^-.Å^{-3}$

Table S2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for $\mathbf{2}_{Cl}\cdot SbF_6\cdot CH_2Cl_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cl(1)	0.64690(8)	0.08164(6)	0.28934(4)	0.028(1)
N(1)	0.5062(2)	0.3170(2)	0.20714(13)	0.018(1)
N(2)	0.5032(2)	0.3191(2)	0.34284(13)	0.015(1)
C(1)	0.5486(3)	0.2430(3)	0.27989(16)	0.016(1)
C(2)	0.4330(3)	0.4457(3)	0.22443(17)	0.021(1)
C(3)	0.4313(3)	0.4473(3)	0.30841(17)	0.020(1)
C(4)	0.5223(3)	0.2677(3)	0.12686(16)	0.020(1)
C(5)	0.6396(3)	0.2684(3)	0.06194(17)	0.024(1)
C(6)	0.6474(3)	0.2252(3)	-0.01507(18)	0.030(1)
C(7)	0.5450(4)	0.1839(3)	-0.02569(19)	0.034(1)
C(8)	0.4307(4)	0.1829(3)	0.04075(19)	0.031(1)
C(9)	0.4167(3)	0.2250(3)	0.11909(17)	0.025(1)
C(10)	0.7547(3)	0.3125(3)	0.07291(18)	0.029(1)
C(11)	0.9025(4)	0.2039(4)	0.0565(3)	0.049(1)
C(12)	0.7525(4)	0.4375(3)	0.0113(2)	0.038(1)
C(13)	0.2908(3)	0.2230(3)	0.19184(18)	0.028(1)
C(14)	0.1510(4)	0.3301(4)	0.1709(3)	0.053(1)
C(15)	0.2780(5)	0.0888(4)	0.2111(3)	0.058(1)
C(16)	0.5137(3)	0.2754(2)	0.43410(15)	0.015(1)
C(17)	0.4044(3)	0.2368(3)	0.48747(16)	0.017(1)
C(18)	0.4100(3)	0.2067(3)	0.57569(16)	0.019(1)
C(19)	0.5197(3)	0.2122(3)	0.60757(16)	0.021(1)
C(20)	0.6282(3)	0.2464(3)	0.55213(17)	0.021(1)
C(21)	0.6277(3)	0.2799(3)	0.46338(16)	0.017(1)
C(22)	0.2846(3)	0.2292(3)	0.45224(17)	0.021(1)
C(23)	0.1473(3)	0.3494(3)	0.4694(2)	0.032(1)
C(24)	0.2582(3)	0.1015(3)	0.48910(19)	0.025(1)
C(25)	0.7476(3)	0.3168(3)	0.40290(17)	0.021(1)
C(26)	0.8909(3)	0.2012(3)	0.4065(2)	0.035(1)
C(27)	0.7544(3)	0.4389(3)	0.4271(2)	0.028(1)
Sb(1)	0.09533(2)	0.79200(2)	0.26912(1)	0.019(1)
F(1)	-0.10206(17)	0.82442(18)	0.29669(11)	0.032(1)
F(2)	0.29395(17)	0.75286(17)	0.24144(11)	0.029(1)
F(3)	0.12711(19)	0.66052(18)	0.36407(11)	0.033(1)
F(4)	0.1196(2)	0.6672(2)	0.19918(12)	0.038(1)
F(5)	0.0687(2)	0.9219(2)	0.17394(12)	0.049(1)
F(6)	0.0731(2)	0.91385(19)	0.34027(13)	0.041(1)
C(28)	0.8069(9)	0.6876(8)	0.1822(6)	0.045(2)
C(28A)	0.8176(8)	0.7023(8)	0.1417(6)	0.044(2)
Cl(2)	0.71952(13)	0.86183(11)	0.13248(7)	0.062(1)

Cl(3)	0.70250(14)	0.60329(12)	0.19787(7)	0.064(1)
H(2A)	0.3915	0.5195	0.1844	0.025
H(3A)	0.3887	0.5223	0.3384	0.023
H(6A)	0.7251	0.2242	-0.0611	0.036
H(7A)	0.5524	0.1557	-0.0790	0.040
H(8A)	0.3614	0.1531	0.0326	0.037
H(10A)	0.7350	0.3318	0.1338	0.034
H(11A)	0.9031	0.1236	0.0959	0.073
H(11B)	0.9746	0.2324	0.0667	0.073
H(11C)	0.9247	0.1860	-0.0036	0.073
H(12A)	0.6576	0.5067	0.0221	0.057
H(12B)	0.7739	0.4194	-0.0487	0.057
H(12C)	0.8245	0.4666	0.0208	0.057
H(13A)	0.3093	0.2410	0.2453	0.034
H(14A)	0.0725	0.3257	0.2184	0.079
H(14B)	0.1324	0.3170	0.1171	0.079
H(14C)	0.1583	0.4166	0.1636	0.079
H(15A)	0.2048	0.0869	0.2627	0.087
H(15B)	0.3701	0.0207	0.2215	0.087
H(15C)	0.2507	0.0723	0.1616	0.087
H(18A)	0.3371	0.1819	0.6146	0.023
H(19A)	0.5206	0.1924	0.6681	0.025
H(20A)	0.7042	0.2471	0.5749	0.025
H(22A)	0.3147	0.2303	0.3880	0.025
H(23A)	0.1648	0.4296	0.4410	0.047
H(23B)	0.1174	0.3528	0.5319	0.047
H(23C)	0.0717	0.3428	0.4461	0.047
H(24A)	0.3493	0.0265	0.4830	0.037
H(24B)	0.1936	0.0926	0.4574	0.037
H(24C)	0.2148	0.1037	0.5505	0.037
H(25A)	0.7284	0.3368	0.3424	0.025
H(26A)	0.8845	0.1229	0.3924	0.053
H(26B)	0.9132	0.1831	0.4649	0.053
H(26C)	0.9666	0.2237	0.3646	0.053
H(27A)	0.6613	0.5112	0.4266	0.041
H(27B)	0.8277	0.4648	0.3850	0.041
H(27C)	0.7786	0.4190	0.4851	0.041
H(28A)	0.8975	0.6441	0.1437	0.054
H(28B)	0.8303	0.6880	0.2384	0.054
H(28C)	0.8933	0.6839	0.1753	0.053
H(28D)	0.8644	0.6757	0.0834	0.053

Table S3. Anisotropic displacement parameters ($Å^2$) for $\mathbf{2_{Cl}}\cdot SbF_6\cdot CH_2Cl_2$.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2 a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1)	0.0469(4)	0.0141(3)	0.0188(3)	-0.0028(2)	-0.0096(3)	-0.0030(3)
N(1)	0.0218(12)	0.0179(11)	0.0142(10)	-0.0013(8)	-0.0039(8)	-0.0076(10)
N(2)	0.0172(11)	0.0153(10)	0.0132(10)	-0.0019(8)	-0.0030(8)	-0.0064(9)
C(1)	0.0189(13)	0.0154(13)	0.0146(12)	-0.0010(9)	-0.0034(9)	-0.0065(11)
C(2)	0.0223(14)	0.0159(13)	0.0203(13)	-0.0006(10)	-0.0048(10)	-0.0033(12)
C(3)	0.0209(14)	0.0140(12)	0.0200(13)	-0.0026(10)	-0.0039(10)	-0.0025(12)
C(4)	0.0285(15)	0.0187(13)	0.0119(12)	-0.0015(10)	-0.0059(10)	-0.0082(12)
C(5)	0.0293(16)	0.0251(15)	0.0164(13)	0.0006(11)	-0.0058(11)	-0.0093(13)
C(6)	0.0337(17)	0.0360(17)	0.0166(13)	-0.0045(12)	-0.0008(11)	-0.0101(15)
C(7)	0.048(2)	0.0397(18)	0.0185(14)	-0.0090(13)	-0.0070(13)	-0.0177(17)
C(8)	0.0440(19)	0.0366(18)	0.0217(14)	-0.0039(12)	-0.0098(13)	-0.0215(16)
C(9)	0.0323(16)	0.0271(15)	0.0172(13)	0.0003(11)	-0.0069(11)	-0.0140(14)
C(10)	0.0302(16)	0.0375(18)	0.0203(14)	-0.0028(12)	-0.0025(11)	-0.0164(15)
C(11)	0.0277(19)	0.046(2)	0.071(3)	-0.0069(19)	-0.0171(17)	-0.0077(18)
C(12)	0.053(2)	0.0406(19)	0.0287(16)	-0.0009(14)	-0.0060(14)	-0.0274(18)
C(13)	0.0340(17)	0.0386(18)	0.0199(14)	-0.0026(12)	-0.0041(12)	-0.0222(15)
C(14)	0.038(2)	0.054(2)	0.053(2)	0.0040(19)	0.0056(17)	-0.017(2)
C(15)	0.062(3)	0.038(2)	0.061(3)	0.0034(18)	0.015(2)	-0.024(2)
C(16)	0.0190(13)	0.0135(12)	0.0124(11)	-0.0027(9)	-0.0035(9)	-0.0038(11)
C(17)	0.0163(13)	0.0141(12)	0.0178(12)	-0.0030(10)	-0.0028(10)	-0.0023(11)
C(18)	0.0210(14)	0.0169(13)	0.0169(12)	-0.0016(10)	-0.0007(10)	-0.0055(12)
C(19)	0.0273(15)	0.0188(13)	0.0120(12)	-0.0030(10)	-0.0060(10)	-0.0030(12)
C(20)	0.0217(14)	0.0195(13)	0.0210(13)	-0.0059(10)	-0.0068(10)	-0.0038(12)
C(21)	0.0182(13)	0.0148(12)	0.0187(12)	-0.0060(10)	-0.0038(10)	-0.0039(11)
C(22)	0.0208(14)	0.0256(15)	0.0181(12)	0.0008(10)	-0.0049(10)	-0.0120(13)
C(23)	0.0225(15)	0.0214(15)	0.053(2)	0.0007(13)	-0.0153(13)	-0.0079(13)
C(24)	0.0228(15)	0.0193(14)	0.0333(15)	-0.0062(11)	-0.0072(12)	-0.0059(13)
C(25)	0.0204(14)	0.0255(15)	0.0217(13)	-0.0038(11)	-0.0048(10)	-0.0115(13)
C(26)	0.0182(15)	0.0234(16)	0.054(2)	-0.0101(14)	0.0112(13)	-0.0053(14)
C(27)	0.0263(16)	0.0242(15)	0.0341(16)	-0.0044(12)	-0.0048(12)	-0.0109(14)
Sb(1)	0.0195(1)	0.0185(1)	0.0146(1)	-0.0014(1)	-0.0020(1)	-0.0022(1)
F(1)	0.0171(8)	0.0404(10)	0.0300(9)	-0.0084(8)	-0.0022(7)	-0.0023(8)
F(2)	0.0195(8)	0.0328(10)	0.0327(9)	-0.0054(7)	-0.0001(7)	-0.0082(8)
F(3)	0.0328(10)	0.0307(10)	0.0241(8)	0.0110(7)	-0.0047(7)	-0.0072(8)
F(4)	0.0327(10)	0.0483(12)	0.0384(10)	-0.0281(9)	-0.0047(8)	-0.0088(9)
F(5)	0.0474(12)	0.0439(12)	0.0312(10)	0.0209(9)	-0.0065(9)	-0.0048(10)
F(6)	0.0423(12)	0.0317(10)	0.0503(12)	-0.0258(9)	-0.0008(9)	-0.0084(9)
Cl(2)	0.0749(7)	0.0539(6)	0.0727(7)	-0.0243(5)	-0.0362(6)	-0.0178(6)
Cl(3)	0.0816(8)	0.0713(7)	0.0452(5)	-0.0086(5)	-0.0083(5)	-0.0356(6)

Table S4. Bond lengths [Å] for $\mathbf{2}_{\mathbf{Cl}}\cdot SbF_6\cdot CH_2Cl_2$.

atom-atom	distance	atom-atom	distance
Cl(1)-C(1)	1.673(3)	N(1)-C(1)	1.337(3)
N(1)-C(2)	1.383(3)	N(1)-C(4)	1.455(3)
N(2)-C(1)	1.335(3)	N(2)-C(3)	1.386(3)
N(2)-C(16)	1.458(3)	C(2)-C(3)	1.347(4)
C(4)-C(5)	1.397(4)	C(4)-C(9)	1.398(4)
C(5)-C(6)	1.394(4)	C(5)-C(10)	1.520(4)
C(6)-C(7)	1.373(5)	C(7)-C(8)	1.389(4)
C(8)-C(9)	1.390(4)	C(9)-C(13)	1.529(4)
C(10)-C(12)	1.526(4)	C(10)-C(11)	1.530(5)
C(13)-C(15)	1.518(5)	C(13)-C(14)	1.524(5)
C(16)-C(21)	1.397(4)	C(16)-C(17)	1.402(4)
C(17)-C(18)	1.394(4)	C(17)-C(22)	1.523(3)
C(18)-C(19)	1.384(4)	C(19)-C(20)	1.384(4)
C(20)-C(21)	1.394(4)	C(21)-C(25)	1.520(4)
C(22)-C(24)	1.528(4)	C(22)-C(23)	1.530(4)
C(25)-C(27)	1.529(4)	C(25)-C(26)	1.533(4)
Sb(1)-F(5)	1.8590(18)	Sb(1)-F(3)	1.8689(16)
Sb(1)-F(6)	1.8701(17)	Sb(1)-F(4)	1.8757(17)
Sb(1)-F(2)	1.8830(16)	Sb(1)-F(1)	1.8840(16)
C(28)-Cl(3)	1.646(8)	C(28)-Cl(2)	1.878(8)
C(28A)-Cl(2)	1.656(8)	C(28A)-Cl(3)	1.890(8)
C(2)-H(2A)	0.9500	C(3)-H(3A)	0.9500
C(6)-H(6A)	0.9500	C(7)-H(7A)	0.9500
C(8)-H(8A)	0.9500	C(10)-H(10A)	1.0000
C(11)-H(11A)	0.9800	C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800	C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800	C(12)-H(12C)	0.9800
C(13)-H(13A)	1.0000	C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800	C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800	C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800	C(18)-H(18A)	0.9500
C(19)-H(19A)	0.9500	C(20)-H(20A)	0.9500
C(22)-H(22A)	1.0000	C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800	C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800	C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800	C(25)-H(25A)	1.0000
C(26)-H(26A)	0.9800	C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800	C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800	C(27)-H(27C)	0.9800
C(28)-H(28A)	0.9900	C(28)-H(28B)	0.9900
C(28A)-H(28C)	0.9900	C(28A)-H(28D)	0.9900

Table S5. Bond angles [°] for $\mathbf{2_{Cl}}\cdot SbF_6\cdot CH_2Cl_2$.

atom-atom-atom	angle	atom-atom-atom	angle
C(1)-N(1)-C(2)	108.0(2)	C(1)-N(1)-C(4)	125.4(2)
C(2)-N(1)-C(4)	126.3(2)	C(1)-N(2)-C(3)	108.1(2)
C(1)-N(2)-C(16)	126.6(2)	C(3)-N(2)-C(16)	125.0(2)
N(2)-C(1)-N(1)	109.0(2)	N(2)-C(1)-Cl(1)	125.6(2)
N(1)-C(1)-Cl(1)	125.3(2)	C(3)-C(2)-N(1)	107.5(2)
C(2)-C(3)-N(2)	107.3(2)	C(5)-C(4)-C(9)	124.1(2)
C(5)-C(4)-N(1)	118.5(2)	C(9)-C(4)-N(1)	117.4(2)
C(6)-C(5)-C(4)	116.4(3)	C(6)-C(5)-C(10)	120.6(3)
C(4)-C(5)-C(10)	123.0(2)	C(7)-C(6)-C(5)	121.3(3)
C(6)-C(7)-C(8)	120.7(3)	C(7)-C(8)-C(9)	120.7(3)
C(8)-C(9)-C(4)	116.7(3)	C(8)-C(9)-C(13)	120.2(3)
C(4)-C(9)-C(13)	123.0(2)	C(5)-C(10)-C(12)	110.5(3)
C(5)-C(10)-C(11)	110.7(3)	C(12)-C(10)-C(11)	109.8(3)
C(15)-C(13)-C(14)	110.5(3)	C(15)-C(13)-C(9)	111.3(3)
C(14)-C(13)-C(9)	111.5(3)	C(21)-C(16)-C(17)	124.3(2)
C(21)-C(16)-N(2)	118.3(2)	C(17)-C(16)-N(2)	117.3(2)
C(18)-C(17)-C(16)	116.3(2)	C(18)-C(17)-C(22)	121.2(2)
C(16)-C(17)-C(22)	122.5(2)	C(19)-C(18)-C(17)	121.2(2)
C(18)-C(19)-C(20)	120.6(2)	C(19)-C(20)-C(21)	121.1(2)
C(20)-C(21)-C(16)	116.5(2)	C(20)-C(21)-C(25)	120.7(2)
C(16)-C(21)-C(25)	122.8(2)	C(17)-C(22)-C(24)	111.9(2)
C(17)-C(22)-C(23)	110.7(2)	C(24)-C(22)-C(23)	111.0(2)
C(21)-C(25)-C(27)	110.7(2)	C(21)-C(25)-C(26)	110.0(2)
C(27)-C(25)-C(26)	110.2(2)	F(5)-Sb(1)-F(3)	178.53(8)
F(5)-Sb(1)-F(6)	91.13(10)	F(3)-Sb(1)-F(6)	88.87(9)
F(5)-Sb(1)-F(4)	89.85(10)	F(3)-Sb(1)-F(4)	90.13(9)
F(6)-Sb(1)-F(4)	178.91(9)	F(5)-Sb(1)-F(2)	90.15(9)
F(3)-Sb(1)-F(2)	88.38(8)	F(6)-Sb(1)-F(2)	90.78(8)
F(4)-Sb(1)-F(2)	88.76(8)	F(5)-Sb(1)-F(1)	91.08(9)
F(3)-Sb(1)-F(1)	90.39(8)	F(6)-Sb(1)-F(1)	90.98(8)
F(4)-Sb(1)-F(1)	89.45(8)	F(2)-Sb(1)-F(1)	177.83(8)
Cl(3)-C(28)-Cl(2)	111.6(4)	Cl(2)-C(28A)-Cl(3)	110.6(4)
C(28A)-Cl(2)-C(28)	19.2(3)	C(28)-Cl(3)-C(28A)	18.9(3)
C(3)-C(2)-H(2A)	126.2	N(1)-C(2)-H(2A)	126.2
C(2)-C(3)-H(3A)	126.4	N(2)-C(3)-H(3A)	126.4
C(7)-C(6)-H(6A)	119.3	C(5)-C(6)-H(6A)	119.3
C(6)-C(7)-H(7A)	119.6	C(8)-C(7)-H(7A)	119.6
C(7)-C(8)-H(8A)	119.6	C(9)-C(8)-H(8A)	119.6
C(5)-C(10)-H(10A)	108.6	C(12)-C(10)-H(10A)	108.6
C(11)-C(10)-H(10A)	108.6	C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5	H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5	H(11A)-C(11)-H(11C)	109.5

H(11B)-C(11)-H(11C)	109.5	C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5	C(15)-C(13)-H(13A)	107.8
C(14)-C(13)-H(13A)	107.8	C(9)-C(13)-H(13A)	107.8
C(13)-C(14)-H(14A)	109.5	C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5	C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5	H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5	C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5	C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5	H(15B)-C(15)-H(15C)	109.5
C(19)-C(18)-H(18A)	119.4	C(17)-C(18)-H(18A)	119.4
C(18)-C(19)-H(19A)	119.7	C(20)-C(19)-H(19A)	119.7
C(19)-C(20)-H(20A)	119.5	C(21)-C(20)-H(20A)	119.5
C(17)-C(22)-H(22A)	107.7	C(24)-C(22)-H(22A)	107.7
C(23)-C(22)-H(22A)	107.7	C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5	H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5	H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5	C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5	H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5	H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5	C(21)-C(25)-H(25A)	108.6
C(27)-C(25)-H(25A)	108.6	C(26)-C(25)-H(25A)	108.6
C(25)-C(26)-H(26A)	109.5	C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5	C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5	H(26B)-C(26)-H(26C)	109.5
C(25)-C(27)-H(27A)	109.5	C(25)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5	C(25)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5	H(27B)-C(27)-H(27C)	109.5
Cl(3)-C(28)-H(28A)	109.3	Cl(2)-C(28)-H(28A)	109.3
Cl(3)-C(28)-H(28B)	109.3	Cl(2)-C(28)-H(28B)	109.3
H(28A)-C(28)-H(28B)	108.0	Cl(2)-C(28A)-H(28C)	109.5
Cl(3)-C(28A)-H(28C)	109.5	Cl(2)-C(28A)-H(28D)	109.5
Cl(3)-C(28A)-H(28D)	109.5	H(28C)-C(28A)-H(28D)	108.1

Table S6. Torsion angles [°] for $\mathbf{2}_{\mathbf{Cl}}\cdot SbF_6\cdot CH_2Cl_2$.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(3)-N(2)-C(1)-N(1)	-1.1(3)	C(16)-N(2)-C(1)-N(1)	173.3(2)
		C(3)-N(2)-C(1)-Cl(1)	177.2(2)
		C(16)-N(2)-C(1)-Cl(1)	-8.4(4)
		C(2)-N(1)-C(1)-N(2)	1.0(3)
		C(4)-N(1)-C(1)-N(2)	-173.4(2)
		C(2)-N(1)-C(1)-Cl(1)	-177.3(2)
		C(4)-N(1)-C(1)-Cl(1)	8.3(4)
		C(1)-N(1)-C(2)-C(3)	-0.5(3)
		C(4)-N(1)-C(2)-C(3)	173.8(2)
		N(1)-C(2)-C(3)-N(2)	-0.2(3)
		C(1)-N(2)-C(3)-C(2)	0.8(3)
		C(16)-N(2)-C(3)-C(2)	-173.7(2)
		C(1)-N(1)-C(4)-C(5)	-96.6(3)
		C(2)-N(1)-C(4)-C(5)	90.0(3)
		C(1)-N(1)-C(4)-C(9)	84.7(3)
		C(2)-N(1)-C(4)-C(9)	-88.6(3)
		C(9)-C(4)-C(5)-C(6)	1.0(4)
		N(1)-C(4)-C(5)-C(6)	-177.5(3)
		C(9)-C(4)-C(5)-C(10)	-178.6(3)
		N(1)-C(4)-C(5)-C(10)	2.9(4)
		C(4)-C(5)-C(6)-C(7)	-0.2(5)
		C(10)-C(5)-C(6)-C(7)	179.4(3)
		C(5)-C(6)-C(7)-C(8)	-0.6(5)
		C(6)-C(7)-C(8)-C(9)	0.7(5)
		C(7)-C(8)-C(9)-C(4)	0.0(5)
		C(7)-C(8)-C(9)-C(13)	-179.8(3)
		C(5)-C(4)-C(9)-C(8)	-0.9(4)
		N(1)-C(4)-C(9)-C(8)	177.6(3)
		C(5)-C(4)-C(9)-C(13)	178.9(3)
		N(1)-C(4)-C(9)-C(13)	-2.6(4)
		C(6)-C(5)-C(10)-C(12)	66.1(4)
		C(4)-C(5)-C(10)-C(12)	-114.3(3)
		C(6)-C(5)-C(10)-C(11)	-55.8(4)
		C(4)-C(5)-C(10)-C(11)	123.8(3)
		C(8)-C(9)-C(13)-C(15)	52.0(4)
		C(4)-C(9)-C(13)-C(15)	-127.8(3)
		C(8)-C(9)-C(13)-C(14)	-72.0(4)
		C(4)-C(9)-C(13)-C(14)	108.2(3)
		C(1)-N(2)-C(16)-C(21)	97.1(3)
		C(3)-N(2)-C(16)-C(21)	-89.4(3)
		C(1)-N(2)-C(16)-C(17)	-85.6(3)
		C(3)-N(2)-C(16)-C(17)	87.9(3)

C(21)-C(16)-C(17)-C(18)	2.6(4)
N(2)-C(16)-C(17)-C(18)	-174.4(2)
C(21)-C(16)-C(17)-C(22)	-178.0(2)
N(2)-C(16)-C(17)-C(22)	4.9(4)
C(16)-C(17)-C(18)-C(19)	-1.3(4)
C(22)-C(17)-C(18)-C(19)	179.3(3)
C(17)-C(18)-C(19)-C(20)	-0.8(4)
C(18)-C(19)-C(20)-C(21)	1.9(4)
C(19)-C(20)-C(21)-C(16)	-0.7(4)
C(19)-C(20)-C(21)-C(25)	-179.8(3)
C(17)-C(16)-C(21)-C(20)	-1.6(4)
N(2)-C(16)-C(21)-C(20)	175.4(2)
C(17)-C(16)-C(21)-C(25)	177.4(2)
N(2)-C(16)-C(21)-C(25)	-5.6(4)
C(18)-C(17)-C(22)-C(24)	-46.8(3)
C(16)-C(17)-C(22)-C(24)	133.9(3)
C(18)-C(17)-C(22)-C(23)	77.6(3)
C(16)-C(17)-C(22)-C(23)	-101.7(3)
C(20)-C(21)-C(25)-C(27)	-61.1(3)
C(16)-C(21)-C(25)-C(27)	119.9(3)
C(20)-C(21)-C(25)-C(26)	60.9(3)
C(16)-C(21)-C(25)-C(26)	-118.1(3)
Cl(3)-C(28A)-Cl(2)-C(28)	59.8(11)
Cl(3)-C(28)-Cl(2)-C(28A)	-92.9(13)
Cl(2)-C(28)-Cl(3)-C(28A)	62.6(12)
Cl(2)-C(28A)-Cl(3)-C(28)	-90.0(13)

Figure S2. Crystal structure for $\mathbf{2}_{\mathbf{Br}}\cdot CF_3SO_3\cdot CH_2Cl_2$.

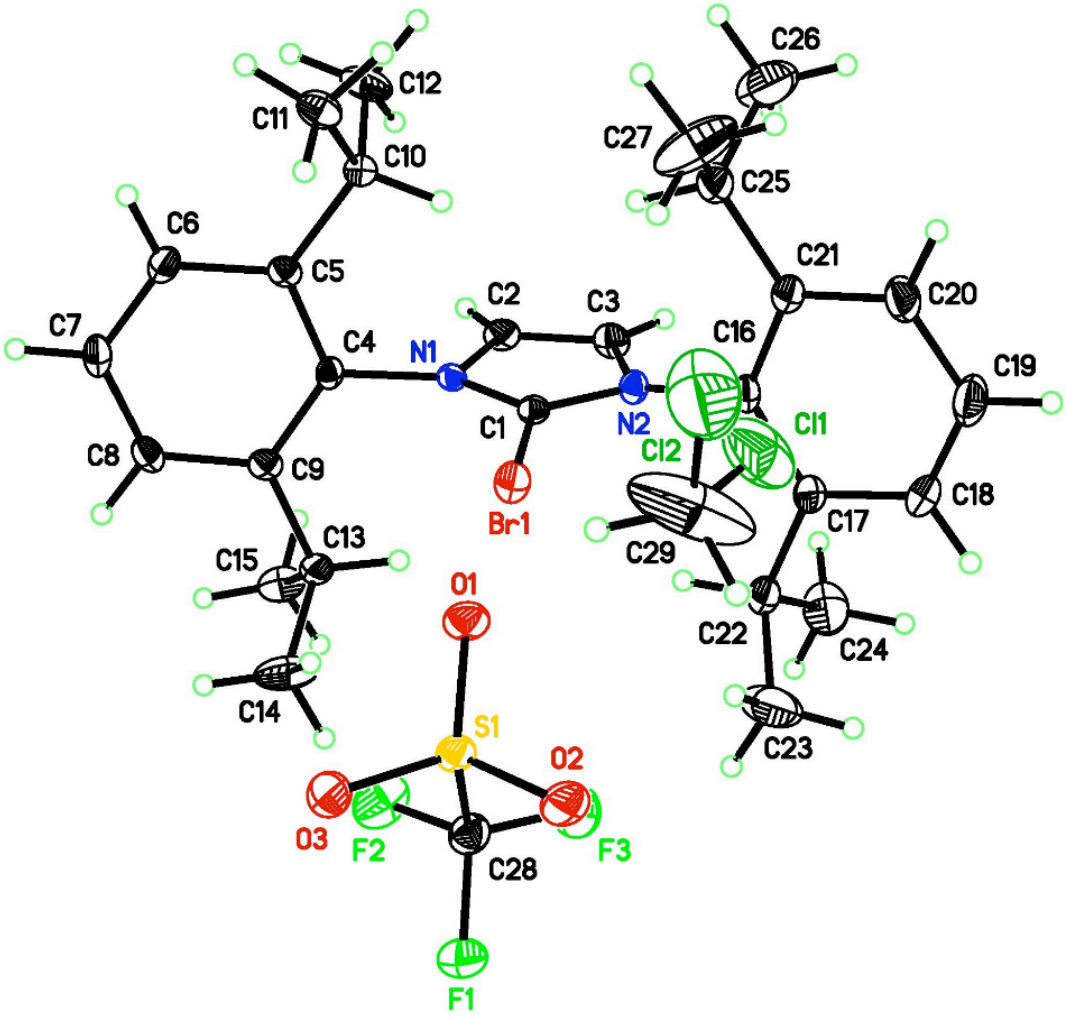

Table S7. Crystal data and structure refinement for $\mathbf{2_{Br}}\cdot CF_3SO_3\cdot CH_2Cl_2$.

Empirical formula	$C_{29}H_{38}BrCl_2F_3N_2O_3S$
Formula weight	702.48
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 10.3704(3) Å α = 89.1950(10)°
	b = 11.6440(3) Å β = 75.2830(10)°
	c = 16.0199(4) Å γ = 63.5760(10)°
Volume	1664.53(8) Å^3
Z	2
Density (calculated)	1.402 g.cm^{-3}
Absorption coefficient (μ)	1.506 mm^{-1}
F(000)	724
Crystal size	0.34 × 0.16 × 0.15 mm^3
θ range for data collection	1.97 to 26.42°
Index ranges	$-12 \le h \le 12$, $-14 \le k \le 14$, $-19 \le l \le 20$
Reflections collected	24895
Independent reflections	6786 [R_{int} = 0.0311]
Completeness to θ = 26.42°	99.3 %
Absorption correction	numerical
Max. and min. transmission	0.8056 and 0.6284
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6786 / 0 / 378
Goodness-of-fit on F^2	1.059
Final R indices [I>2σ(I)]	R_1 = 0.0384, wR_2 = 0.0908
R indices (all data)	R_1 = 0.0466, wR_2 = 0.0953
Largest diff. peak and hole	1.299 and -0.911 e$^-$.Å^{-3}

Table S8. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for $\mathbf{2_{Br}}\cdot CF_3SO_3\cdot CH_2Cl_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Br(1)	0.76760(3)	0.42414(2)	0.28360(2)	0.018(1)
N(1)	0.8297(2)	0.17943(18)	0.34299(12)	0.011(1)
N(2)	0.8356(2)	0.17925(19)	0.20647(12)	0.014(1)
C(1)	0.8116(3)	0.2527(2)	0.27782(15)	0.012(1)
C(2)	0.8671(3)	0.0545(2)	0.31185(16)	0.016(1)
C(3)	0.8710(3)	0.0546(2)	0.22737(16)	0.017(1)
C(4)	0.7964(3)	0.2233(2)	0.43448(14)	0.013(1)
C(5)	0.6499(3)	0.2616(2)	0.48600(15)	0.014(1)
C(6)	0.6226(3)	0.2937(2)	0.57487(15)	0.017(1)
C(7)	0.7357(3)	0.2883(2)	0.60820(16)	0.018(1)
C(8)	0.8786(3)	0.2528(2)	0.55431(16)	0.017(1)
C(9)	0.9125(3)	0.2189(2)	0.46533(15)	0.015(1)
C(10)	0.5260(3)	0.2675(2)	0.44921(16)	0.016(1)
C(11)	0.3771(3)	0.3887(2)	0.48708(17)	0.020(1)
C(12)	0.5056(3)	0.1452(3)	0.4632(2)	0.025(1)
C(13)	1.0685(3)	0.1807(3)	0.40706(16)	0.019(1)
C(14)	1.1073(3)	0.2929(3)	0.4092(2)	0.034(1)
C(15)	1.1855(3)	0.0596(3)	0.43214(19)	0.026(1)
C(16)	0.8055(3)	0.2258(2)	0.12542(15)	0.015(1)
C(17)	0.9216(3)	0.2270(2)	0.05918(16)	0.019(1)
C(18)	0.8878(3)	0.2685(3)	-0.01842(17)	0.026(1)
C(19)	0.7458(3)	0.3075(3)	-0.02729(18)	0.030(1)
C(20)	0.6333(3)	0.3057(3)	0.04044(17)	0.027(1)
C(21)	0.6602(3)	0.2640(3)	0.11876(16)	0.019(1)
C(22)	1.0778(3)	0.1858(3)	0.06793(17)	0.023(1)
C(23)	1.1245(4)	0.2936(4)	0.0478(2)	0.046(1)
C(24)	1.1905(3)	0.0617(3)	0.0085(2)	0.036(1)
C(25)	0.5353(3)	0.2625(3)	0.19260(17)	0.023(1)
C(26)	0.4865(4)	0.1635(4)	0.1699(2)	0.051(1)
C(27)	0.4049(4)	0.3955(3)	0.2195(3)	0.055(1)

S(1)	0.80545(7)	0.75568(6)	0.28162(4)	0.016(1)
F(1)	1.09282(18)	0.68670(16)	0.23778(10)	0.028(1)
F(2)	1.02907(19)	0.56084(16)	0.31868(11)	0.034(1)
F(3)	1.03590(19)	0.55346(16)	0.18316(11)	0.035(1)
O(1)	0.7218(2)	0.68224(17)	0.29617(11)	0.021(1)
O(2)	0.7966(2)	0.82349(18)	0.20531(12)	0.024(1)
O(3)	0.7941(2)	0.82738(18)	0.35812(12)	0.025(1)
C(28)	1.0000(3)	0.6325(3)	0.25390(17)	0.021(1)
Cl(1)	0.55898(12)	0.64591(10)	0.13399(7)	0.058(1)
Cl(2)	0.30823(14)	0.90359(12)	0.19508(7)	0.070(1)
C(29)	0.4976(6)	0.8056(4)	0.1769(5)	0.095(2)
H(2A)	0.8863	-0.0174	0.3443	0.019
H(3A)	0.8939	-0.0174	0.1890	0.021
H(6A)	0.5252	0.3194	0.6128	0.020
H(7A)	0.7153	0.3093	0.6688	0.022
H(8A)	0.9541	0.2516	0.5782	0.021
H(10A)	0.5577	0.2704	0.3851	0.020
H(11A)	0.3948	0.4648	0.4848	0.031
H(11B)	0.3340	0.3810	0.5476	0.031
H(11C)	0.3074	0.3979	0.4531	0.031
H(12A)	0.6003	0.0691	0.4357	0.038
H(12B)	0.4279	0.1493	0.4373	0.038
H(12C)	0.4756	0.1393	0.5256	0.038
H(13A)	1.0695	0.1615	0.3462	0.022
H(14A)	1.0308	0.3696	0.3933	0.051
H(14B)	1.2052	0.2695	0.3680	0.051
H(14C)	1.1108	0.3113	0.4679	0.051
H(15A)	1.1562	-0.0097	0.4330	0.039
H(15B)	1.1922	0.0783	0.4899	0.039
H(15C)	1.2832	0.0326	0.3896	0.039
H(18A)	0.9637	0.2699	-0.0658	0.031
H(19A)	0.7251	0.3359	-0.0804	0.036
H(20A)	0.5361	0.3335	0.0332	0.032
H(22A)	1.0769	0.1685	0.1293	0.028
H(23A)	1.0466	0.3744	0.0828	0.068
H(23B)	1.1375	0.3049	-0.0140	0.068

H(23C)	1.2191	0.2701	0.0618	0.068
H(24A)	1.1600	-0.0063	0.0228	0.054
H(24B)	1.2900	0.0348	0.0167	0.054
H(24C)	1.1938	0.0770	-0.0521	0.054
H(25A)	0.5765	0.2355	0.2436	0.027
H(26A)	0.4069	0.1647	0.2190	0.077
H(26B)	0.5723	0.0773	0.1577	0.077
H(26C)	0.4491	0.1852	0.1186	0.077
H(27A)	0.4399	0.4556	0.2350	0.082
H(27B)	0.3296	0.3929	0.2698	0.082
H(27C)	0.3603	0.4244	0.1712	0.082
H(29A)	0.5234	0.8039	0.2325	0.114
H(29B)	0.5529	0.8439	0.1363	0.114

Table S9. Anisotropic displacement parameters ($Å^2$) for $\mathbf{2_{Br}}\cdot CF_3SO_3\cdot CH_2Cl_2$.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2\, a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br(1)	0.0249(2)	0.0132(1)	0.0161(1)	0.0021(1)	-0.0050(1)	-0.0088(1)
N(1)	0.0125(10)	0.0114(10)	0.0121(9)	0.0018(7)	-0.0038(8)	-0.0069(8)
N(2)	0.0169(10)	0.0123(10)	0.0113(9)	0.0006(8)	-0.0034(8)	-0.0068(8)
C(1)	0.0109(11)	0.0114(11)	0.0134(11)	0.0010(9)	-0.0027(9)	-0.0049(9)
C(2)	0.0200(13)	0.0111(12)	0.0198(12)	0.0031(9)	-0.0047(10)	-0.0099(10)
C(3)	0.0203(13)	0.0126(12)	0.0202(13)	0.0000(10)	-0.0053(10)	-0.0082(10)
C(4)	0.0189(12)	0.0121(11)	0.0101(11)	0.0037(9)	-0.0047(9)	-0.0089(10)
C(5)	0.0169(12)	0.0117(11)	0.0163(12)	0.0041(9)	-0.0060(10)	-0.0088(10)
C(6)	0.0199(13)	0.0164(12)	0.0131(11)	0.0013(9)	-0.0014(10)	-0.0092(10)
C(7)	0.0276(14)	0.0166(12)	0.0118(11)	0.0013(9)	-0.0065(10)	-0.0106(11)
C(8)	0.0232(13)	0.0176(13)	0.0172(12)	0.0052(10)	-0.0111(10)	-0.0119(11)
C(9)	0.0186(13)	0.0126(12)	0.0172(12)	0.0060(9)	-0.0067(10)	-0.0099(10)
C(10)	0.0160(12)	0.0206(13)	0.0148(12)	0.0015(10)	-0.0037(10)	-0.0104(11)
C(11)	0.0195(13)	0.0171(13)	0.0275(14)	0.0046(10)	-0.0107(11)	-0.0088(11)
C(12)	0.0192(14)	0.0173(13)	0.0423(17)	-0.0022(12)	-0.0102(12)	-0.0097(11)
C(13)	0.0179(13)	0.0272(14)	0.0162(12)	0.0067(10)	-0.0070(10)	-0.0137(11)
C(14)	0.0251(16)	0.0276(16)	0.055(2)	0.0180(14)	-0.0094(14)	-0.0172(13)
C(15)	0.0213(14)	0.0217(14)	0.0328(15)	0.0046(12)	-0.0041(12)	-0.0106(12)
C(16)	0.0204(13)	0.0163(12)	0.0104(11)	0.0008(9)	-0.0053(10)	-0.0084(10)
C(17)	0.0208(13)	0.0213(13)	0.0141(12)	-0.0013(10)	-0.0031(10)	-0.0105(11)
C(18)	0.0282(15)	0.0372(17)	0.0139(12)	0.0047(11)	-0.0023(11)	-0.0189(13)
C(19)	0.0312(16)	0.0422(18)	0.0162(13)	0.0091(12)	-0.0090(12)	-0.0147(14)
C(20)	0.0209(14)	0.0389(17)	0.0189(13)	0.0035(12)	-0.0096(11)	-0.0105(13)
C(21)	0.0187(13)	0.0247(14)	0.0138(12)	0.0006(10)	-0.0032(10)	-0.0099(11)
C(22)	0.0208(14)	0.0354(16)	0.0148(12)	0.0019(11)	-0.0037(11)	-0.0144(13)
C(23)	0.039(2)	0.054(2)	0.058(2)	0.0015(18)	-0.0146(17)	-0.0326(18)
C(24)	0.0273(16)	0.0382(18)	0.0324(16)	-0.0014(14)	-0.0083(13)	-0.0065(14)
C(25)	0.0179(13)	0.0304(15)	0.0180(13)	0.0010(11)	-0.0051(10)	-0.0092(12)
C(26)	0.052(2)	0.064(3)	0.041(2)	-0.0132(18)	0.0120(17)	-0.042(2)
C(27)	0.035(2)	0.0341(19)	0.063(2)	0.0033(17)	0.0224(17)	-0.0072(16)

S(1)	0.0201(3)	0.0133(3)	0.0168(3)	0.0022(2)	-0.0033(2)	-0.0097(3)
F(1)	0.0236(8)	0.0371(10)	0.0286(9)	0.0055(7)	-0.0055(7)	-0.0188(8)
F(2)	0.0326(10)	0.0306(9)	0.0356(10)	0.0174(8)	-0.0118(8)	-0.0102(8)
F(3)	0.0339(10)	0.0292(9)	0.0324(9)	-0.0139(7)	0.0002(8)	-0.0104(8)
O(1)	0.0251(10)	0.0174(9)	0.0238(9)	0.0029(7)	-0.0045(8)	-0.0137(8)
O(2)	0.0296(11)	0.0240(10)	0.0252(10)	0.0115(8)	-0.0099(8)	-0.0163(9)
O(3)	0.0331(11)	0.0213(10)	0.0209(9)	-0.0036(8)	-0.0011(8)	-0.0165(9)
C(28)	0.0249(14)	0.0199(13)	0.0192(13)	0.0029(10)	-0.0040(11)	-0.0119(12)
Cl(1)	0.0700(7)	0.0586(6)	0.0750(7)	0.0331(5)	-0.0534(6)	-0.0383(5)
Cl(2)	0.0746(8)	0.0777(8)	0.0585(6)	0.0070(6)	-0.0260(6)	-0.0318(6)
C(29)	0.080(3)	0.055(3)	0.197(7)	0.047(4)	-0.089(4)	-0.046(3)

Table S10. Bond lengths [Å] for $\mathbf{2_{Br}}\cdot CF_3SO_3\cdot CH_2Cl_2$.

atom-atom	distance	atom-atom	distance
Br(1)-C(1)	1.837(2)	N(1)-C(1)	1.336(3)
N(1)-C(2)	1.391(3)	N(1)-C(4)	1.461(3)
N(2)-C(1)	1.339(3)	N(2)-C(3)	1.388(3)
N(2)-C(16)	1.454(3)	C(2)-C(3)	1.344(3)
C(4)-C(9)	1.394(3)	C(4)-C(5)	1.399(3)
C(5)-C(6)	1.401(3)	C(5)-C(10)	1.520(3)
C(6)-C(7)	1.385(4)	C(7)-C(8)	1.388(4)
C(8)-C(9)	1.396(3)	C(9)-C(13)	1.514(3)
C(10)-C(11)	1.534(3)	C(10)-C(12)	1.535(4)
C(13)-C(15)	1.527(4)	C(13)-C(14)	1.531(4)
C(16)-C(17)	1.393(4)	C(16)-C(21)	1.401(4)
C(17)-C(18)	1.399(4)	C(17)-C(22)	1.514(4)
C(18)-C(19)	1.379(4)	C(19)-C(20)	1.384(4)
C(20)-C(21)	1.389(4)	C(21)-C(25)	1.523(4)
C(22)-C(24)	1.526(4)	C(22)-C(23)	1.538(4)
C(25)-C(27)	1.507(4)	C(25)-C(26)	1.530(4)
S(1)-O(3)	1.4426(18)	S(1)-O(1)	1.4455(18)
S(1)-O(2)	1.4463(18)	S(1)-C(28)	1.820(3)
F(1)-C(28)	1.341(3)	F(2)-C(28)	1.333(3)
F(3)-C(28)	1.334(3)	Cl(1)-C(29)	1.760(5)
Cl(2)-C(29)	1.723(5)	C(2)-H(2A)	0.9500
C(3)-H(3A)	0.9500	C(6)-H(6A)	0.9500
C(7)-H(7A)	0.9500	C(8)-H(8A)	0.9500
C(10)-H(10A)	1.0000	C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800	C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800	C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800	C(13)-H(13A)	1.0000
C(14)-H(14A)	0.9800	C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800	C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800	C(15)-H(15C)	0.9800
C(18)-H(18A)	0.9500	C(19)-H(19A)	0.9500
C(20)-H(20A)	0.9500	C(22)-H(22A)	1.0000
C(23)-H(23A)	0.9800	C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800	C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800	C(24)-H(24C)	0.9800
C(25)-H(25A)	1.0000	C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800	C(26)-H(26C)	0.9800
C(27)-H(27A)	0.9800	C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800	C(29)-H(29A)	0.9900
C(29)-H(29B)	0.9900		

Table S11. Bond angles [°] for $\mathbf{2_{Br}}\cdot CF_3SO_3\cdot CH_2Cl_2$.

atom-atom-atom	angle	atom-atom-atom	angle
C(1)-N(1)-C(2)	108.44(19)	C(1)-N(1)-C(4)	126.89(19)
C(2)-N(1)-C(4)	124.16(19)	C(1)-N(2)-C(3)	108.27(19)
C(1)-N(2)-C(16)	125.8(2)	C(3)-N(2)-C(16)	125.2(2)
N(1)-C(1)-N(2)	108.6(2)	N(1)-C(1)-Br(1)	125.93(17)
N(2)-C(1)-Br(1)	125.44(17)	C(3)-C(2)-N(1)	107.2(2)
C(2)-C(3)-N(2)	107.5(2)	C(9)-C(4)-C(5)	124.5(2)
C(4)-C(5)-C(6)	116.3(2)	C(4)-C(5)-C(10)	122.7(2)
C(6)-C(5)-C(10)	121.0(2)	C(7)-C(6)-C(5)	120.8(2)
C(9)-C(4)-N(1)	118.5(2)	C(5)-C(4)-N(1)	117.0(2)
C(6)-C(7)-C(8)	120.9(2)	C(7)-C(8)-C(9)	120.7(2)
C(4)-C(9)-C(8)	116.7(2)	C(4)-C(9)-C(13)	123.0(2)
C(8)-C(9)-C(13)	120.3(2)	C(5)-C(10)-C(11)	112.5(2)
C(5)-C(10)-C(12)	110.6(2)	C(11)-C(10)-C(12)	110.6(2)
C(9)-C(13)-C(15)	111.6(2)	C(9)-C(13)-C(14)	110.2(2)
C(15)-C(13)-C(14)	110.8(2)	C(17)-C(16)-C(21)	124.2(2)
C(17)-C(16)-N(2)	118.8(2)	C(21)-C(16)-N(2)	116.9(2)
C(16)-C(17)-C(18)	116.4(2)	C(16)-C(17)-C(22)	123.4(2)
C(18)-C(17)-C(22)	120.2(2)	C(19)-C(18)-C(17)	121.0(3)
C(18)-C(19)-C(20)	120.7(3)	C(19)-C(20)-C(21)	121.1(3)
C(20)-C(21)-C(16)	116.5(2)	C(20)-C(21)-C(25)	120.4(2)
C(16)-C(21)-C(25)	123.0(2)	C(17)-C(22)-C(24)	110.7(2)
C(17)-C(22)-C(23)	110.8(2)	C(24)-C(22)-C(23)	110.5(3)
C(27)-C(25)-C(21)	111.2(2)	C(27)-C(25)-C(26)	111.8(3)
C(21)-C(25)-C(26)	111.7(2)	O(3)-S(1)-O(1)	115.35(11)
O(3)-S(1)-O(2)	115.44(11)	O(1)-S(1)-O(2)	114.58(11)
O(3)-S(1)-C(28)	101.92(12)	O(1)-S(1)-C(28)	103.72(12)
O(2)-S(1)-C(28)	103.24(12)	F(2)-C(28)-F(3)	107.9(2)
F(2)-C(28)-F(1)	107.3(2)	F(3)-C(28)-F(1)	107.2(2)
F(2)-C(28)-S(1)	111.39(18)	F(3)-C(28)-S(1)	112.15(18)
F(1)-C(28)-S(1)	110.74(18)	Cl(2)-C(29)-Cl(1)	114.4(2)
C(3)-C(2)-H(2A)	126.4	N(1)-C(2)-H(2A)	126.4
C(2)-C(3)-H(3A)	126.2	N(2)-C(3)-H(3A)	126.2
C(7)-C(6)-H(6A)	119.6	C(5)-C(6)-H(6A)	119.6
C(6)-C(7)-H(7A)	119.5	C(8)-C(7)-H(7A)	119.5
C(7)-C(8)-H(8A)	119.7	C(9)-C(8)-H(8A)	119.7
C(5)-C(10)-H(10A)	107.6	C(11)-C(10)-H(10A)	107.6
C(12)-C(10)-H(10A)	107.6	C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5	H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5	H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5	C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5

H(12B)-C(12)-H(12C)	109.5	C(9)-C(13)-H(13A)	108.0
C(15)-C(13)-H(13A)	108.0	C(14)-C(13)-H(13A)	108.0
C(13)-C(14)-H(14A)	109.5	C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5	C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5	H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5	C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5	C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5	H(15B)-C(15)-H(15C)	109.5
C(19)-C(18)-H(18A)	119.5	C(17)-C(18)-H(18A)	119.5
C(18)-C(19)-H(19A)	119.6	C(20)-C(19)-H(19A)	119.6
C(19)-C(20)-H(20A)	119.5	C(21)-C(20)-H(20A)	119.5
C(17)-C(22)-H(22A)	108.3	C(24)-C(22)-H(22A)	108.3
C(23)-C(22)-H(22A)	108.3	C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5	H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5	H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5	C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5	H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5	H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5	C(27)-C(25)-H(25A)	107.3
C(21)-C(25)-H(25A)	107.3	C(26)-C(25)-H(25A)	107.3
C(25)-C(26)-H(26A)	109.5	C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5	C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5	H(26B)-C(26)-H(26C)	109.5
C(25)-C(27)-H(27A)	109.5	C(25)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5	C(25)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5	H(27B)-C(27)-H(27C)	109.5
Cl(2)-C(29)-H(29A)	108.7	Cl(1)-C(29)-H(29A)	108.7
Cl(2)-C(29)-H(29B)	108.7	Cl(1)-C(29)-H(29B)	108.7
H(29A)-C(29)-H(29B)	107.6		

Table S12. Torsion angles [°] for $\mathbf{2}_{\mathbf{Br}}\cdot CF_3SO_3\cdot CH_2Cl_2$.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(2)-N(1)-C(1)-N(2)	0.2(3)	C(4)-N(1)-C(1)-N(2)	-171.8(2)
		C(2)-N(1)-C(1)-Br(1)	-177.85(17)
		C(4)-N(1)-C(1)-Br(1)	10.1(3)
		C(3)-N(2)-C(1)-N(1)	-0.3(3)
		C(16)-N(2)-C(1)-N(1)	170.2(2)
		C(3)-N(2)-C(1)-Br(1)	177.74(18)
		C(16)-N(2)-C(1)-Br(1)	-11.7(3)
		C(1)-N(1)-C(2)-C(3)	0.0(3)
		C(4)-N(1)-C(2)-C(3)	172.3(2)
		N(1)-C(2)-C(3)-N(2)	-0.2(3)
		C(1)-N(2)-C(3)-C(2)	0.3(3)
		C(16)-N(2)-C(3)-C(2)	-170.3(2)
		C(1)-N(1)-C(4)-C(9)	-95.6(3)
		C(2)-N(1)-C(4)-C(9)	93.6(3)
		C(1)-N(1)-C(4)-C(5)	87.2(3)
		C(2)-N(1)-C(4)-C(5)	-83.7(3)
		C(9)-C(4)-C(5)-C(6)	-1.9(4)
		N(1)-C(4)-C(5)-C(6)	175.1(2)
		C(9)-C(4)-C(5)-C(10)	178.8(2)
		N(1)-C(4)-C(5)-C(10)	-4.2(3)
		C(4)-C(5)-C(6)-C(7)	0.7(4)
		C(10)-C(5)-C(6)-C(7)	-179.9(2)
		C(5)-C(6)-C(7)-C(8)	0.9(4)
		C(6)-C(7)-C(8)-C(9)	-1.4(4)
		C(5)-C(4)-C(9)-C(8)	1.4(4)
		N(1)-C(4)-C(9)-C(8)	-175.6(2)
		C(5)-C(4)-C(9)-C(13)	-178.1(2)
		N(1)-C(4)-C(9)-C(13)	5.0(3)
		C(7)-C(8)-C(9)-C(4)	0.3(4)
		C(7)-C(8)-C(9)-C(13)	179.8(2)
		C(4)-C(5)-C(10)-C(11)	-137.7(2)
		C(6)-C(5)-C(10)-C(11)	43.0(3)
		C(4)-C(5)-C(10)-C(12)	98.0(3)
		C(6)-C(5)-C(10)-C(12)	-81.3(3)
		C(4)-C(9)-C(13)-C(15)	-118.3(3)
		C(8)-C(9)-C(13)-C(15)	62.3(3)
		C(4)-C(9)-C(13)-C(14)	118.2(3)
		C(8)-C(9)-C(13)-C(14)	-61.3(3)
		C(1)-N(2)-C(16)-C(17)	94.9(3)
		C(3)-N(2)-C(16)-C(17)	-96.1(3)
		C(1)-N(2)-C(16)-C(21)	-86.5(3)
		C(3)-N(2)-C(16)-C(21)	82.5(3)

C(21)-C(16)-C(17)-C(18)	-0.6(4)
N(2)-C(16)-C(17)-C(18)	177.9(2)
C(21)-C(16)-C(17)-C(22)	179.8(2)
N(2)-C(16)-C(17)-C(22)	-1.8(4)
C(16)-C(17)-C(18)-C(19)	0.9(4)
C(22)-C(17)-C(18)-C(19)	-179.4(3)
C(17)-C(18)-C(19)-C(20)	-0.4(5)
C(18)-C(19)-C(20)-C(21)	-0.4(5)
C(19)-C(20)-C(21)-C(16)	0.7(4)
C(19)-C(20)-C(21)-C(25)	-179.9(3)
C(17)-C(16)-C(21)-C(20)	-0.2(4)
N(2)-C(16)-C(21)-C(20)	-178.7(2)
C(17)-C(16)-C(21)-C(25)	-179.5(2)
N(2)-C(16)-C(21)-C(25)	2.0(4)
C(16)-C(17)-C(22)-C(24)	112.4(3)
C(18)-C(17)-C(22)-C(24)	-67.3(3)
C(16)-C(17)-C(22)-C(23)	-124.7(3)
C(18)-C(17)-C(22)-C(23)	55.6(3)
C(20)-C(21)-C(25)-C(27)	-59.1(4)
C(16)-C(21)-C(25)-C(27)	120.2(3)
C(20)-C(21)-C(25)-C(26)	66.7(4)
C(16)-C(21)-C(25)-C(26)	-114.1(3)
O(3)-S(1)-C(28)-F(2)	59.1(2)
O(1)-S(1)-C(28)-F(2)	-61.1(2)
O(2)-S(1)-C(28)-F(2)	179.11(18)
O(3)-S(1)-C(28)-F(3)	-179.92(18)
O(1)-S(1)-C(28)-F(3)	59.9(2)
O(2)-S(1)-C(28)-F(3)	-59.9(2)
O(3)-S(1)-C(28)-F(1)	-60.26(19)
O(1)-S(1)-C(28)-F(1)	179.60(17)
O(2)-S(1)-C(28)-F(1)	59.78(19)

Figure S3. Crystal structure for $\mathbf{2_I}\cdot I_3$.

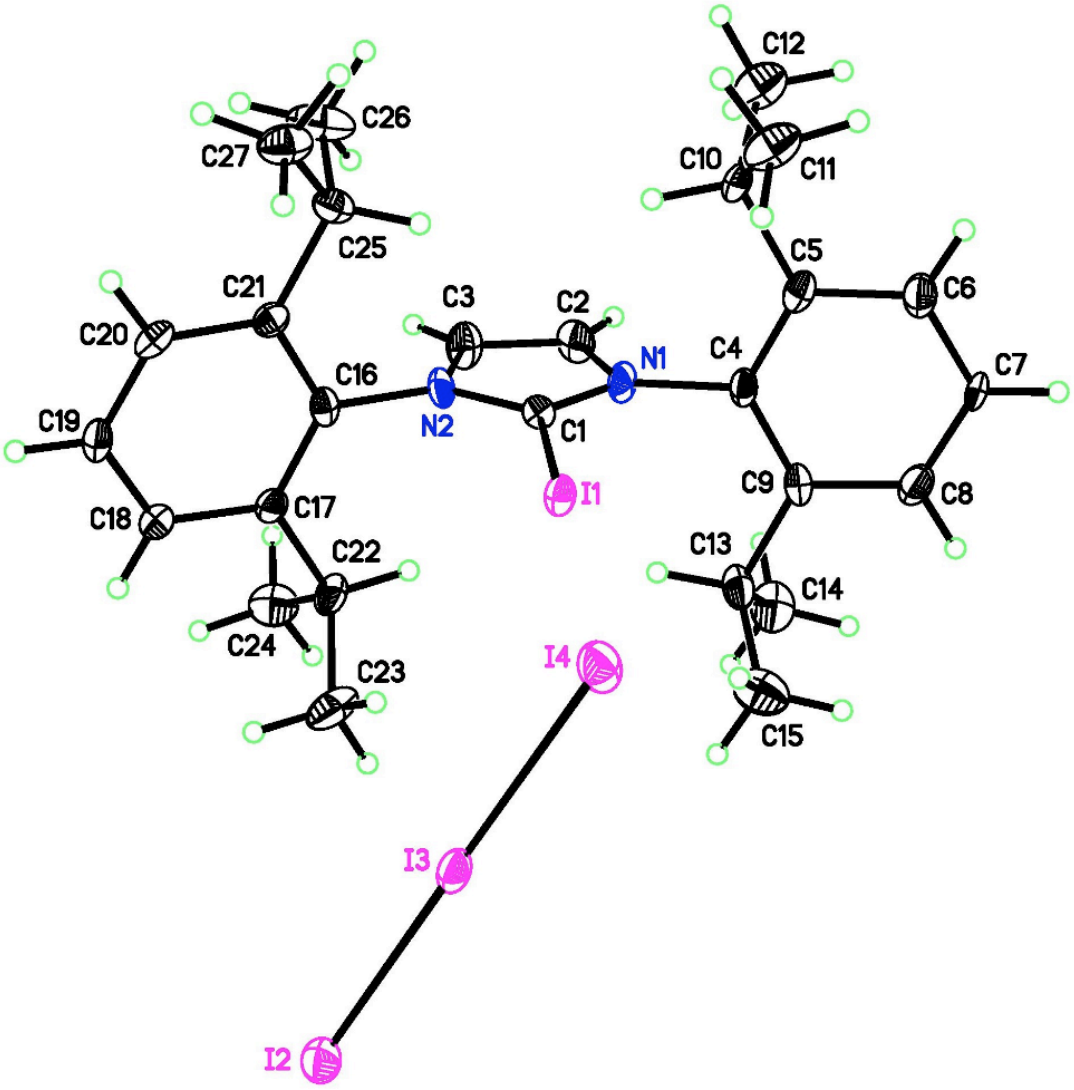

Table S13 Crystal data and structure refinement for $\mathbf{2_I}\cdot I_3$.

Empirical formula	$C_{27}H_{36}I_4N_2$
Formula weight	896.18
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 10.0574(3) Å α = 89.812(2)°
	b = 10.0847(2) Å β = 72.816(2)°
	c = 16.5285(4) Å γ = 77.8020(10)°
Volume	1562.28(7) $Å^3$
Z	2
Density (calculated)	1.905 $g.cm^{-3}$
Absorption coefficient (μ)	31.441 mm^{-1}
F(000)	848
Crystal size	0.17 × 0.08 × 0.04 mm^3
θ range for data collection	2.80 to 69.56°
Index ranges	$-12 \le h \le 11$, $-12 \le k \le 12$, $-18 \le l \le 20$
Reflections collected	15215
Independent reflections	5458 [R_{int} = 0.0427]
Completeness to θ = 69.56°	93.0 %
Absorption correction	numerical
Max. and min. transmission	0.5844 and 0.2559
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5458 / 0 / 306
Goodness-of-fit on F^2	1.028
Final R indices [I>2σ(I)]	R_1 = 0.0350, wR_2 = 0.0779
R indices (all data)	R_1 = 0.0489, wR_2 = 0.0836
Largest diff. peak and hole	1.114 and -1.097 $e^-.Å^{-3}$

Table S14. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for $\mathbf{2_I}\cdot I_3$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij}tensor.

	x	y	z	U(eq)
I(1)	0.41104(4)	0.47752(4)	0.26810(2)	0.016(1)
N(1)	0.5259(5)	0.1899(5)	0.3119(3)	0.019(1)
N(2)	0.5355(5)	0.1912(5)	0.1796(3)	0.019(1)
C(1)	0.5002(6)	0.2710(5)	0.2510(4)	0.014(1)
C(2)	0.5768(7)	0.0565(6)	0.2782(4)	0.023(1)
C(3)	0.5818(7)	0.0585(6)	0.1946(4)	0.024(1)
C(4)	0.5102(6)	0.2316(6)	0.3990(4)	0.017(1)
C(5)	0.6276(7)	0.2612(6)	0.4171(4)	0.019(1)
C(6)	0.6131(7)	0.2889(6)	0.5026(4)	0.023(1)
C(7)	0.4871(6)	0.2865(7)	0.5653(4)	0.021(1)
C(8)	0.3709(7)	0.2601(6)	0.5446(4)	0.023(1)
C(9)	0.3797(7)	0.2307(6)	0.4603(4)	0.019(1)
C(10)	0.7677(6)	0.2639(6)	0.3498(4)	0.021(1)
C(11)	0.8063(7)	0.4016(6)	0.3556(5)	0.030(2)
C(12)	0.8864(7)	0.1488(7)	0.3574(5)	0.033(2)
C(13)	0.2480(7)	0.2064(7)	0.4398(4)	0.023(1)
C(14)	0.2018(8)	0.0831(7)	0.4845(5)	0.033(2)
C(15)	0.1250(8)	0.3332(7)	0.4652(5)	0.035(2)
C(16)	0.5245(6)	0.2367(5)	0.0967(4)	0.015(1)
C(17)	0.4027(6)	0.2256(6)	0.0760(4)	0.017(1)
C(18)	0.3965(6)	0.2640(6)	-0.0045(4)	0.020(1)
C(19)	0.5073(7)	0.3090(6)	-0.0594(4)	0.020(1)
C(20)	0.6262(6)	0.3206(6)	-0.0357(4)	0.022(1)
C(21)	0.6394(6)	0.2837(6)	0.0427(4)	0.017(1)
C(22)	0.2764(7)	0.1789(6)	0.1371(4)	0.022(1)
C(23)	0.1420(7)	0.2950(7)	0.1550(5)	0.033(2)
C(24)	0.2531(7)	0.0513(7)	0.0992(5)	0.030(2)
C(25)	0.7724(6)	0.2889(6)	0.0671(4)	0.020(1)
C(26)	0.8774(7)	0.1505(7)	0.0456(6)	0.039(2)
C(27)	0.8464(7)	0.3997(7)	0.0227(5)	0.028(2)
I(2)	-0.22428(4)	0.69457(4)	0.19300(3)	0.024(1)

I(3)	0.00868(4)	0.75069(4)	0.24538(2)	0.020(1)
I(4)	0.24481(5)	0.81179(4)	0.29950(3)	0.027(1)
H(2A)	0.6030	-0.0211	0.3075	0.027
H(3A)	0.6117	-0.0176	0.1546	0.029
H(6A)	0.6908	0.3096	0.5179	0.028
H(7A)	0.4803	0.3030	0.6231	0.026
H(8A)	0.2842	0.2621	0.5883	0.028
H(10A)	0.7545	0.2519	0.2929	0.025
H(11A)	0.7252	0.4745	0.3547	0.045
H(11B)	0.8891	0.4070	0.3073	0.045
H(11C)	0.8293	0.4115	0.4086	0.045
H(12A)	0.8622	0.0616	0.3493	0.049
H(12B)	0.8985	0.1561	0.4138	0.049
H(12C)	0.9755	0.1541	0.3140	0.049
H(13A)	0.2737	0.1865	0.3772	0.028
H(14A)	0.2826	0.0045	0.4695	0.049
H(14B)	0.1233	0.0627	0.4665	0.049
H(14C)	0.1699	0.1032	0.5461	0.049
H(15A)	0.1572	0.4114	0.4370	0.053
H(15B)	0.0953	0.3519	0.5268	0.053
H(15C)	0.0442	0.3172	0.4479	0.053
H(18A)	0.3150	0.2589	-0.0212	0.024
H(19A)	0.5028	0.3325	-0.1144	0.023
H(20A)	0.7000	0.3547	-0.0742	0.026
H(22A)	0.2980	0.1576	0.1917	0.026
H(23A)	0.0603	0.2648	0.1929	0.049
H(23B)	0.1228	0.3195	0.1015	0.049
H(23C)	0.1577	0.3743	0.1820	0.049
H(24A)	0.3406	-0.0199	0.0865	0.044
H(24B)	0.2284	0.0722	0.0467	0.044
H(24C)	0.1752	0.0197	0.1398	0.044
H(25A)	0.7439	0.3095	0.1298	0.024
H(26A)	0.8304	0.0801	0.0745	0.059
H(26B)	0.9605	0.1532	0.0644	0.059
H(26C)	0.9082	0.1295	-0.0158	0.059
H(27A)	0.7762	0.4861	0.0305	0.042

H(27B)	0.8889	0.3735	-0.0380	0.042
H(27C)	0.9214	0.4102	0.0473	0.042

Table S15. Anisotropic displacement parameters $(Å)^2$ for $\mathbf{2_I}\cdot I_3$.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2[\, h^2a^{*2}\, U_{11} + ... \, + 2\, h\, k\, a^*\, b^*\, U_{12}\,]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I(1)	0.0215(2)	0.0142(2)	0.0122(2)	-0.0009(1)	-0.0047(1)	-0.0026(1)
N(1)	0.025(3)	0.017(2)	0.014(3)	-0.007(2)	-0.006(2)	0.001(2)
N(2)	0.023(3)	0.023(3)	0.012(3)	-0.003(2)	-0.009(2)	-0.005(2)
C(1)	0.016(3)	0.012(3)	0.016(3)	0.002(2)	-0.006(2)	-0.003(2)
C(2)	0.029(3)	0.017(3)	0.022(4)	0.007(3)	-0.011(3)	0.000(3)
C(3)	0.034(4)	0.017(3)	0.021(3)	-0.005(3)	-0.009(3)	-0.004(3)
C(4)	0.022(3)	0.016(3)	0.012(3)	-0.003(2)	-0.007(2)	0.002(2)
C(5)	0.024(3)	0.017(3)	0.012(3)	0.002(2)	-0.002(2)	-0.002(2)
C(6)	0.028(3)	0.024(3)	0.017(3)	-0.002(3)	-0.008(3)	-0.002(3)
C(7)	0.020(3)	0.034(3)	0.006(3)	-0.004(3)	-0.001(2)	-0.002(3)
C(8)	0.024(3)	0.025(3)	0.016(3)	-0.002(3)	-0.001(3)	-0.001(3)
C(9)	0.026(3)	0.020(3)	0.013(3)	0.001(3)	-0.009(2)	-0.006(3)
C(10)	0.020(3)	0.026(3)	0.012(3)	-0.008(3)	0.000(2)	-0.002(3)
C(11)	0.027(3)	0.021(3)	0.034(4)	0.004(3)	0.003(3)	-0.002(3)
C(12)	0.031(4)	0.025(3)	0.035(4)	0.004(3)	-0.001(3)	-0.003(3)
C(13)	0.029(3)	0.030(3)	0.016(3)	0.005(3)	-0.010(3)	-0.014(3)
C(14)	0.041(4)	0.030(4)	0.032(4)	0.003(3)	-0.010(3)	-0.018(3)
C(15)	0.032(4)	0.033(4)	0.046(5)	0.012(4)	-0.017(3)	-0.012(3)
C(16)	0.022(3)	0.009(2)	0.013(3)	-0.002(2)	-0.007(2)	0.000(2)
C(17)	0.016(3)	0.018(3)	0.014(3)	-0.003(2)	-0.003(2)	-0.002(2)
C(18)	0.017(3)	0.023(3)	0.016(3)	-0.001(3)	-0.003(2)	-0.002(2)
C(19)	0.025(3)	0.021(3)	0.011(3)	0.001(3)	-0.005(2)	-0.004(3)
C(20)	0.017(3)	0.026(3)	0.016(3)	0.000(3)	0.003(2)	-0.004(2)
C(21)	0.016(3)	0.016(3)	0.016(3)	-0.003(2)	-0.002(2)	0.001(2)
C(22)	0.024(3)	0.027(3)	0.014(3)	0.003(3)	-0.001(2)	-0.010(3)
C(23)	0.023(3)	0.036(4)	0.031(4)	-0.008(3)	0.007(3)	-0.010(3)
C(24)	0.028(3)	0.025(3)	0.038(4)	0.006(3)	-0.009(3)	-0.012(3)
C(25)	0.016(3)	0.019(3)	0.024(3)	-0.002(3)	-0.008(2)	-0.003(2)
C(26)	0.020(3)	0.032(4)	0.068(6)	-0.004(4)	-0.017(4)	-0.005(3)
C(27)	0.020(3)	0.026(3)	0.036(4)	-0.005(3)	-0.005(3)	-0.007(3)

I(2)	0.0270(2)	0.0257(2)	0.0198(2)	-0.0013(2)	-0.0074(2)	-0.0032(2)
I(3)	0.0244(2)	0.0185(2)	0.0132(2)	-0.0032(2)	-0.0033(1)	-0.0008(2)
I(4)	0.0322(2)	0.0225(2)	0.0254(2)	-0.0048(2)	-0.0137(2)	0.0007(2)

Table S16. Bond lengths [Å] for $\mathbf{2_I}\cdot I_3$.

atom-atom	distance	atom-atom	distance
I(1)-C(1)	2.071(5)	N(1)-C(1)	1.345(8)
N(1)-C(2)	1.388(8)	N(1)-C(4)	1.456(7)
N(2)-C(1)	1.343(7)	N(2)-C(3)	1.369(8)
N(2)-C(16)	1.470(8)	C(2)-C(3)	1.369(9)
C(4)-C(5)	1.389(8)	C(4)-C(9)	1.402(8)
C(5)-C(6)	1.401(8)	C(5)-C(10)	1.521(8)
C(6)-C(7)	1.384(9)	C(7)-C(8)	1.386(9)
C(8)-C(9)	1.399(8)	C(9)-C(13)	1.528(8)
C(10)-C(12)	1.514(9)	C(10)-C(11)	1.529(8)
C(13)-C(14)	1.530(8)	C(13)-C(15)	1.539(9)
C(16)-C(17)	1.392(8)	C(16)-C(21)	1.406(8)
C(17)-C(18)	1.400(9)	C(17)-C(22)	1.532(8)
C(18)-C(19)	1.374(8)	C(19)-C(20)	1.390(9)
C(20)-C(21)	1.382(9)	C(21)-C(25)	1.518(8)
C(22)-C(24)	1.524(8)	C(22)-C(23)	1.544(9)
C(25)-C(26)	1.533(9)	C(25)-C(27)	1.538(8)
I(2)-I(3)	2.8847(5)	I(3)-I(4)	2.9491(6)
C(2)-H(2A)	0.9500	C(3)-H(3A)	0.9500
C(6)-H(6A)	0.9500	C(7)-H(7A)	0.9500
C(8)-H(8A)	0.9500	C(10)-H(10A)	1.0000
C(11)-H(11A)	0.9800	C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800	C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800	C(12)-H(12C)	0.9800
C(13)-H(13A)	1.0000	C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800	C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800	C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800	C(18)-H(18A)	0.9500
C(19)-H(19A)	0.9500	C(20)-H(20A)	0.9500
C(22)-H(22A)	1.0000	C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800	C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800	C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800	C(25)-H(25A)	1.0000
C(26)-H(26A)	0.9800	C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800	C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800	C(27)-H(27C)	0.9800

Table S17. Bond angles [°] for $\mathbf{2_I}\cdot I_3$.

atom-atom-atom	angle	atom-atom-atom	angle
C(1)-N(1)-C(2)	109.3(5)	C(1)-N(1)-C(4)	126.9(5)
C(2)-N(1)-C(4)	123.7(5)	C(1)-N(2)-C(3)	110.3(5)
C(1)-N(2)-C(16)	125.9(5)	C(3)-N(2)-C(16)	123.7(5)
N(2)-C(1)-N(1)	107.0(5)	N(2)-C(1)-I(1)	127.3(4)
N(1)-C(1)-I(1)	125.6(4)	C(3)-C(2)-N(1)	106.7(6)
C(2)-C(3)-N(2)	106.7(5)	C(5)-C(4)-C(9)	124.2(6)
C(5)-C(4)-N(1)	118.2(5)	C(9)-C(4)-N(1)	117.5(5)
C(4)-C(5)-C(6)	116.7(6)	C(4)-C(5)-C(10)	123.7(6)
C(6)-C(5)-C(10)	119.6(6)	C(7)-C(6)-C(5)	120.9(6)
C(6)-C(7)-C(8)	120.7(6)	C(7)-C(8)-C(9)	120.8(6)
C(8)-C(9)-C(4)	116.6(6)	C(8)-C(9)-C(13)	119.2(6)
C(4)-C(9)-C(13)	124.1(6)	C(12)-C(10)-C(5)	111.3(6)
C(12)-C(10)-C(11)	111.1(5)	C(5)-C(10)-C(11)	110.1(5)
C(9)-C(13)-C(14)	110.0(6)	C(9)-C(13)-C(15)	111.1(5)
C(14)-C(13)-C(15)	110.7(6)	C(17)-C(16)-C(21)	124.4(6)
C(17)-C(16)-N(2)	117.5(5)	C(21)-C(16)-N(2)	118.1(5)
C(16)-C(17)-C(18)	116.8(5)	C(16)-C(17)-C(22)	123.5(6)
C(18)-C(17)-C(22)	119.7(5)	C(19)-C(18)-C(17)	120.5(6)
C(18)-C(19)-C(20)	120.9(6)	C(21)-C(20)-C(19)	121.6(6)
C(20)-C(21)-C(16)	115.8(5)	C(20)-C(21)-C(25)	121.8(5)
C(16)-C(21)-C(25)	122.3(6)	C(24)-C(22)-C(17)	110.1(5)
C(24)-C(22)-C(23)	110.9(5)	C(17)-C(22)-C(23)	109.1(5)
C(21)-C(25)-C(26)	110.0(5)	C(21)-C(25)-C(27)	112.2(5)
C(26)-C(25)-C(27)	109.5(5)	I(2)-I(3)-I(4)	179.251(18)
	C(3)-C(2)-H(2A)	126.7	N(1)-C(2)-H(2A)
	126.7	C(2)-C(3)-H(3A)	126.7
N(2)-C(3)-H(3A)	126.7	C(7)-C(6)-H(6A)	119.6
C(5)-C(6)-H(6A)	119.6	C(6)-C(7)-H(7A)	119.6
C(8)-C(7)-H(7A)	119.6	C(7)-C(8)-H(8A)	119.6
C(9)-C(8)-H(8A)	119.6	C(12)-C(10)-H(10A)	108.1
C(5)-C(10)-H(10A)	108.1	C(11)-C(10)-H(10A)	108.1
C(10)-C(11)-H(11A)	109.5	C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5	C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5	H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5	C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5	C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5	H(12B)-C(12)-H(12C)	109.5
C(9)-C(13)-H(13A)	108.3	C(14)-C(13)-H(13A)	108.3
C(15)-C(13)-H(13A)	108.3	C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	C(13)-C(15)-H(15A)	109.5

C(13)-C(15)-H(15B)	109.5	H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5	C(19)-C(18)-H(18A)	119.8
C(17)-C(18)-H(18A)	119.8	C(18)-C(19)-H(19A)	119.6
C(20)-C(19)-H(19A)	119.6	C(21)-C(20)-H(20A)	119.2
C(19)-C(20)-H(20A)	119.2	C(24)-C(22)-H(22A)	108.9
C(17)-C(22)-H(22A)	108.9	C(23)-C(22)-H(22A)	108.9
C(22)-C(23)-H(23A)	109.5	C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5	C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5	H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5	C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5	C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5	H(24B)-C(24)-H(24C)	109.5
C(21)-C(25)-H(25A)	108.3	C(26)-C(25)-H(25A)	108.3
C(27)-C(25)-H(25A)	108.3	C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5	H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5	H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5	C(25)-C(27)-H(27A)	109.5
C(25)-C(27)-H(27B)	109.5	H(27A)-C(27)-H(27B)	109.5
C(25)-C(27)-H(27C)	109.5	H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5		

Table S18. Torsion angles [°] for $\mathbf{2_I}\cdot I_3$.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(3)-N(2)-C(1)-N(1)	1.0(7)	C(16)-N(2)-C(1)-N(1)	179.9(5)
		C(3)-N(2)-C(1)-I(1)	-175.5(4)
		C(16)-N(2)-C(1)-I(1)	3.4(8)
		C(2)-N(1)-C(1)-N(2)	-0.7(7)
		C(4)-N(1)-C(1)-N(2)	176.9(5)
		C(2)-N(1)-C(1)-I(1)	175.9(4)
		C(4)-N(1)-C(1)-I(1)	-6.5(8)
		C(1)-N(1)-C(2)-C(3)	0.2(7)
		C(4)-N(1)-C(2)-C(3)	-177.5(5)
		N(1)-C(2)-C(3)-N(2)	0.4(7)
		C(1)-N(2)-C(3)-C(2)	-0.9(7)
		C(16)-N(2)-C(3)-C(2)	-179.8(5)
		C(1)-N(1)-C(4)-C(5)	-90.8(7)
		C(2)-N(1)-C(4)-C(5)	86.5(7)
		C(1)-N(1)-C(4)-C(9)	93.2(7)
		C(2)-N(1)-C(4)-C(9)	-89.6(7)
		C(9)-C(4)-C(5)-C(6)	1.4(9)
		N(1)-C(4)-C(5)-C(6)	-174.3(5)
		C(9)-C(4)-C(5)-C(10)	-179.0(6)
		N(1)-C(4)-C(5)-C(10)	5.3(9)
		C(4)-C(5)-C(6)-C(7)	0.0(9)
		C(10)-C(5)-C(6)-C(7)	-179.6(6)
		C(5)-C(6)-C(7)-C(8)	-1.8(10)
		C(6)-C(7)-C(8)-C(9)	2.3(10)
		C(7)-C(8)-C(9)-C(4)	-0.9(9)
		C(7)-C(8)-C(9)-C(13)	-178.2(6)
		C(5)-C(4)-C(9)-C(8)	-0.9(9)
		N(1)-C(4)-C(9)-C(8)	174.8(5)
		C(5)-C(4)-C(9)-C(13)	176.2(6)
		N(1)-C(4)-C(9)-C(13)	-8.0(9)
		C(4)-C(5)-C(10)-C(12)	-112.0(7)
		C(6)-C(5)-C(10)-C(12)	67.6(8)
		C(4)-C(5)-C(10)-C(11)	124.3(7)
		C(6)-C(5)-C(10)-C(11)	-56.1(8)
		C(8)-C(9)-C(13)-C(14)	-61.5(8)
		C(4)-C(9)-C(13)-C(14)	121.5(7)
		C(8)-C(9)-C(13)-C(15)	61.5(8)
		C(4)-C(9)-C(13)-C(15)	-115.6(7)
		C(1)-N(2)-C(16)-C(17)	-96.2(7)
		C(3)-N(2)-C(16)-C(17)	82.5(7)
		C(1)-N(2)-C(16)-C(21)	86.0(7)
		C(3)-N(2)-C(16)-C(21)	-95.3(7)

C(21)-C(16)-C(17)-C(18)	0.2(9)
N(2)-C(16)-C(17)-C(18)	-177.4(5)
C(21)-C(16)-C(17)-C(22)	-177.7(5)
N(2)-C(16)-C(17)-C(22)	4.6(8)
C(16)-C(17)-C(18)-C(19)	0.5(9)
C(22)-C(17)-C(18)-C(19)	178.6(6)
C(17)-C(18)-C(19)-C(20)	-1.6(9)
C(18)-C(19)-C(20)-C(21)	2.0(10)
C(19)-C(20)-C(21)-C(16)	-1.1(9)
C(19)-C(20)-C(21)-C(25)	176.6(5)
C(17)-C(16)-C(21)-C(20)	0.1(9)
N(2)-C(16)-C(21)-C(20)	177.7(5)
C(17)-C(16)-C(21)-C(25)	-177.7(5)
N(2)-C(16)-C(21)-C(25)	0.0(8)
C(16)-C(17)-C(22)-C(24)	-120.2(6)
C(18)-C(17)-C(22)-C(24)	61.9(8)
C(16)-C(17)-C(22)-C(23)	118.0(6)
C(18)-C(17)-C(22)-C(23)	-59.9(7)
C(20)-C(21)-C(25)-C(26)	-92.7(7)
C(16)-C(21)-C(25)-C(26)	84.9(7)
C(20)-C(21)-C(25)-C(27)	29.5(8)
C(16)-C(21)-C(25)-C(27)	-152.9(6)

Figure S4. Crystal structure for IPrCu(CF_3SO_3).

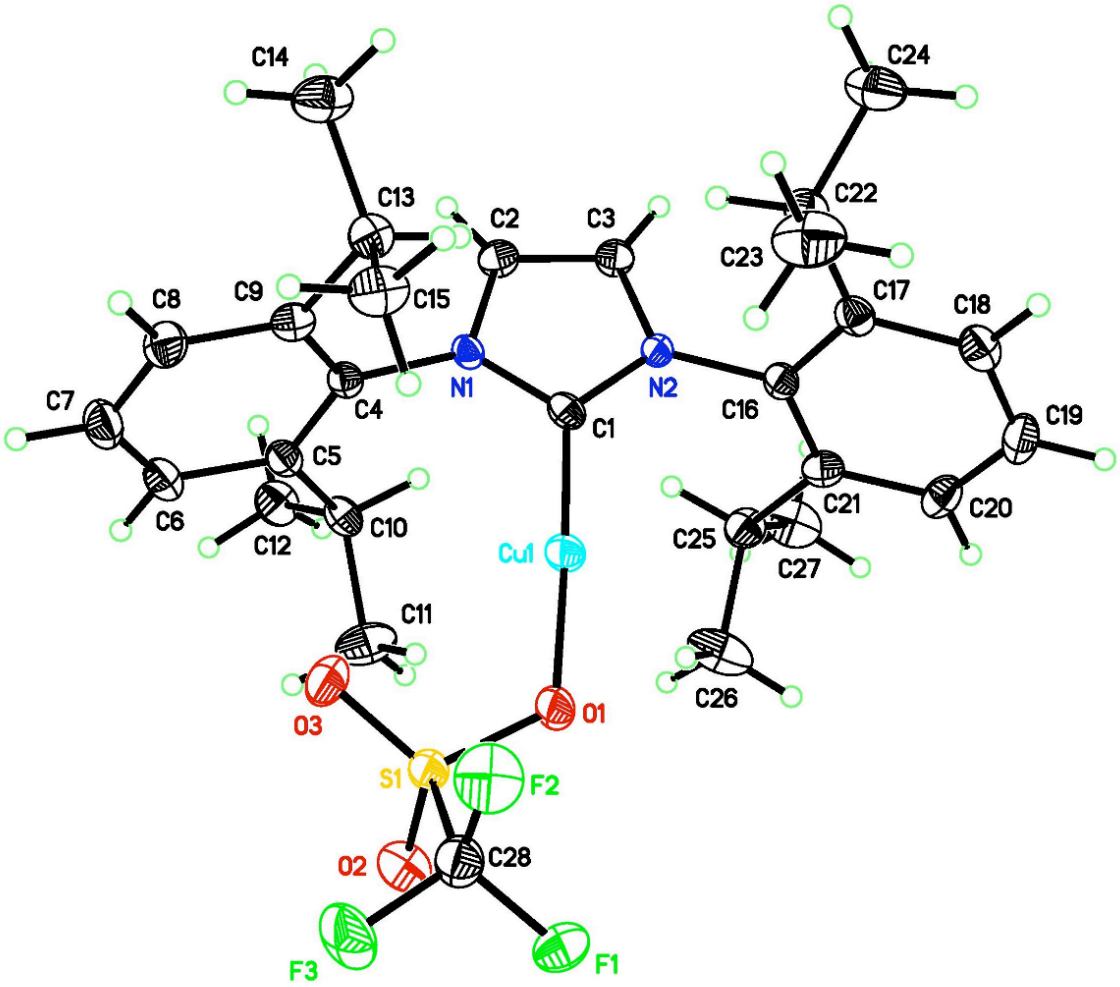

Table S19. Crystal data and structure refinement for IPrCu(CF_3SO_3).

Empirical formula	$C_{28}H_{36}CuF_3N_2O_3S$
Formula weight	601.19
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 10.4856(4) Å α = 90°
	b = 14.0928(5) Å β = 90°
	c = 20.2195(7) Å γ = 90°
Volume	2987.87(19) $Å^3$
Z	4
Density (calculated)	1.336 $g.cm^{-3}$
Absorption coefficient (μ)	0.850 mm^{-1}
F(000)	1256
Crystal size	0.27 × 0.15 × 0.10 mm^3
θ range for data collection	1.76 to 28.11°
Index ranges	$-13 \le h \le 13$, $-18 \le k \le 18$, $-26 \le l \le 26$
Reflections collected	50329
Independent reflections	7256 [R_{int} = 0.0530]
Completeness to θ = 28.11°	99.6 %
Absorption correction	Empiricial
Max. and min. transmission	0.9198 and 0.8030
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7256 / 0 / 351
Goodness-of-fit on F^2	1.070
Final R indices [I>2σ(I)]	R_1 = 0.0333, wR_2 = 0.0689
R indices (all data)	R_1 = 0.0426, wR_2 = 0.0721
Absolute structure parameter	-0.004(8)
Largest diff. peak and hole	0.270 and -0.325 $e^-.Å^{-3}$

Table S20. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for IPrCu(CF_3SO_3). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cu(1)	0.60443(2)	0.53807(2)	0.97853(1)	0.019(1)
S(1)	0.64954(5)	0.44091(4)	1.10440(2)	0.020(1)
F(1)	0.58311(13)	0.52828(10)	1.21322(6)	0.034(1)
F(2)	0.43102(12)	0.45148(10)	1.16630(7)	0.039(1)
F(3)	0.57766(15)	0.37566(10)	1.21889(6)	0.040(1)
O(1)	0.61260(15)	0.53069(10)	1.07105(6)	0.025(1)
O(2)	0.77868(14)	0.44183(12)	1.12738(7)	0.029(1)
O(3)	0.60488(18)	0.35790(11)	1.07163(7)	0.030(1)
N(1)	0.62754(14)	0.46433(12)	0.84724(8)	0.014(1)
N(2)	0.59181(16)	0.61351(12)	0.84298(8)	0.015(1)
C(1)	0.60625(19)	0.54080(15)	0.88623(9)	0.017(1)
C(2)	0.6254(2)	0.48859(15)	0.78086(10)	0.020(1)
C(3)	0.6034(2)	0.58216(15)	0.77803(9)	0.020(1)
C(4)	0.64160(19)	0.36806(15)	0.87136(9)	0.016(1)
C(5)	0.76456(19)	0.33505(15)	0.88546(10)	0.018(1)
C(6)	0.7751(2)	0.24000(16)	0.90531(11)	0.023(1)
C(7)	0.6681(2)	0.18361(17)	0.91038(11)	0.026(1)
C(8)	0.5477(2)	0.21896(16)	0.89710(11)	0.024(1)
C(9)	0.53177(19)	0.31340(16)	0.87801(10)	0.019(1)
C(10)	0.8807(2)	0.39832(16)	0.88097(10)	0.022(1)
C(11)	0.9271(2)	0.42632(19)	0.95032(11)	0.035(1)
C(12)	0.9889(2)	0.35330(17)	0.84153(12)	0.028(1)
C(13)	0.3998(2)	0.35542(16)	0.86664(10)	0.022(1)
C(14)	0.3314(2)	0.30715(19)	0.80982(11)	0.033(1)
C(15)	0.3225(2)	0.35237(18)	0.93067(11)	0.030(1)
C(16)	0.5671(2)	0.71007(15)	0.86232(9)	0.017(1)
C(17)	0.4404(2)	0.74196(16)	0.86033(10)	0.020(1)
C(18)	0.4186(2)	0.83625(16)	0.87935(10)	0.023(1)
C(19)	0.5180(2)	0.89401(17)	0.89877(11)	0.026(1)
C(20)	0.6420(2)	0.85990(16)	0.89986(11)	0.023(1)
C(21)	0.6697(2)	0.76706(16)	0.88122(10)	0.020(1)
C(22)	0.3310(2)	0.67928(16)	0.83813(11)	0.023(1)
C(23)	0.2398(2)	0.6567(2)	0.89499(13)	0.041(1)
C(24)	0.2586(2)	0.72246(19)	0.78014(12)	0.036(1)
C(25)	0.8060(2)	0.73017(17)	0.88126(11)	0.023(1)
C(26)	0.8554(2)	0.7149(2)	0.95169(12)	0.041(1)
C(27)	0.8967(2)	0.79498(19)	0.84348(12)	0.036(1)
C(28)	0.5542(2)	0.45021(17)	1.17944(11)	0.026(1)
H(2A)	0.6373	0.4470	0.7444	0.024
H(3A)	0.5969	0.6198	0.7392	0.023

H(6A)	0.8565	0.2143	0.9153	0.028
H(7A)	0.6773	0.1191	0.9233	0.032
H(8A)	0.4754	0.1787	0.9010	0.029
H(10A)	0.8547	0.4578	0.8576	0.026
H(11A)	0.8580	0.4581	0.9742	0.052
H(11B)	1.0001	0.4694	0.9464	0.052
H(11C)	0.9530	0.3693	0.9746	0.052
H(12A)	0.9560	0.3306	0.7990	0.041
H(12B)	1.0243	0.2998	0.8664	0.041
H(12C)	1.0558	0.4006	0.8338	0.041
H(13A)	0.4114	0.4236	0.8544	0.026
H(14A)	0.3864	0.3072	0.7706	0.049
H(14B)	0.2523	0.3415	0.8000	0.049
H(14C)	0.3111	0.2416	0.8221	0.049
H(15A)	0.3716	0.3819	0.9664	0.045
H(15B)	0.3040	0.2862	0.9422	0.045
H(15C)	0.2423	0.3870	0.9245	0.045
H(18A)	0.3342	0.8607	0.8788	0.028
H(19A)	0.5013	0.9577	0.9115	0.032
H(20A)	0.7092	0.9006	0.9136	0.028
H(22A)	0.3684	0.6179	0.8227	0.028
H(23A)	0.2865	0.6243	0.9304	0.062
H(23B)	0.1712	0.6155	0.8789	0.062
H(23C)	0.2032	0.7157	0.9121	0.062
H(24A)	0.3173	0.7325	0.7431	0.054
H(24B)	0.2217	0.7834	0.7936	0.054
H(24C)	0.1903	0.6793	0.7665	0.054
H(25A)	0.8060	0.6671	0.8585	0.028
H(26A)	0.9403	0.6860	0.9500	0.061
H(26B)	0.7970	0.6728	0.9756	0.061
H(26C)	0.8604	0.7761	0.9746	0.061
H(27A)	0.8635	0.8056	0.7988	0.054
H(27B)	0.9809	0.7651	0.8408	0.054
H(27C)	0.9038	0.8559	0.8666	0.054

Table S21. Anisotropic displacement parameters ($Å^2$) for IPrCu(CF_3SO_3).
The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2 a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	0.0248(1)	0.0198(1)	0.0137(1)	0.0012(1)	0.0001(1)	0.0021(1)
S(1)	0.0253(3)	0.0179(3)	0.0162(2)	0.0012(2)	0.0005(2)	0.0005(2)
F(1)	0.0467(9)	0.0336(8)	0.0204(6)	-0.0073(6)	0.0010(6)	0.0046(7)
F(2)	0.0255(7)	0.0458(9)	0.0454(8)	0.0009(8)	0.0071(6)	-0.0029(7)
F(3)	0.0578(10)	0.0336(8)	0.0277(7)	0.0143(7)	0.0101(7)	0.0053(8)
O(1)	0.0418(9)	0.0179(8)	0.0140(7)	0.0028(6)	0.0008(7)	0.0047(9)
O(2)	0.0224(8)	0.0346(10)	0.0290(9)	0.0048(8)	0.0013(7)	0.0006(7)
O(3)	0.0447(10)	0.0195(8)	0.0267(8)	-0.0057(7)	-0.0017(8)	-0.0002(8)
N(1)	0.0169(9)	0.0136(9)	0.0129(7)	0.0027(7)	0.0004(6)	0.0008(8)
N(2)	0.0198(9)	0.0129(9)	0.0125(8)	0.0005(7)	-0.0011(7)	0.0007(8)
C(1)	0.0127(9)	0.0190(11)	0.0182(9)	0.0030(9)	-0.0001(8)	0.0013(10)
C(2)	0.0245(12)	0.0226(12)	0.0125(9)	-0.0014(9)	0.0024(9)	0.0015(9)
C(3)	0.0264(11)	0.0198(11)	0.0124(9)	0.0009(8)	0.0013(9)	0.0009(10)
C(4)	0.0192(11)	0.0164(11)	0.0125(9)	0.0009(8)	0.0016(8)	0.0016(9)
C(5)	0.0190(11)	0.0187(12)	0.0161(10)	0.0007(9)	0.0001(8)	0.0034(9)
C(6)	0.0259(12)	0.0220(12)	0.0217(11)	0.0052(10)	-0.0007(9)	0.0038(10)
C(7)	0.0344(14)	0.0201(12)	0.0251(12)	0.0056(10)	0.0010(10)	0.0024(11)
C(8)	0.0281(12)	0.0210(12)	0.0236(12)	0.0036(10)	0.0007(10)	-0.0065(10)
C(9)	0.0171(11)	0.0232(13)	0.0157(10)	-0.0011(9)	0.0015(8)	-0.0012(9)
C(10)	0.0181(11)	0.0228(12)	0.0238(11)	0.0036(9)	-0.0007(9)	0.0043(10)
C(11)	0.0240(13)	0.0502(17)	0.0296(12)	-0.0097(12)	-0.0009(10)	-0.0080(12)
C(12)	0.0211(11)	0.0311(14)	0.0305(13)	0.0011(11)	0.0028(10)	0.0045(10)
C(13)	0.0170(10)	0.0242(12)	0.0232(11)	-0.0010(9)	0.0021(9)	0.0010(10)
C(14)	0.0261(13)	0.0452(16)	0.0270(13)	-0.0115(12)	-0.0014(10)	0.0070(12)
C(15)	0.0227(12)	0.0401(15)	0.0266(12)	-0.0052(11)	0.0024(10)	0.0003(11)
C(16)	0.0235(11)	0.0148(11)	0.0133(10)	0.0031(8)	0.0006(8)	0.0000(9)
C(17)	0.0221(11)	0.0209(12)	0.0154(10)	0.0033(9)	0.0012(8)	0.0021(9)
C(18)	0.0241(12)	0.0239(13)	0.0222(11)	0.0037(9)	0.0023(9)	0.0045(10)
C(19)	0.0382(14)	0.0169(12)	0.0243(12)	-0.0016(10)	0.0052(11)	0.0030(10)
C(20)	0.0289(12)	0.0184(12)	0.0229(11)	-0.0029(10)	0.0018(10)	-0.0053(9)
C(21)	0.0198(11)	0.0233(13)	0.0164(10)	0.0007(9)	0.0009(9)	-0.0019(10)
C(22)	0.0192(12)	0.0238(13)	0.0276(12)	0.0004(10)	-0.0041(9)	0.0001(10)
C(23)	0.0354(15)	0.0515(18)	0.0368(15)	0.0062(14)	-0.0008(12)	-0.0181(13)
C(24)	0.0307(14)	0.0429(16)	0.0334(14)	0.0047(13)	-0.0101(11)	-0.0046(12)
C(25)	0.0189(11)	0.0250(13)	0.0262(12)	-0.0027(10)	-0.0004(9)	-0.0002(10)
C(26)	0.0271(13)	0.063(2)	0.0319(13)	0.0122(13)	-0.0036(11)	0.0024(13)
C(27)	0.0239(12)	0.0500(17)	0.0336(13)	0.0060(12)	0.0045(12)	-0.0029(13)
C(28)	0.0305(12)	0.0241(13)	0.0245(11)	0.0005(10)	0.0025(9)	0.0009(11)

Table S22. Bond lengths [Å] for IPrCu(CF_3SO_3).

atom-atom	distance	atom-atom	distance
Cu(1)-C(1)	1.8669(19)	Cu(1)-O(1)	1.8754(13)
S(1)-O(3)	1.4235(16)	S(1)-O(2)	1.4317(16)
S(1)-O(1)	1.4852(15)	S(1)-C(28)	1.822(2)
F(1)-C(28)	1.330(3)	F(2)-C(28)	1.319(3)
F(3)-C(28)	1.342(3)	N(1)-C(1)	1.354(3)
N(1)-C(2)	1.385(2)	N(1)-C(4)	1.449(3)
N(2)-C(1)	1.355(2)	N(2)-C(3)	1.391(2)
N(2)-C(16)	1.439(3)	C(2)-C(3)	1.340(3)
C(4)-C(9)	1.392(3)	C(4)-C(5)	1.400(3)
C(5)-C(6)	1.403(3)	C(5)-C(10)	1.512(3)
C(6)-C(7)	1.378(3)	C(7)-C(8)	1.384(3)
C(8)-C(9)	1.396(3)	C(9)-C(13)	1.522(3)
C(10)-C(12)	1.525(3)	C(10)-C(11)	1.536(3)
C(13)-C(14)	1.516(3)	C(13)-C(15)	1.528(3)
C(16)-C(21)	1.395(3)	C(16)-C(17)	1.404(3)
C(17)-C(18)	1.402(3)	C(17)-C(22)	1.516(3)
C(18)-C(19)	1.379(3)	C(19)-C(20)	1.386(3)
C(20)-C(21)	1.392(3)	C(21)-C(25)	1.522(3)
C(22)-C(24)	1.524(3)	C(22)-C(23)	1.529(3)
C(25)-C(27)	1.523(3)	C(25)-C(26)	1.530(3)
C(2)-H(2A)	0.9500	C(3)-H(3A)	0.9500
C(6)-H(6A)	0.9500	C(7)-H(7A)	0.9500
C(8)-H(8A)	0.9500	C(10)-H(10A)	1.0000
C(11)-H(11A)	0.9800	C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800	C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800	C(12)-H(12C)	0.9800
C(13)-H(13A)	1.0000	C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800	C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800	C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800	C(18)-H(18A)	0.9500
C(19)-H(19A)	0.9500	C(20)-H(20A)	0.9500
C(22)-H(22A)	1.0000	C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800	C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800	C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800	C(25)-H(25A)	1.0000
C(26)-H(26A)	0.9800	C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800	C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800	C(27)-H(27C)	0.9800

Table 23. Bond angles [°] for IPrCu(CF_3SO_3).

atom-atom-atom	angle	atom-atom-atom	angle
C(1)-Cu(1)-O(1)	176.22(8)	O(3)-S(1)-O(2)	118.01(11)
O(3)-S(1)-O(1)	113.76(9)	O(2)-S(1)-O(1)	112.72(10)
O(3)-S(1)-C(28)	105.44(11)	O(2)-S(1)-C(28)	104.37(10)
O(1)-S(1)-C(28)	100.00(10)	S(1)-O(1)-Cu(1)	120.80(9)
C(1)-N(1)-C(2)	111.41(17)	C(1)-N(1)-C(4)	124.47(16)
C(2)-N(1)-C(4)	123.97(17)	C(1)-N(2)-C(3)	111.05(17)
C(1)-N(2)-C(16)	124.03(16)	C(3)-N(2)-C(16)	124.92(16)
N(1)-C(1)-N(2)	104.16(16)	N(1)-C(1)-Cu(1)	124.57(14)
N(2)-C(1)-Cu(1)	131.24(16)	C(3)-C(2)-N(1)	106.68(18)
C(2)-C(3)-N(2)	106.69(18)	C(9)-C(4)-C(5)	123.9(2)
C(9)-C(4)-N(1)	117.80(18)	C(5)-C(4)-N(1)	118.25(18)
C(4)-C(5)-C(6)	116.6(2)	C(4)-C(5)-C(10)	122.24(19)
C(6)-C(5)-C(10)	121.14(19)	C(7)-C(6)-C(5)	120.5(2)
C(6)-C(7)-C(8)	121.4(2)	C(7)-C(8)-C(9)	120.4(2)
C(4)-C(9)-C(8)	117.1(2)	C(4)-C(9)-C(13)	121.5(2)
C(8)-C(9)-C(13)	121.4(2)	C(5)-C(10)-C(12)	112.65(18)
C(5)-C(10)-C(11)	110.62(18)	C(12)-C(10)-C(11)	110.38(18)
C(14)-C(13)-C(9)	111.73(18)	C(14)-C(13)-C(15)	112.22(19)
C(9)-C(13)-C(15)	110.09(18)	C(21)-C(16)-C(17)	123.6(2)
C(21)-C(16)-N(2)	118.69(19)	C(17)-C(16)-N(2)	117.72(19)
C(18)-C(17)-C(16)	116.7(2)	C(18)-C(17)-C(22)	120.67(19)
C(16)-C(17)-C(22)	122.6(2)	C(19)-C(18)-C(17)	120.9(2)
C(18)-C(19)-C(20)	120.6(2)	C(19)-C(20)-C(21)	121.1(2)
C(20)-C(21)-C(16)	117.0(2)	C(20)-C(21)-C(25)	121.1(2)
C(16)-C(21)-C(25)	121.8(2)	C(17)-C(22)-C(24)	111.85(19)
C(17)-C(22)-C(23)	111.84(19)	C(24)-C(22)-C(23)	110.52(19)
C(21)-C(25)-C(27)	112.41(19)	C(21)-C(25)-C(26)	111.49(19)
C(27)-C(25)-C(26)	109.9(2)	F(2)-C(28)-F(1)	108.40(19)
F(2)-C(28)-F(3)	108.07(19)	F(1)-C(28)-F(3)	107.49(17)
F(2)-C(28)-S(1)	111.75(15)	F(1)-C(28)-S(1)	111.22(16)
F(3)-C(28)-S(1)	109.75(15)	C(3)-C(2)-H(2A)	126.7
N(1)-C(2)-H(2A)	126.7	C(2)-C(3)-H(3A)	126.7
N(2)-C(3)-H(3A)	126.7	C(7)-C(6)-H(6A)	119.7
C(5)-C(6)-H(6A)	119.7	C(6)-C(7)-H(7A)	119.3
C(8)-C(7)-H(7A)	119.3	C(7)-C(8)-H(8A)	119.8
C(9)-C(8)-H(8A)	119.8	C(5)-C(10)-H(10A)	107.7
C(12)-C(10)-H(10A)	107.7	C(11)-C(10)-H(10A)	107.7
C(10)-C(11)-H(11A)	109.5	C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5	C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5	H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5	C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5	C(10)-C(12)-H(12C)	109.5

H(12A)-C(12)-H(12C)	109.5	H(12B)-C(12)-H(12C)	109.5
C(14)-C(13)-H(13A)	107.5	C(9)-C(13)-H(13A)	107.5
C(15)-C(13)-H(13A)	107.5	C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5	H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5	C(19)-C(18)-H(18A)	119.5
C(17)-C(18)-H(18A)	119.5	C(18)-C(19)-H(19A)	119.7
C(20)-C(19)-H(19A)	119.7	C(19)-C(20)-H(20A)	119.4
C(21)-C(20)-H(20A)	119.4	C(17)-C(22)-H(22A)	107.5
C(24)-C(22)-H(22A)	107.5	C(23)-C(22)-H(22A)	107.5
C(22)-C(23)-H(23A)	109.5	C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5	C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5	H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5	C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5	C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5	H(24B)-C(24)-H(24C)	109.5
C(21)-C(25)-H(25A)	107.6	C(27)-C(25)-H(25A)	107.6
C(26)-C(25)-H(25A)	107.6	C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5	H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5	H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5	C(25)-C(27)-H(27A)	109.5
C(25)-C(27)-H(27B)	109.5	H(27A)-C(27)-H(27B)	109.5
C(25)-C(27)-H(27C)	109.5	H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5		

Table S24. Torsion angles [°] for IPrCu(CF_3SO_3)..

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
O(3)-S(1)-O(1)-Cu(1)	-35.50(14)	O(2)-S(1)-O(1)-Cu(1)	102.29(12)
C(28)-S(1)-O(1)-Cu(1)	-147.41(12)		
C(1)-Cu(1)-O(1)-S(1)	-41.9(13)		
C(2)-N(1)-C(1)-N(2)	-0.5(2)		
C(4)-N(1)-C(1)-N(2)	-176.31(17)		
C(2)-N(1)-C(1)-Cu(1)	-178.88(15)		
C(4)-N(1)-C(1)-Cu(1)	5.3(3)		
C(3)-N(2)-C(1)-N(1)	0.3(2)		
C(16)-N(2)-C(1)-N(1)	-179.98(18)		
C(3)-N(2)-C(1)-Cu(1)	178.56(16)		
C(16)-N(2)-C(1)-Cu(1)	-1.7(3)		
O(1)-Cu(1)-C(1)-N(1)	46.8(13)		
O(1)-Cu(1)-C(1)-N(2)	-131.1(11)		
C(1)-N(1)-C(2)-C(3)	0.5(2)		
C(4)-N(1)-C(2)-C(3)	176.33(19)		
N(1)-C(2)-C(3)-N(2)	-0.3(2)		
C(1)-N(2)-C(3)-C(2)	0.0(3)		
C(16)-N(2)-C(3)-C(2)	-179.7(2)		
C(1)-N(1)-C(4)-C(9)	88.7(2)		
C(2)-N(1)-C(4)-C(9)	-86.6(2)		
C(1)-N(1)-C(4)-C(5)	-92.4(2)		
C(2)-N(1)-C(4)-C(5)	92.3(2)		
C(9)-C(4)-C(5)-C(6)	2.1(3)		
N(1)-C(4)-C(5)-C(6)	-176.70(18)		
C(9)-C(4)-C(5)-C(10)	-176.8(2)		
N(1)-C(4)-C(5)-C(10)	4.4(3)		
C(4)-C(5)-C(6)-C(7)	-0.1(3)		
C(10)-C(5)-C(6)-C(7)	178.8(2)		
C(5)-C(6)-C(7)-C(8)	-0.9(3)		
C(6)-C(7)-C(8)-C(9)	0.1(3)		
C(5)-C(4)-C(9)-C(8)	-2.9(3)		
N(1)-C(4)-C(9)-C(8)	175.88(18)		
C(5)-C(4)-C(9)-C(13)	175.55(19)		
N(1)-C(4)-C(9)-C(13)	-5.6(3)		
C(7)-C(8)-C(9)-C(4)	1.8(3)		
C(7)-C(8)-C(9)-C(13)	-176.7(2)		
C(4)-C(5)-C(10)-C(12)	-130.9(2)		
C(6)-C(5)-C(10)-C(12)	50.2(3)		
C(4)-C(5)-C(10)-C(11)	105.0(2)		
C(6)-C(5)-C(10)-C(11)	-73.8(3)		
C(4)-C(9)-C(13)-C(14)	118.1(2)		
C(8)-C(9)-C(13)-C(14)	-63.4(3)		

C(4)-C(9)-C(13)-C(15)	-116.5(2)
C(8)-C(9)-C(13)-C(15)	62.0(3)
C(1)-N(2)-C(16)-C(21)	82.4(3)
C(3)-N(2)-C(16)-C(21)	-98.0(2)
C(1)-N(2)-C(16)-C(17)	-98.3(2)
C(3)-N(2)-C(16)-C(17)	81.4(3)
C(21)-C(16)-C(17)-C(18)	-0.7(3)
N(2)-C(16)-C(17)-C(18)	-179.97(17)
C(21)-C(16)-C(17)-C(22)	178.6(2)
N(2)-C(16)-C(17)-C(22)	-0.7(3)
C(16)-C(17)-C(18)-C(19)	0.2(3)
C(22)-C(17)-C(18)-C(19)	-179.1(2)
C(17)-C(18)-C(19)-C(20)	0.0(3)
C(18)-C(19)-C(20)-C(21)	0.3(3)
C(19)-C(20)-C(21)-C(16)	-0.8(3)
C(19)-C(20)-C(21)-C(25)	178.9(2)
C(17)-C(16)-C(21)-C(20)	1.0(3)
N(2)-C(16)-C(21)-C(20)	-179.73(18)
C(17)-C(16)-C(21)-C(25)	-178.7(2)
N(2)-C(16)-C(21)-C(25)	0.6(3)
C(18)-C(17)-C(22)-C(24)	56.7(3)
C(16)-C(17)-C(22)-C(24)	-122.6(2)
C(18)-C(17)-C(22)-C(23)	-67.9(3)
C(16)-C(17)-C(22)-C(23)	112.8(2)
C(20)-C(21)-C(25)-C(27)	-51.3(3)
C(16)-C(21)-C(25)-C(27)	128.3(2)
C(20)-C(21)-C(25)-C(26)	72.6(3)
C(16)-C(21)-C(25)-C(26)	-107.8(2)
O(3)-S(1)-C(28)-F(2)	-55.78(19)
O(2)-S(1)-C(28)-F(2)	179.21(16)
O(1)-S(1)-C(28)-F(2)	62.46(18)
O(3)-S(1)-C(28)-F(1)	-177.09(15)
O(2)-S(1)-C(28)-F(1)	57.90(18)
O(1)-S(1)-C(28)-F(1)	-58.84(17)
O(3)-S(1)-C(28)-F(3)	64.10(18)
O(2)-S(1)-C(28)-F(3)	-60.91(18)
O(1)-S(1)-C(28)-F(3)	-177.66(16)

Computational Methods. All computations were performed using the Gaussian03 software package. All Cu(I) and Cu(III) species were treated as singlets. All Cu(0) and Cu(II) species were treated as doublets. Geometries were optimized by density functional theory method (B3LYP) with 6-311+G** basis set unless otherwise stated. A harmonic oscillator model was used for vibration frequency analysis of the optimized structures. All frequencies of the minima were positive, while transition states had one and only one negative frequency. The vibration mode of the negative frequency in the transition state was confirmed to be the one that corresponding to the reaction coordinate.

Gas phase enthalpies and entropies (pressure = 1 atm, 298.15 K) of all species were obtained via frequency calculations. No scaling factor was used for the calculated frequencies. An implicit solvation model, the PCM/UA0 polarizable continuum model, was employed for the calculation of solvation energies. The gas phase entropies were converted to corresponding entropies (1 M in MeCN) according to an empirical method developed by Wertz.[s5]

The transition state (**TS_3**) for the reaction of **3** and **4** to **5** and **6** was located at the level of B3LYP/LANL2DZ. Single-point and solvation energies were calculated for **3**, **4**, and **TS_3** at the level of B3LYP/6-311+G**. These numbers and thermal corrections at the level of B3LYP/LANL2DZ were used to obtain the activation free energy.

Full reference for 14(a):

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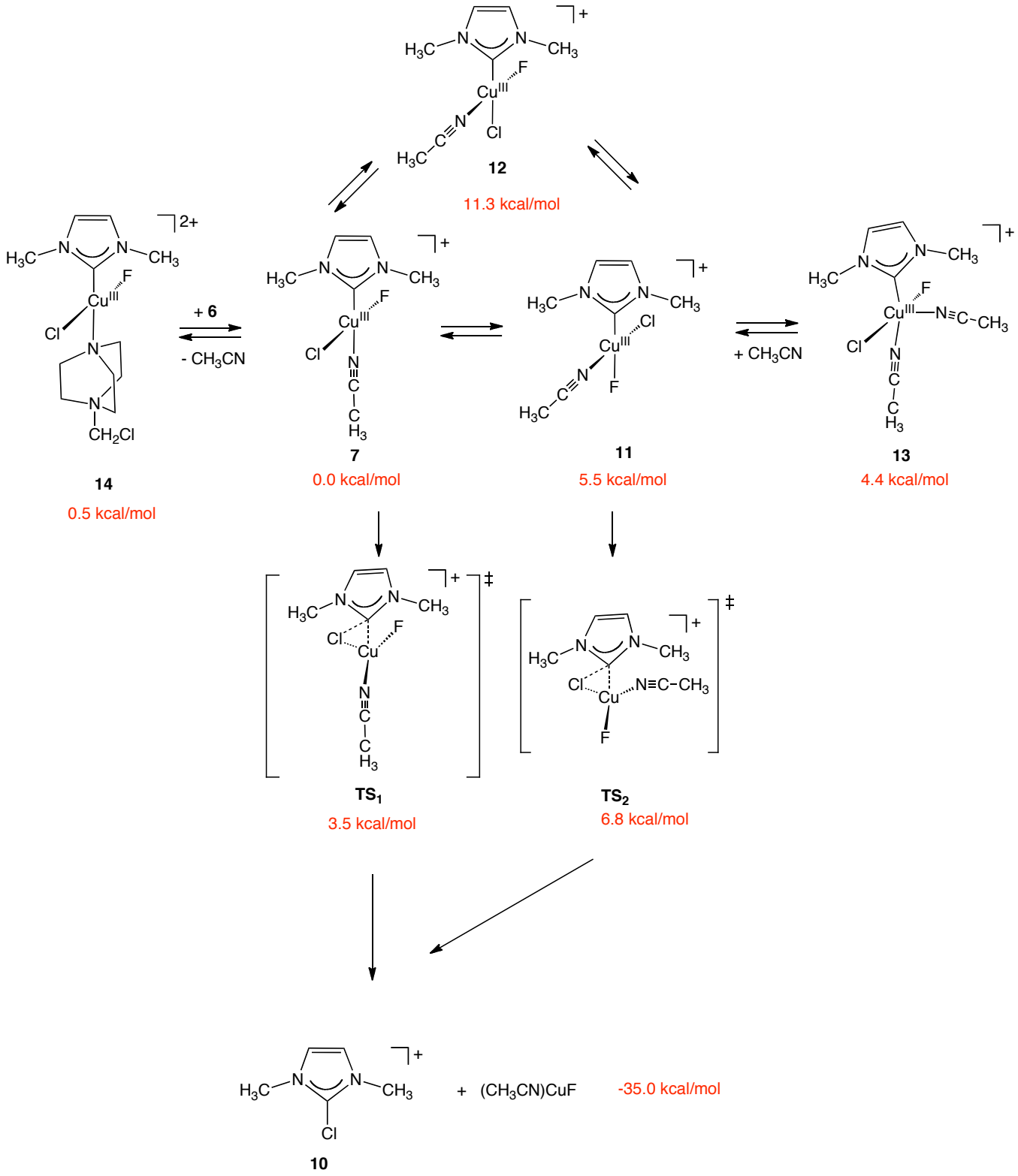
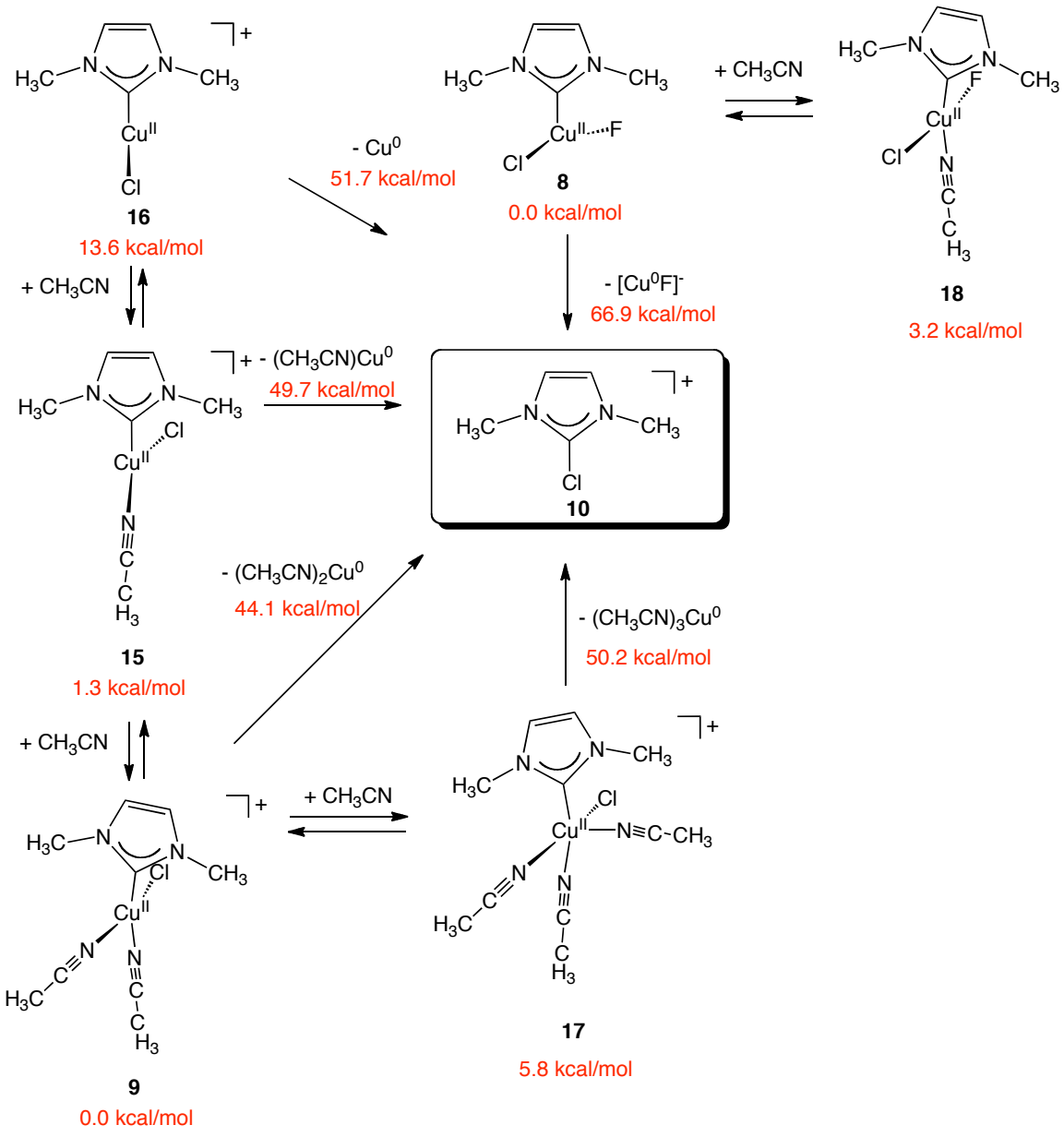
Scheme S1. Relative energies of various Cu(III) species, reductive elimination transition states, and **10**.



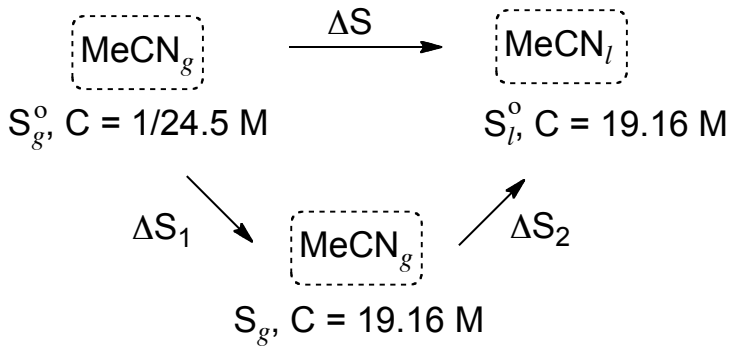
Scheme S2. Relative energies of various Cu(II) species and corresponding reaction free energies to form **10**.



Wertz Method

Wertz's method is composed of two steps, each of which requires a thermodynamic cycle. In the first step, the entropy change from the gaseous state of MeCN (standard state, S_g° = 0.261 kJ mol^{-1} K^{-1}) to liquid state (S_l° = 0.150 kJ mol^{-1} K^{-1}) is separated into two steps: (*i*) the adiabatic compression of an ideal MeCN gas in the standard state to a hypothetical ideal gas state with the concentration equal to that of the liquid state (d=0.786 g/ml, 298 K, 19.16 M); and (*ii*) conversion of the hypothetical state to the final liquid state. (Scheme S3)

Scheme S3.



The entropy change of the first substep (ΔS_1) can be estimated according to Maxwell's relation, while that of the second step (ΔS_2) can be derived from the thermodynamic cycle. The fraction of entropy lost in second step is defined as a coefficient, α, which was calculated to be 0.29.

$$dG = -SdT + VdP = VdP \quad (dT = 0) \quad Maxwell \quad Relation$$

$$\Delta G = \int_{P_1}^{P_2} VdP = \int_{P_1}^{P_2} \frac{RT}{P} dP = RTLn\frac{P_2}{P_1} = -T\Delta S$$

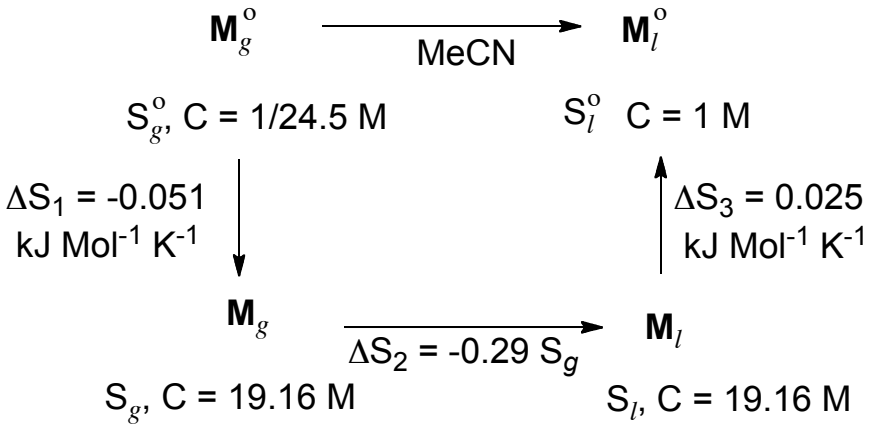
$$\Delta S_1 = -RLn\frac{P_2}{P_1} = -0.051 \quad kJ \quad Mol^{-1} \quad K^{-1}$$

$$\alpha = \frac{\Delta S_2}{S_g} = \frac{S_g - S_l^o}{S_g} = \frac{S_g^o + \Delta S_1 - S_l^o}{S_g} = 0.29$$

$$\Delta S_2 = 0.29 S_g$$

In the second step, the entropy change from the gas state of any given molecule, **M**, in standard state to its 1 M state in MeCN is composed of three substeps: (*i*) adiabatic compression of ideal **M** gas in standard state to a hypothetical ideal gas state with the concentration equal to that of the liquid state (19.16 M); (*ii*) conversion of the hypothetical ideal gas state to a hypothetical liquid state; and (*iii*) expansion of the hypothetical liquid state to the 1 M state in MeCN. (Scheme S4)

Scheme S4.



The entropy change of the first and the third step can be estimated according to Maxwell's relations. The fraction of entropy loss in the second step is assumed to be equal to α. The calculated gas phase entropy of **M** in standard state is then converted to the corresponding entropy in its 1 M state in MeCN according to the following equation and used for the calculations of free energies in MeCN.

$$S_l^o = S_g^o + \Delta S_1 + \Delta S_2 + \Delta S_3 = 0.71 \times S_g^o - 0.0112 \quad kJ \quad Mol^{-1} \quad K^{-1}$$

See references s6-17 for examples of other applications of Wertz method.

Reference:

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s17. Hesp, K. D.; Tobisch, S.; Stradiotto, M. *J. Am. Chem. Soc.* **2010**, *132*, 413-426.

Calculated energies and coordinates (B3LYP/6-311+G):**

3

Sum of electronic and zero-point Energies= -2405.613910
Sum of electronic and thermal Energies= -2405.603230
Sum of electronic and thermal Enthalpies= -2405.602286
Sum of electronic and thermal Free Energies= -2405.652374
<psi(f)| H |psi(f)> (a.u.) = -2405.738482
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -2405.768425
Total free energy in solution:
with all non electrostatic terms (a.u.) = -2405.750477

N	0.002786	0.000679	0.016064
C	0.003889	0.001266	1.377928
N	1.325009	0.000677	1.708562
C	2.126836	-0.000290	0.579394
C	1.292429	-0.000301	-0.488679
Cu	-1.499691	0.003383	2.552561
Cl	-3.174730	0.005676	3.861140
C	1.834639	0.001909	3.076785
C	-1.201443	0.001888	-0.809521
H	1.503311	-0.001120	-1.544571
H	3.202376	-0.001097	0.630299
H	0.986379	-0.002996	3.758555
H	2.443075	-0.887129	3.252939
H	2.434265	0.896544	3.254968
H	-2.068224	-0.002896	-0.151457
H	-1.229171	0.896458	-1.434539
H	-1.225176	-0.887217	-1.442405

4

Sum of electronic and zero-point Energies= -943.910120
Sum of electronic and thermal Energies= -943.900390
Sum of electronic and thermal Enthalpies= -943.899446
Sum of electronic and thermal Free Energies= -943.945029
<psi(f)| H |psi(f)> (a.u.) = -944.127132
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -944.419994
Total free energy in solution:
with all non electrostatic terms (a.u.) = -944.408894

N	0.010486	0.002496	-0.004985

C	0.007167	0.008303	1.519397
C	1.467019	-0.006323	2.035954
N	2.343280	0.399148	0.878825
C	1.851811	1.682702	0.261102
C	0.538548	1.348822	-0.488986
C	0.952290	-1.096932	-0.479773
C	2.410438	-0.696773	-0.154321
F	3.625403	0.615603	1.364777
C	-1.430342	-0.249332	-0.492595
Cl	-1.573031	-0.150164	-2.242955
H	-0.530776	0.899236	1.842883
H	-0.530424	-0.872718	1.869652
H	1.625483	0.715498	2.837119
H	1.801539	-0.989554	2.365572
H	0.687654	1.275468	-1.564059
H	-0.220797	2.105842	-0.294152
H	2.629332	2.038752	-0.414633
H	1.721082	2.400831	1.070137
H	2.952485	-0.297647	-1.011122
H	2.975847	-1.522527	0.277603
H	0.817395	-1.225376	-1.552539
H	0.657451	-2.016410	0.026074
H	-1.707060	-1.247502	-0.156982
H	-2.058467	0.508640	-0.027216

5

Sum of electronic and zero-point Energies= -2505.159141
Sum of electronic and thermal Energies= -2505.146773
Sum of electronic and thermal Enthalpies= -2505.145829
Sum of electronic and thermal Free Energies= -2505.201158
<psi(f)| H |psi(f)> (a.u.) = -2505.287555
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -2505.380777
Total free energy in solution:
with all non electrostatic terms (a.u.) = -2505.362321

C	0.012290	0.002600	0.005462
N	0.011783	0.016160	1.392691
C	1.284062	0.011352	1.795758
N	2.099341	-0.042537	0.740487
C	1.309074	-0.033859	-0.399685
C	-1.179624	0.082279	2.257302
Cu	1.847025	0.228738	3.578252
F	1.887983	1.970708	3.553147

C	3.572522	-0.051287	0.772602
Cl	1.824968	-1.846260	3.693845
H	-0.903364	0.034113	-0.560537
H	1.740304	-0.040208	-1.386483
H	3.917933	-0.882625	1.386275
H	3.932487	-0.184089	-0.244809
H	3.934573	0.898628	1.166158
H	-1.156783	-0.740235	2.971427
H	-1.204100	1.042904	2.771991
H	-2.060683	-0.015231	1.627570

6

Sum of electronic and zero-point Energies= -844.517817
Sum of electronic and thermal Energies= -844.508972
Sum of electronic and thermal Enthalpies= -844.508027
Sum of electronic and thermal Free Energies= -844.552037
<psi(f)| H |psi(f)> (a.u.) = -844.731720
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -844.816382
Total free energy in solution:
with all non electrostatic terms (a.u.) = -844.805783

N	0.008646	0.000695	-0.004886
C	0.006604	-0.003316	1.523302
C	1.485888	0.004319	2.017413
N	2.402709	0.184888	0.894950
C	2.065452	1.410885	0.172065
C	0.652950	1.300522	-0.478574
C	0.847110	-1.179639	-0.485848
C	2.314109	-0.962666	-0.007687
C	-1.424969	-0.113183	-0.460614
Cl	-1.616255	-0.059300	-2.226096
H	-0.546255	0.882826	1.836618
H	-0.540972	-0.890635	1.842300
H	1.630878	0.810530	2.737297
H	1.722759	-0.934380	2.519601
H	0.690731	1.254877	-1.564852
H	-0.016289	2.110693	-0.186494
H	2.815224	1.590577	-0.598911
H	2.101391	2.250095	0.867929
H	2.970019	-0.787400	-0.861124
H	2.673542	-1.854994	0.506155
H	0.755188	-1.222339	-1.569160

H	0.391163	-2.074013	-0.058959
H	-1.812993	-1.063701	-0.102344
H	-1.977667	0.718192	-0.029506

MeCN

Sum of electronic and zero-point Energies= -132.751002
Sum of electronic and thermal Energies= -132.747390
Sum of electronic and thermal Enthalpies= -132.746446
Sum of electronic and thermal Free Energies= -132.775018
<psi(f)| H |psi(f)> (a.u.) = -132.794058
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -132.804984
Total free energy in solution:
with all non electrostatic terms (a.u.) = -132.796362

C	0.000035	-0.000177	0.007141
C	0.001243	-0.000713	1.463641
N	0.006588	0.000812	2.616207
H	-1.021552	0.076082	-0.370418
H	0.576557	0.846622	-0.370497
H	0.444780	-0.922609	-0.371478

7

Sum of electronic and zero-point Energies= -2637.965706
Sum of electronic and thermal Energies= -2637.948647
Sum of electronic and thermal Enthalpies= -2637.947703
Sum of electronic and thermal Free Energies= -2638.015074
<psi(f)| H |psi(f)> (a.u.) = -2638.143430
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -2638.215871
Total free energy in solution:
with all non electrostatic terms (a.u.) = -2638.190086

C	0.016747	0.004357	0.022446
N	0.016306	0.001759	1.410643
C	1.284358	-0.003360	1.832769
N	2.095577	-0.012232	0.769963
C	1.312620	-0.001311	-0.377131
C	-1.172894	0.027105	2.272680
Cu	1.806652	0.160335	3.630690
Cl	1.984680	-1.978058	3.557045
C	3.563752	0.010199	0.802653

N	2.360066	0.374352	5.496687
C	2.675381	0.565040	6.583067
C	3.072873	0.809092	7.953738
F	1.527751	1.913210	3.410737
H	-0.897405	0.013515	-0.545735
H	1.748369	0.003955	-1.361356
H	3.921184	-0.745054	1.501559
H	3.932166	-0.225971	-0.193187
H	3.912912	1.000739	1.095409
H	-1.215197	-0.884893	2.868542
H	-1.133902	0.906840	2.914734
H	-2.054416	0.082711	1.638139
H	2.359681	0.335493	8.632063
H	4.066383	0.390127	8.128001
H	3.094049	1.884414	8.143368

TS_1

Sum of electronic and zero-point Energies= -2637.956418
Sum of electronic and thermal Energies= -2637.939856
Sum of electronic and thermal Enthalpies= -2637.938912
Sum of electronic and thermal Free Energies= -2638.004139
<psi(f)| H |psi(f)> (a.u.) = -2638.131348
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -2638.209715
Total free energy in solution:
with all non electrostatic terms (a.u.) = -2638.184232

C	-0.005749	-0.007841	0.007065
N	0.014634	0.002898	1.358638
C	1.334997	0.007758	1.773102
C	2.112245	-0.050193	0.662066
N	1.269141	-0.090637	-0.434608
C	-1.151769	0.151762	2.233555
C	1.695537	-0.060446	-1.836539
Cu	-1.310772	1.091999	-0.963288
F	-0.431917	2.594228	-0.427295
Cl	-1.393441	-1.162299	-0.903462
N	-2.819712	1.805776	-2.055601
C	-3.616680	2.388257	-2.643325
C	-4.618978	3.128281	-3.382866
H	3.183167	-0.048620	0.553259
H	1.601465	0.069308	2.814218
H	-1.950292	-0.505987	1.892318
H	-0.863189	-0.137454	3.241897

H	-1.484345	1.190973	2.229253
H	1.068813	-0.731117	-2.423168
H	1.627709	0.959002	-2.219565
H	2.726247	-0.404783	-1.888943
H	-4.588121	2.841334	-4.436131
H	-5.610734	2.911010	-2.980538
H	-4.421020	4.198808	-3.295060

8

Sum of electronic and zero-point Energies= -2505.473357
Sum of electronic and thermal Energies= -2505.461344
Sum of electronic and thermal Enthalpies= -2505.460400
Sum of electronic and thermal Free Energies= -2505.513742
<psi(f)| H |psi(f)> (a.u.) = -2505.600515
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -2505.630652
Total free energy in solution:
with all non electrostatic terms (a.u.) = -2505.612668

N	0.014681	-0.002377	0.001707
C	0.014476	0.001222	1.385466
C	1.312541	0.004249	1.776066
N	2.077722	0.011477	0.624172
C	1.284392	0.003801	-0.474603
C	3.545593	-0.019758	0.623568
Cu	1.908237	0.000658	-2.364130
Cl	0.549924	-1.049584	-3.694860
C	-1.208032	0.053589	-0.803030
F	3.491947	0.892923	-2.215904
H	1.752669	0.000037	2.758469
H	-0.895410	0.005752	1.960736
H	-0.976499	-0.242941	-1.823170
H	-1.940489	-0.637584	-0.385053
H	-1.614608	1.066835	-0.793618
H	3.897963	0.327848	-0.347133
H	3.908918	0.644830	1.407911
H	3.893977	-1.036303	0.817462

9

Sum of electronic and zero-point Energies= -2670.893716
Sum of electronic and thermal Energies= -2670.872413
Sum of electronic and thermal Enthalpies= -2670.871469

Sum of electronic and thermal Free Energies= -2670.951147
<psi(f)| H |psi(f)> (a.u.) = -2671.112787
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -2671.184532
Total free energy in solution:
with all non electrostatic terms (a.u.) = -2671.150611

N	0.071399	-0.126957	0.070823
C	0.160987	-0.020506	1.449050
C	1.468936	0.174008	1.744256
N	2.151350	0.177085	0.537223
C	1.293717	-0.007587	-0.492452
C	3.586563	0.428229	0.412946
Cu	1.729488	0.024404	-2.431587
N	3.095885	0.328801	-3.955459
C	3.678494	0.782160	-4.836502
C	4.398862	1.376378	-5.945394
C	-1.180284	-0.340659	-0.660251
Cl	0.730441	1.984597	-2.753074
N	1.693101	-2.026538	-2.797871
C	1.639742	-3.150651	-3.032561
C	1.572232	-4.568608	-3.332675
H	1.965031	0.313841	2.689476
H	-0.701820	-0.088097	2.089352
H	-1.122191	0.171090	-1.618768
H	-1.359907	-1.407263	-0.806184
H	-1.999811	0.087038	-0.084626
H	3.895696	0.224343	-0.610446
H	3.808334	1.469398	0.651854
H	4.135764	-0.228480	1.088258
H	5.432591	1.574542	-5.654781
H	4.390598	0.700613	-6.802856
H	3.918987	2.317200	-6.224625
H	2.524358	-4.904689	-3.748510
H	1.360676	-5.132531	-2.421908
H	0.779642	-4.754115	-4.060752

10

Sum of electronic and zero-point Energies= -764.787667
Sum of electronic and thermal Energies= -764.779177
Sum of electronic and thermal Enthalpies= -764.778233
Sum of electronic and thermal Free Energies= -764.822238
<psi(f)| H |psi(f)> (a.u.) = -764.917363
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -764.993216

Total free energy in solution:
with all non electrostatic terms (a.u.) = -764.979740

C	0.010359	0.014595	0.008169
N	0.012084	0.000247	1.350084
C	1.329318	-0.027233	1.775141
C	2.114593	-0.029082	0.666867
N	1.276945	-0.002722	-0.435029
C	-1.180056	0.011761	2.213990
C	1.696782	0.004921	-1.846177
Cl	-1.369065	0.049031	-0.969301
H	3.186072	-0.046621	0.564568
H	1.587977	-0.042877	2.819980
H	-1.789651	-0.868890	2.014072
H	-0.844629	-0.005181	3.248016
H	-1.758507	0.917215	2.033245
H	1.305204	-0.876584	-2.352870
H	1.335395	0.909546	-2.334203
H	2.783516	-0.013160	-1.872480

$Cu^{I}F(MeCN)$

Sum of electronic and zero-point Energies= -1873.191214
Sum of electronic and thermal Energies= -1873.184426
Sum of electronic and thermal Enthalpies= -1873.183482
Sum of electronic and thermal Free Energies= -1873.222188
<psi(f)| H |psi(f)> (a.u.) = -1873.235283
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -1873.268395
Total free energy in solution:
with all non electrostatic terms (a.u.) = -1873.254949

C	0.000058	-0.000047	0.017786
C	0.002196	0.000823	1.468454
N	0.004566	0.001049	2.619390
Cu	0.007716	0.003323	4.448287
F	0.010788	0.005507	6.225442
H	0.998298	0.236588	-0.356734
H	-0.294766	-0.983642	-0.354143
H	-0.704978	0.746275	-0.354599

11

Sum of electronic and zero-point Energies= -2637.947689

Sum of electronic and thermal Energies= -2637.930683
Sum of electronic and thermal Enthalpies= -2637.929739
Sum of electronic and thermal Free Energies= -2637.995998
<psi(f)| H |psi(f)> (a.u.) = -2638.121568
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -2638.208100
Total free energy in solution:
with all non electrostatic terms (a.u.) = -2638.181907

C	0.031688	0.013504	0.010690
C	0.025881	0.005248	1.367298
N	1.349675	0.012441	1.780040
C	2.145434	0.027607	0.698169
N	1.359069	0.017031	-0.390473
C	1.798606	-0.114751	3.172752
Cu	4.058444	0.083871	0.714812
F	5.839590	0.031090	0.723397
C	1.817560	0.014548	-1.785572
Cl	3.815241	-2.036776	0.695912
N	4.191401	2.013214	0.746512
C	4.629076	3.074372	0.765654
C	5.200159	4.403256	0.789367
H	-0.791053	0.001708	2.068574
H	-0.779162	0.025911	-0.697573
H	2.770085	-0.509067	-1.849251
H	1.087254	-0.519557	-2.390679
H	1.921152	1.036071	-2.153316
H	2.685245	0.497313	3.331647
H	1.004846	0.239526	3.827448
H	2.025984	-1.157764	3.394752
H	4.863000	4.937128	1.680591
H	6.289875	4.320891	0.806644
H	4.892955	4.955670	-0.101388

TS_2

Sum of electronic and zero-point Energies= -2637.939771
Sum of electronic and thermal Energies= -2637.923012
Sum of electronic and thermal Enthalpies= -2637.922067
Sum of electronic and thermal Free Energies= -2637.988825
<psi(f)| H |psi(f)> (a.u.) = -2638.111234
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -2638.203844
Total free energy in solution:
with all non electrostatic terms (a.u.) = -2638.177684

N	0.030017	0.050751	0.033680
C	0.046051	-0.078423	1.408491
C	1.347138	-0.149829	1.798357
N	2.127361	-0.064375	0.662136
C	1.313097	0.100408	-0.414727
C	3.594099	-0.105179	0.629130
Cu	1.823093	1.307165	-1.895497
N	1.671741	3.084514	-1.064070
C	1.755916	4.229610	-1.134895
C	1.867946	5.668151	-1.244775
Cl	1.750961	-0.929634	-2.064799
C	-1.173593	0.156358	-0.799540
F	2.341937	1.962707	-3.506524
H	1.779336	-0.242322	2.780249
H	-0.860503	-0.097456	1.989232
H	-1.050547	-0.451883	-1.694710
H	-2.019408	-0.219100	-0.227454
H	-1.353833	1.195787	-1.077689
H	4.000595	0.902239	0.528435
H	3.944802	-0.547800	1.559053
H	3.921847	-0.723284	-0.205701
H	2.603682	6.042007	-0.529596
H	2.189505	5.919745	-2.258741
H	0.900841	6.135047	-1.046592

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Sum of electronic and zero-point Energies= -2637.938282
Sum of electronic and thermal Energies= -2637.921402
Sum of electronic and thermal Enthalpies= -2637.920458
Sum of electronic and thermal Free Energies= -2637.987388
<psi(f)| H |psi(f)> (a.u.) = -2638.111707
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -2638.198562
Total free energy in solution:
with all non electrostatic terms (a.u.) = -2638.172259

C	-0.039229	0.015859	0.020361
N	-0.019139	0.050115	1.361835
C	1.292838	-0.039248	1.798946
C	2.077323	-0.115189	0.695183
N	1.231284	-0.079878	-0.404932
C	-1.195870	0.203740	2.231160
C	1.689580	-0.027100	-1.797729

Cu	-1.629308	0.287594	-1.070748
N	-1.693193	-1.484813	-1.684382
C	-1.902142	-2.528425	-2.112777
C	-2.189939	-3.832411	-2.667816
Cl	-3.398461	0.727403	-2.260005
F	-1.541196	1.923652	-0.423443
H	3.146654	-0.188645	0.592501
H	1.547432	-0.041845	2.845107
H	-1.735504	-0.740697	2.309022
H	-0.855033	0.505306	3.219291
H	-1.835795	0.982972	1.820548
H	0.854040	-0.236493	-2.462281
H	2.084796	0.964683	-2.019521
H	2.464345	-0.777561	-1.950318
H	-1.982049	-4.608945	-1.928468
H	-3.243981	-3.873171	-2.954544
H	-1.570863	-3.998423	-3.552772

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Sum of electronic and zero-point Energies= -2770.731464
Sum of electronic and thermal Energies= -2770.709055
Sum of electronic and thermal Enthalpies= -2770.708111
Sum of electronic and thermal Free Energies= -2770.789204
<psi(f)| H |psi(f)> (a.u.) = -2770.955162
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -2771.024289
Total free energy in solution:
with all non electrostatic terms (a.u.) = -2770.990827

N	-0.011397	-0.064560	0.034710
C	0.021779	-0.028478	1.374401
N	1.302213	0.058158	1.762597
C	2.108093	0.090519	0.635718
C	1.289321	0.019606	-0.442209
Cu	-1.407295	0.020683	2.610845
F	-0.854198	1.692647	3.008047
C	1.783538	0.110154	3.150146
C	-1.197334	-0.167697	-0.823998
Cl	-1.566642	-2.091081	2.156720
N	-3.343343	0.965117	1.368214
C	-4.217409	1.666738	1.104779
C	-5.316759	2.559132	0.775755
N	-2.599519	-0.060411	4.194771
C	-3.216677	-0.107121	5.160139

C	-3.997724	-0.164449	6.379878
H	1.506776	0.022981	-1.496284
H	3.179464	0.166025	0.705076
H	1.658532	-0.865487	3.621381
H	2.839794	0.369883	3.133733
H	1.224780	0.875185	3.685663
H	-1.949730	-0.770634	-0.323859
H	-1.594024	0.825636	-1.030403
H	-0.901536	-0.652523	-1.752503
H	-5.434936	2.625582	-0.307573
H	-6.246232	2.184268	1.208632
H	-5.115134	3.556527	1.171671
H	-4.047124	0.827422	6.833698
H	-5.008794	-0.510189	6.155054
H	-3.531952	-0.858745	7.082426

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Sum of electronic and zero-point Energies= -3349.647221
Sum of electronic and thermal Energies= -3349.624886
Sum of electronic and thermal Enthalpies= -3349.623942
Sum of electronic and thermal Free Energies= -3349.701434
<psi(f)| H |psi(f)> (a.u.) = -3349.993959
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -3350.230101
Total free energy in solution:
with all non electrostatic terms (a.u.) = -3350.202864

N	0.011385	0.013655	0.010177
C	0.012010	-0.000847	1.348413
N	1.279222	-0.028922	1.781155
C	2.116849	-0.042968	0.674434
C	1.327309	-0.014206	-0.428098
Cu	-1.577342	-0.079966	2.405603
F	-1.778853	-1.761981	1.855523
C	1.741524	-0.014944	3.176734
C	-1.171728	0.023173	-0.863568
N	-3.336728	-0.233618	3.578802
C	-4.347921	0.778122	3.143239
C	-5.705607	0.518132	3.842062
N	-5.482636	-0.417758	5.018393
C	-5.068974	-1.780343	4.485701
C	-3.946288	-1.594050	3.440428
C	-4.328225	0.132575	5.840683
C	-3.021773	0.001403	5.020171

C	-6.707462	-0.511414	5.916427
Cl	-8.160717	-1.020178	5.047397
Cl	-1.198993	1.966193	2.875755
H	3.188412	-0.085656	0.773988
H	1.577253	-0.028246	-1.475628
H	-1.662113	0.996043	-0.815616
H	-0.843505	-0.158974	-1.884336
H	-1.845610	-0.776079	-0.558354
H	1.656483	0.990736	3.587162
H	1.155449	-0.720136	3.764490
H	2.782047	-0.331652	3.193551
H	-6.427673	0.039108	3.184533
H	-6.145718	1.438375	4.226241
H	-4.475768	0.710427	2.063020
H	-3.959524	1.768075	3.375318
H	-4.744405	-2.366375	5.346237
H	-5.948232	-2.253582	4.052817
H	-3.174956	-2.350536	3.563503
H	-4.324836	-1.691561	2.424532
H	-2.419113	-0.835594	5.374250
H	-2.434134	0.913534	5.112371
H	-4.275062	-0.431697	6.771714
H	-4.567807	1.170109	6.074203
H	-6.485721	-1.240156	6.693313
H	-6.875241	0.474895	6.344255

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Sum of electronic and zero-point Energies= -2538.117765
Sum of electronic and thermal Energies= -2538.101772
Sum of electronic and thermal Enthalpies= -2538.100828
Sum of electronic and thermal Free Energies= -2538.166779
<psi(f)| H |psi(f)> (a.u.) = -2538.289823
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -2538.366438
Total free energy in solution:
with all non electrostatic terms (a.u.) = -2538.340893

N	0.002768	0.013254	-0.003041
C	-0.000987	0.014303	1.377189
C	1.299018	-0.000592	1.774607
N	2.067518	-0.010431	0.628157
C	1.273956	0.019958	-0.468021
C	3.533288	-0.042948	0.612125
Cu	1.836605	-0.069411	-2.310802
Cl	1.841362	-2.264794	-2.439149

C	-1.204055	0.011195	-0.835716
N	2.385735	0.612309	-4.069092
C	2.717233	0.854302	-5.142880
C	3.134939	1.150282	-6.496610
H	1.731366	-0.008277	2.760725
H	-0.910811	0.022012	1.953016
H	-0.978494	-0.466851	-1.787491
H	-1.978911	-0.566710	-0.334356
H	-1.556520	1.030634	-0.999260
H	3.868228	-0.530888	-0.301711
H	3.938149	0.968436	0.670573
H	3.883493	-0.625606	1.462745
H	3.223892	0.219137	-7.061287
H	2.396961	1.795367	-6.978586
H	4.102559	1.656807	-6.482078

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Sum of electronic and zero-point Energies= -2405.317478
Sum of electronic and thermal Energies= -2405.306572
Sum of electronic and thermal Enthalpies= -2405.305628
Sum of electronic and thermal Free Energies= -2405.358722
<psi(f)| H |psi(f)> (a.u.) = -2405.435347
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -2405.530603
Total free energy in solution:
with all non electrostatic terms (a.u.) = -2405.512655

N	0.003065	-0.001592	0.015457
C	0.005523	0.000772	1.383614
N	1.328986	-0.001588	1.730467
C	2.119195	0.008249	0.619025
C	1.277660	0.008263	-0.469458
Cu	-1.507987	-0.005768	2.553808
Cl	-3.149499	-0.186277	3.823473
C	1.844291	0.007805	3.107295
C	-1.199668	0.007825	-0.829898
H	1.505532	0.016169	-1.522996
H	3.196166	0.016141	0.663753
H	1.017172	-0.149284	3.796170
H	2.568700	-0.796959	3.228874
H	2.315180	0.968166	3.318774
H	-2.074585	-0.149438	-0.202888
H	-1.285861	0.968253	-1.338721
H	-1.134872	-0.796824	-1.561700

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Sum of electronic and zero-point Energies= -2803.656608
Sum of electronic and thermal Energies= -2803.629757
Sum of electronic and thermal Enthalpies= -2803.628812
Sum of electronic and thermal Free Energies= -2803.722869
<psi(f)| H |psi(f)> (a.u.) = -2803.922182
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -2803.990528
Total free energy in solution:
with all non electrostatic terms (a.u.) = -2803.948513

N	0.007281	0.013233	-0.001549
C	-0.001875	0.010267	1.352229
N	1.301297	-0.012883	1.716262
C	2.122544	-0.018612	0.598596
C	1.306070	-0.005781	-0.481876
Cu	-1.639113	0.110412	2.510198
N	-1.152708	0.786575	4.769935
C	-1.176235	1.679507	5.496926
C	-1.214048	2.827911	6.384896
C	1.806605	0.026474	3.087245
C	-1.185553	0.034102	-0.851175
N	-3.693663	-0.056378	2.917109
C	-4.824799	0.121274	3.010814
C	-6.249314	0.375493	3.118809
Cl	-1.962727	2.275357	1.862954
N	-1.469107	-1.928384	3.108661
C	-1.394081	-3.030479	3.425442
C	-1.302739	-4.422021	3.830571
H	1.531959	-0.005292	-1.534367
H	3.196651	-0.023568	0.670808
H	0.973112	-0.075327	3.776158
H	2.513424	-0.790121	3.241797
H	2.306814	0.978861	3.271083
H	-1.909161	0.728414	-0.427612
H	-0.901080	0.380227	-1.843616
H	-1.615967	-0.965883	-0.930422
H	-1.116924	-4.483473	4.904781
H	-2.237831	-4.937137	3.601564
H	-0.486137	-4.913668	3.298176
H	-6.579654	0.228788	4.148976
H	-6.457529	1.404865	2.818759

H	-6.801460	-0.304449	2.467060
H	-1.497469	3.715218	5.814247
H	-1.943085	2.665948	7.181114
H	-0.231528	2.991416	6.831899

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Sum of electronic and zero-point Energies= -2638.228628
Sum of electronic and thermal Energies= -2638.211225
Sum of electronic and thermal Enthalpies= -2638.210281
Sum of electronic and thermal Free Energies= -2638.279312
<psi(f)| H |psi(f)> (a.u.) = -2638.400723
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -2638.439643
Total free energy in solution:
with all non electrostatic terms (a.u.) = -2638.413782

C	0.067814	-0.142780	-0.108108
N	-0.098821	0.097862	1.216560
C	1.119615	0.326146	1.833463
C	2.067319	0.216793	0.870562
N	1.404360	-0.063132	-0.311904
C	-1.388454	0.168973	1.901758
C	2.077215	-0.299104	-1.592800
Cu	-1.331582	-0.576299	-1.481077
F	-0.498114	0.438037	-2.828938
Cl	-2.162381	-2.402601	-0.400250
H	3.138525	0.309375	0.922469
H	1.203306	0.544778	2.884155
H	-2.080807	-0.514693	1.414134
H	-1.254613	-0.140837	2.938392
H	-1.777868	1.189306	1.875962
H	1.366127	-0.078264	-2.389565
H	2.936308	0.369018	-1.664837
H	2.416652	-1.335765	-1.649629
N	-3.092096	-0.415053	-2.607958
C	-3.976145	-0.448289	-3.338485
C	-5.091493	-0.500204	-4.266538
H	-5.464612	-1.523745	-4.338783
H	-5.898118	0.147525	-3.917700
H	-4.768368	-0.165780	-5.254216

Cu^0F

Cu	0.000000	0.000000	-0.006632
F	0.000000	0.000000	1.874508

Cu^0

Sum of electronic and zero-point Energies= -1640.472257
Sum of electronic and thermal Energies= -1640.470841
Sum of electronic and thermal Enthalpies= -1640.469897
Sum of electronic and thermal Free Energies= -1640.488767
<psi(f)| H |psi(f)> (a.u.) = -1640.472204
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -1640.473461
Total free energy in solution:
with all non electrostatic terms (a.u.) = -1640.466967

Cu^0(MeCN)

Sum of electronic and zero-point Energies= -1773.231317
Sum of electronic and thermal Energies= -1773.225407
Sum of electronic and thermal Enthalpies= -1773.224463
Sum of electronic and thermal Free Energies= -1773.263949
<psi(f)| H |psi(f)> (a.u.) = -1773.274884
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -1773.284076
Total free energy in solution:
with all non electrostatic terms (a.u.) = -1773.271405

C	0.001545	-0.000072	0.010406
C	0.007994	0.000976	1.462869
N	0.042369	0.002465	2.616595
Cu	0.930887	-0.000937	4.433447
H	-0.585528	-0.842140	-0.361794
H	-0.436123	0.928118	-0.362705
H	1.023513	-0.086541	-0.367411

$Cu^0(MeCN)_2$

Sum of electronic and zero-point Energies= -1905.997152
Sum of electronic and thermal Energies= -1905.986533
Sum of electronic and thermal Enthalpies= -1905.985589
Sum of electronic and thermal Free Energies= -1906.037347
<psi(f)| H |psi(f)> (a.u.) = -1906.081731
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -1906.105859
Total free energy in solution:
with all non electrostatic terms (a.u.) = -1906.087375

C	-0.048360	0.004246	0.076708
C	0.085263	-0.006458	1.520591
N	0.123841	-0.011927	2.676436
Cu	0.050291	-0.014558	4.514122
N	0.108622	-0.023742	6.316409
C	-0.023229	-0.021106	7.510710
C	-1.172787	0.033154	8.472079
H	-1.104785	0.019295	-0.210941
H	0.441718	0.888324	-0.337274
H	0.420043	-0.885578	-0.349937
H	-2.135004	0.083876	7.939179
H	-1.159269	-0.850652	9.114462
H	-1.070555	0.905883	9.121559

$Cu^0(MeCN)_3$

Sum of electronic and zero-point Energies= -2038.747849
Sum of electronic and thermal Energies= -2038.731500
Sum of electronic and thermal Enthalpies= -2038.730556
Sum of electronic and thermal Free Energies= -2038.799169
<psi(f)| H |psi(f)> (a.u.) = -2038.875698
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -2038.909134
Total free energy in solution:
with all non electrostatic terms (a.u.) = -2038.882446

C	0.005961	0.068632	0.075701
C	0.023301	0.041350	1.575385
N	0.845746	0.003418	2.444312
Cu	2.259221	-0.054537	3.663057
N	2.976029	-1.726623	4.432417
C	3.337229	-2.774641	4.755835
C	3.806042	-4.102870	5.108934
N	3.078042	1.541719	4.485017
C	3.511347	2.550952	4.841692
C	4.072377	3.830970	5.235951
H	-0.553445	-0.787739	-0.308630
H	-0.499591	0.971043	-0.276649
H	1.031253	0.044721	-0.330136
H	2.956204	-4.766992	5.281556
H	4.414228	-4.517005	4.298965
H	4.410673	-4.064167	6.017553
H	4.684179	3.718135	6.133524
H	4.697062	4.233558	4.432701
H	3.271352	4.543467	5.445191

Calculated energies and coordinates (B3LYP/6-311+G// B3LYP/6-311+G**//B3LYP/LANL2DZ):**

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LANL2DZ:

Electronic energy = -515.979460826
Sum of electronic and zero-point Energies= -515.848580
Sum of electronic and thermal Energies= -515.837915
Sum of electronic and thermal Enthalpies= -515.836971
Sum of electronic and thermal Free Energies= -515.887116

6-311+G**:

<psi(f)| H |psi(f)> (a.u.) = -2405.736092
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -2405.767052
Total free energy in solution:
with all non electrostatic terms (a.u.) = -2405.748824

C	-0.020222	-0.046213	-0.014913
N	-0.002116	0.000614	1.365147
C	1.309600	0.074166	1.856122
C	2.139424	0.073477	0.763094
N	1.313968	-0.000481	-0.368373
C	-1.206465	-0.022290	2.207748
C	1.801918	-0.024811	-1.754831
Cu	-1.543559	-0.145518	-1.171357
Cl	-3.275987	-0.258608	-2.486532
H	3.214740	0.117508	0.701597
H	1.539361	0.118903	2.908374
H	-2.083364	-0.088847	1.560085
H	-1.189726	-0.891182	2.874761
H	-1.273331	0.894187	2.804267
H	0.942382	-0.091237	-2.425379
H	2.359211	0.891079	-1.980237
H	2.448245	-0.894311	-1.917291

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LANL2DZ:

Electronic energy = -498.663418322
Sum of electronic and zero-point Energies= -498.441766
Sum of electronic and thermal Energies= -498.431821
Sum of electronic and thermal Enthalpies= -498.430877

Sum of electronic and thermal Free Energies= -498.477052

6-311+G**:

<psi(f)| H |psi(f)> (a.u.) = -944.120943
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -944.412844
Total free energy in solution:
with all non electrostatic terms (a.u.) = -944.401246

C	-1.047266	1.025197	-0.979573
C	-1.404767	2.452930	-0.461939
H	-0.782985	1.029371	-2.040127
H	-1.888007	0.343404	-0.827703
H	-1.578257	3.154663	-1.281825
H	-2.266265	2.468050	0.209647
C	1.419593	1.315422	-0.599411
H	2.237574	1.029005	0.063132
H	1.692297	1.049555	-1.623772
C	1.082402	2.835300	-0.495554
H	1.864986	3.392827	0.025391
H	0.891840	3.305707	-1.462975
C	-0.060664	2.201927	1.654466
H	0.873980	2.526444	2.117610
H	-0.897899	2.496334	2.292546
C	-0.089012	0.680514	1.317607
H	0.684128	0.147239	1.874715
H	-1.059789	0.229921	1.540035
F	-0.410775	4.350094	0.628326
C	0.355828	-1.012753	-0.540533
H	-0.510005	-1.554857	-0.157952
H	0.450255	-1.102541	-1.623405
Cl	1.862530	-1.703260	0.236996
N	-0.196216	2.943164	0.327994
N	0.174964	0.488708	-0.194125

TS_3

LANL2DZ:

Electronic energy = -1014.71676194
Sum of electronic and zero-point Energies= -1014.365128
Sum of electronic and thermal Energies= -1014.342545
Sum of electronic and thermal Enthalpies= -1014.341601
Sum of electronic and thermal Free Energies= -1014.422326

6-311+G**:

<psi(f)| H |psi(f)> (a.u.) = -3349.929152
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -3350.171640
Total free energy in solution:
with all non electrostatic terms (a.u.) = -3350.139519

N	-0.063532	0.116465	0.102371
C	0.078830	0.245055	1.639784
C	1.585133	-0.001430	2.022221
N	2.279083	-0.477808	0.807214
C	1.680784	-1.714192	0.262707
C	0.269118	-1.334433	-0.323489
C	2.409376	0.587594	-0.215183
C	0.956728	1.075336	-0.569001
C	-1.466282	0.524076	-0.366918
Cl	-2.781392	-0.484114	0.429248
F	4.289985	-0.672853	1.431076
Cu	5.590781	0.630111	1.705001
F	5.102201	2.338469	1.329276
C	7.202046	-0.263228	2.249124
N	7.492259	-1.562510	2.551095
C	8.848144	-1.668152	2.890219
C	9.392913	-0.410035	2.782995
N	8.364650	0.450681	2.379540
C	6.556676	-2.707544	2.551395
C	8.549552	1.905853	2.148492
H	9.302016	-2.603109	3.177472
H	10.399569	-0.066250	2.960653
H	8.905896	2.378582	3.067872
H	9.280010	2.058548	1.349192
H	7.602257	2.367707	1.858162
H	6.477386	-3.116964	3.562826
H	5.576739	-2.368796	2.214137
H	6.927851	-3.481767	1.873662
H	1.661965	-0.754219	2.809429
H	2.062981	0.917358	2.367774
H	-0.588787	-0.490866	2.090193
H	-0.255425	1.246925	1.921589
H	1.592189	-2.452540	1.062329
H	2.323599	-2.121957	-0.520236
H	0.258822	-1.357205	-1.416604
H	-0.519600	-1.986414	0.055902
H	0.773216	1.060915	-1.646528

H	0.759204	2.079180	-0.183546
H	2.915453	0.179198	-1.092442
H	3.008431	1.409986	0.181312
H	-1.530912	0.366876	-1.443699
H	-1.632742	1.567006	-0.097302