

Supplementary Information

Lewis-acid Trapping of an Elusive Copper-Tosylnitrene Intermediate Using Scandium Triflate

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1. Experimental Section

1.1. Materials. All chemicals were purchased from Sigma-Aldrich, Acros, ABCR, TCI and used without further purification unless otherwise mentioned. ^{15}N -*p*-toluene sulfonamide (98+ atom% ^{15}N) was purchased from Isotec (Sigma-Aldrich). Anhydrous solvents (dichloromethane, acetone, *n*-hexane) were purchased from Carl-Roth GmbH ($\geq 99.5\%$, < 50 ppm H_2O) and degassed by freeze-pump-thaw method prior to use. d_4 -DHAⁱ was prepared by following the similar published procedure. All the liquid substrates, for reactivity studies, were distilled under argon prior to use.

1.2. Instrumentations and Physical Methods. Preparation and handling of air sensitive materials were performed in a N_2 glove box OMNI-Lab 2 (VAC) with O_2 and moisture concentrations less than 1 ppm. ^1H NMR spectra were recorded either on a Bruker AV 400 NMR spectrometer or on a Bruker DPX 300 spectrometer. Elemental analyses were performed with a Leco CHNS-932 elemental analyser. UV-vis spectra were recorded by Agilent 8453 diode array spectrometer connected with a cryostat from Unisoku Scientific Instruments, Japan. IR spectra was measured either by preparation of KBr pellet of solid sample with Shimadzu FTIR-8400S spectrometer. Raman spectra were measured at -92 °C (Bruker cryostat) with 514-nm excitation, by using a Horiba Jobin-Yvon LabRAM HR800 confocal Raman spectrometer.

X-band EPR derivative spectra were recorded on a Bruker ELEXSYS E500 spectrometer equipped with the Bruker dual-mode cavity (ER4116DM) and a Helium flow cryostat (Oxford Instrument ESR 910). Microwave frequencies were calibrated with a Hewlett-Packard frequency counter(HP5352B), and field control was calibrated with a Bruker NMR field probe (ER035M). The spectrum was simulated with the program GFIT (by Dr. Eckhard Bill) for the calculation of spectra with effective g values and anisotropic line widths (Gaussian line shapes were used).

The analysis of the different substrate oxidations were done by GC-MS/FID (Varian GC/MS 4000). The products of reactivity studies were identified by comparison of retention time of the authentic compounds and ^1H -NMR. The product quantification was done by ^1H -NMR using known amount of nitromethane as internal standard. The chemical shifts are reported in ppm relative to the residual solvent signal.

X-ray absorption spectroscopy was carried out on beamline X3B of the National Synchrotron Lightsource (Brookhaven National Laboratory, Upton, NY, USA). A sagittally focusing Si(111) monochromator was used for energy selection, while a cylindrically-bent nickel-coated mirror located downstream of the monochromator provided vertical focusing and harmonic rejection. Sample temperatures were maintained at approximately 20 K using a He Displex cryostat. A Cu metal foil was used for internal energy calibration, with the first inflection point of the reference foil edge set to 8979.0 eV. XAS data were collected as fluorescence spectra using a 31 element solid state germanium detector (Canberra), over an energy range of 8779 – 9540 eV. A Ni filter of 3 absorption lengths was used to reduce scatter and maintain detector linearity. Samples were monitored for photoreduction during data collection (based upon red-shifts in the absorption edge), and typically only 2 scans were collected at a given position on the sample. Tandem Mossbauer/XAS cups with a sample window of ~ 6mm x 10mm were used to provide at least 5 independent beam spots on each sample. Averaging and normalization of the XAS data was performed using Athena, a graphical implementation of the IFEFFIT package.ⁱⁱ Careful alignment and examination of individual scans suggested some photoreduction of **2** and **3-Sc** occurred during data collection (**1-BF₄** was unaffected), and so only the first scan at each spot was included in the final average. First and second derivative spectra were calculated using a 0.75 eV polynomial smooth.

1.3. Crystal structure determination. Data collection was performed at 100 K on a Stoe IPDS 2 Θ diffractometer using Mo- K_α radiation ($\lambda = 0.71073$ Å); radiation source was a sealed tube generator with graphite monochromator. Multi-scan (PLATON)ⁱⁱⁱ absorption correction for **2**. The

structure was solved by direct methods (SHELXS-97)^{iv} and refined by full matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-97)^{iv}. All non-hydrogen atoms were refined anisotropically. H atoms were introduced in their idealized positions and refined as riding except for the N bonded ones which were located in the Fourier electron density map.

1.4. Determination of k_2 by UV/vis-spectroscopy. The reactivity studies of **3-Sc** were done at -90 °C, under inert atmosphere, by injecting the CH₂Cl₂ solution of substrate to the preformed **3-Sc**. The pseudo-first order decay of 530 nm band was monitored by acquiring an UV-Vis spectrum in every 1 second. The pseudo-first order fitting of the decay curves yielded the rate constants (k_{obs}) which were found to be linearly increasing with the increment of substrate concentrations. The slope of the rate constant (k_{obs}) versus substrate concentration fitting plot provided the second order rate constants (k_2). In case of second order rate constant (k_2) determinations, the concentration of **1-BF₄** starting solutions were in between 0.2 mM to 0.5 mM.

1.5. Product analysis. Calculated amount of substrate in 0.1 ml CD₂Cl₂ was added to the preformed **3-Sc** in CD₂Cl₂/CD₃COCD₃ at -90 °C. In case of 1,4-cyclohexadiene, cyclohexene and PPh₃, 5 equivalent substrate was added to **3-Sc** and the reaction mixture was stirred at -90 °C until the 530 nm band disappeared completely. In case of toluene and cyclohexane, 25 equivalent substrate was added to **3-Sc** and the reaction mixture was stirred at -90 °C for 1 hour and then at room temperature for 2 hours. Then the reaction mixtures were passed through celite to remove undissolved particles prior to the NMR measurements. For the quantification of products by ¹H- NMR, 2 µl of nitromethane were used as internal standard. For the qualitative product analysis by GC, the reaction mixtures were passed through the silica layer to remove the metal complex and eluted with ethylacetate.

The absorption spectra of final decay solutions of **3-Sc**, in presence of substrates, displayed no broad absorption band in the range from 600 nm to 1000 nm. This indicated that the final decay solutions contained Cu^I. This was also confirmed by EPR studies, which showed EPR silent product.

1.6. Syntheses and Characterizations.

[Cu(L1)][BF₄] (**1-BF₄**) complex (L1 = 3,3'-iminobis(*N,N*-dimethylpropylamine): **1-BF₄** was prepared by following the similar literature procedure.^v A solution of ligand L1 (0.345 g, 1.84 mmol) in CH₂Cl₂ (5 mL) was added to [Cu(MeCN)₄][BF₄] (0.579 gm, 1.84 mmol), and the resultant solution was stirred for 30 min under a nitrogen atmosphere. Then the resultant clear, colorless solution was treated with *n*-hexane (25 mL) to produce a cloudy solution and that was kept at -35 °C for 2 hrs. After that the solvent was decanted and the resultant clear, colorless oil was dried *in vacuo* to yield a white solid. Yield: 0.509 g, 82%. Elemental analysis Calcd. for C₁₀H₂₅N₃BCuF₄: C, 35.57; H, 7.46; N, 12.44. Found: C, 35.81; H, 7.53; N, 12.30.

IR (KBr-pellet): $\tilde{\nu}$ (cm⁻¹) = 3289 s, 2924 s, 2844 s, 2794 s, 1480 s, 1466 s, 1429 s, 1387 m, 1345 m, 1324 m, 1293 m, 1263 m, 1239 m, 1203 m, 1139 s, 1107 s, 1054 s, 978 s, 950 m, 919 w, 899 m, 859 s, 851 s, 771 s, 756 w, 523 m, 492 w, 458 w.

2-(tert-butylsulfonyl)(p-toluenesulfonyliminoiodo)benzene (⁶PhINTs): 2-(tert-butylsulfonyl)(diacetoxyiodo)benzene was prepared by following the previously reported procedure.^{vi}

p-Toluenesulfonamide (0.401 g, 2.34 mmol) and KOH (0.320 g, 5.85 mmol, an excess KOH was used to ensure the neutralization of residual acetic acid which came from the synthetic step of 2-(tert-butylsulfonyl)(diacetoxyiodo)benzene) was dissolved in MeOH (40 mL) and the resultant solution was kept in an ice bath for 15 min. To that cold solution, 2-(tert-butylsulfonyl)(diacetoxyiodo)benzene (1.036 g, 2.34 mmol) was added and stirred for 1 hour at 0 °C to form a white suspension. Then the white suspension was stirred for additional 2 hours at room temperature. After that the reaction mixture was poured to crushed ice and filtered through a Büchner funnel. The white residue was washed thoroughly with water to remove the extra KOH and which was confirmed by pH paper

indicator. Then finally the white residue was washed with Et₂O to remove unreacted starting materials and dried under *vacuo*. Yield: 0.870 g, 76%.

¹H NMR (CDCl₃, 300 MHz): 8.33 (d, 1H), 7.93-7.80 (m, 4H), 7.73 -7.66 (m, 1H), 7.23 (d, 2H), 2.38 (s, 3H), 1.43 (s, 9H).

ESI-MS(+): [C₁₇H₂₀I¹⁴NO₄S₂ +H]⁺: 494.1002 (calc: 493.9956).

IR (KBr-pellet): ¹⁴N-^sPhINTs $\bar{\nu}$ (cm⁻¹) = 3429 br, 3076 m, 2980 m, 2961 m, 2917 w, 1598 m, 1569 m, 1560 m, 1490 m, 1475 m, 1442 m, 1423 m, 1398 m, 1368 m, 1275 s, 1249 w, 1190 w, 1139 s, 1107 s, 1080 s, 1017 m, 996 m, 961 w, 880 w, 850 s, 811 s, 795 m, 767 s, 735 s, 707 m, 698 m, 666 s, 641 s, 628 m, 617 m, 573 s, 560 s, 547 s, 518 m, 462 m.

(¹⁵N-^sPhINTs). For the preparation of ¹⁵N-^sPhINTs, ¹⁵N-*p*-toluene sulfonamide (98+ atom% ¹⁵N) was used.

ESI-MS(+): [C₁₇H₂₀I¹⁵NO₄S₂ +H]⁺: 495.1008 (calc: 494.9956).

IR (KBr-pellet): ¹⁵N-^sPhINTs $\bar{\nu}$ (cm⁻¹) = 3429 br, 3076 m, 2980 m, 2961 m, 2917 w, 1598 m, 1569 m, 1560 m, 1490 m, 1475 m, 1442 m, 1423 m, 1398 m, 1368 m, 1275 s, 1249 w, 1190 w, 1138 s, 1107 s, 1080 s, 1017 m, 996 m, 961 w, 880 w, 834 s, 811 s, 793 m, 767 s, 735 s, 707 m, 698 m, 664 s, 641 s, 628 m, 606 m, 573 s, 557 s, 545 s, 518 m, 462 m.

[(L1)Cu(NHTs)][BF₄] (**2**). The bluish-green complex **2** was synthesized by treatment of a colorless solution of **1-BF₄** in CH₂Cl₂ at 25 °C with the solution of 2 equivalent of ^sPhINTs in CH₂Cl₂.

[(L1)Cu(NTs)][Sc(OTf)₃][BF₄] (**3-Sc**). The colorless solution of **1-BF₄** in CH₂Cl₂ (2mL) was cooled to -90 °C. Then 1 equivalent Sc(OTf)₃ in acetone (0.1 mL) and 1.1 equivalent of ^sPhINTs in CH₂Cl₂ (0.15 ml) were added, respectively, to the previous solution to yield deep purple intermediate **3-Sc**. The generation of the deep purple species **3-Sc** was monitored by the growth of 530 nm in UV/vis spectrum.

The concentration of rRaman and XAS samples were in between 8 mM to 10 mM (with respect to Cu).

2. DFT Methods.

DFT calculations have been carried out using the pure functional BP86^{vii} and a valence triple- ζ basis set with polarization on all atoms (TZVP).^{viii} Calculations have been carried out with the TURBOMOLE 6.3 suite^{ix} applying the resolution-of-the-identity technique^x and using the COSMO continuum solvent model^{xi} at the dielectric constant of acetone (i.e., $\epsilon = 21$). Stationary points of the energy hypersurface have been located by means of energy gradient techniques, and full vibrational analysis has been carried out using the numerical approach implemented in TURBOMOLE (NumForce routine). As far as the electronic structure of **3-Sc** is concerned, XANES data supports a Cu^{II} assignment, thereby, implying an open-shell singlet Cu^{II}-N*(Sc)Ts ground state; even though this would call for high level ab-initio multiconfigurational calculations, such an approach would be clearly unfeasible for theoretical analysis of vibrational frequencies on geometry-optimized structures. In such context, the choice of BP86 density functional calculations is based on previous observations, which demonstrate that this functional is well suited for direct comparisons between computed harmonic frequencies and experimental wave numbers.^{xii} Our open-shell BP86/TZVP calculations indicated the absence of broken symmetry solutions at this level of theory; based on previous results^{xiii} showing non-significant variation in the Cu-N_{imido} distances while going from broken symmetry to

closed shell singlet representations of a β -diketiminato Cu-nitrene complex, we proceeded by using the available closed-shell wavefunction. As far as the connectivity of the Sc-bound model (**3-Sc**) is concerned, the choice of considering direct N_{imido} -Sc bonding stems from an extensive preliminary analysis of the potential energy surface of such species (data not shown): among the various geometric arrangements considered the model presented in the main text turned out to be the most stable. The effect of $\text{Sc}(\text{OTf})_3$ has been modeled by incorporating ScF_3 in the calculation.

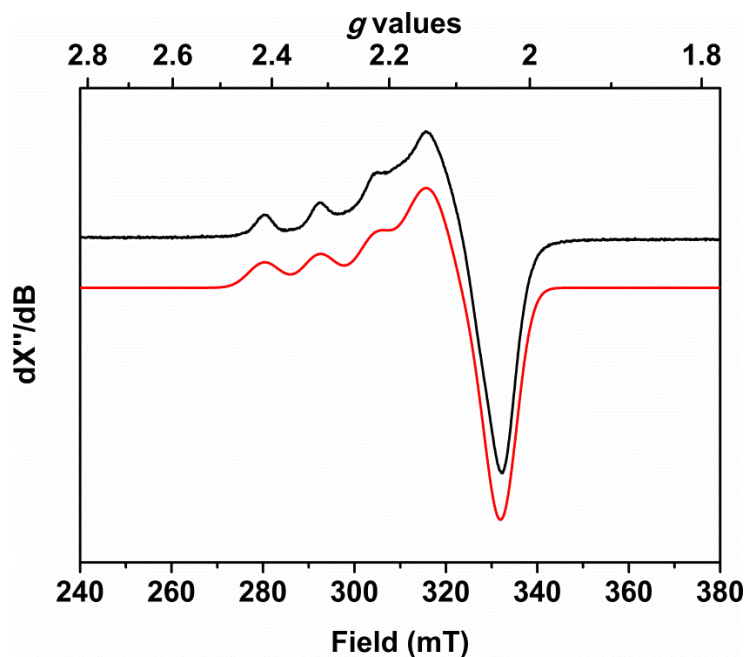


Figure S1: X-band EPR Spectra of **2**, Experimental spectra (black trace) and simulated spectra (red trace) (at 10 K, 0.05 mW power) ($g_x = 2.089$, $g_y = 2.074$, $g_z = 2.268$; $A_x = 54.132 \times 10^{-4} \text{ cm}^{-1}$, $A_y = 14.757 \times 10^{-4} \text{ cm}^{-1}$, $A_z = 127.922 \times 10^{-4} \text{ cm}^{-1}$).

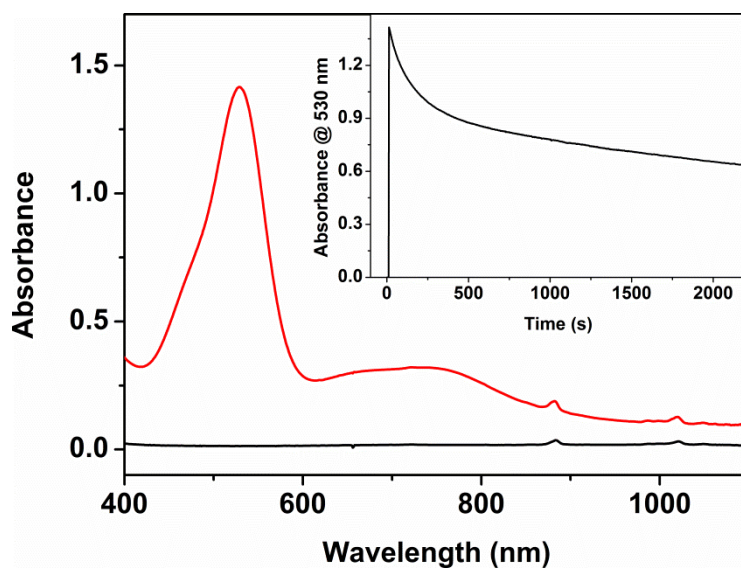


Figure S2: UV/vis spectrum (0.41 mM) of **1-BF₄** (black trace) and **3-Sc** (red trace). Inset: immediate conversion of **1-BF₄** to **3-Sc** upon the addition of ^sPhINTs in presence of Sc(OTf)₃ and slow decay of **3-Sc** at -90 °C.

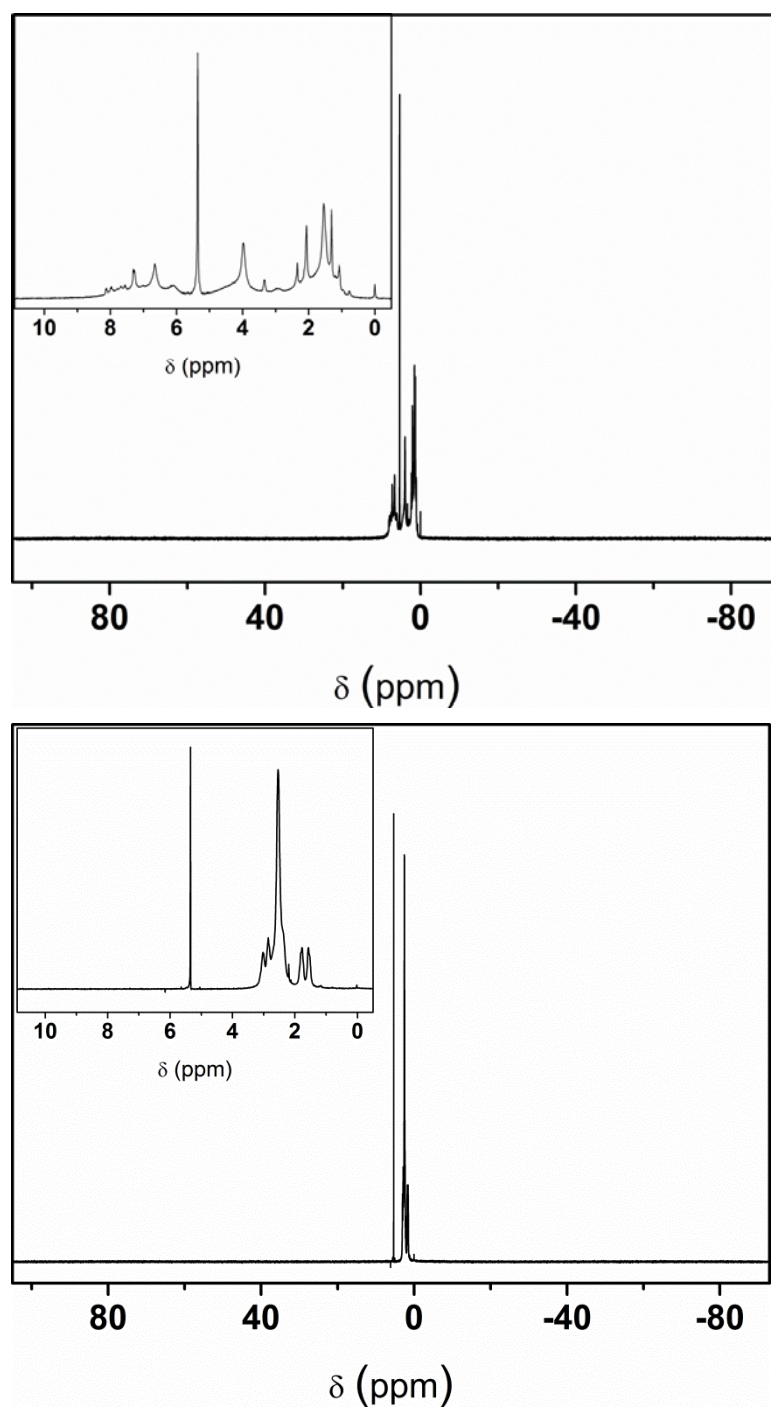


Figure S3 Top: ¹H-NMR spectra of **3-Sc** in CD₂Cl₂ at -90 °C. Inset: expansion of -0.5 to 10.9 ppm region of ¹H-NMR spectra. **Bottom:** ¹H-NMR spectra of **1-BF₄** in CD₂Cl₂ at -90 °C. Inset: expansion of -0.5 to 10.9 ppm region of ¹H-NMR spectra.

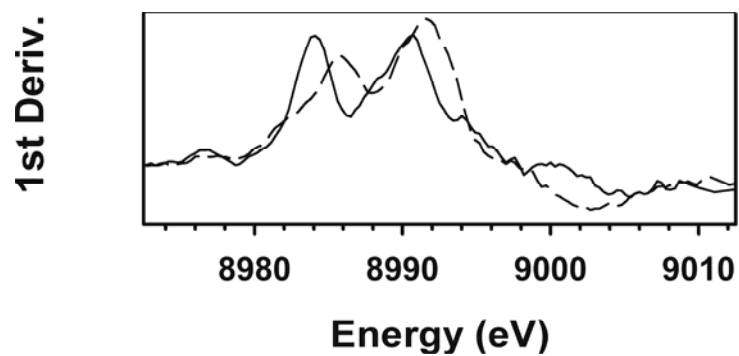


Figure S4: First derivative of the XANES spectra for **2** (solid trace) and **3-Sc** (dashed trace).

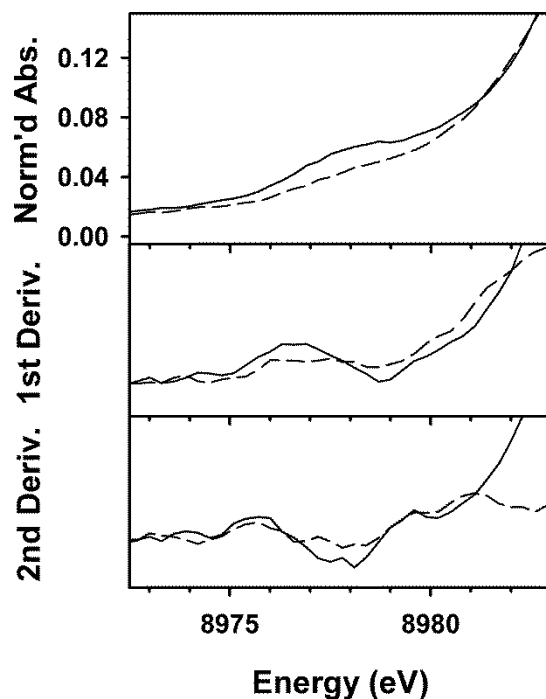


Figure S5: Expansion of the 1s-to-3d pre-edge transition for **2** (solid lines) and **3-Sc** (dashed lines), with first and second derivatives shown on the same energy axis. The pre-edge intensity is weakened in **3-Sc**, but there is no evidence for a hypsochromic shift relative to **2**.

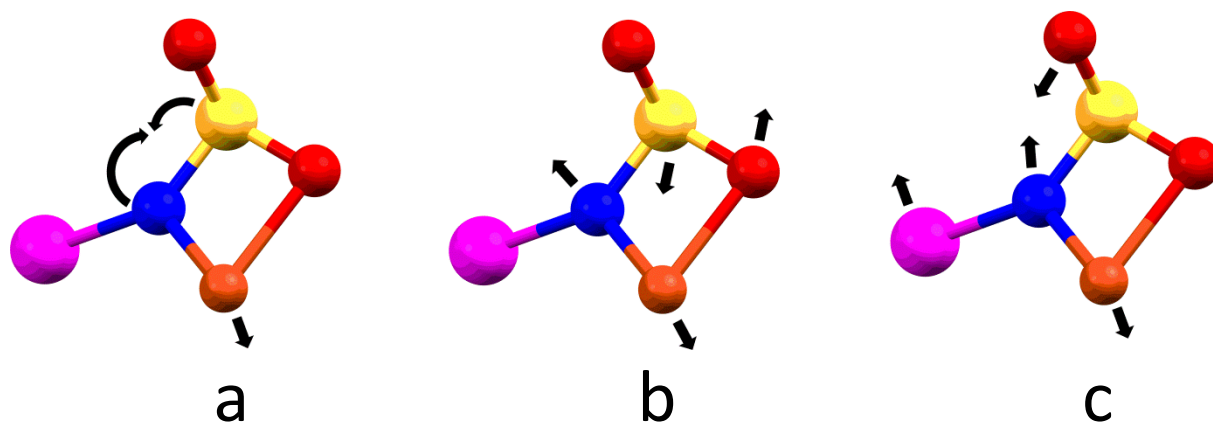


Figure S6: ^{15}N sensitive vibrational modes calculated for the $\text{Cu}^{11}\text{N}\cdot(\text{Sc})\text{Ts}$ core in **3-Sc** at a) 882 cm^{-1} (^{15}N shift of 16 cm^{-1}), b) 654 cm^{-1} (^{15}N -shift of 3 cm^{-1}) and c) 589 cm^{-1} (^{15}N -shift of 1 cm^{-1}). Sc: purple; N: blue; S: yellow; O: red; Cu: orange. Videos of all the ^{15}N sensitive vibrational modes are available.

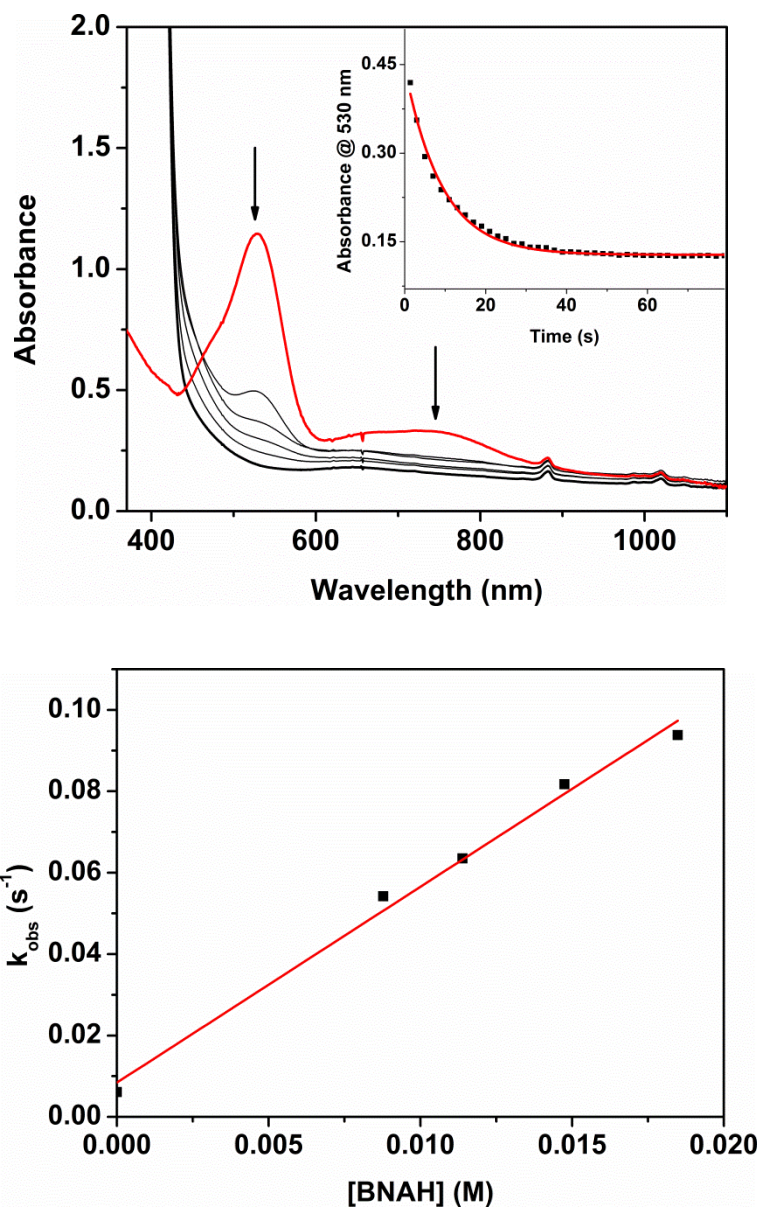


Figure S7 Top: Changes in the absorption spectra associated with the reaction of **3-Sc** (0.32 mM) with 1-Benzyl-1,4-dihydronicotinamide (BNAH) (0.0087 M) at $-90\text{ }^{\circ}\text{C}$. Inset: The Pseudo-first order decay of the absorption band at 530 nm as a function of time. **Bottom:** Linear dependence of k_{obs} on the substrate concentration. Positive intercept at zero substrate concentration corresponds to the rate constant for the self decay of **3-Sc** at $-90\text{ }^{\circ}\text{C}$.

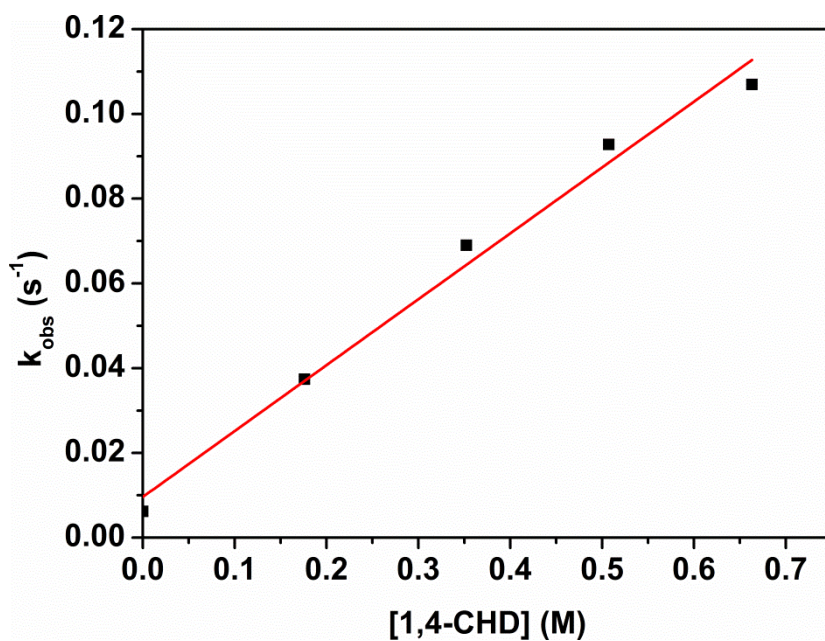
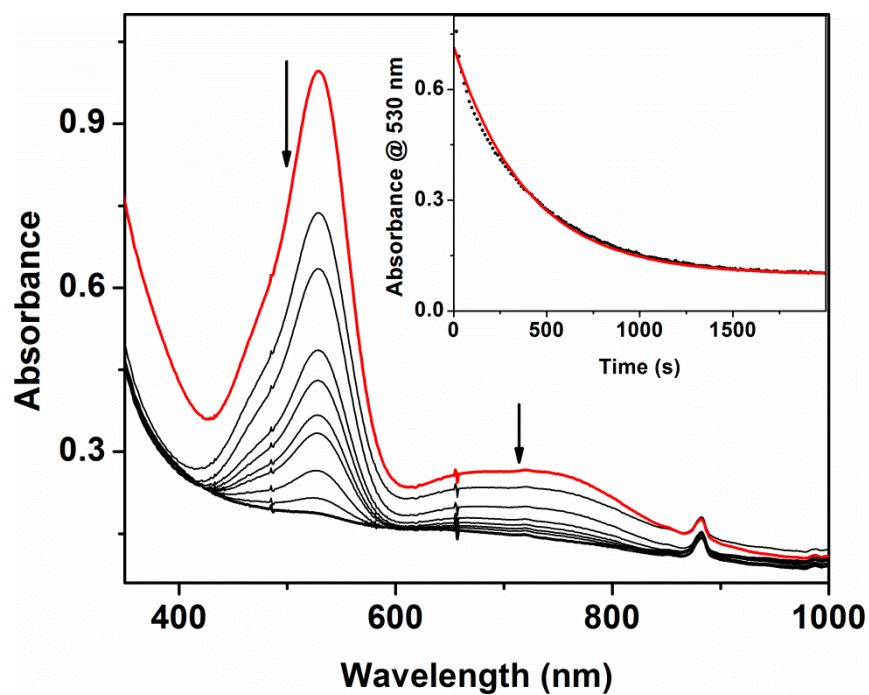


Figure S8 Top: Changes in the absorption spectra associated with the reaction of **3-Sc** (0.29 mM) with 1,4-cyclohexadiene (0.35 M) at $-90\text{ }^{\circ}\text{C}$. Inset: The Pseudo-first order decay of the absorption band at 530 nm as a function of time. **Bottom:** Linear dependence of k_{obs} on the substrate concentration. Positive intercept at zero substrate concentration corresponds to the rate constant for the self decay of **3-Sc** at $-90\text{ }^{\circ}\text{C}$.

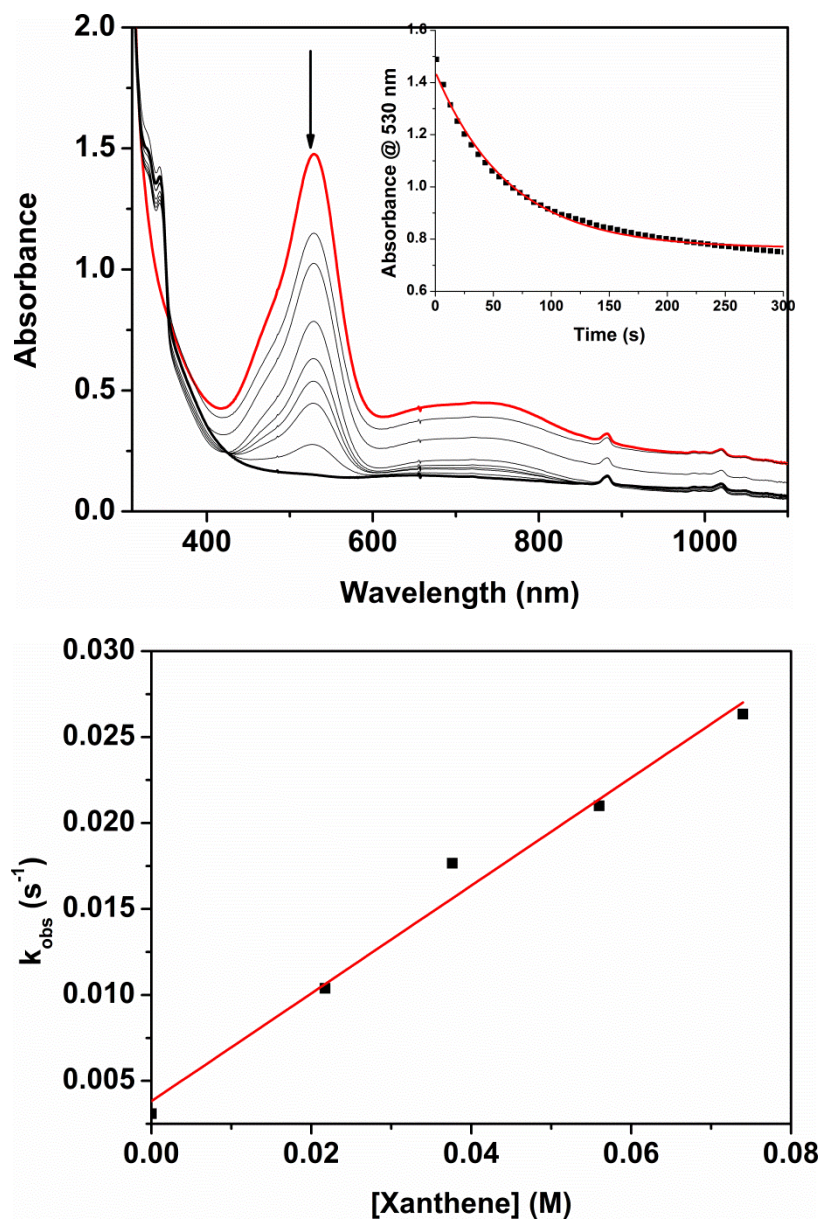


Figure S9 Top: Changes in the absorption spectra associated with the reaction of **3-Sc** (0.38 mM) with Xanthene (0.074 M) at -90 °C. Inset: The Pseudo-first order decay of the absorption band at 530 nm as a function of time. **Bottom:** Linear dependence of k_{obs} on the substrate concentration. Positive intercept at zero substrate concentration corresponds to the rate constant for the self decay of **3-Sc** at -90 °C

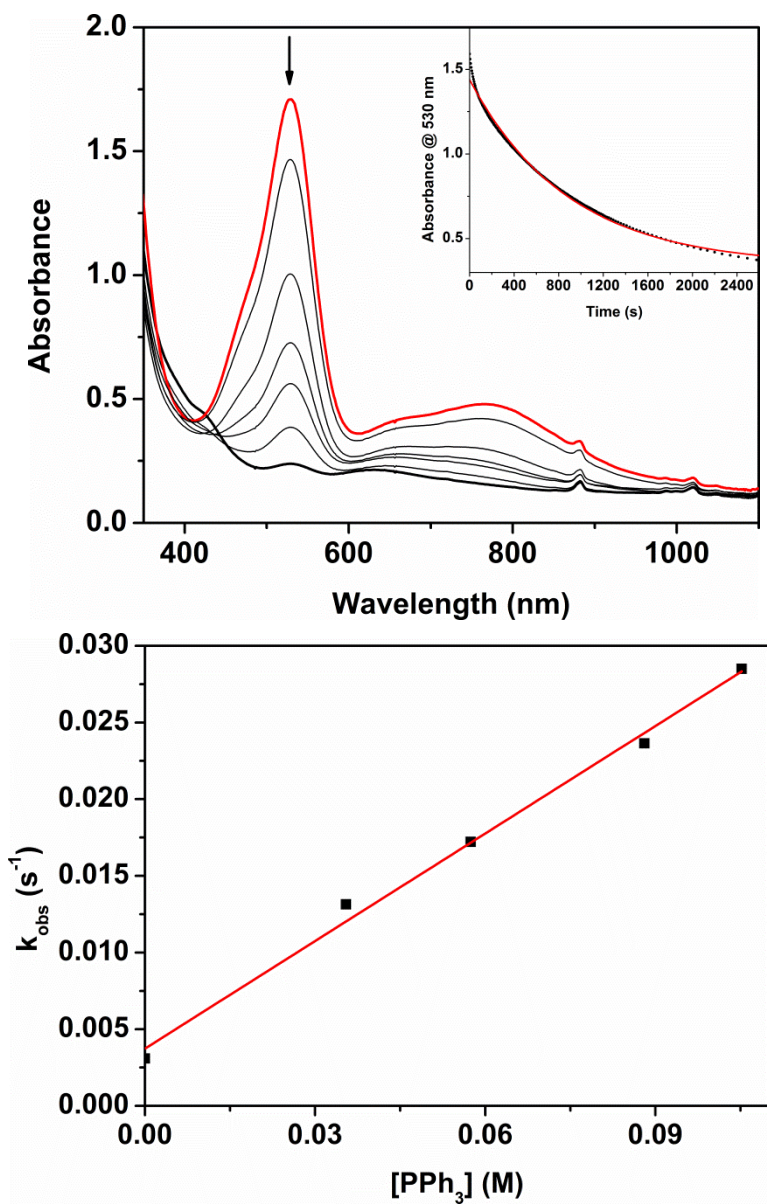


Figure S10 Top: Changes in the absorption spectra associated with the reaction of **3-Sc** (0.48 mM) with PPh₃ (0.088 M) at -90 °C. Inset: The Pseudo-first order decay of the absorption band at 530 nm as a function of time. **Bottom:** Linear dependence of k_{obs} on the substrate concentration. Positive intercept at zero substrate concentration corresponds to the rate constant for the self decay of **3-Sc** at -90 °C.

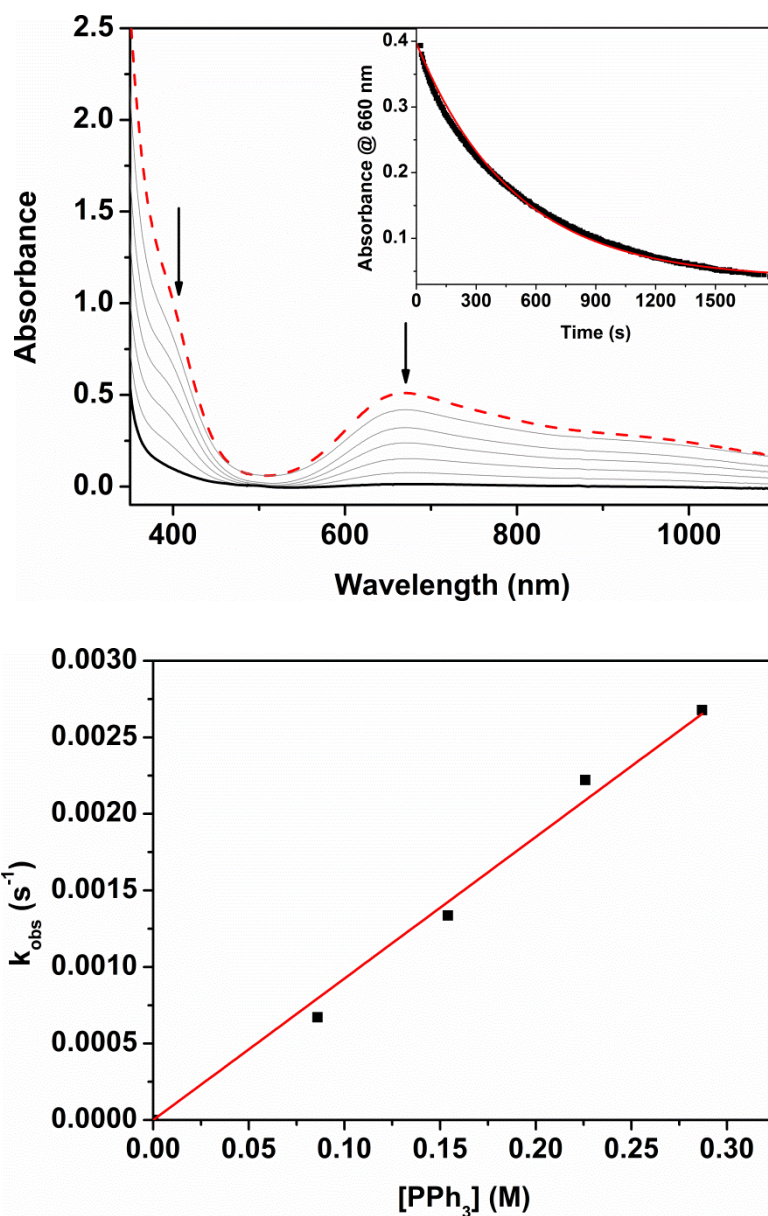
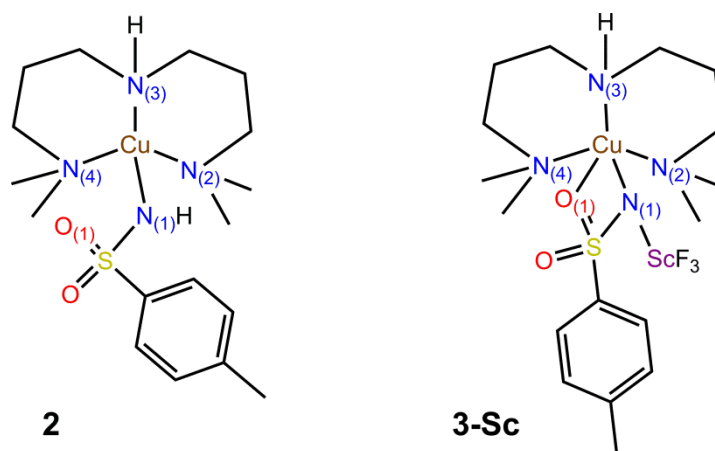


Figure S11 Top: Changes in the absorption spectra associated with the reaction of **2** (2 mM) with PPh₃ (0.286 M) at 25 °C. Inset: The Pseudo-first order decay of the absorption band at 660 nm as a function of time. **Bottom:** Linear dependence of k_{obs} on the substrate concentration.

Table S1: Experimental X-ray diffraction parameters and crystal data for complex **2**

Complex 2	
Empirical formula	C ₁₇ H ₃₃ BCuF ₄ N ₄ O ₂ S
Formula mass	507.88
Crystal habit, color	Elongated plate, bright greenish blue
Crystal dim. (mm)	0.02 x 0.08 x 0.48
Crystal system	Monoclinic
Space Group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	15.4539(6)
<i>b</i> [Å]	13.8231(9)
<i>c</i> [Å]	11.1606(7)
β [°]	108.116(4)
<i>V</i> [Å ³]	2266.0(2)
<i>Z</i>	4
<i>D</i> [g.cm ⁻³]	1.489
<i>F</i> 000	1060
μ (Mo- <i>K</i> α) [cm ⁻¹]	1.109
Diffractometer	STOE IPDS 20
<i>T</i> [K]	100
θ range	2.42- 27.50
Refl. collected	22042
Unique refl.	5162
<i>R</i> _{int}	0.1067
Parameters refined	281
<i>R</i> ₁	0.0416
<i>wR</i> ₂	0.1007
<i>Goof</i>	0.996
Diff. peak/ hole [e/Å ³]	-1.33/ 0.73

Table S2: Selected interatomic distances for **2** (X-ray), **2** (DFT optimized) and **3-Sc** (DFT optimized) structures.



Distances (in Å)	2 (X-Ray)	2 (DFT)	3-Sc (DFT)
Cu-N ₁	1.934(2)	1.985	1.940
Cu-N ₂	2.0542(19)	2.143	2.153
Cu-N ₃	1.994(2)	2.046	2.004
Cu-N ₄	2.0383(19)	2.107	2.193
Cu-S	2.963	3.036	2.692
Cu-O ₁	2.889	3.037	2.232
Cu-Sc	-	-	3.760

Table S3: DFT optimized Cartesian XYZ coordinates of **2**.

C	1.6346546	7.0958520	7.8148940
C	1.0614445	6.0526163	7.0831402
C	1.7253140	4.8299365	6.9281285
C	2.9738002	4.6553942	7.5252226
C	3.5767237	5.6859035	8.2720551
C	2.8880231	6.9036440	8.4035853
S	-0.5578872	6.2893327	6.2922034
N	-0.2369325	6.5385702	4.6946119
Cu	-1.7057979	5.9344708	3.5043077
N	-3.0985742	7.5129244	3.5906221
C	-2.4609595	8.7749630	4.0552418
C	4.9131022	5.4750760	8.9357289
N	-0.4257148	5.0837707	2.0110198
C	0.8785123	5.7938644	2.0004498
N	-3.0971623	4.4414744	3.3534910
C	-4.1637014	4.6261106	4.3839254
C	-4.9811951	5.8977777	4.1859767
C	-4.2457681	7.1991166	4.4949981
O	-1.3032986	4.9787600	6.3593043
O	-1.2061191	7.4567403	7.0008135
C	-0.1833887	3.6447643	2.3263480
C	-1.4392919	2.7813989	2.4176545
C	-2.3994912	3.1326264	3.5498003
C	-1.0668154	5.2458029	0.6803168
C	-3.5568833	7.7070497	2.1883242
H	0.1684178	7.4776889	4.5900798
H	-3.5540377	4.4190270	2.4342147
H	1.2690930	4.0217327	6.3553146

H	3.4917289	3.7008853	7.4081743
H	3.3370764	7.7180534	8.9762691
H	1.1056681	8.0421773	7.9303737
H	5.5779901	4.8615869	8.3117675
H	4.7899430	4.9470307	9.8952990
H	5.4111807	6.4307773	9.1462608
H	0.3582207	3.6192579	3.2827055
H	0.4887002	3.2312824	1.5515873
H	-1.9764388	2.7559722	1.4569620
H	-1.0989631	1.7495244	2.5921072
H	-3.1648801	2.3429123	3.6363633
H	-1.8697514	3.1932801	4.5119778
H	-3.6653274	4.6304572	5.3642392
H	-4.8323939	3.7497998	4.3479196
H	-5.4248449	5.9160854	3.1781332
H	-5.8329647	5.8484894	4.8807506
H	-4.9574798	8.0438531	4.4427944
H	-3.8429429	7.1679162	5.5176585
H	-2.7051954	8.0122728	1.5687409
H	-4.3241230	8.5001375	2.1476860
H	-3.9847771	6.7850856	1.7818851
H	-3.1872347	9.6030850	3.9873888
H	-1.5992451	9.0080209	3.4183082
H	-2.1311843	8.6592180	5.0932553
H	-0.4516540	4.7666697	-0.1014880
H	-1.1559985	6.3140638	0.4494284
H	-2.0636351	4.7935039	0.6630635
H	1.5413048	5.3537074	1.2354816
H	1.3416864	5.7110836	2.9890131

H 0.7177601 6.8528691 1.7650007

Table S4: DFT optimized Cartesian XYZ coordinates of **3-Sc**. The Sc(OTf)₃ has been replaced by ScF₃.

C 3.0929180 6.5733060 6.6823311
C 2.0070276 7.2949448 7.2073758
C 0.8092759 6.6622112 7.5440456
C 0.6961267 5.2817569 7.3459198
C 1.7582347 4.5327042 6.8277321
C 2.9491055 5.1838541 6.5063942
S -0.8729914 4.4747573 7.7459856
O -0.6072267 2.9467539 7.7231366
C 4.3865943 7.2594133 6.3310400
O -1.3249890 5.0559333 9.0513249
N -1.9599466 4.6313198 6.5593117
Cu -2.0476100 2.7671988 6.0276015
N -4.0465434 2.4580008 6.8760075
C -3.9506026 1.5147043 8.0300164
C -3.3776417 0.1452960 7.7031899
C -1.9236943 0.1525168 7.2680130
N -1.6893645 0.7977540 5.9363051
C -0.2786111 0.5484286 5.4997892
C 0.0022567 0.9585659 4.0651578
C -0.0245610 2.4565624 3.8120198
N -1.3469609 3.1208981 4.0231091
C -1.1900106 4.5640081 3.6927243
C -2.3988752 2.5560719 3.1298211
C -4.8807550 1.9124704 5.7699429
C -4.6800117 3.7111043 7.3608430

H	-2.3172307	0.3558243	5.2523475
H	1.6696929	3.4529681	6.7122596
H	3.7846820	4.5986977	6.1167970
H	2.0984140	8.3719312	7.3599411
H	-0.0133207	7.2401816	7.9660479
H	4.6736762	7.0500740	5.2897707
H	5.2070343	6.8966911	6.9696065
H	4.3114641	8.3468082	6.4573967
H	0.7009717	2.9723317	4.4572146
H	0.2706801	2.6533413	2.7666134
H	-0.6619910	0.4207745	3.3721212
H	1.0191863	0.6161249	3.8254480
H	-0.0958765	-0.5319289	5.6082310
H	0.3778140	1.0691099	6.2104303
H	-1.2871676	0.6724462	7.9968585
H	-1.5646497	-0.8851762	7.1860199
H	-4.0011663	-0.3890261	6.9705523
H	-3.4317228	-0.4486674	8.6268617
H	-4.9713064	1.3928733	8.4332916
H	-3.3468923	2.0121899	8.8016911
H	-4.9855929	2.6748962	4.9906095
H	-5.8832388	1.6619230	6.1552980
H	-4.4416635	1.0066976	5.3423288
H	-5.6618299	3.4623345	7.7963676
H	-4.8488838	4.3852159	6.5138631
H	-4.0557112	4.1855007	8.1231111
H	-2.0742591	2.6523819	2.0804139
H	-3.3261120	3.1238169	3.2639637
H	-2.5782406	1.4972873	3.3381751

H	-0.8105482	4.6455570	2.6612335
H	-0.4861594	5.0395066	4.3807845
H	-2.1669456	5.0559095	3.7359038
Sc	-3.0839876	6.3815826	5.9729507
F	-3.9873671	7.1375566	7.4590637
F	-1.8598365	7.6405559	5.2610338
F	-4.2736017	5.6809272	4.6496215.

Table S5: Reactivity of **2** and **3-Sc**.

Substrate for 3-Sc	BDE (kcal/mol)	k_2 (@ -90 °C) (M ⁻¹ s ⁻¹)	Product (yield)
BNAH	67.9	4.8109	-
Xanthene	74	0.3135	-
DHA	76.3	0.2085	Anthracene (82%)
1,4-CHD	76.9	0.1554	Benzene (85%)
Triphenylmethane	81.0	0.0261	-
Fluorene	81.2	0.0583	-
Toluene	88.6	0.0051	N-Tosylbenzaldimine (10%) + N-Tosylbenzylamine (21%)
Cyclohexane	99.5	nd	(Tosylamino)cyclohexane (35%)
PPh ₃	-	0.1960	N-Tosyliminotriphenylphosphorane (85%)
Cyclohexene	-	0.0323	Cyclohexene-N-tosylaziridine (60%)
Substrate for 2	BDE (kcal/mol)	k_2 (@ 25 °C) (M ⁻¹ s ⁻¹)	Product (yield)
PPh ₃	-	0.0092	N-Tosyliminotriphenylphosphorane (75%)

nd = not determined; Yields are reported with respect to Cu.

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