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Supplementary Information

A Cobalt(II) Iminoiodane Complex and its Scandium Adduct: Mechanistic Promiscuity in Hydrogen Atom Abstraction Reactions.

Subrata Kundu,[a] Petko Chernev,[b] Xenia Engelmann,[a] Chan Siu Chung,[e] Holger Dau,[b] Eckhard Bill,[c] Jason England,*[,e] Wonwoo Nam*[,d] and Kallol Ray*[,a]

[a]*Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Straße 2, D-12489 Berlin, Germany. E-mail: kallol.ray@chemie.hu-berlin.de;*

[b]*Freie* Universität Berlin, FB Physik, *Arnimallee 14, D-14195-Berlin (Germany);*

[c]*Max-Plank-Institut für Chemische Energiekonversion, Stiftstraße 34-36, D-45470-Mülheim an der Ruhr (Germany);*

[d]*Department of Chemistry and Nano Science, Center for Biomimetic System, Ewha Womans University, Seoul 120-750, Korea. E-mail: wwnam@ewha.ac.kr;*

[e]*Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637731. E-mail: jengland@ntu.edu.sg*

Experimental Section

1. Materials

All chemicals were purchased from Sigma-Aldrich, Acros, ABCR, TCI and used without further purification unless otherwise mentioned. Anhydrous solvents were purchased from Carl-Roth GmbH (≥ 99.5%, < 50 ppm H_2O) and degassed by freeze-pump-thaw method prior to use. Complex **1**,[1] [N-(p-toluenesulfonyl)imino](2-tert-butylsulfonyl)phenyliodinane] (^{s}PhINTs),[2] and deuterated substrates were prepared by following the previously published procedures. All the liquid substrates for reactivity studies were distilled under argon prior to use.

2. Instrumentation 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. 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 were measured either by preparation of KBr pellet of solid sample with Shimadzu FTIR-8400S spectrometer. ^{1}H NMR spectra were recorded either on a Bruker AV 400 NMR spectrometer or on a Bruker DPX 300 spectrometer. The products of reactivity studies were identified by ^{1}H- and ^{31}P-NMR. The product quantification was done by using known amount of nitromethane as internal standard. The chemical shifts are reported in ppm relative to the residual solvent signal.

EPR spectroscopy: 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). Samples of **2** and **2-Sc** were generated (as mentioned in section 3: Synthesis) in a UV-Vis cuvette and transferred to EPR tubes and frozen immediately under liquid nitrogen for EPR measurements.

Electrospray ionization mass spectrometry experiments were carried out on precooled CH_2Cl_2 solutions (@ -100 ºC) of **2/2-Sc** in an Agilent 1200 mass spectrometer using a spray chamber voltage of 4000 V and a gas carrier temperature of 50°C.

X-Ray absorption Spectroscopy: Co *K*-edge XAS data for the samples of **1**, **2**, and **2-Sc** were collected at beamline KMC-1 of the Helmholtz-Zentrum Berlin for Materials and Energy 3 (formerly known as BESSY II, Berlin). The data were collected at a bending-magnet beamline at 20 K in a liquid-helium cryostat, as described elsewhere.[3] A relatively large sample was irradiated (~3 mm^2) and in each scan different spots of the sample were exposed to the X-ray beam, thereby excluding any significant radiation-induced modification (radiation damage) of the investigated molecules. All spectra were

recorded in fluorescence mode using an energy-resolving 13-element Ge detector (Canberra). Calibration to the first inflection point in the spectrum of a simultaneously measured Co foil[4] was used for energy calibration. Edge energy was determined from the center of gravity of the slope of the normalized spectrum calculated between absorption units of 0.2 to 1. For EXAFS analysis, the extracted spectra were weighted by k^3 as described elsewhere.[5] All EXAFS simulations were performed using in-house software (SimX) after calculation of the phase functions with the FEFF program[6,7] (version 8.4, self-consistent field option activated). Atomic coordinates of the FEFF input files were generated for several reasonable structural models; the EXAFS phase functions did not depend strongly on the details of the used model. An amplitude reduction factor S_0^2 of 0.8 was used. The data range used in the simulation was 30–500 eV (2.8–11.4 $Å^{-1}$). The EXAFS simulation was optimized by a minimization of the error sum obtained by summation of the squared deviations between measured and simulated values (least-squares fit).

3. Syntheses:

*Generation of **2**:* Solution of the orange complex **2** was obtained by treatment of a solution of **1** in CH_2Cl_2 or acetone (2 ml) at -40 °C with a solution of ^{s}PhINTs (1.0 equiv.) in CH_2Cl_2 (0.1 mL). The formation of **2** was monitored by following the development of the 420 nm absorption band in the UV/vis spectrum.

*Generation of **2-Sc**:* The solution of **1** in CH_2Cl_2 or acetone (2 mL) was cooled to -40 °C. Then one equivalent $Sc(OTf)_3$ in acetone (0.1 mL) and one equivalent of ^{s}PhINTs in CH_2Cl_2 (0.15 mL) were added, respectively, to yield a deep orange intermediate **2-Sc**. The generation of the deep orange species **2-Sc** was monitored by following the growth of the 450 nm absorption band in the UV/vis spectrum.

4. Reactivity Studies:

Determination of k_2: The reactivity studies of **2** and **2-Sc** were done at -20 – -40 °C, under inert atmosphere, by injecting acetone solution of the substrate into the preformed solution of **2** or **2-Sc**. The pseudo-first order decay of the characteristic absorption bands were monitored by acquiring an UV/vis spectrum in every 1 - 3 seconds. 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).

Product analysis: Calculated amount of substrate (1 - 5 equivalents) in 0.1 mL d_6-acetone was added to the preformed solution of **2** or **2-Sc** in d_6-acetone at -40 °C in a NMR tube and left for 2 hours at -40 °C. After adding 2 μ L of nitromethane as an internal standard, the resultant solution was analyzed for products by ^{1}H-NMR spectroscopy. Phenoxyl radicals were identified and quantified by EPR.

Blank reactions with different substrates in absence of complex **1** were also performed under similar reaction conditions. The product analyses of the resultant reaction mixtures did not show the formation of corresponding products. Ph_3P=NTs was identified on the basis of the characteristic ^{31}P-NMR in d_6-acetone/CD_2Cl_2 solvent mixture: δ= 14.06 ppm

5. Calculations. All DFT calculations were performed using version 3.0 of the ORCA software package.[8] The geometries of all complexes were optimized, in redundant internal coordinates without imposing geometry constraints at the BP86 level of theory.[9] Calculation of single-point energies and other electronic properties of these optimized structures were performed using the B3LYP functional.[10] In all calculations, def2-TZVP basis sets[11] were applied to all atoms except C and H, which were described by slightly smaller polarized split-valence def2-SV(P) basis sets.[12] Auxiliary basis sets, used to expand the electron density in the calculations, were chosen to match the orbital basis sets.[13] The RI and RIJCOSX approximations were used to accelerate the calculations.[14] All calculations were performed with inclusion of dispersion forces via implementation of the D3ZERO empirical correction.[15] The authenticity of each converged structure was confirmed by the absence of imaginary vibrational frequencies.

The self-consistent field calculations were tightly converged (1×10^{-8} E_h in energy, 1×10^{-7} E_h in the density charge, and 1×10^{-7} in the maximum element of the DIIS[16] error vector). In all cases, the geometries were considered converged after the energy change was less than 1×10^{-6} E_h, the gradient norm and maximum gradient element were smaller than 3×10^{-5} and 1×10^{-4} E_h Bohr^{-1}, respectively, and the root mean displacements of all atoms were smaller than 6×10^{-4} and 1×10^{-3} Bohr, respectively.

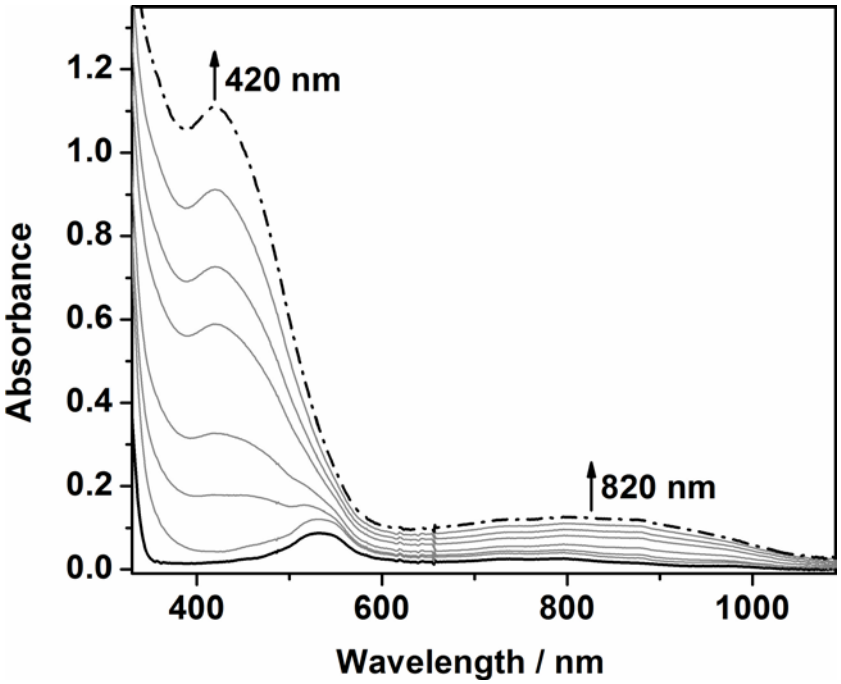


Figure S1: Changes in the absorption spectra of **1** (1.0 mM in acetone/CH_2Cl_2 (95:5 % by volume) upon addition of 1 equiv of ^{s}PhINTs at -40 °C.

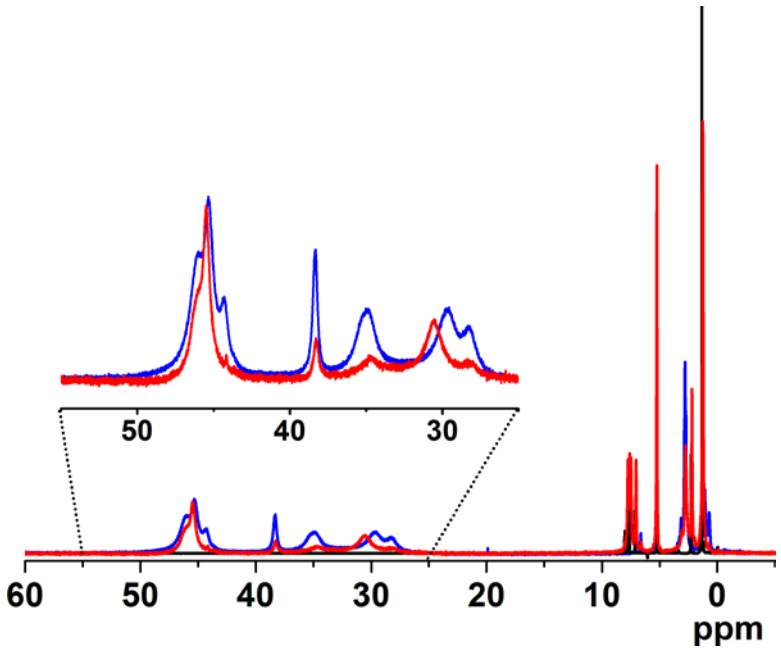


Figure S2: ^{1}H-NMR spectra of ^{s}PhINTs (black trace), **1** (blue trace), and **2** (red trace) in CD_2Cl_2 at 193 K. The inset shows an expansion of the broad peaks for **1** and **2**. An expansion of the 8.5-0.5 ppm region of these ^{1}H-NMR spectra is shown in Figure S3. Note that because of the solubility of ^{s}PhINTs in only chlorinated solvents, CD_2Cl_2 was the obvious choice of solvent for all NMR studies.

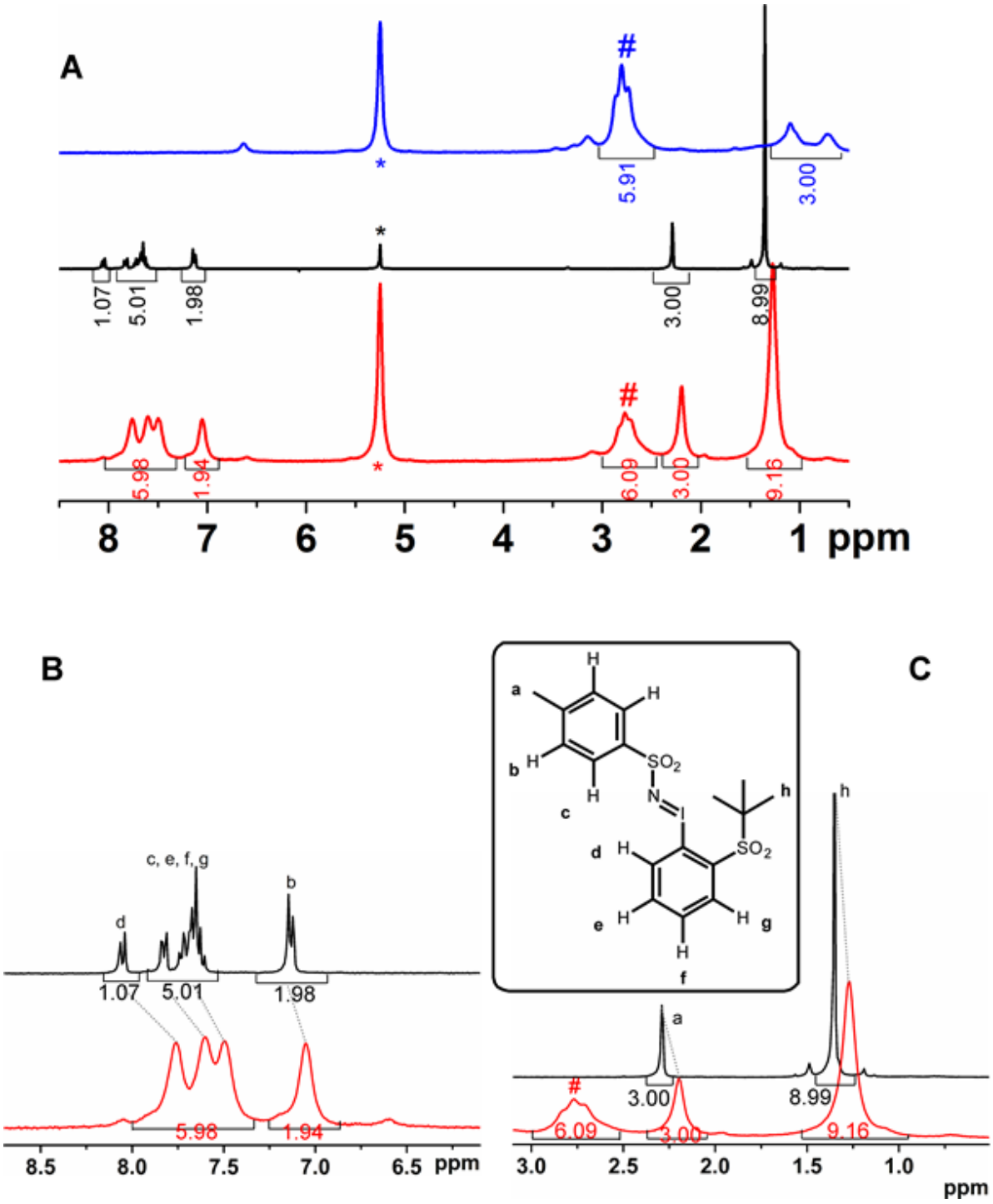


Figure S3: A) Comparison of the ^{1}H-NMR spectra (8.5-0.5 ppm region) of ^{s}PhINTs (black trace), **1** (blue trace) and **2** (red trace) in CD_2Cl_2 at 193 K. Solvent peaks are marked by asterisks (*) and the peak originating from a -CH_2- of TMG_3tren ligand backbone is marked by (#). Integrals of the peaks are mentioned below the respective peaks. B) and C) are the expanded view of the aromatic (8.5-6.5 ppm) and non-aromatic (3.0-0.7 ppm) region of the spectra, respectively. Note that because of the solubility of ^{s}PhINTs in only chlorinated solvents, CD_2Cl_2 was the obvious choice of solvent for all NMR studies.

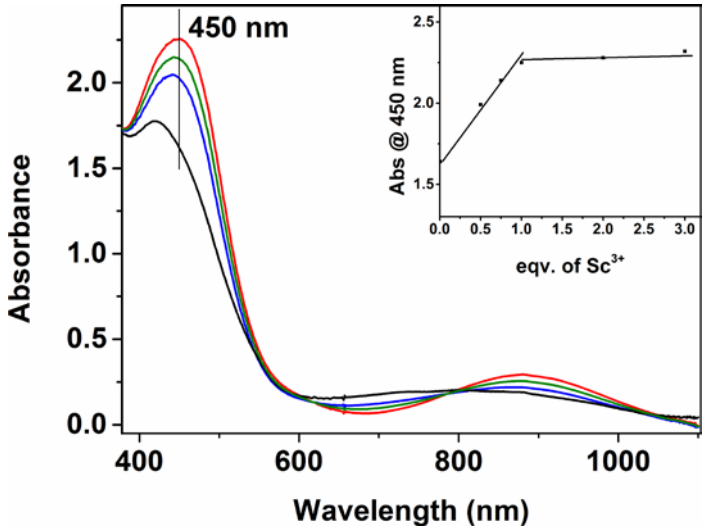


Figure S4: Changes in the absorption spectra of **2** (1.5 mM in acetone CH_2Cl_2 (95:5 % by volume)) upon addition of 0 equiv (black trace), 0.5 equiv (blue trace), 0.75 equiv (green trace), and 1 equiv (red trace) of Sc^{3+} at -40 °C. Inset: Plot of the absorbance at 450 nm band of **2-Sc** against the equivalents of Sc^{3+} ion added to **2**.

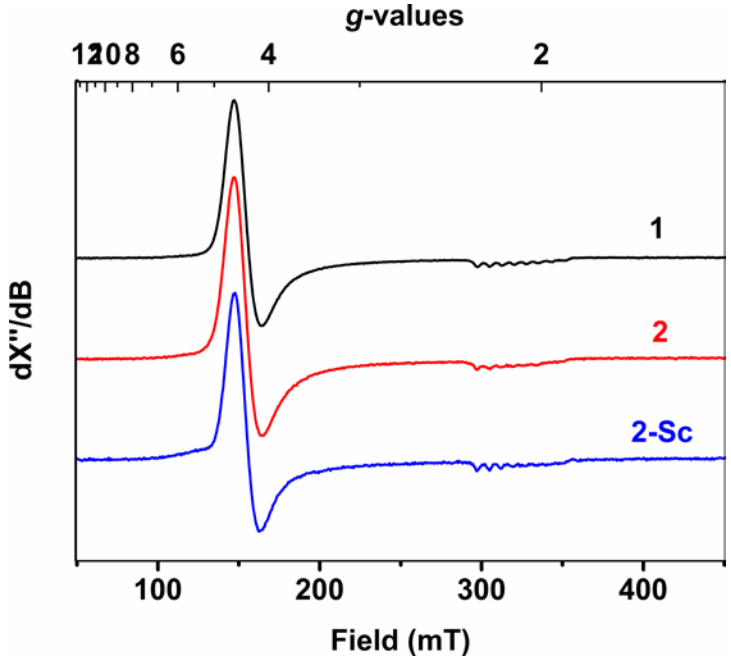


Figure S5: X-band EPR spectra of **1**, **2**, and **2-Sc** in acetone/CH_2Cl_2 (95:5 % by volume) at 10 K (frequency 9.467 GHz; power 0.05 mW; modulation 1.0 mT).

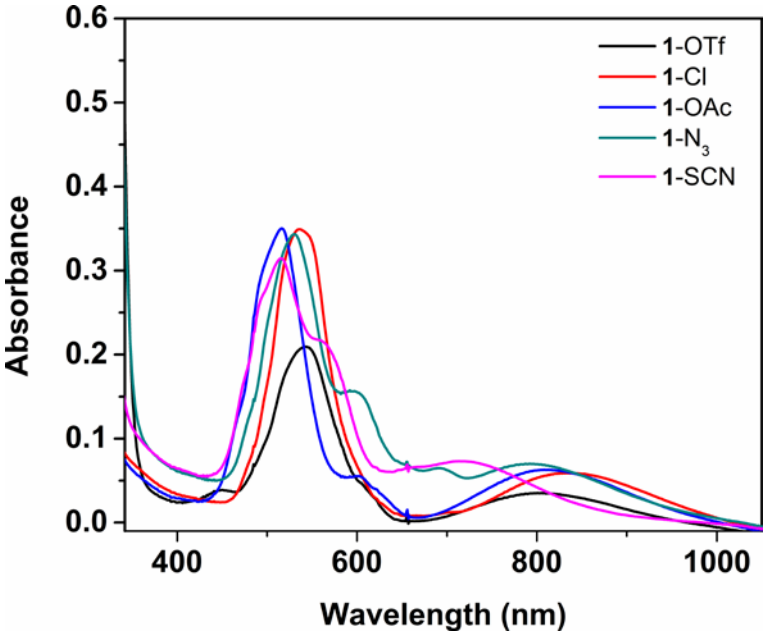


Figure S6: Comparison of the absorption spectra of **1**-X (X = Cl, OAc, N_3, and SCN) (2 mM, in acetone at 25 °C). **1**-X (X = Cl, OAc, N_3, and SCN) were generated by treating **1**-OTf with 2 equivalents of *n*Bu_4NX in acetone at 25 °C. All the **1**-X complexes show EPR spectra identical to **1**, **2** and **2-Sc** (Figure S5).

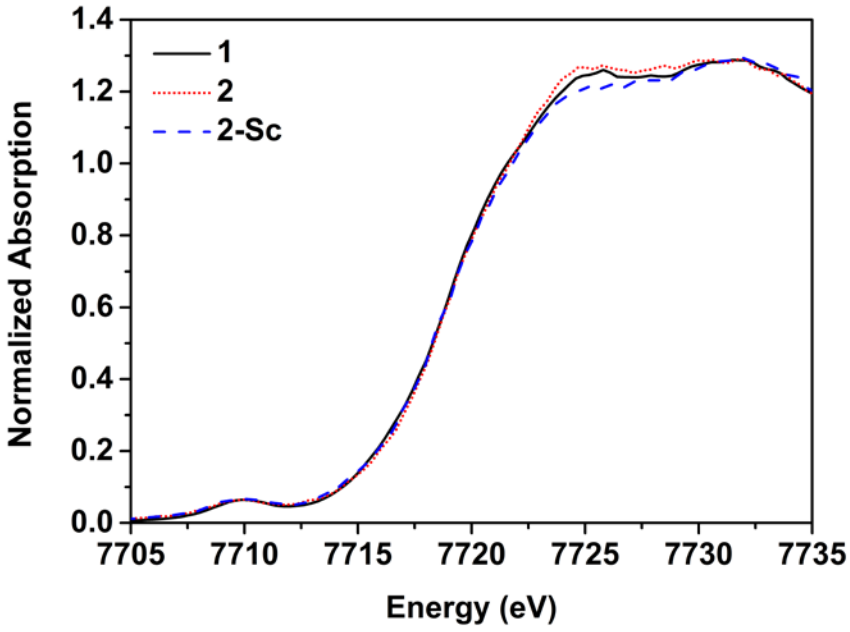


Figure S7: Co-*K* edge XANES spectra of **1**, **2**, and **2-Sc** in frozen acetone/CH_2Cl_2 (95:5 % by volume) solutions**.** Concentration of CH_2Cl_2, needed to dissolve the ^{s}PhINTs oxidant, was kept minimum to improve the signal/noise ratio, as chlorinated solvents are known to absorb X-rays.

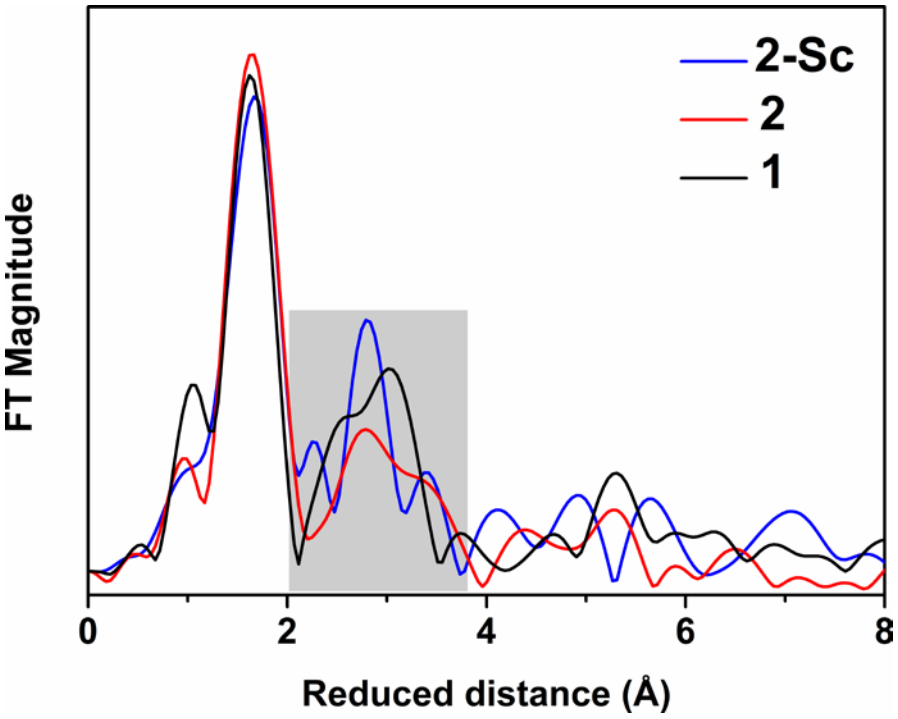


Figure S8: Comparison of Fourier transformed Co *K*-edge EXAFS data of frozen acetone/CH_2Cl_2 (95:5 % by volume) solutions of **1**, **2**, and **2-Sc**. The highlighted part (reduced distance > 2 Å) depicts the changes in the outer-shell features for **1**, **2**, and **2-Sc**. Concentration of CH_2Cl_2, needed to dissolve the ^{s}PhINTs oxidant, was kept at a minimum to improve the signal/noise ratio, as chlorinated solvents are known to absorb X-rays.

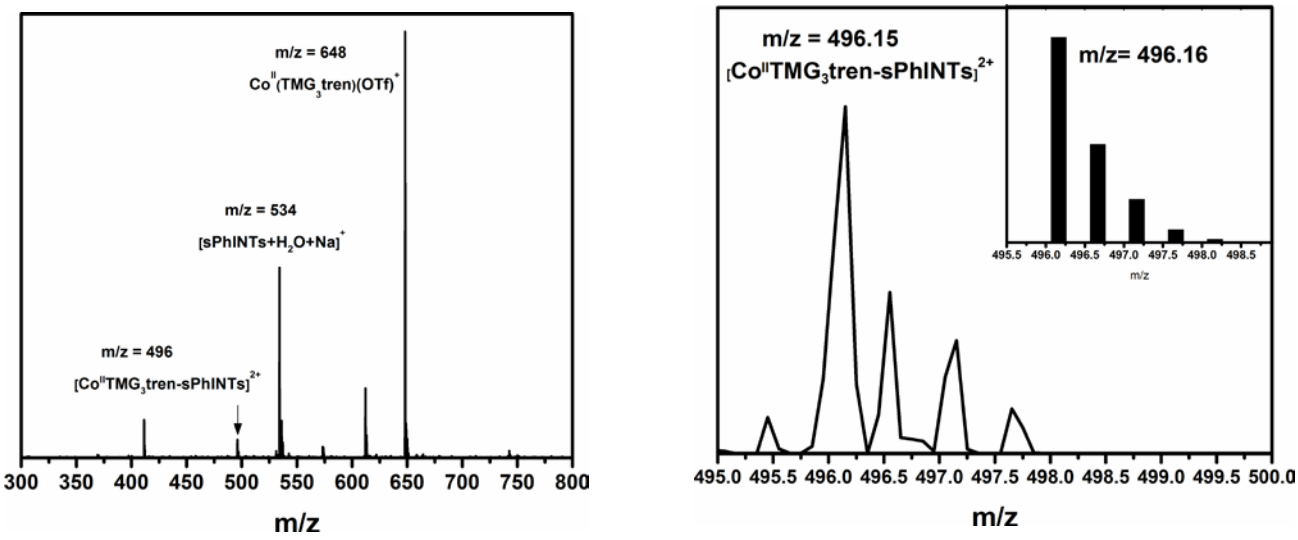


Figure S9: Left: ESI-MS spectrum of **2** in CH_2Cl_2. Right: The experimentally observed isotope distribution pattern of the low intense molecular ion peak at m/z=496.15; in the inset is given the theoretically predicted mass distribution pattern. Identical spectrum was obtained for **2-Sc.**

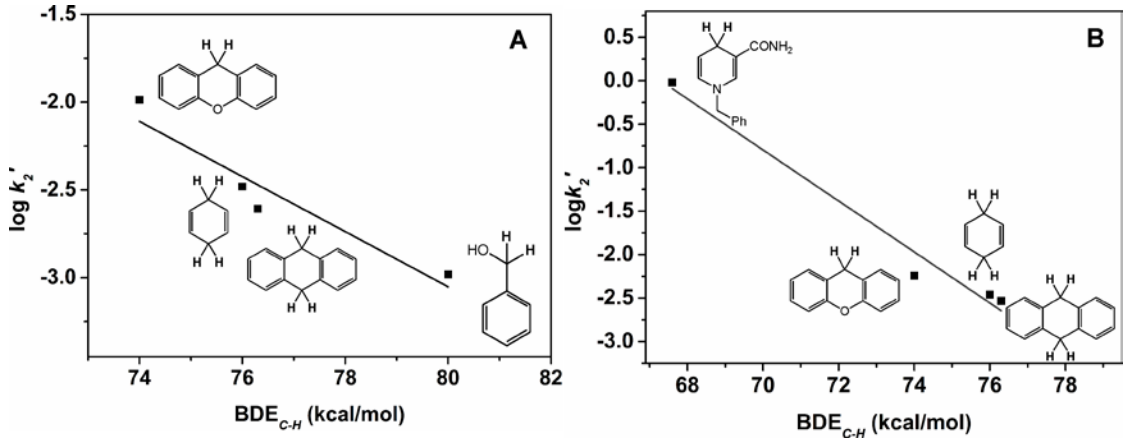


Figure S10: Plot of log k_2' (where, $k_2' = k_2$ / number of equivalent target C-H bonds in the substrate) for **2** (A) and **2-Sc** (B) at -40 °C against BDE[19] of different C-H substrates. Reactions were performed in acetone/CH_2Cl_2 (95:5 % by volume) solvent mixtures.

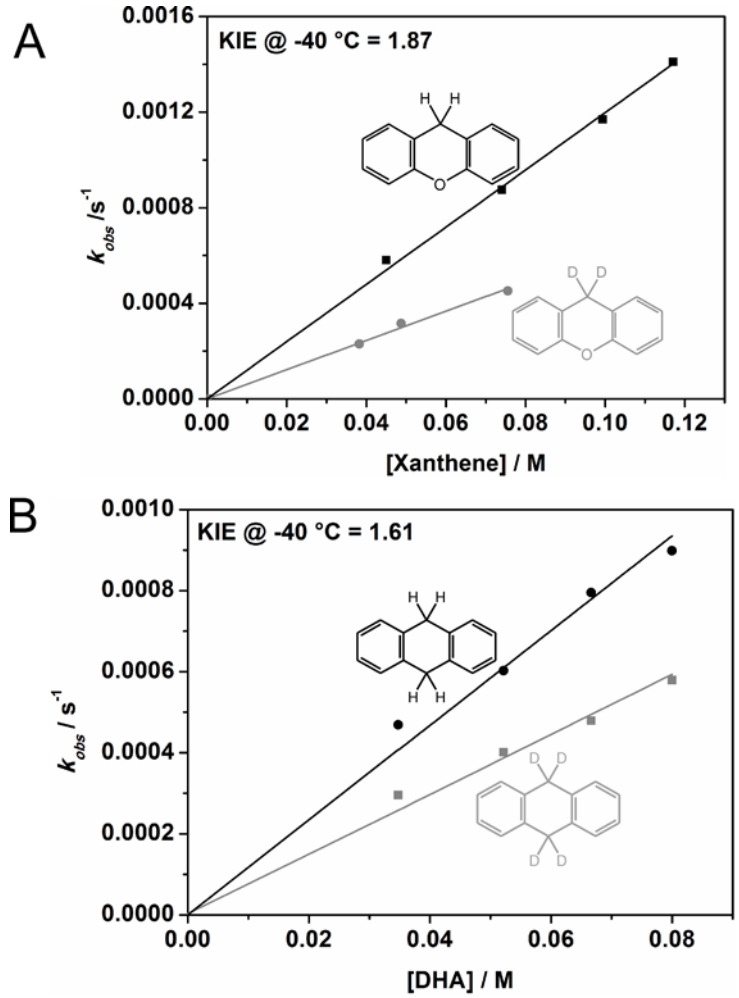


Figure S11: Linear dependences of k_{obs} on the concentrations of different substrates and their deuterated analogues for the reactions with **2** at -40 °C. Reactions were performed in acetone/CH_2Cl_2 (95:5 % by volume) solvent mixtures.

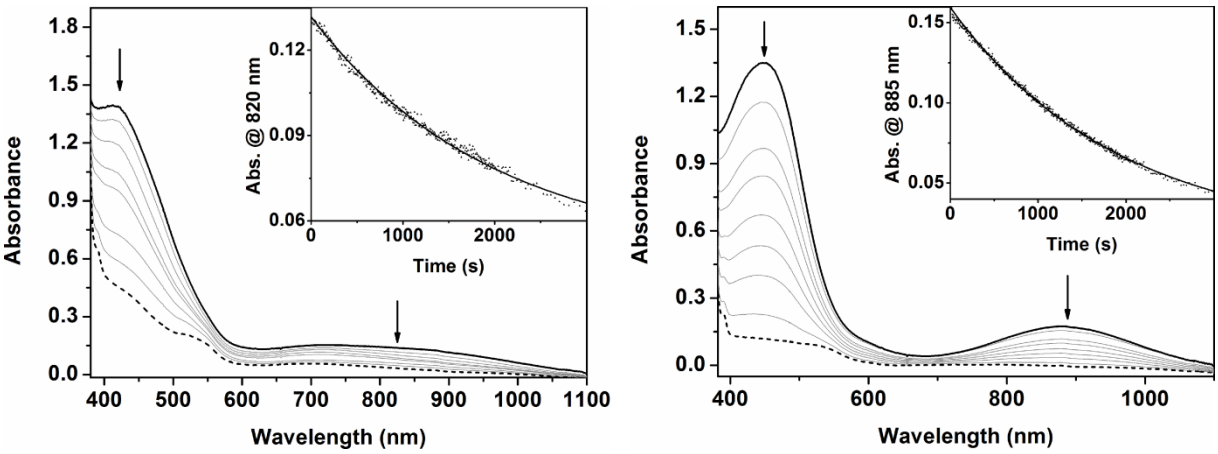


Figure S12: Changes in the absorption spectra of **2** (left) and **2-Sc** (right) upon addition of benzyl alcohol (80 equiv.) at -40 °C. The insets show the time traces monitored at 820 nm for **2** (left inset) and 885 nm for **2-Sc** (right-inset). Reactions were performed in acetone/CH_2Cl_2 (95:5 % by volume) solvent mixtures.

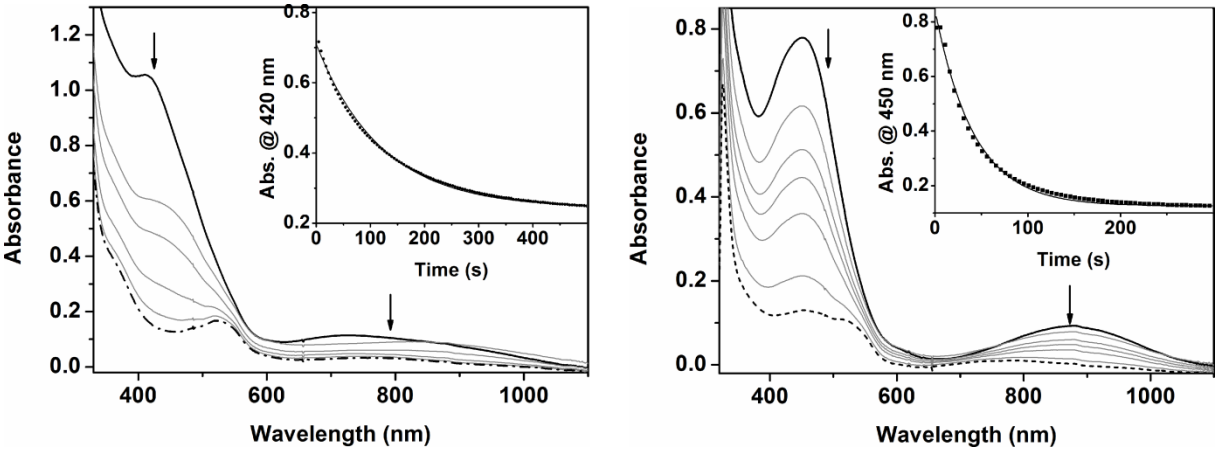


Figure S13: Changes in the absorption spectra of **2** (left) and **2-Sc** (right) upon addition of 4-methoxy-2,6-ditert-butylphenol (MeO-DTBP) (40 equiv.) at -40 °C. The insets show the time traces monitored at 420 nm for **2** (left inset) and 450 nm for **2-Sc** (right-inset). The reaction of MeO-DTBP was found to be too fast to be followed at -20 °C. Thus, the k_2 value for MeO-DTBP was determined at -40 °C and was adjusted for -20 °C by multiplying k_2 by four; the rate of reaction is considered to be doubled for every 10 °C rise in temperature. Reactions were performed in acetone/CH_2Cl_2 (95:5 % by volume) solvent mixtures.

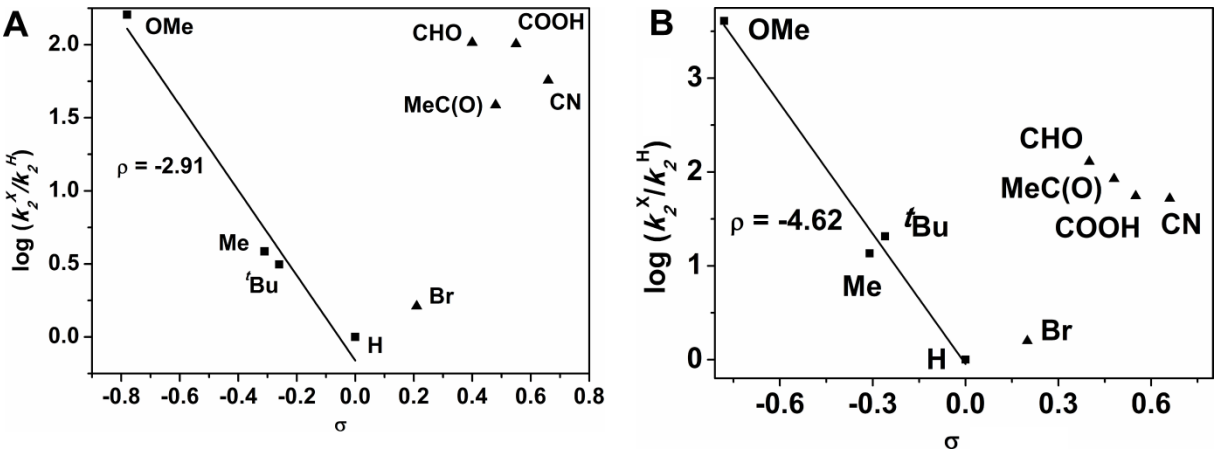


Figure S14: Hammett plot for the reaction of *para*-substituted 2,6-ditert-butylphenol substrates [X-DTBP; X = MeO, Me, ^{t}Bu, H, Br, CN, CHO, COOH, MeC(O)] with **2** (A) and **2-Sc** (B) at -20 ^{o}C. [k_2^X = second-order rate constant (k_2) for the *para*-substituted 2,6-ditert-butylphenol with *para*-substituent X; k_2^H = second-order rate constant (k_2) for 2,6-ditert-butylphenol (DTBP)]. Reactions were performed in acetone/CH_2Cl_2 (95:5 % by volume) solvent mixtures.

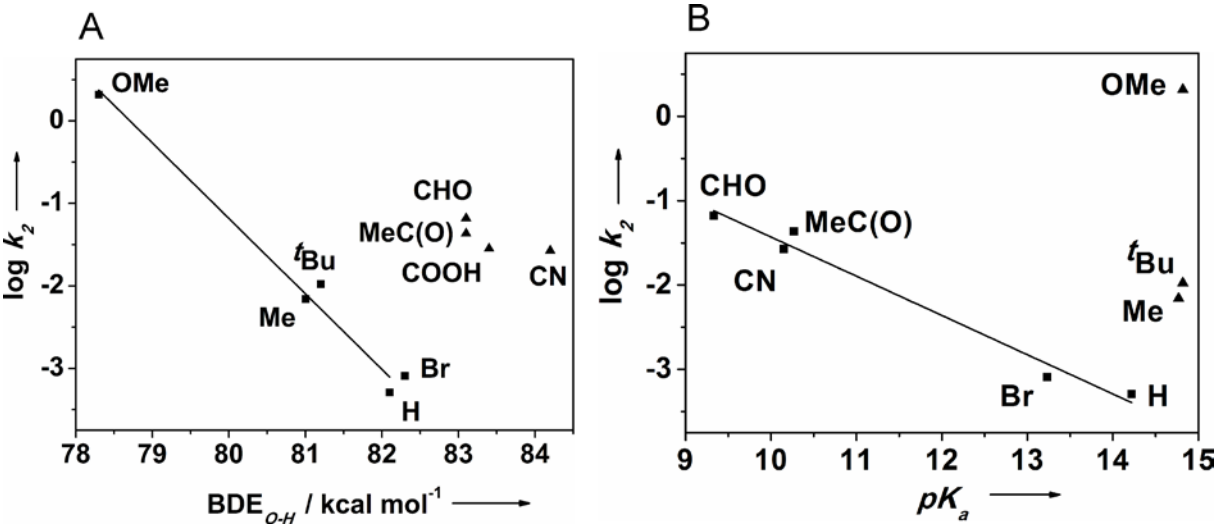


Figure S15: A) Plot of log k_2 for **2-Sc** at -20 ^{o}C against O-H bond dissociation energies (BDE_{O-H}) of *para*-substituted 2,6-ditert-butylphenol substrates [X-DTBP; X = MeO, Me, ^{t}Bu, H, Br, CN, CHO, COOH, MeC(O)]. B) log k_2 *versus* pK_a plot for the reaction of *para*-substituted 2,6-di-tert-butylphenol

substrates [X-DTBP; X = MeO, Me, ^{t}Bu, H, CN, CHO, Br] with **2-Sc** at -20 ^{o}C. Reactions were performed in acetone/CH_2Cl_2 (95:5 % by volume) solvent mixtures.

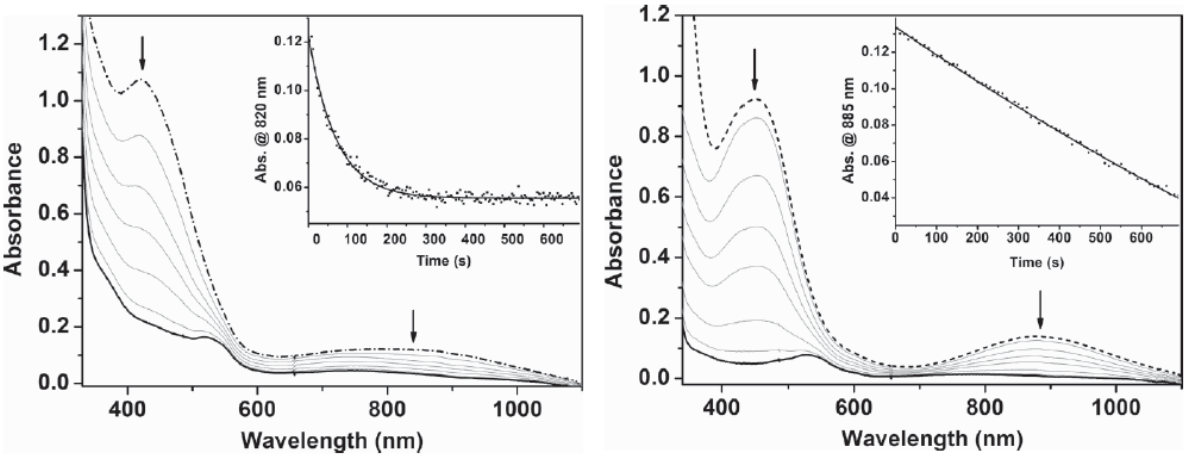


Figure S16: Changes in the absorption spectra of **2** (left) and **2-Sc** (right) upon addition of triphenyl phosphine (30 eqv.) at -40 °C. The insets show the time traces monitored at 820 nm for **2** (left inset) and at 885 nm for **2-Sc** (right-inset). Reactions were performed in acetone/CH_2Cl_2 (95:5 % by volume) solvent mixtures.

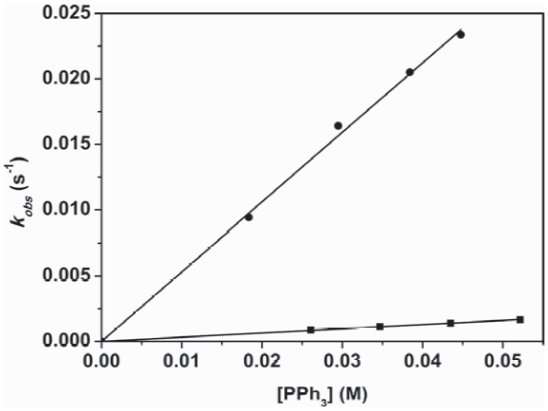


Figure S17: Linear dependence of k_{obs} on the triphenyl phosphine concentration. at -40 °C. The solid-circles and solid-squares represent the experimental data points for **2** and **2-Sc**, respectively. Reactions were performed in acetone/CH_2Cl_2 (95:5 % by volume) solvent mixtures.

Table S1: Structural parameters obtained from the least square simulation of the EXAFS analysis of **1**, **2**, and **2-Sc**.

Complex	EXAFS analysis			Assigned to
	Coordination	r (Å)	σ (Å)	
1	5 Co-N/O	2.05	0.07	4 Co-N_{ligand} 1 Co-$O_{triflate}$
	8 Co-C	2.94	0.12	8 Co-C_{ligand}
	6 Co-C/N	3.45	0.04	6 Co-C/N_{ligand}
2	5 Co-N/O	2.05	0.07	4 Co-N_{ligand} 1 Co-$O_{(sPhINTs)}$
	8 Co-C	3.00	0.12	8 Co-C_{ligand}
	6 Co-C/N	3.49	0.07	6 Co-C/N_{ligand}
	1 Co-S	3.78	0.03	1 Co-$S_{(sPhINTs)}$
2-Sc	5 Co-N/O	2.05	0.08	4 Co-N_{ligand} 1 Co-$O_{(sPhINTs)}$
	8 Co-C	2.98	0.12	8 Co-C_{ligand}
	6 Co-C/N	3.35	0.04	6 Co-C/N_{ligand}
	1 Co-Sc	3.62	0.03	1 Co-Sc
	1 Co-S	3.66	0.33	1 Co-$S_{(sPhINTs)}$

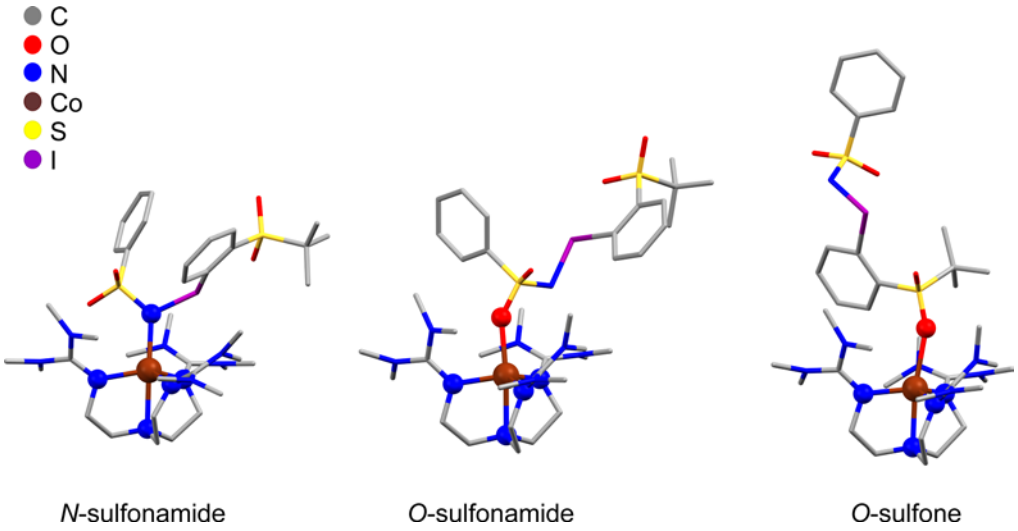
Table S2: Results of EXAFS simulations (fit) for **2**. The best fits are shown in bold. The parameters indicated with * (asterisk) were fixed during the simulation.

	Co-N	**Co-N**	**Co-C**	**Co-C/N**	**Co-I**	**Co-S**	
Fit	**N R [Å] σ [Å]**	**N R [Å] σ [Å]**	**N R [Å] σ [Å]**	**N R [Å] σ [Å]**	**N R [Å] σ [Å]**	**N R [Å] σ [Å]**	**R_F [%]**
1	5* 2.05 0.07						34.4
2	3* 2.02 0.04	2* 2.13 0.04					33.7
3	5* 2.05 0.07		8* 3.00 0.12	6* 3.51 0.09			18.3
4	5* 2.05 0.07		8* 3.00 0.12	6* 3.51 0.06	1* 3.74 0.07		12.6
5	**5* 2.05 0.07**		**8* 3.00 0.12**	**6* 3.51 0.06**		**1* 3.78 0.03**	**13.5**

Table S3: Results of EXAFS simulations (fit) for **2-Sc**. The best fits are shown in bold. The parameters indicated with * (asterisk) were fixed during the simulation.

	Co-N	**Co-N**	**Co-C**	**Co-C/N**	**Co-I**	**Co-S**	**Co-Sc**	
Fit	**N R [Å] σ [Å]**	**N R [Å] σ [Å]**	**N R [Å] σ [Å]**	**N R [Å] σ [Å]**	**N R [Å] σ [Å]**	**N R [Å] σ [Å]**	**N R [Å] σ [Å]**	**R_F [%]**
1	5* 2.06 0.08							43.9
2	3* 2.10 0.01	2* 1.96 0.01						44.5
3	5* 2.05 0.08		8* 2.96 0.12	6* 3.37 0.04*				38.7
4	5* 2.04 0.08		8* 2.95 0.13	6* 3.40 0.04*	1* 3.63 0.03*			28.1
5	5* 2.06 0.08		8* 2.99 0.11	6* 3.39 0.04*			1.5 3.60 0.03*	21.2
6	5* 2.05 0.08		8* 2.98 0.12	6* 3.42 0.04*	1* 3.62 0.03*		1.1 3.66 0.03*	26.7
7	5* 2.05 0.08		8* 2.98 0.11	6* 3.40 0.07*		1* 3.71 0.03*		23.0
8	**5* 2.05 0.08**		**8* 2.98 0.12**	**6* 3.39 0.04***		**1* 3.66 0.03***	**1.2 3.62 0.03***	**20.1**

Table S4: Selected interatomic distances for different DFT optimized geometries of **2**.



Geometries of **2**	Coordinate/path	distance (Å)	Average Co-N/O distance (Å)
N-sulfonamide (*S* = 3/2)	Co-N_{eq} Co-N_{ax} Co-$N_{(sPhINTs)}$ Co···$S_{(Tosyl)}$ Co···I	2.07, 2.09, 2.12 2.30 2.25 3.54 3.67	2.17
O-sulfonamide (*S* = 3/2)	Co-N_{eq} Co-N_{ax} Co-$O_{(Tosyl)}$ Co···$S_{(Tosyl)}$ Co···I	2.02, 2.02, 2.04 2.25 2.21 3.55 5.99	2.10
O-sulfone (*S* = 3/2)	Co-N_{eq} Co-N_{ax} Co-$O_{(sulfone)}$ Co···$S_{(sulfone)}$ Co···I	2.00, 2.03, 2.04 2.26 2.35 3.77 7.07	2.14

Table S5: Relative energies for different DFT optimized geometries of **2**.

Geometries of **2**	*S* = 3/2	*S* = ½
N-sulfonamide	+15.33	+30.25
O-sulfonamide	0.00	+18.29
O-sulfone	+26.51	-

Table S6: DFT geometry optimized atomic xyz coordinates for **2** (*N*-sulfonamide) in *S* = 3/2 ground state.

C	11.458098	0.154410	3.941183
N	10.762596	0.288821	5.213947
C	9.397503	0.165248	5.277162
N	8.878472	-0.425179	6.381364
C	7.502710	-0.196077	6.787101
C	11.596304	0.680008	6.349586
N	8.607506	0.661318	4.290941
Co	7.050987	-0.123823	3.177230
N	6.653835	-0.460917	1.150946
C	5.977025	0.710733	0.570405
C	6.895090	1.903443	0.810748
N	7.190101	1.981748	2.257946
C	6.178234	2.784489	2.983759
C	5.755805	2.157585	4.313543
N	5.357020	0.755822	4.097954
C	4.150314	0.424024	4.565696
N	3.409121	-0.591016	4.006374
C	3.447323	-0.856823	2.575720
C	8.977674	2.052662	3.940876
C	8.584355	2.381653	2.518357
N	3.548930	1.079893	5.624411
C	2.181861	1.596617	5.537247
C	4.277381	1.455405	6.829772
N	7.226089	-2.347795	3.496336
S	8.318056	-3.155132	4.506409
C	7.040014	-1.414234	0.292309
N	6.282859	-1.793182	-0.795391
C	6.874799	-2.086226	-2.102529
N	8.227217	-2.061526	0.463144
C	9.348778	-1.429760	1.150345
C	8.434021	-3.456211	0.076392
C	9.636283	-1.350167	7.229610
C	4.825618	-1.813140	-0.751450

C	2.304275	-1.231034	4.716915
I	5.873804	-3.559290	2.643755
C	4.557106	-3.849129	4.339148
C	4.826639	-3.058731	5.460380
C	3.587301	-4.864819	4.376724
C	2.932978	-5.147974	5.593574
C	4.134541	-3.316280	6.655173
C	3.205912	-4.369008	6.728642
O	9.574662	-2.429718	4.327795
O	7.747864	-3.273072	5.846756
C	8.576992	-4.828924	3.931856
C	9.635679	-5.092699	3.044037
C	7.744006	-5.860364	4.409942
C	7.949611	-7.169055	3.949413
C	9.838175	-6.410063	2.600443
C	8.989681	-7.441835	3.041336
H	11.917576	1.113810	3.615387
H	10.745370	-0.191615	3.175448
H	12.265920	-0.599856	4.040420
H	7.059953	0.559641	6.120017
H	7.470607	0.151914	7.841003
H	6.920087	-1.134991	6.702674
H	12.228670	1.542470	6.049594
H	12.266914	-0.138829	6.684219
H	10.967080	1.002767	7.196733
H	5.788096	0.605209	-0.516215
H	4.999108	0.883392	1.065505
H	6.460601	2.852186	0.424254
H	7.843397	1.728898	0.268070
H	5.275244	2.848267	2.346342
H	6.539156	3.825497	3.146011
H	4.919383	2.767992	4.708592
H	6.576270	2.214247	5.055426
H	4.456561	-0.660801	2.180390

H	2.701840	-0.236643	2.029057
H	3.203300	-1.920339	2.395589
H	8.473985	2.753763	4.645747
H	10.060673	2.256200	4.056608
H	8.750796	3.462994	2.301719
H	9.224227	1.795924	1.829491
H	1.773304	1.445219	4.522804
H	2.191994	2.689682	5.735746
H	1.504387	1.120439	6.277310
H	5.256960	0.954276	6.846398
H	3.702061	1.128384	7.721568
H	4.435025	2.552861	6.909947
H	6.744912	-3.150738	-2.390543
H	7.951485	-1.842893	-2.098110
H	6.382302	-1.458462	-2.874635
H	10.280766	-1.625265	0.582010
H	9.458606	-1.814874	2.182431
H	9.177826	-0.340950	1.204398
H	9.168138	-3.550595	-0.750576
H	7.481635	-3.915092	-0.240660
H	8.818110	-4.022187	0.948921
H	10.480246	-1.769164	6.658068
H	8.972538	-2.186001	7.514128
H	10.005811	-0.852008	8.149055
H	4.457837	-2.791376	-1.126386
H	4.374664	-1.013306	-1.377616
H	4.483497	-1.687230	0.288369
H	1.315449	-0.830097	4.407456
H	2.422185	-1.103579	5.805125
H	2.320010	-2.316021	4.497395
H	5.581926	-2.263010	5.398914
H	2.234734	-5.993559	5.653968
H	4.346439	-2.700944	7.542241
H	2.697972	-4.595924	7.677410

H	10.310566	-4.279165	2.741901
H	6.951676	-5.632662	5.138280
H	7.300574	-7.981622	4.307792
H	10.672614	-6.635134	1.919441
H	9.152130	-8.471603	2.689448
S	3.266354	-5.883938	2.922908
O	4.091329	-5.243905	1.859888
O	3.503756	-7.272837	3.271553
C	1.500003	-5.659770	2.378795
C	1.425869	-6.500781	1.088339
C	0.550530	-6.208917	3.452082
C	1.275430	-4.167958	2.109188
H	2.141609	-6.147398	0.321891
H	0.401347	-6.403401	0.676690
H	1.614730	-7.572423	1.290348
H	-0.467995	-6.265959	3.017995
H	0.836904	-7.230369	3.769062
H	0.490577	-5.547186	4.337282
H	1.403587	-3.563424	3.028981
H	0.233873	-4.023366	1.758558
H	1.958972	-3.788632	1.325501

Table S7: DFT geometry optimized atomic xyz coordinates for **2** (*O*-sulfonamide) in *S* = 3/2 ground state.

C	11.326051	0.158755	2.826528
N	10.877833	0.355510	4.199641
C	9.543779	0.342797	4.541153
N	9.226830	-0.166806	5.764292
C	8.052455	0.286172	6.498539
C	11.937028	0.664153	5.161577
N	8.582645	0.808765	3.728939
Co	6.759454	0.013484	3.396955
N	6.015916	-1.021445	1.832130
C	5.165885	-0.117579	1.046784
C	6.050653	1.063852	0.637395

N	6.665697	1.653136	1.853435
C	5.801361	2.702530	2.446148
C	5.789082	2.658118	3.974816
N	5.528170	1.281914	4.411277
C	4.702812	1.101069	5.445298
N	4.009375	-0.069391	5.561429
C	3.668697	-0.846986	4.380569
C	8.850643	2.046969	2.977827
C	8.078342	2.048732	1.662570
N	4.455261	2.061227	6.401965
C	3.108804	2.306960	6.921291
C	5.493923	2.926421	6.952147
N	5.822774	-3.820518	3.964941
S	6.640084	-3.068830	5.154872
C	6.212432	-2.253553	1.354419
N	5.207547	-2.967607	0.742206
C	5.399898	-3.722569	-0.493355
N	7.444819	-2.831376	1.410606
C	8.635856	-2.016637	1.599081
C	7.643032	-4.276929	1.452203
C	9.987541	-1.232408	6.411582
C	3.848687	-2.923315	1.263396
C	3.640456	-0.641366	6.854952
I	5.398698	-5.755271	4.302823
C	3.471028	-5.543103	5.279347
C	3.057166	-4.243260	5.577534
C	2.700055	-6.656166	5.646171
C	1.510616	-6.464859	6.376946
C	1.848850	-4.059775	6.273706
C	1.083835	-5.164367	6.685184
O	7.187293	-1.862987	4.485189
O	5.860218	-2.828509	6.370246
C	8.051306	-4.056619	5.644418
C	9.195483	-4.101468	4.825924

C	7.982827	-4.794153	6.841160
C	9.075487	-5.596567	7.211338
C	10.279950	-4.905034	5.206266
C	10.218717	-5.656038	6.395725
H	11.811841	1.070349	2.415388
H	10.470884	-0.108400	2.183347
H	12.070892	-0.664667	2.790480
H	7.603749	1.135643	5.960552
H	8.350642	0.597417	7.521383
H	7.289307	-0.514298	6.568734
H	12.582316	1.466552	4.746580
H	12.578177	-0.216600	5.376676
H	11.500268	1.031848	6.106181
H	4.752087	-0.599859	0.137215
H	4.304880	0.238818	1.652178
H	5.486167	1.822604	0.051781
H	6.858810	0.678180	-0.012396
H	4.767017	2.515683	2.099947
H	6.096107	3.713601	2.084457
H	5.004956	3.356563	4.334442
H	6.753528	3.026377	4.380545
H	3.629899	-0.181663	3.500651
H	2.670715	-1.308671	4.523418
H	4.408319	-1.646184	4.171382
H	8.542758	2.914300	3.601980
H	9.923513	2.213117	2.753556
H	8.165346	3.040239	1.161299
H	8.534559	1.294716	0.992196
H	2.359585	1.777126	6.307488
H	2.892958	3.394438	6.865641
H	3.000755	1.989848	7.980404
H	6.490402	2.596081	6.618631
H	5.470707	2.870919	8.061107
H	5.350780	3.987957	6.658195

H	5.258682	-4.815103	-0.344932
H	6.411749	-3.545087	-0.898361
H	4.662574	-3.383208	-1.251878
H	9.495186	-2.498365	1.093210
H	8.868390	-1.879149	2.675450
H	8.471350	-1.013987	1.166604
H	8.173372	-4.637565	0.546013
H	6.670184	-4.785733	1.531338
H	8.239594	-4.550122	2.344812
H	10.656544	-1.723955	5.685473
H	9.279649	-1.994428	6.792251
H	10.586867	-0.855761	7.266864
H	3.459692	-3.959024	1.365003
H	3.156543	-2.357651	0.602122
H	3.862234	-2.462924	2.264472
H	2.549455	-0.554526	7.047923
H	4.188555	-0.129034	7.664245
H	3.937696	-1.705926	6.877766
H	3.685584	-3.390475	5.290298
H	0.941531	-7.343552	6.713562
H	1.519612	-3.038037	6.515402
H	0.156147	-5.015942	7.256794
H	9.242647	-3.480763	3.922235
H	7.086911	-4.726663	7.474507
H	9.032428	-6.177008	8.144938
H	11.182248	-4.941765	4.577327
H	11.070843	-6.286458	6.690742
S	3.214119	-8.334820	5.250298
O	4.617619	-8.174214	4.783531
O	2.933242	-9.191984	6.385716
C	2.216837	-8.882144	3.783476
C	2.774430	-10.282676	3.464816
C	0.737561	-8.940690	4.188215
C	2.468012	-7.887376	2.642402

H	3.854289	-10.250200	3.223315
H	2.233156	-10.676193	2.581183
H	2.616044	-10.984170	4.306130
H	0.165897	-9.398270	3.355893
H	0.585794	-9.567914	5.087628
H	0.313104	-7.933167	4.366270
H	2.140622	-6.861216	2.908200
H	1.877754	-8.207320	1.760296
H	3.535342	-7.866531	2.348777

Table S8: DFT geometry optimized atomic xyz coordinates for **2** (*O*-sulfone) in *S* = 3/2 ground state.

C	11.960706	0.877917	4.074907
N	11.194831	1.494943	5.149765
C	9.823966	1.557645	5.102930
N	9.152159	1.462343	6.282280
C	7.861302	2.112792	6.478055
C	11.994774	2.176444	6.171253
N	9.159011	1.722413	3.937616
Co	7.425127	0.958329	3.307878
N	7.071700	-0.373611	1.815407
C	6.438048	0.395123	0.726807
C	7.458662	1.455637	0.307045
N	7.814971	2.260092	1.502474
C	6.913824	3.431004	1.644192
C	6.512511	3.682682	3.095804
N	6.059648	2.421843	3.691911
C	5.013659	2.442584	4.523573
N	4.275960	1.305697	4.698488
C	4.109909	0.352274	3.612614
C	9.698189	2.776834	3.047428
C	9.257558	2.566895	1.603523
N	4.569321	3.561971	5.188389
C	3.141066	3.797861	5.421330
C	5.445758	4.573127	5.774522

N	9.583844	-3.384478	10.432289
S	9.509281	-5.048323	10.100696
C	7.395988	-1.638896	1.518534
N	6.518547	-2.470842	0.869935
C	6.918478	-3.377300	-0.210967
N	8.631689	-2.139612	1.846294
C	9.818340	-1.293316	1.717388
C	8.915975	-3.567775	1.995046
C	9.709513	0.839307	7.481526
C	5.078055	-2.347547	1.078553
C	3.779266	0.906692	6.013516
I	8.166806	-2.377359	9.499050
C	9.191485	-2.358946	7.539681
C	10.529905	-2.753904	7.623563
C	8.654233	-1.947384	6.308022
C	9.474504	-1.873933	5.163177
C	11.342898	-2.706687	6.478726
C	10.821359	-2.249371	5.254381
O	8.704765	-5.325501	8.902349
O	10.914734	-5.423963	10.136430
C	8.680377	-5.760763	11.504863
C	7.310649	-6.068706	11.416482
C	9.413110	-5.973787	12.686992
C	8.749870	-6.501002	13.805330
C	6.661800	-6.595596	12.544238
C	7.378631	-6.808236	13.735741
H	12.527409	1.627549	3.480194
H	11.276998	0.328663	3.407366
H	12.692896	0.165079	4.507487
H	7.607179	2.674877	5.568382
H	7.919427	2.799482	7.347944
H	7.062713	1.368236	6.660508
H	12.770309	2.789826	5.667291
H	12.505799	1.462508	6.849939

H	11.362889	2.857979	6.765817
H	6.180566	-0.233488	-0.149811
H	5.502197	0.876127	1.077880
H	7.082266	2.093495	-0.522325
H	8.365653	0.938974	-0.059004
H	5.990215	3.211707	1.075906
H	7.371396	4.341415	1.196558
H	5.714694	4.453935	3.110972
H	7.371304	4.101208	3.661473
H	4.186170	0.878234	2.644817
H	3.105375	-0.110324	3.688291
H	4.881496	-0.443787	3.636783
H	9.338230	3.762749	3.416011
H	10.804932	2.842834	3.059576
H	9.536724	3.452425	0.987835
H	9.803006	1.696837	1.192112
H	2.534450	3.119338	4.797245
H	2.900668	4.843860	5.140664
H	2.861927	3.656146	6.486913
H	6.504859	4.308172	5.640835
H	5.248176	4.648529	6.865227
H	5.268321	5.571664	5.323585
H	6.761935	-4.442154	0.059000
H	7.977243	-3.220403	-0.478400
H	6.306652	-3.156782	-1.110509
H	10.235176	-1.343125	0.687741
H	10.599884	-1.646690	2.414218
H	9.568420	-0.249238	1.969350
H	9.486754	-3.967859	1.130929
H	7.980741	-4.139313	2.099375
H	9.525139	-3.722049	2.909381
H	10.491374	0.110564	7.209938
H	8.893840	0.307567	8.004144
H	10.128003	1.588647	8.184748

H	4.644024	-3.356585	1.233429
H	4.566497	-1.882184	0.209061
H	4.889057	-1.731613	1.973795
H	2.671978	0.832138	6.029795
H	4.103601	1.633437	6.777621
H	4.212445	-0.073395	6.290338
H	10.935314	-3.096384	8.594938
H	9.030567	-1.517269	4.222762
H	12.393717	-3.024922	6.552739
H	11.471852	-2.200100	4.369065
H	6.775720	-5.915105	10.468302
H	10.486319	-5.737807	12.717251
H	9.309197	-6.679687	14.735797
H	5.593265	-6.853221	12.490237
H	6.866205	-7.225512	14.615638
S	6.932328	-1.520119	6.108142
O	6.452499	-0.974783	7.385027
O	6.825077	-0.655686	4.911361
C	6.034885	-3.122288	5.748329
C	4.545504	-2.757874	5.668035
C	6.571370	-3.638769	4.412483
C	6.296696	-4.115405	6.886395
H	4.178238	-2.330595	6.620794
H	3.975117	-3.688468	5.475834
H	4.334059	-2.053297	4.843959
H	6.012077	-4.553917	4.133802
H	6.442425	-2.889792	3.609572
H	7.640709	-3.909454	4.490562
H	7.366847	-4.363910	7.023235
H	5.774299	-5.061220	6.638222
H	5.887290	-3.753836	7.847471

Table S9: DFT geometry optimized atomic xyz coordinates for **2** (*N*-sulfonamide) in *S* = 1/2 excited state.

C	11.451577	0.054791	4.087962
N	10.752790	0.076208	5.366380
C	9.387070	-0.026752	5.411551
N	8.840774	-0.668191	6.470742
C	7.486217	-0.379076	6.909604
C	11.584101	0.361548	6.535852
N	8.635299	0.549081	4.433876
Co	7.404898	-0.079877	2.969487
N	6.909727	-0.382992	1.059084
C	6.336610	0.852093	0.502139
C	7.301857	1.944843	0.915043
N	7.450771	1.859538	2.400128
C	6.330330	2.625621	3.063255
C	5.695208	1.907193	4.249936
N	5.166433	0.620495	3.803368
C	3.930752	0.332025	4.186158
N	3.121737	-0.495804	3.428916
C	3.090575	-0.408951	1.978823
C	8.994912	1.977832	4.257728
C	8.789014	2.358729	2.816306
N	3.344547	0.819218	5.344067
C	1.979702	1.345328	5.363911
C	4.082991	0.974142	6.587693
N	7.285530	-2.047263	3.330108
S	8.236512	-3.065678	4.286629
C	7.261297	-1.328739	0.175215
N	6.521020	-1.578945	-0.960778
C	7.150043	-1.856523	-2.253383
N	8.383384	-2.079708	0.347822
C	9.561058	-1.547381	1.022749
C	8.453711	-3.477091	-0.075115
C	9.556531	-1.678422	7.255118
C	5.066431	-1.495859	-0.978188

C	2.043121	-1.291628	4.003543
I	5.610537	-2.942935	2.626122
C	4.524732	-3.248132	4.473052
C	4.851749	-2.398658	5.529293
C	3.586731	-4.284282	4.621278
C	2.987666	-4.488057	5.878190
C	4.227080	-2.590498	6.772126
C	3.306153	-3.636652	6.948746
O	9.561860	-2.453477	4.239883
O	7.581481	-3.283225	5.572702
C	8.380477	-4.685241	3.541636
C	9.548437	-4.995389	2.818273
C	7.387922	-5.657613	3.776460
C	7.538735	-6.935891	3.220224
C	9.700476	-6.288493	2.291975
C	8.690718	-7.250346	2.476878
H	11.849859	1.056843	3.812768
H	10.757183	-0.293928	3.306223
H	12.305410	-0.650258	4.149905
H	6.993715	0.241566	6.142740
H	7.493831	0.152910	7.885082
H	6.932023	-1.329045	7.024677
H	12.232385	1.234911	6.311450
H	12.238334	-0.493430	6.805587
H	10.953181	0.623201	7.402533
H	6.242136	0.824222	-0.600580
H	5.332901	1.046187	0.929712
H	6.980832	2.963608	0.610486
H	8.288536	1.741926	0.457891
H	5.538870	2.780811	2.307481
H	6.705142	3.627348	3.360074
H	4.900841	2.583071	4.636641
H	6.437190	1.783820	5.064709
H	3.990214	0.119861	1.628295

H	2.182375	0.133813	1.632125
H	3.067418	-1.424321	1.531820
H	8.356911	2.607544	4.919429
H	10.038700	2.199232	4.555377
H	8.875212	3.453700	2.641620
H	9.539905	1.840582	2.188502
H	1.569089	1.390166	4.340206
H	1.989762	2.379514	5.768973
H	1.304040	0.734127	5.999851
H	5.036966	0.428266	6.525907
H	3.489886	0.547238	7.424033
H	4.297785	2.037336	6.832013
H	6.961414	-2.897170	-2.591840
H	8.239708	-1.691170	-2.191169
H	6.736710	-1.165552	-3.017824
H	10.466462	-1.812668	0.439400
H	9.660244	-1.941779	2.051458
H	9.483509	-0.446628	1.081233
H	9.149862	-3.617947	-0.928319
H	7.451397	-3.835877	-0.367429
H	8.805775	-4.096990	0.771343
H	10.405928	-2.066265	6.669918
H	8.866503	-2.519756	7.450277
H	9.913203	-1.270800	8.222943
H	4.644324	-2.426381	-1.412856
H	4.702175	-0.638753	-1.585185
H	4.687225	-1.384420	0.049844
H	1.042948	-0.834253	3.840940
H	2.205034	-1.434101	5.085803
H	2.042296	-2.287215	3.518100
H	5.587489	-1.600245	5.364900
H	2.273383	-5.307325	6.025037
H	4.469707	-1.920451	7.609889
H	2.830024	-3.797450	7.926967

H	10.339428	-4.241279	2.704466
H	6.514485	-5.427762	4.402061
H	6.753388	-7.687883	3.382503
H	10.617546	-6.548203	1.742318
H	8.813141	-8.259865	2.056579
S	3.272584	-5.302494	3.158873
O	3.384590	-4.305230	2.056843
O	4.212809	-6.415206	3.173162
C	1.522337	-5.950022	3.107249
C	1.415700	-6.498371	1.668170
C	1.373765	-7.090657	4.125549
C	0.552384	-4.786686	3.343019
H	1.542980	-5.703411	0.910050
H	0.402748	-6.932371	1.550337
H	2.154009	-7.301752	1.480166
H	0.409886	-7.601327	3.928731
H	2.182608	-7.838250	4.021891
H	1.343665	-6.738501	5.173211
H	0.656159	-4.344361	4.352731
H	-0.482555	-5.173774	3.252641
H	0.682384	-3.991214	2.584397

Table S10: DFT geometry optimized atomic xyz coordinates for **2** (*O*-sulfonamide) in *S* = 1/2 excited state.

C	11.353870	-0.064345	2.884756
N	10.924520	0.203638	4.249466
C	9.587019	0.189174	4.605565
N	9.282587	-0.377078	5.805901
C	8.086757	-0.001164	6.548224
C	11.973417	0.653745	5.163873
N	8.638659	0.689622	3.799912
Co	6.902263	-0.069438	3.192023
N	5.827054	-0.972288	1.840405
C	5.065006	0.042334	1.099629
C	6.103542	1.094097	0.718882

N	6.811064	1.502109	1.979929
C	6.035710	2.613182	2.643545
C	6.005281	2.489672	4.161539
N	5.570800	1.136413	4.486488
C	4.697263	1.005669	5.477526
N	3.851493	-0.069541	5.510316
C	3.517637	-0.754771	4.276618
C	8.982706	1.907829	3.042231
C	8.232744	1.882213	1.723699
N	4.518451	1.943021	6.481739
C	3.188566	2.332036	6.948723
C	5.625630	2.632877	7.131067
N	5.796645	-3.734568	3.821854
S	6.556936	-2.866212	4.959334
C	5.989393	-2.165376	1.260307
N	4.947961	-2.786778	0.609315
C	5.099467	-3.428407	-0.694865
N	7.196691	-2.803902	1.237741
C	8.449188	-2.075393	1.355436
C	7.317056	-4.257642	1.222860
C	10.165753	-1.328196	6.477263
C	3.595395	-2.731013	1.147452
C	3.381412	-0.663472	6.758132
I	5.457077	-5.659024	4.304206
C	3.479421	-5.469420	5.175687
C	2.983025	-4.174026	5.332447
C	2.752326	-6.588456	5.608039
C	1.519679	-6.401876	6.264420
C	1.732514	-3.999879	5.953266
C	1.008818	-5.105734	6.430764
O	7.195701	-1.747856	4.207855
O	5.724614	-2.489178	6.099279
C	7.943905	-3.791982	5.604637
C	9.057027	-4.045036	4.781610

C	7.881503	-4.280341	6.922138
C	8.960151	-5.030955	7.421172
C	10.126170	-4.796021	5.290494
C	10.078138	-5.288777	6.608986
H	11.773703	0.837899	2.385828
H	10.498643	-0.431443	2.291055
H	12.146576	-0.842996	2.887012
H	7.422924	0.586982	5.894925
H	8.363969	0.577044	7.456163
H	7.524887	-0.901646	6.860317
H	12.535508	1.491715	4.698218
H	12.695983	-0.155197	5.403135
H	11.528974	1.027327	6.102842
H	4.576902	-0.356124	0.187231
H	4.279335	0.483279	1.745280
H	5.675556	1.981415	0.206610
H	6.845339	0.630560	0.041648
H	4.993048	2.541028	2.284827
H	6.441940	3.592216	2.313257
H	5.304376	3.262973	4.543135
H	6.998601	2.717262	4.599151
H	3.455036	-0.023569	3.451684
H	2.530396	-1.245189	4.387652
H	4.276606	-1.510520	3.990597
H	8.687800	2.803435	3.631168
H	10.065737	2.024571	2.844695
H	8.292465	2.852970	1.185305
H	8.664254	1.098877	1.070831
H	2.412909	1.917409	6.281144
H	3.103203	3.439340	6.931611
H	2.989446	1.990624	7.987608
H	6.588278	2.207889	6.807091
H	5.550800	2.506204	8.232653
H	5.624614	3.722886	6.912870

H	4.908757	-4.522115	-0.644941
H	6.118729	-3.262483	-1.086282
H	4.376621	-2.987388	-1.414140
H	9.216427	-2.557690	0.717633
H	8.812501	-2.044086	2.403492
H	8.311268	-1.034416	1.013659
H	7.793174	-4.613631	0.285018
H	6.320898	-4.716814	1.322444
H	7.933472	-4.591178	2.082561
H	10.848913	-1.797271	5.749374
H	9.551485	-2.123649	6.939372
H	10.763000	-0.846928	7.280386
H	3.135245	-3.739299	1.083161
H	2.940985	-2.021415	0.594690
H	3.643084	-2.436961	2.208987
H	2.294913	-0.487629	6.914573
H	3.937334	-0.237019	7.610481
H	3.579975	-1.751099	6.750539
H	3.577997	-3.315475	4.993756
H	0.981988	-7.277964	6.655099
H	1.335260	-2.982086	6.083357
H	0.046508	-4.960414	6.942838
H	9.089937	-3.633227	3.764309
H	7.001468	-4.063255	7.543950
H	8.924501	-5.417314	8.450643
H	11.005460	-4.995525	4.659680
H	10.918752	-5.878241	7.004567
S	3.375723	-8.261912	5.386271
O	4.787871	-8.057359	4.961001
O	3.096782	-9.031054	6.583386
C	2.478489	-8.996368	3.937127
C	3.129728	-10.382553	3.768345
C	0.988564	-9.110560	4.287112
C	2.722872	-8.091187	2.722391

H	4.215877	-10.305842	3.568623
H	2.652666	-10.883261	2.902144
H	2.973379	-11.016818	4.661808
H	0.482731	-9.674784	3.477982
H	0.833343	-9.664175	5.233017
H	0.498192	-8.119768	4.355220
H	2.329194	-7.066731	2.883842
H	2.188707	-8.519946	1.850826
H	3.798783	-8.033811	2.467620

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