Supplementary Information for

Cleaner and Stronger: How 8-Quinolinolate Facilitates Formation of Co(III)-thiolate from Co(II)-disulfide Complexes

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Part 1 – Experimental Data

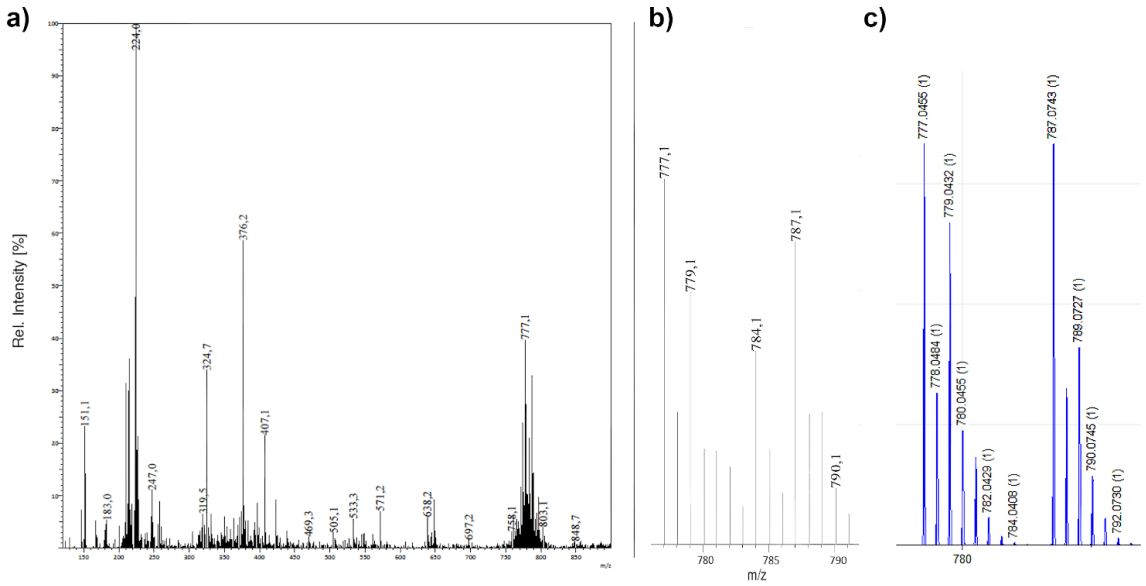

Figure S1. ESI−MS spectrum of a) compound [**2**ss] dissolved in methanol b) the experimental isotopic distribution of the main signal; c) simulated isotopic distribution. ESI−MS found (calcd.) for $[\mathbf{2}ss - 4Cl^- + 2HCOO^-]^{2+}$ m/z 376.2 (376.04), for $[\mathbf{2}ss - 2Cl^- + HCOO^-]^+$ m/z 777.1 (777.05), and for $[\mathbf{2}ss - 3Cl^- + 2HCOO^-]^+$ m/z 787.1 (787.07).

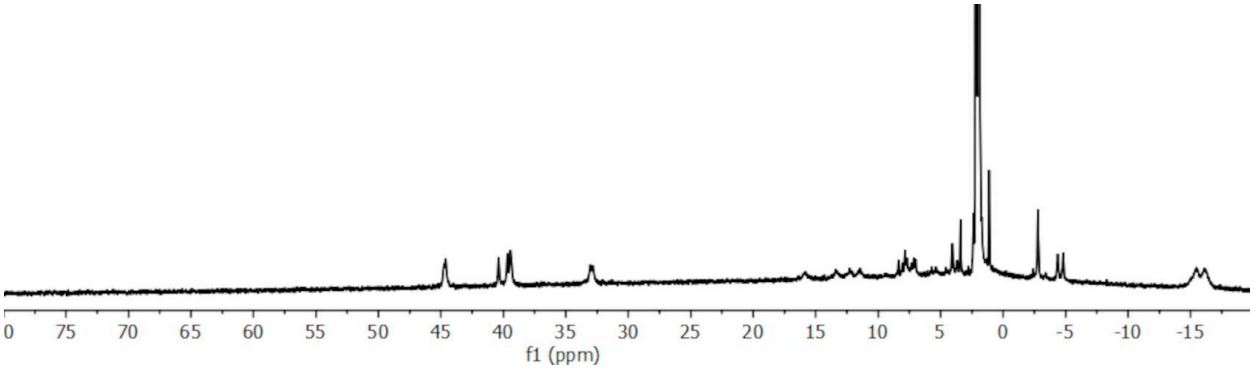

Figure S2. ^{1}H-NMR spectrum of compound [**2**ss] dissolved in CD_3CN.

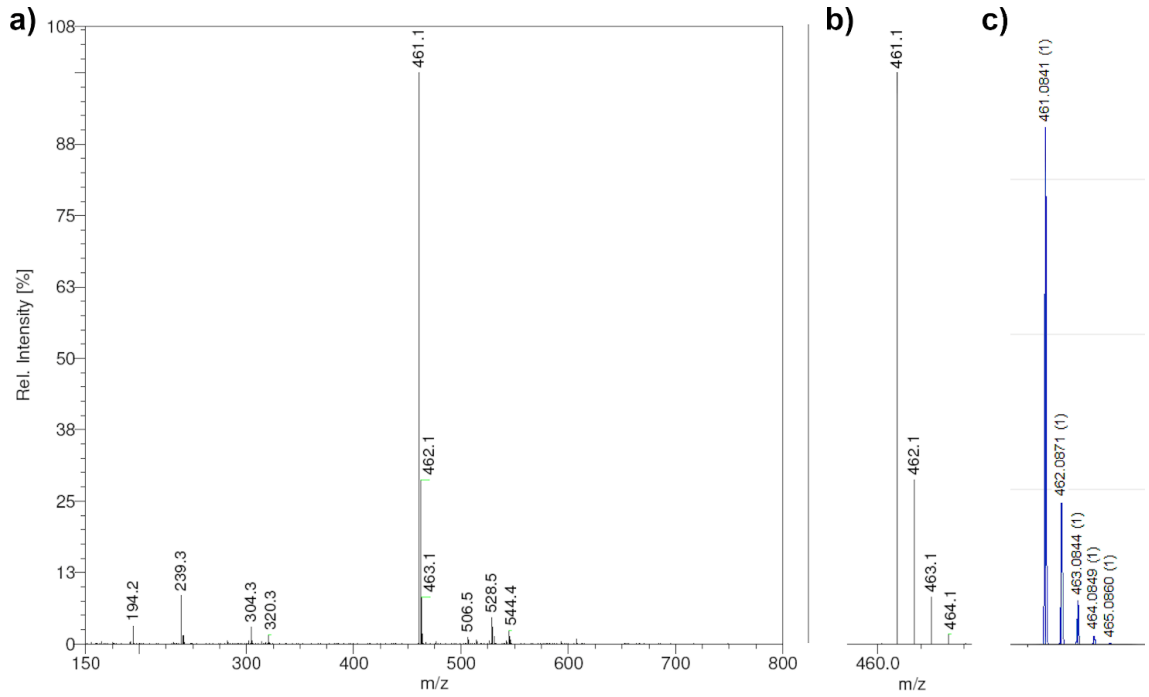

Figure S3. ESI−MS spectrum of a) [**1**s]Cl dissolved in methanol; b) the experimental isotopic distribution of the main signal; c) simulated isotopic distribution. ESI−MS found (calcd.) for [**1**s]$^+$ m/z 461.1 (461.08).

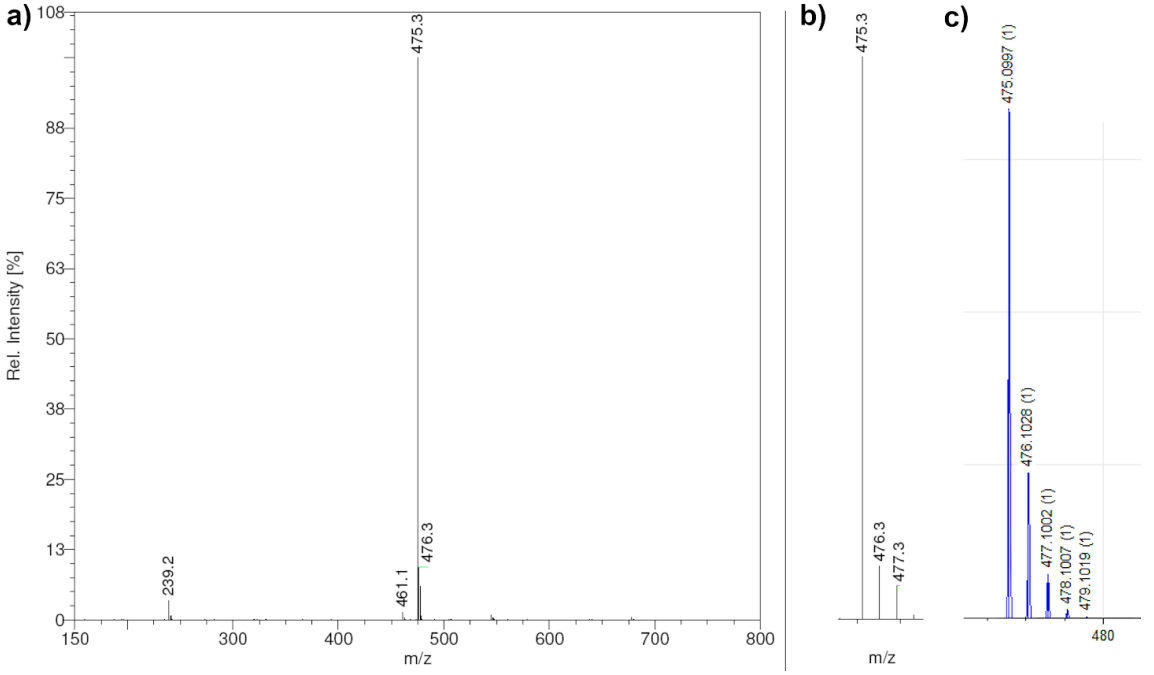

Figure S4. ESI−MS spectrum of a) [**2**s]Cl dissolved in acetonitrile; b) the experimental isotopic distribution of the main signal; c) simulated isotopic distribution. ESI−MS found (calcd.) for [**2**s]$^+$ m/z 475.3 (475.1).

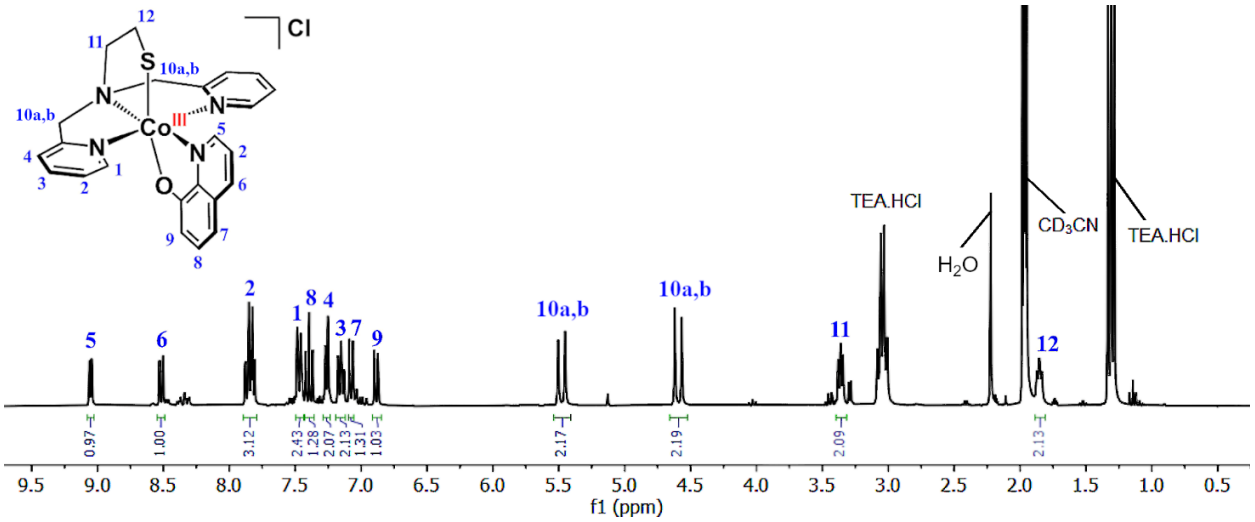

Figure S5. ^{1}H-NMR spectrum of [**1s**]Cl dissolved in CD_3CN.

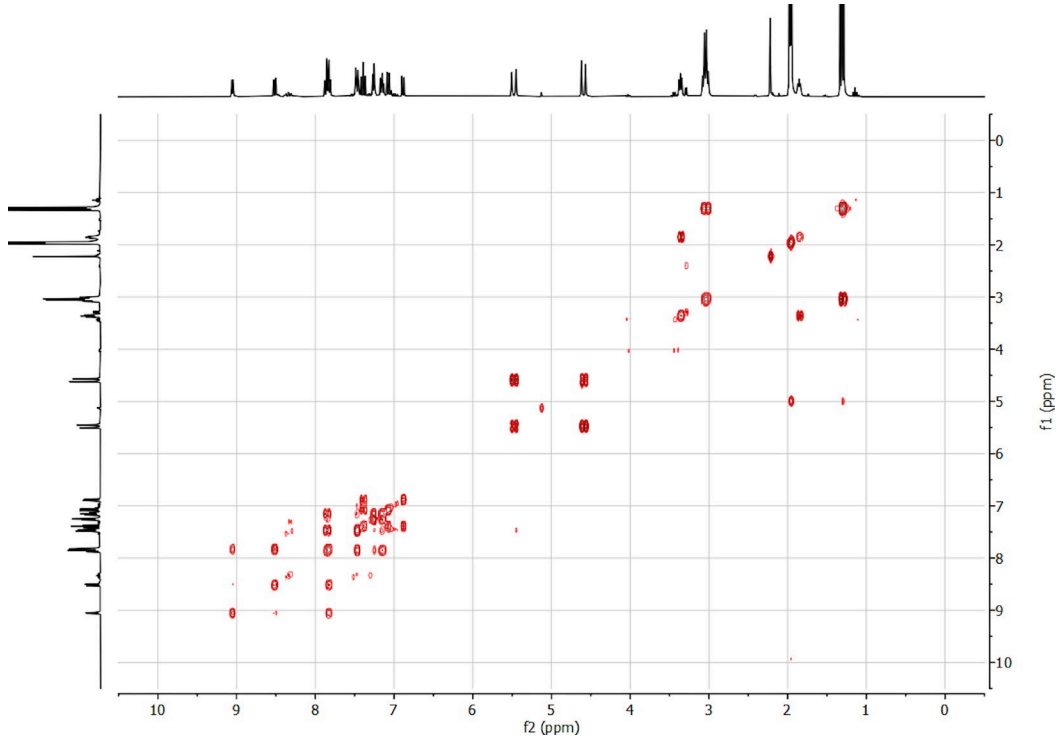

Figure S6. ^{1}H–^{1}H-COSY NMR spectrum of [**1s**]Cl dissolved in CD_3CN.

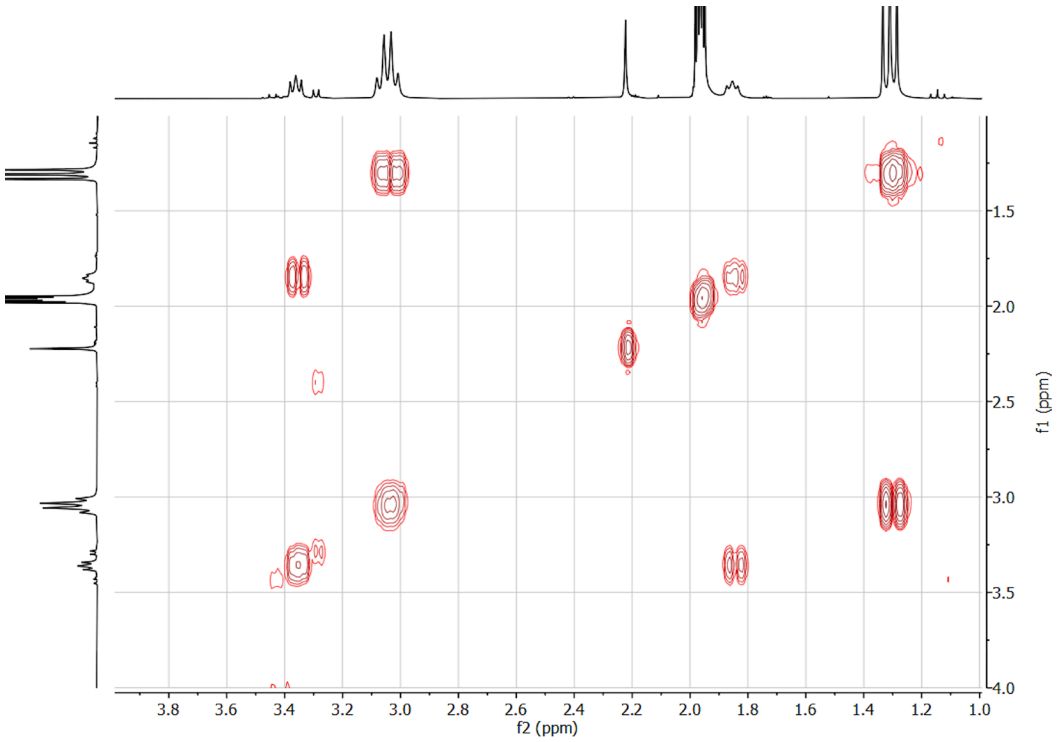

Figure S7. ^{1}H–^{1}H-COSY NMR spectrum of [**1s**]Cl dissolved in CD_3CN. The spectrum shows the correlation of protons in N-C**H**$_2$-C**H**$_2$-S (3.2–3.4 ppm and 1.84−1.87 ppm).

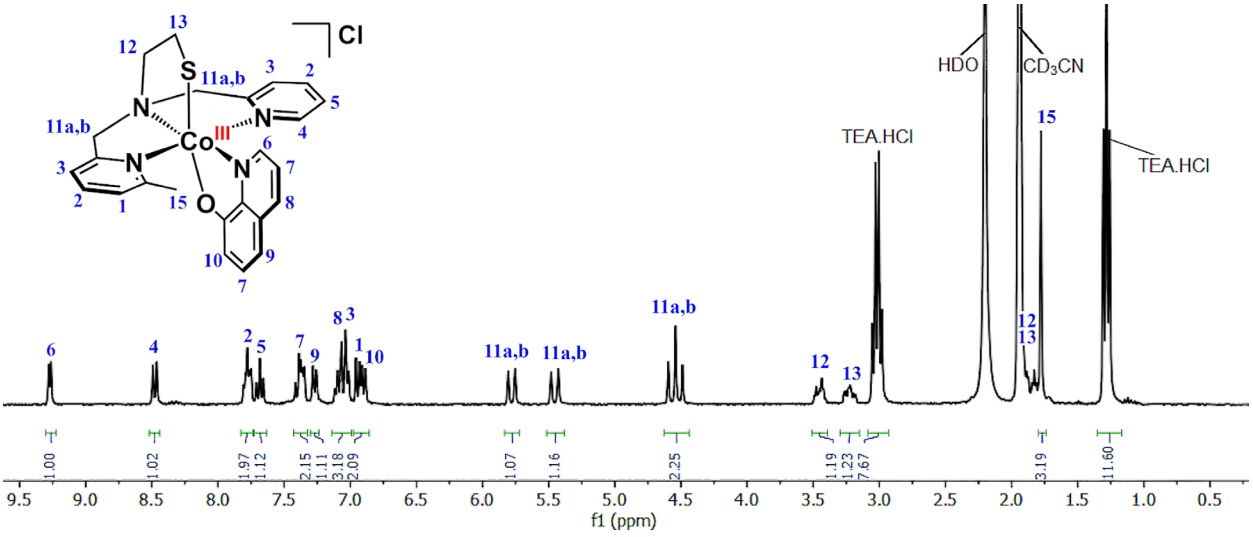

Figure S8. ^{1}H-NMR spectrum of [**2s**]Cl dissolved in CD_3CN.

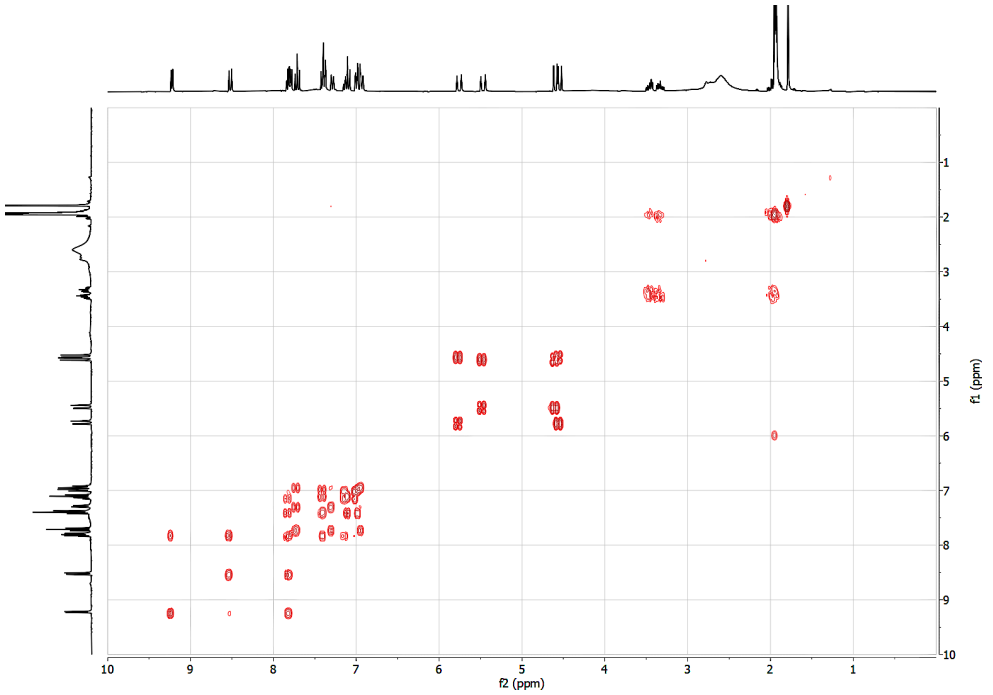

Figure S9. $^{1}H-^{1}H$-COSY NMR spectrum of [**2**$_S$]Cl dissolved in CD_3CN.

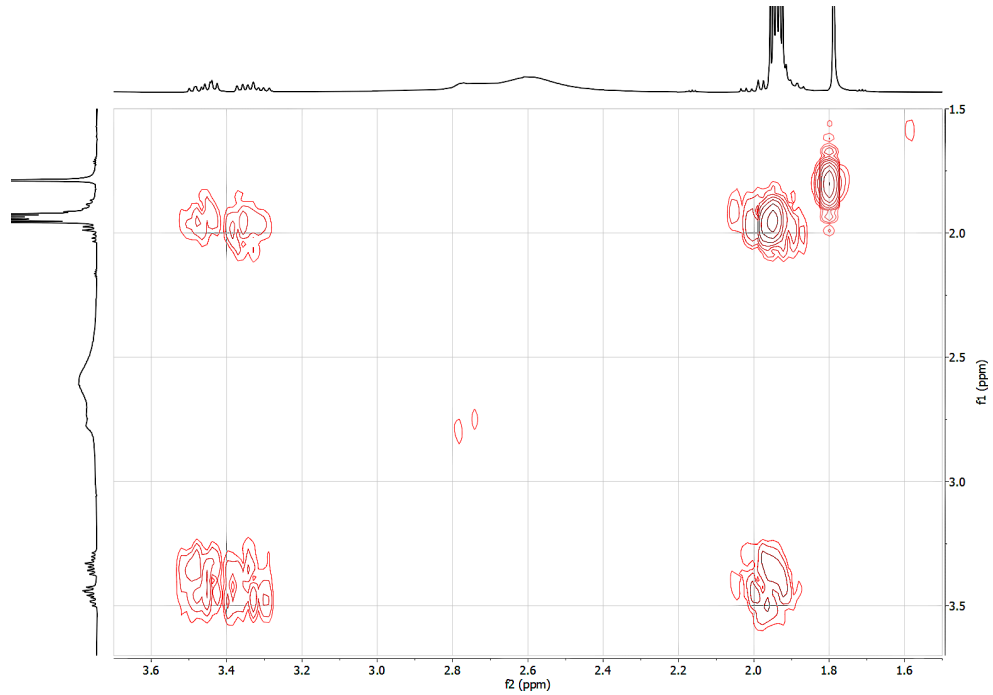

Figure S10. $^{1}H-^{1}H$-COSY NMR spectrum of [**2**$_S$]Cl dissolved in CD_3CN. The spectrum shows the correlation of protons in N-C**H**$_2$-C**H**$_2$-S (3.18–3.50 ppm) with the solvent peak (1.9 ppm), indicating that the solvent peak obscures the proton peak of interest.

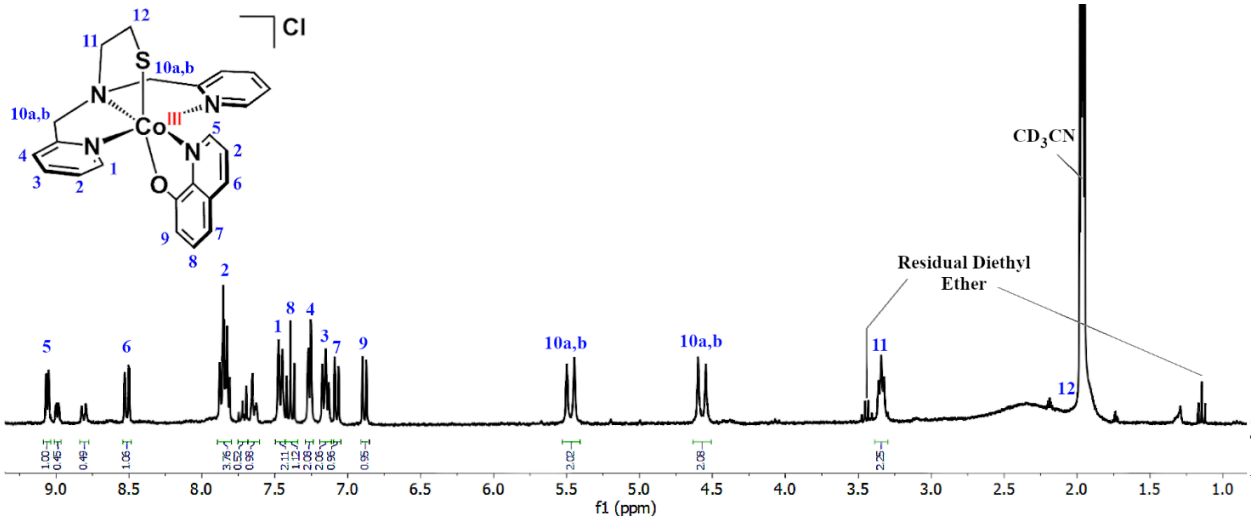

Figure S11. ^{1}H-NMR spectrum of [**1**$_{S}$]Cl dissolved in CD_3CN. The synthesis was done in absence of triethylamine. Impurities (as unlabeled peaks) are present mostly in the aromatic region.

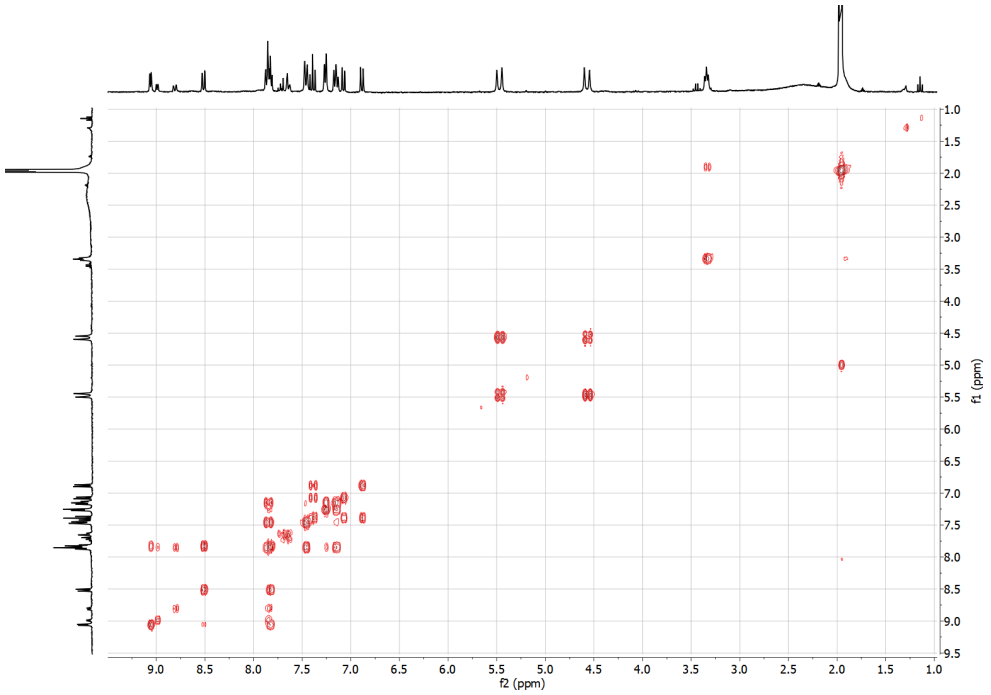

Figure S12. ^{1}H–^{1}H-COSY NMR spectrum of [**1**$_{S}$]Cl dissolved in CD_3CN. The synthesis was done in absence of triethylamine.

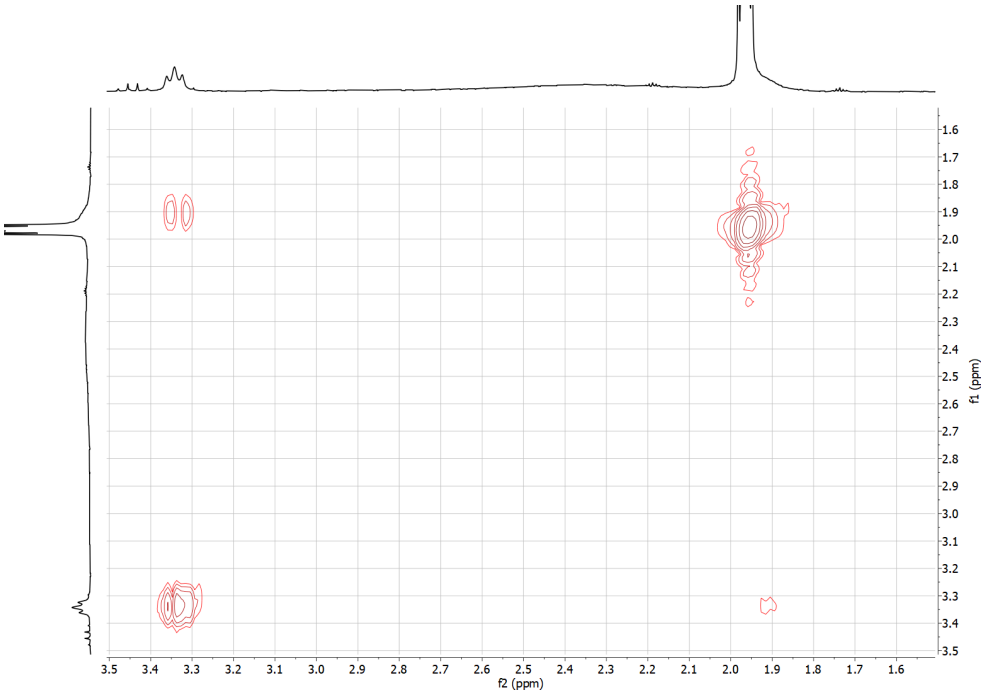

Figure S13. ^{1}H−^{1}H-COSY NMR spectrum of [**1**s]Cl dissolved in CD_3CN. The synthesis was done in absence of triethylamine. The spectrum shows the correlation of protons in N-C**H**$_2$-C**H**$_2$-S (3.2–3.4 ppm and 1.84−1.87 ppm).

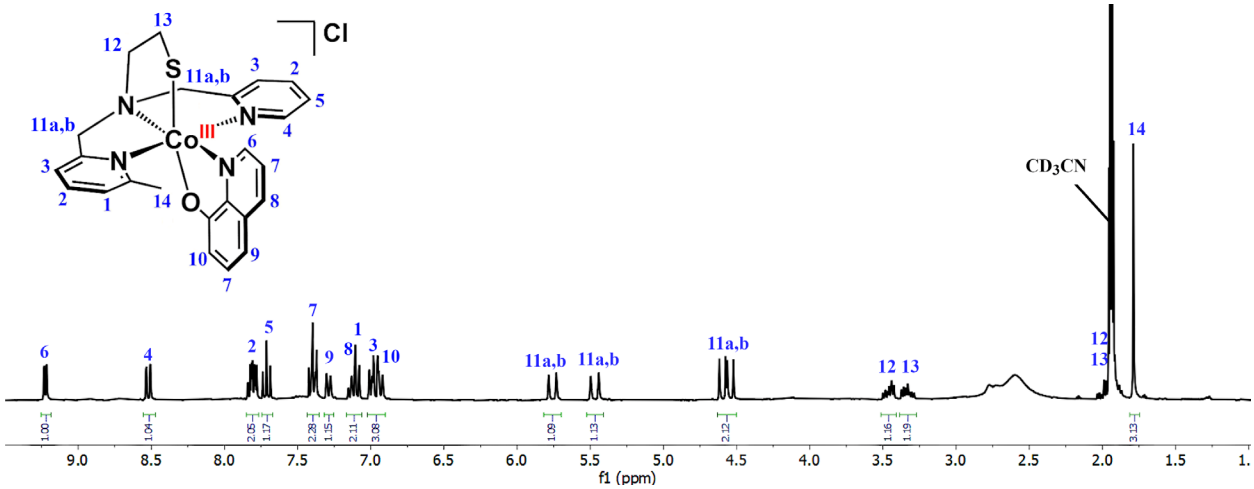

Figure S14. ^{1}H-NMR spectrum of [**2**s]Cl dissolved in CD_3CN. The synthesis was done in absence of triethylamine.

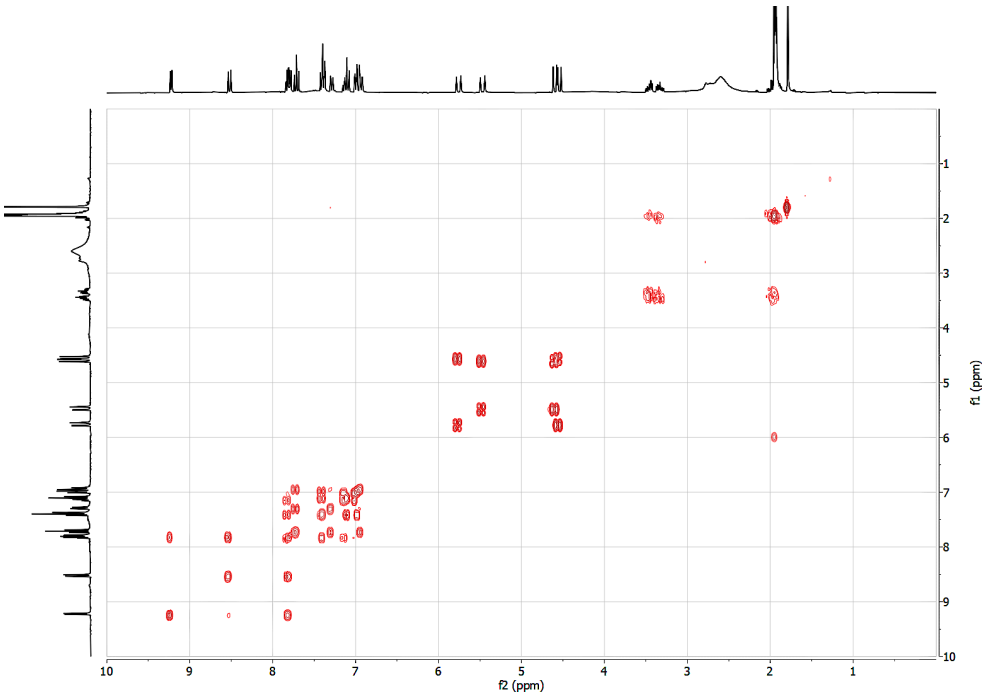

Figure S15. $^{1}H-^{1}H$-COSY NMR spectrum of [**2s**]Cl dissolved in CD_3CN. The synthesis was done in absence of triethylamine.

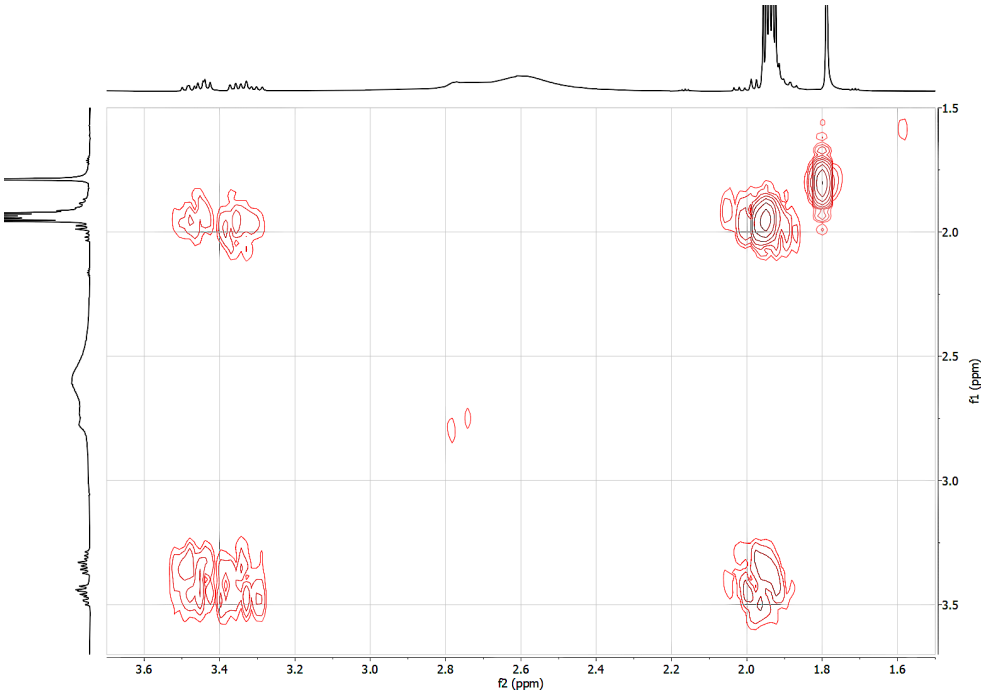

Figure S16. $^{1}H-^{1}H$-COSY NMR spectrum of [**2s**]Cl dissolved in CD_3CN. The synthesis was done in absence of triethylamine. The spectrum shows the correlation of protons in N-C**H**$_2$-C**H**$_2$-S (3.18–3.50 ppm) with the solvent peak (1.9 ppm), indicating that the solvent peak obscures the proton peak of interest.

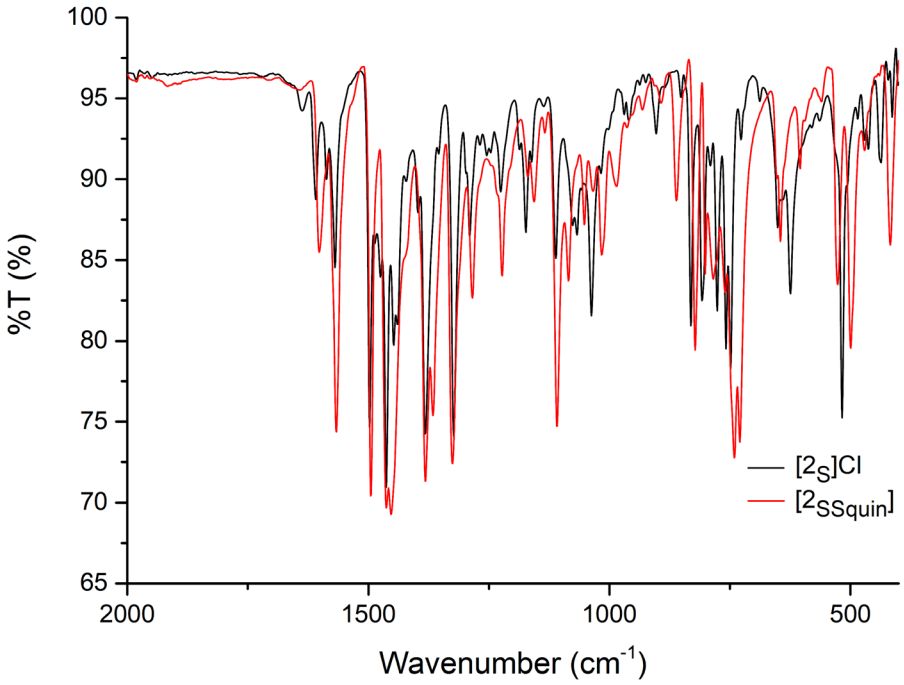

Figure S17. Infrared spectra of [**2**$_{S}$]Cl (black trace) and [**2**$_{SSquin}$] (red trace).

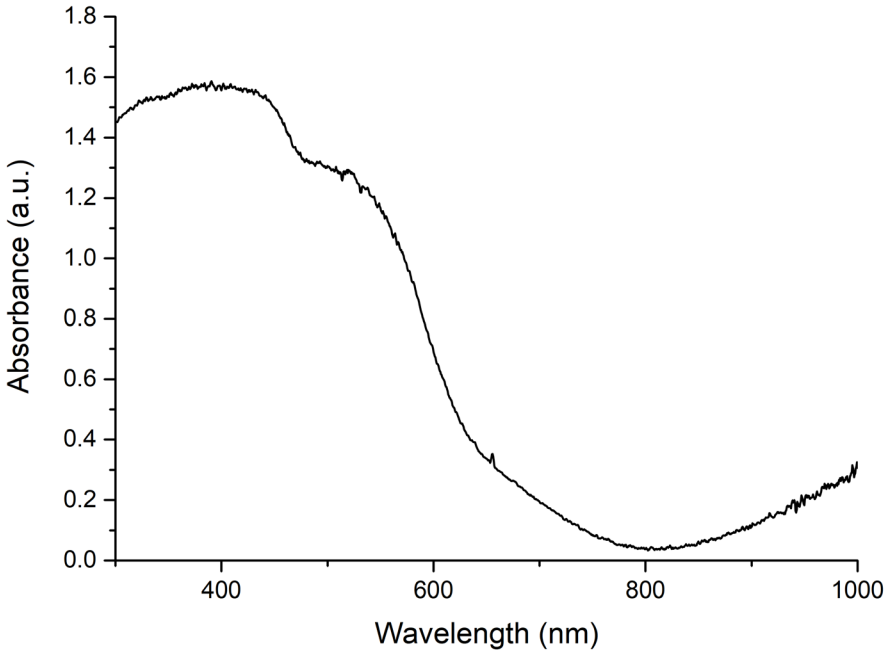

Figure S18. UV-visible diffuse reflectance spectrum of [**2**$_{SSquin}$].

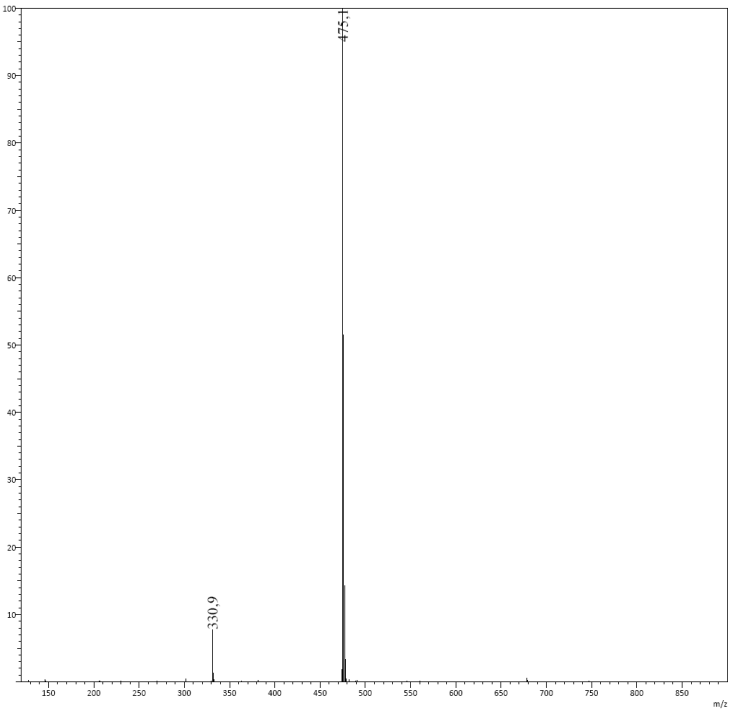

Figure S19. ESI−MS spectrum of [$\mathbf{2}_{\mathbf{SSquin}}$] dissolved in methanol. ESI−MS found (calcd.) for $[\mathbf{2}_{\mathbf{S}}]^+$ m/z 475.1 (475.1).

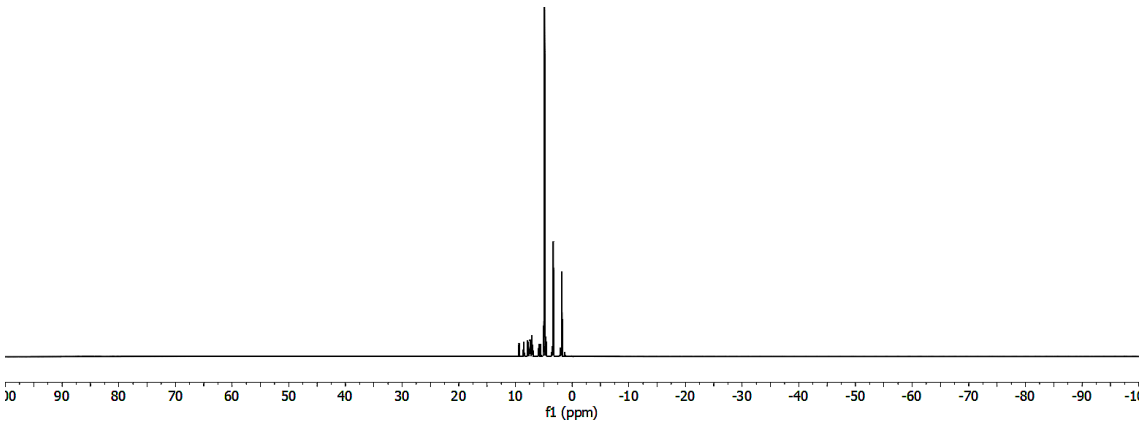

Figure S20. ^{1}H-NMR spectrum of [$\mathbf{2}_{\mathbf{SSquin}}$] dissolved in CD_3OD. The spectrum shows no presence of signals in the paramagnetic region.

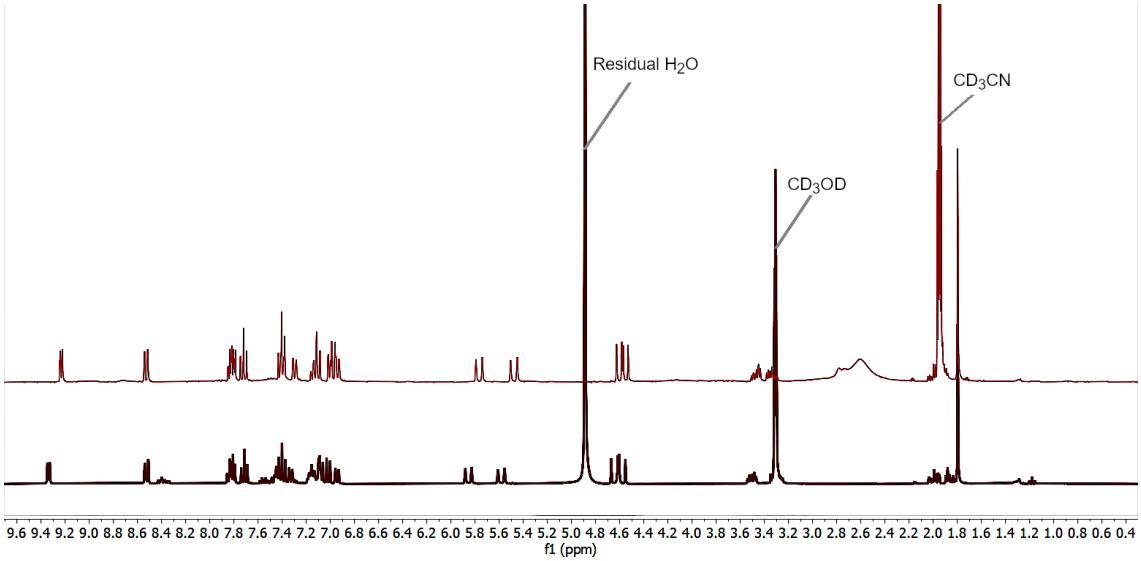

Figure S21. ^{1}H-NMR spectra of [**2**$_{\mathbf{SSquin}}$] dissolved in CD_3OD (bottom spectrum) compared to that of [**2s**]Cl in CD_3CN (top spectrum).

Part 2 – Crystallographic Data

Table S1. Crystallographic data in the present work.

	[**1**$_S$]Cl	[**2**$_S$**-Ag-2**$_S$](SbF$_6$)$_3$	[**2**$_{SSquin}$]
Chemical formula	$C_{23}H_{22}CoN_4OS\cdot 3(CH_4O)\cdot Cl$	$C_{50}H_{51}AgCo_2N_9O_2S_2\cdot 3(F_6Sb)\cdot 0.969(C_2H_3N)$	$C_{48}H_{48}Cl_2Co_2N_8O_2S_2\cdot 0.903(C_2H_3N)$
M_r	593.01	1846.88	1058.87
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/c$	$P2_1/n$
Cell lengths (*a, b, c*) (Å)	8.8184(3), 13.0506(5), 13.3362(5)	15.7072(5), 27.0793(6), 19.3101(6)	18.4673(4), 14.9350(4), 19.1135(4)
Cell angles (α, β, γ) (°)	63.783(4), 73.530(3), 84.488(3)	90, 112.171(3), 90	90, 97.898(2), 90
Cell volume (Å^3)	1319.66(10)	7606.1 (4)	5221.7(2)
Z	2	4	4
μ (mm^{-1})	7.11	1.87	0.86
Crystal size (mm)	0.41 × 0.33 × 0.18	0.52 × 0.37 × 0.22	0.35 × 0.22 × 0.20
Temperature (K)	110(2)	110(2)	110(2)
Diffractometer	SuperNova, Dual, Cu at zero, Atlas detector	SuperNova, Dual, Cu at zero, Atlas detector	SuperNova, Dual, Cu at zero, Atlas detector
Radiation type	Cu *K*α	Mo *K*α	Mo *K*α
T_{min}, T_{max}	0.161, 0.410	0.295, 1.000	0.425, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16974, 5155, 5078	61799, 21893, 14227	62110, 11982, 9923
R_{int}	0.025	0.048	0.045
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.616	0.650	0.650
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.071, 1.05	0.072, 0.231, 1.07	0.048, 0.128, 1.03
No. of reflections	5155	21893	11982
No. of parameters	340	1385	618
No. of restraints	-	2501	2
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, −0.46	1.75, −1.28	0.69, −0.59

Part 3 – Computational Data

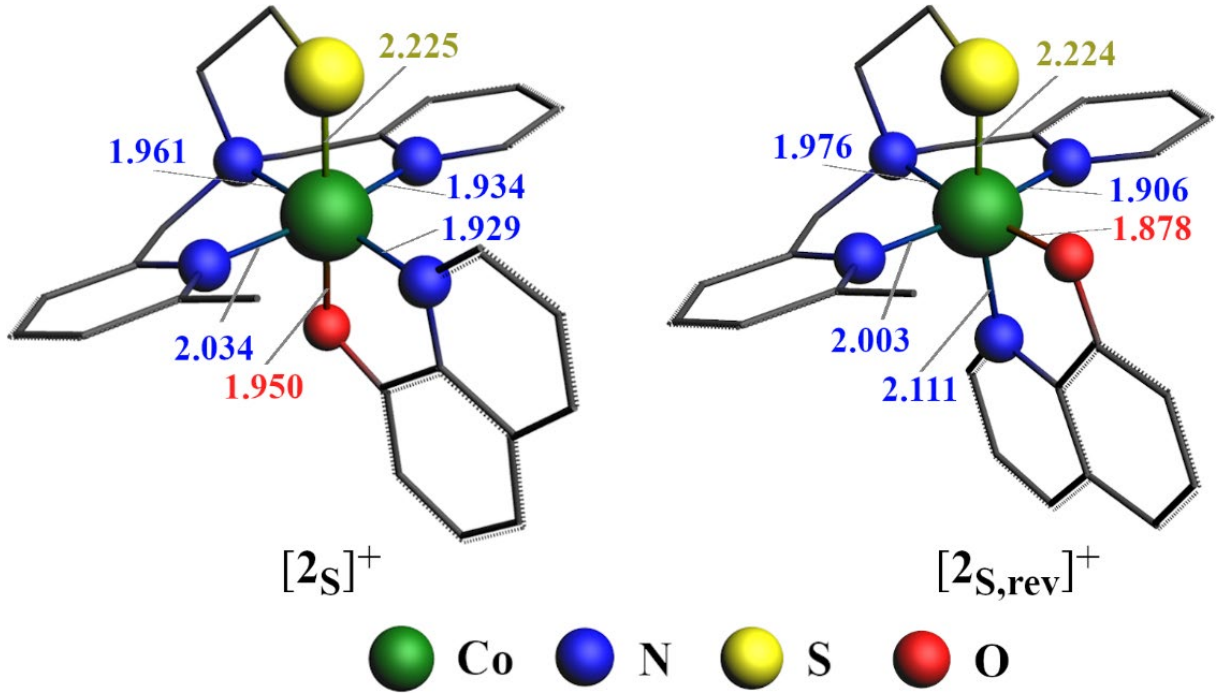

Figure S22. Optimized geometries of $[\mathbf{2}_{S}]^{+}$ and $[\mathbf{2}_{S,rev}]^{+}$ with selected bond distances (Å).

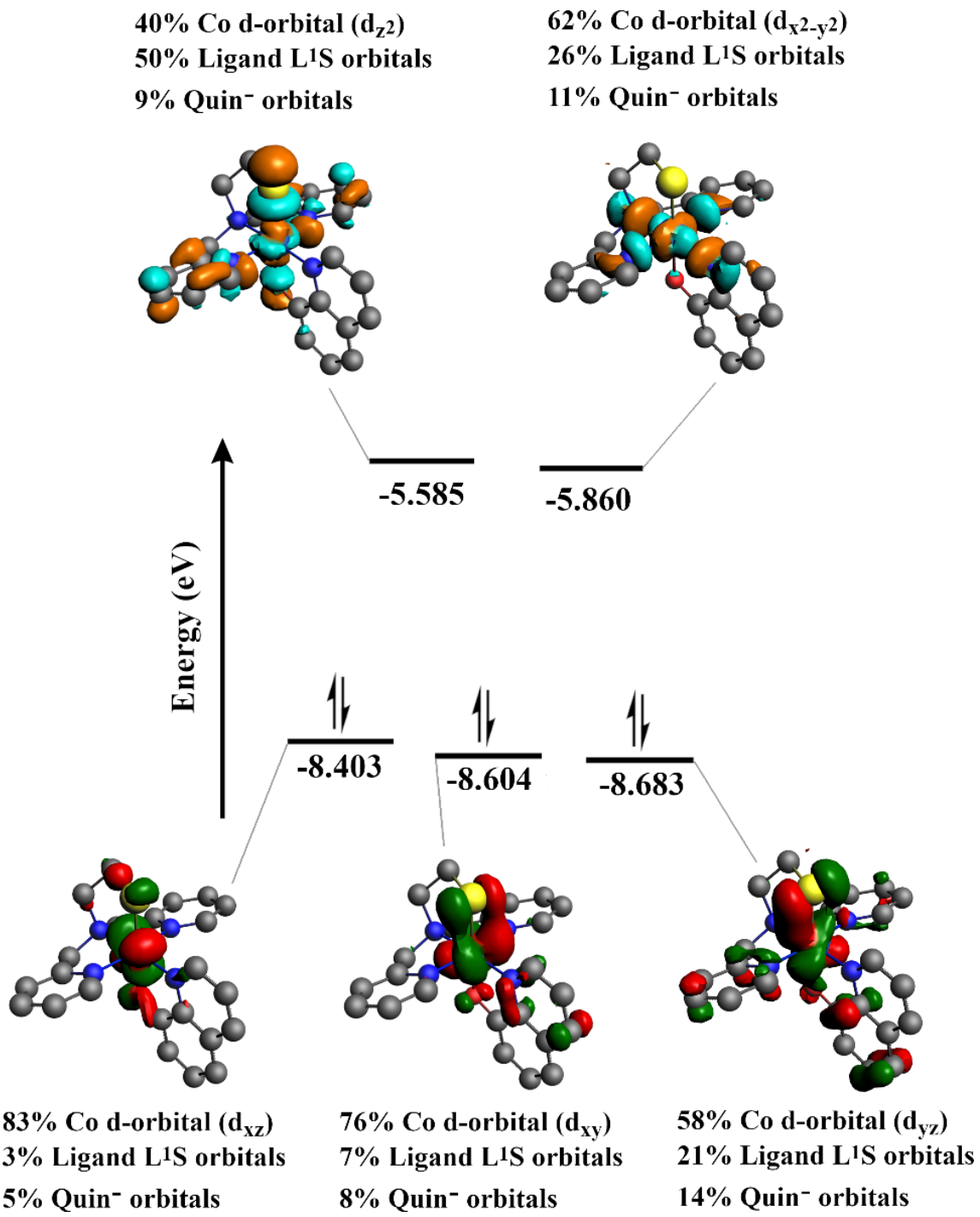

Figure S23. Several frontier orbitals of $[\mathbf{1}_S]^+$ associated with Co d-orbitals along with their energies, orbital visualization, and orbital composition.

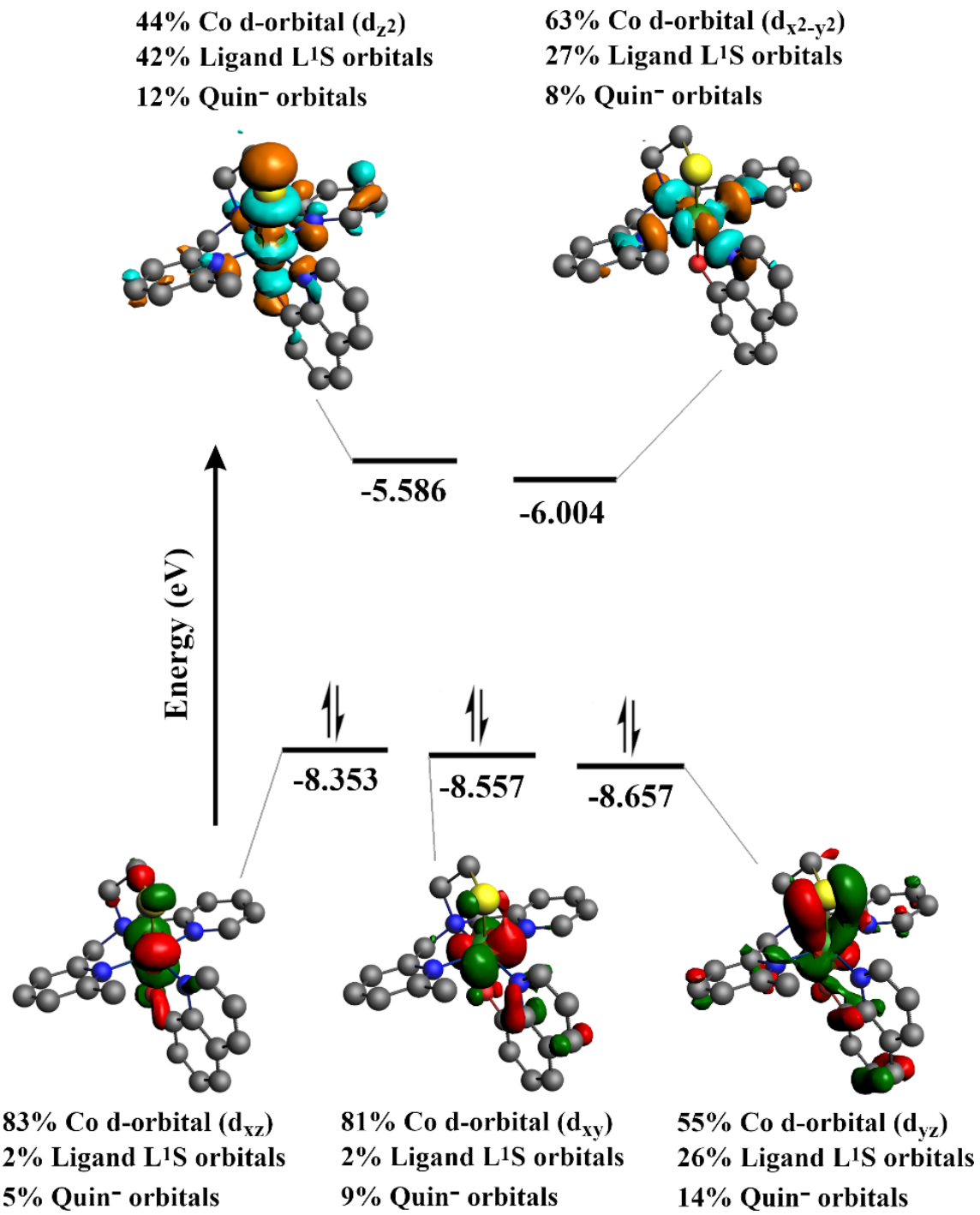

Figure S24. Several frontier orbitals of $[\mathbf{2s}]^+$ associated with Co d-orbitals along with their energies, orbital visualization, and orbital composition.

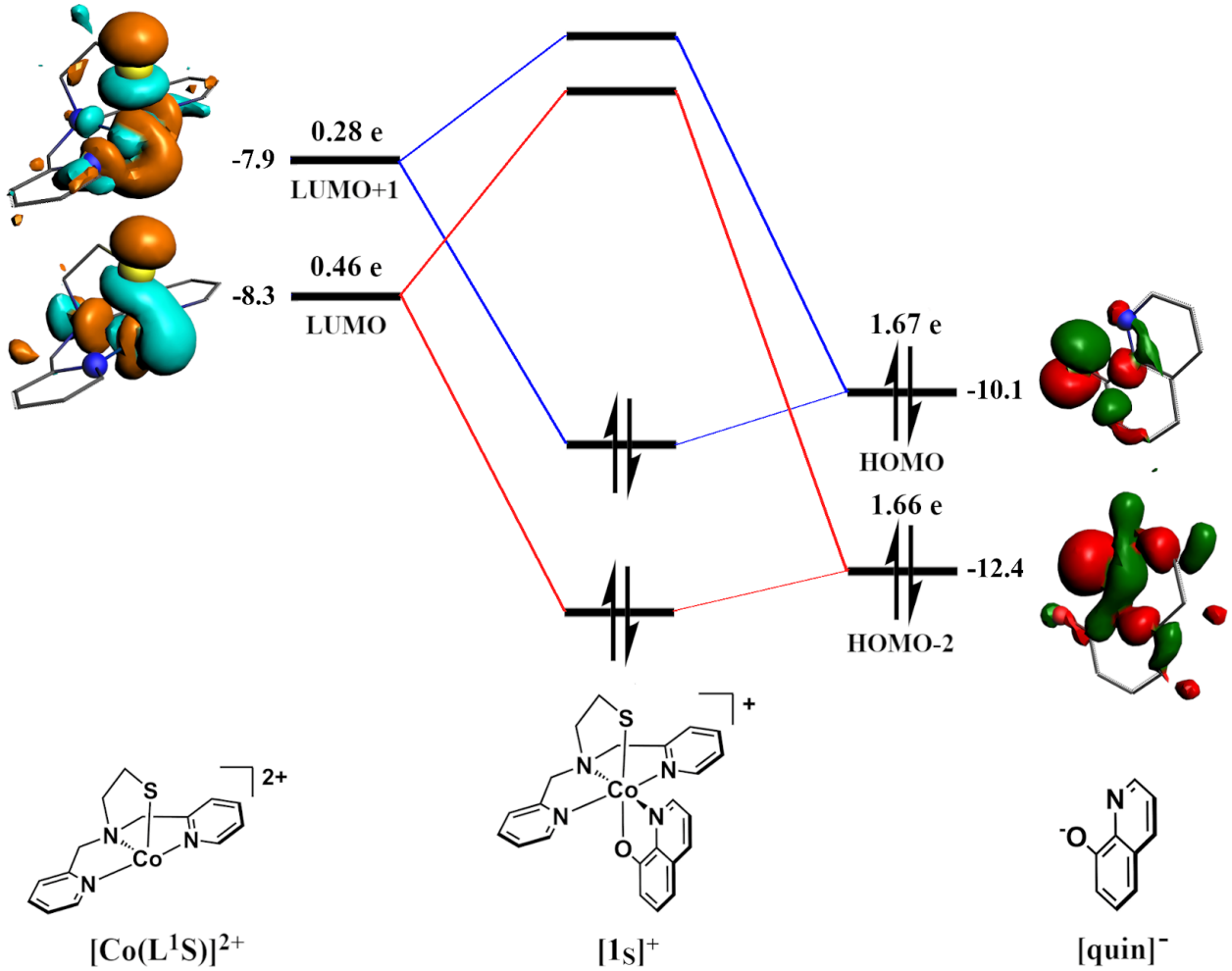

Figure S25. Molecular orbital diagram for the interaction between the fragments $[Co(L^1S)]^{2+}$ and $[quin]^-$ in $[\mathbf{1}s]^+$. Fragment molecular orbital energies (in eV) obtained from the Kohn-Sham Fock matrix diagonal elements (see references[1-3] for details).

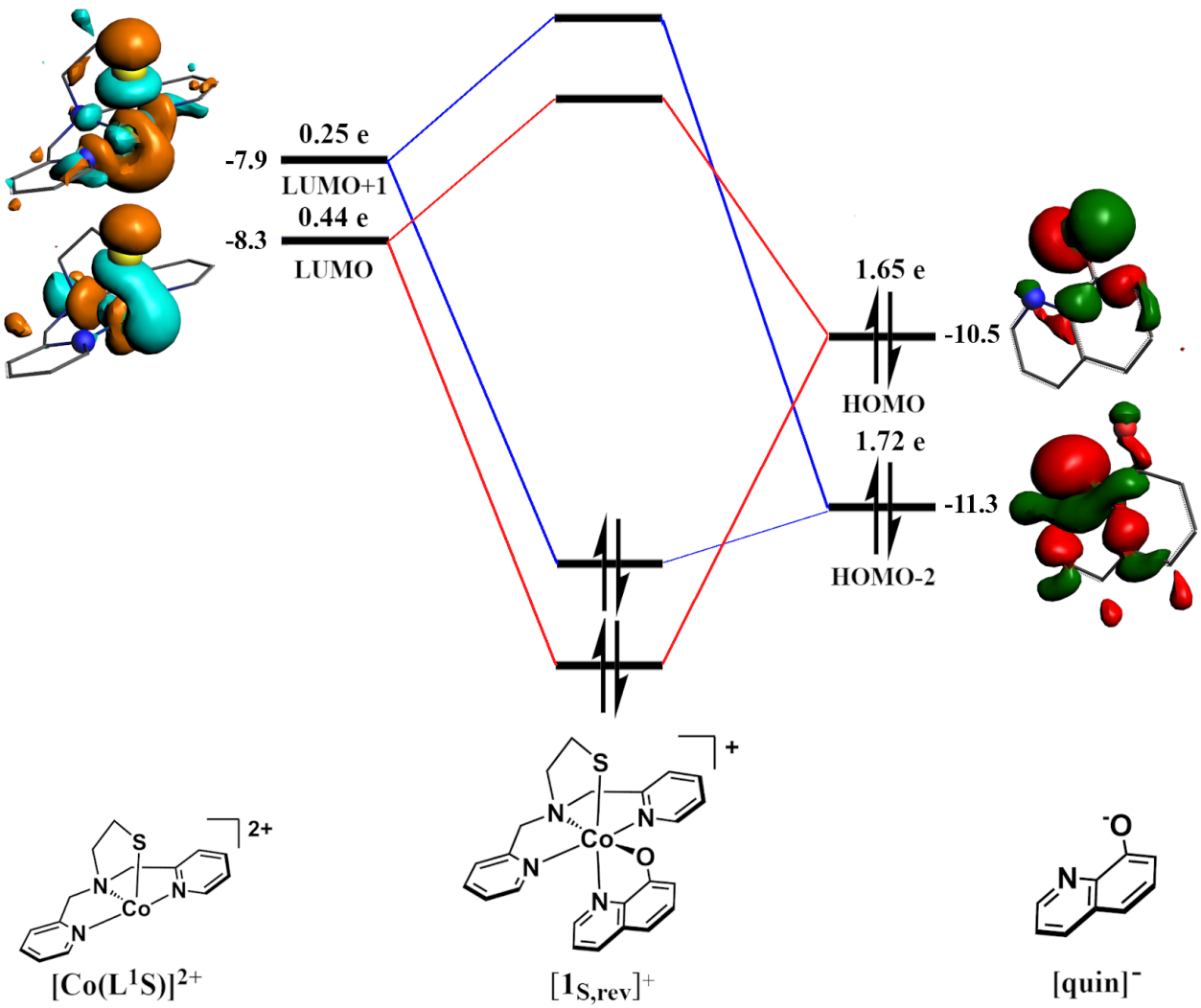

Figure S26. Molecular orbital diagram for the interaction between the fragments $[Co(L^1S)]^{2+}$ and $[quin]^-$ in $[\mathbf{1}_{S,rev}]^+$. Fragment molecular orbital energies (in eV) obtained from the Kohn-Sham Fock matrix diagonal elements (see references[1-3] for details).

Table S2. Coordinates of optimized structure of $[\mathbf{1}_S]^+$ and $[\mathbf{1}_{S,rev}]^+$ with $S = 0$ in gas phase and its respective bond energies.

$[\mathbf{1}_S]^+$ E = −7679.01 kcal/mol				$[\mathbf{1}_{S,rev}]^+$ E = −7670.11 kcal/mol			
1.Co	3.279748	10.503220	2.619490	1.Co	3.362363	10.390019	2.731247
2.C	3.882402	7.550336	2.684559	2.C	3.839856	7.416124	2.322387
3.H	4.589879	6.733148	2.874284	3.H	4.525238	6.560191	2.373994
4.H	2.872634	7.154426	2.845957	4.H	2.820460	7.025831	2.433893
5.C	4.087507	8.064243	1.282862	5.C	4.049562	8.135736	1.019628
6.H	5.148175	8.301013	1.156863	6.H	5.115049	8.365680	0.926076
7.H	3.801230	7.336994	0.507684	7.H	3.740196	7.553406	0.137179
8.C	4.039056	10.133217	0.001366	8.C	4.053077	10.340320	0.048227
9.H	3.344516	10.882988	-0.390274	9.H	3.396794	11.153518	-0.272255
10.H	4.372071	9.494365	-0.826931	10.H	4.363840	9.797019	-0.854698
11.C	1.915321	9.096503	0.668040	11.C	1.888974	9.261954	0.647997
12.H	1.817325	8.195318	0.050239	12.H	1.752736	8.408608	-0.028560
13.H	1.570377	9.952293	0.077991	13.H	1.529517	10.146696	0.113089
14.C	5.180680	10.842227	0.656538	14.C	5.234510	10.909247	0.780580
15.C	6.350936	11.199438	-0.001414	15.C	6.417136	11.296710	0.164635
16.H	6.484933	10.933555	-1.048134	16.H	6.533341	11.180029	-0.911113
17.C	7.335539	11.892321	0.694154	17.C	7.443003	11.824971	0.943234
18.H	8.259622	12.185632	0.198521	18.H	8.378827	12.137226	0.482215
19.C	7.121767	12.186072	2.035499	19.C	7.258188	11.925334	2.317022
20.H	7.865091	12.714781	2.628297	20.H	8.037973	12.314066	2.968635
21.C	5.936552	11.783688	2.634418	21.C	6.056469	11.505438	2.870866
22.H	5.746258	11.977403	3.684078	22.H	5.865683	11.537338	3.939211
23.C	1.071863	9.018473	1.899572	23.C	1.083506	9.087489	1.904384
24.C	-0.149919	8.357037	1.950615	24.C	-0.158663	8.464732	1.938841
25.H	-0.513314	7.823641	1.074376	25.H	-0.583420	8.047077	1.027861
26.C	-0.886172	8.385938	3.128721	26.C	-0.836353	8.377207	3.150324
27.H	-1.847051	7.877627	3.192271	27.H	-1.810976	7.894156	3.201351
28.C	-0.363168	9.062033	4.225474	28.C	-0.238668	8.896554	4.293864
29.H	-0.893101	9.103719	5.174603	29.H	-0.722124	8.833758	5.266455
30.C	0.868621	9.688299	4.107769	30.C	1.008935	9.494474	4.192032
31.H	1.319312	10.203537	4.948117	31.H	1.540177	9.889450	5.052495
32.C	2.565748	12.935113	3.638929	32.C	2.527772	12.988420	3.481121
33.C	2.364011	14.047149	4.507509	33.C	2.016957	14.318426	3.583513
34.C	2.816281	13.900787	5.838943	34.C	1.414523	14.858254	2.425930
35.H	2.688468	14.720345	6.545644	35.H	1.007769	15.868959	2.447202
36.C	3.412101	12.723837	6.233835	36.C	1.341402	14.094862	1.284894
37.H	3.766298	12.582646	7.253002	37.H	0.876043	14.473280	0.376869
38.C	3.570326	11.672793	5.314947	38.C	1.879034	12.796658	1.283400
39.H	4.025622	10.730938	5.611194	39.H	1.806846	12.208780	0.373891
40.C	2.153944	12.949468	2.277115	40.C	3.123197	12.345931	4.599477
41.C	1.532904	14.107898	1.803654	41.C	3.215710	13.050978	5.800943
42.H	1.203775	14.150219	0.766868	42.H	3.668012	12.566651	6.664731
43.C	1.335969	15.203042	2.658766	43.C	2.723464	14.361096	5.888526
44.H	0.848789	16.091516	2.257143	44.H	2.809417	14.885689	6.839976
45.C	1.734658	15.195374	3.983668	45.C	2.131789	14.998320	4.813681
46.H	1.568210	16.059449	4.623171	46.H	1.750165	16.012927	4.905457

47.O	2.381248	11.876598	1.558462	47.O	3.549579	11.110027	4.460062
48.S	4.265607	8.903673	3.812138	48.S	4.279877	8.571608	3.627390
49.N	3.331548	9.342443	1.040060	49.N	3.320526	9.456257	0.986598
50.N	4.974697	11.136824	1.958919	50.N	5.057389	11.025339	2.115064
51.N	1.568541	9.685143	2.962259	51.N	1.645482	9.607496	3.015377
52.N	3.161850	11.775229	4.051192	52.N	2.469730	12.243248	2.337247

Table S3. Coordinates of optimized structure of $[\mathbf{2_S}]^+$ and $[\mathbf{2_{S,rev}}]^+$ with $S = 0$ in gas phase and its respective bond energies.

$[\mathbf{2_S}]^+$ E = −8053.87 kcal/mol				$[\mathbf{2_{S,rev}}]^+$ E = −8046.52 kcal/mol			
1.Co	3.304817	10.529338	2.660171	1.Co	3.273435	10.505905	2.688802
2.C	3.909025	7.569890	2.707034	2.C	3.839606	7.516793	2.538756
3.H	4.624952	6.760303	2.897134	3.H	4.554478	6.695593	2.677757
4.H	2.902577	7.157822	2.849209	4.H	2.832445	7.098184	2.658947
5.C	4.125771	8.104276	1.314865	5.C	4.055882	8.137379	1.187188
6.H	5.182922	8.362544	1.204929	6.H	5.113854	8.399292	1.095465
7.H	3.862192	7.380918	0.527914	7.H	3.787009	7.475019	0.349208
8.C	4.016190	10.166803	0.028446	8.C	3.975205	10.245299	0.028971
9.H	3.308569	10.919119	-0.331458	9.H	3.288279	11.000401	-0.358135
10.H	4.313921	9.531405	-0.816386	10.H	4.297890	9.637029	-0.827850
11.C	1.938749	9.100497	0.704654	11.C	1.863047	9.149652	0.693304
12.H	1.857024	8.188491	0.100856	12.H	1.767796	8.236784	0.091746
13.H	1.587066	9.940407	0.095853	13.H	1.486247	9.973483	0.078565
14.C	5.192667	10.864545	0.623502	14.C	5.150993	10.914063	0.676045
15.C	6.282914	11.198810	-0.166205	15.C	6.258273	11.266322	-0.079055
16.H	6.287745	10.929891	-1.220402	16.H	6.278614	11.050620	-1.145381
17.C	7.348283	11.869470	0.415245	17.C	7.329044	11.881468	0.555950
18.H	8.218744	12.159935	-0.171238	18.H	8.215292	12.181317	-0.001451
19.C	7.285328	12.127296	1.772512	19.C	7.252483	12.066851	1.923517
20.H	8.112262	12.619289	2.279226	20.H	8.084429	12.509323	2.466645
21.C	6.172921	11.749491	2.534006	21.C	6.119840	11.678214	2.652501
22.N	3.069740	11.782490	4.108263	22.N	2.332746	12.297774	2.088531
23.C	1.090538	9.034039	1.927316	23.C	1.044337	9.062415	1.944942
24.C	-0.128685	8.367342	1.973603	24.C	-0.178515	8.406395	2.021570
25.H	-0.479738	7.826164	1.097099	25.H	-0.576526	7.896683	1.146093
26.C	-0.875796	8.400582	3.143623	26.C	-0.869424	8.405015	3.228162
27.H	-1.834849	7.888487	3.203995	27.H	-1.829725	7.898547	3.312470
28.C	-0.361294	9.087639	4.237037	28.C	-0.300263	9.041056	4.326266
29.H	-0.895618	9.135097	5.183449	29.H	-0.791493	9.048278	5.296943
30.C	0.867751	9.719201	4.123322	30.C	0.929366	9.667069	4.184845
31.H	1.301755	10.241529	4.966376	31.H	1.438541	10.151907	5.011272
32.C	2.500906	12.947248	3.672746	32.C	2.261734	13.118329	3.179079
33.C	2.199950	14.033661	4.545453	33.C	1.683025	14.423894	3.152228
34.C	2.494818	13.845447	5.914971	34.C	1.154756	14.859532	1.917390
35.H	2.283974	14.642168	6.627949	35.H	0.703301	15.848100	1.838311
36.C	3.032841	12.651001	6.339156	36.C	1.206525	14.020301	0.830054
37.H	3.258114	12.472703	7.388811	37.H	0.798843	14.314477	-0.135129
38.C	3.309552	11.635133	5.409629	38.C	1.799451	12.753119	0.959482
39.H	3.734134	10.686294	5.727168	39.H	1.820095	12.106303	0.088391

40.C	2.199198	12.985147	2.283847	40.C	2.784829	12.576395	4.383294
41.C	1.621368	14.152381	1.778743	41.C	2.735142	13.355848	5.541621
42.H	1.378532	14.211964	0.719231	42.H	3.127199	12.948038	6.471701
43.C	1.348615	15.231105	2.634001	43.C	2.179862	14.642927	5.501340
44.H	0.897247	16.127314	2.208421	44.H	2.156883	15.227829	6.420768
45.C	1.619618	15.193247	3.990212	45.C	1.660213	15.183831	4.340383
46.H	1.383982	16.039479	4.631850	46.H	1.228096	16.182175	4.332378
47.O	2.469144	11.916701	1.574666	47.O	3.277732	11.360569	4.361545
48.S	4.256132	8.913710	3.858501	48.S	4.201317	8.789438	3.756052
49.N	3.349203	9.369906	1.079663	49.N	3.281109	9.421447	1.036672
50.N	5.105536	11.148358	1.946468	50.N	5.050043	11.136490	2.011489
51.N	1.580479	9.714993	2.984274	51.N	1.576514	9.699566	3.008125
52.C	6.209113	12.006485	4.001431	52.C	6.138908	11.868456	4.131148
53.H	5.883225	11.124659	4.554796	53.H	5.663539	11.039308	4.652886
54.H	5.571611	12.852255	4.273165	54.H	5.610362	12.785244	4.413480
55.H	7.229693	12.248130	4.306859	55.H	7.173990	11.963607	4.468572

Table S4. Coordinates of optimized structure of $[\mathbf{1}_S]^+$ and $[\mathbf{1}_{S,rev}]^+$ with $S = 0$ in methanol (COSMO) and its respective bond energies.

$[\mathbf{1}_S]^+$ E = −7717.66 kcal/mol				$[\mathbf{1}_{S,rev}]^+$ E = −7711.76 kcal/mol			
1.Co	3.281551	10.499477	2.621793	1.Co	3.365927	10.377737	2.745372
2.C	3.891030	7.538448	2.679468	2.C	3.857080	7.401503	2.314888
3.H	4.598583	6.721902	2.867654	3.H	4.543692	6.547182	2.356621
4.H	2.880432	7.145594	2.835866	4.H	2.837602	7.015040	2.424753
5.C	4.101034	8.062790	1.284370	5.C	4.067111	8.140241	1.023935
6.H	5.160146	8.303309	1.157886	6.H	5.130339	8.377174	0.929558
7.H	3.817360	7.339782	0.507709	7.H	3.760929	7.565025	0.139292
8.C	4.043029	10.119406	0.000019	8.C	4.049427	10.337807	0.054046
9.H	3.346774	10.854866	-0.412224	9.H	3.387786	11.138225	-0.282557
10.H	4.381643	9.469796	-0.814928	10.H	4.363009	9.785422	-0.839561
11.C	1.924541	9.073050	0.669395	11.C	1.899154	9.241464	0.649686
12.H	1.841153	8.158557	0.072902	12.H	1.783057	8.371607	-0.005690
13.H	1.576916	9.906681	0.051568	13.H	1.537427	10.103812	0.083100
14.C	5.177320	10.838891	0.651801	14.C	5.221797	10.922189	0.780324
15.C	6.343674	11.201793	-0.010139	15.C	6.390152	11.334833	0.152770
16.H	6.473673	10.930021	-1.055037	16.H	6.491287	11.220740	-0.923871
17.C	7.325414	11.901926	0.681429	17.C	7.413598	11.880572	0.920380
18.H	8.246355	12.197861	0.182528	18.H	8.337563	12.211138	0.449530
19.C	7.114880	12.199404	2.023236	19.C	7.242361	11.976884	2.297019
20.H	7.855498	12.734205	2.613107	20.H	8.019477	12.381347	2.941434
21.C	5.934227	11.792347	2.627175	21.C	6.054999	11.534378	2.862163
22.H	5.748555	11.990396	3.676578	22.H	5.880160	11.569968	3.932347
23.C	1.075728	9.013322	1.895260	23.C	1.082145	9.090199	1.896049
24.C	-0.147492	8.354099	1.943816	24.C	-0.170653	8.487609	1.914410
25.H	-0.500811	7.813895	1.068571	25.H	-0.581851	8.073823	0.996538
26.C	-0.890885	8.393383	3.116560	26.C	-0.870220	8.419262	3.113255
27.H	-1.851474	7.885187	3.177533	27.H	-1.852186	7.951178	3.150239

28.C	-0.376381	9.078802	4.212476	28.C	-0.287021	8.942069	4.263536
29.H	-0.911841	9.129691	5.157540	29.H	-0.789217	8.899920	5.227187
30.C	0.856286	9.703003	4.098843	30.C	0.970075	9.520387	4.178182
31.H	1.297203	10.225547	4.939528	31.H	1.479701	9.922770	5.047234
32.C	2.567887	12.938040	3.648442	32.C	2.542346	12.971335	3.493414
33.C	2.365560	14.048654	4.514138	33.C	2.035052	14.300196	3.577154
34.C	2.817983	13.906657	5.847153	34.C	1.427434	14.825662	2.413897
35.H	2.689078	14.726597	6.552647	35.H	1.023702	15.837471	2.422104
36.C	3.415914	12.731021	6.239664	36.C	1.346667	14.043016	1.287538
37.H	3.772816	12.588773	7.257238	37.H	0.877425	14.403557	0.374850
38.C	3.574607	11.680459	5.320130	38.C	1.882639	12.743316	1.300904
39.H	4.035944	10.744401	5.621069	39.H	1.802875	12.143251	0.402604
40.C	2.156010	12.950668	2.284190	40.C	3.138198	12.340027	4.619972
41.C	1.533558	14.110857	1.808042	41.C	3.236527	13.062106	5.812718
42.H	1.205600	14.152707	0.770252	42.H	3.689589	12.591093	6.684102
43.C	1.335459	15.206928	2.663567	43.C	2.748336	14.376418	5.882921
44.H	0.847954	16.095595	2.261067	44.H	2.838843	14.914718	6.826907
45.C	1.734149	15.199046	3.989722	45.C	2.155250	14.999603	4.799467
46.H	1.568339	16.062145	4.631482	46.H	1.775475	16.016747	4.874857
47.O	2.382472	11.881743	1.567442	47.O	3.554769	11.102259	4.489233
48.S	4.259039	8.892072	3.817713	48.S	4.285707	8.552465	3.632392
49.N	3.337255	9.336883	1.046925	49.N	3.326336	9.454170	1.002082
50.N	4.975379	11.136146	1.955018	50.N	5.057804	11.031546	2.117821
51.N	1.565144	9.686488	2.958067	51.N	1.634565	9.606706	3.014265
52.N	3.164841	11.777619	4.057335	52.N	2.479926	12.209616	2.359961

Table S5. Coordinates of optimized structure of $[\mathbf{2}_{\mathbf{S}}]^+$ and $[\mathbf{2}_{\mathbf{S,rev}}]^+$ with $S = 0$ in methanol (COSMO) and its respective bond energies.

$[\mathbf{2}_{\mathbf{S}}]^+$ E = −8091.55 kcal/mol				$[\mathbf{2}_{\mathbf{S,rev}}]^+$ E = −8086.64 kcal/mol			
1.Co	3.309270	10.526650	2.660899	1.Co	3.279460	10.495889	2.701587
2.C	3.909977	7.558311	2.699900	2.C	3.844644	7.501531	2.535654
3.H	4.622151	6.745605	2.886939	3.H	4.554454	6.675637	2.666026
4.H	2.900998	7.155080	2.840803	4.H	2.834163	7.094349	2.654599
5.C	4.129790	8.099676	1.312893	5.C	4.064621	8.136853	1.192495
6.H	5.186677	8.355051	1.199166	6.H	5.121884	8.398966	1.099841
7.H	3.861477	7.381721	0.526004	7.H	3.795247	7.481511	0.352742
8.C	4.020633	10.152126	0.026393	8.C	3.975945	10.235555	0.032361
9.H	3.313291	10.893061	-0.354194	9.H	3.286642	10.972723	-0.380617
10.H	4.322663	9.505708	-0.805994	10.H	4.307550	9.613861	-0.808412
11.C	1.943469	9.086914	0.704757	11.C	1.870827	9.135244	0.696601
12.H	1.871211	8.166252	0.116576	12.H	1.789960	8.210516	0.115371
13.H	1.591628	9.910600	0.075811	13.H	1.495036	9.937978	0.056134
14.C	5.191461	10.856371	0.620329	14.C	5.139007	10.924133	0.673787
15.C	6.283053	11.187464	-0.169277	15.C	6.230589	11.304999	-0.091504
16.H	6.287665	10.907600	-1.219954	16.H	6.238276	11.093516	-1.158066
17.C	7.346857	11.861466	0.410403	17.C	7.295246	11.937734	0.533964
18.H	8.219120	12.145524	-0.175790	18.H	8.168028	12.258429	-0.032225
19.C	7.281026	12.132220	1.765937	19.C	7.232709	12.114024	1.904710
20.H	8.105692	12.628976	2.271199	20.H	8.062123	12.568454	2.441413

21.C	6.166989	11.760892	2.527086	21.C	6.116620	11.699513	2.641767
22.N	3.072981	11.784413	4.114427	22.N	2.349463	12.267975	2.110814
23.C	1.092655	9.034165	1.923200	23.C	1.042056	9.069433	1.937899
24.C	-0.128112	8.370011	1.967593	24.C	-0.191280	8.430920	1.999382
25.H	-0.471982	7.826125	1.090889	25.H	-0.577640	7.924455	1.117913
26.C	-0.878274	8.408136	3.134914	26.C	-0.901285	8.445595	3.193470
27.H	-1.836932	7.896136	3.193487	27.H	-1.868702	7.951865	3.264509
28.C	-0.368079	9.098103	4.229403	28.C	-0.344415	9.084524	4.297071
29.H	-0.904079	9.149432	5.174112	29.H	-0.852263	9.109277	5.258380
30.C	0.861683	9.727683	4.118669	30.C	0.894381	9.693678	4.170981
31.H	1.289863	10.250363	4.964033	31.H	1.384609	10.183934	5.004551
32.C	2.502772	12.949518	3.682532	32.C	2.277209	13.102030	3.191732
33.C	2.198766	14.033034	4.553335	33.C	1.698700	14.403675	3.147923
34.C	2.491560	13.847612	5.924716	34.C	1.169409	14.825317	1.907066
35.H	2.277859	14.643614	6.637002	35.H	0.718063	15.812653	1.815947
36.C	3.031192	12.654040	6.346640	36.C	1.220537	13.970482	0.832854
37.H	3.255186	12.472636	7.395501	37.H	0.812160	14.247108	-0.136673
38.C	3.310913	11.640010	5.415869	38.C	1.813947	12.704150	0.976294
39.H	3.737826	10.695108	5.738372	39.H	1.830560	12.046979	0.115628
40.C	2.202626	12.987043	2.290781	40.C	2.798012	12.570501	4.403290
41.C	1.623537	14.156222	1.783443	41.C	2.745234	13.362643	5.554875
42.H	1.382947	14.216102	0.722834	42.H	3.135182	12.967038	6.491577
43.C	1.346926	15.234358	2.640128	43.C	2.190381	14.650643	5.498890
44.H	0.894740	16.130738	2.214156	44.H	2.165597	15.246071	6.412200
45.C	1.615950	15.194810	3.997921	45.C	1.673424	15.179069	4.329517
46.H	1.378633	16.038830	4.642594	46.H	1.240193	16.177257	4.306826
47.O	2.472316	11.923273	1.582575	47.O	3.288159	11.356299	4.387256
48.S	4.256263	8.901659	3.857736	48.S	4.207934	8.769736	3.762367
49.N	3.352185	9.365562	1.084477	49.N	3.285702	9.419228	1.050466
50.N	5.103707	11.148879	1.942465	50.N	5.050240	11.138616	2.011983
51.N	1.578775	9.716498	2.981700	51.N	1.566634	9.703119	3.007578
52.C	6.196714	12.044459	3.990398	52.C	6.150760	11.884771	4.122182
53.H	5.857573	11.182099	4.565115	53.H	5.686961	11.050729	4.646206
54.H	5.567810	12.903543	4.240535	54.H	5.620647	12.797446	4.413780
55.H	7.218381	12.283373	4.293767	55.H	7.189713	11.986310	4.445466

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