Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Controlling Helical Chirality of Cobalt Complexes by Chirality Transfer with Vicinal Diamines

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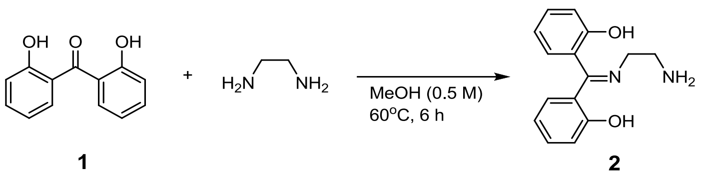
I. General Information

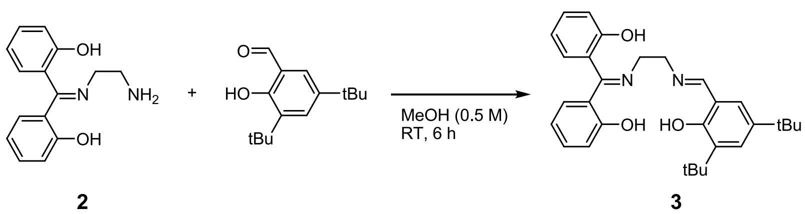
Commercially available compounds were used without further purification or drying. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Ascend 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) and are reported in ppm, relative to residual protonated solvent peak (DMSO-d_6). The high-resolution mass spectra (HRMS) were obtained on a Jeol JMS700 spectrometer at the Korea Basic Science Center, Daegu, Korea. Circular dichroism (CD) and UV-vis spectra were performed on a JASCO J-815 spectrometer at the KAIST Research Analyst Center. All calculations were performed using Gaussian 09. *Rac*-, (*R*,*R*)-, and (*S*,*S*)-1,2-diphenylethylenediamines were purchased and 1,2-bis(2,4,6-trimethylphenyl)ethylenediamine was prepared from hpen (mother diamine) by the diaza-Cope rearrangement.[1]

II. Experimental Procedures



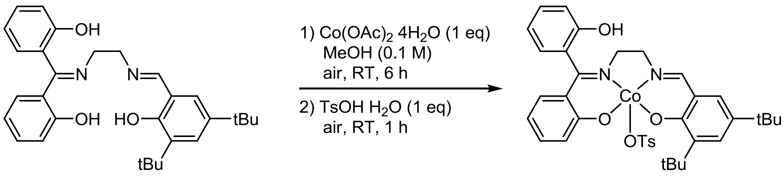
To a stirred solution of 2,2'-dyhydroxybenzophenone (**1**, 10.0 g, 46.7 mmol)[2] in methanol (93 mL) was added 2 equiv of ethylenediamine (6.24 mL, 93.4 mmol) at 25 °C. Heating the reaction mixture at 60 °C for 6 h afforded the product as a yellow precipitate. After allowed to ambient temperature, the mixture was mixed with diethyl ether (93 mL), and stirred for additional 1 h. The resulting cloudy solution was then filtered and washed with diethyl ether to give the product **2** as a yellow solid (10.2 g, 85% yield).

Yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.31 (ddd, *J* = 8.3, 7.3, 1.8 Hz, 1H), 7.25 (ddd, *J* = 8.4, 7.1, 1.8 Hz, 1H), 7.03 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.95 (dd, *J* = 8.2, 0.8 Hz, 1H), 6.91 (td, *J* = 7.4, 1.0 Hz, 1H), 6.85 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.75 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.64 (ddd, *J* = 8.1, 7.2, 1.2 Hz, 1H), 4.49 (br, 3H), 3.32 (td, *J* = 6.4, 0.8 Hz, 2H), 2.81 (td, *J* = 6.4, 2.5 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.0, 163.0, 154.5, 132.1, 130.7, 130.5, 128.5, 120.7, 119.4, 118.7, 117.5, 117.0, 116.6, 54.2, 41.8; HRMS (EI) m/z calcd for $C_{15}H_{16}N_2O_2$ $[M]^+$: 256.1212, found : 256.1214.



To a stirred suspension of **2** (5.08g, 19.8 mmol) in methanol (40 mL) was added 1.2 equiv of 3,5-di-tert-butyl-2-hydroxybenzaldehyde (5.57 g, 23.8 mmol) and the resulting mixture was stirred for 6 h at 25 °C. After adding diethyl ether (40 mL), the mixture was stirred for additional 1 h. The resulting solution was then filtered and washed with diethyl ether to give the product **3** as a yellow solid (7.84 g, 84%).

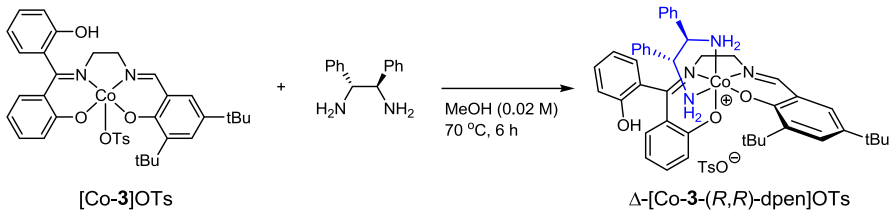
Yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 15.34 (s, 1H), 13.88 (br, 1H), 9.96 (br, 1H), 8.59 (s, 1H), 7.34 (ddd, *J* = 8.3, 7.3, 1.8 Hz, 1H), 7.31 (d, *J* = 2.4 Hz, 1H), 7.25 (m, 2H), 7.01(m, 2H), 6.91 (td, *J* = 7.4, 0.9 Hz, 1H), 6.85 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.77 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.66 (m, 1H), 3.87 (m, 2H), 3.62 (m, 2H), 1.38 (s, 9H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.0, 168.1, 162.2, 157.5, 153.8, 139.5, 135.6, 132.2, 130.7, 130.7, 128.4, 126.4, 126.2, 120.3, 119.5, 119.1, 117.7, 117.4, 117.3, 115.9, 58.8, 51.8, 34.6, 33.8, 31.3, 29.2; HRMS (EI) m/z calcd for $C_{30}H_{36}N_2O_3$ $[M]^+$: 472.2726, found : 472.2722.



3 [Co-**3**]OTs

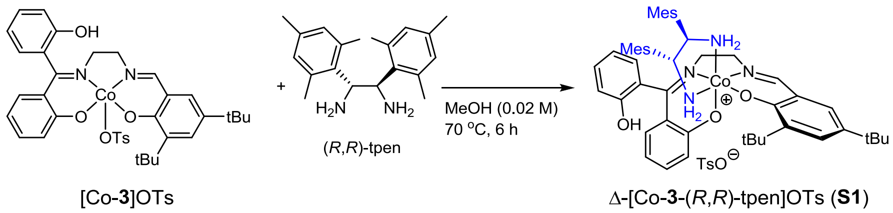
To a stirred suspension of **3** (2.36 g, 5 mmol) in methanol (50 mL) was added $Co(OAc)_2$•$4H_2O$ (1.25 g, 5 mmol). After stirring at 25 °C for 6 h, p-toluenesulfonic acid monohydrate (TsOH•H_2O) (951 mg, 5 mmol) was added and the mixture was stirred for 30 min at the atmospheric environment. All volatiles were removed under reduced pressure and further dried in a vacuum oven overnight at 60 °C to give the product [Co-**3**]OTs as a dark green solid (3.33 g, 95%).

Dark green solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.08 (s, 1H), 8.20 (s, 1H), 7.51 (dd, *J* =8.4, 0.8 Hz, 1H), 7.48 - 7.46 (m, 3H), 7.40 (d, *J* = 2.8 Hz, 1H), 7.35 (m, 1H), 7.27 (d, *J* = 2.4 Hz, 1H), 7.11 - 7.01 (m, 5H), 6.87 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.50 (m, 1H), 4.12 (m, 2H), 3.73 (m, 2H), 2.28 (s, 3H), 1.73 (s, 9H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.9, 167.6, 166.1, 161.8, 153.6, 141.7, 137.3, 135.4, 133.3, 132.9, 130.8, 128.3, 127.8, 125.2, 123.6, 121.8, 120.1, 119.2, 117.7, 116.0, 114.7, 57.6, 55.1, 35.3, 33.2, 31.2, 30.0, 20.5; HRMS (FAB) m/z calcd for $C_{30}H_{34}N_2O_3Co^+$: 529.1901, found : 529.1900.



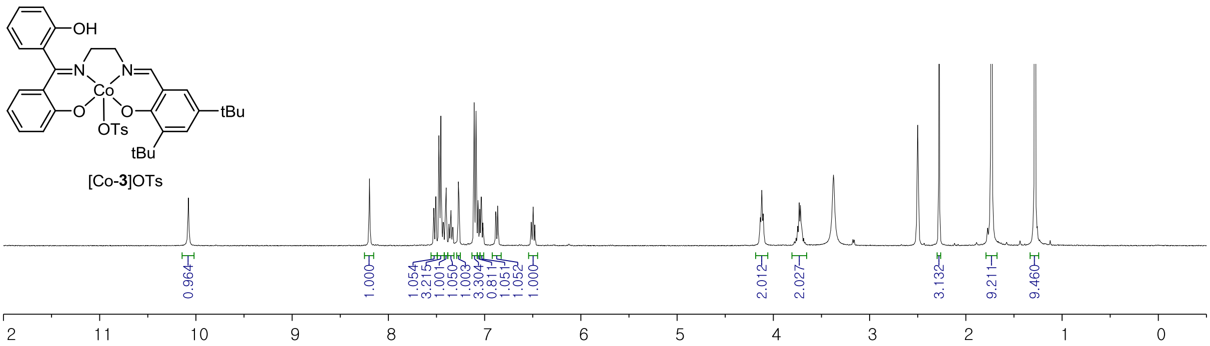
To a stirred solution of [Co-**3**]OTs (210 mg, 0.3 mmol) in methanol (3 mL) was added (*R*,*R*)-1,2-diphenylethylenediamine (dpen) (64 mg, 0.3 mmol), and the mixture was stirred for 6 h at 70 °C. Aliquot ^{1}H NMR indicated full conversion and the product ratio of 7:1. The pure major Δ-[Co-**3**-(*R*,*R*)-dpen]OTs was obtained by slow addition of pentane (36 mL) to a crude mixture (274 mg) dissolved in EtOH (4 mL). After stored in a refrigerator at 5 °C for 3 h, the solution were filtrated to give the pure Δ-[Co-**3**-(*R*,*R*)-dpen]OTs as a brown solid.

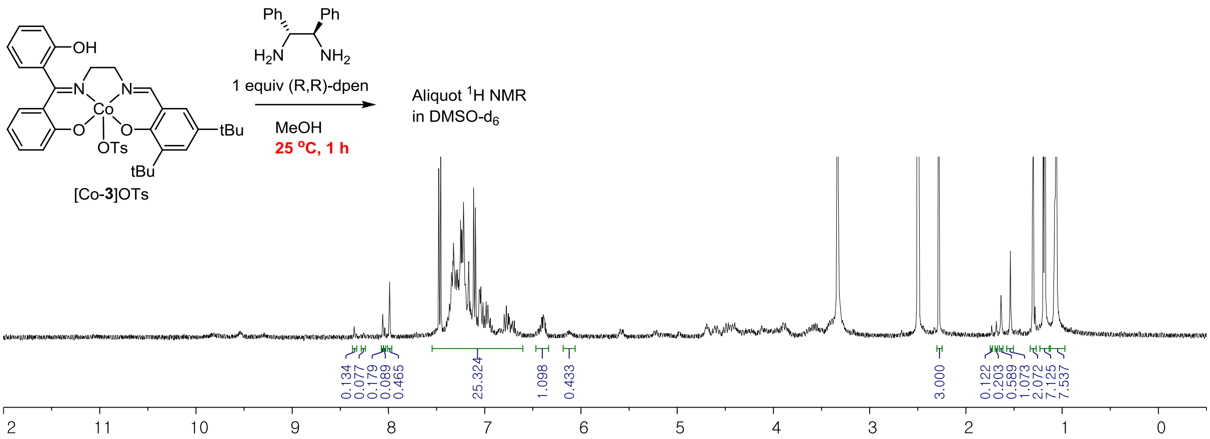
Brown solid (55 mg, 20%); ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 11.01 (br, 1H), 8.36 (s, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 2.6 Hz, 1H), 7.25 - 7.06 (m, 15H), 6.98 (m, 1H), 6.84 (m, 2H), 6.69 (dd, *J* = 8.8, 0.8, 1H), 6.45 (t, *J* = 7.2 Hz, 1H), 6.10 (m, 1H), 5.10 (m, 1H), 4.35 (m, 1H), 4.02 (m, 3H), 3.88 (m, 2H), 3.61 (m, 1H), 3.52 (m, 1H), 2.28 (s, 3H), 1.54 (s, 9H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 171.3, 168.8, 168.7, 161.7, 155.8, 145.8, 141.0, 138.3, 137.5, 136.7, 134.8, 134.3, 132.7, 132.6, 131.2, 128.9, 128.5, 128.4, 128.3, 128.3, 128.2, 128.0, 127.3, 125.7, 125.5, 122.8, 121.2, 119.5, 118.3, 116.1, 115.0, 64.9, 63.4, 59.9, 57.3, 35.3, 33.5, 31.4, 30.2, 20.8; HRMS (FAB) m/z calcd for $C_{44}H_{50}N_4O_3Co^+$: 741.3209, found : 741.3218.

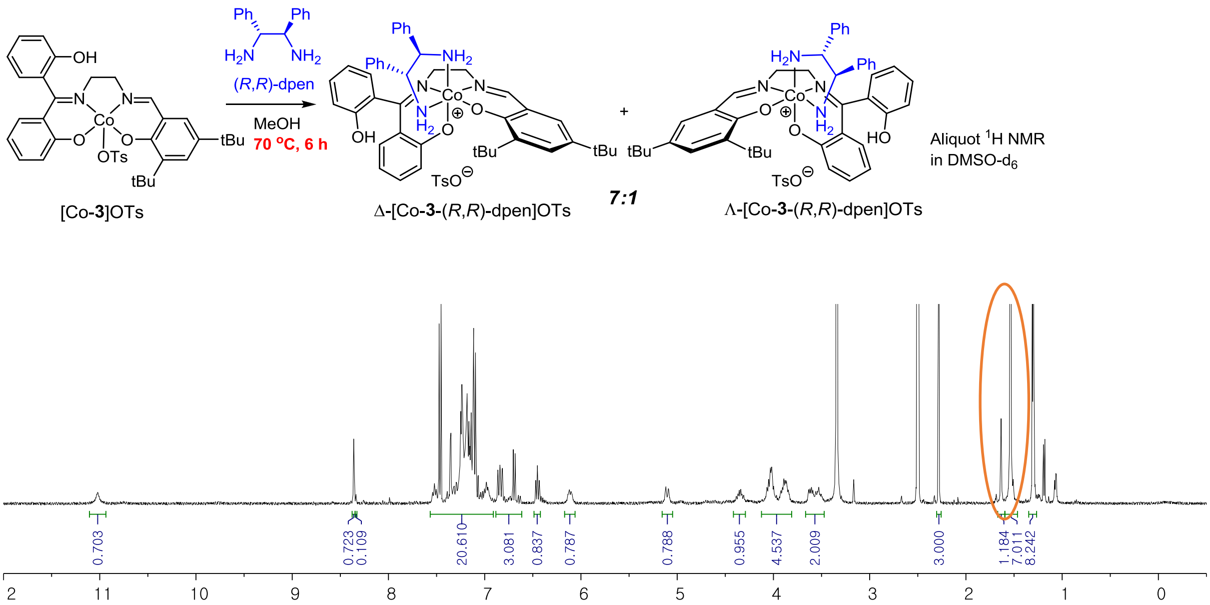


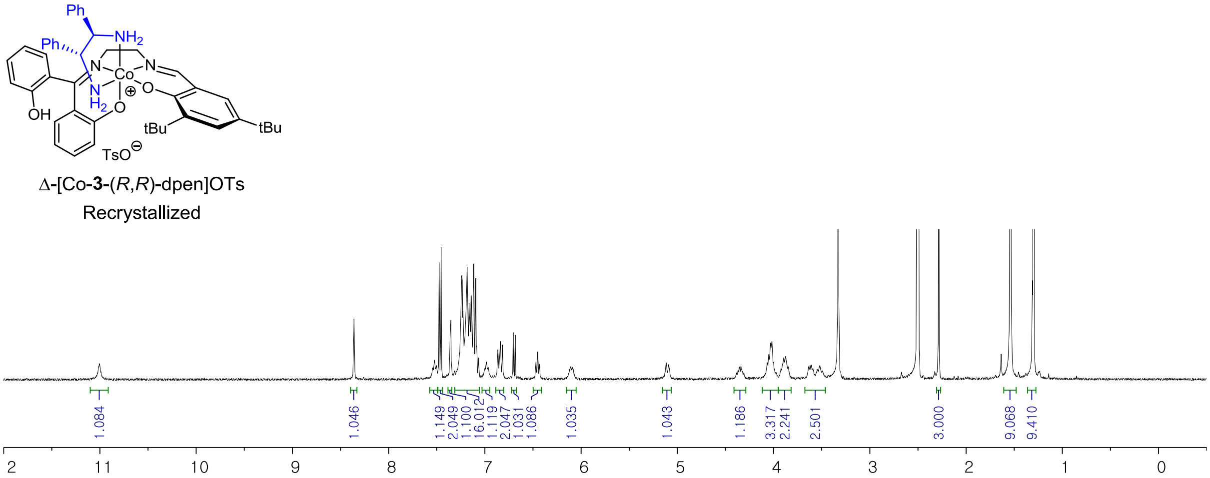
Brown solid (84 mg, 28%); ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.82 (br, 1H), 8.37 (s, 1H), 7.50 - 7.46 (m, 3H), 7.36 (d, *J* = 2.6 Hz, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.15 - 7.09 (m, 3H), 6.91 (t, *J* = 8.0 Hz, 1H), 6.81 (dd, *J*= 8.0, 1.2 Hz, 1H), 6.77 - 6.70 (m, 4H), 6.65 - 6.60 (m, 2H), 6.54 (t, *J* = 7.6 Hz, 1H), 5.87 (m, 1H), 5.43 (m, 1H), 4.85 (m, 1H), 4.64 (m, 1H), 4.43 (m, 2H), 3.98 (m, 1H), 3.79 (m, 1H), 3.60 (m, 1H), 3.01 (m, 1H), 2.46 (s, 3H), 2.35 (s, 3H), 2.28 (s, 3H), 2.08 (s, 6H), 1.96 (s, 3H), 1.90 (s, 3H), 1.50 (s, 9H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 171.7, 169.5, 169.0, 161.2, 145.7, 141.1, 138.0, 137.5, 137.5, 137.2, 137.1, 135.5, 134.9, 134.6, 133.9, 133.1, 132.9, 132.0, 131.1, 130.7, 129.7, 129.5, 129.4, 129.1, 128.8, 128.7, 128.0, 126.6, 125.5, 122.7, 120.4, 119.2, 116.2, 115.2, 59.1, 58.8, 57.6, 56.4, 35.4, 33.6, 31.3, 30.4, 20.9, 20.9, 20.8, 20.8, 20.4, 20.2, 20.1; HRMS (FAB) m/z calcd for $C_{50}H_{62}N_4O_3Co^+$: 825.4148, found : 825.4150.

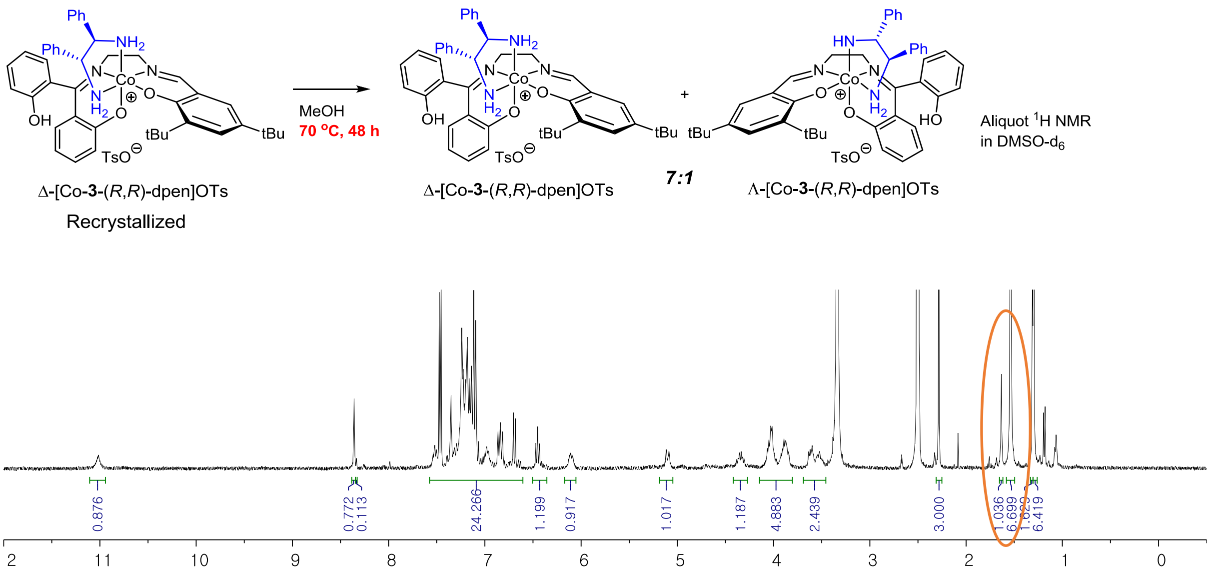
III. Reactions between [Co-3]OTs and Chiral Diamines

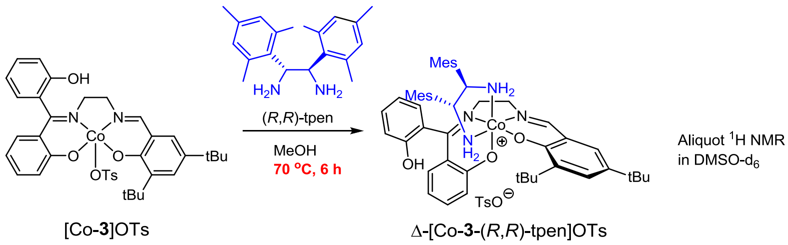


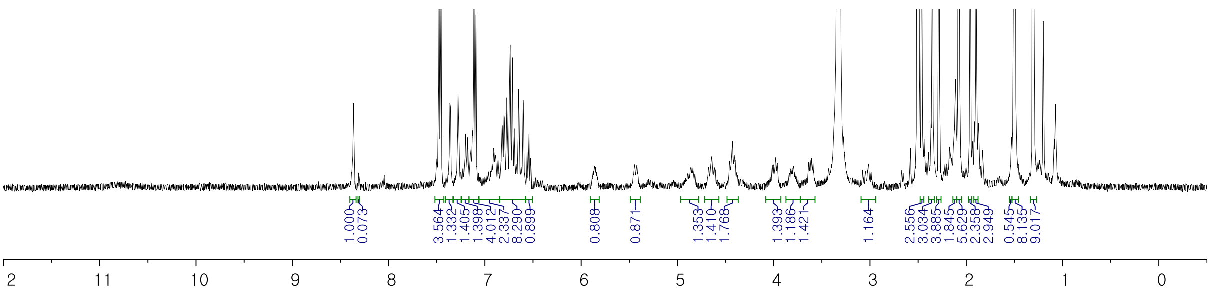


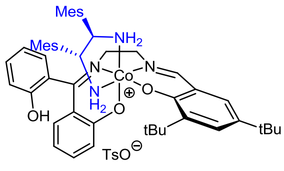



Ph
NH2
Ph
N
Co
N
N
H2
O
O
OH
tBu
tBu
TsO
Δ-[Co-3-(R,R)-dpen]OTs
Recrystallized
1.084
1.046
1.149
2.049
2.100
16.012
1.119
2.047
1.031
1.086
1.035
1.043
1.186
3.317
2.241
2.501
3.000
9.068
9.410
12
11
10
9
8
7
6
5
4
3
2
1
0

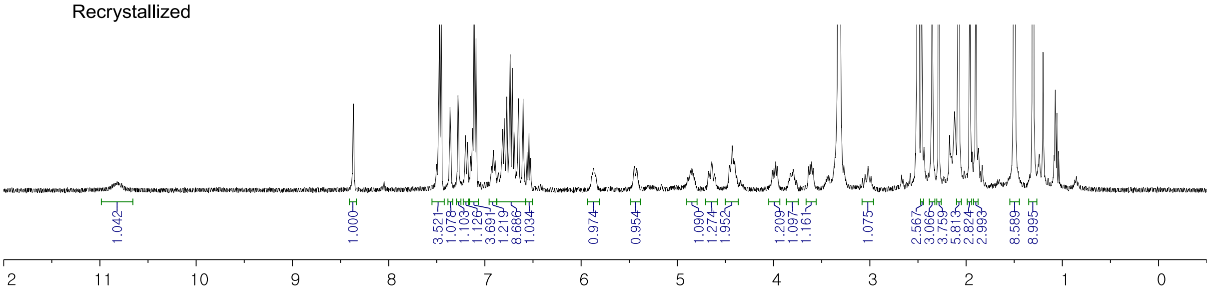

Δ-[Co-3-(R,R)-dpen]OTs
Recrystallized
MeOH
70 °C, 48 h
Δ-[Co-3-(R,R)-dpen]OTs
+
7:1
Λ-[Co-3-(R,R)-dpen]OTs
Aliquot 1H NMR
in DMSO-d6
0.876
0.772
0.113
24.266
1.199
0.917
1.017
1.187
4.883
2.439
3.000
1.036
6.699
6.419
12
11
10
9
8
7
6
5
4
3
2
1
0

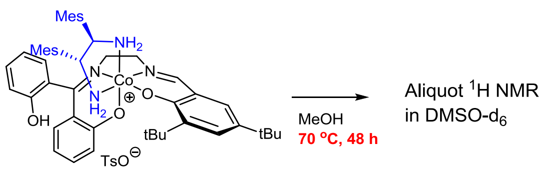




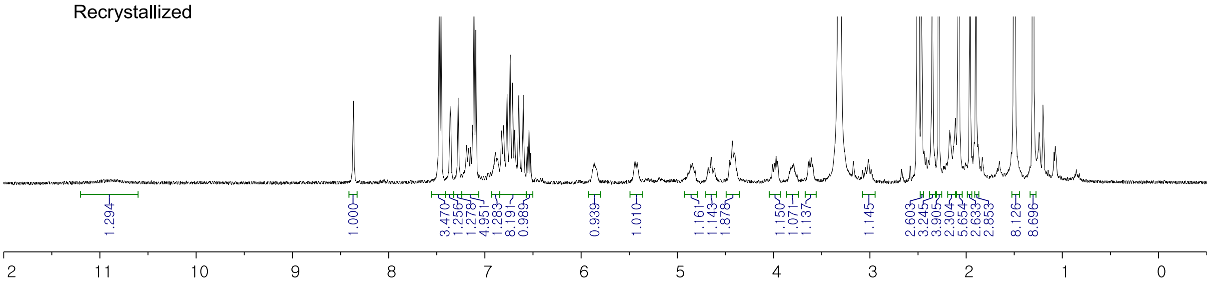


Δ-[Co-**3**-(*R*,*R*)-tpen]OTs
Recrystallized





Δ-[Co-**3**-(*R*,*R*)-tpen]OTs
Recrystallized



IV. CD Spectra

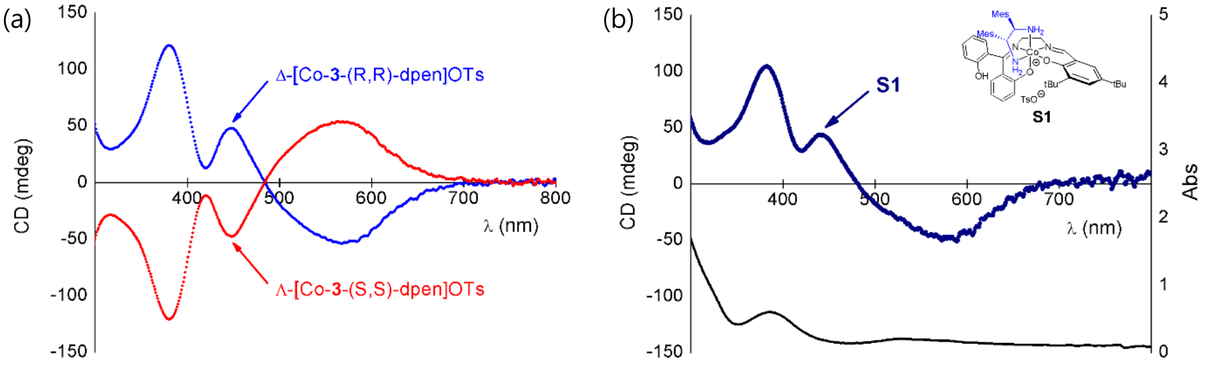


Figure S1. Circular dichroism spectra of recrystallized (a) Δ-[Co-**3**-(*R*,*R*)-dpen]OTs and Λ-[Co-**3**-(*S*,*S*)-dpen]OTs and (b) Δ-[Co-**3**-(*R*,*R*)-tpen]OTs (**S1**) (100 μM in acetonitrile, 10 mm cell, at 20 °C).

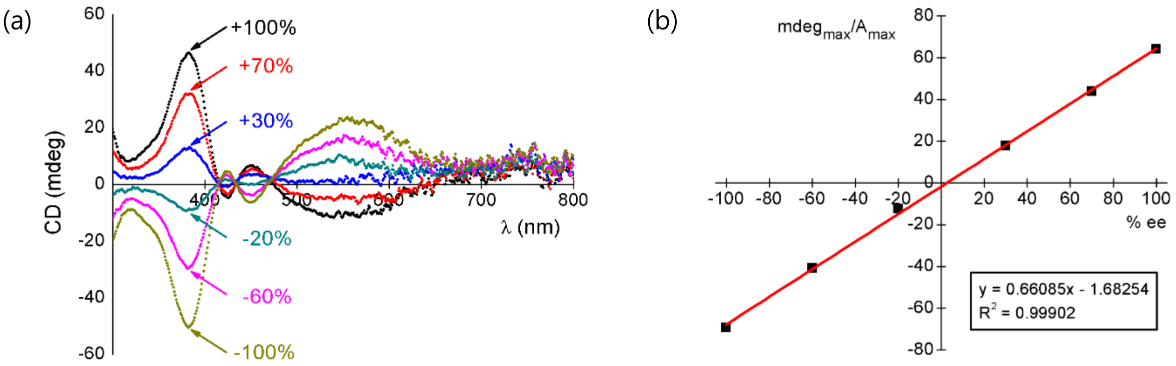
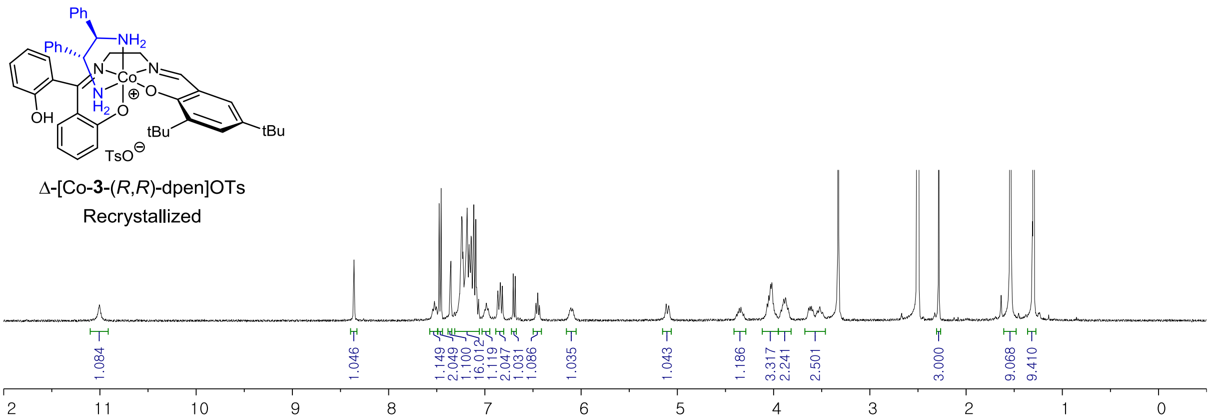
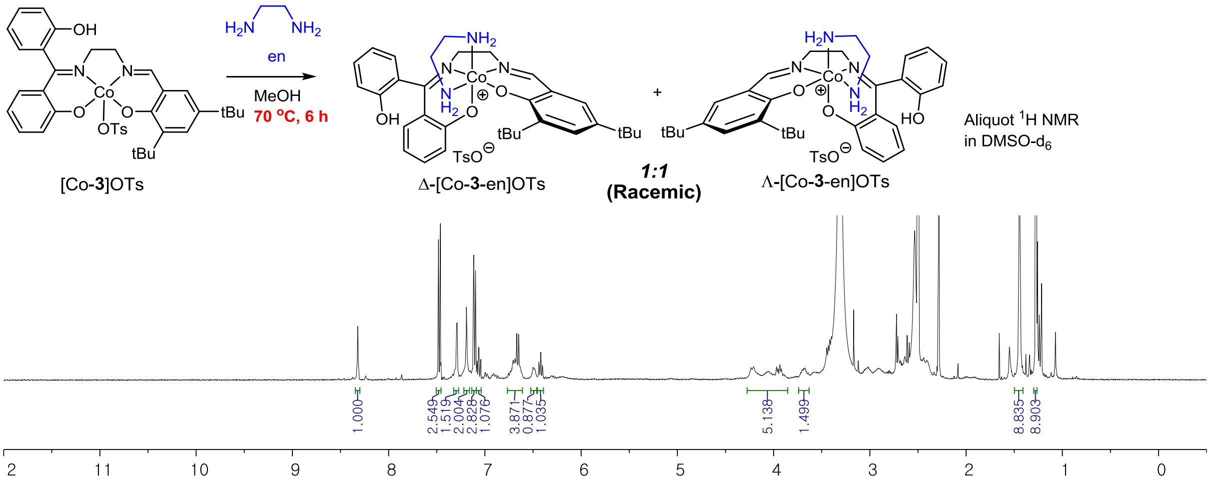
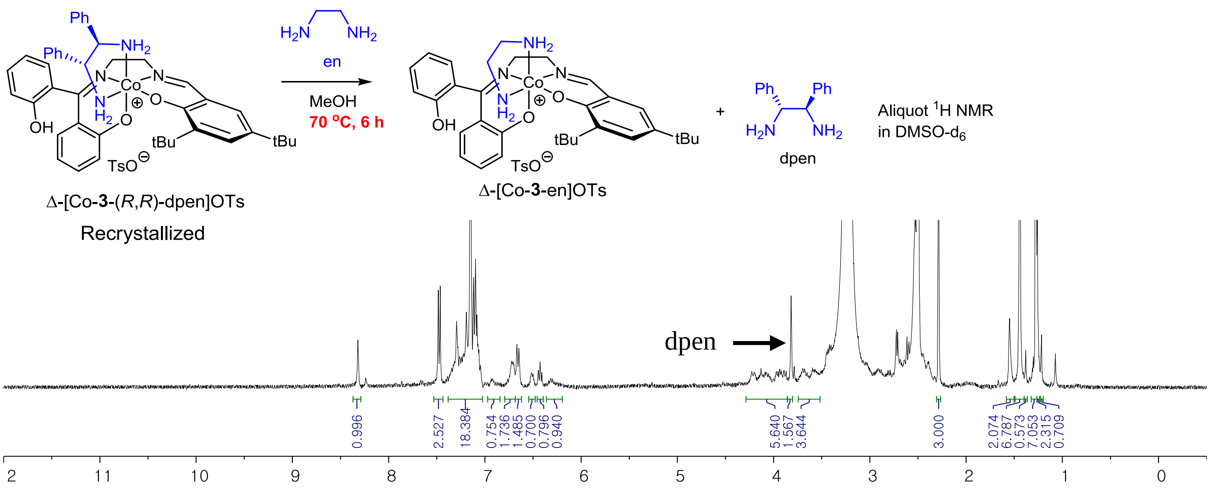


Figure S2. (a) Circular dichroism spectra of [Co-**3**-dpen]OTs with varied enantiopurities of dpen and (b) a linear plot between CD/UV-vis ratios and enantiopurities of dpen. (100 μM in acetonitrile, 10 mm cell, at 20 °C).

V. Asymmetric Coordination Chemistry







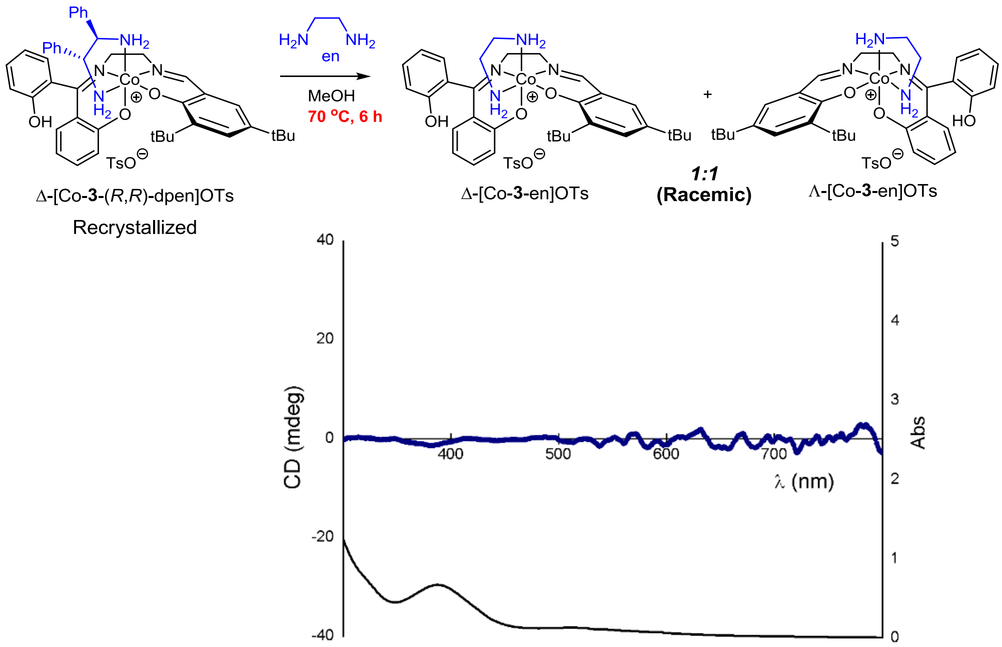
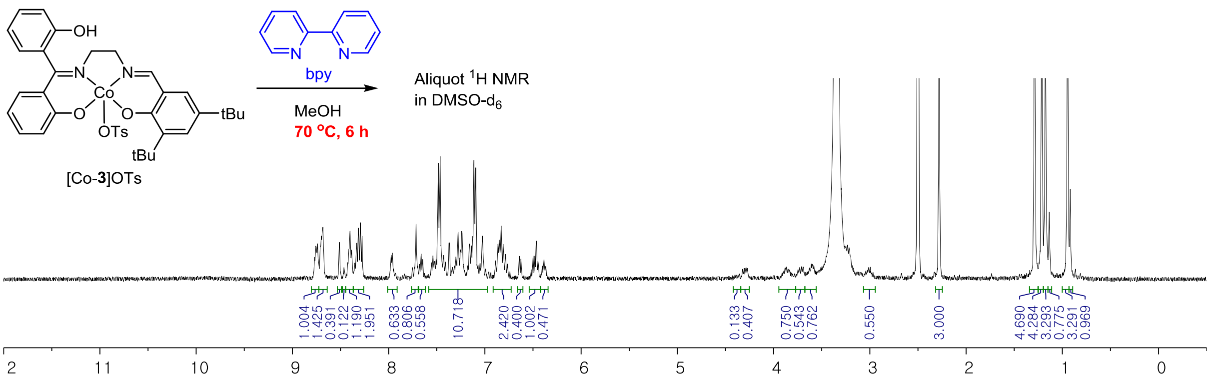
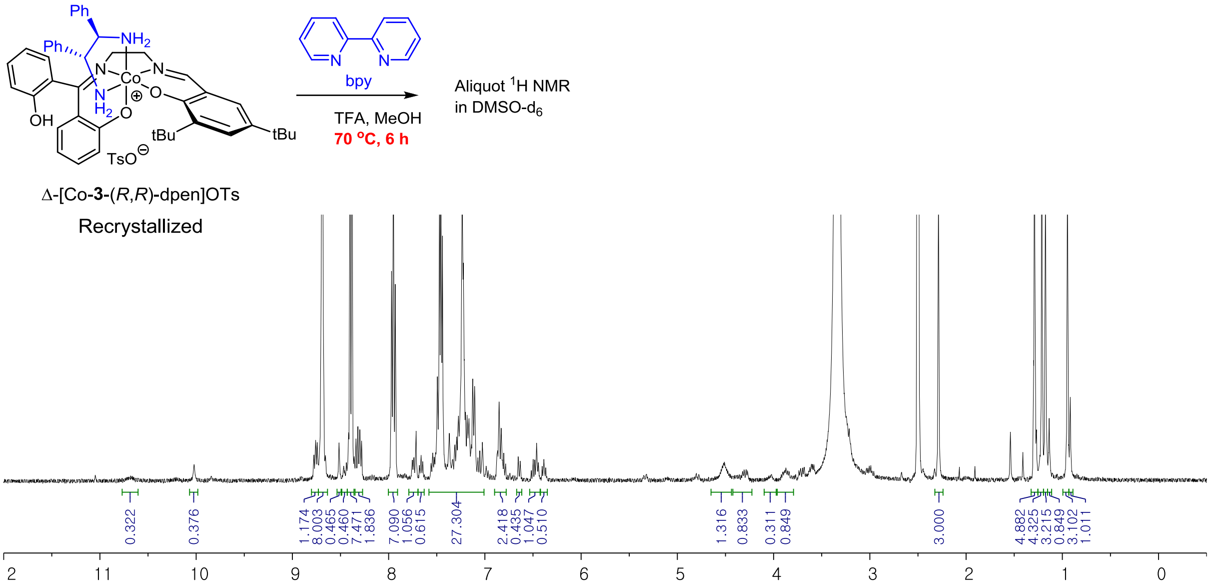


Figure S3. Circular dichroism spectrum of [Co-**3**-en]OTs prepared from Δ-[Co-**3**-(*R*,*R*)-dpen]OTs (100 μM in acetonitrile, 10 mm cell, at 20 °C) and its UV-vis spectrum.





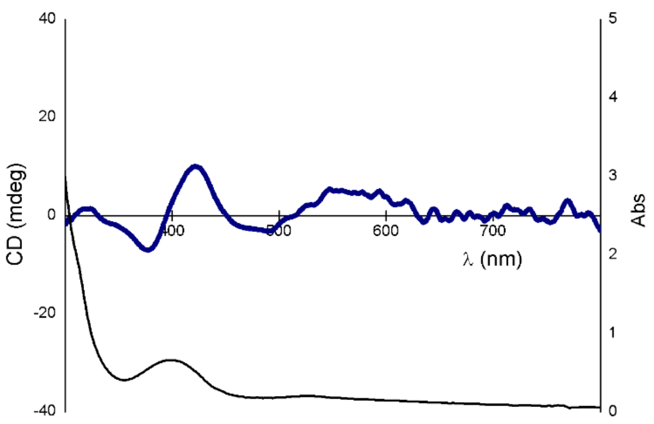
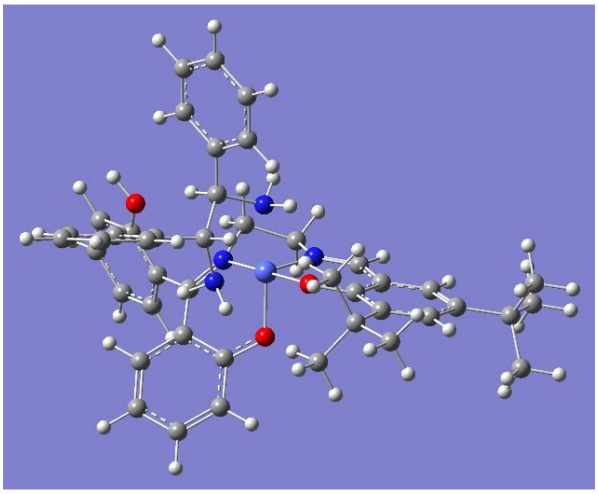


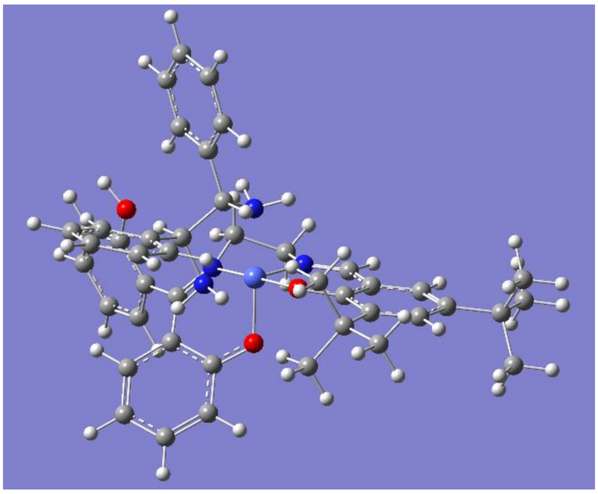
Figure S4. Circular dichroism spectrum of [Co-**3**-bpy]OTs prepared from Δ-[Co-**3**-(*R*,*R*)-dpen]OTs (100 μM in acetonitrile, 10 mm cell, at 20 °C) and its UV-vis spectrum.

VI. Calculation Results

The Gaussian 09 was used for all calculations. We used B3LYP/ 6-31G(d,p) basis for C, H, N and O and LANL2DZ for Co.



Δ-[Co-**3**-(*R*,*R*)-dpen]$^+$



Δ-[Co-**3**-(*S*,*S*)-dpen]$^+$

(Enantiomer of Λ-[Co-**3**-(*R*,*R*)-dpen]$^+$)

Molecule	E (hartree)	E + ZPVE (hartree)	G_{298K} (hartree)	Imaginary Frequency (cm^{-1})
Δ-[Co-**3**-(*R*,*R*)-dpen]$^+$	-2296.53567290	-2295.673060	-2295.755018	-
Δ-[Co-**3**-(*S*,*S*)-dpen]$^+$	-2296.53437244	-2295.671454	-2295.753156	-

Simulated CD Spectra

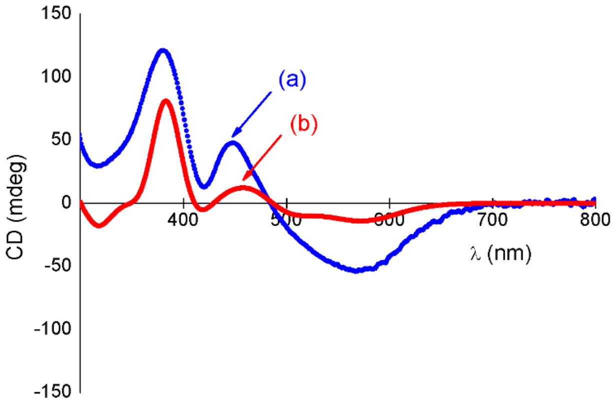


Figure S5. (a) Circular dichroism spectrum of recrystallized Δ-[Co-**3**-(*R*,*R*)-dpen]OTs and (b) simulated circular dichroism spectrum of Δ-[Co-**3**-(*R*,*R*)-dpen]$^+$ by TD-DFT calculation (Gaussian 09 TD-SCF, B3LYP/ 6-31G(d,p) basis for C, H, N and O and LANL2DZ for Co and CD spectra were generated using the program SpecDis v. 1.61).

Cartesian Coordinates of Calculated Compounds

Δ-[Co-**3**-(*R*,*R*)-dpen]$^{+}$

		Coordinates (Angstroms)		
	ATOM	X	Y	Z
1	Co	0.055	-0.569	-0.238
2	N	0.907	-1.548	-1.631
3	N	-1.544	-1.473	-0.859
4	O	0.277	-1.951	1.021
5	C	-2.39	-2.12	-0.093
6	C	-2.109	-2.31	1.318
7	C	-1.502	-3.121	3.938
8	C	-0.739	-2.313	1.766
9	C	-3.137	-2.673	2.231
10	C	-2.849	-3.055	3.525
11	C	-0.475	-2.767	3.085
12	H	-4.167	-2.644	1.893
13	H	-3.647	-3.314	4.212
14	H	0.563	-2.805	3.401
15	H	-1.266	-3.443	4.949
16	C	-3.618	-2.737	-0.676
17	C	-5.943	-3.908	-1.733
18	C	-3.886	-4.105	-0.495
19	C	-4.55	-1.96	-1.394
20	C	-5.708	-2.546	-1.912
21	C	-5.029	-4.695	-1.027
22	H	-3.177	-4.703	0.067
23	H	-6.424	-1.935	-2.455
24	H	-5.21	-5.755	-0.887
25	H	-6.844	-4.352	-2.144
26	C	-1.425	-1.729	-2.296
27	H	-2.181	-2.43	-2.656
28	H	-1.544	-0.796	-2.857
29	C	-0.015	-2.315	-2.479
30	H	0.295	-2.289	-3.531
31	H	-0.024	-3.361	-2.149
32	C	2.193	-1.665	-1.758
33	H	2.557	-2.315	-2.559
34	C	3.2	-1.036	-0.964
35	C	5.276	0.092	0.45
36	C	2.893	-0.1	0.076
37	C	4.546	-1.371	-1.27
38	C	5.605	-0.824	-0.581
39	C	3.989	0.473	0.809
40	H	4.714	-2.085	-2.069
41	H	6.099	0.525	1.003
42	O	1.66	0.274	0.351
43	N	-0.886	0.581	1.106
44	H	-1.751	0.136	1.412
45	H	-0.268	0.613	1.916
46	N	-0.182	1.048	-1.41
47	H	-0.263	0.881	-2.411
48	H	0.709	1.525	-1.261
49	C	-1.319	1.888	-0.925
50	H	-2.226	1.319	-1.15
51	C	-1.159	1.97	0.61
52	H	-0.257	2.55	0.822
53	C	3.746	1.466	1.967
54	C	5.061	1.944	2.617
55	H	4.827	2.634	3.434
56	H	5.701	2.481	1.91
57	H	5.635	1.117	3.045
58	C	3.016	2.729	1.448
59	H	2.848	3.434	2.27
60	H	2.052	2.473	1.006
61	H	3.62	3.239	0.689
62	C	2.911	0.78	3.077
63	H	2.691	1.493	3.88
64	H	3.467	-0.055	3.514
65	H	1.971	0.386	2.687
66	C	7.079	-1.153	-0.874
67	C	7.224	-2.186	-2.007
68	H	6.743	-3.137	-1.756
69	H	8.283	-2.392	-2.186
70	H	6.799	-1.822	-2.949
71	C	7.745	-1.734	0.396
72	H	7.245	-2.654	0.715
73	H	7.718	-1.031	1.234
74	H	8.796	-1.97	0.199
75	C	7.82	0.138	-1.298
76	H	7.783	0.905	-0.518
77	H	7.381	0.563	-2.207
78	H	8.875	-0.077	-1.499

79	O	-4.292	-0.621	-1.554
80	H	-5.043	-0.211	-2.003
81	C	-2.336	2.614	1.318
82	C	-4.491	3.79	2.678
83	C	-3.628	2.078	1.201
84	C	-2.139	3.742	2.122
85	C	-3.21	4.33	2.797
86	C	-4.697	2.663	1.88
87	H	-3.811	1.206	0.576
88	H	-1.143	4.167	2.218
89	H	-3.042	5.206	3.415
90	H	-5.693	2.241	1.784
91	H	-5.324	4.244	3.205
92	C	-1.393	3.238	-1.612
93	C	-1.552	5.722	-2.912
94	C	-2.539	3.594	-2.332
95	C	-0.323	4.145	-1.55
96	C	-0.402	5.378	-2.197
97	C	-2.621	4.828	-2.977
98	H	-3.376	2.902	-2.382
99	H	0.58	3.899	-0.994
100	H	0.432	6.07	-2.141
101	H	-3.518	5.091	-3.53
102	H	-1.612	6.683	-3.413

Δ-[Co-**3**-(*S*,*S*)-dpen]$^+$

		Coordinates (Anstroms)		
	ATOM	X	Y	Z
1	Co	-0.017	-0.636	-0.196
2	N	0.797	-1.729	-1.53
3	N	-1.645	-1.549	-0.73
4	O	0.189	-1.941	1.147
5	C	-2.501	-2.098	0.099
6	C	-2.201	-2.188	1.517
7	C	-1.565	-2.839	4.174
8	C	-0.821	-2.216	1.935
9	C	-3.221	-2.44	2.474
10	C	-2.918	-2.742	3.786
11	C	-0.544	-2.59	3.277
12	H	-4.257	-2.389	2.157
13	H	-3.709	-2.916	4.506
14	H	0.498	-2.647	3.573
15	H	-1.319	-3.099	5.2
16	C	-3.756	-2.721	-0.415
17	C	-6.134	-3.901	-1.336
18	C	-4.076	-4.052	-0.097
19	C	-4.663	-1.984	-1.205
20	C	-5.848	-2.575	-1.653
21	C	-5.245	-4.648	-0.56
22	H	-3.384	-4.619	0.518
23	H	-6.546	-1.993	-2.251
24	H	-5.464	-5.681	-0.314
25	H	-7.056	-4.348	-1.696
26	C	-1.546	-1.955	-2.134
27	H	-2.316	-2.679	-2.408
28	H	-1.659	-1.091	-2.798
29	C	-0.147	-2.575	-2.271
30	H	0.146	-2.675	-3.323
31	H	-0.161	-3.575	-1.82
32	C	2.078	-1.843	-1.703
33	H	2.415	-2.544	-2.473
34	C	3.11	-1.158	-0.993
35	C	5.233	0.017	0.306
36	C	2.837	-0.186	0.023
37	C	4.445	-1.495	-1.343
38	C	5.528	-0.921	-0.716
39	C	3.959	0.401	0.706
40	H	4.587	-2.236	-2.124
41	H	6.075	0.464	0.819
42	O	1.616	0.199	0.324
43	N	-0.89	0.636	1.062
44	H	-1.513	0.182	1.729
45	H	-0.098	1.01	1.588
46	N	-0.235	0.889	-1.506
47	H	-0.882	0.667	-2.26
48	H	0.676	1.043	-1.937
49	C	3.758	1.408	1.86
50	C	5.095	1.883	2.467
51	H	4.889	2.578	3.286
52	H	5.717	2.412	1.738
53	H	5.677	1.054	2.883
54	C	3.026	2.671	1.346
55	H	2.878	3.384	2.165
56	H	2.053	2.417	0.923
57	H	3.614	3.172	0.57

58	C	2.951	0.74	3.001
59	H	2.754	1.465	3.799
60	H	3.52	-0.088	3.437
61	H	2.001	0.339	2.646
62	C	6.991	-1.248	-1.058
63	C	7.099	-2.301	-2.177
64	H	6.635	-3.251	-1.89
65	H	8.153	-2.503	-2.392
66	H	6.635	-1.957	-3.108
67	C	7.707	-1.803	0.197
68	H	7.224	-2.72	0.551
69	H	7.706	-1.084	1.023
70	H	8.752	-2.036	-0.034
71	C	7.709	0.039	-1.531
72	H	7.697	0.819	-0.764
73	H	7.234	0.445	-2.43
74	H	8.756	-0.175	-1.768
75	O	-4.359	-0.68	-1.503
76	H	-5.108	-0.287	-1.971
77	C	-0.691	2.15	-0.823
78	H	0.208	2.598	-0.393
79	C	-1.615	1.72	0.335
80	H	-2.506	1.247	-0.089
81	C	-2.046	2.857	1.243
82	C	-2.881	4.932	2.939
83	C	-3.407	3.14	1.406
84	C	-1.104	3.627	1.942
85	C	-1.52	4.657	2.786
86	C	-3.824	4.172	2.247
87	H	-4.146	2.55	0.869
88	H	-0.04	3.431	1.836
89	H	-0.782	5.245	3.322
90	H	-4.883	4.38	2.363
91	H	-3.203	5.734	3.596
92	C	-1.319	3.131	-1.794
93	C	-2.446	4.942	-3.619
94	C	-2.477	2.792	-2.51
95	C	-0.735	4.385	-2.003
96	C	-1.296	5.288	-2.908
97	C	-3.035	3.691	-3.419
98	H	-2.955	1.825	-2.358
99	H	0.16	4.661	-1.452
100	H	-0.833	6.258	-3.059
101	H	-3.932	3.42	-3.969
102	H	-2.882	5.642	-4.325

VII. Crystal Structure of [Co-3-(*rac*)-dpen]OTs

X-ray quality crystals for [Co-**3**-(*rac*)-dpen]OTs were obtained by slow diffusion of hexane to its solution in EtOH at 5 °C.

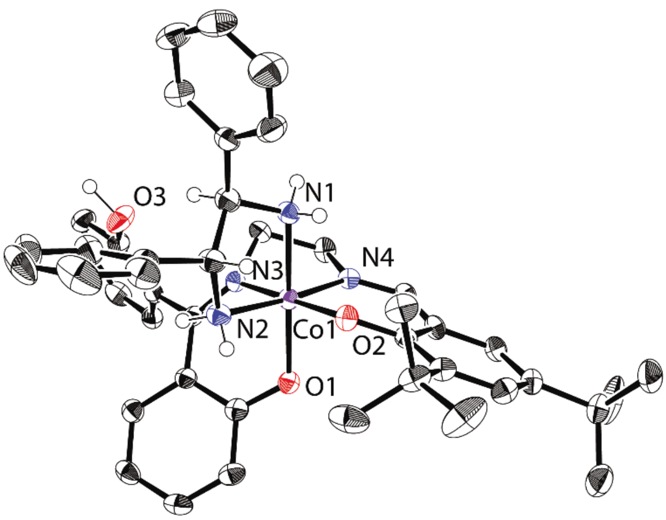


Figure S6. ORTEP representation (50% probability) of the crystal structure of Δ-[Co-**3**-(*R*,*R*)-dpen]OTs. Its enantiomer Λ-[Co-**3**-(*S*,*S*)-dpen]OTs, tosylate, and solvent ethanol are not shown. All hydrogens except for those in dpen and phenols are omitted for clarity.

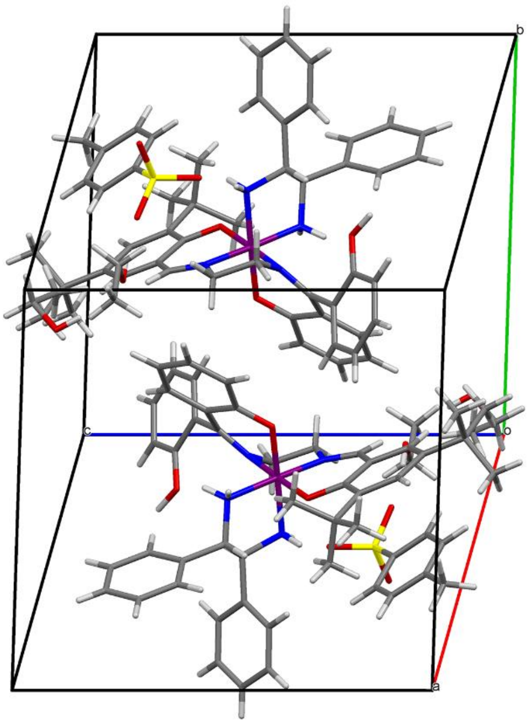
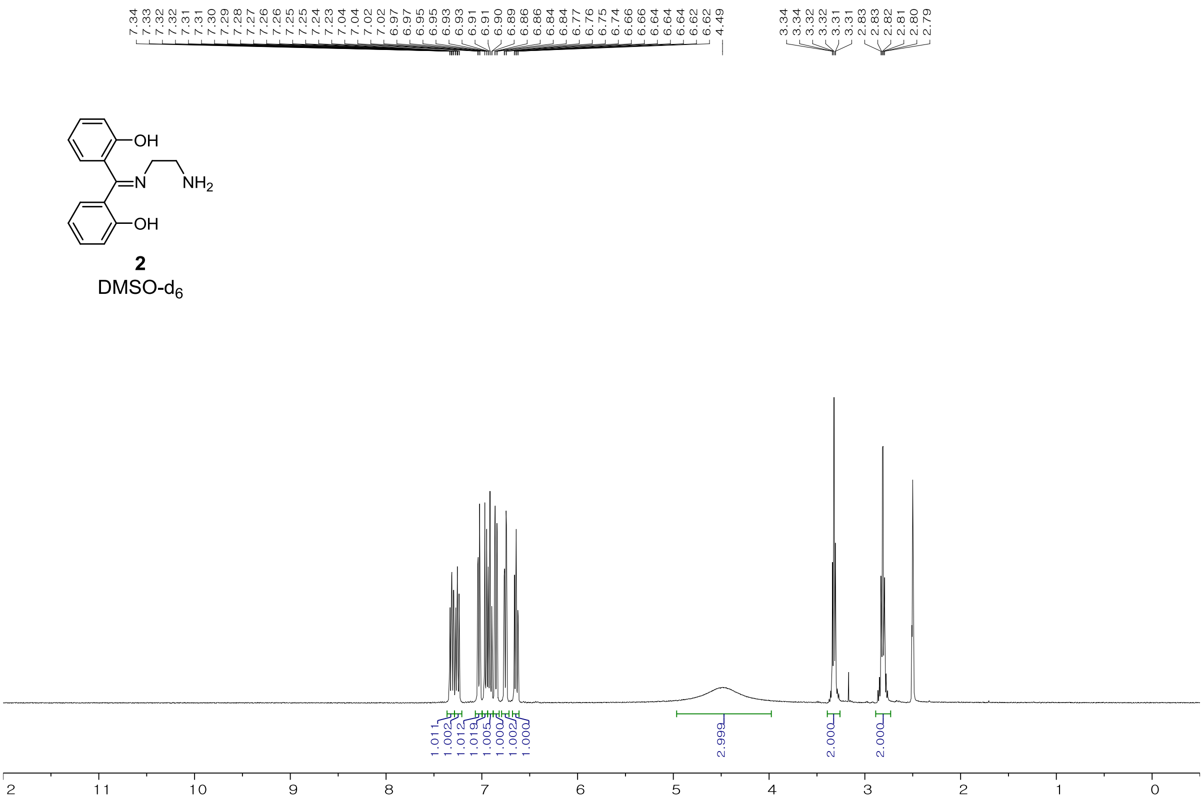
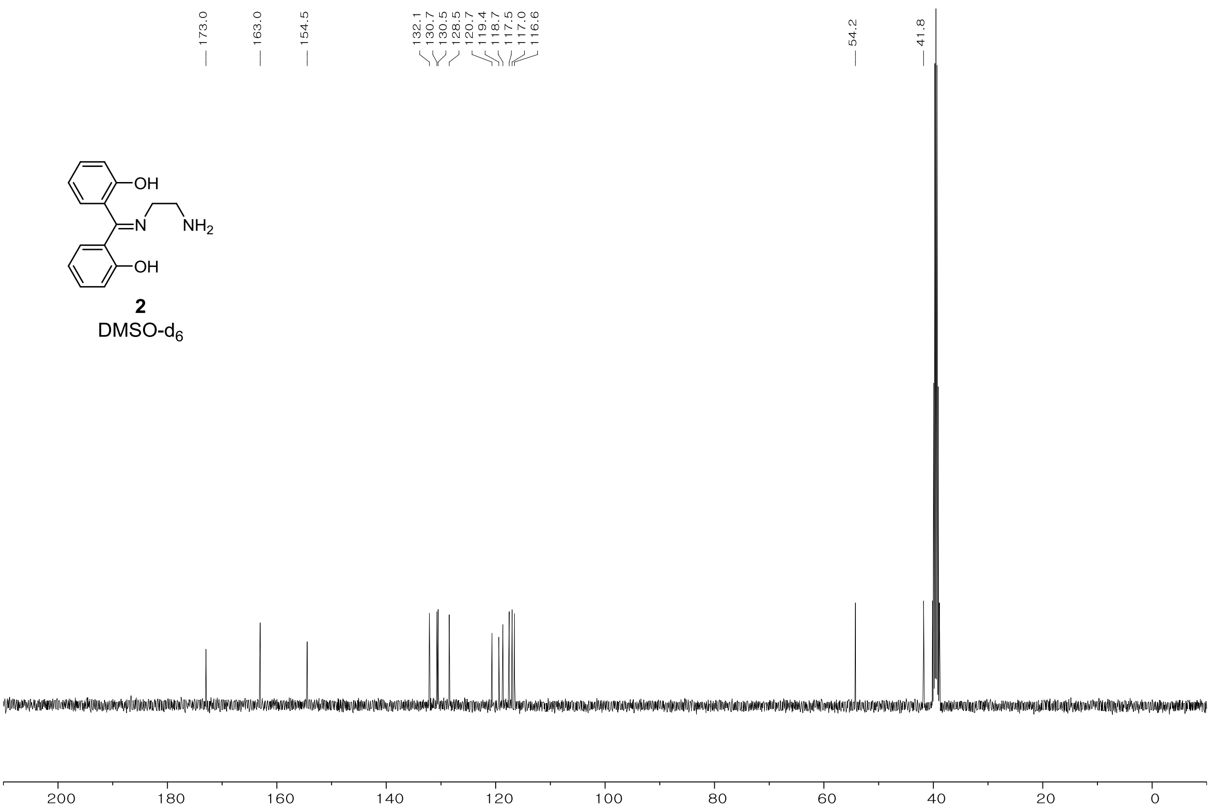


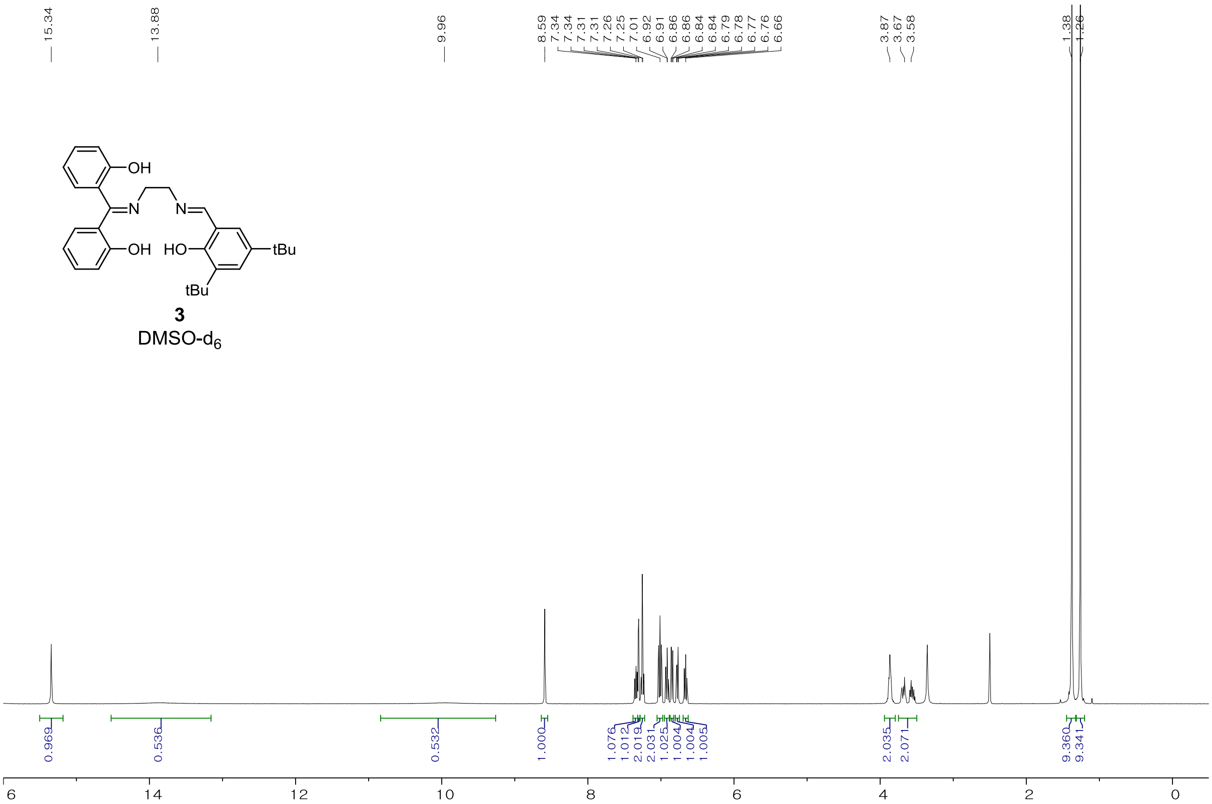
Figure S7. The unit-cell structure of [Co-**3**-(*rac*)-dpen]OTs.

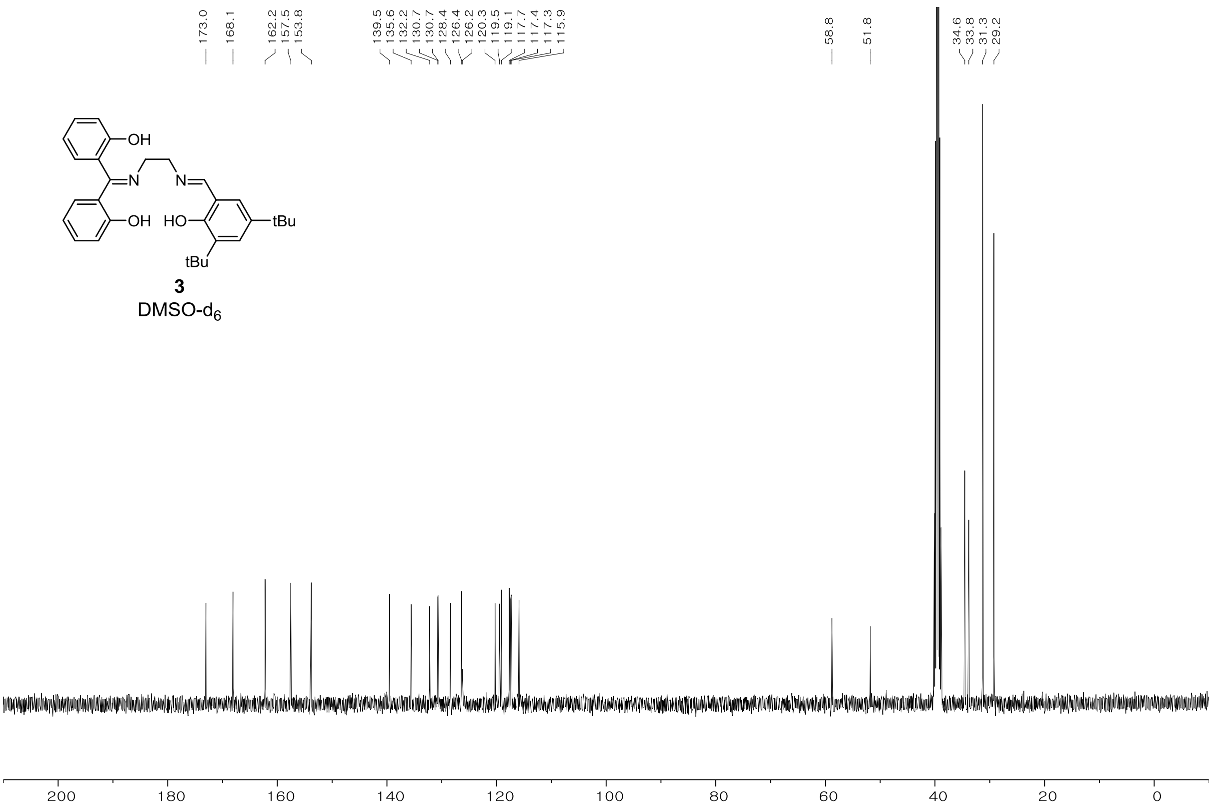
Empirical formula	C55 H69 Co N4 O8 S	
Formula weight	1005.13	
Temperature	147(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.631(3) Å	α=98.858(5)°
	b = 14.137(3) Å	β=95.100(5)°
	c = 14.402(3) Å	γ=105.071(5)°
Volume	2623.6(10) $Å^3$	
Z	2	
Density (calculated)	1.272 Mg/m^3	
Absorption coefficient	0.424 mm^{-1}	
F(000)	1068	
Crystal size	0.22 x 0.22 x 0.12 mm^3	
Theta range for data collection	1.52 to 27.55°.	
Index ranges	-17<=h<=17, -18<=k<=12, -18<=l<=18	
Reflections collected	45043	
Independent reflections	11987 [R(int) = 0.0749]	
Completeness to theta = 27.55°	98.90%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6243	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11987 / 1 / 651	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0570, wR2 = 0.1228	
R indices (all data)	R1 = 0.1071, wR2 = 0.1430	
Largest diff. peak and hole	0.968 and -0.536 e.$Å^{-3}$	

VIII. NMR Spectra






15.34
13.88
9.96
8.59 7.34 7.34 7.31 7.31 7.26 7.25 7.01 6.92 6.91 6.86 6.86 6.84 6.84 6.79 6.78 6.77 6.76 6.66
3.87 3.67 3.58
1.38 1.26
OH
N
N
OH
HO
tBu
tBu
3
DMSO-d6
0.969
0.536
0.532
1.000
1.076 1.012 2.019 2.031 1.025 1.004 1.004 1.005
2.035 2.071
9.360 9.341
16 14 12 10 8 6 4 2 0


173.0
168.1
162.2 157.5 153.8
139.5 135.6 132.2 130.7 130.7 128.4 126.4 126.2 120.3 119.5 119.1 117.7 117.4 117.3 115.9
58.8
51.8
34.6 33.8 31.3 29.2
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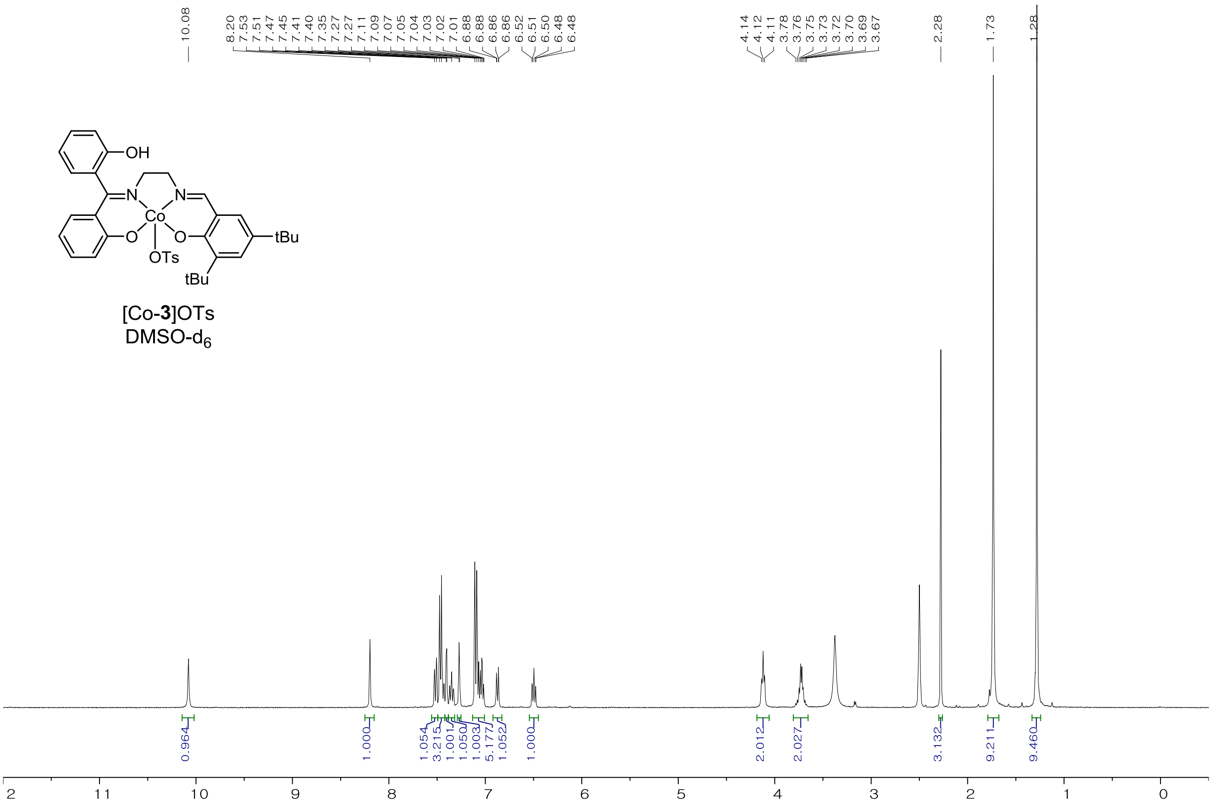
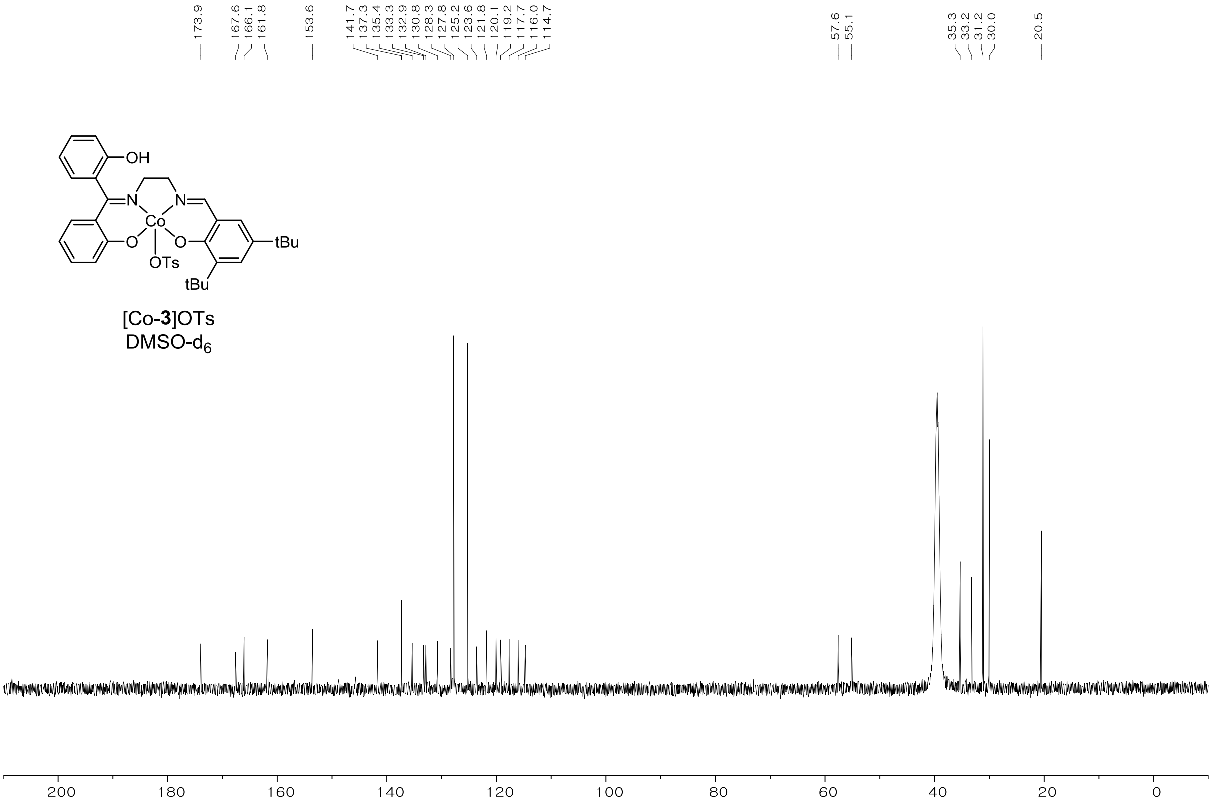
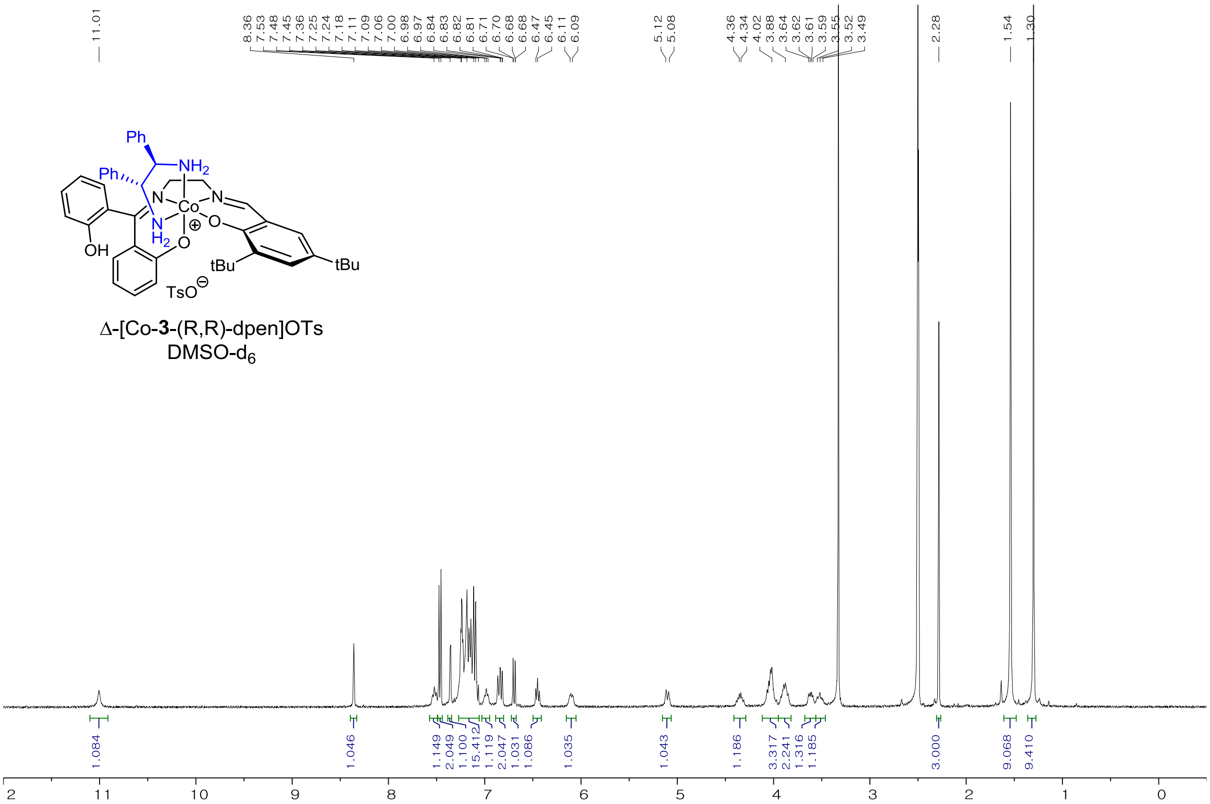
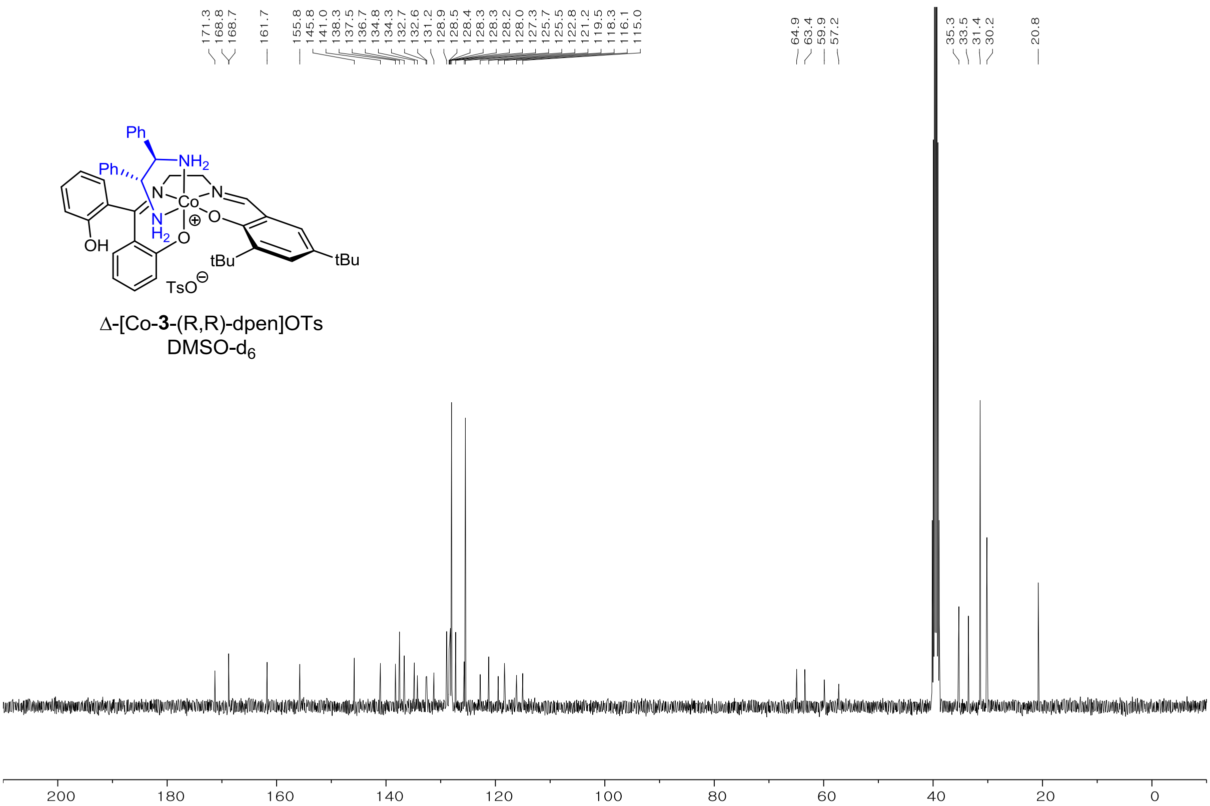
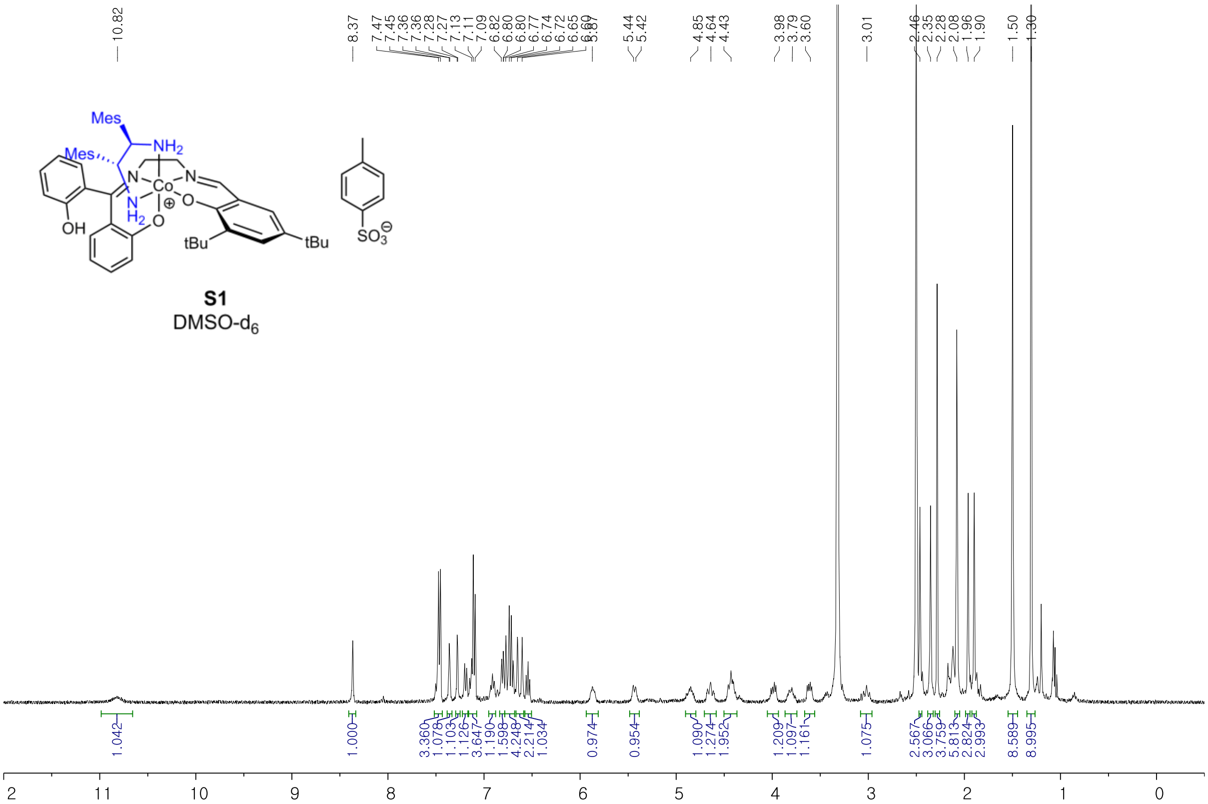
N
N
OH
HO
tBu
tBu
3
DMSO-d6
200 180 160 140 120 100 80 60 40 20 0

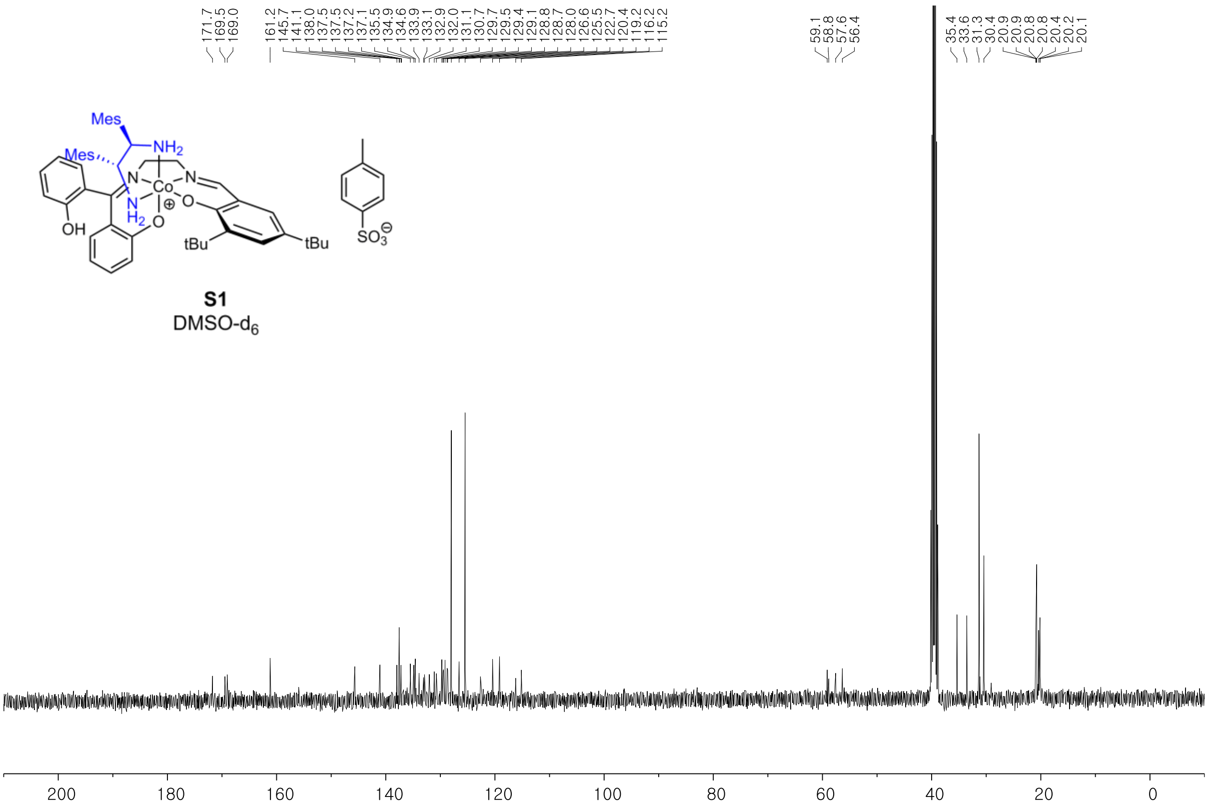

OH
N
N
Co
O
O
tBu
OTs
tBu
[Co-3]OTs
DMSO-d6


OH
N
N
Co
O
O
tBu
OTs
tBu
[Co-3]OTs
DMSO-d6


Δ-[Co-3-(R,R)-dpen]OTs
DMSO-d6


Δ-[Co-3-(R,R)-dpen]OTs
DMSO-d6


10.82
8.37 7.47 7.45 7.36 7.36 7.28 7.27 7.13 7.11 7.09 6.82 6.80 6.80 6.77 6.74 6.72 6.65 6.60 5.87
5.44 5.42
4.85 4.64 4.43
3.98 3.79 3.60
3.01
2.46 2.35 2.28 2.08 1.96 1.90
1.50 1.30
Mes
Mes
NH2
N
N
Co
O
N
H2
OH
O
tBu
tBu
SO3
S1
DMSO-d6
1.042
1.000
3.360 1.076 1.103 1.126 3.647 1.190 1.598 4.249 2.214 1.034
0.974
0.954
1.090 1.274 1.952
1.209 1.097 1.161
1.075
2.567 3.066 3.759 5.813 2.824 2.993
8.589 8.995
2 11 10 9 8 7 6 5 4 3 2 1 0


171.7 169.5 169.0
161.2 145.7 141.1 138.0 137.5 137.2 137.1 135.5 134.9 134.6 133.9 133.1 132.9 132.0 131.1 130.7 129.7 129.5 129.4 129.1 128.8 128.7 128.0 126.6 125.5 122.7 120.4 119.2 116.2 115.2
59.1 58.8 57.6 56.4
35.4 33.6 31.3 30.4 20.9 20.9 20.8 20.8 20.4 20.2 20.1
Mes
Mes
NH2
N
N
Co
O
N
H2
OH
O
tBu
tBu
SO3
S1
DMSO-d6
200 180 160 140 120 100 80 60 40 20 0

IX. References

[1] (a) H. Kim, Y. Nguyen, A. J. Lough, J. Chin, *J. Angew. Chem. Int. Ed.*, 2008, **47**, 8678. (b) H. Kim, Y. Nguyen, C. P.-H. Yen, L. Chagal, A. J. Lough, B. M. Kim, J. Chin, *J. Am. Chem. Soc.*, 2008, **130**, 12184.

[2] Y. Gardikis, P. G. Tsoungas, C. Potamitis, M. Zervou, M, P. Cordopatis, *Heterocycles.*, 2011, **83**, 1077.