Supporting Information

Pyridylbenzimidazole based Re(I)$(CO)_3$ complexes: antimicrobial activity, spectroscopic and density functional theory calculations

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Figure S1	AT IR spectra of the studied Re(I) complexes.
Figure S2	NMR analysis of **1** in DMSO-d_6, a) ^{1}H, b) ^{13}C, c) {^{1}H, ^{1}H} COS90 and d) {^{1}H, ^{13}C} HSQC.
Figure S3	NMR analysis of **2** in DMSO-d_6, a) ^{1}H, b) ^{13}C, c) {^{1}H, ^{1}H} COS90 and d) {^{1}H, ^{13}C} HSQC.
Figure S4	NMR analysis of **3** in DMSO-d_6, a) ^{1}H, b) ^{13}C, c) {^{1}H, ^{1}H} COS90 and d) {^{1}H, ^{13}C} HSQC.
Figure S5	NMR analysis of **4** in DMSO-d_6, a) ^{1}H, b) ^{13}C, c) {^{1}H, ^{1}H} COS90 and d) {^{1}H, ^{13}C} HSQC.
Figure S6	NMR analysis of **5** in DMSO-d_6, a) ^{1}H, b) ^{13}C, c) {^{1}H, ^{1}H} COS90 and d) {^{1}H, ^{13}C} HSQC.
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	Evaluation of antimicrobial properties
	Cytotoxicity Assay
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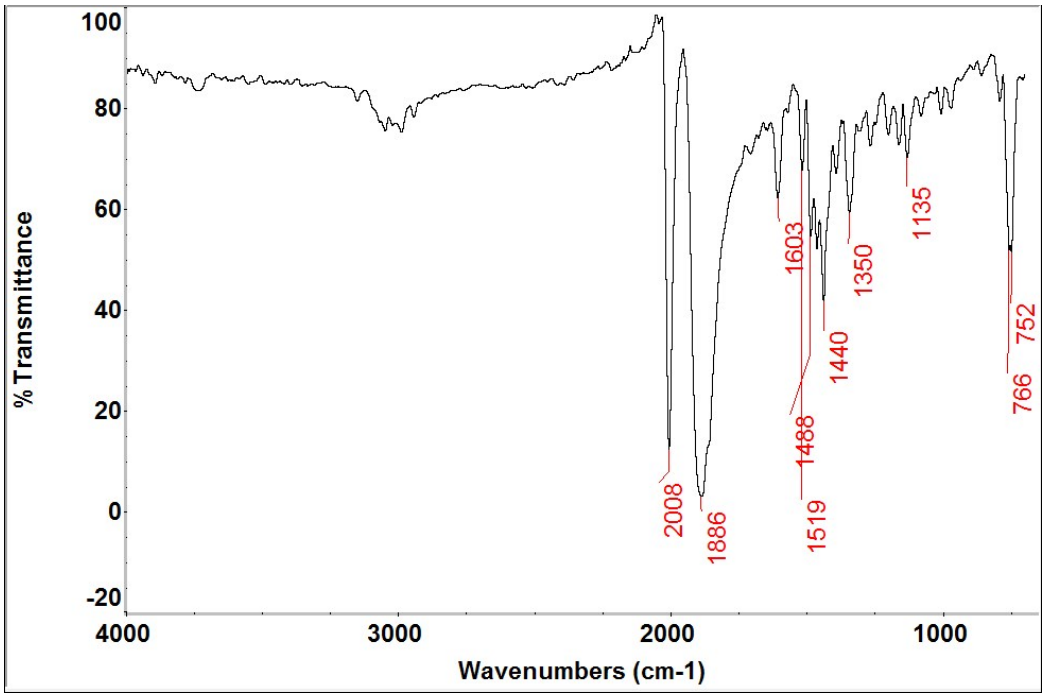
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80
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3000
2000
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Wavenumbers (cm-1)
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1603
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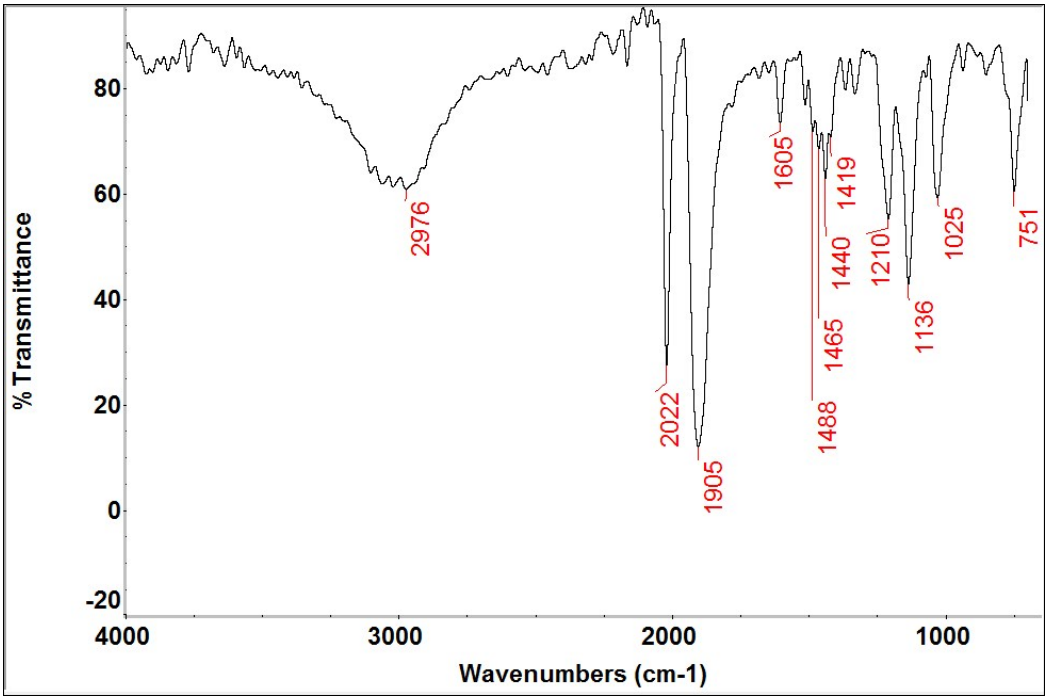
1488
1440
1350
1135
766
752

a) **1**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Wavenumbers (cm-1)
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1440
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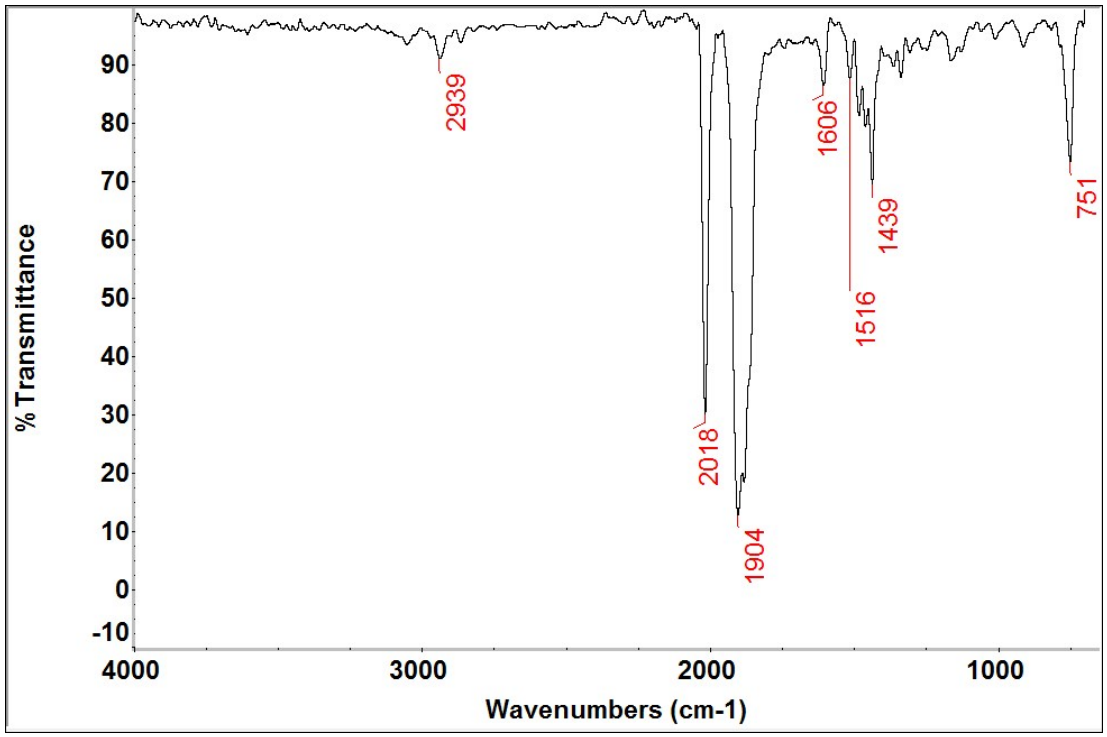
1025
751

b) **2**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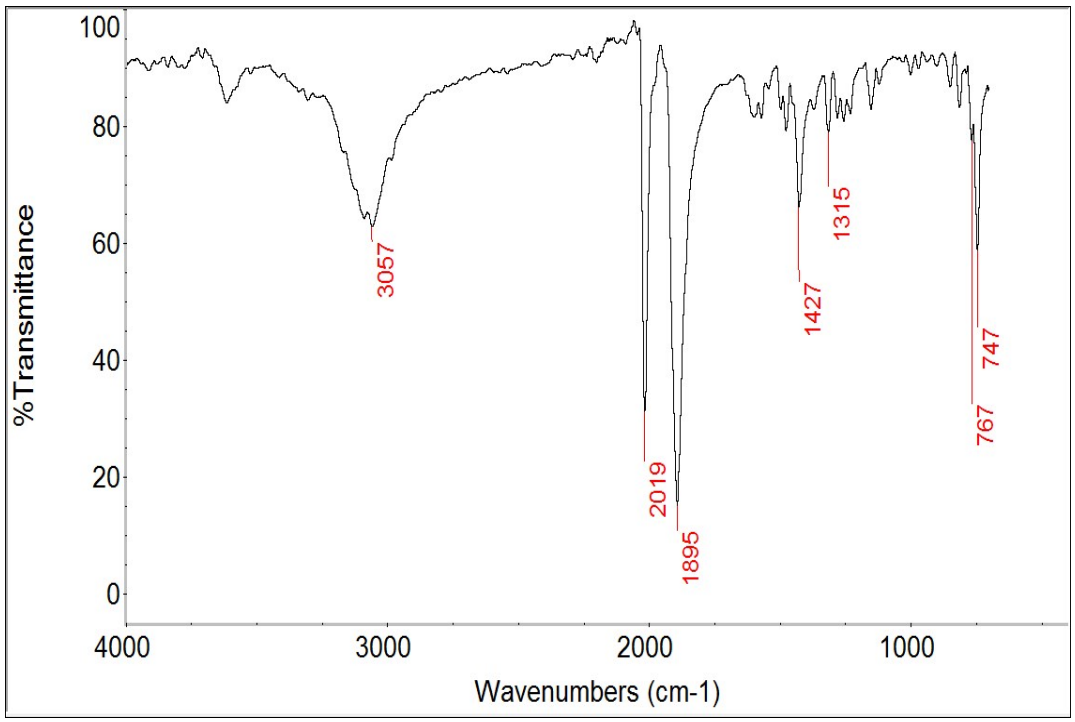
2018
1904
1606
1516
1439
751

c) **3**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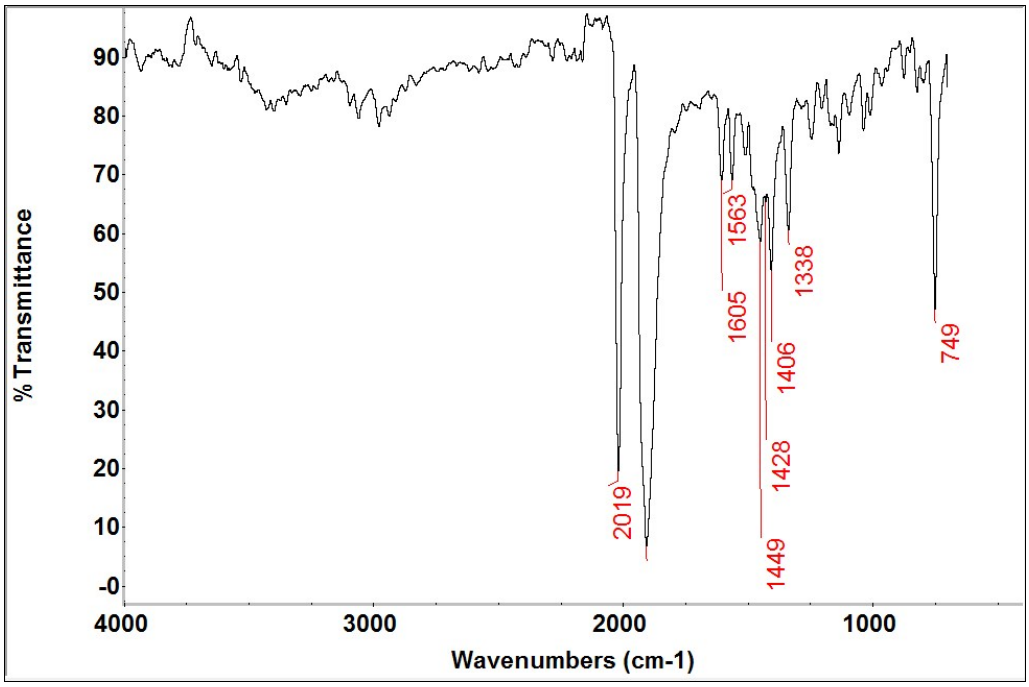
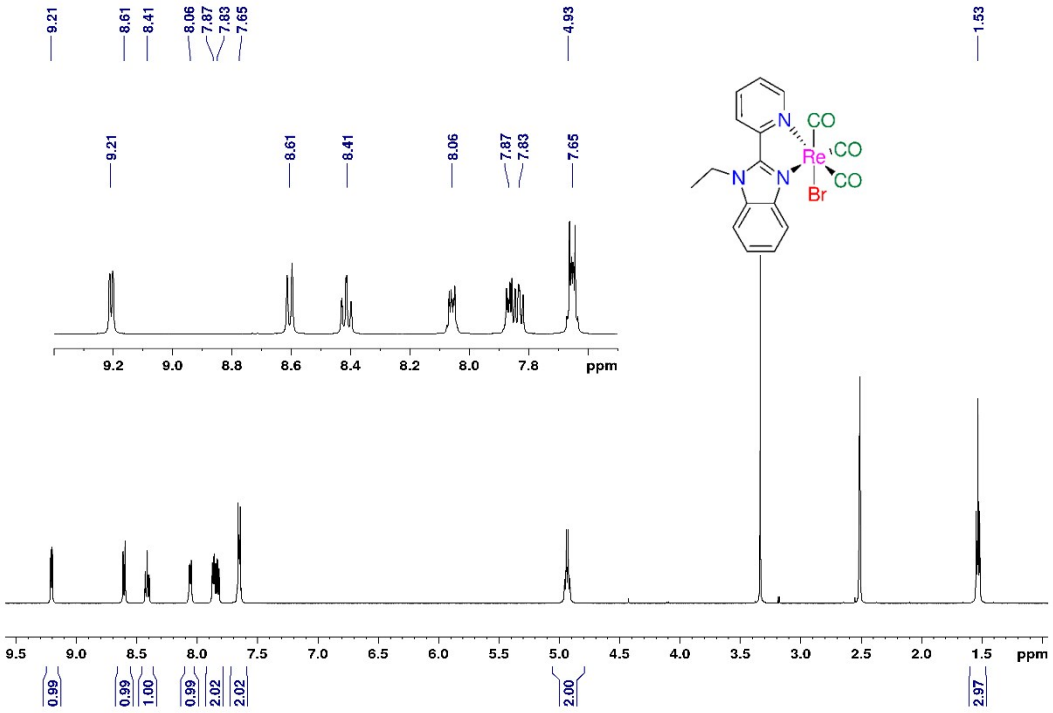
1315
767
747

c) **4**



d) **5**

Figure S1 AT IR spectra of the studied Re(I) complexes.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7.65
4.93
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CO
CO
CO
Re
Br
N
N
N
ppm
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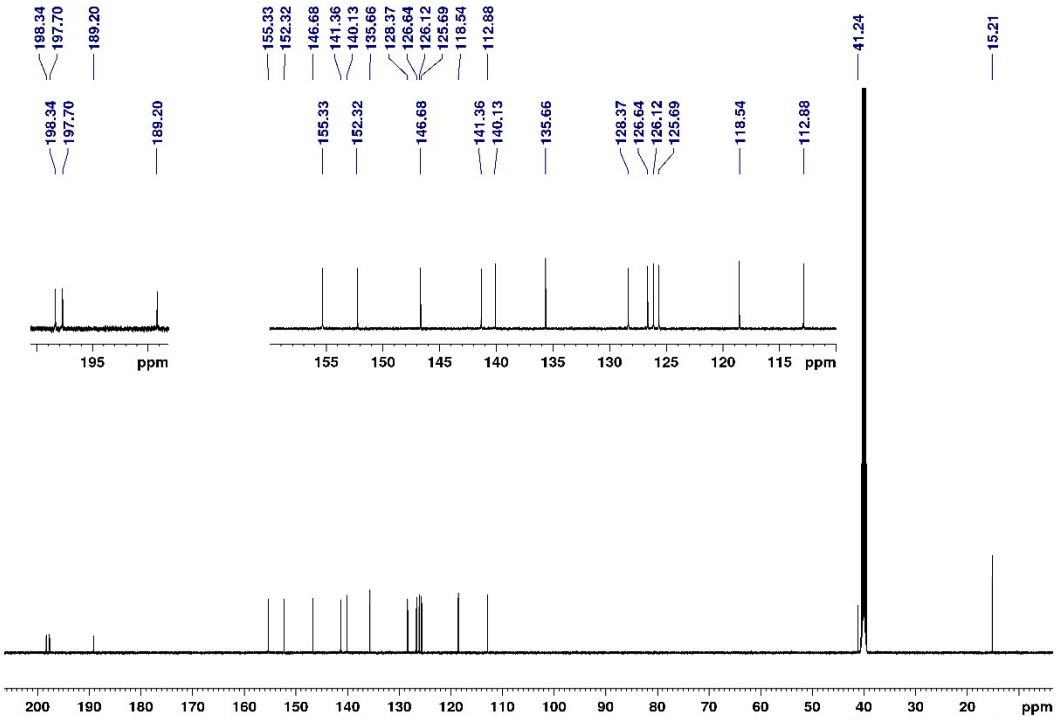
0.99
1.00
0.99
2.02
2.02
2.00
2.97

a)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189.20
155.33
152.32
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141.36
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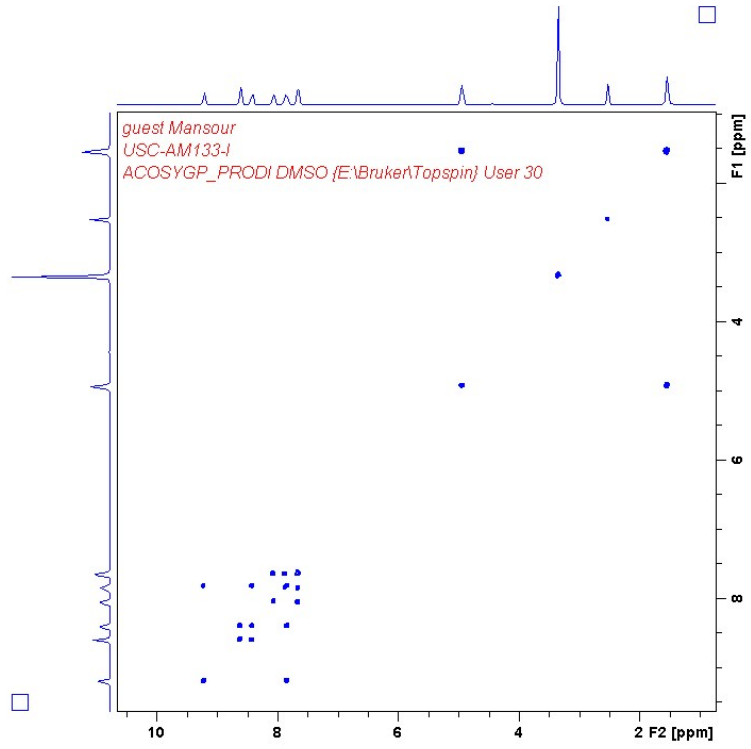
126.12
125.69
118.54
112.88
41.24
15.21
ppm

b)



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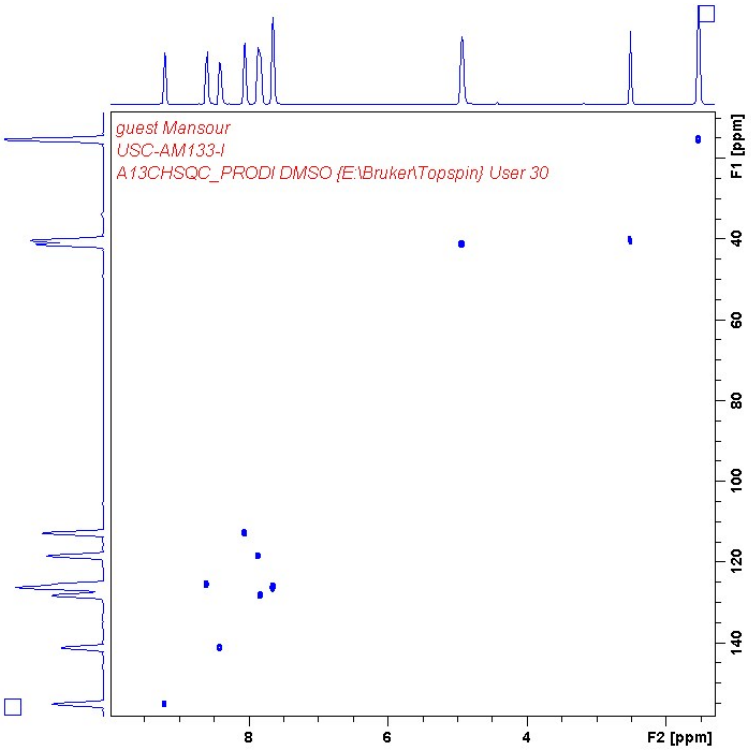
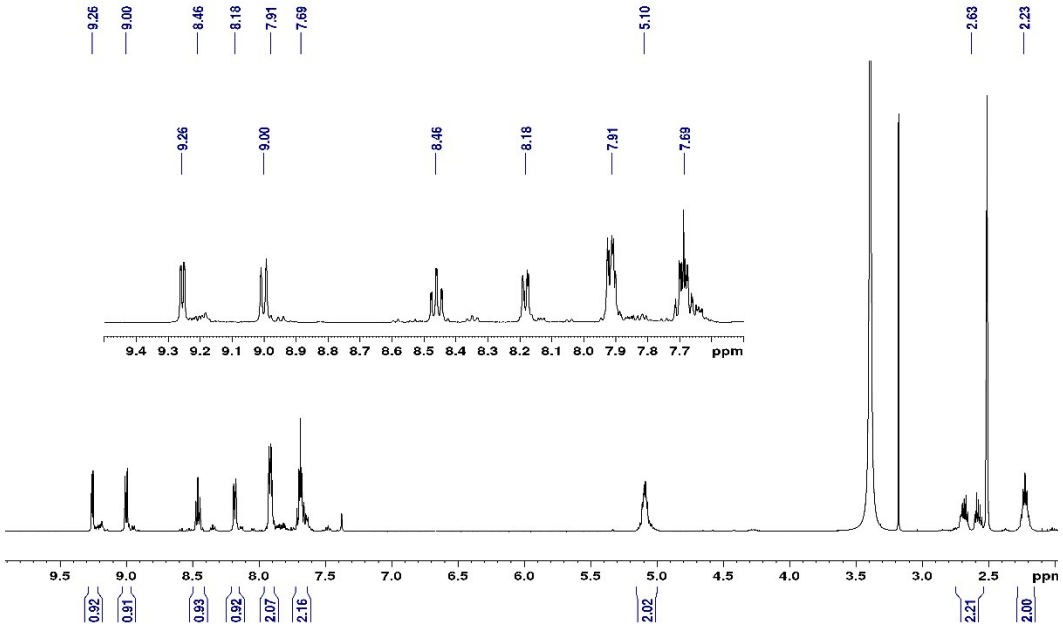


Figure S2 NMR analysis of **1** in DMSO-d_6, a) ^{1}H, b) ^{13}C, c) {^{1}H, ^{1}H} COS90 and d) {^{1}H, ^{13}C} HSQC.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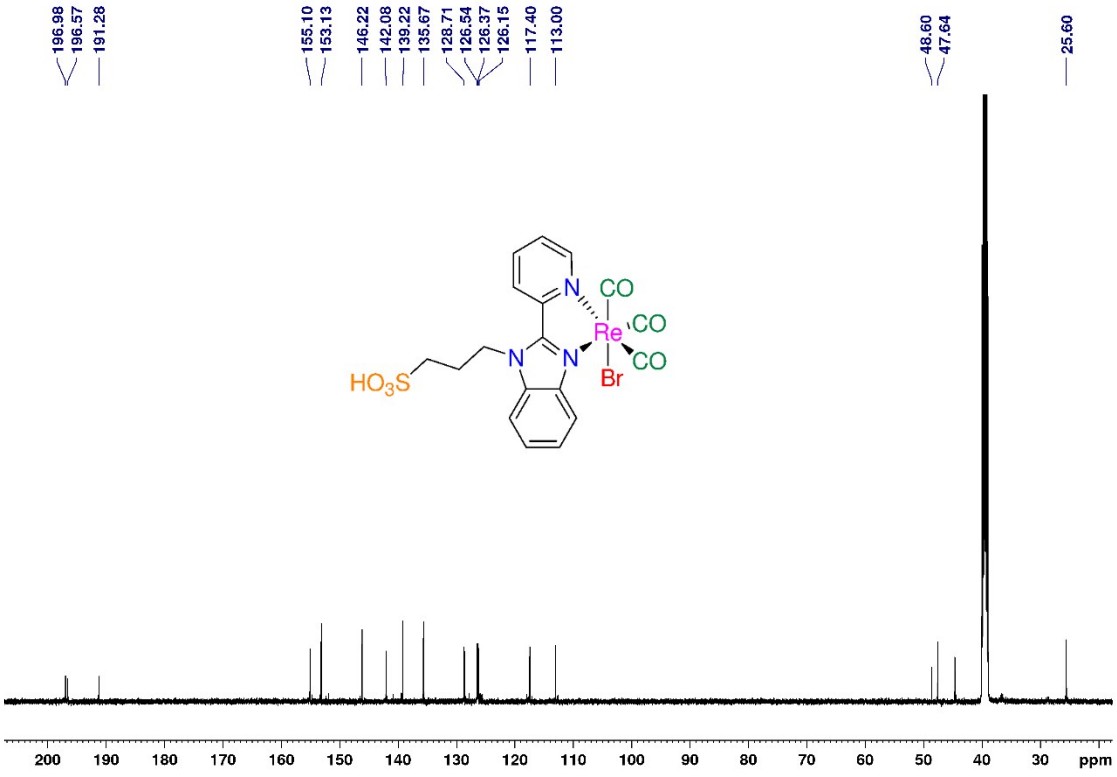
8.18
7.91
7.69
5.10
2.63
2.23
ppm
0.92
0.91
0.93
0.92
2.07
2.16
2.02
2.21
2.00

a)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196.57
191.28
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153.13
146.22
142.08
139.22
135.67
128.71
126.54
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126.15
117.40
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47.64
25.60
N
CO
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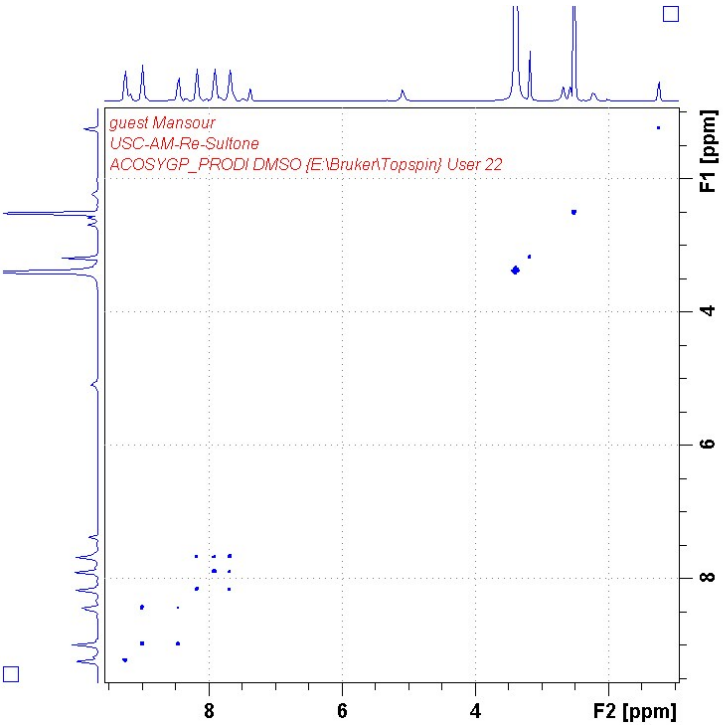
CO
CO
N
N
Br
HO3S
ppm

b)



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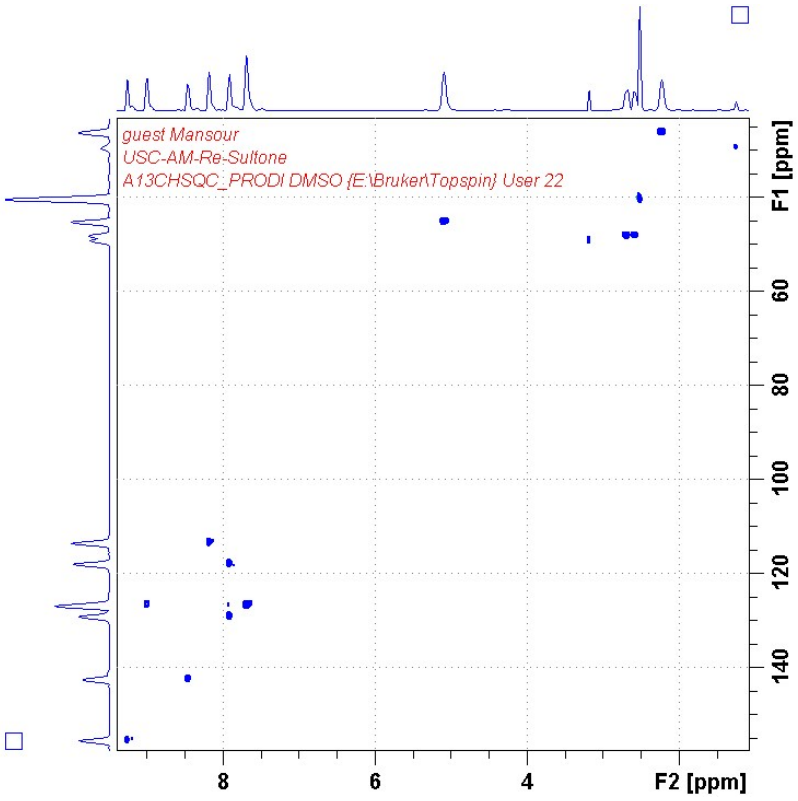
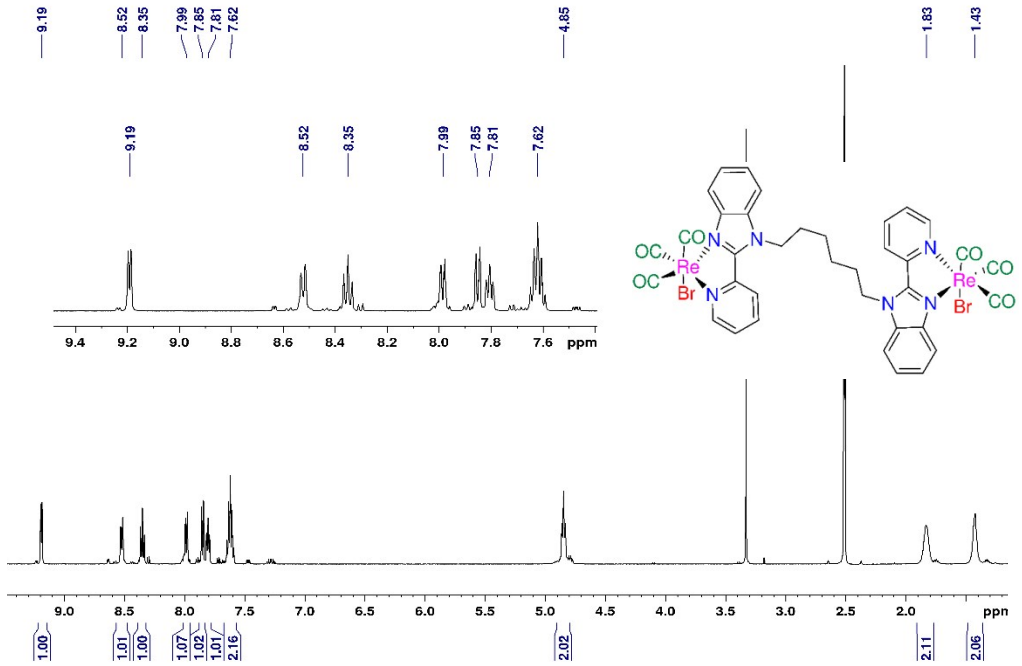


Figure S3 NMR analysis of **2** in DMSO-d_6, a) ^{1}H, b) ^{13}C, c) {^{1}H, ^{1}H} COS90 and d) {^{1}H, ^{13}C} HSQC.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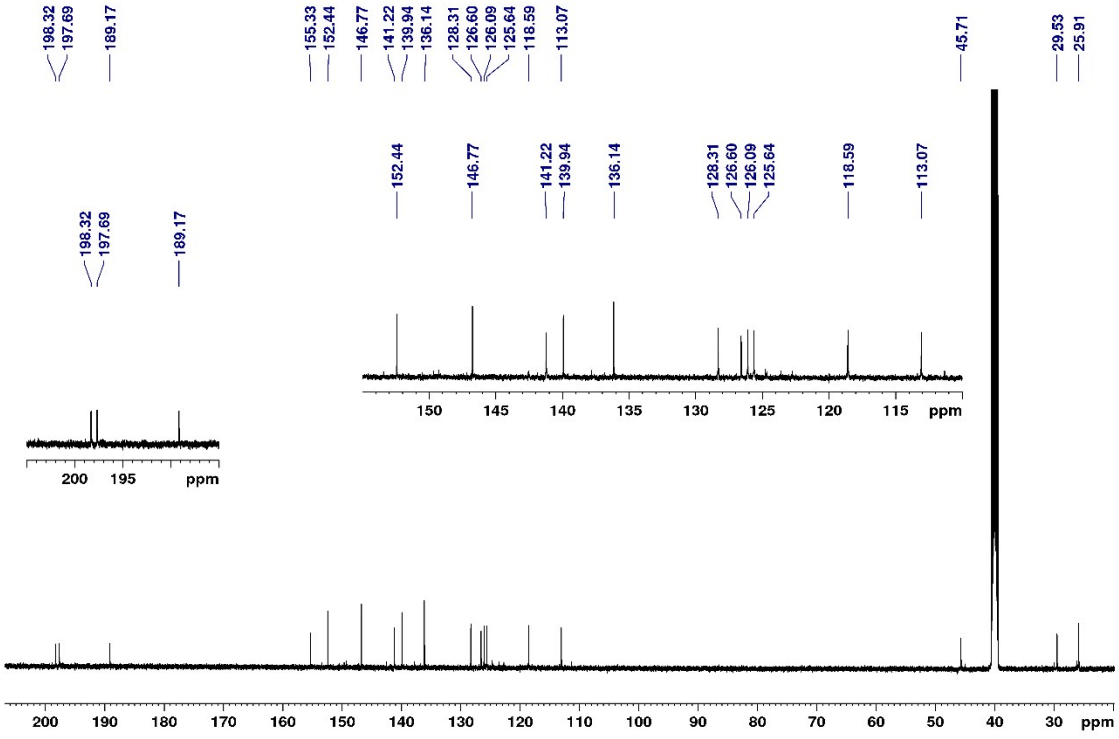
OC
CO
Re
Br
N
CO
ppm

a)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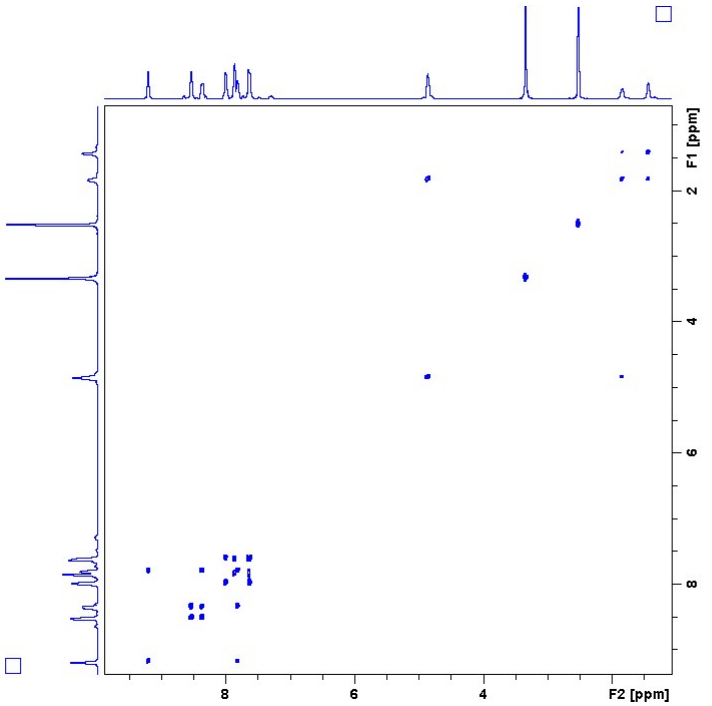
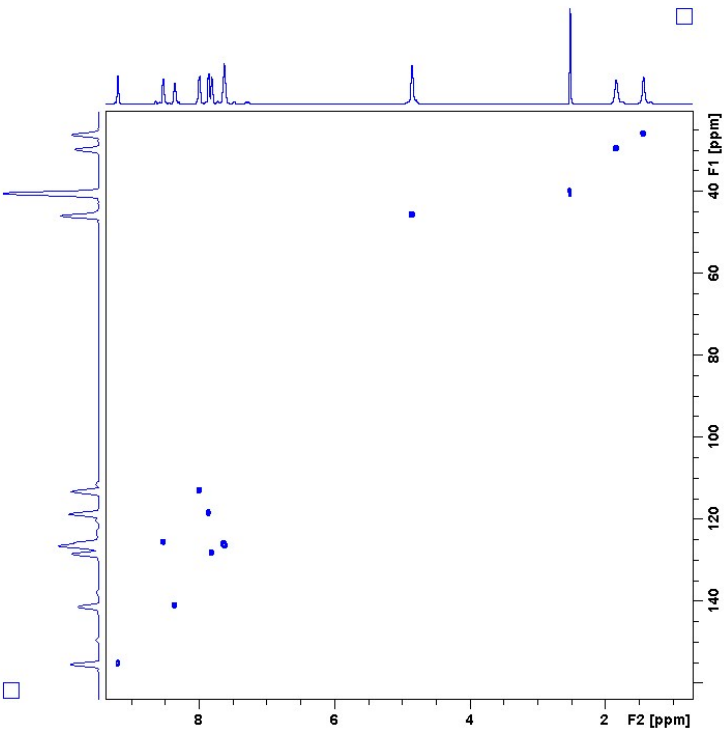
125.64
118.59
113.07
45.71
29.53
25.91
ppm

b)

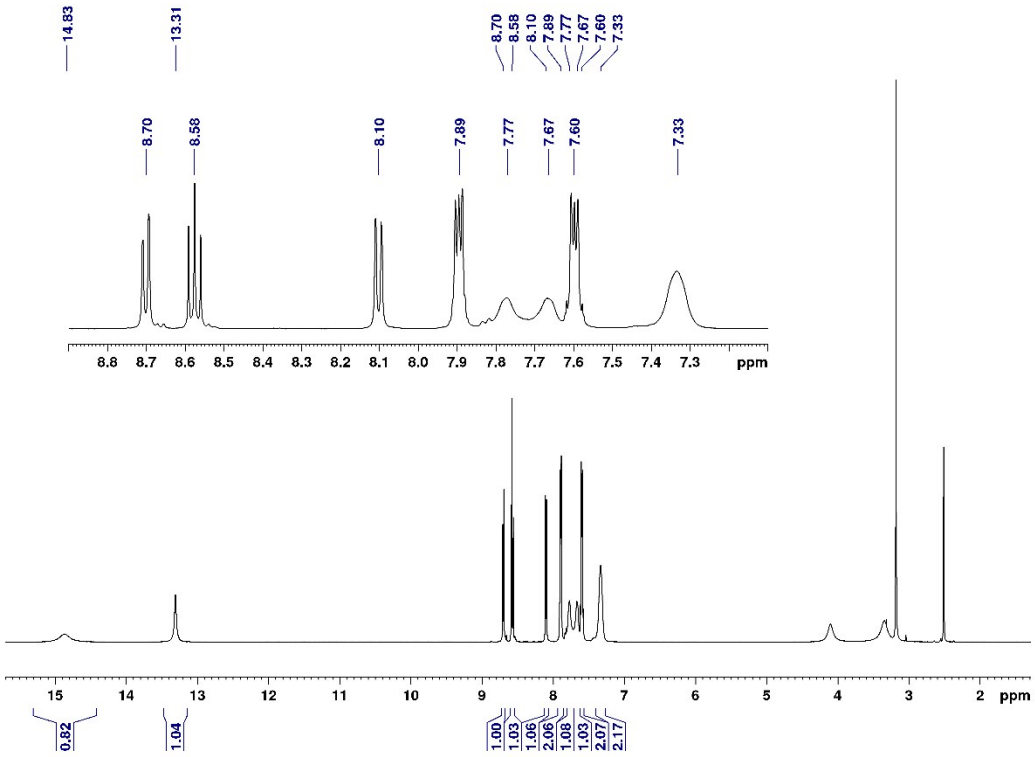


c)



d)

Figure S4 NMR analysis of **3** in DMSO-d_6, a) ^{1}H, b) ^{13}C, c) {^{1}H, ^{1}H} COS90 and d) {^{1}H, ^{13}C} HSQC.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8.70
8.58
8.10
7.89
7.77
7.67
7.60
7.33
ppm
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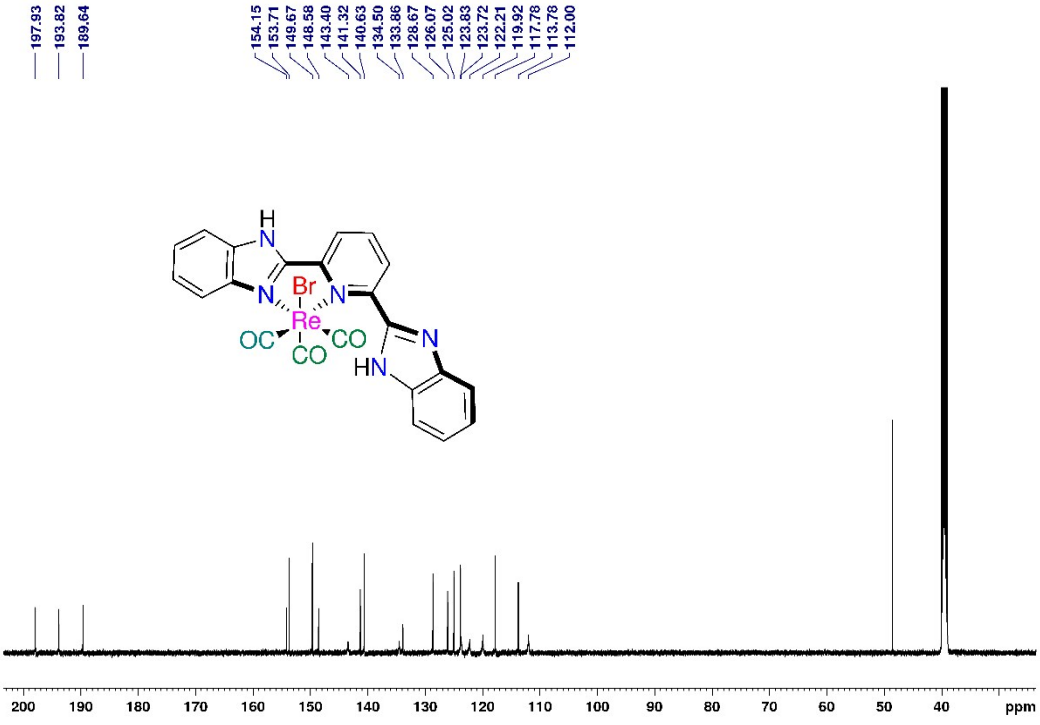
1.00
1.03
1.06
2.06
1.08
1.03
2.07
2.17

a)


197.93
193.82
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153.71
149.67
148.58
143.40
141.32
140.63
134.50
133.86
128.67
126.07
125.02
123.83
123.72
122.21
119.92
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112.00
H
N
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Br
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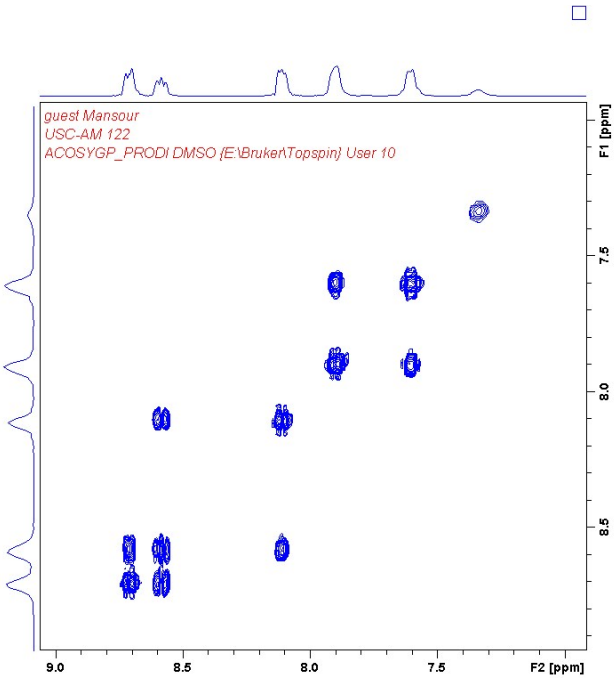
Re
OC
CO
CO
N
HN
ppm

b)



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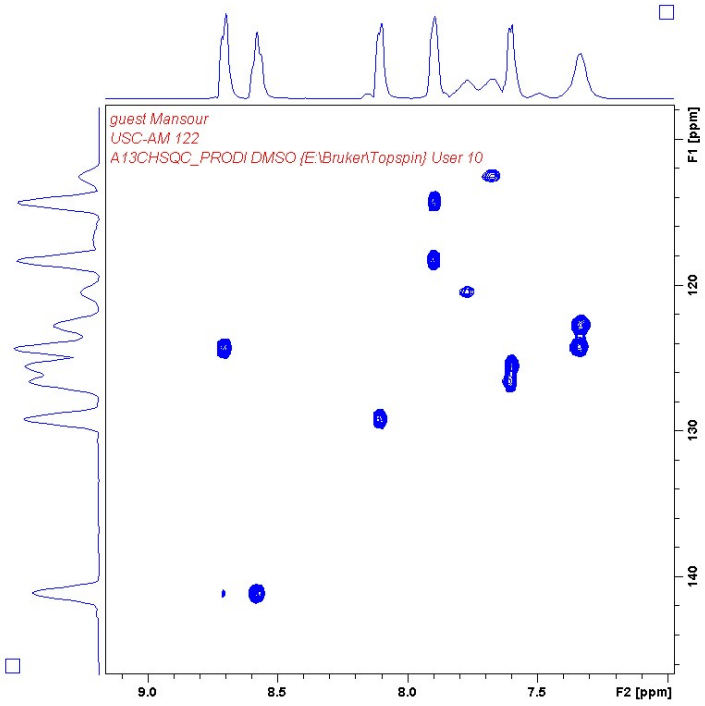
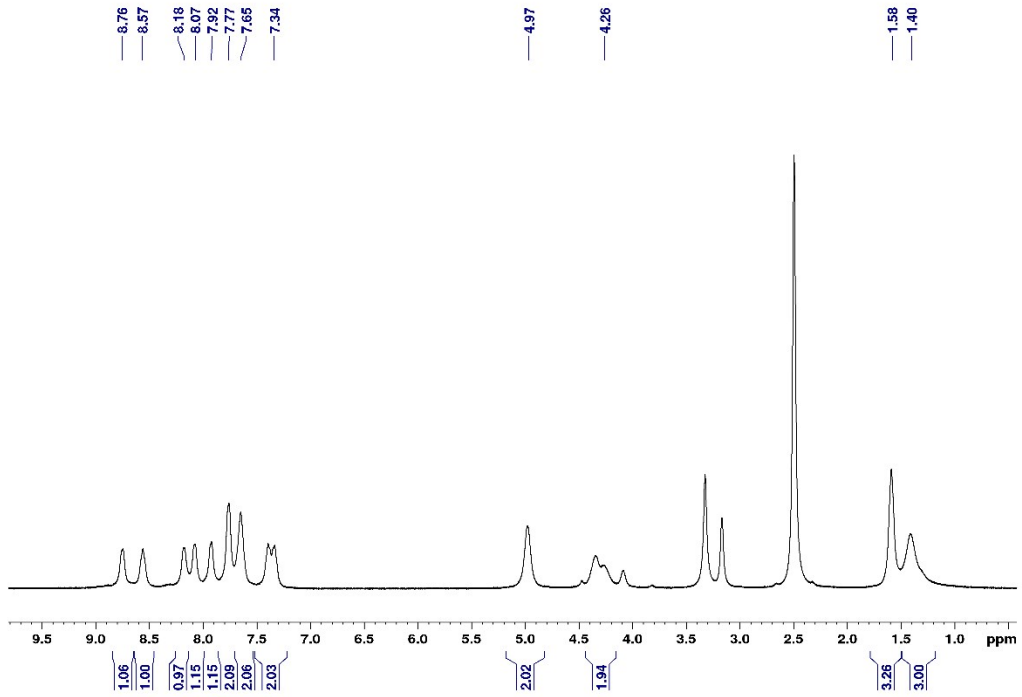


d)

Figure S5 NMR analysis of **4** in DMSO-d_6, a) ^{1}H, b) ^{13}C, c) {^{1}H, ^{1}H} COS90 and d) {^{1}H, ^{13}C} HSQC.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8.07
7.92
7.77
7.65
7.34
4.97
4.26
1.58
1.40
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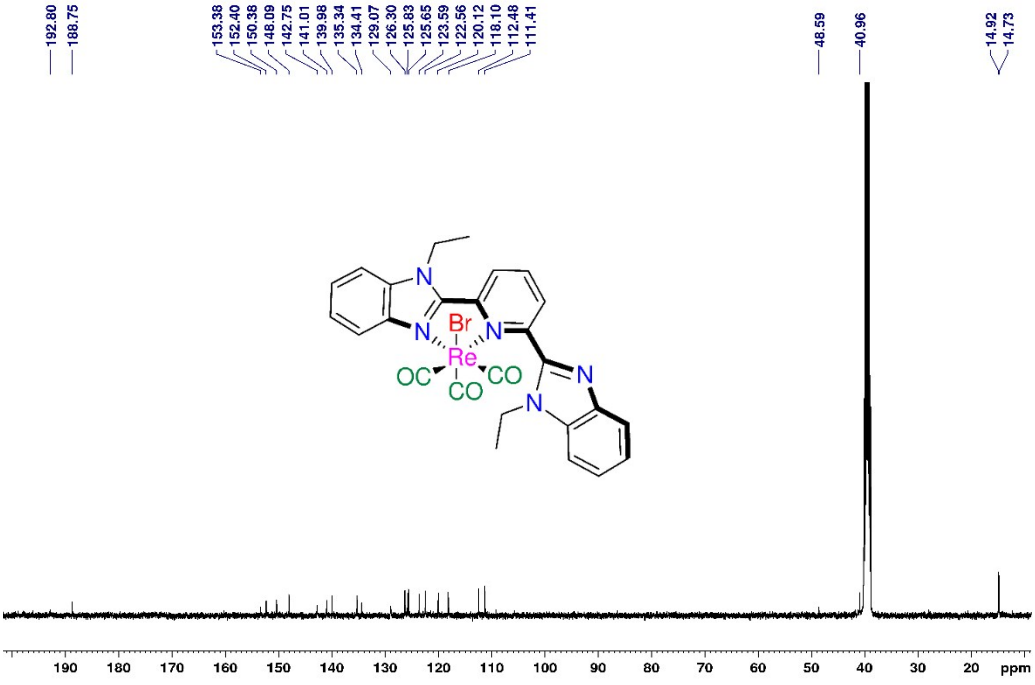
1.06
1.00
0.97
1.15
1.15
2.09
2.06
2.03
2.02
1.94
3.26
3.00

a)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134.41
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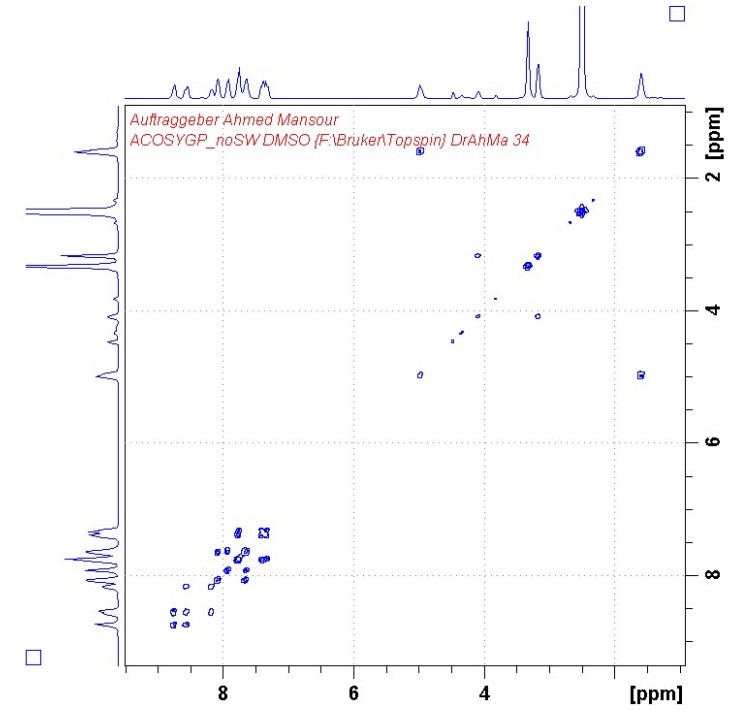
b)



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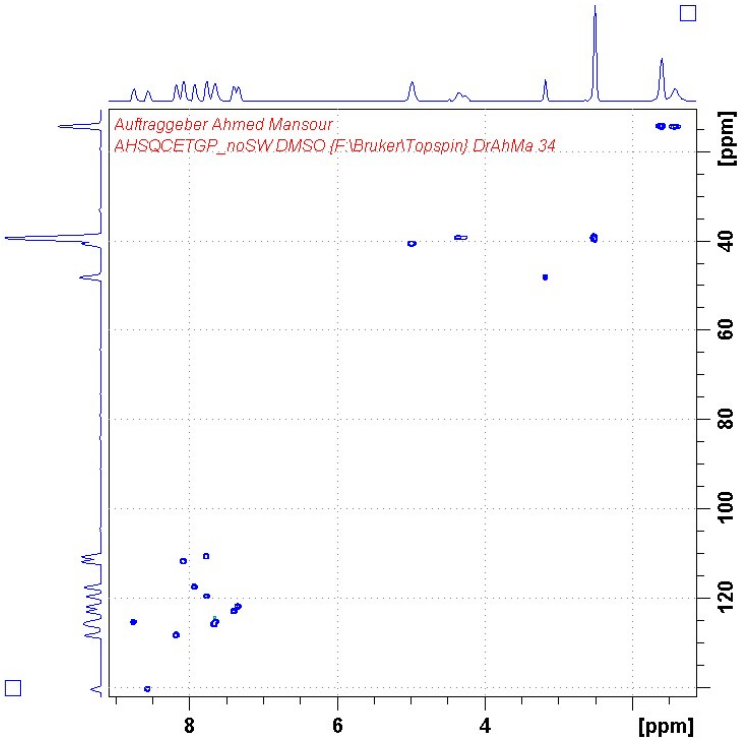


d)

Figure S6 NMR analysis of **5** in DMSO-d_6, a) ^{1}H, b) ^{13}C, c) {^{1}H, ^{1}H} COS90 and d) {^{1}H, ^{13}C} HSQC.

Table S1: ^{1}H and ^{13}C chemical shifts for complexes **1**—**5**.

1		**2**		**3**		**4**		**5**	
Atom	δ	Atom	δ	Atom	δ	Atom	δ	Atom	δ
bim-H4	8.05	bim-H4	7.92	bim-H4	7.98	bim-H4	7.89	bim-H4	8.07
bim-H5	7.65	bim-H5	7.68	bim-H5	7.62	bim-H5	7.60	bim-H5	7.65
bim-H6	7.65	bim-H6	7.68	bim-H6	7.62	bim-H6	7.60	bim-H6	7.65
bim-H7	7.86	bim-H7	7.92	bim-H7	7.85	bim-H7	7.89	bim-H7	7.92
py-H3	8.61	py-H3	9.00	py-H3	8.52	py-H3	8.70	py-H3	8.75
py-H4	8.42	py-H4	8.46	py-H4	8.35	py-H4	8.58	py-H4	8.56
py-H5	7.83	py-H5	8.18	py-H5	7.81	py-H5	8.10	py-H5	8.18
py-H6	9.20	py-H6	9.25	py-H6	9.19	bim-H4`	7.77	bim-H4`	7.76
NCH_2	4.93	NCH_2	5.08	NCH_2	4.85	bim-H5`	7.33	bim-H5`	7.36
CH_3	1.53	CH_2SO_3H	2.62	NCH_2CH_2	1.82	bim-H6`	7.33	bim-H6`	7.36
		CH_2CH_2CH_2	2.22	NCH_2CH_2CH_2	1.42	bim-H7`	7.67	bim-H7`	7.76
						NH	14.83	NCH_2	4.97
						NH	13.31	CH_3	1.59
								NCH_2`	4.30
								CH_3`	1.41
C≡O	198.3	C≡O	197.5	C≡O	198.3	C≡O	197.9	C≡O	192.8
C≡O	197.7	C≡O	197.0	C≡O	197.7	C≡O	193.8	C≡O	188.8
C≡O	189.2	C≡O	191.8	C≡O	189.1	C≡O	189.6	C≡O	
bim-C2	146.6	bim-C2	146.6	bim-C2	146.7	bim-C2	149.7	bim-C2	150.5
bim-C3a	140.1	bim-C3a	139.7	bim-C3a	139.9	bim-C3a	143.3	bim-C3a	142.7
bim-C4	112.8	bim-C4	129.2	bim-C4	113.0	bim-C4	113.8	bim-C4	112.5
bim-C5	126.6	bim-C5	126.9	bim-C5	126.6	bim-C5	125.0	bim-C5	125.8
bim-C6	126.1	bim-C6	126.8	bim-C6	126.1	bim-C6	126.1	bim-C6	125.6
bim-C7	118.5	bim-C7	117.9	bim-C7	118.6	bim-C7	117.8	bim-C7	118.2
bim-C7a	135.6	bim-C7a	136.1	bim-C7a	136.1	bim-C7a	141.3	bim-C7a	139.9
py-C2	152.3	py-C2	153.6	py-C2	152.4	py-C2	154.1	py-C2	153.4
py-C3	125.6	py-C3	126.6	py-C3	125.6	py-C3	123.8	py-C3	126.3
py-C4	141.3	py-C4	142.5	py-C4	141.2	py-C4	140.6	py-C4	141.0
py-C5	128.3	py-C5	113.5	py-C5	128.3	py-C5	128.7	py-C5	129.0
py-C6	155.3	py-C6	155.6	py-C6	155.3	py-C6	153.7	py-C6	152.4
*N*CH$_2$	41.2	NCH_2	45.1	NCH_2	45.7	bim-C2`	148.6	bim-C2`	148.1
*C*H$_3$	15.2	CH_2SO_3H	48.1	NCH_2CH_2	29.5	bim-C3a`	134.5	bim-C3a`	135.3
		CH_2CH_2CH_2	26.1	NCH_2CH_2CH_2	25.9	bim-C4`	112.0	bim-C4`	111.3
						bim-C5`	122.2	bim-C5`	123.6
						bim-C6`	123.7	bim-C6`	122.5
						bim-C7`	119.9	bim-C7`	120.1
						bim-C7a`	133.8	bim-C7a`	134.5
								NCH_2	48.6
								CH_3	14.9
								NCH_2`	40.9
								CH_3`	14.7

bim: benzimidazole; py = pyridine

Table S2 Atomic coordinates of the optimized structure of **1** in the singlet state ground-state.					
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.969517	-1.264177	-0.182324
2	6	0	3.181643	-0.561065	0.067709
3	6	0	4.417685	-1.222691	0.184008
4	6	0	4.403939	-2.617258	0.0445
5	6	0	3.196439	-3.327902	-0.202726
6	6	0	1.968428	-2.666667	-0.317425
7	6	0	1.476061	0.891965	-0.044035
8	1	0	5.346331	-0.691854	0.370693
9	1	0	5.335946	-3.170068	0.127624
10	1	0	3.229646	-4.409348	-0.299424
11	1	0	1.052661	-3.216573	-0.495806
12	6	0	0.589486	2.05224	-0.077112
13	6	0	-1.678721	2.680855	-0.271155
14	6	0	-0.006893	4.409002	-0.044532
15	6	0	-1.356849	4.040813	-0.176549
16	1	0	-2.706232	2.358223	-0.378207
17	1	0	0.280022	5.454313	0.019778
18	1	0	-2.148135	4.781671	-0.210121
19	7	0	0.931085	-0.328711	-0.240334
20	7	0	2.845976	0.799764	0.163683
21	6	0	3.829016	1.857047	0.470021
22	6	0	4.439722	2.499297	-0.791886
23	1	0	4.939146	1.743658	-1.408654
24	1	0	3.677372	2.986351	-1.411074
25	1	0	3.357788	2.603271	1.115707
26	1	0	4.61744	1.392216	1.070843
27	7	0	-0.737847	1.701519	-0.230066
28	1	0	2.012462	3.68464	0.087837
29	6	0	0.971961	3.406313	0.000983
30	75	0	-1.217658	-0.431329	-0.331118
31	6	0	-1.27323	-0.450391	-2.238449
32	6	0	-3.12809	-0.227275	-0.213783
33	6	0	-1.426228	-2.341151	-0.250756
34	35	0	-1.041292	-0.296223	2.376176
35	8	0	-1.306947	-0.453311	-3.430789
36	8	0	-4.299483	-0.051897	-0.130363
37	8	0	-1.534318	-3.521517	-0.189994
38	1	0	5.18331	3.253068	-0.504258
Rotational constants (GHz)			0.2090366	0.1558915	0.1209087
E (a.u.)			-1137.87551035		

Table S3 Atomic coordinates of the optimized structure of **2** in the singlet state ground-state.					
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.323840	2.313217	-0.140978
2	6	0	-1.048812	2.526734	0.159606
3	6	0	-1.59296	3.817056	0.288337
4	6	0	-0.715765	4.895558	0.103205
5	6	0	0.658056	4.690434	-0.19923
6	6	0	1.196264	3.403553	-0.322015
7	6	0	-0.631046	0.319088	0.056195
8	1	0	-2.638724	3.988863	0.526525
9	1	0	-1.092224	5.910828	0.19606
10	1	0	1.305444	5.552603	-0.330967
11	1	0	2.246707	3.256844	-0.540159
12	6	0	-0.660868	-1.143643	0.04332
13	6	0	0.71992	-3.043129	-0.205684
14	6	0	-1.643802	-3.359905	0.17184
15	6	0	-0.367541	-3.909733	-0.032596
16	1	0	1.718619	-3.427566	-0.366917
17	1	0	-2.513362	-3.995557	0.306712
18	1	0	-0.206412	-4.982011	-0.059076
19	7	0	0.545147	0.931767	-0.193833
20	7	0	-1.636303	1.254732	0.288649
21	6	0	-3.056345	1.071073	0.616263
22	6	0	-3.939427	1.095571	-0.657349
23	6	0	-5.441031	1.117663	-0.370137
24	1	0	-5.729871	1.722367	0.495306
25	1	0	-6.047037	1.371857	-1.242183
26	1	0	-3.718321	2.011571	-1.222714
27	1	0	-3.689062	0.257635	-1.318692
28	1	0	-3.19943	0.149797	1.180525
29	1	0	-3.345113	1.89418	1.281205
30	7	0	0.589249	-1.691911	-0.174164
31	1	0	-2.785137	-1.561477	0.35285
32	6	0	-1.793111	-1.964871	0.204646
33	8	0	-6.306703	-1.124047	-1.648913
34	8	0	-4.910947	-1.537794	0.7183
35	8	0	-7.530419	-0.560322	0.813747
36	16	0	-6.094757	-0.629883	0.078481
37	1	0	-6.722169	-2.019626	-1.711295
38	75	0	2.286352	-0.322809	-0.366936
39	6	0	2.241203	-0.34159	-2.274066
40	6	0	3.6609	-1.669534	-0.318935
41	6	0	3.641217	1.040604	-0.353036
42	35	0	2.214704	-0.306908	2.348034
43	8	0	2.205833	-0.356275	-3.466615

44	8	0	4.473972	-2.533426	-0.275463
45	8	0	4.462059	1.898024	-0.33165
Rotational constants (GHz)			0.1738411	0.0681058	0.0580799
E (a.u.)			-1412.73808986		

Table S4 Atomic coordinates of the optimized structure of **3** in the singlet state ground-state.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	5.390337	2.933269	0.687422
2	6	0	6.578236	2.319185	0.200778
3	6	0	7.586002	3.088047	-0.413758
4	6	0	7.371133	4.466446	-0.523188
5	6	0	6.179372	5.07311	-0.037797
6	6	0	5.168967	4.317864	0.573497
7	6	0	5.311733	0.723612	1.075106
8	1	0	8.492504	2.631349	-0.791438
9	1	0	8.128009	5.08814	-0.99269
10	1	0	6.050596	6.146913	-0.144624
11	1	0	4.264846	4.795324	0.938905
12	6	0	5.006542	-0.644711	1.488028
13	6	0	3.876005	-1.077344	2.209272
14	6	0	5.86552	-2.845997	1.476937
15	6	0	3.753324	-2.426915	2.568918
16	1	0	3.099685	-0.381208	2.492313
17	6	0	4.767224	-3.327895	2.200219
18	1	0	6.661461	-3.509394	1.164351
19	1	0	2.885828	-2.766162	3.127181
20	1	0	4.715349	-4.380055	2.457881
21	6	0	3.2063	2.107177	1.671747
22	6	0	2.202884	1.750005	0.551605
23	6	0	0.733655	1.904019	0.99729
24	6	0	-0.250241	1.726166	-0.181029
25	6	0	-1.726253	1.713703	0.269761
26	6	0	-2.698315	1.713187	-0.932556
27	6	0	-4.922233	2.763426	-0.322652
28	6	0	-4.898118	0.52026	-0.251893
29	6	0	-6.204531	2.282826	0.06425
30	6	0	-4.648321	4.137533	-0.448762
31	6	0	-7.256839	3.180002	0.33314
32	6	0	-5.702448	5.020415	-0.17692
33	1	0	-3.672788	4.511419	-0.744713

34	6	0	-6.987671	4.547641	0.209143
35	1	0	-8.240209	2.826927	0.617653
36	1	0	-5.536826	6.090913	-0.265074
37	1	0	-7.778318	5.265991	0.405933
38	6	0	-5.539724	-3.049128	-0.013168
39	6	0	-3.195323	-2.883006	-0.567658
40	6	0	-4.320902	-3.679154	-0.294823
41	1	0	-6.428601	-3.627761	0.202161
42	1	0	-2.233683	-3.337367	-0.786761
43	1	0	-4.26658	-4.762271	-0.298846
44	1	0	3.012192	1.535347	2.583998
45	1	0	3.099952	3.161293	1.948017
46	1	0	2.401908	2.39765	-0.313339
47	1	0	2.380386	0.720219	0.212901
48	1	0	0.503426	1.165476	1.781895
49	1	0	0.578435	2.896519	1.448864
50	1	0	-0.089131	2.538631	-0.906549
51	1	0	-0.017291	0.789243	-0.711476
52	1	0	-1.91427	0.832275	0.899321
53	1	0	-1.936749	2.5934	0.893916
54	7	0	6.489567	0.946274	0.451499
55	7	0	4.603918	1.907866	1.242563
56	7	0	5.992631	-1.540692	1.122131
57	7	0	-4.112887	1.633191	-0.526484
58	7	0	-6.152003	0.88555	0.094696
59	6	0	-4.584389	-0.906264	-0.288192
60	1	0	-2.578403	2.63943	-1.504833
61	1	0	-2.47361	0.899172	-1.62795
62	6	0	-3.329072	-1.487422	-0.557833
63	1	0	-2.464729	-0.871511	-0.759901
64	7	0	-5.680336	-1.697645	-0.003057
65	6	0	-9.185145	0.373151	0.482356
66	6	0	-8.671801	-2.288895	0.365723
67	6	0	-7.394658	-0.736747	2.252788
68	35	0	-7.724581	-0.635987	-2.354874
69	8	0	-10.157265	1.050565	0.547556
70	8	0	-9.298016	-3.297278	0.354581
71	8	0	-7.260481	-0.767341	3.437986
72	35	0	5.715065	-0.961089	-2.087157
73	6	0	8.299219	-2.513058	-0.658838
74	6	0	8.830495	0.056795	-1.362714
75	6	0	8.863621	-0.653438	1.293558
76	8	0	8.682875	-3.59561	-0.958117
77	8	0	9.564146	0.599571	-2.120593
78	8	0	9.641203	-0.571439	2.19339
79	75	0	-7.591213	-0.695474	0.355329

80	75	0	7.610896	-0.79078	-0.139361
Rotational constants (GHz)			0.0817289	0.0090089	0.0085925
E (a.u.)			-2353.15729511		

Table S5 Atomic coordinates of the optimized structure of **4** in the singlet state ground-state.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	35	0	-0.876893	0.112240	2.641823
2	6	0	-3.555057	-0.177408	-0.621708
3	7	0	-2.217655	0.210797	-0.430235
4	8	0	0.259749	-1.602949	-2.839093
5	8	0	-1.546955	-3.521983	0.726423
6	6	0	-4.164214	-1.447171	-0.668842
7	1	0	-3.590724	-2.358053	-0.545508
8	7	0	-3.438435	2.074681	-0.700961
9	8	0	2.372816	-1.809306	1.123503
10	6	0	-6.316757	-0.305848	-1.056159
11	1	0	-7.386923	-0.388875	-1.223093
12	7	0	3.690423	1.321254	0.578268
13	7	0	0.177287	1.4274	-0.274636
14	6	0	-5.547627	-1.492487	-0.888195
15	1	0	-6.047927	-2.455608	-0.932147
16	7	0	2.940119	0.356268	-1.331385
17	6	0	-5.724311	0.964698	-1.012236
18	1	0	-6.309682	1.869107	-1.141803
19	6	0	-2.186372	1.55607	-0.488345
20	6	0	-4.336362	1.005371	-0.793533
21	6	0	-0.81731	3.659385	-0.335159
22	1	0	-1.704136	4.279426	-0.397944
23	6	0	-0.919783	2.259823	-0.362231
24	6	0	0.449839	4.244285	-0.212794
25	1	0	0.560093	5.322291	-0.173204
26	6	0	1.574746	3.408055	-0.174149
27	1	0	2.573436	3.827223	-0.13594
28	6	0	1.416297	2.007	-0.231774
29	6	0	2.639064	1.182102	-0.321413
30	6	0	4.251894	-0.083177	-1.076183
31	6	0	5.071078	-0.966131	-1.81091
32	1	0	4.712116	-1.424179	-2.727859
33	6	0	6.356082	-1.229277	-1.314298

34	1	0	7.01287	-1.905166	-1.855336
35	6	0	6.82344	-0.629035	-0.109102
36	1	0	7.826117	-0.860068	0.240998
37	6	0	6.022426	0.25223	0.634389
38	1	0	6.383357	0.707057	1.551644
39	6	0	4.736693	0.514983	0.128358
40	6	0	0.02721	-1.261808	-1.719833
41	6	0	-1.08351	-2.455668	0.463743
42	6	0	1.350689	-1.383414	0.690561
43	1	0	-3.676804	3.05505	-0.790244
44	1	0	3.672382	1.862783	1.433976
45	75	0	-0.35319	-0.73938	0.065833
Rotational constants (GHz)			0.2055870	0.0787227	0.0724626
E (a.u.)			-1437.90845985		

Table S6 Atomic coordinates of the optimized structure of **5** in the singlet state ground-state.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	35	0	-0.545348	0.282454	2.516149
2	6	0	-3.510859	-0.763028	-0.372541
3	7	0	-2.215965	-0.231014	-0.335679
4	8	0	0.074145	-2.299301	-2.675601
5	8	0	-1.243133	-3.671814	1.349922
6	6	0	-3.990553	-2.069843	-0.154825
7	1	0	-3.322987	-2.883173	0.099699
8	7	0	-3.630321	1.448947	-0.86478
9	8	0	2.597177	-1.850112	1.004992
10	6	0	-6.259297	-1.221963	-0.601354
11	1	0	-7.323306	-1.429031	-0.679995
12	7	0	3.509304	0.995396	0.282991
13	7	0	0.066817	1.10827	-0.563202
14	6	0	-5.368866	-2.281926	-0.274802
15	1	0	-5.769556	-3.278245	-0.111112
16	7	0	2.92705	0.302503	-1.81471
17	6	0	-5.794949	0.082432	-0.81885
18	1	0	-6.48481	0.885209	-1.060994
19	6	0	-2.310927	1.083807	-0.619201
20	6	0	-4.408771	0.291383	-0.699761
21	6	0	-1.030106	3.274829	-0.768824
22	1	0	-1.936132	3.861977	-0.785336
23	6	0	-1.08314	1.872778	-0.663854
24	6	0	0.211862	3.918541	-0.811615
25	1	0	0.269836	5.000232	-0.883651

26	6	0	1.373714	3.138902	-0.77285
27	1	0	2.356766	3.58874	-0.853105
28	6	0	1.275511	1.737944	-0.657312
29	6	0	2.534355	0.9573	-0.71991
30	6	0	4.230251	-0.139485	-1.528895
31	6	0	5.119907	-0.895065	-2.317633
32	1	0	4.829967	-1.220311	-3.312109
33	6	0	6.368791	-1.215079	-1.768062
34	1	0	7.078276	-1.799855	-2.348029
35	6	0	6.727319	-0.79818	-0.45508
36	1	0	7.702214	-1.074947	-0.060767
37	6	0	5.852744	-0.046295	0.343191
38	1	0	6.133283	0.254588	1.348539
39	6	0	4.605665	0.282291	-0.217895
40	6	0	3.366756	1.487899	1.667699
41	1	0	3.727819	0.698203	2.337533
42	1	0	2.299675	1.608424	1.881447
43	6	0	4.130359	2.801016	1.924192
44	1	0	5.197358	2.69613	1.695475
45	1	0	4.032007	3.084164	2.979589
46	1	0	3.73025	3.620214	1.314588
47	6	0	-4.20458	2.753736	-1.246954
48	1	0	-5.086659	2.544645	-1.8616
49	1	0	-3.499126	3.277763	-1.897579
50	6	0	-4.604108	3.613868	-0.030787
51	1	0	-3.742381	3.844331	0.605975
52	1	0	-5.341545	3.091003	0.588103
53	1	0	-5.04778	4.558147	-0.370325
54	6	0	-0.049025	-1.795897	-1.605249
55	6	0	-0.85369	-2.654657	0.873162
56	6	0	1.523214	-1.50622	0.638251
57	75	0	-0.264656	-1.000901	0.118669
Rotational constants (GHz)			0.1614926	0.0682052	0.0608587
E (a.u.)			-1595.08432982		

Table S7 Selected bond lengths obtained from the local minimum structures of **1**–**5** that optimized at B3LYP/LANL2DZ level of theory.

1		**2**		**3**		**4**		**5**	
Re–N19	2.15311	Re–N19	2.15307	Re–N54	2.15031	Re–N3	2.15062	Re–N3	2.14634
Re–N27	2.18849	Re–N30	2.18901	Re–N56	2.18461	Re–N13	2.25661	Re–N13	2.24130
Re–Br	2.71639	Re–Br	2.71596	Re–Br	2.72343	Re–Br	2.76320	Re–Br	2.73381
Re–CO35	1.90824	Re–CO43	1.90776	Re–CO76	1.92611	Re–CO4	1.89901	Re–CO4	1.91060
Re–CO36	1.92488	Re–CO44	1.92493	Re–CO77	1.92416	Re–CO5	1.90718	Re–CO5	1.91079
Re–CO37	1.92286	Re–CO45	1.92217	Re–CO78	1.90826	Re–CO9	1.92568	Re–CO9	1.92919
				Re–N58	2.15381				
				Re–N64	2.18729				
				Re–Br	2.71413				
				Re–CO69	1.92320				
				Re–CO70	1.92530				
				Re–CO71	1.90806				

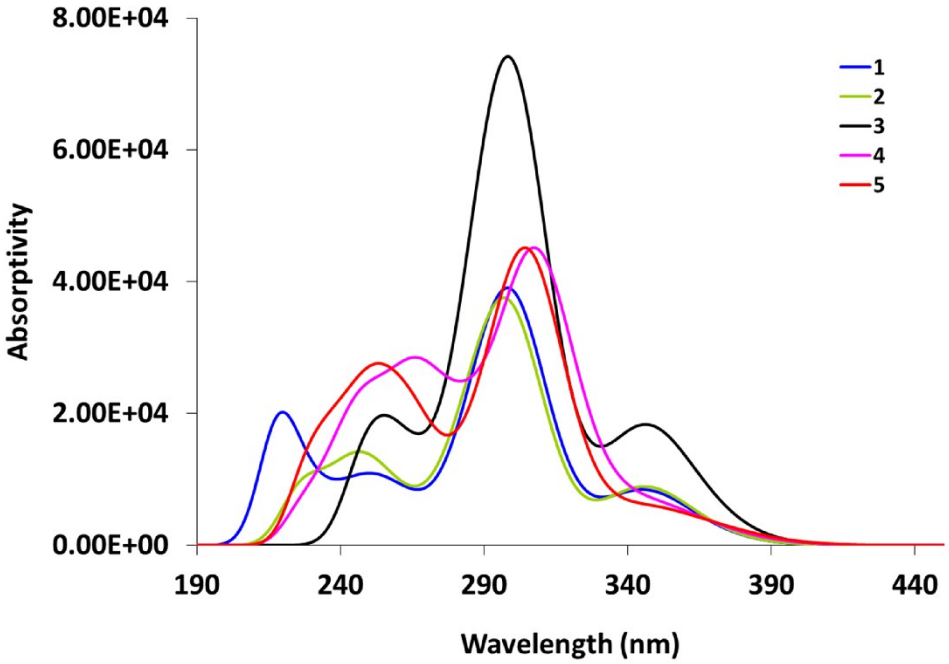
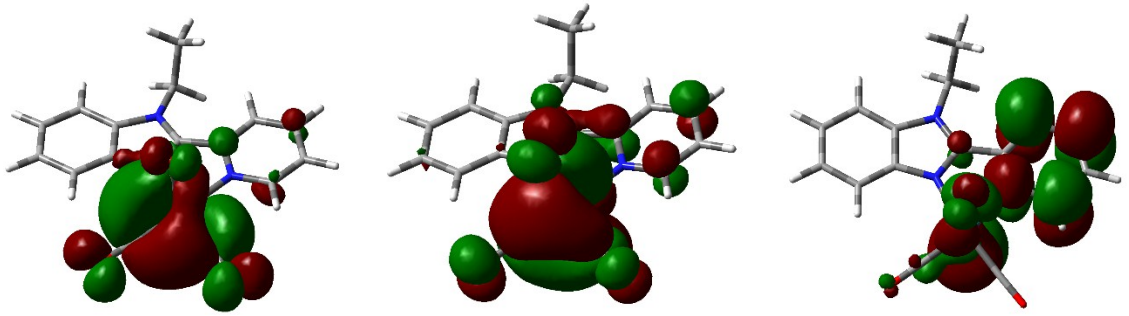
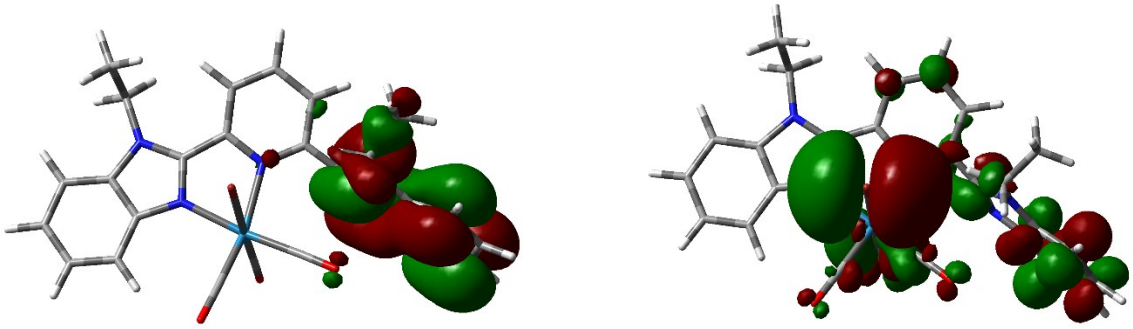


Figure S7 TD/CAM-B3LYP/LANL2DZ calculated spectra of the investigated tricarbonyl Re(I) complexes bearing *N,N*-bidentate benzimidazole ligands.



HSOMO-3(β) **HSOMO-4(β)** **LSOMO(β)**

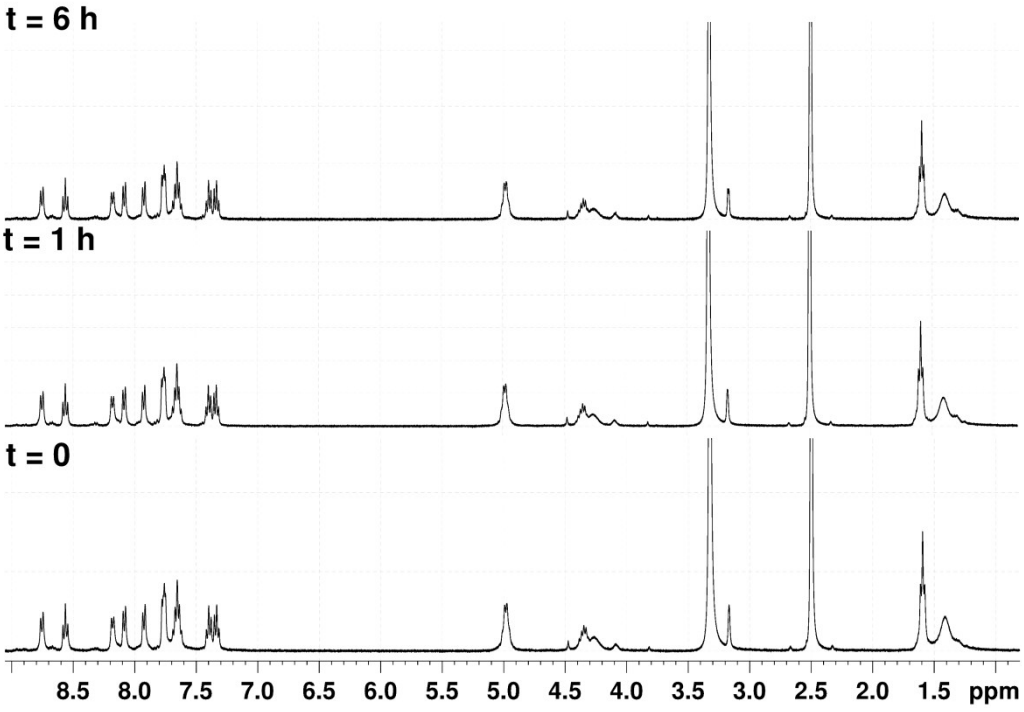
a)



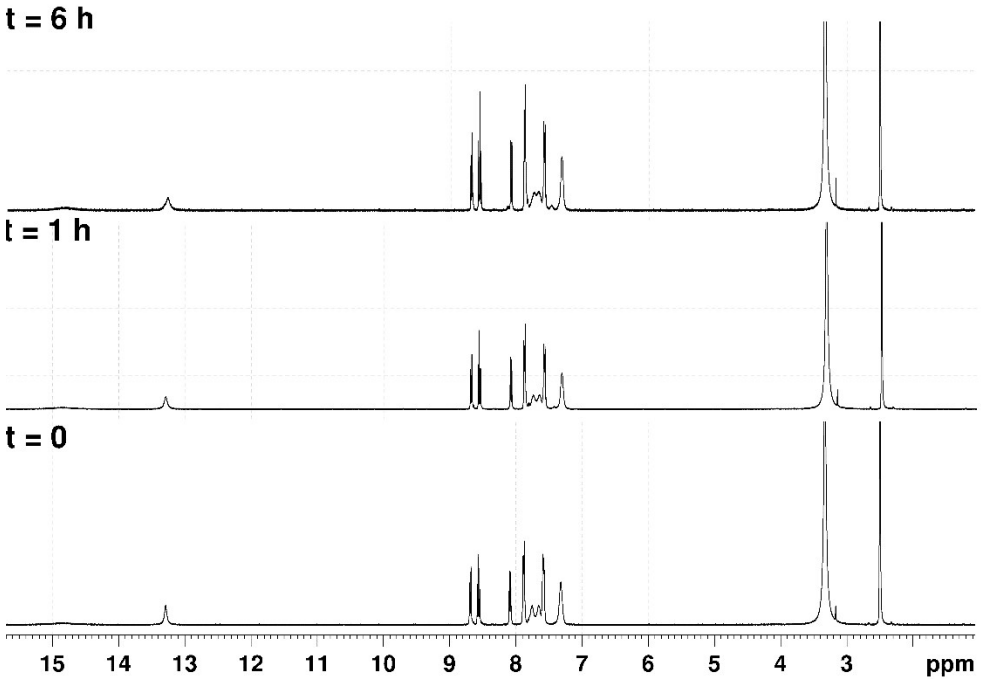
HSOMO-6(α) **LSOMO(α)**

b)

Figure S8 HSOMO and LSOMO orbitals involved in the triplet state calculations of a) **1** and b) **5**.



a)



b)

Figure S9 ^{1}H NMR spectral changes of a) **4** and b) **5** (in DMSO-d_6) upon the illumination at 365 nm.

Biological activity testing

Evaluation of antimicrobial properties

The antimicrobial activities of the benzimidazole ligands and their complexes were evaluated against cultures of *Staphylococcus aureus* ATCC 43300, *Escherichia coli* ATCC 25922, *Klebsiella pneumoniae* ATCC 700603, *Acinetobacter baumannii* ATCC 19606, *Pseudomonas aeruginosa* ATCC 27853, as well as two fungi, *Candida albicans* ATCC 90028 and *Cryptococcus neoformans var. grubii* H99; ATCC 208821. The samples were prepared in DMSO to a final testing concentration of 32 µg/mL and serially diluted 1:2 fold for 8 times. Each concentration was prepared in 384-well plates, non-binding surface plate (NBS; Corning 3640) for each bacterial/fungal strain, all in duplicate (n=2), and keeping the final DMSO concentration to a maximum of 0.5%. All bacteria were cultured in Cation-adjusted Mueller Hinton broth at 37 °C overnight. A sample of each culture was then diluted 40-fold in fresh broth and incubated at 37 °C for 1.5-3 h. The resultant mid-log phase cultures were diluted (CFU/mL, measured the absorbance at 600 nm), then added to each well of the compound containing plates, giving a cell density of 5×10^5 CFU/mL and a total volume of 50 µL. All the plates were covered and incubated at 37 °C for 18 h without shaking. The inhibition of the bacterial growth was determined by OD_{600} using a Tecan M1000 Pro monochromator plate reader. The percentage of growth inhibition was calculated for each well, using the negative control (media only) and positive control (bacteria without inhibitors) on the same plate as references. The MIC was determined as the lowest concentration at which the growth was fully inhibited, defined by an inhibition ≥ 80%. In addition, the maximal percentage of growth inhibition is reported as D_{Max}, indicating any compounds with partial activity plates.

Fungi strains were cultured for 3 days on Yeast Extract-peptone Dextrose agar at 30 °C. A yeast suspension of 1×10^6 to 5×10^6 CFU/mL (determined by OD_{600}) was prepared from five colonies. The suspension was subsequently diluted and added to each well of the sample-containing plates giving a cell density of fungi suspension of 2.5×10^3 CFU/mL and total volume of 50 µL. All plates were covered and incubated at 35 °C for 36 h without shaking. The growth inhibition of *Candida albicans* was measured at 630 nm, while that of *Cryptococcus neoformans* was determined by measuring the difference in absorbance at 600 and 570 nm, after the addition of resazurin (0.001%, final concentration) and incubation at 35 °C for 2 h. The absorbance was measured using a Biotek Multiflo Synergy HTX plate reader and controls. The MIC was determined as the lowest concentration at which the growth was fully inhibited, defined by an inhibition = 80% for *Candida albicans* and an inhibition =

70% for *Cryptococcus neoformans*. Due to a higher variance in the growth and inhibition, a lower threshold was applied to the data for *Cryptococcus neoformans*. In addition, the maximal percentage of growth inhibition is reported as D_{Max}, indicating any compounds with marginal activity.

Cytotoxicity Assay

Human embryonic kidney HEK293 cells were counted manually in a Neubauer haemocytometer and then plated in the 384-well plates containing complex **5** to give a density of 5000 cells/well in a final volume of 50 µL. Dulbecco's Modified Eagle Medium (DMEM) supplemented with 10% FBS was used as growth media and the cells were incubated together with the compounds for 20 h at 37 °C in 5% CO_2. Cytotoxicity (or cell viability) was measured by Fluorescence (excitation 560/10, emission 590/10 nm) ($F_{560/590}$), after addition of 5 µL of 25 µg/mL resazurin (2.3 µg/mL final concentration) and after incubation for further 3 h at 37 37 °C in 5% CO_2. The intensity was measured using Tecan M1000 Pro monochromator plate reader, using automatic gain calculation. CC_{50} (the concentration at 50% cytotoxicity) was calculated by curve fitting the inhibition values *vs.* logC using a sigmoidal dose-response function, with variable fitting values for bottom, top and slope. The curve fitting was implemented using Pipeline Pilot's dose-response component, resulting in similar values to curve fitting tools such as GraphPad's Prism and IDBS's XlFit.

Table S8: Antibacterial and antifungal data of the benzimidazole ligands and their complexes tested at 32 µg/mL.										
	L^1	**L^2**	**L^3**	**L^4**	**L^5**	**1**	**2**	**3**	**4**	**5**
Staphylococcus aureus ATCC 43300	28.68	33.23	20.37	36.08	30.31	21.87	12.43	14.37	49.76	93.2
Escherichia coli ATCC 25922	0.00	2.56	2.02	0.43	4.91	0.00	2.9	0.00	0.37	2.94
Klebsiella pneumoniae ATCC 700603	10.03	25.16	13.31	24.05	17.71	8.84	-2.72	11.96	14.41	14.35
Acinetobacter baumannii ATCC 19606	3.94	8.92	8.18	5.88	5.6	6.95	4.54	13.84	10.88	27.58
Pseudomonas aeruginosa ATCC	25.49	20.31	24.45	24.8	23.58	17.88	20.89	6.1	10.17	10.39
Candida albicans ATCC 90028	5.02	3.31	5.56	1.53	5.88	4.81	8.43	30.37	53.07	1.12
Cryptococcus neoformans var. grubii H99; ATCC 208821	0.00	0.00	0.00	0.00	0.00	0.00	2.73	0.00	0.00	0.00

*Inhibition of bacterial growth was determined measuring absorbance at 600 nm (OD600), using a Tecan M1000 Pro monochromator plate reader. The percentage of growth inhibition was calculated for each well, using the negative control (media only) and positive control (bacteria without inhibitors) on the same plate as references.

**Growth inhibition of C. albicans was determined measuring absorbance at 530 nm (OD530), while the growth inhibition of C. neoformans was determined measuring the difference in absorbance between 600 and 570 nm (OD600-570), after the addition of resazurin (0.001% final concentration) and incubation at 35 °C for additional 2 h. The absorbance was measured using a Biotek Synergy HTX plate reader. The percentage of growth inhibition was calculated for each well, using the negative control (media only) and positive control (bacteria without inhibitors) on the same plate as references.