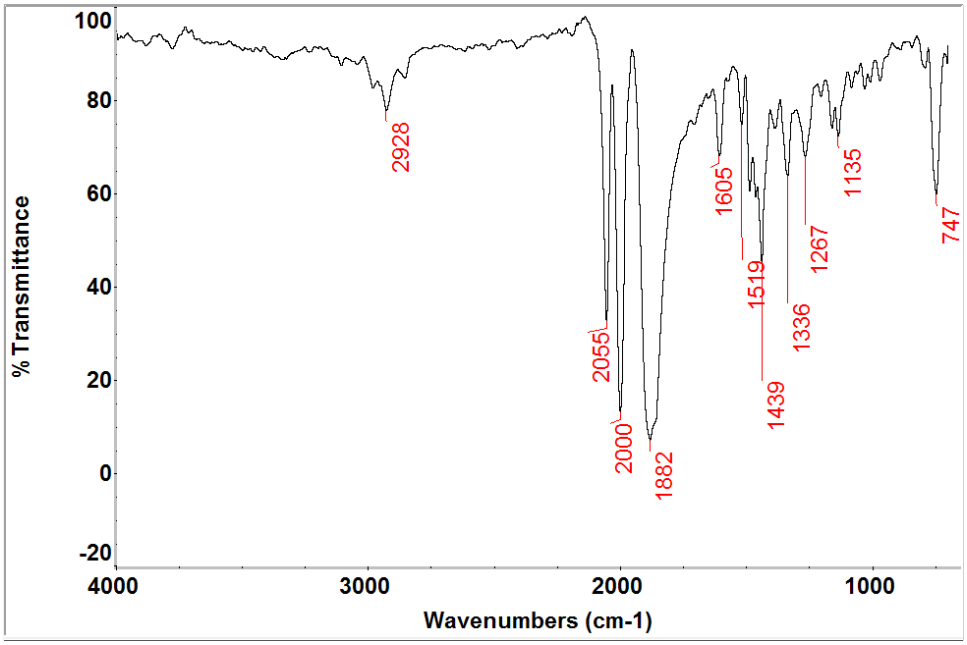
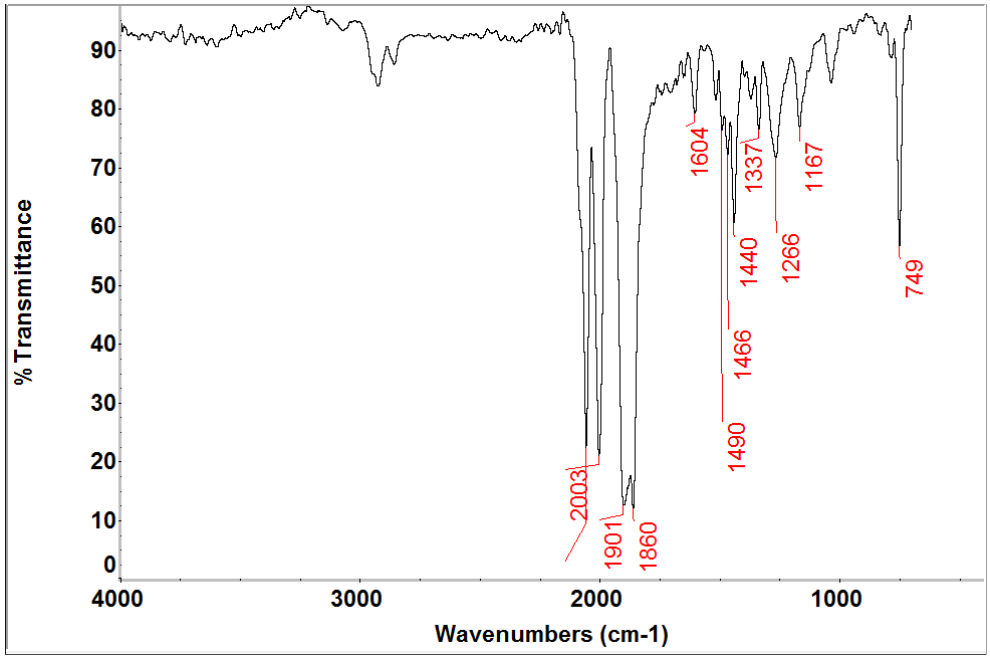
**Supporting information**

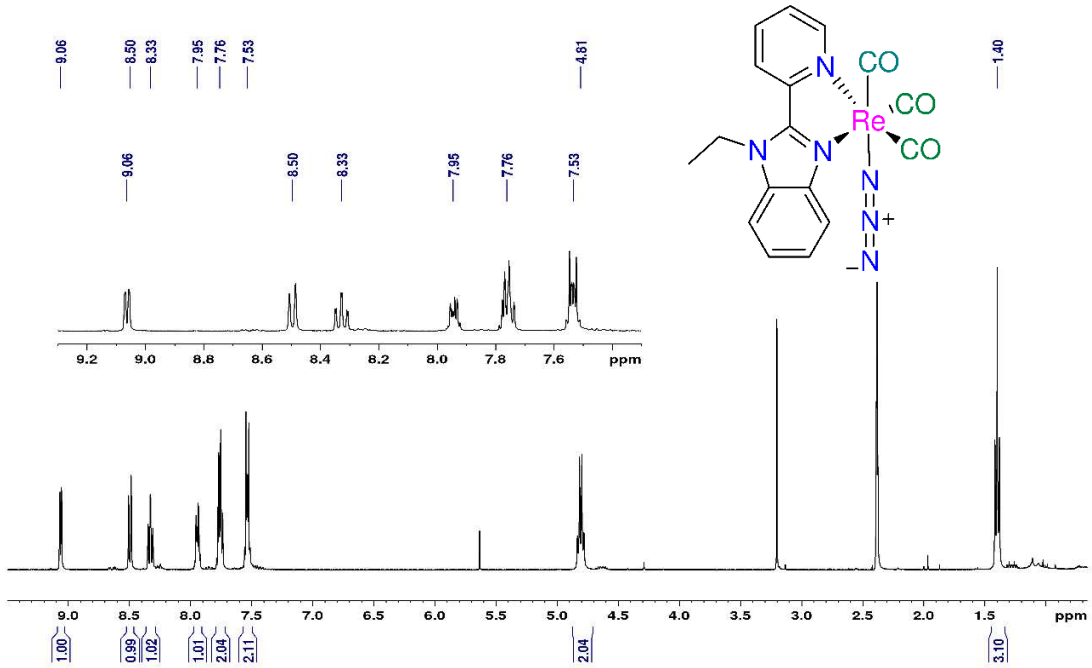



a)

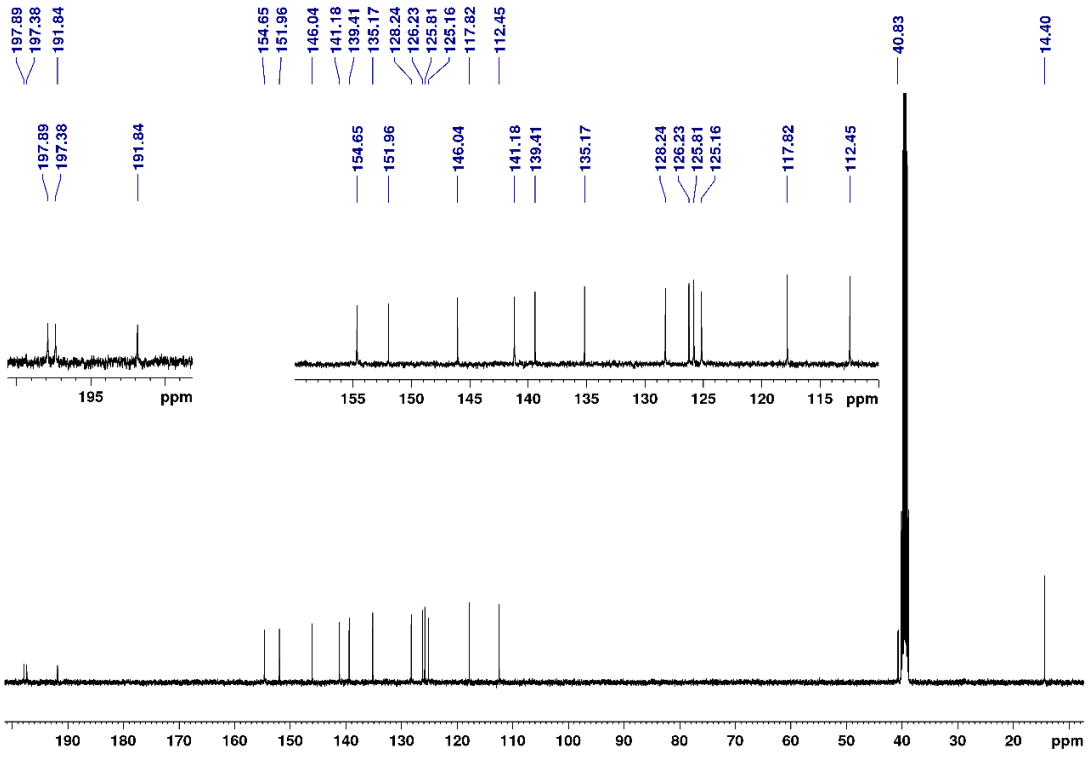



b)

**Fig. S1** AT IR spectra of the Re(I) azide complexes, a) **2** and b) **5**.

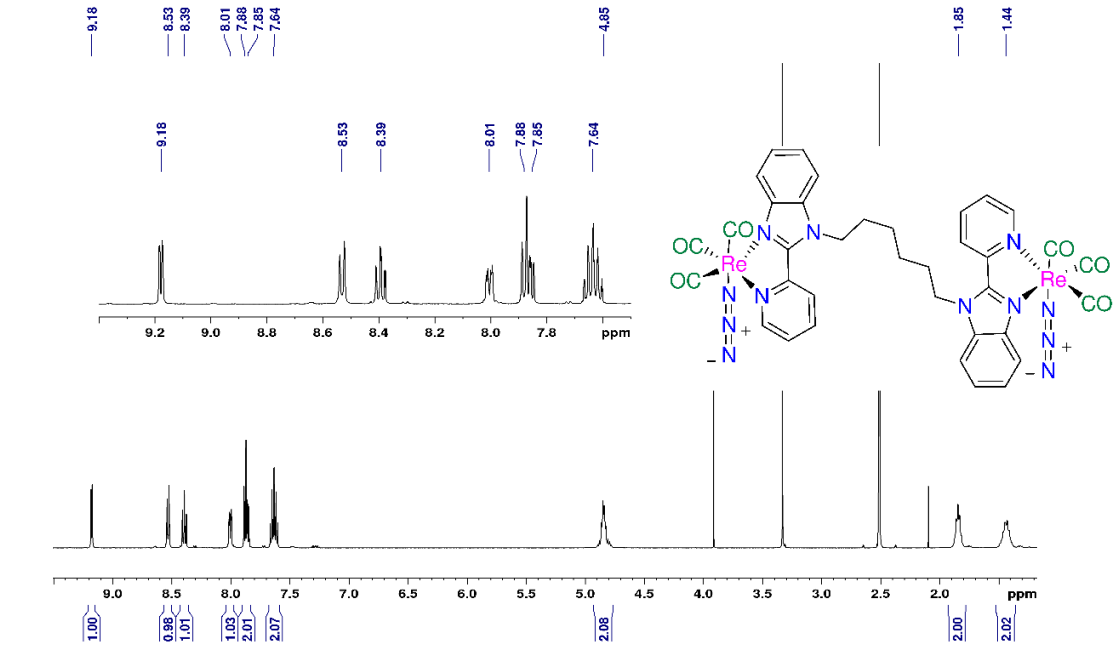



a)

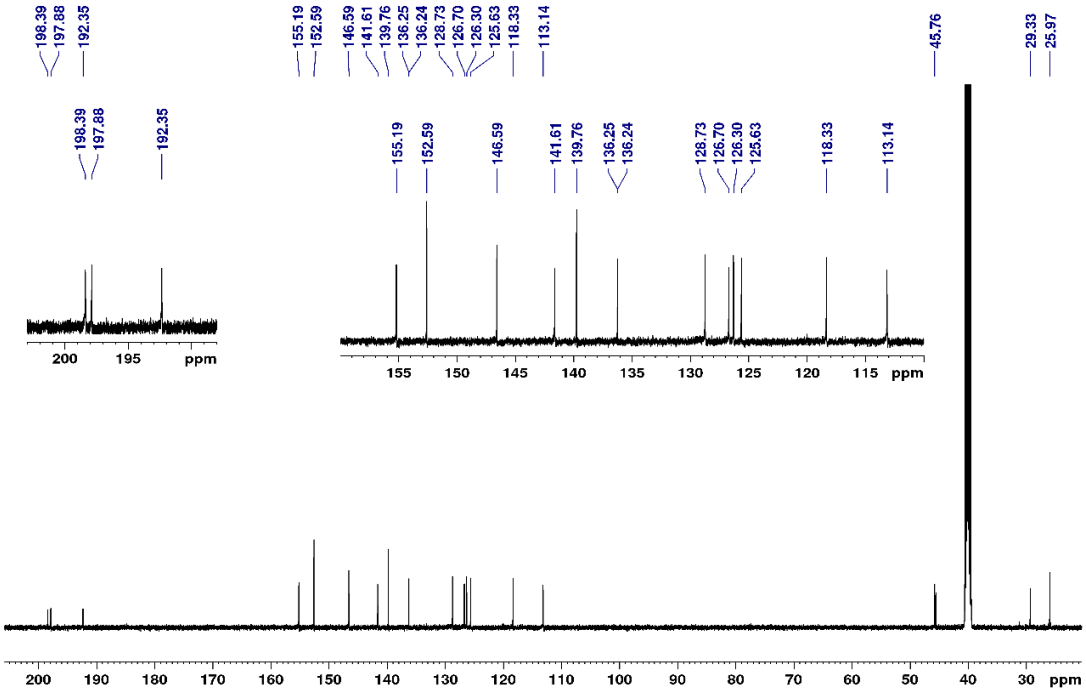



b)

**Fig. S2** NMR analysis of **2** in DMSO-$d_6$, a) $^{1}H$, and b) $^{13}C$ spectra.

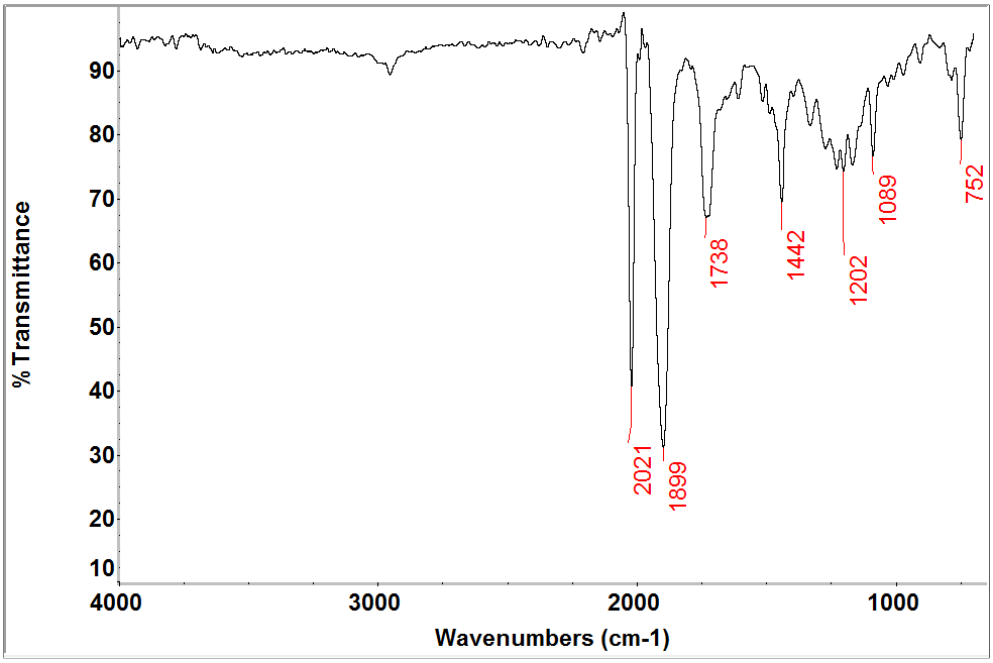



a)

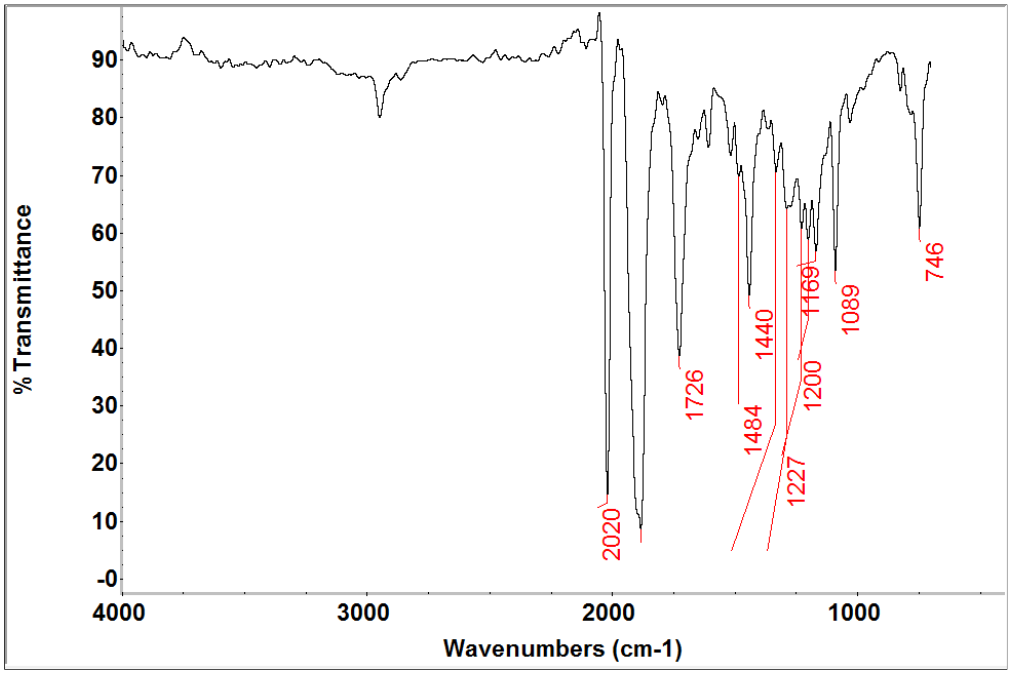



b)

**Fig. S3** NMR analysis of **5** in DMSO-$d_6$, a) $^{1}H$, and b) $^{13}C$ spectra.

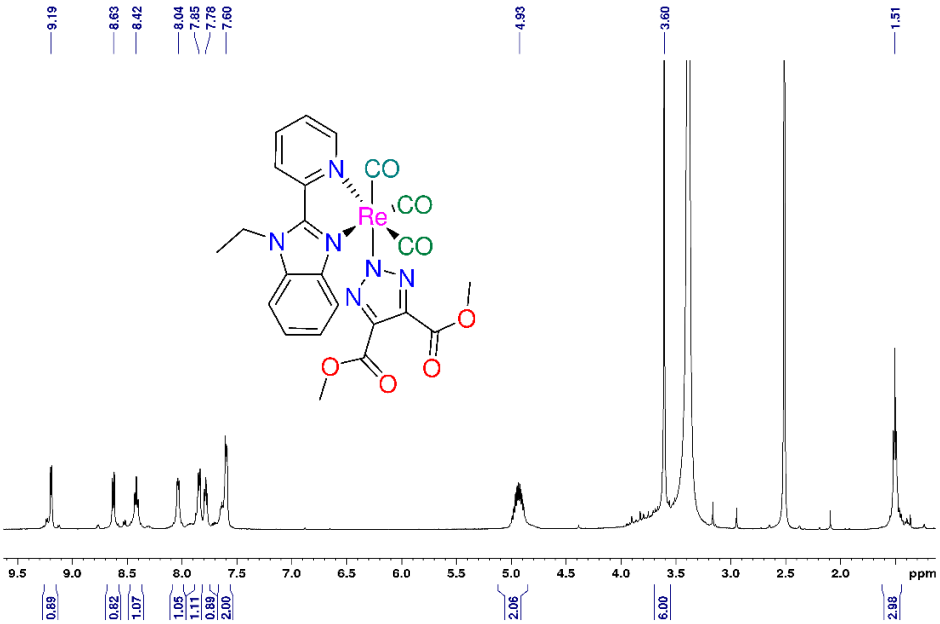



a)

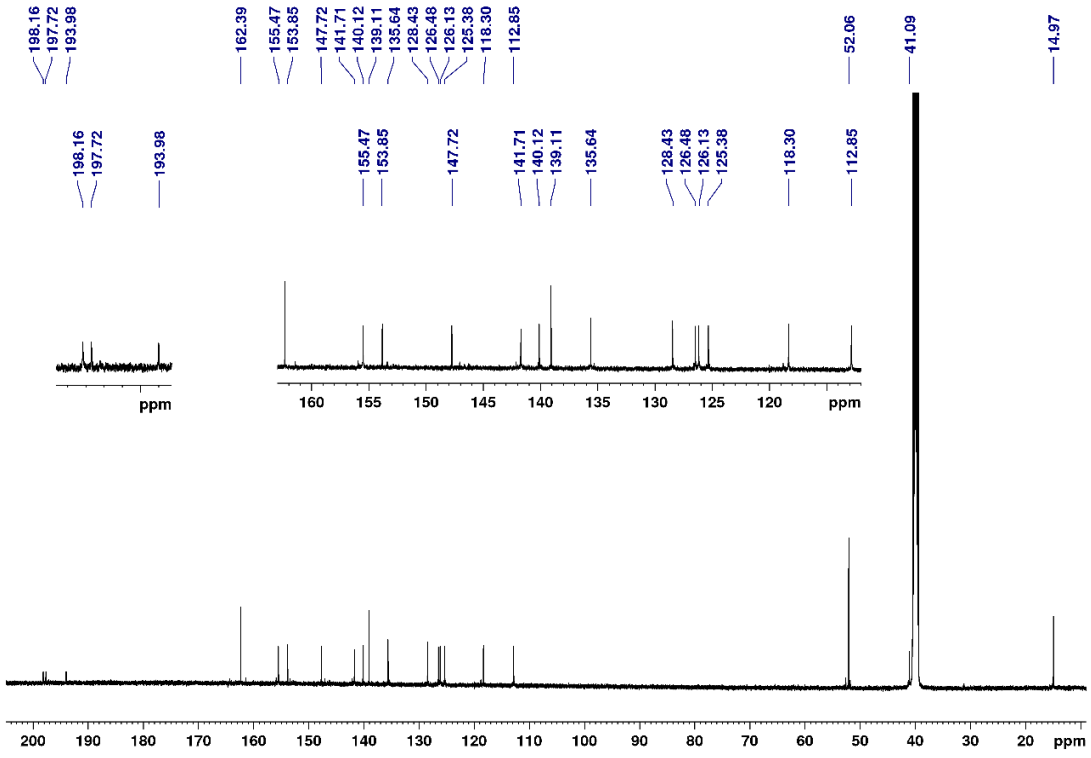



b)

**Fig. S4** AT IR spectra of the Re(I) azide complexes, a) **3** and b) **6**.

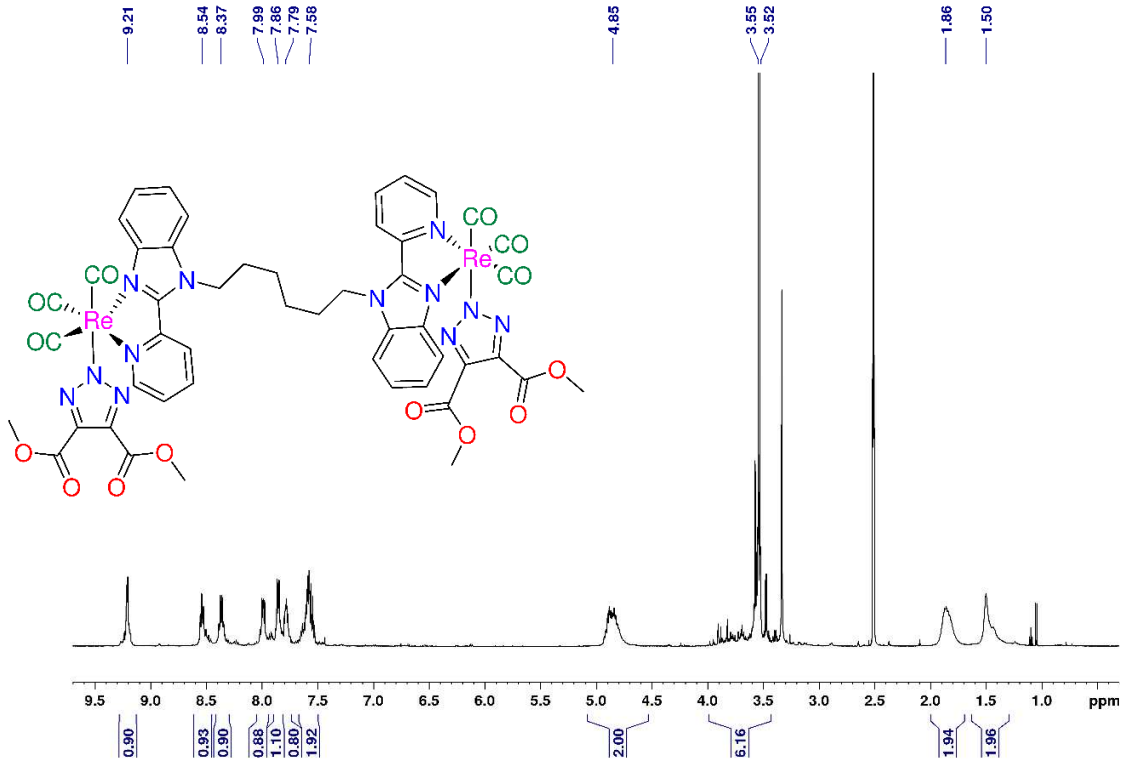



a)

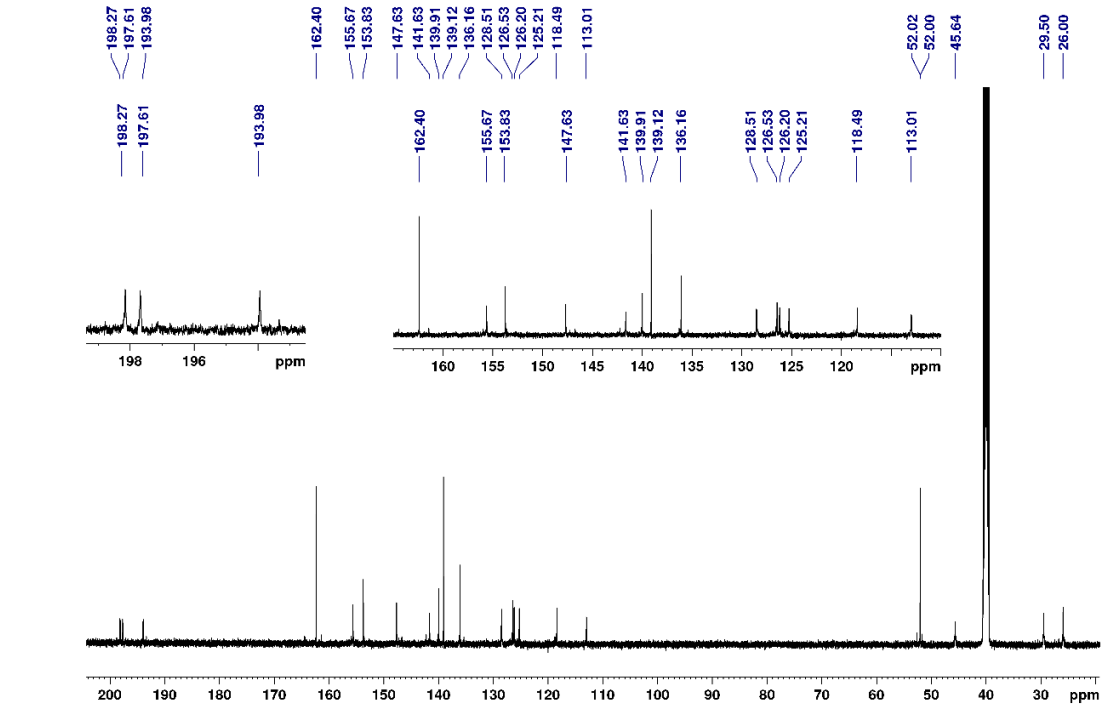



b)

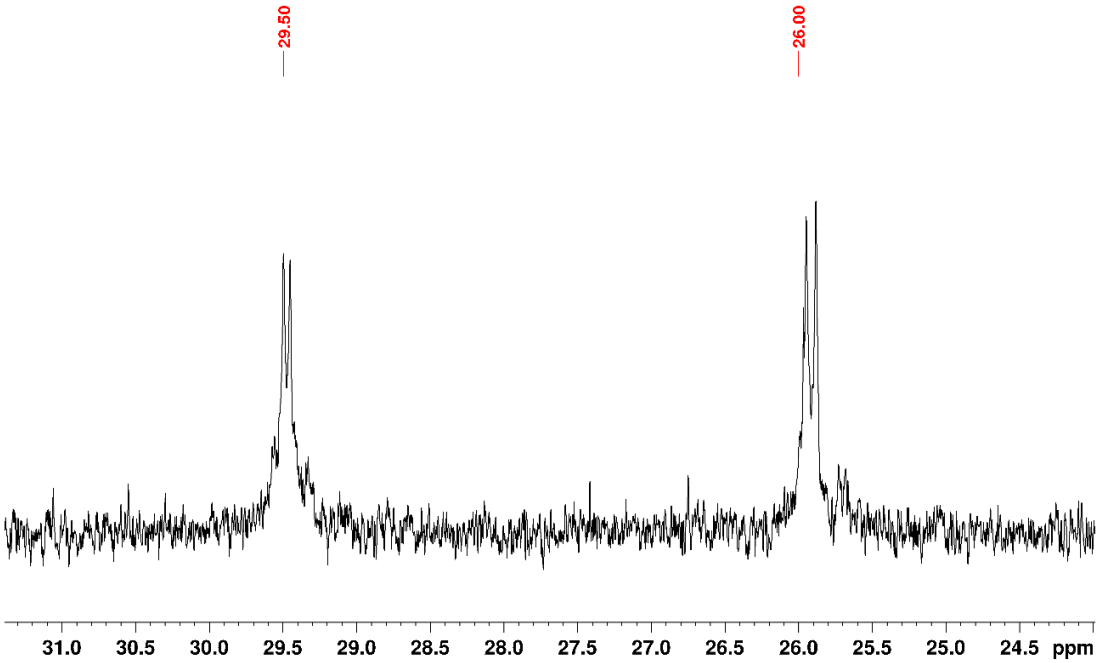
**Fig. S5** NMR analysis of **3** in DMSO-$d_6$, a) $^{1}H$, and b) $^{13}C$ spectra.


9.21
8.54
8.37
7.99
7.86
7.79
7.58
4.85
3.55
3.52
1.86
1.50
CO
OC
Re
N
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.90
0.93
0.90
0.88
1.10
0.80
1.92
2.00
6.16
1.94
1.96

a)


198.27
197.61
193.98
162.40
155.67
153.83
147.63
141.63
139.91
139.12
136.16
128.51
126.53
126.20
125.21
118.49
113.01
52.02
52.00
45.64
29.50
26.00
198 196 ppm
160 155 150 145 140 135 130 125 120 ppm
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

b)




c)

**Fig. S6** NMR analysis of **6** in DMSO-$d_6$, a) $^{1}H$, b) $^{13}C$ and c) representative zoom in section of $^{13}C$ spectra.

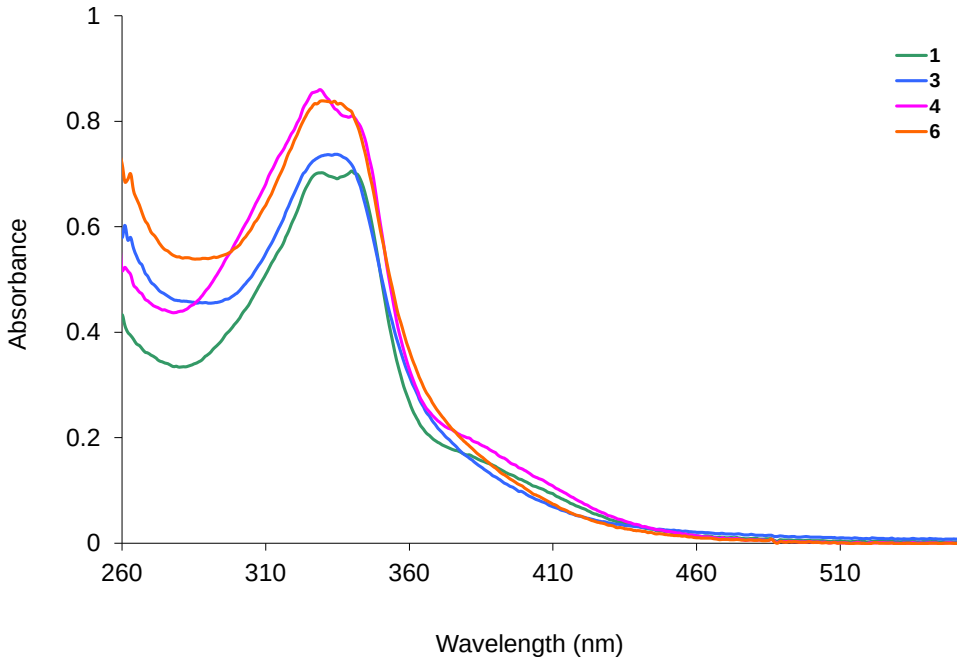



**Fig. S7** Electronic absorption spectra of the complexes in DMSO.

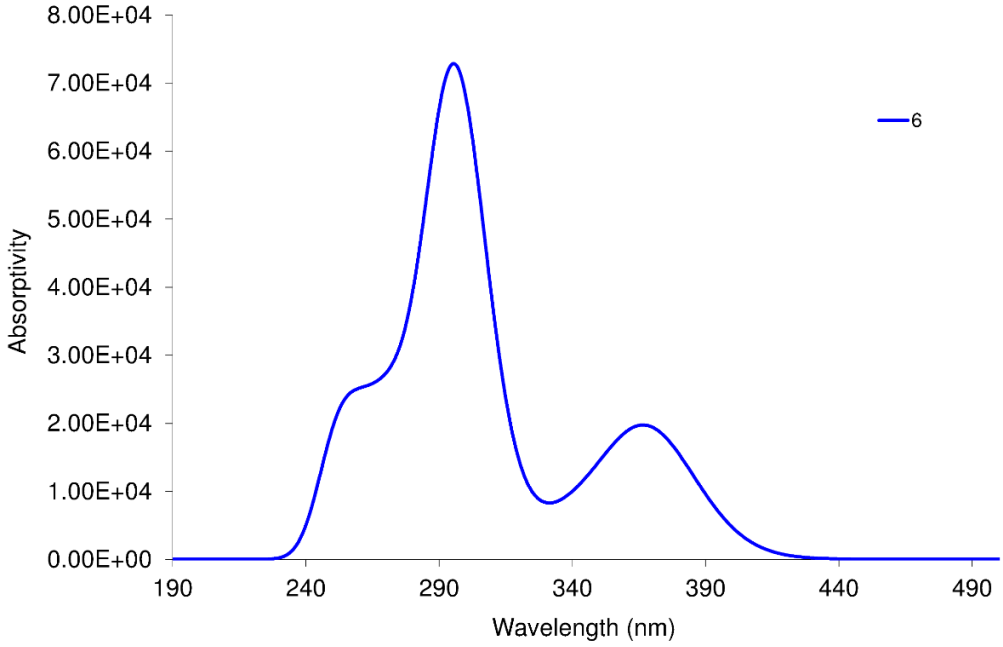
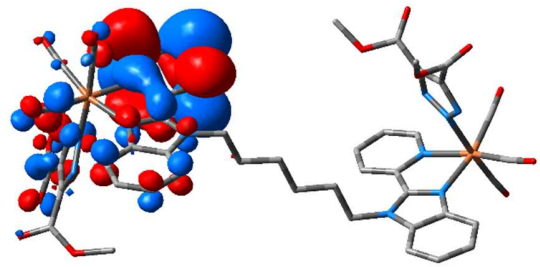
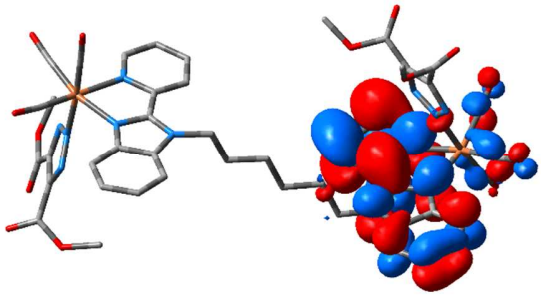
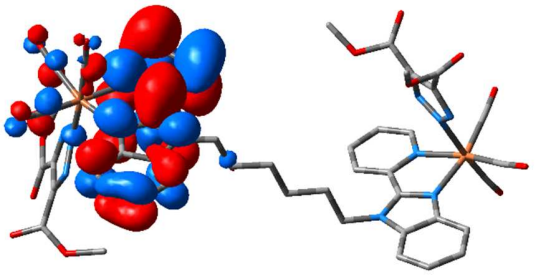
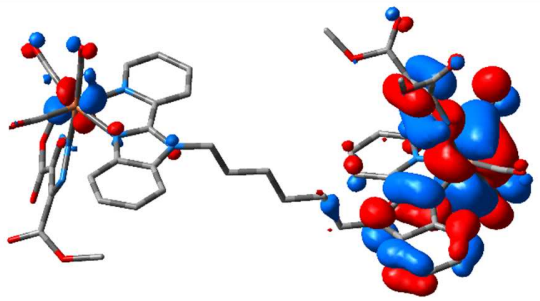
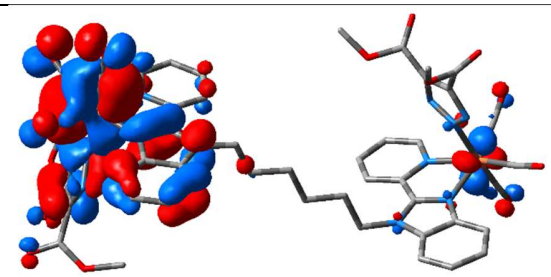
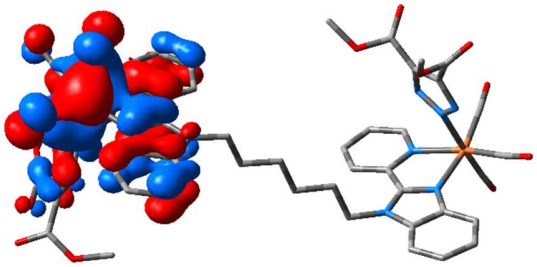
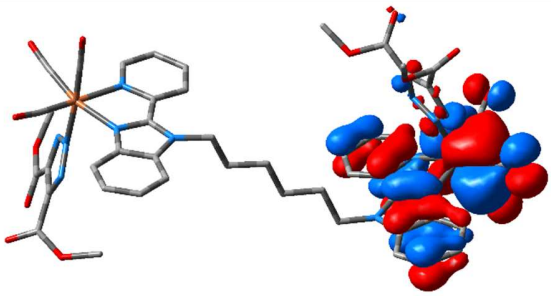
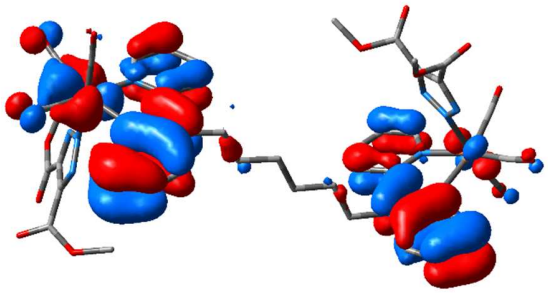
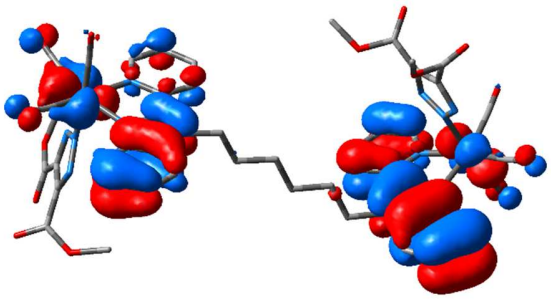



**Fig. S8** Calculated electronic spectra of **6** at TD/PCM(DMSO)/CAM-B3LYP/LANL2DZ level of theory in the singlet state.

| **Table S1** Selected frontiers molecular orbitals of **6** in the singlet state calculated at B3LYP/LANL2DZ level of theory. | |
|---|---|
| Orbital | Frontier molecular orbital |
| LUMO+2 |  |
| LUMO+1 |  |
| LUMO |  |
| HOMO |  |

| | |
|---|---|
| HOMO–1 |  |
| HOMO–2 |  |
| HOMO–3 |  |
| HOMO–5 |  |
| HOMO–6 |  |