Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

The CO release properties of $\kappa^2 N^1,N^2$ Mn(I) tricarbonyl PhotoCORMs with tridentate benzimidazole coligands

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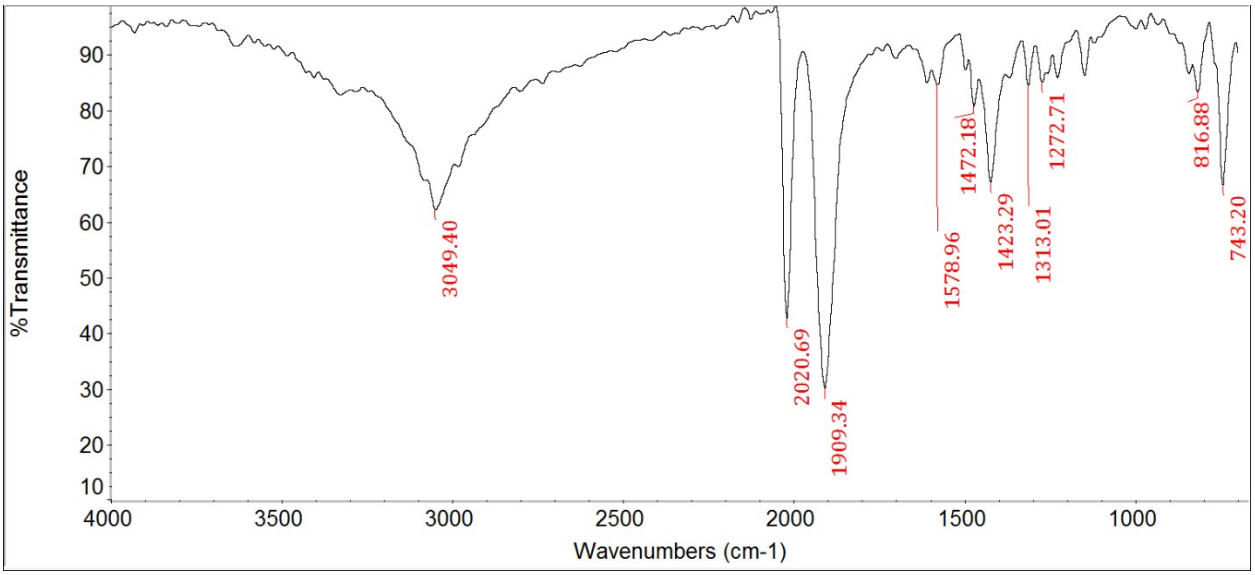
* Corresponding author

Supporting Information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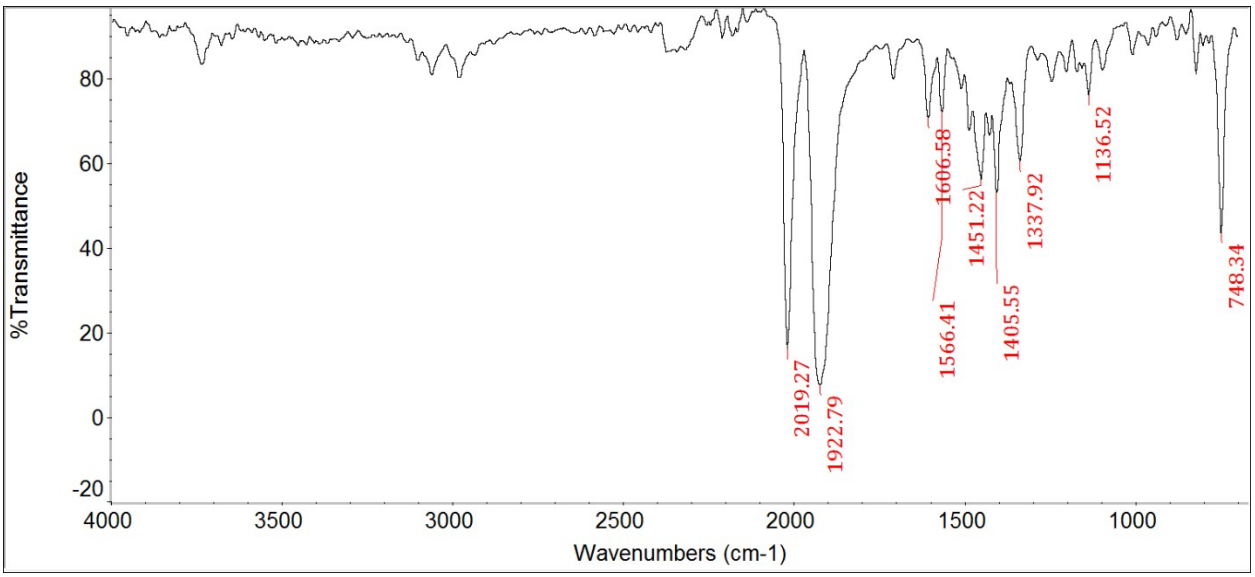
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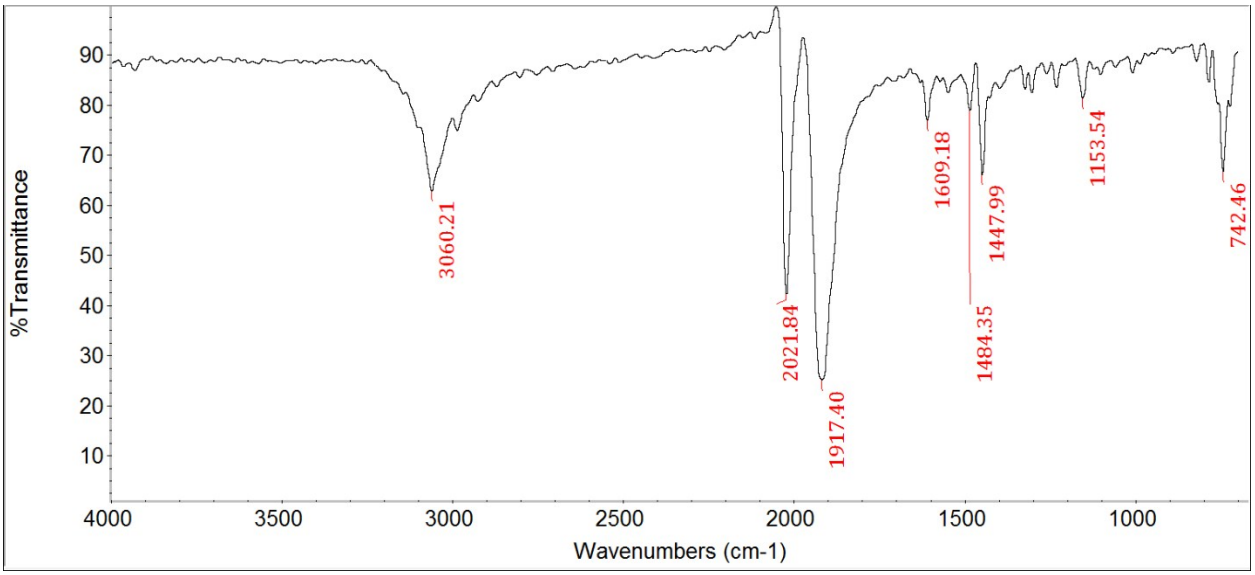
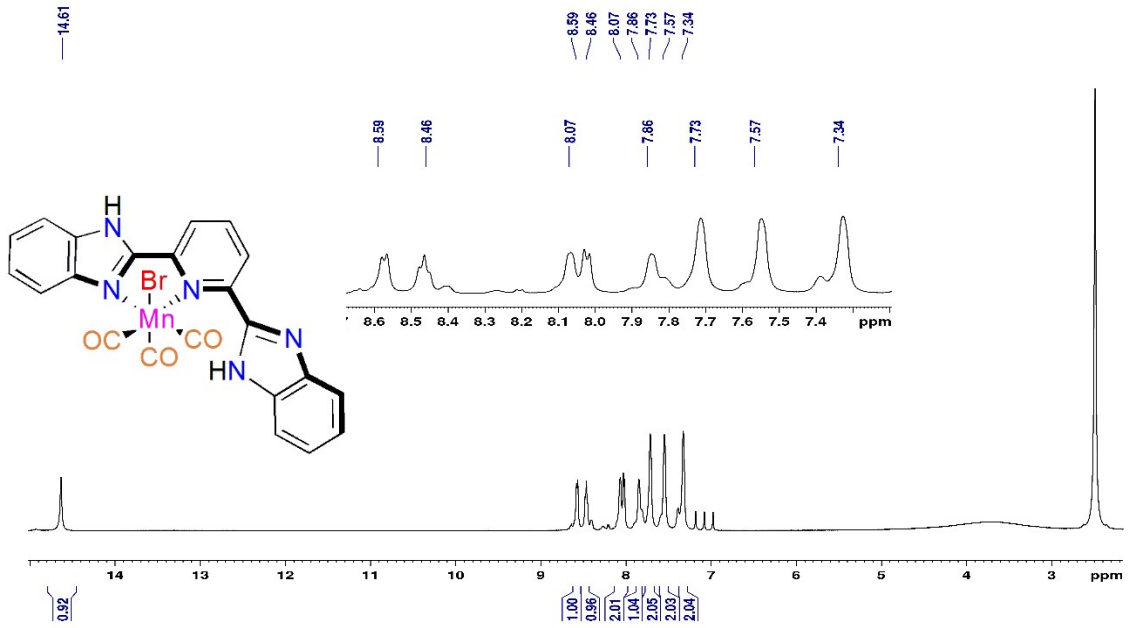
b)



c)

Fig. S1†: AT IR spectra of a) **1**, b) **2** and c) **3**.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ppm

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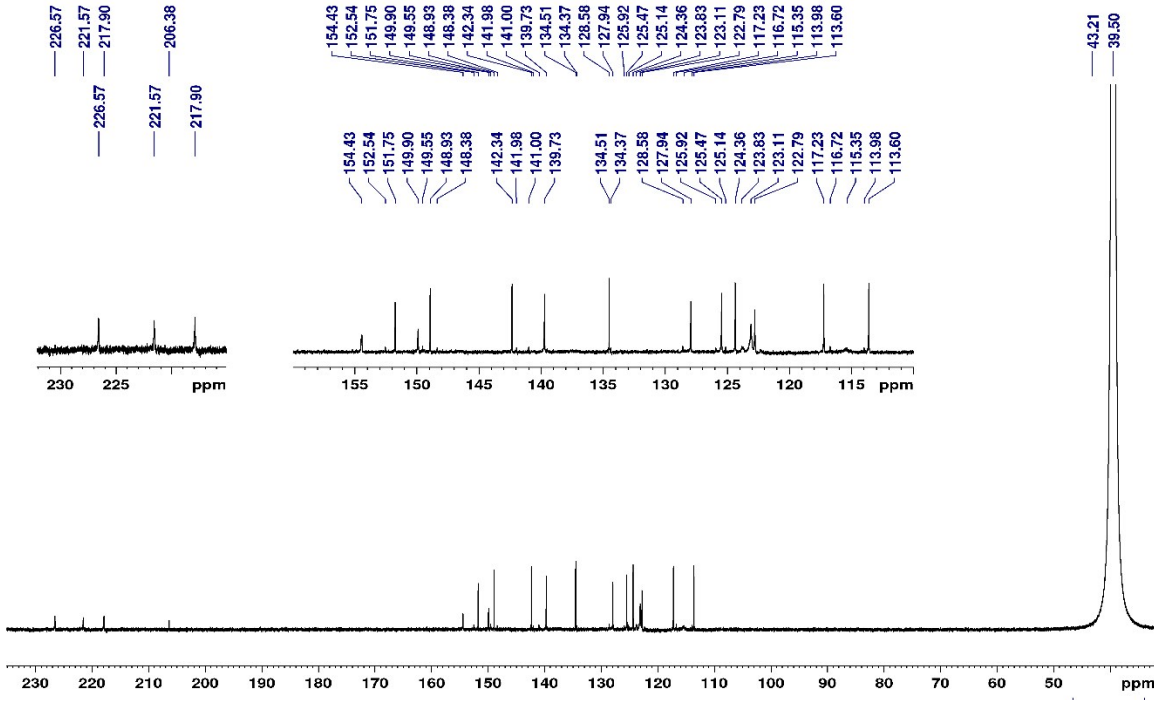
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b)

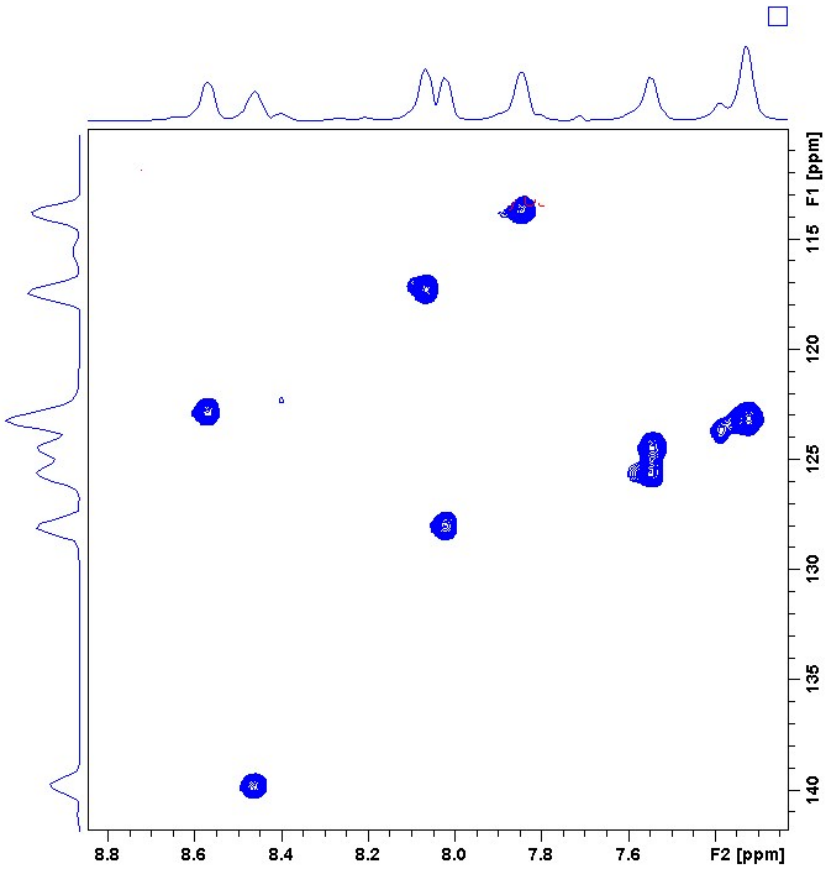
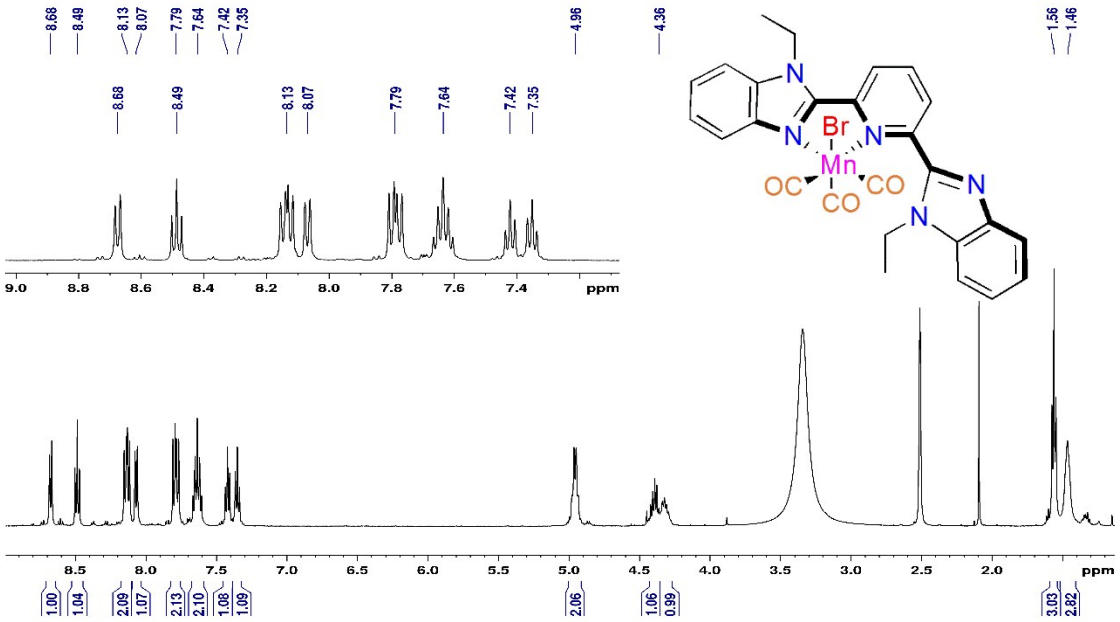


Fig. S2†: NMR analysis of **1** in DMSO-d_6, a) ^{1}H, b) ^{13}C and c) {^{13}C, ^{1}H} HSQC.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CO
CO
N
ppm
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1.09
2.06
1.06
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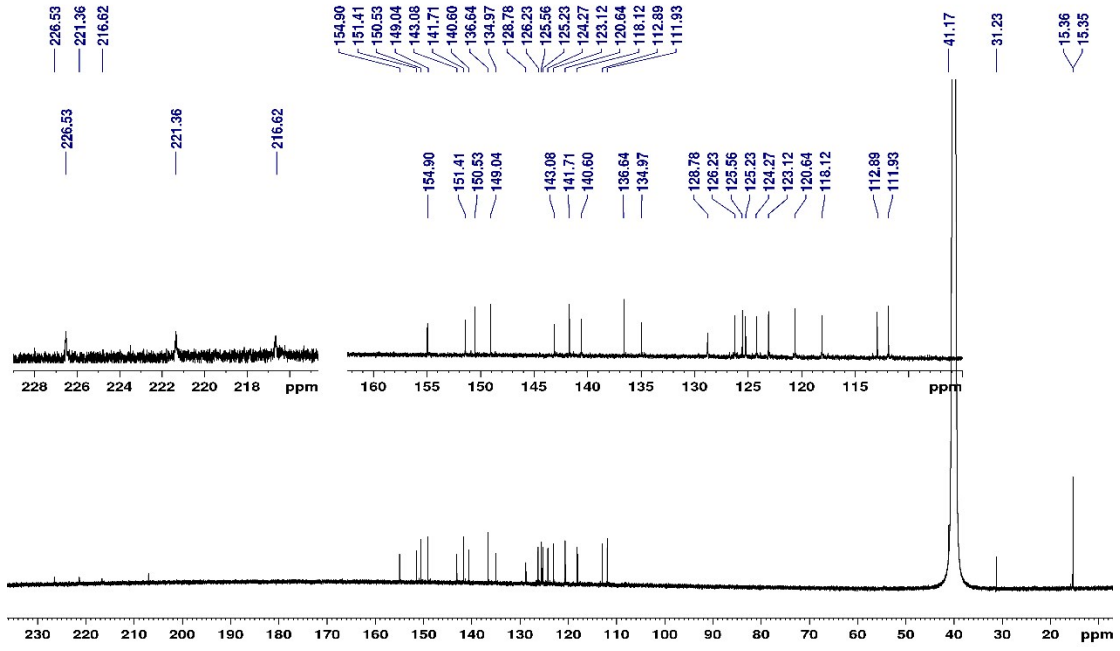
3.03
2.82

a)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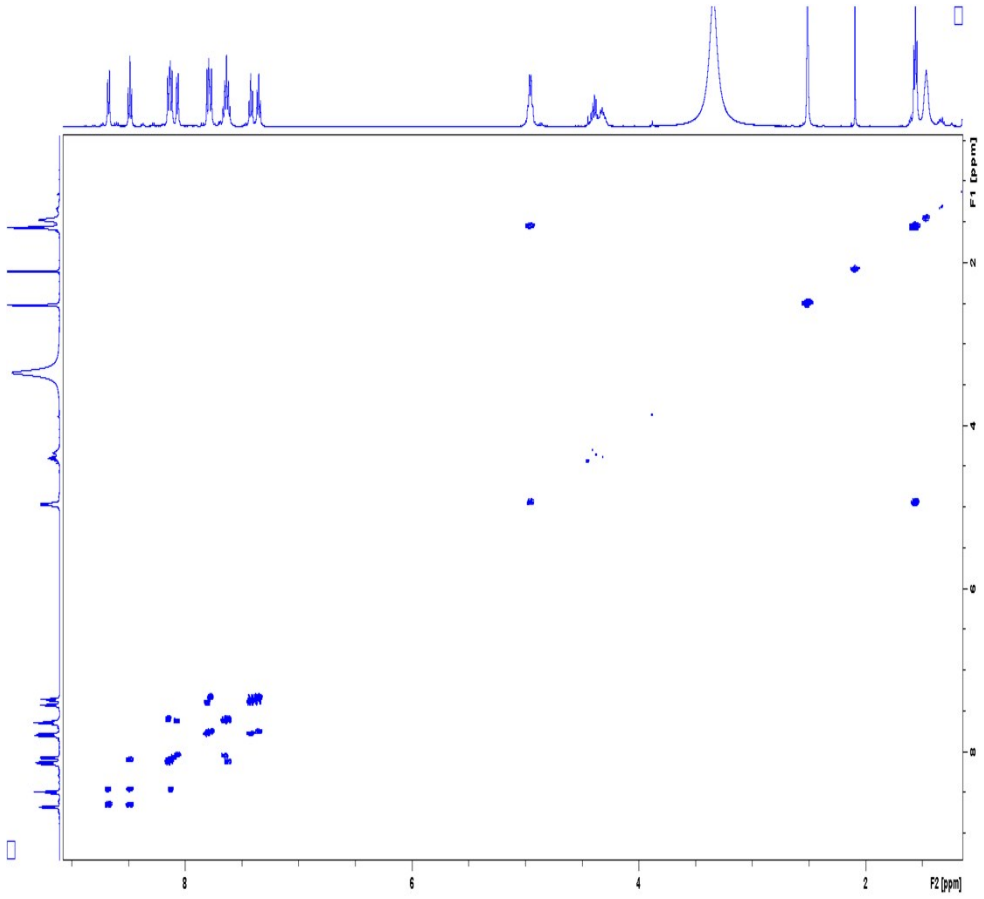
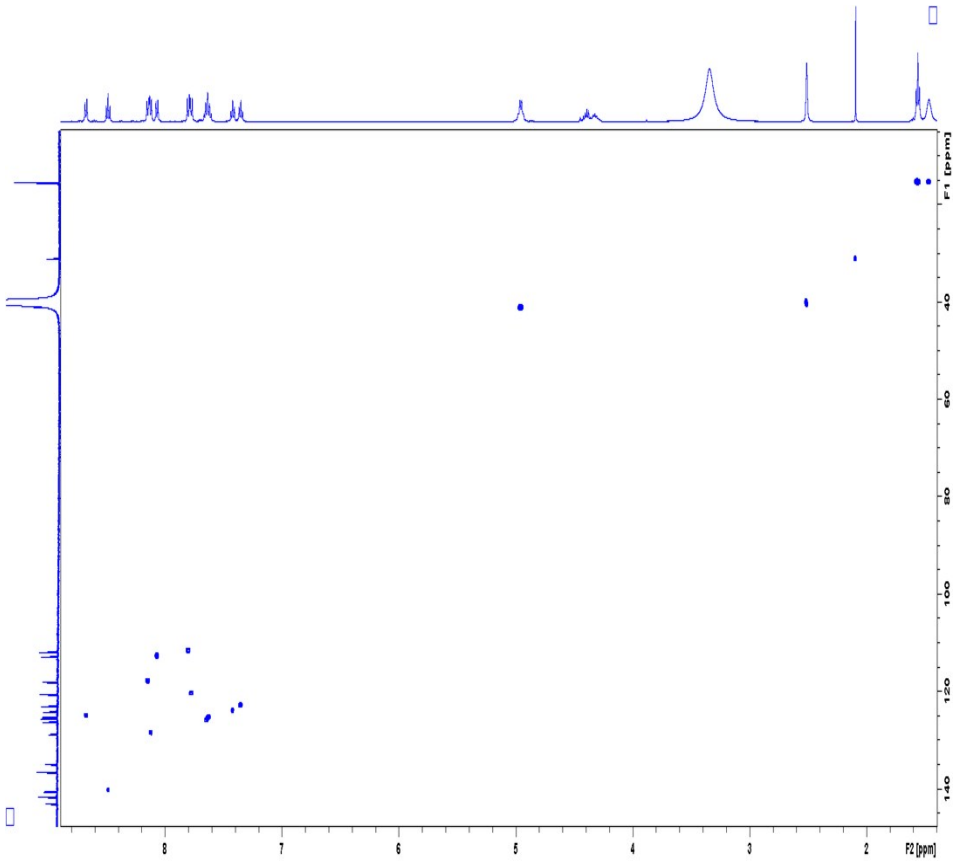
b)

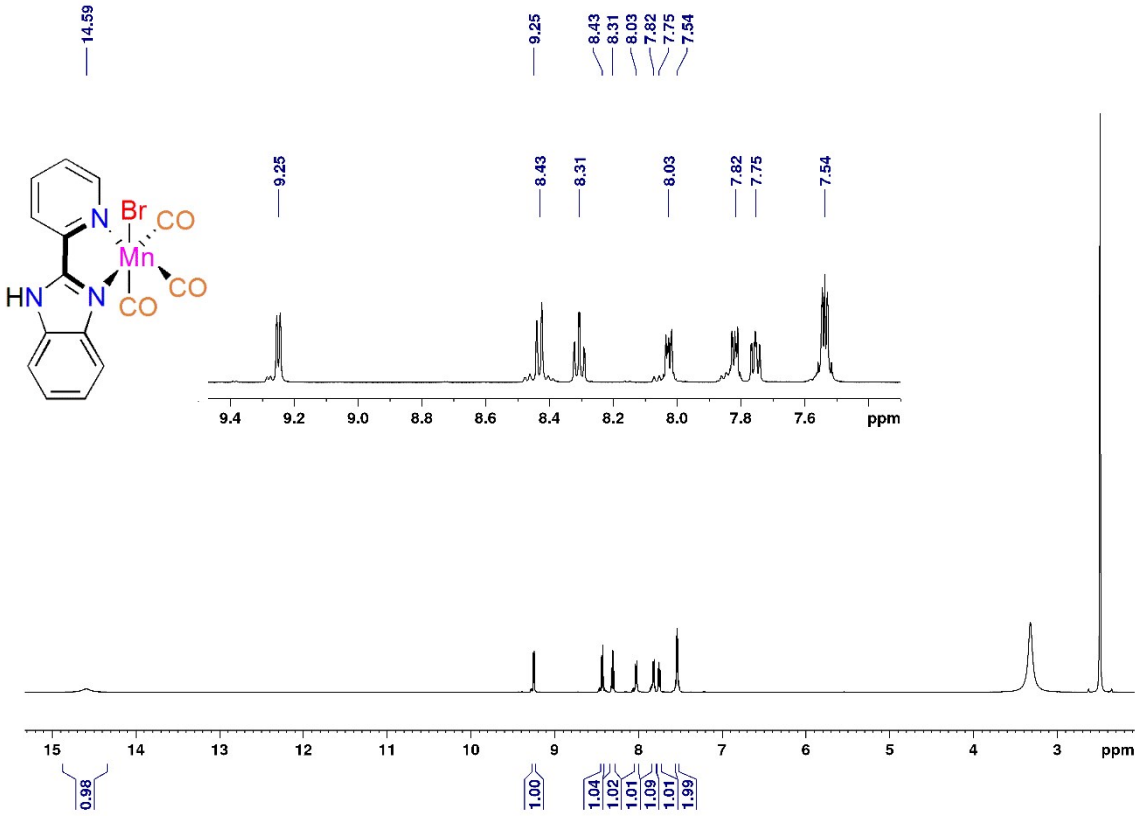


c)



d)

Fig. S3†: NMR analysis of **2** in DMSO-d_6, a) ^{1}H, b) ^{13}C, c) {^{1}H, ^{1}H} COS90 and d) {^{13}C, ^{1}H} HSQC.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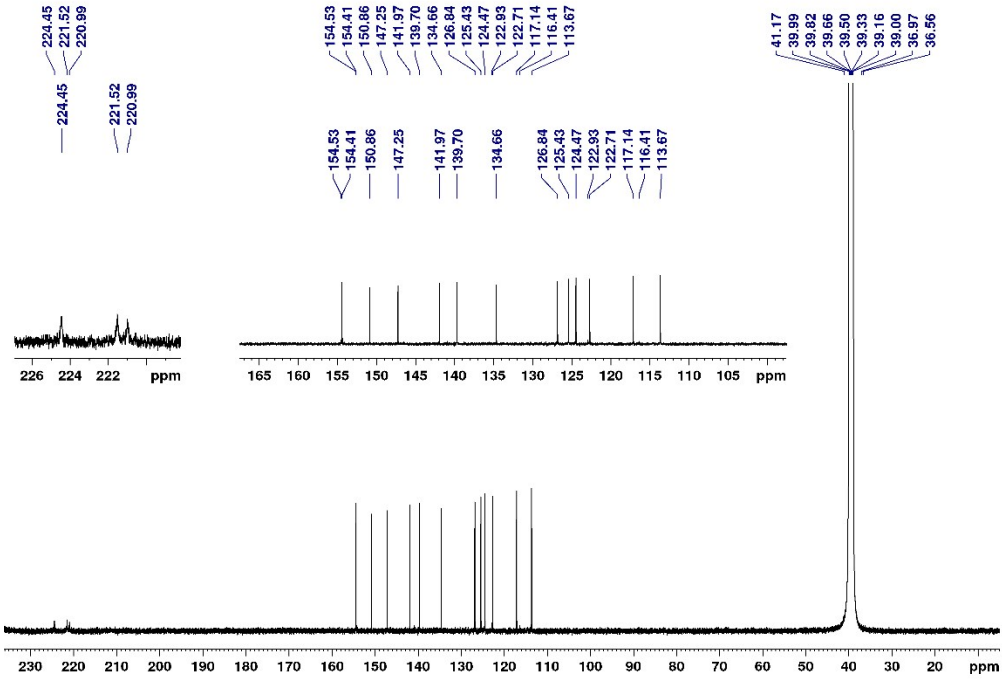
a)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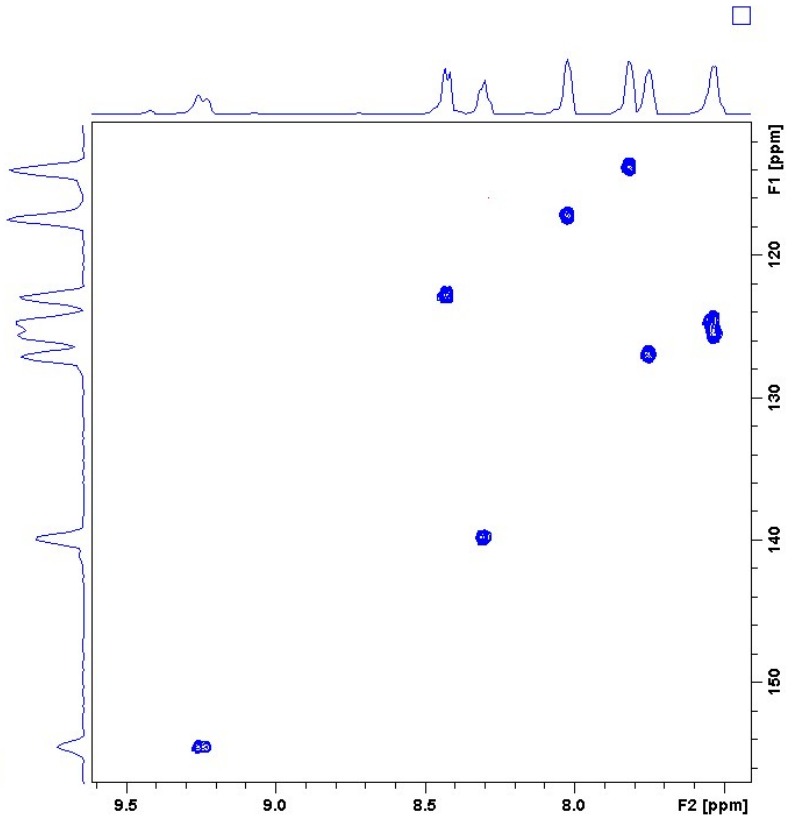
ppm

b)



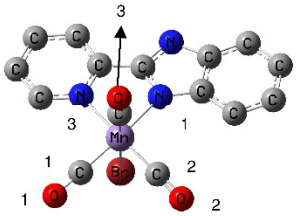
c)

Fig. S4†: NMR analysis of **3** in DMSO-d_6, a) ^{1}H, b) ^{13}C and c) {^{13}C, ^{1}H} HSQC.

Table S1†: Selected experimental and theoretical bond lengths (Å) and angles (°) of complexes **1** and **2**.											
	1						**2**				
	Exp.	B3LYP/ LANL2DZ	B3LYP/ Gen*	B3LYP/ def2-SVP	M05/ def2-SVP		Exp.	B3LYP/ LANL2DZ	B3LYP/ Gen*	B3LYP/ def2-SVP	M05/ def2-SVP
Mn-C(1)	1.809(3)	1.819	1.812	1.823	1.794	Mn-C(1)	1.807 (2)	1.819	1.811	1.821	1.792
Mn-C(2)	1.805(3)	1.805	1.796	1.808	1.778	Mn-C(2)	1.804 (2)	1.819	1.796	1.808	1.777
Mn-C(3)	1.847(3)	1.801	1.791	1.813	1.792	Mn-C(3)	1.800 (2)	1.800	1.790	1.812	1.792
Mn-N(1)	2.028(3)	2.034	2.054	2.074	2.080	Mn-N(1)	2.027 (2)	2.024	2.045	2.063	2.069
Mn-N(3)	2.130(2)	2.123	2.144	2.175	2.197	Mn-N(3)	2.110 (2)	2.111	2.134	2.163	2.186
Mn-Br	2.534(1)	2.622	2.660	2.572	2.530	Mn-Br	2.5457 (8)	2.630	2.666	2.577	2.536
C(1)-O(1)	1.153(4)	1.179	1.154	1.149	1.153	C(1)-O(1)	1.139 (2)	1.179	1.155	1.151	1.153
C(2)-O(2)	1.138(3)	1.180	1.156	1.151	1.154	C(2)-O(2)	1.135 (3)	1.180	1.156	1.150	1.154
C(3)-O(3)	1.068(3)	1.180	1.156	1.150	1.153	C(3)-O(3)	1.137 (3)	1.180	1.156	1.150	1.153
C(1)-Mn-C(2)	85.7(1)	87.8	88.6	89.4	87.9	C(1)-Mn-C(2)	85.57 (9)	86.6	87.3	87.4	85.9
C(1)-Mn-C(3)	86.1(1)	94.1	93.8	94.5	92.9	C(1)-Mn-C(3)	88.37 (9)	93.5	93.1	93.5	85.9
C(1)-Mn-N(1)	177.0(1)	171.5	171.8	170.7	171.9	C(1)-Mn-N(1)	175.05 (8)	173.7	174.1	173.6	174.
C(1)-Mn-N(3)	100.2(1)	97.6	97.8	97.4	98.9	C(1)-Mn-N(3)	100.06 (8)	99.2	99.4	99.8	101.1
C(1)-Mn-Br	96.32(9)	84.5	85.3	85.0	86.3	C(1)-Mn-Br	87.39 (6)	85.1	85.9	85.7	86.9
C(2)-Mn-C(3)	92.2(1)	93.7	92.8	93.7	169.7	C(2)-Mn-C(3)	90.53 (9)	94.4	93.45	94.6	92.9
N(1)-Mn-C(2)	96.2(1)	94.1	94.2	94.2	95.3	N(1)-Mn-C(2)	95.91 (8)	94.4	94.7	94.5	95.9
C(2)-Mn-N(3)	173.9(1)	169.3	169.4	168.5	169.7	C(2)-Mn-N(3)	169.00 (8)	168.1	168.3	167.4	169.1
C(2)-Mn-Br	87.64(9)	87.2	88.6	88.2	90.1	C(2)-Mn-Br	87.63 (7)	86.9	88.4	88.2	89.9
N(1)-Mn-C(3)	91.4(1)	93.9	93.7	93.8	94.4	N(1)-Mn-C(3)	96.33 (8)	92.6	92.3	92.3	93.1
C(3)-Mn-N(3)	89.9(1)	95.1	95.1	94.9	95.0	C(3)-Mn-N(3)	99.02 (8)	95.6	95.7	95.1	95.1
C(3)-Mn-Br	177.52(9)	178.3	178.2	83.2	177.4	C(3)-Mn-Br	175.50 (7)	178.0	177.9	177.1	177.1
N(1)-Mn-N(3)	77.98(9)	79.2	78.2	77.7	76.9	N(1)-Mn-N(3)	77.71 (6)	78.7	77.6	77.1	76.3
N(1)-Mn-Br	86.17(7)	87.4	87.1	86.5	86.3	N(1)-Mn-Br	87.95 (5)	88.7	88.6	88.3	87.5
N(3)-Mn-Br	90.01(6)	84.2	83.5	83.2	82.7	N(3)-Mn-Br	83.23 (4)	83.2	82.6	82.2	82.2

*Gen: LANL2DZ for bromine atom and 6-31G(d) for the rest of the elements

Table S2†: Selected theoretical bond lengths (Å) and angles (°) of complex **3**.				
	B3LYP/ LANL2DZ	B3LYP/ Gen*	B3LYP/ def2-SVP	M05/ def2-SVP
Mn-C(1)	1.812	1.803	1.817	1.789
Mn-C(2)	1.812	1.806	1.817	1.789
Mn-C(3)	1.793	1.784	1.804	1.785
Mn-N(1)	2.042	2.064	2.085	2.089
Mn-N(3)	2.072	2.093	2.113	2.131
Mn-Br	2.603	2.635	2.554	2.515
C(1)-O(1)	1.180	1.156	1.150	1.153
C(2)-O(2)	1.179	1.155	1.149	1.153
C(3)-O(3)	1.184	1.159	1.153	1.156
C(1)-Mn-C(2)	89.8	90.9	91.0	90.0
C(1)-Mn-C(3)	93.9	93.0	94.0	92.5
C(1)-Mn-N(1)	170.8	170.4	169.8	170.8
C(1)-Mn-N(3)	94.3	93.9	94.3	95.2
C(1)-Mn-Br	85.9	87.2	86.6	88.0
C(2)-Mn-C(3)	93.9	93.2	94.0	92.5
N(1)-Mn-C(2)	95.6	96.1	95.7	96.7
C(2)-Mn-N(3)	170.7	171.6	170.3	171.2
C(2)-Mn-Br	86.1	87.9	87.2	88.6
N(1)-Mn-C(3)	93.2	93.1	93.0	93.4
C(3)-Mn-N(3)	94.1	93.3	93.7	94.2
C(3)-Mn-Br	179.7	178.9	178.7	178.7
N(1)-Mn-N(3)	79.3	78.3	78.0	77.3
N(1)-Mn-Br	87.0	86.6	86.2	85.9
N(3)-Mn-Br	85.8	85.6	85.0	84.5



*Gen: LANL2DZ for bromine atom and 6-31G(d) for the rest of the elements

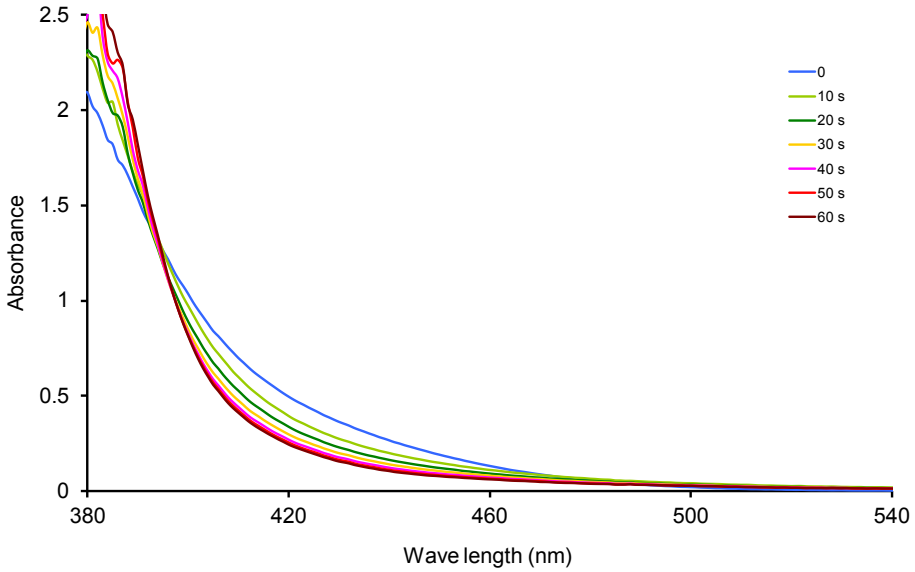


Fig. S5†: UV/Vis spectral changes of **1** upon the photolysis at 468 nm for one minute after pre-incubation in the dark for 16 h.

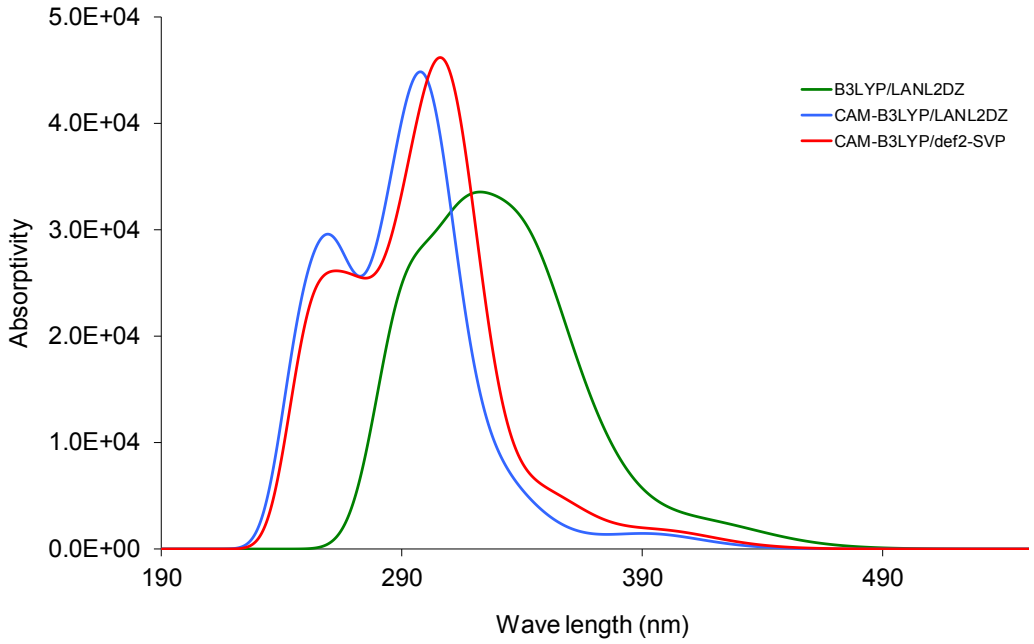
Table S3†: Computed excitation energies (eV), electronic transition configurations and oscillator strengths (*f*) of the studied complexes

(selected, (f > 0.02)			
Energy (cm^{-1})	Wavelength (nm)	f	Major contributions (>20%)
• Complex **3**			
• B3LYP/LANL2DZ			
23264	429	0.0024	HOMO→LUMO (76%)
24228	412	0.0302	HOMO-1→LUMO (76%)
28401	352	0.0694	HOMO-2→LUMO (78%)
30033	332	0.0787	HOMO-5→LUMO (37%), HOMO-3→LUMO (43%)
31255	319	0.2111	HOMO-5→LUMO (31%), HOMO-3→LUMO (34%)
37519	266	0.1025	HOMO-3→LUMO+1 (68%)
• CAM-B3LYP/LANL2DZ			
25746	388	0.0208	HOMO-1→LUMO+2 (25%)
31729	315	0.0605	HOMO→LUMO (38%)
32146	311	0.0214	HOMO-1→LUMO (62%)
33917	294	0.345	HOMO-2→LUMO (86%)
35658	280	0.1213	HOMO-4→LUMO (26%), HOMO-3→LUMO (46%)
40942	244	0.0516	HOMO→LUMO+1 (50%)
• CAM-B3LYP/def2-SVP			
25242	396	0.02	HOMO-1→LUMO+2 (26%)
28766	347	0.0028	HOMO→LUMO (44%)
34017	293	0.4256	HOMO-2→LUMO (77%)
35862	278	0.1555	HOMO-4→LUMO (78%)
37269	268	0.0482	HOMO-5→LUMO (64%)
40603	246	0.0349	HOMO-6→LUMO (70%)
• Complex **1**			
• B3LYP/LANL2DZ			
22621	442	0.0042	HOMO→LUMO (79%)
23988	416	0.0269	HOMO-1→LUMO (84%)

27461	364	0.0817	HOMO-3→LUMO (74%)
29314	341	0.1100	HOMO-4→LUMO (65%)
31381	318	0.2451	HOMO-7→LUMO (47%)
34036	293	0.1086	HOMO-6→LUMO+1 (71%)
34690	288	0.1179	HOMO-5→LUMO+1 (49%)
• CAM-B3LYP/LANL2DZ			
25461	392	0.0176	HOMO-1→LUMO+3 (20%)
29545	338	0.0216	HOMO→LUMO (25%)
33138	301	0.4448	HOMO-3→LUMO (52%), HOMO-2→LUMO (24%)
34965	285	0.2086	HOMO-5→LUMO (52%)
39844	251	0.0583	HOMO-8→LUMO (34%), HOMO-2→LUMO+1 (23%)
• CAM-B3LYP/def2-SVP			
23783	420	0.0017	HOMO→LUMO+3 (29%)
25088	398	0.0206	HOMO-1→LUMO+3 (30%)
27898	358	0.0131	HOMO→LUMO (44%)
28233	354	0.0052	HOMO-1→LUMO (23%)
28728	348	0.0301	HOMO-1→LUMO (23%)
32147	311	0.4179	HOMO-3→LUMO (65%)
33886	295	0.2371	HOMO-5→LUMO (70%)
37226	268	0.1479	HOMO-7→LUMO (23%), HOMO-2→LUMO+1 (41%)
39026	256	0.0553	HOMO-8→LUMO (29%)
• Complex **2**			
• B3LYP/LANL2DZ			
22662	441	0.0087	HOMO→LUMO (75%)
24183	413	0.0248	HOMO-1→LUMO (77%)
25368	394	0.0021	HOMO→LUMO+2 (22%)
28918	345	0.0472	HOMO→LUMO+1 (32%)
29350	340	0.1068	HOMO-5→LUMO (51%)
31065	321	0.2522	HOMO-7→LUMO (59%), HOMO-5→LUMO (23%)
34904	286	0.0784	HOMO-5→LUMO+1 (43%)

• CAM-B3LYP/LANL2DZ			
24212	413	0.0023	HOMO→LUMO+3 (23%)
30673	326	0.0503	HOMO→LUMO (46%)
31782	314	0.0154	HOMO-2→LUMO (21%), HOMO→LUMO+4 (22%)
33273	300	0.2946	HOMO-4→LUMO (54%)
34361	291	0.1874	HOMO-3→LUMO (23%)
39150	255	0.0337	HOMO-2→LUMO+1 (34%), HOMO-1→LUMO+1 (36%)
• CAM-B3LYP/def2-SVP			
25150	397	0.0195	HOMO-1→LUMO+3 (26%)
27797	359	0.015	HOMO→LUMO (28%)
28509	350	0.0114	HOMO-1→LUMO (20%), HOMO→LUMO (20%)
32200	310	0.2338	HOMO-4→LUMO (57%)
32526	307	0.2624	HOMO-2→LUMO (27%)
33672	296	0.1951	HOMO-5→LUMO (70%)
37104	269	0.1185	HOMO-1→LUMO+1 (59%)

Only strong transitions with an oscillator strength > 0.01 in the 250–800 nm range are reported. Only contributions >20% are listed. The reversed order is due to state experiencing a smaller solvent shift than most of the others.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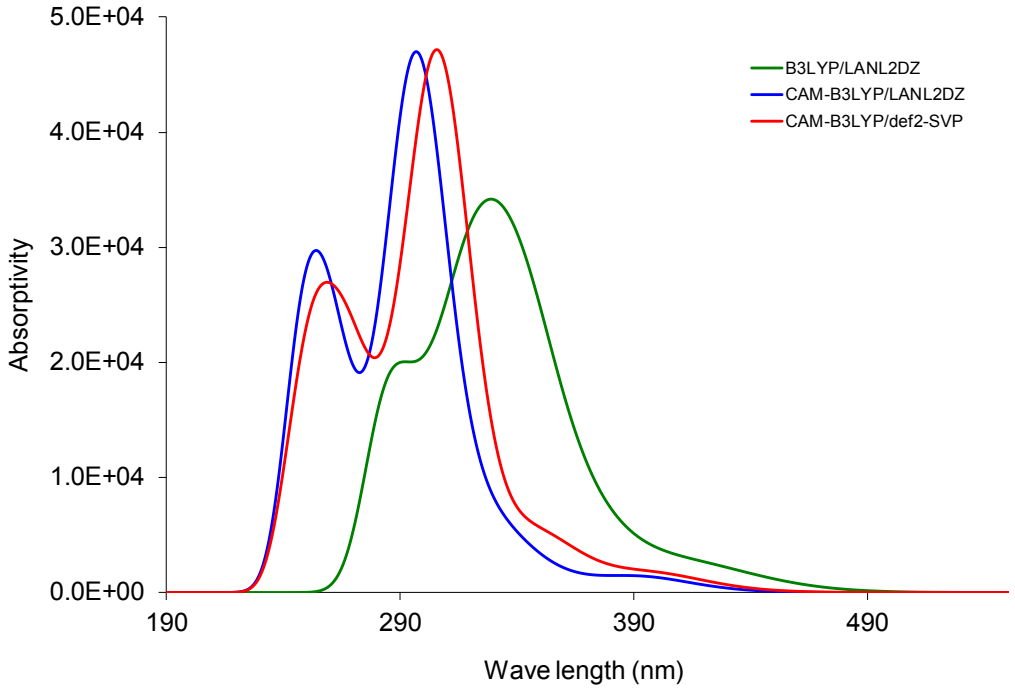
Wave length (nm)
B3LYP/LANL2DZ
CAM-B3LYP/LANL2DZ
CAM-B3LYP/def2-SVP

a)


5.0E+04
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Absorptivity
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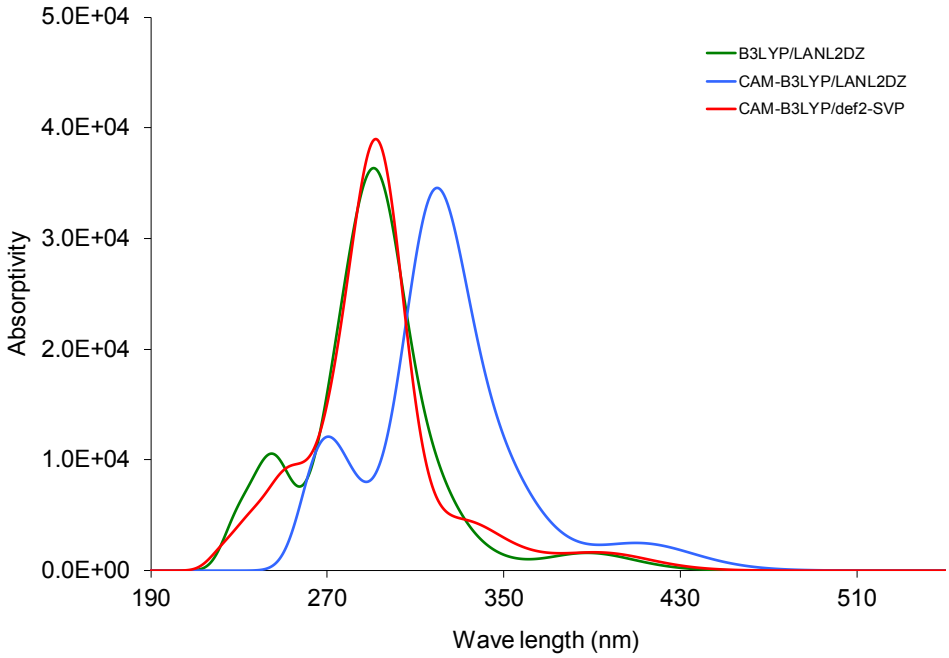
290
390
490
Wave length (nm)
B3LYP/LANL2DZ
CAM-B3LYP/LANL2DZ
CAM-B3LYP/def2-SVP

b)



c)

Fig. S6†: TD-DFT calculated spectra of **1**-**3**.