Electronic Supplementary Material (ESI) for Dalton Transactions.

Insight into the mechanism of CO-release from trypto-CORM using ultra-fast spectroscopy and computational chemistry.

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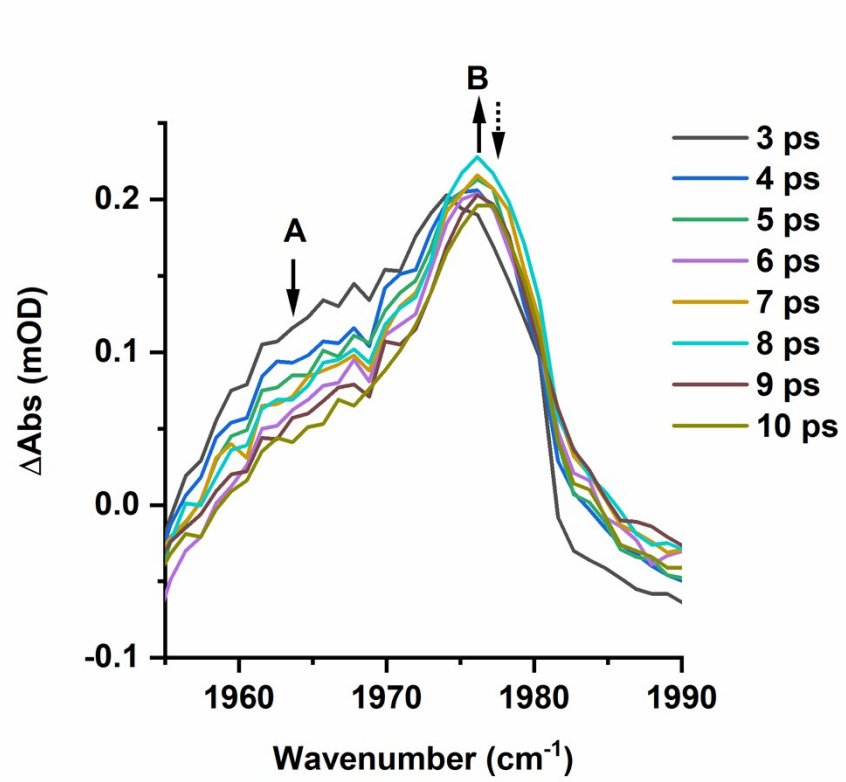
1. TRIR spectra for trypto-CORM with pump-probe delays between 3 and 10 ps

The TRIR spectra recorded with pump-probe delays between 3 and 10 ps are shown in Figure S1. The band for vibrationally excited ^{3}[Mn(tryp)(CO)$_2$(NCMe)], **A**, decreases in intensity over this period, whereas those for the complex in v = 0 (**B**) reach a maximum at 8 ps before beginning to decay to [Mn(tryp)(CO)$_2$(NCMe)$_2$], **C**. In the absence of being



able to model the kinetics for the loss of **A**, these data provide some support for the mechanistic picture **A** → **B** → **C**.

Figure S1 TRIR of spectra for the photolysis of trypto-CORM at 400 nm in the region between 1955 and 1990 cm^{-1} with pump-probe delays between 3 and 10 ps.

2. Results from TD-DFT Calculations

TD-DFT calculations were performed at two different levels of theory using Gaussian 18 and Turbomole. Although the results share many common features (notably in the higher energy region), the calculations in Turbomole at the D3-PBE0/def2-TZVPP//BP86/SV(P) level did not predict a low-energy HOMO-LUMO transition which appears to be present on examination of the experimental spectrum (Figure 2). Hence the model at the PBE0/dgdzvp/def2tzv level with cpcm solvation in acetonitrile is believed to better represent the experimental situation.

Results from calculations at the PBE0/dgdzvp/def2tzv level with cpcm solvation in acetonitrile

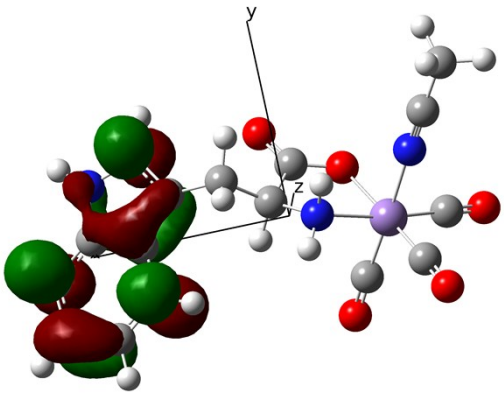
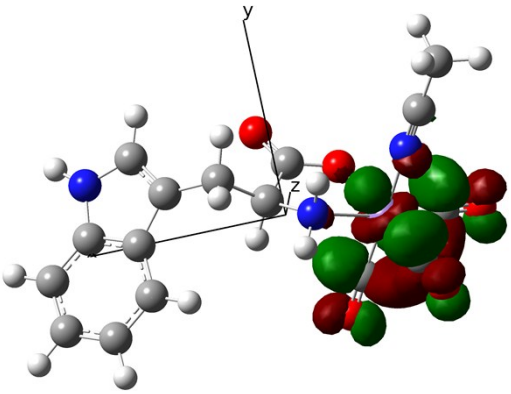
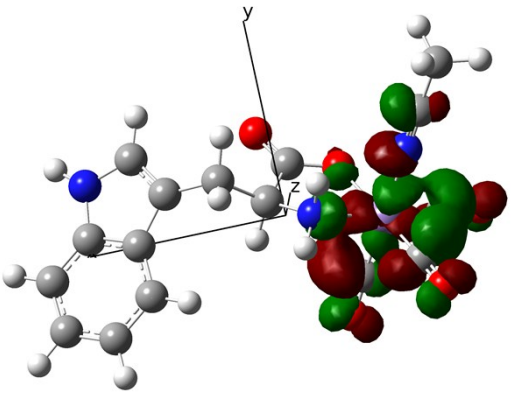
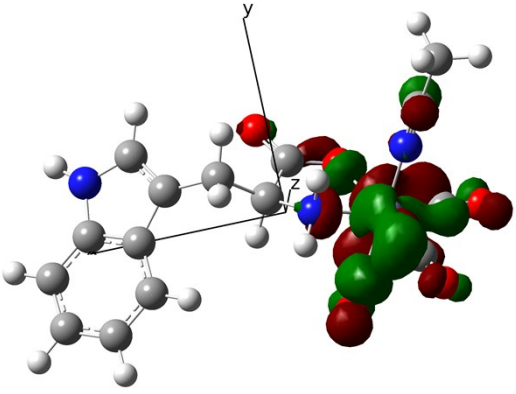
Table S1 Frontier Orbital Energies

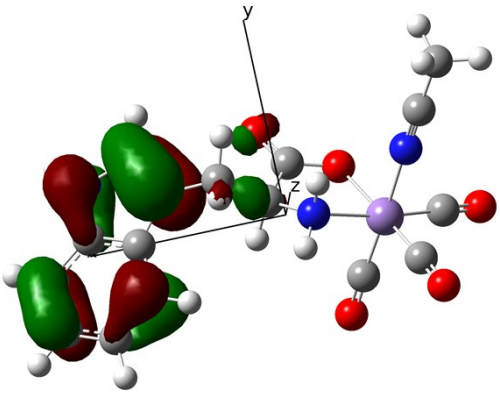
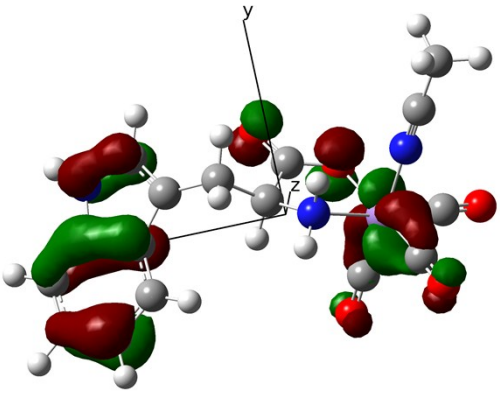
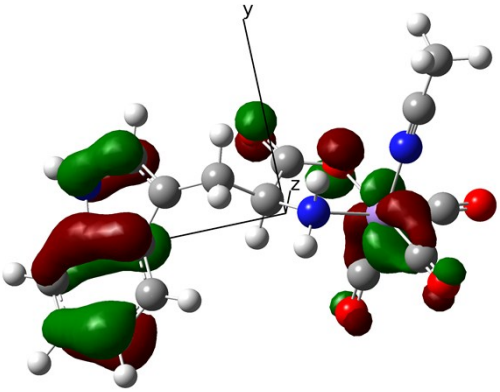
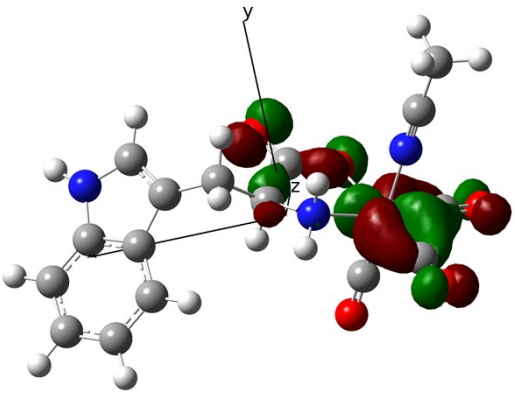
Orbital	Designation	Energy / Hartree	Energy / eV
102	LUMO+3	-0.04284	-1.1657364
101	LUMO+2	-0.05380	-1.4639733
100	LUMO+1	-0.06640	-1.806837
99	LUMO	-0.07255	-1.9741871
98	HOMO	-0.17792	-4.8414523
97	HOMO-1	-0.19949	-5.4284022
96	HOMO-2	-0.19986	-5.4384704
95	HOMO-3	-0.20446	-5.5636428

Table S2 Calculated Excitation Energies and Transitions

Excited State	Energy / nm	Oscillator Strength	From	To	Contribution / %
1	431	0.0212	98	99	100
2	408	0.0006	98	100	100
3	370	0.0085	97	99	35
			96	99	30
			96	100	6
			95	99	6
			97	100	7
			94	100	5
			95	100	5
4	367	0.0001	98	101	99
5	363	0.0047	95	99	46
			97	100	13
			97	99	13
			96	100	11
			94	101	4
			95	101	3
			96	99	3
			94	99	2
6	358	0.0008	96	99	58
			97	99	41
7	355	0.0071	95	99	30
			94	99	24
			97	100	13
			96	100	11
			95	100	6
			95	101	4
			97	101	3
			94	100	3
8	342	0.0007	97	100	51
			96	100	47
9	339	0.0050	95	100	30
			94	100	19
			96	100	14
			94	99	11
			97	101	6
			96	101	5
			97	100	4
			95	99	2
10	325	0.0002	98	103	98

Figure S2 Diagrams of the frontier orbitals at the 0.04 iso value level. Manganese shown in purple, carbon grey, hydrogen white, nitrogen blue and oxygen red.

Orbital	Designation	
102	LUMO+3	
101	LUMO+2	
100	LUMO+1	
99	LUMO	

98	HOMO	
97	HOMO-1	
96	HOMO-2	
95	HOMO-3	

Results from calculations at the D3-PBE0/def2-TZVPP//BP86/SV(P) level in the gas phase

Table S3 Frontier Orbital Energies

Orbital	Designation	Energy / Hartree	Energy / eV
102	LUMO+3	-0.013390	-0.3643606
101	LUMO+2	-0.020081	-0.5464321
100	LUMO+1	-0.033338	-0.9071737
99	LUMO	-0.043408	-1.1811925
98	HOMO	-0.208870	-5.6836451
97	HOMO-1	-0.231198	-6.2912213
96	HOMO-2	-0.244179	-6.6444524
95	HOMO-3	-0.246188	-6.6991201

Table S4 Calculated Excitation Energies and Transitions (with a contribution > 3 %)

Excited State	Energy / nm	Oscillator Strength	From	To	Contribution / %
1	368	0.0031	95	99	27
			94	99	15
			96	100	10
			95	111	8
			94	111	5
			95	100	3
			95	104	3
			96	101	3
2	358	0.0048	96	100	22
			96	99	12
			93	99	9
			96	111	8
			95	99	7
			96	104	7
			96	101	6
3	351	0.0050	96	99	42
			96	100	10
			96	103	8
			96	112	8
			93	100	4
4	344	0.0141	93	99	35
			93	112	11
			93	103	7
			96	99	6
			93	111	5
			95	100	4
			95	101	3
			93	101	3
			96	101	3
5	323	0.0095	95	100	21
			94	100	12
			96	99	9
			95	101	7
			94	112	5
			94	101	4
			95	103	4
			95	112	4
			94	99	3
			94	103	3
			95	99	3
6	316	0.0058	98	99	35
			93	100	27
			93	104	5
			93	101	4
			93	99	4
			93	112	3
			93	111	3
7	314	0.0085	98	99	63
			93	100	13
			93	99	4
			93	104	3
8	297	0.0011	96	101	32

			95	101	18
			94	101	7
			96	104	5
			95	104	5
			96	105	5
			95	105	3
			96	100	3
9	292	0.0018	98	100	97
10	286	0.0023	94	101	15
			93	101	14
			95	101	11
			96	101	11
			93	104	9
			94	104	5
			96	106	4
			94	105	3
			93	100	3

3. Collated energies and vibrational spectra.

[**1a**]

SCF Energy (au) BP86/SV(P)	-2328.3109983610
SCF Energy (au) PBE0/def2-TZVPP	-2327.919444269
Zero Point Energy (au)	0.3133890
Chemical potential (kJ mol^{-1})	656.59
Dispersion correction (au) PBE0/def2-TZVPP	-0.04982762
SCF Energy (au) PBE0/def2-TZVPP COSMO (NCMe)	-2327.9693616435

xyz coordinates

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O	-2.25565	0.99108	1.23436
O	-0.39848	2.24715	1.44821
C	-1.02933	1.30445	0.95762
C	-0.33877	0.34944	-0.07026
C	0.86573	0.97657	-0.81176
N	-1.39671	-0.16240	-0.98664
H	0.01560	-0.53152	0.50792
H	-1.57696	0.52948	-1.73282
Mn	-3.19401	-0.39749	0.09347
H	0.61443	2.03418	-1.05388
H	0.99145	0.44330	-1.78234
C	2.17433	0.89972	-0.06454
C	2.49751	1.53643	1.12695
N	3.78889	1.20221	1.50002
H	1.85794	2.19139	1.73172
H	4.26057	1.54285	2.33760
C	4.33851	0.34130	0.56754
C	4.91277	-1.33257	-1.58585
C	5.88223	-1.10407	-0.57555
C	5.60770	-0.26420	0.51206
C	3.33828	0.12464	-0.44189
C	3.65132	-0.72786	-1.52799
H	5.16131	-1.99601	-2.43087
H	6.86834	-1.59207	-0.64778
H	6.36221	-0.08415	1.29583
H	2.91284	-0.91403	-2.32658
C	-3.89021	-1.58467	-1.04155
N	-2.33135	-1.73861	1.14836
N	-3.87884	1.11051	-0.86208
O	-4.31148	-2.36589	-1.80913
C	-1.81294	-2.52928	1.84331
C	-4.28268	2.08451	-1.37645
C	-4.64761	-0.44363	1.14013
O	-5.59595	-0.47325	1.82022
H	-1.08828	-1.02688	-1.45775
C	-4.83017	3.29951	-1.96571
H	-5.89382	3.42753	-1.66481
H	-4.78393	3.26282	-3.07645
H	-4.26096	4.18964	-1.61788
C	-1.19917	-3.50845	2.73085
H	-1.60145	-3.40158	3.76280
H	-0.09667	-3.36650	2.77164
H	-1.40653	-4.54362	2.37997

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
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2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	9.02	0.28371	YES	YES
8	a	21.58	0.08763	YES	YES
9	a	24.11	0.27269	YES	YES
10	a	30.39	0.02165	YES	YES
11	a	34.85	2.34477	YES	YES
12	a	40.53	6.62361	YES	YES
13	a	44.25	5.64670	YES	YES
14	a	54.42	3.30103	YES	YES
15	a	64.85	0.13506	YES	YES
16	a	74.09	0.80917	YES	YES
17	a	80.34	3.53917	YES	YES
18	a	90.13	0.31953	YES	YES
19	a	98.57	5.11297	YES	YES
20	a	133.99	3.26022	YES	YES
21	a	147.13	0.16147	YES	YES
22	a	150.25	1.91526	YES	YES
23	a	170.31	0.71773	YES	YES
24	a	201.67	1.57964	YES	YES
25	a	219.25	3.29242	YES	YES
26	a	225.22	2.57075	YES	YES
27	a	227.98	2.69092	YES	YES
28	a	237.44	1.23095	YES	YES
29	a	246.03	1.31838	YES	YES
30	a	274.79	5.49643	YES	YES
31	a	291.59	0.75683	YES	YES
32	a	307.29	11.41295	YES	YES
33	a	337.99	7.75372	YES	YES
34	a	361.76	43.90404	YES	YES
35	a	372.09	21.82034	YES	YES
36	a	403.34	4.76664	YES	YES
37	a	419.47	10.64061	YES	YES
38	a	422.73	14.62726	YES	YES
39	a	450.37	3.08538	YES	YES
40	a	454.75	10.74644	YES	YES
41	a	462.29	50.42097	YES	YES
42	a	465.42	2.05815	YES	YES
43	a	476.18	1.62453	YES	YES
44	a	484.57	6.75512	YES	YES
45	a	507.80	1.20281	YES	YES
46	a	539.04	9.26693	YES	YES
47	a	542.05	7.80254	YES	YES
48	a	561.33	1.15600	YES	YES
49	a	568.92	8.32073	YES	YES
50	a	578.98	23.40503	YES	YES

[**1b**]

SCF Energy (au) BP86/SV(P)	-2328.3032678590
SCF Energy (au) PBE0/def2-TZVPP	-2327.911281741
Zero Point Energy (au)	0.3129730
Chemical potential (kJ mol^{-1})	656.38
Dispersion correction (au) PBE0/def2-TZVPP	-0.04933641
SCF Energy (au) PBE0/def2-TZVPP COSMO (NCMe)	-2327.9644134476

xyz coordinates

43

O	-1.90085	1.05183	1.73315
O	-0.05180	2.32769	1.85422
C	-0.67112	1.34369	1.43737
C	0.02044	0.31889	0.48276
C	1.23520	0.88946	-0.28548
N	-1.04068	-0.22715	-0.41109
H	0.35373	-0.53209	1.11784
H	-1.21468	0.43512	-1.18578
Mn	-2.81084	-0.41832	0.71058
H	0.99231	1.93218	-0.59441
H	1.36271	0.29558	-1.21995
C	2.53898	0.84977	0.47297
C	2.83539	1.49599	1.66627
N	4.13208	1.19669	2.04950
H	2.17749	2.14176	2.26150
H	4.58258	1.53855	2.89816
C	4.71174	0.35013	1.12241
C	5.34923	-1.30521	-1.02760
C	6.30314	-1.05272	-0.00822
C	5.99667	-0.22217	1.07794
C	3.72647	0.10747	0.10439
C	4.07161	-0.73469	-0.97987
H	5.62245	-1.96160	-1.87054
H	7.30180	-1.51581	-0.07126
H	6.73835	-0.02508	1.86972
H	3.34464	-0.94034	-1.78426
N	-3.50380	-1.65967	-0.53881
C	-2.12649	-1.69615	1.75450
N	-3.53836	1.09789	-0.35358
C	-3.90305	-2.42866	-1.33725
O	-1.70732	-2.53892	2.44925
C	-3.96270	2.07135	-0.84650
C	-4.27281	-0.41501	1.73720
O	-5.23216	-0.41431	2.40546
H	-0.74073	-1.11449	-0.84427
C	-4.51104	3.30381	-1.39766
H	-5.56729	3.43219	-1.07364
H	-4.48168	3.29364	-2.50893
H	-3.92539	4.17694	-1.03487
C	-4.44638	-3.40999	-2.26874
H	-3.98955	-3.30598	-3.27823
H	-5.54802	-3.28707	-2.37563
H	-4.25029	-4.44519	-1.90864

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
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3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	12.85	0.66636	YES	YES
8	a	23.32	1.72261	YES	YES
9	a	31.86	5.43166	YES	YES
10	a	32.64	0.06994	YES	YES
11	a	33.22	0.62289	YES	YES
12	a	38.67	3.65167	YES	YES
13	a	42.66	0.15658	YES	YES
14	a	52.57	0.97642	YES	YES
15	a	61.20	0.23517	YES	YES
16	a	71.57	1.46744	YES	YES
17	a	82.33	0.54994	YES	YES
18	a	95.42	0.44170	YES	YES
19	a	96.77	3.48789	YES	YES
20	a	134.85	0.02317	YES	YES
21	a	149.77	4.71228	YES	YES
22	a	152.21	2.49060	YES	YES
23	a	164.82	0.10978	YES	YES
24	a	190.72	1.06229	YES	YES
25	a	213.86	5.80496	YES	YES
26	a	219.07	2.62535	YES	YES
27	a	225.07	1.94983	YES	YES
28	a	230.75	5.31514	YES	YES
29	a	245.21	7.35961	YES	YES
30	a	261.70	16.82440	YES	YES
31	a	278.49	11.22016	YES	YES
32	a	298.22	12.93450	YES	YES
33	a	334.09	9.14481	YES	YES
34	a	364.28	5.87335	YES	YES
35	a	383.75	8.68358	YES	YES
36	a	401.95	4.34112	YES	YES
37	a	416.76	4.36233	YES	YES
38	a	422.85	15.30393	YES	YES
39	a	426.08	3.53981	YES	YES
40	a	453.65	13.07355	YES	YES
41	a	455.61	1.56050	YES	YES
42	a	463.46	50.82765	YES	YES
43	a	475.91	9.13315	YES	YES
44	a	491.99	4.81840	YES	YES
45	a	503.47	21.69104	YES	YES
46	a	533.69	10.10289	YES	YES
47	a	541.75	0.25286	YES	YES
48	a	547.50	19.94687	YES	YES
49	a	572.97	2.15453	YES	YES
50	a	582.40	10.46961	YES	YES

[**1c**]

SCF Energy (au) BP86/SV(P)	-2328.3078648380
SCF Energy (au) PBE0/def2-TZVPP	-2327.917075970
Zero Point Energy (au)	0.3133947
Chemical potential (kJ mol^{-1})	656.11
Dispersion correction (au) PBE0/def2-TZVPP	-0.04930500
SCF Energy (au) PBE0/def2-TZVPP COSMO (NCMe)	-2327.9686362922

xyz coordinates
43

O	-1.75367	0.60032	1.20412
O	0.08418	1.88090	1.44439
C	-0.52340	0.92300	0.95393
C	0.18895	-0.03654	-0.05097
C	1.39716	0.58755	-0.78716
N	-0.85910	-0.54925	-0.98600
H	0.53041	-0.91774	0.53668
H	-1.02408	0.15001	-1.73002
Mn	-2.62760	-0.81865	0.04845
H	1.14005	1.64054	-1.04592
H	1.53485	0.04280	-1.74991
C	2.70150	0.52962	-0.03096
C	2.98842	1.12088	1.19264
N	4.29095	0.82615	1.55927
H	2.31909	1.72350	1.81951
H	4.73766	1.13438	2.42263
C	4.88401	0.03727	0.59043
C	5.54638	-1.49916	-1.63861
C	6.49773	-1.27986	-0.60929
C	6.17887	-0.50903	0.51655
C	3.90139	-0.17228	-0.43729
C	4.25904	-0.95429	-1.56180
H	5.82895	-2.10941	-2.51251
H	7.50414	-1.72196	-0.69589
H	6.91846	-0.33784	1.31631
H	3.53431	-1.13449	-2.37421
C	-3.34986	-1.97225	-1.09948
C	-1.96282	-2.17243	1.00819
N	-3.33391	0.75020	-0.94702
O	-3.79088	-2.73390	-1.87761
O	-1.56310	-3.07082	1.64162
C	-3.73453	1.72171	-1.46326
N	-4.14732	-0.70520	1.19825
C	-5.03289	-0.58443	1.95696
H	-0.53143	-1.40338	-1.46219
C	-4.24394	2.93857	-2.08300
H	-5.30966	3.09685	-1.80738
H	-4.17463	2.87664	-3.19108
H	-3.65861	3.81952	-1.73950
C	-6.11777	-0.45489	2.92137
H	-6.96980	0.11525	2.48929
H	-5.76672	0.07934	3.83210
H	-6.49080	-1.45720	3.22835

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	13.51	0.47096	YES	YES
8	a	16.10	0.05956	YES	YES
9	a	24.23	2.47368	YES	YES
10	a	30.68	0.00304	YES	YES
11	a	31.68	1.56262	YES	YES
12	a	40.02	2.59512	YES	YES
13	a	43.47	2.67803	YES	YES
14	a	48.66	3.82620	YES	YES
15	a	62.30	2.04994	YES	YES
16	a	73.04	2.52817	YES	YES
17	a	82.89	0.80725	YES	YES
18	a	91.70	0.37704	YES	YES
19	a	98.54	6.86107	YES	YES
20	a	140.19	5.18759	YES	YES
21	a	141.63	1.97542	YES	YES
22	a	152.87	1.80034	YES	YES
23	a	168.97	1.49637	YES	YES
24	a	202.88	0.80788	YES	YES
25	a	210.48	1.94471	YES	YES
26	a	221.93	7.56124	YES	YES
27	a	226.98	1.31002	YES	YES
28	a	234.21	5.20262	YES	YES
29	a	240.65	2.62917	YES	YES
30	a	268.54	18.87783	YES	YES
31	a	283.28	1.53302	YES	YES
32	a	307.72	14.16843	YES	YES
33	a	337.16	6.34623	YES	YES
34	a	339.94	12.78841	YES	YES
35	a	376.55	5.92223	YES	YES
36	a	404.57	2.93402	YES	YES
37	a	418.99	0.71073	YES	YES
38	a	422.55	12.40612	YES	YES
39	a	424.53	3.56782	YES	YES
40	a	454.14	13.14983	YES	YES
41	a	459.59	0.87647	YES	YES
42	a	461.13	54.11320	YES	YES
43	a	495.53	10.81240	YES	YES
44	a	498.82	3.90871	YES	YES
45	a	507.20	22.38410	YES	YES
46	a	531.72	13.94171	YES	YES
47	a	541.98	0.81047	YES	YES
48	a	558.57	9.01868	YES	YES
49	a	573.44	1.82744	YES	YES
50	a	583.09	6.02266	YES	YES

[**1d**]

SCF Energy (au) BP86/SV(P)	-2328.2836323860
SCF Energy (au) PBE0/def2-TZVPP	-2327.891903135
Zero Point Energy (au)	0.3123734
Chemical potential (kJ mol^{-1})	653.05
Dispersion correction (au) PBE0/def2-TZVPP	0.04909866
SCF Energy (au) PBE0/def2-TZVPP COSMO (NCMe)	-2327.9404071538

xyz coordinates

43

O	-1.76887	1.42838	1.19579
O	0.11762	2.61130	1.52288
C	-0.51751	1.69784	0.98687
C	0.18501	0.73079	-0.01898
C	1.42452	1.32969	-0.72372
N	-0.86011	0.25680	-0.97778
H	0.49256	-0.16577	0.56533
H	-0.98016	0.96849	-1.71664
Mn	-2.63340	-0.00745	0.07299
H	1.20290	2.39259	-0.97392
H	1.56439	0.79319	-1.69090
C	2.71291	1.22491	0.05512
C	2.99865	1.80513	1.28436
N	4.28482	1.46873	1.67167
H	2.33774	2.42662	1.90165
H	4.72818	1.76525	2.54087
C	4.86858	0.66307	0.71128
C	5.52007	-0.88932	-1.50969
C	6.46084	-0.70101	-0.46461
C	6.14713	0.07755	0.65737
C	3.89653	0.48566	-0.33275
C	4.24892	-0.30513	-1.45283
H	5.79877	-1.50546	-2.38076
H	7.45492	-1.17274	-0.53606
H	6.87863	0.22580	1.46907
H	3.53310	-0.46016	-2.27829
N	-3.30097	-1.32659	-1.10248
C	-1.90050	-1.35358	1.11122
C	-3.49149	1.29835	-0.92220
C	-3.68235	-2.15840	-1.84779
O	-1.54380	-2.24618	1.76851
O	-4.08427	2.08008	-1.54778
N	-4.12844	-0.00594	1.24929
C	-5.00882	0.05737	2.02391
H	-0.55069	-0.60219	-1.45997
C	-6.08112	0.16272	3.00515
C	-4.19669	-3.19367	-2.73642
H	-6.95974	0.69251	2.57461
H	-5.73788	0.73154	3.89849
H	-6.41344	-0.84428	3.34272
H	-3.75725	-3.10990	-3.75631
H	-5.30370	-3.11957	-2.83605
H	-3.95558	-4.20701	-2.34323

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	15.21	0.19504	YES	YES
8	a	25.25	0.80856	YES	YES
9	a	26.50	1.13283	YES	YES
10	a	27.41	0.06336	YES	YES
11	a	30.36	1.61758	YES	YES
12	a	38.94	4.63917	YES	YES
13	a	43.90	0.55296	YES	YES
14	a	56.46	0.27625	YES	YES
15	a	58.63	2.69186	YES	YES
16	a	60.92	0.77732	YES	YES
17	a	71.10	0.95125	YES	YES
18	a	77.54	0.49061	YES	YES
19	a	97.98	3.92064	YES	YES
20	a	139.98	1.04175	YES	YES
21	a	145.10	6.50023	YES	YES
22	a	148.89	1.93560	YES	YES
23	a	162.36	2.39923	YES	YES
24	a	186.71	5.55594	YES	YES
25	a	196.87	0.47284	YES	YES
26	a	200.88	1.33158	YES	YES
27	a	216.20	2.07002	YES	YES
28	a	224.60	7.80370	YES	YES
29	a	240.56	0.66902	YES	YES
30	a	268.18	12.53891	YES	YES
31	a	298.43	12.14844	YES	YES
32	a	333.74	6.35770	YES	YES
33	a	342.96	15.95238	YES	YES
34	a	368.36	2.91295	YES	YES
35	a	376.71	11.26861	YES	YES
36	a	403.18	0.99614	YES	YES
37	a	410.16	7.55520	YES	YES
38	a	416.02	3.75043	YES	YES
39	a	420.47	6.61805	YES	YES
40	a	423.41	14.03050	YES	YES
41	a	453.84	23.85393	YES	YES
42	a	456.48	57.73929	YES	YES
43	a	462.33	53.80090	YES	YES
44	a	465.70	16.68770	YES	YES
45	a	494.48	1.75202	YES	YES
46	a	509.22	0.35808	YES	YES
47	a	533.23	34.20814	YES	YES
48	a	541.72	0.67879	YES	YES
49	a	547.18	21.20943	YES	YES
50	a	573.26	1.58969	YES	YES

[1][**2a**]

SCF Energy (au) BP86/SV(P)	-2195.6211283900
SCF Energy (au) PBE0/def2-TZVPP	-2195.246541176
Zero Point Energy (au)	0.2667541
Chemical potential (kJ mol^{-1})	552.06
Dispersion correction (au) PBE0/def2-TZVPP	-0.04567120
SCF Energy (au) PBE0/def2-TZVPP COSMO (NCMe)	-2195.291547595

xyz coordinates
37

O	-1.57057	0.14491	1.95641
O	-0.64713	2.18410	2.23502
C	-0.57147	1.00149	1.92377
C	0.80223	0.37484	1.54672
C	1.71824	1.32858	0.73792
N	0.54951	-0.92761	0.88074
H	1.29778	0.15789	2.52048
H	0.48155	-0.74589	-0.14073
Mn	-1.28836	-1.70755	1.52053
H	2.77161	0.98005	0.83432
H	1.65089	2.31612	1.24358
C	1.36912	1.45227	-0.72331
C	1.97761	0.75312	-1.76316
N	1.41845	1.12078	-2.97422
H	2.81306	0.03974	-1.73103
H	1.69810	0.76006	-3.88619
C	0.43230	2.06900	-2.75706
C	-1.38305	3.92426	-1.75778
C	-1.30331	3.67590	-3.15252
C	-0.39729	2.74446	-3.67243
C	0.36725	2.30145	-1.34328
C	-0.56262	3.24852	-0.84856
H	-2.11339	4.66039	-1.38359
H	-1.96895	4.22362	-3.84015
H	-0.33570	2.54940	-4.75560
H	-0.64889	3.42673	0.23492
C	-1.86407	-2.13713	-0.06163
O	-2.24214	-2.38070	-1.14733
C	-2.85785	-2.20139	2.21306
O	-3.88000	-2.54325	2.66163
H	1.34066	-1.58016	1.00327
N	-0.47842	-3.36193	1.85019
C	0.09073	-4.35524	2.13858
C	0.70916	-5.61556	2.53002
H	0.26698	-5.99385	3.47957
H	1.80505	-5.49774	2.68270
H	0.55293	-6.38966	1.74513

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	14.53	0.58980	YES	YES

8	a	20.39	1.25374	YES	YES
9	a	22.04	0.21608	YES	YES
10	a	31.61	0.69865	YES	YES
11	a	46.15	1.04285	YES	YES
12	a	60.83	0.42242	YES	YES
13	a	69.86	0.84726	YES	YES
14	a	83.11	7.14959	YES	YES
15	a	95.00	2.84456	YES	YES
16	a	96.54	0.60489	YES	YES
17	a	115.60	0.75727	YES	YES
18	a	135.75	3.80984	YES	YES
19	a	155.18	2.23274	YES	YES
20	a	164.94	0.73052	YES	YES
21	a	193.86	2.44121	YES	YES
22	a	207.30	2.60966	YES	YES
23	a	219.20	5.05331	YES	YES
24	a	266.50	2.91277	YES	YES
25	a	282.88	8.44551	YES	YES
26	a	299.80	14.65058	YES	YES
27	a	342.85	22.14009	YES	YES
28	a	380.59	4.90140	YES	YES
29	a	394.10	5.43877	YES	YES
30	a	413.49	34.91466	YES	YES
31	a	425.14	7.15928	YES	YES
32	a	429.43	16.09375	YES	YES
33	a	449.52	37.13057	YES	YES
34	a	455.13	6.67686	YES	YES
35	a	460.49	2.82461	YES	YES
36	a	492.53	0.05479	YES	YES
37	a	502.41	8.15391	YES	YES
38	a	520.82	0.54548	YES	YES
39	a	531.07	4.34085	YES	YES
40	a	549.42	35.33081	YES	YES
41	a	568.95	2.80054	YES	YES
42	a	574.46	7.45277	YES	YES
43	a	579.38	21.33790	YES	YES
44	a	586.59	9.05927	YES	YES
45	a	612.73	1.66593	YES	YES
46	a	654.03	4.77129	YES	YES
47	a	667.89	7.43125	YES	YES
48	a	695.80	1.07776	YES	YES
49	a	698.48	13.01092	YES	YES
50	a	735.97	75.74678	YES	YES

[1][**2b**]

SCF Energy (au) BP86/SV(P)	-2195.6241671690
SCF Energy (au) PBE0/def2-TZVPP	-2195.249102436
Zero Point Energy (au)	0.2669995
Chemical potential (kJ mol^{-1})	553.18
Dispersion correction (au) PBE0/def2-TZVPP	-0.04571178
SCF Energy (au) PBE0/def2-TZVPP COSMO (NCMe)	-2195.2931205951

xyz coordinates
37

O	-0.91657	-0.45584	2.69596
O	0.06457	1.53979	3.07111
C	0.06221	0.41585	2.58168
C	1.28581	-0.12092	1.78621
C	2.12028	0.98938	1.09786
N	0.78764	-1.16989	0.85970
H	1.92199	-0.63321	2.54227
H	0.51691	-0.70206	-0.03001
Mn	-0.86779	-2.10739	1.71901
H	3.16798	0.63318	0.98038
H	2.13814	1.84078	1.81321
C	1.60682	1.43521	-0.24909
C	2.14671	1.06079	-1.47658
N	1.44531	1.65843	-2.50946
H	3.01903	0.42741	-1.68938
H	1.67477	1.58011	-3.50007
C	0.43170	2.44255	-1.98314
C	-1.38011	3.85004	-0.40942
C	-1.42892	3.94888	-1.82398
C	-0.52476	3.24784	-2.63085
C	0.49682	2.32273	-0.55454
C	-0.43105	3.04801	0.23400
H	-2.10672	4.41725	0.19505
H	-2.19031	4.59027	-2.29801
H	-0.55783	3.32876	-3.72993
H	-0.40428	2.96817	1.33266
N	-1.06678	-3.15977	0.17388
C	-1.22549	-3.74682	-0.83709
C	-2.39130	-2.69170	2.44598
O	-3.38593	-3.09045	2.90945
H	1.52995	-1.84035	0.60781
C	0.01356	-3.30083	2.61919
O	0.63768	-4.07414	3.24804
C	-1.49114	-4.50738	-2.05108
H	-1.64645	-3.82927	-2.91994
H	-2.40856	-5.12696	-1.92996
H	-0.64393	-5.18844	-2.29091

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	13.90	1.20042	YES	YES

8	a	20.71	0.25384	YES	YES
9	a	21.01	0.22465	YES	YES
10	a	32.20	0.92056	YES	YES
11	a	55.49	1.80850	YES	YES
12	a	60.90	1.54071	YES	YES
13	a	62.21	0.46300	YES	YES
14	a	82.96	1.31844	YES	YES
15	a	95.75	0.71531	YES	YES
16	a	103.77	6.64772	YES	YES
17	a	123.56	1.86150	YES	YES
18	a	142.19	1.40013	YES	YES
19	a	157.44	2.18457	YES	YES
20	a	174.38	1.83850	YES	YES
21	a	198.48	2.53276	YES	YES
22	a	208.57	0.71474	YES	YES
23	a	219.29	5.29389	YES	YES
24	a	263.27	4.42842	YES	YES
25	a	280.09	11.02389	YES	YES
26	a	302.52	12.00990	YES	YES
27	a	349.46	13.53624	YES	YES
28	a	387.51	5.52751	YES	YES
29	a	395.92	4.67652	YES	YES
30	a	406.10	24.51926	YES	YES
31	a	424.24	35.20364	YES	YES
32	a	434.43	7.61998	YES	YES
33	a	448.89	31.19952	YES	YES
34	a	452.76	5.23166	YES	YES
35	a	456.17	1.36606	YES	YES
36	a	490.47	0.50443	YES	YES
37	a	505.31	12.07263	YES	YES
38	a	519.72	1.07393	YES	YES
39	a	527.47	4.13487	YES	YES
40	a	550.27	18.05918	YES	YES
41	a	572.85	1.92039	YES	YES
42	a	577.23	12.19199	YES	YES
43	a	584.27	25.70309	YES	YES
44	a	597.74	7.98329	YES	YES
45	a	617.45	1.79909	YES	YES
46	a	637.02	5.94599	YES	YES
47	a	665.70	1.85002	YES	YES
48	a	698.52	0.02729	YES	YES
49	a	704.12	10.14782	YES	YES
50	a	738.13	70.92771	YES	YES

[1][**2c**]

SCF Energy (au) BP86/SV(P)	-2195.6325229470
SCF Energy (au) PBE0/def2-TZVPP	-2195.258922628
Zero Point Energy (au)	0.2675361
Chemical potential (kJ mol^{-1})	554.74
Dispersion correction (au) PBE0/def2-TZVPP	-0.04558551
SCF Energy (au) PBE0/def2-TZVPP COSMO (NCMe)	-2195.2991311080

xyz coordinates
37

O	-0.98229	-0.83534	1.69729
O	-0.01898	0.98199	2.62910
C	0.03596	-0.04391	1.96184
C	1.38122	-0.56453	1.38712
C	2.39514	0.55761	1.04771
N	1.05483	-1.45455	0.23985
H	1.81113	-1.20995	2.18563
H	0.98847	-0.85462	-0.60810
Mn	-0.75202	-2.37392	0.55778
H	3.42567	0.14129	1.09722
H	2.30116	1.30507	1.86654
C	2.19624	1.20845	-0.29851
C	2.95157	0.94131	-1.43725
N	2.50593	1.71122	-2.49685
H	3.81139	0.26861	-1.56134
H	2.91006	1.71519	-3.43329
C	1.44814	2.50111	-2.07851
C	-0.57189	3.84382	-0.71543
C	-0.33156	4.11061	-2.08811
C	0.68096	3.44436	-2.78872
C	1.21907	2.20952	-0.69203
C	0.18846	2.90399	-0.01062
H	-1.37679	4.38761	-0.19434
H	-0.95113	4.85568	-2.61411
H	0.87082	3.65303	-3.85449
H	-0.01217	2.69404	1.05222
C	-0.81386	-3.12702	-1.03961
O	-0.85865	-3.56460	-2.12946
N	-2.55512	-2.78421	0.98963
C	-3.67193	-2.95168	1.30551
H	1.82157	-2.11702	0.04868
C	-0.10608	-3.86354	1.17866
O	0.34002	-4.84482	1.65023
C	-5.05537	-3.16798	1.70543
H	-5.23516	-2.75410	2.72224
H	-5.29259	-4.25462	1.72123
H	-5.75221	-2.66809	0.99686

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN

^{3}[**2a**]

SCF Energy (au) BP86/SV(P)	-2195.6064991540
SCF Energy (au) PBE0/def2-TZVPP	-2195.25098729
Zero Point Energy (au)	0.2653253
Chemical potential (kJ mol^{-1})	543.99
Dispersion correction (au) PBE0/def2-TZVPP	-0.04510102
SCF Energy (au) PBE0/def2-TZVPP COSMO (NCMe)	-2195.2953244998
<s^2> PBE0/def2-TZVPP	2.15834922

xyz coordinates
37

O	-1.03889	-0.58584	1.60549
O	0.29642	1.10562	2.27951
C	0.06740	0.10912	1.59642
C	1.17452	-0.45456	0.65290
C	2.02679	0.64939	-0.02360
N	0.54548	-1.40126	-0.30632
H	1.84081	-1.05819	1.30930
H	0.17784	-0.84943	-1.10646
Mn	-1.12266	-2.27842	0.63078
H	3.00416	0.21377	-0.33201
H	2.23264	1.39661	0.77341
C	1.38423	1.30602	-1.21906
C	1.66255	1.00598	-2.55001
N	0.90497	1.80609	-3.38740
H	2.38646	0.29283	-2.96829
H	0.94272	1.79429	-4.40647
C	0.11317	2.64960	-2.62547
C	-1.20568	4.08524	-0.64177
C	-1.45897	4.35396	-2.01185
C	-0.80492	3.64028	-3.02300
C	0.38345	2.35918	-1.24677
C	-0.29609	3.09824	-0.24717
H	-1.74289	4.66356	0.12780
H	-2.18519	5.13697	-2.28656
H	-1.00020	3.84800	-4.08794
H	-0.12030	2.87948	0.81834
C	-1.11451	-3.73104	-0.43057
O	-1.08574	-4.66380	-1.14293
C	-2.90007	-2.21789	0.18146
O	-4.02449	-2.21488	-0.12984
H	1.23935	-2.05081	-0.70760
N	-0.48614	-3.28591	2.24072
C	-0.23288	-3.75824	3.28337
C	0.05429	-4.34590	4.58405
H	-0.79383	-4.16096	5.27949
H	0.96995	-3.89326	5.02346
H	0.20625	-5.44382	4.49458

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	15.80	1.51736	YES	YES

8	a	17.66	1.83862	YES	YES
9	a	20.34	0.67829	YES	YES
10	a	28.63	2.89171	YES	YES
11	a	35.42	2.00840	YES	YES
12	a	45.60	0.59300	YES	YES
13	a	59.93	1.06846	YES	YES
14	a	73.92	2.36733	YES	YES
15	a	88.09	0.28986	YES	YES
16	a	95.34	12.12399	YES	YES
17	a	105.20	2.73460	YES	YES
18	a	128.47	1.42540	YES	YES
19	a	142.00	0.20874	YES	YES
20	a	160.17	4.87288	YES	YES
21	a	166.74	3.97003	YES	YES
22	a	210.99	0.19537	YES	YES
23	a	219.38	5.25391	YES	YES
24	a	243.66	6.51459	YES	YES
25	a	274.16	3.21409	YES	YES
26	a	289.40	2.34357	YES	YES
27	a	307.05	9.16900	YES	YES
28	a	347.01	19.52844	YES	YES
29	a	364.03	1.42716	YES	YES
30	a	379.39	2.83697	YES	YES
31	a	400.59	2.85701	YES	YES
32	a	408.25	23.99586	YES	YES
33	a	430.05	22.76672	YES	YES
34	a	447.66	22.30679	YES	YES
35	a	451.93	12.02415	YES	YES
36	a	454.36	11.29883	YES	YES
37	a	458.08	9.50069	YES	YES
38	a	485.75	1.85147	YES	YES
39	a	510.13	13.01191	YES	YES
40	a	517.38	23.21182	YES	YES
41	a	530.34	1.28690	YES	YES
42	a	543.82	10.20304	YES	YES
43	a	569.29	1.73271	YES	YES
44	a	576.70	14.03112	YES	YES
45	a	604.99	1.33663	YES	YES
46	a	622.38	1.94842	YES	YES
47	a	627.48	7.97181	YES	YES
48	a	657.81	2.45594	YES	YES
49	a	696.17	1.58486	YES	YES
50	a	736.60	72.40771	YES	YES

^{3}[**2b**]

SCF Energy (au) BP86/SV(P)	-2195.6087849860
SCF Energy (au) PBE0/def2-TZVPP	-2196.974458343
Zero Point Energy (au)	0.2655588
Chemical potential (kJ mol^{-1})	552.92
Dispersion correction (au) PBE0/def2-TZVPP	-0.08691920
SCF Energy (au) PBE0/def2-TZVPP COSMO (NCMe)	-2195.2950263680
<s^2> PBE0/def2-TZVPP	2.16125154

xyz coordinates
37

O	-1.00836	-0.82139	2.61181
O	-0.86296	1.42706	2.73827
C	-0.37265	0.31445	2.54538
C	1.15736	0.17600	2.26945
C	1.75001	1.38357	1.49981
N	1.42442	-1.13499	1.61720
H	1.62471	0.13939	3.27855
H	1.46168	-0.98737	0.58934
Mn	-0.18241	-2.46935	1.96647
H	2.84139	1.45021	1.70714
H	1.26973	2.28307	1.94326
C	1.54092	1.35024	0.00619
C	2.50243	0.98797	-0.93292
N	1.98064	1.07361	-2.21273
H	3.55296	0.70428	-0.77986
H	2.50022	0.89814	-3.07273
C	0.66539	1.49846	-2.14372
C	-1.87296	2.38724	-1.42556
C	-1.53712	2.20014	-2.79279
C	-0.26455	1.75092	-3.17083
C	0.34680	1.67809	-0.75473
C	-0.94966	2.13043	-0.40453
H	-2.88083	2.74937	-1.16323
H	-2.28480	2.42296	-3.57244
H	0.00138	1.61517	-4.23214
H	-1.21835	2.26348	0.65616
N	-1.13272	-2.22375	0.19600
C	-1.77338	-1.86775	-0.71745
C	-0.74553	-3.57012	3.31505
O	-1.07296	-4.30107	4.16424
H	2.34372	-1.51528	1.88583
C	0.74972	-3.92261	1.46105
O	1.38702	-4.85747	1.14675
C	-2.57452	-1.39923	-1.83742
H	-2.30675	-0.34422	-2.07812
H	-3.65355	-1.43696	-1.57144
H	-2.40644	-2.03270	-2.73532

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
#		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-

6		0.00	0.00000	-	-
7	a	22.84	1.02140	YES	YES
8	a	33.67	0.27156	YES	YES
9	a	35.71	2.40924	YES	YES
10	a	40.38	0.25497	YES	YES
11	a	52.71	2.64130	YES	YES
12	a	70.13	5.43466	YES	YES
13	a	79.44	2.59574	YES	YES
14	a	89.10	1.17375	YES	YES
15	a	92.20	0.07960	YES	YES
16	a	106.12	1.12417	YES	YES
17	a	109.73	10.38027	YES	YES
18	a	136.33	2.20401	YES	YES
19	a	150.12	4.96299	YES	YES
20	a	162.40	5.39853	YES	YES
21	a	174.23	1.03926	YES	YES
22	a	210.39	0.89078	YES	YES
23	a	221.21	4.43101	YES	YES
24	a	242.13	1.20557	YES	YES
25	a	262.02	6.46527	YES	YES
26	a	289.06	1.42062	YES	YES
27	a	309.87	7.57357	YES	YES
28	a	348.44	13.99299	YES	YES
29	a	366.83	3.57924	YES	YES
30	a	385.53	0.85266	YES	YES
31	a	398.47	1.08942	YES	YES
32	a	412.03	16.18545	YES	YES
33	a	430.30	24.89082	YES	YES
34	a	449.99	6.56599	YES	YES
35	a	454.37	24.82871	YES	YES
36	a	456.30	14.68192	YES	YES
37	a	466.56	15.85845	YES	YES
38	a	475.12	1.93889	YES	YES
39	a	506.97	7.06706	YES	YES
40	a	516.96	18.03004	YES	YES
41	a	523.90	5.21341	YES	YES
42	a	542.79	13.19100	YES	YES
43	a	563.76	6.73177	YES	YES
44	a	577.06	11.62014	YES	YES
45	a	587.62	3.50182	YES	YES
46	a	605.92	2.97700	YES	YES
47	a	628.74	0.65456	YES	YES
48	a	658.73	1.50981	YES	YES
49	a	695.70	1.34052	YES	YES
50	a	743.92	80.65586	YES	YES