Supporting Information

LEWIS ACID CATALYSIS IN INTERMOLECULAR [2+2] PHOTOCYCLOADDITION OF COUMARIN-3-CARBOXAMIDE BEARING 2-OXAZOLIDINONE AUXILIARY WITH *n*-PROPYL VINYL ETHER AND VINYL PIVALATE

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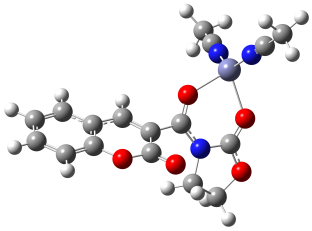
Computational study

- **Table S1.** Energy and NPA charge of complexes **A** and **B** optimized by DFT and TD-DFT calculations in acetonitrile.

Compound	Method	State	Energy (*E*) (a.u.)	Δ*E* (kcal/mol)	Charge of C3 (e)	Charge of C4 (e)
Coumarin **1**	DFT	S_0	-931.569772152	-	-0.246	-0.066
Complex **A**	DFT	S_0	-2976.19663806	1.34	-0.280	0.016
Complex **B**	DFT	S_0	-2976.19877970	0.00	-0.176	0.011
Photoexcited complex **A**	TD-DFT	T_1	-2976.11006471	-	0.008	-0.275
Photoexcited complex **B**	TD-DFT	T_1	-2976.10919731	-	-0.005	-0.249

- Complex **B** was 1.34 kcal/mol more stable than complex **A** in the ground state (S_0) as shown in Δ*E* value in Table S1. Therefore, the abundance ratio between complex **A** and **B** was 1 to 10 at 300 K.
- Electron density of C3 was lower than that of C4 position in triplet state (T_1) of photoexcited complexes **A** and **B**.



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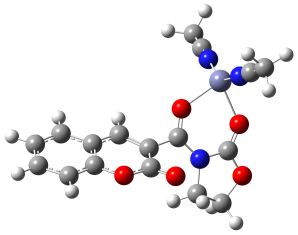

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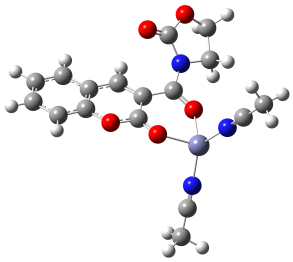
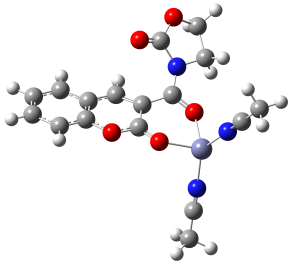


Complex **B** (S_0)



Complex **B** (T_1)

Table S2. Coordinates and NPA charges of the optimized geometry of complex **A** in dicationic S_0 state calculated by CAM-B3LYP/6-311++G(*d*,*p*).

No.	Element	Coordinates (Å)			NPA Charge
		x	y	z	
1	C	-2.279519	-1.436343	0.131313	0.80511
2	C	-4.250145	-0.090062	0.399634	0.36782
3	C	-1.544664	-0.213445	-0.166659	-0.27985
4	C	-2.150322	0.994367	-0.093872	0.01605
5	C	-3.547696	1.094938	0.173153	-0.17057
6	H	-6.122736	-1.027276	0.837554	0.24251
7	C	-5.610093	-0.090457	0.664969	-0.24135
8	C	-4.243200	2.313097	0.217748	-0.13652
9	H	-1.577261	1.900276	-0.255004	0.24966
10	C	-5.594499	2.325508	0.480932	-0.21875
11	C	-6.272770	1.122467	0.703919	-0.14217
12	H	-3.701730	3.234574	0.041742	0.23363
13	H	-6.133350	3.263067	0.516543	0.22988
14	H	-7.335363	1.137467	0.911517	0.22925
15	O	-3.610310	-1.296486	0.375345	-0.50461
16	O	-1.798692	-2.540037	0.205689	-0.62271
17	C	-0.083158	-0.266048	-0.400489	0.78440
18	O	0.648752	0.475441	0.255564	-0.66067
19	C	-0.373830	-1.923551	-2.308993	-0.21075
20	C	0.661413	-2.188847	-3.395284	-0.02954
21	H	-1.235259	-1.377008	-2.683929	0.24445
22	H	-0.693346	-2.830878	-1.804436	0.24506
23	H	0.592897	-1.497848	-4.232341	0.21328
24	H	0.669594	-3.215859	-3.743312	0.22676
25	N	0.407943	-1.092256	-1.372771	-0.50143
26	O	1.935443	-1.937726	-2.738565	-0.49197
27	C	1.764716	-1.221439	-1.659043	1.01882
28	O	2.700437	-0.764093	-1.029587	-0.66312
29	Zn	2.667586	0.506924	0.607758	1.42059
30	N	3.237008	2.275829	-0.024019	-0.53132
31	C	3.566070	3.282863	-0.451318	0.57667
32	N	2.817458	-0.828095	2.073571	-0.52598
33	C	2.913235	-1.579708	2.928576	0.56823
34	C	3.034267	-2.526596	4.010029	-0.71186
35	H	4.086892	-2.647072	4.265820	0.28015
36	H	2.487283	-2.153858	4.876006	0.28012
37	H	2.620083	-3.485638	3.699636	0.28002
38	C	3.980383	4.552984	-0.994136	-0.71257
39	H	3.247047	5.314786	-0.729994	0.28100
40	H	4.953068	4.820591	-0.581498	0.28131
41	H	4.051569	4.473444	-2.078946	0.28113

Table S3. Coordinates and NPA charges of the optimized geometry of complex **B** in dicationic S_0 state calculated by CAM-B3LYP/6-311++G(*d*,*p*).

No.	Element	Coordinates (Å)			NPA Charge
		x	y	z	
1	C	0.600670	-0.991142	0.633230	0.82524
2	C	2.897776	-1.591113	0.783998	0.37492
3	C	0.966422	0.174355	-0.139647	-0.17556
4	C	2.270162	0.344486	-0.500990	0.01089
5	C	3.280902	-0.543300	-0.054962	-0.17131
6	H	3.476007	-3.283550	1.959313	0.24759
7	C	3.812127	-2.484528	1.312612	-0.24594
8	C	4.641739	-0.401681	-0.378839	-0.12094
9	H	2.557352	1.160031	-1.150352	0.24910
10	C	5.562049	-1.282761	0.137542	-0.21949
11	C	5.144284	-2.318701	0.982637	-0.11244
12	H	4.947240	0.408672	-1.028449	0.23552
13	H	6.611047	-1.177506	-0.104890	0.23374
14	H	5.876695	-3.006913	1.385224	0.23682
15	O	1.579551	-1.774054	1.093011	-0.46849
16	O	-0.539233	-1.348746	0.928946	-0.68560
17	C	-0.098881	1.086036	-0.586371	0.74525
18	O	-1.259403	0.706382	-0.787706	-0.67422
19	C	-0.842388	3.235304	-1.494642	-0.20074
20	C	-0.070949	4.535695	-1.654123	-0.03497
21	H	-1.707223	3.339104	-0.839508	0.22613
22	H	-1.152952	2.804179	-2.442495	0.24120
23	H	-0.671188	5.422385	-1.478682	0.22074
24	H	0.441100	4.604961	-2.612233	0.20592
25	N	0.176766	2.395332	-0.851338	-0.52781
26	O	0.938054	4.471212	-0.618599	-0.52542
27	C	1.141007	3.221600	-0.220349	0.97146
28	O	1.983196	2.891340	0.560305	-0.60840
29	Zn	-2.291835	-0.852823	0.033193	1.40090
30	N	-3.308097	0.118745	1.434652	-0.52095
31	C	-3.878340	0.673355	2.254617	0.56608
32	N	-2.639464	-2.396629	-1.156924	-0.52295
33	C	-2.785406	-3.275783	-1.871654	0.57083
34	C	-2.962596	-4.384247	-2.777572	-0.71206
35	H	-2.807903	-5.318891	-2.238717	0.28059
36	H	-3.972669	-4.359152	-3.186079	0.28038
37	H	-2.237805	-4.304564	-3.587846	0.28032
38	C	-4.595565	1.376904	3.289817	-0.71166
39	H	-5.104566	2.236654	2.854396	0.27965
40	H	-5.328162	0.707096	3.739677	0.27992
41	H	-3.891726	1.714112	4.050610	0.27986

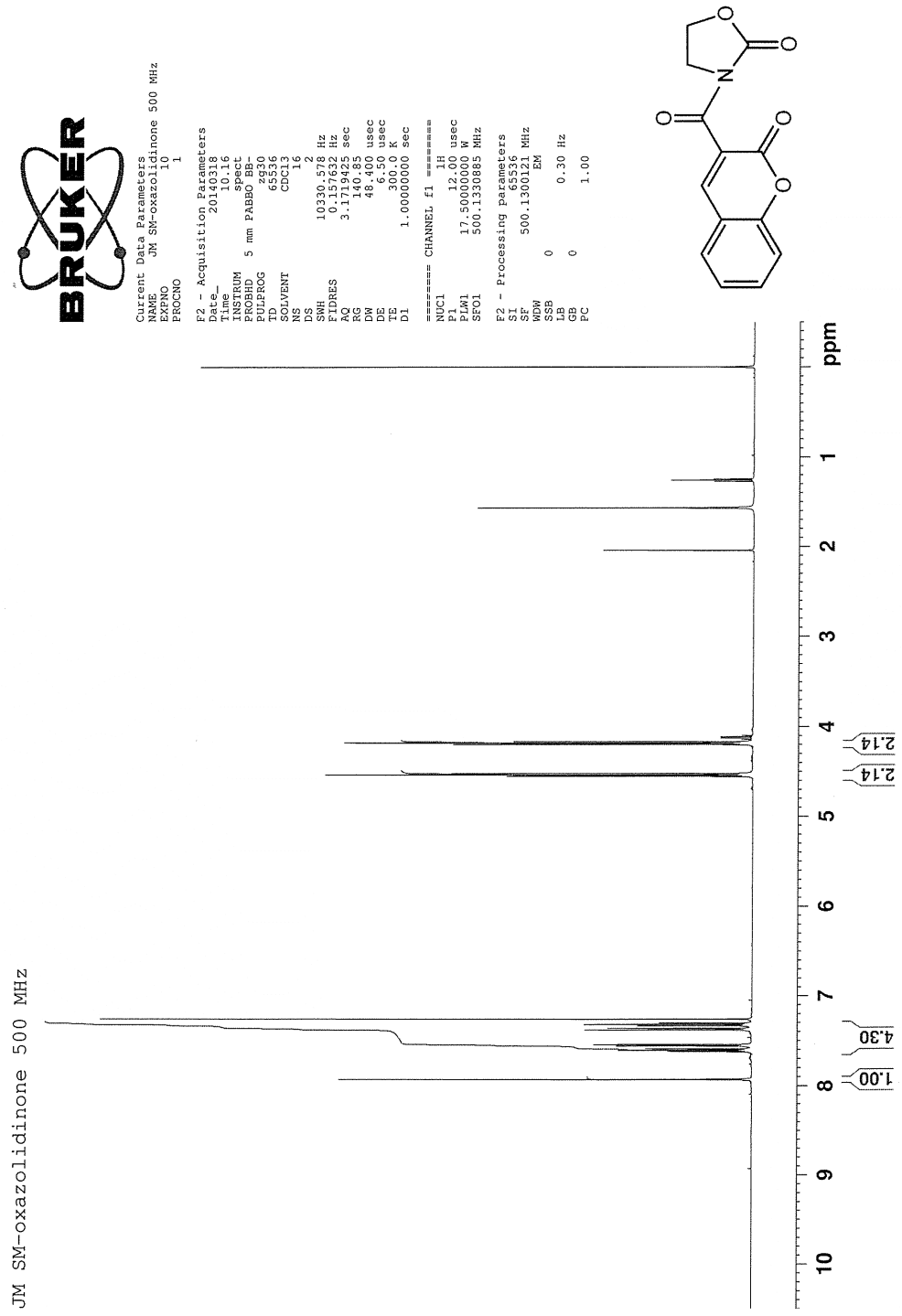
Table S4. Coordinates and NPA charges of the optimized geometry of photoexcited complex **A** in dicationic T_1 state calculated by TD-CAM-B3LYP/6-311++G(*d*,*p*).

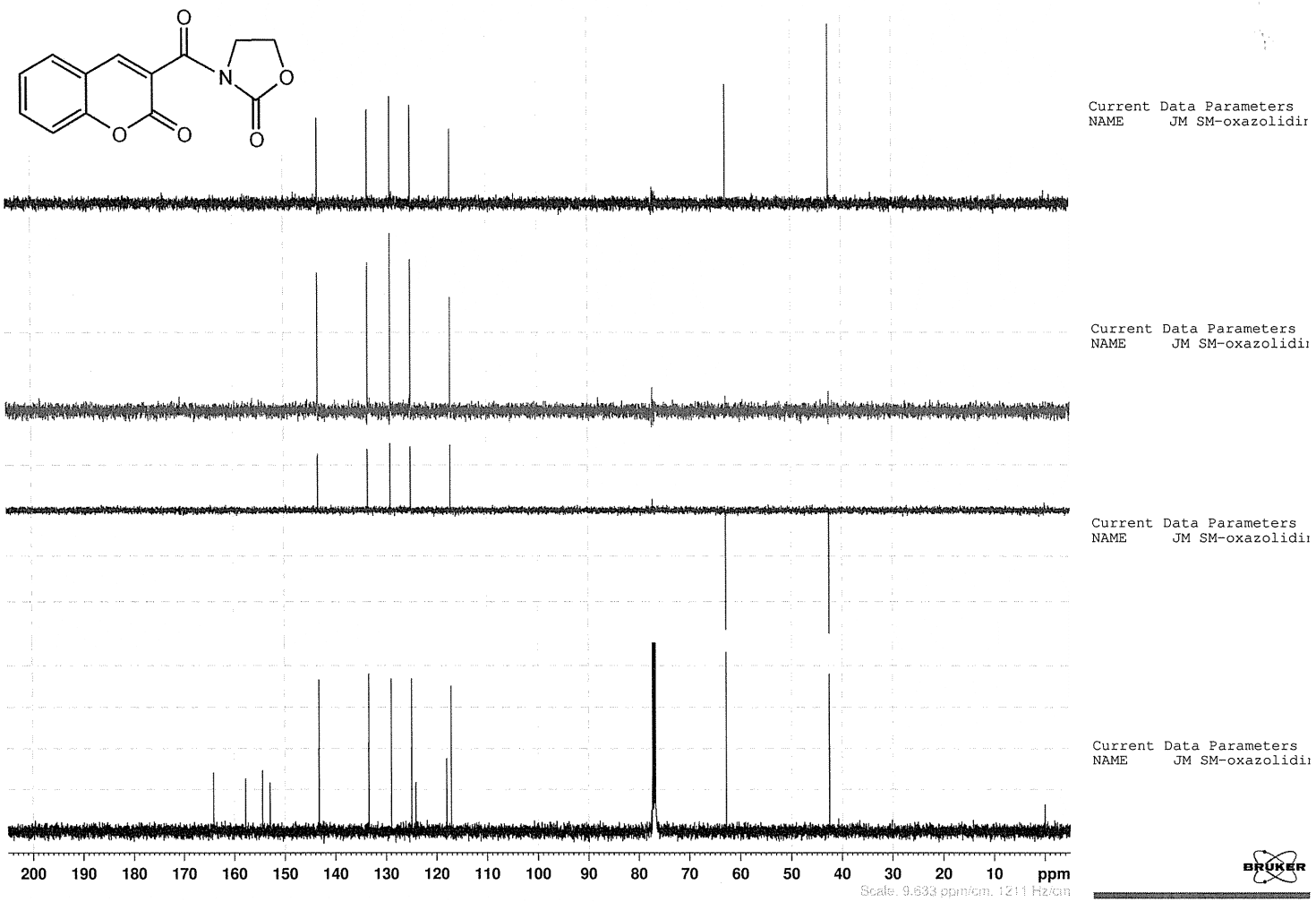
No.	Element	Coordinates (Å)			NPA Charge
		x	y	z	
1	C	-2.257143	-1.430902	0.149081	0.77057
2	C	-4.244658	-0.110959	0.403577	0.28313
3	C	-1.538455	-0.208046	-0.221765	0.00843
4	C	-2.181793	1.084890	-0.131616	-0.27505
5	C	-3.525500	1.114013	0.149007	-0.00074
6	H	-6.065328	-1.088723	0.837979	0.23956
7	C	-5.579209	-0.139815	0.651390	-0.22209
8	C	-4.310296	2.331980	0.193150	-0.19043
9	H	-1.617298	1.983624	-0.328039	0.23931
10	C	-5.653981	2.296043	0.440649	-0.20388
11	C	-6.316991	1.071747	0.670635	-0.14967
12	H	-3.798208	3.268680	0.014291	0.22565
13	H	-6.219691	3.219048	0.461262	0.22687
14	H	-7.379881	1.048487	0.866064	0.21921
15	O	-3.565549	-1.330428	0.432305	-0.53135
16	O	-1.717002	-2.505395	0.239667	-0.56044
17	C	-0.081300	-0.274005	-0.443423	0.72988
18	O	0.623390	0.485132	0.224178	-0.64153
19	C	-0.330647	-1.971920	-2.322317	-0.20799
20	C	0.722477	-2.235146	-3.392543	-0.02980
21	H	-1.196234	-1.446341	-2.717978	0.24521
22	H	-0.639750	-2.878435	-1.809854	0.24340
23	H	0.654350	-1.555302	-4.238564	0.21450
24	H	0.749501	-3.266200	-3.727190	0.22792
25	N	0.428080	-1.115347	-1.389244	-0.50205
26	O	1.984519	-1.957429	-2.723057	-0.49042
27	C	1.790236	-1.229357	-1.656217	1.01930
28	O	2.707646	-0.746778	-1.020033	-0.66180
29	Zn	2.653677	0.517792	0.623839	1.42709
30	N	3.222485	2.284499	-0.010943	-0.53323
31	C	3.554690	3.285629	-0.449542	0.57804
32	N	2.791732	-0.814754	2.088274	-0.52876
33	C	2.876092	-1.548495	2.959862	0.57065
34	C	2.982433	-2.472000	4.062598	-0.71208
35	H	4.033062	-2.602207	4.321888	0.28048
36	H	2.440850	-2.070657	4.919215	0.28050
37	H	2.553786	-3.431554	3.774362	0.28030
38	C	3.973864	4.546662	-1.009224	-0.71272
39	H	3.157807	5.265023	-0.931021	0.28126
40	H	4.841213	4.914088	-0.461022	0.28139
41	H	4.236488	4.403193	-2.057466	0.28140

Table S5. Coordinates and NPA charges of the optimized geometry of photoexcited complex **B** in dicationic T_1 state calculated by TD-CAM-B3LYP/6-311++G(*d*,*p*).

No.	Element	Coordinates (Å)			NPA Charge
		x	y	z	
1	C	-0.526870	-1.007042	-0.653065	0.83771
2	C	-2.825338	-1.610775	-0.858920	0.27034
3	C	-0.924692	0.117863	0.205354	-0.00512
4	C	-2.267691	0.156166	0.714992	-0.24901
5	C	-3.212448	-0.661862	0.143009	0.00564
6	H	-3.349706	-3.129091	-2.230599	0.24438
7	C	-3.703572	-2.426165	-1.487733	-0.18578
8	C	-4.624549	-0.631962	0.480503	-0.16857
9	H	-2.535829	0.869735	1.478432	0.24378
10	C	-5.515325	-1.458997	-0.150747	-0.20949
11	C	-5.088641	-2.356385	-1.145601	-0.13467
12	H	-4.947581	0.066846	1.240916	0.22855
13	H	-6.563969	-1.417852	0.114565	0.23081
14	H	-5.793796	-3.001255	-1.650400	0.22236
15	O	-1.470679	-1.763392	-1.176569	-0.48999
16	O	0.629484	-1.297815	-0.931983	-0.63638
17	C	0.098251	1.095406	0.595094	0.71054
18	O	1.279418	0.775402	0.807341	-0.66249
19	C	0.658528	3.327559	1.476108	-0.20060
20	C	-0.258536	4.534914	1.625586	-0.03400
21	H	1.508835	3.525065	0.823008	0.22736
22	H	1.010140	2.937976	2.427796	0.24229
23	H	0.237888	5.482534	1.444608	0.22100
24	H	-0.774929	4.550739	2.583596	0.20664
25	N	-0.261183	2.382758	0.835329	-0.51659
26	O	-1.254713	4.352440	0.589281	-0.52584
27	C	-1.299678	3.088461	0.187265	0.96973
28	O	-2.066787	2.649069	-0.616462	-0.60232
29	Zn	2.370017	-0.743125	0.011840	1.40689
30	N	3.356707	0.223961	-1.406270	-0.52472
31	C	3.895226	0.758566	-2.260290	0.57022
32	N	2.695934	-2.287608	1.200820	-0.52626
33	C	2.849160	-3.173741	1.905280	0.57432
34	C	3.035625	-4.290835	2.798183	-0.71235
35	H	2.881671	-5.220179	2.249942	0.28103
36	H	4.048043	-4.265879	3.200935	0.28088
37	H	2.315111	-4.222534	3.613259	0.28077
38	C	4.571890	1.432110	-3.341401	-0.71196
39	H	5.286169	2.145932	-2.931540	0.28028
40	H	5.097027	0.695878	-3.949891	0.28045
41	H	3.838393	1.956733	-3.953527	0.28019

^{1}H NMR and ^{13}C NMR spectra

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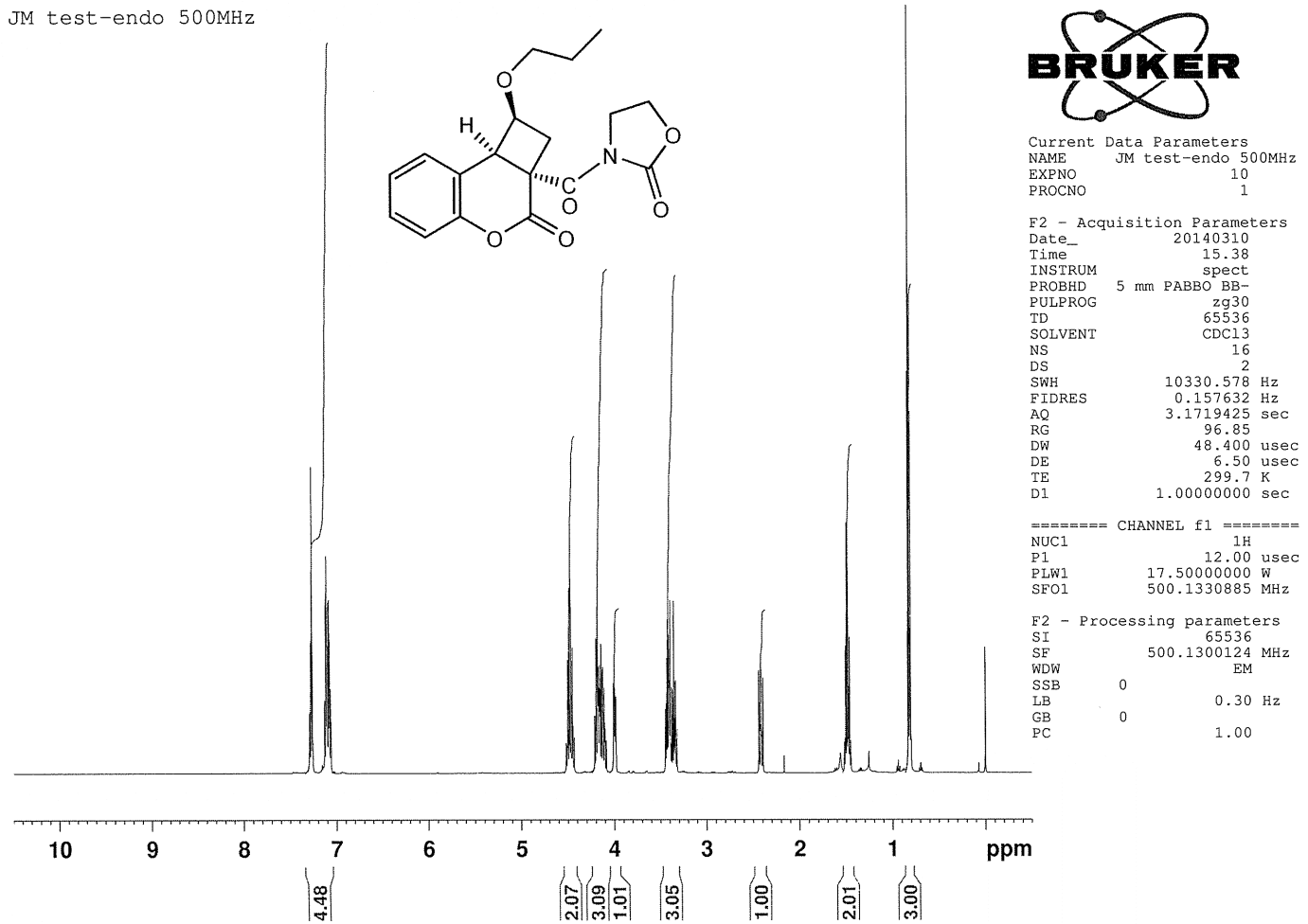
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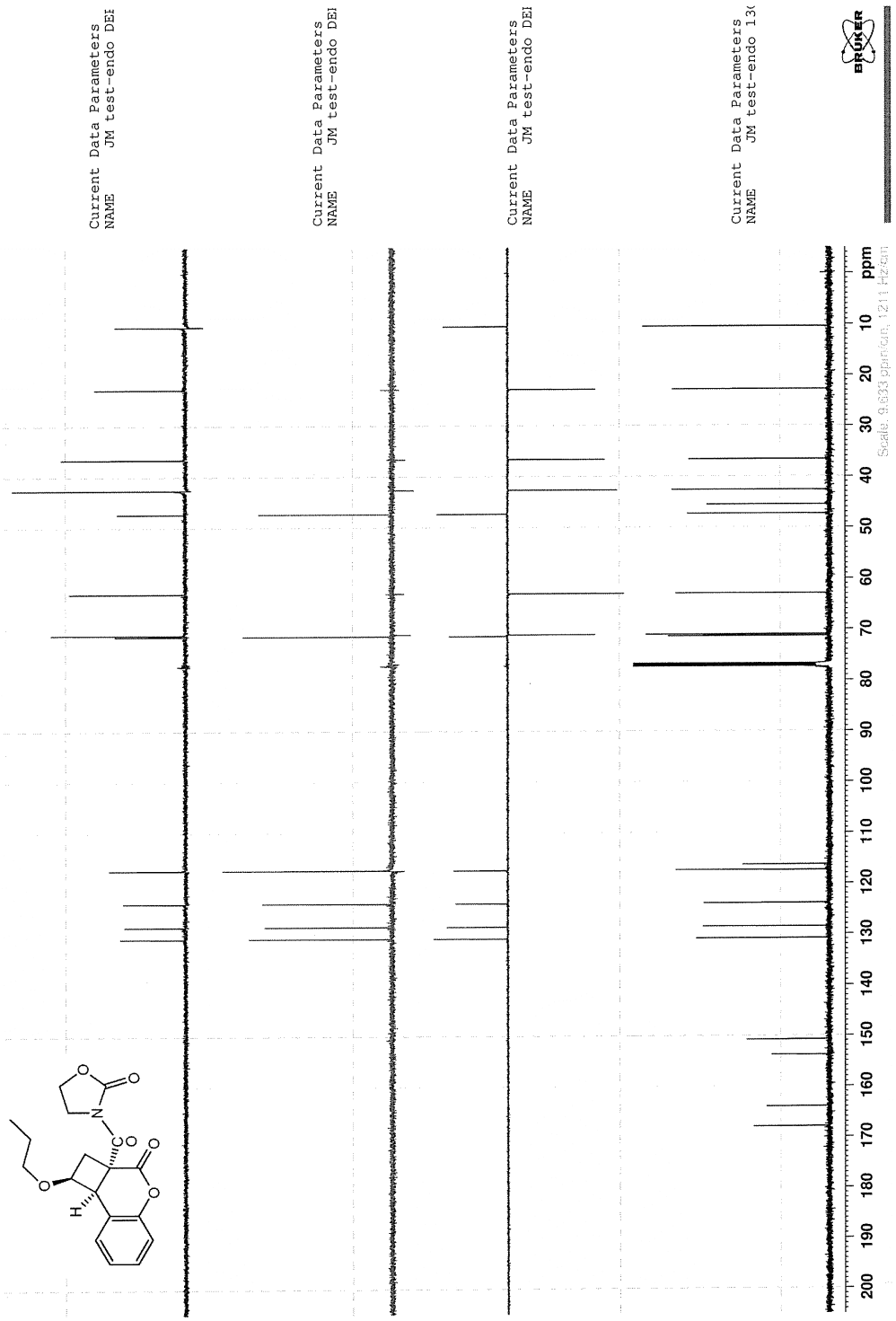
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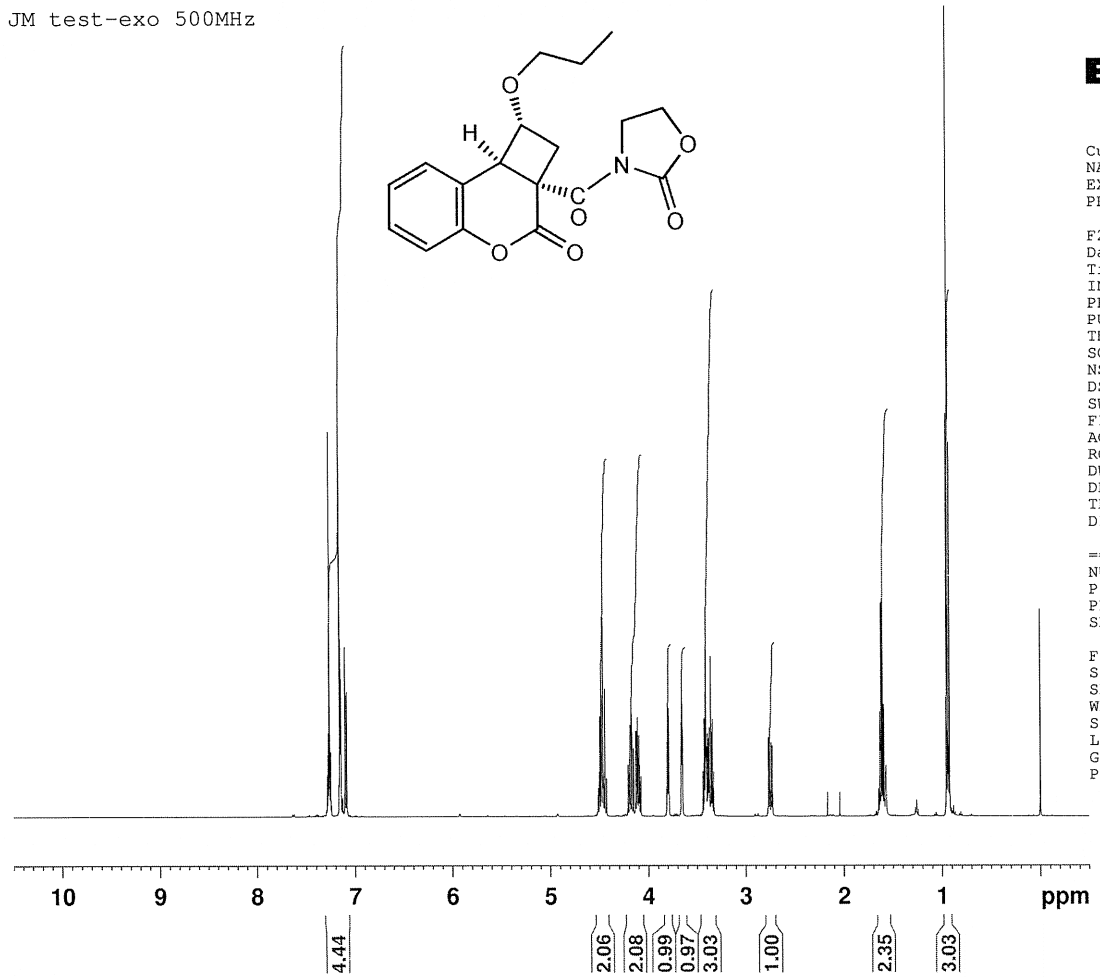

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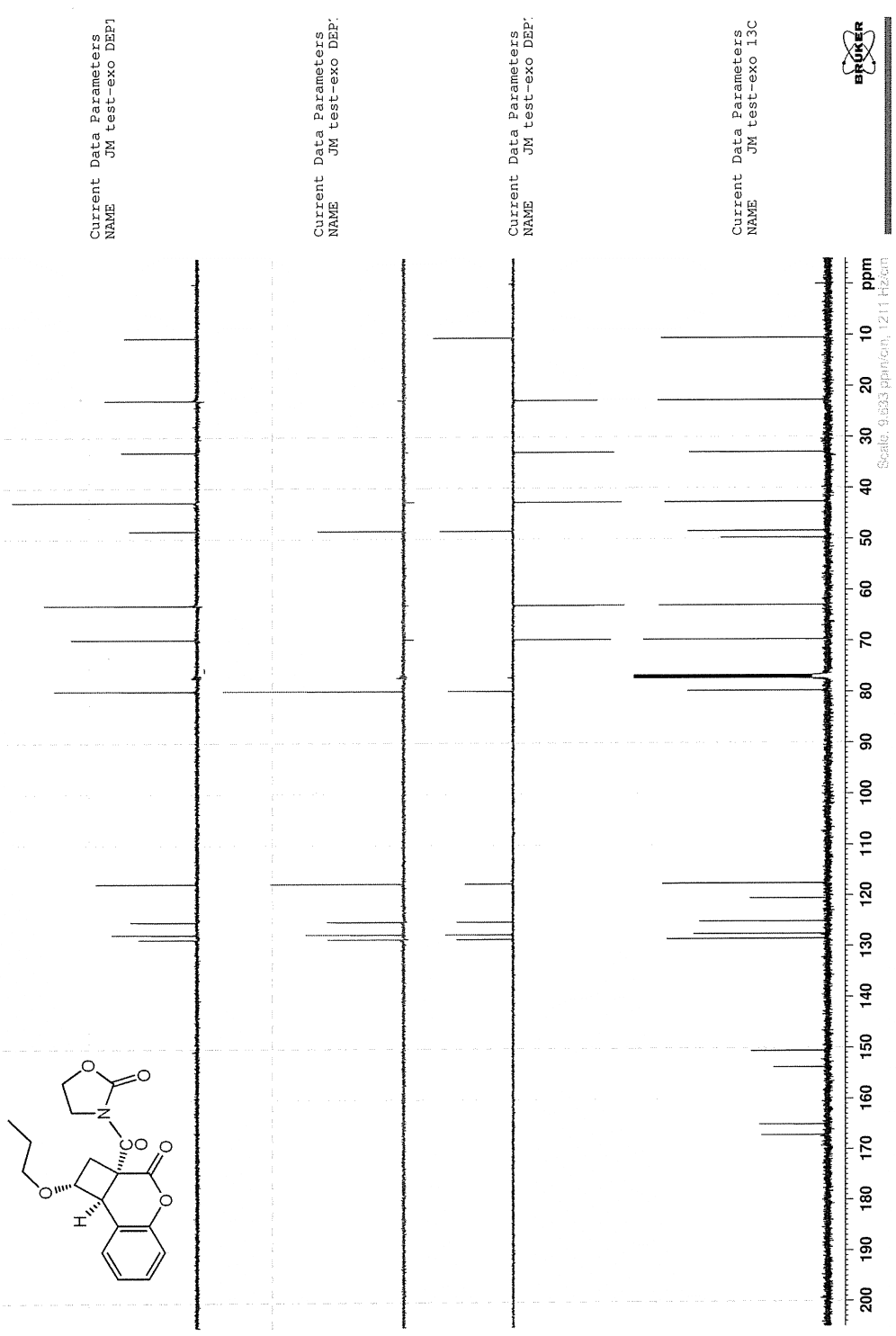
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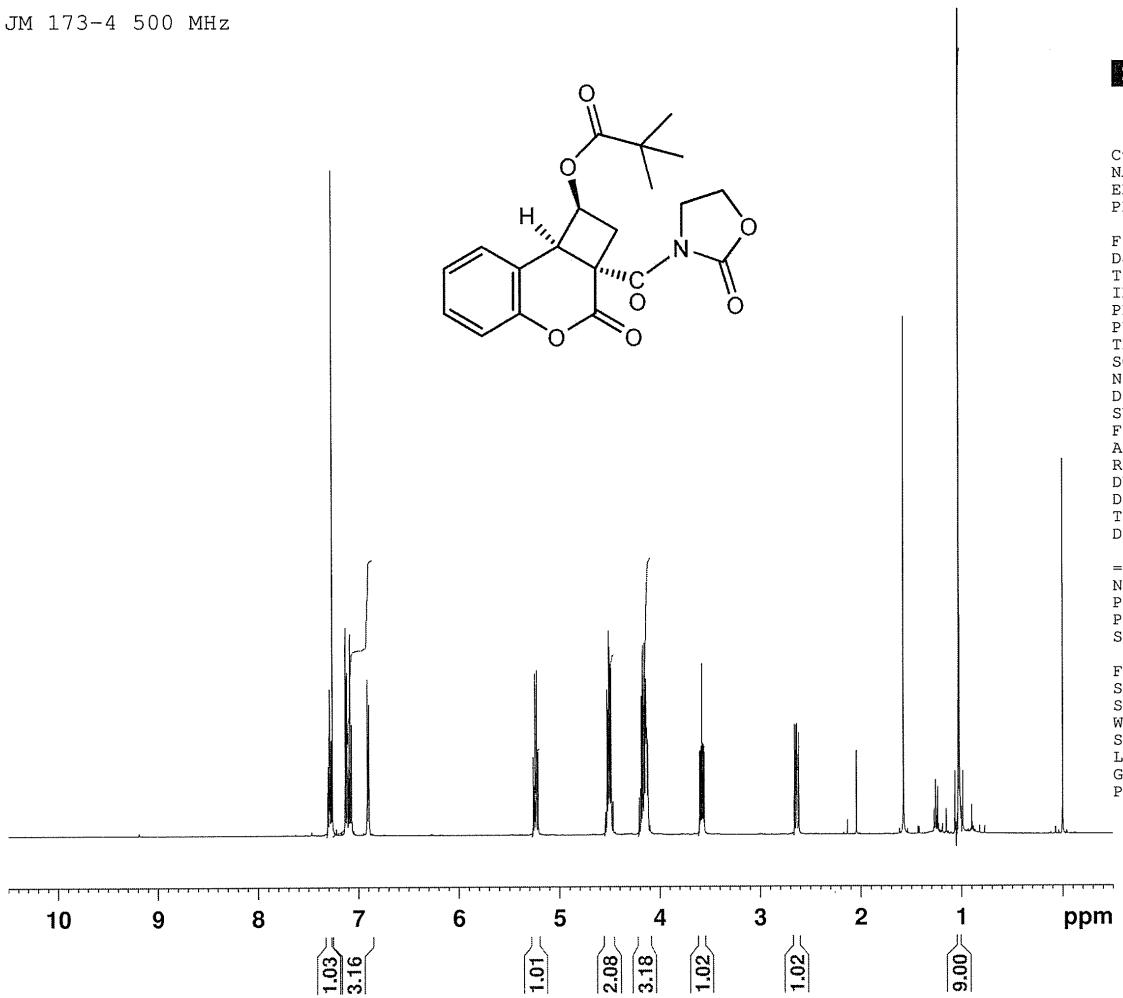

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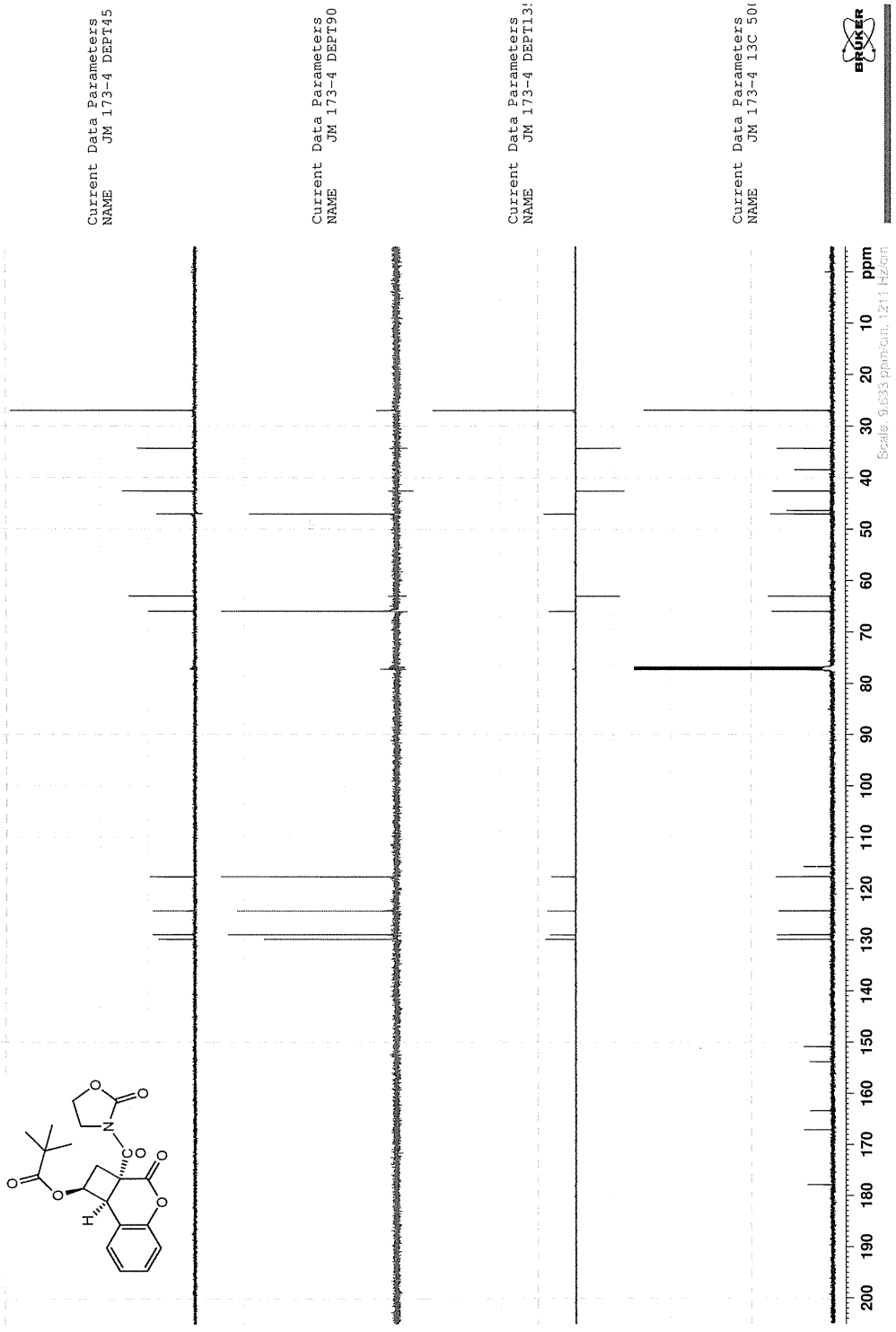
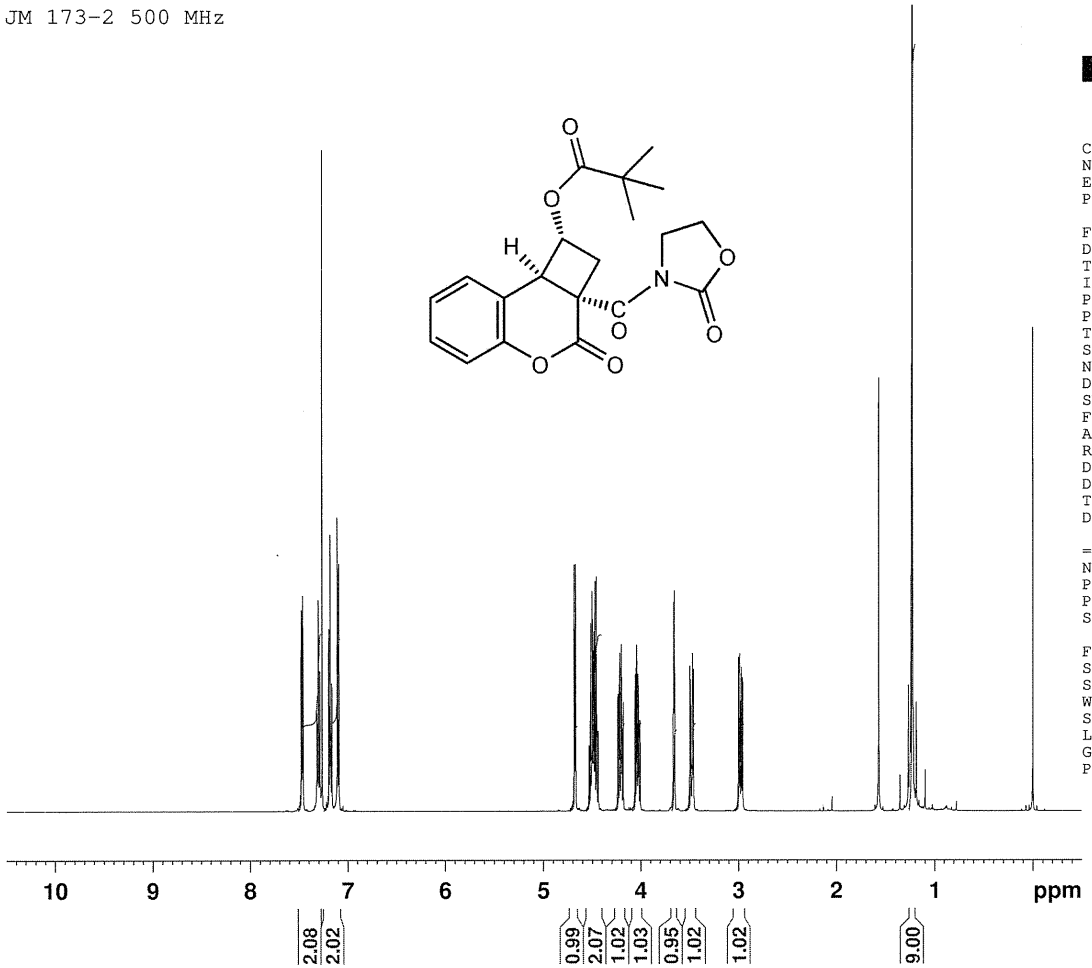
F2 - Acquisition Parameters
Date_ 20131125
Time 18.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719425 sec
RG 115.91
DW 48.400 usec
DE 6.50 usec
TE 298.7 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PLW1 17.50000000 W
SFO1 500.1330885 MHz

F2 - Processing parameters
SI 65536
SF 500.1300113 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


Current Data Parameters
NAME JM 173-4 DEPT45
Current Data Parameters
NAME JM 173-4 DEPT90
Current Data Parameters
NAME JM 173-4 DEPT13
Current Data Parameters
NAME JM 173-4 13C 50
BRUKER
ppm



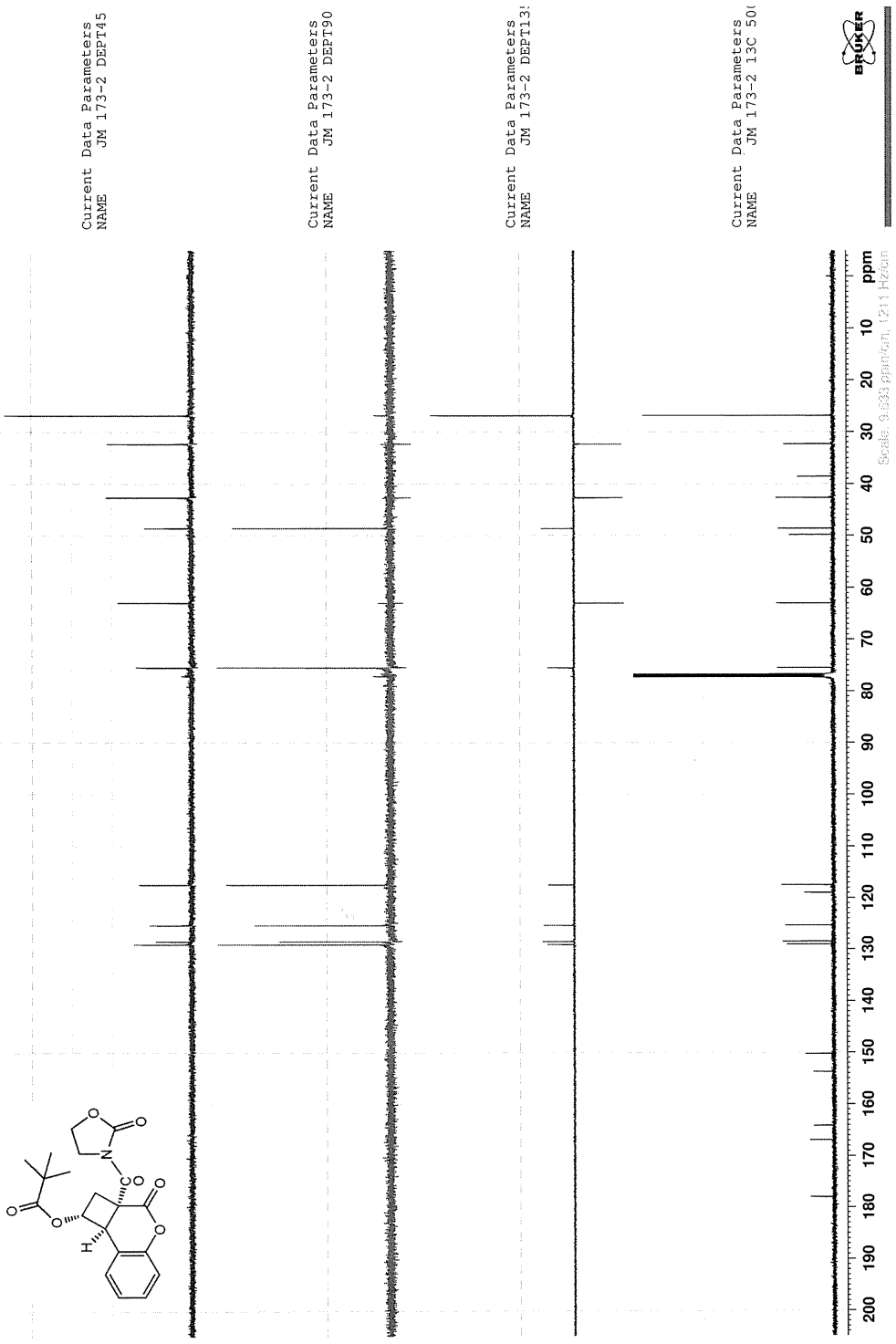
BRUKER

Current Data Parameters
NAME JM 173-2 500 MHz
EXPNO 10
PROCNO 1

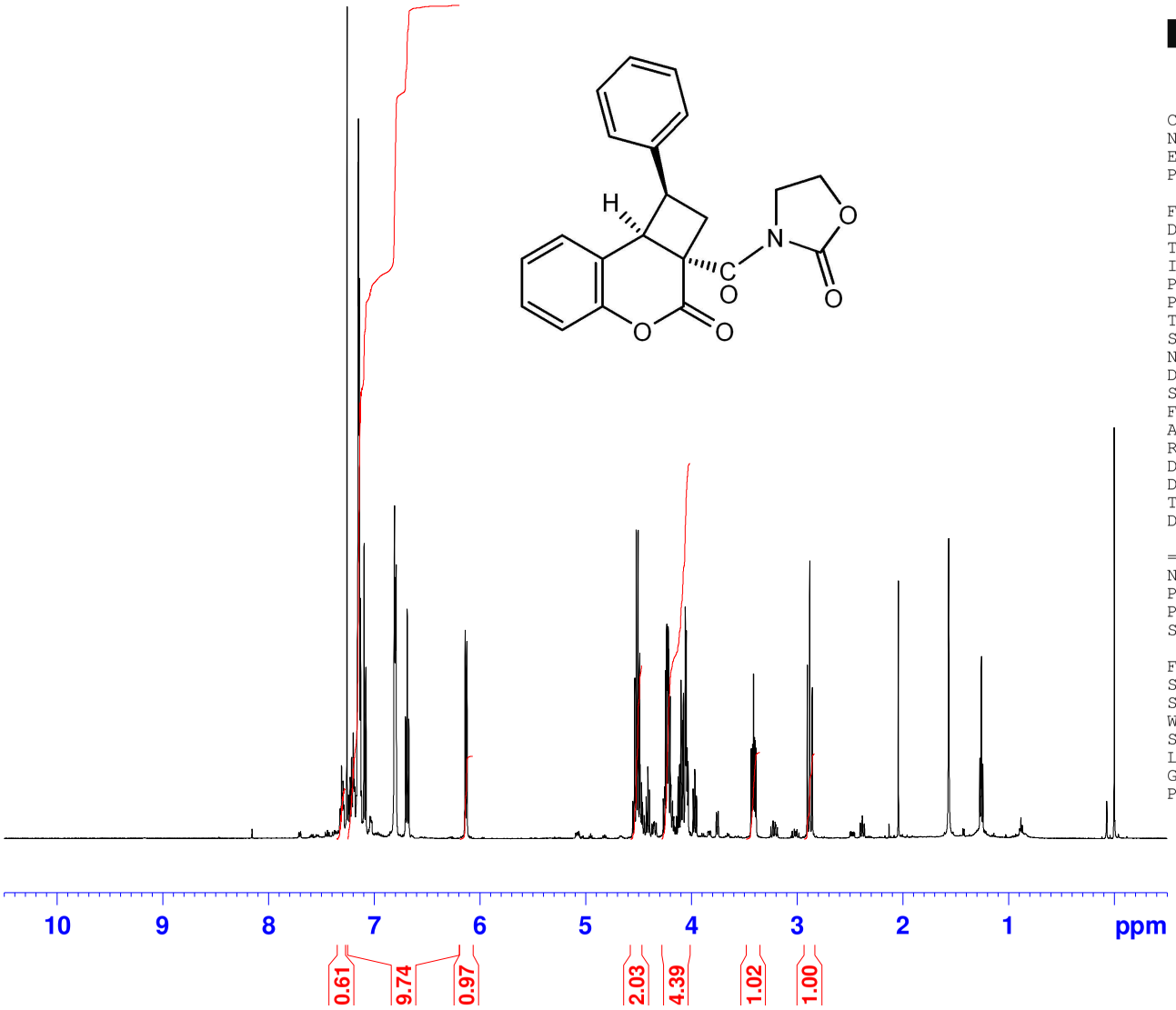
F2 - Acquisition Parameters
Date_ 20131125
Time 12.58
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719425 sec
RG 115.91
DW 48.400 usec
DE 6.50 usec
TE 298.8 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PLW1 17.50000000 W
SFO1 500.1330885 MHz

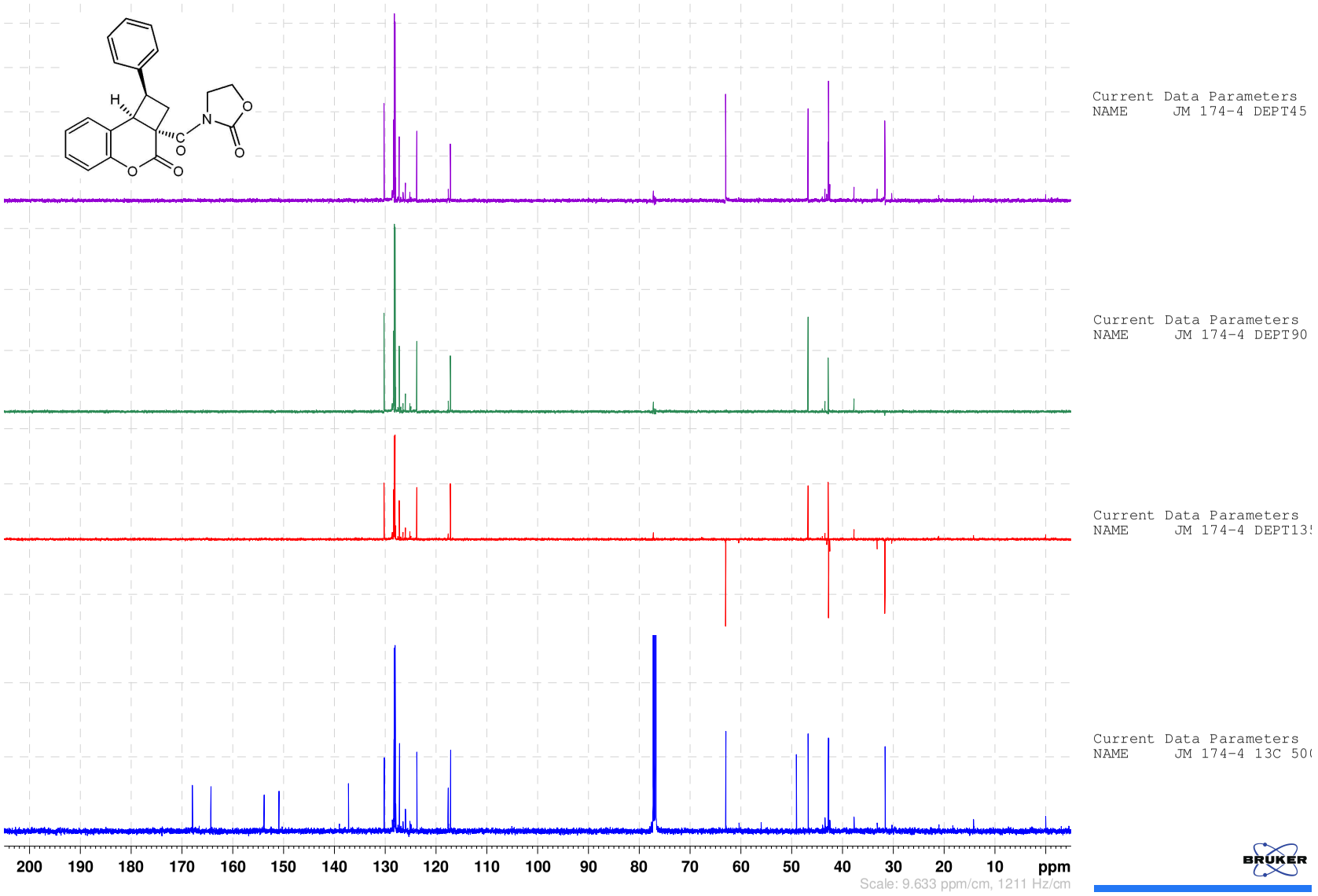
F2 - Processing parameters
SI 65536
SF 500.1300117 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


Current Data Parameters
NAME JM 173-2 DEPT45
Current Data Parameters
NAME JM 173-2 DEPT90
Current Data Parameters
NAME JM 173-2 DEPT13
Current Data Parameters
NAME JM 173-2 13C 50
BRUKER
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

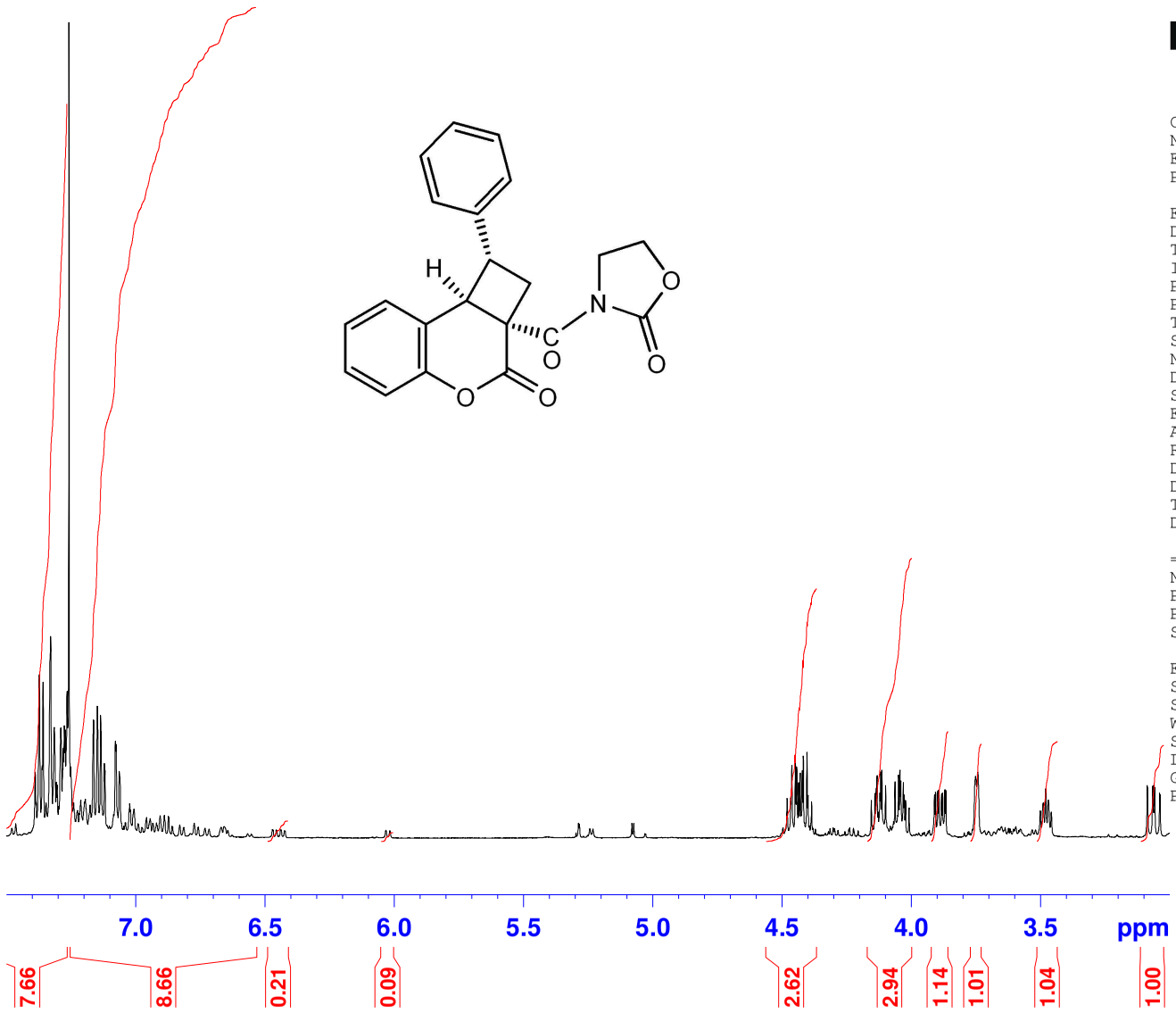
JM 174-4 500 MHz



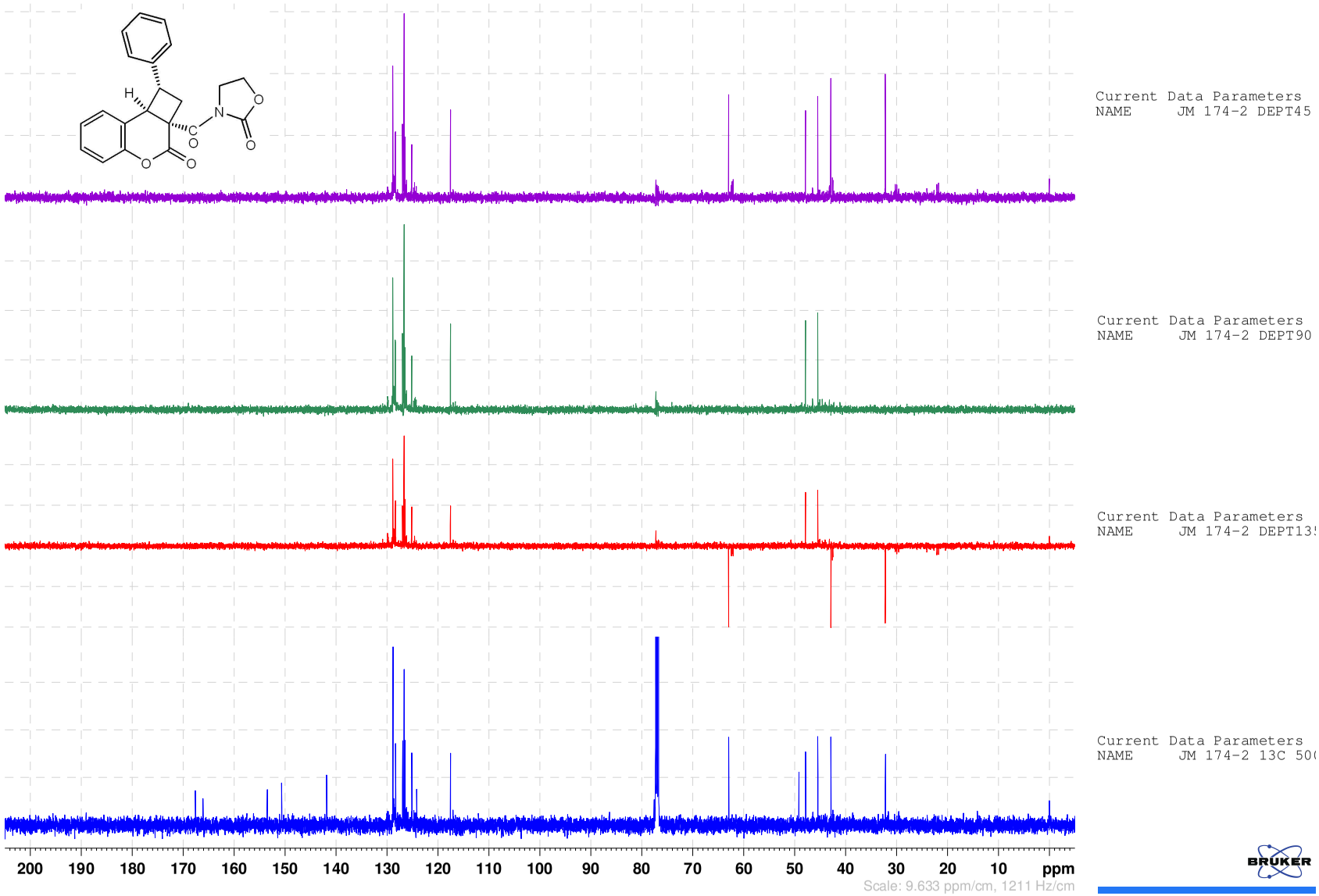

```
Current Data Parameters
NAME      JM 174-4 500 MHz
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_           20131126
Time                6.11
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719425 sec
RG                115.91
DW                48.400 usec
DE                 6.50 usec
TE                298.9 K
D1           1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.00 usec
PLW1         17.50000000 W
SFO1         500.1330885 MHz

F2 - Processing parameters
SI                 65536
SF           500.1300138 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

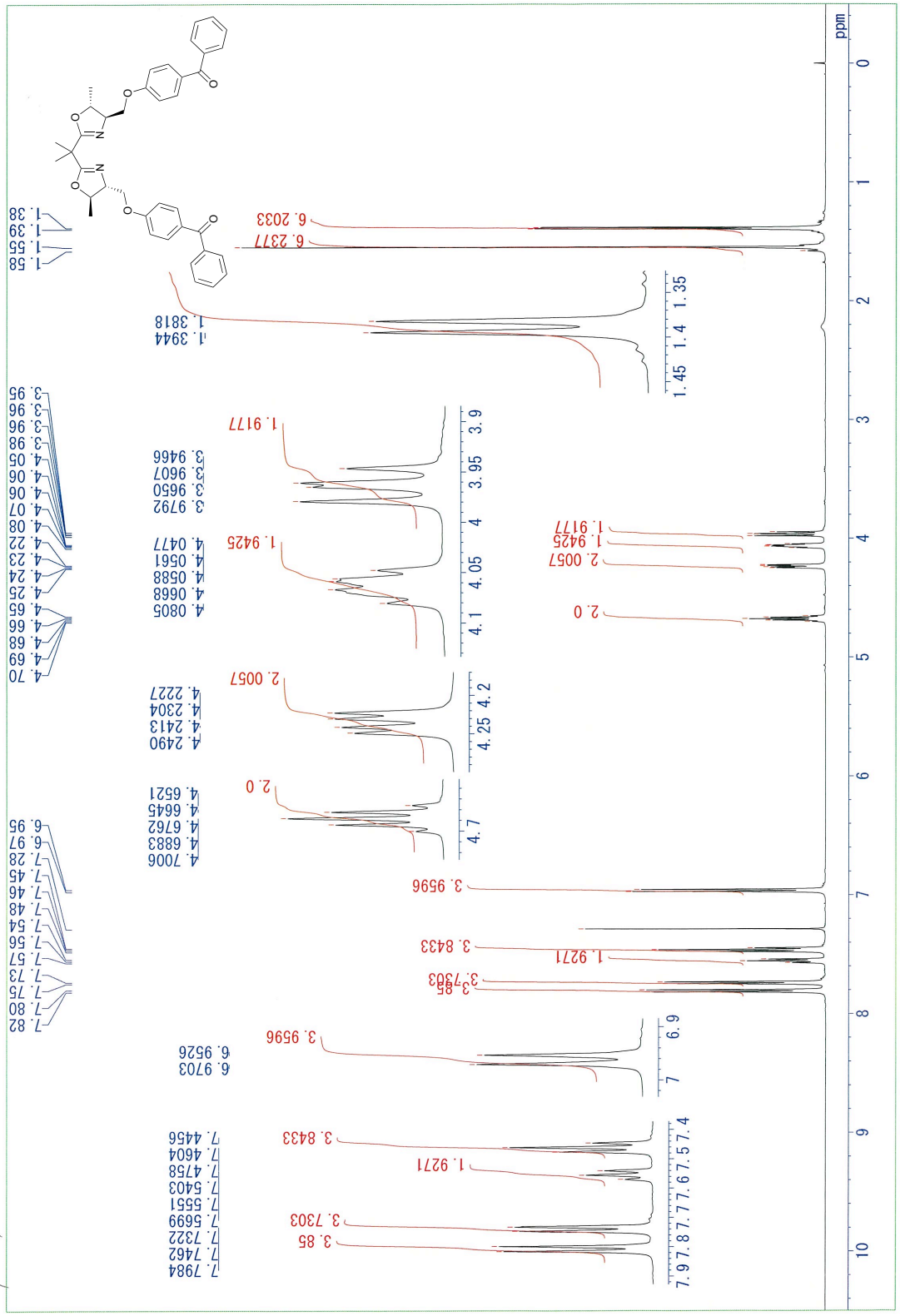

Current Data Parameters
NAME JM 174-4 DEPT45
Current Data Parameters
NAME JM 174-4 DEPT90
Current Data Parameters
NAME JM 174-4 DEPT13
Current Data Parameters
NAME JM 174-4 13C 50
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
Scale: 9.633 ppm/cm, 1211 Hz/cm
BRUKER

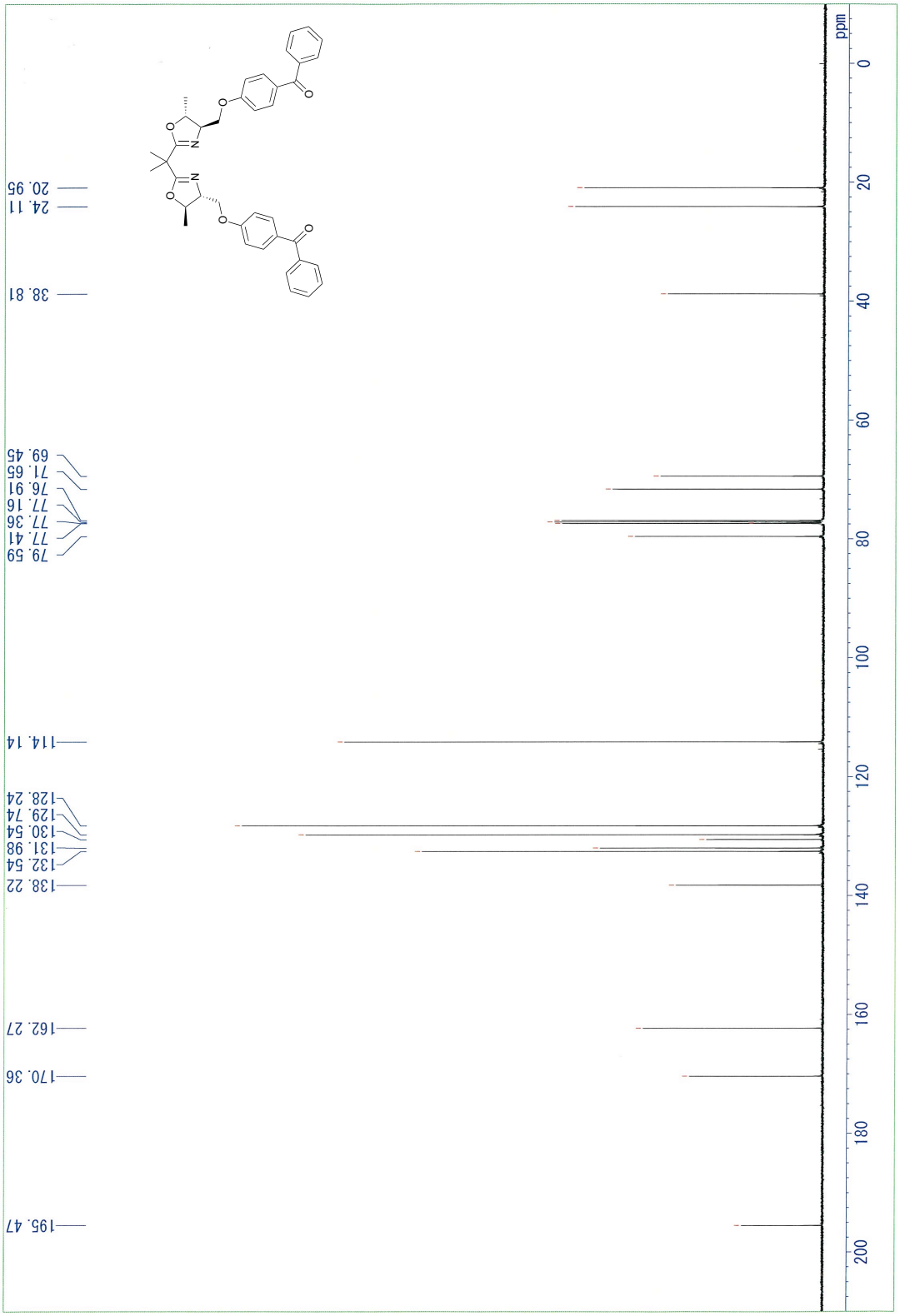
JM 174-2 500 MHz

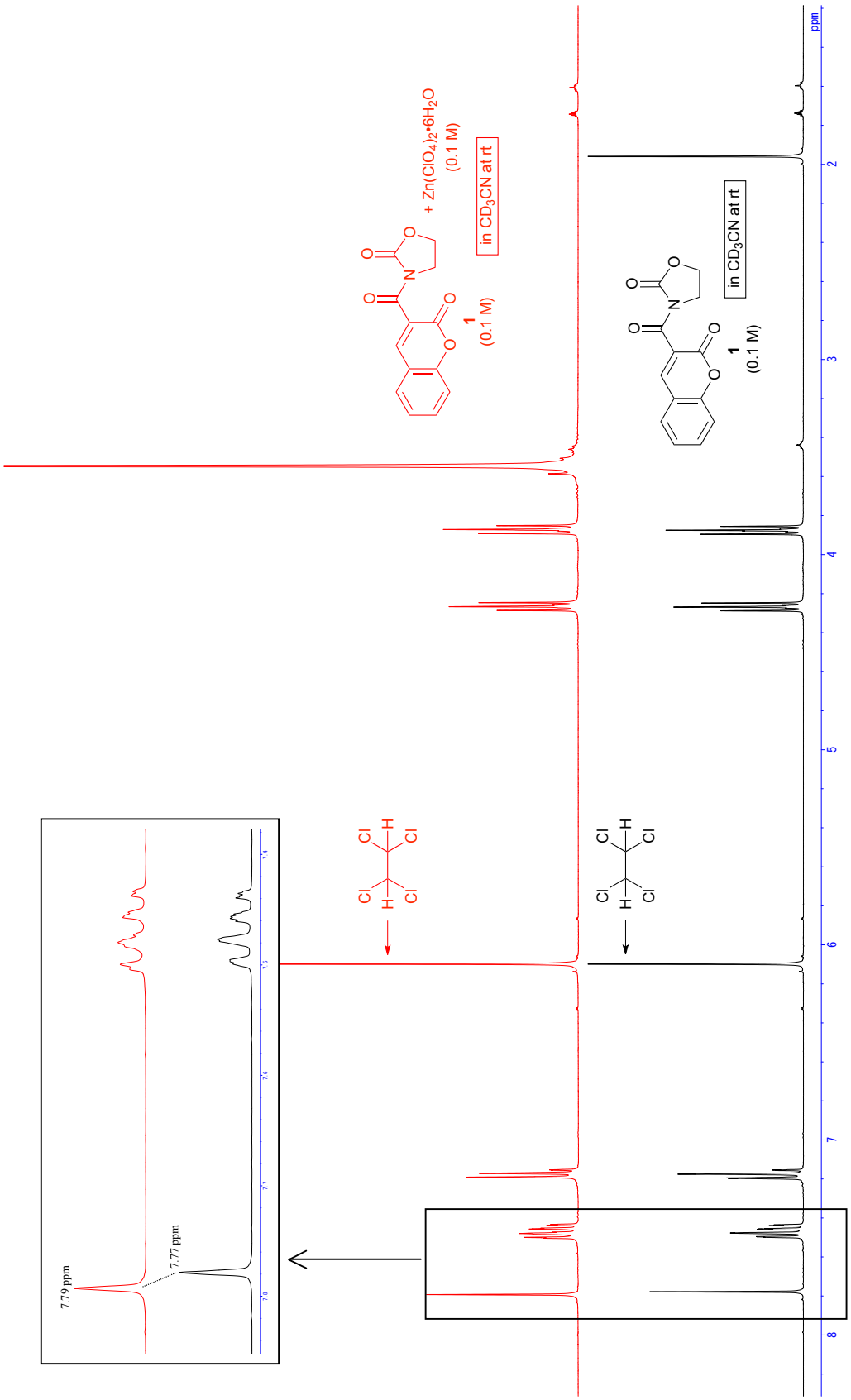



```
Current Data Parameters
NAME      JM 174-2 500 MHz
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_           20131125
Time               22.52
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ              3.1719425 sec
RG                 140.85
DW                 48.400 usec
DE                  6.50 usec
TE                 298.4 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.00 usec
PLW1         17.50000000 W
SFO1         500.1330885 MHz

F2 - Processing parameters
SI                 65536
SF          500.1300138 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

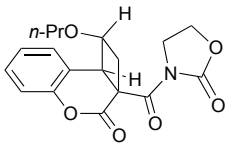

Current Data Parameters
NAME JM 174-2 DEPT45
Current Data Parameters
NAME JM 174-2 DEPT90
Current Data Parameters
NAME JM 174-2 DEPT13
Current Data Parameters
NAME JM 174-2 13C 50
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
Scale: 9.633 ppm/cm, 1211 Hz/cm
BRUKER



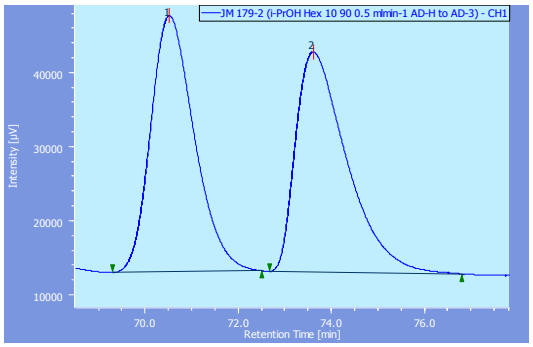

ppm
0
20
40
60
80
100
120
140
160
180
200
20.95
24.11
38.81
69.45
71.65
76.91
77.16
77.36
77.41
79.59
114.14
128.24
129.74
130.54
131.98
132.54
138.22
162.27
170.36
195.47


+ Zn(ClO4)2•6H2O
(0.1 M)
in CD3CN at rt
1
(0.1 M)
in CD3CN at rt
1
(0.1 M)
7.79 ppm
7.77 ppm
ppm

Chiral HPLC chromatograms



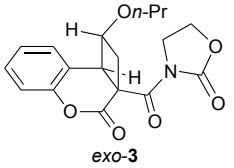
endo-**3**



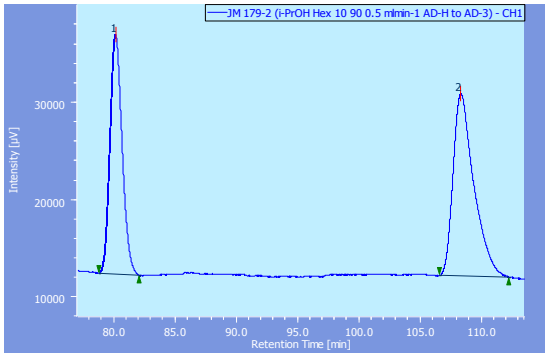
Sample Information

#	ピーク名	CH	tR	面積	高さ	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数
1	Unknown	1	70.525	2240119	34456	49.807	53.773	N/A	27406	1.682	1.271
2	Unknown	1	73.608	2257494	29620	50.193	46.227	N/A	22300	N/A	1.803

Date	2014/1/21	Chiral Column	a doubly-connected AD-H/AD-3
Solvent	iPrOH : Hexane = 10 : 90	Wavelength (nm)	254
Temp. (℃)	35	Injection Volume (μl)	5
Comment		% ee	0.386



exo-**3**



Sample Information

#	ピーク名	CH	tR	面積	高さ	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数
1	Unknown	1	80.15	1689820	24548	43.489	56.745	N/A	31519	11.779	1.178
2	Unknown	1	108.283	2195841	18712	56.511	43.255	N/A	21074	N/A	1.542

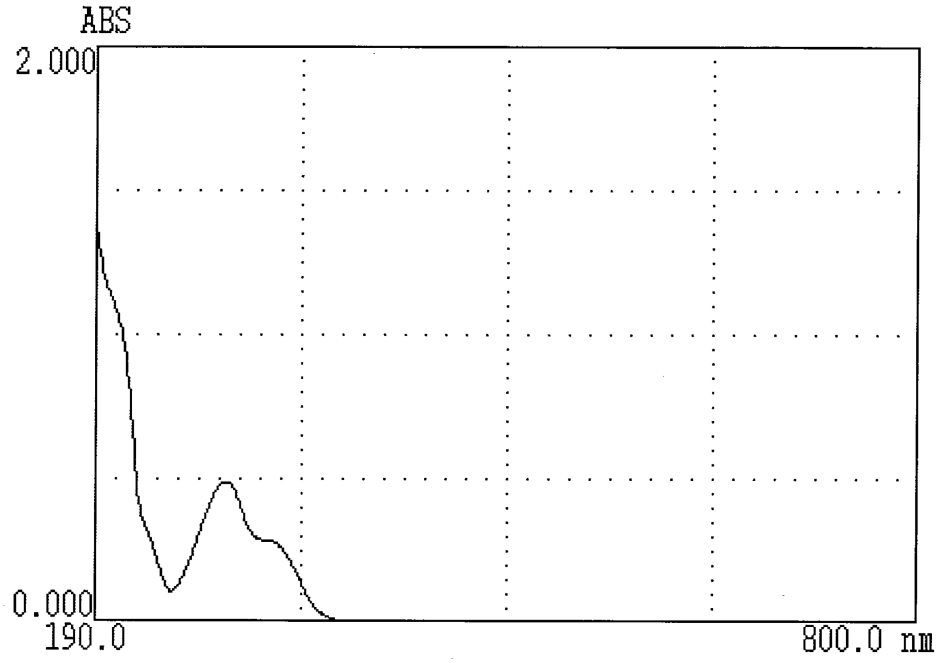
Date	2014/1/21	Chiral Column	a doubly-connected AD-H/AD-3
Solvent	iPrOH : Hexane = 10 : 90	Wavelength (nm)	254
Temp. (℃)	35	Injection Volume (μl)	5
Comment		% ee	13.022

UV-vis spectra

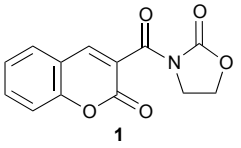
(1) **1** in MeCN (4.00 x 10^{-5} M)

U-2800形　分光光度計

シリアル番号	1612007
プログラムバージョン	09
サンプル名	SAMP-1
日付	17/04/07 20:36
分析者	



波長スキャン	
データモード	ABS
スタート波長(nm)	800.0
ストップ波長(nm)	190.0
スキャン速度(nm/min)	200
サンプリング間隔(nm)	1.0
ベースライン設定	ユーザ1
レスポンス	標準
バンドパス(nm)	1.5
セル長(mm)	10.0
光源切替波長(nm)	340.0
光源切替	自動切替



in MeCN (4.00 x 10^{-5} M)

1

365.0	nm	0.009	ABS

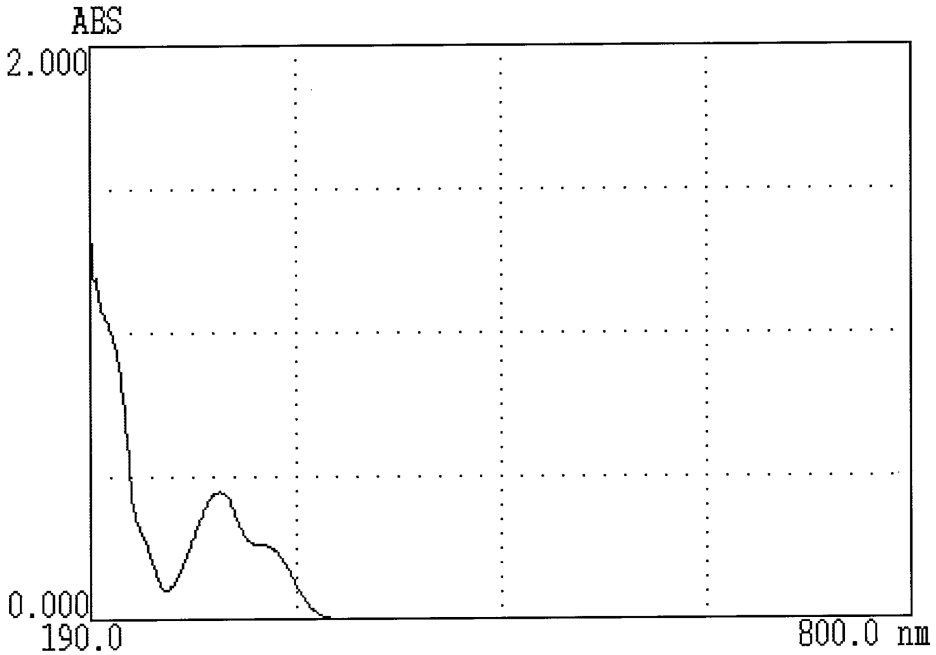
ピーク

ID	WL(nm)	ABS	ID	WL(nm)	ABS	ID	WL(nm)	ABS
1	738.0	0.000	2	286.0	0.483			

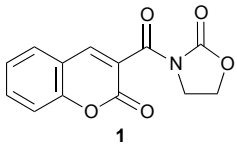
(2) **1** and $Zn(ClO_4)_2 \cdot 6H_2O$ in MeCN (4.00×10^{-5} M)

U-2800形　分光光度計

シリアル番号	1612007
プログラムバージョン	09
サンプル名	SAMP-1
日付	17/04/05 13:48
分析者	



波長スキャン	
データモード	ABS
スタート波長(nm)	800.0
ストップ波長(nm)	190.0
スキャン速度(nm/min)	200
サンプリング間隔(nm)	1.0
ベースライン設定	ユーザ1
レスポンス	標準
バンドパス(nm)	1.5
セル長(mm)	10.0
光源切替波長(nm)	340.0
光源切替	自動切替



1 + $Zn(ClO_4)_2 \cdot 6H_2O$ in MeCN (4.00×10^{-5} M)

365.0	nm	0.008	ABS

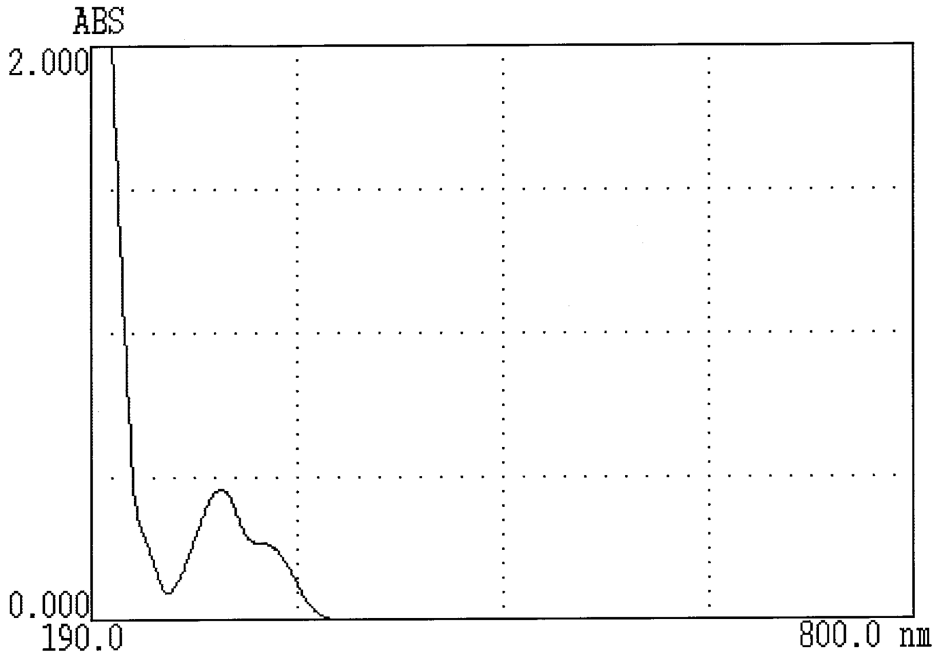
ピーク

ID	WL(nm)	ABS	ID	WL(nm)	ABS	ID	WL(nm)	ABS
1	739.0	0.001	2	594.0	0.001	3	404.0	0.003
4	385.0	0.003	5	286.0	0.443			

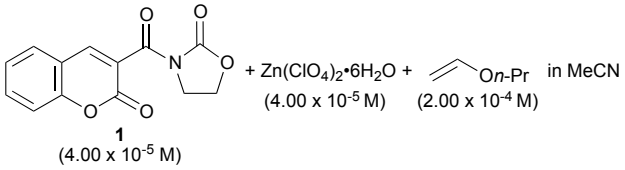
(3) **1**, $Zn(ClO_4)_2 \cdot 6H_2O$ (4.00×10^{-5} M) and n-propyl vinyl ether (2.00×10^{-4} M) in MeCN

U-2800形　分光光度計

シリアル番号	1612007
プログラムバージョン	09
サンプル名	SAMP-1
日付	17/04/05　20:19
分析者	



波長スキャン	
データモード	ABS
スタート波長(nm)	800.0
ストップ波長(nm)	190.0
スキャン速度(nm/min)	200
サンプリング間隔(nm)	1.0
ベースライン設定	ユーザ1
レスポンス	標準
バンドパス(nm)	1.5
セル長(mm)	10.0
光源切替波長(nm)	340.0
光源切替	自動切替



1
(4.00×10^{-5} M)

365.0	nm	0.008	ABS

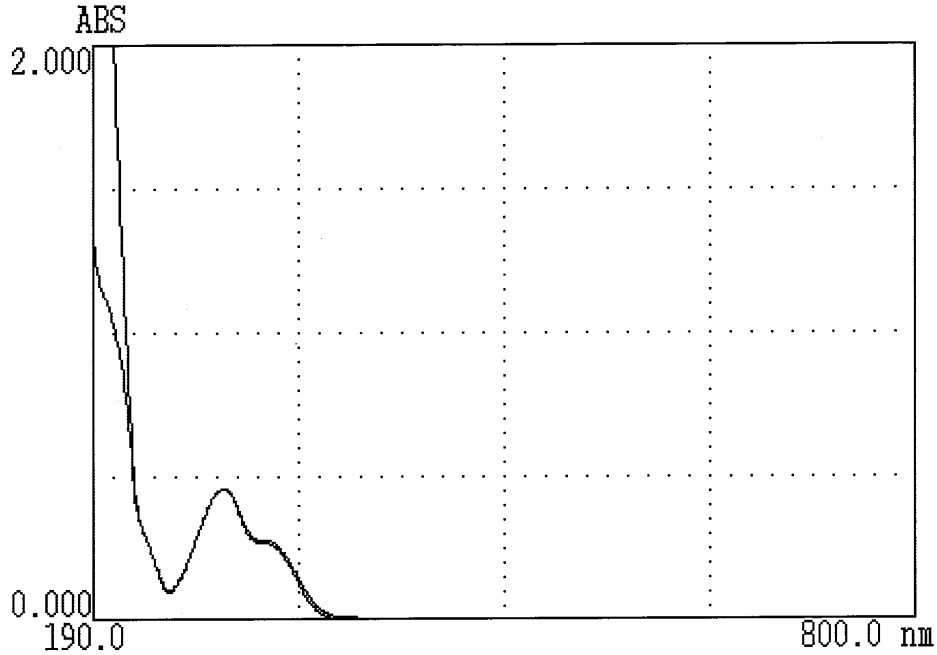
ピーク

ID	WL(nm)	ABS	ID	WL(nm)	ABS	ID	WL(nm)	ABS
1	780.0	-0.000	2	517.0	-0.000	3	504.0	-0.000
4	404.0	-0.000	5	286.0	0.453	6	196.0	2.543

(4) Superimposed spectra of (1), (2) and (3)

U-2800形　分光光度計

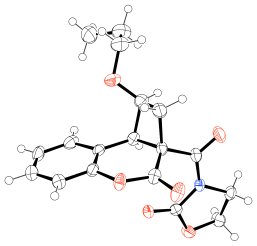
シリアル番号	1612007
プログラムバージョン	09
サンプル名	SAMP-1
日付	17/04/05　20:23
分析者	



波長スキャン	
データモード	ABS
スタート波長(nm)	800.0
ストップ波長(nm)	190.0
スキャン速度(nm/min)	200
サンプリング間隔(nm)	1.0
ベースライン設定	ユーザ1
レスポンス	標準
バンドパス(nm)	1.5
セル長(mm)	10.0
光源切替波長(nm)	340.0
光源切替	自動切替

Crystal data

endo-**4**



Crystal data

$C_{18}H_{19}NO_6$	V = 1688.0 (4) Å^3
M_r = 345.34	Z = 4
a = 14.3156 (19) Å	F(000) = 728
b = 10.5343 (14) Å	D_x = 1.359 Mg m^{-3}
c = 11.2428 (14) Å	Mo Ka radiation, l = 0.71073 Å
a = 90°	m = 0.10 mm^{-1}
b = 95.387 (2)°	T = 296 K
g = 90°	

Data collection

Radiation source: fine-focus sealed tube	R_{int} = 0.036
Graphite monochromator	q_{max} = 25.9°, q_{min} = 1.4°
8466 measured reflections	h = -17®17
3251 independent reflections	k = -11®12
2379 reflections with $I > 2s(I)$	l = -12®13

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2s(F^2)]$ = 0.057	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.172	$w = 1/[s^2(F_o^2) + (0.0774P)^2 + 1.7122P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.05	$(D/s)_{max} < 0.001$
3251 reflections	$D\rho_{max}$ = 0.67 e Å^{-3}
228 parameters	$D\rho_{min}$ = -0.39 e Å^{-3}
0 restraints	Extinction correction: *SHELXL*, $Fc^* = kFc[1+0.001xFc^2l^3/sin(2q)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0007 (12)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement.

R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$) for *endo*-**4**

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.45238 (12)	0.83230 (16)	0.09999 (15)	0.0244 (4)
O2	0.54474 (13)	0.69070 (18)	0.20108 (18)	0.0340 (5)
N1	0.40676 (15)	0.62285 (19)	0.12096 (18)	0.0224 (5)
C1	0.46596 (17)	0.7267 (2)	0.1376 (2)	0.0233 (6)
C2	0.5342 (2)	0.5634 (3)	0.2480 (3)	0.0384 (7)
H2A	0.5215	0.5663	0.3312	0.046*
H2B	0.5905	0.5136	0.2414	0.046*
C3	0.45181 (19)	0.5077 (3)	0.1713 (2)	0.0296 (6)
H3A	0.4723	0.4530	0.1094	0.036*
H3B	0.4105	0.4606	0.2188	0.036*
O3	0.27137 (15)	0.52333 (19)	0.0627 (2)	0.0434 (6)
C4	0.31653 (19)	0.6214 (2)	0.0659 (2)	0.0268 (6)
O4	0.37876 (15)	0.72262 (19)	-0.14005 (16)	0.0350 (5)
C5	0.33521 (19)	0.7919 (3)	-0.0802 (2)	0.0265 (6)
O5	0.32989 (14)	0.91605 (18)	-0.10939 (16)	0.0305 (5)
C6	0.27638 (18)	0.7447 (2)	0.0130 (2)	0.0247 (6)
C7	0.24662 (18)	0.8398 (3)	0.1088 (2)	0.0261 (6)
H7	0.2761	0.8224	0.1894	0.031*
C8	0.1708 (2)	0.7316 (3)	-0.0331 (3)	0.0375 (7)
H8A	0.1517	0.7847	-0.1016	0.045*
H8B	0.1503	0.6446	-0.0468	0.045*
C9	0.1458 (2)	0.7869 (3)	0.0865 (3)	0.0388 (7)
H9	0.1348	0.7194	0.1434	0.047*
O6	0.07504 (14)	0.8793 (2)	0.0832 (2)	0.0519 (7)
C10	-0.0180 (2)	0.8298 (4)	0.0809 (4)	0.0559 (10)
H10A	-0.0206	0.7482	0.0407	0.067*
H10B	-0.0609	0.8867	0.0351	0.067*
C11	-0.0493 (3)	0.8140 (4)	0.2012 (4)	0.0604 (10)
H11A	-0.0056	0.7585	0.2474	0.072*
H11B	-0.1102	0.7729	0.1942	0.072*
C12	-0.0565 (3)	0.9388 (4)	0.2687 (4)	0.0678 (12)
H12A	-0.1019	0.9928	0.2256	0.102*
H12B	0.0035	0.9803	0.2762	0.102*
H12C	-0.0756	0.9220	0.3468	0.102*
C13	0.2418 (2)	1.2010 (3)	0.1058 (3)	0.0382 (7)
H13	0.2243	1.2670	0.1540	0.046*
C14	0.2794 (2)	1.2278 (3)	0.0015 (3)	0.0396 (8)
H14	0.2862	1.3117	-0.0220	0.048*
C15	0.22950 (19)	1.0758 (3)	0.1405 (3)	0.0345 (7)
H15	0.2026	1.0590	0.2110	0.041*
C16	0.3070 (2)	1.1309 (3)	-0.0684 (3)	0.0359 (7)
H16	0.3330	1.1486	-0.1393	0.043*
C17	0.29597 (18)	1.0062 (3)	-0.0324 (2)	0.0270 (6)
C18	0.25698 (17)	0.9746 (2)	0.0709 (2)	0.0251 (6)

Atomic displacement parameters ($Å^2$) for *endo*-**4**

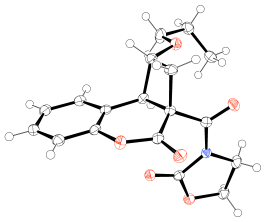
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0279 (10)	0.0197 (10)	0.0255 (9)	0.0001 (7)	0.0023 (7)	0.0021 (7)
O2	0.0259 (10)	0.0294 (11)	0.0447 (12)	-0.0023 (8)	-0.0065 (8)	0.0137 (9)
N1	0.0280 (11)	0.0182 (11)	0.0211 (11)	0.0018 (9)	0.0026 (9)	0.0018 (8)
C1	0.0232 (13)	0.0267 (14)	0.0202 (13)	0.0010 (10)	0.0035 (10)	0.0003 (10)
C2	0.0344 (16)	0.0297 (16)	0.0496 (18)	0.0027 (13)	-0.0044 (14)	0.0191 (14)
C3	0.0340 (15)	0.0224 (14)	0.0327 (15)	0.0066 (11)	0.0045 (12)	0.0066 (11)
O3	0.0417 (12)	0.0221 (11)	0.0636 (15)	-0.0053 (9)	-0.0096 (11)	0.0007 (10)
C4	0.0328 (14)	0.0199 (14)	0.0273 (14)	-0.0004 (11)	0.0000 (11)	-0.0027 (10)
O4	0.0503 (13)	0.0349 (11)	0.0197 (10)	0.0147 (9)	0.0028 (9)	-0.0037 (8)
C5	0.0331 (14)	0.0275 (15)	0.0176 (13)	0.0049 (12)	-0.0039 (11)	-0.0014 (10)
O5	0.0433 (11)	0.0250 (10)	0.0240 (10)	0.0086 (8)	0.0077 (8)	0.0038 (7)
C6	0.0285 (14)	0.0194 (13)	0.0251 (13)	0.0008 (10)	-0.0028 (11)	-0.0020 (10)
C7	0.0284 (13)	0.0273 (14)	0.0228 (13)	0.0037 (11)	0.0039 (11)	0.0010 (11)
C8	0.0317 (16)	0.0297 (16)	0.0477 (18)	-0.0013 (12)	-0.0143 (13)	0.0023 (13)
C9	0.0297 (15)	0.0334 (17)	0.054 (2)	0.0010 (13)	0.0072 (14)	0.0112 (14)
O6	0.0262 (11)	0.0451 (14)	0.0862 (18)	0.0024 (10)	0.0148 (11)	0.0122 (12)
C10	0.0355 (18)	0.053 (2)	0.081 (3)	-0.0003 (16)	0.0143 (18)	0.006 (2)
C11	0.044 (2)	0.063 (3)	0.076 (3)	-0.0038 (18)	0.0101 (19)	0.006 (2)
C12	0.056 (2)	0.046 (2)	0.105 (3)	0.0005 (18)	0.029 (2)	0.000 (2)
C13	0.0352 (16)	0.0241 (15)	0.054 (2)	0.0076 (12)	-0.0033 (14)	-0.0153 (13)
C14	0.0358 (16)	0.0243 (16)	0.059 (2)	0.0009 (12)	0.0044 (15)	-0.0021 (14)
C15	0.0274 (14)	0.0394 (18)	0.0366 (16)	0.0063 (12)	0.0023 (12)	-0.0091 (13)
C16	0.0356 (16)	0.0277 (16)	0.0450 (18)	0.0000 (12)	0.0069 (13)	0.0052 (13)
C17	0.0254 (13)	0.0235 (14)	0.0315 (14)	0.0040 (11)	0.0001 (11)	-0.0016 (11)
C18	0.0195 (12)	0.0251 (14)	0.0299 (14)	0.0031 (10)	-0.0024 (11)	-0.0049 (11)

Geometric parameters (Å, º) for *endo*-**4**

O1—C1	1.199 (3)	C6—C7	1.560 (4)
O2—C1	1.332 (3)	C7—C18	1.494 (4)
O2—C2	1.454 (3)	C7—C9	1.546 (4)
N1—C4	1.379 (3)	C8—C9	1.538 (5)
N1—C1	1.386 (3)	C9—O6	1.402 (4)
N1—C3	1.462 (3)	O6—C10	1.429 (4)
C2—C3	1.513 (4)	C10—C11	1.473 (5)
O3—C4	1.217 (3)	C11—C12	1.527 (6)
C4—C6	1.519 (4)	C13—C14	1.364 (5)
O4—C5	1.205 (3)	C13—C15	1.392 (4)
C5—O5	1.348 (3)	C14—C16	1.369 (4)
C5—C6	1.490 (4)	C15—C18	1.400 (4)
O5—C17	1.402 (3)	C16—C17	1.388 (4)
C6—C8	1.558 (4)	C17—C18	1.376 (4)
C1—O2—C2	110.2 (2)	C8—C6—C7	88.1 (2)
C4—N1—C1	127.2 (2)	C18—C7—C9	114.4 (2)
C4—N1—C3	121.7 (2)	C18—C7—C6	111.9 (2)
C1—N1—C3	111.1 (2)	C9—C7—C6	88.1 (2)
O1—C1—O2	123.6 (2)	C9—C8—C6	88.5 (2)
O1—C1—N1	127.4 (2)	O6—C9—C8	117.8 (3)
O2—C1—N1	108.9 (2)	O6—C9—C7	114.5 (2)

O2—C2—C3	104.6 (2)	C8—C9—C7	89.3 (2)
N1—C3—C2	101.0 (2)	C9—O6—C10	114.7 (3)
O3—C4—N1	119.7 (2)	O6—C10—C11	112.8 (3)
O3—C4—C6	122.3 (2)	C10—C11—C12	113.6 (3)
N1—C4—C6	118.1 (2)	C14—C13—C15	120.5 (3)
O4—C5—O5	118.2 (2)	C13—C14—C16	119.8 (3)
O4—C5—C6	123.1 (2)	C13—C15—C18	121.0 (3)
O5—C5—C6	118.2 (2)	C14—C16—C17	119.4 (3)
C5—O5—C17	121.4 (2)	C18—C17—C16	122.7 (3)
C5—C6—C4	110.1 (2)	C18—C17—O5	123.3 (2)
C5—C6—C8	113.0 (2)	C16—C17—O5	114.0 (2)
C4—C6—C8	112.0 (2)	C17—C18—C15	116.4 (3)
C5—C6—C7	118.7 (2)	C17—C18—C7	122.0 (2)
C4—C6—C7	113.4 (2)	C15—C18—C7	121.6 (2)

exo-**4**



Crystal data

$C_{18}H_{19}NO_6$	V = 3205.6 (6) Å^3
M_r = 345.34	Z = 8
a = 13.9812 (15) Å	F(000) = 1456
b = 11.6104 (13) Å	D_x = 1.431 Mg m^{-3}
c = 19.748 (2) Å	Mo Ka radiation, l = 0.71073 Å
a = 90°	m = 0.11 mm^{-1}
b = 90°	T = 296 K
g = 90°	0.40 × 0.20 × 0.10 mm

Data collection

Radiation source: fine-focus sealed tube	R_{int} = 0.043
Graphite monochromator	q_{max} = 27.3°, q_{min} = 2.5°
17043 measured reflections	h = -16®17
3581 independent reflections	k = -14®14
2686 reflections with $I > 2s(I)$	l = -20®25

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2s(F^2)]$ = 0.039	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.094	$w = 1/[s^2(F_o^2) + (0.0374P)^2 + 1.3573P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.02	$(D/s)_{max} < 0.001$
3581 reflections	$D\rho_{max}$ = 0.28 e Å^{-3}
228 parameters	$D\rho_{min}$ = -0.21 e Å^{-3}

0 restraints	Extinction correction: *SHELXL*, $Fc^{*}=kFc[1+0.001xFc^{2}l^{3}/sin(2q)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0023 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 >$ 2sigma(F^2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$) for *exo*-**4**

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.33086 (7)	0.87119 (9)	0.43825 (5)	0.0203 (3)
O8	0.42172 (7)	0.77609 (10)	0.36385 (5)	0.0218 (3)
N1	0.27943 (8)	0.83766 (11)	0.32826 (6)	0.0157 (3)
O4	0.14323 (8)	0.88472 (10)	0.27521 (5)	0.0244 (3)
O5	0.23852 (8)	1.09833 (9)	0.37858 (5)	0.0209 (3)
O6	0.20750 (7)	1.05501 (9)	0.48453 (5)	0.0198 (3)
O7	-0.01341 (8)	0.75692 (9)	0.38095 (5)	0.0220 (3)
C1	0.34207 (10)	0.83152 (13)	0.38276 (8)	0.0168 (3)
C3	0.41553 (11)	0.73942 (14)	0.29388 (8)	0.0221 (4)
H3A	0.4199	0.6562	0.2907	0.027*
H3B	0.4669	0.7731	0.2674	0.027*
C4	0.31855 (11)	0.78126 (14)	0.26829 (8)	0.0218 (4)
H4A	0.3257	0.8351	0.2311	0.026*
H4B	0.2786	0.7174	0.2539	0.026*
C5	0.18805 (10)	0.88347 (13)	0.32778 (8)	0.0168 (3)
C6	0.14806 (10)	0.92736 (13)	0.39479 (7)	0.0159 (3)
C7	0.20390 (10)	1.03043 (13)	0.41768 (7)	0.0167 (3)
C8	0.18554 (10)	0.97198 (13)	0.53368 (7)	0.0175 (3)
C9	0.20494 (11)	1.00565 (14)	0.59958 (8)	0.0210 (3)
H9	0.2292	1.0786	0.6087	0.025*
C10	0.18752 (10)	0.92865 (15)	0.65163 (8)	0.0220 (4)
H10	0.2004	0.9499	0.6961	0.026*
C11	0.15108 (11)	0.82006 (14)	0.63793 (8)	0.0222 (4)
H11	0.1397	0.7684	0.6730	0.027*
C12	0.13175 (11)	0.78892 (14)	0.57151 (8)	0.0196 (3)
H12	0.1069	0.7162	0.5625	0.024*
C13	0.14885 (10)	0.86429 (13)	0.51812 (8)	0.0170 (3)
C14	0.12582 (11)	0.82991 (13)	0.44681 (7)	0.0168 (3)
H14	0.1537	0.7555	0.4341	0.020*
C15	0.01752 (11)	0.84008 (14)	0.42813 (8)	0.0198 (3)
H15	-0.0249	0.8488	0.4673	0.024*
C16	0.03842 (10)	0.95323 (14)	0.39070 (8)	0.0206 (3)
H16A	0.0192	1.0214	0.4156	0.025*
H16B	0.0137	0.9551	0.3448	0.025*

C17	-0.03000 (14)	0.64639 (15)	0.41143 (8)	0.0297 (4)
H17A	-0.0865	0.6493	0.4399	0.036*
H17B	0.0242	0.6246	0.4392	0.036*
C18	-0.04399 (12)	0.55989 (15)	0.35525 (8)	0.0262 (4)
H18A	-0.0990	0.5822	0.3284	0.031*
H18B	-0.0573	0.4850	0.3749	0.031*
C19	0.04265 (11)	0.55047 (15)	0.30944 (8)	0.0252 (4)
H19A	0.0541	0.6233	0.2879	0.038*
H19B	0.0312	0.4928	0.2756	0.038*
H19C	0.0976	0.5293	0.3359	0.038*

Atomic displacement parameters (Å^2) for *exo*-**4**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0180 (5)	0.0256 (6)	0.0171 (5)	0.0016 (5)	-0.0005 (4)	-0.0018 (5)
O8	0.0159 (5)	0.0286 (6)	0.0209 (6)	0.0063 (5)	0.0005 (4)	-0.0023 (5)
N1	0.0161 (6)	0.0162 (7)	0.0148 (6)	0.0012 (5)	0.0008 (5)	-0.0013 (5)
O4	0.0218 (6)	0.0326 (7)	0.0187 (6)	0.0051 (5)	-0.0040 (5)	0.0007 (5)
O5	0.0216 (6)	0.0179 (6)	0.0233 (6)	0.0002 (5)	0.0029 (5)	0.0030 (5)
O6	0.0247 (6)	0.0162 (6)	0.0184 (6)	-0.0013 (5)	0.0025 (4)	-0.0003 (4)
O7	0.0242 (6)	0.0220 (6)	0.0198 (6)	-0.0066 (5)	0.0004 (5)	-0.0016 (4)
C1	0.0151 (7)	0.0160 (8)	0.0193 (8)	-0.0003 (6)	0.0017 (6)	0.0030 (6)
C3	0.0221 (8)	0.0245 (9)	0.0198 (8)	0.0056 (7)	0.0042 (6)	-0.0027 (6)
C4	0.0234 (8)	0.0242 (9)	0.0178 (8)	0.0053 (7)	0.0026 (6)	-0.0034 (6)
C5	0.0166 (7)	0.0141 (8)	0.0197 (8)	-0.0006 (6)	-0.0005 (6)	0.0014 (6)
C6	0.0155 (7)	0.0146 (7)	0.0177 (7)	0.0024 (6)	0.0004 (6)	-0.0006 (6)
C7	0.0146 (7)	0.0162 (8)	0.0193 (8)	0.0050 (6)	0.0010 (6)	-0.0009 (6)
C8	0.0140 (7)	0.0202 (8)	0.0182 (8)	0.0022 (6)	0.0032 (6)	0.0023 (6)
C9	0.0170 (7)	0.0228 (9)	0.0231 (8)	0.0019 (6)	0.0005 (6)	-0.0035 (6)
C10	0.0165 (8)	0.0318 (9)	0.0175 (8)	0.0031 (7)	-0.0002 (6)	-0.0014 (7)
C11	0.0175 (8)	0.0284 (9)	0.0205 (8)	0.0035 (7)	0.0027 (6)	0.0065 (7)
C12	0.0164 (7)	0.0199 (8)	0.0226 (8)	0.0002 (6)	0.0011 (6)	0.0016 (6)
C13	0.0127 (7)	0.0191 (8)	0.0193 (8)	0.0036 (6)	0.0016 (6)	-0.0006 (6)
C14	0.0173 (7)	0.0152 (8)	0.0179 (8)	-0.0003 (6)	0.0037 (6)	-0.0006 (6)
C15	0.0172 (8)	0.0221 (8)	0.0201 (8)	-0.0019 (6)	0.0025 (6)	-0.0044 (6)
C16	0.0151 (7)	0.0215 (9)	0.0251 (8)	0.0036 (6)	-0.0001 (6)	-0.0016 (6)
C17	0.0383 (10)	0.0296 (10)	0.0213 (9)	-0.0146 (8)	0.0034 (7)	0.0025 (7)
C18	0.0278 (9)	0.0251 (9)	0.0258 (9)	-0.0085 (7)	-0.0037 (7)	0.0016 (7)
C19	0.0244 (8)	0.0234 (9)	0.0276 (9)	0.0027 (7)	-0.0069 (7)	0.0008 (7)

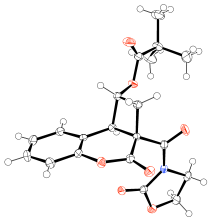
Geometric parameters (Å, º) for *exo*-**4**

O1—C1	1.1990 (18)	C9—H9	0.9300
O8—C1	1.3393 (17)	C10—C11	1.387 (2)
O8—C3	1.4484 (18)	C10—H10	0.9300
N1—C5	1.3839 (19)	C11—C12	1.387 (2)
N1—C1	1.3892 (19)	C11—H11	0.9300
N1—C4	1.4596 (19)	C12—C13	1.391 (2)
O4—C5	1.2126 (18)	C12—H12	0.9300
O5—C7	1.2051 (18)	C13—C14	1.499 (2)
O6—C7	1.3516 (17)	C14—C15	1.563 (2)
O6—C8	1.4020 (18)	C14—H14	0.9800

O7—C15	1.4097 (18)	C15—C16	1.535 (2)
O7—C17	1.436 (2)	C15—H15	0.9800
C3—C4	1.527 (2)	C16—H16A	0.9700
C3—H3A	0.9700	C16—H16B	0.9700
C3—H3B	0.9700	C17—C18	1.509 (2)
C4—H4A	0.9700	C17—H17A	0.9700
C4—H4B	0.9700	C17—H17B	0.9700
C5—C6	1.524 (2)	C18—C19	1.516 (2)
C6—C7	1.499 (2)	C18—H18A	0.9700
C6—C14	1.560 (2)	C18—H18B	0.9700
C6—C16	1.564 (2)	C19—H19A	0.9600
C8—C9	1.386 (2)	C19—H19B	0.9600
C8—C13	1.386 (2)	C19—H19C	0.9600
C9—C10	1.384 (2)		
C1—O8—C3	110.95 (11)	C12—C11—H11	120.2
C5—N1—C1	127.37 (12)	C11—C12—C13	121.29 (15)
C5—N1—C4	120.84 (12)	C11—C12—H12	119.4
C1—N1—C4	111.68 (12)	C13—C12—H12	119.4
C7—O6—C8	121.52 (12)	C8—C13—C12	117.59 (14)
C15—O7—C17	112.61 (12)	C8—C13—C14	121.88 (14)
O1—C1—O8	123.24 (13)	C12—C13—C14	120.51 (14)
O1—C1—N1	127.29 (14)	C13—C14—C6	112.51 (12)
O8—C1—N1	109.44 (12)	C13—C14—C15	114.20 (12)
O8—C3—C4	105.98 (12)	C6—C14—C15	89.01 (11)
O8—C3—H3A	110.5	C13—C14—H14	113.0
C4—C3—H3A	110.5	C6—C14—H14	113.0
O8—C3—H3B	110.5	C15—C14—H14	113.0
C4—C3—H3B	110.5	O7—C15—C16	109.04 (12)
H3A—C3—H3B	108.7	O7—C15—C14	113.67 (12)
N1—C4—C3	101.94 (12)	C16—C15—C14	89.65 (11)
N1—C4—H4A	111.4	O7—C15—H15	114.0
C3—C4—H4A	111.4	C16—C15—H15	114.0
N1—C4—H4B	111.4	C14—C15—H15	114.0
C3—C4—H4B	111.4	C15—C16—C6	89.85 (11)
H4A—C4—H4B	109.2	C15—C16—H16A	113.7
O4—C5—N1	119.19 (14)	C6—C16—H16A	113.7
O4—C5—C6	123.33 (13)	C15—C16—H16B	113.7
N1—C5—C6	117.46 (13)	C6—C16—H16B	113.7
C7—C6—C5	109.74 (12)	H16A—C16—H16B	110.9
C7—C6—C14	118.97 (12)	O7—C17—C18	107.90 (13)
C5—C6—C14	113.73 (12)	O7—C17—H17A	110.1
C7—C6—C16	111.89 (12)	C18—C17—H17A	110.1
C5—C6—C16	112.27 (12)	O7—C17—H17B	110.1
C14—C6—C16	88.74 (11)	C18—C17—H17B	110.1
O5—C7—O6	118.21 (14)	H17A—C17—H17B	108.4
O5—C7—C6	122.57 (14)	C17—C18—C19	112.53 (14)
O6—C7—C6	118.86 (13)	C17—C18—H18A	109.1
C9—C8—C13	122.35 (14)	C19—C18—H18A	109.1
C9—C8—O6	114.41 (14)	C17—C18—H18B	109.1

C13—C8—O6	123.23 (13)	C19—C18—H18B	109.1
C10—C9—C8	118.74 (15)	H18A—C18—H18B	107.8
C10—C9—H9	120.6	C18—C19—H19A	109.5
C8—C9—H9	120.6	C18—C19—H19B	109.5
C9—C10—C11	120.47 (15)	H19A—C19—H19B	109.5
C9—C10—H10	119.8	C18—C19—H19C	109.5
C11—C10—H10	119.8	H19A—C19—H19C	109.5
C10—C11—C12	119.55 (15)	H19B—C19—H19C	109.5
C10—C11—H11	120.2		

exo-**5**



Crystal data

$C_{20}H_{21}NO_7$	$F(000) = 816$
$M_r = 387.38$	$D_x = 1.342$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 16.0143$ (17) Å	Cell parameters from 3065 reflections
$b = 10.7266$ (11) Å	$\theta = 2.3–27.8°$
$c = 11.1665$ (12) Å	$\mu = 0.10$ mm^{-1}
$\beta = 90.938$ (1)°	$T = 296$ K
$V = 1917.9$ (4) Å^3	Block, colorless
$Z = 4$	0.40 × 0.40 × 0.10 mm

Data collection

Bruker D8 goniometer diffractometer	$\theta_{max} = 28.6°$, $\theta_{min} = 1.3°$
10891 measured reflections	$h = -20 \rightarrow 19$
4512 independent reflections	$k = -14 \rightarrow 12$
3405 reflections with $I > 2\sigma(I)$	$l = -14 \rightarrow 11$
$R_{int} = 0.028$	

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.041$	H-atom parameters constrained
$wR(F^2) = 0.113$	$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.13$	$(\Delta/\sigma)_{max} = 0.005$
4512 reflections	$\Delta\rho_{max} = 0.30$ e Å^{-3}
256 parameters	$\Delta\rho_{min} = -0.25$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal

symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for exo-***5**

	x	*y*	*z*	U_{iso}*/U_{eq}
C5	0.69500 (8)	0.72305 (12)	0.98191 (12)	0.0138 (3)
C6	0.73019 (8)	0.80522 (12)	0.87940 (12)	0.0144 (3)
H6	0.711091	0.778778	0.799530	0.017*
C8	0.78660 (8)	0.70010 (13)	1.02723 (13)	0.0168 (3)
H8A	0.801371	0.746376	1.099137	0.020*
H8B	0.800798	0.612628	1.036011	0.020*
C16	0.71898 (8)	0.94191 (12)	0.90101 (13)	0.0165 (3)
C4	0.65310 (9)	0.60315 (12)	0.93907 (13)	0.0167 (3)
C1	0.52829 (8)	0.71811 (12)	0.86333 (12)	0.0156 (3)
C9	0.92352 (9)	0.62168 (13)	0.84719 (13)	0.0192 (3)
C15	0.68242 (9)	0.98656 (13)	1.00379 (14)	0.0191 (3)
C2	0.53646 (9)	0.50172 (13)	0.82775 (14)	0.0199 (3)
H2A	0.514925	0.448314	0.890176	0.024*
H2B	0.573734	0.453992	0.777762	0.024*
C7	0.81909 (8)	0.75918 (12)	0.91185 (12)	0.0154 (3)
H7	0.859622	0.826360	0.925420	0.018*
C17	0.74669 (9)	1.02882 (13)	0.81749 (15)	0.0234 (3)
H17	0.771425	1.001339	0.747496	0.028*
C18	0.73777 (10)	1.15545 (14)	0.83764 (18)	0.0326 (4)
H18	0.756217	1.212380	0.781102	0.039*
C10	0.94292 (9)	0.51017 (14)	0.76892 (14)	0.0227 (3)
C3	0.46658 (10)	0.56086 (13)	0.75458 (16)	0.0263 (4)
H3A	0.480376	0.562918	0.670338	0.032*
H3B	0.414875	0.515018	0.763824	0.032*
C19	0.70149 (10)	1.19743 (14)	0.94166 (19)	0.0351 (4)
H19	0.696055	1.282551	0.955316	0.042*
C13	0.91582 (13)	0.53254 (18)	0.63915 (16)	0.0406 (5)
H13A	0.856314	0.543009	0.634799	0.061*
H13B	0.931583	0.462355	0.591202	0.061*
H13C	0.942508	0.606336	0.609755	0.061*
C20	0.67326 (10)	1.11300 (14)	1.02549 (17)	0.0285 (4)
H20	0.648491	1.140696	1.095381	0.034*
C12	0.89452 (11)	0.39938 (15)	0.82112 (19)	0.0384 (4)
H12A	0.913516	0.384110	0.901782	0.058*
H12B	0.903917	0.326525	0.773259	0.058*
H12C	0.835938	0.418371	0.820894	0.058*
C11	1.03653 (10)	0.48391 (16)	0.77701 (18)	0.0368 (4)
H11A	1.066654	0.553781	0.745779	0.055*
H11B	1.049082	0.410769	0.731151	0.055*
H11C	1.052710	0.470670	0.859187	0.055*
O5	0.84522 (6)	0.66737 (9)	0.82628 (9)	0.0182 (2)
O4	0.60132 (6)	0.72507 (9)	1.14455 (9)	0.0204 (2)
O2	0.54231 (6)	0.82104 (8)	0.90114 (9)	0.0173 (2)
O1	0.45900 (6)	0.68721 (9)	0.80242 (9)	0.0216 (2)
O6	0.96874 (7)	0.66496 (10)	0.92313 (11)	0.0304 (3)

O3	0.68474 (7)	0.50168 (9)	0.95433 (11)	0.0293 (3)
N1	0.57799 (7)	0.61206 (10)	0.87794 (10)	0.0150 (2)
C21	0.64235 (8)	0.78377 (12)	1.07542 (12)	0.0158 (3)
O7	0.65016 (6)	0.90828 (9)	1.09273 (9)	0.0204 (2)

*Atomic displacement parameters (Å^2) for exo-***5**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C5	0.0136 (6)	0.0118 (6)	0.0161 (7)	-0.0003 (5)	-0.0008 (5)	0.0003 (5)
C6	0.0148 (7)	0.0153 (6)	0.0132 (6)	-0.0011 (5)	-0.0003 (5)	0.0007 (5)
C8	0.0147 (7)	0.0184 (7)	0.0172 (7)	0.0004 (5)	-0.0031 (5)	0.0014 (6)
C16	0.0105 (6)	0.0146 (6)	0.0242 (8)	-0.0007 (5)	-0.0033 (5)	0.0019 (6)
C4	0.0182 (7)	0.0141 (6)	0.0179 (7)	-0.0006 (5)	0.0014 (6)	0.0002 (5)
C1	0.0149 (7)	0.0183 (7)	0.0136 (6)	-0.0012 (5)	0.0028 (5)	0.0020 (6)
C9	0.0172 (7)	0.0206 (7)	0.0199 (7)	0.0024 (6)	0.0016 (6)	0.0043 (6)
C15	0.0146 (7)	0.0153 (7)	0.0272 (8)	-0.0027 (5)	-0.0017 (6)	0.0003 (6)
C2	0.0213 (8)	0.0158 (7)	0.0226 (8)	-0.0059 (5)	-0.0004 (6)	-0.0032 (6)
C7	0.0146 (7)	0.0154 (6)	0.0161 (7)	0.0010 (5)	0.0001 (5)	-0.0029 (5)
C17	0.0158 (7)	0.0220 (7)	0.0323 (9)	0.0000 (6)	0.0008 (6)	0.0073 (7)
C18	0.0229 (8)	0.0206 (8)	0.0543 (12)	-0.0043 (6)	0.0013 (8)	0.0141 (8)
C10	0.0202 (8)	0.0230 (7)	0.0247 (8)	0.0072 (6)	0.0002 (6)	-0.0023 (6)
C3	0.0254 (8)	0.0208 (7)	0.0327 (9)	-0.0024 (6)	-0.0062 (7)	-0.0080 (7)
C19	0.0292 (9)	0.0117 (7)	0.0643 (13)	-0.0003 (6)	0.0013 (9)	-0.0010 (8)
C13	0.0503 (11)	0.0446 (11)	0.0269 (9)	0.0230 (9)	-0.0017 (8)	-0.0082 (8)
C20	0.0248 (8)	0.0180 (7)	0.0429 (10)	0.0015 (6)	0.0024 (7)	-0.0077 (7)
C12	0.0366 (10)	0.0244 (9)	0.0544 (12)	0.0020 (7)	0.0065 (9)	-0.0041 (8)
C11	0.0256 (9)	0.0392 (10)	0.0457 (11)	0.0125 (7)	0.0020 (8)	-0.0060 (9)
O5	0.0160 (5)	0.0197 (5)	0.0189 (5)	0.0049 (4)	-0.0005 (4)	-0.0035 (4)
O4	0.0209 (5)	0.0247 (5)	0.0156 (5)	-0.0029 (4)	0.0012 (4)	0.0016 (4)
O2	0.0180 (5)	0.0142 (5)	0.0197 (5)	0.0006 (4)	0.0007 (4)	-0.0016 (4)
O1	0.0165 (5)	0.0210 (5)	0.0272 (6)	-0.0012 (4)	-0.0048 (4)	-0.0047 (4)
O6	0.0211 (6)	0.0331 (6)	0.0365 (7)	0.0060 (5)	-0.0092 (5)	-0.0095 (5)
O3	0.0300 (6)	0.0126 (5)	0.0449 (7)	0.0023 (4)	-0.0115 (5)	0.0002 (5)
N1	0.0166 (6)	0.0119 (5)	0.0164 (6)	-0.0020 (4)	-0.0002 (5)	-0.0011 (5)
C21	0.0160 (7)	0.0166 (7)	0.0148 (7)	-0.0010 (5)	-0.0026 (5)	-0.0006 (6)
O7	0.0244 (6)	0.0162 (5)	0.0206 (5)	-0.0014 (4)	0.0024 (4)	-0.0052 (4)

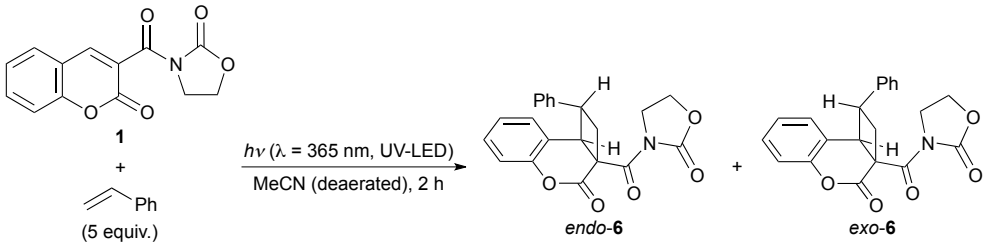
*Geometric parameters (Å, º) for exo-***5**

C5—C21	1.5014 (18)	C7—O5	1.4391 (16)
C5—C4	1.5240 (18)	C7—H7	0.9800
C5—C6	1.5576 (18)	C17—C18	1.385 (2)
C5—C8	1.5633 (18)	C17—H17	0.9300
C6—C16	1.4971 (18)	C18—C19	1.383 (3)
C6—C7	1.5444 (18)	C18—H18	0.9300
C6—H6	0.9800	C10—C13	1.525 (2)
C8—C7	1.5343 (19)	C10—C11	1.527 (2)
C8—H8A	0.9700	C10—C12	1.539 (2)
C8—H8B	0.9700	C3—O1	1.4626 (17)
C16—C15	1.383 (2)	C3—H3A	0.9700
C16—C17	1.396 (2)	C3—H3B	0.9700
C4—O3	1.2115 (17)	C19—C20	1.384 (2)

C4—N1	1.3767 (18)	C19—H19	0.9300
C1—O2	1.2019 (16)	C13—H13A	0.9600
C1—O1	1.3338 (16)	C13—H13B	0.9600
C1—N1	1.3964 (17)	C13—H13C	0.9600
C9—O6	1.1995 (18)	C20—H20	0.9300
C9—O5	1.3630 (16)	C12—H12A	0.9600
C9—C10	1.516 (2)	C12—H12B	0.9600
C15—C20	1.386 (2)	C12—H12C	0.9600
C15—O7	1.4053 (17)	C11—H11A	0.9600
C2—N1	1.4645 (17)	C11—H11B	0.9600
C2—C3	1.514 (2)	C11—H11C	0.9600
C2—H2A	0.9700	O4—C21	1.2003 (16)
C2—H2B	0.9700	C21—O7	1.3550 (16)
C21—C5—C4	109.57 (11)	C17—C18—C19	120.13 (15)
C21—C5—C6	118.66 (11)	C17—C18—H18	119.9
C4—C5—C6	114.18 (11)	C19—C18—H18	119.9
C21—C5—C8	112.20 (11)	C9—C10—C13	111.46 (12)
C4—C5—C8	112.01 (11)	C9—C10—C11	108.76 (13)
C6—C5—C8	88.75 (10)	C13—C10—C11	110.44 (14)
C16—C6—C7	112.82 (11)	C9—C10—C12	106.36 (13)
C16—C6—C5	112.95 (11)	C13—C10—C12	110.14 (15)
C7—C6—C5	89.41 (10)	C11—C10—C12	109.59 (13)
C16—C6—H6	113.2	O1—C3—C2	104.84 (11)
C7—C6—H6	113.2	O1—C3—H3A	110.8
C5—C6—H6	113.2	C2—C3—H3A	110.8
C7—C8—C5	89.57 (10)	O1—C3—H3B	110.8
C7—C8—H8A	113.7	C2—C3—H3B	110.8
C5—C8—H8A	113.7	H3A—C3—H3B	108.9
C7—C8—H8B	113.7	C20—C19—C18	120.10 (15)
C5—C8—H8B	113.7	C20—C19—H19	119.9
H8A—C8—H8B	111.0	C18—C19—H19	119.9
C15—C16—C17	117.82 (13)	C10—C13—H13A	109.5
C15—C16—C6	121.77 (12)	C10—C13—H13B	109.5
C17—C16—C6	120.40 (13)	H13A—C13—H13B	109.5
O3—C4—N1	119.49 (13)	C10—C13—H13C	109.5
O3—C4—C5	122.21 (13)	H13A—C13—H13C	109.5
N1—C4—C5	118.28 (11)	H13B—C13—H13C	109.5
O2—C1—O1	123.82 (12)	C19—C20—C15	119.05 (16)
O2—C1—N1	127.19 (13)	C19—C20—H20	120.5
O1—C1—N1	108.96 (11)	C15—C20—H20	120.5
O6—C9—O5	121.67 (13)	C10—C12—H12A	109.5
O6—C9—C10	125.85 (13)	C10—C12—H12B	109.5
O5—C9—C10	112.42 (12)	H12A—C12—H12B	109.5
C16—C15—C20	122.11 (14)	C10—C12—H12C	109.5
C16—C15—O7	123.04 (12)	H12A—C12—H12C	109.5
C20—C15—O7	114.84 (13)	H12B—C12—H12C	109.5
N1—C2—C3	101.24 (11)	C10—C11—H11A	109.5
N1—C2—H2A	111.5	C10—C11—H11B	109.5

C3—C2—H2A	111.5	H11A—C11—H11B	109.5
N1—C2—H2B	111.5	C10—C11—H11C	109.5
C3—C2—H2B	111.5	H11A—C11—H11C	109.5
H2A—C2—H2B	109.3	H11B—C11—H11C	109.5
O5—C7—C8	112.41 (11)	C9—O5—C7	114.14 (11)
O5—C7—C6	109.87 (11)	C1—O1—C3	110.08 (11)
C8—C7—C6	90.30 (10)	C4—N1—C1	127.32 (12)
O5—C7—H7	114.0	C4—N1—C2	121.41 (11)
C8—C7—H7	114.0	C1—N1—C2	111.06 (11)
C6—C7—H7	114.0	O4—C21—O7	118.39 (12)
C18—C17—C16	120.78 (15)	O4—C21—C5	122.64 (12)
C18—C17—H17	119.6	O7—C21—C5	118.37 (11)
C16—C17—H17	119.6	C21—O7—C15	121.49 (11)

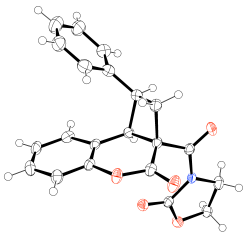
Reaction of **1** with styrene (^{1}H NMR, ^{13}C NMR and crystal structure report)



Photoadduct *endo*-**6**: Colorless needles from *n*-hexane/EtOAc; R_f : 0.34 (1:1 *n*-hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.88 (1H, dd, *J* = 11.6, 11.6 Hz), 3.41 (1H, ddd, *J* = 4.0, 7.9, 11.6 Hz), 4.03-4.13 (2H, m), 4.17-4.27 (2H, m), 4.47-4.56 (2H, m), 6.13 (1H, d, *J* = 7.5 Hz), 6.68-6.71 (1H, m), 6.79-6.81 (2H, m), 7.08-7.31 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.7, 42.8, 42.9, 46.9, 49.2, 63.1, 117.2, 117.7, 123.9, 127.3, 128.2, 128.3, 128.4, 130.3, 137.4, 151.1, 154.0, 164.5, 168.1; HRMS (ESI-TOF) Calcd for $C_{21}H_{17}NO_5Na$ $[M+Na]^+$: 386.0999; Found: 386.1018.
X-Ray diffraction analysis data of *endo*-**6**: monoclinic space group $P2_1/c$, a = 5.8769(9) Å, b = 10.4767(16) Å, c = 28.674(5) Å, α 90°, β 93.594(2)°, γ 90°, V = 1762.0(5) Å^3, Z = 4, ρ = 1.370 g cm^{-3}, μ = 0.100 mm^{-1}. The structure was solved by the direct method. And the refinement was done using the full matrix least-squares, where the final R and wR were 0.0557 and 0.1427 for 8380 reflections. CCDC-1832687.

Photoadduct *exo*-**6**: Pale yellow oil; R_f : 0.28 (1:1 *n*-hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.06 (1H, ddd, *J* = 1.0, 10.3, 13.5 Hz), 3.46-3.50 (m, 2H), 3.74-3.75 (1H, m), 3.88 (1H, ddd, *J* = 2.0, 5.9, 13.5 Hz), 4.01-4.06 (1H, m), 4.10-4.15 (1H, m), 4.39-4.48 (2H, m), 7.06-7.08 (3H, m), 7.25-7.38 (6H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.3, 43.0, 45.6, 48.0, 49.3, 63.0, 117.7, 124.3, 125.3, 126.6, 126.8, 127.1, 128.5, 129.0, 142.0, 150.8, 153.6, 166.3, 167.7.

endo-**6**



Crystal data

$C_{21}H_{17}NO_5$	F(000) = 760
M_r = 363.36	D_x = 1.370 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo *K*a radiation, l = 0.71073 Å
a = 5.8769 (9) Å	Cell parameters from 1526 reflections
b = 10.4767 (16) Å	q = 2.4–23.6°
c = 28.674 (5) Å	m = 0.10 mm^{-1}
b = 93.594 (2)°	T = 296 K
V = 1762.0 (5) Å^3	Block, colorless
Z = 4	0.40 × 0.40 × 0.10 mm

Data collection

Bruker D8 goniometer diffractometer	q_{max} = 25.1°, q_{min} = 1.4°
8380 measured reflections	h = -7®3

3131 independent reflections	k = -12®12
2169 reflections with $I > 2s(I)$	l = -31®34
R_{int} = 0.043	

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2s(F^2)]$ = 0.056	H-atom parameters constrained
$wR(F^2)$ = 0.164	$w = 1/[s^2(F_o^2) + (0.0848P)^2 + 0.8439P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.03	$(D/s)_{max} < 0.001$
3131 reflections	$D\rho_{max}$ = 0.74 e Å^{-3}
244 parameters	$D\rho_{min}$ = -0.34 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for endo-***6**

	x	y	z	U_{iso}*/U_{eq}
O001	0.7229 (3)	0.39133 (18)	0.72281 (7)	0.0220 (5)
O002	0.3414 (3)	0.30641 (18)	0.66235 (7)	0.0235 (5)
O003	0.9498 (3)	0.52403 (18)	0.76505 (7)	0.0248 (5)
O004	0.2697 (3)	0.50529 (19)	0.68111 (8)	0.0287 (5)
O005	0.7044 (4)	0.69509 (18)	0.62933 (7)	0.0300 (5)
N006	0.7956 (4)	0.5974 (2)	0.69756 (8)	0.0173 (5)
C007	0.8140 (5)	0.4938 (3)	0.72769 (9)	0.0188 (6)
C008	0.4922 (5)	0.2129 (3)	0.64716 (10)	0.0191 (6)
C009	0.5843 (5)	0.4760 (3)	0.63378 (10)	0.0188 (6)
C00A	0.7662 (5)	0.3772 (3)	0.61963 (9)	0.0187 (6)
H00A	0.918699	0.395451	0.633847	0.022*
C00B	0.3959 (5)	0.4329 (3)	0.66256 (10)	0.0212 (6)
C00C	0.8291 (5)	0.1400 (3)	0.61439 (10)	0.0228 (7)
H00C	0.964599	0.156010	0.600345	0.027*
C00D	0.6946 (5)	0.2429 (3)	0.62694 (9)	0.0185 (6)
C00E	0.6937 (5)	0.5992 (3)	0.65271 (10)	0.0195 (6)
C00F	0.4249 (5)	0.0887 (3)	0.65497 (11)	0.0242 (7)
H00F	0.287954	0.071980	0.668359	0.029*
C00G	1.0452 (5)	0.6517 (3)	0.76044 (10)	0.0248 (7)
H00B	1.208789	0.647266	0.757773	0.030*
H00D	1.014979	0.703681	0.787339	0.030*
C00H	0.7315 (5)	0.4280 (3)	0.56784 (10)	0.0240 (7)
H00H	0.842291	0.496055	0.563168	0.029*
C00I	0.5054 (5)	0.4883 (3)	0.58086 (10)	0.0258 (7)
H00E	0.372352	0.437183	0.571707	0.031*
H00G	0.485388	0.575786	0.570337	0.031*
C00J	0.9277 (5)	0.7074 (3)	0.71610 (11)	0.0247 (7)
H00I	0.829083	0.778179	0.723106	0.030*

H00J	1.037646	0.735618	0.694441	0.030*
C00K	0.5645 (5)	-0.0104 (3)	0.64255 (11)	0.0272 (7)
H00K	0.522046	-0.094368	0.647896	0.033*
C00L	0.7662 (5)	0.0149 (3)	0.62228 (11)	0.0269 (7)
H00L	0.859684	-0.051851	0.613926	0.032*
C00M	0.7356 (5)	0.3342 (3)	0.52779 (10)	0.0288 (7)
C00N	0.5737 (6)	0.1649 (3)	0.47997 (12)	0.0367 (8)
H00N	0.453119	0.109799	0.472271	0.044*
C00O	0.9287 (6)	0.3283 (3)	0.50184 (11)	0.0330 (8)
H00O	1.050868	0.382355	0.509476	0.040*
C00P	0.5583 (6)	0.2483 (3)	0.51556 (11)	0.0340 (8)
H00P	0.427831	0.248749	0.532301	0.041*
C00Q	0.9425 (6)	0.2425 (3)	0.46446 (12)	0.0385 (9)
H00Q	1.069750	0.241904	0.446731	0.046*
C00R	0.7683 (6)	0.1608 (3)	0.45468 (12)	0.0408 (9)
H00R	0.778274	0.101243	0.430848	0.049*

*Atomic displacement parameters (Å^2) for endo-***6**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O001	0.0260 (11)	0.0183 (11)	0.0215 (11)	-0.0015 (9)	-0.0011 (9)	-0.0001 (8)
O002	0.0174 (10)	0.0200 (11)	0.0330 (12)	-0.0005 (8)	0.0021 (9)	-0.0060 (9)
O003	0.0336 (12)	0.0208 (11)	0.0190 (11)	-0.0047 (9)	-0.0059 (9)	-0.0002 (8)
O004	0.0206 (11)	0.0274 (12)	0.0385 (13)	0.0036 (9)	0.0041 (9)	-0.0103 (10)
O005	0.0475 (14)	0.0145 (11)	0.0276 (12)	0.0023 (10)	-0.0019 (10)	0.0039 (9)
N006	0.0209 (12)	0.0123 (12)	0.0183 (12)	0.0001 (9)	-0.0007 (10)	-0.0021 (9)
C007	0.0192 (15)	0.0200 (16)	0.0172 (15)	0.0031 (12)	0.0015 (12)	-0.0023 (12)
C008	0.0196 (15)	0.0183 (15)	0.0190 (15)	0.0043 (12)	-0.0024 (12)	-0.0041 (12)
C009	0.0216 (15)	0.0163 (15)	0.0180 (14)	0.0021 (11)	-0.0024 (12)	-0.0022 (11)
C00A	0.0200 (15)	0.0194 (15)	0.0167 (14)	0.0032 (12)	0.0008 (11)	0.0004 (12)
C00B	0.0201 (15)	0.0207 (15)	0.0218 (15)	0.0022 (13)	-0.0054 (12)	-0.0054 (12)
C00C	0.0208 (15)	0.0278 (17)	0.0193 (15)	0.0053 (12)	-0.0013 (12)	-0.0037 (12)
C00D	0.0218 (15)	0.0172 (15)	0.0158 (14)	0.0041 (11)	-0.0057 (12)	-0.0036 (11)
C00E	0.0216 (15)	0.0193 (15)	0.0176 (15)	0.0059 (12)	0.0015 (12)	-0.0008 (12)
C00F	0.0220 (16)	0.0227 (16)	0.0276 (16)	-0.0027 (12)	-0.0016 (13)	-0.0019 (13)
C00G	0.0301 (17)	0.0186 (15)	0.0252 (16)	-0.0063 (13)	-0.0004 (13)	-0.0037 (12)
C00H	0.0339 (17)	0.0205 (15)	0.0177 (15)	0.0050 (13)	0.0025 (13)	0.0008 (12)
C00I	0.0344 (18)	0.0222 (16)	0.0196 (16)	0.0051 (13)	-0.0080 (13)	-0.0022 (12)
C00J	0.0291 (17)	0.0156 (15)	0.0289 (17)	-0.0025 (13)	-0.0032 (13)	-0.0034 (13)
C00K	0.0303 (18)	0.0162 (15)	0.0341 (18)	-0.0025 (13)	-0.0053 (14)	-0.0019 (13)
C00L	0.0324 (18)	0.0197 (16)	0.0278 (17)	0.0092 (13)	-0.0044 (14)	-0.0061 (13)
C00M	0.0397 (19)	0.0261 (17)	0.0198 (16)	0.0018 (14)	-0.0036 (14)	0.0030 (13)
C00N	0.042 (2)	0.0307 (18)	0.036 (2)	-0.0045 (15)	-0.0099 (16)	-0.0009 (15)
C00O	0.0404 (19)	0.0310 (18)	0.0276 (18)	-0.0009 (15)	0.0027 (15)	-0.0001 (14)
C00P	0.0379 (19)	0.0344 (19)	0.0294 (18)	0.0014 (15)	-0.0002 (15)	0.0035 (15)
C00Q	0.044 (2)	0.0350 (19)	0.038 (2)	0.0049 (17)	0.0102 (17)	-0.0043 (16)
C00R	0.047 (2)	0.037 (2)	0.038 (2)	0.0106 (17)	-0.0029 (17)	-0.0113 (16)

*Geometric parameters (Å, º) for endo-***6**

O001—C007	1.204 (3)	C00G—C00J	1.525 (4)

O002—C00B	1.363 (3)	C00G—H00B	0.9700
O002—C008	1.409 (3)	C00G—H00D	0.9700
O003—C007	1.333 (3)	C00H—C00M	1.513 (4)
O003—C00G	1.459 (3)	C00H—C00I	1.538 (4)
O004—C00B	1.208 (3)	C00H—H00H	0.9800
O005—C00E	1.212 (3)	C00I—H00E	0.9700
N006—C00E	1.384 (4)	C00I—H00G	0.9700
N006—C007	1.387 (3)	C00J—H00I	0.9700
N006—C00J	1.470 (3)	C00J—H00J	0.9700
C008—C00F	1.382 (4)	C00K—C00L	1.378 (4)
C008—C00D	1.391 (4)	C00K—H00K	0.9300
C009—C00B	1.492 (4)	C00L—H00L	0.9300
C009—C00E	1.526 (4)	C00M—C00O	1.397 (5)
C009—C00A	1.560 (4)	C00M—C00P	1.405 (4)
C009—C00I	1.564 (4)	C00N—C00P	1.350 (5)
C00A—C00D	1.487 (4)	C00N—C00R	1.393 (5)
C00A—C00H	1.579 (4)	C00N—H00N	0.9300
C00A—H00A	0.9800	C00O—C00Q	1.405 (4)
C00C—C00L	1.384 (4)	C00O—H00O	0.9300
C00C—C00D	1.397 (4)	C00P—H00P	0.9300
C00C—H00C	0.9300	C00Q—C00R	1.350 (5)
C00F—C00K	1.383 (4)	C00Q—H00Q	0.9300
C00F—H00F	0.9300	C00R—H00R	0.9300
C00B—O002—C008	121.7 (2)	H00B—C00G—H00D	108.7
C007—O003—C00G	111.0 (2)	C00M—C00H—C00I	120.4 (3)
C00E—N006—C007	126.9 (2)	C00M—C00H—C00A	119.2 (2)
C00E—N006—C00J	120.9 (2)	C00I—C00H—C00A	88.4 (2)
C007—N006—C00J	111.7 (2)	C00M—C00H—H00H	109.1
O001—C007—O003	123.0 (2)	C00I—C00H—H00H	109.1
O001—C007—N006	127.5 (3)	C00A—C00H—H00H	109.1
O003—C007—N006	109.5 (2)	C00H—C00I—C009	89.6 (2)
C00F—C008—C00D	122.7 (3)	C00H—C00I—H00E	113.7
C00F—C008—O002	114.4 (2)	C009—C00I—H00E	113.7
C00D—C008—O002	122.9 (2)	C00H—C00I—H00G	113.7
C00B—C009—C00E	111.7 (2)	C009—C00I—H00G	113.7
C00B—C009—C00A	119.1 (2)	H00E—C00I—H00G	111.0
C00E—C009—C00A	111.9 (2)	N006—C00J—C00G	101.7 (2)
C00B—C009—C00I	112.1 (2)	N006—C00J—H00I	111.4
C00E—C009—C00I	111.6 (2)	C00G—C00J—H00I	111.4
C00A—C009—C00I	88.2 (2)	N006—C00J—H00J	111.4
C00D—C00A—C009	112.8 (2)	C00G—C00J—H00J	111.4
C00D—C00A—C00H	115.5 (2)	H00I—C00J—H00J	109.3
C009—C00A—C00H	88.3 (2)	C00L—C00K—C00F	120.3 (3)
C00D—C00A—H00A	112.7	C00L—C00K—H00K	119.9
C009—C00A—H00A	112.7	C00F—C00K—H00K	119.9
C00H—C00A—H00A	112.7	C00K—C00L—C00C	119.8 (3)
O004—C00B—O002	117.5 (3)	C00K—C00L—H00L	120.1
O004—C00B—C009	123.4 (3)	C00C—C00L—H00L	120.1

O002—C00B—C009	118.3 (2)	C00O—C00M—C00P	116.9 (3)
C00L—C00C—C00D	121.8 (3)	C00O—C00M—C00H	119.0 (3)
C00L—C00C—H00C	119.1	C00P—C00M—C00H	124.0 (3)
C00D—C00C—H00C	119.1	C00P—C00N—C00R	120.6 (3)
C008—C00D—C00C	116.4 (3)	C00P—C00N—H00N	119.7
C008—C00D—C00A	122.0 (2)	C00R—C00N—H00N	119.7
C00C—C00D—C00A	121.6 (3)	C00M—C00O—C00Q	121.5 (3)
O005—C00E—N006	119.4 (2)	C00M—C00O—H00O	119.2
O005—C00E—C009	122.7 (3)	C00Q—C00O—H00O	119.2
N006—C00E—C009	117.9 (2)	C00N—C00P—C00M	121.3 (3)
C008—C00F—C00K	119.0 (3)	C00N—C00P—H00P	119.3
C008—C00F—H00F	120.5	C00M—C00P—H00P	119.3
C00K—C00F—H00F	120.5	C00R—C00Q—C00O	119.0 (3)
O003—C00G—C00J	105.7 (2)	C00R—C00Q—H00Q	120.5
O003—C00G—H00B	110.6	C00O—C00Q—H00Q	120.5
C00J—C00G—H00B	110.6	C00Q—C00R—C00N	120.6 (3)
O003—C00G—H00D	110.6	C00Q—C00R—H00R	119.7
C00J—C00G—H00D	110.6	C00N—C00R—H00R	119.7

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