Supporting Information

Functionalization of Homodiamantane: Oxygen Insertion Reactions without Rearrangement with Dimethyldioxirane

Andrey A. Fokin,[*a,b] Tatyana S. Zhuk,[a] Alexander E. Pashenko,[a] Valeriy V. Osipov,[a] Pavel A. Gunchenko,[a] Michael Serafin,[c] and Peter R. Schreiner[*b]

[a] *Department of Organic Chemistry, Kiev Polytechnic Institute, pr. Pobedy 37, 03056 Kiev, Ukraine, aaf@xtf.kpi.ua*

[b] *Institut für Organische Chemie der Justus-Liebig-Universität, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany, prs@uni–giessen.de*

[c] *Institut für Anorganische Chemie der Justus-Liebig-Universität, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany*

Contents

#		Page
A	The computed HF, Gibb's energies and XYZ-coordinates of of tetramers of diamantine and homodiamantane	S2
B	The computed zero-point vibrational energies (ZPVE), Gibb's energies and XYZ-coordinates of homodiamantyl tertiary cations (B3LYP-D3/6-31G(d,p), M06-2X/6-31G(d,p))	S8
C	The computed zero-point vibrational energies (ZPVE), Gibb's energies and XYZ-coordinates of the transition structures for hydrogen abstraction from homodiamantane with DMD (PCM B3LYP- D3/6-31G(d,p), M06-2X/6-31G(d,p), PCM M06-2X/6-31G(d,p))	S14
D	The X-ray crystal structures and packing of compound **8**	S23
E	The copies of the NMR spectra of new compounds	S24
F	References - SI	S30

A. Table 1s. The computed[1, 2] HF, zero-point vibrational energies (ZPVE), Gibb's energies of tetramers of diamantane and homodiamantane

#	Name	HF, –au	E, –au	G^0_{298}, –au
3	tetramer of diamantane (M06-2X/6-31G(d,p)	-2181.4754548	-2180.198979	-2180.273413
4	tetramer of homodiamantane (M06-2X/6-31G(d,p))	-2338.5955176	-2337.200010	-2337.282243

Table 1s. The XYZ-coordinates of tetramer of diamantane

C	-0.1829916936	-0.0980989454	4.1323456259
C	0.1829916638	0.0980989729	-4.1323456204
C	-3.2538512699	-0.0499511985	1.4476765893
C	3.2538512748	0.0499512258	-1.4476765943
C	-1.2203027854	-0.6575071118	6.3528004124
C	1.2203027630	0.6575072384	-6.3528003800
C	-1.8872166376	0.2600860148	-0.6409696377
C	1.8872166266	-0.2600860368	0.6409696495
C	0.0458209534	1.2657115627	7.4230703530
C	-0.0458208837	-1.2657114261	-7.4230704091
C	-3.4453884982	-1.3008427688	-1.8911773575
C	3.4453886599	1.3008425491	1.8911774404
C	1.0776022698	1.8243998551	5.2000521085
C	-1.0776022345	-1.8243998318	-5.2000521853
C	-4.8170555254	-1.6083930336	0.1937344152
C	4.8170556678	1.6083928611	-0.1937343412
C	-1.4212842119	1.6979864320	5.4297411389
C	1.4212842443	-1.6979863283	-5.4297411973
C	-2.3480645109	-2.0806632146	0.2279288371
C	2.3480646644	2.0806632267	-0.2279286449
C	-1.3796879121	0.2012017749	5.0711863315
C	1.3796878954	-0.2012016867	-5.0711863229
C	-2.0711234518	-0.6191926666	0.6219126933
C	2.0711235154	0.6191927319	-0.6219126296
C	-0.1141867679	2.1025516480	6.1380293025
C	0.1141868125	-2.1025515527	-6.1380293836
C	-3.6305600628	-2.1582672061	-0.6223609094
C	3.6305602637	2.1582670595	0.6223610450
C	1.1235458621	0.3269925439	4.8469440703
C	-1.1235458714	-0.3269925328	-4.8469440951
C	-4.5425663691	-0.1468318163	0.5915982442
C	4.5425663823	0.1468316922	-0.5915982570
C	0.0879278206	-0.2323318071	7.0687976938
C	-0.0879278301	0.2323319281	-7.0687976862
C	-3.1742661597	0.1629560402	-1.4974145878
C	3.1742662003	-0.1629562123	1.4974145686
C	1.2835296020	-0.5298190167	6.1275882932
C	-1.2835296267	0.5298190696	-6.1275882878
C	-4.3577523242	0.7313097013	-0.6739903272
C	4.3577523083	-0.7313099058	0.6739902536
H	-2.2833141488	1.9032133880	6.0789746039
H	2.2833142031	-1.9032132343	-6.0789746462
H	-1.4974775192	-2.4842003797	-0.3367513063
H	1.4974777306	2.4842003901	0.3367515832
H	-1.5575453616	2.2969591932	4.5201265212
H	1.5575454021	-2.2969591178	-4.5201265976
H	-2.4504712750	-2.6969239533	1.1317569612
H	2.4504714048	2.6969240318	-1.1317567212
H	-0.1453457782	3.1697800522	6.3920596357
H	0.1453458747	-3.1697799484	-6.3920597504

H	-3.8259764295	-3.2002244970	-0.9061503374
H	3.8259767165	3.2002243148	0.9061505530
H	-2.3119976766	-0.0814319761	4.5623821396
H	2.3119976520	0.0814320723	-4.5623821207
H	-1.1559439448	-0.5721283414	1.2244672342
H	1.1559439722	0.5721285308	-1.2244671186
H	-0.7887310431	1.4645375355	8.1090567156
H	0.7887311158	-1.4645373495	-8.1090567752
H	-2.6093307499	-1.6894956115	-2.4873858112
H	2.6093309642	1.6894954165	2.4873859487
H	0.9836112445	2.4216851801	4.2824576888
H	-0.9836112072	-2.4216851917	-4.2824577915
H	-4.9718346540	-2.2181033112	1.0942585139
H	4.9718348090	2.2181031883	-1.0942584040
H	-0.2898333795	0.4935034242	3.2131002361
H	0.2898333621	-0.4935034131	-3.2131002420
H	-3.3783208471	-0.6571557195	2.3561354030
H	3.3783208825	0.6571558030	-2.3561353673
H	-2.0717007630	-0.4647215043	7.0212063886
H	2.0717007551	0.4647216798	-7.0212063501
H	-1.0417126914	-0.1256719173	-1.2263244191
H	1.0417127440	0.1256718919	1.2263245249
H	1.9736440160	0.1339305370	4.1803999684
H	-1.9736440411	-0.1339305760	-4.1803999967
H	-5.3888905483	0.2421549618	1.1755321840
H	5.3888905257	-0.2421551060	-1.1755322378
H	0.2009897633	-0.8249692427	7.9879945499
H	-0.2009897629	0.8249693940	-7.9879945235
H	-3.0479765292	0.7726379442	-2.4035748736
H	3.0479765355	-0.7726381628	2.4035748186
C	1.3255601731	-2.0267728301	5.7691656152
C	-1.3255602375	2.0267728733	-5.7691655732
C	-4.0809176749	2.1939620158	-0.2812594907
C	4.0809175251	-2.1939621722	0.2812593338
H	2.2170303214	-0.2460315434	6.6340609261
H	-2.2170303220	0.2460315808	-6.6340609523
H	-5.2730522775	0.6801460248	-1.2808808031
H	5.2730522641	-0.6801463376	1.2808807268
H	0.9677423143	1.5519636539	7.9469539223
H	-0.9677422418	-1.5519635306	-7.9469539881
H	-4.3429630754	-1.3585158835	-2.5214029522
H	4.3429632620	1.3585155436	2.5214030122
H	2.0173945794	2.1244719969	5.6824727049
H	-2.0173945236	-2.1244719720	-5.6824728229
H	-5.7406028763	-1.6679339365	-0.3976826261
H	5.7406030338	1.6679336498	0.3976826830
C	-1.1756827745	-2.1545572419	5.9945758702
C	1.1756827052	2.1545573530	-5.9945757866
C	-1.6117448827	1.7188615162	-0.2348996627
C	1.6117447906	-1.7188614976	0.2348995632
C	-0.1411869607	-1.5943781823	3.7764509431
C	0.1411868763	1.5943781992	-3.7764508985
C	-2.9851641985	1.4137178634	1.8408836572
C	2.9851640869	-1.4137177896	-1.8408837488
H	-1.0877125480	-2.7563567889	6.9093019068
H	1.0877124870	2.7563569402	-6.9093017983
H	-1.4422637320	2.3355009486	-1.1266526917
H	1.4422635716	-2.3355009847	1.1266525416
H	0.6934093699	-1.7889850180	3.0920544526
H	-0.6934094729	1.7889849884	-3.0920544212
H	-3.8190896109	1.7987845722	2.4431676325
H	3.8190894675	-1.7987845153	-2.4431677592
H	1.4618597368	-2.6244014619	6.6806156904
H	-1.4618598008	2.6244015290	-6.6806156309

H	-3.9708083076	2.8084317367	-1.1853173298
H	3.9708081341	-2.8084319583	1.1853171250
H	2.1868014069	-2.2321489179	5.1185574621
H	-2.1868014892	2.2321489191	-5.1185574296
H	-4.9338856115	2.5990759913	0.2797066836
H	4.9338854195	-2.5990761717	-0.2797068938
C	0.0184334639	-2.4318326429	5.0598420143
C	-0.0184335520	2.4318327036	-5.0598419447
C	-2.8013666329	2.2707788346	0.5738207104
C	2.8013664810	-2.2707788435	-0.5738208696
H	0.0502762106	-3.4988068357	4.8046287378
H	-0.0502763442	3.4988068827	-4.8046286273
H	-2.6052858388	3.3128533572	0.8570596181
H	2.6052855854	-3.3128533258	-0.8570598509
H	-1.0608267530	-1.8808562068	3.2492794212
H	1.0608266534	1.8808562322	-3.2492793503
H	-2.0864111769	1.4724832823	2.4643078776
H	2.0864110556	-1.4724831036	-2.4643079610
H	-2.1132398431	-2.4496118453	5.5043893824
H	2.1132397486	2.4496119706	-5.5043892606
H	-0.6939588182	1.7677551239	0.3646062722
H	0.6939587063	-1.7677549515	-0.364606356

Table 3s. The XYZ-coordinates of tetramer of homodiamantane

H	-3.0044308225	0.3283533267	-2.171538103
H	-5.6744150632	-0.7207286595	1.050545257
H	-3.7019735195	-0.9368620463	2.578002323
H	-1.4593456985	-0.2269207144	1.808507023
H	-5.2384776410	-0.4081593919	-1.396135972
H	-4.7869490422	2.0474679500	-1.251683597
H	-0.9907675069	-2.2640623400	0.463464292
H	-5.9658238394	1.4459264334	-0.095246765
H	-2.1334851385	-2.6484149526	1.747691699
H	-2.3562519840	3.2461113397	1.200338897
H	-3.6489736193	-2.0968546838	-2.262787771
H	-3.2193580661	1.5181302158	2.717343506
H	-5.2090165787	-2.7212233826	-0.360748301
H	-4.9186320382	1.0988375333	2.566863890
H	-4.5741443779	-2.9466128538	1.272672655
H	-2.9710280277	3.3964785632	-0.428605589
H	-1.9186310245	-1.9163083146	-1.973720867
C	-2.9080046095	-1.7506846642	-1.529963984
C	-2.7622595955	2.6645794262	0.362345943
C	-4.4511013583	-2.3638761292	0.349608064
C	-3.9656398848	1.1159136890	2.020439295
C	-2.0110146329	-2.0787817420	0.816789208
C	-4.8967331150	1.4303838062	-0.349176941
C	-3.0393827759	-2.5669142185	-0.224939536
C	-4.1061874713	2.0737395164	0.813837289
C	-4.6658134529	-0.8708291691	0.639346178
C	-3.6267184662	-0.3407105368	1.655430759
C	-3.1019290196	-0.2426727054	-1.237236628
C	-1.9778694699	0.1771564767	-0.257937582
C	-2.2050836287	-0.5682845039	1.080250673
C	-4.5222161955	-0.0298365073	-0.651810028
H	-2.8707233765	-3.6300436735	-0.439665349
H	-4.6954449309	2.9352366318	1.159092074
C	-1.6733503152	1.6810614168	-0.138572178
H	-0.7961092732	1.7631052657	0.516703709
H	-1.3327676350	2.0149042483	-1.125908429
H	0.5726491140	0.0012989862	3.110748218
H	-2.2443522847	0.3977609682	6.350342238
H	-0.3840141185	0.0336596400	7.975998983
H	1.9511655246	-0.1008697027	7.195318751
H	-1.7720337123	0.0291907992	3.923884099
H	-0.7289393153	2.2545282110	3.533796997
H	1.8431016555	-2.4282175378	6.312247227
H	-1.9782381184	2.2504812393	4.771356637
H	0.6477823944	-2.2146688783	7.593345419
H	2.0101349551	3.3598991804	5.620161265
H	-0.7084310562	-2.1241108802	3.488868549
H	0.7888391484	2.2156474897	7.561375759
H	-2.3505336359	-1.9005982973	5.405627634
H	-0.9652938538	2.2677235368	7.459196506
H	-1.7773122784	-1.9445132351	7.076594868
H	1.3875054142	3.1068508476	4.006515605
H	1.0103578181	-2.3648058508	3.796889859
C	0.1125949769	-1.8495358918	4.162504556
C	1.4492416518	2.6472618851	5.001821416
C	-1.5145445163	-1.6193893629	6.060852522
C	-0.0659484954	1.8923895233	6.951714095
C	0.9124402919	-1.9072587942	6.572787558
C	-0.9583736194	1.9055282501	4.550414769
C	-0.2178953005	-2.3090693893	5.600808484
C	0.0171206596	2.5589360182	5.554967895

C	-1.3167892816	-0.0960177411	6.025655477
C	-0.1589632998	0.3514667854	6.947126338
C	0.3383771257	-0.3182788951	4.134897681
C	1.5487333521	-0.0225471935	5.061485768
C	1.1366779157	-0.3786882196	6.511379120
C	-0.9740463955	0.3726127582	4.594929810
H	-0.3483819781	-3.3987681248	5.616373042
H	-0.3093986188	3.6006232861	5.681649420
C	2.2618401443	1.3338952273	4.907824038
H	3.0544879596	1.3464161951	5.667769663
H	2.7867530729	1.3240946904	3.947536053
H	-1.0477923712	-0.2343893226	-0.678546517
H	2.3251190387	-0.7514077043	4.781825188
H	0.4136791425	0.0918507333	-7.960527814
H	-2.5791439402	-0.0660473608	-4.857767195
H	-0.7556029353	-0.2318747306	-3.146973620
H	1.6026832252	0.1035424399	-3.825971915
H	-1.9416115563	-0.2196553174	-7.272778574
H	-1.1534195349	2.1491626755	-7.490597571
H	1.9137300767	-2.1895490153	-4.751956931
H	-2.4942048703	1.9094016003	-6.379616462
H	0.6435360315	-2.2049627297	-3.529068290
H	1.2221791104	3.4009279573	-4.971646889
H	-0.5331223825	-2.2227848674	-7.689600628
H	-0.0150452660	2.1373360524	-3.341731610
H	-2.2591079921	-2.3182898216	-5.883765317
H	-1.7322707630	1.8841496062	-3.613616273
H	-1.7918679614	-2.3276689608	-4.182698727
H	0.7553616226	3.4726914002	-6.654519025
H	1.1896333444	-2.1915527459	-7.308835495
C	0.2058261746	-1.8381775859	-6.973909594
C	0.7977360599	2.8011427263	-5.787267788
C	-1.5215754685	-1.9298725572	-5.168105295
C	-0.7378208945	1.7082704236	-4.047334949
C	0.8998795482	-1.8313883080	-4.529889891
C	-1.4208371743	1.7176336509	-6.516174116
C	-0.1071601917	-2.3856115817	-5.563051372
C	-0.6479077589	2.4553005744	-5.396821743
C	-1.5703121988	-0.3942509369	-5.147360793
C	-0.5478336683	0.1859418877	-4.142343412
C	0.1833816591	-0.2901281367	-6.955533695
C	1.2832840479	0.1723436973	-5.968049974
C	0.8737890751	-0.2843210945	-4.546277693
C	-1.2309189256	0.1902576132	-6.539834632
H	-0.0563128524	-3.4819741268	-5.574385697
H	-1.1450412433	3.4255704781	-5.256152557
C	1.7617064977	1.6288565568	-6.109451309
H	2.6567814070	1.7282026287	-5.481112044
H	2.1194415541	1.7392388140	-7.141389936
H	3.6838445353	-0.4883250353	-2.572820129
H	0.8239761522	-0.2908992114	0.646642370
H	2.7098735383	-0.3363781885	2.288983012
H	5.0420614944	-0.1057589360	1.502855293
H	1.3538324184	-0.6823138046	-1.758562359
H	2.2148999710	1.6256906047	-2.246696820
H	5.2797936658	-2.4847795532	0.775726604
H	0.8946179887	1.5372313265	-1.095394224
H	4.0591130205	-2.3589580201	2.044231228
H	4.6798932584	3.0612785303	0.068536652
H	2.7131096825	-2.7455406067	-2.047831187
H	3.4737385503	1.9987367553	1.841410755
H	1.0721432790	-2.6320643981	-0.186715016
H	1.7438957317	1.7486543201	1.656686848
H	1.5906883542	-2.4952534656	1.495303370

H	4.1501111528	3.0084883683	-1.595977904
H	4.4508434011	-2.7142495792	-1.743750625
C	3.4882660076	-2.3121859534	-1.401953324
C	4.2103874793	2.4087632657	-0.678804753
C	1.8368792277	-2.1946613524	0.468806511
C	2.7195190417	1.5134700335	1.207256934
C	4.2826355977	-2.0861947868	1.003994677
C	1.9557867309	1.3037931249	-1.229290834
C	3.2268575416	-2.7150799821	0.066688919
C	2.7739094774	2.1293012815	-0.209734278
C	1.8134268469	-0.6636159836	0.348961474
C	2.8837931001	-0.0137930007	1.252769164
C	3.4909842316	-0.7707963541	-1.527748499
C	4.6391868345	-0.2365582500	-0.633491968
C	4.2810379179	-0.5461184499	0.842883281
C	2.1055598470	-0.2223534708	-1.102734981
H	3.2578733348	-3.8082516215	0.159660470
H	2.2942790566	3.1160963410	-0.142028313
C	5.1332567856	1.1891454625	-0.941434742
H	6.0651979008	1.3278664664	-0.378340982
H	5.4307405936	1.1921369712	-1.998289301
H	2.1802611089	-0.4122691611	-6.223742146
H	5.5143468765	-0.8617752716	-0.866732152

B. The computed absolute energies and zero-point vibrational energies (ZPVE) and XYZ-coordinates of homodiamantyl tertiary cation (B3LYP-D3/6-31G(d,p), M062X/6-31G(d,p))

Table 4s. The computed zero-point vibrational energies (ZPVE) and enthalpies of computed cations at B3LYP-D3/6-31G(d,p).

#	Structure	Name	Point group	E_0, B3PW91/6-31G(d,p) –au	H_{298}, B3PW91/6-31G(d,p) –au
1	**3a**	homodiamantyl-12 cation	C_S	-583,74132	-583,73003
2	**3b**	homodiamantyl-1 cation	C_1	-583,73515	-583,72388
3	**3c**	homodiamantyl-9 cation	C_S	-583,73397	-583,72276
4	**3d**	homodiamantyl-2 cation	C_S	-583,73193	-583,72135
5	**3e**	homodiamantyl-6 cation	C_1	-583,731203	-583,71980
6	**3f**	homodiamantyl-4 cation	C_S	-583,72800	-583,71666

Table 5s. The XYZ geometries of all B3LYP-D3/6-31G(d,p) optimized structures.

1a
H -1.17840 -2.12053 0.10771
H 2.55244 0.00032 -0.42109
H 1.22964 2.16107 -0.44671
H -1.17905 2.12037 0.10745
H 1.23034 -2.16074 -0.44670
H -1.94262 1.29903 -2.15587
H 2.19341 -1.39800 1.65612
H -0.41411 2.16616 -2.28565
H -1.03832 0.88288 3.26672
H -0.41396 -2.16637 -2.28549
H 0.64542 2.16268 1.96469
H 1.76557 -0.88058 -2.61198
H 2.19289 1.39881 1.65608
H 1.76541 0.88073 -2.61212
H -1.03798 -0.88342 3.26646
H -1.94249 -1.29930 -2.15549
C -0.87815 -1.25164 -1.90351
C -0.83861 -0.00015 2.65649
C 1.28188 0.00006 -2.17520
C 1.11256 1.27588 1.52072
C -0.87832 1.25142 -1.90370
C 1.11296 -1.27559 1.52074
C -0.22057 -0.00010 -2.50176
C 0.66139 0.00018 2.27444
C 1.47894 0.00017 -0.64975
C 0.84962 1.23928 0.00820
C -0.71497 -1.24409 -0.35328
C -1.21444 -0.00008 0.23450
C -0.71552 1.24395 -0.35347
C 0.84992 -1.23908 0.00816
H -0.36751 -0.00020 -3.58708
H 1.17418 0.00013 3.24209
C -1.94917 -0.00020 1.49828
H -2.56904 0.89293 1.59741
H -2.56876 -0.89353 1.59733
H 0.64665 -2.16264 1.96483

1b
H -1.19805 -2.11168 0.09908
H 2.54295 -0.17331 -0.35205
H 1.39176 2.02268 -0.47506
H 0.52164 -2.21425 1.88774
H -1.81300 1.38633 -2.21251
H 2.14421 -1.55333 1.51116
H -0.23185 2.14384 -2.35313
H -0.83750 0.82231 3.42756
H -0.41972 -2.17973 -2.33357
H 0.75251 2.09518 1.98931
H 1.78416 -0.98314 -2.62886
H 2.27340 1.31146 1.60794
H 1.85672 0.77499 -2.57797
H -0.91623 -0.91564 3.33567
H -1.92742 -1.28877 -2.17408
C -0.86225 -1.26542 -1.92449
C -0.73554 -0.01873 2.73425
C 1.31956 -0.09511 -2.18755
C 1.18673 1.20750 1.51511
C -0.75924 1.27980 -1.93384
C 1.06767 -1.37686 1.44897
C -0.17536 -0.02211 -2.52252
C 0.72794 -0.04568 2.28437
C 1.49616 -0.14028 -0.66304
C 0.84406 1.21237 0.01992
C -0.72172 -1.25337 -0.38308
C -1.45145 0.08596 0.15459
C -0.63894 1.27761 -0.38898
C 0.66067 -1.06884 0.07688
H -0.30747 -0.02407 -3.60889
C -1.83427 0.09379 1.64002
H -2.39856 1.01969 1.79429
H -2.55977 -0.71303 1.78759
H -2.40638 0.05844 -0.38287
H -1.06405 2.20703 0.01011
H 1.33601 -0.14466 3.18911

1c
H -1.13860 -2.16371 0.09404
H 2.55372 0.00001 -0.44887
H 1.27720 2.15958 -0.40818

1d
H -1.11004 -2.16850 0.02400
H 1.31002 2.11536 -0.46738
H 0.62297 -2.15142 1.96004

H 1.27721 -2.15958 -0.40817
H 0.71718 -2.13487 2.01333
H -1.93694 1.33411 -2.11415
H 2.24142 -1.27959 1.62269
H -0.39666 2.16275 -2.30505
H -0.72333 0.89498 3.45405
H -0.39664 -2.16276 -2.30504
H 0.71716 2.13487 2.01333
H 1.74557 -0.88083 -2.62663
H 2.24141 1.27960 1.62269
H 1.74557 0.88083 -2.62662
H -0.72332 -0.89498 3.45406
H -1.93693 -1.33413 -2.11414
C -0.86954 -1.27190 -1.87612
C -0.61997 0.00000 2.83929
C 1.26132 0.00000 -2.19102
C 1.15003 1.25314 1.53742
C -0.86956 1.27189 -1.87613
C 1.15003 -1.25313 1.53743
C -0.24565 -0.00000 -2.48809
C 0.61611 0.00001 2.07275
C 1.47761 0.00000 -0.66085
C 0.82247 1.23939 -0.02724
C -0.69087 -1.25957 -0.33686
C -1.42140 -0.00001 0.20593
C -0.69088 1.25957 -0.33686
C 0.82248 -1.23939 -0.02724
H -0.40769 -0.00000 -3.57081
C -1.77034 -0.00000 1.71066
H -2.37660 0.88472 1.91456
H -2.37658 -0.88474 1.91456
H -2.41515 -0.00001 -0.25850
H -1.13861 2.16369 0.09403

1e

H -1.16549 -2.11155 0.09504
H 2.51560 0.13375 -0.36880
H 1.15885 2.20627 -0.44196
H 1.29069 -2.10171 -0.45972
H 0.75530 -2.14896 1.95360
H -1.92062 1.32617 -2.15440
H 2.25906 -1.33324 1.57275
H -0.34682 2.17756 -2.29404
H -0.93307 0.62180 3.53240
H -0.35396 -2.16671 -2.32676
H 0.50440 2.15039 2.02314
H 1.82616 -0.81557 -2.60336
H 2.09617 1.52848 1.63934
H 1.76462 0.94139 -2.60556
H -0.90706 -1.08894 3.18590
H -1.89352 -1.33563 -2.18085
C -0.83455 -1.27477 -1.91077
C -0.76210 -0.10386 2.73049
C 1.30187 0.04662 -2.17619
C 1.02606 1.31302 1.54734
C -0.86115 1.30175 -1.89495
C 1.16867 -1.24430 1.49475
C -0.18646 -0.02277 -2.52620
C 0.70549 -0.00403 2.28782
C 1.46454 0.02521 -0.65698
C 0.72947 1.32089 0.03533
C -0.66425 -1.26000 -0.37740
C -1.48073 0.05477 0.15314

H -1.82034 1.34092 -2.26759
H 2.19950 -1.44434 1.66977
H -0.27113 2.16356 -2.34772
H -0.92886 0.87179 3.36191
H -0.27106 -2.16347 -2.34782
H 0.62295 2.15143 1.95998
H 1.89841 -0.90015 -2.48455
H 2.19950 1.44438 1.66973
H 1.89845 0.90013 -2.48453
H -0.92894 -0.87127 3.36231
H -1.82030 -1.34088 -2.26762
C -0.77442 -1.27590 -1.95024
C -0.77101 0.00010 2.71782
C 1.42088 -0.00000 -2.09417
C 1.12491 1.27506 1.53753
C -0.77445 1.27595 -1.95016
C 1.12492 -1.27507 1.53756
C -0.13719 0.00006 -2.52338
C 0.70641 0.00001 2.29841
C 1.25112 -0.00002 -0.64550
C 0.87080 1.24123 0.02125
C -0.70725 -1.24848 -0.41214
C -1.44172 -0.00003 0.11770
C -0.70729 1.24847 -0.41208
C 0.87086 -1.24125 0.02126
C -1.84845 -0.00014 1.60295
H -2.50083 0.86925 1.73976
H -2.50040 -0.86986 1.73969
H -2.40584 -0.00004 -0.40886
H -1.11013 2.16847 0.02409
H 1.27621 0.00001 3.23480
H 1.31004 -2.11539 -0.46737
H -0.14830 0.00008 -3.61691

1f

H -1.18369 -2.16675 -0.03657
H 2.54118 0.00039 -0.47005
H 1.25126 2.14829 -0.47918
H 0.63988 -2.15414 1.94075
H -1.90077 1.26909 -2.25646
H 2.19869 -1.44086 1.57809
H -0.33338 2.13694 -2.39860
H -0.88734 0.87160 3.35767
H -0.33284 -2.13718 -2.39846
H 0.63895 2.15426 1.94075
H 1.75777 -0.90050 -2.64884
H 2.19809 1.44165 1.57821
H 1.75748 0.90088 -2.64892
H -0.88704 -0.87271 3.35705
H -1.90046 -1.26968 -2.25637
C -0.84054 -1.25738 -2.00110
C -0.74280 -0.00029 2.71068
C 1.29011 0.00013 -2.24891
C 1.11798 1.28192 1.48317
C -0.84087 1.25708 -2.00111
C 1.11850 -1.28159 1.48315
C -0.16249 -0.00009 -2.30369
C 0.72374 0.00008 2.25112
C 1.45970 0.00022 -0.63778
C 0.80520 1.25118 -0.03246
C -0.69779 -1.24629 -0.37435
C -1.45462 -0.00015 0.12501
C -0.69815 1.24616 -0.37448

C -0.61598 1.06048 -0.46701
C 0.83282 -1.21377 -0.00444
H -0.35875 0.02827 -3.60472
H 1.29224 0.01090 3.21336
C -1.84027 0.12319 1.64992
H -2.30940 1.10225 1.79401
H -2.64690 -0.60321 1.78897
H -2.43048 0.02074 -0.38747
C 0.80557 -1.25092 -0.03244
C -1.84376 -0.00004 1.62060
H -2.49362 0.86977 1.76362
H -2.49404 -0.86955 1.76370
H -2.42701 -0.00031 -0.38452
H -1.18429 2.16649 -0.03668
H 1.31563 0.00018 3.17410
H 1.25184 -2.14790 -0.47920

Table 6s. The computed zero-point vibrational energies (ZPVE) and enthalpies of computed cations at M062X/6-31G**.

#	Structure	Name	Point group	E_0, M062X/6-31G** –au	G^0_{298}, M062X/6-31G** –au
1	**3a**	homodiamantyl-12 cation	C_S	-583.430261	-583.465549
2	**3b**	homodiamantyl-1 cation	C_1	-583.424435	-583.459477
3	**3c**	homodiamantyl-9 cation	C_S	-583.423970	-583.459266
4	**3d**	homodiamantyl-2 cation	C_S	-583.421077	-583.456008
5	**3e**	homodiamantyl-6 cation	C_1	-583.421057	-583.455850
6	**3f**	homodiamantyl-4 cation	C_S	-583.418141	-583.451991

Table 7s. The XYZ geometries of all M062X/6-31G**(d,p)** optimized structures.

1a

H -1.1693940881 2.1176441073 0.1196832211
H 2.5476992622 0.0029322936 -0.420069743
H 1.2283356368 2.1572162218 -0.4521557229
H -1.1743209129 2.1149771344 0.1190252058
H 1.2333340381 -2.154429873 -0.4516802134
H 0.6461695542 -2.1563813393 1.957836507
H -1.9428860381 1.2927673743 -2.1412747169
H 2.1929302623 -1.3882939903 1.6480950406
H -0.413856696 2.1601001881 -2.2752444801
H -1.0352317692 0.8809099215 3.2521222145
H -0.4087394338 -2.1617099291 -2.274565682
H 0.6407823573 2.158281382 1.9573256507
H 1.755521041 -0.8797358433 -2.607361004
H 2.1894815916 1.3939768336 1.647916511
H 1.753407509 0.8832039613 -2.6075990616
H -1.033027602 -0.8834843706 3.2517261665
H -1.9398255336 -1.2979582394 -2.1409306394
C -0.8755778438 -1.2492057239 -1.8904415793
C -0.836110079 -0.0009023295 2.6404873158
C 1.2738242405 0.0012168875 -2.1693384895
C 1.1091928099 1.2727268714 1.5119086216
C -0.8785147976 1.2466114569,-1.8908164431
C 1.1123262682 -1.2697592462 1.5121848483
C -0.2240807809 -0.0006155121 -2.4881446937
C 0.6588280354 0.0009996886 2.2600197444
C 1.4743338806 0.0016544613 -0.649837556
C 0.8455637432 1.2366374059 0.0042400594
C -0.7045723709 -1.244579156 -0.34735432
C -1.2014207038 -0.0013474706 0.2385525364
C -0.7074414011 1.242862839 -0.3477332639
C 0.8484743938 -1.2346370624 0.0045445397
H -0.376305189 -0.0009634737 -3.5720728957
H 1.1687700682 0.0017391313 3.2287507675
C -1.9459502362 -0.0019600404 1.4926020372
H -2.5627899134 0.8927368587 1.5882140675
H -2.5611693028 -0.897763204 1.5883454495

1b

H -1.1583169818 2.098638497 0.1332789423
H 2.5297239706 -0.0771452478 -0.3132462098
H 1.327848601 2.0687045832 -0.4784991017
H 0.5568110762 -2.1493729196 1.9131808018
H -1.8366711878 1.3382209125 -2.2428887175
H 2.159837832 -1.4282364113 1.5430394238
H -0.2687912584 2.1279233375 -2.3796959906
H -0.9294539634 0.7826676313 3.445874193
H -0.3532617894 -2.1856731678 -2.289285217
H 0.6112682984 2.150110415 1.9691669931
H 1.8169004656 -0.9333068849 -2.5923886252
H 2.174312168 1.427975679 1.6325176275
H 1.833171601 0.8281018304 -2.5588239474
H -0.9522263249 -0.9489540669 3.2630391617
H -1.8856532698 -1.3303889601 -2.1593210121
C -0.8241719532 -1.2777947813 -1.8991832248
C -0.7900625608 -0.0170086283 2.7124309784
C 1.32233624 -0.0558117953 -2.164126756
C 1.0956401732 1.2772710384 1.5159334652
C -0.7837009082 1.2600948689 -1.9528072546
C 1.0778119807 -1.2960621788 1.474956704
C -0.1660039779 -0.0318067645 -2.5100799663
C 0.675300535 0.0173810524 2.2861376097
C 1.4880540072 -0.0787452382 -0.6429387425
C 0.7886509713 1.2518749486 0.0167092044
C -0.7054076275 -1.2344265714 -0.3617744804
C -1.468571891 0.0842294139 0.1350038804
C -0.6817692006 1.2819284057 -0.4146629879
C 0.668370514 -1.0064536405 0.1029943751
H -0.2875263865 -0.0574426929 -3.5968317618
C -1.8680365469 0.1260609037 1.6113634697
H -2.3948577182 1.0764231723 1.7454608978
H -2.6259815024 -0.6480881284 1.7646353165
H -2.4150957312 0.0287888492 -0.4163669347
H -1.1308761268 2.20724737 -0.0320840165
H 1.2710184726 -0.0489978372 3.2016319022

1c

H -0.9956352436 -2.2198871011 0.0674239831
H 2.5391772503 0.1917041769 -0.4025575381
H 1.1158004352 2.2511943633 -0.4140238139
H 1.4193350221 -2.0473804246 -0.3933905082
H 0.7880675947 -2.056134442 2.0129696404
H -1.9903309633 1.1915564804 -2.1665178359

1d

H -0.9326538683 -2.2153474192 0.1205481337
H 1.0809073226 2.2486222652 -0.4759692935
H 0.9669310167 -2.0586667161 1.9606403147
H -1.9712478513 1.1305417431 -2.285010371
H 2.3855466873 -1.0937674305 1.5966276019
H -0.4991529732 2.0825075518 -2.4141748889

H 2.2620519197 -1.0954649799 1.6606973665
H -0.5086248942 2.1295339231 -2.3305187444
H -0.8675782083 0.8694486657 3.4127606243
H -0.2047770304 -2.173510633 -2.3098588332
H 0.4879531102 2.194150121 1.992566754
H 1.840919802 -0.7519081296 -2.5901882836
H 2.0825400879 1.4468089582 1.6484814866
H 1.7167265021 1.0068878835 -2.5986323694
H -0.7411102092 -0.9215595495 3.421347628
H -1.8036966117 -1.4515279441 -2.1538262083
C -0.7480957483 -1.3171519617 -1.894626689
C -0.6906294223 -0.0209369216 2.8098597415
C 1.2889665798 0.0949459331 -2.1682200344
C 0.9983290617 1.3485765612 1.527812072
C -0.926496662 1.2093312629 -1.9067578938
C 1.1748777548 -1.1517147449 1.5398111089
C -0.2027580129 -0.0119650664 -2.4965459647
C 0.54248177 0.0625058018 2.0534492313
C 1.4708933143 0.1151231132 -0.641301705
C 0.7192155964 1.304644249 -0.0312850677
C -0.602303738 -1.2882276158 -0.359473956
C -1.4237695468 -0.0854233114 0.1612713986
C -0.7791242173 1.2158486564 -0.3714973035
C 0.893417162 -1.1623397439 -0.0194397292
H -0.3403401441 -0.0268918138 -3.5818689625
C -1.8026345194 -0.1049995461 1.6543524296
H -2.4748768853 0.7344165962 1.8405172285
H -2.3503925635 -1.0287218052 1.8489920738
H -2.4056601575 -0.1570894766 -0.324286364
H -1.2997581848 2.0870284654 0.0467450375
H -1.012921873 0.4519866235 3.5368029486
H -0.118346398 -2.2156711055 -2.2580441496
H 0.23558467 2.1685282573 1.9375007825
H 1.9381106418 -0.7264601893 -2.4644069736
H 1.9215469456 1.7509357204 1.7104672796
H 1.7312809093 1.0655113075 -2.5159648503
H -0.8140319447 -1.2193119906 3.0821975872
H -1.7334065118 -1.5260863889 -2.1890308402
C -0.6946221338 -1.3628379673 -1.8847932545
C -0.7646089618 -0.197402763 2.6915907117
C 1.3629524207 0.126394174 -2.1008184905
C 0.9005539432 1.3970874221 1.534451696
C -0.9199446353 1.1686851789 -1.9821052435
C 1.293115532 -1.1138104984 1.5154185761
C -0.1778336912 -0.0607215402 -2.5098565978
C 0.6881486357 0.0671662957 2.2836302055
C 1.1986547292 0.1392514797 -0.6539122225
C 0.7147216157 1.3392716287 0.0088963326
C -0.6142543448 -1.2791239669 -0.3518956243
C -1.456312903 -0.0834876669 0.1290266411
C -0.840250791 1.1958756841 -0.4532505172
C 0.9570638268 -1.1270033983 0.0233394754
C -1.8435343609 -0.0037342626 1.6133428895
H -2.3213003298 0.9734723134 1.7471627637
H -2.6368065507 -0.7369393551 1.7875242536
H -2.4169702007 -0.1890142041 -0.3934489402
H -1.3224911986 2.0919736878 -0.0475756901
H 1.2547593112 0.1452783448 3.2176996575
H 1.4590259618 -1.9540926083 -0.4862550416
H -0.1975526478 -0.1087502068 -3.6017648615

1e

H -1.2164543857 -2.0716934543 0.1431517529
H 2.4960075327 0.1012877475 -0.3336624258
H 1.1904421699 2.1836961801 -0.4516613362
H 1.237921722 -2.1142416512 -0.4259098419
H 0.7467283504 -2.1391241787 1.9857019135
H -1.8732270578 1.3208534749 -2.210422887
H 2.2342486691 -1.2976781775 1.5878688511
H -0.2702539973 2.1279657942 -2.3553561712
H -1.019936218 0.4828171311 3.5639297347
H -0.3785977751 -2.2026943944 -2.2604445272
H 0.4474673354 2.150286408 2.0023419876
H 1.8273963558 -0.8943193812 -2.546816193
H 2.048017833 1.5265703076 1.663790701
H 1.7848137313 0.8648160421 -2.6002284327
H -1.0074278238 -1.1637051001 2.9805353924
H -1.9053652516 -1.3384772053 -2.1565857788
C -0.8488055963 -1.2919473462 -1.8750078385
C -0.8253866321 -0.1277400291 2.6768179398
C 1.3082671548 -0.0136632249 -2.1531683013
C 0.9808876946 1.3101323729 1.54461932
C -0.8167032643 1.2787251816 -1.942568723
C 1.1418579817 -1.2329662255 1.5151087743
C -0.1722295691 -0.0729853733 -2.5164884063
C 0.6513269563 0.0000326556 2.2861777404
C 1.4472163242 0.0017109884 -0.6359127592
C 0.7315413774 1.3129413044 0.0254930895
C -0.6979389427 -1.2381325288 -0.3442106113
C -1.4893268787 0.097386845 0.1240131457
C -0.5954457396 1.0612308876 -0.5122976922
C 0.7969929302 -1.2156670388 0.025414556

1f

H -1.1803794558 -2.1608179932 -0.0312141965
H 2.5353784214 -0.0010868967 -0.4662265631
H 1.2506282963 2.1426832179 -0.4841614849
H 0.6270037234 -2.1469030237 1.9330029524
H -1.8998920866 1.2613414804 -2.2425338171
H 2.1910838388 -1.4410096434 1.5714116191
H -0.3276642141 2.130963565 -2.3891250125
H -0.878045966 0.8722997869 3.3468752448
H -0.3294730183 -2.1313555304 -2.3884857157
H 0.6283040482 2.1466730807 1.9325880254
H 1.7472129442 -0.9046909106 -2.6403587424
H 2.1920020369 1.4397374313 1.5712993284
H 1.7479245485 0.902535077 -2.640630829
H -0.8787102017 -0.872058764 3.3462299866
H -1.9009735207 -1.260316297 -2.242140595
C -0.8408969312 -1.2549830708 -1.9889540966
C -0.7366403941 0.0003028542 2.7004324899
C 1.2868420514 -0.0008297093 -2.2401692446
C 1.1126824977 1.2777262419 1.4738104047
C -0.839832941 1.2551681359 -1.9893002151
C 1.1118528889 -1.2783393361 1.4740270866
C -0.1623957708 -0.0002454468 -2.2818274418
C 0.7220910487 -0.0001279967 2.2380243866
C 1.4541026024,-0.00065555,-0.6381916826
C 0.8039949567 1.2464595503 -0.0354001594
C -0.6946421553 -1.24128144 -0.3737810188
C -1.4459363463 0.0006749736 0.1259210215
C -0.6936191741 1.2418448106 -0.3741773397
C 0.8029926089 -1.2471047335 -0.0351291964
C -1.8339531943 0.0011897553 1.6154268158

H -0.3308878536 -0.055150566 -3.5977863666
H 1.2151814743 0.0277416717 3.2244738096
C -1.8419197037 0.2825840499 1.6089762128
H -2.1034261231 1.3390546633 1.7318173752
H -2.7737183918 -0.2650298899 1.7752671456
H -2.4292643886 0.0648373706 -0.43375115
H -2.4830636021 0.8710053898 1.7583271443
H -2.484664084 -0.8673776593 1.7585666651
H -2.4176084257 0.0009879656 -0.3860361869
H -1.1785944539 2.1618809244 -0.0318447472
H 1.3154275097 -0.0002568201 3.1590674293
H 1.2488219139 -2.1437934192 -0.483782315

C. The computed zero-point vibrational energies (ZPVE), Gibb's energies and XYZ-coordinates of the transition structures for hydrogen abstraction from homodiamantane with DMD (PCM B3LYP-D3/6-31G(d,p), M062X/6-31G(d,p), PCM M062X//6-31G(d,p))

Table 8s. The computed zero-point vibrational energies (ZPVE) and enthalpies of TSs at PCM B3LYP-D3/6-31G(d,p).

#	Structure	Position of hydrogen being substituted	Point group	E_0, PCM B3LYP-D3/ 6-31G(d,p) au	G^0_{298}, PCM B3LYP-D3/ 6-31G(d,p) au
1					
2	**TS1**	12	C_1	-852,785807	-852,768171
3	**TS2**	1	C_1	-852,785142	-852,767392
4	**TS3**	9	C_1	-852,786104	-852,767655
5	**TS4**	6	C_1	-852,78445	-852,766638
6	**TS5**	2	C_1	-852,784222	-852,766455
7	**TS6**	4	C_1	-852,781639	-852,763121

Table 9s. The XYZ coordinates of all PCM B3LYP-D3/6-31G(d,p) optimized structures.

TS1
H 0.16450 -2.27693 -0.38758
H -0.83646 0.31700 -3.68899
H -0.64617 2.28514 -2.14197
H 0.23127 1.98105 0.14453
H -0.74654 -1.98035 -2.66999
H 1.73827 -2.06688 -2.50082
H -1.88562 1.06240 1.10851
H 1.14023 -1.14136 -3.86979
H -2.24180 2.09248 -0.28453
H 3.47843 0.68355 -0.83791
H -2.31168 -2.19565 -0.82734
H 1.84253 2.19579 -1.91613
H -2.91324 -0.65445 -2.71888
H 1.22901 1.70473 -3.48782
H -2.87943 1.09747 -2.49431
H 3.35449 -1.05263 -1.04602
H -1.93591 -1.56426 0.77782
C -1.82654 -1.37053 -0.29217
C 2.76302 -0.13237 -0.98881
C -2.39510 0.15908 -2.19527
C 1.28848 1.40256 -2.43445
C -1.78475 1.14437 0.02333
C 1.22320 -1.13749 -2.77531
C -2.49590 -0.03325 -0.67373
C 2.08234 0.07607 -2.34985
C -0.91453 0.18119 -2.60154
C -0.15455 1.33137 -1.90669
C -0.32283 -1.33552 -0.66733
C -0.28338 1.15199 -0.35572
C -0.20814 -1.13643 -2.21784
H -3.54846 -0.05471 -0.36688
H 2.90685 0.15113 -3.07044
C 1.85154 -0.21208 0.27467
H 2.10541 0.61874 0.94074
H 2.08290 -1.13193 0.82062
C 0.35090 -0.17164 0.04972
H -0.02509 -0.31959 1.26374

TS2
H 0.24728 1.89968 0.21467
H -0.22891 -2.34514 -0.18638
H -0.74471 -2.04350 -2.61950
H 2.24307 0.28654 0.59099
H -2.57395 1.15964 -2.82250
H 1.88997 -1.44631 0.62787
H -2.72160 -0.59446 -2.93903
H 3.07853 0.46791 -2.97056
H -2.03290 1.14511 0.95851
H 1.60177 -1.45635 -3.29086
H -2.32809 -1.33562 0.70010
H 1.46927 -2.60173 -1.96400
H -2.60546 -2.04689 -0.89493
H 3.32669 1.17012 -1.39011
H -2.14806 2.22891 -0.43369
C -1.81222 1.23704 -0.10942
C 2.57487 0.68019 -2.02022
C -2.09113 -1.23634 -0.36453
C 1.30996 -1.55095 -2.23739
C -2.21021 0.21421 -2.40184
C 1.69638 -0.51573 0.08293
C -2.54682 0.13160 -0.89750
C 2.23875 -0.66971 -1.37337
C -0.57592 -1.37741 -0.56763
C -0.19212 -1.26212 -2.08035
C -0.28763 1.11919 -0.33939
C -0.02682 1.30328 -1.87171
C -0.67904 0.10914 -2.60920
H -3.62848 0.24219 -0.75644
C 1.40912 1.67200 -2.27899
H 1.37367 1.90204 -3.35058
H 1.64094 2.62285 -1.78438
H -0.61036 2.19287 -2.14766
H -0.44663 0.17964 -3.68011
H 3.19537 -1.19907 -1.27837
C 0.20637 -0.25657 0.09260
H -0.11842 -0.32748 1.32181

O -0.47759 -0.52675 2.37693
C 0.19624 0.06735 3.51796
O -0.80492 -0.46119 4.25030
C 0.21646 1.59093 3.42982
C 1.56430 -0.55461 3.78423
H 2.32452 -0.20327 3.08212
H 0.88324 1.93864 2.63392
H 1.88599 -0.28680 4.79575
H 0.57032 2.01237 4.37601
H 1.48043 -1.64149 3.71697
H -0.79573 1.95244 3.23701

O -0.59568 -0.39984 2.42813
C 0.23368 0.10186 3.50559
O -0.79057 -0.20676 4.32470
C 0.52113 1.59282 3.34176
C 1.48866 -0.74579 3.70486
H 2.22408 -0.58250 2.91174
H 1.20516 1.77992 2.50723
H 1.95490 -0.48483 4.66024
H 0.98388 1.98369 4.25341
H 1.20507 -1.80039 3.72614
H -0.41852 2.12056 3.16504

TS3

H 1.51611 1.93745 -2.07043
H -2.44426 0.46473 -1.21744
H -1.58001 -1.88484 -1.33960
H -0.90924 2.34357 -1.83987
H 0.37877 2.37210 0.29484
H 1.01900 -1.77247 -3.99278
H -1.30809 1.83531 0.47265
H -0.61363 -2.31650 -3.60857
H 1.73102 -0.79080 1.54285
H 0.05419 1.92449 -4.11545
H -0.29753 -1.82572 0.78706
H -2.24338 1.04313 -3.62826
H -1.72275 -0.76222 0.78734
H -2.51766 -0.68843 -3.41989
H 2.00443 0.95457 1.36077
H 1.43036 0.83847 -4.30642
C 0.49885 0.99124 -3.74867
C 1.57078 0.06971 0.89097
C -1.79177 0.11659 -3.25410
C -0.72286 -0.91233 0.36734
C 0.10541 -1.50358 -3.44962
C -0.32508 1.56693 0.07229
C -0.47651 -0.18054 -3.99222
C -1.50687 0.25281 -1.74644
C -0.88967 -1.04617 -1.19223
C 0.81765 1.10809 -2.23847
C 1.48199 -0.22731 -1.80418
C 0.42756 -1.35989 -1.94231
C -0.50134 1.39103 -1.48190
H -0.66780 -0.27928 -5.06699
C 2.29504 -0.19510 -0.49564
H 2.80924 -1.15524 -0.40224
H 3.06078 0.57771 -0.60265
H 2.25278 -0.43910 -2.55700
H 0.84592 -2.30018 -1.56156
C 0.13438 0.26865 0.63302
H -0.44224 0.58446 2.27035
O -0.76748 0.76254 3.19377
C -0.21165 -0.08822 4.28668
O -0.99623 0.23494 5.30168
C 1.26277 0.31710 4.50701
C -0.33145 -1.57109 3.86441
H 0.30421 -1.83814 3.01153
H 1.90584 0.11987 3.64202
H -0.04051 -2.20687 4.70694
H 1.66719 -0.23643 5.36153
H -1.37448 -1.78383 3.61350
H 1.29744 1.38509 4.73861

TS4

H -0.12255 1.92649 -2.78078
H 0.33521 -2.33100 -2.22440
H 0.50502 -1.94986 0.24214
H 0.34429 -0.31919 -3.72669
H -2.06242 0.25202 -3.40028
H 2.23640 1.26371 0.62562
H -1.69923 -1.46650 -3.33848
H 2.38454 -0.49694 0.79280
H -3.34735 0.52384 0.02365
H 2.25362 1.17435 -3.19366
H -1.89632 -1.35678 0.58626
H 2.53100 -1.30492 -2.84431
H -1.60492 -2.54919 -0.67713
H 2.58691 -1.97833 -1.21386
H -3.38818 1.19207 -1.59233
H 2.16114 2.28092 -1.82407
C 1.87221 1.28187 -2.17096
C -2.72527 0.71919 -0.85772
C 2.13606 -1.18865 -1.82748
C -1.48845 -1.48840 -0.42191
C 1.95259 0.30388 0.18315
C -1.57376 -0.52134 -2.79402
C 2.50483 0.19705 -1.27586
C -2.29499 -0.64005 -1.43091
C 0.60928 -1.33862 -1.84377
C 0.02083 -1.20391 -0.40029
C 0.33277 1.14358 -2.16087
C -0.13419 1.36530 -0.67946
C -0.06219 -0.24978 -2.70797
H 3.59301 0.32188 -1.24198
H -3.23187 -1.18155 -1.61729
C -1.61381 1.72299 -0.46458
H -1.71229 1.96512 0.59813
H -1.77457 2.66424 -1.00288
H 0.40675 2.25188 -0.32525
C 0.44249 0.17725 0.07950
H -0.02834 0.28085 1.26293
O -0.64153 0.33411 2.28723
C 0.08902 -0.09219 3.46655
O -1.02173 0.18010 4.17528
C 1.27866 0.82349 3.75256
C 0.46471 -1.57132 3.38227
H 1.24108 -1.74929 2.63056
H 2.08471 0.68260 3.02615
H 0.84658 -1.91152 4.35004
H 1.67662 0.60652 4.74892
H -0.42524 -2.15108 3.12766
H 0.94272 1.86241 3.72395

TS5

TS6

H 0.19256 -2.27294 -2.16776
H 0.31956 2.27975 -0.20656
H -2.01642 -2.06790 -0.76132
H 2.59274 1.12128 -2.87427
H -1.93578 -1.15614 0.74579
H 2.45064 2.12880 -1.43461
H -3.08829 0.74042 -2.86559
H 2.38268 -2.16388 -0.93268
H -1.94680 2.20421 -1.27471
H 2.25003 -0.64845 1.05684
H -1.89876 1.68127 0.40480
H 2.27386 1.11718 0.85460
H -3.10192 -0.99464 -2.65854
H 2.55206 -1.52108 -2.56549
C 2.08018 -1.34131 -1.59235
C -2.48548 -0.10095 -2.50276
C 1.94057 0.17601 0.40561
C -1.60317 1.40064 -0.61196
C 2.11966 1.18607 -1.88729
C -1.64276 -1.14128 -0.30911
C 2.56851 0.00070 -1.00874
C -2.30765 0.07750 -0.98764
C -0.06736 1.34380 -0.62824
C 0.54335 -1.31815 -1.75583
C 0.18505 -0.16232 -2.72124
C 0.58271 1.17312 -2.04586
C -0.10581 -1.13740 -0.33752
C -1.20767 -0.21443 -3.37438
H -1.22363 0.58090 -4.12950
H -1.24902 -1.15294 -3.94058
H 0.86839 -0.27238 -3.57547
H 0.26058 2.01728 -2.66882
H -3.32615 0.14152 -0.58250
H 0.25380 -1.96432 0.28759
H 3.65986 -0.00485 -0.90889
C 0.44677 0.17340 0.19059
H -0.07421 0.32908 1.34881
O -0.72016 0.46163 2.34775
C -0.11466 -0.06047 3.55966
O -1.21983 0.35009 4.20798
C 1.16178 0.69556 3.92679
C 0.07486 -1.57443 3.47720
H 0.85819 -1.84437 2.76106
H 1.98886 0.45650 3.25171
H 0.36276 -1.96613 4.45792
H 1.46450 0.42672 4.94380
H -0.86723 -2.03575 3.17329
H 0.96161 1.76863 3.88948

H -0.97102 2.24558 -1.40825
H 2.63161 -0.12591 -1.73539
H 1.27934 -2.18417 -1.27259
H 0.31355 2.03059 -3.72434
H -1.31961 -1.06101 1.11504
H 1.88167 1.24005 -3.70465
H 0.18911 -1.99926 0.94080
H -1.64373 -0.96432 -4.55393
H 0.41028 2.27351 0.69736
H 0.10918 -2.26111 -3.47678
H 2.44272 0.90853 0.52401
H 1.74529 -1.62432 -3.53462
H 2.35318 -0.87417 0.62671
H -1.56130 0.77758 -4.66940
H -1.18373 1.52177 0.97560
C -0.22396 1.41504 0.46660
C -1.30854 -0.06797 -4.01889
C 1.84482 0.02790 0.27920
C 0.72721 -1.40109 -3.19290
C -0.35181 -1.10927 0.61275
C 0.85018 1.15421 -3.34161
C 0.22346 -0.13464 -3.92126
C 1.63498 -0.05038 -1.28601
C 0.78681 -1.28161 -1.65622
C -0.46477 1.32198 -1.10647
C -1.37898 0.10068 -1.34684
C -0.59124 -1.17085 -0.96402
C 0.91117 1.20887 -1.80091
C -2.11431 0.05910 -2.70096
H -2.82658 -0.77141 -2.63717
H -2.72767 0.96626 -2.74331
H -2.19837 0.18433 -0.62010
H -1.19053 -2.06710 -1.15860
H 0.57377 -0.21208 -4.95864
H 1.49625 2.09534 -1.52440
C 0.45150 0.12686 0.77086
H 0.71132 0.32285 2.38555
O 0.87060 0.44302 3.37549
C -0.20152 -0.04794 4.28506
O 0.25088 0.39101 5.44830
C -0.25415 -1.58828 4.19062
C -1.54032 0.59515 3.85869
H -1.88265 0.27490 2.86686
H -0.55911 -1.95597 3.20508
H -2.31724 0.32532 4.58176
H -0.96634 -1.97256 4.92884
H -1.42468 1.68253 3.86250
H 0.73721 -1.98422 4.42668

Table 10s. The computed zero-point vibrational energies (ZPVE) and enthalpies of TSs at M062X/6-31G(d,p).

#	Structure	Position of hydrogen being substituted	Point group	E_0, M062X/6-31G(d,p) au	ZPVE (NIMAG)	H_{298}, M062X/6-31G(d,p) au
1						
2	**TS1**	12	C_1	-852,30924	1	-852,352731
3	**TS2**	1	C_1	-852,30719	1	-852,351855
4	**TS3**	9	C_1	-852,30608	1	-852,350446
5	**TS4**	6	C_1	-852,30603	1	-852,350564
6	**TS5**	2	C_1	-852,305637	1	-852,349567
7	**TS6**	4	C_1	-852,304793	1	-852,349193

Table 11s. The XYZ coordinates of all M062X/6-31G** optimized structures.

TS1
H 0.38150 -1.92843 0.22476
H -0.98675 -0.44468 -3.57874
H -0.96284 1.88041 -2.63031
H 0.09455 2.28532 -0.42238
H -0.61185 -2.34827 -1.99443
H 1.87956 -2.11691 -1.89120
H -1.89464 1.52140 0.88664
H 1.16385 -1.72484 -3.44748
H -2.39573 2.08563 -0.71814
H 3.21715 1.26252 -1.23269
H -2.10306 -2.16242 -0.04349
H 1.51606 2.09567 -2.63616
H -2.91144 -1.28173 -2.23191
H 0.88354 1.08237 -3.92618
H -3.04361 0.45826 -2.51281
H 3.51625 -0.44719 -0.99082
H -1.70675 -1.06028 1.29041
C -1.67416 -1.18427 0.20488
C 2.72050 0.29401 -1.11606
C -2.45711 -0.31125 -1.99589
C 1.03434 1.13115 -2.84040
C -1.84762 1.30173 -0.18188
C 1.25688 -1.37722 -2.41112
C -2.47304 -0.06886 -0.48408
C 1.97805 -0.01228 -2.42105
C -1.00958 -0.27822 -2.49250
C -0.35191 1.07871 -2.19360
C -0.20654 -1.14493 -0.26956
C -0.37475 1.32055 -0.64890
C -0.15729 -1.36418 -1.81526
H -3.50351 -0.08298 -0.11298
H 2.76294 -0.07257 -3.18473
C 1.88399 0.32226 0.19627
H 2.08983 1.25090 0.73816
H 2.20452 -0.50028 0.84519
C 0.39434 0.20728 0.01493
H 0.10572 0.32186 1.37377
O -0.31902 0.67297 2.30802
C 0.33122 0.16997 3.55407
O -0.59494 0.68963 4.31395
C 1.71333 0.80613 3.70091
C 0.37821 -1.35834 3.49785
H 0.99869 -1.72089 2.66826

TS2
H 0.88193 0.40123 -1.78345
H -0.09665 -0.13831 2.33688
H 2.31241 -0.61412 2.84198
H -0.03429 2.34059 -0.37286
H 3.59132 -2.36517 -0.13493
H -0.62456 1.94897 1.25438
H 3.13379 -2.54288 1.56117
H 3.35521 3.26630 0.61983
H 0.00124 -1.90730 -1.33376
H 3.08990 1.75443 2.51582
H -0.55128 -2.23247 1.06964
H 1.47249 1.57811 3.18219
H 0.73444 -2.49524 2.26590
H 2.07932 3.47707 -0.55258
H 1.67941 -1.96869 -1.91040
C 1.03586 -1.66475 -1.07677
C 2.54245 2.73755 0.11003
C 0.48062 -1.98106 1.33128
C 2.06750 1.43973 2.27107
C 2.87674 -2.02994 0.62621
C 0.20108 1.79640 0.54941
C 1.44160 -2.39619 0.21300
C 1.50992 2.36392 1.17320
C 0.58984 -0.47015 1.54887
C 2.04494 -0.05618 1.93425
C 1.17360 -0.14374 -0.87672
C 2.67184 0.15253 -0.54816
C 2.99809 -0.50404 0.80820
H 1.37080 -3.47707 0.05113
C 3.14403 1.59764 -0.74553
H 4.23056 1.58540 -0.60315
H 2.99242 1.83592 -1.80432
H 3.23383 -0.41306 -1.30490
H 4.02774 -0.24480 1.09064
H 1.22321 3.30731 1.65356
C 0.34894 0.32265 0.29613
H -0.95978 0.06255 -0.05008
O -1.76521 -0.60640 -0.31369
C -2.81169 0.04346 -1.17197
O -3.55907 -1.02095 -1.19783
C -2.15535 0.44092 -2.49625
C -3.38420 1.23825 -0.40611
H -2.64514 2.03607 -0.26614

H 2.43438 0.42596 2.96975
H 0.79986 -1.74716 4.42914
H 2.09626 0.59052 4.70233
H -0.64018 -1.73735 3.39008
H 1.60769 1.88706 3.59132

TS3
H 0.31244 -2.22069 2.49492
H 2.59604 0.07063 -0.33949
H 1.41957 -1.10081 -2.20433
H 2.23326 -0.74837 1.99319
H 0.02592 0.38159 2.32193
H 0.86110 -4.53407 -0.96332
H 1.11829 1.25816 1.23685
H 1.80177 -3.53986 -2.07767
H -2.55171 -0.06740 -0.22681
H 2.60570 -3.17839 2.14119
H -0.78996 0.02394 -1.86311
H 3.92926 -1.86731 0.47418
H 0.59669 1.03108 -1.41963
H 3.59818 -2.01624 -1.25493
H -2.21512 0.06458 1.49968
H 1.35318 -4.31044 1.62553
C 1.81630 -3.34299 1.39737
C -1.82985 -0.32997 0.55412
C 3.13162 -2.02419 -0.26228
C 0.03024 0.13525 -1.14528
C 1.34396 -3.55678 -1.08089
C 0.51515 0.34941 1.34239
C 2.43336 -3.36406 -0.01176
C 2.10258 -0.89407 -0.16179
C 0.97960 -1.08186 -1.19820
C 0.75719 -2.22719 1.49010
C -0.33745 -2.55334 0.44754
C 0.28897 -2.44026 -0.96039
C 1.45134 -0.87373 1.23233
H 3.16031 -4.18109 -0.07961
C -1.70535 -1.88242 0.64679
H -2.38817 -2.32111 -0.08812
H -2.07475 -2.18970 1.63043
H -0.56725 -3.61996 0.58539
H -0.49197 -2.58511 -1.71964
C -0.51361 0.32326 0.24451
H -0.99876 1.61829 0.31091
O -0.76236 2.63802 0.05847
C -1.92552 3.39748 -0.49834
O -1.29082 4.53407 -0.45261
C -3.10345 3.25128 0.46744
C -2.22638 2.85278 -1.89551
H -2.57985 1.81438 -1.86697
H -3.46706 2.21805 0.52483
H -3.00168 3.46338 -2.36647
H -3.92926 3.88373 0.13071
H -1.31604 2.91556 -2.49493
H -2.78340 3.58603 1.45575

TS5
H 2.94131 -0.44270 -1.46092
H 0.10327 0.10149 2.55756
H 1.97797 1.91756 -1.64622
H 2.62032 -2.53404 2.16425
H 0.29175 2.17035 -1.17334
H 1.04100 -2.11803 2.83131

H -1.39728 1.22310 -2.36278
H -4.23056 1.65213 -0.96112
H -2.91734 0.82129 -3.18219
H -3.73758 0.88734 0.56500
H -1.69652 -0.44609 -2.93829

TS4
H -2.23141 0.35513 2.19346
H -2.74530 0.63346 2.07158
H -0.247580.58558 -2.33403
H -3.66677,0.80678,0.24238
H -3.30858 -1.59923 0.88163
H 1.12090 2.23575 0.58867
H -3.77317 -1.30420 -0.78728
H 0.86002 2.32089 -1.16948
H 0.07797 -2.93478 0.05088
H -2.56012 2.73464 1.43478
H -0.04483 -1.84373 -1.89188
H -2.83359 2.90729 -1.01736
H -1.58132 -1.38683 2.63405
H -1.44927 2.75311 -2.10433
H -1.28148 -3.28823 1.10552
H -0.97506 2.49915 2.17411
C -1.59262 2.23376 1.30807
C -0.79766 -2.48876 0.53293
C -1.87394 2.39535 -1.15849
C -0.99378 -1.32991 -1.70863
C 0.42305 1.99339 -0.21994
C -2.94884 -1.19036 -0.07170
C -0.93825 2.72136 0.00866
C -1.75411 -2.03134 -0.57337
C -2.09101 0.88263 1.22561
C -0.73438 0.15153 -1.45099
C -1.78458 0.70898 1.25573
C -0.37074 0.05975 1.12552
C -2.69449 0.32194 0.07444
H -0.74632 3.79858 0.05943
H -2.17367 -2.94991 1.00169
C -0.31530 -1.42024 1.52293
H 0.72289 -1.64614 1.77756
H -0.88881 -1.49164 2.45539
H 0.26478 0.57415 1.85961
C 0.09759 0.51464 -0.23858
H 1.30665 -0.03625 -0.52700
O 1.92383 -0.93181 0.42967
C 3.34653 -0.62652 0.06085
O 3.72131 -1.85480 0.27256
C 3.37679 -0.15258 1.39280
C 3.87687 0.42090 -1.04219
H 3.36310 1.38386 -0.93373
H 2.81621 0.77942 1.53525
H 4.94317 0.58219 -0.86220
H 4.41186 0.02372 1.69923
H 3.74292 0.04288 -2.05714
H 2.95524 -0.93701 2.02448

TS6
H 2.13101 1.04800 -1.34169
H -0.12071 -2.61646 -1.63694
H -2.23007 -1.30812 -1.34192
H 2.09464-0.35410 -3.58153
H -1.33025 1.42946 0.96897
H 1.33810-1.93612 -3.52738

H 3.39876 2.86060 1.63762
H 1.41245 -2.43616 -1.45145
H 1.38922 2.23541 2.58968
H -0.77478 -1.89957 -0.43329
H -0.10435 2.30495 1.64836
H -0.95453 -1.77016 1.33485
H 3.67175 3.01668 -0.08063
H 2.85005 -2.73122 -0.47116
C 1.93434 -2.13203 -0.53590
C 3.20131 2.37668 0.67416
C -0.27454 -1.59708 0.49376
C 0.90732 1.88751 1.66795
C 1.71564 -1.94173 1.98502
C 1.23900 1.72510 -0.85803
C 1.03963 -2.40309 0.68217
C 1.68694 2.40791 0.44965
C 0.75674 0.36664 1.71638
C 2.29863 -0.63858 -0.59317
C 3.05365 -0.28217 0.70285
C 2.08208 -0.44731 1.89116
C 0.99797 0.21144 -0.75772
C 3.89479 0.99956 0.64429
H 4.61168 0.95306 1.47212
H 4.50038 0.92049 -0.26660
H 3.80263 -1.07843 0.82780
H 2.56366 -0.11456 2.82019
H 1.42564 3.46823 0.35054
H 0.49556 -0.12733 -1.67300
H 0.79118 -3.46823 0.74329
C 0.16278 -0.15912 0.43646
H -1.05951 0.45013 0.36595
O -1.63518 1.31219 0.02426
C -2.83838 0.97523 -0.80673
O -3.26974 2.20296 -0.76950
C -3.67787 -0.05432 -0.04871
C -2.36209 0.47398 -2.17020
H -1.84544 -0.49123 -2.10124
H -3.15915 -1.01476 0.05632
H -3.22461 0.35028 -2.83133
H -4.61168 -0.22888 -0.59029
H -1.69394 1.22147 -2.60373
H -3.91211 0.34944 0.93759

H -2.22131 -0.09990 0.80603
H -0.88185 1.48084 -4.67997
H 2.06718 -0.22383 0.84052
H -2.19950 -0.24713 -3.60072
H 0.76357 -2.30690 0.68635
H -1.52265 -1.86497 -3.53544
H -1.01207 -2.26891 0.66530
H 0.862501.43873 -4.68430
H 1.269487 1.35002 0.98784
C 1.20979 0.36805 0.50823
C -0.01451 1.19498 -4.07196
C -0.10767 -1.74180 0.34167
C -1.34356 -0.82567 -3.22917
C -1.318424 0.44000 0.49936
C 1.20811 -0.89026 -3.21829
C -0.05128 -0.32664 -3.90338
C -0.09527 -1.60670 -1.20424
C -1.31582 -0.80817 -1.6941
C 1.20867 0.53083 -1.04454
C -0.01509 1.39540 -1.41059
C -1.28670 0.59742 -1.05919
C 1.16972 -0.87359 -1.68388
C 0.00993 2.06225 -2.79359
H -0.83682 2.75948 -2.82037
H 0.90270 2.69948 -2.81298
H 0.00509 2.25067 -0.71770
H -2.17962 1.16146 -1.36198
H -0.05753 -0.72636 -4.92683
H 2.05259 -1.42137 -1.32443
C -0.07186 -0.33254 0.84334
H -0.28099 -0.53032 2.28076
O 0.37283 -0.68260 3.08906
C 0.07355 0.15324 4.31129
O 0.68057 -0.67180 5.12626
C -1.44860 0.24391 4.48665
C 0.74003 1.52129 4.14259
H 0.29539 2.11121 3.33151
H -1.93950 0.812095 3.68670
H 0.63790 2.09374 5.07056
H -1.67147 0.74218 5.43534
H 1.80353 1.37055 3.94536
H -1.85975 -0.76768 4.52543

Table 12s. The computed zero-point vibrational energies (ZPVE) and enthalpies of TSs at PCM M062X/6-31G(d,p).

#	Structure	Name / position of hydrogen being substituted	Point group	*E*, PCM M06-2X/6-31G(d,p) au	ZPVE (NIMAG)	H^0_{298}, PCM M06-2X /6-31G(d,p) au
1						
2	**TS1**	12	C_1	-852,321676	1	-852,304035
3	**TS2**	1	C_1	-852,320894	1	-852,302896
4	**TS3**	9	C_1	-852,32037	1	-852,302515
5	**TS4**	6	C_1	-852,319539	1	-852,301493
6	**TS5**	2	C_1	-852,319661	1	-852,301684
7	**TS6**	4	C_1	-852,316399	1	-852,298479

Table 13s. The XYZ coordinates of all PCM M06-2X/6-31G(d,p) optimized structures.

TS1
H 0.18944 -2.26463 -0.38305
H -0.83688 0.32290 -3.66892
H -0.65421 2.28391 -2.12440
H 0.22398 1.98343 0.15535
H -0.75504 -1.97079 -2.65253
H 1.72790 -2.05747 -2.51227
H -1.88115 1.04771 1.12345
H 1.11595 -1.11519 -3.86606
H -2.24768 2.07717 -0.27148
H 3.50416 0.62562 -0.84550
H -2.28679 -2.19863 -0.81706
H 1.83617 2.18432 -1.87141
H -2.90426 -0.66082 -2.69698
H 1.22763 1.71881 -3.45429
H -2.87935 1.09232 -2.46373
H 3.29601 -1.10321 -1.04806
H -1.91054 -1.56551 0.79075
C -1.80648 -1.37222 -0.28014
C 2.75091 -0.15578 -0.98819
C -2.39017 0.15430 -2.17289
C 1.28111 1.40206 -2.40539
C -1.78380 1.13293 0.03727
C 1.20966 -1.12609 -2.77286
C -2.48415 -0.04464 -0.65739
C 2.06817 0.07652 -2.33884
C -0.91597 0.18441 -2.58175
C -0.16160 1.33081 -1.88765
C -0.31045 -1.32861 -0.66108
C -0.29040 1.15321 -0.34498
C -0.21076 -1.12820 -2.20461
H -3.53473 -0.07495 -0.34787
H 2.88950 0.15704 -3.06109
C 1.84910 -0.18358 0.27674
H 2.09325 0.68003 0.90560
H 2.08615 -1.07846 0.86158
C 0.35510 -0.16136 0.04394
H -0.02218 -0.30788 1.27936
O -0.45700 -0.55049 2.35054
C 0.19198 0.06520 3.49485
O -0.76967 -0.49746 4.22476
C 0.15506 1.58278 3.39092
C 1.58384 -0.49824 3.74079
H 2.32405 -0.10072 3.04220

TS2
H 0.15446 2.21334 -0.31578
H -0.04951 -2.00598 0.37030
H -0.66732 -2.35454 -2.02652
H 2.25399 0.87359 0.34169
H -2.68603 0.57790 -2.94850
H 2.02205 -0.81787 0.82247
H -2.71968 -1.15623 -2.61470
H 2.93977 0.17571 -3.18945
H -2.05604 1.53697 0.68623
H 1.60910 -1.82545 -2.93641
H -2.18154 -0.91412 1.06721
H 1.59933 -2.60535 -1.35949
H -2.45767 -2.03098 -0.28315
H 3.22613 1.26734 -1.85566
H -2.27061 2.23038 -0.92684
C -1.86386 1.37273 -0.37916
C 2.47397 0.60236 -2.29433
C -1.98503 -1.08401 0.00308
C 1.35974 -1.66934 -1.87941
C -2.25011 -0.20905 -2.32163
C 1.74934 -0.06215 0.07549
C -2.54034 0.07005 -0.83693
C 2.25023 -0.54955 -1.31379
C -0.47556 -1.18678 -0.22353
C -0.14617 -1.43515 -1.72630
C -0.34742 1.29232 -0.63688
C -0.14376 1.09879 -2.16909
C -0.72891 -0.27425 -2.55797
H -3.62205 0.15080 -0.68339
C 1.24582 1.44124 -2.71556
H 1.16023 1.41675 -3.80785
H 1.43114 2.49091 -2.46061
H -0.79922 1.85161 -2.62999
H -0.52543 -0.46238 -3.62082
H 3.24216 -0.98174 -1.13587
C 0.25063 0.10137 0.08715
H -0.01244 0.35606 1.32465
O -0.48419 0.57062 2.37908
C 0.25537 0.03652 3.50560
O -0.68998 0.56621 4.27875
C 1.62930 0.68155 3.62556
C 0.29492 -1.48447 3.45629
H 0.94557 -1.84712 2.65330

H 0.79215 1.94273 2.57583
H 1.89371 -0.23170 4.75530
H 0.51733 2.02437 4.32357
H 1.54517 -1.58624 3.65766
H -0.87376 1.90645 3.22012
H 2.31343 0.33712 2.84457
H 0.67992 -1.87179 4.40369
H 2.06351 0.42486 4.59591
H -0.71846 -1.86113 3.30186
H 1.51798 1.76569 3.56192

TS3

H -1.39749 -2.02032 -2.00225
H 2.42673 -0.29799 -1.04941
H 1.44616 1.98383 -1.33207
H 1.04092 -2.26984 -1.70225
H -0.35320 -2.31132 0.37668
H -1.03480 1.62738 -4.03482
H 1.30248 -1.73111 0.61879
H 0.54929 2.27978 -3.60402
H -1.91247 0.81969 1.46486
H 0.14398 -1.99382 -3.98342
H 0.08064 1.93197 0.75674
H 2.35481 -0.97146 -3.44425
H 1.58222 0.99638 0.85375
H 2.52425 0.78185 -3.28950
H -2.09524 -0.93077 1.35502
H -1.28342 -0.99197 -4.26777
C -0.36892 -1.07658 -3.66831
C -1.67859 -0.05474 0.84809
C 1.84076 -0.05890 -3.11816
C 0.59206 1.03742 0.38425
C -0.13088 1.43370 -3.44502
C 0.33660 -1.48853 0.15971
C 0.54681 0.13462 -3.91461
C 1.50313 -0.15807 -1.62760
C 0.79554 1.11956 -1.14268
C -0.73686 -1.15969 -2.17423
C -1.48879 0.14141 -1.81634
C -0.50201 1.32225 -1.95319
C 0.55975 -1.34400 -1.35993
H 0.77560 0.20818 -4.98381
C -2.35266 0.10697 -0.54703
H -2.93849 1.03161 -0.53198
H -3.07140 -0.70931 -0.67200
H -2.23233 0.28217 -2.61431
H -0.99272 2.24818 -1.62336
C -0.18333 -0.20357 0.76419
H 0.10953 -0.35941 2.01016
O 0.70149 -0.58051 2.98982
C 0.19821 0.09934 4.16304
O 1.18450 -0.49431 4.83449
C -1.20669 -0.37023 4.51315
C 0.31476 1.60875 4.00527
H -0.40369 1.99136 3.27250
H -1.94705 -0.00716 3.79351
H 0.11456 2.09488 4.96401
H -1.47950 0.00676 5.50266
H 1.32919 1.85503 3.68496
H -1.21999 -1.46141 4.53187

TS4

H -0.60808 -2.14380 2.28176
H -0.29929 2.14181 2.56818
H 0.70623 2.17257 0.27762
H -0.62163 -0.09075 3.66450
H -2.74341 -0.63673 2.47733
H 2.68658 -0.89985 0.03427
H -2.50005 1.07703 2.79647
H 2.75217 0.86866 0.19036
H -2.79622 -0.37328 -1.16632
H 1.42552 -1.43902 3.58716
H -1.37954 1.51467 -0.95612
H 1.62944 1.06381 3.73202
H -1.62513 2.56440 0.44965
H 2.18025 1.99594 2.33498
H -3.34531 -1.29109 0.23074
H 1.87563 -2.30042 2.11299
C 1.41893 -1.37868 2.49211
C -2.50954 -0.69966 -0.16182
C 1.60644 1.11112 2.63640
C -1.34767 1.54901 0.14017
C 2.20755 -0.03072 0.49732
C -2.13997 0.23459 2.19162
C 2.23353 -0.15517 2.04470
C -2.37841 0.55297 0.70498
C 0.15862 1.23256 2.15590
C 0.09318 1.32244 0.60513
C -0.02783 -1.26186 1.98008
C 0.03451 -1.24631 0.41332
C -0.67313 0.00780 2.57079
H 3.27411 -0.25537 2.37198
H -3.35632 1.04754 0.64239
C -1.27043 -1.60427 -0.30207
H -1.03594 -1.67487 -1.36958
H -1.51948 -2.61771 0.03402
H 0.72677 -2.05571 0.14282
C 0.74905 0.05460 0.09388
H 0.77157 0.25633 -1.18707
O 0.91567 0.72302 -2.27729
C 0.20225 -0.06965 -3.15924
O -1.05585 -0.10337 -3.08714
C 0.94933 -1.36755 -3.48273
C 0.72398 1.11479 -4.34513
H 1.80112 1.23900 -4.38846
H 2.00455 -1.19588 -3.70139
H 0.32777 0.59926 -5.21995
H 0.46761 -1.87540 -4.31948
H 0.18791 2.03385 -4.13215
H 0.87601 -2.01056 -2.59706

TS5

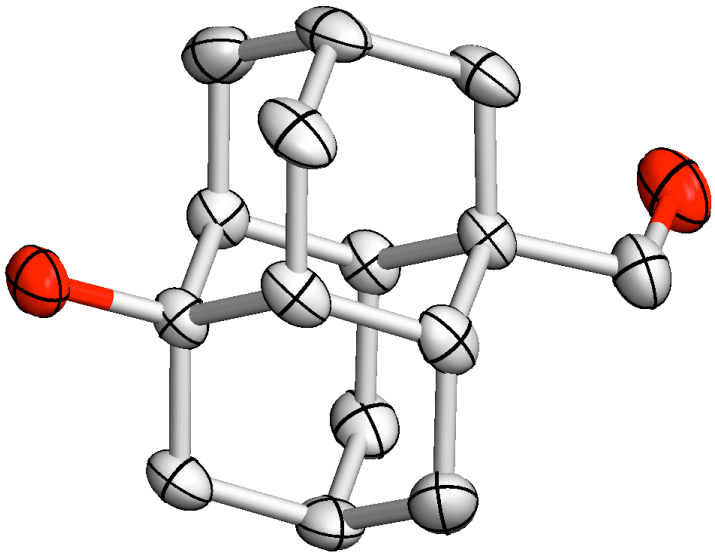
H 0.26111 -2.03394 -2.63376
H 0.27826 1.97665 0.27047
H -1.92891 -2.17934 -1.27568
H 2.50101 1.51274 -2.61090
H -1.88559 -1.69049 0.41590
H 2.35031 2.18177 -0.98419

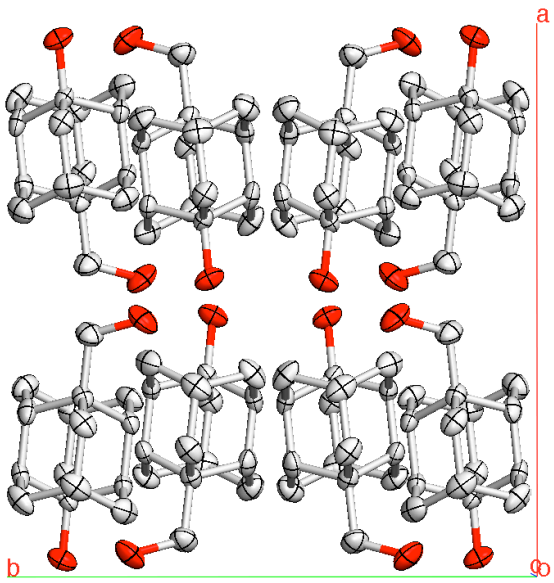
TS6

H -1.11113 2.10924 -1.25323
H 2.61828 -0.00918 -1.66799
H 1.38707 -2.16276 -1.41894
H 0.31147 2.21975 -3.48731
H -1.32258 -1.41104 1.00244
H 1.89621 1.45934 -3.46775

H -3.03269 1.08328 -2.57844
H 2.45977 -2.10628 -1.42142
H -2.01677 2.07027 -0.70869
H 2.30198 -1.08047 0.83811
H -1.89937 1.15044 0.79261
H 2.25847 0.69277 1.02573
H -3.17626 -0.64410 -2.80435
H 2.57046 -1.11634 -2.87935
C 2.11339 -1.17460 -1.88480
C -2.49545 0.13697 -2.44722
C 1.95456 -0.14480 0.38709
C -1.62929 1.14345 -0.26929
C 2.04684 1.34706 -1.62738
C -1.58816 -1.38963 -0.59449
C 2.55721 0.02379 -1.03222
C -2.29687 -0.06712 -0.94391
C -0.10088 1.14388 -0.33702
C 0.58099 -1.17980 -2.02306
C 0.15953 0.13593 -2.70677
C 0.51282 1.30643 -1.76605
C -0.05558 -1.33484 -0.60957
C -1.23678 0.14009 -3.34218
H -1.28128 1.01252 -4.00395
H -1.26870 -0.73188 -4.00614
H 0.83465 0.24199 -3.56851
H 0.14371 2.25101 -2.18638
H -3.30804 -0.13607 -0.52414
H 0.33455 -2.26388 -0.17490
H 3.64875 0.04522 -0.94757
C 0.46373 -0.15723 0.18428
H -0.04089 -0.30809 1.36207
O -0.67324 -0.50569 2.32757
C -0.11043 0.05603 3.54073
O -1.17902 -0.41610 4.17664
C -0.01101 1.57180 3.43414
C 1.20785 -0.61571 3.90151
H 2.01707 -0.32003 3.22725
H 0.75616 1.87349 2.71247
H 1.49043 -0.32995 4.91863
H 0.25561 1.99265 4.40769
H 1.07566 -1.69864 3.86131
H -0.97956 1.97187 3.12621
H 0.23718 -2.24167 0.79062
H -1.55782 -0.59808 -4.73607
H 0.20749 2.04405 0.91071
H 0.18627 -2.06599 -3.62088
H 2.33551 0.80650 0.68534
H 1.81334 -1.40213 -3.61253
H 2.34301 -0.97134 0.62646
H -1.49800 1.12203 -4.43921
H -1.33518 1.18674 1.07208
C -0.36444 1.17769 0.56713
C -1.24808 0.15044 -3.99786
C 1.79089 -0.07336 0.33007
C 0.79165 -1.22717 -3.25305
C -0.34548 -1.35771 0.50973
C 0.85205 1.32399 -3.15745
C 0.27625 0.08884 -3.87082
C 1.62167 -0.02677 -1.20727
C 0.84489 -1.25401 -1.71670
C -0.55763 1.20224 -0.97745
C -1.38556 -0.04759 -1.34583
C -0.53715 -1.29605 -1.03682
C 0.84343 1.23057 -1.62971
C -2.07878 -0.05597 -2.71459
H -2.61000 -1.01307 -2.78029
H -2.86358 0.70809 -2.68102
H -2.22320 -0.07176 -0.63277
H -1.07726 -2.19787 -1.35400
H 0.65208 0.11971 -4.90136
H 1.36493 2.11433 -1.23654
C 0.39074 -0.08841 0.87186
H 0.56972 -0.27370 2.20048
O 0.70593 0.36673 3.07497
C -0.21082 0.03023 4.22393
O 0.50718 0.72972 5.05089
C -0.19114 -1.48603 4.42444
C -1.60096 0.57833 3.90644
H -2.06941 0.05583 3.06312
H -0.63026 -2.02251 3.57456
H -2.24557 0.45763 4.78172
H -0.76630 -1.73929 5.31919
H -1.51007 1.64242 3.67984
H 0.84304 -1.80315 4.56899

D. The X-ray crystal structures and packing of diol 8





E. The copies of the NMR spectra of new compounds

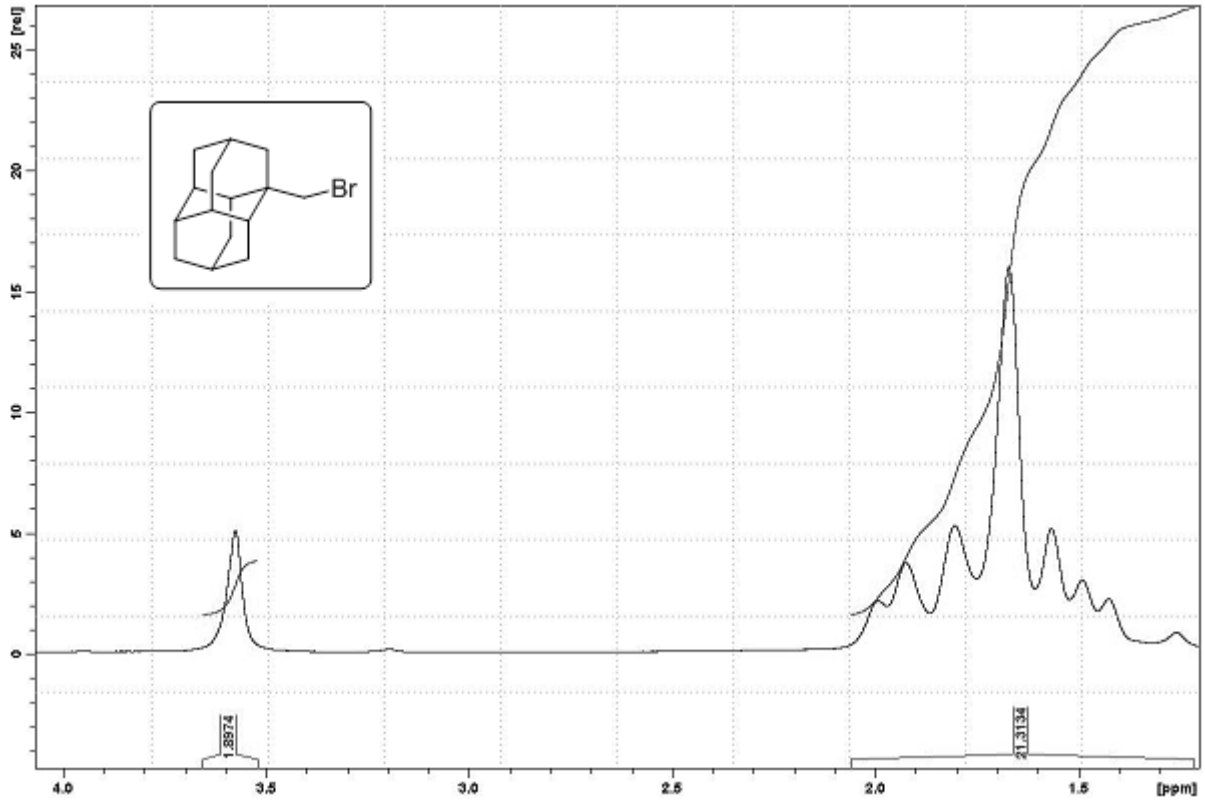


Fig. 1s. The ^{1}H-NMR spectrum of 1-bromomethyldiamantane **5** ($CDCl_3$).

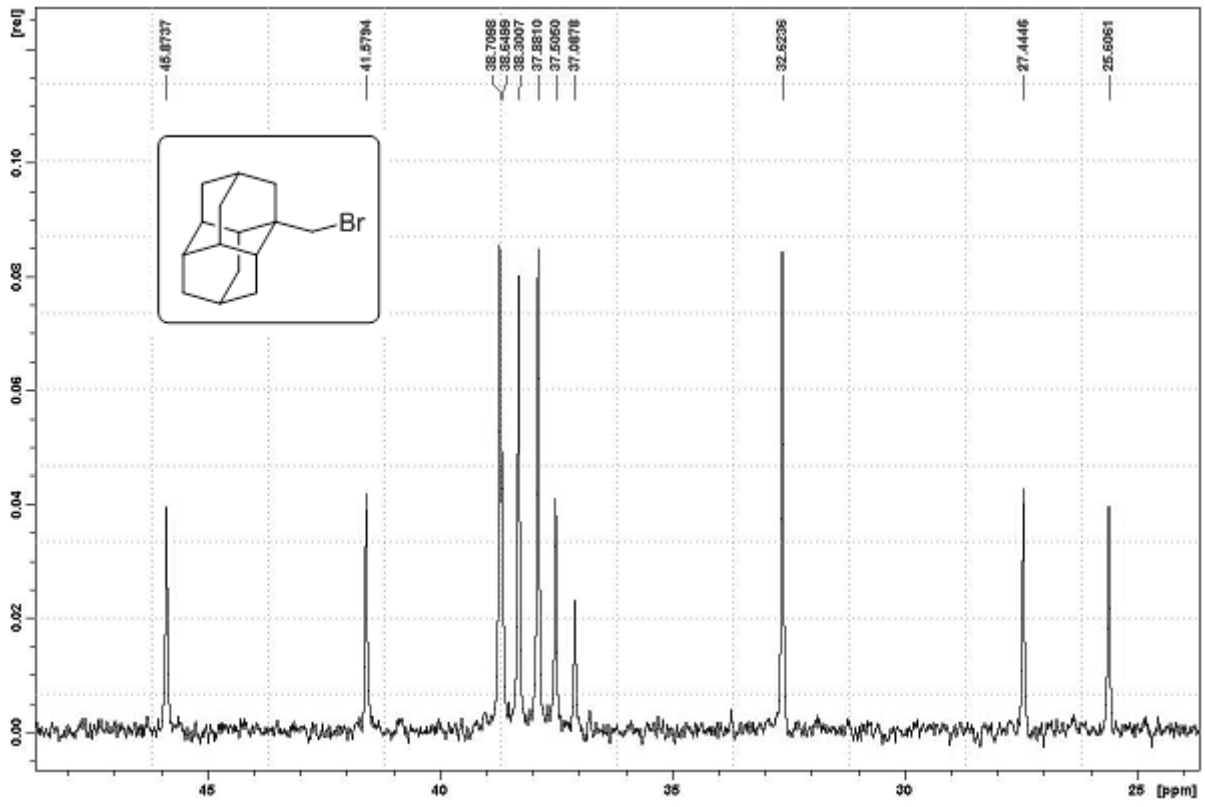


Fig. 2s. The ^{13}C-NMR spectrum of 1-bromomethyldiamantane **5** ($CDCl_3$).

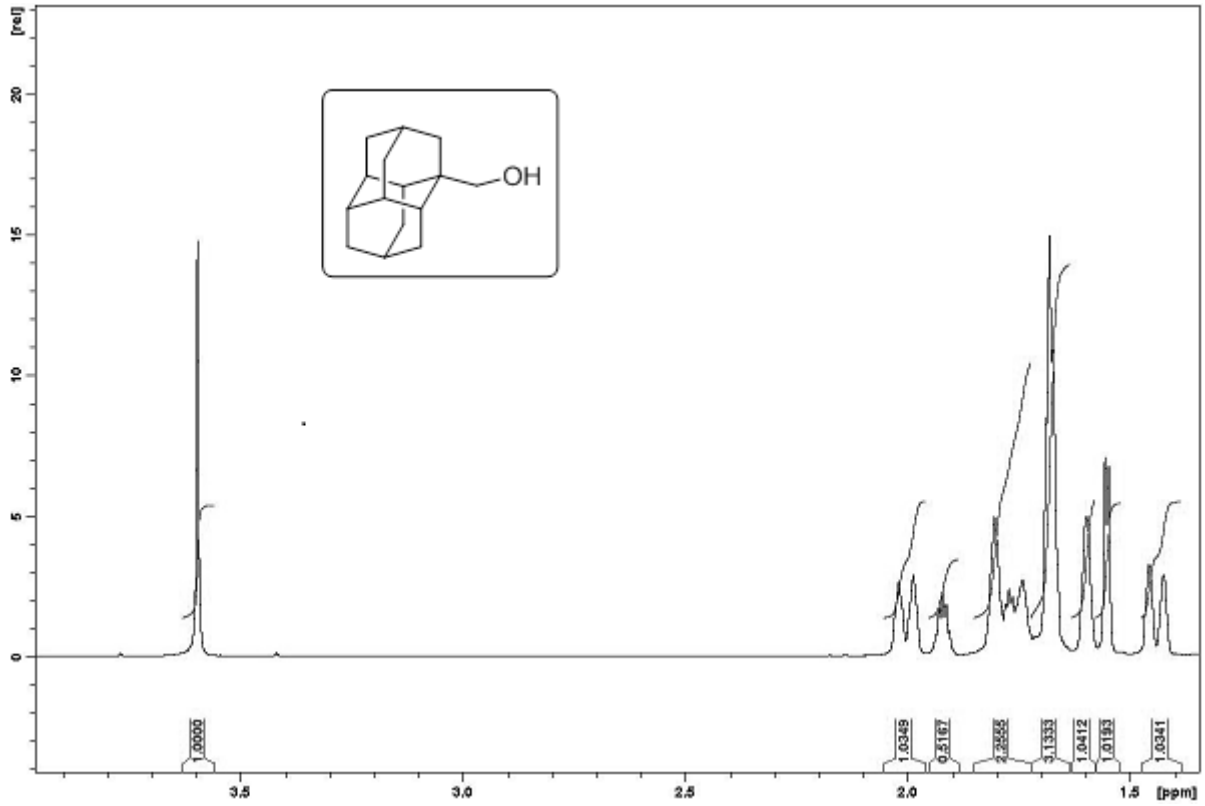


Fig. 3s. The ^{1}H-NMR spectrum of 1-hydroxymethyldiamantane **7** ($CDCl_3$).

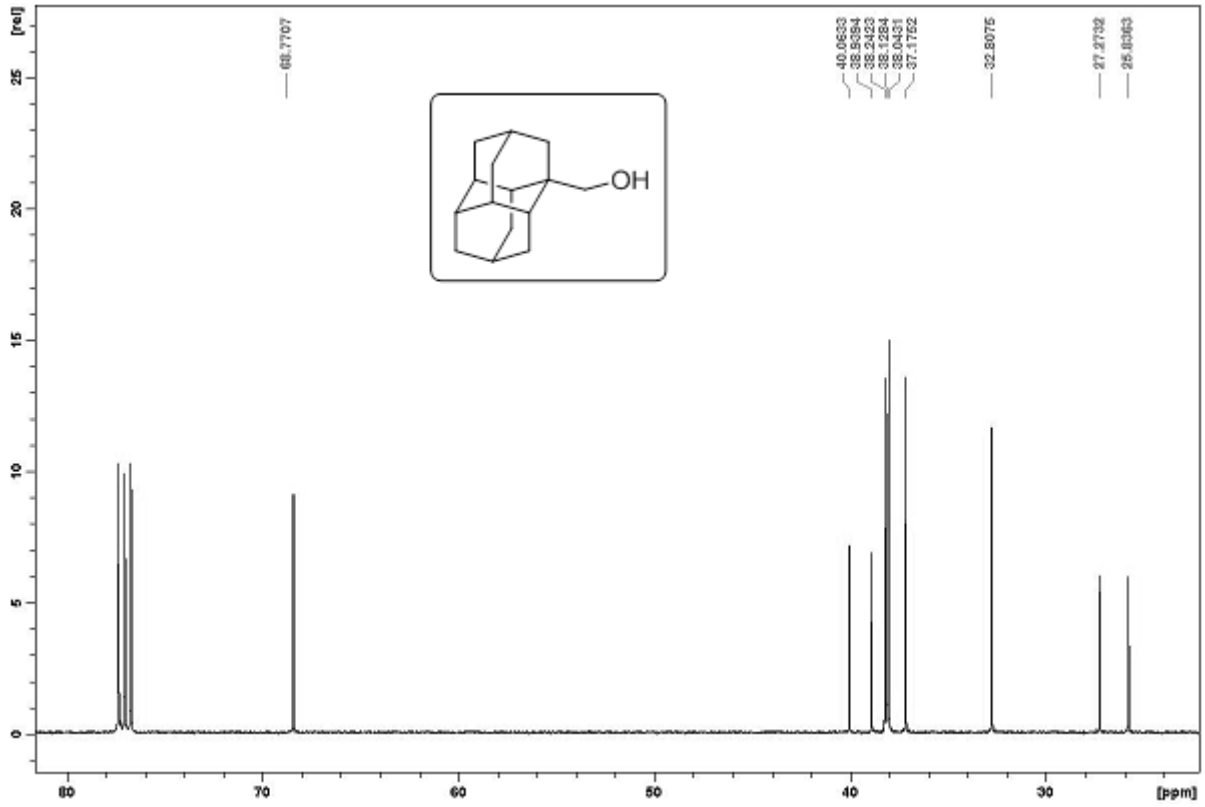


Fig. 4s. The ^{13}C-NMR spectrum 1-hydroxymethyldiamantane **7** ($CDCl_3$).

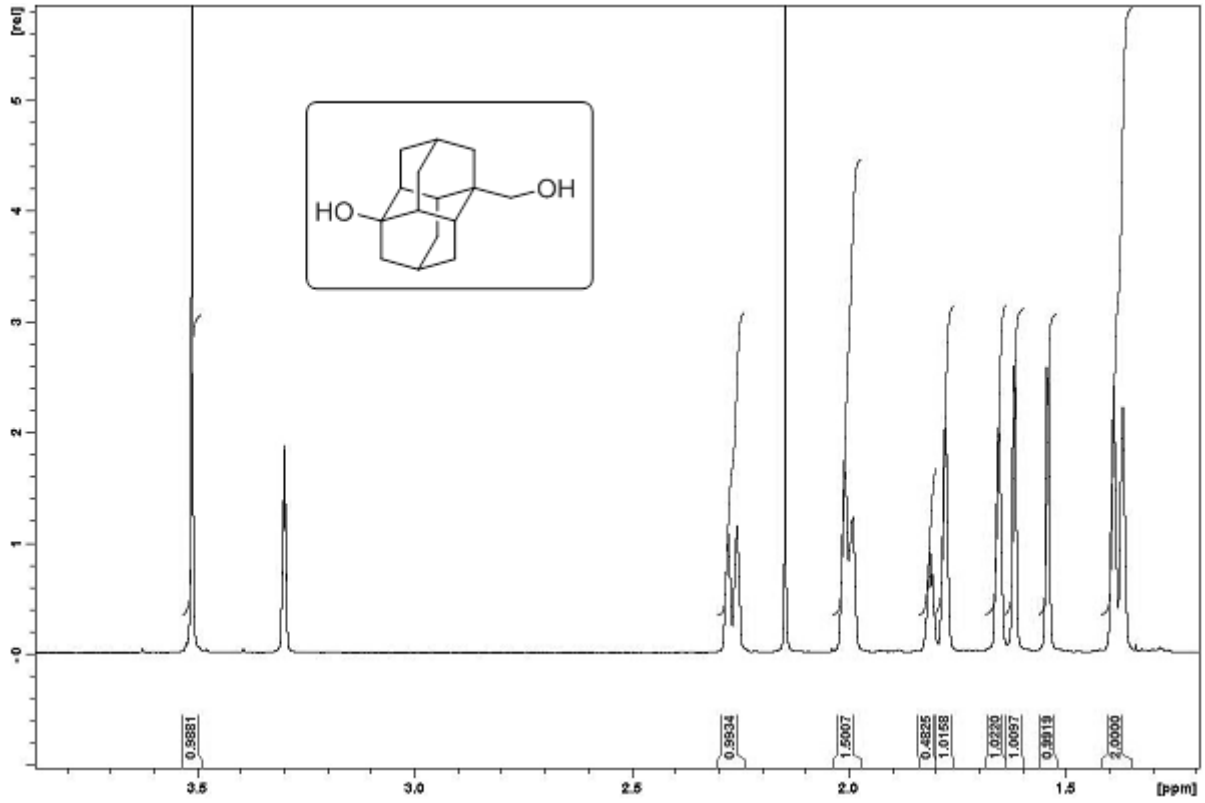


Fig. 5s. The ^{1}H-NMR spectrum of 1-hydroxy-6-hydroxymethyldiamantane **8** (CD_3OD).

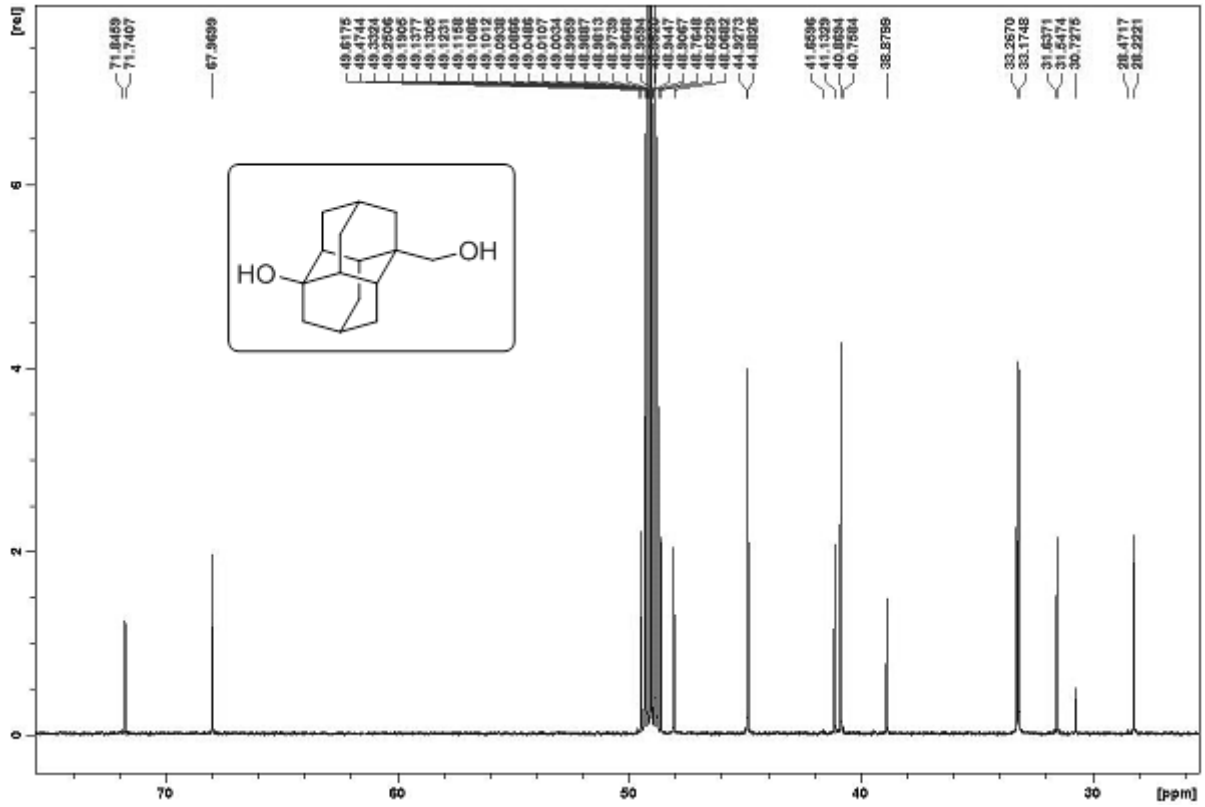


Fig. 6s. The ^{13}C-NMR spectrum of 1-hydroxy-6-hydroxymethyldiamantane **8** (CD_3OD).

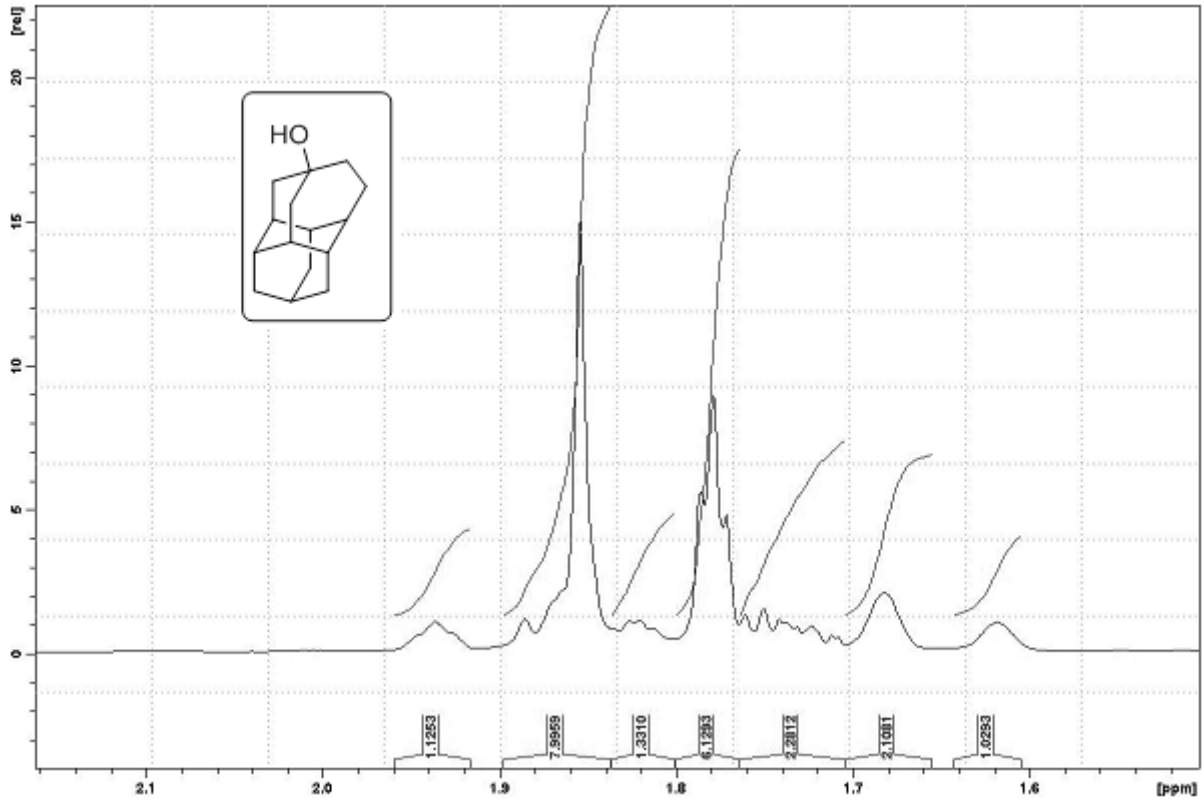


Fig. 7s. The ^{1}H-NMR spectrum of 9-homodiamantanol **9** ($CDCl_3$).

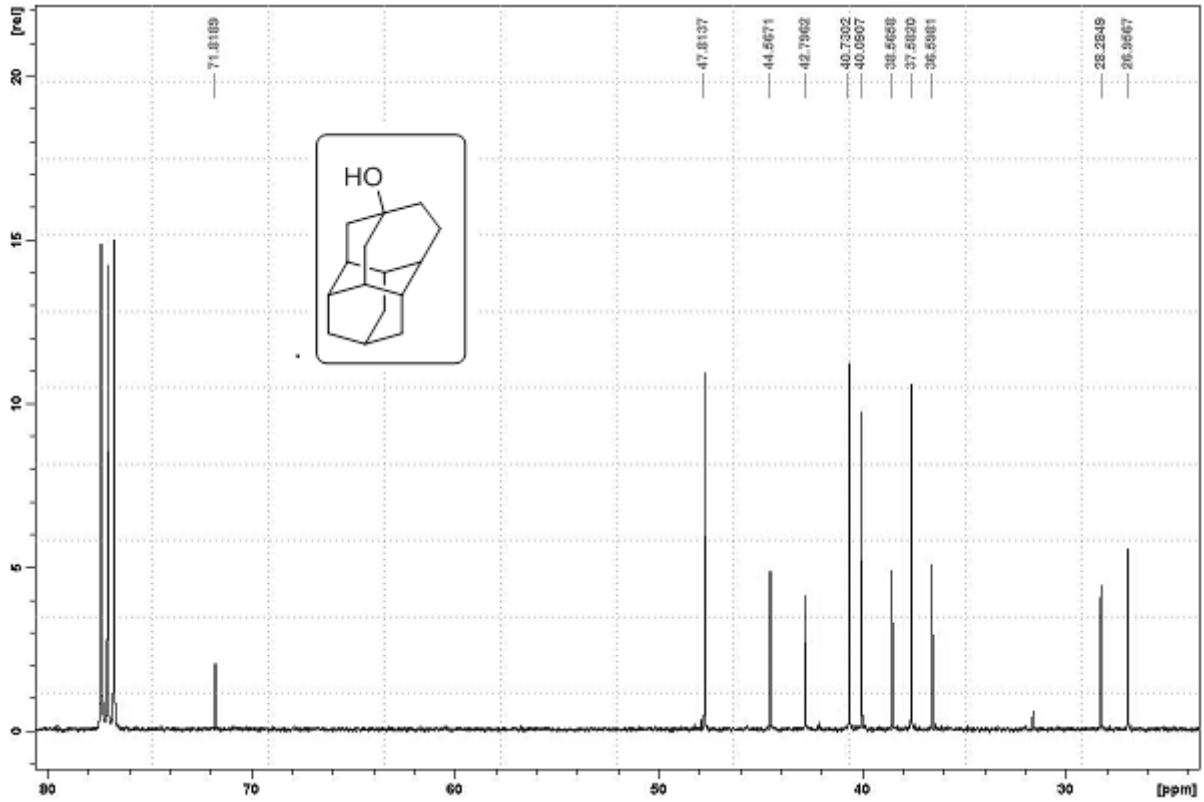


Fig. 8s. The ^{13}C-NMR spectrum of 9-homodiamantanol **9** ($CDCl_3$).

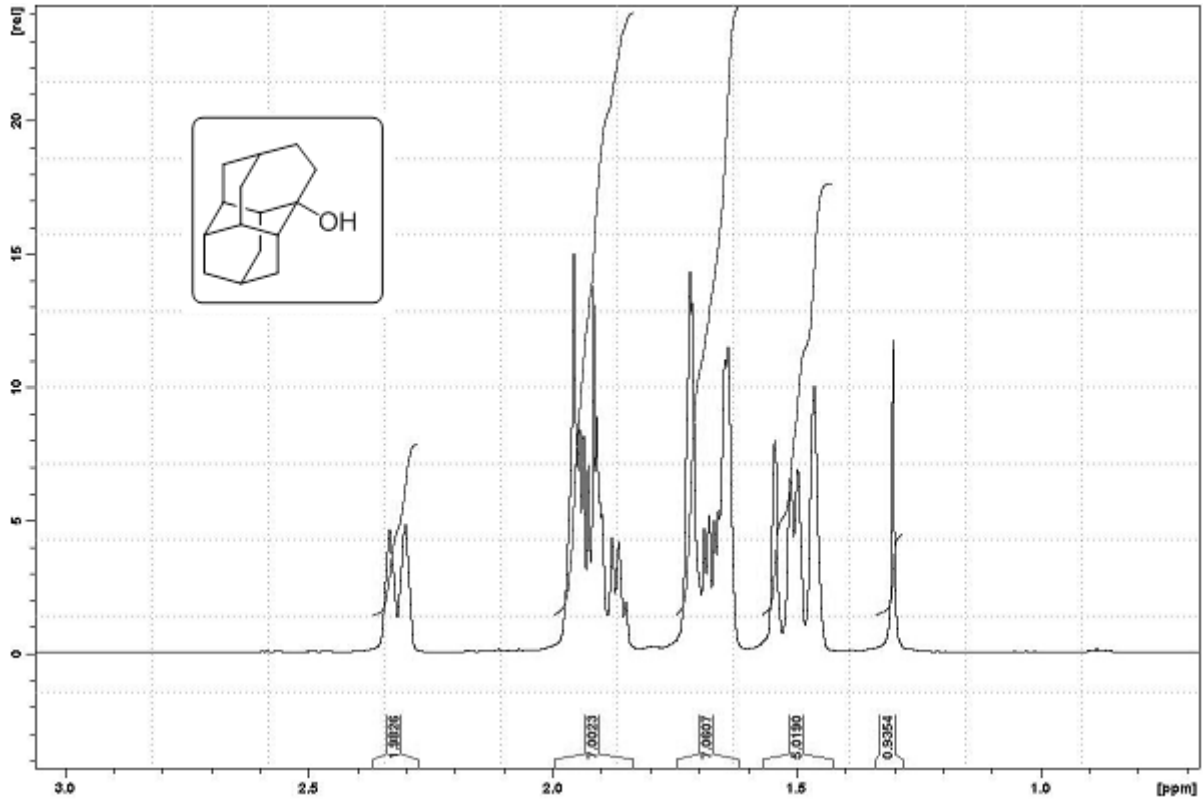


Fig. 9s. The ^{1}H-NMR spectrum of 12-homodiamantanol **10** ($CDCl_3$).

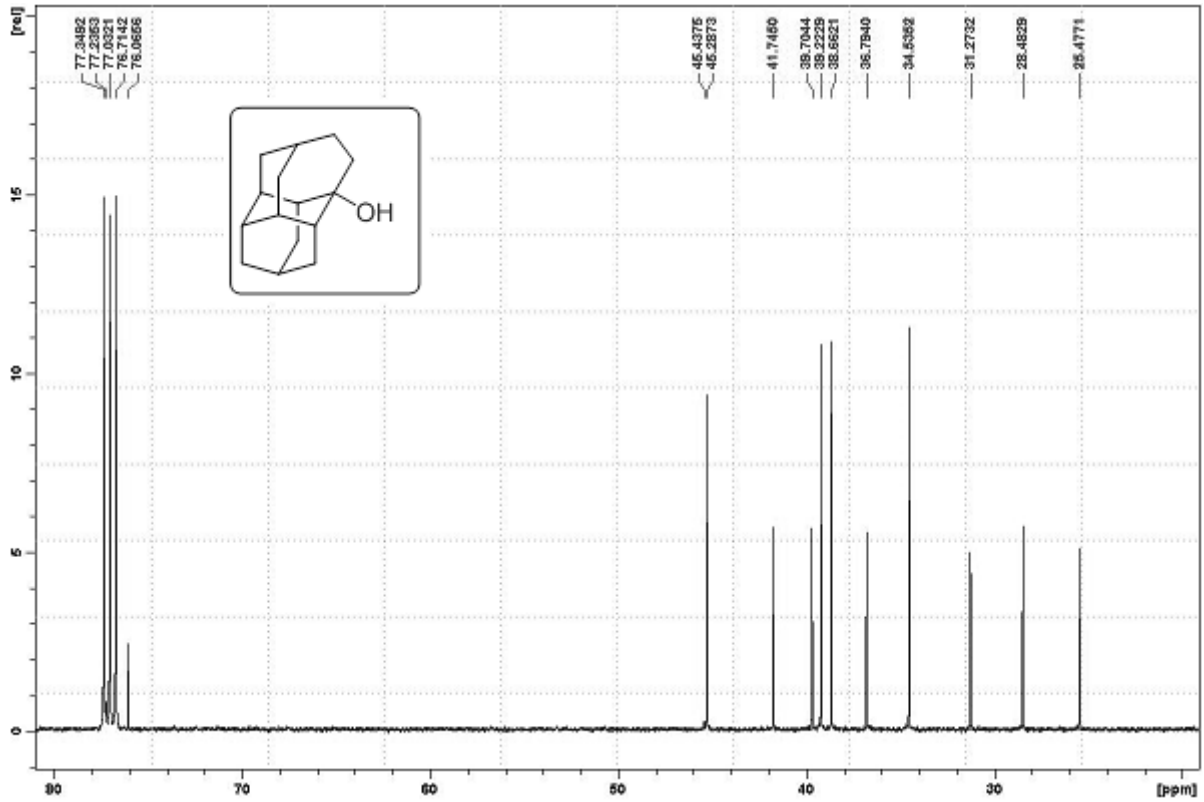


Fig. 10s. The ^{13}C-NMR spectrum 12-homodiamantanol **10** ($CDCl_3$).

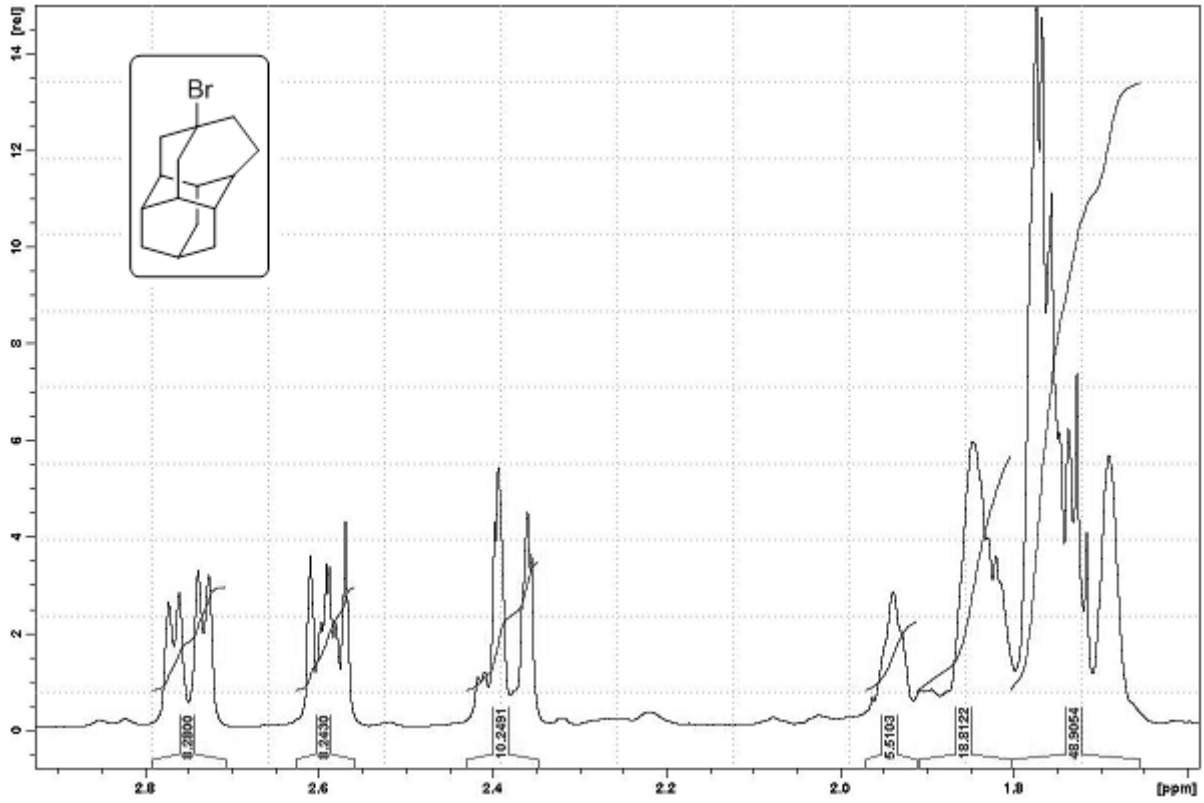


Fig. 11s. The ^{1}H-NMR spectrum of 9-bromohomodiamantane **12** ($CDCl_3$).

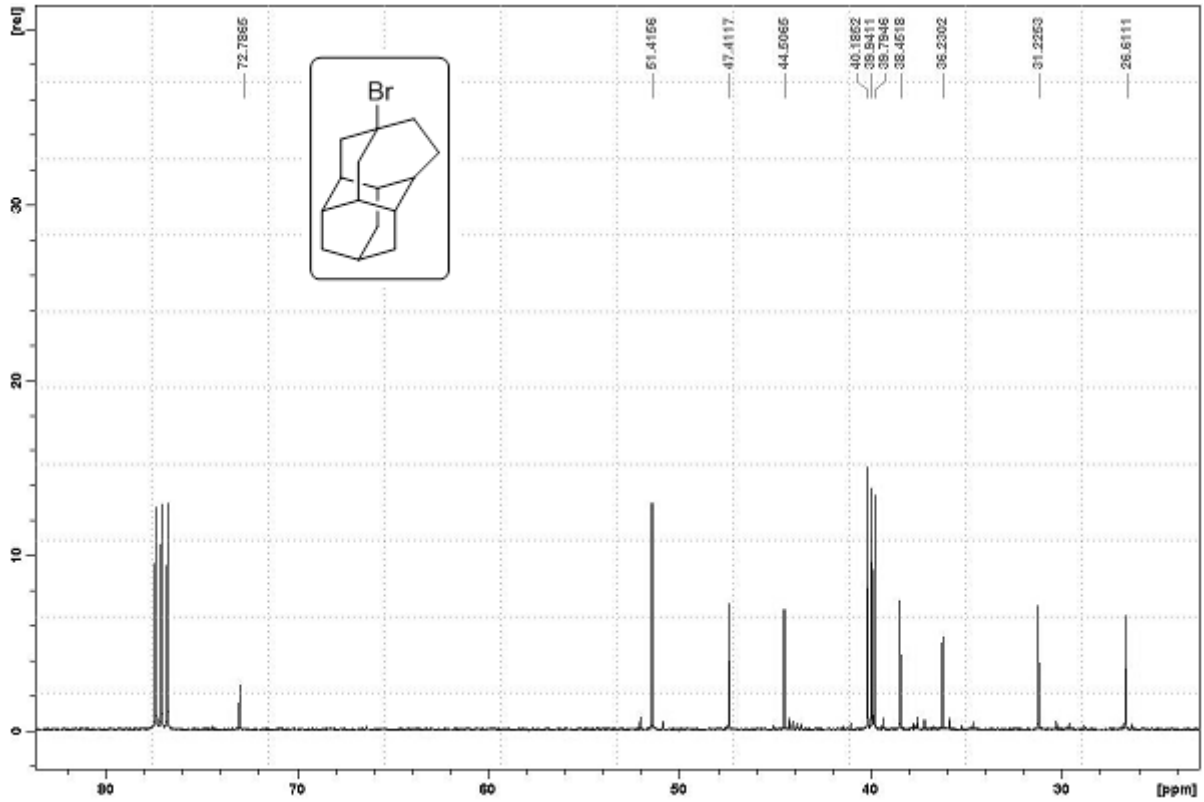


Fig. 12s. The ^{13}C-NMR spectrum of 9-bromohomodiamantane **12** ($CDCl_3$).

References-SI

(1) All computations were performed with the GAUSSIAN09 program suite utilizing analytical first and second energy derivatives. Vibrational frequencies and zero-point vibrational energies (ZPVE) were not scaled; tunneling effects were not considered.

(2) M. J. Frisch; G. W. Trucks; H. B. Schlegel; G. E. Scuseria; M. A. Robb; J. R. Cheeseman; G. Scalmani; V. Barone; B. Mennucci; G. A. Petersson; H. Nakatsuji; M. Caricato; X. Li; H. P. Hratchian; A. F. Izmaylov; J. Bloino; G. Zheng; J. L. Sonnenberg; M. Hada; M. Ehara; K. Toyota; R. Fukuda; J. Hasegawa; M. Ishida; T. Nakajima; Y. Honda; O. Kitao; H. Nakai; T. Vreven; J. A. Montgomery, J.; J. E. Peralta; F. Ogliaro; M. Bearpark; J. J. Heyd; E. Brothers; K. N. Kudin; V. N. Staroverov; R. Kobayashi; J. Normand; K. Raghavachari; A. Rendell; J. C. Burant; S. S. Iyengar; J. Tomasi; M. Cossi; N. Rega; J. M. Millam; M. Klene; J. E. Knox; J. B. Cross; V. Bakken; C. Adamo; J. Jaramillo; R. Gomperts; R. E. Stratmann; O. Yazyev; A. J. Austin; R. Cammi; C. Pomelli; J. W. Ochterski; R. L. Martin; K. Morokuma; V. G. Zakrzewski; G. A. Voth; P. Salvador; J. J. Dannenberg; S. Dapprich; A. D. Daniels; O. Farkas; J. B. Foresman; J. V. Ortiz; J. Cioslowski; D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.