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Displacement of methoxy groups by thiol residues on the fullerene cage

Olga A. Kraevaya, Alexander V. Chernyak, Alexander F. Shestakov and Pavel A. Troshin

Synthetic procedure

The solution of fullerene derivative $C_{60}(OMe)_5Br$ (20 mg, 0.021 mmol) in toluene (20 ml) was placed in three-necked round-bottom flask filled with argon. After that methyl 3-mercapto-propanoate (50 mg, 0.42 mmol) and NPr^i_2Et (54 mg, 0.42 mmol) was added to the solution. The reaction mixture was stirred for 10 minutes at room temperature, and then diluted with toluene and poured out on the top of the column filled with silica gel. Mixtures of toluene with acetonitrile were used as eluents (acetonitrile content varied from 1 to 5% v/v). The fractions obtained after column chromatography were evaporated on a rotary evaporator; the residues after evaporation were washed with hexane and dried in air. Compound **2** was obtained with a yield of 79%.

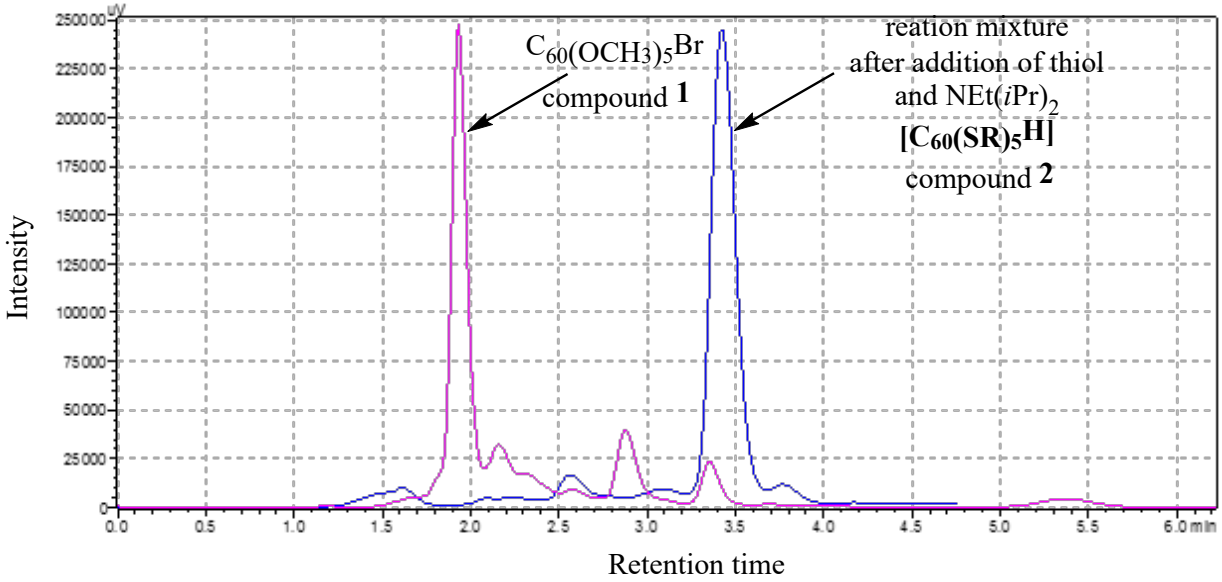

Figure S1. HPLC profile of the reaction mixture before and after the addition of *N*,*N*-diisopropylethylamine. Elution conditions: Orbit C18 column, flow rate 1 ml min^{-1}, 30% toluene/70% acetonitrile, 30°C.

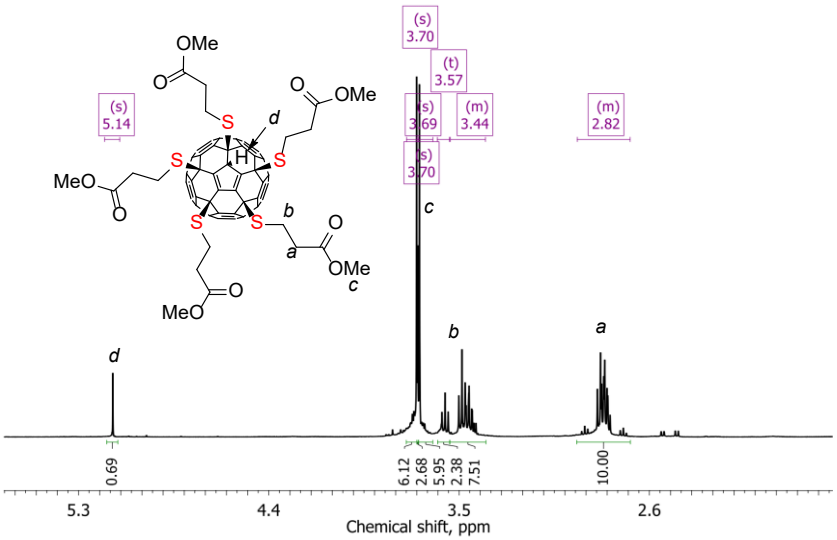

Figure S2. ^{1}H NMR spectrum of compound **2**.

Cartesian coordinates of the optimized structures

$C_{60}(SR)_5H$, R=$CH_2CH_2COOCH_3$, the main isomer

6	-1.69797346	1.08906784	4.04965448
6	-0.98053534	-0.10563824	4.41782526
6	0.23165861	-0.39520579	3.76845384
6	0.80636274	0.51152215	2.80863878
6	0.12221003	1.66561835	2.45679497
6	-1.16018302	1.93014392	3.05714522
6	-3.11941166	0.78287622	4.06101491
6	-3.27659738	-0.61084551	4.43951823
6	-1.95148791	-1.16198637	4.65805147
6	-1.67024783	-2.47920120	4.26957014
6	0.51135428	-1.75809360	3.35337144
6	1.66335604	-0.27926947	1.81484559
6	1.20589779	0.06859780	0.42832884
6	0.60214808	1.23621993	0.06512225
6	0.16631068	2.28583357	1.04473859
6	-1.31913994	2.57929726	0.80529248
6	-2.03894408	2.49655752	2.04860461
6	-3.41771326	2.22588542	2.08050839
6	-3.96607077	1.34365489	3.09572726
6	-4.27668139	-1.39687235	3.84018915
6	-5.15334407	-0.81468147	2.83944634
6	-5.00042296	0.53349875	2.47415502
6	-5.08778532	0.91952398	1.07659388
6	-4.10526945	1.96284491	0.84162506
6	-3.37501651	1.98327311	-0.35708110
6	-1.97595237	2.31747275	-0.38266315
6	-1.33212288	1.72250977	-1.63358424
6	0.06927863	1.09479161	-1.35809426
6	1.24580675	-1.72153857	2.12158452
6	-0.93456572	-2.59285425	-1.86186831

6	-0.10315947	-3.14584286	-0.89988166
6	-0.65782198	-3.98095134	0.13334408
6	-2.02404267	-4.30983803	0.15501306
6	-2.89343591	-3.73353622	-0.83975086
6	-3.06682450	-1.65163699	-2.15444385
6	-2.11021685	-0.61180189	-2.42579539
6	-0.69642744	-1.20870527	-2.49728161
6	0.19299085	-0.40844014	-1.59769812
6	0.95351403	-0.94552932	-0.60158735
6	1.13162894	-2.41885544	-0.35377417
6	0.03111947	-3.70265841	1.38310721
6	-0.65693754	-3.78217355	2.60579992
6	-2.07306182	-4.10389363	2.62167309
6	-2.74404617	-4.35861005	1.41743475
6	-4.06963833	-3.80873218	1.19705876
6	-4.16124776	-3.42016211	-0.19989109
6	-4.85889339	-2.25854307	-0.55620325
6	-4.30818038	-1.36635492	-1.56136182
6	-2.37959026	0.68529040	-2.03467262
6	-3.62353268	0.97859138	-1.37363595
6	-4.59426927	-0.01173354	-1.16019509
6	-5.32767761	-0.05118251	0.09305152
6	-5.49023374	-1.44434171	0.46912981
6	-5.40278680	-1.81997703	1.82047583
6	-4.67999650	-3.02352327	2.19081991
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6	1.01084681	-2.67936783	1.14937687
6	-0.40928108	-2.78617134	3.61783945
6	-2.34841007	-2.86043421	-1.80009929
1	0.79965577	1.58696691	-2.03400521
1	1.03873878	-3.25207874	-3.86236738
1	2.06947007	-1.79643595	-3.77053356
6	1.72722555	-2.50375321	-5.78910448
1	2.65232059	-3.10523503	-5.75839368
1	1.96058228	-1.55060570	-6.28084472
6	1.27185988	-2.29180951	-4.33908549
16	-0.23860153	-1.23147150	-4.32612473
8	0.27615952	-4.37514815	-6.08477649
6	0.72931825	-3.23123140	-6.67716383
8	0.38709012	-2.87451519	-7.78728337
6	-0.69640454	-5.11056937	-6.86309115
1	-0.96655712	-5.97782839	-6.25116699
1	-0.26162477	-5.42944430	-7.81953844
1	-1.57691318	-4.48539002	-7.05996390
1	2.02162716	-5.20471932	-0.63926841
1	3.25281109	-4.65949632	0.54772718
6	4.07534826	-5.33671933	-1.34985745
1	4.30347652	-6.31158191	-0.89057502
1	4.99195640	-4.73228582	-1.35104435
6	2.97016034	-4.66486232	-0.51412286
16	2.77730529	-2.92387661	-1.10063601

8	2.67768313	-6.49866654	-2.86919367
6	3.66920013	-5.56955277	-2.79872616
8	4.15350151	-5.02046255	-3.77047354
6	2.20801342	-6.79800966	-4.20685910
1	1.48514817	-7.61126210	-4.08395048
1	3.04546714	-7.11411149	-4.84233957
1	1.72668341	-5.91603861	-4.64947721
1	-3.17283610	4.00597674	-2.38032628
1	-3.31927291	2.90693864	-3.79459130
6	-2.55404096	4.88042566	-4.27165811
1	-3.56476592	5.22158215	-4.55351920
1	-2.03181087	4.59818038	-5.19511628
6	-2.70454259	3.68453917	-3.31985697
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8	-2.28189403	6.38399303	-2.44344929
6	-1.81675237	6.07787465	-3.68655977
8	-0.95047607	6.71115383	-4.25679146
6	-1.62572709	7.50894215	-1.81503029
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1	0.17097437	4.64123056	2.86924184
1	-0.49699740	5.39834444	1.38537619
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1	0.83115009	7.06825320	2.57987612
1	1.72756104	6.64173682	1.09855122
6	0.42267955	5.07092626	1.89035055
16	1.27084149	3.79856077	0.85412862
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1	4.08115890	6.03132846	5.08288230
1	3.86206955	4.30324653	4.66099238
1	3.22650285	2.12056502	2.74484425
1	3.63616143	1.97909802	1.01091720
6	5.34810814	1.84478448	2.33110030
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1	5.99945370	1.32753646	1.61493433
6	3.86473167	1.60376399	2.01733535
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6	5.78502629	1.41657106	3.72404664
8	6.75411924	0.72791233	3.97552785
6	5.29914565	1.54733409	6.03585041
1	4.54429135	2.02084911	6.67263682
1	6.30525430	1.90149828	6.29612615
1	5.26466410	0.45517352	6.14016684

$C_{60}(SR)_5Br$, R=$CH_2CH_2COOCH_3$

6	-0.59373215	1.93824783	4.01739246
6	-1.97339401	1.85510783	3.61259089
6	-2.40884299	0.71120830	2.92112483
6	-1.52719738	-0.39853787	2.68026159
6	-0.19967861	-0.32584430	3.07125915
6	0.27456061	0.87218268	3.71046570
6	-0.15764679	3.31450704	3.84477837
6	-1.27938566	4.08236771	3.33113910
6	-2.40449483	3.17663041	3.18564501
6	-3.27577846	3.31360232	2.09612504
6	-3.30071971	0.85834382	1.78173960
6	-1.97270887	-1.13176495	1.41370192
6	-0.78700412	-1.21053671	0.49613199
6	0.51389313	-1.23844137	0.88952081
6	0.95665634	-0.99812374	2.30266557
6	1.98439874	0.14123776	2.27391412
6	1.61366946	1.15701492	3.22637154
6	2.04207319	2.48803332	3.08889998
6	1.13941242	3.58575348	3.39089458
6	-1.06555406	5.09700716	2.38148588
6	0.27969736	5.37832407	1.91240793
6	1.36344260	4.63465787	2.40965424
6	2.40417144	4.18053430	1.50454568
6	2.81308852	2.85331310	1.92841331
6	3.10333250	1.86895713	0.97230687
6	2.71175595	0.49636328	1.15254528
6	2.66455011	-0.19644292	-0.21235065
6	1.40168877	-1.11468243	-0.35119489
6	-2.97855128	-0.14876099	0.81023588
6	-0.51817438	1.02289587	-2.93080881
6	-1.80081060	0.75994700	-2.47563315
6	-2.67677126	1.84575169	-2.13106697
6	-2.28859107	3.18531346	-2.30988020
6	-0.95505198	3.46509216	-2.77770760
6	1.30329234	2.47105072	-2.61970577
6	1.74468537	1.15482640	-2.23390472
6	0.69465767	0.11390963	-2.64106226
6	0.39293855	-0.71506869	-1.42769587
6	-0.86080591	-0.88442057	-0.93172964
6	-2.12848057	-0.45443320	-1.60576946
6	-3.44531663	1.47172605	-0.95404907
6	-3.81835171	2.44814893	-0.01365019
6	-3.39738025	3.82719722	-0.19181248
6	-2.64301892	4.18711768	-1.31712788
6	-1.51831908	5.09392249	-1.17444272
6	-0.47197921	4.64413604	-2.07675165
6	0.87017284	4.72642153	-1.68422782
6	1.77344013	3.62534237	-1.97116190
6	2.58843006	1.01415724	-1.14732010
6	3.02807554	2.18639216	-0.43961077
6	2.66611708	3.47800636	-0.85043853

6	2.33144835	4.48744830	0.13813279
6	1.21519677	5.26042754	-0.37685721
6	0.20447251	5.69667672	0.49646459
6	-1.18705332	5.61157350	0.09027336
6	-1.97118640	5.24090842	1.25515104
6	-3.05960057	4.36298794	1.11546342
6	-3.05009866	0.15372062	-0.54269630
6	-3.74465285	2.13307420	1.39071295
6	-0.08414776	2.38926849	-3.04119434
1	2.47609690	0.90783859	-4.88174163
1	0.88953588	0.77625451	-5.71424721
6	2.41953628	-0.55874697	-6.48333154
1	2.67417810	0.15990571	-7.28124605
1	1.73831531	-1.30305551	-6.91627087
6	1.75573515	0.21488619	-5.33570037
16	1.19610468	-1.00472511	-4.06631837
8	4.52173615	-0.50321309	-5.36177064
6	3.70032538	-1.29326410	-6.10540735
8	3.97940192	-2.42488653	-6.44915508
6	5.74855606	-1.14112948	-4.93560108
1	6.29550285	-0.37431793	-4.37674179
1	6.32899071	-1.47770688	-5.80443099
1	5.52283150	-2.00220137	-4.29317945
1	-4.56591745	-0.46158036	-3.34603791
1	-5.08934700	-1.36144105	-1.87359285
6	-5.22242291	-2.50527902	-3.70214522
1	-6.29438753	-2.25658843	-3.78516475
1	-5.15658951	-3.49627146	-3.23468389
6	-4.55711380	-1.43157953	-2.83153180
16	-2.81134823	-1.94753986	-2.51519283
8	-4.49522536	-1.41100793	-5.69193999
6	-4.67736814	-2.63298916	-5.11772729
8	-4.46517910	-3.68370273	-5.69108561
6	-3.97330762	-1.45010002	-7.03992592
1	-3.89032963	-0.40356512	-7.35146521
1	-4.65629990	-1.99959185	-7.70108434
1	-2.99024186	-1.93880006	-7.05215546
1	5.48423655	0.54410921	0.71266950
1	5.45707815	0.89163968	-1.04972731
6	6.91899696	-0.59489511	-0.45575677
1	7.70659610	0.17692681	-0.41648776
1	6.99874244	-1.09845332	-1.42823617
6	5.56080327	0.10422268	-0.28986208
16	4.25335853	-1.18053986	-0.52825931
8	6.98241006	-1.16233598	1.85791851
6	7.25079897	-1.63257605	0.60944728
8	7.73193940	-2.72645776	0.38791379
6	7.26383726	-2.09534688	2.92737169
1	7.00701584	-1.56559687	3.85064630
1	8.32488624	-2.37695348	2.92235239
1	6.65018279	-2.99847598	2.81264949
1	1.42277298	-1.42092402	5.20366535

1	3.09774957	-1.40260277	4.55675483
6	2.54296165	-3.24884480	5.55490683
1	3.01915033	-2.90220941	6.48833554
1	3.26019370	-3.90476924	5.04387527
6	2.19860243	-2.01727133	4.70611872
16	1.57626064	-2.60030965	3.06772448
8	0.31129410	-3.35071459	6.38498627
6	1.35225146	-4.11300247	5.95098839
8	1.33518462	-5.32789451	5.92636839
6	-0.86358895	-4.09912271	6.77324658
1	-1.59423804	-3.34952599	7.09463841
1	-0.62665798	-4.78786396	7.59476723
1	-1.24457891	-4.67508220	5.91954795
1	-4.07732539	-1.66103833	3.16883396
1	-3.77967632	-3.32447420	3.69657948
6	-5.36318088	-3.16575456	2.22316583
1	-6.07636512	-3.30714096	3.05344512
1	-5.24686791	-4.12572777	1.70523959
6	-4.02243759	-2.70185585	2.82404033
16	-2.59152214	-2.89156038	1.66204822
8	-6.32578417	-1.02708902	1.87157019
6	-6.00157562	-2.19310882	1.24632071
8	-6.23272533	-2.41119540	0.07123882
6	-6.99473415	-0.05123896	1.03857948
1	-7.19198276	0.80598392	1.69002833
1	-7.93445456	-0.46583017	0.65019551
1	-6.35737892	0.23854055	0.19293901
35	1.88116354	-3.04301827	-0.79647738

$C_{60}(OMe)_5Br$

6	-1.41436892	3.37834870	1.82612104
6	-0.38691360	3.00565595	2.76763510
6	0.89576200	2.70337797	2.28294506
6	1.21295441	2.83585853	0.88777698
6	0.23974401	3.20263241	-0.02090824
6	-1.10003968	3.43420055	0.45514864
6	-2.66395635	2.78146542	2.26922537
6	-2.40268221	2.03955085	3.49080826
6	-0.99080554	2.17644776	3.79725440
6	-0.28235602	1.09048338	4.33073876
6	1.62487708	1.56895543	2.82652786
6	2.36149724	1.88089796	0.52526021
6	1.88767203	1.03219546	-0.63635204
6	1.00106285	1.42802715	-1.59010041
6	0.19082726	2.70448273	-1.50335575
6	-1.29205727	2.30431216	-1.59369058
6	-2.03749822	2.89387570	-0.51070379
6	-3.25804555	2.34802962	-0.08525755
6	-3.57483888	2.27969516	1.33033230
6	-3.06165833	0.82122876	3.73321992
6	-4.00420751	0.30157738	2.75873483
6	-4.25482741	1.01920447	1.57676143

6	-4.35957450	0.31512136	0.31114863
6	-3.73921427	1.13868656	-0.70927935
6	-2.97016397	0.54432542	-1.71982954
6	-1.74942310	1.14623612	-2.18463012
6	-0.88791129	0.06870201	-2.87618175
6	0.63370134	0.21717578	-2.45146412
6	2.39587039	0.96568165	1.77356763
6	0.87608579	-2.93674262	-0.20854137
6	1.77027778	-2.43797765	0.72260703
6	1.43499293	-2.45458801	2.12219683
6	0.24236946	-3.03949438	2.57967808
6	-0.69446710	-3.55676554	1.61281897
6	-1.41875259	-3.07214488	-0.69856701
6	-0.81685007	-2.28551187	-1.74729094
6	0.72735255	-2.35991028	-1.65609672
6	1.22372111	-0.93840450	-1.64406654
6	2.02036672	-0.43048160	-0.66864841
6	2.68244217	-1.22131672	0.43484657
6	1.91135186	-1.22716854	2.73950255
6	1.20154815	-0.64543800	3.80203952
6	-0.04020888	-1.24378456	4.25931440
6	-0.51284271	-2.41746123	3.65535218
6	-1.92484129	-2.55573801	3.34994454
6	-2.03672211	-3.25998604	2.08415334
6	-3.03572072	-2.89903021	1.17050965
6	-2.72124153	-2.81537900	-0.24513015
6	-1.50430860	-1.20533727	-2.26080579
6	-2.81935298	-0.89642045	-1.76589018
6	-3.44449092	-1.69525946	-0.79758392
6	-4.21411347	-1.08010275	0.26761072
6	-3.95911361	-1.82318597	1.48882131
6	-3.85371813	-1.14278767	2.71402457
6	-2.81844248	-1.51577693	3.66164708
6	-2.32887105	-0.30185529	4.29044634
6	-0.96080365	-0.16843899	4.58362381
6	2.53145028	-0.41325865	1.73273895
6	1.05339651	0.78911904	3.84542584
6	-0.38469509	-3.46197827	0.24306699
8	1.38547063	-3.08686492	-2.69454524
6	0.92258743	-4.42659579	-2.88790657
1	1.08362109	-5.04891075	-1.99056392
1	1.51854807	-4.83112134	-3.71479635
1	-0.14433166	-4.45739585	-3.16663173
8	4.07385392	-1.49011113	0.21938390
6	4.35942685	-2.37457161	-0.87287245
1	3.94759845	-3.38187285	-0.69366012
1	5.45337355	-2.43550424	-0.92315481
1	3.96995037	-1.99116931	-1.82958819
8	-1.11730140	-0.01302892	-4.27993769
6	-1.30753034	1.23286514	-4.97160446
1	-2.28764550	1.67628295	-4.73281487
1	-1.27386017	0.98024569	-6.03839421

1	-0.51192428	1.96096982	-4.75162995
8	0.44780044	3.69974401	-2.49654665
6	1.80584485	4.16024930	-2.53485728
1	2.12347207	4.57908239	-1.56561872
1	1.82921402	4.94912947	-3.29629973
1	2.49635896	3.35131375	-2.82523029
8	3.54280495	2.65106171	0.28535570
6	4.68588396	1.89354748	-0.13372347
1	4.94756773	1.10493489	0.59029760
1	5.50996834	2.61432090	-0.19946755
1	4.52699716	1.43502791	-1.12458149
35	1.81302618	0.33454523	-4.09981289

RSH…N(^{i}Pr)$_2$Et adduct

7	-1.51387618	-0.63553674	-0.13354872
6	-2.32742319	-1.87058210	-0.27861058
1	-3.00409334	-1.97463665	0.58813995
1	-2.99304515	-1.77106526	-1.14959364
6	-1.60565500	-0.07651598	1.24469653
1	-2.67329927	0.11211464	1.49850058
6	-1.77346382	0.35513593	-1.21655324
1	-1.06652321	1.17842008	-1.03653904
6	-1.06097782	-1.08189736	2.27465890
1	-1.17898132	-0.66812379	3.28670896
1	-1.59330881	-2.04179708	2.25197297
1	0.00832481	-1.27284463	2.10017716
6	-1.49535683	-3.14738133	-0.44685607
1	-0.83482584	-3.31737481	0.41442627
1	-2.15891238	-4.02060514	-0.54812074
1	-0.86354527	-3.09018049	-1.34423829
6	-1.41482141	-0.22243203	-2.59499262
1	-0.40341180	-0.65199513	-2.59345330
1	-2.11756927	-1.00591990	-2.91587177
1	-1.45252523	0.57626491	-3.35017915
6	-3.19609106	0.95437605	-1.22413633
1	-3.27591531	1.72619514	-2.00421371
1	-3.95850799	0.18980073	-1.43712144
1	-3.44868575	1.42583091	-0.26316766
6	-0.84377599	1.24879484	1.40362548
1	-1.28620321	2.07589932	0.83255915
1	-0.86042822	1.54161900	2.46320522
1	0.20909530	1.13453423	1.10329560
1	1.72921032	1.16478956	-0.93640577
1	2.22743745	0.29991806	-2.41857949
6	3.85596302	0.74787317	-1.06409447
1	4.11112284	1.65701640	-1.63696637
1	4.53445742	-0.04854783	-1.39777356
6	2.39168302	0.38723285	-1.33550925
16	1.97184693	-1.22645784	-0.52191077
8	3.25446600	1.84106365	0.96692648
6	4.18700209	1.02715241	0.39474382

8	5.17264357	0.62242474	0.97968927
6	3.49875081	2.15360709	2.35688010
1	2.67244824	2.80562202	2.65952922
1	4.46216902	2.66775581	2.47207133
1	3.50840996	1.23462404	2.95757060
1	0.60619189	-1.00417147	-0.40094164

$Br^-[HN(^iPr)_2Et]^+$ adduct

7	0.08477764	-0.07281416	-0.02416648
6	-0.25248114	-1.54873938	-0.09656738
1	-0.62899456	-1.85252365	0.88975217
1	-1.08546406	-1.66623196	-0.80029400
6	0.08350992	0.43930905	1.41988225
1	-0.91611707	0.20382759	1.82131026
6	-0.73885743	0.77399266	-0.99249576
1	-0.29618748	1.77452759	-0.90033100
6	1.15288041	-0.30828138	2.22850041
1	1.13016568	0.06072090	3.26287494
1	0.98456496	-1.39275224	2.26512368
1	2.14951154	-0.11531707	1.80479684
6	0.92381408	-2.42136472	-0.53070693
1	1.77439681	-2.33777427	0.15734089
1	0.59177538	-3.46967666	-0.55778811
1	1.28684367	-2.13918110	-1.52713074
6	-0.49809953	0.31699416	-2.43487694
1	0.58013498	0.27563307	-2.64693262
1	-0.95880190	-0.65687882	-2.65752691
1	-0.95046078	1.05601650	-3.11096438
35	2.94131395	0.67850729	-0.99826850
1	1.13251746	0.09046425	-0.37525894
6	-2.22257349	0.82621210	-0.62382070
1	-2.73426146	1.49485832	-1.33003164
1	-2.70457858	-0.15979068	-0.70076930
1	-2.39718786	1.21960417	0.38719656
6	0.33707620	1.94964295	1.48775756
1	-0.48973407	2.54657276	1.08112914
1	0.45283834	2.22995113	2.54377830
1	1.26767840	2.20449161	0.95848732