

Supporting Information for Ms jo-2012-01983s.R1

Stereoselectivity of additions to N-methyl acetonitrilium fluorosulfonate

Reinhart Keese*, François Berdat, Piero Macchi

Department of Chemistry and Biochemistry, University of Bern,
Freiestrasse 3, 3012 Bern, Switzerland; e-mail: reinhart.keese@ioc.unibe.ch

- ^1H of **7**, **(Z)-8**, **(Z)-9**, **(E)-10**, **(E)-11**, **(E)-8**, **(E)-9**, **13**, **(Z)-14**, **(E)-15**, **(E)-14**,
- **(Z)-8** from N-CH₃-acetamide
- ^1H spectra of **18 a-e**
- Computational results: Cartesian coordinates, absolute energies of **16**, **Z/E-8** and **Z/E-10**, all with *sp* and *ap* conformations

^1H -spectrum of	7	(Z)-8	(E)-8	(Z)-9	(E)-9	(E)-10	(E)-11	13	(Z)-14
page	2	3	4	5	6	7	8	9	10

^1H -spectrum of	(E)-15	(E)-14	(Z)-8
page	11	12	13

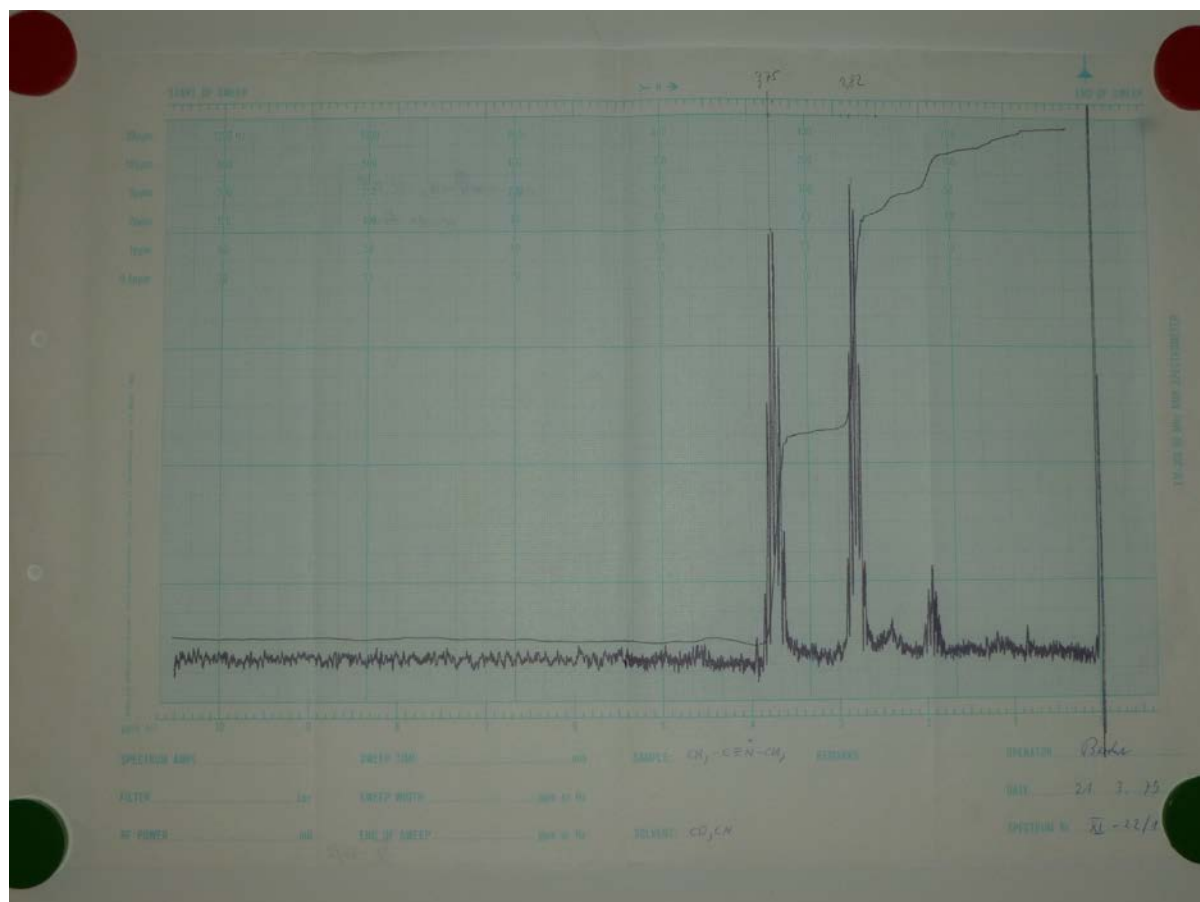
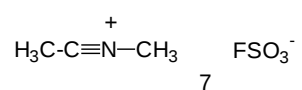
^1H -spectrum of	18a	18b	18c	18d	18e
page	14	15	16	17	18

Comp. results for	(E)-16 ap	(E)-(16) sp	(Z)-16 ap	(Z)-16 sp
page	19	19	20	20

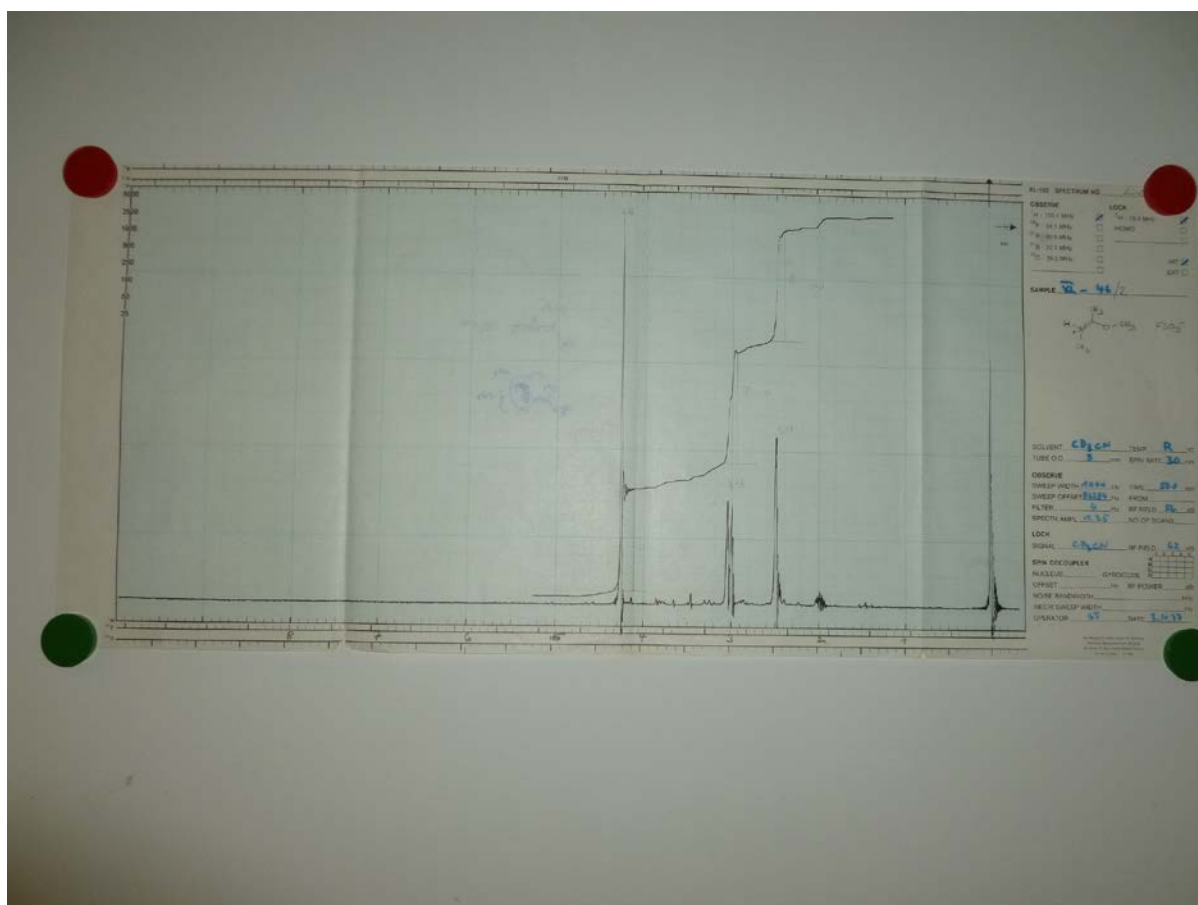
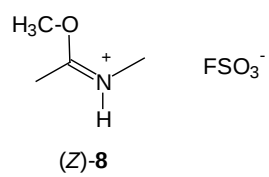
Comp. results for	(Z)-10 ap	(Z)-10 sp	(E)-10 ap	(E)-10 sp
page	21	21	22	22

Comp. results for	(Z)-8 ap	(E)-8 ap	(Z)-8 sp	(E)-8 sp
page	23	23	24	24

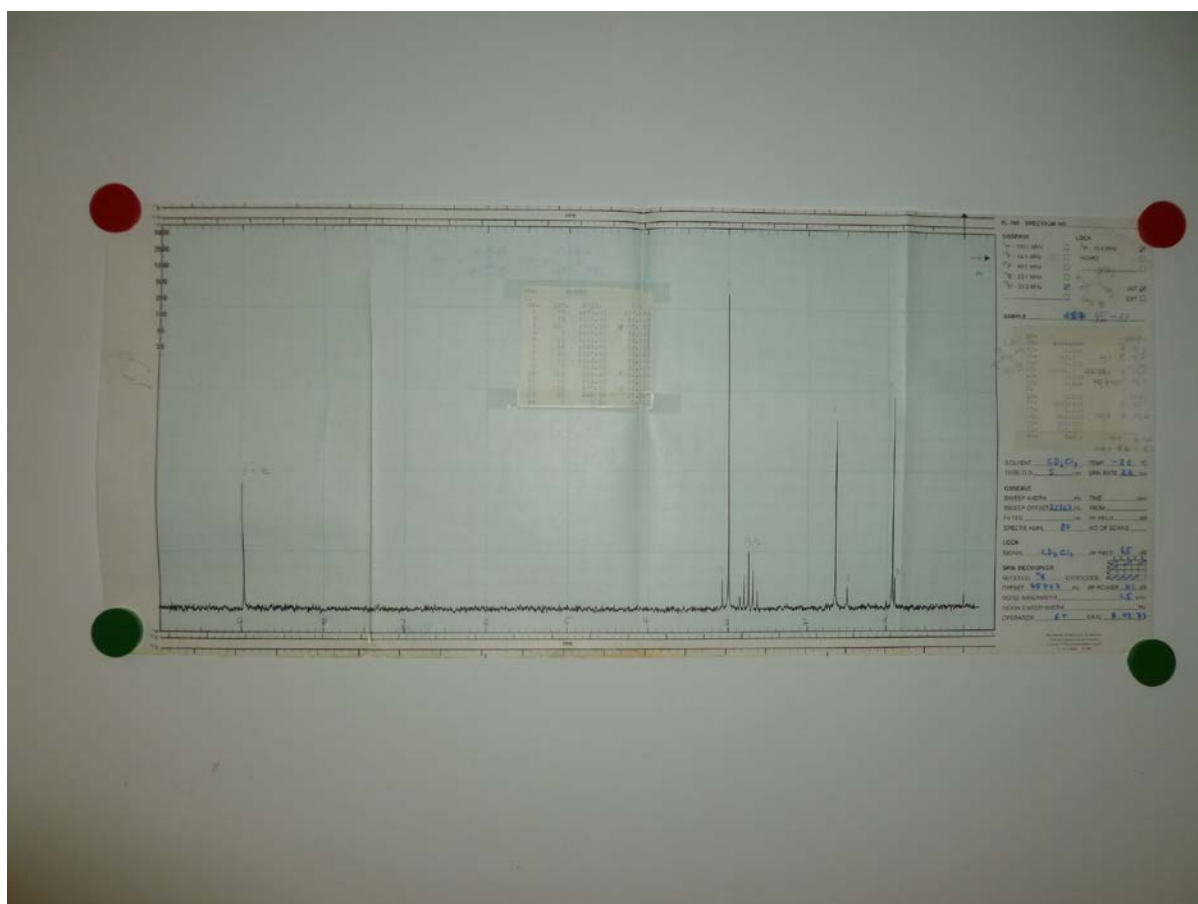
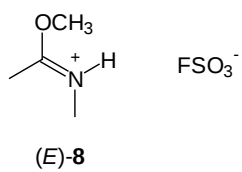
Nitrilium salt 7



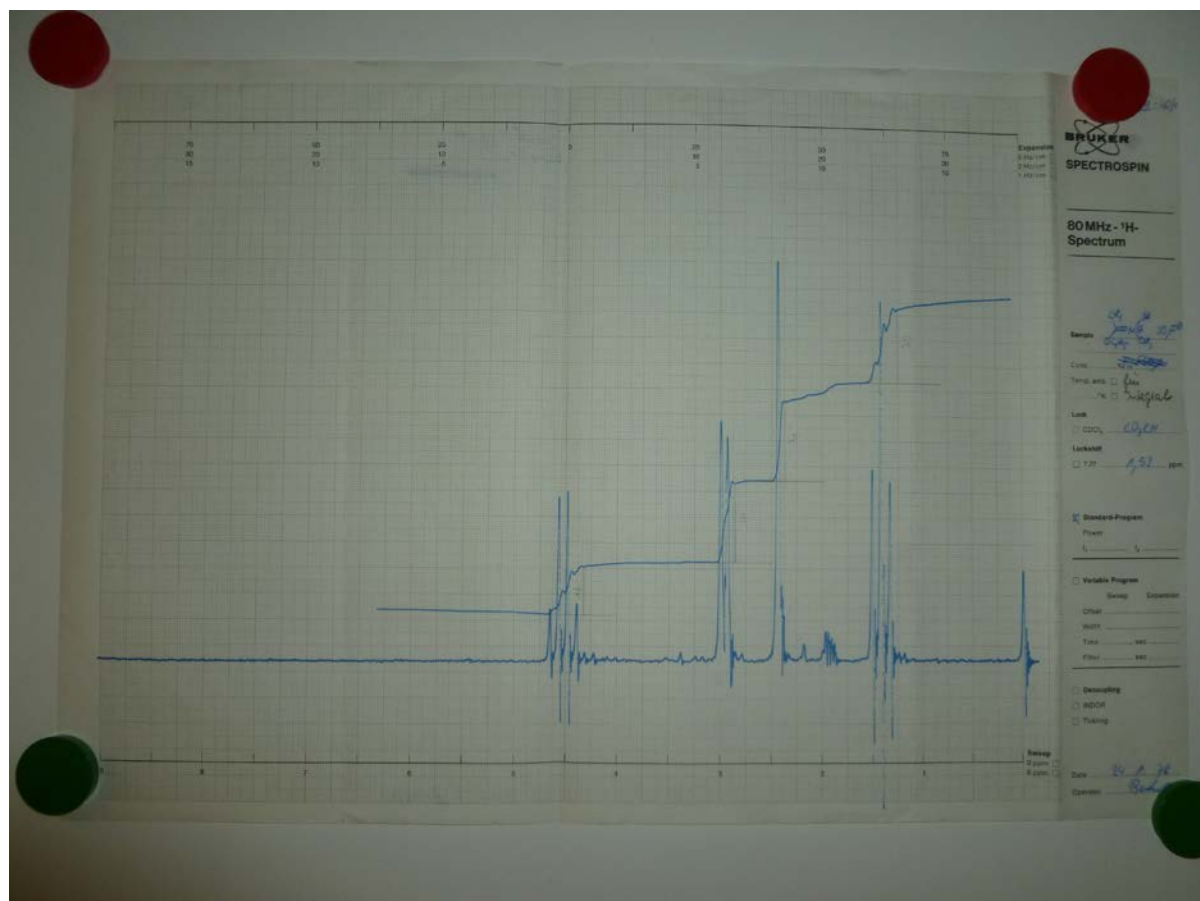
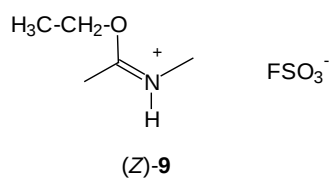
(Z)-N-methyl-methoxyacetiminium salt **(Z)-8**



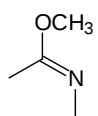
(E)-8 (the minor signals are for (Z)-8)



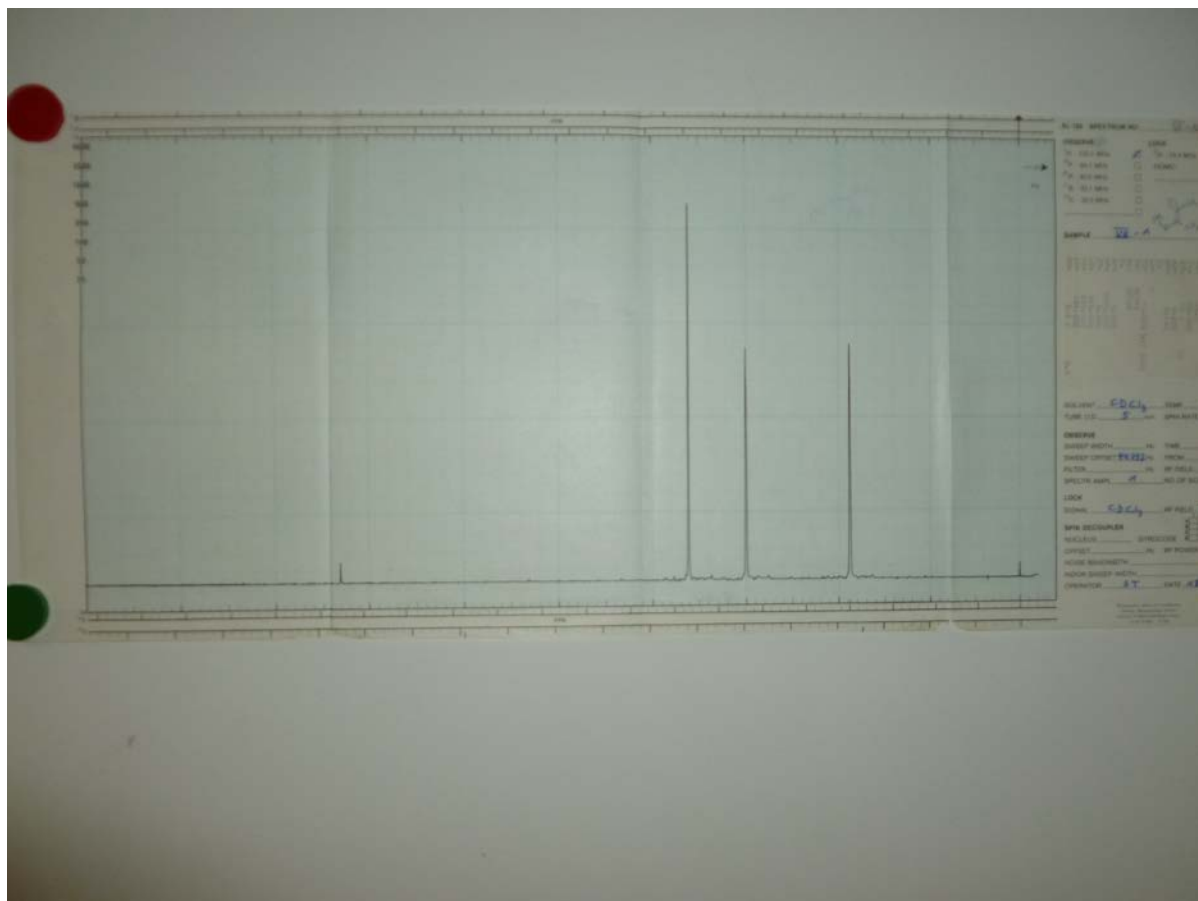
(Z)-9



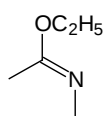
(E)-10



(E)-10



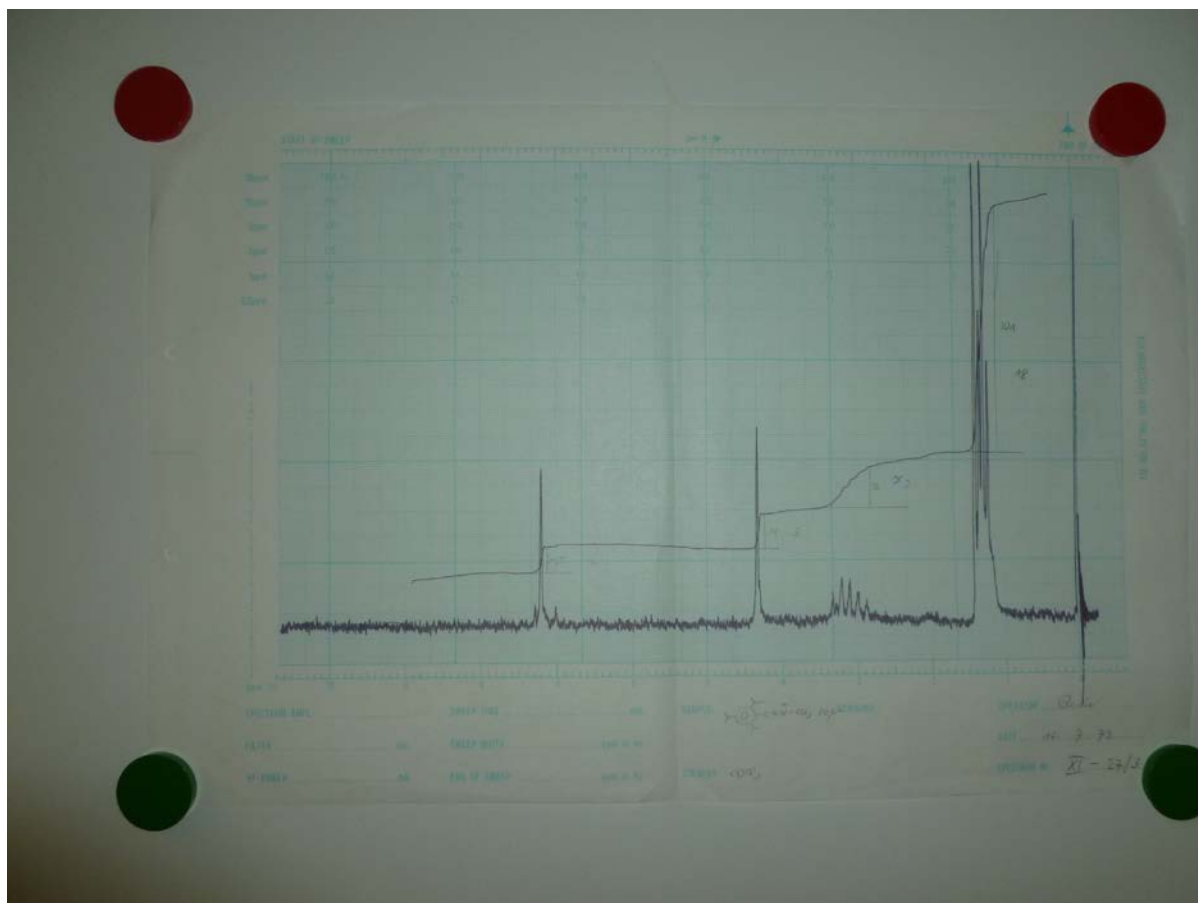
(E)-11



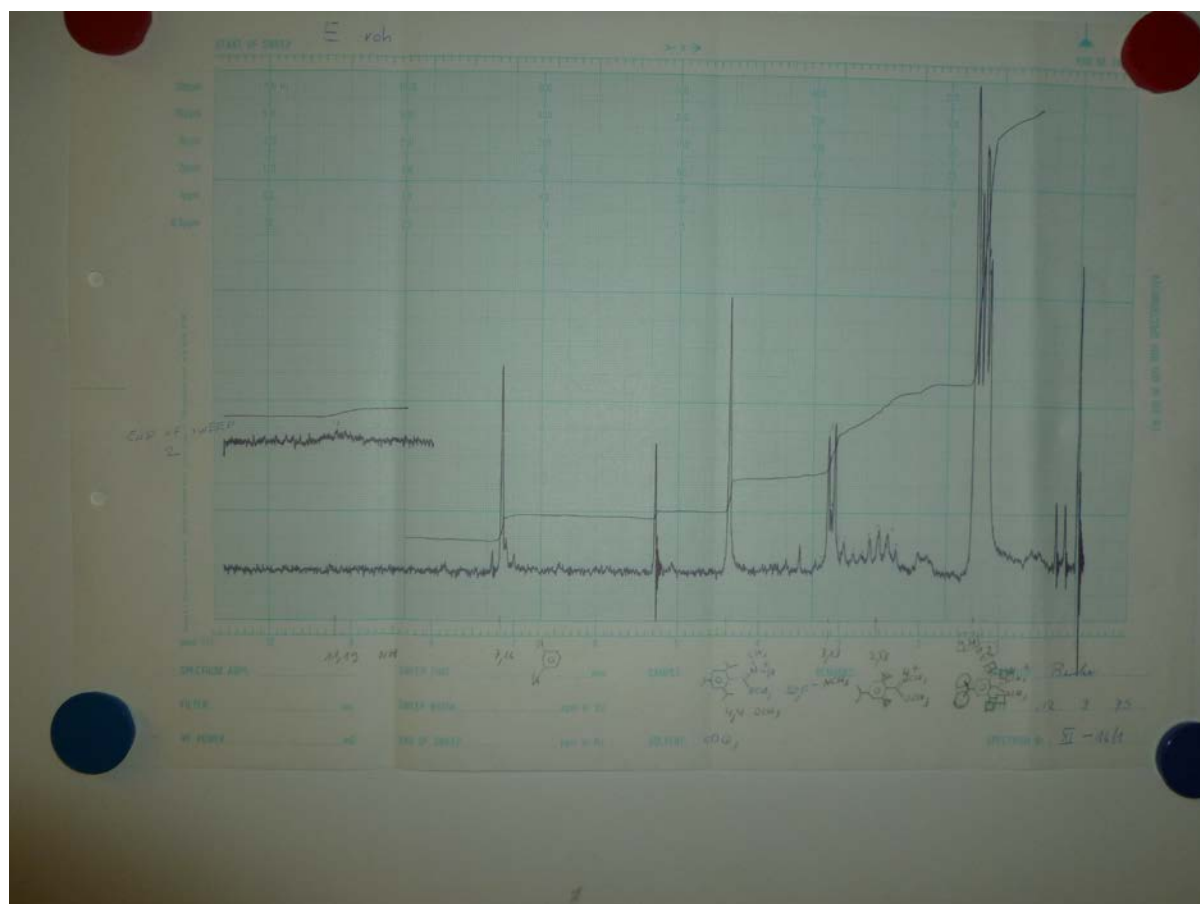
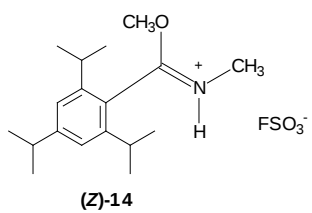
(E)-11



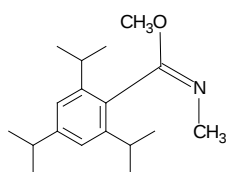
13



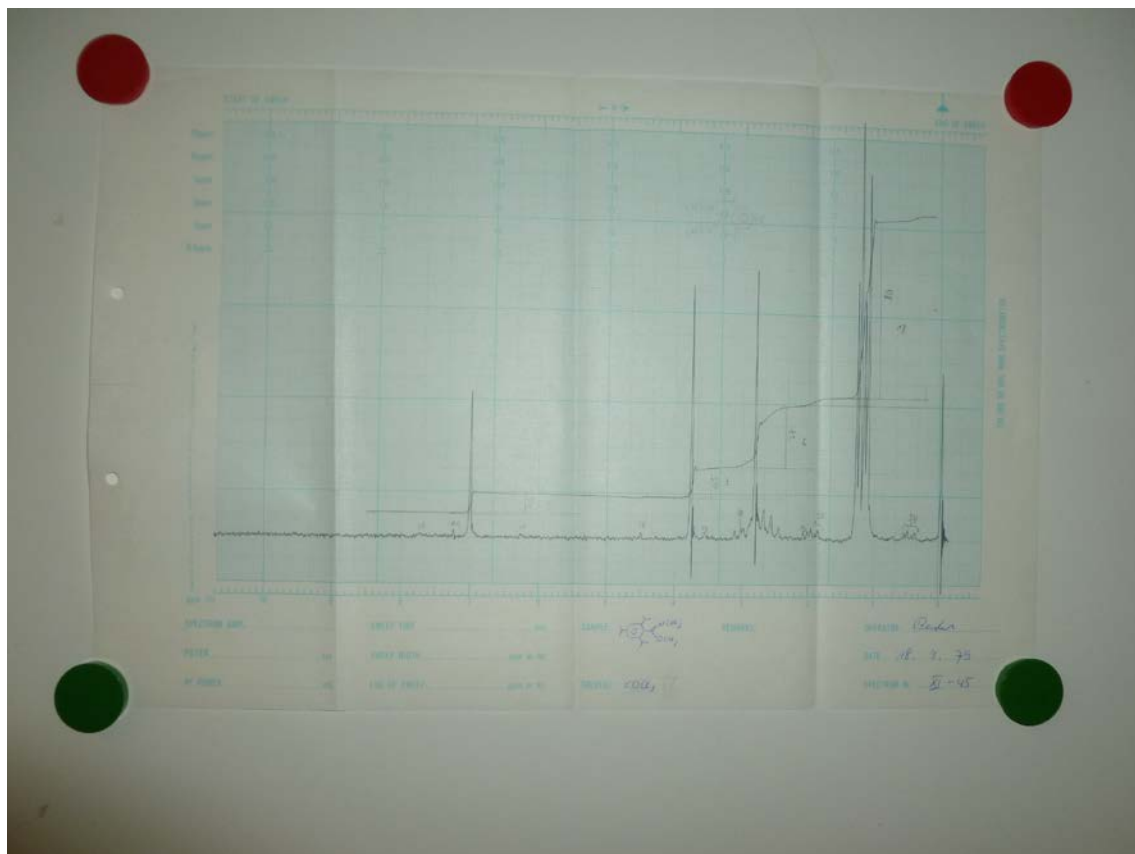
(Z)-14



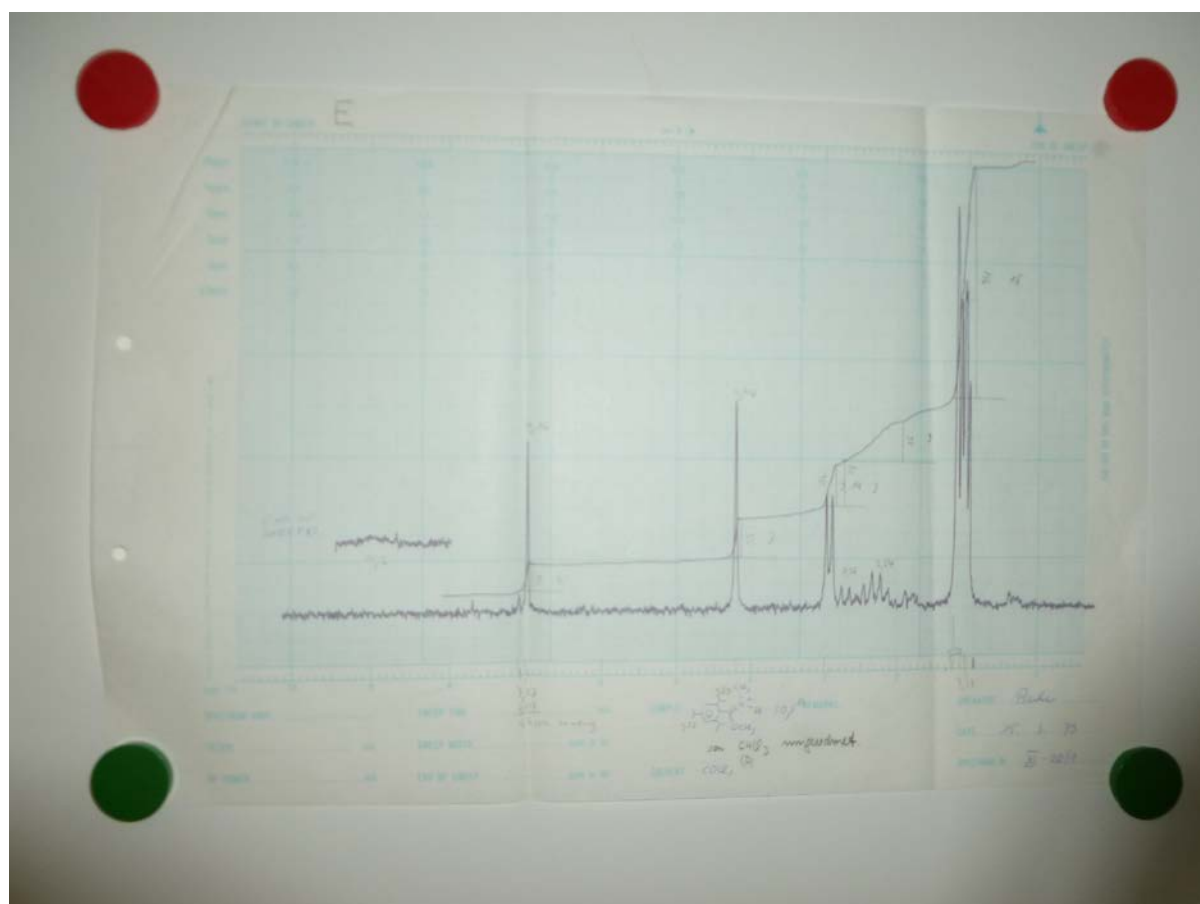
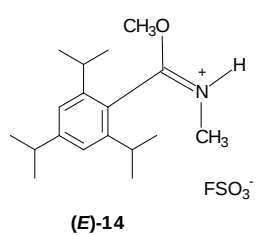
(E)-15



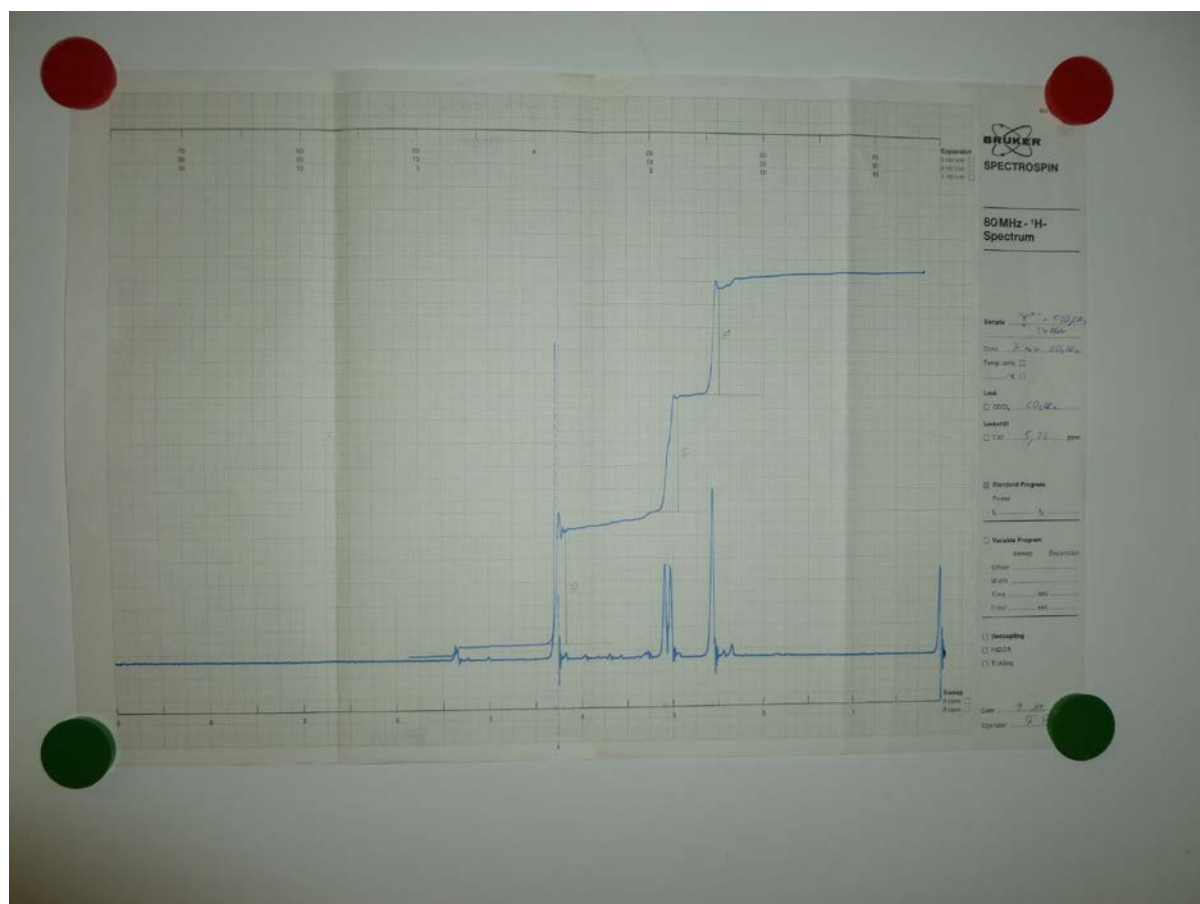
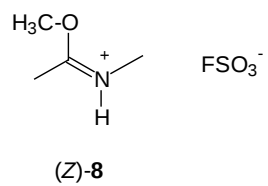
(E)-15



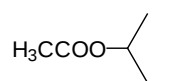
(E)-14



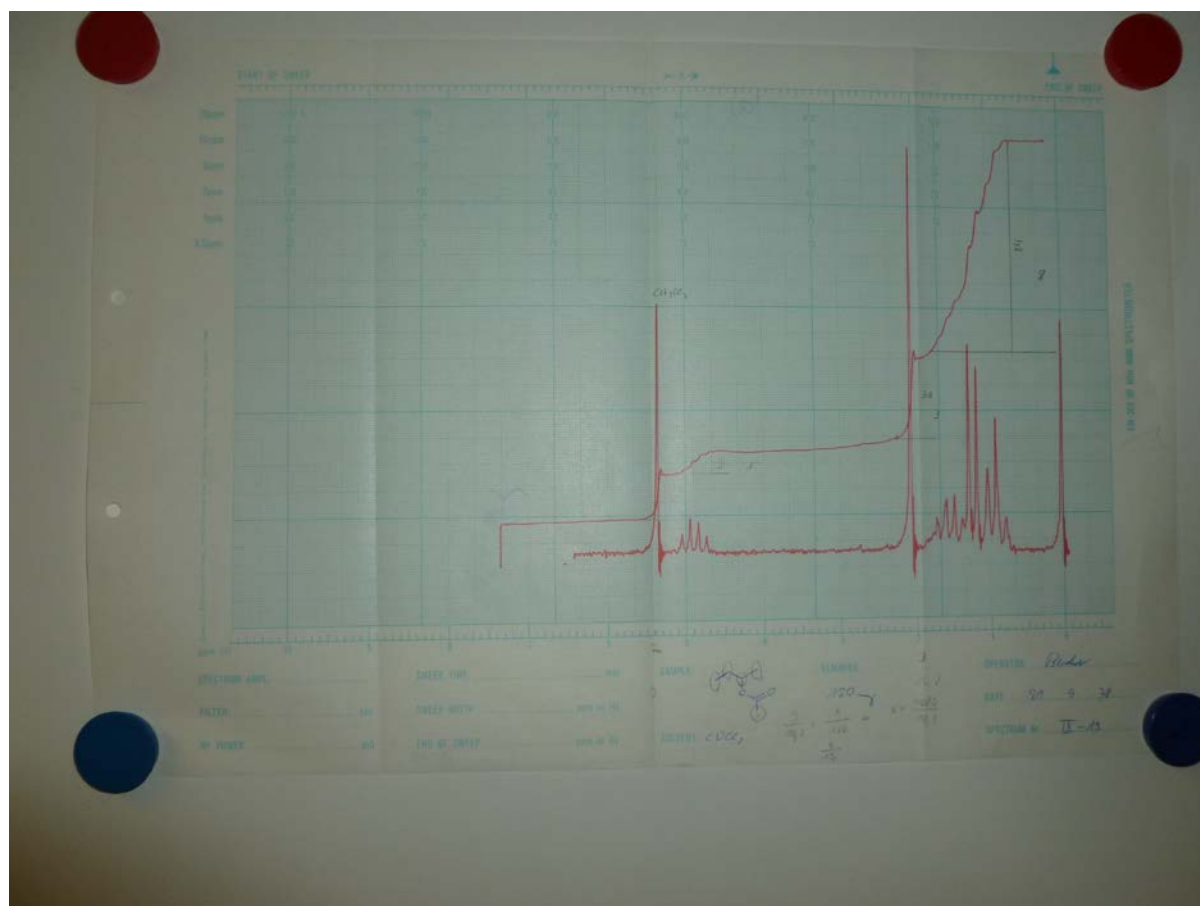
(Z)-8 via methylation of N-methyl-acetamide



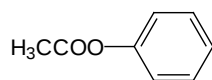
^1H -18a



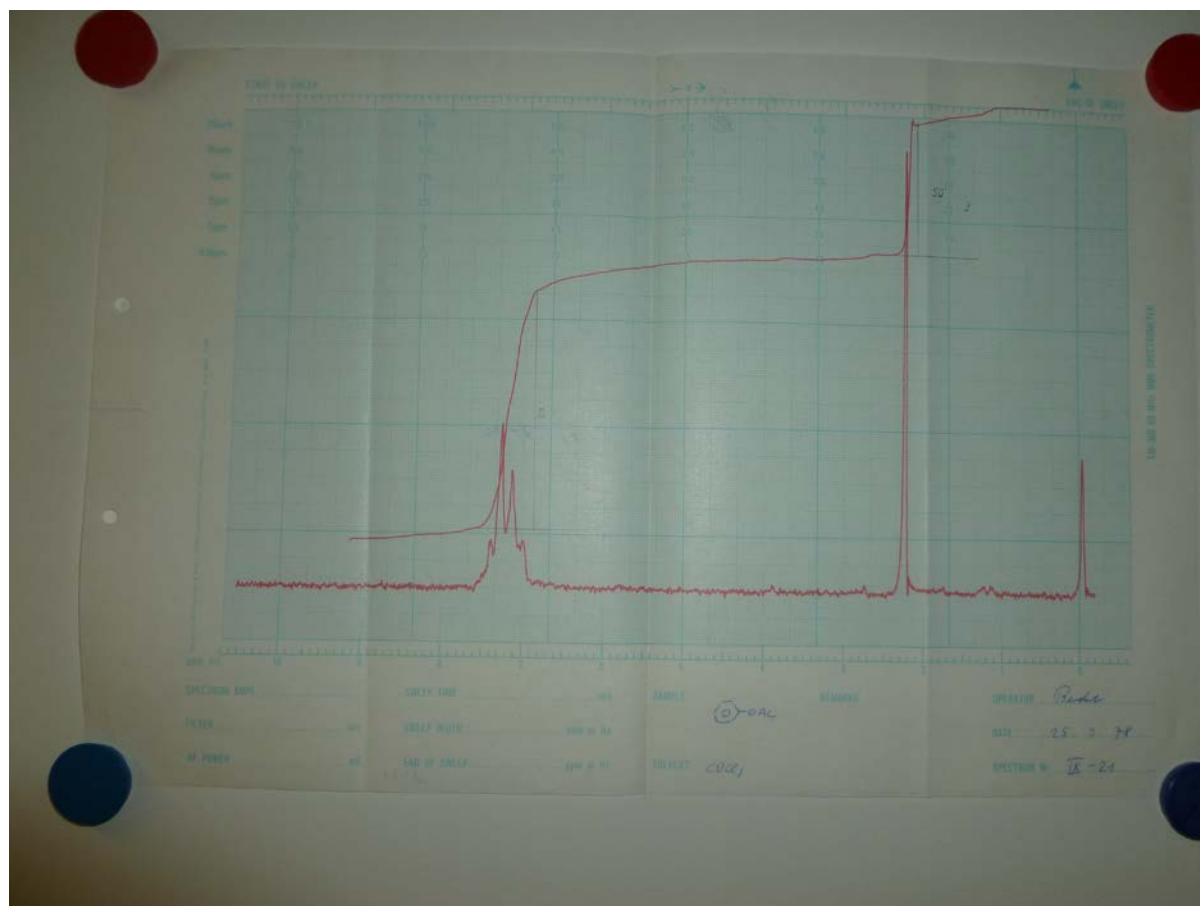
18a



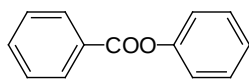
18b



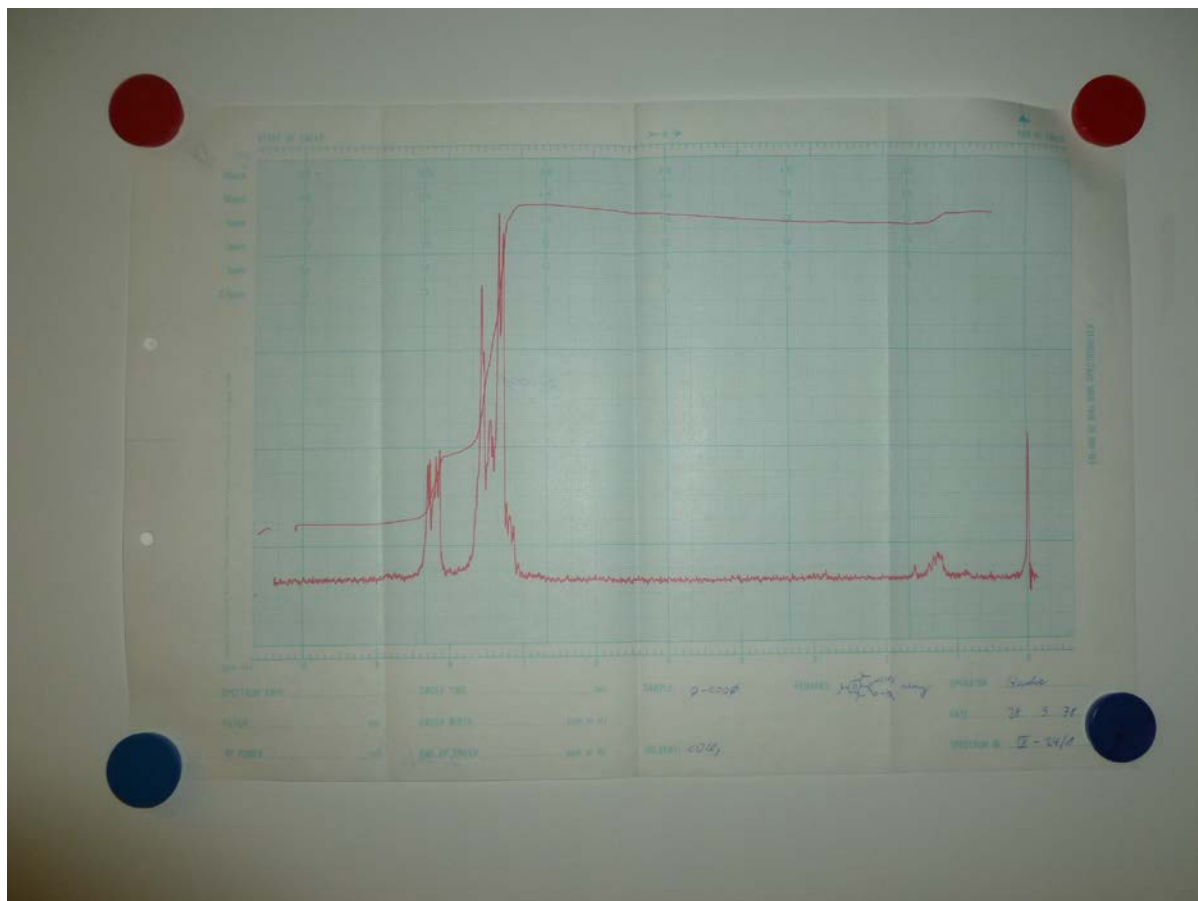
18b



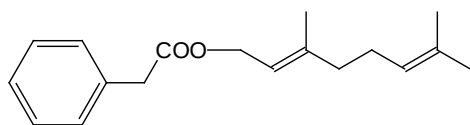
18c



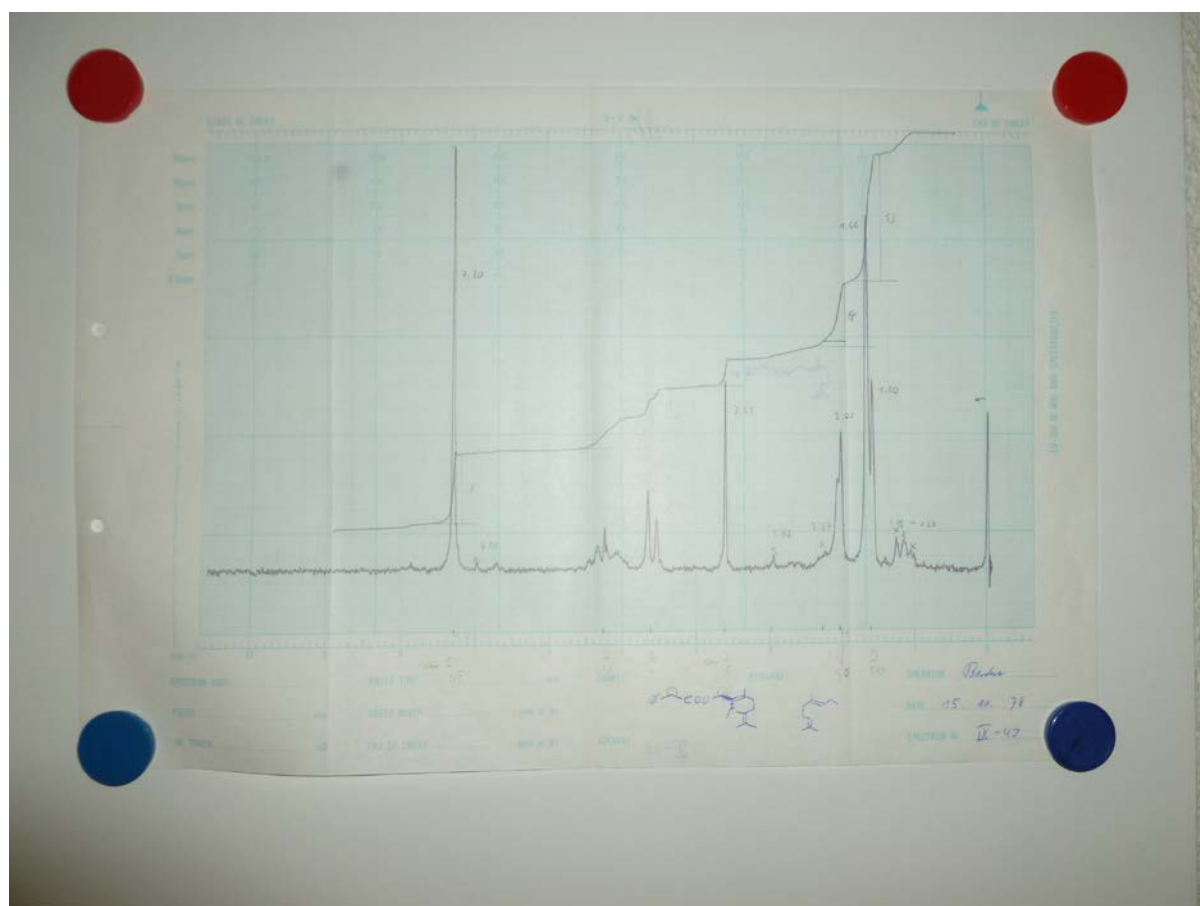
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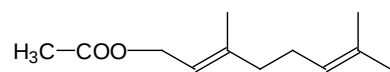
18d



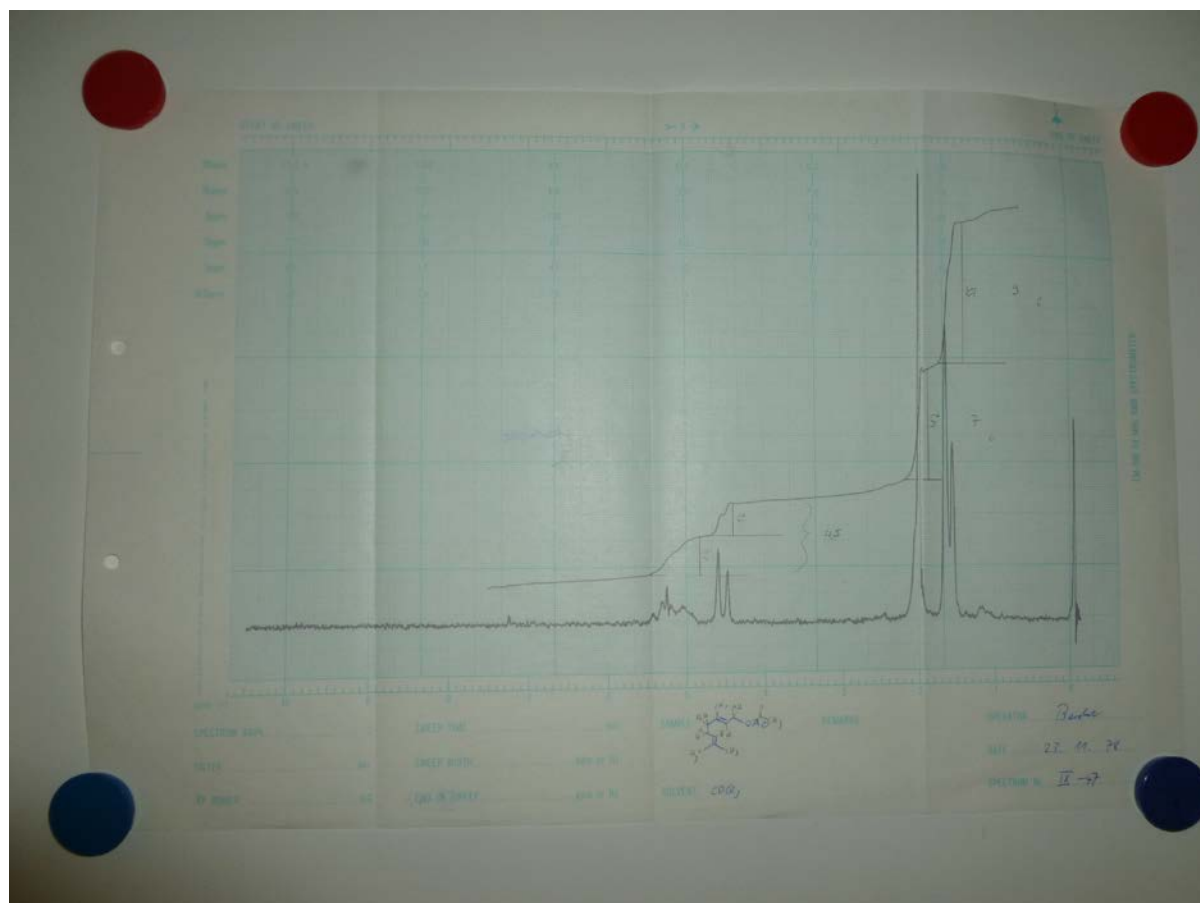
18d



18e



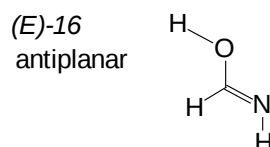
18e



Cartesian coordinates and absolute energies

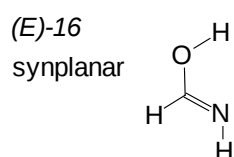
For all these species there were no imaginary frequencies: the symmetries of species showing no true minimum were reduced.

Hydroxyformine 16



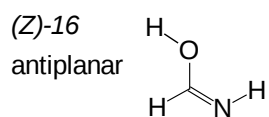
E-anti E = -209.2157204 a.u.

C	0.000000	0.170643	0.000000
N	0.400471	1.372401	0.000000
O	-1.348163	-0.033202	0.000000
C	0.831771	-1.091281	0.000000
H	0.610031	-1.696884	0.885291
H	0.610031	-1.696884	-0.885291
H	1.896210	-0.858011	0.000000
H	-1.541318	-0.976410	0.000000
H	1.416429	1.410830	0.000000



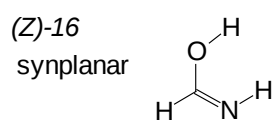
E-syn E = -209.2262816 a.u.

C	0.000000	0.131575	0.000000
N	0.275714	1.372157	0.000000
O	-1.297832	-0.260875	0.000000
C	0.926620	-1.052018	0.000000
H	0.738174	-1.672055	0.880455
H	0.738174	-1.672055	-0.880455
H	1.968604	-0.733287	0.000000
H	-1.831360	0.548350	0.000000
H	1.279345	1.533605	0.000000



Z-anti E = -209.2201685 a.u.

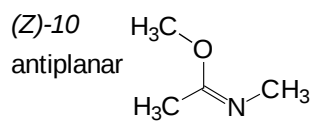
C	0.000000	0.154966	0.000000
N	0.271920	1.391211	0.000000
O	-1.295904	-0.297592	0.000000
C	1.063018	-0.907436	0.000000
H	0.971085	-1.545652	0.885433
H	0.971085	-1.545652	-0.885433
H	2.045167	-0.439334	0.000000
H	-1.317631	-1.261434	0.000000
H	-0.584022	1.949149	0.000000



Z-syn E = -209.2213003 a.u.

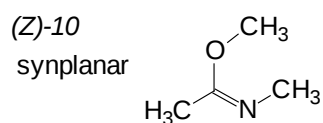
C	0.000000	0.131714	0.000000
N	0.204477	1.385438	0.000000
O	-1.214034	-0.499757	0.000000
C	1.117367	-0.867528	0.000000
H	1.042847	-1.511180	0.880796
H	1.042847	-1.511180	-0.880796
H	2.073463	-0.349226	0.000000
H	-1.920869	0.158376	0.000000
H	-0.661559	1.928085	0.000000

N-CH₃-methoxy acetimine (cf.10)



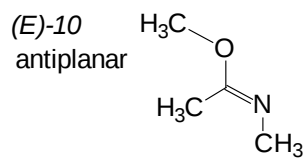
Z- Anti E = -287.82940208a.u.

C	-0.070595	0.434999	-0.014947
N	-1.329481	0.585672	-0.002656
O	0.470567	-0.823866	-0.009517
C	0.847261	1.632568	0.004296
H	1.155570	1.876489	1.023385
H	1.747943	1.485865	-0.596757
H	0.300222	2.483743	-0.398079
C	1.881310	-1.024961	0.005447
H	2.021991	-2.105104	0.044239
H	2.356832	-0.638867	-0.900564
H	2.344262	-0.572025	0.887290
C	-2.181534	-0.595217	0.006680
H	-2.001632	-1.223293	0.887826
H	-3.224942	-0.276101	0.015443
H	-2.017075	-1.223816	-0.876910



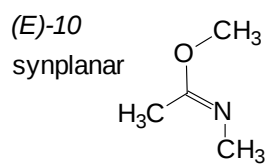
Z-syn E = -287.8234277 a.u.

C	0.590230	-0.230991	-0.030232
N	-0.156019	-1.233206	0.173671
O	0.228512	1.043836	-0.415977
C	2.085724	-0.331525	0.078112
H	2.377868	-1.358116	0.290078
H	2.544134	-0.003287	-0.859662
H	2.456976	0.331881	0.865140
C	-0.879365	1.686974	0.221311
H	-0.652081	2.753926	0.217805
H	-1.813954	1.517664	-0.317166
H	-0.986507	1.345689	1.254086
C	-1.586559	-1.220865	-0.084967
H	-1.868536	-0.600226	-0.943131
H	-1.901556	-2.246420	-0.289907
H	-2.152490	-0.880908	0.789539



E-anti E = -287.821985797 a.u.

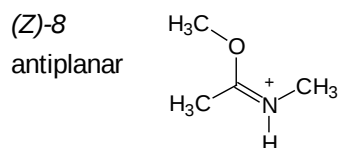
C	0.075565	-0.053553	-0.024793
N	1.138792	-0.737252	0.006741
O	-1.075504	-0.796862	-0.096781
C	-0.088728	1.447968	-0.026210
H	-0.603795	1.779587	-0.932198
H	-0.681486	1.782051	0.829196
H	0.875826	1.948147	0.017062
C	-2.347758	-0.185048	0.071967
H	-2.455117	0.268978	1.062919
H	-2.555671	0.564757	-0.697827
H	-3.071911	-0.993700	-0.022626
C	2.460846	-0.160479	0.035683
H	2.992576	-0.534727	0.916775
H	3.021444	-0.509460	-0.838184
H	2.511067	0.936703	0.052059



E-syn E = -287.835975206 a.u.

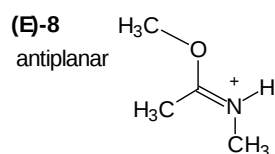
C	-0.112414	-0.074994	0.408837
N	-0.106743	-1.063942	1.202164
O	1.050830	0.525667	0.049797
C	-1.284775	0.605334	-0.259887
H	-1.980228	1.001026	0.484537
H	-0.931543	1.426866	-0.881510
H	-1.835979	-0.099253	-0.887664
C	2.252594	-0.013682	0.608508
H	2.232718	0.046988	1.698660
H	2.377789	-1.059104	0.318831
H	3.058142	0.597492	0.203300
C	-1.344531	-1.710074	1.589875
H	-2.254294	-1.281651	1.150641
H	-1.300395	-2.768740	1.313443
H	-1.444228	-1.673362	2.679763

N-CH₃-methoxy acetiminium (cf. 8)



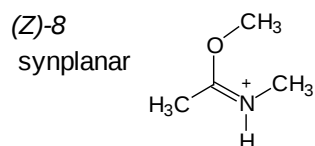
Z- Anti E = -288.218482934 a.u.

C	0.000000	0.407753	0.000000
N	-1.308683	0.427433	0.000000
O	0.542423	-0.772045	0.000000
C	0.795771	1.667420	0.000000
H	0.148742	2.543214	0.000000
H	1.439386	1.703703	0.883143
H	1.439386	1.703703	-0.883143
C	1.990908	-0.952844	0.000000
H	2.127471	-2.030037	0.000000
H	2.418200	-0.515450	-0.901271
H	2.418200	-0.515450	0.901271
C	-2.165670	-0.767498	0.000000
H	-1.970615	-1.366119	0.890058
H	-3.201539	-0.437150	0.000000
H	-1.970615	-1.366119	-0.890058
H	-1.753272	1.335044	0.000000



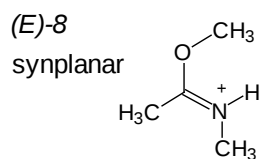
E- Anti E = -288.215069146 a.u.

C	0.000000	0.012423	0.000000
N	1.188969	-0.536213	0.000000
O	0.004423	1.314697	0.000000
C	-1.258376	-0.780414	0.000000
H	-1.065866	-1.849648	0.000000
H	-1.853313	-0.526392	0.882005
H	-1.853313	-0.526392	-0.882005
C	-1.229467	2.092790	0.000000
H	-0.894383	3.125723	0.000000
H	-1.802762	1.879588	-0.901528
H	-1.802762	1.879588	0.901528
C	1.508417	-1.972626	0.000000
H	1.115974	-2.455341	-0.895342
H	2.592293	-2.065405	0.000000
H	1.115974	-2.455341	0.895342
H	1.966557	0.116490	0.000000



Z-syn E = -288.207382633 a.u.

C	0.649534	-0.074945	-0.004331
N	-0.105387	-1.149913	0.022011
O	0.260313	1.157461	-0.042001
C	2.138550	-0.218528	0.004194
H	2.455501	-1.260424	0.015183
H	2.544973	0.276602	-0.881236
H	2.539461	0.296663	0.880572
C	-1.105304	1.676829	0.026739
H	-0.967316	2.740385	0.199834
H	-1.603887	1.514630	-0.926553
H	-1.641632	1.226833	0.858326
C	-1.569080	-1.341805	-0.017102
H	-2.024942	-0.714141	-0.776959
H	-1.744601	-2.382583	-0.282773
H	-2.012090	-1.149526	0.959983
H	0.427535	-2.008043	0.078549



E-syn E = -288.214740815 a.u.

C	-0.021361	0.395494	0.002969
N	0.601854	-0.758066	-0.003837
O	-1.316798	0.486749	0.007003
C	0.708320	1.693335	-0.000641
H	1.240458	1.818183	-0.948997
H	-0.001805	2.508550	0.119864
H	1.447192	1.721913	0.803656
C	-2.170683	-0.691327	-0.003530
H	-1.993193	-1.269434	-0.912667
H	-1.998948	-1.281436	0.899050
H	-3.182911	-0.297982	-0.003551
C	2.065139	-0.933080	0.002280
H	2.527507	-0.277826	-0.734418
H	2.469681	-0.725911	0.994358
H	2.278602	-1.966338	-0.263355
H	0.046339	-1.603778	0.010428

For all these species there were no imaginary frequencies: the symmetries of species showing no true minimum were reduced.