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DFT insights into superelectrophilic activation of α,β-unsaturated nitriles and ketones in superacids

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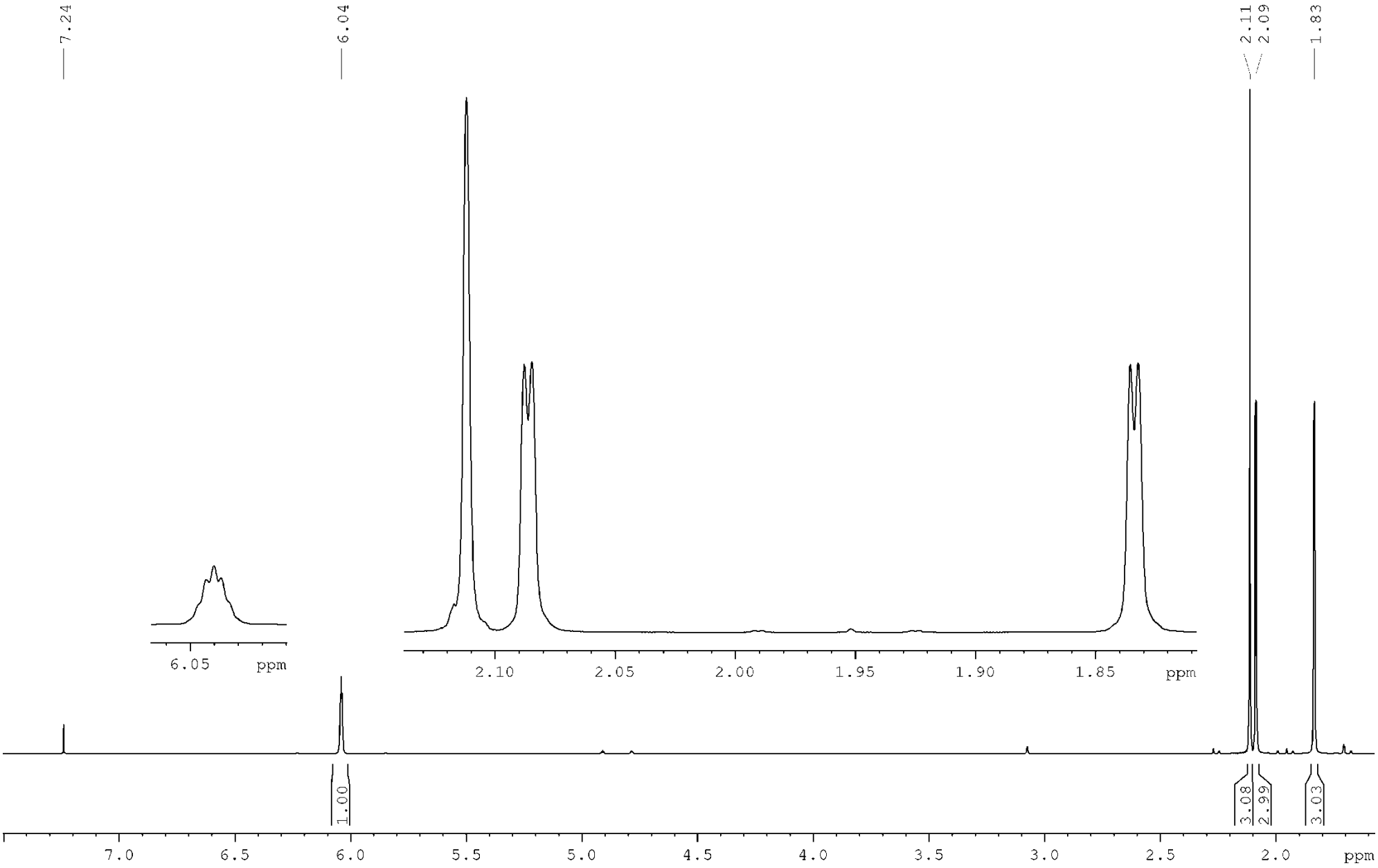
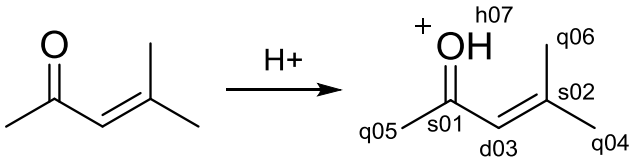
Content

^{1}H NMR spectrum (400 MHz) of mesityl oxide **55** in $CDCl_3$ at 23 °C



NMR spectra of mesityl oxide **55** in FSO_3H-SbF_5/SO_2ClF/CD_2Cl_2 at −91 °C
Pages S4-S6

9.8 mg of compound **55** in 0.1 ml CD_2Cl_2 + 410 mg FSO_3H-SbF_5 (1:1, mol/mol) + 0.3 ml SO_2ClF



55 **56**

Signal assignments

Experiment Bruker_1, 1D 13C: 6 peaks
s01 209.8
s02 206.4
d03 121.8
q04 33.2
q05 28.3
q06 27.7

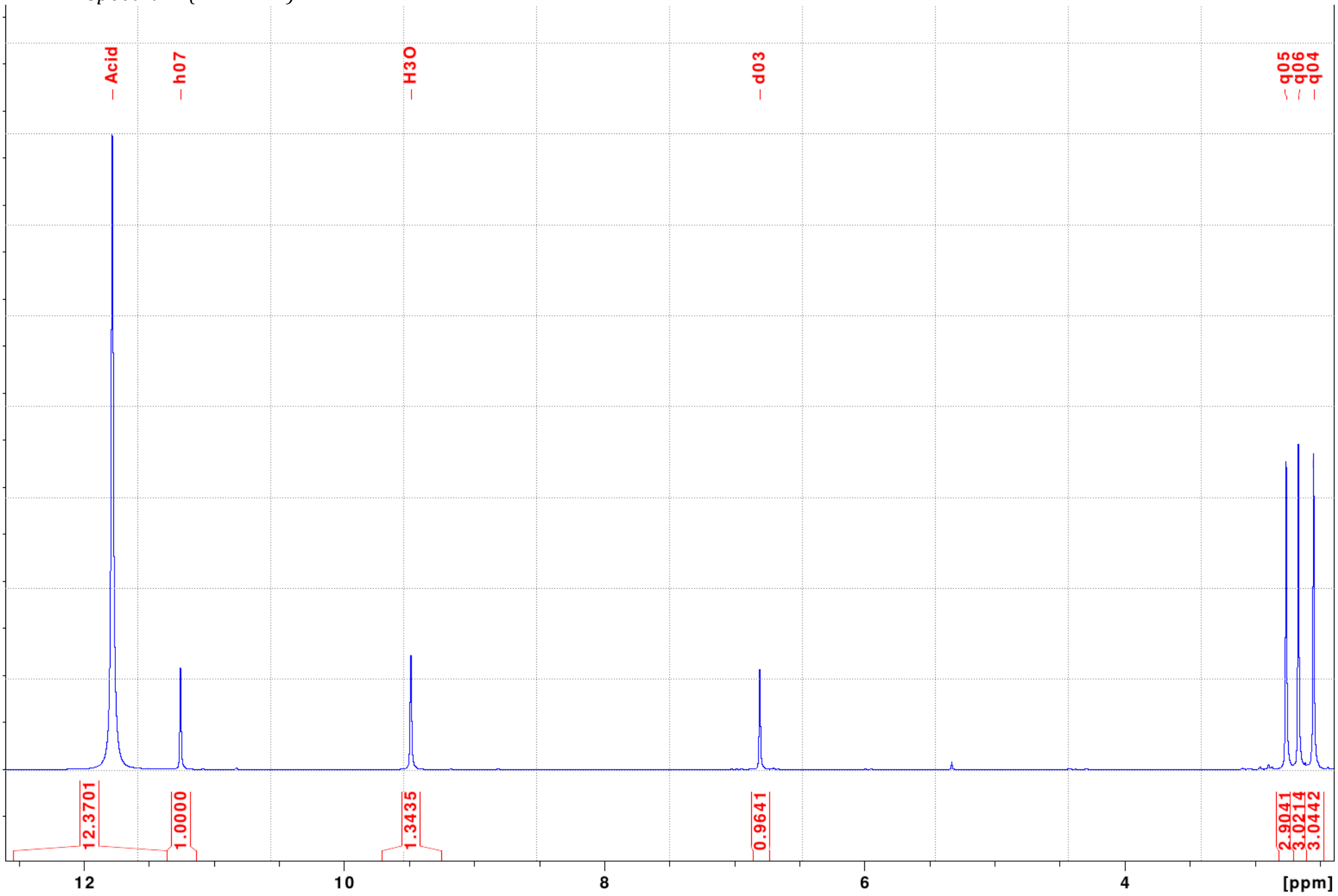
Experiment Bruker_2, 1D 1H: 6 peaks
d03-H 6.81; $^1J_{CH}$ 167.2 Hz
q04-H 2.55
q05-H 2.76
q06-H 2.67
h07-H 11.26
Acid-H 11.78

Experiment Bruker_3, 2D 13C-1H via onebond (HSQC): 4 peaks
d03-H - d03
q04-H - q04
q05-H - q05
q06-H - q06

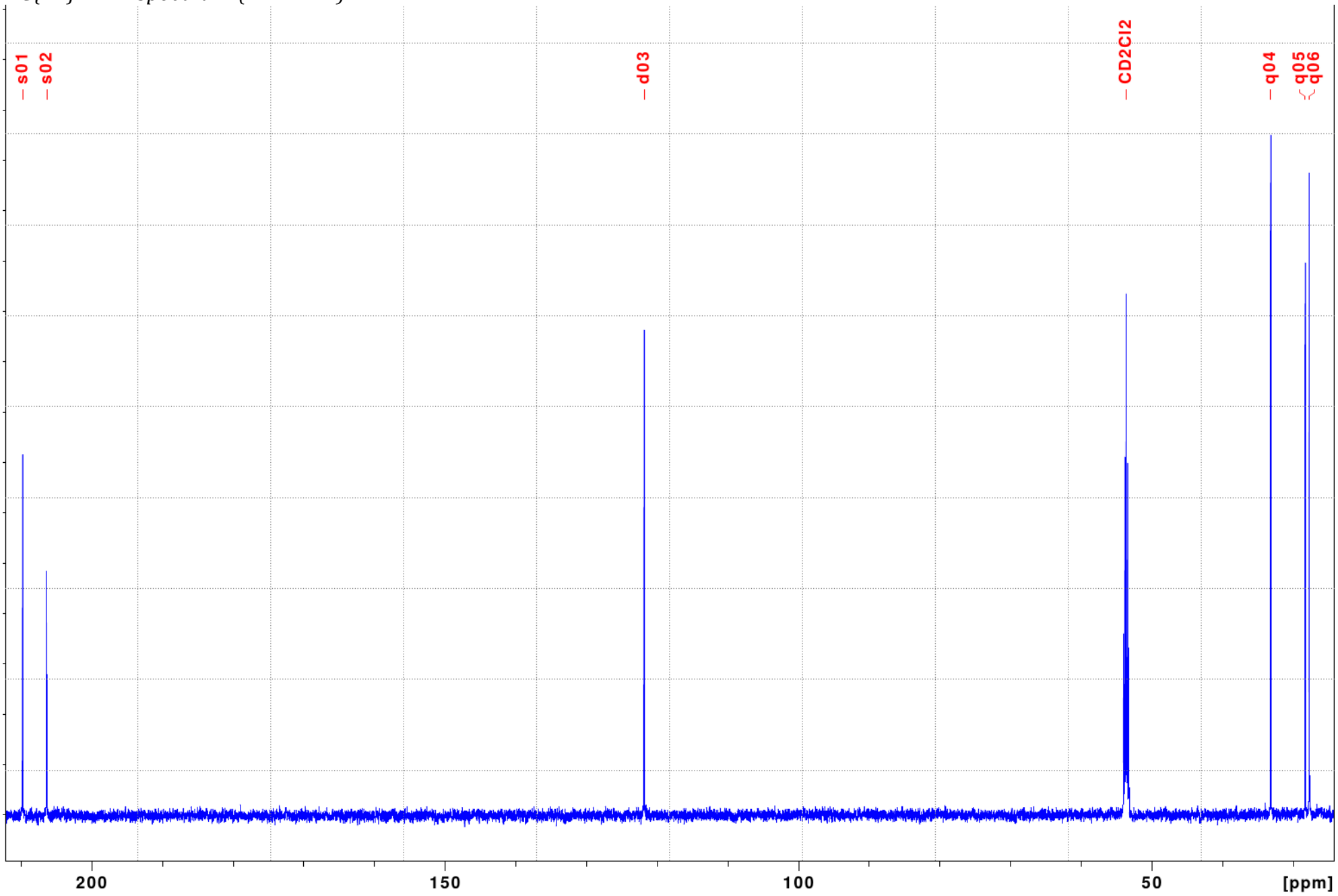
Experiment Bruker_5, 2D 13C-1H via Jcoupling (HMBC): 15 peaks
d03-H - q04 q06 s01
h07-H - d03 q05 s01
q04-H - d03 q06 s02
q05-H - d03 s01 s02(weak)
q06-H - d03 q04 s02

Experiment Bruker_6, 2D 1H-1H via through-space (NOESY): 10 peaks
d03-H - Acid-H? q04-H q05-H
h07-H - Acid-H? q05-H
q04-H - d03-H
q05-H - d03-H h07-H
q06-H - Acid-H? h07-H?

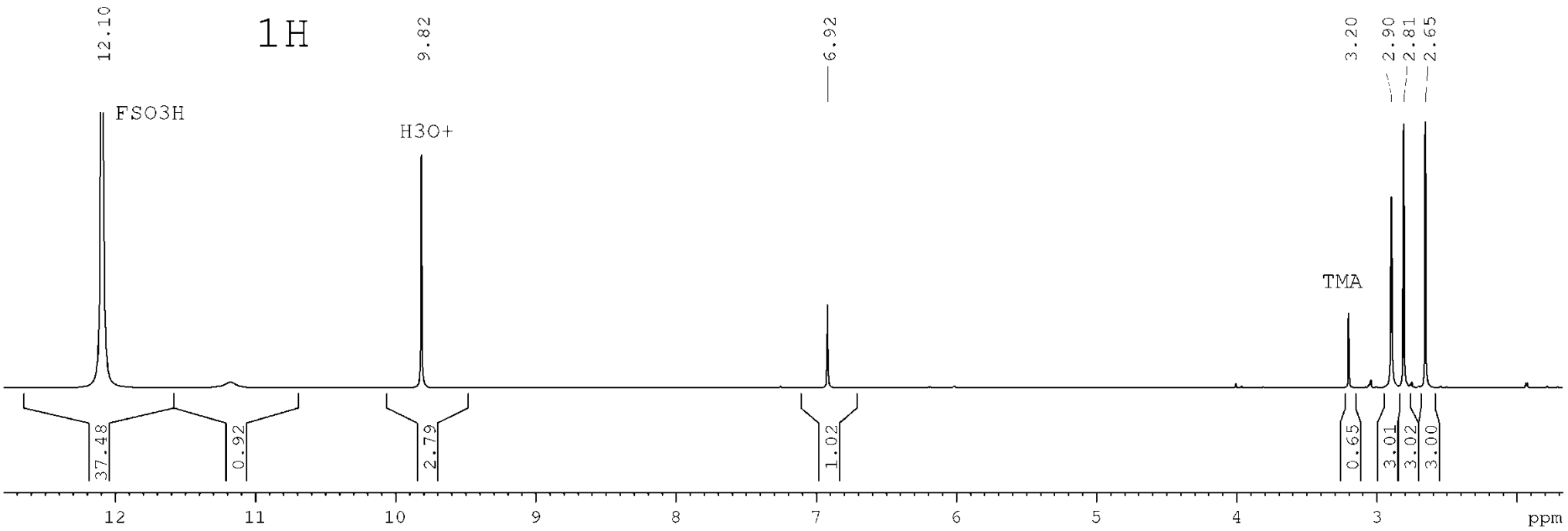
^{1}H NMR spectrum (600 MHz)

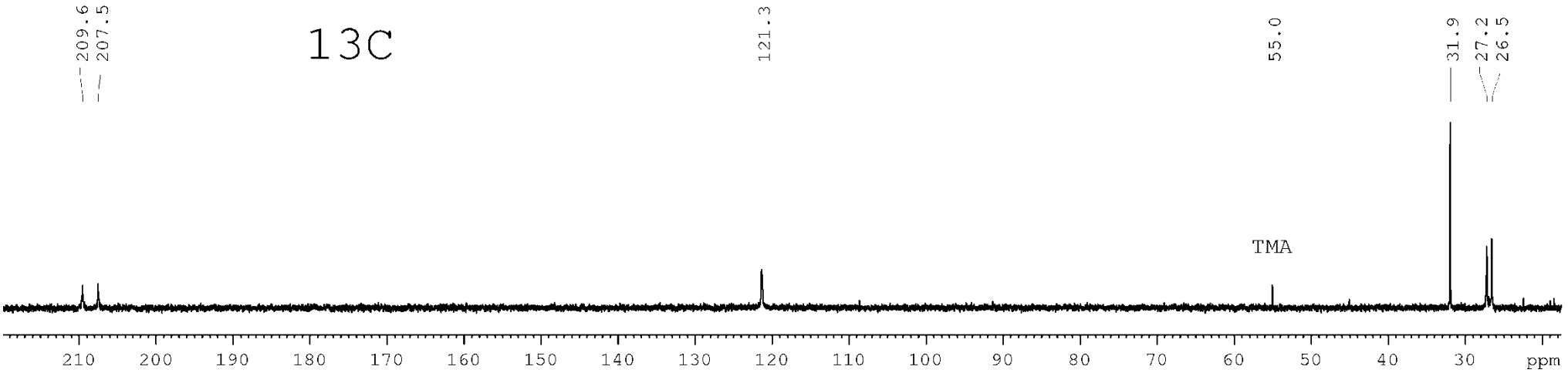


$^{13}C\{^{1}H\}$ NMR spectrum (151 MHz)



^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra of mesityl oxide **55** in FSO_3H-SbF_5 at −1 °C
11.4 mg mesityl oxide + 1 mg $Me_4N^+BF_4^-$ in FSO_3H-SbF_5 (1:1, mol/mol, 0.5 ml)



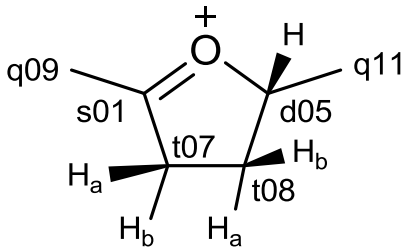


NMR spectra of mesityl oxide **55** in FSO_3H-SbF_5 after destruction
(isomerization, dehydrogenation and cracking)
Pages S8-S15

Reaction mixture from previous page was heated to 53 °C. NMR spectra were then recorded at 30 °C.

Signal assignments

Molecule A (isomerization product)



Experiment Bruker_28, 1D 13C: 6 peaks
s01 240.7
d05 108.8
t07 45.0
t08 26.8
q09 22.3
q11 18.3

Experiment Bruker_26, 1D 1H: 7 peaks
d05-H 6.19 (ddq 8.5, 7.4, 6.5 Hz)
t07-a 3.79 (ddd 23.2, 10.1, 8.6 Hz)
t07-b 3.93 (ddd 23.2, 9.5, 3.5 Hz)
t08-a 2.29 (dddd 13.5, 9.5, 8.6, 8.5 Hz)
t08-b 2.86 (dddd 13.5, 10.1, 7.4, 3.5 Hz)
q09-H 3.04 (s)
q11-H 1.93 (d, 6.5 Hz)
Coupling constants were determinated by total lineshape simulation in xsim in anatolia mode.

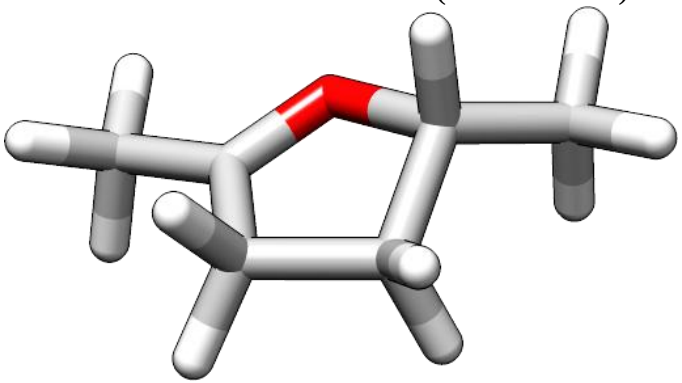
Experiment Bruker_31, 2D 13C-1H via onebond (HSQC): 7 peaks
d05-H - d05
q09-H - q09
q11-H - q11
t07-a - t07
t07-b - t07
t08-a - t08
t08-b - t08

Experiment Bruker_32, 2D 13C-1H via Jcoupling (HMBC): 15 peaks
q09-H - s01 t07
q11-H - d05 t08
t07-a - s01 t08
t07-b - d05 s01 t08
t08-a - d05 q11 s01 t07
t08-b - s01 t07

Experiment Bruker_30, 2D 1H-1H via Jcoupling (COSY): 22 peaks
d05-H - q09-H(weak) q11-H t08-a t08-b
q09-H - d05-H(weak) t07-a
q11-H - d05-H
t07-a - q09-H(weak) t07-b t08-a t08-b
t07-b - t07-a t08-a t08-b
t08-a - d05-H t07-a t07-b t08-b
t08-b - d05-H t07-a t07-b t08-a

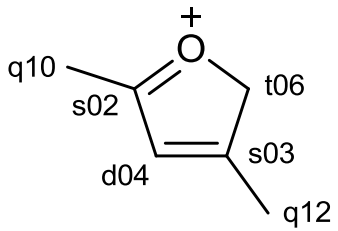
Experiment Bruker_33, 2D 1H-1H via through-space (NOESY): 11 peaks
d05-H - q11-H t08-b
q09-H - t07-b?
q11-H - d05-H t08-a
t07-a - t08-b
t07-b - t08-a
t08-a - q11-H t07-b
t08-b - d05-H t07-a

Lowest conformer of molecule A (DFT/PBE/L1)



Dihedral t08Hb-C-C-t07Hb is close to 90°, and corresponding vicinal coupling constant is 3.5 Hz only.

Molecule B (dehydrogenation product)



Experiment Bruker_28, 1D 13C: 6 peaks
s02 219.5
s03 200.4
d04 127.3
t06 91.3
q10 18.8
q12 14.2

Experiment Bruker_26, 1D 1H: 4 peaks
d04-H 7.25 (s)
t06-H 6.01 (q 3 Hz)
q10-H 3.05 (t 3 Hz)
q12-H 2.75 (s)

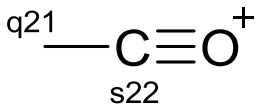
Experiment Bruker_31, 2D 13C-1H via onebond (HSQC): 4 peaks
d04-H - d04
q10-H - q10
q12-H - q12
t06-H - t06

Experiment Bruker_32, 2D 13C-1H via Jcoupling (HMBC): 14 peaks
d04-H - q12 s02 s03 t06
q10-H - d04 s02
q12-H - d04 s02(weak) s03 t06
t06-H - d04 q10(weak) s02 s03

Experiment Bruker_30, 2D 1H-1H via Jcoupling (COSY): 5 peaks
d04-H - q12-H?(weak) t06-a(weak) t06-b(weak)
q10-H - t06-a(weak) t06-b(weak)
t06-H - d04-H(weak) q10-H(weak)

Experiment Bruker_33, 2D 1H-1H via through-space (NOESY): 6 peaks
d04-H - q10-H q12-H
q10-H - d04-H
q12-H - d04-H t06-a t06-b
t06-H - q12-H

Molecule C: product of cracking



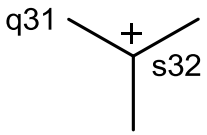
Experiment Bruker_28, 1D 13C: 2 peaks
q21 4.2
s22 151.0

Experiment Bruker_26, 1D 1H: 1 peaks
q21-H 4.00

Experiment Bruker_31, 2D 13C-1H via onebond (HSQC): 1 peaks
q21-H - q21

Experiment Bruker_32, 2D 13C-1H via Jcoupling (HMBC): 1 peaks
q21-H - s22

Molecule D: product of cracking



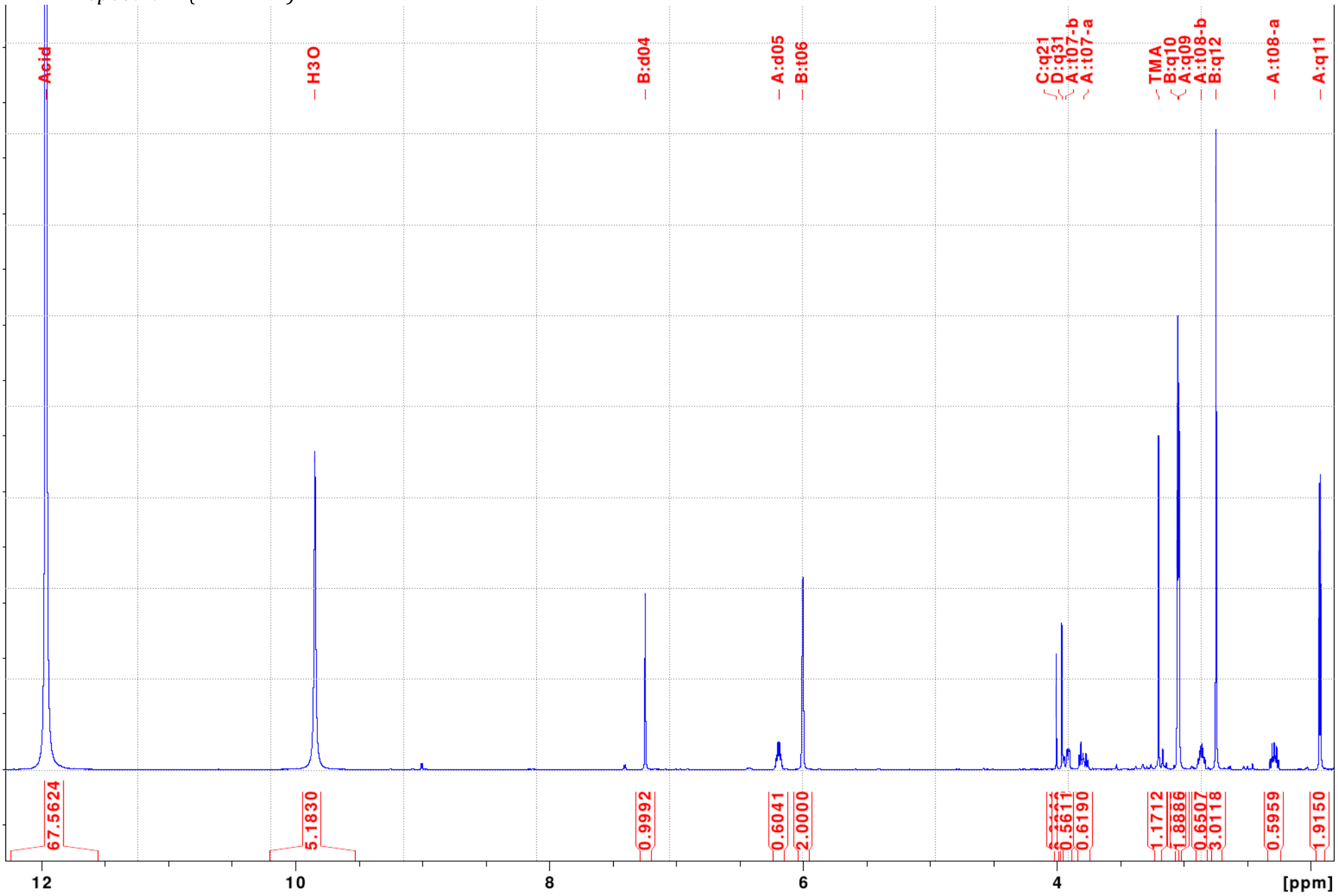
Experiment Bruker_28, 1D 13C: 2 peaks
q31 46.9
s32 336.3

Experiment Bruker_26, 1D 1H: 1 peaks
q31-H 3.96

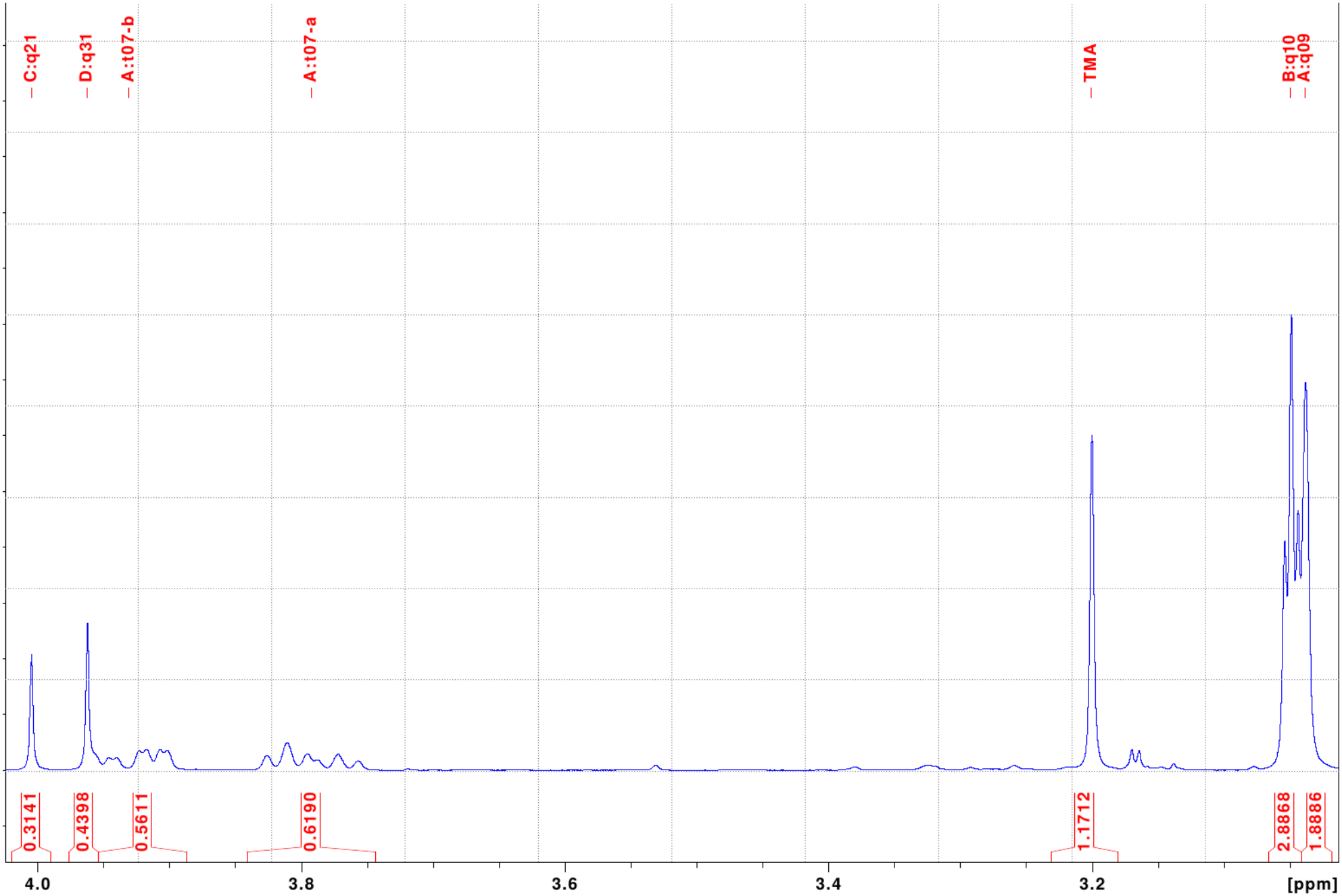
Experiment Bruker_31, 2D 13C-1H via onebond (HSQC): 1 peaks
q31-H - q31

Experiment Bruker_32, 2D 13C-1H via Jcoupling (HMBC): 2 peaks
q31-H - q31 s32

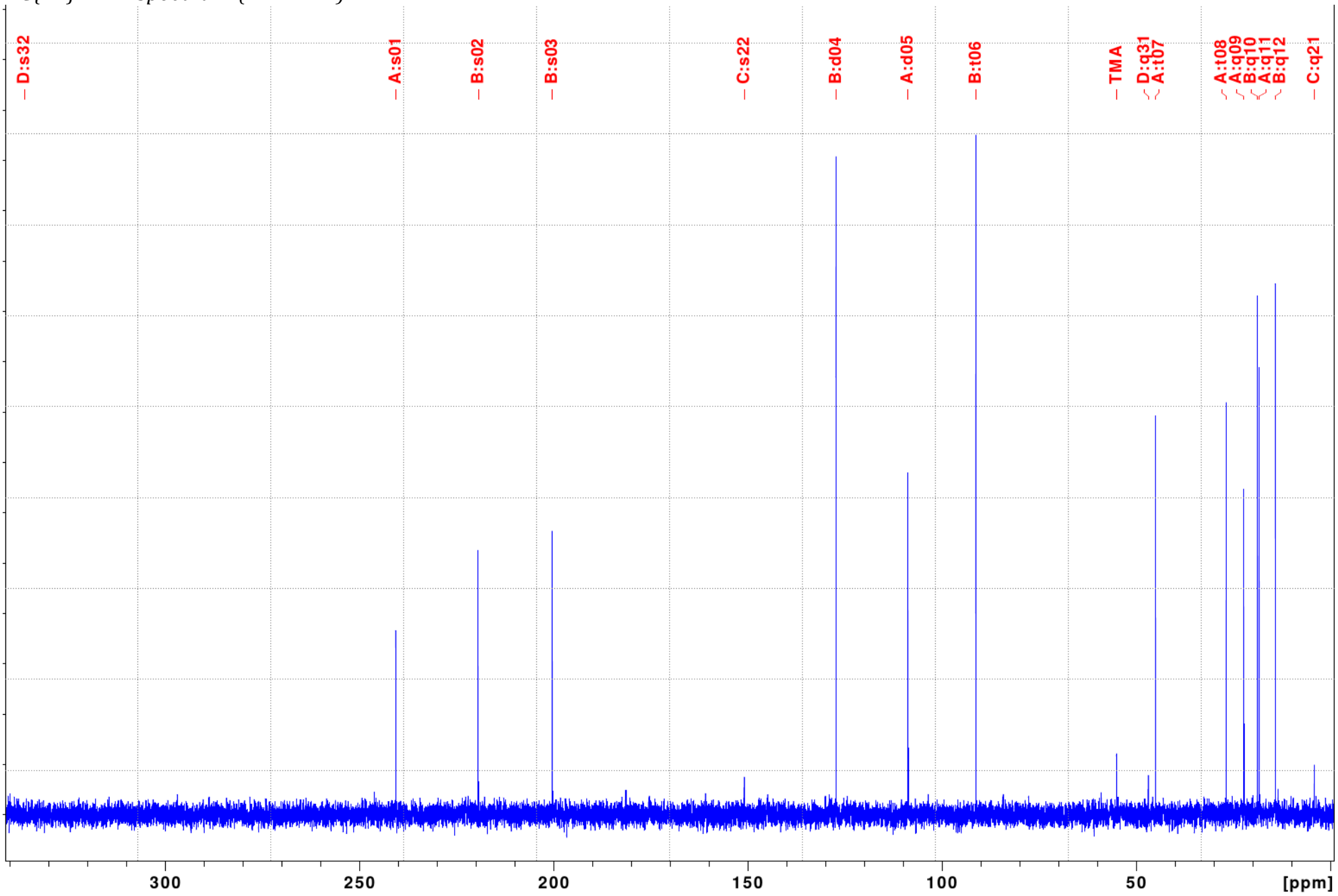
^{1}H NMR spectrum (600 MHz)

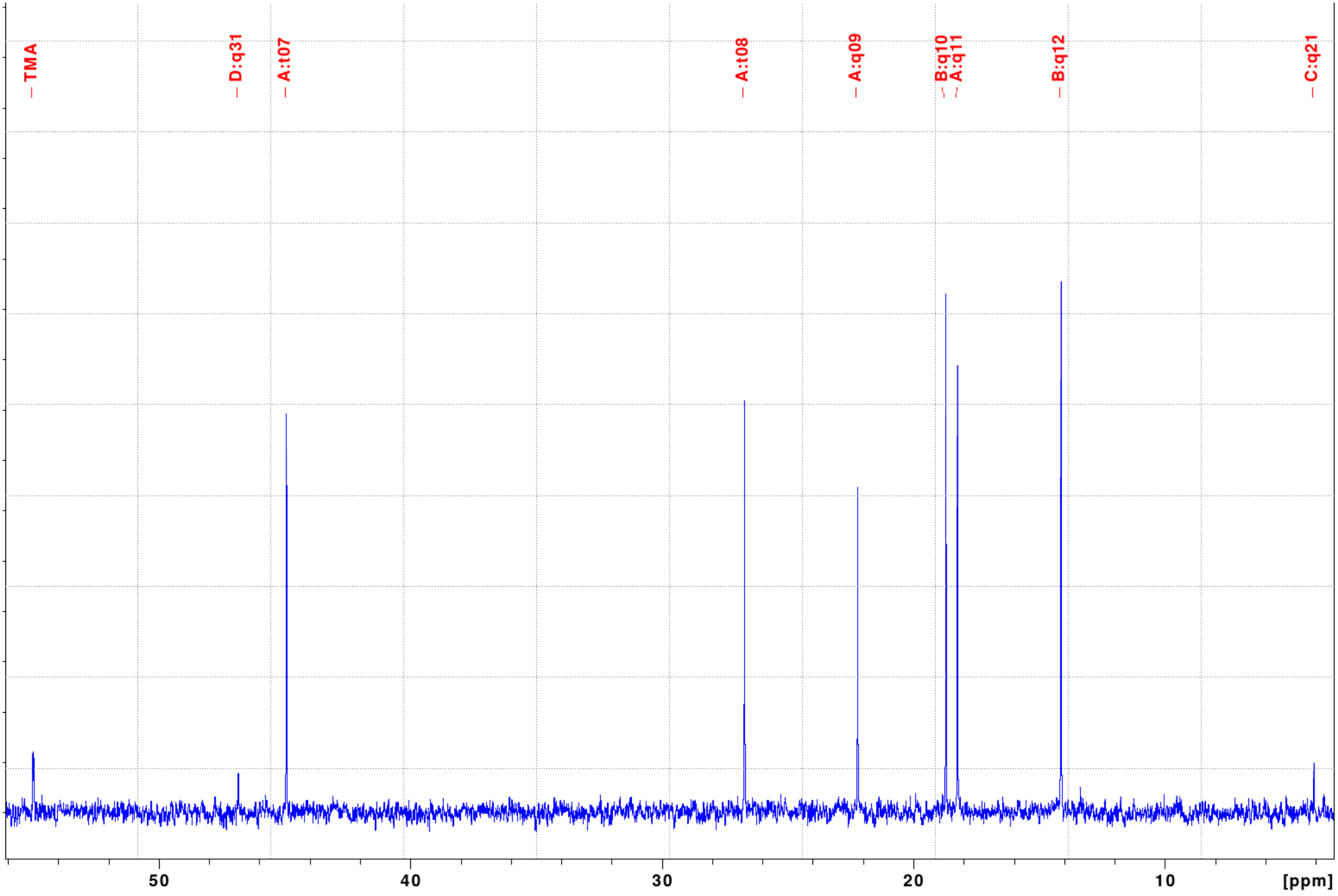



B:d04
A:d05
B:t06
C:q21
D:q31
A:t07-b
A:t07-a
TMA
B:q10
A:q09
A:t08-b
B:q12
A:t08-a
A:q11
0.9992
0.6041
2.0000
0.2141
0.4398
0.5611
0.6190
1.1712
1.8886
0.6507
3.0118
0.5959
1.9150
7
6
5
4
3
[ppm]

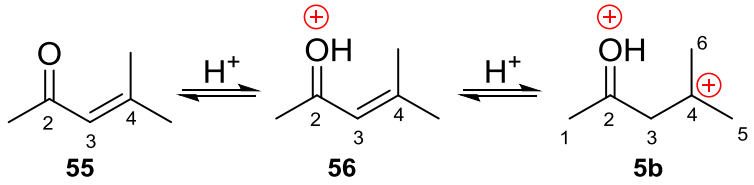

C:q21
D:q31
A:t07-b
A:t07-a
TMA
B:q10
A:q09
0.3141
0.4398
0.5611
0.6190
1.1712
2.8868
1.8886
4.0
3.8
3.6
3.4
3.2
[ppm]

$^{13}C\{^{1}H\}$ NMR spectrum (151 MHz)




TMA
D:q31
A:t07
A:t08
A:q09
B:q10
A:q11
B:q12
C:q21
50
40
30
20
10
[ppm]

Temperature dependence of δ(C4)−δ(C3) of ketone **55** in superacids



The difference in chemical shifts δ(C4) – δ(C3) of mesityl oxide **55** strongly depends on the acidity level, which even contributed to the choice of this compound as an NMR indicator of acidity (see, please, ref. [55] in the main text). Acidity of the system $FSO_3H–SbF_5$ is far outside of the usable range of **55** as indicator since its exhaustive conversion into cation **56**. However, enone **55** can be partially diprotonated to form some amount of dication **5b**. Therefore, the parameter δ(C4) – δ(C3) will reflect the contribution of this dication too. An increase in temperature will lead to an increase in the fraction of the less stable component of the equilibrium mixture, i.e. dication **5b**, and the difference δ(C4) – δ(C3) will increase.*

Indeed, Fig. S1 shows a moderate upward trend for the parameter δ(C4) – δ(C3) with the temperature increase. However, in case of the $FSO_3H–SbF_5/SO_2ClF/CD_2Cl_2$ system, the parameter δ(C4)–δ(C3) increases only up to 200 K, and then it begins to decrease. Obviously, this is due to progressive side reaction: $CD_2Cl_2 + SbF_5 \rightarrow CD_2ClF + CD_2F_2 + SbF_4Cl + SbF_3Cl_2$, leading to partial conversion of SbF_5 into the weaker Lewis acids, such as SbF_4Cl and SbF_3Cl_2, which can be observed by the growth of CD_2ClF and CD_2F_2 signals in the NMR spectra. This decreases the acidity of the medium, thus diminishing content of dication **5b** and influencing the parameter δ(C4) – δ(C3) in general.

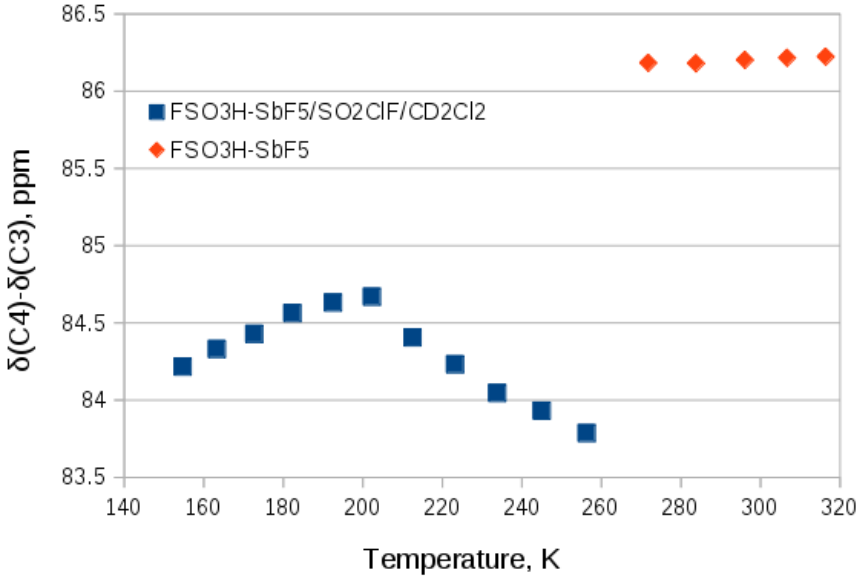
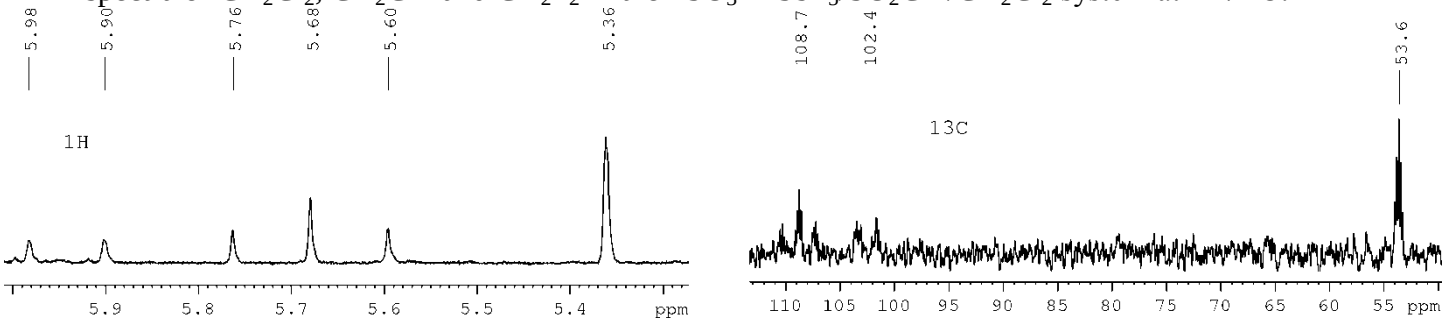


Fig. S1 Temperature dependence of the δ(C4) – δ(C3) parameter of ketone **55** in superacid systems $FSO_3H–SbF_5/SO_2ClF/CD_2Cl_2$ and $FSO_3H–SbF_5$.

NMR spectra of CD_2Cl_2, CD_2ClF and CD_2F_2 in the $FSO_3H–SbF_5/SO_2ClF/CD_2Cl_2$ system at −17 °C:



* The ^{1}H NMR spectrum (200.13 MHz) of **5b** in HF-SbF_5-SO_2ClF at -60 °C: δ 3.55 (s, 3H, C^1H_3), 4.45 (s, 6H, $C^{5,6}H_3$), 6.06 (s, 2H, CH_2), 15.89 (s, 1H, OH); ^{13}C NMR spectrum (50.33 MHz): δ 31.2 (C1), 50.2 (C5,6), 60.5 (C3), 235.8 (C2), 323.0 (C4) (ref. [30] in the main text). Hence, δ(C4) – δ(C3) for **5b** is 323.0 – 60.5 = 262.5 ppm, which is notably higher of magnitudes around 85 ppm for the parent cation **56**. Therefore, the growth of concentration of dication **5b** should become visible through increasing of the δ(C4) – δ(C3) value.

Kinetics data

Chemical exchanges observed for protonated mesityl oxide **55** (cation **56**) and methods for determining their rate constants:

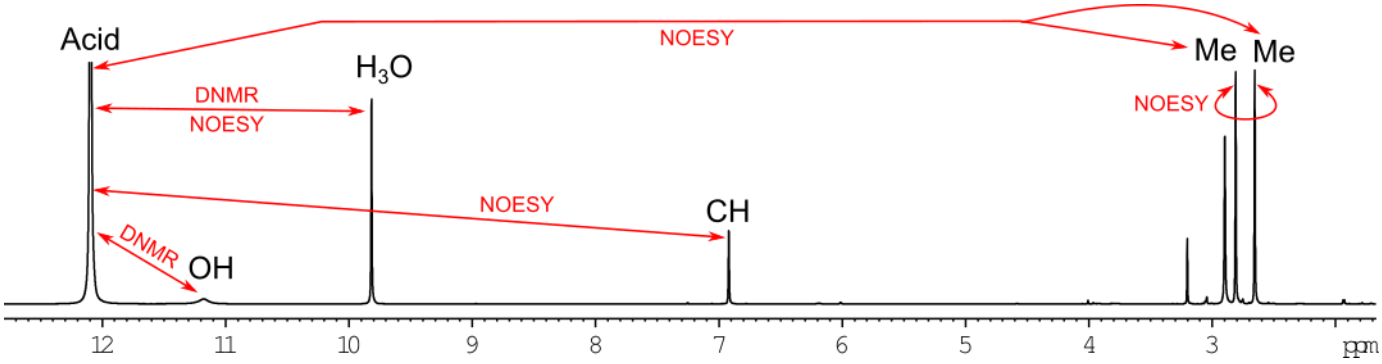


Table S1. Rate constants (s^{-1}) and Eyring's activation parameters for chemical exchanges and irreversible destruction of protonated mesityl oxide **55** (cation **56**) in FSO_3H–SbF_5.

Temperature, K	Process					
	OH-Acid	H_3O^+-Acid [a]	CH-Acid	Me-Me	Me-Acid [a]	Destruction (by integration)
271.7	155	3.2	0.10	0.076		
283.8	284	6.3	0.18	0.171	0.0211	
296.1	455	10.1, 14.7 [b]	0.34	0.354	0.0410	7.4e-05
306.6	703	33.0	0.64	0.668	0.0828	2.2e-04
316.3		98.4	1.54	1.524	0.1519	6.3e-04
326.0						2.1e-03
$\Delta H^{\#}$, kcal mol^{-1}	6.5±0.2	12±2	9.5±1.0	10.6±0.6	10.3±0.6	21±1
$\Delta S^{\#}$, cal mol^{-1} K^{-1}	−24±1	−14±6	−28±3	−25±2	−32±2	−8±4

[a] To calculate the activation parameters, the rate constants were divided by three.
[b] From NOESY and DNMR, respectively.

Quantum chemical calculations by DFT/PBE/Λ01
See also http://limor1.nioch.nsc.ru/quant/H_AlCl3/

Structures are in XMol xyz format.
Energy and ZPE are in hartree, Dipole in D, G(298) is Gibbs energy correction at 298 K in kcal/mol, Edisp is Grimme's DFT-D3/BJ dispersion correction in kcal/mol [S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys. 132 (2010), 154104; S. Grimme, S. Ehrlich and L. Goerigk, J. Comput. Chem. 32 (2011), 1456-1465]).

Benzene C_6H_6

```
12
 Energy -232.0024519633  Dipole 0.000273  ZPE 0.097880  G(298) 45.63  HoF 17.12 kcal
sigma 12  Edisp -6.86
 C   -0.02168251   0.75392639  -1.17665293
 C   -0.67935738   1.22089984  -0.03525456
 C   -0.65789262   0.46684623   1.14132250
 C    0.02167092  -0.75393696   1.17664413
 C    0.67946644  -1.22084201   0.03527875
 C    0.65799486  -0.46679830  -1.14129199
 H   -1.21111378   2.17593570  -0.06292895
 H   -1.17209355   0.83239227   2.03440698
 H    0.03823966  -1.34403257   2.09704463
 H    1.21109333  -2.17595053   0.06295139
 H    1.17231003  -0.83226225  -2.03434517
 H   -0.03863540   1.34382218  -2.09717477
```

*Cation **15***

```
18
 Energy -401.82633783932  Charge 1  Dipole 7.996010  ZPE 0.138536  G(298.15) 65.47  HoF
224.74 kcal  Edisp -11.79
 C    2.17420327  -0.51987839  -0.00012086
 C    1.16807623   0.42576870  -0.00020847
 C   -0.24009410   0.18263880  -0.00004984
 C    3.49901207  -0.14917307  -0.00019521
 C   -1.10414612   1.30914473  -0.00005608
 C   -2.48183704   1.14037696   0.00009753
 C   -3.02095445  -0.15122397   0.00026212
 C   -2.18184846  -1.27789701   0.00023847
 C   -0.80617408  -1.11865721   0.00009272
 N    4.62792013   0.13813367  -0.00026199
 H    1.99152208  -1.59868497   0.00018881
 H    1.46921438   1.47975802  -0.00041877
 H   -0.67426348   2.31484989  -0.00018450
 H   -3.14117989   2.01080398   0.00011769
 H   -4.10563082  -0.28640058   0.00038344
 H   -2.61621490  -2.27982677   0.00035848
 H   -0.16666412  -2.00466856   0.00007245
 H    5.60905931   0.38493578  -0.00031600
```

*Cation **17***

```
18
 Energy -401.791379338  Charge 1  Dipole 4.686244  ZPE 0.139243  G(298.15) 66.42  HoF
246.67 kcal  Edisp -11.96
 C    2.39422656  -0.56298679  -0.00033560
 C    1.32177012   0.46809889  -0.00032638
 C   -0.04820848   0.24166398  -0.00001956
 C    3.74460145  -0.01177150  -0.00026973
 C   -0.91560547   1.39053969   0.00013001
 C   -2.28652241   1.22722544   0.00036416
 C   -2.82433974  -0.07145728   0.00037303
 C   -1.99748915  -1.21705097   0.00016943
 C   -0.62779730  -1.07354605   0.00003170
 N    4.81463404   0.43961971  -0.00008142
 H    2.26864044  -1.22991107  -0.87931229
 H    2.26859848  -1.22997377   0.87858200
 H    1.65699568   1.51374569  -0.00054726
 H   -0.47240889   2.39046538   0.00008741
```

```
 H   -2.94948810   2.09487225   0.00055900
 H   -3.91088069  -0.20053103   0.00053095
 H   -2.45016491  -2.21087168   0.00016078
 H    0.01343839  -1.95813091  -0.00009624
```

*Dication **18***

```
 19
 Energy -401.9828606863  Charge 2  Dipole 9.879303  ZPE 0.149630  G(298.15) 72.84  HoF
495.02 kcal  Edisp -12.21
 C    2.07933775  -0.58331193  -0.00058269
 C    0.99953420   0.48006990  -0.00032820
 C   -0.35073399   0.22303781  -0.00000384
 C    3.43575748  -0.07140821   0.00008133
 C   -1.24146550   1.37424097  -0.00001047
 C   -2.60513420   1.19314635   0.00011942
 C   -3.12745695  -0.11787201   0.00027613
 C   -2.28629086  -1.26259300   0.00025162
 C   -0.92248167  -1.10819373   0.00016248
 N    4.52138473   0.30080902   0.00061085
 H    5.49868117   0.61630893   0.00108467
 H    1.99808828  -1.24465987  -0.89138356
 H    1.99757552  -1.24578371   0.88931170
 H    1.32662292   1.52647157  -0.00054909
 H   -0.81311720   2.38108655  -0.00013681
 H   -3.28156516   2.05141304   0.00015241
 H   -4.21374945  -0.25983167   0.00040290
 H   -2.73396638  -2.25945090   0.00036329
 H   -0.28102070  -1.99347913   0.00017786
```

*Dication **23***

```
 19
Energy -401.9848858883  Charge 2  Dipole 10.215255  ZPE 0.151173  G(298.15) 73.05  HoF
493.75 kcal  Edisp -12.10
 C    1.82301184  -0.12097371   0.79296033
 C    0.69220815   0.65311855   0.31887845
 C   -0.47696261   0.12652427  -0.20517428
 C    2.92011428   0.39947285   1.28549888
 C   -1.49375988   1.07546365  -0.62499668
 C   -2.68115355   0.62782099  -1.15489008
 C   -2.90031986  -0.76209264  -1.28590388
 C   -1.92735979  -1.71476909  -0.88539419
 C   -0.73468747  -1.29028024  -0.35397928
 N    3.98829313   0.84991118   1.76365530
 H    4.81151865   1.06233984   1.16340114
 H    1.82305717  -1.22251541   0.76465550
 H    0.78164447   1.74280986   0.38576966
 H   -1.30252642   2.14689088  -0.51419598
 H   -3.45148085   1.33453347  -1.47316542
 H   -3.84687859  -1.11643337  -1.70835106
 H   -2.13605361  -2.78077301  -1.00361404
 H    0.00754699  -2.03190990  -0.04888829
 H    4.10378796   1.02086184   2.78373392
```

*Structure **19***

```
 22
 Energy -2024.410595006  Charge 1  Dipole 9.980140  ZPE 0.145424  G(298.15) 61.64  Edisp
-17.07
 C    1.28663382  -0.66220119  -0.70195873
 C    0.05504594   0.18870146  -0.62266986
 C   -1.22085156  -0.23137011  -0.28535921
 C    2.46941507   0.06558097  -0.26187801
 C   -2.27891745   0.74932482  -0.32506485
 C   -3.57377591   0.39177034  -0.01456483
 C   -3.85836333  -0.93922032   0.34237871
 C   -2.84481964  -1.92059298   0.39172829
 C   -1.54418853  -1.58327686   0.08891642
 N    3.38515114   0.67402567   0.09480544
 H    1.44821675  -0.94587079  -1.76665270
```

```
 H    1.21496932  -1.60333438  -0.13250018
 H    0.19237897   1.24382167  -0.88914409
 H   -2.03649042   1.77835736  -0.60473837
 H   -4.37475799   1.13345225  -0.04292418
 H   -4.88578237  -1.22032383   0.59113697
 H   -3.09666590  -2.94436400   0.67642585
 H   -0.76483792  -2.34663215   0.13749546
 Al   4.93030566   1.88303477   0.74793431
 Cl   5.04538072   1.25028097   2.77566885
 Cl   6.47772180   1.28434727  -0.57621930
 Cl   3.97423182   3.75448906   0.37718401
```

Pre-reaction complex, TS and product of the reaction ***17***$+C_6H_6\rightarrow$***27***

```
30
 Energy -633.8137028568  Charge 1  Dipole 5.711246  ZPE 0.238783  G(298) 121.80  HoF
251.33 kcal  Edisp -25.65
 C    1.96271805  -1.10180067  -1.53350458
 C    0.87351449  -0.10711012  -1.28873365
 C   -0.47067828  -0.41472739  -1.04892864
 C    3.30214983  -0.56087571  -1.32717079
 C   -1.42748028   0.64951094  -1.11952805
 C   -2.78431095   0.38228291  -1.02312187
 C   -3.21697098  -0.93536008  -0.82893209
 C   -2.29448643  -1.99501114  -0.71550315
 C   -0.94058680  -1.74585480  -0.81355097
 N    4.35884673  -0.11430888  -1.14418834
 H    1.87446869  -1.39869441  -2.60341195
 H    1.83954158  -2.03074714  -0.95406710
 H    1.11918827   0.93313859  -1.52198631
 H   -1.07303685   1.66802360  -1.29393221
 H   -3.51221058   1.19215658  -1.10497621
 H   -4.28750302  -1.14727307  -0.75908953
 H   -2.65551348  -3.01273430  -0.55253716
 H   -0.23267308  -2.57242038  -0.72305114
 C    0.47628180  -0.26443982   2.23756876
 C   -0.56802684   0.65802230   2.31009630
 C   -0.41769782   1.94908947   1.76546742
 C    0.77240490   2.31115866   1.13877241
 C    1.81270310   1.37664063   1.03503112
 C    1.66456484   0.08905650   1.59301561
 H   -1.49736939   0.39271407   2.82090941
 H   -1.22784567   2.67597844   1.86726959
 H    0.90553579   3.32339313   0.74811168
 H    2.76672482   1.65848816   0.58062304
 H    2.50631399  -0.60837535   1.56133533
 H    0.37143357  -1.24992071   2.69801310
 30
 Energy -633.8083589647  Charge 1  Dipole 3.090101  ZPE 0.239204  G(298.15) 123.54  HoF
254.68 kcal  Edisp -25.31
 C    1.62988512  -1.03721512  -1.16335761
 C    0.47972234  -0.15853500  -0.71018287
 C   -0.87476767  -0.62191917  -0.90964458
 C    2.93091617  -0.38184987  -1.16546097
 C   -1.88646605   0.33420315  -1.17950379
 C   -3.18091438  -0.07352783  -1.47232025
 C   -3.49852042  -1.43815471  -1.47056501
 C   -2.51500354  -2.39676486  -1.18657929
 C   -1.21486748  -1.99712135  -0.90921981
 N    3.96641234   0.14592392  -1.17954749
 H    1.39521638  -1.31972914  -2.21006758
 H    1.69005472  -1.98877733  -0.60885408
 H    0.64324527   0.91283467  -0.86831597
 H   -1.63299211   1.39842227  -1.18340304
 H   -3.94904755   0.66765203  -1.70365094
 H   -4.52029774  -1.75841804  -1.68956931
 H   -2.77190330  -3.45825110  -1.18520207
 H   -0.46051172  -2.75657508  -0.68730784
 C    0.73763097   0.01286702   1.44175868
 C   -0.22948186   1.03422077   1.69850336
```

```
 C    0.17642633   2.32845763   1.96348762
 C    1.55056778   2.63366961   2.01081057
 C    2.51856955   1.63763373   1.82725089
 C    2.12102247   0.32994383   1.58274628
 H   -1.29233232   0.78401134   1.65429855
 H   -0.56124882   3.11324780   2.14561600
 H    1.86652412   3.66163250   2.20877489
 H    3.58023518   1.88339767   1.89682632
 H    2.87202349  -0.45903250   1.50806861
 H    0.42990274  -1.03224685   1.54461073
 30
 Energy -633.8126296082  Charge 1  Dipole 4.607619  ZPE 0.240421  G(298) 124.22  HoF
252.00 kcal  Edisp -24.83
 C    1.57331849  -0.96500661  -1.24020340
 C    0.49222526  -0.06127701  -0.59592813
 C   -0.89941371  -0.56813155  -0.86368833
 C    2.88513960  -0.33451353  -1.29332824
 C   -1.80599959   0.24480474  -1.56437025
 C   -3.07955163  -0.22854045  -1.88348206
 C   -3.46587319  -1.51261640  -1.49243681
 C   -2.57398902  -2.32641860  -0.78471369
 C   -1.30025030  -1.85645518  -0.47057918
 N    3.91591711   0.20600964  -1.30540584
 H    1.24224948  -1.16538456  -2.27462002
 H    1.64768664  -1.94654939  -0.74239253
 H    0.60536507   0.95316758  -1.00888190
 H   -1.50631762   1.24938491  -1.87950450
 H   -3.77141272   0.40807641  -2.43986677
 H   -4.46557631  -1.88108897  -1.73453234
 H   -2.87442473  -3.33081179  -0.47775904
 H   -0.61743664  -2.51160635   0.08208414
 C    0.73932861   0.11572849   1.04245254
 C   -0.21635695   1.12774897   1.51137948
 C    0.19771728   2.26752340   2.15336854
 C    1.57666121   2.47536009   2.38095454
 C    2.54109132   1.52037546   2.01659504
 C    2.14220012   0.35310339   1.40055642
 H   -1.27336837   0.96754407   1.27783996
 H   -0.52468876   3.02045559   2.47608372
 H    1.90128743   3.40051259   2.86758566
 H    3.59521789   1.69321598   2.24385982
 H    2.88097857  -0.42426081   1.19576053
 H    0.43827547  -0.89035012   1.40317263
```

Pre-reaction complex, TS and product of the reaction ***18***$+C_6H_6\rightarrow$***28***

```
31
 Energy -634.0138763207  Charge 2  Dipole 6.875100  ZPE 0.248187  G(298) 126.13  HoF
494.22 kcal  Edisp -24.16
 C    1.20446588  -0.67259922  -1.32982857
 C   -0.18834464  -0.08967609  -1.23614284
 C   -1.34718304  -0.85078416  -1.23250935
 C    2.24565983   0.26580989  -0.96795946
 C   -2.60533235  -0.14633613  -1.34200299
 C   -3.79034655  -0.84568635  -1.41384574
 C   -3.76819060  -2.25414497  -1.36903397
 C   -2.55422568  -2.97089441  -1.25389506
 C   -1.35953727  -2.29080538  -1.17985738
 N    3.12129193   0.98493091  -0.77541798
 H    3.87976730   1.62571687  -0.53535425
 H    1.41151729  -0.98470541  -2.38019591
 H    1.34778013  -1.56854972  -0.69694138
 H   -0.27385072   0.99576876  -1.34142194
 H   -2.60406802   0.94673984  -1.38273896
 H   -4.74191677  -0.31713035  -1.50675655
 H   -4.71104921  -2.80763784  -1.42199134
 H   -2.57254279  -4.06270472  -1.22213851
 H   -0.42930042  -2.85695846  -1.08736454
 C    0.26512111   0.93157968   1.54944421
 C    0.52936992   2.29625545   1.31226392
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 C    1.75158997   2.84401170   1.70377851
 C    2.70787671   2.03476672   2.33747736
 C    2.45077828   0.67135100   2.56794526
 C    1.23544213   0.11789909   2.16946264
 H   -0.24300805   2.94120357   0.88351494
 H    1.94371119   3.91154371   1.56548316
 H    3.64383482   2.47666235   2.69317934
 H    3.18641932   0.06067160   3.09825139
 H    1.00602452  -0.92466113   2.40846297
 H   -0.74175420   0.53836321   1.38613302
 31
 Energy -634.011884243  Charge 2  Dipole 9.354475  ZPE 0.248775  G(298.15) 129.08  HoF
495.47 kcal  Edisp -25.18
 C    1.44846427  -1.08012698  -1.06822736
 C    0.28387489  -0.16219865  -0.66743363
 C   -1.04127496  -0.65050933  -0.88799832
 C    2.71194178  -0.41579301  -1.27368198
 C   -2.07649822   0.30197062  -1.12669920
 C   -3.35995938  -0.12210411  -1.42752579
 C   -3.65144244  -1.49591461  -1.46131647
 C   -2.65002393  -2.45052613  -1.20544948
 C   -1.35951337  -2.03841606  -0.91950801
 N    3.72211783   0.07272316  -1.52823751
 H    4.62637324   0.48555155  -1.76973968
 H    1.21524474  -1.54185327  -2.05374220
 H    1.62404218  -1.91971306  -0.36926138
 H    0.44988284   0.90398133  -0.84667492
 H   -1.84525743   1.37106819  -1.10364614
 H   -4.14405609   0.60864859  -1.63862606
 H   -4.66914589  -1.82818734  -1.68439199
 H   -2.89362091  -3.51496962  -1.23053190
 H   -0.59959012  -2.79734157  -0.71071909
 C    0.57974171   0.05825737   1.52798456
 C   -0.36309332   1.10332679   1.77443070
 C    0.07091514   2.38404773   2.07317428
 C    1.44883419   2.65079926   2.15753955
 C    2.39710251   1.62688370   1.97052049
 C    1.97137155   0.33817749   1.68626165
 H   -1.43229940   0.88113397   1.72055567
 H   -0.65022349   3.18224733   2.26479069
 H    1.78878362   3.66219527   2.39849042
 H    3.45929789   1.84438479   2.10864872
 H    2.69804778  -0.48062163   1.65519501
 H    0.23996281  -0.97712178   1.63581937
 31
 Energy -634.0222181129  Charge 2  Dipole 11.481274  ZPE 0.249394  G(298) 129.34  HoF
488.99 kcal  Edisp -24.58
 C    1.48248808  -1.10524552  -1.08594690
 C    0.43787641  -0.04068568  -0.55068569
 C   -0.95903899  -0.54272871  -0.83565937
 C    2.66987821  -0.56315794  -1.68355025
 C   -1.78908521   0.18922892  -1.70137098
 C   -3.06897493  -0.27849572  -2.00500584
 C   -3.52826723  -1.47368650  -1.44556540
 C   -2.70753910  -2.20677055  -0.57919776
 C   -1.42918628  -1.74290075  -0.27272085
 N    3.58668834  -0.11179551  -2.21771278
 H    4.40135106   0.23615688  -2.72716926
 H    0.99339651  -1.67702960  -1.90233428
 H    1.78467754  -1.85402947  -0.33035105
 H    0.59411759   0.90158956  -1.10062195
 H   -1.43640856   1.12488519  -2.14746809
 H   -3.70844190   0.29282016  -2.68197227
 H   -4.53223476  -1.83616991  -1.67967549
 H   -3.06867029  -3.13957363  -0.14023675
 H   -0.80728806  -2.33529749   0.41010063
 C    0.64617942   0.28919060   0.99876641
 C   -0.41340638   1.17428592   1.52466414
 C   -0.14451690   2.14734479   2.45887305
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 C    1.18528719   2.36812756   2.86957045
 C    2.25908338   1.59140808   2.37486747
 C    2.01305002   0.59325425   1.46489176
 H   -1.43294367   1.01103143   1.16059233
 H   -0.94943913   2.76676926   2.86251028
 H    1.39569355   3.16428843   3.59202457
 H    3.27364740   1.78461501   2.73229293
 H    2.84340593  -0.03832392   1.13192544
 H    0.40862077  -0.68910514   1.50616550
```

Pre-reaction complex, TS and product of the reaction ***19*** *+* C_6H_6 *→* ***29***

```
34
 Energy -2256.432181406  Charge 1  Dipole 11.265106  ZPE 0.244961  G(298) 117.73  Edisp -
32.04
 C    0.89877899  -1.31331629  -0.98458638
 C   -0.28648737  -0.40554204  -0.74240474
 C   -1.61672718  -0.86864086  -0.89377926
 C    2.17076795  -0.61205009  -0.98520596
 C   -2.64943656   0.09346411  -1.10614184
 C   -3.95130691  -0.31465163  -1.34049790
 C   -4.26165482  -1.68344105  -1.34326390
 C   -3.26354032  -2.64825276  -1.12221963
 C   -1.95580054  -2.25291479  -0.90016699
 N    3.16887672  -0.02962927  -1.01522255
 H    0.77781681  -1.76229806  -1.99323871
 H    0.95183464  -2.16153646  -0.28006616
 H   -0.10361646   0.66645538  -0.85506512
 H   -2.39587172   1.15726370  -1.10709804
 H   -4.73450077   0.42423457  -1.52297044
 H   -5.29200659  -2.00415534  -1.51837748
 H   -3.52196869  -3.70928576  -1.12746136
 H   -1.19022713  -3.01340145  -0.72720266
 C   -0.07656338   0.01738873   1.73156736
 C   -0.77407552   1.25263038   1.68087324
 C   -0.08007108   2.44893751   1.79774098
 C    1.31221420   2.43141320   1.98330649
 C    2.00984423   1.21567031   2.07550115
 C    1.32068492   0.01541461   1.96149059
 H   -1.86051924   1.25328092   1.55955636
 H   -0.61175089   3.40242142   1.75719830
 H    1.86339485   3.37163771   2.06226875
 H    3.09280706   1.21605998   2.22867581
 H    1.85623524  -0.93121258   2.07987642
 H   -0.64071716  -0.91454402   1.82224861
 Al   4.78723897   1.23554402  -0.84371837
 Cl   5.55129211   0.52719216   1.01890807
 Cl   5.85146046   0.84266651  -2.62536589
 Cl   3.65359519   3.05319723  -0.72515874
 34
 Energy -2256.432171365  Charge 1  Dipole 10.775056  ZPE 0.245046  G(298.15) 119.06
Edisp -32.32
 C    0.89887070  -1.31653632  -0.97259331
 C   -0.26994589  -0.39384095  -0.68884071
 C   -1.60922690  -0.84542637  -0.86045918
 C    2.17892504  -0.63080949  -0.98894658
 C   -2.62518674   0.12312883  -1.10529564
 C   -3.92736157  -0.27450452  -1.36131157
 C   -4.25325506  -1.63895788  -1.35202853
 C   -3.27012565  -2.60966878  -1.09746126
 C   -1.96220716  -2.22385225  -0.85425624
 N    3.18031246  -0.05430278  -1.02937624
 H    0.74775492  -1.74145359  -1.98719052
 H    0.95613443  -2.17967809  -0.28733591
 H   -0.07657198   0.67247283  -0.83528904
 H   -2.36130691   1.18446871  -1.11665292
 H   -4.69773315   0.47083945  -1.57033342
 H   -5.28320347  -1.95110902  -1.54370848
 H   -3.53850123  -3.66824698  -1.09298393
 H   -1.20890277  -2.99025463  -0.65473863
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 C   -0.06015029  -0.02409790   1.68048600
 C   -0.78671742   1.19903369   1.68335729
 C   -0.11866349   2.40528816   1.82798486
 C    1.27702868   2.41357312   1.99426441
 C    2.00387846   1.21271204   2.04556417
 C    1.34113351   0.00165231   1.90546884
 H   -1.87378476   1.17811278   1.57031071
 H   -0.67158304   3.34742402   1.82276200
 H    1.80794397   3.36392175   2.09131721
 H    3.08813446   1.23289664   2.18851052
 H    1.89926820  -0.93498954   1.99549129
 H   -0.60294120  -0.96710726   1.78703681
 Al   4.78458039   1.22766585  -0.85257762
 Cl   5.54065479   0.52998310   1.01846849
 Cl   5.86810570   0.85199394  -2.62502006
 Cl   3.62464302   3.02966912  -0.73462280
 34
 Energy -2256.44117238  Charge 1  Dipole 5.029519  ZPE 0.247022  G(298) 121.81  Edisp -
33.12
 C    0.78930593  -1.40541720  -0.88716222
 C   -0.24997525  -0.33250314  -0.43100201
 C   -1.66335066  -0.78590867  -0.70867185
 C    2.11003104  -0.81329523  -0.97234939
 C   -2.44051555  -0.08602206  -1.64386271
 C   -3.73661969  -0.51157039  -1.94472073
 C   -4.26676171  -1.63635416  -1.31127781
 C   -3.49907325  -2.33908532  -0.37567690
 C   -2.20551994  -1.91562419  -0.07462078
 N    3.10184323  -0.21558068  -1.01270078
 H    0.50103825  -1.74717176  -1.89750106
 H    0.81454527  -2.29830343  -0.24070180
 H   -0.04339143   0.56534341  -1.03498004
 H   -2.02900330   0.79413806  -2.14843937
 H   -4.33226459   0.04034916  -2.67550583
 H   -5.28188480  -1.96758489  -1.54249510
 H   -3.91170855  -3.22073022   0.12010966
 H   -1.62127795  -2.48248727   0.65934607
 C   -0.06353523   0.12413009   1.12782447
 C   -0.54560079   1.51868009   1.20477646
 C    0.26356785   2.54012086   1.62255449
 C    1.58488148   2.25640246   2.04933998
 C    2.05778431   0.92612155   2.15719200
 C    1.27663130  -0.10206629   1.70863442
 H   -1.56306460   1.71670653   0.85150691
 H   -0.09184633   3.57282311   1.61976705
 H    2.22798472   3.07538089   2.38113273
 H    3.05938789   0.74001690   2.55246485
 H    1.63893949  -1.13120093   1.79769972
 H   -0.77581138  -0.53691765   1.66774887
 Al   4.56941368   1.15934644  -0.73769803
 Cl   5.46742510   0.40293456   1.04017314
 Cl   5.60596422   1.23475862  -2.56702156
 Cl   3.25246123   2.86057075  -0.35388284
```

*Structures **25** and **15**+C_6H_6*

```
30
  Energy -633.7928895381  Charge 1  Dipole 6.649794  HoF 264.39
 C   -1.15064769  -0.76940387   1.68378472
 C   -0.63101197  -0.26472134   0.37711478
 C   -0.29149632   1.21838009   0.44912051
 C   -2.30554096  -1.41966018   1.80253208
 C   -0.99500022   2.12286623  -0.35658652
 C   -0.71692515   3.49052191  -0.28975395
 C    0.27123635   3.96346846   0.57521234
 C    0.97945719   3.06586787   1.37969138
 C    0.69884392   1.70026808   1.31608257
 N   -3.43057979  -1.85694066   1.91365728
 H   -3.64829110  -2.85935410   1.95776538
 H   -0.61631220  -0.52584365   2.60719647
```

```
H   -1.39827122  -0.41101725  -0.39923693
H   -1.77581460   1.76069132  -1.03256806
H   -1.27901987   4.18753586  -0.91595275
H    0.49012874   5.03266233   0.62589099
H    1.75009717   3.43092431   2.06265479
H    1.25952677   1.01626048   1.96428366
C    0.65145671  -1.07505562  -0.13144513
C    1.25902618  -0.49019452  -1.33427576
C    1.54966184  -1.24969501  -2.44500325
C    1.29539686  -2.63372151  -2.42958895
C    0.75464967  -3.27047808  -1.29268947
C    0.42673650  -2.52260655  -0.18786035
H    1.46731487   0.58333248  -1.32245527
H    1.98337315  -0.78700581  -3.33440663
H    1.51440082  -3.22868143  -3.32144698
H    0.57482883  -4.34779921  -1.30961726
H   -0.04796937  -2.98896288   0.68088157
H    1.36074489  -0.87163776   0.70701875
30
 Energy -633.8390353571  Charge 1  Dipole 6.863551  HoF 235.43
C   -1.57262331  -0.43028619   1.94788825
C   -0.71012874   0.12781630   1.01511858
C   -0.43128024   1.51750982   0.85628939
C   -1.76044420  -1.78061660   2.02980784
C    0.48742457   1.89192070  -0.16132477
C    0.80346513   3.22753944  -0.36566366
C    0.21216776   4.21076624   0.43660865
C   -0.69919644   3.86016943   1.44750611
C   -1.02088032   2.53070263   1.65932468
N   -2.04898532  -2.92558077   2.05495017
H   -1.76418383  -3.79905734   2.49787696
H   -2.13602147   0.16358086   2.67417862
H   -0.19387699  -0.56008638   0.33282277
H    0.93757837   1.10965100  -0.77957818
H    1.50997478   3.51147614  -1.14836299
H    0.46048236   5.26328910   0.27677671
H   -1.15272419   4.63844238   2.06481491
H   -1.73151796   2.27396898   2.44848617
C    2.04879449  -2.19244855  -0.81412409
C    2.00819468  -1.25004637  -1.84744962
C    0.85469399  -1.11490297  -2.62814115
C   -0.25962810  -1.92223546  -2.37710986
C   -0.21640752  -2.87165014  -1.35049926
C    0.93746990  -3.00621239  -0.56909494
H    2.88897967  -0.63794387  -2.06085835
H    0.83108454  -0.39446746  -3.45032934
H   -1.15332318  -1.82978191  -2.99972225
H   -1.07519174  -3.52802422  -1.18292034
H    0.98859044  -3.77150969   0.21100025
H    2.95751284  -2.31198272  -0.21827127
```

*Structures **26** and **16**+C_6H_6*

```
33
 Energy -2256.065694597  Dipole 13.398734
C   -1.01070317  -0.10869202   1.56088273
C   -0.33860800   0.30222698   0.31613325
C    0.02328534   1.78034829   0.35209778
C   -1.82918216  -1.19579870   1.54742150
C   -0.55562845   2.66067021  -0.57034371
C   -0.24083846   4.02157032  -0.54695969
C    0.66133470   4.51716387   0.39636002
C    1.24396190   3.64536041   1.32014301
C    0.92605757   2.28609310   1.29718640
N   -2.50077976  -2.16326129   1.43377294
Al  -2.71658014  -4.07374075   1.15218071
H   -0.75181195   0.34749039   2.51777429
H   -1.00624440   0.12158676  -0.53986507
H   -1.26600829   2.27811532  -1.30961957
H   -0.70638960   4.69678150  -1.26953983
```

```
H    0.90855309   5.58150060   0.41487660
H    1.94801505   4.02536794   2.06485563
H    1.38649157   1.61757506   2.03311913
C    0.96681078  -0.54854476  -0.04728008
C    1.57441956  -0.02164708  -1.28079331
C    1.58363441  -0.74613081  -2.45070326
C    1.12594234  -2.07819762  -2.46200394
C    0.71064782  -2.70353570  -1.26972612
C    0.65697709  -1.98536819  -0.09940134
H    1.94830835   1.00504248  -1.26573292
H    1.96917470  -0.29876172  -3.37043568
H    1.10856252  -2.63838287  -3.40077595
H    0.39519412  -3.74981991  -1.27327481
H    0.29184959  -2.48254373   0.80561219
H    1.61888333  -0.31621965   0.81512982
Cl  -2.92409924  -4.20775772  -0.98932178
Cl  -4.39568927  -4.70457365   2.30872341
Cl  -0.80554091  -4.86391708   1.80950766
33
 Energy -2256.140973513  Dipole 12.798221
C   -1.44756558   0.10482761   1.71699791
C   -0.57969670   0.65913610   0.82553416
C   -0.21430726   2.05994321   0.73369933
C   -1.72017315  -1.26934283   1.70392666
C    0.70116720   2.43934737  -0.27144051
C    1.09047511   3.76906289  -0.41228710
C    0.57394338   4.74165184   0.44711354
C   -0.33494961   4.37999984   1.45061133
C   -0.72660669   3.05501311   1.59464600
N   -1.96095627  -2.40888347   1.70968436
Al  -2.29257517  -4.36565696   1.62541072
H   -1.97530183   0.68292594   2.48048439
H   -0.10341095  -0.01021523   0.09863859
H    1.10056092   1.66995294  -0.93914604
H    1.79943699   4.04910186  -1.19498743
H    0.87812555   5.78584634   0.33868875
H   -0.73750574   5.14169852   2.12256834
H   -1.43594043   2.79170841   2.38329689
C    2.24605111  -1.77579535  -0.85544123
C    2.37807826  -0.81508725  -1.86381406
C    1.33301750  -0.60478547  -2.77012454
C    0.15679612  -1.35527862  -2.66710407
C    0.02682765  -2.31958183  -1.66233713
C    1.07240638  -2.53005374  -0.75578959
H    3.30302813  -0.23761618  -1.95057554
H    1.43982030   0.13698404  -3.56697090
H   -0.65745392  -1.19622033  -3.37960988
H   -0.88586717  -2.91880551  -1.58328217
H    0.96720503  -3.29191358   0.02322161
H    3.06539273  -1.94539550  -0.15126422
Cl  -3.02241638  -4.59606006  -0.37797679
Cl  -3.71169793  -4.67307763   3.18955610
Cl  -0.32590758  -5.15343049   1.95807253
```

*Structures **30** and **20**+C_6H_6*

```
33
 Energy -2256.040859473  Dipole 14.059794
C   -0.57486091   0.54793175   1.73728237
C   -0.09448717  -0.08582583   0.43872469
C   -0.79856644   0.45405021  -0.79303424
C    0.03730351  -0.05381455   2.87033860
C   -1.60056083  -0.39343551  -1.56909196
C   -2.26942329   0.09812246  -2.69174820
C   -2.13677092   1.43860600  -3.05635527
C   -1.33711976   2.29061564  -2.28969588
C   -0.67201119   1.79881639  -1.16763138
N    0.60717335  -0.61978009   3.72522577
Al  -2.69232969   0.21185513   2.04183654
H   -0.51536508   1.64885868   1.77141786
```

```
H   -0.29332460  -1.16634073   0.51848454
H   -1.73216121  -1.43614144  -1.26655461
H   -2.90526962  -0.57067509  -3.27727456
H   -2.66095792   1.82356938  -3.93469715
H   -1.23860892   3.34431714  -2.56191511
H   -0.06160998   2.48573509  -0.56975179
C    1.48426618   0.03730568   0.20986556
C    1.80684633  -0.87910996  -0.89988189
C    2.67247674  -1.93172877  -0.75059521
C    3.35396835  -2.11455251   0.47347596
C    3.20335732  -1.20478210   1.52715501
C    2.33153341  -0.14007923   1.40277183
H    1.24393441  -0.74651782  -1.82807033
H    2.84062988  -2.63022190  -1.57357292
H    4.03066475  -2.96580366   0.58955598
H    3.78309899  -1.32720068   2.44431702
H    2.29762820   0.61638033   2.18651501
H    1.57390863   1.08944477  -0.12541992
Cl  -3.74960373   1.58988149   0.76940906
Cl  -2.98321112   0.66677678   4.12363973
Cl  -2.95054765  -1.87625706   1.52527490
33
 Energy -2256.099636382  Dipole 7.665359
C   -0.78638709   1.32839743   1.89233638
C   -0.53314975   0.71942566   0.68067235
C   -1.16538783   0.97359044  -0.59171889
C    0.12776644   1.16282635   2.97644249
C   -0.80026324   0.14993952  -1.68058339
C   -1.35849081   0.35235003  -2.93882741
C   -2.28421925   1.38158364  -3.13155830
C   -2.64926561   2.21211820  -2.06341789
C   -2.09789767   2.01331559  -0.80494797
N    0.90174050   1.04814594   3.84128552
Al  -2.53992323  -0.35322057   2.59492955
H   -1.49451121   2.16082827   1.98545858
H    0.25092985  -0.04834739   0.67642678
H   -0.06888487  -0.64790801  -1.51974686
H   -1.07180695  -0.29169242  -3.77334926
H   -2.72268596   1.54359167  -4.11970808
H   -3.36944034   3.01842042  -2.22020051
H   -2.38851554   2.66966729   0.01830964
C    3.50087021  -0.34787111  -0.21451475
C    3.15062256  -1.17181895  -1.28841820
C    2.35507643  -2.30196382  -1.07236980
C    1.90807684  -2.60644029   0.21757612
C    2.26165603  -1.78386119   1.29215269
C    3.05827758  -0.65435445   1.07611240
H    3.50278990  -0.93538777  -2.29632973
H    2.08836157  -2.95181516  -1.91077899
H    1.28317250  -3.48710794   0.38880502
H    1.90951634  -2.01819574   2.30013615
H    3.32648946  -0.01167940   1.91886638
H    4.12443150   0.53430715  -0.38318835
Cl  -4.08690210   0.00844432   1.18159301
Cl  -2.83455868   0.53441755   4.50085382
Cl  -1.49748756  -2.19970527   2.46770150
```

*Structures **31** and **21**+C_6H_6*

```
34
 Energy -2256.396506809  Charge 1  Dipole 9.764540
C   -0.45898488   0.90787003   1.52654997
C   -0.00492829  -0.01395429   0.39731697
C   -0.99343558  -0.04181825  -0.75089536
C    0.08806809   0.82090723   2.75632732
C   -1.58693635  -1.25560676  -1.12719070
C   -2.51302688  -1.29065187  -2.17112164
C   -2.84167842  -0.11948760  -2.85671416
C   -2.24383354   1.09263998  -2.49597384
C   -1.32112810   1.12853862  -1.45215802
```

```
N    0.66764334   0.75728302   3.80663724
H    0.27757276   0.35896033   4.67151098
Al  -2.56578063  -0.06374128   2.50280928
H   -0.91023715   1.87614949   1.27226977
H    0.09780166  -1.03141055   0.80749835
H   -1.34988060  -2.17218440  -0.57941978
H   -2.98506822  -2.23766705  -2.44336582
H   -3.56375987  -0.14859489  -3.67623406
H   -2.49928834   2.01111027  -3.02923372
H   -0.86609969   2.09031760  -1.18494214
C    1.44114648   0.37827838  -0.16395061
C    1.82616177  -0.46456593  -1.30710993
C    3.07882962  -1.02073665  -1.41460165
C    4.02661923  -0.80218276  -0.39556950
C    3.73853493   0.01005698   0.71866934
C    2.49507404   0.58637651   0.83889538
H    1.06364533  -0.65226309  -2.06879659
H    3.33719844  -1.64447500  -2.27329090
H    5.01122336  -1.27428895  -0.47121071
H    4.50367457   0.17921988   1.47964367
H    2.28402199   1.23522797   1.69234827
H    1.23761091   1.39180919  -0.59455770
Cl  -2.62990154   0.87612817   4.41396408
Cl  -1.88727482  -2.09010021   2.50374886
Cl  -3.95358361   0.62285589   1.06814735
34
 Energy -2256.445800682  Charge 1  Dipole 5.796751
C   -2.05584240   0.60145005   0.61133939
C   -1.19200323   0.47493561  -0.45879084
C   -1.50177688   0.73378051  -1.83218383
C   -1.64818697   0.32424898   1.89427739
C   -0.46951661   0.54300441  -2.78655329
C   -0.70439393   0.77952592  -4.13471887
C   -1.96832787   1.20904568  -4.55385357
C   -3.00218033   1.40299741  -3.62326893
C   -2.77663220   1.16945245  -2.27653941
N   -1.31240122   0.19716485   3.01170441
H   -1.18393820  -0.44354084   3.82530727
Al   0.61338552  -0.92470632   6.60130484
H   -3.09907525   0.91449071   0.50944470
H   -0.16734605   0.14653007  -0.24256094
H    0.51255185   0.20611340  -2.44210840
H    0.09376498   0.63127607  -4.86511429
H   -2.15486393   1.39600972  -5.61452627
H   -3.98424195   1.73885016  -3.96292972
H   -3.59098995   1.32641536  -1.56514907
C    2.74441357   0.52074080   0.39770268
C    2.92454078  -0.08568257  -0.84999560
C    2.49442116  -1.40071719  -1.05873942
C    1.88338640  -2.11111554  -0.02017129
C    1.71050829  -1.50723145   1.22959669
C    2.14069912  -0.19178693   1.43928921
H    3.42213637   0.46222378  -1.65494853
H    2.65508080  -1.88258521  -2.02707726
H    1.56294357  -3.14416566  -0.17896278
H    1.26279748  -2.07733000   2.04942960
H    2.03080000   0.27283431   2.42382388
H    3.09626454   1.54217586   0.56498833
Cl   1.48158186   0.77050670   5.72728107
Cl  -0.95170306  -1.82103652   5.43802086
Cl   1.13414374  -1.77387458   8.42468197
```

*Structures **32** and **22**+C_6H_6*

```
37
 Energy -3878.688788456  Dipole 15.968506
C   -0.87107823   0.76393759   1.10866376
C   -0.29351252   0.07584248  -0.13281437
C   -0.93032595   0.56140029  -1.42303560
C   -0.40991363   0.18237132   2.30205283
```

```
C   -1.69566890  -0.32087225  -2.19741493
C   -2.30306275   0.11913194  -3.37525559
C   -2.14436563   1.44020724  -3.79511736
C   -1.37970966   2.32569309  -3.03032574
C   -0.77518079   1.88596342  -1.85394959
N    0.01380068  -0.39365864   3.22735362
Al  -3.04261393   0.50758168   1.27347286
H   -0.79787858   1.86363425   1.13276468
H   -0.50210337  -1.00018834  -0.01986167
H   -1.84807383  -1.34818432  -1.85500097
H   -2.91061122  -0.57527365  -3.96076085
H   -2.62035304   1.78453059  -4.71659959
H   -1.26097582   3.36457379  -3.34713479
H   -0.19315415   2.60078079  -1.25983342
C    1.29501403   0.19283284  -0.28413080
C    1.70002692  -0.74133935  -1.34738353
C    2.62439583  -1.73321659  -1.13191017
C    3.25665549  -1.83777888   0.12523138
C    3.01527157  -0.90537499   1.14740080
C    2.08405285   0.08975255   0.95199579
H    1.16838732  -0.66875515  -2.30068087
H    2.86304446  -2.44975052  -1.92105390
H    3.95895781  -2.65672150   0.30733991
H    3.54300401  -0.96919182   2.10244872
H    1.93859094   0.83119729   1.74194832
H    1.40055483   1.23518772  -0.65665763
Al   1.16256250  -1.24380320   4.57860350
Cl   2.84024695   0.12931946   4.58360674
Cl   0.05751113  -1.36137776   6.38531918
Cl   1.66894171  -3.09846467   3.60642898
Cl  -3.94025587   1.86635720  -0.12172178
Cl  -3.37779417   1.07477535   3.31616969
Cl  -3.29438698  -1.59111927   0.83984236
37
 Energy -3878.738171058  Dipole 12.537524
C   -0.91938145   1.37878218   1.21845898
C   -0.48054048   0.98956955  -0.01447258
C   -1.10746258   1.28853062  -1.28701612
C   -0.19717174   1.06956676   2.38052347
C   -0.51748751   0.75535272  -2.45371845
C   -1.07069755   1.00615270  -3.70621120
C   -2.22027257   1.79259694  -3.81530882
C   -2.81650463   2.32943715  -2.66640237
C   -2.26860395   2.08283034  -1.41416468
N    0.38899743   0.83346706   3.35819504
Al  -3.10488749  -1.52385147   0.94900589
H   -1.82381262   1.97449038   1.37251906
H    0.43857486   0.39162701  -0.05917069
H    0.37939626   0.13647258  -2.35591142
H   -0.60532339   0.58731189  -4.60146194
H   -2.65607705   1.99141019  -4.79775408
H   -3.71432753   2.94562968  -2.75427725
H   -2.74549633   2.51242943  -0.53013370
C    3.26055296  -0.59421153  -0.48215392
C    2.69384347  -1.32309490  -1.53383782
C    1.74211201  -2.31302987  -1.26567659
C    1.36161886  -2.57707161   0.05430851
C    1.93456910  -1.85494875   1.10627199
C    2.88286951  -0.86083880   0.83808696
H    3.00526270  -1.12703052  -2.56414598
H    1.30203844  -2.88773082  -2.08570944
H    0.62175204  -3.35452782   0.26486247
H    1.65074186  -2.06739428   2.14193530
H    3.32854087  -0.30151283   1.66672075
H    4.00838681   0.17596746  -0.69115640
Al   1.47014776   0.37050176   4.96369646
Cl   3.42784261   0.99393671   4.34922279
Cl   0.54709567   1.52591125   6.50132458
Cl   1.19851527  -1.75317834   5.07411971
```

```
 Cl  -4.52057927   0.02958704   1.12219787
 Cl  -2.10594098  -2.22763807   2.65141464
 Cl  -2.76829135  -2.39550178  -0.93418103
```

*Structures **34**, TS **34→33** and **33***

```
31
 Energy -634.0682724196  Charge 2  Dipole 8.255698  ZPE 0.252322  G(298.15) 131.05  HoF
460.09 kcal  Edisp -23.92
 C    1.26067691  -0.05254385  -0.85190192
 C   -0.10887570  -0.15682073  -0.65003905
 C   -1.10363533  -0.47602148  -1.61204533
 C    2.19295310   0.26718833   0.14212688
 C   -2.46306479  -0.53040240  -1.18076515
 C   -3.47580038  -0.83683380  -2.07307121
 C   -3.15960006  -1.09631968  -3.41569528
 C   -1.82656236  -1.04885446  -3.86543877
 C   -0.80819385  -0.74373469  -2.98238858
 N    3.49700450   0.35168079  -0.12998066
 H    3.84347107   0.18464504  -1.07915446
 H    1.66867883  -0.22800257  -1.85269519
 H   -0.49273812   0.02399300   0.36464111
 H   -2.70175182  -0.32686054  -0.13292085
 H   -4.51444950  -0.87736376  -1.73839671
 H   -3.95799227  -1.33876101  -4.12244092
 H   -1.60043483  -1.25388221  -4.91407609
 H    0.22017801  -0.71139281  -3.34845616
 C   -0.14384419   0.79732293   3.65895532
 C    0.16751326   1.93131200   2.87601215
 C    1.05871009   1.81722925   1.83484719
 C    1.76906049   0.53816173   1.58961447
 C    1.30316721  -0.63563874   2.36799917
 C    0.40812643  -0.47713510   3.40002088
 H   -0.30623294   2.89184492   3.09595495
 H    1.32630929   2.68321784   1.22001251
 H    2.71786026   0.75739523   2.16922594
 H    1.75440943  -1.61024473   2.15336181
 H    0.11611094  -1.33242995   4.01534516
 H   -0.84627857   0.90856698   4.49277689
 H    4.20522489   0.58068448   0.56857188
 31
 Energy -634.0105754376  Charge 2  Dipole 10.216218  ZPE 0.250115  G(298.15) 129.68  HoF
496.29 kcal  Edisp -24.59
 C    1.60359490  -0.90309307  -0.71612079
 C    0.43872097  -0.02321616  -0.45138211
 C   -0.77235643  -0.30614688  -1.18319019
 C    2.81168505  -0.50598715  -0.98694805
 C   -1.60499865   0.79334601  -1.53459706
 C   -2.74531453   0.59020366  -2.29547875
 C   -3.09778458  -0.70968357  -2.69470206
 C   -2.29871782  -1.80968666  -2.33850967
 C   -1.14810074  -1.61493996  -1.59163709
 N    3.97904958  -0.15676136  -1.30828370
 H    4.23687427   0.03269756  -2.29455490
 H    1.46306741  -1.99402886  -0.78340103
 H    0.68721487   1.03368830  -0.31817087
 H   -1.32838791   1.80527425  -1.22437172
 H   -3.36964423   1.43906505  -2.58376881
 H   -4.00569588  -0.86895346  -3.28284444
 H   -2.58766059  -2.81639657  -2.64817729
 H   -0.55233478  -2.48926444  -1.31254659
 C    0.06479397  -0.39933129   1.65453749
 C   -0.96183984   0.57459673   1.88299356
 C   -0.70795037   1.68980348   2.65933926
 C    0.56314961   1.85766266   3.24236699
 C    1.57630803   0.89341446   3.07142320
 C    1.32722916  -0.23434103   2.30997137
 H   -1.94669622   0.42777320   1.43126962
 H   -1.49039897   2.43101512   2.83838033
 H    0.76157396   2.74320283   3.85346463
```

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 H    2.53515693   1.02193468   3.57940186
 H    2.08103582  -1.02324717   2.23573515
 H   -0.24958676  -1.41754797   1.39965011
 H    4.73801375  -0.06105239  -0.60984845
 31
 Energy -634.0215161171  Charge 2  Dipole 10.202034  ZPE 0.251008  G(298.15) 130.63  HoF
489.43 kcal  Edisp -24.25
 C    1.67269241  -0.85821664  -0.64495194
 C    0.55860888   0.10295494  -0.21522304
 C   -0.65316651  -0.20913829  -1.07142725
 C    2.72098324  -0.54869224  -1.34023121
 C   -1.11647764   0.76116196  -1.97610736
 C   -2.22498488   0.49267584  -2.77974579
 C   -2.87148957  -0.74395574  -2.69178900
 C   -2.41194637  -1.71659956  -1.79586443
 C   -1.30683976  -1.45188179  -0.98883740
 N    3.68761005  -0.26199622  -2.10162454
 H    3.57454356  -0.23359361  -3.13059232
 H    1.54587684  -1.93295846  -0.44042991
 H    0.88470015   1.13682335  -0.40674092
 H   -0.61761327   1.73279733  -2.04977623
 H   -2.58640327   1.25275459  -3.47640810
 H   -3.73992367  -0.95201801  -3.32163736
 H   -2.91842576  -2.68194881  -1.72696396
 H   -0.96853466  -2.23049996  -0.29414144
 C    0.26380385  -0.00926326   1.34507571
 C   -0.94021150   0.74171782   1.75590658
 C   -0.99481357   1.40104858   2.96090759
 C    0.14584960   1.43218011   3.79038175
 C    1.35042666   0.78342100   3.43480347
 C    1.42693789   0.10011524   2.24622761
 H   -1.80274230   0.72606188   1.08196061
 H   -1.90576839   1.92015994   3.26929979
 H    0.09976440   1.98160754   4.73706829
 H    2.21022202   0.83289212   4.10752278
 H    2.35127952  -0.41898697   1.97270511
 H   -0.07115343  -1.07632659   1.48903602
 H    4.63719546  -0.07229609  -1.73840312
```

*Structures **35** and **24**+C_6H_6*

```
37
  Energy -3878.689946148  Dipole 17.552182
 C   -0.15989169  -0.64214198  -1.40084226
 C    0.40007992   0.03649360  -0.19007558
 C    1.91998590   0.03003980  -0.22838994
 C   -1.27228167  -1.35716006  -1.28876039
 C    2.61947674  -0.77105442   0.68406127
 C    4.01518161  -0.81883357   0.65245677
 C    4.72383763  -0.06503109  -0.28511893
 C    4.03168539   0.73135683  -1.20174599
 C    2.63668991   0.77602846  -1.17390506
 N   -2.28938693  -1.99394682  -1.06739322
 Al  -1.95473018  -3.68380997   0.07202048
 H    0.37520855  -0.62564280  -2.35262353
 H    0.06489076  -0.52093674   0.69958122
 H    2.06383133  -1.37908545   1.40447724
 H    4.54874246  -1.45607948   1.36221874
 H    5.81579690  -0.10247037  -0.30794102
 H    4.57926887   1.31586150  -1.94531476
 H    2.10975627   1.39514359  -1.90936460
 C   -0.13931973   1.52524122   0.03944247
 C    0.50319656   2.12476711   1.21749242
 C   -0.22900005   2.54499639   2.30159325
 C   -1.63720964   2.46776074   2.26882973
 C   -2.32052078   2.01203641   1.12767689
 C   -1.60426379   1.56645432   0.04034128
 H    1.59525862   2.17305902   1.23010551
 H    0.27124900   2.93928323   3.18905437
 H   -2.20961433   2.77148593   3.15043062
```

```
H   -3.41202387   1.96651938   1.10984074
H   -2.13651345   1.18658499  -0.84312786
H    0.23820398   2.03345924  -0.87412508
Al  -4.10926463  -1.23253988  -1.55800416
Cl  -3.86722103  -4.45787447   0.57273369
Cl  -0.90261719  -2.79171777   1.75767046
Cl  -0.68306202  -4.86480397  -1.17683124
Cl  -3.55941187   0.48179260  -2.78162771
Cl  -4.88057295  -0.57776068   0.34088599
Cl  -5.14543460  -2.73747485  -2.63572180
37
 Energy -3878.740883333  Dipole 14.216765
C    0.06647174  -1.69805465  -1.36107466
C    0.68629432  -0.67888804  -0.67587567
C    2.07630787  -0.32036506  -0.74997834
C   -1.28050229  -1.91955374  -1.18904202
C    2.51259361   0.78538792   0.01890189
C    3.84572796   1.17994977  -0.01030713
C    4.76200918   0.48071629  -0.80143416
C    4.34511962  -0.61797609  -1.56796409
C    3.01717395  -1.01725153  -1.54601667
N   -2.44103846  -2.12232975  -1.03527556
Al  -2.97901325  -3.65534401   0.41524519
H    0.57742527  -2.36264801  -2.06284906
H    0.06368111  -0.06769949  -0.00945028
H    1.78764802   1.32693332   0.63487042
H    4.17441570   2.03468923   0.58500700
H    5.81022910   0.78990641  -0.82421776
H    5.06743093  -1.16007075  -2.18239721
H    2.70595426  -1.87571518  -2.14589714
C   -0.47801515   3.28768608   1.04167399
C    0.25351082   2.98612290   2.19592059
C   -0.05134430   1.84016473   2.93876194
C   -1.09393549   1.00079624   2.53261384
C   -1.83180716   1.30817930   1.38392073
C   -1.52021653   2.44867136   0.63521657
H    1.05715785   3.65222411   2.52347342
H    0.51750085   1.60652466   3.84311131
H   -1.34216279   0.10761203   3.11250095
H   -2.66300599   0.66455168   1.07942136
H   -2.09766004   2.67872405  -0.26422304
H   -0.24172388   4.18506856   0.46299552
Al  -3.90502220  -0.95901434  -2.10366645
Cl  -4.80161999  -4.41625670  -0.33575771
Cl  -2.99550224  -2.46075779   2.18158868
Cl  -1.24738722  -4.89995351   0.19676760
Cl  -2.64764208   0.65970486  -2.74781712
Cl  -5.24853777  -0.47254656  -0.53508447
Cl  -4.46051534  -2.31918828  -3.63366243
```

*Cation **38***

```
22
 Energy -462.1711680263  Charge 1  Dipole 2.715640  ZPE 0.177426  G(298) 88.10  HoF
153.00 kcal  Edisp -14.75
C   -0.72721319   1.77575286   0.90775729
C   -1.28880502   0.54280415   0.39608536
C   -0.61864767  -0.67692059   0.25125222
C    0.32614443   2.42388275  -0.17409219
C   -1.28925165  -1.74842885  -0.42602003
C   -0.63749766  -2.94224341  -0.65961925
C    0.69207571  -3.10219992  -0.22717617
C    1.37038565  -2.07285958   0.44595565
C    0.72702658  -0.87485562   0.70001980
O    1.26208993   1.77945764  -0.54305861
H   -0.06759606   1.63281458   1.78038625
H   -1.49624400   2.52556740   1.13001977
H   -2.30991906   0.59099742  -0.00238590
H   -2.31838997  -1.60033440  -0.76502853
```

```
 H   -1.14489804  -3.75840869  -1.17797646
 H    1.20361861  -4.05178243  -0.40812281
 H    2.39763970  -2.22712948   0.78210083
 H    1.24262252  -0.08957183   1.25349808
 C   -0.00166894   3.83693138  -0.54930881
 H    0.76370338   4.22800214  -1.23193987
 H   -0.99702278   3.86679946  -1.02432904
 H   -0.05907222   4.45668120   0.36144777
```

*Dication **5a***

```
 23
 Energy -462.3497151613  Charge 2  Dipole 4.216797  ZPE 0.188158  G(298.15) 93.97  HoF
409.47 kcal  Edisp -14.76
 C    0.54916721   1.58720896   0.42985143
 C   -0.42993181   0.44898802   0.43417683
 C   -0.16046503  -0.87944823   0.18608633
 C    0.03630224   2.91423409  -0.05816358
 C   -1.25251161  -1.82344291   0.36039579
 C   -1.04779823  -3.16880839   0.15829614
 C    0.23336351  -3.62221023  -0.22216553
 C    1.32091281  -2.72950800  -0.40345102
 C    1.13903372  -1.38214621  -0.20900771
 O    0.59709778   4.00450863   0.31656530
 H    1.32826477   3.92466212   0.98338078
 H    1.43899854   1.37214406  -0.19941575
 H    0.94044628   1.69666864   1.46604278
 H   -1.45383942   0.69850761   0.74281439
 H   -2.23625406  -1.45031046   0.66079594
 H   -1.86365821  -3.88366781   0.28999190
 H    0.39460228  -4.69342655  -0.38466209
 H    2.29648719  -3.12248107  -0.69966423
 H    1.98214059  -0.70213862  -0.35351024
 C   -1.07024840   3.05896300  -1.00256372
 H   -1.11307619   2.22022986  -1.71612069
 H   -2.01779380   3.02260155  -0.41648576
 H   -1.04536023   4.03692837  -1.50696067
```

*Structure **39***

```
 26
 Energy -2084.797942273  Charge 1  Dipole 9.325169  ZPE 0.184381  G(298) 86.28  Edisp -
22.39
 C    1.83378836  -0.55627528   0.26980888
 C    0.38762024  -0.99784892   0.30842588
 C    0.05917800  -2.39835652   0.08104956
 C    2.15482375   0.88493640   0.57935205
 C   -1.08371217  -2.92417374   0.72574764
 C   -1.42326215  -4.26272749   0.56858789
 C   -0.63918821  -5.08795659  -0.24503610
 C    0.48792622  -4.57536643  -0.90161489
 C    0.83732963  -3.24001379  -0.74427003
 O    1.31085442   1.80380546   0.51990139
 Al  -0.49351008   2.07841907  -0.03369476
 H    2.31407712  -0.78429014  -0.70167738
 H    2.38497482  -1.17670452   1.00469627
 H   -0.19072344  -0.54181930   1.12577823
 H   -1.69797606  -2.27271205   1.35452299
 H   -2.30159990  -4.66659797   1.07664566
 H   -0.90904658  -6.13923205  -0.37333944
 H    1.09046213  -5.22508062  -1.54001699
 H    1.71172518  -2.85344861  -1.27414274
 C    3.54344032   1.21328669   0.99053800
 H    3.61424576   1.04370350   2.08406341
 H    4.28156878   0.54838176   0.51730932
 H    3.76711983   2.27130414   0.79818435
 Cl  -0.53748533   3.70102631  -1.34461548
 Cl  -1.64383709   1.78294637   1.70633484
 Cl  -0.52070655   0.11737009  -1.23955379
```

Pre-reaction complex, TS and product of the reaction ***38*** *+* C_6H_6 *→* ***49***

```
34
 Energy -694.1843638953  Charge 1  Dipole 3.395273  ZPE 0.276183  G(298) 141.58  HoF
163.38 kcal
 C    1.59027382  -0.10548280  -1.00477545
 C    0.23868295  -0.26423154  -0.50523551
 C   -0.42657303  -1.48274693  -0.30707054
 C    2.66505871  -0.52601202   0.15434211
 C   -1.70879914  -1.45727397   0.33067955
 C   -2.37165343  -2.63545595   0.61338107
 C   -1.77847149  -3.86364252   0.27062111
 C   -0.52503934  -3.91697068  -0.36037393
 C    0.14549956  -2.74469440  -0.66266080
 O    2.68800373  -1.65191317   0.55669882
 H    1.85032237  -0.80498544  -1.81583890
 H    1.79246127   0.93143543  -1.30005915
 H   -0.27639410   0.64645349  -0.17227923
 H   -2.14163248  -0.48876121   0.59634253
 H   -3.34827279  -2.61908565   1.10142392
 H   -2.30800648  -4.79502586   0.48987989
 H   -0.08988811  -4.88274985  -0.62492784
 H    1.10652566  -2.78679894  -1.17612854
 C    3.56687561   0.59595277   0.57095597
 H    2.95175742   1.43429623   0.93886085
 H    4.12399131   0.96320005  -0.30750855
 H    4.26268651   0.24986498   1.34589367
 C    0.21292888   3.28489573   0.88409261
 C   -0.99493117   2.81753563   1.41677143
 C   -2.07539668   2.55224251   0.56827407
 C   -1.94543745   2.74222180  -0.81259949
 C   -0.73694852   3.20685140  -1.34472710
 C    0.34007758   3.48380177  -0.49553217
 H   -1.10230034   2.68954892   2.49720690
 H   -3.03170328   2.22604463   0.98734888
 H   -2.79542985   2.55358007  -1.47380888
 H   -0.64599147   3.38129752  -2.42014666
 H    1.26937649   3.88821511  -0.90736991
 H    1.04207795   3.53243658   1.55336976
34
 Energy -694.1678552274  Charge 1  Dipole 2.092361  ZPE 0.276230  G(298.15) 144.96  HoF
173.74 kcal  Edisp -27.48
 C    1.68422572   0.08621985  -0.55242033
 C    0.39516074   0.05928170   0.23244976
 C   -0.06685616   1.27251875   0.89856634
 C    2.37379328  -1.29315646  -0.62268042
 C   -0.70280914   1.15992519   2.15625422
 C   -1.07494852   2.29765994   2.86376304
 C   -0.84991871   3.56536168   2.31371529
 C   -0.23785776   3.69350881   1.05965138
 C    0.15394552   2.55924468   0.35806510
 O    1.92732875  -2.24210202  -0.01012022
 H    2.38082414   0.74872341  -0.00029166
 H    1.60488752   0.54086157  -1.55455814
 H    0.31285890  -0.86800230   0.81736356
 H   -0.87573694   0.16770305   2.58362019
 H   -1.54149168   2.20174314   3.84678901
 H   -1.15280887   4.45937809   2.86450055
 H   -0.06376942   4.68505534   0.63586006
 H    0.63708631   2.67137545  -0.61665747
 C   -1.05086151  -0.43942075  -1.11565706
 C   -2.22992674  -0.53359861  -0.30456925
 C   -2.79974643  -1.76100414  -0.03347009
 C   -2.24097805  -2.92815709  -0.58967966
 C   -1.13201212  -2.86379036  -1.44343873
 C   -0.56235800  -1.63405727  -1.73272393
 H   -2.64801515   0.37874423   0.12766679
 H   -3.68442210  -1.83191819   0.60312600
 H   -2.68655764  -3.89972126  -0.35889944
 H   -0.72963795  -3.77626146  -1.88766598
```

```
 H    0.26987053  -1.57478142  -2.43779506
 H   -0.87461749   0.50799435  -1.63727198
 C    3.62925749  -1.35112962  -1.45521926
 H    4.07759250  -2.35068409  -1.38814136
 H    3.40427917  -1.11350114  -2.50946333
 H    4.35421981  -0.59401307  -1.11066790
 34
 Energy -694.174514188  Charge 1  Dipole 3.710026  ZPE 0.278397  G(298.15) 146.70  HoF
169.56 kcal  Edisp -27.30
 C    1.64160958   0.06841667  -0.45668632
 C    0.27436762   0.01650129   0.25485443
 C   -0.10524097   1.35898837   0.85455034
 C    2.18775066  -1.30937687  -0.77941708
 C   -0.18357703   1.50395932   2.24613181
 C   -0.51330555   2.73721606   2.81549331
 C   -0.76762417   3.83869101   1.99761561
 C   -0.69017705   3.70505346   0.60802162
 C   -0.36091537   2.47340460   0.04108390
 O    1.44198922  -2.21618163  -1.15869490
 H    2.35709933   0.59247727   0.19650433
 H    1.59761597   0.65890386  -1.39245570
 H    0.38294950  -0.70409059   1.08442382
 H    0.01776209   0.64527284   2.89501636
 H   -0.57295752   2.83409038   3.90218879
 H   -1.02666564   4.80318247   2.44064223
 H   -0.88439481   4.56541438  -0.03680089
 H   -0.29590490   2.39533338  -1.05029146
 C   -0.89586510  -0.54985700  -0.65402252
 C   -1.99154078  -1.07338038   0.20201629
 C   -2.64123808  -2.23135717  -0.09212989
 C   -2.26539412  -2.98029755  -1.24924670
 C   -1.22955981  -2.58919954  -2.07900052
 C   -0.49354993  -1.43350527  -1.77848637
 H   -2.25909721  -0.47793087   1.08052425
 H   -3.45403683  -2.59458711   0.54046118
 H   -2.83090670  -3.88442647  -1.49479209
 H   -0.98193471  -3.17471105  -2.96653976
 H    0.13062940  -0.99510877  -2.55851905
 H   -1.31512073   0.35025074  -1.17122982
 C    3.65469900  -1.55356033  -0.60463305
 H    3.93476639  -2.55067187  -0.96695767
 H    4.22627467  -0.77205155  -1.13473995
 H    3.91149358  -1.45686207   0.46511545
```

Pre-reaction complex, TS and product of the reaction $\mathbf{5a} + C_6H_6 \rightarrow \mathbf{50}$

```
35
 Energy -694.3935639024  Charge 2  Dipole 5.838233  ZPE 0.286441  G(298) 149.71  HoF
400.61 kcal  Edisp -26.67
 C    1.16251240   0.33545007   0.60849440
 C    0.54860200  -0.59760096  -0.38688094
 C    0.15390031  -1.90906481  -0.16265848
 C    2.23510896   1.19390000  -0.01903903
 C   -0.40656039  -2.63553208  -1.28020284
 C   -0.79941924  -3.94813048  -1.13246018
 C   -0.66090596  -4.57465407   0.12180893
 C   -0.12494783  -3.88863143   1.23633236
 C    0.28116398  -2.57964546   1.10655932
 O    1.93967626   2.28984454  -0.59088168
 H    0.94175812   2.58302500  -0.53008521
 H    0.34367113   1.00832822   0.98217295
 H    1.58509458  -0.19749703   1.47327864
 H    0.39521217  -0.19838232  -1.39762241
 H   -0.50579963  -2.13224629  -2.24630452
 H   -1.21429104  -4.50280470  -1.97724300
 H   -0.97340310  -5.61733403   0.23772075
 H   -0.03248381  -4.40497023   2.19457488
 H    0.69493982  -2.05870265   1.97286649
 C    3.64828801   0.80607328   0.01682395
```

```
 H    4.26170849   1.42715561  -0.64984416
 H    3.77225575  -0.27130260  -0.18690690
 H    4.00541326   0.94865233   1.06080345
 C   -2.29388560   1.44260034   0.66668989
 C   -1.60738863   2.34303408   1.49013509
 C   -0.81326637   3.34998439   0.91637852
 C   -0.69435954   3.44044449  -0.48622822
 C   -1.37771239   2.52577711  -1.30633373
 C   -2.17078468   1.52369755  -0.72657913
 H   -1.73404763   2.30387504   2.57553530
 H   -0.32384865   4.09170385   1.55466973
 H   -0.18030592   4.29937253  -0.93507459
 H   -1.33133208   2.63009257  -2.39429240
 H   -2.74683911   0.84963535  -1.36638232
 H   -2.95588574   0.69541020   1.11291093
35
 Energy -694.3773304318  Charge 2  Dipole 4.777340  ZPE 0.288453  G(298.15) 153.02  HoF
410.80 kcal  Edisp -28.33
 C    1.19551064   0.58665190   0.26499628
 C    0.06387539  -0.20757139  -0.46229517
 C   -0.22734347  -1.56058748   0.02126041
 C    2.21504746   1.06073394  -0.71580216
 C   -0.63828708  -2.52931752  -0.92965845
 C   -0.89204152  -3.83750340  -0.53660499
 C   -0.76686475  -4.19598452   0.81213351
 C   -0.37725296  -3.24279692   1.76884363
 C   -0.11681395  -1.93525976   1.38133686
 O    2.04866307   2.17249870  -1.34444627
 H    1.21358829   2.64828083  -1.07712039
 H    0.79255429   1.45158928   0.82273056
 H    1.68956483  -0.07978763   0.98680083
 H    0.17897450  -0.20199651  -1.55554014
 H   -0.73729183  -2.25462912  -1.98504914
 H   -1.18708236  -4.58341100  -1.27817551
 H   -0.97840868  -5.22200036   1.12457461
 H   -0.28278185  -3.53180629   2.81804047
 H    0.17449183  -1.20744415   2.14528192
 C    3.43053034   0.31180655  -1.02441414
 H    3.94914505   0.69425496  -1.91372608
 H    3.21886391  -0.77026149  -1.09015337
 H    4.10725530   0.41170639  -0.14556494
 C   -1.50971845   0.84363639  -0.42750069
 C   -1.82642056   1.04764809   0.96730473
 C   -1.70156510   2.29559593   1.54982653
 C   -1.31297422   3.39687250   0.76184260
 C   -1.07912583   3.25961793  -0.62817460
 C   -1.22010585   2.01927109  -1.22430754
 H   -2.14361260   0.18660262   1.56367172
 H   -1.93271632   2.44110390   2.60832183
 H   -1.22516679   4.38529964   1.22469539
 H   -0.88017105   4.15169615  -1.23172704
 H   -1.12889244   1.91292430  -2.31124714
 H   -2.11342726   0.08256646  -0.94015409
 35
 Energy -694.3990399174  Charge 2  Dipole 5.387414  ZPE 0.288564  G(298.15) 153.09  HoF
397.17 kcal  Edisp -28.06
 C    1.60832256  -0.63951451  -0.39201960
 C    0.38928178   0.26400140  -0.06646545
 C   -0.91055620  -0.27257301  -0.65603340
 C    1.82737465  -0.99106694  -1.83604469
 C   -1.64401184   0.51763788  -1.56931099
 C   -2.83349391   0.03528373  -2.12719051
 C   -3.31086176  -1.22737167  -1.76977968
 C   -2.59893909  -2.01513091  -0.85613417
 C   -1.41000618  -1.54373013  -0.30061753
 O    0.88130006  -0.98205758  -2.69231500
 H   -0.00920510  -0.69681657  -2.27893555
 H    1.52525218  -1.62763247   0.11175067
 H    2.55925433  -0.21070473  -0.03432371
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 H    0.58360019   1.25911673  -0.50306999
 H   -1.28389644   1.51494397  -1.84526209
 H   -3.38774321   0.65372242  -2.83737001
 H   -4.24295890  -1.60136110  -2.20068310
 H   -2.97553759  -3.00173588  -0.57550676
 H   -0.87586513  -2.18006903   0.41453498
 C    0.24660992   0.51654017   1.50736204
 C   -0.98913268   1.24500015   1.86337524
 C   -1.01090187   2.19144799   2.85976533
 C    0.18739342   2.53331759   3.52020667
 C    1.41539420   1.90625821   3.21182726
 C    1.46108986   0.94276590   2.23417317
 H   -1.90546885   0.98596303   1.32415382
 H   -1.94286332   2.69502073   3.12843402
 H    0.16655512   3.30657719   4.29605072
 H    2.31961932   2.18989560   3.75621599
 H    2.40919316   0.43687257   2.03146769
 H    0.04738083  -0.50727622   1.93599756
 C    3.15698554  -1.38020314  -2.32348437
 H    3.73860202  -0.44687376  -2.48457899
 H    3.71223682  -1.95522919  -1.56479127
 H    3.09599613  -1.91501841  -3.28139831
```

Pre-reaction complex, TS and product of the reaction ***39*** *+* C_6H_6 $\rightarrow$ ***51***

```
38
 Energy -2316.812185559  Charge 1  Dipole 7.987037  ZPE 0.282763  G(298) 140.65
 C    0.37960388   0.47474499  -1.35466552
 C   -0.63581526   0.59835463  -0.25392867
 C   -1.50194307   1.76266259  -0.17484758
 C    1.16600474  -0.79876749  -1.49377684
 C   -1.99475857   2.13713692   1.09699989
 C   -2.80691625   3.25568366   1.23481928
 C   -3.15160626   4.00799848   0.10559503
 C   -2.68246503   3.64073553  -1.16245456
 C   -1.86631022   2.52540556  -1.30650283
 O    0.96547454  -1.81977991  -0.79883094
Al   -0.41066338  -2.55298524   0.28765543
 H   -0.02499159   0.72726276  -2.35099817
 H    1.14152201   1.26940282  -1.15209630
 H   -0.27374353   0.24556552   0.72165720
 H   -1.73103572   1.53819759   1.97366058
 H   -3.17934402   3.54319447   2.22045398
 H   -3.79576551   4.88448557   0.21219843
 H   -2.96247007   4.22836249  -2.03942103
 H   -1.52170364   2.24541984  -2.30480076
 C    2.20367836  -0.85722542  -2.55756354
 H    2.64654322   0.12624117  -2.76370698
 H    1.69795517  -1.20361708  -3.48127257
 H    2.96946912  -1.60356930  -2.30623546
Cl   -0.80210667  -4.49176303  -0.38746119
Cl    0.04381793  -1.99833190   2.27506387
Cl   -1.96065945  -1.09661237  -0.54925922
 C    2.83310788   3.02282957  -0.35033834
 C    3.73047330   1.98518701  -0.63329209
 C    3.80808105   0.87543126   0.21640155
 C    2.99302967   0.80470199   1.35166798
 C    2.10682735   1.84850663   1.64208751
 C    2.02474428   2.95609206   0.79167073
 H    4.39188820   2.05834303  -1.50145032
 H    4.52854268   0.07838768   0.01192045
 H    3.06789118  -0.05204875   2.02682556
 H    1.49911064   1.80900282   2.55053369
 H    1.34599714   3.77981322   1.02798997
 H    2.78875452   3.90022422  -1.00130783
38
 Energy -2316.797203149  Charge 1  Dipole 8.395606  ZPE 0.282424  G(298.15) 142.40  Edisp
-36.42
 C    0.61652561  -1.29719302  -0.73482172
 C   -0.44566944  -0.28412622  -0.38307142
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```
 C   -1.83472395  -0.57529489  -0.64511068
 C    1.99981306  -0.72536229  -0.96785469
 C   -2.70429770   0.49702359  -0.97099394
 C   -4.02498245   0.25171119  -1.32156999
 C   -4.51346942  -1.06165308  -1.32107036
 C   -3.67374084  -2.13309398  -0.98243084
 C   -2.34700545  -1.89678253  -0.65013044
 O    2.14033208   0.50909134  -0.91415612
 Al   3.71024877   1.71370907  -1.01951535
 H    0.32603479  -1.76852044  -1.69852456
 H    0.69068111  -2.14915087  -0.03633825
 H   -0.12865596   0.75160677  -0.54746680
 H   -2.31669185   1.52008506  -0.97238786
 H   -4.68122420   1.08025756  -1.59692881
 H   -5.55655087  -1.25326048  -1.58542422
 H   -4.06398257  -3.15316189  -0.98376918
 H   -1.70283081  -2.74060308  -0.38843617
 C   -0.29069964  -0.08027416   1.79083896
 C   -1.13807661   1.05458668   1.97733011
 C   -0.59538535   2.29053970   2.27772370
 C    0.79679946   2.42274139   2.43196428
 C    1.64438381   1.30943925   2.32567151
 C    1.10700987   0.06631788   2.03336497
 H   -2.21765256   0.93952938   1.85281843
 H   -1.24105890   3.16309207   2.39933134
 H    1.22734303   3.40501329   2.64315615
 H    2.72196379   1.42480474   2.46452253
 H    1.76118308  -0.80961366   1.99458825
 H   -0.73328735  -1.07784304   1.87221012
 C    3.11883145  -1.64706988  -1.27606426
 H    3.90397793  -1.50553559  -0.50675126
 H    2.81389245  -2.69946462  -1.33170531
 H    3.59277546  -1.32092209  -2.22181709
 Cl   2.76200417   3.56138673  -0.55248954
 Cl   4.90466403   0.86485111   0.55404279
 Cl   4.37152196   1.35313903  -3.00873427
 38
 Energy -2316.815939997  Charge 1  Dipole 4.287586  ZPE 0.282829  G(298.15) 143.03  Edisp
-36.28
 C   -0.18015497  -0.90124095  -1.46570784
 C    0.56036600   0.15947495  -0.57989810
 C    0.19927046   1.59235030  -0.97886519
 C    0.44503466  -2.26333771  -1.35000498
 C    1.17545346   2.58840275  -0.82915666
 C    0.88501831   3.91853018  -1.13942383
 C   -0.38657314   4.26818243  -1.59725641
 C   -1.36426119   3.28160000  -1.74944765
 C   -1.07569026   1.94947957  -1.44020707
 O   -0.00168517  -3.13899535  -0.58153030
 Al  -1.41259869  -3.73945820   0.57898026
 H   -0.08481404  -0.55844653  -2.50905393
 H   -1.24559308  -0.97059477  -1.20077580
 H    1.64448901   0.04132082  -0.75458797
 H    2.17594156   2.32360350  -0.47275186
 H    1.65789550   4.68235403  -1.02576260
 H   -0.61488668   5.30780506  -1.84333448
 H   -2.35676093   3.54611124  -2.12220517
 H   -1.85403614   1.19507496  -1.58831517
 C    0.34069281  -0.02085946   0.91209395
 C   -0.97465189   0.20678016   1.51092347
 C   -1.08647888   0.20856557   2.96029857
 C   -0.01581559  -0.13336234   3.75438768
 C    1.21328766  -0.43170686   3.14005326
 C    1.39042715  -0.36942031   1.74806267
 H   -1.57082258   0.99134232   1.00810455
 H   -2.06248062   0.43450991   3.39941053
 H   -0.11022414  -0.17108410   4.84131198
 H    2.06581589  -0.71233467   3.76609102
 H    2.38030572  -0.57495139   1.33138881
```

```
H   -1.64658294  -0.71482289   1.20740118
C    1.62768539  -2.59284966  -2.19319506
H    2.20057048  -3.42663847  -1.76577691
H    1.23685815  -2.92042390  -3.17766607
H    2.26103368  -1.71426453  -2.38650321
Cl  -2.92528553  -2.13500376   0.45554776
Cl  -0.43560976  -3.68163070   2.46777797
Cl  -2.05513967  -5.52406119  -0.33040742
```

Structures ***46*** *and* ***36***$+C_6H_6$

```
34
 Energy -694.1585726815  Charge 1  Dipole 5.660481  HoF 179.57
C    1.36578272  -0.98704805  -0.62792679
C    0.27616564  -0.08178501  -0.19589247
C   -1.01269239  -0.33440007  -0.97374377
C    2.59988602  -0.62071416  -1.07070453
C   -1.56180090   0.69844639  -1.74457995
C   -2.73035078   0.48760914  -2.48101850
C   -3.36584555  -0.75465307  -2.44576322
C   -2.82644837  -1.78879181  -1.67536350
C   -1.65632781  -1.57917084  -0.94387024
O    3.40836682  -1.62222087  -1.49763285
H    1.14815029  -2.06053209  -0.65987914
H    0.56336911   0.97008030  -0.34920525
H   -1.06928004   1.67543420  -1.77946009
H   -3.14321892   1.29937665  -3.08487177
H   -4.28109769  -0.91959282  -3.01914724
H   -3.31604750  -2.76514941  -1.64762414
H   -1.24526675  -2.40831807  -0.35679150
C   -0.03234683  -0.21189231   1.36868164
C   -1.22005101   0.54088698   1.79217851
C   -1.18961880   1.40899975   2.86063966
C   -0.00524547   1.55929103   3.60493448
C    1.16107310   0.83315677   3.28351781
C    1.16021918  -0.00784210   2.19722263
H   -2.14019828   0.39484553   1.21968356
H   -2.08240740   1.97244447   3.14128008
H    0.01531545   2.25979535   4.44512754
H    2.06455137   0.96683427   3.88280270
H    2.07359579  -0.52956458   1.89419910
H   -0.30792916  -1.29259175   1.42090747
C    3.15781577   0.76605683  -1.15281519
H    4.12447927   0.82090385  -0.62248851
H    3.33883816   1.04245078  -2.20654137
H    2.48849667   1.52160807  -0.72156821
H    4.24006829  -1.25395334  -1.85428695
34
 Energy -694.218080889  Charge 1  Dipole 3.559709  HoF 142.22
C   -0.47228542  -0.83827857  -0.72298616
C   -1.13730432  -0.10354214  -1.68059893
C   -1.89727902  -0.60620846  -2.78505674
C    0.26138475  -0.27371040   0.33758443
C   -2.50697462   0.33343908  -3.65740183
C   -3.25662911  -0.09188651  -4.74519644
C   -3.41291573  -1.46232538  -4.98450086
C   -2.81801489  -2.40823660  -4.13411847
C   -2.06835638  -1.99131498  -3.04634613
O    0.82436810  -1.14603768   1.14182098
H   -0.48343049  -1.93136599  -0.74480624
H   -1.09562381   0.98942103  -1.61229828
H   -2.38002327   1.40245493  -3.46370411
H   -3.72206481   0.63799871  -5.41083583
H   -4.00276187  -1.80030165  -5.84040854
H   -2.94737409  -3.47448948  -4.33184745
H   -1.61118285  -2.73768770  -2.39332438
C    1.80678835  -0.30628351   4.04001031
C    1.27063501   0.94412279   4.37904877
C    1.90345255   2.11359870   3.94932292
C    3.06695220   2.04002245   3.17353056
```

```
C    3.60065760   0.79645143   2.82683232
C    2.97337022  -0.38041991   3.26269663
H    0.37606376   1.00202755   5.00465422
H    1.50026512   3.08856419   4.23584409
H    3.56988171   2.95740744   2.85634700
H    4.52278702   0.73792722   2.24261040
H    3.42059242  -1.35361211   3.03798739
H    1.33975733  -1.22180113   4.41481130
C    0.45549122   1.17252379   0.61725623
H    0.14333119   1.39233808   1.65329918
H    1.53186882   1.41281646   0.55965513
H   -0.09294256   1.82544287  -0.07005949
H    1.33751589  -0.71905456   1.89017799
```

*Structures **47** and **37**+C_6H_6*

```
37
 Energy -2316.419914718  Dipole 17.343445
C   -0.88921354  -0.97940700  -0.17898169
C   -0.12802066   0.22371337   0.15780439
C   -0.87353021   1.09207904   1.16755293
C   -0.99711954  -1.56827365  -1.43804119
C   -1.25597196   2.39112279   0.81026194
C   -1.94377882   3.20424060   1.71473253
C   -2.25246450   2.72916981   2.99048940
C   -1.87493794   1.43395849   3.35511467
C   -1.19173057   0.62151086   2.44862412
O   -1.71150211  -2.64850601  -1.53965577
H   -1.39783002  -1.51377000   0.63052666
H    0.05896134   0.82798248  -0.74241735
H   -1.02098258   2.76845613  -0.18981725
H   -2.24142498   4.21293181   1.41688248
H   -2.79141401   3.36355765   3.69849213
H   -2.11977824   1.05014750   4.34875320
H   -0.91789909  -0.39605369   2.74790738
C    1.32982247  -0.08208116   0.74191319
C    2.01672823   1.14487108   1.17500207
C    3.21370575   1.54917707   0.62504920
C    3.88269700   0.72787845  -0.29907990
C    3.33968409  -0.52217900  -0.66630327
C    2.11652176  -0.91331245  -0.18135483
H    1.52254096   1.76172360   1.92961614
H    3.66354755   2.49701103   0.93138808
H    4.82844020   1.05779677  -0.73671473
H    3.87829897  -1.16303719  -1.36865075
H    1.65910646  -1.84314014  -0.53383985
H    1.05390234  -0.66788639   1.64236083
C   -0.32779263  -1.03652286  -2.67114202
H    0.32199674  -1.82749724  -3.08888611
H   -1.09610540  -0.84603530  -3.44187116
H    0.25726897  -0.12333025  -2.50187764
Al  -1.98936084  -3.85989656  -2.91943288
Cl  -2.89304162  -2.73925303  -4.53338673
Cl  -3.24207110  -5.38141198  -2.08734096
Cl   0.01274754  -4.54573463  -3.41367728
37
 Energy -2316.493795399  Dipole 12.651383
C   -1.57731600  -0.68229330  -0.28493685
C   -1.20828697   0.59366159   0.00937107
C   -1.60701195   1.37558930   1.16456618
C   -1.12312532  -1.42286349  -1.43583568
C   -1.04274577   2.65923379   1.33168758
C   -1.38527798   3.45477858   2.42138945
C   -2.30207473   2.98364772   3.36506212
C   -2.87417641   1.71368097   3.21356842
C   -2.53258357   0.91638705   2.12817445
O   -1.46808667  -2.64470482  -1.48261645
H   -2.22841256  -1.25757132   0.37988275
H   -0.51663560   1.10330960  -0.67009176
H   -0.32311604   3.02203060   0.59191926
```

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H   -0.93878109   4.44527306   2.53651324
H   -2.57501177   3.60595596   4.22111351
H   -3.59325124   1.34808899   3.95055988
H   -2.99079298  -0.06947562   2.02112714
C    2.32876268  -0.76658022   1.00295307
C    2.55348731   0.60854719   1.12062929
C    3.13893376   1.31384788   0.06453815
C    3.50263051   0.64281503  -1.10741717
C    3.27974332  -0.73252832  -1.22270702
C    2.69062210  -1.43796168  -0.16859918
H    2.27620967   1.13056993   2.04071929
H    3.32390779   2.38771274   0.15905048
H    3.96843150   1.19213825  -1.93030011
H    3.56658882  -1.26121138  -2.13606915
H    2.51007556  -2.51197930  -0.26790300
H    1.87292255  -1.31885041   1.82921352
C   -0.30753537  -0.84033435  -2.53884368
H    0.61608191  -1.43668660  -2.63975799
H   -0.86556561  -0.98137068  -3.48245148
H   -0.05627354   0.21655050  -2.40052522
Al  -1.11185287  -4.06654867  -2.70054911
Cl  -1.90567642  -3.34784232  -4.56882540
Cl  -2.13763478  -5.72568588  -1.84083139
Cl   1.04282776  -4.20933037  -2.67377822
```

Structures ***48*** *and* ***14****+C_6H_6*

```
33
 Energy -693.7252000231  Dipole 2.795095  HoF 83.00
C   -1.09973172  -1.92873880  -1.07996991
C   -0.29979684  -0.85958427  -0.93627198
C   -0.20347576   0.10050467   0.23184225
C   -1.03771394  -2.74276476  -2.33202393
C   -0.47878890   1.46649956  -0.28273882
C   -1.13032866   2.40263348   0.48950443
C   -1.68029505   2.05188663   1.73309895
C   -1.72790709   0.68751187   2.10921669
C   -1.10813221  -0.26536072   1.34737182
O   -0.26735849  -2.49491660  -3.24682061
H   -1.82444824  -2.22246273  -0.31524682
H    0.35699295  -0.63521214  -1.78735296
H   -0.06908568   1.73885881  -1.25782206
H   -1.22656691   3.42930032   0.12457945
H   -2.15356618   2.81076133   2.36064652
H   -2.28960041   0.39494415   3.00169111
H   -1.13256611  -1.31690973   1.65074485
C    1.29663657  -0.01780719   0.77559338
C    1.53994089   0.93310413   1.88096104
C    2.10805546   2.15416354   1.62133956
C    2.62685018   2.43931922   0.33761077
C    2.81127514   1.38404411  -0.58188066
C    2.27759539   0.14526165  -0.31901571
H    1.12857583   0.70793167   2.86722749
H    2.17122013   2.91066229   2.40862627
H    3.01041779   3.43749444   0.11146345
H    3.42045126   1.54685091  -1.47621197
H    2.46476765  -0.69514822  -0.99141644
H    1.29564016  -1.05989942   1.13410808
C   -2.00987189  -3.91072476  -2.39229761
H   -1.88741161  -4.44963031  -3.34108090
H   -1.83458709  -4.59679149  -1.54591741
H   -3.04718663  -3.54578163  -2.29955832
33
 Energy -693.8453558407  Dipole 3.037672  HoF 7.61
C   -1.39713053  -1.99136324  -0.87362132
C   -0.94297038  -0.84271395  -0.32509961
C   -1.69838366   0.21944993   0.32646551
C   -0.45509918  -2.95694447  -1.49789207
C   -0.99233520   1.33438535   0.82520398
C   -1.66147793   2.38103060   1.45776762
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```
C   -3.04966671   2.33624696   1.60565143
C   -3.76561381   1.23645057   1.11602836
C   -3.10018796   0.19099105   0.48468791
O    0.75511300  -2.77581179  -1.54863156
H   -2.46093801  -2.25149984  -0.88035181
H    0.14276158  -0.69008288  -0.37833619
H    0.09541556   1.36836209   0.70872425
H   -1.09613915   3.23604143   1.83722161
H   -3.57684828   3.15574433   2.10116080
H   -4.85216001   1.19840835   1.23040984
H   -3.67199289  -0.66096162   0.10777867
C    3.05233981  -0.05900793   0.97677857
C    3.31173922   1.17689738   1.57652644
C    3.31327313   2.34214541   0.80367885
C    3.05724913   2.26976224  -0.56903248
C    2.79800191   1.03305698  -1.16711338
C    2.79492636  -0.13410570  -0.39610136
H    3.51374649   1.23269169   2.64982096
H    3.51755404   3.30901782   1.27198428
H    3.06003628   3.18058098  -1.17422476
H    2.59421043   0.97608876  -2.23986994
H    2.56719501  -1.09793369  -0.86067779
H    3.04738849  -0.97007243   1.58140046
C   -1.09703541  -4.20679135  -2.08139150
H   -0.32402998  -4.85376718  -2.51658078
H   -1.64564362  -4.75537008  -1.29673263
H   -1.83329771  -3.93092574  -2.85563235
```

*Structure **40** and benzene loss product*

```
37
 Energy -2316.382723939  Dipole 13.947626
C   -0.58774601   0.64901042   1.44620535
C   -0.10924659   0.01046836   0.17065102
C   -0.83505102   0.53969578  -1.06387886
C   -0.02029913   0.12822895   2.73833732
C   -1.59236747  -0.33033853  -1.85842656
C   -2.25504095   0.14360526  -2.99344323
C   -2.15896323   1.48827567  -3.35313159
C   -1.40302180   2.36196171  -2.56755557
C   -0.74725157   1.88837739  -1.43157382
O    0.48308115   0.90277752   3.54202395
Al  -2.71546774   0.39253413   1.69390944
H   -0.48915312   1.74946306   1.44255999
H   -0.27306360  -1.07803308   0.22977285
H   -1.68966651  -1.37967604  -1.56864777
H   -2.85419360  -0.54543398  -3.59414139
H   -2.67870558   1.85903047  -4.24020141
H   -1.33466560   3.42009503  -2.83192834
H   -0.18028480   2.59503568  -0.81427410
C    1.45216456   0.18772962  -0.13030356
C    1.79733602  -0.56621528  -1.34664894
C    2.77697380  -1.53227291  -1.36392347
C    3.55214456  -1.77139368  -0.21423102
C    3.36079390  -1.00182581   0.94915103
C    2.37164167  -0.04608620   0.99341322
H    1.19000053  -0.38026317  -2.23617943
H    2.96425794  -2.10735675  -2.27397532
H    4.32461507  -2.54504367  -0.23151069
H    4.00723228  -1.15871432   1.81610800
H    2.24754648   0.56173064   1.89296190
H    1.46553540   1.27598654  -0.35930998
Cl  -3.69529535   1.95447729   0.58691590
Cl  -3.04098923   0.55531327   3.82140931
Cl  -3.16764296  -1.62662798   1.00878534
C   -0.04280463  -1.36881780   2.99331733
H    0.17561066  -1.55337407   4.05292668
H   -1.01998889  -1.79804500   2.71616162
H    0.72197536  -1.87427855   2.37867478
37
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```
 Energy -2316.451548254  Dipole 7.090715
C   -0.99285151   0.81787186   1.46405088
C   -1.00746496   0.21255330   0.22455376
C   -1.43086194   0.77234907  -1.04230586
C   -0.08631501   0.33374363   2.58030842
C   -1.54536982  -0.09580494  -2.15069764
C   -1.95275670   0.38512927  -3.39068100
C   -2.24356352   1.74398825  -3.54684100
C   -2.12721353   2.61896538  -2.45961690
C   -1.72673753   2.14178737  -1.21758342
O    0.40269651   1.17822768   3.30426240
Al  -3.14594168   0.03235488   1.97939858
H   -1.23673305   1.88560973   1.55760885
H   -0.66345860  -0.82754866   0.17428323
H   -1.32495470  -1.15858680  -2.01640868
H   -2.04650268  -0.29754543  -4.23843897
H   -2.56049202   2.12564039  -4.52089722
H   -2.35210501   3.68047527  -2.58652836
H   -1.63436168   2.83216417  -0.37676130
C    2.75122766   0.26118152  -0.46316915
C    2.38114369  -0.82810345  -1.25838766
C    2.72164543  -2.12682785  -0.86794887
C    3.43617788  -2.33556814   0.31583241
C    3.80874078  -1.24592415   1.10884385
C    3.46469958   0.05253552   0.72069865
H    1.82988613  -0.66176156  -2.18811465
H    2.43634635  -2.97900036  -1.49093551
H    3.70653946  -3.35055687   0.61940162
H    4.36873175  -1.40872158   2.03357524
H    3.75197666   0.90339236   1.34369319
H    2.48628887   1.27658693  -0.76980543
Cl  -4.33195396   1.58562130   1.12276061
Cl  -2.98209256   0.04274896   4.10634227
Cl  -3.35534070  -1.92097444   1.11867938
C    0.22858613  -1.13920363   2.68521864
H    0.64768998  -1.33856135   3.68027954
H   -0.66294303  -1.76537040   2.51732218
H    0.98763733  -1.40286724   1.92800794
```

*Structure **41** and benzene loss product*

```
38
 Energy -2316.765314175  Charge 1  Dipole 8.026312
C    0.10038855   0.72526814   1.40135604
C    0.28961137  -0.05786366   0.15276368
C   -0.63056838   0.43808294  -0.95332055
C    0.11175220   0.16028640   2.63775442
C   -1.60071430  -0.42796478  -1.49231886
C   -2.47441674   0.02074095  -2.49455714
C   -2.39087707   1.33582628  -2.96111665
C   -1.42724724   2.19572540  -2.43236392
C   -0.55369172   1.74833644  -1.43723401
O    0.46866082  -1.14860594   2.73530821
Al  -3.93532318  -0.04412944   0.35644717
H   -0.14346042   1.78601498   1.32579722
H    0.06065655  -1.11370120   0.36475919
H   -1.64440036  -1.47076212  -1.16088204
H   -3.21307454  -0.66619504  -2.91379752
H   -3.07338384   1.68525826  -3.73905039
H   -1.35619086   3.22503913  -2.79221540
H    0.18606188   2.44790735  -1.03194026
C    1.80234701  -0.07045709  -0.36826634
C    1.94877167  -0.76841132  -1.65403348
C    2.85596998  -1.78589803  -1.83010147
C    3.71190516  -2.14984579  -0.77109898
C    3.66977344  -1.48478861   0.46900973
C    2.74354226  -0.48931524   0.67738422
H    1.29306545  -0.46150773  -2.47365031
H    2.92792499  -2.30570559  -2.78815012
H    4.42365624  -2.96813779  -0.91559274
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H     4.35572584  -1.77991976   1.26602892
H     2.66917731   0.00546997   1.64875107
H     1.96534915   1.01377628  -0.56599609
Cl   -5.53565668  -0.62017684  -0.88112262
Cl   -3.57052282   1.98439044   0.80266138
Cl   -3.04183434  -1.52978893   1.58083843
C    -0.25707763   0.87260476   3.89715019
H    -1.16124037   0.41358787   4.33578954
H     0.55288258   0.80964253   4.64467825
H    -0.47643049   1.93110496   3.70477091
H     0.34888853  -1.45588818   3.65556035
38
 Energy -2316.805633556  Charge 1  Dipole 7.269195
C    -0.51699548   1.24253151   2.05176459
C    -0.07579050   0.87618215   0.78867895
C    -0.77595666   1.03600208  -0.44241418
C     0.23983144   1.03336586   3.21001278
C    -0.17846551   0.50387217  -1.61666663
C    -0.82574578   0.60096312  -2.84193930
C    -2.07181213   1.23038006  -2.92239504
C    -2.67668055   1.77382260  -1.77291839
C    -2.04064891   1.68226540  -0.54513481
O     1.44312740   0.48855811   3.09537200
Al   -4.23147423  -1.00642452  -0.03144748
H    -1.49937956   1.69271273   2.19898274
H     0.90581094   0.39066566   0.71481704
H     0.79293956   0.00503434  -1.54617337
H    -0.36198164   0.18437501  -3.73847018
H    -2.58195952   1.30838697  -3.88601245
H    -3.64296130   2.27711027  -1.85377222
H    -2.51059486   2.12419607   0.33598465
C     3.60372388  -0.63898003  -1.35392631
C     3.08444232  -1.27692497  -2.48512206
C     2.20106659  -2.35217850  -2.33897976
C     1.83551085  -2.79010811  -1.06230146
C     2.35913097  -2.15669959   0.06933345
C     3.24322782  -1.08153222  -0.07625442
H     3.38326054  -0.94576021  -3.48332647
H     1.80841772  -2.86132704  -3.22327148
H     1.15478279  -3.63796512  -0.94917720
H     2.09408383  -2.51942085   1.06651957
H     3.67556844  -0.60240164   0.80695902
H     4.30704810   0.19008510  -1.46854637
Cl   -5.77418027  -0.51626594  -1.36090938
Cl   -4.19200720  -0.13934764   1.89629643
Cl   -2.70731713  -2.35347941  -0.55800678
C    -0.24870752   1.39590546   4.56686630
H    -0.26865578   0.50060836   5.21445416
H     0.43489195   2.12770084   5.03434887
H    -1.25708649   1.82673773   4.53454013
H     1.87153588   0.38735419   3.97223507
```

*Structure **42** and benzene loss product*

```
41
 Energy -3939.048841745  Dipole 13.858925
C    -0.74672976   0.72706196   0.88784651
C    -0.25430502   0.04996395  -0.37554844
C    -0.89779709   0.58695053  -1.64572993
C    -0.31516943   0.22514766   2.14379243
C    -1.63142661  -0.26298361  -2.48355485
C    -2.21606829   0.22743732  -3.65379657
C    -2.06538340   1.56909780  -4.00538293
C    -1.32805079   2.42306584  -3.18029787
C    -0.74766471   1.93199986  -2.01175721
O     0.24865633  -0.93668813   2.17401102
Al   -3.00060941   0.21729188   1.04798459
H    -0.91475353   1.81209498   0.85129444
H    -0.47321811  -1.02472975  -0.27542501
H    -1.77458438  -1.30858415  -2.19807332
```

```
H   -2.79822224  -0.44541577  -4.28853861
H   -2.52382705   1.95275458  -4.92027942
H   -1.21128393   3.47696612  -3.44460374
H   -0.18399955   2.62041918  -1.37060678
C    1.33034745   0.11276608  -0.58752117
C    1.69638814  -0.77335550  -1.70837484
C    2.67879348  -1.72029997  -1.59718783
C    3.40899725  -1.83647883  -0.39105345
C    3.18589595  -0.97090087   0.68366168
C    2.17441640  -0.03343969   0.60526540
H    1.10716766  -0.68128787  -2.62508640
H    2.89857361  -2.39214698  -2.42982843
H    4.17106256  -2.61563614  -0.29798614
H    3.77051159  -1.05748521   1.60226666
H    2.04200941   0.66911914   1.43004449
H    1.45899494   1.16452918  -0.93271413
Al   1.07464640  -1.96291243   3.51967271
Cl   1.80518508  -3.66672449   2.43012808
Cl   2.70391280  -0.67507842   4.17582231
Cl  -0.37915728  -2.35557979   5.03151277
Cl  -3.87215804   1.70121579  -0.22874900
Cl  -3.64893910   0.44942051   3.07673889
Cl  -3.04215616  -1.82823076   0.38365928
C   -0.42768369   1.02212692   3.40367142
H   -0.90847690   0.41380104   4.18672566
H    0.59696472   1.24236009   3.75682362
H   -0.99085932   1.95236795   3.26117410
41
 Energy -3939.097358197  Dipole 11.174785
C   -1.55299065   0.84068904   1.48286419
C   -0.79892861   0.62791579   0.33919160
C   -0.95998706   1.21425867  -0.96055001
C   -1.03209823   0.41433547   2.78533583
C   -0.08840951   0.77781407  -1.98882502
C   -0.18111002   1.31902766  -3.26533641
C   -1.13589175   2.30440544  -3.53520129
C   -2.00119616   2.75305496  -2.52609542
C   -1.91848622   2.21682581  -1.25002420
O   -0.06200948  -0.38967753   2.82362605
Al  -3.18144923  -1.01056390   0.90338948
H   -2.35657682   1.58346764   1.50357666
H    0.04335898  -0.06770771   0.44903410
H    0.65458265   0.00541896  -1.77097727
H    0.49423904   0.97266198  -4.05048973
H   -1.20747113   2.73319263  -4.53832780
H   -2.74016283   3.52699925  -2.74512840
H   -2.59326856   2.57437343  -0.47030666
C    3.27760687  -0.89578568  -2.83121256
C    2.37351865  -1.94156824  -3.04572373
C    1.79769738  -2.60254474  -1.95575314
C    2.12930064  -2.22098194  -0.65148085
C    3.03363518  -1.17525189  -0.43699998
C    3.60584443  -0.51142020  -1.52706212
H    2.12275528  -2.24832716  -4.06516166
H    1.09194063  -3.42105704  -2.12190001
H    1.69303569  -2.74076917   0.20612153
H    3.29520181  -0.89282404   0.58687458
H    4.31733014   0.30194954  -1.35925341
H    3.73559525  -0.38489785  -3.68304463
Al   1.07047467  -1.00978231   4.24986463
Cl   2.44356526  -2.28816575   3.22744616
Cl   1.90194709   0.84219377   4.96267246
Cl  -0.26562138  -1.97548217   5.62061125
Cl  -4.58187007   0.23497072  -0.10449761
Cl  -3.66912388  -1.55471933   2.89519838
Cl  -2.04489417  -2.38241937  -0.24740311
C   -1.59976488   1.00680756   4.02717351
H   -1.70857131   0.22192537   4.79479060
H   -0.84921589   1.71996198   4.42074410
```

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 H   -2.55253183   1.52169628   3.85223990
```

Pre-reaction complex, TS and product of the reaction ***43*** *+* C_6H_6 →

```
35
 Energy -694.3582586686  Charge 2  Dipole 12.215958  ZPE 0.286661  G(298) 148.80  HoF
422.76 kcal  Edisp -28.03
 C    1.59183257  -0.71218143  -0.91201300
 C    0.51376209   0.23095699  -0.75641065
 C   -0.84578701  -0.06407308  -0.94030842
 C    2.88025198  -0.34580374  -1.04649802
 C   -1.76183968   1.04309689  -1.02232643
 C   -3.08071994   0.84064074  -1.39165895
 C   -3.53587766  -0.46118738  -1.64688537
 C   -2.67618913  -1.57365396  -1.50963304
 C   -1.35692902  -1.38863957  -1.15590245
 O    3.77073215  -1.58866540  -1.29054755
 H    1.35753958  -1.77787248  -0.98634591
 H    0.77681967   1.28682945  -0.65217043
 H   -1.38692058   2.05508988  -0.85041786
 H   -3.76124122   1.68897953  -1.49302028
 H   -4.57449210  -0.62094536  -1.95095491
 H   -3.06105483  -2.57932023  -1.69321934
 H   -0.70568997  -2.25976537  -1.05794169
 C   -1.09043952  -0.93795522   2.34674334
 C   -2.02631157   0.10209280   2.27345261
 C   -1.60207562   1.44691092   2.20450734
 C   -0.24355715   1.74752076   2.18406403
 C    0.69482370   0.70384697   2.21898584
 C    0.26908055  -0.63939559   2.31741212
 H   -3.09526625  -0.12368606   2.31622823
 H   -2.34479734   2.24889190   2.20889358
 H    0.09127873   2.78810994   2.17508401
 H    1.76271801   0.93816254   2.26222303
 H    1.00844095  -1.43843749   2.41988815
 H   -1.42937421  -1.97072461   2.45828699
 C    3.65401537   0.90259221  -1.03252896
 H    4.43039091   0.90217615  -0.24461633
 H    4.15019886   1.09678900  -2.00129233
 H    2.98122066   1.74963858  -0.83109241
 H    4.08463611  -1.66080919  -2.23074875
 H    4.56082092  -1.62920908  -0.68923618
 35
 Energy -694.3482019791  Charge 2  Dipole 10.075544  ZPE 0.287390  G(298.15) 151.68  HoF
429.07 kcal  Edisp -27.45
 C    1.25005571  -0.90660549  -0.61028714
 C    0.09850951  -0.03965520  -0.28781834
 C   -1.13801408  -0.30140425  -1.01224290
 C    2.47328626  -0.44717837  -0.88327363
 C   -1.92747370   0.81040847  -1.40329421
 C   -3.07762264   0.62456311  -2.15745298
 C   -3.48270742  -0.67266139  -2.50598930
 C   -2.72711244  -1.78527769  -2.10469009
 C   -1.56540355  -1.60609673  -1.36679697
 O    3.39790624  -1.61283428  -1.34270616
 H    1.06870633  -1.97997190  -0.72287902
 H    0.33524877   1.02316123  -0.17430444
 H   -1.61481738   1.82225638  -1.12842903
 H   -3.66835283   1.48654567  -2.47577450
 H   -4.39744996  -0.81899758  -3.08631805
 H   -3.05684537  -2.79225784  -2.36972427
 H   -1.00517719  -2.49001141  -1.04854525
 C   -0.24766233  -0.40762566   1.72696661
 C   -1.39607025   0.41255242   1.99172654
 C   -1.29194514   1.52793391   2.79984042
 C   -0.05270483   1.85074762   3.38575652
 C    1.08070211   1.03962478   3.18610008
 C    0.98256034  -0.08912470   2.39308149
 H   -2.35258577   0.15228780   1.53046457
 H   -2.16659703   2.15153673   2.99892696
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 H    0.02703286   2.73914112   4.01929246
 H    2.01779747   1.28598822   3.69089575
 H    1.84056071  -0.75778892   2.28390554
 H   -0.43700324  -1.46475894   1.50344990
 C    3.16999494   0.84968966  -0.90358275
 H    4.05798664   0.85568744  -0.24566754
 H    3.49069420   1.13541559  -1.92135612
 H    2.48812421   1.63278143  -0.53922054
 H    3.54242367  -1.61888795  -2.32510625
 H    4.28395518  -1.60918329  -0.89494734
 35
 Energy -694.355288044  Charge 2  Dipole 9.595466  ZPE 0.288094  G(298.15) 152.26  HoF
424.63 kcal  Edisp -27.10
 C    1.32635019  -0.81067352  -0.41276428
 C    0.19659239   0.10926921  -0.00470700
 C   -1.00949165  -0.20120360  -0.87717373
 C    2.39399894  -0.42876062  -1.10755944
 C   -1.49650248   0.78515734  -1.74997020
 C   -2.58580240   0.51278098  -2.57894345
 C   -3.19873305  -0.74299580  -2.54103656
 C   -2.72143872  -1.73007167  -1.67164081
 C   -1.63273146  -1.46120122  -0.84267536
 O    3.24027050  -1.67292170  -1.53719201
 H    1.19677715  -1.87984900  -0.20975145
 H    0.48717858   1.15943552  -0.16328152
 H   -1.02796302   1.77402116  -1.78200714
 H   -2.96093576   1.28629085  -3.25323826
 H   -4.05712914  -0.95197948  -3.18402300
 H   -3.20382534  -2.70959873  -1.63678851
 H   -1.28297318  -2.24935589  -0.16522276
 C   -0.14460005  -0.02751905   1.55708755
 C   -1.37707559   0.68181984   1.94643180
 C   -1.46848686   1.36064743   3.13866345
 C   -0.33972113   1.44357214   3.98006965
 C    0.88819398   0.82780853   3.64912184
 C    0.99757342   0.12388479   2.47470791
 H   -2.22979215   0.62952377   1.26195195
 H   -2.39927310   1.85488342   3.42752522
 H   -0.41435550   2.00802704   4.91580742
 H    1.73796468   0.91616760   4.33031559
 H    1.93915241  -0.37132593   2.21726111
 H   -0.43520196  -1.10983938   1.66221856
 C    2.96524559   0.82315162  -1.63748183
 H    4.00235622   0.98890443  -1.29490244
 H    2.95187844   0.85292833  -2.74119030
 H    2.36577071   1.67290702  -1.27744297
 H    3.08210933  -1.92473531  -2.48398895
 H    4.21462001  -1.53915011  -1.40818010
```

*Dication **43***

```
23
 Energy -462.3325434828  Charge 2  Dipole 8.242400  ZPE 0.188187  G(298.15) 94.33  HoF
420.24 kcal  Edisp -14.63
 C    1.25972037  -0.50435019   0.00667810
 C    0.18237046   0.44461863   0.03996400
 C   -1.17708095   0.15518279  -0.04226717
 C    2.55269810  -0.13017655   0.10670502
 C   -2.09613838   1.27137784   0.01134054
 C   -3.45476757   1.06007605  -0.06272736
 C   -3.94276689  -0.25735863  -0.19127708
 C   -3.06966647  -1.37116226  -0.24594410
 C   -1.70992784  -1.18006757  -0.17395859
 O    3.46848968  -1.36991615   0.02241556
 H    1.04175168  -1.57063762  -0.09956944
 H    0.44907810   1.50257184   0.14020813
 H   -1.69738994   2.28505062   0.11117870
 H   -4.15253277   1.89969991  -0.02274092
 H   -5.02315765  -0.42493102  -0.25020825
 H   -3.48443175  -2.37691208  -0.34512037
```

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H   -1.04562001  -2.04558646  -0.21659137
C    3.30437174   1.11462314   0.28050854
H    3.90559259   1.10263380   1.21031664
H    3.99313691   1.30104583  -0.56516968
H    2.61520215   1.96966189   0.34761540
H    3.96555978  -1.43815463  -0.83733813
H    4.11550867  -1.43728919   0.77598183
```

*Structure **44** and benzene loss product*

```
38
 Energy -2316.78096747  Charge 1  Dipole 7.382640
C   -0.78826006   0.93783206  -0.34700979
C   -0.06573494  -0.15030462   0.38534828
C   -0.97524900  -1.33002524   0.69126011
C   -0.96666380   2.19470479   0.07886868
C   -1.15438851  -1.73647222   2.02133302
C   -2.01005683  -2.79650669   2.32873913
C   -2.68617368  -3.46796593   1.30791867
C   -2.50797887  -3.07404237  -0.02197538
C   -1.65641181  -2.01269516  -0.32865152
O   -1.60714545   3.05737272  -0.86157941
H   -1.20560076   0.68623172  -1.32866534
H    0.34293064   0.22893598   1.33543748
H   -0.62971671  -1.21365894   2.82751555
H   -2.14844847  -3.09736795   3.36997191
H   -3.35209839  -4.30060353   1.54666300
H   -3.03745814  -3.59403808  -0.82373791
H   -1.54033362  -1.71576719  -1.37710494
C    1.20014481  -0.62836448  -0.46847092
C    1.86548558  -1.82193323   0.07134807
C    3.23539078  -1.91989698   0.12529805
C    4.02781100  -0.84190709  -0.32199566
C    3.45724049   0.33507352  -0.84142216
C    2.08696637   0.45631994  -0.90779529
H    1.22839844  -2.63723428   0.42737986
H    3.71444644  -2.81792488   0.52177102
H    5.11777575  -0.92178494  -0.25726490
H    4.09969104   1.15037124  -1.18247529
H    1.63871313   1.37776581  -1.30311582
H    0.70315940  -0.98064897  -1.41252706
C   -0.57020333   2.87489538   1.34029557
H    0.13289966   3.69794450   1.12563245
H   -1.45411144   3.30414446   1.84622079
H   -0.10065009   2.17717327   2.04608356
Al  -0.72674412   3.62371128  -2.59101681
H   -2.08684879   3.79828550  -0.42682489
Cl  -1.89577218   5.36645327  -2.86456373
Cl  -0.98069063   1.91147718  -3.83219740
Cl   1.29568605   3.88045016  -1.89869096
38
 Energy -2316.8111221  Charge 1  Dipole 2.617770
C   -1.39826578   0.88983805  -0.25278237
C   -0.93471008  -0.34056623   0.20177135
C   -1.72151652  -1.50709471   0.40656753
C   -0.57656306   1.99152860  -0.43599018
C   -1.06733020  -2.67618831   0.89077721
C   -1.78038806  -3.84277835   1.11347822
C   -3.15860698  -3.86979471   0.85665246
C   -3.82501949  -2.72902884   0.37666207
C   -3.12245696  -1.55857569   0.15176462
O   -1.20186892   3.08954286  -0.92782797
H   -2.45850397   1.03267682  -0.48324881
H    0.13581382  -0.44485344   0.41999007
H    0.00768860  -2.63928937   1.08667841
H   -1.27512461  -4.73619642   1.48597331
H   -3.72302279  -4.78981378   1.03060083
H   -4.89849537  -2.76879658   0.18001010
H   -3.65166446  -0.68024936  -0.22444732
C    3.60169622  -0.41961909  -0.98537701
```

```
C    2.94346363  -1.23798390  -0.06041955
C    2.92763071  -0.88940449   1.29555104
C    3.57061308   0.27755126   1.72651574
C    4.23407633   1.09043863   0.80195621
C    4.24951443   0.74204007  -0.55283085
H    2.47504783  -2.16755934  -0.39758714
H    2.44953402  -1.54514934   2.02974781
H    3.57761538   0.53755805   2.78839062
H    4.75871956   1.98737161   1.14194366
H    4.78792294   1.36612677  -1.27130743
H    3.63302551  -0.70307305  -2.04078479
C    0.87387326   2.12784542  -0.17970212
H    1.40825654   2.26179656  -1.13836322
H    1.06456372   3.02432584   0.43678941
H    1.30793232   1.25938073   0.33111625
Al  -3.05300946   3.48100388  -2.12167943
H   -0.61737040   3.87931046  -1.03819383
Cl  -2.35277930   5.46414498  -2.38526135
Cl  -4.48691860   3.01168624  -0.63831722
Cl  -2.70337291   2.03184815  -3.61881631
```

*Structure **45** and benzene loss product*

```
41
 Energy -3939.052596339  Dipole 21.071528
C   -0.61474500  -0.67954888  -0.00762913
C    0.28469639   0.49403064   0.08120881
C    0.50106509   0.93355378   1.52476538
C   -1.75780467  -0.76138422  -0.72945070
C    0.12906759   2.22679841   1.91346340
C    0.29183708   2.64444742   3.23646648
C    0.83645495   1.77518095   4.18296098
C    1.21078603   0.48332397   3.80300912
C    1.04359256   0.06542006   2.48231607
O   -2.45290147  -1.96713075  -0.68966522
H   -0.33950840  -1.56663890   0.57232292
H   -0.12954725   1.34433037  -0.48236673
H   -0.30865825   2.90953593   1.17862654
H   -0.01564974   3.65198646   3.52748108
H    0.96228114   2.09959456   5.21881601
H    1.62478623  -0.20807486   4.54095887
H    1.32298145  -0.95856470   2.21107755
C    1.70322222   0.18108308  -0.58949934
C    2.66845645   1.27050227  -0.39195361
C    3.37232152   1.81494627  -1.44024121
C    3.20287737   1.29883809  -2.74086713
C    2.32851049   0.22638371  -2.99356688
C    1.59091073  -0.31588503  -1.96505743
H    2.79220968   1.65655413   0.62360765
H    4.06647002   2.64137424  -1.27100405
H    3.75921211   1.74564729  -3.57037238
H    2.21593238  -0.16447714  -4.00775282
H    0.87365399  -1.12119568  -2.17887990
H    2.02859427  -0.68030371   0.04281472
C   -2.39779090   0.27604099  -1.58538312
H   -2.46258192  -0.10103512  -2.61967023
H   -3.42907174   0.45487225  -1.23422688
H   -1.85451661   1.23088754  -1.57256770
Al  -1.63393803  -3.40930926  -1.65005598
Al  -4.06390053  -2.06828407   0.41192111
Cl  -3.14944268  -4.80682481  -2.14464908
Cl   0.01670261  -4.10057093  -0.44194959
Cl  -0.83839088  -2.39808173  -3.42352465
Cl  -3.84298115  -0.33967819   1.69004672
Cl  -3.84307290  -3.92066673   1.44727326
Cl  -5.69212024  -1.85767771  -0.95880291
41
 Energy -3939.103751701  Dipole 14.212780
C   -1.34388460  -0.69793855   0.49473867
C   -0.45624452   0.33897849   0.66209935
```

```
C    0.07197798   0.79901112   1.91679289
C   -1.86450844  -1.09294765  -0.75319948
C    1.07370670   1.80078461   1.89707560
C    1.61135020   2.28579285   3.08291790
C    1.15439287   1.78775214   4.30805015
C    0.15781494   0.80152380   4.34644487
C   -0.38077001   0.30732236   3.16760592
O   -2.67581099  -2.14839412  -0.77281266
H   -1.67278279  -1.29825362   1.34973631
H   -0.08839632   0.86721545  -0.22502628
H    1.43067538   2.17571594   0.93332278
H    2.38636968   3.05516004   3.05861354
H    1.57296640   2.17173846   5.24206372
H   -0.19967347   0.42378219   5.30706978
H   -1.16760242  -0.44985063   3.21083129
C    3.09677134  -0.08090413  -1.32178499
C    3.67512234   1.08113212  -0.80312387
C    3.33329834   2.33025659  -1.33275478
C    2.41444760   2.41668963  -2.38344684
C    1.84313330   1.25262762  -2.90819885
C    2.18309737   0.00320431  -2.37736033
H    4.40048216   1.01263835   0.01225253
H    3.79475555   3.23864295  -0.93521167
H    2.15519640   3.39167250  -2.80508990
H    1.14369503   1.31858553  -3.74683628
H    1.74135613  -0.90980716  -2.78691268
H    3.36326985  -1.05829880  -0.91102519
C   -1.67304964  -0.37145071  -2.03489888
H   -1.76908218  -1.05548088  -2.89147776
H   -2.51373693   0.34758769  -2.10274336
H   -0.72696060   0.18166938  -2.08309275
Al  -2.12033496  -3.72388353  -1.91940021
Al  -4.28845541  -2.15790738   0.43923575
Cl  -2.69069427  -5.38972941  -0.74270017
Cl   0.00976622  -3.36206026  -1.93368698
Cl  -3.04716520  -3.37210665  -3.80612027
Cl  -4.65804858  -0.03688688   0.51247409
Cl  -3.55943043  -2.92380631   2.30370839
Cl  -5.71701404  -3.25977746  -0.66812934
```

*Structure **16***

```
21
 Energy -2024.129849125  Dipole 13.575899  ZPE 0.135194  G(298.15) 54.49  Edisp -16.56
C   -0.84845378   0.99598350   0.07291264
C   -0.22896832  -0.21159528  -0.02638582
C    1.19903797  -0.46436196  -0.01899863
C   -2.24736211   1.09638903   0.05230546
C    1.63828729  -1.80032878  -0.13794258
C    2.99630469  -2.10714757  -0.13771241
C    3.94021316  -1.08434991  -0.01834597
C    3.52064705   0.24722789   0.10089443
C    2.16643630   0.55704127   0.10093632
N   -3.40738675   1.19211292   0.03670395
Al  -5.40471186   1.27974982   0.00875605
H   -0.30614526   1.94009129   0.17275660
H   -0.86612971  -1.09810829  -0.12342584
H    0.89661411  -2.59900028  -0.23120068
H    3.32028740  -3.14630311  -0.23066857
H    5.00706839  -1.32149677  -0.01764692
H    4.26019210   1.04597693   0.19442978
H    1.85794110   1.60113493   0.19532792
Cl  -5.77239843   2.40230115  -1.77269317
Cl  -5.89478452  -0.80184708  -0.07192364
Cl  -5.82668883   2.27653028   1.85192108
```

*Structure **37***

```
25
 Energy -2084.487334966  Dipole 12.891787  ZPE 0.173258  G(298) 78.33  Edisp -20.15
```

```
C    0.05435948   1.33446118   0.00183040
C   -0.68176974   2.47886476   0.00119920
C   -0.18393612   3.84136806   0.00087773
C   -0.49197181  -0.00083688   0.00144143
C    1.19234496   4.16195149   0.00098619
C    1.60684910   5.48777611   0.00026139
C    0.66306771   6.52339506  -0.00068389
C   -0.70218835   6.22552602  -0.00090864
C   -1.12078884   4.89811696  -0.00013335
O    0.35358245  -0.94728012   0.00194263
H    1.14802649   1.35952436   0.00264948
H   -1.77419628   2.39297246   0.00053144
H    1.94057125   3.36613154   0.00149351
H    2.67397487   5.72241924   0.00025896
H    0.99601224   7.56440421  -0.00128345
H   -1.44034033   7.03096401  -0.00175255
H   -2.18919838   4.66221868  -0.00034895
C   -1.95067350  -0.31095402   0.00004543
H   -2.16729695  -0.94503950   0.87927030
H   -2.59859785   0.57238915   0.00066102
H   -2.16591490  -0.94277569  -0.88117299
Al   0.19689760  -2.85196836  -0.00019207
Cl   2.22102533  -3.51785009   0.00120828
Cl  -0.91059952  -3.24506860  -1.80624257
Cl  -0.91425694  -3.24945953   1.80262966
```

Dication ***5b***

```
19
 Energy -310.04032972875  Charge 2  Dipole 2.177546  ZPE 0.160406  G(298.15) 78.85  HoF
391.84 kcal
C    0.69107502   0.06191604  -0.10262790
C    0.13091086   1.39613905   0.30998266
C   -0.17121261  -1.17404782  -0.11855022
O   -0.92725242   1.34159671   1.03208792
C    0.42502474  -2.40901113   0.34792157
C   -1.51149863  -1.16023926  -0.66702587
H    1.59347213  -0.08696594   0.53088987
H    1.11302264   0.14760072  -1.13235798
C    0.80078174   2.64145622  -0.04987976
H    0.48648736   3.50614294   0.55559071
H    1.90091160   2.53020741  -0.03399397
H    0.55549012   2.85595396  -1.11752951
H   -1.25561612   2.22257696   1.36193379
H   -0.10629732  -3.32115956   0.03886392
H    1.51921888  -2.47013456   0.19766459
H    0.32858416  -2.34896634   1.46929967
H   -1.97304909  -0.18407505  -0.85030022
H   -1.41449904  -1.69601010  -1.65086209
H   -2.18555403  -1.85298026  -0.12110719
```

Dication ***57***

```
19
 Energy -310.01484238176  Charge 2  Dipole 6.718744  ZPE 0.160937  G(298.15) 79.61  HoF
407.83 kcal
C    0.80607002   0.04946783  -0.00478390
C    0.30069245   1.30723274   0.06066072
C    0.06727180  -1.19008946  -0.05231296
O    1.37209867   2.34711724   0.09030316
C    0.82861578  -2.41330122   0.20311275
C   -1.35484914  -1.30703819  -0.38250376
H    1.89718586  -0.06723525   0.04100909
C   -1.01137397   1.93226016   0.23374779
H   -1.77617302   1.18188128   0.47028150
H   -0.99133186   2.65433713   1.07486664
H   -1.32136596   2.48047535  -0.67954075
H    1.08091716   3.29784258   0.02045272
H    2.22832308   2.17596241  -0.39038254
H    0.19199722  -3.24504131   0.54816222
```

```
 H    1.20799073  -2.75129815  -0.79775149
 H    1.72170392  -2.27655415   0.83267813
 H   -1.79631662  -0.46454609  -0.92672331
 H   -1.54487149  -2.25564228  -0.91958157
 H   -1.90658463  -1.45583064   0.57830555
```

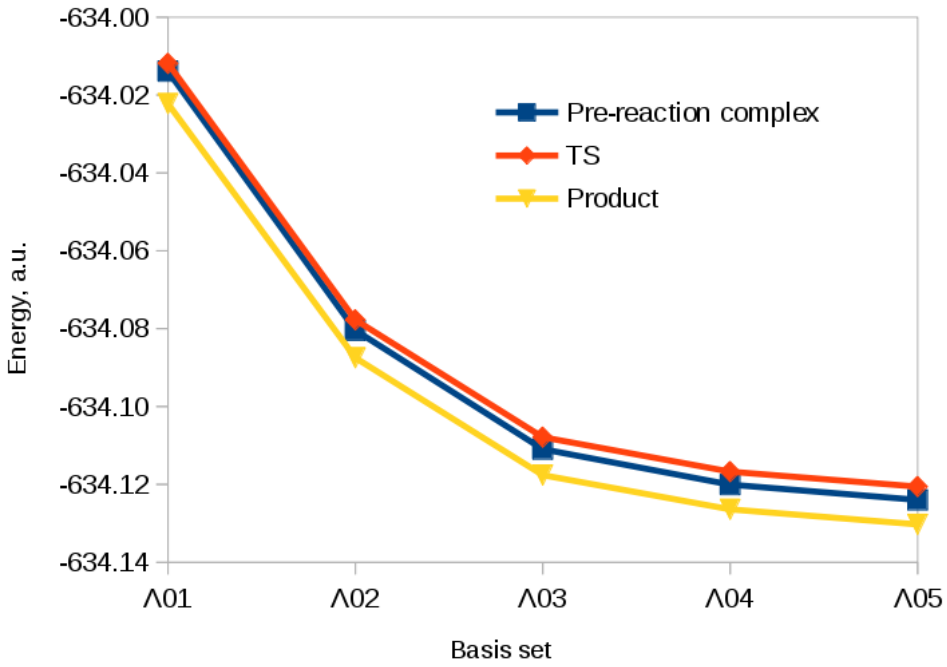
TS of rotation around the α,β-C–C bond in ***5b***

```
19
 Energy -310.0388293211  Charge 2  Dipole 2.127410  ZPE 0.160276  G(298.15) 79.55  HoF
392.78 kcal  Edisp -9.66
 C   -0.31759887  -0.69983483   0.02104527
 C    1.18457419  -0.70659105   0.04825182
 C   -1.00205073   0.65508917   0.03206244
 O    1.73911846   0.43759838   0.22913807
 C   -1.30367586   1.29864867   1.29091683
 C   -1.38299858   1.24955611  -1.22841669
 H   -0.63002753  -1.29905140   0.90448016
 H   -0.62503873  -1.28958560  -0.86743455
 C    1.93468938  -1.94683555  -0.13404487
 H    2.94459402  -1.90794862   0.30838477
 H    1.37916381  -2.82874325   0.22605664
 H    2.06246845  -2.09847480  -1.23279849
 H    2.73468509   0.41884866   0.26642985
 H   -2.18887873   1.96090460   1.23583351
 H   -1.30092264   0.65090888   2.17881445
 H   -0.46748497   2.04245465   1.42531024
 H   -0.77461050   0.95198784  -2.09848323
 H   -2.39186123   0.78067530  -1.42910770
 H   -1.59414505   2.33039282  -1.17643854
```

Complete basis set (CBS) extrapolation of PBE/Λ0n family for the reaction **18** + C_6H_6 → **28**

Basis set	ζ	Basis functions	Energy, a.u.			ΔE, kcal/mol	
			Pre-reaction complex	TS	Product	$\Delta E^{\#}$	ΔE_0
Λ01	2	299	-634.013876	-634.011884	-634.022218	1.25	-5.23
Λ02	3	690	-634.080432	-634.077765	-634.087496	1.67	-4.43
Λ03	4	1330	-634.110949	-634.107874	-634.117612	1.93	-4.18
Λ04	5	2281	-634.120063	-634.116729	-634.126405	2.09	-3.98
Λ05	6	3605	-634.123983	-634.120575	-634.130276	2.14	-3.95
CBS	∞		-634.132453 *	-634.128801 *	-634.138592 *	2.29	-3.85

* Determined by non-linear fitting of the exponential-square root function $E_{\Lambda 0n} = E_{CBS} + A*\exp(-\alpha*\sqrt{\zeta})$, see for example [Kraus, P. (2021). Extrapolating DFT Toward the Complete Basis Set Limit: Lessons from the PBE Family of Functionals. Journal of Chemical Theory and Computation, 17(9), 5651–5660. doi:10.1021/acs.jctc.1c00542]



The expansion of the basis set increases the relative stability of the pre-reaction complex, which consists of two parts that are not linked to each other by valence bonds. The effect of CBS on ΔE does not exceed 2 kcal/mol.

M06/6-311+G(2d,2p)/SMD(benzene)//PBE/Λ01 energies

	Energy, a.u.
Benzene C_6H_6	-232.128197748527
Cation **15**	-402.082829285007
Cation **17**	-402.062056100520
Dication **18**	-402.372212967414
Dication **23**	-402.366954139754
Structure **19**	-2025.331648173970
Pre-reaction complex, TS and product of the reaction **17**+ C_6H_6→**27**	-634.204234402791 -634.192322274779 -634.203719102093
Pre-reaction complex, TS and product of the reaction **18**+ C_6H_6→**28**	-634.513014278514 -634.504118486005 -634.522667765738
Pre-reaction complex, TS and product of the reaction **19**+ C_6H_6→**29**	-2257.469577855388 -2257.468439633262 -2257.482161644868
Structures **25** and **15**+ C_6H_6	-634.173864733437 -634.216537005522
Structures **26** and **16**+ C_6H_6	-2257.054618287183 -2257.127249665506
Structures **30** and **20**+ C_6H_6	-2257.043693803555 -2257.085670360304
Structures **31** and **21**+ C_6H_6	-2257.429065872554 -2257.457001517715
Structures **32** and **22**+ C_6H_6	-3880.341110663898 -3880.373683226672
Structures **34**, TS **34**→**33** and **33**	-634.558128922272 -634.495260272643 -634.515319143663
Structures **35** and **24**+ C_6H_6	-3880.336798871455 -3880.374673356929
Cation **38**	-462.471488862617
Dication **5a**	-462.776335938900
Structure **39**	-2085.740601410303
Pre-reaction complex, TS and product of the reaction **38** + C_6H_6→ **49**	-694.607238410577 -694.594964125878 -694.600834228225
Pre-reaction complex, TS and product of the reaction **5a** + C_6H_6→ **50**	-694.922724302897 -694.912121592158 -694.933696824192
Pre-reaction complex, TS and product of the reaction **39** + C_6H_6→ **51**	-2317.881276543867 -2317.873861267835 -2317.892750362789
Structures **46** and **36**+ C_6H_6	-694.585563388456 -694.634596293241
Structures **47** and **37**+ C_6H_6	-2317.456175830623 -2317.526663268476
Structures **48** and **14**+ C_6H_6	-694.109977342010 -694.229681167878
Structure **40** and benzene loss product	-2317.431416862456 -2317.486444269560
Structure **41** and benzene loss product	-2317.839190083554 -2317.872897410588

Structure **42** and benzene loss product	-3940.745370905198 -3940.776013497543
Dication **43**	-462.746568116341
Structure **44** and benzene loss product	-2317.857435080340 -2317.875608211615
Structure **45** and benzene loss product	-3940.751618138240 -3940.783419548286
Structure **16**	-2024.991373566555
Structure **37**	-2085.391989300991
Dication **5b**	-310.559202239391
Dication **57**	-310.537271755824
TS of rotation around the α,β-C–C bond in **5b**	-310.557175095020