

## Supplementary Material

# Facile Synthesis of Triarylmethanimine Promoted by a Lewis Acid–Base Pair: Theoretical and Experimental Studies

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# Spectra

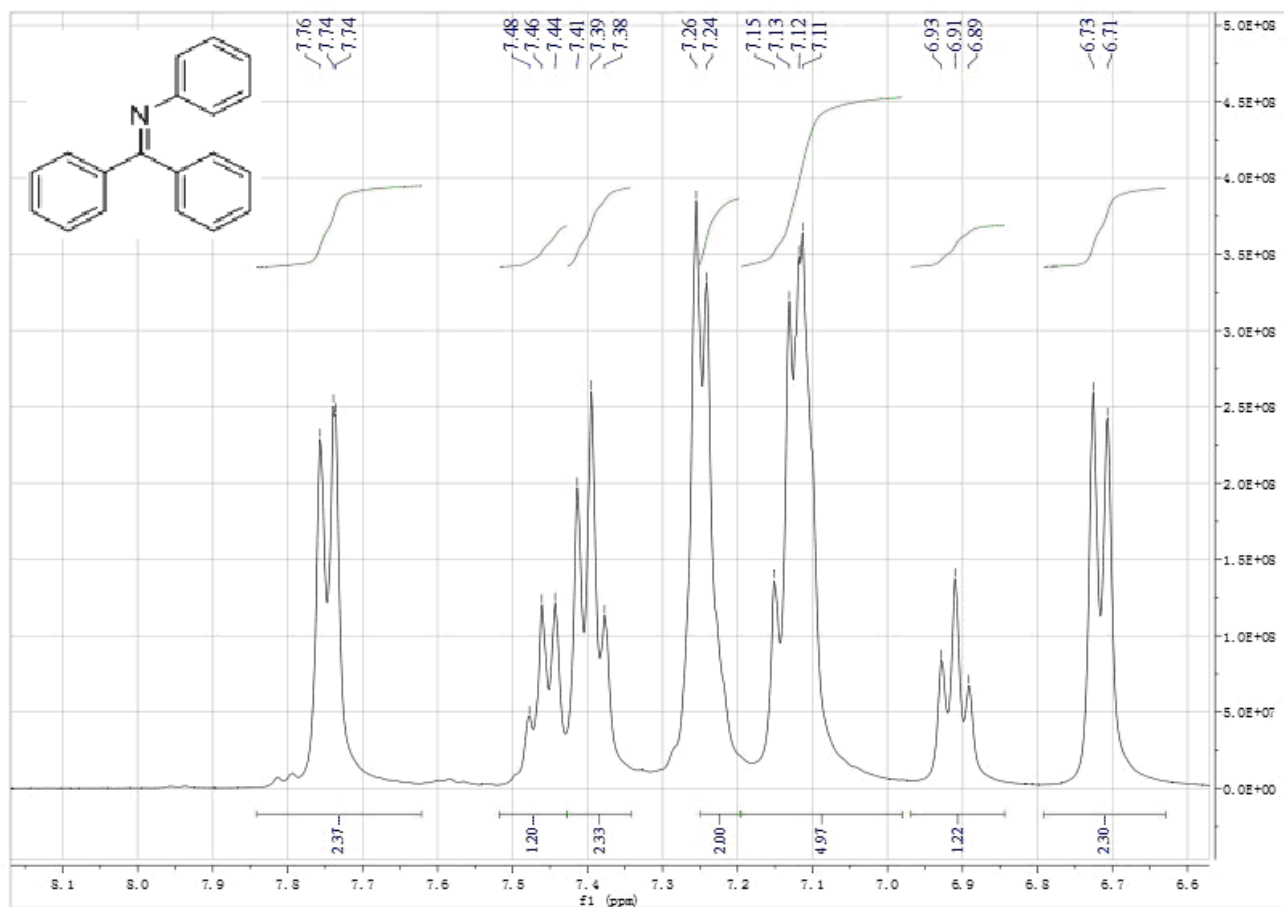


Figure S1:  $^1\text{H}$  NMR spectrum of **3a** in  $\text{CDCl}_3$

### Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	600 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source

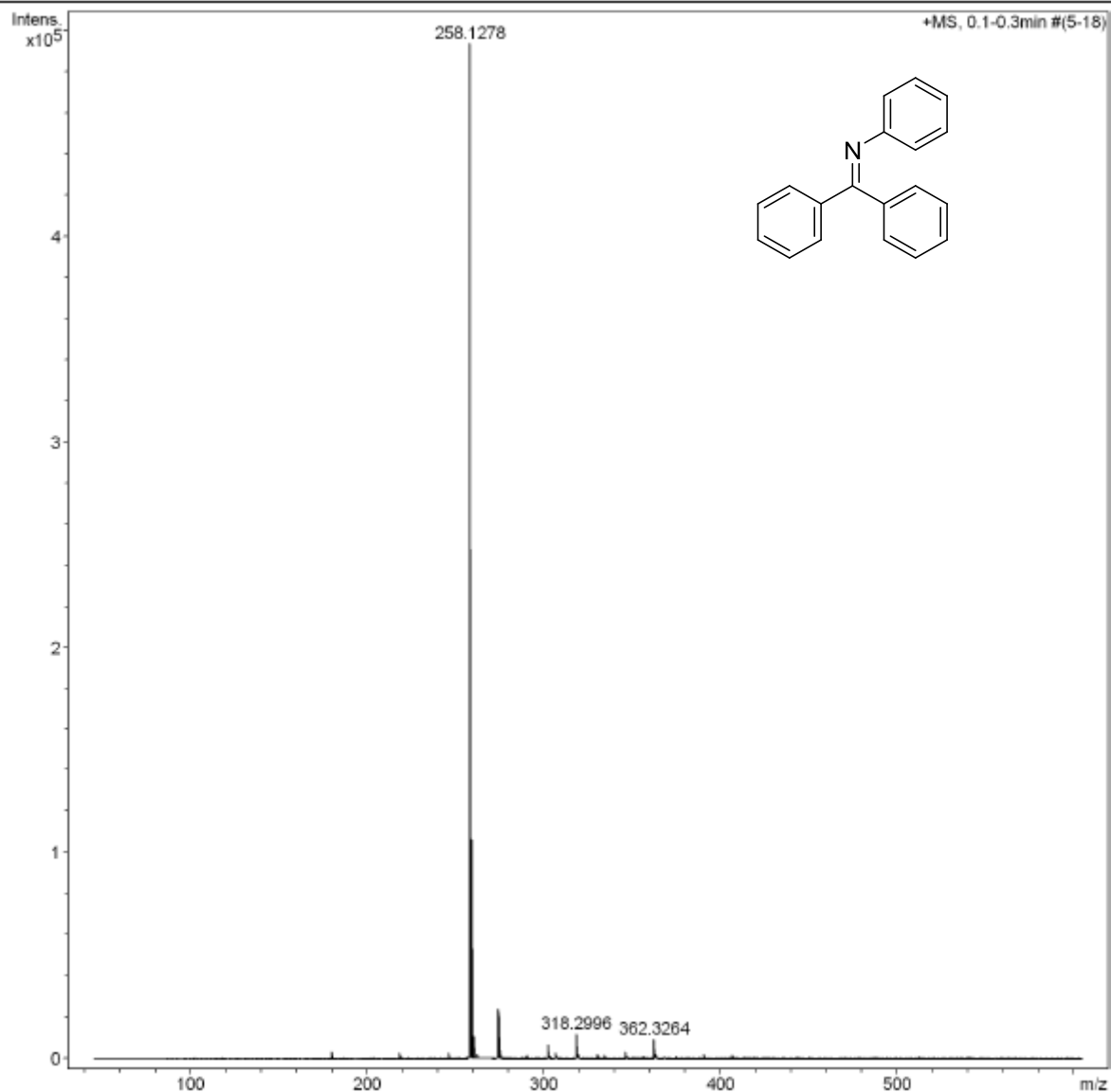


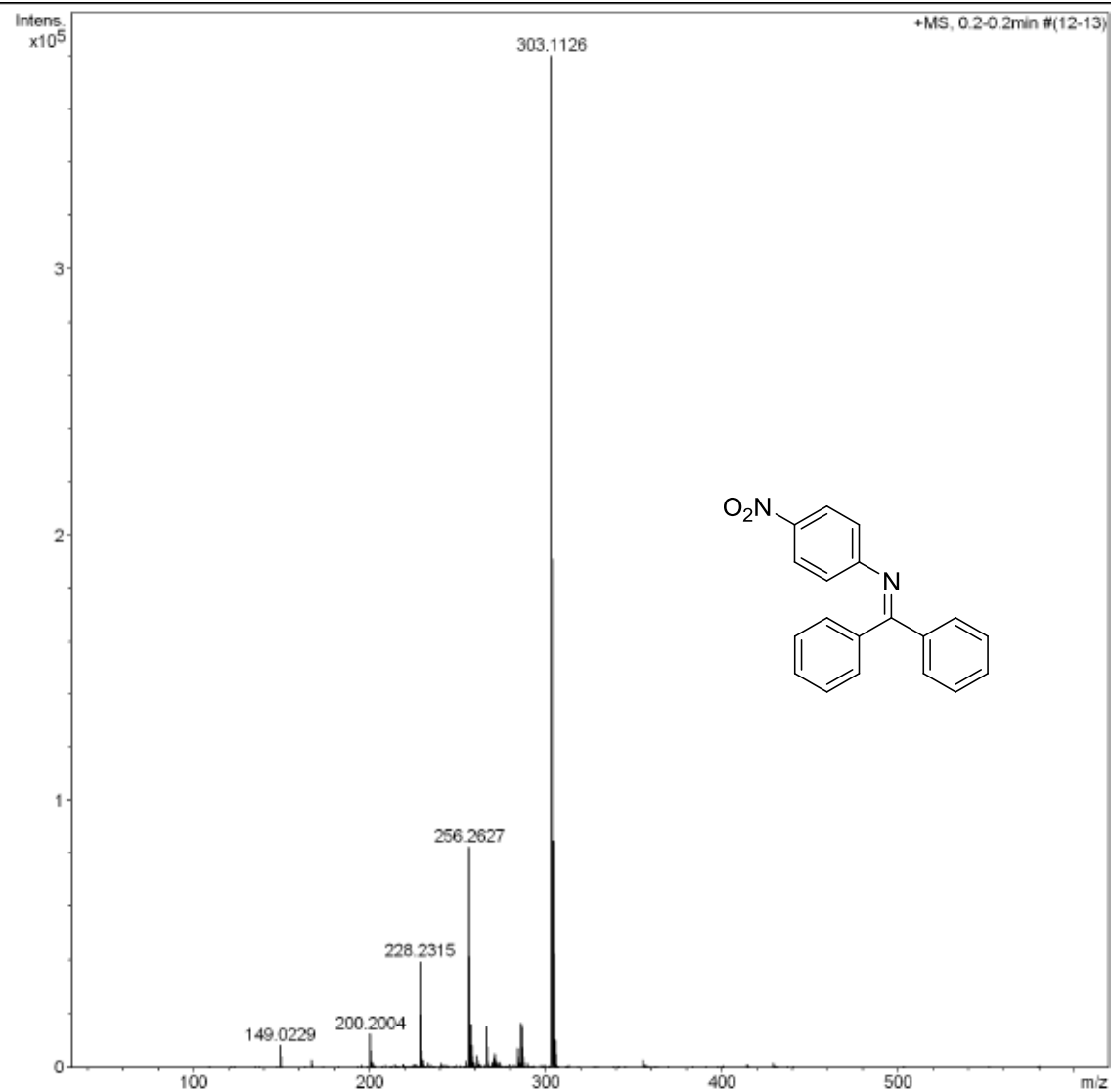
Figure S2: HRMS of **3a** ( $C_{19}H_{16}N^+ = M+H^+$ ), found: 258.1278, requires: 258.1277.



Figure S3:  $^1\text{H}$  NMR spectrum of **3b** in  $\text{CDCl}_3$

**Acquisition Parameter**

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	800 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source



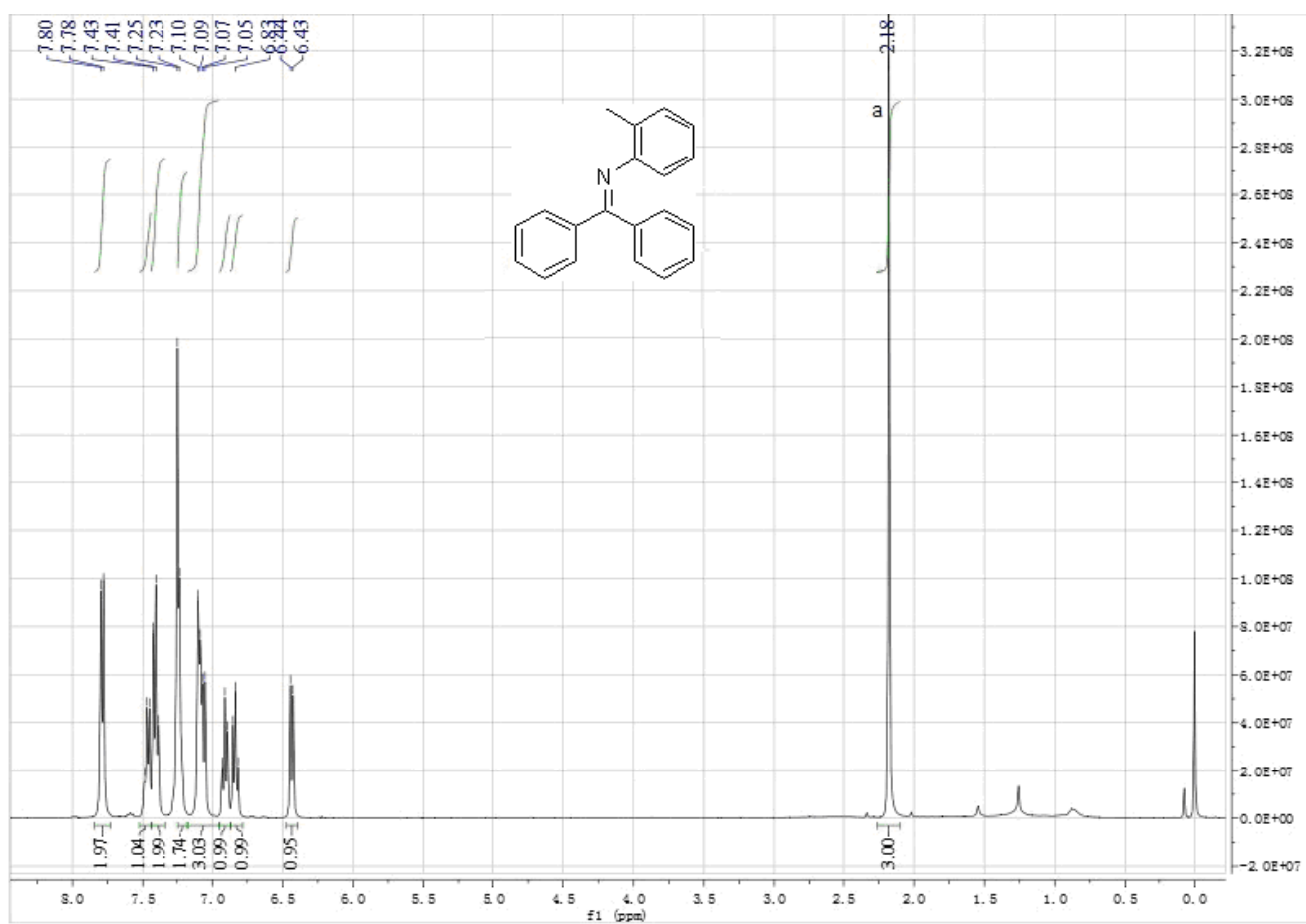


Figure S5:  $^1\text{H}$  NMR spectrum of **3i** in  $\text{CDCl}_3$

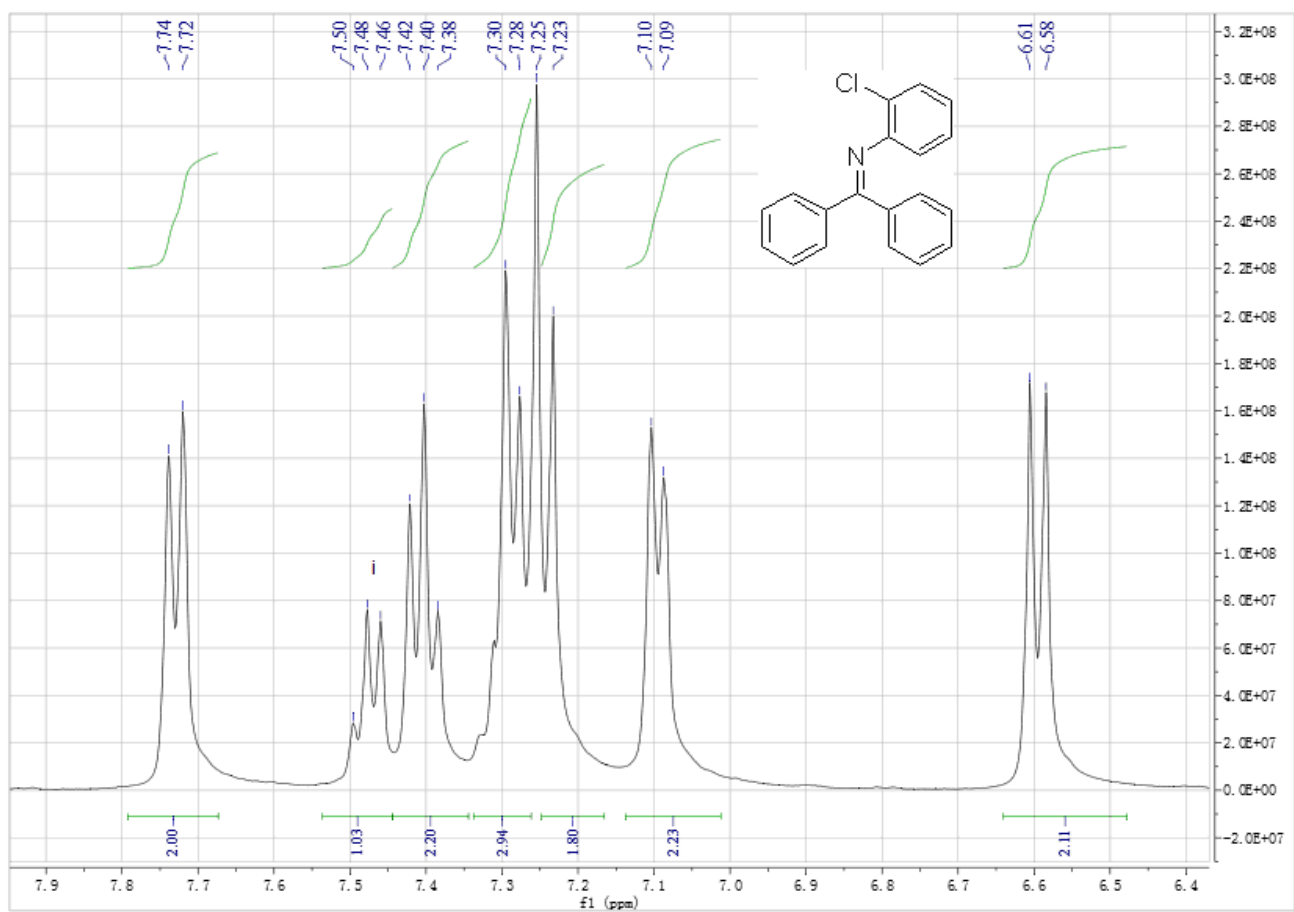


Figure S6:  $^1\text{H}$  NMR spectrum of **3j** in  $\text{CDCl}_3$

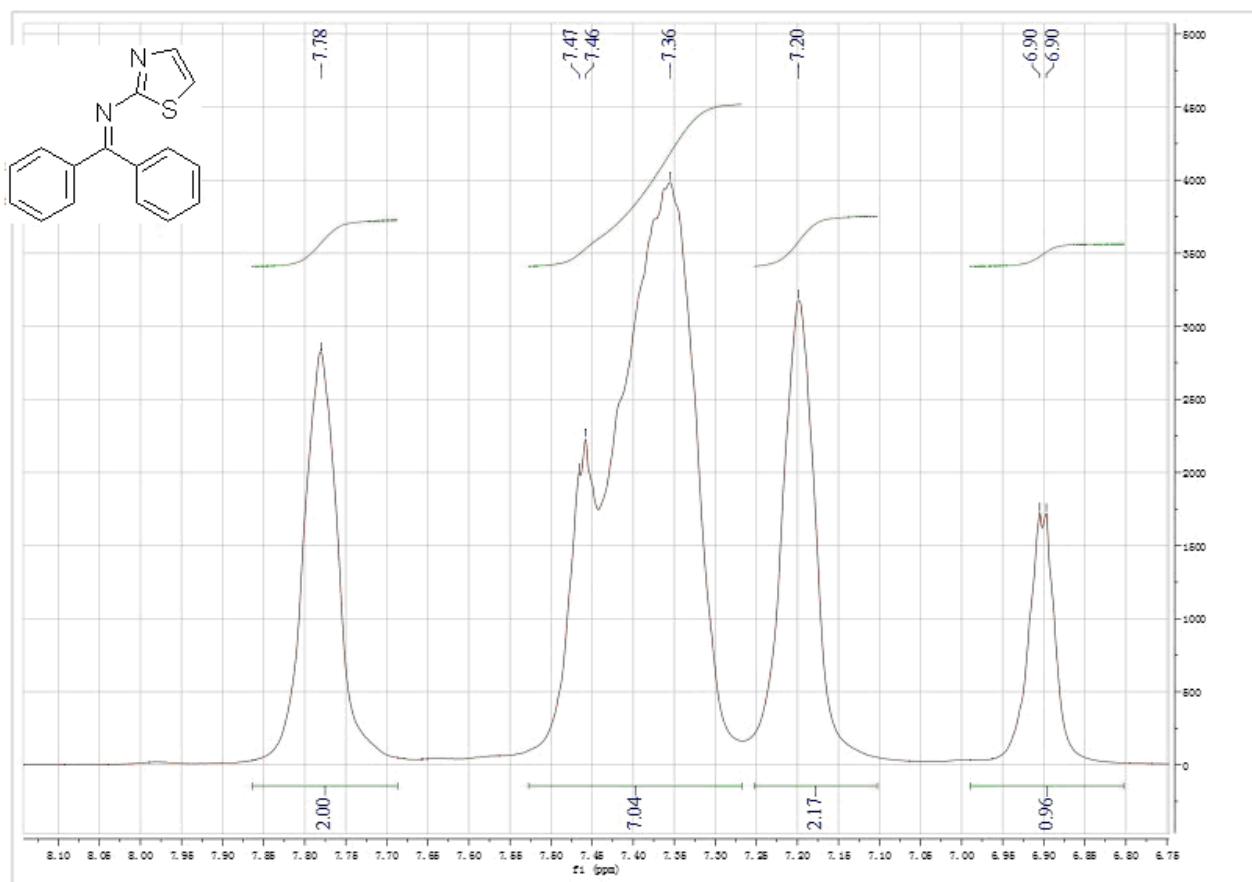


Figure S7:  $^1\text{H}$  NMR spectrum of **3o** in  $\text{CDCl}_3$



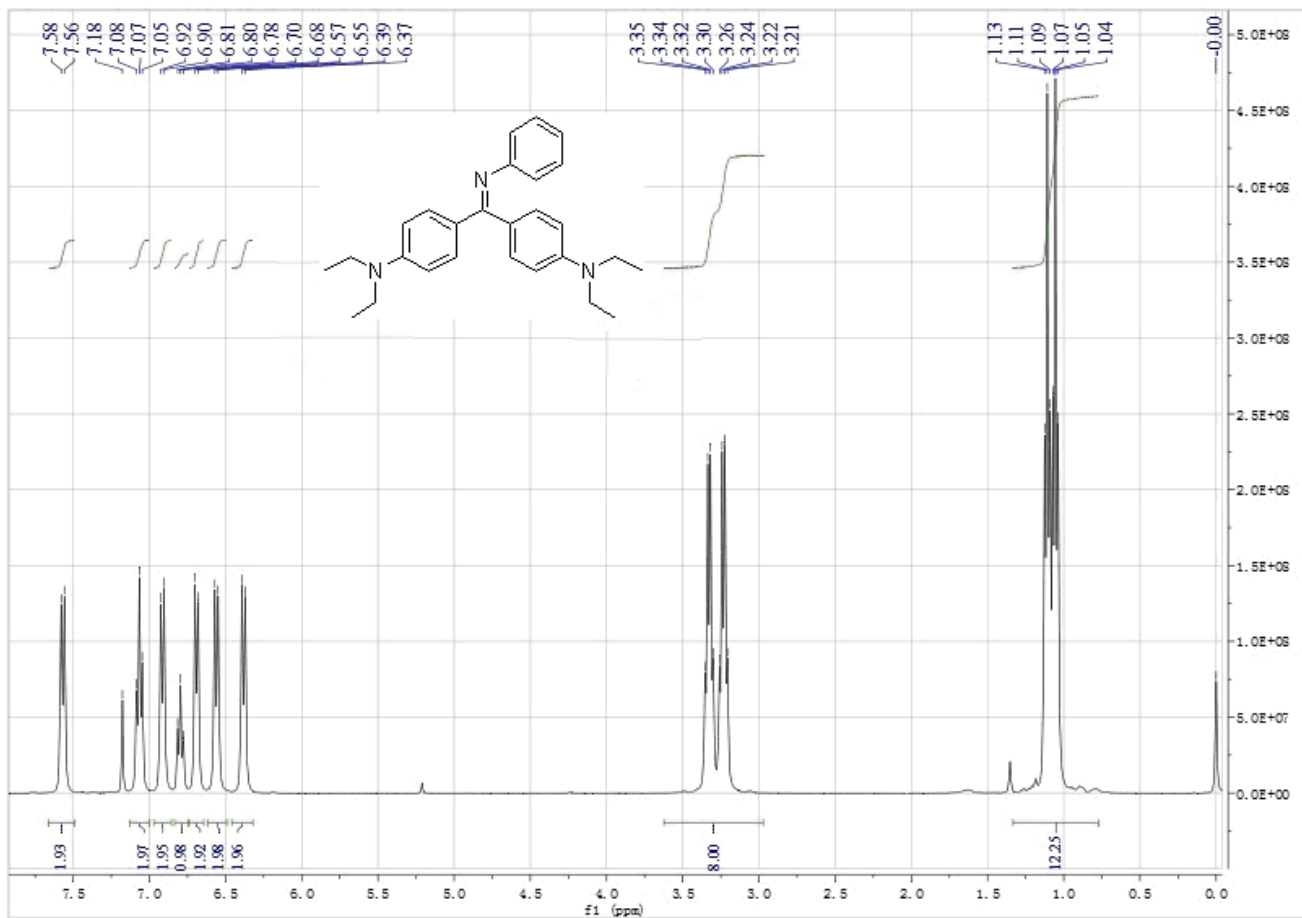


Figure S8:  $^1\text{H}$  NMR spectrum of **3u** in  $\text{CDCl}_3$

### Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	800 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source

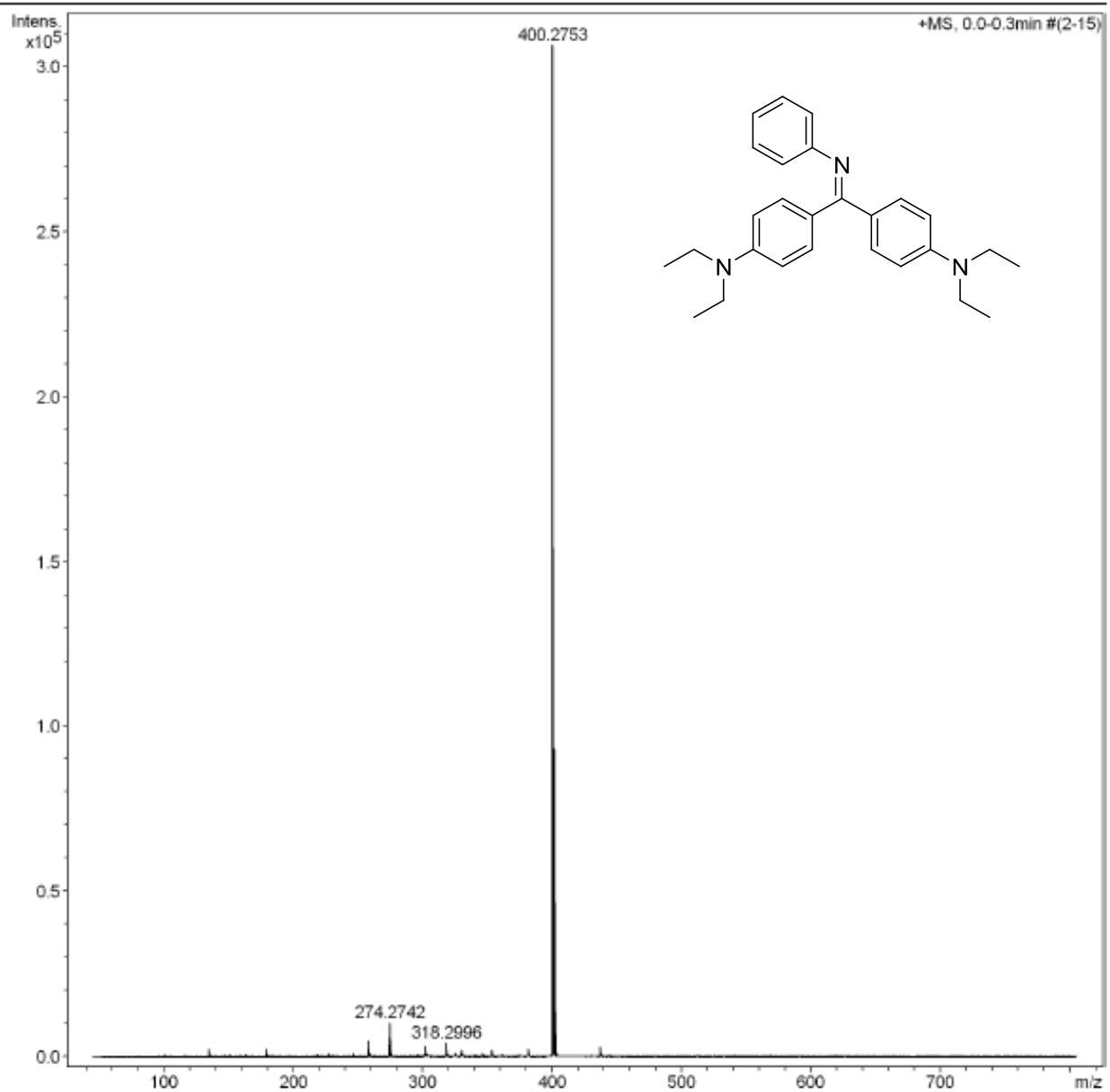


Figure S9: HRMS of **3u** ( $C_{27}H_{34}N_3^+ = M+H^+$ ), found: 400.2753, requires: 400.2747.

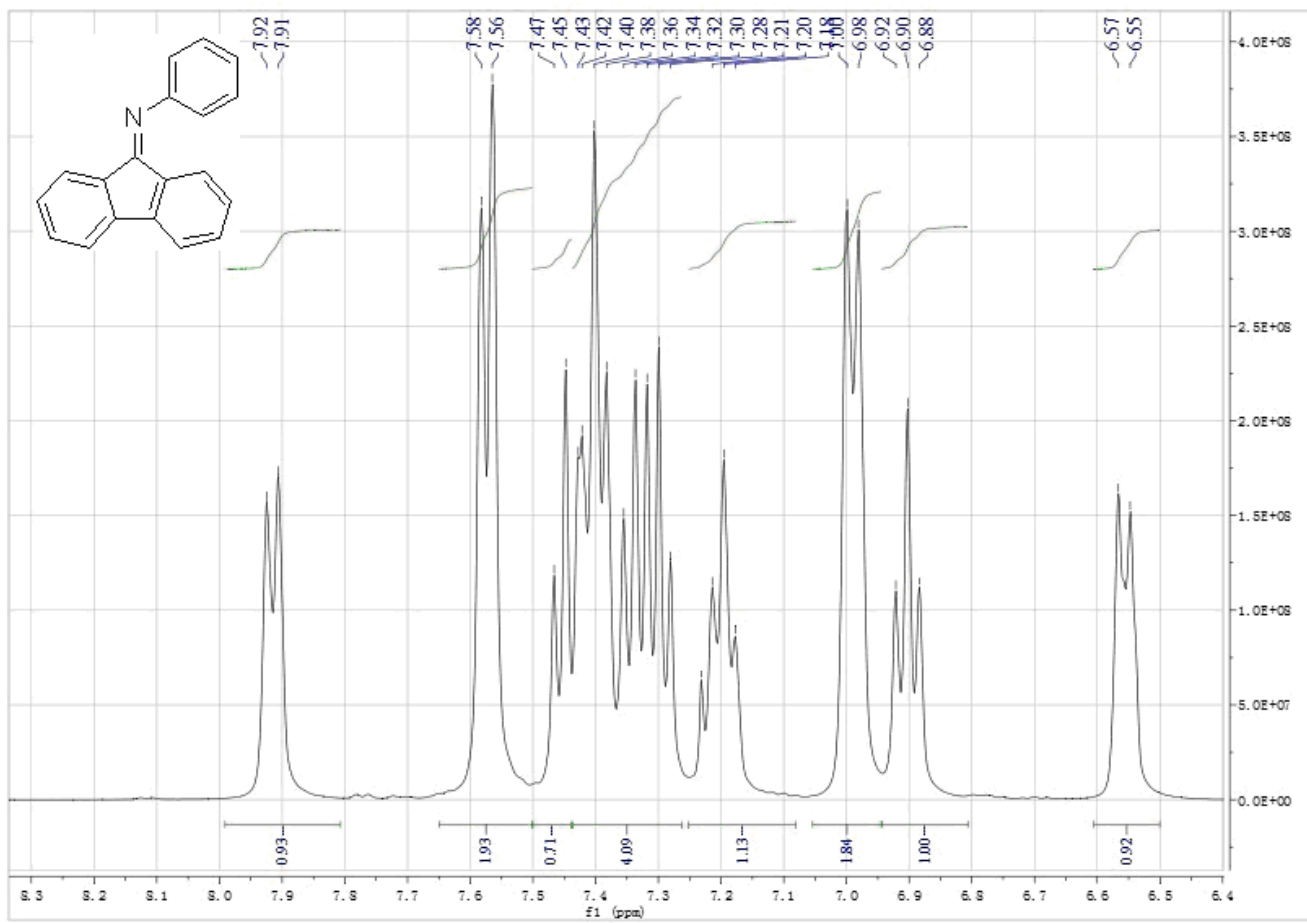


Figure S10:  $^1\text{H}$  NMR spectrum of **3v** in  $\text{CDCl}_3$

## Energy Profiles

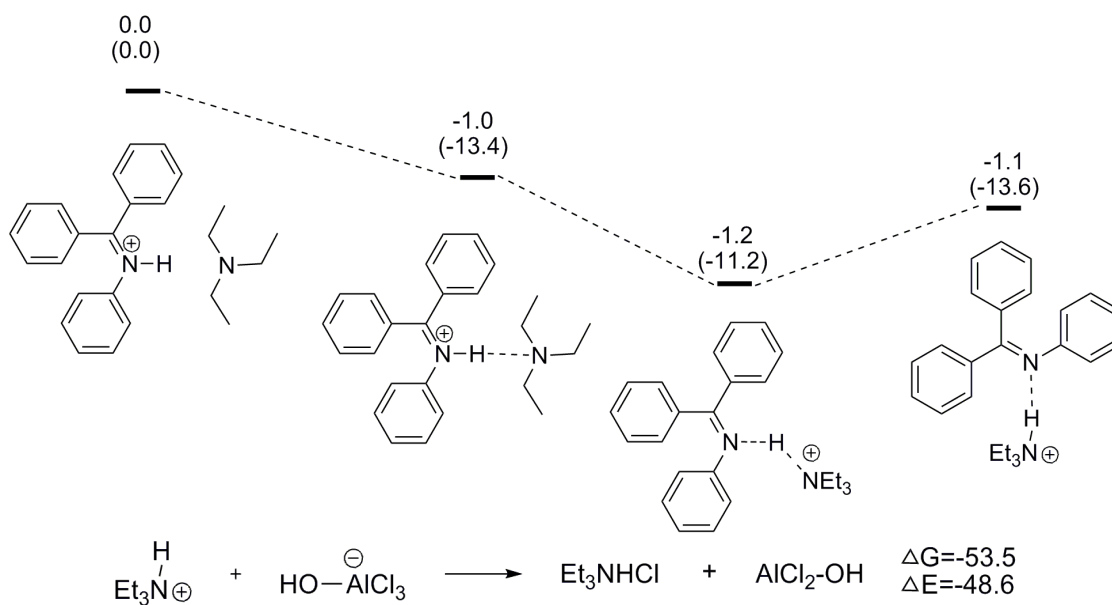


Figure S11: Energy profile of Et<sub>3</sub>N captures the proton. The relative free energies and electronic energies (in parentheses) are given in kcal/mol

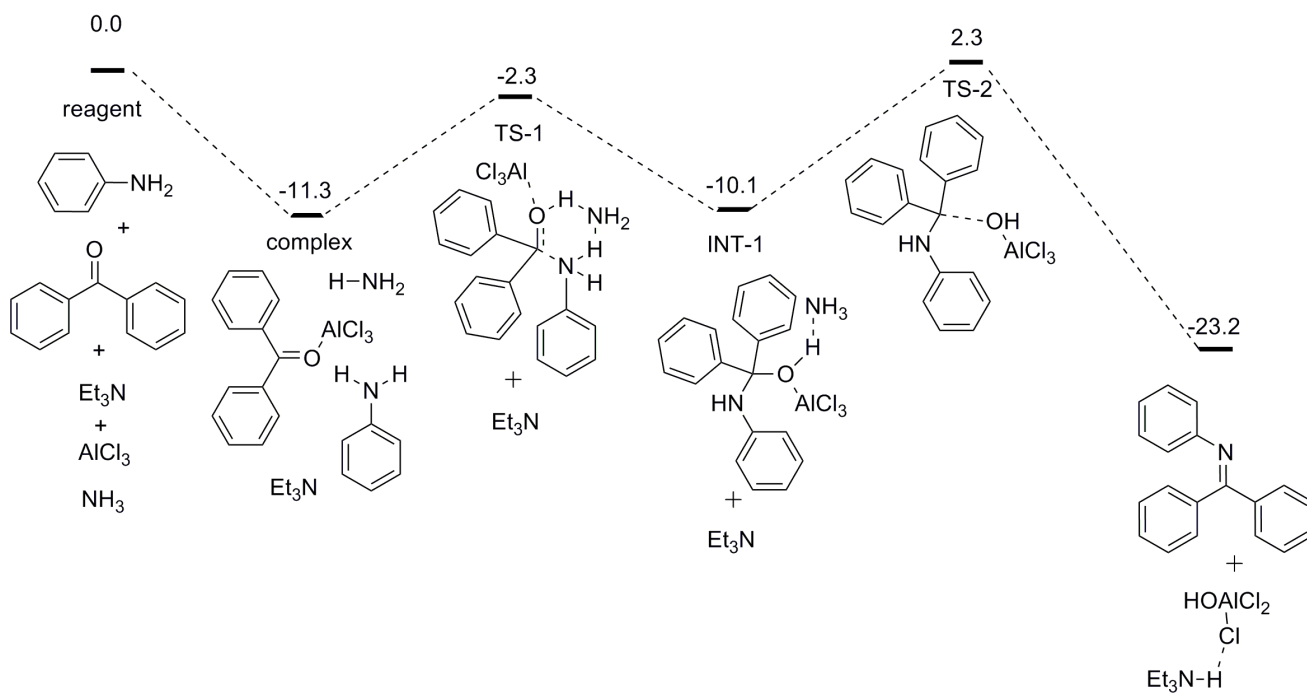


Figure S12: Solvent effect energy profile of the process. The relative free energies considering solvent effect are given in kcal/mol.

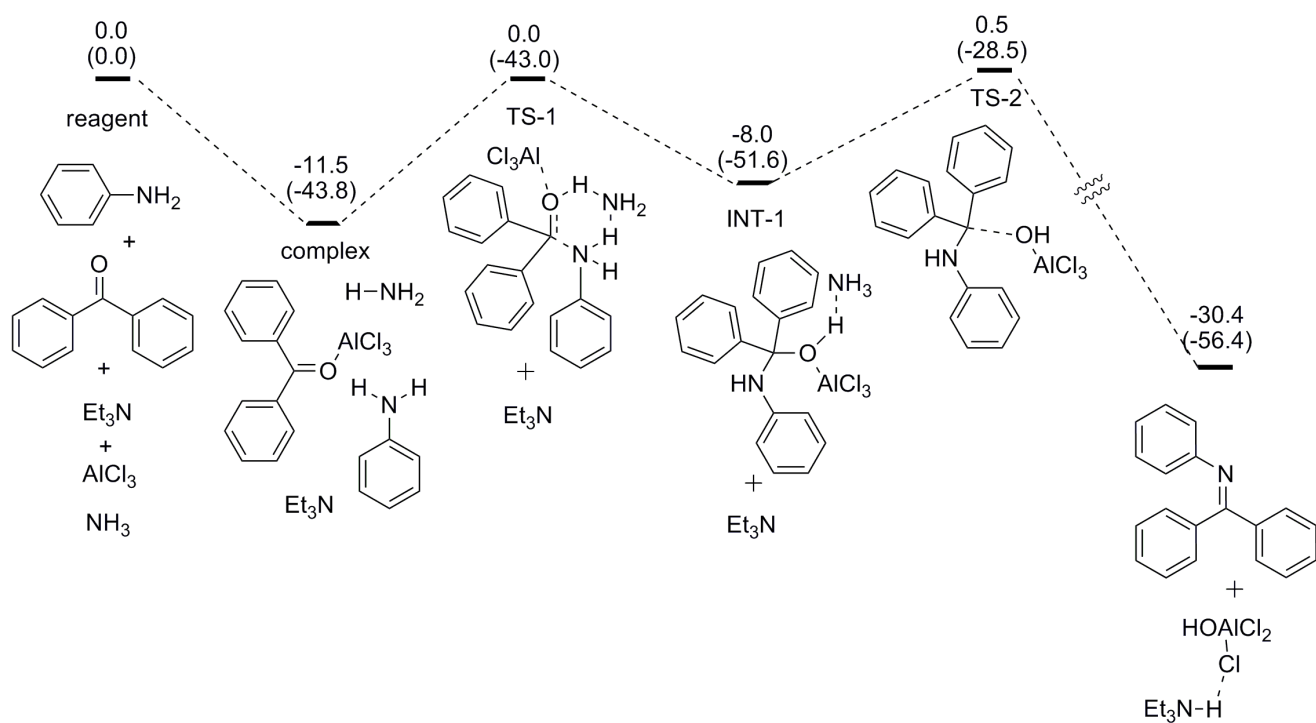


Figure 13: Energy profile of the whole reaction process calculated on B3PW91 functional. The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

# Cartesian coordinates (Å) and energies (hartree) for theoretical structure

## Benzophenone

E(RB+HF-LYP) = -576.636002625 hartree  
Sum of electronic and thermal Free Energies= -576.481741 hartree

6	-0.000045000	1.079109000	0.000252000
8	-0.000096000	2.305677000	0.000216000
6	1.303957000	0.336039000	0.024059000
6	2.433937000	0.984758000	-0.500211000
6	1.455094000	-0.927795000	0.615608000
6	3.681293000	0.369162000	-0.465110000
1	2.307752000	1.973758000	-0.928025000
6	2.710472000	-1.535361000	0.667617000
1	0.597957000	-1.424486000	1.057757000
6	3.821997000	-0.893573000	0.119447000
1	4.546627000	0.873022000	-0.885954000
1	2.819994000	-2.507704000	1.139079000
1	4.796905000	-1.371714000	0.153034000
6	-1.304035000	0.336063000	-0.023744000
6	-2.434186000	0.984793000	0.499886000
6	-1.454825000	-0.927963000	-0.615134000
6	-3.681545000	0.369050000	0.464477000
1	-2.308409000	1.973898000	0.927590000
6	-2.710091000	-1.535606000	-0.667472000
1	-0.597438000	-1.424603000	-1.056831000
6	-3.821921000	-0.893756000	-0.119830000
1	-4.547041000	0.872993000	0.884889000
1	-2.819412000	-2.508098000	-1.138669000
1	-4.796774000	-1.371994000	-0.153677000

## Benzophenone-AlCl<sub>3</sub>

E(RB+HF-LYP) = -623.742979583 hartree  
Sum of electronic and thermal Free Energies= -623.594024 hartree

6	-0.771796000	0.054933000	0.161424000
8	0.280005000	-0.633269000	0.283719000
6	-2.043155000	-0.683190000	0.133448000
6	-2.016014000	-2.047427000	-0.224647000
6	-3.264315000	-0.087915000	0.508043000
6	-3.192659000	-2.785813000	-0.240931000
1	-1.068857000	-2.503544000	-0.492202000
6	-4.435391000	-0.840048000	0.504926000
1	-3.286846000	0.945711000	0.833374000
6	-4.402246000	-2.183795000	0.123001000
1	-3.169591000	-3.831223000	-0.531502000
1	-5.371609000	-0.382434000	0.808454000
1	-5.318993000	-2.766165000	0.117332000
6	-0.701085000	1.519866000	0.071617000
6	0.322318000	2.201085000	0.760212000
6	-1.606231000	2.248098000	-0.726908000
6	0.416773000	3.585226000	0.671592000
1	1.020360000	1.645390000	1.378024000
6	-1.485444000	3.630125000	-0.831661000
1	-2.367278000	1.726175000	-1.296095000
6	-0.481750000	4.299628000	-0.126141000
1	1.197539000	4.105880000	1.216359000
1	-2.168088000	4.184529000	-1.467808000
1	-0.395047000	5.379334000	-0.204421000
13	2.122648000	-0.832128000	-0.045312000
17	2.548698000	0.480533000	-1.719247000
17	2.234656000	-2.945358000	-0.511727000
17	3.043701000	-0.246026000	1.834147000

## TS-1

E(RB+HF-LYP) = -967.918679198 hartree  
Sum of electronic and thermal Free Energies= -967.619146 hartree

6	-0.145248000	0.226071000	0.260287000
7	-0.788089000	-0.912143000	-0.508648000
8	1.029236000	-0.347456000	0.820984000
1	-0.541734000	-2.497454000	0.686917000
1	-0.182078000	-1.077517000	-1.312592000

13	2.616040000	-0.760012000	0.034271000
17	3.090947000	-2.718969000	1.024517000
17	4.211294000	0.643098000	0.465691000
17	2.257584000	-1.173455000	-2.098560000
1	0.800626000	-3.324683000	1.363744000
1	0.494663000	-1.709836000	1.608425000
6	-1.041844000	0.741320000	1.402690000
6	-0.727550000	0.483516000	2.742240000
6	-2.167767000	1.531298000	1.121575000
6	-1.540316000	0.963448000	3.773932000
1	0.186257000	-0.045992000	2.985575000
6	-2.979103000	2.008590000	2.148611000
1	-2.406018000	1.782581000	0.093955000
6	-2.673870000	1.719577000	3.481061000
1	-1.271242000	0.760281000	4.806739000
1	-3.846663000	2.615717000	1.907030000
1	-3.302651000	2.098275000	4.281574000
6	-2.155334000	-1.062005000	-0.892744000
6	-3.188812000	-1.191612000	0.051660000
6	-2.465126000	-1.251762000	-2.251037000
6	-4.494004000	-1.457104000	-0.362829000
1	-2.975233000	-1.084148000	1.108301000
6	-3.768188000	-1.539729000	-2.654798000
1	-1.672435000	-1.186866000	-2.992318000
6	-4.794835000	-1.632532000	-1.714501000
1	-5.278296000	-1.542615000	0.384115000
1	-3.977709000	-1.686348000	-3.710445000
1	-5.811312000	-1.848330000	-2.028384000
6	0.225892000	1.425704000	-0.633636000
6	1.152466000	2.356850000	-0.140788000
6	-0.368864000	1.660726000	-1.877873000
6	1.495927000	3.480673000	-0.889384000
1	1.614901000	2.192416000	0.825832000
6	-0.029639000	2.792383000	-2.623520000
1	-1.102421000	0.970930000	-2.276343000
6	0.905623000	3.703073000	-2.135020000
1	2.228753000	4.179828000	-0.498079000
1	-0.496027000	2.954203000	-3.591106000
1	1.174230000	4.578246000	-2.719387000
7	0.030487000	-2.667270000	1.539964000
1	-0.528289000	-2.925375000	2.350241000

## INT-1

E(RB+HF-LYP) = -967.932302102 hartree  
Sum of electronic and thermal Free Energies= -967.632573 hartree

6	0.300491000	0.692010000	-0.251150000
7	-0.569015000	0.510340000	-1.419078000
8	0.110517000	-0.376161000	0.702233000
1	-2.881145000	0.050151000	1.346116000
1	-0.158535000	-0.226489000	-1.986981000
13	0.597996000	-2.129645000	0.572184000
17	-1.209059000	-3.200627000	1.379456000
17	2.249218000	-2.583996000	1.916953000
17	0.889646000	-2.722450000	-1.515355000
1	-2.289410000	-1.337528000	2.111070000
1	-1.193123000	-0.229916000	1.489002000
6	0.037437000	2.029540000	0.468067000
6	0.146416000	2.137957000	1.859635000
6	-0.204647000	3.191463000	-0.279153000
6	-0.022074000	3.372400000	2.494236000
1	0.393331000	1.257843000	2.443788000
6	-0.375246000	4.421733000	0.353453000
1	-0.267902000	3.119651000	-1.359932000
6	-0.290975000	4.517249000	1.745323000
1	0.069241000	3.437171000	3.575097000
1	-0.570603000	5.308859000	-0.242277000
1	-0.421375000	5.476599000	2.237323000
6	-1.961831000	0.276656000	-1.290429000
6	-2.846377000	1.210901000	-0.712996000
6	-2.504149000	-0.912149000	-1.813017000
6	-4.216640000	0.936773000	-0.638822000

1	-2.470962000	2.156507000	-0.344479000
6	-3.873614000	-1.166184000	-1.753124000
1	-1.837118000	-1.649977000	-2.249587000
6	-4.741577000	-0.251385000	-1.154365000
1	-4.879329000	1.678750000	-0.200239000
1	-4.257381000	-2.096686000	-2.160970000
1	-5.807014000	-0.452444000	-1.101894000
6	1.762798000	0.737231000	-0.741900000
6	2.803605000	0.478992000	0.159457000
6	2.082854000	1.119544000	-2.051530000
6	4.133759000	0.563731000	-0.250425000
1	2.579210000	0.196472000	1.180891000
6	3.414926000	1.207329000	-2.458196000
1	1.291401000	1.350043000	-2.755890000
6	4.445382000	0.926565000	-1.561210000
1	4.924904000	0.341005000	0.459195000
1	3.643734000	1.494636000	-3.480485000
1	5.481680000	0.990912000	-1.879844000
7	-2.168879000	-0.320126000	1.985932000
1	-2.192348000	0.175731000	2.874819000

### Complex of HOAlCl<sub>3</sub> and Et<sub>3</sub>NH

E(RB+HF-LYP) = -298.041412505 hartree  
Sum of electronic and thermal Free Energies= -297.929784 hartree

13	1.28523200	-0.02102400	0.14397000
17	3.24483600	-0.94759100	0.27343600
17	1.32635900	2.12123800	-0.33612200
17	0.00962300	-0.96806500	-1.48243000
8	0.26822000	-0.31020400	1.56620800
1	0.72910400	-0.38649500	2.40864800
7	-2.51666000	-0.08129500	0.10694600
1	-1.63522700	-0.32594000	-0.41021500
7	-2.30000700	1.25217800	0.75742600
1	-2.04819500	1.98105600	-0.01342500
1	-3.21676400	1.54047900	1.27629000
1	-1.45951100	1.14415900	1.44369000
7	-2.70357200	-1.16592000	1.12198600
1	-3.58131600	-0.93620800	1.72958300
1	-2.84340300	-2.11176600	0.59713500
1	-1.78932000	-1.19744200	1.71702300
7	-3.60810500	-0.04666900	-0.90823700
1	-3.37934200	0.72427600	-1.64487700
1	-3.66250000	-1.01759900	-1.40191900
1	-4.55448000	0.17706500	-0.41190500

### Triethylamine

E(RB+HF-LYP) = -174.482835727 hartree  
Sum of electronic and thermal Free Energies= -174.389525 hartree

7	0.000052000	-0.000199000	-0.370867000
6	-0.033947000	1.388483000	0.060781000
1	0.841686000	1.919136000	-0.327252000
1	-0.929613000	1.878428000	-0.335305000
1	-0.041651000	1.506065000	1.163039000
6	1.220042000	-0.664787000	0.060815000
1	1.243368000	-1.687542000	-0.329434000
1	2.092328000	-0.132613000	-0.333023000
1	1.324596000	-0.719440000	1.163094000
6	-1.186061000	-0.723575000	0.060752000
1	-2.083202000	-0.232482000	-0.330528000
1	-1.161633000	-1.745555000	-0.331674000
1	-1.286447000	-0.785336000	1.163063000

### Et<sub>3</sub>NHCl

E(RB+HF-LYP) = -190.066582153 hartree  
Sum of electronic and thermal Free Energies= -189.968716 hartree

7	-0.722562000	0.000440000	-0.000380000
6	-1.140588000	1.357564000	-0.394949000
1	-0.729299000	2.074969000	0.317986000
1	-0.732335000	1.579972000	-1.382875000
1	-2.233706000	1.448762000	-0.419511000
6	-1.129840000	-0.336679000	1.375449000
1	-0.721846000	-1.315823000	1.634091000

1	-0.710641000	0.404017000	2.059408000
1	-2.222257000	-0.354766000	1.476588000
6	-1.137304000	-1.023308000	-0.976418000
1	-0.736284000	-0.759994000	-1.957213000
1	-0.716950000	-1.986031000	-0.678722000
1	-2.230209000	-1.101531000	-1.034848000
1	0.588587000	0.002300000	-0.003381000
17	2.114663000	0.001152000	-0.001962000

### AlCl<sub>3</sub>

E(RB+HF-LYP) = -47.0509341925 hartree  
Sum of electronic and thermal Free Energies= -47.077558 hartree

13	-0.000003000	0.000044000	0.000500000
17	-0.688746000	2.003830000	-0.000127000
17	-1.391039000	-1.598391000	-0.000127000
17	2.079787000	-0.405472000	-0.000127000

### AlCl<sub>3</sub>-OH

E(RB+HF-LYP) = -123.031518645 hartree  
Sum of electronic and thermal Free Energies= -123.048053 hartree

8	-0.18845100	-0.02952600	2.06898000
13	0.00238800	-0.00276400	0.32551900
17	-2.03862900	-0.14254900	-0.58318400
17	1.22719900	-1.70816100	-0.39262900
17	0.96353100	1.86883800	-0.38493900
1	-1.10915600	-0.03604900	2.34919500

### Et<sub>3</sub>NH

E(RB+HF-LYP) = -174.862738147 hartree  
Sum of electronic and thermal Free Energies= -174.754081 hartree

7	-0.000201000	-0.000014000	-0.339137000
6	-1.439919000	-0.058349000	0.103493000
1	-1.963504000	0.817212000	-0.280952000
1	-1.892910000	-0.969785000	-0.287193000
1	-1.465171000	-0.063175000	1.193843000
6	0.669466000	1.275887000	0.103365000
1	1.688595000	1.292180000	-0.283450000
1	0.105096000	2.124098000	-0.284631000
1	0.680754000	1.298471000	1.193697000
6	0.770555000	-1.217497000	0.103381000
1	0.275078000	-2.108815000	-0.282023000
1	1.786777000	-1.152816000	-0.286092000
1	0.786371000	-1.237455000	1.193706000
1	-0.000289000	-0.000066000	-1.364382000

### Product

E(RB+HF-LYP) = -787.806719933 hartree  
Sum of electronic and thermal Free Energies= -787.567669 hartree

6	0.534175000	-0.320401000	-0.048734000
7	-0.255984000	-1.336197000	-0.071643000
6	0.089092000	1.114153000	-0.072172000
6	0.533146000	2.017871000	0.905857000
6	-0.779034000	1.572682000	-1.074437000
6	0.103676000	3.345170000	0.892119000
1	1.211192000	1.675657000	1.682202000
6	-1.193122000	2.903668000	-1.097333000
1	-1.127865000	0.882151000	-1.835461000
6	-0.757423000	3.792173000	-0.111760000
1	0.445631000	4.030312000	1.662615000
1	-1.859085000	3.246341000	-1.883966000
1	-1.085789000	4.827450000	-0.127344000
6	-1.655996000	-1.268113000	0.024091000
6	-2.317682000	-0.624824000	1.085265000
6	-2.417897000	-1.982556000	-0.916900000
6	-3.707028000	-0.681158000	1.183877000
1	-1.736196000	-0.096084000	1.833348000
6	-3.807537000	-2.011121000	-0.825394000
1	-1.899691000	-2.505897000	-1.714643000
6	-4.460755000	-1.363248000	0.226497000
1	-4.202841000	-0.185458000	2.014153000
1	-4.382021000	-2.555079000	-1.570255000
1	-5.543214000	-1.399847000	0.305402000
6	2.001236000	-0.600998000	-0.026181000



6	2.457640000	-1.867978000	0.379273000
6	2.945041000	0.357833000	-0.428986000
6	3.817070000	-2.162499000	0.388276000
1	1.723567000	-2.606699000	0.681552000
6	4.307916000	0.057744000	-0.426319000
1	2.612740000	1.336525000	-0.757618000

6	4.748656000	-1.200057000	-0.014552000
1	4.154103000	-3.143276000	0.711878000
1	5.024127000	0.808199000	-0.748560000
1	5.810191000	-1.430961000	-0.006748000