Electronic Supporting Information

Cross-Benzoin and Stetter-Type Reactions Mediated by KO*t*Bu-DMF via Electron-Transfer process

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Mass spectrometric experiments

The mass spectrometric investigations were carried out on a LCQ Duo (ThermoQuest, San Jose, CA, USA), equipped with an electrospray ionization source operating in negative-ion mode. Instrumental parameters: capillary voltage -10 V, spray voltage 4.50 kV, capillary temperature of 150 °C, mass scan range from m/z 50 to 1200; N_2 was used as sheath gas. The samples were injected into the spectrometer by a syringe pump at a constant flow rate of 8 μL/min using the appropriate eluting solvent.

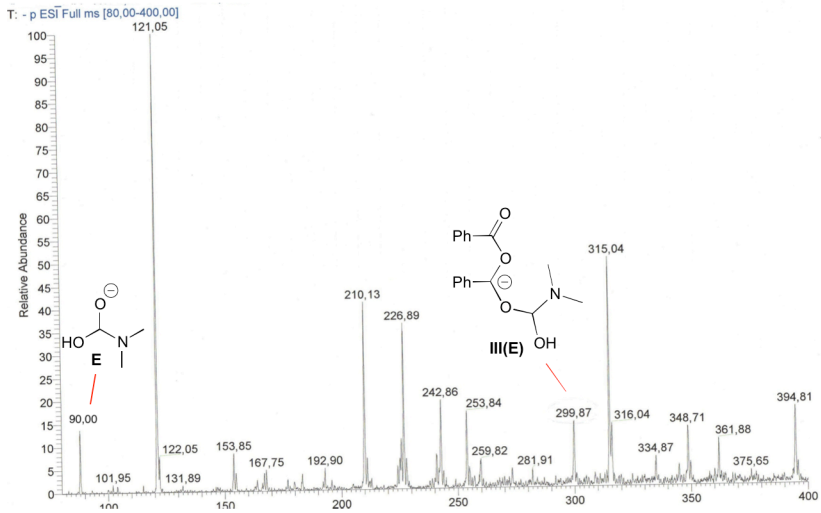


Figure S1. Full scan spectrum of the benzoin-like reaction of **1a** (0.5 M), **2a** (0.5 M) in DMF with KO*t*Bu (0.125 M) showing the presence of anion **E** (*m/z* 90) and isobaric species **I-III(E)** (*m/z* 300).

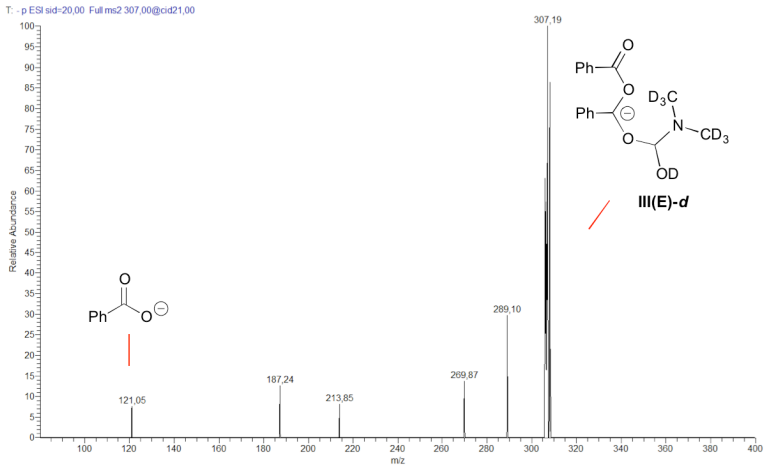


Figure S2. MS/MS mass spectrum of the deuterated adduct **III(E)-*d*** obtained from DMF-d_7 solutions of **1a** (0.5 M), **2a** (0.5 M) and KO*t*Bu (0.125 M).

EPR experiments

EPR investigation was carried out with a Bruker ER200 MRD spectrometer calibrated with α,α'-diphenylpicrylhydrazyl (dpph, resonance at 3457.41 G, g = 2.0023) and equipped with a TE201 resonator (microwave frequency of 9.4 GHz). A flat quartz cell was used for all the experiments. Samples were DMF solutions containing KO*t*Bu (0.125 M) to which benzyl **1a** (0.5 M) and aldehyde **2a** (0.5 M) were added stepwise and when necessary. In the case of EPR spin trapping experiments, DMF solutions contain from the beginning α-phenyl-N-*tert*-butyl nitrone (PBN, 0.5 M) as radical trap. When requested benzyl **1a** (0.5 M) and aldehyde **2a** (0.5 M) were progressively added.

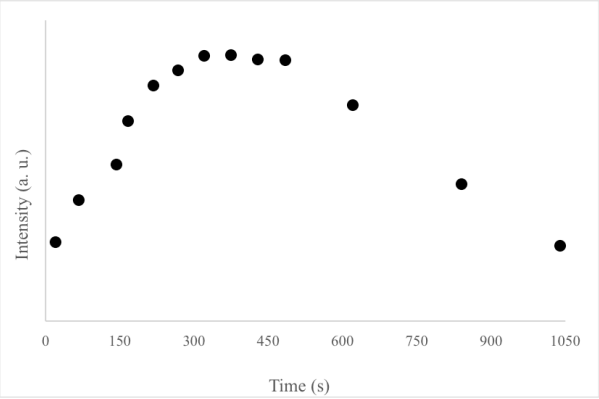


Figure S3. Fixed-field EPR signal intensity of a radical species (g= 2.0017) in time obtained by the addition of aldehyde **2a** (0.5 M) to a DMF solution of KOtBu (0.125 M) and of benzil **1a** (0.5 M).

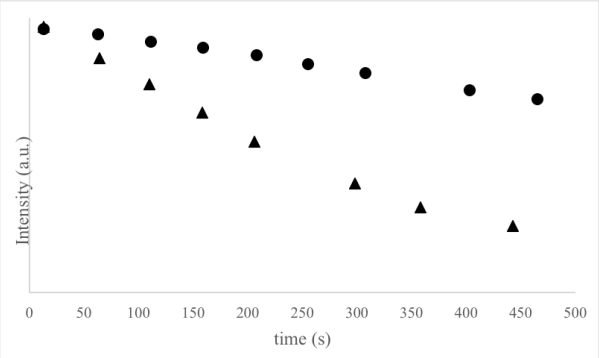


Figure S4. Fixed-field EPR signal intensity of the paramagnetic adduct [PBN-benzyl anion radical **V**]$^{\bullet}$ in time. (●) DMF solution containing KO*t*Bu (0.125 M), benzil **1a** (0.5 M) and PBN (0.5 M). (▲) the same as before with the addition of aldehyde **2a** (0.5 M).

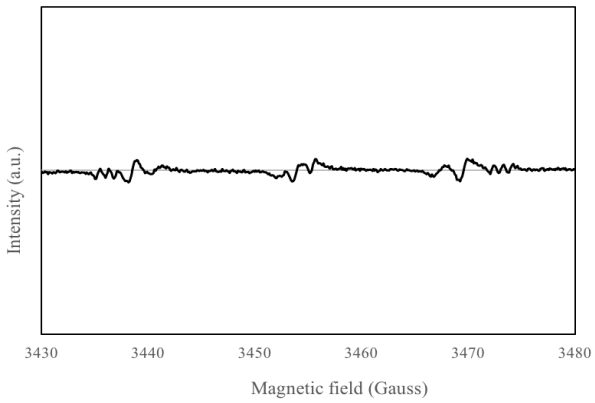


Figure S5. Anaerobic EPR spectrum of a DMF solution containing KO*t*Bu (0.125 M) and PBN (0.5 M).

Computational methods, Cartesian coordinates and energies in Hartree for species calculated

DFT calculations were carried out with the Truhlar M06 hybrid functional,[1] together with the 6-31+G(d,p) basis set within the framework of the Gaussian 09 suite of programs.[2] All the molecular structures were fully optimized by using the PCM continuum model (N,N-dimethylformamide and dimethylsulfoxide)[3] and the Berny analytical gradient optimization method, whereby the stationary points were characterized by frequency calculation. Thermochemical analysis (free energies $\Delta\Delta G$) was performed at 298.15 K, starting from the frequency calculations.

Electronic energies (E, u.a.), Gibbs free energies (ΔG, u.a.), and fully optimized structures [M06//6-31+G(d,p) level using PCM continuum model (N,N-dimethylformamide and dimethylsulfoxide)] are reported in the next pages (pp. S5-S14).

Structures of Figure 3

1a

E = -689.51998
ΔG = -689.36149

C	-0.868844	-0.494326	0.135532
O	-0.179584	-1.497915	0.254542
C	-1.618674	-0.140331	-1.078274
C	-1.501990	-0.953407	-2.213509
C	-2.225261	-0.652366	-3.357817
C	-3.074060	0.456605	-3.372863
C	-3.199710	1.265450	-2.245241
C	-2.471765	0.970338	-1.098263
H	-0.839556	-1.814750	-2.178466
H	-2.133648	-1.278930	-4.240897
H	-3.641473	0.690780	-4.270210
H	-3.862277	2.126359	-2.260793
H	-2.570196	1.607084	-0.221126
C	-0.862894	0.480119	1.314478
O	-0.162156	1.475682	1.195081
C	-1.616089	0.134804	2.528701
C	-1.489398	0.946476	3.663867
C	-2.215464	0.653801	4.808577
C	-3.077001	-0.445295	4.824097
C	-3.212607	-1.252632	3.696547
C	-2.481938	-0.965940	2.549165
H	-0.817082	1.800112	3.628456
H	-2.116133	1.279264	5.691604
H	-3.646586	-0.672904	5.721758
H	-3.885062	-2.105831	3.712468
H	-2.588200	-1.601503	1.672084

E

E = -324.27277
ΔG = -324.18874

C	-1.605229	-0.848889	-0.290468
N	-0.643114	0.221028	-0.429466
C	-0.909573	1.279770	0.519908
C	0.764065	-0.252725	-0.407283
O	1.656935	0.680661	-0.576519
H	0.766997	-1.090730	-1.154536
H	-2.611920	-0.490390	-0.545750
H	-1.354575	-1.670419	-0.974704
H	-1.643083	-1.263229	0.736222
H	-1.885681	1.736745	0.308411
H	-0.930214	0.920469	1.568603
H	-0.136215	2.049365	0.433906
O	0.993418	-0.983299	0.872501
H	1.598088	-0.386835	1.333316

TS reactants- I(E)

E = -1013.80292
ΔG = -1013.53566

C	1.821514	-1.520647	-0.987837
C	1.327215	-1.407429	0.317222
C	2.170695	-1.714647	1.387362
C	3.483801	-2.125374	1.167460
C	3.968057	-2.230668	-0.133088
C	3.132054	-1.926074	-1.209051
C	-0.051995	-0.927358	0.641901
O	-0.358819	-0.642629	1.808998
C	-1.182273	-1.244954	-0.340956
O	-1.020620	-2.119887	-1.181821
C	-2.515299	-0.605025	-0.162852
C	-2.710691	0.629231	0.469286
C	-3.992303	1.157895	0.583810
C	-5.090196	0.460918	0.081272
C	-4.904355	-0.768748	-0.548783
C	-3.623789	-1.293616	-0.673561
O	0.151896	0.928596	-0.468122
C	1.058643	1.652757	0.168104
N	1.444336	2.874280	-0.561333
C	2.457524	3.626272	0.159978
O	0.604906	2.110695	1.467798
C	1.954380	2.516949	-1.873276
H	2.015011	1.078929	0.368821
H	2.753542	4.500779	-0.431442
H	2.071395	3.971580	1.121878
H	3.369520	3.020593	0.349471
H	2.212785	3.426215	-2.428601
H	2.869659	1.889024	-1.807800
H	1.200565	1.959773	-2.434533
H	0.253711	1.309557	1.886904
H	1.784063	-1.619122	2.399392
H	4.127214	-2.359783	2.012477
H	4.993751	-2.545934	-0.311507
H	3.508801	-1.999018	-2.226956
H	1.187340	-1.255149	-1.827329
H	-3.465813	-2.252011	-1.162654
H	-5.757355	-1.316924	-0.941571
H	-6.090269	0.877613	0.178585
H	-4.135237	2.123134	1.064181
H	-1.845847	1.179695	0.823241

IE

E = -1013.81590
ΔG = -1013.54477

C	1.521792	4.081183	-0.044428
N	0.861926	2.911482	-0.607532
C	1.557555	2.490697	-1.815103

C	0.813878	1.836714	0.356630
O	0.198357	2.298183	1.525667
O	0.105153	0.774397	-0.198065
H	1.853188	1.497104	0.603253
H	1.545783	4.874593	-0.798609
H	0.979831	4.446128	0.830035
H	2.566770	3.862886	0.256011
H	1.563228	3.318670	-2.531682
H	2.610490	2.208380	-1.610492
H	1.052532	1.636103	-2.271166
H	0.034323	1.448370	2.006319
C	0.223777	-0.471875	0.599629
C	-0.930071	-1.379529	0.118707
O	0.020773	-0.295191	1.900553
C	1.581844	-1.078932	0.225808
C	2.472381	-1.474566	1.219015
C	3.718583	-2.009844	0.886941
C	4.080389	-2.161214	-0.448802
C	3.188063	-1.775164	-1.451677
C	1.950021	-1.239467	-1.113059
H	2.173738	-1.348597	2.257634
H	4.407613	-2.308844	1.674651
H	5.050739	-2.577546	-0.711069
H	3.461530	-1.892060	-2.498561
H	1.257402	-0.932081	-1.896349
O	-0.731465	-2.583749	-0.011788
C	-2.324669	-0.847860	-0.020478
C	-3.283400	-1.715683	-0.560633
C	-4.601703	-1.309586	-0.731525
C	-4.985720	-0.024070	-0.353633
C	-4.042862	0.846865	0.189422
C	-2.720524	0.444272	0.351211
H	-2.974857	-2.717913	-0.847709
H	-5.329757	-1.995612	-1.158355
H	-6.016537	0.298381	-0.482576
H	-4.338419	1.850058	0.488210
H	-1.989629	1.130846	0.764077

TS1(E)

E = -1013.79682
ΔG = -1013.52580

C	-2.512833	-0.622258	-1.191652
C	-1.766997	-1.323425	-0.239840
C	-2.447412	-2.088893	0.712734
C	-3.838978	-2.141330	0.726978
C	-4.574484	-1.436783	-0.224300
C	-3.904901	-0.682770	-1.186912
C	-0.263445	-1.291252	-0.157727
O	0.326551	-2.385228	0.188497
C	0.408142	0.035589	-0.125963
O	0.323981	-0.486361	-1.408817
C	-0.303509	1.331171	0.130197
C	-0.905270	1.574837	1.364692
C	-1.554311	2.784107	1.603252
C	-1.595546	3.760914	0.608924
C	-0.984726	3.524260	-0.622236
C	-0.342658	2.311012	-0.859621
O	1.696794	0.190718	0.435418
C	2.716179	-0.735624	0.119080
O	2.721171	-1.796247	1.004547
N	3.967036	-0.016046	0.203330
C	5.092633	-0.914965	-0.011938
C	3.999773	1.054338	-0.784573
H	-1.991884	-0.035339	-1.943897
H	-4.469472	-0.138797	-1.941584
H	-5.661382	-1.478425	-0.218860
H	-4.350190	-2.736694	1.480741
H	-1.866785	-2.647327	1.443670
H	0.120233	2.107181	-1.824483
H	-1.014972	4.284581	-1.399728
H	-2.104190	4.704671	0.792599
H	-2.030431	2.964053	2.564669
H	-0.875252	0.803370	2.134360
H	2.538372	-1.099946	-0.915440
H	1.825228	-2.210259	0.829044
H	5.043639	-1.409988	-1.003033
H	5.121807	-1.687546	0.758561
H	6.022847	-0.338929	0.032794
H	3.178718	1.756291	-0.617122
H	3.918362	0.663935	-1.819522
H	4.948173	1.594855	-0.699821

II(E)

E = -1013.79632
ΔG = -1013.52900

C	-2.493403	-1.064633	-1.273116
C	-1.691433	-1.348821	-0.167604
C	-2.304633	-1.753215	1.023032
C	-3.689664	-1.856899	1.112073
C	-4.484325	-1.575847	0.000313
C	-3.880583	-1.185298	-1.192722
C	-0.186921	-1.273851	-0.191336
O	0.437376	-2.356857	0.161233
C	0.431595	0.086699	-0.198520
O	0.301581	-0.517722	-1.449794
C	-0.362665	1.336062	0.034099
C	-0.562604	1.800423	1.336891
C	-1.311599	2.950341	1.567512
C	-1.861896	3.652665	0.494721
C	-1.661346	3.194977	-0.805691
C	-0.918397	2.037731	-1.033523
O	1.731634	0.343102	0.274553
C	2.753974	-0.621760	0.095805
O	2.705468	-1.596854	1.068138
N	4.006614	0.094124	0.179110
C	5.131728	-0.828938	0.115612

C	4.116249	1.072443	-0.894321
H	-1.680571	-1.986911	1.884453
H	-4.150746	-2.162030	2.049272
H	-5.566756	-1.661436	0.065046
H	-4.491932	-0.967666	-2.066290
H	-2.022597	-0.742364	-2.199047
H	-0.774782	1.658309	-2.043253
H	-2.090565	3.736816	-1.645886
H	-2.448546	4.550840	0.674074
H	-1.468480	3.300141	2.585555
H	-0.132407	1.247743	2.171341
H	1.839647	-2.066299	0.850333
H	2.619592	-1.073927	-0.911737
H	5.138050	-1.413087	-0.826946
H	5.105043	-1.527043	0.953879
H	6.063937	-0.256508	0.164336
H	5.073744	1.596172	-0.806125
H	3.310548	1.806896	-0.830505
H	4.077585	0.595656	-1.894657

TS2(E)

E = -1013.76244
ΔG = -1013.49344

C	2.494728	0.812847	-1.247983
C	1.552964	1.166258	-0.240580
C	1.834329	2.348696	0.496338
C	2.951036	3.126304	0.217332
C	3.854044	2.772728	-0.789641
C	3.606542	1.598992	-1.510948
C	0.352035	0.405454	-0.062635
O	0.399008	-0.953527	-0.397867
C	1.202527	-1.763618	0.425341
O	0.523816	-2.070137	1.633960
O	-0.232054	0.579215	1.261618
C	-1.358340	1.324124	1.107188
C	-2.441624	0.769626	0.253507
C	-2.625320	-0.609836	0.088573
C	-3.723334	-1.086417	-0.618843
C	-4.644154	-0.198538	-1.175647
C	-4.471098	1.174525	-1.005058
C	-3.386207	1.654490	-0.280178
O	-1.487703	2.366850	1.724268
N	1.528283	-2.961752	-0.277393
C	0.373971	-3.776634	-0.629912
C	2.546896	-3.744327	0.400162
H	-1.900890	-1.305774	0.502669
H	-3.860854	-2.158955	-0.737391
H	-5.497197	-0.575878	-1.734709
H	-5.187470	1.872424	-1.432276
H	-3.250514	2.723214	-0.131138
H	1.154024	2.651797	1.289188
H	3.126235	4.026052	0.807081
H	4.726910	3.386060	-1.001071
H	4.299385	1.287659	-2.292553
H	2.324371	-0.094521	-1.825965
H	2.140252	-1.228508	0.661425
H	2.886169	-4.548073	-0.263345
H	3.410172	-3.112910	0.639910
H	2.181183	-4.203954	1.335871
H	0.685192	-4.537581	-1.354626
H	-0.064246	-4.290837	0.242869
H	-0.396950	-3.153213	-1.091618
H	0.187743	-1.231980	1.989493

III(E)

E = -1013.76818
ΔG = -1013.50027

C	-1.649869	0.768152	-0.746817
O	-1.622223	1.773224	-1.440990
C	-2.916362	0.187135	-0.221758
C	-2.995764	-1.118425	0.274829
C	-4.207610	-1.620029	0.737293
C	-5.349904	-0.820838	0.715945
C	-5.278578	0.479086	0.217675
C	-4.069499	0.977803	-0.254268
H	-2.111712	-1.750345	0.279411
H	-4.261500	-2.638510	1.113964
H	-6.295078	-1.212387	1.084604
H	-6.167398	1.105032	0.197779
H	-4.000994	1.988505	-0.648949
O	-0.577393	0.086634	-0.360978
C	0.737372	0.351785	-0.946632
O	1.382020	-0.895626	-1.042165
C	1.462018	1.400793	-0.289111
C	0.841575	2.442205	0.450873
C	1.577406	3.500364	0.973538
C	2.960990	3.578877	0.805396
C	3.596617	2.548960	0.099212
C	2.876837	1.490602	-0.430032
H	-0.234229	2.420339	0.605626
H	1.055991	4.277791	1.531822
H	3.529428	4.410243	1.215835
H	4.677587	2.572954	-0.036788
H	3.396882	0.703547	-0.974946
C	1.784296	-1.495049	0.166883
N	2.823177	-2.435653	-0.099932
H	2.180162	-0.720452	0.845484
O	0.685175	-2.137737	0.795617
C	3.470815	-2.904318	1.112333
C	2.423799	-3.543463	-0.955338
H	4.370587	-3.470823	0.846041
H	3.775878	-2.051155	1.729210
H	2.820675	-3.559104	1.720040
H	3.320584	-4.088145	-1.271952
H	1.753065	-4.254480	-0.442489
H	1.917273	-3.163855	-1.846417
H	-0.014915	-1.473385	0.879251

Structures of Figure 6

IX

E = -689.720593
ΔG = -689.56415

C	-0.868841	-0.494330	0.135534
O	-0.179583	-1.497910	0.254564
C	-1.618643	-0.140329	-1.078296
C	-1.501947	-0.953410	-2.213531
C	-2.225244	-0.652381	-3.357827
C	-3.074088	0.456562	-3.372850
C	-3.199733	1.265415	-2.245239
C	-2.471737	0.970330	-1.098275
H	-0.839493	-1.814736	-2.178485
H	-2.133620	-1.278935	-4.240912
H	-3.641544	0.690707	-4.270178
H	-3.862281	2.126336	-2.260787
H	-2.570125	1.607110	-0.221157
C	-0.862945	0.480164	1.314466
O	-0.162210	1.475727	1.195047
C	-1.616113	0.134843	2.528703
C	-1.489387	0.946471	3.663900
C	-2.215432	0.653764	4.808613
C	-3.076995	-0.445312	4.824109
C	-3.212637	-1.252605	3.696535
C	-2.481980	-0.965885	2.549149
H	-0.817034	1.800079	3.628517
H	-2.116058	1.279176	5.691670
H	-3.646588	-0.672923	5.721765
H	-3.885111	-2.105789	3.712428
H	-2.588277	-1.601397	1.672031

2g

E = -345.35472
ΔG = -345.27556

C	0.268305	2.014169	0.000000
O	1.378007	2.519124	0.000000
H	-0.641292	2.654029	0.000000
C	0.000000	0.571178	0.000000
C	-1.326963	0.130471	0.000000
C	-1.608624	-1.231679	0.000000
C	-0.561444	-2.151406	0.000000
C	0.766275	-1.715410	0.000000
C	1.048926	-0.357074	0.000000
H	-2.133888	0.862274	0.000000
H	-2.639057	-1.576747	0.000000
H	-0.779298	-3.216686	0.000000
H	1.575657	-2.440839	0.000000
H	2.074963	0.003485	0.000000

TS IX-2g

E = -1035.07880
ΔG = -1034.81931

C	-1.373562	2.016923	-0.599740
C	-1.014153	1.217668	0.500727
C	-1.943186	1.118646	1.547395
C	-3.165804	1.787335	1.512587
C	-3.501224	2.583029	0.417755
C	-2.593667	2.687096	-0.639082
C	0.245319	0.390473	0.587909
O	0.379115	-0.315110	1.710711
C	1.481740	1.090511	0.109751
C	2.807352	0.371231	0.159028
C	3.813425	0.837095	-0.702062
C	5.066002	0.235878	-0.742134
C	5.347227	-0.845460	0.094111
C	4.360607	-1.318985	0.955387
C	3.099384	-0.723309	0.986148
O	1.484507	2.224217	-0.392723
H	3.587308	1.682046	-1.348588
H	5.825139	0.608909	-1.427035
H	6.329035	-1.314464	0.071713
H	4.572608	-2.161861	1.610953
H	2.305944	-1.070532	1.642571
H	-1.673244	0.482385	2.387773
H	-3.860936	1.687498	2.346098
H	-4.451869	3.112903	0.386152
H	-2.842773	3.295834	-1.508230
H	-0.694223	2.080175	-1.442633
C	0.109835	-0.774120	-0.896751
O	0.295814	-0.244398	-2.083370
H	0.918227	-1.438780	-0.502663
C	-1.212235	-1.439388	-0.648387
C	-1.373634	-2.402177	0.357357
C	-2.618587	-2.972278	0.619015
C	-3.733883	-2.605286	-0.135171
C	-3.582498	-1.667721	-1.159678
C	-2.337033	-1.099643	-1.413413
H	-0.503204	-2.688597	0.943411
H	-2.718885	-3.716660	1.408222
H	-4.705656	-3.054627	0.062048
H	-4.442549	-1.382529	-1.765076
H	-2.208961	-0.364473	-2.206179

X

E = -1035.08485
ΔG = -1013.82566

C	2.303724	1.216051	-1.318569
C	1.253334	1.507293	-0.441406
C	1.488734	2.455525	0.562075
C	2.736318	3.061354	0.711110
C	3.779989	2.740829	-0.157186
C	3.553127	1.817443	-1.179561
C	-0.089732	0.800764	-0.570382
O	-0.368410	0.334459	-1.811115
C	-0.193268	-0.346871	0.546451
C	-1.502770	-1.102323	0.307175
O	-1.590331	-2.332624	0.365297
C	1.011402	-1.271120	0.374325
C	1.244327	-2.008969	-0.794972
C	2.404553	-2.763948	-0.951032
C	3.365182	-2.804735	0.061638
C	3.140868	-2.086556	1.234885
C	1.973112	-1.336775	1.384916
O	-0.370963	0.090793	1.828838
C	-2.786662	-0.330520	0.160847
C	-3.765680	-0.868392	-0.683755
C	-4.983216	-0.221348	-0.873384
C	-5.250771	0.970036	-0.199545
C	-4.290423	1.504858	0.657532
C	-3.065211	0.864798	0.834013
H	-3.554403	-1.800594	-1.204417
H	-5.724815	-0.647084	-1.546317
H	-6.204899	1.474681	-0.337654
H	-4.498866	2.426417	1.198168
H	-2.304738	1.249474	1.508566
H	1.781582	-0.772132	2.296019
H	3.876125	-2.112912	2.038473
H	4.271021	-3.396166	-0.060481
H	2.562926	-3.326216	-1.870882
H	0.513855	-1.949773	-1.597171
H	-0.834119	1.548306	-0.190406
H	0.674257	2.711567	1.239092
H	2.893032	3.793742	1.502131
H	4.754140	3.214095	-0.047235
H	4.355820	1.568639	-1.873125
H	2.115087	0.492564	-2.109964

TS X-XI

E = -1035.07345
ΔG = -1034.81165

C	-3.129480	0.499457	1.023593
C	-2.759025	-0.282798	-0.076843
C	-3.724062	-0.519869	-1.065886
C	-5.004074	0.016238	-0.976948
C	-5.361245	0.797312	0.124532
C	-4.418640	1.030070	1.122095
C	-1.380367	-0.913345	-0.288743
O	-1.407033	-2.060578	-0.828936
C	-0.225832	-0.472496	0.710539
O	-0.526953	-0.400232	2.015942
C	-0.118892	0.880865	-0.125837
O	-0.693851	0.386892	-1.295902
C	1.212987	1.540590	-0.261260
C	2.033145	1.362836	-1.380942
C	3.302235	1.935710	-1.440047
C	3.782563	2.700399	-0.376401
C	2.969739	2.898544	0.740424
C	1.697820	2.333442	0.789162
C	1.055785	-1.288729	0.442623
C	1.467705	-1.751924	-0.816537
C	2.682696	-2.413317	-0.985125
C	3.532838	-2.627935	0.100464
C	3.139757	-2.178138	1.359126
C	1.915279	-1.527635	1.519379
H	-3.446354	-1.139331	-1.917070
H	-5.729555	-0.175608	-1.766361
H	-6.363892	1.213731	0.203610
H	-4.687470	1.627856	1.992406
H	-2.385292	0.652298	1.803354
H	1.588470	-1.181373	2.498356
H	3.785806	-2.337641	2.221928
H	4.483652	-3.141174	-0.033743
H	2.971440	-2.761942	-1.976505
H	0.823470	-1.577570	-1.671684
H	-0.782334	1.594960	0.412731
H	1.060062	2.506508	1.657068
H	3.324901	3.504812	1.572119
H	4.773821	3.146777	-0.422491
H	3.921945	1.784841	-2.322723
H	1.658421	0.758532	-2.204041

XI

E = -1035.07839
ΔG = -1034.81772

C	3.234946	-1.226172	-0.463869
C	2.749166	0.068494	-0.274601
C	3.621635	1.017937	0.274345
C	4.927775	0.687357	0.619896
C	5.403917	-0.610077	0.411486
C	4.550647	-1.564035	-0.134595
C	1.351486	0.524548	-0.714200
O	1.414409	1.518730	-1.553706
O	0.630445	-0.729824	-1.269131
C	0.039100	-0.997726	-0.015802
C	0.317091	0.477228	0.535390
C	-0.938234	1.323846	0.280667
C	-1.342764	-1.539532	-0.043793
C	-1.889748	-2.050639	1.142234
C	-3.213586	-2.474791	1.199261
C	-4.017452	-2.418557	0.059704
C	-3.477530	-1.933457	-1.131557

C	-2.155887	-1.494462	-1.181056
O	0.783452	0.586777	1.781808
H	0.671263	-1.660827	0.610571
H	-1.737726	-1.099222	-2.104008
H	-4.092808	-1.894074	-2.029037
H	-5.050711	-2.757010	0.098194
H	-3.619021	-2.859013	2.133756
H	-1.261758	-2.101626	2.032688
H	3.261889	2.034882	0.424671
H	5.583567	1.443693	1.048981
H	6.428565	-0.869052	0.671672
H	4.907891	-2.578318	-0.308329
H	2.567364	-1.972016	-0.891056
C	-1.732623	1.660798	1.383344
C	-2.941586	2.340563	1.241624
C	-3.382273	2.726718	-0.024069
C	-2.596693	2.415778	-1.133714
C	-1.398815	1.716351	-0.985195
H	-1.367834	1.369075	2.366782
H	-3.538795	2.574973	2.122357
H	-4.320776	3.265654	-0.143323
H	-2.922894	2.717429	-2.128891
H	-0.786092	1.478968	-1.849790

C	4.192712	0.196918	-0.625152
C	5.237084	-0.476930	-0.025891
C	5.013308	-1.624276	0.766530
C	3.683537	-2.068724	0.931722
C	2.622644	-1.410456	0.341563
H	4.384289	1.081047	-1.231226
H	6.255112	-0.112945	-0.169212
H	5.841431	-2.150617	1.236215
H	3.484509	-2.953237	1.537888
H	1.608006	-1.780067	0.480930
C	-1.702965	2.787777	-0.261151
C	-1.956766	3.723499	0.73662
C	-1.317954	3.620635	1.973677
C	-0.423728	2.575988	2.194440
C	-0.172696	1.637245	1.193662
H	-2.200121	2.872622	-1.227414
H	-2.651250	4.539887	0.548027
H	-1.510558	4.353588	2.754054
H	0.087119	2.490328	3.151754
H	0.537981	0.830845	1.368711

3ag

E = -1035.07860
ΔG = -1034.82244

C	1.783794	0.476576	-1.095854
O	0.531324	-0.107788	-0.901044
C	2.833259	-0.239188	-0.464833
C	-0.600803	0.715899	-1.152777
C	-1.857521	-0.119921	-1.403326
C	-0.815273	1.726743	-0.044554
H	-0.439389	1.271166	-2.086357
O	-2.562797	0.229795	-2.416952
C	-2.268742	-1.160389	-0.509269
C	-1.546020	-1.568935	0.656454
C	-2.014726	-2.575075	1.482849
C	-3.219242	-3.247941	1.209687
C	-3.941063	-2.871784	0.065627
C	-3.488125	-1.864657	-0.768549
H	-0.599549	-1.088920	0.889881
H	-1.430544	-2.851043	2.361130
H	-3.578349	-4.039336	1.864204
H	-4.876666	-3.379089	-0.171895
H	-4.062718	-1.583890	-1.648680
O	1.894773	1.515697	-1.790361

Structures of Figure 7

1a

E = -689.52009
ΔG = -689.36163

C	-0.869134	-0.494387	0.135581
O	-0.178820	-1.497332	0.254307
C	-1.618840	-0.140468	-1.078278
C	-1.501431	-0.953149	-2.213748
C	-2.224561	-0.652129	-3.358148
C	-3.073952	0.456405	-3.373052
C	-3.200343	1.264835	-2.245204
C	-2.472546	0.969758	-1.098126
H	-0.838599	-1.814192	-2.178853
H	-2.132421	-1.278383	-4.241388
H	-3.641289	0.690533	-4.270453
H	-3.863429	2.125341	-2.260632
H	-2.571684	1.606113	-0.220787
C	-0.863178	0.480174	1.314430
O	-0.161403	1.475086	1.195310
C	-1.616251	0.134938	2.528705
C	-1.488841	0.946211	3.664103
C	-2.214769	0.653563	4.808904
C	-3.076894	-0.445089	4.824285
C	-3.213232	-1.252009	3.696514
C	-2.482708	-0.965357	2.549033
H	-0.816132	1.799544	3.628837
H	-2.114918	1.278714	5.692088
H	-3.646402	-0.672649	5.722001
H	-3.886200	-2.104801	3.712314
H	-2.589670	-1.600527	1.671753

A

E = -552.55401
ΔG = -552.51673

S	-0.116880	0.155787	-0.414269
O	0.153199	1.497517	0.355873
C	1.306603	-0.836120	0.126744
C	-1.379005	-0.831504	0.192787
H	1.320864	-1.793470	-0.399757
H	2.220072	-0.272396	-0.082114
H	1.209585	-0.998461	1.207457
H	-2.346180	-0.443998	-0.146471
H	-1.325445	-0.958661	1.285016

TS reactants- I(A)

E = -1242.08945
ΔG = -1242.86994

C	2.644689	-0.647187	1.413212
C	1.794993	-0.918882	0.332925
C	2.367569	-1.428634	-0.842519
C	3.740083	-1.653789	-0.924062
C	4.571775	-1.373864	0.158191
C	4.016091	-0.865726	1.330599
C	0.322696	-0.649020	0.560537
O	-0.032105	-0.293977	1.704732
C	-0.688136	-1.056588	-0.464783
O	-0.430573	-1.798205	-1.434276
C	-2.139565	-0.788905	-0.145262
C	-3.053981	-1.770931	-0.540634
C	-4.415342	-1.634402	-0.277942
C	-4.884951	-0.499991	0.378501
C	-3.983132	0.491444	0.766077
C	-2.621969	0.349753	0.512766
C	0.112421	0.952797	-0.991629
S	0.729345	2.323520	-0.033139
C	1.168002	3.462675	-1.384834
O	-0.480674	2.984718	0.638416
H	2.199400	-0.255891	2.324560
H	4.651629	-0.639581	2.184323
H	5.642917	-1.550297	0.088138
H	4.161323	-2.052189	-1.844968
H	1.728688	-1.657067	-1.688543
H	-2.680270	-2.651399	-1.058205
H	-5.107735	-2.414081	-0.588501
H	-5.947354	-0.384279	0.582490
H	-4.344554	1.386570	1.268488
H	-1.932847	1.137777	0.807681
H	0.873773	0.645531	-1.716114
H	-0.826885	1.255372	-1.473480
H	1.518612	4.397156	-0.936365
H	1.962122	3.014774	-1.989370
H	0.271013	3.638495	-1.987745

I(A)

E = -1242.12891
ΔG = -1242.90585

C	0.615146	-1.685936	1.316199
C	0.185170	-1.468723	0.003472
C	0.482167	-2.425119	-0.965791
C	1.196475	-3.575533	-0.634699
C	1.628347	-3.781022	0.674742
C	1.336109	-2.829367	1.651893
C	-0.631713	-0.222743	-0.375554
O	-0.712369	0.048520	-1.699873

C	-0.022443	1.042699	0.253039
O	-0.715892	1.814635	0.916345
C	1.407096	1.383596	-0.018653
C	2.155125	0.796541	-1.047829
C	3.496318	1.125174	-1.214047
C	4.110819	2.032711	-0.350943
C	3.375328	2.618838	0.677376
C	2.031215	2.298203	0.838218
C	-2.026399	-0.456929	0.243863
S	-3.210737	0.825724	-0.326513
O	-4.253739	0.090731	-1.178328
C	-4.030441	1.085728	1.273172
H	0.155490	-2.235080	-1.987022
H	1.421994	-4.313151	-1.402772
H	2.193004	-4.674330	0.932742
H	1.673107	-2.977594	2.675908
H	0.395180	-0.945446	2.088062
H	1.448814	2.747549	1.639229
H	3.849829	3.324308	1.355567
H	5.161381	2.282788	-0.481196
H	4.065909	0.673015	-2.022811
H	1.655975	0.109392	-1.726274
H	-2.442355	-1.388701	-0.160837
H	-2.025675	-0.499144	1.339827
H	-4.855601	1.783120	1.109022
H	-4.413192	0.127899	1.641015
H	-3.305978	1.513985	1.971862

TS1(A)

E = -1242.11413
ΔG = -1242.89217

C	-0.561823	1.514487	1.229301
C	-0.285027	1.393466	-0.135585
C	-0.877561	2.283366	-1.029040
C	-1.734224	3.282392	-0.567858
C	-2.013589	3.392521	0.792841
C	-1.425587	2.502285	1.692916
C	0.656397	0.320222	-0.624825
C	2.087436	0.750189	-0.333207
S	3.415089	-0.506904	-0.134205
C	3.057120	-0.934332	1.595355
C	0.272439	-1.115378	-0.523930
C	-1.184002	-1.423716	-0.311101
C	-2.223000	-0.965519	-1.124820
C	-3.548187	-1.264948	-0.815111
C	-3.855605	-2.017099	0.317916
C	-2.824963	-2.480060	1.133938
C	-1.500472	-2.191175	0.814954
O	1.118665	-2.043667	-0.383151
O	0.436508	-0.139438	-1.927755
O	4.664337	0.382934	-0.027143
H	-0.691572	-2.554117	1.447488
H	-3.052862	-3.069151	2.019928
H	-4.891373	-2.244015	0.560952
H	-4.346184	-0.908318	-1.463366
H	-1.977288	-0.373000	-2.002300
H	-0.675170	2.170123	-2.092914
H	-2.190146	3.973471	-1.274031
H	-2.689280	4.165393	1.152287
H	-1.643614	2.578017	2.756074
H	-0.103940	0.813042	1.929991
H	2.441135	1.347530	-1.185356
H	2.168516	1.373503	0.567825
H	3.804486	-1.664937	1.914960
H	3.159402	-0.014508	2.181292
H	2.054257	-1.361398	1.668367

IIA

E = -1242.11658
ΔG = -1242.89346

C	0.250752	-1.130025	-0.597927
C	-1.179910	-1.412031	-0.209817
C	-1.449430	-1.765616	1.115762
C	-2.743921	-2.073502	1.522659
C	-3.790660	-2.046761	0.599769
C	-3.529821	-1.701177	-0.724335
C	-2.232881	-1.377859	-1.123741
H	-0.627896	-1.795785	1.831638
H	-2.938929	-2.337015	2.560318
H	-4.802972	-2.292848	0.912843
H	-4.340450	-1.678207	-1.450110
H	-2.027995	-1.088971	-2.152498
O	1.102917	-2.080451	-0.415757
C	0.666251	0.332332	-0.630175
O	0.337032	-0.328362	-1.848655
C	-0.257847	1.437466	-0.228936
C	-1.162999	1.986695	-1.138900
C	-2.021483	3.015263	-0.753634
C	-1.994241	3.502831	0.550906
C	-1.099640	2.953674	1.470043
C	-0.239077	1.931971	1.081368
H	-1.192720	1.591441	-2.151929
H	-2.717453	3.435761	-1.476788
H	-2.666544	4.302770	0.852433
H	-1.075153	3.319901	2.494132
H	0.451396	1.502330	1.808680
C	2.123395	0.706271	-0.508842
H	2.295494	1.474378	0.256527
H	2.478287	1.111874	-1.466760
S	3.393192	-0.571899	-0.116366
O	4.655066	0.302283	-0.013655
C	2.922068	-0.838350	1.616053
H	3.633984	-1.550296	2.041374
H	3.007324	0.125636	2.129638
H	1.909101	-1.245421	1.655377

TS2(A)

E = -1242.09899
ΔG = -1242.87697

C	1.369350	2.012493	0.930659
C	0.128337	1.629239	0.365823
C	-0.361115	2.454163	-0.678466
C	0.345983	3.559466	-1.131181
C	1.577423	3.906901	-0.570104
C	2.071579	3.120957	0.470954
C	-0.605704	0.487481	0.852943
C	-2.084082	0.456151	0.830288
S	-2.928516	-0.803342	-0.289288
C	-2.328477	-0.168042	-1.874071
O	-0.018974	-0.164377	1.996219
C	-0.016592	-1.331540	1.262107
O	-0.847302	-2.218374	1.494011
C	1.161000	-1.584918	0.390149
C	2.432143	-1.082415	0.684010
C	3.521286	-1.402183	-0.125639
C	3.354536	-2.225562	-1.235627
C	2.090404	-2.745401	-1.524805
C	1.007800	-2.438593	-0.710949
O	-4.407930	-0.399949	-0.232925
H	0.021081	-2.847139	-0.922687
H	1.952960	-3.395245	-2.386258
H	4.204430	-2.469900	-1.868674
H	4.505881	-1.008960	0.118286
H	2.572401	-0.457810	1.560957
H	1.762025	1.439854	1.765295
H	3.018573	3.378727	0.943535
H	2.131132	4.770560	-0.930582
H	-0.072762	4.159335	-1.937880
H	-1.314035	2.223471	-1.148294
H	-2.545721	1.399342	0.500075
H	-2.506090	0.190955	1.808165
H	-2.693153	-0.836989	-2.657430
H	-2.736938	0.838522	-2.021383
H	-1.233091	-0.158808	-1.869513

III(A)

E = -1242.11389
ΔG = -1242.89445

C	3.926028	0.170508	0.945040
C	2.744429	-0.132678	0.261216
C	2.815243	-0.733918	-1.001352
C	4.052038	-1.026564	-1.566366
C	5.226591	-0.718456	-0.880934
C	5.161244	-0.118778	0.376240
C	1.448622	0.178641	0.919388
O	1.363121	0.663620	2.039295
O	0.410714	-0.122681	0.145416
C	-0.930622	0.071271	0.595787
C	-1.296821	1.440910	0.881390
S	-1.363978	2.597347	-0.671859
O	-1.687801	4.012646	-0.160471
C	-1.779925	-1.023548	0.326351
C	-1.278041	-2.273273	-0.154871
C	-2.110941	-3.362169	-0.368628
C	-3.486388	-3.296588	-0.123295
C	-4.002652	-2.081261	0.346311
C	-3.191091	-0.979531	0.559004
C	-2.920352	1.962315	-1.343486
H	-0.211621	-2.370789	-0.349439
H	-1.672543	-4.290467	-0.736046
H	-4.131815	-4.155257	-0.291835
H	-5.069931	-1.989709	0.548603
H	-3.645565	-0.059582	0.925354
H	1.898862	-0.970994	-1.535200
H	4.100759	-1.494939	-2.546425
H	6.192296	-0.944478	-1.326939
H	6.074909	0.123617	0.913576
H	3.859206	0.635152	1.925555
H	-2.293104	1.551440	1.327004
H	-0.569334	1.993007	1.490363
H	-3.123992	2.473454	-2.287734
H	-2.818354	0.884784	-1.511118
H	-3.718565	2.167248	-0.620656

Other Structures

DMF

E = -248.37578
DG = -248.303206

C	-0.088010	0.178702	0.076812
O	-0.086063	0.018952	1.295257
H	0.645549	0.834461	-0.429528
N	-0.943573	-0.393269	-0.792522
C	-0.863202	-0.140987	-2.216512
C	-1.988168	-1.292837	-0.346679
H	-1.797938	0.303010	-2.579844
H	-0.041294	0.548488	-2.427092
H	-0.687140	-1.076404	-2.761429
H	-2.972151	-0.897994	-0.627153
H	-1.862917	-2.277479	-0.813081
H	-1.935625	-1.396828	0.738180

C (Scheme 1)

E = -247.83143
DG = -247.77322

C	0.020165	0.072202	-0.068182
N	0.116198	0.348413	1.338567
C	1.420347	0.120210	1.924323
C	-1.006929	0.805351	2.052647
O	-0.809993	1.015696	3.282488
H	0.256232	-0.980385	-0.297585
H	-1.006432	0.280059	-0.393927
H	0.710442	0.698054	-0.658206
H	1.735264	-0.929292	1.811656
H	2.190795	0.749781	1.451685
H	1.362098	0.364484	2.989994

F (Scheme 5)

E = -247.71468
DG = -247.65524

247.714678

C	-0.000105	0.079460	-0.077170
N	0.139157	0.343197	1.344975
C	1.456573	0.109132	1.935481
C	-0.886069	0.776118	2.064813
O	-0.976853	1.050810	3.240578
H	0.228418	-0.971222	-0.290270
H	-1.026076	0.295015	-0.383540
H	0.688932	0.712877	-0.647802
H	1.741332	-0.940616	1.802422
H	2.201685	0.744469	1.443672
H	1.421192	0.345334	3.000300

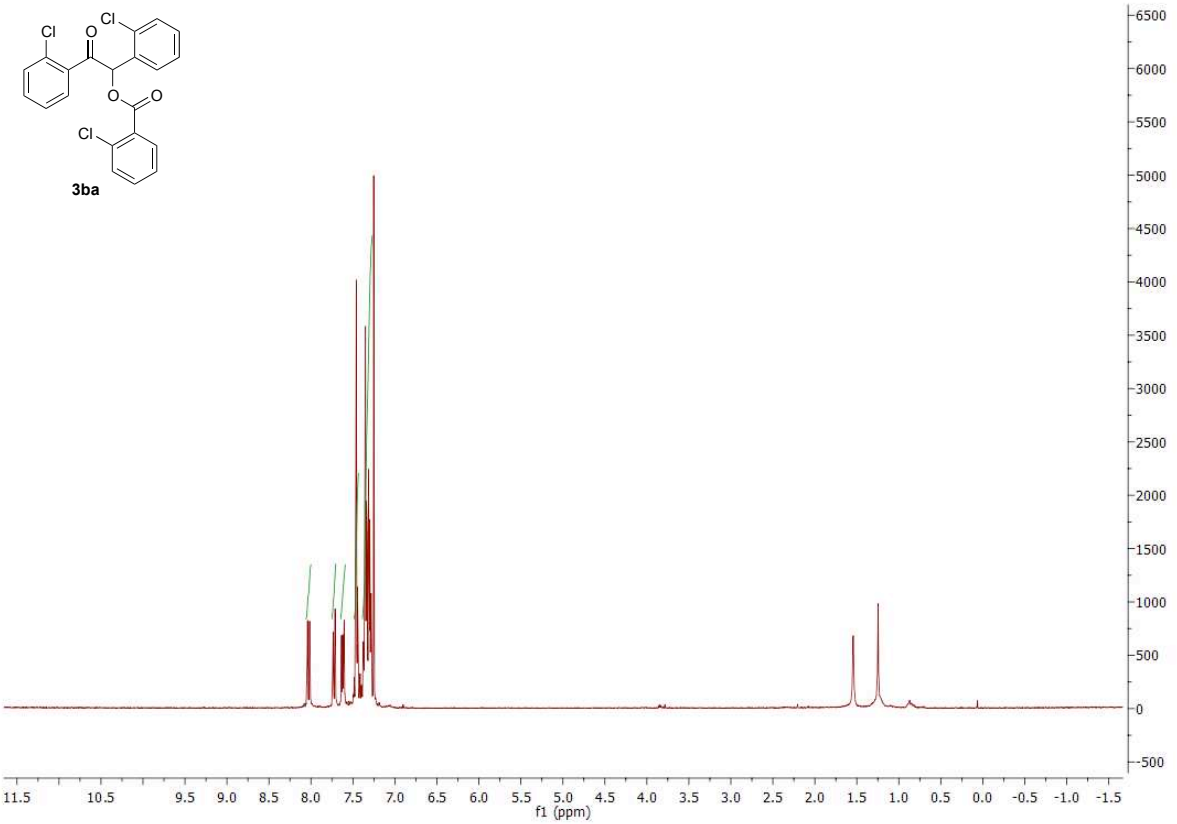
V (Scheme 5)

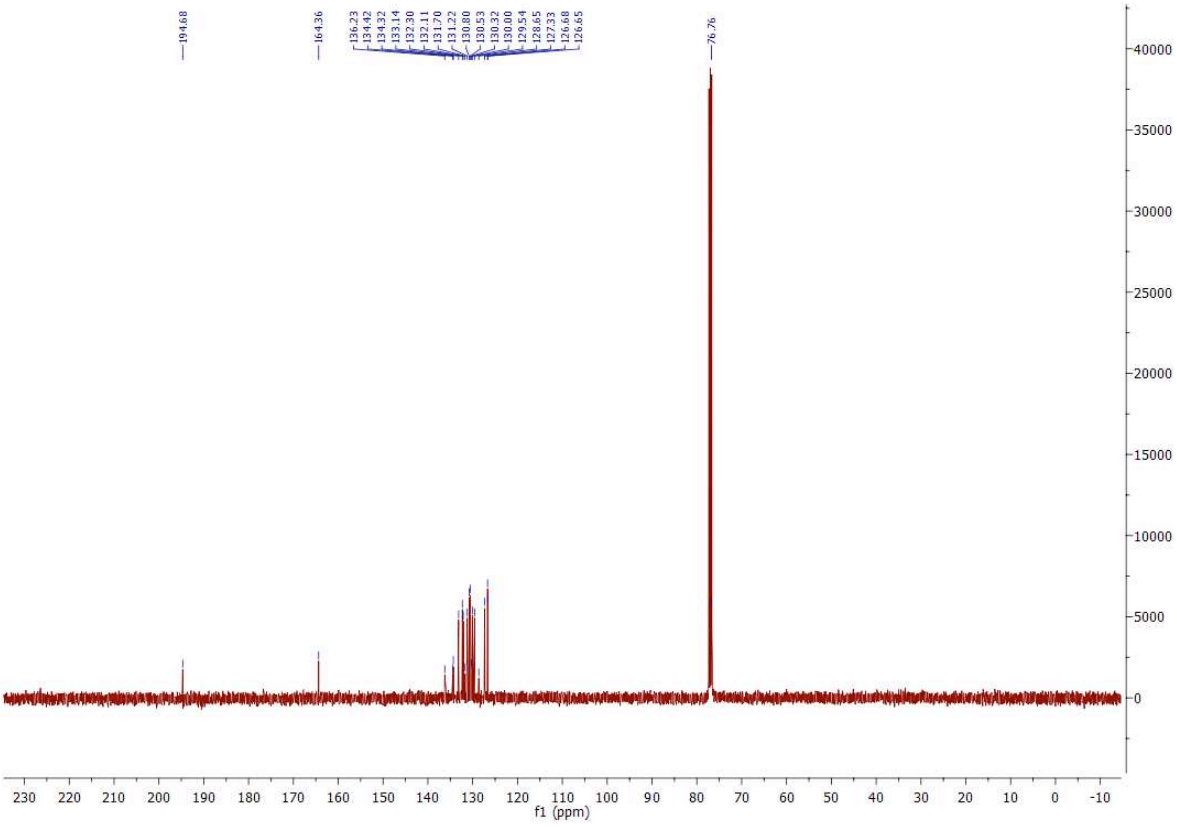
E = -689.63884
DG = -689.48333

C	-1.937592	-0.477647	0.173333
O	-1.812954	-1.725659	0.364292
C	-2.056161	0.002122	-1.235804
C	-1.718255	-0.903956	-2.256781
C	-1.845261	-0.566659	-3.599303
C	-2.331249	0.689209	-3.963280
C	-2.685489	1.596024	-2.964648
C	-2.545950	1.263842	-1.619818
H	-1.353347	-1.886503	-1.966991
H	-1.566221	-1.287015	-4.366140
H	-2.435107	0.956761	-5.012686
H	-3.075239	2.575631	-3.235759
H	-2.814318	1.981640	-0.851438
C	-1.931763	0.475771	1.277266
O	-1.792794	1.722257	1.086230
C	-2.055095	-0.002595	2.686472
C	-1.706194	0.899525	3.707255
C	-1.836351	0.563721	5.049850
C	-2.336604	-0.686453	5.414105
C	-2.701833	-1.589121	4.415674
C	-2.559205	-1.258576	3.070765
H	-1.330126	1.877793	3.417256
H	-1.548596	1.280810	5.816527
H	-2.442969	-0.952784	6.463569
H	-3.102715	-2.564164	4.687007
H	-2.836260	-1.973231	2.302538

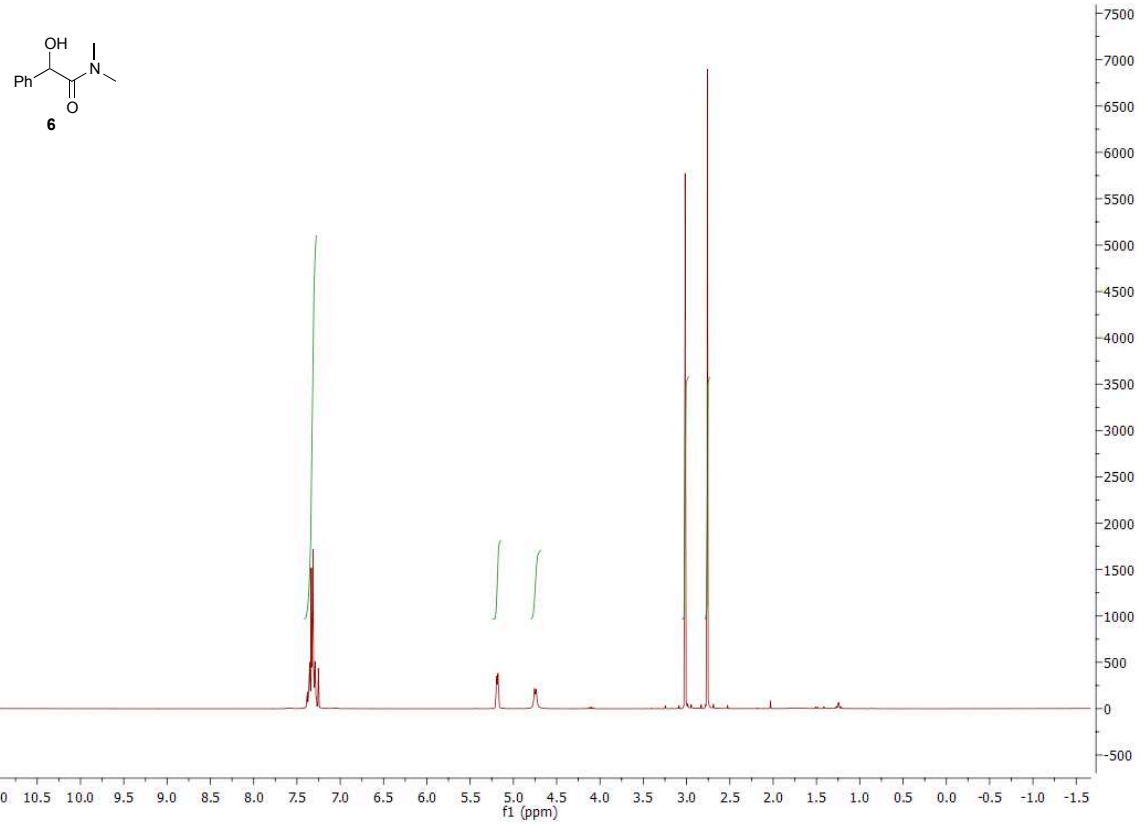
^{1}H (300 MHz) and ^{13}C (75 MHz) spectra ($CDCl_3$) of 3ba

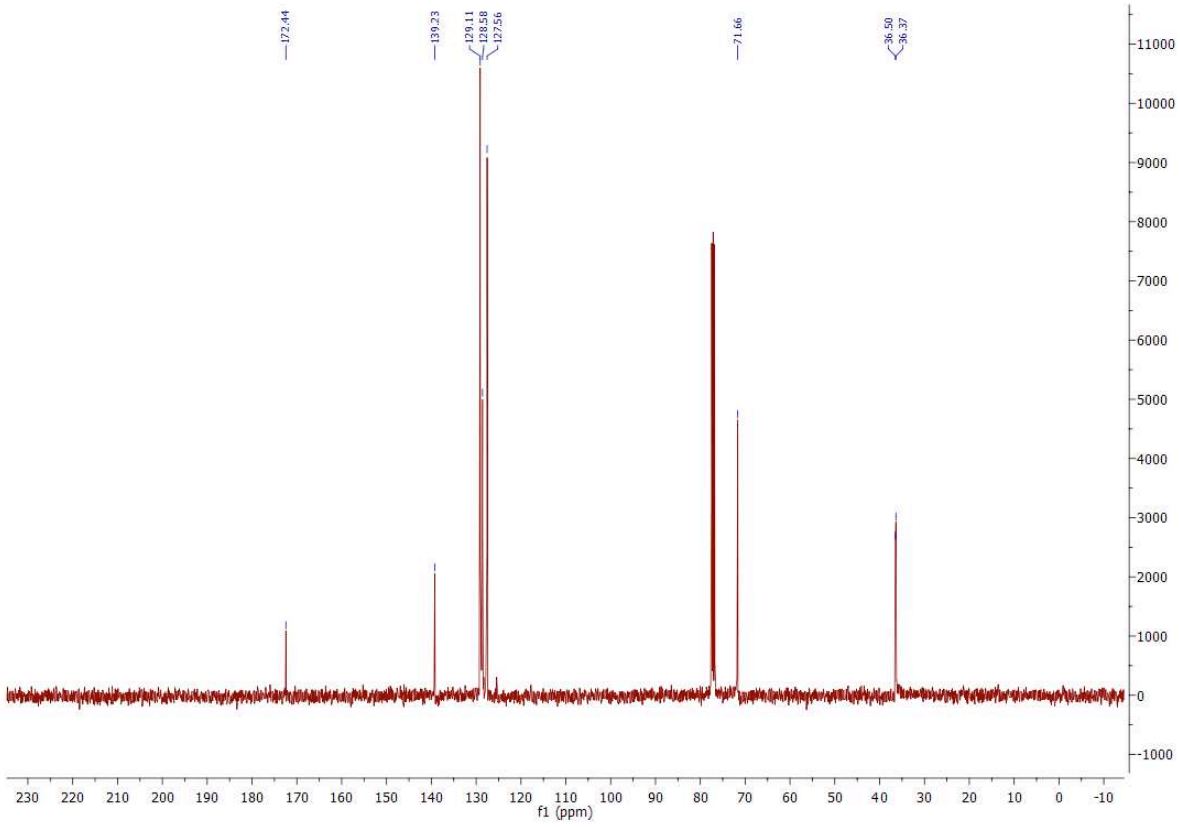
3ba



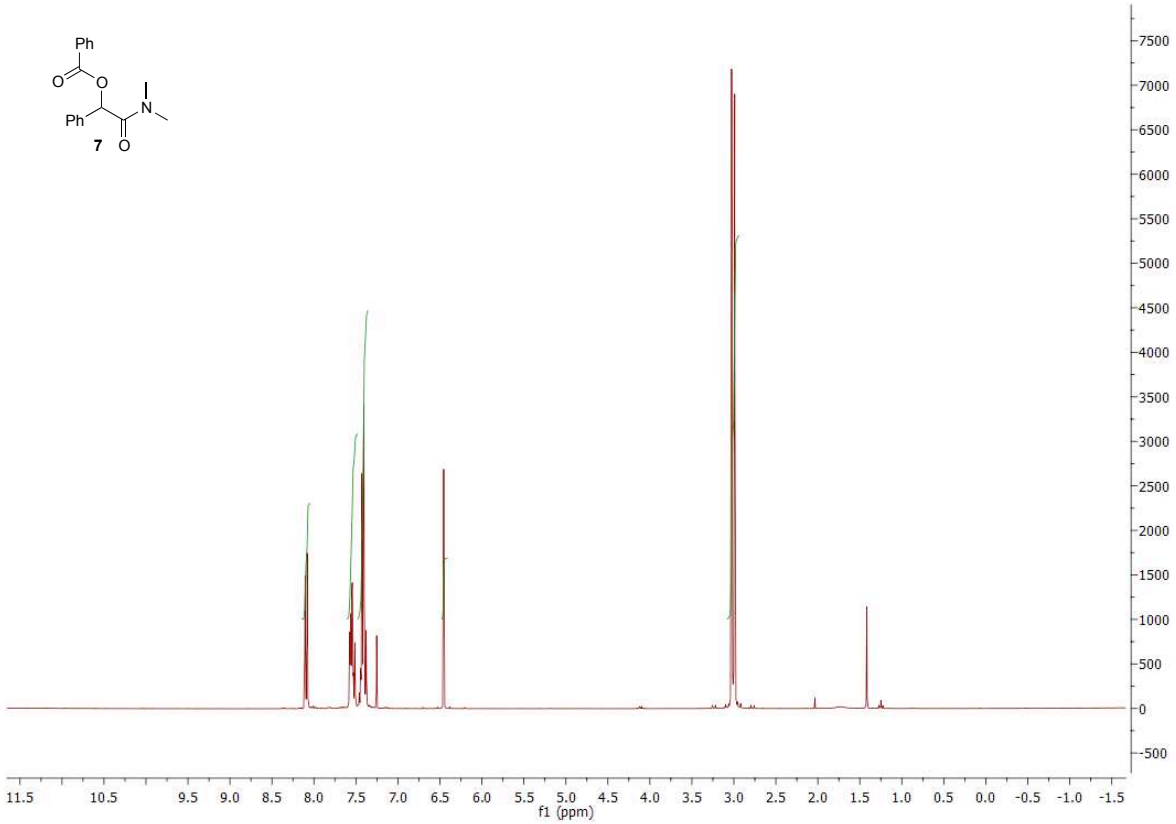


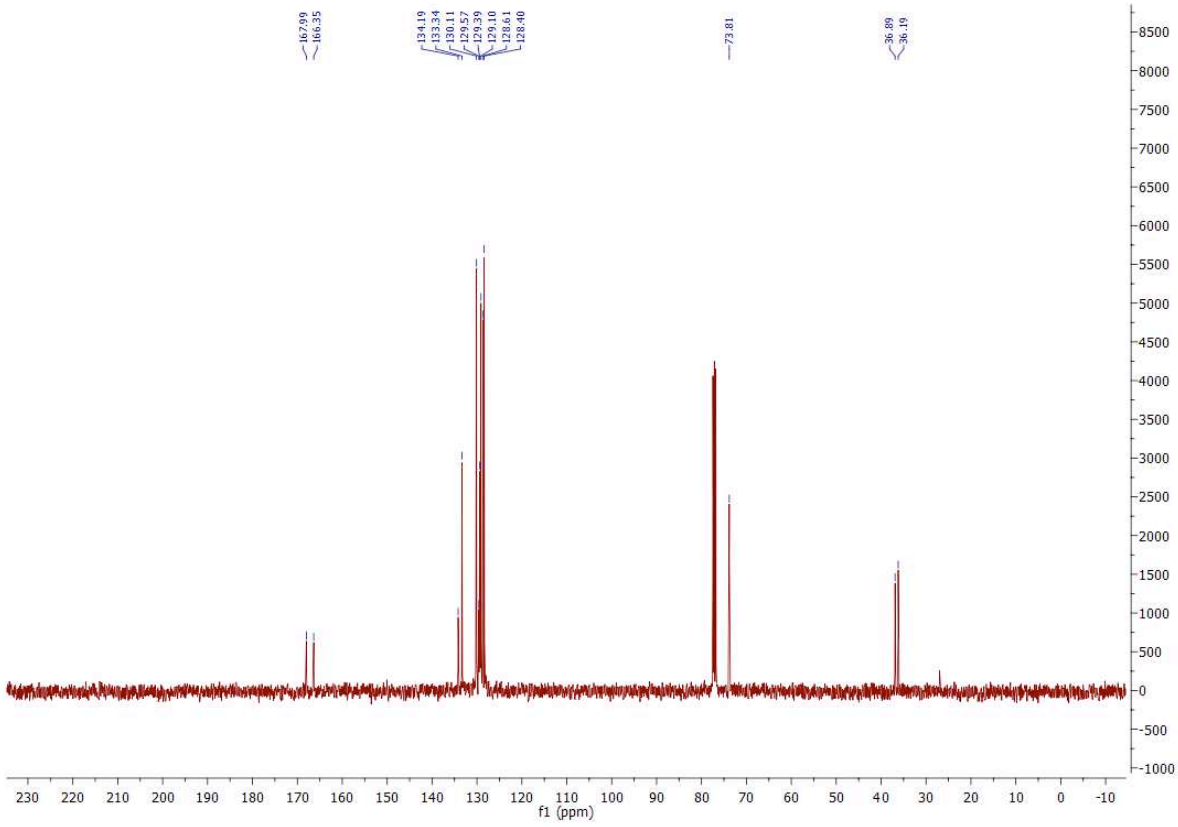
^{1}H (300 MHz) and ^{13}C (75 MHz) spectra ($CDCl_3$) of 6





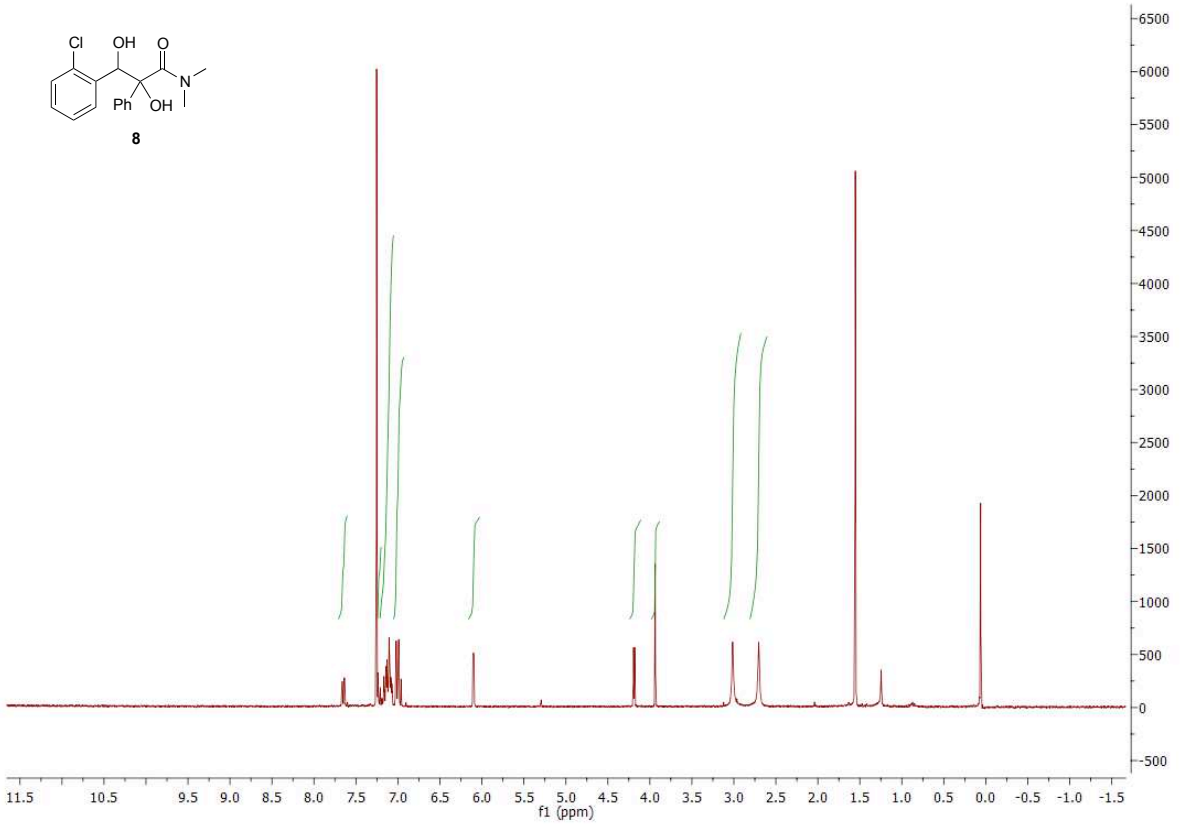
^{1}H (300 MHz) and ^{13}C (75 MHz) spectra ($CDCl_3$) of 7

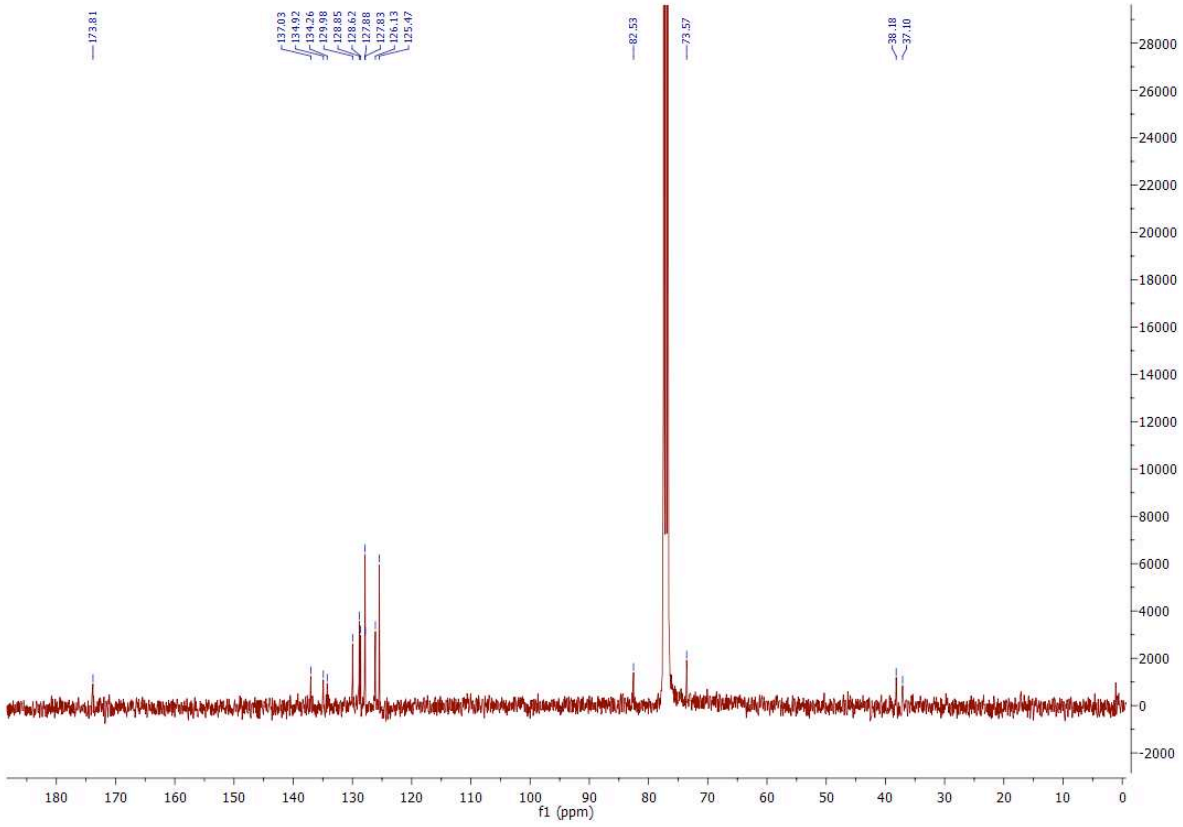




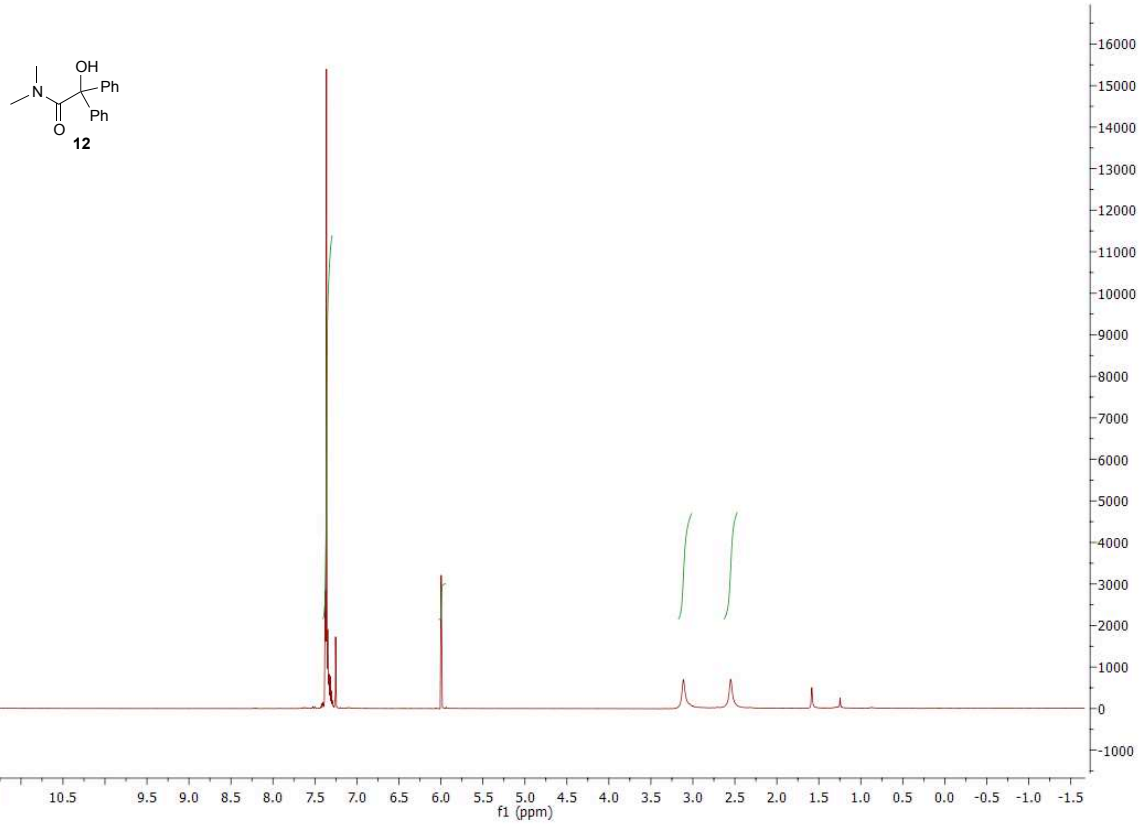
^{1}H (300 MHz) and ^{13}C (75 MHz) spectra ($CDCl_3$) of 8

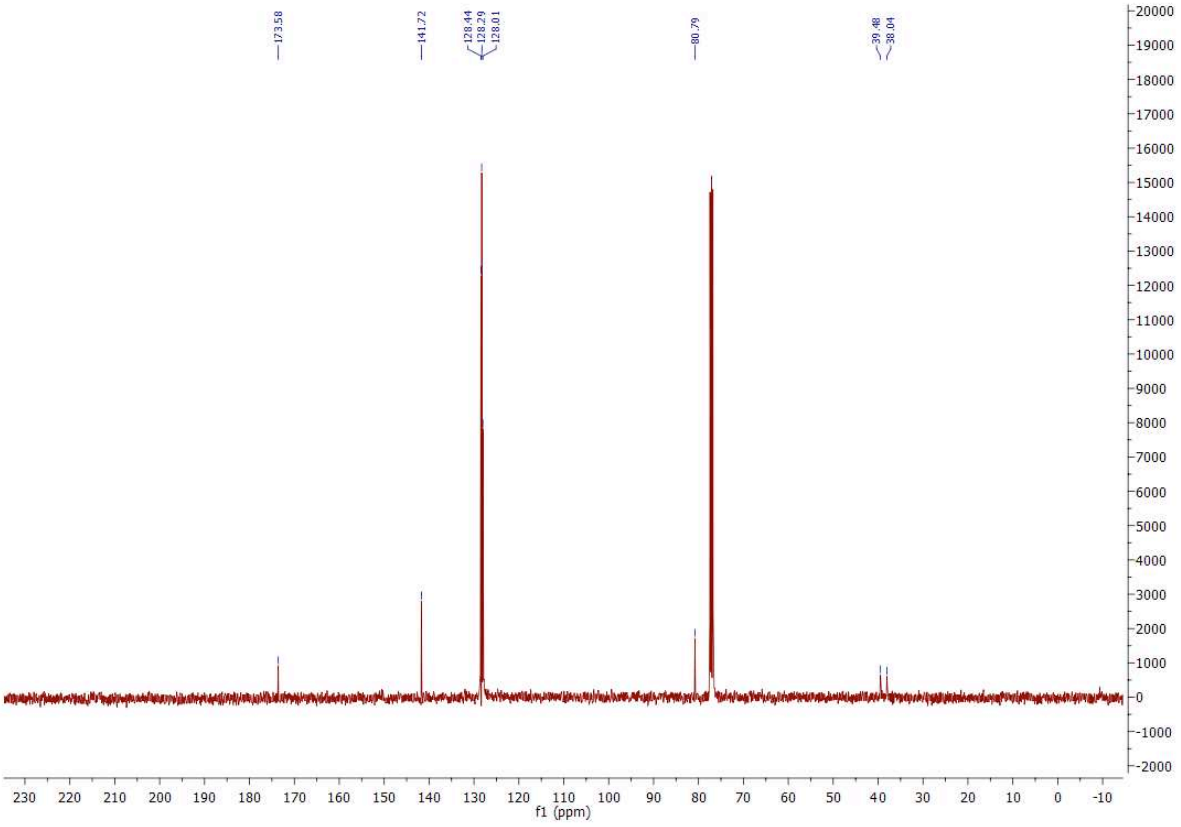
8





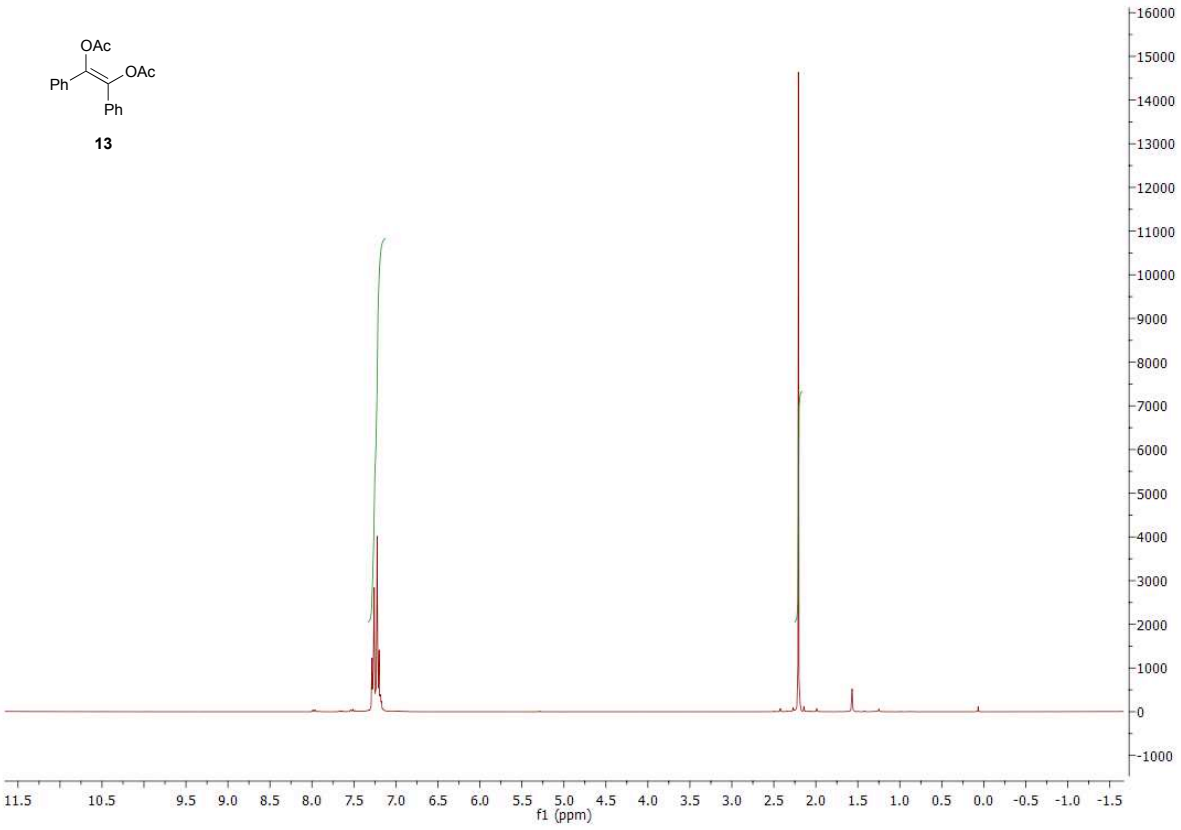
^{1}H (300 MHz) and ^{13}C (75 MHz) spectra ($CDCl_3$) of 12

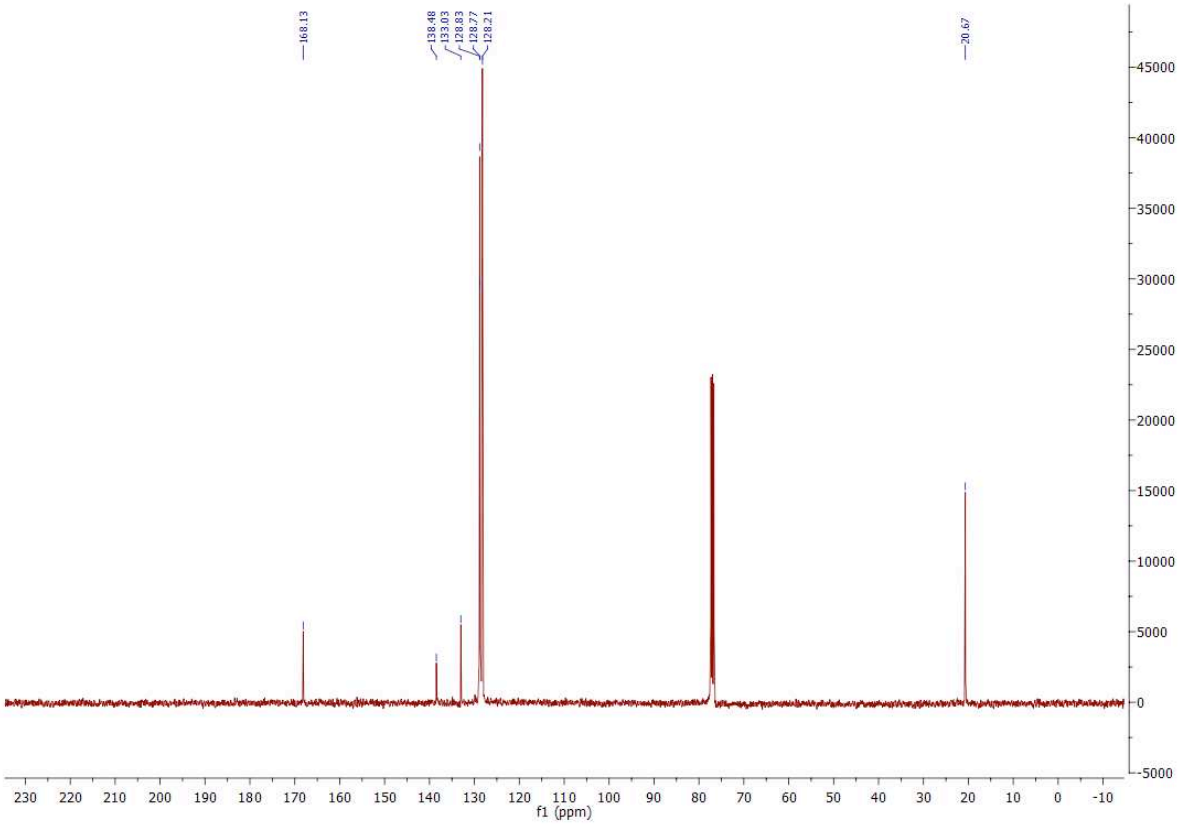




^{1}H (300 MHz) and ^{13}C (75 MHz) spectra ($CDCl_3$) of 13

13





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