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Supporting Information

Mechanistic Study of Silver-Mediated Furan Formation by Oxidative Coupling

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1 Technical details

1.1 Basis set for geometry optimizations and frequency calculations (B_1)

1.1.1 Basis set for main group elements

For C, O and H atoms we have used the 6-31+G* basis set.

1.1.2 Basis set for Ag

****
Ag 0

S	3	1.00	
		2.9500000	-1.7910564
		2.1490000	2.0244570
		0.6684000	0.6072839
S	4	1.00	
		2.9500000	1.0141125
		2.1490000	-1.2413971
		0.6684000	-0.4901427
		0.0997000	1.1128375
S	1	1.00	
		0.0347000	1.0000000
S	1	1.00	
		0.0162000	1.0000000
P	3	1.00	
		6.5530000	-0.1079117
		1.5650000	0.7403645
		0.5748000	0.3721008
P	2	1.00	
Free		0.9085000	-0.0418371
		0.0833000	1.0087586
P	1	1.00	
		0.0252000	1.0000000
P	1	1.00	
		0.0152000	1.0000000
D	3	1.00	
		3.3910000	0.1396938
		1.5990000	0.4744421
		0.6282000	0.5156311
D	1	1.00	
		0.2108000	1.0000000
D	1	1.00	
		0.0620000	1.0000000
F	1	1.00	
		1.3299000	1.0000000
F	1	1.00	
		0.4449000	1.0000000

The basis set was employed with the LANL2 effective core potential.

1.2 Basis set employed for single-point energy calculations (B_2)

1.2.1 Basis set for main group elements

For C, O and H atoms we have employed the 6-311++G(3df,3dp) basis set.

1.2.2 Basis set for Ag

****
Ag 0

S	1	1.00	
		2.9500000	1.0000000
S	1	1.00	
		2.1490000	1.0000000
S	1	1.00	
		0.6684000	1.0000000
S	1	1.00	
		0.0997000	1.0000000
S	1	1.00	
		0.0347000	1.0000000
S	1	1.00	
		0.0151000	1.0000000
P	1	1.00	
		6.5530000	1.0000000
P	1	1.00	
		1.5650000	1.0000000
P	1	1.00	
		0.5748000	1.0000000
P	1	1.00	
		0.0833000	1.0000000
P	1	1.00	
		0.0252000	1.0000000
P	1	1.00	
		0.0132000	1.0000000
D	2	1.00	
		3.3910000	0.1396938
		1.5990000	0.4744421
D	1	1.00	
		0.6282000	1.0000000
D	1	1.00	
		0.2108000	1.0000000
D	1	1.00	
		0.0481000	1.0000000
F	1	1.00	
		2.5431000	1.0000000
F	1	1.00	
		0.7381000	1.0000000
F	1	1.00	
Free		0.2889000	1.0000000
G	1	1.00	
		1.5751000	1.0000000
G	1	1.00	
		0.7090000	1.0000000

The basis set was employed with the LANL2 effective core potential.

1.3 Calculation of free energy contributions

All solvent-corrected Gibbs free energies were calculated with the following approach:

$$\Delta G_{solv} = \Delta G_{vrt}^{B_1} + E_{SMD}^{B_2},$$

where $\Delta G_{vrt}^{B_1}$ is the vibrational, rotational, translational thermal correction to Gibbs free energy (harmonic oscillator – rigid rotor – ideal gas approximation) at 80°C and 1 mol/dm^3 concentration, using basis set B_1. $E_{SMD}^{B_2}$ is the electronic energy calculated with the SMD solvent model applying DMF as solvent and basis set B_2. Basis set B_1 was employed for all geometry optimizations and all the free energy and solvent corrections were computed at the optimal geometries. For all calculations, the "ultrafine" grid was employed.

We also report $E_g^{B_1}$, the vacuum electronic energy calculated with basis set B_1, for each structure.

1.3.1 BSSE

For estimation of the basis set superposition error (BSSE) in our calculations we have examined the transition state of an intermolecular reaction (1.2+2.1⟶3.2+Ag) with the counterpoise method using basis set B_2. The BSSE was found to be 1.6 kcal/mol, much smaller than the typical energy differences along the free energy profiles. We conclude that our results are converged with respect to the size of the basis set.

1.3.2 Calculation of Gibbs free energy of $Ag_{(s)}$

Gibbs free energy of solid Ag was calculated by taking into account available experimental data:

$Ag_{(s)} \longrightarrow Ag_{(g)}$	$\Delta_r G$	=	0.08525 Eh	at 80°C from Ref 1
$Ag_{(g)}$	$\Delta_f G_g$	=	−145.79158 Eh	M06/B_2, 80°C, p=1 atm
$Ag_{(s)}$	$\Delta_f G_s$	=	−145.87683 Eh	

2 Identification of the resting state

Although the free energy change for Ag_2CO_3 solvation in DMF is not easily accessible by computational or experimental methods, the resting state of the solvated species can be deduced from reaction free energy changes of hypothetical reactions. Free energy calculations show that the most stable species are Ag_2CO_3, $AgCO_3^-$ and AgOAc in this order. Formation of other species requires larger free energy investment.

Ag_2CO_3+ OAc^- $\rightleftharpoons$ $AgCO_3^-$ + AgOAc $\Delta_r G = 3.5\ kcal/mol$

Ag_2CO_3+ 2 OAc^- $\rightleftharpoons$ CO_3^{2-} + 2 AgOAc $\Delta_r G = 20.6\ kcal/mol$

3 Excluded reaction pathways

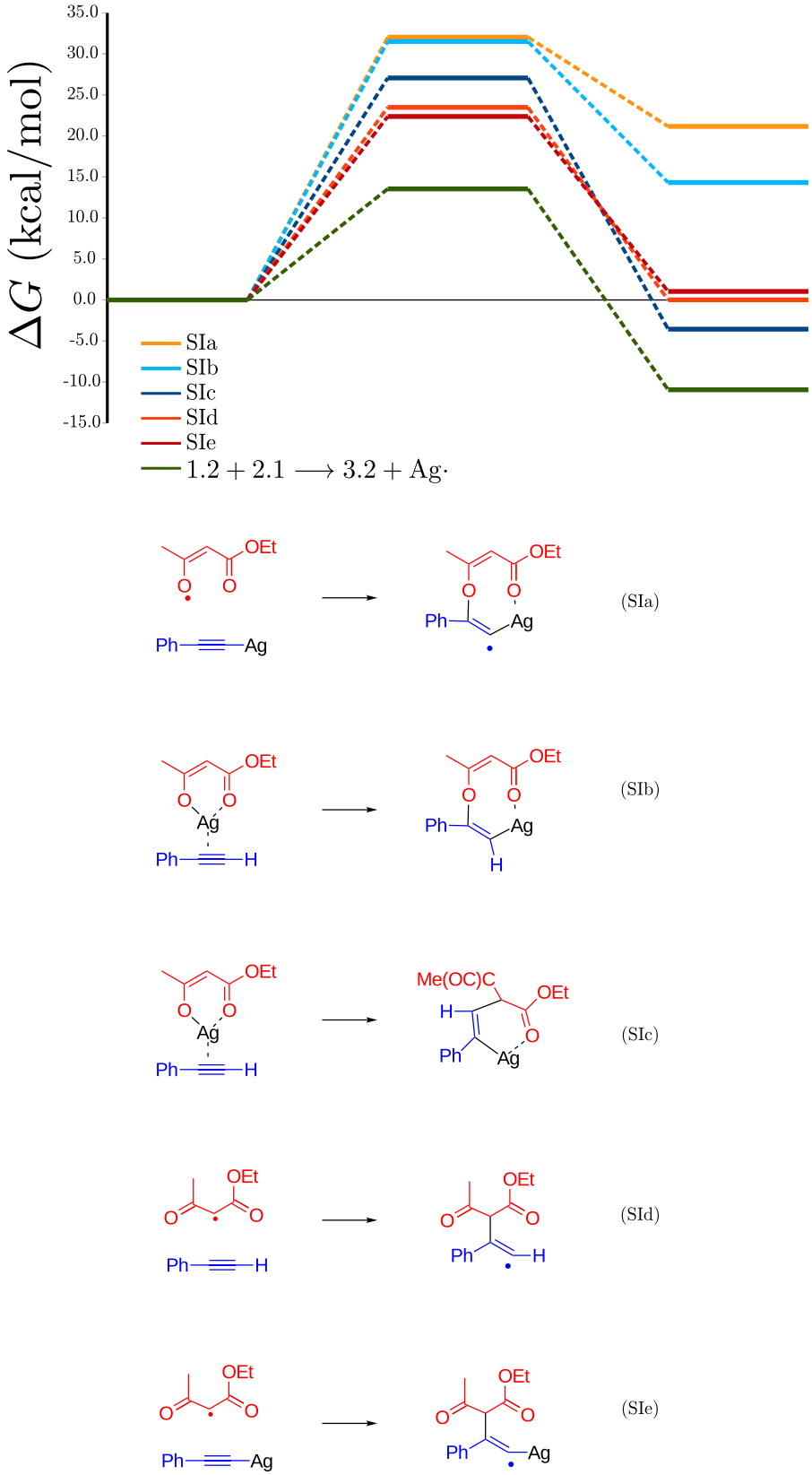
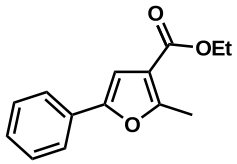


Figure 1: Top: free energy profiles of the excluded pathways in comparison with the proposed pathway (green). All free energy contributions are calculated using basis set B_1. Bottom: reaction schemes for the excluded pathways.

4 Experimental procedures and general experimental methods

Unless otherwise indicated, all starting materials were obtained from commercial suppliers, and were used without further purification. Analytical thin-layer chromatography (TLC) was performed on Merck DC pre coated TLC plates with 0.25 mm Kieselgel 60 F_{254}. Visualization was performed with a 254 nm UV lamp. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-250 spectrometer in $CDCl_3$. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standards (δ 7.26 for ^{1}H, δ 77.0 for ^{13}C). Coupling constants (J) are reported in Hertz (Hz). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), m (multiplet). Combination gas chromatography and low resolution mass spectrometry was obtained on an Agilent 6890N Gas Chromatograph (30 m x 0.25 mm column with 0.25 μm HP-5MS coating, He carrier gas) and Agilent 5973 Mass Spectrometer (Ion source: EI+, 70eV, 230°C; interface: 300°C).

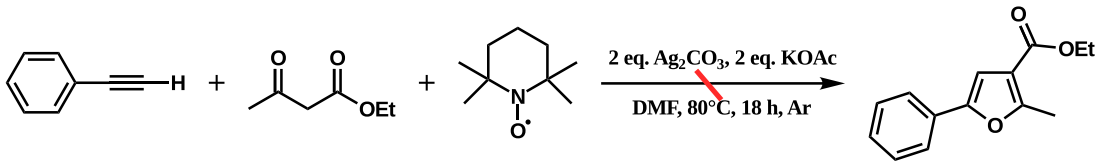
4.1 Procedure for the preparation of ethyl 2-methyl-5-phenylfuran-3-carboxylate



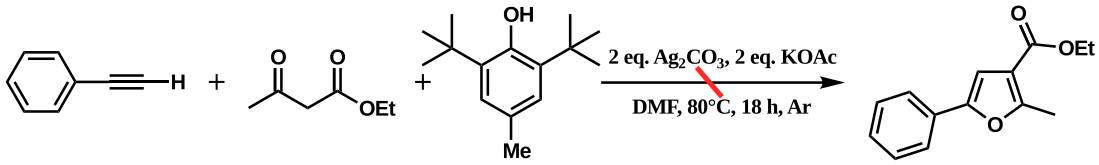
Ag_2CO_3 (0.5518 g; 2 mmol, 2 eq.) and KOAc (0.1970 g; 2 mmol, 2 eq.) were placed in a 20 mL vial. The system was charged with argon. Dry DMF (18 mL) was added. The phenylacetylene (0,11 mL; 1 mmol, 1 eq.) and the ethyl acetoacetate (0.38 mL, 3 mmol, 3 eq.) were added via cannula. The mixture was stirred at 80°C for 18 h. The reaction was quenched with solution of HCl (5 mL, 2 M). The solution was extracted with EtOAc (10 mL) three times. The combined organic layers were dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was purified by column chromatography. Eluent: hexane:EtOAc (5:1). The product was characterized with GC-MS and NMR, and it was consistent with the literature data.

Yellow oil: 197.8 mg, 86 %, ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.54 (d, J = 8.6 Hz, 2H), 7.28 (t, J = 7.3 Hz, 2H), 7.16 (t, J = 7.3 Hz, 1H), 6.79 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 2.55 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H). GC-MS: m/z (%): 230(58%); 201(100%); 185(20%); 157(14%); 128(20%); 115(25%); 105(30%); 77(27%); 63(5%); 51(12%),

4.2 Study of the effect of radical scavengers

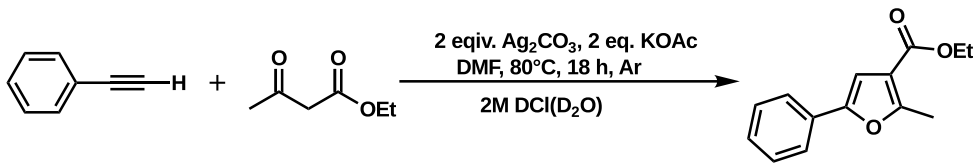


Ag_2CO_3 (0.0918 g; 0.33 mmol, 2 eq.), KOAc (0.0331 g; 0.33 mol, 2 eq.) and TEMPO (0.0027 g, 0.017 mmol, 10 mol %) were placed in a 4 mL vial. The system was charged with argon. Dry DMF (4 mL) was added. The phenylacetylene (19 μL; 0.17 mmol, 1 eq.) and the ethyl acetoacetate (89 μL, 0.5 mmol, 3 eq.) were added via cannula. The mixture was stirred at 80°C for 18 h. The reaction was quenched with solution of HCl (1 mL, 2 M) and sample was taken from it. The sample was monitored by GC-MS. GC-MS conversion: 73% Reaction was repeat with TEMPO (0,0270 g, 0.17mmol, 1 eq.). GC-MS conversion: 15%



Ag_2CO_3 (0.0918 g; 0.33 mmol, 2 eq.), KOAc (0.0331 g; 0.33 mol, 2 eq.) and 2,6-di-tert-butyl-4-methylphenol (0,0037 g, 0,017 mmol, 10 mol %) were placed in a 4 mL vial. The system was charged with argon. Dry DMF (4 mL) was added. The phenylacetylene (19 μL; 0,17 mmol, 1 eq.) and the ethyl acetoacetate (89 μL, 0.5 mmol, 3 eq.) were added via cannula. The mixture was stirred at 80°C for 18 h. The reaction was quenched with solution of HCl (1 mL, 2 M) and sample was taken from it. The sample was monitored by GC-MS. GC-MS conversion: 69%. Reaction was repeated with and 2,6-di-tert-butyl-4-methylphenol (0,0370 g, 0,17 mmol, 1 eq.). GC-MS: Conversion: 0%

4.3 Quenching experiments with DCl



Possible deuterium incorporation into furan ring after quenching the reaction mixture with DCl(D_2O) would provide proof for the existence of silver-furanyl species in the reaction mixture until the work up, as the deuterolysis of this organometallic species could provide deuterated furans.

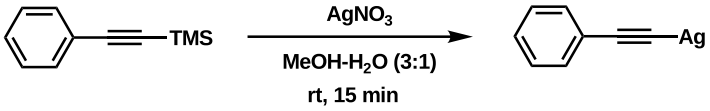
Ag_2CO_3 (0.5518 g; 2 mmol, 2 eq.) and KOAc (0.1970 g; 2 mmol, 2 eq.) were placed in a 20 mL vial. The system was charged with argon. Dry. DMF (18 mL) was added. The phenylacetylene (0,11 mL; 1 mmol, 1 eq.) and the ethyl acetoacetate (0.38 mL, 3 mmol, 3 eq.) were added via cannula. The mixture was stirred at 80°C for 18 h. The reaction was quenched with solution of DCl (5 mL, 2 M). The solution was extracted with EtOAc and the content of the reaction mixture was analyzed by GC-MS. *m/z* (%): 230(60%); 201(100%); 185(20%); 157(15%); 128(20%); 115(25%); 105(30%); 77(30%); 63(%5); 51(10%).

As it was observed in the MS spectra of the product the deuterium atom were not present in the product (the MS spectra was identical with the isolated furan product), which indicates that the silver furanyl molecule is protonated before the quenching procedure.

4.4 Reactions with silver-acetylide

We supposed that the reaction could undergo alternative path if the starting material is silver acetylide instead of terminal acetylene. For this study we prepared the required silver salt, then examined its reactivity.

4.5 Synthesis of silver acetylide[3]



1-trimethylsilyl-2-phenylacetylene (1 mmol, 174 mg, 196 μL) were added to the mixture of MeOH (3 mL) and water (1 mL) at 25°C. At this temperature $AgNO_3$ (1 mmol, 170 mg, 1 eqiuv.) was added and the reaction mixture was stirred for 15 min at 25°C. The formed white solid was filtered, and washed with cold methanol. The desired silver acetylide were obtained as white solid (159 mg, 0.76 mmol, 76% yield).

4.6 Reaction of silver acetylide with ketoesters

The silver derivative of the acetylene was reacted with ethyl acetoacetate under the standard reaction conditions. We examined the deuterium incorporation into the furan ring after quenching the reaction mixture with 2M DCl(D_2O). This experiment provides useful information regarding the supposed mechanistic paths.

Silver acetylide (26 mg, 0.125 mmol), Ag_2CO_3 (34.5 mg; 0.125 mmol, 1 eq.) and KOAc (24.5 mg; 0.25 mmol, 2 eq.) were placed in a 4 mL vial. The system was charged with argon. Dry DMF (3 mL) was added, followed by ethyl acetoacetate (47 μL, 0.375 mmol, 3 eqiv.) were added with syringe. The reaction mixture was stirred at 80°C for 18 h. The reaction was quenched with solution of DCl (2 mL, 2 M in D_2O). The solution was extracted with EtOAc and the content of the reaction mixture was analyzed by GC-MS. *m/z* (%): 230(60%); 201(100%); 185(20%); 157(15%); 128(20%); 115(25%); 105(30%); 77(30%); 63(5%); 51(10%).

The MS spectra of the formed product (it was identical with the MS spectra of the isolated furan compound) clearly shows that the deuterium atom did not build in to the heterocyclic ring.

4.7 MS and NMR spectra

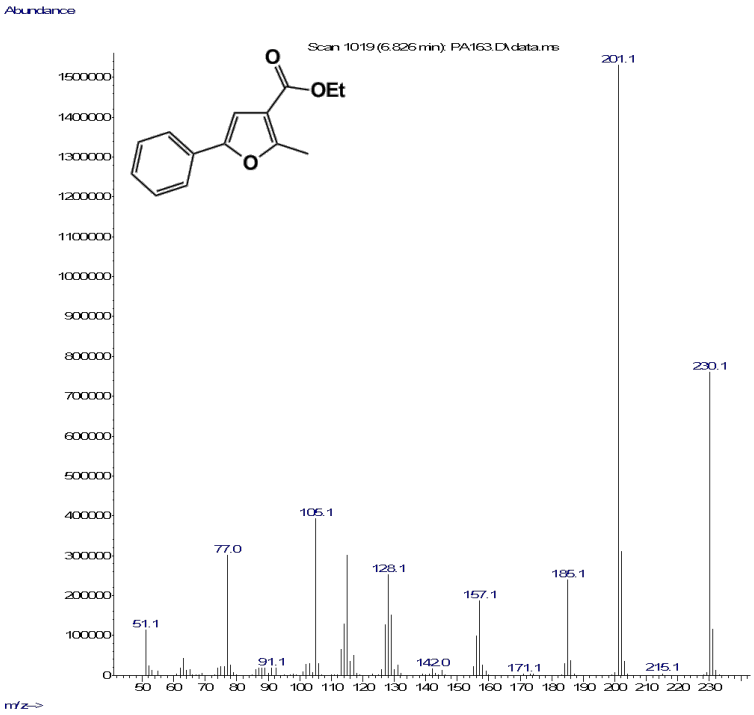


Figure 2: MS spectra of isolated ethyl 2-methyl-5-phenylfuran-3-carboxylate

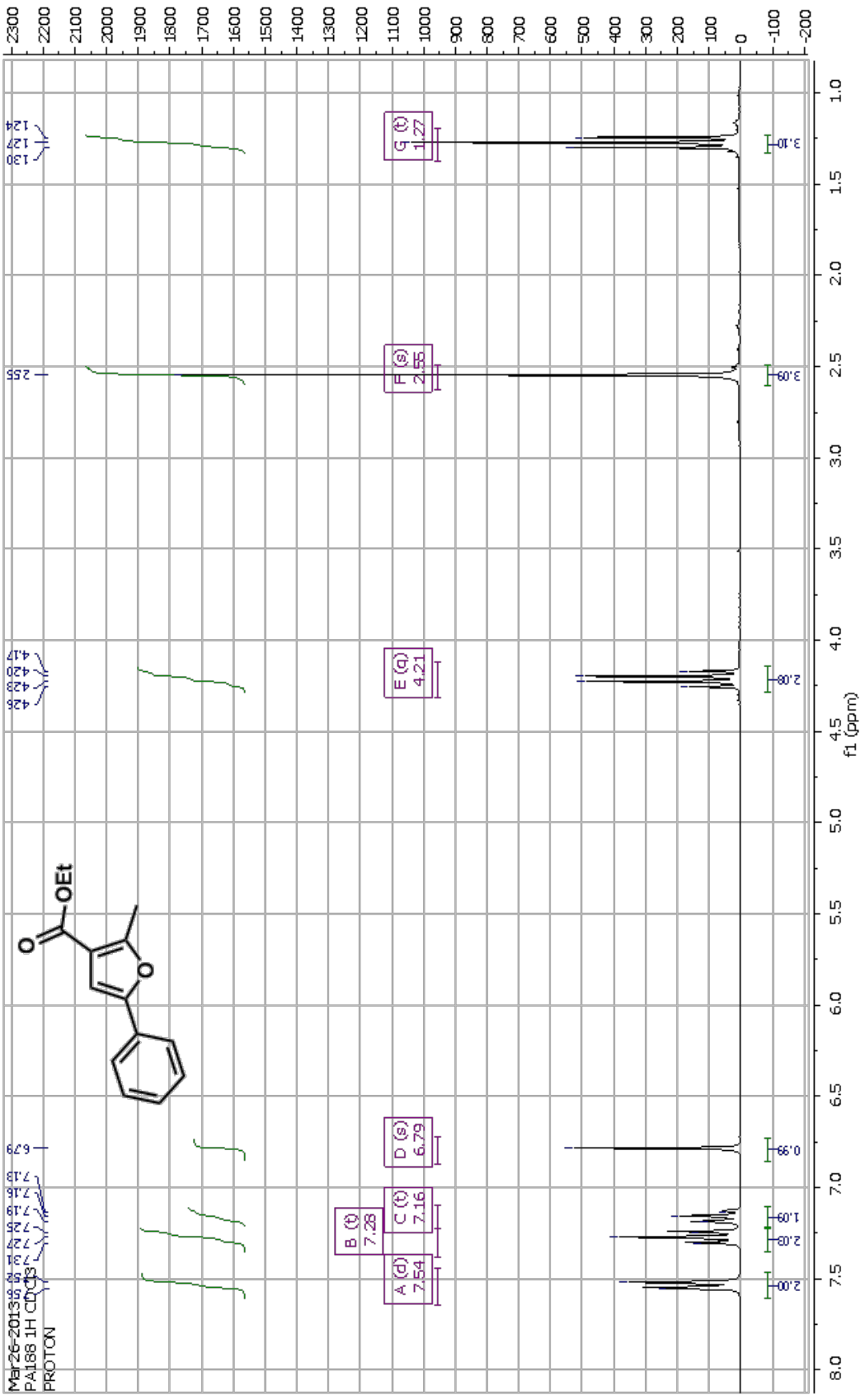


Figure 3: NMR spectra of isolated ethyl 2-methyl-5-phenylfuran-3-carboxylate

5 Stable structures

5.1 Structures in Scheme 2-7

molecule 1:

number of imag. freq.	=	0	
charge	=	0	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−460.226187138	Eh
$\Delta G_{vrt}^{B_1}$	=	0.111749	Eh
ΔG_{solv}	=	−460.114438138	Eh
$E_g^{B_1}$	=	−460.071518580	Eh

XYZ coordinates:
19

C	0.377555	-0.385051	-0.139186
C	-0.021875	-0.535845	1.302888
C	1.377372	0.727182	-0.421806
C	1.556244	0.942032	-1.899912
O	-0.066211	-1.088896	-1.019382
H	-0.593516	-1.458150	1.440754
H	0.856440	-0.534241	1.962040
H	-0.645801	0.318825	1.600508
O	2.494368	0.128950	-2.395178
O	0.920211	1.734424	-2.554292
C	2.670786	0.166701	-3.822321
C	3.731147	-0.843129	-4.171570
H	1.705240	-0.058927	-4.292857
H	2.951525	1.187896	-4.112214
H	3.898736	-0.853013	-5.255459
H	4.681677	-0.602444	-3.679806
H	3.428503	-1.850334	-3.861166
H	1.023188	1.658876	0.039728
H	2.330846	0.458145	0.055735

molecule 1.1:

number of imag. freq.	=	0	
charge	=	−1	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−459.736486865	Eh
$\Delta G_{vrt}^{B_1}$	=	0.099983	Eh
ΔG_{solv}	=	−459.636503865	Eh
$E_g^{B_1}$	=	−459.513300774	Eh

XYZ coordinates:
18

C	-0.126661	-0.070410	0.065520
C	0.072807	0.201946	1.562430
C	1.056674	-0.060712	-0.710669
C	1.139090	-0.283575	-2.108612
O	-1.299052	-0.269551	-0.304673
H	-0.524481	1.080311	1.846754
H	-0.321794	-0.650144	2.134574
H	1.119751	0.372719	1.851824
O	2.488817	-0.194774	-2.528647
O	0.284300	-0.524450	-2.952465
C	2.698992	-0.399046	-3.903350
C	4.183491	-0.269599	-4.163259
H	2.327553	-1.392036	-4.206252
H	2.126681	0.335628	-4.493703
H	4.409696	-0.420494	-5.228856
H	4.543061	0.725984	-3.869715
H	4.745225	-1.012318	-3.580627
H	2.003131	0.134115	-0.207422

molecule 1.2:

number of imag. freq.	=	0	
charge	=	0	
multiplicity	=	2	
$E_{SMD}^{B_2}$	=	−459.567185682	Eh
$\Delta G_{vrt}^{B_1}$	=	0.098223	Eh
ΔG_{solv}	=	−459.468962682	Eh
$E_g^{B_1}$	=	−459.413539261	Eh

XYZ coordinates:
18

C	-0.063061	-0.239351	0.102676
C	-0.001135	0.085514	1.574117
C	1.124773	0.113559	-0.673984
C	1.183207	0.112806	-2.142024
O	-1.029977	-0.792022	-0.402789
H	-0.935971	-0.213012	2.056895
H	0.837499	-0.440239	2.051441
H	0.163697	1.160519	1.729949
O	2.465968	0.015948	-2.547241
O	0.241790	0.221394	-2.894247
C	2.671018	0.019958	-3.969671
C	4.150078	-0.118004	-4.213877
H	2.094538	-0.805778	-4.407565
H	2.263424	0.955039	-4.376861
H	4.354386	-0.119166	-5.291389
H	4.703042	0.713778	-3.760861
H	4.532380	-1.055025	-3.791342
H	2.040346	0.386250	-0.146396

molecule 2:

number of imag. freq.	=	0	
charge	=	0	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−308.243571706	Eh
$\Delta G_{vrt}^{B_1}$	=	0.075265	Eh
ΔG_{solv}	=	−308.168306706	Eh
$E_g^{B_1}$	=	−308.147045028	Eh

XYZ coordinates:
14

C	0.337268	0.056419	-0.277125
C	0.082151	0.030138	1.101974
C	1.135536	-0.013127	2.007517
C	2.452436	-0.030685	1.551258
C	2.713534	-0.004767	0.182339
C	1.665147	0.038521	-0.728939
H	-0.949595	0.044112	1.450050
H	0.927758	-0.033280	3.076308
H	3.275947	-0.064593	2.263032
H	3.741192	-0.018379	-0.177704
H	1.860413	0.058994	-1.800061
C	-0.742566	0.100888	-1.210418
C	-1.658489	0.138612	-2.001913
H	-2.467485	0.171929	-2.701009

molecule 2.1:

number of imag. freq.	=	0	
charge	=	0	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−453.448462971	Eh
$\Delta G_{vrt}^{B_1}$	=	0.059223	Eh
ΔG_{solv}	=	−453.389239971	Eh
$E_g^{B_1}$	=	−453.324936625	Eh

XYZ coordinates:
14

C	0.182535	0.126450	-0.236500
C	0.019442	0.096474	1.157870
C	1.124150	0.001999	1.996076
C	2.409564	-0.064230	1.460790
C	2.582884	-0.035289	0.077913
C	1.481764	0.059071	-0.765019
H	-0.987295	0.148509	1.570258
H	0.981289	-0.020184	3.075880
H	3.273835	-0.138207	2.119510
H	3.584599	-0.086709	-0.347296
H	1.610888	0.082054	-1.846260
C	-0.950172	0.223265	-1.099719
C	-1.921716	0.306410	-1.840579
Ag	-3.539072	0.445155	-3.069649

molecule 3.1:

number of imag. freq.	=	0	
charge	=	0	
multiplicity	=	2	
$E_{SMD}^{B_2}$	=	−767.853561498	Eh
$\Delta G_{vrt}^{B_1}$	=	0.197641	Eh
ΔG_{solv}	=	−767.655920498	Eh
$E_g^{B_1}$	=	−767.611798466	Eh

XYZ coordinates:
32

C	-2.979028	-0.040716	-0.474957
C	-3.485026	-1.373498	-0.430921
C	-4.712051	-1.634866	0.149599
C	-5.477528	-0.600235	0.701131
C	-4.994966	0.713579	0.668336
C	-3.771023	1.000372	0.092558
H	-2.876319	-2.174662	-0.848021
H	-5.081616	-2.658950	0.181698
H	-6.442993	-0.816507	1.155356
H	-5.588098	1.519927	1.098120
H	-3.395644	2.023057	0.058771
C	-1.760111	0.223266	-1.061081
O	0.106577	-1.673065	0.945825
C	0.170114	-0.468797	0.827282
C	0.663744	0.162053	-0.479209
C	-0.513658	0.380567	-1.411639
C	-0.242440	0.484942	1.908962
H	0.662377	0.893043	2.383772
H	-0.803499	1.334728	1.497578
H	-0.840759	-0.033482	2.664279
C	1.705068	-0.738975	-1.113058
O	1.589009	-1.311052	-2.169229
O	2.784628	-0.801423	-0.321830
C	3.801662	-1.753823	-0.689264
H	4.707328	-1.384659	-0.196678
C	3.422282	-3.136201	-0.216880
H	3.943457	-1.716094	-1.775985
H	4.234271	-3.843238	-0.429362
H	3.233050	-3.138376	0.863485
H	2.517312	-3.488924	-0.725113
H	-0.245272	0.652491	-2.439053
H	1.146492	1.128310	-0.252650

molecule 3.2:

number of imag. freq.	=	0	
charge	=	0	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−767.279309577	Eh
$\Delta G_{vrt}^{B_1}$	=	0.187946	Eh
ΔG_{solv}	=	−767.091363577	Eh
$E_g^{B_1}$	=	−767.034363790	Eh

XYZ coordinates:
31

C	0.005438	0.102365	-0.168260
C	-0.023750	0.052325	1.257670
C	1.170365	0.016844	1.993096
C	1.134352	-0.031847	3.381457
C	-0.088094	-0.046615	4.051037
C	-1.278440	-0.012371	3.326201
C	-1.250915	0.036973	1.937724
H	2.120956	0.028478	1.461772
H	2.065918	-0.058861	3.944805
H	-0.113269	-0.085282	5.139084
H	-2.234977	-0.024860	3.846614
H	-2.174704	0.061872	1.361577
C	0.014720	0.125832	-1.380058
C	0.055742	0.219032	-2.829048
C	-1.312110	0.024611	-3.467841
H	0.751851	-0.515549	-3.258657
O	-1.164683	-0.081256	-4.794878
O	-2.372562	0.017230	-2.893844
C	0.617335	1.608630	-3.235324
C	-2.378949	-0.195421	-5.560796
C	-1.987792	-0.309747	-7.009604
H	-2.933300	-1.072709	-5.203346
H	-2.997649	0.690137	-5.360208
H	-2.884829	-0.396213	-7.634552
H	-1.424357	0.572427	-7.336302
H	-1.364231	-1.195685	-7.178740
O	1.732618	1.702350	-3.688940
C	-0.296934	2.778261	-3.016100
H	-0.806285	2.708580	-2.046434
H	0.266839	3.712458	-3.089191
H	-1.079095	2.777492	-3.790269

molecule 3.3:

number of imag. freq.	=	0	
charge	=	1	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−912.943703834	Eh
$\Delta G_{vrt}^{B_1}$	=	0.186877	Eh
ΔG_{solv}	=	−912.756826834	Eh
$E_g^{B_1}$	=	−912.626054001	Eh

XYZ coordinates:

32

C	-2.855895	0.473415	-0.061812
C	-3.746763	1.394773	0.512758
C	-5.083238	1.054199	0.671144
C	-5.537447	-0.198274	0.258426
C	-4.656199	-1.114091	-0.314422
C	-3.316128	-0.785899	-0.475401
H	-3.384918	2.377319	0.816812
H	-5.775325	1.768506	1.112416
H	-6.586451	-0.460733	0.381468
H	-5.015838	-2.088544	-0.638380
H	-2.620461	-1.493181	-0.924133
C	-1.480455	0.824934	-0.228504
O	0.907212	3.060558	1.227994
C	1.365015	2.873121	0.115722
C	1.075609	1.526309	-0.607778
C	-0.308402	1.124742	-0.395863
C	2.246871	3.835175	-0.593188
H	1.739078	4.198125	-1.498643
H	2.497068	4.681438	0.051409
H	3.160332	3.327157	-0.935001
C	2.044702	0.535825	0.054698
O	1.811852	0.021589	1.135943
O	3.141668	0.395738	-0.644504
C	4.224065	-0.407598	-0.071408
H	4.772482	-0.757043	-0.949757
C	5.066522	0.446758	0.838304
H	3.774473	-1.262605	0.443749
H	5.913683	-0.139520	1.213087
H	5.470944	1.313919	0.302267
H	4.493212	0.795330	1.705998
H	1.322915	1.612645	-1.674602
Ag	-0.231542	1.032162	2.113003

molecule 3.4:

number of imag. freq.	=	0	
charge	=	−1	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−766.812836117	Eh
$\Delta G_{vrt}^{B_1}$	=	0.178541	Eh
ΔG_{solv}	=	−766.634295117	Eh
$E_g^{B_1}$	=	−766.507699054	Eh

XYZ coordinates:
30

C	-2.731294	-0.224154	0.057892
C	-3.796404	0.700206	0.121866
C	-5.113927	0.267303	0.199290
C	-5.418613	-1.095529	0.215607
C	-4.374941	-2.021254	0.152655
C	-3.054310	-1.598331	0.075156
H	-3.557993	1.763325	0.109097
H	-5.916999	1.004443	0.247679
H	-6.454045	-1.431113	0.276489
H	-4.594696	-3.090038	0.164265
H	-2.239769	-2.320452	0.025890
C	-1.389908	0.208634	-0.020575
O	0.402637	3.247191	-0.109353
C	1.339862	2.437981	-0.175007
C	1.114337	1.006049	-0.165207
C	-0.225792	0.577894	-0.087914
C	2.743336	3.014657	-0.270733
H	3.266088	2.672605	-1.172548
H	2.647113	4.106530	-0.286901
H	3.365946	2.709712	0.579599
C	2.086611	-0.054196	-0.224573
O	1.848880	-1.258158	-0.236763
O	3.402491	0.376421	-0.269578
C	4.386734	-0.641555	-0.305716
H	5.266914	-0.171203	-0.766945
C	4.714608	-1.153467	1.081589
H	4.046442	-1.464308	-0.948767
H	5.528888	-1.891544	1.040619
H	5.028198	-0.327816	1.734626
H	3.833070	-1.632522	1.523631

molecule 3.5:

number of imag. freq.	=	0	
charge	=	0	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−912.491604293	Eh
$\Delta G_{vrt}^{B_1}$	=	0.175842	Eh
ΔG_{solv}	=	−912.315762293	Eh
$E_g^{B_1}$	=	−912.230092232	Eh

XYZ coordinates:
31

C	-2.873748	0.153331	-0.003786
C	-3.676541	1.301802	0.119360
C	-5.056670	1.178554	0.204196
C	-5.661242	-0.078460	0.168748
C	-4.871442	-1.219755	0.047030
C	-3.488892	-1.106255	-0.038884
H	-3.193213	2.277776	0.146085
H	-5.668028	2.074838	0.299277
H	-6.744263	-0.167764	0.235802
H	-5.334166	-2.205296	0.018481
H	-2.871384	-2.002934	-0.134332
C	-1.460179	0.334113	-0.087327
O	-0.263669	3.429174	0.027135
C	0.845043	2.903320	-0.078324
C	0.946638	1.443223	-0.170108
C	-0.314668	0.811346	-0.128390
C	2.073710	3.777577	-0.111820
H	2.649102	3.629840	-1.033439
H	1.742197	4.818460	-0.043509
H	2.751187	3.549466	0.719756
C	2.113138	0.634354	-0.292274
O	2.128459	-0.622394	-0.378007
O	3.281594	1.294672	-0.321431
C	4.487996	0.525916	-0.422345
H	5.214482	1.228291	-0.846574
C	4.934950	0.021776	0.929486
H	4.336086	-0.296924	-1.130347
H	5.901818	-0.490287	0.840171
H	5.052591	0.853365	1.635344
H	4.208268	-0.687920	1.341470
Ag	0.044659	-1.507055	-0.321618

molecule 3.6:

number of imag. freq.	=	0	
charge	=	−1	
multiplicity	=	2	
$E_{SMD}^{B_2}$	=	−767.377468466	Eh
$\Delta G_{vrt}^{B_1}$	=	0.186615	Eh
ΔG_{solv}	=	−767.190853466	Eh
$E_g^{B_1}$	=	−767.079462733	Eh

XYZ coordinates:
31

C	-2.202634	1.412367	-0.211243
C	-3.009025	0.448553	-0.899646
C	-4.389043	0.523841	-0.884943
C	-5.049974	1.546887	-0.187456
C	-4.284207	2.496645	0.506422
C	-2.903301	2.437455	0.503839
H	-2.500229	-0.353868	-1.433587
H	-4.971554	-0.227391	-1.421754
H	-6.138793	1.598365	-0.178347
H	-4.784492	3.293027	1.060802
H	-2.313104	3.170877	1.053076
C	-0.830461	1.341506	-0.215623
O	0.019584	-0.135840	1.760803
C	1.212542	0.030183	1.441660
C	1.563053	0.830945	0.304724
C	0.464360	1.427649	-0.439246
C	2.256708	-0.650944	2.312027
H	2.954064	0.072014	2.753618
H	1.723897	-1.185256	3.107367
H	2.868239	-1.357102	1.736389
C	2.866605	1.125330	-0.205682
O	3.128285	1.831020	-1.182904
O	3.911128	0.542051	0.495952
C	5.212323	0.792416	-0.001493
H	5.879547	0.657371	0.861975
C	5.579351	-0.163167	-1.118322
H	5.285661	1.832626	-0.346465
H	6.617219	-0.000508	-1.444101
H	5.480427	-1.204835	-0.784044
H	4.916621	-0.008380	-1.977979
H	0.786568	2.027354	-1.301870

molecule 3.7:

number of imag. freq.	=	0	
charge	=	0	
multiplicity	=	2	
$E_{SMD}^{B_2}$	=	−913.073381616	Eh
$\Delta G_{vrt}^{B_1}$	=	0.185961	Eh
ΔG_{solv}	=	−912.887420616	Eh
$E_g^{B_1}$	=	−912.825966422	Eh

XYZ coordinates:
32

C	-2.391427	0.954787	0.136044
C	-3.658443	0.333041	0.104550
C	-4.783038	0.991584	-0.368521
C	-4.686661	2.315116	-0.801176
C	-3.451782	2.964598	-0.758040
C	-2.323712	2.299230	-0.301038
H	-3.729025	-0.700055	0.452347
H	-5.742445	0.476569	-0.394676
H	-5.569953	2.840568	-1.161483
H	-3.371313	4.002420	-1.079400
H	-1.373552	2.830067	-0.258126
C	-1.235961	0.230311	0.621957
O	0.823921	-1.106765	2.564122
C	1.623771	-0.771840	1.678583
C	1.325193	0.264678	0.688991
C	0.046400	0.637720	0.252145
C	2.914396	-1.553152	1.585279
H	3.673238	-1.097529	2.233208
H	2.717394	-2.565875	1.953630
H	3.328068	-1.596993	0.571504
C	2.428058	0.964479	-0.014588
O	2.334088	1.505438	-1.099208
O	3.559384	0.998134	0.719796
C	4.712271	1.593294	0.105477
H	5.326547	1.931182	0.947214
C	5.440369	0.582809	-0.749457
H	4.394582	2.464218	-0.479466
H	6.348263	1.027722	-1.176106
H	5.736047	-0.291214	-0.154406
H	4.805819	0.246773	-1.578887
Ag	-1.483120	-1.413180	1.975539
H	0.105691	1.347150	-0.584374

molecule 4:

number of imag. freq.	=	0	
charge	=	0	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−767.329760520	Eh
$\Delta G_{vrt}^{B_1}$	=	0.195839	Eh
ΔG_{solv}	=	−767.13392152	Eh
$E_g^{B_1}$	=	−767.096311339	Eh

XYZ coordinates:
31

C	0.209226	-0.370003	-0.169331
C	0.072416	0.329191	1.036765
C	1.184343	0.892735	1.653284
C	2.447419	0.769256	1.079723
C	2.590997	0.074457	-0.120968
C	1.484145	-0.490152	-0.740546
H	-0.912389	0.428810	1.489136
H	1.061520	1.433476	2.590788
H	3.316480	1.211384	1.564393
H	3.574027	-0.028663	-0.578412
H	1.607149	-1.031603	-1.678303
C	-0.941842	-0.964584	-0.826741
O	-2.160361	-0.814997	-0.208175
C	-3.103586	-1.427505	-0.955703
C	-2.507192	-1.978482	-2.063554
C	-1.113567	-1.676977	-1.973948
H	-0.361055	-1.972494	-2.695518
C	-4.490731	-1.366511	-0.442130
H	-4.928887	-2.368122	-0.360814
H	-4.497135	-0.892600	0.545216
H	-5.140671	-0.789752	-1.112711
C	-3.118345	-2.734112	-3.155159
O	-2.500397	-3.199231	-4.090495
O	-4.453031	-2.859613	-3.002653
C	-5.150316	-3.580570	-4.032409
H	-6.057698	-3.946954	-3.539676
C	-5.473735	-2.682779	-5.202576
H	-4.539246	-4.437576	-4.339742
H	-6.069302	-3.230394	-5.944128
H	-6.052667	-1.809721	-4.876356
H	-4.556531	-2.335217	-5.691821

molecule 4.1:

number of imag. freq.	=	0	
charge	=	1	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−912.919017798	Eh
$\Delta G_{vrt}^{B_1}$	=	0.189414	Eh
ΔG_{solv}	=	−912.729603798	Eh
$E_g^{B_1}$	=	−912.602682783	Eh

XYZ coordinates:
32

C	-2.490836	0.741116	-0.007128
C	-3.087355	1.811054	0.672293
C	-4.430105	1.748229	1.027101
C	-5.188776	0.624691	0.709242
C	-4.602288	-0.439773	0.025703
C	-3.263636	-0.381121	-0.336370
H	-2.503013	2.692079	0.931126
H	-4.885641	2.582603	1.556729
H	-6.240038	0.580528	0.987027
H	-5.196186	-1.312412	-0.239227
H	-2.811568	-1.197249	-0.900583
C	-1.084344	0.755836	-0.368896
O	-0.520940	2.129999	-0.434629
C	0.706874	2.075374	-0.753813
C	1.099840	0.660757	-1.000568
C	-0.129476	-0.128227	-0.668077
C	1.472682	3.317814	-0.885930
H	2.193099	3.250194	-1.708459
H	0.807912	4.177537	-1.011330
H	2.069810	3.459697	0.027559
C	2.404854	0.132945	-0.388940
O	2.576385	-1.043525	-0.184079
O	3.280430	1.099886	-0.185726
C	4.593295	0.713498	0.337103
H	5.247229	1.523202	0.001865
C	4.553286	0.587126	1.836728
H	4.888056	-0.219135	-0.155148
H	5.560441	0.365916	2.209532
H	4.220875	1.520626	2.306124
H	3.893633	-0.228769	2.153400
H	1.284642	0.618401	-2.097062
Ag	-0.004301	-2.243648	-0.494563

molecule 4.2:

number of imag. freq.	=	0	
charge	=	0	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−912.514118471	Eh
$\Delta G_{vrt}^{B_1}$	=	0.180568	Eh
ΔG_{solv}	=	−912.333550471	Eh
$E_g^{B_1}$	=	−912.266334622	Eh

XYZ coordinates:

31

C	-2.699252	0.609214	-0.009844
C	-3.527939	1.730502	0.141441
C	-4.910090	1.587713	0.205447
C	-5.495946	0.327223	0.120261
C	-4.680091	-0.794038	-0.030351
C	-3.300168	-0.655305	-0.094590
H	-3.080842	2.720259	0.208925
H	-5.534839	2.472591	0.323242
H	-6.578325	0.217634	0.170527
H	-5.124342	-1.786701	-0.098466
H	-2.665645	-1.534340	-0.212569
C	-1.252078	0.745490	-0.078110
O	-0.775219	2.049895	0.014495
C	0.564727	2.011223	-0.065375
C	0.963208	0.700974	-0.207736
C	-0.213807	-0.124863	-0.216476
C	1.265144	3.314600	0.013419
H	1.864814	3.501369	-0.886265
H	0.531910	4.121002	0.122630
H	1.955585	3.347275	0.865651
C	2.319303	0.182303	-0.332574
O	2.601326	-1.001436	-0.460168
O	3.255924	1.148662	-0.299135
C	4.626634	0.732255	-0.405486
H	5.146993	1.612937	-0.798070
C	5.175612	0.314358	0.937819
H	4.695514	-0.079621	-1.139146
H	6.242330	0.071322	0.850194
H	5.068375	1.122966	1.671514
H	4.653093	-0.572921	1.313700
Ag	0.123302	-2.193193	-0.430274

molecule 4.3:

number of imag. freq.	=	1	
charge	=	0	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−1141.58216298	Eh
$\Delta G_{vrt}^{B_1}$	=	0.2359777	Eh
ΔG_{solv}	=	−1141.34618528	Eh
$E_g^{B_1}$	=	−1141.26150187	Eh

XYZ coordinates:

39

C	-2.321295	1.511466	-0.048224
C	-3.104851	2.631908	0.263604
C	-4.491950	2.536484	0.312653
C	-5.129516	1.325472	0.051917
C	-4.361628	0.209113	-0.278621
C	-2.976622	0.304089	-0.338824
H	-2.615411	3.579911	0.480348
H	-5.080882	3.418364	0.563151
H	-6.215378	1.254067	0.094086
H	-4.847641	-0.738284	-0.511948
H	-2.378289	-0.554518	-0.649751
C	-0.868162	1.580625	-0.066426
O	-0.326178	2.854170	-0.206770
C	1.012931	2.731757	-0.183682
C	1.336721	1.403579	-0.021385
C	0.117232	0.647908	0.060501
C	1.789813	3.984804	-0.333903
H	2.429663	3.953591	-1.224957
H	1.105754	4.835970	-0.421064
H	2.453486	4.148932	0.524274
C	2.661129	0.801658	0.077587
O	2.868991	-0.388305	0.245764
O	3.657442	1.705919	-0.040320
C	4.998173	1.203388	0.055128
H	5.604036	1.939596	-0.485194
C	5.433227	1.075517	1.495949
H	5.055456	0.241058	-0.467612
H	6.483280	0.759790	1.547180
H	5.338725	2.035742	2.018493
H	4.826000	0.328448	2.020093
Ag	0.126423	-1.392726	0.446872
O	-0.337861	-3.501288	1.048067
C	-1.434040	-3.774289	1.522760
C	-1.834865	-5.149154	1.935168
O	-2.390926	-2.878005	1.725454
H	-2.081563	-1.985293	1.447044
H	-2.083789	-5.155929	3.002696
H	-2.737702	-5.450941	1.391905

H	-1.022911	-5.850941	1.735430

molecule 4.4:

number of imag. freq.	=	0	
charge	=	−1	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−766.791143752	Eh
$\Delta G_{vrt}^{B_1}$	=	0.183155	Eh
ΔG_{solv}	=	−766.607988752	Eh
$E_g^{B_1}$	=	−766.479653935	Eh

XYZ coordinates:
30

C	-2.522824	-0.089616	0.015514
C	-3.326120	1.063554	0.107654
C	-4.713785	0.969941	0.174974
C	-5.348651	-0.270904	0.153056
C	-4.560479	-1.423994	0.061749
C	-3.178265	-1.338474	-0.005652
H	-2.845543	2.040905	0.125968
H	-5.307799	1.883516	0.245808
H	-6.435726	-0.341680	0.205886
H	-5.036700	-2.406288	0.042923
H	-2.552475	-2.228226	-0.077196
C	-1.079970	-0.047281	-0.057030
O	-0.543849	1.279773	-0.028667
C	0.779562	1.126791	-0.102727
C	1.084022	-0.226059	-0.176057
C	-0.127335	-1.025299	-0.148501
C	1.564230	2.391175	-0.089059
H	2.207364	2.478638	-0.974996
H	0.880129	3.248688	-0.061161
H	2.232176	2.444979	0.781916
C	2.433550	-0.767882	-0.267392
O	2.766075	-1.931566	-0.366146
O	3.396298	0.229157	-0.231932
C	4.744938	-0.203977	-0.304373
H	5.301523	0.654753	-0.705034
C	5.274744	-0.605931	1.055928
H	4.825073	-1.039657	-1.012693
H	6.338917	-0.875163	0.993582
H	5.167781	0.219706	1.772177
H	4.719803	-1.471269	1.436848

molecule 4.5:

number of imag. freq.	=	0	
charge	=	0	
multiplicity	=	2	
$E_{SMD}^{B_2}$	=	−913.048850021	Eh
$\Delta G_{vrt}^{B_1}$	=	0.187471	Eh
ΔG_{solv}	=	−912.861379021	Eh
$E_g^{B_1}$	=	−912.796633037	Eh

XYZ coordinates:

32

C	-2.236166	0.536643	-0.026739
C	-2.951911	1.473821	0.730152
C	-4.223007	1.173902	1.210608
C	-4.805880	-0.061315	0.940430
C	-4.106720	-0.995967	0.177107
C	-2.838271	-0.697927	-0.303247
H	-2.500301	2.440532	0.942219
H	-4.762207	1.914143	1.800592
H	-5.802013	-0.293241	1.314795
H	-4.558758	-1.959847	-0.054394
H	-2.306422	-1.421518	-0.922602
C	-0.893607	0.851394	-0.514589
O	-0.565015	2.197354	-0.439879
C	0.685549	2.349645	-0.990841
C	1.271523	1.016596	-1.307330
C	0.094929	0.090996	-1.024309
C	1.340902	3.655298	-0.802013
H	2.239887	3.724708	-1.428133
H	0.670353	4.482117	-1.077086
H	1.654666	3.821643	0.244850
C	2.422167	0.537587	-0.433169
O	3.186750	-0.347495	-0.755713
O	2.432196	1.141464	0.761728
C	3.321369	0.598698	1.752455
H	3.468792	1.417296	2.464744
C	2.699604	-0.611175	2.408216
H	4.280322	0.357820	1.277972
H	3.337202	-0.972909	3.224889
H	1.713856	-0.362722	2.820883
H	2.579176	-1.425560	1.682903
H	1.637973	0.923588	-2.346263
Ag	0.341428	-1.979008	-1.206550

5.2 Structures for the study of the substituent effects

molecule 2Me:

number of imag. freq.	=	0	
charge	=	0	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−347.546379278	Eh
$\Delta G_{vrt}^{B_1}$	=	0.099313	Eh
ΔG_{solv}	=	−347.447066278	Eh
$E_g^{B_1}$	=	−347.438978363	Eh

XYZ coordinates:

17

C	0.038086	0.000285	0.000262
C	0.751440	1.208878	-0.000618
C	2.141336	1.205142	-0.000747
C	2.840449	-0.000702	-0.000057
C	2.140510	-1.206032	0.000812
C	0.750581	-1.208807	0.000974
H	0.199508	2.147827	-0.001153
H	2.683123	2.150032	-0.001395
H	3.929514	-0.001063	-0.000179
H	2.681659	-2.151283	0.001364
H	0.197954	-2.147353	0.001648
C	-1.390157	0.000658	0.000346
C	-2.603264	0.000812	0.000354
C	-4.056577	-0.000742	0.000390
H	-4.455602	1.020797	-0.043571
H	-4.455179	-0.550517	-0.862428
H	-4.455406	-0.474343	0.907209

molecule 3.1Me:

number of imag. freq.	=	0	
charge	=	0	
multiplicity	=	2	
$E_{SMD}^{B_2}$	=	−807.147889825	Eh
$\Delta G_{vrt}^{B_1}$	=	0.22626	Eh
ΔG_{solv}	=	−806.921629825	Eh
$E_g^{B_1}$	=	−806.900074106	Eh

XYZ coordinates:

35

C	-1.402548	-0.239586	-0.898358
C	-1.260396	-1.324387	-1.808920
C	-1.923277	-2.518544	-1.586987
C	-2.746341	-2.677150	-0.466200
C	-2.900966	-1.619538	0.437482
C	-2.249648	-0.416654	0.231335
H	-0.611454	-1.195990	-2.674980
H	-1.800858	-3.340901	-2.291089
H	-3.265134	-3.619507	-0.297995
H	-3.534291	-1.743818	1.314846
H	-2.351995	0.404324	0.940636
C	-0.744405	0.961355	-1.117893
O	2.609223	3.561872	0.597985
C	1.659960	2.820167	0.753301
C	1.462854	1.651948	-0.218284
C	0.189264	1.878030	-1.048860
C	0.638806	3.037305	1.830114
H	-0.376264	2.811118	1.477696
H	0.837994	2.343074	2.656311
H	0.704986	4.067514	2.193729
C	1.400942	0.304638	0.466559
O	0.993955	0.107928	1.589897
O	1.819199	-0.657258	-0.361589
C	1.690731	-2.015279	0.107608
H	1.642008	-2.609433	-0.811455
C	2.864888	-2.408417	0.970283
H	0.736004	-2.110442	0.641377
H	2.786511	-3.467176	1.248096
H	3.809678	-2.266093	0.431176
H	2.891375	-1.815870	1.891833
C	0.126896	3.201548	-1.761881
H	2.324710	1.669562	-0.902602
H	0.066056	4.039666	-1.051332
H	1.035686	3.361972	-2.359859
H	-0.745079	3.250534	-2.422452

molecule 2Ph:

number of imag. freq.	=	0	
charge	=	0	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−539.193795254	Eh
$\Delta G_{vrt}^{B_1}$	=	0.143442	Eh
ΔG_{solv}	=	−539.050353254	Eh
$E_g^{B_1}$	=	−539.031526005	Eh

XYZ coordinates:
24

C	-2.980117	-1.667963	-0.766109
C	-3.618637	-0.727032	0.057976
C	-4.958763	-0.417809	-0.138358
C	-5.681465	-1.039290	-1.155686
C	-5.055667	-1.974563	-1.978521
C	-3.715829	-2.289049	-1.788389
H	-3.048158	-0.245310	0.850769
H	-5.443446	0.313495	0.506919
H	-6.731792	-0.794861	-1.307162
H	-5.616240	-2.462614	-2.774554
H	-3.220823	-3.018746	-2.427557
C	-1.606762	-1.987285	-0.567723
C	-0.433804	-2.259457	-0.397663
C	0.939634	-2.577510	-0.197816
C	1.673354	-1.954714	0.824879
C	3.013286	-2.267459	1.017012
C	3.641214	-3.202715	0.195754
C	2.920529	-3.825868	-0.821959
C	1.580267	-3.518376	-1.020300
H	1.176661	-1.225067	1.462793
H	3.572271	-1.778100	1.813359
H	4.691628	-3.445802	0.348772
H	3.406878	-4.557141	-1.466015
H	1.011415	-4.001445	-1.813442

molecule 3.1Ph:

number of imag. freq.	=	0	
charge	=	0	
multiplicity	=	2	
$E_{SMD}^{B_2}$	=	−998.795963397	Eh
$\Delta G_{vrt}^{B_1}$	=	0.271961	Eh
ΔG_{solv}	=	−998.524002397	Eh
$E_g^{B_1}$	=	−998.490504429	Eh

XYZ coordinates:
42

C	2.082755	-0.526956	-0.726972
C	2.258525	0.445480	-1.751460
C	3.529913	0.858222	-2.106757
C	4.656906	0.325945	-1.470561
C	4.500474	-0.631735	-0.462876
C	3.238177	-1.061331	-0.092912
H	1.371205	0.866387	-2.222559
H	3.651164	1.612171	-2.883393
H	5.653496	0.658282	-1.756743
H	5.377087	-1.044721	0.034720
H	3.110794	-1.812727	0.686600
C	0.807175	-0.954332	-0.391489
O	0.901582	1.958777	1.408286
C	0.436156	0.879645	1.703229
C	-0.785602	0.307742	0.977239
C	-0.406223	-0.891671	0.118064
C	0.984012	0.044151	2.826793
H	0.427913	0.293857	3.742523
H	0.861688	-1.030592	2.647448
H	2.038468	0.288347	2.990615
C	-1.408231	1.415650	0.147261
O	-1.193281	1.612125	-1.023499
O	-2.212676	2.162658	0.915735
C	-2.735507	3.366258	0.319344
H	-3.626144	3.596171	0.913729
C	-1.712367	4.474188	0.379348
H	-3.038507	3.144426	-0.711014
H	-2.145291	5.406844	-0.004389
H	-1.383434	4.643010	1.411998
H	-0.832147	4.227132	-0.225152
C	-1.444900	-1.909277	-0.165892
H	-1.499929	-0.000919	1.758398
C	-2.800983	-1.670265	0.084793
C	-3.761867	-2.634912	-0.211204
C	-3.385443	-3.856356	-0.759371
C	-2.036242	-4.106533	-1.013227
C	-1.079968	-3.145479	-0.718694
H	-3.128316	-0.717034	0.500835

H	-4.812087	-2.424154	-0.013760
H	-4.136623	-4.611006	-0.987468
H	-1.728510	-5.060663	-1.439248
H	-0.024620	-3.343505	-0.911084

5.3 Small molecules for stoichiometry

molecule Ag_2CO_3:

number of imag. freq.	=	0	
charge	=	0	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−555.403878215	Eh
$\Delta G_{vrt}^{B_1}$	=	−0.022313	Eh
ΔG_{solv}	=	−555.426191215	Eh
$E_g^{B_1}$	=	−555.264154424	Eh

XYZ coordinates:
6

C	0.048032	-0.047124	-0.111201
O	-0.304992	-0.246229	1.155842
O	1.293107	0.005057	-0.387832
O	-0.877820	0.081629	-0.980479
Ag	1.941252	-0.323551	1.730794
Ag	-2.531684	-0.163309	0.509710

molecule $AgCO_3^-$:

number of imag. freq.	=	0	
charge	=	−1	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−409.711030465	Eh
$\Delta G_{vrt}^{B_1}$	=	−0.017868	Eh
ΔG_{solv}	=	−409.728898465	Eh
$E_g^{B_1}$	=	−409.513048094	Eh

XYZ coordinates:
5

C	0.442104	0.357074	-0.126956
O	0.445947	0.056998	1.167350
O	0.733960	1.494676	-0.540149
O	0.108019	-0.627359	-0.952967
Ag	-0.172914	-2.029760	0.743005

molecule HCO_3^-:

number of imag. freq.	=	0	
charge	=	−1	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−264.529121105	Eh
$\Delta G_{vrt}^{B_1}$	=	−0.001017	Eh
ΔG_{solv}	=	−264.530138105	Eh
$E_g^{B_1}$	=	−264.349965800	Eh

XYZ coordinates:
5

C	0.163733	0.023496	-0.029717
O	-0.290103	0.005088	1.136482
O	1.314864	-0.008453	-0.477163
O	-0.853843	0.096587	-1.036791
H	-1.666939	0.113362	-0.511124

molecule OAc^-:

number of imag. freq.	=	0	
charge	=	−1	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−228.571543366	Eh
$\Delta G_{vrt}^{B_1}$	=	0.01885	Eh
ΔG_{solv}	=	−228.552693366	Eh
$E_g^{B_1}$	=	−228.408428387	Eh

XYZ coordinates:
7

C	0.114315	0.157928	-0.045652
H	0.003087	0.062015	1.043220
H	0.862204	-0.565854	-0.402345
H	0.503549	1.158385	-0.286392
C	-1.226921	-0.069254	-0.791662
O	-1.151495	0.015276	-2.042751
O	-2.230068	-0.308473	-0.076413

6 Transition states

6.1 Structures in Scheme 2-7

TS(1.2+2 ⟶ 3.1):

number of imag. freq.	=	1	
charge	=	0	
multiplicity	=	2	
$E_{SMD}^{B_2}$	=	−767.809726917	Eh
$\Delta G_{vrt}^{B_1}$	=	0.1952287	Eh
ΔG_{solv}	=	−767.614498217	Eh
$E_g^{B_1}$	=	−767.565443369	Eh

XYZ coordinates:
32

C	0.034179	0.008339	-0.013661
C	-0.033688	0.074445	1.391134
C	-0.898958	0.968769	2.005487
C	-1.706780	1.805916	1.235219
C	-1.648582	1.744830	-0.157448
C	-0.787618	0.853796	-0.782501
H	0.596628	-0.587953	1.983468
H	-0.946366	1.013842	3.092273
H	-2.384389	2.505913	1.721372
H	-2.280094	2.396915	-0.758619
H	-0.735975	0.796584	-1.868670
C	0.914247	-0.901999	-0.645364
O	5.001836	-1.972610	-0.574451
C	4.358271	-0.936807	-0.501542
C	3.620525	-0.365414	-1.636680
C	1.773382	-1.585333	-1.201984
C	4.264561	-0.141568	0.777745
H	4.861869	0.777228	0.691367
H	3.228725	0.165108	0.980306
H	4.649715	-0.735664	1.611772
C	3.786883	-0.835094	-3.021695
O	3.882496	-1.989972	-3.377357
O	3.772317	0.215372	-3.870579
C	3.918804	-0.090817	-5.267530
H	3.461316	0.762142	-5.780574
C	5.373264	-0.253623	-5.639609
H	3.342742	-0.996853	-5.492084
H	5.469200	-0.416741	-6.720621
H	5.945198	0.644899	-5.376713
H	5.813415	-1.115177	-5.124427
H	2.233784	-2.455212	-1.643870
H	3.230920	0.646736	-1.521933

TS(1.2+2.1 ⟶ 3.2+Ag):

number of imag. freq.	=	1	
charge	=	0	
multiplicity	=	2	
$E_{SMD}^{B_2}$	=	−913.018933923	Eh
$\Delta G_{vrt}^{B_1}$	=	0.1834947	Eh
ΔG_{solv}	=	−912.835439223	Eh
$E_g^{B_1}$	=	−912.755770372	Eh

XYZ coordinates:
32

C	-0.518370	0.785169	0.576202
O	-0.483596	0.821422	1.802327
C	-0.034453	1.958384	-0.233759
C	-0.995362	-0.445036	-0.071518
C	-1.514900	-0.625212	-1.417821
H	-1.396424	-1.176319	0.627632
O	-2.241128	-1.538773	-1.760637
O	-1.050718	0.296676	-2.323882
C	-1.487483	0.135884	-3.675120
H	-1.456536	1.142532	-4.106107
C	-0.580310	-0.814119	-4.429135
H	-2.520394	-0.230474	-3.683491
H	-0.858988	-0.880305	-5.488817
H	0.465867	-0.444301	-4.416186
H	-0.641989	-1.827965	-4.009377
C	1.028505	-1.378735	-0.283990
C	1.335491	-1.761633	0.860557
Ag	1.361610	-1.135594	-2.337202
C	1.591578	-2.142948	2.197503
C	1.929263	-1.173495	3.162242
C	2.180065	-1.553905	4.472783
C	2.102440	-2.896852	4.844075
C	1.765120	-3.864250	3.896526
C	1.509049	-3.495127	2.583760
H	1.961989	-0.126298	2.866165
H	2.431170	-0.797171	5.214495
H	2.300153	-3.189509	5.874355
H	1.699138	-4.912028	4.186352
H	1.241742	-4.241033	1.836522
H	-0.829207	2.362079	-0.872426
H	0.318943	2.733401	0.453092
H	0.783827	1.654574	-0.901472

TS(3.3 ⟶ 4.1):

number of imag. freq.	=	1	
charge	=	1	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−912.909618131	Eh
$\Delta G_{vrt}^{B_1}$	=	0.1908557	Eh
ΔG_{solv}	=	−912.718762431	Eh
$E_g^{B_1}$	=	−912.595945070	Eh

XYZ coordinates:
32

C	0.468704	-0.321502	-0.217636
C	0.221846	0.899764	0.427949
C	1.162531	1.414780	1.307691
C	2.353802	0.726189	1.540057
C	2.604351	-0.486929	0.900717
C	1.661273	-1.020146	0.032074
H	-0.709077	1.431655	0.239217
H	0.971075	2.358939	1.813292
H	3.089740	1.136389	2.229112
H	3.530591	-1.024984	1.091719
H	1.833602	-1.977239	-0.459333
C	-0.458308	-0.868229	-1.161141
O	-2.133492	-0.796506	-0.398733
C	-2.871123	-1.348096	-1.221851
C	-2.138942	-1.896282	-2.440877
C	-0.721106	-1.470113	-2.276831
C	-4.318551	-1.503130	-0.958259
H	-4.685499	-2.474997	-1.305974
H	-4.526545	-1.361533	0.105780
H	-4.867528	-0.744625	-1.533130
C	-2.711772	-1.600283	-3.831401
O	-2.005258	-1.430652	-4.802210
O	-4.029184	-1.619593	-3.839556
C	-4.701528	-1.417450	-5.123274
H	-5.665865	-1.913884	-4.984735
C	-4.847187	0.051322	-5.421130
H	-4.127124	-1.946495	-5.890793
H	-5.415932	0.180189	-6.349639
H	-5.392560	0.566595	-4.621328
H	-3.871591	0.531966	-5.557463
H	-2.222230	-2.998483	-2.342853
Ag	0.548406	-1.494603	-4.014378

TS(4.3 ⟶ 4):

number of imag. freq.	=	1	
charge	=	0	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−1141.55960931	Eh
$\Delta G_{vrt}^{B_1}$	=	0.2291537	Eh
ΔG_{solv}	=	−1141.33045561	Eh
$E_g^{B_1}$	=	−1141.24308016	Eh

XYZ coordinates:

39

C	-0.043423	0.237849	0.164168
C	0.023232	0.032152	1.548838
C	-1.140957	-0.096977	2.298581
C	-2.387710	-0.024980	1.681665
C	-2.462404	0.183062	0.304430
C	-1.303165	0.319715	-0.446928
H	0.995341	-0.032922	2.034051
H	-1.072678	-0.258393	3.373720
H	-3.298042	-0.126371	2.270811
H	-3.432604	0.248749	-0.186366
H	-1.365359	0.501596	-1.519883
C	1.159166	0.370371	-0.642614
O	2.343900	0.484694	0.056432
C	3.349529	0.555445	-0.842569
C	2.815531	0.489617	-2.104919
C	1.376187	0.354206	-1.995299
C	4.705235	0.717947	-0.274704
H	5.442619	0.853911	-1.069379
H	4.741595	1.580608	0.404007
H	4.988978	-0.168069	0.310104
C	3.496859	0.660084	-3.384610
O	2.923934	1.011878	-4.412774
O	4.811758	0.420676	-3.348838
C	5.546851	0.591461	-4.576564
H	6.572810	0.789419	-4.247860
C	5.462992	-0.648690	-5.432491
H	5.160997	1.473735	-5.100344
H	6.090286	-0.530899	-6.325120
H	5.815346	-1.528008	-4.879621
H	4.432870	-0.828721	-5.760494
Ag	0.522872	1.429551	-3.875265
O	-1.111514	-0.017893	-4.583776
C	-0.987175	-1.151147	-4.065061
C	-1.929017	-2.254056	-4.465768
O	-0.110871	-1.474989	-3.185736
H	0.562348	-0.549604	-2.719630
H	-1.357390	-3.138535	-4.769659

H	-2.532695	-2.546626	-3.597675
H	-2.585199	-1.930738	-5.278501

TS(3.4 $\longrightarrow$ 4.4):

number of imag. freq.	=	1	
charge	=	−1	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−766.770403734	Eh
$\Delta G_{vrt}^{B_1}$	=	0.1830537	Eh
ΔG_{solv}	=	−766.587350034	Eh
$E_g^{B_1}$	=	−766.465925761	Eh

XYZ coordinates:
30

C	0.440971	-0.151510	-0.077466
C	0.113332	0.120256	1.266077
C	1.102139	0.435654	2.190950
C	2.446347	0.493072	1.820434
C	2.783228	0.224955	0.490805
C	1.805739	-0.090994	-0.441642
H	-0.932155	0.077904	1.562876
H	0.815031	0.641082	3.224014
H	3.216260	0.741356	2.551481
H	3.827447	0.263205	0.175194
H	2.067135	-0.299824	-1.478661
C	-0.514886	-0.479677	-1.082000
O	-2.202203	-0.485024	-0.314167
C	-2.889670	-0.786382	-1.351541
C	-2.162279	-0.977100	-2.553737
C	-0.757742	-0.782352	-2.322571
C	-4.372447	-0.898605	-1.146024
H	-4.746254	-1.882204	-1.456270
H	-4.604091	-0.736028	-0.087112
H	-4.913796	-0.161841	-1.753212
C	-2.703361	-1.314123	-3.849718
O	-2.085128	-1.513512	-4.882741
O	-4.090278	-1.404811	-3.853788
C	-4.687085	-1.714394	-5.100684
H	-5.656997	-2.167826	-4.851039
C	-4.873733	-0.477003	-5.954008
H	-4.074410	-2.457163	-5.629394
H	-5.397461	-0.724946	-6.888665
H	-5.462966	0.278443	-5.416808
H	-3.898807	-0.043671	-6.206549

TS(3.5 ⟶ 4.2):

number of imag. freq.	=	1	
charge	=	0	
multiplicity	=	1	
$E_{SMD}^{B_2}$	=	−912.470979214	Eh
$\Delta G_{vrt}^{B_1}$	=	0.1791037	Eh
ΔG_{solv}	=	−912.291875514	Eh
$E_g^{B_1}$	=	−912.216952295	Eh

XYZ coordinates:
31

C	0.192501	-0.331419	-0.608831
C	-0.233854	0.705285	0.239279
C	0.701176	1.460006	0.934387
C	2.066409	1.219172	0.780759
C	2.495223	0.196372	-0.063571
C	1.570128	-0.586713	-0.741463
H	-1.301521	0.878790	0.352601
H	0.359856	2.252502	1.598982
H	2.793586	1.823252	1.321141
H	3.559130	-0.004431	-0.183160
H	1.900202	-1.403253	-1.383516
C	-0.741556	-1.109300	-1.338696
O	-2.685137	-1.149921	-0.131388
C	-3.318020	-1.903154	-0.899369
C	-2.664641	-2.385353	-2.091769
C	-1.335423	-1.867079	-2.165880
C	-4.732419	-2.268838	-0.537529
H	-4.845751	-3.354977	-0.440369
H	-4.989245	-1.783890	0.408917
H	-5.433777	-1.952250	-1.318675
C	-3.160695	-3.235596	-3.127172
O	-2.514892	-3.583627	-4.139728
O	-4.421425	-3.676917	-2.957300
C	-4.973754	-4.518113	-3.978079
H	-5.760855	-5.081678	-3.463949
C	-5.535505	-3.702579	-5.118798
H	-4.204556	-5.218051	-4.324668
H	-6.022991	-4.360450	-5.850039
H	-6.281083	-2.984940	-4.754111
H	-4.738907	-3.151141	-5.631584
Ag	-0.380303	-2.543825	-3.999430

TS(3.2+Ag $\longrightarrow$ 4.5):

number of imag. freq.	=	1	
charge	=	0	
multiplicity	=	2	
$E_{SMD}^{B_2}$	=	−913.009625240	Eh
$\Delta G_{vrt}^{B_1}$	=	0.1862067	Eh
ΔG_{solv}	=	−912.82341854	Eh
$E_g^{B_1}$	=	−912.764177330	Eh

XYZ coordinates:
32

C	0.063086	-0.329042	-0.419263
C	-0.313847	0.656867	0.504140
C	0.654686	1.427909	1.135464
C	2.006472	1.237327	0.852948
C	2.386936	0.261882	-0.067303
C	1.427721	-0.522222	-0.695049
H	-1.367934	0.812028	0.723121
H	0.350052	2.188071	1.853633
H	2.760802	1.845204	1.350204
H	3.440715	0.103205	-0.292314
H	1.720236	-1.296241	-1.404940
C	-0.888160	-1.140343	-1.128720
O	-2.408840	-1.167291	-0.252329
C	-3.114192	-1.953604	-0.926151
C	-2.466381	-2.466705	-2.191426
C	-1.096922	-1.859500	-2.194471
C	-4.473192	-2.341157	-0.493201
H	-4.721074	-3.359924	-0.820862
H	-4.575591	-2.255106	0.593643
H	-5.210841	-1.665529	-0.953702
C	-3.244503	-2.092828	-3.447019
O	-3.453241	-2.843917	-4.367327
O	-3.627484	-0.812745	-3.391556
C	-4.201209	-0.252314	-4.592031
H	-4.788013	0.600079	-4.234489
C	-3.113332	0.171730	-5.547921
H	-4.874823	-0.993686	-5.038179
H	-3.553293	0.671513	-6.420371
H	-2.419563	0.868818	-5.061541
H	-2.540077	-0.694367	-5.903474
H	-2.447934	-3.571774	-2.181068
Ag	0.115260	-1.644308	-4.053367

TS(3.1 ⟶ 3.6):

number of imag. freq.	=	1	
charge	=	−1	
multiplicity	=	2	
$E_{SMD}^{B_2}$	=	−996.415648678	Eh
$\Delta G_{vrt}^{B_1}$	=	0.2359327	Eh
ΔG_{solv}	=	−996.179715978	Eh
$E_g^{B_1}$	=	−996.049232419	Eh

XYZ coordinates:
39

C	0.006259	-0.005494	-0.037698
C	0.012366	-0.057313	1.390955
C	-1.103379	0.308183	2.120333
C	-2.272328	0.743510	1.479439
C	-2.296193	0.814225	0.079094
C	-1.190700	0.455599	-0.669542
H	0.926409	-0.380101	1.888419
H	-1.069489	0.261397	3.209864
H	-3.147370	1.030814	2.062056
H	-3.196965	1.160648	-0.429716
H	-1.206331	0.519497	-1.757105
C	1.109723	-0.367712	-0.770675
O	2.841690	1.668980	-0.535829
C	3.569194	1.195644	-1.403973
C	3.289297	-0.131827	-2.005843
C	2.090548	-0.847268	-1.488367
C	4.684480	2.041171	-1.975532
H	4.892875	1.797920	-3.025510
H	4.400336	3.094184	-1.860969
H	5.608093	1.866409	-1.408965
C	4.376078	-1.069665	-2.369019
O	4.189223	-2.203700	-2.775142
O	5.616918	-0.553061	-2.235613
C	6.668354	-1.253864	-2.898379
H	7.395059	-0.475407	-3.164112
C	7.281412	-2.304964	-2.000148
H	6.274300	-1.686891	-3.825144
H	8.138075	-2.781574	-2.497600
H	7.634583	-1.858059	-1.060816
H	6.543227	-3.079810	-1.761660
H	2.044752	-1.897256	-1.807978
H	2.940099	0.211672	-3.219290
O	2.517815	0.494339	-4.475569
C	3.499492	0.472696	-5.305463
O	4.698199	0.359632	-5.013599
C	3.078109	0.596080	-6.762202
H	3.952990	0.665185	-7.418150

H	2.479969	-0.280869	-7.042892
H	2.437484	1.477054	-6.896328

TS(3.7 $\longrightarrow$ 4):

number of imag. freq.	=	1	
charge	=	0	
multiplicity	=	2	
$E_{SMD}^{B_2}$	=	−913.051193843	Eh
$\Delta G_{vrt}^{B_1}$	=	0.1897637	Eh
ΔG_{solv}	=	−912.861430143	Eh
$E_g^{B_1}$	=	−912.802324863	Eh

XYZ coordinates:
32

C	-2.686655	1.922215	0.408419
C	-3.557007	2.899265	0.925578
C	-4.933065	2.760215	0.820427
C	-5.475294	1.642093	0.186307
C	-4.630556	0.667469	-0.347488
C	-3.254437	0.811345	-0.252971
H	-3.127029	3.777263	1.414197
H	-5.588403	3.526528	1.231506
H	-6.555521	1.535352	0.097890
H	-5.050384	-0.202078	-0.851253
H	-2.592358	0.064899	-0.691544
C	-1.255078	2.017809	0.542779
O	-0.323957	3.066373	-0.987093
C	0.741348	2.393317	-1.117091
C	0.841843	1.208507	-0.330052
C	-0.326193	1.004819	0.421091
C	1.776176	2.893396	-2.077082
H	1.985149	2.143730	-2.849450
H	1.415901	3.815223	-2.543204
H	2.726575	3.082268	-1.563981
C	1.899556	0.203503	-0.301690
O	1.852143	-0.813759	0.366573
O	2.947526	0.503966	-1.102134
C	4.030811	-0.438088	-1.115538
H	4.524238	-0.271048	-2.079766
C	4.974680	-0.203563	0.040110
H	3.618619	-1.453959	-1.095938
H	5.832424	-0.884981	-0.028871
H	5.354572	0.825877	0.031231
H	4.470471	-0.385547	0.996199
Ag	-0.496421	3.820862	1.636681
H	-0.496774	0.044079	0.915388

6.2 TS-s for the sutdy of the substituent effects

TS(1.2+2Me $\longrightarrow$ 3.1Me):

number of imag. freq.	=	1	
charge	=	0	
multiplicity	=	2	
$E_{SMD}^{B_2}$	=	−807.109464442	Eh
$\Delta G_{vrt}^{B_1}$	=	0.2217937	Eh
ΔG_{solv}	=	−806.887670742	Eh
$E_g^{B_1}$	=	−806.855949891	Eh

XYZ coordinates:
35

C	0.308077	-0.157278	0.121553
C	0.609100	-0.441240	1.468244
C	-0.198119	0.063732	2.475756
C	-1.307356	0.851060	2.162677
C	-1.608973	1.141633	0.831154
C	-0.809451	0.644041	-0.186123
H	1.501296	-1.021243	1.697276
H	0.045348	-0.144556	3.516238
H	-1.934471	1.247493	2.959954
H	-2.468637	1.764703	0.589587
H	-1.027155	0.869831	-1.229821
C	1.127584	-0.652461	-0.912451
O	2.456808	2.158855	-0.068729
C	2.828070	1.763827	-1.162088
C	3.620443	0.545167	-1.365875
C	1.994261	-0.907127	-1.762094
C	2.451392	2.489969	-2.434042
H	3.345849	2.874533	-2.943972
H	1.946698	1.807662	-3.134302
H	1.785870	3.325386	-2.196292
C	4.250156	-0.210862	-0.278358
O	3.929429	-0.230445	0.889716
O	5.260092	-0.971305	-0.784640
C	5.974981	-1.784582	0.156402
H	6.404921	-2.590522	-0.449177
C	7.046485	-0.988754	0.863918
H	5.260734	-2.214616	0.869530
H	7.628391	-1.643100	1.525691
H	7.734546	-0.533745	0.140473
H	6.601285	-0.194765	1.474573
C	2.556673	-1.670501	-2.883005
H	4.089285	0.427400	-2.344352
H	2.646348	-1.045291	-3.782406
H	3.557934	-2.050857	-2.643007
H	1.908790	-2.522042	-3.125255

TS(1.2+2Ph ⟶ 3.1Ph):

number of imag. freq.	=	1	
charge	=	0	
multiplicity	=	2	
$E_{SMD}^{B_2}$	=	−998.755728747	Eh
$\Delta G_{vrt}^{B_1}$	=	0.2708607	Eh
ΔG_{solv}	=	−998.484868047	Eh
$E_g^{B_1}$	=	−998.447623410	Eh

XYZ coordinates:
42

C	-0.004723	-0.026971	0.066484
C	-0.125075	-0.296749	1.446019
C	-1.309585	-0.007180	2.104021
C	-2.383791	0.550862	1.408268
C	-2.270838	0.826530	0.044260
C	-1.091688	0.542100	-0.627604
H	0.737390	-0.694128	1.979023
H	-1.394641	-0.203579	3.171397
H	-3.310927	0.778245	1.932399
H	-3.108542	1.266826	-0.494363
H	-0.990137	0.750391	-1.692358
C	1.199600	-0.325184	-0.595480
O	1.959007	2.183400	1.333349
C	2.457226	2.173448	0.219406
C	3.515445	1.241054	-0.192235
C	2.357375	-0.400938	-1.046627
C	1.991014	3.117911	-0.863851
H	2.773831	3.857159	-1.086142
H	1.784435	2.574303	-1.797399
H	1.089320	3.642214	-0.532435
C	4.268059	0.412151	0.762655
O	3.835546	-0.124117	1.760102
O	5.541880	0.265373	0.325190
C	6.388794	-0.600079	1.093618
H	7.133619	-0.959847	0.374443
C	7.027081	0.142519	2.243600
H	5.795525	-1.452699	1.448608
H	7.723669	-0.515168	2.779350
H	7.587832	1.013173	1.881217
H	6.265765	0.485372	2.954000
C	3.389036	-1.143643	-1.736789
H	4.059090	1.500414	-1.102550
C	3.943432	-0.677839	-2.934841
C	4.958082	-1.392754	-3.559444
C	5.434324	-2.574140	-2.991803
C	4.884902	-3.042846	-1.800332
C	3.867348	-2.332692	-1.171888

H	3.571246	0.250906	-3.369216
H	5.382682	-1.025619	-4.492608
H	6.233110	-3.129956	-3.480610
H	5.251974	-3.966728	-1.355208
H	3.437695	-2.681498	-0.232948

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