SUPPORTING INFORMATION

Mechanistic Features of the Oxidation-Reductive Coupling of Alcohols Catalyzed by Oxo-Vanadium Complexes

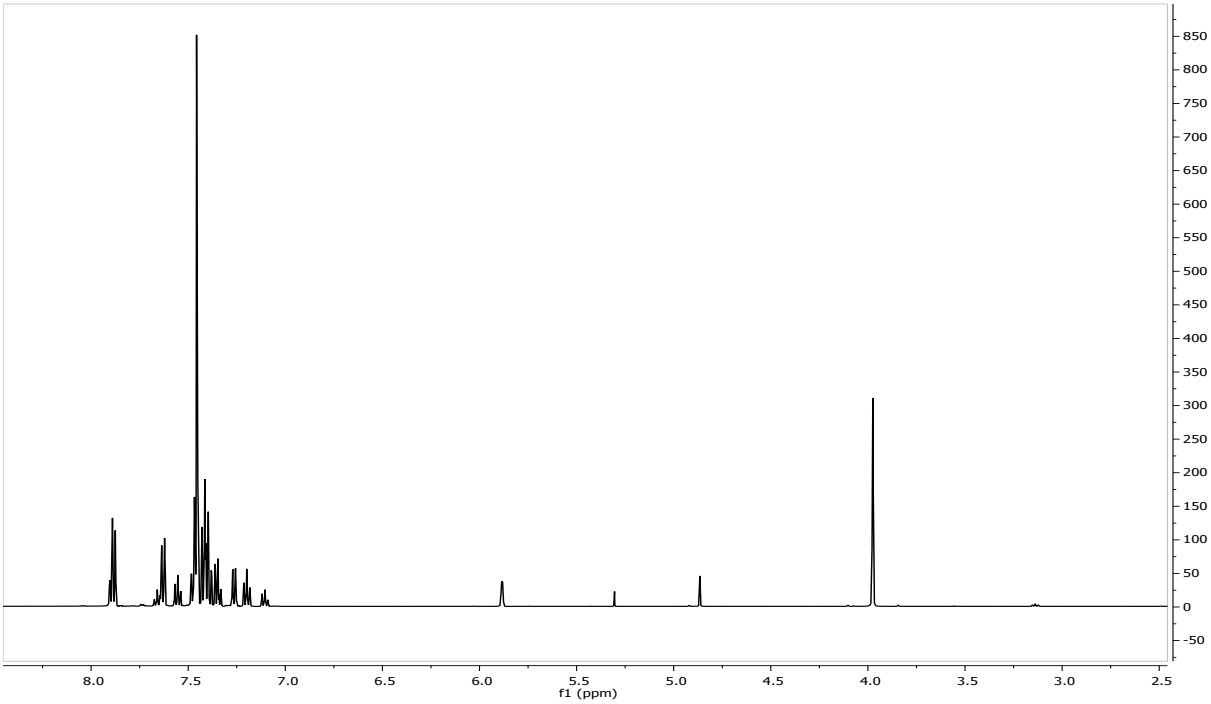
Eric Steffensmeier, Matthew T. Swann and Kenneth M. Nicholas[a]

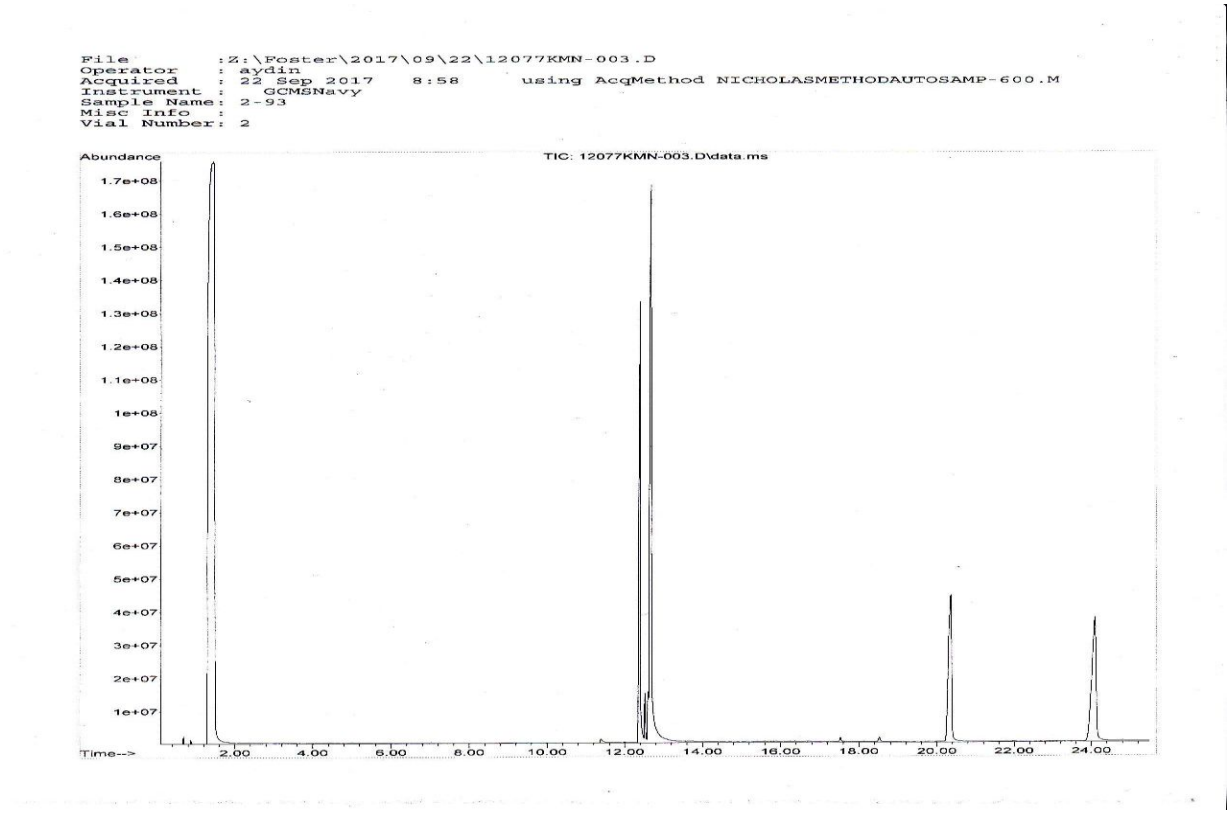
Table of Contents

The supplemental file xyz_coordinates.xyz contains the computed Cartesian coordinates of all of the molecules reported in this study. The file may be opened as a text file to read the coordinates or opened directly by a molecular modeling program such as Mercury (version 3.3 or later, http://www.ccdc.cam.ac.uk/pages/Home.aspx) for visualization and analysis.

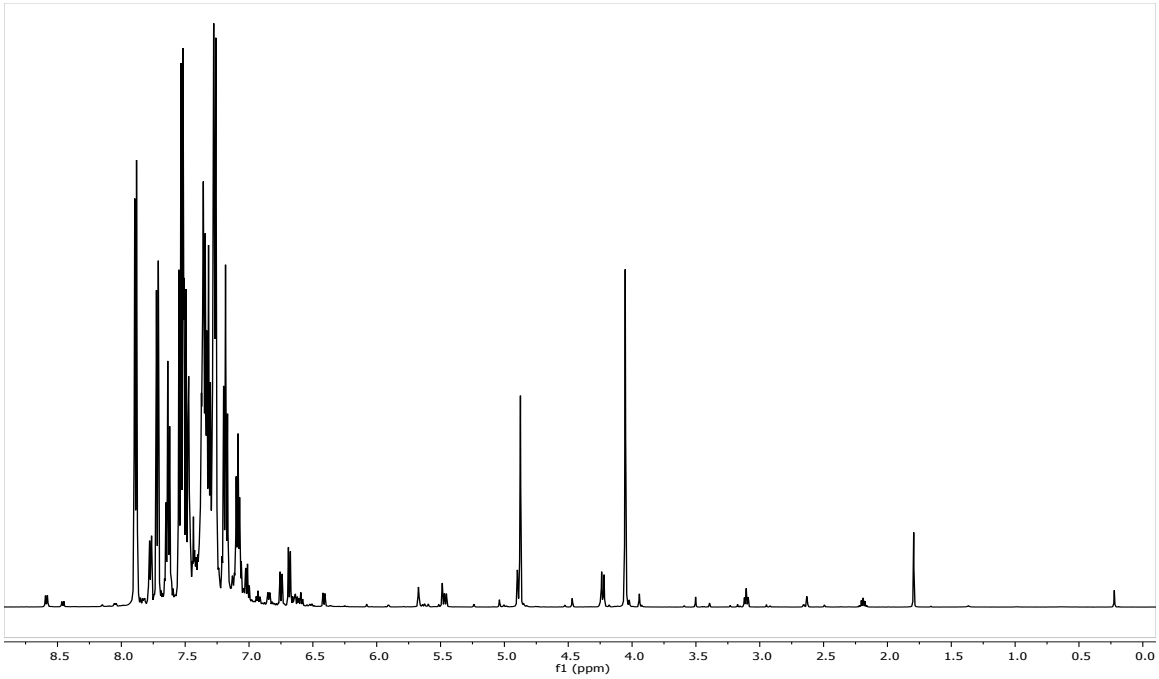
Authentic mixed dimers from Ph_2CHOH/fluorine/base rxn

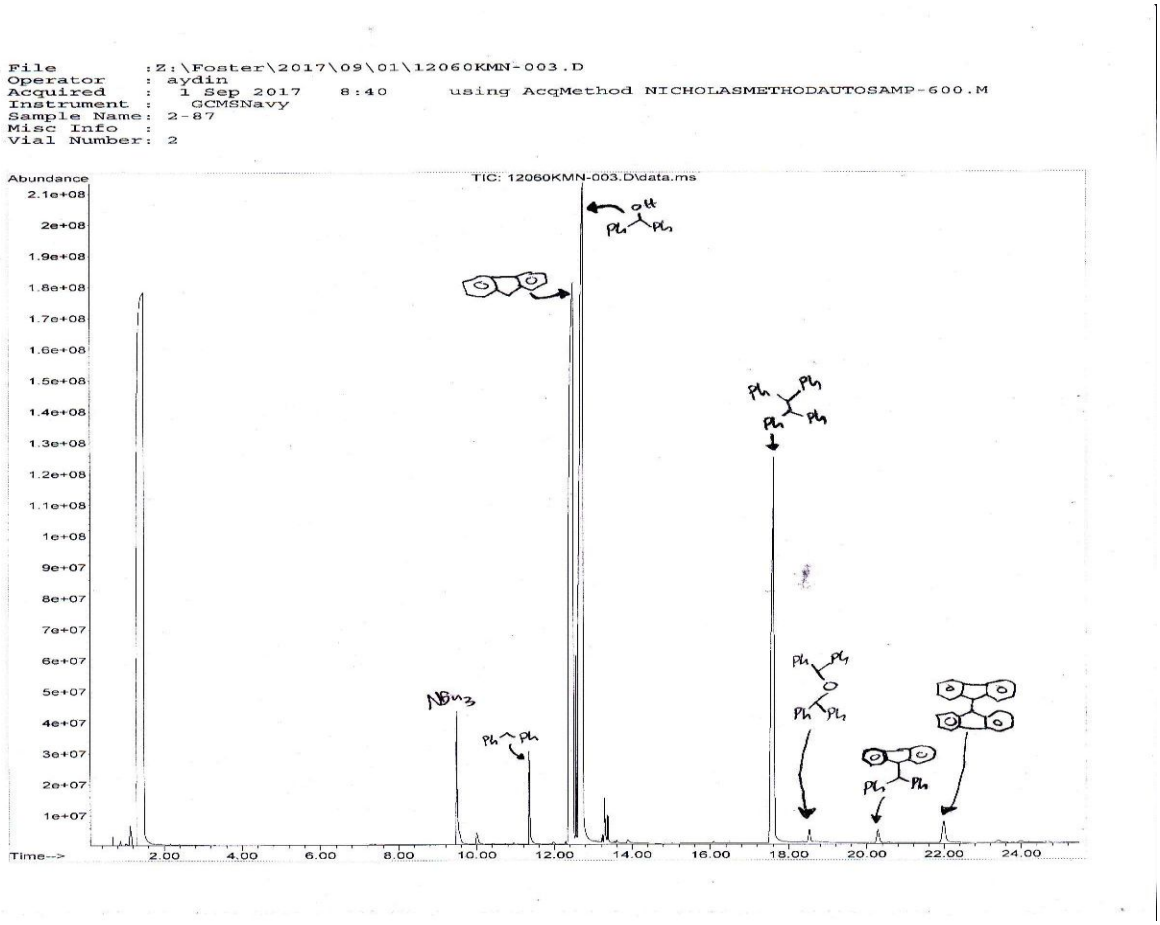
H-NMR/GC-MS



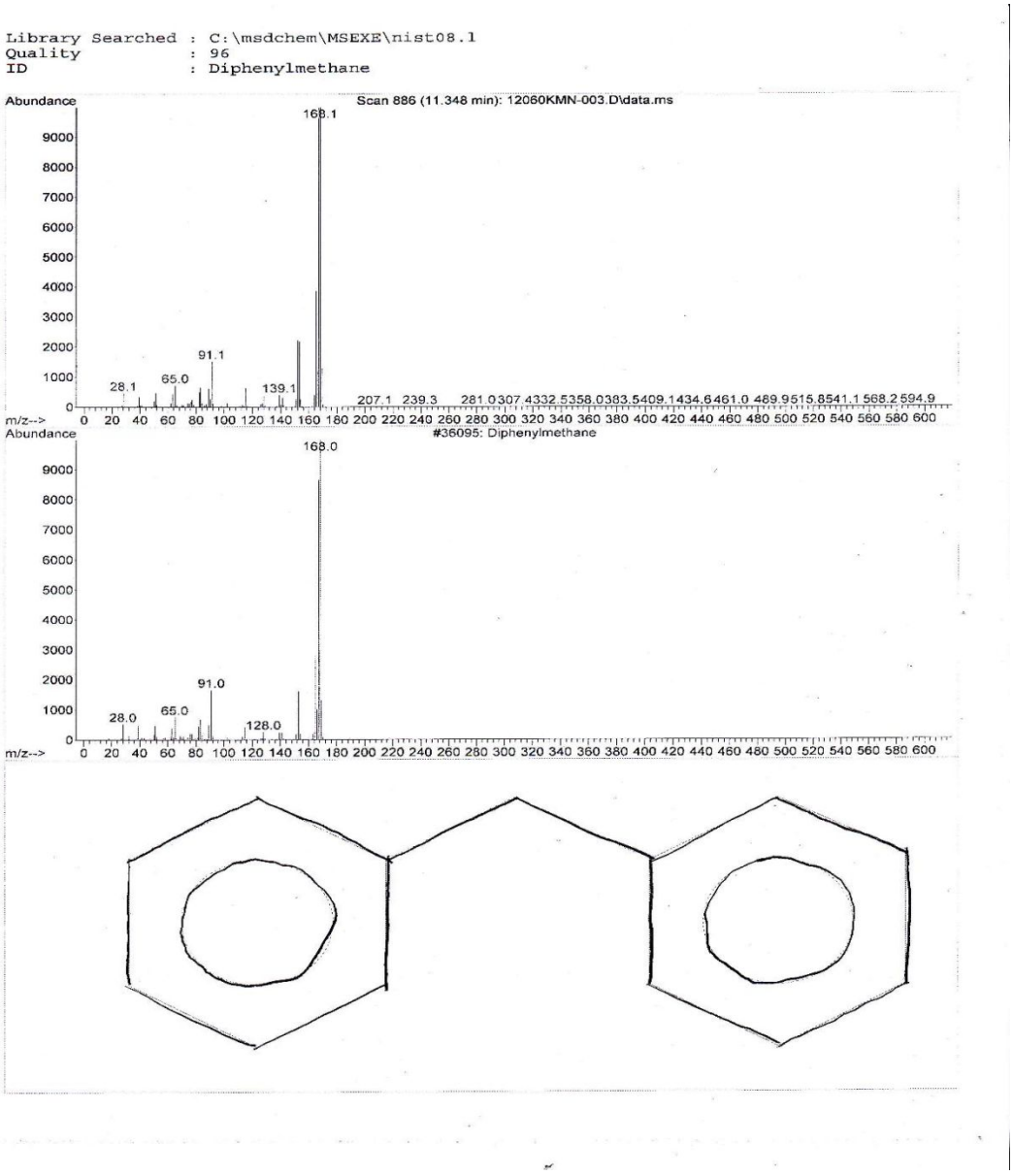


H-NMR and GC/MS for Ph_2CHOH/fluorene/1 reaction mixture

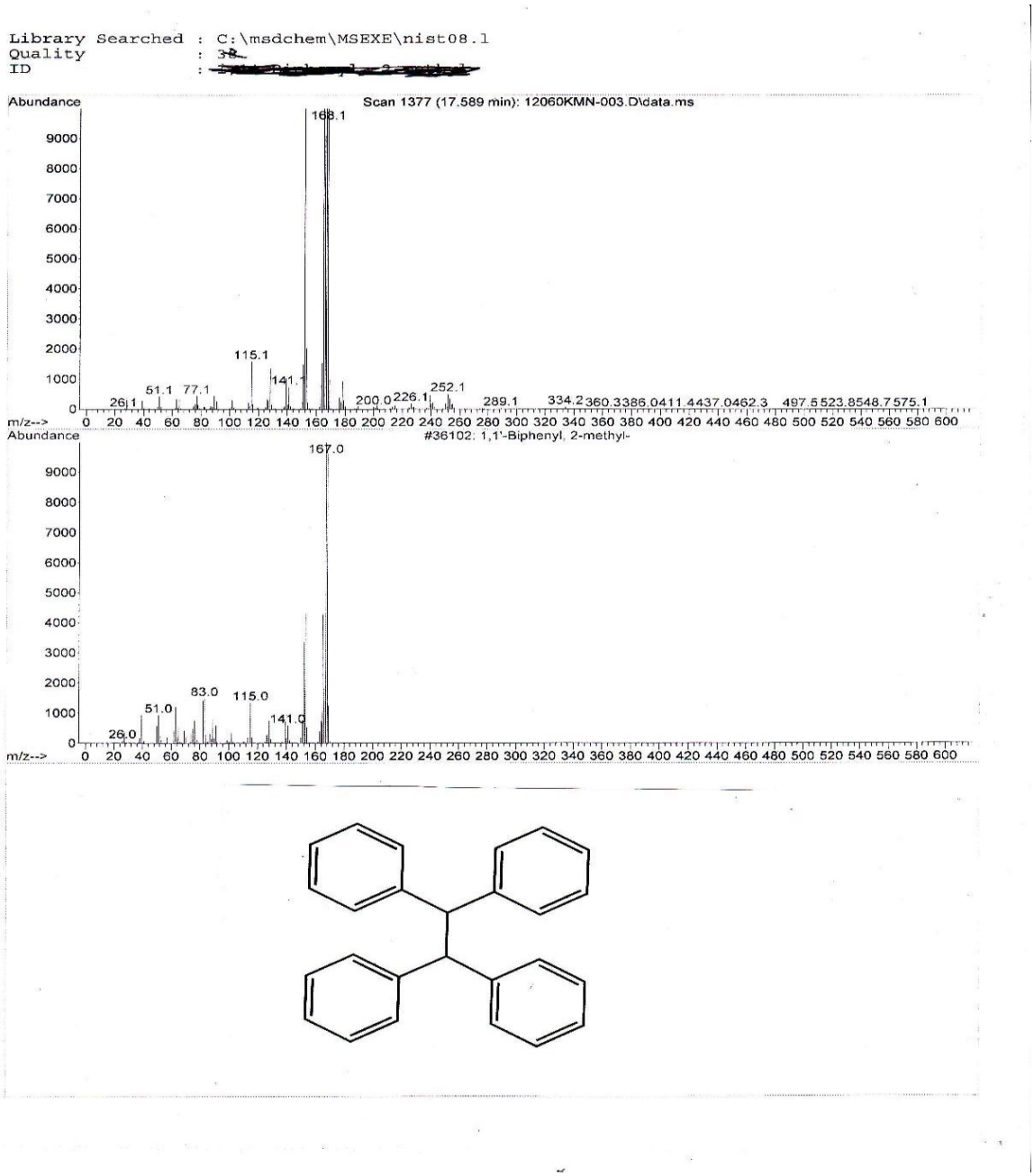




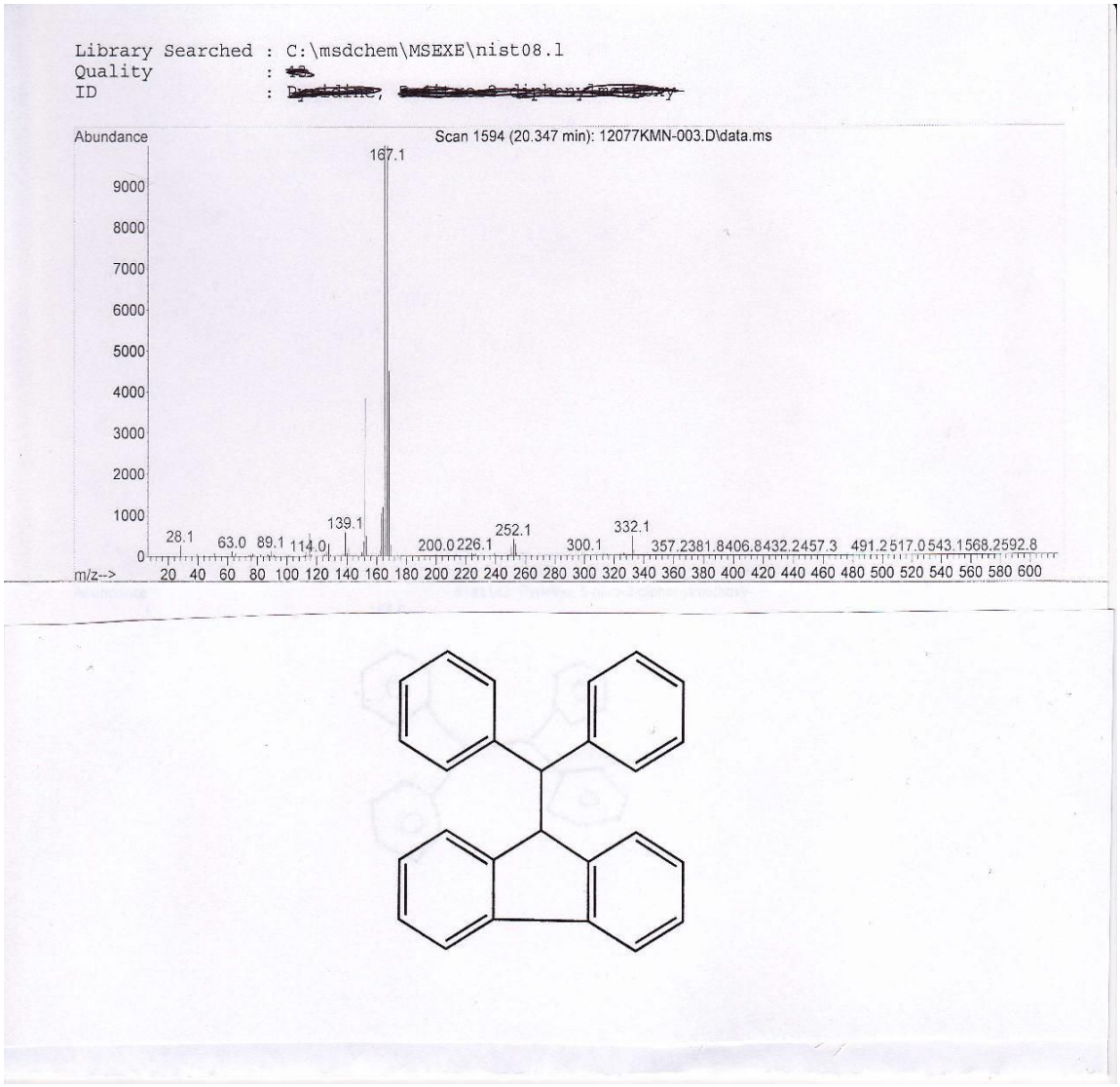
GC-MS component analysis for Ph_2CHOH/fluorene/1 reaction mixture



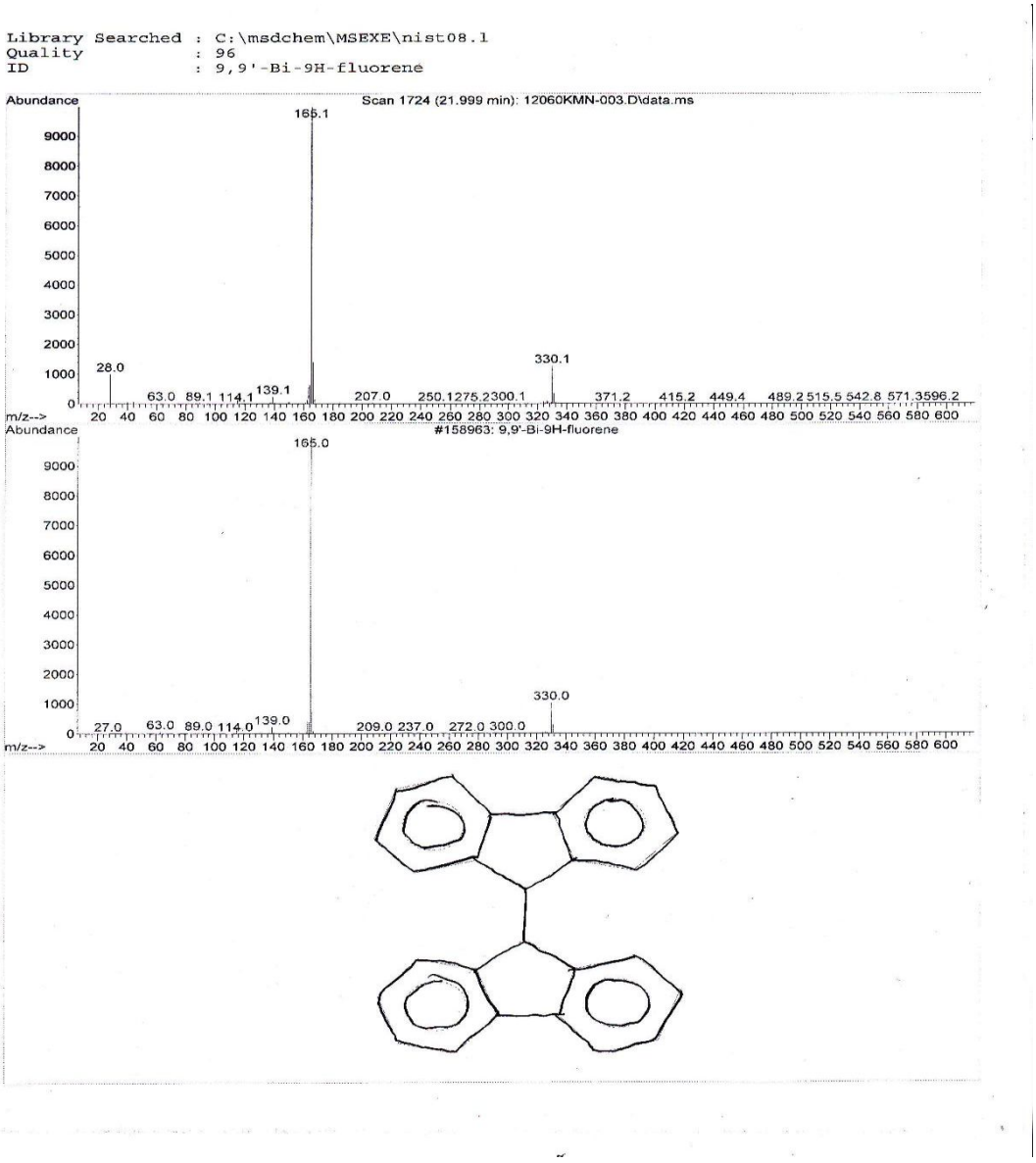
GC-MS component analysis for Ph_2CHOH/fluorene/1 reaction mixture



GC-MS component analysis for Ph_2CHOH/fluorene/1 reaction mixture



GC-MS component analysis for Ph_2CHOH/fluorene/1 reaction mixture



Kinetic data for Z-BnOH/BnOH competition in the reactions catalyzed by

*Bu_4N(Salimin)VO_2 (**1a**); T= 150 C, benzene solvent*

4-Z subst	sigma p-alcohol	sigma p-radical	sigma p-carbocation	benzyl alcohol/ substituted benzyl alcohol	substituted aldehyde/ benzaldehyde
OMe	-0.28	0.24	-0.78	2.24	2.24
Me	-0.14	0.11	-0.31	1.17	1.7
Cl	0.24	0.12	0.11	1.01	0.71
CN	0.7	0.46	0.66	1.91	9.09
H	0	0	0	1	1

*Kinetic data for Ph2CHOH rxn with catalysts **1a, 1b, 1c**: T= 150 C, benzene solvent*

NO2 catalyst 1b

time (hr)	[dimer]	[ketone]	[alcohol]
3.000	--	1.69	21.92
6.000	--	3.25	19.49
9.000	--	5.07	12.99
12.000	0.95	7.1	11.91
12.000	0.00	4.06	10.47
15.000	0.39	4.97	8.38
18.000	1.18	7.07	12.57
21.000	1.440	7.26	10.47

H catalyst 1a

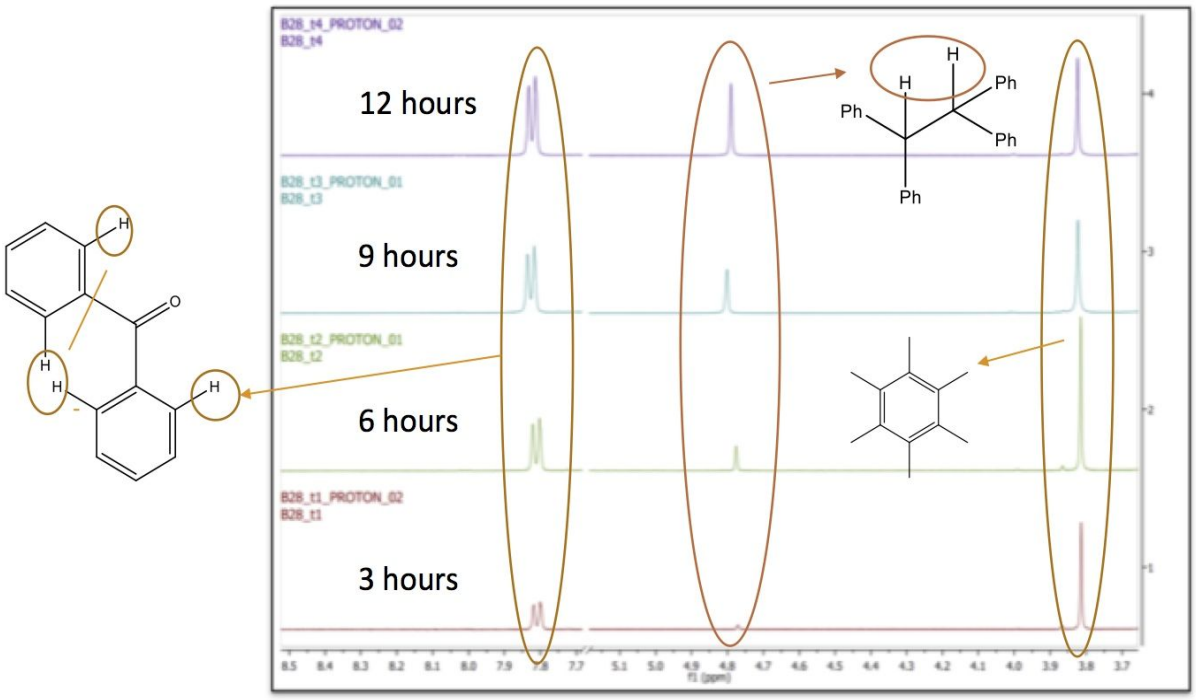
time (hr)	[dimer]	[ketone]	[alcohol]
3.000	--	0.87	19.47
6.000	0.13	1.00	19.20
9.000	0.93	1.60	20.80
12.000	1.60	2.00	21.07
6.000	0.39	1.24	15.46
9.000	0.79	1.64	17.80
12.000	2.09	2.55	19.37
15.000	2.75	3.53	14.90

*Kinetic data for Ph2CHOH rxn with catalysts **1a, 1b, 1c**: T= 150 C, benzene solvent*

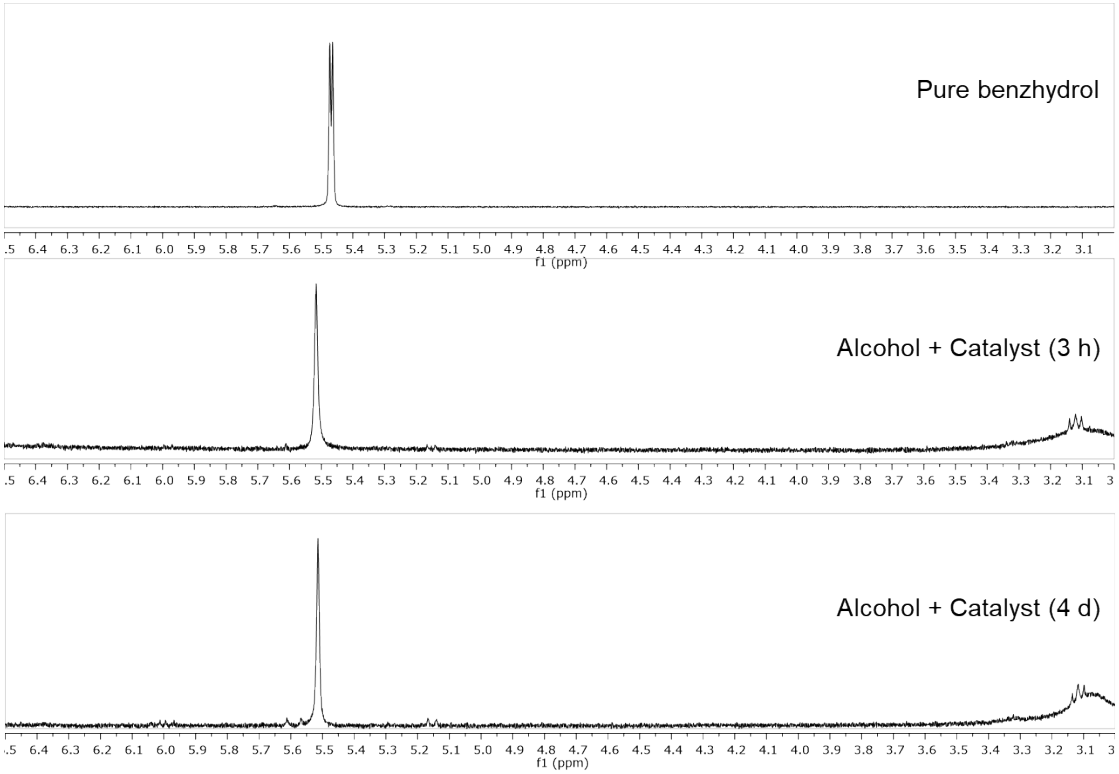
MeO catalyst 1c

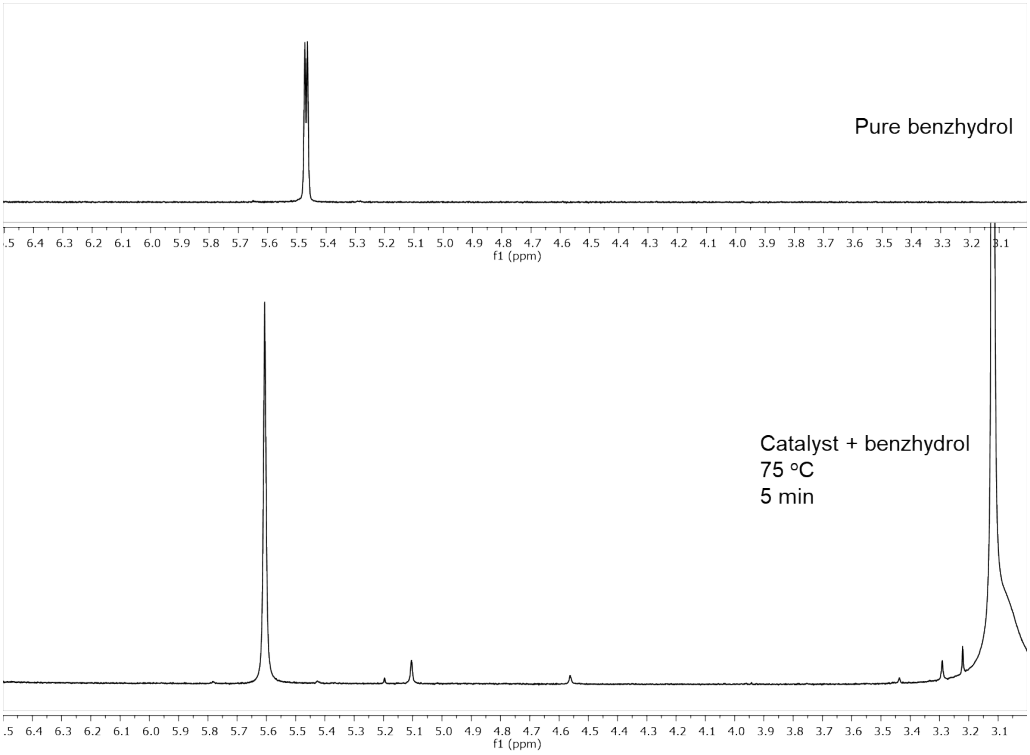
time (hr)	[dimer]	[ketone]	[alcohol]
3.000	--	1.12	23.50
6.000	0.92	1.65	20.59
9.000	1.58	2.24	18.74
12.000	2.38	2.90	17.16
6.000	0.46	1.77	26.05
9.000	1.03	1.71	17.80
12.000	1.49	2.57	22.85
15.000	1.94	2.80	18.51

Sample NMR kinetics plot

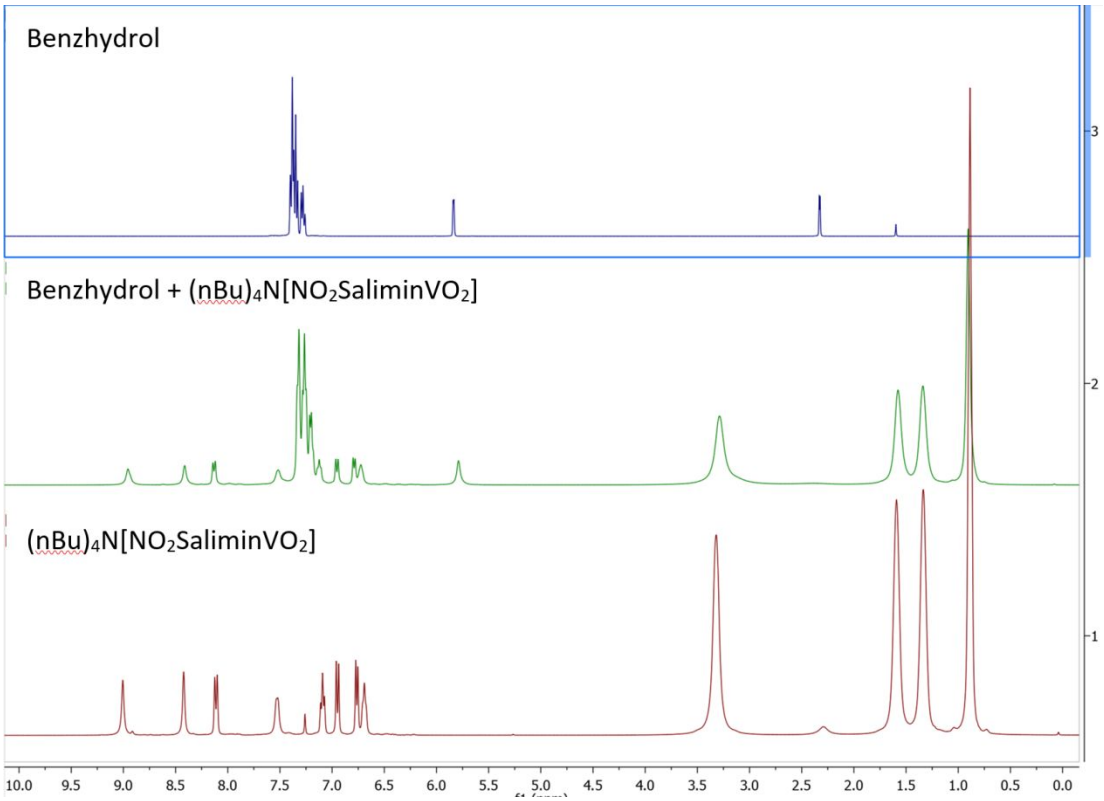


*H-NMR for Ph_2CHOH + complex **1** combination ($CDCl_3$ solvent)*

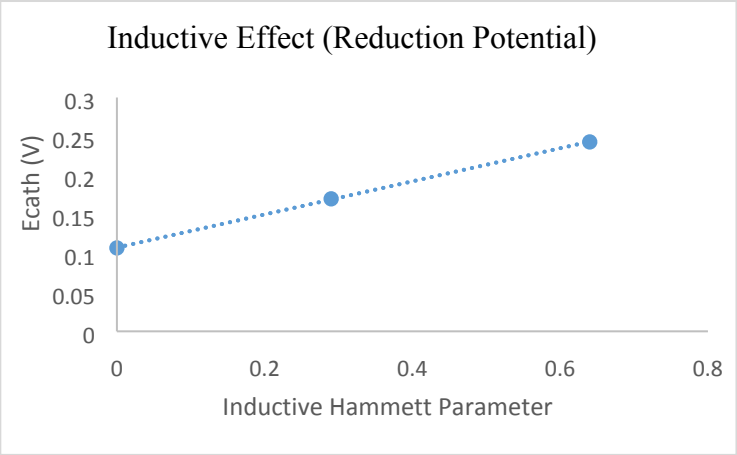




*H-NMR spectra for Ph_2CHOH/**1b** interaction ($CDCl_3$ solvent)*



E-chem correlations:

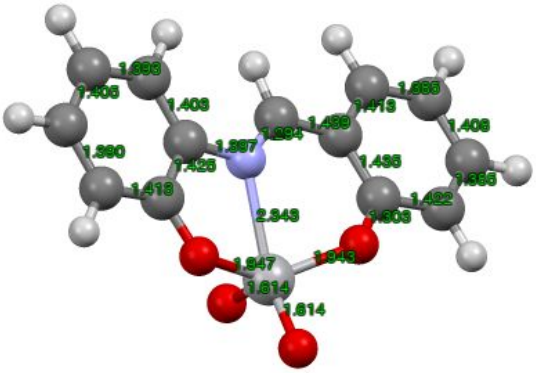


*Relationship between reduction potential of (Z-Salimin)VO_2^- (**1a-c**) and the Hammett inductive sigma parameter*

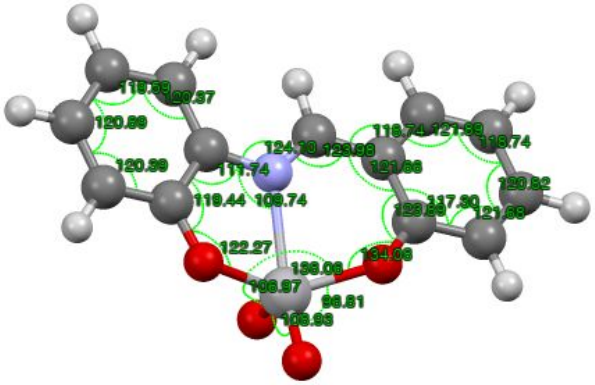
Computational SI

CITATION FOR GAUSSIAN 09

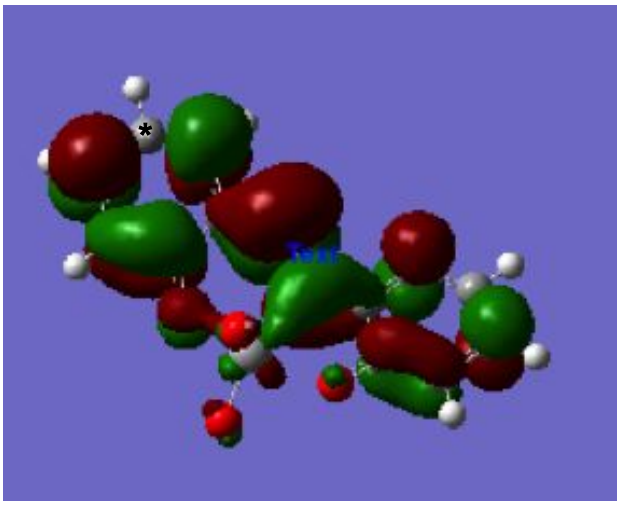
Gaussian 09, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.



B3LYP-Calculated bond lengths for **1a**



B3LYP-Calculated bond angles for **1a**



SOMO of (H-salimin)$VO_2^{(2-)}$; * indicates atom to which Z-groups are attached in **1b,c**.

B3LYP Calculated Energies (in Hartrees) for species in Fig. 8,9

Species	**E**	**Species**	**E**
A	-928.00142	**H**	-1430.02541
Ph_2CHOH	-577.82239	$Ph_2CH\text{-}CHPh_2$	-1004.01806
$TS_{A\text{-}B}$	-1505.78557		
B	-1505.82736		
$TS_{B\text{-}C}$	-1505.81300		
B'	-11505.80317		
$TS_{B'\text{-}D}$	-1505.77538		
C	-929.20813		
D	-929.17955		
H_2O	-76.42257		
E	-852.74443		
F	-1430.60541		
$TS_{F\text{-}G}$	-1430.56415		
G	-928.61471		
$CHPh_2$ rad	-501.97886		