

Supporting Information

Sergiy V. Rosokha,^{*,†} Vasiliy Korotchenko,[‡] Charlotte L. Stern,[§] Vladimir Zaitsev[‡] and

Jeremy T. Ritzert[†]

Substituent-Induced Switch of the Role of Charge-Transfer Complexes

in the Diels-Alder Reactions of o-Chloranil and Styrenes

Department of Biological, Chemical and Physical Sciences, Roosevelt University, Chicago IL 60605

Department of Chemistry, University of Houston, Houston TX 77204

[§] *Department of Chemistry, Northwestern University, Evanston, Illinois 60208*

E-mail: srosokha@roosevelt.edu

Table of Content

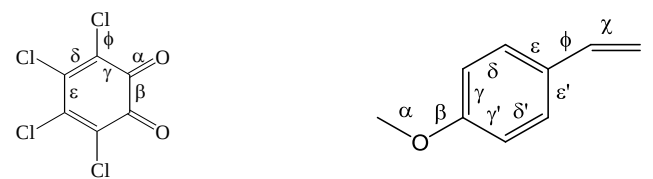
Redox potentials of donors and spectral characteristics of the CT complexes (Table S1).....	S2
Evaluation of charge transfer in the [MeOSty , oCA] complex (Table S2)	S3
Calculated energies of reactants, CT complexes, TS and products (Table S3)	S4
Energies, enthalpies and free energies of the cycloadducts, TS and CT complexes.....	S5
Energy diagram for the oCA/HSty reaction pathway.....	S5
Cartesian coordinates of the calculated structures.....	S7-S27
Temperature dependence of its formation constant (Figure S1)	S28
Spectral changes during the MeOSty/oCA cycloaddition (Figure S2).....	S28
Kinetic curves for cycloaddition reactions (Figure S3).....	S29
Concentration and temperature dependencies of cycloaddition rate (Figure S4).....	S29
ORTEP diagrams of XSty/oCA adducts (Figure S5).....	S30
ORTEP diagrams hydrated cycloadducts (Figure S6).....	S31
NMR spectra of cycloadducts (Figure S7).....	S32-S35
Molecular orbital shapes (Figure S8)).....	S36
Calculated structures of HSty/oCA associates (Figure S9)	S37
Electrostatic potential distributions (Figure S10).....	S37

Table S1. Oxidation potentials of various organic donors and energy of the charge-transfer transitions for their intermolecular complexes with the *o*-chloranil acceptors in dichloromethane, at 22°C, unless noted otherwise. which were used in the Mulliken correlation in Figure 2.^a

N	Donor	E^0_{ox} , V	ν_{CT} , eV
1	<i>p</i> -Methoxystyrene	0.89	2.08
2	<i>p</i> -Methylstyrene	1.23	2.35
3	<i>p</i> -Chlorostyrene	1.34	2.48
4	Styrene	1.39	2.53
	Benzene	2.62	3.31
	Toluene	2.25	3.06
	<i>o</i> -Xylene	2.16	2.98
	Mesitylene	2.11	2.70
	Durene	1.84	2.39
	Pentamethylbenzene	1.71	2.34
	Hexamethylbenzene	1.62	2.22
	Naphthalene	1.54	2.39
	2,6-Dimethylnaphthalene	1.36	2.10
	Pyrene	1.16	1.85
	2,5-dimethyl- <i>p</i> -dimethoxybenzene	1.15	1.78
	Anthracene	1.09	1.77
	9-Methylanthracene	0.96	1.64
	9,10-Dimethylanthracene	0.94	1.50
	Perylene	0.85	1.48
	Octamethylbiphenylene	0.80	1.41
	10-Methylphenothiazine	0.79 ^c	1.55
	Phenothiazine	0.61 ^c	1.39
	Tetrathiafulvalene	0.37	1.13

a) Note: (i) oxidation potentials for styrene donors and energy of their charge-transfer band in the complexes with *o*-chloranil acceptor (entries 1-4) were measured in the current work. Spectral and electrochemical data for the other entries are taken from: Rosokha, S.V.; Dibrov, S.M.; Rosokha, T.Y.; Kochi, J.K. *Photochem. Photobiol. Sci.* **2006**, 5, 914-924 and references therein. (ii) For clarity, numbers are assigned only to the data corresponding to styrene donors in Figure 2.

Table S2. Average bond lengths^a within *o*CA and MeOSty moieties in the [MeOSty, CA] complex in comparison with those in the corresponding neutral molecules and ion-radicals.



Structure	α	β	γ	δ	ϵ	ϕ	χ
<i>o</i> -Chloranil moieties							
CA ^a	1.209	1.549	1.474	1.350	1.476	1.705	
CA ^{•+a}	1.234	1.517	1.453	1.381	1.425	1.758	
<i>o</i> CA/MeOSty	1.206	1.533	1.470	1.360	1.470(5)	1.701	
MeOSty moieties							
MeOSty	1.414	1.377	1.393	1.384	1.376	1.479	1.303
MeOSty ^{•+c}	1.451	1.311	1.386	1.362	1.390		
			1.430,	1.369	1.431	1.429	1.364
			1.423	1.362	1.432		
<i>o</i> CA/MeOSty	1.409	1.389	1.410	1.366	1.406	1.461	1.316
			1.382	1.375	1.407		

a) Rosokha, S.V.; Dibrov, S.M.; Rosokha, T.Y.; Kochi, J.K. *Photochem. Photobiol. Sci.* **2006**, 5, 914-924 and references therein. (c) DFT B3LYP/6-311+G(dp) calculations. c) Byrn, M. P.; Curtis, C. J.; Hsiou, Y.; Khan, S.I.; Sawin, P. A.; Tendick, S.K.; Terzis, A.; Strouse, C.E. *J. Am. Chem. Soc.* **1993**, 115, 9480-9497.

Structural evaluation of the charge transfer in the [MeOSty, *o*CA] complex.

Bondlength measurements in conjunction with the classic Pauling bondlength/bondorder relationship,¹ have often been used for the evaluation of degree of charge transfer.² Accordingly, we first estimated the charge (*q*) on the basis of eq 1:

$$q = 1/n \sum q^i = 1/n \sum (l_{CT}^i - l_0^i)/(l_1 - l_0) \quad (1)$$

where l_{CT}^i , l_0^i and l_1^i were the i^{th} bondlengths in the acceptor moiety within the CT complex, neutral molecule and cation radical, respectively, from Table S2 (so that the value $q^i = (l_{CT}^i - l_0^i)/(l_1 - l_0)$ provided the estimate based on a particular bond), and *n* was the number of equivalent bonds. Thus, the overall charge on the *o*CA moiety in the charge-transfer complex was evaluated as $q = 0.1 \pm 0.2$ (where standard deviation was calculated based on the variation of values calculated from different bonds). In the similar manner, we evaluated charge transfer based on the structure of the MeOSty moiety as: $q = 0.3 \pm 0.4$. Taking into account significant variation of the degree of charge-transfer, such values can be considered as a semi-qualitative evaluation of charge-transfer.

- Pauling, L. *Nature of the Chemical Bond*; Cornell: Ithaca, NY, 1960.
- (a) S.V. Lindeman, S. V. Rosokha, D. Sun, J.K. Kochi, X-ray Structure Analysis and the Intervalent Electron Transfer in Organic Mixed-Valence Crystals with Bridged Aromatic Cation Radicals. *J. Am. Chem. Soc.* 2002, **124**, 843 - 855. (b) J. M. Lu, S.V. Rosokha, S.V. Lindeman, I.S. Neretin, J.K. Kochi, "Separated" versus "Contact" Ion-Pair Structures in Solution from Their Crystalline States: Dynamic Effects on Dinitrobenzenide as a Mixed-Valence Anion. *J. Am. Chem. Soc.* 2005, **127**, 1797 - 1809. (c) D.A. Clemente, A. Marzotto, Structure of two polymorphs of the TTF-TCNE charge-transfer complex and the degree of ionicity, *J. Mater. Chem.* 1996, **6**, 941 - 946. (d) W.F. Cooper, J.W. Edmonds, F. Wudl, P. Coppens, The 2-2'-bi-1,3-dithiole. *Cryst. Struct. Commun.* 1974, **3**, 23 - 26. (e) T.C. Umland, S. Allie, T. Kuhlmann, P. Coppens, Relation between Geometry and Charge Transfer in Low-Dimensional Organic Salts, *J. Phys. Chem.*, 1988, **92**, 6456 - 6460.

Table S3. Energies of the styrenes, their CT complexes, transition states and products of the Diels-Alder reaction with o-chloranil^a obtained from the DFT B3LYP/6-311+G(d,p) computations (including ZPE corrections) and, in italic, from the single-point MP2/6-311+G(d,p) calculations of the optimized structures (including BSSE corrections). For clarity, each structure is designated by a letter (in parenthesis), and their Cartesian coordinates are presented below.

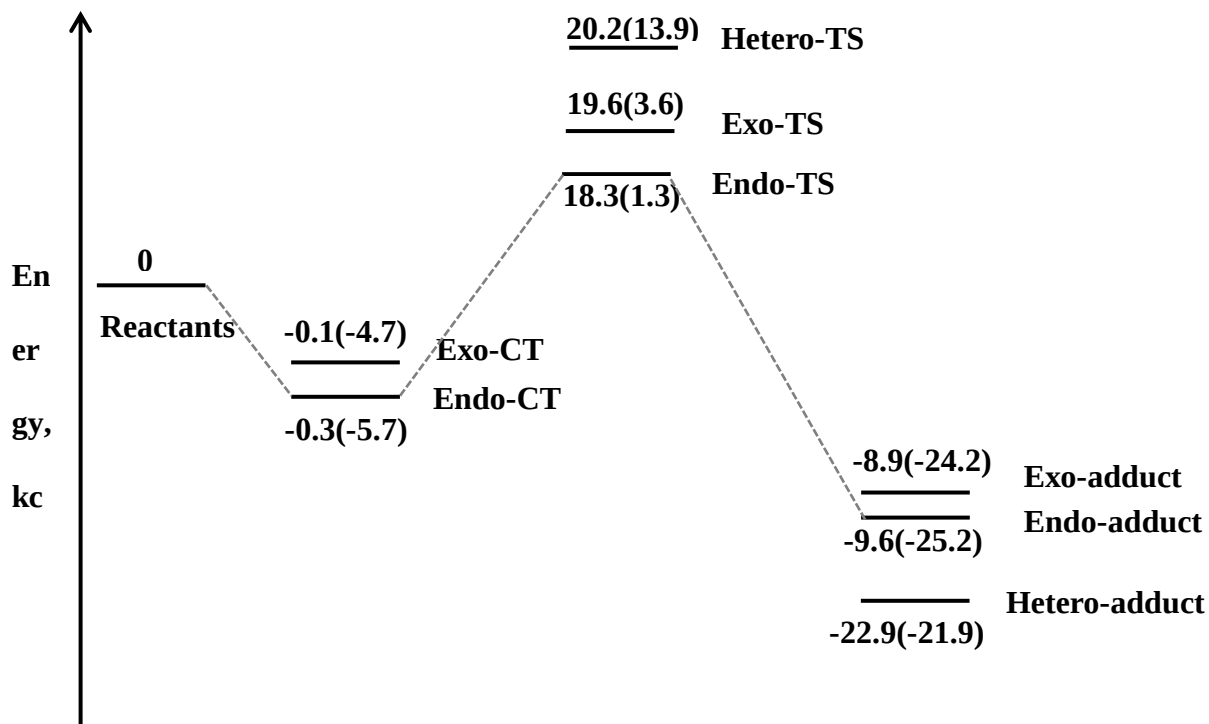
Isomer ^b	Energy (Hartree)			
	HSty	MeSty	ClSty	MeOSty
XSty/oCA Cycloadducts				
Endo	-2529.583599(A) -2525.538549 ^c	-2568.884633(C) -2564.73922	-2989.215293(E) -2984.597996	-2644.108458(G) -2639.797879
Exo	-2529.583161(B) -2525.537488	-2568.884089(D) -2564.738126	-2989.214575(F) -2984.59681	-2644.107913(H) -2639.796919
Hetero	-2529.604621(I) -2525.536645			
Hetero	-2529.609053(J) -2525.538742			
Transition states for the DA reaction				
Endo	-2529.537425(K) -2525.490101		-2989.169347 (X) -2984.550531	-2644.065156(M) -2639.748502
Exo	-2529.535904(L) -2525.486994		-2989.167952 (Y) -2984.547640	-2644.064087(N) -2639.745606
Hetero	-2529.53828(O) -2525.474042			
Charge-transfer complexes				
Endo	-2529.570176(P) -2525.503288			
Exo	-2529.570116(R) -2525.501657			
XSty Reactants				
	-309.597979(S) -308.7618048	-348.898593(T) -347.962071	-769.230433(U) -767.8220272	-424.122501(V) -423.0209883

a) For o-chloranil, energies are -2219.968811 (B3LYP/6-311+G(d,p)) and -2216.7288659 (MP2/6-311+G(d,p)) . b) Note that “endo” denotes the structures of the complexes, transition states and products of the normal Diels-Alder reaction in which p-substituent in the styrene fragment is directed toward chlorine-substituted side of o-chloranil fragment, “exo” denotes the structures in which p-substituent in the styrene fragment is directed toward oxygen-substituted side of o-chloranil, and “hetero” designates products and TS of the hetero-DA reaction.

Table S4. Energies, enthalpies and free energies of the cycloadducts, transition states and CT complexes^a

Adduct	Structure	ΔE (B3LYP) ^b	ΔE (MP2)	ΔH (MP2)	ΔG (MP2) ^b	Charge-transfer ^b
Cycloadducts						
Endo-oCA/HSty	A	-9.6	-25.2	-26.1	-13.5	0.165
Exo-oCA/HSty	B	-8.9	-24.2	-25.0	-12.6	0.165
Endo-oCA/MeSty	C	-9.7	-25.4	-26.2	-13.4	0.168
Exo-oCA/MeSty	D	-8.6	-23.9	-24.8	-12.1	0.169
Endo-oCA/ClSty	E	-9.5	-25.0	-25.8	-13.4	0.159
Exo-oCA/ClSty	F	-8.6	-23.8	-24.6	-12.1	0.158
Endo-oCA/MeOSty	G	-9.6	-25.2	-26.0	-13.7	0.173
Exo-oCA/MeOSty	H	-8.7	-24.1	-24.9	-12.6	0.171
Hetero-oCA/HSty	I	-20.3	-20.6	-21.7	-9.5	0.696
Hetero-oCA/HSty	J	-22.9	-21.9	-22.9	-10.6	0.695
Transition states						
Endo-oCA/HSty	K	18.3	1.3	0.9	12.7	0.353
Exo-oCA/HSty	L	19.6	3.6	3.1	14.7	0.350
Endo-oCA/MeOSty	M	15.8	1.4	1.0	12.8	0.436
Exo-oCA/MeOSty	N	17.2	3.9	3.5	14.8	0.435
Hetero-oCA/HSty	O	20.2	13.9	13.4	24.5	0.566
Endo-oCA/ClSty	X	18.8	1.3	0.9	12.7	0.339
Exo-oCA/ClSty	Y	20.0	3.4	3.0	14.5	0.337
CT complexes						
Endo-oCA/HSty	P	-0.3	-5.7	-4.8	-	0.039
Exo-oCA/HSty	R	-0.1	-4.7	-3.7	-	0.012

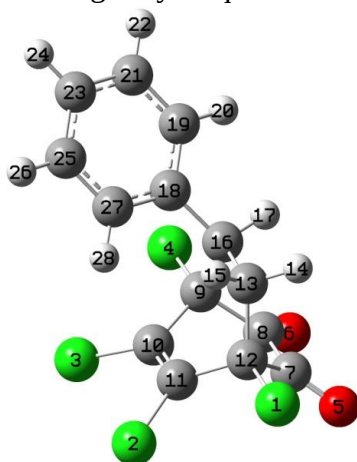
a) In kcal/mol, relative to the reactants state. Energies include ZPE, solvation and BSSE (MP2) corrections. b) At 235 K. b) Charge transfer from XSty to oCA fragments calculated via NBO analysis.



Scheme S1. Energy diagram illustrating possible reaction path for the **oCA/HSty** cycloaddition. The values (including ZPE and solvation) are obtained via B3LYP/6-311+G(dp) computations, and via MP2/6-311+(dp) computations (in parenthesis, including BSSE corrections).

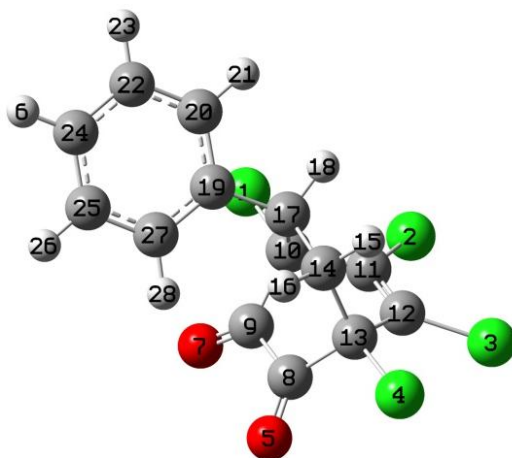
Cartesian coordinates (in Å) for the structures A-V

Structure A. Number of imaginary frequencies: 0.



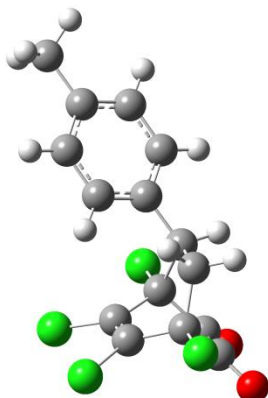
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C	-1.10034000	1.92991400	-0.46583300
C	0.12654800	1.16755100	0.09232600
C	-0.47995700	0.22473100	1.13739000
C	-1.41295700	-0.62392000	0.66740500
C	-1.69196900	-0.51356200	-0.83744500
C	-0.35008800	-0.67566200	-1.60066700
H	-0.54020300	-0.54322900	-2.66721100
H	-0.01224500	-1.70041800	-1.45335500
C	0.72473400	0.33646500	-1.11030400
H	0.89166400	1.07546200	-1.89796300
C	2.06737600	-0.30837800	-0.80987100
C	3.22268100	0.21980200	-1.39382900
H	3.14551800	1.08467000	-2.04410700
C	4.47221200	-0.34554400	-1.14830900
H	5.35468500	0.07780400	-1.61427800
C	4.58522900	-1.44904800	-0.30659400
H	5.55568800	-1.89129200	-0.11291000
C	3.44084100	-1.98451500	0.28205300
H	3.51810600	-2.84445400	0.93759700
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Structure **B**. Number of imaginary frequencies: 0.



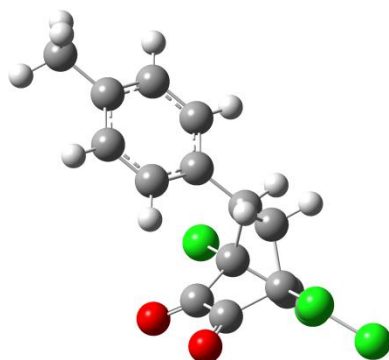
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C	-0.04195000	0.04731000	1.57651000
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C	-2.07684300	0.09280800	-0.36915700
C	-1.33950100	-1.24082600	-0.20419000
C	-0.06134700	-1.22567200	-1.07991200
H	-0.36678500	-1.29633400	-2.12393500
H	0.51856500	-2.11921100	-0.84743200
C	0.78581100	0.06091200	-0.85085100
H	0.68713600	0.69834800	-1.73085000
C	2.26585400	-0.22271600	-0.65464100
C	3.19760000	0.42934100	-1.46768400
H	2.85207300	1.13201400	-2.21850600
C	4.56327100	0.19271700	-1.32479300
H	5.26825100	0.70726400	-1.96774400
C	5.01919100	-0.69911500	-0.35753800
C	4.10067600	-1.35609000	0.45939600
H	4.44443900	-2.05211500	1.21582400
C	2.73619600	-1.12411500	0.30781800
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Structure C. Number of imaginary frequencies: 0.



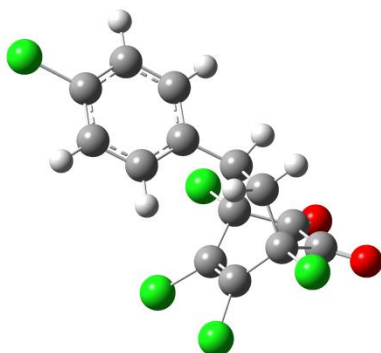
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C	-1.60880700	1.84418200	-0.44620600
C	-0.29433800	1.23400900	0.09767100
C	-0.77290100	0.21402400	1.13726600
C	-1.59739200	-0.73885600	0.66460200
C	-1.89884400	-0.65006700	-0.83736700
C	-0.55276200	-0.63915900	-1.61014700
H	-0.76526600	-0.52014700	-2.67407200
H	-0.09105300	-1.61637900	-1.47616800
C	0.39451000	0.49150600	-1.11578400
H	0.46551200	1.25220600	-1.89732300
C	1.80569800	0.01264800	-0.82421100
C	2.89098000	0.68410000	-1.39235500
H	2.71453100	1.54102300	-2.03403700
C	4.19888200	0.27368000	-1.14705400
H	5.01986700	0.81281000	-1.60844200
C	4.46937000	-0.81880600	-0.31891400
C	3.38056900	-1.49314800	0.24453600
H	3.55661100	-2.35154500	0.88481800
C	2.07241500	-1.08995500	-0.00432200
H	1.26149000	-1.64938300	0.44781400
C	5.88623300	-1.24462100	-0.02283700
H	6.56508700	-0.96062100	-0.82981800
H	6.25093800	-0.77136400	0.89532600
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Structure **D**. Number of imaginary frequencies: 0.



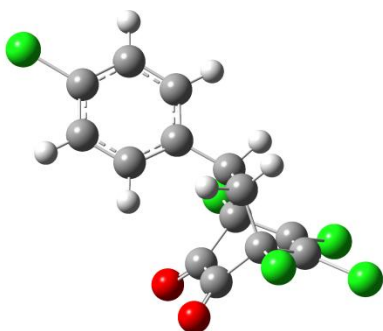
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O	0.06365400	0.33571000	2.67084600
C	-1.13862100	-1.24067100	1.27757400
C	-0.35111000	0.07650900	1.58147300
C	-0.22257600	0.93967800	0.31001300
C	-1.68944500	1.13870600	-0.11458000
C	-2.37159100	0.01000100	-0.38021000
C	-1.56748300	-1.28285200	-0.20341500
C	-0.28318600	-1.20472800	-1.06701100
H	-0.57395600	-1.29872100	-2.11339600
H	0.34096200	-2.06462700	-0.82247200
C	0.49265700	0.12596200	-0.83927500
H	0.36479500	0.75350500	-1.72273100
C	1.98352600	-0.07658400	-0.63380200
C	2.88784700	0.61916600	-1.43815300
H	2.51583300	1.30266000	-2.19429200
C	4.26291200	0.45732000	-1.28121800
H	4.93973300	1.01328300	-1.92170400
C	4.78206200	-0.40245900	-0.31118000
C	3.87382100	-1.09781800	0.49611900
H	4.24448700	-1.76990900	1.26332900
C	2.50149100	-0.94420100	0.33551400
H	1.84337900	-1.51170000	0.98513200
C	6.26937100	-0.59504600	-0.14545800
H	6.58769500	-1.56072700	-0.55220300
H	6.83161500	0.18408600	-0.66382900
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Structure E. Number of imaginary frequencies: 0.



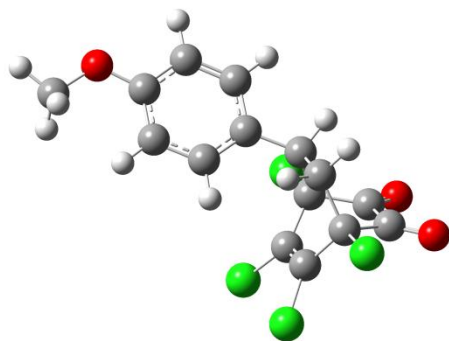
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C	-0.62297400	1.25424100	0.09730600
C	-1.04874000	0.21216500	1.13831600
C	-1.81555600	-0.78740700	0.66451000
C	-2.11324400	-0.72068100	-0.83950200
C	-0.76535300	-0.63742300	-1.60484600
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H	-0.24933100	-1.58588500	-1.46156800
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H	0.13730200	1.31101900	-1.89611200
C	1.54739100	0.15805900	-0.81728100
C	2.58997900	0.88323000	-1.40066200
H	2.36413700	1.72014200	-2.05237100
C	3.92253100	0.55901800	-1.15953000
H	4.72071900	1.12687300	-1.61988000
C	4.21685800	-0.50560300	-0.31576200
C	3.20068200	-1.24677700	0.27941300
H	3.44290700	-2.07497500	0.93282200
C	1.87449300	-0.91351600	0.02180100
H	1.09660600	-1.50551900	0.48889100
Cl	5.89221900	-0.92697600	-0.00249000

Structure F. Number of imaginary frequencies: 0.



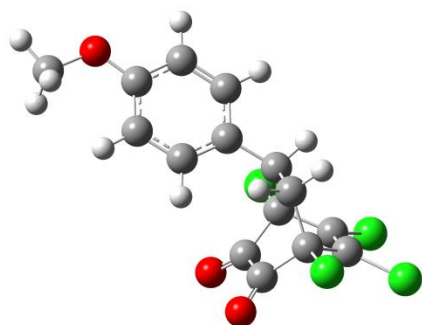
Cl	0.31863900	2.48524300	0.66625200
Cl	-2.70951900	2.67902800	-0.22454900
Cl	-4.29326700	-0.07690200	-0.87153000
Cl	-2.68170000	-2.81406400	-0.58233500
O	-1.58411200	-2.08854700	2.10742400
O	-0.22126200	0.34409000	2.67642600
C	-1.39904500	-1.24805900	1.27971100
C	-0.63358800	0.08101100	1.58714600
C	-0.51565500	0.94861400	0.31720000
C	-1.98318800	1.12094800	-0.11602900
C	-2.64229900	-0.02018500	-0.38740400
C	-1.81639700	-1.29845500	-0.20449600
C	-0.52596800	-1.19856200	-1.05753200
H	-0.80453000	-1.30362300	-2.10612000
H	0.11254900	-2.04519800	-0.80344100
C	0.21892600	0.14933500	-0.82940400
H	0.07952100	0.77244800	-1.71406400
C	1.71409400	-0.01764000	-0.62010200
C	2.60092500	0.69875000	-1.42836600
H	2.21323600	1.36907000	-2.18767000
C	3.97978700	0.57655000	-1.27877800
H	4.65571900	1.13526100	-1.91321500
C	4.48034000	-0.27286300	-0.29906200
C	3.62328400	-0.99899100	0.52216800
H	4.02454000	-1.65655100	1.28240200
C	2.24832100	-0.87044900	0.35266900
H	1.60339200	-1.45206800	1.00203900
Cl	6.21651400	-0.43587400	-0.09707500

Structure **G**. Number of imaginary frequencies: 0.



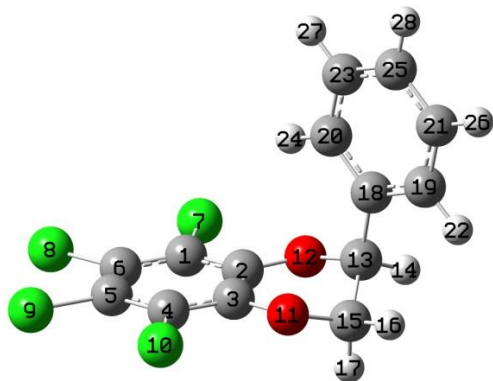
Cl	-3.04409800	-2.02557900	-1.59475400
Cl	-2.29088900	-2.26213100	1.49183900
Cl	-0.51949600	0.11722000	2.80348500
Cl	0.26551500	2.57769800	0.94829600
O	-3.99537800	0.80343300	-1.33040200
O	-2.45058400	2.89897000	-0.18519600
C	-2.90001200	0.62733800	-0.88823000
C	-2.05149800	1.77568600	-0.25637600
C	-0.66885100	1.25482500	0.20249300
C	-1.01260400	0.10278600	1.15266700
C	-1.75199100	-0.88246400	0.61096800
C	-2.10504400	-0.68979300	-0.86985400
C	-0.78900000	-0.47557300	-1.66485100
H	-1.04221400	-0.28513600	-2.70931500
H	-0.23005300	-1.40942500	-1.62887600
C	0.05672600	0.69640600	-1.08762600
H	0.02779700	1.52720900	-1.79721300
C	1.51599900	0.34073400	-0.87254100
C	2.51439400	1.17763100	-1.39000500
H	2.23296000	2.07094500	-1.93744600
C	3.85940800	0.89336500	-1.21562200
H	4.62680100	1.54162300	-1.62074900
C	4.24882800	-0.24702900	-0.50363900
C	3.26940300	-1.09585700	0.01926200
H	3.53801700	-1.98658000	0.57050100
C	1.92038400	-0.79724700	-0.17246900
H	1.18609400	-1.47936800	0.24068200
C	6.05169600	-1.57793500	0.34394000
H	7.13846400	-1.52293800	0.31849000
H	5.71109100	-1.55112900	1.38433200
H	5.72486800	-2.51178500	-0.12567100
O	5.58991200	-0.44405300	-0.38117000

Structure **H**. Number of imaginary frequencies: 0.



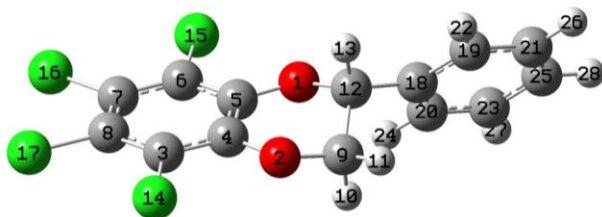
Cl	0.25681200	2.50965400	0.68437400
Cl	-2.80412900	2.62777700	-0.09712100
Cl	-4.32149300	-0.15831300	-0.76727800
Cl	-2.61629400	-2.84872900	-0.61388300
O	-1.43742300	-2.16629000	2.05172300
O	5.85382200	-0.08073600	-0.43080500
O	-0.12971400	0.28961800	2.64359100
C	-1.31126600	-1.29585400	1.24366800
C	-0.57707500	0.04817400	1.56292500
C	-0.53693100	0.95575800	0.31771700
C	-2.02375600	1.09180600	-0.05800700
C	-2.65603700	-0.06168800	-0.33924800
C	-1.78392900	-1.31646500	-0.22425700
C	-0.53120200	-1.14904300	-1.12163300
H	-0.84836200	-1.22759100	-2.16160800
H	0.14118400	-1.98353800	-0.92153600
C	0.18523400	0.21143500	-0.87620400
H	-0.00188300	0.85684100	-1.73599200
C	1.68932100	0.08498300	-0.71889300
C	2.53332800	0.89047100	-1.49594700
H	2.10108800	1.59434800	-2.19923600
C	3.91232100	0.81394600	-1.38393500
H	4.55998800	1.43728400	-1.98829000
C	4.49378900	-0.07726100	-0.47474400
C	3.67099800	-0.89102000	0.30883300
H	4.08880800	-1.59021400	1.01996400
C	2.28542900	-0.80466600	0.17589200
H	1.68179600	-1.45652000	0.79851300
C	6.50736400	-0.94973200	0.48756000
H	7.57308600	-0.77297100	0.35436700
H	6.28439000	-1.99978100	0.27081000
H	6.22766100	-0.72029200	1.52100400

Structure I. Number of imaginary frequencies: 0.



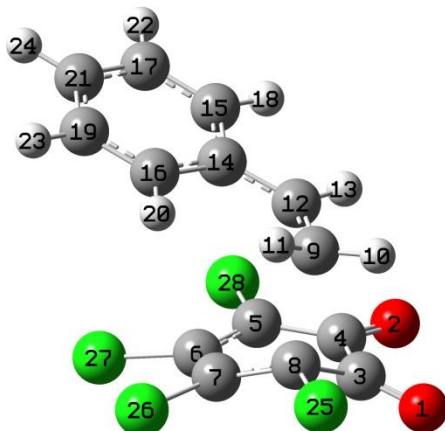
C	1.11077800	-1.32730700	-0.42761300
C	0.03945200	-0.51822000	-0.81961500
C	0.13572700	0.87201600	-0.68844200
C	1.28338800	1.44290900	-0.13088000
C	2.34844900	0.63365600	0.27742600
C	2.26570500	-0.75777000	0.11824300
Cl	0.95038100	-3.04762300	-0.62544100
Cl	3.58838400	-1.77724400	0.60220600
Cl	3.77082700	1.35625500	0.96844700
Cl	1.33952800	3.17231100	0.02754600
O	-0.88057500	1.68629600	-1.07947300
O	-1.07129500	-1.11961800	-1.33152400
C	-2.23897600	-0.29141300	-1.47531200
H	-2.81693900	-0.78584400	-2.26130200
C	-1.79456200	1.07465700	-1.99278600
H	-2.62974100	1.76497000	-2.08762400
H	-1.30865200	0.95680600	-2.96753600
C	-3.07066900	-0.23965700	-0.20006600
C	-4.25727000	0.50284100	-0.18771100
C	-2.70916500	-0.95232200	0.94401000
C	-5.05638800	0.54557800	0.95081200
H	-4.57164700	1.04837200	-1.07178000
C	-3.50852900	-0.90630400	2.08634800
H	-1.81087300	-1.55543800	0.94360100
C	-4.68091800	-0.15646600	2.09561400
H	-5.97188000	1.12618500	0.94338200
H	-3.21150800	-1.46257700	2.96815700
H	-5.30097700	-0.12197300	2.98400500

Structure J. Number of imaginary frequencies: 0.



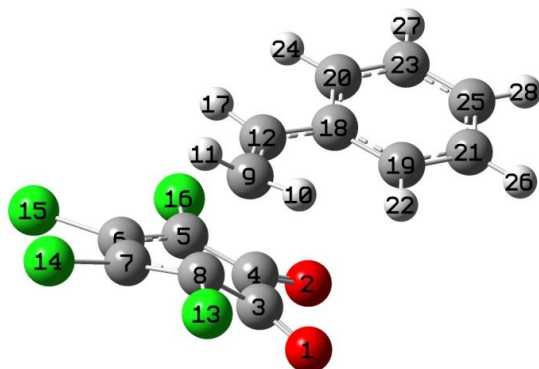
C	-1.02631400	1.29256700	-0.09240900
C	-0.11758600	0.22893100	-0.08366200
C	-0.58847400	-1.08673100	0.00666400
C	-1.96457300	-1.33320900	0.04636100
C	-2.87419200	-0.27153400	0.02226000
C	-2.40221500	1.04860000	-0.03674100
Cl	-0.39181800	2.90835100	-0.18270100
Cl	-3.51952900	2.38070700	-0.05038000
Cl	-4.58229700	-0.59233700	0.07422200
Cl	-2.49550600	-2.98586300	0.13369300
O	0.26541800	-2.14506300	0.03939400
O	1.21266900	0.51149600	-0.15243000
C	2.06776800	-0.60194000	-0.47925000
H	1.93573800	-0.83305500	-1.54252400
C	1.62353100	-1.80805600	0.34244400
H	2.21316800	-2.69031700	0.09835600
H	1.72106900	-1.59031700	1.41164300
C	3.49914600	-0.21487400	-0.20626600
C	4.51295900	-0.68303700	-1.04636600
C	3.83521200	0.56517100	0.90402000
C	5.84708500	-0.38551800	-0.77636700
H	4.25965000	-1.27585400	-1.91975000
C	5.16879400	0.86848400	1.16853200
H	3.05167300	0.95280400	1.54368300
C	6.17725600	0.39114800	0.33263300
H	6.62516400	-0.75106300	-1.43668900
H	5.41983300	1.48180400	2.02647700
H	7.21416500	0.62992000	0.53980200

Structure **K**. Number of imaginary frequencies: 1.



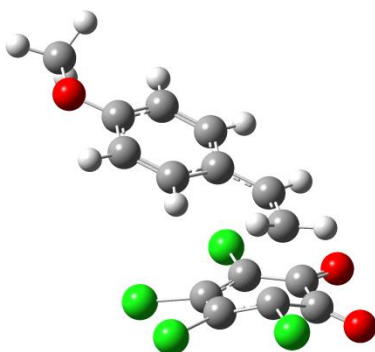
O	-3.27504400	1.69263600	-0.75745800
O	-1.00724300	3.24885300	-0.23556300
C	-2.23962100	1.20214200	-0.41170500
C	-1.03553900	2.06756200	0.03832300
C	-0.02259900	1.34720700	0.79992000
C	-0.23986500	0.04197500	1.26408200
C	-1.22386500	-0.77750200	0.69121500
C	-1.95588000	-0.29027700	-0.43507900
C	-0.76694300	-0.21289300	-1.99098500
H	-1.47748800	0.27002900	-2.65417900
H	-0.71930400	-1.28646400	-2.13369400
C	0.44417000	0.48165200	-1.77384500
H	0.48319400	1.53088200	-2.04437300
C	1.69740300	-0.13399100	-1.41873900
C	1.80745700	-1.50097100	-1.07842100
C	2.87278900	0.65184000	-1.41046400
C	3.03702900	-2.04992400	-0.74419500
H	0.93087800	-2.13655500	-1.07789700
C	4.10020000	0.09399800	-1.08606900
H	2.80579000	1.70235000	-1.66979900
C	4.18725100	-1.25811700	-0.74840800
H	3.10286600	-3.09940900	-0.48170100
H	4.99125800	0.71091700	-1.09073500
H	5.14634500	-1.69352900	-0.49270500
Cl	-3.32462400	-1.24260700	-1.00062400
Cl	-1.42438400	-2.41651000	1.22132600
Cl	0.78092300	-0.59565900	2.51722800
Cl	1.32236900	2.28381600	1.34533300

Structure **L**. Number of imaginary frequencies: 1.



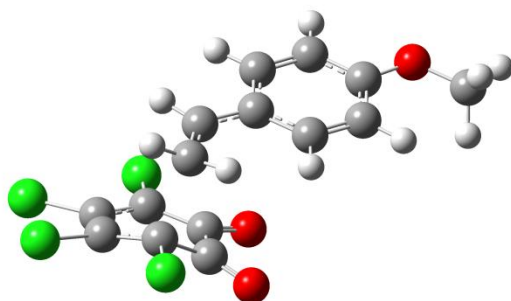
O	0.03585300	-2.11978500	1.92791500
O	-1.37174200	0.27504700	2.01415100
C	0.34945800	-1.19103800	1.23902900
C	-0.34978200	0.18408200	1.36647400
C	0.30576000	1.27914900	0.66859600
C	1.60132600	1.14930900	0.14758200
C	2.17483300	-0.11002700	-0.06930600
C	1.37274300	-1.27604900	0.12391500
C	0.05428400	-1.33329400	-1.33435000
H	-0.33856500	-2.32243700	-1.12589800
H	0.81297400	-1.33162200	-2.10891200
C	-0.86396300	-0.25552600	-1.34862500
Cl	2.16714100	-2.84492700	0.02900300
Cl	3.72943700	-0.24698100	-0.82378900
Cl	2.46843100	2.57737600	-0.33461200
Cl	-0.47696900	2.81871500	0.78020300
H	-0.55394900	0.65102800	-1.85685100
C	-2.25335700	-0.30222200	-0.96687500
C	-2.84909300	-1.41282300	-0.32846200
C	-3.06663200	0.81850000	-1.24925800
C	-4.19743300	-1.40263800	-0.00600300
H	-2.25600600	-2.28337500	-0.07681200
C	-4.41605700	0.81973000	-0.93055600
H	-2.62272400	1.68448600	-1.72753800
C	-4.98713900	-0.29171500	-0.30874400
H	-4.63592800	-2.26049800	0.48993600
H	-5.02407700	1.68716200	-1.15944200
H	-6.04097000	-0.29057500	-0.05520500

Structure **M**. Number of imaginary frequencies: 1.



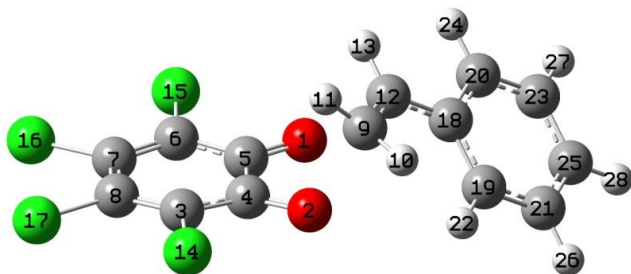
O	-3.95350800	1.26337600	-0.89593100
O	-1.93162500	3.12748400	-0.38507900
C	-2.87621000	0.92937200	-0.49363700
C	-1.81491300	1.96548400	-0.04780100
C	-0.75678700	1.42565100	0.78722800
C	-0.78895800	0.11224400	1.27401700
C	-1.63068800	-0.85865400	0.70974800
C	-2.40301600	-0.51412600	-0.44073200
C	-1.21612100	-0.35866800	-1.99774100
H	-1.97451300	-0.00499300	-2.68860300
H	-1.03023300	-1.42342000	-2.08332500
C	-0.10526400	0.49487400	-1.81236000
H	-0.20616600	1.53018400	-2.11904000
C	1.19944300	0.07877800	-1.39585500
C	1.50143200	-1.24965200	-1.00110300
C	2.25257900	1.02076500	-1.36618200
C	2.77140500	-1.60415900	-0.60227400
H	0.72963700	-2.00887400	-1.00739100
C	3.53502700	0.67161900	-0.97695400
H	2.04940500	2.04427600	-1.65997000
C	3.80282200	-0.64852200	-0.58494200
H	3.00223200	-2.61691200	-0.29592800
H	4.31244100	1.42318500	-0.97138500
Cl	-3.62968800	-1.65947600	-0.97850900
Cl	-1.60057400	-2.49745800	1.28299700
Cl	0.28696500	-0.34158400	2.56332300
Cl	0.43873400	2.55589100	1.32339600
O	5.01162600	-1.09785200	-0.18145700
C	6.10952800	-0.18796300	-0.12233200
H	6.95550500	-0.77252200	0.23287800
H	6.33743600	0.22027700	-1.11162100
H	5.90822600	0.62712300	0.57912200

Structure N. Number of imaginary frequencies: 1.



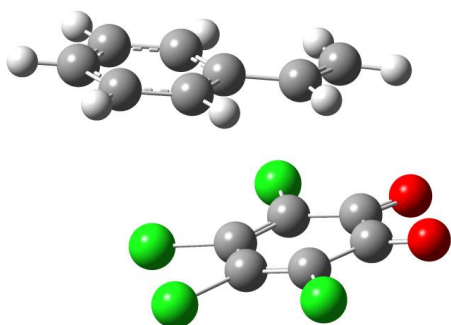
O	0.30513000	-2.04968300	1.87124500
O	-0.86607700	0.46469800	1.89332200
C	0.75039100	-1.15412900	1.20914500
C	0.18608800	0.28254100	1.31077700
C	0.98659500	1.31002900	0.67618200
C	2.27181700	1.04983900	0.18063800
C	2.72704000	-0.25886400	-0.02672400
C	1.81549500	-1.34312000	0.14885700
C	0.54540300	-1.32174900	-1.36495100
H	0.08337900	-2.28215700	-1.16445800
H	1.33322200	-1.37516100	-2.10798100
C	-0.30200800	-0.18805400	-1.42593600
Cl	2.46981000	-2.97906000	0.10324800
Cl	4.27674200	-0.54556700	-0.75407500
Cl	3.28929700	2.38633700	-0.27346300
Cl	0.35965400	2.92341200	0.77336600
H	0.09498900	0.69724000	-1.91162700
C	-1.68864400	-0.12613400	-1.07476400
C	-2.39211800	-1.18703500	-0.46273300
C	-2.41255900	1.06349100	-1.34660500
C	-3.73640700	-1.08060900	-0.15000200
H	-1.88183200	-2.11040800	-0.21795500
C	-3.75100000	1.17685100	-1.04708600
H	-1.89545200	1.90089500	-1.80164200
C	-4.42825400	0.10489400	-0.44031600
H	-4.23438900	-1.91270100	0.32786900
H	-4.30171600	2.08560800	-1.25560900
O	-5.73654300	0.31102600	-0.17538700
C	-6.48353400	-0.71042100	0.48516700
H	-6.05914500	-0.93420600	1.46815900
H	-7.48721000	-0.30786400	0.60454300
H	-6.52531600	-1.62183000	-0.11892800

Structure **O**. Number of imaginary frequencies: 1.



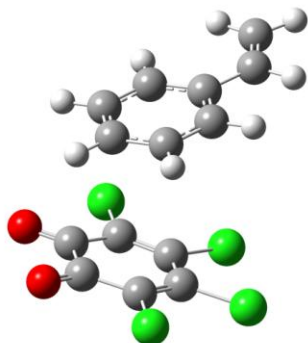
O	1.08239900	0.87816900	-0.12051700
O	0.60359500	-1.71134100	-0.19399900
C	-1.74997500	-1.36865800	-0.08778300
C	-0.39874700	-0.91716000	-0.19741300
C	-0.11413300	0.51822000	-0.16464000
C	-1.23650100	1.42666100	-0.07469600
C	-2.52624200	0.95111600	-0.09907700
C	-2.79107300	-0.46412700	-0.10476600
C	1.70159400	-1.58067000	1.32607400
H	2.20435100	-2.50040600	1.06300800
H	0.93626100	-1.69001000	2.08388600
C	2.41579000	-0.36886700	1.27668300
H	2.13796100	0.41818700	1.96651800
Cl	-2.02204100	-3.08378100	-0.02783300
Cl	-0.87261400	3.12011200	-0.00307000
Cl	-3.86580400	2.05726000	-0.10557000
Cl	-4.43484500	-1.02012400	-0.12985200
C	3.63411100	-0.17281500	0.52967300
C	4.05784500	-1.07398000	-0.46855900
C	4.41517200	0.97403200	0.77602800
C	5.22921800	-0.84120200	-1.17505600
H	3.45319300	-1.94111700	-0.70386400
C	5.59013900	1.19878500	0.07321800
H	4.08411900	1.68741600	1.52267900
C	6.00200400	0.29035800	-0.90363800
H	5.54113300	-1.53758800	-1.94488000
H	6.18262200	2.08312700	0.27705900
H	6.91737700	0.46666300	-1.45705200

Structure **P**. Number of imaginary frequencies: 0.



C	-4.35956900	-0.73226200	0.07189200
C	-3.50954100	-1.71233300	-0.44565800
H	-3.69846200	-2.75898800	-0.23464800
C	-2.42230300	-1.35524100	-1.23334800
H	-1.77899300	-2.13233200	-1.62929300
C	-2.15589500	-0.00588100	-1.52438300
C	-3.02062700	0.96612200	-0.99674900
H	-2.83370000	2.01291800	-1.21322900
C	-4.11127500	0.60935700	-0.20802600
H	-4.76576200	1.37842900	0.18643100
Cl	0.76827100	3.30863400	0.41931600
Cl	-0.45674000	1.22632100	2.46895800
Cl	0.16787700	-1.79778600	2.23806300
Cl	2.10920400	-2.89676200	-0.01183000
C	2.40435900	-0.31284700	-0.82069100
C	2.04560500	1.20177400	-0.74007900
C	1.11574100	1.61941900	0.33338900
C	0.59597900	0.71360400	1.19853600
C	0.90295000	-0.73050900	1.09445200
C	1.73199700	-1.21863200	0.13865700
O	3.21809800	-0.68524800	-1.62676500
O	2.54565800	1.96943800	-1.52193500
C	-1.02290700	0.42890900	-2.35504100
H	-0.94798200	1.50576400	-2.49103400
C	-0.10412500	-0.34207200	-2.95092500
H	0.68560400	0.09688700	-3.54822000
H	-0.11193200	-1.42448000	-2.88431100
H	-5.20753900	-1.01508100	0.68512800

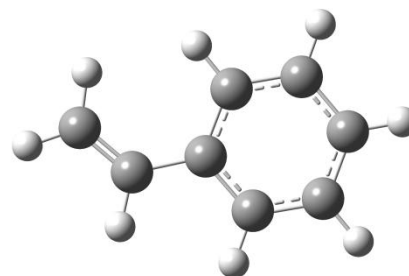
Structure **R**. Number of imaginary frequencies: 0.



C	-0.89482100	-2.19287500	-1.70544600
C	-1.77666300	-1.16268900	-2.04549300
H	-1.70109100	-0.68579600	-3.01636200
C	-2.75274600	-0.74682200	-1.14756800
H	-3.42531200	0.05359600	-1.43269800
C	-2.87484400	-1.34976400	0.11604800
C	-1.97838700	-2.37967000	0.44313800
H	-2.05817700	-2.86031300	1.41300300
C	-0.99997400	-2.79941300	-0.45518800
H	-0.32399600	-3.60169800	-0.18114800
Cl	-0.57802800	3.04089900	-1.11126800
Cl	-0.24099900	2.19759900	1.92293700
Cl	1.55547000	-0.19175100	2.72741700
Cl	3.15361300	-1.84265200	0.54671400
C	2.05360300	-0.18063800	-1.30883200
C	1.12998000	1.00890100	-1.71623600
C	0.42442000	1.72226300	-0.62896100
C	0.58053500	1.34629900	0.66442400
C	1.44681000	0.20800900	1.04967700
C	2.13720500	-0.51135800	0.13109400
O	2.66052200	-0.77308900	-2.16363500
O	1.03361500	1.30553800	-2.87934600
C	-4.86754000	-0.05141200	0.94995600
H	-5.56897200	0.14712300	1.75126700
H	-5.00432600	0.51897800	0.03804300
H	-0.14023500	-2.51948000	-2.41189400
C	-3.89791300	-0.95914100	1.09978900
H	-3.83991600	-1.49174900	2.04663100

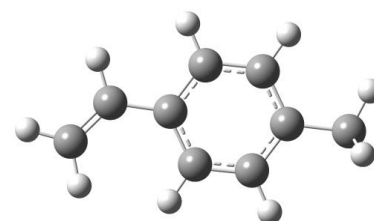
Structure **S**. Number of imaginary frequencies: 0.

C	2.26245900	0.26141100	0.00036100
C	1.77899100	-1.04444700	0.00037100
C	0.40610900	-1.27968100	-0.00005300
C	-0.51416400	-0.22036300	-0.00042300
C	-0.00881300	1.09062900	-0.00053300
C	1.36025000	1.32754600	-0.00012000
C	-1.95356500	-0.52877200	-0.00069800
C	-2.97358100	0.33508800	0.00093100
H	3.33006300	0.44973800	0.00065700
H	2.46925200	-1.88073100	0.00068900
H	0.03617600	-2.30003000	-0.00004900
H	-0.69095600	1.93272300	-0.00106600
H	1.72823900	2.34767000	-0.00024400
H	-2.18643600	-1.59147500	-0.00229400
H	-3.99817700	-0.01675100	0.00052000
H	-2.83427000	1.41039400	0.00277300



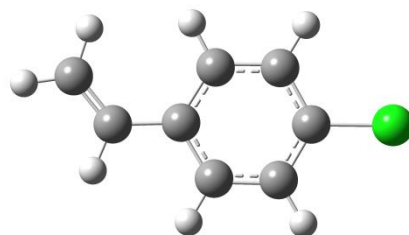
Structure **T**. Number of imaginary frequencies: 0.

C	1.79545800	-0.07257400	-0.00010800
C	1.20505200	1.19206600	-0.00003000
C	-0.18071200	1.33862100	-0.00002600
C	-1.03265700	0.22663900	-0.00011000
C	-0.43511500	-1.04578700	-0.00020600
C	0.94440400	-1.18844200	-0.00021800
C	-2.48809400	0.43641800	-0.00007800
C	-3.44861900	-0.49359800	0.00032000
H	1.83411800	2.07651400	0.00000200
H	-0.61078700	2.33526400	0.00000700
H	-1.05573400	-1.93447100	-0.00035900
H	1.37440500	-2.18557000	-0.00035700
H	-2.79235400	1.48121700	-0.00035500
H	-4.49461600	-0.21155200	0.00031500
H	-3.23868200	-1.55760200	0.00067900
C	3.29354300	-0.24597100	0.00025700
H	3.62896600	-0.80008600	0.88284100
H	3.62878500	-0.80601300	-0.87860900
H	3.80634000	0.71806600	-0.00297400



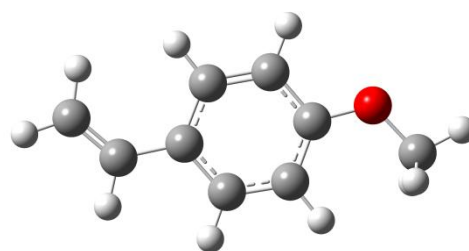
Structure **U**. Number of imaginary frequencies: 0.

C	1.36052800	-0.01343300	-0.00016600
C	0.78281400	1.25028300	-0.00019300
C	-0.60503400	1.35786900	0.00025100
C	-1.43267200	0.22549800	0.00064700
C	-0.81323400	-1.03525200	0.00078900
C	0.56941900	-1.16101600	0.00035300
C	-2.89215500	0.40693600	0.00091700
C	-3.83159500	-0.54366600	-0.00083500
H	1.40666000	2.13496200	-0.00053500
H	-1.05535600	2.34491800	0.00022600
H	-1.41512200	-1.93613000	0.00137000
H	1.03412900	-2.13882800	0.00049500
H	-3.21751400	1.44494400	0.00262400
H	-4.88323500	-0.28400100	-0.00040400
H	-3.59955900	-1.60302300	-0.00280400
Cl	3.11185700	-0.16977400	-0.00067900



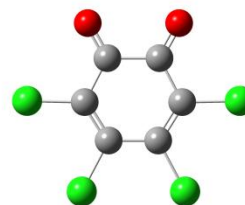
Structure **V**. Number of imaginary frequencies: 0.

C	1.32912000	0.28273000	0.00000400
C	0.86503000	-1.03317600	-0.00000500
C	-0.50938600	-1.27589000	-0.00001400
C	-1.44851800	-0.23948500	-0.00001200
C	-0.95290300	1.07901400	-0.00000400
C	0.40475200	1.33856400	0.00000400
C	-2.88113800	-0.56437100	-0.00001800
C	-3.91488000	0.28453800	0.00001300
C	3.63125700	-0.37717400	0.00001300
O	2.64362300	0.64499800	0.00001300
H	1.55069500	-1.86973000	-0.00000700
H	-0.85731000	-2.30402200	-0.00002100
H	-1.64210900	1.91537000	-0.00000700
H	0.78135800	2.35451300	0.00000900
H	-3.10003400	-1.63035000	-0.00005100
H	-4.93387100	-0.08284200	0.00000400
H	-3.79138600	1.36188000	0.00005000
H	3.55636200	-1.00508700	-0.89442000
H	3.55635200	-1.00509700	0.89443800
H	4.59096400	0.13687700	0.00002100



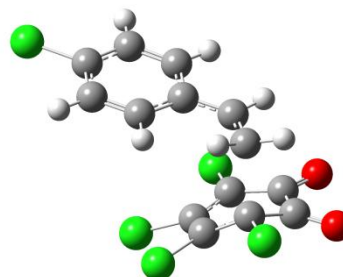
Structure W. Number of imaginary frequencies: 0.

Cl	3.18319700	0.45298500	-0.00026100
Cl	1.54731800	-2.26246800	0.00019400
Cl	-1.54734900	-2.26244100	-0.00016500
Cl	-3.18318300	0.45300200	-0.00001900
C	-0.78009200	1.73338500	0.00010700
C	0.78010100	1.73337200	0.00009200
C	1.45908300	0.41654200	-0.00008600
C	0.74107400	-0.73403500	0.00006600
C	-0.74106900	-0.73402200	0.00000000
C	-1.45908400	0.41655100	0.00008400
O	-1.36808900	2.78319000	-0.00011400
O	1.36811500	2.78317400	0.00045100



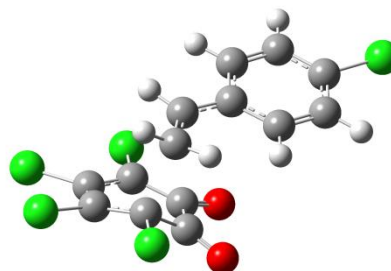
Structure X. Number of imaginary frequencies: 1.

O	-4.00415700	1.13298600	-0.84576600
O	-2.06627000	3.07637600	-0.29619200
C	-2.90755400	0.84006800	-0.46710900
C	-1.88953200	1.91256400	-0.00400700
C	-0.78349100	1.39556100	0.79244200
C	-0.77108200	0.07730700	1.26928700
C	-1.57928600	-0.91300000	0.68969400
C	-2.36303200	-0.57897500	-0.45735600
C	-1.17466200	-0.32194200	-1.99137200
H	-1.94684900	0.00384000	-2.68092500
H	-0.92522000	-1.37113300	-2.10404400
C	-0.11915900	0.59189600	-1.77370200
H	-0.27198900	1.62366600	-2.06960500
C	1.21653000	0.23345700	-1.37645500
C	1.57756500	-1.07889200	-0.99803800
C	2.22309900	1.22626100	-1.35775900
C	2.87473400	-1.38357000	-0.61737900
H	0.84126500	-1.87240200	-1.00024400
C	3.52456200	0.92733700	-0.99022400
H	1.97063500	2.24089000	-1.64337100
C	3.84206700	-0.37854100	-0.61685200
H	3.14134500	-2.39085700	-0.32466900
H	4.28829400	1.69416600	-0.98444400
Cl	-3.52963400	-1.76716400	-1.02967500
Cl	-1.49142400	-2.55531100	1.23841700
Cl	0.32230000	-0.35414900	2.54890000
Cl	0.36057800	2.56403500	1.34754700
Cl	5.48179000	-0.76389600	-0.14425100



Structure **Y**. Number of imaginary frequencies: 1.

O	0.51194700	-2.10144600	1.91640900
O	-0.83119900	0.33089400	1.97819900
C	0.86083400	-1.18259700	1.23134900
C	0.19968000	0.21191500	1.34898200
C	0.89620000	1.28825600	0.66254100
C	2.19201000	1.12084300	0.15335500
C	2.73111300	-0.15493100	-0.05779200
C	1.89490100	-1.29810100	0.12881000
C	0.59205800	-1.32343000	-1.34277400
H	0.17518900	-2.30378300	-1.13892800
H	1.35716700	-1.33950300	-2.11082700
C	-0.30167100	-0.22517100	-1.36629400
Cl	2.64739600	-2.88792900	0.04633400
Cl	4.28855400	-0.33694000	-0.79519100
Cl	3.10436800	2.52274300	-0.32019100
Cl	0.15635700	2.84922100	0.76512100
H	0.03252600	0.67377000	-1.87246800
C	-1.69190300	-0.23854200	-0.99106600
C	-2.31997600	-1.33300500	-0.35573000
C	-2.47931700	0.90076000	-1.27111000
C	-3.66666900	-1.29833400	-0.03538300
H	-1.75367700	-2.22010600	-0.10091500
C	-3.82807600	0.94193700	-0.95978600
H	-2.01812200	1.75952500	-1.74544200
C	-4.41506500	-0.16251600	-0.34365000
H	-4.13670500	-2.13952600	0.45699800
H	-4.42206300	1.81848400	-1.18351100
Cl	-6.11814700	-0.12162300	0.05272300



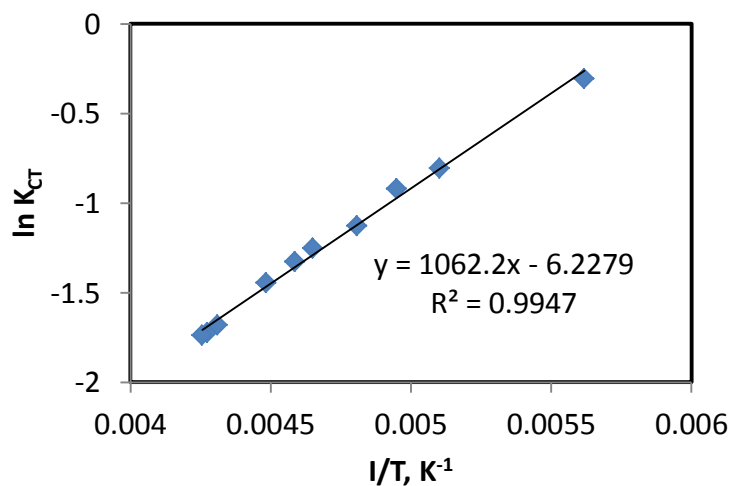


Figure S1. Temperature dependence of the formation constant of the [MeOSty, oCA] complex.

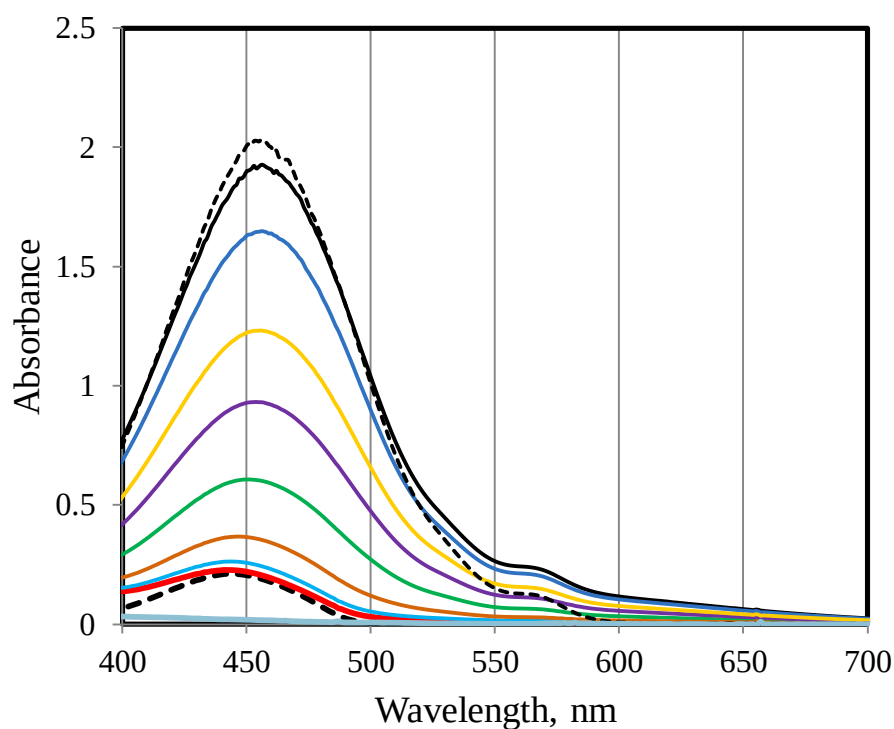


Figure S2. A) Spectral changes occurring in the dichloromethane solution containing the MeOSty donor and the oCA acceptor. Initial concentrations: oCA - 1 mM, MeOSty - 250 mM, 19 °C. Solid lines represent spectra of the solutions immediately after mixing (black), after 3 min (blue), 9 min (yellow), 15 min (violet), 26 min (green), 42 min (brown), 60 min (light blue), 120 min (red). The dashed line represents the spectrum of 1 mM solution of oCA, and the dot-dash line represents the spectrum of the 1 mM solution of crystalline MeOSty/oCA cycloadduct.

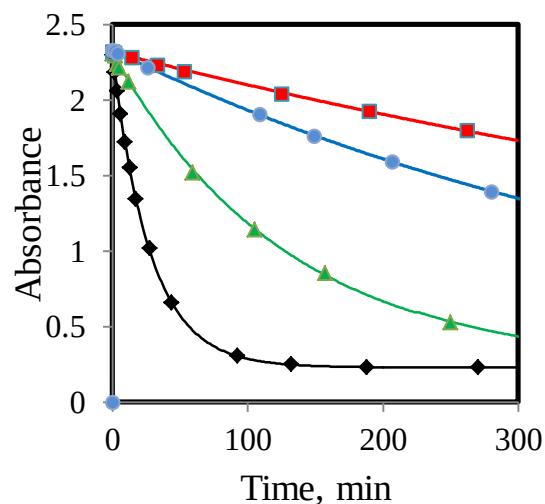


Figure S3. Kinetic curves for the cycloaddition reactions: **MeOSty/oCA** (black), **MeSty/oCA** (green), **HSty/oCA** (blue) and **ClSty/oCA** (red). Experimental points were measured for the reaction in dichloromethane solutions at 20°C. Initial concentrations in all experiments were: **oCA** - 1.2 mM, styrenes – 100 mM. Lines represent spectral changes calculated for the pseudo-first-order reactions according to the equation: $A(t) = A_0 \exp(-k_{\text{obs}}t) + A_\infty[1 - \exp(-k_{\text{obs}}t)]$, where $A_0 = c_0 \varepsilon_{\text{oCA}} l$, and $A_\infty = c_0 \varepsilon_{\text{Add}} l$, c_0 initial concentration of **oCA**, ε_{oCA} - extinction coefficient of **oCA** at $\lambda = 457$ nm, ε_{Add} - extinction coefficient of cycloadduct at $\lambda = 457$ nm and $l = 1$ cm. The values of k_{obs} (in min^{-1}) were: 0.036 (**MeOSty**), 0.0078 (**MeSty**), 0.0021(**HSty**), 0.0011(**ClSty**).

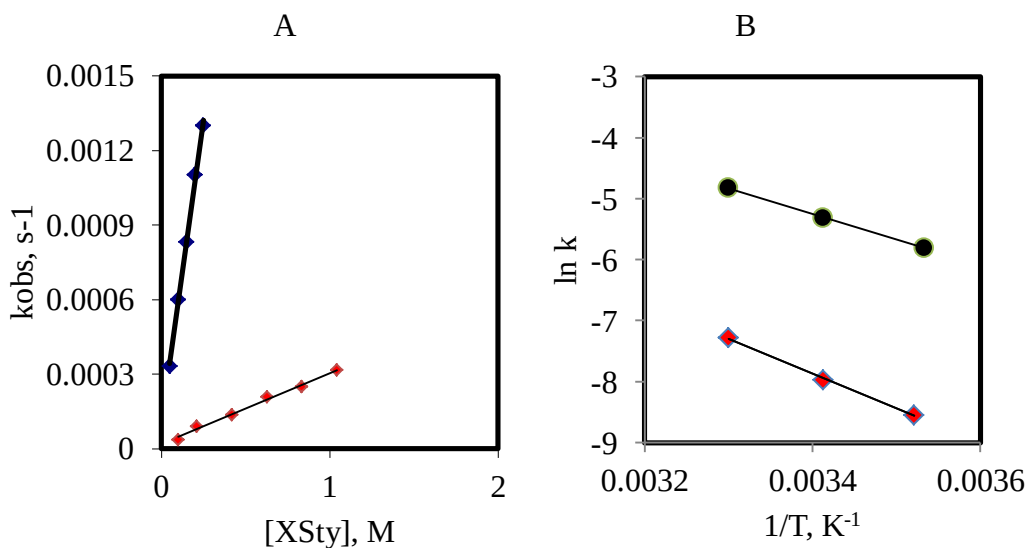


Figure S4. A) Dependences of the pseudo-first-order rate constants k_{obs} for the **XSty/oCA** cycloaddition on concentration of styrene (at 20°C). B) Temperature dependence of rate constants for the **XSty/oCA** cycloaddition. **XSty**: **MeOSty** (black) and **HSty** (red).

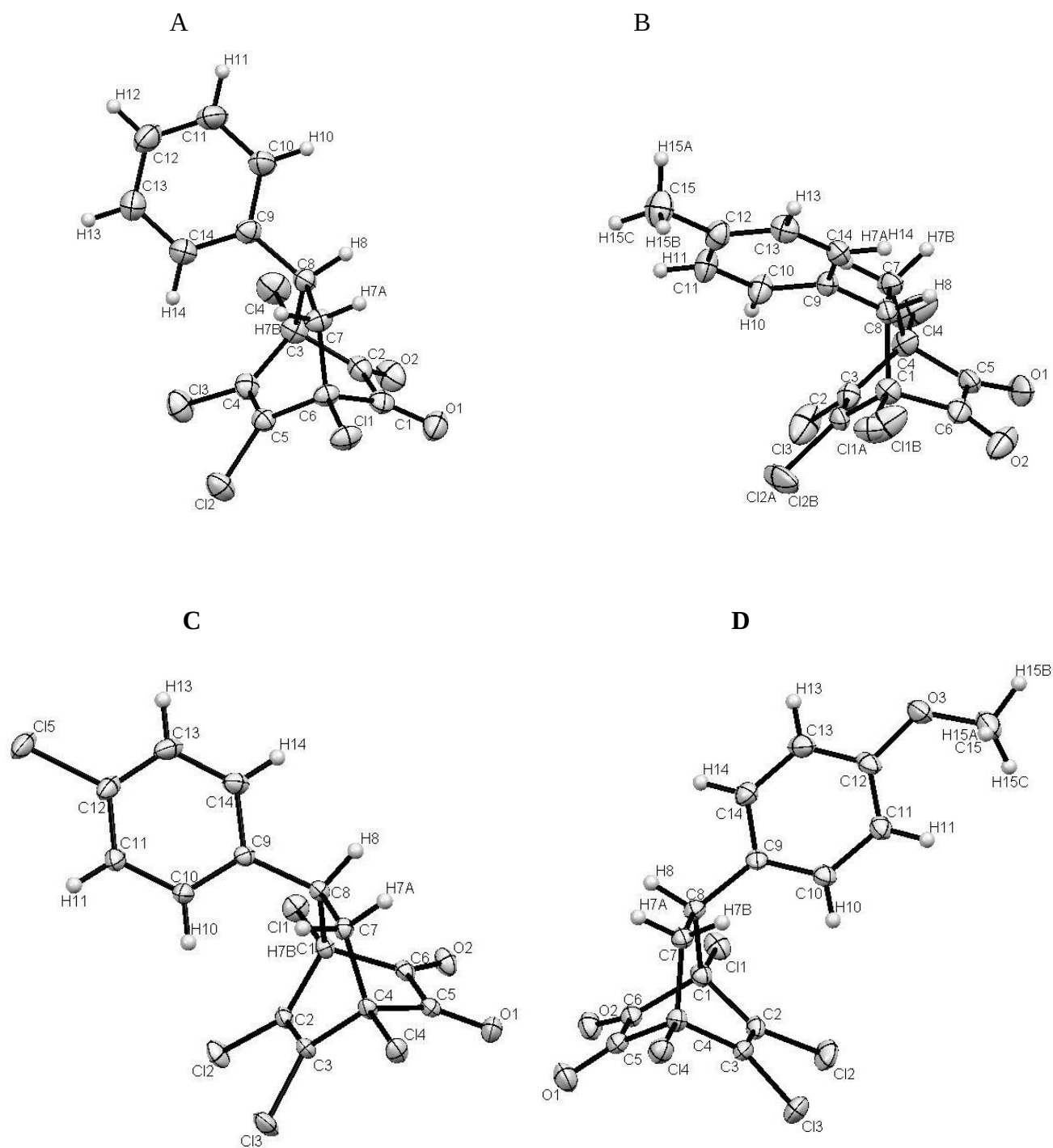


Figure S5. ORTEP diagrams for the **HSty/oCA** (A) and **MeSty/oCA** (B) **ClSty/oCA** (C) and **MeOSty/oCA** (D) adducts. Thermal ellipsoid are shown at 50% probability.

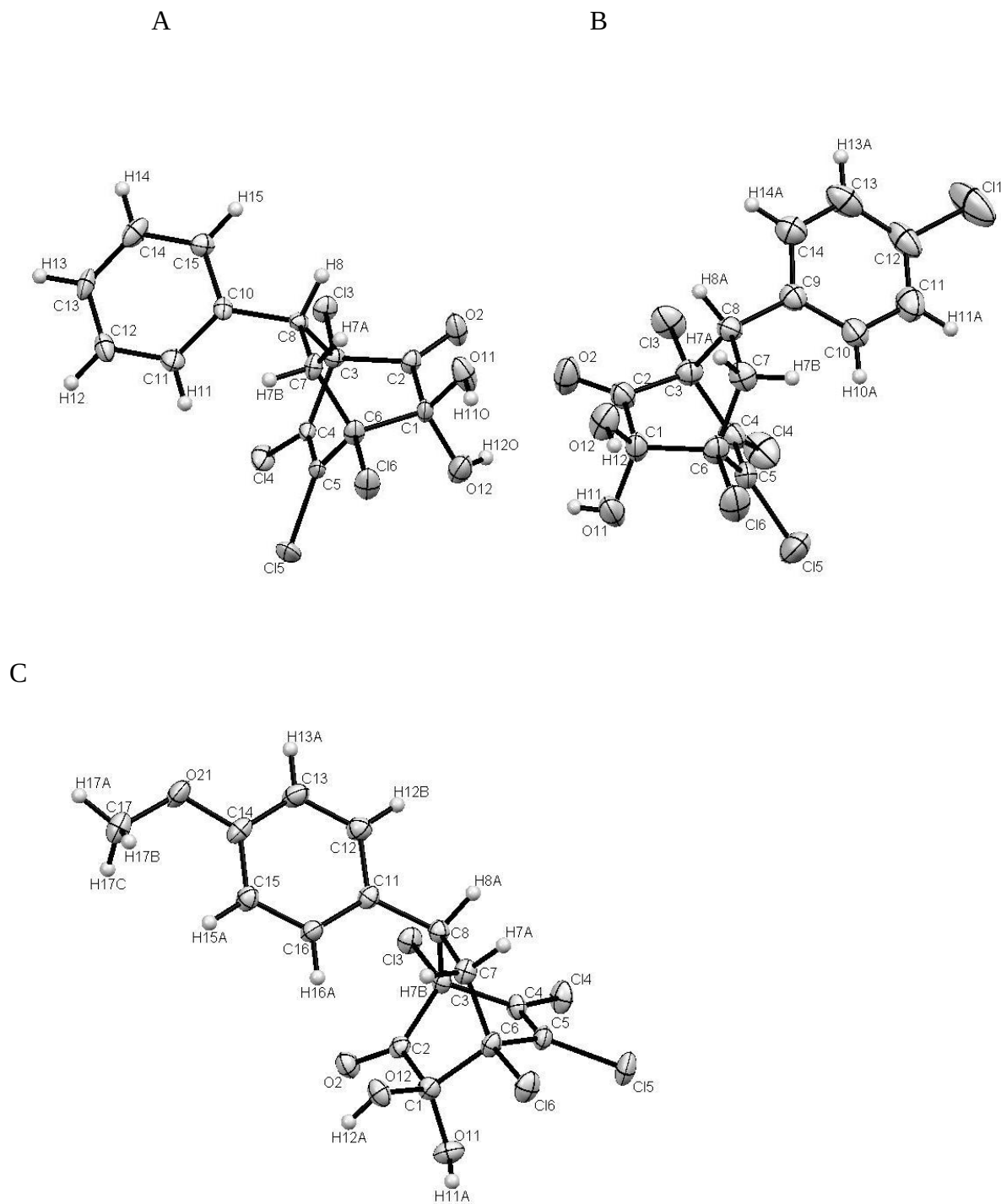


Figure S6. ORTEP diagrams of the hydrated products of XSty/oCA cycloadditions which were carried under air at room temperatures. (A) **Sty/oCA**, (B) **ClSty/oCA**, (C) **MeO Sty/oCA**. Note the exo-configuration of the **MeO Sty/oCA** adduct. Thermal ellipsoids are shown at 50% probability.

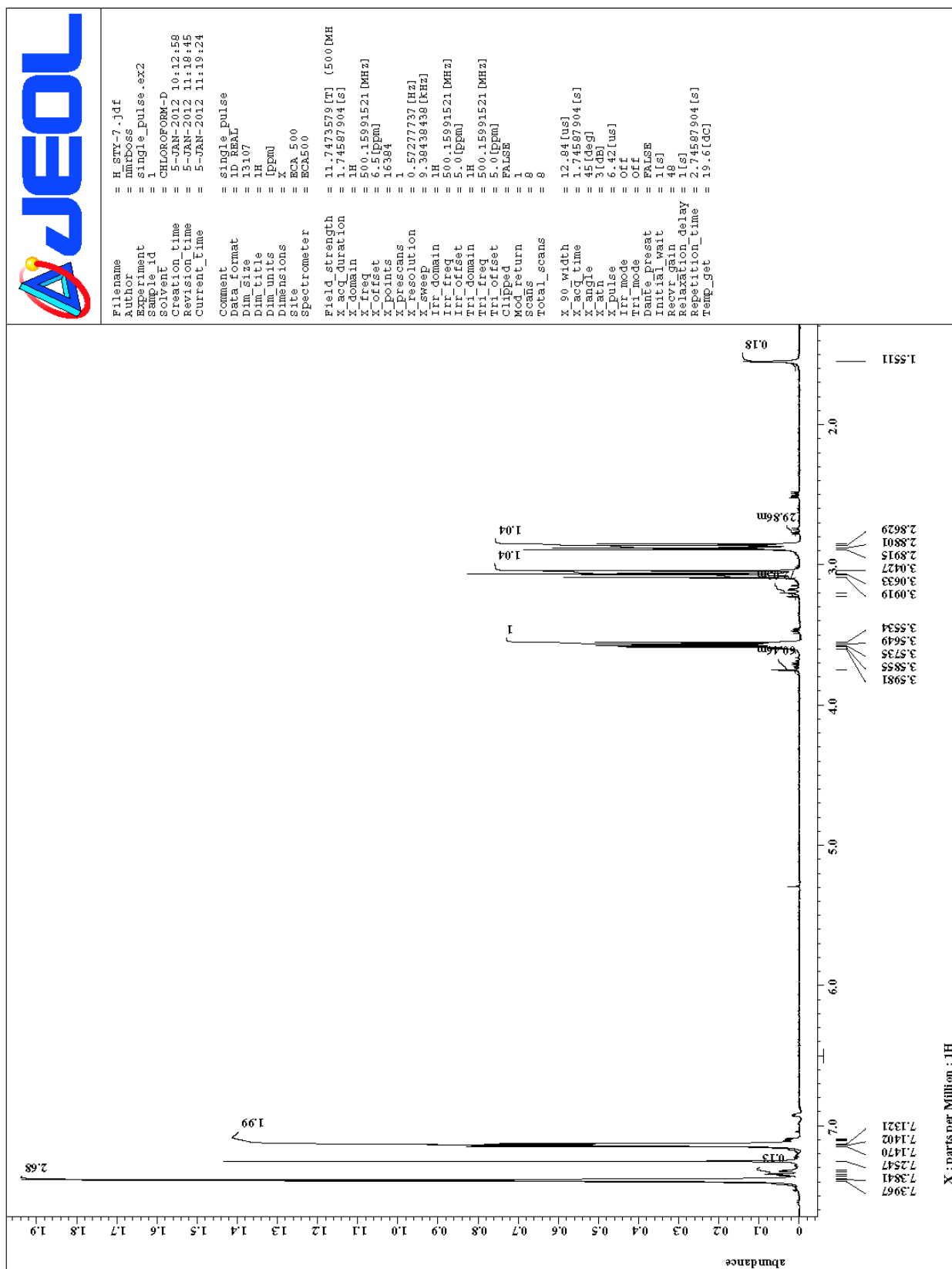
Figure S7A. ¹H NMR spectrum of HSty/oCA adduct (1).

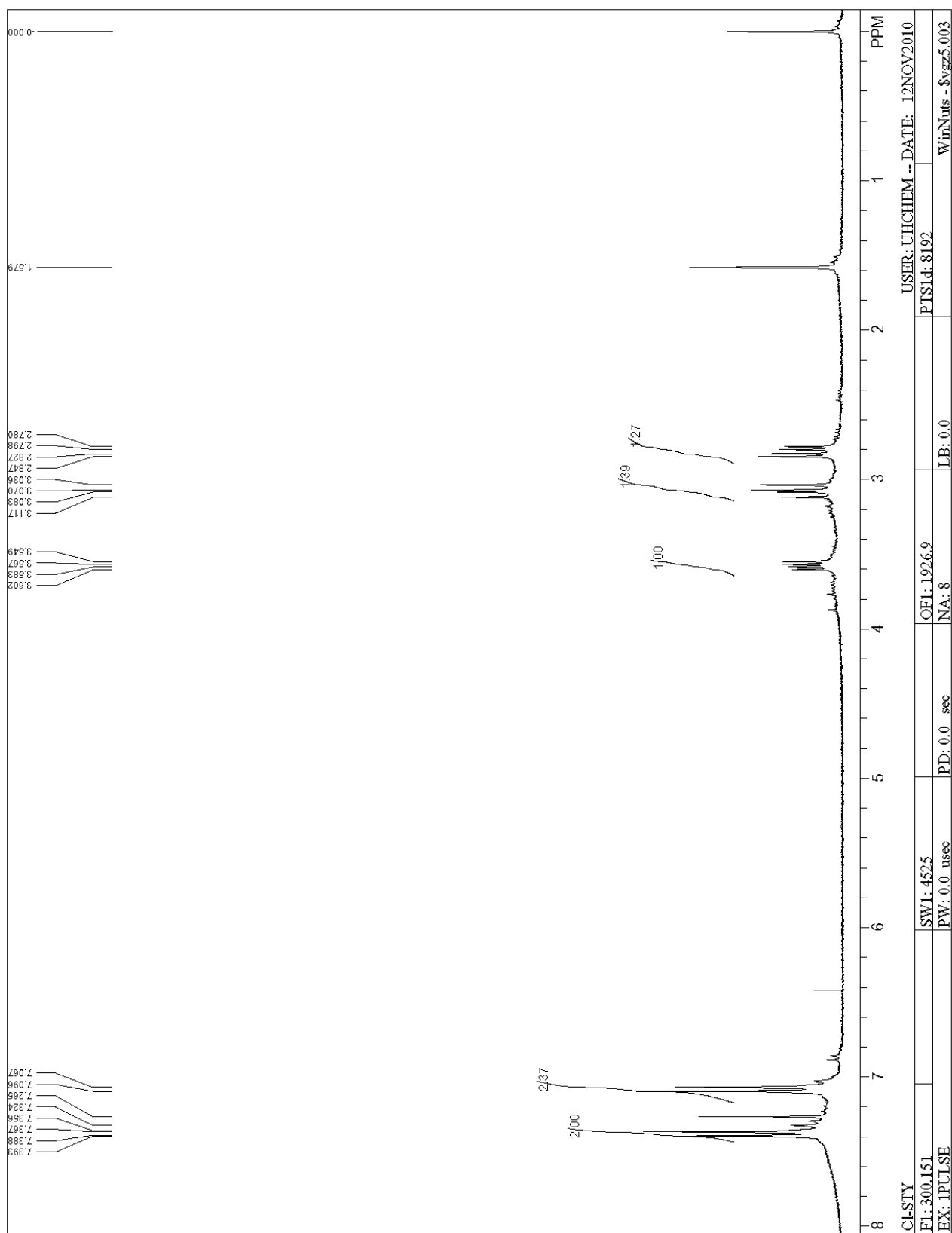
Figure S7B. ^1H NMR spectrum of ClSty/oCA adduct (2).

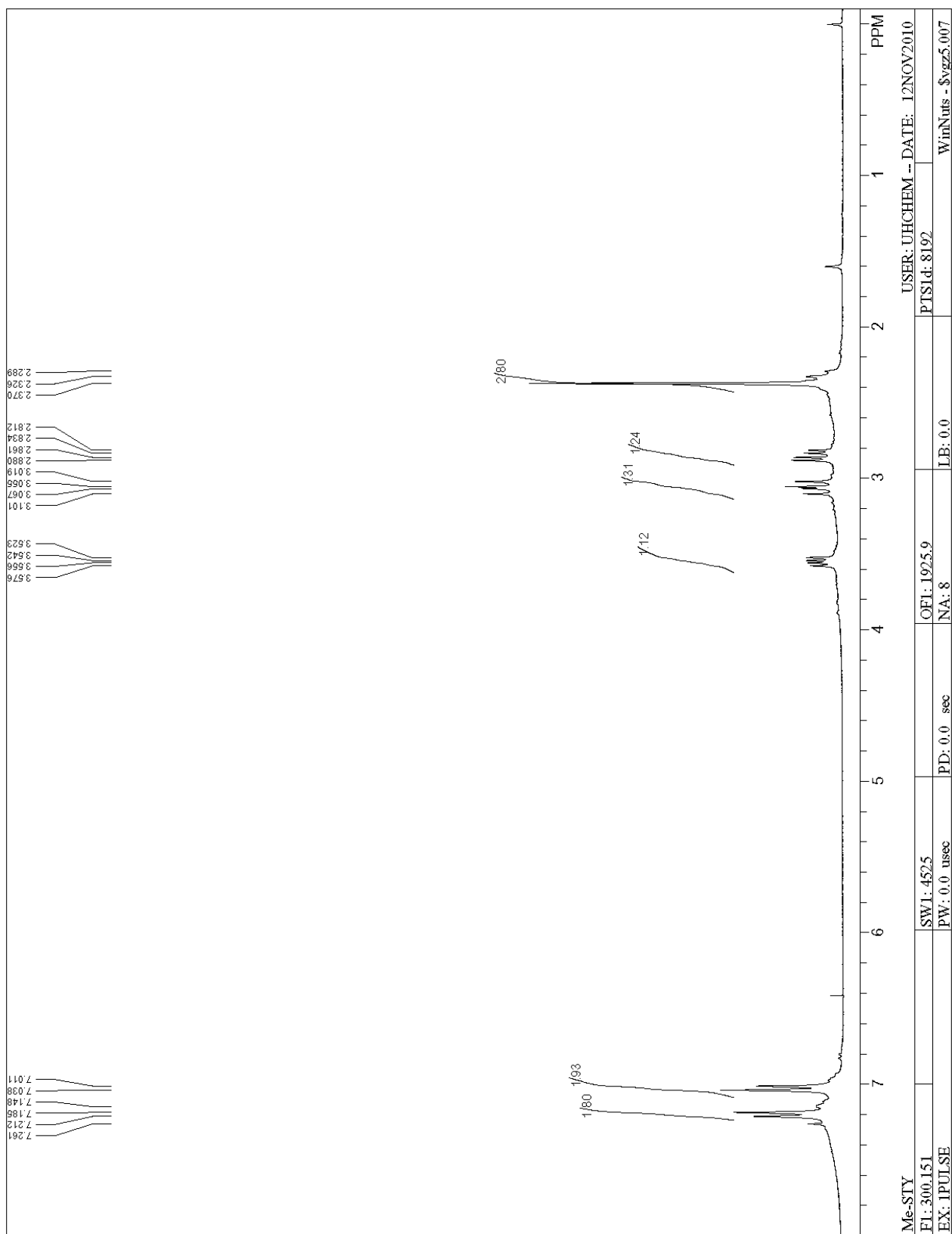
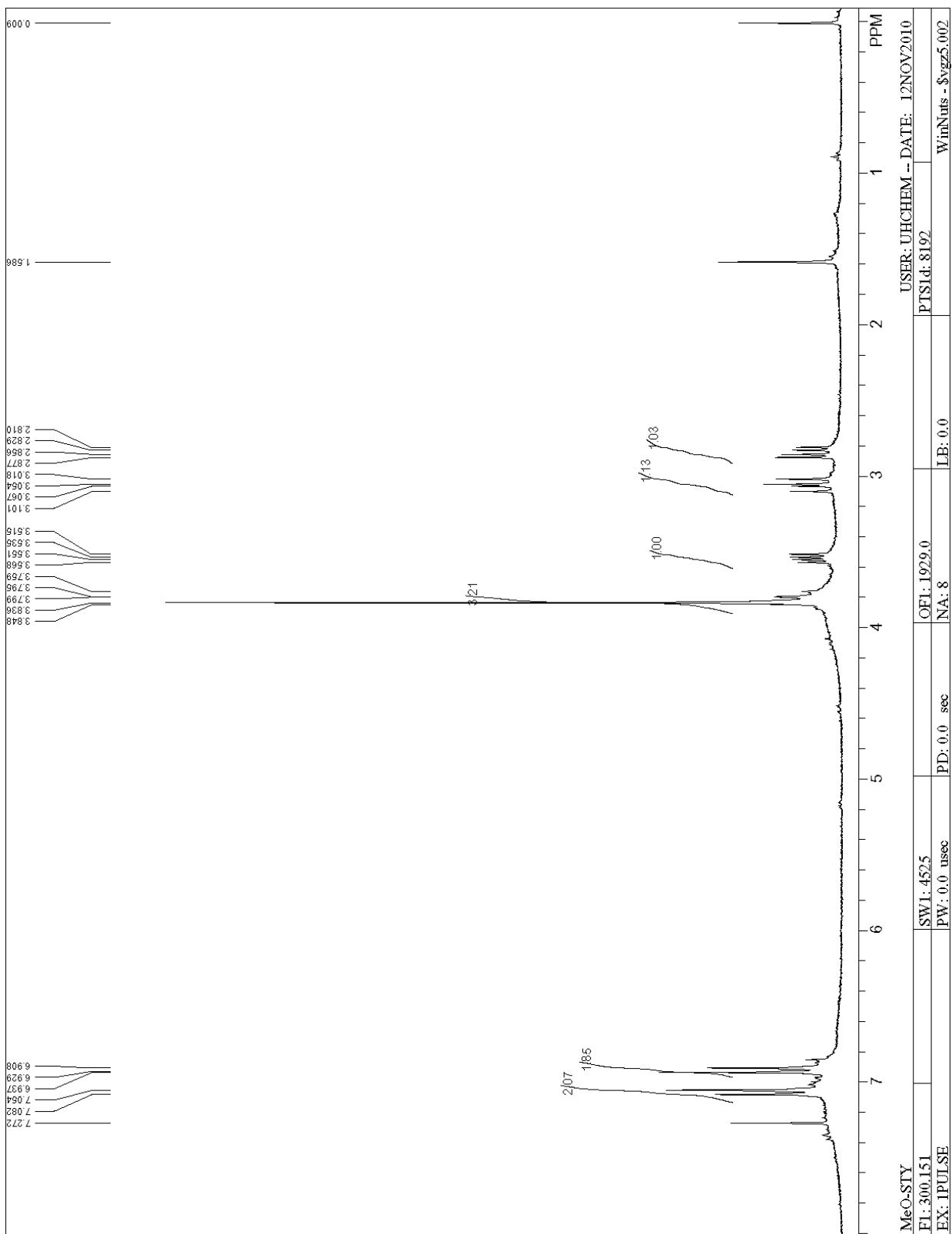
Figure S7C. ^1H NMR spectrum of MeSty/oCA adduct (3).

Figure S7C. ^1H NMR spectrum of MeOSty/oCA adduct (4).



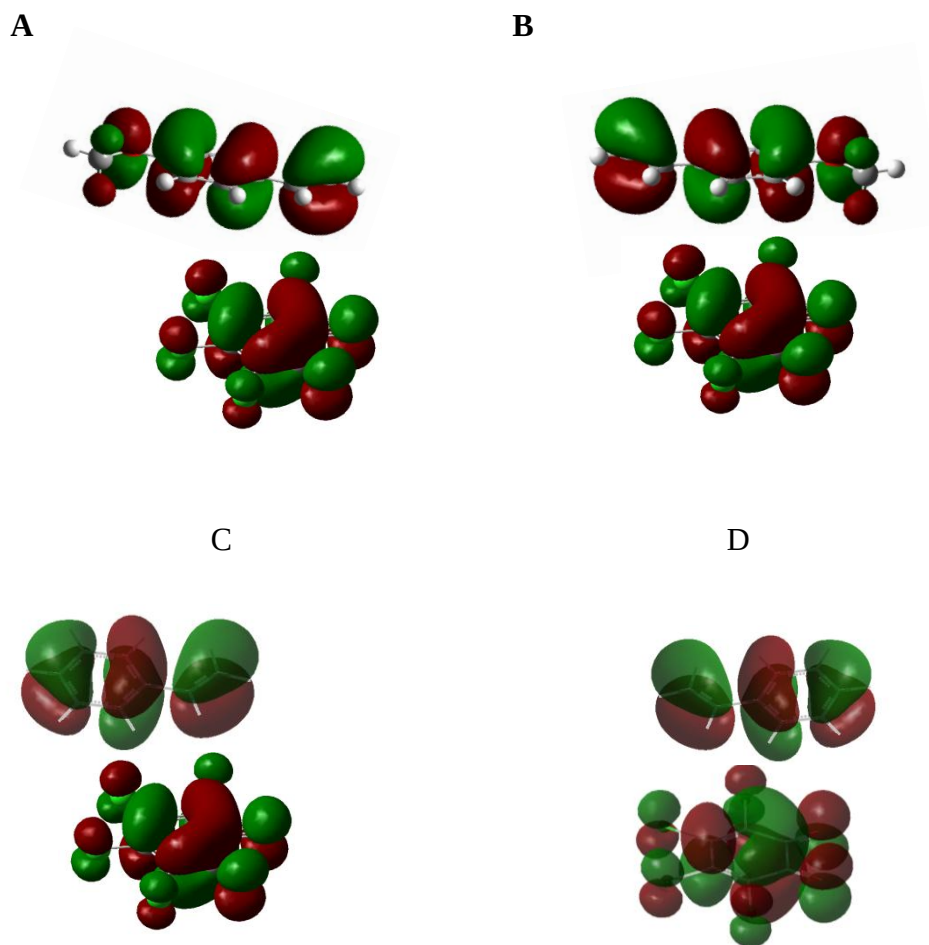


Figure S8. Molecular orbital shapes of HOMO of **XSty** and LUMO of **oCA** illustrating possibility of bonding HOMO/LUMO interaction for endo- (left) and exo-(right) donor/acceptor approach for **MeOSty/oCA** (A and B) and **HSty/oCA** (C and D) dyads.

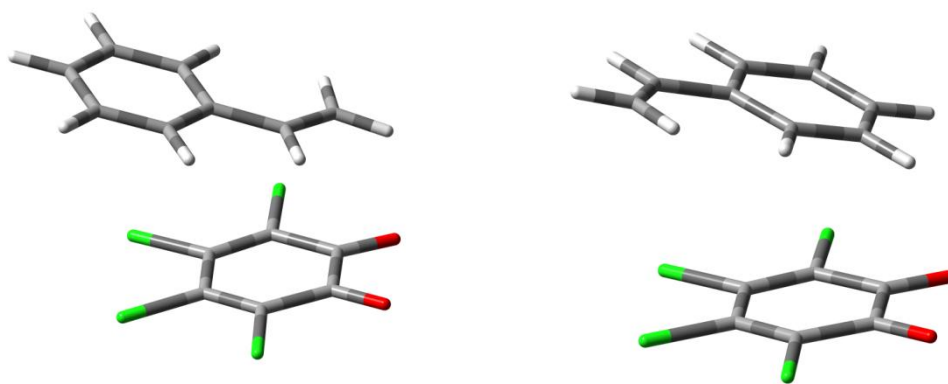


Figure S9. Alternative structures of **HSty/oCA** associates resulted from B3LYP/6-311+G(dp) optimization starting from parallel endo- and exo arrangements of **HSty** and **oCA** moieties. . Single-point calculation at MP2/6-311+G(dp) level indicate that energy of the endo-structure (left) is 1.9 kcal/mol lower than that of the exo-structure (right).

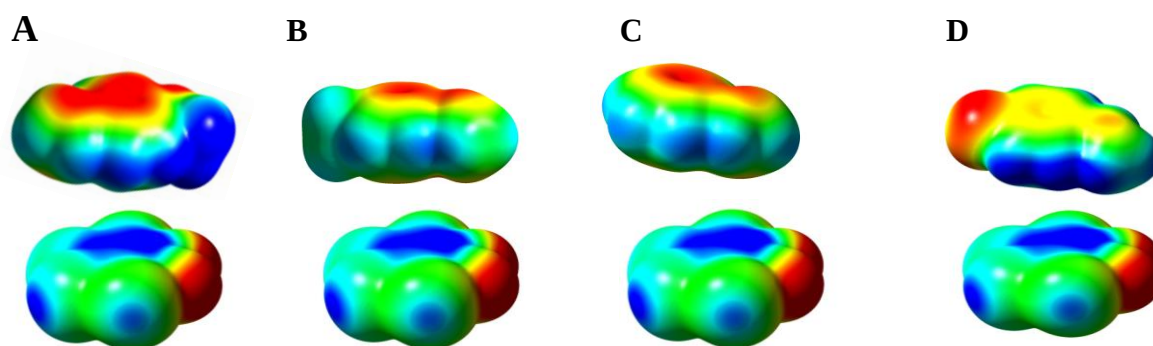


Figure S11. (A) Surface electrostatic potentials of the **MeOSty** (A), **MeSty** (B) **Sty** (C) and **ClSty** (D) donors and **oCA** acceptor (bottom). (Electrostatic potentials were calculated using cubegen/potential option on the 0.0004 electrons bohr⁻³ molecular surfaces; and visualized using GaussView 4.1 program). Note that only **MeOSty** is characterized by the area of the most positive potential (blue) located on the methoxy-substituent side of the donor. In contrast, the area of the most positive ESP of the **ClSty** donor is located on the vinyl side of the ring, while the surface of the chlorine substituent is characterized by the negative potential. For the **MeSty** (B) and **Sty** (C) donors, both sides of the rings are characterized by slightly positive potentials. Accordingly, in **MeOSty/oCA** dyad, the most favorable electrostatic attraction between donor and acceptor is expected when the methoxy-group of the styrene is arranged over the oxygen side of the **oCA** (A). For the **ClSty/oCA** dyad, the most favorable electrostatic interaction is expected when vinyl group is arranged over the oxygen side of **oCA** (D). For the **MeSty/oCA** and **Sty/oCA** pairs, the differences (if any) are less pronounced, but the endo approach (shown in B and C) seems more favorable since the most positive values of ESP for these donors are located near vinyl substituents. Most importantly, only the **MeSty/oCA** pair show clear preference for the exo-arrangement of the donor and acceptor, which makes this complex a dead-end in the Diels-Alder cycloaddition.