Electronic Supplementary Material (ESI) for RSC Advances.

Reactivity Descriptor for Retro Diels-Alder Reaction of Partially Saturated 2-Pyrones: DFT Study on Substituents and Solvents Effect

Tuhin S. Khan[1,*], Shelaka Gupta[1], Md. Imteyaz Alam[1] and M. Ali Haider[1,*]

[1] *Renewable Energy and Chemicals Laboratory, Department of Chemical Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016*

**Corresponding Author*

Tel: +91-11-26591016, Fax: +91-11-2658-2037
E-mail: suvratuhin@gmail.com , haider@iitd.ac.in

Table S1. First order rate constant (k) at 473 K corresponding to 2-pyrone rDA reaction

Entry	2-pyrone[a]	rate constant (k) (min^{-1})	log k (min^{-1})
1	DHHP	2.1	0.3
2	4-Me-DHHP	$1.3x10^{1}$	1.1
3	4-OH-DHHP	$1.3x10^{3}$	3.1
4	4-NH_2-DHHP	$1.4x10^{6}$	6.1
5	4-OMe-DHHP	$1.4x10^{3}$	3.1
6	4-CHO-DHHP	2.2	0.3
7	4-CO_2Me-DHHP	$8.2x10^{-2}$	-1.1

[a] partially saturated

Table S2. rDA reaction activation barriers and reaction energy comparison with different GGA functional and DFT-D dispersion correction

DHHP	Activation Barrier (Ea, kJ/mol)	Reaction Energy (Er, kJ/mol)
PW91	135.7	6.8
PW91+ DFT-D *	128.1	7.5
PBE	136.0	1.5
PBE+ DFT-D	129.9	5.6

4-OH-DHHP	**Activation Barrier (Ea, kJ/mol)**	**Reaction Energy (Er, kJ/mol)**
PW91	110.2	4.8
PW91+DFT-D	98.3	10.2
PBE	110.3	2.7
PBE+ DFT-D	104.3	9.5
4-CHO-DHHP	**Activation Barrier (Ea, kJ/mol)**	**Reaction Energy (Er, kJ/mol)**
PW91	138.2	-4.9
PW91+ DFT-D	130.8	-3.3
PBE	138.6	-8.1
PBE+ DFT-D	132.2	-4.5

* DFT-D refers to the Grimme dispersion correction applied to the GGA functionals.

Table S3: Vibrational modes of transition states in vapor-phase rDA reaction

Transition states	DHHP	4-Me-DHHP	4-OH-DHHP	4-NH2-DHHP	4-OMe-DHHP	4-CHO-DHHP	4-CO_2Me-DHHP
mode	Frequency (cm-1)	Frequency (cm-1)	Frequency (cm-1)	Frequency (cm-1)	Frequency (cm-1)	Frequency (cm-1)	Frequency (cm-1)
#1	-467.1	-398.1	-317	-283.3	-303.6	-450.3	-445.5
#2	119.7	81.7	58.2	95.2	75.1	79.1	59.5
#3	264.9	133.6	110.3	147.8	102.8	110.3	75.9
#4	302.3	166.5	254.9	306.2	189.7	178.8	119.8
#5	382.9	297.2	313.7	349.5	203.6	239.6	171.9
#6	396.9	309.6	346	376.3	259.1	297.9	196.3
#7	452.3	370.6	413.3	385	313.4	328	225.5
#8	582.2	390.3	472.1	422	344	372.3	297.7
#9	615.9	415.3	523.5	473.8	367	392.6	309.9
#10	663.5	520	549.3	527	412.4	471.3	334.2
#11	704.9	559.1	564.1	544.8	486.3	541.1	352.0
#12	852.3	604.6	656.7	586	549.4	595.4	404.6
#13	902.7	681.2	688.7	683.7	556.8	673	435.2
#14	954.4	728.2	755.7	705.6	636.8	698.2	485.4
#15	976.7	819.2	835.3	783.7	683.8	750.4	525.5
#16	1003.5	893.2	874.9	871.1	742.5	831.4	606.9
#17	1036.8	922.2	899	908.2	823.9	893.6	657.7

#18	1054.2	974.1	985.4	914.8	879.9	923.6	682.4
#19	1113.9	988	1013.5	971.3	901.8	991.1	711.5
#20	1188.7	996.5	1104.6	1013.4	964.8	998.1	802.3
#21	1223.2	1017.9	1172.9	1048.4	985.7	1011.9	833.9
#22	1279.7	1054.1	1189.6	1086.9	1024.1	1040.7	902.1
#23	1403.4	1094.8	1239.8	1115.7	1033.7	1071.9	934.3
#24	1469.4	1191.5	1251.5	1220	1097.1	1192.8	952.6
#25	1518.1	1246.3	1324.4	1279.3	1141.8	1230.3	976.2
#26	1542	1289.1	1403.3	1384.6	1176.2	1279.3	999.6
#27	1785.4	1361	1415.7	1417.1	1203.1	1349.5	1039.1
#28	3053.5	1380.9	1524.4	1481	1264.7	1399.3	1067.7
#29	3143.5	1429.9	1592.1	1507	1336.5	1468.4	1140.4
#30	3162.5	1441.9	1723.2	1579.9	1373.9	1493.7	1147.3
#31	3173.2	1475	2910.6	1632.7	1433.5	1555	1191.0
#32	3183.1	1489.6	2973	1721.7	1452	1719.8	1208.2
#33	3254.2	1555.4	3062	3053.2	1462.1	1770.1	1246.5
#34		1758.1	3118.3	3135.7	1468.6	2898.9	1297.9
#35		3004.5	3184.3	3165.4	1482.2	3056.9	1373.6
#36		3061.2	3625.4	3175	1576	3137.7	1440.0
#37		3062.1		3265.6	1756.2	3154.8	1455.5
#38		3113.5		3508.4	3006.3	3161.8	1464.7
#39		3128.2		3633.1	3064.6	3230.5	1467.0
#40		3143.1			3090		1480.9
#41		3164.1			3152.6		1558.1
#42		3238.1			3159.7		1721.7
#43					3165.4		1776.5
#44					3171.7		3037.0
#45					3245.5		3044.9
#46							3119.9
#47							3136.8
#48							3178.3
#49							3191.0
#50							3201.4
#51							3238.2

Table S4: Dipole moment of the transition states

Molecule	TS dipole moment (debye)
DHHP	5.07
4-Me-DHHP	5.64
4-OH-DHHP	6.14
4-NH2-DHHP	7.44
4-OMe-DHHP	7.63
4-CHO-DHHP	3.68

Table S5: Scaling parameters for the fitted lines used in the article:

Molecule	Slope	Constant/Intercept	R^2
Activation energy vs FMO gap (Figure 3)	0.37	- 51.21	0.96
Activation energy vs $\frac{IP_{diene} + EA_{CO_2}}{2}$ (Figure 4)	0.74	- 141.33	0.90
FMO gap vs $\frac{IP_{diene} + EA_{CO_2}}{2}$ (Figure S5)	0.79	-159.19	0.9
$E_{a(vapor-phase)} - E_{a(H2O)}$ vs $\delta Charge_{TS}$	923.85	- 515.04	0.94
$E_{a(vapor-phase)} - E_{a(H2O)}$ vs "$\delta Charge_{Reactant}$-$\delta Charge_{TS}$"	-549.77	122.44	0.98

Table S6: Scaling parameters for the fitted lines in activation energy and FMO gap:

Ea vs FMO	slope	intercept	R^2
vapor-phase	0.38	-55.25	0.96
n-hexane	0.45	-96.69	0.96
benzene	0.48	-109.05	0.96
acetone	0.63	-191.05	0.94
methanol	0.63	-195.45	0.94
water	0.64	-200.98	0.94

Table S7: Scaling parameters for the fitted lines in activation energy and $\frac{IP_{diene} + EA_{CO_2}}{2}$:

Ea vs $\frac{IP_{diene} + EA_{CO_2}}{2}$	slope	intercept	R^2
vapor-phase	0.79	-159.19	0.9
n-hexane	0.96	-244.5	0.92

benzene	1.01	-243.67	0.92
acetone	1.33	-368.89	0.92
methanol	1.35	-376.9	0.92
water	1.37	-385.38	0.92

Table S8: Mullikan change on C6 and O1 atoms of reactant, product and transition state corresponding to rDA of DHHP, 4-Me-DHHP, 4-OH-DHHP, 4-NH_2-DHHP, 4-OMe-DHHP, 4-CHO-DHHP, 4-CO_2Me-DHHP

Atom	charge	charge	charge
DHHP	Reactant	Product	Transition state
C6	0.11	-0.20	-0.04
O1	-0.45	-0.28	-0.39
4-Me-DHHP	Reactant	Product	Transition state
C6	0.11	-0.18	-0.04
O1	-0.44	-0.29	-0.40
4-OH-DHHP	Reactant	Product	Transition state
C6	0.11	-0.21	-0.04
O1	-0.44	-0.30	-0.42
4-NH2-DHHP	Reactant	Product	Transition state
C6	0.10	-0.18	-0.04
O1	-0.43	-0.28	-0.43
4-OMe-DHHP	Reactant	Product	Transition state
C6	0.10	-0.21	-0.06
O1	-0.43	-0.29	-0.43
4-CHO-DHHP	Reactant	Product	Transition state
C6	0.11	-0.19	-0.03
O1	-0.45	-0.29	-0.37
4-CO_2Me-DHHP	Reactant	Product	Transition state
C6	0.11	-0.18	-0.04
O1	-0.45	-0.283	-0.387

Geometry of Reactant, Product and Transition states:

Table S9: Geometry of DHHP – Reactant, Product and Transition state

DHHP		Reactant				Product				Transition State		
#	ATOM	X	Y	Z		X	Y	Z		X	Y	Z
1	H	-2.20	0.23	-0.91		-2.75	-0.85	0.22		0.00	-0.10	0.32
2	C	-1.54	0.20	-0.02		-1.68	-0.69	0.07		1.04	-0.25	0.61

3	O	-0.74	1.40	-0.09		-0.68	3.11	-0.22		2.01	1.48	-0.33
4	C	0.63	1.40	-0.07		0.40	3.56	-0.20		3.25	1.38	-0.32
5	C	1.37	0.08	0.02		1.40	-0.60	0.26		3.81	0.00	0.62
6	C	0.53	-1.15	0.06		0.63	-1.61	-0.18		3.18	-1.16	0.10
7	C	-0.80	-1.08	0.04		-0.82	-1.71	0.00		1.79	-1.27	0.06
8	H	2.02	0.16	0.90		0.99	0.22	0.84		3.44	0.36	1.58
9	H	-1.41	-1.98	0.08		-1.22	-2.73	0.06		1.33	-2.00	-0.61
10	O	1.21	2.46	-0.13		1.49	4.00	-0.17		4.20	2.03	-0.75
11	H	-2.19	0.32	0.85		-1.35	0.35	-0.05		1.36	0.28	1.50
12	H	2.07	0.06	-0.83		2.48	-0.59	0.07		4.90	0.03	0.56
13	H	1.04	-2.11	0.11		1.11	-2.44	-0.70		3.78	-1.87	-0.49

Table S10: Geometry of 4-Me-DHHP – Reactant, Product and Transition state

4-Me-DHHP		Reactant				Product				Transition State		
#	ATOM	X	Y	Z		X	Y	Z		X	Y	Z
1	H	-2.42	0.37	-0.33		-2.76	-0.48	0.87		-2.68	0.19	0.43
2	C	-1.53	0.33	0.31		-1.74	-0.35	0.52		-1.63	0.06	0.69
3	O	-0.73	1.47	-0.11		-0.72	3.35	-0.33		-0.58	1.54	-0.63
4	C	0.63	1.41	-0.21		0.45	3.47	-0.46		0.65	1.33	-0.62
5	C	1.33	0.10	0.07		1.30	-0.12	0.35		1.13	0.17	0.57
6	C	0.47	-1.13	0.10		0.58	-1.25	0.24		0.46	-1.06	0.30
7	C	-0.86	-0.99	0.21		-0.82	-1.32	0.66		-0.95	-1.08	0.34
8	H	1.86	0.22	1.03		0.88	0.78	0.80		0.80	0.71	1.46
9	H	-1.51	-1.87	0.26		-1.14	-2.28	1.09		-1.48	-1.90	-0.16
10	O	1.23	2.42	-0.52		1.61	3.60	-0.57		1.62	1.78	-1.22
11	H	-1.86	0.54	1.34		-1.49	0.60	0.05		-1.25	0.77	1.41
12	H	2.13	0.01	-0.68		2.34	-0.07	0.01		2.22	0.13	0.51
13	C	1.16	-2.45	0.01		1.17	-2.53	-0.29		1.22	-2.21	-0.28
14	H	1.73	-2.54	-0.93		2.22	-2.40	-0.60		1.81	-1.87	-1.14
15	H	0.46	-3.29	0.07		0.60	-2.90	-1.15		0.56	-3.03	-0.59
16	H	1.89	-2.57	0.82		1.14	-3.32	0.47		1.94	-2.60	0.45

Table S11: Geometry of 4-OH-DHHP – Reactant, Product and Transition state

4-OH-DHHP		Reactant				Product				Transition State		
#	ATOM	X	Y	Z		X	Y	Z		X	Y	Z

1	H	-2.45	0.39	-0.80		-2.92	-0.61	0.09		-2.82	0.19	-0.02
2	C	-1.70	0.36	0.00		-1.85	-0.43	0.03		-1.79	0.09	0.33
3	O	-0.91	1.56	-0.19		-0.84	3.23	-0.48		-0.72	1.78	-0.68
4	C	0.45	1.58	-0.14		0.29	3.51	-0.37		0.52	1.66	-0.52
5	C	1.20	0.27	0.08		1.20	-0.27	0.44		0.97	0.37	0.50
6	C	0.38	-0.97	0.02		0.48	-1.33	0.04		0.37	-0.86	0.06
7	C	-0.96	-0.93	-0.01		-0.98	-1.45	0.09		-1.02	-0.97	-0.08
8	H	1.72	0.36	1.04		0.71	0.58	0.90		0.58	0.73	1.46
9	H	-1.54	-1.84	-0.04		-1.35	-2.48	0.16		-1.41	-1.74	-0.74
10	O	1.04	2.63	-0.27		1.43	3.78	-0.25		1.50	2.31	-0.89
11	O	1.04	-2.17	0.04		1.04	-2.49	-0.46		1.11	-1.84	-0.50
12	H	-2.24	0.51	0.95		-1.52	0.60	-0.10		-1.52	0.73	1.16
13	H	2.00	0.25	-0.69		2.29	-0.25	0.35		2.07	0.37	0.51
14	H	2.00	-2.00	0.00		2.01	-2.40	-0.43		2.06	-1.60	-0.43

Table S12: Geometry of 4-NH_2-DHHP – Reactant, Product and Transition state

4-NH_2-DHHP		Reactant				Product				Transition State		
#	ATOM	X	Y	Z		X	Y	Z		X	Y	Z
1	H	-2.65	0.69	-0.32		-2.89	-0.21	0.23		-2.86	0.45	0.15
2	C	-1.68	0.61	0.18		-1.82	-0.24	0.45		-1.82	0.31	0.45
3	O	-0.91	1.74	-0.34		-0.88	3.48	-0.33		-0.71	1.95	-0.61
4	C	0.45	1.71	-0.27		0.19	3.92	-0.52		0.53	1.73	-0.52
5	C	1.07	0.45	0.32		1.22	-0.12	0.29		0.94	0.49	0.52
6	C	0.31	-0.80	0.00		0.45	-1.18	-0.02		0.29	-0.75	0.11
7	C	-1.03	-0.71	-0.08		-1.01	-1.09	-0.21		-1.12	-0.79	0.03
8	H	1.12	0.58	1.41		0.78	0.88	0.34		0.58	0.84	1.49
9	H	-1.67	-1.57	-0.31		-1.43	-1.78	-0.93		-1.59	-1.54	-0.60
10	N	1.06	-1.96	-0.11		0.97	-2.45	-0.29		1.04	-1.75	-0.40
11	H	0.57	-2.76	-0.51		0.40	-3.22	0.05		0.61	-2.52	-0.89
12	H	1.98	-1.85	-0.52		1.94	-2.57	-0.02		2.04	-1.62	-0.52
13	O	1.10	2.65	-0.65		1.26	4.37	-0.71		1.52	2.27	-1.02
14	H	-1.84	0.81	1.25		-1.45	0.44	1.21		-1.48	0.95	1.26
15	H	2.11	0.42	-0.03		2.29	-0.21	0.46		2.03	0.44	0.53

Table S13: Geometry of 4-OMe-DHHP – Reactant, Product and Transition state

4-OMe-DHHP		Reactant				Product				Transition State		
#	ATOM	X	Y	Z		X	Y	Z		X	Y	Z
1	H	-2.55	1.19	-0.40		-2.83	0.31	0.27		-2.83	1.04	0.16

2	C	-1.61	1.13	0.16		-1.76	0.29	0.08		-1.80	0.93	0.48
3	O	-0.82	2.25	-0.36		-0.67	4.08	-0.25		-0.61	2.45	-0.80
4	C	0.54	2.22	-0.25		0.33	4.67	-0.39		0.62	2.28	-0.60
5	C	1.17	0.97	0.33		1.30	0.31	0.47		0.98	1.09	0.58
6	C	0.38	-0.27	0.08		0.48	-0.75	0.44		0.32	-0.15	0.31
7	C	-0.96	-0.20	-0.01		-0.98	-0.68	0.58		-1.09	-0.19	0.17
8	H	1.29	1.13	1.41		0.90	1.30	0.66		0.62	1.60	1.48
9	H	-1.60	-1.06	-0.20		-1.44	-1.49	1.16		-1.56	-1.00	-0.38
10	O	1.17	-1.38	-0.04		1.04	-2.02	0.39		1.13	-1.16	-0.03
11	C	0.48	-2.61	-0.27		0.42	-2.95	-0.50		0.54	-2.41	-0.47
12	H	1.26	-3.38	-0.31		0.94	-3.90	-0.37		1.39	-3.08	-0.61
13	H	-0.07	-2.58	-1.21		0.52	-2.62	-1.55		0.01	-2.27	-1.42
14	H	-0.21	-2.83	0.56		-0.65	-3.09	-0.28		-0.14	-2.81	0.30
15	O	1.18	3.18	-0.61		1.34	5.26	-0.53		1.65	2.81	-1.01
16	H	-1.84	1.36	1.21		-1.34	1.09	-0.53		-1.44	1.68	1.18
17	H	2.18	0.88	-0.09		2.37	0.18	0.35		2.07	1.00	0.59

Table S14: Geometry of 4-CHO-DHHP – Reactant, Product and Transition state

4-CHO-DHHP		Reactant				Product				Transition State		
#	ATOM	X	Y	Z		X	Y	Z		X	Y	Z
1	H	-2.54	0.66	-0.66		-2.82	-0.17	-0.85		-2.68	0.09	-1.11
2	C	-1.75	0.59	0.11		-1.84	-0.10	-0.38		-1.89	-0.02	-0.37
3	O	-0.98	1.81	-0.01		-0.89	3.30	0.00		-0.75	1.84	-0.68
4	C	0.39	1.83	-0.01		0.15	3.84	-0.06		0.34	1.84	-0.07
5	C	1.15	0.53	0.10		1.06	-0.11	0.66		0.54	0.44	0.95
6	C	0.34	-0.72	-0.05		0.39	-1.14	0.11		0.33	-0.73	0.15
7	C	-1.00	-0.67	-0.03		-0.96	-1.11	-0.46		-0.87	-0.94	-0.53
8	H	1.66	0.55	1.08		0.64	0.89	0.74		-0.26	0.68	1.66
9	H	-1.57	-1.60	-0.12		-1.24	-2.02	-0.98		-0.88	-1.66	-1.35
10	C	1.04	-2.02	-0.21		1.10	-2.44	0.06		1.50	-1.60	-0.16
11	O	0.48	-3.10	-0.30		0.65	-3.47	-0.43		1.41	-2.66	-0.76
12	H	2.15	-1.95	-0.24		2.12	-2.42	0.51		2.48	-1.22	0.22
13	O	0.95	2.90	-0.10		1.20	4.37	-0.12		1.29	2.60	0.06
14	H	-2.27	0.63	1.09		-1.62	0.83	0.14		-2.07	0.48	0.58
15	H	1.96	0.58	-0.64		2.06	-0.26	1.06		1.53	0.54	1.40

Table S15: Geometry of 4-CO_2Me-DHHP – Reactant, Product and Transition state

4-CO_2Me-DHHP		Reactant		Product		Transition State

#	ATOM	X	Y	Z		X	Y	Z		X	Y	Z
1	H	-2.32	0.24	-0.98		-1.46	0.81	0.21		-2.01	-0.53	-1.11
2	C	-1.69	0.24	-0.08		-1.75	-0.21	-0.06		-1.79	-1.33	-0.41
3	O	-1.07	1.55	-0.02		-0.82	3.87	0.36		-1.61	0.42	0.93
4	C	0.29	1.73	0.04		0.36	3.93	0.37		-0.53	1.02	0.76
5	C	1.21	0.53	0.06		1.21	0.19	-0.66		0.38	0.40	-0.60
6	C	0.55	-0.81	-0.02		0.60	-0.98	-0.36		0.57	-1.01	-0.40
7	C	-0.78	-0.93	-0.08		-0.85	-1.17	-0.33		-0.53	-1.86	-0.27
8	H	1.82	0.62	0.96		2.29	0.28	-0.65		1.29	1.00	-0.64
9	H	-1.24	-1.91	-0.13		-1.19	-2.19	-0.52		-0.37	-2.84	0.17
10	O	0.71	2.86	0.08		1.53	3.99	0.36		0.04	1.98	1.26
11	C	1.37	-2.06	-0.02		1.40	-2.22	-0.10		1.91	-1.58	-0.07
12	H	-2.38	0.19	0.78		-2.82	-0.43	-0.07		-2.66	-1.84	0.00
13	H	1.92	0.67	-0.77		0.62	1.06	-0.93		-0.34	0.67	-1.37
14	O	2.70	-1.76	0.06		2.73	-1.98	0.01		2.88	-0.64	-0.03
15	O	0.93	-3.19	-0.08		0.92	-3.33	0.00		2.11	-2.77	0.12
16	C	3.57	-2.92	0.07		3.54	-3.16	0.23		4.20	-1.15	0.30
17	H	3.42	-3.52	-0.83		3.43	-3.86	-0.61		4.52	-1.88	-0.45
18	H	3.36	-3.54	0.95		3.24	-3.66	1.16		4.19	-1.62	1.28
19	H	4.58	-2.52	0.11		4.57	-2.80	0.30		4.85	-0.27	0.30

Table 16. Absolute Energies (Total Energies) of the Reactant, Product and Transition states

Solvent	vapor-phase	n-hexane	benzene	acetone	methanol	water
Molecules	Energy (Ha)	Energy (Ha)	Energy (Ha)	Energy (Ha)	Energy (Ha)	Energy (Ha)
DHHP	-344.590	-344.595	-344.596	-344.604	-344.604	-344.605
DHHP-butadiene	-155.968	-155.969	-155.970	-155.972	-155.972	-155.972
DHHP-TS	-344.539	-344.544	-344.546	-344.556	-344.557	-344.558
4-Me-DHHP	-383.905	-383.910	-383.911	-383.919	-383.919	-383.920
2-Me-1,3-butadiene	-195.282	-195.283	-195.283	-195.285	-195.285	-195.285
4-Me-DHHP-TS	-383.856	-383.862	-383.864	-383.876	-383.877	-383.878
4-OH-DHHP	-419.835	-419.842	-419.843	-419.853	-419.854	-419.854
2-OH-1,3-butadiene	-231.214	-231.217	-231.218	-231.222	-231.222	-231.223

4-OH-DHHP-TS	-419.793	-419.803	-419.805	-419.822	-419.823	-419.825
4-NH_2-DHHP	-399.960	-399.967	-399.969	-399.979	-399.979	-399.980
2-NH_2-1,3-butadiene	-211.334	-211.337	-211.338	-211.343	-211.343	-211.344
4-NH_2-DHHP-TS	-399.928	-399.939	-399.942	-399.961	-399.962	-399.963
4-CHO-DHHP	-457.929	-457.935	-457.937	-457.948	-457.948	-457.949
2-CHO-1,3-butadiene	-269.311	-269.314	-269.315	-269.319	-269.320	-269.320
4-CHO-DHHP-TS	-457.876	-457.883	-457.884	-457.895	-457.896	-457.896
4-OMe-DHHP	-459.130	-459.135	-459.137	-459.145	-459.146	-459.146
2-OMe-1,3-butadiene	-270.508	-270.510	-270.511	-270.514	-270.514	-270.514
4-OMe-DHHP-TS	-459.087	-459.096	-459.098	-459.114	-459.115	-459.116
4-CO2Me-DHHP	-572.500	-572.506	-572.508	-572.518	-572.519	-572.519
2-CO_2Me-1,3-butadiene	-383.876	-383.879	-383.880	-383.884	-383.885	-383.885
4-CO_2OMe-DHHP-TS	-572.444	-572.451	-572.453	-572.464	-572.465	-572.466
CO_2	-188.620	-188.621	-188.621	-188.623	-188.623	-188.623

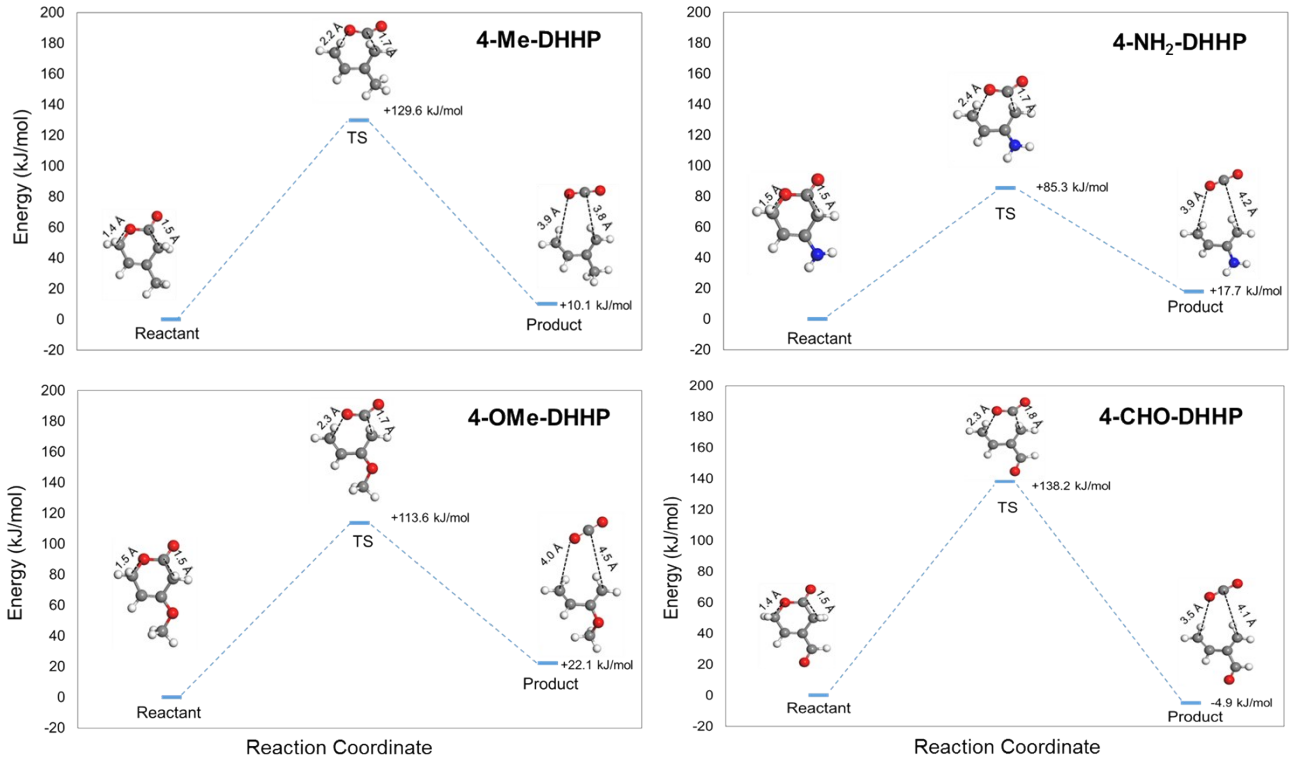

Figure S1. Reaction diagram for rDA reaction of 4-Me-DHHP, 4-NH_2-DHHP, 4-OMe-DHHP and 4-CHO-DHHP in vapor phase.

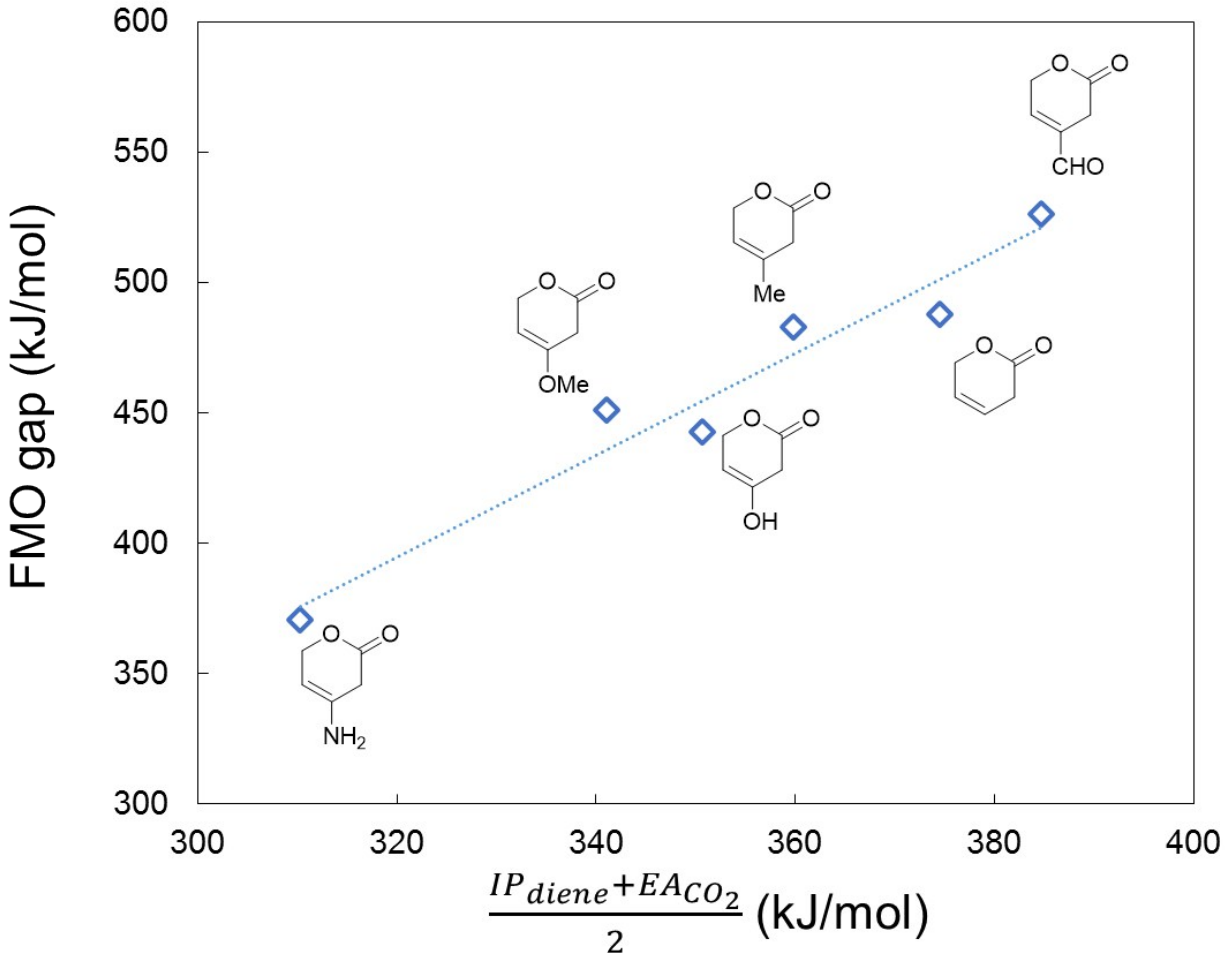

Figure S2. Scaling relation plot for $\frac{IP_{diene} + EA_{CO_2}}{2}$ and FMO gap of rDA reaction of partially saturated 2-pyrones.

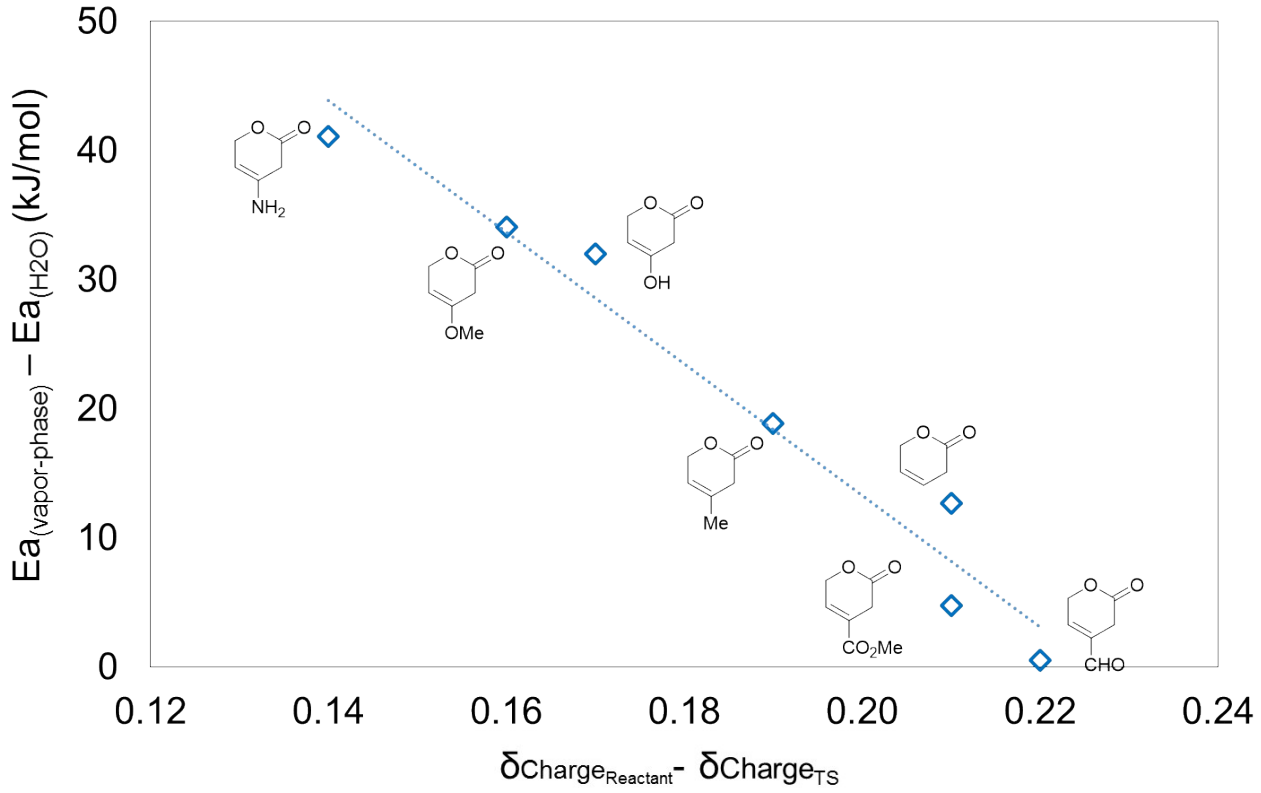

Figure S3. Scaling relationship plot between "$\delta Charge_{Reactant}$- $\delta Charge_{TS}$" and change in activation barrier (Table 5) due to solvent for partially saturated 2-pyrones molecules

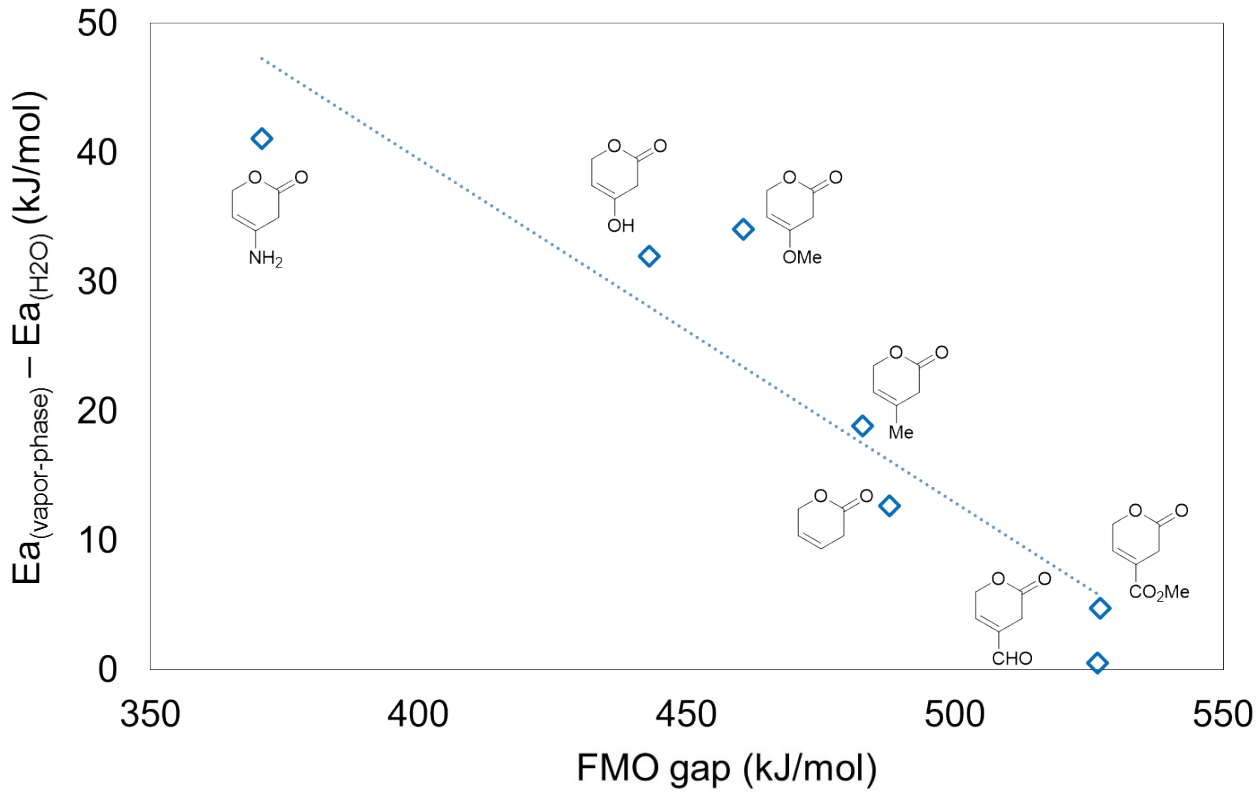

Figure S4. Scaling relationship plot between FMO gap and change in activation barrier (Table 5) due to solvent for partially saturated 2-pyrones molecules

References:

1 S. Gupta, M. I. Alam, T. S. Khan, N. Sinha and M. A. Haider, *RSC Adv.*, 2016, **6**, 60433–60445.