Supporting Information

Theoretical Exploration of the Diene-Transmissive Hetero-Diels-Alder Strategy Toward Boron-Functionalized Octahydroquinolines

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1. Duals descriptor of the reactants

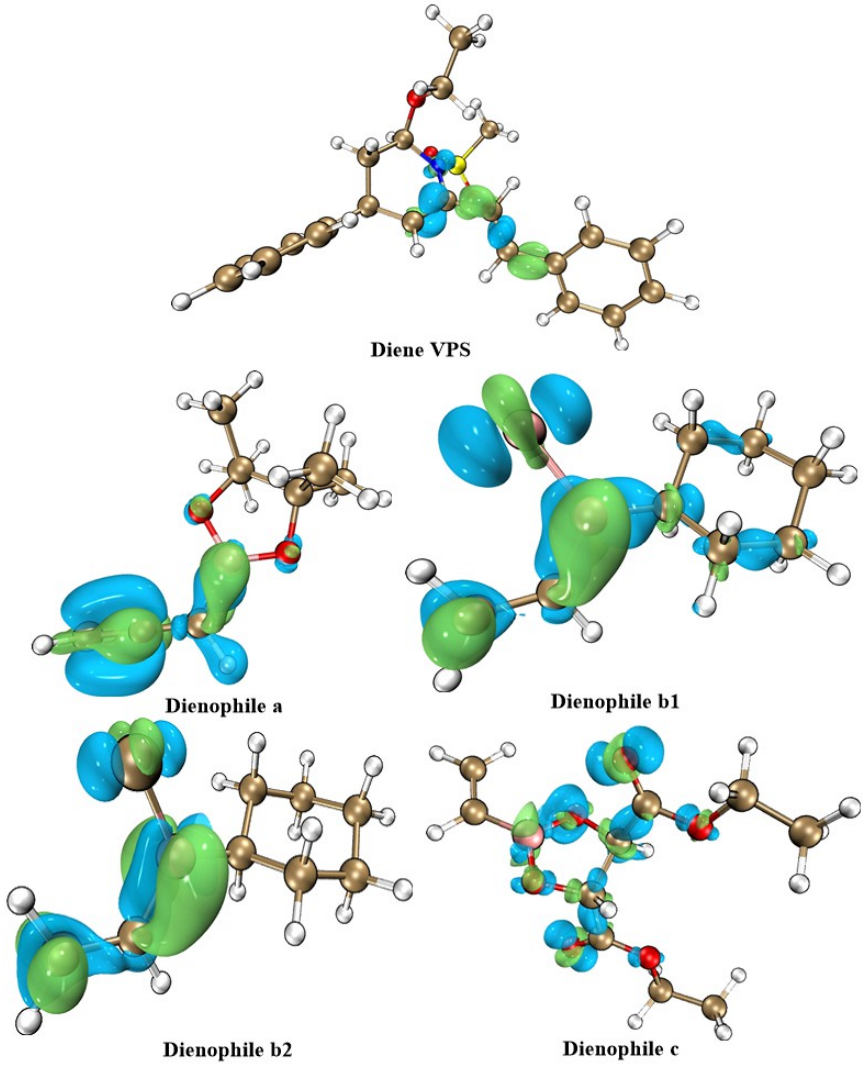

Figure S1: Isosurface (0.005) of the dual descriptor of VPS and dienophiles a, b1, b2, and c. Blue indicates positive regions, while green indicates negative regions.

2. Energies of the reaction of VPS with a

- Gas phase 25 °C

*Table S1: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **a** in the prox approach, according to wB97XD/6-311G(d,p) calculations in the gas phase at 25 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P1-r1-en-f1	-58.87	-35.99	-54.57	-62.33
P1-r1-ex-f1	-53.57	-29.40	-48.83	-65.16
P1-r2-en-f1	-52.89	-31.02	-48.68	-59.23
P1-r2-ex-f1	-55.57	-32.39	-50.94	-62.21
TS1-r1-en-f1	13.75	31.81	14.96	-56.49
TS1-r1-ex-f1	13.07	31.18	14.07	-57.40
TS1-r2-en-f1	11.61	29.32	12.62	-55.99
TS1-r2-ex-f1	10.19	27.97	11.22	-56.18
P1-r1-en-f2	-61.02	-35.38	-56.13	-69.59
P1-r1-ex-f2	-56.68	-33.55	-52.39	-63.20
P1-r2-en-f2	-51.68	-27.85	-47.28	-65.18
P1-r2-ex-f2	-52.46	-29.75	-48.10	-61.52
TS1-r1-en-f2	13.68	32.87	14.92	-60.21
TS1-r1-ex-f2	13.42	31.10	14.32	-56.27
TS1-r2-en-f2	14.62	35.03	16.04	-63.69
TS1-r2-ex-f2	17.11	36.08	18.28	-59.69

*Table S2: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **a** in the dis approach, according to wB97XD/6-311G(d,p) calculations in the gas phase at 25 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P1-r1-E-f1	-60.78	-37.14	-55.60	-61.90
P1-r1-Z-f1	-60.08	-36.92	-54.89	-60.28
P1-r2-E-f1	-55.16	-34.32	-50.78	-55.21
P1-r2-Z-f1	-52.44	-30.92	-47.97	-57.21
TS1-r1-E-f1	16.83	31.77	17.71	-47.14
TS1-r1-Z-f1	22.93	39.26	23.85	-51.69
TS1-r2-E-f1	17.52	33.36	18.40	-50.17
TS1-r2-Z-f1	19.22	37.26	20.26	-57.02
P1-r1-E-f2	-61.49	-38.93	-56.81	-59.98
P1-r1-Z-f2	-61.32	-38.49	-56.37	-59.99
P1-r2-E-f2	-57.39	-36.52	-52.97	-55.17
P1-r2-Z-f2	-59.67	-38.29	-55.00	-56.03
TS1-r1-E-f2	20.34	38.89	21.45	-58.48
TS1-r1-Z-f2	24.11	42.35	24.93	-58.41
TS1-r2-E-f2	21.67	39.63	23.07	-55.57
TS1-r2-Z-f2	22.79	41.19	23.86	-58.13

- Toluene 25 °C

Table S3: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of VPS and a in the prox approach, according to wB97XD/6-311G(d,p) calculations in toluene at 25 C.

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P1-r1-en-f1	-56.60	-33.26	-52.22	-63.58
P1-r1-ex-f1	-51.87	-27.87	-47.15	-64.67
P1-r2-en-f1	-51.10	-28.21	-46.96	-62.88
P1-r2-ex-f1	-54.36	-31.32	-49.76	-61.85
TS1-r1-en-f1	15.85	33.92	17.14	-56.26
TS1-r1-ex-f1	14.44	32.62	15.44	-57.64
TS1-r2-en-f1	12.46	30.31	13.48	-56.43
TS1-r2-ex-f1	11.48	29.07	12.51	-55.55
P1-r1-en-f2	-59.74	-33.92	-54.83	-70.13
P1-r1-ex-f2	-54.60	-30.66	-50.33	-65.95
P1-r2-en-f2	-50.54	-26.58	-46.12	-65.54
P1-r2-ex-f2	-51.20	-29.14	-46.90	-59.59
TS1-r1-en-f2	15.34	34.24	16.64	-59.03
TS1-r1-ex-f2	14.93	33.73	15.99	-59.49
TS1-r2-en-f2	16.13	35.89	17.45	-61.84
TS1-r2-ex-f2	18.07	36.62	19.14	-58.60

*Table S4: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **a** in the dis approach, according to wB97XD/6-311G(d,p) calculations in toluene at 25 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P1-r1-E-f1	-59.30	-35.94	-54.10	-60.92
P1-r1-Z-f1	-58.73	-35.46	-53.53	-60.57
P1-r2-E-f1	-54.07	-33.37	-49.71	-54.80
P1-r2-Z-f1	-50.86	-28.69	-46.43	-59.47
TS1-r1-E-f1	17.72	32.88	18.60	-47.77
TS1-r1-Z-f1	24.41	40.61	25.30	-51.22
TS1-r2-E-f1	18.70	34.70	19.59	-50.57
TS1-r2-Z-f1	21.29	39.74	22.40	-58.04
P1-r1-E-f2	-60.65	-38.55	-55.98	-58.47
P1-r1-Z-f2	-60.37	-37.58	-55.49	-60.05
P1-r2-E-f2	-56.56	-35.06	-52.06	-57.03
P1-r2-Z-f2	-58.38	-36.39	-53.67	-57.96
TS1-r1-E-f2	20.89	38.65	22.05	-55.59
TS1-r1-Z-f2	25.10	43.24	25.89	-58.08
TS1-r2-E-f2	22.92	40.47	24.24	-54.34
TS1-r2-Z-f2	24.13	42.82	25.20	-58.98

- Toluene 70 °C

*Table S5: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **a** in the prox approach, according to wB97XD/6-311G(d,p) calculations in toluene at 70 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P1-r1-en-f1	-56.60	-32.71	-51.19	-60.51
P1-r1-ex-f1	-51.87	-27.27	-46.13	-61.63
P1-r2-en-f1	-51.10	-27.69	-45.92	-59.77
P1-r2-ex-f1	-54.36	-30.85	-48.73	-58.79
TS1-r1-en-f1	15.85	34.12	18.29	-52.80
TS1-r1-ex-f1	14.44	32.89	16.59	-54.16
TS1-r2-en-f1	12.46	30.52	14.65	-52.91
TS1-r2-ex-f1	11.48	29.25	13.68	-52.03
P1-r1-en-f2	-59.74	-33.08	-53.82	-67.11
P1-r1-ex-f2	-54.60	-30.01	-49.30	-62.87
P1-r2-en-f2	-50.54	-25.94	-45.10	-62.47
P1-r2-ex-f2	-51.20	-28.77	-45.86	-56.47
TS1-r1-en-f2	15.34	34.57	17.79	-55.57
TS1-r1-ex-f2	14.93	34.12	17.13	-56.07
TS1-r2-en-f2	16.13	36.35	18.61	-58.35
TS1-r2-ex-f2	18.07	36.93	20.31	-55.11

*Table S6: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **a** in the dis approach, according to wB97XD/6-311G(d,p) calculations in toluene at 70 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P1-r1-E-f1	-59.30	-24.76	-60.22	-80.14
P1-r1-Z-f1	-58.73	-24.28	-59.64	-79.79
P1-r2-E-f1	-54.07	-22.19	-55.83	-74.01
P1-r2-Z-f1	-50.86	-28.33	-45.40	-56.40
TS1-r1-E-f1	17.72	32.71	19.76	-44.28
TS1-r1-Z-f1	24.41	40.59	26.45	-47.76
TS1-r2-E-f1	18.70	34.65	20.75	-47.06
TS1-r2-Z-f1	21.29	40.03	23.57	-54.52
P1-r1-E-f2	-60.65	-27.37	-62.10	-77.68
P1-r1-Z-f2	-60.37	-26.40	-61.61	-79.27
P1-r2-E-f2	-56.56	-23.87	-58.18	-76.24
P1-r2-Z-f2	-58.38	-36.09	-52.66	-54.94
TS1-r1-E-f2	20.89	38.83	23.20	-52.11
TS1-r1-Z-f2	25.10	43.53	27.05	-54.58
TS1-r2-E-f2	22.92	40.59	25.39	-50.87
TS1-r2-Z-f2	24.13	43.15	26.36	-55.49

- Toluene 100 °C

*Table S7: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **a** in the prox approach, according to wB97XD/6-311G(d,p) calculations in toluene at 100 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P1-r1-en-f1	-56.60	-28.46	-52.40	-64.16
P1-r1-ex-f1	-51.87	-22.98	-47.34	-65.29
P1-r2-en-f1	-51.10	-23.46	-47.12	-63.39
P1-r2-ex-f1	-54.36	-26.65	-49.94	-62.44
TS1-r1-en-f1	15.85	38.14	17.16	-56.23
TS1-r1-ex-f1	14.44	36.95	15.46	-57.57
TS1-r2-en-f1	12.46	34.54	13.53	-56.31
TS1-r2-ex-f1	11.48	33.24	12.56	-55.42
P1-r1-en-f2	-59.74	-28.63	-55.04	-70.78
P1-r1-ex-f2	-54.60	-25.69	-50.50	-66.50
P1-r2-en-f2	-50.54	-21.63	-46.30	-66.11
P1-r2-ex-f2	-51.20	-24.64	-47.06	-60.09
TS1-r1-en-f2	15.34	38.67	16.66	-59.00
TS1-r1-ex-f2	14.93	38.24	16.00	-59.47
TS1-r2-en-f2	16.13	40.53	17.48	-61.77
TS1-r2-ex-f2	18.07	41.02	19.18	-58.51

*Table S8: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **a** in the dis approach, according to wB97XD/6-311G(d,p) calculations in toluene at 100 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P1-r1-E-f1	-59.30	-31.33	-54.34	-61.65
P1-r1-Z-f1	-58.73	-30.89	-53.76	-61.30
P1-r2-E-f1	-54.07	-29.23	-49.89	-55.36
P1-r2-Z-f1	-50.86	-24.20	-46.61	-60.05
TS1-r1-E-f1	17.72	36.43	18.65	-47.63
TS1-r1-Z-f1	24.41	44.41	25.34	-51.12
TS1-r2-E-f1	18.70	38.46	19.65	-50.39
TS1-r2-Z-f1	21.29	44.06	22.47	-57.85
P1-r1-E-f2	-60.65	-34.13	-56.19	-59.13
P1-r1-Z-f2	-60.37	-33.05	-55.71	-60.75
P1-r2-E-f2	-56.56	-30.75	-52.25	-57.64
P1-r2-Z-f2	-58.38	-32.01	-53.88	-58.62
TS1-r1-E-f2	20.89	42.79	22.10	-55.45
TS1-r1-Z-f2	25.10	47.56	25.94	-57.92
TS1-r2-E-f2	22.92	44.51	24.28	-54.22
TS1-r2-Z-f2	24.13	47.20	25.25	-58.83

- Acetonitrile 25 °C

*Table S9: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **a** in the prox approach, according to wB97XD/6-311G(d,p) calculations in acetonitrile at 25 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P1-r1-en-f1	-54.39	-31.59	-50.25	-62.47
P1-r1-ex-f1	-49.92	-26.17	-45.26	-63.93
P1-r2-en-f1	-50.66	-27.33	-46.45	-64.02
P1-r2-ex-f1	-53.01	-29.74	-48.35	-62.29
TS1-r1-en-f1	15.25	33.62	16.32	-57.91
TS1-r1-ex-f1	15.85	33.52	16.72	-56.25
TS1-r2-en-f1	12.24	29.44	13.18	-54.42
TS1-r2-ex-f1	11.89	30.16	12.88	-57.84
P1-r1-en-f2	-58.18	-32.23	-53.35	-70.73
P1-r1-ex-f2	-52.57	-29.07	-48.47	-64.94
P1-r2-en-f2	-49.05	-25.06	-44.65	-65.60
P1-r2-ex-f2	-49.57	-27.67	-45.44	-59.50
TS1-r1-en-f2	16.82	35.35	17.83	-58.65
TS1-r1-ex-f2	16.65	35.67	17.60	-60.50
TS1-r2-en-f2	17.54	37.55	18.85	-62.60
TS1-r2-ex-f2	19.17	38.18	20.31	-59.83

*Table S10: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **a** in the dis approach, according to wB97XD/6-311G(d,p) calculations in acetonitrile at 25 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P1-r1-E-f1	-57.70	-33.63	-52.60	-63.48
P1-r1-Z-f1	-56.91	-33.73	-51.84	-60.64
P1-r2-E-f1	-53.09	-31.86	-48.75	-56.54
P1-r2-Z-f1	-49.37	-26.47	-44.79	-61.31
TS1-r1-E-f1	18.45	33.93	19.33	-48.86
TS1-r1-Z-f1	26.21	43.14	27.16	-53.46
TS1-r2-E-f1	19.69	36.02	20.54	-51.78
TS1-r2-Z-f1	23.12	41.00	24.06	-56.70
P1-r1-E-f2	-59.63	-36.85	-54.98	-60.71
P1-r1-Z-f2	-59.07	-36.48	-54.26	-59.52
P1-r2-E-f2	-55.66	-33.33	-51.18	-59.76
P1-r2-Z-f2	-57.22	-35.44	-52.65	-57.60
TS1-r1-E-f2	21.35	39.71	22.39	-58.00
TS1-r1-Z-f2	26.37	44.61	27.12	-58.55
TS1-r2-E-f2	24.10	42.25	25.35	-56.56
TS1-r2-Z-f2	25.33	44.62	26.41	-60.96

- Acetonitrile 70 °C

*Table S11: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **a** in the prox approach, according to wB97XD/6-311G(d,p) calculations in acetonitrile at 70 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P1-r1-en-f1	-54.39	-28.81	-50.34	-62.74
P1-r1-ex-f1	-49.92	-23.32	-45.37	-64.26
P1-r2-en-f1	-50.66	-24.47	-46.54	-64.30
P1-r2-ex-f1	-53.01	-26.97	-48.45	-62.62
TS1-r1-en-f1	15.25	36.18	16.35	-57.81
TS1-r1-ex-f1	15.85	36.02	16.76	-56.13
TS1-r2-en-f1	12.24	31.84	13.23	-54.26
TS1-r2-ex-f1	11.89	32.72	12.92	-57.71
P1-r1-en-f2	-58.18	-29.07	-53.47	-71.09
P1-r1-ex-f2	-52.57	-26.18	-48.56	-65.23
P1-r2-en-f2	-49.05	-22.13	-44.75	-65.90
P1-r2-ex-f2	-49.57	-25.02	-45.53	-59.75
TS1-r1-en-f2	16.82	37.95	17.87	-58.52
TS1-r1-ex-f2	16.65	38.35	17.64	-60.37
TS1-r2-en-f2	17.54	40.33	18.88	-62.51
TS1-r2-ex-f2	19.17	40.84	20.34	-59.74

*Table S12: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **a** in the dis approach, according to wB97XD/6-311G(d,p) calculations in acetonitrile at 70 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P1-r1-E-f1	-57.70	-30.80	-52.72	-63.88
P1-r1-Z-f1	-56.91	-31.03	-51.97	-61.03
P1-r2-E-f1	-53.09	-29.35	-48.85	-56.84
P1-r2-Z-f1	-49.37	-23.74	-44.89	-61.64
TS1-r1-E-f1	18.45	36.09	19.36	-48.75
TS1-r1-Z-f1	26.21	45.51	27.19	-53.39
TS1-r2-E-f1	19.69	38.31	20.58	-51.65
TS1-r2-Z-f1	23.12	43.52	24.12	-56.53
P1-r1-E-f2	-59.63	-34.14	-55.10	-61.07
P1-r1-Z-f2	-59.07	-33.83	-54.38	-59.90
P1-r2-E-f2	-55.66	-30.66	-51.28	-60.09
P1-r2-Z-f2	-57.22	-32.87	-52.75	-57.94
TS1-r1-E-f2	21.35	42.29	22.42	-57.89
TS1-r1-Z-f2	26.37	47.20	27.15	-58.44
TS1-r2-E-f2	24.10	44.76	25.38	-56.46
TS1-r2-Z-f2	25.33	47.33	26.45	-60.85

- Acetonitrile 100 °C

*Table S13: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **a** in the prox approach, according to wB97XD/6-311G(d,p) calculations in acetonitrile at 100 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P1-r1-en-f1	-54.39	-26.92	-50.40	-62.90
P1-r1-ex-f1	-49.92	-21.39	-45.44	-64.46
P1-r2-en-f1	-50.66	-22.54	-46.60	-64.46
P1-r2-ex-f1	-53.01	-25.08	-48.52	-62.81
TS1-r1-en-f1	15.25	37.92	16.36	-57.76
TS1-r1-ex-f1	15.85	37.70	16.78	-56.07
TS1-r2-en-f1	12.24	33.47	13.25	-54.19
TS1-r2-ex-f1	11.89	34.45	12.94	-57.65
P1-r1-en-f2	-58.18	-26.94	-53.54	-71.30
P1-r1-ex-f2	-52.57	-24.22	-48.62	-65.40
P1-r2-en-f2	-49.05	-20.15	-44.81	-66.08
P1-r2-ex-f2	-49.57	-23.23	-45.58	-59.90
TS1-r1-en-f2	16.82	39.71	17.89	-58.46
TS1-r1-ex-f2	16.65	40.16	17.66	-60.31
TS1-r2-en-f2	17.54	42.21	18.89	-62.47
TS1-r2-ex-f2	19.17	42.63	20.35	-59.70

*Table S14: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **a** in the dis approach, according to wB97XD/6-311G(d,p) calculations in acetonitrile at 100 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P1-r1-E-f1	-57.70	-28.88	-52.81	-64.11
P1-r1-Z-f1	-56.91	-29.19	-52.06	-61.27
P1-r2-E-f1	-53.09	-27.64	-48.92	-57.02
P1-r2-Z-f1	-49.37	-21.89	-44.97	-61.84
TS1-r1-E-f1	18.45	37.55	19.38	-48.71
TS1-r1-Z-f1	26.21	47.11	27.19	-53.36
TS1-r2-E-f1	19.69	39.86	20.60	-51.60
TS1-r2-Z-f1	23.12	45.21	24.14	-56.46
P1-r1-E-f2	-59.63	-32.31	-55.18	-61.29
P1-r1-Z-f2	-59.07	-32.03	-54.46	-60.13
P1-r2-E-f2	-55.66	-28.86	-51.36	-60.29
P1-r2-Z-f2	-57.22	-31.13	-52.83	-58.15
TS1-r1-E-f2	21.35	44.02	22.44	-57.84
TS1-r1-Z-f2	26.37	48.96	27.17	-58.39
TS1-r2-E-f2	24.10	46.45	25.40	-56.42
TS1-r2-Z-f2	25.33	49.15	26.46	-60.80

3. Energies of the reaction of VPS with b1

- Gas phase 25 °C

*Table S15: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **b1** according to wB97XD/6-311G(d,p) calculations in the gas phase at 25 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P2-r1-en-f1	-45.22	-22.10	-41.09	-18.99
P2-r1-en-f2	-45.46	-21.71	-42.11	-20.40
P2-r1-ex-f1	-48.38	-25.01	-44.93	-19.93
P2-r1-ex-f2	-44.95	-21.71	-41.99	-21.31
P2-r2-en-f1	-45.25	-22.49	-42.07	-19.58
P2-r2-en-f2	-50.23	-28.07	-46.26	-18.19
P2-r2-ex-f1	-45.81	-22.95	-41.61	-18.66
P2-r2-ex-f2	-50.09	-27.38	-46.09	-18.71
TS2-r1-en-f1	6.57	25.92	7.76	-18.17
TS2-r1-en-f2	17.44	36.40	18.47	-17.93
TS2-r1-ex-f1	4.80	23.90	5.87	-18.02
TS2-r1-ex-f2	13.07	32.03	14.05	-17.98
TS2-r2-en-f1	4.94	23.55	5.88	-17.67
TS2-r2-en-f2	9.03	28.02	10.13	-17.89
TS2-r2-ex-f1	3.52	22.18	4.64	-17.54
TS2-r2-ex-f2	9.94	28.74	11.00	-17.74

- Toluene 25 °C

*Table S16: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **b1** according to wB97XD/6-311G(d,p) calculations in toluene at 25 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P2-r1-en-f1	-46.86	-23.69	-42.71	-19.02
P2-r1-en-f2	-44.17	-21.84	-40.37	-18.53
P2-r1-ex-f1	-46.60	-24.66	-42.73	-18.06
P2-r1-ex-f2	-48.87	-26.33	-44.82	-18.49
P2-r2-en-f1	-43.99	-22.01	-40.21	-18.20
P2-r2-en-f2	-49.34	-26.99	-45.35	-18.36
P2-r2-ex-f1	-35.12	-12.55	-30.71	-18.16
P2-r2-ex-f2	-48.56	-26.34	-44.68	-18.34
TS2-r1-en-f1	7.75	26.86	8.97	-17.89
TS2-r1-en-f2	17.75	36.12	18.77	-17.35
TS2-r1-ex-f1	6.30	24.57	7.20	-17.38
TS2-r1-ex-f2	13.69	32.47	14.72	-17.76
TS2-r2-en-f1	5.75	24.14	6.63	-17.50
TS2-r2-en-f2	8.63	27.92	9.83	-18.09
TS2-r2-ex-f1	3.86	22.30	4.93	-17.37
TS2-r2-ex-f2	9.67	28.34	10.78	-17.56

- Toluene 70 °C

*Table S17: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **b1** according to wB97XD/6-311G(d,p) calculations in toluene at 70 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P2-r1-en-f1	-46.86	-20.65	-42.85	-22.20
P2-r1-en-f2	-44.17	-18.88	-40.50	-21.62
P2-r1-ex-f1	-46.61	-21.75	-42.85	-21.10
P2-r1-ex-f2	-48.87	-23.35	-44.95	-21.60
P2-r2-en-f1	-44.00	-19.06	-40.32	-21.26
P2-r2-en-f2	-49.35	-24.01	-45.48	-21.46
P2-r2-ex-f1	-44.86	-20.50	-40.97	-20.47
P2-r2-ex-f2	-48.57	-23.35	-44.81	-21.46
TS2-r1-en-f1	7.74	29.75	8.95	-20.80
TS2-r1-en-f2	17.75	38.91	18.75	-20.16
TS2-r1-ex-f1	6.29	27.41	7.18	-20.24
TS2-r1-ex-f2	13.68	35.32	14.71	-20.61
TS2-r2-en-f1	5.74	26.97	6.63	-20.34
TS2-r2-en-f2	8.62	30.82	9.82	-21.00
TS2-r2-ex-f1	3.86	25.15	4.92	-20.24
TS2-r2-ex-f2	9.66	31.19	10.77	-20.41

- Toluene 100 °C

*Table S18: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **b1** according to wB97XD/6-311G(d,p) calculations in toluene at 100 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P2-r1-en-f1	-46.86	-18.68	-42.91	-24.23
P2-r1-en-f2	-44.17	-16.96	-40.55	-23.59
P2-r1-ex-f1	-46.61	-19.86	-42.90	-23.04
P2-r1-ex-f2	-48.87	-21.42	-45.01	-23.59
P2-r2-en-f1	-44.00	-17.15	-40.37	-23.22
P2-r2-en-f2	-49.35	-22.08	-45.53	-23.45
P2-r2-ex-f1	-44.86	-18.64	-41.02	-22.38
P2-r2-ex-f2	-48.57	-21.42	-44.87	-23.45
TS2-r1-en-f1	7.74	31.61	8.96	-22.65
TS2-r1-en-f2	17.75	40.70	18.76	-21.94
TS2-r1-ex-f1	6.29	29.25	7.19	-22.06
TS2-r1-ex-f2	13.68	37.15	14.73	-22.43
TS2-r2-en-f1	5.74	28.80	6.65	-22.15
TS2-r2-en-f2	8.62	32.69	9.84	-22.85
TS2-r2-ex-f1	3.86	26.99	4.93	-22.06
TS2-r2-ex-f2	9.66	33.02	10.79	-22.23

- Acetonitrile 25 °C

*Table S19: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **b1** according to wB97XD/6-311G(d,p) calculations in acetonitrile at 25 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P2-r1-en-f1	-46.58	-23.52	-42.43	-18.91
P2-r1-en-f2	-42.91	-20.75	-39.20	-18.45
P2-r1-ex-f1	-44.87	-22.78	-41.04	-18.26
P2-r1-ex-f2	-48.21	-25.64	-44.18	-18.55
P2-r2-en-f1	-42.93	-21.35	-39.24	-17.89
P2-r2-en-f2	-48.41	-26.31	-44.47	-18.16
P2-r2-ex-f1	-44.00	-22.15	-40.05	-17.91
P2-r2-ex-f2	-47.39	-25.49	-43.60	-18.10
TS2-r1-en-f1	8.56	27.38	9.73	-17.65
TS2-r1-en-f2	17.60	36.40	17.83	-18.57
TS2-r1-ex-f1	7.80	25.76	8.58	-17.18
TS2-r1-ex-f2	14.15	32.76	15.11	-17.65
TS2-r2-en-f1	5.64	23.90	6.51	-17.39
TS2-r2-en-f2	7.97	27.10	9.16	-17.94
TS2-r2-ex-f1	3.91	22.19	4.95	-17.24
TS2-r2-ex-f2	9.22	27.61	10.31	-17.30

- Acetonitrile 70 °C

*Table S20: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **b1** according to wB97XD/6-311G(d,p) calculations in acetonitrile at 70 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P2-r1-en-f1	-46.58	-20.59	-42.54	-21.95
P2-r1-en-f2	-42.91	-17.91	-39.29	-21.38
P2-r1-ex-f1	-44.87	-19.96	-41.14	-21.18
P2-r1-ex-f2	-48.21	-22.76	-44.29	-21.53
P2-r2-en-f1	-42.93	-18.56	-39.33	-20.77
P2-r2-en-f2	-48.41	-23.48	-44.57	-21.09
P2-r2-ex-f1	-44.00	-19.34	-40.15	-20.81
P2-r2-ex-f2	-47.39	-22.66	-43.70	-21.04
TS2-r1-en-f1	8.56	30.11	9.73	-20.38
TS2-r1-en-f2	17.60	39.23	17.76	-21.48
TS2-r1-ex-f1	7.80	28.46	8.59	-19.87
TS2-r1-ex-f2	14.15	35.48	15.12	-20.35
TS2-r2-en-f1	5.64	26.62	6.53	-20.09
TS2-r2-en-f2	7.97	29.87	9.18	-20.69
TS2-r2-ex-f1	3.91	24.90	4.97	-19.94
TS2-r2-ex-f2	9.22	30.31	10.33	-19.98

- **Acetonitrile 100 °C**

*Table S21: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **b1** according to wB97XD/6-311G(d,p) calculations in acetonitrile at 100 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P2-r1-en-f1	-46.58	-18.63	-42.60	-23.97
P2-r1-en-f2	-42.91	-16.01	-39.34	-23.33
P2-r1-ex-f1	-44.87	-18.07	-41.19	-23.12
P2-r1-ex-f2	-48.21	-20.83	-44.34	-23.51
P2-r2-en-f1	-42.93	-16.68	-39.37	-22.69
P2-r2-en-f2	-48.41	-21.57	-44.62	-23.05
P2-r2-ex-f1	-44.00	-17.46	-40.20	-22.74
P2-r2-ex-f2	-47.39	-20.75	-43.75	-23.00
TS2-r1-en-f1	8.56	31.94	9.75	-22.19
TS2-r1-en-f2	17.60	41.13	17.72	-23.41
TS2-r1-ex-f1	7.80	30.27	8.61	-21.66
TS2-r1-ex-f2	14.15	37.29	15.15	-22.15
TS2-r2-en-f1	5.64	28.43	6.55	-21.89
TS2-r2-en-f2	7.97	31.71	9.20	-22.51
TS2-r2-ex-f1	3.91	26.72	4.98	-21.73
TS2-r2-ex-f2	9.22	32.12	10.35	-21.77

4. Energies of the reaction of VPS with b2

- Gas phase 25 °C

*Table S22: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **b2** according to wB97XD/6-311G(d,p) calculations in the gas phase at 25 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P2'-r1-en-f1	-44.85	-21.46	-40.64	-19.19
P2'-r1-en-f2	-46.73	-23.55	-42.54	-18.99
P2'-r1-ex-f1	-49.08	-26.19	-45.02	-18.83
P2'-r1-ex-f2	-48.15	-25.19	-43.90	-18.71
P2'-r2-en-f1	-45.76	-22.90	-41.79	-18.89
P2'-r2-en-f2	-50.54	-27.55	-46.34	-18.79
P2'-r2-ex-f1	-46.89	-24.25	-42.82	-18.57
P2'-r2-ex-f2	-50.68	-27.91	-46.64	-18.73
TS2'-r1-en-f1	6.23	25.89	7.58	-18.31
TS2'-r1-en-f2	16.91	36.24	18.10	-18.14
TS2'-r1-ex-f1	3.88	23.15	4.10	-18.15
TS2'-r1-ex-f2	12.43	31.62	13.57	-18.05
TS2'-r2-en-f1	4.33	23.55	5.45	-18.10
TS2'-r2-en-f2	8.35	28.13	9.64	-18.49
TS2'-r2-ex-f1	2.57	21.46	3.73	-17.72
TS2'-r2-ex-f2	9.12	28.12	10.32	-17.80

- Toluene 25 °C

*Table S23: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **b2** according to wB97XD/6-311G(d,p) calculations in toluene at 25 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P2'-r1-en-f1	-47.33	-23.60	-43.08	-19.48
P2'-r1-en-f2	-44.92	-22.61	-41.06	-18.45
P2'-r1-ex-f1	-46.50	-24.38	-42.62	-18.24
P2'-r1-ex-f2	-48.85	-26.03	-44.77	-18.73
P2'-r2-en-f1	-43.70	-21.55	-39.92	-18.37
P2'-r2-en-f2	-49.27	-26.67	-45.23	-18.56
P2'-r2-ex-f1	-45.08	-22.97	-41.11	-18.14
P2'-r2-ex-f2	-48.55	-26.15	-44.65	-18.50
TS2'-r1-en-f1	7.84	27.04	9.07	-17.97
TS2'-r1-en-f2	17.66	37.26	18.11	-19.16
TS2'-r1-ex-f1	5.85	24.28	6.78	-17.50
TS2'-r1-ex-f2	13.57	32.48	14.63	-17.85
TS2'-r2-en-f1	5.61	24.20	6.52	-17.68
TS2'-r2-en-f2	8.31	27.74	9.56	-18.19
TS2'-r2-ex-f1	3.42	22.09	4.59	-17.50
TS2'-r2-ex-f2	9.30	28.17	10.47	-17.69

- Toluene 70 °C

*Table S24: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **b2** according to wB97XD/6-311G(d,p) calculations in toluene at 70 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P2'-r1-en-f1	-47.34	-20.50	-43.22	-22.72
P2'-r1-en-f2	-44.93	-19.67	-41.18	-21.51
P2'-r1-ex-f1	-46.51	-21.45	-42.75	-21.29
P2'-r1-ex-f2	-48.86	-23.04	-44.90	-21.86
P2'-r2-en-f1	-43.71	-18.59	-40.04	-21.45
P2'-r2-en-f2	-49.27	-23.68	-45.36	-21.68
P2'-r2-ex-f1	-45.08	-20.04	-41.23	-21.19
P2'-r2-ex-f2	-48.56	-23.17	-44.78	-21.62
TS2'-r1-en-f1	7.84	29.92	9.05	-20.87
TS2'-r1-en-f2	17.65	40.25	17.99	-22.26
TS2'-r1-ex-f1	5.85	27.12	6.75	-20.37
TS2'-r1-ex-f2	13.56	35.32	14.61	-20.71
TS2'-r2-en-f1	5.60	27.03	6.51	-20.52
TS2'-r2-en-f2	8.31	30.64	9.54	-21.10
TS2'-r2-ex-f1	3.41	24.94	4.57	-20.37
TS2'-r2-ex-f2	9.30	31.02	10.46	-20.56

- Toluene 100 °C

*Table S25: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **b2** according to wB97XD/6-311G(d,p) calculations in toluene at 100 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P2'-r1-en-f1	-47.34	-18.47	-43.29	-24.81
P2'-r1-en-f2	-44.93	-17.75	-41.23	-23.49
P2'-r1-ex-f1	-46.51	-19.54	-42.80	-23.26
P2'-r1-ex-f2	-48.86	-21.08	-44.96	-23.88
P2'-r2-en-f1	-43.71	-16.66	-40.09	-23.43
P2'-r2-en-f2	-49.27	-21.72	-45.42	-23.69
P2'-r2-ex-f1	-45.08	-18.12	-41.28	-23.16
P2'-r2-ex-f2	-48.56	-21.21	-44.84	-23.63
TS2'-r1-en-f1	7.84	31.80	9.06	-22.74
TS2'-r1-en-f2	17.65	42.21	17.94	-24.27
TS2'-r1-ex-f1	5.85	28.97	6.76	-22.21
TS2'-r1-ex-f2	13.56	37.17	14.63	-22.54
TS2'-r2-en-f1	5.60	28.88	6.53	-22.35
TS2'-r2-en-f2	8.31	32.54	9.56	-22.97
TS2'-r2-ex-f1	3.41	26.80	4.58	-22.22
TS2'-r2-ex-f2	9.30	32.88	10.47	-22.41

- Acetonitrile 25 °C

*Table S26: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **b2** according to wB97XD/6-311G(d,p) calculations in acetonitrile at 25 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P2'-r1-en-f1	-45.84	-22.54	-41.69	-19.14
P2'-r1-en-f2	-43.85	-21.84	-40.08	-18.24
P2'-r1-ex-f1	-44.63	-22.13	-40.76	-18.62
P2'-r1-ex-f2	-48.03	-25.47	-43.99	-18.52
P2'-r2-en-f1	-42.63	-20.86	-38.95	-18.09
P2'-r2-en-f2	-48.34	-25.99	-44.36	-18.37
P2'-r2-ex-f1	-44.03	-22.04	-40.05	-18.02
P2'-r2-ex-f2	-47.37	-25.22	-43.56	-18.34
TS2'-r1-en-f1	8.59	27.51	9.77	-17.73
TS2'-r1-en-f2	17.32	35.98	18.29	-17.69
TS2'-r1-ex-f1	7.40	25.82	8.23	-17.59
TS2'-r1-ex-f2	14.04	32.68	15.01	-17.67
TS2'-r2-en-f1	5.31	23.69	6.17	-17.52
TS2'-r2-en-f2	7.60	26.80	8.80	-18.00
TS2'-r2-ex-f1	3.40	21.70	4.51	-17.19
TS2'-r2-ex-f2	8.78	27.38	9.94	-17.44

- Acetonitrile 70 °C

*Table S27: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **b2** according to wB97XD/6-311G(d,p) calculations in acetonitrile at 70 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P2'-r1-en-f1	-45.84	-19.57	-41.80	-22.23
P2'-r1-en-f2	-43.85	-19.01	-40.17	-21.16
P2'-r1-ex-f1	-44.63	-19.24	-40.85	-21.61
P2'-r1-ex-f2	-48.03	-22.59	-44.09	-21.50
P2'-r2-en-f1	-42.63	-18.03	-39.04	-21.01
P2'-r2-en-f2	-48.34	-23.11	-44.47	-21.35
P2'-r2-ex-f1	-44.03	-19.21	-40.15	-20.94
P2'-r2-ex-f2	-47.37	-22.34	-43.66	-21.32
TS2'-r1-en-f1	8.59	30.27	9.78	-20.49
TS2'-r1-en-f2	17.32	38.72	18.31	-20.42
TS2'-r1-ex-f1	7.40	28.59	8.24	-20.35
TS2'-r1-ex-f2	14.04	35.43	15.03	-20.40
TS2'-r2-en-f1	5.31	26.45	6.19	-20.26
TS2'-r2-en-f2	7.60	29.60	8.82	-20.77
TS2'-r2-ex-f1	3.40	24.43	4.52	-19.91
TS2'-r2-ex-f2	8.78	30.12	9.96	-20.16

- **Acetonitrile 100 °C**

*Table S28: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **b2** according to wB97XD/6-311G(d,p) calculations in acetonitrile at 100 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P2'-r1-en-f1	-45.84	-17.58	-41.86	-24.28
P2'-r1-en-f2	-43.85	-17.12	-40.22	-23.10
P2'-r1-ex-f1	-44.63	-17.30	-40.90	-23.60
P2'-r1-ex-f2	-48.03	-20.66	-44.15	-23.49
P2'-r2-en-f1	-42.63	-16.13	-39.08	-22.96
P2'-r2-en-f2	-48.34	-21.18	-44.52	-23.34
P2'-r2-ex-f1	-44.03	-17.30	-40.20	-22.89
P2'-r2-ex-f2	-47.37	-20.41	-43.72	-23.31
TS2'-r1-en-f1	8.59	32.12	9.80	-22.32
TS2'-r1-en-f2	17.32	40.56	18.32	-22.23
TS2'-r1-ex-f1	7.40	30.45	8.26	-22.19
TS2'-r1-ex-f2	14.04	37.26	15.05	-22.21
TS2'-r2-en-f1	5.31	28.29	6.21	-22.08
TS2'-r2-en-f2	7.60	31.46	8.85	-22.61
TS2'-r2-ex-f1	3.40	26.25	4.54	-21.71
TS2'-r2-ex-f2	8.78	31.95	9.98	-21.97

5. Energies of the reaction of VPS with c:

- Gas phase

*Table S29: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **c** according to wB97XD/6-311G(d,p) calculations in the gas phase at 25 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P3-r1-en-f1	-58.03	-32.83	-53.77	-20.94
P3-r1-en-f2	-56.51	-31.88	-52.23	-20.35
P3-r1-ex-f1	-49.63	-25.33	-45.04	-19.71
P3-r1-ex-f2	-53.60	-30.41	-49.60	-19.19
P3-r2-en-f1	-50.75	-25.73	-47.08	-21.35
P3-r2-en-f2	-50.24	-27.51	-46.27	-18.76
P3-r2-ex-f1	-52.64	-28.00	-48.78	-20.78
P3-r2-ex-f2	-56.27	-32.25	-52.22	-19.97
TS3-r1-en-f1	4.92	25.15	5.89	-19.27
TS3-r1-en-f2	10.21	30.03	11.28	-18.75
TS3-r1-ex-f1	5.74	25.19	6.76	-18.43
TS3-r1-ex-f2	8.76	28.23	9.56	-18.67
TS3-r2-en-f1	6.63	25.90	7.59	-18.32
TS3-r2-en-f2	9.97	29.65	10.88	-18.76
TS3-r2-ex-f1	5.94	25.11	7.13	-17.98
TS3-r2-ex-f2	10.67	30.32	11.86	-18.45

- Toluene 25 °C

*Table S30: Relative electronic energies and electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **c** according to wB97XD/6-311G(d,p) calculations in toluene at 25 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P3-r1-en-f1	-54.12	-29.29	-49.93	-20.64
P3-r1-en-f2	-52.92	-28.69	-48.72	-20.03
P3-r1-ex-f1	-47.01	-23.18	-43.40	-20.22
P3-r1-ex-f2	-51.31	-27.38	-47.94	-20.55
P3-r2-en-f1	-48.43	-25.26	-44.33	-19.07
P3-r2-en-f2	-49.40	-27.11	-45.51	-18.40
P3-r2-ex-f1	-49.65	-26.24	-45.30	-19.05
P3-r2-ex-f2	-52.29	-28.97	-48.37	-19.40
TS3-r1-en-f1	8.62	27.93	9.43	-18.50
TS3-r1-en-f2	12.64	33.00	13.64	-19.36
TS3-r1-ex-f1	8.18	27.40	9.11	-18.29
TS3-r1-ex-f2	11.27	30.86	12.14	-18.72
TS3-r2-en-f1	7.69	26.86	8.65	-18.21
TS3-r2-en-f2	10.85	30.29	11.76	-18.54
TS3-r2-ex-f1	9.14	28.92	9.66	-19.26
TS3-r2-ex-f2	12.22	31.58	13.36	-18.22

- Toluene 70 °C

*Table S31: Relative electronic energies and electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **c** according to wB97XD/6-311G(d,p) calculations in toluene at 70 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P3-r1-en-f1	-54.12	-26.20	-50.10	-23.90
P3-r1-en-f2	-52.92	-25.67	-48.88	-23.21
P3-r1-ex-f1	-47.01	-20.17	-43.65	-23.48
P3-r1-ex-f2	-51.31	-24.31	-48.18	-23.87
P3-r2-en-f1	-48.43	-22.38	-44.48	-22.10
P3-r2-en-f2	-49.40	-24.29	-45.65	-21.36
P3-r2-ex-f1	-49.65	-23.34	-45.46	-22.12
P3-r2-ex-f2	-52.29	-26.01	-48.53	-22.51
TS3-r1-en-f1	8.62	30.75	9.39	-21.36
TS3-r1-en-f2	12.64	35.91	13.59	-22.32
TS3-r1-ex-f1	8.18	30.19	9.08	-21.11
TS3-r1-ex-f2	11.27	33.69	12.10	-21.60
TS3-r2-en-f1	7.69	29.63	8.62	-21.02
TS3-r2-en-f2	10.85	33.09	11.73	-21.36
TS3-r2-ex-f1	9.14	31.84	9.54	-22.31
TS3-r2-ex-f2	12.22	56500.91	13.31	-21.06

- Toluene 100 °C

*Table S32: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **c** according to wB97XD/6-311G(d,p) calculations in toluene at 100 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P3-r1-en-f1	-54.12	-24.10	-50.17	-26.07
P3-r1-en-f2	-52.92	-23.61	-48.95	-25.34
P3-r1-ex-f1	-47.01	-18.11	-43.76	-25.65
P3-r1-ex-f2	-51.31	-22.21	-48.30	-26.08
P3-r2-en-f1	-48.43	-20.42	-44.54	-24.12
P3-r2-en-f2	-49.40	-22.37	-45.71	-23.34
P3-r2-ex-f1	-49.65	-21.36	-45.52	-24.16
P3-r2-ex-f2	-52.29	-24.00	-48.58	-24.58
TS3-r1-en-f1	8.62	32.66	9.40	-23.26
TS3-r1-en-f2	12.64	37.89	13.60	-24.29
TS3-r1-ex-f1	8.18	32.09	9.10	-23.00
TS3-r1-ex-f2	11.27	35.62	12.11	-23.51
TS3-r2-en-f1	7.69	31.52	8.63	-22.89
TS3-r2-en-f2	10.85	34.98	11.75	-23.23
TS3-r2-ex-f1	9.14	33.83	9.49	-24.34
TS3-r2-ex-f2	12.22	36.27	13.32	-22.95

- Acetonitrile 25 °C

*Table S33: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **c** according to wB97XD/6-311G(d,p) calculations in acetonitrile at 25 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P3-r1-en-f1	-51.36	-26.95	-47.24	-20.29
P3-r1-en-f2	-50.79	-26.57	-46.81	-20.24
P3-r1-ex-f1	-45.71	-21.77	-42.31	-20.54
P3-r1-ex-f2	-49.52	-25.37	-46.19	-20.82
P3-r2-en-f1	-46.43	-23.54	-42.44	-18.90
P3-r2-en-f2	-48.43	-25.69	-44.60	-18.91
P3-r2-ex-f1	-47.05	-23.84	-42.83	-19.00
P3-r2-ex-f2	-49.11	-26.09	-45.31	-19.22
TS3-r1-en-f1	11.40	30.83	12.14	-18.69
TS3-r1-en-f2	14.65	35.60	15.05	-20.55
TS3-r1-ex-f1	10.03	29.20	10.90	-18.30
TS3-r1-ex-f2	13.38	32.50	14.18	-18.32
TS3-r2-en-f1	7.50	26.12	8.23	-17.89
TS3-r2-en-f2	11.49	30.50	12.28	-18.22
TS3-r2-ex-f1	10.09	28.76	10.92	-17.84
TS3-r2-ex-f2	13.37	32.62	14.38	-18.24

- Acetonitrile 70 °C

*Table S34: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **c** according to wB97XD/6-311G(d,p) calculations in acetonitrile at 70 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P3-r1-en-f1	-51.36	-23.86	-47.36	-23.50
P3-r1-en-f2	-50.79	-23.46	-46.92	-23.46
P3-r1-ex-f1	-45.71	-18.65	-42.50	-23.85
P3-r1-ex-f2	-49.52	-22.22	-46.39	-24.17
P3-r2-en-f1	-46.43	-20.65	-42.54	-21.90
P3-r2-en-f2	-48.43	-22.75	-44.71	-21.96
P3-r2-ex-f1	-47.05	-20.89	-42.95	-22.06
P3-r2-ex-f2	-49.11	-23.12	-45.42	-22.30
TS3-r1-en-f1	11.40	33.72	12.14	-21.58
TS3-r1-en-f2	14.65	38.70	14.96	-23.74
TS3-r1-ex-f1	10.03	32.04	10.91	-21.12
TS3-r1-ex-f2	13.38	35.33	14.19	-21.14
TS3-r2-en-f1	7.50	28.89	8.25	-20.64
TS3-r2-en-f2	11.49	33.31	12.31	-21.00
TS3-r2-ex-f1	10.09	31.52	10.93	-20.59
TS3-r2-ex-f2	13.37	35.47	14.38	-21.09

- **Acetonitrile 100 °C**

*Table S35: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of **VPS** and **c** according to wB97XD/6-311G(d,p) calculations in acetonitrile at 100 C.*

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P3-r1-en-f1	-51.36	-21.79	-47.43	-25.63
P3-r1-en-f2	-50.79	-21.39	-46.98	-25.60
P3-r1-ex-f1	-45.71	-16.56	-42.62	-26.05
P3-r1-ex-f2	-49.52	-20.10	-46.50	-26.40
P3-r2-en-f1	-46.43	-18.71	-42.60	-23.89
P3-r2-en-f2	-48.43	-20.78	-44.76	-23.98
P3-r2-ex-f1	-47.05	-18.91	-43.01	-24.10
P3-r2-ex-f2	-49.11	-21.12	-45.47	-24.35
TS3-r1-en-f1	11.40	35.66	12.16	-23.50
TS3-r1-en-f2	14.65	40.77	14.91	-25.86
TS3-r1-ex-f1	10.03	33.93	10.93	-23.00
TS3-r1-ex-f2	13.38	37.22	14.20	-23.02
TS3-r2-en-f1	7.50	30.75	8.27	-22.48
TS3-r2-en-f2	11.49	35.18	12.33	-22.85
TS3-r2-ex-f1	10.09	33.38	10.95	-22.43
TS3-r2-ex-f2	13.37	37.37	14.39	-22.98

6. Energies of the reaction of VPS6 with b1 in the gas phase at 25 °C

Table S36: Relative electronic energies and thermodynamic properties of the products and transition states of the reaction of VPS6 and b1 according to wB97XD/6-311G(d,p) calculations in the gas phase at 25 C.

	ΔE (kcal/mol)	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol.K)
P2-r1-en-f1	-46.44	-22.75	-42.15	-65.05
P2-r1-ex-f1	-47.32	-25.78	-43.46	-59.31
P2-r2-en-f1	-46.25	-22.36	-41.77	-65.08
P2-r2-ex-f1	-45.49	-22.76	-41.04	-61.31
TS2-r1-en-f1	8.65	28.23	10.23	-60.39
TS2-r1-ex-f1	3.66	22.62	4.68	-60.18
TS2-r2-en-f1	6.35	26.70	8.09	-62.70
TS2-r2-ex-f1	2.58	22.65	4.61	-60.51
P2-r1-en-f2	-43.93	-21.22	-39.98	-62.91
P2-r1-ex-f2	-49.05	-26.28	-44.85	-62.26
P2-r2-en-f2	-49.79	-25.94	-45.00	-63.92
P2-r2-ex-f2	-49.86	-26.41	-45.12	-62.76
TS2-r1-en-f2	16.46	39.00	17.99	-70.46
TS2-r1-ex-f2	13.91	34.04	12.46	-70.48
TS2-r2-en-f2	8.57	26.64	9.59	-57.20
TS2-r2-ex-f2	8.44	27.96	10.14	-59.79

7. IGM maps for the reaction of VPS and a

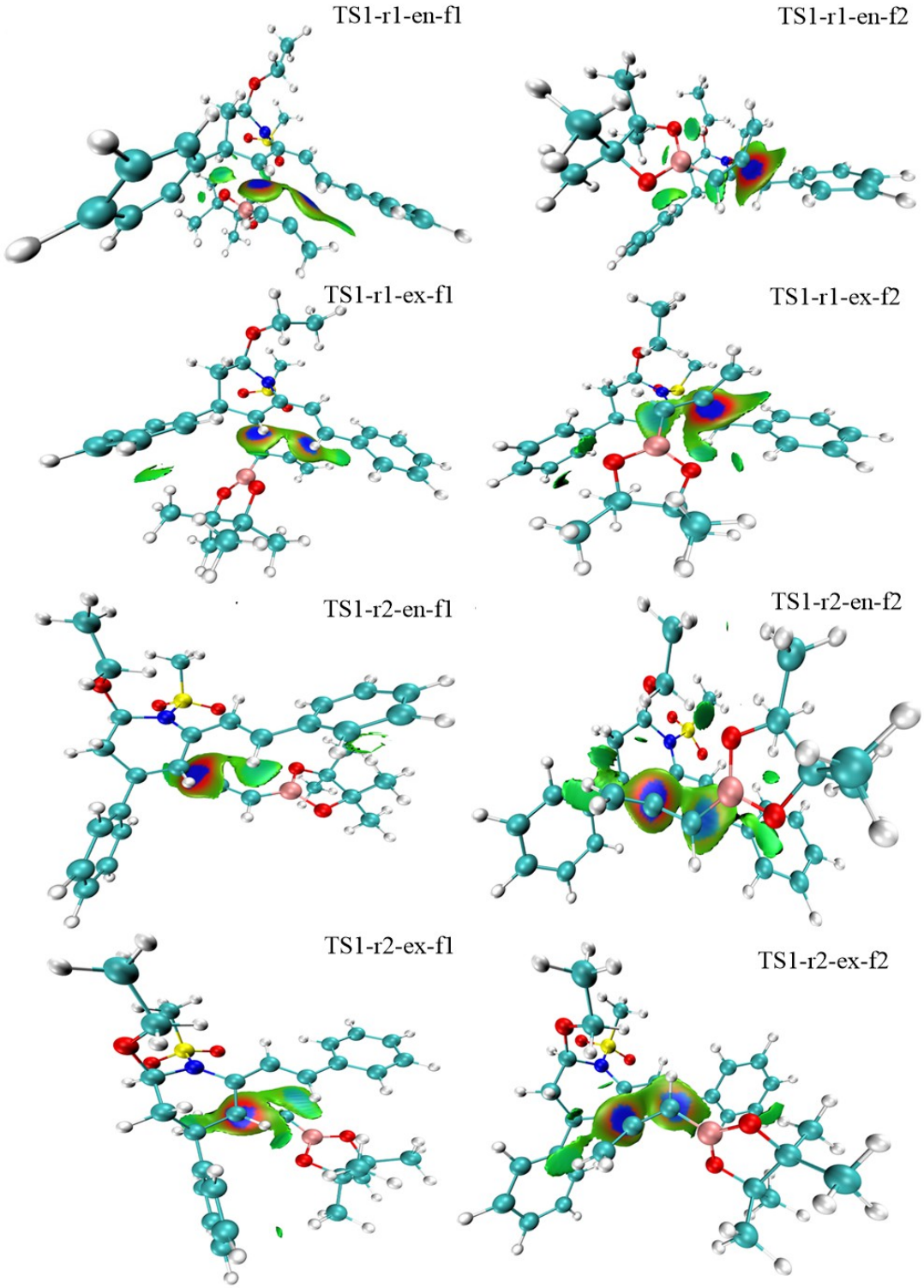

*Figure S2: Sign(λ2)ρ colored isosurfaces of δginter = 0.009 a.u of TSs of reaction of **VPS** and **a** at the proximal bond. Blue is for attractive interactions, red is for repulsive interactions.*

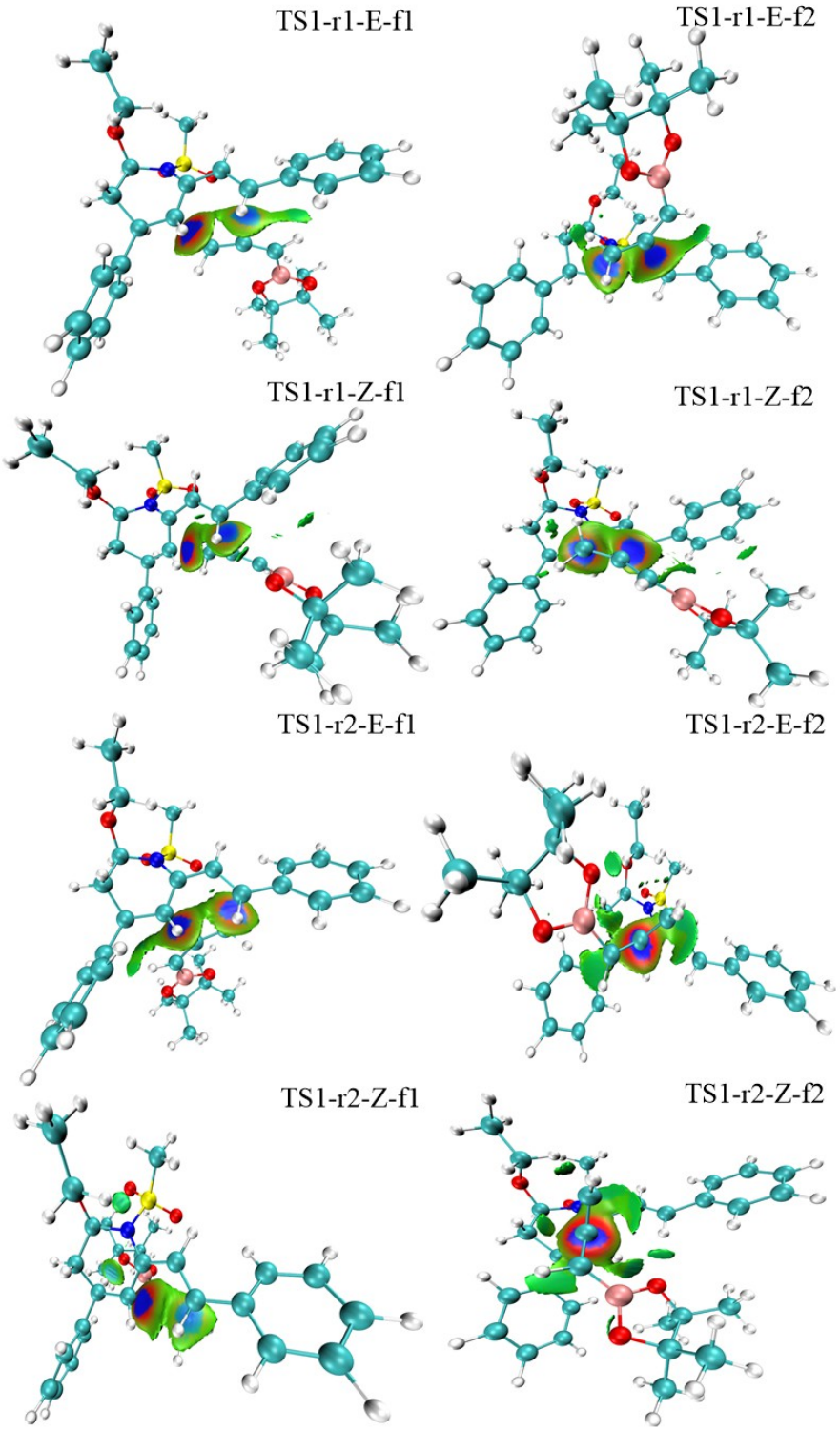

*Figure S3: Sign(λ2)ρ colored isosurfaces of δginter = 0.009 a.u of TSs of reaction of **VPS** and **α** at the distal bond. Blue is for attractive interactions, red is for repulsive interactions.*

8. IGM maps for the reaction of VPS and b1

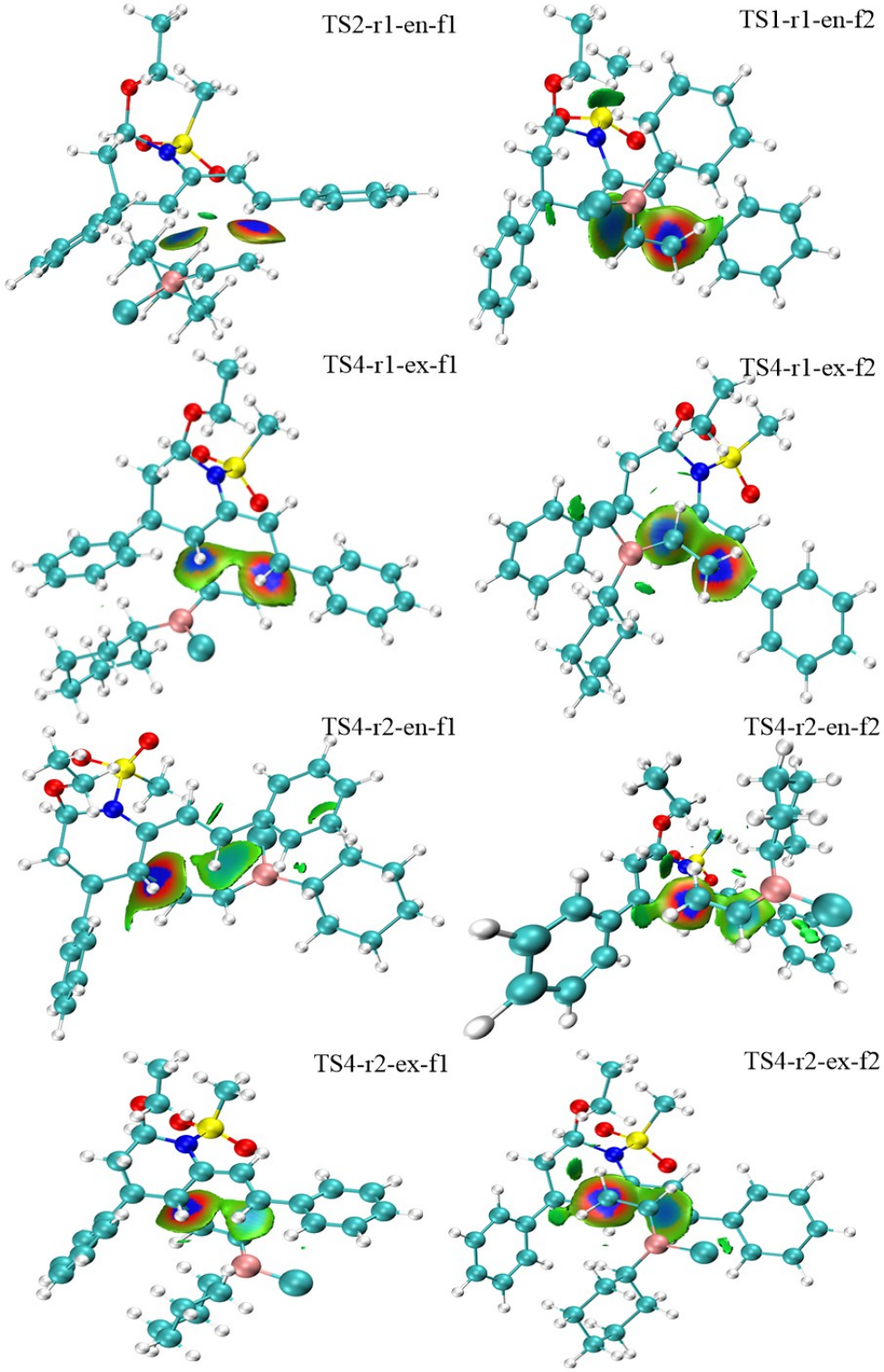

*Figure S4: Sign(λ2)ρ colored isosurfaces of δginter = 0.009 a.u of TSs of reaction of **VPS** and **b1**. Blue is for attractive interactions, red is for repulsive interactions.*

9. IGM maps for the reaction of VPS and c

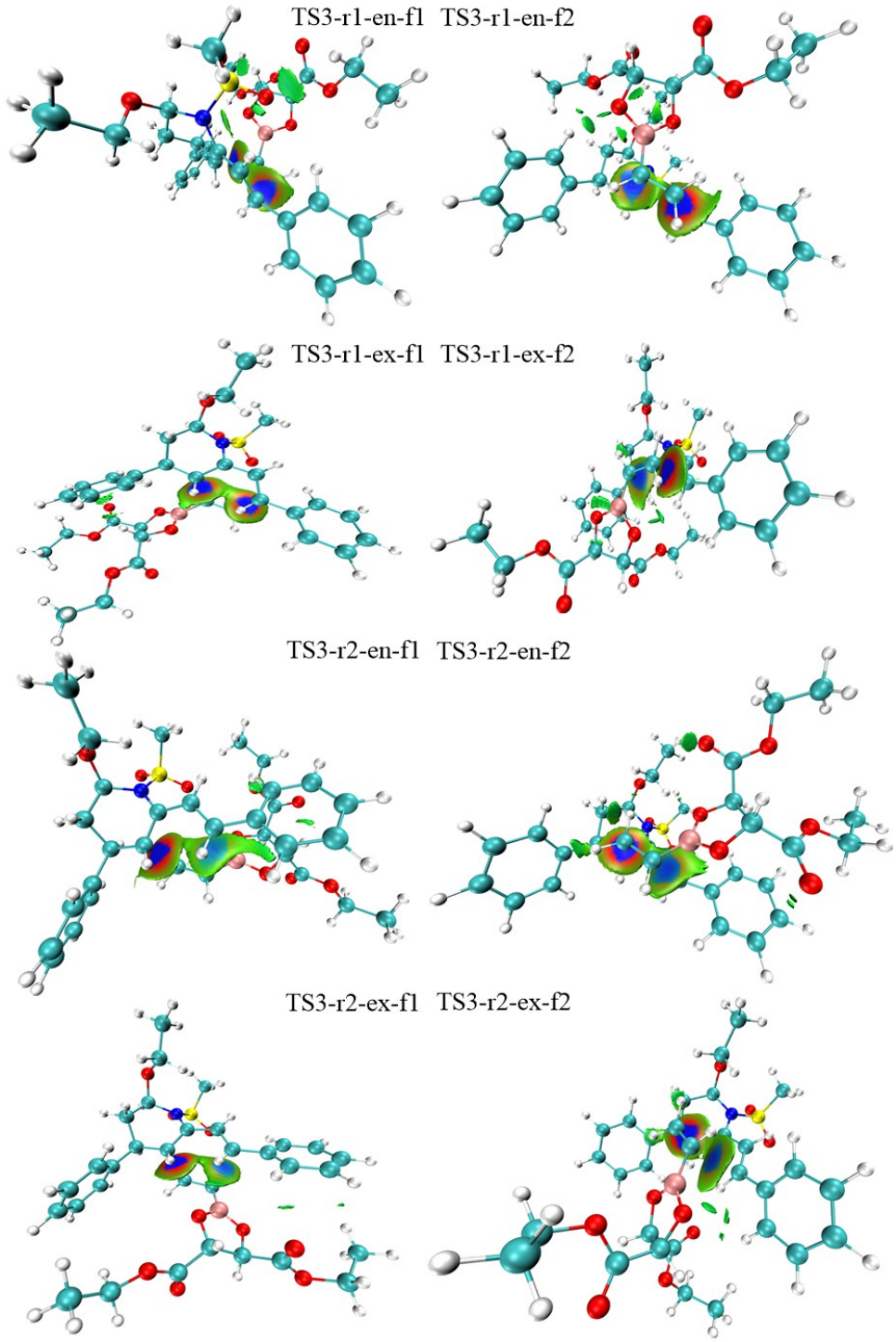

*Figure S5: Sign(λ2)ρ colored isosurfaces of δginter = 0.009 a.u of TSs of reaction of **VPS** and **c**. Blue is for attractive interactions, red is for repulsive interactions,*

10. ELF results of the most stable transition states the reaction of VPS with b1 and c.

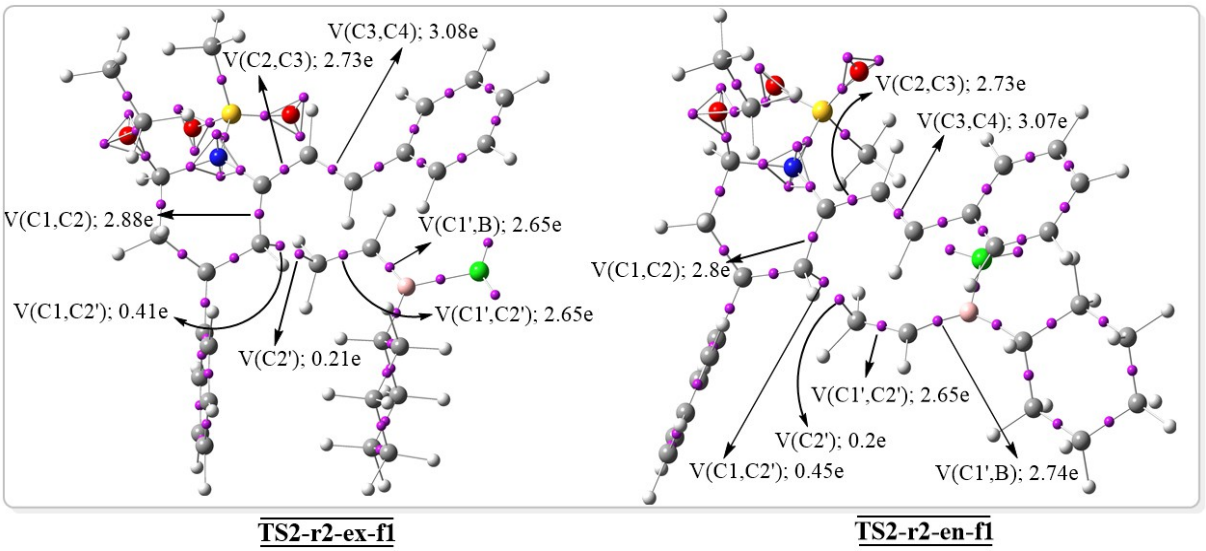

Figure S6: ELF basin attractor positions and population values of TS2-r2-ex-f1 and TS2-r2-en-f1 from the reaction VPS and b1

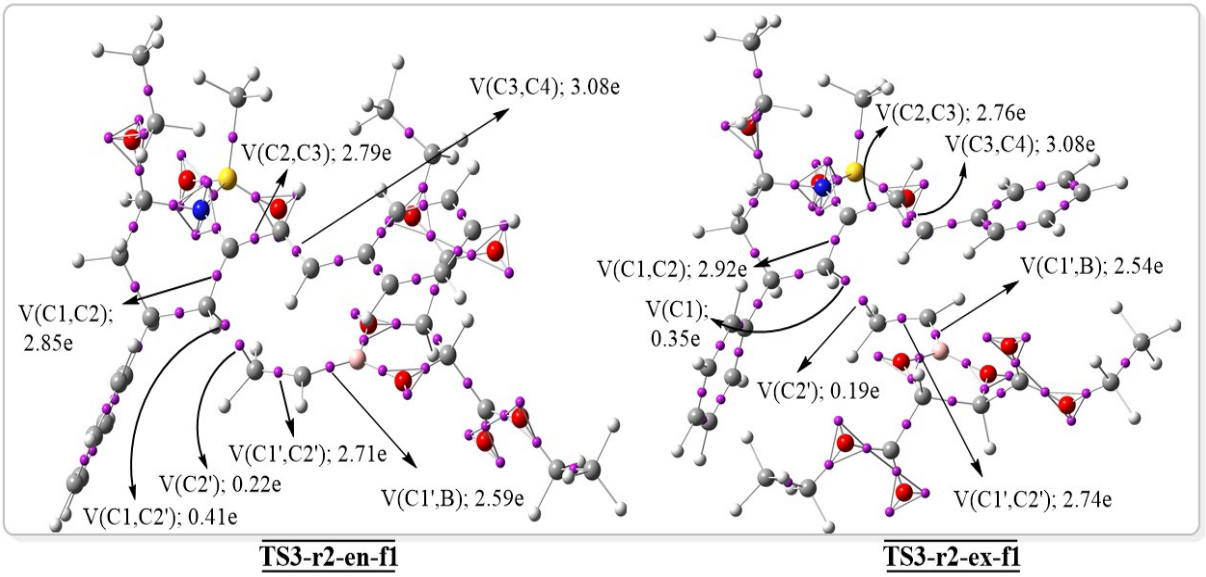

Figure S7: ELF basin attractor positions and population values of TS2-r2-en-f1 and TS2-r2-ex-f1 from the reaction VPS and c

11.Cartesian coordinates of P1-r1-E-f2 from the reaction of VPS and a

C	-2.06999300	-1.64515500	1.39713100
C	-0.78317000	-1.97513600	0.63749800
C	-0.43773900	-0.78512400	-0.30397800
C	-1.71589800	-0.11700900	-0.75716600
C	-3.23933000	-1.68932700	0.41252700
H	-2.26979800	-2.36563700	2.19226200
H	0.06966400	-1.19049900	-1.18734600
N	-2.85604600	-0.97534500	-0.80509400

S	-3.55778700	-1.42582500	-2.25274500
O	-2.72833000	-0.92071800	-3.32205500
O	-3.88165800	-2.83522000	-2.16152700
C	-5.10277900	-0.53481400	-2.25068100
H	-4.88791400	0.53255200	-2.26533100
H	-5.65124100	-0.83037800	-3.14443700
H	-5.64074800	-0.81971400	-1.34739400
C	-4.53451200	0.13607100	1.30642200
H	-3.89882200	0.33472300	2.17925800
H	-4.17736700	0.76770800	0.48472100
C	-5.97769900	0.45342900	1.63400800
H	-6.33771500	-0.19368100	2.43618900
H	-6.07336200	1.49388700	1.95370600
H	-6.61519200	0.30047000	0.76001100
O	-4.46359800	-1.23110000	0.93837800
C	-1.80998900	1.17912900	-1.03302100
H	-2.77096900	1.59803200	-1.31657300
C	-0.65393000	2.13839500	-0.94908400
H	-0.55400700	2.64999200	-1.91214500
H	-3.44589100	-2.72638500	0.14695100
H	-1.99208800	-0.65546600	1.85876200
H	-1.00971200	-2.83101000	-0.00861300
C	-0.89601800	3.20713900	0.11420400
C	-0.30603400	4.46275400	-0.02707000
C	-1.65857400	2.95336000	1.25252100
C	-0.47344600	5.44032200	0.94298300
H	0.29650900	4.67109400	-0.90540400
C	-1.82731000	3.93031400	2.22768900
H	-2.12825800	1.98332400	1.37435300
C	-1.23603500	5.17683900	2.07593600
H	-0.00845300	6.41136400	0.81492400
H	-2.42452300	3.71529300	3.10705400
H	-1.36838600	5.94032900	2.83397000
C	0.38950800	-2.37761500	1.50277200
C	1.36228000	-3.22865600	0.97872100
C	0.56282100	-1.89256600	2.79790200
C	2.47225300	-3.59271800	1.72843100
H	1.24541400	-3.61070900	-0.03053300
C	1.67690600	-2.24747200	3.54942500
H	-0.17555600	-1.22559500	3.22958100
C	2.63530200	-3.10092900	3.01835700
H	3.20858600	-4.26849800	1.30729500
H	1.79309000	-1.85844400	4.55478000
H	3.50066200	-3.38478200	3.60643800
C	0.48250200	0.27162200	0.31503400
C	0.64186400	1.39612800	-0.66773400
C	1.78855900	1.71182700	-1.28057800
H	1.77008900	2.55314400	-1.97250700
C	5.37732700	0.58619700	-1.18944200
C	4.66549100	-0.52533200	-0.34323300
B	3.14340900	0.99260500	-1.07823000
O	4.35324600	1.59912900	-1.29161000
O	3.27927900	-0.31509800	-0.67848900
C	5.04747200	-1.95075900	-0.70482500
H	6.11686100	-2.11453000	-0.54325500
H	4.49282500	-2.64271700	-0.06853800
H	4.80967000	-2.17672100	-1.74418400
C	4.78746400	-0.31420800	1.16549300
H	4.09703100	-0.99462800	1.66929700
H	5.80114000	-0.51910000	1.51878200
H	4.52152400	0.70863700	1.44334600
C	5.70235000	0.13838300	-2.61334500
H	6.00222700	1.01147400	-3.19616300
H	6.51920100	-0.58719900	-2.62835500
H	4.82934300	-0.30774700	-3.09507800
C	6.60650000	1.19416500	-0.53439600
H	7.36766600	0.42754800	-0.36263600
H	7.03133600	1.95739400	-1.18963600
H	6.35925100	1.66327600	0.41776400
H	1.44148600	-0.16899800	0.57034300
H	0.02791700	0.65831100	1.23648300

12.IR spectrum of P1-r1-E-f2 from the reaction of VPS and a

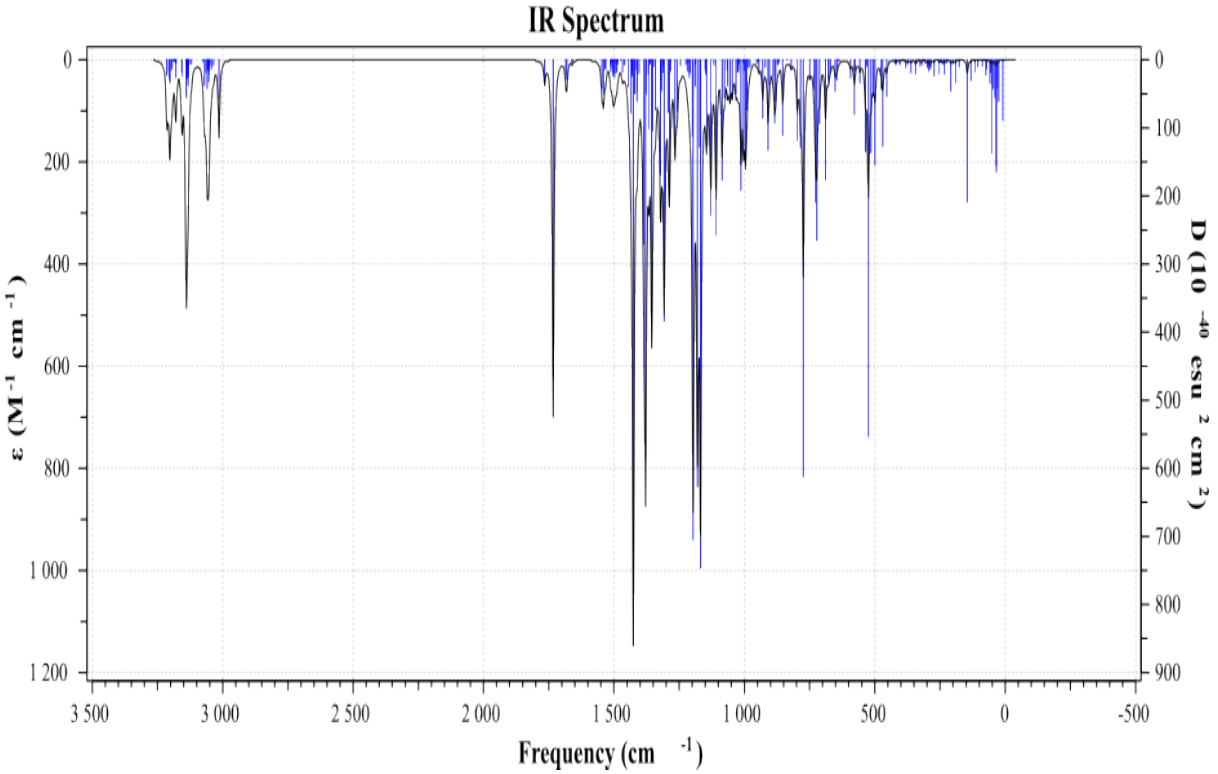

Figure S8: IR spectrum of P1-r1-E-f2 calculated at the wB97XD/6-311G(d,p) level of theory

13. Cartesian coordinates of P1-r2-ex-f1 (toluene) from the reaction of VPS and a

C	0.18717400	-3.07977900	-0.00210700
C	0.13718600	-2.10371500	1.18069600
C	0.01724800	-0.69706900	0.59529000
C	1.20894600	-0.36340000	-0.30102700
C	1.29484300	-2.77221900	-1.02325700
H	0.33150600	-4.09840800	0.36115400
H	-0.86670700	-0.71071000	-0.05598000
N	1.95513100	-1.49976700	-0.72655700
S	3.57289700	-1.39783800	-1.17860800
O	4.19718500	-0.32568900	-0.43600600
O	4.11438000	-2.73912800	-1.08291100
C	3.51330400	-0.97248800	-2.90802400
H	3.01027500	-0.01372800	-3.02362500
H	4.54087600	-0.91360600	-3.26447500
H	2.96329900	-1.76609200	-3.41223300
C	-0.05670800	-1.88769500	-2.81510000
H	-0.92364100	-1.84322000	-2.14569000
H	0.41029400	-0.89509100	-2.81066500
C	-0.49943400	-2.26224800	-4.21217600
H	-0.97174600	-3.24662300	-4.21250000
H	-1.21836400	-1.52962600	-4.58731100
H	0.35419800	-2.28915500	-4.89320600
O	0.86880100	-2.86607800	-2.36800900
C	1.51904700	0.89637900	-0.61331100
H	2.37766300	1.11036500	-1.23592100
C	0.87161000	2.11612900	-0.01516400
H	0.56440500	2.77293200	-0.83565400
H	2.06396000	-3.53403100	-0.95083600
H	-0.78584600	-3.06769100	-0.50013400
H	1.07456300	-2.17850900	1.74276600
C	1.85805600	2.90520200	0.83377200
C	1.68840200	4.28446500	0.96655700
C	2.89618600	2.28794700	1.52787000
C	2.52965200	5.03116900	1.77991100
H	0.88349200	4.77498800	0.42613500
C	3.74096500	3.03458700	2.34300400

H	3.05703200	1.22228600	1.41397700
C	3.56055800	4.40545400	2.47399200
H	2.38487600	6.10233000	1.86906800
H	4.54698100	2.53958200	2.87329000
H	4.22201800	4.98562300	3.10770300
C	-1.00289700	-2.51993500	2.09039600
C	-0.75712600	-3.45132500	3.09826400
C	-2.30707300	-2.05688000	1.91346700
C	-1.78415500	-3.91438400	3.91181900
H	0.25490300	-3.81526400	3.24994700
C	-3.33519800	-2.51802900	2.72640500
H	-2.52569000	-1.30307300	1.16484000
C	-3.08018300	-3.44912000	3.72659400
H	-1.57000400	-4.63544300	4.69284600
H	-4.34084100	-2.13790900	2.58293600
H	-3.88411600	-3.80372000	4.36165000
C	-0.16427200	0.46285500	1.54767400
C	-0.39762300	1.75618200	0.81485700
H	-0.54754300	2.55932500	1.54640700
C	-3.27927600	2.50817500	-1.52175600
C	-3.60231700	1.03872000	-1.08654200
B	-1.69212700	1.75073600	-0.08155700
O	-1.90654900	2.65747700	-1.08317800
O	-2.72846100	0.86412700	0.05402000
C	-5.03628200	0.79546800	-0.65087400
H	-5.72586100	1.01107900	-1.47149300
H	-5.16057100	-0.25204200	-0.36774700
H	-5.30400100	1.41431100	0.20519300
C	-3.17653300	0.00200200	-2.12404000
H	-3.83080700	0.01714600	-2.99833600
H	-2.14943900	0.17703300	-2.45426600
C	-4.10300500	3.54920400	-0.76779800
H	-3.68828200	4.53907500	-0.96738100
H	-5.14637500	3.53904500	-1.09090600
H	-4.06993900	3.37601500	0.31032500
C	-3.34733800	2.76072000	-3.01806700
H	-4.35528800	2.56218300	-3.39253200
H	-3.10702000	3.80560100	-3.22413800
H	-2.64072000	2.13491600	-3.56313900
C	-0.04978900	0.38650600	2.86816200
H	-0.14700100	1.27703900	3.47999900
H	0.12990100	-0.54833600	3.38509500
H	-3.22872700	-0.99143300	-1.67199600

14.IR spectrum of P1-r2-ex-f1 (toluene) from the reaction of VPS and a

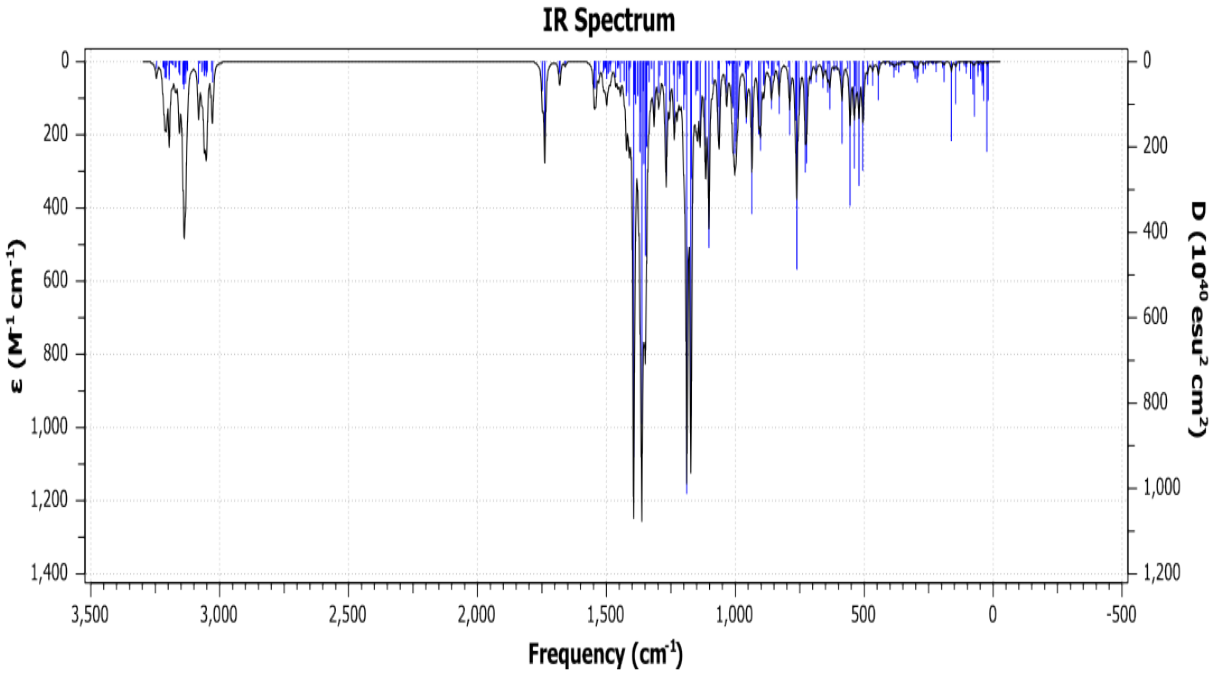

Figure S9: IR spectrum of P1-r2-ex-f1 calculated at the wB97XD/6-311G(d,p) level of theory

15. Cartesian coordinates of P1-r2-en-f1 (acetonitrile) from the reaction of VPS and a

C	-3.80361700	-0.02260400	0.11890900
C	-2.78630300	-1.11778600	-0.22512100
C	-1.47060000	-0.71905900	0.44679800
C	-1.13412300	0.74265900	0.19861100
C	-3.45858100	1.29421600	-0.57471600
H	-4.80943600	-0.30747100	-0.19247600
H	-1.61159700	-0.82284000	1.53213700
N	-2.00060700	1.44050800	-0.68214300
S	-1.43392400	2.48803600	-1.85798000
O	-0.05355500	2.16072400	-2.15266500
O	-2.40646700	2.46686600	-2.93800100
C	-1.50174000	4.09838600	-1.10942600
H	-0.85805600	4.11165500	-0.23165100
H	-1.15423500	4.81625200	-1.85127500
H	-2.53949700	4.28360000	-0.83923800
C	-3.69831100	2.75028300	1.34035000
H	-4.07378400	1.99356100	2.03710200
H	-2.60646400	2.77722000	1.43101600
C	-4.29658900	4.10028500	1.67111000
H	-5.38225200	4.07562900	1.55532000
H	-4.06468900	4.36681000	2.70456300
H	-3.89646700	4.87950700	1.01817500
O	-4.06935900	2.42457400	0.00225100
C	-0.03339200	1.23824000	0.75773200
H	0.26619700	2.26858700	0.62087400
C	0.81825300	0.31513400	1.58601100
H	0.25823400	0.10716300	2.50806300
H	-3.85078900	1.27610200	-1.58916500
H	-3.82596500	0.10359800	1.20461500
H	-2.64309300	-1.12485600	-1.31131800
C	2.15361700	0.89279500	2.01851700
C	2.75403800	0.40601600	3.18119700
C	2.83721800	1.85441400	1.27358400
C	3.99840900	0.86674100	3.59336100
H	2.23667800	-0.34393600	3.77207400
C	4.07773900	2.32640900	1.68854500
H	2.41506900	2.22250300	0.34664800
C	4.66389100	1.83468700	2.84896800
H	4.44501800	0.47426600	4.50002600
H	4.59100600	3.07509200	1.09524600
H	5.63270400	2.20050300	3.16944200
C	-3.30586700	-2.47910100	0.19128100
C	-3.74295800	-3.38257900	-0.77687300
C	-3.41150400	-2.84360200	1.53428800
C	-4.25933600	-4.62274600	-0.41879600
H	-3.67304100	-3.11277500	-1.82622300
C	-3.92633200	-4.08252100	1.89710700
H	-3.09307600	-2.15940300	2.31370600
C	-4.35043500	-4.97842300	0.92172700
H	-4.58835100	-5.31154600	-1.18875500
H	-3.99662200	-4.34806200	2.94598800
H	-4.74972000	-5.94553900	1.20507700
C	-0.22214300	-1.50863300	0.10299200
C	1.01287300	-1.07391300	0.87676400
H	1.17977700	-1.80911600	1.67250500
C	4.36802000	-1.63672900	-0.78337700
C	3.67772100	-0.65145800	-1.79293300
B	2.28442600	-1.09906100	-0.05264100
O	3.25691600	-2.05480400	0.05109700
O	2.52468800	-0.19618600	-1.04561200
C	4.51670300	0.55788000	-2.17077800
H	5.44278800	0.24372100	-2.65933100
H	3.95808100	1.18550400	-2.86847100
H	4.76588200	1.15631200	-1.29402900
C	3.14096100	-1.34135500	-3.04407100
H	2.52072100	-0.63248200	-3.59640100
H	2.52253100	-2.20445700	-2.78652700
C	5.36774100	-0.95082700	0.14466200
H	5.66795300	-1.65721900	0.92162400
H	6.26135400	-0.63491100	-0.39820100
H	4.92325200	-0.07899700	0.62978200

C	4.99401000	-2.86483000	-1.42192400
H	5.78360400	-2.56969800	-2.11797100
H	5.44000400	-3.49275500	-0.64764400
H	4.25548500	-3.45729900	-1.96220200
C	-0.18919700	-2.48645600	-0.79911900
H	0.73655700	-3.00865700	-1.02278100
H	-1.07203900	-2.82123900	-1.32812700
H	3.95238000	-1.67369800	-3.69515000

16. IR spectrum of P1-r2-en-f1 (acetonitrile) from the reaction of VPS and a

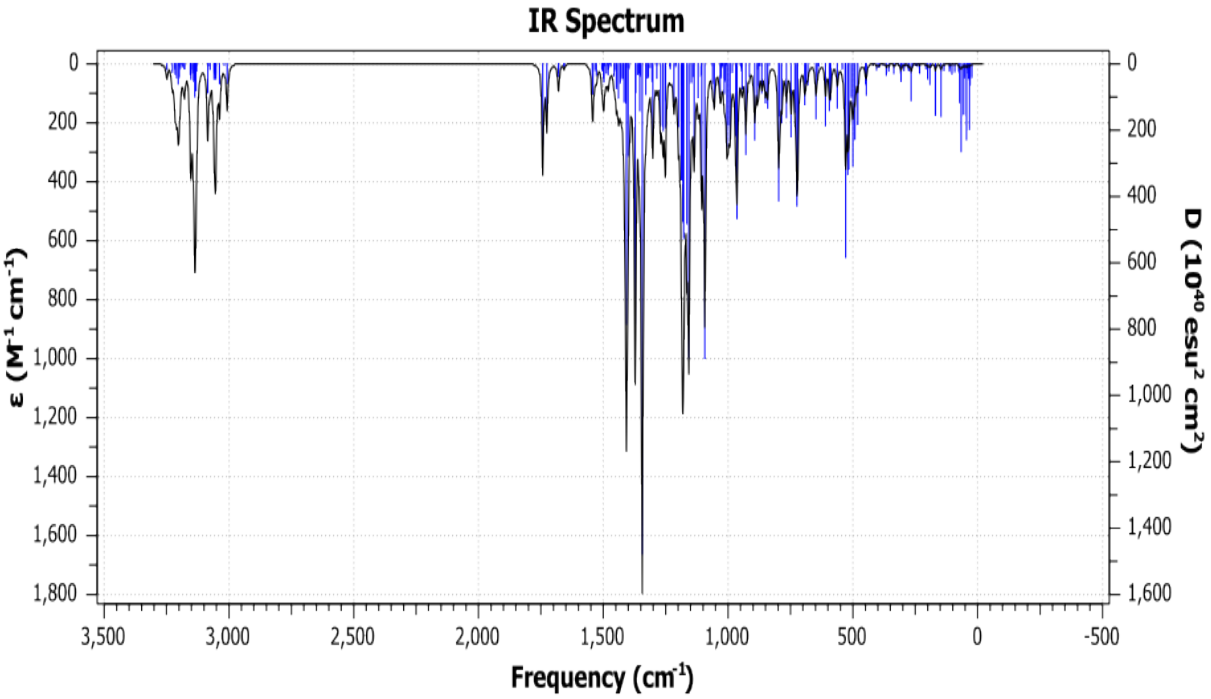

Figure S10: IR spectrum of P1-r2-en-f1 calculated at the wB97XD/6-311G(d,p) level of theory

17. Cartesian coordinates of P2-r2-ex-f1 from the reaction of VPS and b1

C -2.03557100 -2.55620600 0.51671400
C -0.97811700 -2.26510900 -0.55098200
C -0.45261900 -0.84909100 -0.28443400
C -1.56945900 0.12389600 0.00676300
C -3.27678100 -1.69065000 0.29642800
H -2.34781200 -3.60239400 0.50533400
H 0.19164300 -0.91289600 0.60406100
N -2.89102300 -0.35883700 -0.17317900
S -4.00585700 0.46726200 -1.12261500
O -3.30583700 1.48366200 -1.87243400
O -4.80349000 -0.53158200 -1.80222800
C -5.06093400 1.25861700 0.07012200
H -4.46650900 1.95460400 0.66080400
H -5.83497500 1.78800600 -0.48477000
H -5.49032700 0.47487400 0.69268600
C -3.61272500 -1.01930500 2.58934100
H -2.86441900 -1.66975400 3.05975300
H -3.11935500 -0.07163500 2.33806100
C -4.76805100 -0.79107300 3.54089300
H -5.27588300 -1.73400300 3.75349600
H -4.40891300 -0.36824200 4.48239900
H -5.49827600 -0.10120400 3.11093400
O -4.13367300 -1.62767500 1.41573100
C -1.24034200 1.38703100 0.26293600
H -1.98066200 2.16295200 0.41943500

C 0.22066100 1.76223600 0.22629000
H 0.69631400 1.32822200 1.11577000
H -3.89844600 -2.14020800 -0.47691100
H -1.61054000 -2.35709400 1.50525200
H -1.46633100 -2.27883200 -1.53402900
C 0.44297900 3.25783400 0.28494500
C -0.21355300 4.10484200 -0.61025200
C 1.32658200 3.81358000 1.20589400
C 0.01422300 5.47347100 -0.58395200
H -0.90956000 3.68426400 -1.33189600
C 1.56014200 5.18472200 1.23225200
H 1.83324800 3.16593200 1.91659500
C 0.90476200 6.01785900 0.33623400
H -0.50320600 6.11860600 -1.28623800
H 2.25330600 5.60029300 1.95612800
H 1.08474300 7.08742800 0.35371400
C 0.16262600 -3.26012400 -0.57646300
C 0.65068600 -3.73967100 -1.79084200
C 0.79600300 -3.66799500 0.59918800
C 1.74635700 -4.59433400 -1.83462800
H 0.16941900 -3.43286300 -2.71510500
C 1.88467300 -4.52930900 0.56090300
H 0.44201600 -3.30782900 1.56059900
C 2.36765800 -4.99172600 -0.65771700
H 2.11345400 -4.95031900 -2.79132200
H 2.36206200 -4.83460100 1.48610700
H 3.22196800 -5.65922800 -0.68861100
C 0.92569800 1.16420600 -1.03778300
C 0.36949500 -0.23987000 -1.42736400
H 1.17120900 -0.93308100 -1.70890000
H 0.72933900 1.84458500 -1.86906800
B 2.47433300 0.94289900 -0.86761900
C 3.14477300 0.20669000 0.35439400
C 3.70291700 -1.17897600 -0.04546900
C 4.25451900 1.04735400 1.01939600
H 2.37073900 0.02829900 1.11609600
C 4.31464600 -1.89910800 1.15664400
H 4.46606700 -1.04874700 -0.82272700
H 2.91500500 -1.80473800 -0.47952400
C 4.86024500 0.32416600 2.22307300
H 5.04066400 1.24800400 0.28140700
H 3.86411200 2.02495800 1.32338300
C 5.39512400 -1.05466800 1.83287000
H 4.72361900 -2.86420700 0.83994100
H 3.51875700 -2.12233900 1.88027000
H 5.65933900 0.93133500 2.66087400
H 4.09255700 0.20890800 3.00036400
H 5.78781100 -1.57330100 2.71358000
H 6.23850200 -0.92901700 1.14114200
Cl 3.52292300 1.41877200 -2.22899700
H -0.27686400 -0.14366400 -2.30484400

18.IR spectrum of P2-r2-ex-f1 from the reaction of VPS and b1

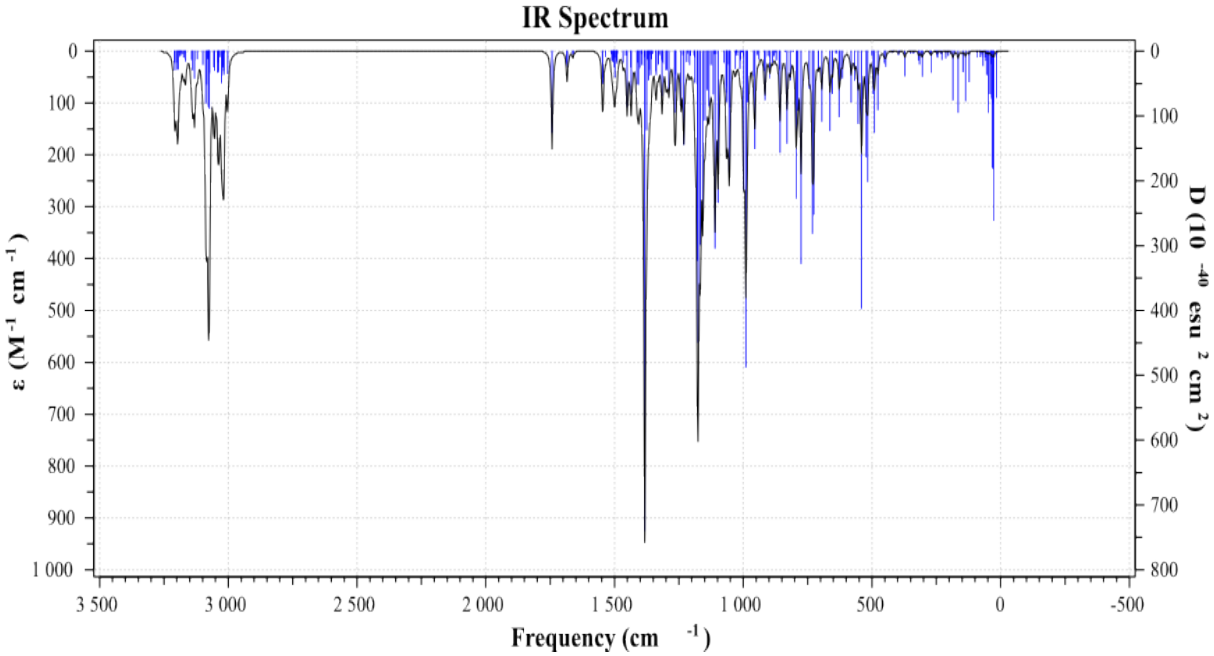

Figure S11: IR spectrum of P2-r2-ex-f1 calculated at the wB97XD/6-311G(d,p) level of theory

19.Cartesian coordinates of P2-r2-en-f2 from the reaction of VPS and b1

C	2.14351800	1.54488500	1.26881100
C	1.54122000	2.19268800	0.02090900
C	0.98876200	1.07452500	-0.91921800
C	1.77961100	-0.19468900	-0.71053800
C	3.41876100	0.80492000	0.87295500
H	2.40817600	2.28862900	2.02360100
H	1.14691300	1.40202600	-1.95523200
N	3.14460200	0.01002300	-0.32733300
S	4.40175500	-0.33688600	-1.35760400
O	3.83737100	-0.70377800	-2.64108500
O	5.35533200	0.75684000	-1.27709200
C	5.17860600	-1.76272200	-0.64114200
H	4.46324400	-2.58377500	-0.63969800
H	6.04502200	-2.00298700	-1.25688900
H	5.47851100	-1.49724600	0.37185400
C	3.20849000	-1.04281900	2.41151800
H	2.34676400	-0.65632000	2.96950200
H	2.82678800	-1.65242300	1.58431100
C	4.09377100	-1.86765100	3.32032500
H	4.49352400	-1.25038000	4.12810000
H	3.52221900	-2.68847100	3.76048000
H	4.93338300	-2.29149500	2.76369400
O	3.99126100	0.03278500	1.90302000
C	1.26986200	-1.41735000	-0.81199300
H	1.90453300	-2.27506800	-0.60271300
C	-0.15980500	-1.71865000	-1.16563000
H	-0.16186900	-2.38230800	-2.03723400
H	4.19531200	1.53181300	0.63051800
H	1.42521400	0.85406700	1.72204500
H	2.36299100	2.68308200	-0.51400700
C	-0.82446600	-2.49324600	-0.03033700
C	-0.72403200	-2.07519300	1.29934600
C	-1.57500100	-3.63610100	-0.31062400
C	-1.37786500	-2.76364700	2.31374900
H	-0.12012300	-1.20731700	1.54499600
C	-2.22140000	-4.33461900	0.70391400
H	-1.65561200	-3.98078700	-1.33735700
C	-2.13022900	-3.89642800	2.01929200
H	-1.29266200	-2.41917400	3.33923000
H	-2.79816900	-5.22146500	0.46316300

H	-2.63665800	-4.43679000	2.81196700
C	0.49590200	3.25214100	0.29854600
C	0.27212200	4.25302500	-0.64841100
C	-0.31151900	3.22379600	1.43574200
C	-0.74199700	5.18725100	-0.47669200
H	0.89746900	4.29308000	-1.53631800
C	-1.32701300	4.15779600	1.61284900
H	-0.15996000	2.45913600	2.19110700
C	-1.55002300	5.13966900	0.65470200
H	-0.90069400	5.95509200	-1.22683900
H	-1.94704700	4.11536500	2.50248900
H	-2.34382100	5.86641000	0.79103700
C	-0.93896300	-0.42683300	-1.56361000
C	-0.49559100	0.77737600	-0.72863100
H	-0.69852600	0.60311000	0.33363700
H	-0.67801600	-0.22372700	-2.61075200
B	-2.49478500	-0.69095300	-1.47681900
C	-3.42475400	-0.19030100	-0.31809800
C	-4.08933400	1.14503400	-0.73864700
C	-4.49556600	-1.18065700	0.16553600
H	-2.77780000	0.03819700	0.54065000
C	-4.90022600	1.73652400	0.41631200
H	-4.75089100	0.96261200	-1.59571600
H	-3.33803800	1.87050900	-1.06983400
C	-5.30681000	-0.59196100	1.32083500
H	-5.16850900	-1.42687600	-0.66531000
H	-4.02370400	-2.11794400	0.47735200
C	-5.94345200	0.74507200	0.93550300
H	-5.38521100	2.66402800	0.09417700
H	-4.21279000	2.00619900	1.22928100
H	-6.07929200	-1.30092900	1.63679500
H	-4.64386900	-0.44449800	2.18429800
H	-6.47812400	1.17234500	1.79028400
H	-6.69249400	0.57157600	0.15136800
Cl	-3.23418300	-1.57048900	-2.85325400
H	-1.07862200	1.65800100	-1.00803900

20.IR spectrum of P2-r2-en-f2 from the reaction of VPS and b1

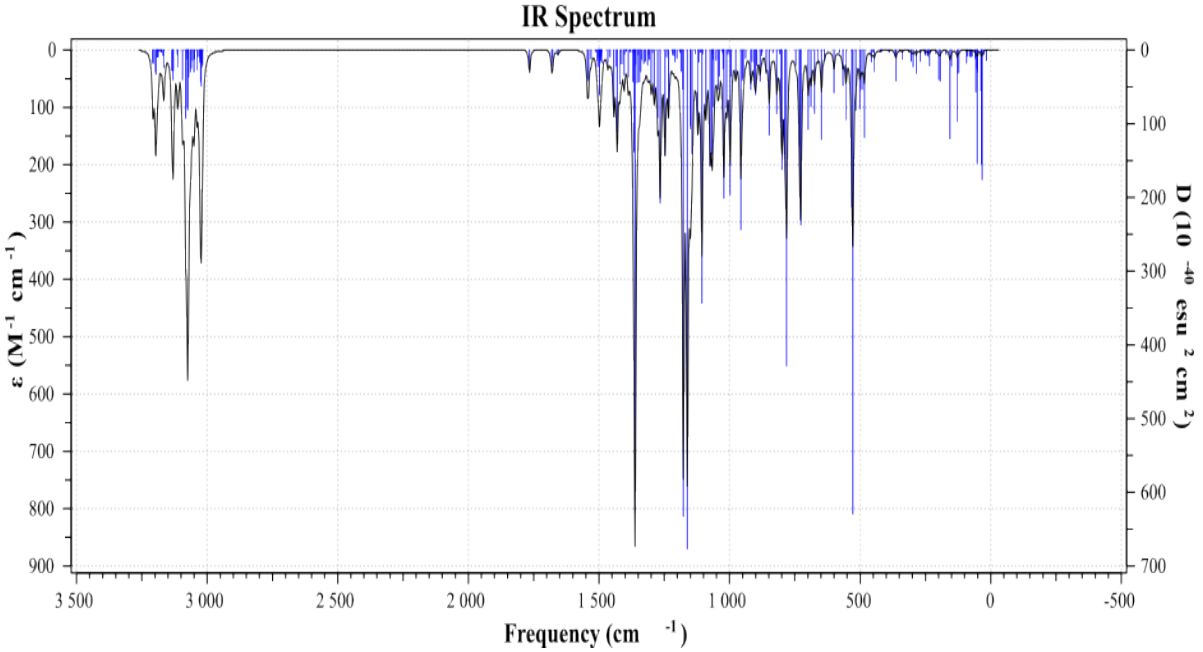

Figure S12: IR spectrum of P2-r2-en-f2 calculated at the wB97XD/6-311G(d,p) level of theory

21.Cartesian coordinates of P3-r2-en-f1 from the reaction of VPS and c

C -4.16157100 1.80193600 0.67391000
C -2.76312600 1.48132200 1.20333300
C -1.93076100 0.96121300 0.02385700
C -2.51686800 -0.34074300 -0.49733500

C -4.81477700 0.62869000 -0.07769200
H -4.82039000 2.08904700 1.49589000
H -2.01119700 1.70939600 -0.77917500
N -3.90396000 -0.51566700 -0.19341200
S -4.64471300 -2.02156500 -0.23433300
O -3.68979300 -3.02249300 0.19340800
O -5.89431800 -1.89225100 0.49128400
C -5.04866000 -2.27249400 -1.94577100
H -4.13563000 -2.24543400 -2.53918700
H -5.53153900 -3.24619600 -2.02401200
H -5.72708300 -1.47024400 -2.23399100
C -4.52304100 1.39974700 -2.35823700
H -3.95827900 2.29147600 -2.05710100
H -3.79940100 0.60608900 -2.58141700
C -5.37244200 1.70245900 -3.57347800
H -6.09712200 2.48772100 -3.34684500
H -4.74317300 2.03735800 -4.40163200
H -5.91872200 0.81132100 -3.89250000
O -5.39760000 0.98641900 -1.31543700
C -1.77033100 -1.24484200 -1.13575800
H -2.20004100 -2.18127700 -1.46829500
C -0.27584200 -1.15804400 -1.30475000
H -0.04550100 -1.32443000 -2.36330600
H -5.66340200 0.27484100 0.49886200
H -4.10618000 2.66476500 0.00529200
H -2.84024600 0.67932600 1.94697400
C 0.41332200 -2.28204600 -0.53169600
C 1.58499000 -2.85565600 -1.03437500
C -0.08689900 -2.75258400 0.68286100
C 2.24896000 -3.85667400 -0.33541200
H 1.97963100 -2.51351500 -1.98601900
C 0.57043500 -3.76065700 1.38017900
H -1.01770600 -2.35143000 1.06963500
C 1.74084100 -4.31468300 0.87573800
H 3.15831400 -4.28581300 -0.74353900
H 0.15654800 -4.12224100 2.31603000
H 2.24808800 -5.10697300 1.41703400
C -2.14087100 2.68319600 1.88169200
C -1.76874300 2.61957700 3.22278200
C -1.91593000 3.87335200 1.18519800
C -1.18679600 3.71298500 3.85689800
H -1.93392800 1.69962000 3.77618900
C -1.33255300 4.96624600 1.81281100
H -2.19042500 3.94898700 0.13666200
C -0.96600700 4.89005100 3.15319000
H -0.90423800 3.64201500 4.90217800
H -1.16252700 5.88076200 1.25392900
H -0.51079900 5.74380200 3.64399400
C -0.44439100 0.78086600 0.31638300
C 0.26759700 0.24552200 -0.92552100
C 4.00651900 0.14485700 -1.39915600
C 3.88141200 0.21434800 0.14170800
B 1.82644100 0.24382000 -0.79842700
O 2.67598200 0.00662500 -1.85397500
O 2.50643800 0.46934100 0.37442900
H -0.01412900 1.74006300 0.61462000
H -0.30680600 0.09821000 1.16356000
H 0.02186400 0.91164400 -1.76512600
H 4.48081300 1.02298100 0.57023900
H 4.61151300 -0.71132800 -1.70188200
C 4.35138400 -1.07214900 0.81724300
O 5.25400100 -1.74327100 0.38338600
O 3.70133700 -1.30293200 1.94283800
C 4.62234700 1.41537000 -1.96538300
O 4.02347600 2.27243300 -2.55613100
O 5.92175900 1.44763000 -1.67876000
C 6.64752400 2.62397800 -2.09945300
H 6.56787800 2.70779800 -3.18575800
H 6.17256600 3.50116300 -1.65370700
C 8.07718400 2.45568700 -1.64407300
H 8.52441600 1.56588800 -2.09209100
H 8.66349000 3.32677000 -1.94551800
H 8.12994400 2.36320100 -0.55712000
C 4.13273500 -2.44860200 2.71139900
H 5.17430100 -2.29291100 3.00354700
H 4.08228000 -3.33030600 2.07024500

C 3.21149300 -2.55707800 3.90161500
H 3.49470000 -3.42070500 4.50795600
H 3.27144000 -1.66170900 4.52400600
H 2.17852800 -2.68701800 3.57213200

22.IR spectrum of P3-r2-en-f1 from the reaction of VPS and c

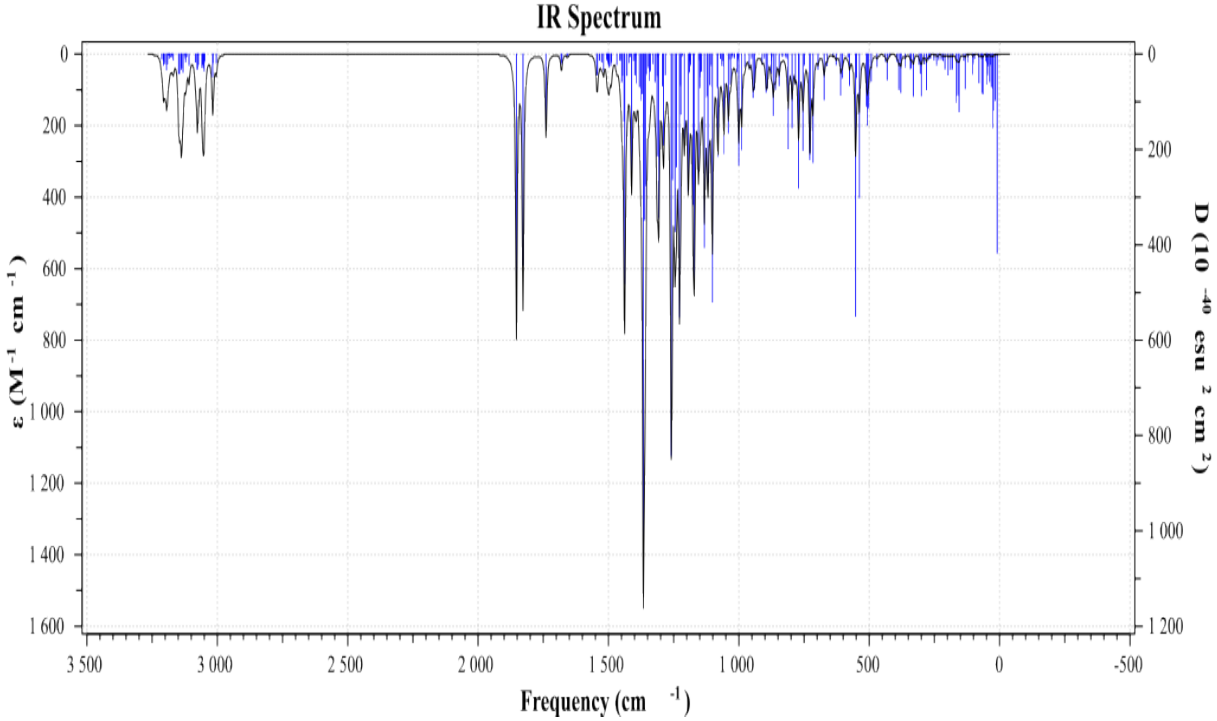

Figure S13: IR spectrum of P3-r2-en-f1 calculated at the wB97XD/6-311G(d,p) level of theory

23.Cartesian coordinates of P3-r1-en-f1 from the reaction of VPS and c

C -3.52537800 0.45032700 -0.62046000
C -2.11337400 1.02254600 -0.73164700
C -1.27283900 -0.03193500 -1.46632100
C -1.24636000 -1.33023300 -0.67660700
C -3.54639400 -0.82503800 0.23542800
H -4.20756600 1.17049200 -0.16371700
H -1.78907300 -0.23524300 -2.41703900
N -2.20850600 -1.40622100 0.37579100
S -1.89122900 -2.14709200 1.84601800
O -0.46178600 -2.28117200 2.02579800
O -2.66005200 -1.43515600 2.85307100
C -2.60711100 -3.76376200 1.67883100
H -2.08608000 -4.29618400 0.88388600
H -2.48065700 -4.27362500 2.63355400
H -3.66141100 -3.63200000 1.43706700
C -4.21836000 -2.46800000 -1.39632800
H -3.98539600 -1.76234400 -2.20450600
H -3.33808300 -3.10733700 -1.25735100
C -5.43311600 -3.29746100 -1.75072700
H -6.30535800 -2.65675100 -1.89867600
H -5.25309800 -3.85971000 -2.67028000
H -5.65888000 -4.00694000 -0.95077800
O -4.50606700 -1.77209700 -0.18943700
C -0.34841300 -2.28274000 -0.92438700
H -0.35550200 -3.20218600 -0.34942000
C 0.81156500 -2.12651300 -1.87481200
H 0.72630700 -2.91368900 -2.63461100
H -3.87254300 -0.56072600 1.23773900
H -3.91596400 0.23555700 -1.61930000
H -1.70789500 1.14393500 0.27743500

C 2.14560300 -2.37053800 -1.17354700
C 3.24770200 -2.76895100 -1.93525700
C 2.31123400 -2.20527400 0.20138300
C 4.48158300 -3.00045200 -1.34244600
H 3.13218300 -2.91031500 -3.00702500
C 3.55047800 -2.42955500 0.79718000
H 1.46353200 -1.91525400 0.81231100
C 4.63674300 -2.83174300 0.03091700
H 5.32170800 -3.32135900 -1.95023600
H 3.66056500 -2.29450700 1.86831800
H 5.59750200 -3.01997800 0.49942900
C -2.07384000 2.37336500 -1.40883700
C -2.61361400 2.57432200 -2.68122400
C -1.45954400 3.45050700 -0.77103700
C -2.53878800 3.81763700 -3.29659400
H -3.09417800 1.75138400 -3.20272600
C -1.38127900 4.69705100 -1.38364800
H -1.03680100 3.30680400 0.21913200
C -1.92118800 4.88412400 -2.64981100
H -2.96301600 3.95534400 -4.28591700
H -0.89624400 5.52048500 -0.86975400
H -1.86181700 5.85419100 -3.13186900
C 0.16374300 0.37559000 -1.82536600
C 0.79475500 -0.77571300 -2.62855800
C 1.51294800 1.15828100 1.60929400
C 2.56822600 1.83013900 0.70261600
B 0.98523700 0.83165600 -0.56899700
O 0.68303000 0.45029100 0.71294300
O 2.04260500 1.70889800 -0.61031100
H 0.12025100 1.24244000 -2.49529900
H 0.20749800 -0.89481400 -3.54613100
H 1.81167600 -0.51858700 -2.93659000
H 2.69530300 2.88594600 0.95685100
H 1.98231700 0.46656800 2.31437200
C 0.71933500 2.15831500 2.44009100
O 1.23987000 3.05562800 3.05204600
O -0.57857600 1.89499200 2.42546900
C 3.94031500 1.18286700 0.84820000
O 4.40238300 0.90419400 1.92623100
O 4.55430100 1.02441400 -0.31063300
C 5.89606700 0.49046200 -0.25916600
H 6.53389500 1.21797900 0.24931200
H 5.87890100 -0.42706300 0.33074700
C 6.32879700 0.24166000 -1.68324400
H 6.32831800 1.16919000 -2.25976200
H 7.33960000 -0.17316400 -1.69318600
H 5.65630400 -0.47250000 -2.16355900
C -1.43429300 2.72744700 3.23764700
H -1.14958000 2.59164600 4.28359200
H -1.26309500 3.77219000 2.96695100
C -2.85379100 2.28554900 2.96892900
H -2.96639200 1.21810500 3.17243100
H -3.54105300 2.84150500 3.61073300
H -3.12728900 2.47563800 1.92765700

24.IR spectrum of P3-r1-en-f1 from the reaction of VPS and c

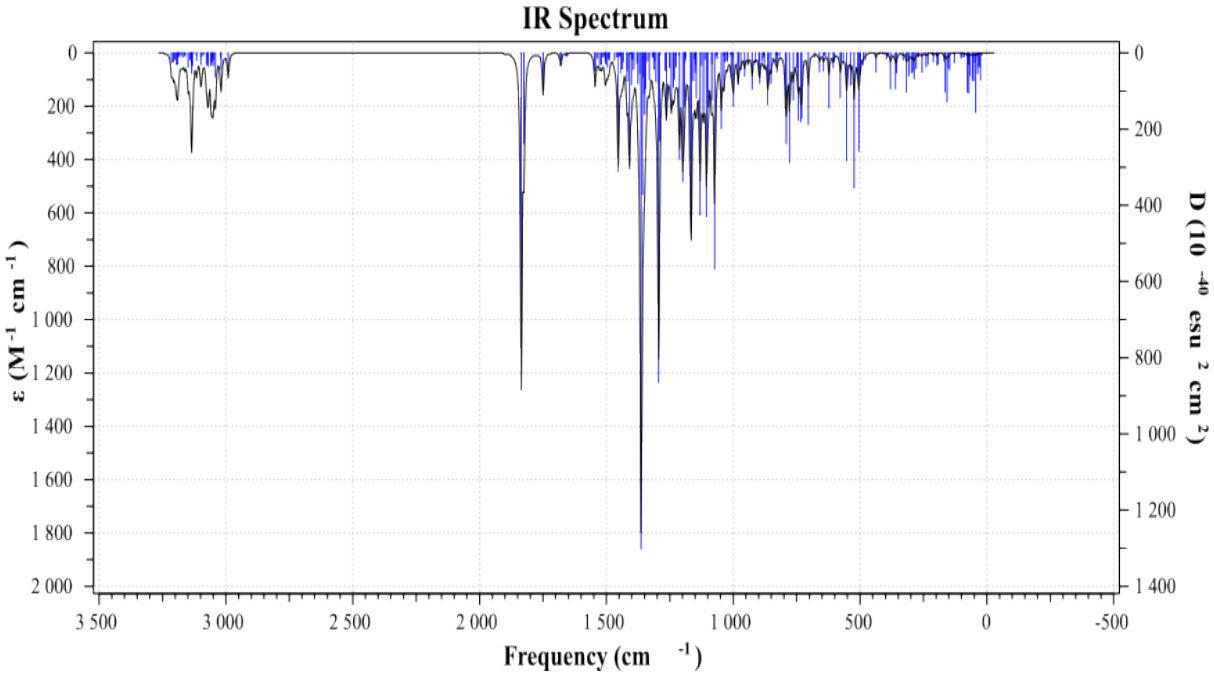

Figure S14: IR spectrum of P3-r1-en-f1 calculated at the wB97XD/6-311G(d,p) level of theory