

Supplementary material for the article:

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Supporting Information for:

Benchmarking Density Functional Tight Binding Models for Barrier Heights and Reaction Energetics of Organic Molecules

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Computed reaction energies and barrier heights with DFTB2 with and without included dispersion for the ISO34 (Table S1), DARC (Table S2), ISOL22 (Table S3), CIT (Table S4), NHTBH38/08 (Table S5), BHPERI (Table S7), Sn2SM (Table S9), Sn2MM (Table S10), PEREP (Table S12) databases; transition state bond distances for NHTBH38/08 (Table S6), BHPERI (Table S8), Sn2SM (Figure S1), Sn2MM (Table S11), PEREP (Table S13); representation of transition states for Sn2MM reactions (Figure S2) and for epoxydation of alkenes (Figure S3); summary of error analysis (Table S14).

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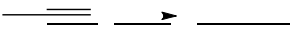
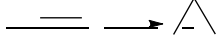
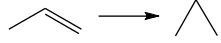
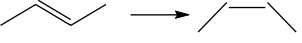
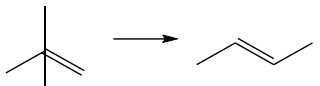

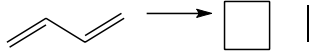
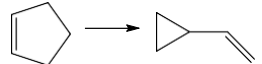
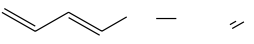
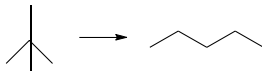
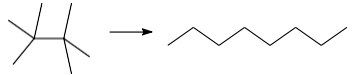
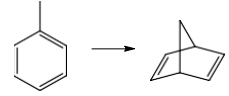
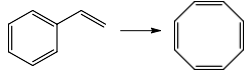
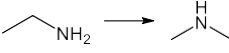
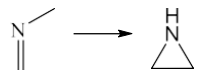
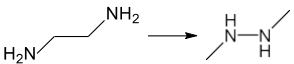
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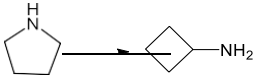
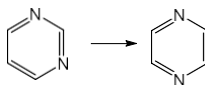
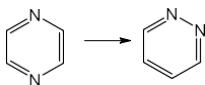
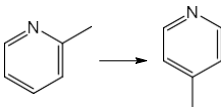
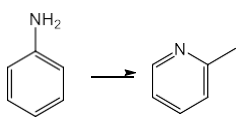
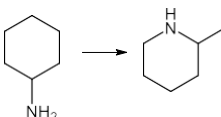
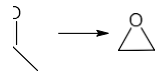
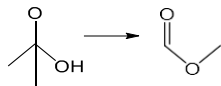
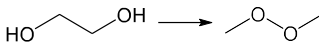
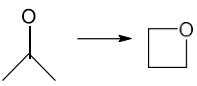
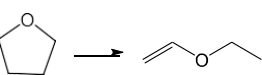
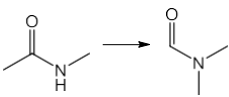
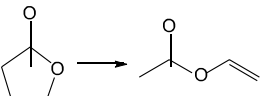
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Table S1. Computed isomerization energies (in kcal/mol) with DFTB2, with and without included dispersion, for ISO34 database;¹⁻³ Comparison to reference values is also given.

No.	Reaction	DFTB2	DFTB2-D3	Ref. value ³
1.		4.7	4.7	1.6
2.		31.1	31.1	21.9
3.		6.4	6.5	7.2
4.		0.9	0.8	1.0
5.		0.1	0.3	0.9
6.		3.8	3.7	2.6
7.		7.4	7.4	11.2
8.		24.3	24.6	22.9
9.		8.2	8.1	6.9
10.		-1.0	-0.3	3.6
11.		-6.7	-3.7	1.9
12.		51.4	51.1	47.0
13.		42.0	41.6	36.0
14.	$\text{CH}_3\text{CN} \longrightarrow \text{CH}_3\text{NC}$	10.2	10.1	24.2
15.		7.5	7.6	7.3
16.		18.9	19.0	10.8
17.		36.9	37.1	27.0

18.		10.4	10.4	11.2
19.		4.2	4.2	4.6
20.		26.8	26.8	20.2
21.		0.8	0.8	0.9
22.		1.7	1.9	3.2
23.		5.9	6.0	5.7
24.	$C_2H_5OH \longrightarrow (CH_3)_2O$	8.7	8.7	12.5
25.		31.8	31.9	26.5
26.		15.2	15.2	18.2
27.		58.6	59.0	64.2
28.		28.5	28.6	31.2
29.		14.3	14.3	11.9
30.		10.3	10.1	9.5
31.		17.3	17.7	14.1

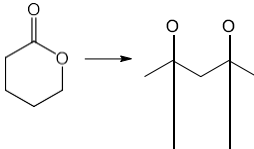
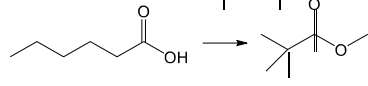
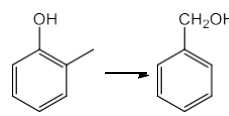
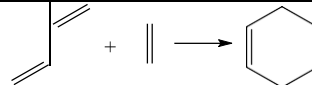
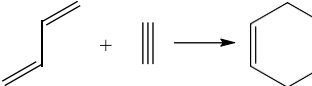
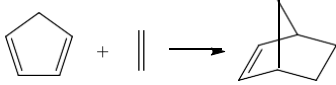
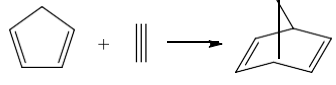
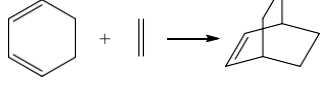
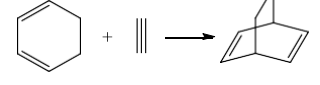
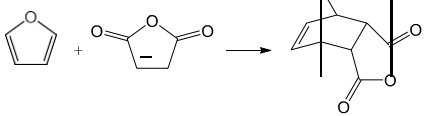
32.		3.4	3.5	7.1
33.		9.2	8.6	5.6
34.		11.8	11.9	7.3
MSE		0.5	0.6	
MAE		3.7	3.6	
RMSE		4.9	4.8	
LE		14.0	14.1	

Table S2. Computed Diels–Alder reaction energies (in kcal/mol) with DFTB2, with and without included dispersion, for DARC database;^{4,6} Comparison to reference values is also given.

No.	Reaction	DFTB2	DFTB2-D3	Ref. value ⁶
1.		-47.2	-49.5	-43.8
2.		-58.6	-60.5	-59.3
3.		-25.1	-27.6	-30.0
4.		-25.9	-28.0	-33.1
5.		-34.5	-37.6	-36.5
6.		-41.6	-44.1	-48.2
7.		-1.8	-5.6	-14.4

8.		-2.8	-6.3	-16.2
9.		-3.3	-7.3	-17.2
10.		-4.4	-8.0	-19.2
11.		-21.6	-25.8	-31.6
12.		-22.1	-26.2	-32.1
13.		-22.7	-27.1	-34.1
14.		-23.2	-27.4	-34.4
MSE		8.2	4.9	
MAE		8.7	6.1	
RMSE		9.8	6.8	
LE		14.8	11.2	

Table S3. Computed isomerization reaction energies (kcal/mol) with DFTB2, with and without included dispersion, for large organic molecules – ISOL22 database;^{7,8} Comparison to reference values is also given.

No.	Reaction	DFTB2	DFTB2-D3	Ref. value ⁸
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1.		26.8	32.6	37.5
2.		8.8	8.7	9.8
3.		35.3	37.9	32.8
4.		27.7	27.2	25.5
5.		12.4	15.4	17.4
6.		47.3	41.2	22.3
7.		16.0	17.3	21.8
8.		1.2	1.8	6.8
9.		38.2	38.3	37.9
10.		-3.7	-3.9	0.2
11.		45.8	46.3	33.5
12.		1.4	2.0	5.3
13.		25.8	27.00	3.1

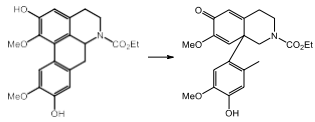
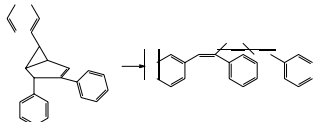
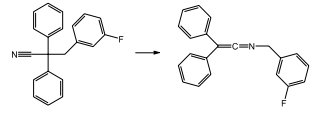
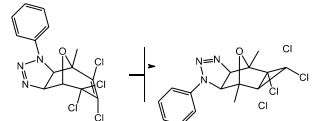
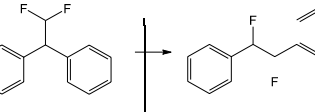
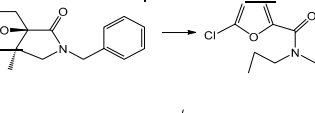
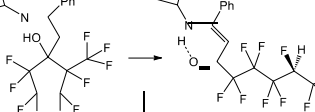
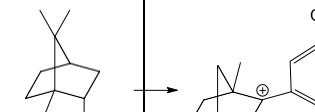
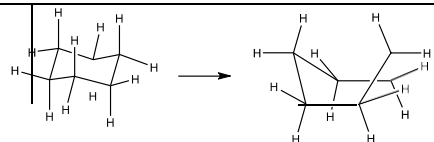
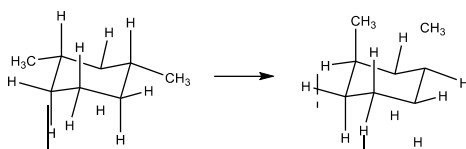
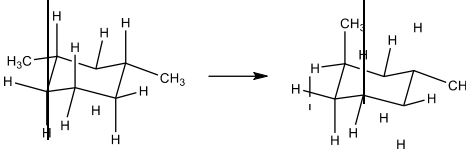
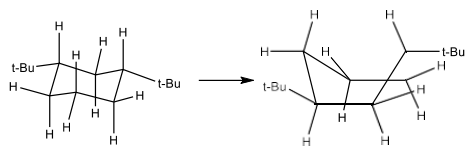
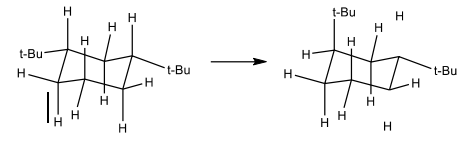
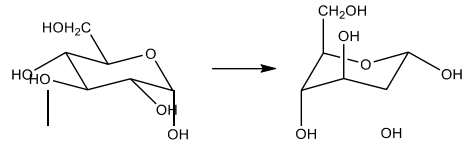
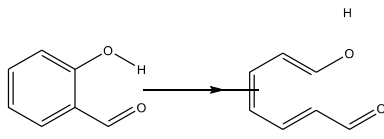
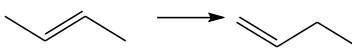
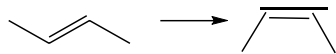
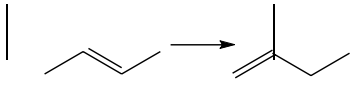
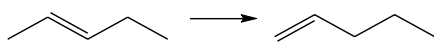
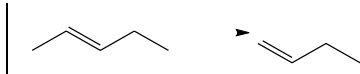
14.		21.9	21.5	22.8
15.		4.0	4.6	10.3
16.		23.8	26.4	22.6
17.		17.2	17.3	18.3
18.		5.1	4.7	4.7
19.		-6.7	-5.6	11.2
20.		-17.3	-16.6	0.8
21.		6.4	7.4	23.4
	MSE	-1.5	-0.8	
	MAE	7.8	7.1	
	RMSE	11.0	10.0	
	LE	25	23.9	

Table S4. Computed reaction energies (kcal/mol) with DFTB2, with and without included dispersion, and DFT (B3LYP-D3) for Conformers, Isomers, Tautomers – CIT database.

No.	Reaction	DFTB2	DFTB2 -D3	B3LYP- D3/TZP
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1.		4.3	4.3	6.3
2.		3.2	2.5	5.2
3.		0.9	0.6	1.9
4.		3.3	-0.8	5.0
5.		4.0	3.2	4.7
6.		3.4	2.7	1.3
7.		5.1	5.2	8.9
8.		3.8	3.7	2.8
9.		1.0	0.8	1.0
10.		2.5	2.4	1.5
11.		3.1	3.1	2.1
12.		0.7	0.6	0.8

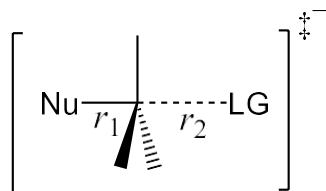
13.		14.2	14.2	13.5
14.		14.7	14.6	11.9
15.		15.2	15.3	13.8
16.		14.8	14.9	11.4
17.		8.8	8.7	10.0
18.		10.1	10.2	7.4
19.		6.1	6.0	3.9
20.		3.0	2.9	5.5
MSE ^[a]		0.2	-0.2	
MAE ^[a]		1.7	1.9	
RMSE ^[a]		1.9	2.3	
LE ^[a]		3.8	5.8	

[a] Compared to B3LYP-D3/TZP results

Table S5. Computed barrier heights (kcal/mol) with DFTB2, with and without included dispersion for S_N2 reactions – subset of NHTBH38/08 database;^{9,10} Comparison to reference values is also given.

No	S _N 2	DFTB2	DFTB2-D3	Ref. value ¹⁰
1.	F ⁻ ...CH ₃ F → FCH ₃ ...F ⁻	2.1	2.0	13.4
2.	Cl ⁻ ...CH ₃ Cl → ClCH ₃ ...Cl ⁻	0.8	0.8	13.4
3.	FCH ₃ ...Cl ⁻ → F ⁻ ...CH ₃ Cl	29.7	29.7	29.4
4.	HOCH ₃ ...F ⁻ → OH ⁻ ...CH ₃ F	49.0	48.7	47.2
	MSE	-5.5	-5.6	
	MAE	6.5	6.5	
	RMSE	8.5	8.5	
	LE	12.6	12.6	

Table S6. TS bond distances (Å) for NHTBH38/08 reactions



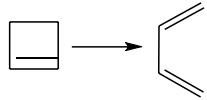
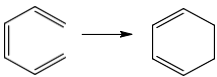
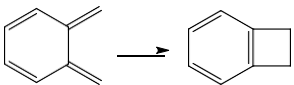



No.	S _N 2	DFTB2		DFTB2 D3		DFTB3		DFTB3 D3		Ref. value ¹⁰	
		r ₁	r ₂	r ₁	r ₂	r ₁	r ₂	r ₁	r ₂	r ₁	r ₂
1.	[F...CH ₃ ...F] ^{‡-}	1.92	1.92	1.92	1.92	1.92	1.92	1.92	1.92	1.82	1.82
2.	[Cl...CH ₃ ...Cl] ^{‡-}	2.35	2.35	2.35	2.35	2.35	2.35	2.35	2.35	2.32	2.32
3.	[F...CH ₃ ...Cl] ^{‡-}	2.51	1.92	2.52	1.92	2.53	1.87	2.53	1.88	2.05	2.11
4.	[F...CH ₃ ...OH] ^{‡-}	1.51	2.42	1.41	2.64	1.75	2.15	1.74	2.15	1.76	1.99

Table S7. Computed barrier heights (kcal/mol) with DFTB2, with and without included dispersion, for pericyclic reactions – BHPERI database¹¹⁻¹³ (excluding reaction with Si as DFTB parameters for Si atom are currently not available); Comparison to reference values is also given.

No.	Reaction	DFTB2	DFTB2- D3	Ref. value ¹¹⁻¹³
1.		41.8	41.7	35.3
2.		26.1	25.0	30.9
3.		34.1	34.3	28.3
4.		35.4	28.0	39.6
5.		25.5	47.7	28.2
6.		28.9	27.1	35.6
7.		14.9	12.1	22.1
8.		17.4	14.4	18.3
9.		20.2	14.7	9.8
10.		31.1	31.5	23.6
11.	$\text{N}_2\text{O} + \text{C}_2\text{H}_4$	35.5	35.1	26.3
12.	$\text{N}_3\text{H} + \text{C}_2\text{H}_4$	25.8	25.0	18.1
13.	$\text{N}_2\text{CH}_2 + \text{C}_2\text{H}_4$	14.3	13.3	12.2

14.	HCNO + C ₂ H ₄	13.0	13.0	11.1
15.	HCNNH + C ₂ H ₄	11.4	11.3	5.3
16.	HCNCH ₂ + C ₂ H ₄	7.5	6.4	4.0
17.	H ₂ COHN + C ₂ H ₄	11.4	8.9	11.5
18.	H ₂ CNHNH + C ₂ H ₄	6.7	4.1	4.0
19.	H ₂ CNHCH ₂ + C ₂ H ₄	0.3	-2.0	-1.4
20.	Furan + C ₂ H ₄	20.5	18.4	19.8
21.	Pyrrole + C ₂ H ₄	28.0	25.4	25.4
22.	C ₄ H ₄ PH + C ₂ H ₄	22.9	19.5	18.1
23.	C ₄ H ₄ PH + C ₂ H ₄	20.4	17.3	18.2
24.	Thiophene + C ₂ H ₄	28.4	25.5	28.1
MSE		2.0	1.1	
MAE		4.3	5.1	
RMSE		5.1	6.7	
LE		10.4	19.5	

Table S8. TS bond distances (Å) for BHPERI reactions

No.	Reaction / kcal/mol	DFTB2	DFTB2-D3	DFTB3	DFTB3-D3	Ref. value ¹¹⁻¹³
1.		2.11	2.11	2.11	2.11	2.14
2.		2.25	2.25	2.24	2.24	2.28
3.		2.25	2.25	2.25	2.25	2.29
4.		1.30	1.30	1.29	1.29	1.43
5.		1.32	1.32	1.33	1.33	1.31
6.		1.32	1.32	1.33	1.33	1.31

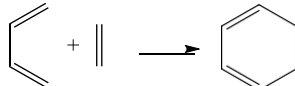
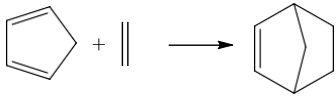
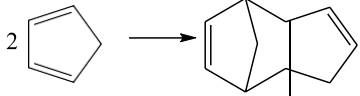
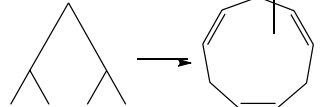
7.		2.22	2.22	2.22	2.22	2.27
8.		2.19	2.19	2.18	2.18	2.22
9.	2 	2.04	2.04	2.04	2.03	1.96
10.		1.86	1.86	1.86	1.86	1.87
11.	$\text{N}_2\text{O} + \text{C}_2\text{H}_4$	1.99	1.99	1.99	1.99	2.00
12.	$\text{N}_3\text{H} + \text{C}_2\text{H}_4$	2.03	2.03	2.03	2.02	2.12
13.	$\text{N}_2\text{CH}_2 + \text{C}_2\text{H}_4$	3.88	2.12	2.37	3.13	2.32
14.	$\text{HCNO} + \text{C}_2\text{H}_4$	2.08	2.08	2.07	2.07	2.19
15.	$\text{HCNNH} + \text{C}_2\text{H}_4$	2.20	2.19	2.18	2.18	2.30
16.	$\text{HCNCH}_2 + \text{C}_2\text{H}_4$	2.29	2.30	2.28	2.28	2.41
17.	$\text{H}_2\text{COHN} + \text{C}_2\text{H}_4$	2.15	2.15	2.14	2.14	2.16
18.	$\text{H}_2\text{CNHNH} + \text{C}_2\text{H}_4$	2.22	2.22	2.20	2.20	2.25
19.	$\text{H}_2\text{CNHCH}_2 + \text{C}_2\text{H}_4$	2.37	2.37	2.34	2.34	2.47
20.	furan + C_2H_4	2.09	2.09	2.09	2.08	2.13
21.	pyrrole + C_2H_4	2.06	2.05	2.05	2.05	2.10
22.	$\text{C}_4\text{H}_4\text{PH} + \text{C}_2\text{H}_4$	2.18	2.18	2.18	2.17	2.23
23.	$\text{C}_4\text{H}_4\text{PH} + \text{C}_2\text{H}_4$	2.17	2.17	2.17	2.16	2.22
24.	thiophene + C_2H_4	2.13	2.12	2.12	2.12	2.16

Table S9. Computed barrier heights (kcal/mol) with DFTB2, with and without included dispersion and DFT (B3LYP-D3) for $\text{S}_{\text{N}}2$ reactions involving different small molecules – Sn2SM database.

No.	$\text{S}_{\text{N}}2$	DFTB2	DFTB2-D3	B3LYP-D3/TZP
1.	$\text{OH}^- + \text{CH}_3\text{OH} \rightarrow [\text{HO}\dots\text{CH}_3\dots\text{OH}]^{\ddagger-}$	-1.8	-2.4	4.8

2.	$\text{CN}^- + \text{CH}_3\text{OH} \rightarrow [\text{NC}\dots\text{CH}_3\dots\text{OH}]^{\ddagger-}$	31.6	30.9	23.1
3.	$\text{PhO}^- + \text{CH}_3\text{OH} \rightarrow [\text{PhO}\dots\text{CH}_3\dots\text{OH}]^{\ddagger-}$	---	---	31.3
4.	$\text{NH}_2^- + \text{CH}_3\text{OH} \rightarrow [\text{H}_2\text{N}\dots\text{CH}_3\dots\text{OH}]^{\ddagger-}$	-0.3	-0.3	2.8
5.	$\text{CN}^- + \text{CH}_3\text{CN} \rightarrow [\text{NC}\dots\text{CH}_3\dots\text{CN}]^{\ddagger-}$	25.5	24.7	21.5
6.	$\text{PhO}^- + \text{CH}_3\text{CN} \rightarrow [\text{PhO}\dots\text{CH}_3\dots\text{CN}]^{\ddagger-}$	30.5	28.8	27.7
7.	$\text{CN}^- + \text{CH}_3\text{NH}_2 \rightarrow [\text{NC}\dots\text{CH}_3\dots\text{NH}_2]^{\ddagger-}$	45.5	44.6	41.0
8.	$\text{PhO}^- + \text{CH}_3\text{OPh} \rightarrow [\text{PhO}\dots\text{CH}_3\dots\text{OPh}]^{\ddagger-}$	8.0	6.4	10.1
9.	$\text{PhO}^- + \text{CH}_3\text{NH}_2 \rightarrow [\text{PhO}\dots\text{CH}_3\dots\text{NH}_2]^{\ddagger-}$	---	---	49.8
10.	$\text{NH}_2^- + \text{CH}_3\text{NH}_2 \rightarrow [\text{H}_2\text{N}\dots\text{CH}_3\dots\text{NH}_2]^{\ddagger-}$	6.9	5.8	18.9
<hr/>				
	MSE ^[a]	-0.5	-1.4	
	MAE ^[a]	5.5	5.4	
	RMSE ^[a]	6.3	6.4	
	LE ^[a]	12.0	13.1	

[a] Compared to B3LYP-D3/TZP results

Figure S1. TS bond distances (Å) for Sn2SM.

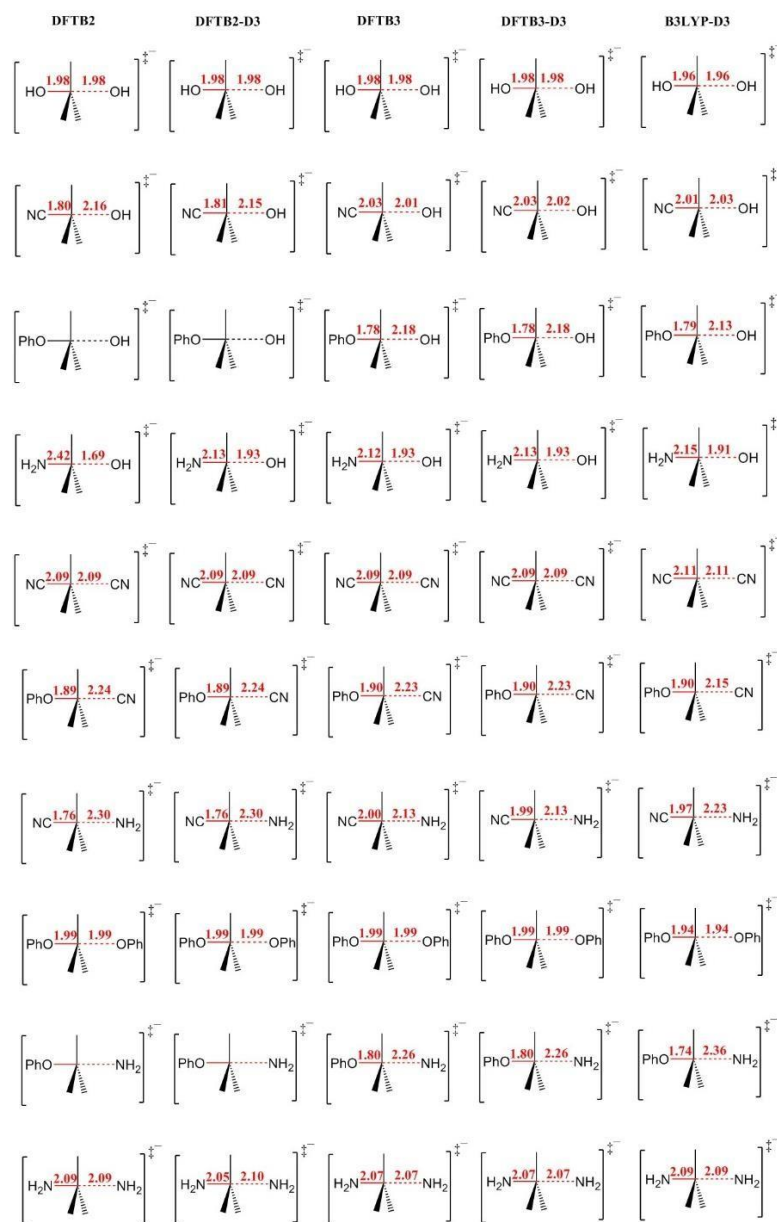


Table S10. Computed barrier heights (kcal/mol) with DFTB2, with and without included dispersion and DFT (B3LYP-D3) for S_N2 reactions involving different medium size molecules – Sn2MM database.

No.	React1	React2	DFTB2	DFTB2-D3	B3LYP-D3/TZP
1.	CN ⁻	CH ₃ -OSO ₂ Ph	-5.7	-8.4	-10.4
2.	CN ⁻	prim-OSO ₂ Ph	-5.4	-7.4	-5.7

3.	CN ⁻	sec- OSO ₂ Ph	-4.2	-7.1	-7.5
4.	NH ₃	CH ₃ - OSO ₂ Ph	42.5	35.7	25.9
5.	NH ₃	prim- OSO ₂ Ph	40.0	32.8	27.6
6.	NH ₃	sec- OSO ₂ Ph	37.1	30.1	27.4
7.	CN ⁻	CH ₃ - OSO ₂ CH ₃	-5.3	-9.0	-10.0
8.	CN ⁻	prim- OSO ₂ CH ₃	-4.2	-7.1	-5.5
9.	CN ⁻	sec- OSO ₂ CH ₃	-4.3	-7.9	-5.3
10.	NH ₃	CH ₃ - OSO ₂ CH ₃	42.7	34.7	25.9
11.	NH ₃	prim- OSO ₂ CH ₃	40.5	32.0	27.6
12.	NH ₃	sec- OSO ₂ CH ₃	36.9	29.3	27.1
MSE ^[a]			7.8	2.6	
MAE ^[a]			7.8	3.5	
RMSE ^[a]			9.7	4.6	
LE ^[a]			16.8	9.8	

[a] Compared to B3LYP-D3/TZP results

Figure S2. Schematic representation of TS for S_N2MM reactions

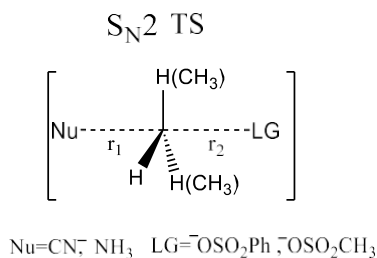
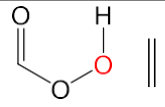
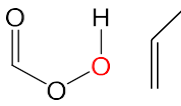
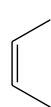
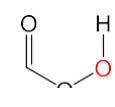
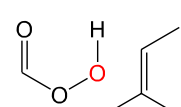
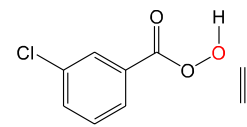
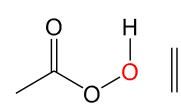


Table S11. TS bond distances (Å) for S_N2MM

No.	TS	DFTB2		DFTB2-D3		DFTB3		DFTB3-D3		B3LYP-D3	
		r ₁	r ₂	r ₁	r ₂	r ₁	r ₂	r ₁	r ₂	r ₁	r ₂
1.	CN ⁻ CH ₃ - OSO ₂ Ph	2.45	1.72	2.45	1.72	2.41	1.75	2.43	1.73	2.40	1.76
2.	CN ⁻ prim- OSO ₂ Ph	2.47	1.82	2.47	1.82	2.46	1.84	2.45	1.84	2.48	1.80
3.	CN ⁻ sec- OSO ₂ Ph	2.52	1.93	2.52	1.93	2.53	1.96	2.52	1.96	2.58	1.99

4.	NH ₃	CH ₃ -OSO ₂ Ph	2.33	1.77	2.33	1.77	2.27	1.82	2.26	1.82	2.06	1.94
5.	NH ₃	prim-OSO ₂ Ph	2.38	1.86	2.39	1.86	2.30	1.93	2.29	1.92	2.13	2.00
6.	NH ₃	sec-OSO ₂ Ph	2.45	2.22	2.44	2.21	2.39	2.28	2.38	2.26	2.20	2.21
7.	CN ⁻	CH ₃ -OSO ₂ CH ₃	2.45	1.73	2.44	1.73	2.42	1.75	2.40	1.75	2.38	1.78
8.	CN ⁻	prim-OSO ₂ CH ₃	2.48	1.82	2.48	1.82	2.48	1.83	2.47	1.83	2.43	1.87
9.	CN ⁻	sec-OSO ₂ CH ₃	2.51	1.94	2.50	1.94	2.53	1.96	2.52	1.96	2.55	1.98
10.	NH ₃	CH ₃ -OSO ₂ CH ₃	2.34	1.77	2.33	1.77	2.27	1.82	2.27	1.82	2.07	1.94
11.	NH ₃	prim-OSO ₂ CH ₃	2.38	1.85	2.38	1.85	2.29	1.93	2.29	1.93	2.13	2.00
12.	NH ₃	sec-OSO ₂ CH ₃	2.45	2.24	2.44	2.23	2.38	2.28	2.38	2.27	2.22	2.22

Table S12. Computed barrier heights (kcal/mol) with DFTB2, with and without included dispersion and DFT (B3LYP-D3) for the epoxidation of alkenes – PEREP database.

No.	Reaction	DFTB2	DFTB2-D3	B3LYP D3/TZP
1.		10.4	9.2	13.3
2.		9.5	7.9	10.5
3.		7.7	5.9	 7.8
4.		6.9	5.1	5.8
5.		11.8	10.5	14.1
6.		12.0	10.8	15.2

7.		12.3	11.0	14.8
8.		10.5	9.2	12.9
9.		6.8	5.7	8.9
	MSE ^[a]	-1.7	-3.1	
	MAE ^[a]	2.0	3.1	
	RMSE ^[a]	2.2	3.3	
	LE ^[a]	3.2	4.4	

[a] Compared to B3LYP-D3/TZP results

Figure S3. Schematic representation of TS for our epoxydation of alkenes compilation

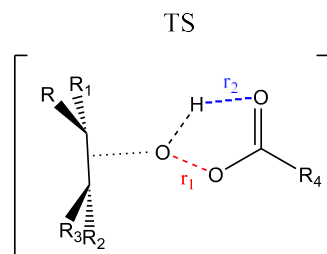


Table S13. TS bond distances (Å) for our compilation – PEREP

No.	DFTB2		DFTB2-D3		DFTB3		DFTB3-D3		B3LYP-D3		
	r ₁	r ₂	r ₁	r ₂	r ₁	r ₂	r ₁	r ₂	r ₁	r ₂	
1.		2.07	1.77	2.07	1.75	1.90	1.82	1.90	1.82	1.86	1.66
2.		2.09	1.66	2.09	1.65	1.79	1.84	1.79	1.83	1.84	1.70

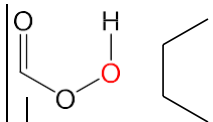
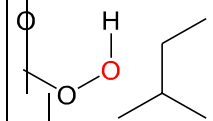
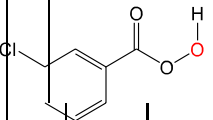
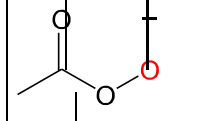
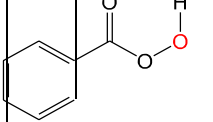
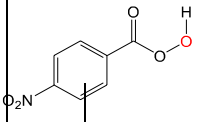
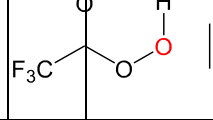
3.		1.81	1.89	1.80	1.88	1.76	1.84	1.77	1.84	1.82	1.73
4.		1.78	1.90	1.78	1.89	1.74	1.85	1.73	1.83	1.80	1.77
5.		2.06	1.68	2.05	1.63	1.91	1.73	1.90	1.73	1.84	1.61
6.		2.06	1.68	2.07	1.66	1.96	1.70	1.90	1.73	1.86	1.59
7.		2.06	1.67	2.06	1.65	1.99	1.65	1.95	1.68	1.84	1.58
8.		2.04	1.69	2.05	1.65	1.84	1.78	1.83	1.77	1.83	1.64
9.		1.80	1.91	1.79	1.90	1.78	1.89	1.78	1.88	1.82	1.77

Table S14. Summary of the error analysis (MSE – mean signed error; MAE – mean absolute error; RMSE – root mean square error; MAD – mean absolute deviation; RMSD – root mean square deviation; LE – largest error in absolute value)¹⁴ in kcal/mol (compared to the reference values)^[a] of different DFT and DFTB methods for all herein studied datasets.

ISO34 ¹⁻³	B3LYP-D3/ def2-QZVP ¹⁵	PBE-D3/ def2-QZVP ¹⁵	DFTB3	DFTB3-D3	B3LYP/TZP//DFTB3-D3	DFTB2	DFTB2-D3
MSE	-0.1	-0.6	1.3	1.4	0.1	0.5	0.6
MAE	1.9	1.6	3.6	3.4	1.8	3.7	3.6
RMSE	2.6	2.1	5.0	4.9	2.5	4.9	4.8
MAD	1.9	1.5	3.4	3.3	1.8	3.7	3.5
RMSD	2.6	2.0	4.8	4.7	2.5	4.9	4.7
LE	9.4	4.6	13.9	14.1	9.1	14.0	14.1

DARC ^{4,6}	B3LYP-D3/def2-QZVP ¹⁵	PBE-D3/ def2-QZVP ¹⁵	DFTB3	DFTB3-D3	B3LYP/TZP//DFTB3-D3	DFTB2	DFTB2-D3
MSE	10.2	3.3	8.4	5.1	5.6	8.2	4.9
MAE	10.2	4.2	8.7	5.8	5.6	8.7	6.1
RMSE	10.5	4.8	9.6	6.5	5.9	9.8	6.8
MAD	2.0	3.1	3.8	3.1	1.5	4.5	3.7
RMSD	2.4	3.5	4.6	4.1	2.1	5.3	4.7
LE	12.4	6.9	14.5	10.8	7.6	14.8	11.2
ISOL22 ^{7,8}	B3LYP-D3/ def2-QZVP ¹⁵	PBE-D3/ def2-QZVP ¹⁶	DFTB3	DFTB3-D3	B3LYP/TZP//DFTB3-D3	DFTB2	DFTB2-D3
MSE	-3.7	-2.7	-1.3	-0.6	-3.2	-1.5	-0.8
MAE	5.9	4.5	7.6	7.0	6.1	7.8	7.1
RMSE	8.0	6.2	10.7	9.8	8.3	11.0	10.0
MAD	5.0	3.8	7.4	6.8	5.3	7.6	6.9
RMSD	7.0	5.6	10.7	9.8	7.7	10.9	10.0
LE	20.2	16.5	24.3	21.7	22.4	25.0	23.9
CIT	B3LYP-D3/TZP	PBE-D3/ TZP	DFTB3	DFTB3-D3	B3LYP/TZP//DFTB3-D3	DFTB2	DFTB2-D3
MSE	-	-0.1	-0.6	-0.7	0.1	0.2	-0.2
MAE	-	1.0	1.3	1.3	0.5	1.7	1.9
RMSE	-	1.4	1.6	1.6	0.9	1.9	2.3
MAD	-	1.0	1.2	1.3	0.6	9.9	10.9
RMSD	-	1.4	1.5	1.5	0.9	10.1	11.2
LE	-	3.9	4.2	4.2	2.1	3.8	5.8
NHTBH38/ O8 ^{9,10}	B3LYP-D3/ TZP	PBE-D3/ TZP	DFTB3	DFTB3-D3	B3LYP/TZP//DFTB3-D3	DFTB2	DFTB2-D3
MSE	-4.1	-5.9	-6.8	-6.8	-3.7	-5.5	-5.6
MAE	4.1	5.9	6.8	6.8	3.7	6.5	6.5
RMSE	4.9	6.2	7.1	7.1	4.1	8.5	8.5
MAD	2.5	1.7	1.6	1.6	1.6	6.5	6.5
RMSD	2.6	2.0	1.9	1.9	1.7	6.5	6.5
LE	7.7	7.6	9.9	9.9	5.9	12.6	12.6
BHPERI ¹¹⁻¹³	B3LYP-D3/def2-QZVP ¹⁵	PBE-D3/ def2-QZVP ¹⁵	DFTB3	DFTB3-D3	B3LYP/TZP//DFTB3-D3	DFTB2	DFTB2-D3
MSE	2.0	-4.2	2.5	0.9	-0.1	2.0	1.1
MAE	2.6	4.2	5.3	5.0	2.6	4.3	5.1
RMSE	3.4	4.8	6.5	6.3	3.4	5.1	6.7
MAD	2.3	1.9	4.5	5.0	2.5	3.7	5.0
RMSD	2.8	2.2	6.0	6.2	3.4	4.7	6.7
LE	6.6	8.5	14.2	14.4	9.9	10.4	19.5
Sn2SM ^[a]	B3LYP-D3/TZP	PBE-D3/ TZP	DFTB3	DFTB3-D3	B3LYP/TZP//DFTB3-D3	DFTB2	DFTB2-D3
MSE	-	-4.7	0.2	-1.0	-0.2	-0.5	-1.4

MAE	-	4.7	5.1	5.3	0.4	5.5	5.4
RMSE	-	5.0	5.9	6.2	0.5	6.3	6.4
MAD	-	1.6	5.1	5.3	0.4	5.5	5.4
RMSD	-	1.8	5.9	6.1	0.5	6.3	6.3
LE	-	7.2	10.2	11.9	1.2	12.0	13.1
SN₂MM^[a]	B3LYP-D3/TZP	PBE-D3/ TZP	DFTB3	DFTB3-D3	B3LYP/TZP// DFTB3-D3	DFTB2	DFTB2-D3
MSE	-	-2.7	2.6	1.2	-0.2	7.8	2.6
MAE	-	2.7	3.5	3.4	1.2	7.8	3.5
RMSE	-	2.8	4.6	4.2	1.2	9.7	4.6
MAD	-	0.7	3.0	3.3	1.2	5.2	3.0
RMSD	-	0.8	3.8	4.0	1.2	5.8	3.8
LE	-	4.1	9.8	8.7	1.8	16.8	9.8
PEREP^[a]	B3LYP-D3/TZP	PBE-D3/ TZP	DFTB3	DFTB3-D3	B3LYP/TZP// DFTB3-D3	DFTB2	DFTB2-D3
MSE	-	-8.6	-3.6	-5.1	1.0	-1.7	-3.1
MAE	-	8.6	3.6	5.1	1.5	2.0	3.1
RMSE	-	8.7	4.1	5.3	1.9	2.2	3.3
MAD	-	0.6	1.6	1.5	1.5	1.1	0.9
RMSD	-	0.7	1.9	1.7	1.6	1.3	1.1
LE	-	9.5	6.1	7.4	3.5	3.2	4.4

[a] Compared to B3LYP-D3/TZP results

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