Electronic Supplementary Information (ESI)

Unsaturated C_6 Fatty Acid Methyl Esters as Reference Molecules for Biodiesel: Kinetics of H-Atom Abstraction and Addition

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S1. Reactions Analyzed

For this study, the reactions investigated involve hydrogen abstraction and addition processes in a specific class of molecules containing carbonyl functional groups. Hydrogen abstraction can occur both at the methyl group and at the carbon atoms located at the α, β, γ, δ, and ϵ positions relative to the carbonyl group. Conversely, hydrogen addition takes place at positions adjacent to the double bond, with the exact sites depending on its location within the molecule.

These positions correspond to α and β in (X)-2mhex, β and γ in (X)-3mhex, γ and δ in (X)-4mhex, and δ and ϵ in 5mhex, where X denotes either the Z or E stereoisomer. These considerations define the following reaction channels:

$\mathrm{R}_{\mathrm{ab},\alpha}^{(\mathrm{X})-2\mathrm{mhex}}$: (x)-2mhex + H $\rightarrow$ $\mathrm{P}_{\mathrm{ab},\alpha}^{(\mathrm{X})-2\mathrm{mhex}}$ + H_2

$\mathrm{R}_{\mathrm{ab},\beta}^{(\mathrm{X})-2\mathrm{mhex}}$: (x)-2mhex + H $\rightarrow$ $\mathrm{P}_{\mathrm{ab},\beta}^{(\mathrm{X})-2\mathrm{mhex}}$ + H_2

$\mathrm{R}_{\mathrm{ab},\gamma}^{(\mathrm{X})-2\mathrm{mhex}}$: (x)-2mhex + H $\rightarrow$ $\mathrm{P}_{\mathrm{ab},\gamma}^{(\mathrm{X})-2\mathrm{mhex}}$ + H_2 (x2)

$\mathrm{R}_{\mathrm{ab},\delta}^{(\mathrm{X})-2\mathrm{mhex}}$: (x)-2mhex + H $\rightarrow$ $\mathrm{P}_{\mathrm{ab},\delta}^{(\mathrm{X})-2\mathrm{mhex}}$ + H_2 (x2)

$\mathrm{R}_{\mathrm{ab},\epsilon}^{(\mathrm{X})-2\mathrm{mhex}}$: (x)-2mhex + H $\rightarrow$ $\mathrm{P}_{\mathrm{ab},\epsilon}^{(\mathrm{X})-2\mathrm{mhex}}$ + H_2

$\mathrm{R}_{\mathrm{ab,m}}^{(\mathrm{X})-2\mathrm{mhex}}$: (x)-2mhex + H $\rightarrow$ $\mathrm{P}_{\mathrm{ab,m}}^{(\mathrm{X})-2\mathrm{mhex}}$ + H_2

$\mathrm{R}_{\mathrm{ad},\alpha}^{(\mathrm{X})-2\mathrm{mhex}}$: (x)-2mhex + H $\rightarrow$ $\mathrm{P}_{\mathrm{ad},\alpha}^{(\mathrm{X})-2\mathrm{mhex}}$ (x2)

$\mathrm{R}_{\mathrm{ad},\beta}^{(\mathrm{X})-2\mathrm{mhex}}$: (x)-2mhex + H $\rightarrow$ $\mathrm{P}_{\mathrm{ad},\beta}^{(\mathrm{X})-2\mathrm{mhex}}$ (x2)

$\mathrm{R}_{\mathrm{ab},\alpha}^{(\mathrm{X})-3\mathrm{mhex}}$: (x)-3mhex + H $\rightarrow$ $\mathrm{P}_{\mathrm{ab},\alpha}^{(\mathrm{X})-2\mathrm{mhex}}$ + H_2 (x2)

$\mathrm{R}_{\mathrm{ab},\beta}^{(\mathrm{X})-3\mathrm{mhex}}$: (x)-3mhex + H $\rightarrow$ $\mathrm{P}_{\mathrm{ab},\beta}^{(\mathrm{X})-2\mathrm{mhex}}$ + H_2

$\mathrm{R}_{\mathrm{ab},\gamma}^{(\mathrm{X})-3\mathrm{mhex}}$: (x)-3mhex + H $\rightarrow$ $\mathrm{P}_{\mathrm{ab},\gamma}^{(\mathrm{X})-2\mathrm{mhex}}$ + H_2

$\mathrm{R}_{\mathrm{ab},\delta}^{(\mathrm{X})-3\mathrm{mhex}}$: (x)-3mhex + H $\rightarrow$ $\mathrm{P}_{\mathrm{ab},\delta}^{(\mathrm{X})-2\mathrm{mhex}}$ + H_2 (x2)

$\mathrm{R}_{\mathrm{ab},\epsilon}^{(\mathrm{X})-3\mathrm{mhex}}$: (x)-3mhex + H $\rightarrow$ $\mathrm{P}_{\mathrm{ab},\epsilon}^{(\mathrm{X})-2\mathrm{mhex}}$ + H_2

$\mathrm{R}_{\mathrm{ab,m}}^{(\mathrm{X})-3\mathrm{mhex}}$: (x)-3mhex + H $\rightarrow$ $\mathrm{P}_{\mathrm{ab,m}}^{(\mathrm{X})-2\mathrm{mhex}}$ + H_2

$\mathrm{R}_{\mathrm{ad},\beta}^{(\mathrm{X})-3\mathrm{mhex}}$: (x)-3mhex + H $\rightarrow$ $\mathrm{P}_{\mathrm{ad},\beta}^{(\mathrm{X})-2\mathrm{mhex}}$ (x2)

$\mathrm{R}_{\mathrm{ad},\gamma}^{(\mathrm{X})-3\mathrm{mhex}}$: (x)-3mhex + H $\rightarrow$ $\mathrm{P}_{\mathrm{ad},\gamma}^{(\mathrm{X})-2\mathrm{mhex}}$ (x2)

$\mathrm{R}_{\mathrm{ab},\alpha}^{(\mathrm{X})-4\mathrm{mhex}}$: (x)-4mhex + H $\rightarrow$ $\mathrm{P}_{\mathrm{ab},\alpha}^{(\mathrm{X})-4\mathrm{mhex}}$ + H_2 (x2)

$R^{(X)-4mhex}_{ab,\beta}$: (x)-4mhex + H $\rightarrow$ $P^{(X)-4mhex}_{ab,\beta}$ + H_2 (x2)

$R^{(X)-4mhex}_{ab,\gamma}$: (x)-4mhex + H $\rightarrow$ $P^{(X)-4mhex}_{ab,\gamma}$ + H_2

$R^{(X)-4mhex}_{ab,\delta}$: (x)-4mhex + H $\rightarrow$ $P^{(X)-4mhex}_{ab,\delta}$ + H_2

$R^{(X)-4mhex}_{ab,\epsilon}$: (x)-4mhex + H $\rightarrow$ $P^{(X)-4mhex}_{ab,\epsilon}$ + H_2

$R^{(X)-4mhex}_{ab,m}$: (x)-4mhex + H $\rightarrow$ $P^{(X)-4mhex}_{ab,m}$ + H_2

$R^{(X)-4mhex}_{ad,\gamma}$: (x)-4mhex + H $\rightarrow$ $P^{(X)-4mhex}_{ad,\gamma}$ (x2)

$R^{(X)-4mhex}_{ad,\delta}$: (x)-4mhex + H $\rightarrow$ $P^{(X)-4mhex}_{ad,\delta}$ (x2)

$R^{5mhex}_{ab,\alpha}$: 5mhex + H $\rightarrow$ $P^{5mhex}_{ab,\alpha}$ + H_2 (x2)

$R^{5mhex}_{ab,\beta}$: 5mhex + H $\rightarrow$ $P^{5mhex}_{ab,\beta}$ + H_2 (x2)

$R^{5mhex}_{ab,\gamma}$: 5mhex + H $\rightarrow$ $P^{5mhex}_{ab,\gamma}$ + H_2 (x2)

$R^{5mhex}_{ab,\delta}$: 5mhex + H $\rightarrow$ $P^{5mhex}_{ab,\delta}$ + H_2

$R^{5mhex}_{ab,\epsilon_1}$: 5mhex + H $\rightarrow$ $P^{5mhex}_{ab,\epsilon}$ + H_2

$R^{5mhex}_{ab,\epsilon_2}$: 5mhex + H $\rightarrow$ $P^{5mhex}_{ab,\epsilon}$ + H_2

$R^{5mhex}_{ab,m}$: 5mhex + H $\rightarrow$ $P^{5mhex}_{ab,m}$ + H_2

$R^{5mhex}_{ad,\delta}$: 5mhex + H $\rightarrow$ $P^{5mhex}_{ad,\gamma}$ (x2)

$R^{5mhex}_{ad,\epsilon}$: 5mhex + H $\rightarrow$ $P^{5mhex}_{ad,\delta}$ (x2)

It is important to highlight that certain hydrogen abstraction reactions involving methylenic carbon sites are counted twice to reflect the presence of two configurational enantiomer transition states (R and S). Due to their energetic equivalence, only one of these pathways is included in the conformational analysis, and the corresponding rate constant is weighted by a factor of two. An exception to this treatment occurs for abstractions at the ϵ carbon in 5mhex, where the associated transition states exhibit significant energetic differences and are therefore treated independently.

Similarly, hydrogen addition reactions are also counted twice to account for hydrogen atom attack occurring on either the same or the opposite face of the double bond. Nonetheless, only one of these pathways is incorporated into the reaction mechanism, with this symmetry incorporated into the calculation of the rate constants.

S2. Conformational Search for Methyl (Z)- and (E)-hex-2-enoate

For methyl (Z)- and (E)-hex-2-enoate, two approaches were considered to account for the possible impact of the mesomeric effect between the double bond and the carbonyl group, which may restrict rotation around the adjacent dihedral angle (see Figure S1.). In the first approach, this torsion (ϕ_2) was excluded, while in the second, all four torsions were included, as shown in Figure S1. of the main text. As expected, the latter led to a larger number of conformers, including some low-energy structures not identified in the first approach, such as conf. 7 and conf. 3 for (Z)-2mhex and (E)-2mhex, respectively, as shown in the tables below. These results highlight the importance of accounting for ϕ_2, as it can influence both thermodynamic and kinetic properties. Therefore, all subsequent analyses were based on the second approach.

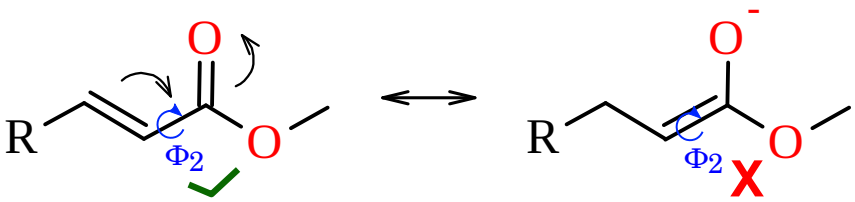

Fig. S1.: Representation of the mesomeric effect between the carbonyl group and the double bond in unsaturated esters.

All dihedral angles are reported in degrees (°), and energy differences are given in kcal/mol.

(Z)-2mhex (four torsion).

	angles	conf	weight	E	E+ZPE
1	180_187_272_182	TT-g-T-	2	0.000	0.083
2	180_181_124_177	TT-A+T+	2	0.066	0.000
3	180_184_253_068	TT-A-G+	2	0.129	0.407
4	180_186_273_300	TT-g-G-	2	0.573	0.598
5	180_350_091_177	TC-a+T+	2	1.652	1.799
6	180_000_180_180	TCTT	1	1.693	1.388

7	180_006_251_068	TC+A-G+	2	1.814	2.077
8	180_352_090_059	TC-g+G+	2	2.190	2.310
9	352_159_093_178	C-T+a+T+	2	8.599	8.529
10	009_204_248_067	C+T-A-G+	2	8.941	9.006
11	352_159_092_060	C-T+a+G+	2	9.248	9.286

(E)-2mhex (four torsion).

	angles	conf	weight	E	E+ZPE
1	180_180_000_180	TTCT	1	0.000	0.000
2	180_180_121_178	TTA+T+	2	0.058	0.031
3	180_180_123_295	TTA+G-	2	0.218	0.199
4	180_000_000_180	TCCT	1	0.681	0.729
5	180_000_121_178	TCA+T+	2	0.697	0.666
6	180_180_119_063	TTA+G+	2	0.710	0.848
7	180_180_351_288	TTC-G-	2	0.848	1.001
8	180_000_123_295	TCA+G-	2	0.872	0.867
9	180_000_241_297	TCA-G-	2	1.362	1.501
10	180_000_009_072	TCC+G+	2	1.539	1.699
11	000_180_000_180	CTCT	1	8.964	8.873
12	000_179_122_178	CT+A+T+	2	9.039	8.991
13	000_181_123_296	CT-A+G-	2	9.175	9.123
14	000_180_119_063	CTA+G+	2	9.689	9.737
15	001_182_009_072	C+T-C+G+	2	9.870	9.989

(Z)-2mhex (three torsion).

	angles	conf	weight	E	E+ZPE
1	180_272_182	Tg-T-	2	0.000	0.083
2	180_124_177	TA+T+	2	0.066	0.000
3	180_253_068	TA-G+	2	0.129	0.407
4	180_273_300	Tg-G-	2	0.573	0.598
5	352_093_178	C-a+T+	2	8.599	8.529

6	009_248_067	C+A-G+	2	8.941	9.006
7	352_092_060	C-a+G+	2	9.248	9.286

(E)-2mhex (three torsion).

	angles	conf	weight	E	E+ZPE
1	180_000_180	TCT	1	0.000	0.063
2	180_121_178	TA+T+	2	0.015	0.000
3	180_123_295	TA+G-	2	0.190	0.200
4	180_241_297	TA-G-	2	0.681	0.835
5	180_009_072	TC+G+	2	0.858	1.033

S3. Nomenclature IUPAC - Dihedral Angles

- C $\Rightarrow \phi_i = 0°$
- C$-$ $\Rightarrow \phi_i \in (-30°, 0°) \Leftrightarrow$ C$+$ $\Rightarrow \phi_i \in (0°, +30°)$;
- G$-$ $\Rightarrow \phi_i \in (-75°, -30°) \Leftrightarrow$ G$+$ $\Rightarrow \phi_i \in (+30°, +75°)$;
- g$-$ $\Rightarrow \phi_i \in (-90°, -75°) \Leftrightarrow$ g$+$ $\Rightarrow \phi_i \in (+75°, +90°)$;
- a$-$ $\Rightarrow \phi_i \in (-105°, -90°) \Leftrightarrow$ a$+$ $\Rightarrow \phi_i \in (+90°, +105°)$;
- A$-$ $\Rightarrow \phi_i \in (-150°, -105°) \Leftrightarrow$ A$+$ $\Rightarrow \phi_i \in (+105°, +150°)$;
- T$-$ $\Rightarrow \phi_i \in (-180°, -105°) \Leftrightarrow$ T$+$ $\Rightarrow \phi_i \in (+150°, +180°)$;
- T $\Rightarrow \phi_i = 180°$.

S4. Partition Functions of the Isomers

	(Z)-2mhex SS-QH	(E)-2mhex SS-QH	(Z)-3mhex SS-QH	(E)-3mhex SS-QH
250.00	3.2399E-089	5.0011E-089	6.1732E-088	4.0820E-088
300.00	2.6481E-072	3.7974E-072	4.5406E-071	2.9077E-071
400.00	1.0867E-050	1.4300E-050	1.6522E-049	1.0202E-049
500.00	3.1408E-037	3.9391E-037	4.4826E-036	2.7116E-036
600.00	7.3886E-028	8.9873E-028	1.0158E-026	6.0637E-027
700.00	7.7350E-021	9.2131E-021	1.0384E-019	6.1402E-020
800.00	2.6565E-015	3.1164E-015	3.5087E-014	2.0604E-014
900.00	9.0790E-011	1.0531E-010	1.1854E-009	6.9243E-010
1000.00	6.0162E-007	6.9175E-007	7.7887E-006	4.5307E-006
1100.00	1.1833E-003	1.3512E-003	1.5220E-002	8.8246E-003
1200.00	9.1875E-001	1.0434E+000	1.1759E+001	6.7995E+000
1300.00	3.4352E+002	3.8840E+002	4.3793E+003	2.5268E+003
1400.00	7.1364E+004	8.0393E+004	9.0686E+005	5.2230E+005
1500.00	9.1566E+006	1.0284E+007	1.1605E+008	6.6740E+007
1600.00	7.8624E+008	8.8078E+008	9.9436E+009	5.7111E+009
1700.00	4.8071E+010	5.3735E+010	6.0686E+011	3.4817E+011

1800.00	2.1976E+012	2.4520E+012	2.7701E+013	1.5878E+013
1900.00	7.8117E+013	8.7024E+013	9.8338E+014	5.6322E+014
2000.00	2.2288E+015	2.4795E+015	2.8026E+016	1.6041E+016

	(Z)-4mhex	(E)-4mhex	5mhex
T(K)	SS-QH	SS-QH	SS-QH
250.00	8.6973E-089	1.7374E-088	8.2370E-089
300.00	6.6032E-072	1.2344E-071	6.2221E-072
400.00	2.4866E-050	4.3121E-050	2.3089E-050
500.00	6.8658E-037	1.1425E-036	6.2954E-037
600.00	1.5723E-027	2.5493E-027	1.4286E-027
700.00	1.6182E-020	2.5776E-020	1.4612E-020
800.00	5.4940E-015	8.6406E-015	4.9398E-015
900.00	1.8627E-010	2.9017E-010	1.6698E-010
1000.00	1.2271E-006	1.8976E-006	1.0977E-006
1100.00	2.4029E-003	3.6945E-003	2.1461E-003
1200.00	1.8594E+000	2.8458E+000	1.6588E+000
1300.00	6.9340E+002	1.0573E+003	6.1807E+002
1400.00	1.4374E+005	2.1851E+005	1.2804E+005
1500.00	1.8411E+007	2.7917E+007	1.6392E+007
1600.00	1.5787E+009	2.3886E+009	1.4050E+009
1700.00	9.6405E+010	1.4561E+011	8.5770E+010
1800.00	4.4028E+012	6.6397E+012	3.9161E+012
1900.00	1.5637E+014	2.3551E+014	1.3906E+014
2000.00	4.4583E+015	6.7069E+015	3.9639E+015

	(Z)-2mhex		(E)-2mhex	
	MS-QH	or MS-T	MS-QH	or MS-T
250.00	3.9596E-088	3.3128E-088	4.8080E-088	3.3194E-088
300.00	3.3965E-071	2.9715E-071	4.1688E-071	3.0391E-071
400.00	1.5175E-049	1.4083E-049	1.9013E-049	1.5193E-049
500.00	4.7070E-036	4.5018E-036	5.9656E-036	5.1071E-036
600.00	1.1739E-026	1.1343E-026	1.4951E-026	1.3435E-026
700.00	1.2903E-019	1.2425E-019	1.6455E-019	1.5256E-019
800.00	4.6174E-014	4.3881E-014	5.8874E-014	5.5516E-014
900.00	1.6349E-009	1.5227E-009	2.0829E-009	1.9748E-009
1000.00	1.1172E-005	1.0147E-005	1.4223E-005	1.3432E-005
1100.00	2.2579E-002	1.9924E-002	2.8733E-002	2.6824E-002
1200.00	1.7962E+001	1.5358E+001	2.2859E+001	2.0965E+001
1300.00	6.8647E+003	5.6757E+003	8.7411E+003	7.8361E+003
1400.00	1.4548E+006	1.1613E+006	1.8543E+006	1.6181E+006
1500.00	1.9009E+008	1.4635E+008	2.4266E+008	2.0540E+008
1600.00	1.6599E+010	1.2315E+010	2.1228E+010	1.7381E+010
1700.00	1.0308E+012	7.3651E+011	1.3210E+012	1.0439E+012
1800.00	4.7809E+013	3.2885E+013	6.1420E+013	4.6751E+013
1900.00	1.7226E+015	1.1403E+015	2.2188E+015	1.6243E+015
2000.00	4.9773E+016	3.1702E+016	6.4288E+016	4.5211E+016

	(Z)-3mhex		(E)-3mhex	
	MS-QH	or MS-T	MS-QH	or MS-T
250.00	2.1126E-087	2.0339E-087	2.9395E-087	2.3167E-087
300.00	1.7257E-070	1.7327E-070	2.2194E-070	1.8376E-070
400.00	7.2934E-049	7.5801E-049	8.4646E-049	7.5040E-049
500.00	2.1863E-035	2.2498E-035	2.3827E-035	2.1860E-035
600.00	5.3188E-026	5.2738E-026	5.5583E-026	5.1404E-026
700.00	5.7347E-019	5.3892E-019	5.8172E-019	5.3182E-019
800.00	2.0209E-013	1.7826E-013	2.0056E-013	1.7872E-013
900.00	7.0660E-009	5.8182E-009	6.8978E-009	5.9315E-009
1000.00	4.7788E-005	3.6629E-005	4.6071E-005	3.7958E-005
1100.00	9.5747E-002	6.8238E-002	9.1435E-002	7.1814E-002
1200.00	7.5618E+001	5.0103E+001	7.1700E+001	5.3490E+001
1300.00	2.8723E+004	1.7703E+004	2.7092E+004	1.9149E+004
1400.00	6.0553E+006	3.4747E+006	5.6904E+006	3.8040E+006
1500.00	7.8775E+008	4.2134E+008	7.3843E+008	4.6632E+008
1600.00	6.8525E+010	3.4208E+010	6.4140E+010	3.8234E+010
1700.00	4.2415E+012	1.9789E+012	3.9674E+012	2.2314E+012
1800.00	1.9618E+014	8.5659E+013	1.8350E+014	9.7360E+013
1900.00	7.0511E+015	2.8854E+015	6.5990E+015	3.3029E+015
2000.00	2.0331E+017	7.8077E+016	1.9046E+017	8.9945E+016

	(Z)-4mhex		(E)-4mhex	
	MS-QH	or MS-T	MS-QH	or MS-T
250.00	1.2765E-087	1.3586E-087	1.6795E-087	1.4541E-087

300.00	1.1133E-070	1.2173E-070	1.3465E-070	1.2138E-070
400.00	5.2009E-049	5.6744E-049	5.6769E-049	5.3602E-049
500.00	1.6778E-035	1.7506E-035	1.7205E-035	1.6450E-035
600.00	4.3137E-026	4.2136E-026	4.2388E-026	4.0094E-026
700.00	4.8536E-019	4.3916E-019	4.6233E-019	4.2587E-019
800.00	1.7690E-013	1.4757E-013	1.6459E-013	1.4609E-013
900.00	6.3555E-009	4.8811E-009	5.8068E-009	4.9315E-009
1000.00	4.3955E-005	3.1089E-005	3.9589E-005	3.2016E-005
1100.00	8.9735E-002	5.8520E-002	7.9902E-002	6.1337E-002
1200.00	7.2010E+001	4.3375E+001	6.3531E+001	4.6195E+001
1300.00	2.7732E+004	1.5459E+004	2.4284E+004	1.6703E+004
1400.00	5.9171E+006	3.0587E+006	5.1500E+006	3.3477E+006
1500.00	7.7798E+008	3.7366E+008	6.7375E+008	4.1370E+008
1600.00	6.8318E+010	3.0547E+010	5.8923E+010	3.4170E+010
1700.00	4.2647E+012	1.7785E+012	3.6658E+012	2.0078E+012
1800.00	1.9877E+014	7.7445E+013	1.7038E+014	8.8149E+013
1900.00	7.1944E+015	2.6233E+015	6.1525E+015	3.0077E+015
2000.00	2.0877E+017	7.1353E+016	1.7820E+017	8.2345E+016

	5mhex		
	MS-QH	or	MS-T
250.00	1.2864E-087		1.1262E-087
300.00	1.1956E-070		1.0759E-070
400.00	6.0827E-049		5.6332E-049
500.00	2.0709E-035		1.9275E-035
600.00	5.5278E-026		5.0892E-026
700.00	6.3955E-019		5.7597E-019
800.00	2.3821E-013		2.0822E-013
900.00	8.7093E-009		7.3475E-009
1000.00	6.1106E-005		4.9557E-005
1100.00	1.2625E-001		9.8142E-002
1200.00	1.0235E+002		7.6096E+001
1300.00	3.9761E+004		2.8230E+004
1400.00	8.5480E+006		5.7893E+006
1500.00	1.1313E+009		7.3028E+008
1600.00	9.9914E+010		6.1446E+010
1700.00	6.2687E+012		3.6716E+012
1800.00	2.9348E+014		1.6369E+014
1900.00	1.0665E+016		5.6641E+015
2000.00	3.1059E+017		1.5709E+017

S5. Mulstistructural Factors

S5.1. (Z)-2mhex

	(Z)-2mhex		Alpha-site(abs)		Beta-site (abs)	
T (K)	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH
250.00	10.23	12.22	1.57	2.13	8.25	9.54
300.00	11.22	12.83	1.67	2.20	8.98	9.83
400.00	12.96	13.97	1.86	2.36	10.24	10.39
500.00	14.33	14.99	2.00	2.53	11.23	10.87
600.00	15.35	15.89	2.11	2.69	11.95	11.28
700.00	16.06	16.68	2.20	2.84	12.43	11.63
800.00	16.52	17.38	2.25	2.98	12.74	11.94
900.00	16.77	18.01	2.28	3.11	12.89	12.22
1000.00	16.87	18.57	2.29	3.24	12.94	12.47
1100.00	16.84	19.08	2.29	3.35	12.90	12.71
1200.00	16.72	19.55	2.27	3.46	12.79	12.93
1300.00	16.52	19.98	2.25	3.56	12.64	13.14
1400.00	16.27	20.39	2.21	3.66	12.45	13.34
1500.00	15.98	20.76	2.18	3.75	12.24	13.53
1600.00	15.66	21.11	2.13	3.84	12.00	13.71
1700.00	15.32	21.44	2.09	3.92	11.75	13.89
1800.00	14.96	21.76	2.04	4.00	11.49	14.06
1900.00	14.60	22.05	1.99	4.07	11.22	14.23
2000.00	14.22	22.33	1.94	4.14	10.95	14.39

	Gamma-site (abs)		Delta-site (abs)		Methyl-site (abs)	
T (K)	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH
250.00	1.71	2.30	14.01	15.87	14.61	22.27

300.00	1.97	2.55	15.61	16.65	15.55	22.53
400.00	2.50	3.03	18.16	17.89	17.39	23.04
500.00	3.01	3.48	19.90	18.82	19.05	23.48
600.00	3.48	3.89	20.98	19.53	20.44	23.88
700.00	3.88	4.27	21.57	20.11	21.55	24.23
800.00	4.22	4.61	21.81	20.59	22.39	24.57
900.00	4.50	4.92	21.79	21.02	22.99	24.90
1000.00	4.72	5.21	21.60	21.41	23.40	25.22
1100.00	4.88	5.47	21.29	21.77	23.63	25.54
1200.00	5.00	5.72	20.91	22.12	23.74	25.86
1300.00	5.09	5.95	20.47	22.45	23.73	26.18
1400.00	5.14	6.17	20.00	22.78	23.63	26.50
1500.00	5.16	6.37	19.52	23.10	23.47	26.82
1600.00	5.16	6.56	19.03	23.41	23.25	27.14
1700.00	5.13	6.75	18.53	23.72	22.98	27.45
1800.00	5.10	6.93	18.04	24.02	22.68	27.76
1900.00	5.05	7.09	17.55	24.31	22.35	28.06
2000.00	4.98	7.26	17.08	24.60	22.00	28.36

	Epsilon-site (abs)		Alpha-site (add)		Beta-site (add)	
T (K)	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH
250.00	9.02	13.13	4.99	5.72	5.35	5.99
300.00	11.34	15.50	5.73	6.27	5.90	6.27
400.00	15.62	19.32	7.18	7.31	7.08	6.95
500.00	19.20	22.24	8.52	8.25	8.22	7.65
600.00	22.03	24.53	9.69	9.08	9.23	8.31
700.00	24.18	26.38	10.66	9.83	10.09	8.92
800.00	25.73	27.91	11.46	10.48	10.79	9.48
900.00	26.79	29.20	12.08	11.07	11.35	9.99
1000.00	27.45	30.31	12.56	11.60	11.77	10.46
1100.00	27.80	31.27	12.91	12.08	12.08	10.89
1200.00	27.89	32.11	13.15	12.52	12.29	11.30
1300.00	27.78	32.87	13.29	12.92	12.41	11.69
1400.00	27.52	33.54	13.35	13.29	12.47	12.06
1500.00	27.15	34.16	13.35	13.63	12.46	12.41
1600.00	26.68	34.72	13.29	13.95	12.41	12.74
1700.00	26.15	35.23	13.18	14.25	12.31	13.06
1800.00	25.57	35.70	13.03	14.53	12.18	13.36
1900.00	24.95	36.14	12.86	14.79	12.02	13.65
2000.00	24.32	36.55	12.65	15.04	11.83	13.93

S5.2. (*E*)-2mhex

	(E)-2mhex		Alpha-site (abs)		Beta-site (abs)		Gamma-site (abs)		Delta-site (abs)	
T (K)	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH
250.00	6.64	9.61	3.48	4.73	6.38	10.36	3.10	4.17	2.87	4.12
300.00	8.00	10.98	4.15	5.27	7.42	11.37	3.56	4.59	3.51	4.74
400.00	10.62	13.30	5.45	6.29	9.27	12.91	4.40	5.28	4.71	5.81
500.00	12.97	15.15	6.60	7.20	10.79	14.01	5.13	5.83	5.75	6.66
600.00	14.95	16.64	7.50	7.98	11.96	14.84	5.77	6.28	6.60	7.36
700.00	16.56	17.86	8.18	8.66	12.82	15.49	6.30	6.64	7.26	7.93
800.00	17.81	18.89	8.64	9.25	13.40	16.03	6.74	6.95	7.75	8.42
900.00	18.75	19.78	8.92	9.78	13.77	16.48	7.10	7.21	8.10	8.84
1000.00	19.42	20.56	9.06	10.24	13.95	16.88	7.39	7.44	8.32	9.21
1100.00	19.85	21.27	9.10	10.65	14.00	17.25	7.61	7.65	8.44	9.55
1200.00	20.09	21.91	9.05	11.02	13.94	17.59	7.77	7.84	8.48	9.85
1300.00	20.18	22.51	8.94	11.36	13.80	17.91	7.87	8.02	8.46	10.13
1400.00	20.13	23.07	8.78	11.67	13.59	18.23	7.94	8.19	8.39	10.39
1500.00	19.97	23.60	8.59	11.95	13.34	18.53	7.96	8.34	8.28	10.64
1600.00	19.73	24.10	8.37	12.21	13.05	18.82	7.95	8.49	8.14	10.87
1700.00	19.43	24.58	8.13	12.46	12.74	19.11	7.91	8.64	7.98	11.09
1800.00	19.07	25.05	7.88	12.68	12.41	19.39	7.85	8.78	7.79	11.30
1900.00	18.67	25.50	7.63	12.90	12.07	19.67	7.76	8.91	7.60	11.50
2000.00	18.23	25.93	7.38	13.09	11.72	19.94	7.66	9.04	7.40	11.70

	Methyl-site (abs)		Epsilon-site (abs)		Alpha-site (add)		Beta-site (add)	
T (K)	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH
250.00	8.03	14.37	13.21	20.28	3.12	4.66	4.45	6.42
300.00	9.78	16.59	16.15	23.53	3.62	5.12	5.40	7.36
400.00	13.43	20.41	21.92	29.21	4.56	5.92	7.24	8.98
500.00	17.13	23.50	27.25	33.86	5.37	6.58	8.87	10.29

600.00	20.69	26.00	31.90	37.68	6.06	7.11	10.25	11.37
700.00	23.97	28.06	35.79	40.85	6.60	7.55	11.37	12.27
800.00	26.88	29.80	38.91	43.54	7.03	7.92	12.25	13.03
900.00	29.39	31.29	41.32	45.86	7.36	8.24	12.92	13.69
1000.00	31.49	32.59	43.10	47.90	7.59	8.52	13.40	14.28
1100.00	33.19	33.74	44.32	49.73	7.75	8.77	13.72	14.81
1200.00	34.52	34.77	45.08	51.40	7.84	9.00	13.91	15.30
1300.00	35.50	35.71	45.45	52.94	7.87	9.20	13.99	15.75
1400.00	36.18	36.57	45.49	54.37	7.87	9.39	13.98	16.17
1500.00	36.58	37.37	45.27	55.72	7.82	9.56	13.90	16.57
1600.00	36.76	38.11	44.83	56.99	7.74	9.72	13.76	16.95
1700.00	36.73	38.80	44.22	58.20	7.64	9.87	13.57	17.32
1800.00	36.54	39.45	43.47	59.36	7.51	10.01	13.34	17.67
1900.00	36.20	40.06	42.62	60.47	7.37	10.15	13.09	18.00
2000.00	35.75	40.64	41.69	61.53	7.22	10.28	12.81	18.33

S5.3. (Z)-3mhex

	(Z)-3mhex		Alpha-site (abs)		Beta-site (abs)		Gamma-site (abs)		Delta-site (abs)	
T (K)	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH
250.00	3.30	3.42	1.96	2.15	32.34	31.50	3.74	4.08	1.42	1.67
300.00	3.82	3.80	2.26	2.32	38.00	35.42	4.28	4.37	1.76	1.91
400.00	4.59	4.41	2.83	2.61	45.95	41.51	5.10	4.80	2.35	2.35
500.00	5.02	4.88	3.31	2.85	50.17	46.03	5.59	5.09	2.79	2.72
600.00	5.19	5.24	3.69	3.05	51.79	49.56	5.80	5.31	3.06	3.03
700.00	5.19	5.52	3.96	3.23	51.72	52.40	5.83	5.49	3.20	3.29
800.00	5.08	5.76	4.13	3.39	50.65	54.77	5.73	5.62	3.24	3.51
900.00	4.91	5.96	4.23	3.53	49.01	56.79	5.55	5.74	3.22	3.70
1000.00	4.70	6.14	4.26	3.66	47.07	58.56	5.33	5.84	3.16	3.87
1100.00	4.48	6.29	4.24	3.78	45.01	60.15	5.08	5.93	3.07	4.02
1200.00	4.26	6.43	4.19	3.89	42.92	61.58	4.83	6.01	2.97	4.16
1300.00	4.04	6.56	4.11	3.99	40.87	62.90	4.59	6.09	2.86	4.29
1400.00	3.83	6.68	4.02	4.08	38.90	64.13	4.35	6.16	2.75	4.40
1500.00	3.63	6.79	3.91	4.17	37.01	65.27	4.12	6.22	2.64	4.51
1600.00	3.44	6.89	3.80	4.26	35.21	66.35	3.90	6.29	2.53	4.61
1700.00	3.26	6.99	3.68	4.34	33.51	67.37	3.70	6.35	2.42	4.70
1800.00	3.09	7.08	3.56	4.42	31.91	68.34	3.50	6.40	2.32	4.79
1900.00	2.93	7.17	3.45	4.49	30.40	69.26	3.32	6.46	2.22	4.88
2000.00	2.79	7.25	3.33	4.56	28.98	70.14	3.15	6.51	2.13	4.96

	Methyl-site (abs)		Epsilon-site (abs)		Beta-site (add)		Gamma-site (add)	
T (K)	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH
250.00	6.68	8.58	5.19	5.98	2.60	2.99	2.34	2.74
300.00	7.92	9.57	6.19	6.79	2.99	3.26	2.60	2.94
400.00	10.03	11.12	7.75	8.11	3.61	3.73	3.06	3.34
500.00	11.55	12.27	8.73	9.10	4.03	4.11	3.39	3.69
600.00	12.52	13.13	9.25	9.87	4.27	4.42	3.59	3.98
700.00	13.05	13.80	9.44	10.48	4.39	4.68	3.69	4.22
800.00	13.24	14.34	9.42	10.98	4.43	4.90	3.71	4.44
900.00	13.18	14.79	9.26	11.40	4.40	5.10	3.68	4.62
1000.00	12.95	15.16	9.02	11.76	4.33	5.28	3.62	4.78
1100.00	12.61	15.49	8.74	12.08	4.24	5.44	3.53	4.92
1200.00	12.20	15.77	8.42	12.37	4.14	5.59	3.42	5.05
1300.00	11.74	16.01	8.10	12.64	4.02	5.73	3.30	5.17
1400.00	11.26	16.24	7.77	12.88	3.90	5.86	3.18	5.28
1500.00	10.77	16.44	7.45	13.11	3.78	5.99	3.06	5.39
1600.00	10.28	16.62	7.14	13.32	3.65	6.12	2.94	5.48
1700.00	9.81	16.78	6.84	13.52	3.53	6.24	2.82	5.57
1800.00	9.34	16.94	6.54	13.71	3.40	6.35	2.71	5.66
1900.00	8.90	17.08	6.26	13.89	3.28	6.46	2.59	5.74
2000.00	8.47	17.21	6.00	14.07	3.17	6.57	2.49	5.81

S5.4. (E)-3mhex

	(E)-3mhex		Alpha-site (abs)		Beta-site (abs)		Gamma-site (abs)		Delta-site (abs)	
T (K)	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH
250.00	5.68	7.20	5.22	6.52	1.36	3.46	7.94	9.08	2.85	3.53
300.00	6.32	7.63	5.86	6.95	1.49	3.59	8.89	9.62	3.27	3.87

400.00	7.36	8.30	7.24	7.87	1.69	3.80	10.48	10.51	3.98	4.43
500.00	8.06	8.79	8.64	8.78	1.80	3.96	11.60	11.20	4.50	4.85
600.00	8.48	9.17	9.92	9.64	1.84	4.08	12.27	11.74	4.85	5.19
700.00	8.66	9.47	11.02	10.43	1.83	4.18	12.56	12.17	5.07	5.47
800.00	8.67	9.73	11.91	11.17	1.79	4.26	12.58	12.54	5.18	5.71
900.00	8.57	9.96	12.59	11.84	1.73	4.33	12.41	12.85	5.21	5.92
1000.00	8.38	10.17	13.08	12.45	1.66	4.39	12.11	13.12	5.18	6.10
1100.00	8.14	10.36	13.40	13.02	1.58	4.45	11.73	13.38	5.10	6.26
1200.00	7.87	10.55	13.58	13.54	1.51	4.50	11.31	13.61	5.00	6.41
1300.00	7.58	10.72	13.63	14.02	1.43	4.55	10.86	13.83	4.88	6.55
1400.00	7.28	10.90	13.60	14.47	1.35	4.59	10.40	14.05	4.75	6.68
1500.00	6.99	11.06	13.48	14.89	1.28	4.63	9.95	14.25	4.61	6.81
1600.00	6.70	11.23	13.31	15.28	1.21	4.67	9.51	14.46	4.46	6.93
1700.00	6.41	11.40	13.08	15.64	1.15	4.71	9.08	14.65	4.32	7.04
1800.00	6.13	11.56	12.83	15.99	1.08	4.75	8.67	14.84	4.17	7.15
1900.00	5.86	11.72	12.54	16.32	1.03	4.78	8.28	15.03	4.03	7.26
2000.00	5.61	11.87	12.23	16.62	0.97	4.82	7.90	15.22	3.89	7.36

	Methyl-site (abs)		Epsilon-site (abs)		Beta-site (add)		Gamma-site (add)	
T (K)	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH
250.00	8.02	12.36	10.31	13.26	8.84	11.28	7.63	8.70
300.00	9.09	13.26	11.90	14.71	10.09	12.28	8.73	9.48
400.00	10.99	14.69	14.55	17.12	12.30	14.11	10.53	10.78
500.00	12.53	15.78	16.45	19.02	14.01	15.72	11.75	11.81
600.00	13.70	16.66	17.68	20.56	15.20	17.13	12.47	12.64
700.00	14.54	17.38	18.36	21.85	15.94	18.37	12.78	13.33
800.00	15.10	18.00	18.62	22.95	16.31	19.45	12.81	13.91
900.00	15.42	18.55	18.58	23.91	16.40	20.42	12.63	14.41
1000.00	15.55	19.04	18.32	24.76	16.29	21.29	12.33	14.86
1100.00	15.53	19.48	17.92	25.54	16.02	22.07	11.94	15.26
1200.00	15.39	19.90	17.43	26.25	15.66	22.79	11.51	15.62
1300.00	15.17	20.28	16.87	26.91	15.23	23.46	11.05	15.96
1400.00	14.88	20.65	16.28	27.54	14.76	24.08	10.58	16.27
1500.00	14.54	20.99	15.68	28.13	14.26	24.66	10.11	16.56
1600.00	14.16	21.32	15.07	28.70	13.75	25.21	9.65	16.84
1700.00	13.76	21.63	14.46	29.24	13.24	25.72	9.21	17.11
1800.00	13.34	21.93	13.87	29.75	12.73	26.21	8.78	17.36
1900.00	12.91	22.22	13.29	30.25	12.23	26.68	8.37	17.60
2000.00	12.48	22.50	12.73	30.73	11.73	27.12	7.98	17.83

S5.5. (Z)-4mhex

	(Z)-4mhex		Alpha-site (abs)		Beta-site (abs)		Gamma-site (abs)		Delta-site (abs)	
T (K)	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH
250.00	15.62	14.68	3.79	3.66	2.67	2.57	6.71	6.19	11.36	10.62
300.00	18.43	16.86	4.87	4.46	3.06	2.82	8.26	7.38	14.86	13.48
400.00	22.82	20.92	6.91	5.99	3.62	3.22	11.04	9.83	21.34	19.17
500.00	25.50	24.44	8.63	7.36	3.95	3.53	13.11	12.16	26.41	24.48
600.00	26.80	27.44	9.95	8.57	4.11	3.78	14.46	14.29	29.93	29.27
700.00	27.14	30.00	10.90	9.64	4.17	3.98	15.20	16.18	32.11	33.52
800.00	26.86	32.20	11.54	10.59	4.14	4.15	15.51	17.87	33.26	37.30
900.00	26.21	34.12	11.93	11.44	4.07	4.31	15.51	19.38	33.66	40.67
1000.00	25.34	35.82	12.12	12.20	3.97	4.44	15.31	20.74	33.54	43.70
1100.00	24.35	37.35	12.17	12.89	3.86	4.57	14.97	21.97	33.07	46.45
1200.00	23.33	38.73	12.10	13.52	3.73	4.69	14.55	23.11	32.36	48.97
1300.00	22.29	39.99	11.96	14.10	3.60	4.80	14.08	24.16	31.50	51.28
1400.00	21.28	41.17	11.76	14.63	3.48	4.91	13.59	25.14	30.55	53.43
1500.00	20.30	42.26	11.51	15.12	3.35	5.01	13.09	26.06	29.55	55.43
1600.00	19.35	43.28	11.24	15.57	3.23	5.11	12.59	26.92	28.52	57.31
1700.00	18.45	44.24	10.95	16.00	3.11	5.21	12.09	27.74	27.49	59.08
1800.00	17.59	45.15	10.64	16.39	2.99	5.30	11.61	28.51	26.47	60.75
1900.00	16.78	46.01	10.33	16.77	2.88	5.39	11.14	29.25	25.46	62.33
2000.00	16.00	46.83	10.01	17.11	2.77	5.48	10.69	29.95	24.48	63.83

	Methyl-site (abs)		Epsilon-site (abs)		Gamma-site (add)		Delta-site (add)	
T (K)	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH
250.00	35.21	41.55	11.51	14.49	14.24	17.72	26.57	28.43
300.00	42.38	48.00	15.35	18.78	17.31	21.35	36.09	37.36
400.00	55.47	60.06	23.32	27.61	22.45	28.55	54.26	55.97
500.00	65.91	70.60	30.67	36.05	26.06	35.27	68.77	74.10
600.00	73.47	79.63	36.77	43.73	28.31	41.33	78.86	90.85
700.00	78.46	87.35	41.50	50.58	29.50	46.72	85.10	106.02

800.00	81.38	94.00	44.96	56.67	29.94	51.52	88.37	119.66
900.00	82.71	99.80	47.36	62.10	29.87	55.79	89.51	131.94
1000.00	82.86	104.89	48.90	66.98	29.45	59.63	89.18	143.04
1100.00	82.15	109.42	49.77	71.39	28.80	63.10	87.87	153.14
1200.00	80.82	113.49	50.12	75.42	28.01	66.26	85.91	162.38
1300.00	79.06	117.16	50.07	79.11	27.13	69.16	83.54	170.88
1400.00	77.00	120.51	49.72	82.53	26.21	71.83	80.93	178.74
1500.00	74.74	123.59	49.14	85.71	25.26	74.31	78.19	186.05
1600.00	72.37	126.42	48.39	88.67	24.31	76.61	75.39	192.88
1700.00	69.94	129.05	47.52	91.46	23.37	78.77	72.60	199.28
1800.00	67.49	131.49	46.54	94.08	22.45	80.78	69.84	205.30
1900.00	65.05	133.78	45.50	96.55	21.56	82.68	67.13	210.97
2000.00	62.65	135.91	44.41	98.90	20.69	84.47	64.51	216.33

S5.6. (E)-4mhex

	(E)-4mhex		Alpha-site (abs)		Beta-site (abs)		Gamma-site (abs)		Delta-site (abs)	
T (K)	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH
250.00	8.37	9.67	3.18	3.78	3.15	3.50	3.99	4.05	5.61	5.99
300.00	9.83	10.91	4.04	4.52	3.71	3.90	4.71	4.62	6.97	7.22
400.00	12.43	13.17	5.76	5.86	4.64	4.52	5.98	5.71	9.49	9.61
500.00	14.40	15.06	7.36	7.01	5.32	4.98	6.89	6.66	11.45	11.76
600.00	15.73	16.63	8.72	8.00	5.78	5.34	7.45	7.47	12.78	13.63
700.00	16.52	17.94	9.82	8.85	6.06	5.62	7.75	8.16	13.60	15.25
800.00	16.91	19.05	10.66	9.60	6.22	5.86	7.84	8.75	14.01	16.66
900.00	17.00	20.01	11.27	10.25	6.28	6.05	7.80	9.26	14.14	17.89
1000.00	16.87	20.86	11.69	10.84	6.27	6.23	7.66	9.72	14.07	18.99
1100.00	16.60	21.63	11.95	11.37	6.21	6.38	7.46	10.12	13.87	19.98
1200.00	16.23	22.32	12.08	11.85	6.12	6.53	7.23	10.49	13.58	20.89
1300.00	15.80	22.97	12.11	12.28	6.00	6.66	6.98	10.83	13.23	21.71
1400.00	15.32	23.57	12.06	12.69	5.87	6.78	6.72	11.15	12.85	22.48
1500.00	14.82	24.13	11.95	13.06	5.73	6.90	6.45	11.44	12.45	23.20
1600.00	14.31	24.67	11.79	13.41	5.58	7.01	6.19	11.71	12.04	23.87
1700.00	13.79	25.18	11.59	13.74	5.42	7.12	5.93	11.97	11.63	24.50
1800.00	13.28	25.66	11.36	14.04	5.27	7.22	5.68	12.21	11.22	25.10
1900.00	12.77	26.12	11.11	14.33	5.11	7.32	5.43	12.45	10.82	25.67
2000.00	12.28	26.57	10.84	14.60	4.96	7.42	5.20	12.67	10.43	26.21

	Methyl-site (abs)		Epsilon-site (abs)		Gamma-site (add)		Delta-site (add)	
T (K)	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH
250.00	12.77	18.36	13.95	18.12	14.24	17.72	26.57	28.43
300.00	15.18	20.72	16.07	20.16	17.31	21.35	36.09	37.36
400.00	19.94	25.04	19.88	23.87	22.45	28.55	54.26	55.97
500.00	24.17	28.68	23.04	27.03	26.06	35.27	68.77	74.10
600.00	27.62	31.71	25.53	29.69	28.31	41.33	78.86	90.85
700.00	30.24	34.24	27.39	31.95	29.50	46.72	85.10	106.02
800.00	32.10	36.39	28.73	33.89	29.94	51.52	88.37	119.66
900.00	33.32	38.24	29.62	35.60	29.87	55.79	89.51	131.94
1000.00	34.01	39.85	30.16	37.11	29.45	59.63	89.18	143.04
1100.00	34.29	41.29	30.43	38.48	28.80	63.10	87.87	153.14
1200.00	34.23	42.58	30.47	39.74	28.01	66.26	85.91	162.38
1300.00	33.92	43.75	30.34	40.91	27.13	69.16	83.54	170.88
1400.00	33.41	44.82	30.08	42.00	26.21	71.83	80.93	178.74
1500.00	32.76	45.81	29.71	43.03	25.26	74.31	78.19	186.05
1600.00	32.00	46.73	29.26	44.01	24.31	76.61	75.39	192.88
1700.00	31.17	47.59	28.74	44.94	23.37	78.77	72.60	199.28
1800.00	30.28	48.39	28.18	45.83	22.45	80.78	69.84	205.30
1900.00	29.37	49.15	27.57	46.68	21.56	82.68	67.13	210.97
2000.00	28.43	49.86	26.94	47.49	20.69	84.47	64.51	216.33

S5.7. 5mhex

	5mhex		Alpha-site (abs)		Beta-site (abs)		Gamma-site (abs)		Delta-site (abs)	
T (K)	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH
250.00	13.67	15.62	7.47	8.83	7.99	8.56	7.29	8.12	8.11	8.75
300.00	17.29	19.22	9.32	10.49	10.30	10.54	9.03	9.82	10.74	11.24
400.00	24.40	26.34	13.11	13.62	14.96	14.46	12.47	13.23	15.97	16.29
500.00	30.62	32.90	16.70	16.42	19.16	18.08	15.57	16.43	20.57	21.05
600.00	35.62	38.69	19.89	18.87	22.62	21.31	18.20	19.31	24.26	25.34
700.00	39.42	43.77	22.58	21.02	25.30	24.17	20.34	21.87	27.05	29.15

800.00	42.15	48.22	24.78	22.92	27.25	26.70	22.00	24.15	29.06	32.52
900.00	44.00	52.16	26.51	24.60	28.60	28.96	23.26	26.18	30.42	35.52
1000.00	45.15	55.67	27.83	26.10	29.44	30.99	24.18	28.01	31.26	38.21
1100.00	45.73	58.83	28.78	27.46	29.88	32.83	24.80	29.66	31.70	40.64
1200.00	45.87	61.70	29.43	28.69	30.01	34.50	25.19	31.17	31.82	42.84
1300.00	45.68	64.33	29.81	29.81	29.91	36.04	25.39	32.55	31.70	44.87
1400.00	45.21	66.76	29.97	30.84	29.61	37.46	25.42	33.83	31.39	46.73
1500.00	44.55	69.01	29.96	31.79	29.18	38.78	25.33	35.01	30.94	48.47
1600.00	43.74	71.12	29.79	32.67	28.64	40.01	25.14	36.12	30.38	50.08
1700.00	42.81	73.09	29.51	33.49	28.02	41.16	24.87	37.15	29.74	51.59
1800.00	41.80	74.94	29.13	34.26	27.35	42.25	24.52	38.13	29.05	53.01
1900.00	40.73	76.70	28.67	34.98	26.64	43.28	24.13	39.04	28.31	54.35
2000.00	39.63	78.35	28.15	35.65	25.91	44.25	23.69	39.91	27.55	55.61

	Methyl-site (abs)		Epsilon1-site (abs)		Epsilon2-site (abs)		Delta-site (add)		Epsilon-site (add)	
T (K)	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH	MS-T	MS-QH
250.00	30.95	44.38	11.23	12.83	19.40	21.59	55.92	58.74	7.63	8.83
300.00	39.73	54.46	14.25	15.85	25.17	27.23	68.04	69.33	10.23	11.40
400.00	58.39	74.12	20.13	21.85	36.67	38.77	91.02	90.19	15.48	16.56
500.00	76.81	92.01	25.24	27.42	46.89	49.79	110.35	109.34	20.24	21.40
600.00	93.63	107.78	29.33	32.39	55.20	59.82	125.43	126.37	24.20	25.77
700.00	108.21	121.55	32.42	36.78	61.57	68.78	136.58	141.40	27.33	29.65
800.00	120.36	133.60	34.63	40.65	66.22	76.75	144.45	154.71	29.69	33.09
900.00	130.13	144.21	36.13	44.09	69.44	83.85	149.65	166.60	31.40	36.15
1000.00	137.71	153.61	37.05	47.16	71.50	90.22	152.77	177.30	32.58	38.90
1100.00	143.34	162.01	37.52	49.93	72.65	95.98	154.26	187.02	33.32	41.39
1200.00	147.28	169.56	37.62	52.45	73.07	101.21	154.47	195.94	33.72	43.66
1300.00	149.77	176.40	37.45	54.75	72.92	106.00	153.69	204.17	33.85	45.73
1400.00	151.04	182.64	37.07	56.88	72.34	110.41	152.15	211.82	33.75	47.65
1500.00	151.30	188.35	36.52	58.85	71.42	114.49	150.02	218.97	33.49	49.43
1600.00	150.73	193.61	35.85	60.68	70.24	118.28	147.44	225.68	33.09	51.09
1700.00	149.47	198.47	35.08	62.40	68.86	121.83	144.52	232.01	32.58	52.64
1800.00	147.67	202.98	34.25	64.01	67.34	125.15	141.35	237.99	31.99	54.10
1900.00	145.43	207.19	33.37	65.52	65.72	128.28	138.00	243.66	31.34	55.48
2000.00	142.84	211.11	32.47	66.95	64.03	131.23	134.53	249.04	30.65	56.78

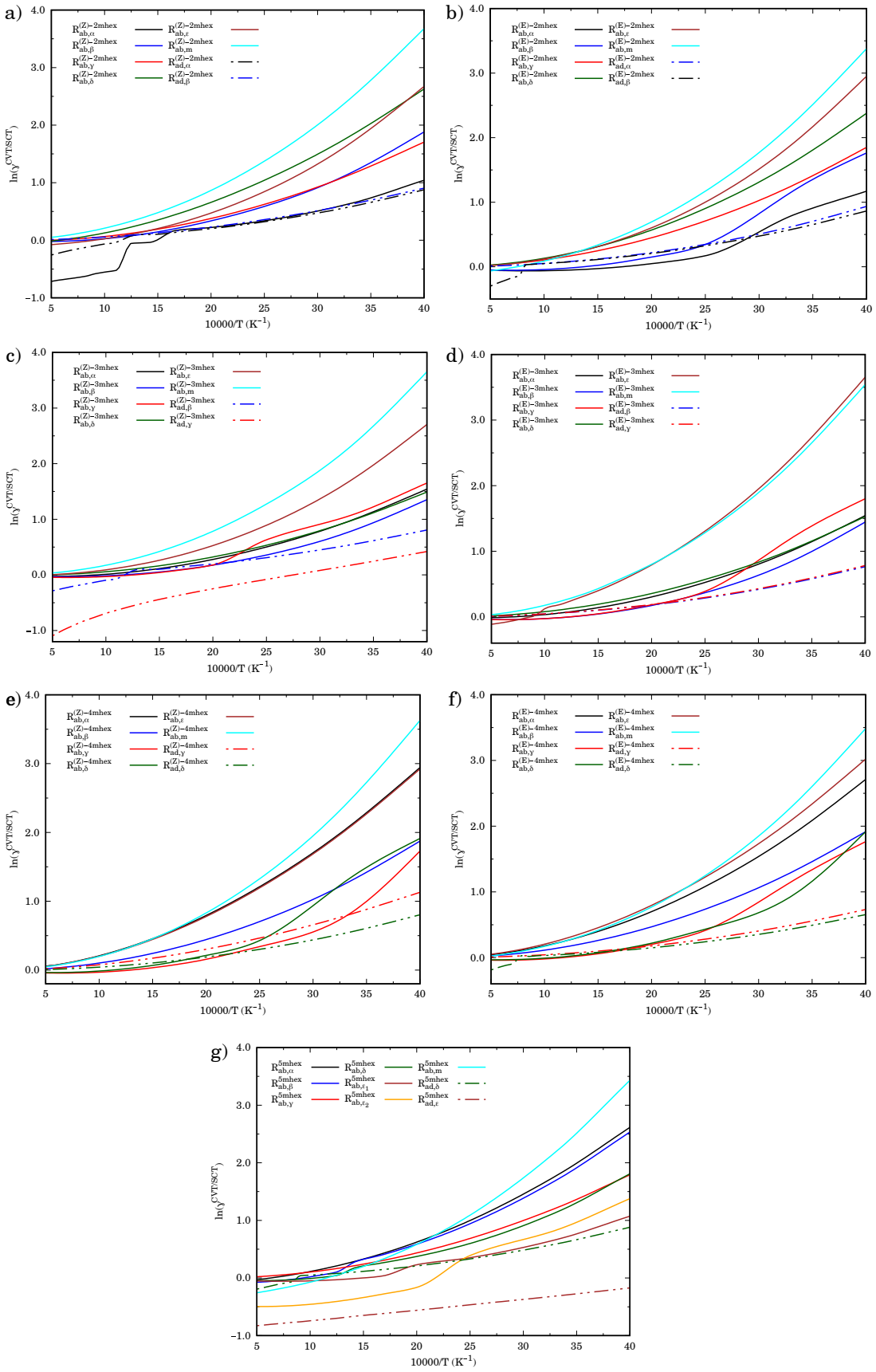

Fig. S2.: Transmission coefficient $\gamma^{\mathrm{CVT/SCT}}$ for the most stable transition state at each site of H-abstraction and addition in: (a) methyl (*Z*)-hex-2-enoate, (b) methyl (*E*)-hex-2-enoate, (c) methyl (*Z*)-hex-3-enoate, (d) methyl (*E*)-hex-3-enoate, (e) methyl (*Z*)-hex-4-enoate, (f) methyl (*E*)-hex-4-enoate, and (g) methyl hex-5-enoate.

S6. Calculation of Overall Rate Constants

The overall rate constants listed below are given in cm^3 $molecule^{-1}$ s^{-1}.

		(Z)-2mhex	
	Overall	Abs-total	Add-total
250.00	2.77E-13	8.20E-15	2.69E-13
300.00	5.28E-13	2.23E-14	5.06E-13
400.00	1.45E-12	1.04E-13	1.35E-12
500.00	3.11E-12	3.26E-13	2.78E-12
600.00	5.69E-12	8.01E-13	4.89E-12
700.00	9.38E-12	1.67E-12	7.71E-12
800.00	1.44E-11	3.10E-12	1.13E-11
900.00	2.03E-11	5.26E-12	1.50E-11
1000.00	2.80E-11	8.36E-12	1.97E-11
1100.00	3.75E-11	1.26E-11	2.50E-11
1200.00	4.89E-11	1.81E-11	3.08E-11
1300.00	6.23E-11	2.51E-11	3.72E-11
1400.00	7.79E-11	3.38E-11	4.41E-11
1500.00	9.58E-11	4.43E-11	5.15E-11
1600.00	1.16E-10	5.67E-11	5.94E-11
1700.00	1.39E-10	7.12E-11	6.76E-11
1800.00	1.64E-10	8.78E-11	7.63E-11
1900.00	1.92E-10	1.07E-10	8.54E-11
2000.00	2.23E-10	1.28E-10	9.49E-11

		(E)-2mhex	
	Overall	Abs-total	Add-total
250.00	1.90E-13	5.35E-15	1.84E-13
300.00	4.22E-13	1.61E-14	4.06E-13
400.00	1.35E-12	8.29E-14	1.27E-12
500.00	3.06E-12	2.72E-13	2.78E-12
600.00	5.70E-12	6.91E-13	5.00E-12
700.00	9.42E-12	1.48E-12	7.94E-12
800.00	1.44E-11	2.83E-12	1.16E-11
900.00	2.08E-11	4.94E-12	1.59E-11
1000.00	2.89E-11	8.02E-12	2.08E-11
1100.00	3.88E-11	1.23E-11	2.64E-11
1200.00	5.07E-11	1.81E-11	3.26E-11
1300.00	6.16E-11	2.55E-11	3.61E-11
1400.00	7.72E-11	3.48E-11	4.24E-11
1500.00	9.51E-11	4.61E-11	4.90E-11
1600.00	1.16E-10	5.97E-11	5.59E-11
1700.00	1.39E-10	7.58E-11	6.33E-11
1800.00	1.65E-10	9.44E-11	7.09E-11
1900.00	1.95E-10	1.16E-10	7.90E-11
2000.00	2.27E-10	1.40E-10	8.72E-11

		(Z)-3mhex	
	Overall	Abs-total	Add-total
250.00	3.90E-13	1.70E-14	3.73E-13
300.00	7.17E-13	4.49E-14	6.72E-13
400.00	1.80E-12	1.97E-13	1.60E-12
500.00	3.56E-12	5.79E-13	2.98E-12
600.00	6.13E-12	1.33E-12	4.80E-12
700.00	9.68E-12	2.62E-12	7.06E-12
800.00	1.43E-11	4.63E-12	9.72E-12
900.00	1.95E-11	7.59E-12	1.19E-11
1000.00	2.67E-11	1.17E-11	1.50E-11
1100.00	3.54E-11	1.73E-11	1.82E-11
1200.00	4.61E-11	2.45E-11	2.17E-11
1300.00	5.90E-11	3.36E-11	2.54E-11
1400.00	7.42E-11	4.48E-11	2.94E-11
1500.00	9.19E-11	5.84E-11	3.35E-11
1600.00	1.12E-10	7.45E-11	3.79E-11
1700.00	1.36E-10	9.33E-11	4.24E-11
1800.00	1.62E-10	1.15E-10	4.71E-11
1900.00	1.92E-10	1.40E-10	5.19E-11
2000.00	2.24E-10	1.67E-10	5.70E-11

		(E)-3mhex	
	Overall	Abs-total	Add-total

250.00	3.91E-13	1.08E-14	3.81E-13
300.00	8.27E-13	3.14E-14	7.96E-13
400.00	2.45E-12	1.52E-13	2.30E-12
500.00	5.28E-12	4.68E-13	4.81E-12
600.00	9.44E-12	1.11E-12	8.33E-12
700.00	1.51E-11	2.22E-12	1.28E-11
800.00	2.23E-11	3.99E-12	1.83E-11
900.00	3.12E-11	6.59E-12	2.46E-11
1000.00	4.20E-11	1.02E-11	3.18E-11
1100.00	5.48E-11	1.51E-11	3.97E-11
1200.00	6.97E-11	2.14E-11	4.83E-11
1300.00	8.70E-11	2.93E-11	5.77E-11
1400.00	1.07E-10	3.92E-11	6.76E-11
1500.00	1.29E-10	5.10E-11	7.82E-11
1600.00	1.54E-10	6.51E-11	8.93E-11
1700.00	1.82E-10	8.15E-11	1.01E-10
1800.00	2.14E-10	1.00E-10	1.13E-10
1900.00	2.48E-10	1.22E-10	1.26E-10
2000.00	2.85E-10	1.46E-10	1.39E-10

(Z)-4mhex

	Overall	Abs-total	Add-total
250.00	4.59E-13	3.52E-15	4.56E-13
300.00	8.74E-13	1.19E-14	8.62E-13
400.00	2.31E-12	7.25E-14	2.23E-12
500.00	4.70E-12	2.63E-13	4.43E-12
600.00	8.20E-12	7.05E-13	7.49E-12
700.00	1.30E-11	1.56E-12	1.14E-11
800.00	1.92E-11	3.03E-12	1.61E-11
900.00	2.70E-11	5.32E-12	2.17E-11
1000.00	3.66E-11	8.67E-12	2.79E-11
1100.00	4.83E-11	1.33E-11	3.49E-11
1200.00	6.21E-11	1.96E-11	4.26E-11
1300.00	7.84E-11	2.76E-11	5.09E-11
1400.00	9.74E-11	3.76E-11	5.98E-11
1500.00	1.19E-10	4.98E-11	6.93E-11
1600.00	1.44E-10	6.43E-11	7.94E-11
1700.00	1.71E-10	8.15E-11	8.99E-11
1800.00	2.02E-10	1.01E-10	1.01E-10
1900.00	2.37E-10	1.24E-10	1.13E-10
2000.00	2.74E-10	1.49E-10	1.25E-10

(E)-4mhex

	Overall	Abs-total	Add-total
250.00	4.92E-13	3.47E-15	4.89E-13
300.00	9.93E-13	1.22E-14	9.81E-13
400.00	2.74E-12	7.58E-14	2.67E-12
500.00	5.60E-12	2.74E-13	5.32E-12
600.00	9.65E-12	7.26E-13	8.93E-12
700.00	1.50E-11	1.58E-12	1.34E-11
800.00	2.17E-11	3.03E-12	1.87E-11
900.00	3.00E-11	5.26E-12	2.48E-11
1000.00	4.00E-11	8.49E-12	3.15E-11
1100.00	5.18E-11	1.29E-11	3.89E-11
1200.00	6.57E-11	1.88E-11	4.69E-11
1300.00	8.18E-11	2.64E-11	5.54E-11
1400.00	9.72E-11	3.57E-11	6.15E-11
1500.00	1.17E-10	4.71E-11	7.01E-11
1600.00	1.40E-10	6.07E-11	7.91E-11
1700.00	1.65E-10	7.66E-11	8.84E-11
1800.00	1.93E-10	9.49E-11	9.80E-11
1900.00	2.24E-10	1.16E-10	1.08E-10
2000.00	2.58E-10	1.39E-10	1.18E-10

5mhex

	Overall	Abs-total	Add-total
250.00	1.18E-12	3.86E-15	1.17E-12
300.00	1.87E-12	1.24E-14	1.86E-12
400.00	3.75E-12	6.98E-14	3.68E-12
500.00	6.29E-12	2.44E-13	6.05E-12
600.00	9.64E-12	6.43E-13	8.99E-12
700.00	1.39E-11	1.41E-12	1.25E-11
800.00	1.91E-11	2.68E-12	1.64E-11

900.00	2.56E-11	4.68E-12	2.09E-11
1000.00	3.35E-11	7.61E-12	2.59E-11
1100.00	4.30E-11	1.17E-11	3.13E-11
1200.00	5.32E-11	1.71E-11	3.61E-11
1300.00	6.60E-11	2.40E-11	4.20E-11
1400.00	8.09E-11	3.26E-11	4.82E-11
1500.00	9.79E-11	4.32E-11	5.48E-11
1600.00	1.17E-10	5.58E-11	6.15E-11
1700.00	1.39E-10	7.06E-11	6.86E-11
1800.00	1.64E-10	8.77E-11	7.61E-11
1900.00	1.91E-10	1.07E-10	8.38E-11
2000.00	2.21E-10	1.29E-10	9.19E-11

S7. Site-Specific MS-CVT/SCT Rate Constants

In this section, we present the individual rate constants for each site of H-abstraction and addition for all molecules studied. The values for addition reactions and abstractions at methylenic carbons do not include the weight 2, as discussed in Section S1. The site-specific rate constants listed below are given in cm^3 $molecule^{-1}$ s^{-1}.

S7.1. (Z)-2mhex

T (K)	Alpha-site	Beta-site	Gamma-site	Delta-site	Methyl-site	Epsilon-site
250.00	1.14E-23	2.15E-20	3.99E-15	1.03E-16	3.23E-18	1.01E-18
300.00	1.13E-21	4.80E-19	1.06E-14	5.31E-16	2.47E-17	1.18E-17
400.00	4.60E-19	3.30E-17	4.63E-14	5.29E-15	4.71E-16	3.74E-16
500.00	1.98E-17	5.05E-16	1.35E-13	2.46E-14	3.57E-15	3.76E-15
600.00	2.65E-16	3.40E-15	3.06E-13	7.50E-14	1.57E-14	1.96E-14
700.00	1.49E-15	1.41E-14	5.92E-13	1.77E-13	4.93E-14	6.85E-14
800.00	6.47E-15	4.30E-14	1.02E-12	3.50E-13	1.23E-13	1.83E-13
900.00	1.33E-14	1.06E-13	1.62E-12	6.17E-13	2.61E-13	4.08E-13
1000.00	3.38E-14	2.23E-13	2.42E-12	9.94E-13	4.92E-13	7.94E-13
1100.00	7.36E-14	4.18E-13	3.42E-12	1.50E-12	8.46E-13	1.40E-12
1200.00	1.41E-13	7.19E-13	4.66E-12	2.15E-12	1.36E-12	2.27E-12
1300.00	2.51E-13	1.15E-12	6.15E-12	2.95E-12	2.06E-12	3.47E-12
1400.00	4.16E-13	1.75E-12	7.89E-12	3.92E-12	2.97E-12	5.05E-12
1500.00	6.50E-13	2.54E-12	9.89E-12	5.07E-12	4.14E-12	7.04E-12
1600.00	9.69E-13	3.54E-12	1.22E-11	6.40E-12	5.59E-12	9.49E-12
1700.00	1.39E-12	4.78E-12	1.47E-11	7.93E-12	7.35E-12	1.24E-11
1800.00	1.91E-12	6.28E-12	1.75E-11	9.65E-12	9.44E-12	1.59E-11
1900.00	2.57E-12	8.07E-12	2.06E-11	1.16E-11	1.19E-11	1.99E-11
2000.00	3.35E-12	1.02E-11	2.40E-11	1.37E-11	1.47E-11	2.45E-11

T (K)	Alpha-site (add)	Beta-site (add)
250.00	2.45E-14	1.10E-13
300.00	5.61E-14	1.97E-13
400.00	1.90E-13	4.84E-13
500.00	4.47E-13	9.43E-13
600.00	8.54E-13	1.59E-12
700.00	1.43E-12	2.43E-12
800.00	2.17E-12	3.46E-12
900.00	2.82E-12	4.69E-12
1000.00	3.74E-12	6.11E-12
1100.00	4.77E-12	7.70E-12
1200.00	5.92E-12	9.48E-12
1300.00	7.17E-12	1.14E-11
1400.00	8.52E-12	1.35E-11
1500.00	9.96E-12	1.58E-11
1600.00	1.15E-11	1.82E-11
1700.00	1.31E-11	2.08E-11
1800.00	1.47E-11	2.35E-11
1900.00	1.64E-11	2.63E-11
2000.00	1.82E-11	2.92E-11

S7.2. (E)-2mhex

T (K)	Alpha-site	Beta-site	Gamma-site	Delta-site	Methyl-site	Epsilon-site
250.00	7.36E-25	3.86E-23	2.63E-15	4.35E-17	2.82E-18	1.42E-18
300.00	1.27E-22	2.85E-21	7.76E-15	2.75E-16	2.29E-17	1.51E-17
400.00	7.23E-20	5.79E-19	3.74E-14	3.63E-15	4.84E-16	4.45E-16
500.00	4.58E-18	2.07E-17	1.12E-13	2.03E-14	3.95E-15	4.31E-15
600.00	7.87E-17	2.45E-16	2.55E-13	7.05E-14	1.85E-14	2.22E-14
700.00	6.29E-16	1.51E-15	4.90E-13	1.82E-13	6.06E-14	7.69E-14
800.00	3.09E-15	6.16E-15	8.41E-13	3.89E-13	1.57E-13	2.06E-13
900.00	1.09E-14	1.89E-14	1.33E-12	7.24E-13	3.44E-13	4.59E-13
1000.00	3.06E-14	4.75E-14	1.97E-12	1.22E-12	6.64E-13	8.96E-13
1100.00	7.21E-14	1.03E-13	2.79E-12	1.91E-12	1.17E-12	1.58E-12
1200.00	1.49E-13	1.98E-13	3.80E-12	2.81E-12	1.90E-12	2.59E-12
1300.00	2.79E-13	3.50E-13	5.01E-12	3.96E-12	2.92E-12	3.98E-12

1400.00	4.81E-13	5.76E-13	6.44E-12	5.37E-12	4.27E-12	5.82E-12
1500.00	7.78E-13	8.95E-13	8.09E-12	7.05E-12	6.00E-12	8.17E-12
1600.00	1.19E-12	1.33E-12	9.98E-12	9.02E-12	8.14E-12	1.11E-11
1700.00	1.75E-12	1.89E-12	1.21E-11	1.13E-11	1.08E-11	1.46E-11
1800.00	2.47E-12	2.61E-12	1.45E-11	1.39E-11	1.38E-11	1.88E-11
1900.00	3.38E-12	3.49E-12	1.71E-11	1.68E-11	1.75E-11	2.37E-11
2000.00	4.50E-12	4.57E-12	2.00E-11	2.00E-11	2.16E-11	2.93E-11

T (K)	Alpha-site (add)	Beta-site (add)
250.00	3.55E-14	5.66E-14
300.00	8.01E-14	1.23E-13
400.00	2.59E-13	3.74E-13
500.00	5.83E-13	8.09E-13
600.00	1.07E-12	1.44E-12
700.00	1.71E-12	2.26E-12
800.00	2.52E-12	3.26E-12
900.00	3.49E-12	4.44E-12
1000.00	4.62E-12	5.80E-12
1100.00	5.90E-12	7.31E-12
1200.00	7.33E-12	8.99E-12
1300.00	8.91E-12	9.16E-12
1400.00	1.06E-11	1.06E-11
1500.00	1.25E-11	1.20E-11
1600.00	1.45E-11	1.35E-11
1700.00	1.66E-11	1.51E-11
1800.00	1.88E-11	1.67E-11
1900.00	2.11E-11	1.83E-11
2000.00	2.36E-11	2.00E-11

S7.3. (Z)-3mhex

T (K)	Alpha-site	Beta-site	Gamma-site	Delta-site	Methyl-site	Epsilon-site
250.00	4.09E-15	3.71E-22	4.67E-21	4.39E-15	2.73E-18	8.61E-19
300.00	9.85E-15	1.84E-20	1.54E-19	1.26E-14	2.20E-17	1.02E-17
400.00	3.88E-14	3.20E-18	1.67E-17	5.95E-14	5.27E-16	3.31E-16
500.00	1.07E-13	8.34E-17	2.56E-16	1.78E-13	4.66E-15	3.38E-15
600.00	2.39E-13	8.00E-16	2.05E-15	4.05E-13	2.30E-14	1.79E-14
700.00	4.56E-13	4.26E-15	9.66E-15	7.76E-13	7.81E-14	6.36E-14
800.00	7.82E-13	1.56E-14	3.22E-14	1.32E-12	2.07E-13	1.73E-13
900.00	1.24E-12	4.40E-14	8.49E-14	2.07E-12	4.61E-13	3.93E-13
1000.00	1.84E-12	1.04E-13	1.89E-13	3.03E-12	9.01E-13	7.78E-13
1100.00	2.61E-12	2.13E-13	3.70E-13	4.24E-12	1.59E-12	1.39E-12
1200.00	3.55E-12	3.95E-13	6.59E-13	5.70E-12	2.61E-12	2.31E-12
1300.00	4.68E-12	6.74E-13	1.09E-12	7.43E-12	4.02E-12	3.59E-12
1400.00	6.00E-12	1.08E-12	1.69E-12	9.43E-12	5.89E-12	5.30E-12
1500.00	7.52E-12	1.64E-12	2.49E-12	1.17E-11	8.27E-12	7.52E-12
1600.00	9.25E-12	2.38E-12	3.53E-12	1.43E-11	1.12E-11	1.03E-11
1700.00	1.12E-11	3.33E-12	4.84E-12	1.71E-11	1.48E-11	1.37E-11
1800.00	1.33E-11	4.52E-12	6.44E-12	2.03E-11	1.90E-11	1.78E-11
1900.00	1.57E-11	5.97E-12	8.35E-12	2.37E-11	2.39E-11	2.26E-11
2000.00	1.83E-11	7.72E-12	1.06E-11	2.75E-11	2.96E-11	2.81E-11

T (K)	Beta-site (add)	Gamma-site (add)
250.00	9.81E-14	8.84E-14
300.00	1.76E-13	1.60E-13
400.00	4.23E-13	3.77E-13
500.00	8.02E-13	6.88E-13
600.00	1.32E-12	1.08E-12
700.00	1.98E-12	1.55E-12
800.00	2.79E-12	2.07E-12
900.00	3.32E-12	2.64E-12
1000.00	4.21E-12	3.27E-12
1100.00	5.18E-12	3.91E-12
1200.00	6.24E-12	4.60E-12
1300.00	7.39E-12	5.32E-12
1400.00	8.63E-12	6.04E-12
1500.00	9.96E-12	6.80E-12
1600.00	1.14E-11	7.59E-12
1700.00	1.28E-11	8.37E-12
1800.00	1.44E-11	9.16E-12

1900.00	1.60E-11	9.97E-12
2000.00	1.77E-11	1.08E-11

S7.4. (*E*)-3mhex

T (K)	Alpha-site	Beta-site	Gamma-site	Delta-site	Methyl-site	Epsilon-site
250.00	2.43E-15	1.18E-22	3.33E-21	2.98E-15	1.96E-18	1.86E-18
300.00	6.48E-15	7.27E-21	1.17E-19	9.19E-15	1.73E-17	1.68E-17
400.00	2.90E-14	1.71E-18	9.75E-18	4.67E-14	4.09E-16	3.94E-16
500.00	8.66E-14	5.38E-17	2.02E-16	1.44E-13	3.57E-15	3.36E-15
600.00	2.02E-13	5.83E-16	1.68E-15	3.34E-13	1.74E-14	1.59E-14
700.00	4.02E-13	3.37E-15	8.04E-15	6.50E-13	5.81E-14	5.21E-14
800.00	7.10E-13	1.30E-14	2.72E-14	1.12E-12	1.54E-13	1.34E-13
900.00	1.15E-12	3.84E-14	7.22E-14	1.77E-12	3.41E-13	2.91E-13
1000.00	1.75E-12	9.32E-14	1.61E-13	2.62E-12	6.69E-13	5.59E-13
1100.00	2.53E-12	1.96E-13	3.17E-13	3.70E-12	1.19E-12	9.14E-13
1200.00	3.49E-12	3.68E-13	5.66E-13	5.01E-12	1.96E-12	1.48E-12
1300.00	4.66E-12	6.36E-13	9.36E-13	6.58E-12	3.04E-12	2.26E-12
1400.00	6.05E-12	1.03E-12	1.45E-12	8.40E-12	4.48E-12	3.30E-12
1500.00	7.65E-12	1.57E-12	2.15E-12	1.05E-11	6.34E-12	4.63E-12
1600.00	9.49E-12	2.29E-12	3.05E-12	1.29E-11	8.68E-12	6.30E-12
1700.00	1.16E-11	3.21E-12	4.18E-12	1.55E-11	1.15E-11	8.35E-12
1800.00	1.39E-11	4.36E-12	5.57E-12	1.85E-11	1.49E-11	1.08E-11
1900.00	1.64E-11	5.76E-12	7.24E-12	2.17E-11	1.89E-11	1.37E-11
2000.00	1.92E-11	7.44E-12	9.20E-12	2.52E-11	2.36E-11	1.71E-11

T (K)	Beta-site (add)	Gamma-site
250.00	8.38E-14	1.07E-13
300.00	1.75E-13	2.23E-13
400.00	5.06E-13	6.45E-13
500.00	1.07E-12	1.34E-12
600.00	1.87E-12	2.30E-12
700.00	2.90E-12	3.52E-12
800.00	4.18E-12	4.97E-12
900.00	5.67E-12	6.64E-12
1000.00	7.38E-12	8.51E-12
1100.00	9.28E-12	1.06E-11
1200.00	1.14E-11	1.28E-11
1300.00	1.37E-11	1.52E-11
1400.00	1.61E-11	1.77E-11
1500.00	1.87E-11	2.04E-11
1600.00	2.15E-11	2.32E-11
1700.00	2.44E-11	2.61E-11
1800.00	2.74E-11	2.92E-11
1900.00	3.06E-11	3.24E-11
2000.00	3.39E-11	3.56E-11

S7.5. (*Z*)-4mhex

T (K)	Alpha-site	Beta-site	Gamma-site	Delta-site	Methyl-site	Epsilon-site
250.00	1.14E-16	1.31E-15	6.96E-21	1.15E-20	2.08E-18	6.76E-16
300.00	4.95E-16	4.21E-15	1.41E-19	3.13E-19	1.80E-17	2.47E-15
400.00	4.24E-15	2.32E-14	1.33E-17	1.84E-17	4.21E-16	1.71E-14
500.00	1.90E-14	7.65E-14	2.48E-16	3.22E-16	3.68E-15	6.77E-14
600.00	5.83E-14	1.87E-13	1.93E-15	2.40E-15	1.81E-14	1.92E-13
700.00	1.41E-13	3.80E-13	8.89E-15	1.08E-14	6.15E-14	4.39E-13
800.00	2.88E-13	6.79E-13	2.92E-14	3.47E-14	1.64E-13	8.64E-13
900.00	5.25E-13	1.11E-12	7.61E-14	8.91E-14	3.66E-13	1.53E-12
1000.00	8.75E-13	1.68E-12	1.68E-13	1.95E-13	7.17E-13	2.48E-12
1100.00	1.36E-12	2.43E-12	3.27E-13	3.76E-13	1.28E-12	3.79E-12
1200.00	2.01E-12	3.35E-12	5.79E-13	6.61E-13	2.10E-12	5.51E-12
1300.00	2.83E-12	4.48E-12	9.52E-13	1.08E-12	3.25E-12	7.67E-12
1400.00	3.84E-12	5.81E-12	1.47E-12	1.66E-12	4.79E-12	1.03E-11
1500.00	5.07E-12	7.36E-12	2.17E-12	2.44E-12	6.76E-12	1.35E-11
1600.00	6.52E-12	9.14E-12	3.08E-12	3.45E-12	9.23E-12	1.73E-11
1700.00	8.20E-12	1.12E-11	4.21E-12	4.70E-12	1.22E-11	2.16E-11
1800.00	1.01E-11	1.34E-11	5.60E-12	6.24E-12	1.58E-11	2.66E-11
1900.00	1.23E-11	1.59E-11	7.26E-12	8.07E-12	2.00E-11	3.22E-11

2000.00	1.47E-11	1.87E-11	9.22E-12	1.02E-11	2.48E-11	3.84E-11

T (K)	Gamma-site (add)	Delta-site
250.00	1.51E-13	7.69E-14
300.00	2.69E-13	1.62E-13
400.00	6.42E-13	4.75E-13
500.00	1.21E-12	1.01E-12
600.00	1.99E-12	1.76E-12
700.00	2.96E-12	2.74E-12
800.00	4.15E-12	3.92E-12
900.00	5.52E-12	5.31E-12
1000.00	7.09E-12	6.88E-12
1100.00	8.84E-12	8.62E-12
1200.00	1.08E-11	1.05E-11
1300.00	1.28E-11	1.26E-11
1400.00	1.51E-11	1.48E-11
1500.00	1.75E-11	1.72E-11
1600.00	2.00E-11	1.97E-11
1700.00	2.27E-11	2.23E-11
1800.00	2.55E-11	2.50E-11
1900.00	2.84E-11	2.79E-11
2000.00	3.15E-11	3.09E-11

S7.6. (E)-4mhex

T (K)	Alpha-site	Beta-site	Gamma-site	Delta-site	Methyl-site	Epsilon-site
250.00	7.76E-17	1.18E-15	1.96E-21	2.48E-21	2.00E-18	9.56E-16
300.00	3.62E-16	4.03E-15	7.44E-20	6.13E-20	1.77E-17	3.38E-15
400.00	3.37E-15	2.34E-14	7.34E-18	7.15E-18	4.19E-16	2.18E-14
500.00	1.58E-14	7.86E-14	1.59E-16	1.49E-16	3.68E-15	8.10E-14
600.00	4.96E-14	1.94E-13	1.36E-15	1.24E-15	1.81E-14	2.19E-13
700.00	1.22E-13	3.93E-13	6.64E-15	5.92E-15	6.13E-14	4.81E-13
800.00	2.51E-13	7.01E-13	2.27E-14	1.99E-14	1.62E-13	9.19E-13
900.00	4.60E-13	1.14E-12	6.09E-14	5.29E-14	3.61E-13	1.59E-12
1000.00	7.69E-13	1.73E-12	1.37E-13	1.18E-13	7.05E-13	2.54E-12
1100.00	1.20E-12	2.48E-12	2.71E-13	2.32E-13	1.25E-12	3.83E-12
1200.00	1.77E-12	3.43E-12	4.86E-13	4.15E-13	2.05E-12	5.50E-12
1300.00	2.49E-12	4.56E-12	8.06E-13	6.86E-13	3.15E-12	7.59E-12
1400.00	3.39E-12	5.91E-12	1.26E-12	1.07E-12	4.62E-12	1.02E-11
1500.00	4.48E-12	7.48E-12	1.86E-12	1.58E-12	6.51E-12	1.32E-11
1600.00	5.76E-12	9.28E-12	2.65E-12	2.25E-12	8.85E-12	1.69E-11
1700.00	7.25E-12	1.13E-11	3.64E-12	3.09E-12	1.17E-11	2.10E-11
1800.00	8.95E-12	1.36E-11	4.85E-12	4.13E-12	1.51E-11	2.58E-11
1900.00	1.09E-11	1.61E-11	6.31E-12	5.38E-12	1.90E-11	3.12E-11
2000.00	1.30E-11	1.89E-11	8.02E-12	6.86E-12	2.35E-11	3.72E-11

T (K)	Gamma-site (add)	Delta-site
250.00	1.38E-13	1.06E-13
300.00	2.72E-13	2.18E-13
400.00	7.22E-13	6.11E-13
500.00	1.42E-12	1.24E-12
600.00	2.37E-12	2.10E-12
700.00	3.53E-12	3.17E-12
800.00	4.91E-12	4.44E-12
900.00	6.49E-12	5.89E-12
1000.00	8.24E-12	7.51E-12
1100.00	1.02E-11	9.28E-12
1200.00	1.22E-11	1.12E-11
1300.00	1.45E-11	1.32E-11
1400.00	1.68E-11	1.39E-11
1500.00	1.93E-11	1.57E-11
1600.00	2.20E-11	1.76E-11
1700.00	2.47E-11	1.95E-11
1800.00	2.76E-11	2.14E-11
1900.00	3.05E-11	2.34E-11
2000.00	3.36E-11	2.55E-11

S7.7. 5mhex

T (K)	Alpha-site	Beta-site	Gamma-site	Delta-site	Methyl-site	Epsilon1-site	Epsilon2-site
250.00	9.34E-17	1.48E-17	1.82E-15	9.58E-21	2.09E-18	4.57E-24	6.77E-24
300.00	4.30E-16	1.04E-16	5.65E-15	2.58E-19	1.72E-17	5.09E-22	6.32E-22
400.00	3.90E-15	1.64E-15	2.92E-14	2.21E-17	3.75E-16	2.38E-19	2.46E-19
500.00	1.79E-14	1.04E-14	9.18E-14	3.85E-16	3.13E-15	1.11E-17	7.23E-18
600.00	5.56E-14	3.96E-14	2.17E-13	2.84E-15	1.49E-14	1.36E-16	9.35E-17
700.00	1.35E-13	1.11E-13	4.30E-13	1.24E-14	4.94E-14	9.41E-16	6.16E-16
800.00	2.76E-13	2.24E-13	7.53E-13	3.57E-14	1.29E-13	4.19E-15	2.64E-15
900.00	5.00E-13	4.36E-13	1.21E-12	8.98E-14	2.83E-13	1.38E-14	8.48E-15
1000.00	8.31E-13	7.64E-13	1.81E-12	1.93E-13	5.48E-13	3.67E-14	2.21E-14
1100.00	1.29E-12	1.23E-12	2.58E-12	3.69E-13	9.62E-13	8.33E-14	4.94E-14
1200.00	1.89E-12	1.87E-12	3.54E-12	6.43E-13	1.57E-12	1.67E-13	9.82E-14
1300.00	2.65E-12	2.70E-12	4.68E-12	1.04E-12	2.41E-12	3.06E-13	1.78E-13
1400.00	3.59E-12	3.74E-12	6.03E-12	1.60E-12	3.52E-12	5.19E-13	3.00E-13
1500.00	4.72E-12	5.01E-12	7.59E-12	2.34E-12	4.93E-12	8.27E-13	4.75E-13
1600.00	6.04E-12	6.52E-12	9.36E-12	3.28E-12	6.69E-12	1.25E-12	7.18E-13
1700.00	7.57E-12	8.28E-12	1.14E-11	4.46E-12	8.82E-12	1.82E-12	1.04E-12
1800.00	9.31E-12	1.03E-11	1.36E-11	5.90E-12	1.14E-11	2.56E-12	1.45E-12
1900.00	1.13E-11	1.26E-11	1.60E-11	7.61E-12	1.43E-11	3.48E-12	1.97E-12
2000.00	1.35E-11	1.52E-11	1.87E-11	9.63E-12	1.77E-11	4.61E-12	2.61E-12

T (K)	Delta-site (add)	Epsilon-site (add)
250.00	2.23E-14	5.64E-13
300.00	5.49E-14	8.75E-13
400.00	1.94E-13	1.65E-12
500.00	4.56E-13	2.57E-12
600.00	8.54E-13	3.64E-12
700.00	1.40E-12	4.84E-12
800.00	2.08E-12	6.13E-12
900.00	2.90E-12	7.54E-12
1000.00	3.86E-12	9.07E-12
1100.00	4.95E-12	1.07E-11
1200.00	5.59E-12	1.25E-11
1300.00	6.70E-12	1.43E-11
1400.00	7.89E-12	1.62E-11
1500.00	9.14E-12	1.82E-11
1600.00	1.04E-11	2.03E-11
1700.00	1.18E-11	2.25E-11
1800.00	1.33E-11	2.48E-11
1900.00	1.48E-11	2.71E-11
2000.00	1.64E-11	2.96E-11

S8. Fit Parameters MS-CVT/SCT Rate Constants

To facilitate the use of rate constants for each reaction site of the isomers studied, we performed fits using various analytical functions implemented in the Pilgrim code, as shown in Table S1. Note that addition reactions and abstractions at methylenic carbons were not weighted here. In such cases, the pre-exponential factor A can be multiplied by 2.

Table S1.: Analytical expressions for rate constants and corresponding parameters.

Label	**Equation**	**Parameters**	**Units**
analytic1	$k = Ae^{-B/T}$	A, B	A: molecule cm^{-3} s^{-1} B: K
analytic2	$k = AT^n e^{-B/T}$	A, B, n	AT^n: molecule cm^{-3} s^{-1} B: K
analytic3	$k = A\left(\frac{T}{300}\right)^n e^{-B/T}$	A, B, n, T_r	A: molecule cm^{-3} s^{-1} B: K
analytic4[a]	$k = A\left(\frac{T}{300}\right)^n e^{-B(T+T_0)/(T^2+T_0^2)}$	A, B, n, T_0	A: molecule cm^{-3} s^{-1} B and T_0: K

[a] J. Zheng and D. G. Truhlar, *Phys. Chem. Chem. Phys.*, 2010, **12**, 7782–7793.

S8.1. (Z)-2mhex

```
Alpha-site
analytic1  9.0815E-11  7.5489E+03                                  # r^2 = 0.84383905
analytic2  9.2421E-16  6.6309E+03  1.5031E+00                     # r^2 = 0.99307036
analytic3  4.8869E-12  6.6309E+03  1.5031E+00  3.0000E+02         # r^2 = 0.99307036
analytic4  4.9974E-13  5.0448E+03  2.3567E+00  3.0000E+02  7.7301E+01 # r^2 = 0.99746765

Beta-site
analytic1  9.8749E-11  5.7939E+03                                  # r^2 = 0.75199015
analytic2  2.1110E-19  4.1997E+03  2.6103E+00                     # r^2 = 0.99765679
analytic3  6.1732E-13  4.1997E+03  2.6103E+00  3.0000E+02         # r^2 = 0.99765679
analytic4  3.3237E-13  3.3473E+03  2.7489E+00  3.0000E+02  1.2755E+02 # r^2 = 0.99964381

Gamma-site
nalytic1  4.3912E-11  2.5679E+03                                 # r^2 = 0.70055517
analytic2  1.6386E-20  8.3431E+02  2.8385E+00                     # r^2 = 0.99733257
analytic3  1.7614E-13  8.3431E+02  2.8385E+00  3.0000E+02         # r^2 = 0.99733257
analytic4  2.9585E-13  8.6900E+02  2.5749E+00  3.0000E+02  1.9863E+02 # r^2 = 0.99975370

Delta-site
analytic1  4.1646E-11  3.4385E+03                                  # r^2 = 0.75507057
analytic2  2.4068E-19  1.9237E+03  2.4803E+00                     # r^2 = 0.99904620
analytic3  3.3523E-13  1.9237E+03  2.4803E+00  3.0000E+02         # r^2 = 0.99904620
analytic4  2.8886E-13  1.5713E+03  2.4812E+00  3.0000E+02  1.3744E+02 # r^2 = 0.99988940

Methyl-site
analytic1  6.4009E-11  4.4998E+03                                  # r^2 = 0.65224859
analytic2  4.8426E-22  2.4549E+03  3.3483E+00                     # r^2 = 0.99311495
analytic3  9.5306E-14  2.4549E+03  3.3483E+00  3.0000E+02         # r^2 = 0.99311495
analytic4  1.6249E-13  2.2285E+03  3.0190E+00  3.0000E+02  1.6867E+02 # r^2 = 0.99960575

Epsilon-site
analytic1  1.5457E-10  4.9702E+03                                  # r^2 = 0.73599743
analytic2  6.6305E-20  3.2478E+03  2.8203E+00                     # r^2 = 0.99297827
analytic3  6.4237E-13  3.2478E+03  2.8203E+00  3.0000E+02         # r^2 = 0.99297827
analytic4  8.2727E-13  2.8050E+03  2.5905E+00  3.0000E+02  1.5541E+02 # r^2 = 0.99949140

Alpha-site (add)
analytic1  3.2035E-11  1.9400E+03                                  # r^2 = 0.85811294
analytic2  9.9861E-17  9.2756E+02  1.6578E+00                     # r^2 = 0.99953168
analytic3  1.2761E-12  9.2756E+02  1.6578E+00  3.0000E+02         # r^2 = 0.99953168
analytic4  1.5607E-12  8.4189E+02  1.5334E+00  3.0000E+02  1.6850E+02 # r^2 = 0.99995117
```

```
Beta-site (add)
analytic1  4.0567E-11  1.6495E+03                                  # r^2 = 0.79559985
analytic2  6.5440E-18  4.0058E+02  2.0450E+00                      # r^2 = 0.99910347
analytic3  7.6117E-13  4.0058E+02  2.0450E+00  3.0000E+02          # r^2 = 0.99910347
analytic4  1.0751E-12  4.5009E+02  1.8755E+00  3.0000E+02  2.1264E+02 # r^2 = 0.99993653
```

S8.2. (*E*)-2mhex

```
Alpha-site
analytic1  1.8684E-10  8.4828E+03                                  # r^2 = 0.81679995
analytic2  7.1295E-18  7.1187E+03  2.2335E+00                      # r^2 = 0.99619906
analytic3  2.4301E-12  7.1187E+03  2.2335E+00  3.0000E+02          # r^2 = 0.99619906
analytic4  5.1956E-13  5.5451E+03  2.7001E+00  3.0000E+02  1.1597E+02 # r^2 = 0.99852337

Beta-site
analytic1  9.9393E-11  7.3692E+03                                  # r^2 = 0.76460515
analytic2  2.0390E-19  5.7717E+03  2.6157E+00                      # r^2 = 0.99504799
analytic3  6.1487E-13  5.7717E+03  2.6157E+00  3.0000E+02          # r^2 = 0.99504799
analytic4  2.4193E-13  4.5780E+03  2.8445E+00  3.0000E+02  1.2542E+02 # r^2 = 0.99890404

Gamma-site
analytic1  3.7713E-11  2.6150E+03                                  # r^2 = 0.70876798
analytic2  3.9826E-20  9.6450E+02  2.7025E+00                      # r^2 = 0.99939420
analytic3  1.9707E-13  9.6450E+02  2.7025E+00  3.0000E+02          # r^2 = 0.99939420
analytic4  1.9374E-13  8.0485E+02  2.6765E+00  3.0000E+02  1.4491E+02 # r^2 = 0.99986079

Delta-site
analytic1  7.3257E-11  3.8036E+03                                  # r^2 = 0.75793597
analytic2  2.9642E-19  2.2604E+03  2.5269E+00                      # r^2 = 0.99781682
analytic3  5.3860E-13  2.2604E+03  2.5269E+00  3.0000E+02          # r^2 = 0.99781682
analytic4  5.1520E-13  1.8848E+03  2.4679E+00  3.0000E+02  1.4464E+02 # r^2 = 0.99974221

Methyl-site
analytic1  1.0181E-10  4.6622E+03                                  # r^2 = 0.64890015
analytic2  3.8236E-22  2.5614E+03  3.4398E+00                      # r^2 = 0.98916428
analytic3  1.2687E-13  2.5614E+03  3.4398E+00  3.0000E+02          # r^2 = 0.98916428
analytic4  2.7000E-13  2.3895E+03  3.0064E+00  3.0000E+02  1.7525E+02 # r^2 = 0.99920799

Epsilon-site
analytic1  1.7206E-10  4.9315E+03                                  # r^2 = 0.70418317
analytic2  1.4395E-20  3.0785E+03  3.0340E+00                      # r^2 = 0.99257903
analytic3  4.7193E-13  3.0785E+03  3.0340E+00  3.0000E+02          # r^2 = 0.99257903
analytic4  6.7923E-13  2.6977E+03  2.7595E+00  3.0000E+02  1.5947E+02 # r^2 = 0.99952593

Alpha-site (add)
analytic1  3.8662E-11  1.8986E+03                                  # r^2 = 0.82973964
analytic2  3.6247E-17  7.9022E+02  1.8149E+00                      # r^2 = 0.99984246
analytic3  1.1347E-12  7.9022E+02  1.8149E+00  3.0000E+02          # r^2 = 0.99984246
analytic4  1.0731E-12  6.4700E+02  1.8128E+00  3.0000E+02  1.3829E+02 # r^2 = 0.99998645

Beta-site (add)
analytic1  3.5555E-11  1.7265E+03                                  # r^2 = 0.92218899
analytic2  3.0214E-15  9.7801E+02  1.2256E+00                      # r^2 = 0.99622108
analytic3  3.2816E-12  9.7801E+02  1.2256E+00  3.0000E+02          # r^2 = 0.99622108
analytic4  6.3642E-12  1.0372E+03  8.9229E-01  3.0000E+02  2.0212E+02 # r^2 = 0.99805096
```

S8.3. (Z)-3mhex

```
Alpha-site
analytic1  3.1325E-11  2.4913E+03                                  # r^2 = 0.68170266
analytic2  3.9353E-21  6.7079E+02  2.9809E+00                     # r^2 = 0.99622191
analytic3  9.5273E-14  6.7079E+02  2.9809E+00  3.0000E+02         # r^2 = 0.99622191
analytic4  2.1762E-13  8.3979E+02  2.5871E+00  3.0000E+02  2.3068E+02 # r^2 = 0.99976839

Beta-site
analytic1  1.3186E-10  6.8607E+03                                  # r^2 = 0.77285926
analytic2  1.0419E-18  5.3709E+03  2.4394E+00                     # r^2 = 0.99867559
analytic3  1.1493E-12  5.3709E+03  2.4394E+00  3.0000E+02         # r^2 = 0.99867559
analytic4  3.4072E-13  4.1711E+03  2.8160E+00  3.0000E+02  1.1407E+02 # r^2 = 0.99949590

Gamma-site (add)
analytic1  1.2861E-10  6.2264E+03                                  # r^2 = 0.75435472
analytic2  2.6688E-19  4.6298E+03  2.6142E+00                     # r^2 = 0.99711352
analytic3  7.9791E-13  4.6298E+03  2.6142E+00  3.0000E+02         # r^2 = 0.99711352
analytic4  2.5908E-13  3.5775E+03  2.9755E+00  3.0000E+02  1.1083E+02 # r^2 = 0.99785931

Delta-site (add)
analytic1  5.3431E-11  2.5665E+03                                  # r^2 = 0.74073064
analytic2  2.0427E-19  1.0187E+03  2.5343E+00                     # r^2 = 0.99875377
analytic3  3.8721E-13  1.0187E+03  2.5343E+00  3.0000E+02         # r^2 = 0.99875377
analytic4  4.8317E-13  9.2476E+02  2.3976E+00  3.0000E+02  1.6867E+02 # r^2 = 0.99990173

Methyl-site
analytic1  1.5199E-10  4.7787E+03                                  # r^2 = 0.66583469
analytic2  8.5781E-22  2.7104E+03  3.3866E+00                     # r^2 = 0.98547005
analytic3  2.1006E-13  2.7104E+03  3.3866E+00  3.0000E+02         # r^2 = 0.98547005
analytic4  6.5164E-13  2.6378E+03  2.7778E+00  3.0000E+02  1.8468E+02 # r^2 = 0.99942742

Epsilon-site
analytic1  1.7173E-10  5.0544E+03                                  # r^2 = 0.69182100
analytic2  1.0087E-20  3.1732E+03  3.0803E+00                     # r^2 = 0.99436296
analytic3  4.3051E-13  3.1732E+03  3.0803E+00  3.0000E+02         # r^2 = 0.99436296
analytic4  4.8568E-13  2.7015E+03  2.9136E+00  3.0000E+02  1.5118E+02 # r^2 = 0.99952970

Beta-site (add)
analytic1  2.4312E-11  1.5182E+03                                  # r^2 = 0.82961909
analytic2  6.0894E-17  4.8828E+02  1.6864E+00                     # r^2 = 0.99984797
analytic3  9.1606E-13  4.8828E+02  1.6864E+00  3.0000E+02         # r^2 = 0.99984797
analytic4  9.1623E-13  4.1006E+02  1.6691E+00  3.0000E+02  1.4657E+02 # r^2 = 0.99968512

Gamma-site (add)
analytic1  1.5701E-11  1.4095E+03                                  # r^2 = 0.88749731
analytic2  4.7691E-16  5.7886E+02  1.3601E+00                     # r^2 = 0.99955740
analytic3  1.1156E-12  5.7886E+02  1.3601E+00  3.0000E+02         # r^2 = 0.99955740
analytic4  1.2285E-12  5.1609E+02  1.2958E+00  3.0000E+02  1.6412E+02 # r^2 = 0.99995204
```

S8.4. (E)-3mhex

```
Alpha-site
analytic1  3.5401E-11  2.6558E+03                                  # r^2 = 0.67628795
analytic2  3.0151E-21  8.0418E+02  3.0317E+00                     # r^2 = 0.99612482
analytic3  9.7540E-14  8.0418E+02  3.0317E+00  3.0000E+02         # r^2 = 0.99612482
analytic4  1.9522E-13  9.0386E+02  2.6912E+00  3.0000E+02  2.1274E+02 # r^2 = 0.99963156
```

```
Beta-site
analytic1  1.5846E-10  7.1845E+03                                  # r^2 = 0.80563875
analytic2  5.1031E-18  5.8069E+03  2.2556E+00                    # r^2 = 0.99776644
analytic3  1.9740E-12  5.8069E+03  2.2556E+00  3.0000E+02        # r^2 = 0.99776644
analytic4  6.0802E-13  4.5434E+03  2.5980E+00  3.0000E+02  1.1845E+02 # r^2 = 0.99942143

Gamma-site
analytic1  1.1644E-10  6.3005E+03                                  # r^2 = 0.75792054
analytic2  1.5901E-19  4.6705E+03  2.6689E+00                    # r^2 = 0.99428126
analytic3  6.4954E-13  4.6705E+03  2.6689E+00  3.0000E+02        # r^2 = 0.99428126
analytic4  4.0247E-13  3.7813E+03  2.7256E+00  3.0000E+02  1.3414E+02 # r^2 = 0.99907601

Delta-site
analytic1  5.0522E-11  2.6467E+03                                  # r^2 = 0.73482556
analytic2  1.6616E-19  1.0869E+03  2.5540E+00                    # r^2 = 0.99920328
analytic3  3.5239E-13  1.0869E+03  2.5540E+00  3.0000E+02        # r^2 = 0.99920328
analytic4  3.6146E-13  9.2047E+02  2.5042E+00  3.0000E+02  1.4960E+02 # r^2 = 0.99986996

Methyl-site
analytic1  8.0652E-11  4.6313E+03                                  # r^2 = 0.66361532
analytic2  1.8539E-21  2.6751E+03  3.2030E+00                    # r^2 = 0.99657391
analytic3  1.5929E-13  2.6751E+03  3.2030E+00  3.0000E+02        # r^2 = 0.99657392
analytic4  2.3567E-13  2.3679E+03  2.9301E+00  3.0000E+02  1.6213E+02 # r^2 = 0.99999275

Epsilon-site
nalytic1  1.7173E-10  5.0544E+03                                 # r^2 = 0.69182100
analytic2  1.0087E-20  3.1732E+03  3.0803E+00                    # r^2 = 0.99436296
analytic3  4.3051E-13  3.1732E+03  3.0803E+00  3.0000E+02        # r^2 = 0.99436296
analytic4  4.8568E-13  2.7015E+03  2.9136E+00  3.0000E+02  1.5118E+02 # r^2 = 0.99952970

Beta-site (add)
analytic1  5.2939E-11  1.7579E+03                                  # r^2 = 0.83879736
analytic2  8.0567E-17  6.8820E+02  1.7515E+00                    # r^2 = 0.99966575
analytic3  1.7574E-12  6.8820E+02  1.7515E+00  3.0000E+02        # r^2 = 0.99966575
analytic4  1.8299E-12  5.9030E+02  1.7088E+00  3.0000E+02  1.5343E+02 # r^2 = 0.99996538

Gamma-site (add)
analytic1  5.6322E-11  1.6975E+03                                  # r^2 = 0.86291131
analytic2  3.6187E-16  7.4280E+02  1.5632E+00                    # r^2 = 0.99983176
analytic3  2.6964E-12  7.4280E+02  1.5632E+00  3.0000E+02        # r^2 = 0.99983176
analytic4  2.5970E-12  6.1257E+02  1.5544E+00  3.0000E+02  1.4086E+02 # r^2 = 0.99998754
```

S8.5. (Z)-4mhex

```
Alpha-site
analytic1  3.9834E-11  3.4613E+03                                  # r^2 = 0.67327532
analytic2  1.7226E-21  1.5556E+03  3.1203E+00                    # r^2 = 0.99549420
analytic3  9.2383E-14  1.5556E+03  3.1203E+00  3.0000E+02        # r^2 = 0.99549420

Beta-site
analytic1  3.8727E-11  2.8051E+03                                  # r^2 = 0.70900789
analytic2  2.7907E-20  1.1240E+03  2.7525E+00                    # r^2 = 0.99875413
analytic3  1.8363E-13  1.1240E+03  2.7525E+00  3.0000E+02        # r^2 = 0.99875413
analytic4  2.0962E-13  9.8483E+02  2.6525E+00  3.0000E+02  1.5945E+02 # r^2 = 0.99983953

Gamma-site
analytic1  1.0477E-10  6.1416E+03                                  # r^2 = 0.74049848
```

```
analytic2  4.6342E-20  4.4216E+03  2.8163E+00                  # r^2 = 0.99271491
analytic3  4.3881E-13  4.4216E+03  2.8163E+00  3.0000E+02      # r^2 = 0.99271491
analytic4  5.6591E-13  3.7908E+03  2.5443E+00  3.0000E+02  1.5317E+02 # r^2 = 0.99995746

Delta-site
analytic1  1.0492E-10  5.9846E+03                              # r^2 = 0.72574800
analytic2  2.2052E-20  4.2051E+03  2.9136E+00                  # r^2 = 0.99248045
analytic3  3.6372E-13  4.2051E+03  2.9136E+00  3.0000E+02      # r^2 = 0.99248045
analytic4  2.9974E-13  3.4736E+03  2.8550E+00  3.0000E+02  1.4154E+02 # r^2 = 0.99890151

Methyl-site
analytic1  1.2512E-10  4.7948E+03                              # r^2 = 0.64997316
analytic2  4.0770E-22  2.6826E+03  3.4584E+00                  # r^2 = 0.98770945
analytic3  1.5039E-13  2.6826E+03  3.4584E+00  3.0000E+02      # r^2 = 0.98770945
analytic4  3.5340E-13  2.5233E+03  2.9759E+00  3.0000E+02  1.7715E+02 # r^2 = 0.99921919

Epsilon-site
analytic1  9.0461E-11  3.2272E+03                              # r^2 = 0.65809225
analytic2  2.1170E-21  1.2725E+03  3.2006E+00                  # r^2 = 0.99566259
analytic3  1.7948E-13  1.2725E+03  3.2006E+00  3.0000E+02      # r^2 = 0.99566259
analytic4  3.2680E-13  1.2610E+03  2.8844E+00  3.0000E+02  1.8860E+02 # r^2 = 0.99964001

Gamma-site (add)
analytic1  4.3103E-11  1.5720E+03                              # r^2 = 0.80980038
analytic2  1.8638E-17  4.0181E+02  1.9160E+00                  # r^2 = 0.99946665
analytic3  1.0392E-12  4.0181E+02  1.9160E+00  3.0000E+02      # r^2 = 0.99946665
analytic4  1.2549E-12  3.9800E+02  1.8165E+00  3.0000E+02  1.8855E+02 # r^2 = 0.99993581

Delta-site (add)
analytic1  4.8782E-11  1.7539E+03                              # r^2 = 0.84781784
analytic2  1.2446E-16  7.2541E+02  1.6840E+00                  # r^2 = 0.99974809
analytic3  1.8467E-12  7.2541E+02  1.6840E+00  3.0000E+02      # r^2 = 0.99974809
analytic4  1.8869E-12  6.1574E+02  1.6486E+00  3.0000E+02  1.5026E+02 # r^2 = 0.99998642
```

S8.6. (E)-4mhex

```
Alpha-site
analytic1  3.7225E-11  3.5322E+03                              # r^2 = 0.68579425
analytic2  3.2648E-21  1.6830E+03  3.0279E+00                  # r^2 = 0.99617343
analytic3  1.0333E-13  1.6830E+03  3.0279E+00  3.0000E+02      # r^2 = 0.99617343
analytic4  1.4692E-13  1.5234E+03  2.8084E+00  3.0000E+02  1.6798E+02 # r^2 = 0.99959521

Beta-site
analytic1  4.0437E-11  2.8297E+03                              # r^2 = 0.72264039
analytic2  6.9105E-20  1.2176E+03  2.6396E+00                  # r^2 = 0.99928876
analytic3  2.3880E-13  1.2176E+03  2.6396E+00  3.0000E+02      # r^2 = 0.99928876
analytic4  2.2997E-13  1.0112E+03  2.6141E+00  3.0000E+02  1.4330E+02 # r^2 = 0.99987639

Gamma-site
analytic1  1.0940E-10  6.4077E+03                              # r^2 = 0.77073754
analytic2  3.6447E-19  4.8490E+03  2.5523E+00                  # r^2 = 0.99563088
analytic3  7.6558E-13  4.8490E+03  2.5523E+00  3.0000E+02      # r^2 = 0.99563088
analytic4  3.9458E-13  3.8791E+03  2.6882E+00  3.0000E+02  1.2923E+02 # r^2 = 0.99919251

Delta-site
analytic1  8.8613E-11  6.3389E+03                              # r^2 = 0.75954320
analytic2  1.5269E-19  4.7275E+03  2.6385E+00                  # r^2 = 0.99524671
analytic3  5.2441E-13  4.7275E+03  2.6385E+00  3.0000E+02      # r^2 = 0.99524671
```

```
analytic4  4.9181E-13  3.9506E+03  2.5017E+00  3.0000E+02  1.4525E+02 # r^2 = 0.99999171

Methyl-site
analytic1  1.2071E-10  4.7872E+03                                     # r^2 = 0.66256063
analytic2  7.8446E-22  2.7302E+03  3.3681E+00                         # r^2 = 0.98833158
analytic3  1.7292E-13  2.7302E+03  3.3681E+00  3.0000E+02             # r^2 = 0.98833159
analytic4  3.8537E-13  2.5458E+03  2.9078E+00  3.0000E+02  1.7513E+02 # r^2 = 0.99926851

Epsilon-site
analytic1  8.2362E-11  3.1063E+03                                     # r^2 = 0.65793786
analytic2  3.0275E-21  1.1876E+03  3.1416E+00                         # r^2 = 0.99752371
analytic3  1.8328E-13  1.1876E+03  3.1416E+00  3.0000E+02             # r^2 = 0.99752371
analytic4  2.5035E-13  1.0955E+03  2.9580E+00  3.0000E+02  1.7261E+02 # r^2 = 0.99968912

Gamma-site (add)
analytic1  5.0039E-11  1.6046E+03                                     # r^2 = 0.85299339
analytic2  2.3308E-16  6.2419E+02  1.6053E+00                         # r^2 = 0.99989051
analytic3  2.2075E-12  6.2419E+02  1.6053E+00  3.0000E+02             # r^2 = 0.99989051
analytic4  2.1148E-12  5.1142E+02  1.6031E+00  3.0000E+02  1.3856E+02 # r^2 = 0.99999026

Delta-site (add)
analytic1  4.2640E-11  1.6120E+03                                     # r^2 = 0.91722894
analytic2  2.9393E-15  8.4680E+02  1.2529E+00                         # r^2 = 0.99699677
analytic3  3.7316E-12  8.4680E+02  1.2529E+00  3.0000E+02             # r^2 = 0.99699677
analytic4  5.7384E-12  8.4979E+02  1.0285E+00  3.0000E+02  1.9133E+02 # r^2 = 0.99902255
```

S8.7. 5mhex

```
Alpha-site
analytic1  3.8176E-11  3.4870E+03                                     # r^2 = 0.69493577
analytic2  5.2750E-21  1.6741E+03  2.9684E+00                         # r^2 = 0.99611896
analytic3  1.1895E-13  1.6741E+03  2.9684E+00  3.0000E+02             # r^2 = 0.99611896
analytic4  1.6718E-13  1.5122E+03  2.7546E+00  3.0000E+02  1.6747E+02 # r^2 = 0.99954477

Beta-site
analytic1  6.0026E-11  4.0342E+03                                     # r^2 = 0.73451838
analytic2  9.4277E-20  2.4154E+03  2.6506E+00                         # r^2 = 0.99861787
analytic3  3.4696E-13  2.4154E+03  2.6506E+00  3.0000E+02             # r^2 = 0.99861787
analytic4  2.7999E-13  1.9650E+03  2.6645E+00  3.0000E+02  1.3587E+02 # r^2 = 0.99980110

Gamma-site
analytic1  3.7602E-11  2.7079E+03                                     # r^2 = 0.71800517
analytic2  4.6238E-20  1.0695E+03  2.6826E+00                         # r^2 = 0.99886800
analytic3  2.0424E-13  1.0695E+03  2.6826E+00  3.0000E+02             # r^2 = 0.99886800
analytic4  2.2701E-13  9.3069E+02  2.5968E+00  3.0000E+02  1.5758E+02 # r^2 = 0.99982732

Delta-site
nalytic1  1.0558E-10  5.9940E+03                                    # r^2 = 0.76602827
analytic2  8.3979E-19  4.5047E+03  2.4385E+00                         # r^2 = 0.99934965
analytic3  9.2177E-13  4.5047E+03  2.4385E+00  3.0000E+02             # r^2 = 0.99934965
analytic4  3.4607E-13  3.5082E+03  2.7353E+00  3.0000E+02  1.1570E+02 # r^2 = 0.99984185

Methyl-site
analytic1  8.5780E-11  4.6938E+03                                     # r^2 = 0.65698468
analytic2  4.2968E-22  2.6159E+03  3.4022E+00                         # r^2 = 0.98830085
analytic3  1.1501E-13  2.6159E+03  3.4022E+00  3.0000E+02             # r^2 = 0.98830085
analytic4  2.6974E-13  2.4669E+03  2.9230E+00  3.0000E+02  1.7774E+02 # r^2 = 0.99929445
```

```
Epsilon1-site
analytic1  1.3880E-10  7.9511E+03                                  # r^2 = 0.78625050
analytic2  3.0531E-18  6.5430E+03  2.3055E+00                     # r^2 = 0.99945833
analytic3  1.5694E-12  6.5430E+03  2.3055E+00  3.0000E+02         # r^2 = 0.99945833
analytic4  3.3150E-11  7.4854E+03  7.3581E-01  3.0000E+02  2.0398E-05 # r^2 = 0.89151089

Epsilon2-site
analytic1  6.4796E-11  7.6743E+03                                  # r^2 = 0.75313120
analytic2  1.9202E-19  6.1061E+03  2.5676E+00                     # r^2 = 0.99878651
analytic3  4.4013E-13  6.1061E+03  2.5676E+00  3.0000E+02         # r^2 = 0.99878651
analytic4  6.3019E-14  4.6366E+03  3.2693E+00  3.0000E+02  9.0833E+01 # r^2 = 0.99689596

Delta-site (add)
analytic1  3.0053E-11  1.9248E+03                                  # r^2 = 0.89043466
analytic2  6.1213E-16  1.0622E+03  1.4123E+00                     # r^2 = 0.99941654
analytic3  1.9292E-12  1.0622E+03  1.4123E+00  3.0000E+02         # r^2 = 0.99941654
analytic4  2.1624E-12  9.2722E+02  1.3229E+00  3.0000E+02  1.5841E+02 # r^2 = 0.99959503

Epsilon-site (add)
analytic1  3.5201E-11  1.1510E+03                                  # r^2 = 0.83694016
analytic2  3.0920E-16  2.2131E+02  1.5223E+00                     # r^2 = 0.99993547
analytic3  1.8247E-12  2.2131E+02  1.5223E+00  3.0000E+02         # r^2 = 0.99993547
analytic4  1.7025E-12  1.7848E+02  1.5494E+00  3.0000E+02  4.3696E+01 # r^2 = 0.99996035
```

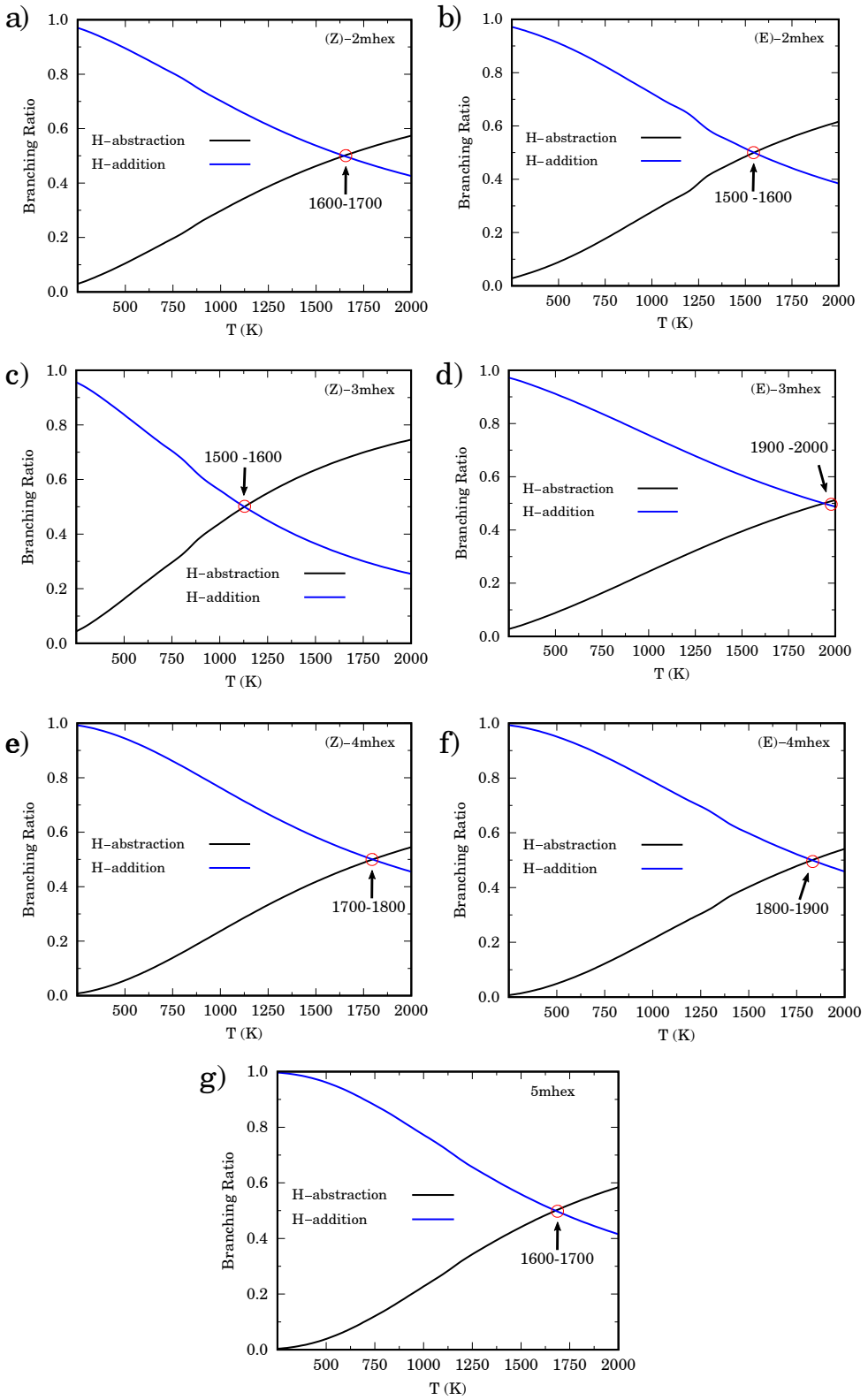

Fig. S3.: Branching ratio of the summed contributions from H-abstraction and addition reaction sites for (a) methyl (*Z*)-hex-2-enoate, (b) methyl (*E*)-hex-2-enoate, (c) methyl (*Z*)-hex-3-enoate, (d) methyl (*E*)-hex-3-enoate, (e) methyl (*Z*)-hex-4-enoate, (f) methyl (*E*)-hex-4-enoate, and (g) methyl hex-5-enoate.