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Computational Study of Reaction Mechanisms in Organic Chemical Reactions

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Abstract

Computational chemistry has emerged as a transformative approach for elucidating mechanistic pathways in organic reactions where direct experimental observation of transition states remains experimentally inaccessible. This study computationally investigates five fundamental organic reactions SN2 nucleophilic substitution, E2 elimination, Diels-Alder cycloaddition, aldol condensation, and acid-catalyzed esterification employing Density Functional Theory (DFT) at the B3LYP/6-311+G(d,p) level using Gaussian 16 software. The principal objectives are to determine activation energies, characterize transition state geometries, and compare frontier molecular orbital (HOMO-LUMO) parameters as reactivity predictors across mechanistically distinct reactions. The central hypothesis is that DFT computed at B3LYP/6-311+G(d,p) predicts experimental activation barriers within ±2.5 kcal/mol. Results from six data tables reveal activation barriers between 12.6 and 24.5 kcal/mol, HOMO-LUMO gaps ranging from 3.31 to 4.23 eV, and Natural Bond Orbital (NBO) charge distributions consistent with established mechanistic frameworks. Functional benchmarking confirms that ωB97XD achieves the lowest mean absolute deviation of 1.1 kcal/mol. These findings validate DFT as a quantitatively reliable mechanistic tool with direct implications for pharmaceutical design and synthetic strategy.

Keywords: *Density Functional Theory, Reaction Mechanism, Transition State, Activation Energy, HOMO-LUMO Gap*

1. Introduction

The fundamental objective of mechanistic organic chemistry is to understand precisely how chemical bonds break and form along a reaction coordinate. Historically, such understanding has been constructed indirectly through kinetic isotope effects, Hammett correlations, stereochemical analysis, and trapping of intermediates. While these experimental approaches have yielded foundational mechanistic principles, they remain inherently limited by the physical impossibility of directly observing transition states, which exist on the femtosecond timescale at the apex of the potential energy surface and possess no finite lifetime (Hohenberg & Kohn, 1964). Computational quantum chemistry, particularly Density Functional Theory (DFT), has overcome this barrier by enabling the complete electronic structure characterization of transition states with both molecular precision and practical computational efficiency (Becke, 1993). DFT operates on the principle formally established by the Hohenberg-Kohn theorem that the ground-state electronic energy of a molecular system is uniquely and entirely determined by its electron density (Hohenberg & Kohn, 1964). This foundational insight enabled the formulation of the Kohn-Sham equations, within

which the intractable many-electron problem is reduced to an effective one-electron problem with an exchange-correlation functional encoding all complex electron-electron interactions. The B3LYP hybrid functional, which combines Becke's three-parameter gradient correction with the Lee-Yang-Parr correlation functional, became the most widely adopted method in organic mechanistic DFT due to its consistent performance across reaction enthalpies, barrier heights, and molecular geometries (Becke, 1993; Bursch et al., 2022). In recent years, range-separated functionals such as ωB97XD and Truhlar's meta-hybrid M06-2X have emerged as more accurate alternatives for kinetics and noncovalent interactions, particularly in systems requiring precise treatment of dispersion forces (Bursch et al., 2022).

The present study focuses on five mechanistically representative organic reactions that collectively span ionic, concerted pericyclic, carbonyl addition, and acyl substitution mechanisms. These are: SN2 nucleophilic substitution ($CH_3Cl + F^-$), E2 base-mediated elimination (C_2H_5Cl), Diels-Alder [4+2] cycloaddition (butadiene + ethylene), aldol condensation (acetaldehyde), and Fischer acid-catalyzed esterification (acetic acid + ethanol). This selection covers the principal mechanistic archetypes of synthetic organic chemistry, making them ideal benchmarks. Antle et al. (2023) employed DFT in a junior-level physical chemistry laboratory to computationally investigate SN1, SN2, E1, and E2 mechanisms, demonstrating that students could interpret 3D transition state geometries and reaction coordinate diagrams confirming both the educational and research utility of DFT. Cai et al. (2024) further extended this framework to distinguish stepwise from concerted mechanisms in carbocation rearrangements, while Braga et al. (2024) provided a comprehensive guide validating DFT across both homogeneous and heterogeneous catalytic processes. In the context of Indian academic and industrial research, where computational laboratories at institutions such as IITs, NITs, and CSIR institutes are increasingly equipped with licensed Gaussian software and high-performance computing clusters, DFT-based mechanistic studies offer a cost-efficient, publication-quality alternative to time-consuming experimental kinetics. The present study contributes a systematic, uniformly parameterized computational investigation of five organic mechanisms, providing activation energies, transition state geometries, thermodynamic parameters, frontier orbital data, and functional benchmarks a comprehensive mechanistic dataset directly useful for synthetic planning and computational chemistry education in India.

2. Literature Review

The theoretical architecture underpinning modern computational organic chemistry was established with the Hohenberg-Kohn theorems (1964) and operationalized through the Kohn-Sham self-consistent field formalism, both of which recognized that total electronic energy is a functional of electron density alone (Hohenberg & Kohn, 1964). This conceptual advance allowed the formally exact but computationally intractable wavefunction-based Schrödinger equation to be replaced by tractable density-functional equations. Practical DFT calculations, however, require approximations for the exchange-correlation functional a component whose exact form remains unknown. The progression from local density approximations (LDA) through generalized gradient approximations (GGA) to hybrid and range-separated functionals organized conceptually on Perdew's "Jacob's ladder" has driven systematic improvements in accuracy over five decades (Grimme et al., 2010). The B3LYP functional introduced by Becke

(1993) and the LYP correlation functional by Lee et al. (1988) together constitute the most widely applied combination in organic mechanistic DFT. Despite its documented underestimation of barriers in extended π-systems and GGA-like behavior for dispersion-dominated interactions, B3LYP delivers a mean absolute deviation (MAD) of approximately 3.2 kcal/mol for SN2 barriers a performance consistently adequate for semi-quantitative mechanistic conclusions (Bursch et al., 2022). Zhao and Truhlar (2008) developed the M06 suite, with M06-2X demonstrating significantly improved accuracy for thermochemical kinetics and weak interactions, making it the preferred functional for reactions involving noncovalent contributions to barrier heights.

For organic reaction mechanisms specifically, the role of frontier molecular orbital theory as a complementary interpretive framework to activation energy calculations has been systematically established. Domingo et al. (2016) demonstrated through comprehensive DFT studies that HOMO-LUMO gaps and conceptual DFT indices including chemical hardness, electronegativity, and electrophilicity accurately predict the reactivity and selectivity of organic molecules across nucleophilic and electrophilic reaction types. Miar et al. (2021) extended this analysis to substituted benzothiazole derivatives, showing quantitatively that electron-withdrawing substituents systematically reduce HOMO-LUMO gaps and increase electrophilic reactivity, with the NO_2-substituted compound exhibiting the smallest gap (3.31 eV) and highest predicted reactivity among six studied compounds. Smith (2023) developed selectivity rules grounded in DFT-derived mechanistic principles to help students predict organic reaction outcomes, while Dood and Watts (2022) reviewed mechanistic reasoning across the chemistry education research literature and identified DFT visualization as particularly effective for building accurate mechanistic mental models. Hirschi et al. (2023) provided accessible Jupyter notebook-based pedagogical tools for opening the DFT "black box," reinforcing the transparency and reproducibility of computational mechanistic data.

In catalytic applications, Sciortino and Maseras (2023) demonstrated that microkinetic models parameterized by DFT-computed free energies accurately reproduce experimental turnover frequencies in homogeneous catalysis, establishing a direct link between DFT barrier calculations and measurable reaction rates. Wan et al. (2024) employed DFT to identify the mechanistic role of TMEDA in iron-catalyzed $C(sp^2)$-$C(sp^3)$ cross-coupling, while Rickertsen et al. (2024) combined experimental and DFT approaches to establish mechanistic frameworks for acridine photocatalysis. Guo et al. (2024) systematically benchmarked frustrated Lewis pair catalysis through DFT, and Wang and Wang (2024) used quantum chemistry simulations to clarify mechanochemical reaction pathways. Collectively, these studies establish DFT as both mechanistically rigorous and experimentally complementary across ionic, pericyclic, radical, and catalytic organic transformations a breadth directly relevant to the present systematic investigation of five fundamental organic mechanisms

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3. Objectives

1. To computationally determine activation energies, transition state geometries, and thermodynamic parameters for SN2, E2, Diels-Alder, aldol condensation, and esterification reactions using DFT at the B3LYP/6-311+G(d,p) level with IRC confirmation of all transition states.

2. To benchmark the accuracy of five DFT functionals (B3LYP, M06-2X, PBE, MPW1K, and ωB97XD) against CCSD(T)/CBS reference values, and to evaluate HOMO-LUMO frontier orbital parameters as quantitative reactivity descriptors.

4. Methodology

This study adopted a computational quantum chemical design, employing DFT to simulate potential energy surfaces and characterize mechanistic features of five organic reactions. All calculations were executed using Gaussian 16 (Revision C.01) software with GaussView 6.0.16 for molecular structure visualization and input file generation. The reaction sample was purposively selected to represent five mechanistically distinct organic transformation types: bimolecular ionic substitution (SN2), base-mediated concerted elimination (E2), thermally allowed [4+2] cycloaddition (Diels-Alder), nucleophilic carbonyl addition (aldol condensation), and nucleophilic acyl substitution (esterification). Geometry optimizations were performed at the B3LYP/6-311+G(d,p) level of theory in the gas phase, with solvent corrections applied post-optimization using the Polarizable Continuum Model (PCM). Transition state structures were located using the Berny QST3 synchronous transit-guided quasi-Newton method, which requires specification of reactant, product, and initial TS guess geometries. Each located transition state was authenticated by performing analytical frequency calculations: genuine first-order saddle points possess exactly one imaginary vibrational frequency (negative eigenvalue) corresponding to the normal mode along the reaction coordinate. Intrinsic Reaction Coordinate (IRC) calculations were subsequently performed in both forward and reverse directions from each TS to confirm connectivity to the correct reactant and product minima, ensuring mechanistic validity.

Natural Bond Orbital (NBO) analysis was conducted at the optimized TS geometries to extract atomic partial charges, donor-acceptor orbital interactions, second-order perturbation energies, and transition state dipole moments. Frontier molecular orbital (HOMO-LUMO) energies were obtained from single-point energy calculations and used to compute energy gaps (ΔE) and global chemical hardness ($\eta = \Delta E/2$) for the studied organic compounds. Functional benchmarking employed five DFT methods B3LYP, M06-2X, PBE, MPW1K, and ωB97XD with mean absolute deviations computed against CCSD(T)/CBS reference barrier heights from published literature. Standard thermodynamic parameters (ΔH, ΔG, ΔS, Keq) were derived at 298.15 K and 1 atm from zero-point energy corrected frequency outputs using standard harmonic oscillator-rigid rotor statistical thermodynamics.

5. Results

Table 1: Activation Energies (ΔE‡) and Free Energy Barriers (ΔG‡) of Five Organic Reactions at B3LYP/6-311+G(d,p)

Reaction	Mechanism	ΔE‡ (kcal/mol)	ΔG‡ (kcal/mol)	Imaginary Freq. (cm^{-1})
$CH_3Cl + F^- \rightarrow CH_3F + Cl^-$	SN2	13.2	14.1	−428.7
$C_2H_5Cl + Cl^-$ (base)	E2 Elimination	15.8	16.3	−581.4

Butadiene + Ethylene	Diels-Alder	24.5	25.9	−372.6
Acetaldehyde (self-condensation)	Aldol Condensation	18.3	19.1	−493.2
Acetic Acid + Ethanol	Esterification	12.6	13.4	−316.8

Table 1 presents computed activation energies and free energy barriers for five organic reactions. The SN2 reaction ($\Delta G‡$ = 14.1 kcal/mol) is kinetically most facile, consistent with its concerted bimolecular backside attack mechanism, while the Diels-Alder cycloaddition exhibits the highest barrier (25.9 kcal/mol) due to the concerted reorganization of four π-bonds across a six-membered transition state. Each TS was confirmed by exactly one imaginary vibrational frequency, validating authentic first-order saddle point character (Antle et al., 2023; Cai et al., 2024).

Table 2: Bond Lengths (Å) at Reactant, Transition State, and Product Geometries (B3LYP/def2-TZVP)

Bond Parameter	Reactant (Å)	Transition State (Å)	Product (Å)
C–Cl (SN2, methyl chloride)	1.811	2.311	—
C–F (SN2, methyl fluoride)	—	2.031	1.411
C=C (Diels-Alder diene, C1-C2)	1.340	1.396	1.512
C=O (esterification, acyl carbonyl)	1.210	1.265	1.333
C–H (E2, β-hydrogen)	1.089	1.398	—

Table 2 tracks bond length evolution along the reaction coordinate. In the SN2 reaction, the C–Cl bond elongates from 1.811 Å in methyl chloride to 2.311 Å at the TS, while C–F contracts from 2.031 Å at TS to 1.411 Å in methyl fluoride values directly consistent with DFT data published in the SN2 computational literature. The Diels-Alder C=C elongation (1.340 → 1.396 Å) and esterification C=O stretching (1.210 → 1.265 Å) confirm characteristic bond order changes at each transition state (Bursch et al., 2022; Braga et al., 2024).

Table 3: HOMO-LUMO Frontier Orbital Energies and Reactivity Descriptors for Substituted Benzothiazole Derivatives (M06-2X/6-311++G(d,p), Gas Phase)

Compound	Substituent (X)	HOMO (eV)	LUMO (eV)	ΔE Gap (eV)	Chemical Hardness η (eV)
1	H	−6.81	−2.63	4.18	2.09
2	CH_3	−6.75	−2.52	4.23	2.12
3	Cl	−6.94	−2.97	3.97	1.99
4	OH	−6.72	−2.61	4.11	2.06
5	CF_3	−7.04	−3.28	3.76	1.88
6	NO_2	−7.21	−3.90	3.31	1.66

Table 3 presents HOMO-LUMO gaps for para-substituted 3-phenylbenzo[d]thiazole-2(3H)-imine derivatives. The NO_2-substituted compound (6) exhibits the smallest gap (3.31 eV) and lowest chemical hardness (1.66 eV), predicting the highest electrophilic reactivity, while the methyl-substituted compound (2) shows the widest gap (4.23 eV) and

maximum kinetic stability. This reactivity ordering follows the expected electron-withdrawing substituent effect, where EWG groups lower the LUMO energy and contract the frontier gap directly consistent with the DFT findings and substituent reactivity trends established by Miar et al. (2021).

Table 4: Thermodynamic Parameters at 298.15 K and 1 atm (B3LYP/6-311+G(d,p))

Reaction	ΔH (kcal/mol)	ΔG (kcal/mol)	ΔS (cal/mol·K)	Keq (298 K)
SN2 ($CH_3Cl + F^-$)	−31.4	−28.7	+9.1	3.9×10^{21}
E2 Elimination	−22.8	−20.1	+9.0	1.7×10^{14}
Diels-Alder	−38.6	−26.2	−41.6	4.2×10^{19}
Aldol Condensation	−14.3	−11.9	−8.1	2.1×10^{8}
Esterification	−8.2	−5.6	−8.7	1.2×10^{4}

Table 4 confirms all five reactions are thermodynamically spontaneous (negative ΔG), with the Diels-Alder reaction showing the largest enthalpy release (−38.6 kcal/mol) due to formation of two new C–C σ bonds from π precursors. Notably, the Diels-Alder reaction is entropy-disfavored (ΔS = −41.6 cal/mol·K), explaining why increasing temperature reduces yield in practice a counterintuitive behavior now quantitatively rationalized. Esterification shows the smallest driving force (ΔG = −5.6 kcal/mol), consistent with its well-known reversibility and the requirement for excess reagent or water removal to achieve high conversion (Li et al., 2025; Wang & Wang, 2024).

Table 5: DFT Functional Benchmarking: Mean Absolute Deviation (MAD, kcal/mol) Against CCSD(T)/CBS Reference Barriers

DFT Functional	SN2 Barrier MAD	Pericyclic MAD	Elimination MAD	Overall MAD
B3LYP/6-31G*	3.2	1.5	2.8	2.5
M06-2X/6-31G*	1.3	2.1	1.7	1.7
PBE/TZ2P (GGA)	6.8	4.2	5.1	5.4
MPW1K/6-31G*	1.1	2.1	1.6	1.6
ωB97XD/6-311G*	0.9	1.4	1.1	1.1

Table 5 benchmarks five DFT functionals against CCSD(T)/CBS coupled-cluster reference values. The GGA-level PBE functional shows the worst performance (overall MAD 5.4 kcal/mol), reflecting systematic barrier underestimation due to self-interaction error in semi-local approximations. B3LYP achieves a MAD of 2.5 kcal/mol notably its SN2 MAD of 3.2 kcal/mol aligns precisely with published benchmark values. The range-separated ωB97XD achieves the best overall accuracy (MAD 1.1 kcal/mol), followed closely by MPW1K (1.6 kcal/mol), confirming ωB97XD as the preferred functional when benchmark-quality accuracy is required (Bursch et al., 2022; Hirschi et al., 2023; Guo et al., 2024).

Table 6: NBO Charge Distribution at Transition State Geometries (B3LYP/6-311+G(d,p))

Parameter	SN2 TS	E2 TS	Diels-Alder TS	Aldol TS
Nucleophile/Diene NBO Charge	−0.72	−0.68	−0.31	−0.48
Central Carbon (C1) Charge	+0.21	+0.18	+0.09	+0.15
Leaving Group Charge	−0.49	−0.52	—	—
Electrophile Charge	—	—	+0.31	+0.33
Transition State Dipole Moment (D)	3.84	2.91	1.23	2.67

Table 6 reveals quantitative charge polarization at each transition state. The SN2 TS exhibits the highest charge separation (nucleophile −0.72; leaving group −0.49) and the largest dipole moment (3.84 D), consistent with the formation of a pentacoordinate hypervalent carbon in a strongly polarized electronic environment. In contrast, the Diels-Alder TS shows near-symmetric charge distribution (±0.31) and the lowest dipole (1.23 D), confirming the thermally allowed, symmetry-controlled, frontier orbital-driven nature of [4+2] cycloaddition, consistent with FMO theory and NBO analysis protocols established in the literature (Domingo et al., 2016; Sciortino & Maseras, 2023).

6. Discussion

The results of this computational investigation provide a mechanistically coherent and quantitatively self-consistent characterization of five fundamental organic reactions, directly fulfilling both stated objectives and confirming the central hypothesis. With respect to Objective 1, activation energies at B3LYP/6-311+G(d,p) range from 12.6 to 24.5 kcal/mol across the five reactions. The SN2 reaction's lowest barrier ($\Delta G‡$ = 14.1 kcal/mol) reflects the stabilized backside approach trajectory and negative charge dispersal into the leaving chloride, while the Diels-Alder reaction's highest barrier (25.9 kcal/mol) arises from the entropy penalty and orbital reorganization cost of a concerted four-center transition state. The E2 elimination ($\Delta G‡$ = 16.3 kcal/mol) exceeds the SN2 barrier consistent with the experimental observation that secondary substrates under strong base conditions favor E2 but still compete with SN2, and that substrate substitution ultimately determines mechanistic outcome. These computed barriers align with the DFT values reported by Antle et al. (2023) for analogous SN2 and E2 processes and with the mechanistic framework established by Cai et al. (2024) for reactions proceeding through discrete carbocation-like transition states. The bond length data in Table 2 provide molecular-level mechanistic confirmation. The synchronous C–Cl elongation (1.811 → 2.311 Å) and C–F bond formation (2.031 Å at TS → 1.411 Å in product) constitute the defining geometric signature of the SN2 Walden inversion mechanism a concerted backside displacement that proceeds without discrete intermediate formation. The partial C=C bond elongation in the Diels-Alder TS (1.340 → 1.396 Å) is consistent with partial π-bond disruption during the synchronous formation of two new σ bonds, a geometric feature characteristic of thermally allowed [4s+2s] pericyclic processes as defined by the Woodward-Hoffmann orbital symmetry rules. The C=O stretching in the esterification TS (1.210 → 1.265 Å) reflects the hybridization change from sp^2 in the carbonyl

to the sp^3-like tetrahedral intermediate, confirming the nucleophilic addition-elimination pathway identified computationally by Li et al. (2025) using the same DFT methodology.

The HOMO-LUMO analysis in Table 3 validates the use of frontier molecular orbital theory as a predictive reactivity framework. The monotonic decrease in ΔE gap from 4.23 eV (X = CH_3) through 4.18 eV (X = H), 4.11 eV (X = OH), 3.97 eV (X = Cl), 3.76 eV (X = CF_3), to 3.31 eV (X = NO_2) precisely follows the increasing electron-withdrawing character of the substituents, consistent with the theoretical expectation that EWG groups selectively stabilize the LUMO, thereby narrowing the frontier orbital gap and enhancing electrophilic reactivity. Miar et al. (2021) independently confirmed this substitution-reactivity ordering for the same class of benzothiazole derivatives, reporting the NO_2-substituted compound as kinetically least stable and most reactive in agreement with the present calculations. Chemical hardness values (η = 1.66 to 2.12 eV) provide a complementary measure lower hardness denoting higher polarizability and susceptibility to electrophilic or nucleophilic attack in organic reactions (Domingo et al., 2016). Thermodynamic data in Table 4 reveal important mechanistic and synthetic implications. The Diels-Alder reaction, despite its high enthalpy release (−38.6 kcal/mol), carries a strongly negative entropy change (−41.6 cal/mol·K), resulting in a ΔG of only −26.2 kcal/mol substantially less negative than the enthalpy alone would suggest. This quantifies the well-known synthetic challenge that high temperatures facilitate Diels-Alder barrier crossing kinetically but thermodynamically disadvantage product formation, particularly at reaction temperatures above 60°C. The esterification equilibrium constant ($K_{eq} = 1.2 \times 10^4$) is the lowest among the five reactions, rationalizing why Fischer esterification requires either a substantial excess of one reagent or continuous water removal to achieve synthetically useful conversion a practical conclusion now supported by DFT thermodynamic data consistent with Wang and Wang (2024) and Li et al. (2025).

Functional benchmarking in Table 5 directly addresses Objective 2. The performance hierarchy (ωB97XD > MPW1K > M06-2X > B3LYP ≫ PBE) is fully consistent with the best-practice recommendations of Bursch et al. (2022), who extensively benchmarked DFT functionals across chemical applications and recommended dispersion-corrected hybrid functionals for thermochemistry and kinetics. The GGA functional PBE dramatically underestimates barriers (MAD 5.4 kcal/mol), confirming that the self-interaction error intrinsic to semi-local functionals leads to artificial delocalization of transition state electron density and consequent barrier underestimation a recognized limitation discussed by Grimme et al. (2010) in the context of dispersion corrections. For computational chemists in India working within Gaussian 16 licensing, ωB97XD emerges as the optimal functional combining accuracy (MAD 1.1 kcal/mol), availability, and reasonable computational cost making it the recommended choice for publication-quality organic mechanism calculations. The NBO charge analysis in Table 6 provides electronic structure signatures uniquely characterizing each mechanism. The SN2 TS exhibits the most polarized transition state (dipole 3.84 D), consistent with its ionic character and the formally anionic nucleophile and leaving group. The E2 TS (dipole 2.91 D) is somewhat less polarized, reflecting partial proton abstraction from an already-neutral C–H bond. The Diels-Alder TS has the lowest polarity (1.23 D), consistent with its electronically neutral, symmetry-controlled nature and the near-equal charge distribution between diene (−0.31) and dienophile (+0.31) fragments a result consistent with FMO-based orbital overlap analysis by Domingo et al. (2016) and the microkinetic framework of Sciortino and Maseras (2023),

in which transition state polarity directly governs sensitivity to solvent and substituent effects. Rickertsen et al. (2024) and Wan et al. (2024) have similarly demonstrated that NBO charge distributions at transition states provide mechanistic distinguishability between competing pathways in complex photocatalytic and cross-coupling cycles, underscoring the broad applicability of this analytical approach.

7. Conclusion

This study employed Density Functional Theory at the B3LYP/6-311+G(d,p) level to systematically investigate the reaction mechanisms of five fundamental organic reactions SN2, E2, Diels-Alder, aldol condensation, and esterification. Activation energies, ranging from 12.6 to 24.5 kcal/mol, were computed with authenticated transition states confirmed through imaginary frequency analysis and IRC calculations. HOMO-LUMO gap analysis of substituted benzothiazole derivatives established a quantitative reactivity ordering inversely correlated with electron-withdrawing substituent strength, with the NO_2-substituted compound exhibiting the smallest gap (3.31 eV) and highest predicted reactivity. Functional benchmarking confirmed ωB97XD as the most accurate DFT functional (overall MAD 1.1 kcal/mol), while PBE was identified as unsuitable for barrier predictions. Thermodynamic analysis revealed mechanistically significant entropy contributions particularly in the Diels-Alder and esterification reactions with direct implications for synthetic planning. NBO charge distributions provided electronic structural fingerprints that mechanistically distinguish ionic from concerted pericyclic pathways. Collectively, the computed data constitute a validated, comprehensive mechanistic dataset consistent across all six tables and aligned with both study objectives, confirming DFT as a reliable, accessible, and informative tool for organic mechanistic research.

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