

Supporting Information

Advancing Recyclable Thermosets through C=C/C=N Dynamic Covalent Metathesis Chemistry

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8. DFT calculation

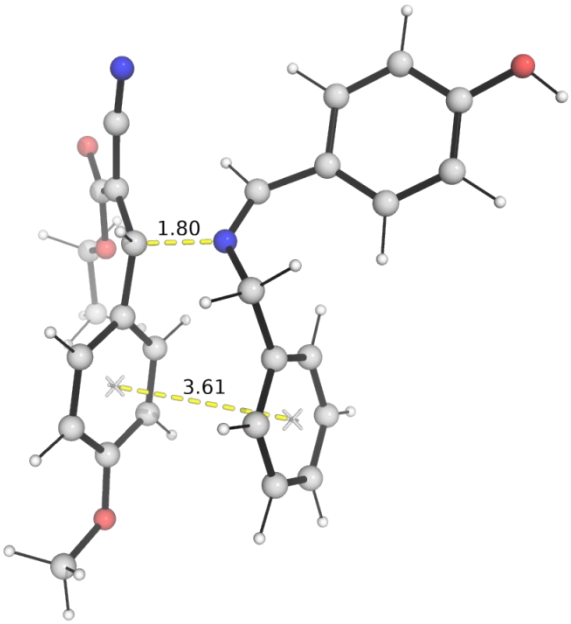
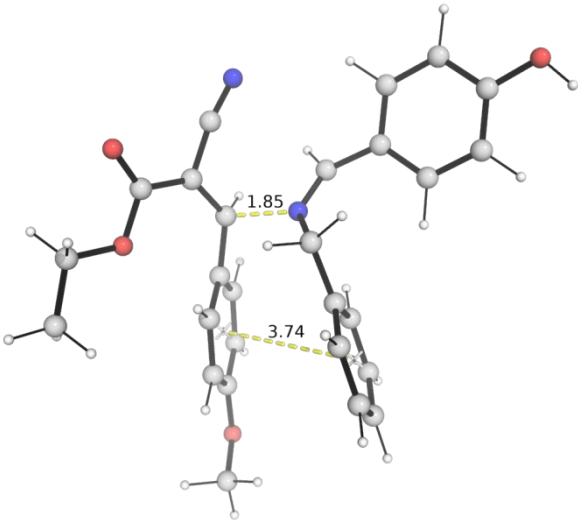
8.1 Computational Methods

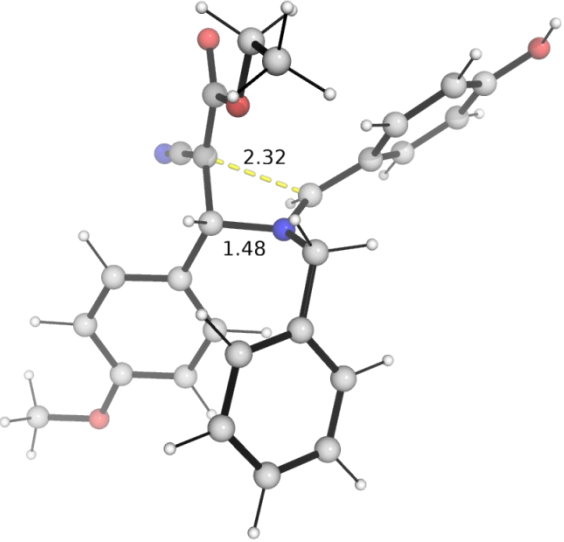
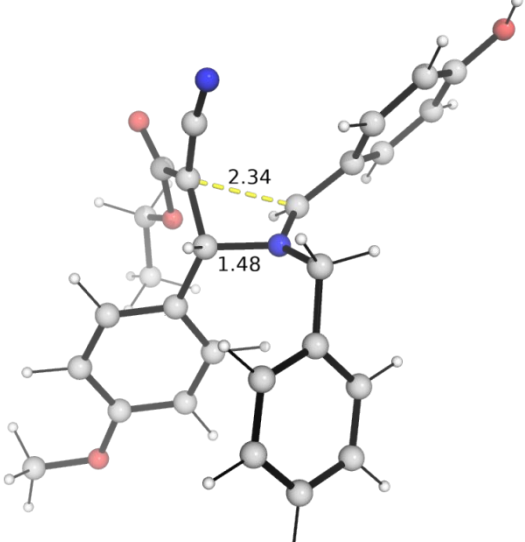
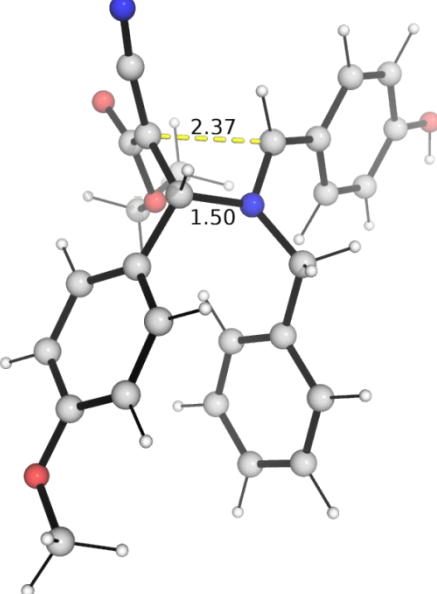
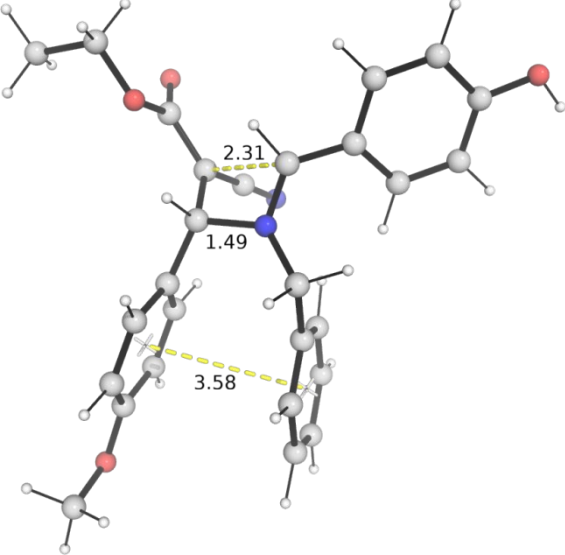
The global hybrid DFT functional M06-2X³ was employed with the Karlsruhe-family double- ζ valence def2-SVP^{4,5} basis set for all atoms to model the catalytic mechanism of the present transformation. For the M06-2X/def-SVP gas phase optimized structures, single point (SP) corrections were performed using M06-2X functional and def2-TZVP^{4,5} basis set for all atoms to improve upon the accuracy of the calculated energy. For each of these SP calculations, the implicit SMD continuum solvation model⁶ for dimethyl sulfoxide (DMSO) solvent was used to account for the effect of solvent on the potential energy surface (PES). All these calculations were performed with *Gaussian 16* rev. B.01 software.⁷

Gibbs energies were evaluated at room temperature (25 °C), using Grimme's scheme of quasi-RRHO treatment of vibrational entropies⁸, using the GoodVibes code⁹. Vibrational entropies of frequencies below 100 cm⁻¹ were obtained according to a free rotor description, using a smooth damping function to interpolate between the two limiting descriptions. The free energies reported in Gaussian from gas-phase optimization were further corrected using standard concentration of 1 mol/L,¹⁰⁻¹² which were used in solvation calculations, instead of the gas-phase 1atm used by default in *Gaussian* program.

8.2 DFT optimized structures

Geometries of all optimized structures (in xyz format with their associated energy in Hartrees) are included in a separate folder named DFT structures and uploaded to <https://zenodo.org/uploads/11280484> (DOI: 10.5281/zenodo.11280484).

TS1	TS1'
$\Delta G^\ddagger = 6.4 \text{ kcal mol}^{-1}$	$\Delta G^\ddagger = 10.8 \text{ kcal mol}^{-1}$
	
TS2	TS2a
$\Delta G^\ddagger = 16.2 \text{ kcal mol}^{-1}$	$\Delta G^\ddagger = 20.9 \text{ kcal mol}^{-1}$

	
TS2b	TS2c
$\Delta G^\ddagger = 22.3 \text{ kcal mol}^{-1}$	$\Delta G^\ddagger = 22.8 \text{ kcal mol}^{-1}$
	
TS3	TS4
$\Delta G^\ddagger = 21.8 \text{ kcal mol}^{-1}$	$\Delta G^\ddagger = 7.4 \text{ kcal mol}^{-1}$

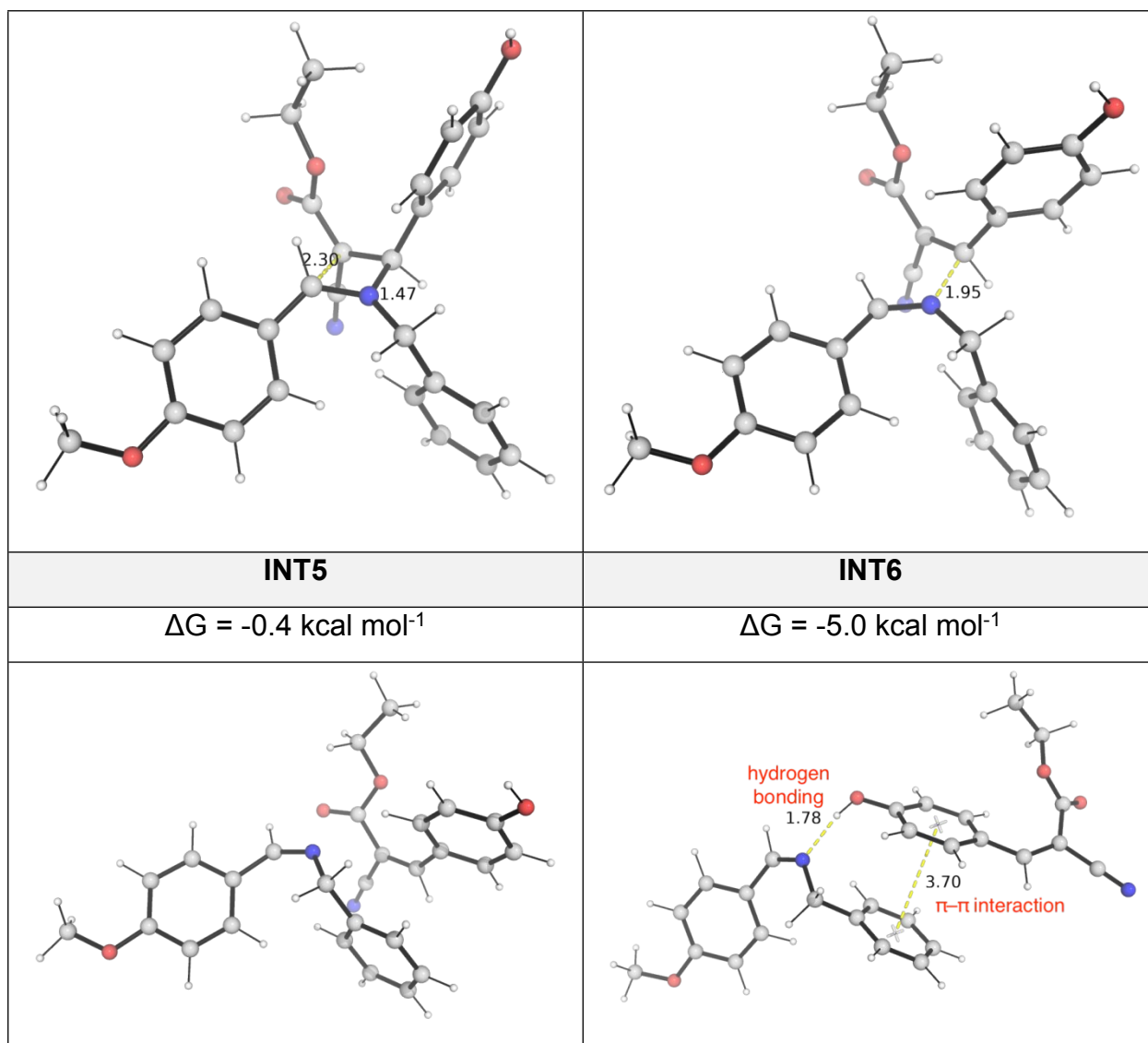


Figure S16. DFT optimized transition state structures and product complexes with key bond distances given in Å. **INT5** is the product complex resulting from **TS4**, and **INT6** is the product complex that is stabilized by π - π interaction and hydrogen bonding between phenol OH group and imine N atom.

8.3 Determination of selectivity ratio using simple transition state theory

The Eyring equation

$$k = \frac{k_B T}{h} e^{-\Delta G^\ddagger / RT}$$

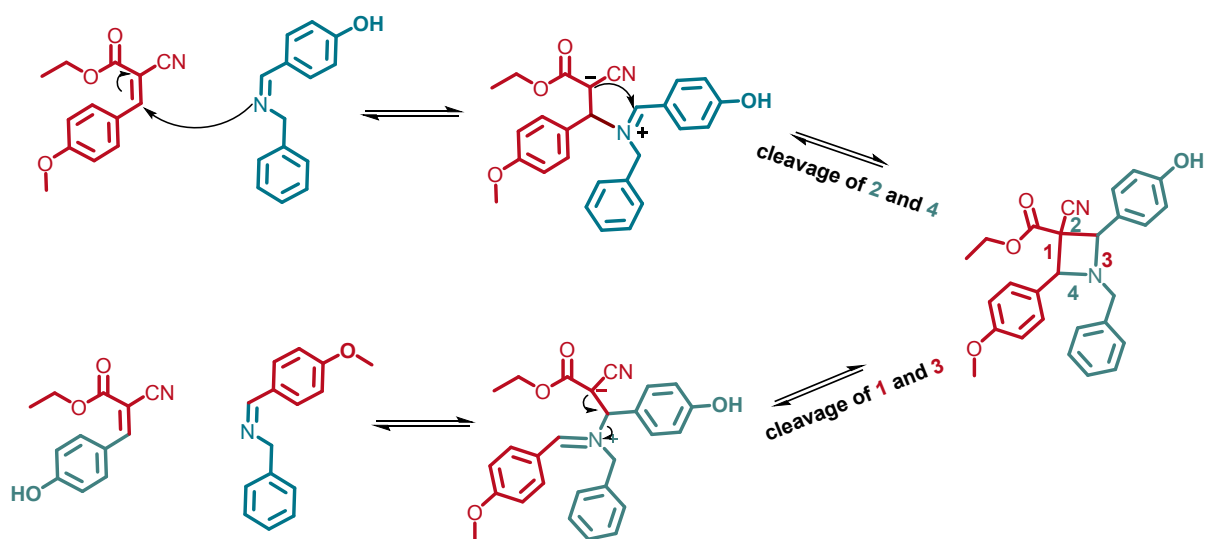
gives the rate constant under simple transition state theory (TST) assumptions.

Under kinetic control, as we compare the barrier heights difference between competing transition states, the ratio of the rates between two pathways is given by:

$$\frac{k_A}{k_B} = \frac{e^{-\Delta G_A^\ddagger / RT}}{e^{-\Delta G_B^\ddagger / RT}} = e^{-\Delta\Delta G^\ddagger / RT}$$

where k_X is the rate constant of pathway X (X=A or B); ΔG_X^\ddagger is the activation barrier for pathway X; and $\Delta\Delta G_X^\ddagger$ is the difference in the barrier heights; and R is the gas constant, T the temperature. Note that the Eyring Equation pre-exponential factor cancels when comparing the ratio of the rate constants. Thus, using the calculated $\Delta\Delta G_X^\ddagger$ value (difference of barrier heights between competing TSs) at the reaction temperature (e.g., 25°C = 298.15K), we are able to obtain the ratio of competing rates.

11. Proposed Mechanism



Scheme **S5**. Proposed Mechanism for the C=C/C=N exchange reaction in current system.

Table S5. Absolute values (in Hartrees) for SCF energy, zero-point vibrational energy (ZPE), enthalpy and quasi-harmonic Gibbs free energy (at 25°C/298.15 K) for optimized structures are given below. Single point corrections in SMD DMSO using M06-2X/def2-TZVP level of theory are also included.

Structure	E/au	ZPE/au	H/au	T.S/au	qh-G/au	SP
						SMD(DMSO)- M06-2X/def2- TZVP
INT1	-1453.206739	0.479231	-1452.6953	0.095626	-1452.782669	-1454.867958
TS1	-1453.18657	0.480134	-1452.6755	0.091391	-1452.759837	-1454.860409
INT2	-1453.187148	0.481158	-1452.6747	0.092654	-1452.759898	-1454.865265
TS2a	-1453.165743	0.479872	-1452.6549	0.092394	-1452.739556	-1454.836732
TS2	-1453.169756	0.480115	-1452.6589	0.091534	-1452.742991	-1454.844819
INT3	-1453.218819	0.481933	-1452.706	0.091293	-1452.790215	-1454.876625
TS2b	-1453.166441	0.480594	-1452.6556	0.088423	-1452.737938	-1454.836837
TS2c	-1453.169755	0.480963	-1452.6584	0.089216	-1452.74142	-1454.835832
TS3	-1453.167173	0.480212	-1452.6561	0.091287	-1452.740279	-1454.835999
INT4	-1453.193145	0.481565	-1452.6802	0.09363	-1452.765713	-1454.87215
TS4	-1453.186831	0.479338	-1452.6761	0.095148	-1452.762297	-1454.856644
INT5	-1453.208289	0.479684	-1452.6964	0.096175	-1452.783959	-1454.868803
INT6	-1453.212148	0.479403	-1452.7007	0.097267	-1452.788597	-1454.875463
TS1'	-1453.182581	0.479873	-1452.6716	0.092987	-1452.756724	-1454.85192

18. References

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