Supporting information

Mechanism of N-Heterocylic-carbene-Catalyzed Annulation of Allenals with Chalcones to 3-pyrancarbaldehydes or Cyclopentene

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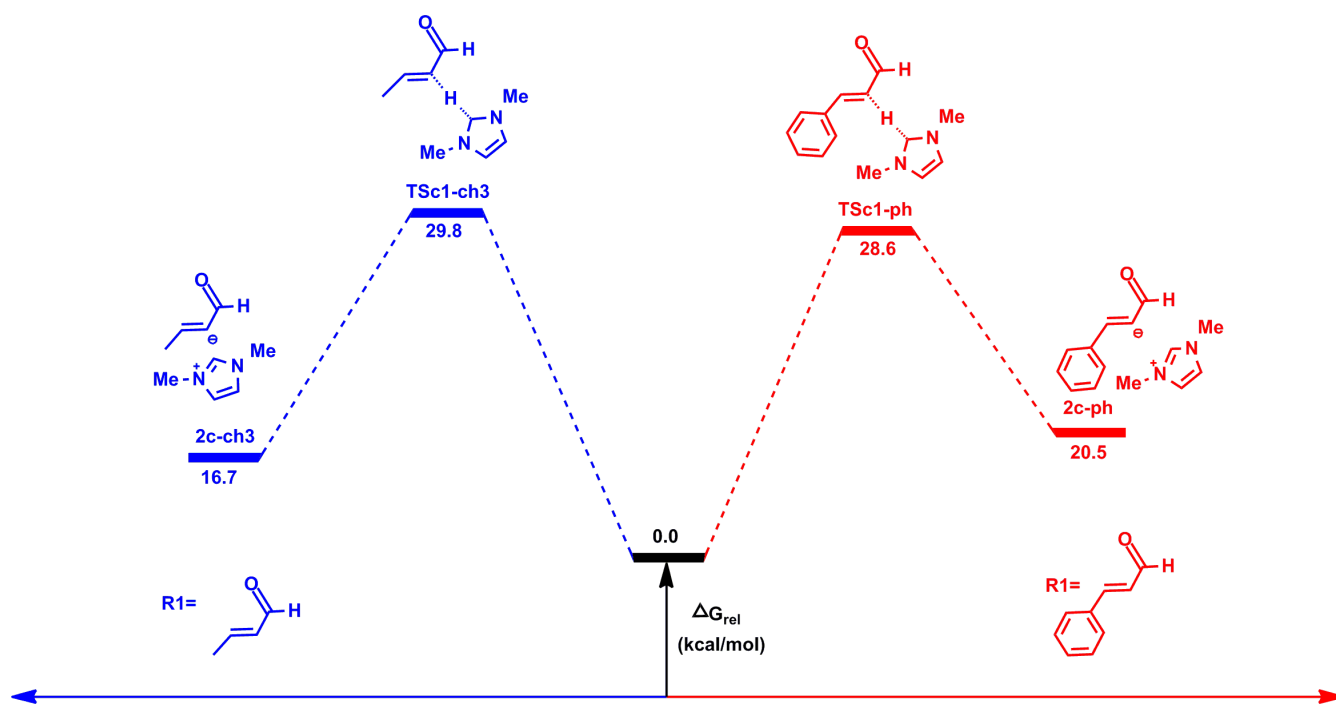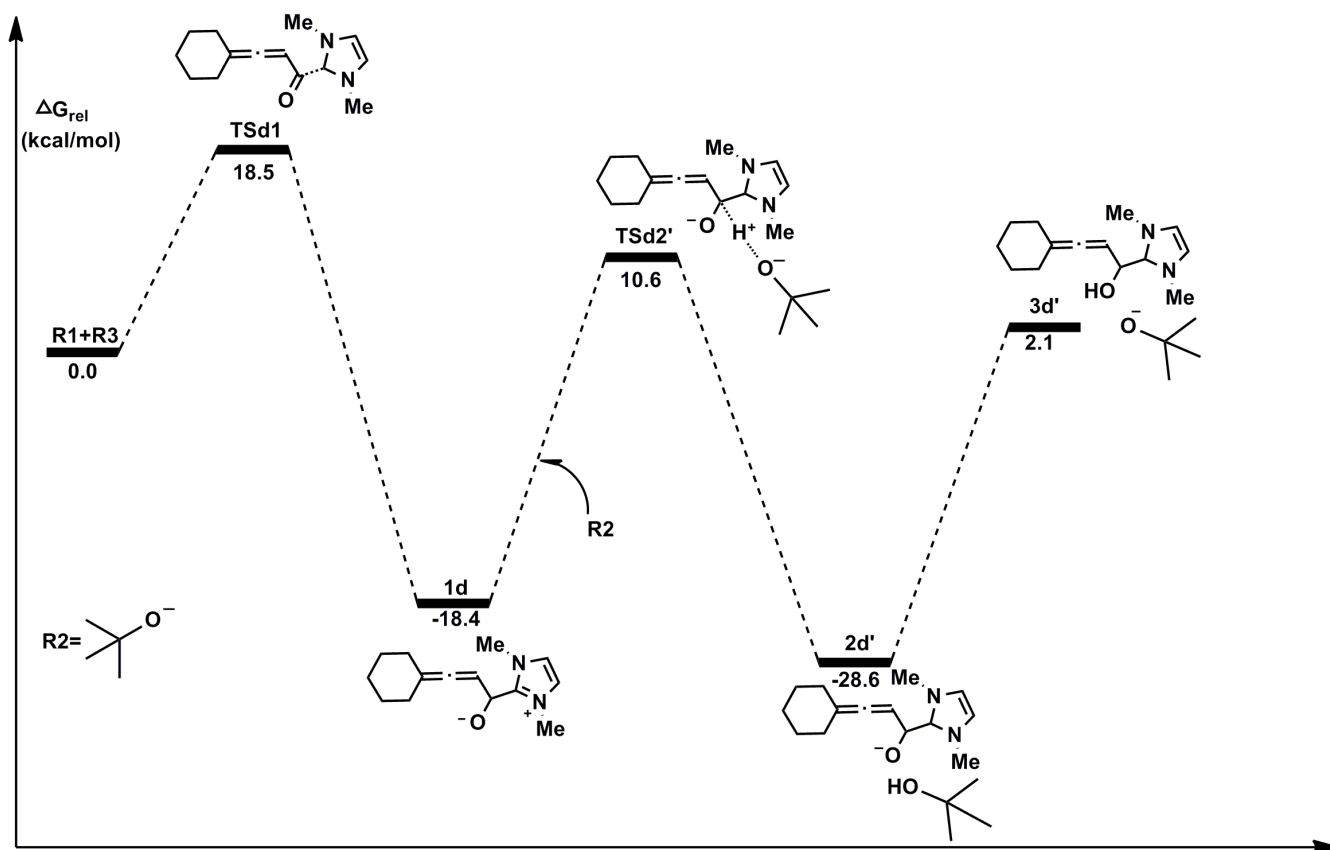
Table of contents

Figure S1. Energy profiles for the rate-determining step of pathway **c** for (E)-3-phenylacrylaldehyde and (E)-but-2-enal (carbene as a base to abstract hydrogen atom); the relative energies are given in kcal/mol.

Figurer S2 Energy profiles for proton migration assisted by *t*-BuO⁻ for aldehyde ; the relative energies are given in kcal/mol.
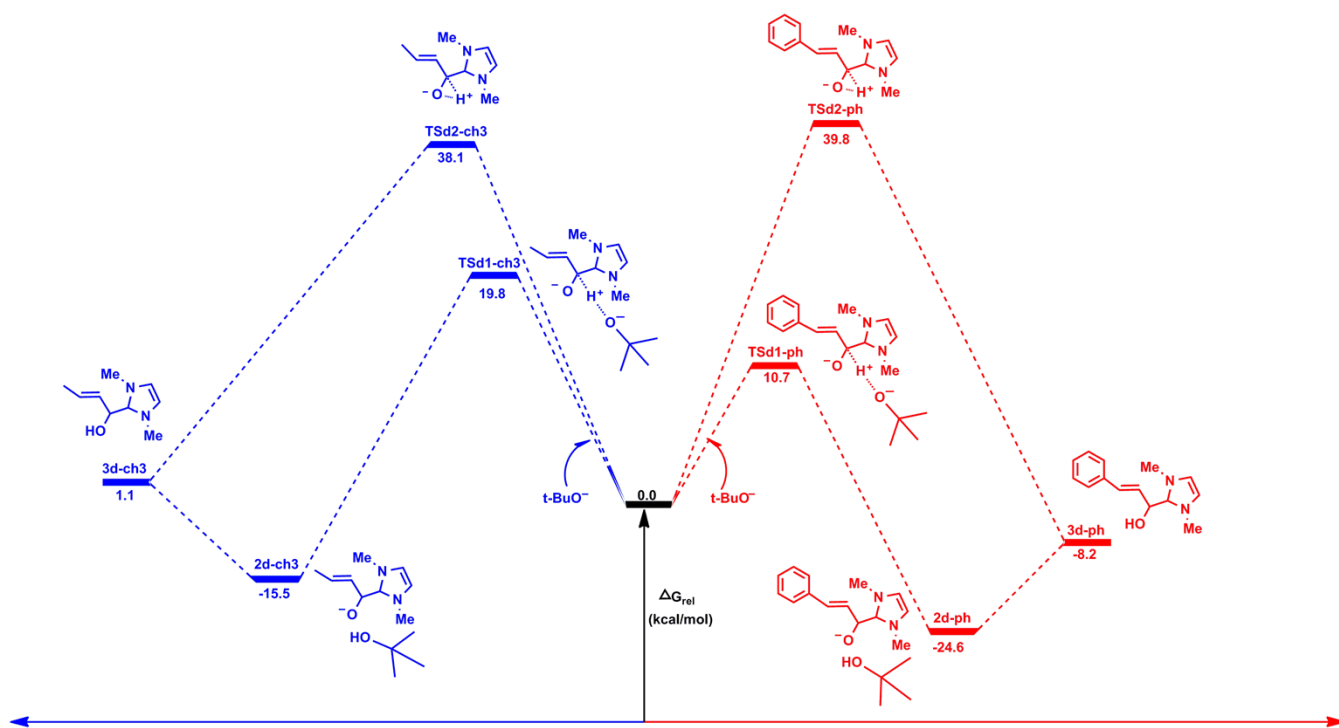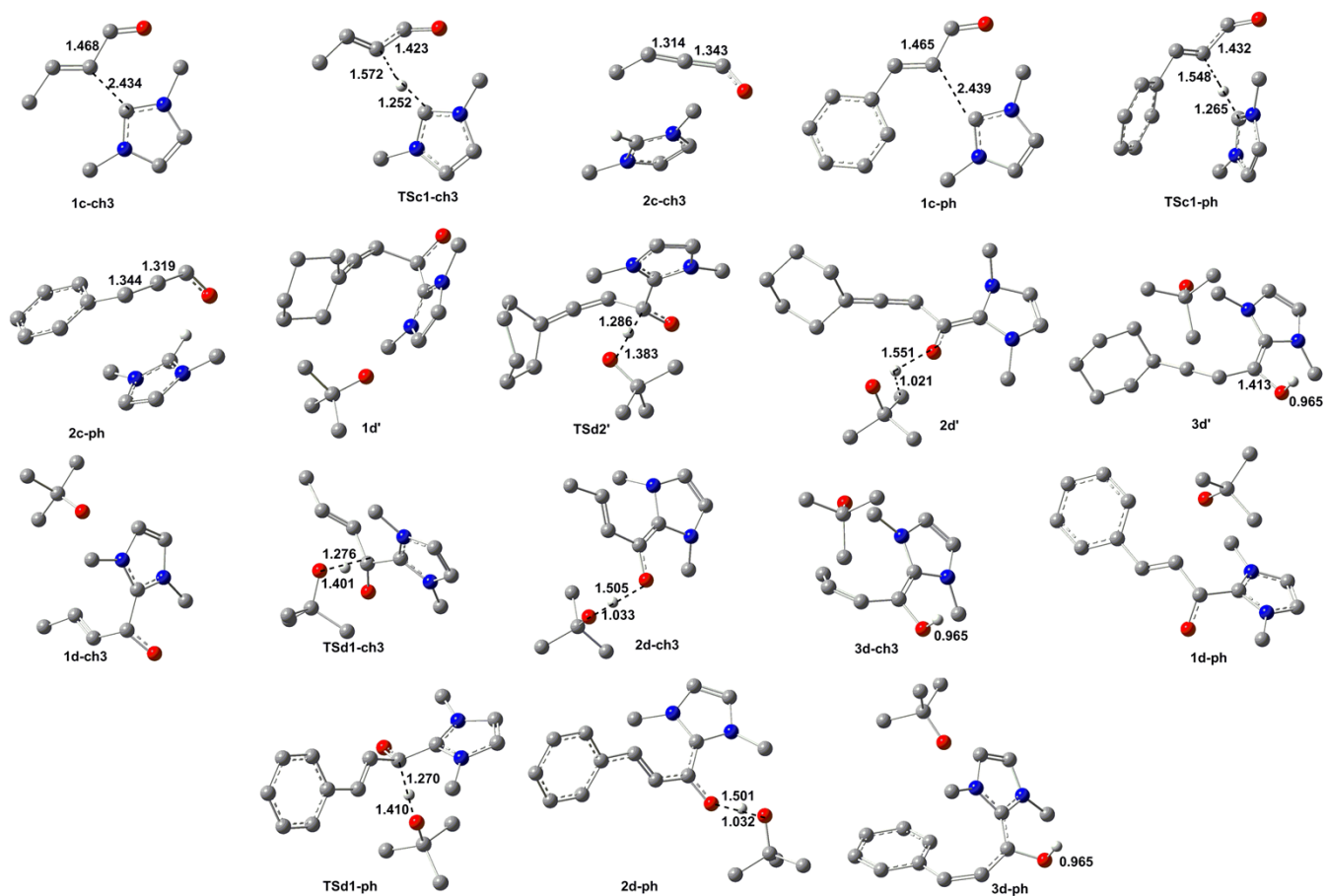
Figure S3. Energy profiles for direct proton migration and assisted by t-BuO⁻ for (E)-3-phenylacrylaldehyde and (E)-but-2-enal; the relative energies are given in kcal/mol.

Figurer S4 Optimized structures for paths shown in Figure S1, S2 and S3, with selected structural parameters (bond lengths in Å).

Table S1. Thermodynamic Properties (Relative Free Energies and Activation Free Energies in Gas Phase and in Solution) of the Structures in Figure 3[a]

System	$\Delta E^{\text{rel}}_{\text{gas}}$	$\Delta G^{\text{rel}}_{\text{gas}}$	$\Delta E^{\neq}_{\text{gas}}$	$\Delta G^{\neq}_{\text{gas}}$	$\Delta E^{\text{rel}}_{\text{sol}}$	$\Delta G^{\text{rel}}_{\text{sol}}$	$\Delta E^{\neq}_{\text{sol}}$	$\Delta G^{\neq}_{\text{sol}}$

R1+R3	0	0			0	0		
TSa1	1.5	14.6	1.5	14.6	10.0	25.8	10.0	25.8
1a	-27.2	-13.1			-30.4	-14.4		
TSa2	-37.5	-5.9	-10.3	7.3	-30.6	10.2	-0.3	24.6
2a	-44.1	-13.5			-35.7	-2.6		
TSa3	-44.6	-14.5	-0.5	-1.0	-31.7	1.0	4.0	3.6
3a	-53.8	-23.8			-44.8	-4.1		
TSa4	-39.1	-8.2	14.7	15.5	-24.8	12.3	20.0	16.3
4a	-50.1	-19.3			-39.7	0		
TSa5	-29.0	2.3	21.2	21.5	-21.1	16.9	18.6	16.9
5a	-36.0	-4.4			-32.0	7.2		
TSa6	-41.9	-0.3	-5.8	-4.9	-26.2	14.1	5.9	6.9
6a+R2	-36.8	-21.1			-31.37	-15.2		
TSb3	-13.8	16.6	30.3	30.1	-6.7	29.3	29.0	31.9
3b	-63.8	-31.1			-54.1	-10.9		
TSb4	-23.6	7.3	40.2	38.4	-7.3	32.5	46.8	43.4
4b	-31.6	-3.2			-19.9	17.2		
TSb5	-17.4	11.7	14.2	14.8	-2.8	31.4	17.1	14.2
5b	-25.7	3.6			-18.9	19.6		
TSb6	-19.2	11.8	6.6	8.2	-10.4	27.5	8.5	7.9
6b	-47.6	-16.3			-36.2	3.4		
TSb7	-31.3	-0.6	16.3	15.6	-7.4	20.7	28.8	17.3
TSc1+R2	16.4	27.1	16.4	27.1	25.9	35.1	25.9	35.1
1c+R2	3.1	16.1			5.6	21.4		
TSc2	-6.7	22.1	-9.8	6.0	2.9	41.5	-2.7	20.1

Table S2. Thermodynamic Properties (Relative Free Energies and Activation Free Energies in Gas Phase and in Solution) of the Structures in Figure 5 [a]

System	$\Delta E^{\mathrm{rel}}_{\mathrm{gas}}$	$\Delta G^{\mathrm{rel}}_{\mathrm{gas}}$	$\Delta E^{\neq}_{\mathrm{gas}}$	$\Delta G^{\neq}_{\mathrm{gas}}$	$\Delta E^{\mathrm{rel}}_{\mathrm{sol}}$	$\Delta G^{\mathrm{rel}}_{\mathrm{sol}}$	$\Delta E^{\neq}_{\mathrm{sol}}$	$\Delta G^{\neq}_{\mathrm{sol}}$
R1+R3	0	0			0	0		
TSd1	0.8	14.2	0.8	14.2	6.9	22.8	6.9	22.8
1d	-2.9	10.0			-3.3	13.3		
TSd2	37.5	51.3	40.3	41.2	43.1	59.5	46.5	46.2
2d	-10.3	3.2			-1.2	16.9		
3d	-18.7	8.5			-6.1	30.2		
TSd3	-7.6	22.8	17.8	19.6	1.8	40.8	7.9	10.6
4d	-32.3	-0.9			-31.9	9.1		
TSd4	-20.0	11.8	12.3	12.7	-6.6	30.1	25.2	20.9
5d	-61.6	-30.1			-52.8	-11.4		
TSd5	-50.3	-17.7	11.3	12.5	-42.9	-3.6	9.9	7.9
6d	-57.4	-24.8			-47.8	-6.2		
TSd6	-51.2	-18.9	6.1	5.8	-36.1	-2.0	11.7	4.3
7d	-61.0	-31.4			-49.0	-10.5		
TSd7	-29.5	-0.7	31.5	30.7	-19.9	15.8	29.2	26.3
8d	-78.7	-51.4			-64.1	-25.2		

Complete List of Authors for References with more than 10 Authors

[20] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09*, Revision A.01; Gaussian, Inc., Wallingford CT, 2009.