Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information of DFT calculation:

Pursuing High Efficiency in Photocatalytic Oxidative Couplings of Heteroarenes and Aliphatic C-H bonds

Contents

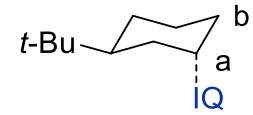
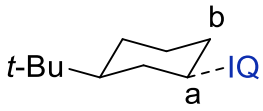
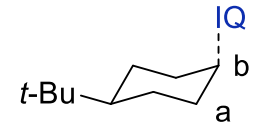
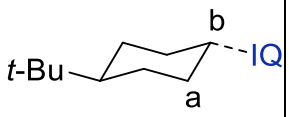
Method
The UB3LYP density functional theory (DFT) method implemented in Gaussian 16 software was used with the 6-31+G* basis set to optimize the geometries of transition states (TSs) for the reactions between 3- and 4-*t*-butylcyclohexyl radicals to isoquinoline [1-3].

[1] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

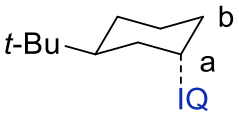
[2] (a) A. D. Becke, “Density-functional thermochemistry. III. The role of exact exchange,” *J. Chem. Phys.*, **98** (1993) 5648-52. (b) C. Lee, W. Yang, and R. G. Parr, “Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density,” *Phys. Rev. B*, **37** (1988) 785-89. (c) S. H. Vosko, L. Wilk, and M. Nusair, “Accurate spin-dependent electron liquid correlation energies for local spin density calculations: A critical analysis,” *Can. J. Phys.*, **58** (1980) 1200-11.

[3] (a) Clark, Timothy, Chandrasekhar, Jayaraman, Spitznagel, W. Günther, Schleyer, Paul Von Ragué, “Efficient diffuse function-augmented basis sets for anion calculations. III. The 3-21+G basis set for first-row, Li-F,” *J. Comput. Chem.*, **4**, (1983) 294-301 (b) R. Ditchfield, W. J. Hehre, J. A. Pople, “Self-Consistent Molecular-Orbital Methods. IX. An Extended Gaussian-Type Basis for Molecular-Orbital Studies of Organic Molecules,” *J. Chem. Phys.*, **54** (1971) 724-728. (c) P. C. Hariharan, J. A. Pople, “The influence of polarization functions on molecular orbital hydrogenation energies,” *Theor. Chim. Acta*, **28** (1973) 213-222. (d) W. J. Hehre, R. Ditchfield, J. A. Pople, “Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules,” *J. Chem. Phys.*, **56** (1972) 2257-2261.

Table S1 Transition state energies of axial or equatorial addition of 3- and 4-*t*-butylcyclohexyl radicals to isoquinoline (the energy of transitions states refers to the sum of electronic energy and zero-point energy)

TS structure	Energy (hartrees)	Energy difference (kcal/mol)	Free energy (hartrees)	Free energy difference (kcal/mol)
	-793.997243	1.11	-794.045369	1.58
	**-793.999010**	**0.00**	**-794.047884**	**0.00**
	-793.997279	1.09	-794.045698	1.37
	-793.998357	0.41	-794.047056	0.52

XYZ coordinates of TS structures



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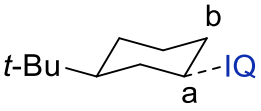

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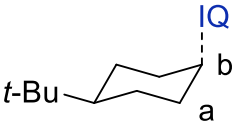

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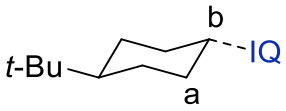

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