Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

Pd(II)-Promoted Direct Cross-Coupling Reaction of Arenes via Highly Regioselective Aromatic C-H Activation: A Theoretical Study

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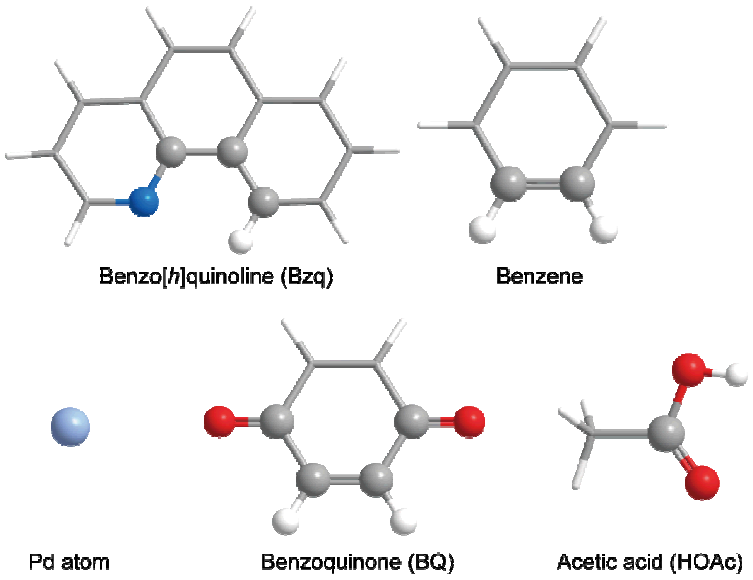
Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision D.02*, Gaussian, Inc., Wallingford CT, 2004.



Scheme S1. Large model for ONIOM method. Atoms shown by balls are included in high level region which is calculated with the CCSD(T) while whole system is calculated by the lower level of theory.

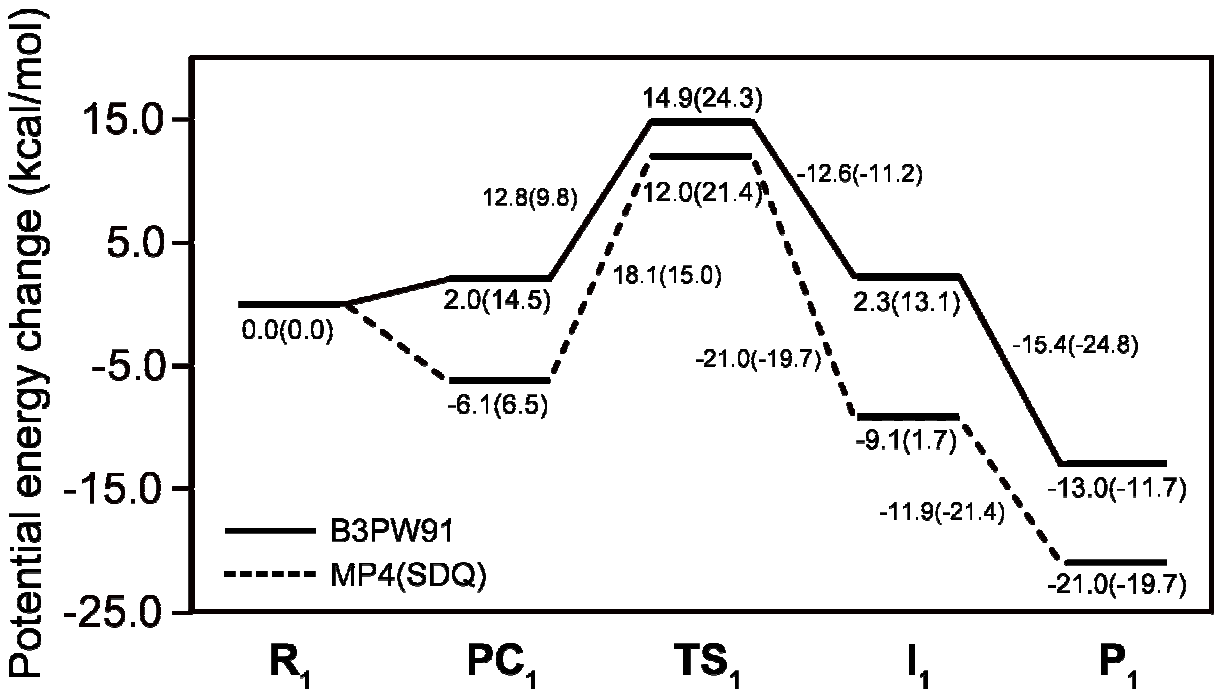


Fig. S1. Potential energy changes by the C-H activation of Bzq by $Pd(\eta^2\text{-}OAc)_2$ in gas phase. Energies[a)] are given in kcal/mol unit. [a)] In parentheses are Gibbs free energy changes.

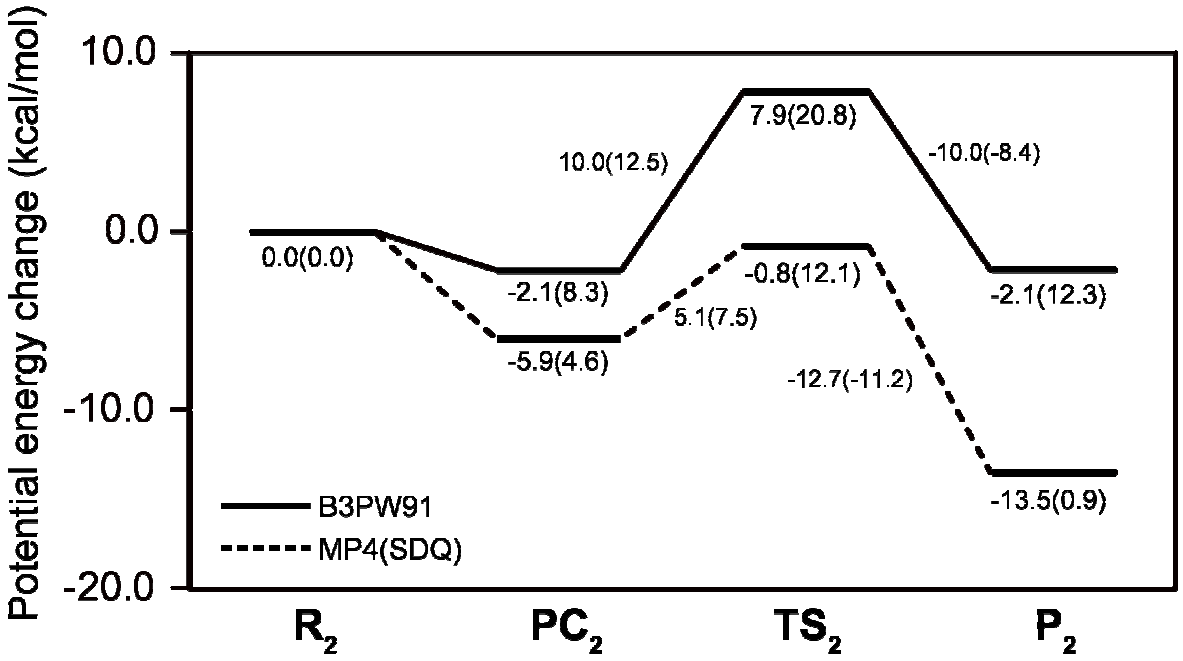


Fig. S2. Potential energy changes by BQ coordination to Pd(Bzq)(OAc) in gas phase. Energies[a)] are given in kcal/mol unit. [a)] In parentheses are Gibbs free energy changes.

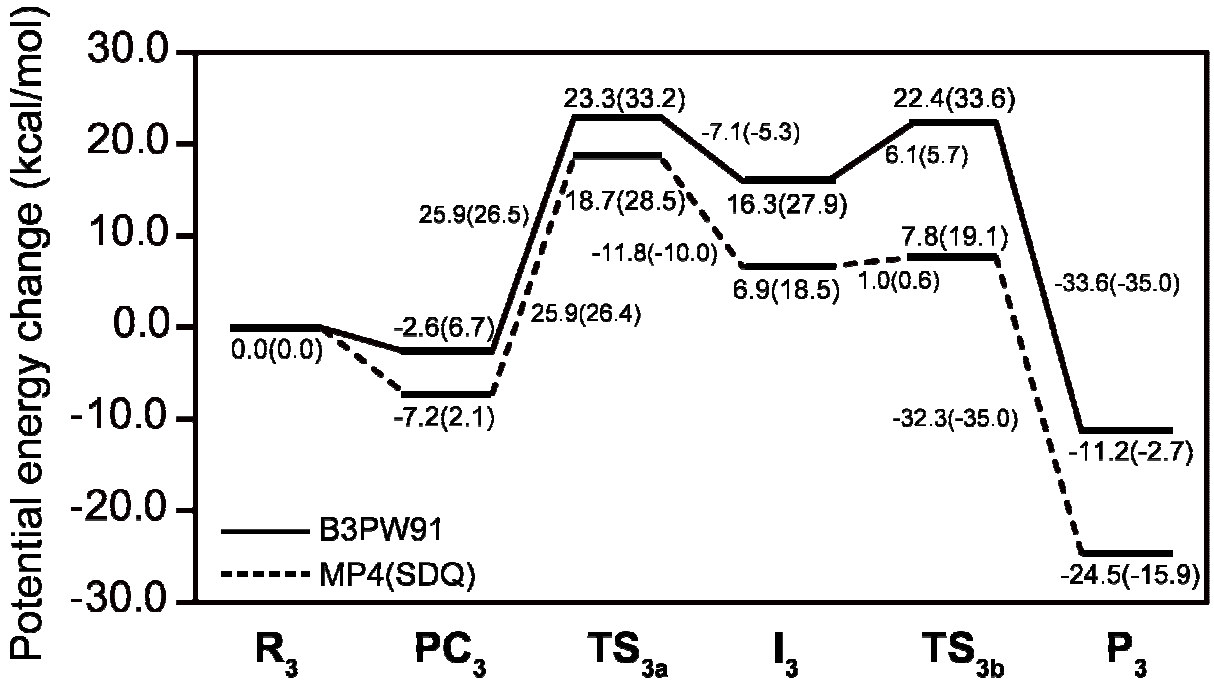


Fig. S3. Potential energy changes for the C-H activation of benzene by Pd(Bzq)(OAc)(BQ) in gas phase. Energies[a)] are given in kcal/mol unit. [a)] In parentheses are Gibbs free energy changes.

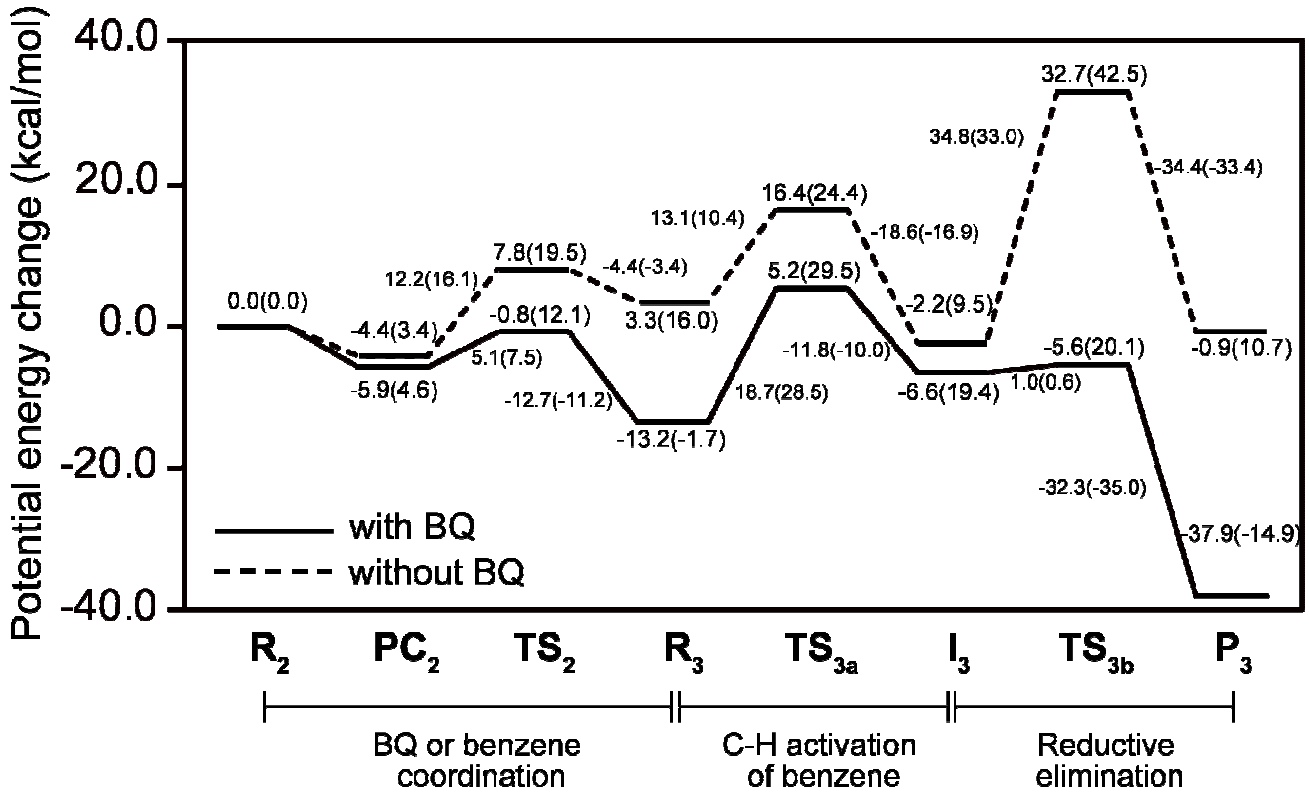


Fig. S4. Potential energy changes for the C-H activation of benzene by Pd(Bzq)(OAc)(BQ) in gas phase. Energies[a)] are given in kcal/mol unit. [a)] In parentheses are Gibbs free energy changes.

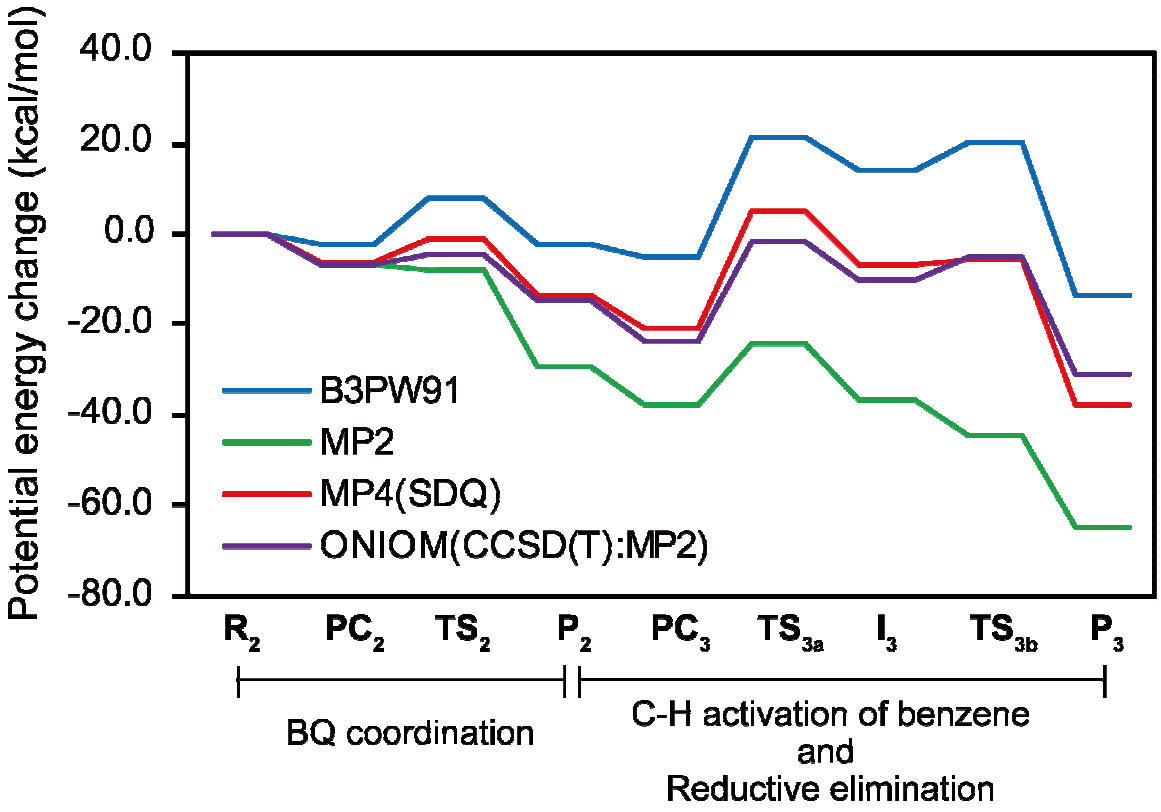


Fig. S5. Potential energy change of the BQ coordination, the C-H activation of benzene, and the reductive elimination in gas phase calculated with DFT, MP2, MP4(SDQ), and ONIOM(CCSD(T):MP2) methods. Energies are given in kcal/mol unit.

Table S1.Relative electronic energies of the C-H activation of HBzq, BQ coordination, and the C-H activation of benzene, calculated by Hartree-Fock, MP2, MP3, MP4(DQ), MP4(SDQ), and DFT(B3PW91) methods.[a)] Energies are given in kcal/mol unit.

		HF	MP2	MP3	MP4(DQ)	MP4(SDQ)	B3PW91/BS-I	B3PW91
First C-H activation	$\mathbf{R_1}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	$\mathbf{PC_1}$	12.7	-14.1	-2.5	-4.8	-6.1	-0.4	2.0
	$\mathbf{TS_{1a}}$	35.2	1.6	14.2	13.4	12.0	14.5	14.9
	$\mathbf{I_1}$	12.5	-19.8	-6.7	-9.7	-9.1	1.6	2.3
	$\mathbf{P_1}$	-1.7	-32.8	-17.5	-21.9	-21.0	-13.3	-13.0
BQ coordination	$\mathbf{R_2}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	$\mathbf{PC_2}$	-2.4	-7.0	-5.5	-5.5	-5.9	-4.0	-2.1
	$\mathbf{TS_2}$	21.2	-7.7	4.0	2.0	-0.8	7.7	7.9
	$\mathbf{P_2}$	25.7	-29.0	-1.0	-9.3	-13.5	-0.4	-2.1
Second C-H activation and Reductive Elimination	$\mathbf{R_3}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	$\mathbf{PC_3}$	-3.4	-8.8	-7.0	-7.0	-7.2	-2.9	-2.6
	$\mathbf{TS_{3a}}$	45.3	5.1	23.3	19.4	18.7	24.5	23.3
	$\mathbf{I_3}$	30.0	-7.3	12.5	6.2	6.9	16.0	16.3
	$\mathbf{TS_{3b}}$	43.4	-15.4	21.6	6.7	7.8	20.2	22.4
	$\mathbf{P_3}$	-14.9	-35.6	-18.2	-27.3	-24.5	-16.8	-11.2

a) BS-II was used unless otherwise stated.