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Electronic Supplementary Information (ESI)

Lithium-bromine exchange reaction on C_{60}: First theoretical proposal of stable singlet fullerene carbene without heteroatom†

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† Dedicated to Professor Eiji Ōsawa on the occasion of his 85th birthday.

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1. Calculation details on the nucleophilicity index (N) and global electrophilicity (ω).

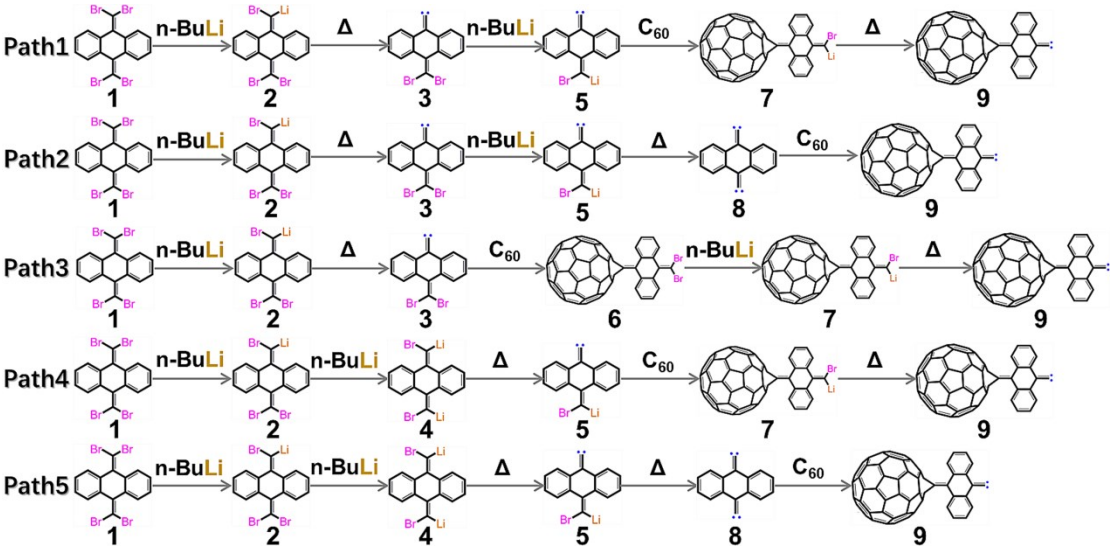
Calculation details

The nucleophilicity index (N), which was defined by Domingo et al,[1] was calculated following $N = \Delta E_{HOMO(Nu)} - \Delta E_{HOMO(TCNE)}$, in which tetracyanoethylene (TCNE) is chosen as the reference. The global electrophilicity ω,[2] was calculated as $\omega = \mu^2/(2\eta)$, where μ represents the chemical potential $\mu = (E_{HOMO} + E_{LUMO})/2$, and η is the chemical hardness $\eta = E_{HOMO} - E_{LUMO}$.[3] The energies of HOMO and LUMO were calculated on the B3LYP/6-311G(2df,2p).

[1] L. R. Domingo, E. Chamorro, P. Pérez, *J. Org. Chem.*, 2008, **73**, 4615-4624.
[2] R. G. Parr, L. Szentpaly, S. Liu, *J. Am. Chem. Soc.*, 1999, **121**, 1922-1924.
[3] R. G. Parr, R. G. Pearson, *J. Am. Chem. Soc.*, 1983, **105**, 7512-7516.

2. Five pathways proposed to generate the stable singlet fullerene carbene.

Scheme S1 Five pathways proposed on the basis of lithium-bromine exchange reactions and qusi carbene insertions to generated the stable singlet fullerene carbene.



3. Kinetic study on the lithium-halogen exchange reactions on **1,1-dibromo-2-methylpropene** (**DM**).

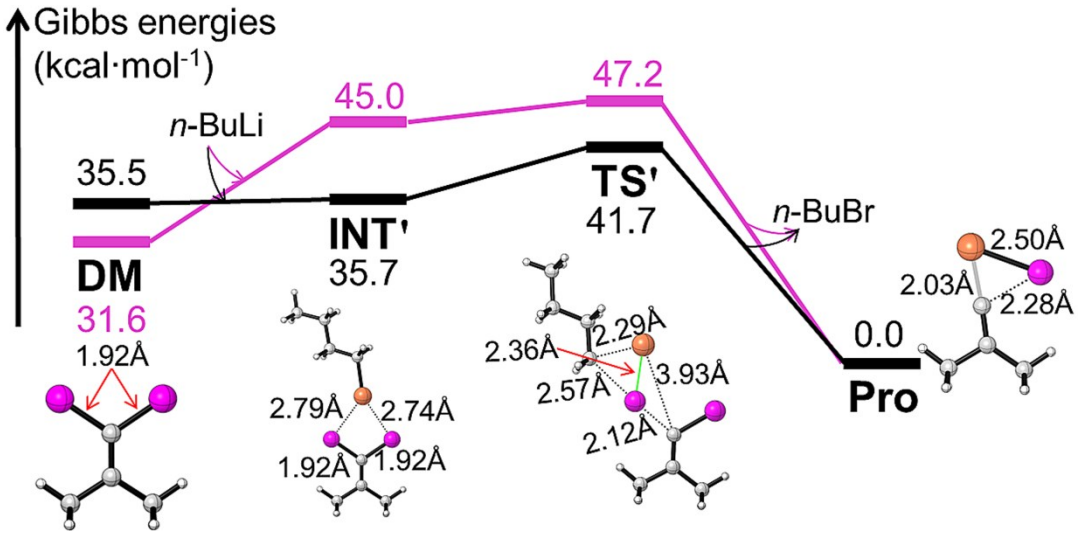


Figure S1 Kinetic study on the lithium-halogen exchange reactions on **1,1-dibromo-2-methylpropene** (**DM**). The results based on the B3LYP-PCM(THF)/6-31G(d) and B3LYP-PCM(THF)/6-311+G(2df,2p)// B3LYP-PCM(THF)/6-31G(d) were marked in black and pink, respectively.

4. Relative potential energies and geometrical parameters (Table S1) for *cis*- and *trans*-configurations of **4** based on the Figure S2.

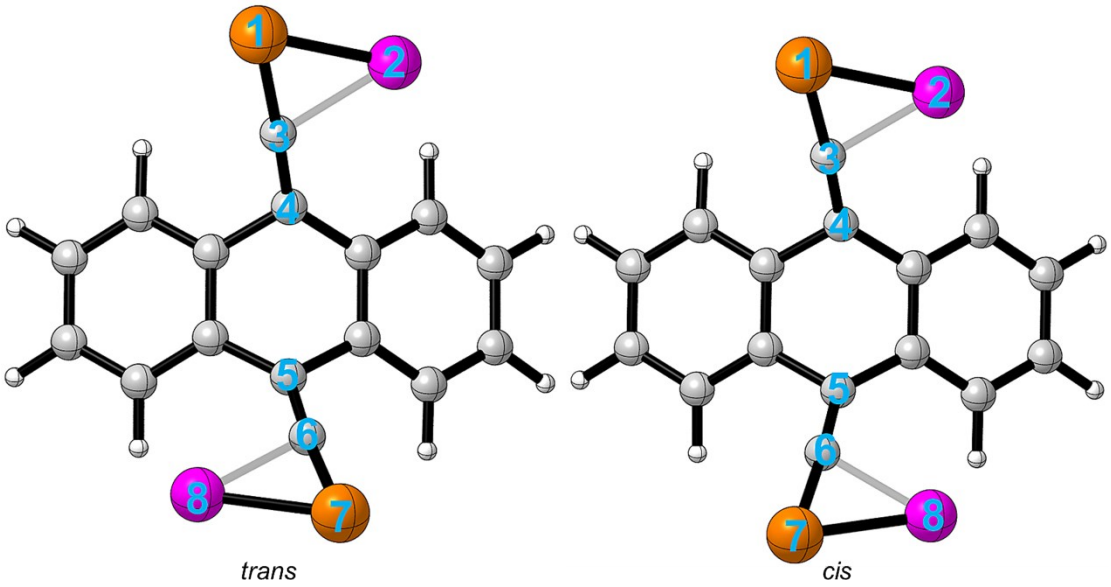


Figure S2 Geometries of *cis*- and *trans*-configurations of **4**.

Table S1 Relative potential energies including zero-point energy correction on the B3LYP-PCM(THF)/6-311G(2df,2p)//B3LYP/6-31G(d) level and geometrical parameters for cis- and trans-configurations of **4** based on the Figure S2.

		cis-4	*trans*-4
Relative Energy/kcal·mol^{-1}		0.3	0
bond	1-2	2.32	2.32
	1-3	1.94	1.94
	2-3	2.25	2.26
	3-4	1.34	1.34
	5-6	1.34	1.34
	6-7	1.94	1.94
	6-8	2.25	2.26
	7-8	2.32	2.32
angle	1-2-3	50.2	50.1
	1-3-2	66.7	66.6
	2-1-3	63.0	63.3
	1-3-4	172.4	172.0
	5-6-7	172.4	172.0
	6-7-8	63.1	63.3
	6-8-7	50.2	50.1
	7-6-8	66.7	66.6
dihedral angle	1-2-3-4	-172.0	-171.5
	7-8-6-5	172.0	-171.5

5. Configurations of **6** based on the reaction sites and the orientation of TDD, and their relative energy Figure S3.

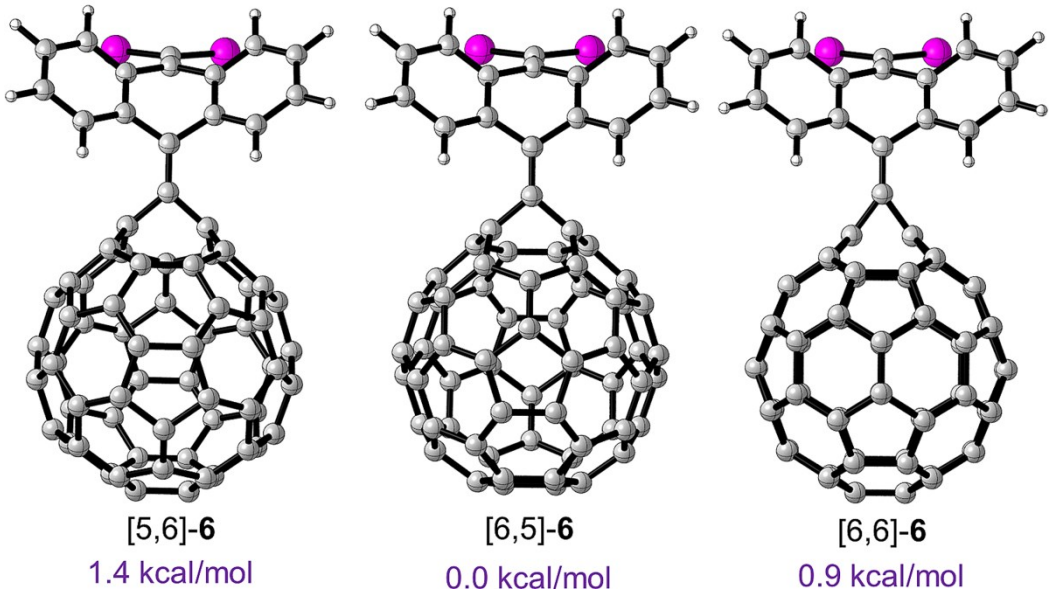


Figure S3 Configurations of **6** based on the reaction sites and the orientation of TDD, and their relative energy (in purple) on the B3LYP-PCM(THF)/6-311G(2df,2p)//B3LYP/6-31G(d).

6. Configurations of **7** based on the reaction sites and the orientation of TDD, and their relative energy Figure S4.

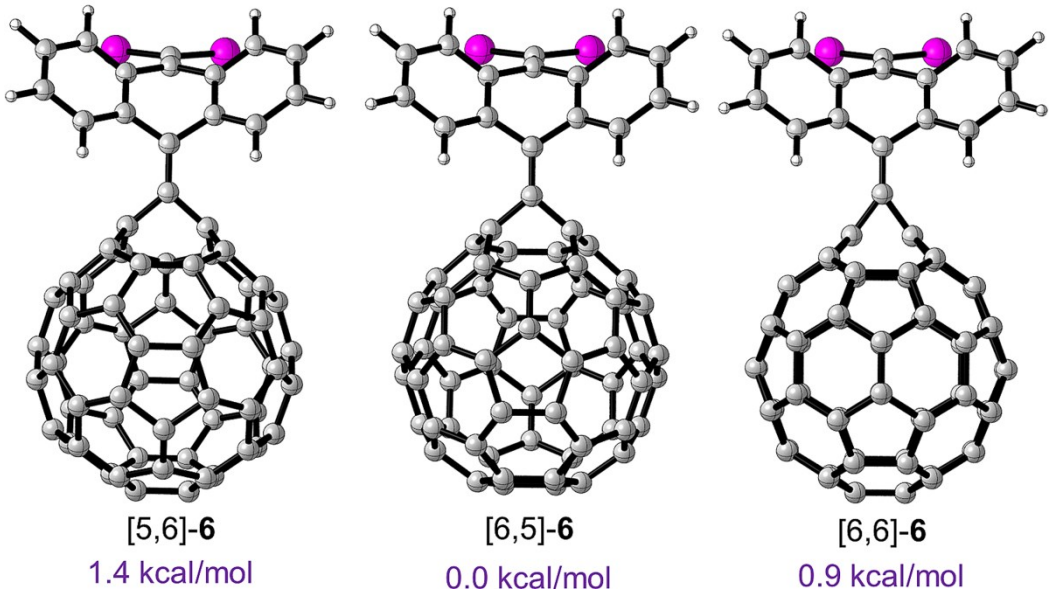


Figure S4 Configurations of **7** based on the reaction sites and the orientation of TDD, and their relative energy (in purple) on the B3LYP-PCM(THF)/6-311G(2df,2p)//B3LYP/6-31G(d).

7. Geometries of INT1, TS1, INT3, and TS2 Figure S5.

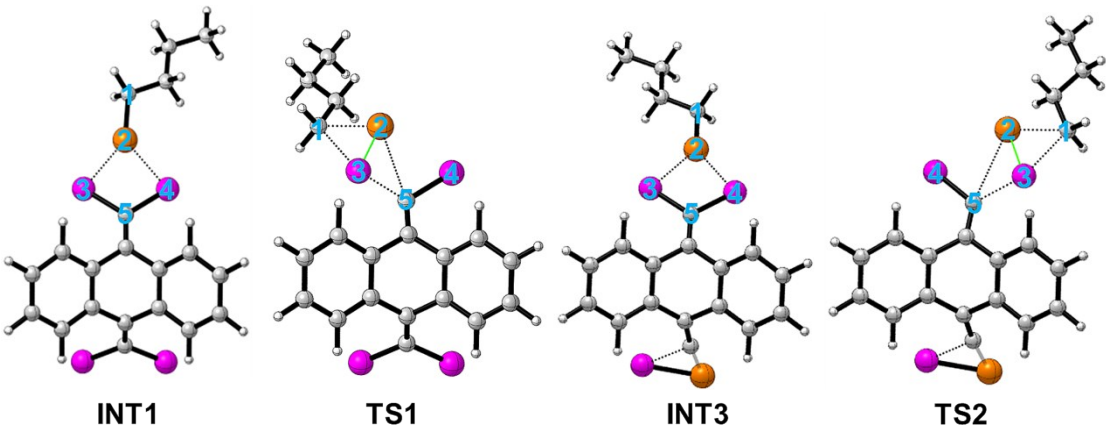


Figure S5 Geometries of INT1, TS1, INT3, and TS2 on the B3LYP/6-31G(d).

8. Natural bond orbital charge for the atoms labelled in Figure S5 of INT1, TS1, INT3, and TS2 Table S2.

Table S2 Natural bond orbital charge for the atoms labelled in Figure S5 of INT1, TS1, INT3, and TS2.

atoms	NBO Charge			
	INT1	TS1	INT3	TS2
1	-1.048	-0.791	-1.048	-0.787
2	0.762	0.890	0.761	0.884
3	0.117	-0.035	0.117	-0.036
4	0.124	0.005	0.108	-0.006
5	-0.203	-0.205	-0.209	-0.200

9. Parameters of bond critical points (BCPs) and Mayer bond orders (MBO) between specific atoms in **2**, **4**, LiBr, and n-BuLi Table S3.

Table S3 Parameters of bond critical points (BCPs) and Mayer bond orders (MBO) between specific atoms in **2**, **4**, LiBr, and n-BuLi, including density of all electrons (ρ_{BCP}), Potential energy density (V_{BCP}), Laplacian of electron density ($\nabla^2\rho_{BCP}$), Energy density (H_{BCP}), and the ratio between $|V_{BCP}|$ and Lagrangian kinetic energy (G_{BCP}).

Molecules	Bonds	ρ_{BCP}	V_{BCP}	$\nabla^2\rho_{BCP}$	H_{BCP}	$\lvert V_{BCP}\rvert/G_{BCP}$	MBO
4	C3-C4	0.347	-0.523	-1.017	-0.389	3.887	1.888
	C3-Li1	0.039	-0.046	0.240	0.007	0.871	0.610
	C3-Br2	0.078	-0.057	0.054	-0.022	1.617	0.596
	Li1-Br2	0.025	-0.026	0.149	0.006	0.818	0.584
	C6-C5	0.347	-0.523	-1.016	-0.389	3.887	1.888
	C6-Li7	0.039	-0.046	0.240	0.007	0.871	0.610
	C6-Br8	0.078	-0.057	0.054	-0.022	1.618	0.597
	Li7-Br8	0.025	-0.026	0.149	0.006	0.818	0.584
2	C3-C4	0.346	-0.522	-1.013	-0.388	3.885	1.891
	C3-Li1	0.039	-0.046	0.238	0.007	0.870	0.605
	C3-Br2	0.083	-0.062	0.045	-0.025	1.689	0.622
	Br2-Li1	-	-	-	-	-	0.562
LiBr	Li-Br	0.037	-0.043	0.218	0.006	0.878	1.134
n-BuLi	C-Li	0.041	-0.045	0.202	0.003	0.936	0.897

10. Kinetic study of Path2, geometries of reactants and products in Path2 with several important bond parameters, and the change in the Gibbs free energy ΔG (kcal/mol) Figure S6.

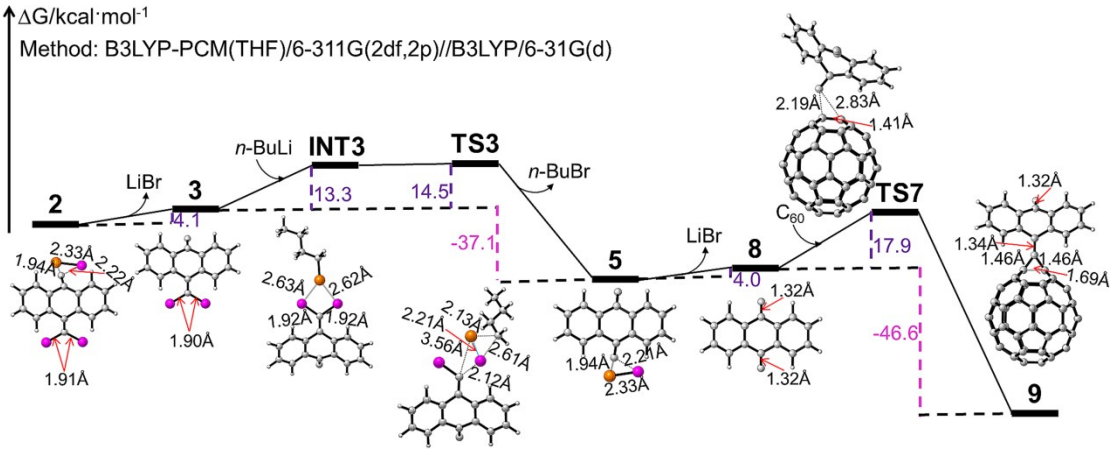


Figure S6 Kinetic study of Path2, geometries of reactants and products in Path2 with several important bond parameters, and the change in the Gibbs free energy ΔG (kcal/mol).

11. Kinetic study of Path3, geometries of reactants and products in Path3 with several important bond parameters, and the change in the Gibbs free energy ΔG (kcal/mol) Figure S7

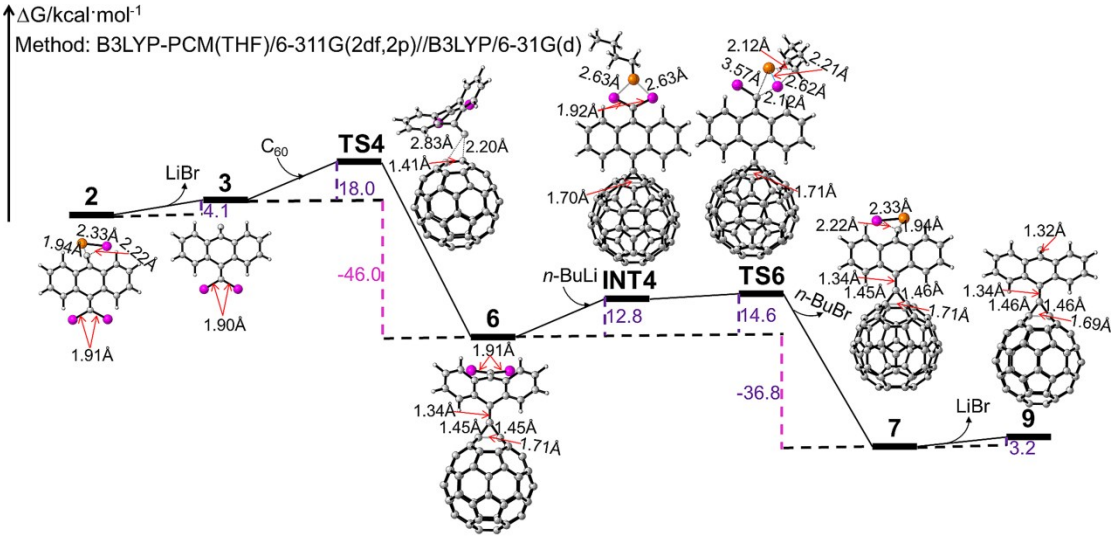


Figure S7 Kinetic study of Path3, geometries of reactants and products in Path3 with several important bond parameters, and the change in the Gibbs free energy ΔG (kcal/mol).

12. Geometries of 3 and 5 including some angles in them Figure S8.

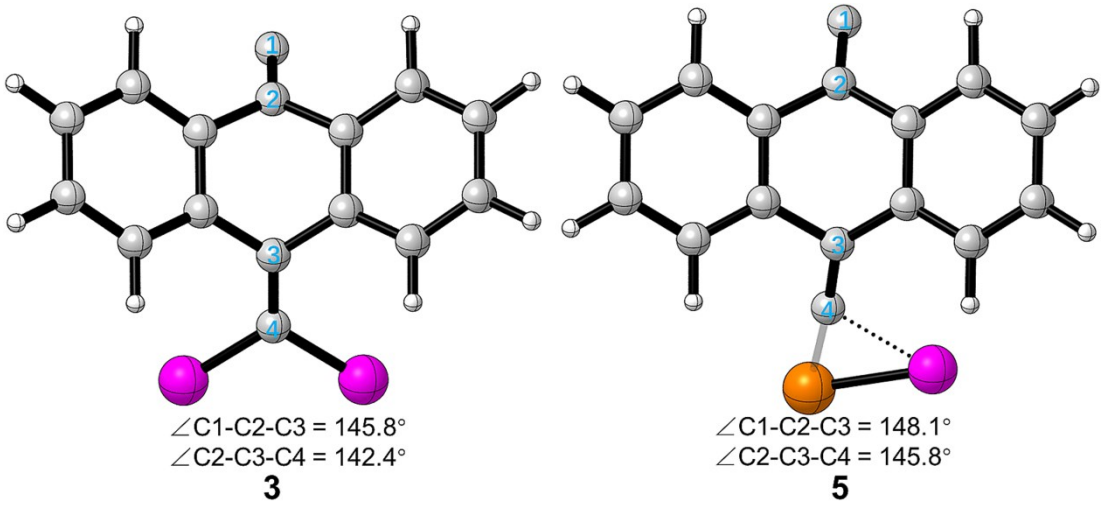


Figure S8 Geometries of **3** and **5** including some angles in them.

13. Kinetic study of Path4, geometries of reactants and products in Path4 with several important bond parameters, and the change in the Gibbs free energy ΔG (kcal/mol) Figure S9.

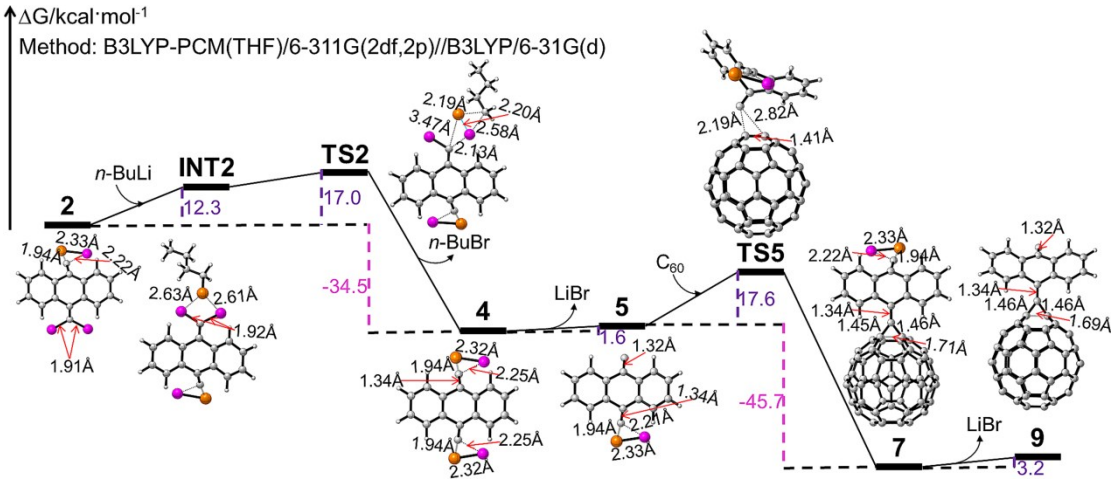


Figure S9 Kinetic study of Path4, geometries of reactants and products in Path4 with several important bond parameters, and the change in the Gibbs free energy ΔG (kcal/mol).

14. Kinetic study of Path5, geometries of reactants and products in Path5 with several important bond parameters, and the change in the Gibbs free energy ΔG (kcal/mol) Figure S10.

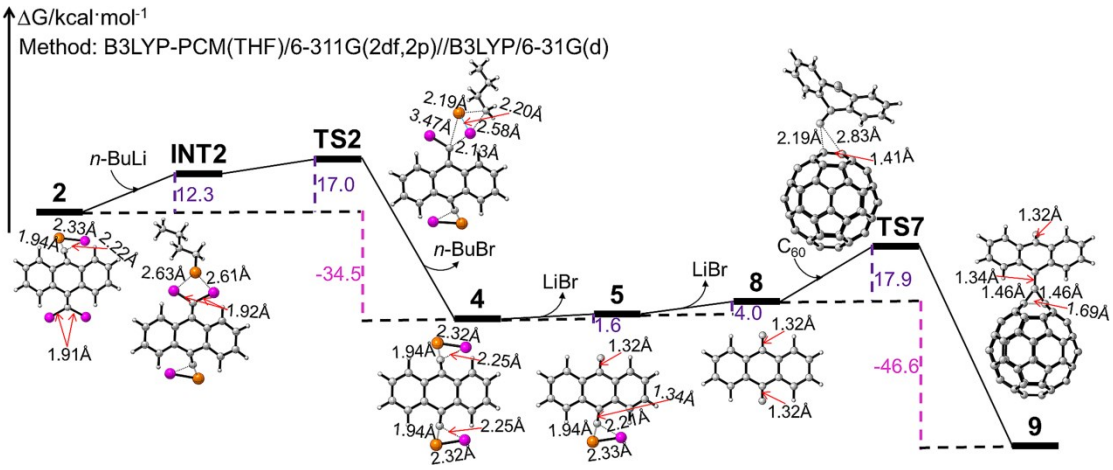


Figure S10 Kinetic study of Path5, geometries of reactants and products in Path5 with several important bond parameters, and the change in the Gibbs free energy ΔG (kcal/mol).

15. Interaction between carbene C atom and LiBr in **7** and **5**, Figure S11.

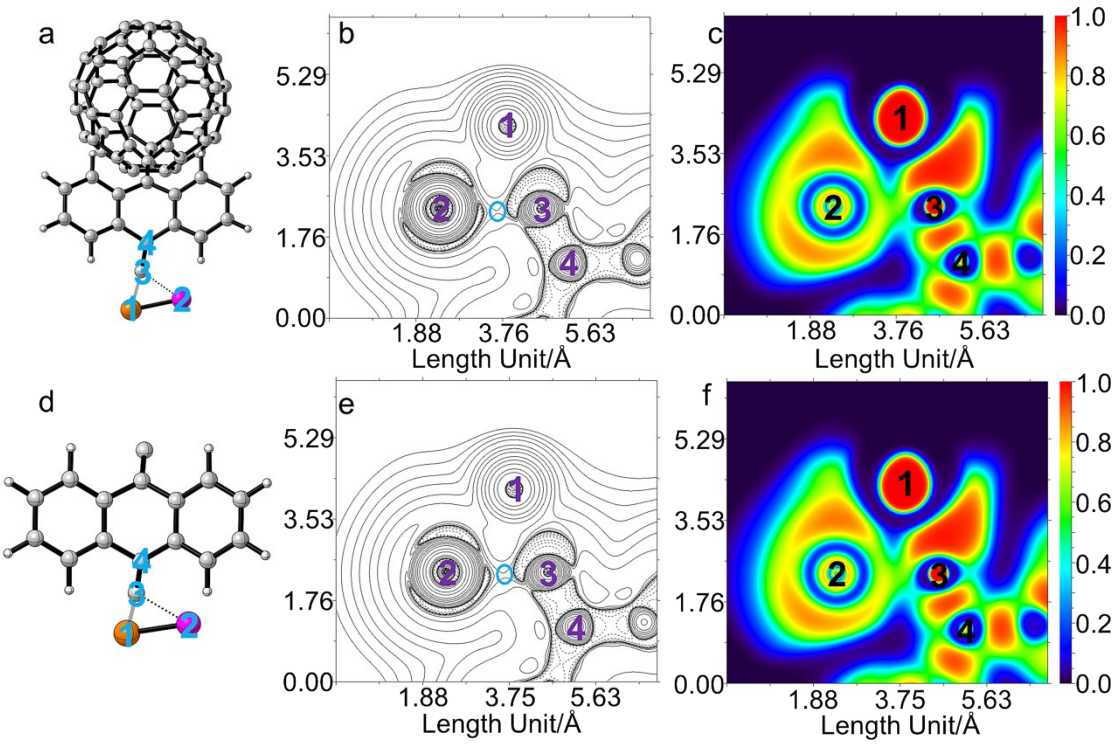


Figure S11 Geometries of **7** (a) and **5** (d), Laplacian of electron density contour line map of **7** (b) and **5** (e), and electron localization function (ELF) color-filled map for of **7** (c) and **5** (f). The bromine and lithium atoms are marked in yellow and pink, respectively.

16. Geometry of by-product **10** generated from dicarbene **8** Figure S12.

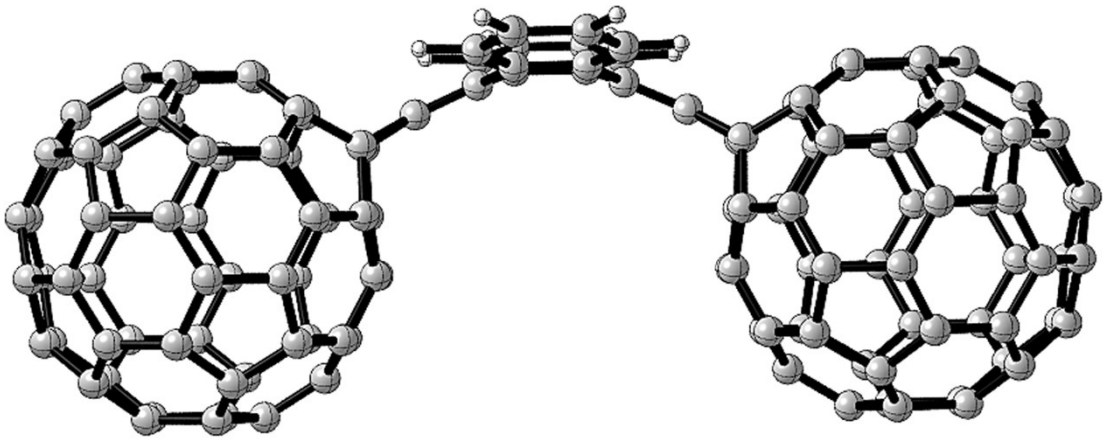


Figure S12 Geometry of by-product **10** generated from dicarbene **8**.

17. Reaction process to generate by-product **10** from **9** Figure S13.

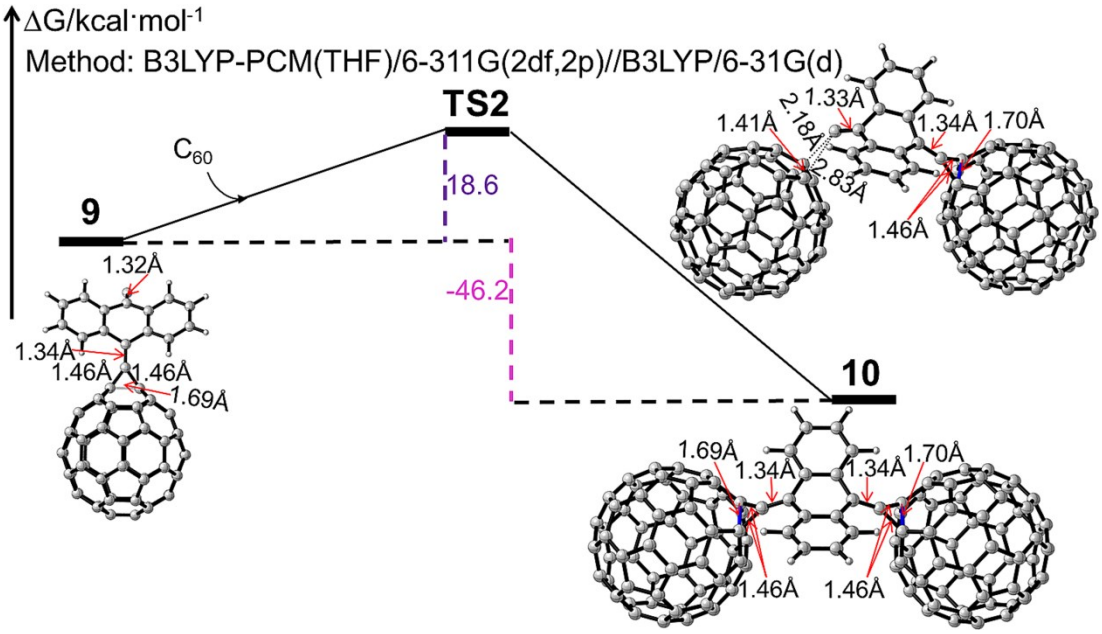


Figure S13 Reaction process to generate by-product **10** from **9**.

18. Geometries of carbenes Ref1, Ref2, and Ref3 acknowledged in experiment Figure S14.

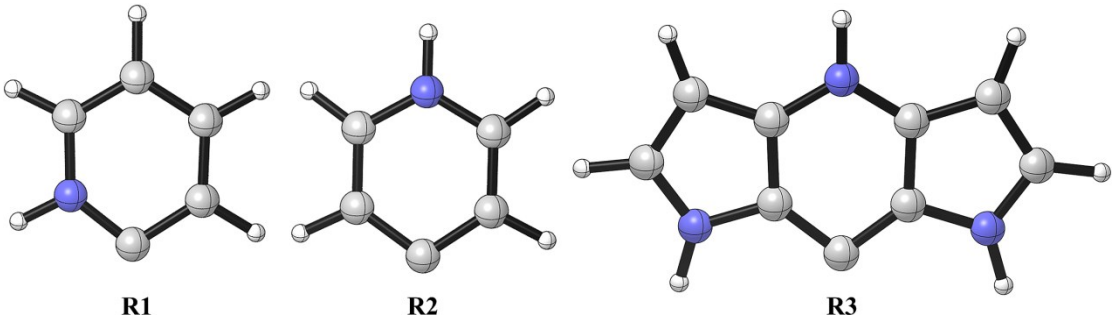


Figure S14 Geometries of carbenes Ref1, Ref2, and Ref3 acknowledged in experiment.