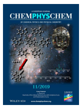
Supporting Information



Reactivity of the Indenyl Radical (C_9H_7) with Acetylene (C_2H_2) and Vinylacetylene (C_4H_4)

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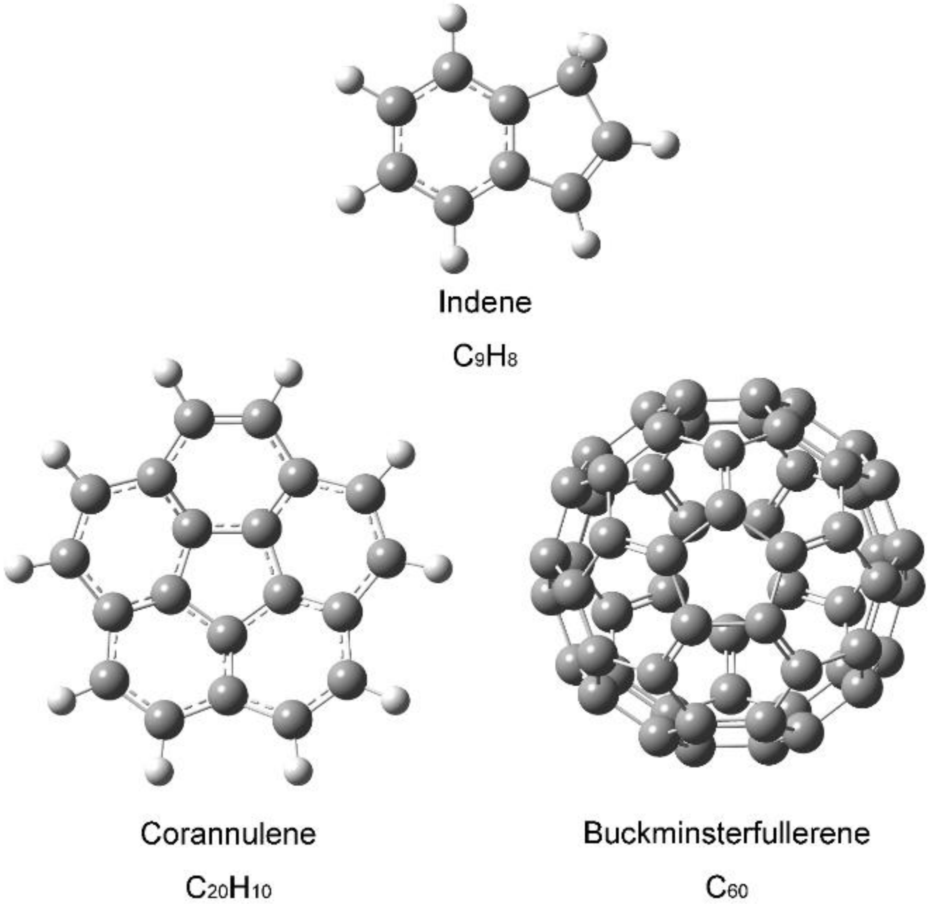
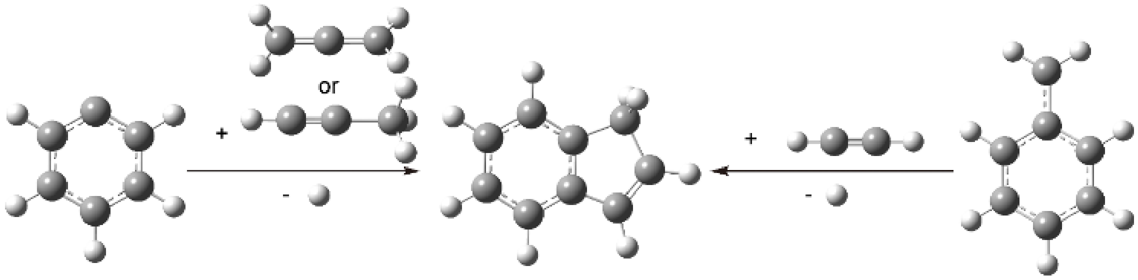


Scheme S1. Molecular structures of indene, corannulene and buckminsterfullerene carrying five-membered rings.



Scheme S2. Formation routes to indene via reactions of phenyl radicals with allene/ methylacetylene (C6-C3 route) and benzyl with acetylene (C7-C2 route).

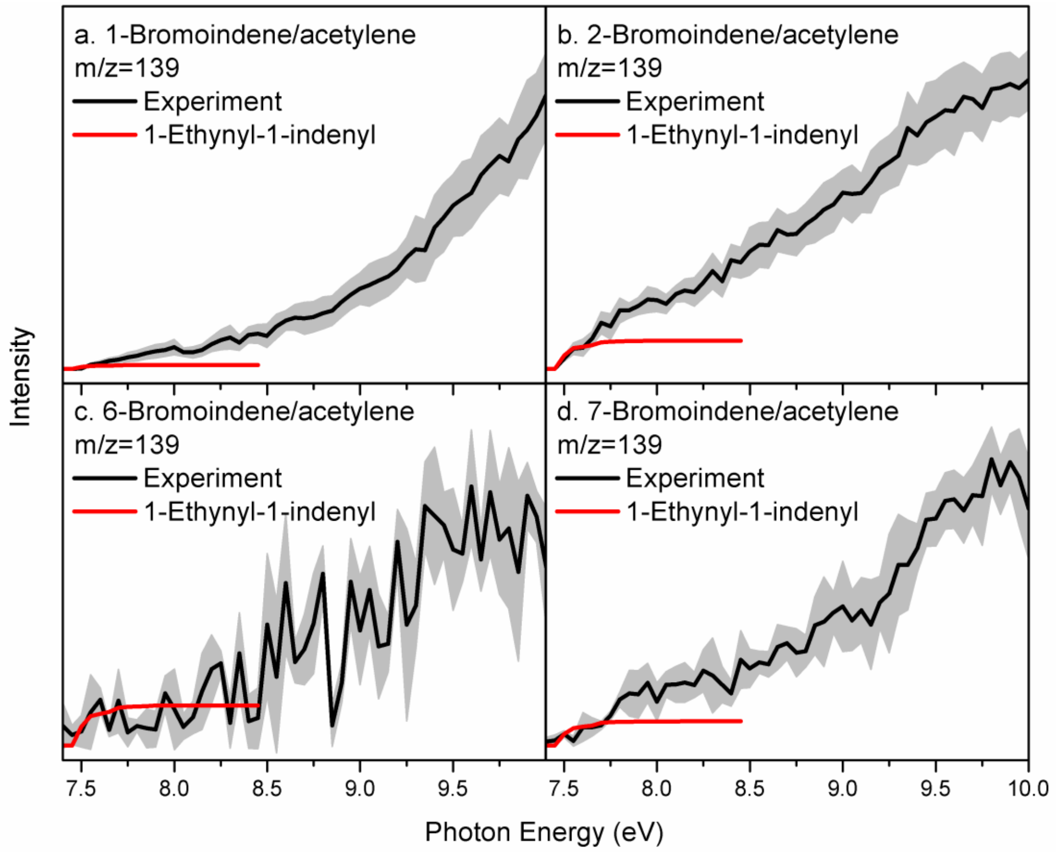


Figure S1. Experimental photoionization efficiency curves (PIE, black lines) curves for *m/z* = 139 in the reaction systems 1-bromoindene/acetylene (a), 2-bromoindene (b), 6-bromoindene (c) and 7-bromoindene (d), along with the experimental error (gray area), and the reference PIE curves (red lines).

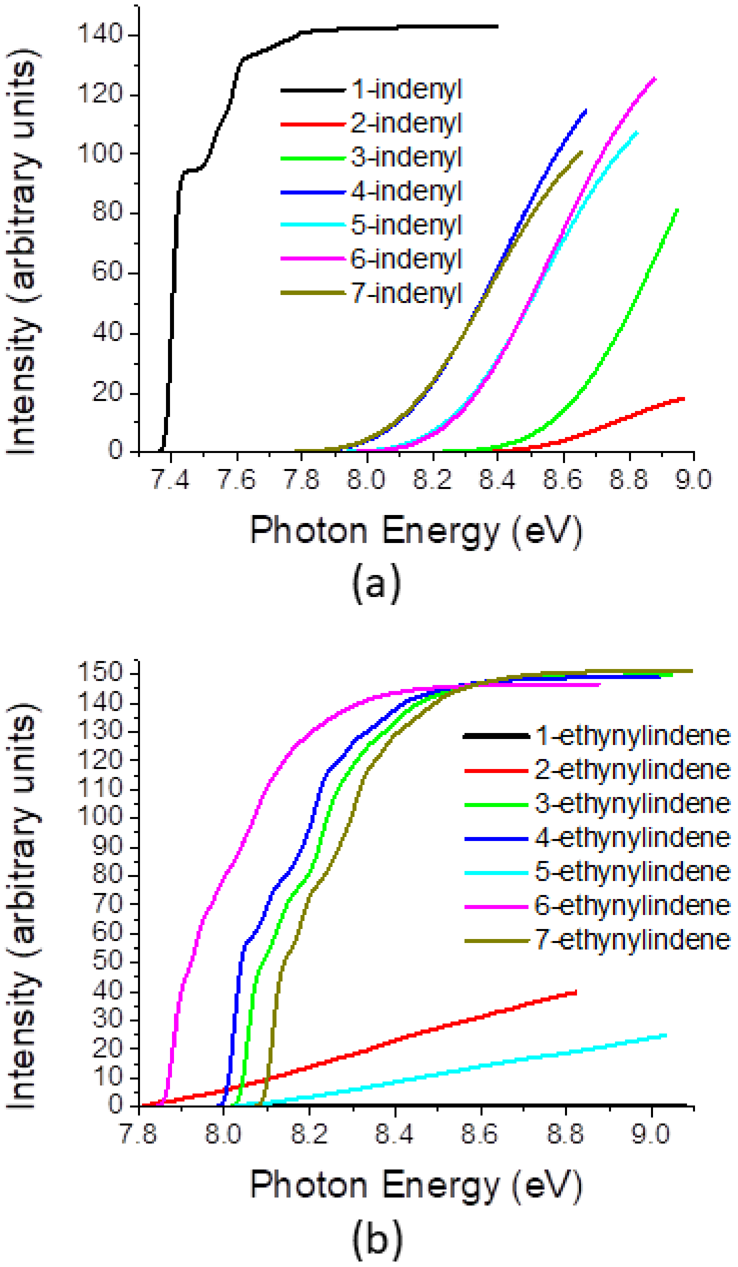
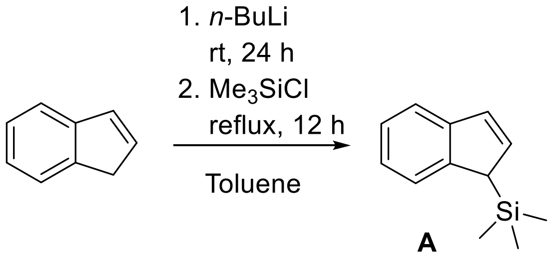


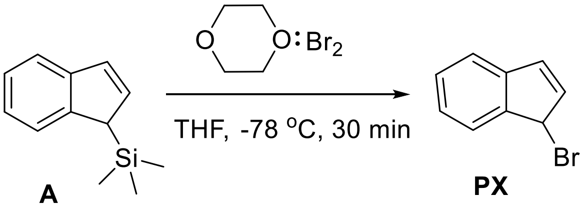
Figure S2. Theoretical photoionization efficiency curves based on calculated ionization Franck-Condon factors: (a) n-indenyl radical isomers; (b) n-ethynylindene isomers.

Synthesis of 1-Trimethylsilylindene; A.



The indene (5.0 g, 43 mmol) and dry toluene (30 mL) were placed in the flame-dried flask under N_2 at 0 °C (ice-bath). Then butyllithium (1.6 M/hexane, 28 mL, 44.8 mmol) was added slowly into the stirring solution. The reaction mixture was allowed to warm to room temperature and stirring was continued for 30 h. During this time, the reaction mixture became pale yellow in color. Then trimethylchlorosilane (5.7 mL, 4.88 g, 44.9 mmol) was added slowly to cooled reaction mixture at -10 °C (ice/NaCl). The reaction mixture was refluxed under N_2 at 115 °C for 12 h and was poured into crushed ice and extracted with EtOAc. The organic phase was separated, dried over anhydrous Na_2SO_4, filtered, and evaporated at reduced pressure. The residue was column chromatographed (*n*-hexane) to give light yellow liquid, which upon ^{1}H NMR analysis, showed to be mixture of product and indene substrate (70:30). Distillation of this mixture at reduced pressure gave pure 1-trimethylsilylindene A^{S1} (4.86 g, 60%) as pale yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ -0.04 (s, 9 H), 3.35 (s, 1H), 6.65 (dd, J = 5.6, 2.0 Hz, 1H), 6.92 (d, J = 6.0 Hz, 1H), 7.16-7.26 (m, 2H), 7.46 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ -2.41, 46.62, 121.16, 122.87, 123.67, 124.92, 128.96, 135.86, 144.23, 145.50.

Synthesis of 1-Bromoindene; PX.



The 1-trimethylsilylindene (**A**; 14.80 g, 25.5 mmol) was dissolved in dry THF (100 mL) in foil-covered flame dry flask and cooled to -78 °C. Dioxane dibromide (6.95 g, 28.0 mmol) was dissolved in dry THF (25 mL) and was added dropwise via addition funnel. The reaction mixture was allowed to warm to ambient temperature and volatiles were evaporated at reduced pressure. The residue was column chromatographed (*n*-hexane) to give **PX**^{S1} (3.38 g, 68%) as pale yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.49 (s, 1H), 6.47 (dd, J = 5.6, 2.0 Hz, 1H), 6.82 (d, J = 5.6 Hz, 1H), 7.23-7.32 (m, 3H), 7.56 (d, J = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 47.04, 121.97, 124.95, 126.53, 128.76, 132.88, 136.60, 141.71, 144.70.

Figure S3. ^{1}H NMR and ^{13}C NMR spectra of compound **A** in $CDCl_3$

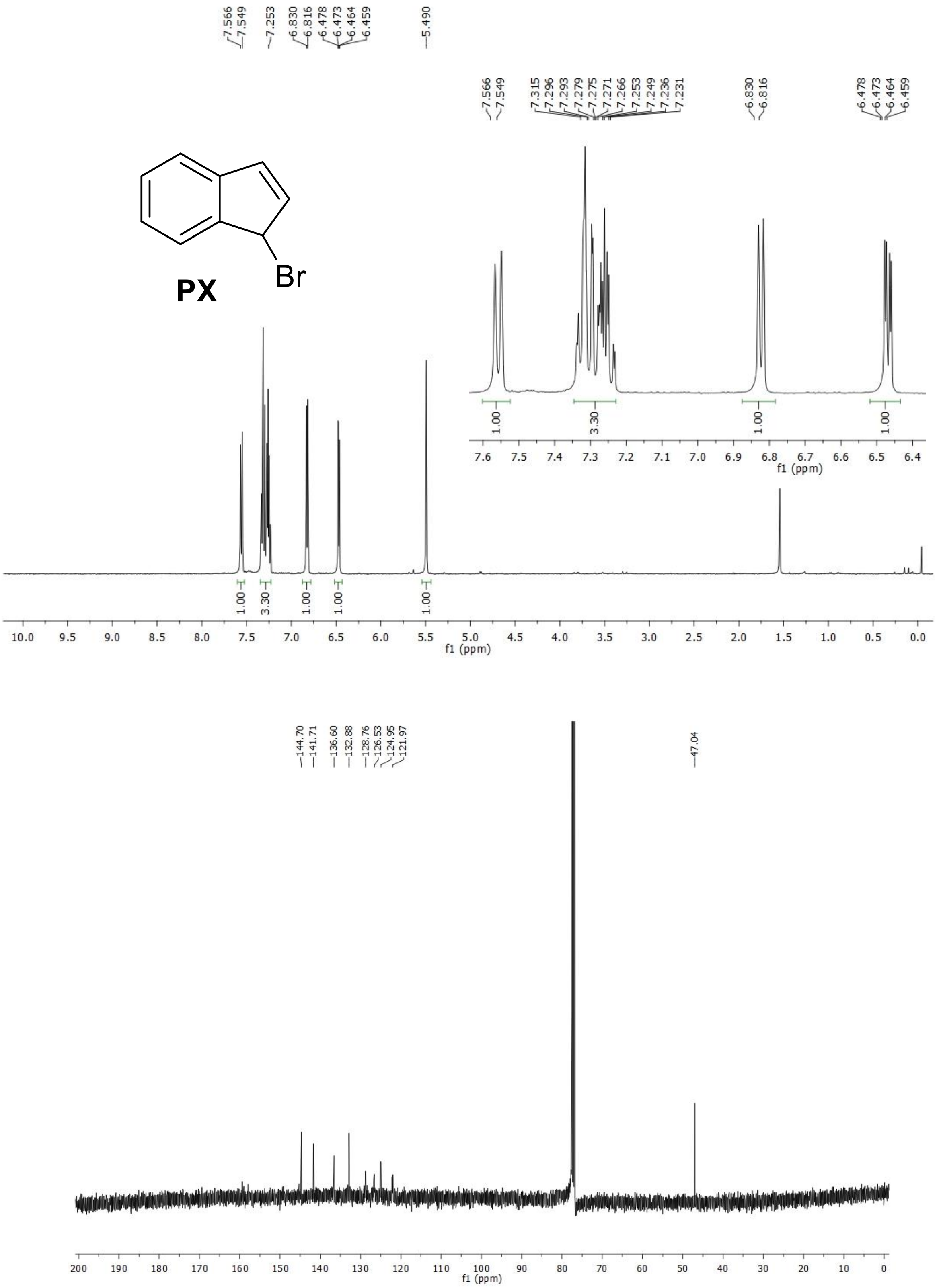


Figure S4. ^{1}H NMR and ^{13}C NMR spectra of compound **PX** in $CDCl_3$.

References

S1. Murphy, J. A.; Patterson, C. W., Regioselectivity of radical-induced bond cleavages in epoxides. *J. Chem. Soc., Perkin Trans. 1* **1993,** 405-410.