Table S1. The relative energy (B3LYP/6-31G**) for the syn and anti mono radicals and its values derived from the equations shown in Schemes 4.

R	E_{tot}(synMR), au	E_{tot}(antiMR), au	$\Delta E_{synMR-antiMR}$, kcal/mol	E(Syn1-Anti1) E(Syn2-Anti2)	SE (synMR) kcal/mol	SE (antiMR) kcal/mol
NO_2	-589.71246	-589.70917	2.06	2.1	1.82	-0.25
CHO	-498.54005	-498.53567	2.75	2.7	2.65	-0.10
CN	-477.45665	-477.45753	-0.55	-0.5	-1.02	-0.46
CF_3	-722.25051	-722.25017	0.21	0.2	-0.02	-0.23
H	-385.21615	-385.21615	0.00	0.0	0.00	0.00
F	-484.44682	-484.44795	-0.71	-0.7	-0.99	-0.28
Cl	-844.80914	-844.80910	0.02	0.0	-0.15	-0.18
CH_3	-424.53752	-424.53587	1.03	1.1	1.13	0.09
Ohsyn	-460.43874	-460.43376	3.13	3.1	3.02	-0.11
Ohanti	-460.43556	-460.43640	-0.53	-0.5	-0.64	-0.12
NH_2	-440.57539	-440.57079	2.89	2.9	2.94	0.05
$NH3^+$st	-440.93627	-440.93049	3.63	3.6	1.74	-1.89
$NH3^+$ec	-440.93669	-440.92824	5.30	5.3	3.43	-1.87
OMe (syn)	-499.73644	-499.72729	5.74	5.7	5.93	0.19
OMe (anti)	-499.74090	-499.74150	-0.38	-0.4	-0.49	-0.12

Table S2. The stabilization energies of aryl radical and arene by subsequent hydrogen abstraction from aryl diradical (i.e. Bergman cyclization intermediate) calculated by three hydrogen donors viz. methane (CH_4), methanol (CH_3OH) and 1,4-cyhexadiene (C_6H_8).

enediyne	H-donor	ΔE (kcal mol^{-1})				
		step **1**	step **2a**	step **2b**	step **3a**	step **3b**
	CH_4 CH_3OH C_6H_8	3.3	-3.9 -15.3 -38.2	-4.9 -16.2 -39.3	-	-
	CH_4 CH_3OH C_6H_8	11.0	-3.7 -15.0 -38.1	-5.1 -16.4 -39.5	-	-
	CH_4 CH_3OH C_6H_8	10.8	-4.1 -16.1 -38.5	-6.1 -17.3 -40.5	-4.8 -15.4 -39.2	-5.4 -16.6 -39.7
	CH_4 CH_3OH C_6H_8	10.0	-4.3 -15.5 -38.6	-5.2 -16.5 -39.6	-4.2 -15.5 -38.6	-5.3 -16.5 -39.6
	CH_4 CH_3OH C_6H_8	9.2	-4.1 -15.3 -38.5	-5.1 -16.4 -39.5	-3.9 -15.1 -38.2	-5.3 -16.6 -39.7
	CH_4 CH_3OH C_6H_8	10.0	-4.4 -15.6 -38.8	-6.1 -17.4 -40.5	-4.9 -16.1 -39.3	-5.5 -16.8 -39.9

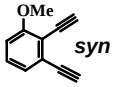
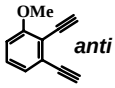
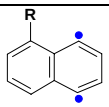
	CH_4 CH_3OH C_6H_8	9.4	-3.8 -15.2 -38.2	-2.4 -13.7 -36.8	-1.0 -12.5 -35.4	-5.2 -16.5 -39.6
	CH_4 CH_3OH C_6H_8	6.6	-4.2 -15.5 -38.6	-3.3 -14.5 -37.6	-2.2 -13.4 -36.5	-5.3 -16.6 -39.7
	CH_4 CH_3OH C_6H_8	12.4	-3.9 -15.1 -38.2	-2.1 -13.4 -36.5	-1.0 -12.2 -35.3	-5.0 -16.3 -39.4
	CH_4 CH_3OH C_6H_8	10.9	-3.8 -15.1 -38.2	-4.0 -15.2 -38.3	-2.7 -14.0 -37.1	-5.0 -16.3 -39.4
	CH_4 CH_3OH C_6H_8	8.9	-3.8 -15.0 -38.1	0.9 -10.4 -33.5	-2.0 -9.3 -32.4	-4.9 -16.2 -39.3
	CH_4 CH_3OH C_6H_8	10.3	-4.0 -15.3 -38.4	-5.6 -16.9 -40.0	-4.4 -15.7 -38.8	-5.2 -16.5 -39.6

Table S3. The deflection angles (deg) calculated from both θ_1 and θ_2 defined in Figure 8.

 R	θ_1	θ_2	$\theta_1 + \theta_2$
NO_2	11.7	10.8	22.5
CF_3	12.6	9.5	22.1
CN	10.2	6.4	16.6
H	2.2	0.8	3
F	3.4	2.5	5.9
Cl	10.2	7.6	17.8
CH_3	11.4	7.6	19