Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information for

"Computational Realization of Dirac Nodal Point and Dirac Nodal Loop Fermions in Novel β–Graphyne Analogues"

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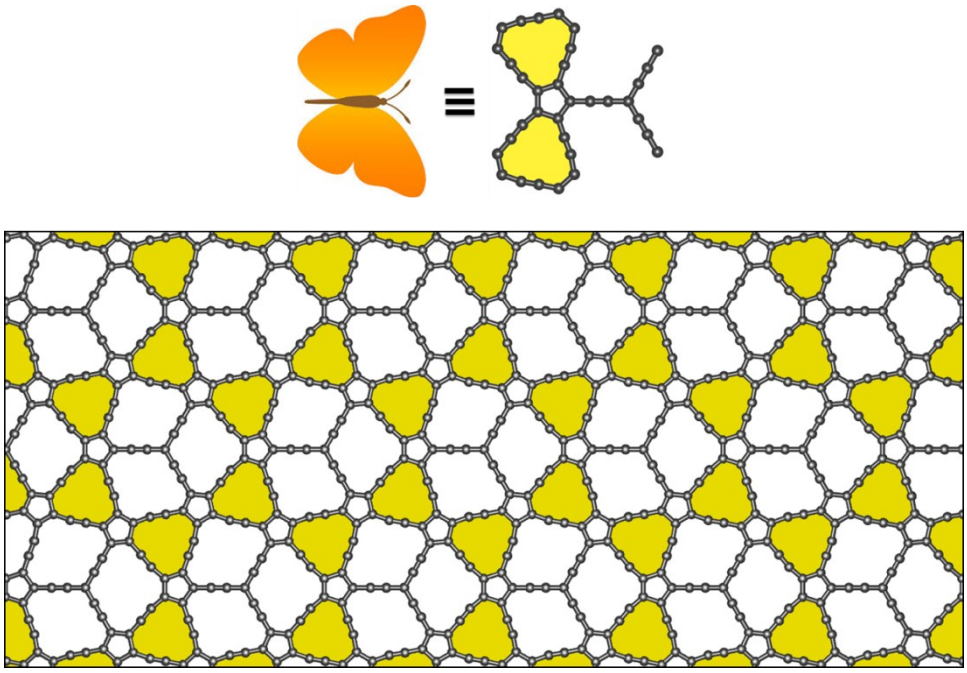


Fig. S1 Geometrical features of butterfly-graphyne.

Table S1. The inequivalent of C atoms in β4-, β5-, β6- and B-graphynes.

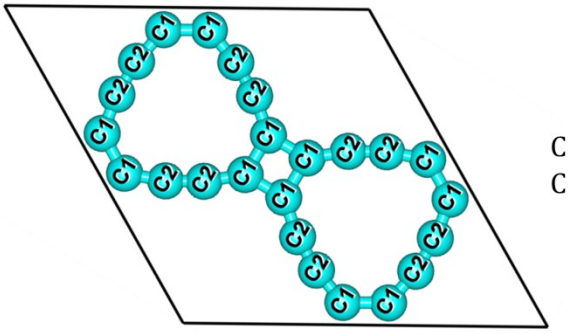
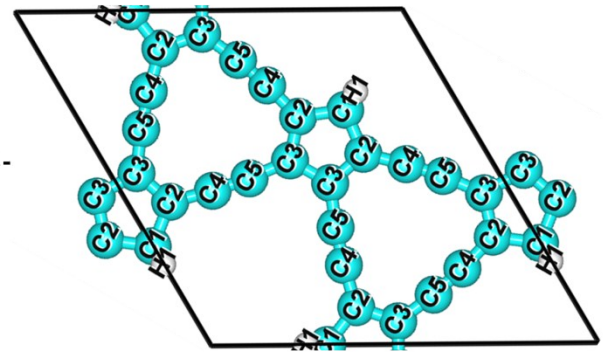
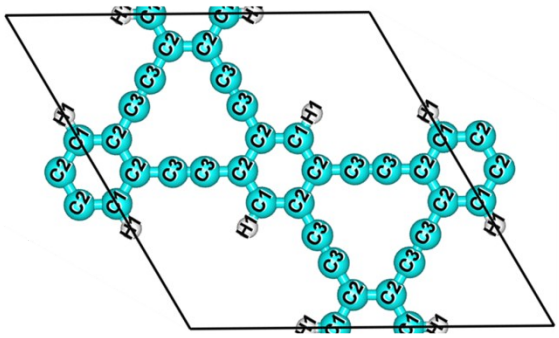
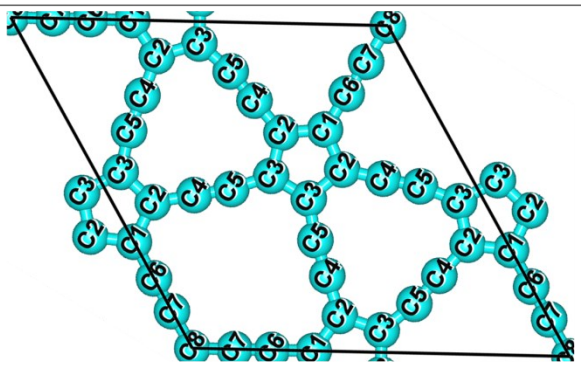
Graphyne	Carbon Allotrope	C	Wyckoff position	X	Y	Z
β4-		C1	12q	0.47283	0.40178	0.50000
		C2	12q	0.72229	0.54998	0.50000
β5-		C1	3g	0.29912	0.00000	0.50000
		C2	6k	0.68117	0.56939	0.50000
		C3	6k	0.55158	0.48280	0.50000
		C4	6k	0.77538	0.53730	0.50000
		C5	6i	0.49884	0.35133	0.50000
		H1	6i	0.24477	0.00000	0.42813
β6-		C1	6k	0.60134	0.00000	0.50000
		C2	12q	0.89705	0.39647	0.50000
		C3	12q	0.79525	0.50180	0.50000
		H1	6k	0.68037	0.00000	0.50000
B-		C1	3g	0.32184	0.00000	0.50000
		C2	6k	0.66509	0.55636	0.50000
		C3	6k	0.53267	0.46537	0.50000
		C4	6k	0.76175	0.53146	0.50000
		C5	6k	0.48950	0.33891	0.50000
		C6	3g	0.21106	0.00000	0.50000
		C7	3g	0.11202	0.00000	0.50000
		C8	1b	0.00000	0.00000	0.50000

Table S2. Optimized bond lengths (Å) and bond angles (deg) of β4-, β5-, β6- and B-graphynes. The bond lengths and bond angles in or around the carbon polygons, at the central acetylenic linker and at the terminal bonds of the acetylenic linker are represented by the black, red and blue colored values, respectively (*Ci atoms are same as those of inequivalent Wyckoff positions of C atoms).

System	Bond lengths (Å)		Bond angles (deg)	
β4-graphyne	C1-C1*	1.45	C1-C1-C1	90.00
	C1-C2	1.35	C1-C1-C2	140.06
	C2-C2	1.25	C1-C2-C2	170.06
β5-graphyne	C1-C2	1.50	H1-C1-H1	105.87
	C2-C3	1.40	H1-C1-C2	111.77
	C3-C3	1.46	C2-C1-C2	104.02
	C2-C4	1.39	C1-C2-C3	108.98
	C4-C5	1.23	C1-C2-C4	126.16
	C3-C5	1.40	C3-C2-C4	124.86
	C1-H1	1.10	C2-C3-C3	109.01
			C2-C3-C5	124.48
			C3-C3-C5	126.51
			C2-C4-C5	175.94
			C4-C5-C3	174.71
β6-graphyne	C1-C2	1.40	H1-C1-C2	118.93
	C2-C2	1.43	C2-C1-C2	122.13
	C2-C3	1.41	C1-C2-C2	118.93
	C3-C3	1.22	C1-C2-C3	120.48
	C1-H1	1.09	C2-C2-C3	120.59
			C2-C3-C3	179.41
B-graphyne	C1-C2	1.44	C2-C1-C2	108.78
	C2-C3	1.45	C2-C1-C6	125.61
	C3-C3	1.44	C1-C2-C3	107.80
	C2-C4	1.38	C1-C2-C4	125.57
	C4-C5	1.24	C3-C2-C4	126.63
	C3-C5	1.38	C2-C3-C3	107.81
	C1-C6	1.37	C2-C3-C5	121.81
	C6-C7	1.23	C3-C3-C5	130.38
	C7-C8	1.39	C2-C4-C5	179.30
			C4-C5-C3	170.86
			C1-C6-C7	180.00
			C6-C7-C8	180.00
			C7-C8-C7	120.00

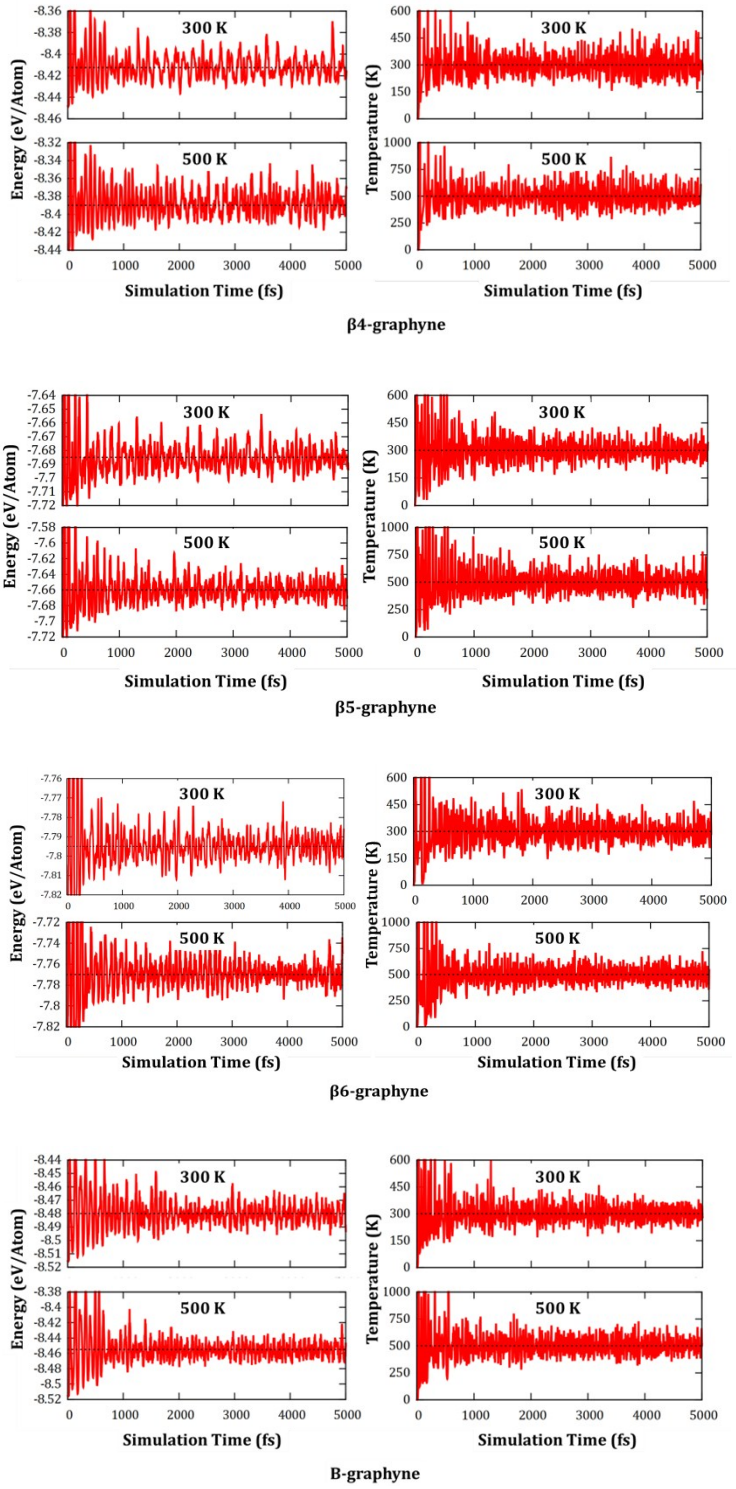


Fig. S2 Total energy and temperature fluctuations of β4-, β5-, β6- and B-graphynes at 300 and 500 K

Genaralized Synthetic Procedure

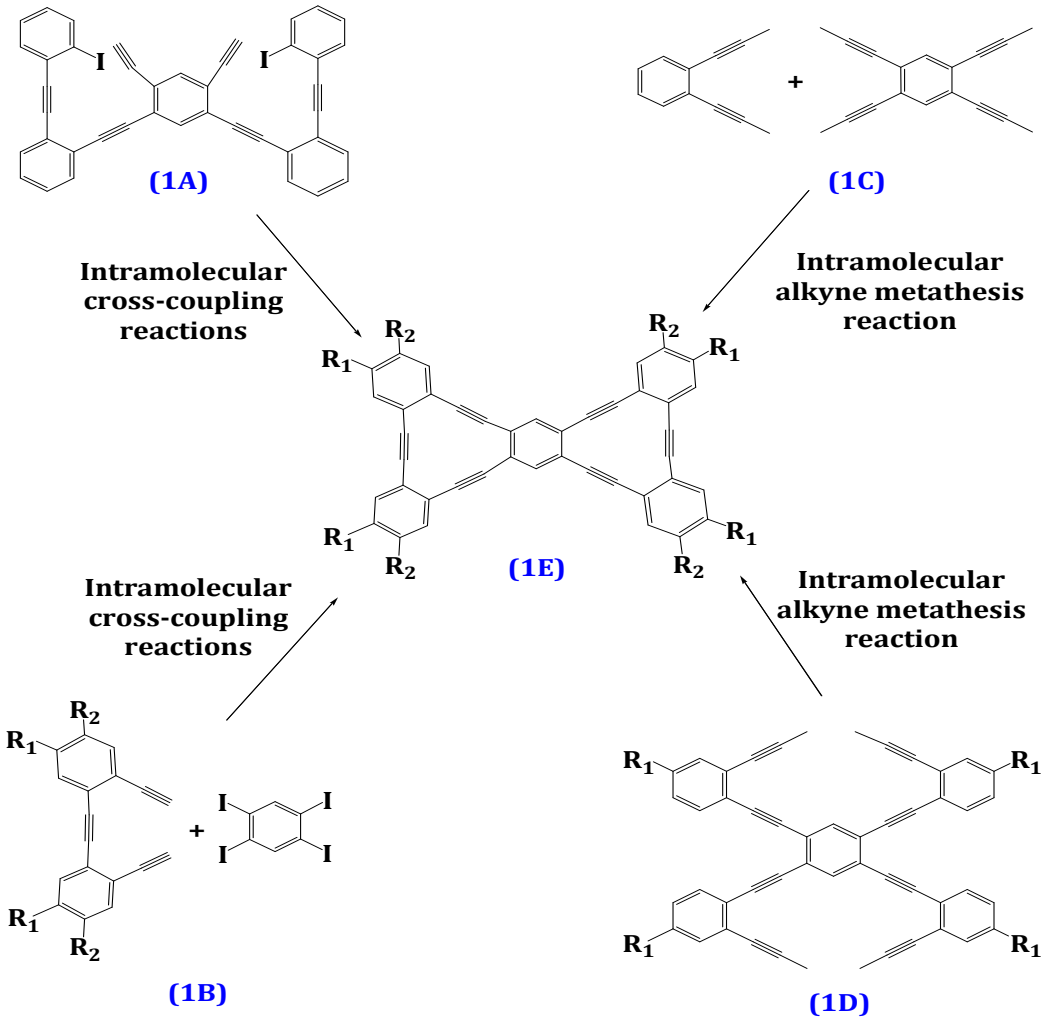
Dehydrotribenzo[12]annulenes, dehydrotribenzo[18]annulenes and perethynylated expanded radialenes, cyclo[12]carbon are considered as the potential candidates for the synthesis of small graphyne flakes using the most promising metal-catalyzed cross-coupling reactions, alkyne metathesis and templated synthesis techniques[1-6].

β6-Graphyne

In the same direction, intramolecular cross-coupling reactions of (**1A**) or (**1B**) and alkyne metathesis reaction of (**1C**) or (**1D**) eventually results the formation of small flakes of β6-graphyne (**1E**) as presented in step I and step II.

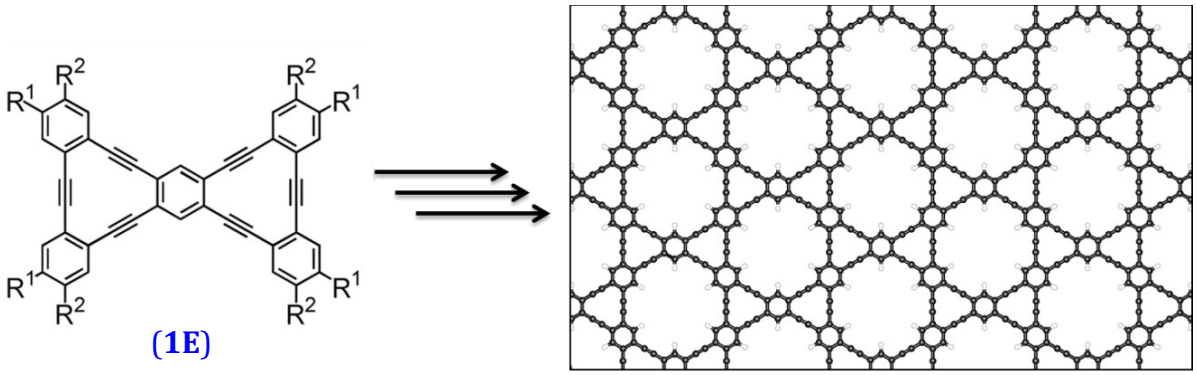
Scheme-S1:

Step I



$R_1 = R_2 = t$-Bu

Step II

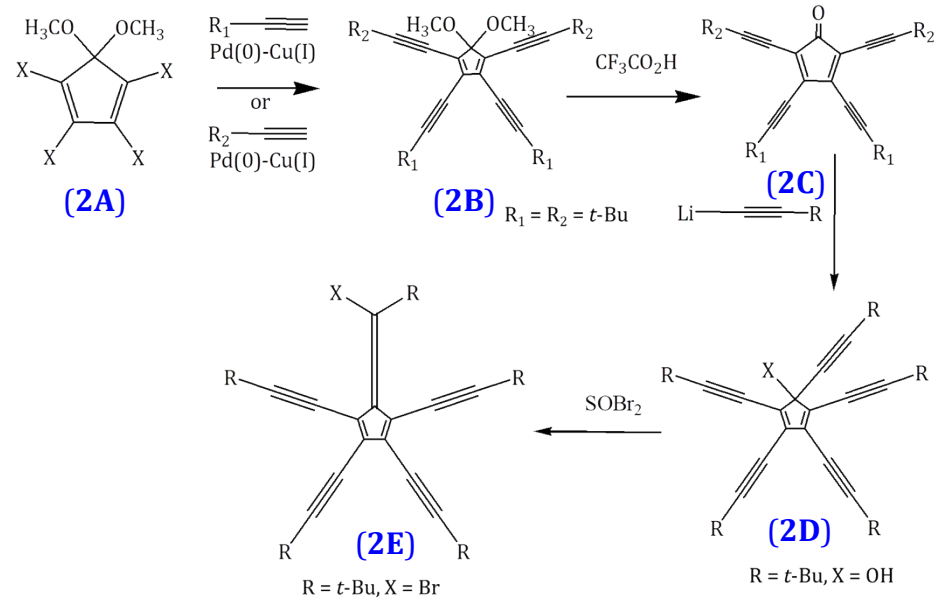


B-Graphyne

Similarly, tetrabromocyclopentadienone acetal (**2A**) *catalyzed with appropriate acetylene unit in the presence of Pd(0)–Cu(I) leads to the tetraethynyl compounds* (**2B**). *The subsequent hydrolysis afforded the corresponding dienones* (**2C**). *Treatment of these dienones with appropriate alkynyllithium reagents gave the corresponding alcohols* (**2D**), *which were converted to chlorides or bromides* (**2E**) *by treatment with either* $SOCl_2$ *or* $SOBr_2$.

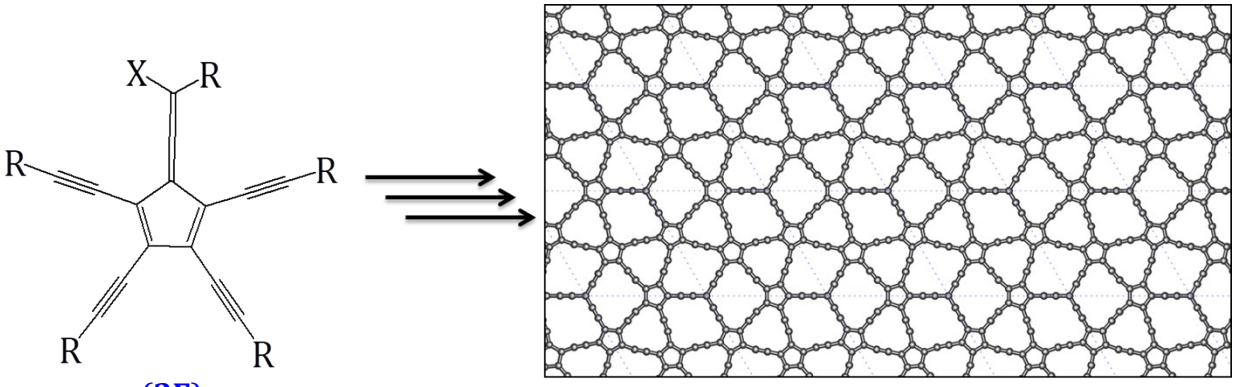
Scheme-S2:

Step I



Step II

The compound (**2E**) of step I in scheme 2 may serve as the precursor for the intramolecular cross-coupling reactions or alkyne metathesis reaction which may leads to the formation of small flakes of B-Graphyne as presented in step II.

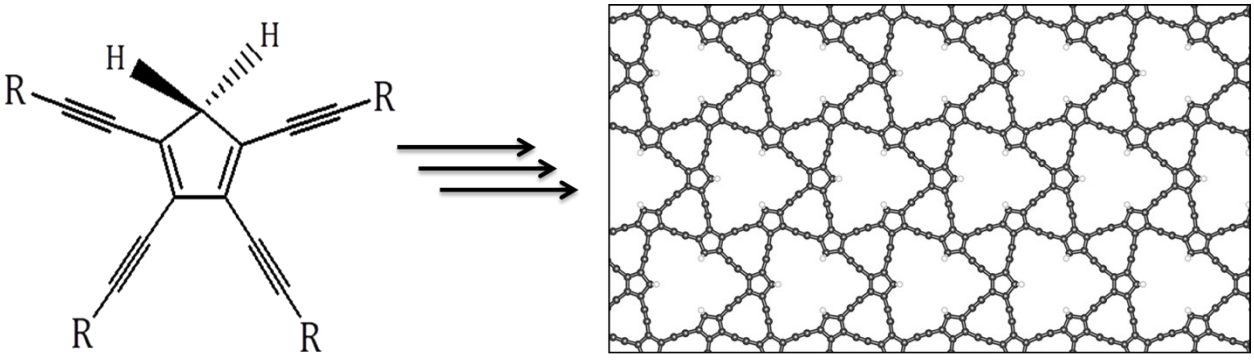


(2E) **B-Graphyne**

β5-Graphyne

Scheme-S3:

The complete reduction of carbonyl group of compound (**2C**) in scheme 2 with a suitable reducing agent and fallowed by treatment with appropriate alkynyllithium reagent lead to the formation of compound (**3A**) as shown below. The compound (**3A**) may serve as the starting material for the synthesis of small patches of β5-graphyne using promising metal-catalyzed cross-coupling reactions, alkyne metathesis and templated synthesis techniques.

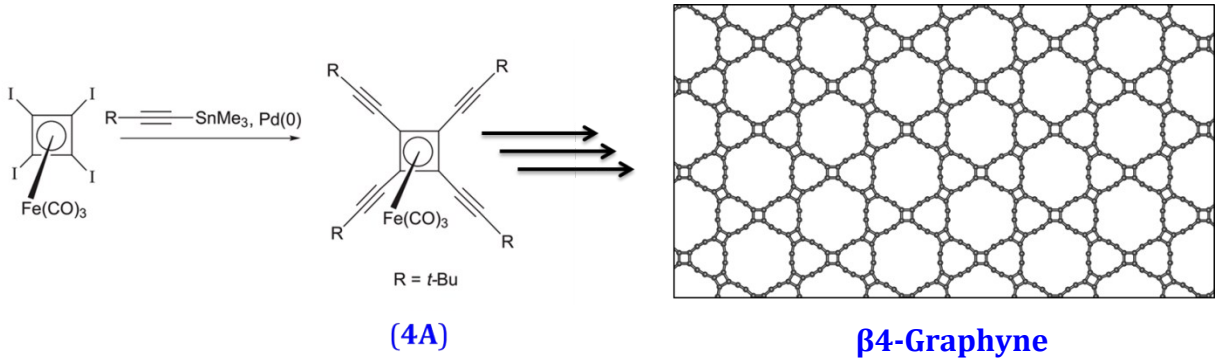


(3A) **β5-Graphyne**

β5-Graphyne

Scheme-S4:

Similar to the previous synthetic procedures, the acetylic scaffolds of carbon tetragon (**4A**) may serve as starting point for the synthesis of β4-graphyne.



(4A) **β4-Graphyne**

By removing the metal carbonyl unit using a proper reagent like (Trimethylamine N-Oxide, Me_3NO) and suitable metallic support, free standing monolayer of β4-graphyne may be synthesized.

References:

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