Electronic Supplementary Material (ESI) for Dalton Transactions
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Supplementary Information

S-1 FTIR spectra of samples prepared using different boron sources

For investigating the effect of different boron sources on the content of cBN, and examining the applicability of this modified solid state metathesis reaction method to other reaction systems, three other boron sources including $NaBH_4$, KBH_4 and B were used. As a result, four samples were prepared and their FTIR spectra and a TEM photo were shown in Fig. S1. The FTIR spectra revealed that the dominant phase in the samples prepared at 250 °C and 24 h was tBN, only a little amount of cBN was detected in them. However, when B was used as the boron source and the reaction duration was prolonged to 144 h, the dominant phase became cBN. To our disappointment, the yield of the sample prepared by using B as the boron source was very poor.

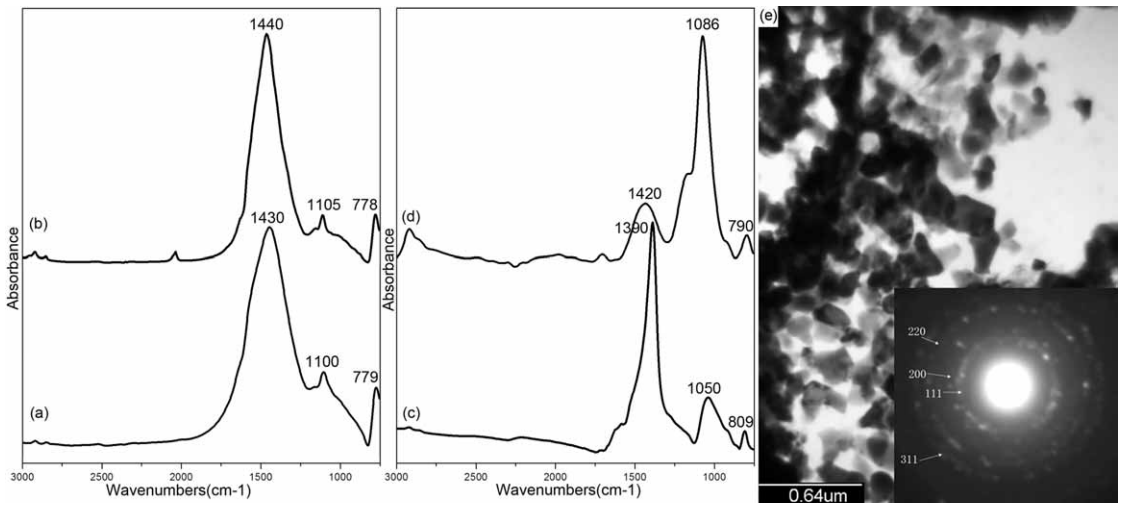

Figure S1. FTIR spectra and TEM image of BN prepared using different boron sources.(a) $NaBH_4$: 250 °C /24 h; (b) KBH_4: 250 °C /24 h; (c) B: 250 °C /24 h; (d) B: 250 °C /144h; (e) TEM image of cBN nanocrystals in (d). Inset is the corresponding SAED pattern of cBN.

S-2 tBN micro-flakes from sample S-1

Fig. S2 shows typical TEM image and corresponding SAED pattern of the tBN micro-flakes, which were obtained by the reaction of NH_4BF_4 and NaN_3 at 250 ˚C for 24 h with the reactants pre-pressed into dense pellets.

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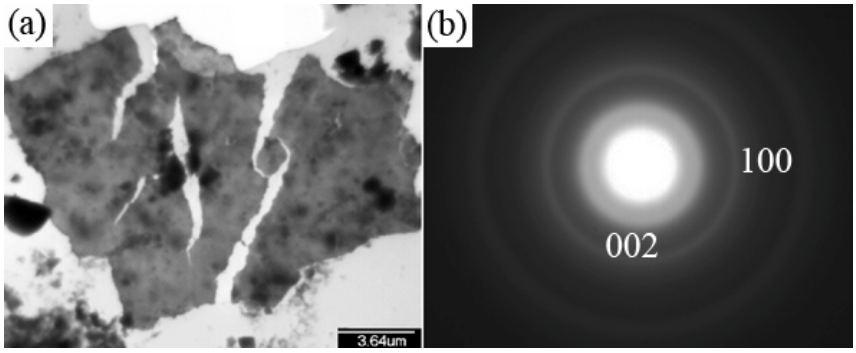

Figure S2. (a) TEM image and (b) SAED pattern of tBN micro-flakes.

S-3 Variation of the contents of tBN and cBN with the pressure and temperature

In order to increase cBN content, a pressure was applied onto the reactants during the reaction process of synthesizing BN by reacting NH_4BF_4 and NaN_3. The results indicated that all the temperature, pressure and reaction duration affected the contents of tBN and cBN, and the detailed information can be found in table S1.

For intuitionistically displaying the variation of tBN and cBN contents with the increase of temperature and pressure, a chart was presented in Fig. S3. From this figure, it was found that the content of cBN increased with the increase of pressure, while that of tBN decreased obviously. Especially, the content of cBN increased to a large extent when the reaction duration prolonged from 24 h to 48 h. On the other hand, it seems that higher reaction temperature favored the formation of tBN.

Table S1. Relative contents of tBN and cBN in the samples prepared at different temperature and pressure

Press. / Temp.	0 MPa/24h		125 MPa/24h		300 MPa/24h		450 MPa/24h		450 MPa/48h	
	t/%	c/%	t/%	c/%	t/%	c/%	t/%	c/%	t/%	c/%
220°C	86	14	64	36	56	44	53	47	24	76
250°C	89	11	85	15	78	22	60	40	45	55
300°C	100	0	92	8	79	21	63	37	48	52

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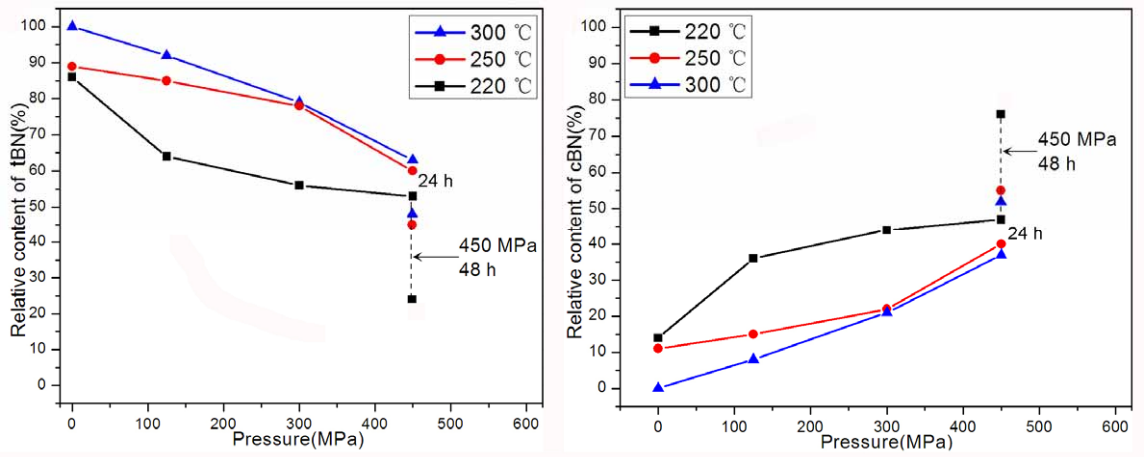

Figure S3. Relative contents of tBN and cBN vs pressure and temperature. * The contents of tBN and cBN were calculated using $C_{tBN}=I_{1386\sim1415}/(I_{1050\sim1108}+I_{1386\sim1415})$ and $C_{cBN}=I_{1050\sim1108}/(I_{1050\sim1108}+I_{1386\sim1415})$, and the value of I was obtained through fitting the FTIR peaks by multi-Lorentzian curves.

S-4 The structure induction effect at another temperature and reactants system

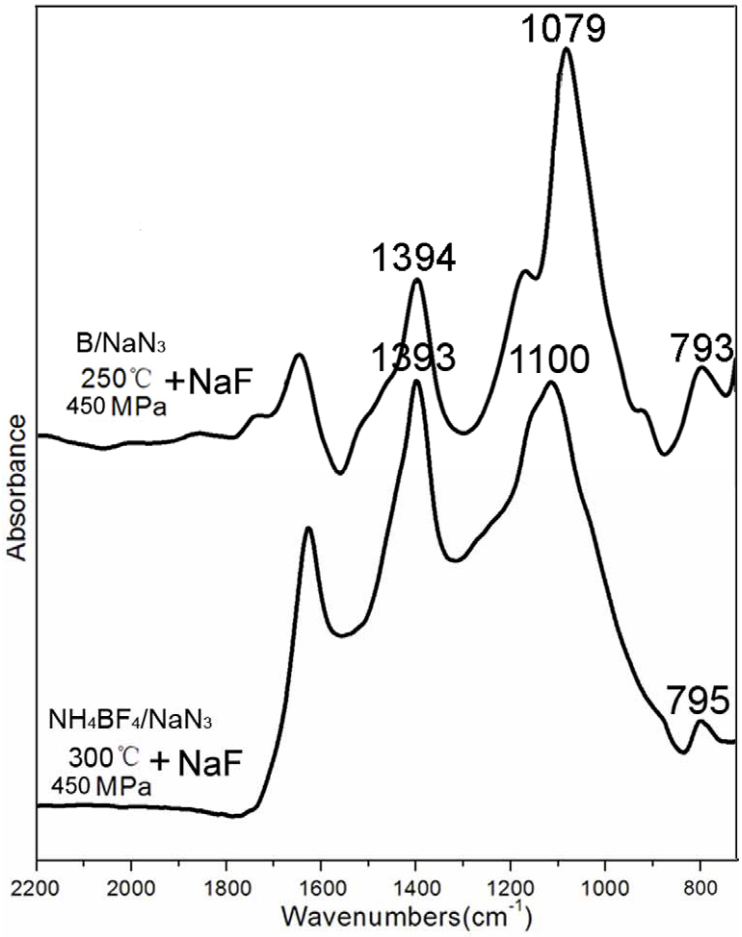

Figure S4. FTIR spectra of BN samples prepared under structural induction effect.

S-5 The XRD pattern of sample S22

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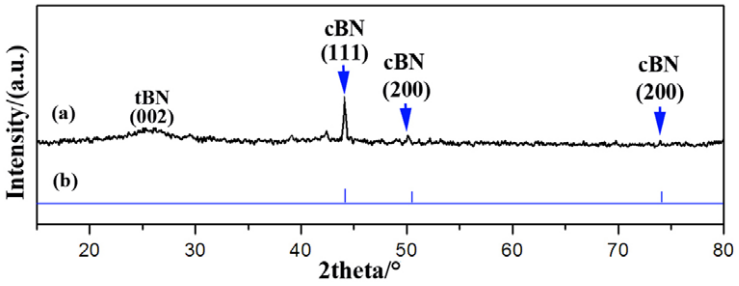

Figure S5. (a) the XRD pattern of sample S22; (b) the 2D transformation result of SAED pattern.