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Multicomponent reaction (MCR) for constructing *bis*-spirocyclohexane skeletons using β -nitrostyrene derived MBH acetates, 1,3-indanedione and aldehydes via [1 + 1 + 1 + 3] annulation†

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An AB₂C type four-component quadruple cascade reaction has been established between nitroallylic MBH acetate, 1,3-indanedione and aldehyde for generating *bis*-spirocyclohexanes. This reaction progressed in an unusual [1 + 1 + 1 + 3] annulation manner via a Knoevenagel/Michael/Michael/Michael sequence, resulting in the generation of three/four chiral centres, and two all-carbon quaternary centres through the formation of 3 new C–C bonds.

Introduction

The development of novel synthetic strategies for constructing new chiral spirocyclic compounds with varied medicinal potentials is a great challenge in organic and pharmaceutical chemistry.¹ In this regard, Multicomponent Reactions (MCRs)² are preferred for the synthesis of chiral spirocyclic compounds³ by virtue of their advantages, *i.e.*, one-pot synthesis, avoiding isolation of intermediates and atom economy.

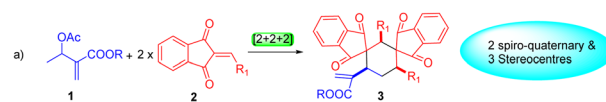
In recent times, the β -nitrostyrene derived Morita–Baylis–Hillman (MBH)⁴ adducts have been explored extensively towards the construction of various MCRs.⁵ The β -nitrostyrene derived MBH adducts^{6–8} are one of the essential classes of molecules in medicinal chemistry, due to their utility as building blocks for constructing complex and biologically sound molecules.⁹

Among the various β -nitrostyrene derived MBH adducts, nitroallylic MBH acetates have been explored extensively to give various spirocycles,¹⁰ heterocycles,¹¹ carbocycles,¹² bicyclic skeletons,¹³ and arenes.¹⁴ But to date there are no available reports for the construction of *bis*-spirocyclohexanes utilizing nitrostyrene derived MBH acetate with 1,3-indanedione¹⁵ or arylidene indanedione.^{16,17}

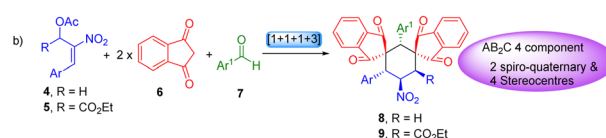
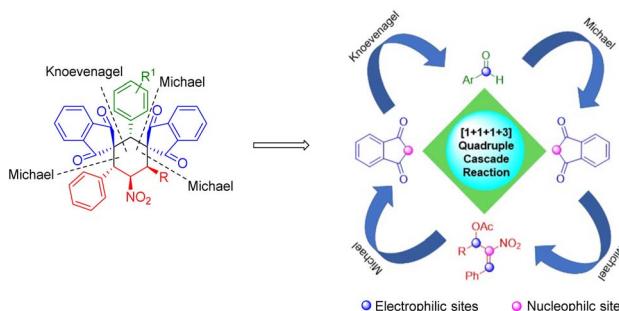
In 2015, He *et al.* successfully utilized acrylate derived MBH adducts along with 2-arylidene-1,3-indanediones to

demonstrate a [2 + 2 + 2] annulation protocol for producing substituted *bis*-spirocyclohexanes (eqn (a), Scheme 1).¹⁸

Hereby, we propose an MCR strategy to explore the utility of nitroallylic MBH acetate for generating fully substituted *bis*-spirocyclohexanes in a unique [1 + 1 + 1 + 3] annulation fashion (eqn (b), Scheme 1).

 Annulation reaction using acrylic MBH acetates (He *et al.*)


Annulation reaction using nitroallylic MBH acetates (Present work)


 Scheme 1 Construction of substituted *bis*-spirocyclohexanes using MBH acetates.

 Scheme 2 AB₂C type four component quadruple cascade reaction.

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In continuation of our perpetual study on heterocycles and spirocycles,¹⁹ we have demonstrated an AB₂C type four-component reaction²⁰ between 1,3-indanedione, aryl aldehydes, and β -nitrostyrene derived MBH acetates *via* [1 + 1 + 1 + 3] cyclization strategy (Scheme 2).

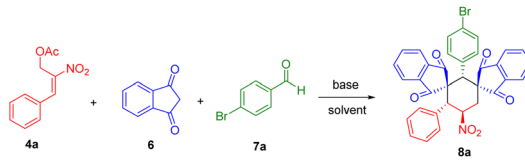
Results and discussion

Optimization studies of quadruple cascade reactions were carried out and the obtained results were tabulated (Table 1). The reaction initially carried out with potassium carbonate (1.5 equiv.) in acetonitrile at ambient temperature, gave the desired compound **8a** in 24% yield (entry 1, Table 1). Increasing the amount of indanedione to 2 equiv. gave a marginal increase in the yield *i.e.*, 25% for the product formation **8a** (entry 2, Table 1). The use of chlorinated solvents, *i.e.*, chloroform, didn't alter the yield even after 24 h (entry 3, Table 1). The yield for product **8a** improved to 35% with the use of potassium carbonate in 3 equiv. amounts (entry 4, Table 1). There is no improvement was observed with the change in reaction time as well as temperature (entries 5 and 6, Table 1). The use of methanol as solvent decreased the diastereomeric excess and yield due to the poor

solubility of *in situ*-formed KC product (entry 7, Table 1). Utilisation of organic bases such as DABCO, urea and thiourea couldn't improve the yield for the product formation **8a** (entries 8–15, Table 1). We also examined the effect of other inorganic bases such as Cs₂CO₃ but, there is no appreciable improvement was observed for the formation of desired product **8a** (entries 16 and 17, Table 1). It was observed that, there is no improvement in the yield with the higher concentrations of aldehyde (entries 18–20, Table 1). As the base concentration increases, the yield of **8a** gets decreases due to the high amount of side products formation (entries 21 and 22 Table 1). The use of mixture of solvents did not improve the yield and delivered the compound **8a** in 25% of yield (entry 23, Table 1). This is due to the less solubility of *in situ* formed KC side product for further cascade process.

The lower yield for **8a** is due to the formation of side product **11** (*i.e.*, double Michael reaction of MBH acetate **4a** with 1,3-indanedione **6**) and **10a** (Knoevenagel condensation between aldehyde **7a** and 1,3-indanedione **6**). It was also observed that, recovery of aldehyde for the most of the reactions was predominant. In conclusion of the optimization studies, the use of potassium carbonate (3 equiv.) in acetonitrile solvent gave

Table 1 Optimization studies for quadruple cascade reaction^a



| S. no | 6 (equiv.) | Base (equiv.) | Solvent | Temp (°C)/time (h) | Yield (%) ^b | <i>dr</i> ^c |
|-----------------|------------|---------------------------------------|-------------------|--------------------|------------------------|------------------------|
| 1 | 1 | K ₂ CO ₃ (1.5) | ACN | 30 (4) | 24 | >20 : 1 |
| 2 | 2 | K ₂ CO ₃ (1.5) | ACN | 30 (4) | 25 | >20 : 1 |
| 3 | 2 | K ₂ CO ₃ (1.5) | CHCl ₃ | 30 (24) | 20 | >20 : 1 |
| 4 | 2 | K ₂ CO ₃ (3) | ACN | 30 (4) | 35 | >20 : 1 |
| 5 | 2 | K ₂ CO ₃ (3) | ACN | 30 (12) | 20 | >20 : 1 |
| 6 | 2 | K ₂ CO ₃ (3) | ACN | 60 (4) | 20 | >20 : 1 |
| 7 | 1 | K ₂ CO ₃ (3) | MeOH | 30 (4) | 18 | 19 : 1 |
| 8 | 1 | DABCO (3) | MeOH | 30 (4) | 15 | 16 : 1 |
| 9 | 1 | Thiourea (3) | MeOH | 30 (4) | 22 | 10 : 1 |
| 10 | 2 | Thiourea (3) | MeOH | 30 (4) | 20 | 10 : 1 |
| 11 | 2 | Urea (3) | MeOH | 30 (4) | 20 | nd |
| 12 | 1 | Thiourea (3) | ACN | 30 (4) | 24 | nd |
| 13 | 2 | Thiourea (3) | ACN | 30 (4) | 25 | nd |
| 14 | 1 | Urea (3) | ACN | 30 (4) | 23 | nd |
| 15 | 2 | Urea (3) | ACN | 30 (4) | 25 | nd |
| 16 | 1 | Cs ₂ CO ₃ (1.5) | ACN | 30 (4) | 21 | nd |
| 17 | 2 | Cs ₂ CO ₃ (1.5) | ACN | 30 (4) | 27 | nd |
| 18 ^d | 2 | K ₂ CO ₃ (3) | ACN | 30 (4) | 25 | nd |
| 19 ^e | 2 | K ₂ CO ₃ (3) | ACN | 30 (4) | 23 | nd |
| 20 ^f | 2 | K ₂ CO ₃ (3) | ACN | 30 (4) | 20 | nd |
| 21 | 2 | K ₂ CO ₃ (4) | ACN | 30 (4) | 26 | nd |
| 22 | 2 | K ₂ CO ₃ (5) | ACN | 30 (4) | 20 | nd |
| 23 ^g | 2 | K ₂ CO ₃ (3) | ACN | 30 (4) | 25 | nd |

^a Compound **4a** (110.5 mg, 0.5 mmol), **6** (0.5 or 1.0 mmol), **7a** (92.5 mg, 0.5 mmol) and base (0.75 or 1.5 mmol) were dissolved in 5 mL of solvent.

^b Isolated yields. ^c Determined by ¹H NMR. ^d 1.5 equiv. of aldehyde was used. ^e 2.0 equiv. of aldehyde was used. ^f 3.0 equiv. of aldehyde was used.

^g ACN and H₂O (1 : 1) used; nd = not determined.



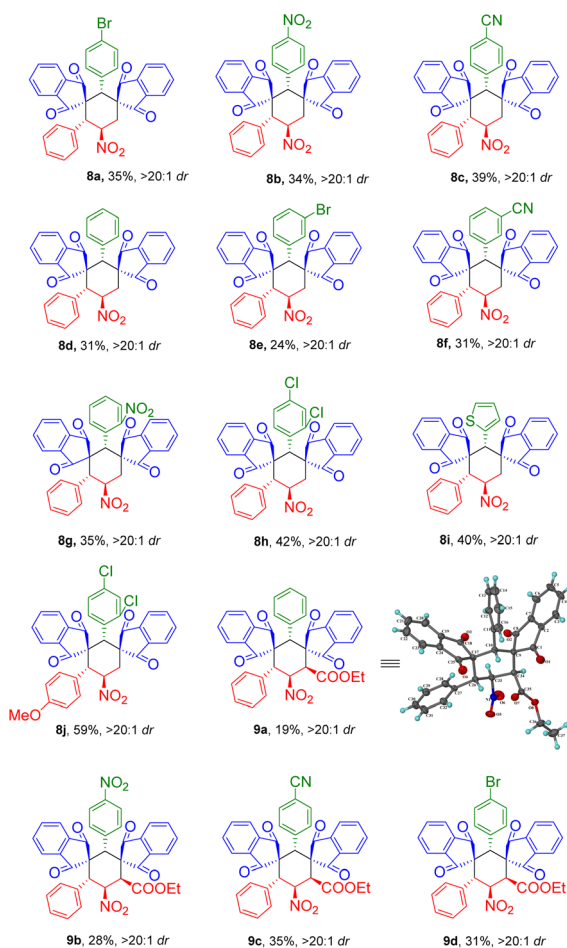
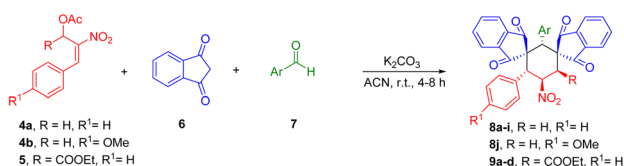
the maximum yield. The final product **8a** obtained with highly diastereoselectivity was fully characterized by ^1H NMR, ^{13}C NMR, DEPT-135 and the structure was further confirmed by single crystal X-ray analysis.²¹

The studies for the formation of *bis*-spirocyclohexane were further explored into substrate scope study with various MBH acetates **4/5** and aldehydes **7a–i** possessing electron withdrawing and donating substituents (Table 2). This reaction when employed with *p*-nitrobenzaldehyde resulted in 34% yield for product **8b**. When the reaction was carried out with *p*-cyano benzaldehyde, the corresponding *bis*-spirocyclohexane **8c** was obtained in a 39% yield. Compound **8d** was obtained in 31% of yield with the use of unsubstituted benzaldehyde. *m*-

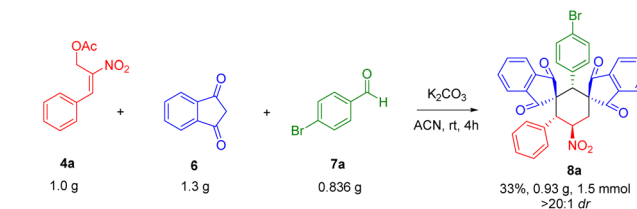
bromobenzaldehyde on reacting with indanedione **6** and MBH acetate **4** retained high diastereoselectivity for product **8e** in 24% of yield. It was observed that the substitution of an electron-withdrawing group *i.e.*, *m*-cyano, gave **8f** with a yield of 31%. The *ortho*-nitro substituted benzaldehyde delivered the corresponding *bis*-spirocyclohexane **8g** in 35% yield.

A good yield of 42% for the formation of compound **8h** was observed when *o,p*-dichlorobenzaldehyde was employed in the reaction. Heteroaromatic aldehydes also tolerated the reaction conditions towards the formation of *bis*-spirocyclohexanes. The quadruple cascade reaction with 2-thiophenyl aldehyde produced compound **8i** in a good yield of 40%. An impressive yield of 59% was observed for compound **8j**, by the reaction of *p*-methoxy MBH acetate **4b**, 1,3-indanedione and *o,p*-dichloro benzaldehyde. We further explored the utility of secondary nitroallylic MBH acetate **5** to develop fully substituted *bis*-spirocyclohexanes **9a–d**. The reaction involving unsubstituted benzaldehyde, gave the desired compound **9a** in 19% yield. The substitution of electron-withdrawing groups like $-\text{NO}_2$, $-\text{CN}$ at the para position of the benzaldehyde resulted in compounds **9b** and **9c** in 28% and 35%, respectively. Whereas, the *p*-bromo benzaldehyde delivered the compound **9d** in 31% of the yield. Attempts using aliphatic aldehydes led to trace amounts of corresponding *bis*-spirocyclohexanes. This may be presumably due to poor reactivity of 2-alkylidene indanediones.

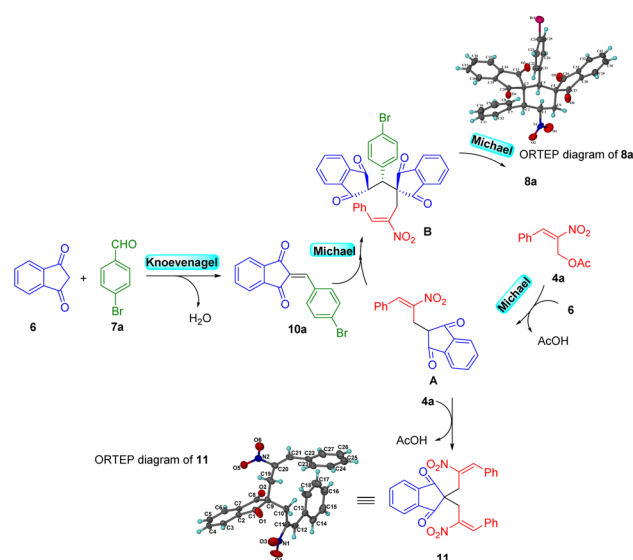
Table 2 Substrate scope for construction of *bis*-spirocyclohexanes^{a,b,c}



^a Compound **4/5** (0.5 mmol), **6** (1.0 mmol), aldehyde **7** (0.5 mmol) and K_2CO_3 (1.5 mmol) were dissolved in 5 mL of ACN and stirred at 30 °C.
^b Isolated yields. ^c *dr* was determined by ^1H NMR.



Scheme 3 Gram scale synthesis of *bis*-spirocyclohexane **8a**.



Scheme 4 Plausible reaction mechanism for the quadruple cascade sequence.



We further examined the scalability of our protocol by gram scale preparation of *bis*-spirocyclohexane **8a** (Scheme 3). To our delight the reaction retained with high diastereoselectivity for product **8a** formation.

A possible mechanistic pathway for the formation of *bis*-spirocyclohexane products **8/9** is explained in Scheme 4. Base assisted MBH acetate **4a** on reaction with 1,3-indanedione *via* S_N2 manner generates intermediate **A** as a Michael adduct. Intermediate **A** undergoes another Michael addition with *in situ* generated KC product arylideneindanedione **10a** to form intermediate **B** which further undergoes 6-*endo-trig* cyclization *via* Michael addition to produce **8a**. The overall reaction follows a Knoevenagel/Michael/Michael/Michael quadruple cascade reaction sequence *via* [1 + 1 + 1 + 3] annulation. This plausible mechanism is further supported by the isolation of side product **11**. The formation of side product **11** is due to a parallel reaction of intermediate **A** with MBH acetate **4a** in a Michael addition manner *via* double S_N2 fashion.

Conclusions

A multicomponent reaction was demonstrated for developing fully substituted *bis*-spirocyclohexanes derived from β-nitrostyrene derived MBH acetates. This AB₂C type four-component cascade protocol between nitroallylic MBH acetate, 1,3-indanedione, and aldehyde resulted in synthesis of *bis*-spirocyclohexanes in high diastereoselectivity.

Conflicts of interest

There are no conflicts of interest.

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- 21 CCDC 2149813 for **8a** compound contains the crystallographic data for this paper. See ESI† for complete XRD data of **9a** (CCDC 2149825) and **11** (CCDC 2175054).

