Supporting Information

Transition Metal-free Efficient Synthesis of Bis(indolyl)propynes (BIPs)

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Experimental Section:

1. Synthesis of α,β-unsaturated aromatic acetylenic aldehydes:

\[ \text{R}^1\text{CHO} \xrightarrow{\text{CBr}_4, \text{PPh}_3, \text{DCM}} \text{R}^1\text{CHO} \]

- \[ \text{R}^1\text{CHO} \xrightarrow{\text{CBr}_4, \text{PPh}_3, \text{DCM}} \text{R}^1\text{CHO} \]
  \( \text{R}^1 = \text{cyclopropyl, hexyl} \)

Scheme S1. Synthesis of α,β-unsaturated aromatic acetylenic aldehydes

Synthesis of α,β-unsaturated aliphatic acetylenic aldehydes:

\[ \text{R}^1\text{CHO} \xrightarrow{\text{CBr}_4, \text{PPh}_3, \text{DCM}} \text{R}^1\text{CHO} \]

- \[ \text{R}^1\text{CHO} \xrightarrow{\text{CBr}_4, \text{PPh}_3, \text{DCM}} \text{R}^1\text{CHO} \]

Scheme S2. Synthesis of α,β-unsaturated aliphatic acetylenic aldehydes:
General Procedure for the Synthesis of the intermediate \textit{gem}-dibromolefins 1a:

Under an atmosphere of argon, a solution of triphenylphosphine (3 eq., 0.141 mol) and tetrabromomethane (1.5 eq., 0.071 mol) in anhydrous DCM was stirred at 0 °C for 30 minutes. The aldehyde (1, 1.0 eq., 0.047 mol) was added over a period of five minutes and the mixture as stirred at 0 °C for one hour. After addition of water, the layers were separated, and the aqueous layer was extracted with DCM (3 x 100 mL). The combined organic layers were dried over Na$_2$SO$_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel with 100% hexane as the eluent to afford the intermediate \textit{gem}-dibromolefins 1a with 95% yield.

Procedure for the synthesis of \(\alpha,\beta\)-unsaturated acetylenic aldehydes 12:

Under an atmosphere of argon, n-BuLi (14.4 mL, 1.2 eq., 1.6 M in \textit{n}-hexane) was added over a period of 30 minutes via syringe pump to a solution of \textit{gem}-dibromoolefine (1a, 5.0 g, 1.0 eq.) in anhydrous THF at \(-78\) °C, and the mixture was stirred at \(-40\) °C for 15 minutes. After addition of DMF (3 mL, 2.0 eq.) in one lot, the mixture was allowed to warm to room temperature and stirred for one hour. The mixture was added to a stirring solution of KH$_2$PO$_4$ (aq.)/diethyl ether (1:1). After five minutes, the layers were separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over Na$_2$SO$_4$, the solvent was removed under reduced pressure and the crude product was subjected to column chromatography (hexane/EtOAc, 99:1, v/v) to obtain 3-phenylpropioaldehyde (12) in 84% yield.
Fig. S1. $^1$H-NMR spectrum of 12a in CDCl$_3$.

Figure S2. $^{13}$C-NMR spectrum of 12a in CDCl$_3$.
Figure S3: $^1$H-NMR spectrum of 12b in CDCl$_3$.

Figure S4: $^{13}$C-NMR spectrum of 12b in CDCl$_3$. 
Figure S5 $^1$H-NMR spectrum of 12c in CDCl$_3$.

Figure S6 $^{13}$C-NMR spectrum of 12c in CDCl$_3$. 
Figure S7. $^1$H-NMR spectrum of 12d in CDCl$_3$.

Figure S8. $^{13}$C-NMR spectrum of 12d in CDCl$_3$. 
Figure S9 $^1$H-NMR spectrum of $12e$ in CDCl$_3$.

Figure S10 $^{13}$C-NMR of spectrum $12e$ in CDCl$_3$. 
Figure S11 $^1$H-NMR spectrum of 12f in CDCl$_3$. $^{13}$C-NMR Could not be recorded due to solubility problem.

Figure S12 $^1$H-NMR spectrum of 12h in CDCl$_3$. 
Figure S13 $^{13}$C-NMR spectrum of 12h in CDCl$_3$.

Figure S14 $^1$H-NMR spectrum of 12i in CDCl$_3$. 

Figure S15 $^{13}$C-NMR spectrum of 12i in CDCl$_3$.

Figure S16 $^1$H-NMR spectrum of 12j in CDCl$_3$. 
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Figure S20: H-NMR spectrum of 12l in CDCl$_3$. 
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Figure S24 $^{13}$C-NMR spectrum of 12o in CDCl$_3$. 
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Figure S28 $^{13}$C-NMR spectrum of 13a in CDCl$_3$. 
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Figure S30 $^{13}$C-NMR spectrum of 13c in CDCl$_3$. 
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Figure S38 $^{13}$C-NMR spectrum of 14f in CDCl$_3$ + DMSO-d$_6$. 
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Figure S52 $^{13}$C-NMR spectrum of 17a in CDCl$_3$.  

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Figure S53 $^1$H-NMR spectrum of $17i$ in CDCl$_3$.

Figure S54 $^{13}$C-NMR spectrum of $17i$ in CDCl$_3$. 

Figure S55 $^1$H-NMR spectrum of $17k$ in CDCl$_3$.

Figure S56 $^{13}$C-NMR spectrum of $17k$ in CDCl$_3$. 
Figure S57 $^1$H-NMR spectrum of 18a in CDCl$_3$.

Figure S58 $^{13}$C-NMR spectrum of 18a in CDCl$_3$. 
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Figure S60 $^{13}$C-NMR spectrum of 18d in CDCl$_3$. 
Figure S61 $^1$H-NMR spectrum of 18e in CDCl$_3$.

Figure S62 $^{13}$C-NMR spectrum of 18e in CDCl$_3$. 
Figure S63 $^1$H-NMR spectrum of 19a in CDCl$_3$.

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Figure S71 $^1$H-NMR spectrum of 20a in CDCl$_3$.

Figure S72 $^{13}$C-NMR spectrum of 20a in CDCl$_3$. 
Figure S73 $^1$H-NMR spectrum of 20d in CDCl$_3$.

Figure S74 $^{13}$C-NMR spectrum of 20d in CDCl$_3$. 
Figure S75 $^1$H-NMR spectrum of 21a in CDCl$_3$.

Figure S76 $^{13}$C-NMR spectrum of 21a in CDCl$_3$. 
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Figure S78: $^{13}$C-NMR spectrum of 21c in CDCl$_3$. 

Figure S79 \(^1\)H-NMR spectrum of 21h in CDCl\(_3\).

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Figure S88 $^{13}$C-NMR spectrum of 22c in CDCl$_3$. 
Figure S89 $^1$H NMR spectrum of 22d in CDCl$_3$.

Figure S90 $^{13}$C NMR spectrum of 22d in CDCl$_3$. 
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Figure S92 $^{13}$C NMR spectrum of 22e in CDCl$_3$. 
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Figure S94 $^{13}$C NMR spectrum of 22k in CDCl$_3$. 
Figure S95 $^1$H NMR spectrum of 22n in CDCl$_3$ + DMSO-d$_6$.

Figure S96 $^{13}$C NMR spectrum of 22n in CDCl$_3$ + DMSO-d$_6$. 
Figure S97 $^1$H NMR spectrum of $22o$ in CDCl$_3$.

Figure S98 $^{13}$C NMR spectrum of $22o$ in CDCl$_3$. 