

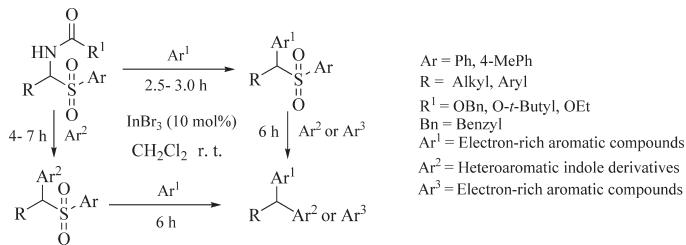
# InBr<sub>3</sub>: A Versatile Catalyst for the Different Types of Friedel–Crafts Reactions

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Mild and efficient InBr<sub>3</sub>-catalyzed Friedel–Crafts alkylation of heteroaromatic or electron-rich aromatic compounds with  $\alpha$ -amido sulfones at room temperature in CH<sub>2</sub>Cl<sub>2</sub> has been developed. The products undergo further Friedel–Crafts alkylation with heteroaromatic or electron-rich aromatic compounds leading to unsymmetrical or bis-symmetrical triaryl methanes in good yield.  $\alpha$ -Amido sulfones are employed for the synthesis of the unsymmetrical and bis-symmetrical triaryl methanes. The use of mild reaction condition, low catalytic loading, and high yield are the advantages of the present procedures.

## Introduction

Friedel–Crafts alkylation is one of the most important C–C bond-forming reactions in organic chemistry.<sup>1</sup> These reactions are usually assisted by either protic acid or Lewis acid catalyst. Indoles and many of its derivatives are present in numerous substances commonly found in nature,<sup>2</sup> as well as in the compounds that show pharmacological and biological

activities.<sup>3</sup> The introduction of functionalized alkyl framework at the 3-position in the indole system is a common practice directed to the synthesis of biologically active compounds.<sup>4</sup> A variety of methods have been explored for the Friedel–Crafts alkylation of indole due to its electron-rich nature.<sup>5</sup>

Recently several workers have demonstrated that  $\alpha$ -amido sulfones **1** are useful precursors of *N*-acyliminium ions **2** that can further react with several nucleophiles such as allylsilanes, silyl ketene acetals, trimethylsilyl cyanide, and electron-rich aromatics leading to the corresponding adducts **3** (Scheme 1).<sup>6</sup> Petrini and co-workers have demonstrated that the Friedel–Crafts reactions of heteroaromatic indoles with

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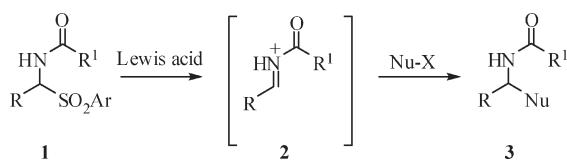
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## SCHEME 1



$\alpha$ -amido sulfones catalyzed by montmorillonite K-10 give the unexpected 3-(1-arylsulfonylalkyl)indoles.<sup>7</sup> Moreover 3-(1-arylsulfonylalkyl)indoles have further scope for various synthetic transformations.<sup>8</sup>

In recent years the utility of indium salts as Lewis acids in organic synthesis has received a great deal of attention due to the relatively low toxicity, stability in air and water, and strong tolerance to oxygen- and nitrogen-containing substrates.<sup>9</sup> The application as Lewis acid catalyst to fundamental reactions such as Diels–Alder,<sup>10</sup> Friedel–Crafts,<sup>11</sup> Mukaiyama aldol,<sup>12</sup> and Sakurai–Hosomi allylation reactions<sup>13</sup> has been extensively investigated.<sup>14</sup> In continuation of the development of useful synthetic methodology for C–C bond-forming reactions,<sup>15</sup> we report herein an efficient InBr<sub>3</sub>-catalyzed Friedel–Crafts alkylation of heteroaromatic or electron-rich aromatic compounds with  $\alpha$ -amido sulfones. The products undergo further Friedel–Crafts alkylation with heteroaromatic or electron-rich aromatic compounds giving rise to triaryl methanes.

Triaryl methanes display interesting properties and have received a great deal of attention as leuco dyes,<sup>16</sup> photochromic

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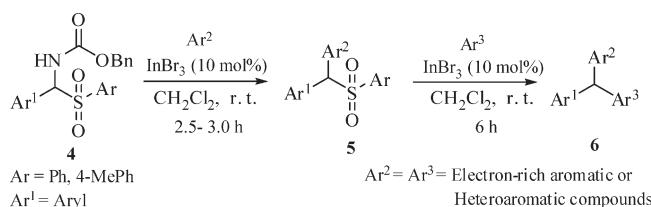
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## SCHEME 2



agents,<sup>17</sup> suitable building blocks for generating dendrimers,<sup>18</sup> and substrates for theoretical<sup>19</sup> and biological<sup>20</sup> studies. While many methods have been reported for the preparation of symmetrical triaryl methanes,<sup>21</sup> the synthesis of unsymmetrical derivatives is far less studied.<sup>22–24</sup> We describe here a broad scope of InBr<sub>3</sub>-catalyzed Friedel–Crafts alkylations that allow the selective preparation of structurally diverse triaryl methanes through sequential reactions with same or different electron-rich aromatic compounds (Scheme 2; Table 1).

## Result and Discussion

We have carried out the reaction of  $\alpha$ -amido sulfone **4** with heteroaromatic indole **8** in CH<sub>2</sub>Cl<sub>2</sub> in the presence of molecular iodine that produces the desired 3-(1-arylsulfonylalkyl)-indole in 58% yield (entry 1). In the absence of any catalyst no product could be detected (entry 2). Then the Lewis acids such as ZrOCl<sub>2</sub>·8H<sub>2</sub>O, Rh(acac)<sub>3</sub>, Co(acac)<sub>3</sub>, In(acac)<sub>3</sub>, and InBr<sub>3</sub> were screened (entries 3–7). InBr<sub>3</sub> (10 mol %) is found to be the most effective catalyst (entry 7). The effect of various solvents also has been studied. CH<sub>2</sub>Cl<sub>2</sub> is found to be the solvent of choice in terms of yield and reaction time (entry 12).

On the basis of the optimized reaction conditions, the scope of the Friedel–Crafts alkylation reaction is evaluated and the results are outlined in Table 2. The  $\alpha$ -amido sulfone (R = CO<sub>2</sub>Et, Ar = Ph, R<sup>1</sup> = Ph) is reacted with a variety of indoles (**11a–e**) to give the Friedel–Crafts alkylation products in good yield. The methyl group at the 2-position of indoles (entry 3 and 6) gives less yield than in case of the reaction of entry 1 because of the steric hindrance exerted by the methyl group. The reactions of 5-methoxy indole (entry 4) or methyl

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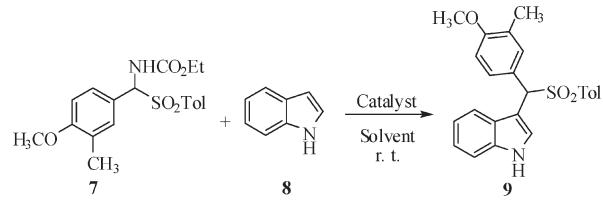
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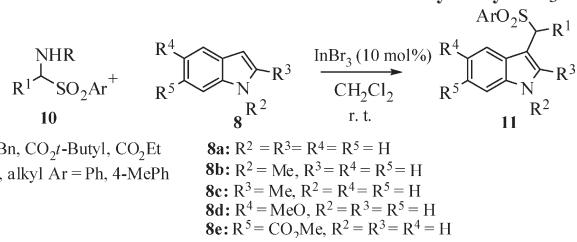
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**TABLE 1.** Friedel–Crafts Alkylation of Heteroaromatic Indoles with  $\alpha$ -Amido Sulfones under Various Reaction Conditions<sup>a</sup>

entry	catalyst (mol %)	solvent	reaction time (h)	isolated yield (%) <sup>b</sup>
1	I <sub>2</sub> (20)	CH <sub>2</sub> Cl <sub>2</sub>	6	58
2		CH <sub>2</sub> Cl <sub>2</sub>	12	NR
3	ZrOCl <sub>2</sub> ·8H <sub>2</sub> O (10)	CH <sub>2</sub> Cl <sub>2</sub>	8	63
4	Rh(acac) <sub>3</sub> (10)	CH <sub>2</sub> Cl <sub>2</sub>	12	NR
5	Co(acac) <sub>3</sub> (10)	CH <sub>2</sub> Cl <sub>2</sub>	12	NR
6	In(acac) <sub>3</sub> (10)	CH <sub>2</sub> Cl <sub>2</sub>	12	NR
7	InBr <sub>3</sub> (10)	CH <sub>2</sub> Cl <sub>2</sub>	4	89
8	InBr <sub>3</sub> (3)	CH <sub>2</sub> Cl <sub>2</sub>	10	67
9	InBr <sub>3</sub> (5)	CH <sub>2</sub> Cl <sub>2</sub>	8	73
10	InBr <sub>3</sub> (15)	CH <sub>2</sub> Cl <sub>2</sub>	4	89
11	InBr <sub>3</sub> (20)	CH <sub>2</sub> Cl <sub>2</sub>	4	90
		CHCl <sub>3</sub>	5	70
		1,4-dioxane	6	83
12	InBr <sub>3</sub> (10)	THF	8	61
		1,4-dioxane:H <sub>2</sub> O (3:1)	10	44
		MeOH	7	40
		H <sub>2</sub> O	12	trace

<sup>a</sup>Reaction conditions:  $\alpha$ -amido sulfone (1.0 mmol), heteroaromatic indole (1.1 mmol), and solvent (2.0 mL) at r.t. <sup>b</sup>Yield of isolated product after flash column chromatography.

**TABLE 2.** Friedel–Crafts Alkylation of Heteroaromatic Indoles with  $\alpha$ -Amido Sulfones Catalyzed by InBr<sub>3</sub><sup>a</sup>

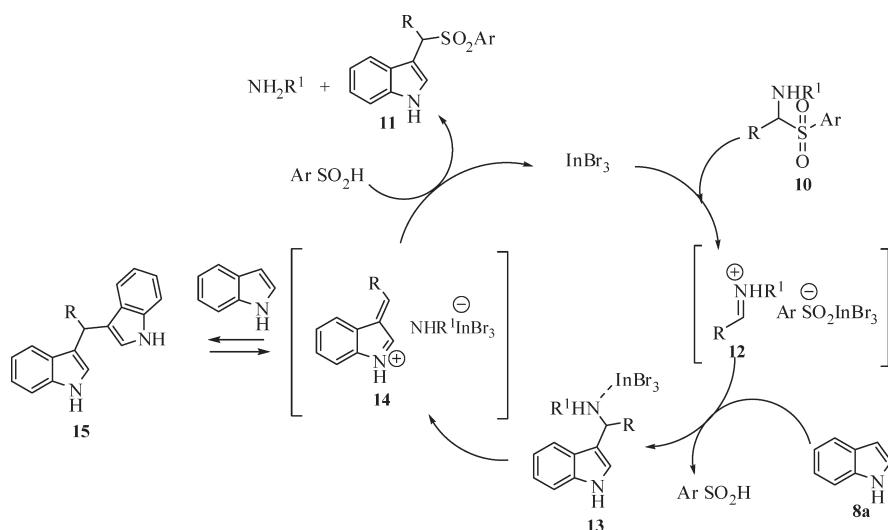
$\alpha$ -amido sulfone 10				indole 8	product 11	reaction time (h)	isolated yield (%) <sup>b</sup>
entry	R <sup>1</sup>	R	Ar				
1	Ph	CO <sub>2</sub> Et	4-MePh	8a	11a	6	83
2	Ph	CO <sub>2</sub> Et	4-MePh	8b	11b	6	76
3	Ph	CO <sub>2</sub> Et	4-MePh	8c	11c	7	80
4	Ph	CO <sub>2</sub> Et	4-MePh	8d	11d	6	78
5	Ph	CO <sub>2</sub> Et	4-MePh	8e	11e	7	75
6	Ph	CO <sub>2</sub> Et	Ph	8c	11f	7	78
7	Ph	CO <sub>2</sub> t-Butyl	4-MePh	8a	11a	6	61
8	Ph	CO <sub>2</sub> Bn	4-MePh	8a	11a	6	68
9	4-MePh	CO <sub>2</sub> Et	4-MePh	8a	11g	5	84
10	4-MeOPh	CO <sub>2</sub> Et	4-MePh	8a	11h	5	86
11	3-Me, 4-MeOPh	CO <sub>2</sub> Et	4-MePh	8a	11i	4	90
12	4-ClPh	CO <sub>2</sub> Et	4-MePh	8a	11j	6	83
13	3-ClPh	CO <sub>2</sub> Et	4-MePh	8a	11k	6	80
14	2-ClPh	CO <sub>2</sub> Et	4-MePh	8a	11l	7	76
15	C <sub>6</sub> H <sub>11</sub>	CO <sub>2</sub> Et	4-MePh	8a	11m	6	73

<sup>a</sup>Reaction conditions:  $\alpha$ -amido sulfone (1.0 mmol), indole (1.1 mmol), InBr<sub>3</sub> (0.1 mmol), and CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) at r.t. <sup>b</sup>Yield of isolated product after flash column chromatography.

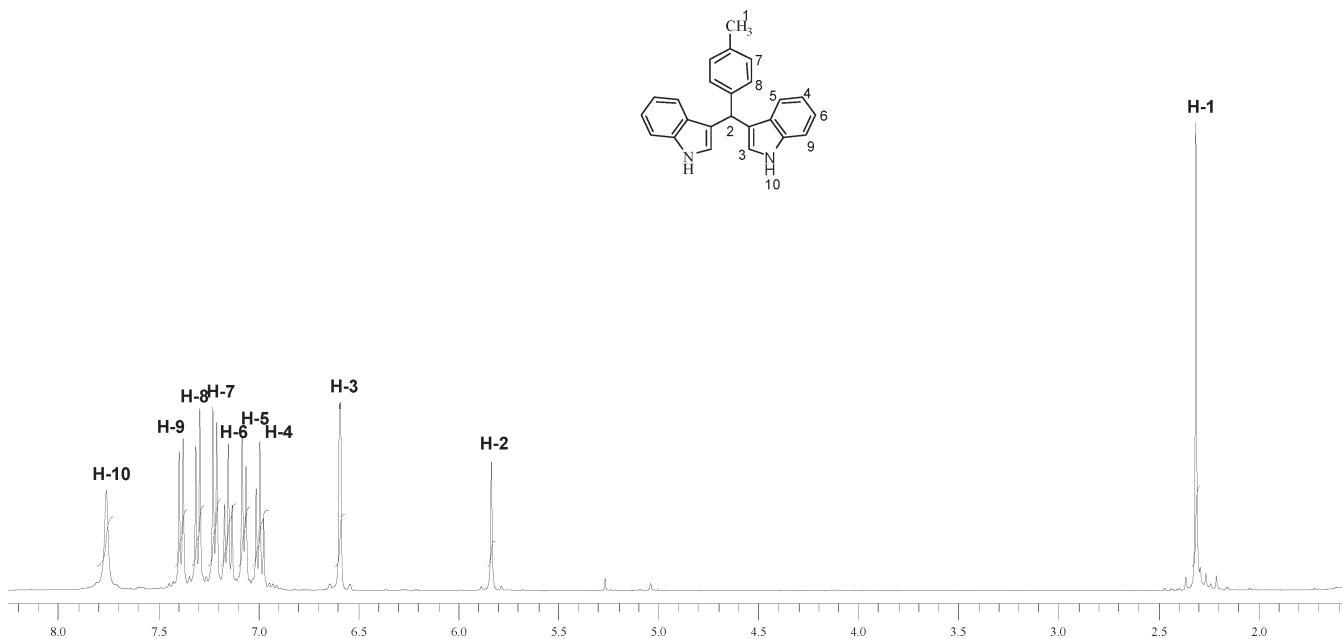
indole-6-carboxylate (entry 5) with  $\alpha$ -amido sulfone ( $R = \text{CO}_2\text{Et}$ , Ar = Ph, R<sup>1</sup> = Ph) produce corresponding 3-(1-arylsulfonylalkyl)indoles in 78% and 75% yield, respectively.

Indole 8a is used as a substrate to react with various  $\alpha$ -amido sulfones for the Friedel–Crafts alkylation reactions (Table 2, entries 7–15). The alkoxy group in the carbamoyl moiety in

$\alpha$ -amido sulfones plays an important role for the yield of product. Among the alkoxy groups OEt, O-*tert*-butyl, and OBn in  $\alpha$ -amido sulfones (entries 1, 6 and 7), the ethyloxy (OEt) group is found to give the best result (entry 1). The  $\alpha$ -amido sulfones with an electron-donating group attached to the benzene ring are able to undergo Friedel–Crafts alkylation



**FIGURE 1.** Plausible mechanism of InBr<sub>3</sub>-catalyzed Friedel–Crafts alkylation of  $\alpha$ -amido sulfones with indoles.



**FIGURE 2.** <sup>1</sup>H NMR of bis-indole 15 (R = 4-MePh).

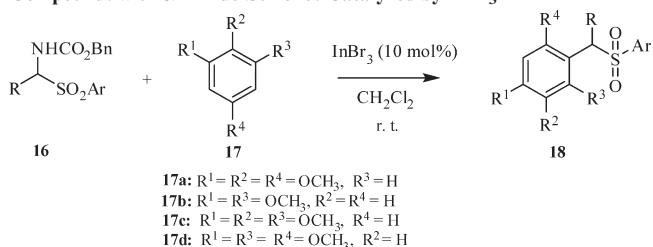
smoothly and generate the corresponding products in very good yield (entries 9–11). The reactions of *p*-, *m*-, and *o*-chloro- $\alpha$ -amido sulfones with indole 8a give the corresponding 3-(1-arylsulfonylalkyl)indoles in 83%, 80%, and 76% yield, respectively (entries 12–14). The *o*-chloro isomer indicates slight steric effects that are responsible for the lower yield (entry 14). Cyclohexyl  $\alpha$ -amido sulfone brings about the corresponding 3-(1-arylsulfonylalkyl)indole derivative in good yield (entry 15).

A plausible mechanism for the formation of 11 may start from the *N*-acyliminium ion 12 that is formed by elimination of arenesulfonic acid from the  $\alpha$ -amido sulfone 10 by the action of InBr<sub>3</sub>. Reaction of the strong electrophile 12 with indole 8a gives the Friedel–Crafts product 13 (Figure 1).

InBr<sub>3</sub> catalyzes the elimination of carbamate from 13 leading to the second iminium ion 14.<sup>25</sup> The iminium ion 14 then reacts with indole 8a in a second Friedel–Crafts reaction giving rise to bis-indole 15 through reversible reaction. Formation of bis-indole 15 has been observed during the course of the reaction that completely disappeared at the end of the reaction. After 1.0 h of reaction time 15 (R = 4-MePh) was isolated and characterized by NMR analysis (see Figure 2 and the Supporting Information). The arenesulfonic acid (ArSO<sub>2</sub>H) reacts with the second iminium ion 14 to afford the desired product 11 (Figure 1).

We have further examined the scope of the Friedel–Crafts alkylation reactions using  $\alpha$ -amido sulfones 16 with other electron-rich aromatic compounds 17 and the results are summarized in Table 3. The  $\alpha$ -amido sulfone (R = Ph, Ar = 4-MePh) was treated with 1,2,4-trimethoxybenzene 17a to afford the corresponding diarylsulfone 18a in excellent yield

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**TABLE 3.** Friedel–Crafts Alkylation of Electron-Rich Aromatic Compounds with  $\alpha$ -Amido Sulfones Catalyzed by  $InBr_3$ <sup>a</sup>

		$\alpha$ -amido sulfone 16		isolated yield (%) <sup>b,c</sup>	
entry	Ar	R	arene 17	product 18	
1	4-MePh	Ph	17a	18a	92
2	4-MePh	Ph	17b	18b	80
3	4-MePh	Ph	17c	18c	87
4	4-MePh	Ph	17d	18d	90
5	Ph	Ph	17a	18e	86
6	Ph	4-MeOPh	17a	18f	89
7	4-MePh	4-MePh	17a	18g	90
8	4-MePh	4-MeOPh	17a	18h	92
9	4-MePh	3,4-MeOPh	17a	18i	92
10	4-MePh	4-NO <sub>2</sub> Ph	17a	18j	87
11	4-MePh	4-ClPh	17a	18k	90
12	4-MePh	3-ClPh	17a	18l	87
13	4-MePh	2-ClPh	17a	18m	83
14	4-MePh	PhCH <sub>2</sub> CH <sub>2</sub>	17a	18n	85
15	4-MePh	C <sub>6</sub> H <sub>11</sub>	17a	18o	81
16	4-MePh	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub>	17a	18p	79

<sup>a</sup>Reaction conditions:  $\alpha$ -amido sulfone (1.0 mmol), aromatic compounds (1.1 mmol),  $InBr_3$  (0.1 mmol), and  $\text{CH}_2\text{Cl}_2$  (2.0 mL) at r.t. <sup>b</sup>Yield of isolated product after flash column chromatography. <sup>c</sup>All the reaction times were 2.5 h except for entries 2, 6, 11, and 14–16 that took 3.0 h.

(entry 1). The synthetic utility of the method is further demonstrated by the reaction of  $\alpha$ -amido sulfone ( $R = \text{Ph}$ ,  $\text{Ar} = 4\text{-MePh}$ ) with electron-rich aromatic compounds such as 1,3-dimethoxy-, 1,2,3-trimethoxy-, and 1,3,5-trimethoxybenzene for formation of aryl sulfones (entries 2–4). The reactions of various  $\alpha$ -amido sulfones containing electron-donating or electron-withdrawing groups attached to the benzene ring with 1,2,4-trimethoxybenzene produce (1-alkyl-1-aryl)methylphenyl or tolylsulfones in excellent yield (entries 5–13). The reactions of aralkyl, cyclic and acyclic aliphatic  $\alpha$ -amido sulfones with 1,2,4-trimethoxybenzene give the corresponding (1-alkyl-1-aryl)methyl tolylsulfones in 85%, 81%, and 79%, respectively (entries 14–16).

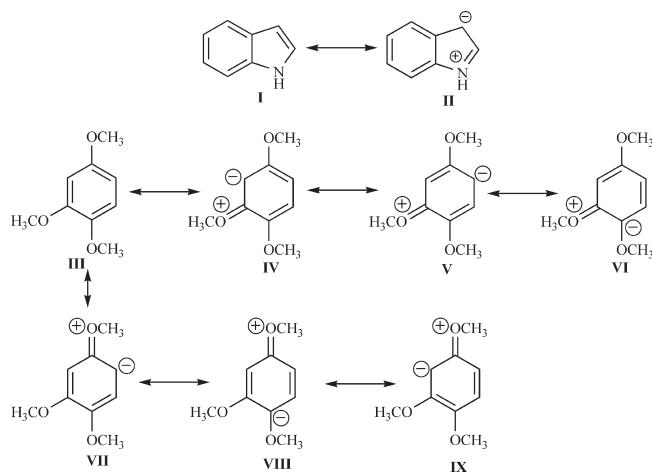
Table 4 shows the Friedel–Crafts alkylation reaction of diaryl sulfones with nucleophilic arene partners. Both heteroaromatic and electron-rich aromatic compounds prove to be very effective to afford the Friedel–Crafts substitution products in good yield as a single regioisomer. The reactions of diaryl sulfones **21** with heteroaromatic indole **22** give corresponding unsymmetrical triaryl methane in 68%, 61%, and 63% yield, respectively (entries 1–3). Similarly, unsubstituted, methoxy- and chloro-substituted diaryl sulfones were also reacted smoothly with 1,2,4-trimethoxybenzene to afford the corresponding bis-symmetrical triaryl methanes in good yield (entries 5–8). The reactions of *o*- and *p*-chloro diarylsulfones with 1,2,4-trimethoxybenzene gave corresponding products in 56% and 64% yield, respectively (entries 7 and 8). The *o*-chloro isomer shows less yield, which might be due to the steric and electronic effects of the chlorine substituent (entry 7).

We propose a plausible mechanism that could explain the formation of compounds **23** in the following manner (Figure 3).  $InBr_3$  catalyzes the formation of *N*-acyliminium ion **12** by elimination of arenesulfinic acid ( $\text{ArSO}_2\text{H}$ ) from the  $\alpha$ -amido sulfones **10**. Reaction of the strong electrophiles **12** with electron-rich arene **17** gives the Friedel–Crafts products **24**. The elimination of carbamate from **24** by  $InBr_3$  may lead to formation of oxonium ions **25**. The oxonium ions **25** can react with arenesulfinic acid ( $\text{ArSO}_2\text{H}$ ) to produce the diaryl sulfones **18**. The diaryl sulfones **18** in presence of  $InBr_3$  result in the second oxonium ions **26** that react with indole **8** in a second Friedel–Crafts reaction to afford triaryl methanes **23**.<sup>26,27</sup>

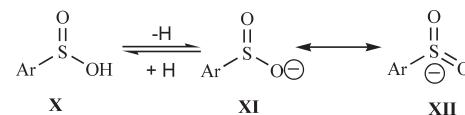
### Conclusion

In conclusion, we have demonstrated  $InBr_3$ -catalyzed Friedel–Crafts alkylations of heteroaromatic or electron-rich aromatic compounds with  $\alpha$ -amido sulfones. The catalyst system also allows a controlled double electrophilic aromatic substitution that provides access to unsymmetrical and bis-symmetrical triaryl methanes with wide structural diversity.  $\alpha$ -Amido sulfones are employed for the first time in the synthesis of the unsymmetrical and bis-symmetrical triaryl methanes. Further investigation of the reaction under other reaction conditions is currently in progress.

(26) The electron-rich arene (e.g., indole or 1,2,4-trimethoxybenzene) having various resonance structures (**I** to **X**). The active resonance structures are **II**, **V**, and **VII** for the addition reaction.

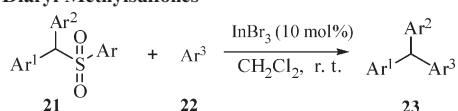


The deprotonation of arenesulfinic acid (**X**) leads to the formation of sulfinate ion. This shows two resonance structures, *O*-sulfinate (**XI**) and *S*-sulfinate (**XII**). The *S*-sulfinate (**XII**) could be more nucleophilic than *O*-sulfinate (**XI**).



In the synthesis of triaryl methanes, the addition of carbanion (**II** or **V**) derived from electron-rich arene is more favorable than *S*-sulfinate (**XII**) from arenesulfinic acid. This may be due to the higher nucleophilicity of the **II** or **V**.

(27) Kice, J. C.; Large, G. B. *J. Am. Chem. Soc.* **1968**, 90, 4069.

TABLE 4. Synthesis of Triaryl Methanes from Diaryl Methylsulfones<sup>a,b</sup>

$\text{Ar} = \text{Ph}, 4\text{-MePh} \quad \text{Ar}^1 = \text{Aryl}$   
 $\text{Ar}^2 = \text{Ar}^3 = \text{Electron-rich aromatic or heteroaromatic indole compounds}$

entry	diaryl sulfone 21			$\text{Ar}^3 \text{ 22}$	product 23	isolated yields (%) <sup>c</sup>
	Ar	$\text{Ar}^1$	$\text{Ar}^2$			
1	Ph	4-MeOPh	1,2,4-(OCH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	indole	23a	68
2	4-MePh	4-MeOPh	1,2,4-(OCH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	indole	23a	61
3	4-MePh	4-MeOPh	indole	1,2,4-(OCH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	23a	63
4	Ph	Ph	1,2,4-(OCH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	1,2,4-(OCH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	23b	65
5	4-MePh	Ph	1,2,4-(OCH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	1,2,4-(OCH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	23b	59
6	4-MePh	4-MeOPh	1,2,4-(OCH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	1,2,4-(OCH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	23c	67
7	4-MePh	2-ClPh	1,2,4-(OCH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	1,2,4-(OCH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	23d	56 <sup>d</sup>
8	4-MePh	4-ClPh	1,2,4-(OCH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	1,2,4-(OCH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	23e	64

<sup>a</sup>Reaction conditions: diaryl sulfone (1.0 mmol), heteroaromatic indole or electron-rich aromatic compound (1.1 mmol), InBr<sub>3</sub> (0.1 mmol), and CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) at r.t. <sup>b</sup>Reaction time is 6.0 h. <sup>c</sup>Yield of isolated product after flash column chromatography. <sup>d</sup>Isolated yield after 7.0 h of reaction time.

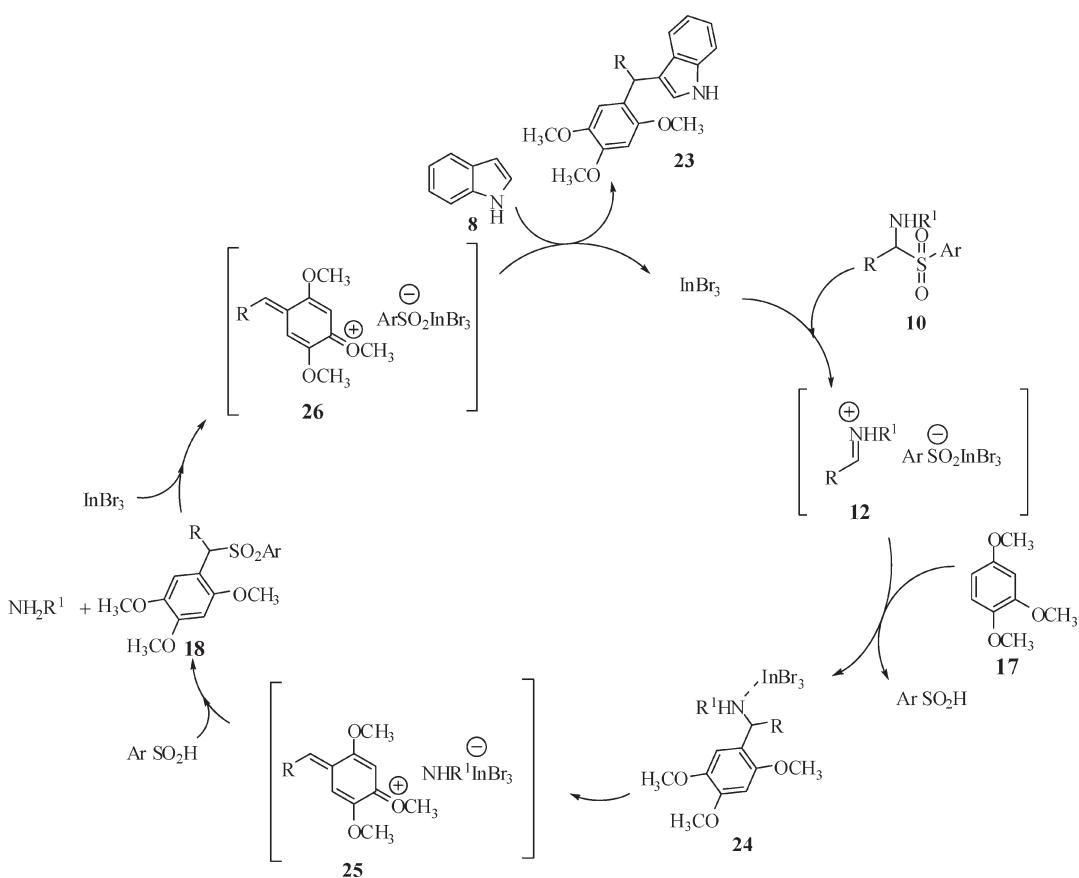


FIGURE 3. Plausible mechanism of InBr<sub>3</sub>-catalyzed Friedel-Crafts alkylation of  $\alpha$ -amido sulfone with electron-rich aromatic compounds and synthesis of triarylmethanes.

## Experimental Section

### A. Experimental Procedure for the Friedel-Crafts Alkylation of Heteroaromatic or Electron-Rich Aromatic Compounds.

InBr<sub>3</sub> (10 mol %) was added to a solution of  $\alpha$ -amido sulfones (1 mmol) and heteroaromatic indoles or electron-rich aromatic compounds in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) under nitrogen. The mixture was stirred at r.t. and the reaction was monitored by

TLC. After completion, the reaction was quenched with distilled water (5 mL) and the mixture was extracted with EtOAc (5 mL). The combined organic portions were washed with water (5 mL) and saturated aqueous NH<sub>4</sub>Cl (5 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum. The crude product was subjected to flash column chromatography (silica gel, hexane-EtOAc, 4:1 to 3:1) to obtain the pure product.

**11a:** brown solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.63 (d,  $J = 6.5$  Hz, 1H), 7.56 (s, 1H), 7.50–7.40 (m, 5H), 7.23–7.19 (m, 4H), 7.06–6.99 (m, 4H), 5.68 (s, 1H), 2.25 (s, 3H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  144.3, 135.4, 135.1, 133.4, 130.0, 129.2, 129.1, 128.8, 128.3, 126.9, 124.9, 122.2, 119.8, 118.1, 111.5, 106.8, 69.0, 21.4.<sup>7</sup>

**18a:** white solid, mp 110–111 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 7.2$  Hz, 1H), 7.64 (d,  $J = 7.5$  Hz, 2H), 7.56 (d,  $J = 7.5$  Hz, 2H), 7.36–7.33 (m, 3H), 7.19 (d,  $J = 7.2$  Hz, 2H), 6.62 (d,  $J = 7.5$  Hz, 1H), 6.32 (s, 1H), 6.03 (s, 1H), 3.82 (s, 3H), 3.54 (s, 3H), 2.40 (s, 3H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  160.9, 157.9, 144.1, 136.0, 133.7, 130.8, 130.2, 129.0, 128.5, 128.2, 114.3, 104.7, 98.3, 66.4, 55.4, 55.3, 21.6; HRMS-EI ( $m/z$ ) [M]<sup>+</sup> calcd for  $\text{C}_{22}\text{H}_{22}\text{O}_4\text{S}$  382.1239, found 382.1263.

**B. Experimental Procedure for the Synthesis of Triaryl Methanes.** To a mixture of diaryl sulfone (1 mmol) and heteroaromatic indole or electron-rich aromatic compound (1.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) under nitrogen,  $\text{InBr}_3$  (10 mol %) was added and stirred for 6.0 h at r.t. The progress of the reaction mixture was monitored by TLC. After completion of the reaction, the mixture was quenched with distilled water (5 mL) and then extracted with EtOAc (5 mL). The combined organic portions were washed with water (5 mL) and saturated

aqueous  $\text{NH}_4\text{Cl}$  (5 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated under vacuum. The crude product was subjected to flash column chromatography (silica gel, hexane–EtOAc, 4:1 to 3:1) to obtain the pure product.

**23a:** white solid, mp 179–180 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (br s, 1H), 7.31 (d,  $J = 7.2$  Hz, 1H), 7.25 (d,  $J = 7.2$  Hz, 1H), 7.13 (d,  $J = 7.6$  Hz, 3H), 6.99 (t,  $J = 7.4$  Hz, 1H), 6.80 (d,  $J = 7.2$  Hz, 2H), 6.61 (s, 1H), 6.58 (d,  $J = 7.6$  Hz, 1H), 5.98 (s, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 3.74 (s, 3H), 3.59 (s, 3H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  157.7, 151.2, 147.9, 142.9, 136.8, 136.4, 129.7, 127.1, 124.7, 123.8, 121.9, 120.2, 120.1, 119.2, 114.3, 113.4, 111.0, 98.2, 57.0, 56.6, 56.1, 55.2, 40.0; HRMS-EI ( $m/z$ ) [M]<sup>+</sup> calcd for  $\text{C}_{25}\text{H}_{25}\text{NO}_4$  403.1784, found 403.1786.

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**Supporting Information Available:** Experimental procedure and characterization data of compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.