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Friedel−Crafts Arylation Reactions of *N*-Sulfonyl Aldimines or Sulfonamidesulfones with Electron-Rich Arenes Catalyzed by $FeCl_3 \cdot 6H_2O$: Synthesis of Triarylmethanes and Bis-heteroarylarylmethanes

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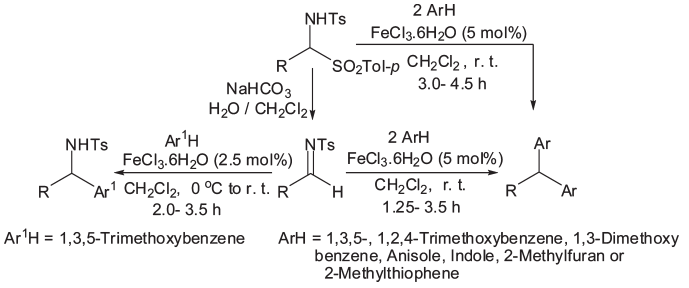

The $FeCl_3 \cdot 6H_2O$-catalyzed Friedel−Crafts arylation reactions of *N*-sulfonyl aldimines or sulfonamidesulfones with electron-rich arenes and heteroarenes, which lead to the formation of triarylmethanes and bis-heteroarylarylmethanes, are developed. The use of mild reaction conditions, low catalytic loading, high yield, and single step synthesis are the advantages of the present procedure.

Introduction

Friedel−Crafts alkylation is one of the most important C−C bond-forming reactions in organic chemistry.[1,2] These reactions are usually assisted by either protic acid or Lewis acid catalyst. The Friedel−Crafts arylation reactions of carbonyl compounds,[3] epoxides,[4] and electron-deficient olefins[5] as substrates have been extensively studied. The same reactions with imine substrates are completely atom-economical access to obtain functionalized molecules, which are potential starting materials for many biologically active compounds. However, the study of the Lewis acid-catalyzed Friedel−Crafts arylation of imines is limited to synthesis of 3-substituted indole derivatives.[6] Very recently You and co-workers report an enantioselective synthesis of unsymmetriacal triarylmethanes by chiral phosphoric acid.[6d] Tian and co-workers have demonstrated the formation of bis-arylation of imines with $Bi_2(SO_4)_3$-TMSCl.[7] Triarylmethanes and bis-heteroarylarylmethanes have been prepared by using Lewis acid- or protic acid-catalyzed Friedel−Crafts arylation reactions of aldehydes with electron-rich arenes and

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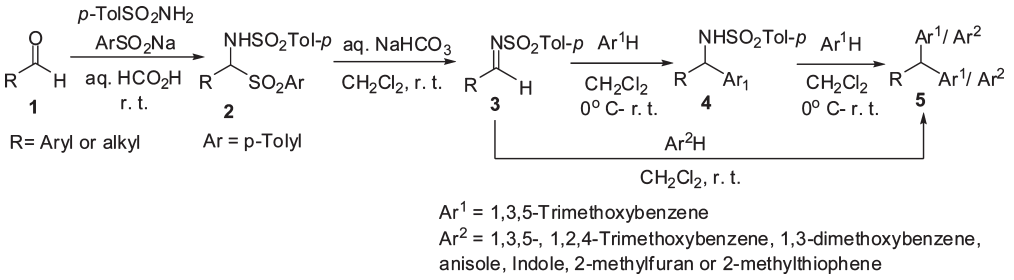
SCHEME 1. General Preparation Method for the Synthesis of *N*-Sulfonyl Aldimines and Triarylmethanes



Ar^1 = 1,3,5-Trimethoxybenzene
Ar^2 = 1,3,5-, 1,2,4-Trimethoxybenzene, 1,3-dimethoxybenzene, anisole, Indole, 2-methylfuran or 2-methylthiophene

heteroarenes.[8] The alcohols[9] and α-amido sulfones[10] are also utilized for the Friedel−Crafts arylation reactions for the preparation of triarylmethanes and bis-heteroarylarylmethane.

However, many of these methods are associated with one or more drawbacks such as elevated temperature, long reaction time, and multistep process with low yields. In continuation of the development of useful synthetic methodology for C−C bond forming reactions,[9c,10,11] we report herein an efficient $FeCl_3 \cdot 6H_2O$-catalyzed synthesis of triarylmethanes and bis-heteroarylarylmethanes by Friedel−Crafts alkylation reactions of *N*-sulfonyl aldimines or sulfonamidesulfones. Iron salts have attracted attention from synthetic organic chemists since iron is one of the most abundant metals. Many iron salts are inexpensive and commercially available.[12] These iron salts have been found to show promising catalytic ability in many organic transformations including Friedel−Crafts arylation reactions.[12a,g−j] Friedel−Crafts arylation reactions of electron-rich arenes are a well-known process for the formation of the C−C bond from the aromatic C−H bond.[2]

The triarylmethanes, bis-heteroarylarylmethanes, and diarylalkanes have attracted considerable attention[13] due to biological activity as antiviral,[14] antitumor,[15] antitubercular,[9a,16] antifungal,[17] and anti-inflammatory agents.[17] Moreover, these compounds have found widespread application in synthetic, medicinal, and industrial chemistry.[18] The triarylmethyl derivatives are useful as protective groups,[19] photochromic agents,[20] and dyes.[21] Ring-hydroxylated triarylmethanes exhibit antitumor and antioxidant activities.[8a] Moreover, diheteroarylmethanes are of interest for the food industry as natural components of certain food and beverage items as well as flavor agents in coffee.[22]

Result and Discussion

We have directed our studies toward the synthesis of triarylmethanes and bis-heterotriarylarylmethanes from *N*-sulfonyl aldimines by Friedel−Crafts arylation reactions. The *N*-sulfonyl aldimines (**3**) were prepared from the condensation of aldehydes (**1**), sulfonamides, and sodium salt of arenesulfinic acid to produce the sulfonamidesulfone (**2**) followed by treatment with saturated aq $NaHCO_3$ (Scheme 1).[23]

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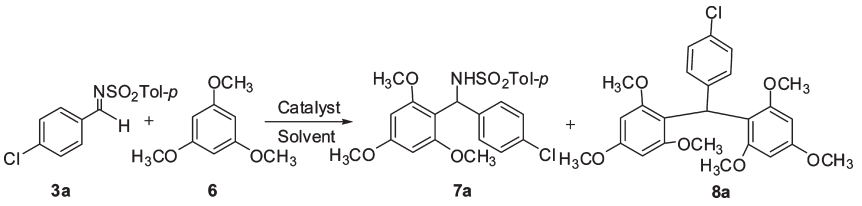
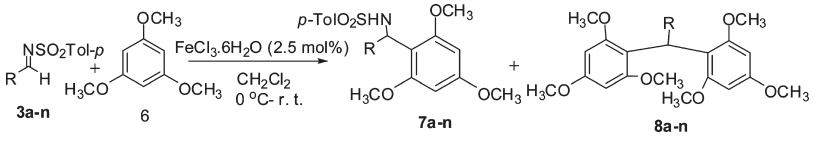
TABLE 1. Optimization of the Reaction Conditions for Friedel−Crafts Arylation Reactions of *N*-Tosyl(4-chlorobenzylidene)-4-methylbenzenesulfonamide with 1,3,5-Trimethoxybenzene[a]



					yield (%)[b]	
entry	catalyst (mol %)	solvent	reaction time (h)	reaction temp (°C)	**7a**	**8a**
1		CH_2Cl_2	16	rt	NR	NR
2	CuI (10)	CH_2Cl_2	12	rt	NR	NR
3	$RhI_3 \cdot H_2O$ (10)	CH_2Cl_2	12	rt	NR	NR
4	$BiCl_3$ (10)	CH_2Cl_2	12	rt	49	0
5	$Fe(acac)_3$ (10)	CH_2Cl_2	5.0	rt	37	0
6	$Fe(NO_3)_3 \cdot 9H_2O$ (10)	CH_2Cl_2	5.0	rt	37	0
7	$Fe(ClO_4)_3 \cdot xH_2O$ (10)	CH_2Cl_2	4.0	rt	78	10
8	$FeCl_2 \cdot 4H_2O$ (10)	CH_2Cl_2	5.0	rt	48	0
9	$FeCl_3 \cdot 6H_2O$ (10)	CH_2Cl_2	2.0	rt	83	13
10	$FeCl_3$ (10)	CH_2Cl_2	2.0	rt	82	7
11	$FeBr_3$ (10)	CH_2Cl_2	3.0	rt	80	10
12	$FeCl_3 \cdot 6H_2O$ (5)	CH_2Cl_2	2.0	rt	86	10
13	$FeCl_3 \cdot 6H_2O$ (2.5)	CH_2Cl_2	2.0	rt	88	7
14	$FeCl_3 \cdot 6H_2O$ (2.5)	CH_2Cl_2	2.0	0−rt	90	4
15	$FeCl_3 \cdot 6H_2O$ (2.5)	CH_2Cl_2	4.5	0	27	0
16	$FeCl_3 \cdot 6H_2O$ (2.5)	CH_2Cl_2	4.5	−10	NR	NR
17	$FeCl_3 \cdot 6H_2O$ (2.5)	$CHCl_3$	3.5	0−rt	78	11
18	$FeCl_3 \cdot 6H_2O$ (2.5)	CH_3CN	2.5	0−rt	89	7
19	$FeCl_3 \cdot 6H_2O$ (2.5)	CH_3OH	3.5	0−rt	60	16
20	$FeCl_3 \cdot 6H_2O$ (2.5)	THF	4.0	0−rt	47	14
21	$FeCl_3 \cdot 6H_2O$ (2.5)	CH_3NO_2	2.5	0−rt	79	15

[a]Reaction condition: *N*-tosyl(4-chlorobenzylidene)-4-methylbenzenesulfonamide (1.0 mmol) and 1,3,5-trimethoxybenzene (1.0 mmol) are used. [b]Yield of isolated product after column chromatography.

TABLE 2. Friedel−Crafts Arylation Reactions of Various *N*-Sulfonyl Aldimines with 1,3,5-Trimethoxybenzene[a]



			yield (%)[b]	
entry	R in **3**	reaction time (h)	**7**	**8**
1	**3a**, 4-ClC_6H_4	2.0	**7a**, 90	**8a**, 4
2	**3b**, 3-ClC_6H_4	3.0	**7b**, 88	**8b**, 6
3	**3c**, 2-ClC_6H_4	3.5	**7c**, 84	**8c**, 5
4	**3d**, 4-BrC_6H_4	2.0	**7d**, 91	**8d**, 0
5	**3e**, C_6H_5	2.5	**7e**, 87	**8e**, 5
6	**3f**, 4-$NO_2C_6H_4$	3.5	**7f**, 87	**8f**, 4
7	**3g**, 4-CNC_6H_4	3.5	**7g**, 89	**8g**, 6
8	**3h**, 3-CNC_6H_4	3.5	**7h**, 86	**8h**, 4
9	**3i**, 4-$MeOC_6H_4$	2.0	**7i**, 82	**8i**,14
10	**3j**, 4-MeC_6H_4	2.0	**7j**, 90	**8j**, 0
11	**3k**, 2-furanyl	2.0	**7k**,86	**8k**, 0
12	***3l***, 2-pyridinyl	3.0	***7l***, 81	***8l***, 0
13	**3m**, $C_6H_5CH_2CH_2$	2.5	**7m**, 85	**8m**, 0
14	**3n**, $(CH_3)_2CH$	2.5	**7n**, 78	**8n**, 0

[a]Reaction condition: *N*-sulfonyl aldimines (1.0 mmol) and 1,3,5-trimethoxybenzene (1.0 mmol) are used at 0 °C−rt. [b]Yield of isolated product after column chromatography.

The reaction between *N*-tosyl(4-chlorobenzylidene)-4-methylbenzenesulfonamide **3a** and 1,3,5-trimethoxybenzene **6** for 16 h in the absence of catalyst did not take place at all (entry 1). The reactions have been screened in the presence of various Lewis acids such as CuI, $RhI_3 \cdot H_2O$, $BiCl_3$, $Fe(acac)_3$, $Fe(NO_3)_3 \cdot 9H_2O$, $Fe(ClO_4)_3 \cdot XH_2O$, $FeCl_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$, $FeCl_3$, and $FeBr_3$ (entries 2−10). By considering the amount of catalyst, the reaction time, and the yield, $FeCl_3 \cdot 6H_2O$ (2.5 mol %) is suitable for the reaction (entry 13). The temperature effect on the reaction is studied in CH_2Cl_2 (entries

13−16). The reaction carried out at 0 °C−rt is found to be the most effective (entry 14). The effect of various solvents is tested (entries 14 and 17−21). CH_2Cl_2 is found to be the solvent of choice in terms of yield and reaction time (entry 14) (Table 1).

The scope of the Friedel−Crafts arylation reactions of various *N*-sulfonyl aldimines with 1,3,5-trimethoxybenzene is evaluated and the results are summarized in Table 2. The reaction of *N*-tosyl(4-chlorobenzylidene)-4-methylbenzenesulfonamide (**3a**) with 1,3,5-trimethoxybenzene (**6**) produces the arylation product **7a** in 90% yield, along with 4% of triarylmethane **8a** (entry 1). *N*-Tosyl(3-chlorobenzylidene)- (**3b**), *N*-tosyl(2-chlorobenzylidene)- (**3c**), and *N*-tosyl(4-bromobenzylidene)-4-methylbenzenesulfonamide (**3d**) react with 1,3,5-trimethoxybenzene (**6**) to afford the arylation products in 88%, 84%, and 91%, respectively (entries 2−4). The reaction of *N*-tosyl(benzylidene)-4-methylbenzenesulfonamide (**3e**) with 1,3,5-trimethoxybenzene (**6**) gave the product **7e** (entry 5). The reaction of *N*-sulfonyl aldimines bearing electron-withdrawing groups on the phenyl ring proceeded smoothly to give the arylation products in good yields (entries 6−8). *N*-Sulfonyl aldimines with an electron-donating group on the phenyl ring react with 1,3,5-trimethoxybenzene (**6**) to obtain **7i** and **7j** in 82% and 90% yield, respectively (entries 9 and 10). Conspicuously there is hardly any substituent electronic effect on the Friedel−Crafts arylation reactions (compare the yield of entries 6−10). 2-Furanyl (**3k**) and 2-pyridinyl *N*-sulfonyl aldimines (**3*l***) exhibit similar reactivity toward the arylations (entries 11 and 12). The reactions of aralkyl (**3m**) and aliphatic *N*-sulfonyl aldimines (**3n**) give the corresponding products in 85% and 78%, respectively (entries 13 and 14). The pure aliphatic structure without benzene ring (entry 14) appears to yield a little lower yield.

A plausible mechanism for the formation of **7** and **8** is proposed in Figure 1. The first step is the formation of **A**, which is formed by coordination of the *N*-sulfonyl aldimines **3** to Fe(III) ion. *N*-Sulfonyl aldimine **3** is activated by Fe(III) ion to give more electrophilicity at the imine carbon of **A**. The nucleophilic carbon of 1,3,5-trimethoxybenzene **6** attacks on the imine carbon of **A** leading to the formation of the Fredel−Crafts product **7**. Again the Fe(III) ion forms coordination with the nitrogen atom to produce **B**. Subsequently the elimination of *p*-tolylsulfanimide from **B** and Fe(III) ion leads to the formation of oxonium ion **C**. Oxonium ion **C** then reacts with 1,3,5-trimethoxybenzene **6** giving rise to the formation of triarylmethane **8**.[10b]

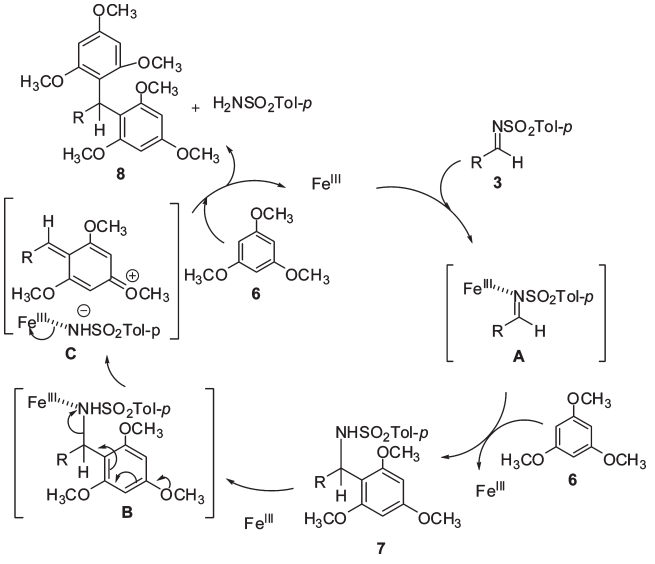
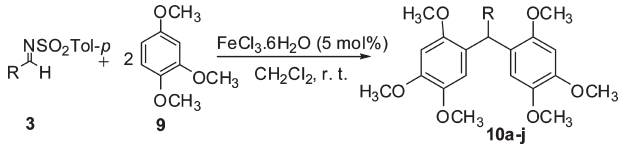


FIGURE 1. Plausible mechanism of $FeCl_3 \cdot 6H_2O$-catalyzed Friedel−Crafts arylation of *N*-sulfonyl aldimines with 1,3,5-trimethoxybenzene.

TABLE 3. Synthesis of Triarylmethanes from *N*-Sulfonyl Aldimines and 1,2,4-Trimethoxybenzene[a]



entry	R in **3**	product **10**	reaction time (h)	yield (%)[b]
1	**3e**, C_6H_5	**10a**	2.5	76
2	**3i**, 4-$MeOC_6H_4$	**10b**	2.0	88
3	**3o**, 3,4-$(MeO)_2C_6H_3$	**10c**	2.0	90
4	**3j**, 4-MeC_6H_4	**10d**	2.0	85
5	**3d**, 4-BrC_6H_4	**10e**	2.5	86
6	**3a**, 4-ClC_6H_4	**10f**	2.5	85
7	**3b**, 3-ClC_6H_4	**10g**	2.5	82
8	**3c**, 2-ClC_6H_4	**10h**	2.5	78
9	**3h**, 3-CNC_6H_4	**10i**	3.0	80
10	**3g**, 4-CNC_6H_4	**10j**	3.0	83

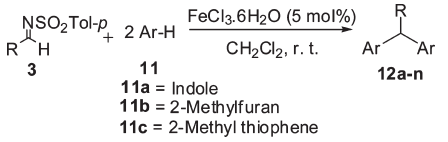
[a]Reaction condition: *N*-sulfonyl aldimines (1.0 mmol) and 1,2,4-trimethoxybenzene (2.0 mmol) are used. [b]Yield of isolated product after column chromatography.

The Friedel−Crafts arylation reactions of *N*-sulfonyl aldimines with 1,2,4-trimethoxybenzene generate the triarylmethanes (Table 3). Recently Deutsch and co-workers have demonstrated the synthesis of triarylmethanes through amidoalkylation of arenes in two steps with poor yield (18−22%).[24] Previously we have also reported the synthesis of triarylmethanes from α-amido sulfones in two steps with moderate yield (56−67%).[10a,b] We are herein reporting the one-step synthesis of triarylmethanes using *N*-sulfonyl aldimines (**3**). The reaction of *N*-tosyl(benzylidene)-4-methylbenzenesulfonamide (**3e**) with 1,2,4-trimethoxybenzene (**9**) affords **10a** in 76% yield (entry 1). *N*-Tosyl(4-methoxybenzylidene)- (**3i**), *N*-tosyl(3,4-dimethoxybenzylidene)- (**3o**), and *N*-tosyl(4-methylbenzylidene)-4-methylbenzenesulfonamide (**3j**) react with 1,2,4-trimethoxybenzene (**11**) to give the triarylmethanes in 88%, 90%, and 85%, respectively (entries 2−4). The reactions of *N*-sulfonyl aldimines (**3**) containing halogen groups of chlorine and bromine on the phenyl ring proceed smoothly to produce **10e**, **10f**, **10g**, and **10h** (entries 5−8). Interestingly, *N*-tosyl(3-cyanobenzylidene)- (**3h**) and *N*-tosyl(4-cyanobenzylidene)-4-methylbenzenesulfonamide (**3g**) treated with 1,2,4-trimethoxybenzene (**9**) produce the triarylmethanes in 80% and 83%, respectively (entries 9 and 10). The present method is equally applicable for both electron-donating as well as electron-withdrawing substrates for a similar yield of triarylmethanes. This method shows better yield in "one-step" compared to the "two-step" synthesis.[10a,b,24]

The Friedel−Crafts arylation reactions of *N*-sulfonyl aldimines with various electron-rich heteroarenes are examined (Table 4). The *N*-tosyl(benzylidene)-4-methylbenzenesulfonamide (**3e**) is treated with indole (**11a**) in the presence of 5.0%

(24) Deutsch, J.; Checinski, M.; Kockritz, A.; Beller, M. *Catal. Commun.* **2009**, *10*, 373.

TABLE 4. Synthesis of Bis-heterotriarylarylmethanes from *N*-Sulfonyl Aldimines and Electron-Rich Heteroarenes[a]



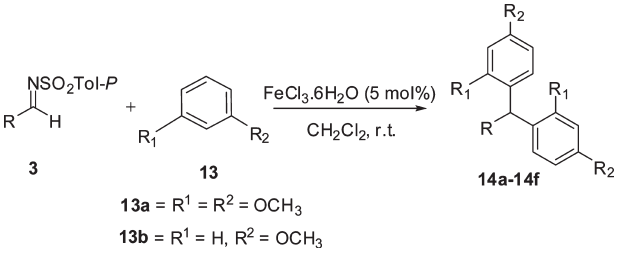
entry	R in **3**	**11**	product **12**	reaction time (h)	yield (%)[b]
1	**3e**, C_6H_5	**11a**	**12a**	2.5	88
2	**3e**, C_6H_5	**11b**	**12b**	2.0	90
3	**3e**, C_6H_5	**11c**	**12c**	2.5	82
4	**3i**, 4-$MeOC_6H_4$	**11a**	**12d**	2.0	87
5	**3p**, 4-MeO-3-MeC_6H_3	**11a**	**12e**	2.5	86
6	**3j**, 4-MeC_6H_4	**11a**	**12f**	2.0	84
7	**3a**, 4-ClC_6H_4	**11a**	**12g**	2.5	82
8	**3i**, 4-$MeOC_6H_4$	**11b**	**12h**	2.0	92
9	**3j**, 4-MeC_6H_4	**11b**	**12i**	2.0	90
10	**3d**, 4-BrC_6H_4	**11b**	**12j**	2.0	87
11	**3b**, 3-ClC_6H_4	**11b**	**12k**	3.0	85
12	**3h**, 3-CNC_6H_4	**11b**	**12l**	3.0	78
13	**3g**, 4-CNC_6H_4	**11b**	**12m**	3.0	80
14	**3n**, $(CH_3)_2CH$	**11b**	**12n**	3.0	71

[a]Reaction condition: *N*-sulfonyl aldimines (1.0 mmol) and heteroarene (2.0 mmol) are used. [b]Yield of isolated product after column chromatography.

$FeCl_3 \cdot 6H_2O$. The reaction was taking place to produce bis-heteroarylarylmethane **12a** in 88% yield (entry 1). The reactions of *N*-tosyl(benzylidene)-4-methylbenzenesulfonamide (**3e**) with 2-methylfuran (**11b**) or 2-methylthiopene (**11c**) give bis-heteroarylarylmethanes (entries 2 and 3). Similarly, *N*-tosyl-(4-methoxybenzylidene)- (**3i**), *N*-tosyl(4-methoxy-3-methylbenzylidene)- (**3p**), *N*-tosyl(4-methylbenzylidene)- (**3j**) and *N*-tosyl(4-chlorobenzylidene)-4-methylbenzenesulfonamide (**3a**) react smoothly with indole (**11a**) to generate **12d**, **12e**, **12f**, and **12g**, respectively (entries 4−7). The reactions of *N*-tosyl(4-methoxybenzylidene)- (**3i**), *N*-tosyl(4-methylbenzylidene)- (**3j**), *N*-tosyl(4-bromobenzylidene)- (**3d**), and *N*-tosyl(3-chlorobenzylidene)-4-methylbenzenesulfonamide (**3b**) with 2-methylfuran (**11b**) were taking place to yield the products in 92%, 90%, 87%, and 85% yield, respectively (entries 8−11). The reactions of *N*-sulfonyl aldimines (**3h** and **3g**) bearing an electron-withdrawing group on the phenyl ring proceed smoothly to yield the bis-heteroarylarylmethanes (entries 12 and 13). The presence of a strongly electron-withdrawing group such as a cyano group in R more or less reduces the yield. The isobutaryl group in *N*-sulfonyl aldimine (**3n**) significantly decreases the yield of diarylalkane **12n** to 71% (entry 14).

The Friedel−Crafts arylation reactions of *N*-sulfonyl aldimines with less activated arenes such as 1,3-dimethoxybenzene and anisole are examined and the results are summarized in Table 5. The reaction of *N*-tosyl(benzylidene)-4-methylbenzenesulfonamide (**3e**) with 1,3-dimethoxybenzene (**13a**) was completed to afford **14a** in 55% yield

TABLE 5. Friedel−Crafts Arylation of *N*-Sulfonyl Aldimines with 1,3-Dimethoxybenzene and Anisole[a]



entry	R in **3**	**13**	product **14**	reaction time (h)	yield (%)[b]
1	**3e**, C_6H_5	**13a**	**14a**	2.0	55
2	**3j**, 4-MeC_6H_4	**13a**	**14b**	2.0	61
3	**3a**, 4-ClC_6H_4	**13a**	**14c**	2.0	58
4	**3b**, 3-ClC_6H_4	**13a**	**14d**	2.0	54
5	**3f**, 4-$NO_2C_6H_4$	**13a**	**14e**	3.0	52
6	**3e**, C_6H_5	**13b**	**14f**	6.0	53

[a]Reaction condition: *N*-sulfonyl aldimines (1.0 mmol) and **13** (2.0 mmol) are used. [b]Yield of isolated product after column chromatography.

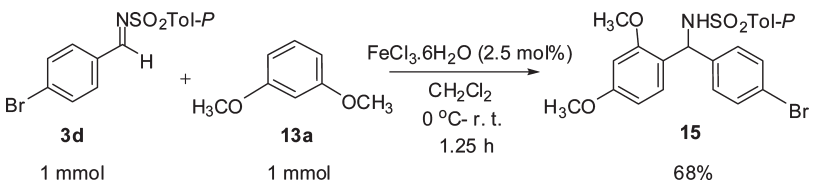
(entry 1). *N*-Tosyl(4-methylbenzylidene)- (**3j**), *N*-tosyl(4-chlorobenzylidene)- (**3a**), *N*-tosyl(3-chlorobenzylidene)- (**3b**), and *N*-tosyl(4-nitrobenzylidene)-4-methylbenzenesulfonamide (**3f**) were treated with 1,3-dimethoxybenzene (**13a**) to produce the corresponding triarylmethanes (entries 2−5). Similarly, *N*-tosyl(benzylidene)-4-methylbenzenesulfonamide (**3e**) also reacts with anisole (**13b**) to afford the regioselctive triarylmethane (entry 6).

The reaction of *N*-tosyl(4-bromobenzylidene)-4-methylbenzenesulfonamide (**3d**) with 1,3-dimethoxybenzene (**13a**) in the presence of 2.5 mol % of $FeCl_3 \cdot 6H_2O$ produces the alkylation product **15** in 68% yield (Scheme 2).

The Friedel−Crafts arylation reactions of various sulfonamidesulfones (precursors of *N*-sulfonyl aldimines) with 1,2,4-trimethoxybenzene or 2-methylfuran were examined (Scheme 2). 4-Methyl-*N*-(phenyl(tosyl)methyl)sulfonamide (**16a**) is treated with 1,2,4-trimethoxybenzene (**9**) for 4.5 h to produce **10a** in 58% yield. The reactions of *N*-(4-methoxyphenyl(tosyl)methyl)- (**16b**) with 4-methyl-*N*-(*p*-tolyl(tosyl)-methyl)benzenesulfonamide (**16c**) bring about the triarylmethanes in good yield. Similarly, 4-methyl-*N*-(phenyl(tosyl)-methyl)- (**16a**), *N*-(4-methoxyphenyl(tosyl)methyl)- (**16b**), 4-methyl-*N*-(*p*-tolyl(tosyl)methyl)- (**16c**), and 4-methyl-*N*-(4-bromophenyl(tosyl)methyl)benzenesulfonamide (**16d**) underwent reaction smoothly with 2-methylfuran (**11b**) to afford the **12b**, **12i**, **12j**, and **12k** in 65%, 71%, 70%, and 67% yield, respectively (Scheme 3).

To investigate the applications and advantages of mono-Friedel−Crafts arylation of *N*-sulfonyl aldimines with electron-rich arenes, we focused on the one-pot synthesis of unsymmetrical triarylmethanes (Table 6). The reaction between *N*-tosyl-(4-chlorobenzylidene)-4-methylbenzenesulfonamide (**3a**) and

SCHEME 2. Friedel−Crafts Arylation of *N*-Tosyl(4-bromobenzylidene)-4-methylbenzenesulfonamide with 1,3-Dimethoxybenzene



SCHEME 3. Synthesis of Triarylmethanes and Bis-heteroarylarylmethanes from Sulfonamidesulfones

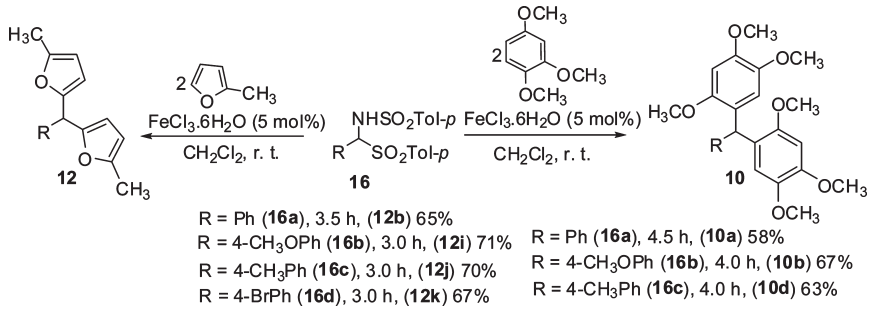
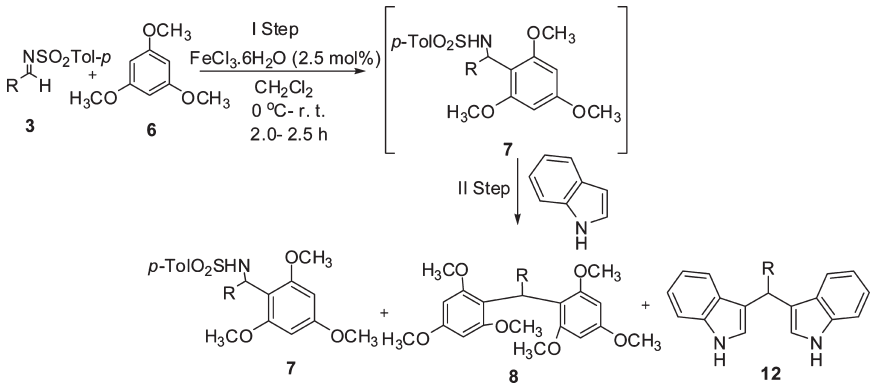


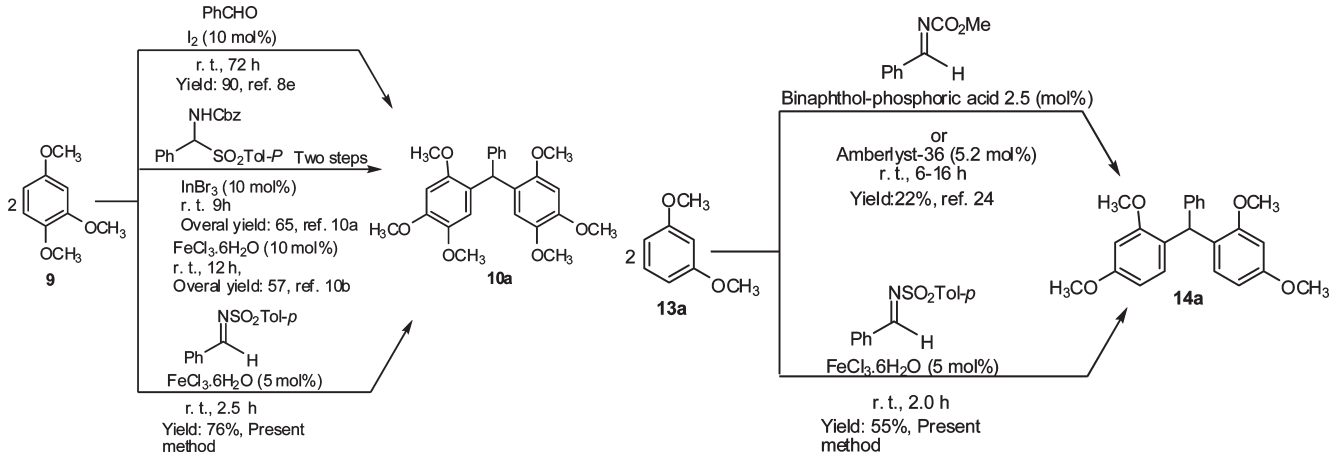
TABLE 6. Friedel–Crafts Arylation Reactions of *N*-Sulfonyl Aldimines with 1,3,5-Trimethoxybenzene Followed by Addition of Indole[a]



		reaction temp and time (h)		yield (%)[b]		
entry	**R**	step I	step II	**7**	**8**	**12**
1	**3a**, 4-ClC_6H_4	0 °C–rt, 2.0	rt, 24	**7a**, 5	**8a**, 5	**12g**, 18
2	**3a**, 4-ClC_6H_4	0 °C–rt, 2.0	reflux, 8	**7a**, 60	**8a**, 8	**12g**, 21
3	**3e**, C_6H_4	0 °C–rt, 2.5	rt, 24	**7e**, 68	**8e**, 4	**12a**, 12
4	**3i**, 4-$CH_3OC_6H_4$	0 °C–rt, 2.0	rt, 8	**7i**, 41	**8i**, 12	**12h**, 38

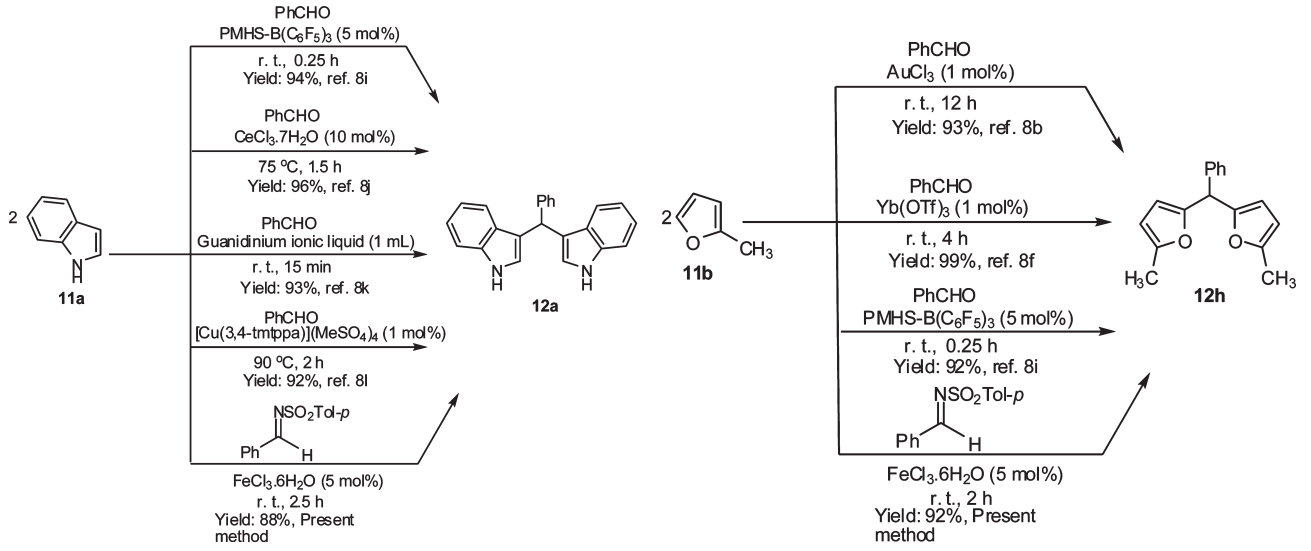
[a]Reaction condition: *N*-sulfonyl aldimines (1.0 mmol), 1,3,5-trimethoxybenzene (1.0 mmol), and indole (1.0 mmol) are used. [b]Yield of isolated product after column chromatography.

SCHEME 4. Synthesis of Triarylmethanes: Comparison of Present Method with Literature



1,3,5-trimethoxybenzene (**6**) in the presence of 2.5% $FeCl_3 \cdot 6H_2O$ at 0 °C–rt was stirred for 2.0 h and then 1 equiv of indole (**11a**) was added to the mixture in same reaction pot. The reaction mixture was again stirred for 24 h at rt. The major product obtained in this reaction is mono-Friedel–Crafts arylation product **7a** (65%) and the second Friedel–Crafts arylation product **8a** (5%). Unexpectedly, bis-indolylmethane (**12g**) is also obtained in 18% yield (entry 1). After addition of indole (**11a**) the reaction temperature was raised to reflux but there was not much improvement in the yield (entry 2). Similarly,

SCHEME 5. Synthesis of Bis-heteroarylmethanes: Comparison of Present Method with Literature



N-tosyl(benzylidene)- (**3e**) and *N*-tosyl(4-methoxybenzylidene)-4-methylbenzenesulfonamide (**3i**) give **7e**, **8e**, and **12a** and **7i**, **8i**, and **12h** in 68%, 4%, and 12% and 41%, 12%, and 38%, respectively (entries 3 and 4).

The synthesis of triarylmethane and bis-heteroarylmethane by Friedel−Crafts arylation of *N*-sulfonyl aldimines with electron-rich arenes is compared with other literature (Scheme 4 and Scheme 5).

Conclusions

$FeCl_3 \cdot 6H_2O$-catalyzed Friedel−Crafts arylation reactions of electron-rich arenes with *N*-sulfonyl aldimines or sulfonamidesulfones are described. The identical catalytic system is employed for the consecutive Friedel−Crafts reactions. The advantages of the method include (1) low catalyst loading and (2) mild reaction conditions.

Experimental Section

A. Experimental Procedure for the Friedel−Crafts Alkylation of *N*-Sulfonyl Aldimines with 1,3,5-Trimethoxybenzne. To a stirred solution of *N*-sulfonyl aldimines (1 mmol) and $FeCl_3 \cdot 6H_2O$ (2.5 mol %) in CH_2Cl_2 (3 mL) under nitrogen atmosphere at 0 °C is added 1,3,5-trimethoxybenzne (1 mmol). The mixture is stirred at 0 °C−rt and monitored by TLC. After completion, the reaction mixture is filtered, and the residue is washed with diethyl ether (3 × 5 mL). The filtrate is dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product is subject to flash column chromatography (silica gel, hexane−EtOAc, 4:1 to 3:1) to obtain the pure product.

ACS reagent grade $FeCl_3 \cdot 6H_2O$ is used for the reaction. The purity of $FeCl_3 \cdot 6H_2O$ is 97% (CAS No 10025-77-1, Sigma-Aldrich).

The products were characterized by ^1H and ^{13}C NMR data that are consistent with literature values. Melting point, HRMS-FAB, and ^1H and ^{13}C NMR values for the new products are given below.

7a: white solid, mp 168−169 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 7.6 Hz, 2H), 7.14 (d, J = 7.6 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 6.33 (d, J = 10.6 Hz, 1H), 6.05 (d, J = 10.6 Hz, 1H), 5.90 (s, 2H), 3.74 (s, 3H), 3.62 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 157.6, 142.4, 140.0, 137.2, 132.0, 128.6, 127.7, 126.6, 108.0, 90.4, 55.4, 55.2, 50.8, 21.2; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{23}H_{24}O_5NClS$ 461.1064, found 461.1061.

7b: white solid, mp 131−132 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.4 Hz, 2H), 7.25 (s, 1H), 7.16−7.12 (m, 3H), 7.02 (d, J = 8.4 Hz, 2H), 6.33 (d, J = 10.6 Hz, 1H), 6.08 (d, J = 10.6 Hz, 1H), 5.87 (s, 2H), 3.71 (s, 3H), 3.59 (s, 6H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 157.6, 143.6, 142.3, 137.2, 133.4, 129.0, 128.6, 126.6, 126.5, 126.4, 124.5, 107.9, 90.4, 55.4, 55.2, 50.9, 21.2; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{23}H_{24}O_5NClS$ 461.1064, found 461.1064.

7c: white solid, mp 124 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.4 Hz, 2H), 7.37−7.34 (m, 1H), 7.28−7.26 (m, 1H), 7.11−7.07 (m, 2H), 7.02 (d, J = 8.4 Hz, 2H), 6.41 (d, J = 10.2 Hz, 1H), 5.98 (d, J = 10.2 Hz, 1H), 5.87 (s, 2H), 3.72 (s, 3H), 3.62 (s, 6H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 158.1, 142.3, 138.2, 137.7, 133.5, 129.7, 129.4, 128.6, 128.1, 126.9, 125.9, 107.5, 90.6, 55.4, 55.2, 50.3, 21.3; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{23}H_{24}O_5NClS$ 461.1064, found 461.1064.

7d:. white solid, mp 155 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 6.35 (d, J = 11.0 Hz, 1H), 6.03 (d, J = 10.6 Hz, 1H), 5.85 (s, 2H), 3.70 (s, 3H), 3.58 (s, 6H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 157.5, 142.4, 140.6, 137.2, 130.7, 128.5, 128.1, 126.6, 120.1, 108.0, 90.3, 55.4, 55.1, 50.8, 21.1; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{23}H_{24}O_5NBrS$ 505.0559, found 505.0560.

7e: white solid, mp 167−168 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.0 Hz, 2H), 7.24−7.15 (m, 5H), 6.99 (d, J = 8.0 Hz, 2H), 6.21 (d, J = 11.0 Hz, 1H), 6.10 (d, J = 11.0 Hz, 1H), 5.88 (s, 2H), 3.74 (s, 3H), 3.62 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 157.9, 142.3, 141.3, 137.6, 128.6, 127.9, 126.8, 126.5, 126.4, 90.6, 55.6, 55.3, 51.5, 21.3; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{23}H_{24}O_5NS$ 427.1453, found 427.1455.

7f: yellow solid, mp 135 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 6.22 (d, J = 10.6 Hz, 1H), 6.14 (d, J = 10.6 Hz, 1H), 5.91 (s, 2H), 3.75 (s, 3H), 3.63 (s, 6H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 157.6, 149.4, 146.6, 142.8, 137.2, 128.8, 127.1, 126.8, 123.1, 107.8, 90.5, 55.6, 51.0, 21.3; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{23}H_{24}O_7N_2S$ 472.1304, found 472.1302.

7g: white solid, mp 164−165 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.35 (d,

J = 8.4 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 6.39 (d, J = 10.6 Hz, 1H), 6.09 (d, J = 10.2 Hz, 1H), 5.86 (s, 2H), 3.73 (s, 3H), 3.61 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 157.5, 147.2, 142.8, 137.1, 131.5, 128.6, 126.9, 126.9, 126.6, 118.8, 109.9, 107.5, 90.3, 55.4, 55.1, 51.0, 21.1; HRMS-FAB (m/z) $[M]^+$ calcd. for $C_{24}H_{24}O_5N_2S$ 452.1406, found 452.1404.

7h: white solid, mp 145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.44−7.40 (m, 2H), 7.34−7.29 (m, 1H), 7.02 (d, J = 8.0 Hz, 2H), 6.25 (d, J = 10.6 Hz, 1H), 6.07 (d, J = 10.6 Hz, 1H), 5.89 (s, 2H), 3.74 (s, 3H), 3.61 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 157.6, 143.2, 142.7, 137.2, 131.1, 130.2, 129.9, 128.8, 128.7, 126.8, 119.0, 111.8, 107.6, 90.5, 55.6, 55.3, 50.8, 21.3; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{24}H_{24}O_5N_2S$ 452.1406, found 452.1405.

7i: white solid, mp 153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.1 Hz, 2H), 6.74 (d, J = 8.8 Hz, 2H), 6.21 (d, J = 10.6 Hz, 1H), 6.05 (d, J = 11.0 Hz, 1H), 5.87 (s, 2H), 3.74 (s, 3H), 3.73 (s, 3H), 3.62 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 158.3, 157.8, 142.3, 137.5, 133.3, 128.6, 127.6, 127.8, 113.2, 198.7, 90.5, 55.5, 55.2, 55.1, 51.1, 21.3; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{24}H_{27}O_6NS$ 457.1559, found 457.1561.

7j: white solid, mp 165−166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 6.24 (d, J = 11.0 Hz, 1H), 6.07 (d, J = 11.0 Hz, 1H), 5.87 (s, 2H), 3.72 (s, 3H), 3.61 (s, 6H), 2.28 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.8, 142.2, 138.2, 137.5, 136.0, 128.5, 126.7, 126.3, 108.6, 90.5, 55.5, 55.2, 51.3, 21.2, 20.9; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{24}H_{27}O_5NS$ 441.1610, found 441.1612.

7k: white solid, mp 127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.0 Hz, 2H), 7.22 (s, 1H), 7.02 (d, J = 8.0 Hz, 2H), 6.20−6.18 (m, 1H), 6.15 (d, J = 11.0 Hz, 1H), 6.12 (d, J = 10.6 Hz, 1H), 5.98 (d. J = 3.3 Hz, 1H), 5.90 (s, 2H), 3.74 (s, 3H), 3.67 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 158.1, 153.6, 142.4, 141.6, 137.6, 128.7, 126.8, 110.0, 106.7, 106.3, 94.4, 90.7, 55.7, 55.2, 46.9, 21.3; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{21}H_{23}O_6NS$ 417.1246, found 417.1245.

7*l*: white solid, mp 162−163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 5.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 7.3 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 8.0 Hz, 3H), 6.57 (d, J = 9.5 Hz, 1H), 6.17 (d, J = 9.1 Hz, 1H), 5.89 (s, 2H), 3.71 (s, 3H), 3.58 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 159.9, 158.1, 148.1, 142.2, 137.6, 135.9, 128.6, 126.9, 121.3, 120.9, 109.5, 90.7, 55.6, 55.1, 52.1, 21.3; HRMS-FAB (m/z) $[M + H]^+$ calcd for $C_{22}H_{25}O_5N_2S$ 429.1484, found 429.1485.

7m: white solid, mp 114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 2H), 7.24−7.19 (m, 2H), 7.13−7.10 (m, 3H), 6.94 (d, J = 8.0 Hz, 2H), 5.84 (d, J = 11.0 Hz, 1H), 5.80 (s, 2H), 4.91−4.84 (m, 1H), 3.70 (s, 3H), 3.64 (s, 6H), 2.80−2.72 (m, 1H), 2.51−2.43 (m, 1H), 2.25 (s, 3H), 2.16−2.07 (m, 1H), 1.93−1.83 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 142.2, 142.1, 137.6, 128.5, 128.3, 128.1, 126.7, 125.5, 108.9, 90.3, 55.4, 55.2, 49.3, 37.2, 32.6, 21.2; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{25}H_{29}O_5NS$ 455.1766, found 455.1765.

7n: white solid, mp 139−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 5.83 (s, 2H), 5.76 (d, J = 11.0 Hz, 1H), 4.44−4.38 (m, 1H), 3.70 (s, 6H), 3.58 (s, 3H), 2.25 (s, 3H), 2.05−1.95 (m, 1H), 1.09 (d, J = 8.0 Hz, 3H), 0.63 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 157.8, 157.7, 141.9, 137.6, 129.6, 128.3, 126.6, 126.4, 108.7, 90.5, 89.8, 55.6, 55.2, 32.6, 21.2, 20.1, 19.3; HRMS-FAB (m/z) $[M + H]^+$ calcd for $C_{20}H_{27}NO_5S$ 394.1688, found 394.1688.

8a: white solid, mp 170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 6.15 (s, 1H), 6.10 (s, 4H), 3.78 (s, 6H), 3.51 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 159.1, 144.2, 129.4, 129.0, 126.9, 113.4, 91.6, 55.9, 55.9, 55.0, 36.4; HRMS-EI (m/z) $[M]^+$ calcd for $C_{25}H_{27}ClO_6$ 458.1496, found 458.1497.

8b: white solid; mp 160−161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07−7.00 (m, 3H), 6.91 (d, J = 7.4 Hz, 1H), 6.17 (s, 1H), 6.12 (s, 4H), 3.80 (s, 6H), 3.53 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 159.3, 148.1, 132.8, 128.1, 127.9, 126.0, 124.2, 113.2, 91.6, 56.0, 55.0, 36.8; HRMS-EI (m/z) $[M]^+$ calcd for $C_{25}H_{27}ClO_6$ 458.1496, found 458.1497.

8c: white solid; mp 200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.4 Hz, 1H), 7.05−7.03 (m, 3H), 6.30 (s, 1H), 6.11 (s, 4H), 3.78 (s, 6H), 3.50 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 159.1, 142.8, 133.4, 130.4, 128.1, 125.8, 125.6, 113.7, 92.0, 56.3, 56.3, 55.1, 35.8; HRMS-EI (m/z) $[M]^+$ calcd for $C_{25}H_{27}ClO_6$ 458.1496, found 458.1492.

8e: white solid; mp 191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16−7.12 (m, 2H), 7.05−7.03 (m, 3H), 6.21 (s, 1H), 6.11 (s, 4H), 3.78 (s, 6H), 3.49 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1159.7, 159.1, 142.8, 133.4, 130.4, 128.1, 125.8, 125.6, 113.7, 92.0, 56.3, 56.3, 55.1, 35.8.[8b]

8f: yellow solid; mp 159−160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 6.26 (s, 1H), 6.10 (s, 4H), 3.79 (s, 6H), 3.52 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 159.6, 154.8, 145.1, 128.4, 122.4, 112.2, 91.4, 55.9, 55.2, 37.2.[8b]

8g: white solid; mp 153−154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 6.24 (s, 1H), 6.10 (s, 4H), 3.79 (s, 6H), 3.51 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 159.5, 152.2, 130.9, 128.4, 119.9, 112.3, 107.5, 91.5, 55.9, 55.1, 37.2; HRMS-EI (m/z) $[M]^+$ calcd for $C_{26}H_{27}NO_6$ 449.1838, found 449.1840.

8h: white solid; mp 139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.22 (m, 4H), 6.20 (s, 1H), 6.10 (s, 4H), 3.79 (s, 6H), 3.52 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 159.5, 147.4, 132.5, 131.6, 128.0, 127.6, 120.0, 112.3, 110.7, 91.4, 55.8, 55.1, 36.7; HRMS-EI (m/z) $[M]^+$ calcd for $C_{26}H_{27}NO_6$ 449.1838, found 449.1836.

8i: white solid; mp 133−134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, J = 8.4 Hz, 2H), 6.70 (d, J = 8.0 Hz, 2H), 6.15 (s, 1H), 6.10 (s, 4H), 3.78 (s, 6H), 3.50 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 159.0, 156.6, 137.7, 133.7, 129.7, 128.7, 127.9, 114.6, 112.4, 91.9, 56.2, 55.1, 36.3; HRMS-EI (m/z) $[M]^+$ calcd for $C_{26}H_{30}O_7$ 454.1992, found 454.1993.

B. Experimental Procedure for the Synthesis of Triarylmethanes or Heterotriarylmethanes. To a mixture of of *N*-sulfonyl aldimines or sulfonamidesulfones (1 mmol) and $FeCl_3 \cdot 6H_2O$ (5.0 mol %) in CH_2Cl_2 (3 mL) under nitrogen, electron-rich arene or heteroarene (2.0 mmol) is added and the mixture is stirred at rt. The progress of the reaction mixture is monitored by TLC. After completion of the reaction, the mixture is filtered, and the residue is washed with diethyl ether (3 × 5 mL). The combined organic portions were washed with water (5 mL) and saturated aqueous NH_4Cl (5 mL), dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude product is subjected to flash column chromatography (silica gel, hexane−EtOAc, 4:1 to 3:1) to obtain pure product.

10a: white solid, mp 126−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.21 m 2H), 7.17−7.13 (m, 1H), 7.04 (d, J = 8.2 Hz, 2H), 6.54 (s, 2H), 6.42 (s, 2H), 6.07 (s, 1H), 3.87 (s, 6H), 3.65 (s, 6H), 3.62 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 151.5, 147.9, 144.2, 142.6, 128.9, 127.9, 125.7, 124.5, 114.5, 98.3, 57.0, 56.6, 56.0, 42.5.[8e,10a,b]

10b: white solid, mp 131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 8.2 Hz, 2H), 6.93 (d, J = 8.2 Hz, 2H), 6.69 (s, 2H), 6.58 (s, 2H), 6.17 (s, 1H), 4.02 (s, 6H), 3.91 (s, 3H), 3.80 (s, 6H), 3.79 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.2, 152.1, 148.5, 143.2, 136.8, 130.5, 125.5, 115.0, 113.9, 99.0, 57.6, 57.2, 56.6, 55.7, 42.2.[8e,10a,b]

10c: white solid, mp 110−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 6.76 (d, J = 8.0 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 6.56 (s, 2H), 6.53 (s, 1H), 6.45 (s, 2H), 6.03 (s, 1H), 3.90 (s, 6H), 3.86 (s, 3H), 3.78 (s, 3H), 3.69 (s, 6H), 3.65 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C) δ 151.5, 148.5, 148.0, 147.0, 142.7, 136.7, 124.8, 120.9, 114.4, 112.6, 110.5, 98.4, 57.1, 56.7, 56.0, 55.7, 42.0.[8e,10a,b]

10d: white solid; mp 142−143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.0 Hz, 2H), 6.51 (s, 2H), 6.42 (s, 2H), 6.02 (s, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.63 (s, 6H), 3.61 (s, 6H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 147.9, 142.6, 141.0, 135.0, 128.8,128.6, 124.8, 114.5, 98.4, 57.0, 56.6, 56.0, 42.0, 20.9.[8e]

10e: white solid; mp 141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 6.50 (s, 2H), 6.36 (s, 2H), 5.96 (s, 1H), 3.82 (s, 6H), 3.62 (s, 6H), 3.60 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 151.5, 148.2,142.7, 131.0, 130.7, 128.8, 123.6, 119.5, 114.4, 98.2, 56.8, 56.7, 56.0, 42.1.[8e]

10f: white solid; mp 168−169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 6.53 (s, 2H), 6.39 (s, 2H), 6.01 (s, 1H), 3.87 (s, 6H), 3.65 (s, 6H), 3.63 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 148.1, 142.9, 142.6, 131.3, 130.2, 128.0, 123.7, 114.3, 98.1, 56.8, 56.6, 56.0, 41.9.[8e,10a,b]

10g: white solid; mp 169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16−7.14 (m, 2H), 7.03−7.01 (m, 1H), 6.94−6.91 (m, 1H), 6.54 (s, 2H), 6.40 (s, 2H), 6.03 (s, 1H), 3.87 (s, 6H), 3.64 (s, 6H), 3.61 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 148.2, 146.7, 133.8, 129.1, 129.0, 127.1, 125.9, 123.5, 114.5, 98.2, 56.8, 56.7, 56.0, 42.3; HRMS-EI (m/z) $[M]^+$ calcd for $C_{25}H_{27}ClO_6$ 458.1496, found 458.1497.

10h: white solid; mp 126−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.2 Hz, 1H), 7.13−7.10 (m, 2H), 6.87 (d, J = 7.2 Hz, 1H), 6.54 (s, 2H), 6.32 (s, 1H), 6.31 (s, 2H), 3.87 (s, 6H), 3.66 (s, 6H), 3.61 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 151.6, 148.1, 142.5, 142.0, 134.3, 129.8, 129.4, 127.2, 126.0, 122.8, 114.1, 98.2, 56.8, 56.5, 55.9, 40.2.[10a,b]

10i: white solid; mp 141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.5 Hz, 2H), 6.54 (s, 2H), 6.36 (s, 2H), 6.06 (s, 1H), 3.88 (s, 3H), 3.65 (s, 6H), 3.63 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 150.6, 148.5, 142.7, 131.7, 129.5, 122.4, 119.2, 114.4, 109.4, 98.0, 56.7, 56.6, 56.0, 43.0; HRMS-EI (m/z) $[M]^+$ calcd for $C_{26}H_{27}NO_6$ 449.1838, found 449.1841.

10j: white solid; mp 139−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.5 Hz, 1H), 7.33−7.29 (m, 3H), 6.54 (s, 2H), 6.36 (s, 2H), 6.04 (s, 1H), 3.90 (s, 6H), 3.67 (s, 3H), 3.64 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 148.8, 146.5, 143.0, 133.7, 132.5, 129.8, 128.8, 122.7, 199.5, 114.7, 112.1, 98.3, 56.9, 56.8, 56.3, 42.7; HRMS-EI (m/z) $[M]^+$ calcd for $C_{26}H_{27}NO_6$ 449.1838, found 449.1840.

12a: brown solid; mp 141−142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (br s, 2H), 7.40−7.29 (m, 5H), 7.28−7.25 (m, 3H), 7.22−7.14 (m, 3H), 7.02−7.00 (m, 2H), 6.65 (s, 2H), 5.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 243.9, 136.7, 128.7, 128.2, 127.0, 126.1, 123.6, 121.9, 119.9, 119.7, 119.2, 111.0, 40.2.[8i−l]

12b: viscous mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.27 (m, 2H), 7.23 (d, J = 8.5 Hz, 3H), 5.87−5.85 (m, 4H), 5.32 (s, 1H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 151.4, 128.4, 128.3, 126.9, 108.1, 106.0, 45.1, 13.6.[8b,f,i]

12c: viscous mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.22 (m, 5H), 6.59−6.55 (m, 4H), 5.66 (s, 1H), 2.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 143.8, 139.0, 128.4, 128.3, 126.9, 125.6, 124.5, 47.6, 15.3.[8b]

12d: brown solid; mp 187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (br s, 2H), 7.40 (d, J = 7.8 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.18 (t, J = 7.6 Hz, 2H), 7.02 (t, J = 7.6 Hz, 2H), 6.82 (d, J = 8.0 Hz, 2H), 6.61 (d, J = 1.6 Hz, 2H), 5.85 (s, 1H), 3.81 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 136.6, 136.2, 129.6, 127.0, 123.5, 121.8, 120.0, 119.9, 119.1, 113.5, 110.9, 60.4, 55.2.[8i]

12e: brown solid; mp 137−138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (br s, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 7.22 (d, J = 1.5 Hz, 1H), 7.20 (t, J = 8.0 Hz, 2H), 7.13 (dd, J = 8.2, 1.5 Hz, 1H), 7.06 (d, J = 8.0 Hz, 2H), 6.75 (d, J = 8.2 Hz, 1H), 6.58 (d, J = 1.5 Hz, 1H), 5.86 (s, 1H), 3.82 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 136.6, 135.7, 130.9, 127.0, 126.6, 125.9, 123.7, 121.7, 119.9, 119.8, 119.0, 111.0, 109.6, 60.4, 55.2, 16.3.[10a]

12f: pale brown solid; mp 96−97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (br s, 2H), 7.38 (d, J = 7.2 Hz, 2H), 7.30 (d, J = 7.5 Hz, 2H), 7.21 (d, J = 7.5 Hz, 2H), 7.15 (t, J = 7.2 Hz, 2H), 7.07 (d, J = 7.2 Hz, 2H), 6.99 (d, J = 7.2 Hz, 2H), 6.59 (d, J = 1.5 Hz, 2H), 5.83 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 141.0, 136.7, 135.5, 128.9, 128.6, 127.1, 123.6, 121.9, 120.0, 119.9, 119.2, 111.0, 39.8, 21.1.[8i]

12g: pale brown solid; mp 79−80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (br s, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.33−7.22 (m, 8H), 7.06 (t, J = 7.8 Hz, 2H), 6.54 (s, 2H), 5.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 136.6, 131.6, 129.9, 129.8, 126.7, 123.5, 121.9, 119.7, 199.2, 188.9, 111.1, 60.5.[8i]

12h: viscous mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 8.2 Hz, 2H), 6.84 (d, J = 8.2 Hz, 2H), 5.88−5.84 (m, 4H), 5.29 (s, 1H), 3.77 (s, 3H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 153.1, 151.3, 132.1, 129.3, 113.7, 107.9, 106.0, 55.1, 44.3, 13.5; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{18}H_{18}O_3$ 282.1256, found 282.1251.

12i: viscous mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 7.8 Hz, 2H), 7.17 (d, J = 7.8 Hz, 2H), 5.93 (s, 4H), 5.37 (s, 1H), 2.38 (s, 3H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 151.2, 137.0, 136.4, 129.0, 128.2, 107.9, 106.0, 44.7, 21.0, 13.5; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{18}H_{18}O_2$ 266.1307, found 266.1304.

12j: viscous mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 5.88−5.87 (m, 4H), 5.29 (s, 1H), 2.24 (s, 6H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 152.1, 151.6, 139.0, 131.5, 130.1, 120.8, 108.3, 106.1, 44.5, 13.5; HRMS-FAB (m/z) $[M + H]^+$ calcd for $C_{17}H_{15}BrO_2$ 331.0334, found 331.0331.

12k: viscous mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.14 (m, 3H), 7.16−7.14 (m, 1H), 5.91−5.90 (m, 4H), 5.31 (s, 1H), 2.25 (s, 6H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 151.9, 151.7, 142.0, 134.2, 129.6, 128.5, 127.1, 126.6, 108.4, 106.1, 44.7, 13.5; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{17}H_{15}ClO_2$ 286.0761, found 286.0763.

12l: viscous mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.5 Hz, 1H), 7.53 (d, J = 1.5 Hz, 1H), 7.50 (d, J = 8.5 Hz, 1H), 7.41 (d, J = 8.5 Hz, 1H), 5.92−5.91 (m, 4H), 5.36 (s, 1H), 2.24 (s, 6H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 151.9, 151.1, 141.6, 132.9, 131.9, 130.6, 129.1, 118.8, 112.4, 108.7, 106.2, 44.5, 13.5; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{18}H_{15}NO_2$ 277.1103, found 277.1103.

12m: viscous mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 5.92−5.91 (m, 4H), 5.38 (s, 1H), 2.24 (s, 6H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 151.9, 151.1, 145.4, 132.2, 129.1, 118.8, 110.8, 108.7, 106.2, 44.9, 13.5; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{18}H_{15}NO_2$ 277.1103, found 277.1102.

12n: viscous mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 (d, J = 2.0 Hz, 2H), 5.85 (d, J = 2.0 Hz, 2H), 5.67 (d, J = 7.6 Hz, 1H), 2.30−2.26 (s, 1H), 2.25 (s, 6H), 0.88 (d, J = 7.6 Hz, 6H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 153.3, 150.3, 106.8, 105.8, 46.3, 31.8, 20.7, 13.5.[8e]

14a: white solid; mp 123−124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.21 (m, 2H), 7.17 (d, J = 8.2 Hz, 1H), 7.05 (d, J = 8.4 Hz, 2H), 6.69 (d, J = 8.6 Hz, 2H), 6.46 (d, J = 1.6 Hz,

2H), 6.37 (dd, J = 8.4, 1.6 Hz, 2H), 6.02 (s, 1H), 3.80 (s, 6H), 3.68 (s, 6H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 159.2, 158.0, 144.6, 130.4, 129.1, 127.8, 125.5, 125.3, 103.5, 98.7, 55.7, 55.2, 42.1.[24]

14b: white solid; mp109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, J = 8.2 Hz, 2H), 6.94 (d, J = 8.2 Hz, 2H), 6.70 (d, J = 8.6 Hz, 2H), 6.45 (d, J = 1.6 Hz, 2H), 6.37 (dd, J = 8.4, 1.6 Hz, 2H), 5.99 (s, 1H), 3.80 (s, 6H), 3.72 (s, 6H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 159.1, 158.1, 141.4, 134.9, 130.3, 129.0, 128.6, 125.6, 103.5, 98.7, 55.7, 55.2, 41.6, 21.0; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{24}H_{26}O_4$ 378.1831, found 378.1833.

14c: white solid; mp 153−154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 8.2 Hz, 2H), 6.99 (d, J = 8.2 Hz, 2H), 6.68 (d, J = 8.6 Hz, 2H), 6.48 (d, J = 1.6 Hz, 2H), 6.39 (dd, J = 8.4, 1.6 Hz, 2H), 5.99 (s, 1H), 3.79 (s, 6H), 3.69 (s, 6H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 159.4., 158.0, 143.3, 131.2, 130.4, 130.3, 127.9, 124.7, 103.6, 98.7, 55.6, 55.2, 41.7; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{23}H_{23}ClO_4$ 398.1285, found 398.1285.

14d: white solid; mp 105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18−7.14 (m, 2H), 7.05 (s, 1H), 6.96−6.94 (m, H), 6.70 (d, J = 8.6 Hz, 2H), 6.48 (d, J = 1.6 Hz, 2H), 6.40 (dd, J = 8.4, 1.6 Hz, 2H), 6.01 (s, 1H), 3.82 (s, 6H), 3.76 (s, 6H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 159.4, 157.9, 147.0, 133.7, 130.3, 129.1, 127.3, 125.8, 124.4, 103.6, 98.7, 55.6, 55.2, 41.9; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{23}H_{23}ClO_4$ 398.1285, found 398.1289.

14e: white solid; mp 151−152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 6.65 (d, J = 9.1 Hz, 2H), 6.48 (d, J = 1.4 Hz, 2H), 6.39 (dd, J = 9.0, 1.4 Hz, 2H), 6.07 (s, 1H), 3.80 (s, 6H), 3.69 (s, 6H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 159.7, 157.9, 146.0, 130.3, 129.6, 123.4, 123.1, 103.7, 98.7, 55.5, 55.2, 42.5; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{23}H_{23}NO_6$ 409.1525, found 409.1527.

14f: white solid; mp 97−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.25 (m, 2H), 7.21−7.19 (m, 1H), 7.10 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.8 Hz, 4H), 6.81 (d, J = 8.8 Hz, 4H), 5.44 (s, 1H), 3.78 (s, 6H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 157.9, 144.6, 136.4, 130.2, 129.3, 128.2, 126.1, 113.6, 55.2, 55.1.[7,8f]

15: white solid, mp 184−185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.8 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.80 (d, J = 8.0 Hz, 1H), 6.28 (dd, J = 8.0, 2.0 Hz, 1H), 6.23 (d, J = 2.0 Hz, 1H), 5.67 (d, J = 9.2 Hz, 1H), 5.51 (d, J = 9.0 Hz, 1H), 3.75 (s, 3H), 3.56 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 160.8, 157.2, 142.8, 140.0, 137.4, 131.1,130.1, 129.1, 128.5, 127.0, 120.9, 119.7, 104.1, 99.1, 58.1, 55.3, 21.4; HRMS-FAB (m/z) $[M]^+$ calcd for $C_{22}H_{22}O_4NBrS$ 475.0453, found 475.0454.

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