DOI: 10.1002/ejoc.200901186

Regioselective Arylations of α-Amido Sulfones with Electron-Rich Arenes through Friedel–Crafts Alkylations Catalyzed by Ferric Chloride Hexahydrate: Synthesis of Unsymmetrical and Bis-Symmetrical Triarylmethanes

Ponnaboina Thirupathi[a] and Sung Soo Kim*[a]

Keywords: Iron / C–C coupling / α-Amido sulfones / Arenes / Heteroarenes / Triarylmethanes

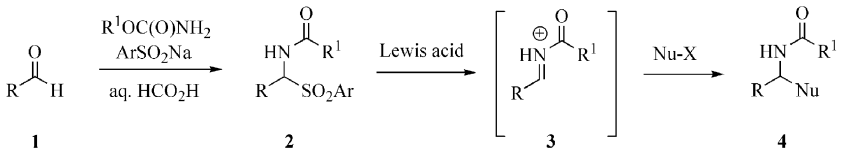
Ferric chloride hexahydrate is a highly efficient catalyst for the regioselective arylation of α-amido sulfones. The products undergo further Friedel–Crafts alkylations with heteroaromatic or electron-rich arenes to afford unsymmetrical or bis-symmetrical triarylmethanes.

Introduction

Friedel–Crafts alkylations[1] belong to the most important C–C bond-forming reactions in organic chemistry.[2] These reactions are usually assisted by protic acid or Lewis acid catalysts. Recently, iron salts have attracted the attention of synthetic organic chemists, because iron is one of the most abundant metals. Many iron salts are inexpensive and commercially available.[3] These iron salts were found to have promising catalytic abilities in many organic transformations including Friedel–Crafts reactions.[3a,3g–3j] Friedel–Crafts reactions of electron-rich arenes are a well-known process for the formation of C–C bonds from aromatic C–H bonds.[2] Here we would like to disclose our recent discovery of $FeCl_3 \cdot 6H_2O$-catalyzed Friedel–Crafts reactions between electron-rich arenes and α-amido sulfones.

Recently several workers have demonstrated that α-amido sulfones **2** (Scheme 1) can be prepared from a variety of aldehydes **1** by treatment with carbamates and sodium sulfinates in the presence of aqueous formic acid.[4] These are useful precursors of the *N*-acyliminium ions **3**, which can further react with several nucleophiles such as allylsilanes, silyl ketene acetals, trimethylsilyl cyanide, and electron-rich aromatics, leading to the formation of the corresponding adducts **4**.[5]

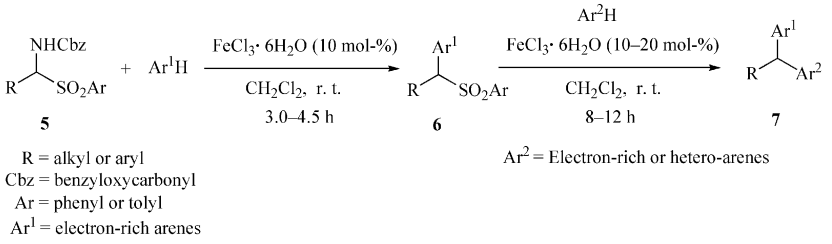
In continuation of the development of useful synthetic methodologies for C–C bond-forming reactions,[6] here we report efficient $FeCl_3 \cdot 6H_2O$-catalyzed Friedel–Crafts alkylations of electron-rich arenes with α-amido sulfones. The products undergo further Friedel–Crafts alkylations with heteroaromatic or electron-rich arenes, giving rise to unsymmetrical or bis-symmetrical triarylmethanes. Triarylmethanes display interesting properties and have received a great deal of attention as leuco dyes,[7] photochromic agents,[8] building blocks for generating dendrimers,[9] and substrates for theoretical[10] and biological studies.[11] Although many methods for the preparation of symmetrical triarylmethanes are known,[12] the synthesis of unsymmetrical derivatives is far less studied.[13–15] Here we describe a broad range of $FeCl_3 \cdot 6H_2O$-catalyzed Friedel–Crafts alkylations that allow the selective preparation of structurally diverse triarylmethanes through sequential reactions either with the same electron-rich arene or with different ones (Scheme 2).



Scheme 1. General equation for Lewis-acid-catalyzed nucleophilic substitution of α-amido sulfones.

[a] Department of Chemistry, Inha University, Incheon 402-751, South Korea
E-mail: sungsoo@inha.ac.kr

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200901186.



Scheme 2. Synthesis of triarylmethanes.

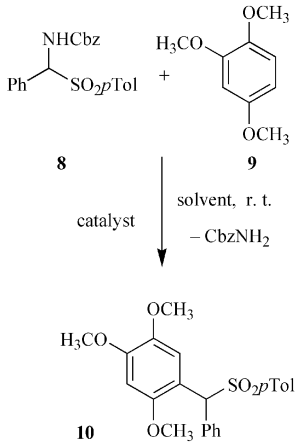
Results and Discussion

Initially we investigated the reaction behavior of [(benzyloxycarbonyl)amino](phenyl)methyl *p*-tolyl sulfone (**8**) and 1,2,4-trimethoxybenzene (**9**). In the absence of catalyst (Table 1, Entry 1) this did not give rise to any reaction. We next examined the reaction behavior in the presence of various Lewis acids such as CuCl, CuI, $Fe(ClO_4)_3 \cdot x H_2O$, $Fe(acac)_3$, $Fe(NO_3)_3 \cdot 9 H_2O$, $FeCl_3$, and $FeCl_3 \cdot 6 H_2O$ (Entries 2–8). With regard to the amount of the catalyst, reaction time, and yield, $FeCl_3 \cdot 6 H_2O$ (10 mol-%) was found to be the most effective (Entry 8). The effects of various solvents were also studied. CH_2Cl_2 was found to be the solvent of choice in terms of yield and reaction time (Entries 8 and 12–15).

The optimized reaction conditions were used as a basis for study of the scope of the Friedel–Crafts alkylation of sulfone **8** with other activated arenes. The results are outlined in Table 2. The reasonably highly activated 1,3-dimethoxybenzene (Entry 1) afforded a lower yield and required a longer reaction time than 1,2,3-, 1,3,5-, or 1,2,4-trimethoxybenzene (Entries 2–4). This indicates that highly activated benzenes are the best substrates for these Friedel–Crafts alkylation reactions. 1,2,4-Trimethoxybenzene was the most effective arene for Friedel–Crafts alkylation reaction in relation to the other activated arenes (Table 2).

We then examined the scope of the Friedel–Crafts alkylation reactions between various α-amido sulfones **13** and 1,2,4-trimethoxybenzene (**9**) and the results are summarized in Table 3. The α-amido sulfones were treated with 1,2,4-trimethoxybenzene (**9**) for 3.0–4.5 h to produce the corresponding (1-alkyl)(1-aryl)methyl phenyl/tolyl sulfones **14** in good to excellent yields. α-Amido sulfones with electron-donating groups attached to the benzene rings reacted with 1,2,4-trimethoxybenzene (**9**) to yield (alkyl)(aryl)methyl phenyl/tolyl sulfones in excellent yields (Entries 2–9). The presence of electron-withdrawing groups in the α-amido sulfones prolonged the reaction times and reduced the yields relative to those observed in the case of electron-donating groups (Entries 10 and 11). The *p*-, *m*-, and *o*-chloro α-amido sulfones gave the corresponding products in 89, 86 and 83% yields, respectively (Entries 12–14). The *o*-chloro isomer showed slight steric and electron effects that were responsible for the lower yield and longer reaction time (Entry 14). 2-Naphthyl, 2-furyl, and 2-thiophenyl α-amido sulfones reacted with 1,2,4-trimethoxybenzene (**9**) to afford the corresponding products in high yields (Entries 15–17). Cyclohexyl and cyclohex-2-enyl α-amido sulfones afforded the corresponding (1-alkyl)(1-aryl)methyl phenyl/tolyl sulfone derivatives in good yields (Entry 18 and 19). The reactions of arylalkyl and acyclic aliphatic α-amido sulfones give the corresponding (1-alkyl)(1-aryl)methyl tolyl sulfones in 85% and in 77 and 75% yields, respectively (Entries 20–22).

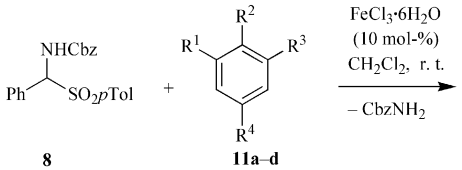
Table 1. Friedel–Crafts alkylations of 1,2,4-trimethoxybenzene with [(benzyloxycarbonyl)amino](phenyl)methyl *p*-tolyl sulfone (**8**) catalyzed by various catalysts.[a]

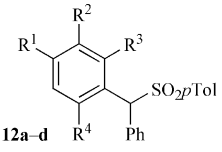


Entry	Catalyst (mol-%)	Solvent	Reaction time [h]	% Isolated yield[b]
1	–	CH_2Cl_2	12	trace
2	CuCl (10)	CH_2Cl_2	12	NR
3	CuI (10)	CH_2Cl_2	12	NR
4	$Fe(ClO_4)_3$ (10)	CH_2Cl_2	3.5	64
5	$Fe(acac)_3$ (10)	CH_2Cl_2	10.0	47
6	$Fe(NO_3)_3$ (10)	CH_2Cl_2	8	56
7	$FeCl_3$ (10)	CH_2Cl_2	3.5	90
8	$FeCl_3 \cdot 6 H_2O$ (10)	CH_2Cl_2	3.5	91
9	$FeCl_3 \cdot 6 H_2O$ (15)	CH_2Cl_2	3.5	89
10	$FeCl_3 \cdot 6 H_2O$ (20)	CH_2Cl_2	3.5	90
11	$FeCl_3 \cdot 6 H_2O$ (5)	CH_2Cl_2	5.5	86
12	$FeCl_3 \cdot 6 H_2O$ (10)	CH_3Cl	5.0	53
13	$FeCl_3 \cdot 6 H_2O$ (10)	CH_3CN	4.0	85
14	$FeCl_3 \cdot 6 H_2O$ (10)	CH_3NO_2	4.0	87
15	$FeCl_3 \cdot 6 H_2O$ (10)	1,4-dioxane	5.0	65

[a] Reaction conditions: sulfone **8** (1.0 mmol), 1,2,4-trimethoxybenzene (**9**) (1.0 mmol), solvent (2.0 mL), room temp. [b] Yield of isolated product after flash column chromatography.

Table 2. $FeCl_3 \cdot 6H_2O$-catalyzed Friedel–Crafts alkylations of sulfone **8** with electron-rich arenes.[a]



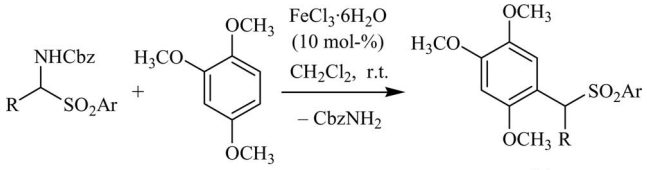


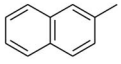
a: $R^1 = R^3 = OCH_3$, $R^2 = R^4 = H$
b: $R^1 = R^2 = R^3 = OCH_3$, $R^4 = H$
c: $R^1 = R^3 = R^4 = OCH_3$, $R^2 = H$
d: $R^1 = R^2 = R^4 = OCH_3$, $R^3 = H$

Entry	Arene **11**	Product	Reaction time [h]	% Isolated yield[b]
1	**11a**	**12a**	4.5	83
2	**11b**	**12b**	4.0	86
3	**11c**	**12c**	3.5	89
4	**11d**	**12d**	3.5	91

[a] Reaction conditions: sulfone **8** (1.0 mmol), electron-rich arene (1.0 mmol), CH_2Cl_2 (2.0 mL) at room temp. [b] Yield of isolated product after flash column chromatography.

Table 3. $FeCl_3 \cdot 6H_2O$-catalyzed Friedel–Crafts alkylations of 1,2,4-trimethoxybenzene with α-amido sulfones.[a]



Entry	**13** R	Ar	**14**	Reaction time [h]	% Isolated yield[b]
1	C_6H_5	Ph	**14a**	3.5	89
2	4-MeC_6H_4	4-MeC_6H_4	**14b**	4.0	90
3	4-$MeOC_6H_4$	4-MeC_6H_4	**14c**	3.5	93
4	4-$MeOC_6H_4$	Ph	**14d**	3.5	93
5	3-Me,4-$MeOC_6H_3$	Ph	**14e**	3.0	92
6	3-Me,4-$MeOC_6H_3$	4-MeC_6H_4	**14f**	3.0	92
7	3-F,4-$MeOC_6H_3$	4-MeC_6H_4	**14g**	3.5	88
8	3,4-$(MeO)_2C_6H_3$	4-MeC_6H_4	**14h**	3.0	93
9	3,4,5-$(MeO)_3C_6H_2$	4-MeC_6H_4	**14i**	3.0	90
10	4-$NO_2C_6H_4$	4-MeC_6H_4	**14j**	4.5	83
11	4-CNC_6H_4	4-MeC_6H_4	**14k**	4.5	82
12	4-ClC_6H_4	4-MeC_6H_4	**14l**	3.5	89
13	3-ClC_6H_4	4-MeC_6H_4	**14m**	3.5	86
14	2-ClC_6H_4	4-MeC_6H_4	**14n**	4.5	83
15		4-MeC_6H_4	**14o**	4.0	89
16		4-MeC_6H_4	**14p**	3.0	84
17		4-MeC_6H_4	**14q**	4.5	79
18		4-MeC_6H_4	**14r**	3.5	89
19		4-MeC_6H_4	**14s**	3.5	83
20	$PhCH_2CH_2$	4-MeC_6H_4	**14t**	3.5	86
21	$(CH_3)_2CH$	4-MeC_6H_4	**14u**	4.5	77
22	$CH_3CH_2CH_2$	4-MeC_6H_4	**14v**	4.5	75

[a] Reaction conditions: α-amido sulfone (1.0 mmol), 1,2,4-trimethoxybenzene (1.0 mmol), and CH_2Cl_2 (2.0 mL) at room temp. [b] Yield of isolated product after flash column chromatography.

A plausible mechanism for the formation of **14** may start from the *N*-acyliminium ion **B** (Figure 1) formed by elimination of arenesulfinic acid from the α-amido sulfone **13** through the action of the Fe^{III} in $FeCl_3 \cdot 6H_2O$. A reaction between the strong electrophile **B** and 1,2,4-trimethoxybenzene (**9**) would then give the Friedel–Crafts product **C**. Fe^{III} could catalyze the elimination of carbamate from **C**, leading to the formation of oxonium ion **D**.[16] The oxonium ion **D** could then react once more with 1,2,4-trimethoxybenzene (**9**), giving rise to the bis-arene **E** through the reversible reaction. The formation of the bis-arene **E** was observed by TLC (just above the spot for the desired product) during the course of the reaction but had completely disappeared at end of the reaction. After a reaction time of 1.0 h, **E** (R = 4-MePh) was isolated and characterized by NMR analysis (see Figure 2, Exp. Section, and Supporting Information). The oxonium ion **D** could then react in a second Friedel–Crafts reaction with an arenesulfinic acid ($ArSO_2H$), leading to the formation of product **14**.

The reusability of the $FeCl_3 \cdot 6H_2O$ catalyst was tested in the reaction between sulfone **8** and 1,2,4-trimethoxybenzene (**9**) under the same reaction conditions. The reaction mixture was filtered, washed with diethyl ether (3×15 mL), and used in a second run by charging with the same substrates. The catalytic system shows high efficiency of reusability and could be recycled four times with a very little decrease in the yield (Scheme 3).

We studied the scope of the Friedel–Crafts alkylation reactions further with (1-alkyl)(1-aryl)methyl phenyl/tolyl sulfones **14** and the other electron-rich indole derivatives **15**, giving rise to unsymmetrical triarylmethanes. The results are summarized in Table 4. The reaction between the (1-alkyl)(1-aryl)methyl tolyl sulfones **14** (R = Ph, Ar = 4-MeC_6H_4) and indole in the presence of $FeCl_3 \cdot 6H_2O$ afforded the unsymmetrical triarylmethane **16a** in 38% yield (Entry 1). An improvement in the reaction yield (46%) was observed on changing the amount of $FeCl_3 \cdot 6H_2O$ to 20 mol-% (Entry 1). Similarly, 4-methoxy-, 3-methyl-4-methoxy-, 3-fluoro-, 4-methoxy-, and 3,4-dimethoxy-substituted (1-alkyl)(1-aryl)methyl sulfones **14** also reacted smoothly with indole or 5-methoxyindole to give rise to the corresponding unsymmetrical triarylmethanes in moderate yields (Entries 2–10).

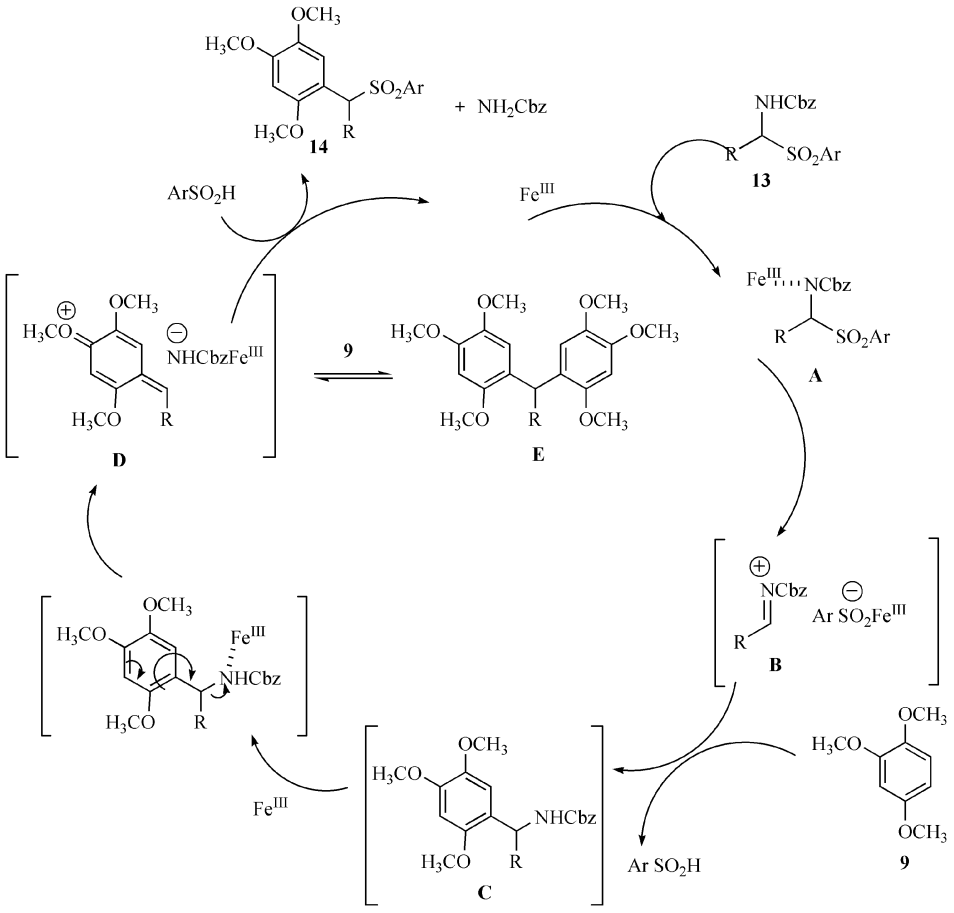


Figure 1. Proposed mechanism of $FeCl_3 \cdot 6H_2O$-catalyzed Friedel–Crafts alkylations of α-amido sulfones with 1,2,4-trimethoxybenzene.

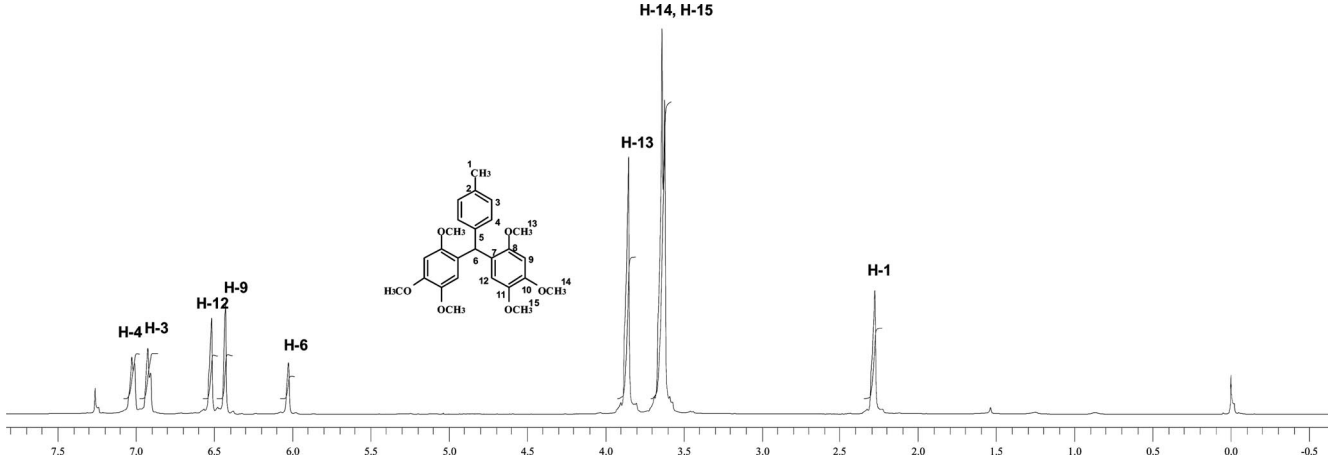
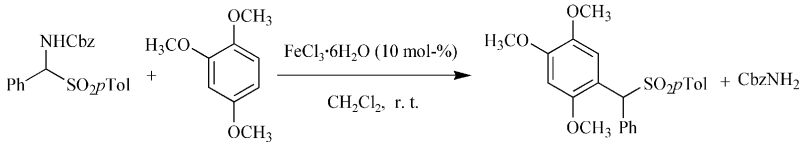


Figure 2. ^1H NMR of bis-arene **E** (R = 4-MePh).

The scope of the Friedel–Crafts alkylation reactions was next examined (Table 5) with various (1-alkyl)(1-aryl)-methyl tolyl sulfones **14** and 1,2,4-trimethoxybenzene (**9**). The sulfone **14** (R = Ph) was treated with **9** in the presence of $FeCl_3 \cdot 6H_2O$ at room temp. The reaction mixture were stirred for 9.0 h to afford the corresponding bis-symmetrical triarylmethane **17a** in good yield (Entry 1). The corresponding reactions of 4-methoxy-, 3-methyl-4-methoxy-,

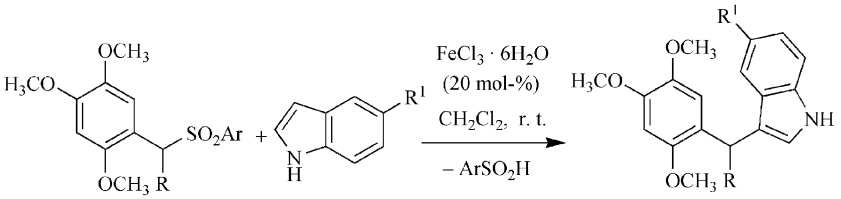


8 **9** **10**

Cycles	1	2	3	4
Reaction time (h)	3.5	4.0	4.0	4.5
Yield (%)	91	87	81	70

Scheme 3. Reusability of catalyst.

Table 4. $FeCl_3 \cdot 6H_2O$-catalyzed synthesis of unsymmetrical triarylmethanes.[a]



14 **15** **16**

Entry	**14** R	Ar	R^1 in **15**	Product **16**	% Isolated yield[b]
1	Ph	4-MeC_6H_4	H	**16a**	38[c] 40[d] 44[e] 46[a]
2	4-$MeOC_6H_4$	4-MeC_6H_4	H	**16b**	51
3	4-$MeOC_6H_4$	Ph	H	**16b**	55
4	4-$MeOC_6H_4$	Ph	CH_3O	**16c**	60
5	3-Me, 4-$MeOC_6H_3$	4-MeC_6H_4	H	**16d**	53
6	3-Me, 4-$MeOC_6H_3$	4-MeC_6H_4	CH_3O	**16e**	56
7	3-Me, 4-$MeOC_6H_3$	Ph	CH_3O	**16e**	58
8	3-F, 4-$MeOC_6H_3$	4-MeC_6H_4	H	**16f**	49
9	3,4-$(MeO)_2C_6H_3$	4-MeC_6H_4	H	**16g**	54
10	3,4-$(MeO)_2C_6H_3$	4-MeC_6H_4	CH_3O	**16h**	57

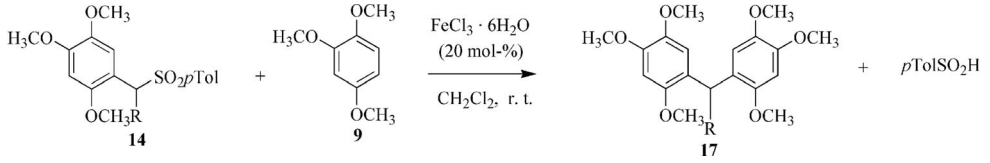
[a] Reaction conditions: (1-alkyl)(1-aryl)methyl phenyl/tolyl sulfones (1.0 mmol), indole derivative (1.0 mmol), and CH_2Cl_2 (2.0 mL) at room temp.; the reaction time is 12 h. [b] Yield of isolated product after flash column chromatography. [c] Catalyst (10 mol-%) was used. [d] Catalyst (15 mol-%) was used. [e] Catalyst (30 mol-%) was used.

3,4-dimethoxy-, and 3,4,5-trimethoxy-substituted tosyl sulfones **14** proceeded to produce the corresponding bis-symmetrical triarylmethanes in 64, 59, 63, and 60% yields, respectively (Entries 2–5). The tolyl sulfones **14** (R = 4-Cl and 2-Cl) gave the corresponding products in 56 and 52% yields, respectively (Entries 6 and 7).

A likely mechanism for the formation of **16** or **17** could start from the oxonium ion **C** (Figure 3) formed by elimination of arenesulfinic acid from the tolyl sulfones **14** through the catalytic action of Fe^{III}, by way of **A** and **B**. The oxonium ion **C** could react with indole derivatives **15** or 1,2,4-trimethoxybenzene (**9**) to yield the corresponding Friedel–Crafts products **16** or **17** by elimination of arenesulfinic acid ($ArSO_2H$).

Under similar reaction conditions the reaction between [(benzyloxycarbonyl)amino](4-methoxy-3-methylphenyl)-methyl *p*-tolyl sulfone (**18**) and 1,2,3-trimethoxybenzene (**19**) afforded the product **20**. Compound **20** further underwent Friedel–Crafts alkylation with the electron-rich indole to form the unsymmetrical triarylmethane **21** (Scheme 4).

Table 5. $FeCl_3 \cdot 6H_2O$-catalyzed synthesis of bis-symmetrical triarylmethanes.[a]



Entry	R in **14**	Product	Reaction time [h]	% Isolated yield[b]
1	C_6H_5	**17a**	9.0	57
2	4-$MeOC_6H_4$	**17b**	8.0	64
3	3-Me,4-$MeOC_6H_3$	**17c**	8.5	59
4	3,4-$(MeO)_2C_6H_3$	**17d**	8.0	63
5	3,4,5-$(MeO)_3C_6H_2$	**17e**	8.0	60
6	4-ClC_6H_4	**17f**	9.0	56
7	2-ClC_6H_4	**17g**	12.0	52

[a] Reaction conditions: (1-alkyl)(1-aryl)methyl phenyl/tolyl sulfones (1.0 mmol), 1,2,4-trimethoxybenzene (1.0 mmol), and CH_2Cl_2 (2.0 mL) at room temp. [b] Yield of isolated product after flash column chromatography.

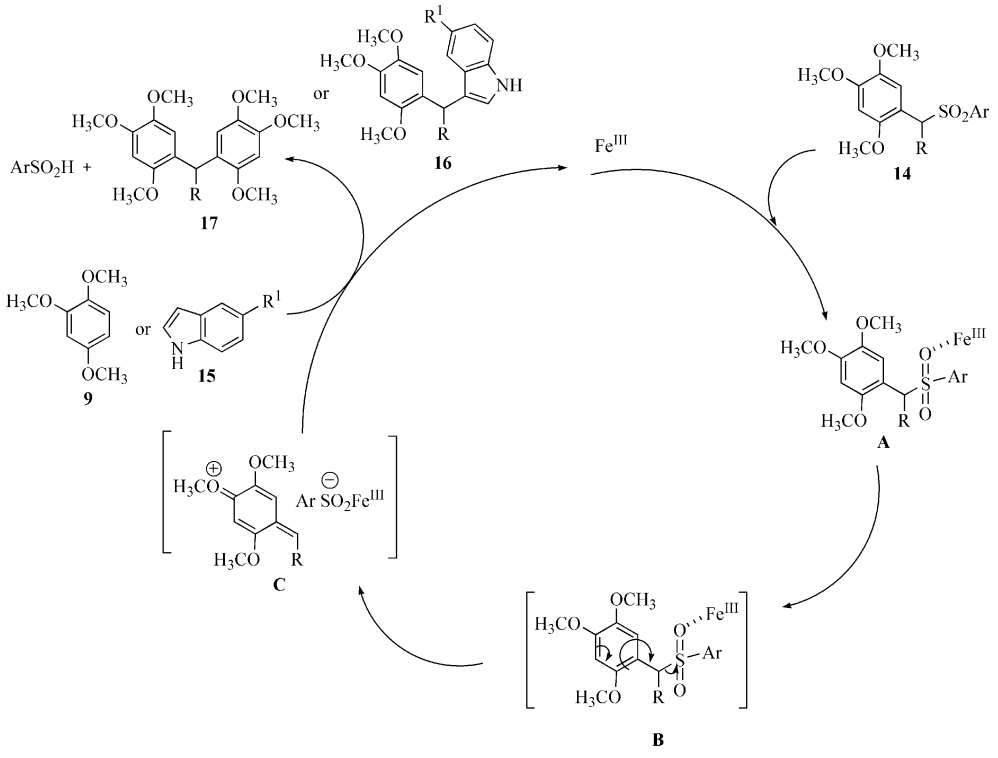
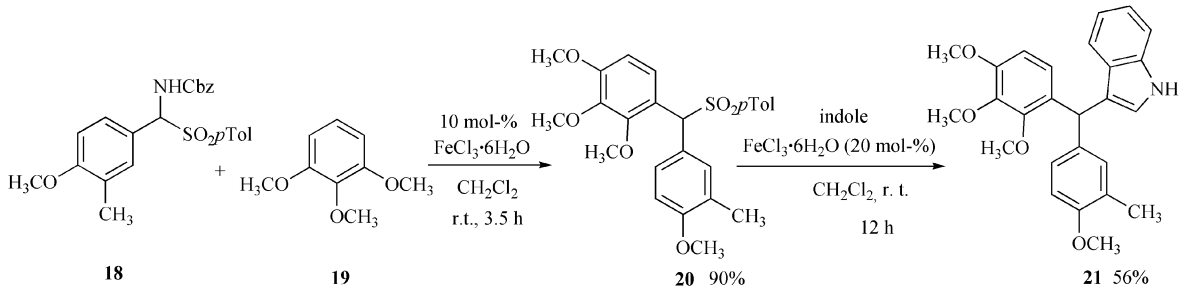


Figure 3. Proposed mechanism for the $FeCl_3 \cdot 6H_2O$-catalyzed synthesis of unsymmetrical or bis-symmetrical triarylmethanes.



Scheme 4. Synthesis of an unsymmetrical triarylmethane from 1,2,3-trimethoxybenzene.

Conclusions

We have described the action of $FeCl_3 \cdot 6H_2O$ as a highly effective catalyst for Friedel–Crafts reactions between electron-rich arenes and α-amido sulfones. This catalyst shows high efficiency in regioselective substitution reactions between α-amido sulfones and electron-rich arenes. The products undergo further Friedel–Crafts alkylations with heteroaromatic or electron-rich arenes, giving rise to unsymmetrical or bis-symmetrical triarylmethanes. This provides a facile and convenient route for the synthesis of unsymmetrical and bis-symmetrical triarylmethanes of wide structural diversity. The advantages of this method include: 1) high efficiency and excellent regioselectivity, 2) mild conditions, and 3) reusability of the catalyst.

Experimental Section

a) Regioselective Friedel–Crafts Arylation of α-Amido Sulfones with Electron-Rich Arenes: An electron-rich arene (1 mmol) was added under nitrogen to a stirred solution of the α-amido sulfone (1 mmol) and $FeCl_3 \cdot 6H_2O$ (10 mol-%) in CH_2Cl_2 (2 mL). The mixture was stirred at room temp. and the reaction was monitored by TLC. After completion, the reaction mixture was filtered, and the residue was washed with diethyl ether (3 × 5 mL). In the recycling experiment, the residue was used in the next run. The filtrate was dried with anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was subjected to flash column chromatography (silica gel, hexane/EtOAc 4:1 to 3:1) to afford the pure product.

b) Experimental Procedure for the Synthesis of Unsymmetrical or Bis-Symmetrical Triarylmethanes: $FeCl_3 \cdot 6H_2O$ (10–20 mol-%) was added under nitrogen to a mixture of a (1-alkyl)(1-aryl)methyl phenyl/tolyl sulfone (1 mmol) and either 1,2,4-trimethoxybenzene (1.1 mmol) or a heteroaromatic indole derivative in CH_2Cl_2 (2 mL). The resulting solution was stirred at room temp. for 8.0–12.0 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was quenched with distilled water (5 mL) and extracted with EtOAc (5 mL). The combined organic portions were washed with water (5 mL) and saturated aqueous NH_4Cl (5 mL), dried with anhydrous Na_2SO_4, and concentrated under vacuum. The crude product was subjected to flash column chromatography (silica gel, hexane/EtOAc 3:1) to provide pure product.

c) Characterization Data for the Products

Compound 12a: White solid; m.p. 110–111 °C; yield 317 mg (83.0%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.00 (d, J = 8.0 Hz, 1 H), 7.64 (d, J = 8.5 Hz, 2 H), 7.56 (d, J = 8.5 Hz, 2 H), 7.36–7.33 (m, 3 H), 7.19 (d, J = 8.0 Hz, 2 H), 6.62 (d, J = 8.5 Hz, 1 H), 6.32 (s, 1 H), 6.03 (s, 1 H), 3.82 (s, 3 H), 3.54 (s, 3 H), 2.40 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 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 ppm. HRMS-EI calcd. for $C_{22}H_{22}O_4S$ $[M]^+$: 382.1239; found 382.1263.

Compound 12b: White solid; m.p. 88–90 °C; yield 354 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.82 (d, J = 8.2 Hz, 1 H), 7.53–7.49 (m, 4 H), 7.29–7.27 (m, 3 H), 7.14 (d, J = 8.5 Hz, 2 H), 6.74 (d, J = 8.2 Hz, 1 H), 5.88 (s, 1 H), 3.84 (s, 3 H), 3.71 (s, 3 H), 3.58 (s, 3 H), 2.33 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 153.9, 152.0, 144.2, 135.8, 133.6, 130.1, 129.2, 129.0, 128.6, 128.4, 124.4, 119.5, 107.3, 67.2, 61.0, 60.6, 55.9, 21.6 ppm. HRMS-EI calcd. for $C_{23}H_{24}O_5S$ $[M]^+$: 412.1344; found 412.1342.

Compound 12c: White solid; m.p. 128 °C; yield 366 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.64 (d, J = 8.4 Hz, 2 H), 7.50 (d, J = 8.5 Hz, 2 H), 7.25–7.39 (m, 3 H), 7.17 (d, J = 8.4 Hz, 2 H), 6.15 (s, 1 H), 6.06 (s, 2 H), 3.77 (s, 3 H), 3.64 (s, 6 H), 2.37 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 161.6, 143.3, 138.2, 134.4, 130.2, 128.8, 128.7, 127.8, 127.5, 104.3, 91.0, 67.7, 55.6, 55.2, 21.5 ppm. HRMS-EI calcd. for $C_{23}H_{24}O_5S$ $[M]^+$: 412.1344; found 412.1316.

Compound 12d: Light yellow solid; m.p. 171 °C; yield 374 mg (91%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.58 (s, 1 H), 7.57 (d, J = 8.4 Hz, 2 H), 7.50 (d, J = 8.0 Hz, 2 H), 7.31–7.29 (m, 3 H), 7.14 (d, J = 8.4 Hz, 2 H), 6.23 (s, 1 H), 5.98 (s, 1 H), 3.91 (s, 3 H), 3.82 (s, 3 H), 3.51 (s, 3 H), 2.35 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 151.6, 149.8, 144.0, 143.0, 135.9, 133.5, 129.9, 128.9, 128.8, 128.5, 128.2, 113.1, 112.9, 96.8, 66.3, 56.5, 56.3, 55.9, 21.5 ppm. HRMS-EI calcd. for $C_{23}H_{24}O_5S$ $[M]^+$: 412.1344; found 412.1343.

Compound 14a: White solid; yield 354 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.63 (d, J = 8.6 Hz, 2 H), 7.58–7.56 (m, 3 H), 7.48 (t, J = 8.6 Hz, 2 H), 7.37–6.29 (m, 5 H), 6.29 (s, 1 H), 6.00 (s, 1 H), 3.91 (s, 3 H), 3.81 (s, 3 H), 3.47 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 151.6, 149.9, 143.1, 138.8, 133.3, 133.1, 129.9, 128.8, 128.5, 128.3, 113.2, 112.7, 96.7, 66.2, 56.6, 56.2, 55.9 ppm.[3]

Compound 14b: White solid; m.p. 122–123 °C; yield 383 mg (90%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.57 (s, 1 H), 7.51 (d, J = 8.4 Hz, 2 H), 7.45 (d, J = 8.0 Hz, 2 H), 7.14 (d, J = 8.0 Hz, 2 H), 7.12 (d, J = 8.4 Hz, 2 H), 6.31 (s, 1 H), 5.95 (s, 1 H), 3.91 (s, 3 H), 3.82 (s, 3 H), 3.50 (s, 3 H), 2.36 (s, 3 H), 2.31 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 151.6, 149.8, 143.9, 143.1, 138.2, 136.1, 129.9, 129.3, 129.0, 128.9, 113.3, 113.2, 96.9, 66.1, 56.6, 56.4, 56.0, 21.6, 21.1 ppm. HRMS-EI calcd. for $C_{24}H_{26}O_5S$ $[M]^+$: 426.1501; found 426.1511.

Compound 14c: White solid; m.p. 143.0 °C; yield 411 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.58 (s, 1 H), 7.52–7.48 (m, 4 H), 7.14 (d, J = 8.0 Hz, 2 H), 6.84 (d, J = 8.6 Hz, 2 H), 6.32 (s, 1 H), 5.93 (s, 1 H), 3.92 (s, 3 H), 3.82 (s, 3 H), 3.76 (s, 3 H), 3.51 (s, 3 H), 2.35 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 159.6, 151.6, 149.8, 144.0, 143.1, 136.0, 131.3, 129.0, 128.8, 125.3, 114.0, 113.3, 113.1, 97.0, 65.8, 56.6, 56.5, 56.0, 55.2, 21.5 ppm. HRMS-EI calcd. for $C_{24}H_{26}O_6S$ $[M]^+$: 442.1450; found 442.1460.

Compound 14d: White solid; yield 398 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.61 (d, J = 8.3 Hz, 2 H), 7.55 (s, 1 H), 7.49–7.46 (m, 3 H), 7.32 (t, J = 8.3 Hz, 1 H), 6.83 (d, J = 8.3 Hz, 2 H), 6.28 (s, 1 H), 5.95 (s, 1 H), 3.90 (s, 3 H), 3.79 (s, 3 H), 3.74 (s, 3 H), 3.46 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 159.6, 151.6, 149.9, 143.1, 138.9, 133.2, 131.3, 128.8,128.4, 125.1, 114.0,113.2, 113.0, 96.9, 65.8, 56.7, 56.4, 56.0, 55.2 ppm.[3]

Compound 14e: White solid; m.p. 131–133 °C; yield 406 mg (92%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.62 (d, J = 8.4 Hz, 2 H), 7.57 (s, 1 H), 7.49–7.42 (m, 2 H), 7.33 (t, J = 7.6 Hz, 2 H), 7.27 (s, 1 H), 6.76 (d, J = 8.4 Hz, 1 H), 6.27 (s, 1 H), 5.92 (s, 1 H), 3.91 (s, 3 H), 3.80 (s, 3 H), 3.77 (s, 3 H), 3.45 (s, 3 H), 2.16 (s, 3 H), 2.12 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 157.8, 151.5, 149.8, 143.0, 138.9, 132.9, 128.7, 128.4, 128.2, 126.7, 124.3, 113.3, 113.1, 109.8, 96.8, 65.7, 56.5, 56.2, 55.8, 55.1, 16.1 ppm. HRMS-EI calcd. for $C_{24}H_{26}O_6S$ $[M]^+$: 442.1450; found 442.1460.

Compound 14f: White solid; m.p. 146–147 °C; yield 419 mg (92%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.55 (s, 1 H), 7.47 (d, J = 8.2 Hz, 2 H), 7.37 (d, J = 8.0 Hz, 1 H), 7.22 (s, 1 H), 7.08 (d, J = 8.2 Hz, 2 H), 6.71 (d, J = 8.0 Hz, 1 H), 6.26 (s, 1 H), 5.86 (s, 1 H), 3.87 (s, 3 H), 3.76 (s, 3 H), 3.73 (s, 3 H), 3.44 (s, 3 H), 2.29 (s, 3 H), 2.12 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 157.6, 151.4, 149.6, 143.7, 142.9, 135.9, 132.3, 128.8, 128.7, 128.3, 126.5, 124.5, 113.2, 113.1, 109.7, 96.8, 65.6, 56.5, 56.2, 55.8, 55.1, 21.3, 16.1 ppm. HRMS-EI calcd. for $C_{25}H_{28}O_6S$ [M]$^+$: 456.1607; found 456.1597.

Compound 14g: White solid; m.p. 131–132 °C; yield 404 mg (88%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.51 (s, 1 H), 7.50 (d, J = 8.0 Hz, 2 H), 7.31–7.25 (m, 2 H), 7.15 (d, J = 8.6 Hz, 2 H), 6.89 (t, J = 8.4 Hz, 1 H), 6.31 (s, 1 H), 5.88 (s, 1 H), 3.91 (s, 3 H), 3.85 (s, 3 H), 3.82 (s, 3 H), 3.50 (s, 3 H), 2.35 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 153.1, 151.6, 150.7, 150.0, 147.7, 147.6, 144.2, 143.2, 135.7, 129.0, 128.8, 117.8, 117.7, 113.1, 112.7, 96.9, 65.3, 56.6, 56.4, 56.1, 55.9, 21.5 ppm. HRMS-EI calcd. for $C_{24}H_{25}FO_6S$ [M]$^+$: 460.1356; found 460.1344.

Compound 14h: White solid; m.p. 186–187 °C; yield 438 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.59 (s, 1 H), 7.52 (d, J = 8.6 Hz, 2 H), 7.16 (d, J = 8.2 Hz, 2 H), 7.14 (d, J = 8.6 Hz, 1 H), 7.06 (s, 1 H), 6.82 (d, J = 8.2 Hz, 2 H), 6.35 (s, 1 H), 5.92 (s, 1 H), 3.92 (s, 3 H), 3.85 (s, 3 H), 3.83 (s, 3 H), 3.53 (s, 3 H), 2.36 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 151.7, 149.9, 149.1, 148.7, 144.0, 143.1, 136.0, 129.0, 128.9, 125.6, 122.6, 113.2, 113.1, 111.0, 97.1, 66.0, 56.6, 56.4, 56.0, 55.8 (×2) 21.5 ppm. HRMS-EI calcd. for $C_{25}H_{28}O_7S$ [M]$^+$: 472.1556; found 472.

Compound 14i: White solid; m.p. 156 °C; yield 454 mg (90%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.55 (s, 1 H), 7.49 (d, J = 8.0 Hz, 2 H), 7.13 (d, J = 8.4 Hz, 2 H), 6.77 (s, 1 H), 6.29 (s, 1 H), 5.87 (s, 1 H), 3.88 (s, 3 H), 3.80 (s, 3 H), 3.78 (s, 9 H), 3.47 (s, 3 H), 2.33 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 153.0, 151.7, 150.0, 144.1, 143.1, 135.9, 129.0, 128.9, 128.8, 113.2, 112.7, 107.3, 96.9, 66.2, 60.8, 56.6, 56.3, 56.0, 56.0, 21.5 ppm. HRMS-EI calcd. for $C_{26}H_{30}O_8S$ [M]$^+$: 502.1661; found 502.1661.

Compound 14j: Yellow solid; m.p. 148 °C; yield 379 mg (83%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.09 (d, J = 8.6 Hz, 2 H), 7.73 (d, J = 8.2 Hz, 2 H), 7.46 (d, J = 8.6 Hz, 2 H), 7.43 (s, 1 H), 7.11 (d, J = 8.2 Hz, 2 H), 6.28 (s, 1 H), 6.04 (s, 1 H), 3.84 (s, 3 H), 3.76 (s, 3 H), 3.44 (s, 3 H), 2.30 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 151.5, 150.2, 147.2, 144.5, 142.9, 140.8, 135.0, 130.7, 129.0, 128.5, 123.3, 112.6, 111.2, 96.5, 65.5, 56.4, 56.0, 55.7, 21.3 ppm. HRMS-EI calcd. for $C_{23}H_{23}NO_7S$ [M]$^+$: 457.1195; found 457.1189.

Compound 14k: Yellow solid; yield 358 mg (82%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.65 (d, J = 8.4 Hz, 2 H), 7.56 (d, J = 8.4 Hz, 2 H), 7.46 (d, J = 8.0 Hz, 2 H), 7.44 (s, 1 H), 7. 13 (d, J = 8.4 Hz, 2 H), 6.27 (s, 1 H), 5.96 (s, 1 H), 3.86 (s, 3 H), 3.79 (s, 3 H), 3.46 (s, 3 H), 2.33 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 151.6, 150.3, 144.5, 143.1, 138.9, 135.3, 132.1, 130.6, 129.1, 128.7, 118.3, 112.8, 111.9, 111.5, 96.7, 66.9, 56.6, 56.1, 55.9, 21.5. MS (EI): m/z = 437 [M]$^+$, 283, 282, 266 ppm.

Compound 14l: White solid; m.p. 137 °C; yield 396 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.50–7.47 (m, 5 H), 7.25 (d, J = 8.5 Hz, 2 H), 7.17 (d, J = 8.5 Hz, 2 H), 6.29 (s, 1 H), 5.93 (s, 1 H), 3.88 (s, 3 H), 3.79 (s, 3 H), 3.46 (s, 3 H), 2.32 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 151.5, 149.9, 144.1, 143.0, 135.5, 134.1, 132.0, 131.2, 128.9, 128.6, 128.5, 112.9, 112.3, 96.7, 65.5, 56.5, 56.1, 55.8, 21.3 ppm. HRMS-EI calcd. for $C_{23}H_{23}ClO_5S$ [M]$^+$: 446.0955; found 446.0955.

Compound 14m: White solid; m.p. 157–158 °C; yield 383 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.57–7.54 (m, 5 H), 7.32 (s, 2 H), 7.22 (d, J = 8.5 Hz, 2 H), 6.37 (s, 1 H), 5.99 (s, 1 H), 3.97 (s, 3 H), 3.88 (s, 3 H), 3.56 (s, 3 H), 2.42 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 151.6, 150.1, 144.3, 143.1, 135.6, 135.5, 134.3, 130.1, 129.7, 129.1, 128.8, 128.4, 128.0, 112.9, 112.2, 96.7, 65.7, 56.6, 56.3, 55.9, 21.5 ppm. HRMS-EI calcd. for $C_{23}H_{23}ClO_5S$ [M]$^+$: 446.0955; found 446.0949.

Compound 14n: White solid; m.p. 146–147 °C; yield 370 mg (83%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.36 (d, J = 8.6 Hz, 1 H), 7.64 (d, J = 8.2 Hz, 2 H), 7.62 (s, 1 H), 7.46 (t, J = 8.6 Hz, 1 H), 7.41 (d, J = 7.6 Hz, 1 H), 7.33 (t, J = 8.6 Hz, 1 H), 7.29 (d, J = 8.2 Hz, 2 H), 6.73 (s, 1 H), 6.47 (s, 1 H), 4.02 (s, 3 H), 3.95 (s, 3 H), 3.62 (s, 3 H), 2.49 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 152.1, 150.0, 144.2, 142.8, 135.7, 135.1, 131.9, 130.4, 129.5, 129.2, 128.9, 128.8, 126.7, 113.4, 111.9, 96.6, 61.9, 56.4, 56.1, 55.7, 21.3 ppm. HRMS-EI calcd. for $C_{23}H_{23}ClO_5S$ [M]$^+$: 446.0955; found 446.0955.

Compound 14o: White solid; m.p. 141–142 °C; yield 411 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.03 (s, 1 H), 7.81–7.78 (m, 3 H), 7.70 (dd, J = 8.0, 1.6 Hz, 1 H), 7.64 (d, J = 1.6 Hz, 1 H), 7.54 (d, J = 8.5 Hz, 2 H), 7.47–7.45 (m, 2 H), 7.14 (d, J = 8.5 Hz, 2 H), 6.34 (s, 1 H), 6.16 (s, 1 H), 3.93 (s, 3 H), 3.83 (s, 3 H), 3.53 (s, 3 H), 2.35 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 151.7,149.9, 144.0, 143.1, 136.0, 133.1, 132.8, 131.0, 129.5, 129.0, 128.8, 128.2, 128.1, 127.5, 127.2, 126.3, 126.1, 113.4, 113.0, 96.9, 66.5, 56.6, 55.9, 21.5 ppm. HRMS-EI calcd. for $C_{23}H_{23}ClO_5S$ [M]$^+$: 462.1501; found 462.1505.

Compound 14p: White solid; m.p. 173 °C; yield 337 mg (84%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.48 (d, J = 8.0 Hz, 2 H), 7.42 (s, 1 H), 7.17 (d, J = 8.0 Hz, 2 H), 6.53 (d, J = 3.4 Hz, 1 H), 6.37–6.36 (m, 1 H), 6.34 (s, 1 H), 6.12 (s, 1 H), 3.87 (s, 3 H), 3.85 (s, 3 H), 3.55 (s, 3 H), 2.38 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 151.9, 150.4, 146.2, 144.2, 143.4, 143.3, 135.2, 129.1, 129.0, 114.0, 111.8, 110.8, 110.4, 96.7, 61.3, 56.5, 56.4, 56.0, 21.6 ppm. HRMS-EI calcd. for $C_{21}H_{22}O_6S$ [M]$^+$: 402.1137; found 402.1141.

Compound 14q: White solid; m.p. 147 °C; yield 330 mg (79%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.47 (d, J = 8.0 Hz, 2 H), 7.44 (s, 1 H), 7.26 (d, J = 5.1 Hz, 1 H), 7.20 (d, J = 4.4 Hz, 1 H), 7.11 (d, J = 8.0 Hz, 2 H), 6.95 (dd, J = 5.1, 4.4 Hz, 1 H), 6.28 (s, 1 H), 6.23 (s, 1 H), 3.86 (s, 3 H), 3.81 (s, 3 H), 3.49 (s, 3 H), 2.33 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 151.6, 150.1, 144.1, 142.9, 134.9, 134.4, 129.4, 128.9, 128.8, 126.6, 124.5, 113.1, 112.1, 96.6, 62.2, 56.8, 56.3, 55.8, 21.3 ppm. HRMS-EI calcd. for $C_{21}H_{22}O_5S_2$ [M]$^+$: 418.0909; found 418.0915.

Compound 14r: White solid; m.p. 127–129 °C; yield 372 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.39–7.30 (m, 3 H), 7.16 (s, 1 H), 7.04 (d, J = 8.8 Hz, 2 H), 6.12 (s, 1 H), 4.69 (d, J = 6.5 Hz, 1 H), 3.89 (s, 3 H), 3.78 (s, 3 H), 3.35 (s, 3 H), 2.52–2.48 (m, 2 H), 2.42–2.38 (m, 2 H), 2.30 (s, 3 H), 1.80–1.76 (m, 2 H), 1.70–1.63 (m, 2 H), 1.39–1.14 (m, 3 H), 1.00–0.95 (m, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 152.3, 149.5, 143.2, 143.0, 136.9, 128.4, 128.3, 128.1, 128.0, 112.6, 112.5, 96.3, 66.8, 66.1, 56.6, 56.0, 55.9, 38.2, 32.0, 30.6, 26.1, 25.9, 21.4 ppm. HRMS-EI calcd. for $C_{23}H_{30}O_5S$ [M]$^+$: 418.1814; found 418.1797.

Compound 14s: White solid; m.p. 117 °C; yield 345 mg (83%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.35 (d, J = 8.4 Hz, 2 H), 7.32 (s, 1 H), 7.31 (s, 1 H), 7.30–7.25 (m, 2 H), 7.10 (d, J = 14.0 Hz, 2 H), 7.01 (d, J = 8.0 Hz, 2 H), 6.09 (d, J = 5.6 Hz, 1 H), 5.06–5.00 (m, 4 H), 4.74 (t, J = 8.0 Hz, 1 H), 3.85 (s, 3 H), 3.75 (s, 3 H),

3.33 (s, 3 H), 2.79–2.56 (m, 2 H), 2.27 (s, 3 H), 2.04–1.89 (m, 3 H), 1.72–1.57 (m, 2 H), 1.29–1.20 (m, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 156.8, 152.1, 151.9, 149.5, 143.0, 142.8, 136.3, 136.0, 128.1, 127.7, 111.9, 96.0, 66.3, 56.3, 55.5, 33.8, 29.3, 24.5, 24.4, 21.0 ppm. HRMS-EI calcd. for $C_{23}H_{28}O_5S$ $[M]^+$: 416.1657; found 416.1665.

Compound 14t: White solid; m.p. 123–124 °C; yield 378 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.43 (d, J = 8.5 Hz, 2 H), 7.36 (s, 1 H), 7.28–7.23 (m, 2 H), 7.20–7.13 (m, 3 H), 7.07 (d, J = 8.5 Hz, 2 H), 6.99 (s, 1 H), 6.30 (s, 1 H), 4.79 (d, J = 6.5 Hz, 1 H), 3.87 (s, 6 H), 3.37 (s, 3 H), 2.80–2.77 (m, 1 H), 2.68–2.43 (m, 1 H), 2.42–2.38 (m, 1 H), 2.37 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 151.9, 149.1, 143.0, 142.3, 139.6, 134.3, 128.0, 127.8, 127.5, 127.5, 127.4, 127.2, 127.1, 125.2, 110.5, 95.5, 65.7, 55.6, 55.0, 54.9, 31.7, 27.9, 20.6 ppm. HRMS-EI calcd. for $C_{25}H_{28}O_5S$ $[M]^+$: 440.1657; found 440.1656.

Compound 14u: White solid; m.p. 79 °C; yield 291 mg (77%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.37–7.29 (m, 4 H), 7.11 (s, 1 H), 7.00 (d, J = 7.4 Hz, 2 H), 6.10 (s, 1 H), 4.57 (d, J = 6.5 Hz, 1 H), 3.84 (s, 3 H), 3.75 (s, 3 H), 3.32 (s, 3 H), 2.77–2.74 (m, 1 H), 2.27 (s, 3 H), 1.26 (d, J = 6.5 Hz, 1 H), 0.89 (d, J = 6.5 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 152.2, 149.5, 143.2, 142.9, 136.7, 128.4, 128.3, 128.1, 112.5, 96.2, 66.7, 56.5, 55.9, 55.8, 28.7, 21.4, 21.3, 20.9 ppm. HRMS-EI calcd. for $C_{20}H_{26}O_5S$ $[M]^+$: 378.1501; found 378.1508.

Compound 14v: White solid; m.p. 85 °C; yield 283 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.39 (d, J = 8.0 Hz, 2 H), 7.10 (d, J = 8.0 Hz, 2 H), 6.91 (s, 1 H), 6.21 (s, 1 H), 4.88 (d, J = 12.0 Hz, 1 H), 3.81 (s, 3 H), 3.80 (s, 3 H), 3.33 (s, 3 H), 2.33 (s, 3 H), 2.34–2.30 (m, 1 H), 2.14–1.98 (m, 1 H), 1.31–1.11 (m, 2 H), 0.84 (t, J = 7.6 Hz, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 152.6, 149.8, 143.6, 143.2, 135.4, 128.8, 128.7, 128.7, 111.9, 96.5, 61.3, 56.5, 56.0, 55.8, 28.8, 21.5, 19.8, 13.5 ppm. HRMS-EI calcd. for $C_{20}H_{26}O_5S$ $[M]^+$: 378.1501; found 378.1508.

Compound 16a: White solid; m.p. 169 °C; yield 171 mg (46%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.96 (br. s, 1 H), 7.33 (d, J = 8.6 Hz, 1 H), 7.28–7.13 (m, 6 H), 7.13 (d, J = 8.6 Hz, 1 H), 6.98 (t, J = 8.6 Hz, 1 H), 6.62 (s, 1 H), 6.58 (d, J = 1.6 Hz, 1 H), 6.03 (s, 1 H), 3.89 (s, 3 H), 3.73 (s, 3 H), 3.58 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 151.2, 148.0, 144.2, 142.8, 136.7, 128.8, 128.0, 127.1, 125.9, 124.3, 123.8, 121.9, 120.0, 119.2, 114.4, 111.0, 98.1, 56.9, 56.6, 56.0, 40.8 ppm. HRMS-EI calcd. for $C_{24}H_{23}NO_3$ $[M]^+$: 373.1678; found 373.1700.

Compound 16b: White solid; m.p. 179–180 °C; yield 221 mg (55%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.96 (br. s, 1 H), 7.31 (d, J = 8.2 Hz, 1 H), 7.25 (d, J = 8.2 Hz, 1 H), 7.13 (d, J = 8.6 Hz, 3 H), 6.99 (t, J = 8.4 Hz, 1 H), 6.80 (d, J = 8.2 Hz, 2 H), 6.61 (s, 1 H), 6.58 (d, J = 8.6 Hz, 1 H), 5.98 (s, 1 H), 3.89 (s, 3 H), 3.78 (s, 3 H), 3.74 (s, 3 H), 3.59 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 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 ppm. HRMS-EI calcd. for $C_{25}H_{25}NO_4$ $[M]^+$: 403.1784; found 403.1786.

Compound 16c: White solid; m.p. 150–152 °C; yield 259 mg (60%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.98 (br. s, 1 H), 7.22 (d, J = 8.5 Hz, 1 H), 7.18 (d, J = 8.5 Hz, 2 H), 6.86–6.84 (m, 3 H), 6.71 (d, J = 1.5 Hz, 1 H), 6.67 (s, 1 H), 6.62 (s, 1 H), 6.58 (d, J = 1.5 Hz, 1 H), 5.96 (s, 1 H), 3.92 (s, 3 H), 3.81 (s, 3 H), 3.76 (s, 3 H), 3.72 (s, 3 H), 3.64 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 157.6, 153.5, 151.2, 147.9, 142.8, 136.2, 131.9, 129.6, 127.4, 124.5, 119.6, 114.3, 113.3, 111.7, 111.5, 98.2, 56.9, 56.7, 56.0, 55.7, 55.1, 40.0 ppm. HRMS-EI calcd. for $C_{26}H_{27}NO_5$ $[M]^+$: 433.1889; found 433.1885.

Compound 16d: White solid; m.p. 170 °C; yield 221 mg (53%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.09 (br. s, 1 H), 7.32 (d, J = 7.6 Hz, 1 H), 7.30 (d, J = 7.6 Hz, 1 H), 7.17 (t, J = 7.6 Hz, 1 H), 7.11 (s, 1 H), 7.06–7.00 (m, 2 H), 6.75 (d, J = 8.0 Hz, 1 H), 6.72 (s, 1 H), 6.64 (s, 1 H), 6.58 (s, 1 H), 6.03 (s, 1 H), 3.92 (s, 3 H), 3.82 (s, 3 H), 3.78 (s, 3 H), 3.64 (s, 3 H), 2.23 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 155.8, 151.1, 147.8, 142.7, 136.6, 135.7, 131.1, 126.9, 126.7, 125.8, 124.8, 123.7, 121.6, 119.9, 119.8, 118.5, 114.4, 111.0, 109.3, 98.1, 56.8, 56.5, 55.9, 55.1, 39.8, 16.2 ppm. HRMS-EI calcd. for $C_{26}H_{27}NO_4$ $[M]^+$: 417.1940; found 417.1942.

Compound 16e: White solid; m.p. 172.9 °C; yield 250 mg (56%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.97 (br. s, 1 H), 7.17 (d, J = 8.8 Hz, 1 H), 7.05 (d, J = 2.0 Hz, 1 H), 6.99 (dd, J = 8.4, 2.0 Hz, 1 H), 6.81 (dd, J = 8.4, 2.0 Hz, 1 H), 7.72 (d, J = 8.8 Hz, 1 H), 7.71 (s, 1 H), 6.67 (s, 1 H), 6.59 (s, 1 H), 6.56 (d, J = 2.0 Hz, 1 H), 5.92 (s, 1 H), 3.89 (s, 3 H), 3.80 (s, 3 H), 3.75 (s, 3 H), 3.70 (s, 3 H), 3.62 (s, 3 H), 2.18 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 155.8, 151.1, 147.8, 142.7, 136.6, 135.7, 131.1, 126.9, 126.7, 125.8, 124.8, 123.7, 121.6, 119.9, 119.8, 118.5, 114.4, 111.0, 109.3, 98.1, 56.8, 56.5, 55.9, 55.1, 39.8, 16.2 ppm. HRMS-EI calcd. for $C_{27}H_{29}NO_5$ $[M]^+$: 447.2046; found 447.2050.

Compound 16f: White solid; m.p. 145–147 °C; yield 206 mg (49%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.95 (br. s, 1 H), 7.30 (d, J = 8.4 Hz, 1 H), 7.23 (s, 1 H), 7.19 (d, J = 8.0 Hz, 3 H), 7.12 (t, J = 7.4 Hz, 1 H), 6.96 (d, J = 7.6 Hz, 1 H), 6.93 (d, J = 7.6 Hz, 1 H), 6.89 (d, J = 7.6 Hz, 1 H), 6.82 (t, J = 8.4 Hz, 1 H), 6.56–6.54 (m, 3 H), 5.92 (s, 1 H), 3.86 (s, 3 H), 3.83 (s, 3 H), 3.71 (s, 3 H), 3.56 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 153.3, 151.1, 151.0, 148.1, 145.6, 142.8, 137.5, 136.7, 126.9, 124.2, 123.8, 123.9, 122.0, 119.8, 119.4, 119.2, 116.5, 116.3, 114.1, 112.9, 110.9, 98.0, 56.9, 56.7, 56.1, 56.0, 40.0 ppm. MS (EI): m/z = 421 $[M]^+$, 420, 319, 151 ppm.

Compound 16g: White solid; m.p. 157–158 °C; yield 233 mg (54%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.02 (br. s, 1 H), 7.27 (d, J = 8.0 Hz, 1 H), 7.22 (d, J = 8.0 Hz, 1 H), 7.11 (t, J = 8.5 Hz, 1 H), 6.94 (t, J = 8.5 Hz, 1 H), 6.79 (d, J = 2.0 Hz, 1 H), 6.73 (d, J = 8.4 Hz, 1 H), 6.68 (dd, J = 8.4, 1.8 Hz, 1 H), 6.59 (s, 1 H), 6.55 (s, 1 H), 6.54 (d, J = 1.5 Hz, 1 H), 5.94 (s, 1 H), 3.86 (s, 3 H), 3.81 (s, 3 H), 3.73 (s, 3 H), 3.71 (s, 3 H), 3.56 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 151.2, 148.5, 148.0, 147.1, 136.8, 136.7, 127.0, 124.4, 123.7, 121.8, 120.6, 119.9, 119.1, 114.3, 112.4, 111.0, 110.7, 98.1, 56.9, 56.6, 56.0, 55.7, 40.3 ppm. HRMS-EI calcd. for $C_{26}H_{27}NO_5$ $[M]^+$: 433.1889; found 433.1902.

Compound 16h: White solid; m.p. 175–177 °C; yield 263 mg (57%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.96 (br. s, 1 H), 7.19 (d, J = 8.8 Hz, 1 H), 6.81 (s, 1 H), 6.70 (d, J = 2.0 Hz, 1 H), 6.75 (d, J = 8.4 Hz, 1 H), 6.74 (d, J = 1.8 Hz, 1 H), 6.69 (d, J = 8.8 Hz, 1 H), 6.68 (d, J = 2.0 Hz, 1 H), 6.62 (s, 1 H), 6.56 (s, 1 H), 5.91 (s, 1 H), 3.86 (s, 3 H), 3.84 (s, 3 H), 3.75 (s, 3 H), 3.73 (s, 3 H), 3.69 (s, 3 H), 3.59 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 153.5, 151.2, 148.5, 147.9, 147.1, 142.8, 136.7, 131.9, 127.5, 124.5, 120.6, 119.6, 114.3, 112.4, 111.7, 110.7, 102.0, 98.1, 57.0, 56.6, 56.0, 55.7, 40.3 ppm. HRMS-EI calcd. for $C_{27}H_{29}NO_6$ $[M]^+$: 463.1995; found 463.1995.

Compound 17a: White solid; m.p. 126–127 °C; yield 241 mg (57%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.26–7.21 (m 2 H), 7.17–7.13 (m, 1 H), 7.04 (d, J = 8.2 Hz, 2 H), 6.54 (s, 2 H), 6.42 (s, 2 H), 6.07 (s, 1 H), 3.87 (s, 6 H), 3.65 (s, 6 H), 3.62 (s, 6 H) ppm. ^{13}C

NMR (50 MHz, $CDCl_3$, 25 °C): 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 ppm. HRMS-EI calcd. for $C_{25}H_{28}O_6$ $[M]^+$: 424.1886; found 424.1884.

Compound 17b: White solid; m.p. 131 °C; yield 290 mg (64%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.11 (d, J = 8.2 Hz, 2 H), 6.93 (d, J = 8.2 Hz, 2 H), 6.69 (s, 2 H), 6.58 (s, 2 H), 6.17 (s, 1 H), 4.02 (s, 6 H), 3.91 (s, 3 H), 3.80 (s, 6 H), 3.79 (s, 6 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): 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 ppm. HRMS-EI calcd. for $C_{26}H_{30}O_7$ $[M]^+$: 454.1992; found 454.1993.

Compound 17c: White solid; m.p. 119–121 °C; yield 276 mg (59%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.84 (s, 1 H), 6.77 (d, J = 8.0 Hz, 1 H), 6.68 (s, 2 H), 6.53 (s, 2 H), 6.44 (s, 2 H), 5.99 (s, 1 H), 3.87 (s, 6 H), 3.78 (s, 3 H), 3.66 (s, 6 H), 3.64 (s, 6 H), 2.13 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 155.8, 151.6, 147.9, 142.7, 135.6, 131.5, 126.9, 125.2, 114.6, 109.3, 98.5, 57.1, 56.7, 56.0, 55.2, 41.5, 16.3 ppm. HRMS-EI calcd. for $C_{27}H_{32}O_7$ $[M]^+$: 468.2128; found 468.2142.

Compound 17d: White solid; m.p. 110–111 °C; yield 304 mg (63%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.76 (d, J = 8.0 Hz, 1 H), 6.67 (d, J = 8.0 Hz, 1 H), 6.56 (s, 2 H), 6.53 (s, 1 H), 6.45 (s, 2 H), 6.03 (s, 1 H), 3.90 (s, 6 H), 3.86 (s, 3 H), 3.78 (s, 3 H), 3.69 (s, 6 H), 3.65 (s, 6 H) ppm. ^{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 ppm. HRMS-EI calcd. for $C_{27}H_{32}O_8$ $[M]^+$: 484.2097; found 484.2096.

Compound 17e: White solid; m.p. 97–99 °C; yield 308 mg (60%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.53 (s, 2 H), 6.44 (s, 2 H), 6.27 (s, 2 H), 5.99 (s, 1 H), 3.87 (s, 6 H), 3.81 (s, 3 H), 3.70 (s, 6 H), 3.68 (s, 6 H), 3.64 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 152.8, 151.6, 148.1, 139.8, 124.4, 114.4, 106.3, 98.3, 60.8, 57.1, 56.8, 56.0, 42.5 ppm. HRMS-EI calcd. for $C_{28}H_{34}O_9$ $[M]^+$: 514.2203; found 514.2201.

Compound 17f: White solid; m.p. 168–169 °C; yield 256 mg (56%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.19 (d, J = 8.4 Hz, 2 H), 6.97 (d, J = 8.4 Hz, 2 H), 6.53 (s, 2 H), 6.39 (s, 2 H), 6.01 (s, 1 H), 3.87 (s, 6 H), 3.65 (s, 6 H), 3.63 (s, 6 H) ppm. ^{13}C NMR (50 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 ppm. HRMS-EI calcd. for $C_{25}H_{27}ClO_6$ $[M]^+$: 458.1496; found 458.1497.

Compound 17g: White solid; m.p. 126–127 °C; yield 238 mg (52%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.34 (d, J = 7.2 Hz, 1 H), 7.13–7.10 (m, 2 H), 6.87 (d, J = 7.2 Hz, 1 H), 6.54 (s, 2 H), 6.32 (s, 1 H), 6.31 (s, 2 H), 3.87 (s, 6 H), 3.66 (s, 6 H), 3.61 (s, 6 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): 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 ppm. HRMS-EI calcd. for $C_{25}H_{27}ClO_6$ $[M]^+$: 458.1496; found 458.1492.

Compound 20: White solid; m.p. 138–140 °C; yield 410 mg (90%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.81 (d, J = 8.7 Hz, 1 H), 7.51 (d, J = 8.0 Hz, 2 H), 7.37–7.34 (m, 2 H), 7.27 (s, 1 H), 7.15 (d, J = 8.4 Hz, 2 H), 6.74 (d, J = 8.7 Hz, 2 H), 5.80 (s, 1 H), 5.09 (s, 1 H), 3.84 (s, 3 H), 3.78 (s, 3 H), 3.70 (s, 3 H), 3.57 (s, 3 H), 2.34 (s, 3 H), 2.16 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 157.8, 153.7, 151.9, 144.0, 141.7, 135.9, 132.3, 129.1, 129.0, 128.7, 128.5, 128.1, 126.7, 124.7, 124.3, 119.9, 109.8, 107.3, 66.6, 61.0, 60.5, 55.9, 55.2, 21.5, 16.2 ppm. HRMS-EI calcd. for $C_{25}H_{28}O_6S$ $[M]^+$: 456.1607; found 456.1597.

Compound 21: White solid; m.p. 173 °C; yield 233 mg (56%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.95 (br. s, 1 H), 7.29 (d, J = 8.0 Hz, 1 H), 7.25 (d, J = 8.0 Hz, 1 H), 7.12 (t, J = 8.0 Hz, 1 H), 7.00 (d, J = 1.5 Hz, 1 H), 6.97–6.94 (m, 2 H), 6.69 (d, J = 8.7 Hz, 1 H), 6.53 (s, 1 H), 6.50 (d, J = 8.7 Hz, 1 H), 5.88 (s, 1 H), 3.87 (s, 3 H), 3.78 (s, 3 H), 3.77 (s, 3 H), 3.61 (s, 3 H), 2.19 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 155.9, 151.9, 151.5, 142.2, 136.7, 135.9, 131.2, 130.7, 127.0, 126.8, 126.0, 123.9, 121.9, 120.6, 119.9, 119.1, 110.9, 109.5, 106.7, 60.8, 60.7, 55.8, 55.2, 40.6, 16.3 ppm. HRMS-EI calcd. for $C_{26}H_{27}NO_4$ $[M]^+$: 417.1940; found 417.1953.

Compound E (R = 4-MePh): White solid; yield 332 mg (76%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.08 (d, J = 8.0 Hz, 2 H), 6.87 (d, J = 8.0 Hz, 2 H), 6.51 (s, 2 H), 6.42 (s, 2 H), 6.02 (s, 1 H), 3.87 (s, 3 H), 3.84 (s, 3 H), 3.63 (s, 6 H), 3.61 (s, 6 H), 2.27 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): 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 ppm.

Supporting Information (see also the footnote on the first page of this article): General procedures, preparation of α-amido sulfones, ^1H NMR and ^{13}C NMR spectra and references.

Acknowledgments

The authors thank the Centre for Biological Modulators of the Korea Research Institute of Chemical Technology for the financial support. We also acknowledge the assistance by BK21 provided by the Korea Research Council.

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Received: October 20, 2009
Published Online: January 20, 2010

