Tetrahedron 67 (2011) 7301–7310

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Tris(pentafluorophenyl)borane [$B(C_6F_5)_3$]-catalyzed Friedel–Crafts reactions of activated arenes and heteroarenes with α-amidosulfones: the synthesis of unsymmetrical triarylmethanes

Ponnaboina Thirupathi *, Lok Nath Neupane, Keun-Hyeung Lee *

Bioorganic Chemistry Lab, Department of Chemistry, Inha University, 253-Yunghyun-dong, Nam-gu, Incheon 402-751, South Korea

ARTICLE INFO

Article history:
Received 20 June 2011
Received in revised form 13 July 2011
Accepted 14 July 2011
Available online 23 July 2011

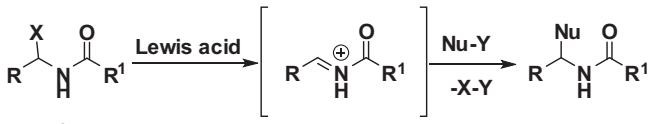
Keywords:
Friedel–Crafts reactions
Tris(pentafluorophenyl)borane [$B(C_6F_5)_3$]
α-Amidosulf-ones
(1-Alkyl-1-aryl)methyl sulfones
Triarylmethanes (TRAMs)

ABSTRACT

Tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] has found to be an efficient catalyst for Friedel–Crafts reactions between activated arenes or heteroarenes and α-amidosulfones. The products undergo further Friedel–Crafts reactions with activated heteroarenes leading to the synthesis of unsymmetrical triarylmethanes. The present synthetic method displayed significant advantages such as low catalyst loading, mild reaction conditions, highly regioselective, high yield, and broad applicability to various substrates.

1. Introduction

Friedel–Crafts alkylation reactions have proven to be an excellent and efficient method for C–C bond formation in organic transformations.[1,2] Generally, these reactions are carried out by either protic acid or Lewis acid catalyst. The Friedel–Crafts alkylation reactions of carbonyl compounds,[3] imines,[4] epoxides,[5] and electron-deficient olefins[6] as substrates have been extensively studied. Recently, the α-amidosulfones are subjected to Friedel–Crafts alkylation reactions as alkylating agents.[7] The application of α-amidosulfones has been explained through the formation of *N*-acyl iminiumions on treatment with Lewis acid (Scheme 1).[8] Compared with *N*-alkylimines, *N*-acylimines and their corresponding iminiumions are considerably more reactive toward nucleophiles in the addition reactions. Similarly, the enhanced electrophilic character of *N*-acyliminium ions of α-amidosulfones allows their reactions with a variety of nucleophiles.[7,8] Petrini et al. have demonstrated that the Montmorillonite K-10 could be an efficient catalyst for the Friedel–Crafts reactions of α-amidosulfones with indoles for the synthesis of 3-substituted indoles.[7a] Reutrakul et al. have reported that the $Yb(OTf)_3$-catalyzed Friedel–Crafts reactions of α-amidosulfones with electron-rich arenes.[7b] Kim et al. have developed Friedel–Crafts type alkylation of electron-rich arenes or heteroarenes with α-amidosulfones using $InBr_3$,[7c] Amberlyst-15[7d] and $FeCl_3 \cdot 6H_2O$[7e] as catalysts, respectively.



Scheme 1. Nucleophilic substitution of α-amidosulfones through *N*-acyliminium ion (**2**).

With increasing environmental concern, the new environmentally benign methods have been extensively studied. Thus synthetic methods should be designed to use substances that exhibit little or no toxicity to human health and environment.[9] In this regard, tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] have recently attracted considerable attention because $B(C_6F_5)_3$ is remarkably nontoxic, air-stable, non-conventional, water-tolerant, and thermally stable Lewis acid.[10] Recently, various research groups were engaged in exploring the potential utility of $B(C_6F_5)_3$ for various organic transformations, such as ring-opening of epoxides, aza-Ferrier glycosylation,[11–13] hydrosilylation of imines,[14] reduction of alcohols with silane,[15] and hydrogenation of imines.[16] In this context, $B(C_6F_5)_3$ has been utilized to catalyze the regio- and stereoselective cyclizations of unsaturated alkoxysilanes.[17] $B(C_6F_5)_3$ is also as an efficient activator for polymethylhydrosiloxane in the reduction of

* Corresponding authors. E-mail addresses: pthiruchem2@gmail.com (P. Thirupathi), leekh@inha.ac.kr (K.-H. Lee).

0040-4020/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2011.07.041

different functional groups.[18,19] In this present work, we would like to report tris(pentafluorophenyl)borane [$B(C_6F_5)_3$]-catalyzed Friedel–Crafts alkylation reaction of activated arenes and heteroarenes with α-amidosulfones as an alkylating agent to synthesize the (1-alkyl-1-aryl)methyl sulfones and triarylmethanes (TRAMs).[7c,e]

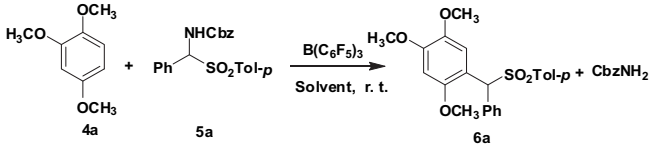
The synthesis of triarylmethanes (TRAMs) has attracted considerable attention due to their various biological activities.[20] These compounds have been found in widespread applications in synthetic, medicinal, and industrial chemistry.[21] The triarylmethyl derivatives are useful as protective groups,[22] photochromic agents,[23]and dyes.[24] The ring-hydroxylated triarylmethanes exhibit antitumor and antioxidant activities.[24c] Different types of methods have been reported for the synthesis of symmetrical triarylmethanes from various substrates.[25] The synthesis of unsymmetrical triarylmethanes is far less explored.[20f,26,27] In this present paper, we also report the $B(C_6F_5)_3$-catalyzed sequential Friedel–Crafts alkylation reactions of α-amidosulfones with different activated arenes leads to the selective synthesis of unsymmetrical triarylmethanes. The present method displayed significant advantages, such as low catalyst loading, mild reaction conditions, highly regioselective, high yield, and broad applicability to various substrates.

2. Result and discussion

Initially, we screened the reaction conditions for Friedel–Crafts alkylation of 1,2,4-trimethoxy benzene **4a** with *N*-benzyloxycarbonylamino phenyl *p*-tolylsulfone **5a** in the absence and presence of tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] (Table 1). In the absence of catalyst, no product was detected (entry 1). When **4a** is treated with **5a** using 1 mol % $B(C_6F_5)_3$ in dichloromethane, the Friedel–Crafts product **6a** was isolated in 39% yield (entry 2). By increasing the quantity of the catalyst results to an increased yields (entries 3–5). Among the various solvents tested, dichloromethane provided the expected product with high yield (entries 4 and 6–10). Thus, dichloromethane was selected as the solvent of choice. Interestingly, when **4a** was reacted with **5a** in presence of 5 mol % $B(C_6F_5)_3$ in dichloromethane at 40 °C, the corresponding product **6a** was obtained in an excellent yield (entry 11). The entry 11 was found to be the best in terms of loading of catalyst, reaction time and yield. This optimized reaction conditions were applied for the various substrates in this study.

On the basis of the optimized reaction conditions, the reactivity of various activated and non-activated arenes with *N*-benzyloxycarbonylamino phenyl *p*-tolylsulfone are investigated for the Friedel–Crafts reaction (Table 2). The Friedel–Crafts alkylation

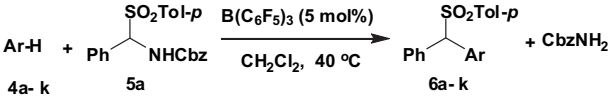
Table 1
Optimization of the reaction conditions for Friedel–Crafts reactions of 1,2,4-trimethoxy benzene with *N*-benzyloxycarbonylamino phenyl *p*-tolylsulfone[a]



Entry	$B(C_6F_5)_3$ mol %	Solvent	Reaction time (h)	Isolated yield[b] (%)
1	—	CH_2Cl_2	14.0	NR
2	1.0	CH_2Cl_2	8.0	39
3	2.5	CH_2Cl_2	6.0	58
4	5.0	CH_2Cl_2	4.0	87
5	10.0	CH_2Cl_2	3.5	89
6	5.0	CH_3CN	8.0	56
7	5.0	1,4-Dioxane	8.0	23
8	5.0	$CHCl_3$	8.0	42
9	5.0	THF	8.0	34
10	5.0	CH_3NO_2	6.0	69
11	**5.0**	**CH_2Cl_2**	**2.5**	**91**[c]

[a] Reaction condition: 1,2,4-trimethoxy benzene (1.0 mmol) and *N*-benzyloxycarbonylamino phenyl *p*-tolylsulfone (1.0 mmol) are used.
[b] Isolated yield of product after column chromatography.
[c] Reaction was carried out at 40 °C.

Table 2
Friedel–Crafts reactions of various activated and non-activated arenes with *N*-benzyloxycarbonylamino phenyl *p*-tolylsulfone catalyzed by $B(C_6F_5)_3$[a]



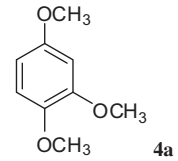
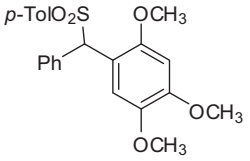
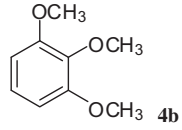
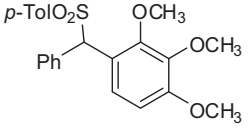
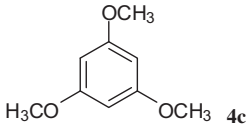
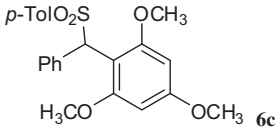
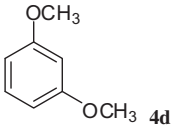
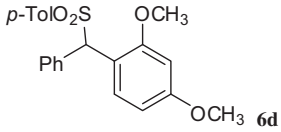
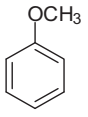
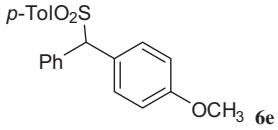
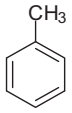
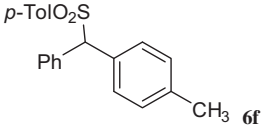
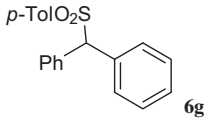
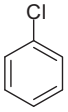
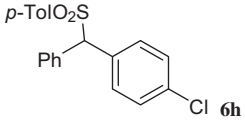
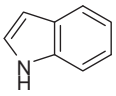
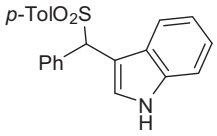
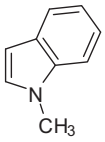
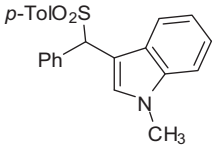
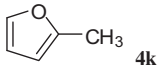
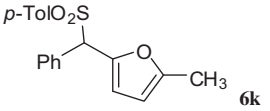
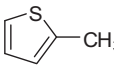
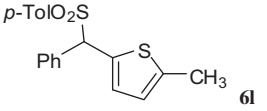
Entry	Ar–H	Product	Reaction time (h)	Isolated yield[b] (%)
1	 **4a**	 **6a**	2.5	91
2	 **4b**	 **6b**	2.5	87

Table 2 (*continued*)

Entry	Ar–H	Product	Reaction time (h)	Isolated yield[b] (%)
3	 **4c**	 **6c**	2.5	85
4	 **4d**	 **6d**	3.5	77
5	 **4e**	 **6e**	4.0	NR
6	 **4f**	 **6f**	4.0	NR
7	 **4g**	 **6g**	6.0	NR
8	 **4h**	 **6h**	6.0	NR
9	 **4i**	 **6i**	2.5	78
10	 **4j**	 **6j**	2.5	75
11	 **4k**	 **6k**	2.0	83
12	 **4l**	 **6l**	2.0	80

[a] Reaction condition: Activated or non-activated arenes **4** (1.0 mmol), *N*-benzyloxycarbonylamino phenyl *p*-tolylsulfone **5a** (1.0 mmol) and $B(C_6F_5)_3$ (5 mol %) were used.
[b] Isolated yield of product after column chromatography.

reactions between the activated trimethoxy benzenes (**4a**, **4b**, or **4c**) and *N*-benzyloxycarbonylamino phenyl *p*-tolylsulfone **5a** give the products in high yield (entries 1–3). However, the 1,3-dimehtoxy benzene **4d** furnishes the product in less yield and the reaction requires a longer reaction time in comparison with entries 1–3 (entry 4). Less activated arenes such as anisole **4e** and toluene **4f** as well as non-activated benzene **4g** give no product under the same reaction condition (entries 5–7). Similarly deactivated arene, chlorobenzene **4h** was also unable to give the corresponding Friedel–Crafts product at all (entry 8). The reactions of heteroarenes,

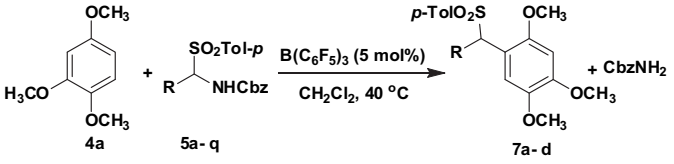
such as indole **4i** and *N*-methyl indole **4j** gave the good yield of corresponding products (entries 9–10). 2-Methyl furan **4k** and 2-methyl thiophene **4l** produce the products in 83 and 80% yield, respectively (entries 11–12). The above results indicate that the highly activated arenes (activation of C–H bond) are more facile substrates for the Friedel–Crafts reactions over non-activated or deactivated arenes (Table 2).

The substitution effect of the arenes on the reaction yield can be well observed. The substitution of electron-donating group of the arenes improves reaction with and decreases the completion of reaction time.

The substrate scope of the Friedel–Crafts alkylation reactions of 1,2,4-trimethoxy benzene **4a** with various α-amidosulfones **5** has been examined and the results are summarized in Table 3. The 1,2,4-trimethoxy benzene **4a** reacts with *N*-benzyloxycarbonylamino 2-naphthyl *p*-tolylsulfone **5b** to afford the Friedel–Crafts product **7b** in high yield (entry 1). The reactions of *p*-chloro- **5c**, *m*-chloro- **5d** and *o*-chloro α-amidosulfones **5e** gave the corresponding products in 90, 87, and 85% yield, respectively (entries 2–4). *o*-Chloro isomer shows slight steric and electronic effects that are responsible for the longer reaction time and less yield (entry 4). The electron-donating substituent's attached to the phenyl ring of α-amidosulfones **5f**–**k** react with 1,2,4-trimethoxy benzene **4a** achieve the Friedel–Crafts product in excellent yield (entries 5–10). The electron-withdrawing substituents like NO_2– **5l** and CN– **5m** in α-amidosulfones require longer reaction time for the completion of the reaction (entries 11–12). The electron-donating substituent in α-amidosulfones enhance the formation of oxonium ion intermediates compare with electron-withdrawing substrates. As a result higher yield of the Friedel–Crafts products were observed (entries 5–10; see the proposed mechanism in Scheme 2). 2-Furyl **5n** and 2-thiophenyl **5o** containing α-amidosulfones react with 1,2,4-trimethoxy benzene **4a** to afford the respective products in good yield (entries 13–14). The reactions of arylalkyl **5p**, cyclic aliphatic **5q** or acyclic aliphatic **5r** α-amidosulfones also result in the Friedel–Crafts products in 83, 85, and 78% yield, respectively (entries 15–17).

Table 4 shows the effect of sulfonyl group in α-amidosulfone. 1,2,4-Trimethoxy benzene **4a** react with *N*-benzyloxycarbonylamino phenyl- **8a** or 4-methoxy phenyl phenylsulfone **8b** to bring about the

Table 3
Friedel–Crafts reactions of 1,2,4-trimethoxy benzene with various α-amidosulfone catalyzed by $B(C_6F_5)_3$[a]



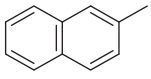
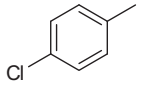
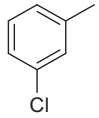
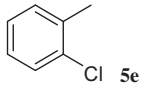
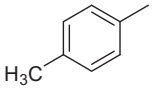
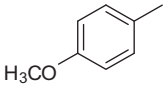
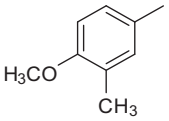
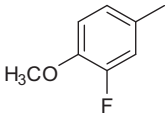
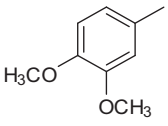
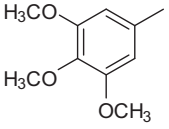
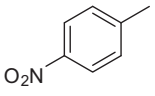
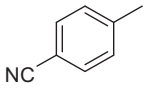
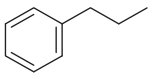
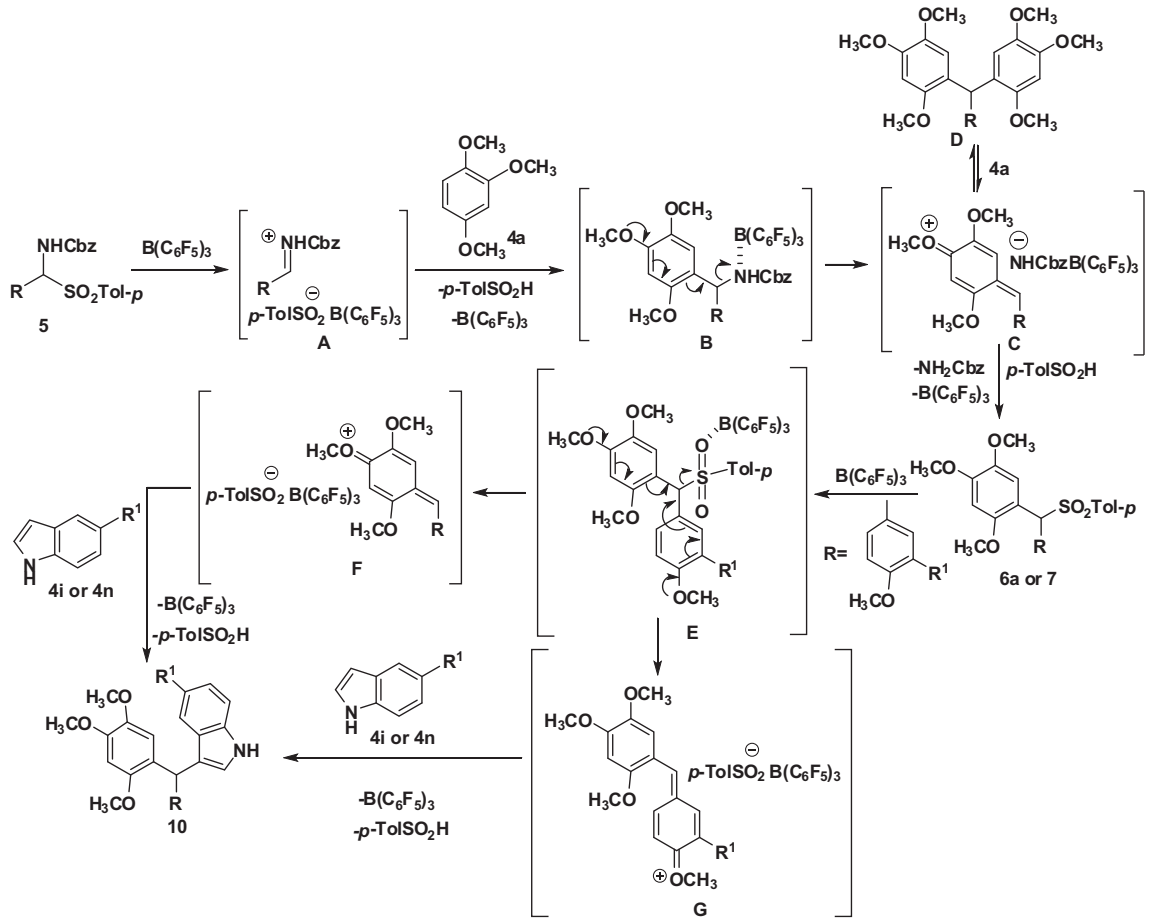
Entry	R in **5**	Product (**7**)	Reaction time (h)	Isolated yield[b] (%)
1	 **5b**	**7a**	3.0	88
2	 **5c**	**7b**	2.5	90
3	 **5d**	**7c**	2.5	87
4	 **5e**	**7d**	3.0	85
5	 **5f**	**7e**	2.5	90

Table 3 (*continued*)

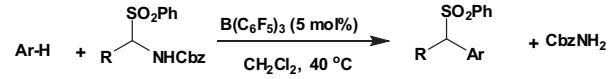
Entry	R in **5**	Product (**7**)	Reaction time (h)	Isolated yield[b] (%)
6	 **5g**	**7f**	2.0	92
7	 **5h**	**7g**	2.0	90
8	 **5i**	**7h**	2.5	89
9	 **5j**	**7i**	2.0	92
10	 **5k**	**7j**	2.0	90
11	 **5l**	**7k**	3.0	84
12	 **5m**	**7l**	3.0	86
13	 **5n**	**7m**	3.0	88
14	 **5o**	**7n**	3.0	85
15	 **5p**	**7o**	3.0	83
16	 **5q**	**7p**	3.0	85
17	 **5r**	**7q**	3.0	78

[a] Reaction condition: α-amidosulfone (1.0 mmol), 1,2,4-trimethoxy benzene (1.0 mmol), and $B(C_6F_5)_3$ (5 mol %) were used.
[b] Isolated yield of product after column chromatography.

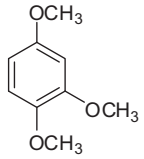
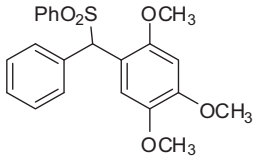
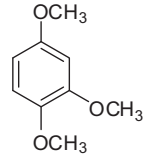
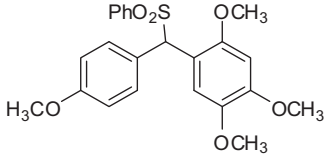
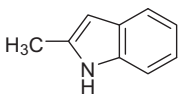
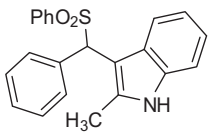


Scheme 2. Plausible mechanism of $B(C_6F_5)_3$ catalyzed (a) Friedel–Crafts reaction of activated arene with α-amidosulfone (**5** to **6a** or **7**) and (b) Synthesis of unsymmetrical triarylmethanes from (1-alkyl-1-aryl)methyl *p*-tolylsulfones **7** (**6a** or**7** to **10**).

Table 4
Friedel–Crafts reactions of activated arenes with α-amidosulfone catalyzed by $B(C_6F_5)_3$[a]



4a and **4m** **8a:** R= C_6H_5
8b: R= 4-$CH_3OC_6H_4$

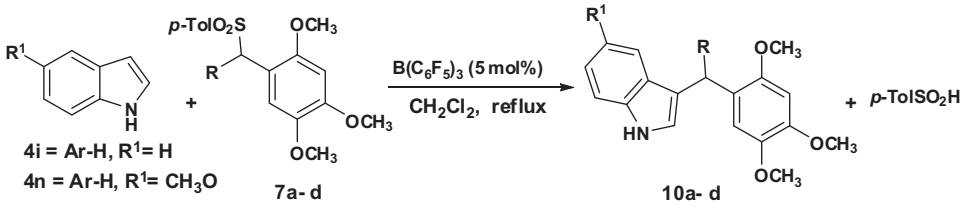
Entry	Ar–H (**4**)	R (**8**)	Product (**9**)	Reaction time (h)	Isolated yield[b] (%)
1	 **4a**	**8a**	 **9a**	2.5	89
2	 **4a**	**8b**	 **9b**	2.5	91
3	 **4m**	**8a**	 **9c**	3.0	73

[a] Reaction condition: α-amidosulfone (1.0 mmol), electron-rich aromatic compound (1.0 mmol) and $B(C_6F_5)_3$ (5 mol %) were used.
[b] Isolated yield of product after column chromatography.

corresponding Friedel–Crafts product in 89 and 90% yield, respectively (entries 1 and -2). The reaction of *N*-benzyloxycarbonylamino phenyl phenylsulfone **8a** and 2-methylindole **4m** gives 73% yield (entry 3). The substrates **8a** or **8b** did not provide the product with considerable different yields in comparison to yields of the substrate in Tables 2 and 3. The above results suggest that the sulfonyl moiety does not show great influence on the Friedel–Crafts alkylation reaction catalyzed by $B(C_6F_5)_3$.

The synthetic utility of the present method was explored further for the synthesis of unsymmetrical triarylmethanes **10**. The Friedel–Crafts alkylation reactions of activated heteroarenes, such as indole **4i** or 5-methoxyindole **4n** and (1-alkyl-1-aryl)methyl *p*-tolylsulfones **7** in the presence of tris(pentafluorophenyl)borane $[B(C_6F_5)_3]$ at 40 °C afforded the unsymmetrical triarylmethanes **10** (Table 5). The 4-methoxy-**7f**, 3-methyl-4-methoxy- **7g**, and 3,4-dimethoxy-**7h** substituted (1-alkyl-1-aryl)methyl *p*-tolylsulfones react with indole **4i** or 5-methoxyindole **4n** smoothly to give rise to the corresponding unsymmetrical triarylmethanes **10a–f** in moderate yield (entries 1–6). The reaction of 4-nitro substituted (1-alkyl-1-aryl)methyl *p*-tolylsulfones **7k** and indole **4i** or 5-methoxyindole **4n** were unable to produce the Friedel–Crafts products at all (entry 7 and 8). Because, the electron-donating substituent in (1-alkyl-1-aryl)methyl *p*-tolylsulfones **7** was more favor the formation of oxonium ion **G** intermediates compare with that of electron-withdrawing substrates. As a result the no reaction took place in electron-withdrawing substrates (see the proposed mechanism in Scheme 2).

Table 5
Synthesis of unsymmetrical triarylmethanes catalyzed by $B(C_6F_5)_3$[a]



Entry	Ar–H (**4**)	**7**	Product (**10**)	Reaction time (h)	Isolated yield[b] (%)
1	**4i**	**7f**	**10a**	4.5	53
2	**4n**	**7f**	**10b**	4.0	58
3	**4i**	**7g**	**10c**	4.5	52
4	**4n**	**7g**	**10d**	4.5	55
5	**4i**	**7i**	**10e**	4.5	54
6	**4n**	**7i**	**10f**	4.0	58
7	**4i**	**7k**	**10g**	6.0	NR
8	**4n**	**7k**	**10h**	6.0	NR

[a] Reaction condition: (1-alkyl-1-aryl)methyl *p*-tolylsulfones **7** (1.0 mmol), indole **4i** or 5-methoxyindole **4n** (1.0 mmol), and $B(C_6F_5)_3$ (5 mol %) were used.
[b] Isolated yield of product after column chromatography.

A plausible mechanism for the Friedel–Crafts alkylation reactions are shown in Scheme 2. (a) The α-amidosulfone on treatment with tris(pentafluorophenyl)borane $[B(C_6F_5)_3]$ to produce the *N*-acyliminium ion **A** through the elimination of *p*-tolunesulfinic acid. The *N*-acyliminium ion **A** (more electrophilic in nature) react with 1,2,4-trimethoxy benzene **4a** gives the Friedel–Crafts product **B**. $B(C_6F_5)_3$ catalyzes the elimination of carbamate from **B** generating the oxonium ion **C**. The oxonium ion **C** undergoes second Friedel–Crafts reactions with *p*-tolunesulfinic acid (*p*-TolSO$_2$H) leading to the formation of product **6a** or **7**. Along with the desired Friedel–Crafts product **6a** or **7**, very small quantity of bis-arene **D** was also isolated. The formation of bis-arene **D** explained by the reversible reaction between the oxonium ion **C** and 1,2,4-trimethoxy benzene **5a**.[8] (b) The Lewis acid $B(C_6F_5)_3$ react with (1-alkyl-1-aryl)methyl *p*-tolylsulfones **7** like **E**, which facilitate the removal of *p*-toluenesulfinic acid from **7** leads to the second oxonium ion **F**. If R=4-methoxyphenyl derivatives generate additional oxonium ion **G**. Both the oxonium ions **F** and **G** react with indole derivatives **4i** or **4n** to afford the corresponding unsymmetrical triarylmethanes **10** (Scheme 2).

3. Conclusion

We have demonstrated an extremely facile and efficient Friedel–Crafts alkylation reactions of activated arenes and heteroarenes with α-amidosulfones using 5 mol % of tris(pentafluorophenyl) borane $[B(C_6F_5)_3]$. In addition, the present method utilized further to synthesis of unsymmetrical triarylmethanes from (1-alkyl-1-aryl)methyl *p*-tolylsulfones and heteroarenes. $B(C_6F_5)_3$-Catalyzed Friedel–Crafts reactions displayed significant advantages such as low catalyst loading, easy-to-handle, mild reaction conditions, highly regioselective, high yield, and broad applicability to various substrates.

4. Experimental section

4.1. General procedures

In all the cases the ^{1}H NMR spectra were recorded with Varian Gemini 200 or 400 MHz instrument. Chemical shifts are reported in parts per million in $CDCl_3$ with tetramethylsilane as an internal standard. ^{13}C NMR data were collected on Varian Gemini 200 or 400 MHz instrument (50 or 100 MHz). Compounds have been also identified by HRMS (EI) with Jeol DMX 303.

4.2. General Procedure for the $B(C_6F_5)_3$-Catalyzed Friedel–Crafts alkylation reactions of activated arenes with α-amidosulfones

To a solution of equimolar quantities of the α-amidosulfones (1 mmol) and electron-rich arenes or heteroarenes (1 mmol) in dichloromethane (4 mL) at room temperature was added $B(C_6F_5)_3$ (5 mol %) as a solid under a purge of nitrogen. Then the temperature slowly rises to 40 °C and stirred the reaction mixture for appropriate time. The reactions were monitored by TLC. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with dichloromethane (5 mL), washed with water (5 mL), and followed by brine (5 mL). The organic layers were collected, dried over Na_2SO_4 and evaporated in rotavapour. The crude compound was purified by column chromatography (hexanes–ethyl acetate (3:1)) to afford the corresponding Friedel–Crafts products.

The products were characterized by IR, Mass, ^{1}H and ^{13}C NMR data that are consistent with literature values. Melting point, IR, Mass, ^{1}H, and ^{13}C NMR values for new products are given below.[7a–e]

4.2.1. Compound ***6a***. Pale yellow solid, mp 171 °C; IR (KBr): ν_{max} 2941, 1518, 1316, 1138, 1023 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (s, 1H), 7.57 (d, J=8.4 Hz, 2H), 7.50 (d, J=8.0 Hz, 2H), 7.31–7.29 (m, 3H), 7.14 (d, J=8.4 Hz, 2H), 6.23 (s, 1H), 5.98 (s, 1H), 3.91 (s, 3H), 3.82 (s, 3H), 3.51 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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; HRMS-EI (m/z): [M]$^+$ calcd for $C_{23}H_{24}O_5S$: 412.1344, found: 412.1343.[7c–e]

4.2.2. Compound ***6b***. White solid, mp 88–90 °C; IR (KBr): ν_{max} 2949, 1339, 1140, 1069 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, J=8.2 Hz, 1H), 7.53–7.49 (m, 4H), 7.29–7.27 (m, 3H), 7.14 (d, J=8.5 Hz, 2H), 6.74 (d, J=8.2 Hz, 1H), 5.88 (s, 1H), 3.84 (s, 3H), 3.71 (s, 3H), 3.58 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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; HRMS-EI (m/z): [M]$^+$ calcd for $C_{23}H_{24}O_5S$: 412.1344, found: 412.1342.[7c–e]

4.2.3. Compound ***6c***. White solid, mp 127–128 °C; IR (KBr): ν_{max} 2937, 1513, 1310, 1143, 1023 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, J=8.4 Hz, 2H), 7.50 (d, J=8.5 Hz, 2H), 7.25–7.39 (m, 3H), 7.17 (d, J=8.4 Hz, 2H), 6.15 (s, 1H), 6.06 (s, 2H), 3.77 (s, 3H), 3.64 (s, 6H), 2.37 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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; HRMS-EI (m/z): [M]$^+$ calcd for $C_{23}H_{24}O_5S$: 412.1344, found: 412.1316.[7c–e]

4.2.4. Compound ***6d***. White solid, mp 110–111 °C; IR (KBr): ν_{max} 2946, 1502, 1293, 1208, 1138, 1031 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (d, J=8.0 Hz, 1H), 7.64 (d, J=8.5 Hz, 2H), 7.56 (d, J=8.5 Hz, 2H), 7.36–7.33 (m, 3H), 7.19 (d, J=8.0 Hz, 2H), 6.62 (d, J=8.5 Hz, 1H), 6.32 (s, 1H), 6.03 (s, 1H), 3.82 (s, 3H), 3.54 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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; HRMS-EI (m/z): [M]$^+$ calcd for $C_{22}H_{22}O_4S$: 382.1239, found: 382.1263.[7c–e]

4.2.5. Compound ***6i***. Brown solid, mp 52–53 °C; IR (KBr): ν_{max} 3397, 3049, 1456, 1316, 1146, 1085 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.63 (d, J=6.5 Hz, 1H), 7.56 (s, 1H), 7.50–7.40 (m, 5H), 7.23–7.19 (m, 4H), 7.06–6.99 (m, 4H), 5.68 (s, 1H), 2.25 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 144.3, 135.4, 135.1, 133.4, 130.0, 129.2, 129.1, 128.8, 128.3, 126.9, 124.9, 122.2, 119.8, 118.1, 111.5, 106.8, 69.0, 21.4.[7a,c,d]

4.2.6. Compound ***6j***. Brown solid, mp 137–138 °C; (KBr): ν_{max} 2958, 1401, 1345, 1073 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (s, 1H), 7.50 (d, J=7.6 Hz, 2H), 7.48–7.39 (m, 2H), 7.38 (d, J=7.2 Hz, 1H), 7.26–7.22 (m, 4H), 7.17 (t, J=7.2 Hz, 1H), 7.08 (d, J=7.6 Hz, 2H), 7.02 (t, J=7.2 Hz, 1H), 5.65 (s, 1H), 3.77 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 144.2, 136.4, 135.4, 133.9, 130.1, 129.2, 129.0, 128.4, 127.7, 122.0, 119.6, 118.5, 109.4, 105.8, 69.0, 33.1, 21.5; HRMS-EI (m/z): [M]$^+$ calcd for $C_{23}H_{21}NO_2S$: 375.1293, found: 375.1297.[7a,c,d]

4.2.7. Compound ***6k***. White solid, mp 148–149 °C; IR (KBr): ν_{max} 2944, 1499, 1310, 1143, 1085 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48–7.45 (m, 4H), 7.34–7.32 (m, 3H), 7.18 (d, J=8.4 Hz, 2H), 6.42 (d, J=3.0 Hz, 1H), 5.95 (dd, J=3.0, 1.0 Hz, 1H), 5.33 (s, 1H), 2.39 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 153.2, 144.5, 143.8, 134.8, 131.0, 130.4, 129.2, 129.1, 128.9, 128.4, 112.7, 107.0, 71.0, 21.6, 13.5; HRMS-FAB (m/z): [M–H]$^+$ calcd for $C_{19}H_{17}O_3S$: 325.0896, found: 325.0898.

4.2.8. Compound ***6l***. White solid, mp 180 °C; IR (KBr): ν_{max} 2930, 1485, 1310, 1136, 1080 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50–7.47 (m, 4H), 7.31–7.30 (m, 3H), 7.16 (d, J=8.0 Hz, 2H), 6.95 (d, J=3.6 Hz, 1H), 6.22 (dd, J=3.6, 1.4 Hz, 1H), 5.42 (s, 1H), 2.44 (s, 3H), 2. 73 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 144.5, 141.9, 134.6, 132.9, 131.2, 129.9, 129.7, 129.2, 129.1, 128.8, 128.5, 125.0, 72.6, 21.6, 15.3; EI (m/z): [M]$^+$ calcd for $C_{19}H_{18}O_2S2$: 342.0748, found: 342. 1, 187 [M–155]$^+$.

4.2.9. Compound ***7a***. White solid, mp 141–142 °C; IR (KBr): ν_{max} 2949, 1518, 1316, 1208, 1146, 1031 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (s, 1H), 7.81–7.78 (m, 3H), 7.70–7.64 (m, 2H), 7.54 (d, J=8.5 Hz, 2H), 7.47–7.45 (m, 2H), 7.14 (d, J=8.5 Hz, 2H), 6.34 (s, 1H), 6.16 (s, 1H), 3.93 (s, 3H), 3.83 (s, 3H), 3.53 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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; HRMS-EI (m/z): [M]$^+$ calcd for $C_{27}H_{26}O_5S$: 462.1501, found: 462.1505.[7c–e]

4.2.10. Compound ***7b***. White solid, mp 137 °C; IR (KBr): ν_{max} 2941, 1510, 1332, 1216, 1138, 1031 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50–7.47 (m, 5H), 7.25 (d, J=8.5 Hz, 2H), 7.17 (d, J=8.5 Hz, 2H), 6.29 (s, 1H), 5.93 (s, 1H), 3.88 (s, 3H), 3.79 (s, 3H), 3.46 (s, 3H), 2.32 (s, 3H); ^{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; HRMS-EI (m/z): [M]$^+$ calcd for $C_{23}H_{23}ClO_5S$: 446.0955, found: 446.0955.[7c–e]

4.2.11. Compound ***7c***. White solid, mp 157–158 °C; ν_{max} 2937, 1520, 1307, 12.13, 1143, 1031 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57–7.54 (m, 5H), 7.32 (s, 2H), 7.22 (d, J=8.5 Hz, 2H), 6.37 (s, 1H), 5.99 (s, 1H), 3.97 (s, 3H), 3.88 (s, 3H), 3.56 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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; HRMS-EI (m/z): [M]$^+$ calcd for $C_{23}H_{23}ClO_5S$: 446.0955, found: 446.0949.[7c–e]

4.2.12. Compound ***7d***. White solid, mp 146–147 °C; IR (KBr): ν_{max} 2941, 1510, 1332, 1216, 1138, 1023 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36 (d, J=8.6 Hz, 1H), 7.64 (d, J=8.2 Hz, 2H), 7.62 (s, 1H), 7.46 (t, J=8.6 Hz, 1H), 7.41 (d, J=7.6 Hz, 1H), 7.33 (t, J=8.6 Hz, 1H), 7.29 (d, J=8.2 Hz, 2H), 6.73 (s, 1H), 6.47 (s, 1H), 4.02 (s, 3H), 3.95 (s, 3H), 3.62 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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; HRMS-EI (m/z): [M]$^+$ calcd for $C_{23}H_{23}ClO_5S$: 446.0955, found: 446.0955.[7c–e]

4.2.13. Compound ***7e***. White solid, mp 122–123 °C; IR (KBr): ν_{max} 2937, 1520, 1307, 12.13, 1143, 1031 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (s, 1H), 7.51 (d, J=8.4 Hz, 2H), 7.45 (d, J=8.0 Hz, 2H), 7.14 (d, J=8.0 Hz, 2H), 7.12 (d, J=8.4 Hz, 2H), 6.31 (s, 1H), 5.95 (s, 1H), 3.91 (s, 3H), 3.82 (s, 3H), 3.50 (s, 3H), 2.36 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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; HRMS-EI (m/z): [M]$^+$ calcd for $C_{24}H_{26}O_5S$: 426.1501, found: 426.1511.[7c–e]

4.2.14. Compound ***7f***. White solid, mp 143 °C; IR (KBr): ν_{max} 2949, 1510, 1316, 1254, 1146, 1031 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (s, 1H), 7.52–7.48 (m, 4H), 7.14 (d, J=8.0 Hz, 2H), 6.84 (d, J=8.6 Hz, 2H), 6.32 (s, 1H), 5.93 (s, 1H), 3.92 (s, 3H), 3.82 (s, 3H), 3.76 (s, 3H), 3.51 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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; HRMS-EI (m/z): [M]$^+$ calcd for $C_{24}H_{26}O_6S$: 442.1450, found: 442.1460.[7b–e]

4.2.15. Compound ***7g***. White solid, mp 146–147 °C; IR (KBr): ν_{max} 2930, 1513, 1325, 1143, 1219, 1150, 1023 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.55 (s, 1H), 7.47 (d, J=8.2 Hz, 2H), 7.37 (d, J=8.0 Hz, 1H), 7.22 (s, 1H), 7.08 (d, J=8.2 Hz, 2H), 6.71 (d, J=8.0 Hz, 1H), 6.26 (s, 1H), 5.86 (s, 1H), 3.87 (s, 3H), 3.76 (s, 3H), 3.73 (s, 3H), 3.44 (s, 3H), 2.29 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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; HRMS-EI (m/z): $[M]^+$ calcd for $C_{25}H_{28}O_6S$: 456.1607, found: 456.1597.[7c–e]

4.2.16. Compound ***7h***. White solid, mp 131–132 °C; IR (KBr): ν_{max} 2944, 1520, 1310, 1213, 1136, 1010 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.51 (s, 1H), 7.50 (d, J=8.0 Hz, 2H), 7.31–7.25 (m, 2H), 7.15 (d, J=8.6 Hz, 2H), 6.89 (t, J=8.4 Hz, 1H), 6.31 (s, 1H), 5.88 (s, 1H), 3.91 (s, 3H), 3.85 (s, 3H), 3.82 (s, 3H), 3.50 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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; HRMS-EI (m/z): $[M]^+$ calcd for $C_{24}H_{25}FO_6S$: 460.1356, found: 460.1344.[7c–e]

4.2.17. Compound ***7i***. White solid, mp 186–187 °C; IR (KBr): ν_{max} 2925, 1518, 1308, 1216, 1138, 1023 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.59 (s, 1H), 7.52 (d, J=8.6 Hz, 2H), 7.16 (d, J=8.2 Hz, 2H), 7.14 (d, J=8.6 Hz, 1H), 7.06 (s, 1H), 6.82 (d, J=8.2 Hz, 1H), 6.35 (s, 1H), 5.92 (s, 1H), 3.92 (s, 3H), 3.85 (s, 3H), 3.83 (s, 3H), 3.82 (s, 3H), 3.53 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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 (x2) 21.5; EI (m/z): $[M]^+$ calcd for $C_{25}H_{28}O_7S$: 472.1556, found: 472.1, 317 $[M-155]^+$.[7c–e]

4.2.18. Compound ***7j***. White solid, mp 156 °C; IR (KBr): ν_{max} 2949, 1518, 1316, 1213, 1130, 1023 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.55 (s, 1H), 7.49 (d, J=8.0 Hz, 2H), 7.13 (d, J=8.4 Hz, 2H), 6.77 (s, 1H), 6.29 (s, 1H), 5.87 (s, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 3.78 (s, 9H), 3.47 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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; HRMS-EI (m/z): $[M]^+$ calcd for $C_{26}H_{30}O_8S$: 502.1661, found: 502.1661.[7c–e]

4.2.19. Compound ***7k***. Yellow solid, mp 148 °C; IR (KBr): ν_{max} 2941, 1525, 1347, 1223, 1138, 1031 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.09 (d, J=8.6 Hz, 2H), 7.73 (d, J=8.2 Hz, 2H), 7.46 (d, J=8.6 Hz, 2H), 7.43 (s, 1H), 7. 11 (d, J=8.2 Hz, 2H), 6.28 (s, 1H), 6.04 (s, 1H), 3.84 (s, 3H), 3.76 (s, 3H), 3.44 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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; HRMS-EI (m/z): $[M]^+$ calcd for $C_{23}H_{23}NO_7S$: 457.1195, found: 457.1189.[7c–e]

4.2.20. Compound ***7l***. Yellow solid, mp 138–139 °C; IR (KBr): ν_{max} 2941, 2210, 1518, 1316, 1138, 1023 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 7.65 (d, J=8.4 Hz, 2H), 7.56 (d, J=8.4 Hz, 2H), 7.46 (d, J=8.0 Hz, 2H), 7.44 (s, 1H), 7. 13 (d, J=8.4 Hz, 2H), 6.27 (s, 1H), 5.96 (s, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 3.46 (s, 3H), 2.33 (s, 3H); ^{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; EI (m/z): $[M]^+$ 437, 283, 282, 266.[7c–e]

4.2.21. Compound ***7m***. White solid, mp 172–173 °C; IR (KBr): ν_{max} 2949, 1518, 1301, 1208, 1138, 1015 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.48 (d, J=8.0 Hz, 2H), 7.42 (s, 2H), 7.17 (d, J=8.0 Hz, 2H), 6.53 (d, J=3.4 Hz, 1H), 6.37–6.36 (m, 1H), 6.34 (s, 1H), 6.12 (s, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.55 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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; HRMS-EI (m/z): $[M]^+$ calcd for $C_{21}H_{22}O_6S$: 402.1137, found: 402.1141.[7c–e]

4.2.22. Compound ***7n***. White solid, mp 147 °C; IR (KBr): ν_{max} 2933, 1510, 1324, 1200, 1031 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.47 (d, J=8.0 Hz, 2H), 7.44 (s, 1H), 7.26 (d, J=5.1 Hz, 1H), 7.20 (d, J=4.4 Hz, 1H), 7.11 (d, J=8.0 Hz, 2H), 6.95 (dd, J=5.1, 4.4 Hz, 1H), 6.28 (s, 1H), 6.23 (s, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.49 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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; HRMS-EI (m/z): $[M]^+$ calcd for $C_{21}H_{22}O_5S_2$: 418.0909, found: 418.0915.[7c-e]

4.2.23. Compound ***7o***. White solid, mp 123–124 °C; IR (KBr): ν_{max} 2933, 1518, 1316, 1209, 1138, 1023 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, J=8.5 Hz, 2H), 7.36 (s, 1H), 7.28–7.23 (m, 2H), 7.20–7.13 (m, 3H), 7.07 (d, J=8.5 Hz, 2H), 6.99 (s, 1H), 6.30 (s, 1H), 4.79 (d, J=6.5 Hz, 1H), 3.87 (s, 6H), 3.37 (s, 3H), 2.80–2.77 (m, 1H), 2.68–2.43 (m, 1H), 2.42–2.38 (m, 1H), 2.37 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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; HRMS-EI (m/z): $[M]^+$ calcd for $C_{25}H_{28}O_5S$: 440.1657, found: 440.1656.[7c–e]

4.2.24. Compound ***7p***. White solid, mp 127–129 °C; IR (KBr): ν_{max} 2933, 1518, 1308, 1138, 1031 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.39–7.30 (m, 3H), 7.16 (s, 1H), 7.04 (d, J=8.8 Hz, 2H), 6.12 (s, 1H), 4.69 (d, J=6.5 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 3.35 (s, 3H), 2.52–2.48 (m, 2H), 2.42–2.38 (m, 2H), 2.30 (s, 3H), 1.80–1.76 (m, 1H), 1.70–1.63 (m, 1H), 1.39–1.14 (m, 3H), 1.00–0.95 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) 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; HRMS-EI (m/z): $[M]^+$ calcd for $C_{23}H_{30}O_5S$: 418.1814, found: 418.1797.[7c–e]

4.2.25. Compound ***7q***. White solid, mp 78–79 °C; IR (KBr): ν_{max} 2951, 1448, 1347, 1213, 1136, 1023 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.37–7.29 (m, 3H), 7.11 (s, 1H), 7.00 (d, J=7.4 Hz, 2H), 6.10 (s, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 3.32 (s, 3H), 2.77–2.74 (m, 1H), 2.27 (s, 3H), 1.26 (d, J=6.5 Hz, 3H), 0.89 (d, J=6.5 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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; HRMS-EI (m/z): $[M]^+$ calcd for $C_{20}H_{26}O_5S$: 378.1501, found: 378.1508.[7c–e]

4.2.26. Compound ***9a***. White solid, IR (KBr): ν_{max} 2949, 1518, 1316, 1208, 1146, 1031 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, J=8.6 Hz, 2H), 7.58–7.56 (m, 3H), 7.48 (t, J=8.6 Hz, 2H), 7.37–6.29 (m, 4H), 6.29 (s, 1H), 6.00 (s, 1H), 3.91 (s, 3H), 3.81 (s, 3H), 3.47 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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.[7b–e]

4.2.27. Compound ***9b***. White solid, IR (KBr): ν_{max} 2933, 1518, 1308, 1200, 1146, 1031 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.61 (d, J=8.3 Hz, 2H), 7.55 (s, 1H), 7.49–7.46 (m, 3H), 7.32 (m, 2H), 6.83 (d, J=8.3 Hz, 2H), 6.28 (s, 1H), 5.95 (s, 1H), 3.90 (s, 3H), 3.79 (s, 3H), 3.74 (s, 3H), 3.46 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 159.6, 151.6, 149.9, 143.1, 138.9, 133.2, 131.3, 128.8128.4, 125.1, 114.0.113.2, 113.0, 96.9, 65.8, 56.7, 56.4, 56.0, 55.2.[7c–e]

4.2.28. Compound ***9c***. Brown solid, 169 °C; (KBr): ν_{max} 3384, 3064, 1450, 1297, 1143, 1080 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.98 (br s, 1H), 7.81–7.73 (m, 3H), 7.55–7.52 (m, 3H), 7.43–7.41 (m, 1H), 7.32–7.23 (m, 5H), 7.22–7.02 (m, 2H), 5.66 (s, 1H), 2.12 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 138.8, 135.5, 135.1, 133.2, 132.8, 129.9, 128.6, 128.5, 128.4, 128.2, 127.1, 121.5, 121.1, 120.1, 110.4, 103.9, 69.6, 11.8; HRMS-EI (m/z): $[M]^+$ calcd for $C_{22}H_{19}NO_2S$: 361.1136, found: 361.1136.[7a–c]

4.3. Experimental procedure for the synthesis of unsymmetrical triarylmethanes

The $B(C_6F_5)_3$ (5 mol %) was added to a solution of (1-alkyl-1-aryl)methyl *p*-tolylsulfone (1 mmol) and heteroaromatic indole derivatives in dichloromethane (4 mL) under nitrogen atmosphere. The resulting solution was refluxed with constant stirring for 4.0–6.0 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was diluted with water (5 mL), and extracted with dichloromethane (3×5 mL). The combined organic layer was washed with water (5 mL), saturated aqueous NaCl (5 mL), dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude product was subject to column chromatography (silica gel, hexane–EtOAc (3:1)) to obtain pure product.

The products were characterized by IR, Mass, ^1H, and ^{13}C NMR data that are consistent with literature values.[7c,e]

4.3.1. Compound ***10a***. White solid, mp 179–180 °C; (KBr): ν_{max} 3342, 2930, 1560, 1213, 1038 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 7.96 (br s, 1H), 7.31 (d, *J*=8.2 Hz, 1H), 7.25 (d, *J*=8.2 Hz, 1H), 7.13 (d, *J*=8.6 Hz, 3H), 6.99 (t, *J*=8.4 Hz, 1H), 6.80 (d, *J*=8.2 Hz, 2H), 6.61 (s, 1H), 6.58 (d, *J*=8.6 Hz, 2H), 5.98 (s, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 3.74 (s, 3H), 3.59 (s, 3H); ^{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; HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{25}H_{25}NO_4$: 403.1784, found: 403.1786.[7c,e]

4.3.2. Compound ***10b***. White solid, mp 150–152 °C; (KBr): ν_{max} 3335, 2930, 1513, 1206, 1048 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 7.98 (br s, 1H), 7.22 (d, *J*=8.5 Hz, 1H), 7.18 (d, *J*=8.5 Hz, 2H), 6.86–6.84 (m, 3H), 6.71 (d, *J*=1.5 Hz, 1H), 6.67 (s, 1H), 6.62 (s, 1H), 6.58 (d, *J*=1.5 Hz, 1H), 5.96 (s, 1H), 3.92 (s, 3H), 3.81 (s, 3H), 3.76 (s, 3H), 3.72 (s, 3H), 3.64 (s, 3H); ^{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; HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{26}H_{27}NO_5$: 433.1889, found: 433.1885.[7e]

4.3.3. Compound ***10c***. White solid, mp 170 °C; (KBr): ν_{max} 3370, 2937, 1507, 1213, 1032 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 8.09 (br s, 1H), 7.32 (d, *J*=7.6 Hz, 1H), 7.30 (d, *J*=7.6 Hz, 1H), 7.17 (t, *J*=7.6 Hz, 1H), 7.11 (s, 1H), 7.06–7.00 (m, 2H), 6.75 (d, *J*=8.0 Hz, 1H), 6.72 (s, 1H), 6.64 (s, 1H), 6.58 (s, 1H), 6.03 (s, 1H), 3.92 (s, 3H), 3.82 (s, 3H), 3.78 (s, 3H), 3.64 (s, 3H), 2.23 (s, 3H); ^{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; HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{26}H_{27}NO_4$: 417.1940, found: 417.1942.[7e]

4.3.4. Compound ***10d***. White solid, mp 172.9 °C; (KBr): ν_{max} 3340, 2935, 1508, 1213, 1048 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 7.97 (br s, 1H), 7.17 (d, *J*=8.8 Hz, 1H), 7.05 (d, *J*=2.0 Hz, 1H), 6.99 (dd, *J*=8.4, 2.0 Hz, 1H), 6.81 (dd, *J*=8.4, 2.0 Hz, 1H), 7.72 (d, *J*=8.8 Hz, 1H), 7.71 (s, 1H), 6.67 (s, 1H), 6.59 (s, 1H), 6.56 (d, *J*=2.0 Hz, 1H), 5.92 (s, 1H), 3.89 (s, 3H), 3.80 (s, 3H), 3.75 (s, 3H), 3.70 (s, 3H), 3.62 (s, 3H), 2.18 (s, 3H); ^{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; HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{27}H_{29}NO_5$: 447.2046, found: 447.2050.[7e]

4.3.5. Compound ***10e***. White solid, mp 157–158 °C; (KBr): ν_{max} 3356, 2930, 1506, 1206, 1032 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 8.02 (br s, 1H), 7.27 (d, *J*=8.0 Hz, 1H), 7.22 (d, *J*=8.0 Hz, 1H), 7.11 (t, *J*=8.5 Hz, 1H), 6.94 (t, *J*=8.5 Hz, 1H), 6.79 (d, *J*=2.0 Hz, 1H), 6.73 (d, *J*=8.4 Hz, 1H), 6.68 (dd, *J*=8.4, 1.8 Hz, 1H), 6.59 (s, 1H), 6.55 (s, 1H), 6.54 (d, *J*=1.5 Hz, 1H), 5.94 (s, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.73 (s, 3H), 3.71 (s, 3H), 3.56 (s, 3H); ^{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; HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{26}H_{27}NO_5$: 433.1889, found: 433.1902.[7e]

4.3.6. Compound ***10f***. White solid, mp 175–177 °C; (KBr): ν_{max} 3356, 2930, 1506, 1206, 1032 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.96 (br s, 1H), 7.19 (d, *J*=8.8 Hz, 1H), 6.81 (s, 1H), 6.70 (d, *J*=2.0 Hz, 1H), 6.75 (d, *J*=8.4 Hz, 1H), 6.74 (d, *J*=1.8 Hz, 1H), 6.69 (d, *J*=8.8 Hz, 1H), 6.68 (d, *J*=2.0 Hz, 1H), 6.62 (s, 1H), 6.56 (s, 1H), 5.91 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.75 (s, 3H), 3.73 (s, 3H), 3.69 (s, 3H), 3.59 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 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; HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{27}H_{29}NO_6$: 463.1995, found: 463.1995.[7e]

Acknowledgements

Authors thank the Department of Chemistry, Inha University. This work was supported by grant of Inha University in Korea.

References and notes

1. (a) Friedel, C.; Crafts, J. M. *Compt. Rend.* **1877**, *84*, 1392–1450.
2. (a) Olah, G. A. *Friedel–Crafts and Related Reactions*; Wiley-Interscience: New York, NY, 1964; Vol. II; part 1; (b) Roberts, R. M.; Khalaf, A. A. *Friedel–Crafts Alkylation Chemistry: A Century of Discovery*; Dekker: New York, NY, 1984; (c) Olah, G. A. *Friedel–Crafts and Related Reactions*; Wiley: New York, NY, 1973; (d) Heaney, H. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 2, p 733; (e) Olah, G. A.; Krishnamurthi, R.; Prakash, G. K. S. *Friedel–Crafts Alkylations in Comprehensive Organic Synthesis*, 1st ed.; Pergamon: Oxford, UK, 1991; (f) Bandini, M.; Melloni, A.; Umani-Ronchi, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 550.
3. (a) Ishii, A.; Kojima, J.; Mikami, K. *Org. Lett.* **1999**, *1*, 2013; (b) Ishii, A.; Soloshonok, V. A.; Mikami, K. *J. Org. Chem.* **2000**, *65*, 1597; (c) Gathergood, N.; Zhuang, W.; Jorgensen, K. A. *J. Am. Chem. Soc.* **2000**, *122*, 12517; (d) Zhuang, W.; Gathergood, N.; Hazell, R. G.; Jørgensen, K. A. *J. Org. Chem.* **2001**, *66*, 1009; (e) Lyle, M. P. A.; Draper, N. D.; Wilson, P. D. *Org. Lett.* **2005**, *7*, 901.
4. (a) Esquivias, J.; Gomez Arrays, R.; Carretero, J. C. *Angew. Chem.* **2006**, *118*, 645; (b) Jia, Y.-X.; Xie, J.-H.; Duan, H.-F.; Wang, L.-X.; Zhou, Q.-L. *Org. Lett.* **2006**, *8*, 1621; (c) Kang, Q.; Zhao, Z.-A.; YouS-, L. *J. Am. Chem. Soc.* **2007**, *129*, 1484; (d) He, Q. L.; Sun, F. L.; Zheng, X. J.; You, S. L. *Synlett* **2009**, 1111; (e) Sun, F.-L.; Zheng, X.-J.; Gu, Q.; He, Q.-L.; You, S.-L. *Eur. J. Org. Chem.* **2010**, 47.
5. (a) Bandini, M.; Cozzi, P. G.; Melchiorre, P.; Umani-Ronchi, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 84; (b) Das, B.; Thirupathi, P.; Aravind Kumar, R.; Ravinder Reddy, K. *Catal. Commun.* **2008**, *9*, 635.
6. (a) Jensen, K. B.; Thorhauge, J.; Hazell, R. G.; Jorgensen, K. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 160; (b) Zhou, J.; Tang, Y. *J. Am. Chem. Soc.* **2002**, *124*, 9030; (c) Evans, D. A.; Scheidt, K. A.; Frandrick, K. R.; Lam, H. W.; Wu, J. *J. Am. Chem. Soc.* **2003**, *125*, 10780; (d) Palomo, C.; Oiarbide, M.; Kardak, B. G.; Garcia, J. M.; Linden, A. *J. Am. Chem. Soc.* **2005**, *127*, 4154; (e) Evans, D. A.; Fandrick, K. R.; Song, H. J. *J. Am. Chem. Soc.* **2005**, *127*, 8942; (f) Jia, Y.-X.; Yang, Y.; Zhu, S.-F.; Zhou, Q.-L. *J. Org. Chem.* **2006**, *71*, 75.
7. (a) Ballini, R.; Palmieri, A.; Petrini, M.; Torregiani, E. *Org. Lett.* **2006**, *8*, 4093; (b) Kuhakarn, C.; Tangdenpaisal, K.; Kongsaeree, P.; Prabpai, S.; Tuchinda, P.; Pohmakotr, M.; Reutrakul, V. *Tetrahedron Lett.* **2007**, *48*, 2467; (c) Thirupathi, P.; Kim, S. S. *J. Org. Chem.* **2009**, *74*, 7755; (d) Kadam, S. T.; Thirupathi, P.; Kim, S. S. *Tetrahedron* **2009**, *65*, 10383; (e) Thirupathi, P.; Kim, S. S. *Eur. J. Org. Chem.* **2010**, 1798.
8. (a) Petrini, M. *Chem. Rev.* **2005**, *105*, 3949; (b) Petrini, M.; Torregiani, E. *Tetrahedron Lett.* **2005**, *46*, 5999; (c) Das, B.; Damodar, K.; Saritha, D.; Chowdhury, N.; Krishnaiah, M. *Tetrahedron Lett.* **2007**, *48*, 7930; (d) Das, B.; Damodar, K.; Shashikanth, B.; Srinivas, Y.; Kalavathi, I. *Synlett* **2008**, 3133; (e) Reingruber, R.; Baumann, T.; Dahmen, S.; Brase, S. *Adv. Synth. Catal.* **2009**, *351*, 1019; (f) Thirupathi, P.; Kim, S. S. *Tetrahedron* **2010**, *66*, 8623; (g) Patrizia, G.; Dario, A.; Giorgio, B.; Letizia, S.; Giuseppe, B.; Paolo, M. *Chem.—Eur. J.* **2010**, *16*, 6069.
9. Anastas, P.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University: Oxford, 1998.
10. Blackwell, J. M.; Piers, W. E.; Parvez, M. *Org. Lett.* **2000**, *2*, 695.
11. Chandrasekhar, S.; Reddy, C. R.; Babu, B. N.; Chandrashekar, G. *Tetrahedron Lett.* **2002**, *43*, 3801.
12. Chandrasekhar, S.; Reddy, C. R.; Chandrashekar, G. *Tetrahedron Lett.* **2004**, *45*, 6481.
13. Srihari, P.; Yaragorla, S. R.; Basu, D.; Chandrasekhar, S. *Synthesis* **2006**, 2646.

14. Gevorgyan, V.; Rubin, M.; Benson, S.; Liu, J.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 6179.
15. Blackwell, J. M.; Sonmor, E. R.; Scoccitti, T.; Piers, W. E. *Org. Lett.* **2000**, *2*, 3921.
16. Chen, D.; Klankermayer, J. *Chem. Commun.* **2008**, 2130.
17. Shchepin, R.; Xu, C.; Dussault, P. *Org. Lett.* **2010**, *12*, 4772.
18. Chandrasekhar, S.; Chandrashekar, G.; Vijeender, K.; Reddy, M. S. *Tetrahedron Lett.* **2006**, *47*, 3474.
19. Chandrasekhar, S.; Reddy, C. R.; Babu, B. N. *J. Org. Chem.* **2002**, *67*, 9080.
20. (a) Duxbury, D. F. *Chem. Rev.* **1993**, *93*, 381; (b) Shchepinov, M. S.; Korshun, V. A. *Chem. Soc. Rev.* **2003**, *32*, 170; (c) Dinger, M. B.; Scott, M. J. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1741; (d) Nair, V.; Thomas, S.; Mathew, S. C.; Abhilash, K. G. *Tetrahedron* **2006**, *62*, 6731; (e) Mibu, N.; Yokomizo, K.; Uyeda, M.; Sumoto, K. *Chem. Pharm. Bull.* **2005**, *53*, 1171; (f) Katritzky, A. R.; Toader, D. *J. Org. Chem.* **1997**, *62*, 4137; (g) Panda, G.; Shagufta; Mishra, J. K.; Chaturvedi, V.; Srivastava, A. K.; Srivastava, R.; Srivastava, B. S. *Bioorg. Med. Chem.* **2004**, *12*, 5269; (h) Parai, M. K.; Panda, G.; Chaturvedi, V.; Manju, Y. K.; Sinha, S. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 289; (i) Podder, S.; Choudhury, J.; Roy, U. K.; Roy, S. *J. Org. Chem.* **2007**, *72*, 3100.
21. Schnitzer, R. J.; Hawking, F. *Experimental Chemotherapy*; Academic: New York, NY, 1963; Vol. I.
22. Greene, T. W.; Wuts, P. G. M. *Protecting Groups in Organic Synthesis*, 3rd ed.; Wiley: New York, NY, 1999.
23. (a) Aldag, R. Photochromism based on dissociation processes In *Photochromism: Molecules and Systems*; Durr, H., Bouas-Laurent, H., Eds.; Elsevier: London, 1990; (b) Irie, M. *J. Am. Chem. Soc.* **1983**, *105*, 2078.
24. (a) Rys, P.; Zollinger, H. *Fundamentals of the Chemistry and Application of Dyes*; Wiley-Interscience: New York, NY, 1972; (b) Muthyala, R.; Katritzky, A. R.; Lan, X. *Dyes Pigm.* **1994**, *25*, 303; (c) Mibu, N.; Sumoto, K. *Chem. Pharm. Bull.* **2000**, *48*, 1810.
25. (a) Hoffmann, M.; Hampel, N.; Kanzian, T.; Mayr, H. *Angew. Chem.* **2004**, *116*, 5518; (b) Shanmuga, P.; Varma, L. *Indian J. Chem., Sect. B* **2001**, *40*, 1258; (c) Zhang, Z.-H.; Yang, F.; Li, T.-S.; Fu, C.-G. *Synth. Commun.* **1997**, *27*, 3823.
26. (a) Das, S. K.; Shagufta Panda, G. *Tetrahedron Lett.* **2005**, *46*, 3097; (b) Burmester, A.; Stegmann, H. B. *Synthesis* **1981**, 125; (c) Pratt, E. F.; Green, L. Q. *J. Am. Chem. Soc.* **1953**, *75*, 275; (d) Katrizky, A. R.; Gupta, V.; Garot, C.; Stevens, C. V.; Gordeev, M. F. *Heterocycles* **1994**, 38; (e) Katrizky, A. R.; Lan, X.; Lam, J. M. *Chem. Ber.* **1991**, *124*, 1809.
27. (a) Esquivias, J.; Arrayas, R. G.; Carretero, J. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 629; (b) Lin, S.; Lu, X. *J. Org. Chem.* **2007**, *72*, 9757.