



Indium triflate-catalyzed allylation reactions of *N*-sulfonyl aldimines or *N*-alkoxycarbonylamino *p*-tolylsulfones with allyltrimethylsilane: synthesis of protected homoallylic amines

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ABSTRACT

Indium triflate-catalyzed allylation reactions of *N*-sulfonyl aldimines or *N*-alkoxyloxycarbonylamino *p*-tolylsulfone with allyltrimethylsilane have been successfully developed to produce protected homoallylic amines.

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1. Introduction

The allylation of carbonyl derivatives, such as aldehydes, ketones, and imines is one of the important carbon–carbon bond forming reactions because of the versatility of homoallylic alcohols and amines as synthetic intermediates.¹ In particular, Lewis acid-catalyzed allylation of imines has attracted increasing attention because of the significance for the preparation of nitrogen containing molecules.^{1,2} The homoallylic amines are useful fundamental building blocks for the synthesis of many nitrogen containing natural products and bioactive molecules.^{3,4} The development of new methods for the synthesis of homoallylic amines is a significant task for synthetic chemist. A number of methods have been reported for the preparation of protected homoallylic amines using various substrates.^{5,6}

In continuation of the development of useful synthetic methodologies for C–C bond forming reactions⁷ we report herein the Indium triflate-catalyzed allylation reactions of *N*-sulfonyl aldimines or *N*-alkoxycarbonylamino *p*-tolylsulfone with allyltrimethylsilane. In recent years the utility of indium salts as Lewis acid in organic synthesis has received a great deal of attention due to the relatively low toxicity, stability in air and water, strong tolerance to oxygen- and nitrogen-containing substrates.⁸

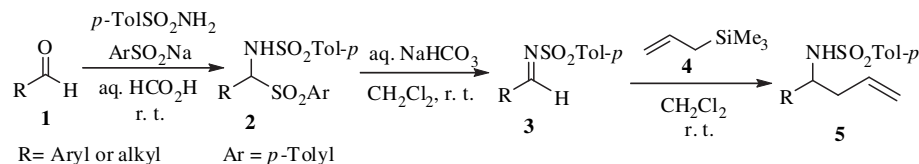
2. Results and discussions

2.1. Allylation of *N*-sulfonyl aldimines

Recently, Batey and Li reported the synthesis of protected homoallylic amines by palladium pincer complex.^{6f} Szabo and co-workers have demonstrated the preparation of protected homoallylic amines with the reaction of *N*-sulfonyl aldimines with potassium trifluoro (allyl)borate.^{6g} The *N*-sulfonyl aldimines (**3**) were prepared from the condensation of aldehydes (**1**), sulfonamides, and sodium salt of arenesulfonic acid to produce the sulfonamidesulfone (**2**) followed by the treatment with saturated aq NaHCO₃ (Scheme 1).⁹

The reactions of *N*-tosyl(phenylbenzylidene)-4-methylbenzenesulfonamide (**3a**) with allyltrimethylsilane (**4**) were examined under reaction conditions employing various catalysts (Table 1). The reaction of *N*-tosyl(phenylbenzylidene)-4-methylbenzenesulfonamide (**3a**) and allyltrimethylsilane (**4**) in the absence of the catalyst did not take place at all (entry 1). The reactions have been screened in the presence of various Lewis acids. Among the various iron and indium catalysts tested, In(OTf)₃ was shown to be the most effective one (entry 11). In(NO₃)₃·XH₂O and In(acac)₃·XH₂O did not allow the reaction to proceed at all (entries 6 and 7). Other metal triflates La(OTf)₃, Ce(OTf)₃, heteropoly acids H₃PO₄·12WO₃·XH₂O, H₃PMo₁₂O₄₀ (PMA), and heterogeneous catalysts Amberlyst-15, PMA·SiO₂ also catalyzed the reaction with only decreased yields (entries 12–17).

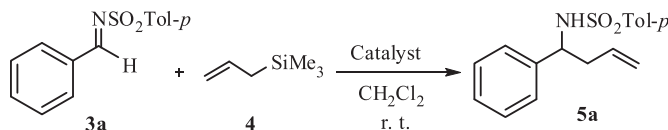
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Scheme 1. General preparation method for the synthesis of *N*-sulfonyl aldimines and synthesis of protected homoallyl amines.

Table 1

The reaction conditions for allylation of *N*-tosyl(phenylbenzylidene)-4-methylbenzenesulfonamide with allyltrimethylsilane^a



Entry	Catalyst (mol %)	Reaction time (h)	Isolated yield (%) ^b
1	—	16	NR
2	FeCl ₃ ·6H ₂ O (10)	10	21
3	FeBr ₃ (10)	10	49
4	FeCl ₃ (10)	10	57
5	InCl ₃ (10)	8	80
6	In(NO ₃) ₃ ·XH ₂ O (10)	10	NR
7	In(acac) ₃ ·XH ₂ O (10)	10	NR
8	InBr ₃ (10)	6	81
9	In(ClO ₄) ₃ ·XH ₂ O (10)	8	46
10	In(OTf) ₃ (10)	6	85
11	In(OTf) ₃ (5)	6	84
12	La(OTf) ₂ (10)	16	76
13	Ce(OTf) ₃ (10)	8	82
14	H ₃ PO ₄ ·12WO ₃ ·XH ₂ O (1)	8	76
15	H ₃ PMo ₁₂ O ₄₀ (PMA) (1)	6	80
16	Amberlyst-15 (100 mg)	16	56
17	PMA·SiO ₂ (100 mg)	16	74

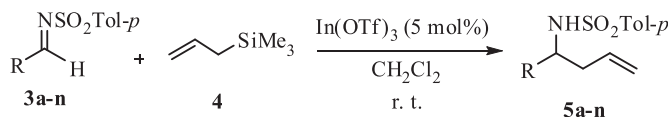
^a Reaction condition: *N*-Tosyl-(phenylbenzylidene)-4-methylbenzenesulfonamide (1.0 mmol) and allyltrimethylsilane (1.5 mmol) are used.

^b Yield of isolated product after column chromatography.

The In(OTf)₃-catalyzed reactions of various *N*-sulfonyl aldimine with allyltrimethylsilane that proceeded smoothly to give the corresponding protected homoallyl amines (Table 2). The reaction of *N*-tosyl(phenylbenzylidene)-4-methylbenzenesulfonamide (**3a**) with allyltrimethylsilane (**4**) produces the protected homoallyl amine (**5a**) in 84% yield (entry 1). The reaction of *N*-sulfonyl aldimines

Table 2

Allylation of various *N*-sulfonyl aldimines with allyltrimethylsilane catalyzed by In(OTf)₃^a



Entry	R in 3	Reaction time (h)	Product 5	Isolated yield ^b (%)
1	3a , C ₆ H ₄	6.0	5a	84
2	3b , 4-ClC ₆ H ₄	5.0	5b	88
3	3c , 3-ClC ₆ H ₄	6.0	5c	85
4	3d , 2-ClC ₆ H ₄	6.0	5d	82
5	3e , 4-BrC ₆ H ₄	6.0	5e	89
6	3f , 4-MeC ₆ H ₄	5.0	5f	87
7	3g , 4-MeOC ₆ H ₄	4.0	5g	88
8	3h , 3,4,5-(MeO) ₃ C ₆ H ₂	3.5	5h	91
9	3i , 4-NO ₂ C ₆ H ₄	6.0	5i	78
10	3j , 4-CNC ₆ H ₄	6.0	5j	82
11	3k , 3-CNC ₆ H ₄	6.0	5k	76

^a Reaction condition: *N*-sulfonyl aldimine (1.0 mmol), trimethylsilane (1.5 mmol), and In(OTf)₃ (5 mol % with respect to *N*-sulfonyl aldimine) are used.

^b Yield of isolated product after column chromatography.

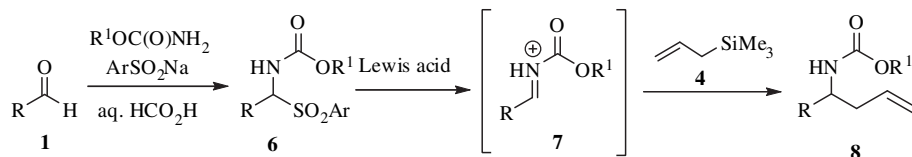
containing halogen groups, such as chlorine and bromine on the phenyl ring proceeded smoothly to give the corresponding products in good yields (entries 2–5). *N*-Tosyl(4-methylbenzylidene) (**3f**), *N*-tosyl(4-methoxybenzylidene) (**3g**), and *N*-tosyl(3,4,5-trimethoxybenzylidene)-4-methylbenzenesulfonamide (**3h**) react with allyltrimethylsilane (**4**) to give **5f**, **5g**, and **5h** in 87, 88, and 91%, respectively (entries 6–8). The reactions of *N*-sulfonyl aldimines bearing an electron-withdrawing group on the phenyl ring took place in slightly lower yields (entries 9–11).

2.2. Allylation of *N*-alkoxycarbonylamino *p*-tolylsulfone

The acylated homoallylic amines are important synthons for many synthetic applications, notably for acyliminium chemistry.¹⁰ The varieties of synthetic methods have been reported for the synthesis of homoallylic amines. The in situ generations of imines are highly attractive, among which the three-component allylation reaction have been introduced by Panek^{5a} and developed by Veenstra.^{5b} Yet, many Lewis acids cannot be used in this reaction because they decompose or are deactivated in the presence of the amine or water produced during imine formation. Thus the Sakurai reaction of *N*-alkoxycarbonylamino *p*-tolylsulfone (**6**) with allyltrimethylsilane (**4**) in the presence of a suitable Lewis acid constitutes an important method for the synthesis of *N*-alkoxycarbonyl-protected homoallylic amines. This reaction proceeds through a very reactive *N*-acyliminium species or *N*-alkoxycarbonyliminium derivative (**7**, Scheme 2).

Recently, very few Lewis acid catalysts, such as TiCl₄, SnCl₄, GaCl₃, InCl₃, or Bi(OTf)₃ have been employed for the preparation of alkoxycarbonyl-protected homoallylic amines.¹¹ However, TiCl₄ or SnCl₄ is moisture sensitive and required in stoichiometric quantity or in large excess. Some of these methods show longer reaction time and lower yield. To overcome these limitations, we report herein In(OTf)₃-catalyzed Sakurai reaction of *N*-alkoxycarbonylamino *p*-tolylsulfone with allyltrimethylsilane. Under optimized reaction conditions as in Table 1, the scope of allylation reactions have been studied using *N*-alkoxycarbonylamino *p*-tolylsulfone (**6**) and allyltrimethylsilane (**4**). The results are summarized in Table 3.

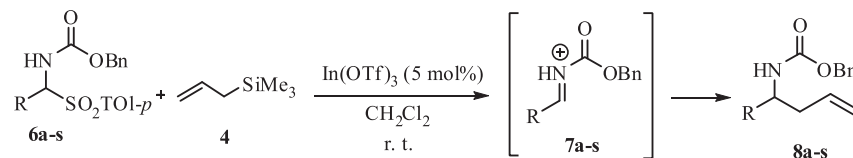
N-Alkoxycarbonylamino *p*-tolylsulfones (**6**) with electron-donating group attached to the benzene ring react with allyltrimethylsilane (**4**) to produce the Cbz-protected homoallylic amines in good yield (entries 2–6). The reactions of *p*-, *m*-, and *o*-halogen containing *N*-alkoxycarbonylamino *p*-tolylsulfone gave corresponding products in 90, 83, 89, 87, 84, and 83% yield, respectively (entries 7–12). This shows no serious electron-withdrawing effects of halogen atoms. *o*-Isomers exhibit a slight steric and electron effect, that is responsible for the less yield and longer reaction time (entries 8 and 11). The electron-withdrawing *p*-CN group also (**6k**) proceeds smoothly to give the allylation product in good yield (entry 13). 2-Furyl (**6n**) and 2-naphthyl *N*-alkoxycarbonylamino *p*-tolylsulfone (**6o**) react with allyltrimethylsilane (**4**) to afford the corresponding products (entries 14 and 15). The reactions of acyclic aliphatic *N*-alkoxycarbonylamino *p*-tolylsulfone give the Cbz-protected homoallylic amines in comparatively low yield (entries 16 and 17). Cyclohexyl and 2-cyclohexenyl *N*-alkoxycarbonylamino *p*-tolylsulfone bring about the corresponding allylation derivatives (entry 18 and 19).



Scheme 2. General equation for Lewis acid-catalyzed allylation of *N*-benzyloxycarbonylamino *p*-tolylsulfone.

Table 3

Allylation of various *N*-alkoxycarbonylamino *p*-tolylsulfone with allyltrimethylsilane catalyzed by $\text{In}(\text{OTf})_3^a$



Entry	R in 6	Reaction time (h)	Product 8	Isolated yield (%) ^b
1	6a , C ₆ H ₄	8.0	8a	87
2	6b , 4-MeC ₆ H ₄	9.0	8b	89
3	6c , 2-MeC ₆ H ₄	9.0	8c	85
4	6d , 4-MeOC ₆ H ₄	8.0	8d	91
5	6e , 3,4-(MeO) ₂ C ₆ H ₂	8.0	8e	91
6	6f , 3-PhOC ₆ H ₄	9.0	8f	87
7	6g , 4-BrC ₆ H ₄	9.0	8g	92
8	6h , 2-BrC ₆ H ₄	9.0	8h	83
9	6i , 4-ClC ₆ H ₄	8.0	8i	89
10	6j , 3-ClC ₆ H ₄	9.0	8j	87
11	6k , 2-ClC ₆ H ₄	9.0	8k	84
12	6l , 3-FC ₆ H ₄	9.0	8l	83
13	6m , 4-CNC ₆ H ₄	9.0	8m	80
14	6n ,	9.0	8n	76
15	6o ,	9.0	8o	84
16	6p , CH ₃ (CH ₂) ₂	10.0	8p	70
17	6q , CH ₃ (CH ₂) ₆	10.0	8q	76
18	6r ,	10.0	8r	75
19	6s ,	10.0	8s	78

^a Reaction condition: *N*-alkoxycarbonylamino *p*-tolylsulfone (**6**) (1.0 mmol), trimethylsilane (1.5 mmol), and $\text{In}(\text{OTf})_3$ (5 mol % with respect to *N*-sulfonyl aldimine) are used.

^b Yield of isolated product after column chromatography.

3. Conclusion

An effective Indium triflate-catalyzed allylation reaction of *N*-sulfonyl aldimines or *N*-alkoxycarbonylamino *p*-tolylsulfone with allyltrimethylsilane is described. The present method provides a facile and convenient route for the synthesis of protected homoallylic amines. The advantages of the present method include: (1) low catalyst loading and (2) mild reaction conditions.

4. Experimental section

4.1. Experimental procedure for the allylation of *N*-sulfonyl aldimines with allyltrimethylsilane

To a stirred solution of *N*-sulfonyl aldimines (1 mmol) and $\text{In}(\text{OTf})_3$ (5 mol %) in CH_2Cl_2 (3 mL) under nitrogen atmosphere at rt, allyltrimethylsilane (1.5 mmol) is added. The mixture is stirred at rt

and monitored by TLC. After the completion, the reaction mixture is filtered, and the residue is washed with CH_2Cl_2 (2 × 5 mL). The filtrate is dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product is subject to flash column chromatography (silica gel, hexane–EtOAc, 9:1) to obtain the pure product.

4.2. Experimental procedure for the allylation of *N*-alkoxycarbonylamino *p*-tolylsulfone with allyltrimethylsilane

Allyltrimethylsilane (1.5 mmol) was added drop-wise to a stirred solution of *N*-alkoxycarbonylamino *p*-tolylsulfone (1 mmol) and $\text{In}(\text{OTf})_3$ (5 mol %) in CH_2Cl_2 (3 mL) under nitrogen atmosphere at rt. The mixture is stirred at rt and monitored by TLC. After the completion, the reaction mixture is filtered, and the residue is washed with CH_2Cl_2 (2 × 5 mL). The filtrate is dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product is subject to flash column chromatography (silica gel, hexane–EtOAc, 90:10 to 95:5) to obtain the pure product.

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

4.2.1. Compound 5a. White solid, mp 75–76 °C; IR (KBr): ν_{max} 3261, 1458, 1314, 1159, 1088 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J=8.4$ Hz, 2H), 7.14–7.01 (m, 7H), 5.50–5.43 (m, 1H), 5.11 (br s, 1H), 4.99 (d, $J=14.0$ Hz, 2H), 4.33 (q, $J=7.0$ Hz, 1H), 2.46–2.36 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.0, 137.4, 133.1, 129.2, 128.3, 127.3, 127.1, 126.5, 119.1, 57.2, 41.8, 21.4.^{5c,6g,l}

4.2.2. Compound 5b. White solid, mp 159–160 °C; IR (KBr): ν_{max} 3261, 1456, 1314, 1159, 1076 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, $J=8.4$ Hz, 2H), 7.13–7.07 (m, 4H), 6.98 (d, $J=8.0$ Hz, 2H), 5.51–5.44 (m, 2H), 5.03 (s, 1H), 5.00–4.98 (m, 1H), 4.32 (q, $J=7.0$ Hz, 1H), 2.43–2.36 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.2, 138.8, 137.2, 132.9, 132.7, 129.2, 128.3, 128.0, 127.0, 119.2, 56.7, 41.5, 21.3.^{5c,6l}

4.2.3. Compound 5c. Viscous mass; IR (KBr): ν_{max} 3273, 1589, 1422, 1291, 1148, 1088 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, $J=8.4$ Hz, 2H), 7.14 (d, $J=8.4$ Hz, 2H), 7.09 (d, $J=6.0$ Hz, 2H), 7.02–6.98 (m, 1H), 6.94 (s, 1H), 5.54–5.44 (m, 2H), 5.06 (s, 1H), 5.02 (d, $J=5.8$ Hz, 1H), 4.34 (q, $J=7.0$ Hz, 1H), 2.44–2.38 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.2, 142.3, 137.1, 134.0, 132.6, 129.5, 129.2, 127.3, 127.0, 126.8, 124.8, 119.4, 56.8, 41.5, 21.3; HRMS-FAB (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{19}\text{ClNO}_2\text{S}$ 336.0825, found 336.0825.

4.2.4. Compound 5d. White solid, mp 113–114 °C; IR (KBr): ν_{max} 3261, 1446, 1327, 1159, 1086 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J=8.4$ Hz, 2H), 7.21–7.17 (m, 2H), 7.12 (d, $J=7.0$ Hz, 2H), 7.08–7.05 (m, 2H), 5.58–5.44 (m, 2H), 5.03 (d, $J=15$ Hz, 2H), 4.83 (q, $J=7.0$ Hz, 1H), 2.48–2.38 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.1, 137.8, 136.8, 132.7, 131.9, 129.4, 129.2, 128.3, 128.2, 127.1, 126.7, 119.3, 54.0, 40.3, 21.4; HRMS-FAB (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{19}\text{ClNO}_2\text{S}$ 336.0825, found 336.0826.

4.2.5. Compound 5e. White solid, mp 129–130 °C; IR (KBr): ν_{max} 3249, 1446, 1327, 1159, 1064 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, $J=8.4$ Hz, 2H), 7.25 (d, $J=8.4$ Hz, 2H), 7.13 (d, $J=8.4$ Hz, 2H), 6.93 (d, $J=8.4$ Hz, 2H), 5.54–5.45 (m, 1H), 5.34 (d, $J=6.6$ Hz, 1H), 5.05 (s, 1H), 5.02 (d, $J=8.4$ Hz, 1H), 4.32 (q, $J=7.0$ Hz, 1H), 2.43–2.38 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 143.3, 139.3, 137.2, 132.6, 131.3, 129.3, 128.3, 127.0, 121.1, 119.4, 56.6, 41.5, 21.4; HRMS-FAB (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{19}\text{BrNO}_2\text{S}$ 380.0143, found 380.0137.

4.2.6. Compound 5f. White solid, mp 118–119 °C; IR (KBr): ν_{max} 3261, 1446, 1314, 1159, 1088 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, $J=8.4$ Hz, 2H), 7.14 (d, $J=8.7$ Hz, 2H), 7.01–6.93 (m, 4H), 5.55–5.45 (m, 1H), 5.02 (dd, $J=12.0, 2.0$ Hz, 3H), 4.31 (q, $J=7.0$ Hz, 1H), 2.49–2.39 (m, 2H), 2.37 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.9, 137.5, 137.3, 137.0, 129.6, 129.2, 128.9, 127.1, 126.4, 119.0, 56.9, 41.7, 21.4, 20.9.^{5c,6g,l}

4.2.7. Compound 5g. White solid, mp 86–87 °C; IR (KBr): ν_{max} 3261, 1530, 1314, 1159, 1028 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, $J=7.8$ Hz, 2H), 7.09 (d, $J=8.0$ Hz, 2H), 6.94 (d, $J=8.8$ Hz, 2H), 6.64 (d, $J=8.4$ Hz, 2H), 5.49–5.43 (m, 1H), 5.24 (br s, 1H), 4.99 (d, $J=6.6$ Hz, 2H), 4.27 (q, $J=7.0$ Hz, 1H), 3.69 (s, 3H), 2.44–2.36 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 158.7, 142.8, 137.5, 133.3, 132.4, 131.9, 129.2, 127.7, 127.0, 118.7, 113.6, 56.8, 55.1, 41.7, 21.3.^{5c}

4.2.8. Compound 5h. White solid, mp 67–68 °C; IR (KBr): ν_{max} 3257, 1458, 1314, 1159, 1111 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, $J=7.8$ Hz, 2H), 7.08 (d, $J=7.8$ Hz, 2H), 6.21 (s, 2H), 5.58–5.52 (m, 2H), 5.05 (d, $J=8.4$ Hz, 1H), 5.02 (s, 1H), 4.30 (q, $J=7.0$ Hz, 1H), 3.72 (s,

3H), 3.67 (s, 6H), 2.45–2.39 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.8, 142.9, 137.6, 136.8, 135.8, 133.2, 129.5, 129.0, 127.1, 126.3, 118.8, 103.5, 60.4, 57.7, 55.8, 41.7, 21.3; HRMS-FAB (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{26}\text{NO}_5\text{S}$ 391.1453, found 391.1453.

4.2.9. Compound 5i. White solid, mp 127 °C; IR (KBr): ν_{max} 3285, 1518, 1362, 1148, 1064 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J=8.8$ Hz, 2H), 7.55 (d, $J=8.4$ Hz, 2H), 7.28 (d, $J=8.8$ Hz, 2H), 7.14 (d, $J=8.0$ Hz, 2H), 5.60 (d, $J=6.2$ Hz, 1H), 5.50–5.48 (m, 1H), 5.04 (d, $J=5.5$ Hz, 1H), 5.02 (d, $J=12.5$ Hz, 1H), 4.44 (q, $J=7.0$ Hz, 1H), 2.44–2.39 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 147.9, 146.9, 143.8, 131.9, 129.4, 127.5, 127.0, 123.4, 120.1, 56.6, 41.4, 21.3.^{6g}

4.2.10. Compound 5j. White solid, mp 148–149 °C; IR (KBr): ν_{max} 3297, 2210, 1338, 1135, 1064 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J=8.4$ Hz, 2H), 7.39 (d, $J=7.8$ Hz, 2H), 7.17 (d, $J=8.0$ Hz, 2H), 7.10 (d, $J=8.0$ Hz, 2H), 5.65 (d, $J=6.6$ Hz, 1H), 5.42–5.39 (m, 1H), 4.99 (d, $J=4.7$ Hz, 1H), 4.97 (d, $J=11.7$ Hz, 1H), 4.35 (q, $J=7.0$ Hz, 1H), 2.37–2.33 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 145.9, 143.5, 136.9, 132.0, 129.3, 127.4, 127.0, 119.8, 118.5, 110.9, 56.8, 41.3, 21.3.

4.2.11. Compound 5k. White solid, mp 84–85 °C; IR (KBr): ν_{max} 3249, 2210, 1327, 1159, 1052 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, $J=8.4$ Hz, 2H), 7.39–7.34 (m, 2H), 7.27–7.22 (m, 2H), 7.10 (d, $J=8.4$ Hz, 2H), 5.60 (br s, 1H), 5.47–5.39 (m, 1H), 5.03–4.96 (m, 2H), 4.35 (q, $J=6.7$ Hz, 1H), 2.40–2.35 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.5, 141.9, 137.0, 132.1, 131.2, 130.7, 130.2, 129.4, 129.0, 126.9, 119.8, 118.3, 112.1, 56.6, 41.4, 21.3; HRMS-FAB (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_2\text{S}$: 327.1167, found: 327.1165.

4.2.12. Compound 8a. White solid, mp 67 °C; IR (KBr): ν_{max} 3367, 1685, 1530, 1257, 1028 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.31–7.22 (m, 10H), 5.70–5.59 (m, 1H), 5.20 (br s, 1H), 5.10–5.01 (m, 4H), 4.79 (br s, 1H), 2.51 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.7, 142.0, 136.5, 133.8, 128.6, 128.5, 128.1, 127.3, 126.3, 118.4, 66.8, 54.6, 41.1.^{5g}

4.2.13. Compound 8b. White solid, mp 63–64 °C; IR (KBr): ν_{max} 3357, 1697, 1518, 1267, 1040 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.27 (s, 5H), 7.11–7.07 (m, 5H), 5.68–5.58 (m, 1H), 5.32 (br s, 1H), 5.07–4.98 (m, 4H), 4.74 (br s, 1H), 2.46 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.6, 138.9, 136.7, 136.4, 133.8, 129.1, 128.3, 127.9, 126.1, 118.1, 66.5, 54.2, 40.9, 20.9.^{11f}

4.2.14. Compound 8c. White solid, mp 51–52 °C; IR (KBr): ν_{max} 3344, 1673, 1541, 1267, 1028 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.35 (s, 5H), 7.25–7.18 (m, 5H), 5.80–5.70 (m, 1H), 5.23 (br s, 1H), 5.17–5.04 (m, 5H), 2.52 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.7, 140.3, 136.5, 135.4, 134.0, 130.7, 128.5, 128.1, 127.2, 126.3, 125.1, 118.3, 66.8, 50.8, 40.3, 19.3.^{11h}

4.2.15. Compound 8d. White solid, mp 69–70 °C; IR (KBr): ν_{max} 3309, 1684, 1541, 1255, 1028 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.30 (s, 5H), 7.16 (d, $J=7.8$ Hz, 2H), 6.83 (d, $J=8.4$ Hz, 2H), 5.70–5.59 (m, 1H), 5.14 (br s, 1H), 5.10–5.00 (m, 4H), 4.72 (br s, 1H), 3.76 (s, 3H), 2.49 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.7, 155.6, 136.4, 133.8, 128.4, 128.0, 127.3, 118.2, 113.8, 66.6, 55.1, 54.0, 40.9.^{5g}

4.2.16. Compound 8e. White solid, mp 70 °C; IR (KBr): ν_{max} 3344, 1697, 1530, 1243, 1124 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.35–7.25 (m, 5H), 6.46 (s, 2H), 5.73–5.62 (m, 1H), 5.18–5.08 (m, 6H), 4.75 (br s, 1H), 3.81 (s, 9H), 2.51 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.3, 153.8, 138.3, 137.6, 136.9, 134.3, 129.0, 128.6, 119.0, 103.7, 67.4, 61.3, 56.6, 55.3, 41.7.^{11f}

4.2.17. Compound 8f. White solid, mp 45–46 °C; IR (KBr): ν_{max} 3311, 1679, 1534, 1255, 1056 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3)

δ 7.36–7.28 (m, 7H), 7.14–7.10 (m, 1H), 7.03–6.97 (m, 4H), 6.90 (d, $J=8.0$ Hz, 2H), 5.73–5.64 (m, 1H), 5.19 (br s, 1H), 5.14–5.05 (m, 4H), 4.82 (br s, 1H), 2.48 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.3, 157.0, 155.6, 144.1, 136.3, 133.4, 129.8, 129.7, 128.4, 128.0, 123.2, 121.0, 118.8, 118.5, 117.4, 116.6, 66.7, 54.1, 40.9; HRMS-FAB (m/z) [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{24}\text{H}_{24}\text{NO}_3$ 373.1756, found 374.1755.

4.2.18. Compound 8g. White solid, mp 87–88 °C; IR (KBr): ν_{max} 3344, 1684, 1541, 1267, 1040 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, $J=8.4$ Hz, 2H), 7.33 (s, 5H), 7.14 (d, $J=7.0$ Hz, 2H), 5.68–5.60 (m, 1H), 5.20 (br s, 1H), 5.13–5.06 (m, 4H), 4.75 (br s, 1H), 2.49 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.6, 141.0, 136.2, 133.2, 131.6, 128.5, 128.1, 127.9, 121.0, 118.8, 66.8, 53.9, 40.8; HRMS-FAB (m/z) [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{18}\text{H}_{19}\text{BrNO}_2$ 360.0599, found 360.0597.

4.2.19. Compound 8h. White solid, mp 73 °C; IR (KBr): ν_{max} 3311, 1693, 1547, 1268, 1030 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, $J=8.0$ Hz, 2H), 7.34–7.24 (m, 6H), 7.14–7.09 (m, 1H), 5.75–5.64 (m, 1H), 5.31 (br s, 1H), 5.16–5.03 (m, 5H), 2.56 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.5, 141.0, 136.3, 133.5, 133.2, 128.7, 128.5, 128.2, 127.6, 127.3, 122.7, 118.7, 66.8, 54.0, 39.4; HRMS-FAB (m/z) [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{18}\text{H}_{19}\text{BrNO}_2$ 360.0599, found 360.0597.

4.2.20. Compound 8i. White solid, mp 63 °C; IR (KBr): ν_{max} 3347, 1675, 1543, 1267, 1040 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.40–7.27 (m, 6H), 7.17 (d, $J=7.0$ Hz, 2H), 5.68–5.60 (m, 1H), 5.23 (br s, 1H), 5.17–5.01 (m, 4H), 4.78 (br s, 1H), 2.51 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.2, 141.3, 136.9, 133.8, 133.6, 129.2, 129.1, 121.0, 128.9, 128.7, 128.2, 128.1, 119.4, 67.4, 54.5, 41.4.^{11h}

4.2.21. Compound 8j. White solid, mp 61–62 °C; IR (KBr): ν_{max} 3344, 1673, 1530, 1255, 1028 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.34–7.24 (m, 8H), 7.15 (d, $J=2.0$ Hz, 1H), 5.73–5.60 (m, 1H), 5.26 (br s, 1H), 5.14–5.04 (m, 4H), 4.89 (br s, 1H), 2.50 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.6, 144.2, 136.2, 134.3, 133.1, 129.7, 128.4, 128.1, 127.4, 126.3, 124.4, 118.8, 66.8, 54.0, 40.8; HRMS-FAB (m/z) [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{18}\text{H}_{19}\text{ClNO}_2$ 316.1104, found 316.1105.

4.2.22. Compound 8k. White solid, mp 65–66 °C; IR (KBr): ν_{max} 3309, 1673, 1541, 1267, 1028 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.37–7.17 (m, 8H), 5.75–5.63 (m, 1H), 5.33 (br s, 1H), 5.21–5.03 (m, 5H), 2.54 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.1, 140.1, 136.9, 134.0, 133.7, 130.5, 129.0, 128.7, 127.9, 127.5, 119.4, 67.4, 52.6, 39.8.^{5g,h}

4.2.23. Compound 8l. Viscous mass; IR (KBr): ν_{max} 3320, 1684, 1530, 1243, 1028 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.31–7.22 (m, 6H), 7.03 (d, $J=7.0$ Hz, 1H), 6.97–6.90 (m, 2H), 5.68–5.90 (m, 1H), 5.26 (d, $J=5.4$ Hz, 1H), 5.11–5.02 (m, 4H), 4.79 (br s, 1H), 2.48 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.1, 161.6, 155.6, 144.7, 136.2, 133.2, 130.0, 129.9, 128.4, 128.1, 121.8, 118.7, 114.2, 113.9, 113.2, 113.0, 66.8, 54.0, 40.8; HRMS-FAB (m/z) [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{18}\text{H}_{19}\text{FNO}_2$ 300.1400, found 300.1398.

4.2.24. Compound 8m. Viscous mass; IR (KBr): ν_{max} 3366, 2208, 1689, 1540, 1255, 1040 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J=7.8$ Hz, 2H), 7.37–7.32 (m, 1H), 5.66–5.56 (m, 1H), 5.41 (d, $J=5.8$ Hz, 1H), 5.13–5.05 (m, 4H), 4.82 (br s, 1H), 2.48 (d, $J=4.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.5, 147.5, 136.0, 132.6, 132.2, 128.4, 128.1, 128.0, 126.9, 119.2, 118.6, 110.9, 66.8, 54.2, 40.5.^{11h}

4.2.25. Compound 8n. Viscous mass; IR (KBr): ν_{max} 3333, 1697, 1506, 1219, 1040 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.30 (s, 6H), 6.26 (dd, $J=3.0, 1.0$ Hz, 1H), 6.13 (s, 1H), 5.71–5.61 (m, 1H), 5.09–5.03 (m, 5H), 4.89 (br s, 1H), 2.55 (t, $J=6.7$ Hz, 2H); ^{13}C NMR

(100 MHz, CDCl_3) δ 154.9, 153.4, 141.2, 135.7, 132.6, 127.8, 127.4, 117.9, 109.5, 105.5, 66.2, 48.0, 37.8.^{5g}

4.2.26. Compound 8o. White solid, mp 66–67 °C; IR (KBr): ν_{max} 3368, 1673, 1518, 1243, 1028 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.75–7.66 (m, 3H), 7.42–7.28 (m, 6H), 5.68–5.59 (m, 1H), 5.41 (br s, 1H), 5.09–4.95 (m, 5H), 2.54 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.7, 139.3, 136.3, 133.6, 133.2, 132.6, 128.4, 128.3, 128.0, 127.8, 127.5, 126.1, 125.7, 124.8, 124.4, 118.4, 66.7, 54.6, 40.8.^{11f}

4.2.27. Compound 8p. Viscous mass; IR (KBr): ν_{max} 3320, 1697, 1530, 1219, 1088 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.32 (s, 5H), 5.82–5.74 (m, 1H), 5.17–5.06 (m, 4H), 4.78 (br s, 1H), 3.64–3.59 (m, 1H), 2.36–2.23 (m, 1H), 2.18–2.13 (m, 1H), 1.42–1.38 (m, 2H), 0.99–0.93 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.3, 136.8, 134.8, 128.5, 128.0, 117.4, 66.5, 55.2, 41.4, 36.7, 29.7, 28.3, 26.4, 26.2, 26.1.^{5d}

4.2.28. Compound 8q. Viscous mass; IR (KBr): ν_{max} 3320, 1684, 1541, 1267, 1064 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.33 (s, 5H), 5.82–5.74 (m, 1H), 5.66 (s, 2H), 5.14–5.05 (m, 4H), 4.67 (br s, 1H), 3.68–3.64 (m, 1H), 2.43–2.30 (m, 1H), 2.22–2.14 (m, 1H), 2.08–2.00 (m, 3H), 1.85–1.75 (m, 2H), 1.67–1.63 (m, 1H), 1.48–1.20 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.2, 136.5, 134.3, 128.4, 127.9, 126.9, 125.9, 117.7, 66.5, 54.4, 37.4, 36.7, 28.6, 26.9, 25.6, 25.2, 24.3; HRMS-FAB (m/z) [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{18}\text{H}_{24}\text{NO}_2$ 290.2120, found 290.2120.

4.2.29. Compound 8r. White solid, mp 64–65 °C; IR (KBr): ν_{max} 3309, 1673, 1541, 1255 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.39–7.28 (s, 5H), 5.82–5.76 (m, 1H), 5.09–5.05 (m, 4H), 4.67 (br s, 1H), 3.68–3.58 (m, 1H), 2.31–2.13 (m, 3H), 1.80–1.76 (m, 1H), 0.87–0.77 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.0, 136.7, 134.8, 134.3, 128.5, 128.0, 117.8, 66.5, 50.4, 39.5, 36.8, 19.1, 13.9.^{3e,5h}

4.2.30. Compound 8s. Viscous mass; IR (KBr): ν_{max} 3320, 1684, 1518, 1243, 1040 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.36–7.28 (m, 5H), 5.82–5.73 (m, 1H), 5.10–5.04 (m, 4H), 4.74 (br s, 1H), 3.71 (br s, 1H), 2.28–2.16 (m, 2H), 1.47 (br s, 1H), 1.44–1.26 (m, 9H), 0.89 (t, $J=7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.9, 136.6, 134.2, 128.3, 128.0, 127.8, 117.6, 66.3, 50.6, 39.3, 34.5, 31.6, 29.0, 25.7, 22.4, 13.9; HRMS-FAB (m/z) [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{18}\text{H}_{28}\text{NO}_2$ 286.1807, found 286.1806.

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