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Palladium-catalyzed alkenyl C–H bond sulfonylation reaction using organosulfonyl chlorides

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ABSTRACT

A Pd-catalyzed alkenyl C–H bond direct sulfonylation of vinyl pyridine and enamides was developed. Various arylsulfonyl chlorides were tested in this reaction and the desired products were obtained in good yields. Moreover, the alkyl sulfonyl chloride could also be used though the yield was lower. A possible Pd(II)/Pd(IV) catalytic pathway involved in this coupling reaction was proposed.

1. Introduction

Organosulfones are important synthetic intermediate in organic chemistry.[1] Therefore, the preparation of organosulfur has gained much attention.[2] Among the methods developed, the addition of sulfonyl radicals generated from the sulfonyl halides to olefins is one of the most common methods.[3] Kharasch reported the first example of addition of sulfuryl chloride induced by peroxide into the olefinic double bond.[4] Since then a number of arenesulphonyl halides and alkane–sulphonyl chlorides were added to olefins by the reduction with metallic reagents at high temperature,[5] or exposure to uv light.[6] In 2004, palladium-catalyzed coupling reaction of aryl boronic acids with arylsulfonyl chloride was developed by professor Bandgar.[7] Recently, palladium-mediated C–H activation/cross-coupling of 2-phenyl pyridine and derivatives with arylsulfonyl chlorides was elegantly disclosed by Dong.[8] Due to our recent interest in the development of palladium-catalyzed alkenyl C–H bond functionalization reaction,[9] herein, we report a sulfonylation reaction of olefins generated by coupling with organosulfonyl chloride and catalyzed by palladium.

2. Results and discussion

Initially, 2-(prop-1-en-2-yl)pyridine as substrate was chosen to investigate the conditions. We first examined different palladium catalysts in dioxane with 0.5 equiv of K_2CO_3. The best result (product in 71% yield) was obtained with 10 mol % $Pd(PhCN)_2Cl_2$; both $Pd(CH_3CN)_2Cl_2$ and $Pd(OAc)_2$ also could afford the desired product in moderate yields, but only low yield was obtained when the $Pd(TFA)_2$ (Table 1, entry 3) or $Pd(acac)_2$ (Table 1, entry 4) was used as catalyst. It was noted that improving the amount or decreasing the use of K_2CO_3 would lower the product's yield (Table 1, entry 8). Other bases such as Na_2CO_3 (Table 1, entry 9) or K_3PO_4 (Table 1, entry 10) applied in this reaction could also provide the product in moderate yield also, while low yields were obtained when organic bases like triethylamine (Table 1, entry 11) or pyridine (Table 1, entry 12) was used. It was further found that the choice of solvent was crucial important for this reaction, no any desired product was formed when the reaction was carried in DMF or THF (Table 1, entry 15, 16, respectively). Only recovery of the starting materials was found in the control experiment in the absence of palladium catalyst (Table 1, entry 13).

Next, in the presence of 10 mol % $Pd(PhCN)_2Cl_2$ and 0.5 equiv of K_2CO_3 in dioxane with 4 Å m s and heating under 120 °C, the scope of the sulfonyl chloride was examined. The results are shown as in Table 2. We found that not only the arylsulfonyl chloride with electron-donating groups but also the substrates containing even strong electron-withdrawing groups all could afford the corresponding products in reasonable yields. Notably, 25% yield of product could be obtained when 1-butanesulfonyl chloride was used to react with 2-(prop-1-en-2-yl)pyridine (Table 2, **3g**). The

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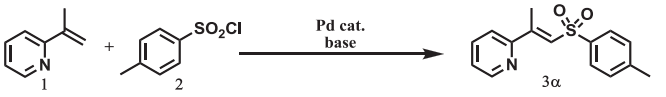
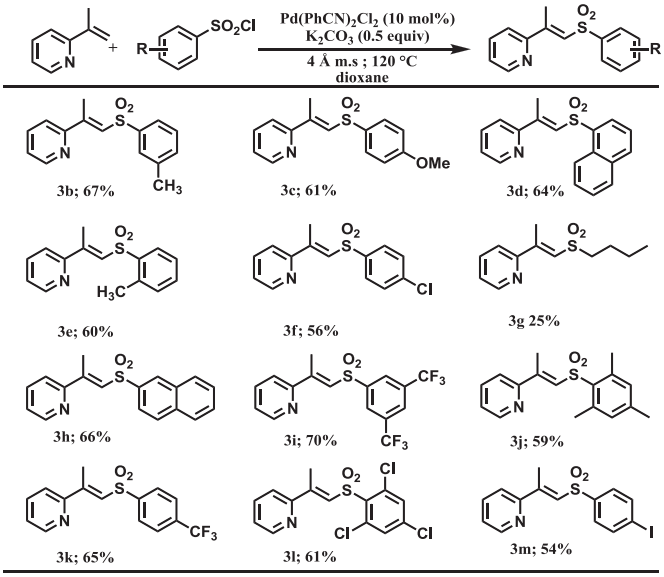
Table 1
Optimization of the coupling reaction condition of α-methyl vinyl pyridine with *p*-toluene sulfonyl chloride[a]



Entry	Cat/mol %	Base/equiv	Solvent	Time/h	Yield (%)
1	$Pd(CH_3CN)_2Cl_2$/10	K_2CO_3/0.5	Dioxane	24	59
2	$Pd(OAc)_2$/10	K_2CO_3/0.5	Dioxane	24	65
3	$Pd(TFA)_2$/10	K_2CO_3/0.5	Dioxane	24	26
4	$Pd(acac)_2$/10	K_2CO_3/0.5	Dioxane	24	13
5	$PdCl_2$/10	K_2CO_3/0.5	Dioxane	24	60
6	$Pd(PhCN)_2Cl_2$/10	K_2CO_3/0.5	Dioxane	24	71
7	$Pd(PhCN)_2Cl_2$/10	K_2CO_3/0.2	Dioxane	24	51
8	$Pd(PhCN)_2Cl_2$/10	K_2CO_3/2	Dioxane	24	40
9	$Pd(PhCN)_2Cl_2$/10	Na_2CO_3/0.5	Dioxane	24	61
10	$Pd(PhCN)_2Cl_2$/10	K_3PO_4/0.5	Dioxane	24	52
11	$Pd(PhCN)_2Cl_2$/10	Et_3N/0.5	Dioxane	24	34
12	$Pd(PhCN)_2Cl_2$/10	Pyridine/0.5	Dioxane	24	25
13	—	K_2CO_3/0.5	Dioxane	24	—
14	$Pd(PhCN)_2Cl_2$//10	K_2CO_3/0.5	Dioxane	48	32
15	$Pd(PhCN)_2Cl_2$/10	K_2CO_3/0.5	DMF	24	—
16	$Pd(PhCN)_2Cl_2$/10	K_2CO_3/0.5	THF	24	—

[a] Conditions: α-methyl vinyl pyridine (0.2 mmol) and sulfonyl chloride (0.3 mmol), Pd(II) (10 mol %), base and 50 mg 4 Å molecular sieves in corresponding solvent (1 ml) were heated at 120 °C.

Table 2
Sulfonylation of α-methyl vinyl pyridine with various sulfonyl chlorides

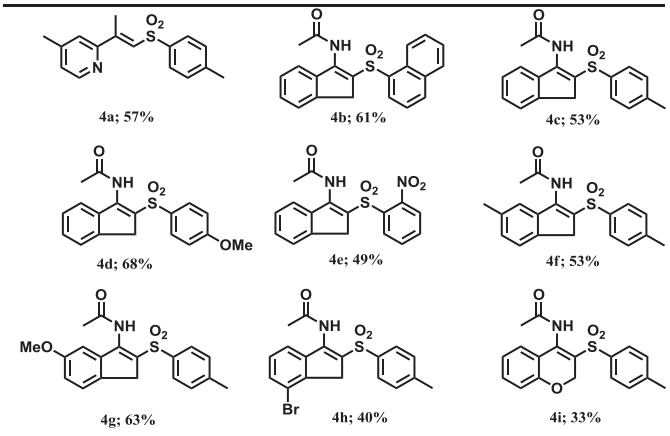


Conditions: α-methyl vinylpyridine (0.2 mmol) and sulfonyl chloride (0.3 mmol), $Pd(PhCN)_2Cl_2$ (10 mol%), K_2CO_3 (0.1 mmol) and 50 mg 4Å molecular sieves in dioxane (1 ml) were heated for 24 h at 120 °C.

tolerance of halides substituents on the phenyl ring permits possible further transformation of the product.

Other functionalized olefins were found to be compatible with this protocol (Table 3). The substituent on the pyridine ring affects the yield dramatically. The electron-donating group such as methyl group slightly decreased the yield. On the basis of this result, we tested the enamide scope for this reaction under slightly modified conditions. It was found some differences happened comparing with the previous results, only the arylsulfonyl chloride with electron-donating groups could afforded the products in high yields. The indanone-derivatived enamides with electro-donating groups easily gave the products in good yields, while only

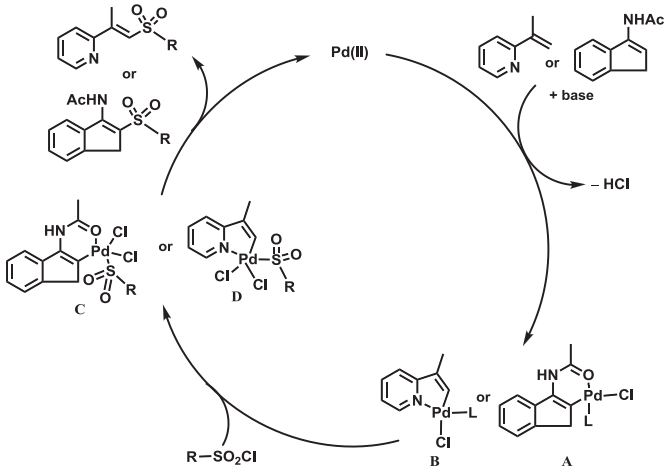
Table 3
Palladium-catalyzed sulfonylation of vinyl pyridine derivatives and enamides



Conditions for vinylpyridine derivatives: **1** (0.2 mmol) and **2** (0.3 mmol), $Pd(PhCN)_2Cl_2$ (10 mol%), K_2CO_3 (0.1 mmol) and 50 mg 4Å molecular sieves in dioxane (1 ml) were heated for 24 h at 120 °C. Conditons for enamides: **1** (0.2 mmol) and **2** (0.3 mmol), $Pd(CH_3CN)_2Cl_2$ (10 mol%), K_2CO_3 (0.1 mmol) and 50 mg 4Å molecular sieves in dioxane (1 ml) were heated for 24 h at 120 °C.

comparable low yields were obtained for the substrates with halide substituent. It was also found that chromenone-derivatived enamide could afford the desired product in 33% yield (Table 3, **4i**).

A possible mechanism for the olefinic C–H bond sulfonylation reaction is proposed as shown in Scheme 1. Firstly the olefin reacted with Pd(II) under the basic condition to give a cyclic vinylpalladium species **A** or **B**, then the five-, or six-membered palladacyclic intermediate reacted with the sulfonyl chloride and a new Pd(IV) complex **C** was generated via an oxidation.[10] After a reductive elimination, the Pd(II) catalyst was involved again into the next catalytic cycle (Scheme 1).



Scheme 1. Proposed mechanism for the sulfonylation of olefins.

3. Conclusion

In conclusion, we have developed a Pd-catalyzed alkenyl C–H bond direct sulfonylation of vinyl pyridine and enamides. Various arylsulfonyl chlorides were tested in this reaction and the desired products were obtained in good yields. A possible Pd(II)/Pd(IV) catalytic pathway involved in this coupling reaction was proposed. Further study focused on extending the scope and establishing the exact mechanism are currently underway in this laboratory.

4. Experimental section

4.1. General

All commercially obtained reagents for the cross-coupling reaction were used as received: anhydrous dioxane was obtained from Sigma–Aldrich and used as received. The enamides and vinyl pyridines were prepared according to the reported references.[11] All cross-coupling reactions were run under 1 atm O_2 and no precautions taken to exclude moisture. Thin-layer chromatography (TLC) was conduced with Merck 60 F254 precoated silicon gel plate (0.2 mm thickness) and visualized with UV and potassium permanganate staining, followed by heating on the hot plate. Flash chromatography was performed using Merck silica gel 60 with distill solvents. ^{1}H NMR spectra were performed on a Brucker Advance 300, 400 NMR spectrometer and are reported in parts per million downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (J=7.26, singlet). Data reported as: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, coupling constant(s) in Hertz; integration. Proton-decoupled ^{13}C NMR spectra were recorded on a Bruker Advance 300 (75 MHz), Bruker Advance 400 (100 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.23 ppm). IR spectra were recorded as thin films on NaCl plates on a Bio-Rad FTS 165 FTIR spectrometer and are reported in frequency of absorption (cm^{-1}). High resolution mass spectral analysis (HRMS) was performed on Waters Q-Tof Premier Mass Spectrometer.

4.2. General procedures for direct cross-coupling reaction of α-methyl vinyl pyridines with *p*-toluene sulfonyl chloride

*4.2.1. Compound **3a**.* A 10 ml dried round bottom flask was charged sequentially with a stirring bar, $Pd(PhCN)_2Cl_2$ (0.02 mmol, 10 mol %), K_2CO_3 (05 equiv), *p*-toluene sulfonyl chloride (1.5 equiv) and 4 Å molecular sieve (50 mg). Dry dioxane (1 ml) and α-methyl vinyl pyridine (0.2 mmol, 1 equiv) were added into the mixture in sequence, and the resultant mixture was stirred at 120 °C under 1 atm of oxygen (balloon pressure) for 24 h. After cooling down, the mixture was diluted with ethyl acetate and filtered via Celite. After removing the organic solvent under reduced pressure, the crude product was purified by silica gel flash column chromatography (EtOAc/hexane mixtures). And 3a was obtained in 71% yield as a white solid. Mp=98–99 °C; R_f=0.35 (EA/Hexane=3:7). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (d, J=4.23 Hz, 1H), 7.87 (d, J=8.25 Hz, 2H), 7.68–7.74 (td, J=7.77, 1.70 Hz, 1H), 7.50 (d, J=7.95 Hz, 1H), 7.34 (d, J=8.25 Hz, 2H), 7.25–7.29 (m, 2H), 2.59 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.8, 149.6, 149.3, 144.2, 139.0, 136.8, 129.9, 127.4, 124.1, 121.0, 21.5, 15.0; IR (film, cm^{-1}): 3020, 1597, 1581, 1568, 1465, 1431, 1311, 1301, 1215, 1145, 1085; HRMS *m*/*z* calculated for $C_{14}H_{13}O_2$ $[M+H]^+$: 213.2887; found 213.2882.

*4.2.2. Compound **3b**.* This compound was prepared by the general procedure and was obtained as a white solid. Yield=67%. Mp=65–66 °C; R_f=0.35 (EA/Hexane=3:7). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57–8.60 (m, 2H), 7.77–7.80 (m, 2H), 7.69–7.74 (td, J=7.76, 1.7 Hz, 1H), 7.50–7.53 (m, 1H), 7.41–7.43 (m, 2H), 7.25–7.30 (m, 2H), 2.60 (d, J=1.23 Hz, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7, 149.9, 149.4, 141.7, 139.5, 136.9, 134.1, 129.8, 129.1, 127.7, 124.5, 124.2, 121.1, 21.3, 15.1; IR (film, cm^{-1}): 3020, 1610, 1581, 1566, 1465, 1431, 1313, 1300, 1215, 1139, 1083; HRMS *m*/*z* calculated for $C_{15}H_{16}NO_2S$ $[M+H]^+$: 274.0902; found 274.0901.

*4.2.3. Compound **3c**.* This compound was prepared by the general procedure and was obtained as a white solid. Yield=61%. Mp=50–51 °C; R_f=0.36 (EA/Hexane=3:7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J=4.52 Hz, 1H), 7.89 (d, J=9.00 Hz, 2H), 7.70 (t, J=7.84 Hz, 1H), 7.48 (d, J=7.84 Hz, 1H), 7.23–7.26 (m, 2H), 6.98 (d, J=9.00 Hz, 2H), 3.85 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 155.8, 149.3, 149.1, 136.9, 133.5, 130.2, 129.6, 124.2, 121.1, 55.7, 14.9; IR (film, cm^{-1}): 3020, 1595, 1579, 1568, 1496, 1431, 1315, 1296, 1261, 1141, 1026; HRMS *m*/*z* calculated for $C_{15}H_{16}NO_3S$ $[M+H]^+$: 290.0851; found 290.0849.

*4.2.4. Compound **3d**.* This compound was prepared by the general procedure and was obtained as a white solid. Yield=64%. Mp=102–104 °C; R_f=0.33 (EA/Hexane=3:7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J=8.60 Hz, 1H), 8.53 (d, J=4.60 Hz, 1H), 8.43 (d, J=7.36 Hz, 1H), 8.09 (d, J=8.24 Hz, 1H), 7.93 (d, J=8.12 Hz, 1H), 7.55–7.69 (m, 4H), 7.45–7.47 (m, 2H), 7.21–7.26 (m, 1H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 150.2, 149.4, 136.9, 136.8, 134.9, 134.2, 130.2, 129.2, 129.1, 128.7, 128.4, 126.9, 124.5, 124.3, 124.2, 121.0, 15.2; IR (film, cm^{-1}): 3018, 1618, 1581, 1564, 1508, 1465, 1431, 1305, 1215, 1155, 1124; HRMS *m*/*z* calculated for $C_{18}H_{16}NO_2S$ $[M+H]^+$: 310.0902; found 310.0900.

*4.2.5. Compound **3e**.* This compound was prepared by the general procedure and was obtained as a white solid. Yield=60%. Mp=63–65 °C; R_f=0.37 (EA/Hexane=3:7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J=4.16 Hz, 1H), 8.12 (d, J=7.84 Hz, 1H), 7.71 (t, J=7.74 Hz, 2H), 7.45–7.51 (dd, J=8.00, 7.44 Hz, 2H), 7.36 (t, J=7.60 Hz, 1H), 7.25–7.31 (m, 3H), 2.65 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 150.2, 149.4, 139.8, 137.9, 137.0, 133.3, 132.5, 129.5, 128.7, 126.3, 124.3, 121.0, 20.4, 15.1; IR (film, cm^{-1}): 3020, 1639, 1465, 1431, 1305, 1215, 1149, 1058; HRMS *m*/*z* calculated for $C_{15}H_{16}NO_2S$ $[M+H]^+$: 274.0902; found 274.0901.

*4.2.6. Compound **3f**.* This compound was prepared by the general procedure and was obtained as a white solid. Yield=56%. Mp=65–67 °C; R_f=0.30 (EA/Hexane=3:7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J=4.48 Hz, 1H), 7.91 (d, J=8.52 Hz, 2H), 7.71 (td, J=7.76, 1.40 Hz, 1H), 7.51 (d, J=8.4 Hz, 3H), 7.26–7.29 (m, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 150.6, 149.4, 140.4, 140.0, 137.0, 129.5, 129.2, 128.9, 124.5, 121.1, 15.1; IR (film, cm^{-1}): 3020, 1612, 1581, 1568, 1465, 1431, 1394, 1315, 1215, 1147, 1085, 1014; HRMS *m*/*z* calculated for $C_{14}H_{13}NO_2SCl$ $[M+H]^+$: 294.0356; found 294.0350.

*4.2.7. Compound **3g**.* This compound was prepared by the general procedure and was obtained as a yellow oil. Yield=25%. R_f=0.4 (EA/Hexane=3:7). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63–8.65 (m, 1H), 7.76 (td, J=7.85, 1.80 Hz, 1H), 7.53–7.56 (m, 1H), 7.30–7.34 (m, 1H), 7.18–7.20 (m, 1H), 3.08–3.13 (m, 2H), 2.62 (d, J=1.29 Hz, 3H), 1.81–1.91 (m, 2H), 1.42–1.55 (m, 2H), 0.96 (t, J=7.19 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 151.4, 149.4, 137.0, 127.2, 124.4, 121.1, 55.7, 24.2, 21.7, 15.2, 13.5; IR (film, cm^{-1}): 2962, 1618, 1581, 1568, 1465, 1431, 1298, 1128; HRMS *m*/*z* calculated for $C_{12}H_{18}NO_2S$ $[M+H]^+$: 240.1058; found 240.1053.

*4.2.8. Compound **3h**.* This compound was prepared by the general procedure and was obtained as a white solid. Yield=66%. Mp=75–77 °C; R_f=0.33 (EA/Hexane=3:7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55–8.56 (m, 2H), 7.88–7.98 (m, 4H), 7.58–7.71 (m, 3H), 7.49 (d, J=7.92 Hz, 1H), 7.37 (s, 1H), 7.23–7.26 (m, 1H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 150.2, 149.4, 138.7, 136.9, 135.1, 132.2, 129.6, 129.6, 129.4, 129.1, 128.8, 127.9, 127.6, 124.3, 122.4, 121.1, 15.1; IR (film, cm^{-1}): 3018, 1618, 1581, 1568, 1465, 1431, 1309, 1215, 1145, 1126, 1070; HRMS *m*/*z* calculated for $C_{18}H_{16}NO_2S$ $[M+H]^+$: 310.0902; found 310.0896.

*4.2.9. Compound **3i**.* This compound was prepared by the general procedure and was obtained as a white solid. Yield=70%. Mp=98–100 °C; R_f=0.31 (EA/Hexane=3:7). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60–8.62 (m, 1H), 8.43 (s, 2H), 8.11 (s, 1H), 7.76 (td, J=7.80,

1.80 Hz, 1H), 7.55–7.58 (m, 1H), 7.30–7.37 (m, 2H), 2.66 (d, J=1.23 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 152.5, 149.5, 144.6, 137.1, 133. 4, 132.9, 127.8 (m), 127.6, 126.9 (m), 124.5 (d, J=52.03 Hz), 120.9 (d, J=60.46 Hz), 15.21; IR (film, cm^{-1}): 3018, 1612, 1581, 1568, 1433, 1359, 1330, 1313, 1280, 1215, 1186, 1149, 1107; HRMS m/z calculated for $C_{16}H_{12}NO_2SF_6$ $[M+H]^+$: 396.0493; found 396.0493.

4.2.10. Compound ***3j***. This compound was prepared by the general procedure and was obtained as a white solid. Yield=59%. Mp=120–122 °C; R_f=0.35 (EA/Hexane=3:7). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57–8.59 (m, 1H), 7.69–7.74 (td, J=7.80, 1.93 Hz, 1H), 7.50 (d, J=7.95 Hz, 1H), 7.32–7.34 (m, 1H), 7.24–7.29 (m, 1H), 6.94 (s, 2H), 2.69 (s, 3H), 2.49 (d, J=1.23 Hz, 3H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.8, 149.4, 147.9, 142.9, 139.4, 136.9, 135.5, 132.1, 131.9, 124.1, 120.9, 22.6, 21.0, 14.9; IR (film, cm^{-1}): 3018, 1602, 1581, 1566, 1465, 1431, 1301, 1215, 1134, 1053; HRMS m/z calculated for $C_{17}H_{20}NO_2S$ $[M+H]^+$: 302.1215 Found 302.1218.

4.2.11. Compound ***3k***. This compound was prepared by the general procedure and was obtained as a white solid. Yield=65%. Mp=67–69 °C; R_f=0.32 (EA/Hexane=3:7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55–8.59 (m, 1H), 8.12 (d, J=8.16 Hz, 2H), 7.81 (d, J=8.16 Hz, 2H), 7.73 (t, J=8.60 Hz, 1H), 7.52 (d, J=7.92 Hz, 1H), 7.25–7.32 (m, 2H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 151.5, 149.5, 145.4, 137.0, 134.9 (q, J=33.07 Hz), 128.6, 128.0, 126.4 (q, J=3.39 Hz), 124.5 (d, J=9.07 Hz), 121.5 (d, J=59.06 Hz), 15.1; IR (film, cm^{-1}): 3024, 1606, 1581, 1566, 1465, 1433, 1404, 1321, 1215, 1172, 1149, 1085, 1062, 1016; HRMS m/z calculated for $C_{15}H_{13}NO_2SF_3$ $[M+H]^+$: 328.0619; found 328.0618.

4.2.12. Compound ***3l***. This compound was prepared by the general procedure and was obtained as a white solid. Yield=61%. Mp=122–124 °C; R_f=0.28 (EA/Hexane=3:7). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61–8.63 (m, 1H), 7.72–7.78 (td, J=7.77, 1.80 Hz, 1H), 7.53–7.56 (m, 1H), 7.50–7.52 (m, 1H), 7.47 (s, 2H), 7.29–7.33 (m, 1H), 2.51 (d, J=1.20 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.2, 151.7, 149.6, 138.9, 137.0, 136.5, 135.2, 131.3, 130.1, 124.6, 121.2, 15.4; IR (film, cm^{-1}): 3020, 1581, 1562, 1537, 1431, 1363, 1328, 1215, 1159, 1136; HRMS m/z calculated for $C_{14}H_{11}NO_2SCl_3$ $[M+H]^+$: 361.9576; found 361.9579.

4.2.13. Compound ***3m***. This compound was prepared by the general procedure and was obtained as a white solid. Yield=59%. Mp=97–99 °C; R_f=0.30 (EA/Hexane=3:7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56–8.61 (m, 1H), 7.90 (d, J=8.40 Hz, 2H), 7.68–7.74 (m, 3H), 7.51 (d, J=7.92 Hz, 1H), 7.25–7.30 (m, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 152.9, 133.4, 133.0, 131.5, 128.4, 128.4, 127.6, 126.6, 126.5, 124.0, 122.6, 102.7, 21.0; IR (film, cm^{-1}): 3018, 1612, 1581, 1568, 1467, 1431, 1384, 1315, 1215, 1147, 1082, 1055, 1006; HRMS m/z calculated for $C_{14}H_{13}NO_2SI$ $[M+H]^+$: 385.9712; found 385.9716.

4.2.14. Compound ***4a***. This compound was prepared by the general procedure and was obtained as a white solid. Yield=57%. Mp=61–63 °C; R_f=0.35 (EA/Hexane=3:7). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (d, J=4.89 Hz, 1H), 7.84 (d, J=8.22 Hz, 2H), 7.33 (s, 1H), 7.30 (s, 2H), 7.21 (m, 1H), 7.07 (d, J=4.77 Hz, 1H), 2.57 (s, 3H), 2.41 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.8, 150.0, 149.1, 148.1, 144.2, 139.1, 129.8, 127.4, 125.1, 122.1, 21.5, 21.1, 15.1; IR (film, cm^{-1}): 3020, 1597, 1444, 1379, 1311, 1301, 1215, 1145, 1085; HRMS m/z calculated for $C_{16}H_{18}NO_2S$ $[M+H]^+$: 288.1058; found 288.1056.

4.2.15. Compound ***4b***. This compound was prepared by the general procedure except using $Pd(CH_3CN)_2Cl_2$ as the catalyst and was obtained as a white solid. Yield=61%. Mp=188–189 °C; R_f=0.31 (EA/Hexane=2:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 8.61–8.35 (dd, J=7.40, 1.08 Hz, 1H), 8.07 (d, J=8.24 Hz, 1H), 7.90 (d, J=7.84 Hz, 1H), 7.81–7.83 (m, 1H), 7.52–7.63 (m, 3H), 7.25–7.30 (s, 3H), 3.48 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 147.4, 142.3, 137.5, 135.7, 135.3, 134.2, 129.2, 128.9, 128.6, 128.6, 127.1, 126.9, 126.4, 124.4, 123.9, 123.5, 121.3, 36.5, 24.4; IR (film, cm^{-1}): 3018, 1710, 1612, 1595, 1566, 1506, 1371, 1357, 1296, 1215, 1153, 1124, 1109; HRMS m/z calculated for $C_{21}H_{17}NO_3SNa$ $[M+Na]^+$: 386.0827; found 386.0828.

4.2.16. Compound ***4c***. This compound was prepared by the general procedure except using $Pd(CH_3CN)_2Cl_2$ as the catalyst and was obtained as a white solid. Yield=53%. Mp=173–174 °C; R_f=0.33 (EA/Hexane=2:3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.83–7.86 (m, 1H), 7.80–7.82 (m, 1H), 7.77–7.79 (m, 1H), 7.30–7.35 (m, 5H), 3.57 (s, 2H), 2.41 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 146.8, 144.7, 142.4, 138.2, 137.5, 130.0, 128.8, 126.9, 126.5, 123.9, 121.4, 36.2, 24.4, 21.5; IR (film, cm^{-1}): 3018, 1708, 1612, 1597, 1568, 1371, 1359, 1298, 1215, 1145, 1076; HRMS m/z calculated for $C_{18}H_{17}NO_3SNa$ $[M+Na]^+$: 350.0827; found 350.0826.

4.2.17. Compound ***4d***. This compound was prepared by the general procedure except using $Pd(CH_3CN)_2Cl_2$ as the catalyst and was obtained as a white solid. Yield=68%. Mp=165–167 °C; R_f=0.35 (EA/Hexane=2:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 7.79–7.81 (m, 3H), 7.31–7.33 (m, 3H), 6.94–6.96 (m, 2H), 3.81 (s, 3H), 3.53 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 163.7, 146.2, 142.3, 137.5, 132.6, 129.2, 128.8, 126.9, 126.4, 123.9, 122.0, 114.7, 55.7, 36.2, 24.4; IR (film, cm^{-1}): 3018, 1708, 1612, 1595, 1568, 1496, 1371, 1359, 1294, 1261, 1215, 1143, 1118; HRMS m/z calculated for $C_{18}H_{17}NO_4SNa$ $[M+Na]^+$: 366.0776; found 366.0779.

4.2.18. Compound ***4e***. This compound was prepared by the general procedure except using $Pd(CH_3CN)_2Cl_2$ as the catalyst and was obtained as a white solid. Yield=49%. Mp=166–167 °C; R_f=0.30 (EA/Hexane=2:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 8.20–8.24 (m, 1H), 7.89–7.93 (m, 1H), 7.73–7.79 (m, 3H), 7.32–7.36 (m, 3H), 3.62 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 152.9, 133.4, 133.0, 131.5, 128.4, 128.4, 127.6, 126.6, 126.5, 124.0, 122.6, 102.7, 21.0; IR (film, cm^{-1}): 2945, 2833, 1654, 1448, 1417, 1217, 1112, 1029; HRMS m/z calculated for $C_{17}H_{14}N_2O_5SNa$ $[M+Na]^+$: 381.0521 Found 381.0519.

4.2.19. Compound ***4f***. This compound was prepared by the general procedure except using $Pd(CH_3CN)_2Cl_2$ as the catalyst and was obtained as a white solid. Yield=53%. Mp=187–189 °C; R_f=0.30 (EA/Hexane=2:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (s, 1H), 7.74 (d, J=8.08 Hz, 2H), 7.61 (s, 1H), 7.28 (d, J=8.08 Hz, 2H), 7.21 (d, J=9.0 Hz, 1H), 7.12 (d, J=7.72 Hz, 1H), 3.49 (s, 2H), 2.38 (s, 3H), 2.35 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 146.8, 144.6, 139.6, 138.2, 137.6, 136.7, 130.0, 129.9, 126.9, 126.6, 123.6, 121.7, 35.8, 24.4, 21.5, 21.5; IR (film, cm^{-1}): 2252, 1707, 1595, 1571, 1350, 1298, 1215, 1141; HRMS m/z calculated for $C_{19}H_{19}NO_3SNa$ $[M+Na]^+$: 364.0983 Found 364.0983.

4.2.20. Compound ***4g***. This compound was prepared by the general procedure except using $Pd(CH_3CN)_2Cl_2$ as the catalyst and was obtained as a white solid. Yield=63%. Mp=157–159 °C; R_f=0.30 (EA/Hexane=2:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.74 (d, J=8.08 Hz, 2H), 7.38–7.39 (m, 1H), 7.28 (d, J=8.08 Hz, 1H), 7.20 (d, J=8.32 Hz, 1H), 6.87–6.90 (m, 1H), 3.78 (s, 3H), 3.47 (s, 2H), 2.38 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 158.8, 146.7, 144.7, 138.6, 138.1, 134.8, 130.1, 126.9, 124.4, 122.4, 116.8, 110.5, 55.6, 35.5, 24.5, 21.6; IR (film, cm^{-1}): 3018, 2945, 2835, 1708, 1595,

1571, 1474, 1350, 1288, 1215, 1026; HRMS *m*/*z* calculated for $C_{19}H_{19}NO_4SNa$ $[M+Na]^+$: 380.0932 Found 380.0939.

*4.2.21. Compound **4h**.* This compound was prepared by the general procedure except using $Pd(CH_3CN)_2Cl_2$ as the catalyst and was obtained as a white solid. Yield=40%. Mp=204–206 °C; R_f=0.30 (EA/Hexane=2:3). ^1H NMR (300 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.82 (d, *J*=8.08 Hz, 2H), 7.81 (s, 1H), 7.50 (d, *J*=7.88 Hz, 1H), 7.36 (d, *J*=8.08 Hz, 2H), 7.23–7.28 (m, 1H), 3.55 (s, 2H), 2.45 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 146.0, 145.0, 142.3, 138.9, 137.7, 131.8, 130.2, 128.7, 127.0, 125.6, 122.3, 118.6, 37.7, 24.3, 21.6; IR (film, cm^{-1}): 3018, 2399, 1712, 1606, 1589, 1475, 1371, 1357, 1215, 1141; HRMS *m*/*z* calculated for $C_{18}H_{16}NO_3SBrNa$ $[M+Na]^+$: 427.9932 Found 427.9931.

*4.2.22. Compound **4i**.* This compound was prepared by the general procedure except using $Pd(CH_3CN)_2Cl_2$ as the catalyst and was obtained as a white solid. Yield=33%. Mp=172–174 °C; R_f=0.31 (EA/Hexane=3:2). ^1H NMR (300 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.77 (d, *J*=8.08 Hz, 2H), 7.30–7.35 (m, 2H), 7.26 (d, *J*=8.08 Hz, 2H), 6.93–6.99 (m, 1H), 6.87 (d, *J*=7.43 Hz, 1H), 4.84 (s, 2H), 2.43 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.7, 156.0, 145.3, 139.9, 137.6, 132.8, 130.2, 127.3, 126.9, 121.7, 118.7, 117.1, 63.7, 24.1, 21.6; IR (film, cm^{-1}): 3018, 1670, 1618, 1477, 1369, 1301, 1215, 1138, 1016; HRMS *m*/*z* calculated for $C_{18}H_{17}NO_4SNa$ $[M+Na]^+$: 366.0776; found 366.0780.

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