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Palladium-catalyzed coupling of vinyl tosylates with arylsulfinate salts

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ABSTRACT

The first palladium-catalyzed coupling of vinyl tosylates with arylsulfinate salts is described. A variety of cyclic and acyclic vinyl tosylates were coupled with aryl sulfinate salts using 2.5 mol % $Pd_2(dba)_3$/5.0 mol % XantPhos to give vinyl aryl sulfone products in good yields. The coupling was extended to the preparation of a cyclopropyl vinyl sulfone.

1. Introduction

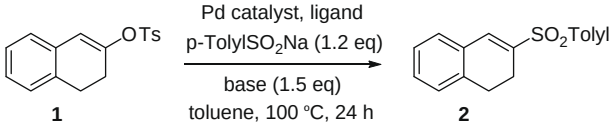
Aryl vinyl sulfones are useful synthetic intermediates,[1] and have been shown to have interesting biological activities.[2] While numerous procedures based on copper or palladium catalysis have been reported for the synthesis of diaryl sulfones and aryl alkyl sulfones, comparatively little work has been done on aryl vinyl sulfone preparations. In 1950 Baker reported the low yielding thermal displacement of β-bromostyrene and β-bromo-4-nitrostyrene with an arylsulfinate sodium salt.[3] In 2004, Cacchi et al. described a Pd-catalyzed coupling of vinyl triflates with arylsulfinate salts.[4] Subsequently, Bao and Wang reported a CuI/L-proline-catalyzed coupling of vinyl bromides with sulfinate salts in ionic liquids.[5] Ma and coworkers reported the CuI-catalyzed coupling of vinyl bromides with sulfinate salts in anion-functionalized ionic liquids.[6]

The use of vinyl tosylates as electrophiles in palladium-catalyzed cross-couplings is attractive due to their simple one-step synthesis from ketone or aldehyde precursors, their lower cost of preparation compared to vinyl triflates (compare the cost of Ts_2O and $PhNTf_2$),[7] and their generally high crystallinity which aids in isolation and purification.[8] Herein we describe our work on the development of a palladium-catalyzed coupling of arylsulfinate salts with vinyl tosylates.

Initial screening experiments employed β-tetralone derived vinyl tosylate **1** and *p*-toluenesulfinic acid sodium salt in toluene solvent at 100 °C for 24 h. Key results for catalyst, ligand, and base screening are summarized in Table 1. The combination of $Pd_2(dba)_3$ as catalyst and XantPhos as ligand was found to be optimal for the coupling. The choice of base proved to be critical, with K_3PO_4 giving the best results. The catalyst loading could be lowered from 5.0 to 2.5 mol % $Pd_2(dba)_3$ with no reduction in yield. Thus, the optimal reaction conditions (entry 4) were defined as 1.2 equiv of sulfinate salt, 1.5 equiv of K_3PO_4, 2.5 mol % $Pd_2(dba)_3$ and 5.0 mol % of XantPhos in toluene at 100 °C for 24 h.

The optimized reaction conditions were applied to the coupling of a variety of ketone and aldehyde derived vinyl tosylates as summarized in Table 2. A variety of cyclic (entries 1–6) vinyl sulfones were prepared, including the functionalized *N*-Boc piperidine substrate **12**. Acyclic substrates could also be prepared (entries 7–9, 11–12), and in the case of sulfones **14**, **16,** and **21** a mixture of

Table 1
Catalyst, ligand, and base screening for the conversion of **1** to **2**



1 **2**

Entry	Pd cat. (mol %)	Ligand (mol %)	Base	Yield[a] (%)
1	$Pd_2(dba)_3$ (5.0)	XantPhos (10.0)	K_2CO_3	62
2	$Pd_2(dba)_3$ (5.0)	XantPhos (10.0)	Cs_2CO_3	45
3	$Pd_2(dba)_3$ (5.0)	XantPhos (10.0)	K_3PO_4	84
4	*$Pd_2(dba)_3$ (2.5)*	*XantPhos (5.0)*	*K_3PO_4*	*84*
5	$Pd_2(dba)_3$ (5.0)	dppf (10.0)	K_3PO_4	50
6	$PdCl_2$	d(iPr)pf	K_3PO_4	60

[a] HPLC assay yield.

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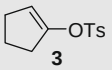
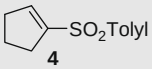
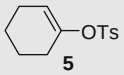
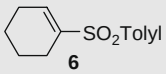
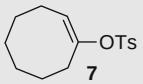
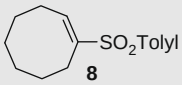
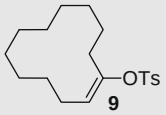
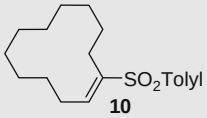
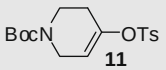
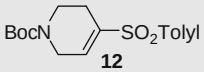
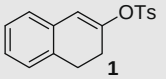
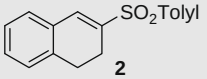
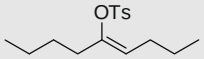
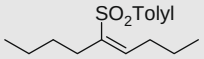
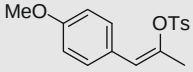
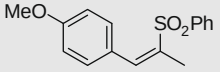
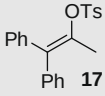
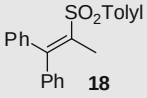
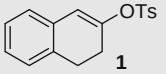
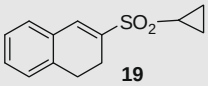
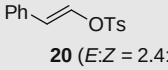
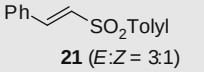
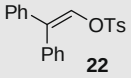
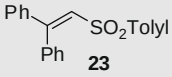
Table 2
Pd-catalyzed coupling of vinyl tolsylates with arylsulfinate salts

Entry	Vinyl tosylate[a]	Vinyl sulfone	Yield[b] (%)
1	 **3**	 **4**	59
2	 **5**	 **6**	69
3	 **7**	 **8**	53
4	 **9**	 **10**	63
5	 **11**	 **12**	75
6	 **1**	 **2**	70
7	 **13** (*Z*:*E* = 3:1)	 **14** (*Z*:*E* = 3:1)	65
8	 **15** (*Z*:*E* = 10:1)	 **16** (*Z*:*E* = 4:1)	50
9	 **17**	 **18**	52
10	 **1**	 **19**	74
11	 **20** (*E*:*Z* = 2.4:1)	 **21** (*E*:*Z* = 3:1)	67
12	 **22**	 **23**	40

[a] Vinyl tosylates were prepared from the corresponding ketones or aldehydes using either NaO*t*-Bu or KHMDS and Ts_2O. See Supplementary data for experimental details.
[b] Isolated yields after chromatography on SiO_2.

isomeric trans and cis olefins was produced with near retention of the olefin geometries of the starting vinyl tosylates. While the coupling of sodium methanesulfinate failed to give any coupling products, we were gratified to find that sodium cyclopropylmethanesulfinate coupled with vinyl tosylate **1** to provide vinyl cyclopropyl sulfone **19** in good yield (74%). To the best of our knowledge, this is the first example of a palladium-catalyzed coupling of an *alkyl sulfinate salt* with any type of electrophile.

In conclusion, a palladium-catalyzed cross-coupling of vinyl tosylates with aryl and cyclopropyl sulfinate salts has been developed. The reaction gives moderate to good yields of vinyl sulfones from a variety of ketone and aldehyde-derived vinyl tolsylates. The successful coupling of cyclopropylsulfinic acid sodium salt represents the first palladium-catalyzed coupling of an alkyl sulfinate salt. The procedure described herein complements existing copper (vinyl bromides) and palladium (vinyl triflates)-based methods and provides an alternative starting material (vinyl tosylates) for vinyl sulfone synthesis.

2. Experimental

2.1. General procedure A for tosylate synthesis

2.1.1. Cyclopentenyl 4-methylbenzenesulfonate 3

To a 200 mL round-bottomed flask under nitrogen atmosphere and magnetic stirring was added cyclopentanone (2.00 g, 23.78 mmol) in tetrahydrofuran (100 mL) to give a yellow solution. The reaction mixture was cooled to −15 °C. Potassium bis(trimethylsilyl)amide 0.5 M in toluene (52.3 mL, 26.20 mmol) was added in one portion. The orange brown solution was stirred at −15 °C for 1 h. *p*-Toluenesulfonic anhydride (8.54 g, 26.20 mmol) was then added at −15 °C. The resulting brown solution was stirred at −15 °C for 30 min then allowed to reach room temperature and stirred for 14 h, and finally quenched with aq $NaHCO_3$ (20 mL). MTBE was added (100 mL) and the organic phase was separated and was washed with water (4 × 100 mL), dried on $MgSO_4$, and concentrated. The residue was dissolved in dichloromethane (2 mL) and purified by CombiFlash (hexane/EtOAc from 10% EtOAc to 30% EtOAc). A tan oil (3.50 g, 62% yield) was obtained which solidified under vacuum removal of solvent.

2.2. General procedure B for tosylate synthesis

2.2.1. 1,1-Diphenylprop-1-en-2-yl 4-methylbenzenesulfonate 17

In a 200 mL round-bottomed flask under magnetic stirring and nitrogen atmosphere was added 1,1-diphenylacetone (4.00 g, 19.02 mmol) in THF (47.6 mL) to give a pale yellow solution. The reaction mixture was cooled to −20 °C. Sodium *tert*-butoxide (2.01 g, 20.93 mmol) was added in one portion. The solution was stirred at −5 °C for 1 h and then at room temperature for 30 min. The solution was cooled to −15 °C. *p*-Toluenesulfonic anhydride (6.83 g, 20.93 mmol) was added in one portion. The resulting solution was stirred at −15 to −5 °C for 1.5 h and quenched with aq $NaHCO_3$ (20 mL). MTBE was added (100 mL) and the organic phase was washed with water (4 × 100 mL), dried on $MgSO_4$, and concentrated. The white solid was separated by recrystallization from hexane/EtOAc. Alternatively the residue was dissolved in dichloromethane (2 mL) and purified by CombiFlash (hexane/EtOAc from 10% EtOAc to 30% EtOAc). A white powder (5.20 g, 75% yield) was obtained.

2.2.2. 3,4-Dihydronaphthalen-2-yl 4-methylbenzenesulfonate 1

White solid mp 70–71 °C. Yield 73%, general procedure B. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (d, J = 7.0 Hz, 2H), 7.37 (d, J = 7.0 Hz, 2H), 7.29–7.09 (m, 3H), 7.00–6.93 (m, 1H), 6.13 (s, 1H), 2.91 (t, J = 6.9 Hz, 2H), 2.49 (s, 3H), 2.47 (t, J = 6.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.7, 145.3, 133.1, 133.1, 132.3, 129.8, 128.4, 127.5, 127.3, 126.7, 126.7, 117.3, 28.5, 26.6, 21.7. HRMS calcd for $C_{17}H_{20}NO_3S$ $[M+NH_4]^+$: 318.1159; found: 318.1169. HRMS calcd for $C_{17}H_{17}NO_3S$ $[M+H]^+$: 301.0892; found: 301.0896. IR (neat) ν 1372.9, 1174.7, 1078.4, 888.4, 747.2 cm^{-1}.

2.3. General procedure for tosylate coupling

2.3.1. 3-(Cyclopropylsulfonyl)-1,2-dihydronaphthalene (19)

In a 10 mL sealed tube equipped with magnetic stirrer was added 3,4-dihydronaphthalen-2-yl 4-methylbenzenesulfonate **1** (0.50 g, 1.67 mmol) in toluene (7 mL) to give a colorless solution.

Cyclopropane sulfinic acid sodium salt (0.26 g, 2.00 mmol), potassium phosphate (0.53 g, 2.50 mmol), $Pd_2(dba)_3$ (0.04 g, 0.04 mmol), and XantPhos (0.05 g, 0.08 mmol) were added to give a brown suspension. The reaction mixture was stirred at 110 °C for 18 h. After cooling down to 22 °C the crude reaction mixture was filtered, the solids were washed with ethyl acetate (10 mL), and the combined organic solutions were concentrated under reduced pressure. The residue was dissolved in dichloromethane (2 mL) and purified by column chromatography on SiO_2 (hexane/EtOAc from 10% EtOAc to 30% EtOAc) to provide 0.29 g (74% yield) of **19** as an orange oil.

2.3.2. 3-Tosyl-1,2-dihydronaphthalene (2)

White solid mp 118–119 °C. Yield 70%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 (d, J = 8.4 Hz, 2H), 7.76 (s, 1H), 7.52 (d, J = 8.3 Hz, 2H), 7.48–7.41 (m, 3H), 7.32 (d, J = 6.5 Hz, 1H), 3.06 (t, J = 8.0 Hz, 2H), 2.69 (t, J = 8.0 Hz, 2H), 2.63 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.3, 134.7, 130.4, 130.0, 129.1, 128.1, 127.8, 127.1, 27.6, 21.8, 21.6. HRMS calcd for $C_{17}H_{20}NO_2S$ $[M+NH_4]^+$: 302.1209; found: 302.1210, difference = 0.2406 ppm. HRMS calcd for $C_{17}H_{17}O_2S$ $[M+H]^+$: 285.0943; found: 285.0938, difference = 2.0280 ppm. IR (neat) ν 1319.6, 1143.8, 1083.1, 759.8 cm^{-1}.

2.3.3. 1-(Cyclopentenylsulfonyl)-4-methylbenzene (4)

Light orange solid mp 106–107 °C. Yield 59%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 6.73–6.70 (m, 1H), 2.54–2.52 (m, 4H), 2.44 (s, 3H), 2.09–1.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 144.2, 142.7, 133.0, 129.7, 128.0, 32.9, 30.9, 23.6, 21.6. HRMS calcd for $C_{12}H_{14}SO_2$ $(M+H)^+$: 223.0787, found 223.0785, difference = 1.0225 ppm. IR (neat) ν 1288.8, 1147.1, 661.9 cm^{-1}.

2.3.4. 1-(Cyclohexenylsulfonyl)-4-methylbenzene (6)

Yellow solid mp 64–65 °C. Yield 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.3 Hz, 2H), 7.04–7.01 (m, 1H), 2.43 (s, 3H), 2.29–2.23 (m, 2H), 2.19–2.14 (m, 2H),1.68–1.53 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 140.0, 136.5, 129.7, 128.1, 25.5, 22.8, 21.8, 21.6, 20.8. HRMS calcd for $C_{13}H_{17}SO_2$ $(M+H)^+$: 237.0943, found 237.09331, difference = 4.5474 ppm. IR (neat) ν 1286.4, 1141.3, 814.2 cm^{-1}.

2.3.5. (*E*)-1-Tosylcyclooct-1-ene (8)

White solid mp 76–77 °C. Yield 53%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 7.07 (t, J = 8.5 Hz, 1H), 2.42 (s, 3H), 2.40–2.36 (m, 2H), 2.33–2.26 (m, 2H), 1.67–1.61 (m, 2H), 1.44–1.36 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.9, 142.0, 137.0, 134.9, 129.7, 128.2, 29.1, 28.2, 26.5, 25.8, 25.6, 25.0, 21.6. HRMS calcd for $C_{15}H_{21}O_2S$ $[M+H]^+$: 265.1256; found: 265.1249, difference = 2.9357 ppm. IR (neat) ν 1284.3, 1145.2, 713.3 cm^{-1}.

2.3.6. (*E*)-1-Tosylcyclododec-1-ene (10)

Light yellow solid mp 101–102 °C. Yield 63%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 6.95 (t, J = 9.5 Hz, 1H), 2.43 (s, 3H), 2.32 (t, J = 6.0 Hz, 2H), 2.21 (t, J = 8.4 Hz, 2H), 1.59–1.52 (m, 4H), 1.42–1.31 (m, 10H), 1.22–1.16 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.4, 142.7, 137.6, 134.8, 129.7, 129.0, 128.4, 127.9, 26.5, 25.8, 25.6, 25.5, 25.2, 24.6, 23.5, 23.3, 23.1, 22.0, 21.6. HRMS calcd for $C_{19}H_{32}NO_2S$ $[M+NH_4]^+$: 338.2148; found: 338.2165, difference = 4.9441 ppm. HRMS calcd for $C_{19}H_{29}O_2S$ $[M+NH]^+$: 321.1882; found: 321.1884, difference = 0.3777 ppm. IR (neat) ν 1286.8, 1134.3, 981.9, 690.2 cm^{-1}.

2.3.7. *tert*-Butyl-4-tosyl-5,6-dihydropyridine-1(2*H*)-carboxylate (12)

Orange oil. Yield 75%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 (d, J = 7.2 Hz, 2H), 7.36 (d, J = 7.2 Hz, 2H), 7.19–7.06 (m, 1H), 4.76–4.74 (m, 1H), 3.71–3.68 (m, 2H), 3.57–3.52 (m, 1H), 2.45 (s, 3H), 2.25 (br s, 1H), 2.00 (br s, 1H), 1.47 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 1144.8, 134.4, 131.2, 129.7, 128.9, 94.9, 94.4, 81.5, 58.1, 39.1, 37.9, 28.1, 21.5. HRMS calcd for $C_{17}H_{27}N_2O_4S$ $[M+NH_4]^+$: 355.1686; found: 355.1688, difference = 0.5465 ppm. HRMS calcd for $C_{17}H_{24}NO_4S$ $[M+H]^+$: 338.1420; found: 355.1433, difference = 3.6766 ppm. IR (neat) ν 1701.9, 1311.7, 1142.6, 715.0 cm^{-1}.

2.3.8. (*Z*)-1-Methyl-4-(non-4-en-5-ylsulfonyl)benzene (*Z*:*E* = 3:1) (14)

Yellow oil. Yield 65%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 6.85 (t, J = 7.5 Hz, 1H), 2.40 (s, 3H), 2.20–2.13 (m, 4H), 1.53–1.46 (m, 2H), 1.32–1.18 (m, 4H), 0.94 (t, J = 7.3 Hz, 3H), 0.80 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.8, 141.5, 129.7, 129.0, 128.4, 128.0, 31.2, 30.3, 26.2, 22.7, 21.8, 21.5, 13.8, 13.6. HRMS calcd for $C_{16}H_{24}O_2S$ $[M+H]^+$: 281.1569; found: 281.1575, difference = 1.8548 ppm. IR (neat) ν 1287.8, 1134.7, 717.3 cm^{-1}.

2.3.9. (*Z*)-1-Methoxy-4-(2-(phenylsulfonyl)prop-1-enyl) benzene (*Z*:*E* = 4:1) (16)

Light yellow oil. Yield 50%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (d, J = 8.4 Hz, 2H), 7.57–7.48 (m, 1H), 7.41–7.36 (m, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.00 (s, 1H), 6.80 (d, J = 8.6 Hz, 2H), 3.82 (s, 3H), 2.19 (d, J = 1.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.8, 138.9, 133.2, 131.5, 131.0, 129.2, 128.6, 128.1, 127.7, 113.1, 55.3, 21.09. HRMS calcd for $C_{16}H_{16}O_2S$ $[M+H]^+$: 289.0892; found: 289.0890, difference = 1.0129 ppm. IR (neat) ν 1508.5, 1249.4, 1146.0, 728.3 cm^{-1}.

2.3.10. (2-Tosylprop-1-ene-1,1-diyl)dibenzene (18)

White solid mp 141–142 °C. Yield 52%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, J = 8.2 Hz, 2H), 7.55–7.38 (m, 8H), 7.33–7.28 (m, 4H), 2.63 (s, 3H), 2.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.4, 141.1, 139.5, 137.3, 129.7, 129.2, 128.5, 128.4, 128.3, 128.2, 127.8, 127.6, 127.4, 21.5, 18.0. HRMS calcd for $C_{22}H_{24}NO_2S$ $[M+NH_4]^+$: 366.1522; found: 366.1532, difference = 2.6560 ppm. HRMS calcd for $C_{22}H_{21}O_2S$ $[M+H]^+$: 349.1256; found: 349.1280, difference = 0.9213 ppm. IR (neat) ν 1312.6, 1156.1, 1077.2, 749.6 cm^{-1}.

2.3.11. 3-(Cyclopropylsulfonyl)-1,2-dihydronaphthalene (19)

Orange oil. Yield 74%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38 (s, 1H), 7.32–7.14 (m, 4H), 2.98 (t, J = 8.0 Hz, 2H), 2.73 (t, J = 8.0 Hz, 2H), 2.45–2.39 (m, 1H), 1.28–1.24 (m, 2H), 1.06–1.01 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.6, 135.5, 134.8, 133.2, 130.2, 128.8, 127.7, 127.0, 29.8, 27.5, 22.1, 4.9. HRMS calcd for $C_{13}H_{14}O_2S$ $[M+H]^+$: 235.0787; found: 235.0783, difference = 1.8210 ppm. IR (neat) ν 1288.5, 1132.4, 883.4 cm^{-1}.

2.3.12. (*E*)-1-Methyl-4-(styrylsulfonyl)benzene (*E*:*Z* = 3:1) (21)

White solid mp 98–99 °C. Yield 67%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (d, J = 8.3 Hz, 2H), 7.67 (d, J = 15.4 Hz, 1H), 7.50–7.32 (m, 7H), 6.86 (d, J = 15.4 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.4, 141.9, 137.8, 133.0, 132.5, 131.1, 130.0, 129.9, 129.0, 127.7, 21.6. HRMS calcd for $C_{15}H_{18}NO_2S$ $[M+NH_4]^+$: 276.1052; found: 276.1047, difference = 2.0906 ppm. HRMS calcd for $C_{15}H_{15}O_2S$ $[M+H]^+$: 259.0787; found: 259.0781, difference = 2.4243 ppm. IR (neat) ν 1303.3, 1141.8, 810.3 cm^{-1}.

2.3.13. (2-Tosylethene-1,1-diyl)dibenzene (23)

White solid, mp 94–95 °C. Yield 40%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49 (t, J = 8.0 Hz, 2H), 2.73 (d, J = 8.3 Hz, 2H), 7.41–7.10 (m, 12H), 7.01 (s, 1H), 2.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.7, 143.7, 139.3, 138.6, 135.6, 132.9, 130.22, 129.8, 129.4, 128.8, 128.6, 128.2,

127.8, 127.7, 21.5. HRMS calcd for $C_{21}H_{22}NO_2S$ $[M+NH_4]^+$: 352.1365; found: 352.1358, difference = 2.2076 ppm. HRMS calcd for $C_{21}H_{19}O_2S$ $[M+H]^+$: 335.1100; found: 335.1083, difference = 5.1573 ppm. IR (neat) ν 1299.6, 1134.8, 696.3 cm^{-1}.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.03.174.

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