Stereoselective synthesis of vinyl sulfones by the Stille coupling of (*E*)-α-stannylvinyl sulfones with aryl halides

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Palladium-catalysed hydrostannylation of acetylenic sulfones (R–C≡C–SO_2Ar) in benzene at room temperature gives stereoselectively (*E*)-α-stannylvinyl sulfones in good to high yields. (*E*)-α-Stannylvinyl sulfones are difunctional group reagents which undergo Stille coupling reaction with aryl halides in the presence of $Pd(PPh_3)_4$ and CuI co-catalyst to afford stereoselectively (*Z*)-1,2-disubstituted vinyl sulfones in good yields.

Keywords: acetylenic sulfone, hydrostannylation, (*E*)-α-stannylvinyl sulfone, Stille coupling, (*Z*)-1,2-disubstituted vinyl sulfone

Many biologically active compounds contain the structural unit of polysubstituted alkenes and the stereoselective synthesis of polysubstituted alkenes remains a challenging problem in organic synthesis.[1-5] Stereodefined vinyl sulfones are useful precursors of alkenes since the sulfone group provides a useful functional group for further transformation by various desulfonylation methods.[6,7] In addition, vinyl sulfones are excellent acceptors for Michael additions[8] and 2π partners in cycloaddition reactions.[9] The available methods for the synthesis of vinyl sulfones mainly consist of Horner–Emmons reactions of carbonyl compounds and sulfonyl phosphoranes,[10] Peterson reactions,[11] β-elimination of selenosulfones[12] and selenosulfonation of acetylene.[13] Alternative convergent processes involve the combination of a sulfone-stabilised carbanion with a carbonyl compound. In this regard, Knoevenagel condensation[14] and Horner–Wittig reaction[15] have achieved great success giving the (*E*)-vinyl sulfone as the exclusive product. The preparation of the starting materials such as sulfonomethylphosphonates, however, could be both inconvenient and time-consuming. Considering the importance of vinyl sulfones, it is still of interest to develop new routes to the synthesis of stereodefined polysubstituted vinyl sulfones. We report here that (*Z*)-1,2-disubstituted vinyl sulfones can be synthesised stereoselectively by palladium-catalysed hydrostannylation of acetylenic sulfones, followed by Stille coupling reaction with aryl halides in the presence of $Pd(PPh_3)_4$ and CuI co-catalyst.

Palladium-catalysed hydrostannylation of phenylthioalkynes,[16] alkynyl selenides,[17] and alkynyl sulfoxides[18] has been reported to be highly regio- and stereoselective, providing a direct route for the stereoselective synthesis of 1,1-difunctional group reagents containing a heteroatom and tin. Xiang and coworkers reported that palladium-catalysed hydrostannylation of acetylenic triflones with tributyltin hydride provided α-stannylated vinyl triflones regiospecifically, but the reaction was not stereospecific, affording a 1:1.7 ratio of *E* and *Z* stereoisomers.[19]

We have now investigated the palladium-catalysed hydrostannylation of acetylenic sulfones in order to provide a simple general route for the stereoselective synthesis of (*E*)-α-stannylvinyl sulfones although there have been examples of these compounds in the literature.[20-23] We found that the palladium-catalysed hydrostannylation of acetylenic sulfones **1** with Bu_3SnH in benzene at room temperature was also highly regio- and stereoselective, giving the corresponding (*E*)-α-stannylvinyl sulfones **2** in good to high yields (Scheme 1). The experimental results are summarised in Table 1.

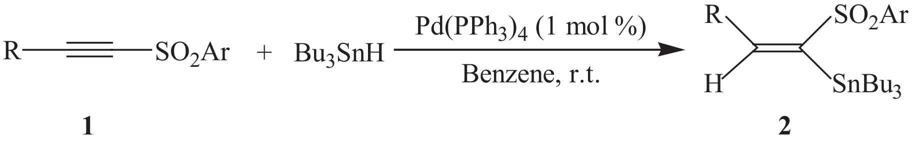
Investigations of the crude products **2** by ^1H NMR spectroscopy (400 MHz) showed their isomeric purities to be more than 98%. One olefinic proton signal of compounds **2a**, **2b**, **2d** and **2e** splits characteristically into a triplet at δ = 6.25–6.42 with coupling constant *J* = 5–7 Hz, which indicated that the hydrostannylation to the acetylenic sulfones had taken place with strong preference for the addition of the tin atom at the carbon adjacent to the sulfonyl group. The stereochemistry of the addition was readily apparent from the ^1H NMR spectra of compounds **2** which showed a ($^3J_{Sn\text{-}H}$) coupling constant of 48–52 Hz, fully in accord with an *E* geometry and overall *cis* addition of tin hydride.[24]

(*E*)-α-Stannylvinyl sulfones **2** are difunctional group reagents in which two synthetically versatile groups are linked to the same olefinic carbon atom and can be considered both as vinylstannanes and as vinyl sulfones. The palladium-catalysed cross-coupling of organostannanes with organic halides and triflates is known as the Stille reaction[25-27] and has become an extremely powerful tool for the formation of carbon–carbon bonds. This coupling reaction has been widely applied in organic synthesis since a wide variety of functionality can be tolerated on either partner, the yields of coupled products are high, and the organotin reagents can be readily synthesised, purified, and stored. With a convenient route to the (*E*)-α-stannylvinyl sulfones **2**, we decided to

Table 1 Synthesis of (*E*)-α-stannylvinyl sulfones **2a–e**[a]

Entry	R	Ar	Product	Yield[b]/%
1	*n*-C_4H_9	Ph	**2a**	90
2	*n*-C_4H_9	4-$CH_3C_6H_4$	**2b**	88
3	Ph	Ph	**2c**	82
4	CH_3OCH_2	Ph	**2d**	83
5	CH_3OCH_2	4-$CH_3C_6H_4$	**2e**	80

[a]Reactions were performed in the presence of **1** (1 mmol), Bu_3SnH (1.05 mmol), $Pd(PPh_3)_4$ (0.01 mmol), using benzene (4 ml) as solvent, at room temperature for 4 h under Ar.
[b]Isolated yield based on the **1** used.



Scheme 1

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establish the feasibility of using **2** in Stille coupling reactions with aryl iodides **3**. Gratifyingly, when the Stille coupling reactions of **2** with a variety of aryl iodides **3** were conducted in DMF at room temperature using $Pd(PPh_3)_4$ and CuI as co-catalyst (Scheme 2), fairly rapid reactions occurred affording stereoselectively the desired coupled products **4** in good yields. The experimental results are summarised in Table 2. The nature of the substituents in the aryl iodides has no influence on the Stille reaction. The Stille coupling reactions of (*E*)-α-stannylvinyl sulfones **2** with heteroaryl iodides and 1-iodonaphthalene also proceeded smoothly to give the corresponding coupled products in good yields (entries 7 and 8). However, we found that when Stille coupling reactions of (*E*)-α-stannylvinyl sulfones **2** with aryl bromides were attempted under the same conditions, the Stille coupling reactions did not occur at all.

It is well documented that the Stille coupling reaction of vinylstannanes with organic halides, in the presence of a palladium catalyst, occurs with retention of configuration.[25-27] In addition, the *Z*-configuration of compound **4f** was confirmed by NOESY experiments. An enhancement of the allylic protons was observed as the vinylic proton of **4f** was irradiated. A correlation between the allylic protons and the aromatic protons of (4-methylphenyl)sulfonyl group was observed. The NOE results indicate that compound **4f** has the expected *Z*-configuration and that the cross-coupling reaction of (*E*)-α-stannylvinyl sulfones with aryl iodides occurs with retention of configuration.

In conclusion, a convenient synthetic method for (*Z*)-1,2-disubstituted vinyl sulfones has been developed by the palladium-catalysed hydrostannylation of acetylenic sulfones, followed by the Stille coupling reaction with aryl iodides in the presence of $Pd(PPh_3)_4$ and CuI. The present method has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions, and good yields.

Experimental

^1H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard using $CDCl_3$ as the solvent. ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer using $CDCl_3$ as the solvent. IR spectra were determined on an FTS-185 instrument as neat films. Mass spectra were obtained on a Finnigan 8239 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyser. All reactions were carried out in pre-dried glassware (150°C, 4 h) and cooled under a stream of dry Ar. Benzene was distilled from sodium prior to use. DMF was dried by distillation over calcium hydride.

General procedure for the synthesis of (E)-α-stannylvinyl sulfones **2a–e**

A 25 ml, two-necked, round-bottom flask equipped with a magnetic stir bar, and argon was charged sequentially with acetylenic sulfone **1** (1 mmol), benzene (4 ml), $Pd(PPh_3)_4$ (0.01 mmol) and Bu_3SnH (1.05 mmol). The mixture was stirred at room temperature for 4 h. After removal of the solvent under reduced pressure, the residue was diluted with light petroleum ether (20 ml) and filtered to remove the palladium catalyst. The resulting solution was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent: light petroleum ether/Et_2O, 7 : 1).

2a: Oil. IR (film): ν (cm^{-1}) 3066, 2958, 2927, 1713, 1587, 1446, 1285, 1138, 1082, 822, 689; ^1H NMR ($CDCl_3$): δ 7.86–7.84 (m, 2H), 7.56–7.48 (m, 3H), 6.28 (t, J = 7.6 Hz, $^3J_{Sn\text{-}H}$ = 52 Hz, 1H), 2.40–2.36 (m, 2H), 1.56–1.48 (m, 6H), 1.38–1.29 (m, 6H), 1.22–1.15 (m, 4H), 1.11–1.06 (m, 6H), 0.90 (t, J = 7.2 Hz, 9H), 0.80 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 157.4, 149.0, 143.5, 132.5, 128.8, 127.1, 31.0, 30.6, 28.8, 27.3, 22.3, 13.8, 13.7, 11.4; MS: *m/z* 513 (M^+, 1.2), 457 (16), 291 (11), 197 (18), 111 (27), 73 (100); Found: C, 55.89; H, 8.02. Calcd for $C_{24}H_{42}SO_2Sn$: C, 56.19; H, 8.19%.

2b: Oil. IR (film): ν (cm^{-1}) 2957, 2926, 1588, 1456, 1285, 1138, 1082, 812, 665; ^1H NMR ($CDCl_3$): δ 7.73 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 6.25 (t, J = 7.6 Hz, $^3J_{Sn\text{-}H}$ = 52 Hz, 1H), 2.42 (s, 3H), 2.41–2.34 (m, 2H), 1.57–1.49 (m, 6H), 1.36–1.30 (m, 6H), 1.22–1.16 (m, 4H), 1.10–1.05 (m, 6H), 0.91 (t, J = 7.2 Hz, 9H), 0.81 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 156.9, 149.3, 143.2, 140.6, 129.4, 127.2, 30.9, 30.7, 28.8, 27.3, 22.3, 21.5, 13.8, 13.7, 11.4; MS: *m/z* 527 (M^+, 1.4), 471 (100), 469 (71), 213 (22), 211 (33), 209 (24), 91 (18); Found: C, 56.75; H, 8.09. Calcd for $C_{25}H_{44}SO_2Sn$: C, 56.98; H, 8.35%.

2c: Oil. IR (film): ν (cm^{-1}) 3063, 2957, 2921, 1585, 1446, 1286, 1136, 1081, 878, 745; ^1H NMR ($CDCl_3$): δ 7.39 (d, J = 8.4 Hz, 2H), 7.27–7.09 (m, 9H), 1.67–1.61 (m, 6H), 1.43–1.37 (m, 6H), 1.27–1.22 (m, 6H), 0.95 (t, J = 7.2 Hz, 9H); ^{13}C NMR ($CDCl_3$): δ 154.4, 149.7, 141.4, 135.3, 131.9, 128.9, 128.2, 127.9, 127.7, 127.4, 29.0, 27.3, 13.7, 11.9; MS: *m/z* 533 (M^+, 1.1), 477 (100), 475 (71), 199 (17), 197 (35), 195 (24), 102 (21); Found: C, 58.32; H, 6.94. Calcd for $C_{26}H_{38}SO_2Sn$: C, 58.59; H, 7.13%.

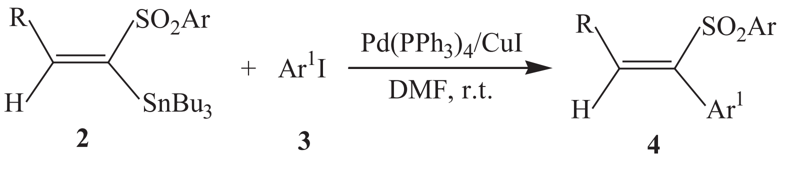
2d: Oil. IR (film): ν (cm^{-1}) 2958, 2926, 1712, 1597, 1455, 1285, 1138, 1083, 830, 667; ^1H NMR ($CDCl_3$): δ 7.86–7.83 (m, 2H), 7.60–7.53 (m, 3H), 6.42 (t, J = 5.6 Hz, $^3J_{Sn\text{-}H}$ = 48 Hz, 1H), 4.39 (d, J = 5.6 Hz, 2H), 3.30 (s, 3H), 1.48–1.41 (m, 6H), 1.32–1.26 (m, 6H), 1.05–1.00 (m, 6H), 0.88 (t, J = 7.2 Hz, 9H); ^{13}C NMR ($CDCl_3$): δ 153.8, 148.4, 142.3, 133.0, 129.0, 127.0, 70.7, 58.5, 28.7, 27.2, 13.7, 11.3; MS: *m/z* 501 (M^+, 1.7), 445 (100), 443 (72), 441 (34),

Table 2 Synthesis of (*Z*)-1,2-disubstituted vinyl sulfones **4a–j**[a]

Entry	R	Ar	Ar^1	Product	Yield/%[b]
1	n-C_4H_9	Ph	Ph	**4a**	83
2	n-C_4H_9	Ph	4-$MeOCOC_6H_4$	**4b**	80
3	$MeOCH_2$	4-MeC_6H_4	4-MeC_6H_4	**4c**	79
4	Ph	Ph	Ph	**4d**	75
5	n-C_4H_9	4-MeC_6H_4	4-ClC_6H_4	**4e**	86
6	n-C_4H_9	4-MeC_6H_4	4-$O_2NC_6H_4$	**4f**	87
7	Ph	Ph	2-thienyl	**4g**	86
8	n-C_4H_9	Ph	1-naphthyl	**4h**	81
9	Ph	Ph	3-NCC_6H_4	**4i**	85
10	n-C_4H_9	4-MeC_6H_4	4-$MeOC_6H_4$	**4j**	84

[a]Reactions were performed with **2** (1 mmol), **3** (1.1 mmol), $Pd(PPh_3)_4$ (0.05 mmol), CuI (0.75 mmol), using DMF (8 ml) as solvent, at room temperature for 20–24 h under Ar.

[b]Isolated yield based on the **2** used.



Scheme 2

197 (27), 195 (21), 41 (22); Found: C, 52.48; H, 7.41. Calcd for $C_{22}H_{38}SO_3Sn$: C, 52.74; H, 7.58%.

2e: Oil. IR (film): ν (cm^{-1}) 2959, 2925, 1713, 1598, 1456, 1285, 1138, 1085, 831, 809; ^{1}H NMR ($CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 6.39 (t, J = 5.6 Hz, $^3J_{Sn-H}$ = 48 Hz, 1H), 4.39 (d, J = 5.6 Hz, 2H), 3.30 (s, 3H), 2.43 (s, 3H), 1.47–1.42 (m, 6H), 1.32–1.26 (m, 6H), 1.04–1.00 (m, 6H), 0.88 (t, J = 7.2 Hz, 9H); ^{13}C NMR ($CDCl_3$): δ 153.3, 148.7, 143.8, 139.4, 129.6, 127.1, 70.7, 58.5, 28.7, 27.2, 21.6, 13.6, 11.3; MS: m/z 515 (M$^+$, 1.4), 459 (100), 457 (86), 455 (44), 211 (25), 209 (17), 91 (8); Found: C, 53.43; H, 7.52. Calcd for $C_{23}H_{40}SO_3Sn$: C, 53.64; H, 7.77%.

General procedure for the synthesis of (Z)-1,2-disubstituted vinyl sulfones **4a–j**

(E)-α-Stannylvinyl sulfone **2** (1.0 mmol) and aryl iodide **3** (1.1 mmol) were dissolved in DMF (8 ml) under Ar at room temperature. $Pd(PPh_3)_4$ (0.05 mmol) and CuI (0.75 mmol) were then added. The mixture was stirred for 20–24 h at room temperature and monitored by TLC (SiO_2) for the disappearance of the starting (E)-α-stannylvinyl sulfone **2**. The reaction mixture was diluted with diethyl ether (30 ml), filtered and then treated with 20% aqueous KF (10 ml) for 30 min before being dried and concentrated. The residue was purified by column chromatography on silica gel (eluent: light petroleum ether/Et_2O, 5 : 1).

4a: Oil. IR (neat): ν (cm^{-1}) 3061, 2958, 2928, 1628, 1585, 1490, 1446, 1306, 1153, 1086, 760; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 7.6 Hz, 2H), 7.54–7.37 (m, 3H), 7.28–7.17 (m, 5H), 6.18 (t, J = 7.6 Hz, 1H), 2.91–2.85 (m, 2H), 1.49–1.35 (m, 4H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 142.0, 141.1, 135.9, 133.0, 130.2, 128.7, 128.5, 128.0, 127.7, 31.5, 28.5, 22.4, 13.9; MS (EI): m/z 300 (M$^+$, 100), 196 (28), 117 (47); Found: C, 72.23; H, 6.93. Calcd for $C_{18}H_{20}SO_2$: C, 71.97; H, 6.71%.

4b: Oil. IR (neat): ν (cm^{-1}) 3066, 2956, 2927, 1717, 1607 1584, 1446, 1275, 1154, 1103, 1086, 772; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.90 (m, 2H), 7.66–7.63 (m, 2H), 7.53–7.51 (m, 1H), 7.43–7.39 (m, 2H), 7.29–7.26 (m, 2H), 6.21 (t, J = 7.6 Hz, 1H), 3.91 (s, 3H), 2.93–2.87 (m, 2H), 1.52–1.38 (m, 4H), 0.95 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 147.8, 141.4, 140.8, 140.4, 133.3, 130.2, 130.1, 129.2, 128.9, 127.7, 52.2, 31.4, 28.5, 22.4, 13.9; MS (EI): m/z 359 (M$^+$ + 1, 100), 358 (M$^+$, 85), 217 (99), 115 (78); Found: C, 66.84; H, 6.25. Calcd for $C_{20}H_{22}SO_4$: C, 67.02; H, 6.19%.

4c: Oil. IR (neat): ν (cm^{-1}) 2957, 2925, 1643, 1595, 1510, 1314, 1148, 1112, 816, 696; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 6.25 (t, J = 4.8 Hz, 1H), 4.77 (d, J = 4.8 Hz, 2H), 3.43 (s, 3H), 2.38 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 143.3, 141.2, 138.8, 137.1, 131.8, 129.7, 129.4, 128.8, 127.9, 69.8, 58.6, 21.6, 21.2; MS (EI): m/z 316 (M$^+$, 3.6), 269 (100), 267 (67), 91 (23); Found: C, 68.15; H, 6.21. Calcd for $C_{18}H_{20}SO_3$: C, 68.34; H, 6.37%.

4d: White solid, m.p. 129–130 °C (lit.,[28] 131 °C). IR (KBr): ν (cm^{-1}) 3063, 2958, 2923, 1623, 1578, 1495, 1304, 1145, 1085, 776; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.24 (m, 15H), 7.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 141.5, 140.3, 135.8, 133.7, 132.9, 129.9, 129.4, 128.8, 128.7, 128.4, 128.2, 128.1, 127.8; MS (EI): m/z 320 (M$^+$, 56), 269 (23), 179 (100), 77 (31).

4e: Oil. IR (neat): ν (cm^{-1}) 2957, 2926, 1629, 1596, 1487, 1456, 1319, 1152, 1087, 684; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 8.4 Hz, 2H), 7.23–7.20 (m, 4H), 7.14–7.12 (m, 2H), 6.13 (t, J = 7.6 Hz, 1H), 2.89–2.84 (m, 2H), 2.39 (s, 3H), 1.48–1.32 (m, 4H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 144.2, 141.2, 138.0, 134.7, 134.5, 131.5, 129.5, 128.2, 127.7, 31.5, 28.5, 22.4, 21.6, 13.9; MS (EI): m/z 350 (M$^+$, ^{37}Cl, 21), 348 (M$^+$, ^{35}Cl, 45), 151 (100), 91 (48); Found: C, 65.13; H, 5.88. Calcd for $C_{19}H_{21}SO_2Cl$: C, 65.40; H, 6.07%.

4f: Oil. IR (neat): ν (cm^{-1}) 3067, 2958, 2927, 1626, 1597, 1520, 1492, 1348, 1152, 1086, 814; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12–8.10 (m, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.41–7.38 (m, 2H), 7.23 (d, J = 8.4 Hz, 2H), 6.22 (t, J = 7.6 Hz, 1H), 2.93–2.87 (m, 2H), 2.40 (s, 3H), 1.53–1.39 (m, 4H), 0.95 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 147.8, 144.6, 142.6, 140.8, 137.6, 131.1, 129.7, 127.7, 123.2, 31.3, 28.6, 22.5, 21.6, 13.9; MS (EI): m/z 359 (M$^+$, 52), 269 (100), 267 (87), 91 (56); Found: C, 63.21; H, 5.74. Calcd for $C_{19}H_{21}NSO_4$: C, 63.49; H, 5.89%.

4g: White solid, m.p. 78–79 °C. IR (KBr): ν (cm^{-1}) 3110, 1582, 1330, 1148, 1079, 728; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.0 Hz, 2H), 7.48–7.40 (m, 4H), 7.35–7.30 (m, 7H), 7.00–6.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 140.4, 137.3, 136.1, 133.6, 133.1, 129.9, 129.4, 128.9, 128.6, 128.0, 127.9, 127.8, 127.2; MS (EI) m/z 326 (M$^+$, 2.2), 185 (56), 77 (100); Found: C, 66.41; H, 4.55. Calcd for $C_{18}H_{14}S_2O_2$: C, 66.23; H, 4.32%.

4h: Oil. IR (neat): ν (cm^{-1}) 3061, 2956, 2920, 1630, 1506, 1447, 1306, 1151, 1085, 803; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80–7.60 (m, 5H), 7.44–7.18 (m, 7H), 6.24 (t, J = 7.6 Hz, 1H), 2.93–2.86 (m, 2H), 1.47–1.32 (m, 4H), 0.95 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 140.4, 140.3, 133.4, 133.1, 132.9, 132.7, 129.3, 129.1, 128.6, 128.2, 128.1, 126.4, 125.9, 125.5, 124.7, 31.4, 28.6, 22.5, 14.0; MS (EI): m/z 350 (M$^+$, 1.2), 209 (92), 139 (93), 91 (100); Found: C, 75.13; H, 6.44. Calcd for $C_{22}H_{22}SO_2$: C, 75.39; H, 6.33%.

4i: White solid, m.p. 85–86 °C. IR (KBr): ν (cm^{-1}) 3065, 2227, 1625, 1597, 1304, 1146, 1083, 749, 685; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71–7.63 (m, 3H), 7.49–7.44 (m, 6H), 7.38–7.28 (m, 5H), 7.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 142.4, 139.7, 137.2, 134.4, 133.4, 133.3, 132.9, 132.3, 129.4, 129.3, 129.2, 128.7, 128.1, 128.0, 118.1, 112.7; MS (EI): m/z 345 (M$^+$, 17), 203 (100), 91 (26); Found: C, 72.75; H, 4.21. Calcd for $C_{21}H_{15}NSO_2$: C, 73.02; H, 4.38%.

4j: Oil. IR (neat): ν (cm^{-1}) 2957, 2926, 1606, 1575, 1509, 1464, 1316, 1178, 1150, 688; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.13–7.11 (m, 2H), 6.78–6.76 (m, 2H), 6.11 (t, J = 7.6 Hz, 1H), 3.79 (s, 3H), 2.86–2.82 (m, 2H), 2.38 (s, 3H), 1.47–1.32 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 146.4, 143.8, 141.6, 138.3, 131.5, 129.4, 128.3, 127.7, 113.3, 55.3, 31.6, 28.5, 22.4, 21.6, 14.0; MS (EI): m/z 344 (M$^+$, 1.4), 209 (46), 178 (50), 165 (100), 91 (38). Found: C, 69.51; H, 6.80. Calcd for $C_{20}H_{24}SO_3$: C, 69.74; H, 7.02%.

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