A facile stereoselective synthesis of (*Z*)-2-arylsulfonyl-substituted 1,3-enynes from (*E*)-α-stannylvinyl sulfones and alkynyl bromides

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Palladium-catalysed hydrostannylation of acetylenic sulfones **1** in benzene at room temperature gives stereoselectively (*E*)-α-stannylvinyl sulfones **2** in good to high yields. (*E*)-α-Stannylvinyl sulfones **2** are difunctional group reagents which undergo cross-coupling reactions with alkynyl bromides **3** in the presence of $Pd(PPh_3)_4$ and CuI co-catalyst to afford stereoselectively (*Z*)-2-arylsulfonyl-substituted 1,3-enynes **4** in good yields.

Keywords: acetylenic sulfone, hydrostannylation, (*E*)-α-stannylvinyl sulfone, (*Z*)-2-arylsulfonyl-substituted 1,3-enyne, stereoselective synthesis

The discovery of strong antifungal agents[1] and new powerful antitumor antibiotics[2] has stimulated intense interest in the chemistry of enynes,[3] as this type of structure is considered the origin of the biological properties of these substances. Conjugated enynes are also important synthetic intermediates since the conjugated enyne moiety can be readily converted in a stereospecific manner into the corresponding diene system.[4] Recently, Takahashi and coworkers described the formation of highly substituted enynes using a coupling reaction between alkenylzirconium compounds and alkynyl halides.[5] Gimeno and coworkers reported the stereoselective synthesis of chiral terminal (*E*)-1,3-enynes derived from optically active aldehydes.[6] The synthesis of 1,3-enynes containing metal or heteroatom functional groups has also attracted considerable interest in organic synthesis because many useful functional group transformations can be achieved by the introduction and removal of metal or heteroatom functions. The stereoselective synthesis of 1,3-enynylsulfides,[7] 1,3-enynyltellurides,[8] 1,3-enynylselenides,[9] 1,3-enynylsilanes,[10] 1,3-enynylstannanes[11] and fluoro or CF_3-substituted 1,3-enynes[12] has already been described in the literature. 1,3-Enynylsulfones are important synthetic intermediates since the sulfone group both activates the adjacent multiple carbon–carbon bonds and provides a useful functional group for further transformation by various desulfonylation methods.[13] Yoshimatsu and Hasegawa[14] described regio- and stereoselective additions of sodium selenides to conjugate enyne sulfones providing a convenient synthesis of 4-seleno-1-sulfonylbuta-1,3-dienes. Kataoka and coworkers[15] reported a one-pot synthesis of diyne alcohols by dehydrosulfonylation of enyne sulfones. 1-Sulfonyl-substituted 1,3-enynes can be conveniently prepared by palladium-catalysed additions of terminal alkynes to acetylenic sulfones.[16] However, the synthesis of 2-sulfonyl-substituted 1,3-enynes is limited.[17] Here we report that (*Z*)-2-arylsulfonyl-substituted 1,3-enynes can be synthesised by palladium-catalysed hydrostannylation of acetylenic sulfones, followed by a cross-coupling reaction with alkynyl bromides in the presence of $Pd(PPh_3)_4$ and CuI co-catalysts.

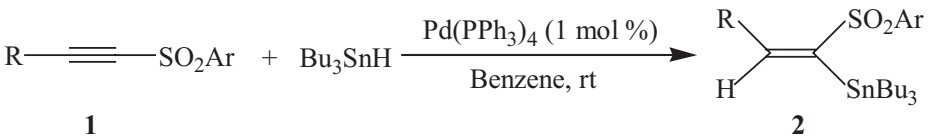
Stille[18] has reported the use of organotin reagents to obtain enynes by the cross-coupling reaction of vinyl triflates or vinyl iodides with alkynylstannanes in the presence of palladium catalysts. An advantage of the method is a high tolerance for functional groups such as allylic ethers vinylic thioethers, esters, ketones or trimethylsilyl ether.[19] However, the cross-coupling reaction of vinylstannanes with haloalkynes has rarely been reported.[9b,20] Palladium-catalysed hydrostannylation of phenylthioalkynes,[21] alkynyl selenides,[22] and alkynyl sulfoxides[23] 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[24] 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. We have 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.[25] We have found that the palladium-catalysed hydrostannylation of acetylenic sulfones **1** with Bu_3SnH in benzene at room temperature is 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 isomeric purities of more than 98%. One olefinic proton signal of compounds **2a**, **2b**, **2d,** and **2e** splits characteristically into one triplet at $\delta = 6.25$–

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.



1 **2**

Scheme 1

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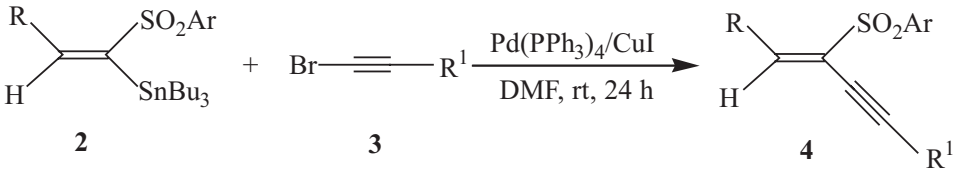

Scheme 2

6.42 with a 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 ^{1}H 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.[26]

(*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. As we had now found a convenient route to the (*E*)-α-stannylvinyl sulfones **2**, we decided to establish the feasibility of using **2** in cross-coupling reactions with alkynyl bromides **3**. Gratifyingly, when the cross-coupling reactions of **2** with a variety of alkynyl bromides **3** were conducted in DMF at room temperature using $Pd(PPh_3)_4$ and CuI as co-catalysts (Scheme 2), fairly rapid reactions occurred affording stereoselectively the desired coupling products **4** in good yields. The experimental results are summarised in Table 2. However, we found that when the cross-coupling reactions of (*E*)-α-stannylvinyl sulfones **2** with alkynyl iodides were performed under the same conditions, only traces of coupling products were obtained.

In summary, a convenient synthetic method for (*Z*)-2-arylsulfonyl-substituted 1,3-enynes has been developed by the palladium-catalysed hydrostannylation of acetylenic sulfones, followed by a cross-coupling reaction with alkynyl bromides 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

^{1}H 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 Finigan 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 containing Ar was charged sequentially with the 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).

Compound **2a**: IR (film): ν (cm^{-1}) 3066, 2958, 2927, 1713, 1587, 1446, 1285, 1138, 1082, 822, 689; ^{1}H NMR ($CDCl_3$): δ 7.86–7.84 (m, 2H), 7.56–7.48 (m, 3H), 6.28 (t, J = 7 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 Hz, 9H), 0.80 (t, J = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 157.4 (CH), 149.0 (C), 143.5 (C), 132.5 (CH), 128.8 (CH × 2), 127.1 (CH × 2), 31.0 (CH_2), 30.6 (CH_2), 28.8 (CH_2 × 3), 27.3 (CH_2 × 3), 22.3 (CH_2), 13.8 (CH_3), 13.7 (CH_3 × 3), 11.4 (CH_2 × 3); MS: *m/z* 513 (M$^+$, 1.2), 457 (16), 291 (11), 197 (18), 111 (27), 73 (100); Anal. Calc. for $C_{24}H_{42}SO_2Sn$: C, 56.19; H, 8.19. Found: C, 55.9; H, 8.0%.

Compound **2b**: IR (film): ν (cm^{-1}) 2957, 2926, 1588, 1456, 1285, 1138, 1082, 812, 665; ^{1}H NMR ($CDCl_3$): δ 7.73 (d, J = 8 Hz, 2H), 7.29 (d, J = 8 Hz, 2H), 6.25 (t, J = 7 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 Hz, 9H), 0.81 (t, J = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 156.9 (CH), 149.3 (C), 143.2 (C), 140.6 (C), 129.4 (CH × 2), 127.2 (CH × 2), 30.9 (CH_2), 30.7 (CH_2), 28.8 (CH_2 × 3), 27.3 (CH_2 × 3), 22.3 (CH_2), 21.5 (CH_3), 13.8 (CH_3), 13.7 (CH_3 × 3), 11.4 (CH_2 × 3); MS: *m/z* 527 (M$^+$, 1.4), 471 (100), 469 (71), 213 (22), 211 (33), 209 (24), 91 (18); Anal. Calc. for $C_{25}H_{44}SO_2Sn$: C, 56.98; H, 8.35. Found: C, 56.75; H, 8.1%.

Compound **2c**: IR (film): ν (cm^{-1}) 3063, 2957, 2921, 1585, 1446, 1286, 1136, 1081, 878, 745; ^{1}H NMR ($CDCl_3$): δ 7.39 (d, J = 8 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 Hz, 9H); ^{13}C NMR ($CDCl_3$): δ 154.4 (C), 149.7 (CH), 141.4 (C), 135.3 (C), 131.9 (CH), 128.9 (CH × 2), 128.2 (CH), 127.9 (CH × 2), 127.7 (CH × 2), 127.4 (CH × 2), 29.0 (CH_2 × 3), 27.3 (CH_2 × 3), 13.7 (CH_3 × 3), 11.9 (CH_2 × 3); MS: *m/z* 533 (M$^+$, 1.1), 477 (100), 475 (71), 199 (17), 197 (35), 195 (24), 102 (21); Anal. Calc. for $C_{26}H_{38}SO_2Sn$: C, 58.59; H, 7.13. Found: C, 58.3; H, 6.9%.

Compound **2d**: IR (film): ν (cm^{-1}) 2958, 2926, 1712, 1597, 1455, 1285, 1138, 1083, 830, 667; ^{1}H NMR ($CDCl_3$): δ 7.86–7.83 (m, 2H), 7.60–7.53 (m, 3H), 6.42 (t, J = 5 Hz, $^3J_{Sn\text{-}H}$ = 48 Hz, 1H), 4.39 (d, J = 5 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 Hz, 9H); ^{13}C NMR ($CDCl_3$): δ 153.8 (CH), 148.4 (C), 142.3 (C), 133.0 (CH), 129.0 (CH × 2), 127.0 (CH × 2), 70.7 (CH_2), 58.5 (CH_3), 28.7 (CH_2 × 3), 27.2 (CH_2 × 3), 13.7 (CH_3 × 3), 11.3 (CH_2 × 3); MS: *m/z* 501 (M$^+$, 1.7), 445 (100), 443 (72), 441 (34), 197 (27), 195 (21), 41 (22); Anal. Calc. for $C_{22}H_{38}SO_3Sn$: C, 52.74; H, 7.58. Found: C, 52.5; H, 7.4%.

Compound **2e**: 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 Hz, 2H), 7.31 (d, J = 8 Hz, 2H), 6.39 (t, J = 5 Hz, $^3J_{Sn\text{-}H}$ = 48 Hz, 1H), 4.39 (d, J = 5 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 Hz, 9H); ^{13}C NMR ($CDCl_3$): δ 153.3 (CH), 148.7 (C), 143.8 (C), 139.4 (C), 129.6 (CH × 2), 127.1 (CH × 2), 70.7 (CH_2), 58.5 (CH_3), 28.7 (CH_2 × 3), 27.2 (CH_2 × 3), 21.6 (CH_3), 13.6 (CH_3 × 3), 11.3 (CH_2 × 3); MS: *m/z* 515 (M$^+$, 1.4), 459 (100), 457 (86), 455 (44), 211 (25), 209 (17), 91 (8); Anal. Calc. for $C_{23}H_{40}SO_3Sn$: C, 53.64; H, 7.77. Found: C, 53.4; H, 7.5%.

Table 2 Synthesis of (*Z*)-2-arylsulfonyl-substituted 1,3-enynes **4a–i**

Entry	R	Ar	R^1	Product	Yield/%[a]
1	*n*-C_4H_9	Ph	*n*-C_4H_9	**4a**	80
2	*n*-C_4H_9	Ph	Ph	**4b**	75
3	CH_3OCH_2	4-$CH_3C_6H_4$	Ph	**4c**	69
4	Ph	Ph	Ph	**4d**	77
5	*n*-C_4H_9	4-$CH_3C_6H_4$	*n*-C_4H_9	**4e**	78
6	Ph	Ph	*n*-C_4H_9	**4f**	75
7	*n*-C_4H_9	4-$CH_3C_6H_4$	CH_3OCH_2	**4g**	72
8	CH_3OCH_2	Ph	*n*-C_4H_9	**4h**	70
9	*n*-C_4H_9	Ph	*n*-C_6H_{13}	**4i**	76

[a]Isolated yield based on the (*E*)-α-stannylvinyl sulfone **2** used.

General procedure for the synthesis of (Z)-2-arylsulfonyl-substituted 1,3-enynes **4a–i**

The (*E*)-α-stannylvinyl sulfone **2** (1.0 mmol) and alkynyl bromide **3** (1.1 mmol) were dissolved in DMF (10 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).

Compound **4a**: IR (film): ν (cm^{-1}) 2958, 2931, 2873, 2222, 1711, 1553, 1448, 1325, 1154, 726, 688; ^1H NMR ($CDCl_3$): δ 7.96–7.94 (m, 2H), 7.66–7.52 (m, 3H), 6.46 (t, *J* = 8 Hz, 1H), 2.83–2.76 (m, 2H), 2.24 (t, *J* = 7 Hz, 2H), 1.46–1.25 (m, 8H), 0.92 (t, *J* = 7 Hz, 3H), 0.86 (t, *J* = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 150.4 (CH), 140.3 (C), 133.5 (CH), 128.8 (CH × 2), 128.2 (CH × 2), 127.2 (C), 95.3 (C), 74.8 (C), 31.2 (CH_2), 30.2 (CH_2), 28.3 (CH_2), 22.4 (CH_2), 21.9 (CH_2), 19.1 (CH_2), 13.9 (CH_3), 13.6 (CH_3); MS: *m/z* 304 (M^+, 14), 269 (54), 267 (38), 179 (42), 163 (35), 125 (58), 109 (100), 91 (42), 77 (60); Anal. Calc. for $C_{18}H_{24}SO_2$: C, 71.06; H, 7.89. Found: C, 70.8; H, 7.7%.

Compound **4b**: IR (film): ν (cm^{-1}) 2957, 2929, 2874, 2206, 1720, 1593, 1447, 1323, 1158, 756, 688; ^1H NMR ($CDCl_3$): δ 8.06–8.03 (m, 2H), 7.69–7.56 (m, 3H), 7.36–7.28 (m, 5H), 6.66 (t, *J* = 8 Hz, 1H), 2.93–2.87 (m, 2H), 1.54–1.32 (m, 4H), 0.98 (t, *J* = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 151.5 (CH), 140.2 (C), 133.6 (CH), 131.5 (CH × 2), 128.9 (CH × 2), 128.6 (C), 128.4 (CH × 2), 128.3 (CH × 2), 127.4 (CH), 122.0 (C), 93.5 (C), 83.4 (C), 31.1 (CH_2), 28.5 (CH_2), 22.4 (CH_2), 13.9 (CH_3); MS: *m/z* 324 (M^+, 21), 295 (9), 183 (37), 167 (53), 155 (37), 141 (100), 115 (44), 77 (27); Anal. Calc. for $C_{20}H_{20}SO_2$: C, 74.08; H, 6.17. Found: C, 73.9; H, 5.9%.

Compound **4c**: IR (film): ν (cm^{-1}) 3064, 2927, 2206, 1721, 1597, 1450, 1324, 1153, 814, 691; ^1H NMR ($CDCl_3$): δ 7.89 (d, *J* = 8 Hz, 2H), 7.38–7.31 (m, 7H), 6.65 (t, *J* = 5 Hz, 1H), 4.76 (d, *J* = 5 Hz, 2H), 3.42 (s, 3H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 147.5 (CH), 145.2 (C), 136.2 (C), 131.6 (CH × 2), 129.7 (CH × 2), 129.2 (CH), 128.5 (CH × 2), 128.4 (CH × 2), 127.0 (C), 121.7 (C), 94.0 (C), 82.5 (C), 69.2 (CH_2), 58.8 (CH_3), 21.8 (CH_3); MS: *m/z* 326 (M^+, 3.7), 269 (36), 141 (29), 122 (61), 105 (100), 91 (34), 77 (48), 45 (44); Anal. Calc. for $C_{19}H_{18}SO_3$: C, 69.94; H, 5.52. Found: C, 69.7; H, 5.4%.

Compound **4d**: IR (film): ν (cm^{-1}) 2924, 2202, 1717, 1583, 1447, 1321, 1153, 754, 688; ^1H NMR ($CDCl_3$): δ 7.97–7.95 (m, 2H), 7.65–7.61 (m, 3H), 7.54–7.50 (m, 3H), 7.42–7.38 (m, 3H), 7.35–7.25 (m, 3H), 7.19–7.16 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 144.9 (CH), 139.6 (C), 133.7 (CH), 132.7 (C), 131.5 (CH × 2), 130.3 (CH × 2), 130.0 (CH), 129.2 (CH), 128.9 (CH × 2), 128.7 (CH × 2), 128.4 (CH × 2), 128.0 (CH × 2), 127.6 (C), 121.7 (C), 96.4 (C), 84.7 (C); MS: *m/z* 344 (M^+, 22), 203 (100), 202 (94), 77 (12); Anal. Calc. for $C_{22}H_{16}SO_2$: C, 76.75; H, 4.65. Found: C, 76.5; H, 4.4%.

Compound **4e**: IR (film): ν (cm^{-1}) 2958, 2930, 2875, 2220, 1714, 1598, 1465, 1325, 1151, 813, 684; ^1H NMR ($CDCl_3$): δ 7.83 (d, *J* = 8 Hz, 2H), 7.33 (d, *J* = 8 Hz, 2H), 6.43 (t, *J* = 8 Hz, 1H), 2.82–2.76 (m, 2H), 2.45 (s, 3H), 2.24 (t, *J* = 7 Hz, 2H), 1.45–1.26 (m, 8H), 0.94–0.89 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 149.9 (CH), 144.4 (C), 137.4 (C), 129.4 (CH × 2), 128.2 (CH × 2), 127.5 (C), 95.0 (C), 74.9 (C), 31.2 (CH_2), 30.2 (CH_2), 28.2 (CH_2), 22.4 (CH_2), 21.9 (CH_3), 21.7 (CH_2), 19.1 (CH_2), 13.9 (CH_3), 13.6 (CH_3); MS: *m/z* 318 (M^+, 17), 269 (26), 179 (24), 139 (43), 105 (41), 91 (100), 65 (32), 41 (30); Anal. Calc. for $C_{19}H_{26}SO_2$: C, 71.70; H, 8.17. Found: C, 71.4; H, 8.05%.

Compound **4f**: IR (film): ν (cm^{-1}) 3062, 2957, 2929, 2875, 2214, 1717, 1586, 1447, 1321, 1148, 751, 688; ^1H NMR ($CDCl_3$): δ 7.97–7.94 (m, 4H), 7.88 (s, 1H), 7.63–7.35 (m, 6H), 2.45 (t, *J* = 7 Hz, 2H), 1.56–1.47 (m, 2H), 1.38–1.28 (m, 2H), 0.90 (t, *J* = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 140.6 (CH), 139.1 (C), 133.4 (CH), 133.0 (C), 131.1 (CH), 130.0 (CH × 2), 128.8 (CH × 2), 128.7 (CH × 2), 128.6 (CH × 2), 124.7 (C), 105.2 (C), 73.2 (C), 30.0 (CH_2), 21.9 (CH_2), 19.7 (CH_2), 13.5 (CH_3); MS: *m/z* 324 (M^+, 49), 269 (18), 240 (31), 155 (36), 141 (100), 139 (44), 115 (55), 77 (23); Anal. Calc. for $C_{20}H_{20}SO_2$: C, 74.08; H, 6.17. Found: C, 73.8; H, 6.0%.

Compound **4g**: IR (film): ν (cm^{-1}) 2957, 2931, 2873, 2210, 1717, 1597, 1453, 1324, 1151, 814, 685; ^1H NMR ($CDCl_3$): δ 7.84 (d, *J* = 8 Hz, 2H), 7.34 (d, *J* = 8 Hz, 2H), 6.57 (t, *J* = 8 Hz, 1H), 4.16 (s, 2H), 3.29 (s, 3H), 2.83–2.76 (m, 2H), 2.44 (s, 3H), 1.44–1.35 (m, 4H), 0.92 (t, *J* = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 152.5 (CH), 144.7 (C), 137.3 (C), 129.6 (CH × 2), 128.1 (CH × 2), 127.0 (C), 89.2 (C), 80.7 (C), 60.1 (CH_2), 57.7 (CH_3), 31.0 (CH_2), 28.4 (CH_2), 22.4 (CH_2), 21.7 (CH_2), 13.8 (CH_3); MS: *m/z* 306 (M^+, 1.2), 274 (62), 269 (35), 209 (42), 157 (34), 139 (76), 119 (98), 91 (100); Anal. Calc. for $C_{17}H_{22}SO_3$: C, 66.67; H, 7.18. Found: C, 66.4; H, 7.2%.

Compound **4h**: IR (film): ν (cm^{-1}) 2958, 2931, 2875, 2222, 1715, 1583, 1448, 1322, 1152, 733, 687; ^1H NMR ($CDCl_3$): δ 7.95–7.92 (m, 2H), 7.66–7.53 (m, 3H), 6.51 (t, *J* = 5 Hz, 1H), 4.69 (d, *J* = 5 Hz, 2H), 3.39 (s, 3H), 2.24 (t, *J* = 7 Hz, 2H), 1.41–1.37 (m, 2H), 1.31–1.26 (m, 2H), 0.86 (t, *J* = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 146.8 (CH), 139.4 (C), 133.8 (CH), 128.9 (CH × 2), 128.4 (CH × 2), 126.9 (C), 96.4 (C), 73.9 (C), 69.1 (CH_2), 58.7 (CH_3), 30.0 (CH_2), 21.8 (CH_2), 19.0 (CH_2), 13.5 (CH_3); MS: *m/z* 292 (M^+, 1.5), 151 (100), 109 (57), 77 (59), 45 (61); Anal. Calc. for $C_{16}H_{20}SO_3$: C, 65.76; H, 6.84. Found: C, 65.5; H, 6.7%.

Compound **4i**: IR (film): ν (cm^{-1}) 2957, 2933, 2873, 2238, 1712, 1448, 1330, 1155, 721, 688; ^1H NMR ($CDCl_3$): δ 7.96–7.94 (m, 2H), 7.63–7.51 (m, 3H), 6.45 (t, *J* = 8 Hz, 1H), 2.83–2.78 (m, 2H), 2.22 (t, *J* = 7 Hz, 2H), 1.44–1.22 (m, 12H), 0.93–0.85 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 150.5 (CH), 140.2 (C), 133.6 (CH), 128.7 (CH × 2), 128.3 (CH × 2), 127.1 (C), 95.5 (C), 74.6 (C), 31.2 (CH_2), 30.5 (CH_2), 29.2 (CH_2), 28.7 (CH_2), 28.3 (CH_2), 22.6 (CH_2), 22.4 (CH_2), 19.7 (CH_2), 13.9 (CH_3), 13.8 (CH_3); MS: *m/z* 332 (M^+, 1.1), 207 (26), 181 (96), 168 (58), 151 (34), 137 (100), 111 (64), 77 (89), 55 (64), 43 (71); Anal. Calc. for $C_{20}H_{28}SO_2$: C, 72.29; H, 8.43. Found: C, 72.05; H, 8.2%.

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