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A facile stereoselective synthesis of (*Z*)-α-arylsulfonyl-α,β-unsaturated ketones

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ABSTRACT

Palladium-catalyzed hydrostannylation of acetylenic sulfones 1 in benzene at room temperature gives highly regio- and stereoselectively (*E*)-α-stannylvinyl sulfones 2 in high yields. (*E*)-α-Stannylvinyl sulfones 2 are new difunctional group reagents which undergo Stille coupling reactions with acyl chlorides 3 to afford stereoselectively (*Z*)-α-arylsulfonyl-α,β-unsaturated ketones 4 in good yields. A one-pot stereoselective synthesis of (*Z*)-α-arylsulfonyl-α,β-unsaturated ketones 4 has also been achieved by tandem hydrostannylation-Stille coupling reaction of acetylenic sulfones 1 under mild conditions.

1. Introduction

α,β-Unsaturated ketones are one of the most widely used synthetic building blocks and a variety of synthetic methods for the synthesis of α,β-unsaturated ketones have been reported. Of these methods, the aldol condensation is one of the most powerful synthetic tools for them.[1,2] The Friedel–Crafts reaction of acyl chlorides, acids, or anhydrides with olefins is also an important route to the α,β-unsaturated ketones.[3] The hydrozirconation of alkynes, followed by aluminum chloride promoted acylation of the resulting vinylzirconium compounds, has provided a convenient method for stereoselective synthesis of α,β-unsaturated ketones.[4] The synthesis of functionalized α,β-unsaturated ketones is also of considerable interest in organic synthesis because they are important intermediates in the synthesis of a wide variety of organic compounds. Sung et al. reported that hydrozirconation of acetylenic tellurides, followed by the reaction with acyl halides in the presence of CuI, gave α-organotelluro-α,β-unsaturated ketones.[5] Zhao et al. described the synthesis of (*Z*)-β-selenyl-α,β-unsaturated ketones by CuX-catalyzed selenocarbonylation addition reaction of selenoesters to nonactivated terminal alkynes.[6] (*Z*)-α-Selenyl-α,β-unsaturated ketones could be prepared by utilizing either a Wittig-type reaction of α-phenylselanyl arsonium ylides with carbonyl compounds[7] or through palladium-catalyzed acylation of (*E*)-α-selanylvinylstannanes with acyl halides.[8] Some methods for the synthesis of α-aryl(alkyl)thio-α,β-unsaturated ketones have been developed including Pummerer rearrangement of 2-arylsulfinyl ketones,[9–11] the NaOH-catalyzed thiolysis of α,β-epoxyketones,[12] and the Rh-catalyzed diazo decomposition of β-thio group α-diazo ketones.[13]

Recently, α-arylsulfonyl-α,β-unsaturated ketones have attracted considerable interest because of their utility as synthetic intermediates, particularly for the synthesis of heterocyclic systems.[14–19] A common route to α-arylsulfonyl-α,β-unsaturated ketones involves the Knoevenagel condensation of β-keto sulfones with aldehydes.[20–22] Alternatively, α-arylsulfonyl-α,β-unsaturated ketones can also be obtained via peracid oxidation of 4-arylsulfonyl-substituted 4-isoxazolines.[23] However, the stereoselective synthesis of α-arylsulfonyl-α,β-unsaturated ketones has received less attention. (*E*)-α-Arylsulfonyl-α,β-unsaturated ketones can be synthesized by utilizing either a reaction of α-lithiated vinyl sulfones with acyl chlorides[24] or a reaction of α-arylsulfonyl-substituted alkenylmagnesium reagents with acyl chlorides in the presence of stoichiometric amount of CuCN·2LiCl.[25] To the best of our knowledge, no well-established method has been used to prepare stereoselectively (*Z*)-α-arylsulfonyl-α,β-unsaturated ketones to date. Herein we wish to report that (*Z*)-α-arylsulfonyl-α,β-unsaturated ketones can be conveniently synthesized by palladium-catalyzed hydrostannylation of acetylenic sulfones, followed by the Stille coupling with acyl halides in the presence of a catalytic amount of $Pd(PPh_3)_4$ and CuI cocatalyst.

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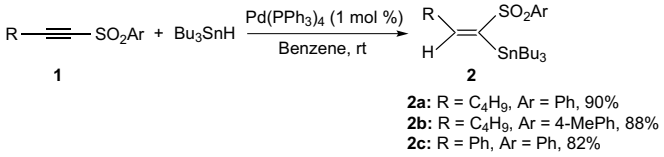
2. Results and discussion

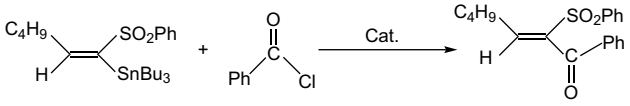
Palladium-catalyzed hydrostannylation of alkynes provides a simple general route for the synthesis of vinylstannanes.[26] In 1991, Magriotis reported that the palladium-catalyzed hydrostannylation of phenylthioalkynes with Bu_3SnH was highly regio- and stereoselective, giving (*E*)-α-stannylvinyl sulfides in high yields.[27] Paley et al. reported that the palladium-catalyzed hydrostannylation of chiral alkynyl sulfoxides at −78 °C was also highly regio- and stereoselective, affording chiral (*E*)-α-stannylvinyl sulfoxides in good yields.[28] Huang et al. demonstrated that alkynyl selenides can also undergo the palladium-catalyzed hydrostannylation to afford stereoselectively (*E*)-α-stannylvinyl selenides.[29] Xiang et al. reported that palladium-catalyzed 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.[30] Recently, we investigated the palladium-catalyzed hydrostannylation of acetylenic sulfones in order to prepare (*E*)-α-stannylvinyl sulfones. We found that the hydrostannylation reaction of acetylenic sulfones with tributyltin hydride proceeded smoothly in benzene in the presence of catalytic amount of $Pd(PPh_3)_4$ at room temperature to afford the corresponding (*E*)-α-stannylvinyl sulfones in high yields with high regio- and stereoselectivities (Scheme 1). Investigations of the crude products **2** by ^1H NMR spectroscopy (400 MHz) showed their isomeric purities of more than 98%. One olefinic proton signal of compounds **2a** and **2b** splits characteristically into one triplet at δ=6.25–6.28 with coupling constant J=7.2 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 ($^3J_{Sn117-H}$) coupling constant of 52 Hz, fully in accord with an *E* geometry and overall cis addition of tin hydride.[31]



Scheme 1.

(*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. Vinylstannanes can undergo the Stille coupling reaction with organic electrophiles.[32] Huang et al. reported palladium-catalyzed acylation reaction of (*E*)-α-selanylvinylstannanes with acyl halides, providing a new route for the stereoselective synthesis of (*Z*)-α-selenyl-α,β-unsaturated ketones.[8] However, to the best of our knowledge, there has been no general study of Stille coupling of (*E*)-α-arylsulfonylvinylstannanes with acyl halides described to date. With a convenient route to the (*E*)-α-arylsulfonylvinylstannanes **2** we decided to establish the feasibility of using **2** in cross-coupling reactions with acyl halides **3**. Initially, to determine the optimum conditions, the cross-coupling reaction of benzoyl chloride (1.1 equiv) with (*E*)-1-phenylsulfonyl-1-tributylstannyl-1-hexene was examined under various reaction conditions. The results are summarized in Table 1. Among the palladium–phosphine complexes screened, $Pd(PPh_3)_4$ showed the best catalytic activity (yield 84%); while the yields were low in the presence of other palladium–phosphine complexes such as $PdCl_2(PPh_3)_2$ (12%) and $PdBnCl(PPh_3)_2$ (22%) even under sealed-tube conditions. It was found that benzene was the best solvent among those tested, such as DMF and THF. The cross-coupling reaction proceeded smoothly in benzene at reflux temperature in the presence of 5 mol% $Pd(PPh_3)_4$ and 75 mol% CuI, affording the corresponding coupled product in 84% yield after 7 h; while the same reaction under sealed-tube conditions gave the coupled product in 85% yield. In general, the amount of $Pd(PPh_3)_4$ and CuI in their co-catalyzed organic transformation only is less than 10 mol%. However, we found that the amount of CuI affected the reaction rate of the Stille coupling. When 10 mol% CuI was used as the co-catalyst, the cross-coupling reaction of benzoyl chloride (1.1 equiv) with (*E*)-1-phenylsulfonyl-1-tributylstannyl-1-hexene in benzene at reflux temperature in the presence of 5 mol% $Pd(PPh_3)_4$ proceeded slowly, giving the coupled product in only 47% yield after 48 h. The reaction did not occur in the presence of $Pd(PPh_3)_4$ without the co-catalyst (CuI) after 72 h even under sealed-tube conditions. On the other hand, the reaction did not also occur in the presence of CuI without any palladium catalyst.

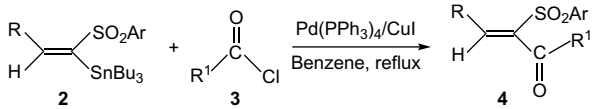
Table 1
Stille coupling reaction of (*E*)-1-phenylsulfonyl-1-tributylstannyl-1-hexene with benzoyl chloride[a]



Catalyst[b]	Additive[c]	Solvent	Temp (°C)	Time (h)	Yield[d] (%)
$PdCl_2(PPh_3)_2$	CuI	DMF	rt (or 65 °C)	72	0
$PdCl_2(PPh_3)_2$	CuI	C_6H_6	rt (or refux)	72	0
$PdCl_2(PPh_3)_2$	CuI	C_6H_6	120 (sealed tube)	72	12
$PdCl_2(PPh_3)_2$	CuI	THF	rt (or refux)	72	0
$PdCl_2(PPh_3)_2$	CuI	THF	120 (sealed tube)	72	0
$PdBnCl(PPh_3)_2$	CuI	DMF	rt (or 65 °C)	72	0
$PdBnCl(PPh_3)_2$	CuI	C_6H_6	120 (sealed tube)	72	22
$PdBnCl(PPh_3)_2$	CuI	THF	120 (sealed tube)	72	Trace
$Pd(PPh_3)_4$	CuI	DMF	rt (or 65 °C)	72	0
$Pd(PPh_3)_4$	CuI	THF	120 (sealed tube)	72	0
$Pd(PPh_3)_4$	CuI	C_6H_6	rt	72	0
$Pd(PPh_3)_4$	CuI	C_6H_6	Reflux	4	79
$Pd(PPh_3)_4$	CuI	C_6H_6	Reflux	7	84
$Pd(PPh_3)_4$	CuI	C_6H_6	120 (sealed tube)	7	85
$Pd(PPh_3)_4$		C_6H_6	Reflux or 120	72	0
	CuI	C_6H_6	Reflux or 120	72	0

[a] Reaction was carried out with 1.0 mmol of (*E*)-1-phenylsulfonyl-1-tributylstannyl-1-hexene and 1.1 mmol of benzoyl chloride in solvent (2 mL) under Ar.
[b] 5 mol% of Pd catalyst was used.
[c] 0.75 equiv CuI was used.
[d] Isolated yield.

The Stille coupling reactions of (*E*)-α-arylsulfonylvinylstannanes with a variety of acyl halides were examined in the presence of a catalytic amount (5 mol%) of $Pd(PPh_3)_4$ and CuI (0.75 equiv) in benzene at reflux temperature (Scheme 2) and the results are summarized in Table 2. In all cases, the reaction proceeded smoothly to afford the corresponding (*Z*)-α-arylsulfonyl-α,β-unsaturated ketones in good yields. Electron donating and electron withdrawing groups such as CH_3, CH_3O, Cl, NO_2 on aromatic acyl halides were well tolerated. Unfortunately, the Stille coupling of (*E*)-α-arylsulfonylvinylstannanes with aliphatic acyl halides did not occur under the same conditions. 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.[32] In addition, the *Z*-configuration of compound **4d** was confirmed by NOESY experiments. An enhancement of the allylic protons was



Scheme 2.

observed as the vinylic proton of **4d** was irradiated. A correlation between the allylic protons and the aromatic protons (δ=7.68) of (4-methylphenyl)sulfonyl group was observed. The NOE results indicate that compound **4d** has the expected *Z*-configuration and that the cross-coupling reaction of (*E*)-α-arylsulfonylvinylstannanes with acyl halides occurs with retention of configuration.

Table 2
Synthesis of (*Z*)-α-arylsulfonyl-α,β-unsaturated ketones[a]

Entry	R	Ar	R^1	Product	Yield[b] (%)
1	n-C_4H_9	Ph	Ph	**4a**	84
2	n-C_4H_9	4-$CH_3C_6H_4$	Ph	**4b**	80
3	n-C_4H_9	Ph	4-$O_2NC_6H_4$	**4c**	81
4	n-C_4H_9	4-$CH_3C_6H_4$	4-ClC_6H_4	**4d**	79
5	n-C_4H_9	Ph	4-ClC_6H_4	**4e**	82
6	n-C_4H_9	4-$CH_3C_6H_4$	4-$O_2NC_6H_4$	**4f**	81
7	n-C_4H_9	Ph	4-$CH_3C_6H_4$	**4g**	84
8	n-C_4H_9	Ph	4-$CH_3OC_6H_4$	**4h**	85
9	Ph	Ph	Ph	**4i**	87
10	Ph	Ph	4-ClC_6H_4	**4j**	86
11	Ph	Ph	4-$O_2NC_6H_4$	**4k**	84
12	Ph	Ph	4-$CH_3C_6H_4$	**4l**	78

[a] Reaction was carried out with 1.0 mmol of (*E*)-α-arylsulfonylvinylstannane, 1.1 mmol of acyl chloride, 0.05 mmol of $Pd(PPh_3)_4$, and 0.75 mmol of CuI in benzene (2 mL) at reflux under Ar.
[b] Isolated yield based on the (*E*)-α-arylsulfonylvinylstannane **2** used.

The tandem reaction has recently been of interest for organic synthesis because it offers a convenient and economical method to prepare desired organic molecules.[33–35] Recently, Huang et al. described the synthesis of functionalized allylic alcohols by Michael-aldol tandem reaction of acetylenic sulfones with phenylselenomagnesium bromides and aldehydes.[36] Considering the fact that both the hydrostannylation and Stille reactions were catalyzed by $Pd(PPh_3)_4$, we tried to combine the two reactions in one pot to prepare stereoselectively (*Z*)-α-arylsulfonyl-α,β-unsaturated ketones (Scheme 3). We found that, after the hydrostannylation reaction of acetylenic sulfones **1** with Bu_3SnH using 5 mol % $Pd(PPh_3)_4$ in benzene at room temperature for 2 h, acyl chlorides and 75 mol % CuI were added and the resulting mixture was stirred at reflux for 7–10 h, the desired (*Z*)-α-arylsulfonyl-α,β-unsaturated ketones **4** were obtained in good yields. The experimental results are summarized in Table 3. As shown in Table 3, the hydrostannylation–Stille tandem reaction of acetylenic sulfones with Bu_3SnH and a variety of acyl chlorides proceeded smoothly under very mild conditions to afford stereoselectively the corresponding (*Z*)-α-arylsulfonyl-α,β-unsaturated ketones **4**.

3. Conclusions

In summary, we have developed an efficient and stereoselective one-pot method for the synthesis of (*Z*)-α-arylsulfonyl-α,β-unsaturated ketones by the tandem hydrostannylation-Stille coupling reactions of acetylenic sulfones with tributyltin hydride and acyl chlorides. The present method has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions and good yields.

4. Experimental

4.1. Materials

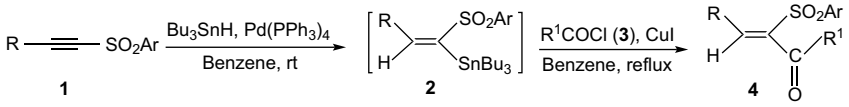
All chemicals were of reagent grade and used as purchased. Benzene and THF were distilled from sodium prior to use. DMF was dried by distillation over calcium hydride. All reactions were carried out in pre-dried glassware (150 °C, 4 h) and cooled under a stream of dry Ar. IR spectra were determined on a Perkin–Elmer 683 instrument. ^1H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. ^{13}C NMR spectra were recorded on a Bruker AC-P400 (100 MHz) spectrometer in $CDCl_3$ as solvent. Mass spectra were determined on a Finnigan 8230 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyzer.

4.2. General procedure for the hydrostannylation of acetylenic sulfones

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 vacuum and the residue was purified by flash chromatography on silica gel (eluent: light petroleum ether/Et_2O, 7:1).

*4.2.1. (E)-1-Phenylsulfonyl-1-tributylstannyl-1-hexene (**2a**)*

Oil. IR (film): ν (cm^{-1}) 3066, 2958, 2927, 1713, 1587, 1446, 1285, 1138, 1082, 822, 689. ^1H NMR (400 MHz, $CDCl_3$): δ 7.86–7.84 (m, 2H), 7.56–7.48 (m, 3H), 6.28 (t, J=7.2 Hz, $^3J_{Sn-H}$=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 (100 MHz, $CDCl_3$): δ 157.42, 149.03, 143.51, 132.50, 128.84, 127.13, 31.04, 30.62, 28.81, 27.32, 22.34, 13.80, 13.73, 11.40. MS (EI, 70 eV): *m*/*z* 513 (M^+, 1.2), 457 (16), 291 (11), 197 (18), 111 (27), 73 (100). Anal. Calcd for $C_{24}H_{42}SO_2Sn$: C, 56.19; H, 8.19. Found: C, 55.89; H, 8.02.



Scheme 3.

Table 3
One-pot synthesis of (*Z*)-α-arylsulfonyl-α,β-unsaturated ketones[a]

Entry	R	Ar	R^1	Product	Yield[b] (%)
1	n-C_4H_9	Ph	Ph	**4a**	79
2	n-C_4H_9	4-$CH_3C_6H_4$	Ph	**4b**	76
3	n-C_4H_9	4-$CH_3C_6H_4$	4-ClC_6H_4	**4d**	73
4	n-C_4H_9	4-$CH_3C_6H_4$	4-$O_2NC_6H_4$	**4f**	75
5	n-C_4H_9	Ph	4-$CH_3OC_6H_4$	**4h**	81
6	Ph	Ph	4-ClC_6H_4	**4j**	80
7	Ph	Ph	4-$CH_3C_6H_4$	**4l**	71

[a] Reaction was carried out with 1.0 mmol of acetylenic sulfone, 1.05 mmol of Bu_3SnH, 1.1 mmol of acyl chloride, 0.05 mmol of $Pd(PPh_3)_4$, and 0.75 mmol of CuI in benzene (3 mL) under Ar.
[b] Isolated yield based on the acetylenic sulfone **1** used.

*4.2.2. (E)-1-(p-Tolylsulfonyl)-1-tributylstannyl-1-hexene (**2b**)*

Oil. IR (film): ν (cm^{-1}) 2957, 2926, 1588, 1456, 1285, 1138, 1082, 812, 665. ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J*=8.4 Hz, 2H), 7.29 (d, *J*=8.4 Hz, 2H), 6.25 (t, *J*=7.2 Hz, $^3J_{Sn-H}$=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 (100 MHz, $CDCl_3$): δ 156.93, 149.34, 143.20, 140.63, 129.41, 127.23, 30.90, 30.71, 28.84, 27.33, 22.31, 21.50, 13.81, 13.74, 11.41. MS (EI, 70 eV): m/z 527 (M^+, 1.4), 471 (100), 469 (71), 213 (22), 211 (33), 209 (24), 91 (18). Anal. Calcd for $C_{25}H_{44}SO_2Sn$: C, 56.98; H, 8.35. Found: C, 56.75; H, 8.09.

*4.2.3. (E)-1-Phenylsulfonyl-1-tributylstannyl-2-phenylethene (**2c**)*

Oil. IR (film): ν (cm^{-1}) 3063, 2957, 2921, 1585, 1446, 1286, 1136, 1081, 878, 745. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J=8.0 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 (100 MHz, $CDCl_3$): δ 154.43, 149.72, 141.40, 135.31, 131.93, 128.91, 128.20, 127.94, 127.73, 127.41, 29.04, 27.32, 13.74, 11.92. MS (EI, 70 eV): m/z 533 (M^+, 1.1), 477 (100), 475 (71), 199 (17), 197 (35), 195 (24), 102 (21). Anal. Calcd for $C_{26}H_{38}SO_2Sn$: C, 58.59; H, 7.13. Found: C, 58.32; H, 6.94.

4.3. General procedure for the Stille coupling reaction

To a solution of (*E*)-α-arylsulfonylvinylstannane (1.0 mmol) and acyl chloride (1.1 mmol) in benzene (2.0 mL) under Ar, $Pd(PPh_3)_4$ (0.05 mmol) and CuI (0.75 mmol) were added, the resulting mixture was stirred at reflux for 7 h, cooled to room temperature, and diluted with light petroleum. The supernatant was filtered through a short plug of silica gel and the filtrate evaporated. The residue was purified by preparative TLC on silica gel to afford the corresponding compounds.

*4.3.1. (Z)-1-Benzoyl-1-phenylsulfonyl-1-hexene (**4a**)*

Oil. IR (film): ν (cm^{-1}) 2927, 1667, 1596, 1448, 1319, 1154, 732. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.82 (m, 4H), 7.64–7.59 (m, 2H), 7.54–7.44 (m, 4H), 7.24 (t, J=7.6 Hz, 1H), 2.04–1.98 (m, 2H), 1.42–1.36 (m, 2H), 1.27–1.22 (m, 2H), 0.76 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.13, 146.82, 141.63, 139.84, 136.37, 134.52, 133.64, 129.82, 129.07, 128.86, 128.38, 30.09, 29.60, 22.16, 13.60. MS (EI, 70 eV): m/z 328 (M^+, 73), 187 (21), 105 (100). Anal. Calcd for $C_{19}H_{20}SO_3$: C, 69.48; H, 6.14. Found: C, 69.20; H, 6.03.

*4.3.2. (Z)-1-Benzoyl-1-(p-tolylsulfonyl)-1-hexene (**4b**)*

Oil. IR (film): ν (cm^{-1}) 2928, 1668, 1597, 1450, 1320, 1145, 717. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90–7.88 (m, 2H), 7.70 (d, J=8.4 Hz, 2H), 7.61 (t, J=7.2 Hz, 1H), 7.46 (t, J=7.6 Hz, 2H), 7.30 (d, J=8.0 Hz, 2H), 7.20 (t, J=7.6 Hz, 1H), 2.42 (s, 3H), 2.03–1.97 (m, 2H), 1.41–1.17 (m, 4H), 0.78 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.28, 146.17, 144.66, 141.90, 136.83, 136.41, 134.46, 129.85, 129.74, 128.83, 128.43, 30.10, 29.53, 22.16, 21.69, 13.61. MS (EI, 70 eV): m/z 342 (M^+, 8.5), 177 (100), 119 (62), 91 (42). Anal. Calcd for $C_{20}H_{22}SO_3$: C, 70.15; H, 6.48. Found: C, 69.88; H, 6.23.

*4.3.3. (Z)-1-(4-Nitrobenzoyl)-1-phenylsulfonyl-1-hexene (**4c**)*

Oil. IR (film): ν (cm^{-1}) 3068, 2928, 1623, 1600, 1520, 1348, 1306, 1152, 847, 729. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J=8.4 Hz, 2H), 7.66 (d, J=7.6 Hz, 2H), 7.60–7.56 (m, 1H), 7.47–7.39 (m, 4H), 6.27 (t, J=7.6 Hz, 1H), 2.93–2.87 (m, 2H), 1.44–1.32 (m, 4H), 0.95 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.07, 148.93, 142.40, 140.54, 133.63, 131.09, 129.21, 129.11, 127.61, 127.25, 123.21, 31.28, 28.66, 22.45, 13.88. MS (EI, 70 eV): m/z 373 (M^+, 4.1), 225 (100), 143 (39), 116 (46). Anal. Calcd for $C_{19}H_{19}NSO_5$: C, 61.11; H, 5.13. Found: C, 60.87; H, 4.92.

*4.3.4. (Z)-1-(4-Chlorobenzoyl)-1-(p-tolylsulfonyl)-1-hexene (**4d**)*

Oil. IR (film): ν (cm^{-1}) 2930, 1669, 1587, 1320, 1154, 1086, 911, 733. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J=8.8 Hz, 2H), 7.68 (d, J=8.0 Hz, 2H), 7.45 (d, J=8.4 Hz, 2H), 7.31 (d, J=8.0 Hz, 2H), 7.19 (t, J=8.0 Hz, 1H), 2.43 (s, 3H), 2.03–1.97 (m, 2H), 1.43–1.19 (m, 4H), 0.78 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.10, 146.26, 144.80, 141.77, 141.17, 136.64, 134.76, 131.21, 129.78, 129.23, 128.40, 30.12, 29.51, 22.17, 21.68, 13.60. MS (EI, 70 eV): m/z 376 (M^+, ^{35}Cl, 2.5), 235 (37), 177 (39), 120 (100), 91 (41). Anal. Calcd for $C_{20}H_{21}SO_3Cl$: C, 63.73; H, 5.62. Found: C, 63.44; H, 5.38.

*4.3.5. (Z)-1-(4-Chlorobenzoyl)-1-phenylsulfonyl-1-hexene (**4e**)*

Oil. IR (film): ν (cm^{-1}) 2928, 1670, 1587, 1320, 1152, 1087, 813. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85–7.80 (m, 4H), 7.64–7.44 (m, 5H), 7.23 (t, J=7.6 Hz, 1H), 2.04–1.98 (m, 2H), 1.42–1.21 (m, 4H), 0.80 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.93, 146.91, 141.50, 141.23, 139.68, 134.74, 133.72, 131.18, 129.26, 129.11, 128.35, 30.10, 29.69, 22.16, 13.58. MS (EI, 70 eV): m/z 362 (M^+, ^{35}Cl, 7.3), 177 (100), 109 (66). Anal. Calcd for $C_{19}H_{19}SO_3Cl$: C, 62.88; H, 5.28. Found: C, 62.59; H, 5.37.

*4.3.6. (Z)-1-(4-Nitrobenzoyl)-1-(p-tolylsulfonyl)-1-hexene (**4f**)*

Oil. IR (film): ν (cm^{-1}) 2927, 1625, 1597, 1521, 1347, 1152, 1086, 848. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J=8.8 Hz, 2H), 7.53 (d, J=8.4 Hz, 2H), 7.40 (d, J=8.8 Hz, 2H), 7.23 (d, J=8.4 Hz, 2H), 6.23 (t, J=7.6 Hz, 1H), 2.95–2.87 (m, 2H), 2.40 (s, 3H), 1.44–1.32 (m, 4H), 0.95 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.67, 148.44, 147.72, 144.67, 142.58, 140.75, 137.55, 131.07, 129.72, 127.67, 123.19, 31.33, 28.60, 22.46, 21.63, 13.90. MS (EI, 70 eV): m/z 387 (M^+, 1.2), 360 (11), 295 (15), 157 (50), 139 (61), 115 (70), 109 (100), 91 (32). Anal. Calcd for $C_{20}H_{21}NSO_5$: C, 62.00; H, 5.46. Found: C, 61.71; H, 5.23.

*4.3.7. (Z)-1-(4-Methylbenzoyl)-1-phenylsulfonyl-1-hexene (**4g**)*

Oil. IR (film): ν (cm^{-1}) 2928, 1669, 1597, 1446, 1320, 1152, 733. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J=7.6 Hz, 2H), 7.79 (d, J=8.0 Hz, 2H), 7.63–7.48 (m, 3H), 7.27–7.24 (m, 2H), 7.20 (t, J=7.6 Hz, 1H), 2.42 (s, 3H), 2.05–1.98 (m, 2H), 1.42–1.36 (m, 2H), 1.26–1.18 (m, 2H), 0.78 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.56, 146.41, 145.76, 141.77, 139.93, 133.98, 133.56, 130.02, 129.58, 129.03, 128.37, 30.13, 29.57, 22.18, 21.86, 13.63. MS (EI, 70 eV): m/z 342 (M^+, 8.9), 119 (100), 91 (67). Anal. Calcd for $C_{20}H_{22}SO_3$: C, 70.15; H, 6.48. Found: C, 70.33; H, 6.34.

*4.3.8. (Z)-1-(4-Methoxybenzoyl)-1-phenylsulfonyl-1-hexene (**4h**)*

Oil. IR (film): ν (cm^{-1}) 2926, 1667, 1596, 1445, 1318, 1150, 1109, 724. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.81 (m, 4H), 7.63–7.49 (m, 3H), 7.18 (t, J=7.6 Hz, 1H), 6.95–6.92 (m, 2H), 3.88 (s, 3H), 2.06–2.01 (m, 2H), 1.44–1.35 (m, 2H), 1.28–1.19 (m, 2H), 0.81 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.22, 164.75, 146.09, 141.81, 139.91, 133.54, 132.43, 129.51, 129.03, 128.35, 114.12, 55.64, 30.16, 29.56, 22.20, 13.65. MS (EI, 70 eV): m/z 358 (M^+, 5.4), 269 (100), 135 (34). Anal. Calcd for $C_{20}H_{22}SO_4$: C, 67.01; H, 6.19. Found: C, 66.73; H, 5.95.

*4.3.9. (Z)-1-Benzoyl-1-phenylsulfonyl-2-phenylethene (**4i**)*

White solid, 97–98 °C. IR (KBr): ν (cm^{-1}) 1659, 1614, 1447, 1304, 1230, 1141, 1085, 687. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.91–7.87 (m, 4H), 7.65–7.18 (m, 11H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.20, 141.57, 139.72, 139.44, 135.45, 134.50, 133.75, 131.38, 131.16, 130.30, 129.85, 129.13, 128.92, 128.82, 128.63. MS (EI, 70 eV): m/z 348 (M^+, 5.7), 207 (31), 177 (100), 105 (89), 77 (49). Anal. Calcd for $C_{21}H_{16}SO_3$: C, 72.39; H, 4.63. Found: C, 72.11; H, 4.40.

*4.3.10. (Z)-1-(4-Chlorobenzoyl)-1-phenylsulfonyl-2-phenylethene (**4j**)*

White solid, 108–109 °C. IR (KBr): ν (cm^{-1}) 2957, 1659, 1616, 1582, 1307, 1228, 1146, 1086, 687. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.89 (d, J=8.4 Hz, 2H), 7.82 (d, J=8.4 Hz, 2H), 7.67–7.52 (m,

3H), 7.34–7.22 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.07, 141.77, 141.18, 139.53, 139.06, 133.87, 133.83, 131.37, 131.20, 131.15, 130.22, 129.26, 129.19, 129.03, 128.62. MS (EI, 70 eV): m/z 382 (M^+, ^{35}Cl, 8.6), 185 (26), 177 (100), 120 (91). Anal. Calcd for $C_{21}H_{15}SO_3Cl$: C, 65.87; H, 3.95. Found: C, 65.59; H, 3.77.

*4.3.11. (Z)-1-(4-Nitrobenzoyl)-1-phenylsulfonyl-2-phenylethene (**4k**)*

Yellow solid, 124–125 °C. IR (KBr): ν (cm^{-1}) 3059, 1669, 1605, 1529, 1345, 1150, 853. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J=8.8 Hz, 2H), 7.61 (d, J=8.8 Hz, 2H), 7.51–7.22 (m, 11H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.04, 143.08, 139.71, 133.46, 132.76, 130.89, 130.69, 130.14, 129.48, 129.18, 128.73, 128.67, 128.05, 127.98, 123.44. MS (EI, 70 eV): m/z 393 (M^+, 3.4), 185 (100). Anal. Calcd for $C_{21}H_{15}NSO_5$: C, 64.11; H, 3.84. Found: C, 63.84; H, 3.65.

*4.3.12. (Z)-1-(4-Methylbenzoyl)-1-phenylsulfonyl-2-phenylethene (**4l**)*

White solid, 95–96 °C. IR (KBr): ν (cm^{-1}) 1654, 1615, 1449, 1306, 1232, 1145, 1087, 689. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.90–7.88 (m, 2H), 7.79 (d, J=8.4 Hz, 2H), 7.63–7.51 (m, 3H), 7.30–7.19 (m, 5H), 7.16 (d, J=8.0 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.67, 145.78, 141.17, 139.74, 139.59, 133.69, 133.12, 131.47, 131.07, 130.31, 130.05, 129.60, 129.10, 128.90, 128.60, 21.84. MS (EI, 70 eV): m/z 362 (M^+, 2.1), 119 (100), 91 (78), 77 (38). Anal. Calcd for $C_{22}H_{18}SO_3$: C, 72.90; H, 5.01. Found: C, 72.63; H, 4.86.

4.4. General procedure for one-pot stereoselective synthesis of (*Z*)-α-arylsulfonyl-α,β-unsaturated ketones

A 25 mL, two-necked, round-bottom flask equipped with a magnetic stirring bar under argon atmosphere, was charged sequentially with acetylenic sulfone (1 mmol), benzene (3 mL), $Pd(PPh_3)_4$ (0.05 mmol) and Bu_3SnH (1.05 mmol). The mixture was stirred at room temperature for 2 h. Then acyl chloride (1.1 mmol) and CuI (0.75 mmol) were added and the mixture was stirred at reflux for 7–10 h, cooled to room temperature, and diluted with light petroleum. The supernatant was filtered through a short plug of silica gel and the filtrate evaporated. The residue was purified by preparative TLC on silica gel to afford the corresponding compounds.

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